Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Synthesis of 3-stannyl and 3-silyl propargyl phosphanes and the formation of a phosphinoallene

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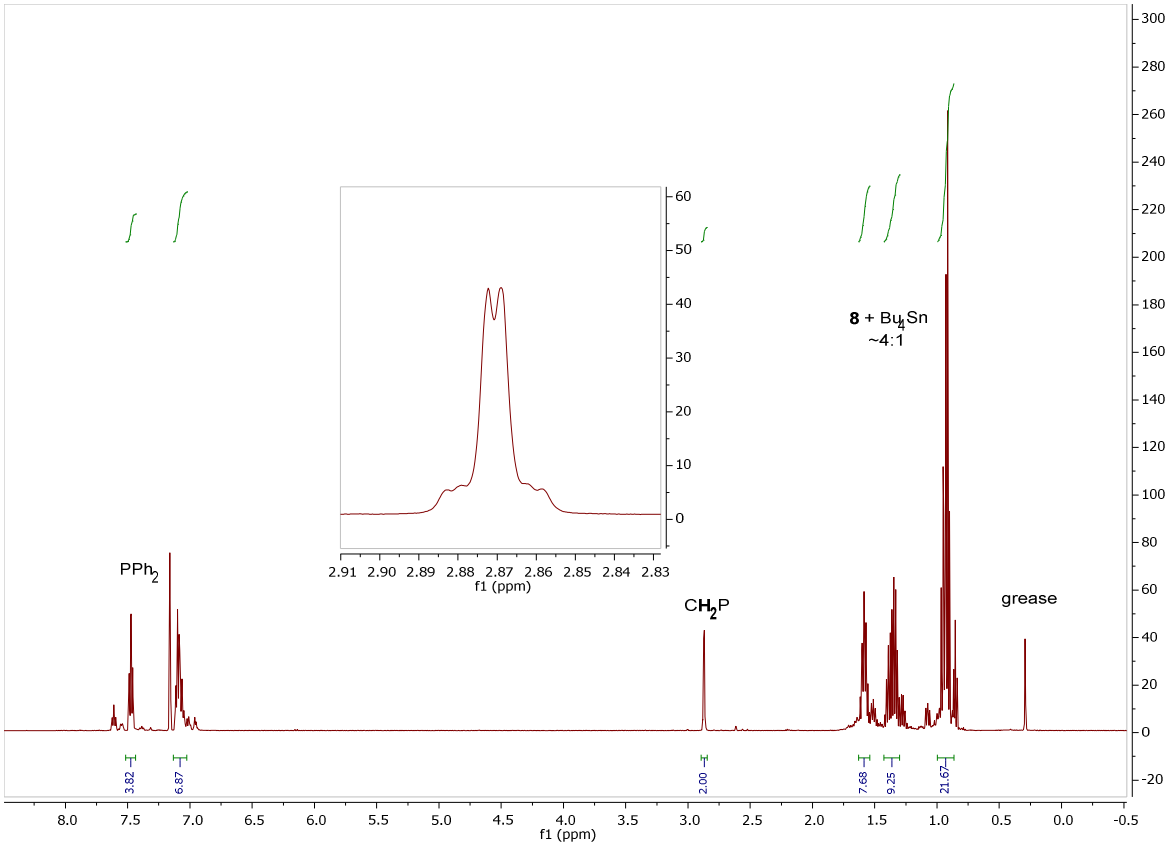

Figure S1. ^{1}H-NMR spectrum of compound **8**. Key data: ^{1}H-NMR: δ_H 0.93 (m, C*H*$_3$), 1.36 (m, 12H, 2 x C*H*$_2$), 1.58 (m, 6H, C*H*$_2$), 2.87 (d, J_{PH} 1.6 Hz, J_{117SnC} 8.7 Hz, J_{119SnC} 12.4 Hz, 2H, CH_2P), 7.02 – 7.13 (m, 6H, *m/p*-C$_6$*H*$_5$), 7.43 – 7.51 (m, 4H, *o*-C$_6$*H*$_5$).

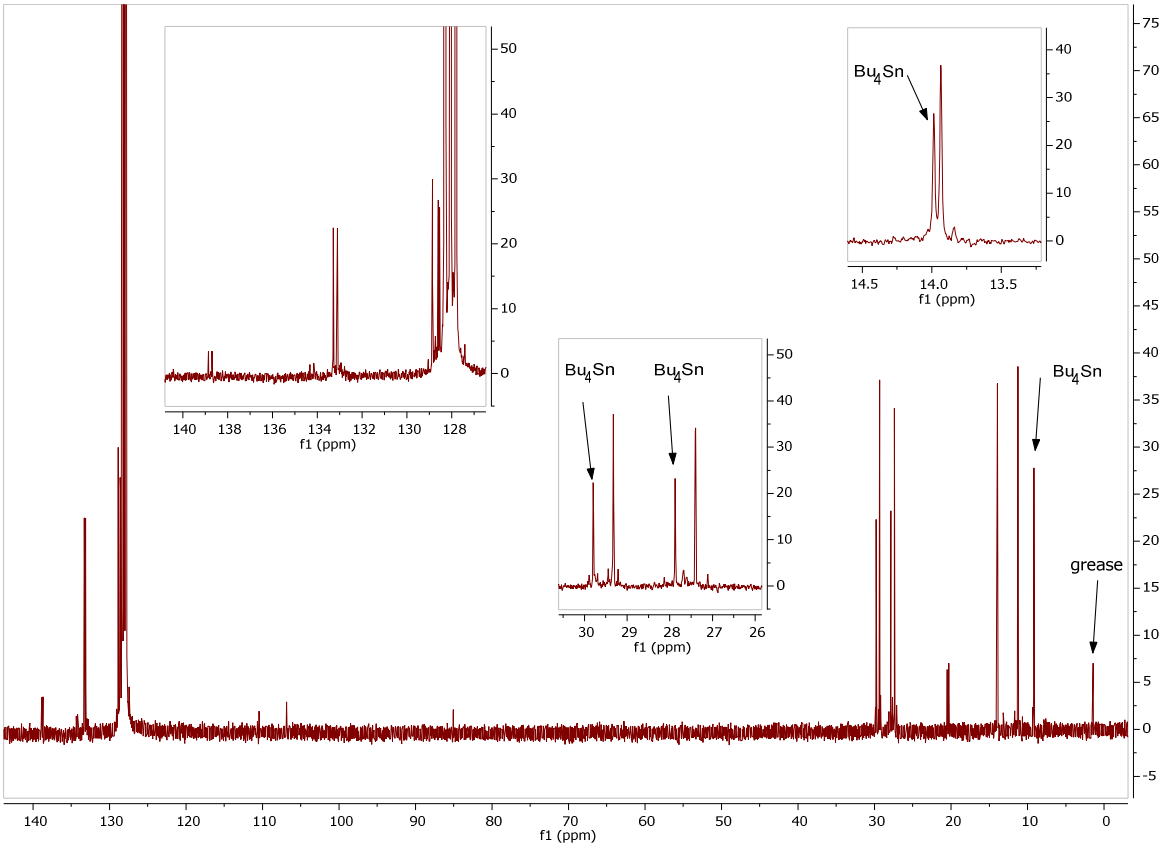

Figure S2. $^{13}C\{^{1}H\}$-NMR spectrum of compound **8**. Key data: $^{13}C\{^{1}H\}$-NMR: δ_C 11.3 (s, $\underline{C}H_2Sn$, $^{1}J_{117SnC}$ 366 Hz, $^{1}J_{119SnC}$ 383 Hz), 13.9 (s, $\underline{C}H_3$), 20.4 (d, $^{1}J_{PC}$ 18Hz, $\underline{C}H_2PPh_2$), 27.4 (s, $\underline{C}H_2CH_2Sn$, J_{SnC} 58 Hz) 85.0 (d, J_{PC} 6 Hz, $\underline{C}$=CCH_2PPh_2), 106.8 (d, J_{PC} 5 Hz, C$\underline{C}CH_2PPh_2$), 128.6 (d, J_{PC} 6 Hz, *m*-C_6H_5), 128.9 (s, *p*-C_6H_5), 133.2 (d, J_{PC} 19 Hz, *o*-C_6H_5), 138.8 (d, J_{PC} 17 Hz, *i*-C_6H_5).

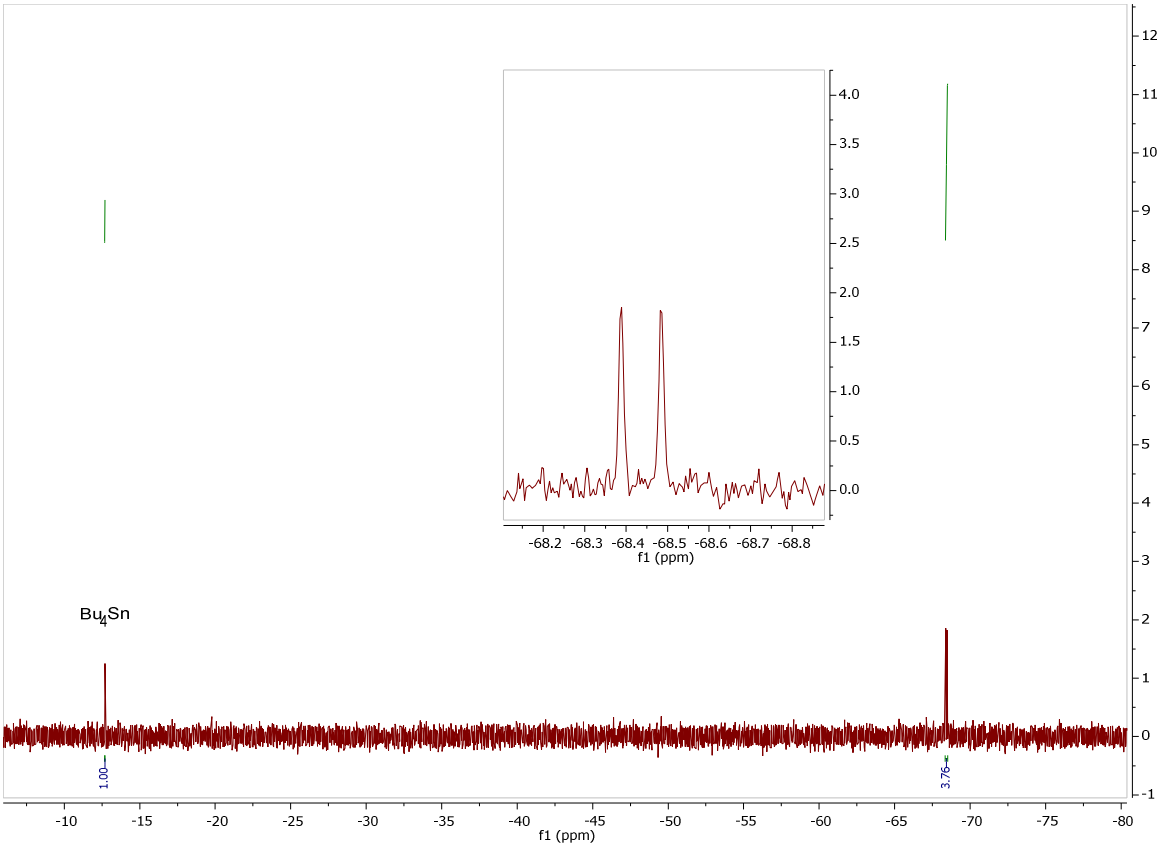

Figure S3. $^{119}Sn\{^{1}H\}$-NMR spectrum of compound **8**, illustrating relative proportions of **8** and Bu_4Sn.

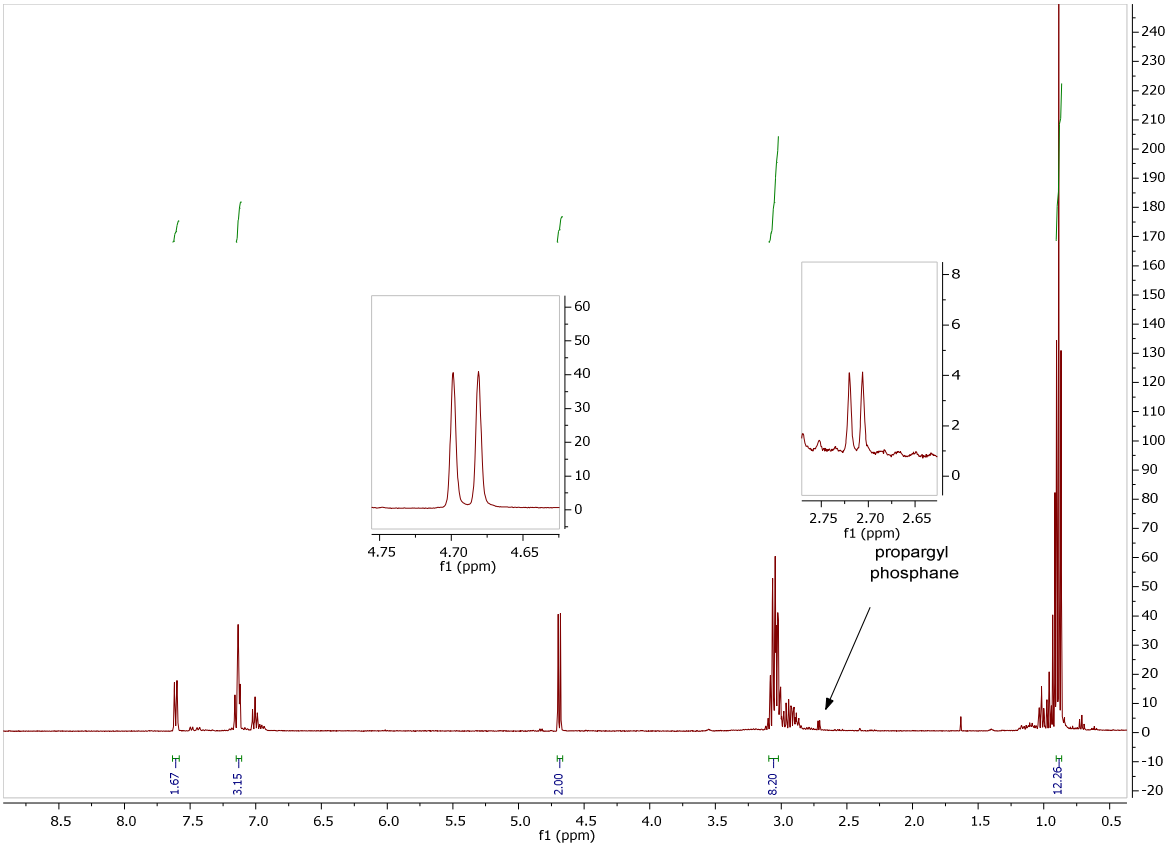

Figure S4. ^{1}H-NMR spectrum of compound **15** (74 %) indicating assigned resonances and the presence of trace (ca 5 %) of the propargyl isomer. Key data: ^{1}H-NMR (**15**): δ_H 0.89 (t, $^{3}J_{HH}$ 7.0 Hz, 12H, CH_3), 3.05 (q, $^{3}J_{HH}$ 7.0 Hz, 8H, CH_2), 4.69 (d, J_{PH} 7.0 Hz, 2H, =CH_2), 7.11 – 7.15 (m, 3H, *m/p*- C_6H_5), 7.63 – 7.59 (m, 2H, *o*-C_6H_5). ^{1}H-NMR (propargyl): δ_H 1.02 (t, $^{3}J_{HH}$ 7.2 Hz, 12H, CH_3), 2.71 (d, J_{PH} 5.8 Hz, 2H, CH_2P), 2.87 (m, 8H, NCH_2).

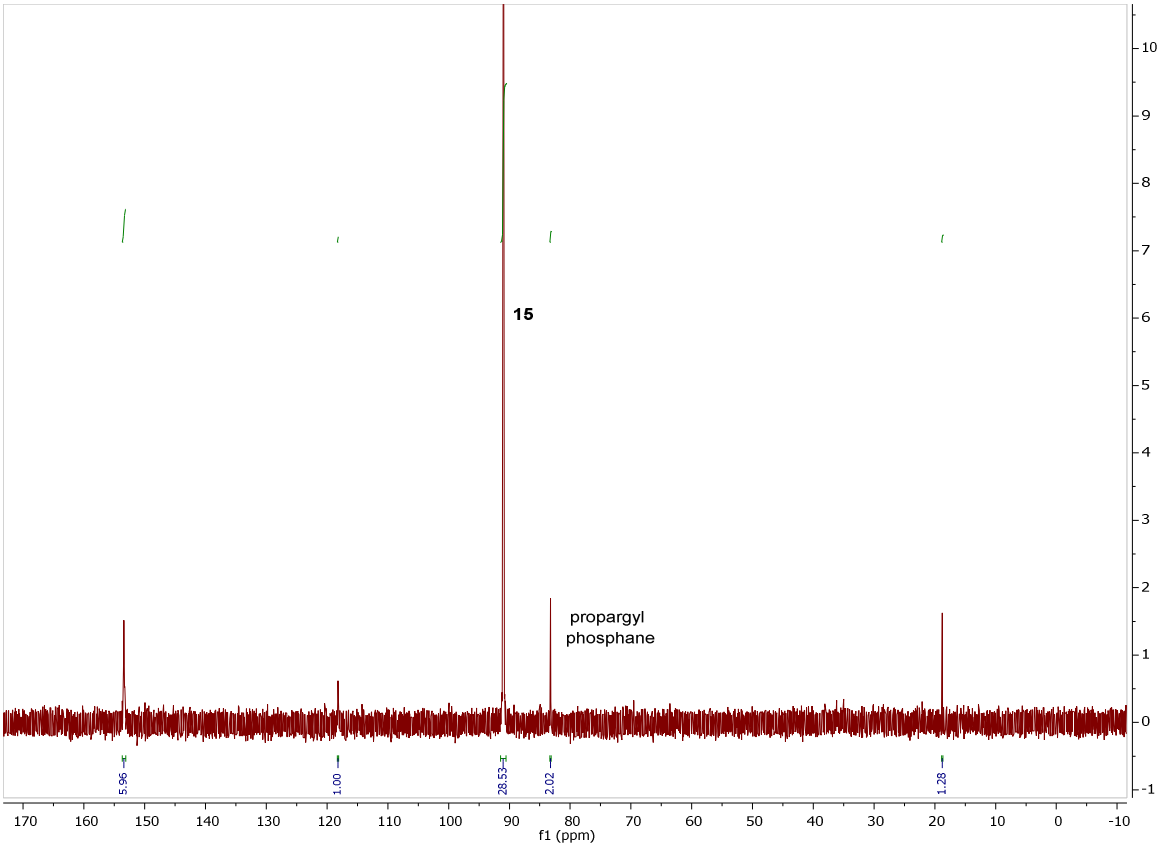

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of compound **15**, within product mixture also containing (inter alia) the propargyl phosphane $(Et_2N)_2PCH_2C{\equiv}CPh$. Key data: $^{31}P\{^{1}H\}$-NMR: δ_P 91.0 (s, br, 74 %, **15**), $^{31}P\{^{1}H\}$-NMR: δ_P 83.2 (s, br, 5 %, propargyl).

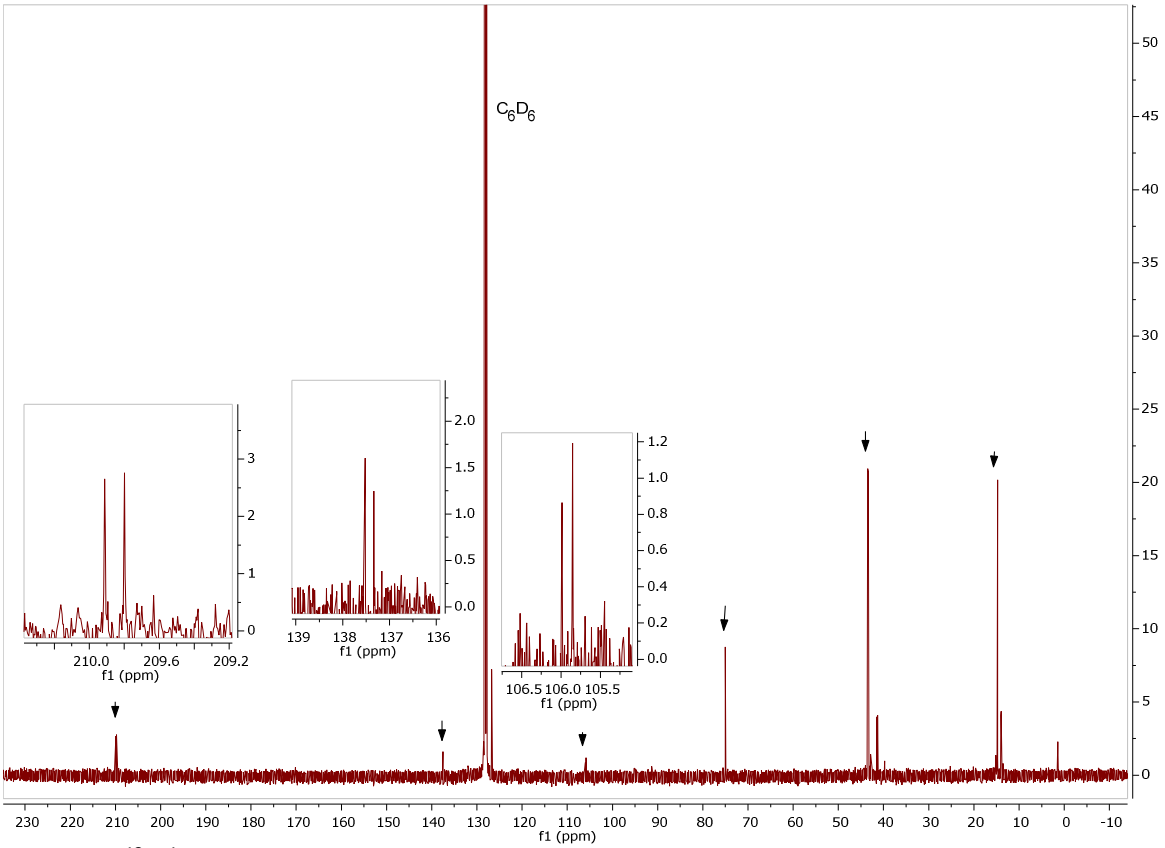

Figure S6. $^{13}C\{^{1}H\}$-NMR for compound **15**, illustrating key resonances within the mixture. Key data: $^{13}C\{^{1}H\}$-NMR: δ_C 14.8 (d, $^{3}J_{PC}$ 3.2 Hz, $\underline{C}H_3$), 43.4 (d, $^{3}J_{PC}$ 17.4 Hz, N$\underline{C}H_2$), 75.0 (s, =$\underline{C}H_2$), 105.9 (d, J_{PC} 13.5 Hz, *i*-C_6H_5), 137.4 (d, J_{PC} 19 Hz, Ph$\underline{C}\{P(NEt_2)_2\}$C), 127.8 (s, *o*-$C_6H_5$), 127.9 (overlapped *m*-/*p*-C_6H_5), 209.9 (d, J_{PC} 11.4 Hz, =$\underline{C}$=).

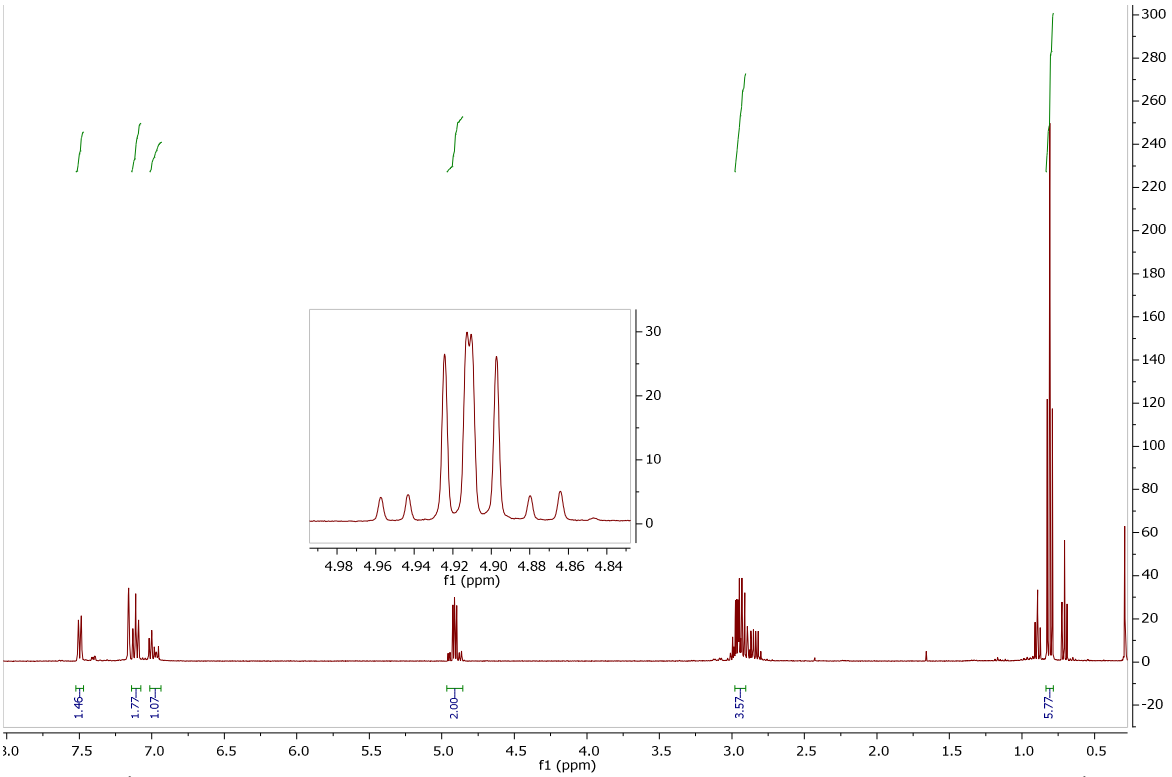

Figure S7. ^{1}H NMR spectrum for compound **16** (77 %) in crude reaction mixture. Key data: ^{1}H-NMR: δ_H 0.81 (t, $^{3}J_{HH}$ 6.9 Hz, 6H, CH_3), 2.94 (q, $^{3}J_{HH}$ 7.4 Hz, 4H, CH_2), 4.89 (dd, $^{2}J_{HH}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, =CH_2), 4.93 (dd, $^{2}J_{HH}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, =CH_2), 6.94 – 7.02 (m, 1H, *p*-C_6H_5), 7.11 (7, J_{HH} 7.8 Hz, 2H, *m* - C_6H_5), 7.50 (d, J_{HH} 7.8 Hz, 2H, *o*-C_6H_5).

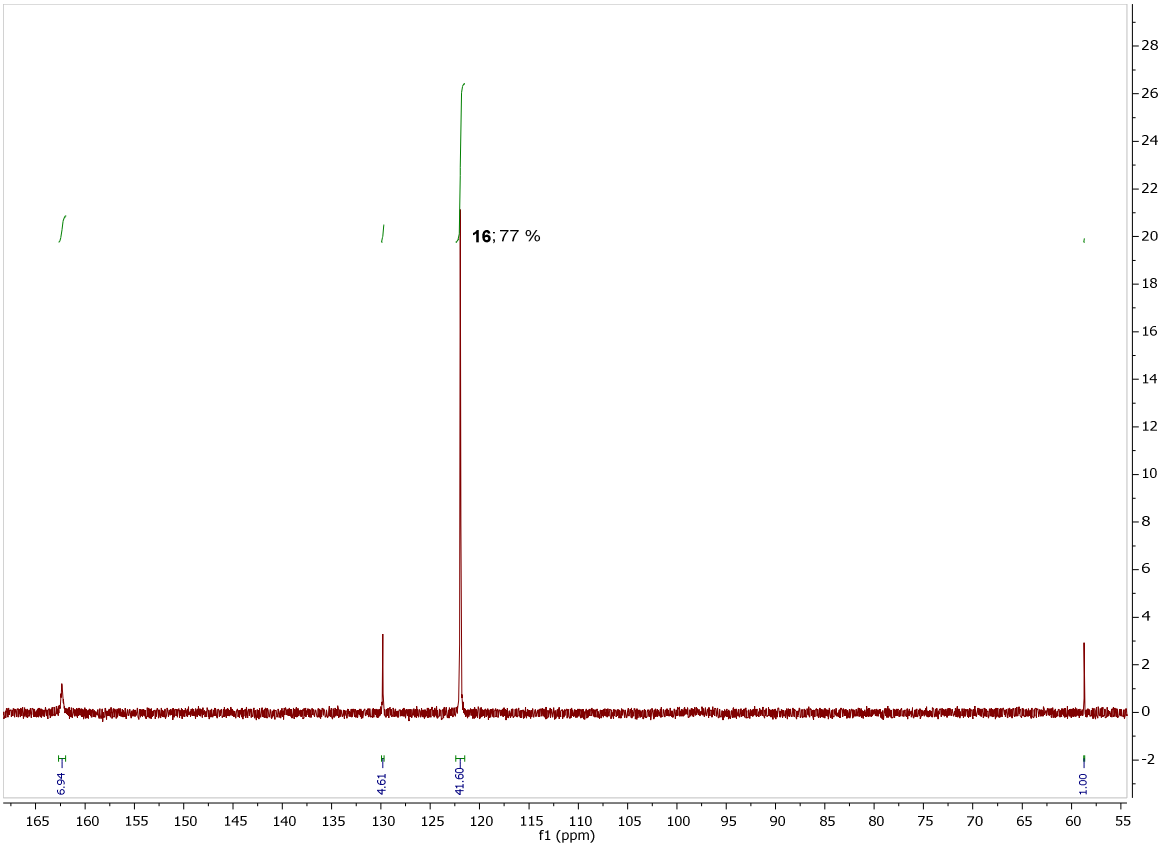

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum for compound **16** (77 %) in crude reaction mixture. Key data: $^{31}P\{^{1}H\}$-NMR: δ_P 122.0 (s, br, 77 %).

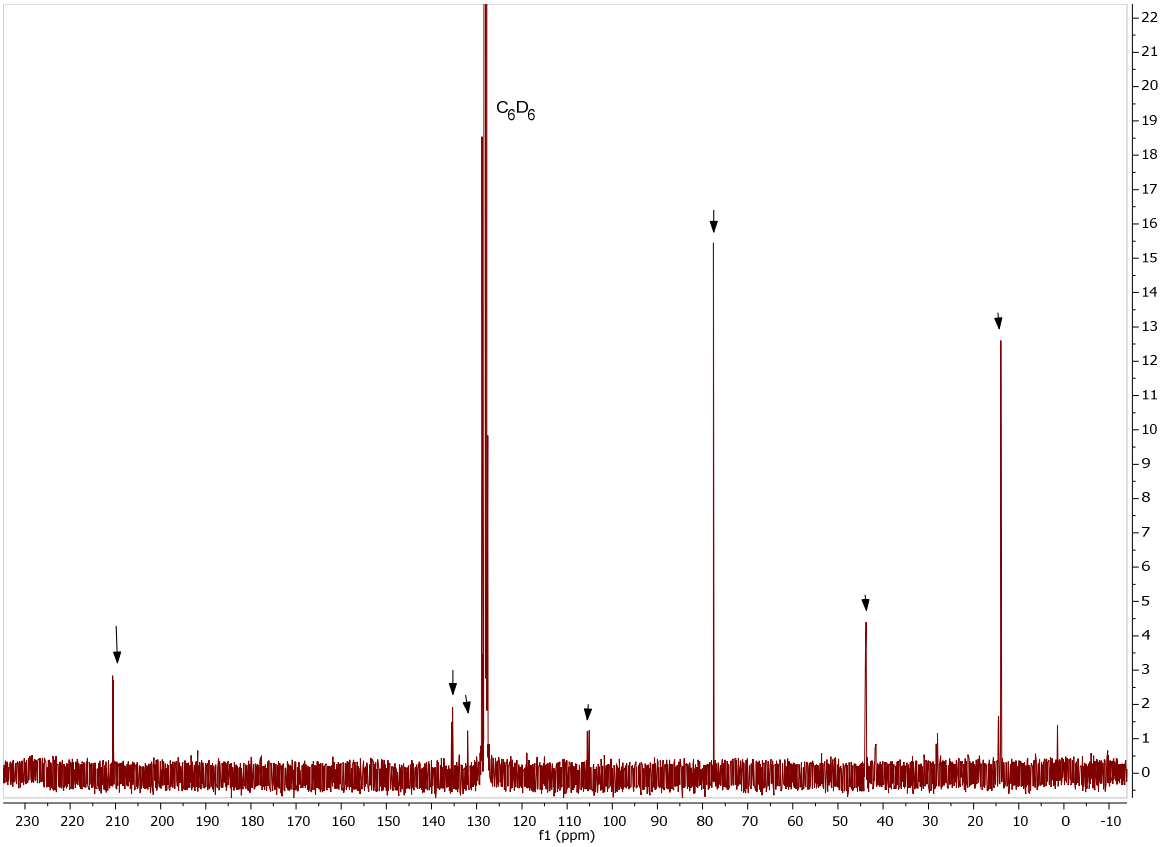

Figure S9. $^{13}C\{^{1}H\}$-NMR spectrum for compound **16**, illustrating the associated resonances within the mixture. Key data: $^{13}C\{^{1}H\}$-NMR: δ_C 13.9 (d, $^{3}J_{PC}$ 6.2 Hz, $\underline{C}H_3$), 43.9 (d, $^{3}J_{PC}$ 13 Hz, N$\underline{C}H_2$), 77.6 (s, =$\underline{C}H_2$), 105.3 (d, J_{PC} 40 Hz, Ph$\underline{C}$\{PCl(NEt$_2$)\}C), 135.4 (d, J_{PC} 24 Hz, *i*-C_6H_5), 127.6 (d, J_{PC} 1.5 Hz, *o*-C_6H_5), 127.98 (s, *p*-C_6H_5) 128.9 (s, *m*-C_6H_5), 210.6 (d, J_{PC} 8.4 Hz, =$\underline{C}$=).