Supporting information

A Brønsted Acid-Catalyzed Generation of Palladium Complexes: Efficient Head-to-Tail Dimerization of Alkynes

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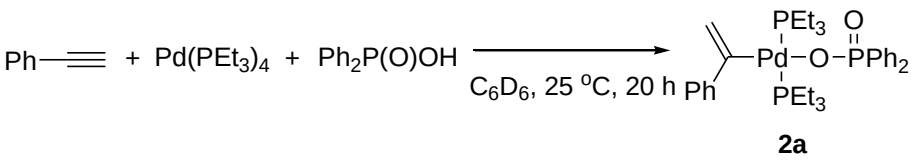
A. General information

The intermediates were prepared in a glove box (O_2<0.1 ppm, H_2O<0.1 ppm). All other reactions were carried out in oven-dried Schlenk tubes or NMR tube under N_2 atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica Gel 60 (particle size 40-50 μm) purchased from Kanto Chemical Co. Inc. The pure products were obtained by column chromatography or GPC (LC-908). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR data were acquired on a JEOL LA-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 160 MHz for ^{31}P NMR spectroscopy) or a JEOL LA-500 instrument (500 MHz for ^{1}H, 125.4 MHz for ^{13}C, and 201.9 MHz for ^{31}P NMR spectroscopy) in deuterated solvents as indicated. Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d*, and those for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm). X-ray analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology, Japan.

B. The synthesis and characterization of the intermediate 2

1). The synthesis of complex 2a



2a

In glove box, 0.065 mmol of phenylacetylene, 0.065 mmol of $Pd(PEt_3)_4$, 0.065 mmol of $Ph_2P(O)OH$ were dissolved in 0.5 mL of dry and degassed C_6D_6 in a NMR tube. The reaction was complete after standing the mixture at room temperature for 20 h as

indicated from ^{1}H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt_3) under high vacuum afforded a white solid. Recrystallization of the solid from hexane and toluene at -30 ^{o}C gave analytically pure product **2a**, 35.3 mg, yield: 82%. ^{1}H NMR (400 MHz, C_6D_6) δ 8.23-8.28 (m, 4H), 8.02 (d, *J* = 6.8 Hz, 2H), 7.10-7.23 (m, 8H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.02 (t, *J* = 3.6 Hz, 1H), 5.09 (s, 1H), 1.52-1.63 (m, 6H), 1.38-1.49 (m, 6H), 0.86-0.94 (m, 18H); ^{31}P NMR (161.8 MHz, C_6D_6) δ 19.22 (s, 1P), 10.72 (s, 2P).

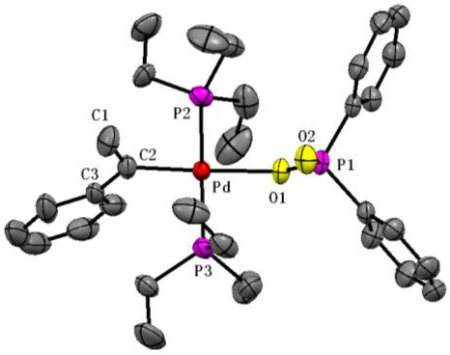
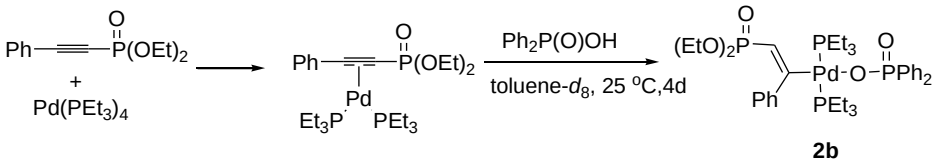


Figure 1. ORTEP Drawing of alkenylpalladium complex **2a**. Thermal ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1-C2 = 1.322(4), C2-C3 = 1.477(4), C2-Pd = 2.015(3), O1-Pd = 2.1368(17), P2-Pd = 2.3124(7), P3-Pd = 2.3209(6); C1-C2-Pd = 119.2(2), C3-C2-Pd = 119.2(2), C2-Pd-P2 = 90.44(8), C2-Pd-P3 = 91.11(8), O1-Pd-P2 = 88.37(5).

2). The synthesis of complex 2b



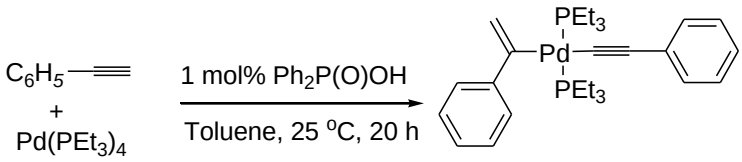
2b

In glove box, 0.06 mmol of $Pd(PEt_3)_4$ and 1 equiv of alkynes were mixed in 0.5 mL of toluene, 30 min later, the volatiles was removed under high vacuum, then 1 equiv of $Ph_2P(O)OH$ and 0.5 mL of toluene-d_8 were added, as followed by ^{1}H NMR and ^{31}P NMR spectroscopies, the reaction was complete in 4 days at room temperature, the analytical pure product was obtained by precipitation from toluene/hexane solution at

-30 °C, colorless oil, 34 mg, yield, 71%. ^{1}H NMR (400 MHz, Tol-d_8) δ 8.43 (d, J = 8.0 Hz, 2H), 8.22 (t, J = 8.8 Hz, 6H), 7.23-7.34 (m, 7H), 6.19 (d, J = 18.0 Hz, 1H), 3.99-4.07 (m, 4H), 1.60-1.78 (m, 12H), 1.35-1.44 (m, 3H), 1.01-1.11 (m, 21H); ^{31}P NMR (161.8 MHz, Tol-d_8) δ 20.51 (s, 1P), 10.44 (s, 1P), 9.96 (s, 2P).

C. The synthesis and characterization of the intermediates 1

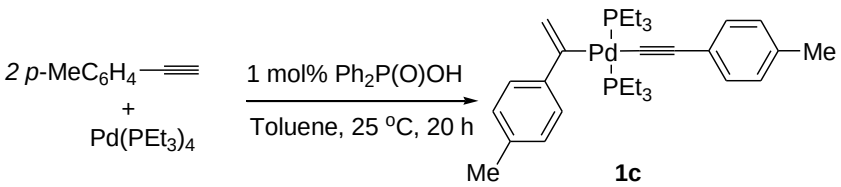
1).



1a

In glove box, 1 mmol of phenylacetylene, 0.5 mmol of Pd(PEt$_3$)$_4$, and 1 mol% Ph$_2$P(O)OH (based on Pd atom) were dissolved in 0.5 mL of dry and degassed Toluene-d_8 in a NMR tube, The reaction was complete after standing the mixture at room temperature for 20 h as indicated from ^{1}H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt$_3$) under high vacuum afforded a yellow oil. After precipitation from toluene/hexane solution at -80 °C, the analytical pure product was obtained. 227 mg, yield: 83%.^{1}H NMR (400 MHz, Tol-d_8) δ 7.93 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H), 7.27 (dd, J = 7.6 Hz, J = 6.0 Hz, 2H), 7.20 (d, J = 6.0 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.59 (b, 1H), 5.33 (b, 1H), 1.94-1.97 (m, 6H), 1.75-1.78 (m, 6H), 1.16 (dt, J_{P-H} = 8.0 Hz, J_{H-H} = 8.0 Hz, 18H). ^{31}P NMR (161.8 MHz, Tol-d_8) δ 13.95.

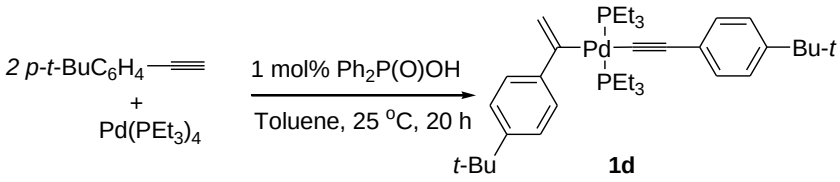
2).



1c

In glove box, 1 mmol of *p*-methylphenylacetylene, 0.5 mmol of $Pd(PEt_3)_4$, and 1 mol% $Ph_2P(O)OH$ (based on Pd atom) were dissolved in 0.5 mL of dry and degassed Toluene-d_8 in a NMR tube, The reaction was complete after standing the mixture at room temperature for 20 h as indicated from ^1H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt_3) under high vacuum afforded a yellow oil. After precipitation from toluene/hexane solution at -80 ^oC, the analytical pure product was obtained. 215 mg, yield: 75%. ^1H NMR (500 MHz, Tol-d_8) δ 7.83 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 6.54 (dt, $J_{P\text{-}H}$ = 4.0 Hz, $J_{H\text{-}H}$ = 2.5 Hz, 1H), 5.23 (d, $J_{H\text{-}H}$ = 2.5 Hz, 1H), 2.19 (s, 3H), 2.12 (s, 3H), 1.81-1.90 (m, 6H), 1.62-1.70 (m, 6H), 1.01 (dt, $J_{P\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 18H). ^{31}P NMR (202 MHz, Tol-d_8) δ 13.99.

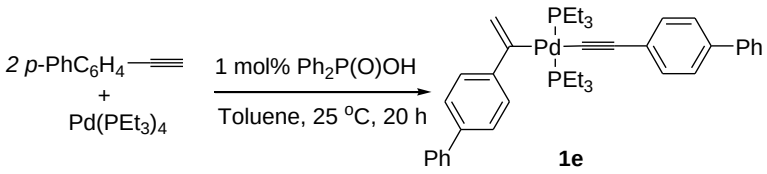
3).



1d

In glove box, 1 mmol of *p*-*t*-butylphenylacetylene, 0.5 mmol of $Pd(PEt_3)_4$, and 1 mol% $Ph_2P(O)OH$ (based on Pd atom) were dissolved in 0.5 mL of dry and degassed Toluene-d_8 in a NMR tube, The reaction was complete after standing the mixture at room temperature for 20 h as indicated from ^1H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt_3) under high vacuum afforded a yellow oil. After precipitation from toluene/hexane solution at -80 ^oC, the analytical pure product was obtained. 287 mg, yield: 87%. ^1H NMR (500 MHz, Tol-d_8) δ 7.79 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.50 (dt, $J_{P\text{-}H}$ = 4.0 Hz, $J_{H\text{-}H}$ = 2.5 Hz, 1H), 5.23 (d, J = 2.5 Hz, 1H), 1.82-1.90 (m, 6H), 1.62-1.70 (m, 6H), 1.29 (s, 9H), 1.24 (s, 9H), 1.05 (dt, $J_{P\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 18H). ^{31}P NMR (202 MHz, Tol-d_8) δ 13.97.

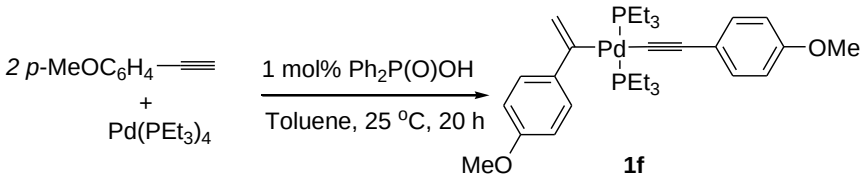
4).



1e

In glove box, 1 mmol of *p*-phenylphenylacetylene, 0.5 mmol of $Pd(PEt_3)_4$, and 1 mol% $Ph_2P(O)OH$ (based on Pd atom) were dissolved in 0.5 mL of dry and degassed Toluene-d_8 in a NMR tube, The reaction was complete after standing the mixture at room temperature for 20 h as indicated from ^1H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt_3) under high vacuum afforded a yellow oil. After precipitation from toluene/hexane solution at -80 °C, the analytical pure product was obtained. 280 mg, yield: 80%. ^1H NMR (500 MHz, Tol-d_8) δ 7.93 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.54-7.58 (m, 4H), 7.46 (d, J = 8.0 Hz, 4H), 7.17-7.21 (m, 4H), 7.07-7.11 (m, 2H), 6.57 (d, J = 1.5 Hz, 1H), 5.28 (d, J = 2.0 Hz, 1H), 1.81-1.89 (m, 6H), 1.62-1.70 (m, 6H), 1.03 (dt, J_{P-H} = 8.5 Hz, J_{H-H} = 8.5 Hz, 18H). ^{31}PNMR (202 MHz, Tol-d_8) δ 14.12.

5).



1f (X-ray)

In glove box, 1 mmol of *p*-anisylacetylene, 0.5 mmol of $Pd(PEt_3)_4$, and 1 mol% $Ph_2P(O)OH$ (based on Pd atom) were dissolved in 0.5 mL of dry and degassed Toluene-d_8 in a NMR tube, The reaction was complete after standing the mixture at room temperature for 20 h as indicated from ^1H NMR spectra and ^{31}P NMR spectra. Removal of the volatile (solvent and PEt_3) under high vacuum afforded a yellow solid. Recrystallization of the solid from hexane and toluene at -30 °C gave analytically pure product **1f**, 212 mg, yield: 70%. Crystals suitable for X-ray crystallography was obtained from the recrystallization of the solid from hexane and toluene at -30 °C. ^1H

NMR (500 MHz, Tol-d_8) δ 7.86 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 6.49 (dt, J_{P-H} = 3.5 Hz, J_{H-H} = 2.0 Hz, 1H), 5.23 (d, J = 2.0 Hz, 1H), 3.38 (s, 3H), 3.30 (s, 3H), 1.84-1.92 (m, 6H), 1.63-1.72 (m, 6H), 1.05 (dt, J_{P-H} = 8.0 Hz, J_{H-H} = 8.0 Hz, 18H). ^{31}P NMR (202 MHz, Tol-d_8) δ 14.03.

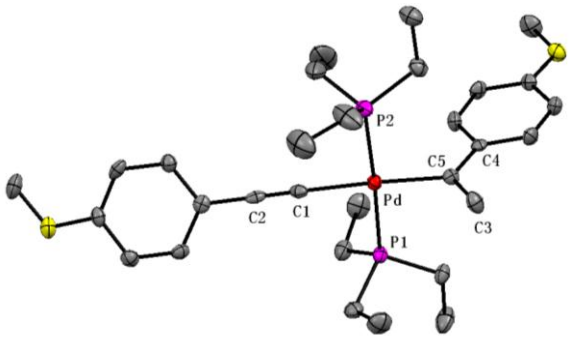


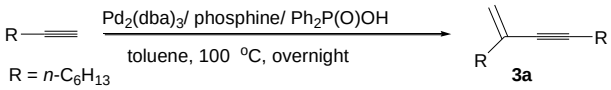
Figure 1. The ORTEP drawing of intermediate vinyl(alkynyl)palladium complex **1f**. The hydrogen atoms were omitted for clarity. The selected bond length and bond angles: C2-C1 = 1.166(5), C1-Pd = 2.046(4), Pd-P1 = 2.2943(12), Pd-P2 = 2.2977(13), Pd-C5 = 2.064(4), C5-C3 = 1.336(5), C5-C4 = 1.497(5); C2-C1-Pd = 177.3(4), C1-Pd-P1 = 87.20(12), C1-Pd-P2 = 89.92(12), Pd-C5-C3 = 119.1(3), Pd-C5-C4 = 120.0(3).

D. Typical procedure for Pd(0)/$Ph_2P(O)OH$ catalyzed dimerization.

A mixture of $Pd_2(dba)_3$ (2.3 mg), DPPE (2.0 mg), and $Ph_2P(O)OH$ (2.2 mg) in toluene (0.5 mL)was stirred at room temperature for 10 minutes. 1-Octyne (110 mg) was added. The mixture was heated at 80 ^{o}C overnight. Isolation of the product on silica chromatography using hexane as an eluent gave pure **3a** as an oil (99.5 mg, 90% yield).

E. Screening conditions for the Selective head-to-tail dimerization of 1-octyne

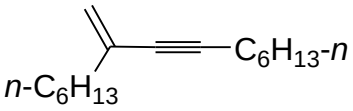
Selective head-to-tail dimerization of 1-octyne catalyzed by the combination of Pd(0)/Brønsted acid.[a]



Run	Condition	% NMR yield
1	PPh_3	39
2	P(*p*-anisyl)$_3$	13
3	$PhPCy_2$	12
5	dppf	trace
6	$Ph_2P(CH_2)_4PPh_2$	46
7	$Ph_2P(CH_2)_3PPh_2$	68
8	dppe	95
9[b]	dppe	trace
10[c]	dppe	92
11[d]	dppe	65

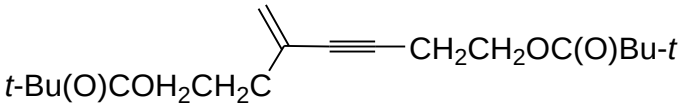
[a] Conditions: In a glass tube, 1 mol% $Pd_2(dba)_3$, phosphine ligand (Pd/P = 1/2), and $Ph_2P(O)OH$ (Pd/acid = 1/2) were mixed in toluene (0.5 mL) at 25 °C for 10 min, and 1-Octyne (0.5 mmol) was added, then the mixture was heated overnight. [b] In the absence of $Ph_2P(O)OH$. [c] Heated at 80 °C using 0.25 mol% $Pd_2(dba)_3$, C = 2 mol/L. [d] HOAc was used instead of $Ph_2P(O)OH$.

F. Analytical and spectral data of products



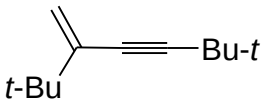
3a[1]

1 mmol of terminal alkynes was loaded, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 5.11 (s, 1H), 2.30 (t, *J* = 6.0 Hz, 2H), 2.12 (t, *J* = 8.0 Hz, 2H), 1.48-1.56 (m, 4H), 1.37-1.44 (m, 2H), 1.29 (b, 10H), 0.90 (b, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.42, 119.23, 90.06, 81.04, 37.66, 31.74, 31.40, 28.80, 28.67, 28.58, 28.13, 22.66, 22.61, 19.32, 14.11, 14.06.



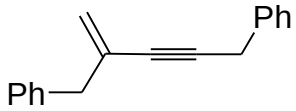
3b

1 mmol of terminal alkynes was loaded, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.19 (s, 1H), 4.11-4.18 (m, 4H), 2.60 (t, *J* = 6.0 Hz, 2H), 2.39 (t, *J* = 6.0 Hz, 2H), 1.17 (s, 9H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.31, 178.16, 127.52, 122.47, 86.00, 81.36, 62.16, 62.05, 38.72, 36.56, 27.16, 27.14, 19.77.



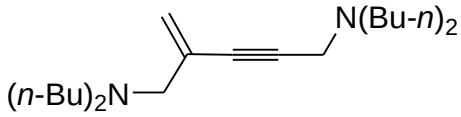
3c[1]

1 mmol of terminal alkynes was loaded, yield: 93%. ^{1}H NMR (400 MHz, Toluene-d_8) δ 5.40 (s, 1H), 5.23 (s, 1H), 1.34 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, Toluene-d_8) δ 143.1, 116.6, 100.1, 80.5, 33.6, 32.5, 31.7, 29.9.



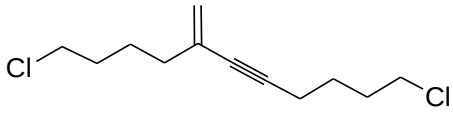
3d[2]

1 mmol of terminal alkynes was loaded, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.40 (m, 10H), 5.48 (s, 1H), 5.31 (s, 1H), 3.74 (s, 2H), 3.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.74, 136.69, 131.21, 129.18, 128.52, 128.43, 127.94, 126.57, 126.49, 121.41, 88.10, 83.21, 43.95, 25.67.



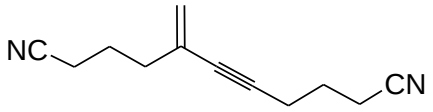
3e

1 mmol of terminal alkynes was loaded, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 1H), 5.38 (s, 1H), 3.48 (s, 2H), 3.04 (s, 2H), 2.39-2.46 (m, 8H), 1.26-1.46 (m, 16H), 0.86-0.92 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.87, 121.83, 85.36, 84.65, 59.65, 53.65, 53.54, 42.61, 29.78, 29.55, 20.72, 20.63, 14.13, 14.08.



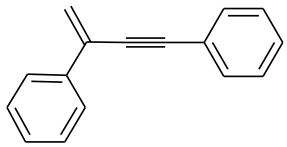
3f

1 mmol of terminal alkynes was loaded, yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 5.15 (s, 1H), 3.52-3.58 (m, 4H), 2.35 (t, *J* = 8.0 Hz, 2H), 2.15 (t, *J* = 8.0 Hz, 2H), 1.86-1.93 (m, 2H), 1.74-1.81 (m, 2H), 1.62-1.72 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.31, 120.33, 89.39, 81.26, 44.93, 44.59, 36.67, 31.77, 31.63, 25.92, 25.32, 18.62.



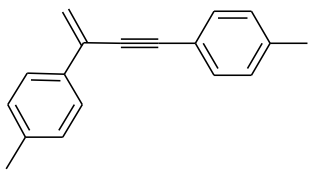
3g

1 mmol of terminal alkynes was loaded, yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (s, 1H), 5.26 (s, 1H), 2.47-2.50 (m, 4H), 2.26-2.37 (m, 4H), 1.84-1.90 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.00, 122.58, 119.43, 119.07, 87.73, 81.68, 35.86, 24.53, 23.71, 18.43, 16.28, 16.14.



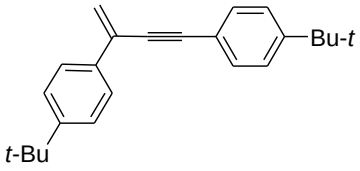
3h[3]

1 mmol of terminal alkynes was loaded, yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.0 Hz, 2H), 7.54 (t, *J* = 4.0 Hz, 2H), 7.32-7.41 (m, 6H), 5.99 (s, 1H), 5.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.29, 131.70, 130.64, 128.44, 128.38, 127.98, 127.86, 126.13, 123.13, 120.71, 90.81, 88.59.



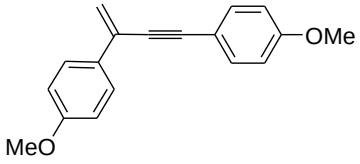
3i

1 mmol of terminal alkynes was loaded, yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.16-7.21 (m, 4H), 5.95 (s, 1H), 5.72 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.52, 138.23, 134.63, 131.59, 130.56, 129.14, 129.12, 126.05, 120.14, 119.48, 90.84, 88.16, 21.59, 21.25.



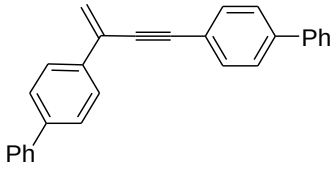
3j[1]

1 mmol of terminal alkynes was loaded, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.6 Hz, 2H), 7.50 (d, *J* = 10.0 Hz, 2H), 7.39-7.45 (m, 4H), 5.97 (s, 1H), 5.73 (s, 1H), 1.38 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.65, 151.45, 134.67, 131.45, 130.53, 125.90, 125.38, 125.36, 120.23, 119.62, 90.82, 88.20, 34.87, 34.68, 31.38, 31.26.



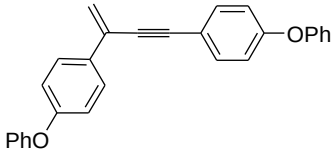
3k

1 mmol of terminal alkynes was loaded, yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 10.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 10.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.85 (s, 1H), 5.63 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.74, 159.68, 133.11, 130.08, 127.36, 118.11, 115.28, 114.00, 113.70, 90.59, 87.54, 55.35, 55.32.



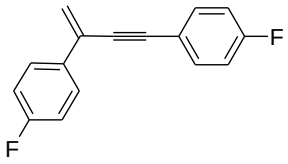
3l

1 mmol of terminal alkynes was loaded, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.61-7.66 (m, 10H), 7.47 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 4H), 7.38 (t, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 5.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.21, 140.59, 140.33, 136.25, 132.16, 130.25, 128.91, 128.86, 127.72, 127.51, 127.17, 127.09, 126.59, 122.00, 120.63, 90.86, 89.24.



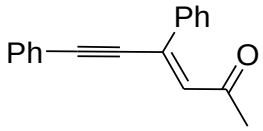
3m

1 mmol of terminal alkynes was loaded, yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 10.0 Hz, 2H), 7.35-7.40 (m, 4H), 7.13-7.19 (m, 2H), 6.97-7.07 (m, 8H), 5.93 (s, 1H), 5.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.78, 157.59, 156.93, 156.40, 133.31, 132.37, 129.94, 129.88, 129.84, 127.62, 123.92, 123.56, 119.52, 119.48, 119.15, 118.53, 118.41, 117.59, 90.46, 88.02.



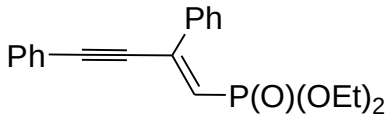
3n

1 mmol of terminal alkynes was loaded, yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.71 (m, 2H), 7.50-7.54 (m, 2H), 7.04-7.10 (m, 4H), 5.92 (s, 1H), 5.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01 (d, J_{F-C} = 21.9 Hz), 161.54 (d, J_{F-C} = 23.8 Hz), 133.59 (d, J_{F-C} = 8.5 Hz), 133.33 (d, J_{F-C} = 3.8 Hz), 129.49, 127.85 (d, J_{F-C} = 7.6 Hz), 120.50, 119.05 (d, J_{F-C} = 3.8 Hz), 115.74 (d, J_{F-C} = 22.0 Hz), 115.34 (d, J_{F-C} = 21.9 Hz), 89.91, 88.06.



3p[4]

0.5 mmol of terminal alkynes and 0.5 mmol of internal alkynes were loaded, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.81 (m, 2H), 7.60-7.62 (m, 2H), 7.39-7.44 (m, 6H), 6.82 (s, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.62, 137.26, 133.90, 131.97, 131.80, 129.95, 129.51, 128.66, 128.51, 127.21, 122.20, 102.59, 87.57, 30.68.



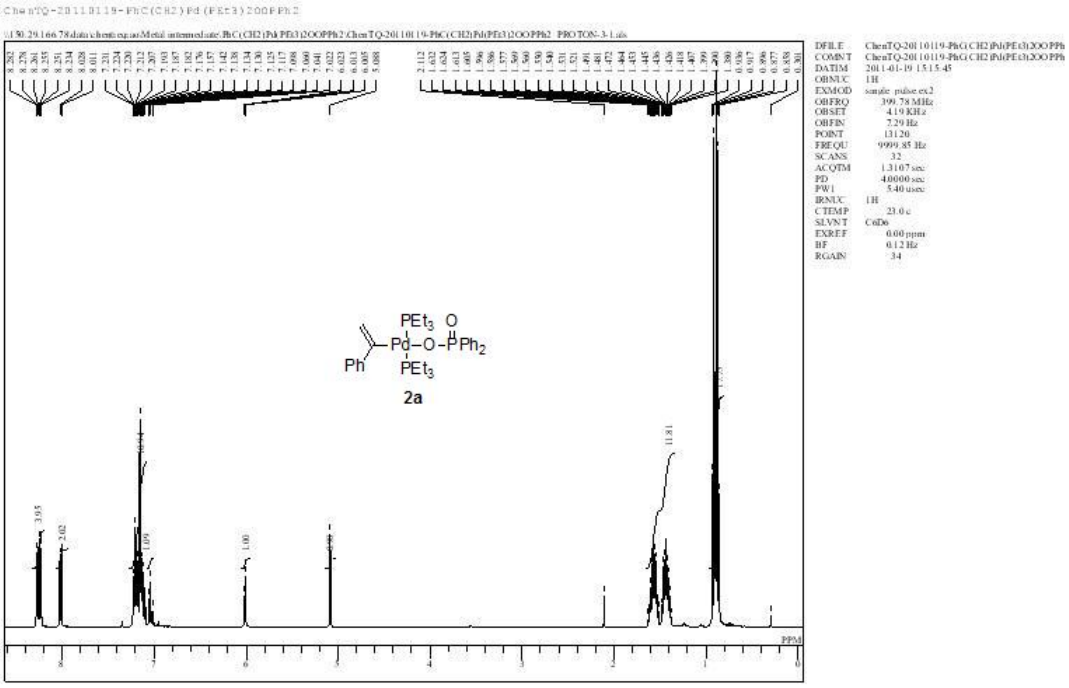
3q

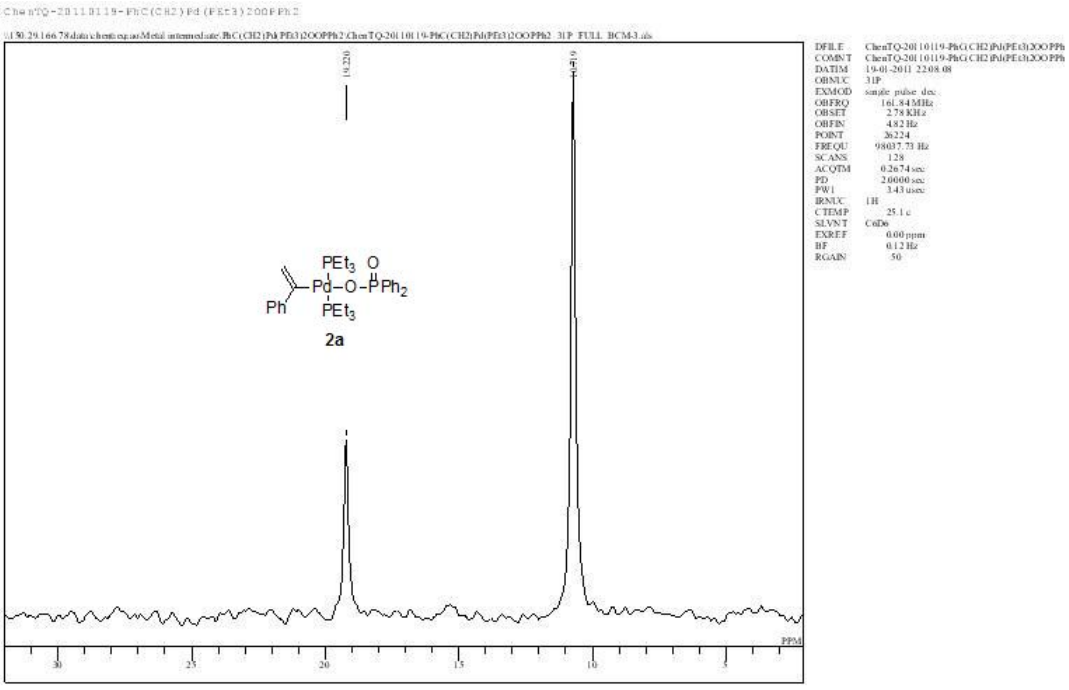
0.5 mmol of terminal alkynes and 0.5 mmol of internal alkynes were loaded, yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.72 (m, 2H), 7.27-7.43 (m, 8H), 6.24 (d, J = 14.0Hz, 1H), 3.79-3.94 (m, 4H), 1.08 (t, J = 7.0 Hz, 6H); ^{31}P NMR (161.8 MHz, $CDCl_3$) δ 14.39; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.63 (d, J = 9.5 Hz), 136.88 (d, J = 5.7 Hz), 131.86, 129.38, 129.20, 128.80, 128.43, 128.01, 123.37, 121.81 (d, J = 64.9 Hz), 94.56 (d, J = 1.9 Hz), 90.19 (d, J = 32.4 Hz), 61.88 (d, J = 5.7 Hz), 16.12 (d, J = 6.7 Hz).

G. Reference

1. Dash, A. K. Eisen, M. S. *Org. Lett.* **2000**, *2*, 737-740.
2. Slugovc, C. Doberer, D. Gemel, C. Schmid, R. Kirchner, K. Winkler, B. Stelzer, F. *Monatsh. Chem.* **1998**, *129*, 221-233.
3. Trost, B. M. Chan, C. Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486-3487.
4. Trost, B. M. Sorum, M. T. Chan, C. Harms, A. E. Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698-708

H. Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra





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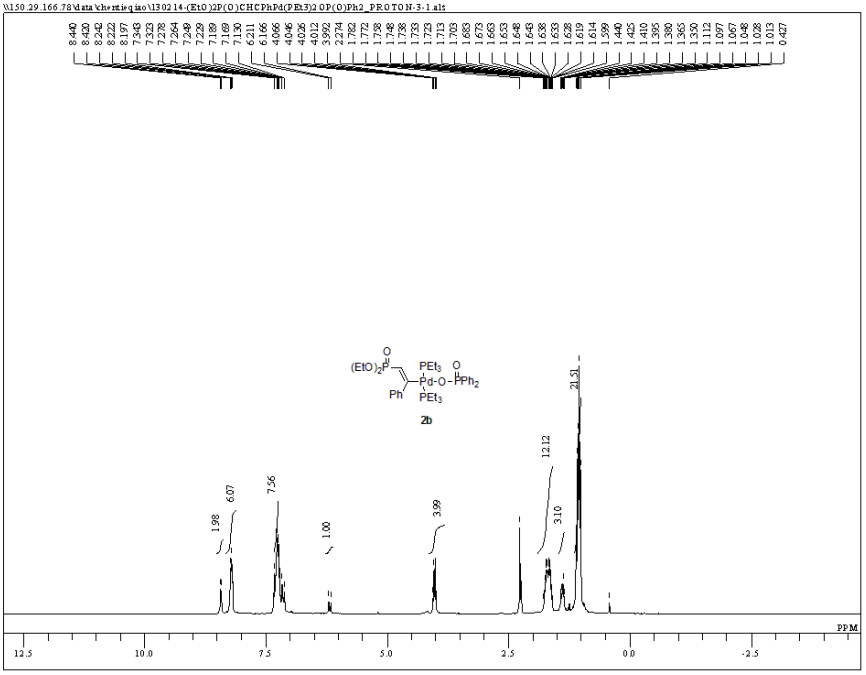

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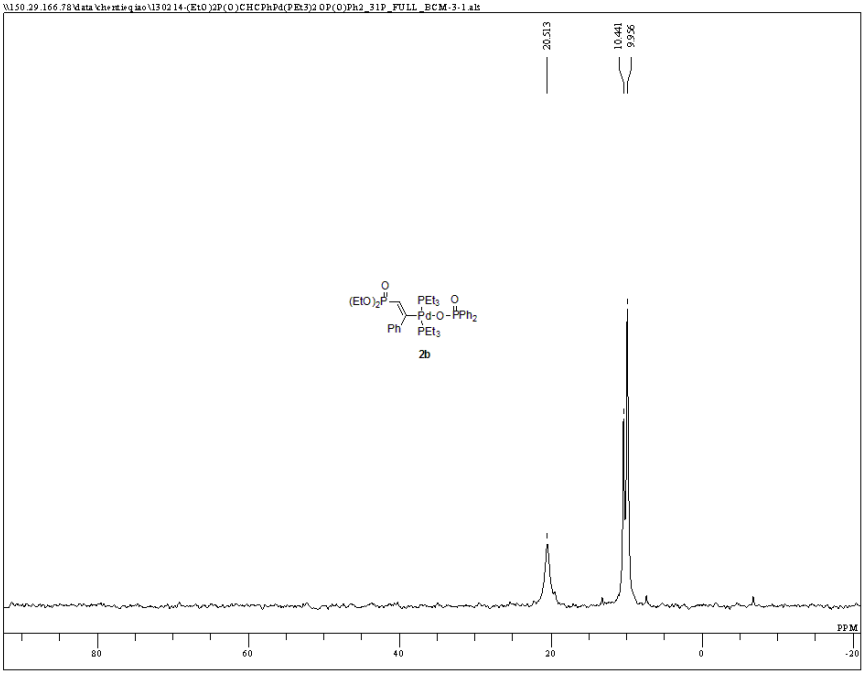

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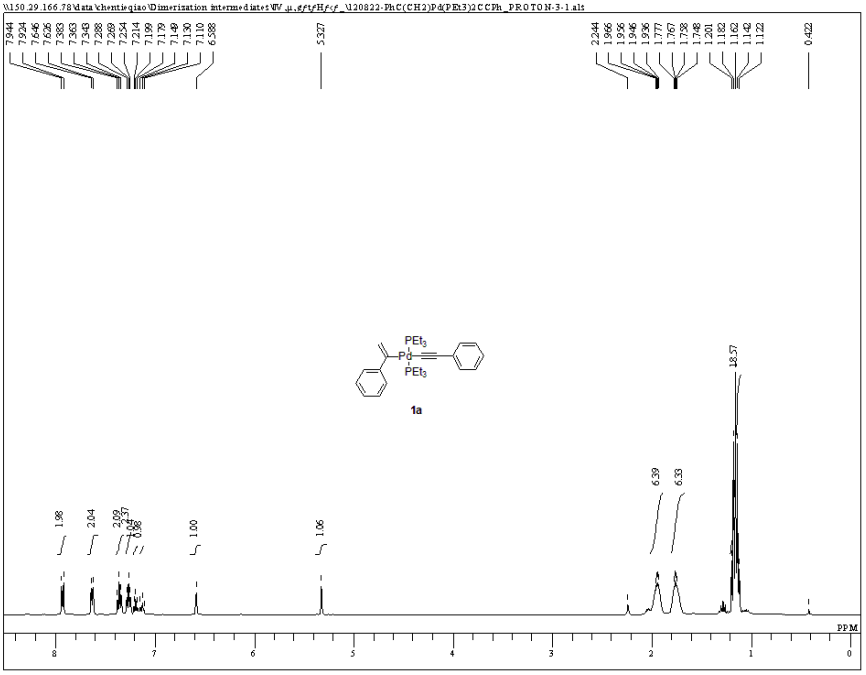

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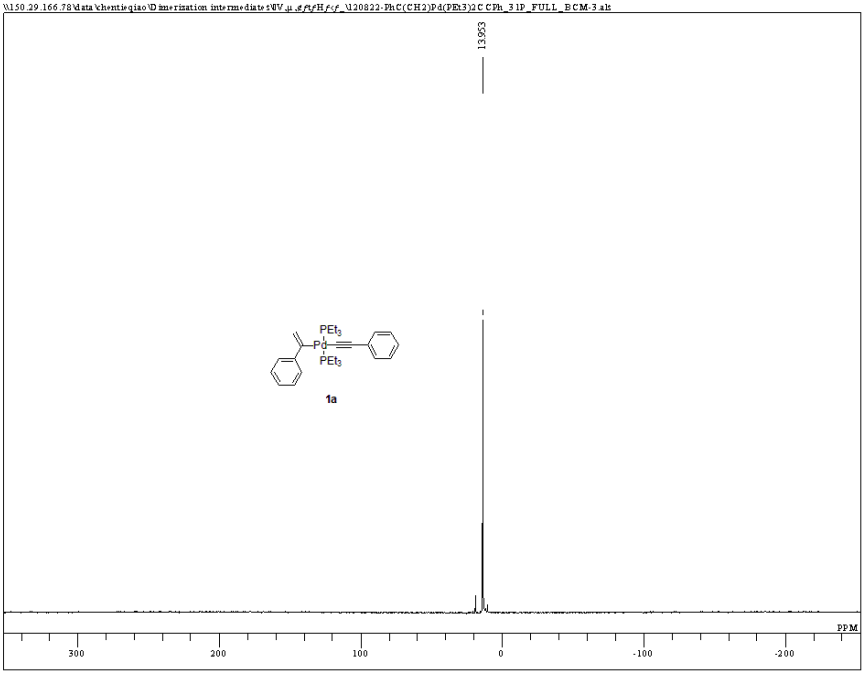

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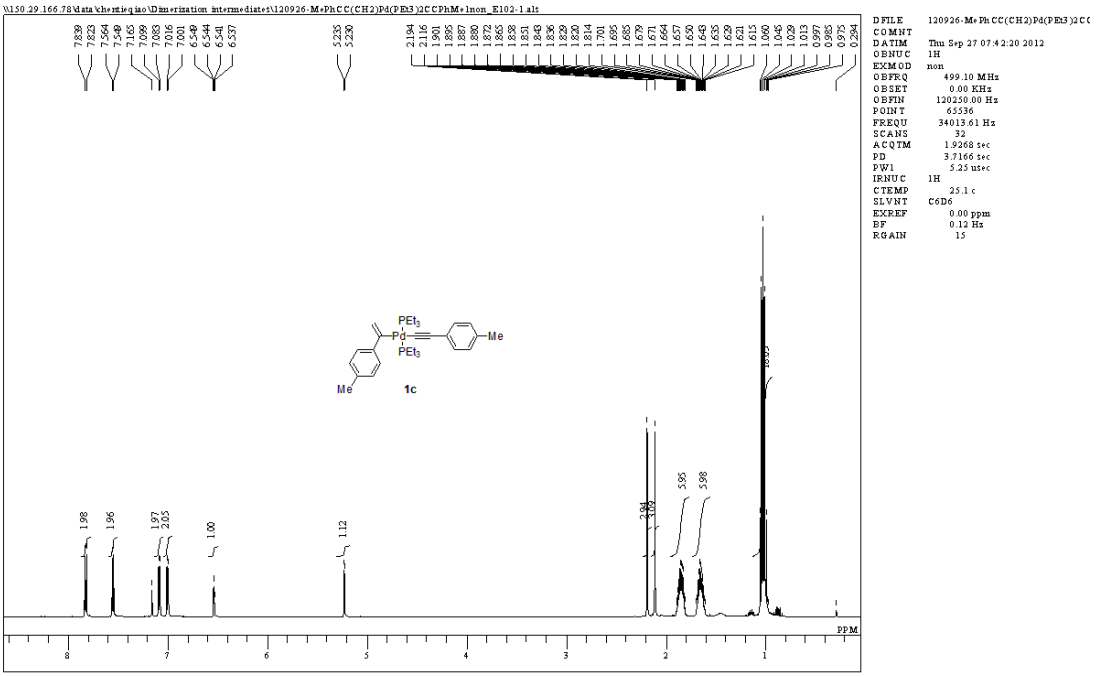
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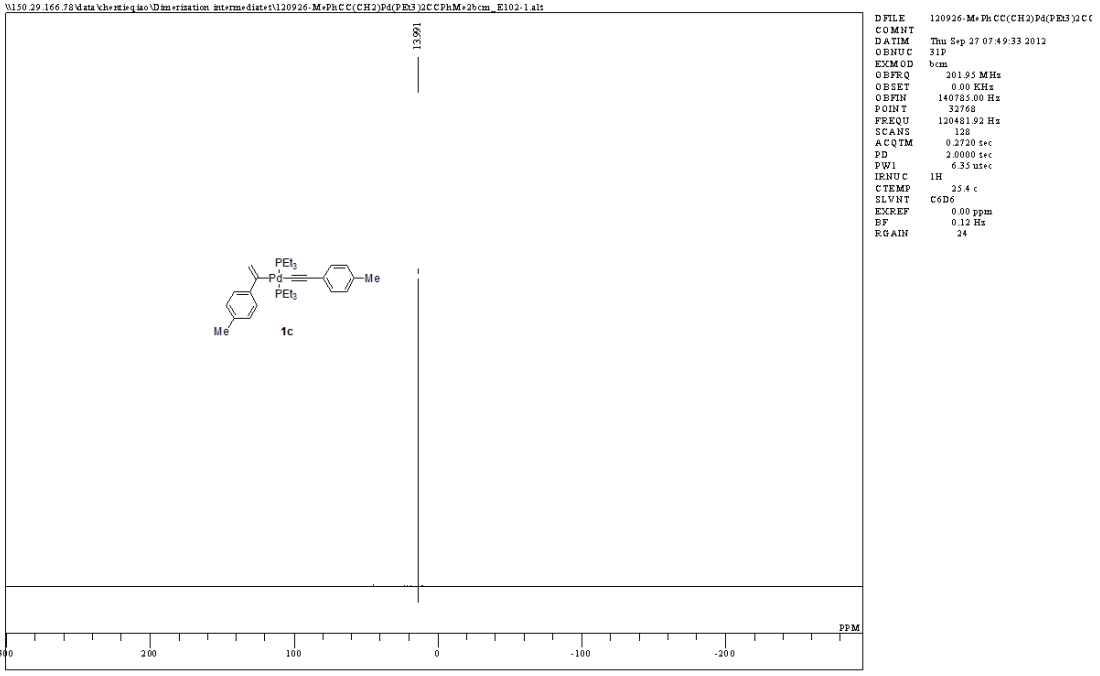
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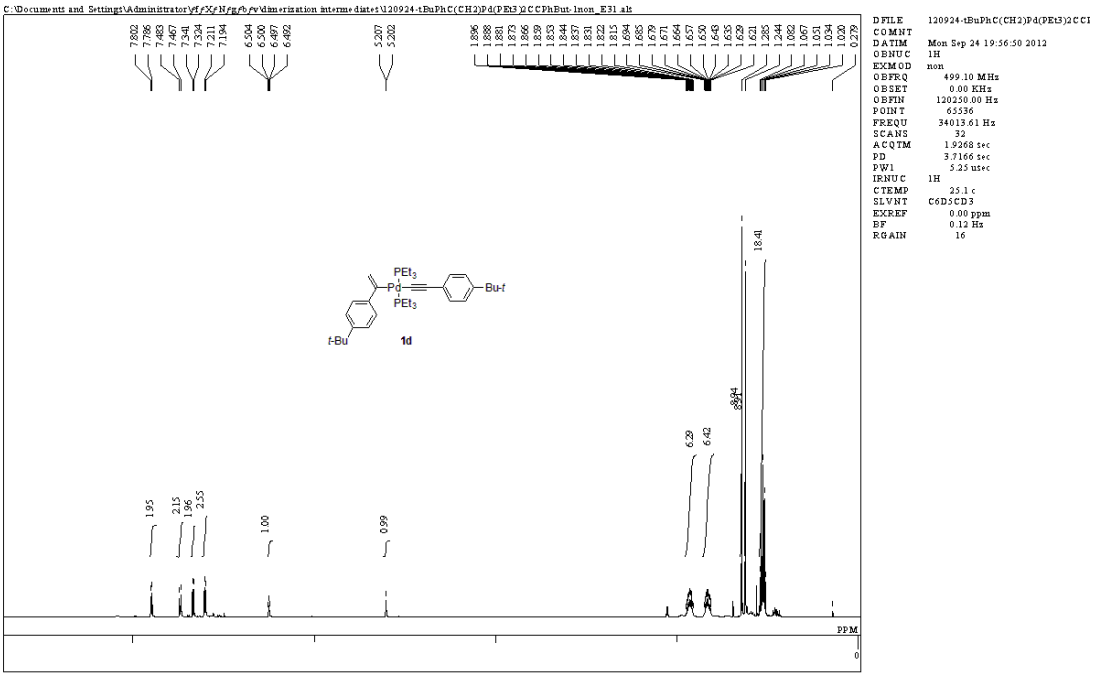
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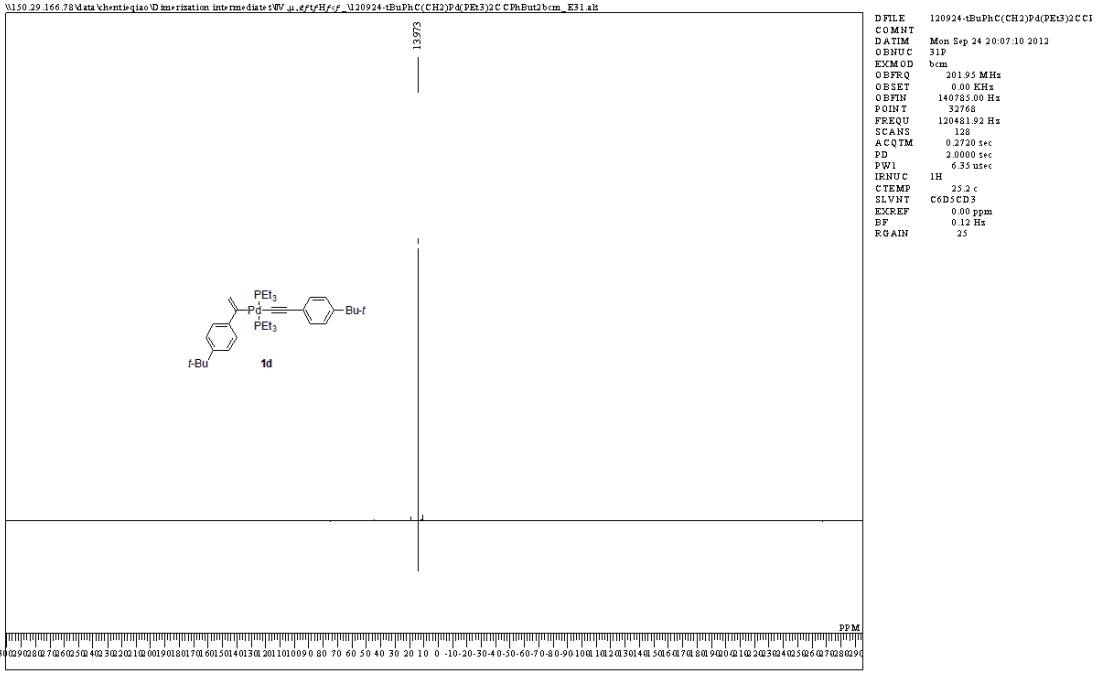
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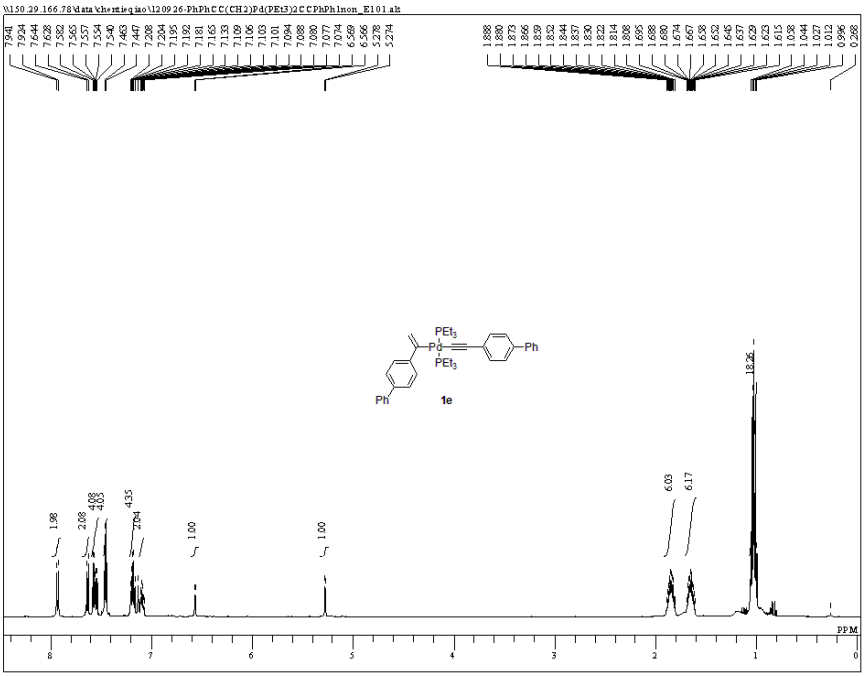


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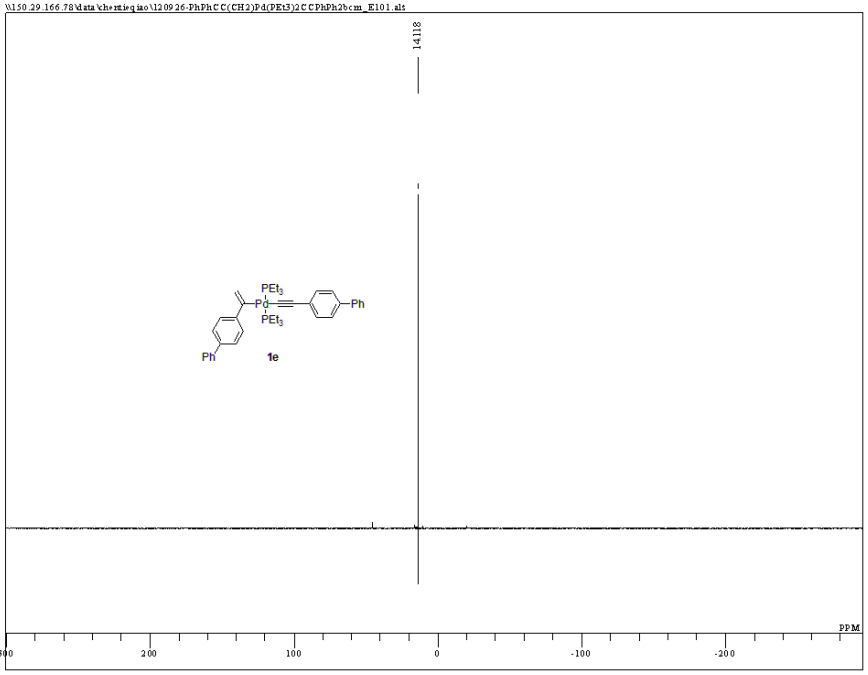


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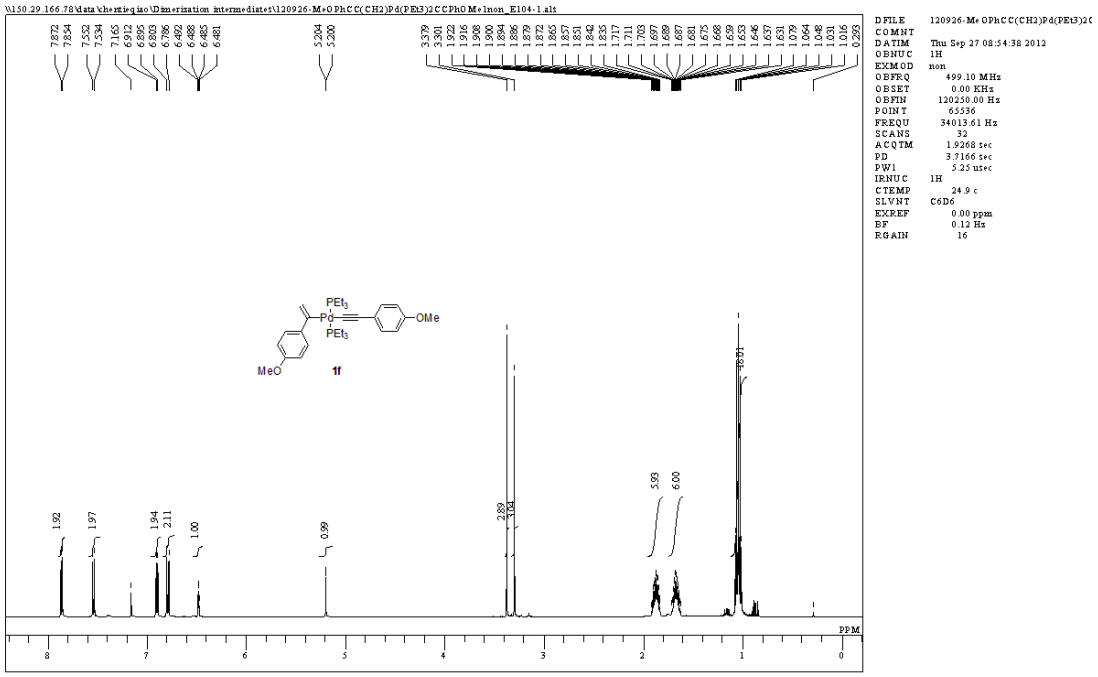
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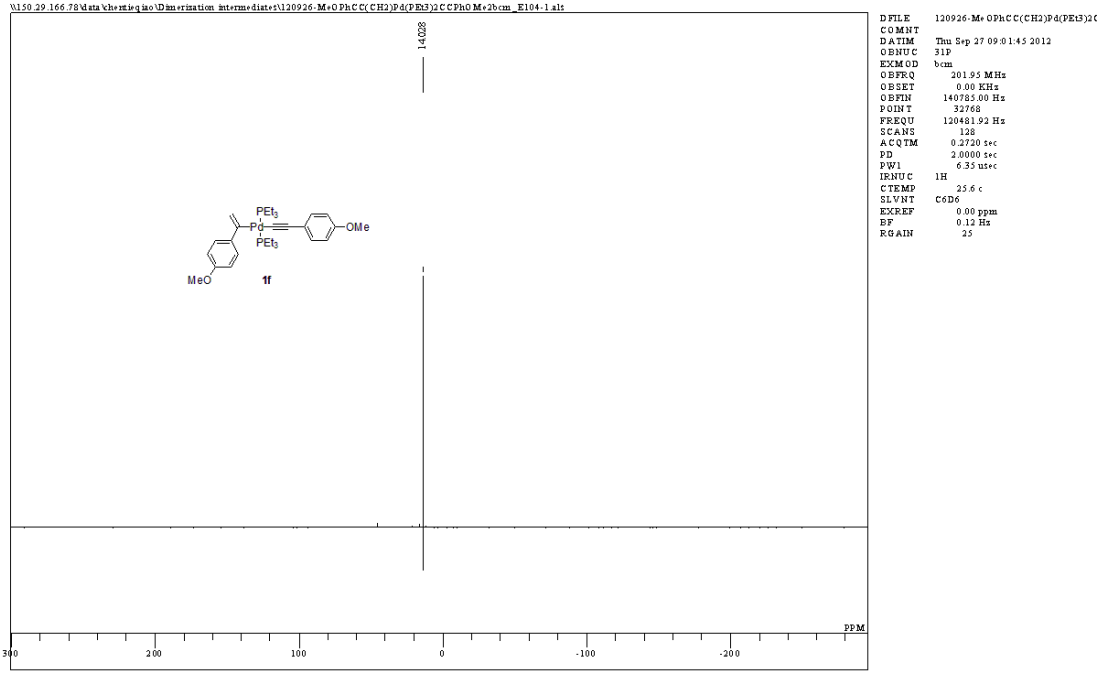
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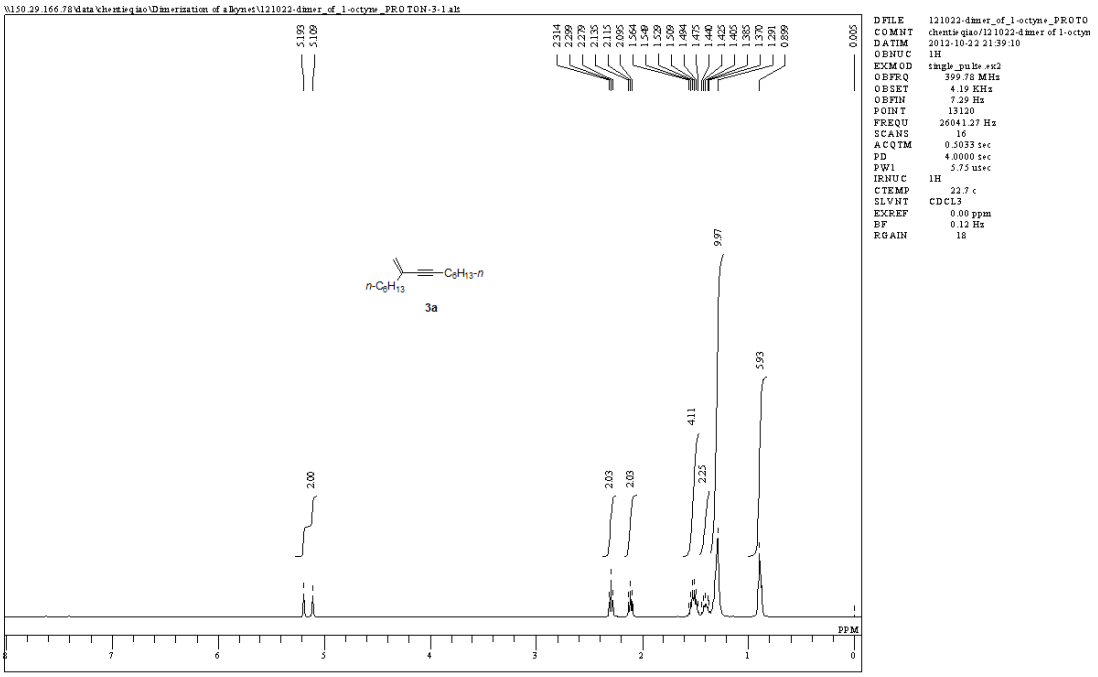
chentieqiao/121022-dimer of 1-octyne



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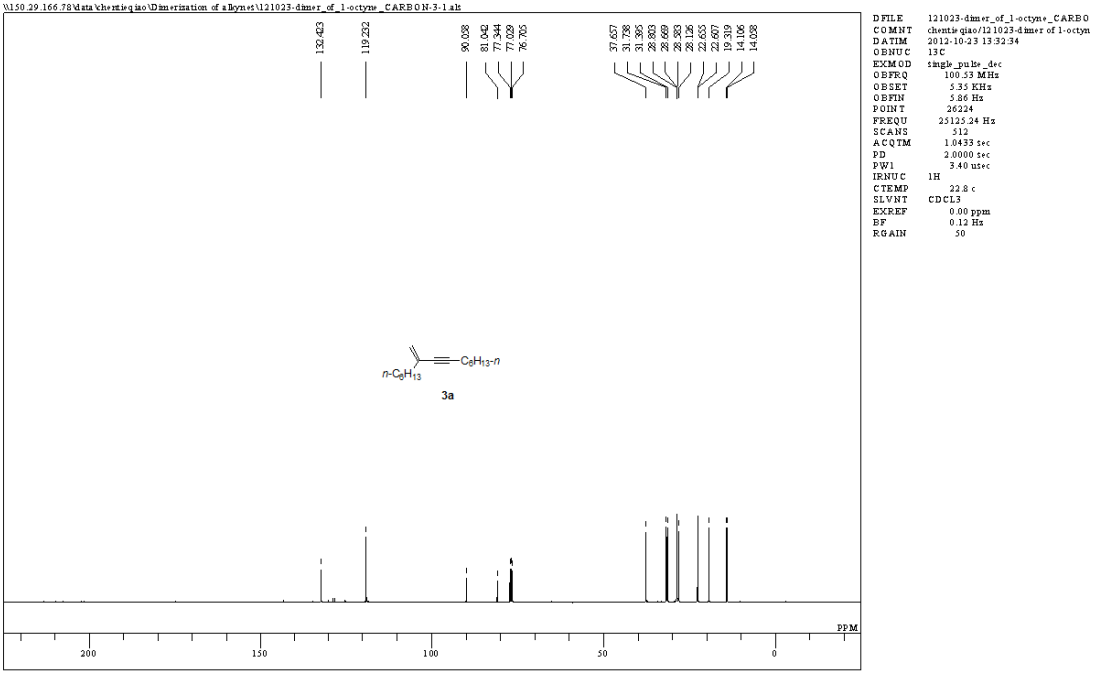
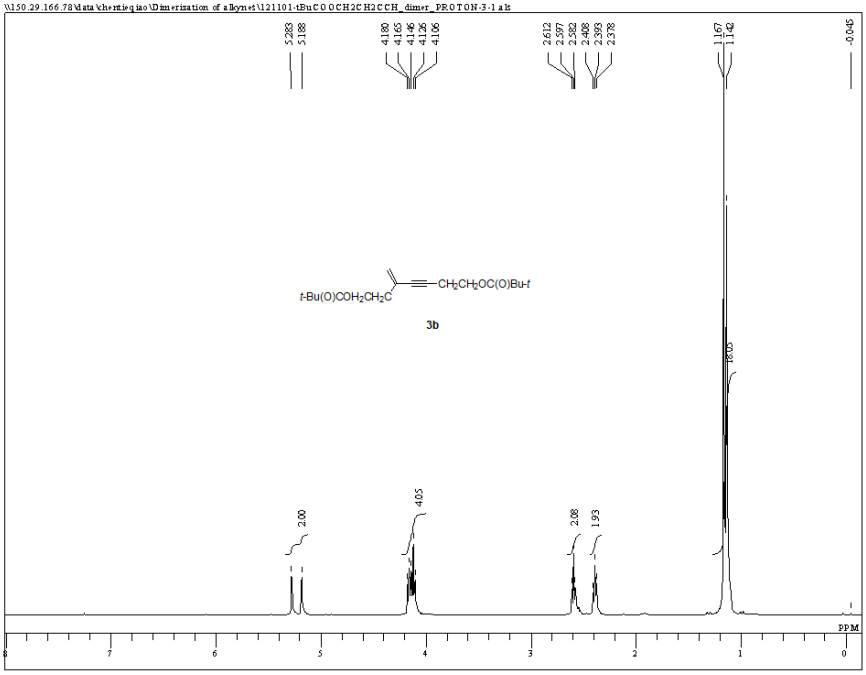
RGAIN 18

chentieqiao/121023-dimer of 1-octyne



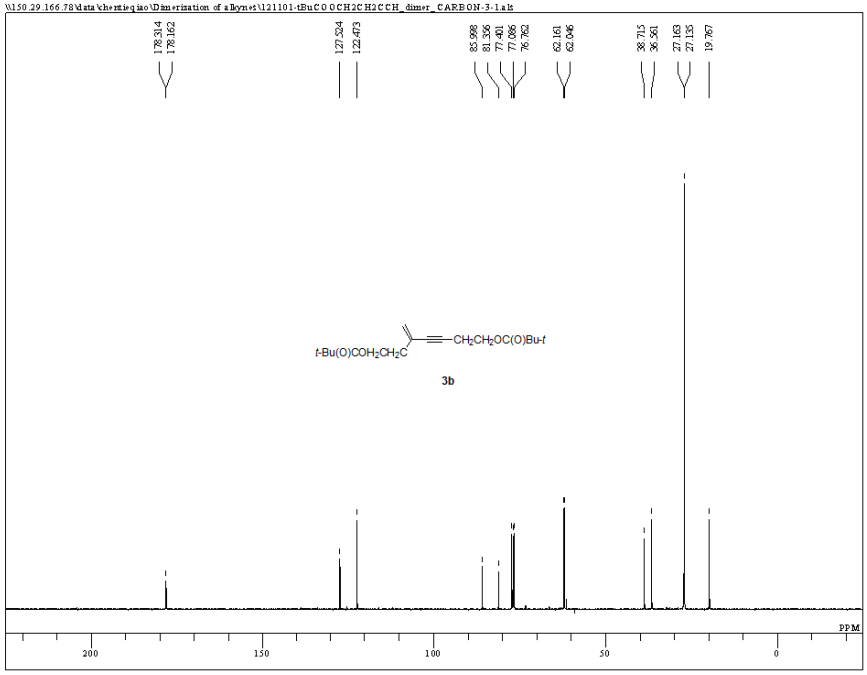
DFILE 121023-dimer_of_1-octyne_CARBO
COMNT chentieqiao/121023-dimer of 1-octyn
DATIM 2012-10-23 13:32:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.24 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

chentieqiao/121101-tBuC00CH2CH2CCH dimer



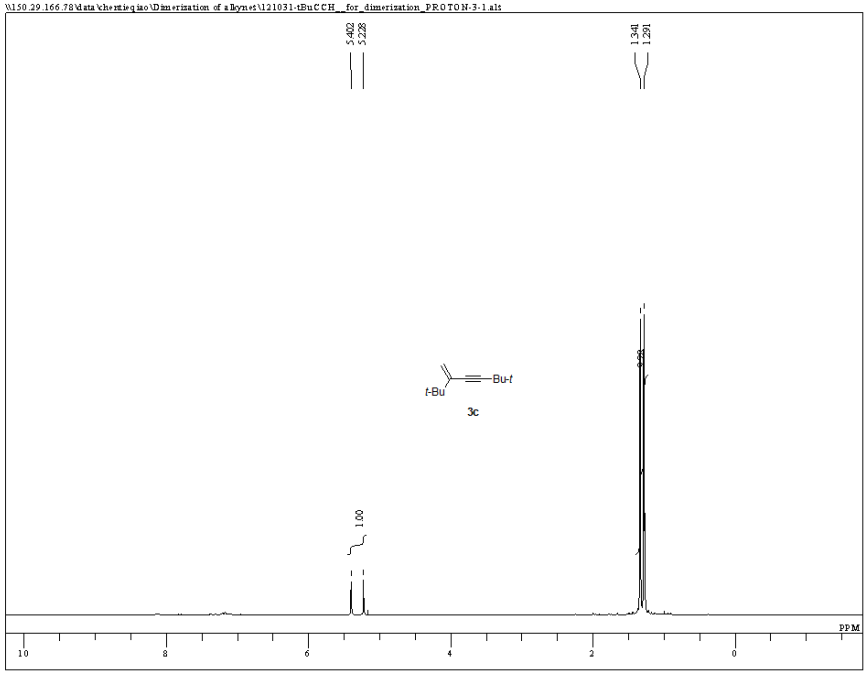
DFILE 121101-tBuC00CH2CH2CCH_dim
COMNT chentieqiao/121101-tBuC00CH2CH
DATIM 2012-11-01 11:32:41
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 32552.08 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18

chentieqiao/121101-tBuC00CH2CH2CCH dimer



DFILE 121101-tBuC00CH2CH2CCH_dim
COMNT chentieqiao/121101-tBuC00CH2CH
DATIM 2012-11-01 11:59:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32781
FREQU 31407.03 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48

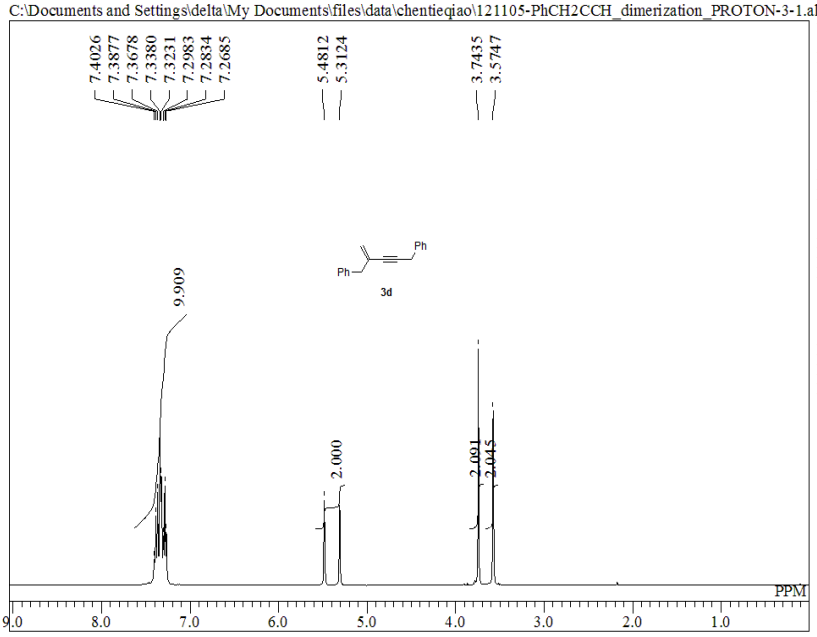
chentieqiao/121031-tBuCCH for dimerization



DFILE	121031-tBuCCH__for_dimerization_
COMNT	chentieqiao/121031-tBuCCH for dim
DATIM	2012-10-31 10:07:25
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16400
FREQU	32552.08 Hz
SCANS	16
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	C6D5CD3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	16

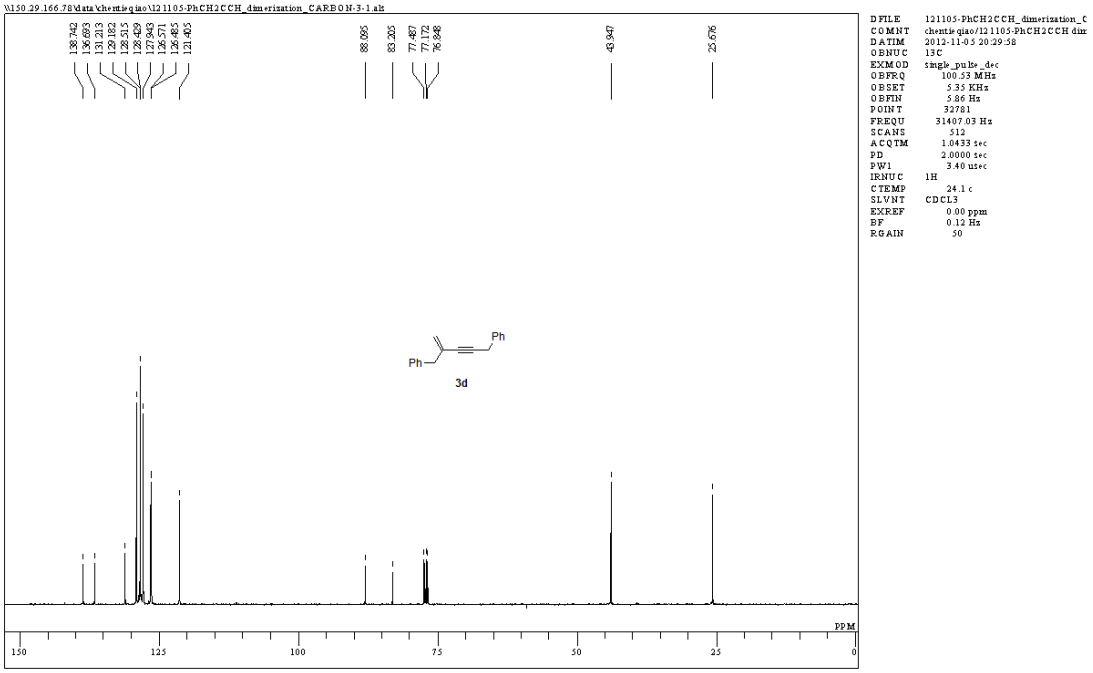
chentieqiao/121105-PhCH2CCH dimerization

C:\Documents and Settings\delta\My Documents\files\data\chentieqiao\121105-PhCH2CCH_dimerization_PROTON-3-1.als

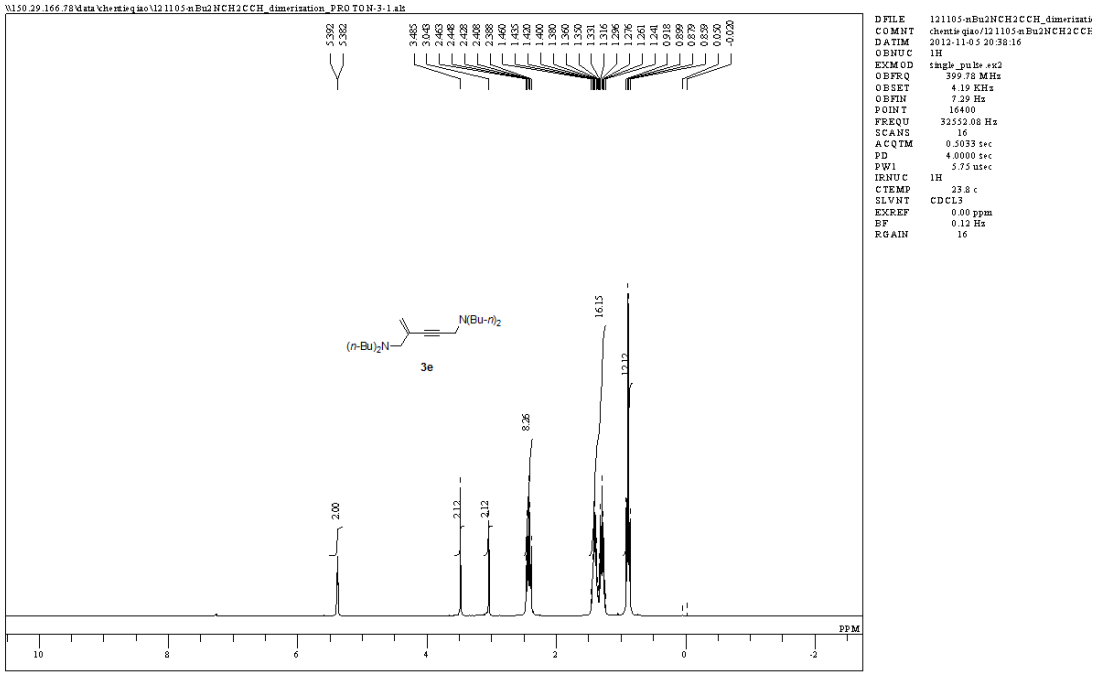


DFILE	121105-PhCH2CCH_dimerization_PROTO
COMNT	chentieqiao/121105-PhCH2CCH dimerizati
DATIM	05-11-2012 20:00:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16400
FREQU	32552.08 Hz
SCANS	16
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	22

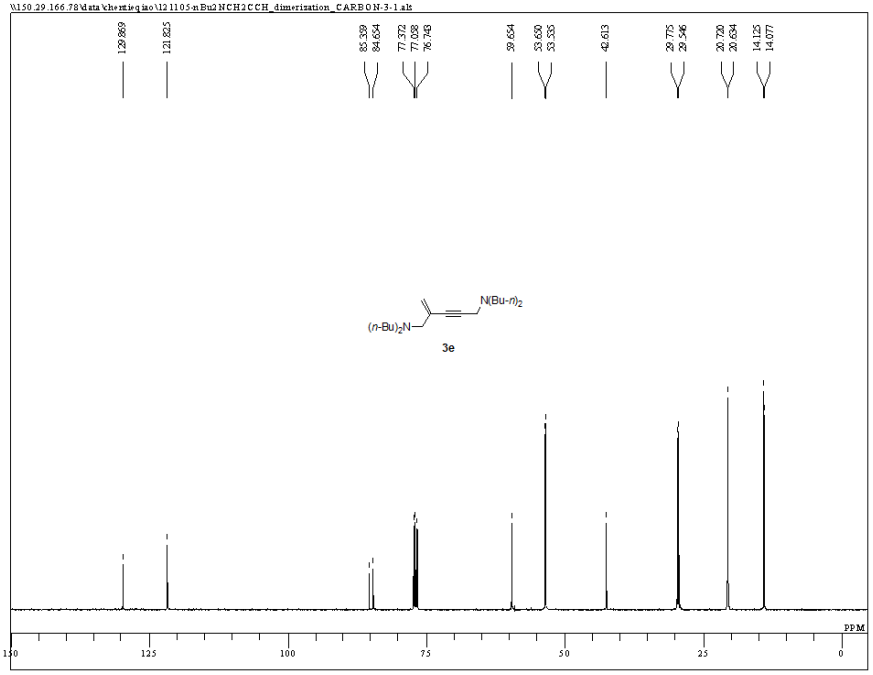
chentieqiao/121105-PhCH2CCH dimerization



chentieqiao/121105-nBu2NCH2CCH dimerization

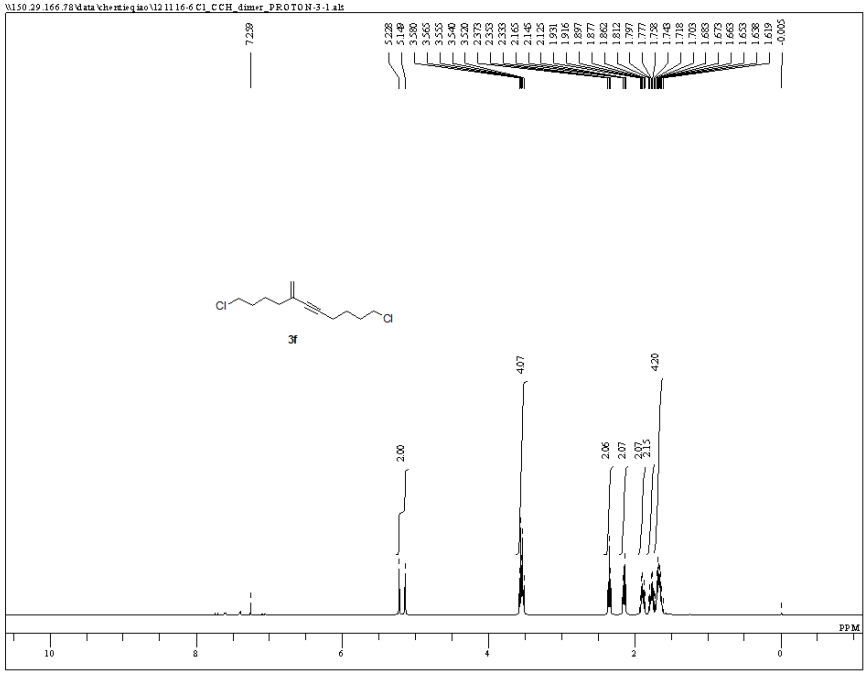


chentieqiao/121105-nBu2NCH2CCH dimerization



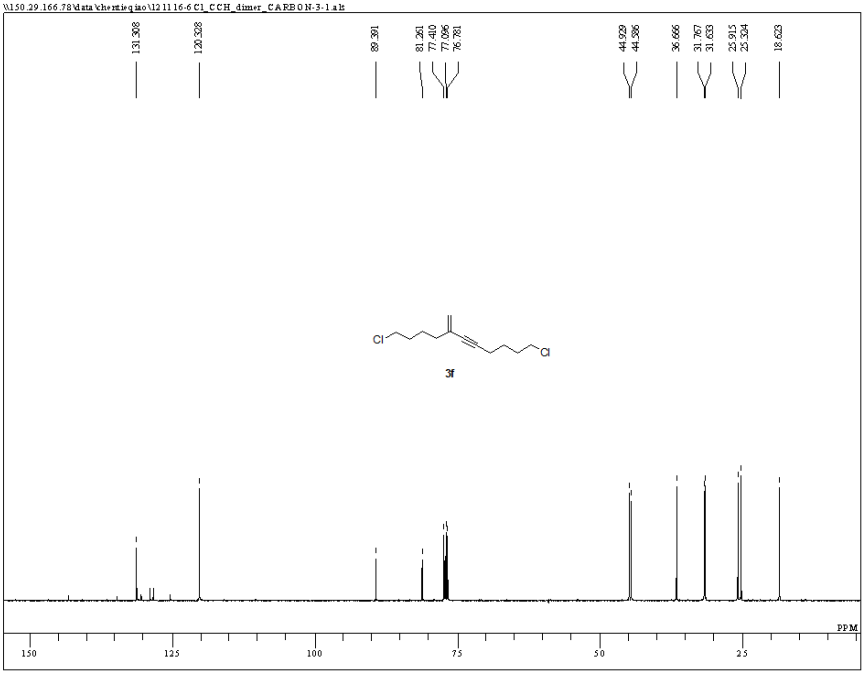
DFILE 121105-nBu2NCH2CCH_dimerizati
COMNT chentieqiao/121105-nBu2NCH2CCH
DATIM 2012-11-05 21:05:04
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32781
FREQU 31407.03 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

chentieqiao/121116-6Cl CCH dimer



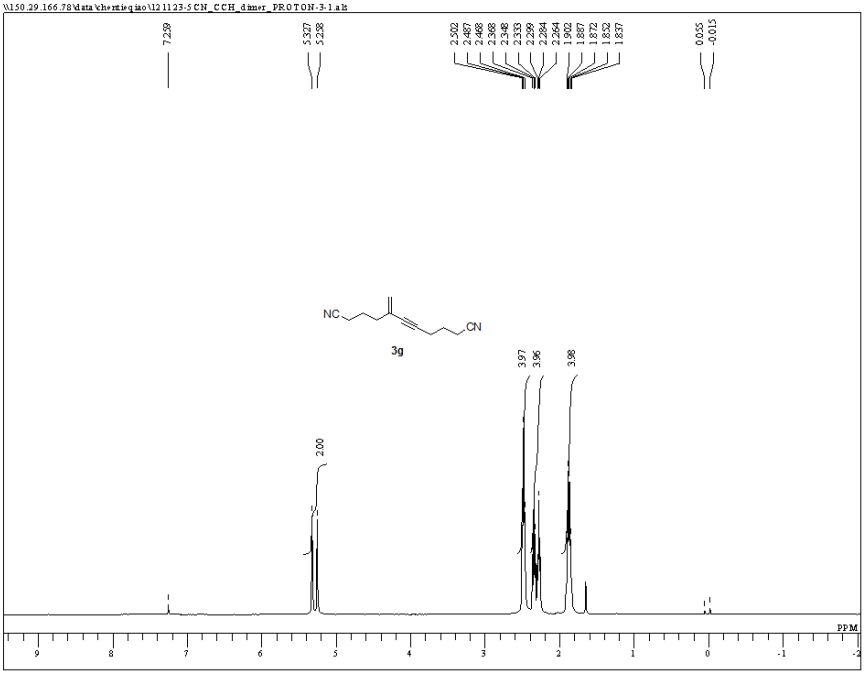
DFILE 121116-6Cl_CCH_dimer_PROTON-
COMNT chentieqiao/121116-6Cl CCH dimer
DATIM 2012-11-16 15:29:04
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 32552.08 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20

chentieqiao/121116-6Cl CCH dimer



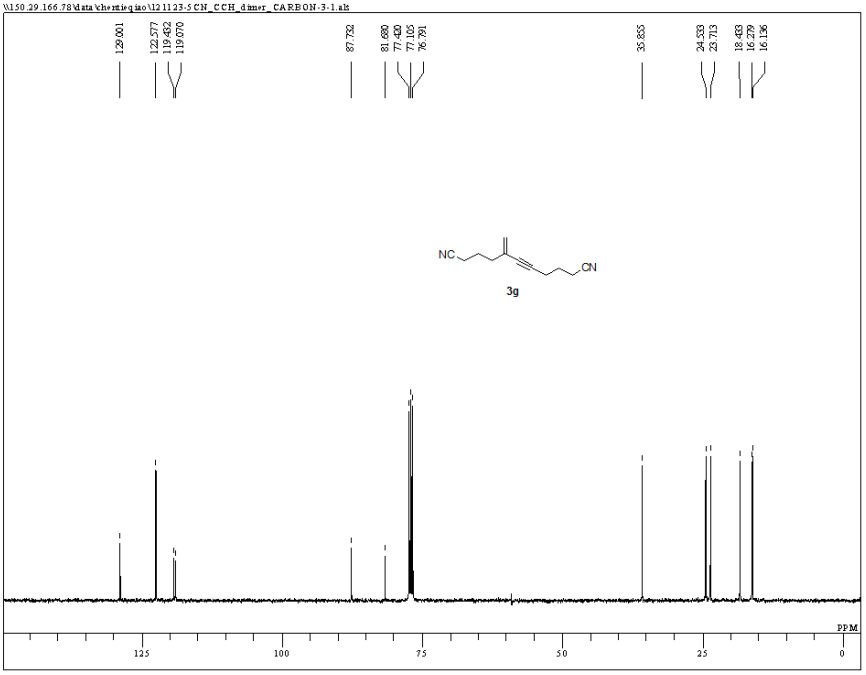
DFILE 121116-6Cl_CCH_dimer_CARBON
COMNT chentieqiao/121116-6Cl CCH dimer
DATIM 2012-11-16 15:42:50
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32781
FREQU 31407.03 Hz
SCANS 256
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 0.00 ppm
EF 0.12 Hz
RGAIN 50

chentieqiao/121123-5CN CCH dimer



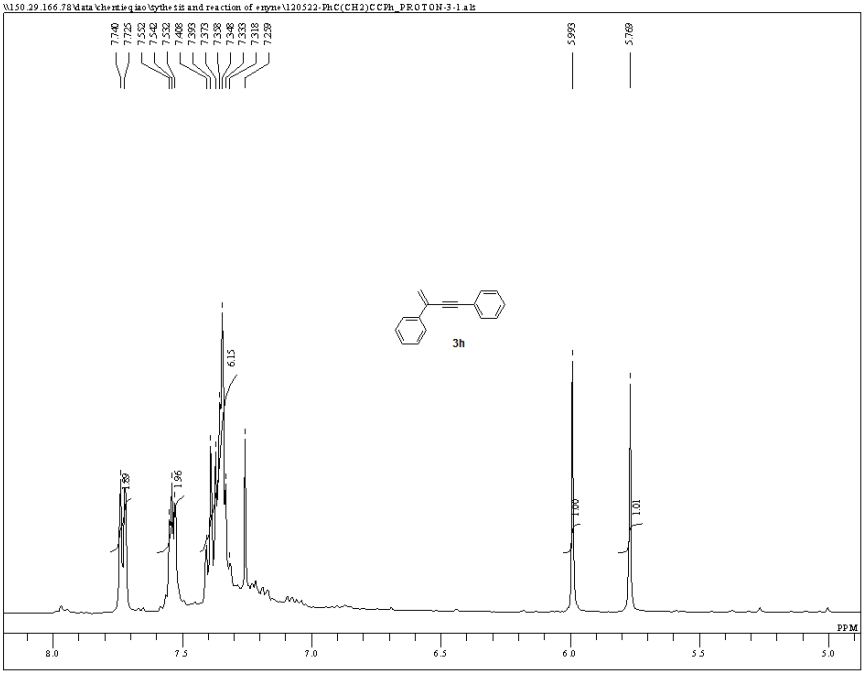
DFILE 121123-5CN_CCH_dimer_PROTON
COMNT chentieqiao/121123-5CN CCH dimer
DATIM 2012-11-23 18:21:12
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 32552.08 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 400.4 c
SLVNT CDCL3
EXREF 0.00 ppm
EF 0.12 Hz
RGAIN 30

chentieqiao/121123-5CN CCH dimer



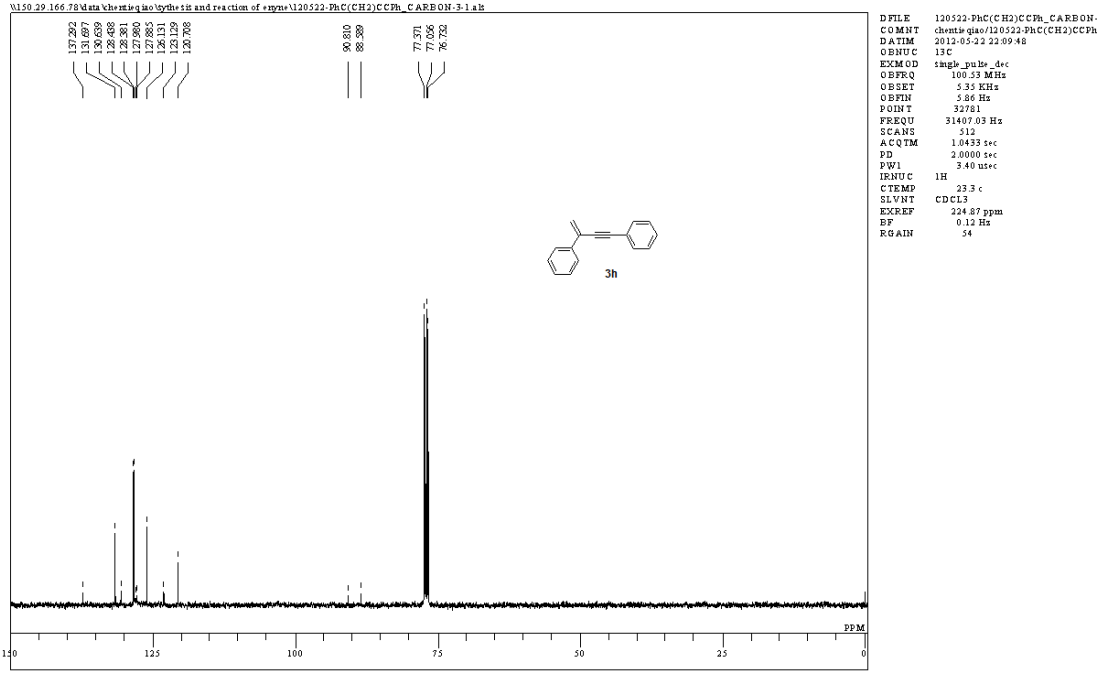
DFILE	121123-5CN_CCH_dimer_CARBO
COMNT	chentieqiao/121123-5CN CCH dime
DATIM	2012-11-23 18:49:10
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32781
FREQU	31407.03 Hz
SCANS	512
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	400.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50

chentieqiao/120522-PhC(CH2)CCPh

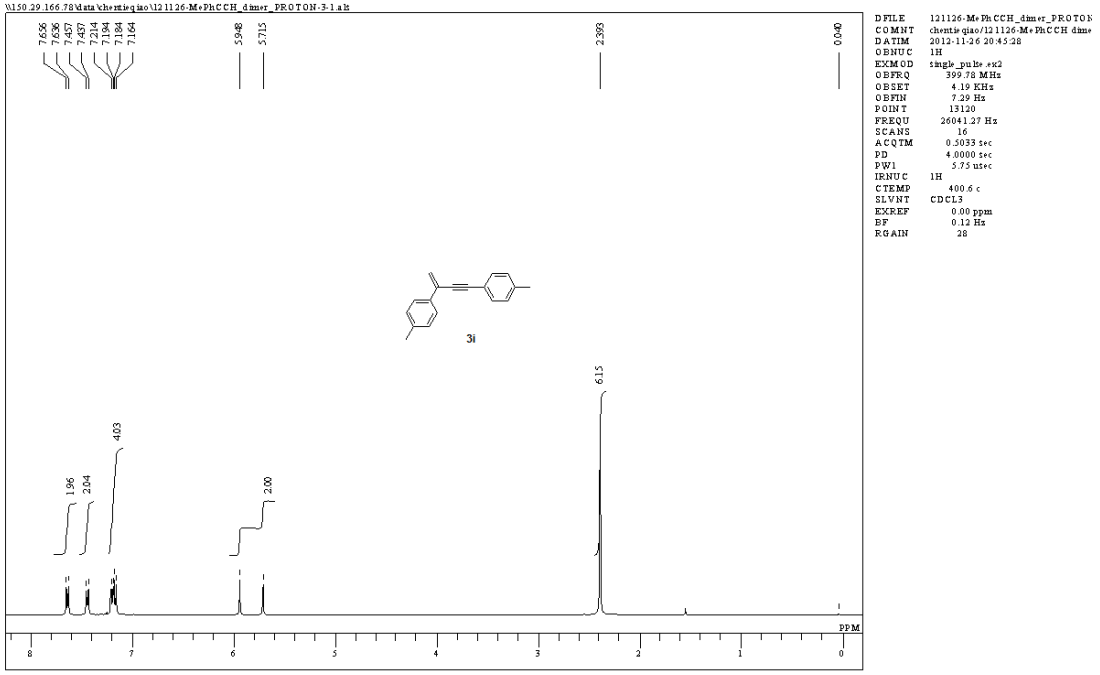


DFILE	120522-PhC(CH2)CCPh_PROTON-
COMNT	chentieqiao/120522-PhC(CH2)CCPh
DATIM	2012-05-22 21:41:57
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16400
FREQU	32552.08 Hz
SCANS	32
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	32

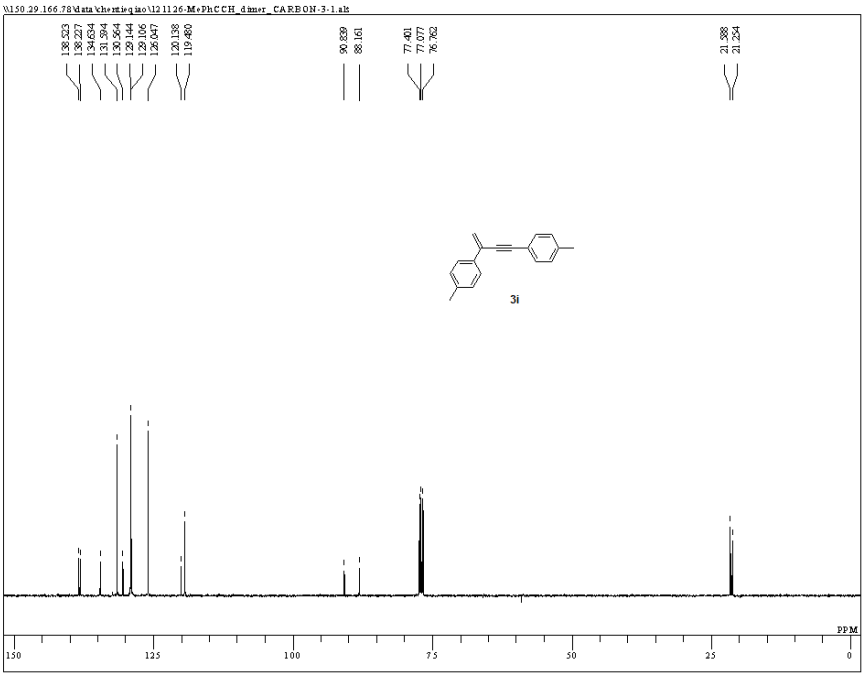
chentieqiao/120522-PhC(CH2)CCPh



chentieqiao/121126-MePhCCH dimer

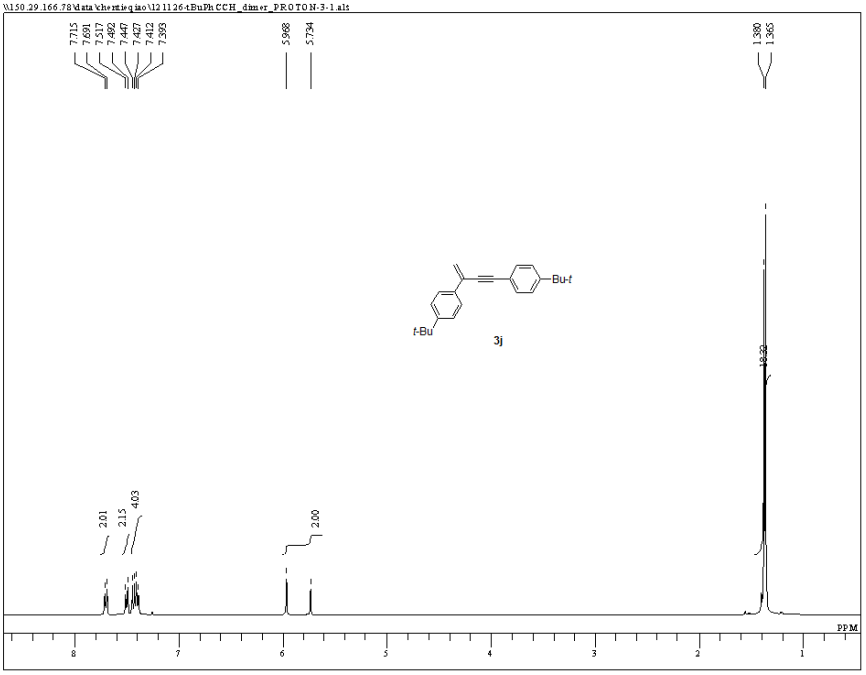


chentieqiao/121126-MePhCCH dimer



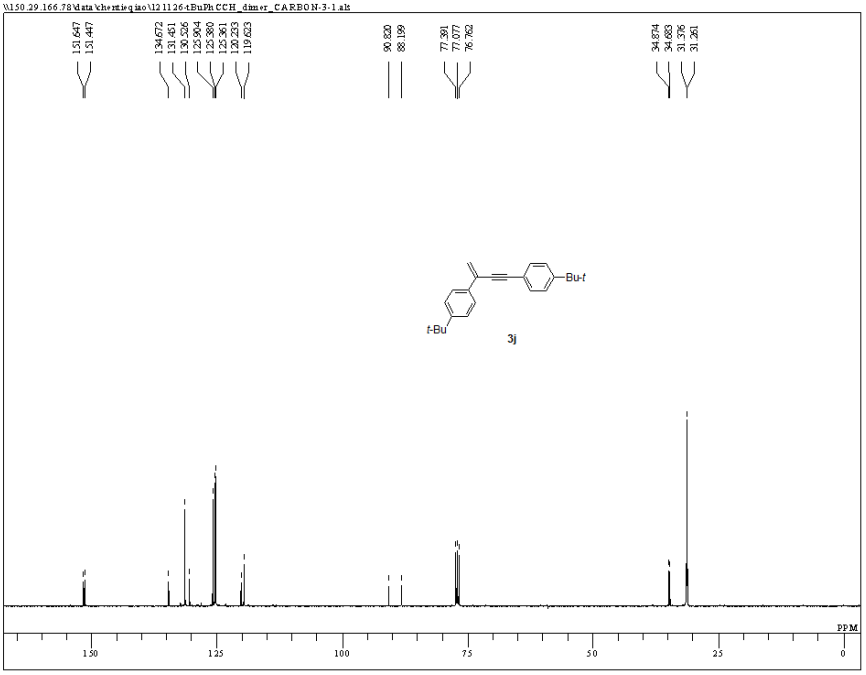
DFILE 121126-MePhCCH_dimer_CARBO
COMNT chentieqiao/121126-MePhCCH dime
DATIM 2012-11-26 21:12:33
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.24 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 400.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48

chentieqiao/121126-tBuPhCCH dimer



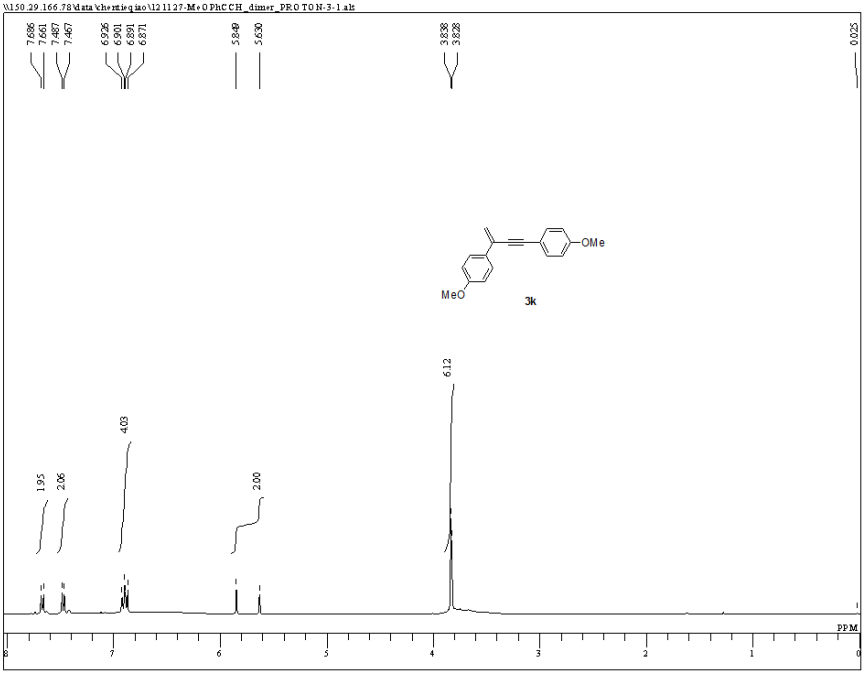
DFILE 121126-tBuPhCCH_dimer_PROTO
COMNT chentieqiao/121126-tBuPhCCH dime
DATIM 2012-11-26 20:10:15
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13120
FREQU 26041.27 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 400.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22

chentieqiao/121126-tBuPhCCH dimer



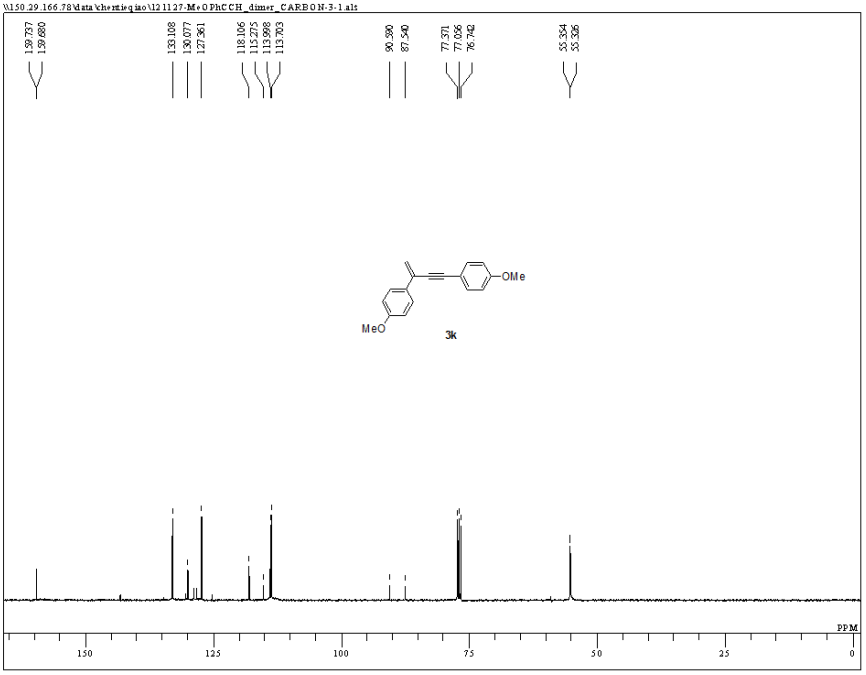

```
DFILE     121126-tBuPhCCH_dimer_CARBO
COMNT     chentieqiao/121126-tBuPhCCH dime
DATIM     2012-11-26 20:37:19
OBNUC     13C
EXMOD     single_pulse_dec
OBFRQ       100.53 MHz
OBSET         5.35 KHz
OBFIN         5.86 Hz
POINT        26224
FREQU        25125.24 Hz
SCANS          512
ACQTM         1.0433 sec
PD            2.0000 sec
PW1           3.40 usec
IRNUC     1H
CTEMP       400.6 c
SLVNT     CDCL3
EXREF         0.00 ppm
EF            0.12 Hz
RGAIN          48
```

chentieqiao/121127-MeOPhCCH dimer



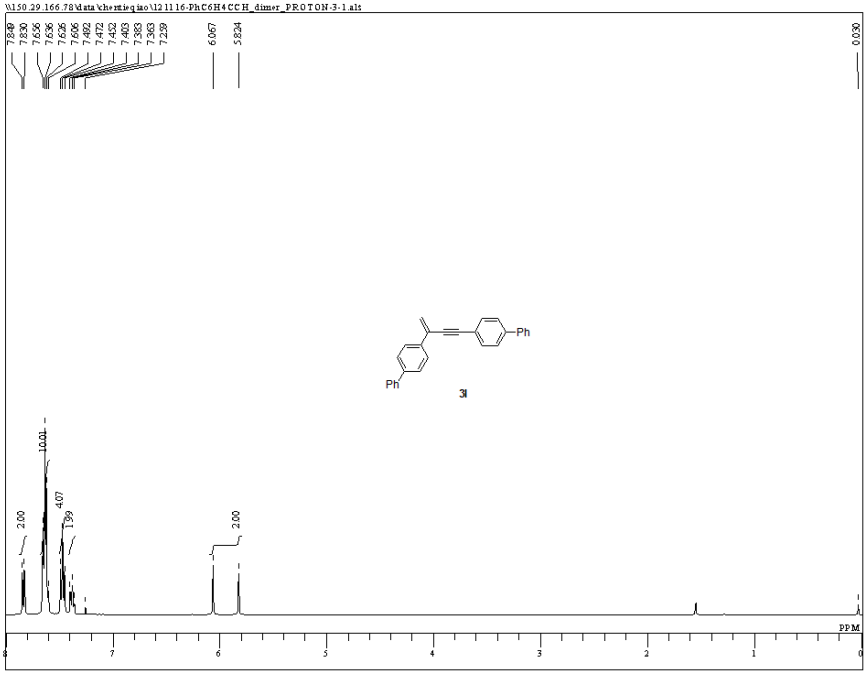

```
DFILE     121127-MeOPhCCH_dimer_PROTO
COMNT     chentieqiao/121127-MeOPhCCH dim
DATIM     2012-11-27 21:59:17
OBNUC     1H
EXMOD     single_pulse.exp
OBFRQ       399.78 MHz
OBSET         4.19 KHz
OBFIN         7.29 Hz
POINT        13120
FREQU        26041.27 Hz
SCANS          16
ACQTM         0.5033 sec
PD            4.0000 sec
PW1           5.75 usec
IRNUC     1H
CTEMP       400.4 c
SLVNT     CDCL3
EXREF         0.00 ppm
EF            0.12 Hz
RGAIN          26
```

chentieqiao/121127-MeOPhCCH dimer



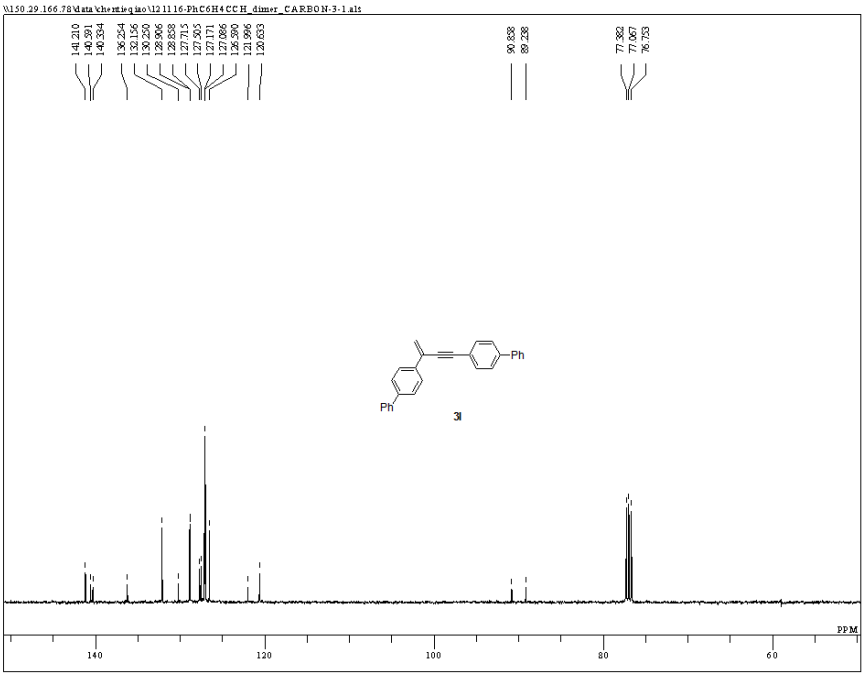
DFILE 121127-MeOPhCCH_dimer_CARBO
COMNT chentieqiao/121127-MeOPhCCH dim
DATIM 2012-11-27 22:29:56
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.24 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 400.4 c
SLVNT CDCL3
EXREF 224.83 ppm
EF 0.12 Hz
RGAIN 48

chentieqiao/121116-PhC6H4CCH dimer



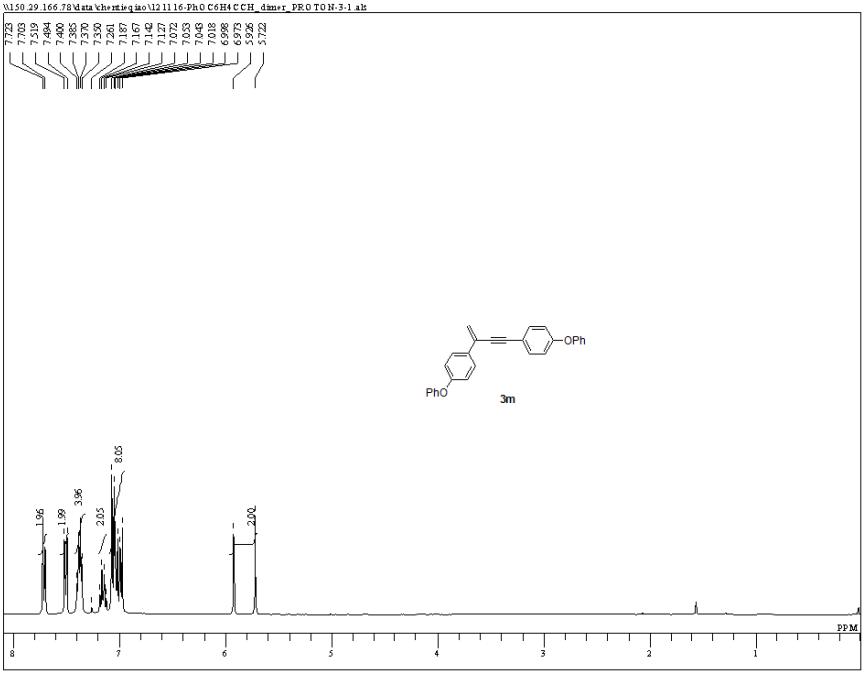
DFILE 121116-PhC6H4CCH_dimer_PROT
COMNT chentieqiao/121116-PhC6H4CCH di
DATIM 2012-11-16 13:05:59
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 32552.08 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
EF 0.12 Hz
RGAIN 30

chentieqiao/121116-PhC6H4CCH dimer



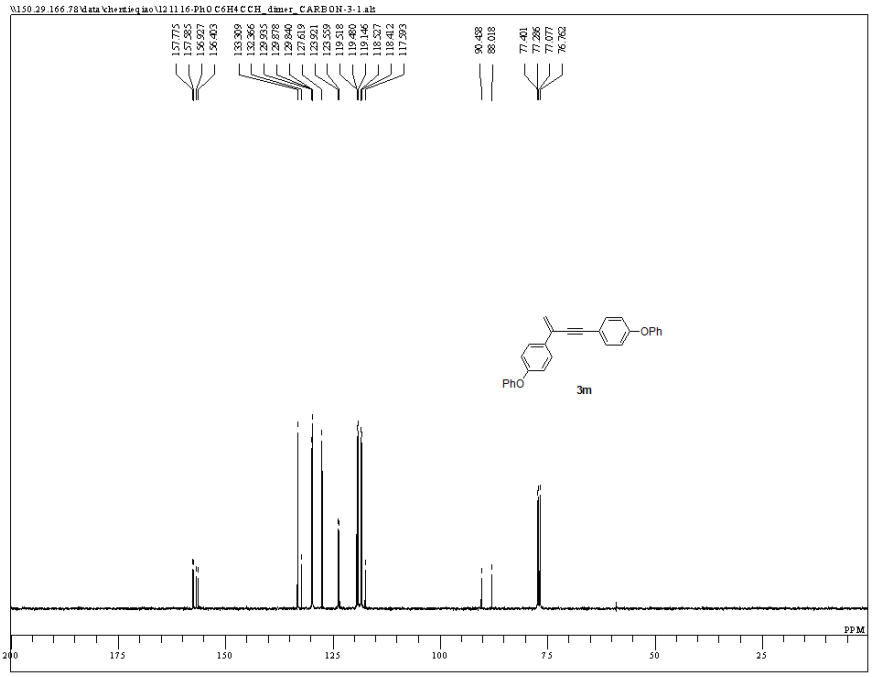
DFILE 121116-PhC6H4CCH_dimer_CARB
COMNT chentieqiao/121116-PhC6H4CCH di
DATIM 2012-11-16 15:20:39
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32781
FREQU 31407.03 Hz
SCANS 256
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50

chentieqiao/121116-PhOC6H4CCH dimer



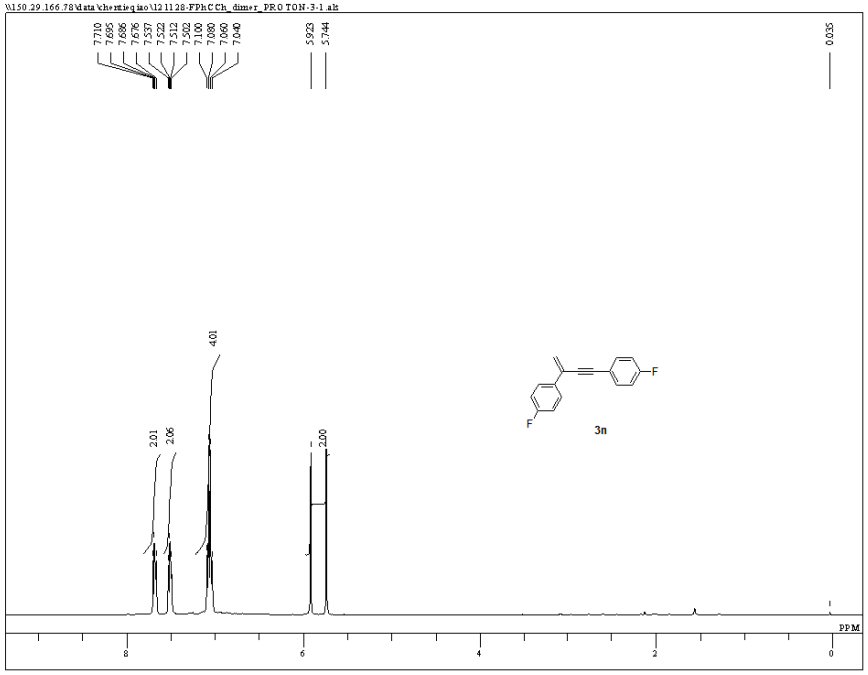
DFILE 121116-PhOC6H4CCH_dimer_PRO
COMNT chentieqiao/121116-PhOC6H4CCH
DATIM 2012-11-16 20:24:04
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 32552.08 Hz
SCANS 16
ACQTM 0.5033 sec
PD 4.0000 sec
PW1 5.75 usec
IRNUC 1H
CTEMP 400.5 c
SLVNT CDCL3
EXREF 37.55 ppm
BF 0.12 Hz
RGAIN 28

chentieqiao/121116-PhOC6H4CCH dimer



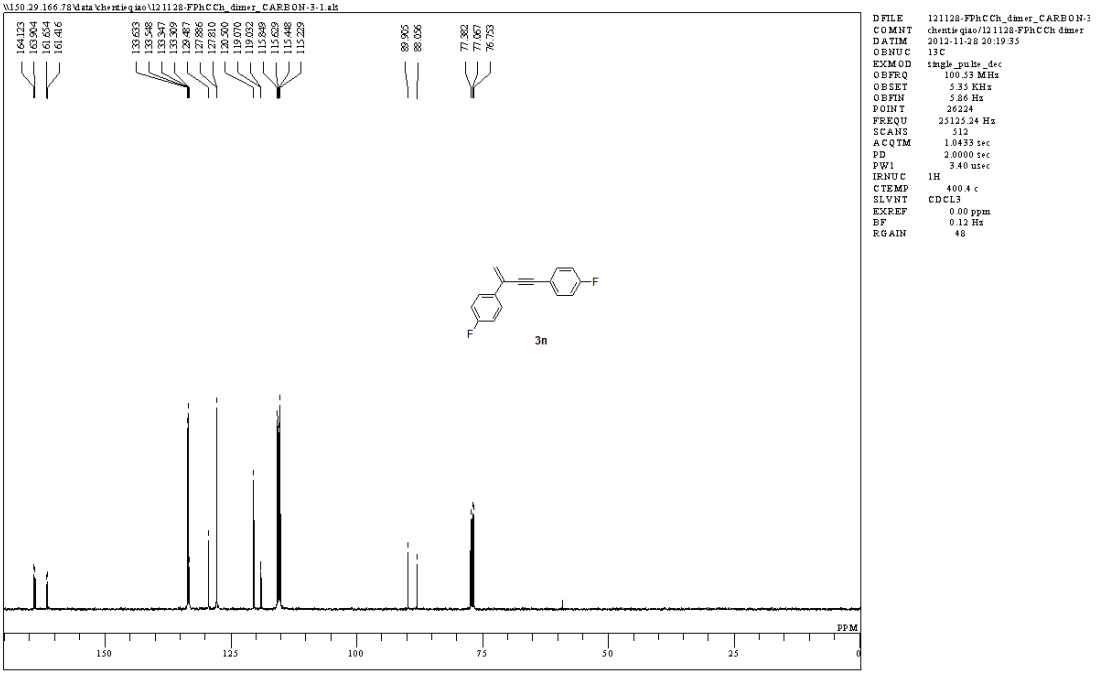
DFILE	121116-PhOC6H4CCH_dimer_CAR
COMNT	chentieqiao/121116-PhOC6H4CCH
DATIM	2012-11-16 20:55:02
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32781
FREQU	31407.03 Hz
SCANS	512
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	400.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	48

chentieqiao/121128-FPhCCh dimer



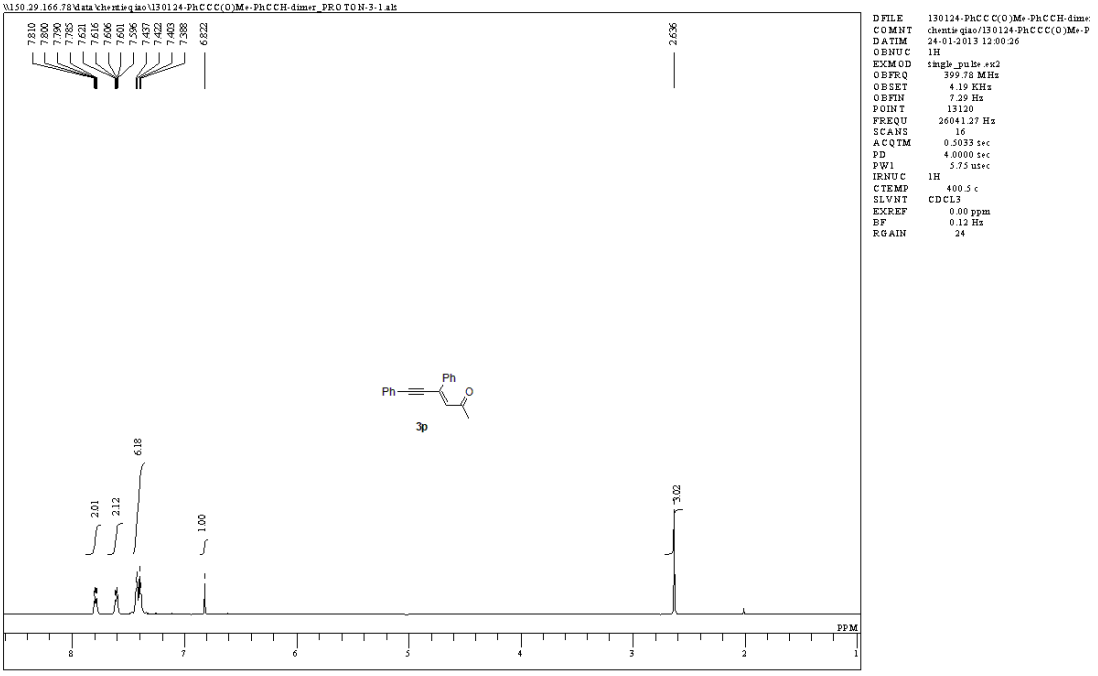
DFILE	121128-FPhCCh_dimer_PROTON-3
COMNT	chentieqiao/121128-FPhCCh dimer
DATIM	2012-11-28 19:52:38
OBNUC	1H
EXMOD	single_pulse.exp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13120
FREQU	26041.27 Hz
SCANS	16
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	400.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	26

chentieqiao/121128-FPhCCh dimer



DFILE	121128-FPhCCh_dimer_CARBON-3
COMNT	chentieqiao/121128-FPhCCh dimer
DATIM	2012-11-28 20:19:35
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26224
FREQU	25125.24 Hz
SCANS	512
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	400.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
EF	0.12 Hz
RGAIN	48

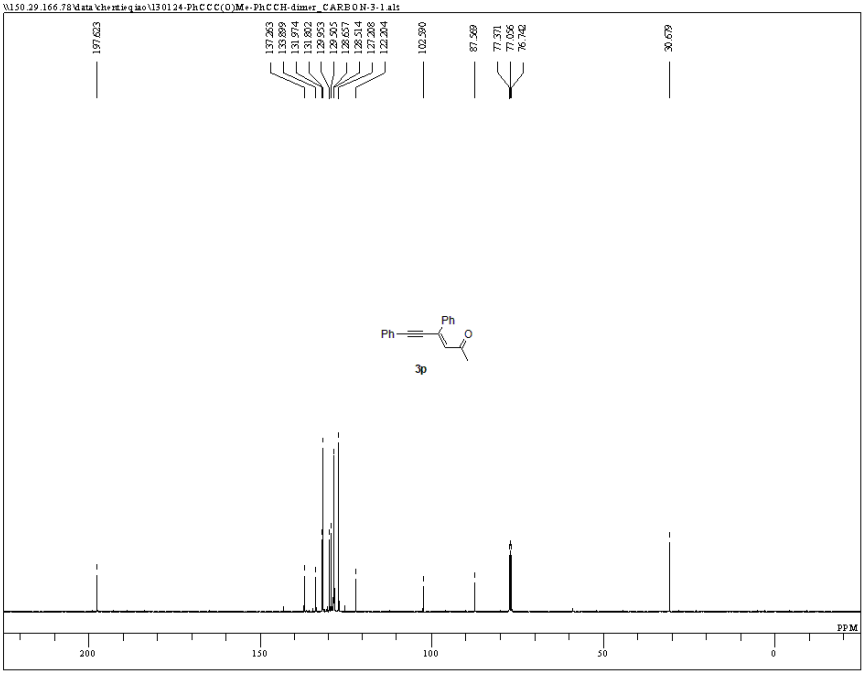
chentieqiao/130124-PhCCC(O)Me-PhCCH-dimer



DFILE	130124-PhCCC(O)Me-PhCCH-dime
COMNT	chentieqiao/130124-PhCCC(O)Me-P
DATIM	24-01-2013 12:00:26
OBNUC	1H
EXMOD	single_pulse.exp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13120
FREQU	26041.27 Hz
SCANS	16
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	400.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
EF	0.12 Hz
RGAIN	24

chentieqiao/130124-PhCCC(O)Me-PhCCH-dimer

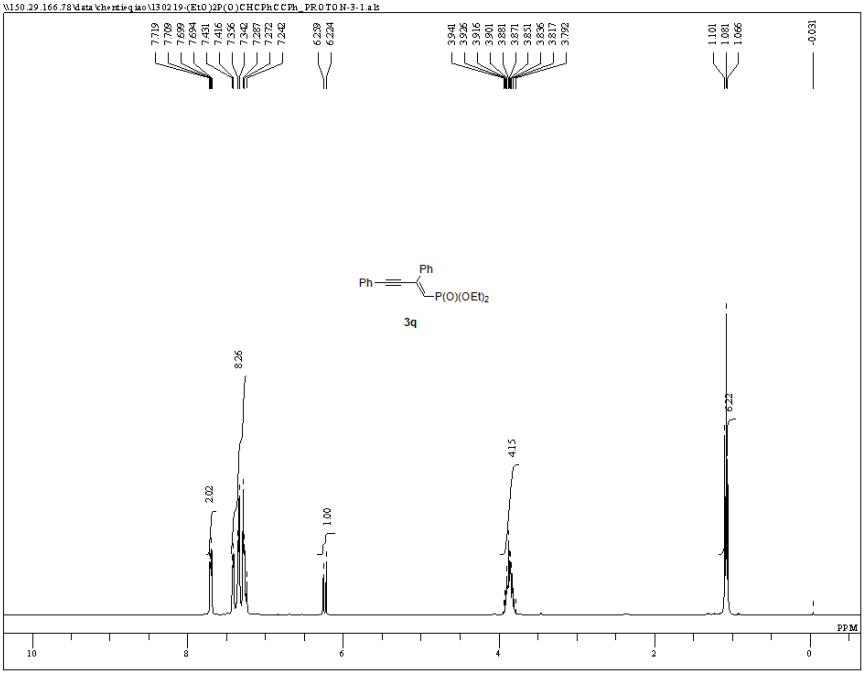
\\150.29.166.78\data\chentieqiao\130124-PhCCC(O)Me-PhCCH-dimer_CARBON-3-1.alt



DFILE	130124-PhCCC(O)Me-PhCCH-dime
COMNT	chentieqiao/130124-PhCCC(O)Me-P
DATIM	2013-01-24 10:42:04
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26224
FREQU	25125.24 Hz
SCANS	256
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	400.6 c
SLVNT	CDCL3
EXREF	224.74 ppm
BF	0.12 Hz
RGAIN	48

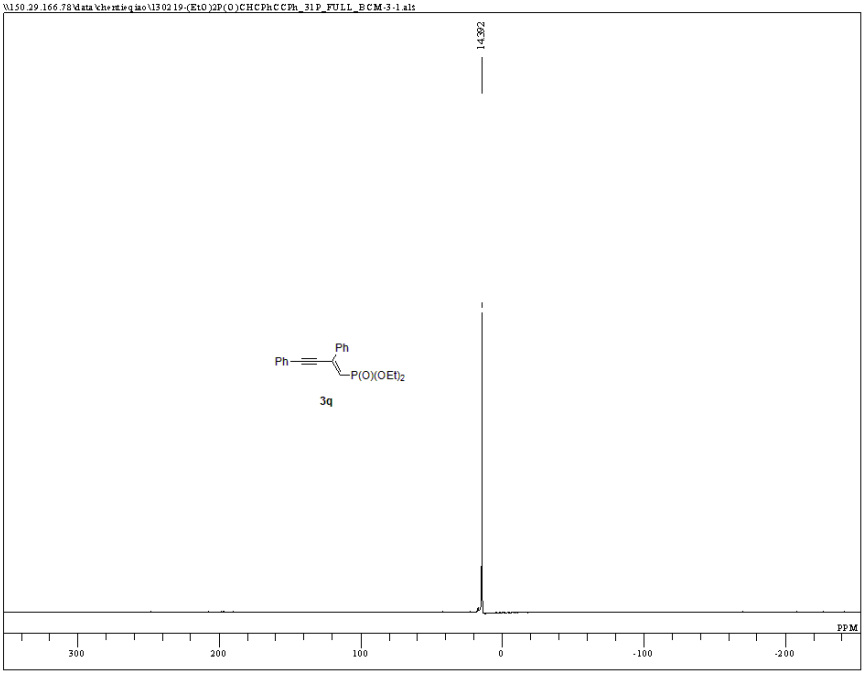
chentieqiao/130219-(EtO)2P(O)CHCPhCCPh

\\150.29.166.78\data\chentieqiao\130219-(EtO)2P(O)CHCPhCCPh_PROTON-3-1.alt



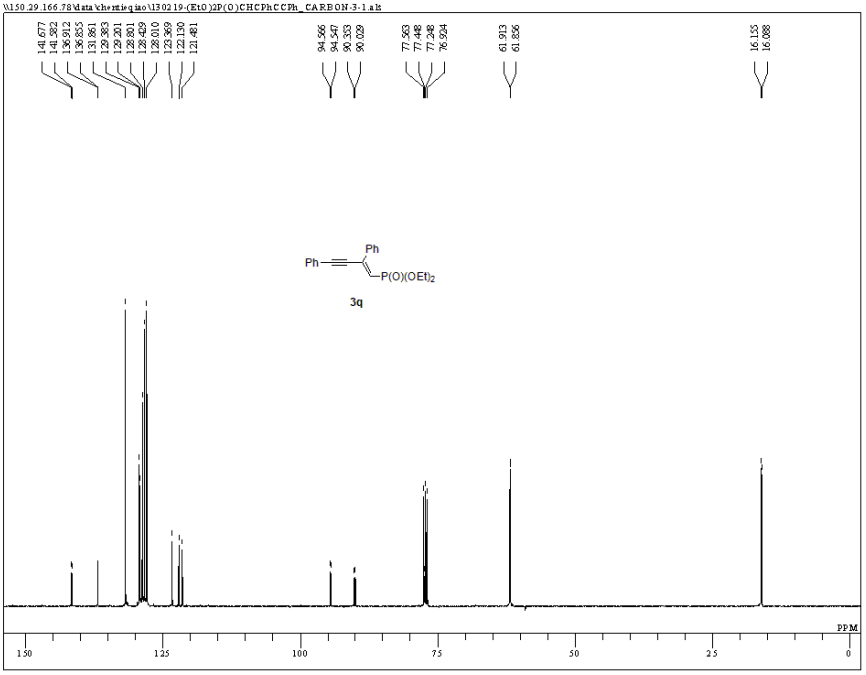
DFILE	130219-(EtO)2P(O)CHCPhCCPh_PI
COMNT	chentieqiao/130219-(EtO)2P(O)CHC
DATIM	2013-02-19 17:48:21
OBNUC	1H
EXMOD	single_pulse.exp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16400
FREQU	32552.08 Hz
SCANS	16
ACQTM	0.5033 sec
PD	4.0000 sec
PW1	5.75 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	12.50 ppm
BF	0.12 Hz
RGAIN	18

chentieqiao/130219-(EtO)2P(O)CHCPhCCPh



DFILE	130219-(EtO)2P(O)CHCPhCCPh_31
COMNT	chentieqiao/130219-(EtO)2P(O)CHC
DATIM	2013-02-19 18:20:44
OBNUC	31P
EXMOD	single_pulse_dec
OBFRQ	161.84 MHz
OBSET	2.78 KHz
OBFIN	4.82 Hz
POINT	32781
FREQU	122549.03 Hz
SCANS	128
ACQTM	0.2674 sec
PD	2.0000 sec
PW1	3.43 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46

chentieqiao/130219-(EtO)2P(O)CHCPhCCPh



DFILE	130219-(EtO)2P(O)CHCPhCCPh_C.
COMNT	chentieqiao/130219-(EtO)2P(O)CHC
DATIM	2013-02-19 20:25:48
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32781
FREQU	31407.03 Hz
SCANS	512
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	48

I. CheckCIF / PLATON report

1. CheckCIF / PLATON report of complex 2a.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: hanchen2aa

Bond precision: C-C = 0.0050 A Wavelength=0.71073

Cell: a=18.456(3) b=14.233(2) c=12.5508(19)
alpha=90 beta=90 gamma=90
Temperature: 183 K

	Calculated	Reported
Volume	3296.9(9)	3296.9(9)
Space group	P c a 21	Pca2(1)
Hall group	P 2c -2ac	?
Moiety formula	C32 H47 O2 P3 Pd	?
Sum formula	C32 H47 O2 P3 Pd	C32 H47 O2 P3 Pd
Mr	663.01	663.01
Dx,g cm-3	1.336	1.336
Z	4	4
Mu (mm-1)	0.734	0.734
F000	1384.0	1384.0
F000'	1381.63	
h,k,lmax	23,18,16	23,18,16
Nref	3968[7578]	7483
Tmin,Tmax	0.753,0.929	0.758,0.930
Tmin'	0.738	

Correction method= MULTI-SCAN

Data completeness= 1.89/0.99 Theta(max)= 27.500

R(reflections)= 0.0241(6950) wR2(reflections)= 0.0610(7483)

S = 1.022 Npar= 349

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
PLAT230_ALERT_2_C Hirshfeld Test Diff for P1 -- C27 .. 5.7 su

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites ....          4
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF          ?
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......          6
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

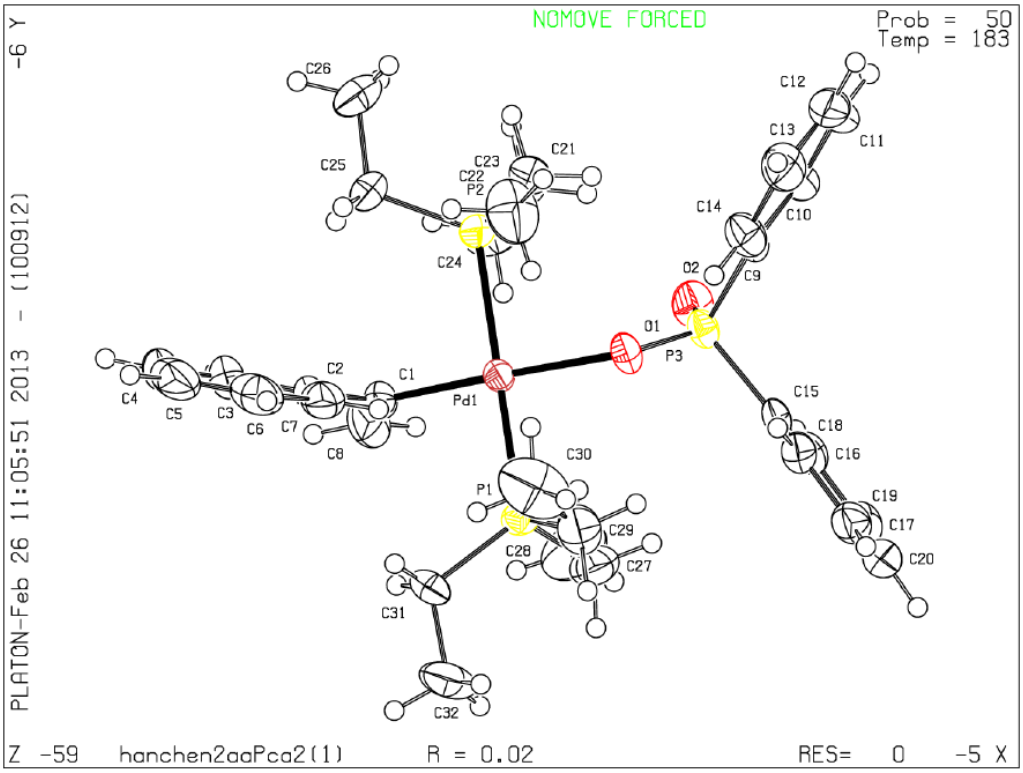
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock hanchen2aa - ellipsoid plot



2. CheckCIF / PLATON report of complex 1f.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: hanchenpd

Bond precision: C-C = 0.0063 A Wavelength=0.71073

Cell: a=11.7501(14) b=14.1473(17) c=18.600(2)
alpha=90 beta=101.676(1) gamma=90
Temperature: 93 K

	Calculated	Reported
Volume	3027.9(6)	3028.0(6)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C30 H46 O2 P2 Pd	?
Sum formula	C30 H46 O2 P2 Pd	C30 H46 O2 P2 Pd
Mr	607.01	607.01
Dx,g cm-3	1.332	1.332
Z	4	4
Mu (mm-1)	0.742	0.742
F000	1272.0	1272.0
F000'	1269.20	
h,k,lmax	13,16,22	13,16,22
Nref	5319	5280
Tmin,Tmax	0.915,0.928	0.896,0.929
Tmin'	0.895	

Correction method= MULTI-SCAN

Data completeness= 0.993 Theta(max)= 25.000

R(reflections)= 0.0607(3772) wR2(reflections)= 0.0777(5280)

S = 1.255 Npar= 316

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.8 Ratio

Alert level C

```
PLAT222_ALERT_3_C Large Non-Solvent    H    Uiso(max)/Uiso(min) ..        4.7 Ratio
```

Alert level G

```
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF          ?
PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c   .......      P21/n
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C2     -   C3     ...       1.46 Ang.
```

```
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   1 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock hanchenpd - ellipsoid plot