Supplementary Material (ESI) for Chemical Communications
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Exploitation of an unprecedented silica-promoted acetylene-allene rearrangement for the preparation of *C,C*-diacetylenic phosphaalkenes

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Supporting Information

Contents

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General Procedure All reactions were performed under argon using Schlenk techniques. Diethyl ether and THF were freshly distilled from sodium/benzophenone prior to use. ^{1}H, ^{13}C and ^{31}P spectra were recorded on a JEOL 400 MHz spectrometer. Chemical shifts (ppm) were reported and referenced to the internal signal of residual protic solvent. UV-Vis spectroscopy was performed on a Varian Cary 5000 instrument. Cyclic voltammetry (CV) was carried out using a computer-controlled potentiostat (Autolab) and a standard three electrode arrangement. All electrochemical measurements were carried out in Ar-purged dry dichloromethane with 100 mM Bu_4NPF_4 as the supporting electrolyte. The working electrode was a glassy carbon disc (diameter 3 mm). Potentials were measured *vs*. a Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in CH_3CN) with the ferrocenium/ferrocene ($Fc^{+/0}$) as internal standard. Preparative HPLC was performed on Dionex Ultimate 3000 system on a C18 column (15×21.2 mm, 10 μ) with a solvent mixture of THF and methanol as eluent. High resolution mass spectral analyses (HRMS) were performed on high resolution ESI–FTICR mass spectrometer (Varian 7.0 T).

Experimental section

Synthesis of 2a and 2b To a solution of alcohol **1**[1] (1.15 g, 5 mmol) in 50 ml dry Et_2O was added thionyl chloride (2.4 g, 20 mmol) dropwise at room temperature (20 °C). Then 2 drops of DMF were added as catalyst. The reaction was allowed to stir at room temperature for 2–3 hours. When all starting material was consumed (as judged by TLC), the reaction mixture was poured into a vigorously stirred mixture of ice water and hexane (30 ml /120 ml). The organic phase was separated and washed with sat. aq. Na_2CO_3, H_2O and brine, then dried over $MgSO_4$ and concentrated in *vacuo*. (**2a**/**2b** = 10/1, by NMR). The residue was allowed to pass through a chromatographic column filled with silica gel (hexane as eluent), affording allene **2b** as the sole product. (880 mg, 72 %) **2b**: colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 0.26 (s, 9H), 5.77 (s, 1H), 7.31–7.32 (m, 3H), 7.44–7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100MHz) δ = –2.3, 80.2, 81.1, 93.5, 100.8, 122.9, 128.3, 128.5, 131.6, 211.7. IR (hexane): 1375, 1445, 1963, 2187, 2841, 2929. EI MS (70 eV): *m*/*z* (%) 211.1 (100 %)[*M-Cl*], 246.1 (15 %)$[M]^+$**.** Compound **2b** is presumably a racemic mixture and unstable in its pure form, but stable in hexane solution when kept in the freezer under inert atmosphere.

Synthesis of 3b: To a solution of supermesityl bromide (325 mg, 1 mmol) in dry THF (10 ml) was added *n*-BuLi (0.5 ml, 1.25 mmol, 2.5 M in hexane) at –78 °C. The solution was allowed to stir for 5 min before PCl_3 (0.3 ml, 3 mmol) was added in one portion. The reaction mixture was then heated to 50 °C. After stirring for 3 hours, the volatiles of the reaction mixture were removed under *vacuo*. Then, a solution of **2b** (295 mg, 1.2 mmol, freshly purified) in THF (15 ml) was added to the flask of the aforementioned residue under argon. After cooling to –98 °C, a solution of freshly prepared LDA (2.5 mol) in THF (10 ml) was added to this resulting mixture. The reaction mixture was allowed to stir for 20 min at -98 °C and gradually warmed to room temperature within another 30 min. The reaction was quenched by addition of NH_4Cl (aq.), diluted with hexane and washed with water and brine. The hexane layer was dried over Na_2SO_4 and concentrated in *vacuo*. After purification by column chromatography on silica gel (hexane as eluent), ***E/Z*** isomer mixture of **3b** was obtained as light yellow solid. (265 mg, total yield: 55 %, ***E*-3b**/***Z*-3b** = $\tilde{3}$/1, estimated by ^{31}P–NMR). The isomers were separated by preparative HPLC. (Phenomenex® Gemini 110A C18, methanol:THF = 95:5, flow rate 2.5 ml/min) 254 nm, $t_{Z\text{-}3b}$ = 25.4 min and $t_{E\text{-}3b}$ = 28.5 min).

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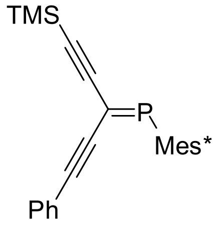
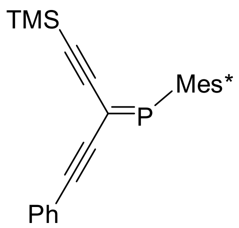
[1] K. A. Tallman, J. B. Roschek, N. A. Porter, *J. Am. Chem. Soc.* 2004, **126**, 9240-9247.

Compound *E*-3b:



Light yellow solid. mp 136 °C (from methanol). ^{1}H NMR ($CDCl_3$, 400MHz) δ = 0.28 (s, 9H), 1.32 (s, 9H), 1.52 (s, 18H), 6.86 (*d* , J = 7.2 Hz, 2H), 7.13–7.18 (m, 3H), 7.48 (s, 2H). ^{13}C NMR ($CDCl_3$, 100MHz) δ = 0.03, 31.4, 33.2 (*d*, J(P,C) = 6.3 Hz), 35.1, 38.2, 89.2 (*d*, J(P,C) = 20.2 Hz), 101.2 (*d*, J(P,C) = 14.9 Hz), 103.3 (*d*, J(P,C) = 9.5 Hz), 104.1 (*d*, J(P,C) = 25.4 Hz), 122.3, 123.2 (*d*, J(P,C) = 6.3 Hz), 128.0, 128.2 (d, J(P,C) = 1.9 Hz), 131.4 (*d*, J(P,C) = 3.7 Hz), 135.1 (*d*, ^{1}J(P,C) = 57.6 Hz), 141.5 (*d*, ^{1}J(P,C) = 35.7 Hz), 150.7, 154.3. ^{31}P NMR ($CDCl_3$, 162MHz) δ = 338.3 ppm. UV/Vis (CH_2Cl_2) λ/nm (ε [$M^{-1}cm^{-1}$]) 368 (15000), 276 (20000). IR (CH_2Cl_2): 1250, 1283, 1422, 2304, 2679, 2984. EI MS (70 eV): *m*/*z* (%) 486.14 (30 %)[M^+], 430.2 (15 %)[*M*H–*t*Bu]$^+$, 275.47 (100 %) [Mes*P]$^+$, 219.4 (24 %) [Mes*–2^{t}Bu]. HRMS (ESI) for $C_{32}H_{43}PSi$: Calcd for $[M+H]^+$ 487.2944, found 487.2944.

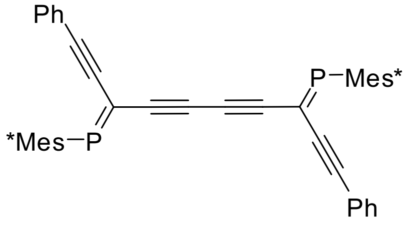
Compound *Z*-3b:



Light yellow solid. mp 147 °C (from methanol). ^{1}H NMR ($CDCl_3$, 400MHz) δ= –0.10 (s, 9H), 1.34 (s, 9H), 1.52 (s, 18H), 7.31–7.33 (m, 3H), 7.49 (s, 2H), 7.53–7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 100MHz) δ = -0.41, 31.4, 33.0 (*d*, J(P,C) = 6.3 Hz), 35.2, 38.3, 89.9 (*d*, J(P,C) = 26.2 Hz), 96.3 (*d*, J(P,C) = 16.5 Hz), 102.8 (*d*, J(P,C) = 18.4 Hz), 108.2 (*d*, J(P,C) = 9.4 Hz), 122.5, 123.3 (*d*, J(P,C) = 7.6 Hz), 128.2, 128.3 (d, J(P,C) = 1.9 Hz) 131.6 (*d*, J(P,C) = 5.7 Hz), 134.6 (*d*, ^{1}J(P,C) = 57.1 Hz), 141.0 (*d*, ^{1}J(P,C) = 35.5 Hz), 150.5, 153.7. ^{31}P NMR ($CDCl_3$, 162MHz) δ = 339.9 ppm. UV/Vis (CH_2Cl_2) λ/(nm) (ε [$M^{-1}cm^{-1}$]) 367 (15000), 277 (20500). IR (CH_2Cl_2) 1270, 1421, 2107, 2245, 2695, 2983. EI MS (70 eV): *m*/*z* (%) 486.46 (75 %)[M^+], 430.5 (15 %)[*M*H–*t*Bu]$^+$, 275.4 (100 %) [Mes*P]$^+$. 219.4 (20 %) [Mes*–2^{t}Bu]. HRMS (ESI) for $C_{32}H_{43}PSi$ Calcd for $[M+H]^+$ 487.2944, found 487.2946.

Synthesis of 4

To a solution of cupric acetate (45 mg, 0.25 mmol) and potassium carbonate (35 mg, 0.25 mmol) in pyridine/methanol (10 ml, v/v=1/1) was added a solution of ***E*-3b** (50 mg, 0.1 mmol) in ether and methanol (1 ml, v/v=1/1) dropwise at room temperature. The reaction progress was monitored by TLC. After 1h, the reaction was quenched by addition of water (2 ml), and extracted with three 20 ml portions of hexane. The combined hexane extracts were then washed with 0.1 N HCl (aq.), water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane to 2 % EtOAc in hexane as eluent), affording **4** as an orange solid (27 mg, 68 %). This solid was further recrystallized from CH_2Cl_2/CH_3OH.



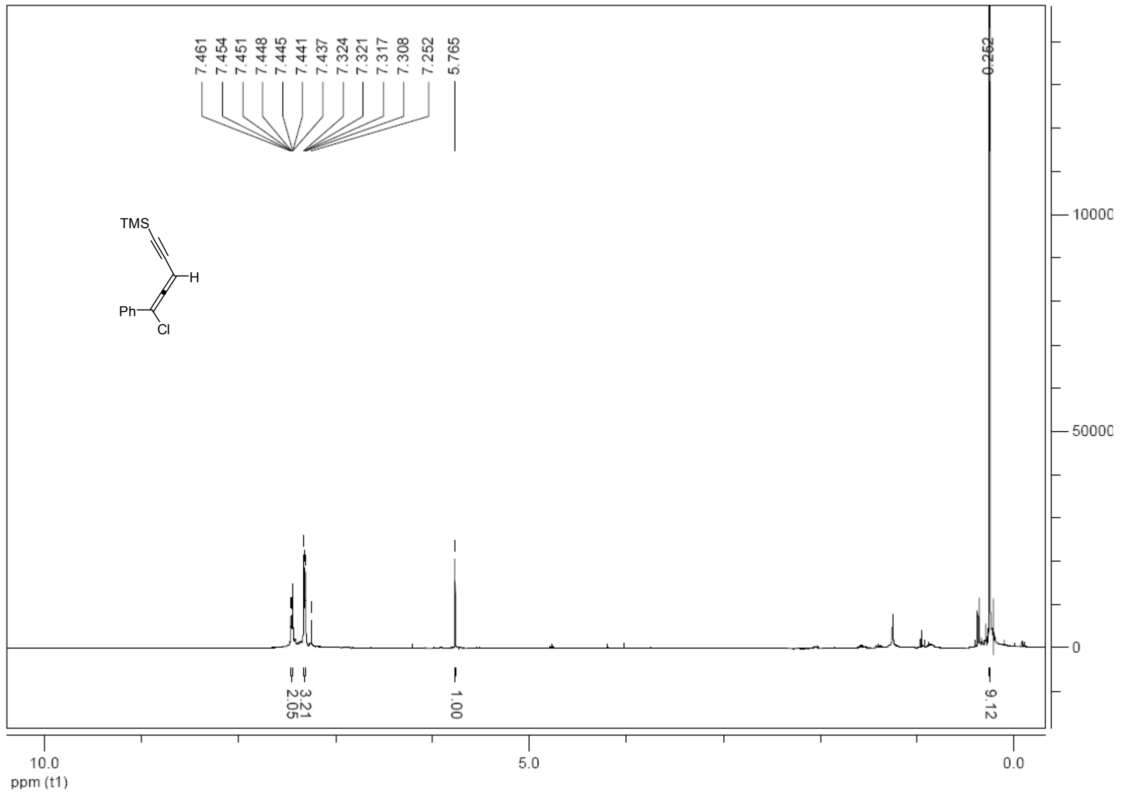
Orange solid. mp 246 °C (from hexane, decomp.). ^{1}H NMR ($CDCl_3$, 400MHz) δ = 1.32 (s, 18 H), 1.51 (s, 36H), 6.86–6.88 (d, *J* = 6.8 Hz, 4H), 7.15–7.17 (m, 6H), 7.48 (s, 4H). ^{13}C NMR ($CDCl_3$, 100MHz) δ = 31.3, 33.2, 35.1, 38.2, 81.2, 86.7 (t, *J* = 15.5 Hz), 88.2 (t, *J* = 6.8 Hz), 103.4, 122.4, 123.0, 128.0, 128.4, 131.4, 134.9 (m), 140.0 (m), 150.9, 154.3. ^{31}P NMR ($CDCl_3$, 162MHz) δ = 348.9. UV/Vis (CH_2Cl_2) λ/nm (ε [$M^{-1}cm^{-1}$]) 275 (24000), 373 (16500), 445 (12300). IR (CH_2Cl_2) 1254, 1423, 2307, 2525, 2692, 1985. HRMS (ESI) for $C_{58}H_{68}P_2$ Calcd for $[M+H]^+$ 827.4869, found 827.4854.

The X-ray structure of **4** was solved by direct methods (Shelxs 97) and refined by using the SHELXTL 5.0 software package. Crystallographic data for the structure of **4** reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 743457.

Crystal data and structure refinement for 4.

Identification code	r90605d
Empirical formula	$C_{58} H_{68} P_2$
Formula weight	827.06
Crystal color	orange
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.4252(19) A alpha = 90 deg. b = 26.239(5) A beta = 99.39(3) deg. c = 10.502(2) A gamma = 90 deg.
Volume	2562.5(9) A^3
Z, Calculated density	2, 1.072 Mg/m^3
Absorption coefficient	0.119 mm^-1
F(000)	892
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	2.11 to 25.02 deg.
Limiting indices	-11<=h<=11, -31<=k<=28, -11<=l<=12
Reflections collected / unique	18817 / 4524 [R(int) = 0.0560]
Completeness to theta = 25.02	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9858 and 0.9765
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	4524 / 72 / 300
Goodness-of-fit on F^2	1.105
Final R indices [I>2sigma(I)]	R1 = 0.0841, wR2 = 0.1989
R indices (all data)	R1 = 0.1153, wR2 = 0.2211
Extinction coefficient	0.012(2)
Largest diff. peak and hole	0.217 and -0.217 e.A^-3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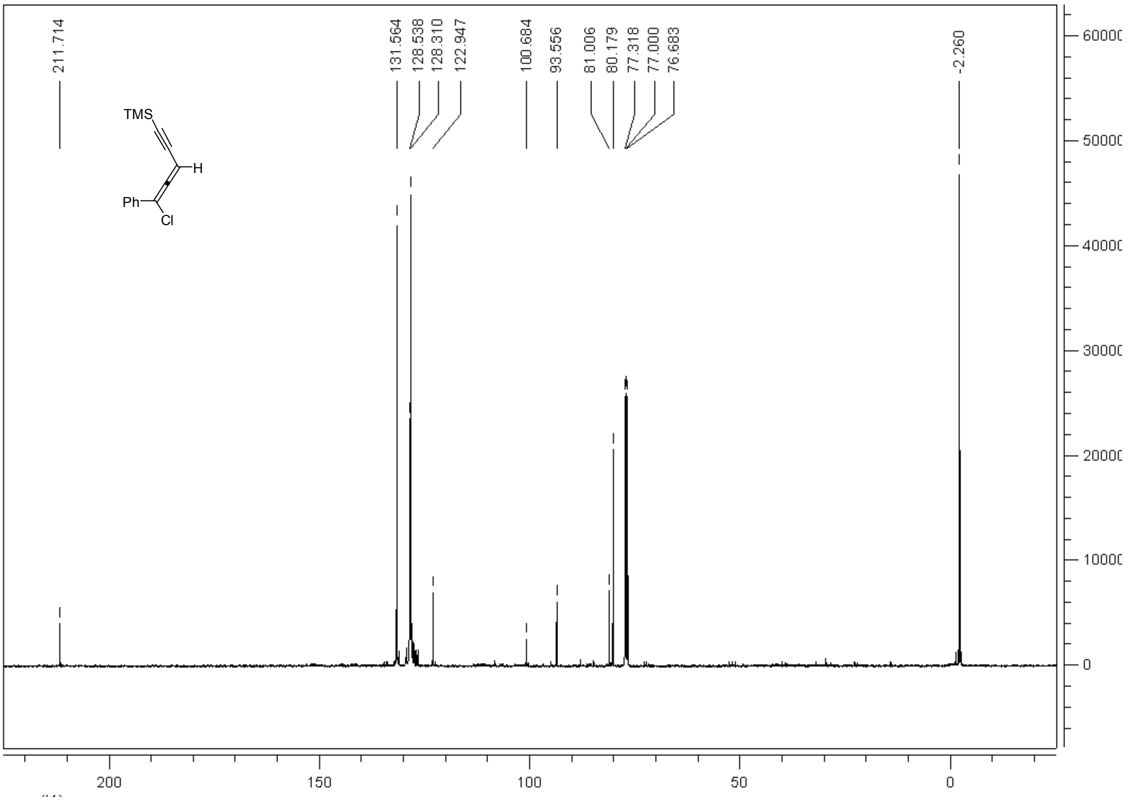
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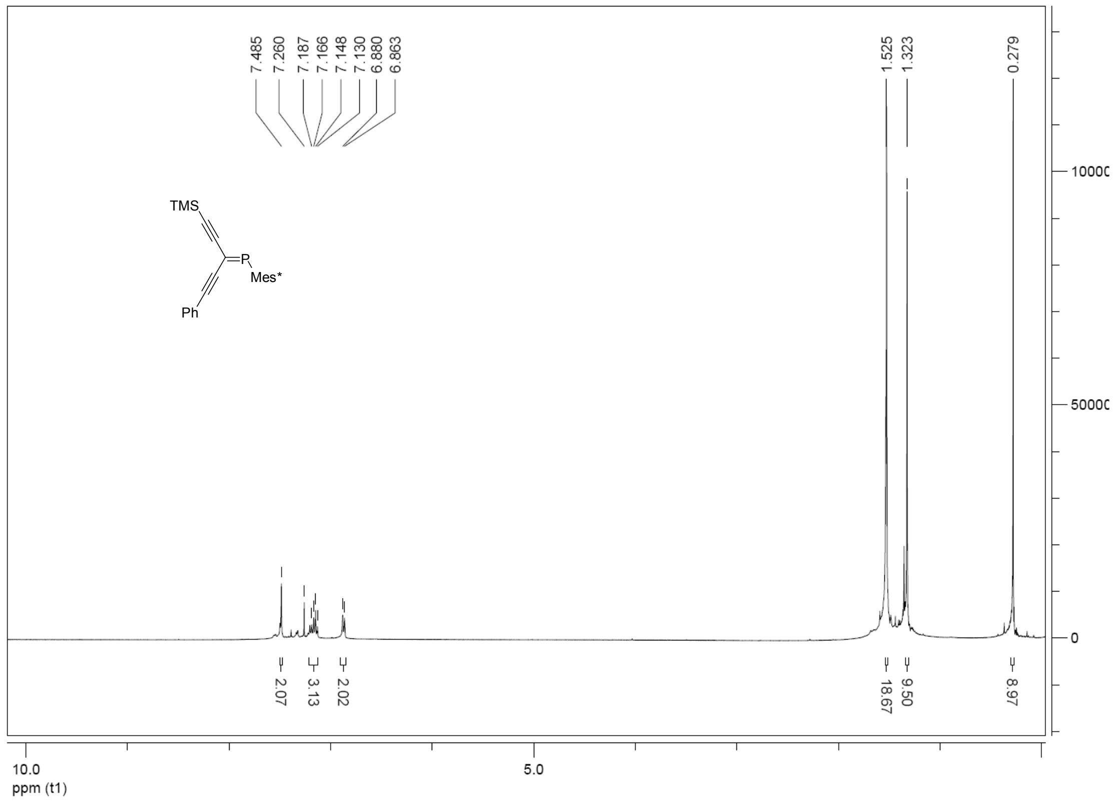
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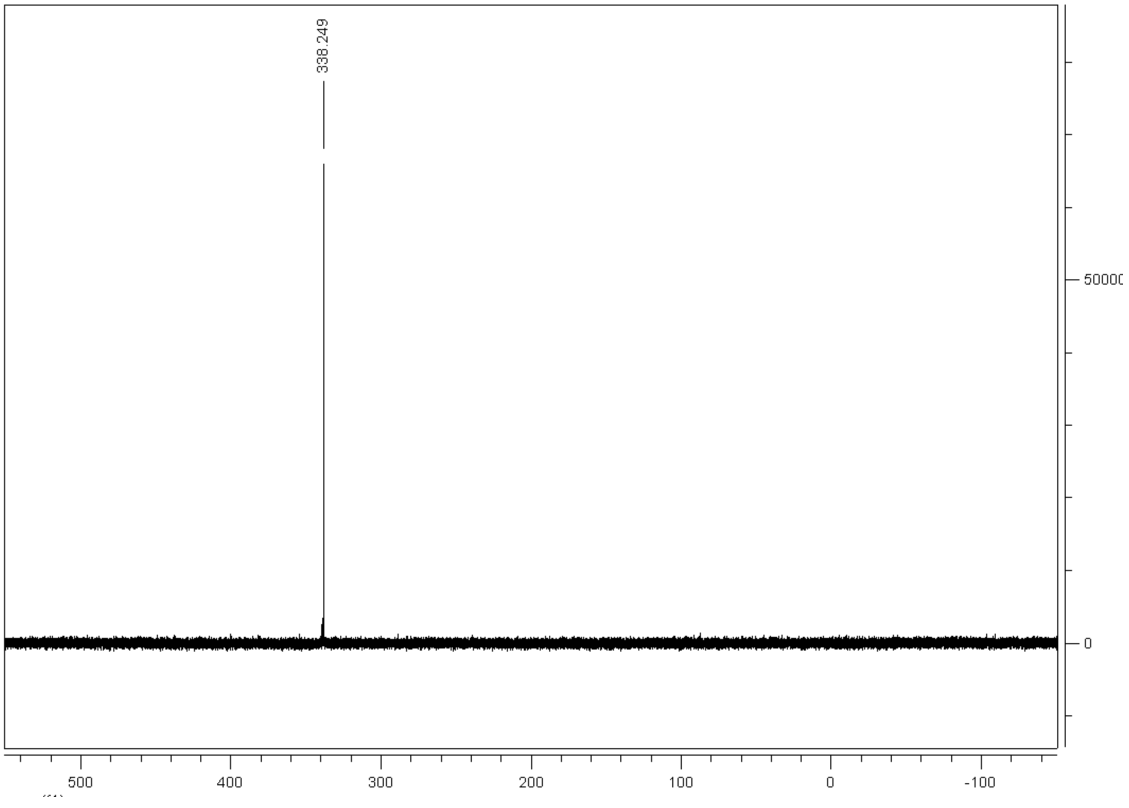
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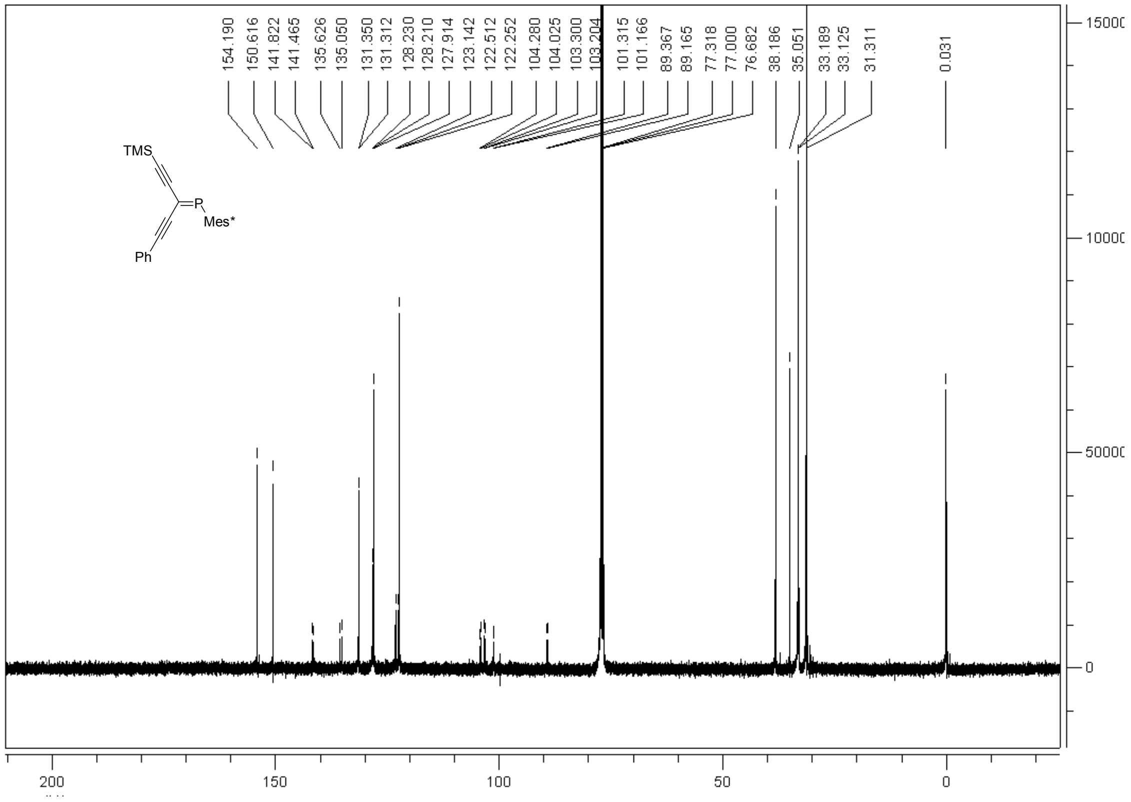
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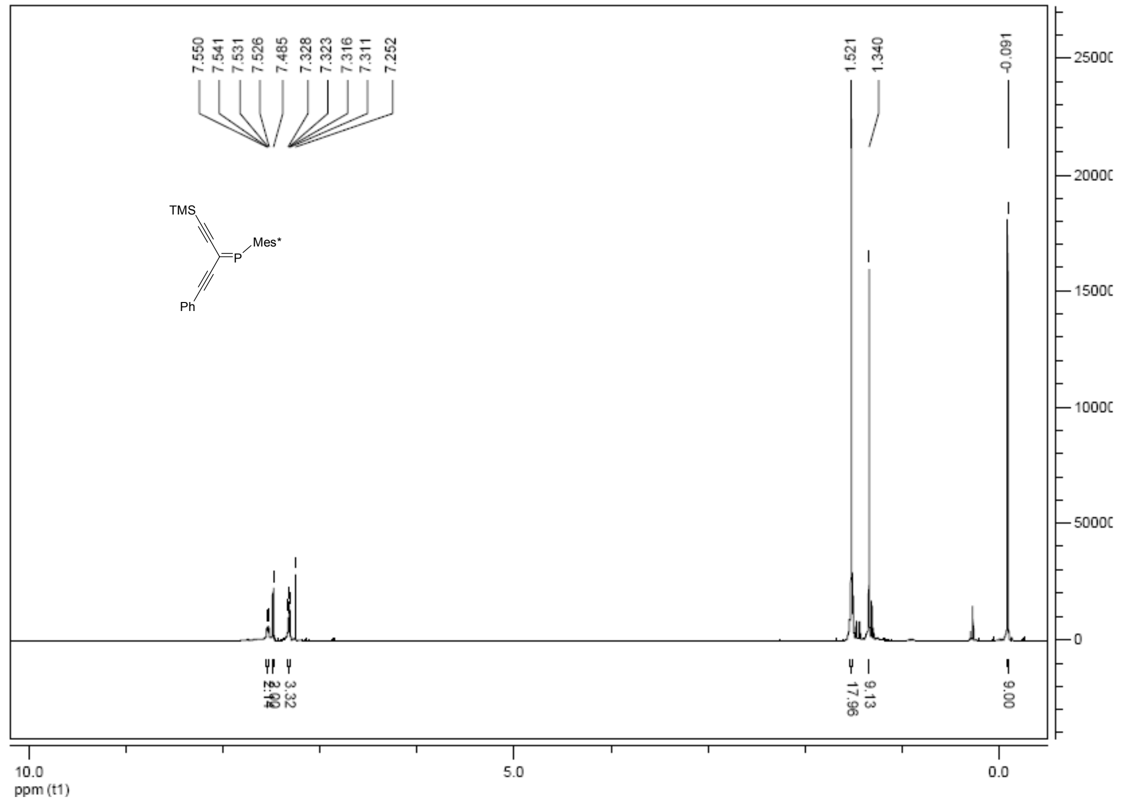
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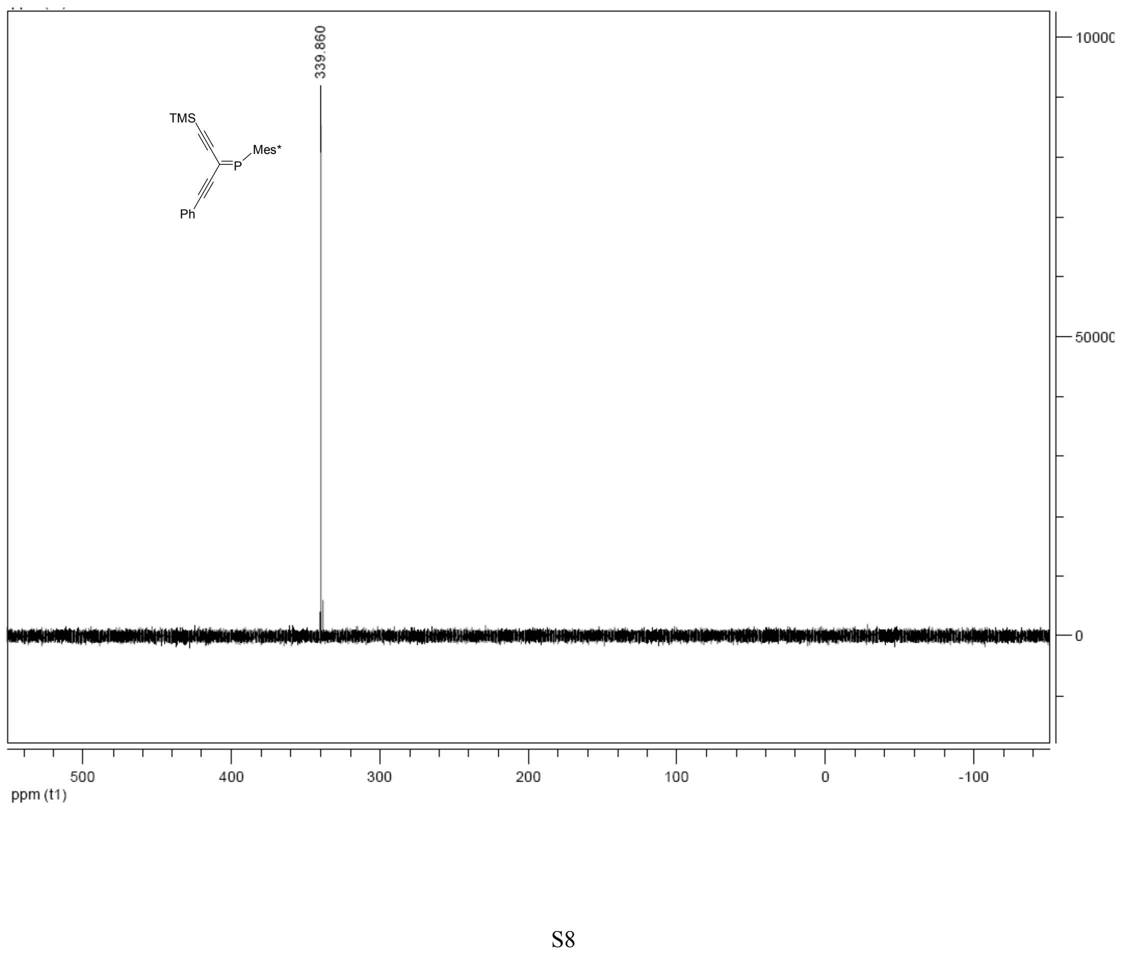
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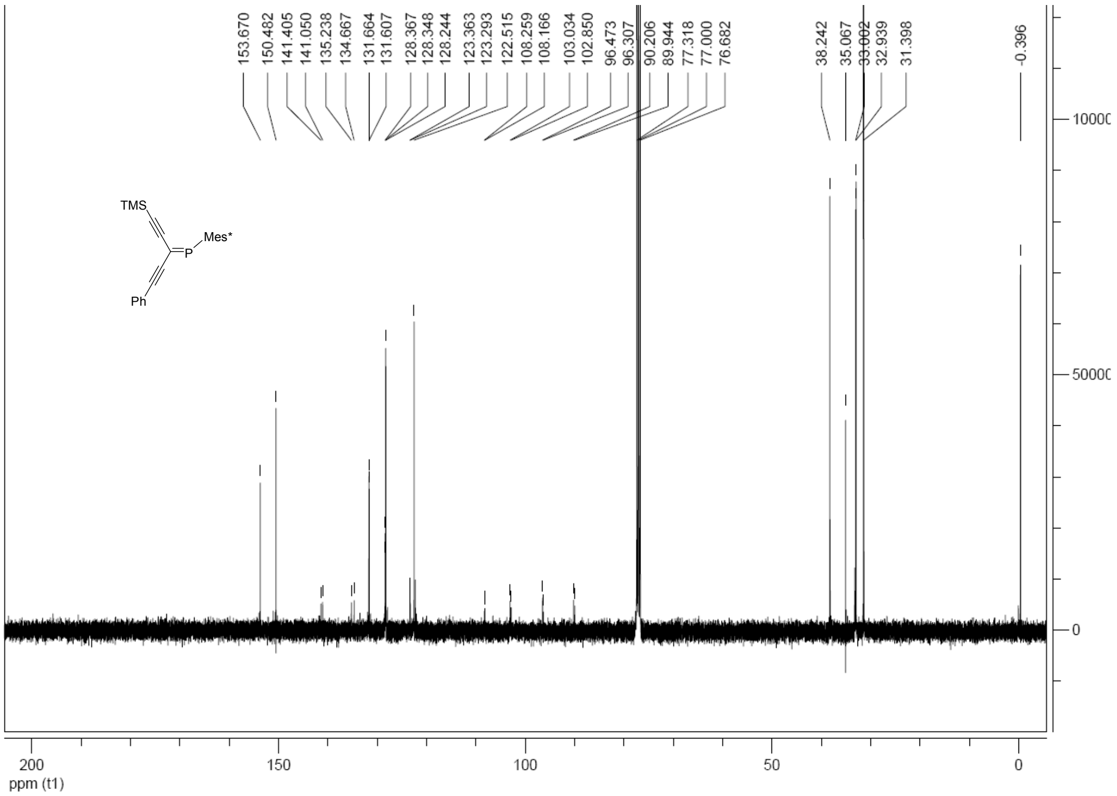
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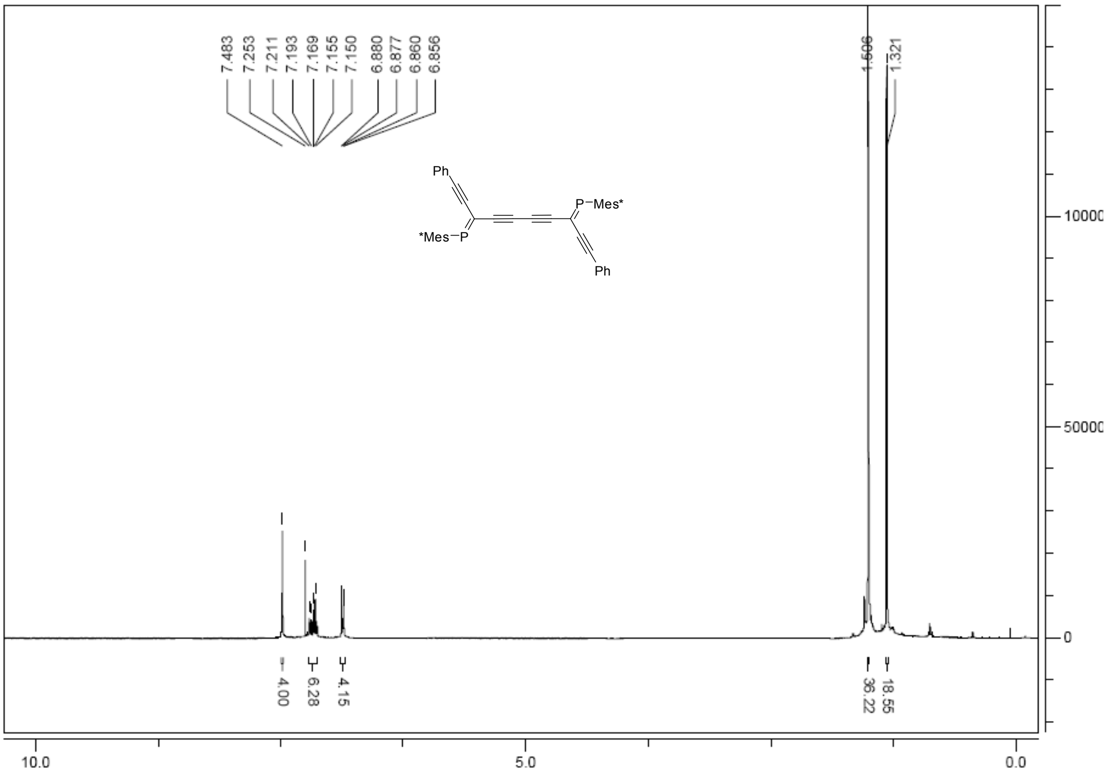
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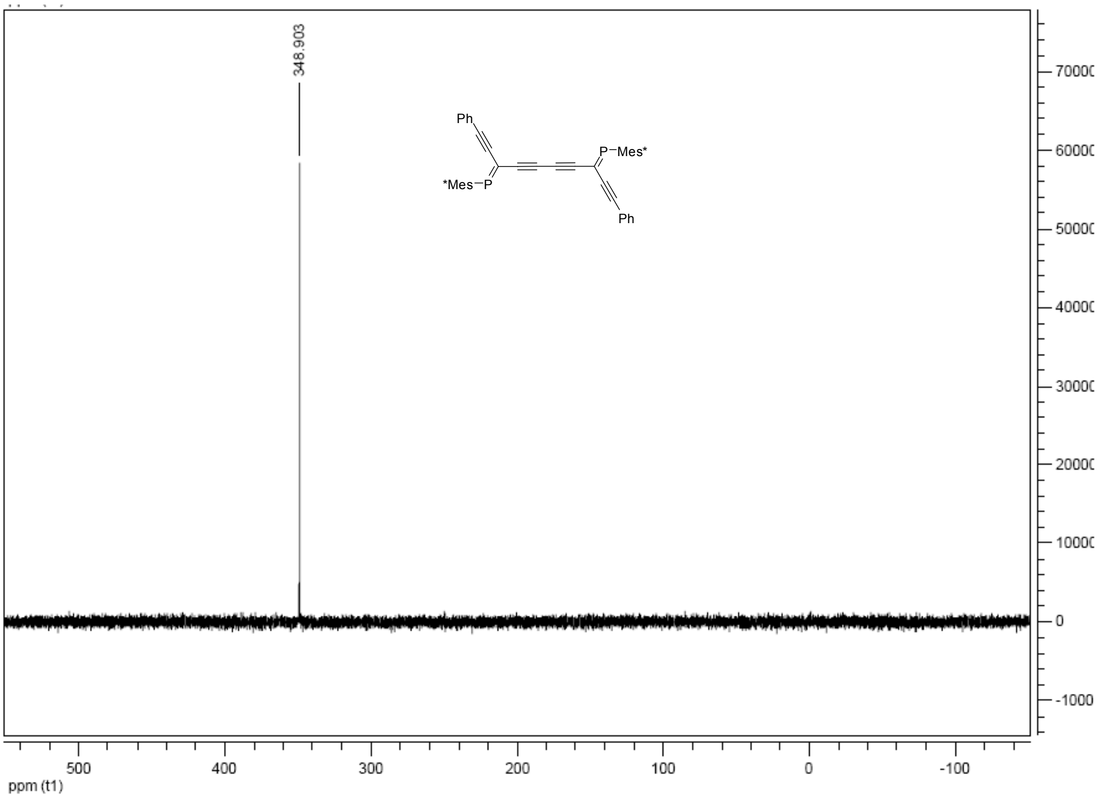
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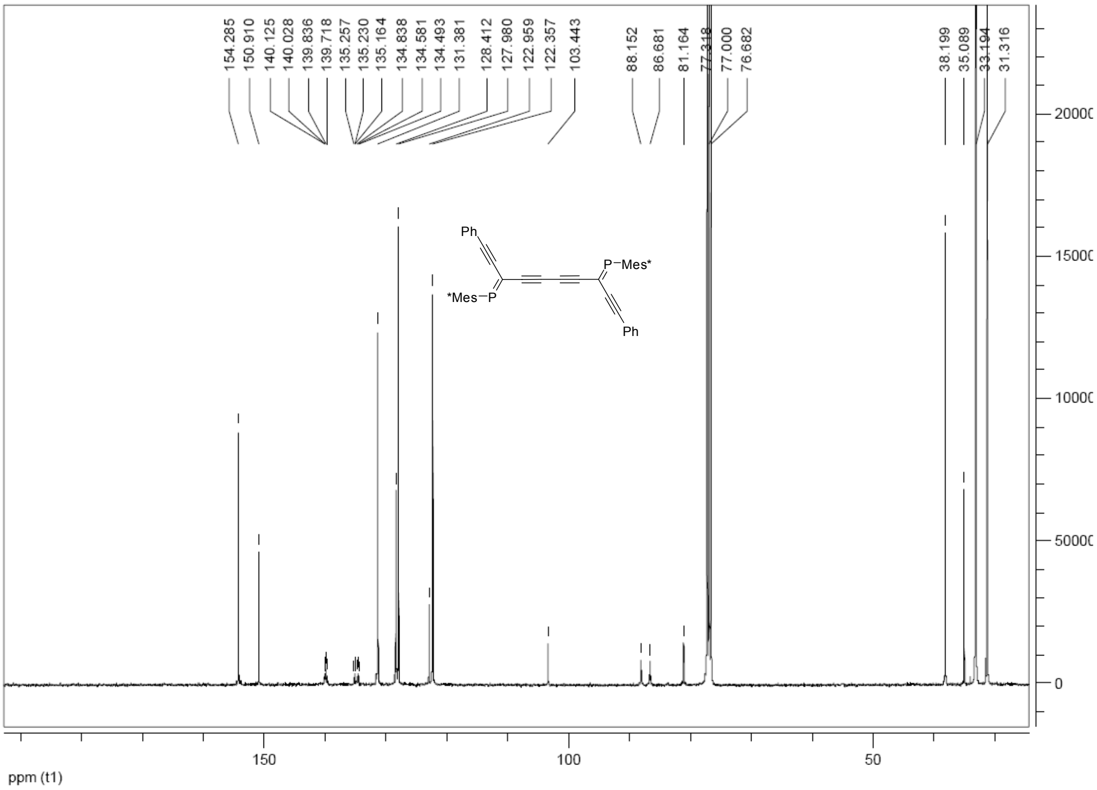
ppm (t1)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ppm (t1)