Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Au(I)-Mediated N_2-Elimination from Triazaphospholes: A One-Pot Synthesis of Novel N_2P_2-Heterocycles

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Table of Content

1. Experimental Procedures

1.1 General information

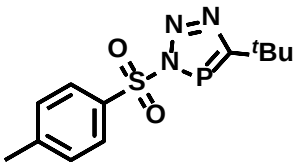
General Remarks

All reactions were performed under an argon atmosphere in oven-dried glassware using modified Schlenk techniques or in an MBraun glovebox. All common solvents and chemicals were commercially available. Tosyl azide **1a** and mesitylsulfonyl azide **1b** were prepared according to literature methods.[1] *Tert*-butylphosphaalkyne was prepared according to the previous literature.[2] Commercially available chemicals were used without further purification. Dry Toluene, EtOH, *n*-hexane, *n*-pentane and CH_2Cl_2 were prepared by using an MBraun Solvent Purification System. Et_2O was dried over Na/benzophenone and THF was dried over K/benzophenone under argon. The deuterated dry solvents benzene-d_6 and DCM-d_2 were dried over CaH_2 and THF-d_8 over sodium-potassium alloy. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded by using a JEOL ECS400 spectrometer (400 MHz), or a JEOL ECZ600 spectrometer (600Hz). All chemical shifts are reported relative to the residual resonance in the deuterated solvents. ESI-MS spectra were recorded on an Agilent 6210 ESI-TOF (4 kV) from Agilent Technologies. EI measurements were conducted with a modified device of a MAT 711 from Varian MAT. CHN-Analysis was performed on an ELEMENTAR VARIO EL.

Caution: Azides are potentially hazardous compounds and adequate safety measures should be taken when weighing, heating and working up.

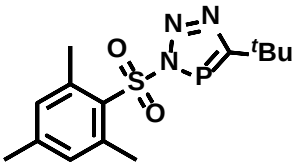
1.2 Synthesis and characterization

Synthesis of 5-(*tert*-butyl)-3-tosyl-3*H*-1,2,3,4-triazaphosphole (2a)



The tosyl azide **1a** (739.6 mg, 3.75 mmol) was dissolved in 20 mL of dry toluene and the solution was frozen at T = -78 °C and degassed. The freshly prepared *tert*-butyl phosphaalkyne (412.9 mg, 4.13 mmol, 1.5 eq.) in 30 mL dry toluene was added by means of trap-to-trap condensation. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Excess alkyne and the solvent were removed under vacuum. The crude product was recrystallized from a hot saturated solution of dry pentane. **2a** was obtained as a white solid (948.4 mg, 85%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.06 (d, J = 8.5 Hz, 2H, *m*-tosyl-H), 7.44 (d, J = 8.5 Hz, 2H, *o*-tosyl-H), 2.47 (s, 3H, $CH_{3\text{-tosyl}}$), 1.47 (d, J = 3.2 Hz, 9H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ (ppm) = 200.0 (d, J = 61.8 Hz, Ar-C), 147.0 (s, Ar-C), 133.9 (s, Ar-C), 130.2 (s, Ar-C), 128.5 (s, Ar-C), 33.5 (d, J = 14.5 Hz, CMe$_3$), 30.8 (d, J = 8.5 Hz, CMe$_3$), 21.5 (s, *p*-Ar-Me). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ (ppm) = 177.2 (s). EI-MS(m/z): 297.078 m/z (Calc.: 297.0701). Elemental analysis: N: 11.51; C: 48.61; H: 5.513; (Calc.: N: 14.13; C: 48.48; H: 5.42).

Synthesis of 5-(*tert*-butyl)-3-(2-mesitylenesulfonyl)-3*H*-1,2,3,4-triazaphosphole (2b)

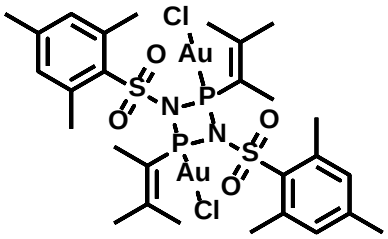


The 2-mesitylenesulfonyl azide **1b** (1500 mg, 6.66 mmol) was dissolved in 20 mL toluene and the solution was frozen at T = -78 °C and degassed. The freshly prepared *tert*-butyl phosphaalkyne (998.8 mg, 9.99 mmol, 1.5 eq.) in 30 mL dry toluene was added by means of trap-to-trap condensation. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Excess alkyne and the solvent was removed under vacuum. The crude product was recrystallized from a hot saturated solution of dry pentane. **2b** was obtained as a white solid (998.0 mg, 46%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.04 (s, 2H, Ar-H), 2.71 (s, 6H, Ar_{Me}-H), 2.31 (s, 3H, Ar_{Me}-H), 1.43 (s, 9H, CMe$_3$-H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ (ppm) = 199.5 (d, J = 61.0 Hz, TAP-C), 146.3 (s, Ar-C), 142.1 (s, Ar-C), 133.0 (s, Ar-C), 131.5 (s, Ar-C), 36.0 (d, J = 15.0 Hz, CMe$_3$), 31.4 (d, J = 8.0 Hz, CMe$_3$), 23.6 (s, *o*-Ar-Me), 21.4 (s, *p*-Ar-Me). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ (ppm) = 175.2 (s). Elemental analysis: N: 12.93; C: 51.72; H: 6.614 (Calc.: N: 12.91; C: 51.68; H: 6.20).

Reaction of 2a with AuCl(SMe_2):

In a *J*-Young NMR tube, tosyl-substituted triazaphosphole **2a** (50.0 mg, 0.17 mmol) and AuCl(SMe_2) (48.5 mg, 0.17 mmol) was dissolved in 0.5 mL of CD_2Cl_2 under an argon atmosphere. A gas evolution was immediately observed, while the reaction solution turned yellow. The reaction is not selective and several resonances were found by means of NMR spectroscopy (see Figure S9). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ (ppm) = 11.5 (s), 16.7 (s), 115.4 (s), 120.5 (s), 130.2 (s), 138.4 (s). Crystals of diauro 2,4-bis(3-methylbut-2-en-2-yl)-1,3-ditosyl-1,3,2,4-diazadiphosphetidine dichloride **(3a)**, suitable for single crystal X-ray diffraction analysis, were obtained from the reaction mixtures at low temperature.

Synthesis of diauro 2,4-bis(3-methylbut-2-en-2-yl)-1,3-bis(2-mesitylenesulfonyl)-1,3,2,4-diazadiphosphetidine dichloride (3b).



Mesitylsulfonyl-substituted triazaphosphole **2b** (50.0 mg, 0.15 mmol) and AuCl(SMe_2) (45.3 mg, 0.15 mmol) was dissolved in 2.0 mL of CH_2Cl_2 under an argon atmosphere. A gas evolution was immediately observed (Figure S1). The reaction solution was first heated to T = 60°C for 2h and then left to cool to room temperature over the next 12 h. The Solvent was evaporated and a yellow solid was obtained. When adding 1.0 mL of toluene the product precipitated as a white solid. The desired complex was obtained as a white solid (28.6 mg, 36%). Crystals suitable for single crystal X-ray diffraction analysis were obtained from the reaction mixtures at low temperature.

^1H NMR (401 MHz, CD_2Cl_2): δ = 7.03 (s, 2H), 2.74 (d, J = 1.2 Hz, 3H), 2.72 (s, 6H), 2.32 (s, 3H), 1.95 (d, J = 11.5 Hz, 3H), 1.88 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ = 169.57 – 169.15 (m)145.98, 140.47, 132.96, 131.08, 125.55 – 125.03 (m), 26.83 – 26.56 (m), 25.35 – 24.95 (m), 24.56, 20.93, 16.28. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 133.9 (s). Elemental analysis: N: 2.658; C: 31.88; H: 4.73 (Calc.: N: 2.64; C: 31.75; H: 3.81).

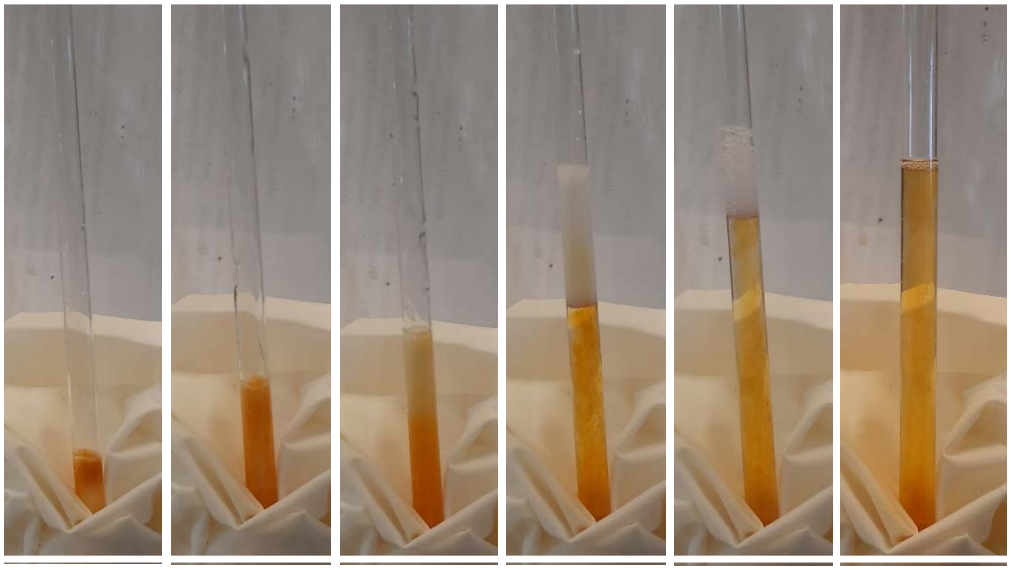


Figure S1. Nitrogen generation upon addition of DCM to a mixture of **2b** and $AuCl(SMe_2)$. Left picture: start, right picture: after one minute.

1.3 Low-temperature $^{31}P\{^1H\}$ NMR spectroscopy

Under exclusion of light gold(I)chloride dimethylsulfide (18.1 mg, 0.06 mmol) was dissolved in DCM-d_2 in a *J*-Young-NMR-tube and cooled to T = -78 °C. A prestirred solution of 5-(*tert*-butyl)-3-(mesitylsulfonyl)-3*H*-1,2,3,4-triazaphosphole **2b** (20.0 mg, 0.06 mmol) in DCM-d_2 (0.3 mL) was likewise cooled to T = -78 °C and then carefully added. The low temperature $^{31}P\{^1H\}$ NMR-measurement was started at T = -70 °C, the temperature of the reaction solution was increased by T = 10 °C every 30 minutes until reaching room temperature (Figure S2).

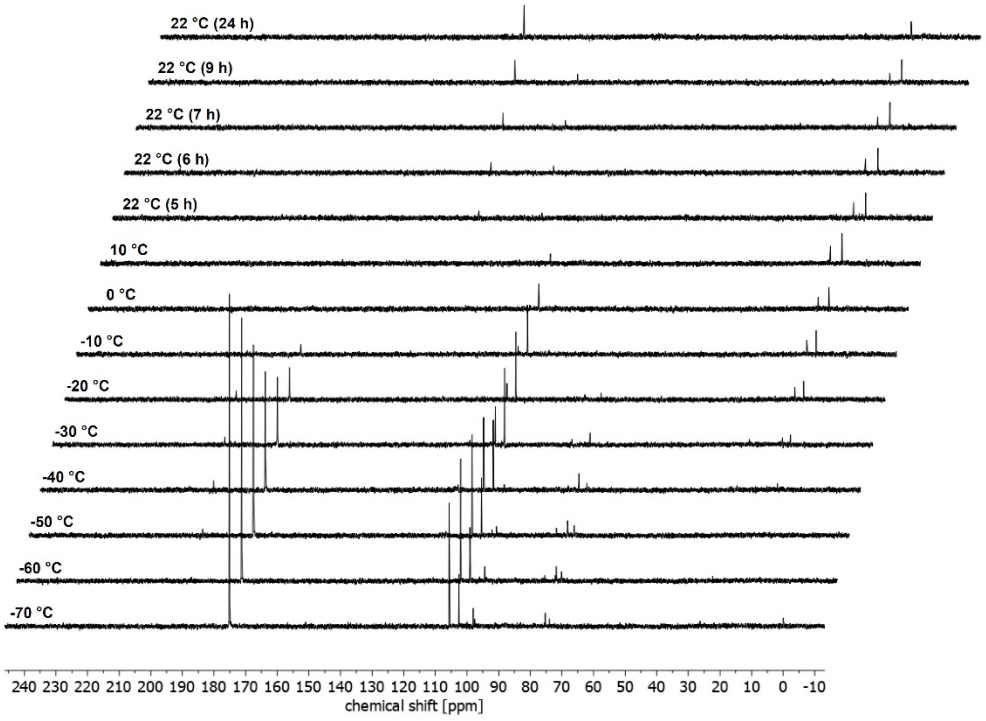


Figure S2. Temperature-dependent $^{31}P\{^{1}H\}$ NMR spectra for the reaction of **2b** with an equimolar amount of $AuCl{\cdot}SMe_2$.

At T = -70 °C, free ligand and a new species with a sharp resonance at δ(ppm) = 105.4 is present in solution in a ratio of 3:2. The strong upfield shift of the signal is consistent with the formation of the Au(I)-complex [(**2b**)AuCl], in which coordination of the heterocycle to the AuCl-fragment proceeds *via* the phosphorus donor. The presence of larger amounts of free ligand might be attributed to the low solubility of $AuCl{\cdot}S(CH_3)_2$ in CH_2Cl_2 at T = -70 °C. Indeed, with increasing temperature up to T = -10°C, both the signal of the free ligand and the proposed [(**2b**)AuCl] complex decrease in intensity, which indicates that fluxional coordination processes start to take place, while the AuCl-fragment can coordinate to the donor atoms P^4, N^1 and N^2 of the ambidentate triazaphosphole. Between T = 0 °C and r.t., the formation of the products with the resonances at δ(ppm) = 133.81 (**3b**) and δ(ppm) = 2.18 can be observed. It should be noted that during the temperature dependent NMR spectroscopic investigations, also several minor, unidentified phosphorus compounds were detected. However, the exclusive formation of the above-mentioned two phosphorus species in the ratio of approximately 4:1 is completed within 24 h.

1.4 Trapping Experiment

In a *J*-Young NMR tube, *N*-tosyl-triazaphosphole **2a** (20 mg, 0.067 mg) and AuCl(SMe_2) (20 mg, 0.067 mmol) were cooled to *T* = -196 °C. Subsequently, a solution of dimethylbutadiene (22 mg, 0.26 mmol, 4 eq.) as a trapping reagent in CD_2Cl_2 was condensed into the reaction vessel. The solution was first placed into a dry ice bath (*T* = -78 °C) and then slowly warmed to room temperature over 6-8 hours. The reaction solution was analysed by means of NMR spectroscopy (*T* = 25 °C) ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.91–7.85 (m, 3 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.40 (dd, *J* = 8.5, 0.5 Hz, 2H), 7.37–7.33 (m, 2H), 7.10 (dd, *J* = 8.6, 0.7 Hz, 1H), 2.67 (s, 3H), 2.52–2.25 (m), 1.57 (s, 9H), 1.49–1.44 (m), 1.32 (s, 1H), 1.13 (s, 1H), 1.24 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 143.41, 132.24, 131.34, 130.95, 129.74, 129.29, 128.75, 128.65, 128.39, 128.34, 128.23, 127.57, 126.25, 126.12, 124.70, 112.77, 30.94, 28.12, 27.64, 21.62, 20.26, 0.70. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 133.2 (s), 104.8 (s, main species), 13.6 (s). ESI-TOF-MS (m/z): [(**6a**)AuCl] m/z calc. for $C_{18}H_{26}AuClNO_2PS$ $[M + Na]^+$: 606.0668; found 606.0655; [(**6a**)AuCl] m/z calc. for $C_{18}H_{26}AuClNO_2PS$ $[M + K]^+$: 622.0407; found 622.0392.

1.5 Crossover Experiment

Tosyl-substituted triazaphosphole **2a** (30.0 mg, 0.10 mmol), mesitylsulfonyl-substituted triazaphosphole **2b** (32.8 mg, 0.10 mmol) and AuCl(SMe_2) (29.7 mg, 0.10 mmol) were dissolved in 2.0 mL of CH_2Cl_2 under an argon atmosphere. A gas evolution was immediately observed. The reaction solution was first heated to *T* = 60°C for 2 h and then left to cool to room temperature over the next 12 h. The reaction solution was analysed by means of NMR spectroscopy. ^{31}P{^{1}H} NMR (162 MHz, NONE): δ = 133.9 (s), 133.0 (s), 132.3 (s). The above-mentioned three phosphorus species are in the ratio of approximately 4:4:1 (see Figure S13).

2. Crystallographic Details

Crystals of **2b** suitable for X-ray diffraction were obtained by laying diethyl ether on a dichloromethane solution of **2b** at low temperature. Crystals of **3a** and **3b** suitable for X-ray diffraction were obtained from their reaction mixtures at low temperature. X-ray studies were carried out on a D8 Venture, Bruker Photon CMOS diffractometer[3] with a rotating anode (MoKα radiation; λ = 0.71073 Å) up to a resolution of $(\sin\Theta/\lambda)_{max}$ = 0.60 Å at 104(2) K (**2b**), 100(2) K (**3a**) and 102(2) K (**3b**). The structures were solved with SHELXT-2014/5[4a] by using direct methods and refined with SHELXL-2017/1[4b] on F^2 for all reflections. Non-

hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[5] Crystal data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Database Center: CCDC number: 1983603 (**2b**), CCDC number: 1983601 (**3a**) and CCDC number: 1983602 (**3b**). Details of the X-ray structure determinations and refinements are provided in Table S1.

Table S1. Crystal data and structure refinement for **2b**, **3a** and **3b** (CCDC: 1983603, 1983601, 1983602).

Identification code	**2b**	**3a**	**3b**
Empirical formula	$C_{14}H_{20}N_3O_2PS$	$C_{24}H_{32}Au_2Cl_2N_2O_4P_2S_2$	$C_{28}H_{40}Au_2Cl_2N_2O_4P_2S_2$
Formula weight	325.36	1003.42	1059.52
Temperature/K	104(2)	100(2)	102(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	10.6589(3)	8.8016(5)	9.6463(2)
b/Å	17.7200(4)	9.8055(4)	17.8725(4)
c/Å	8.8396(2)	17.4622(9)	10.9159(2)
α/°	90	90	90
β/°	102.6651(9)	96.710(2)	114.0878(7)
γ/°	90	90	90
Volume/Å^3	1628.96(7)	1496.74(13)	1718.06(6)
Z	4	2	2
ρ_{calc}g/cm^3	1.327	2.227	2.048
μ/mm^{-1}	0.304	10.250	8.935
F(000)	688	952	1016
Crystal size/mm^3	0.660×0.110×0.050	0.115×0.035×0.020	0.170×0.100×0.040
Radiation	MoKα(λ = 0.71073)	MoKα(λ = 0.71073)	MoKα(λ = 0.71073)
2Θ range for	4.54 to 52.83	4.70 to 52.89	4.62 to 51.44

data collection/°			
Index ranges	$-13 \le h \le 13$, $-22 \le k \le 21$, $-11 \le l \le 11$	$-11 \le h \le 11$, $-12 \le k \le 10$, $-21 \le l \le 21$	$-11 \le h \le 11$, $-21 \le k \le 21$, $-13 \le l \le 13$
Reflections collected	17318	18922	24932
Independent reflections	3335 [R_{int} = 0.0524, R_{sigma} = 0.0408]	3072 [R_{int} = 0.0245, R_{sigma} = 0.0423]	3267 [R_{int} = 0.0452, R_{sigma} = 0.0236]
Data/restraints/parameters	3335/0/196	3072/0/176	3267/0/196
Goodness-of-fit on F^2	1.033	1.186	1.133
Completeness to θ	99.9%	99.7%	99.8%
Final R indexes [I>=2σ (I)]	R1 = 0.0370 wR2 = 0.0817	R1 = 0.0335 wR2 = 0.0582	R1 = 0.0233 wR2 = 0.0465
Final R indexes [all data]	R1 = 0.0575 wR2 = 0.0896	R1 = 0.0434 wR2 = 0.0582	R1 = 0.0296 wR2 = 0.0465
Largest diff. peak/hole/e Å^{-3}	0.292/-0.408	1.832/-1.617	1.369/-0.778

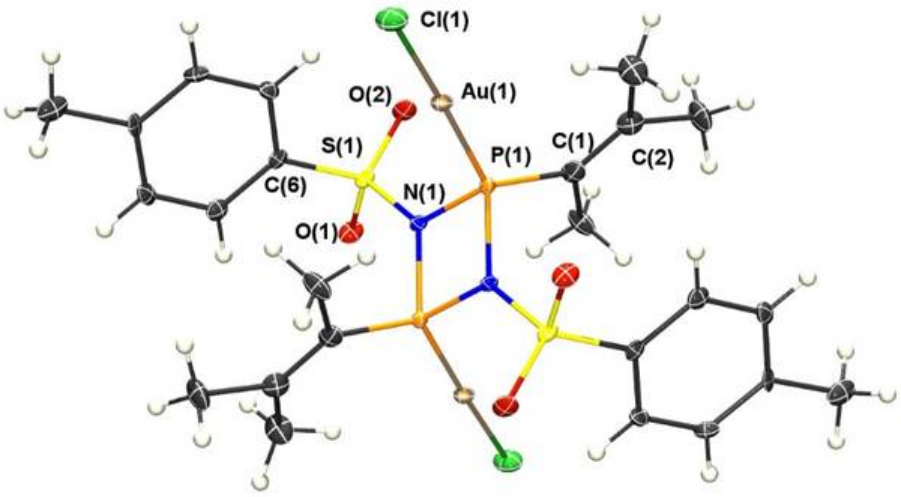


Figure S3. Molecular structure of **3a** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angels (°): P(1)-N(1): 1.720(5), N(1)-P(1)_i: 1.732 (5), N(1)-S(1): 1.658(5), P(1)-Au(1): 2.203(1), P(1)-C(1): 1.796(7), C(1)-C(2): 1.337(9), N(1)-P(1)-N(1)_i: 79.9(2), P(1)-N(1)-P(1)_i: 100.1(2).

3. NMR Spectroscopic Data

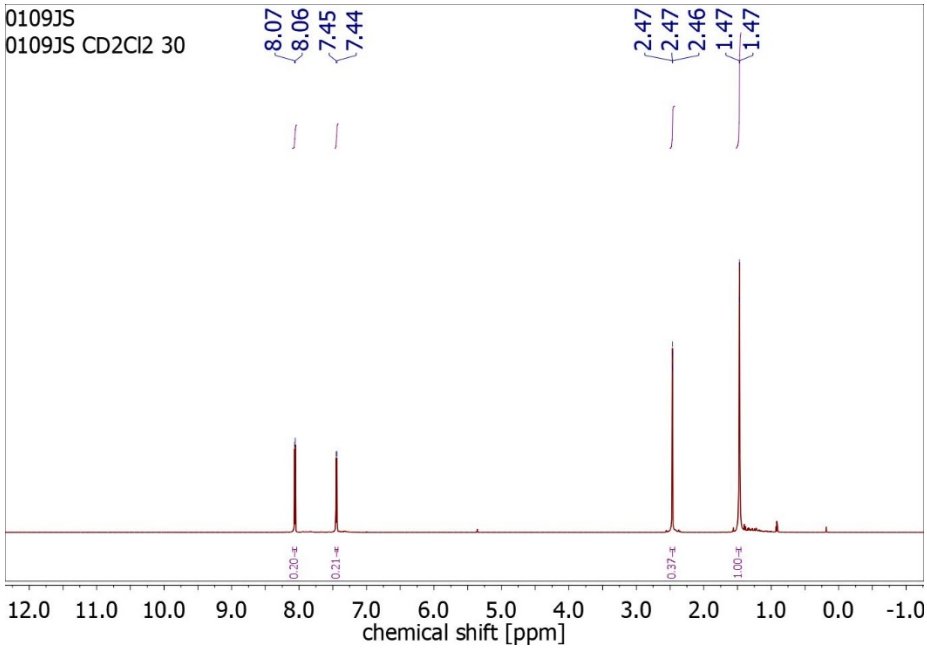


Figure S4. ^{1}H NMR spectrum of **2a** in CD_2Cl_2

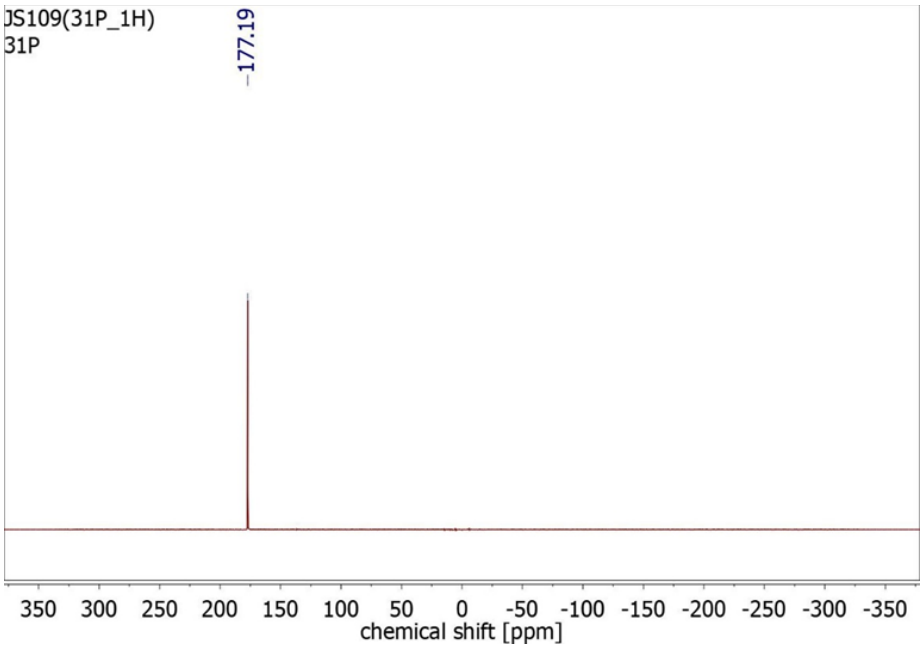


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in CD_2Cl_2.

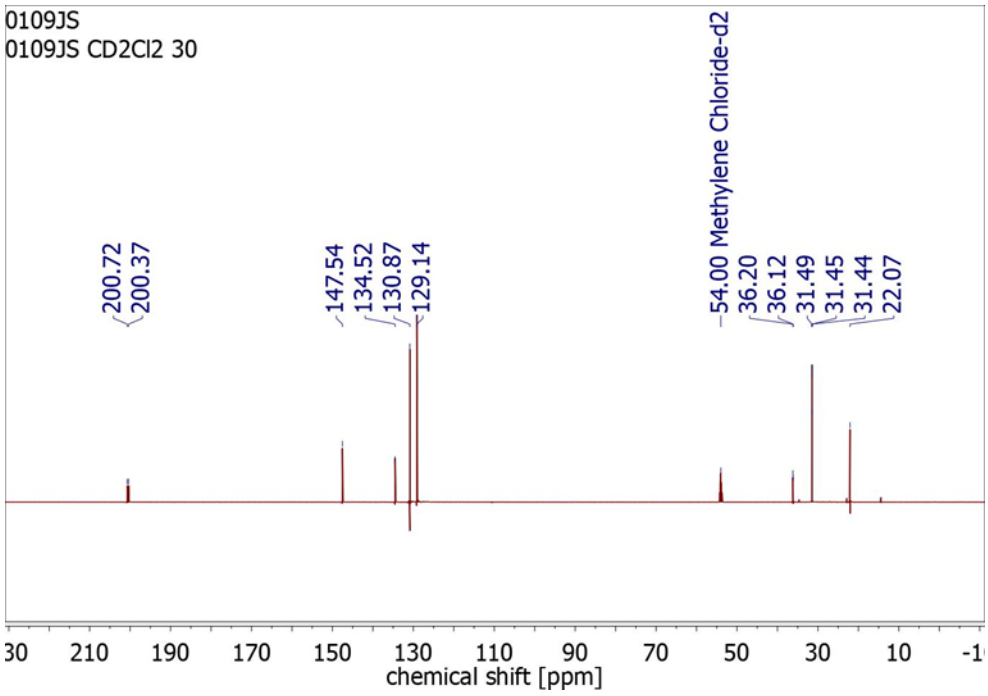


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in CD_2Cl_2.

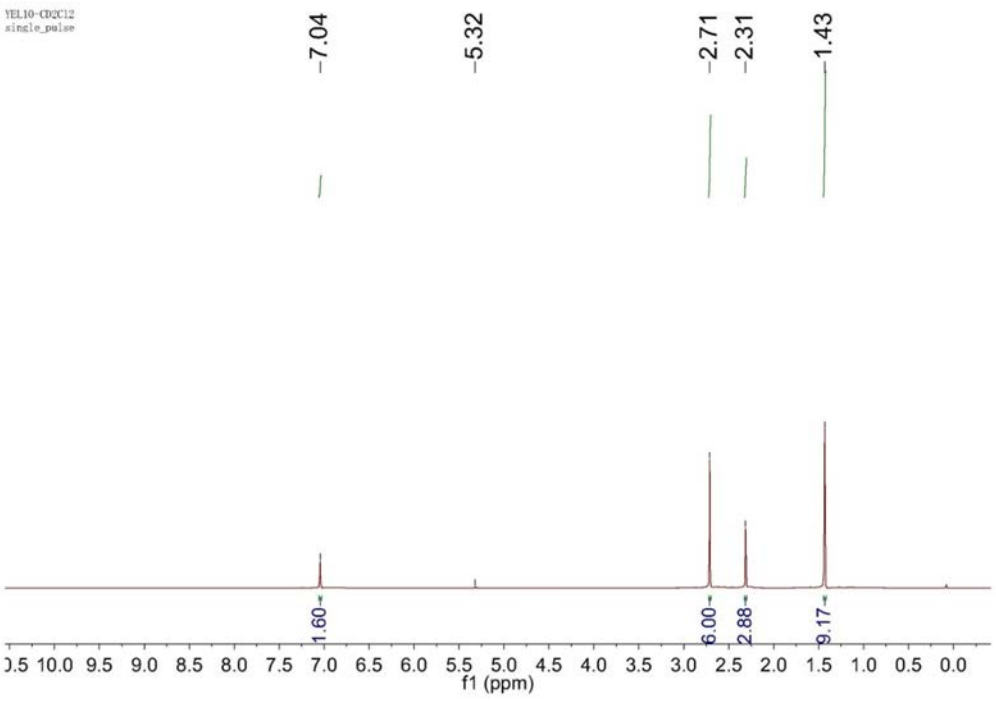


Figure S7. ^{1}H NMR spectrum of **2b** in CD_2Cl_2.

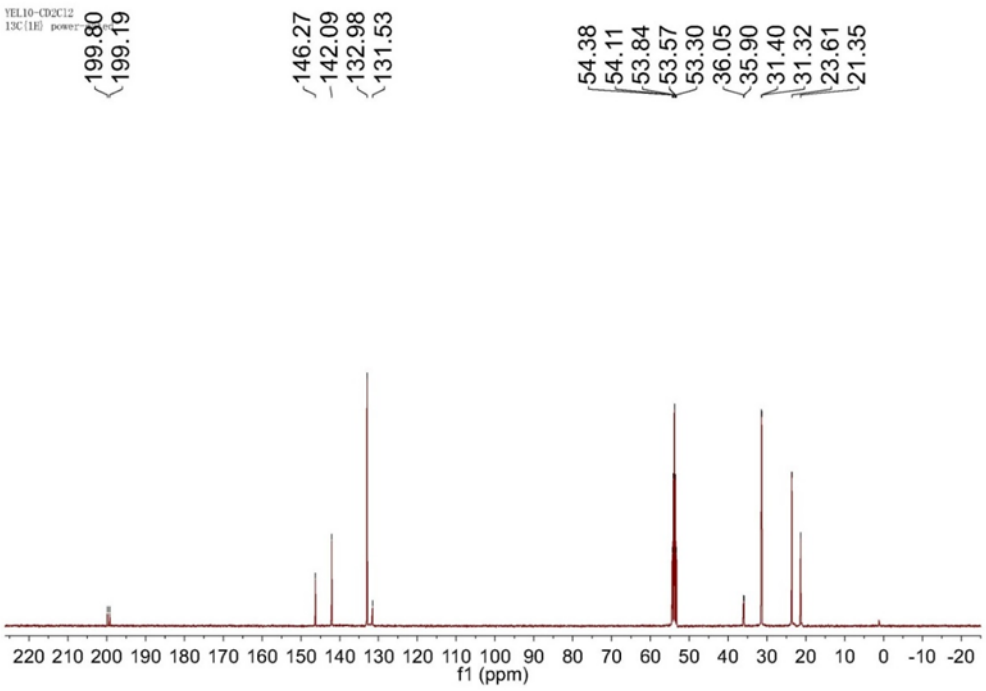


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2.

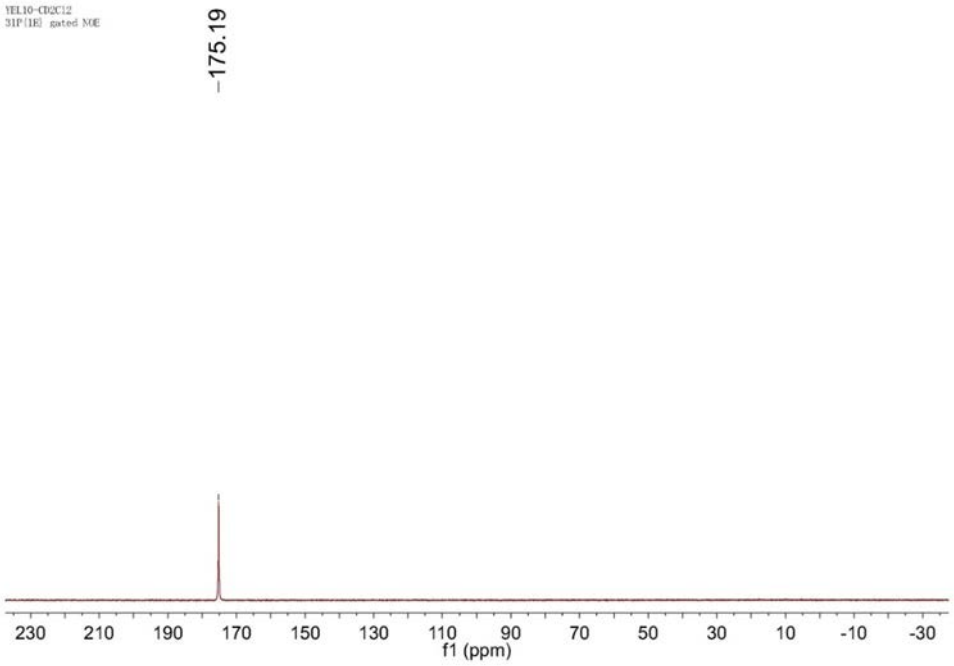


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2.

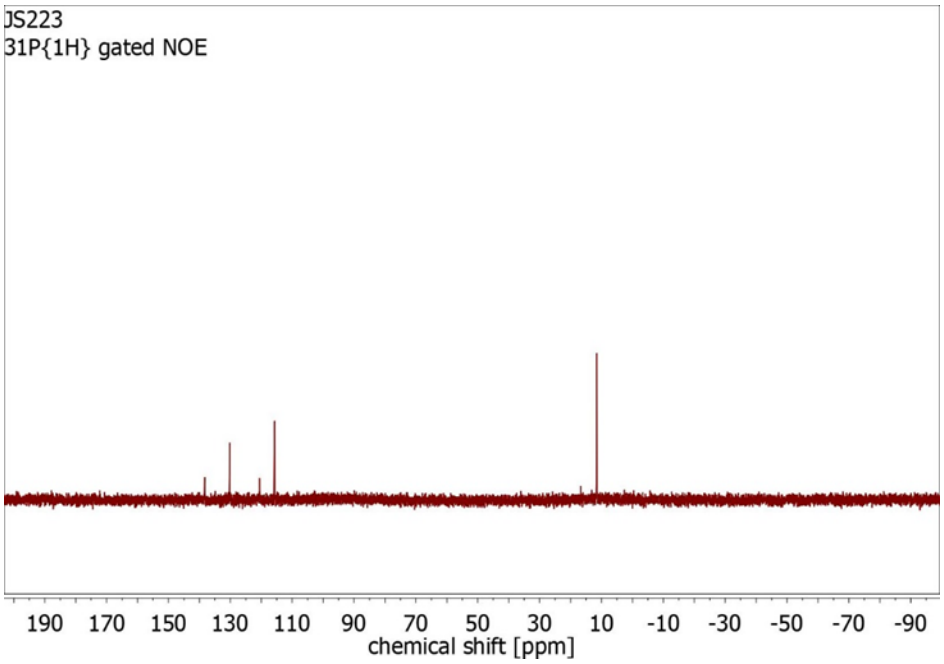


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum for the unselective reaction of **2a** with $AuCl{\cdot}SMe_2$ in CD_2Cl_2.

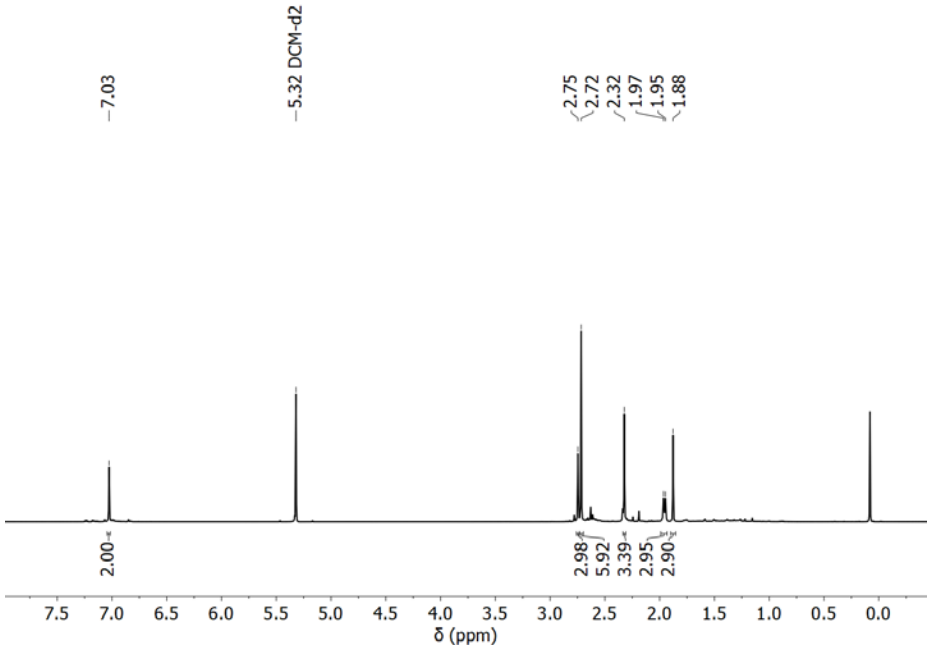


Figure S10. ^{1}H NMR spectrum of **3b** in CD_2Cl_2.

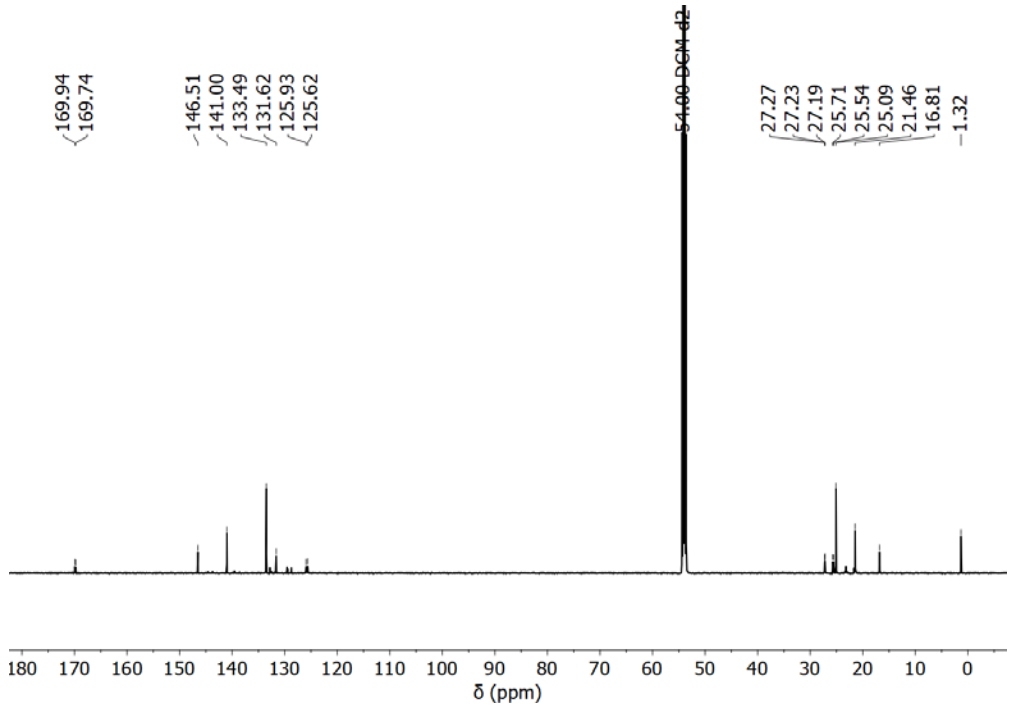


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in CD_2Cl_2.

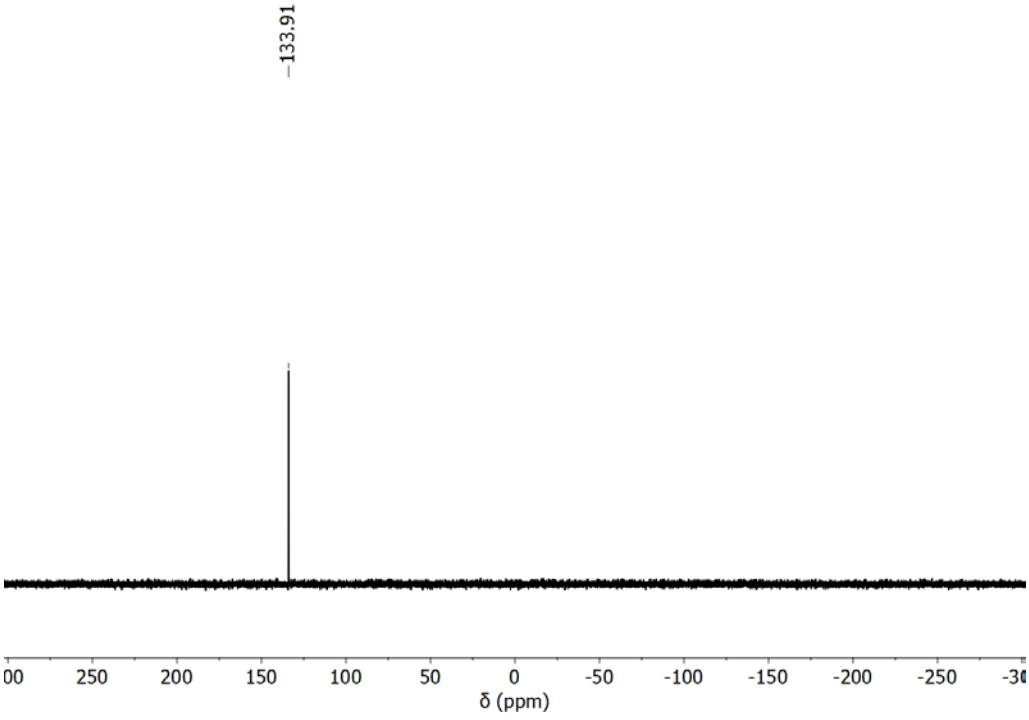


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **3b** in CD_2Cl_2.

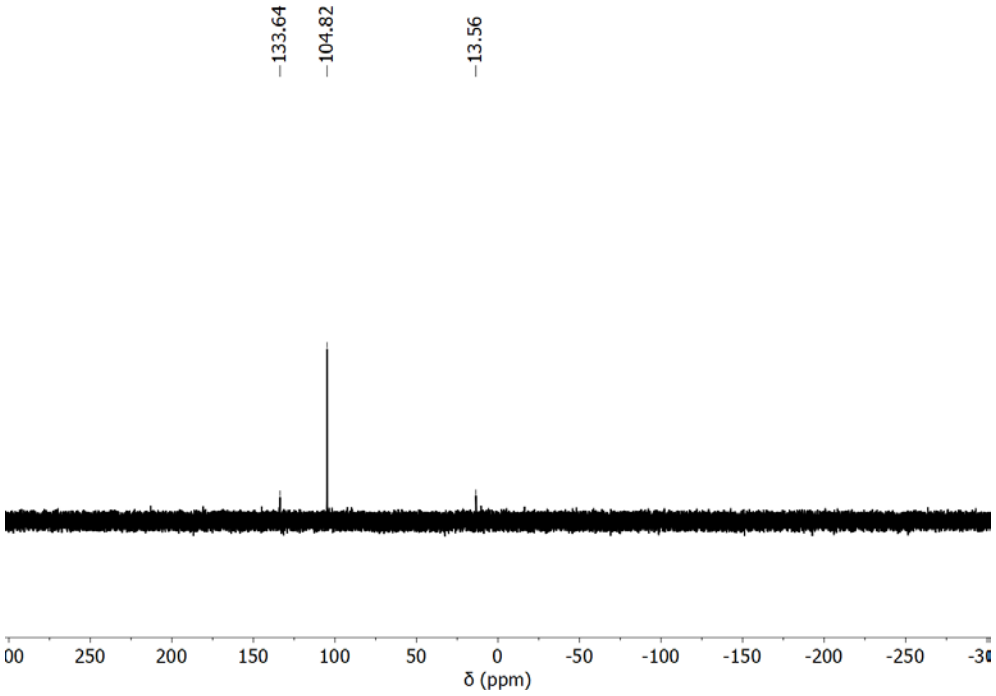


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of trapping experiment.

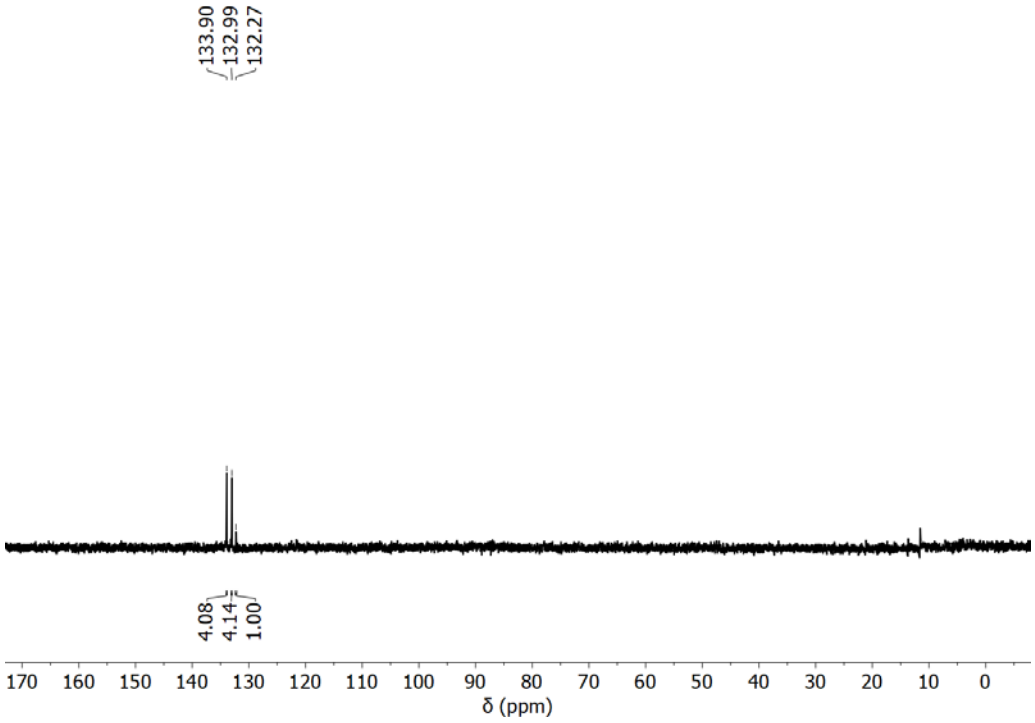


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of crossover experiment.

4. References

[1] a) T. J. Curphey, *Org. Prep. Proced. Int.* 1981, **13**, 112; b) R. A. Abramovitch, T.Chellathurai, D. W. Holcomb, T. I. McMaster, D. P. Vanderpool, *J. Org. Chem.* 1977, **42**, 2920.

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