Supplementary Information

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Contents

General Comments

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or a glovebox. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). All solvents were degassed using freeze pump technique. ^{1}H, ^{13}C, ^{31}P, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance III HD 500 (equipped with a prodigy probe), Avance III HD 400, Avance II 300 and Avance I 300 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ^{1}H and ^{13}C solvent signals. External $BF_3.OEt_2$, 85% H_3PO_4 and $CFCl_3$ were used as reference for ^{11}B, ^{31}P and ^{19}F NMR respectively. Mass spectra were recorded on a Waters LCT mass spectrometer. Elemental analyses were recorded on a PERKIN ELMER 2400 II.

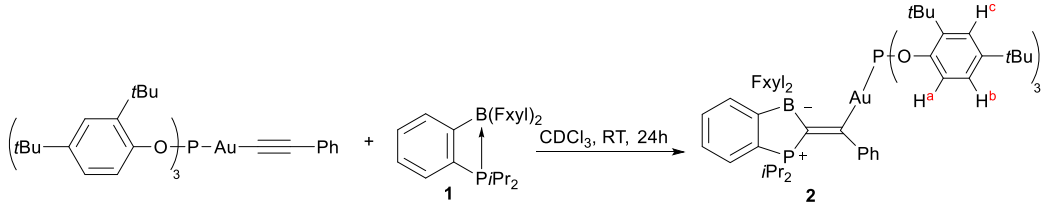
The phosphine-borane **1** was prepared as previously reported by our group.[1] $((ArO)_3P)Au(C{\equiv}CPh)$ was synthetized following the *modus operandi* described in literature.[2] All others reagents were purchased from Sigma-Aldrich, Fluorochem, ACROS Organics or TCI chemicals and used as received.

Abbreviations

THT	tetrahydrothiophene
THF	tetrahydrofuran
DCM	dichloromethane
DMS	tetrahydrothiophene
Fxyl	3,5-bis(trifluoromethyl)phenyl
HMDSO	hexamethyldisiloxane
Xyl	2,6-dimethylphenyl

[1] Boudjelel, M.; Carrizo, E. D. S.; Mallet−Ladeira, S.; Massou, S.; Miqueu, M.; Bouhadir, G.; Bourissou, D. *ACS Catal.* **2018**, *8*, 4459−4464.
[2] Hosseyni, S; Smith, C.A.; Shi, X. *Org. Lett.* **2016**, *18*, 6336–6339

Synthesis of 2:



A J. Young cap NMR tube was charged with $((ArO)_3P)Au(C{\equiv}CPh)$ (152.5 mg, 0.16 mmol) in 0.4 mL of $CDCl_3$ and the phosphine-borane **1** (101 mg, 0.16 mmol, 1 equiv.) was added at room temperature as a solution in 0.3 mL of $CDCl_3$. After 1 day at this temperature, a clear orange solution was obtained. The solvent was removed under vacuum to afford a yellow solid. The latter was solubilized in pentane and the mixture was allowed to stand at room temperature for another day. The volatiles were evaporated *in vacuo*. The yellow solid was redispersed in HMDSO (2 mL) and the solution placed at –20°C for 2 days yielding to the partial precipitation of a white solid identified as free $P(OAr)_3$. The supernatant was then collected and the HMDSO removed under high vacuum. Finally a column over neutral Al_2O_3 was performed in the glovebox using a pentane/toluene gradient (from 100/0 to 75/25) to remove the remaining $P(OAr)_3$ and traces of unidentified by-products. All volatiles were removed under high vacuum to afford a white solid identified as a mixture of 95% of **2** and 5% of $P(OAr)_3$ (57.1 mg of solid, estimated yield of **2**: 22%). Crystals suitable for X-Ray diffraction were obtained by crystallization from a HMDSO/pentane mixture at room temperature.

m.p.: 114.8°C

^{1}H NMR ($CDCl_3$, 500.1 MHz, 298 K): δ (in ppm) 8.11 (br.s, 4H, $H_{o\text{-Fxyl}}$), 7.47 (br.s, 2H, $H_{p\text{-Fxyl}}$), 7.42-7.37 (m, 1H, H_{Ar}), 7.31-7.24 (m, 5H, $2H_{Ar}$ and $3H_c$), 7.21-7.14 (m, 3H, $1H_{Ar}$ and $2H_{m\text{-Ph}}$), 7.08 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 1.4 Hz, 3H, H_a), 7.11-7.02 (m, 1H, $H_{p\text{-Ph}}$), 6.76 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 3H, H_b), 6.73 (d br., J_{HH} = 8.0 Hz, 2H, $H_{o\text{-Ph}}$), 2.35-2.20 (m, 2H, C*H*$_{i\text{Pr}}$), 1.27 (s, 27H, $H_{t\text{Bu}}$), 1.13 (s, 27H, $H_{t\text{Bu}}$), 1.10 (dd, $^3J_{PH}$ = 15.7 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, C*H*$_{3i\text{Pr}}$), 0.56 (dd, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, C*H*$_{3i\text{Pr}}$).

Jmod (^{13}C{^{1}H}) NMR ($CDCl_3$, 125.8 MHz, 298 K): δ (in ppm) 210.3 (dd, $^2J_{CP}$ = 165.1 Hz and 10.0 Hz, P-C=*C*-Au-$P(OAr)_3$), 173.17 (br.s, B-C$_{ipso\text{-Ar}}$), 162.0 (br.q, B-C$_{ipso\text{-Fxyl}}$), 153.8 (d, J_{PC} = 21.3 Hz, $C_{ipso\text{-Ph}}$), 147.7 (d, $^2J_{PC}$ = 5.0 Hz, O-C$_{ipso\text{-P(OAr)3}}$), 147.0 (s, C-*t*Bu), 138.9 (d, J_{PC} = 5.3 Hz, C-*t*Bu), 134.4 (s, $CH_{o\text{-Fxyl}}$), 134.0 (d, J_{PC} = 12.1 Hz, CH_{Ar}), 132.2 (s, CH_{Ar}), 129.3 (d, J_{PC} = 11.3 Hz, CH_{Ar}), 128.7 (q, $^2J_{FC}$ = 31.8 Hz, *C*-CF_3), 128.4 (s, $CH_{m\text{-Ph}}$), 125.7 (d, J_{PC} = 9.9 Hz, CH_{Ar}), 125.1 (s, $CH_{p\text{-Ph}}$), 125.0 (s, $CH_{o\text{-Ph}}$), 124.7 (s, CH_c), 124.6 (q, $^1J_{CF}$ = 272.8 Hz, CF_3), 123.7 (s, CH_b), 119.6 (d, $^4J_{PC}$ = 10.4 Hz, CH_a), 117.9 (m, $CH_{p\text{-Fxyl}}$), 34.8 (s, $C_{t\text{Bu}}$), 34.6 (s, $C_{t\text{Bu}}$), 31.5 (s, $CH_{3t\text{Bu}}$), 30.3 (s, $CH_{3t\text{Bu}}$), 27.6 (s, $CH_{i\text{Pr}}$), 27.3 (s, $CH_{i\text{Pr}}$), 17.0 (d, $^3J_{PC}$ = 2.9 Hz, $CH_{3i\text{Pr}}$), 16.6 (s, $CH_{3i\text{Pr}}$).

NB: P-*C*=C-Au-$P(OAr)_3$ *not visible.*

^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz, 298 K): δ (in ppm) 137.4 (d, $^4J_{PP}$ = 85.5 Hz, $P_{P(OAr)3}$), 41.6 (d pseudo-q, $^4J_{PP}$ = 85.5 Hz, $^2J_{PB}$ = 21.3 Hz, $P_{i\text{Pr2P}}$).

^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz, 298 K): δ (in ppm) -5.08 (d, J_{PB} = 21.3 Hz)

^{19}F NMR ($CDCl_3$, 470.5 MHz, 298 K): δ (in ppm) -62.08 (s)

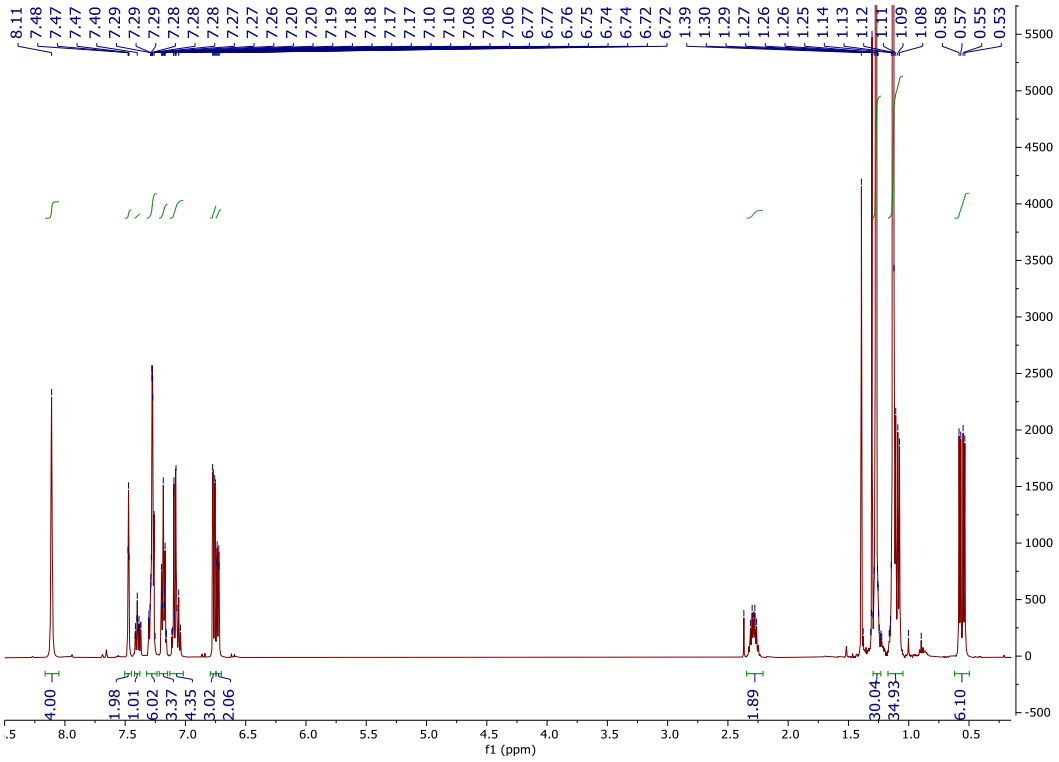


Figure S1. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K).

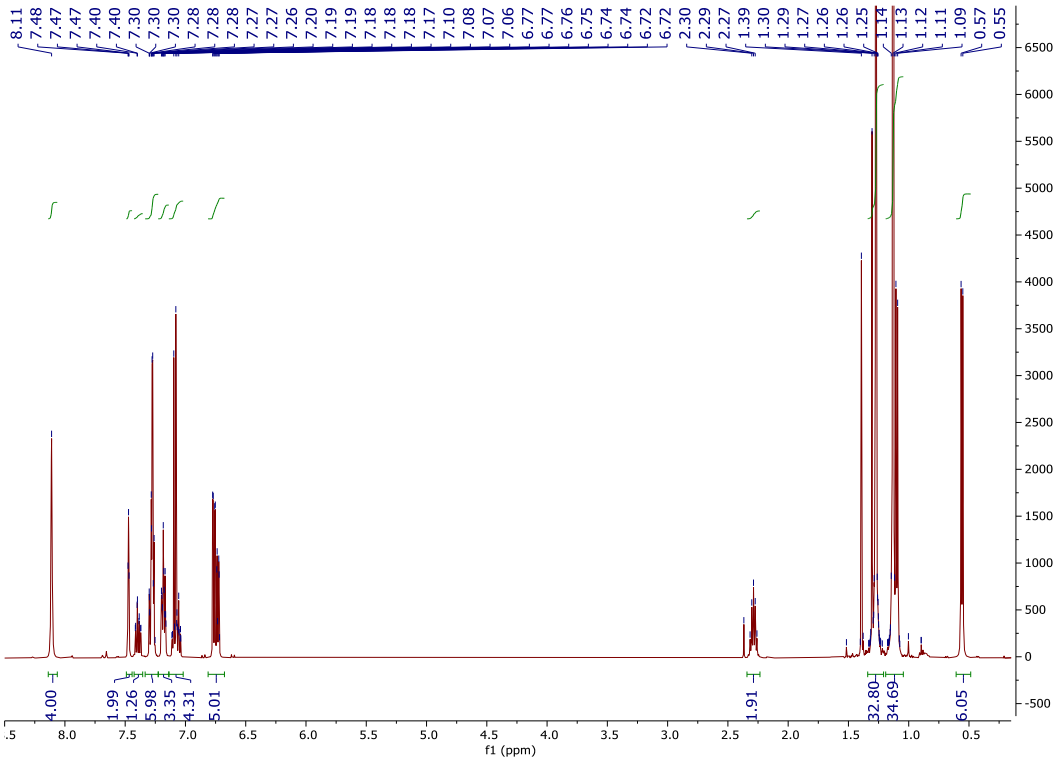


Figure S2. ^{1}H{^{31}P} NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K).

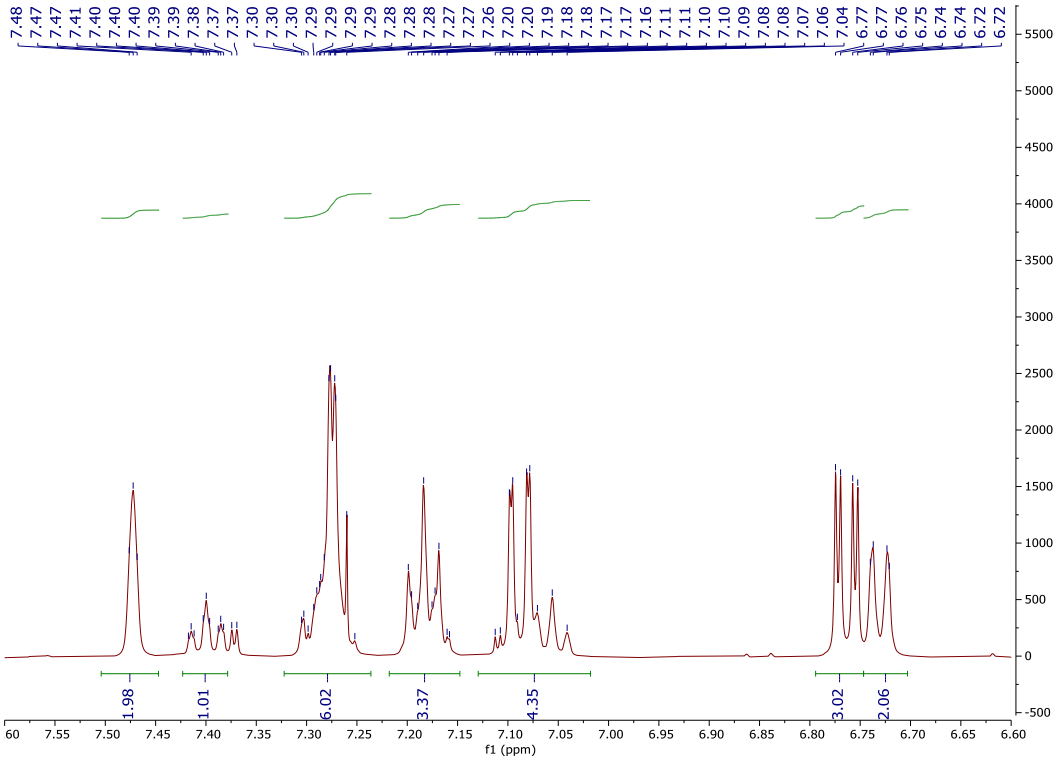


Figure S3. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aromatic area.

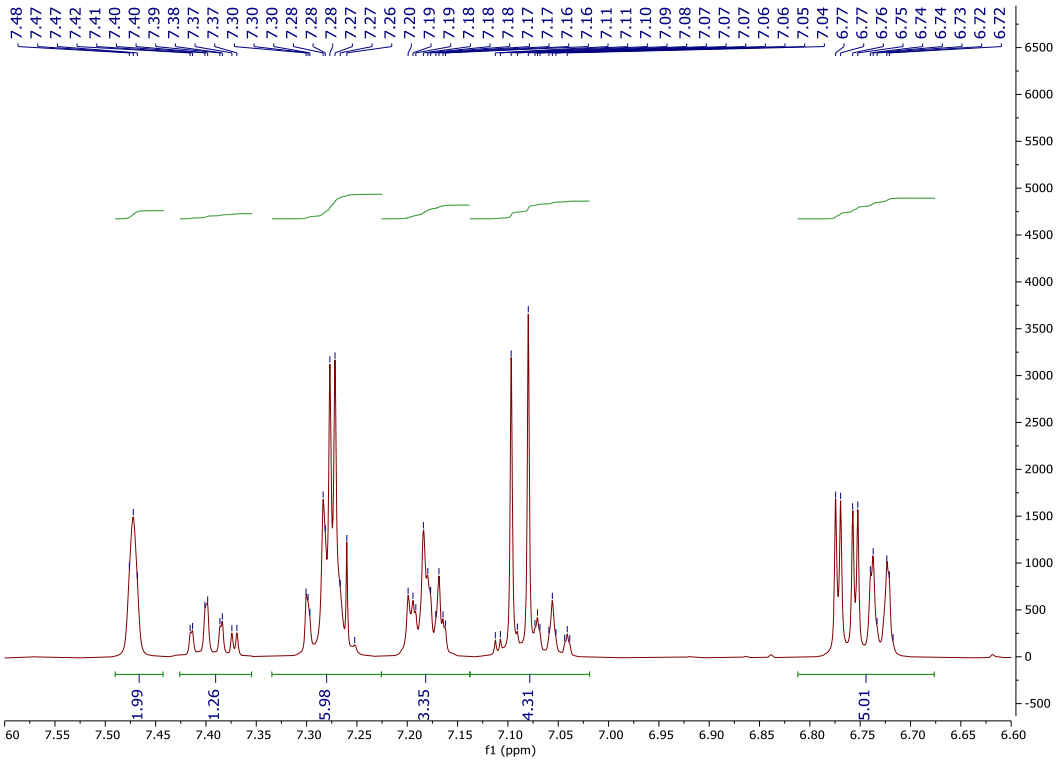


Figure S4. ^{1}H{^{31}P} NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aromatic area.

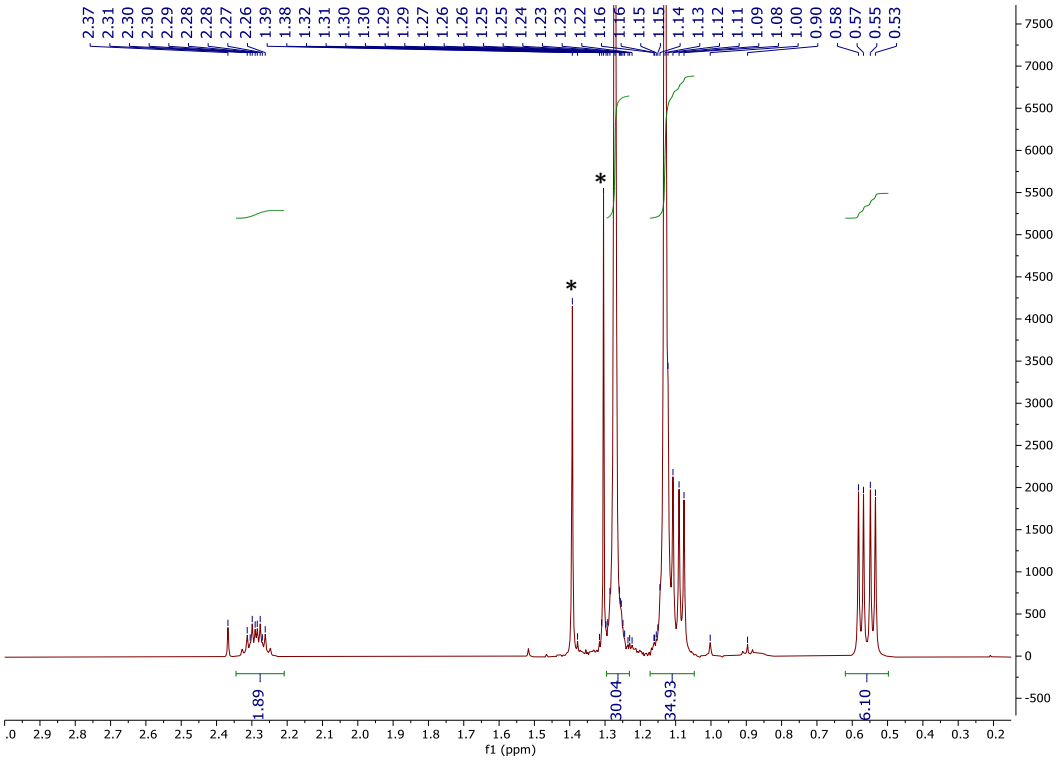


Figure S5. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aliphatic area.
** tBu resonances of remaining traces of free P(OAr)$_3$ (<5%)*

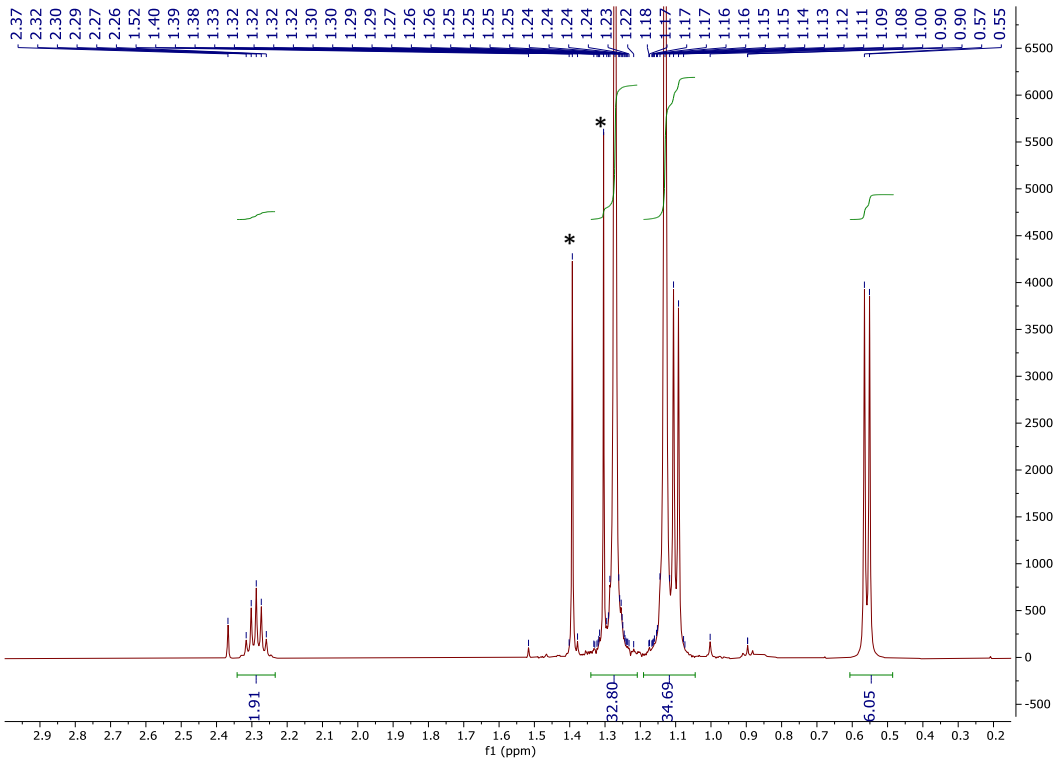


Figure S6. ^{1}H{^{31}P} NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aliphatic area.
** tBu resonances of remaining traces of free P(OAr)$_3$ (<5%).*

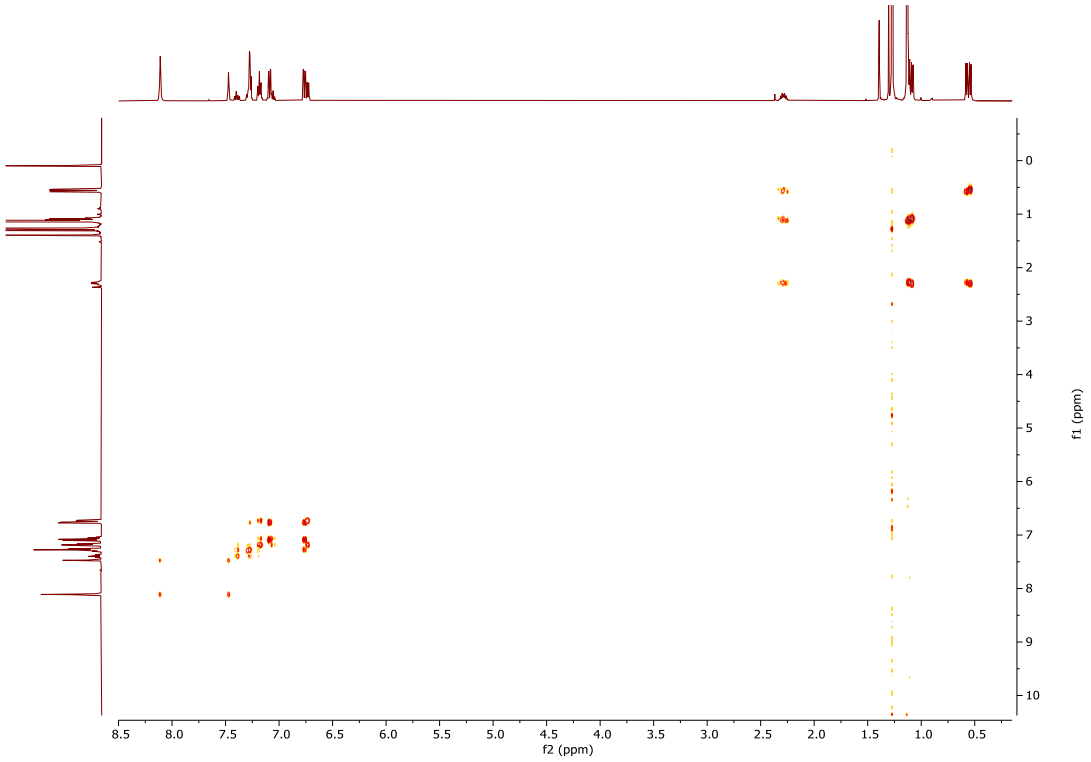


Figure S7. COSY (^{1}H ;^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K).

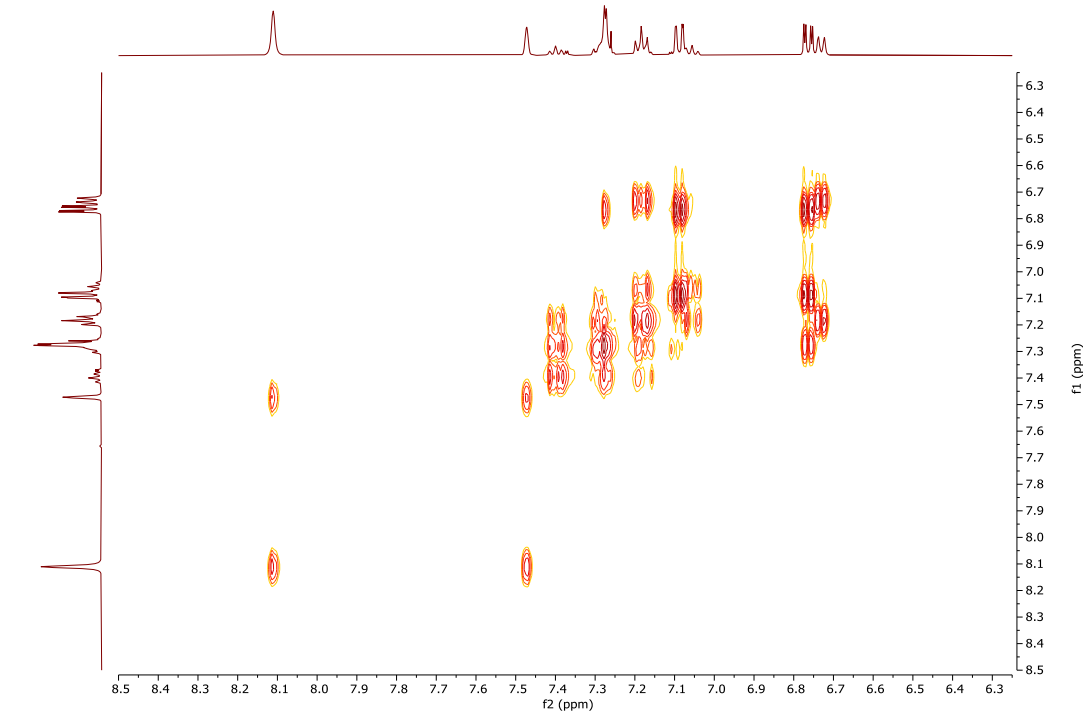


Figure S8. COSY (^{1}H ;^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aromatic area.

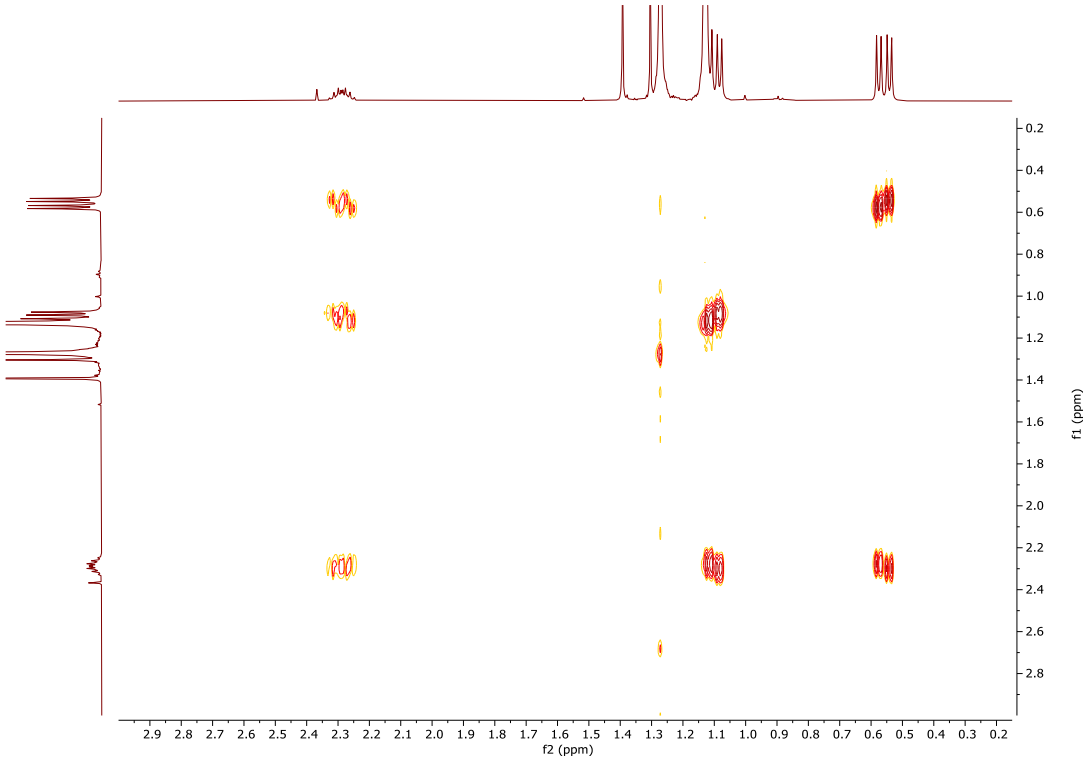


Figure S9. COSY (^{1}H ;^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aliphatic area.

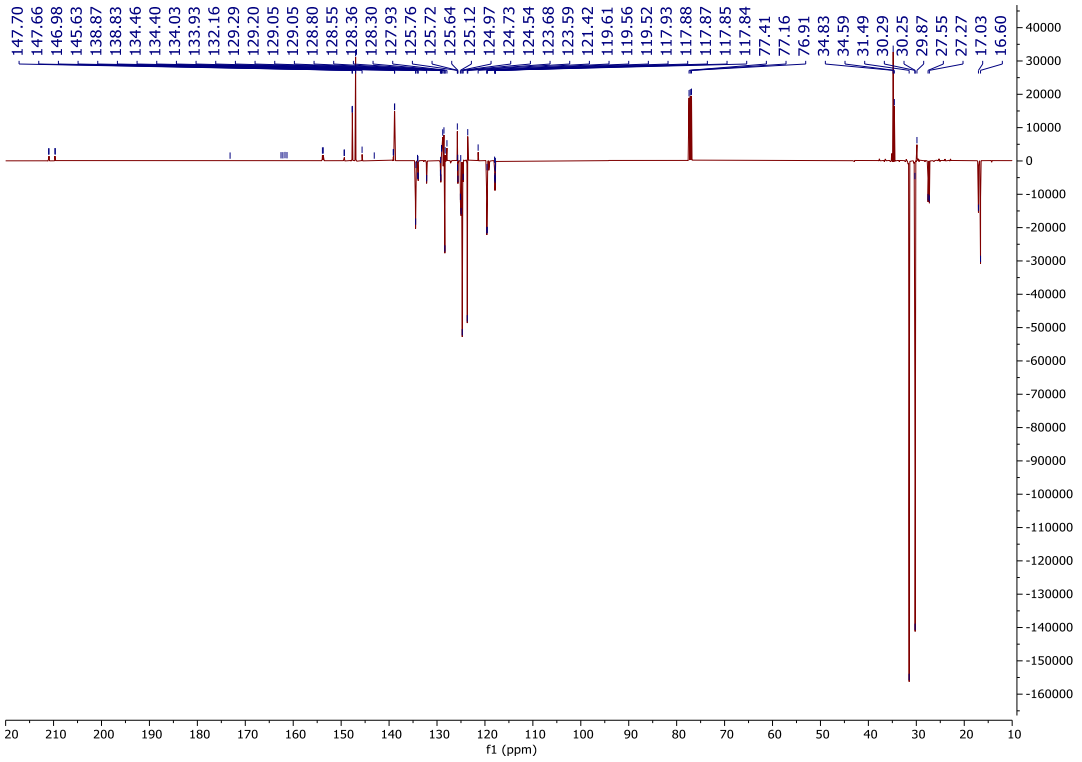


Figure S10. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K).

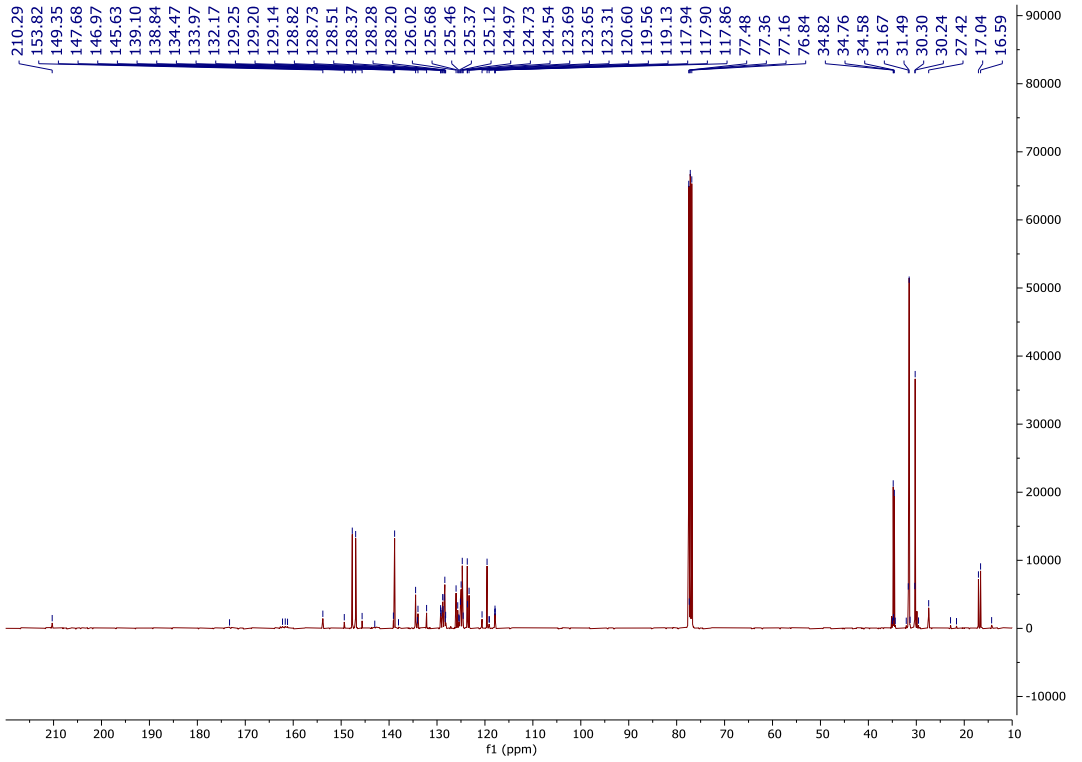


Figure S11. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K).

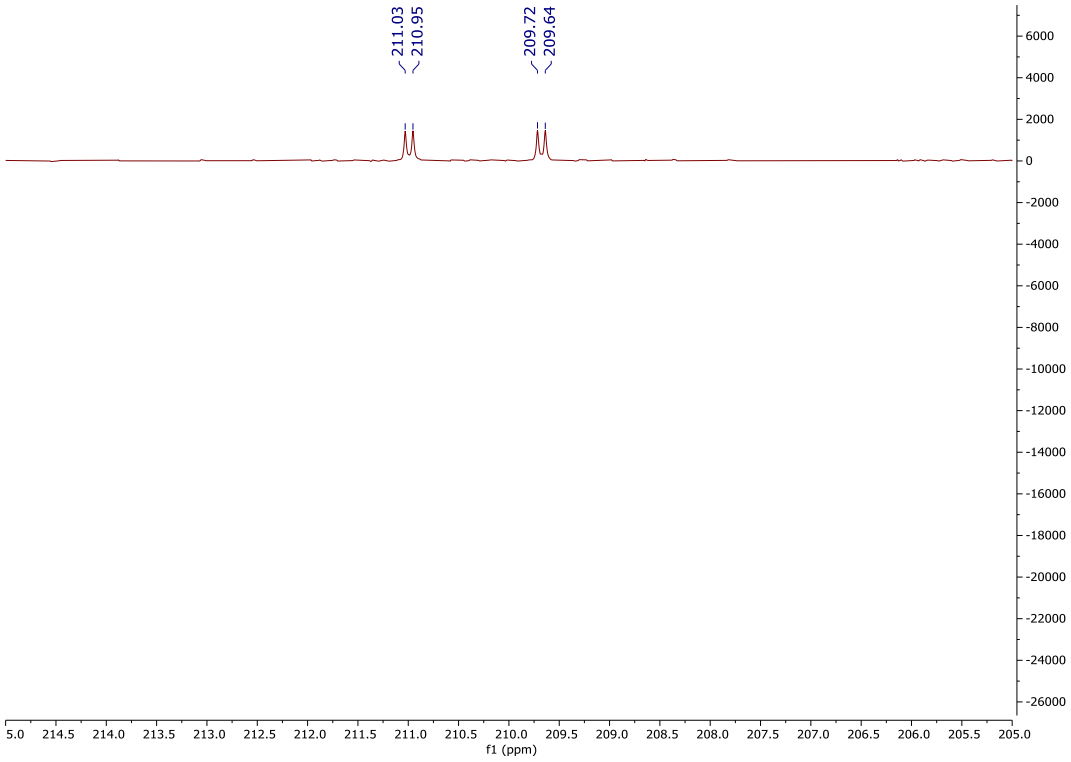


Figure S12. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K); Au-C(sp^2) area.

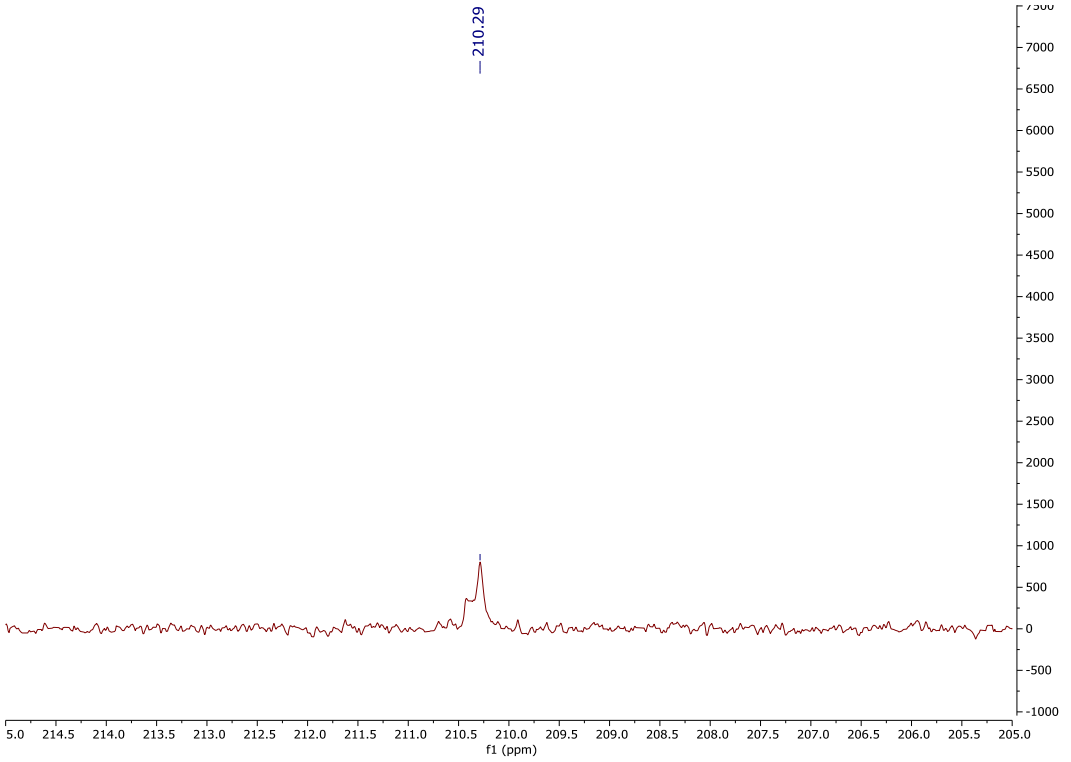


Figure S13. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K); Au-C(sp^2) area.

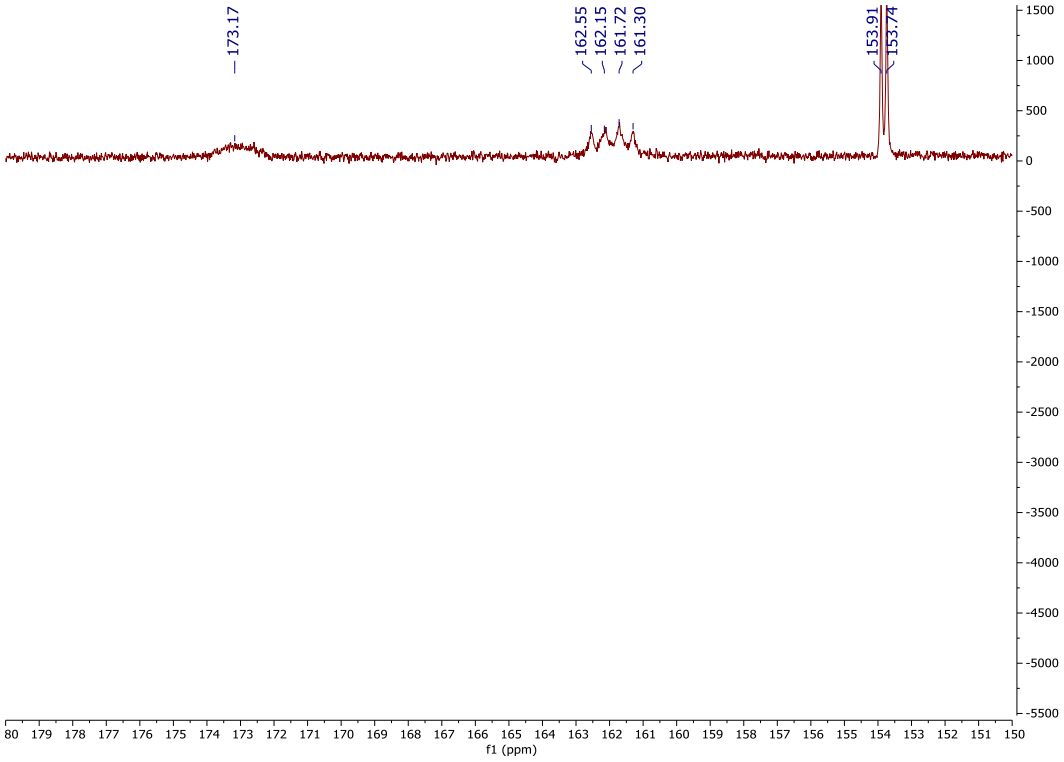


Figure S14. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K); aromatic area.

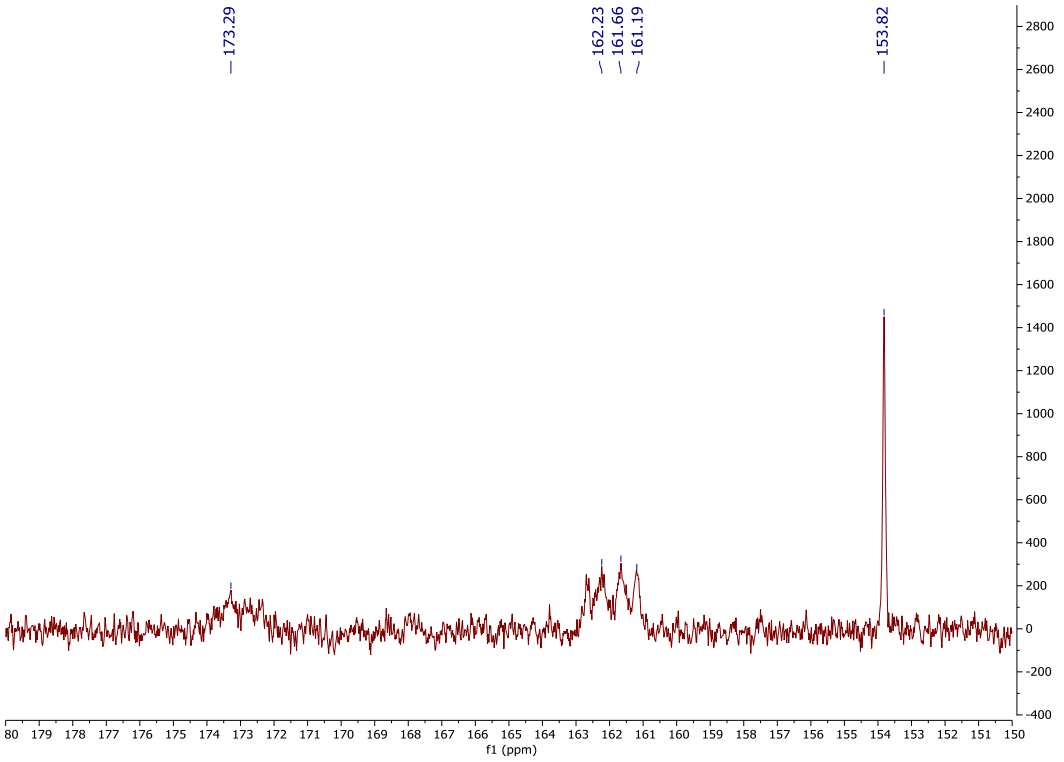


Figure S15. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area.

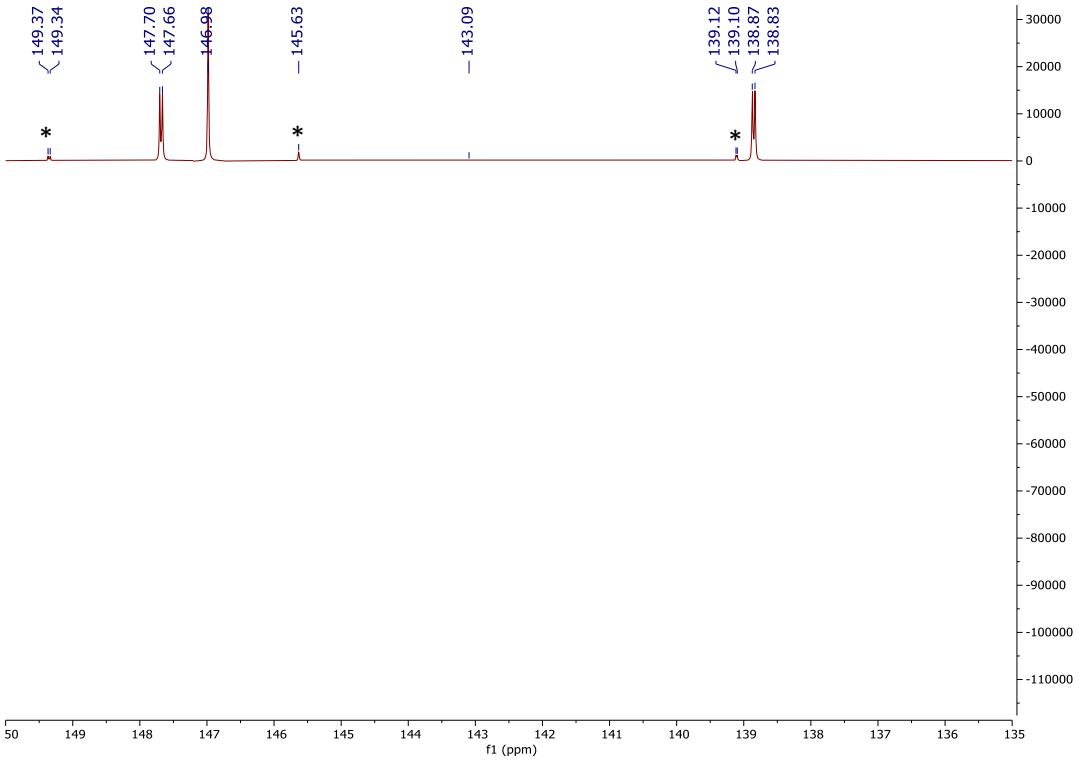


Figure S16. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K); aromatic area. * *C_q resonances of remaining traces of free P(OAr)$_3$ (<5%).*

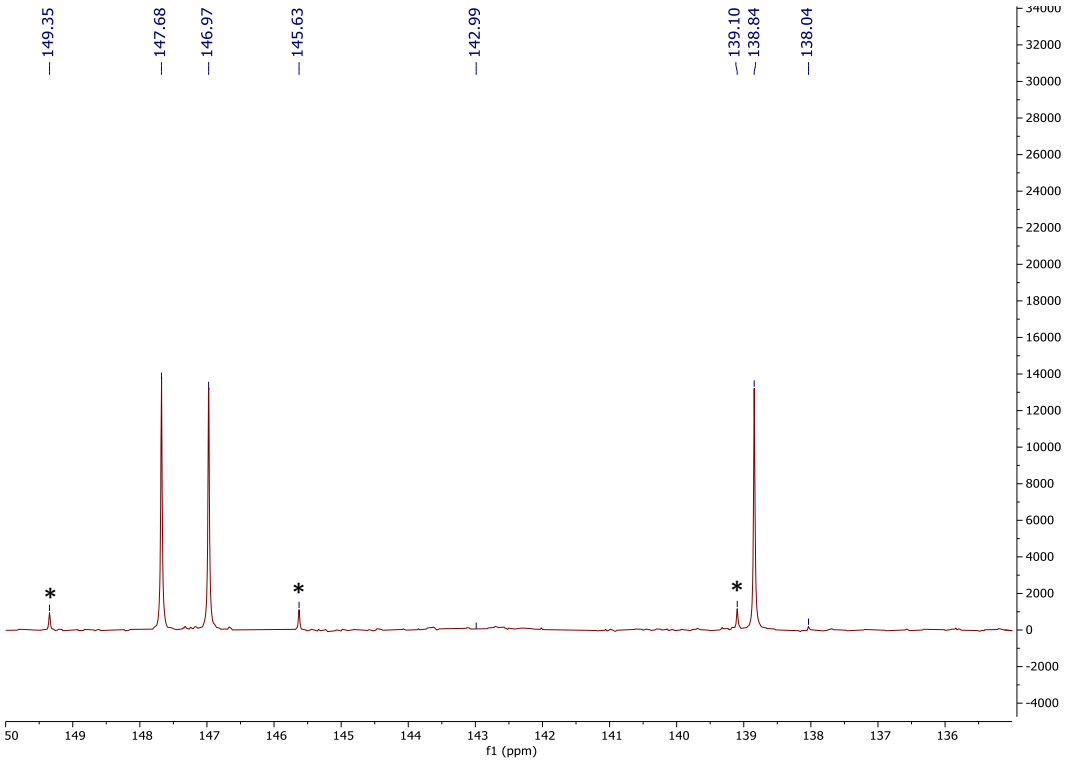


Figure S17. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area. * *C_q resonances of remaining traces of free P(OAr)$_3$ (<5%)*

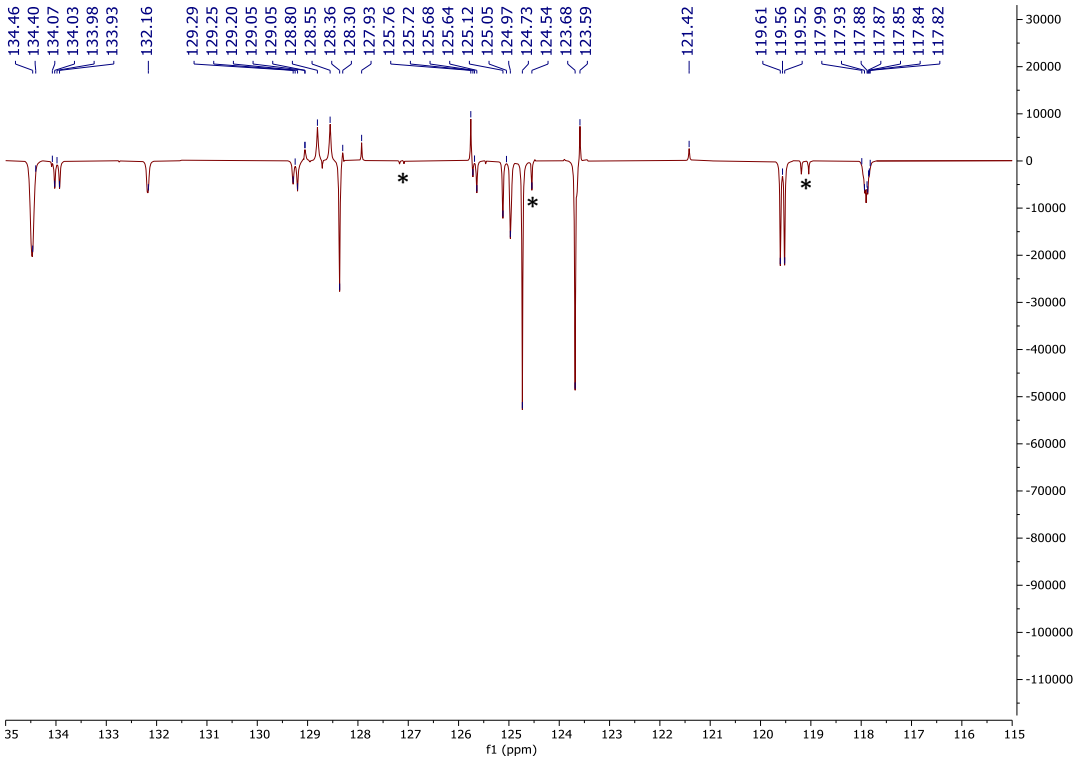


Figure S18. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K); aromatic area.* *CH resonances of remaining traces of free P(OAr)$_3$ (<5%).*

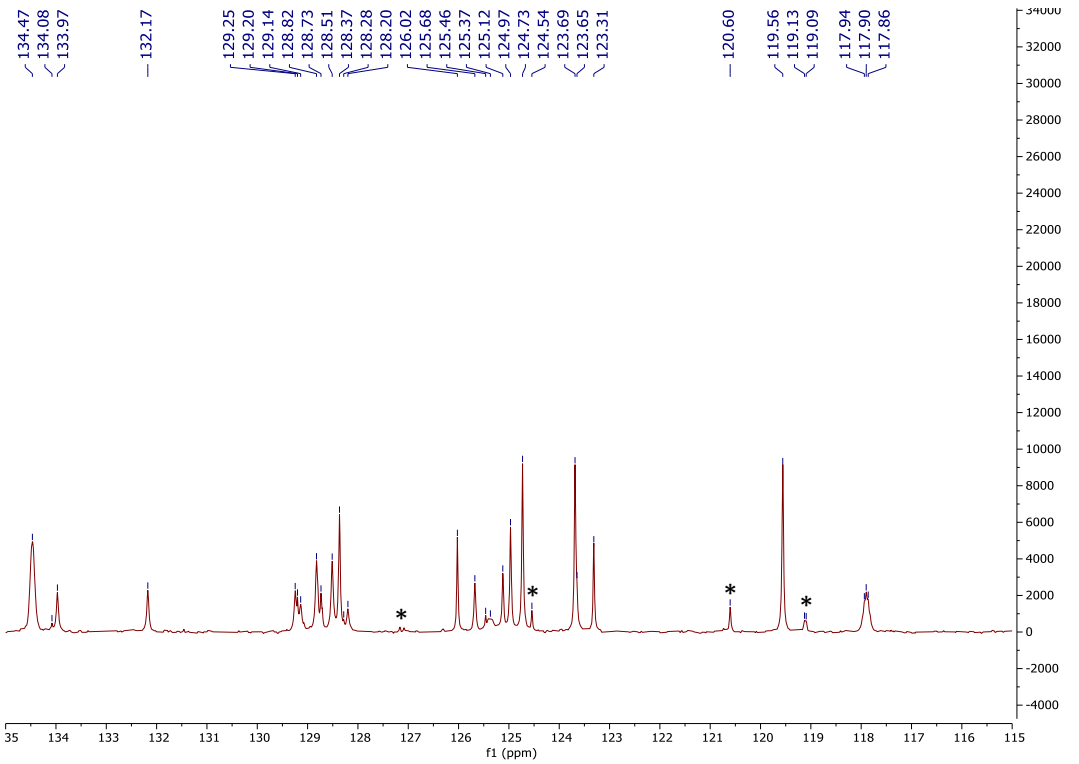


Figure S19. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area. * *impurities.*

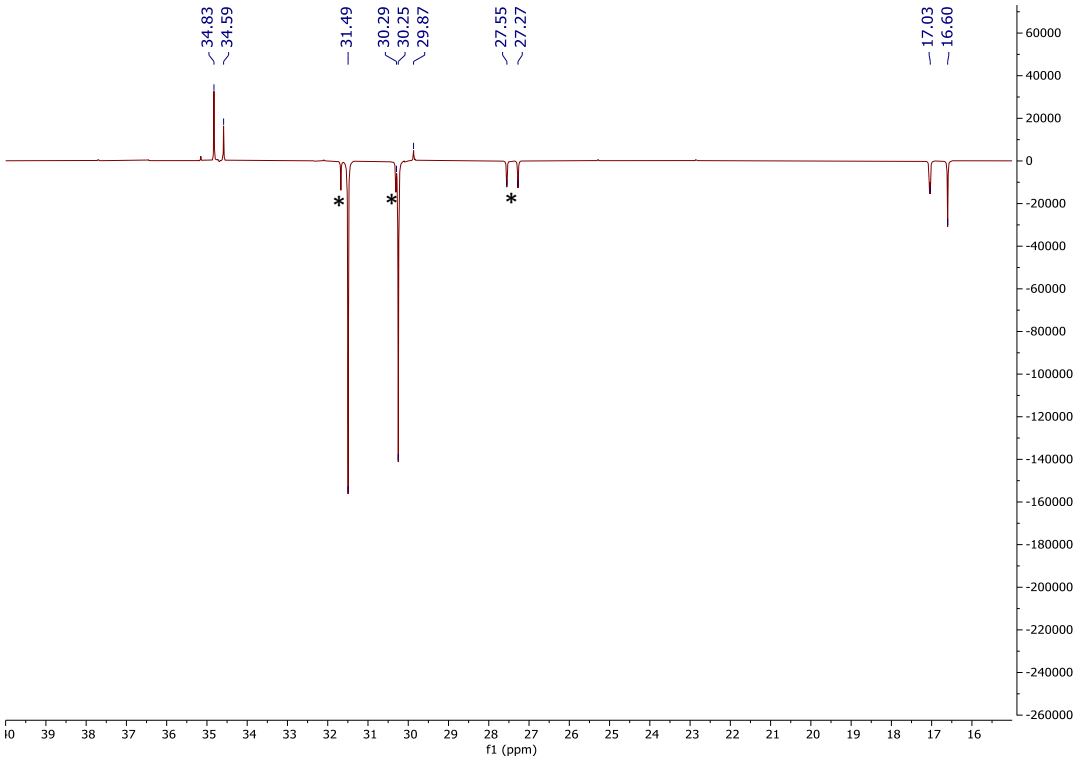


Figure S20. Jmod ($^{13}C\{^{1}H\}$) NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz, 298 K); aliphatic area. **impurities*.

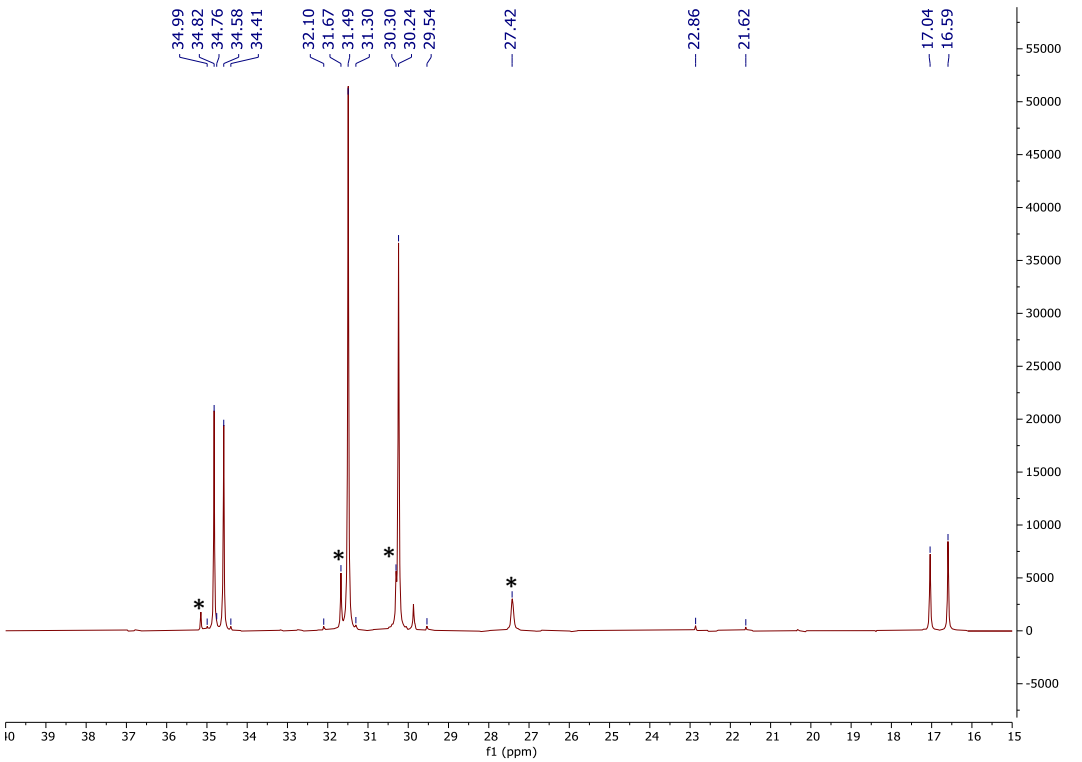


Figure S21. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 100.6 MHz, 298 K); aliphatic area. **impurities*.

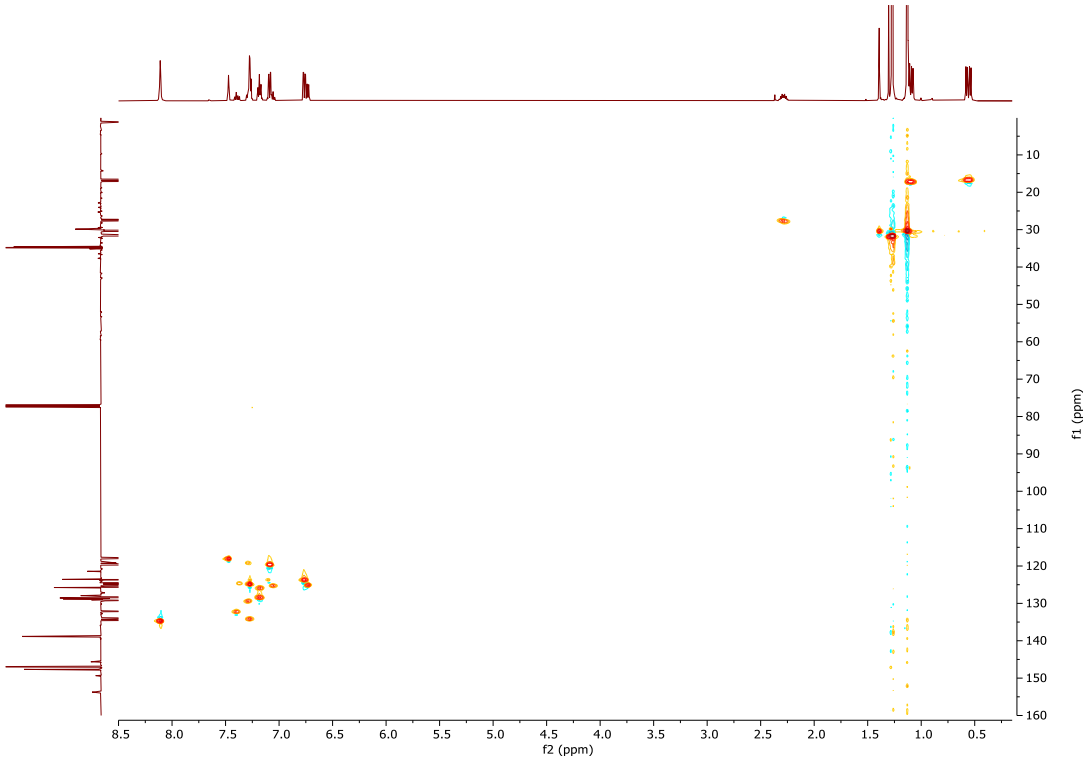


Figure S22. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

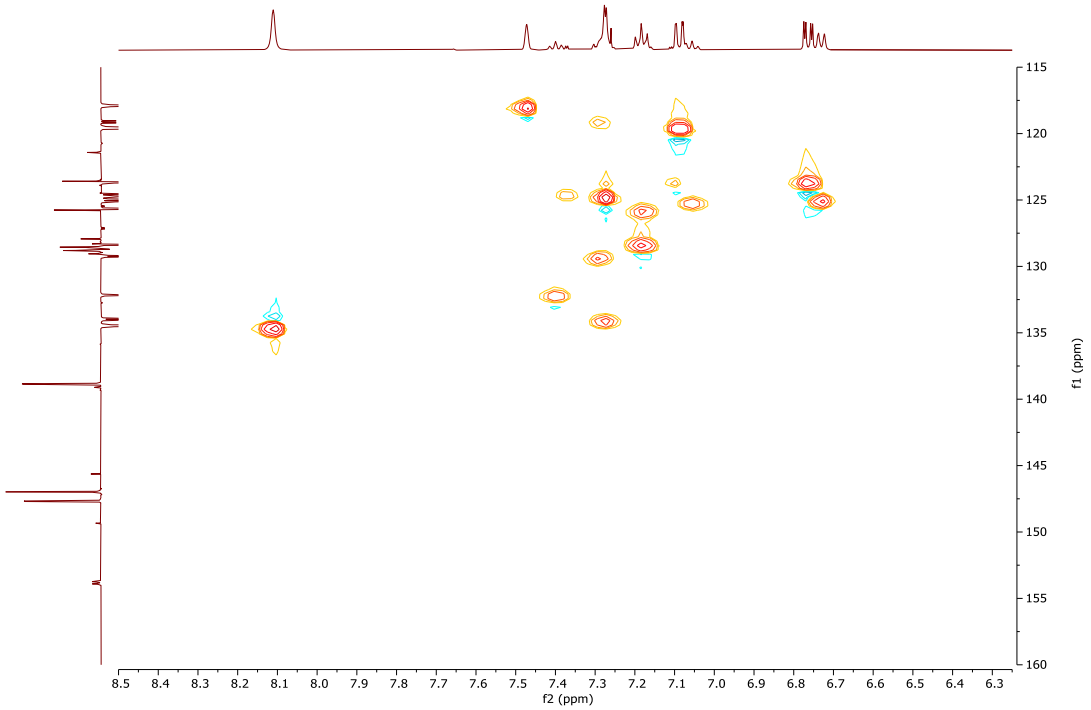


Figure S23. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aromatic area.

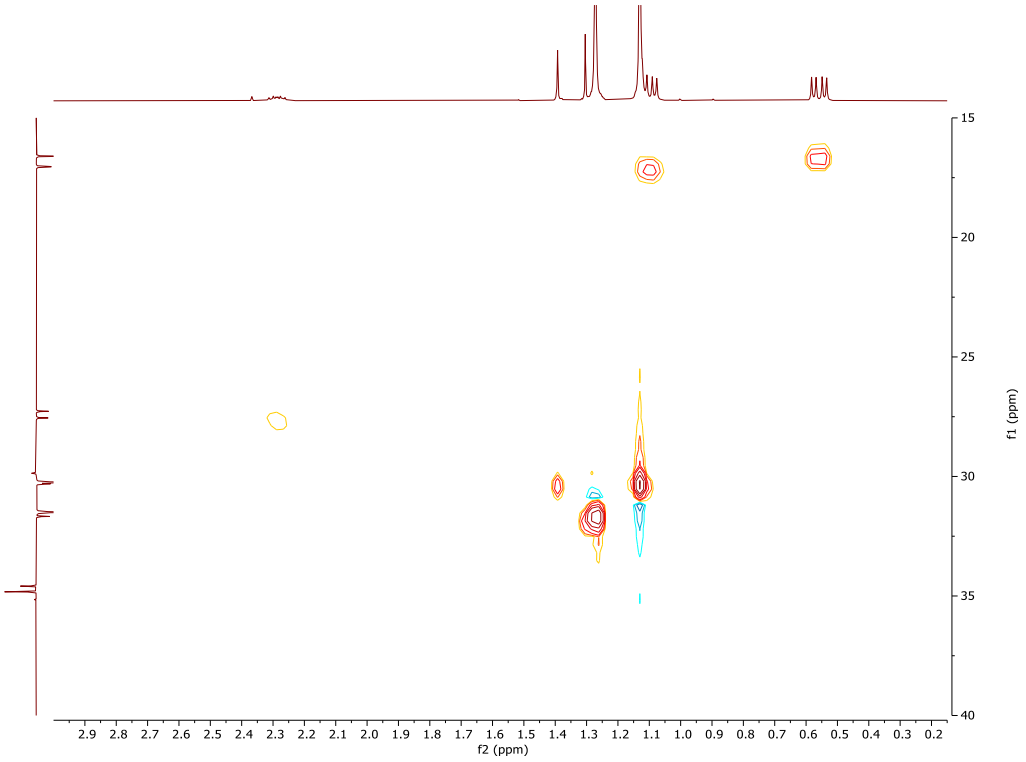


Figure S24. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aliphatic area.

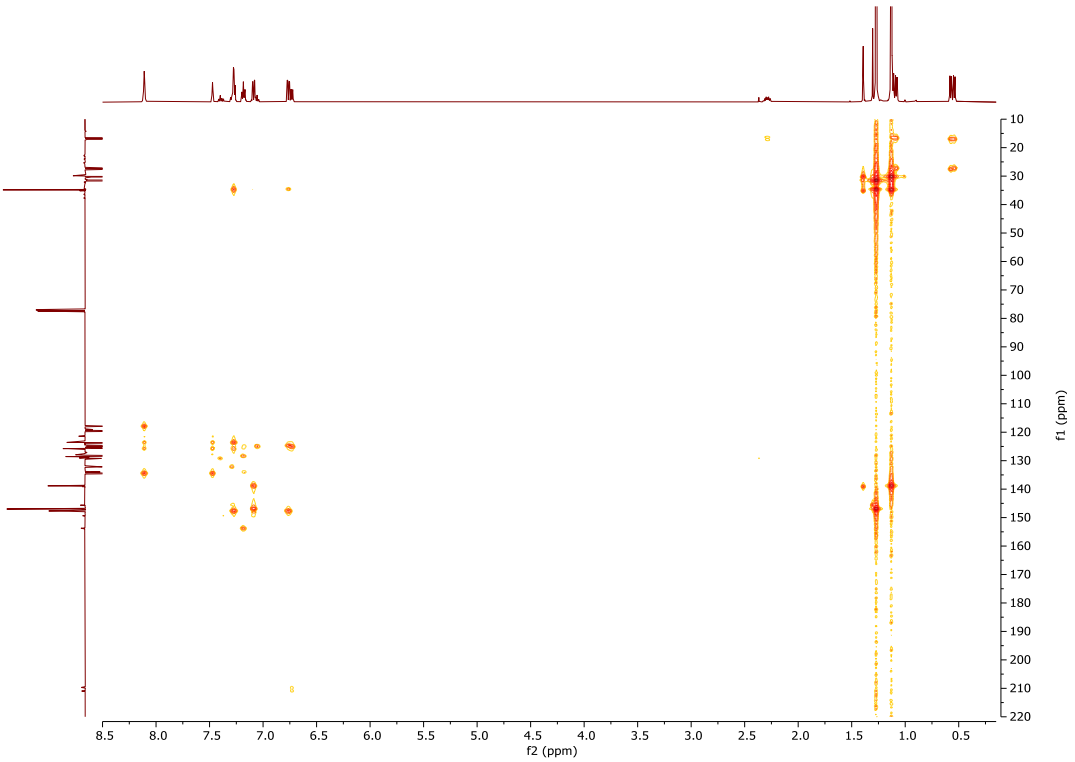


Figure S25. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

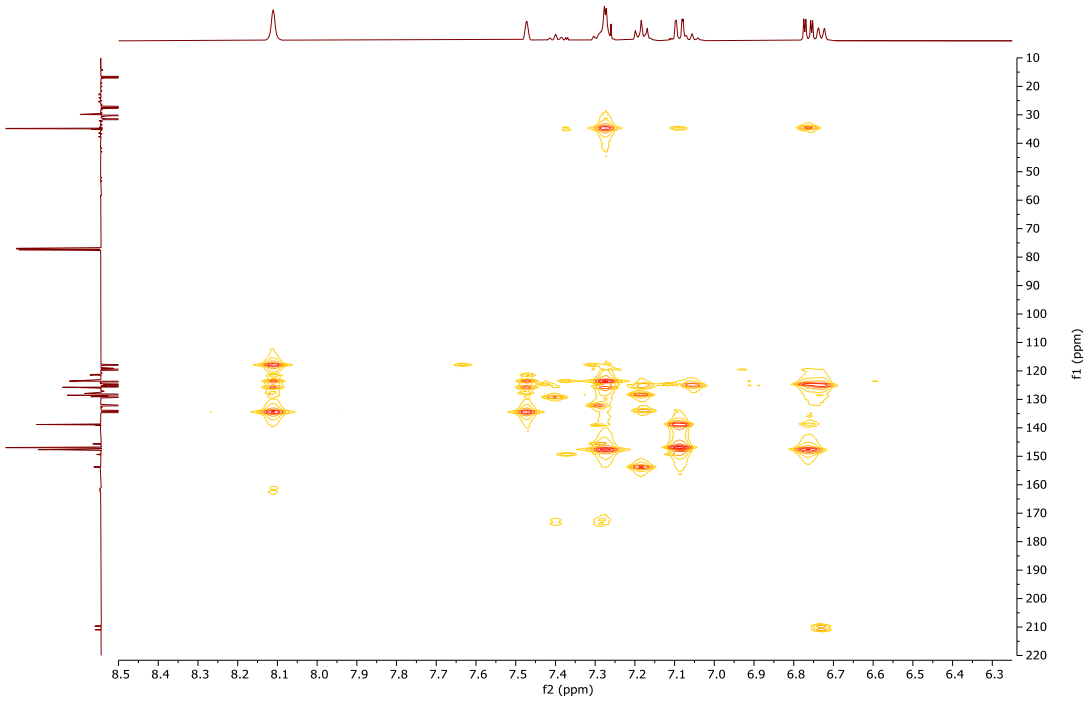


Figure S26. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aromatic area.

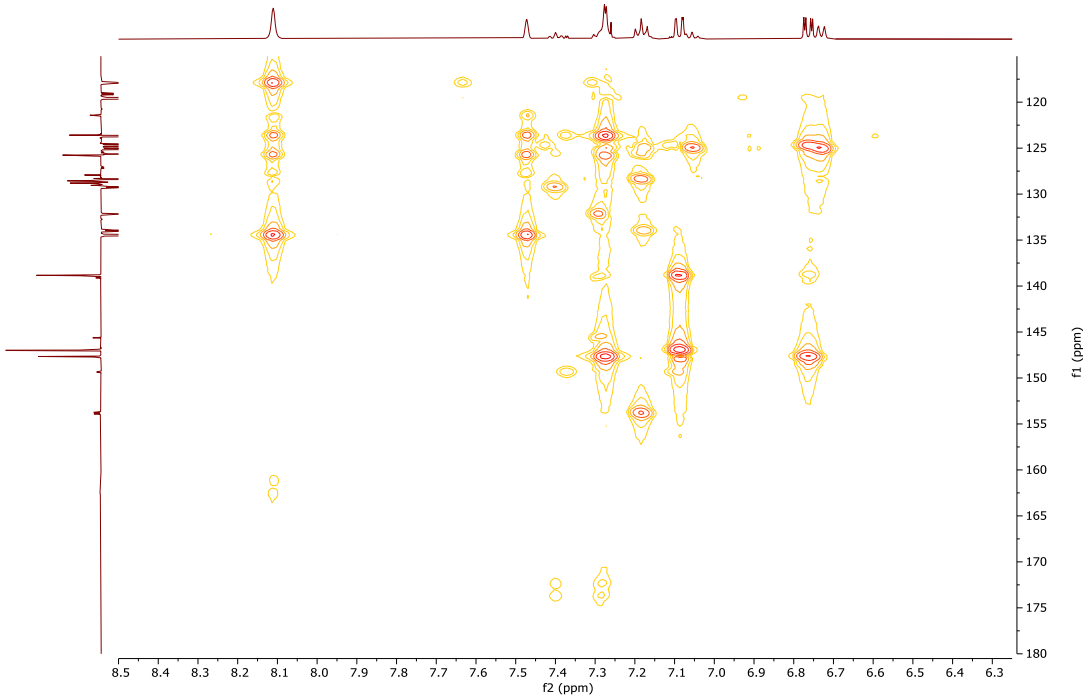


Figure S27. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aromatic area, zoom-in.

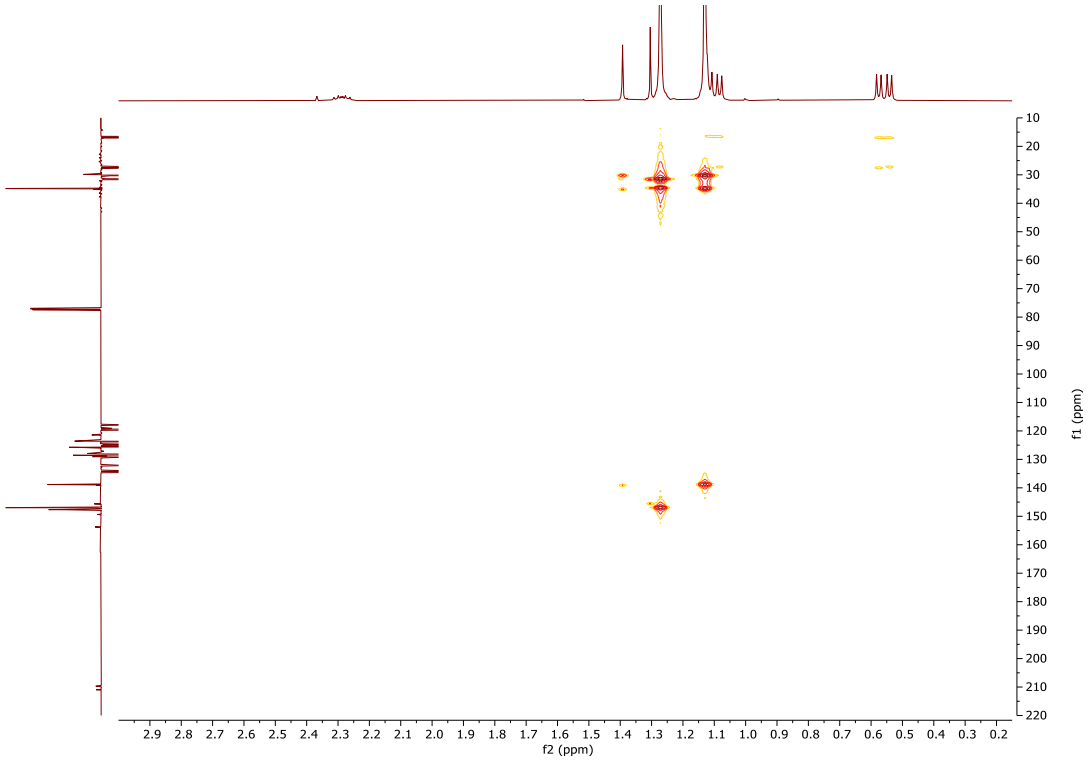


Figure S28. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aliphatic area.

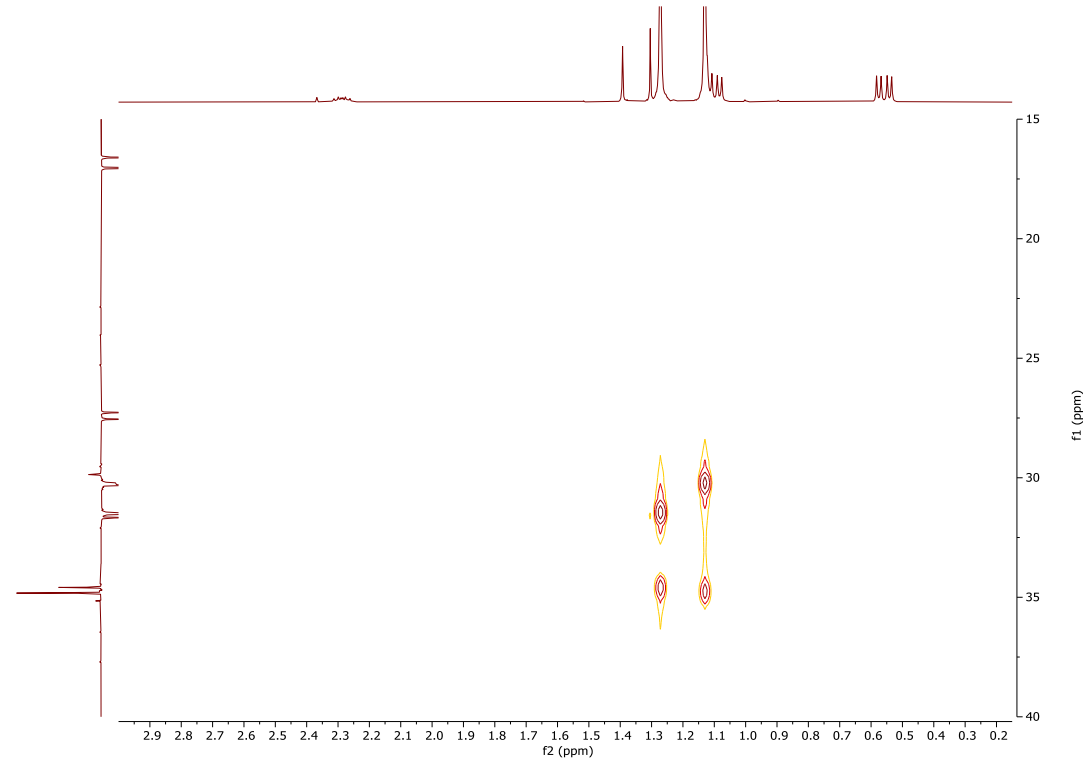


Figure S29. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **2** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aliphatic area, zoom-in.

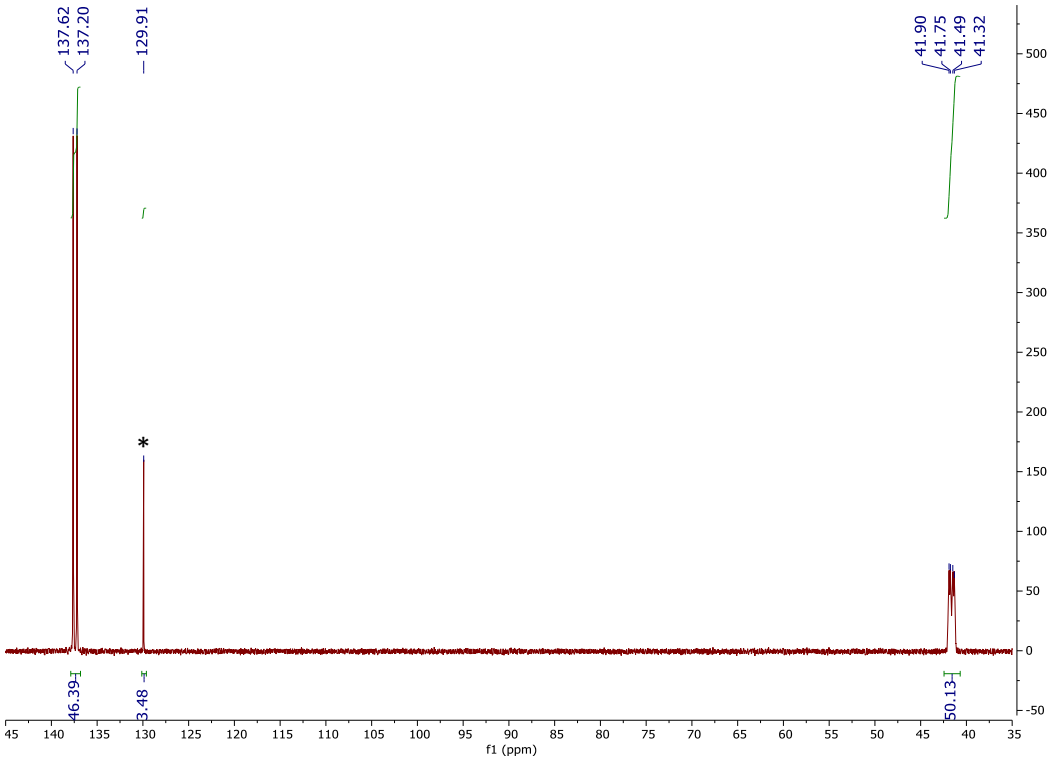


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** ($CDCl_3$, 202.5 MHz, 298 K). ** resonance of remaining traces of free P(OAr)$_3$ (<5%)*

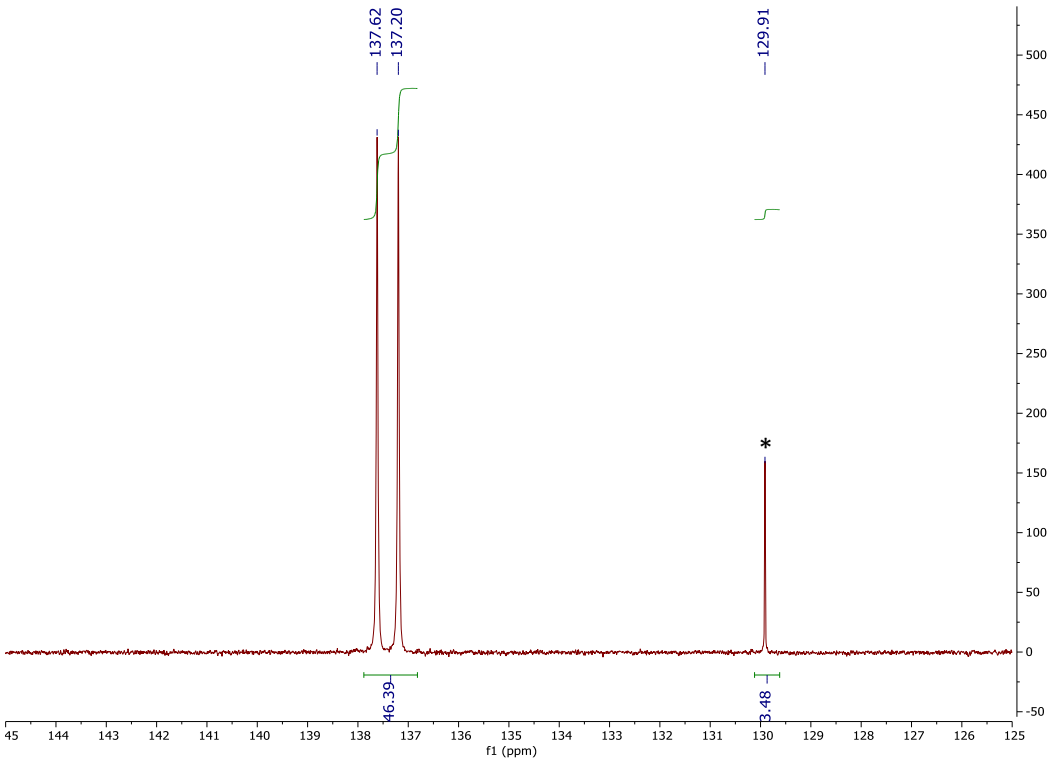


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** ($CDCl_3$, 202.5 MHz, 298 K), zoom-in phosphite area. ** resonance of remaining traces of free P(OAr)$_3$ (<5%).*

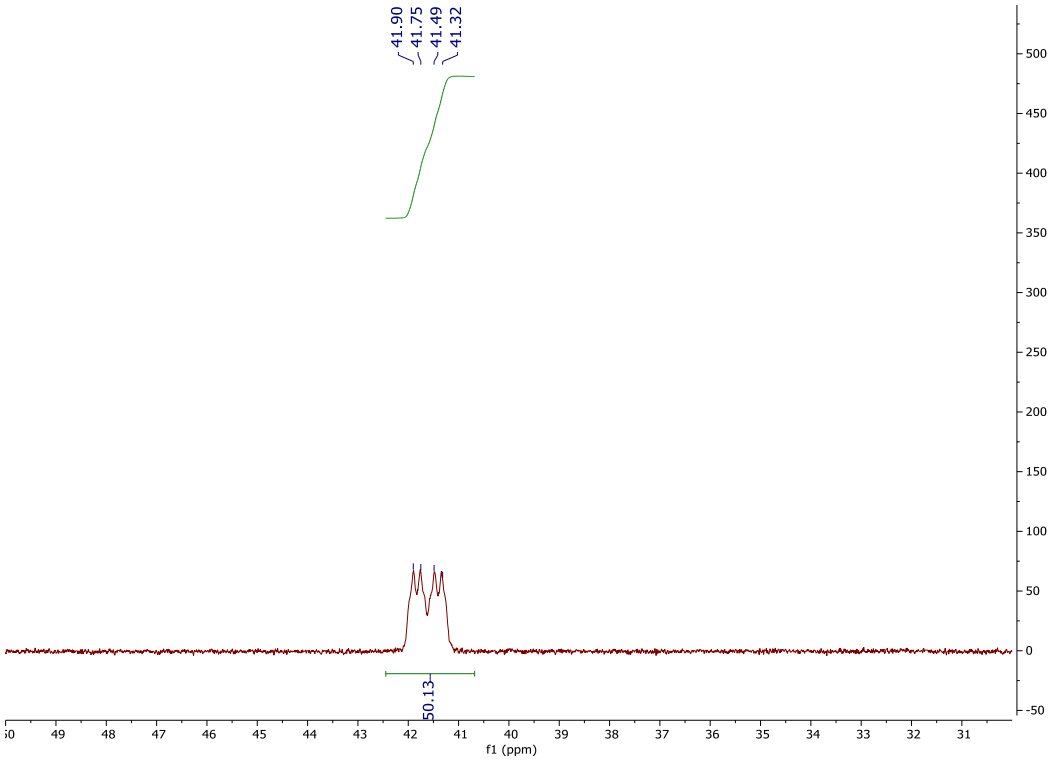


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** ($CDCl_3$, 202.5 MHz, 298 K); phosphine area, zoom-in.

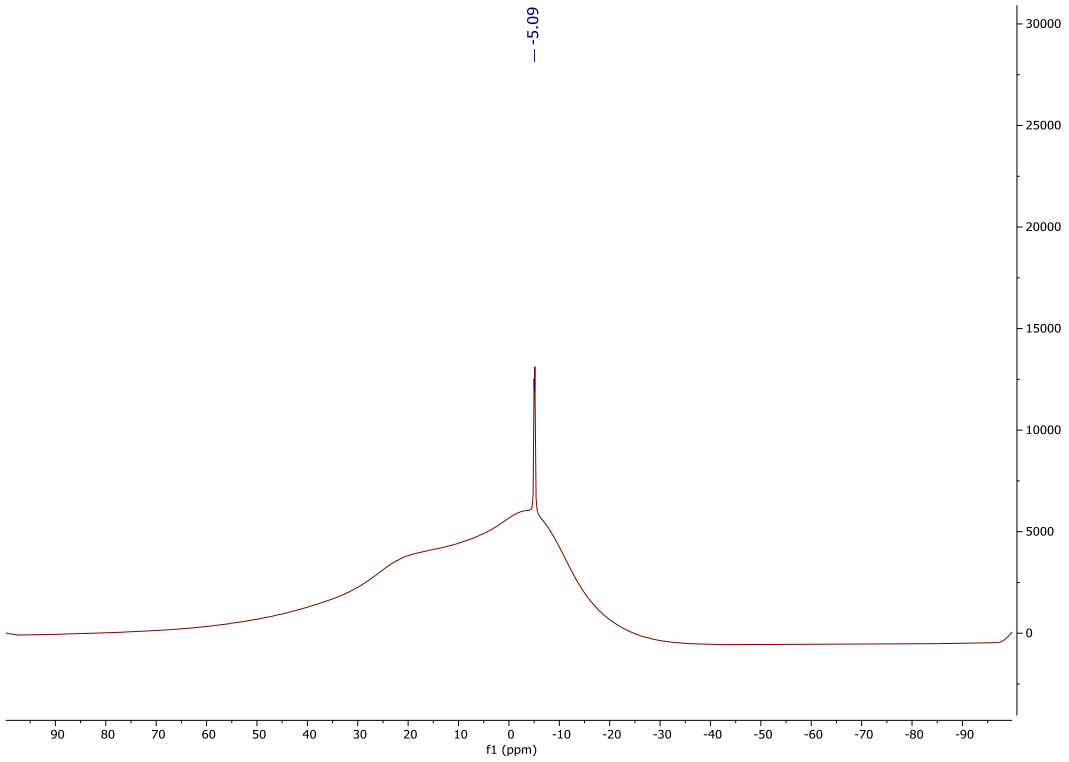


Figure S33. $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** ($CDCl_3$, 128.4 MHz, 298 K).

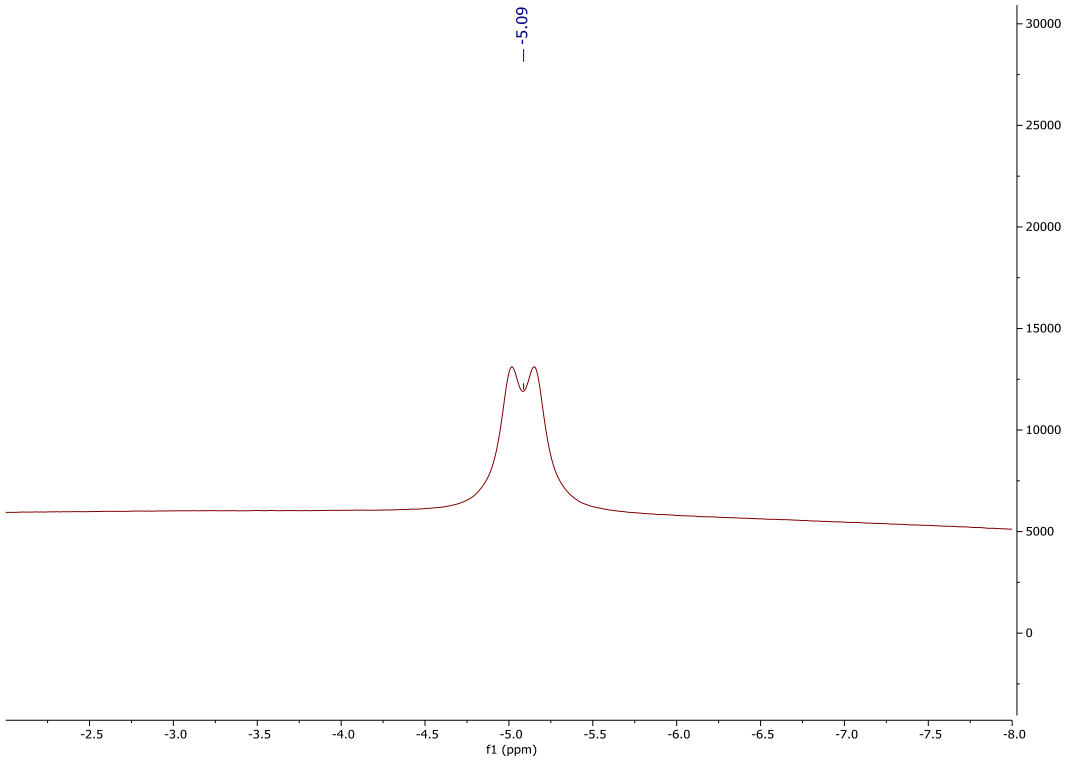


Figure S34. $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** ($CDCl_3$, 128.4 MHz, 298 K); zoom-in.

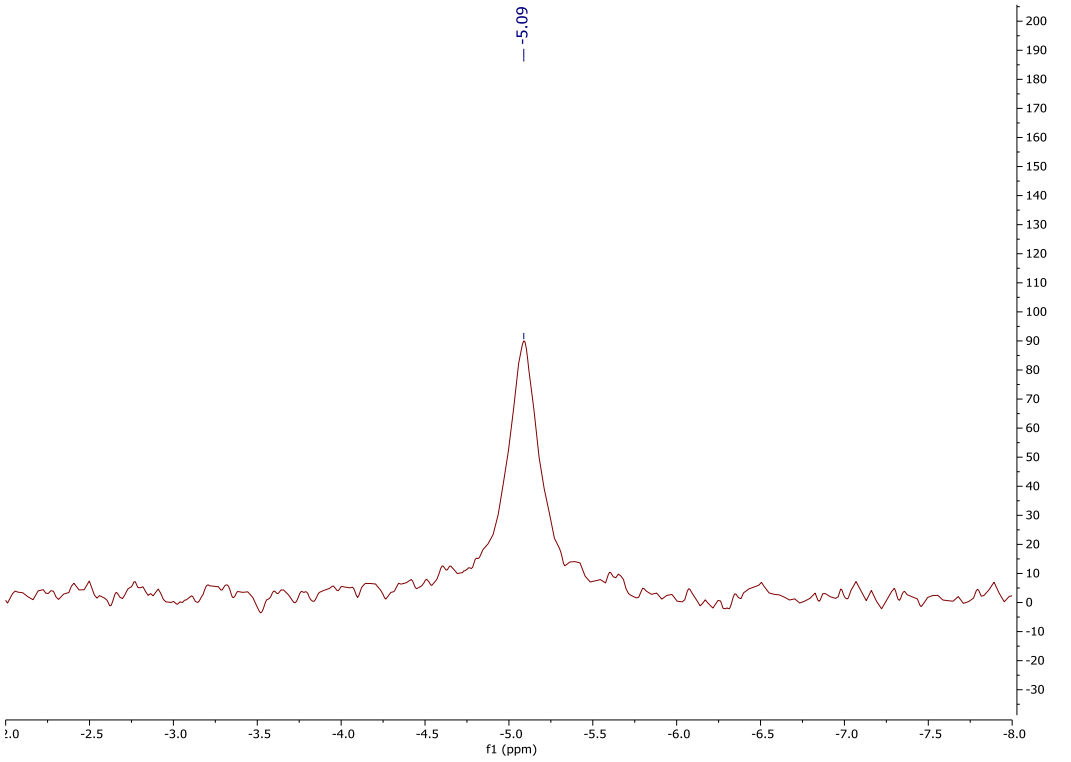


Figure S35. $^{11}B\{^{1}H, ^{31}P\}$ NMR spectrum of compound **2** ($CDCl_3$, 128.4 MHz, 298 K); zoom-in.

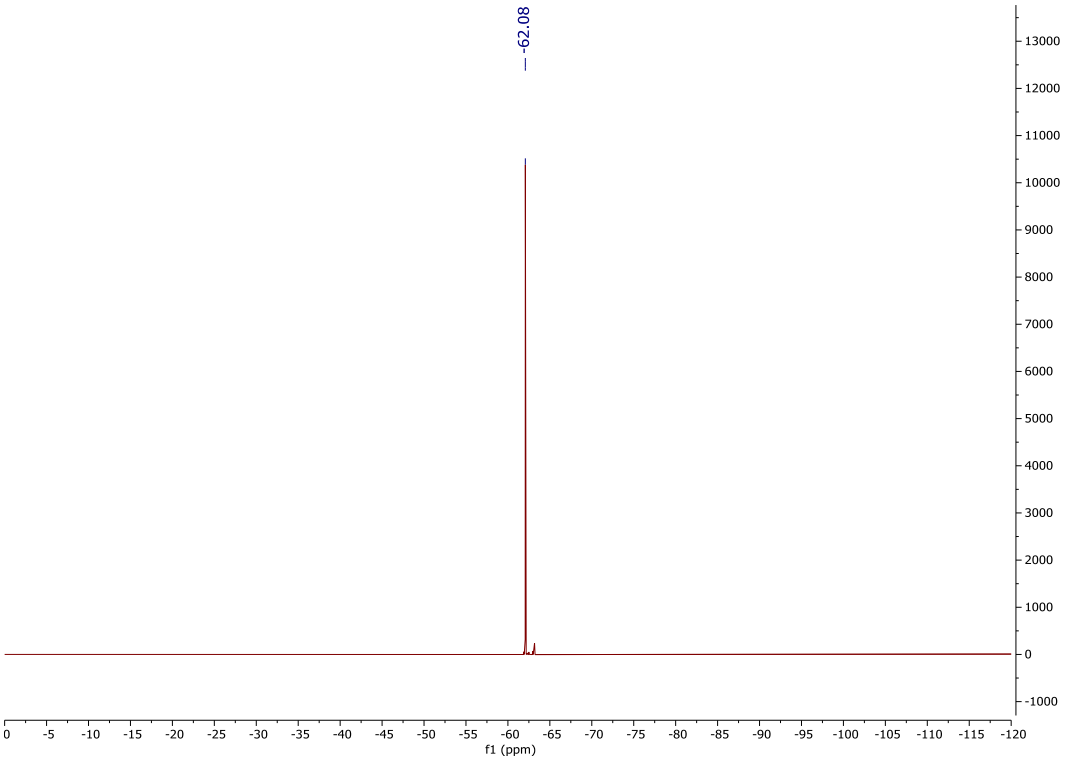


Figure S36. ^{19}F NMR spectrum of compound **2** ($CDCl_3$, 470.5 MHz, 298 K).

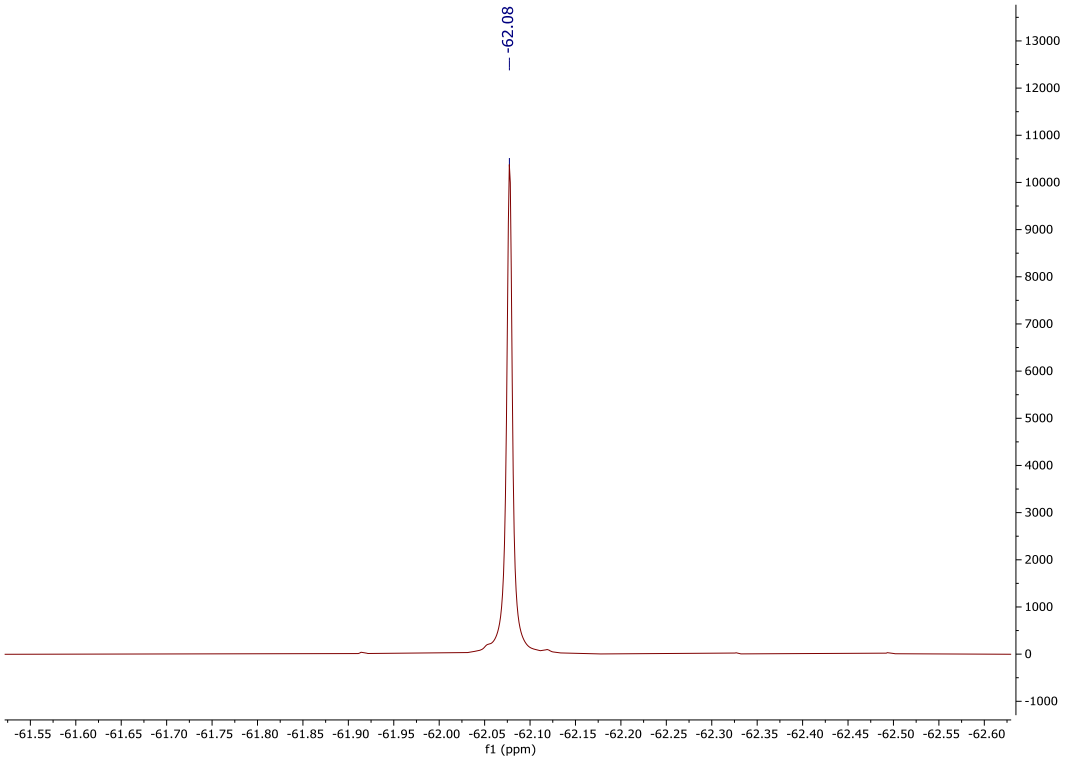


Figure S37. ^{19}F NMR spectrum of compound **2** ($CDCl_3$, 470.5 MHz, 298 K); zoom-in.

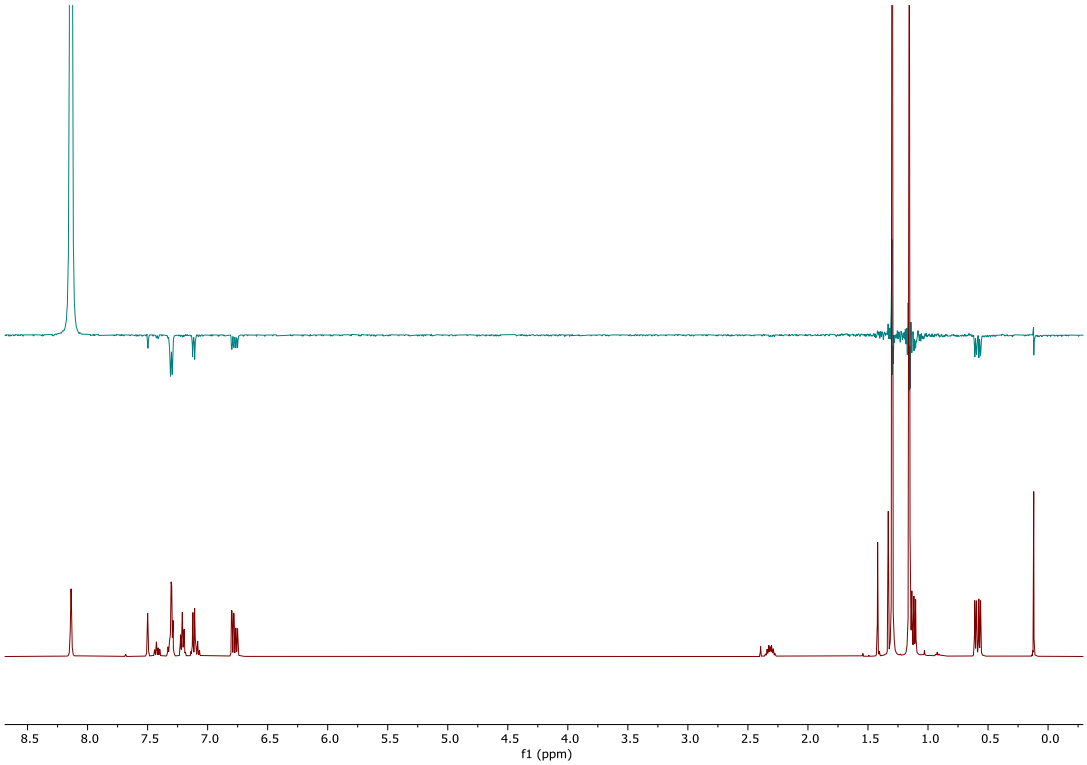


Figure S38. Stacked view: ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K) (bottom) and NOESY (^{1}H) NMR spectrum ($CDCl_3$, 500.1 MHz, 298 K, selective pulse at δ 8.14 ppm).

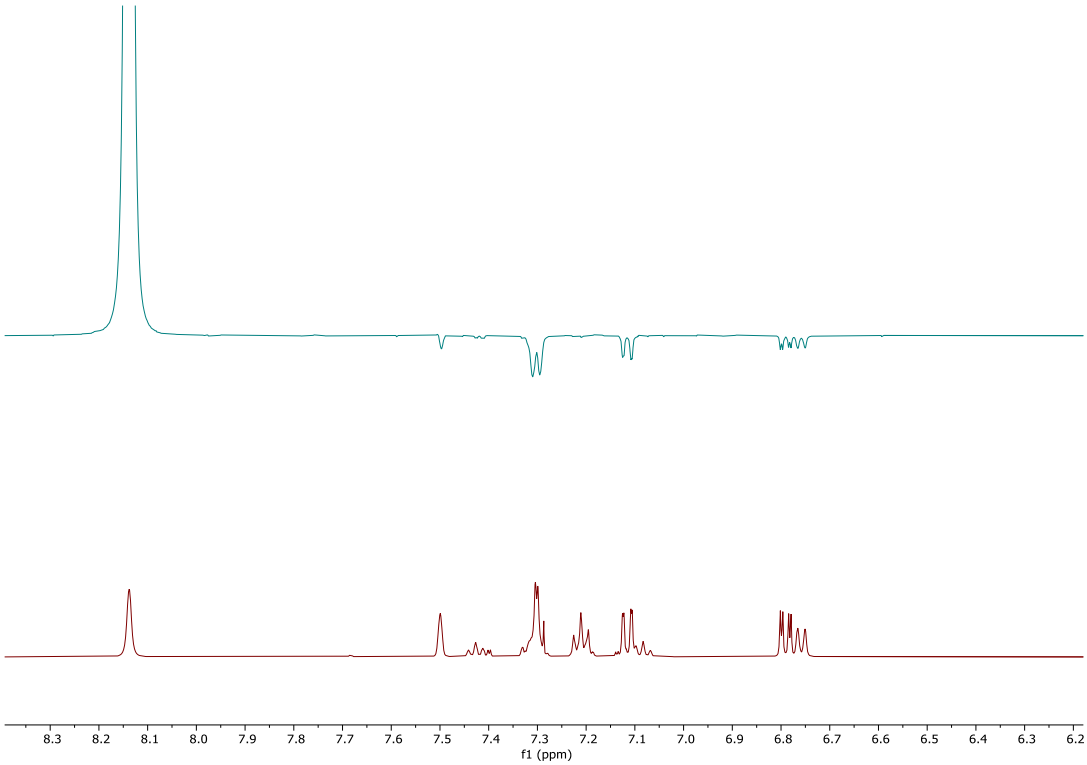


Figure S39. Stacked view: ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K) (bottom) and NOESY (^{1}H) NMR spectrum ($CDCl_3$, 500.1 MHz, 298 K, selective pulse at δ 8.14 ppm); aromatic area.

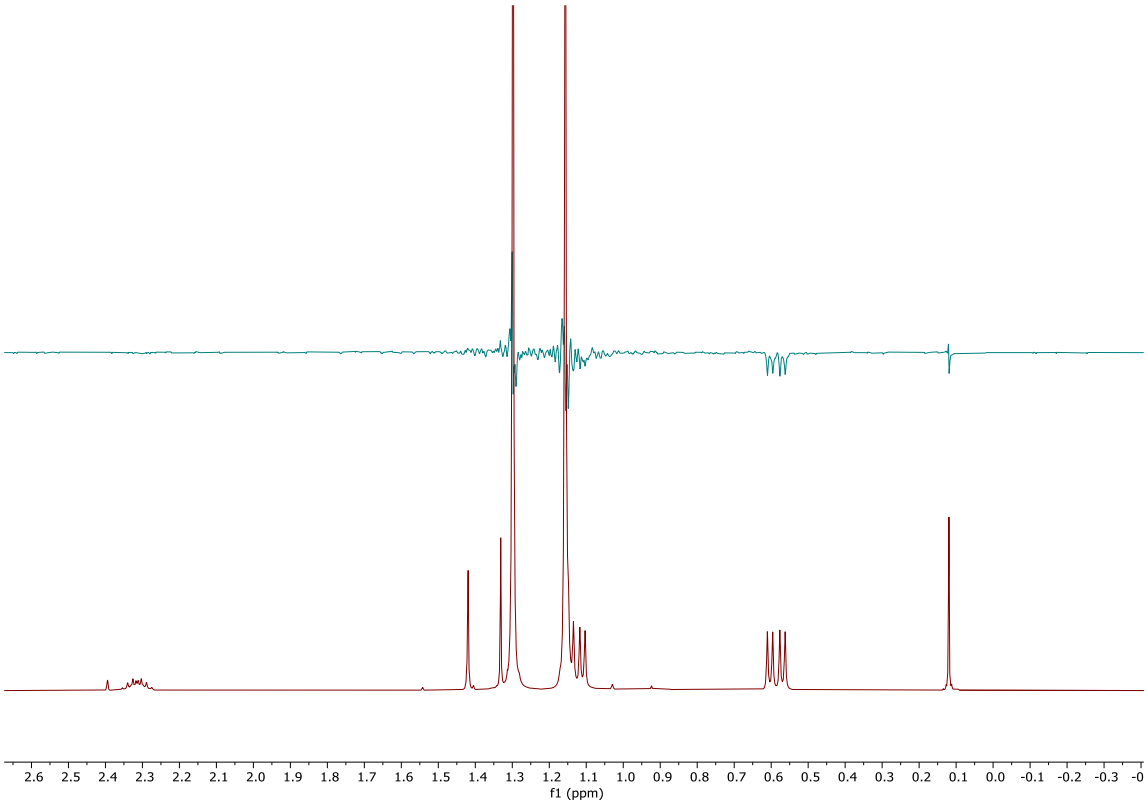


Figure S40. Stacked view: ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K) (bottom) and NOESY (^{1}H) NMR spectrum ($CDCl_3$, 500.1 MHz, 298 K, selective pulse at δ 8.14 ppm); aliphatic area.

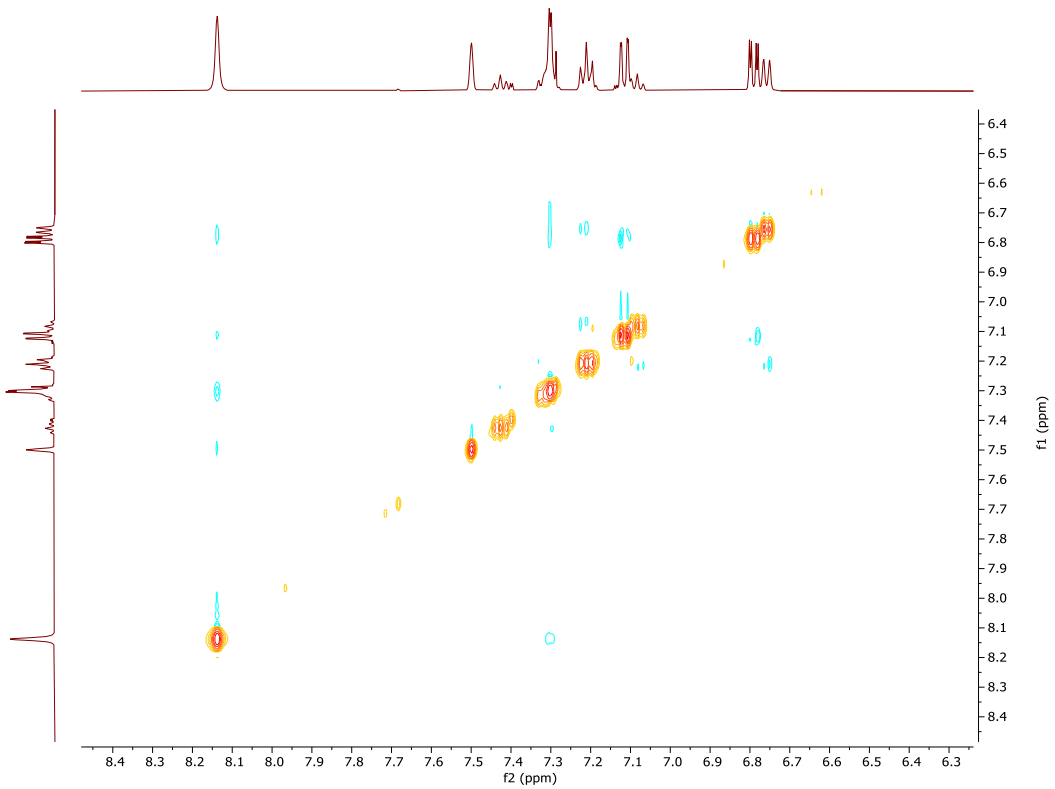


Figure S41. NOESY (^{1}H-^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aromatic area. *NB: in blue are represented NOESY correlations and in red scalar correlations.*

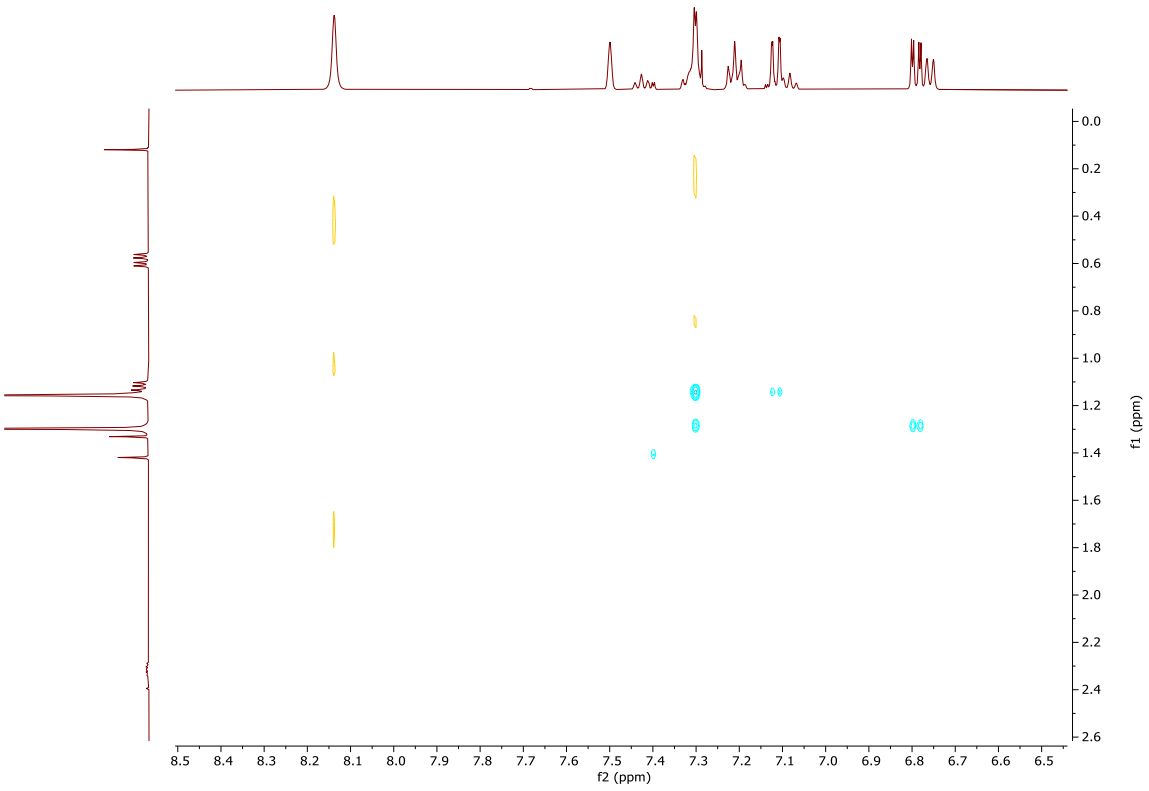


Figure S42. NOESY (^{1}H-^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aromatic area, zoom-in.

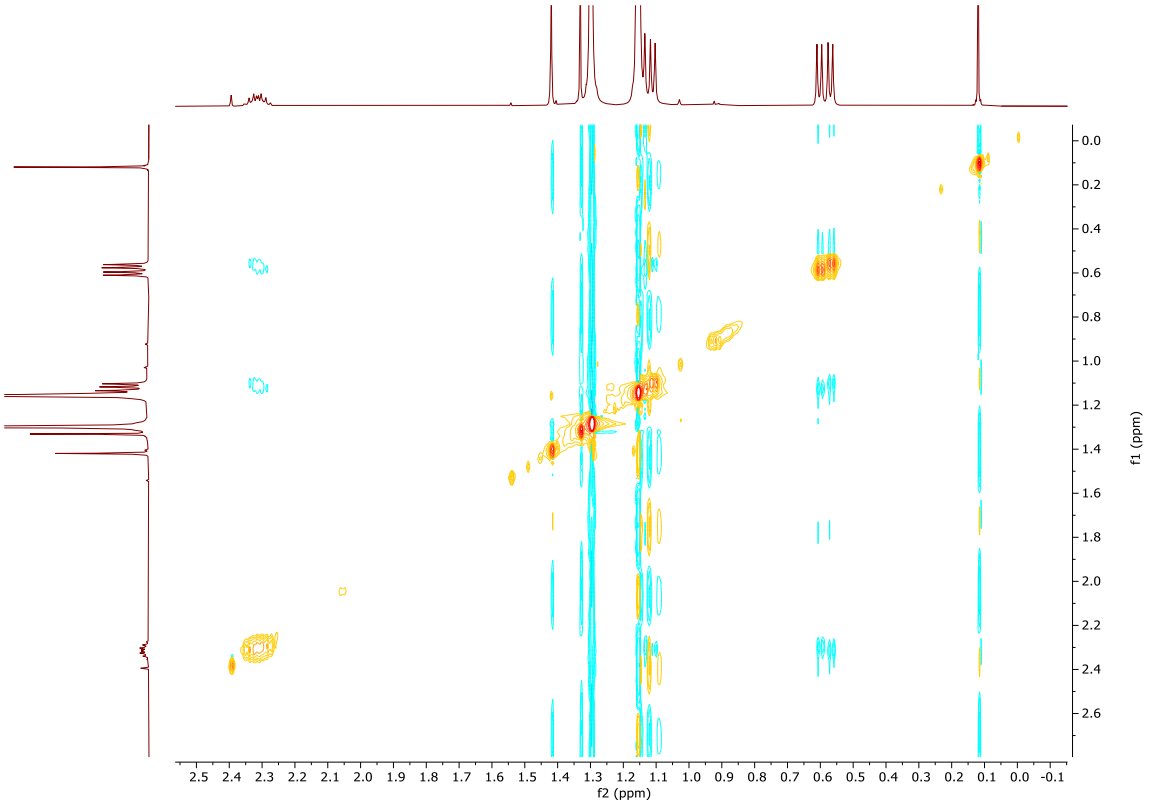


Figure S43. NOESY (^{1}H-^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aliphatic area.

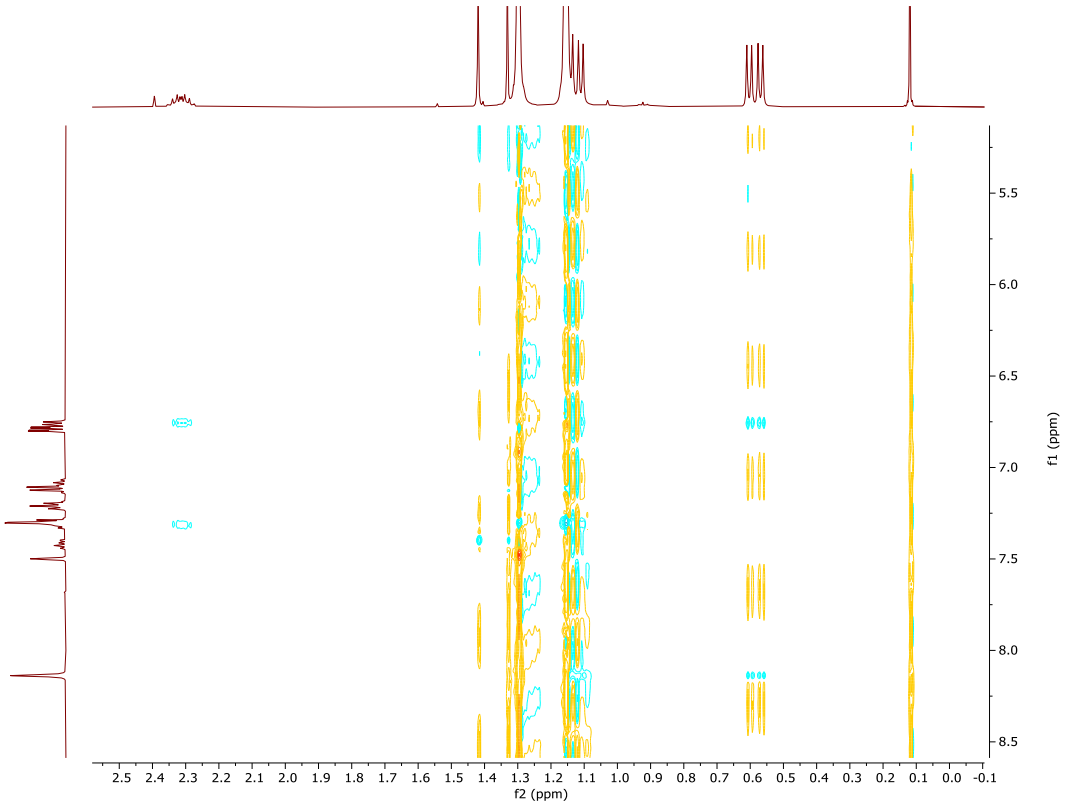
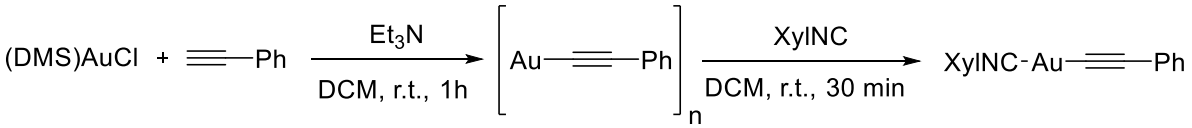


Figure S44. NOESY (^{1}H-^{1}H) NMR spectrum of compound **2** ($CDCl_3$, 500.1 MHz, 298 K); aliphatic area, zoom-in.

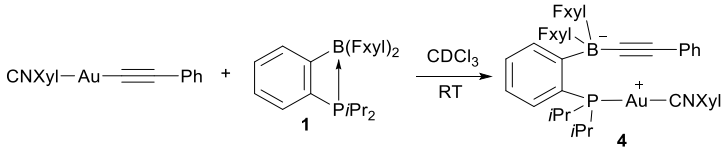
Synthesis of (XylNC)AuCCPh



(XylNC)AuCCPh was synthetized via the following procedure adapted from literature.[3] A solution of (DMS)AuCl (516.2 mg, 1.75 mmol, 1 equiv.) and phenylacetylene (0.21 mL, 1.93 mmol, 1.1 equiv.) was first prepared in DCM (15 mL). Triethylamine (0.42 mL, 2.98 mmol, 1.7 equiv.) was added dropwise at room temperature leading to the immediate formation of a bright yellow precipitate. The dispersion was further stirred at the same temperature for 1 h. The supernatant was removed using filtered cannula and the solid was abundantly washed with DCM (2x20 mL) and Et_2O (2x20 mL) to quantitatively yield $[AuCCPh]_n$. Next, the solid was dispersed in DCM (15 mL) and XylNC (231.3 mg, 1.75 mmol, 1 equiv.) was added at room temperature as a solid. A clear solution is obtained after 30 min. The volatiles were removed under high vacuum. The residue was then washed with pentane (2x5 mL) and Et_2O (2x5 mL) to give a white solid identified as **(XylNC)AuCCPh** (683.6 mg, 1.59 mmol, 91%) by comparison with reported NMR characterization.[4]

[3] Dong, Y.-B.; Chen, Z.; Yang, L. ; Hu, Y-X.; Wang, X-Y.; Yin, J.; Liu, S. H. *Dyes Pigm.* **2018**, *150*, 315–322.
[4] Canovese, L.; Levi, C.; Visentin, F.; Santo, C.; Bertolasi, V. *Inorg. Chim. Acta* **2013**, *404*, 105–112.

Synthesis of 4



In an J. Young cap NMR tube, a solution of **1** (218.5 mg, 0.347 mmol, 1 equiv.) in $CDCl_3$ (3 mL) was added at room temperature to a solution of **(XylNC)AuCCPh** (148.8 mg, 0.347 mmol, 1 equiv.) in $CDCl_3$ (3 mL). After 1 day at this temperature, the solvent was removed under high vacuum to yield an orange residue. The latter was dispersed in pentane (5 mL) and let stand at room temperature for another day leading to a turbid orange solution containing a dark greenish solid. The solid was filtered-off and the solution transferred into a vial placed at –20°C. Overnight standing led to the massive formation of orange crystals (by-products) and a clear yellow solution*. The supernatant was separated and the volatiles were removed *in vacuo*. The oily residue was then solubilized in HMDSO (1.5 mL) and pentane was added (1.5mL). The solution was kept at –20°C for 2 days yielding to the precipitation of a white solid. The supernatant was removed and the solid washed with HMDSO (2x1 mL), dried under vacuum to afford a compound **4** as a white solid (154.1 mg, 0.145 mmol, 42 %). Crystals suitable for X-Ray diffraction were obtained from a saturated solution of **4** in a mixture of DCM/pentane after 2 days standing at –20°C.

* A by-product disclosing a phosphorus resonance at 30 ppm was authenticated as the **1**/CNXyl adduct (which was independently prepared).

Anal. Calcd. for $C_{45}H_{38}AuBF_{12}NP/0.45C_5H_{12}$: C, 51.97; H, 4.01; N, 1.28. Found: C, 52.01; H, 3.92, N, 1.25. HRMS (ES-MS$^+$): exact mass (monoisotopic) calcd. for $[M+H]^+$ $(C_{45}H_{39}AuBF_{12}NP)^+$: 1060.2395; found: 1060.2397.

m.p.: 137.6 °C.

^{1}H NMR ($CDCl_3$, 400.2 MHz, 298 K): δ (in ppm) 7.79 (br.s, 4H, $H_{o\text{-Fxyl}}$), 7.59 (br.s, 2H, $H_{p\text{-Fxyl}}$), 7.51 (pseudo-ddd, $^3J_{HH}$ = 7.7 Hz, $^5J_{HH}$ = 1.5 Hz, J_{PH} = 9.2 Hz, HAr), 7.49-7.44 (m, 2H, H_{Ph}), 7.34 (t, $^3J_{HH}$ = 7.7 Hz, 1H, $H_{p\text{-Xyl}}$)*, 7.30-7.17 (m, 5H, $2H_{Ar}$ and $3H_{Ph}$)*,#, 7.14 (d, $^3J_{HH}$ = 7.7 Hz, 2H, $H_{m\text{-Xyl}}$)*, 6.85 (pseudo-t, $^3J_{HH}$ = 7.3 Hz ≈ J_{PH}, 1H, H_{Ar}), 2.70 (dhept, $^2J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_{i\text{Pr}}$), 2.26 (s, 6H, $CH_{3\text{Xyl}}$), 1.32 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 16.9 Hz, 6H, $CH_{3i\text{Pr}}$), 1.09 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 17.7 Hz, 6H, $CH_{3i\text{Pr}}$).

* assigned according to COSY (^{1}H-^{1}H) NMR.

visible in HSQC (^{13}C{^{1}H}-^{1}H) NMR.

Jmod (^{13}C{^{1}H}) NMR ($CDCl_3$, 100.6 MHz, 298 K): δ (in ppm) 161.2 (br.s, B-$C_{ipso\text{-Fxyl}}$)$, 138.5 (d, J_{PC} = 14.1 Hz, CH_{Ar}), 136.3 (s, *C*-$CH_{3\text{Xyl}}$), 135.1 (br.s, $CH_{o\text{-Fxyl}}$), 131.9 (d, J_{PC} = 5.4 Hz, CH_{Ar}), 131.3 (s, CH_{Ph}), 131.2 (s, $CH_{p\text{-Xyl}}$), 130.9 (d, $^1J_{PC}$ = 52.2 Hz, P-C_{Ar}), 130.4 (d, J_{PC} = 3.1 Hz, CH_{Ar})#, 129.0 (q, $^2J_{CF}$ = 31.7 Hz, *C*-CF_3), 128.5 (s, $CH_{m\text{-Xyl}}$), 128.3 (s, CH_{Ph}), 126.9 (s, CH_{Ph}), 125.4 (d, J_{PC} = 8.4 Hz, CH_{Ar})#, 124.7 (q, $^1J_{CF}$ = 272.9 Hz, CF_3), 124.0 (br.s, $C_{ipso\text{-Xyl}}$)£, 118.4 (hept, $^3J_{CF}$ = 3.9 Hz, $CH_{p\text{-Fxyl}}$), 101.8 (br.s, $C_{ipso\text{-Ph}}$)£, 27.7 (d, $^1J_{PC}$ = 27.5 Hz, $CH_{i\text{Pr}}$), 21.3 (d, $^2J_{PC}$ = 3.8 Hz, $CH_{3i\text{Pr}}$), 20.0 (d, $^2J_{PC}$ = 3.8 Hz, $CH_{3i\text{Pr}}$), 18.4 (s, $CH_{3o\text{-Xyl}}$).

$ assigned according to a coupling seen in HMBC (^{13}C{^{1}H}-^{1}H) NMR.

assigned according to HSQC (^{13}C{^{1}H}-^{1}H) NMR.

£ assigned according to HMBC (^{13}C{^{1}H}-^{1}H) NMR.

B-*C*≡C-Ph, B-C≡*C*-Ph, Au-*C*≡N-Xyl, B-$C_{ipso\text{-Ar}}$ *not visible despite extended acquisition time.*

^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz, 298 K): δ (in ppm) 49.97 (s)

^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz, 298 K): δ (in ppm) -11.49 (s)

^{19}F NMR ($CDCl_3$, 470.5 MHz, 298 K): δ (in ppm) -62.36 (s)

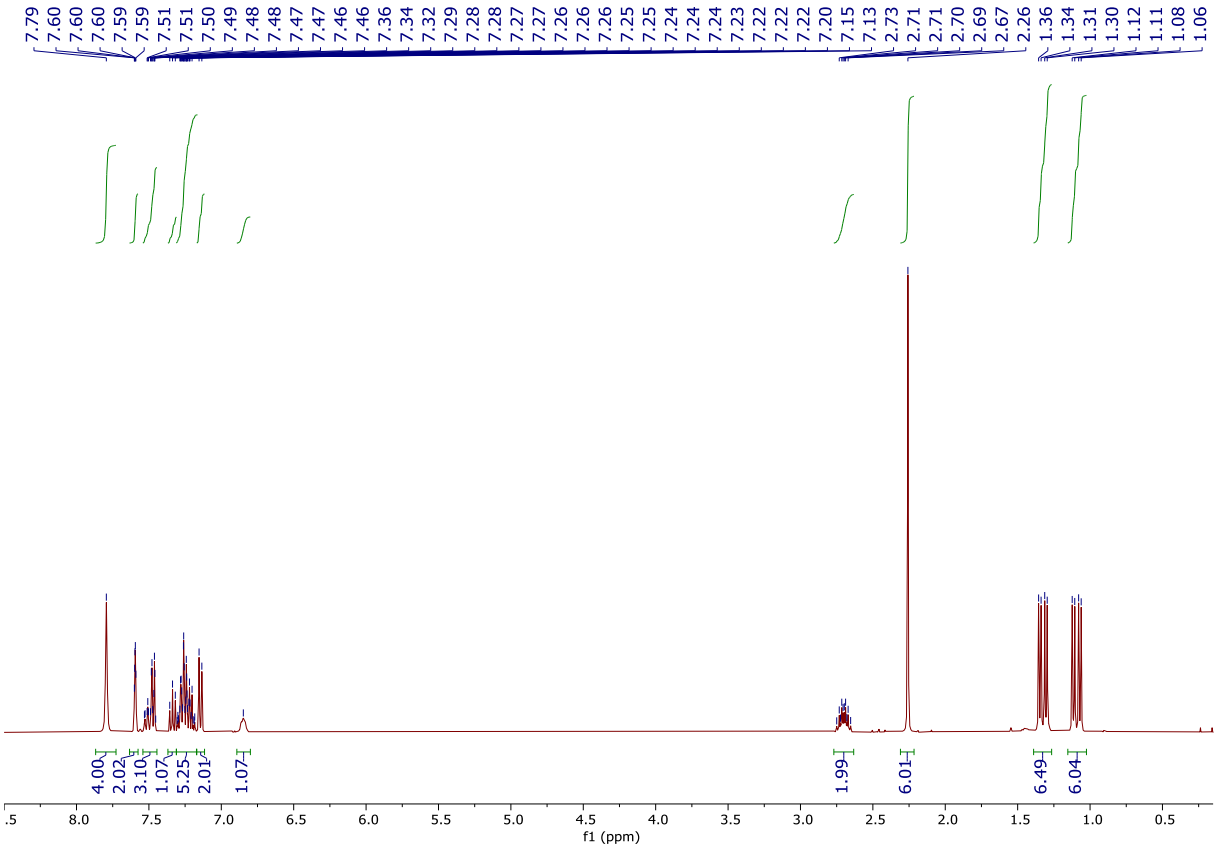


Figure S45. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K).

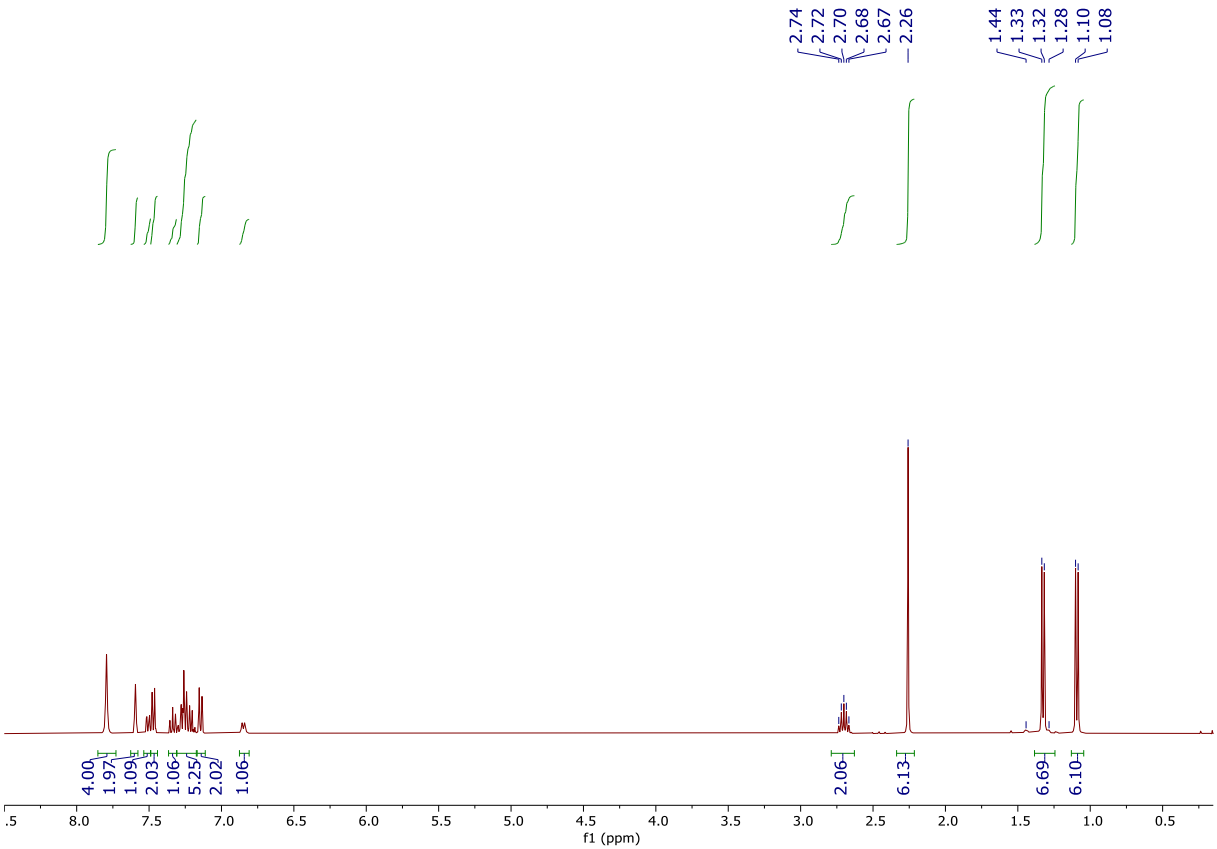


Figure S46. $^{1}H\{^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K).

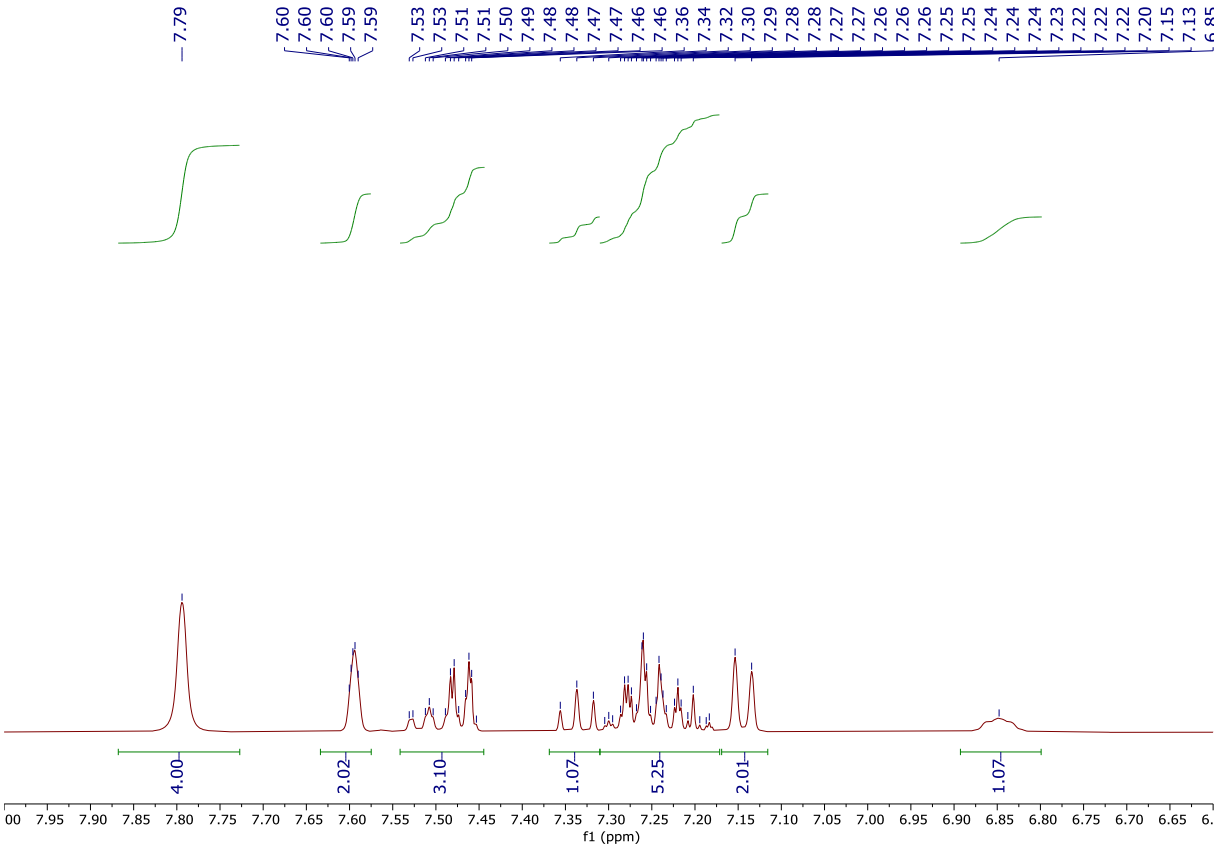


Figure S47. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

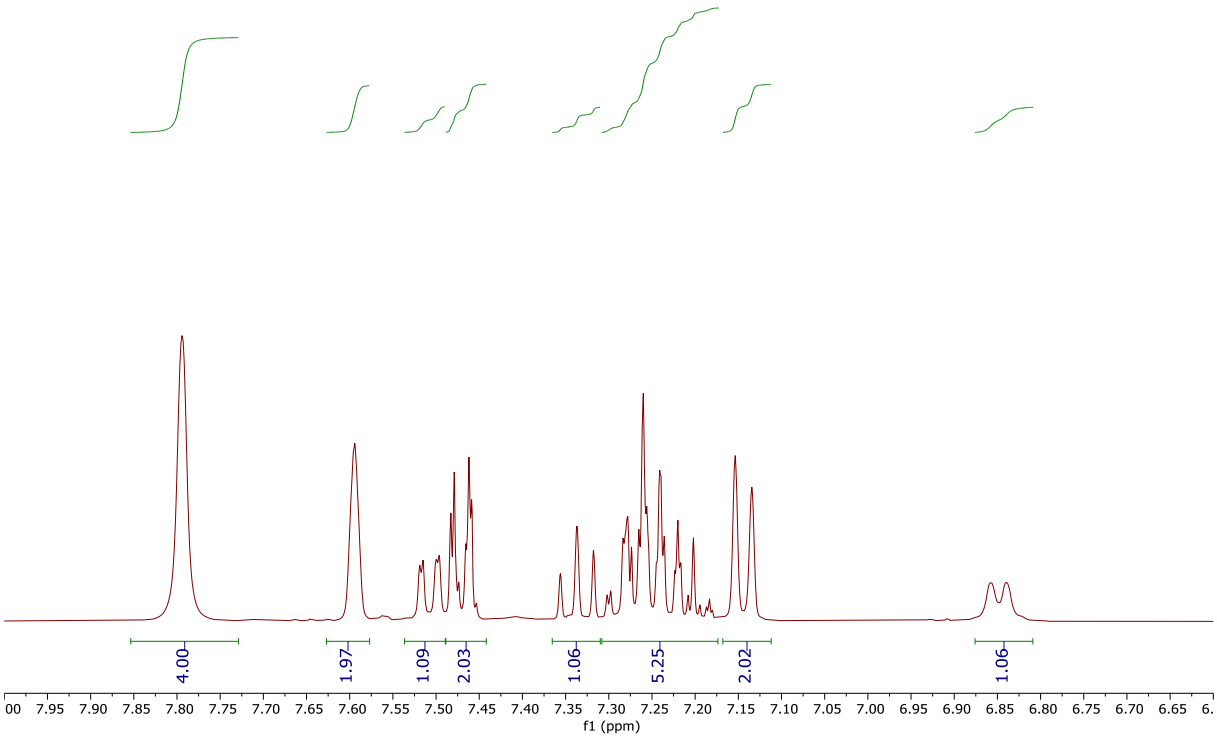


Figure S48. ^{1}H{^{31}P} NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

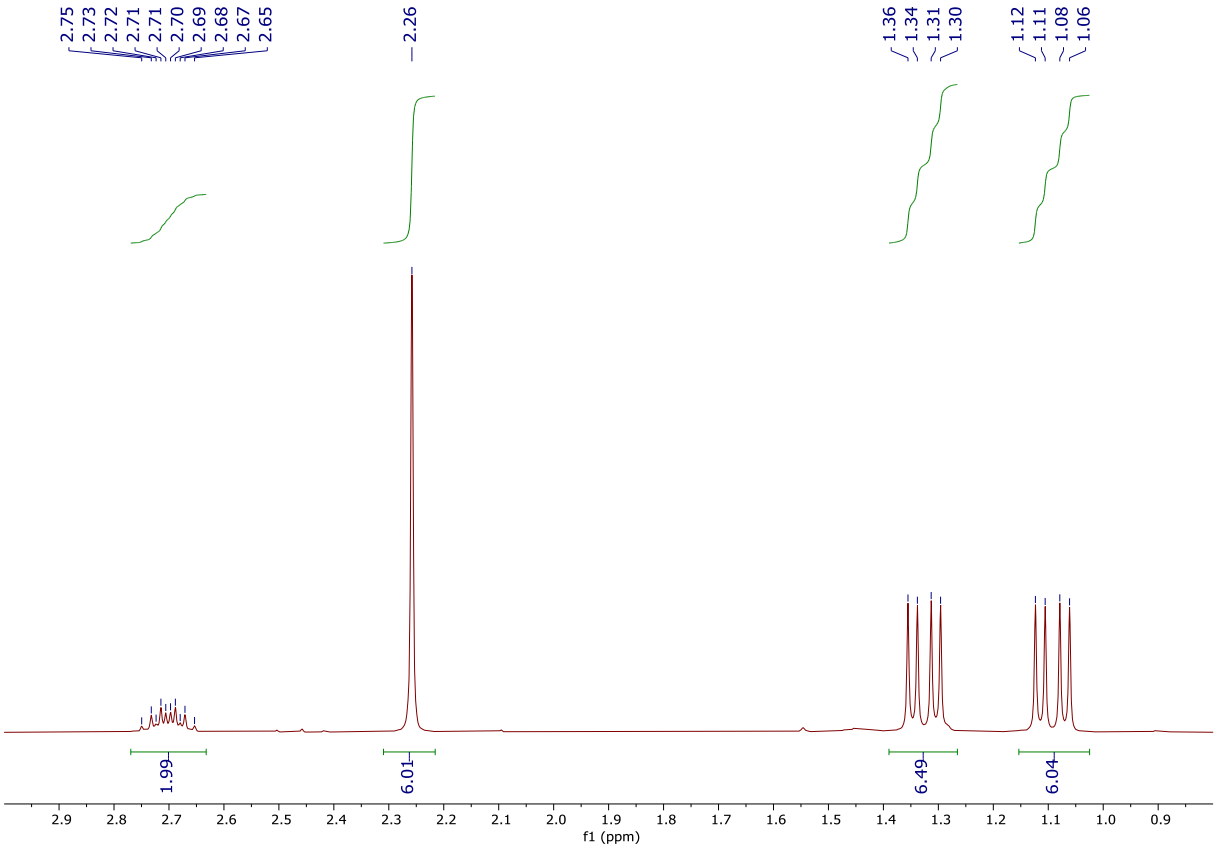


Figure S49. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

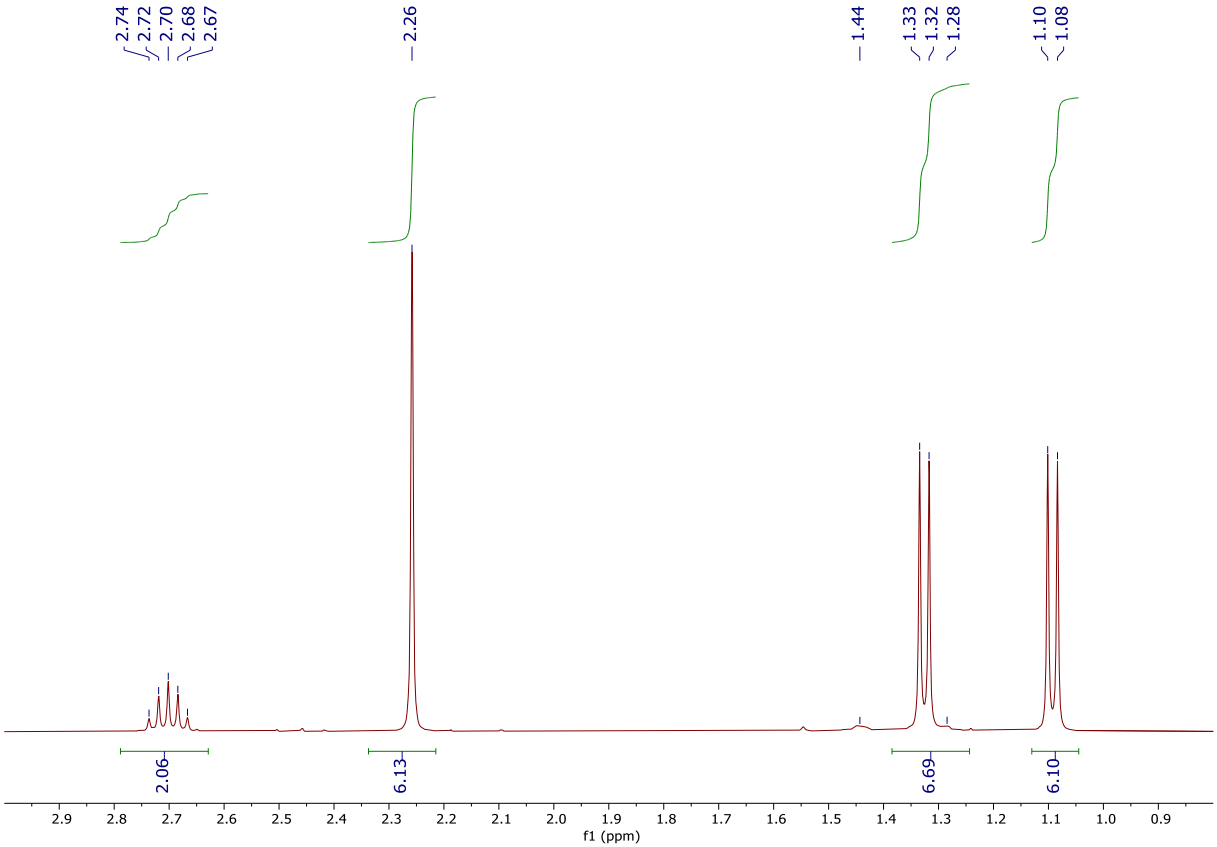


Figure S50. $^{1}H\{^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

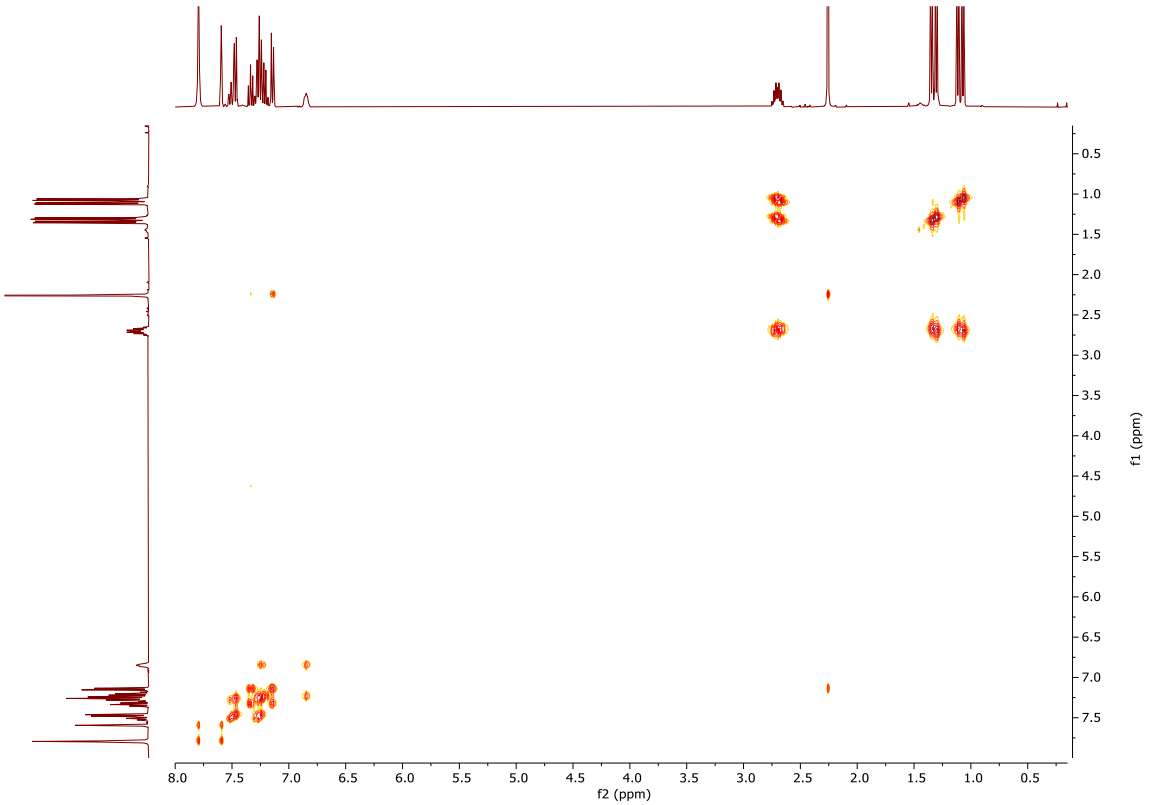


Figure S51. COSY (^{1}H-^{1}H) NMR of compound **4** ($CDCl_3$, 400.2 MHz, 298 K).

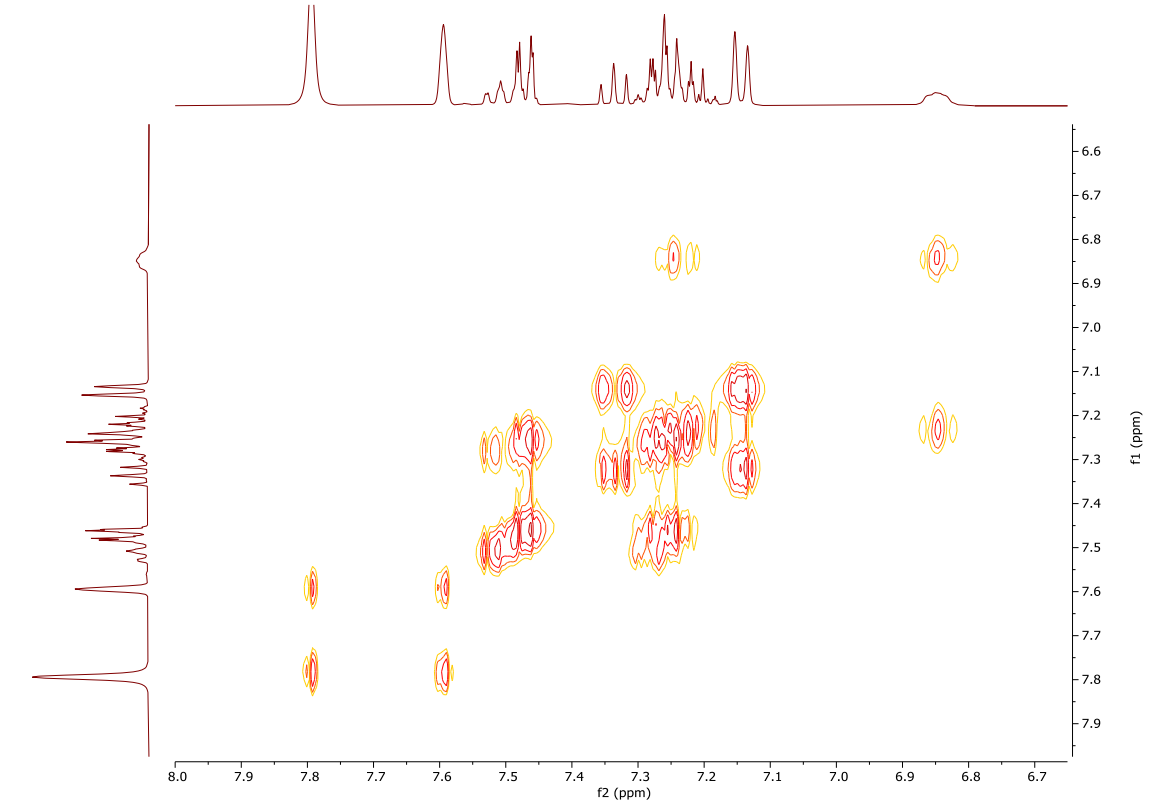


Figure S52. COSY (^{1}H-^{1}H) NMR of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

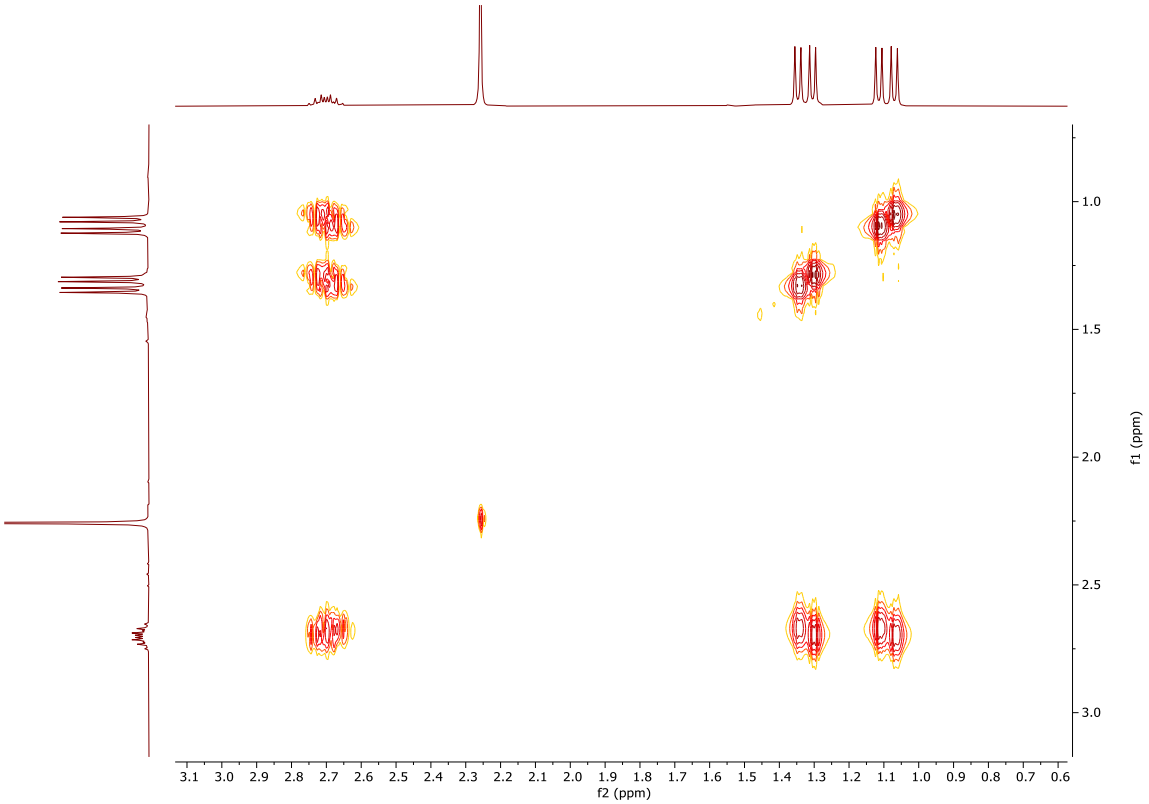


Figure S53. COSY (^{1}H-^{1}H) NMR of compound **4** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

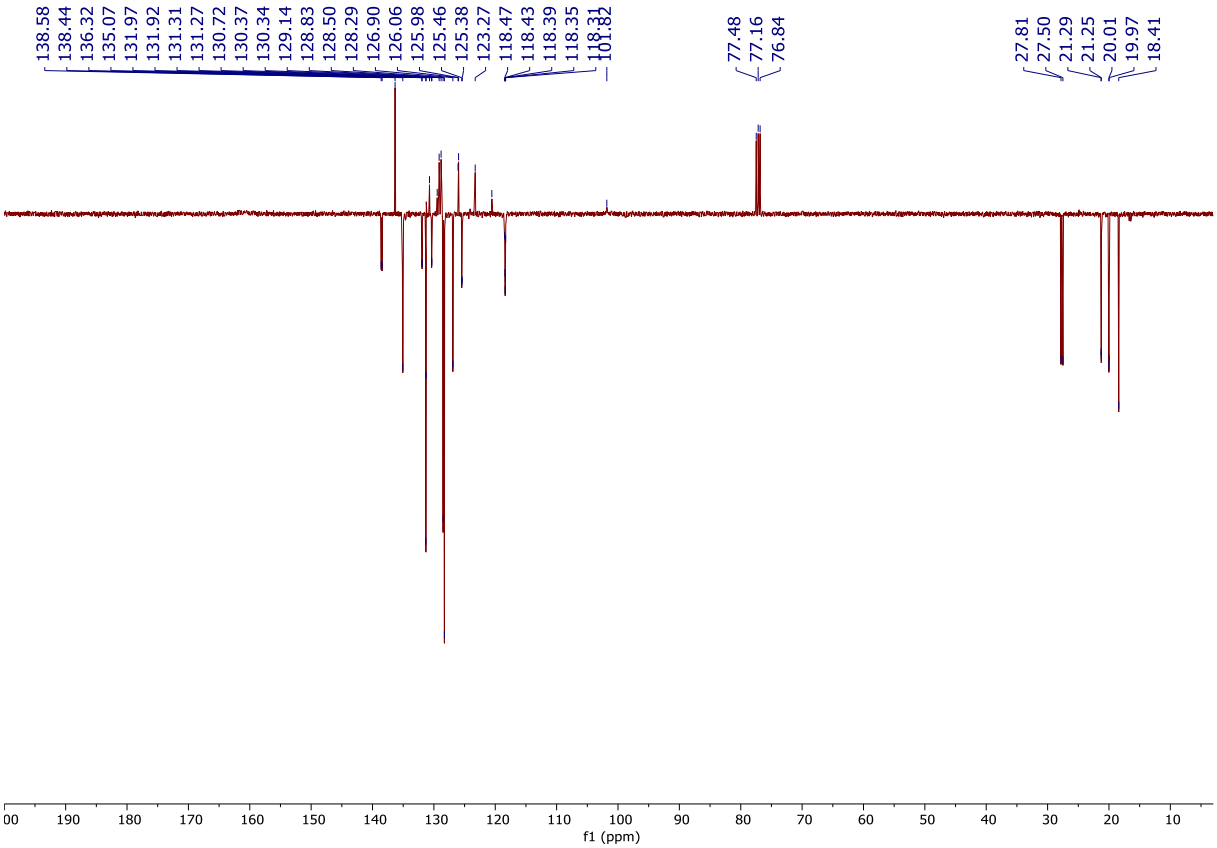


Figure S54. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K).

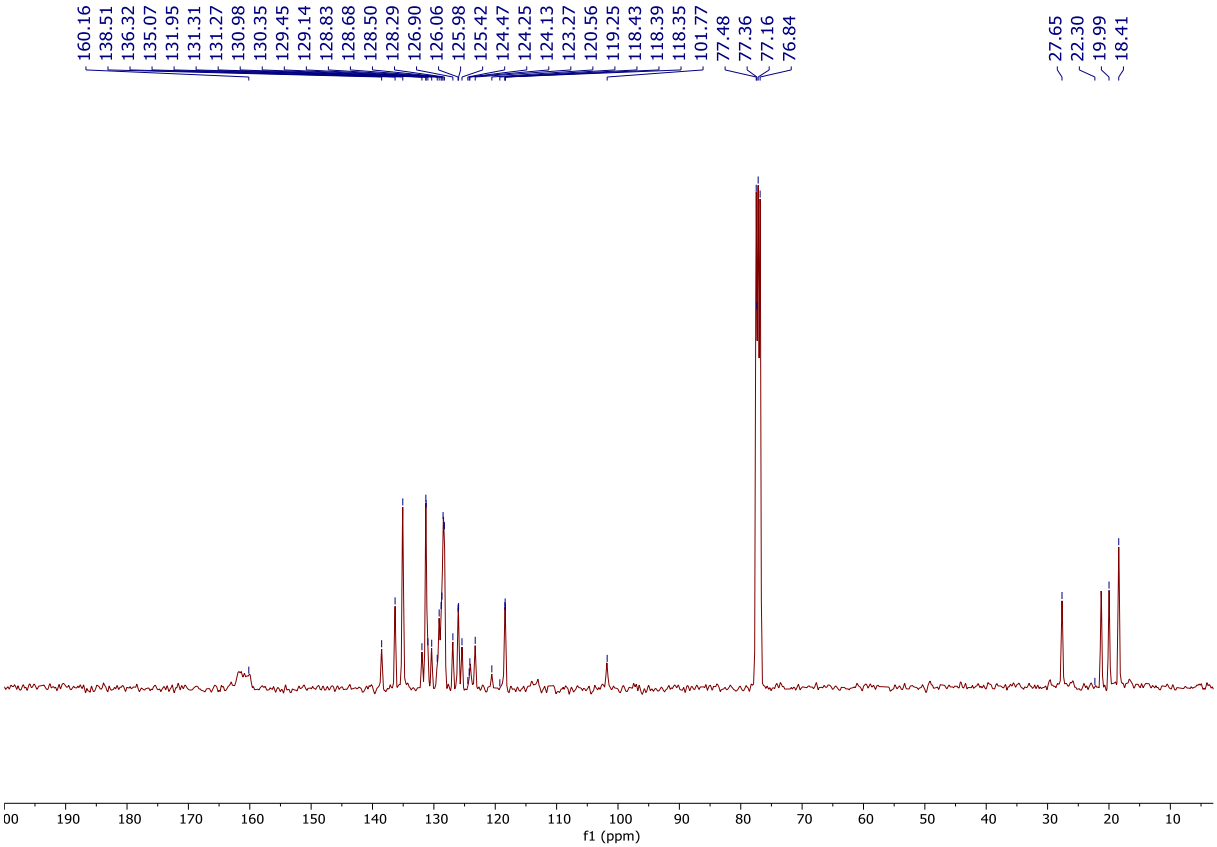


Figure S55. $^{13}C\{^{1}H\ ;\ ^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K).

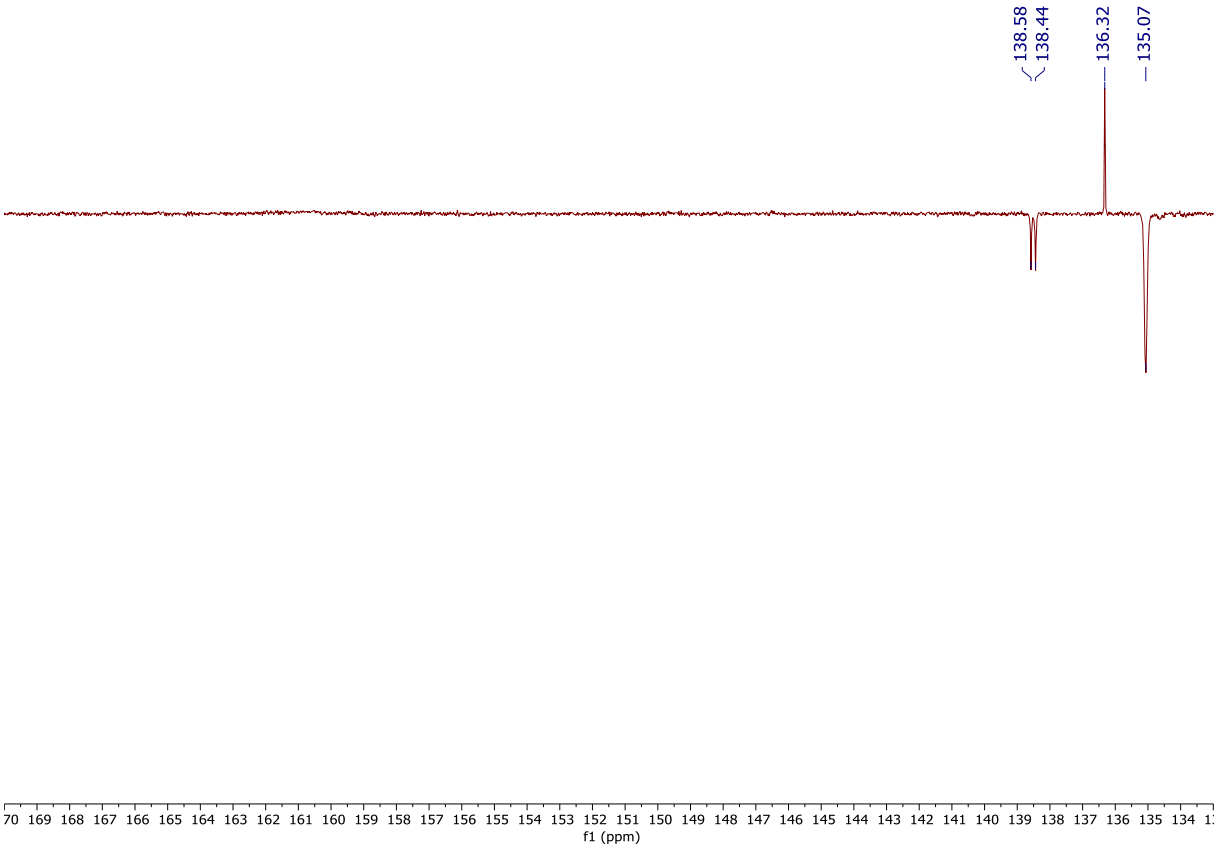


Figure S56. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

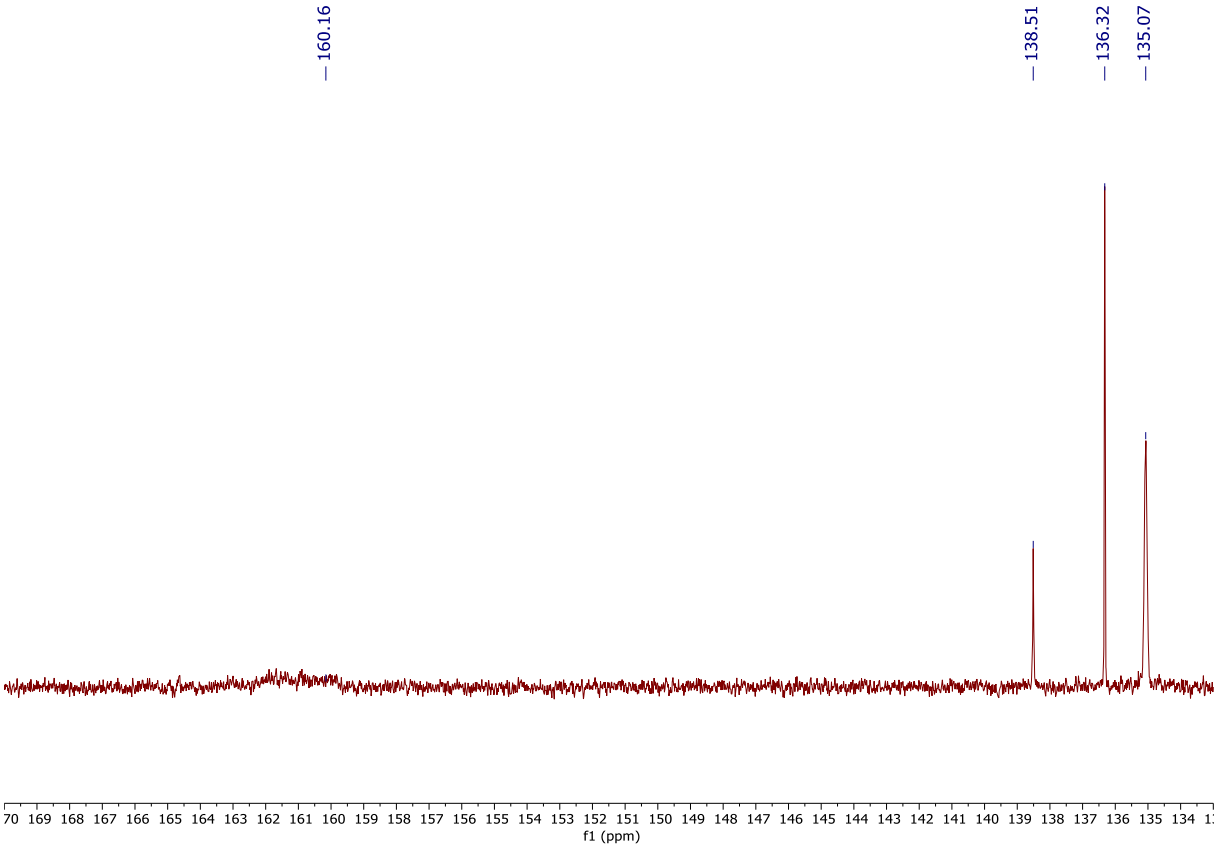


Figure S57. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

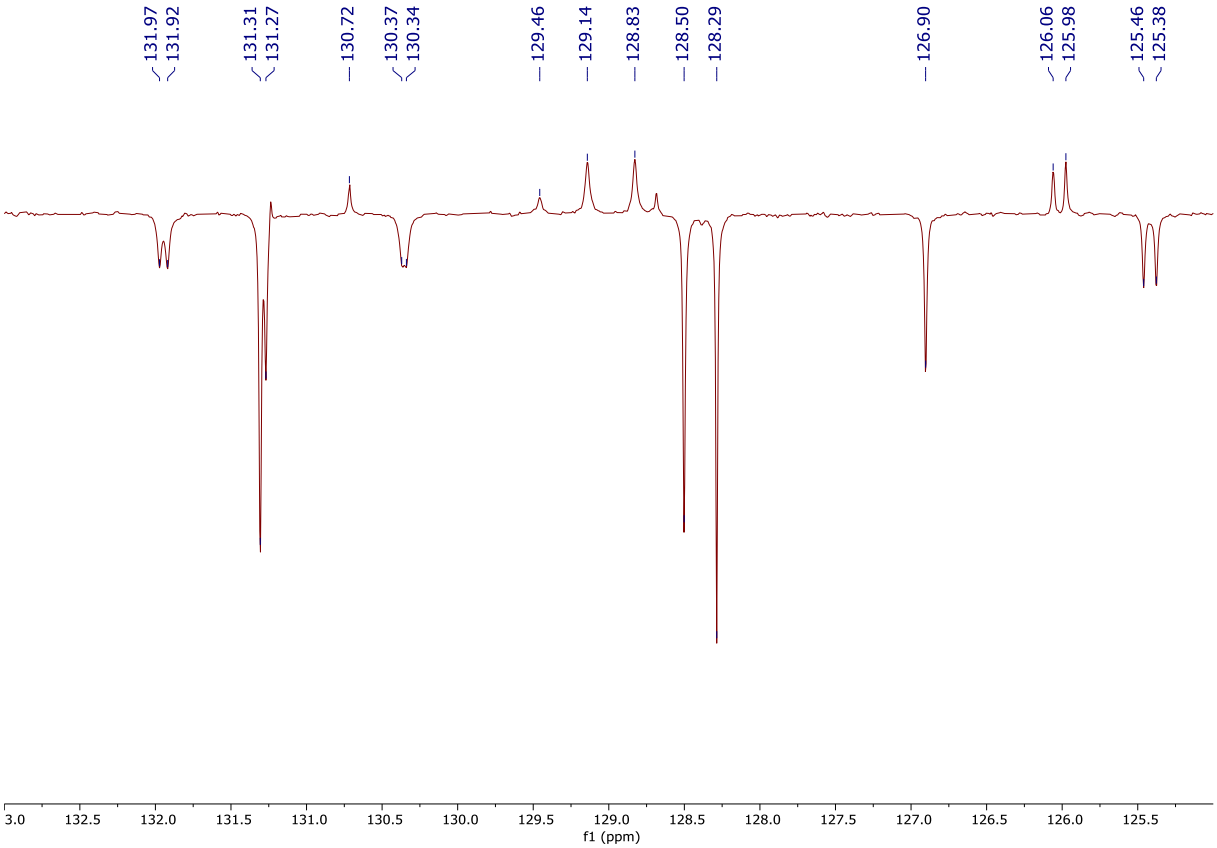


Figure S58. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

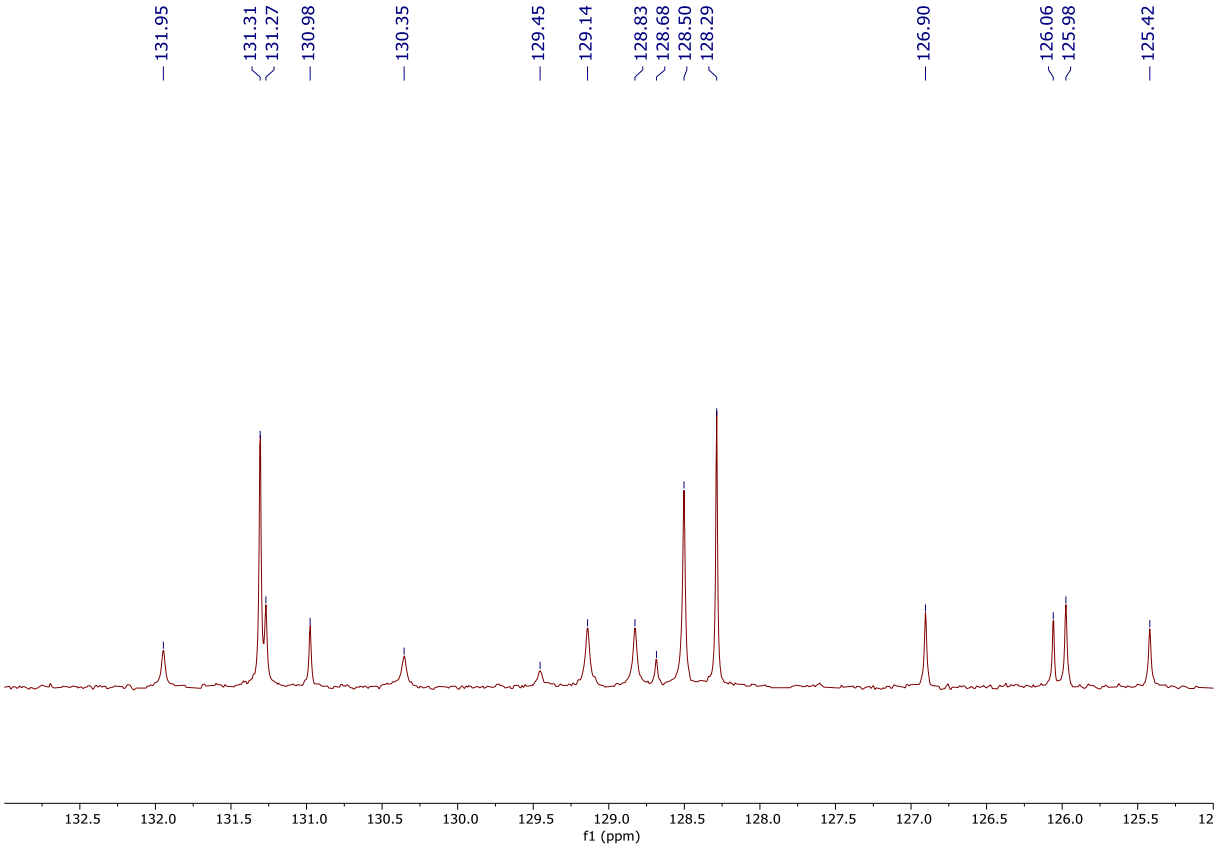


Figure S59. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

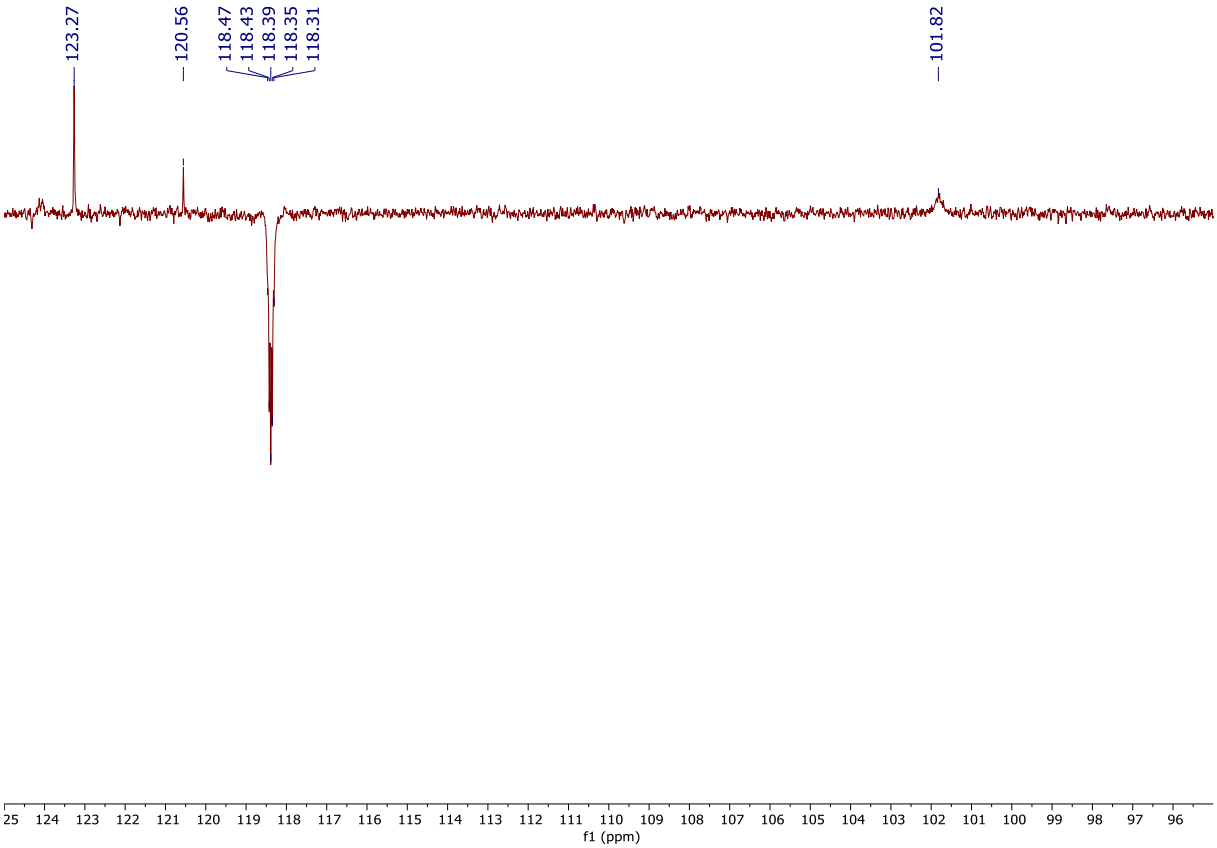


Figure S60. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

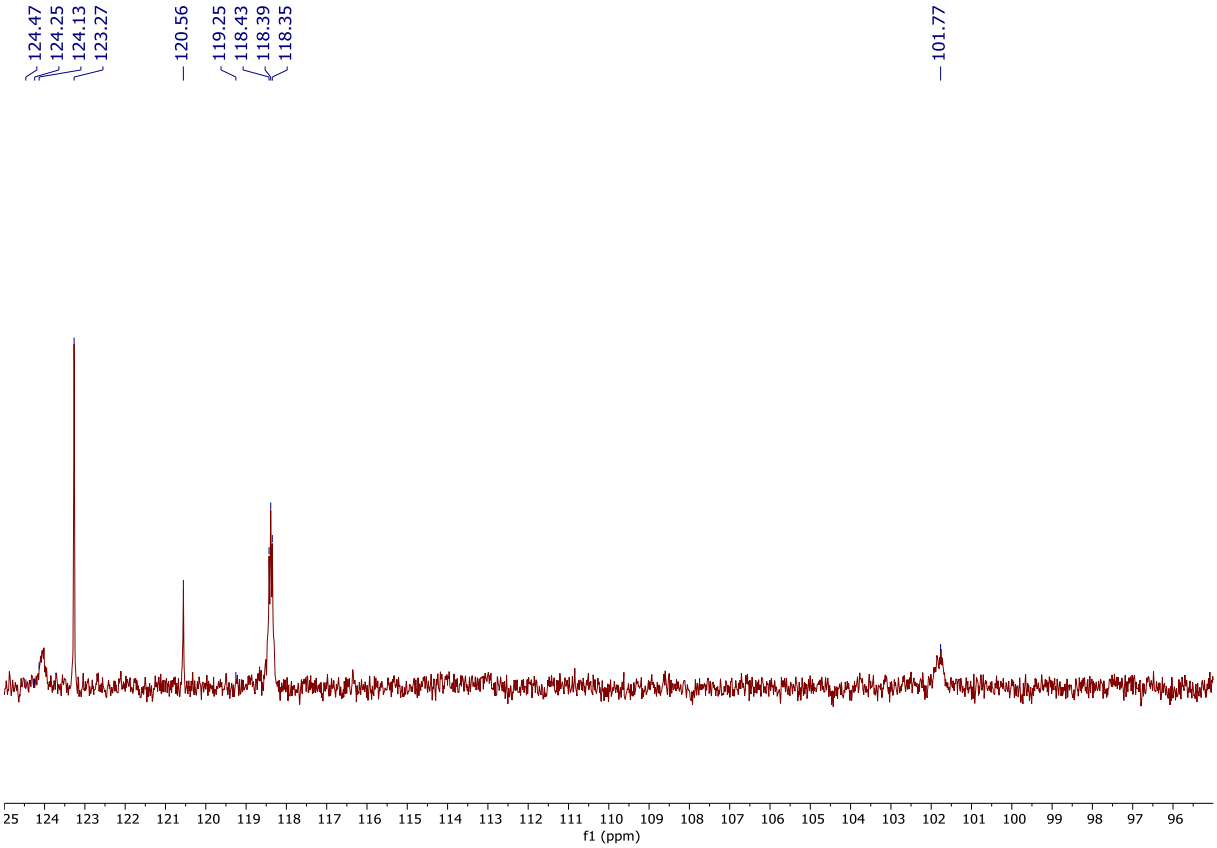


Figure S61. $^{13}C\{^{1}H\ ;\ ^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, zoom-in.

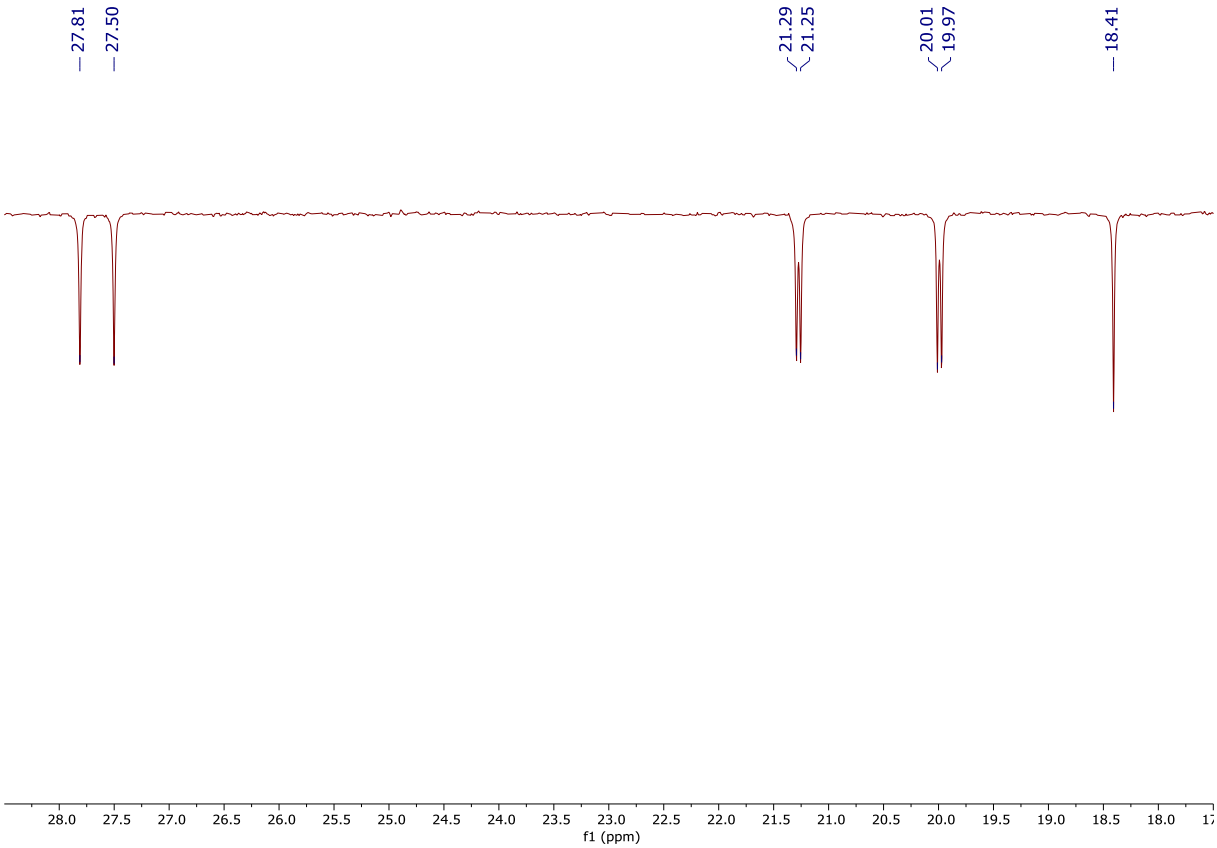


Figure S62. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aliphatic area, zoom-in.

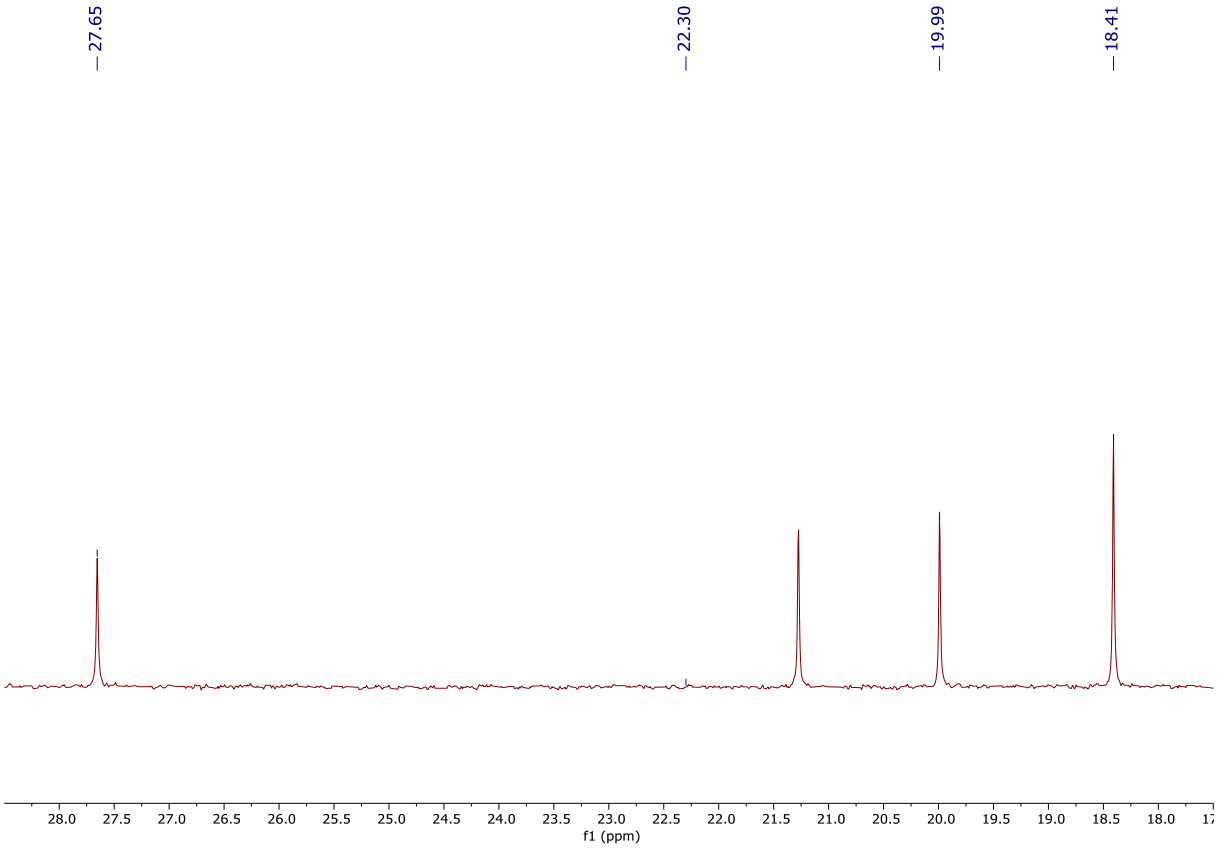


Figure S63. $^{13}C\{^{1}H\ ;\ ^{31}P\}$ NMR spectrum of compound **4** ($CDCl_3$, 100.6 MHz, 298 K); aliphatic area, zoom-in.

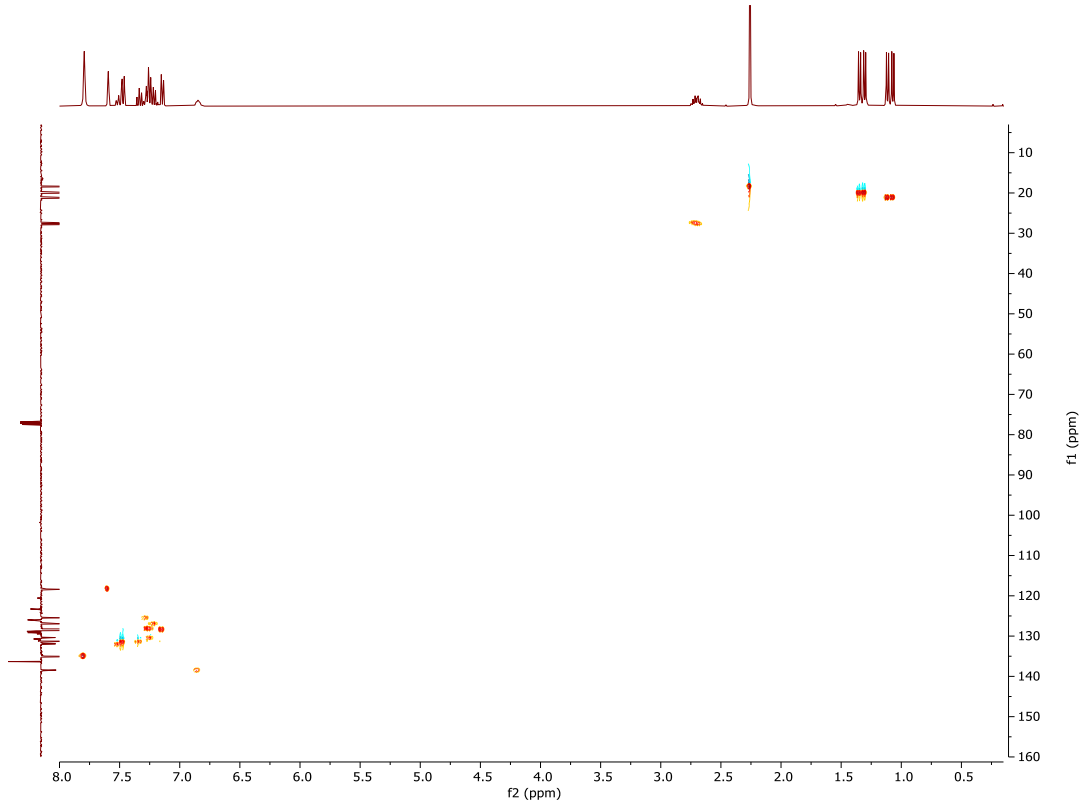


Figure S64. HSQC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}).

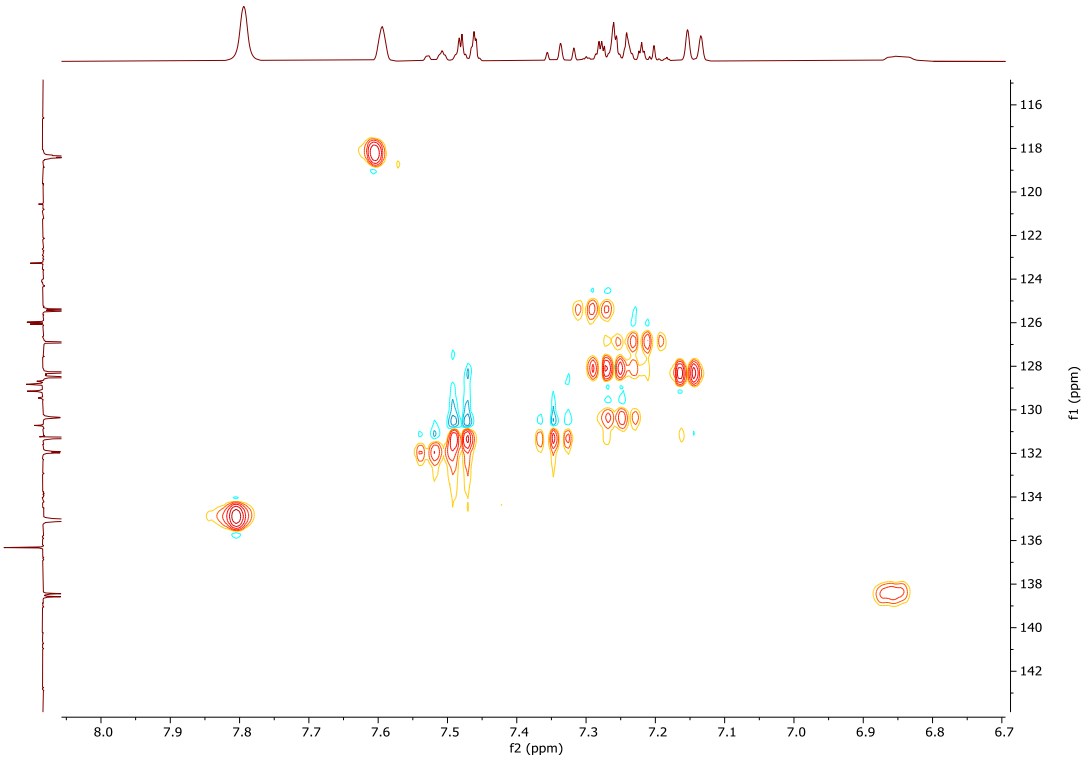


Figure S65. HSQC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area.

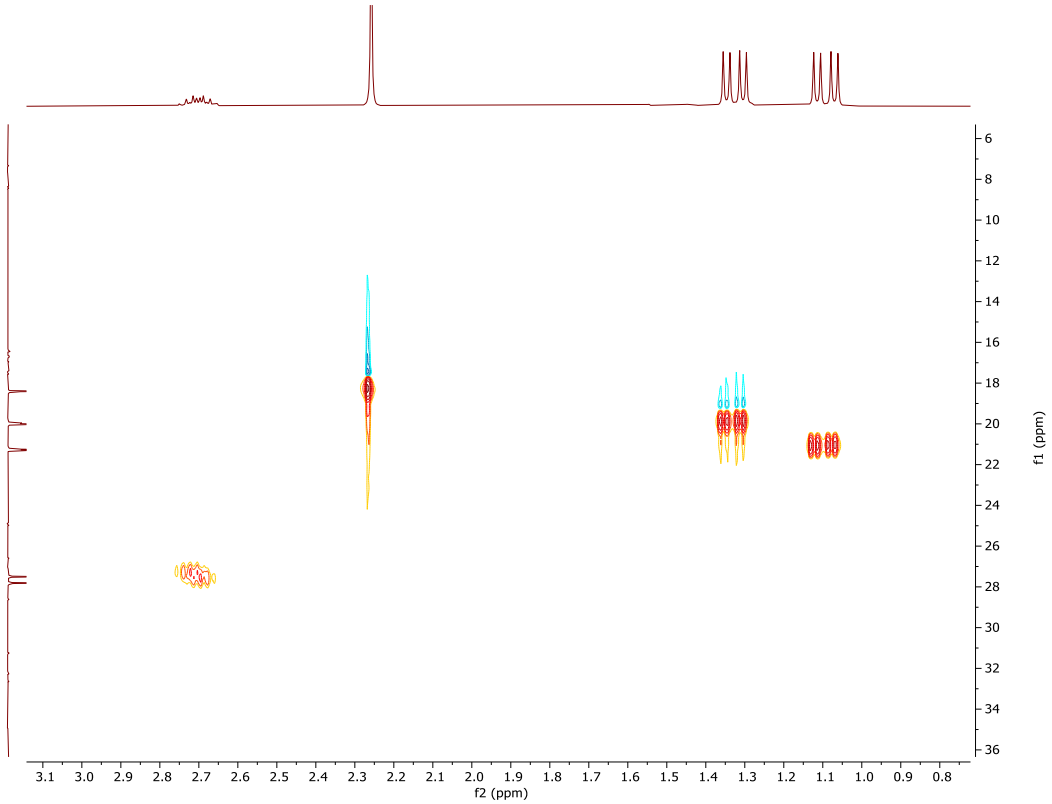


Figure S66. HSQC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aliphatic area.

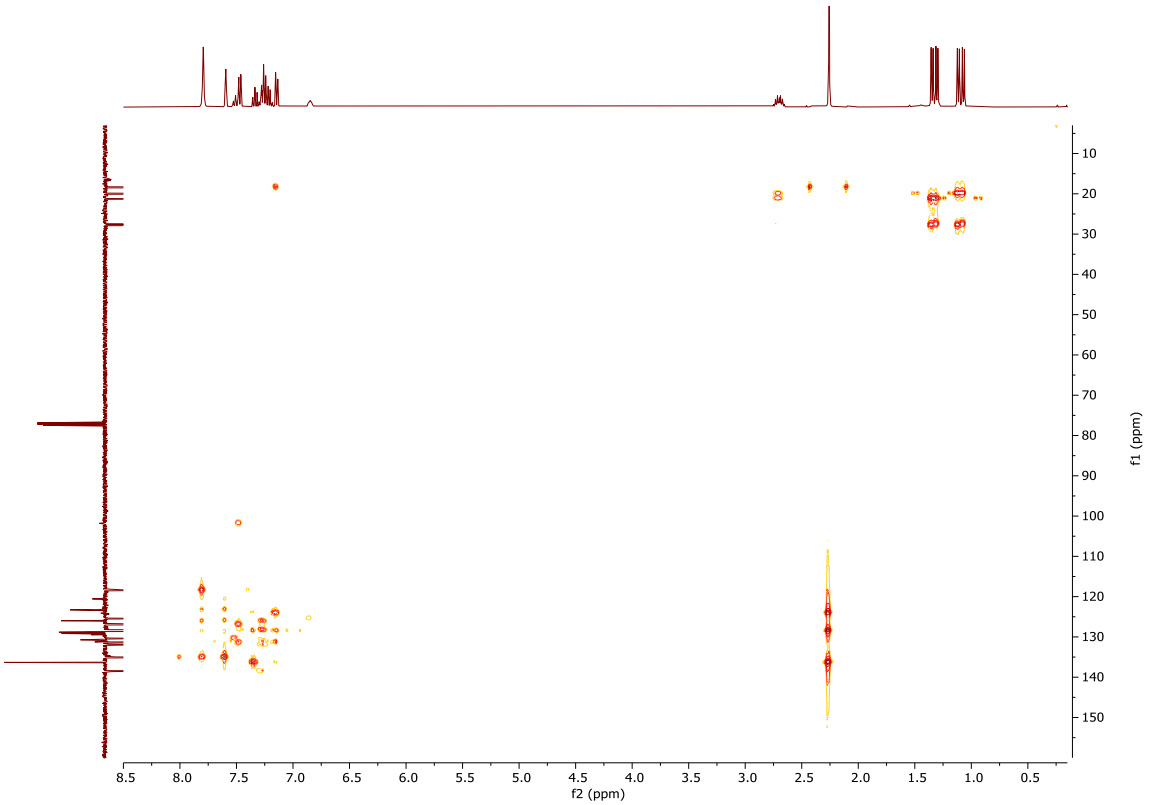


Figure S67. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}).

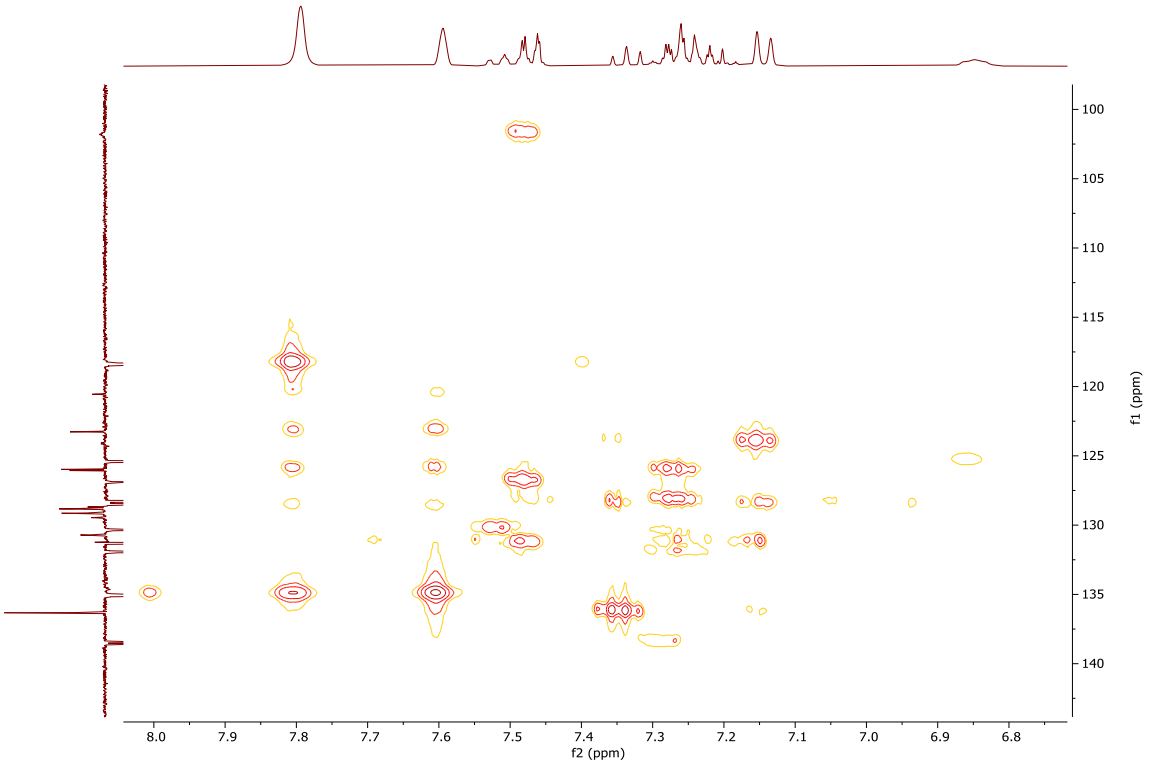


Figure S68. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area.

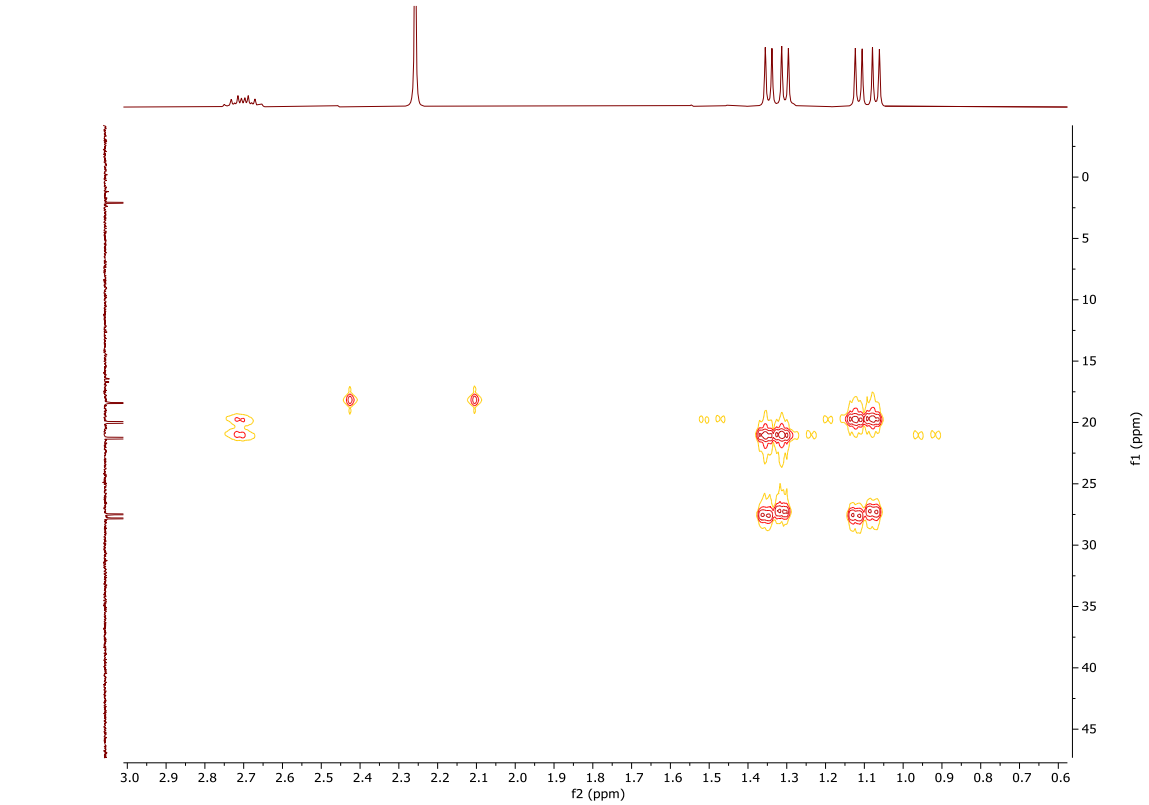


Figure S69. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **4** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area.

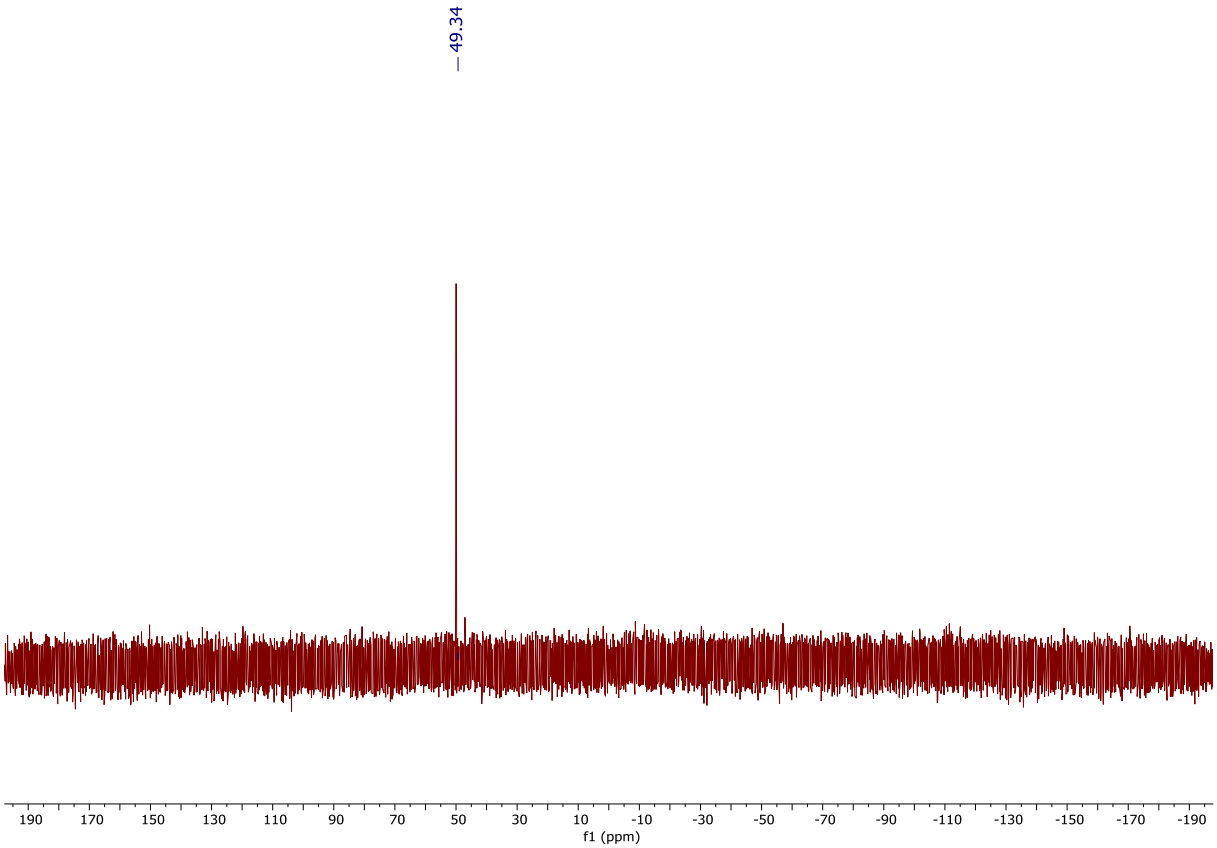


Figure S70. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4** ($CDCl_3$, 162.0 MHz, 298 K).

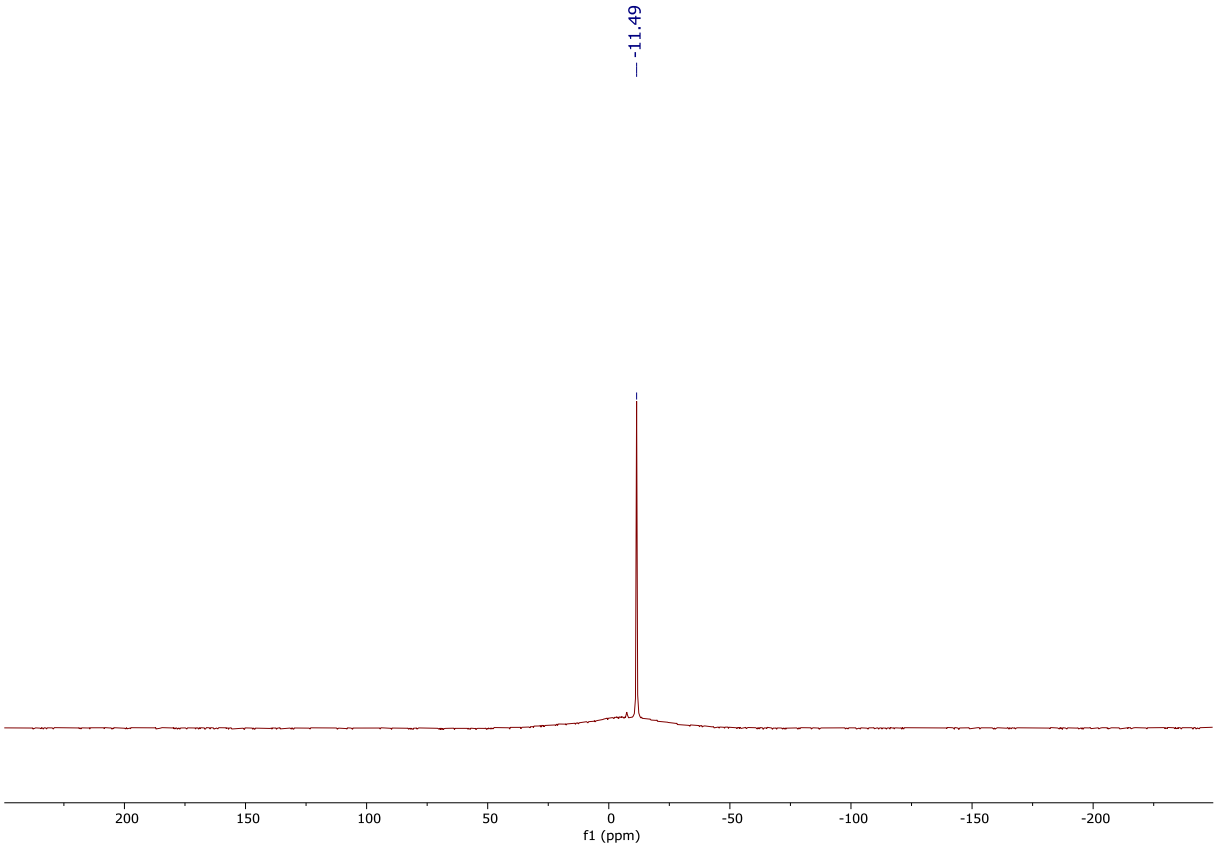


Figure S71. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4** ($CDCl_3$, 128.4 MHz, 298 K).

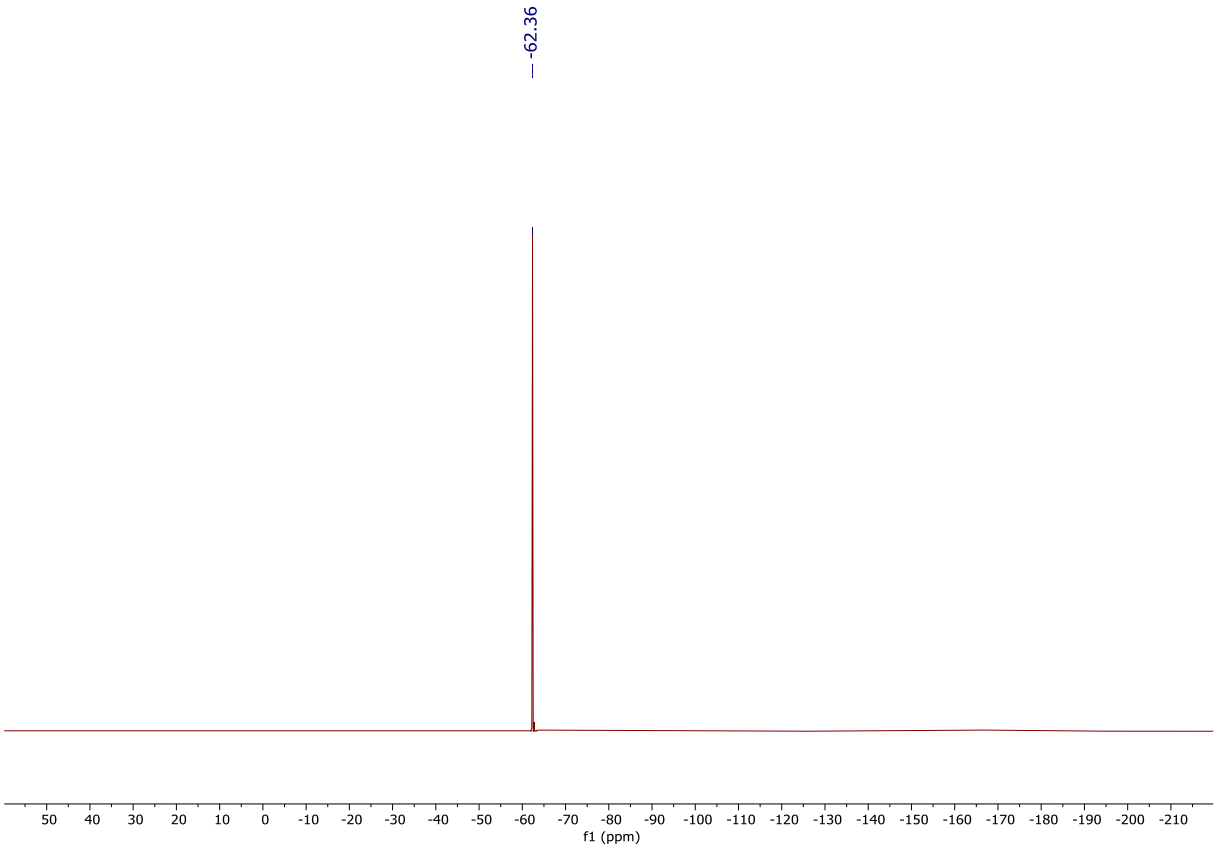
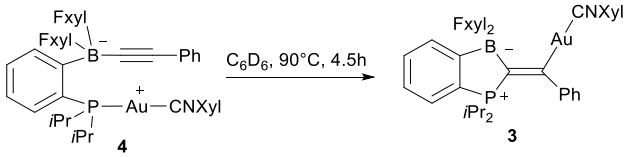


Figure S72. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4** ($CDCl_3$, 470.5 MHz, 298 K)

Synthesis of 3 from 4



A solution of **4** (50 mg, 0.047 mmol, 1 equiv.) in C_6D_6 (0.6 mL) was prepared in an NMR pressure tube and heated at 90°C for 4h30. The solution turned from colorless to pale yellow. The volatiles were removed under high vacuum. The residue was then redispersed into pentane and the solution was filtered. Crystals suitable for X-ray diffraction analysis were obtained after 3 days standing at –20°C. The supernatant was removed and the crystals were washed with chilled pentane (2x0.3 mL). Finally, the solid was dried *in vacuo* to afford the pure product **3** in 67% isolated yield (33.7 mg, 0.032 mmol).

Anal. Calcd. for $C_{45}H_{38}AuBF_{12}NP/0.15\ CDCl_3$: C, 50.32; H, 3.55; N, 1.30. Found: C, 50.12; H, 3.93, N, 1.28. HRMS (ES-MS$^+$): exact mass (monoisotopic) calcd. for $[M+H]^+$ $(C_{45}H_{39}BF_{12}NPAu)^+$: 1060.2395; found: 1060.2415.
^{1}H NMR ($CDCl_3$, 400.2 MHz, 298 K): δ (in ppm) 8.02 (br.s, 4H, H$_{o\text{-Fxyl}}$), 7.53 (br.s, 2H, H$_{p\text{-Fxyl}}$), 7.47 (pseudo-tt, J_{HH} = 7.4 Hz, J_{HH} = 1.2 Hz ≈ J_{PH} ≈ 1.3 Hz, 1H, H$_{Ar}$), 7.40 (pseudo-dd, J_{HH} = 7.6 Hz ≈ J_{PH} ≈ 6.8 Hz, 1H, H$_{Ar}$), 7.36 (br.d, J_{HH} = 7.6 Hz, 1H, H$_{Ar}$), 7.31-7.23 (m, 4H, 1H$_{Ar}$ + 2H$_{m\text{-Ph}}$ + 1H$_{p\text{-Xyl}}$)*, 7.11 (pseudo-tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H$_{p\text{-Ph}}$), 7.08 (br.d, $^3J_{HH}$ = 7.8 Hz, 2H, H$_{m\text{-Xyl}}$), 7.02 (pseudo-dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H$_{o\text{-Ph}}$), 2.31 (dhept, $^2J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH$_{i\text{Pr}}$), 2.23 (s, 6H, CH$_{3\text{Xyl}}$), 1.18 (dd, $^3J_{PH}$ = 15.7 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, CH$_{3i\text{Pr}}$), 0.57 (dd, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, CH$_{3i\text{Pr}}$).

* assigned according to COSY (^{1}H-^{1}H) NMR.

visible in HSQC (^{13}C{^{1}H}-^{1}H) NMR.

Jmod (^{13}C{^{1}H}) NMR ($CDCl_3$, 125.8 MHz, 298 K): δ (in ppm) 203.6 (d, $^2J_{PC}$ = 8.2 Hz, P-C=*C*-Au), 172.0 (br.s, B-C$_{ipso\text{-Ar}}$) $, 163.2 (br.q, B-C$_{ipso\text{-Fxyl}}$) $, 160.8 (br.q, P-*C*=C-Au), 154.4 (d, $^3J_{PC}$ = 20.5 Hz, C$_{ipso\text{-Ph}}$) $, 145.6 (br.s, C$_{CNXyl}$)£, 136.1 (s, *C*-CH$_{3\text{Xyl}}$), 135.0 (s, CH$_{o\text{-Fxyl}}$), 134.1 (d, J_{PC} = 11.8 Hz, CH$_{Ar}$), 132.3 (d, J_{PC} = 2.9 Hz, CH$_{Ar}$), 130.5 (s, CH$_{p\text{-Xyl}}$) #, 129.5 (d, J_{PC} = 11.0 Hz, CH$_{Ar}$), 128.7 (q, $^2J_{FC}$ = 31.1 Hz, *C*-CF$_3$), 128.5 (s, CH$_{m\text{-Ph}}$) #, 128.3 (s, CH$_{m\text{-Xyl}}$), 126.5 (d, $^1J_{PC}$ = 90.7 Hz, P-C$_{ipso\text{-Ar}}$), 126.0 (d, J_{PC} = 9.7 Hz, CH$_{Ar}$), 125.7 (s, CH$_{p\text{-Ph}}$), 125.3 (d, $^5J_{PC}$ = 2.6 Hz, CH$_{o\text{-Ph}}$), 124.8 (q, $^1J_{FC}$ = 125.9 Hz, CF$_3$), 124.7 (br.s, C$_{ipso\text{-Xyl}}$) $, 117.6 (hept, $^3J_{FC}$ = 4.0 Hz, C$_{p\text{-Fxyl}}$), 27.5 (d, $^1J_{PC}$ = 35.5 Hz, CH$_{i\text{Pr}}$), 18.3 (s, Me$_{Xyl}$), 17.0 (d, $^2J_{PC}$ = 2.9 Hz, CH$_{3i\text{Pr}}$).

$ assigned according to HMBC (^{13}C{^{1}H}-^{1}H) NMR.

assigned according to HSQC (^{13}C{^{1}H}-^{1}H) NMR.

£ only visible in ^{13}C{^{1}H, ^{31}P} NMR.

^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz, 298 K): δ (in ppm) 41.2 (pseudo-q, $^2J_{BP}$ ~ 22 Hz)

^{11}B{^{1}H} NMR ($CDCl_3$, 160.5 MHz, 298 K): δ (in ppm) -4.74 (d, $^2J_{PB}$ ~ 22Hz)

^{19}F NMR ($CDCl_3$, 470.5 MHz, 298 K): δ (in ppm) -62.33 (s)

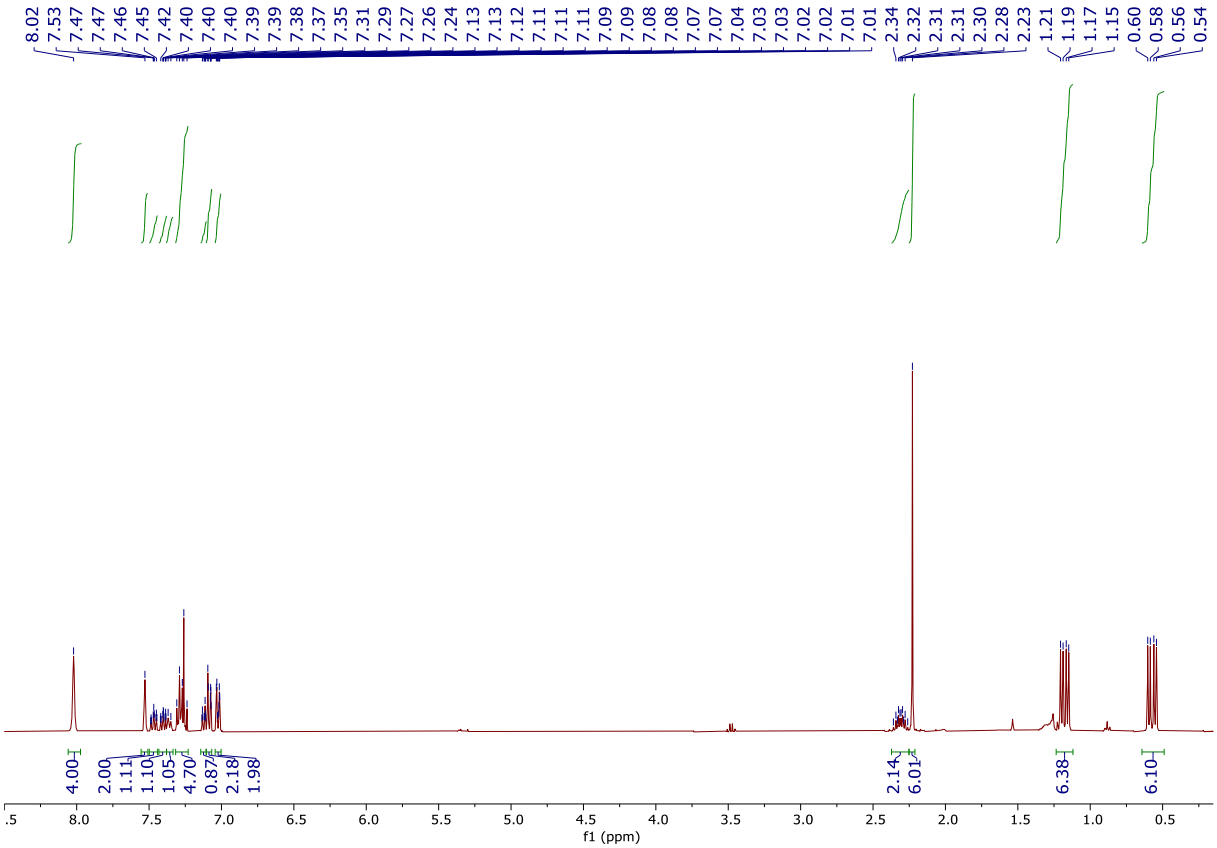


Figure S73. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K).

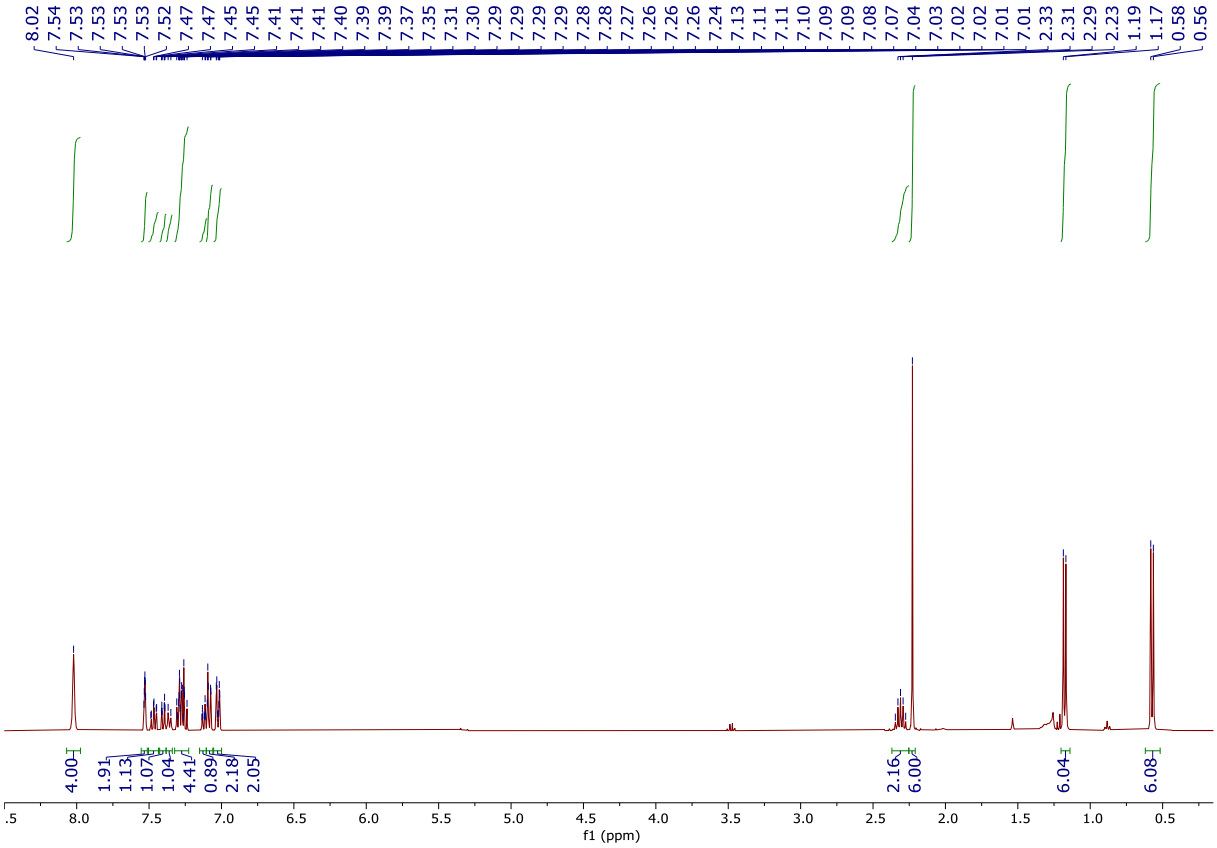


Figure S74. ^{1}H{^{31}P} NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K).

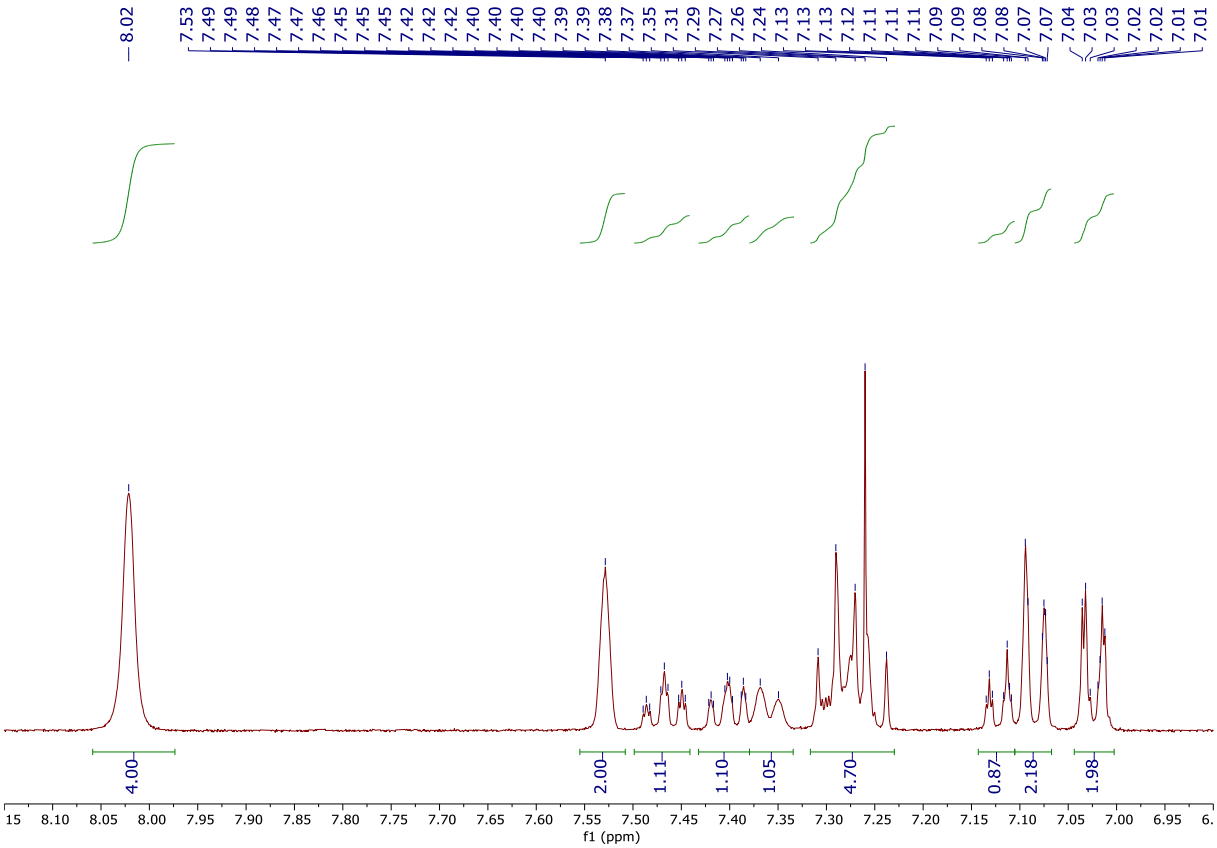


Figure S75. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

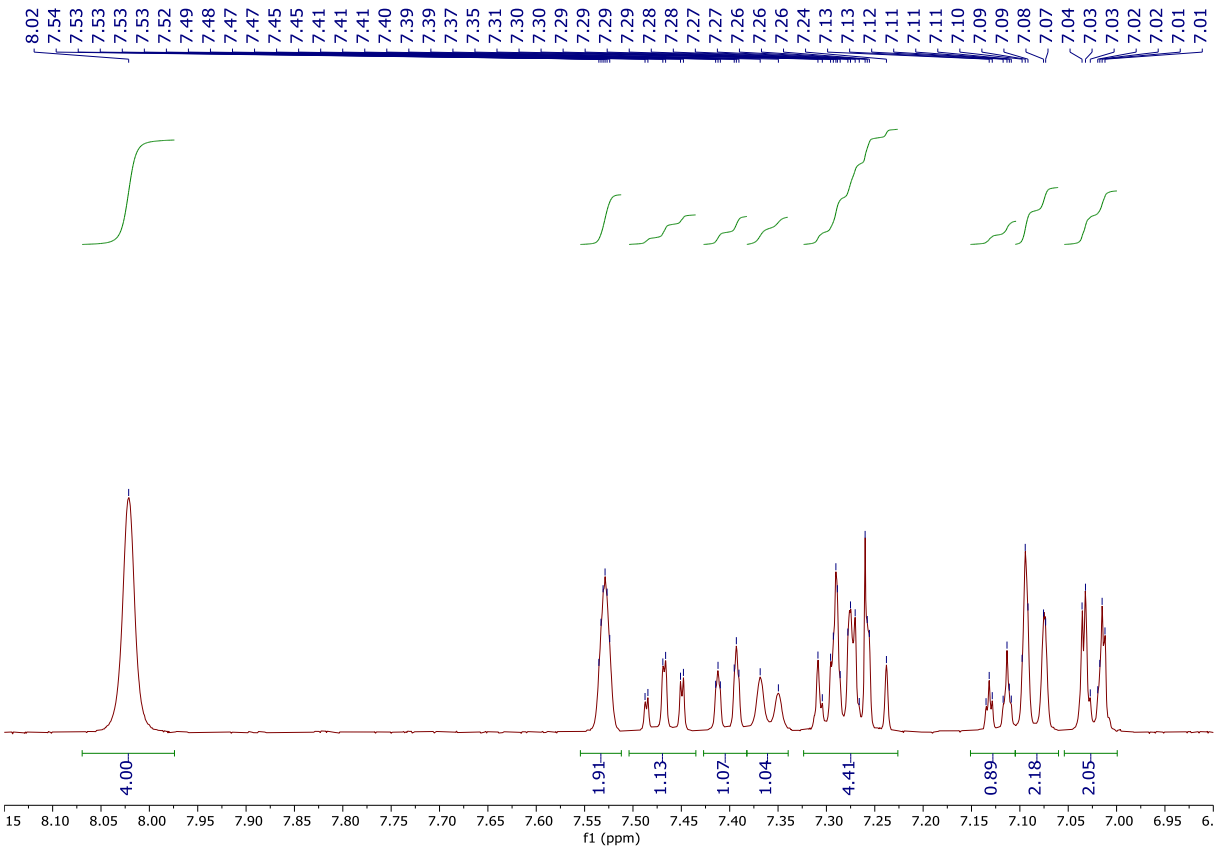


Figure S76. $^{1}H\{^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

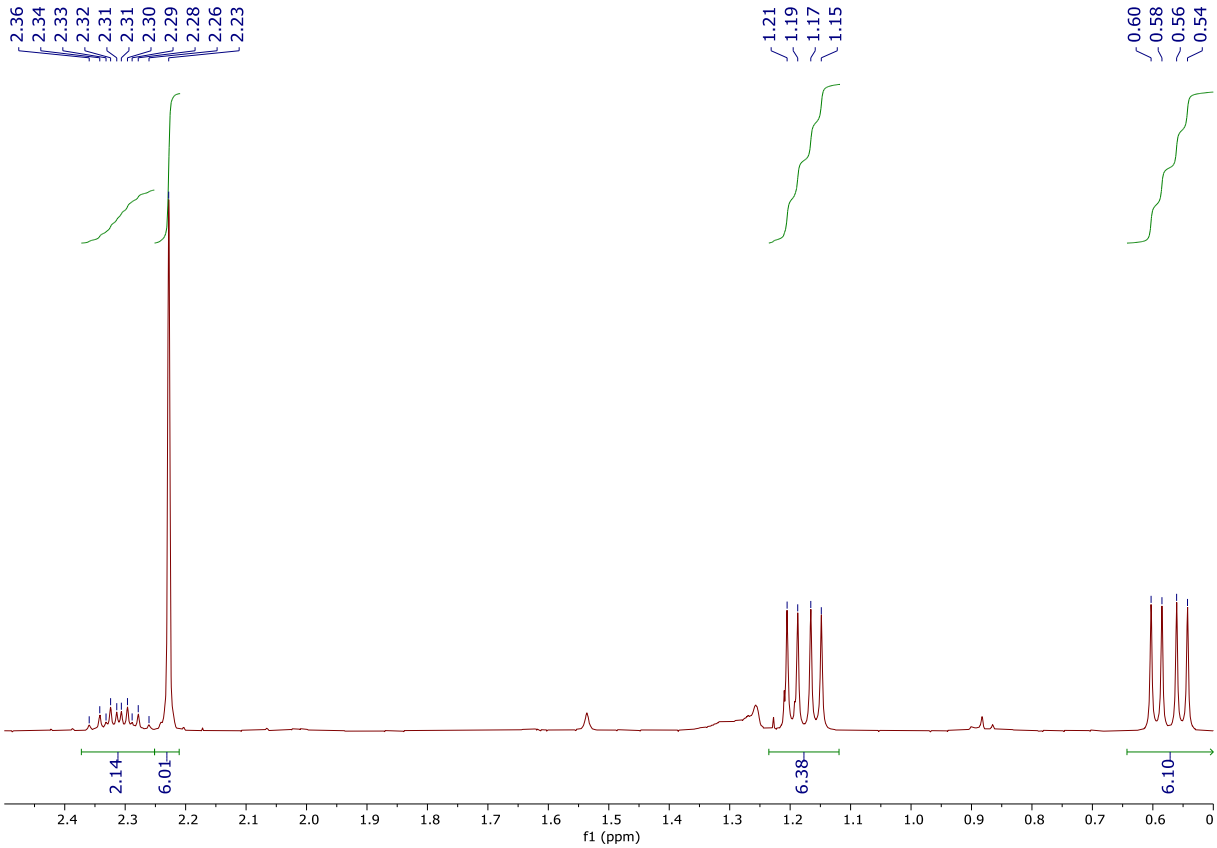


Figure S77. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

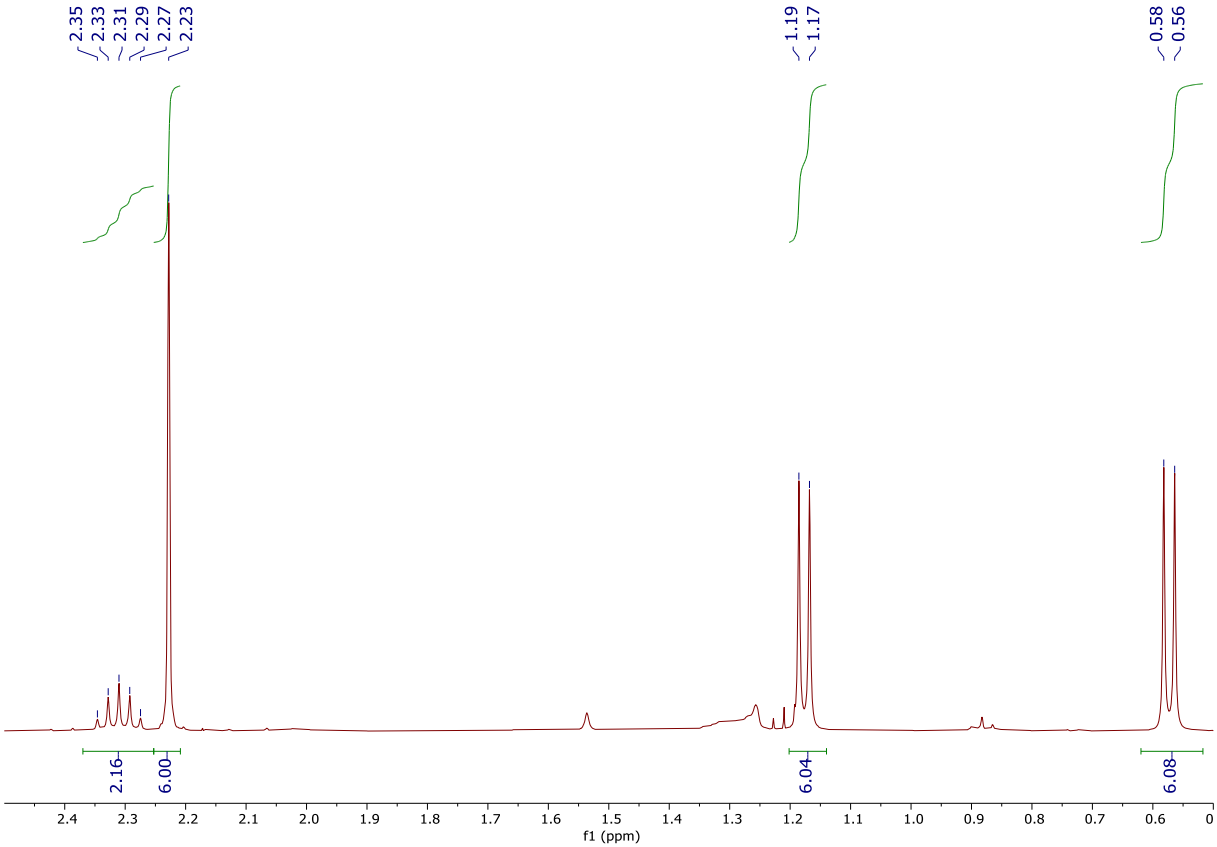


Figure S78. $^{1}H\{^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

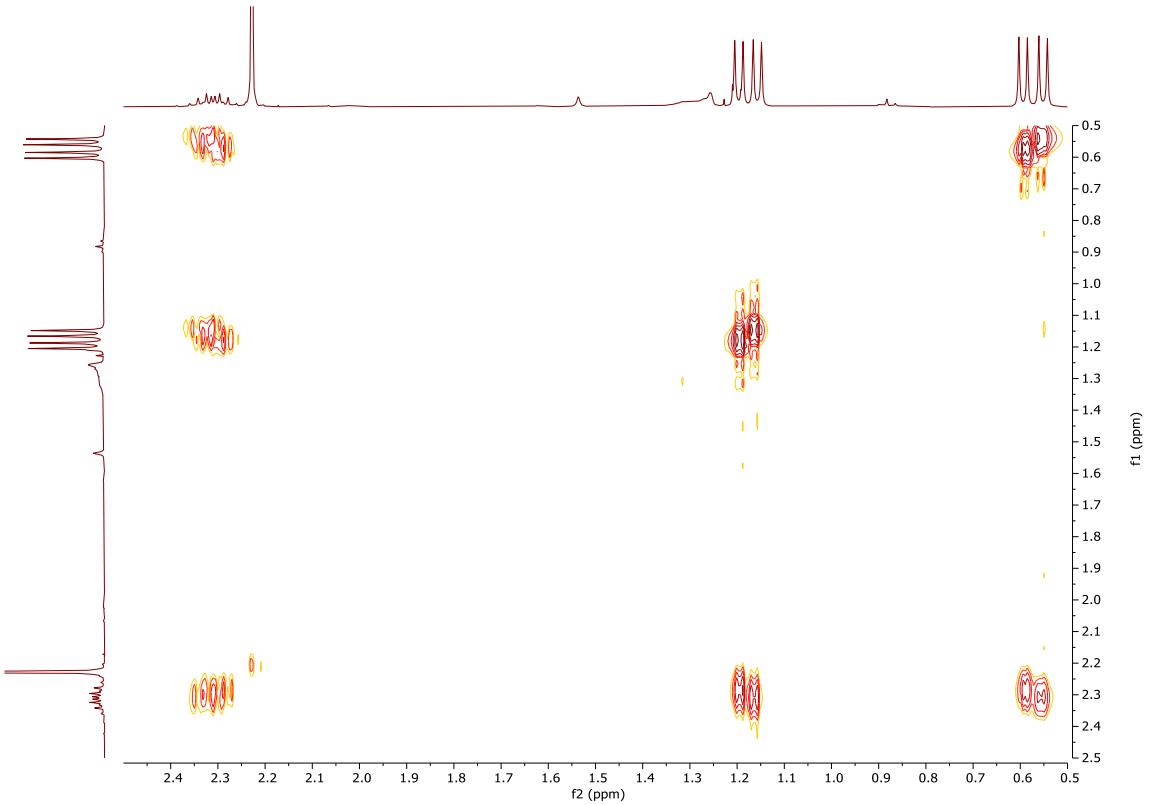


Figure S79. COSY (^{1}H-^{1}H) NMR of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aromatic area.

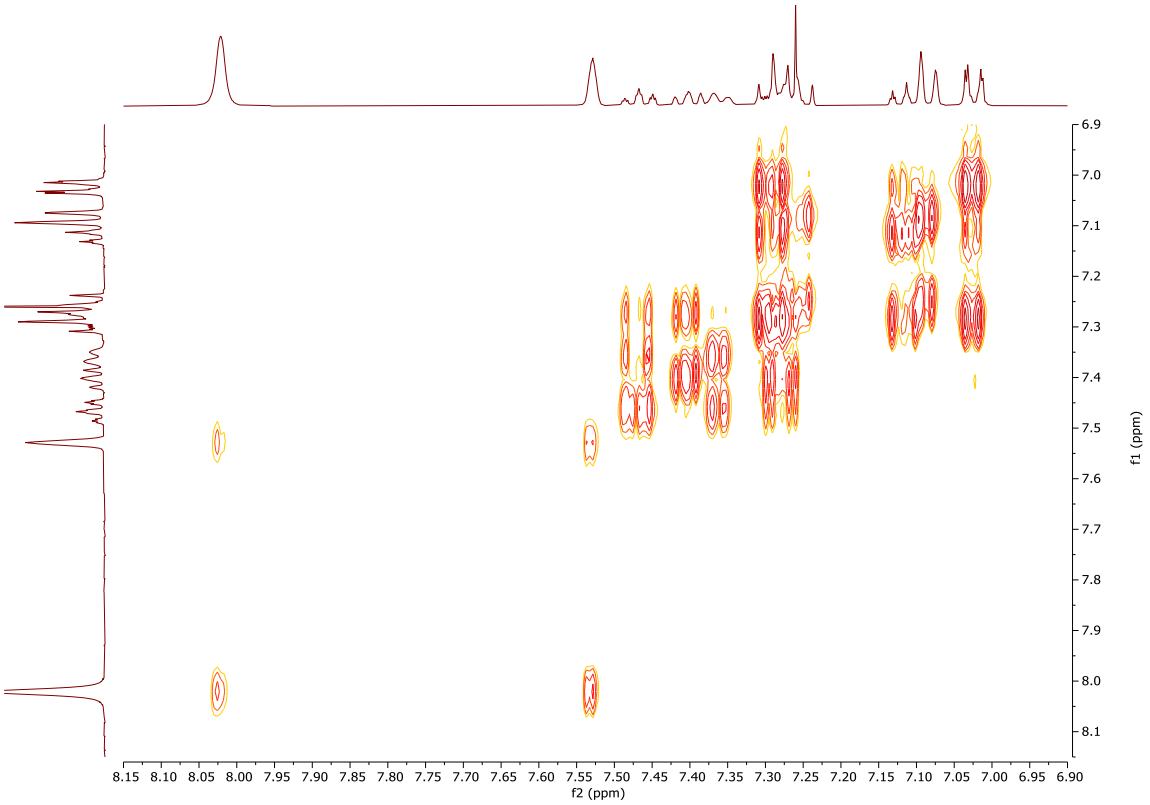


Figure S80. COSY (^{1}H-^{1}H) NMR of compound **3** ($CDCl_3$, 400.2 MHz, 298 K); aliphatic area.

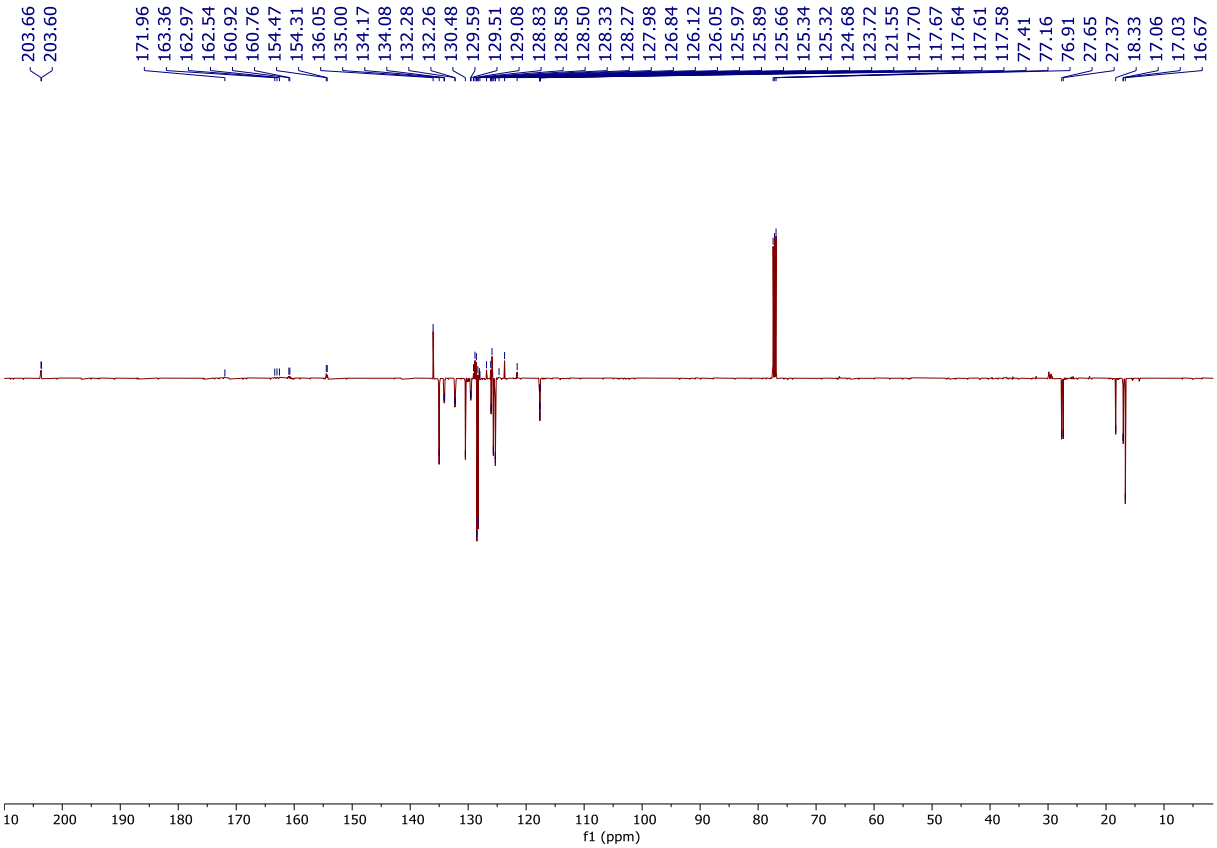


Figure S81. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **3** ($CDCl_3$, 125.8 MHz, 298 K).

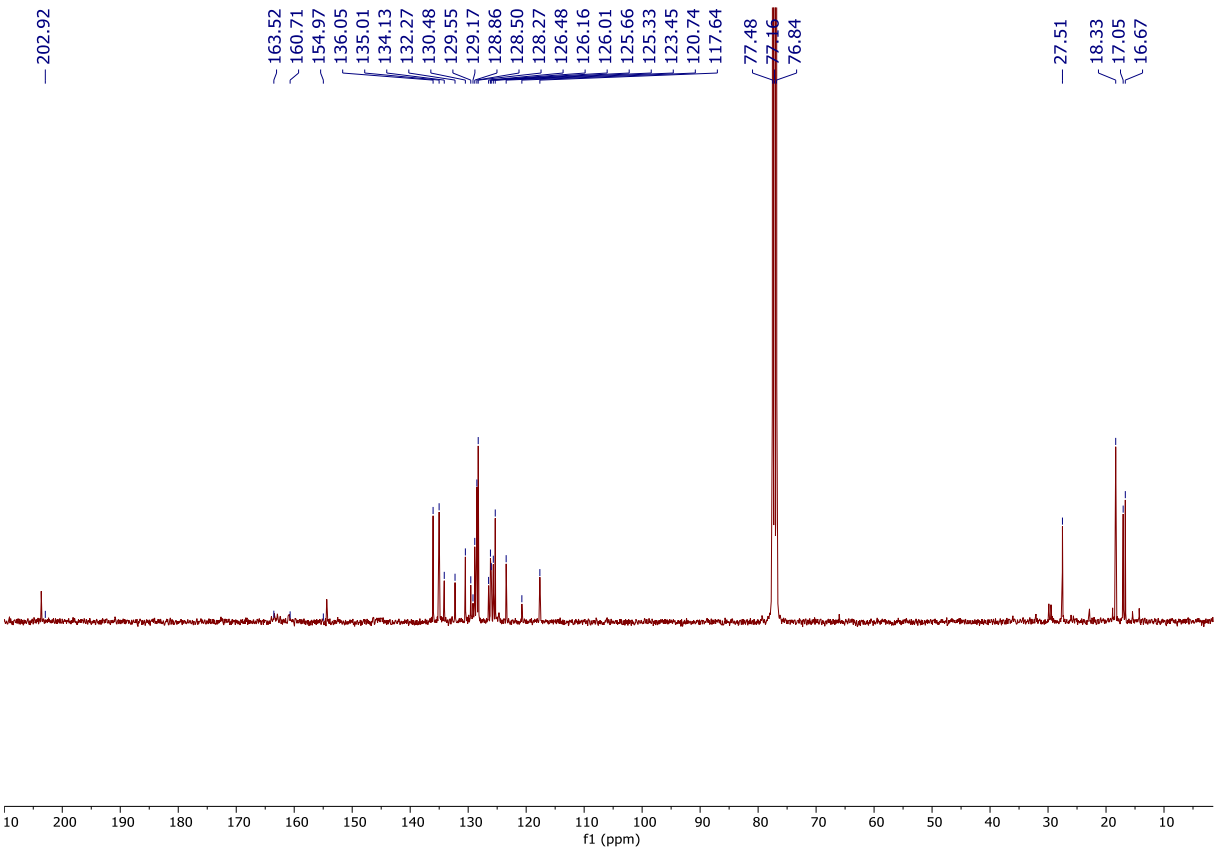


Figure S82. $^{13}C\{^{1}H\ ;\ ^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 100.6 MHz, 298 K).

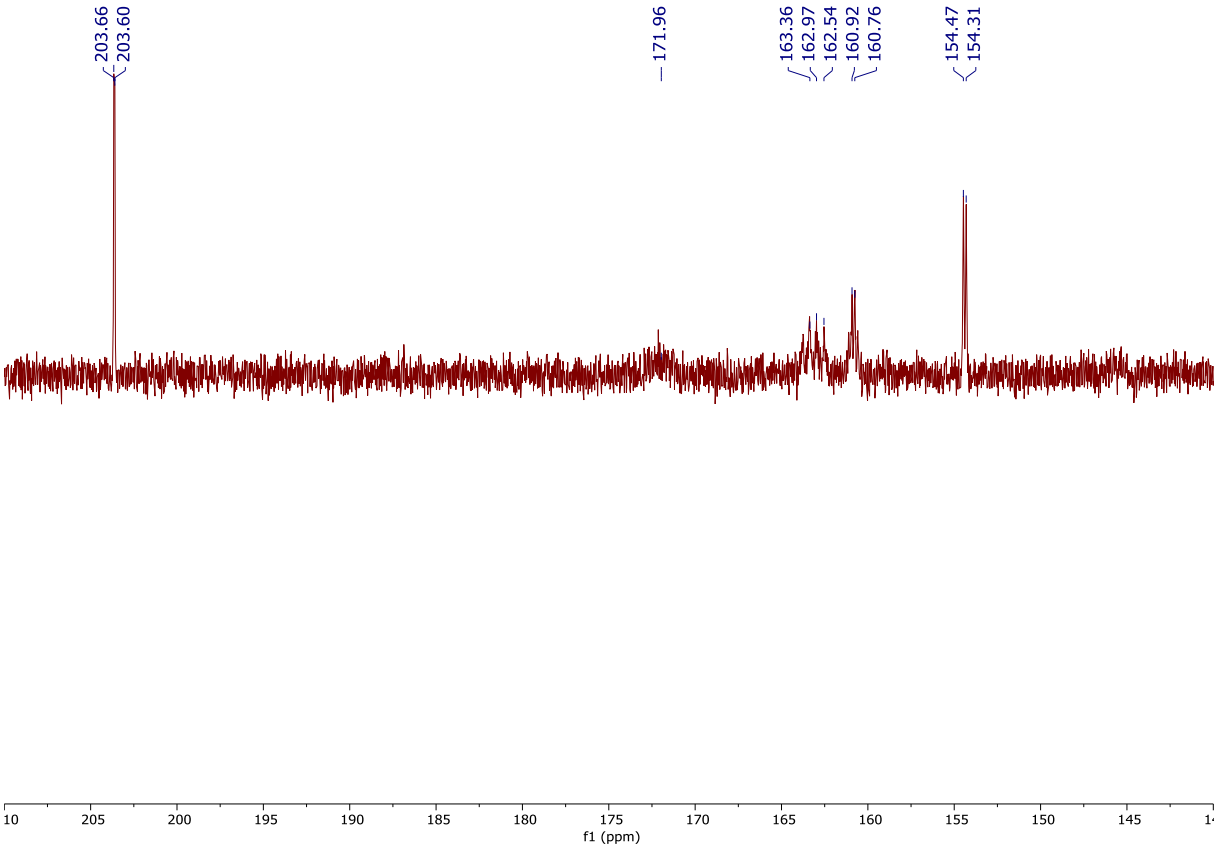


Figure S83. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **3** ($CDCl_3$, 125.8 MHz, 298 K); aromatic area, quaternary carbons.

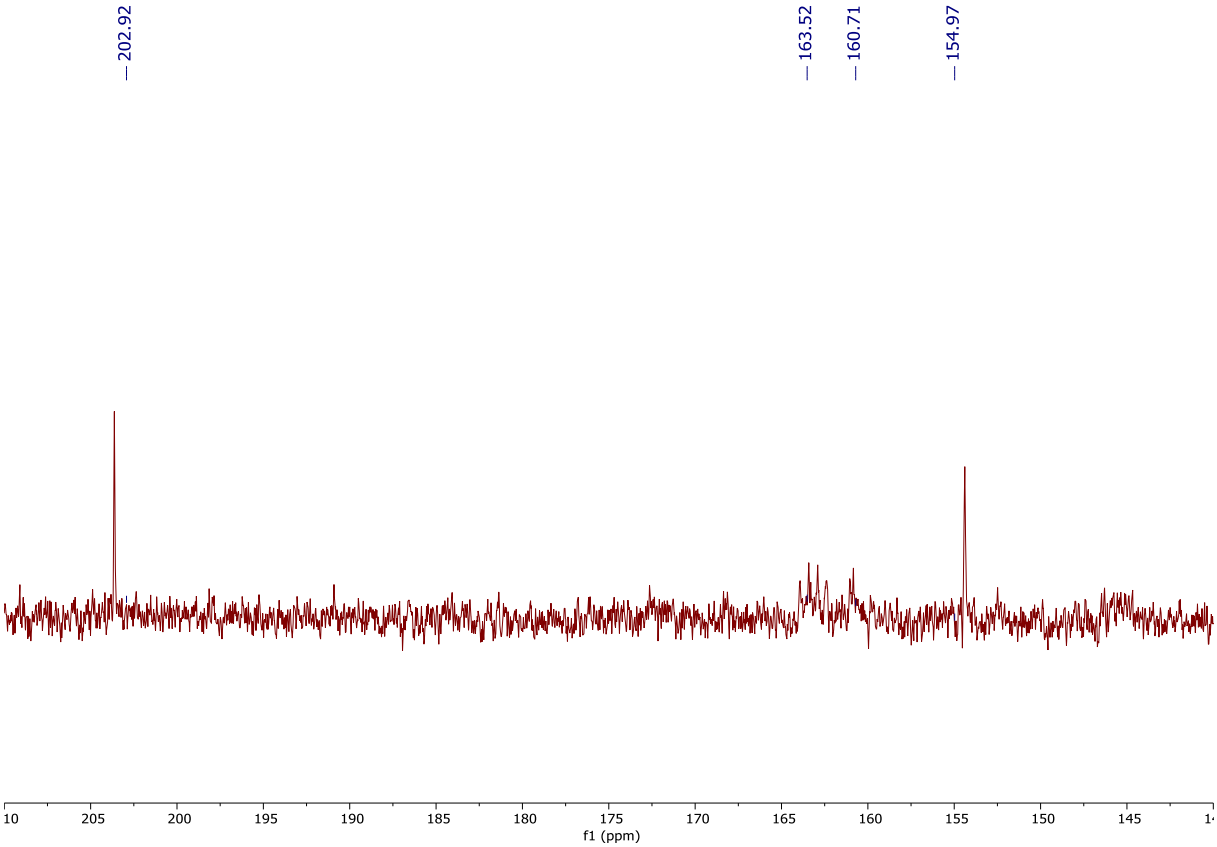


Figure S84. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area, quaternary carbons.

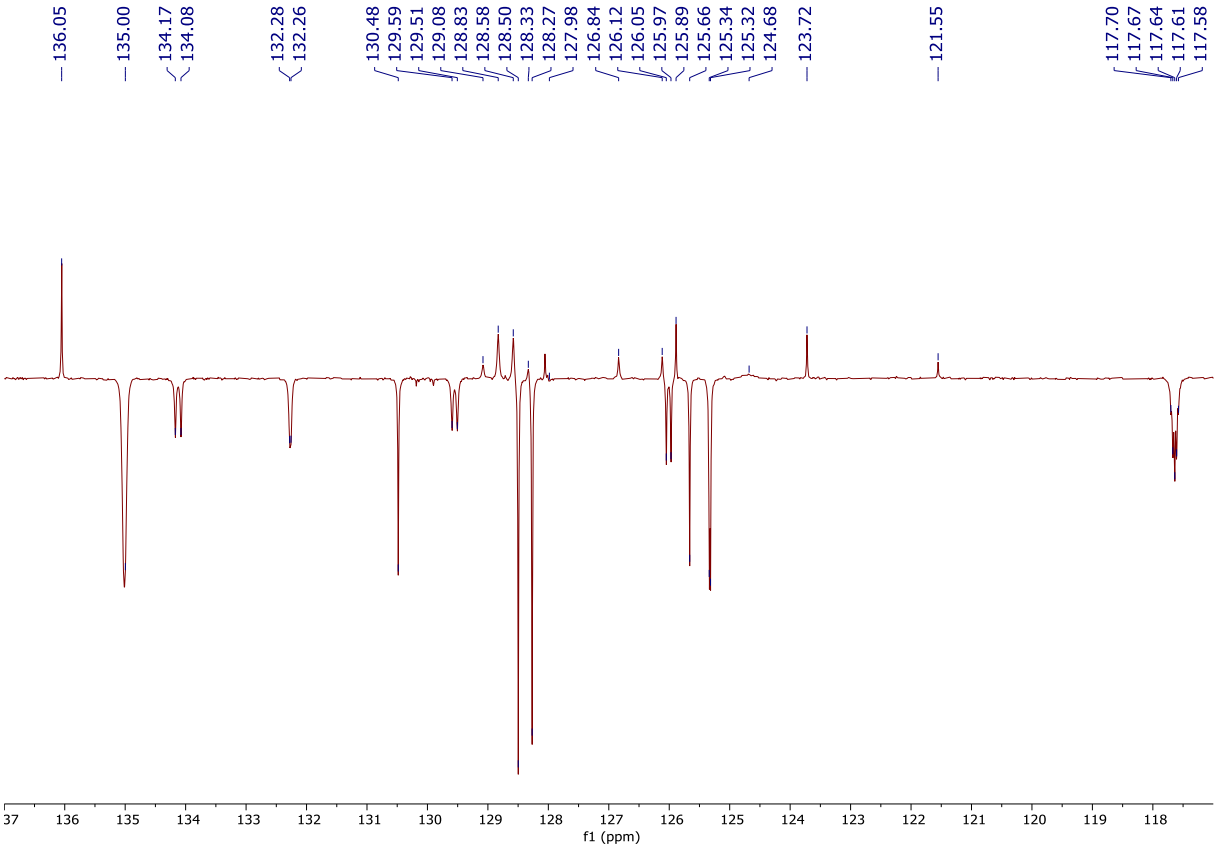


Figure S85. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **3** ($CDCl_3$, 125.8 MHz, 298 K); aromatic area.

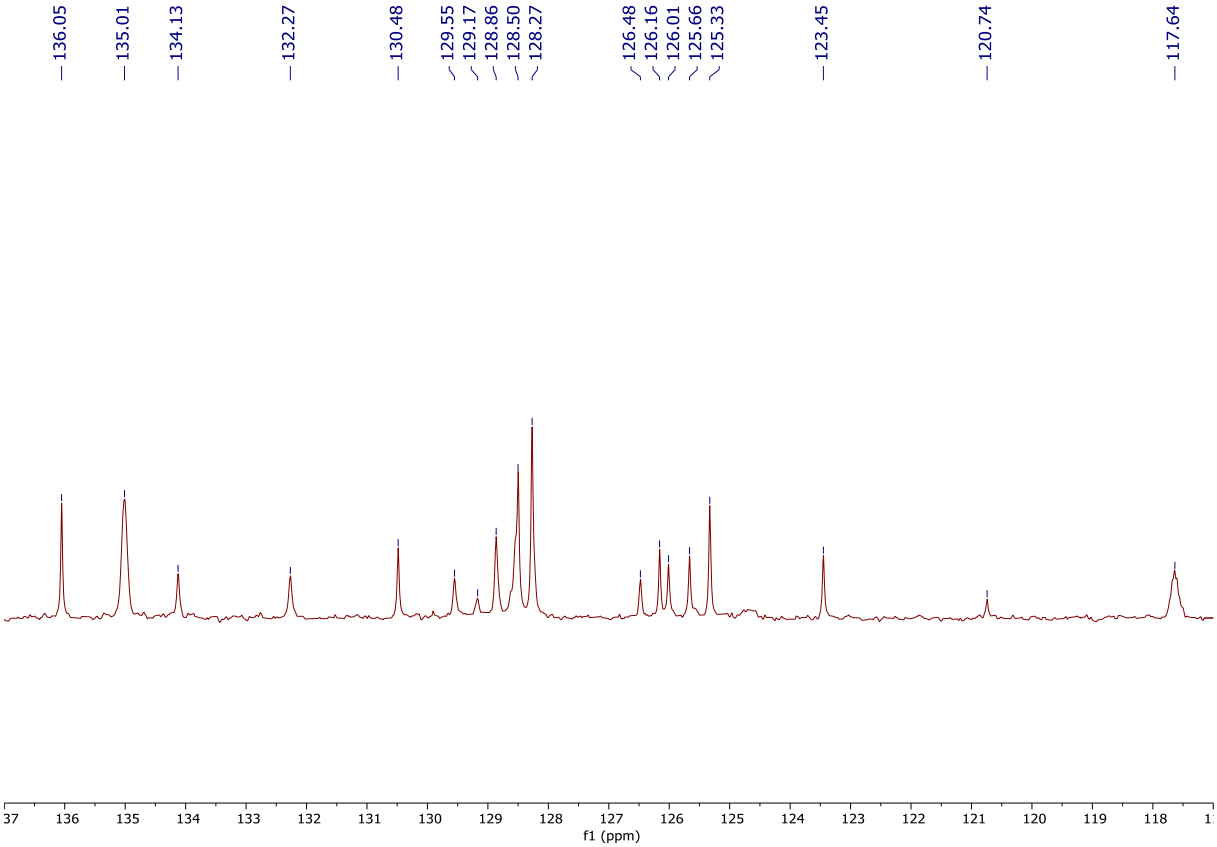


Figure S86. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area.

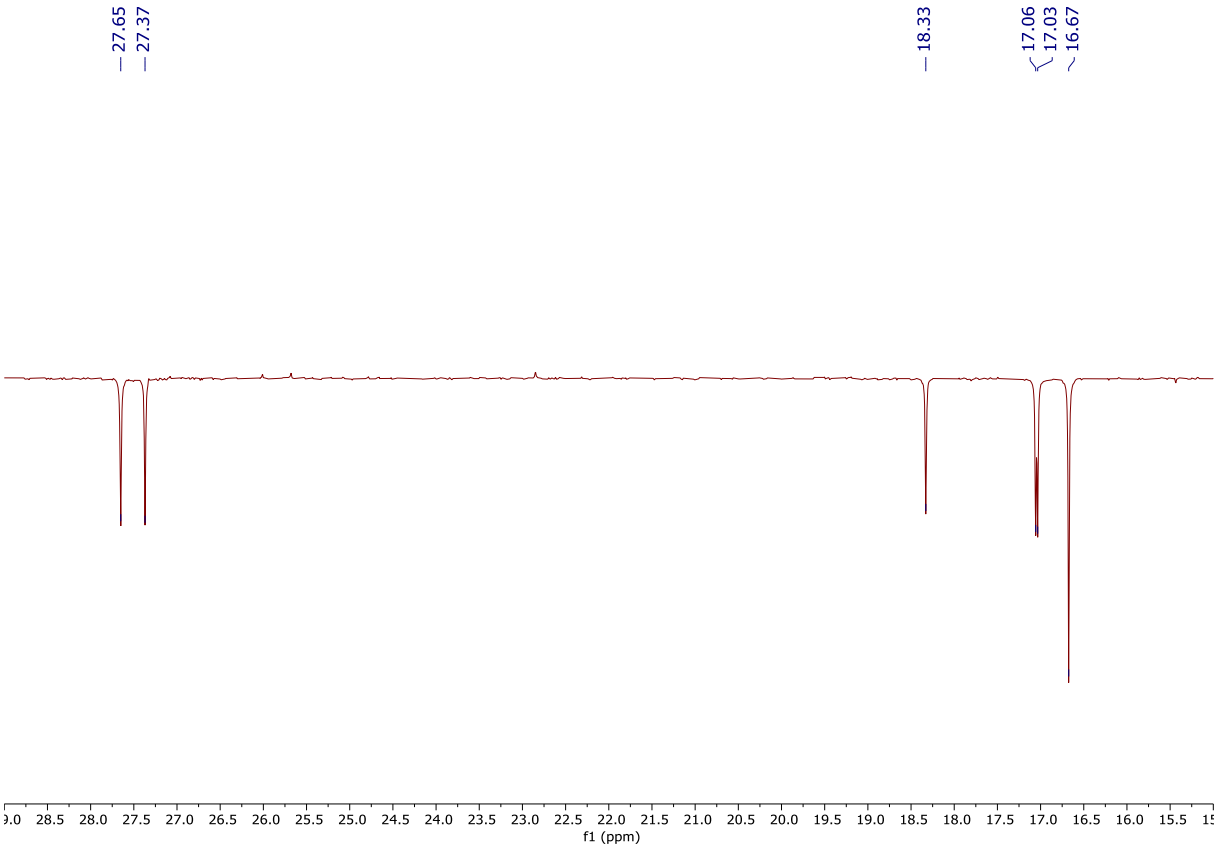


Figure S87. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **3** ($CDCl_3$, 125.8 MHz, 298 K); aliphatic area.

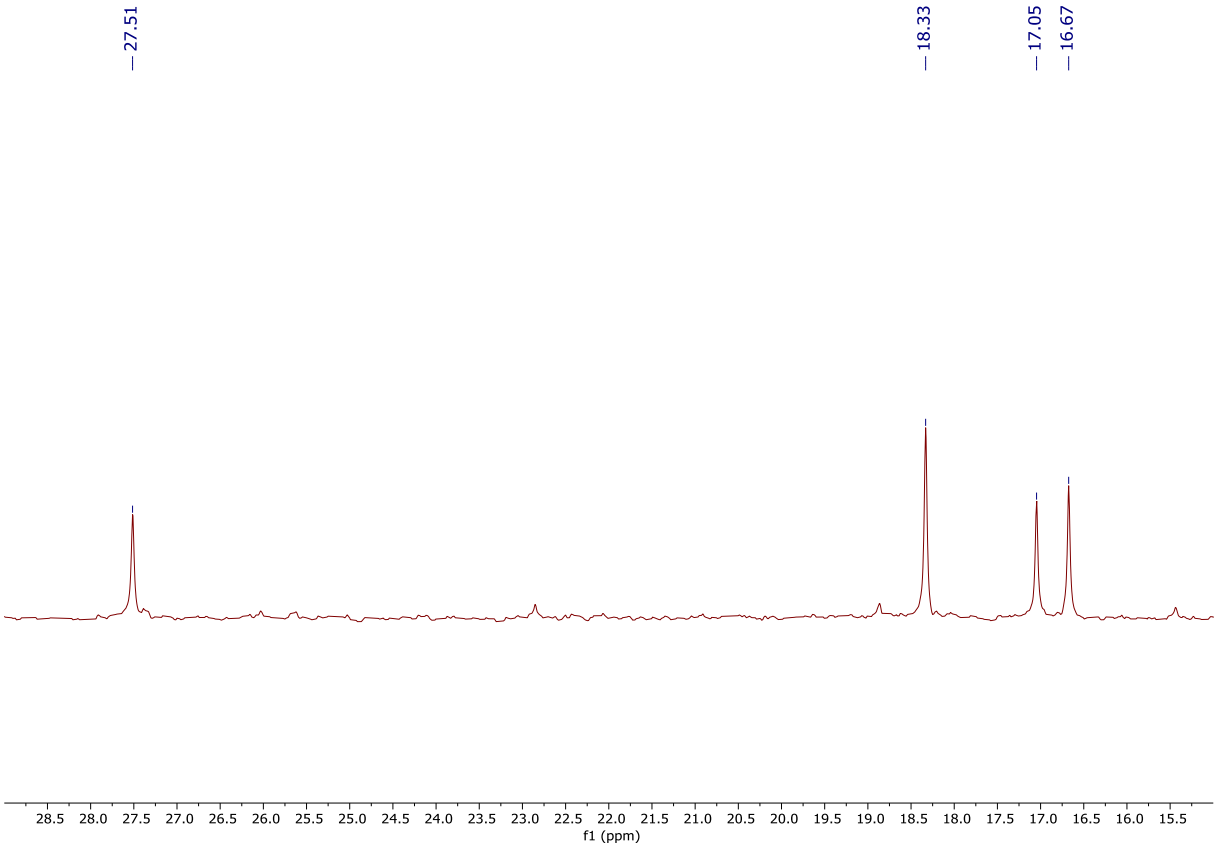


Figure S88. $^{13}C\{^{1}H\ ;\ ^{31}P\}$ NMR spectrum of compound **3** ($CDCl_3$, 100.6 MHz, 298 K); aliphatic area.

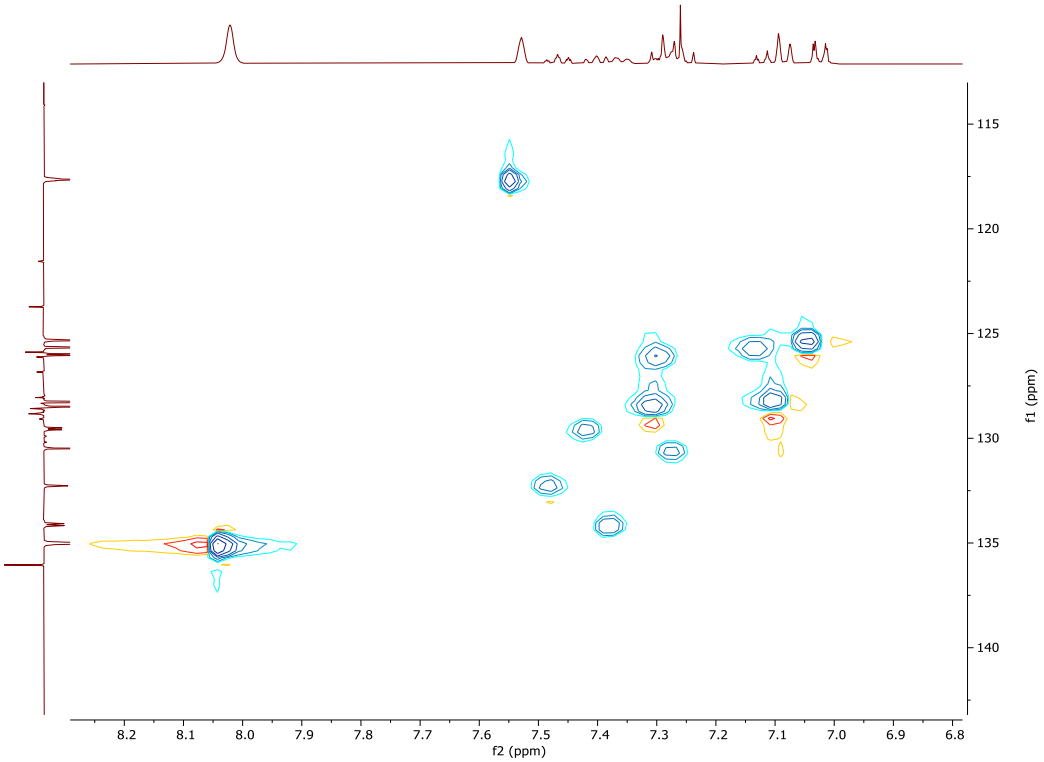


Figure S89. HSQC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **3** ($CDCl_3$, 400.2 / 125.8 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area.

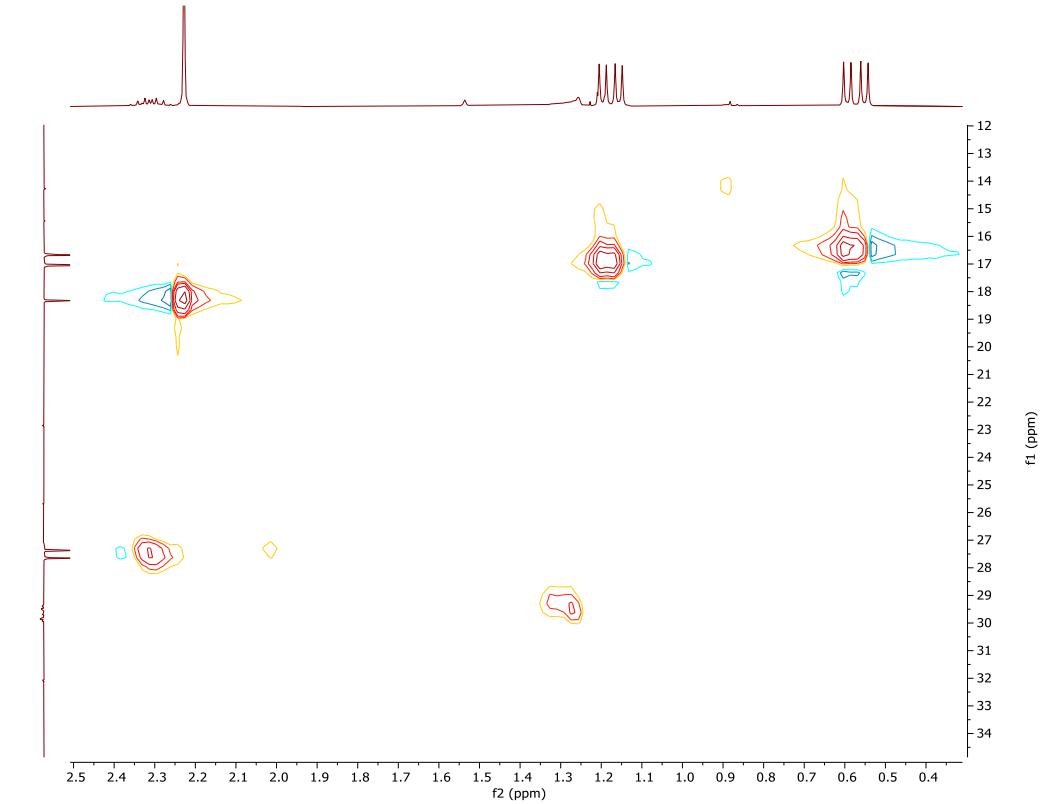


Figure S90. HSQC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **3** ($CDCl_3$, 400.2 / 125.8 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aliphatic area.

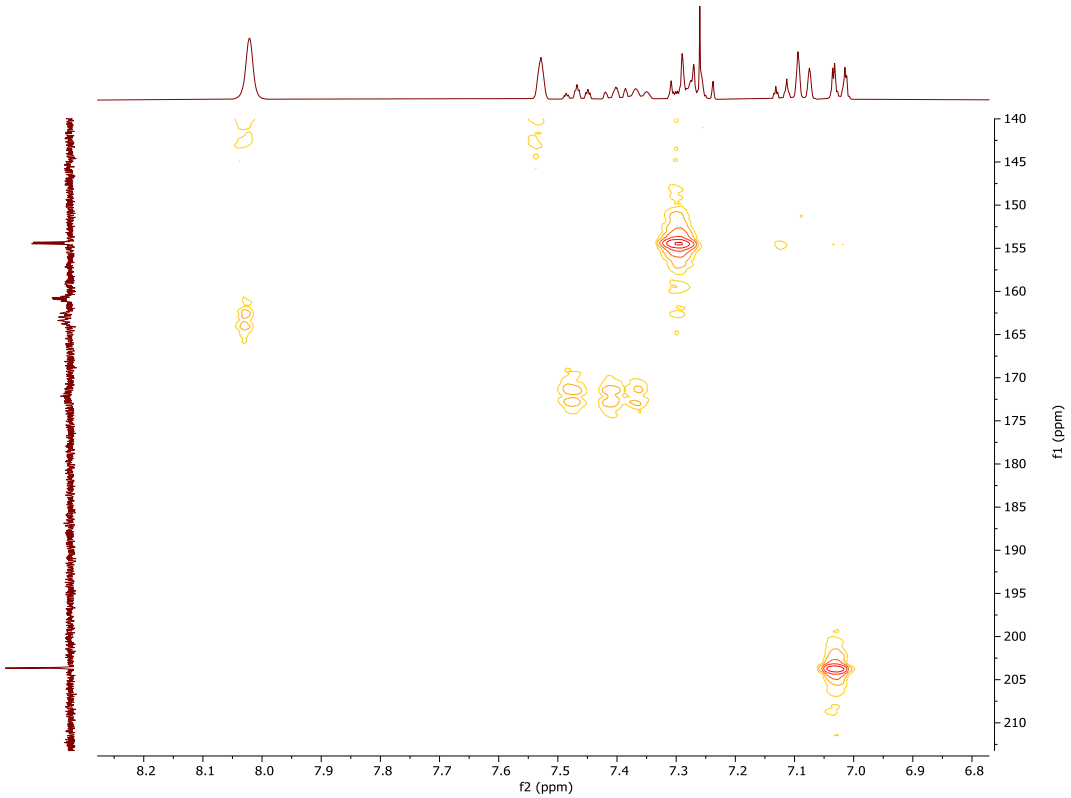


Figure S91. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **3** ($CDCl_3$, 400.2 / 125.8 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area, quaternary carbons.

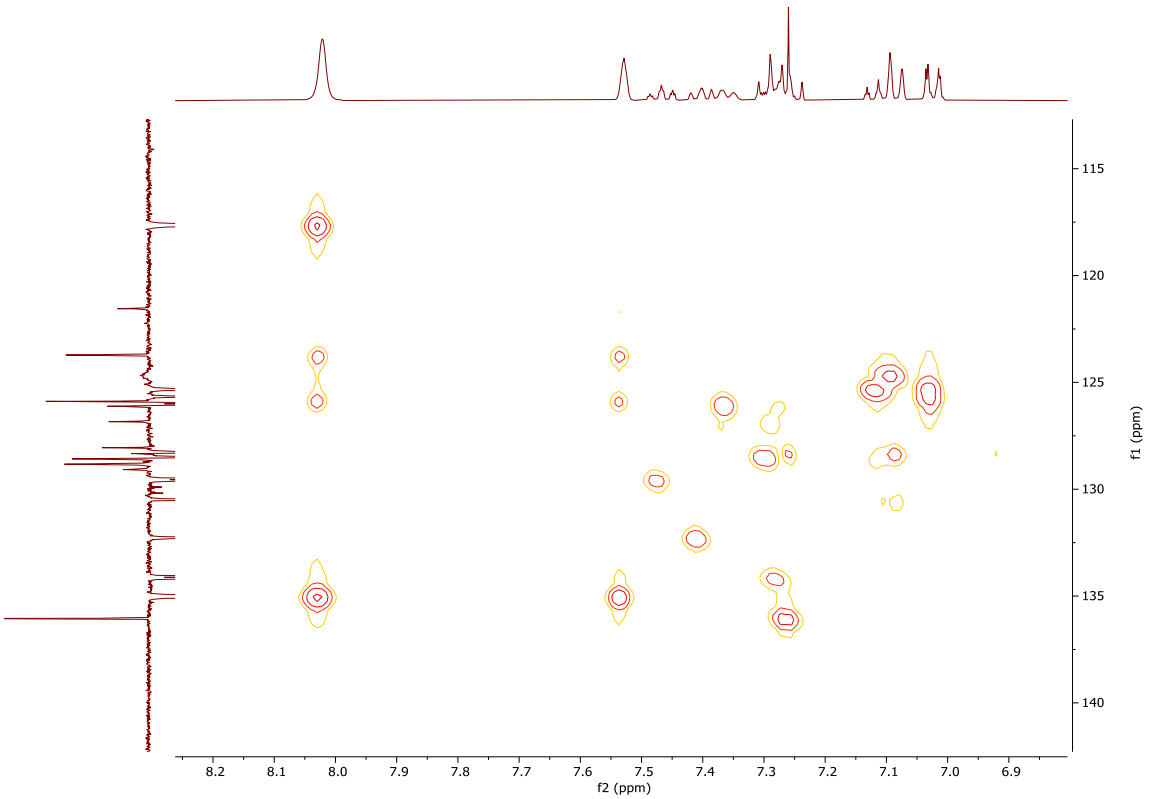


Figure S92. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **3** ($CDCl_3$, 400.2 / 125.8 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aromatic area.

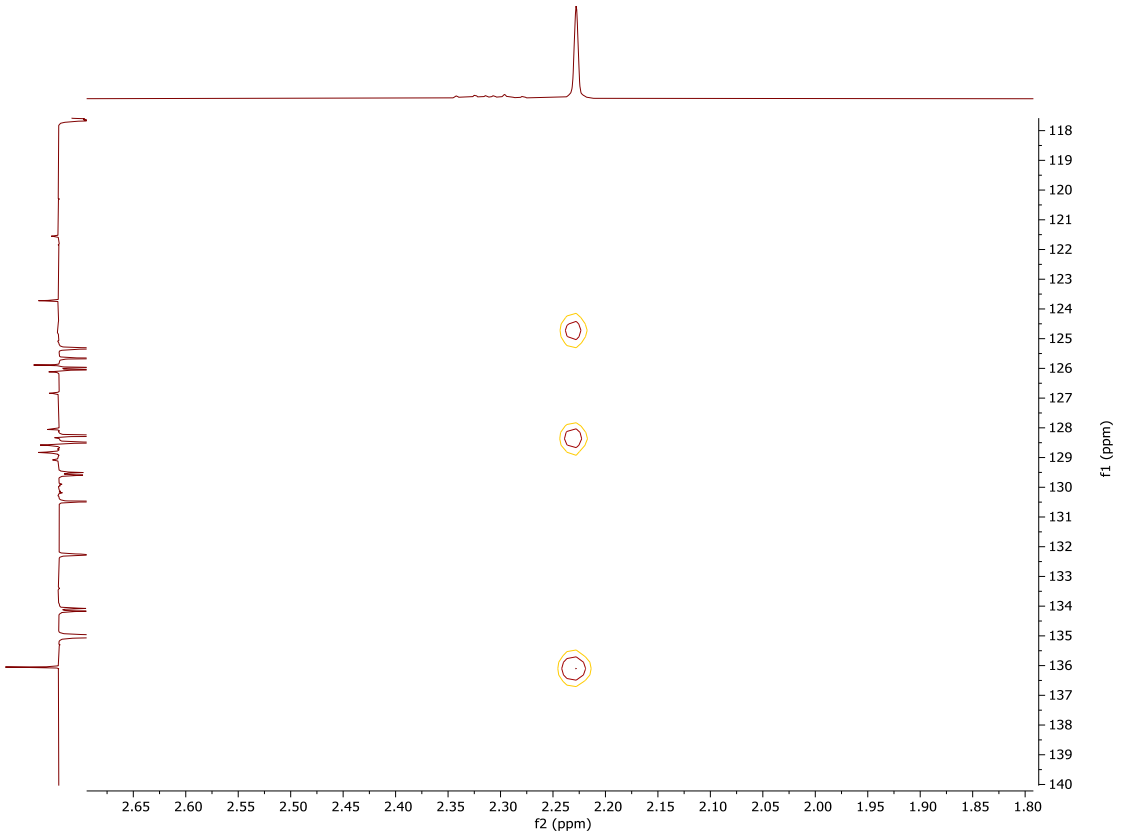


Figure S93. HMBC (^{1}H-^{13}C{^{1}H}) NMR spectrum of compound **3** ($CDCl_3$, 400.2 / 125.8 MHz, 298 K). Projection along the x-axis : ^{1}H ; projection along the y-axis : Jmod(^{13}C{^{1}H}); aliphatic area, zoom-in.

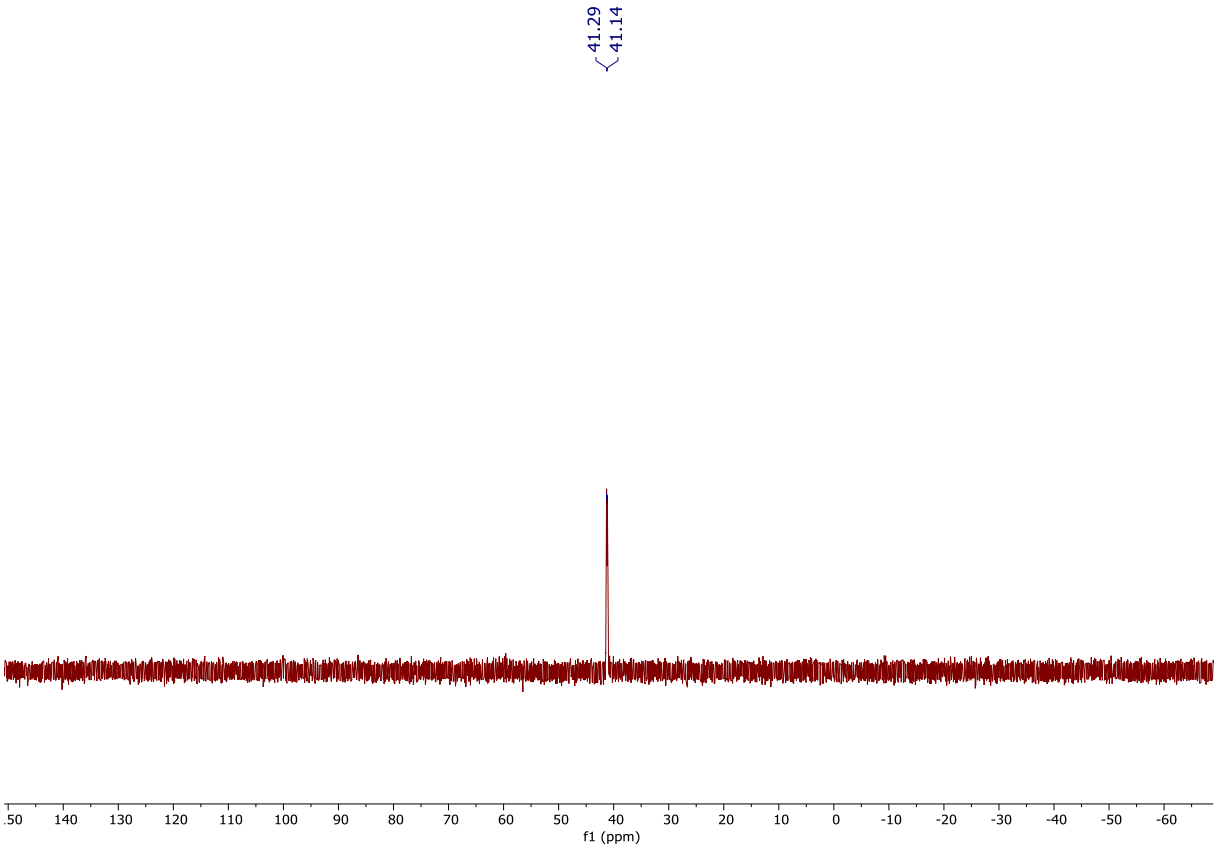


Figure S94. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** ($CDCl_3$, 202.5 MHz, 298 K).

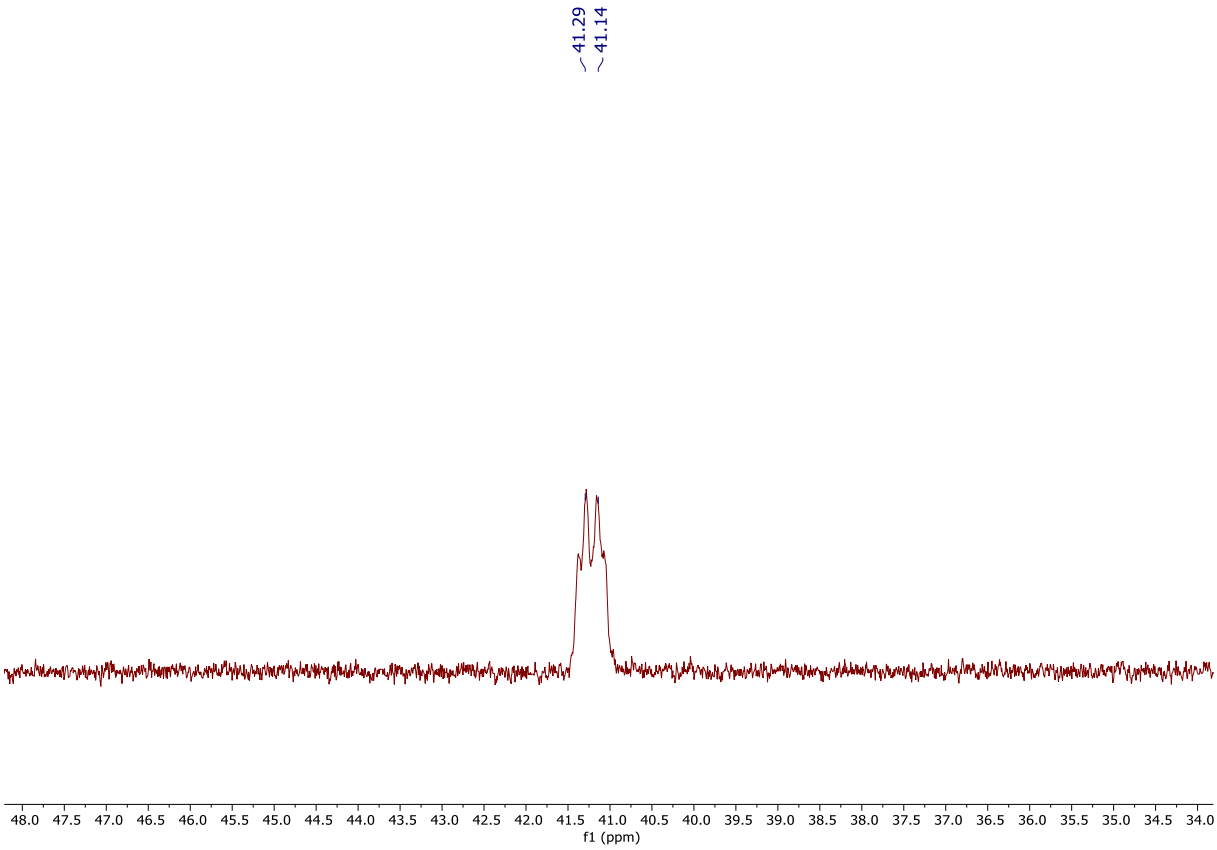


Figure S95. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** ($CDCl_3$, 202.5 MHz, 298 K); zoom-in.

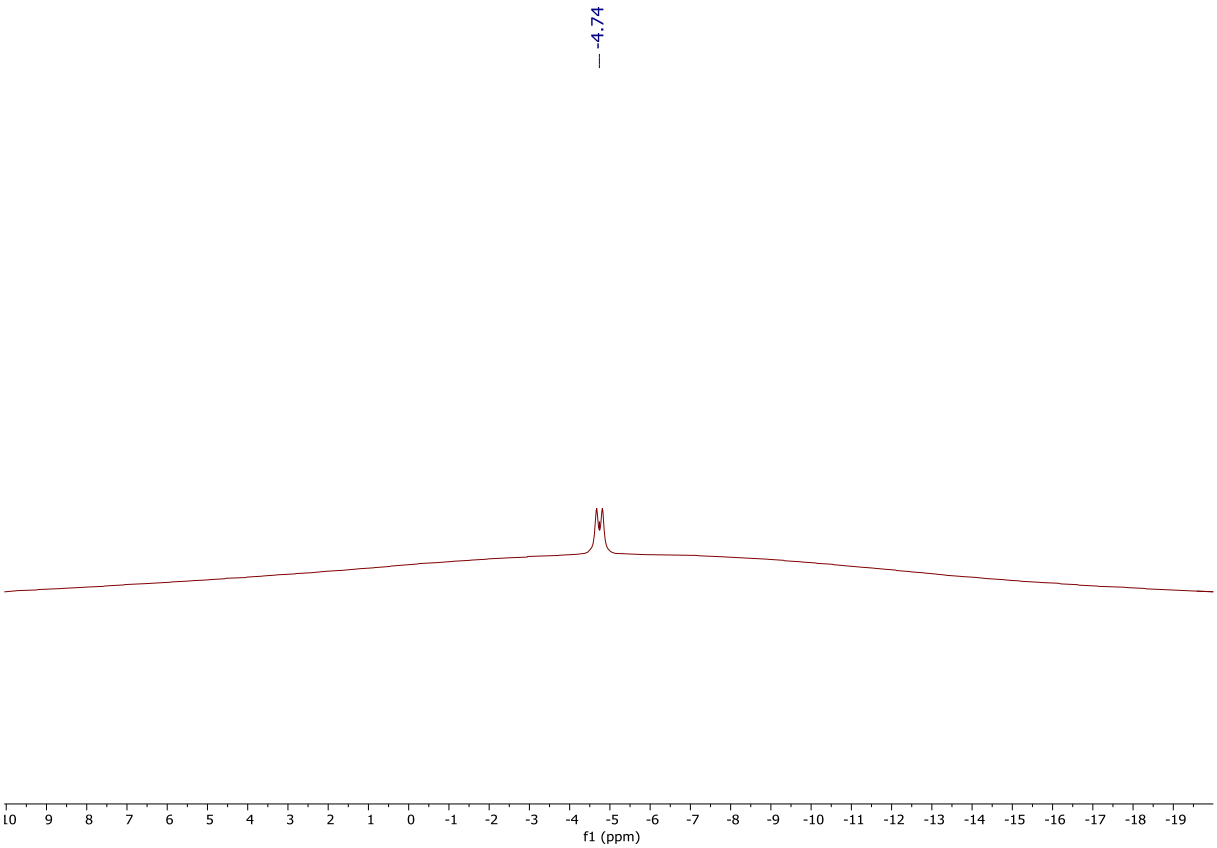


Figure S96. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3** ($CDCl_3$, 160.5 MHz, 298 K).

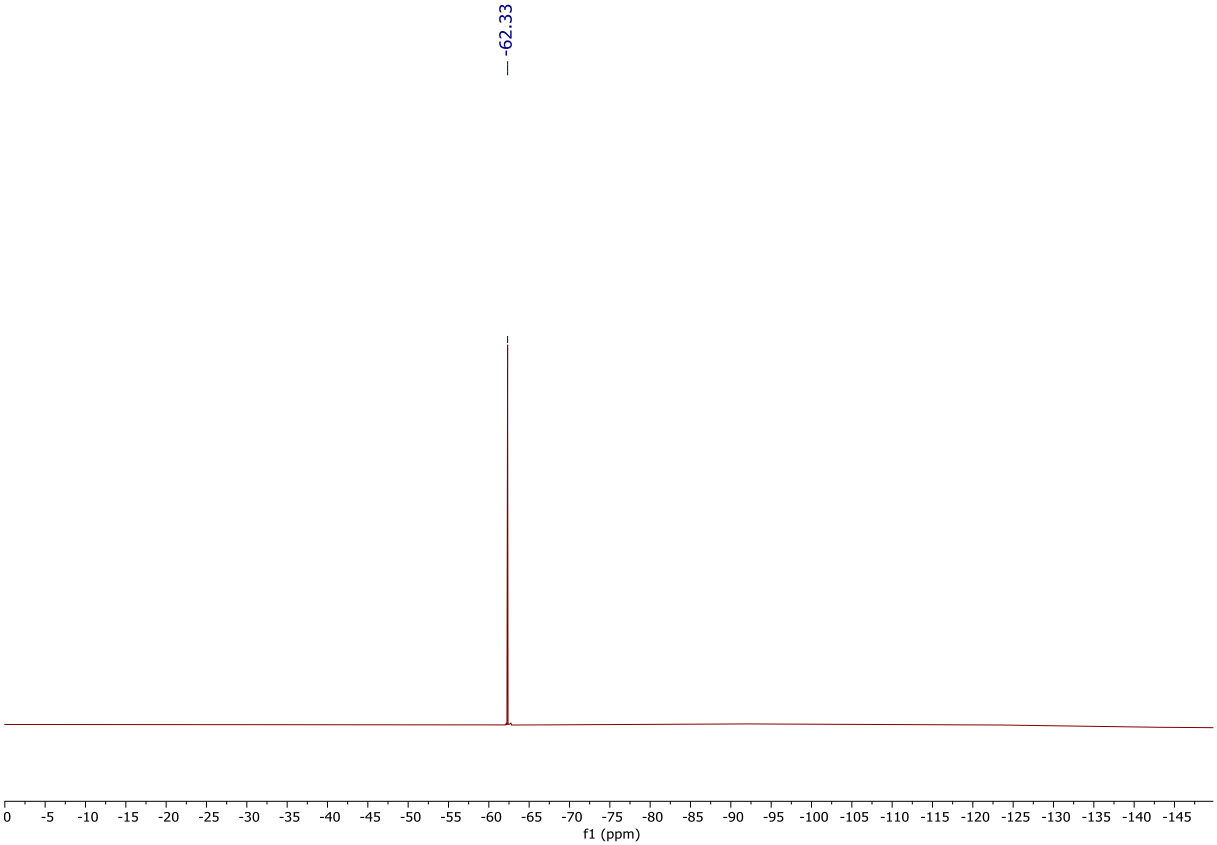
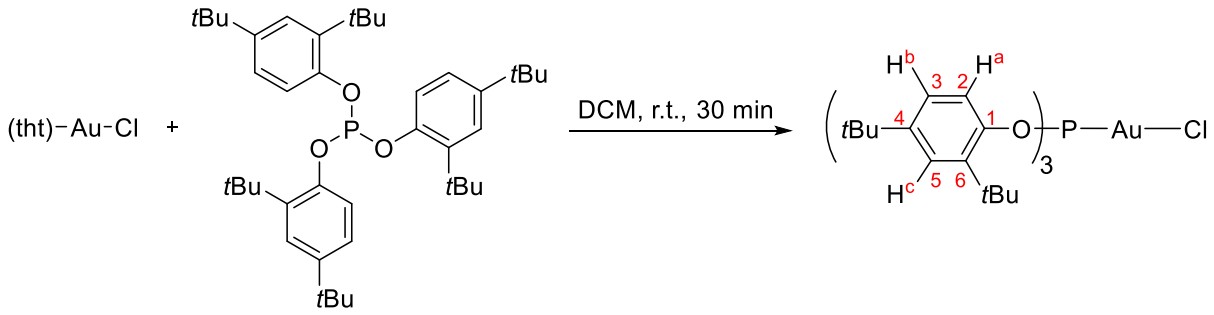


Figure S97. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3** ($CDCl_3$, 470.5 MHz, 298 K).

Synthesis of ((ArO)$_3$P)AuCl



DCM (10 mL) was added to a mixture of tris(2,4-di-*tert*-butylphenyl)phosphite (1.816 g, 2.81 mmol, 1 equiv.) and (tht)AuCl (900 mg, 2.81 mmol, 1 equiv.) leading to a white turbid suspension. Fastly the mixture became clear and colourless. The solution was stirred for 30 min at room temperature. All the volatiles were then removed under reduced pressure. The white solid was washed with 5 mL of pentane using a filtered cannula. The procedure was repeated two times and the resulting product was dried under vacuum. The reaction led to **((ArO)$_3$P)AuCl** as a white solid (2.289 g, 2.60 mmol, 93%).

^{1}H NMR ($CDCl_3$, 500.1 MHz, 298 K): δ 7.43 (3H, H_c, masked by H_a), 7.42 (dd, 3H, $^3J_{HH}$ = 8.5 Hz, $^5J_{HH}$ = 1.5 Hz, H_a), 7.14 (dd, 3H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, H_b), 1.45 (s, 27H, CH_{3tBu}), 1.30 (s, 27H, CH_{3tBu}).

^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz, 298 K): δ 148.2 (s, C_4), 147.4 (d, $^3J_{PC}$ = 5.9 Hz, C_6), 139.2 (d, $^2J_{PC}$ = 6.9 Hz, C_1), 125.5 (s, C_5), 124.3 (s, C_3), 119.3 (d, $^3J_{PC}$ = 8.9 Hz, C_2), 35.2 (s, C_{tBu}), 34.8 (s, C_{tBu}), 31.5 (s, CH_{3tBu}), 30.7 (s, CH_{3tBu}).

^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz, 298 K) : δ 100.7 (s).

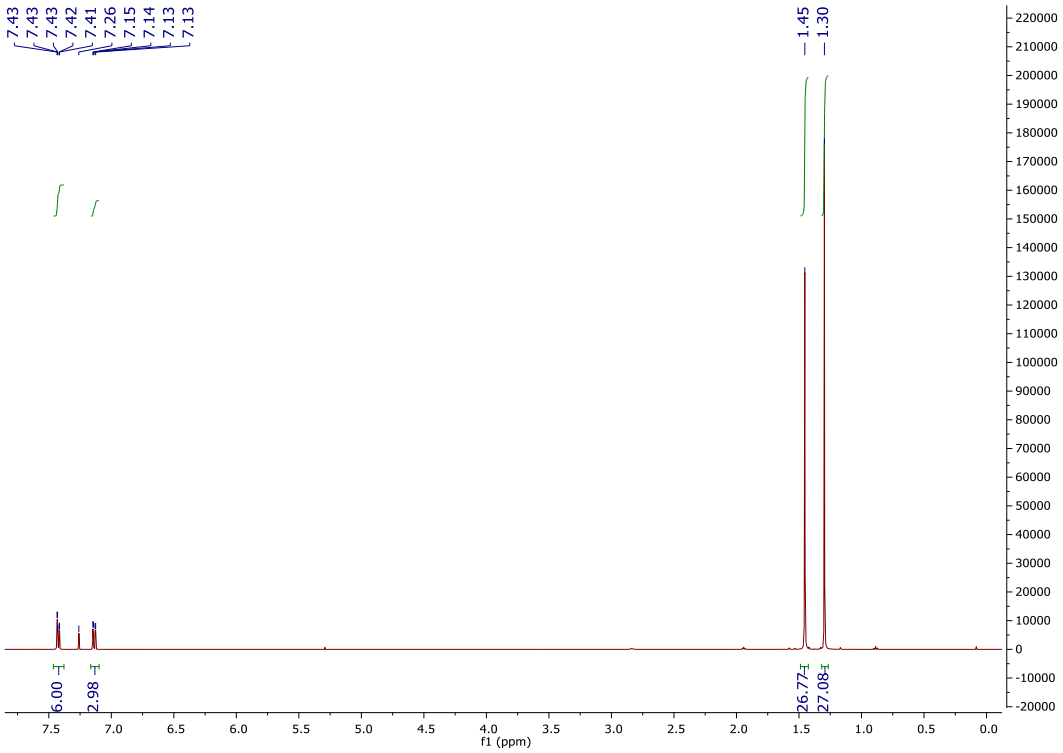


Figure S98. ^{1}H NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 500.1 MHz, 298 K).

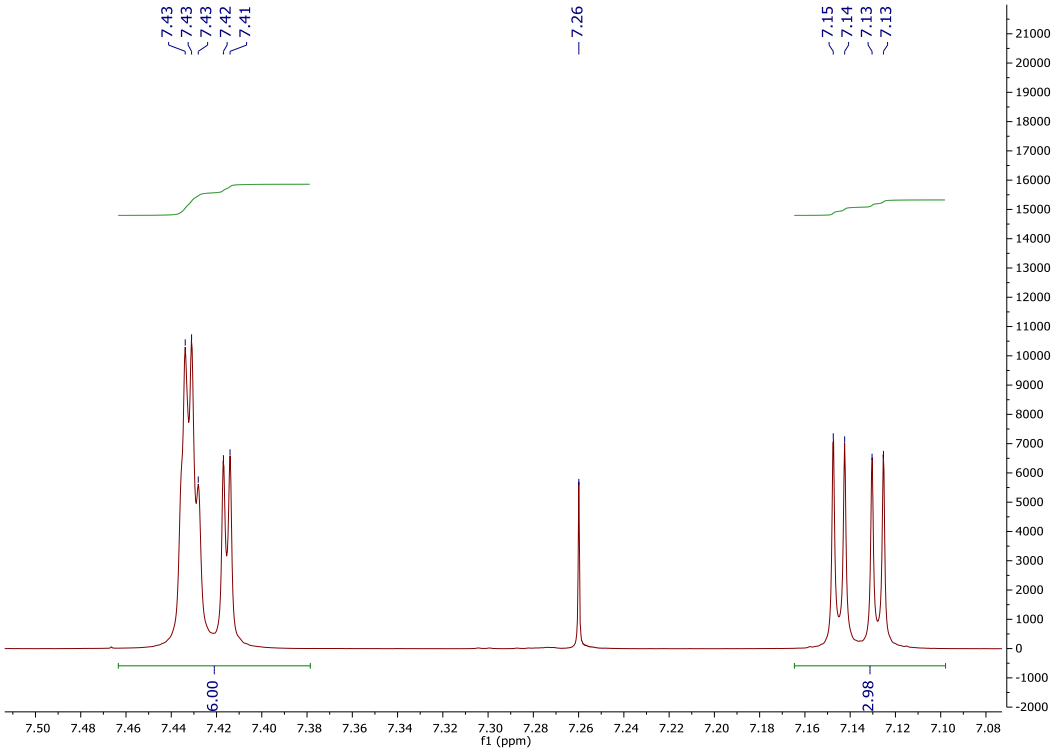


Figure S99. ^{1}H NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 500.1 MHz, 298 K) ; aromatic region.

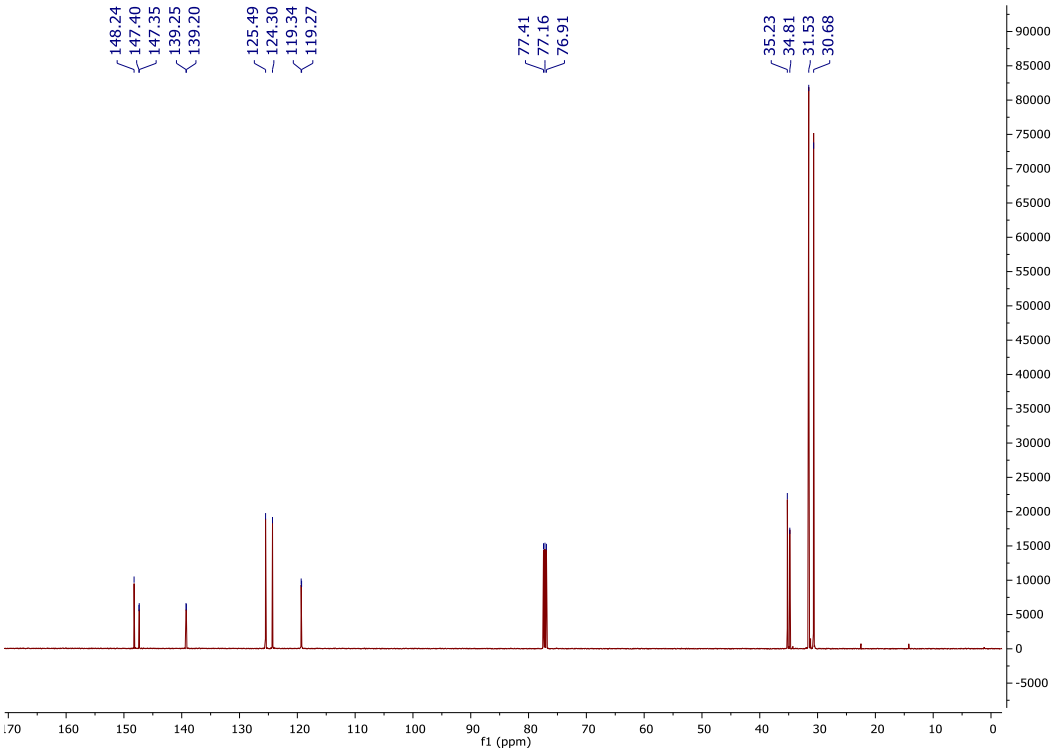


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 125.8 MHz, 298 K).

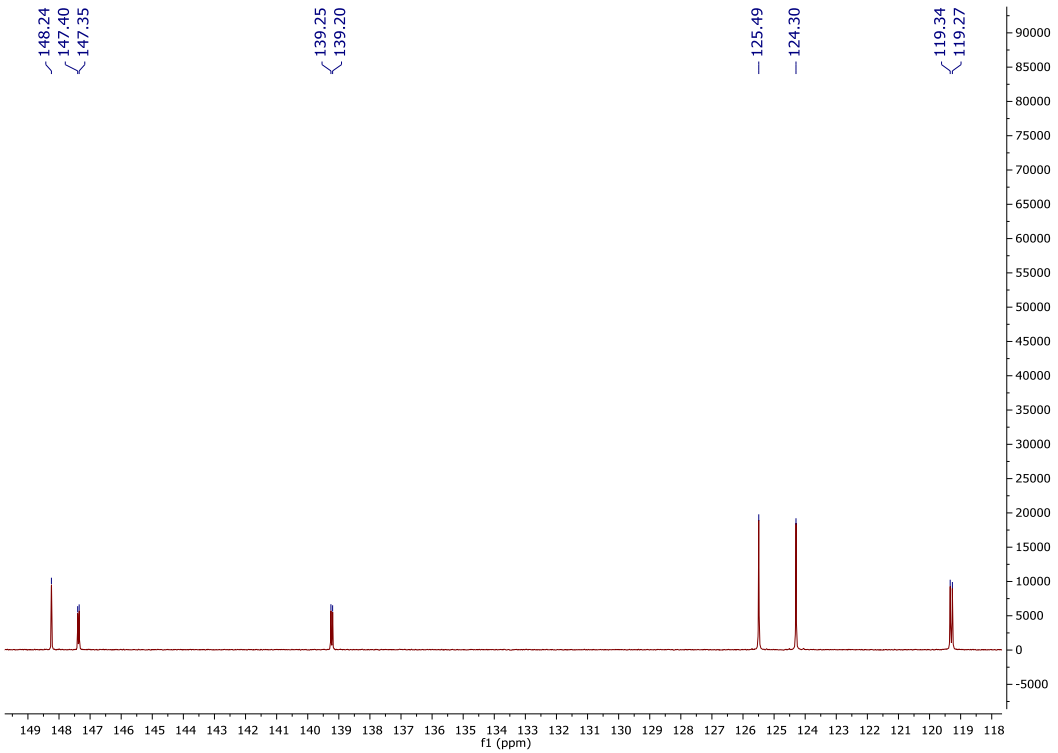


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 125.8 MHz, 298 K) ; aromatic region.

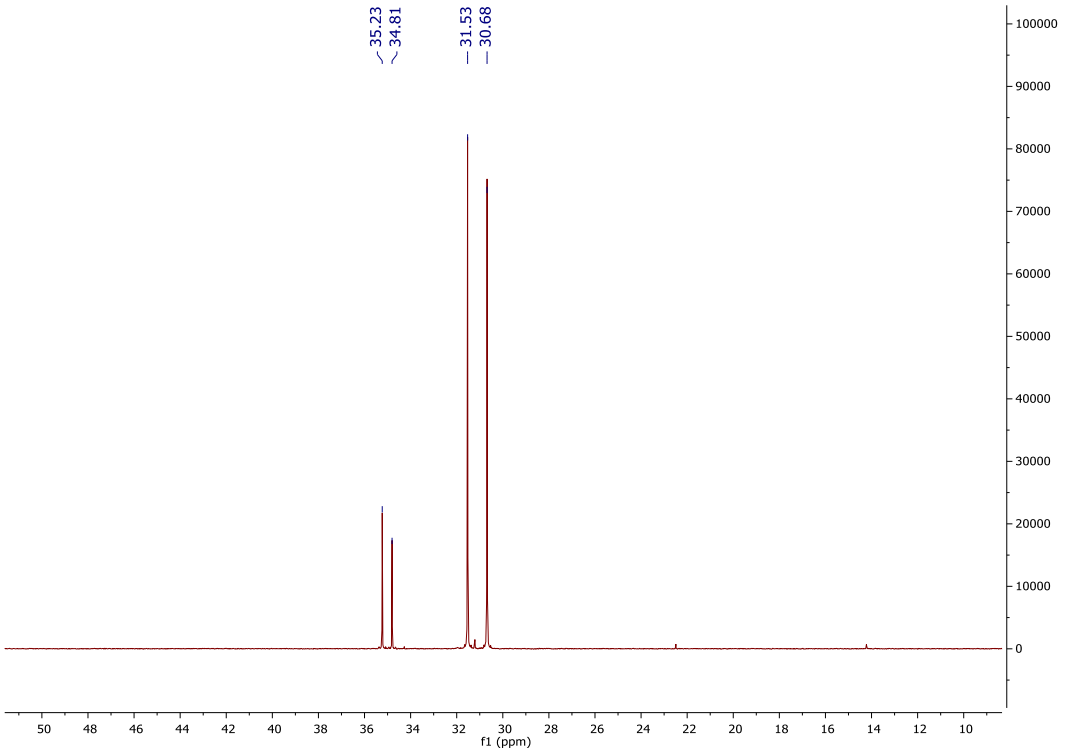


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 125.8 MHz, 298 K) ; aliphatic region.

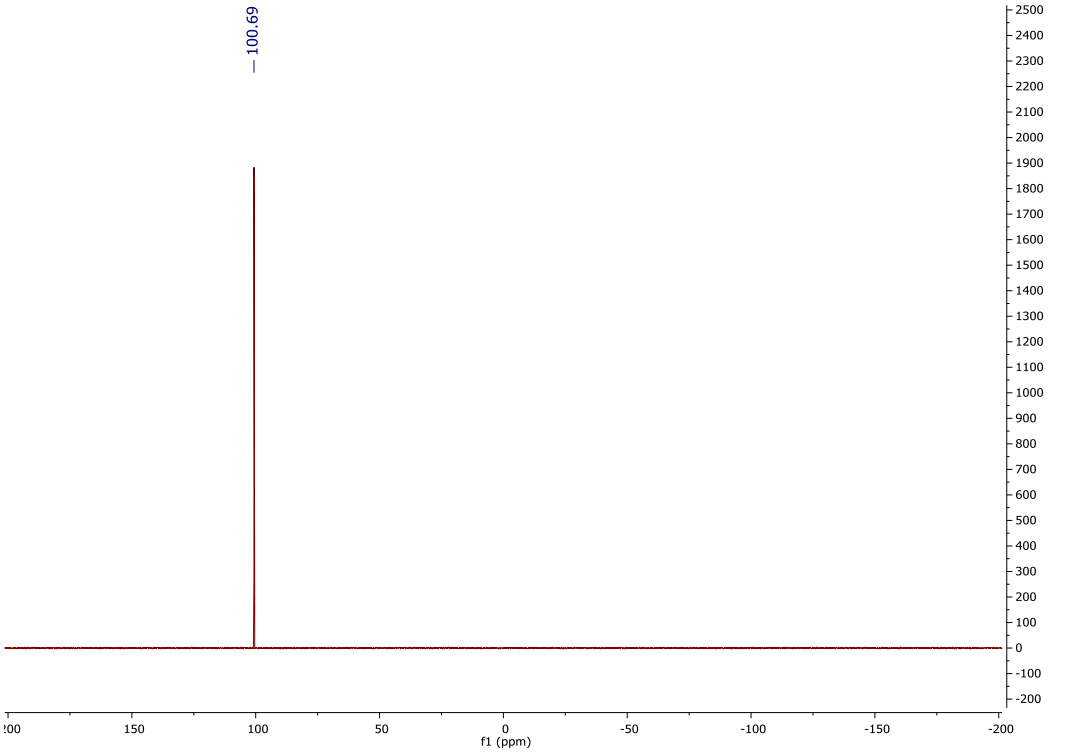
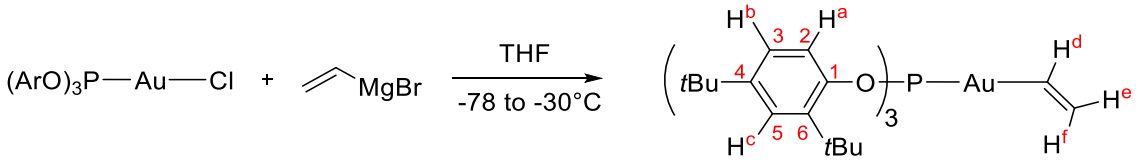


Figure S103. $^{31}P\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)AuCl** ($CDCl_3$, 202.5 MHz, 298 K).

Synthesis of $((ArO)_3P)Au(CH=CH_2)$



To a solution of **$((ArO)_3P)AuCl$** (300 mg, 0.34 mmol, 1 equiv.) in THF (20 mL) at –78°C was added dropwise a solution of vinylmagnesium bromide in THF (0.37 mL, 0.90 M, 1 equiv.). The mixture was allowed to reach –30°C over 1h30 and stirred an additional 1h30 at the same temperature before aqueous quenching using a saturated KH_2PO_4 solution (20 mL). The mixture was warmed-up to room temperature prior to the addition of Et_2O (40 mL) and water (20 mL). After two extractions with Et_2O (2x40 mL), the organic layer was dried on Na_2SO_4, filtered, concentrated and filtered in order to remove the deep purple degradation product. All volatiles are removed and the residue was dried overnight under vacuum using a P_2O_5 trap. Since the desired compound is poorly stable in solution, no further purification was performed. **$((ArO)_3P)Au(CH=CH_2)$** *was obtained as a 9/1 mixture with phosphite* (235 mg, 0.28 mmol of **$((ArO)_3P)Au(CH=CH_2)$**, 81%).

^{1}H NMR of **$((ArO)_3P)Au(CH=CH_2)$*** (C_6D_6, 300.1 MHz, 298 K) : δ 7.97 (dd, 3H, $^3J_{HH}$ = 8.5 Hz, $^5J_{HH}$ =1.4 Hz, H_a), 7.61 (ddd, 1H, $^3J_{HH}$ = 20.5 and 13.9 Hz, $^3J_{PH}$ = 11.4 Hz, H_d), 7.51 (m, 3H, H_c), 6.96 (dd, 3H, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.4 Hz, H_b), 6.23 (ddd, 1H, $^3J_{HH}$ = 13.9 Hz, $^2J_{HH}$ = 4.9 Hz, $^4J_{PH}$ = 29.4 Hz, H_e), 5.76 (ddd, 1H, $^3J_{HH}$ = 20.5 Hz, $^2J_{HH}$ = 4.9 Hz, $^4J_{PH}$ = 13.5 Hz, H_f), 1.50 (s, 27H, CH_{3tBu}), 1.16 (s, 27H, CH_{3tBu}).

^{31}P{^{1}H} NMR of **$((ArO)_3P)Au(CH=CH_2)$*** (C_6D_6, 121.5 MHz, 298 K) : δ 149.8 (s, 89% relative integration, $((ArO)_3P)Au(CH=CH_2)$), 108.4 (s, 11% relative integration, phosphite).

spectroscopic data of the 9/1 mixture* **$((ArO)_3P)Au(CH=CH_2)$*/phosphite*

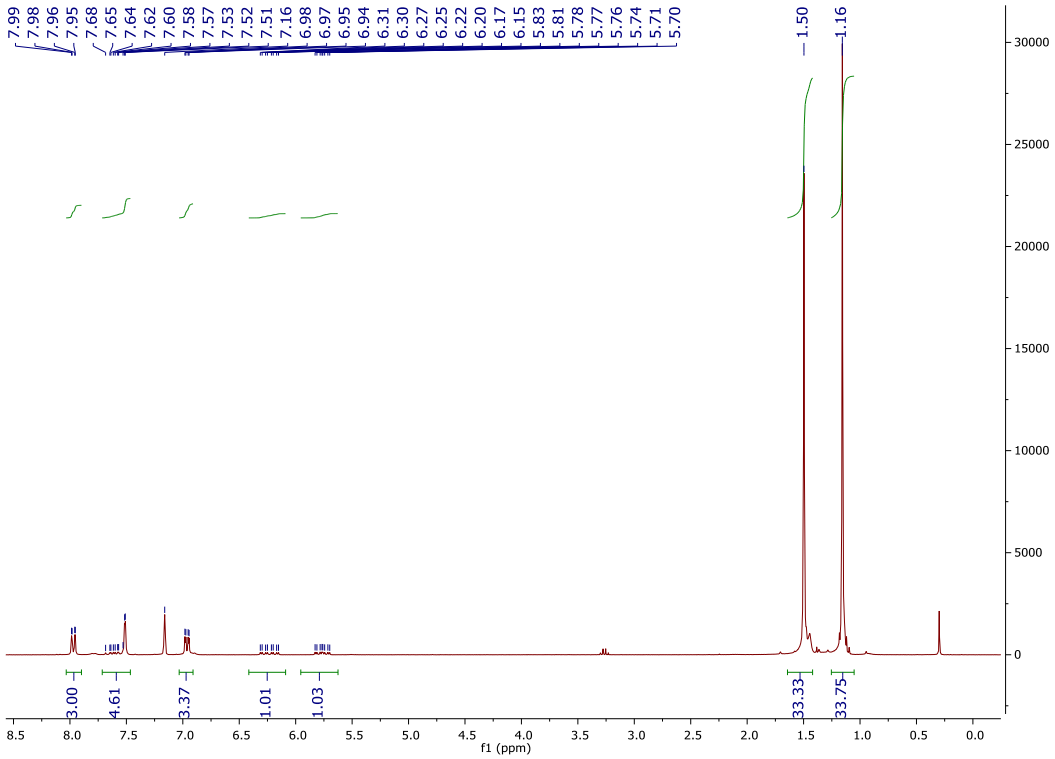


Figure S104. ^{1}H NMR spectrum of **((ArO)$_3$P)Au(CH=CH$_2$)*** (C_6D_6, 300.1 MHz, 298 K).

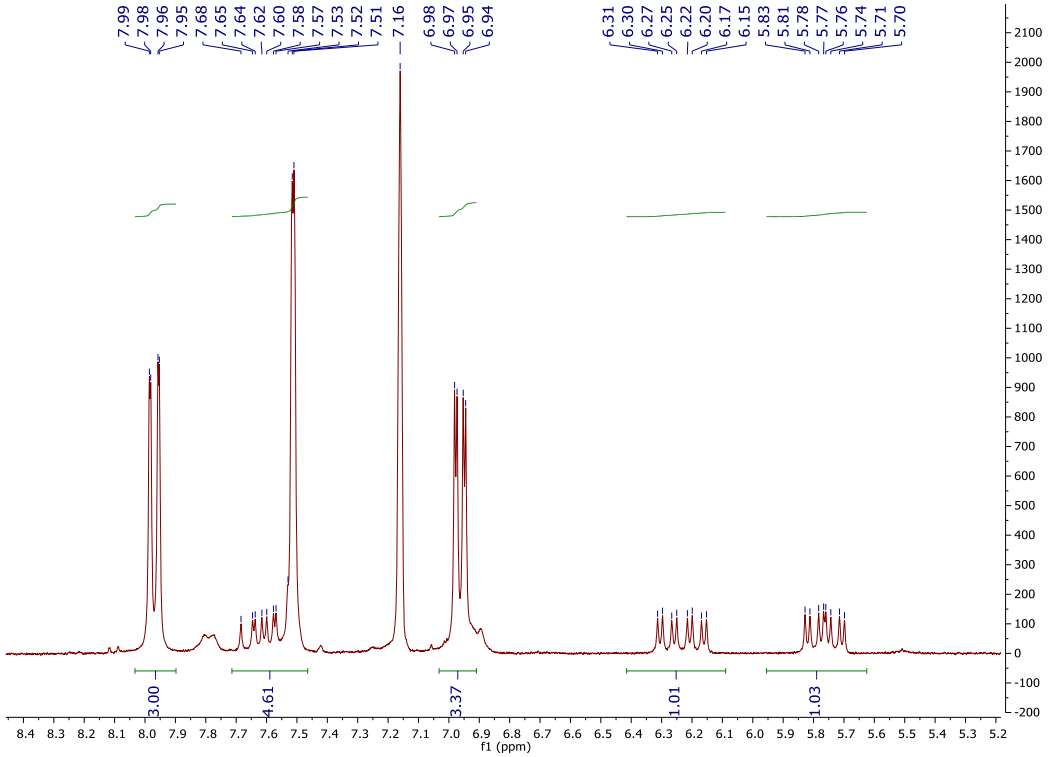


Figure S105. ^{1}H NMR spectrum of **((ArO)$_3$P)Au(CH=CH$_2$)*** (C_6D_6, 300.1 MHz, 298 K) ; aromatic and vinylic regions.

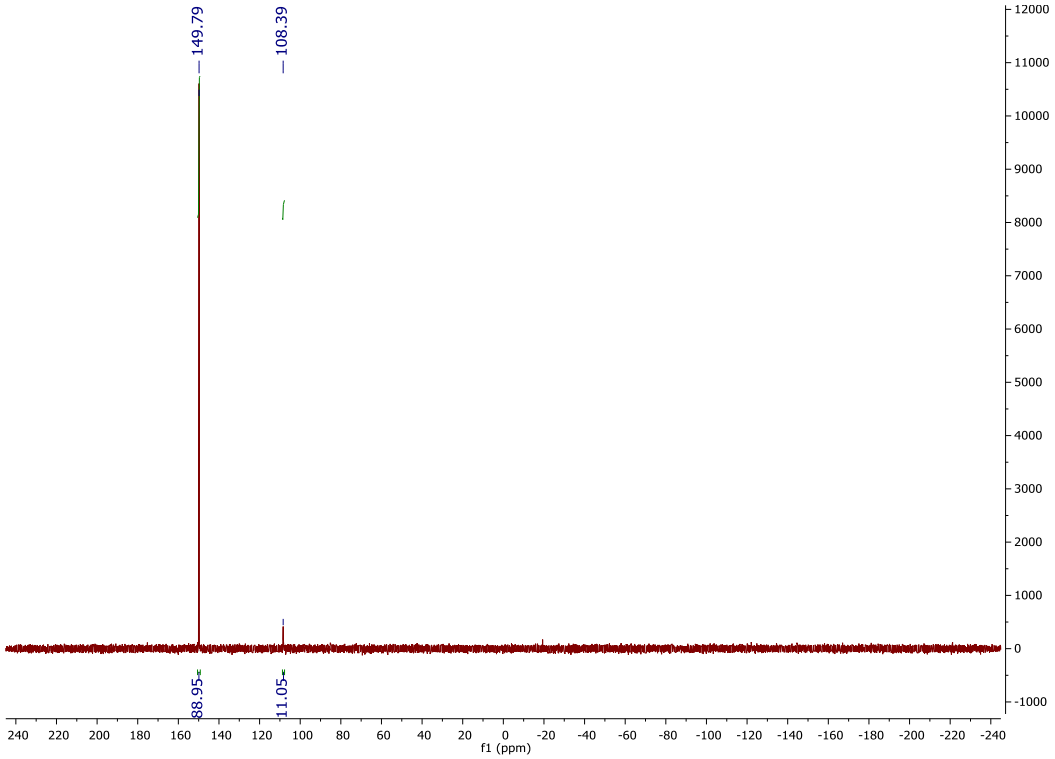


Figure S106. $^{31}P\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)Au(CH=CH$_2$)*** (C_6D_6, 121.5 MHz, 298 K).

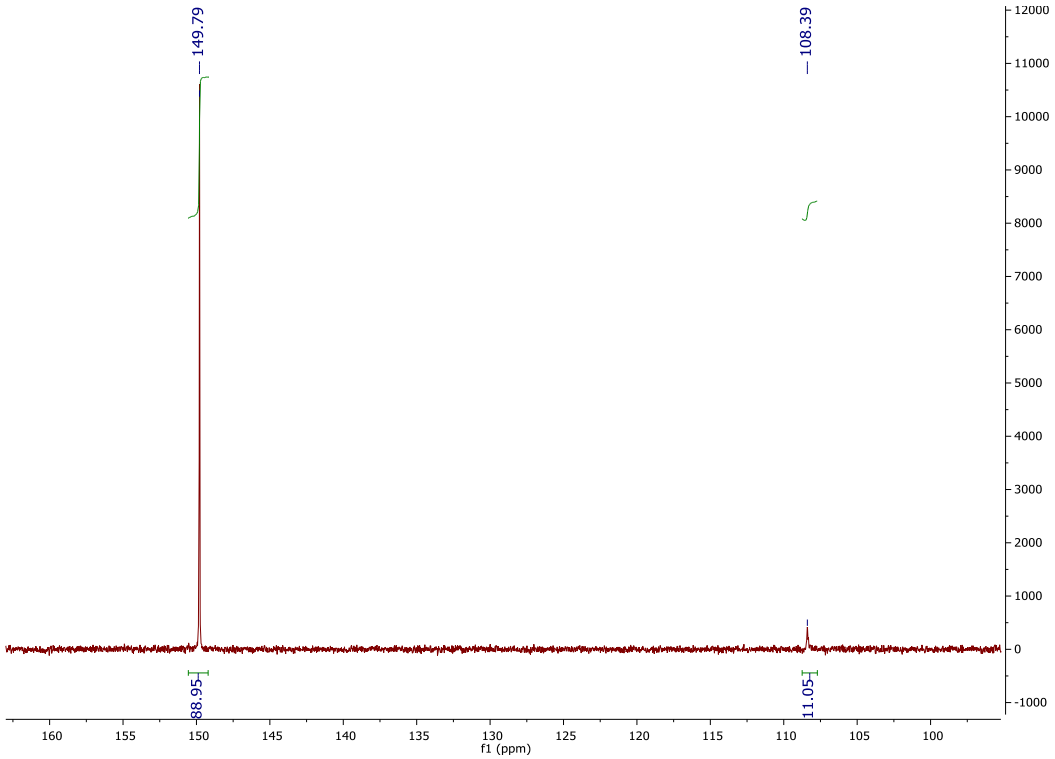
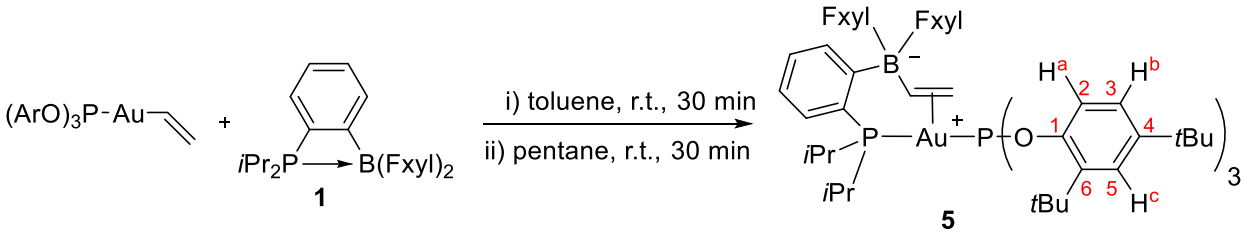


Figure S107. $^{31}P\{^{1}H\}$ NMR spectrum of **((ArO)$_3$P)Au(CH=CH$_2$)*** (C_6D_6, 121.5 MHz, 298 K) ; zoom in.

Synthesis of 5



To a solution of **1** (172 mg, 0.27 mmol, 1 equiv.) in toluene (4 mL) at room temperature was added dropwise a solution of **((ArO)$_3$P)Au(CH=CH$_2$)** (235 mg, 0.27 mmol, 1 equiv.) in toluene (4 mL). After 30 min, the solution became yellow. Toluene was removed under vacuum and residual traces were removed by adding 5 mL of pentane, stirring and co-evaporation of volatiles. Pentane (10 mL) was added to the resulting pale-yellow powder and the mixture was stirred at room temperature for 30 minutes. Next the solution was placed overnight at –20°C for precipitation. The yellow solution was removed by filtration and the solid was washed with cold pentane (2x5 mL). **5** was isolated as a white solid (149 mg, 37 %). Crystals suitable for X-ray diffraction analysis were obtained by DCM/heptane layering at –20°C over 1 week.

NB : The yield is low despite a clean reaction. It is due to the purification conditions. Some of the compound is lost because it is slightly soluble in pentane.

^{1}H NMR ($CDCl_3$, 400.1 MHz, 298 K) : δ 7.54 (br. s, 2H, H$_{p\text{-Fxyl}}$), 7.53-7.45 (br. m, 5H, 1H$_{Ar}$ and 4H$_{o\text{-Fxyl}}$), 7.37 (dd, 3H, $^{4}J_{HH}$ = 2.5 Hz, $^{5}J_{HH}$ = 1.0 Hz, H$_c$), 7.18 (dd, 3H, $^{3}J_{HH}$ = 8.5 Hz, $^{5}J_{HH}$ = 1.0 Hz, H$_a$), 7.09 (br. m, 2H, H$_{Ar}$), 6.97 (dd, 3H, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 2.5 Hz, H$_b$), 6.92 (br. s, 1H, H$_{Ar}$), 5.40 (m, 1H, CH$_{vinyl}$), 3.85 (br. s, 1H, CH$_{2vinyl}$), 3.71 (br. d, 1H, $^{3}J_{HH}$ = 18.4 Hz, CH$_{2vinyl}$), 2.33 (m, 2H, CH$_{i\text{Pr}}$), 1.35 (s, 27H, CH$_{3t\text{Bu}}$), 1.25 (s, 27H, CH$_{3t\text{Bu}}$), 0.90 (dd, 6H, $^{3}J_{PH}$ = 15.5 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH$_{3i\text{Pr}}$), 0.80 (dd, 6H, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH$_{3i\text{Pr}}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K) : δ 167.6 (br.s, B-C$_{ipso}$), 162.0 (br.s, B-C$_{ipso}$), 147.8 (s, C$_4$), 147.7 (d, $^{3}J_{PC}$ = 6.5 Hz, C$_6$), 140.5 (d, J_{PC} = 14.7 Hz, CH$_{Ar}$), 138.9 (d, $^{2}J_{PC}$ = 6.0 Hz, C$_1$), 134.8 (s, CH$_{o\text{-Fxyl}}$), 131.3* (s, CH$_{Ar}$ and CH$_{vinyl}$), 129.6 (s, CH$_{Ar}$), 128.9 (q, $^{2}J_{FC}$ = 31.7 Hz, C$_{ipso\text{-CF3}}$), 127.1 (dd, $^{1}J_{PC}$ = 41.9 Hz, $^{3}J_{PC}$ = 10.4 Hz, P-C$_{ipso}$), 124.5 (q, $^{1}J_{CF}$ = 272.7 Hz, C$_{CF3}$), 125.4 (s, C$_5$), 124.7 (d, $^{3}J_{PC}$ = 6.5 Hz, CH$_{Ar}$), 123.9 (s, C$_3$), 118.6 (d, $^{3}J_{PC}$ = 10 Hz, C$_2$), 117.9 (m, CH$_{p\text{-Fxyl}}$), 85.2 (d, J_{PC} = 7.4 Hz, CH$_{2\ vinyl}$), 35.15 (s, C$_{t\text{Bu}}$), 34.71 (s, C$_{t\text{Bu}}$), 31.49 (s, CH$_{3t\text{Bu}}$) , 30.39 (s, CH$_{3t\text{Bu}}$), 27.7 (d,$^{1}J_{PC}$ = 24.6 Hz, CH$_{i\text{Pr}}$), 19.9 (d, $^{2}J_{PC}$ = 6.9 Hz, CH$_{3i\text{Pr}}$), 19.0 (s, CH$_{3i\text{Pr}}$).

*CH$_{vinyl}$ assigned according to HSQC NMR ($CDCl_3$, 100.6 and 400.1 MHz, 298 K).

^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz, 298 K) : δ 136.3 (d, $^{2}J_{PP}$ = 240.5 Hz, P$_{phosphite}$), 54.0 (br. pseudo-dd, $^{2}J_{PP}$ = 240.5 Hz, J_{PB} ~ 8 Hz, P$_{phosphine}$).

^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz, 298 K) : δ -9.5 (d, J_{PB} ~ 8Hz).

^{19}F{^{1}H} NMR ($CDCl_3$, 376.5 MHz, 298 K) : δ -62.33 (s, CF_3).

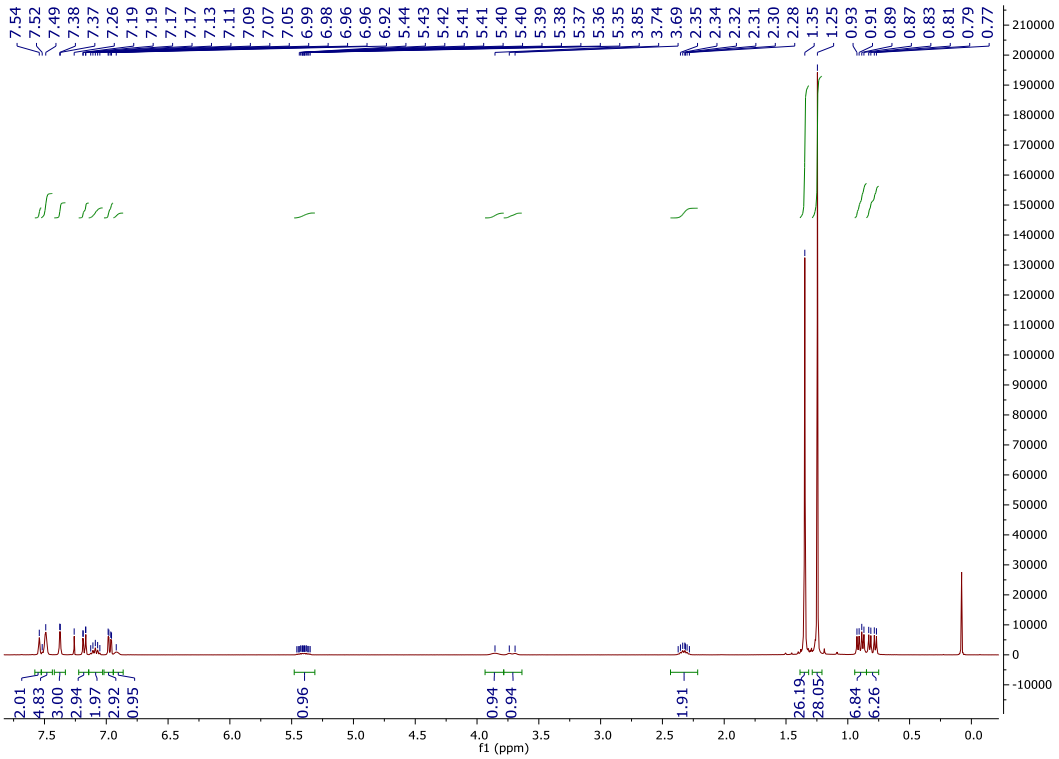


Figure S108. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400.1 MHz, 298 K).

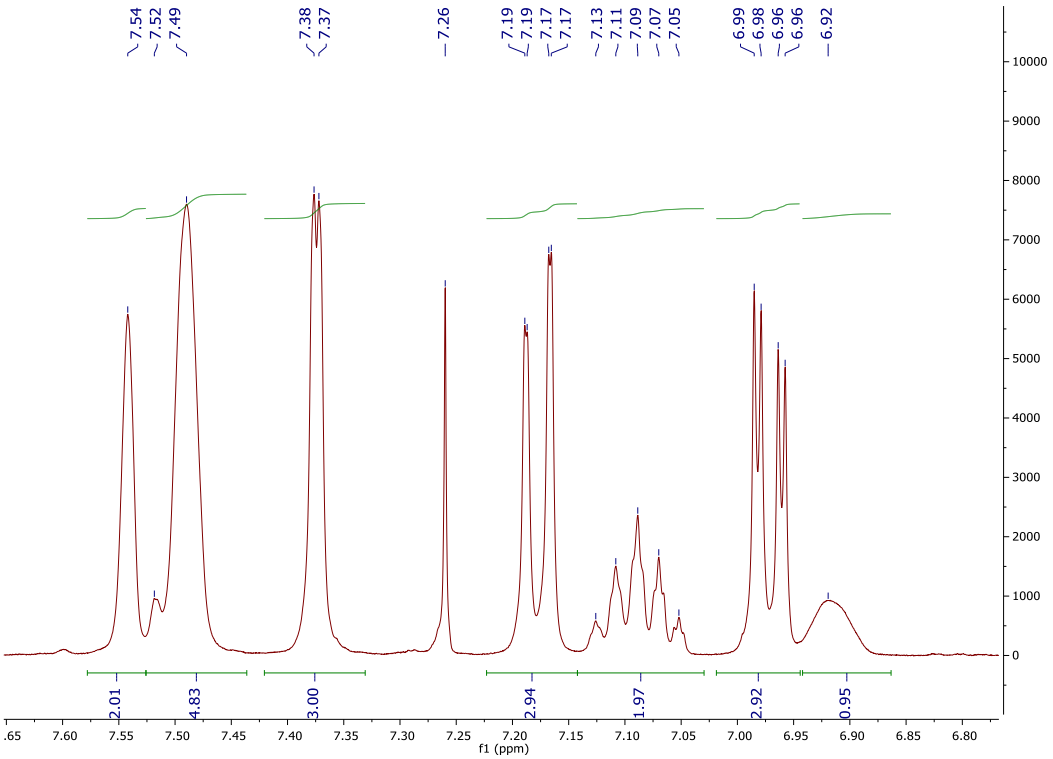


Figure S109. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400.1 MHz, 298 K) ; aromatic region.

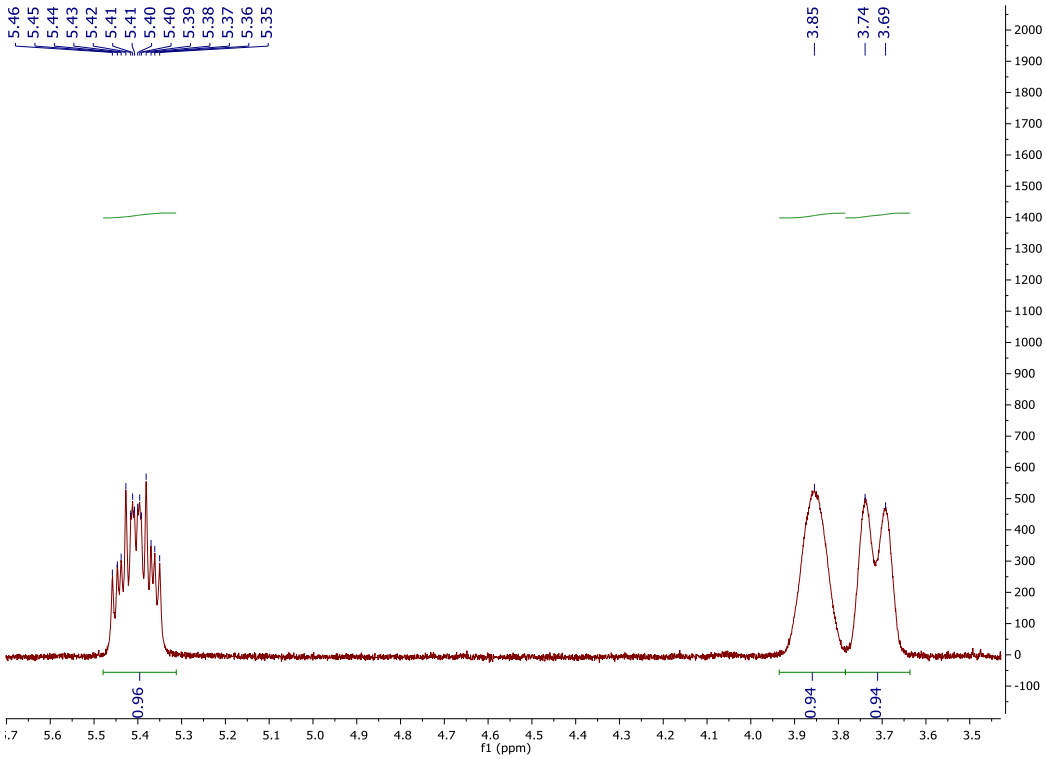


Figure S110. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400.1 MHz, 298 K) ; vinylic region.

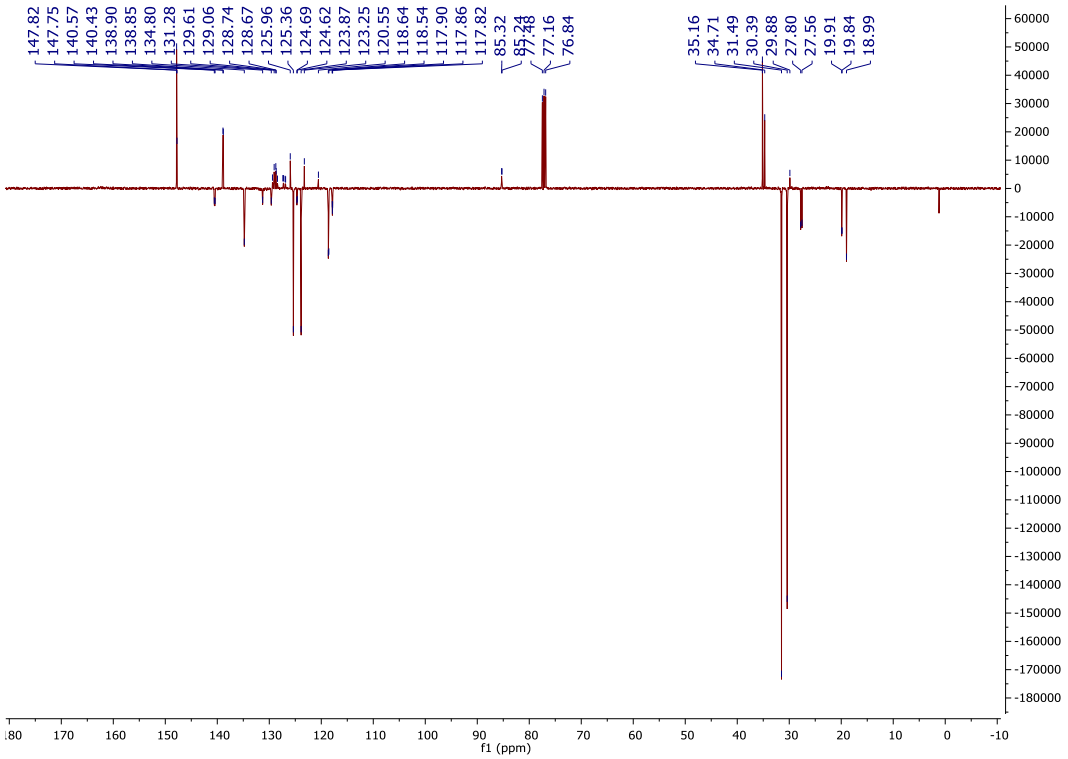


Figure S111. Jmod ($^{13}C\{^{1}H\}$)spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K).

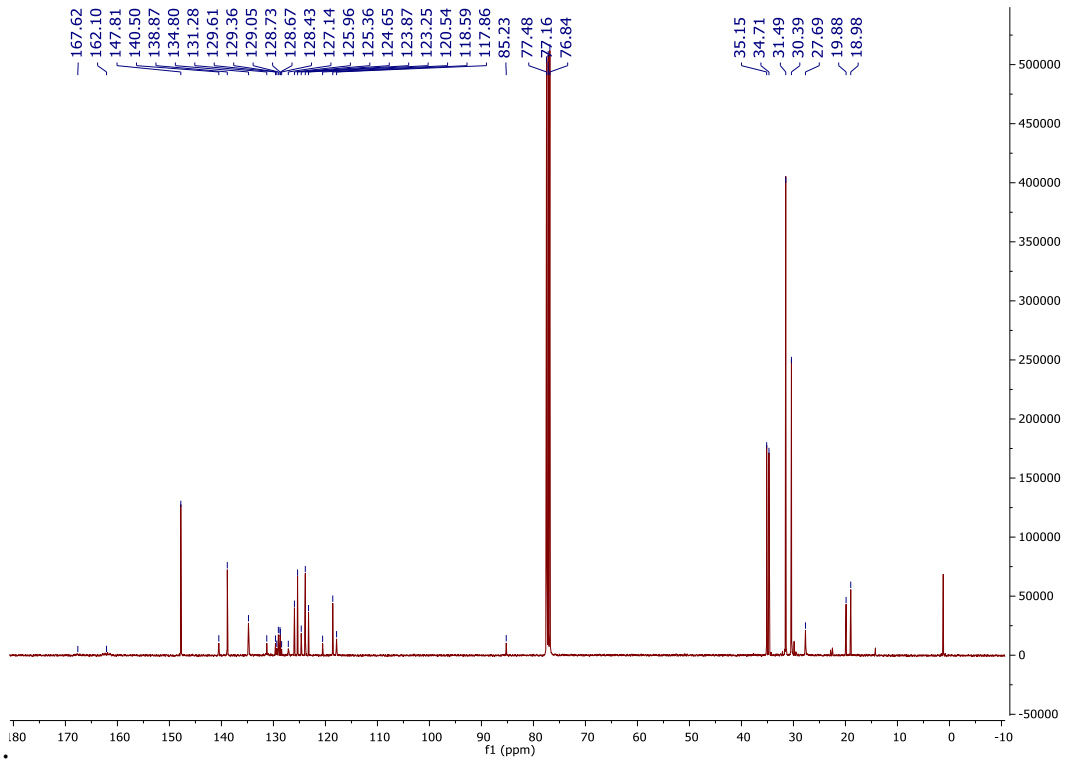


Figure S112. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K).

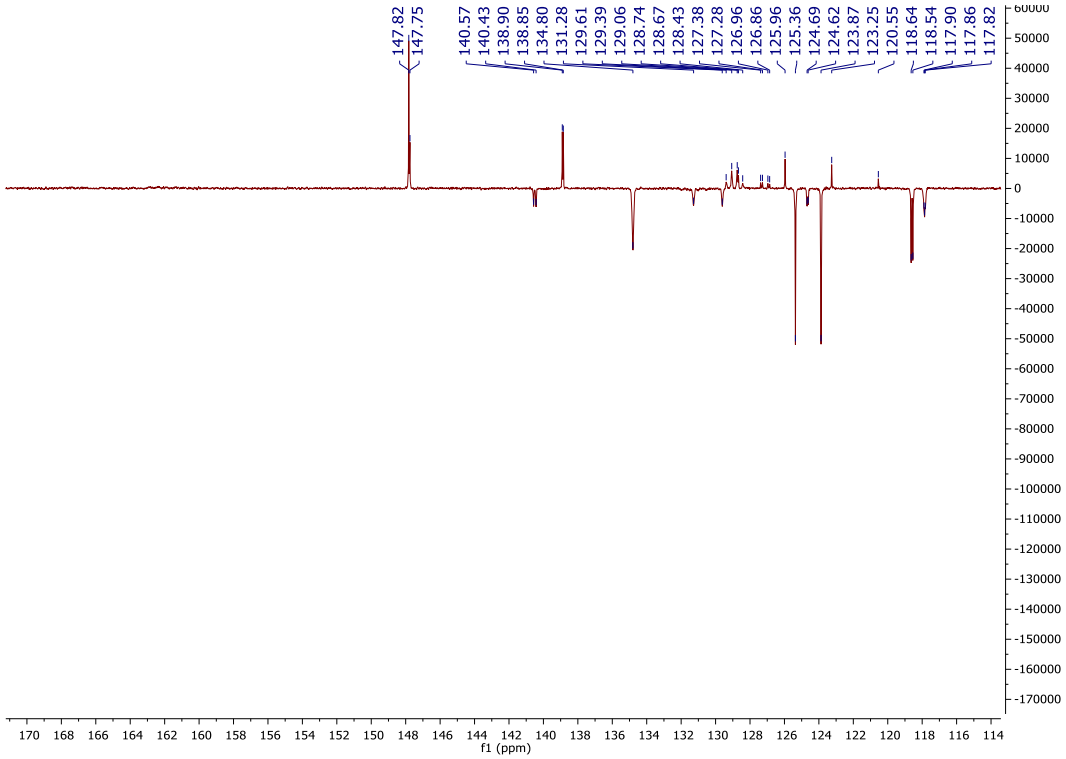


Figure S113. Jmod ($^{13}C\{^{1}H\}$)spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; area of the quaternary and aromatic carbons.

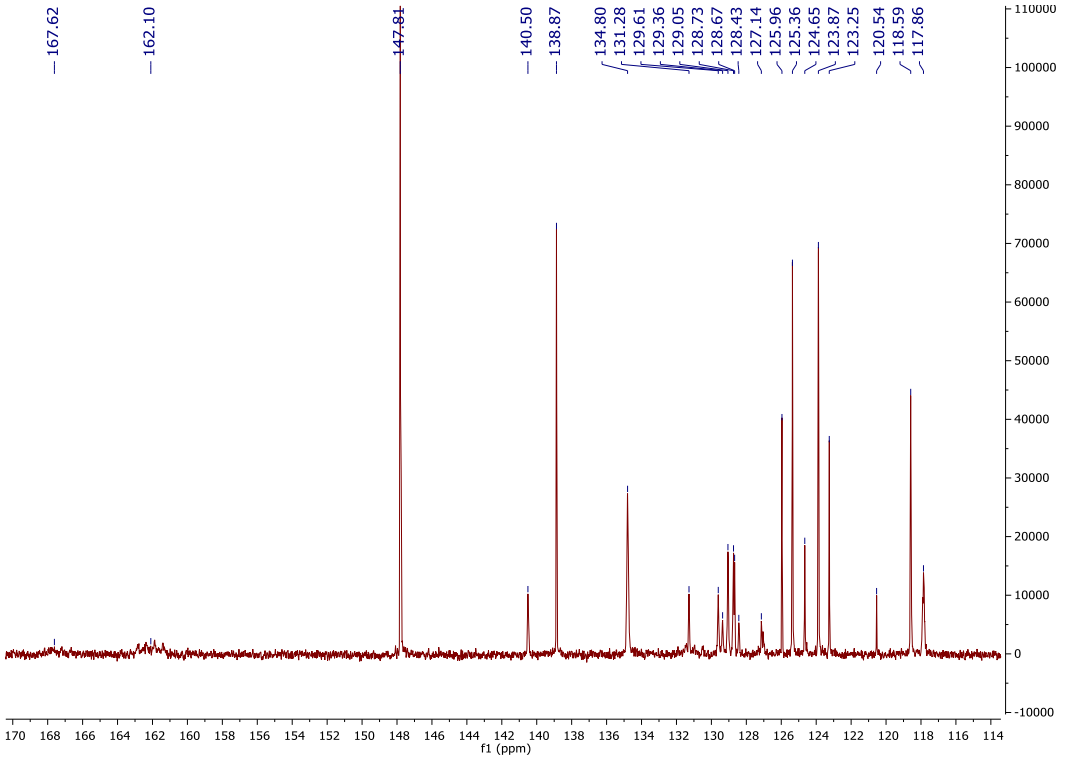


Figure S114. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; area of the quaternary and aromatic carbons.

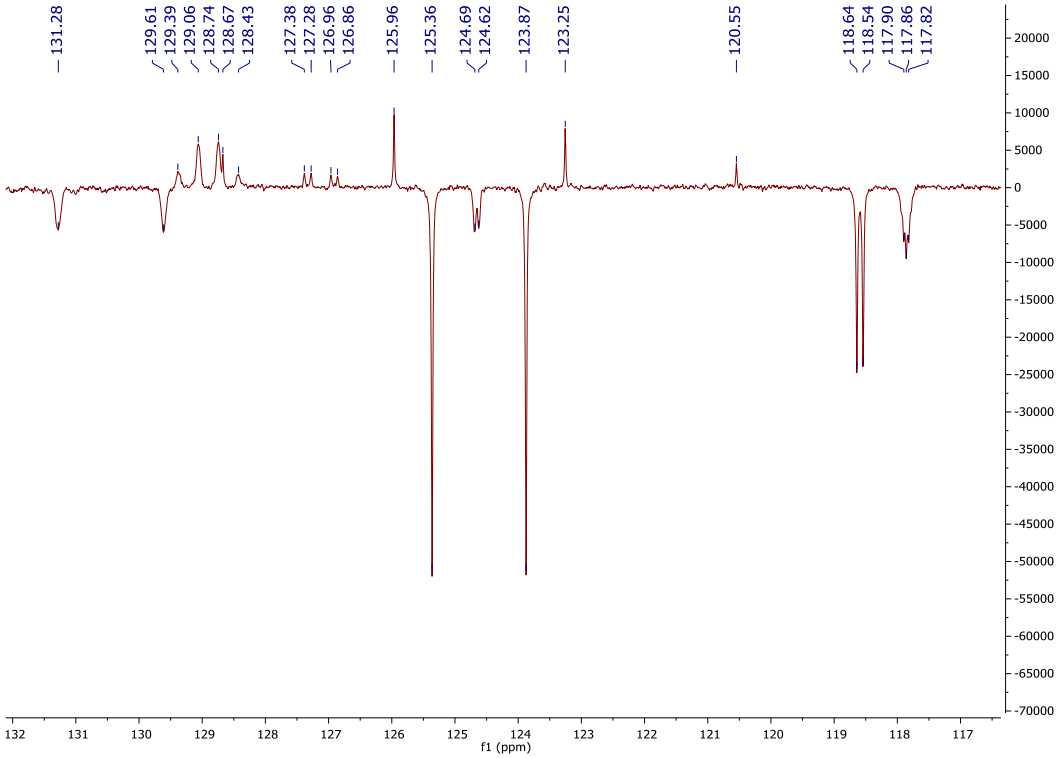


Figure S115. Jmod ($^{13}C\{^{1}H\}$)spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; area of the quaternary and aromatic carbons.

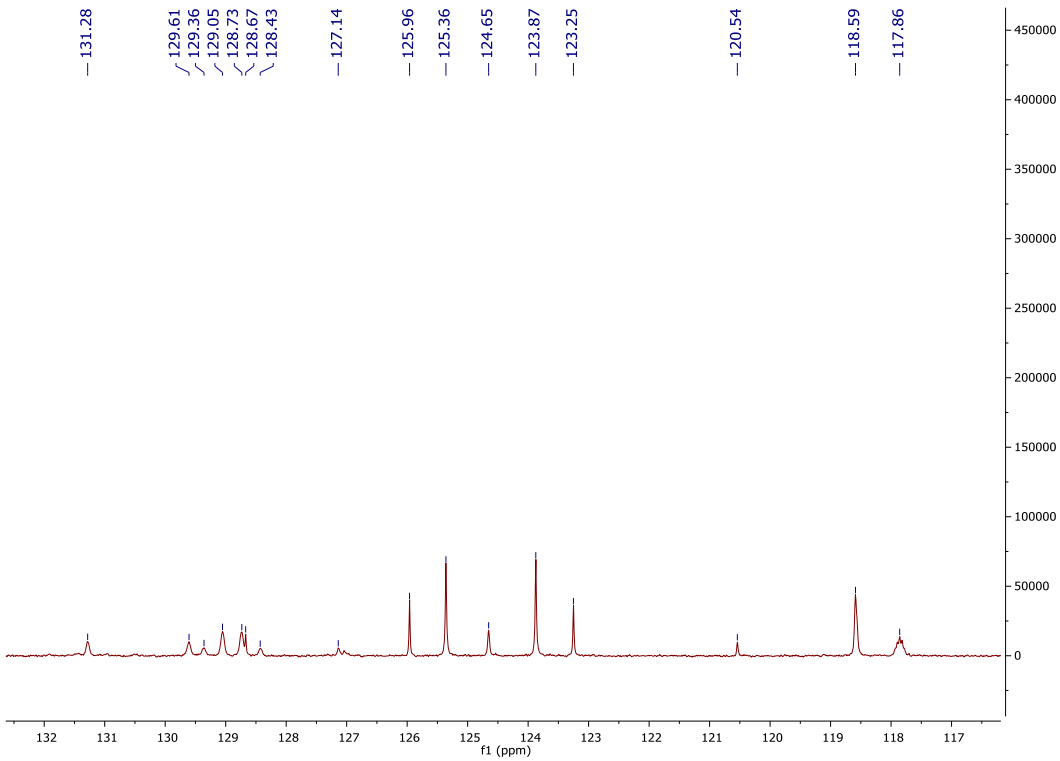


Figure S116. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; area of the quaternary and aromatic carbons

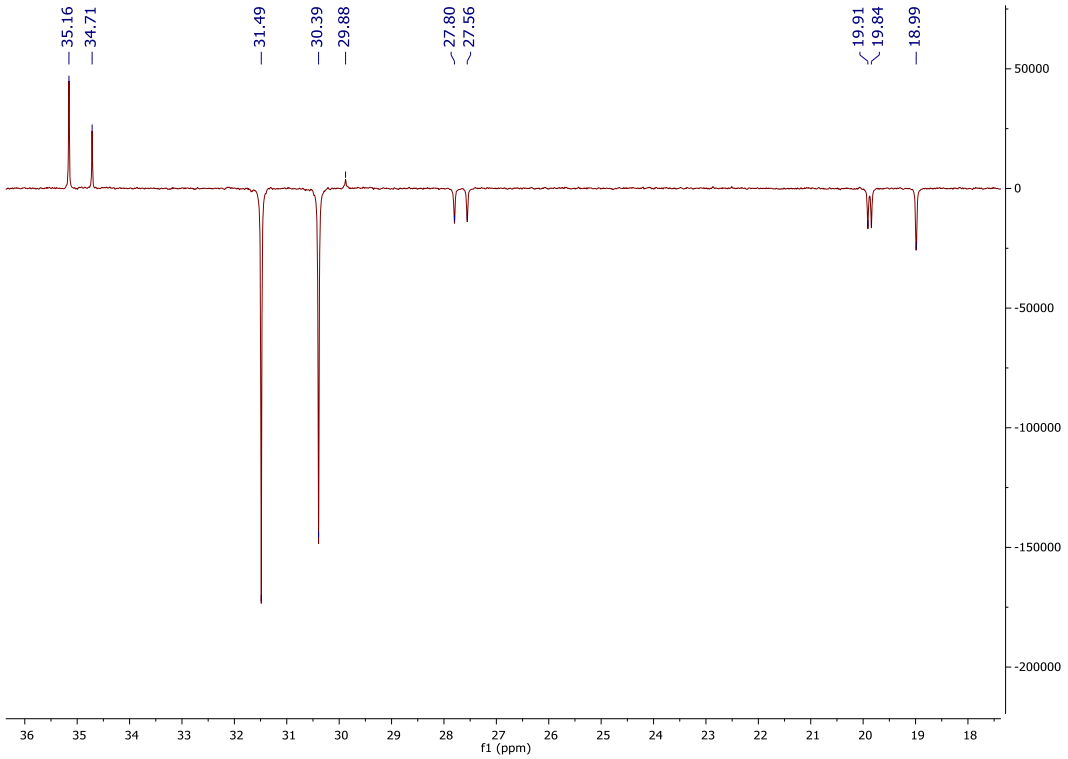


Figure S117. Jmod ($^{13}C\{^{1}H\}$)spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; aliphatic area.

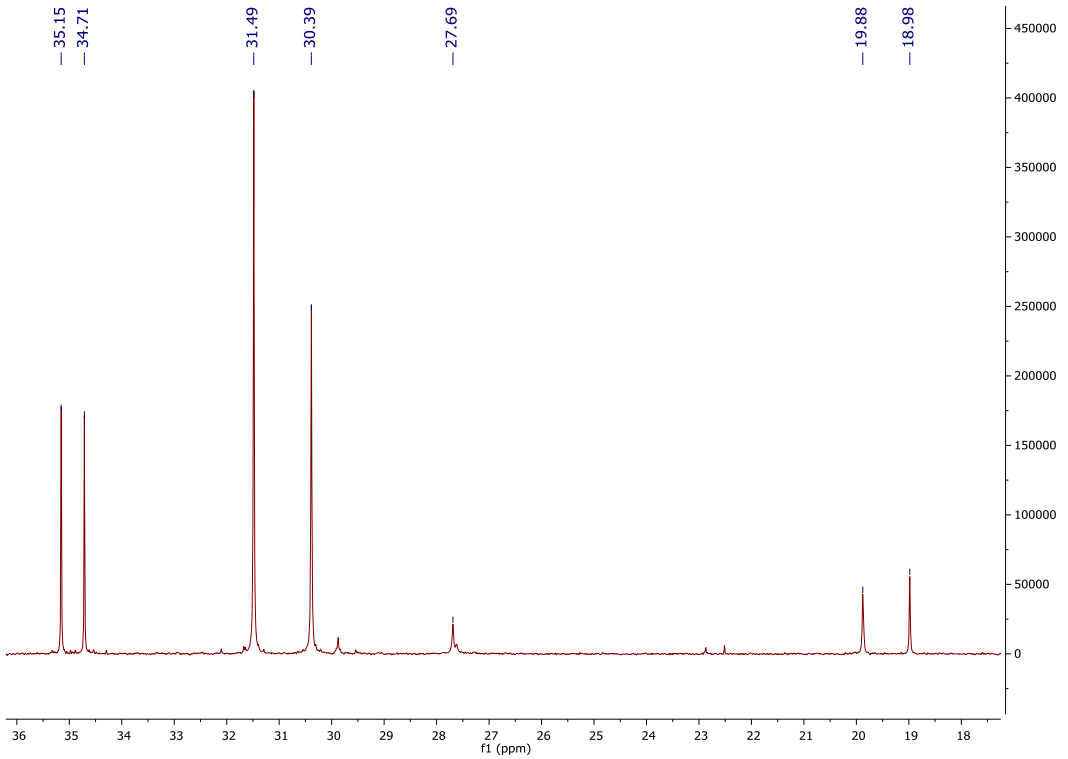


Figure S118. $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum of compound **5** ($CDCl_3$, 100.6 MHz, 298 K) ; aliphatic area.

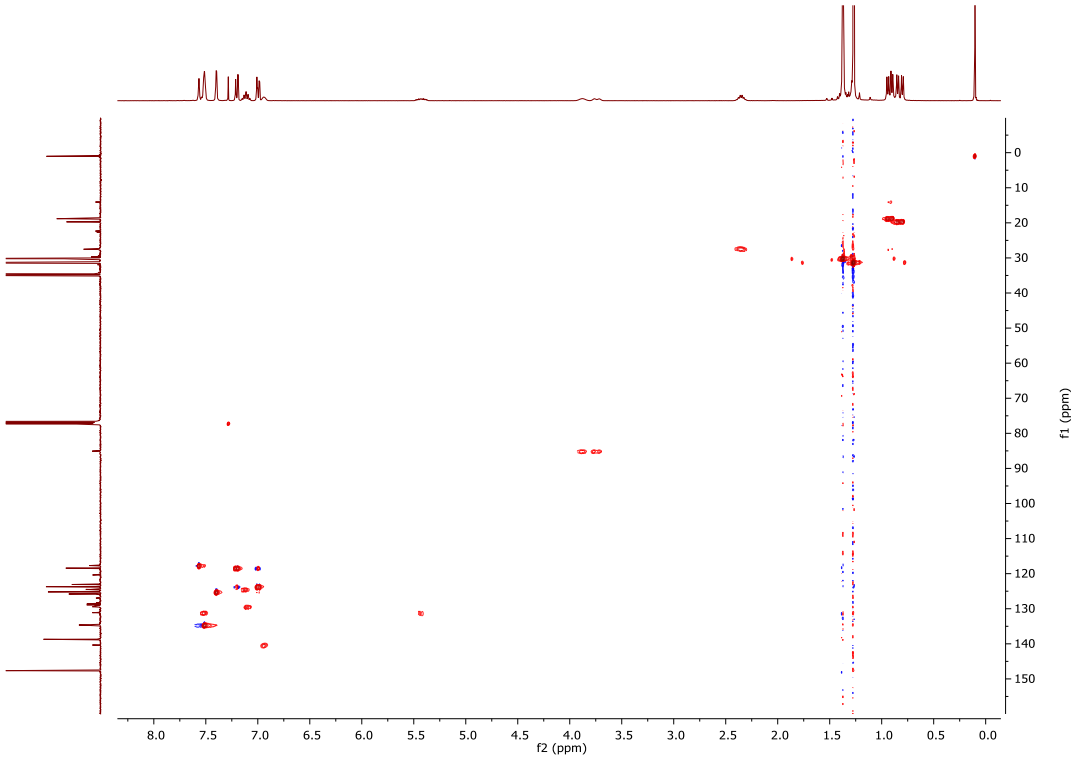


Figure S119. HSQC (^{1}H-^{13}C{^{1}H ; ^{31}P}) spectrum of compound **5** ($CDCl_3$, 400.1 / 100.6 MHz, 298 K).

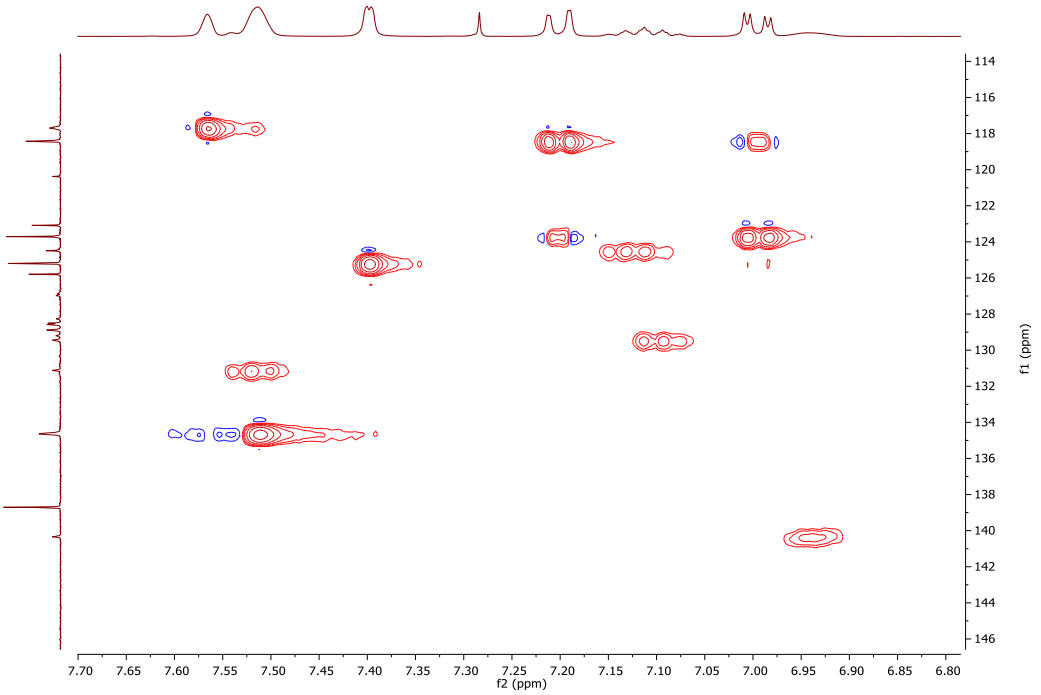


Figure S120. HSQC (^{1}H-^{13}C{^{1}H ; ^{31}P}) spectrum of compound **5** ($CDCl_3$, 400.1 / 100.6 MHz, 298 K).

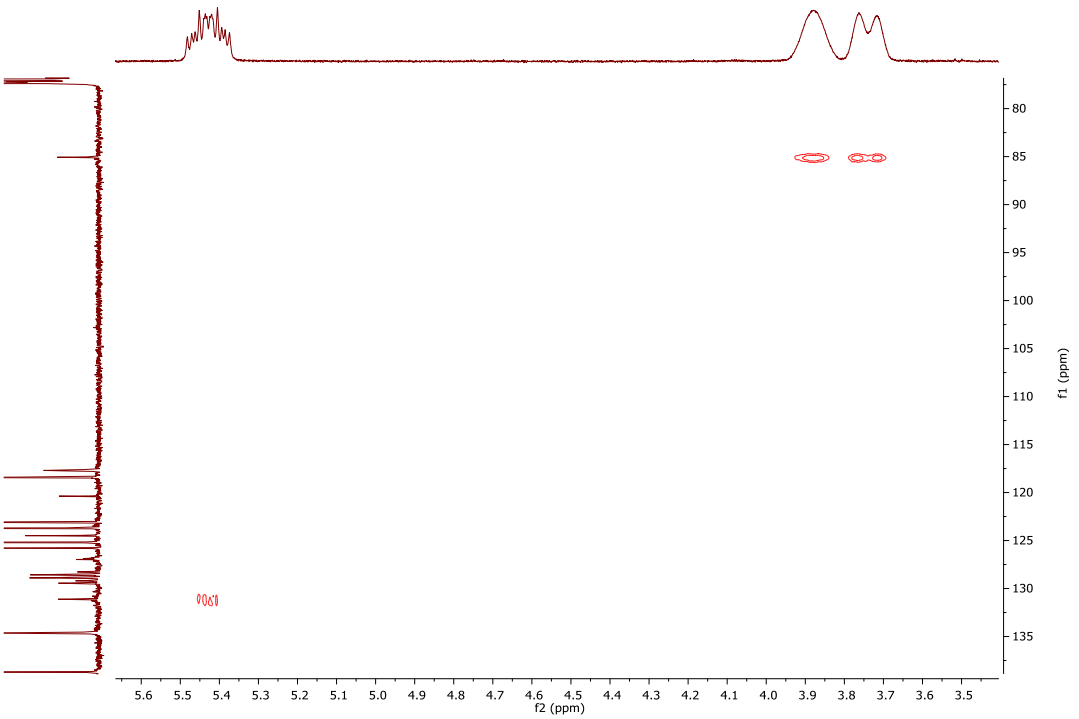


Figure S121. HSQC (^{1}H-^{13}C{^{1}H ; ^{31}P}) spectrum of compound **5** ($CDCl_3$, 400.1 / 100.6 MHz, 298 K).

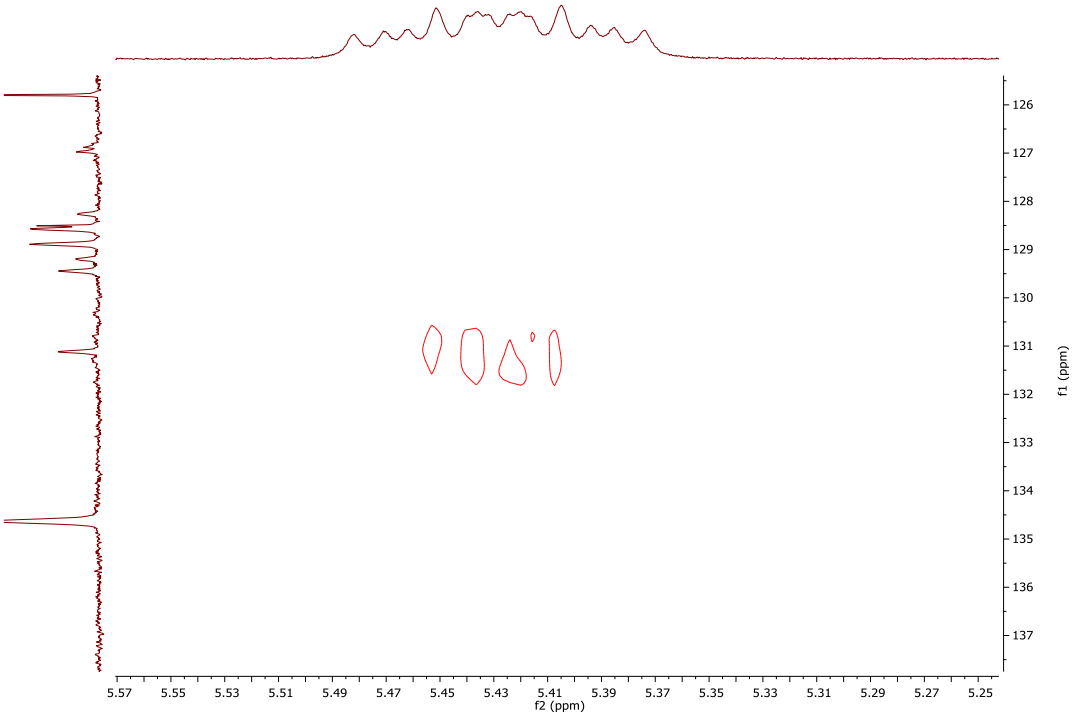


Figure S122. HSQC (^{1}H-^{13}C{^{1}H ; ^{31}P}) spectrum of compound **5** ($CDCl_3$, 400.1 / 100.6 MHz, 298 K); vinylic area, zoom-in.

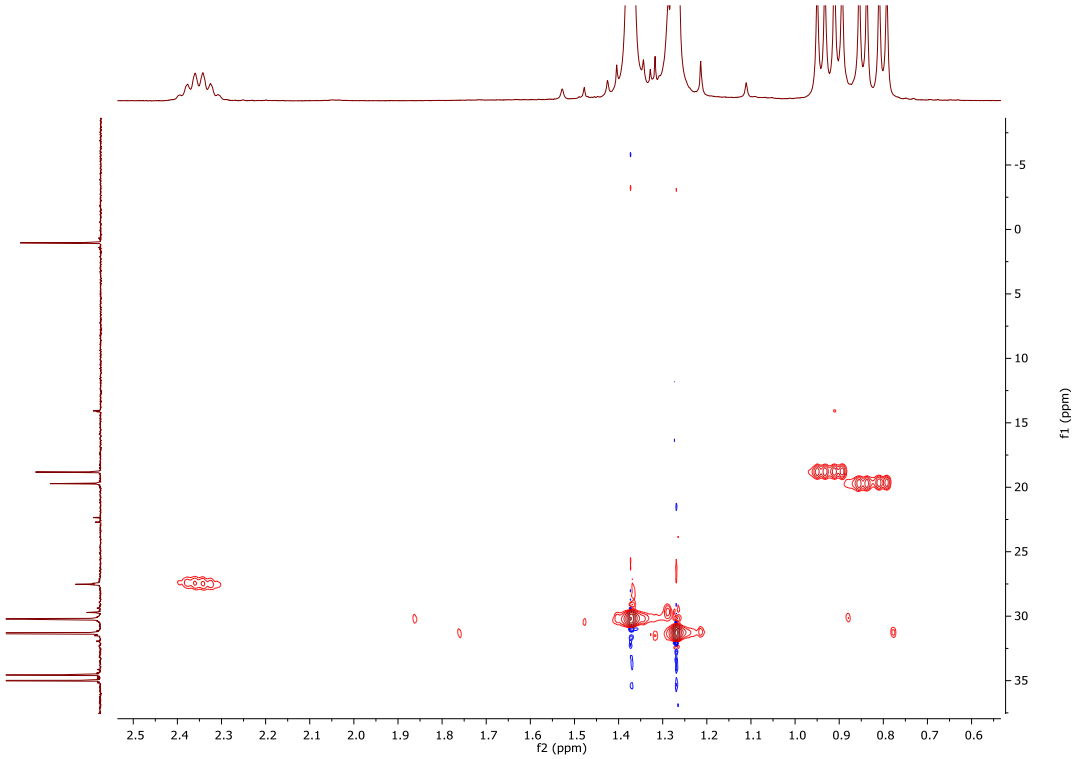


Figure S123. HSQC (^{1}H-^{13}C{^{1}H ; ^{31}P}) spectrum of compound **5** ($CDCl_3$, 400.1 / 100.6 MHz, 298 K).

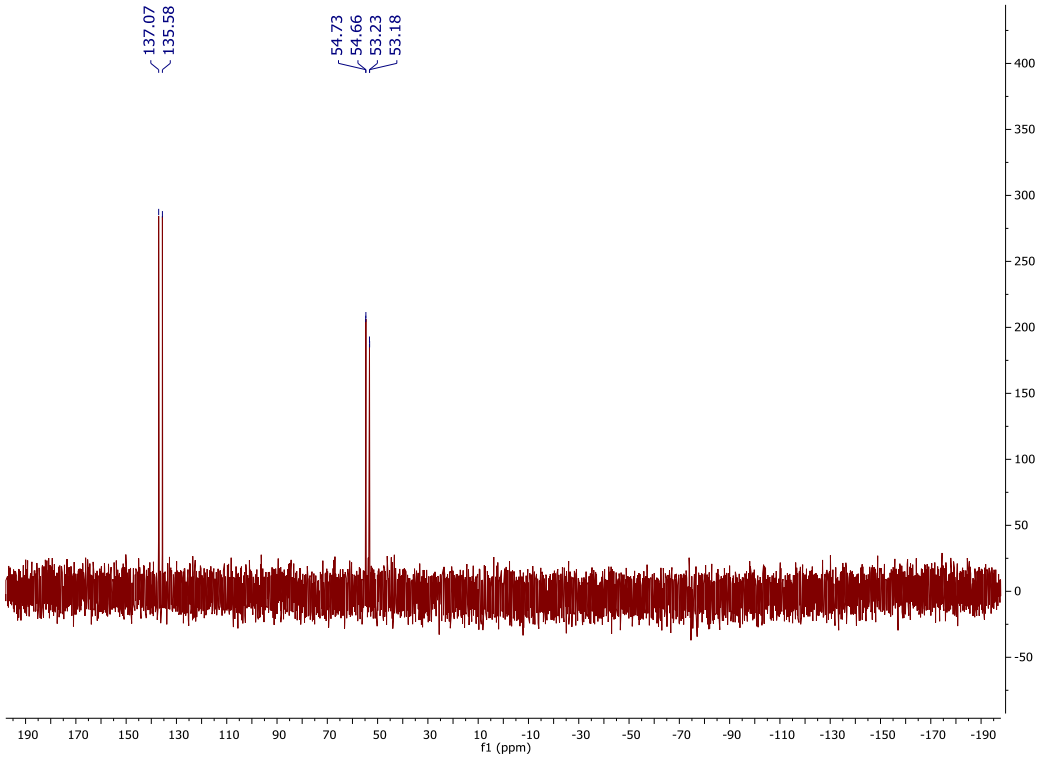


Figure S124. ^{31}P{^{1}H} NMR spectrum of compound **5** ($CDCl_3$, 162.0 MHz, 298 K).

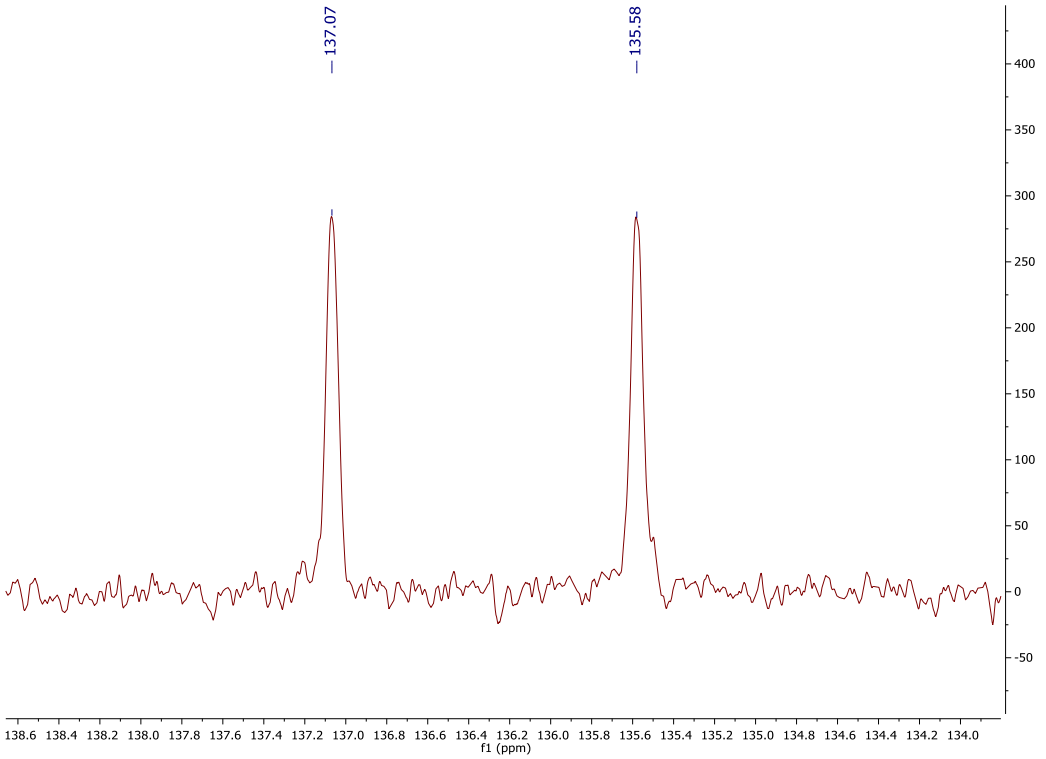


Figure S125. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 162.0 MHz, 298 K) ; phosphite area.

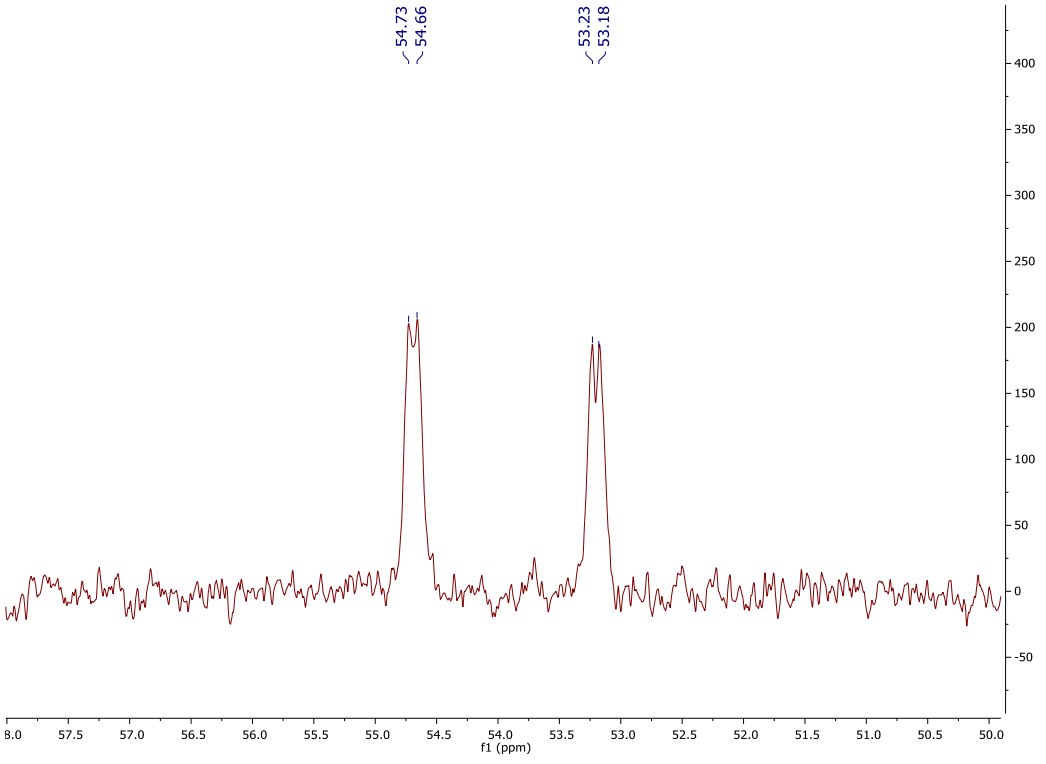


Figure S126. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 162.0 MHz, 298 K) ; phosphine area.

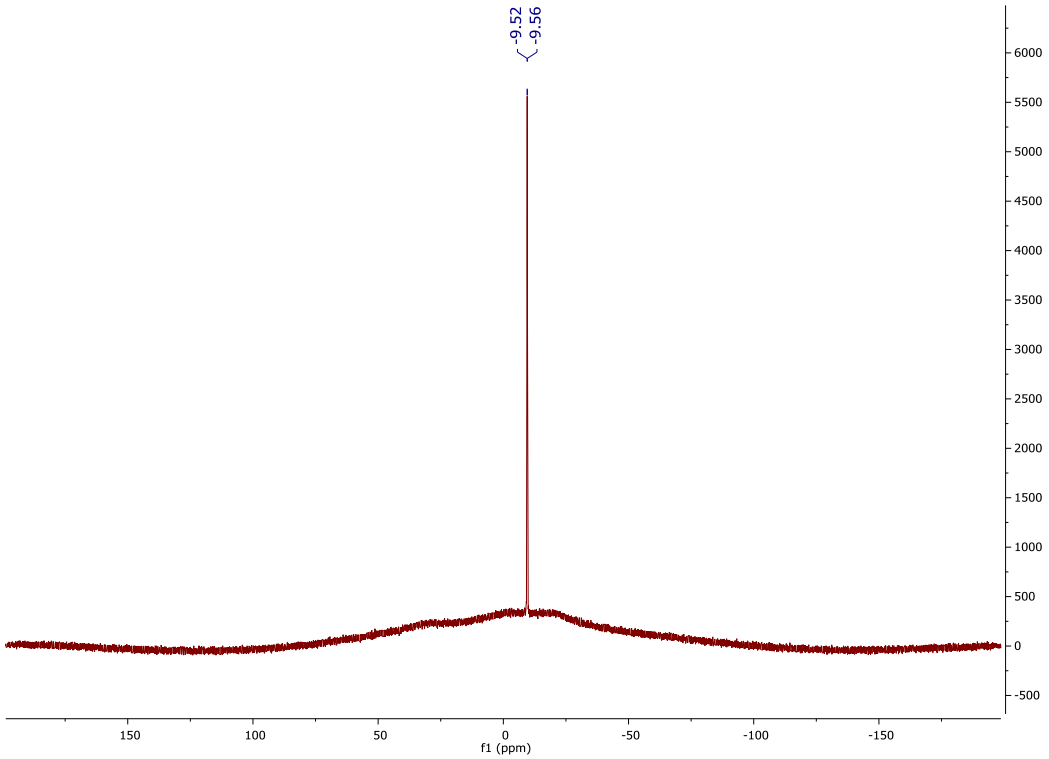


Figure S127. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 128.4 MHz, 298 K).

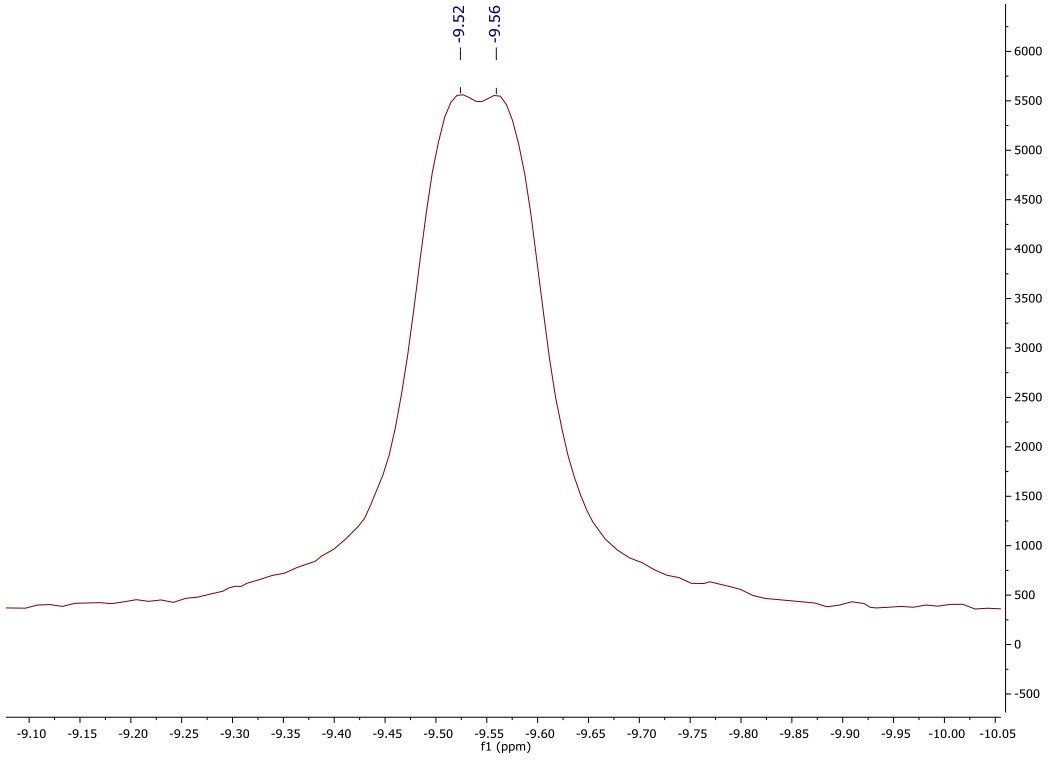


Figure S128. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 128.4 MHz, 298 K) ; zoom-in.

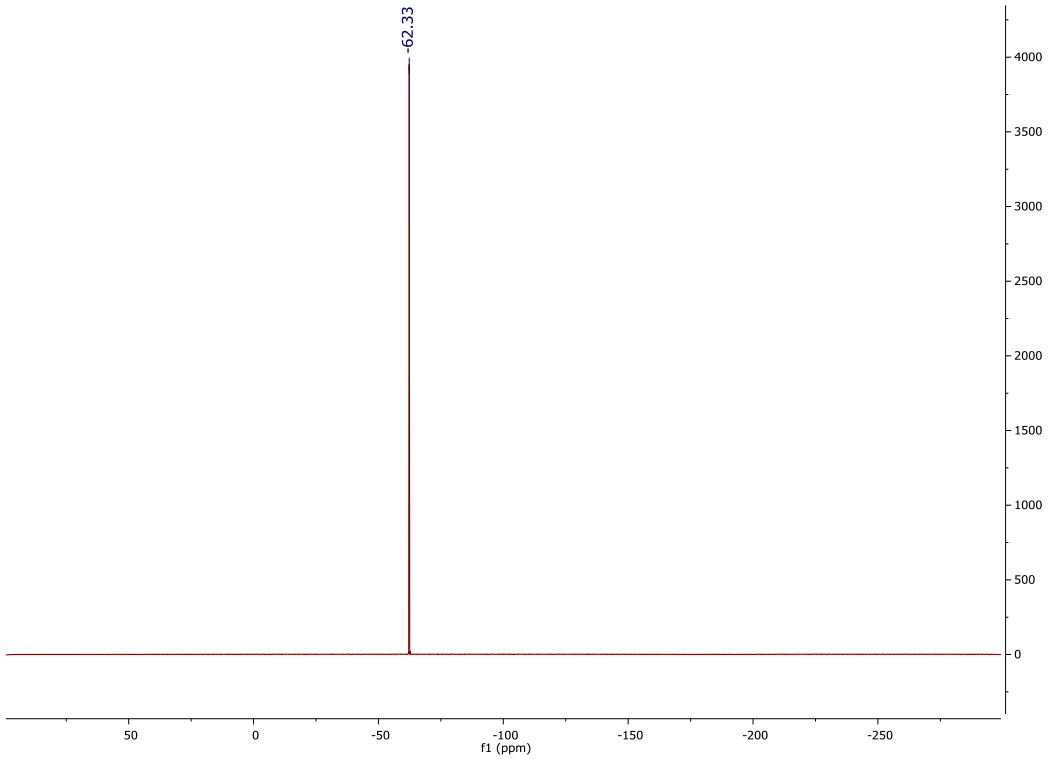
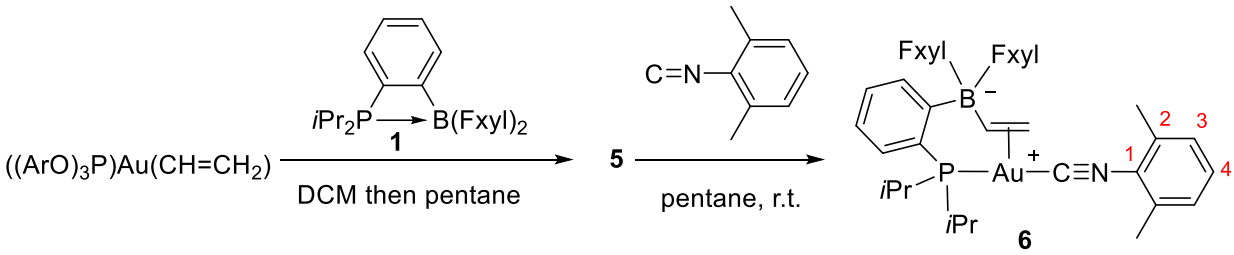


Figure S129. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5** ($CDCl_3$, 376.5 MHz, 298 K).

Synthesis of 6



To a solution of **1** (236.3 mg, 0.375 mmol, 1 equiv.) in DCM (5 mL) at room temperature was added dropwisely a solution of **((ArO)$_3$P)Au(CH=CH$_2$)** (326.7 mg, 0.375 mmol, 1 equiv.) in DCM (5 mL). After 40 min, the solution became yellow. DCM was removed under vacuum and pentane (10 mL) was added to the resulting pale-yellow powder. The mixture was stirred at room temperature for 1 h. Then XylNC (49.6 mg, 0.375 mmol, 1 equiv.) was added at room temperature as a solid and the crude was stirred for another 40 min. The volatiles were removed *in vacuo* and the obtained residue was redispersed in a mixture of HMDSO (1.5 mL) and pentane (1.5 mL). This mixture was then cooled to –20°C leading to the precipitation of a white solid after 2 days. The supernatant was removed and the solid was washed with cold pentane (2x1 mL). Finally, after drying under high vacuum, **6** was isolated as a white solid (143.2 mg, 0.145 mmol, 39 % from **1**).

* A by-product disclosing a ^{31}P NMR resonance at 30 ppm was authenticated as the **1**/CNXyl adduct (which was prepared independently).

m.p.: 107.4 °C

^{1}H NMR ($CDCl_3$, 400.2 MHz, 298 K) : δ 7.64 (br. s, 4H, $CH_{o\text{-}Fxyl}$), 7.58-7.50 (br. m, 3H, $2CH_{p\text{-}Fxyl}$ and CH_{Ar}), 7.32 (m, 1H, CH_{Ar}), 7.25-7.15 (m, 4H, CH_{Ar}), 7.07 (br. s, 1H, CH_{Ar}), 6.17 (ddd, 1H, $^{3}J_{HH}$ = 17.4 and 12.2 Hz, J_{PH} = 4.7 Hz, CH_{vinyl}), 4.49 (br. d, 1H, $^{3}J_{HH}$ = 17.4 Hz, $CH_{2vinyl\ trans}$), 4.35 (br. s, 1H, $CH_{2vinyl\ cis}$), 2.55 (m, 2H, CH_{iPr}), 2.38 (s, 6H, $CH_{3o\text{-}Xyl}$), 1.29 (dd, $^{3}J_{PH}$ = 16.9 Hz, $^{3}J_{HH}$ = 6.8 Hz, CH_{3iPr}), 1.05 (dd, $^{3}J_{PH}$ = 17.4 Hz, $^{3}J_{HH}$ = 7.1 Hz, CH_{3iPr}).

^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz, 298 K) : δ 166.6 (pseudo-qd, $^{1}J_{BC}$ = 51.5 Hz, $^{2}J_{PC}$ = 23.6 Hz, B-C_{ipso}),162.1 ((pseudo-q, $^{1}J_{BC}$ = 49.7 Hz, B-$C_{ipso\text{-}Fxyl}$), 159.1 (br. s, C_{CN}), 139.6 (d, J_{PC} = 14.8 Hz, CH_{Ar}), 135.8 (s, C_2), 134.7 (s, $CH_{o\text{-}Fxyl}$), 131.2 (br. s, CH_{Ar}), 130.9* (s, C_4 and CH_{vinyl}), 129.9 (br.s , CH_{Ar}), 129.8 (d, $^{1}J_{PC}$ = 46.6 Hz, P-C_{ipso}), 129.0 (q, $^{2}J_{FC}$ = 31.6 Hz, $C_{ipso\text{-}CF3}$), 128.5 (s, C_3), 125.1 (d, J_{PC} = 7.3 Hz, CH_{Ar}), 124.7 (q, $^{1}J_{FC}$ = 272.3 Hz, CF_3), 117.8 (m, $CH_{p\text{-}Fxyl}$), 91.8* (br. s, CH_{2vinyl}), 27.7 (d, $^{1}J_{PC}$ = 25.9 Hz, CH_{iPr}), 20.6 (d, $^{2}J_{PC}$ = 4.4 Hz, CH_{3iPr}), 19.8 (d, $^{2}J_{PC}$ = 5.2 Hz, CH_{3iPr}), 18.7 (s, CH_{3Xyl}).

NB : C_1 not visible

CH$_{vinyl}$ and CH$_{2vinyl}$ are assigned according to HSQC (^{1}H; ^{13}C{^{1}H,^{31}P}) NMR. $^{1}J_{CH}$ were determined from HSQC (^{1}H; ^{13}C) NMR: for CH_{vinyl} : δ 129.9 ppm, $^{1}J_{CH}$ = 130.91 Hz, and for CH_{2vinyl} : δ 91.8 ppm, $^{1}J_{CH}$ = 157.91 and 160.52 Hz, see **Figure S141 and S142. Texte Didier*

^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz, 298 K) : δ 53.7 (pseudo-q, J_{PB} = 8.0 Hz).

^{11}B{^{1}H} NMR ($CDCl_3$, 128.4 MHz, 298 K) : δ -9.0 (d, J_{PB} = 8.0 Hz).

^{19}F NMR ($CDCl_3$, 470.5 MHz, 298 K) : δ -62.4 (s, CF_3).

HRMS (ES-MS^{+}): exact mass (monoisotopic) calcd. for $[M+H]^{+}$ $(C_{39}H_{37}AuBF_{12}NP)^{+}$: 986.22; found: 986.2225.

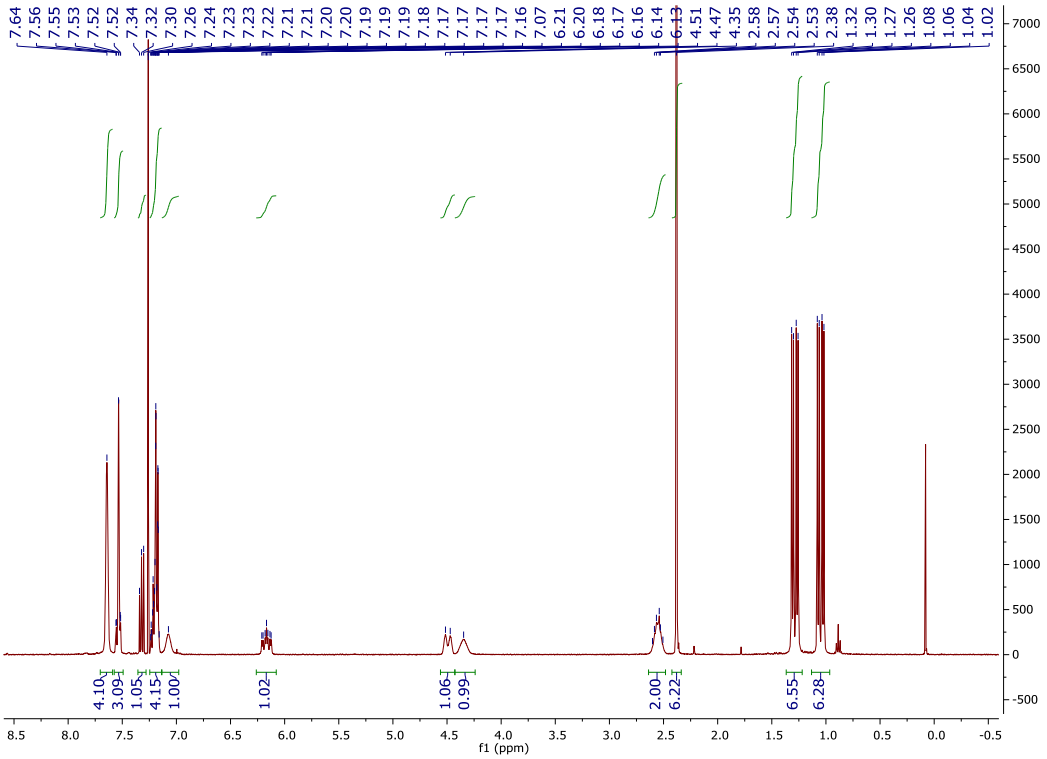


Figure S130. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400.2 MHz, 298 K).

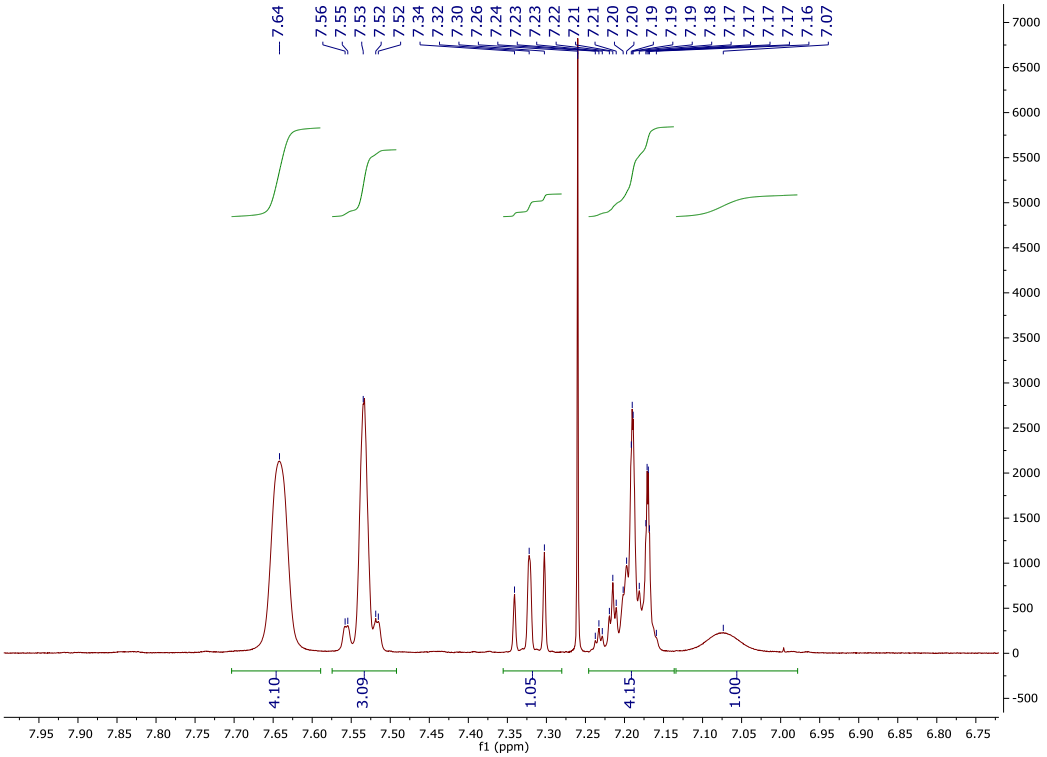


Figure S131. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400.2 MHz, 298 K) ; aromatic area.

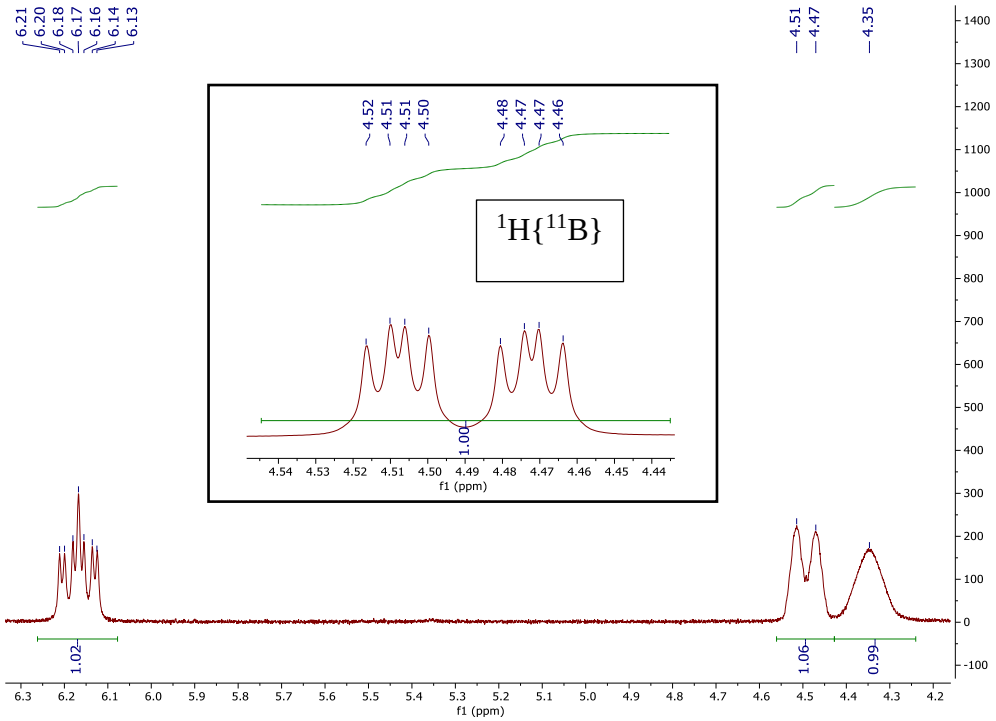


Figure S132. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400.2 MHz, 298 K) ; vinylic area. Zoom-in: $^{1}H\{^{11}B\}$ NMR of one CH_{2vinyl} ($CDCl_3$, 500.1 MHz, 298 K)

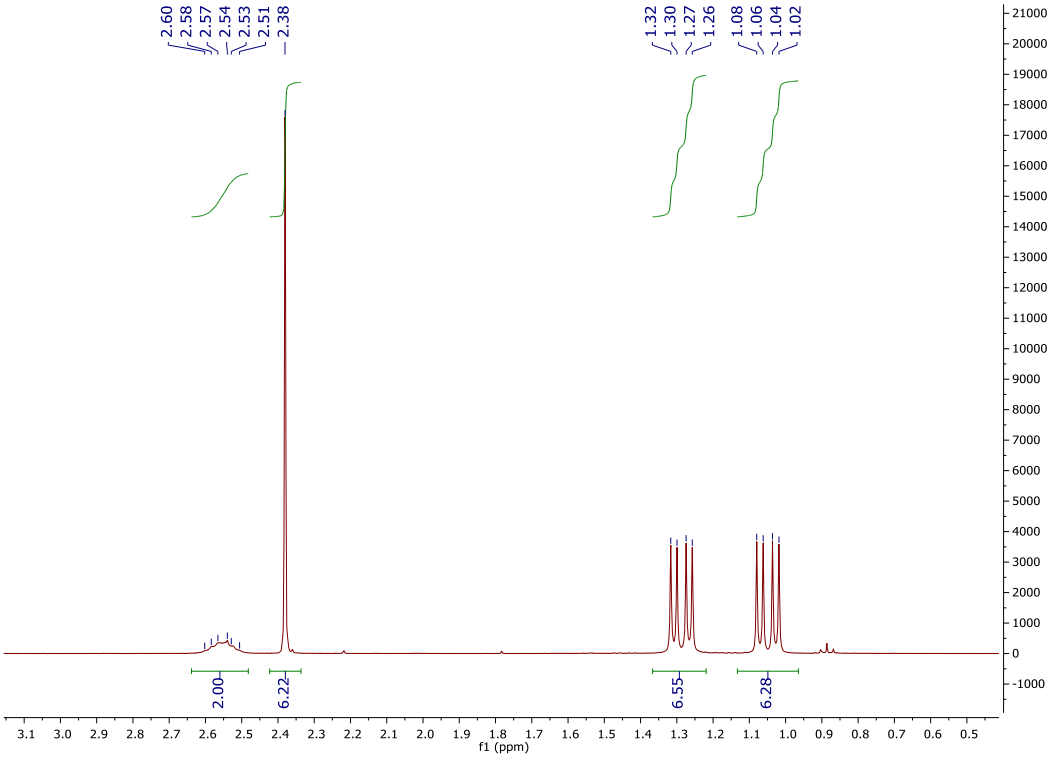


Figure S133. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400.2 MHz, 298 K) ; aliphatic area.

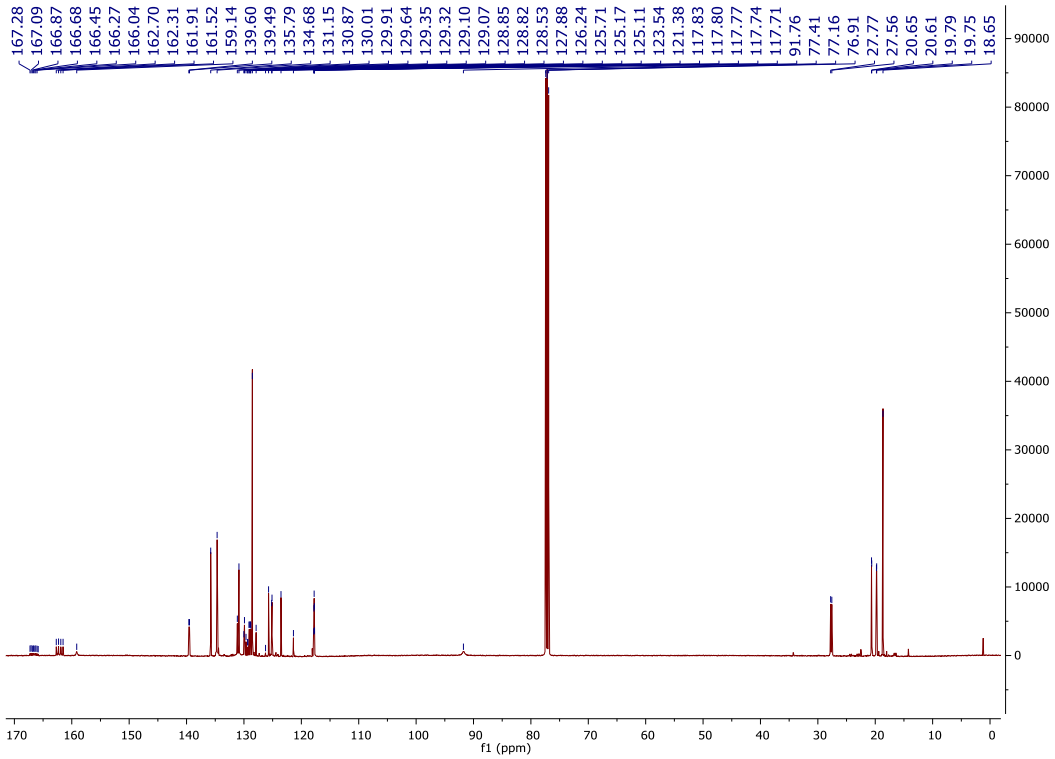


Figure S134. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 125.8 MHz, 298 K).

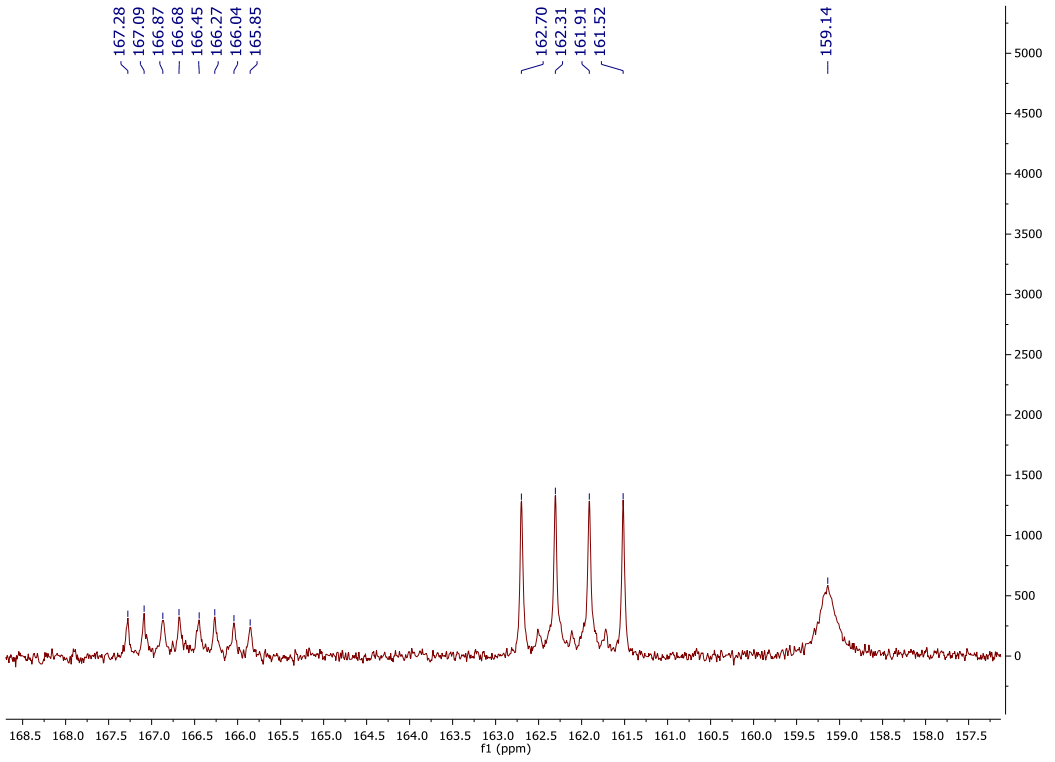


Figure S135. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 125.8 MHz, 298 K) ; area of the quaternary and aromatic carbons.

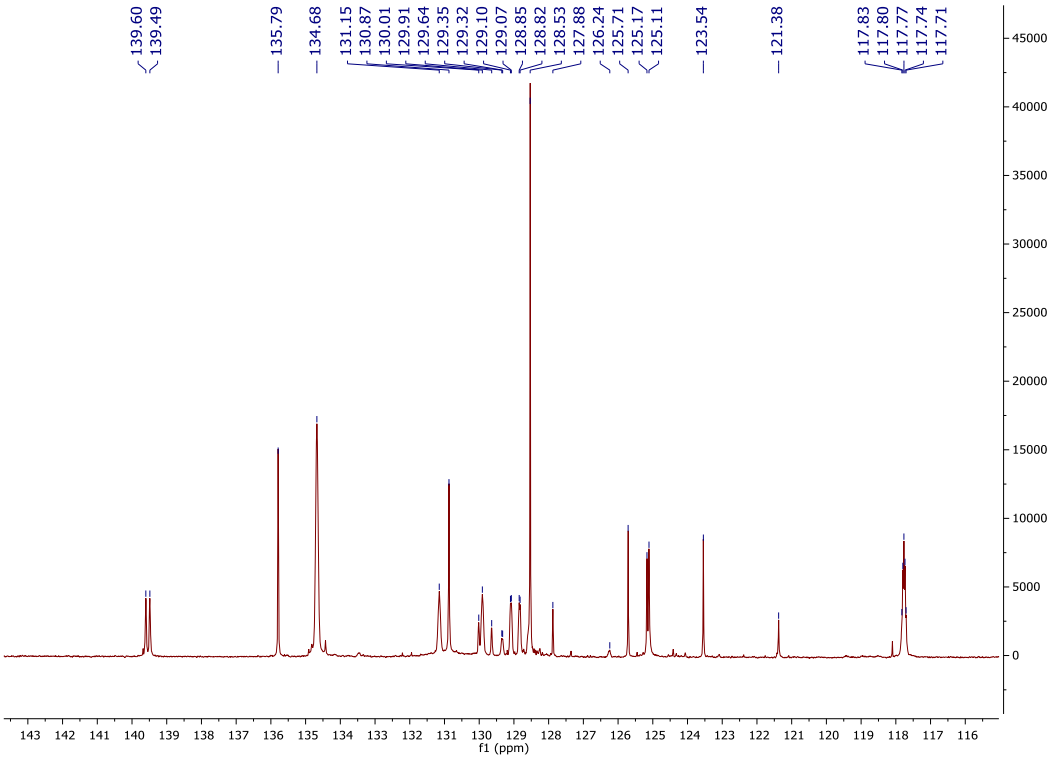


Figure S136. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 125.8 MHz, 298 K) ; area of the quaternary and aromatic carbons.

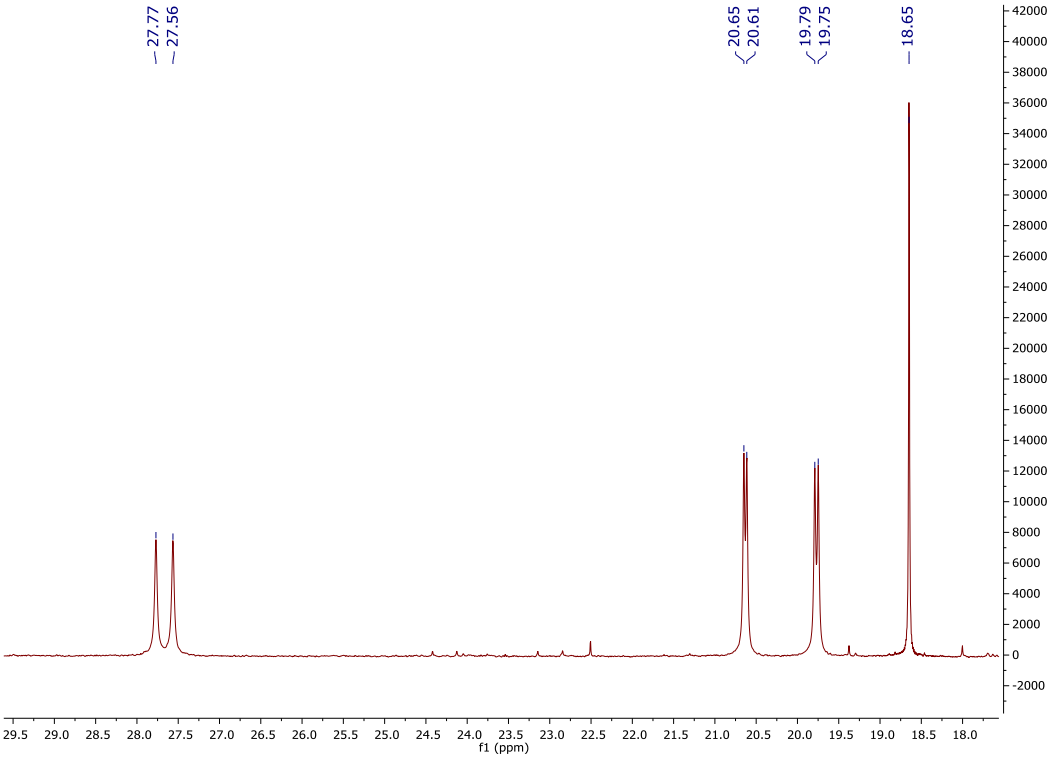


Figure S137. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 125.8 MHz, 298 K) ; aliphatic area.

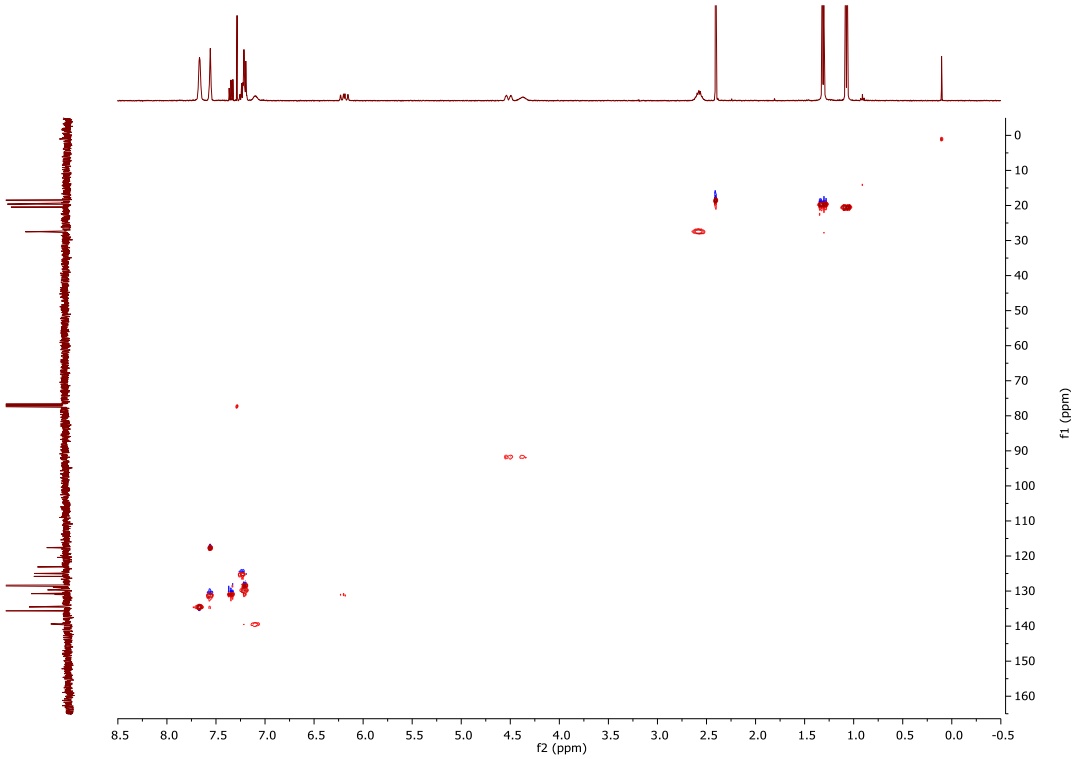


Figure S138. HSQC (^{1}H ;^{13}C{^{1}H ;^{31}P}) spectrum of compound **6** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K).

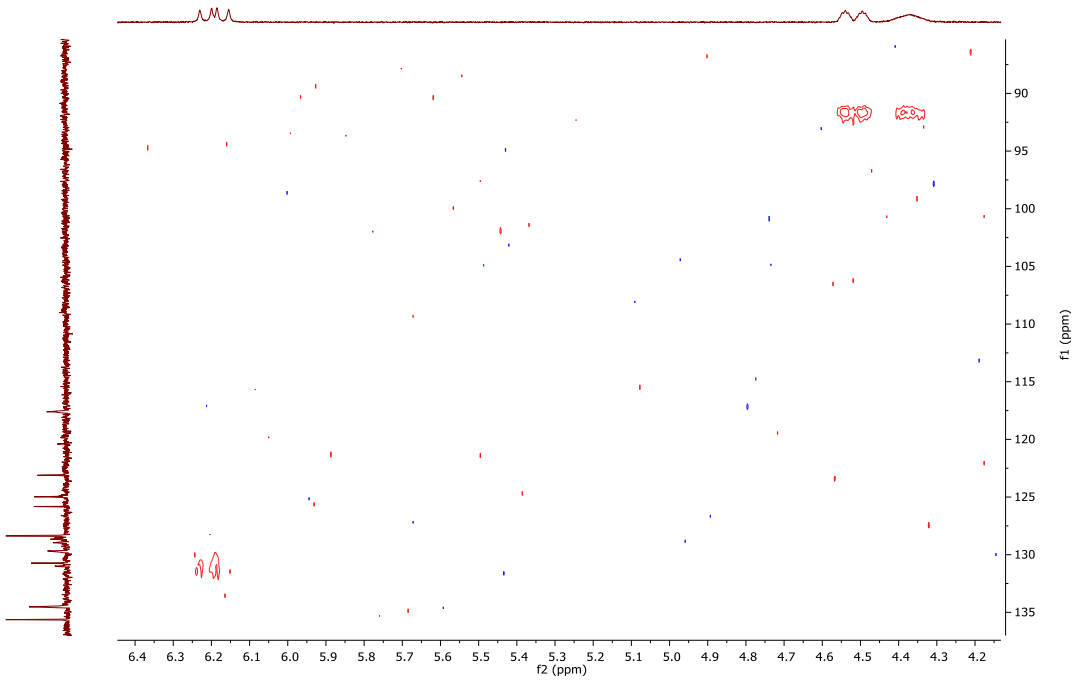


Figure S139. HSQC (^{1}H ;^{13}C{^{1}H ;^{31}P}) spectrum of compound **6** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K); vinylic area.

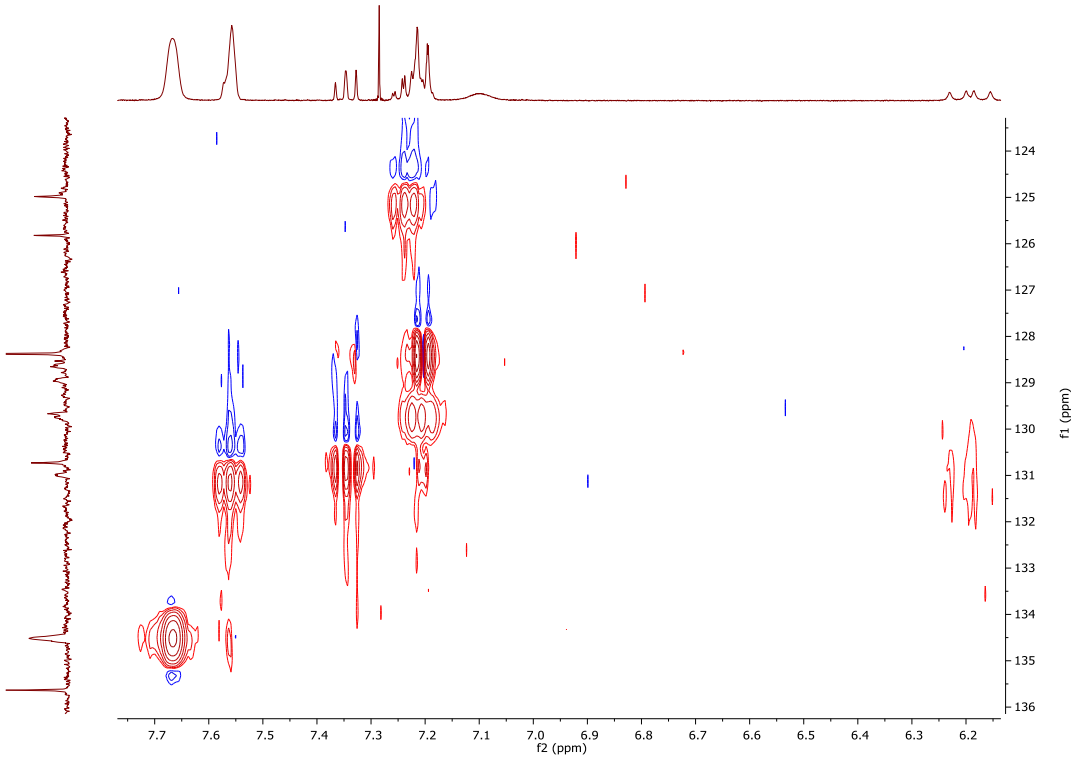


Figure S140. HSQC (^{1}H ;^{13}C{^{1}H ;^{31}P}) spectrum of compound **6** ($CDCl_3$, 400.2 / 100.6 MHz, 298 K); area of the quaternary and aromatic carbons, zoom-in.

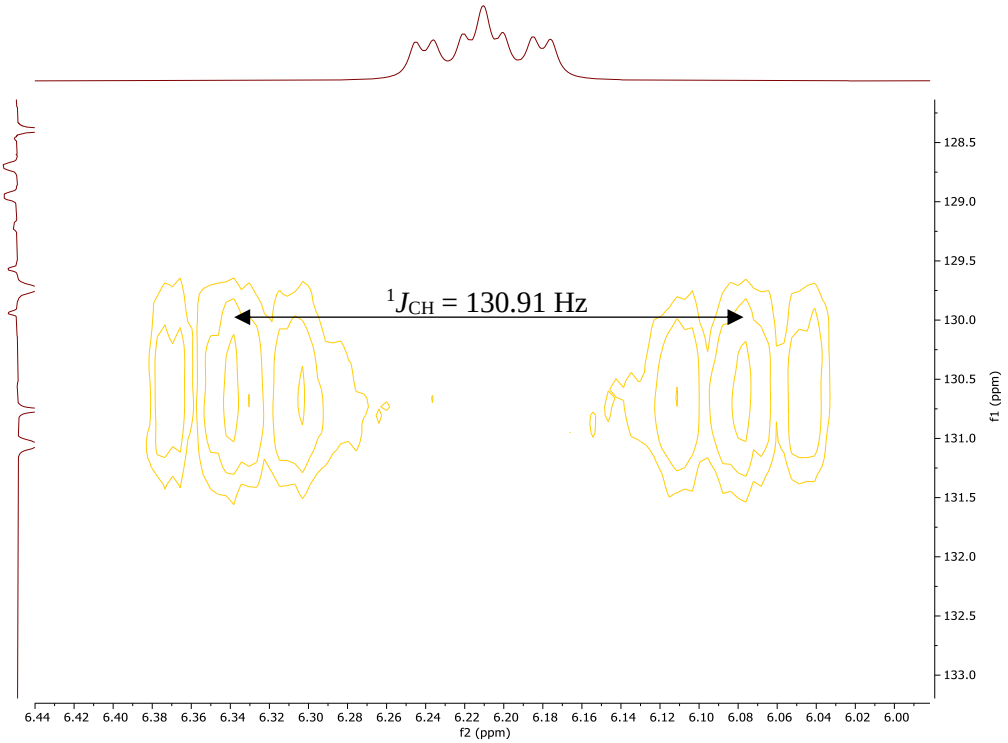


Figure S141. Selected vinylic area of HSQC (^{1}H ;^{13}C) spectrum of compound **6** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

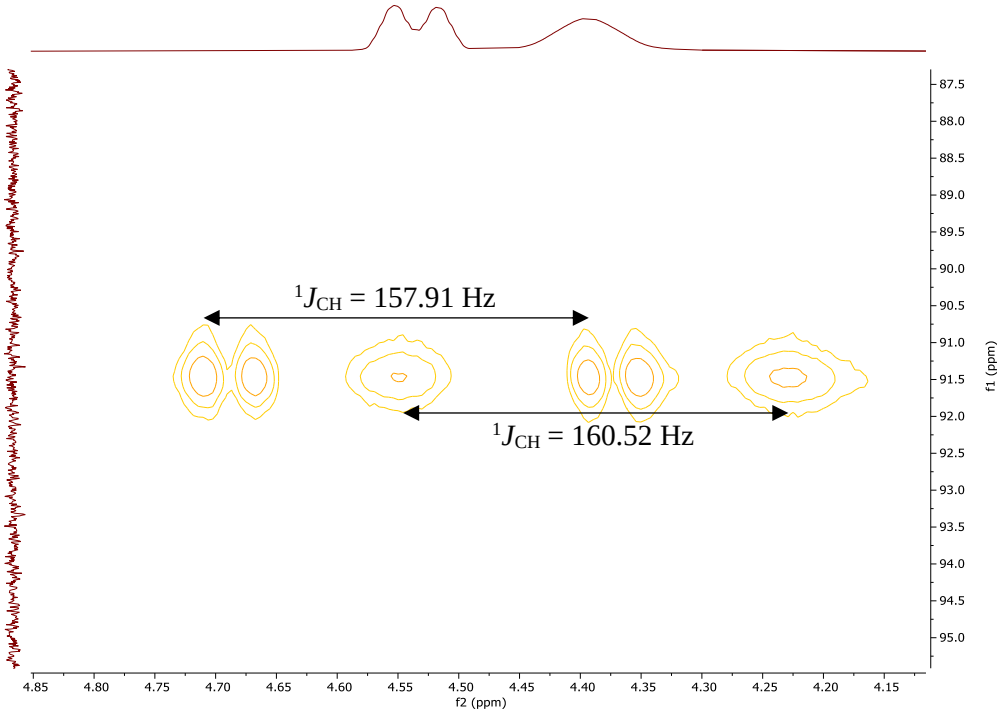


Figure S142. Selected vinylic area HSQC (^{1}H ;^{13}C) spectrum of compound **6** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

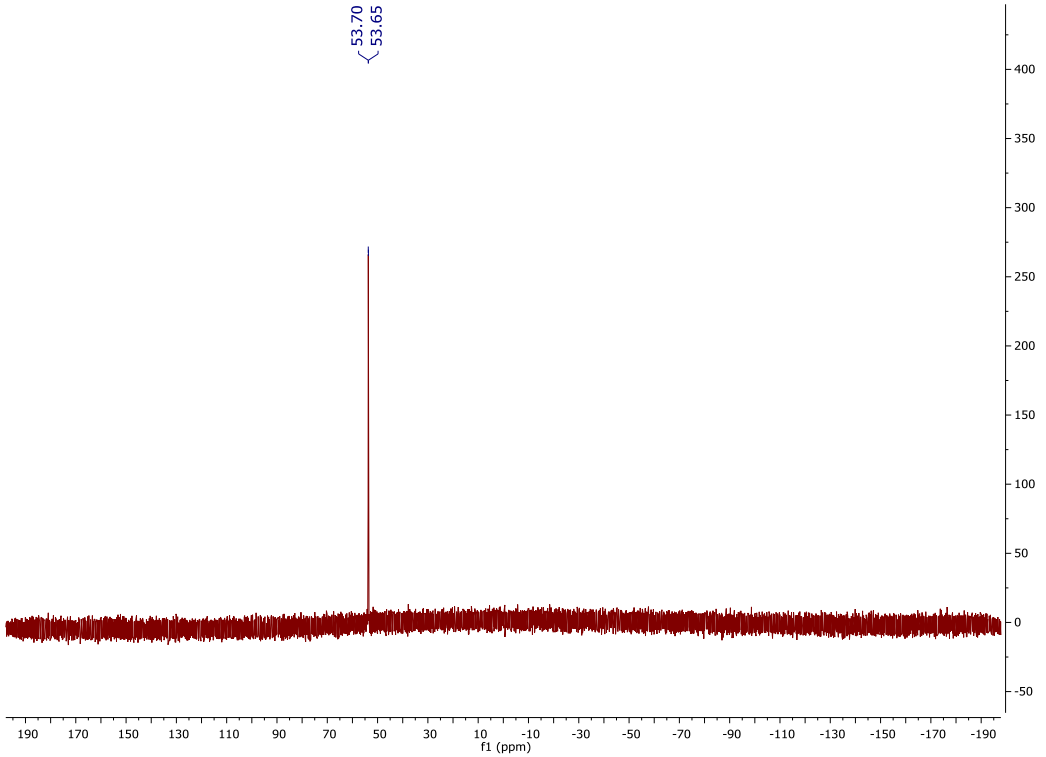


Figure S143. ^{31}P{^{1}H} NMR spectrum of compound **6** ($CDCl_3$, 162.0 MHz, 298 K).

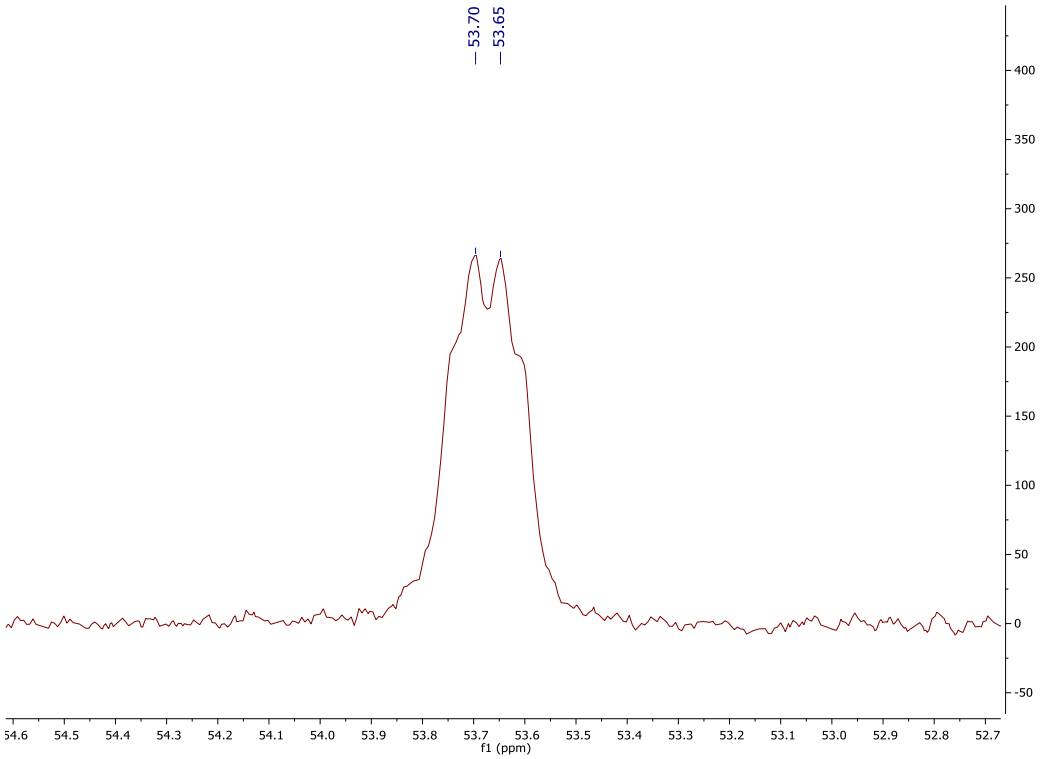


Figure S144. $^{31}P\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 162.0 MHz, 298 K); zoom-in.

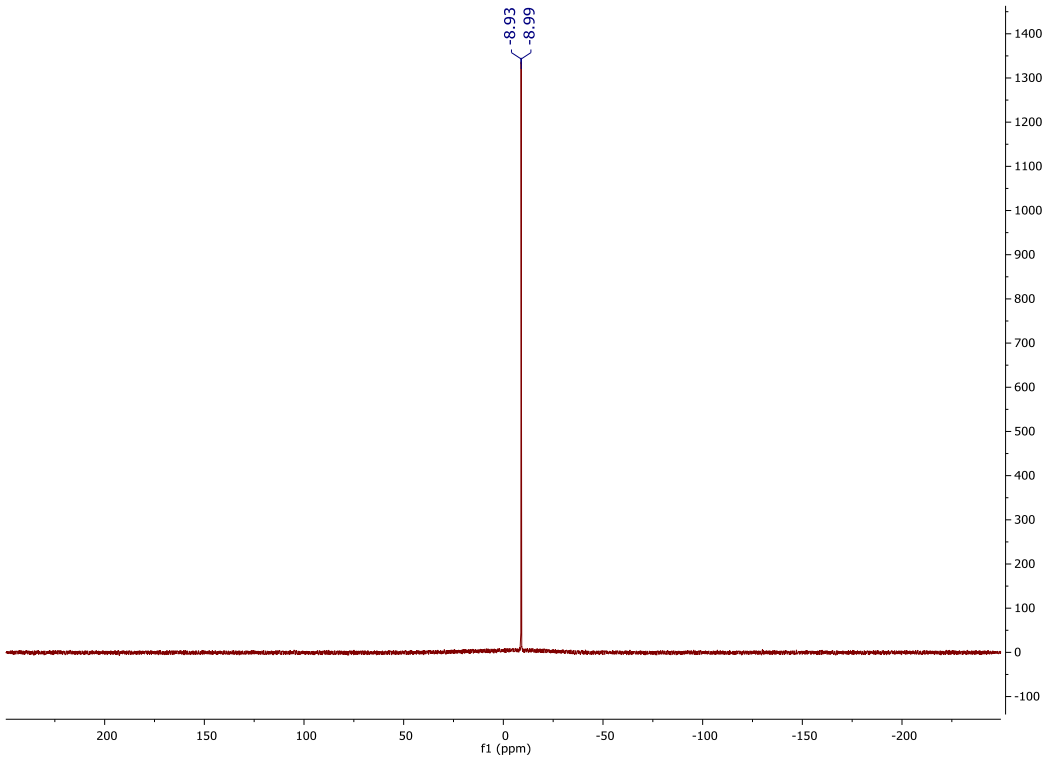


Figure S145. $^{11}B\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 128.4 MHz, 298 K).

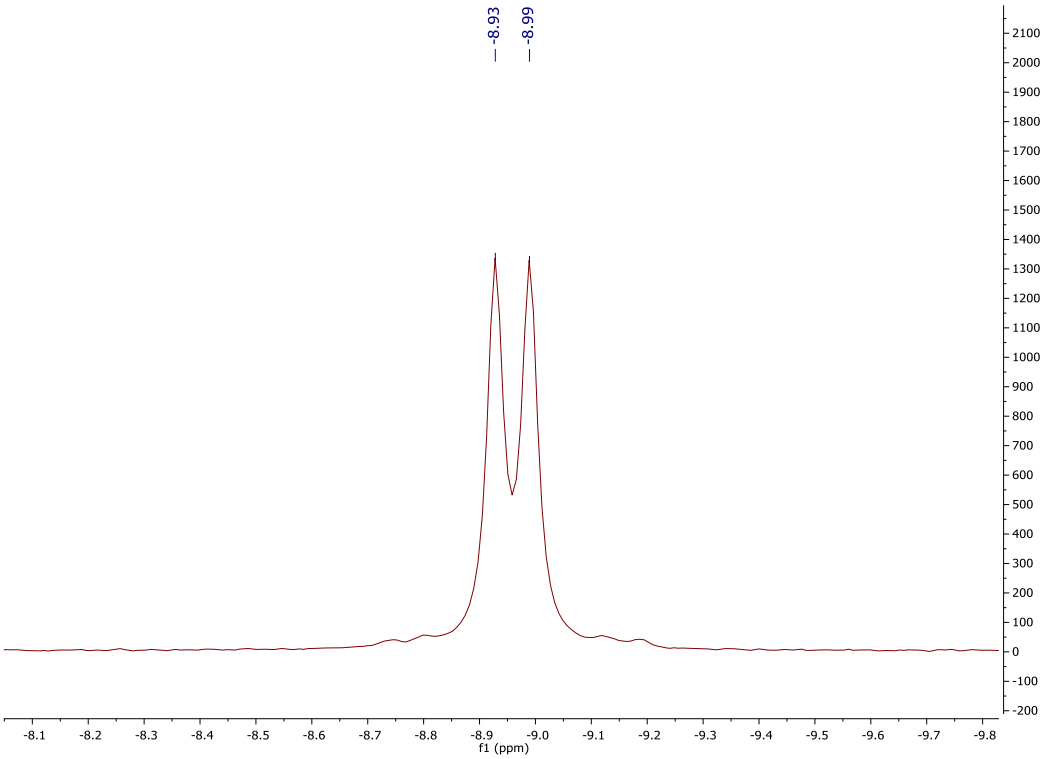


Figure S146. $^{11}B\{^{1}H\}$ NMR spectrum of compound **6** ($CDCl_3$, 128.4 MHz, 298 K); zoom-in.

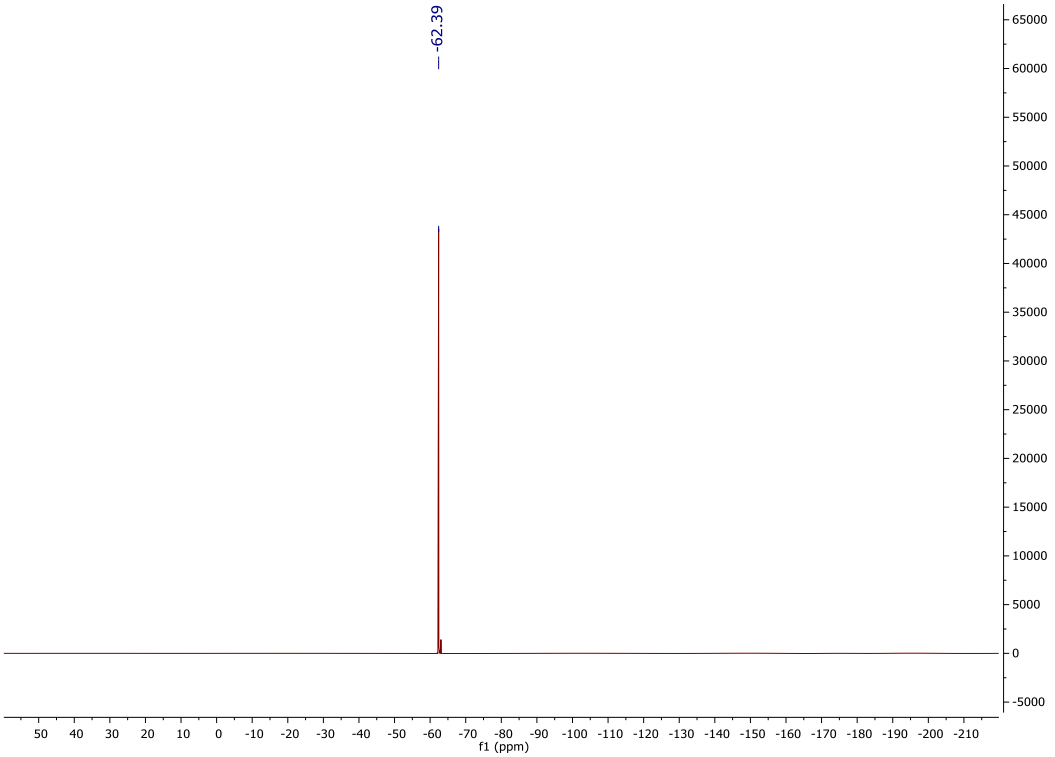


Figure S147. ^{19}F NMR spectrum of compound **6** ($CDCl_3$, 470.5 MHz, 298 K).

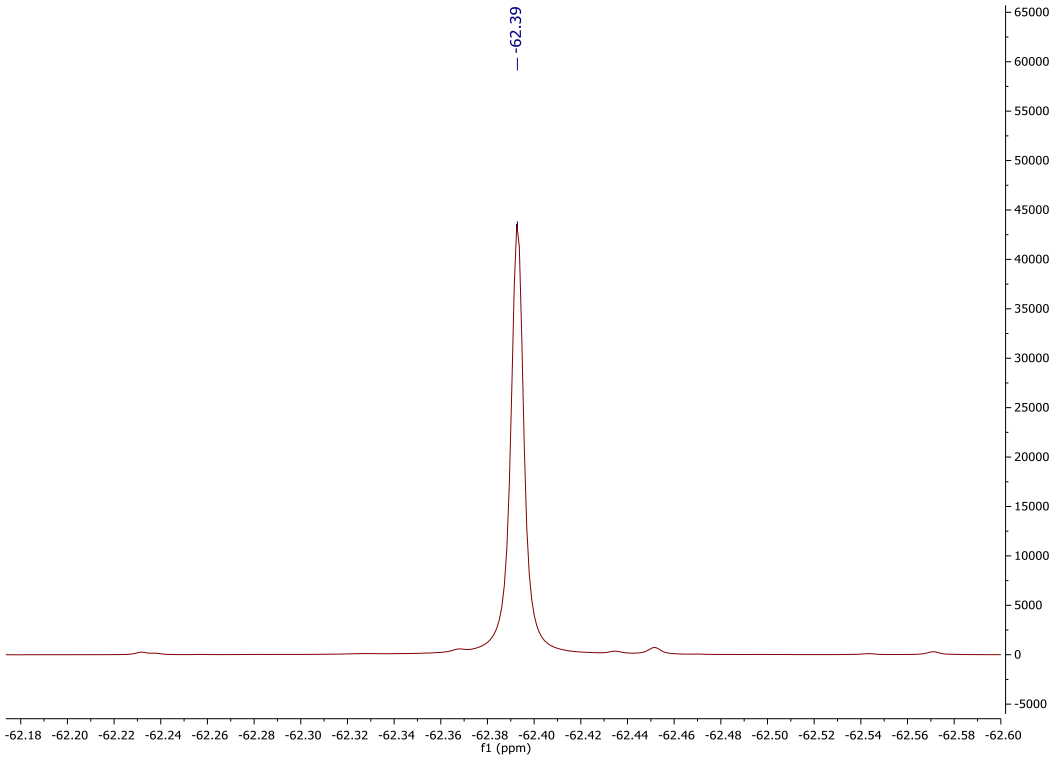
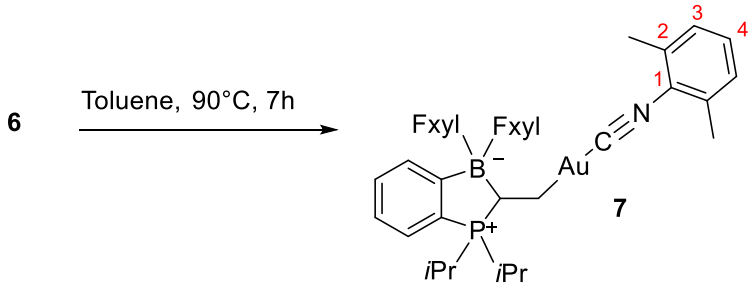


Figure S148. ^{19}F NMR spectrum of compound **6** ($CDCl_3$, 470.5 MHz, 298 K); zoom-in.

Synthesis of 7



An NMR pressure tube was charged with **6** (13 mg, 0.0132 mmol) in 0.6 mL of toluene. The tube was heated at 90°C for 7h. The pale yellow solution turned to red. The volatiles were evaporated and the red oily residue was dispersed in 0.5 mL of pentane. The black solid was filtered out. This solution was kept at –20°C and after 2h, the by-product* that selectively precipitated was eliminated by filtration. The supernatant was concentrated and gave compound **7** as white solid after crystallization at –80°C for 3 weeks (4.7 mg, 0.0048 mmol, 36 %). *The low isolated yield is due to the high solubility of the compound. N.B.: many crystallization tests have been performed using different methods and solvent systems based on THF, Et_2O, DCM, heptane, benzene, toluene mixtures*. Crystals suitable for X-ray diffraction analysis were obtained from a saturated pentane solution after 3 weeks at –20°C.

** The by-product disclosing a ^{31}P NMR resonance at 30 ppm was authenticated as the **1**/CNXyl adduct (which was prepared independently).*

HRMS (DCI-CH_4): exact mass (monoisotopic) calcd. for $[M+H]^+$ $(C_{39}H_{37}AuBF_{12}NP)^{+\cdot}$:986.2238; found 986.2208.

^1H NMR ($CDCl_3$, 500.1 MHz, 298 K) : δ 7.90 (br. s, 2H, $H_{o\text{-Fxyl}}$), 7.75 (br. s, 2H, $H_{o\text{-Fxyl}}$), 7.57 (br. s, 1H, $H_{p\text{-Fxyl}}$), 7.51 (br. s, 1H, $H_{p\text{-Fxyl}}$), 7.49-7.43 (m, 2H, H_{Ar}), 7.30 (m, 2H, H_{Ar}), 7.28 (t, 1H, $^3J_{HH}$ = 7.6 Hz, H_4), 7.12 (d, 2H, $^3J_{HH}$ = 7.6 Hz, H_3), 2.82[£] (pseudo-t br, 1H, $^3J_{HH}$ = $^2J_{PH}$ = 12.5 Hz, B-CH), 2.73 (heptd, 1H, $^3J_{HH}$ = 7.1 Hz, $^2J_{PH}$ = 11.6 Hz, $CH_{i\text{Pr}}$), 2.30 (s, 6H, $CH_{3\text{Xyl}}$), 2.17 (heptd, 1H, $^3J_{HH}$ = 7.3 Hz and $^2J_{PH}$ =11.4 Hz, $CH_{i\text{Pr}}$), 1.46[£$] (br, 1H, B-CH-C$H_2$), 1.43 (dd, 3H, $^3J_{HH}$ =7.1 Hz, $^3J_{PH}$ =15.1 Hz, $CH_{3i\text{Pr}}$), 1.33 (dd, 3H, $^3J_{HH}$ = 7.2 Hz and $^3J_{PH}$ = 14.4 Hz, $CH_{3i\text{Pr}}$), 1.28 (dd, 3H, $^3J_{HH}$ =7.2 Hz, $^3J_{PH}$ = 14.7 Hz, $CH_{3i\text{Pr}}$), 0.90 (dd, 3H, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 15.8 Hz, $CH_{3i\text{Pr}}$), 0.82 (pseudo-td, 1H, $^3J_{HH}$ = $^2J_{HH}$ =12.5 Hz, $^3J_{PH}$ = 7.8 Hz, B-CH-CH_2).

[£] very broad signals were observed due to the presence of boron in α/β position.

[$] partially masked by the CH_3 signal of *i*Pr at 1.43 ppm.

Jmod($^{13}C\{^1H\}$) NMR ($CDCl_3$, 125.8 MHz, 298 K) δ 171.9 (br. s, B-C_{ipso}), 166.4 (br. s, C_{CNXyl}), 161.92 (br. s, B-C_{ipso}), 159.2 (br. s, B-C_{ipso}), 136.0 (s, C_2), 135.7 (s, $CH_{o\text{-Fxyl}}$), 134.1 (d, J_{PC} = 14.7 Hz, CH_{Ar}), 133.9 (s, $CH_{o\text{-Fxyl}}$), 132.5 (s, CH_{Ar}), 130.3 (s, C_4), 129.5 (d, J_{PC} = 9.6 Hz, CH_{Ar}), 129.1 (q, $^2J_{FC}$ = 31.6 Hz, $C_{ipso\text{-CF3}}$), 128.3 (q, J_{FC} = 31.7 Hz, $C_{ipso\text{-CF3}}$), 128.3 (s, C_3), 127.3 (d, J_{PC} = 82.1 Hz, P-C_{ipso}), 126.4 (d, J_{PC} = 9.5 Hz, CH_{Ar}), 125.0 (br. s, C_1), 124.8 (q, $^1J_{FC}$ = 272.7 Hz, CF_3), 124.7 (q, $^1J_{FC}$ = 272.7 Hz, CF_3), 118.2 (hept, $^3J_{FC}$ = 4.1 Hz, $CH_{p\text{-Fxyl}}$), 118.0 (hept, $^3J_{FC}$ = 3.9 Hz, $CH_{p\text{-Fxyl}}$), 28.8[&] (br. s, B-CH), 22.7 (d, $^1J_{PC}$ = 38.0 Hz, $CH_{i\text{Pr}}$), 21.2 (d, $^1J_{PC}$ = 41.1 Hz, $CH_{i\text{Pr}}$), 18.5 (s, $CH_{3\text{Xyl}}$), 18.3 (d, $^2J_{PC}$ = 3.0 Hz, $CH_{3i\text{Pr}}$), 17.4 (d, $^2J_{PC}$ = 3.0 Hz, $CH_{3i\text{Pr}}$),17.0 (d, $^2J_{PC}$ = 3.6 Hz, $CH_{3i\text{Pr}}$), 16.9 (d, $^2J_{PC}$ = 1.3 Hz, $CH_{3i\text{Pr}}$), 15.8 (d, $^2J_{PC}$ = 6.9 Hz, CH_2).

[&] very broad signal due to the presence of boron, attributed by HSQC.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.5 MHz, 298 K) : δ 57.0 (s).

^{19}F NMR ($CDCl_3$, 470.5 MHz, 298 K) : δ -62.3 (s, 6F, CF_3), -62.4 (s, 6F, CF_3).

$^{11}B\{1H\}$ ($CDCl_3$, 160.5 MHz, 298 K) : δ -5.6 (s).

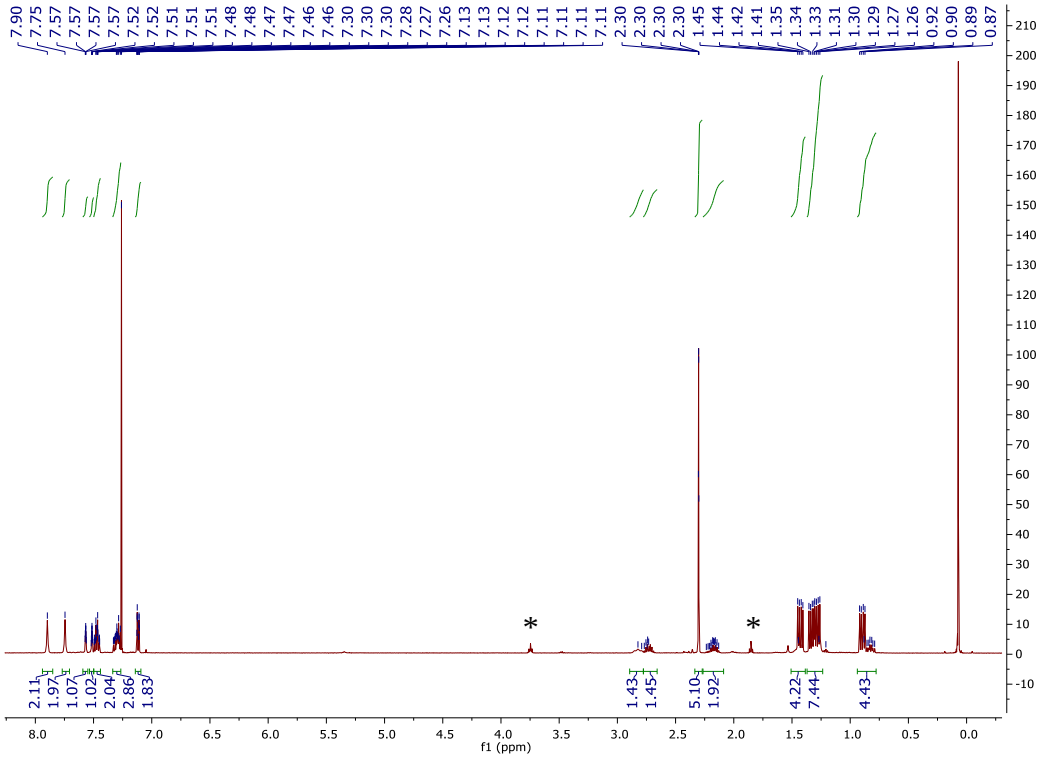


Figure S149. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K). * remaining traces of THF coming from crystallization attempts.

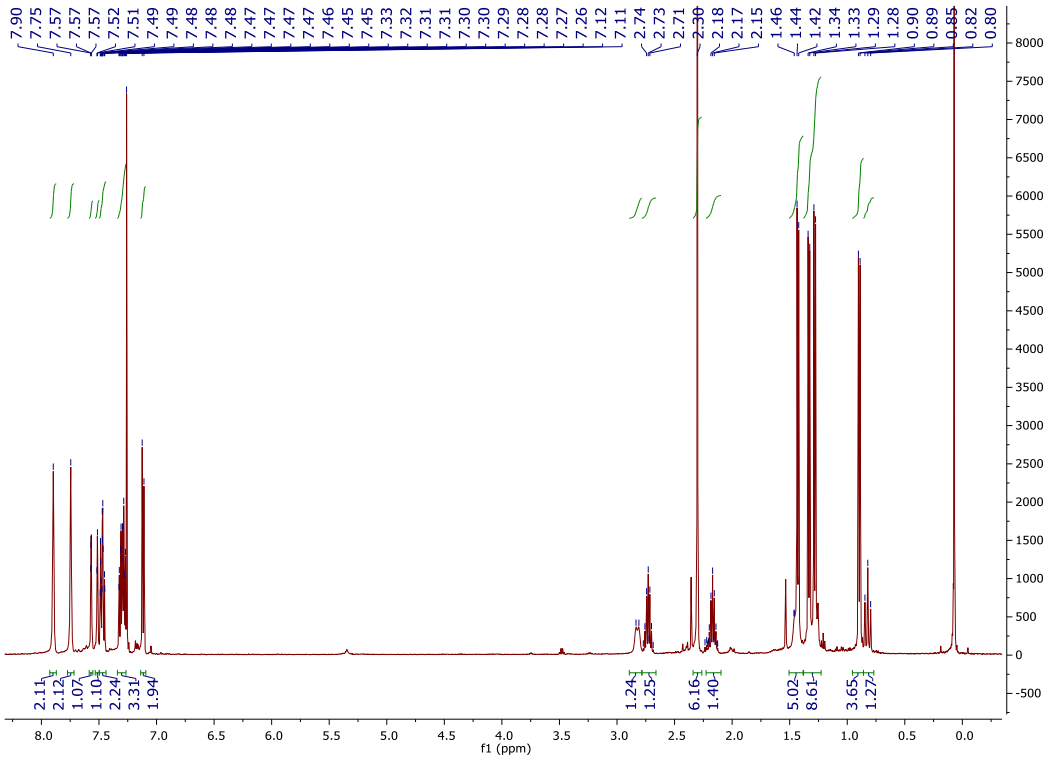


Figure S150. ^{1}H{^{31}P} NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K).

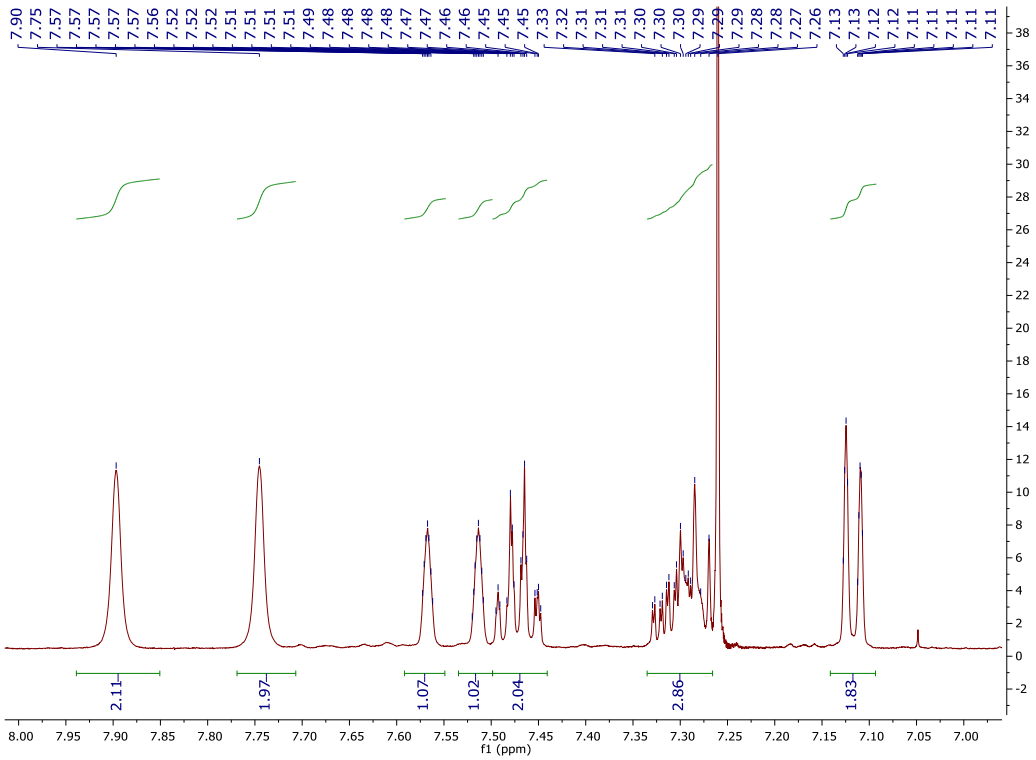


Figure S151. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aromatic area.

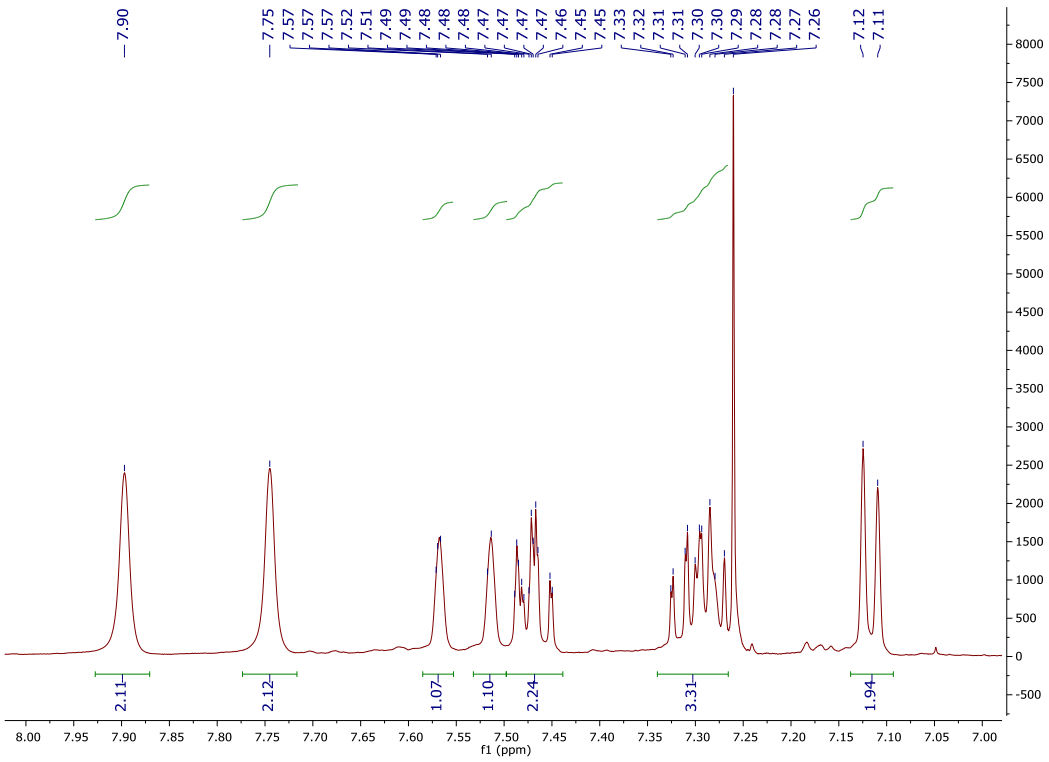


Figure S152. $^{1}H\{^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aromatic area

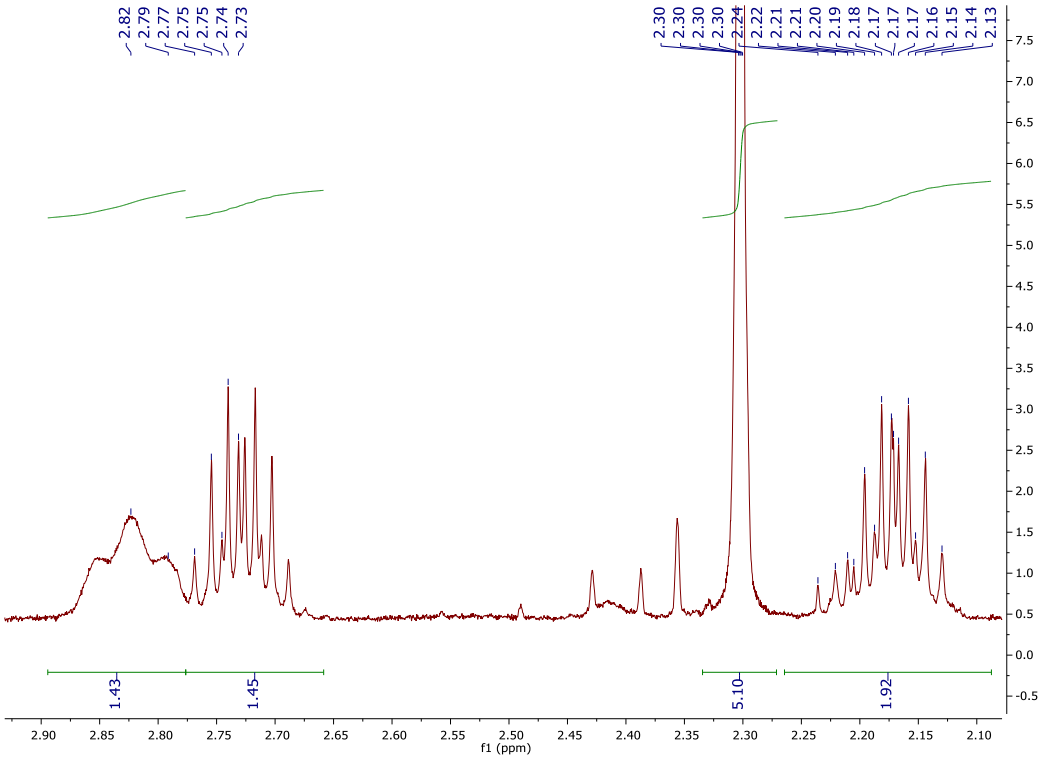


Figure S153. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aliphatic area.

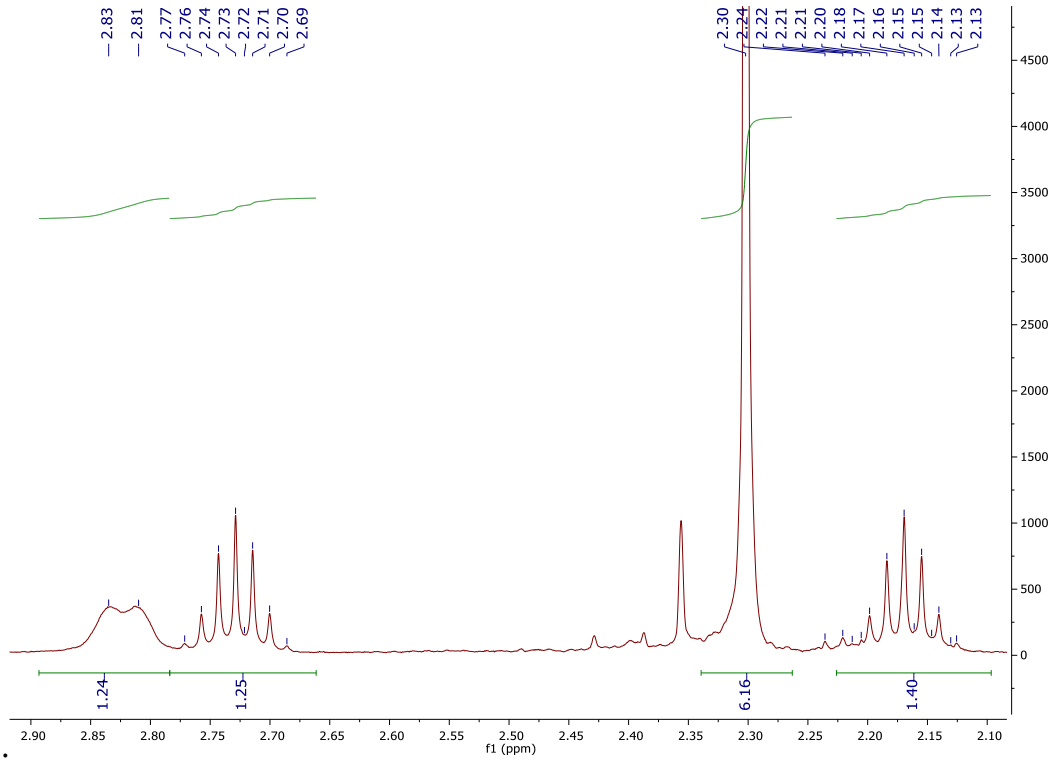


Figure S154. $^{1}H\{^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aliphatic area.

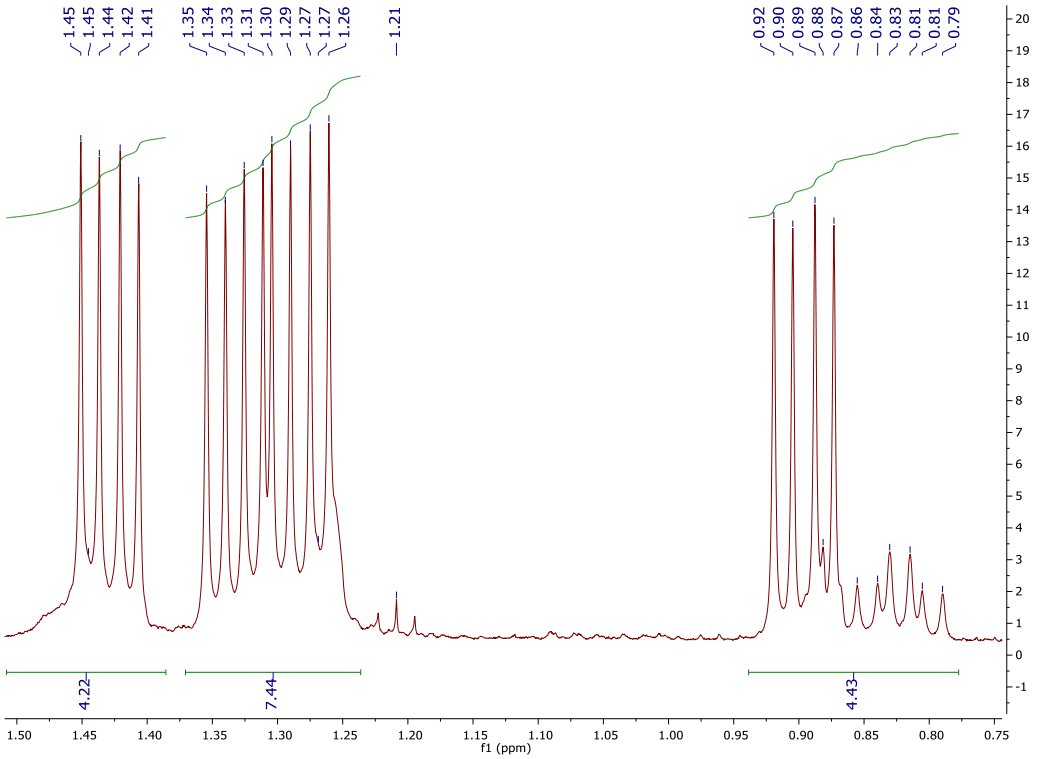


Figure S155. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aliphatic area.

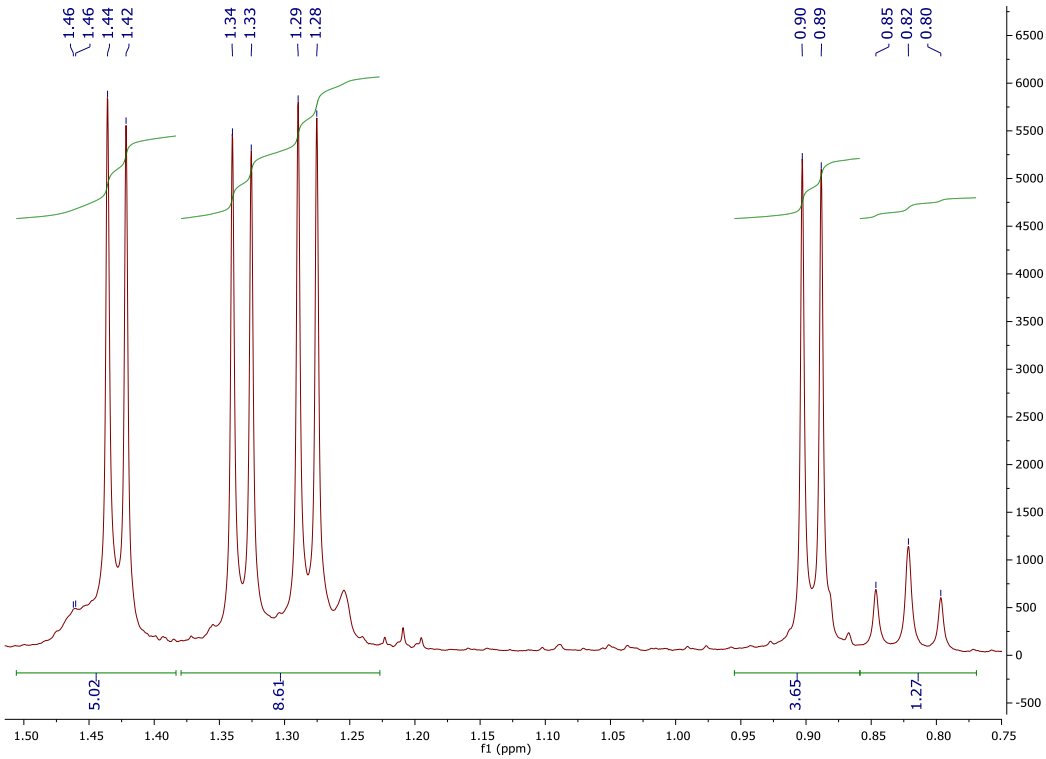


Figure S156. $^{1}H\{^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K) ; aliphatic area.

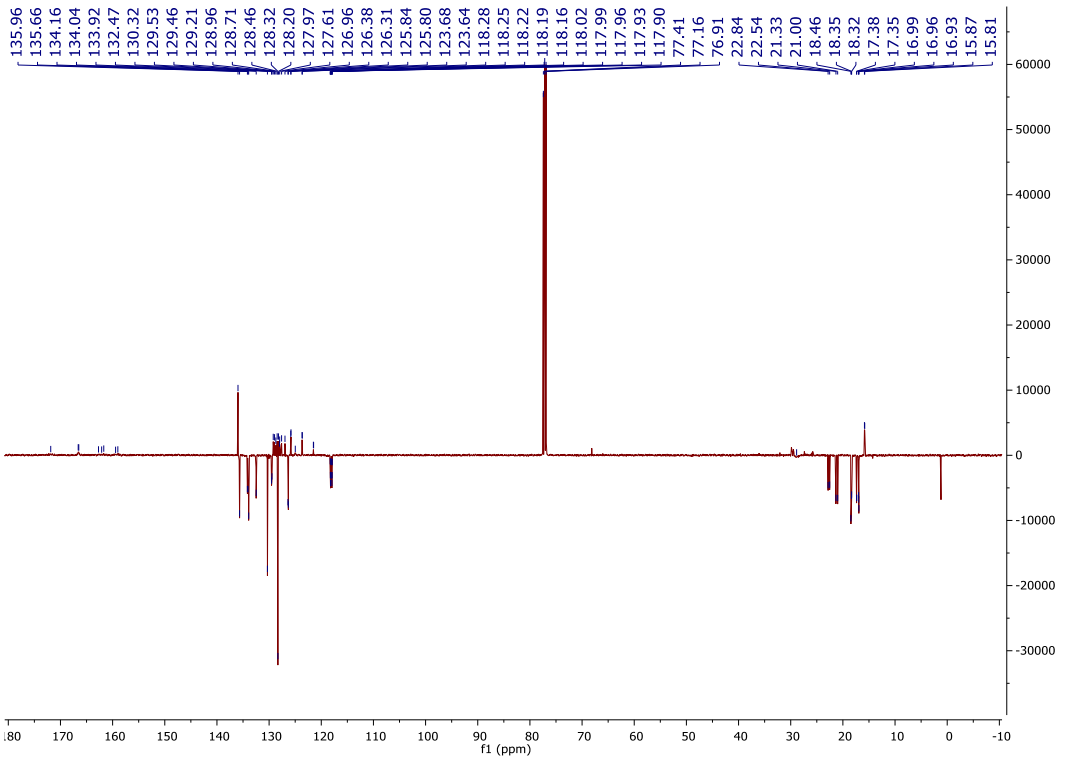


Figure S157. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **7** ($CDCl_3$, 125.8 MHz, 298 K).

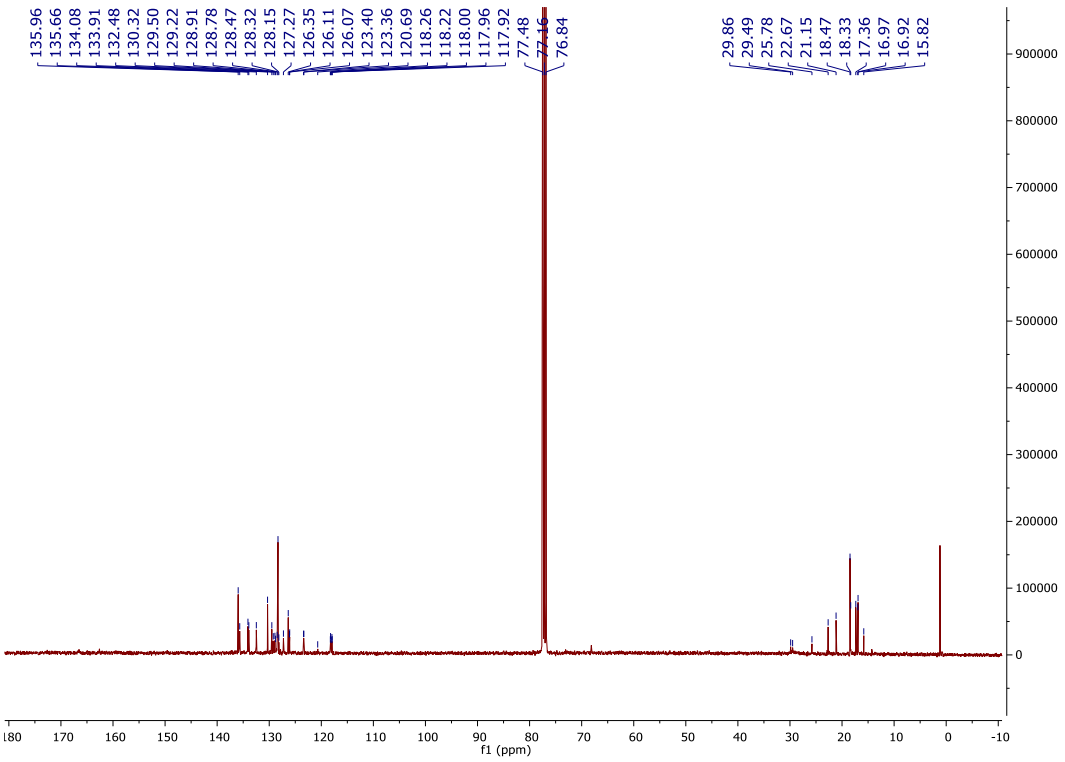


Figure S158. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 100.6 MHz, 298 K).

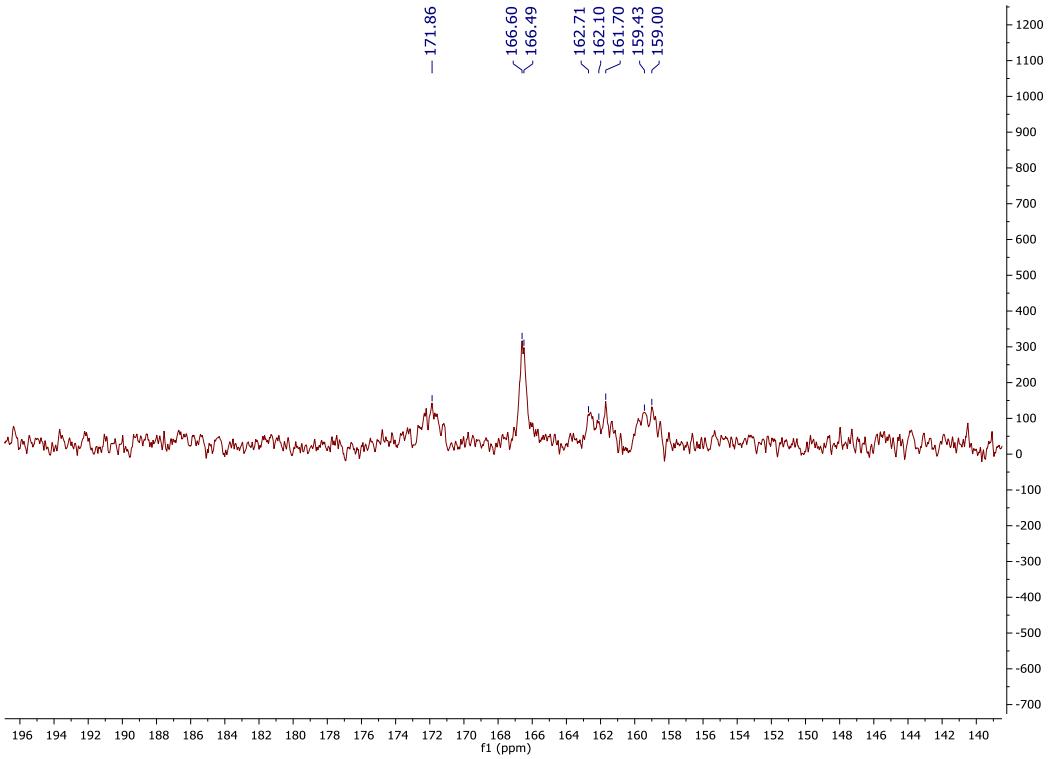


Figure S159. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **7** ($CDCl_3$, 125.8 MHz, 298 K) ; aromatic area.

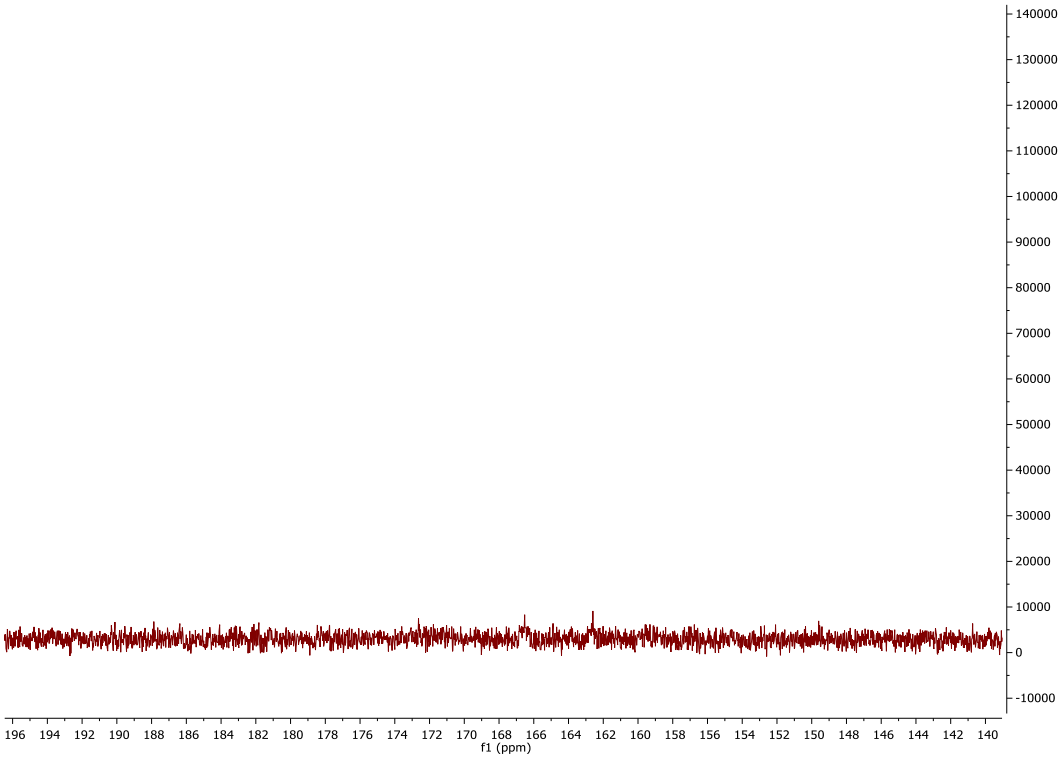


Figure S160. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 100.6 MHz, 298 K); aromatic area.

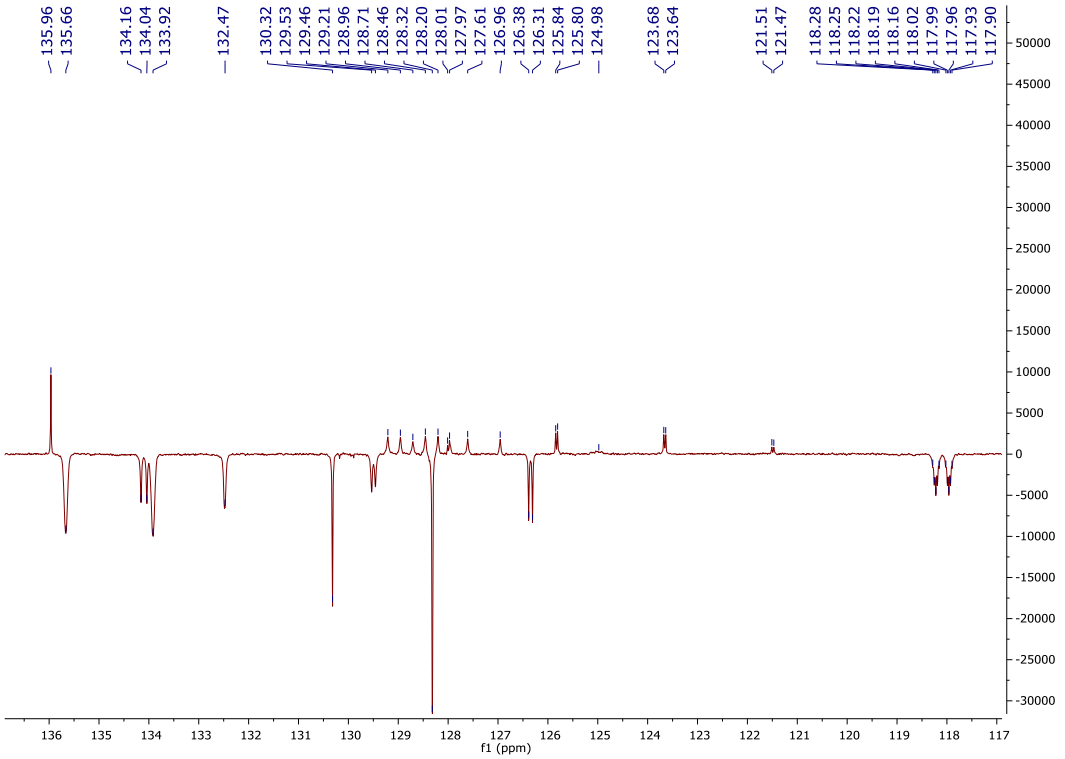


Figure S161. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **7** ($CDCl_3$, 125.8 MHz, 298 K) ; aromatic area.

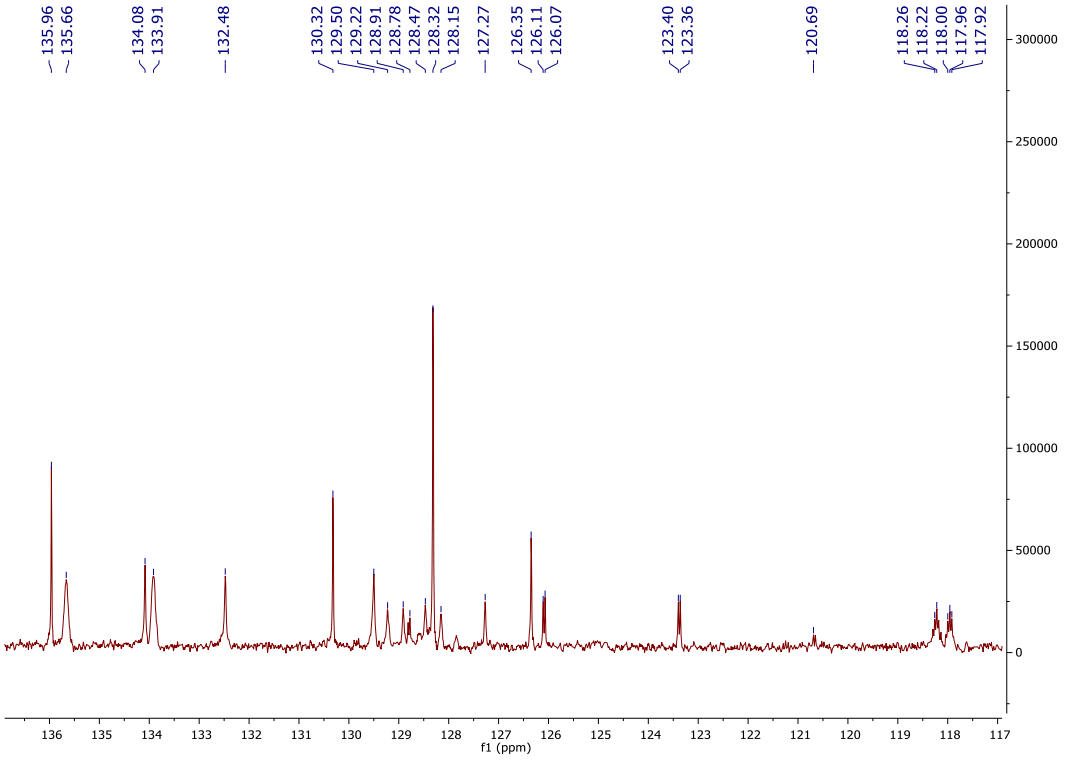


Figure S162. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 100.6 MHz, 298 K) ; aromatic area.

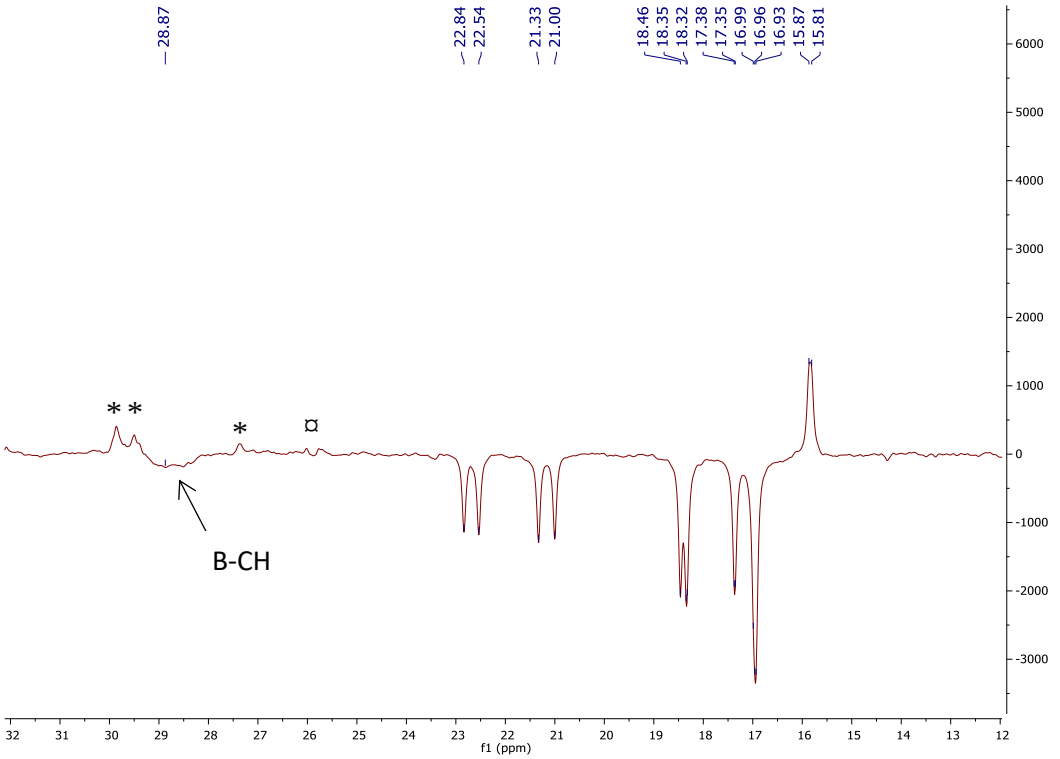


Figure S163. Jmod($^{13}C\{^{1}H\}$) NMR spectrum of compound **7** ($CDCl_3$, 125.8 MHz, 298 K) ; aliphatic area. * non-identified impurity and ¤ remaining traces of THF.

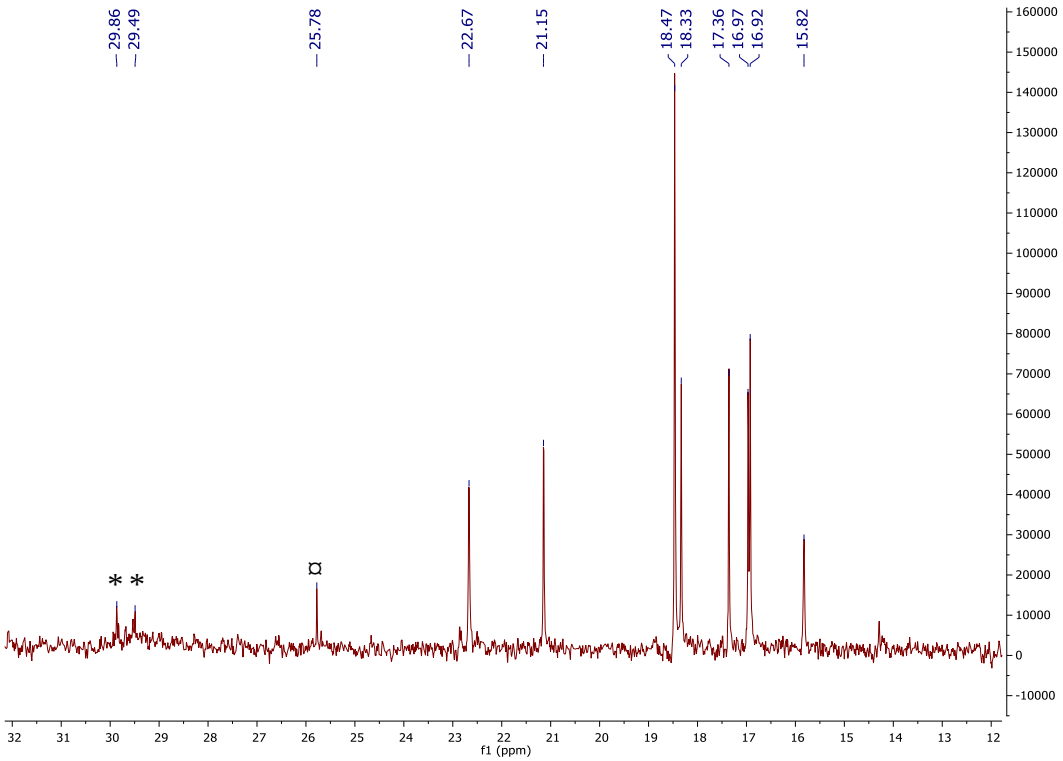


Figure S164. $^{13}C\{^{1}H$; $^{31}P\}$ NMR spectrum of compound **7** ($CDCl_3$, 100.6 MHz, 298 K) ; aliphatic area. * non-identified impurity and ¤ remaining traces of THF.

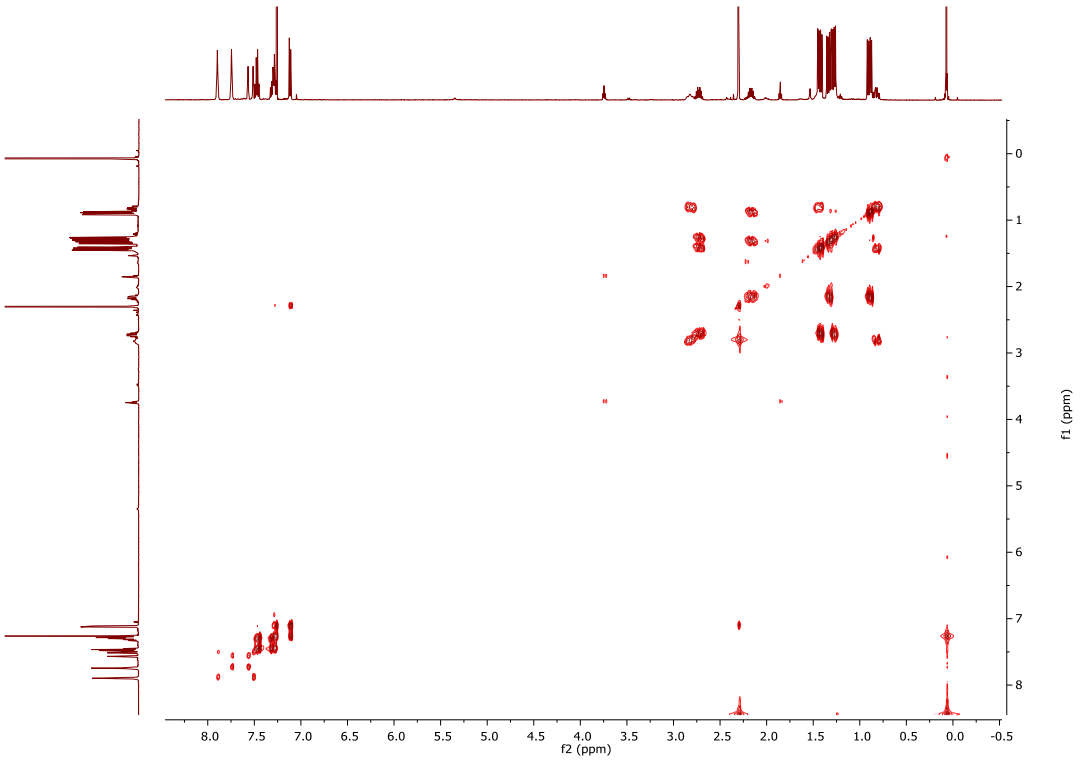


Figure S165. COSY (^{1}H ;^{1}H) NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K).

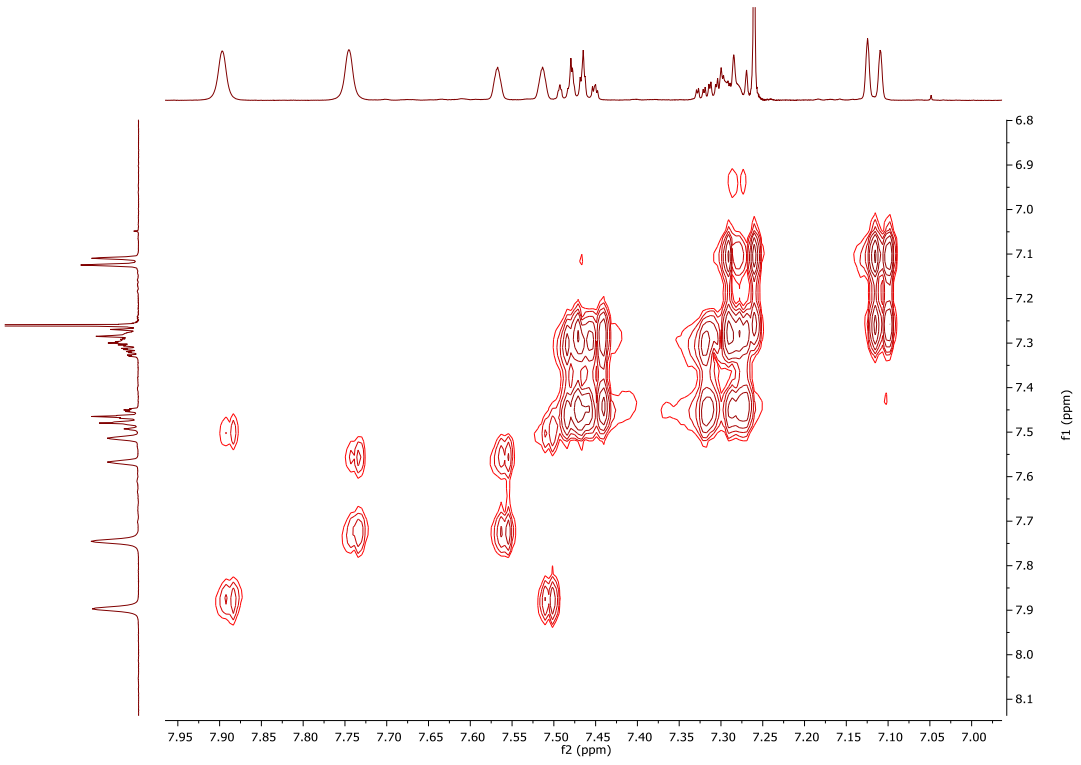


Figure S166 COSY (^{1}H ;^{1}H) NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K).

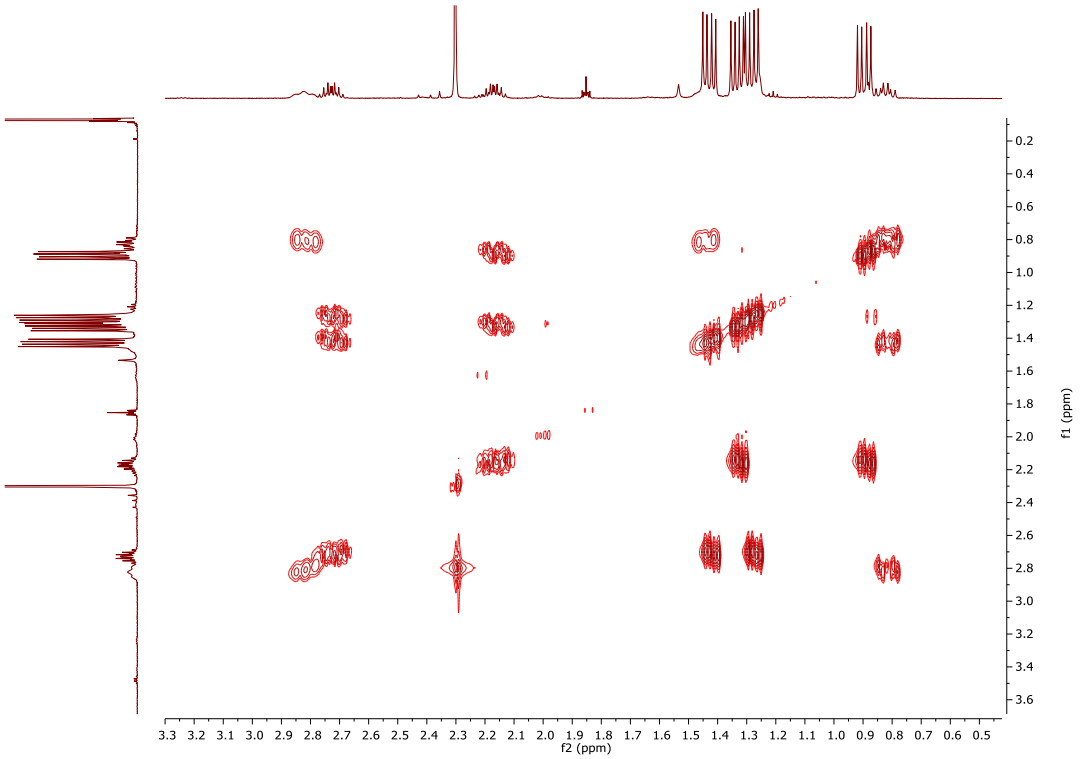


Figure S167. COSY (^{1}H ;^{1}H) NMR spectrum of compound **7** ($CDCl_3$, 500.1 MHz, 298 K).

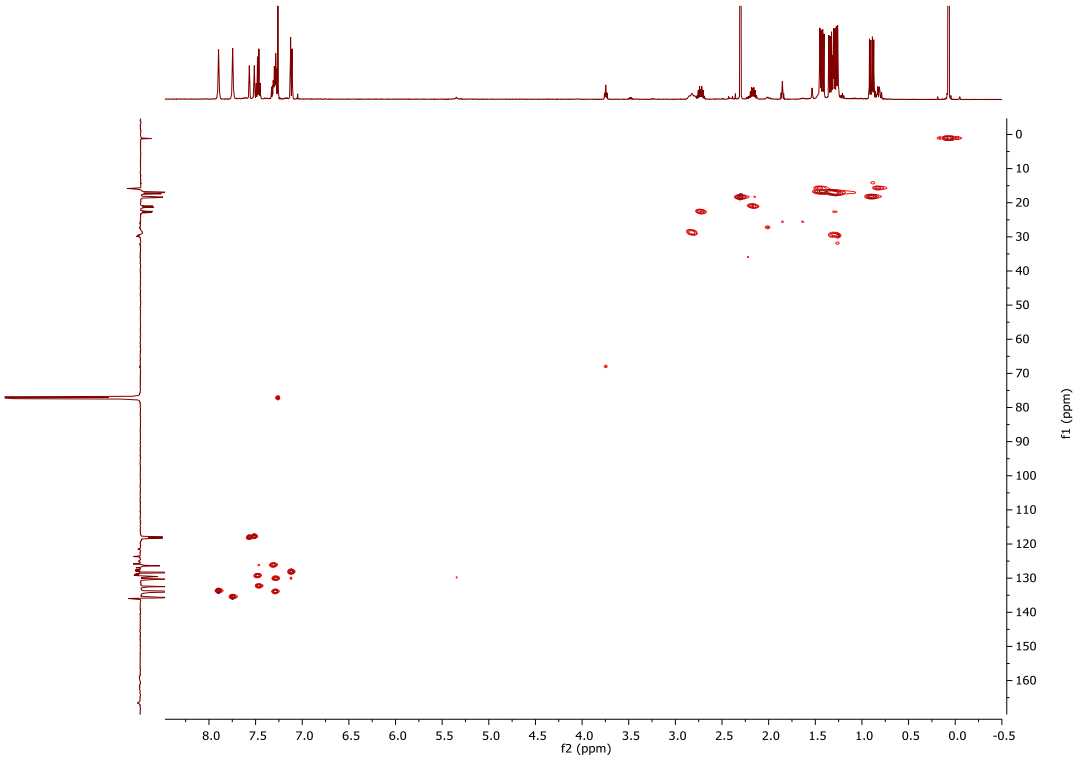


Figure S168. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

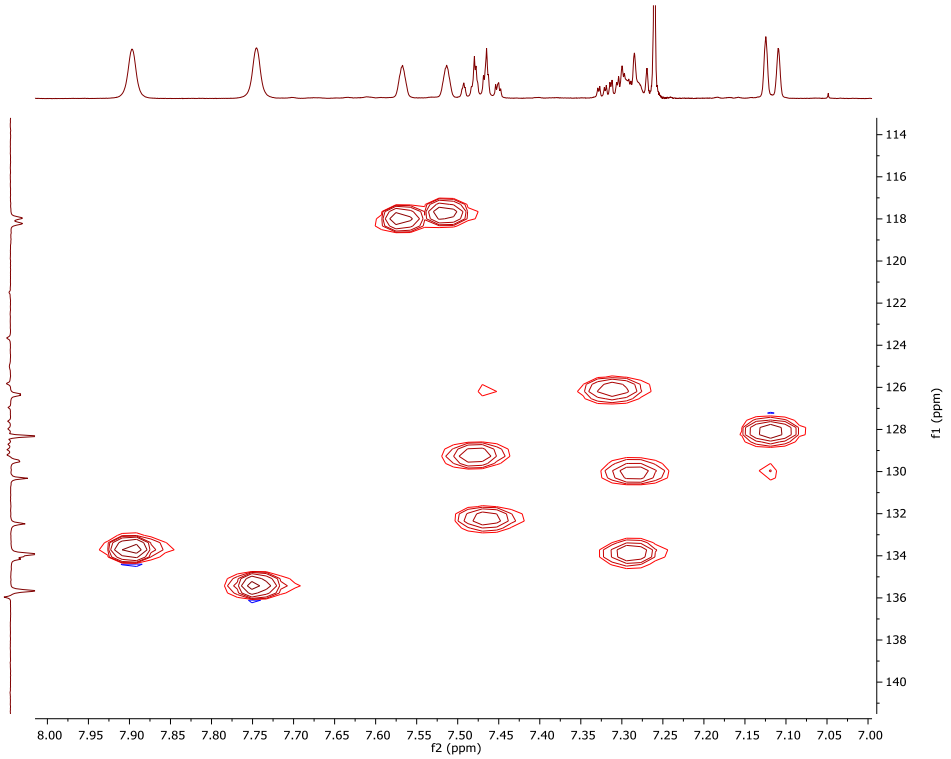


Figure S169. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

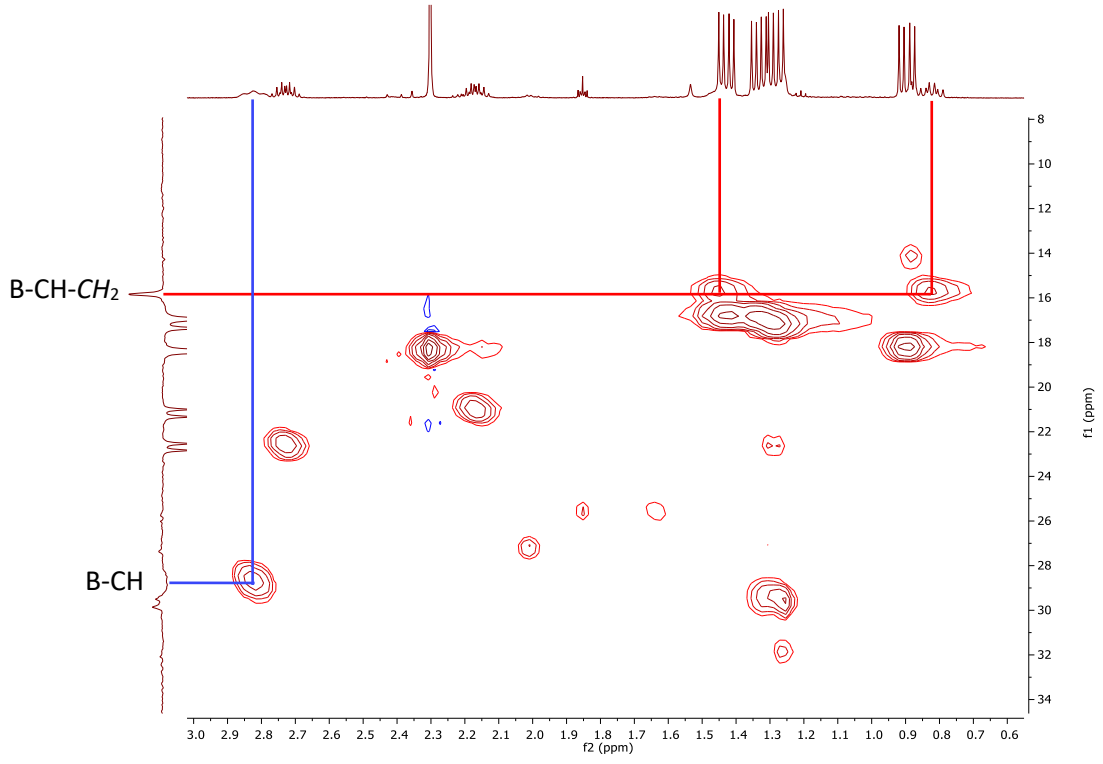


Figure S170. HSQC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

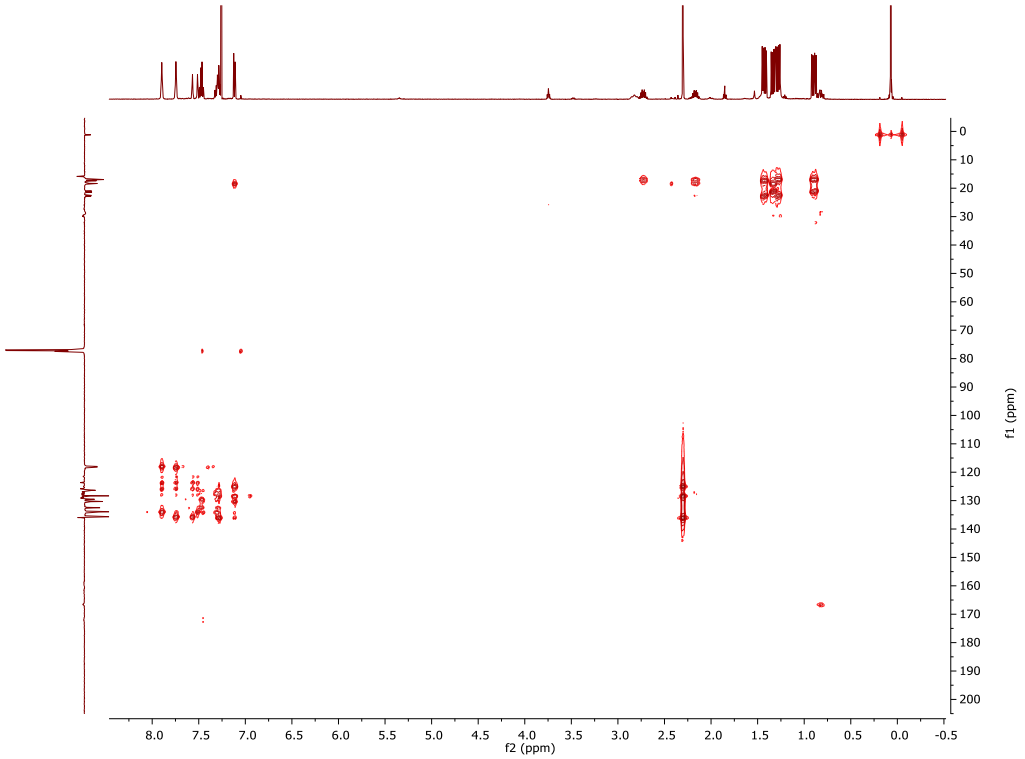


Figure S171. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

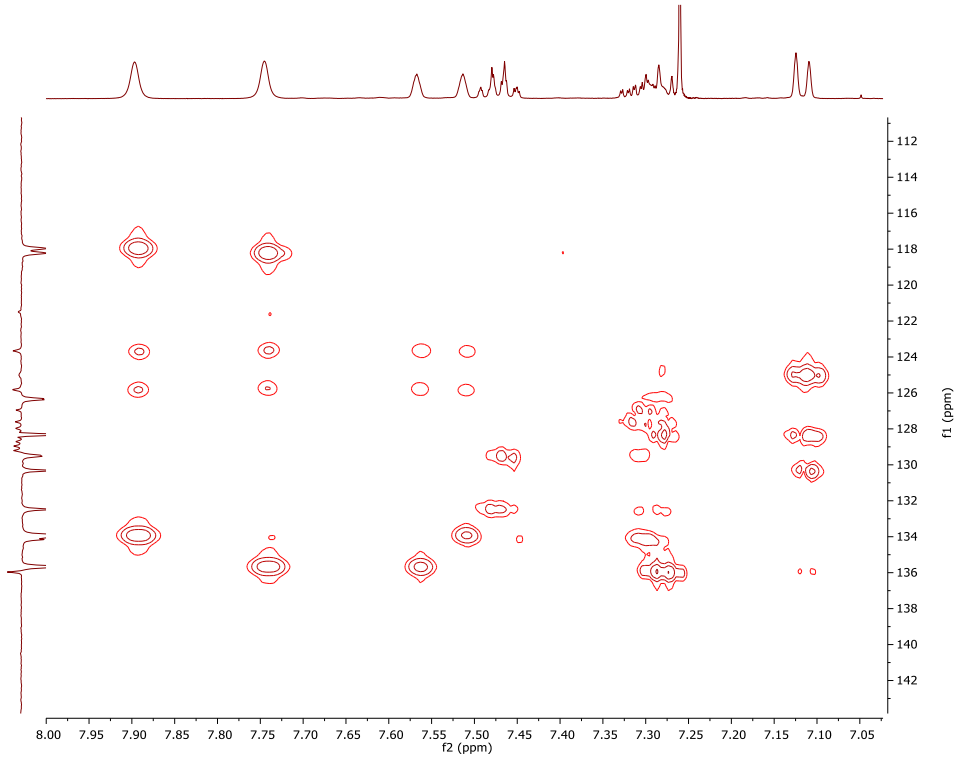


Figure S172. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

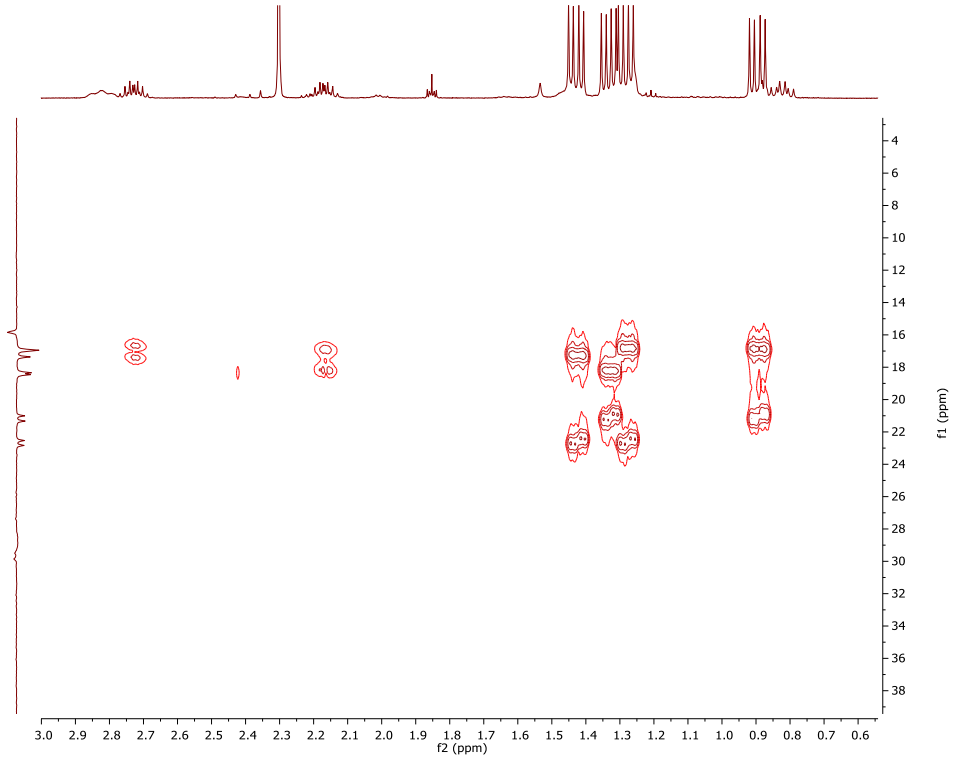


Figure S173. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K).

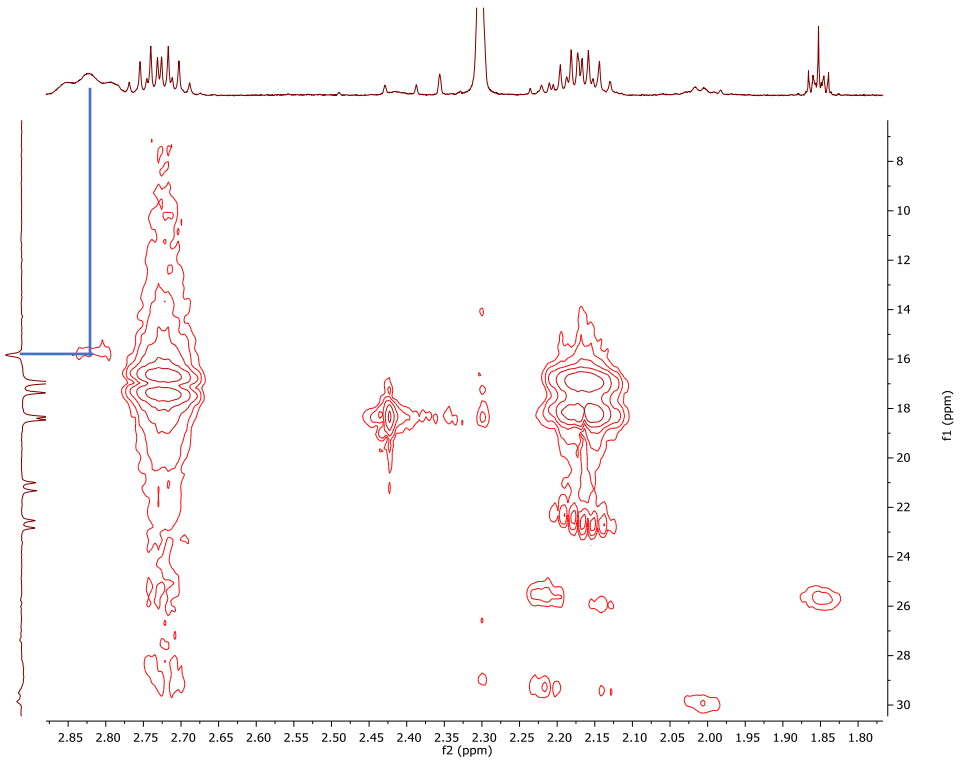


Figure S174. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aliphatic area, zoom-in.

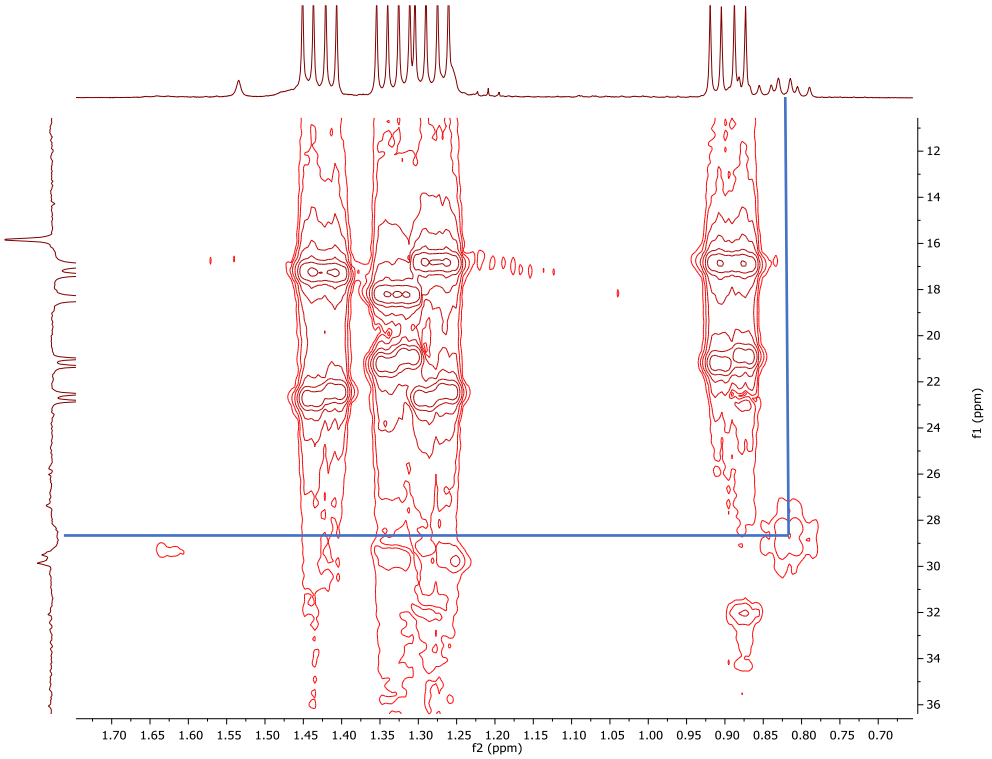


Figure S175. HMBC (^{1}H ; ^{13}C{^{1}H}) NMR spectrum of compound **7** ($CDCl_3$, 500.1 / 125.8 MHz, 298 K); aliphatic area, zoom-in.

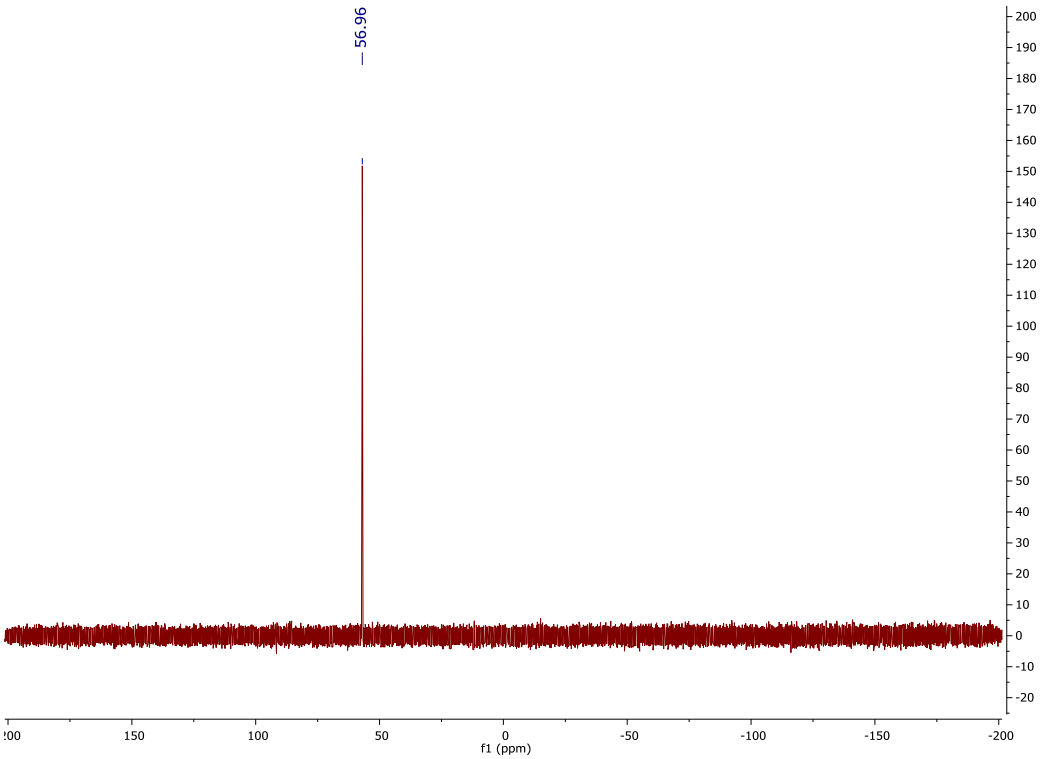


Figure S176. ^{31}P{^{1}H} NMR spectrum of compound **7** ($CDCl_3$, 202.5 MHz, 298 K).

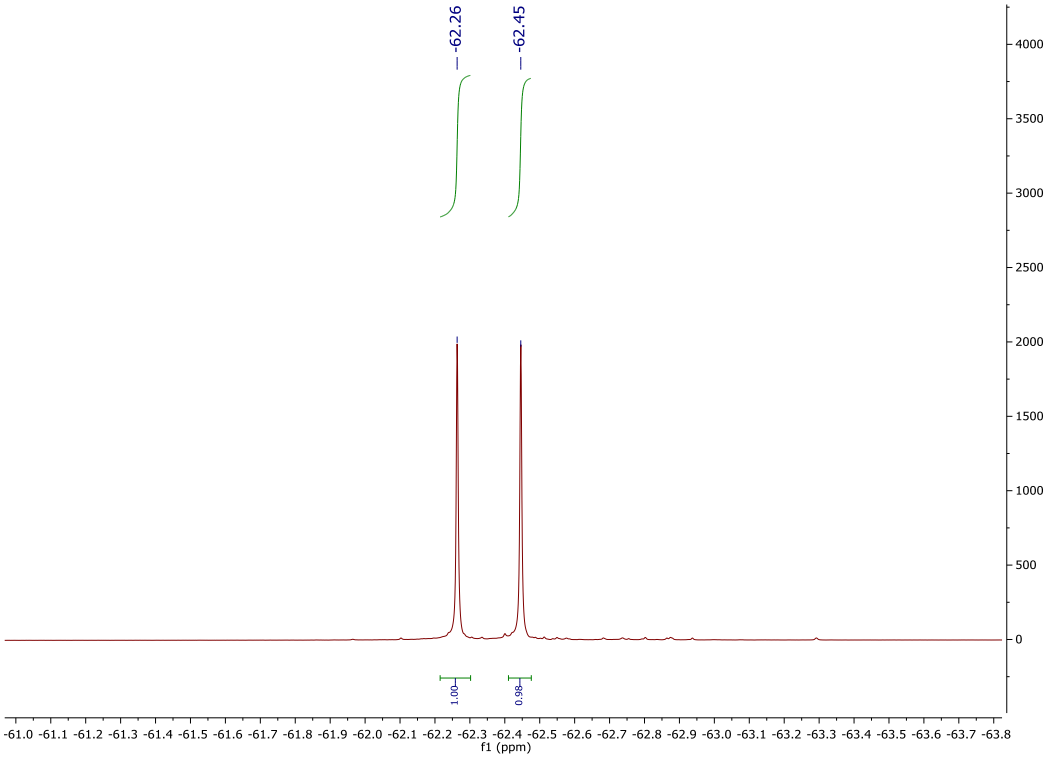


Figure S177. ^{19}F NMR spectrum of compound **7** ($CDCl_3$, 470.5 MHz, 298 K).

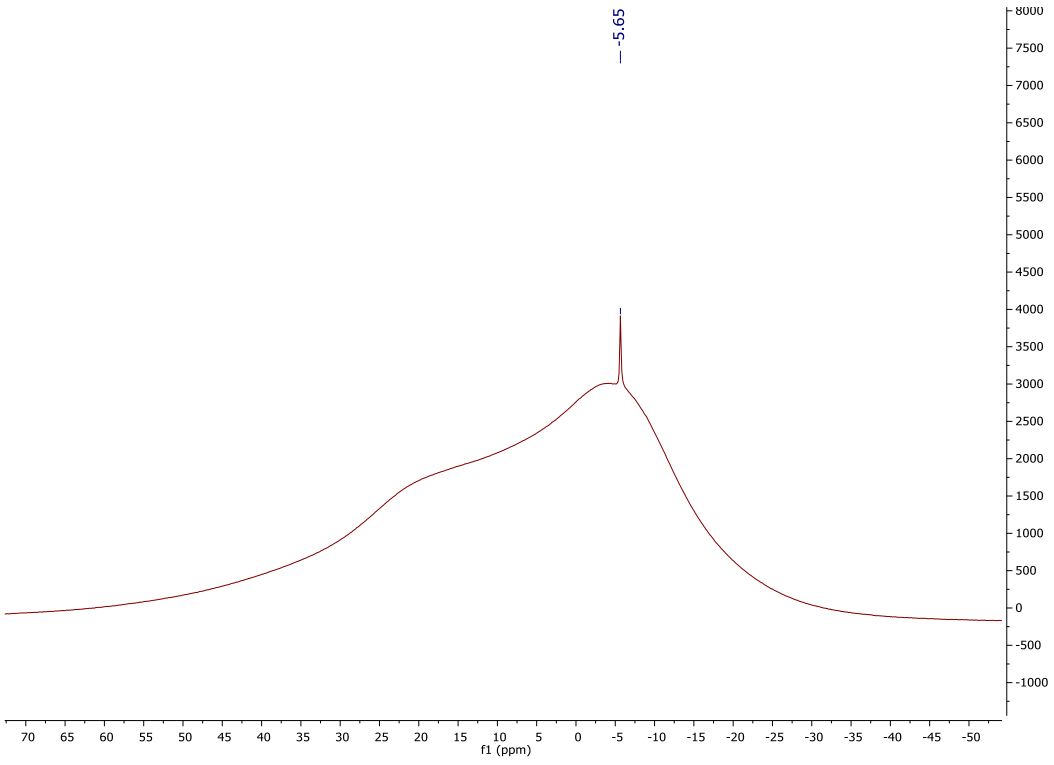
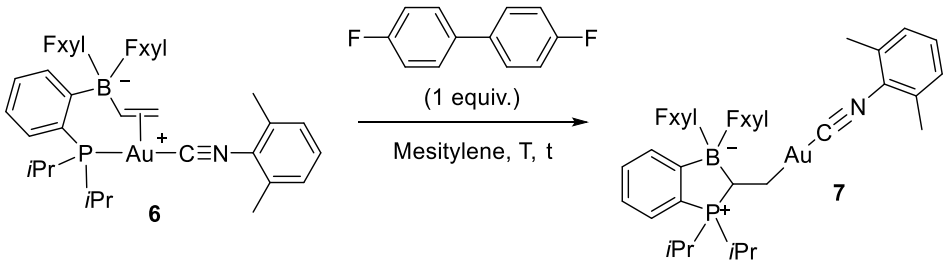


Figure S178. $^{11}B\{^1H\}$ NMR spectrum of compound **7** ($CDCl_3$, 470.5 MHz, 298 K).

Kinetic investigation

Experimental results:



Kinetic experiments were performed using NMR techniques on Bruker Avance III HD 400 spectrometer equipped with a 5 mm Z-gradient broadband probe. In a glovebox, an NMR pressure tube was charged with compound **6** (0.01 mmol). In parallel a 0.02131 M stock solution of 4,4'-difluorobiphenyl (internal standard) in mesitylene was prepared. The NMR tube was filled with 0.5 mL of this solution and the pressure NMR tube was tightly sealed with a teflon cap. The NMR tube was then taken out of the glovebox. No reaction is observed at r.t. so there is no need to freeze the mixture prior to the NMR monitoring. Once the set temperature correctly adjusted, the NMR tube was injected and a multi-scan sequence was launched. The progress of the reaction was monitored by quantitative $^{19}F\{^{1}H\}$zgig NMR (32 scans, 5 s relaxation delay, 13.70 μs pulse width). The reaction was carried out at four temperatures: 343, 353, 368 and 383 K. An example of stacked spectra extracted from the experiment run at 353 K is depicted in **Figure S179**. All spectra were phased and integrated using Mnova 11.0 Mestrelab software. Experimental kinetic data were analyzed, plotted and modeled using Microsoft Excel software from Office Pack 2013.

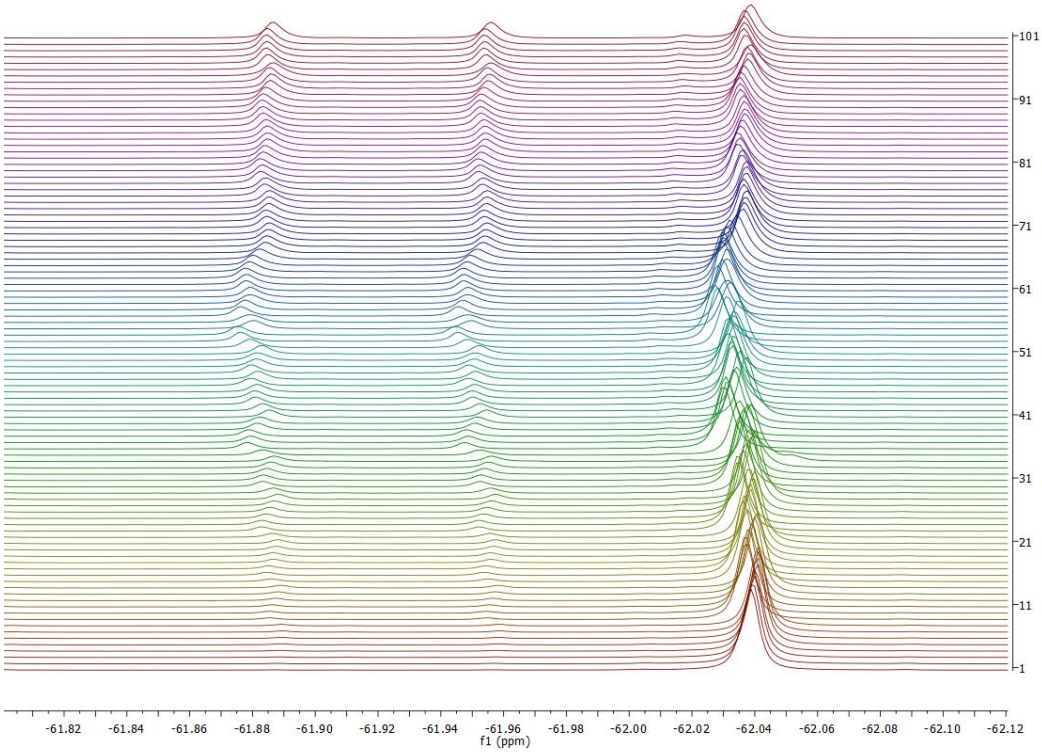


Figure S179. $^{19}F\{^{1}H\}$ NMR spectra (mesitylene, 376.5 MHz, 353 K) showing consumption of **6** (as a singlet at δ –62.04 ppm) and formation of **7** (as two singlets at δ –61.89 and –61.96 ppm).

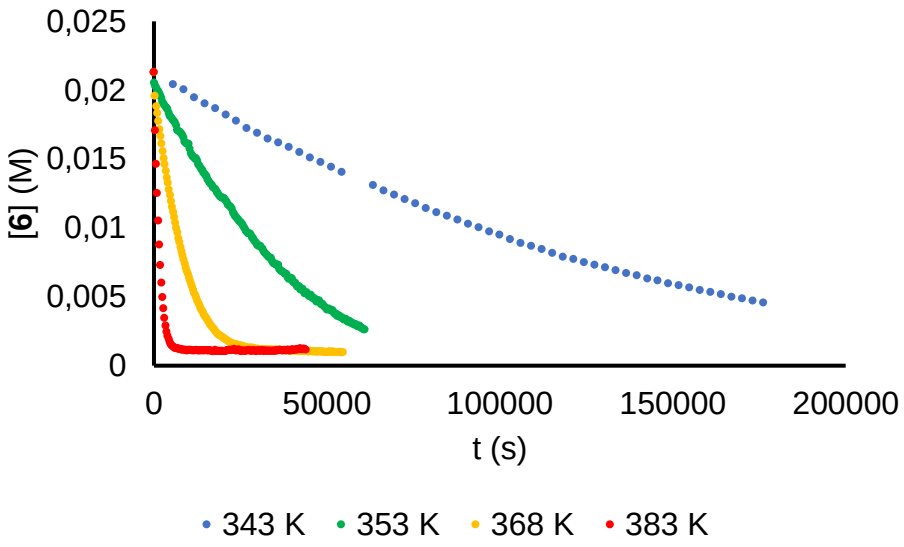


Figure S180. Plots of **[6]** over time at 343, 353, 368 and 383 K.

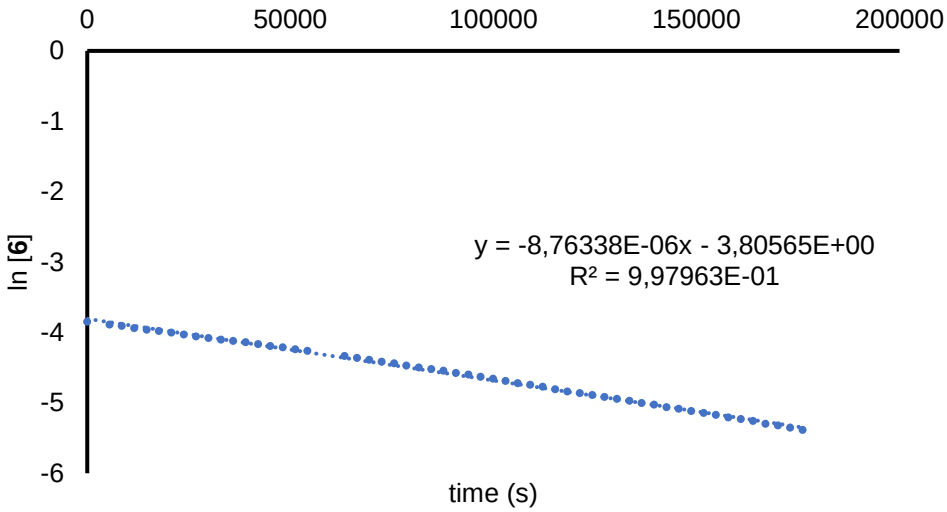


Figure S181. Plot of ln [**6**] over time at 343 K.

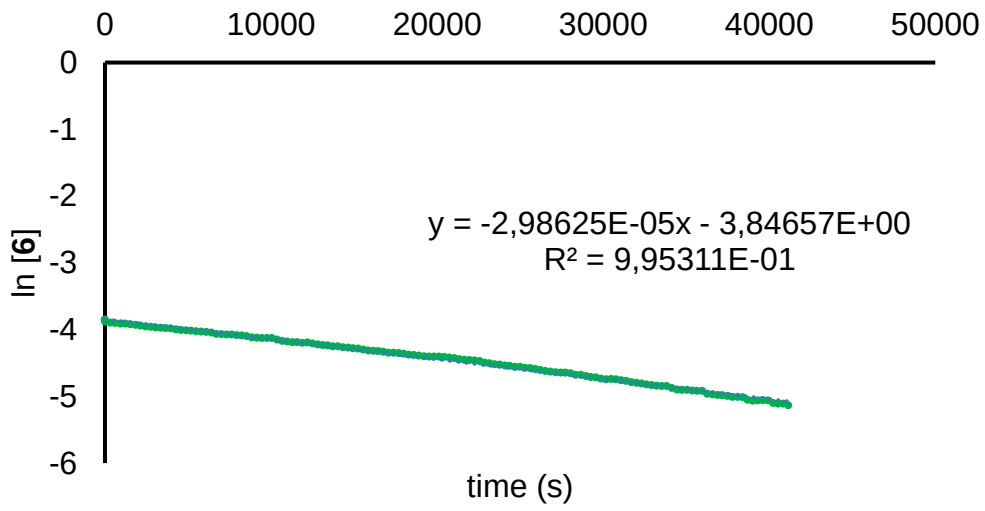


Figure S182. Plot of ln [**6**] over time at 353 K.

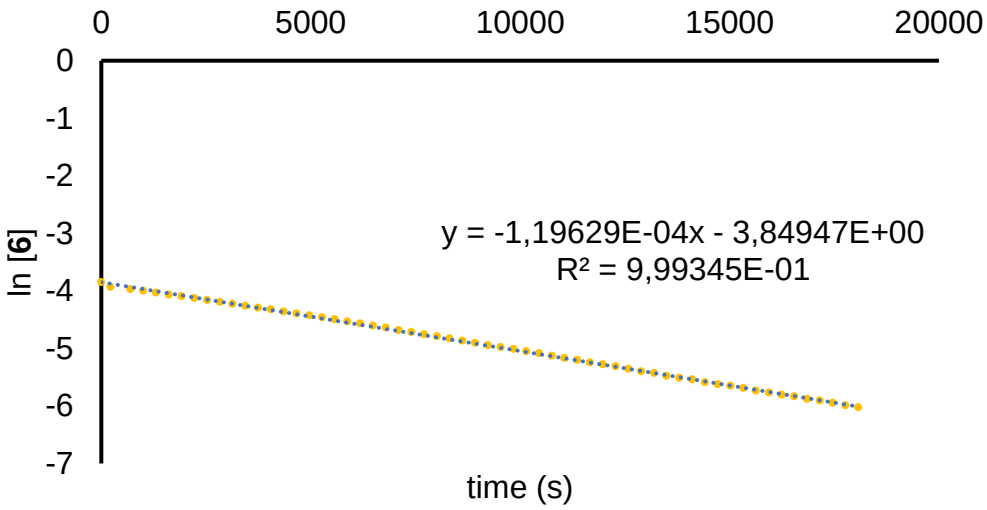


Figure S183. Plot of ln [**6**] over time at 368 K.

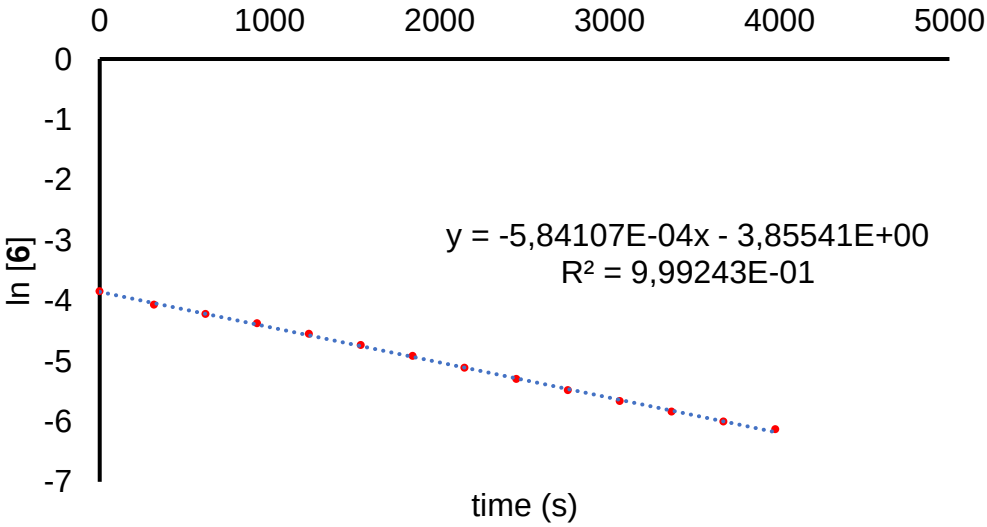


Figure S184. Plot of ln [**6**] over time at 383 K

Kinetic modeling of the insertion:

For a first-order reaction, as expected for an intramolecular rearrangement:

$$v = -\frac{d[6]}{dt} = -k_{obs} * [6]$$

Giving, after integration:

$$\ln[6] = -k_{obs} * t + \ln[6]_0$$

The plots of ln[**6**] against time (**Figures S181-184**) show very good linear correlations (R_{corr}^2 close to 1), in line with this kinetic model. The corresponding parameters are gathered in **Table S1**.

T (K)	R_{corr}^2	ln $[5]_0$	k_{obs} (s^{-1})
343	0.998	-3.806	$8.763\ 10^{-6}$
353	0.995	-3.847	$2.986\ 10^{-5}$
368	0.999	-3.849	$1.196\ 10^{-4}$
383	0.999	-3.855	$5.841\ 10^{-4}$

Table S1. Kinetic parameters for the rearrangement of **6** into **7** at 343, 353, 368 and 383 K.

Determination of the activation parameters:

T (K)	k_{obs} (s^{-1})	1/T (K^{-1})	ln (k_{obs}/T)
343	$8.763\ 10^{-6}$	0.002915	-17.483
353	$2.986\ 10^{-5}$	0.002833	-16.285
368	$1.196\ 10^{-4}$	0.002717	-14.939
383	$5.841\ 10^{-4}$	0.002611	-13.393

Table S2. Eyring parameters for the rearrangement of **6** into **7** at 343, 353, 368 and 383 K.

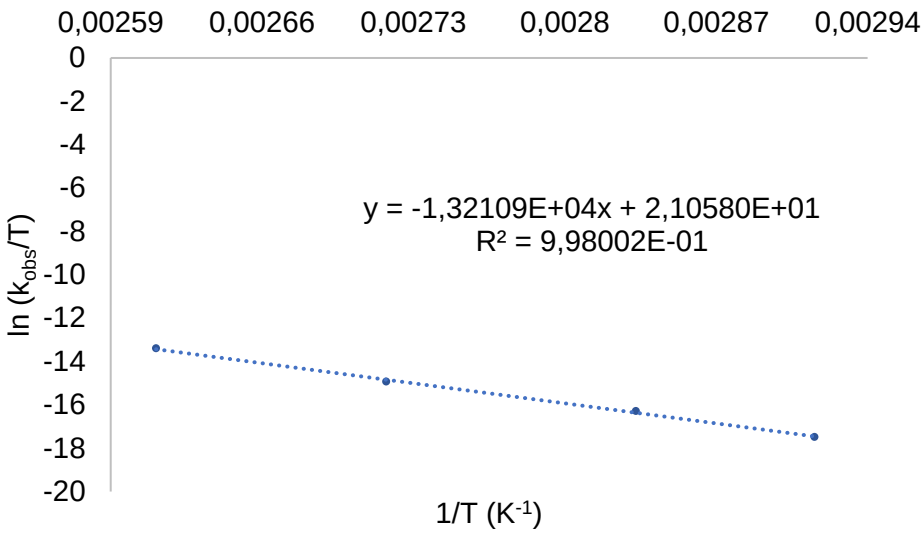


Figure S185. Eyring plot for the rearrangement of **6** into **7** (353-383 K temperature range).

The Eyring equation states the following relationship between k_{obs} and $\Delta G^{\neq}$:

$$\ln\left(\frac{k_{obs}}{T}\right) = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln\left(\frac{k_b}{h}\right)$$

With : $k_b = 1.38064852 \times 10^{-23}$ m^2.kg.s^{-2}.K^{-1}

$h = 6.62607004 \times 10^{-34}$ m^2.kg.s^{-1}

$R = 1.9858775 \times 10^{-3}$ kcal.K^{-1}.mol^{-1}

The plot of ln[k_{obs}/T] against 1/T (**Figure S185**) shows a very good linear correlations (R_{corr}^2 = 0.998) from which the following activation parameters can be extracted:

$\Delta H^{\neq} = 26.24 \pm 1.66$ kcal.mol^{-1}

$\Delta S^{\neq} = -5.37 \pm 4.5$ cal.K^{-1}.mol^{-1}

leading to $\Delta G^{\neq} = 28.2 \pm 3.3$ kcal.mol^{-1} (at 90°C)

Selected Crystallographic Data

Crystallographic data for compound **2**, **3**, **4**, **5**, **6** and **7** were collected at 193(2) K on a Bruker-AXS APEX II CCD Quazar diffractometer equipped with a 30 W air-cooled microfocus source (**2**, **5** and **6**), or on a Bruker-AXS D8-Venture diffractometer (**3**, **4** and **7**) equipped with a Photon III detector, using Mo K_α radiation (λ=0.71073 Å). Phi- and omega-scans were used. Space group were determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed.[5] The structures were solved using an intrinsic phasing method (SHELXT),[6] and refined using the least-squares method on F^2.[7] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2 times for all other carbon atoms.

All structures were disordered. Several restraints (SAME, SIMU, DELU, ISOR) were applied to refine some moieties of the molecules and to avoid the collapse of the structures during the least-squares refinement by the large anisotropic displacement parameters. The details of data collection and crystal structures refinement are summarized in **Table S3**.

CCDC-2036098 (**2**), CCDC-2035740 (**3**), CCDC-2035741 (**4**), CCDC-2035742 (**5**), CCDC-2035743 (**6**), and CCDC-2035744 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

[5] Bruker, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2008**. SADABS-2016/2 Krause, L., Herbst-Irmer, R., Sheldrick G. M. & Stalke D., *J. Appl. Cryst.* **2015**, *48*, 3–10

[6] ShelXT, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

[7] ShelXL, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8

Table S3. Crystallographic data for the compounds **2**, **3**, **4**, **5**, **6** and **7**

Compound	**2**	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{78}H_{92}AuBF_{12}O_3P_2$	$C_{45}H_{38}AuBF_{12}NP$	$C_{45}H_{38}AuBF_{12}NP$, $CHCl_3$	$C_{75}H_{96}AuBCl_6F_{12}O_3P_2$	$C_{39}H_{36}AuBF_{12}NP$	$C_{39}H_{36}AuBF_{12}NP$
M_r	1575.23	1059.51	1178.88	1755.93	985.43	985.43
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\ \bar{1}$	$P\ 2_1/n$	P bca	P bca	$P\ \bar{1}$	C 2/c
a [Å]	14.4357(8)	10.0600(5)	18.4404(10)	24.8443(18)	11.2978(7)	15.7366(8)
b [Å]	21.5653(15)	12.6560(7)	22.2609(11)	22.0162(17)	13.6927(10)	17.7379(9)
c [Å]	25.4588(17)	34.5461(19)	23.8142(10)	30.643(2)	14.2787(10)	29.4924(17)
α [°]	87.595(3)	90	90	90	108.722(2)	90
β [°]	77.238(3)	92.8652(18)	90	90	100.2329(19)	105.0068(17)
γ [°]	83.387(3)	90	90	90	102.5317(19)	90
V [Å^3]	7677.2(9)	4392.9(4)	9775.7(8)	16761(2)	1967.7(2)	7951.6(7)
Z	4	4	8	8	2	8
ρ [g cm^{-3}]	1.363	1.602	1.602	1.392	1.663	1.646
μ($Mo_{K\alpha}$) [mm^{-1}]	2.032	3.469	3.285	2.054	3.865	3.826
Reflections collected	217596	191226	292862	326738	50155	112297
Independent reflections	37995 R(int)=0.0841	10938 R(int)=0.0650	8931 R(int)=0.0625	17087 R(int)=0.1001	7406 R(int)=0.0801	9900 R(int)=0.0731
Data/ restraints/ parameters	37995/402/1909	10938/336/649	8931/750/802	17087/737/1162	7406/138/558	9900/174/558
Crystal size [mm^3]	0.2x0.2x0.04	0.12x0.10x0.06	0.20x0.08×0.04	0.15x0.08x0.05	0.20×0.15×0.02	0.20×0.18×0.16
GOOF on F^2	1.048	1.094	1.047	1.063	1.029	1.068
R ($I > 2\sigma(I)$)	0.0387	0.0305	0.0281	0.0362	0.0349	0.0332
wR2 (all data)	0.0832	0.0701	0.0763	0.0959	0.0635	0.0627
Largest difference peak and hole, [e Å^{-3}]	0.709 and -0.708	1.308 and -0.918	0.800 and -0.561	1.207 and -0.759	0.731 and -0.639	1.296 and -1.019
CCDC number	2036098	2035740	2035741	2035742	2035743	2035744

Computational details

All calculations were performed using the Gaussian 16 package[8] and the B3PW91[9] hybrid functional. For the alkynyl group, a model complex (**4***), where the Ph substituent of the triple C≡C bond was replaced by hydrogen (with C≡CH instead of C≡CPh), was computed. For the alkenyl group, the real complex was considered (**6**). All stationary points involved were fully optimized in gas phase. The gold atom was described with the relativistic electron core potential SDD and associated basis set,[10] augmented by a set of f-orbital polarization functions.[11] The 6-31G** basis set was employed for all other atoms (C, H, P, B, N, F). Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS), corresponding to the expected process, and all of them positive for *minima*. The connectivity of the transition states and their adjacent *minima* was confirmed by intrinsic reaction coordinate (IRC) calculations.[12] In order to have better accuracy on energies (activation barriers and reaction energies), single points calculations have been carried out by taking into account solvent effect (benzene) by means of the universal Solvation Model based on solute electron Density (SMD)[13] at SMD(benzene)-B3PW91/6-311G(2df,2pd), SDD+2fg(Au) level of theory on the geometry optimized in gas phase at B3PW91/6-31G(d,p), SDD+f(Au), level of theory. For the alkenyl group, the bonding situation of π-complexes (interacting **6** and perpendicular **6**$_\perp$ forms) and the intermediate **INT-TS1** involved in the two steps *anti* insertion process, was analyzed through Natural Bond Orbital[14] calculations (NBO, 5.9 version).[15] NMR calculations were also carried out in the gas phase in order to determine the $^1J_{CH}$ coupling constants within the B–CH=CH$_2$ moiety for both **6** and **6**$_\perp$ by employing the direct implementation of the Gauge Including Atomic Orbitals (GIAO) method,[16] with the IGLOII[17] basis set on B, C, P, F, N and H atoms and SDD+f on gold.

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[8] Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[9] (a) Becke A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652; (b) Perdew J. P., in *Electronic Structure of Solids '91*, Ed. P. Ziesche and H. Eschrig, Akademie Verlag, Berlin, **1991**, 11.

[10] D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123-141

[11] Ehlers, A. W.; Biihme, M.; Dapprich, S.; Gobbi, A.; Hijllwarth, A.; Jonas, V.; Kiihler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Letters* **1993**, *208*, 111-114.

[12] (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363; (b) Hratchian, H. P.; Schlegel, H. B. in *Theory and Applications of Computational Chemistry: The First 40 Years*, Ed. Dykstra, C. E.; Frenking, G.; Kim, K. S.; Scuseria, G.; Elsevier, Amsterdam, **2005**, 195.

[13] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[14] (a) Reed, E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899; (b) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211-7218; (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736-1740.

[15] NBO 5.9, Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold F. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2004**); http://www.chem.wisc.edu/~nbo5.

[16] (a) F. London, *J. Phys. Radium* **1937**, *8*, 397-409; (b) R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028-1034; (c) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789-807; (d) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260; (e) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497-5509.

[17] W. Kutzelnigg, U. Fleischer, M. Schindler, *The IGLO-Method: Ab Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities*, Springer-Verlag, Heidelberg, **1990**, vol. 23.

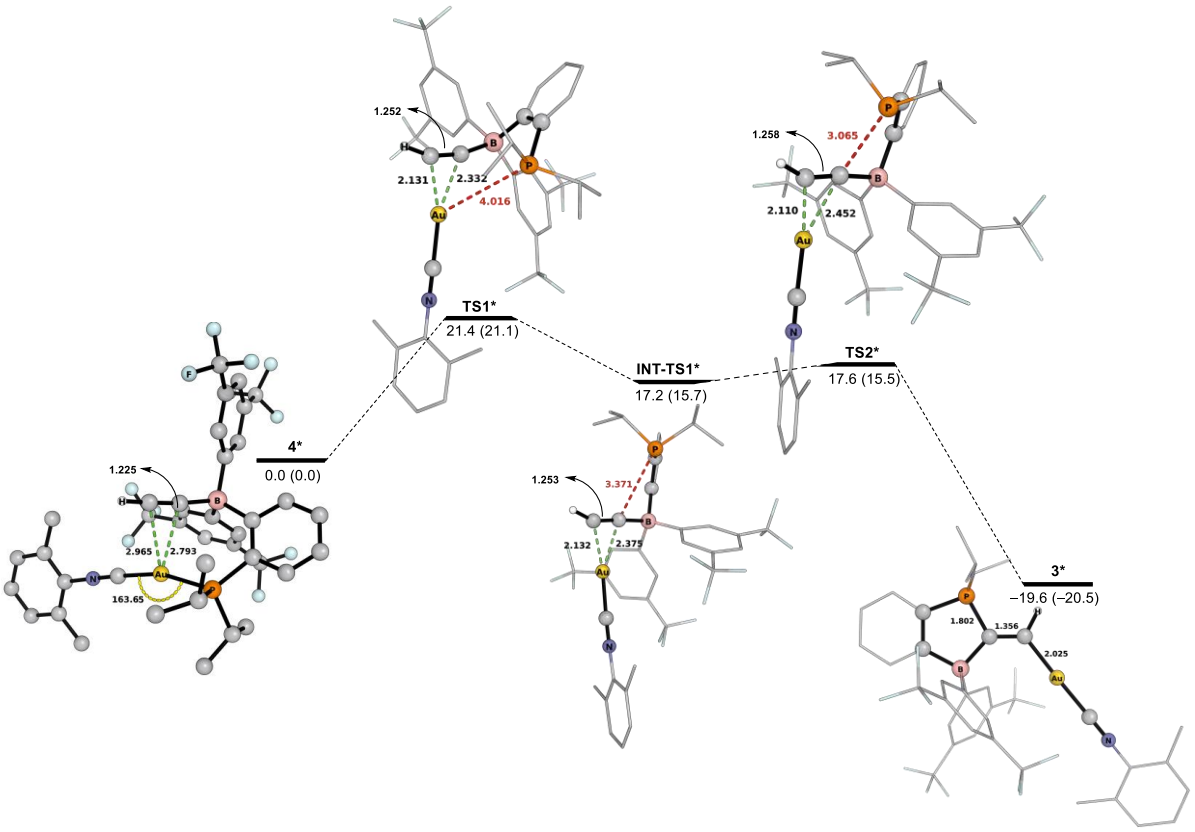


Figure S186. Two-step mechanism accounting for the *trans*-phosphaboration of the C≡C triple bond at gold for model compound **4*** to **3***. Corrected Gibbs free energies computed at SMD(benzene)-B3PW91/6-311G(2df,2pd),SDD+2fg(Au)//B3PW91/6-31G(d,p),SDD+f(Au) level and Gibbs free energies (in parentheses) at B3PW91/6-31G(d,p),SDD+f(Au). Energy values, ΔG, in kcal/mol

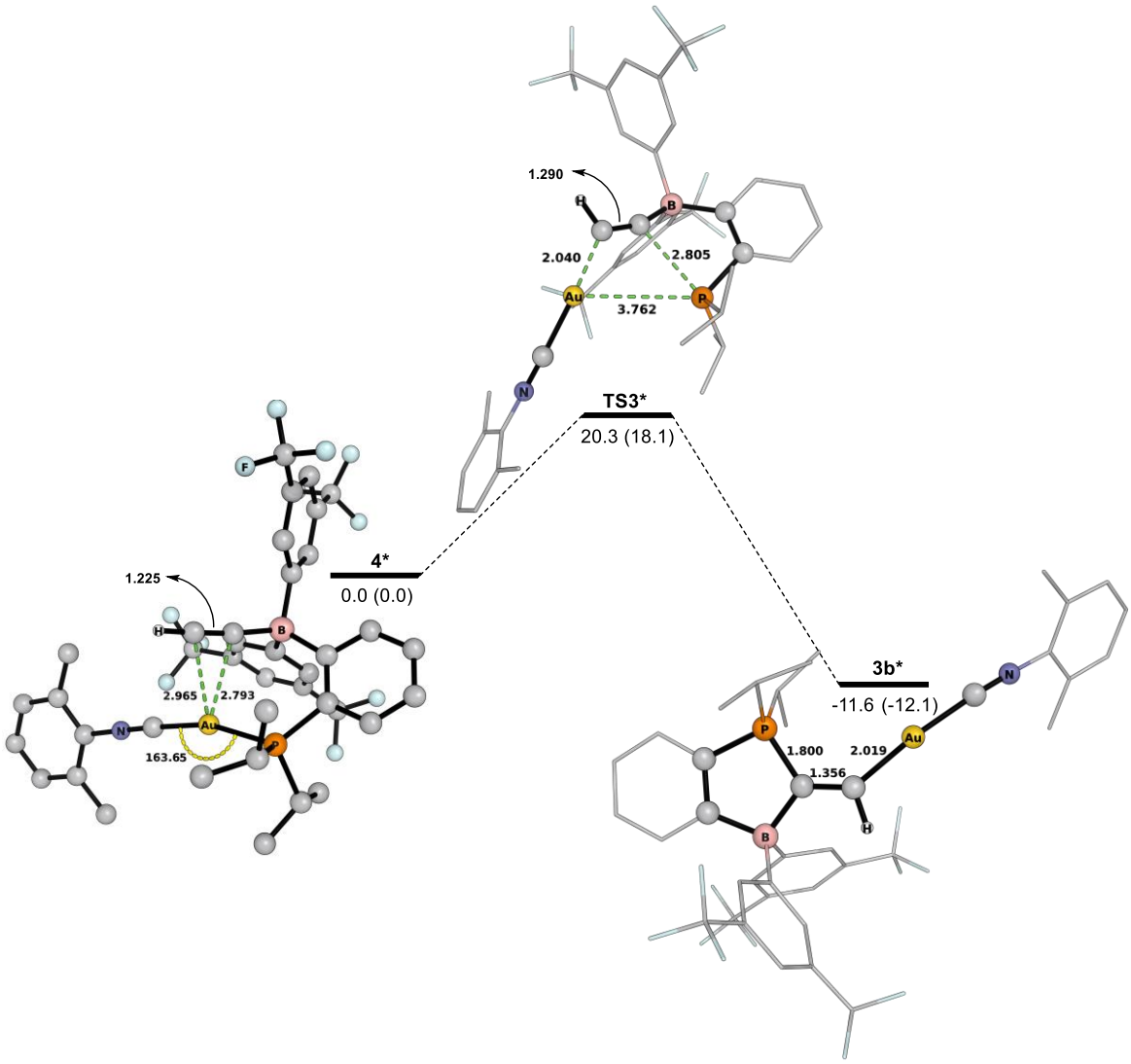


Figure S187. Concerted *syn* insertion of the C≡C triple bond into the P–Au bond for model compound **4*** to **3***. Corrected Gibbs free energies computed at SMD(benzene)-B3PW91/6-311G(2df,2pd),SDD+2fg(Au)//B3PW91/6-31G(d,p),SDD+f(Au) level and Gibbs free energies (in parentheses) at B3PW91/6-31G(d,p),SDD+f(Au). Energy values, ΔG, in kcal/mol.

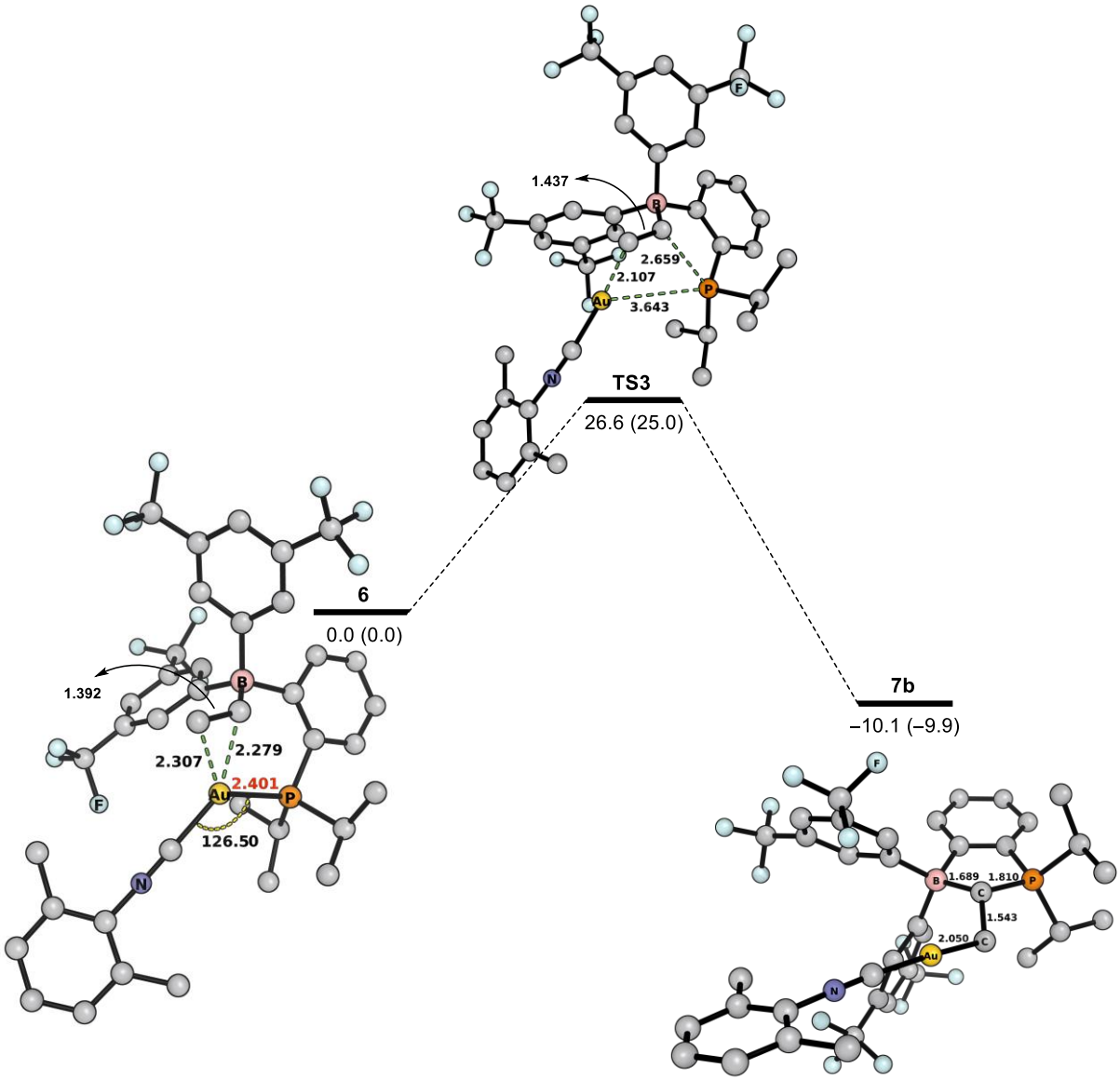
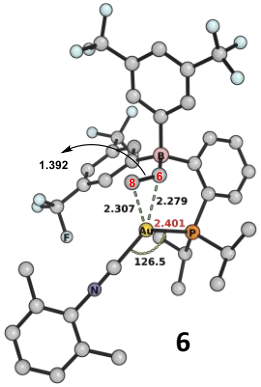
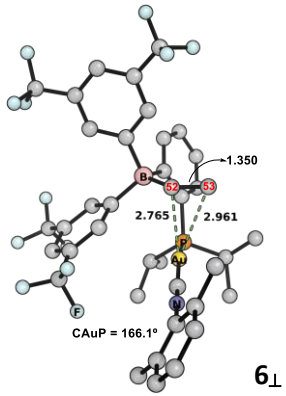


Figure S188. Concerted *syn* insertion of the C=C bond into the P–Au bond of **6**. Corrected Gibbs free energies computed at SMD(benzene)-B3PW91/6-311G(2df,2pd),SDD+2fg(Au)//B3PW91/6-31G(d,p),SDD+f(Au) level and Gibbs free energies (in parentheses) at B3PW91/6-31G(d,p),SDD+f(Au). Energy values, ΔG, in kcal/mol.

Two *minima* have been localized on the potential energy surface (PES) for the initial reactant: *i*) a form with C=C→Au interaction (complex **6**, see NBO analysis below) and *ii*) a form with the C=C bond about perpendicular to the P-Au-C fragment (**6**$_{\perp}$, see Table S4). They are close in energy (ΔΔG = 0.9 (0.2) kcal/mol), in favor of **6**.

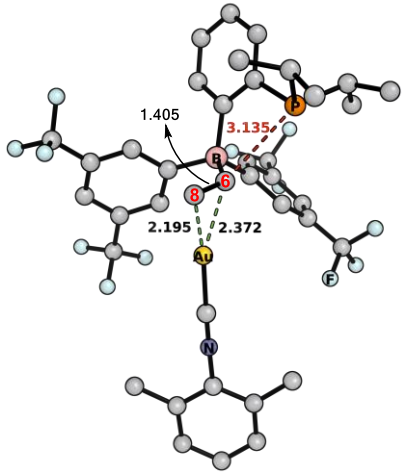
Table S4. NBO analysis for the π-complex **6** and the associated perpendicular form **6⊥**. Stabilizing energies, ΔE(2) in kcal/mol, corresponding to donation and back-donation C=C/Au, at 2nd order perturbation theory. Associated Natural Localized Molecular Orbital (NLMO), with percentage of main atoms and hybridization. Wiberg Bond indexes (WBI) for Au-C and C=C bonds.

	ΔE(2) in kcal/mol	**NLMO**	**WBI**
 **6**	**Donation : $\pi_{C=C} \rightarrow s(Au)^*$** BD (2) C6-C 8 → LP*(6)Au 1 : **91.6** **Back-Donation : LP(Au) → $\pi^*_{C=C}$** LP (5)Au 1 → BD*(2) C6- C8 : **20.7**	**$\pi_{C6=C8}$** 5.7 % Au : s (88.9 %), p (5.1 %), d (5.9 %) 40.1% C6 : s (1.7 %), p (98.2 %) 48.8 % C8 : s (2.3 %), p (97.6 %) **LP(Au)** 91.4 % Au : s (0.9 %), p (0.0 %), d (99.1 %) 3.6 % C6 : s (2.4 %), p (97.4 %) 2.8 % C8 : s (4.0 %), p (95.8 %)	Au-C6 : 0.231 Au-C8 : 0.213 C6-C8 : 1.598
 **6⊥**	**Donation : $\pi_{C=C} \rightarrow s(Au)^*$** BD (2) C 52- C53 → LP*(6)Au 73 : **8.7** **Back-Donation : LP(Au) → $\pi^*_{C=C}$** LP (5)Au 73 → BD*(2) C 52-C53 : **0.09**	**$\pi_{C52=C53}$** 1.1 % Au : s (51.9 %), p (36.8 %), d (9.3%) 50.7 % C53 : s (0.07 %), p (99.9 %) 45.0 % C52 : s (0.1 %), p (99.8 %) **LP(Au)** 95.8 % Au : s (0.4 %), p (0.0 %), d (99.5 %) 0.3 % P : s (3.8 %), p (78.9 %), d (17.3 %) 2.4 % C_{CNAryl} : p (99.0 %), d (1.0 %)	Au -C52 : 0.041 Au-C53 : 0.032 C52-C53 : 1.893

* The acceptor NBO orbital presents a strong s character (96 % of s character for **6** and 89 % of s character for **6⊥**).

In complex **6**, the alkene is η^2-coordinated to gold with almost identical Au–C bond lengths (2.28 and 2.31 Å, quasi-symmetric structure) and Wiberg Bond indexes (WBI : 0.21 and 0.23). The C=C bond is weakened upon coordination to gold, as indicated by the lengthening of the CC distance (1.392 in **6** *vs* 1.350 Å in **6⊥**, where there is almost no interaction) and the decrease of the WBI (1.60 in **6** *versus* 1.89 in **6⊥**). NBO analysis indicates strong donation ($\pi_{C=C} \rightarrow$Au) and non-negligible back-donation (Au$\rightarrow \pi^*_{C=C}$). The stabilizing energies of the associated donor-acceptor interactions are 91.6 and 20.7 kcal/mol, respectively.

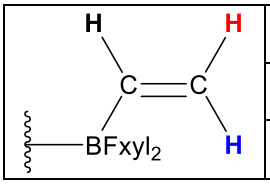
Table S5. NBO analysis for the intermediate **INT-TS1** involved in the two-step mechanism accounting for the *trans*-phosphaboration of the C=C double bond at gold from **6** to **7**. Stabilizing energies, ΔE(2) in kcal/mol, corresponding to donation and back-donation C=C/Au, at 2nd order perturbation theory. Associated Natural Localized Molecular Orbital (NLMO), with percentage of main atoms and hybridization. Wiberg Bond indexes (WBI) for Au-C and C=C bonds.

	ΔE(2) in kcal/mol	**NLMO**	**WBI**
 **INT-TS1**	**Donation : $\pi_{C=C} \rightarrow$ s(Au)*** 14. BD (2) C6-C 8 → 213. LP*(6)Au 1 : **168.6** **Back-Donation : LP(Au) → $\pi^*_{C=C}$** 172. LP (5)Au 1 → 948. BD*(2) C6- C8 : **18.7**	**$\pi_{C6=C8}$** 11.8% Au : s (85.4 %), p (0.8 %), d (13.7 %) 32.5 % C6 : s (0.7 %), p (99.2 %) 51.4 % C8 : s (3.6 %), p (96.3 %) **LP(Au)** 93.5 % Au : s (0.2 %), p (0.0 %), d (99.8 %) 2.2 % C6 : s (0.8 %), p (99.0 %), d (1.2 %) 1.5 % C8 : s (7.6 %), p (92.0 %), d (0.4 %)	Au-C6 : 0.224 Au-C8 : 0.317 C6-C8 : 1.574

* The acceptor NBO orbital presents a strong s character (86 % of s character for **INT-TS1**).

In the intermediate **INT-TS1**, where the phosphine is decoordinated, the alkene is still η^2-coordinated but more assymmetrically than in complex **6**, as shown by the Au-C bond lengths (2.20 and 2.37 Å) and the Wiberg Bond indices (0.22 and 0.32). As expected from the 2-coordinate linear structure of **INT-TS1** *vs* 3-coordinate bent structure of **6**, the donation / backdonation balance, as estimated by NBO, is much larger in **INT-TS1** (168.6 / 18.7 kcal/mol) than in **6** (91.6 / 20.7 kcal/mol).

Table S6. $^{1}J_{CH}$ coupling constants (in Hz) within the B–CH=CH_2 computed in the gas phase with the GIAO method at B3PW91/SDD+f (Au), IGLO-II (all other atoms) level of theory.

		$^{1}J_{CH}$ (Hz)		
		6	**6⊥**	**Experimental**
	**–CH**	124.6	118.1	130
	–CH(H)	147.5	141.8	158
	–CH(H)	148.1	144.8	161

The data computed for **6** match well those measured experimentally. In line with reported data,[18] only small changes are observed upon coordination of the C=C double bond to gold, but all the $^{1}J_{CH}$ couplings were found to slightly increase upon strengthening the coordination to gold and increasing Au→π*(C=C) back-donation (by 4 to 6 Hz).

[18] Dias, H. V. R.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, 509-522.

Cartesian coordinates, electronic ZPE corrected energies and Gibbs free energies (in a.u.) of all the stationary points discussed in the text and ESI.

Alkenyl group :

6:

Sum of electronic and zero-point Energies= -3261.088138
Sum of electronic and thermal Free Energies= -3261.191164

Au	1.574535000	-1.064808000	-0.450046000
P	0.985938000	-2.214835000	1.574242000
N	4.484955000	-0.110214000	-1.314375000
B	-1.580791000	-0.408719000	0.114450000
C	3.415435000	-0.467921000	-0.994299000
C	-0.631304000	-1.120071000	-1.018306000
H	-0.817405000	-2.195545000	-1.115549000
C	0.046236000	-0.581529000	-2.109129000
H	0.081643000	0.490285000	-2.285939000
H	0.307995000	-1.197705000	-2.967840000
C	-1.784462000	-1.415072000	1.414069000
C	-0.782073000	-2.169372000	2.075972000
C	-1.084187000	-2.942220000	3.214518000
H	-0.305238000	-3.527988000	3.698467000
C	-2.366223000	-2.988227000	3.742875000
H	-2.577208000	-3.592180000	4.620817000
C	-3.367178000	-2.244739000	3.123628000
H	-4.381080000	-2.255524000	3.515346000
C	-3.069335000	-1.491275000	1.994096000
H	-3.876785000	-0.936574000	1.524440000
C	1.404927000	-4.042821000	1.427022000
H	1.493087000	-4.420950000	2.455223000
C	0.293690000	-4.815244000	0.709477000
H	0.151649000	-4.440304000	-0.310289000
H	-0.663549000	-4.750736000	1.229623000
H	0.572975000	-5.872036000	0.634275000
C	2.737021000	-4.259184000	0.700416000
H	2.993735000	-5.324657000	0.710138000
H	3.567561000	-3.710153000	1.147961000
H	2.656540000	-3.945036000	-0.346075000
C	1.855498000	-1.590870000	3.112096000
H	1.434936000	-2.175641000	3.940778000
C	1.500034000	-0.117670000	3.328803000
H	1.922491000	0.226122000	4.279353000
H	0.420062000	0.045345000	3.360969000
H	1.912319000	0.509924000	2.532170000
C	3.370156000	-1.792686000	3.087541000
H	3.818100000	-1.327465000	2.202318000
H	3.654417000	-2.848171000	3.108617000
H	3.814198000	-1.317710000	3.969476000
C	-2.985723000	-0.244245000	-0.734192000
C	-3.433652000	0.990683000	-1.222592000
H	-2.894709000	1.896497000	-0.960070000
C	-4.562732000	1.101057000	-2.038540000
C	-5.291343000	-0.027474000	-2.397996000
H	-6.167191000	0.056084000	-3.030191000
C	-4.867781000	-1.268390000	-1.926233000
C	-3.739032000	-1.368854000	-1.114475000
H	-3.440247000	-2.353779000	-0.765054000
C	-4.949951000	2.448751000	-2.577768000
F	-4.812317000	3.418855000	-1.652204000
F	-4.176587000	2.804757000	-3.627826000
F	-6.227851000	2.479976000	-3.006004000
C	-5.666006000	-2.500237000	-2.243618000
F	-6.379998000	-2.365384000	-3.379207000
F	-6.546471000	-2.794181000	-1.261783000
F	-4.878540000	-3.586236000	-2.392141000
C	-1.089358000	1.047247000	0.704015000
C	-1.836979000	1.659132000	1.730705000
H	-2.734131000	1.168819000	2.096279000
C	-1.470661000	2.872418000	2.307195000
C	-0.321030000	3.542922000	1.886761000
H	-0.031578000	4.486525000	2.333555000
C	0.430813000	2.971231000	0.870936000
C	0.043518000	1.757582000	0.290560000
H	0.664747000	1.373288000	-0.512266000
C	-2.272936000	3.433602000	3.447956000
F	-2.201273000	4.779215000	3.499022000
F	-3.573969000	3.100605000	3.365939000
F	-1.825612000	2.975614000	4.638741000
C	1.692358000	3.618999000	0.387951000
F	2.784311000	2.857727000	0.674341000
F	1.907073000	4.826986000	0.933130000
F	1.700352000	3.775125000	-0.955858000
C	5.729511000	0.342253000	-1.707301000
C	6.855011000	-0.447865000	-1.405525000
C	8.098321000	0.031477000	-1.815484000
H	8.986195000	-0.555718000	-1.599304000
C	8.211289000	1.244397000	-2.490009000
H	9.189669000	1.600782000	-2.798448000
C	7.078766000	2.003083000	-2.771905000
H	7.174774000	2.948175000	-3.298432000
C	5.808276000	1.571165000	-2.390692000
C	6.711392000	-1.751437000	-0.674788000
H	6.250226000	-1.608375000	0.308547000
H	7.685882000	-2.221227000	-0.526331000
H	6.077440000	-2.453196000	-1.228093000
C	4.576182000	2.374218000	-2.687248000
H	4.057319000	2.672407000	-1.771323000
H	3.861729000	1.799697000	-3.287244000
H	4.830361000	3.279730000	-3.241861000

$6_{\perp}$:

Sum of electronic and zero-point Energies= -3261.088318
Sum of electronic and thermal Free Energies= -3261.190901

C	-0.999877000	-2.343585000	-2.066532000
C	-1.482718000	-3.374874000	-2.894620000
H	-0.809386000	-4.141626000	-3.264584000
C	-2.818089000	-3.447242000	-3.270121000
H	-3.162655000	-4.253870000	-3.911013000
C	-3.690838000	-2.471806000	-2.805388000
H	-4.744169000	-2.502257000	-3.072291000
C	-3.211796000	-1.445675000	-1.996485000
H	-3.919810000	-0.697023000	-1.657863000
C	-1.867300000	-1.314529000	-1.594142000
C	0.812562000	-3.785028000	-0.241033000
H	-0.050549000	-3.490124000	0.364666000
C	0.570633000	-5.212741000	-0.734893000
H	1.402976000	-5.587418000	-1.340138000
H	-0.350719000	-5.297860000	-1.316713000
H	0.471133000	-5.876899000	0.130104000
C	2.048399000	-3.689589000	0.657206000
H	1.915708000	-4.355167000	1.516826000
H	2.193069000	-2.674468000	1.036412000
H	2.964910000	-3.990533000	0.140920000
C	1.655846000	-3.202921000	-3.090298000
H	1.183255000	-4.166204000	-3.315179000
C	1.492506000	-2.277498000	-4.299152000
H	1.945866000	-1.299109000	-4.105355000
H	0.442743000	-2.120086000	-4.558670000
H	1.996014000	-2.714024000	-5.168839000
C	3.136575000	-3.461880000	-2.797369000

H	3.624474000	-3.844810000	-3.700758000
H	3.285083000	-4.199672000	-2.005224000
H	3.648989000	-2.540058000	-2.501335000
C	-0.887213000	-0.501740000	0.807060000
C	-1.409052000	-1.636496000	1.450506000
H	-2.176613000	-2.220043000	0.947295000
C	-0.986786000	-2.037662000	2.721118000
C	-0.008713000	-1.320140000	3.402765000
H	0.322443000	-1.630814000	4.386816000
C	0.521121000	-0.185246000	2.793511000
C	0.079448000	0.217810000	1.532295000
H	0.488646000	1.133224000	1.117196000
C	-1.538710000	-3.302576000	3.314122000
C	-2.769631000	0.967001000	-0.376284000
C	-3.217870000	1.860501000	-1.364018000
H	-2.697457000	1.897035000	-2.317311000
C	-4.314938000	2.699925000	-1.169805000
C	-5.011559000	2.686284000	0.035869000
H	-5.866859000	3.333041000	0.190411000
C	-4.589982000	1.811798000	1.031941000
C	-3.490580000	0.974097000	0.826552000
H	-3.200490000	0.305327000	1.631369000
C	-4.704843000	3.664152000	-2.253027000
C	-5.283075000	1.804469000	2.364711000
C	-0.407145000	0.973237000	-1.420047000
C	-0.039978000	0.965362000	-2.719187000
H	-0.368600000	0.178123000	-3.395489000
C	3.225549000	0.883509000	-0.531240000
C	4.891787000	2.720398000	0.064466000
C	4.776520000	3.954277000	-0.604310000
C	5.694592000	4.946727000	-0.263670000
H	5.634306000	5.911210000	-0.759309000
C	6.675180000	4.716366000	0.697705000
H	7.378986000	5.504476000	0.948485000
C	6.759459000	3.484771000	1.341438000
H	7.525824000	3.314761000	2.091967000
C	5.869449000	2.453753000	1.041743000
C	3.707357000	4.182527000	-1.632845000
H	3.777239000	5.190662000	-2.045936000
H	2.707040000	4.062216000	-1.202516000
H	3.788819000	3.470276000	-2.461405000
C	5.935889000	1.121968000	1.729978000
H	5.017117000	0.915690000	2.287948000
H	6.773508000	1.091671000	2.429725000
H	6.065595000	0.305988000	1.010311000
Au	1.895972000	-0.504834000	-1.027958000
B	-1.455844000	-0.011070000	-0.654973000
F	-0.934208000	-4.395392000	2.780424000
F	-2.855067000	-3.440737000	3.078822000
F	-1.352120000	-3.369702000	4.645106000
F	-3.907692000	4.756164000	-2.260965000
F	-4.608127000	3.110458000	-3.479400000
F	-5.970519000	4.106900000	-2.112384000
F	-6.532572000	2.306753000	2.291977000
F	-4.617062000	2.545148000	3.277822000
F	-5.380233000	0.560195000	2.874966000
P	0.777168000	-2.490243000	-1.599819000
N	3.994643000	1.719872000	-0.256212000
H	-0.060906000	1.848926000	-0.857689000
C	1.641281000	0.551482000	3.464306000
F	1.549694000	0.524463000	4.804991000
F	2.846330000	-0.005807000	3.151486000
F	1.715337000	1.841798000	3.085761000
H	0.567301000	1.753935000	-3.162982000

TS1:

Sum of electronic and zero-point Energies= -3261.048908

Sum of electronic and thermal Free Energies= -3261.150222

Au	-1.246518000	-0.388534000	-1.661437000
P	-0.271851000	3.445293000	-0.327627000
N	-4.278730000	-1.108128000	-1.302289000
B	1.663697000	0.620104000	0.003574000
C	-3.156992000	-0.815859000	-1.422328000
C	0.900213000	0.644413000	-1.468106000
H	0.641562000	1.627263000	-1.867040000
C	0.799229000	-0.367184000	-2.415350000
H	1.198804000	-1.359799000	-2.209104000
H	0.642314000	-0.134756000	-3.470667000
C	2.218004000	2.143765000	0.348248000
C	1.517849000	3.370805000	0.186032000
C	2.147440000	4.588422000	0.503759000
H	1.617430000	5.524143000	0.340571000
C	3.430716000	4.641327000	1.032594000
H	3.889268000	5.597878000	1.268912000
C	4.102949000	3.446306000	1.269472000
H	5.096625000	3.449813000	1.710482000
C	3.501223000	2.240815000	0.925554000
H	4.058834000	1.326502000	1.108827000
C	-0.264168000	4.649978000	-1.799496000
H	-0.255560000	5.670778000	-1.390064000
C	0.954862000	4.491121000	-2.711462000
H	0.994960000	3.489471000	-3.156176000
H	1.895828000	4.657675000	-2.183614000
H	0.896056000	5.206169000	-3.540944000
C	-1.547052000	4.458558000	-2.618936000
H	-1.605256000	5.202221000	-3.423203000
H	-2.454718000	4.546897000	-2.016263000
H	-1.559818000	3.465347000	-3.083162000
C	-0.958747000	4.552359000	1.042414000
H	-0.353393000	5.468470000	1.063230000
C	-0.832013000	3.859282000	2.400627000
H	-1.154634000	4.538797000	3.198586000
H	0.196439000	3.555850000	2.612149000
H	-1.465861000	2.969460000	2.447392000
C	-2.412999000	4.948636000	0.776825000
H	-3.049732000	4.065091000	0.653066000
H	-2.520915000	5.576233000	-0.112311000
H	-2.805065000	5.520021000	1.626765000
C	2.881732000	-0.453030000	-0.309706000
C	2.755273000	-1.820422000	-0.023447000
H	1.901958000	-2.170112000	0.551339000
C	3.691812000	-2.764496000	-0.455249000
C	4.806414000	-2.372381000	-1.187035000
H	5.535317000	-3.100565000	-1.521680000
C	4.957468000	-1.019724000	-1.487610000
C	4.010433000	-0.087675000	-1.065278000
H	4.152419000	0.954119000	-1.338435000
C	3.436793000	-4.218112000	-0.177506000
F	3.042918000	-4.426959000	1.093638000
F	2.449765000	-4.702777000	-0.969220000
F	4.523253000	-4.982856000	-0.395164000
C	6.174637000	-0.553108000	-2.235438000
F	6.719404000	-1.536491000	-2.980455000
F	7.139170000	-0.116735000	-1.397953000
F	5.891269000	0.469676000	-3.067472000
C	0.785478000	0.133819000	1.301994000
C	1.446994000	-0.380496000	2.433208000
H	2.527625000	-0.483793000	2.415127000
C	0.766137000	-0.774596000	3.582925000
C	-0.622985000	-0.680895000	3.653297000
H	-1.156909000	-1.004985000	4.538700000
C	-1.300607000	-0.152393000	2.561811000
C	-0.603870000	0.263676000	1.421391000
H	-1.160843000	0.755268000	0.626775000
C	1.531035000	-1.254360000	4.785312000
F	0.819298000	-2.144500000	5.508137000
F	2.690650000	-1.846021000	4.445661000
F	1.837468000	-0.235619000	5.616471000
C	-2.796175000	-0.077139000	2.575679000
F	-3.255067000	1.072849000	2.018730000

F	-3.315046000	-0.153283000	3.811646000
F	-3.361890000	-1.081216000	1.854411000
C	-5.602720000	-1.465184000	-1.136319000
C	-6.500880000	-0.488285000	-0.666438000
C	-7.829666000	-0.881432000	-0.510927000
H	-8.552230000	-0.156351000	-0.148450000
C	-8.234082000	-2.179960000	-0.809015000
H	-9.274494000	-2.462508000	-0.678837000
C	-7.316601000	-3.120760000	-1.270017000
H	-7.641339000	-4.131854000	-1.496989000
C	-5.974471000	-2.787573000	-1.445554000
C	-6.037542000	0.901037000	-0.340574000
H	-5.280236000	0.891655000	0.449548000
H	-6.873874000	1.516368000	-0.003419000
H	-5.589699000	1.389027000	-1.213564000
C	-4.965321000	-3.784733000	-1.935857000
H	-4.160188000	-3.929736000	-1.207064000
H	-4.499288000	-3.457315000	-2.872000000
H	-5.435610000	-4.753365000	-2.115258000

INT-TS1:

Sum of electronic and zero-point Energies= -3261.061083

Sum of electronic and thermal Free Energies= -3261.166512

Au	-1.134979000	-0.386696000	-1.713633000
P	3.944610000	1.325395000	-1.709417000
N	-4.118293000	0.480257000	-1.284766000
B	1.599223000	-0.429911000	0.105407000
C	-3.011870000	0.138582000	-1.423356000
C	1.217014000	-0.201752000	-1.470729000
H	1.376430000	0.793408000	-1.889281000
C	0.804687000	-1.139191000	-2.413646000
H	0.787808000	-2.202863000	-2.174410000
H	0.818728000	-0.896531000	-3.477290000
C	3.242379000	-0.566528000	0.339231000
C	4.280902000	0.130743000	-0.330306000
C	5.620491000	-0.049185000	0.060234000
H	6.408274000	0.474445000	-0.477003000
C	5.978641000	-0.884467000	1.110222000
H	7.022648000	-1.005265000	1.386753000
C	4.972983000	-1.556021000	1.798019000
H	5.215802000	-2.208896000	2.632732000
C	3.647748000	-1.394994000	1.408365000
H	2.890555000	-1.944962000	1.960153000
C	5.090936000	0.719355000	-3.090484000
H	6.117147000	1.038614000	-2.856767000
C	5.069388000	-0.806067000	-3.219769000
H	4.050365000	-1.171386000	-3.393761000
H	5.452705000	-1.304844000	-2.327465000
H	5.679455000	-1.118638000	-4.075815000
C	4.664498000	1.350481000	-4.422473000
H	5.355747000	1.057427000	-5.222035000
H	4.636159000	2.442183000	-4.390794000
H	3.663469000	1.006091000	-4.705853000
C	4.841704000	2.850139000	-1.049507000
H	5.845733000	2.536076000	-0.733157000
C	4.093604000	3.381149000	0.176294000
H	4.642979000	4.221752000	0.616764000
H	3.977323000	2.615281000	0.947832000
H	3.095409000	3.742267000	-0.092582000
C	4.991664000	3.946994000	-2.105501000
H	4.022678000	4.224671000	-2.536309000
H	5.657483000	3.652890000	-2.921673000
H	5.417078000	4.848355000	-1.648254000
C	0.820814000	-1.806501000	0.561985000
C	-0.426110000	-1.784513000	1.209153000
H	-0.838181000	-0.834275000	1.536176000
C	-1.151042000	-2.950074000	1.466219000
C	-0.654940000	-4.194542000	1.085719000
H	-1.210341000	-5.102433000	1.290703000
C	0.580029000	-4.246213000	0.447285000
C	1.298639000	-3.075622000	0.194171000
H	2.269956000	-3.155600000	-0.287317000
C	-2.520118000	-2.868602000	2.071459000
F	-2.713256000	-1.740647000	2.776599000
F	-3.479066000	-2.884427000	1.101223000
F	-2.789087000	-3.908614000	2.880899000
C	1.123618000	-5.559351000	-0.040706000
F	0.520034000	-6.612289000	0.543215000
F	2.445605000	-5.673046000	0.186709000
F	0.947044000	-5.694860000	-1.375576000
C	1.085265000	0.856870000	0.992461000
C	1.239229000	0.859570000	2.390957000
H	1.708267000	0.007561000	2.874338000
C	0.804364000	1.916503000	3.187162000
C	0.199142000	3.035767000	2.614739000
H	-0.147626000	3.855956000	3.232097000
C	0.042733000	3.064105000	1.235279000
C	0.480244000	1.995028000	0.445953000
H	0.336683000	2.072015000	-0.627822000
C	1.037939000	1.884938000	4.671966000
F	0.098290000	2.584260000	5.342260000
F	1.027972000	0.629368000	5.158824000
F	2.231186000	2.423493000	5.000132000
C	-0.547558000	4.265860000	0.562029000
F	0.397931000	5.039396000	-0.011814000
F	-1.240307000	5.049156000	1.408485000
F	-1.399285000	3.912900000	-0.437243000
C	-5.419281000	0.916338000	-1.117236000
C	-5.682976000	2.289794000	-1.289104000
C	-7.002131000	2.703309000	-1.108001000
H	-7.243275000	3.755113000	-1.229580000
C	-8.001281000	1.792113000	-0.776422000
H	-9.021399000	2.138464000	-0.639530000
C	-7.704875000	0.440702000	-0.620868000
H	-8.491365000	-0.262977000	-0.364935000
C	-6.404641000	-0.034452000	-0.787375000
C	-4.593595000	3.256110000	-1.649963000
H	-3.810639000	3.293744000	-0.886349000
H	-4.997394000	4.263762000	-1.765460000
H	-4.108957000	2.978192000	-2.592661000
C	-6.066049000	-1.486875000	-0.626701000
H	-5.342488000	-1.648618000	0.177681000
H	-5.625575000	-1.897939000	-1.542030000
H	-6.962177000	-2.066385000	-0.396486000

TS2:

Sum of electronic and zero-point Energies= -3261.064232

Sum of electronic and thermal Free Energies= -3261.164568

Au	1.138531000	0.857055000	-1.645052000
P	-4.071190000	-0.160539000	-1.984769000
N	4.114887000	-0.070261000	-1.309838000
B	-1.650884000	0.321796000	0.206861000
C	3.016378000	0.307854000	-1.415453000
C	-1.307479000	0.409915000	-1.400919000
H	-1.331088000	-0.514885000	-1.976391000
C	-0.859038000	1.519505000	-2.137877000
H	-0.948533000	2.520258000	-1.713831000
H	-0.888873000	1.484086000	-3.228398000
C	-3.214768000	0.736006000	0.547065000
C	-4.325976000	0.552013000	-0.307862000
C	-5.625097000	0.872920000	0.122153000
H	-6.466037000	0.734160000	-0.554489000
C	-5.864582000	1.372160000	1.396342000
H	-6.875616000	1.618989000	1.708984000
C	-4.786877000	1.547096000	2.261592000
H	-4.946951000	1.928690000	3.267042000
C	-3.499036000	1.236075000	1.835299000
H	-2.677207000	1.392398000	2.529337000
C	-5.008669000	1.002441000	-3.144638000
H	-6.081314000	0.773680000	-3.060544000

C	-4.789316000	2.474050000	-2.783707000
H	-3.725192000	2.732988000	-2.817481000
H	-5.159220000	2.718316000	-1.785967000
H	-5.305628000	3.116354000	-3.507169000
C	-4.561198000	0.755399000	-4.591847000
H	-5.144465000	1.377271000	-5.281369000
H	-4.676298000	-0.284868000	-4.905036000
H	-3.505545000	1.020383000	-4.718103000
C	-5.207047000	-1.667076000	-1.885043000
H	-6.181568000	-1.305129000	-1.527478000
C	-4.652048000	-2.654420000	-0.856064000
H	-5.329762000	-3.510010000	-0.752993000
H	-4.536873000	-2.197683000	0.129776000
H	-3.673553000	-3.039461000	-1.162870000
C	-5.411800000	-2.353337000	-3.236623000
H	-4.456110000	-2.639832000	-3.690493000
H	-5.954336000	-1.724737000	-3.947837000
H	-5.998006000	-3.270160000	-3.101730000
C	-0.628205000	1.364005000	0.978952000
C	0.532145000	0.937259000	1.642692000
H	0.740615000	-0.126028000	1.716749000
C	1.435931000	1.837704000	2.216080000
C	1.211912000	3.208014000	2.148836000
H	1.909975000	3.908936000	2.590702000
C	0.059835000	3.659070000	1.506884000
C	-0.841863000	2.754776000	0.946543000
H	-1.747807000	3.141692000	0.487979000
C	2.640705000	1.302861000	2.933060000
F	2.334602000	0.785494000	4.136561000
F	3.237216000	0.307676000	2.227877000
F	3.581391000	2.249709000	3.133880000
C	-0.172807000	5.134768000	1.349491000
F	0.458939000	5.854334000	2.297346000
F	-1.479609000	5.451201000	1.404585000
F	0.284171000	5.578089000	0.154356000
C	-1.347551000	-1.217733000	0.702772000
C	-1.980361000	-1.798787000	1.813609000
H	-2.746412000	-1.237526000	2.341233000
C	-1.658100000	-3.078203000	2.269007000
C	-0.676913000	-3.837602000	1.634416000
H	-0.422846000	-4.828134000	1.992467000
C	-0.032258000	-3.286529000	0.532899000
C	-0.370655000	-2.009283000	0.081760000
H	0.162464000	-1.624630000	-0.784769000
C	-2.422222000	-3.662245000	3.424076000
F	-2.678497000	-2.741134000	4.373210000
F	-3.615469000	-4.157310000	3.029794000
F	-1.754323000	-4.674211000	4.014783000
C	1.082302000	-4.017169000	-0.152911000
F	0.989489000	-3.935653000	-1.499577000
F	1.131015000	-5.320674000	0.168186000
F	2.294242000	-3.488329000	0.165358000
C	5.400717000	-0.563429000	-1.195138000
C	5.686677000	-1.804479000	-1.797981000
C	6.991021000	-2.280054000	-1.668656000
H	7.248510000	-3.234304000	-2.118834000
C	7.954808000	-1.552927000	-0.974738000
H	8.964229000	-1.944000000	-0.887285000
C	7.635971000	-0.329536000	-0.391183000
H	8.394133000	0.229696000	0.149277000
C	6.348533000	0.197939000	-0.484474000
C	4.630211000	-2.578168000	-2.531583000
H	3.828269000	-2.896152000	-1.857353000
H	5.058284000	-3.471904000	-2.990000000
H	4.171049000	-1.978767000	-3.325558000
C	5.980035000	1.506308000	0.151740000
H	5.247327000	1.363863000	0.952020000
H	5.538907000	2.197547000	-0.574774000
H	6.861222000	1.986779000	0.581791000

7:

Sum of electronic and zero-point Energies= -3261.104602

Sum of electronic and thermal Free Energies= -3261.205566

Au	1.323744000	-0.904266000	-1.594317000
P	-3.046747000	-2.498739000	-0.751306000
N	4.365426000	-0.170513000	-1.245920000
B	-1.758125000	-0.417730000	0.591268000
C	3.238763000	-0.456454000	-1.381402000
C	-0.681909000	-1.354139000	-1.852268000
H	-1.140901000	-0.511432000	-2.384305000
H	-0.723095000	-2.211143000	-2.541657000
C	-1.450588000	-1.641935000	-0.548747000
H	-0.902933000	-2.412808000	0.012580000
C	-3.895419000	-1.912043000	0.715489000
C	-3.124544000	-0.917780000	1.353940000
C	-3.638898000	-0.426099000	2.565344000
H	-3.080922000	0.329696000	3.112281000
C	-4.843334000	-0.887025000	3.089042000
H	-5.211998000	-0.482620000	4.028432000
C	-5.584380000	-1.870515000	2.425344000
H	-6.521036000	-2.227238000	2.843862000
C	-5.106455000	-2.395029000	1.231425000
H	-5.664623000	-3.175522000	0.719795000
C	-3.934382000	-2.119769000	-2.334381000
H	-3.193155000	-2.362773000	-3.107918000
C	-5.180342000	-2.988485000	-2.537184000
H	-5.922219000	-2.808803000	-1.752215000
H	-4.959584000	-4.058782000	-2.568088000
H	-5.649587000	-2.724560000	-3.490649000
C	-4.278153000	-0.632954000	-2.446081000
H	-4.713390000	-0.437734000	-3.431701000
H	-3.401194000	0.005543000	-2.331577000
H	-5.011213000	-0.333967000	-1.691757000
C	-2.896032000	-4.348910000	-0.655333000
H	-3.929116000	-4.719286000	-0.699407000
C	-2.292375000	-4.792799000	0.681221000
H	-2.318483000	-5.885675000	0.743772000
H	-2.841055000	-4.390269000	1.535974000
H	-1.246007000	-4.486018000	0.773125000
C	-2.109101000	-4.918703000	-1.840958000
H	-1.079435000	-4.547252000	-1.844948000
H	-2.561159000	-4.676464000	-2.807190000
H	-2.065730000	-6.010068000	-1.762079000
C	-2.008297000	1.042922000	-0.114466000
C	-3.248916000	1.692240000	-0.161183000
H	-4.112279000	1.227540000	0.307300000
C	-3.422862000	2.927907000	-0.793592000
C	-2.351548000	3.570334000	-1.402957000
H	-2.482912000	4.526737000	-1.894180000
C	-1.099994000	2.958562000	-1.350693000
C	-0.938064000	1.731388000	-0.711726000
H	0.055866000	1.292717000	-0.674403000
C	-4.797713000	3.528743000	-0.827035000
F	-5.318374000	3.662391000	0.410366000
F	-5.659921000	2.747400000	-1.520010000
F	-4.818157000	4.744995000	-1.403838000
C	0.079469000	3.585071000	-2.036292000
F	0.327686000	3.001964000	-3.232532000
F	-0.101994000	4.898582000	-2.274352000
F	1.211259000	3.460927000	-1.310512000
C	-0.524231000	-0.272882000	1.666146000
C	-0.429183000	0.872721000	2.475847000
H	-1.137634000	1.684118000	2.331261000
C	0.556812000	1.022456000	3.452301000
C	1.518230000	0.034552000	3.644715000
H	2.289355000	0.149388000	4.397168000
C	1.463812000	-1.101026000	2.842271000
C	0.459089000	-1.248738000	1.883812000
H	0.462119000	-2.160930000	1.294958000
C	0.545990000	2.242772000	4.328529000

F	0.265021000	3.359964000	3.630005000
F	-0.387624000	2.148577000	5.300648000
F	1.730961000	2.439820000	4.942380000
C	2.536400000	-2.142944000	2.951567000
F	3.114415000	-2.162813000	4.167300000
F	2.072790000	-3.383938000	2.703333000
F	3.536481000	-1.926869000	2.054763000
C	5.689304000	0.177201000	-1.062249000
C	6.033406000	0.906489000	0.091696000
C	7.377963000	1.243413000	0.248560000
H	7.678212000	1.806263000	1.127633000
C	8.327940000	0.870247000	-0.698121000
H	9.369011000	1.144025000	-0.554031000
C	7.953148000	0.148583000	-1.828491000
H	8.699766000	-0.139292000	-2.563120000
C	6.623682000	-0.215486000	-2.038611000
C	6.194965000	-0.992137000	-3.249810000
H	5.724062000	-1.941029000	-2.970014000
H	7.051257000	-1.214198000	-3.890018000
H	5.462149000	-0.434203000	-3.843264000
C	4.992876000	1.293959000	1.100964000
H	4.208253000	1.910568000	0.648976000
H	5.440783000	1.862847000	1.918285000
H	4.503272000	0.411706000	1.525080000

TS3:

Sum of electronic and zero-point Energies= -3261.049243

Sum of electronic and thermal Free Energies= -3261.151282

Au	1.408577000	-0.527244000	-1.647743000
P	-0.157339000	-2.993528000	0.528075000
N	4.468685000	-0.156724000	-1.180446000
B	-1.750689000	-0.263415000	0.456224000
C	3.327860000	-0.352645000	-1.345323000
C	-1.296641000	-1.053975000	-0.889019000
H	-1.826104000	-1.993022000	-1.073086000
C	-0.657056000	-0.525859000	-2.062593000
H	-0.805661000	0.549328000	-2.189613000
H	-0.851788000	-1.067640000	-2.991221000
C	-2.021998000	-1.303455000	1.691484000
C	-1.360743000	-2.544087000	1.828304000
C	-1.603523000	-3.379604000	2.932849000
H	-1.092791000	-4.336692000	3.018049000
C	-2.497098000	-2.999542000	3.926046000
H	-2.679932000	-3.650379000	4.776801000
C	-3.155877000	-1.773834000	3.815420000
H	-3.856779000	-1.461991000	4.585671000
C	-2.920054000	-0.953642000	2.717685000
H	-3.450335000	-0.006776000	2.646035000
C	-0.755290000	-4.634761000	-0.207252000
H	-0.309197000	-5.427605000	0.410454000
C	-2.275831000	-4.806313000	-0.175993000
H	-2.781432000	-4.047362000	-0.783330000
H	-2.682632000	-4.746699000	0.835333000
H	-2.544463000	-5.782399000	-0.596458000
C	-0.235209000	-4.776401000	-1.643895000
H	-0.487946000	-5.764981000	-2.044654000
H	0.848642000	-4.653035000	-1.717598000
H	-0.694118000	-4.027741000	-2.298731000
C	1.358882000	-3.535163000	1.507588000
H	1.016972000	-4.330973000	2.185370000
C	1.898427000	-2.379565000	2.349388000
H	2.777669000	-2.706889000	2.916184000
H	1.157172000	-2.017769000	3.065439000
H	2.200878000	-1.535554000	1.721614000
C	2.447971000	-4.112671000	0.601245000
H	2.767112000	-3.381527000	-0.150110000
H	2.124137000	-5.017482000	0.079602000
H	3.326491000	-4.378702000	1.200582000
C	-3.214257000	0.324219000	-0.054249000
C	-3.534318000	1.686806000	-0.119109000
H	-2.802298000	2.429092000	0.181560000
C	-4.789505000	2.131076000	-0.543545000
C	-5.770146000	1.225265000	-0.932328000
H	-6.741094000	1.569976000	-1.267611000
C	-5.479736000	-0.135760000	-0.868662000
C	-4.231085000	-0.571497000	-0.430041000
H	-4.058705000	-1.641146000	-0.351546000
C	-5.096784000	3.602444000	-0.518125000
F	-5.445960000	4.016192000	0.718633000
F	-4.032811000	4.342307000	-0.888691000
F	-6.115496000	3.921400000	-1.340876000
C	-6.497878000	-1.139296000	-1.331272000
F	-7.756957000	-0.673142000	-1.219667000
F	-6.428782000	-2.287734000	-0.628604000
F	-6.316204000	-1.468365000	-2.629464000
C	-0.670771000	0.894266000	0.884886000
C	0.015688000	0.825172000	2.108127000
H	-0.231751000	0.033825000	2.807173000
C	1.003563000	1.743537000	2.467779000
C	1.343446000	2.790412000	1.617118000
H	2.099024000	3.514794000	1.899829000
C	0.676327000	2.893583000	0.400519000
C	-0.308280000	1.968083000	0.049436000
H	-0.810287000	2.111361000	-0.901004000
C	1.780947000	1.550908000	3.736683000
F	1.073195000	0.916731000	4.686575000
F	2.893741000	0.799593000	3.516682000
F	2.208735000	2.717930000	4.256638000
C	1.098624000	3.952111000	-0.575571000
F	2.163310000	3.536527000	-1.315105000
F	1.485257000	5.086958000	0.037968000
F	0.127446000	4.269197000	-1.447988000
C	5.808835000	0.104489000	-0.970899000
C	6.755079000	-0.691108000	-1.644463000
C	8.100389000	-0.406142000	-1.416078000
H	8.857088000	-1.000162000	-1.920296000
C	8.478472000	0.623587000	-0.558189000
H	9.532219000	0.829504000	-0.395173000
C	7.516269000	1.392729000	0.090032000
H	7.820032000	2.195527000	0.755422000
C	6.154591000	1.154343000	-0.098363000
C	6.323354000	-1.793025000	-2.568356000
H	5.723607000	-2.544581000	-2.043090000
H	7.190278000	-2.295830000	-3.001693000
H	5.708865000	-1.408580000	-3.389984000
C	5.104728000	1.971900000	0.595758000
H	4.528174000	1.369578000	1.306438000
H	4.390756000	2.403375000	-0.112991000
H	5.565897000	2.790635000	1.152128000

7b:

Sum of electronic and zero-point Energies= -3261.104796

Sum of electronic and thermal Free Energies= -3261.207284

Au	-1.322287000	-0.856011000	-1.626726000
P	3.081672000	-2.417953000	-0.893680000
N	-4.360812000	-0.128461000	-1.242747000
B	1.762881000	-0.439415000	0.567019000
C	-3.237096000	-0.421090000	-1.387984000
C	0.685789000	-1.272262000	-1.917007000
H	1.130824000	-0.402765000	-2.417051000
H	0.733403000	-2.098893000	-2.641849000
C	1.469263000	-1.607233000	-0.633898000
H	0.941997000	-2.417491000	-0.109805000
C	3.926181000	-1.899503000	0.601554000
C	3.137399000	-0.960396000	1.298730000
C	3.643316000	-0.532189000	2.537414000
H	3.070982000	0.178278000	3.128796000
C	4.857621000	-0.999446000	3.032055000
H	5.219561000	-0.645169000	3.994015000
C	5.617421000	-1.925626000	2.309634000

H	6.562012000	-2.287645000	2.705130000
C	5.147981000	-2.387545000	1.086787000
H	5.721188000	-3.124452000	0.529020000
C	3.948988000	-1.929469000	-2.457501000
H	3.207416000	-2.144374000	-3.239132000
C	5.212405000	-2.757188000	-2.718533000
H	5.956523000	-2.606404000	-1.929577000
H	5.015638000	-3.828743000	-2.809948000
H	5.667758000	-2.427867000	-3.658267000
C	4.260764000	-0.431641000	-2.487293000
H	4.689943000	-0.173639000	-3.461091000
H	3.370968000	0.181160000	-2.337164000
H	4.989068000	-0.159474000	-1.718380000
C	2.971610000	-4.273259000	-0.906388000
H	4.012666000	-4.616492000	-0.976404000
C	2.385409000	-4.808123000	0.404407000
H	2.436046000	-5.901946000	0.402720000
H	2.929808000	-4.444150000	1.279045000
H	1.332904000	-4.530881000	0.518287000
C	2.192602000	-4.792088000	-2.120304000
H	1.151747000	-4.454630000	-2.094328000
H	2.628103000	-4.475157000	-3.072346000
H	2.184402000	-5.887072000	-2.110141000
C	1.993764000	1.060404000	-0.058816000
C	3.221447000	1.736078000	-0.052821000
H	4.088017000	1.264674000	0.402966000
C	3.377838000	3.007427000	-0.614871000
C	2.301730000	3.660890000	-1.204232000
H	2.420393000	4.645103000	-1.640684000
C	1.062654000	3.022508000	-1.202685000
C	0.917905000	1.759458000	-0.632730000
H	-0.067693000	1.300735000	-0.632685000
C	4.741393000	3.634317000	-0.600040000
F	5.259544000	3.681411000	0.644560000
F	5.617690000	2.924677000	-1.350176000
F	4.739674000	4.891681000	-1.081530000
C	-0.124020000	3.660899000	-1.864474000
F	-0.375640000	3.109583000	-3.075090000
F	0.046996000	4.981756000	-2.065974000
F	-1.250769000	3.508301000	-1.136101000
C	0.528806000	-0.369197000	1.649967000
C	0.400302000	0.741287000	2.502719000
H	1.083464000	1.578650000	2.388700000
C	-0.588563000	0.823503000	3.484437000
C	-1.518293000	-0.200535000	3.640762000
H	-2.291833000	-0.137703000	4.396915000
C	-1.429664000	-1.303347000	2.796723000
C	-0.422252000	-1.383518000	1.833214000
H	-0.397390000	-2.272937000	1.211193000
C	-0.613849000	2.007564000	4.408819000
F	-0.334302000	3.156047000	3.762654000
F	0.299333000	1.886465000	5.397308000
F	-1.814765000	2.163082000	5.003677000
C	-2.469444000	-2.381295000	2.868124000
F	-3.036950000	-2.470171000	4.085836000
F	-1.970471000	-3.595856000	2.564557000
F	-3.482581000	-2.158134000	1.987816000
C	-5.681674000	0.227300000	-1.053277000
C	-6.040860000	0.834856000	0.164709000
C	-7.381883000	1.184059000	0.325251000
H	-7.693371000	1.654995000	1.253125000
C	-8.313982000	0.938760000	-0.679250000
H	-9.352560000	1.219832000	-0.531256000
C	-7.924319000	0.336444000	-1.872736000
H	-8.656946000	0.148970000	-2.652507000
C	-6.597691000	-0.034075000	-2.089329000
C	-6.152841000	-0.682920000	-3.368025000
H	-5.715228000	-1.670382000	-3.183915000
H	-6.994810000	-0.807348000	-4.052170000
H	-5.388279000	-0.083819000	-3.874956000
C	-5.018819000	1.089328000	1.233516000
H	-4.216561000	1.741247000	0.870689000
H	-5.478116000	1.569403000	2.100033000
H	-4.549061000	0.158417000	1.566128000

Alkynyl group :

4*:

Sum of electronic and zero-point Energies= -3259.873218

Sum of electronic and thermal Free Energies= -3259.976337

Au	1.708707000	-1.210044000	-0.607489000
P	0.562306000	-3.188306000	-0.067210000
N	3.993165000	0.872717000	-1.206977000
B	-1.613632000	-0.479540000	-0.200475000
C	3.123448000	0.128474000	-0.972543000
C	-0.824957000	-0.562581000	-1.588585000
C	-0.292354000	-0.543572000	-2.691539000
H	0.134602000	-0.519737000	-3.669727000
C	-2.031336000	-1.979251000	0.361349000
C	-1.198062000	-3.123487000	0.455200000
C	-1.694261000	-4.345229000	0.949245000
H	-1.055547000	-5.224417000	0.978626000
C	-3.002242000	-4.470577000	1.396618000
H	-3.362995000	-5.423215000	1.773851000
C	-3.829976000	-3.353788000	1.351211000
H	-4.856581000	-3.415727000	1.702849000
C	-3.345416000	-2.154396000	0.840022000
H	-4.021476000	-1.306628000	0.801171000
C	0.621562000	-4.408078000	-1.501262000
H	0.694795000	-5.396483000	-1.025103000
C	-0.649645000	-4.366274000	-2.354466000
H	-0.810367000	-3.367829000	-2.771656000
H	-1.539748000	-4.638953000	-1.784771000
H	-0.547209000	-5.071955000	-3.186576000
C	1.858591000	-4.186322000	-2.378700000
H	1.928090000	-4.984846000	-3.126210000
H	2.792542000	-4.173773000	-1.811905000
H	1.780622000	-3.233307000	-2.912321000
C	1.438131000	-4.047842000	1.345580000
H	0.901090000	-4.989711000	1.513161000
C	1.342856000	-3.196826000	2.612681000
H	1.829596000	-3.715785000	3.445505000
H	0.306652000	-3.002741000	2.898009000
H	1.844026000	-2.232760000	2.479862000
C	2.893034000	-4.380034000	1.008820000
H	3.452386000	-3.476769000	0.740443000
H	2.981366000	-5.097768000	0.188644000
H	3.376051000	-4.824495000	1.886036000
C	-2.964633000	0.411863000	-0.526447000
C	-3.473398000	1.370497000	0.359471000
H	-2.962672000	1.557503000	1.299710000
C	-4.631121000	2.100698000	0.075247000
C	-5.324070000	1.894452000	-1.112414000
H	-6.219202000	2.462100000	-1.337176000
C	-4.838381000	0.944527000	-2.008994000
C	-3.681806000	0.222843000	-1.718402000
H	-3.319093000	-0.497597000	-2.445859000
C	-5.088716000	3.160491000	1.036440000
F	-4.928102000	2.777560000	2.319501000
F	-4.391050000	4.307306000	0.885359000
F	-6.390505000	3.470805000	0.870516000
C	-5.597977000	0.655174000	-3.272021000
F	-6.345554000	1.705633000	-3.667796000
F	-6.443196000	-0.388341000	-3.119755000
F	-4.776878000	0.339956000	-4.294349000
C	-0.702337000	0.324312000	0.906678000
C	-0.696443000	-0.008952000	2.268450000
H	-1.268195000	-0.868067000	2.606953000
C	0.007396000	0.744000000	3.212731000
C	0.727590000	1.869191000	2.826958000
H	1.259367000	2.464128000	3.560598000

C	0.730847000	2.226719000	1.479469000
C	0.033637000	1.466184000	0.541309000
H	0.037954000	1.776362000	-0.499974000
C	0.039070000	0.295140000	4.645854000
F	-1.127412000	-0.253701000	5.031649000
F	0.994500000	-0.645358000	4.846045000
F	0.311329000	1.307371000	5.491626000
C	1.549689000	3.403063000	1.038941000
F	2.838841000	3.047410000	0.789517000
F	1.597472000	4.373670000	1.968067000
F	1.085919000	3.955212000	-0.101866000
C	5.031369000	1.746107000	-1.463795000
C	6.285398000	1.471421000	-0.885355000
C	7.320593000	2.362723000	-1.163027000
H	8.300758000	2.181879000	-0.731517000
C	7.111034000	3.471515000	-1.978984000
H	7.931516000	4.153281000	-2.182455000
C	5.857899000	3.714108000	-2.534472000
H	5.702636000	4.583058000	-3.167171000
C	4.783959000	2.858265000	-2.290370000
C	6.486299000	0.271352000	-0.006249000
H	5.820305000	0.298391000	0.863271000
H	7.515171000	0.225827000	0.356332000
H	6.274789000	-0.659431000	-0.544434000
C	3.420865000	3.114377000	-2.862390000
H	2.701238000	3.339084000	-2.068966000
H	3.042136000	2.244594000	-3.409542000
H	3.443826000	3.963110000	-3.548863000

TS1*:

Sum of electronic and zero-point Energies= -3259.841258

Sum of electronic and thermal Free Energies= -3259.942758

Au	-1.286821000	-0.053142000	-1.720985000
P	0.037882000	3.479379000	-0.343753000
N	-4.237751000	-1.008307000	-1.358766000
B	1.683059000	0.549655000	0.123307000
C	-3.138909000	-0.639831000	-1.488995000
C	0.922946000	0.560723000	-1.300998000
C	0.618511000	0.480119000	-2.512373000
H	0.762033000	0.458474000	-3.575587000
C	2.369052000	2.010277000	0.454452000
C	1.782448000	3.287784000	0.269894000
C	2.503919000	4.443762000	0.616872000
H	2.064810000	5.422828000	0.440484000
C	3.769764000	4.379886000	1.186399000
H	4.302067000	5.291467000	1.444887000
C	4.332890000	3.130832000	1.430267000
H	5.311327000	3.047834000	1.896547000
C	3.640490000	1.982529000	1.061600000
H	4.110716000	1.020985000	1.249151000
C	0.231297000	4.590842000	-1.872958000
H	0.282099000	5.632147000	-1.522294000
C	1.497832000	4.292752000	-2.678335000
H	1.520565000	3.248064000	-3.006252000
H	2.407703000	4.478033000	-2.104008000
H	1.526908000	4.921929000	-3.576414000
C	-1.003644000	4.432050000	-2.769219000
H	-0.954911000	5.123546000	-3.619529000
H	-1.940635000	4.621577000	-2.238440000
H	-1.055468000	3.413086000	-3.169495000
C	-0.624933000	4.715886000	0.922561000
H	0.053612000	5.579185000	0.949881000
C	-0.653341000	4.078138000	2.313483000
H	-0.979556000	4.813533000	3.058835000
H	0.330591000	3.708561000	2.614254000
H	-1.355404000	3.239568000	2.347022000
C	-2.016971000	5.221548000	0.535549000
H	-2.720211000	4.390845000	0.403782000
H	-2.006797000	5.809071000	-0.387036000
H	-2.415094000	5.867234000	1.327586000
C	2.784607000	-0.618318000	-0.285395000
C	2.524164000	-1.976757000	-0.055265000
H	1.635006000	-2.265446000	0.497895000
C	3.374463000	-2.981893000	-0.518801000
C	4.524670000	-2.662083000	-1.233203000
H	5.187386000	-3.439820000	-1.593193000
C	4.800237000	-1.319847000	-1.482362000
C	3.941094000	-0.321065000	-1.023649000
H	4.177088000	0.714343000	-1.251444000
C	2.993166000	-4.418618000	-0.302251000
F	2.504917000	-4.628536000	0.935764000
F	2.028222000	-4.808137000	-1.167657000
F	4.033546000	-5.256400000	-0.474144000
C	6.056219000	-0.935085000	-2.212397000
F	6.535431000	-1.945742000	-2.964994000
F	7.040531000	-0.579543000	-1.360043000
F	5.855478000	0.116235000	-3.033060000
C	0.772016000	0.105169000	1.402585000
C	1.385899000	-0.481060000	2.522871000
H	2.454675000	-0.672282000	2.506363000
C	0.665369000	-0.840730000	3.660041000
C	-0.712400000	-0.638278000	3.721067000
H	-1.277422000	-0.934316000	4.596976000
C	-1.339940000	-0.043681000	2.632987000
C	-0.604763000	0.335351000	1.505323000
H	-1.116151000	0.866096000	0.705588000
C	1.379869000	-1.403791000	4.857496000
F	0.590173000	-2.238796000	5.564188000
F	2.484494000	-2.089549000	4.510832000
F	1.771464000	-0.428422000	5.704254000
C	-2.826918000	0.138938000	2.632980000
F	-3.198208000	1.319025000	2.079034000
F	-3.360886000	0.090803000	3.864107000
F	-3.452933000	-0.820192000	1.899471000
C	-5.534465000	-1.446067000	-1.180615000
C	-6.474898000	-0.540132000	-0.653200000
C	-7.775856000	-1.012946000	-0.485858000
H	-8.529119000	-0.344569000	-0.079526000
C	-8.114391000	-2.319656000	-0.827693000
H	-9.134400000	-2.664971000	-0.687556000
C	-7.157180000	-3.189168000	-1.344772000
H	-7.430882000	-4.207313000	-1.605058000
C	-5.839839000	-2.774747000	-1.533875000
C	-6.081473000	0.859084000	-0.281061000
H	-5.308426000	0.860615000	0.493649000
H	-6.942733000	1.413753000	0.096197000
H	-5.678992000	1.404558000	-1.142033000
C	-4.788015000	-3.693941000	-2.083083000
H	-3.959452000	-3.819680000	-1.377378000
H	-4.362160000	-3.305667000	-3.015056000
H	-5.207096000	-4.680440000	-2.289990000

INT-TS1*:

Sum of electronic and zero-point Energies= -3259.848694

Sum of electronic and thermal Free Energies= -3259.951335

Au	1.182425000	0.452233000	-1.847923000
P	-4.310597000	-0.133208000	-1.575585000
N	4.045428000	-0.650177000	-1.287223000
B	-1.518627000	0.800542000	0.116121000
C	2.990756000	-0.197158000	-1.492834000
C	-1.109685000	0.913990000	-1.428881000
C	-0.709100000	1.080375000	-2.604034000
H	-0.847008000	1.272928000	-3.651076000
C	-2.988594000	1.515935000	0.385951000
C	-4.213849000	1.167210000	-0.245347000
C	-5.402343000	1.808425000	0.142039000
H	-6.333798000	1.553248000	-0.358177000
C	-5.432868000	2.771690000	1.144447000
H	-6.369945000	3.249053000	1.418876000
C	-4.246433000	3.105172000	1.787095000

H	-4.238392000	3.844560000	2.583988000
C	-3.059113000	2.487583000	1.402682000
H	-2.149752000	2.770166000	1.924008000
C	-5.152943000	0.801051000	-2.997993000
H	-6.233715000	0.836888000	-2.796713000
C	-4.639311000	2.235431000	-3.144490000
H	-3.550696000	2.254342000	-3.272592000
H	-4.878766000	2.854755000	-2.277952000
H	-5.081407000	2.703725000	-4.032383000
C	-4.916948000	0.038052000	-4.308282000
H	-5.452732000	0.520579000	-5.135047000
H	-5.243731000	-1.003573000	-4.262129000
H	-3.850373000	0.030833000	-4.559695000
C	-5.730890000	-1.187915000	-0.913672000
H	-6.575047000	-0.522656000	-0.685257000
C	-5.298784000	-1.882217000	0.378998000
H	-6.122253000	-2.486431000	0.777748000
H	-5.006969000	-1.165709000	1.150397000
H	-4.449530000	-2.550801000	0.203754000
C	-6.201287000	-2.217232000	-1.944499000
H	-5.372025000	-2.845111000	-2.290093000
H	-6.664064000	-1.751166000	-2.818922000
H	-6.950824000	-2.879587000	-1.495010000
C	-0.275822000	1.623593000	0.845168000
C	0.577554000	1.044331000	1.792698000
H	0.394966000	0.028061000	2.127501000
C	1.668855000	1.739750000	2.324655000
C	1.944374000	3.042848000	1.927603000
H	2.786194000	3.584131000	2.343031000
C	1.105350000	3.642967000	0.989443000
C	0.021830000	2.944596000	0.462199000
H	-0.612266000	3.440469000	-0.268046000
C	2.598595000	1.031850000	3.266303000
F	3.356731000	1.884814000	3.980143000
F	1.945169000	0.241568000	4.133345000
F	3.460449000	0.224988000	2.587202000
C	1.425679000	5.016017000	0.471416000
F	2.162579000	5.730519000	1.343956000
F	0.317080000	5.727037000	0.197669000
F	2.139173000	4.950074000	-0.678545000
C	-1.520718000	-0.756209000	0.610945000
C	-2.057155000	-1.083955000	1.865788000
H	-2.539387000	-0.308993000	2.455654000
C	-1.989818000	-2.378907000	2.382054000
C	-1.364071000	-3.397704000	1.667055000
H	-1.297220000	-4.399609000	2.073967000
C	-0.828906000	-3.095602000	0.418583000
C	-0.925672000	-1.803939000	-0.100873000
H	-0.529066000	-1.622341000	-1.095930000
C	-2.654892000	-2.684189000	3.694633000
F	-2.499461000	-1.682143000	4.581398000
F	-3.984686000	-2.867600000	3.543549000
F	-2.167058000	-3.805071000	4.263011000
C	-0.061079000	-4.130387000	-0.348492000
F	-0.264911000	-4.038456000	-1.677939000
F	-0.365673000	-5.386144000	0.022657000
F	1.279367000	-3.984282000	-0.161188000
C	5.278918000	-1.221532000	-1.046252000
C	5.487870000	-2.546173000	-1.478564000
C	6.742586000	-3.097930000	-1.223898000
H	6.942407000	-4.117008000	-1.541408000
C	7.730253000	-2.364058000	-0.571712000
H	8.699780000	-2.815905000	-0.384033000
C	7.486787000	-1.057482000	-0.156330000
H	8.262890000	-0.495272000	0.354356000
C	6.252056000	-0.450525000	-0.381766000
C	4.406609000	-3.320127000	-2.174940000
H	3.529966000	-3.459251000	-1.533349000
H	4.769083000	-4.307910000	-2.466067000
H	4.066104000	-2.806325000	-3.080902000
C	5.957794000	0.948217000	0.075174000
H	5.181038000	0.952266000	0.846891000
H	5.603801000	1.576701000	-0.749105000
H	6.852969000	1.412358000	0.493659000

TS2*:

Sum of electronic and zero-point Energies= -3259.850198

Sum of electronic and thermal Free Energies= -3259.951605

Au	1.126847000	0.466886000	-1.820835000
P	-4.133850000	-0.287213000	-1.696559000
N	4.050213000	-0.477723000	-1.276201000
B	-1.611848000	0.654590000	0.190984000
C	2.970540000	-0.077776000	-1.464104000
C	-1.266548000	0.743811000	-1.366474000
C	-0.808363000	0.930255000	-2.523414000
H	-0.998115000	1.095747000	-3.568075000
C	-3.127834000	1.229236000	0.484431000
C	-4.282215000	0.850061000	-0.242445000
C	-5.544538000	1.326004000	0.147240000
H	-6.425514000	1.045040000	-0.425831000
C	-5.703053000	2.160394000	1.248470000
H	-6.690661000	2.517032000	1.528821000
C	-4.579249000	2.527244000	1.982722000
H	-4.677146000	3.170962000	2.853234000
C	-3.322121000	2.069991000	1.596101000
H	-2.460694000	2.376046000	2.183281000
C	-5.017747000	0.673679000	-3.072867000
H	-6.102364000	0.558159000	-2.931529000
C	-4.681244000	2.166933000	-3.049090000
H	-3.599306000	2.331982000	-3.112975000
H	-5.034924000	2.658771000	-2.140868000
H	-5.140047000	2.668260000	-3.909894000
C	-4.630200000	0.081051000	-4.434216000
H	-5.182703000	0.579416000	-5.240069000
H	-4.828951000	-0.990853000	-4.507164000
H	-3.560996000	0.225403000	-4.625931000
C	-5.421952000	-1.587181000	-1.228343000
H	-6.348744000	-1.058623000	-0.965125000
C	-4.940864000	-2.362987000	-0.000156000
H	-5.696086000	-3.098696000	0.300823000
H	-4.754842000	-1.705977000	0.853078000
H	-4.013270000	-2.904375000	-0.213930000
C	-5.726664000	-2.543290000	-2.383620000
H	-4.814970000	-3.024248000	-2.756369000
H	-6.216181000	-2.041568000	-3.223052000
H	-6.401209000	-3.337625000	-2.042383000
C	-0.447589000	1.628436000	0.848292000
C	0.590099000	1.142919000	1.652389000
H	0.607631000	0.091515000	1.924100000
C	1.619132000	1.975644000	2.108087000
C	1.640152000	3.324788000	1.778196000
H	2.436786000	3.969861000	2.128211000
C	0.613264000	3.830673000	0.980726000
C	-0.406054000	2.997485000	0.528432000
H	-1.190808000	3.419651000	-0.093605000
C	2.703192000	1.382142000	2.959280000
F	3.735404000	2.229932000	3.145272000
F	2.259329000	1.017551000	4.175062000
F	3.219213000	0.263518000	2.387234000
C	0.652006000	5.263043000	0.528866000
F	1.420857000	6.028728000	1.327747000
F	-0.574581000	5.815666000	0.495865000
F	1.160025000	5.368619000	-0.721088000
C	-1.458984000	-0.879296000	0.735997000
C	-1.898900000	-1.209356000	2.027559000
H	-2.403756000	-0.456180000	2.626295000
C	-1.706357000	-2.480345000	2.569720000
C	-1.049024000	-3.471132000	1.842727000
H	-0.884262000	-4.453457000	2.269540000
C	-0.610088000	-3.167404000	0.558113000

C	-0.830407000	-1.900329000	0.014130000
H	-0.503474000	-1.715458000	-1.005077000
C	-2.268934000	-2.803017000	3.925816000
F	-2.219373000	-1.743848000	4.756212000
F	-3.563495000	-3.178532000	3.847903000
F	-1.603997000	-3.814024000	4.521187000
C	0.190365000	-4.167005000	-0.222484000
F	-0.049295000	-4.093643000	-1.546987000
F	-0.043425000	-5.434100000	0.162327000
F	1.525622000	-3.954676000	-0.066996000
C	5.308667000	-1.006183000	-1.065597000
C	5.559950000	-2.311537000	-1.533248000
C	6.837692000	-2.823051000	-1.311037000
H	7.069162000	-3.826115000	-1.656871000
C	7.808345000	-2.069571000	-0.655887000
H	8.796692000	-2.489574000	-0.494174000
C	7.523532000	-0.783346000	-0.205328000
H	8.286640000	-0.204805000	0.306780000
C	6.263926000	-0.216881000	-0.397215000
C	4.496616000	-3.109438000	-2.230271000
H	3.645446000	-3.311311000	-1.571130000
H	4.895499000	-4.068653000	-2.566029000
H	4.108187000	-2.580600000	-3.107728000
C	5.928586000	1.158076000	0.101454000
H	5.197568000	1.111569000	0.914837000
H	5.498586000	1.782022000	-0.689164000
H	6.822073000	1.658834000	0.479442000

3*:

Sum of electronic and zero-point Energies= -3259.905981

Sum of electronic and thermal Free Energies= -3260.009083

Au	1.146338000	-0.060716000	-1.778378000
P	-3.462097000	-0.978674000	-1.892707000
N	4.211793000	0.407202000	-1.232686000
B	-1.898741000	-0.333050000	0.359688000
C	3.072902000	0.240013000	-1.438410000
C	-0.805540000	-0.425667000	-2.176040000
H	-1.039547000	-0.567409000	-3.238540000
C	-1.820540000	-0.550121000	-1.285798000
C	-4.346333000	-0.953408000	-0.334503000
C	-3.467085000	-0.654647000	0.728501000
C	-4.039877000	-0.645289000	2.011426000
H	-3.416436000	-0.419306000	2.872255000
C	-5.388222000	-0.920935000	2.215408000
H	-5.794678000	-0.905003000	3.223549000
C	-6.228123000	-1.224025000	1.138650000
H	-7.278370000	-1.444210000	1.306449000
C	-5.705605000	-1.245038000	-0.147401000
H	-6.347832000	-1.494790000	-0.988397000
C	-4.096587000	0.248080000	-3.131889000
H	-3.344854000	0.207425000	-3.933189000
C	-5.466808000	-0.110958000	-3.714027000
H	-6.241879000	-0.096923000	-2.941245000
H	-5.482213000	-1.089095000	-4.202967000
H	-5.747081000	0.634778000	-4.465419000
C	-4.088601000	1.658285000	-2.535532000
H	-4.345934000	2.384314000	-3.313560000
H	-3.109468000	1.925103000	-2.131695000
H	-4.825766000	1.753250000	-1.732848000
C	-3.635218000	-2.668518000	-2.646292000
H	-4.713016000	-2.760987000	-2.842163000
C	-3.233367000	-3.759207000	-1.649014000
H	-3.449196000	-4.741399000	-2.082468000
H	-3.780492000	-3.676452000	-0.706908000
H	-2.164161000	-3.722250000	-1.424937000
C	-2.875117000	-2.807042000	-3.968406000
H	-1.796656000	-2.710737000	-3.810825000
H	-3.181042000	-2.069638000	-4.716726000
H	-3.058793000	-3.800405000	-4.390879000
C	-1.544806000	1.233944000	0.693324000
C	-2.522621000	2.238162000	0.731462000
H	-3.568279000	1.967020000	0.615724000
C	-2.202599000	3.585545000	0.913527000
C	-0.879579000	3.983877000	1.078161000
H	-0.627302000	5.027705000	1.219231000
C	0.109562000	3.003855000	1.066364000
C	-0.221496000	1.660064000	0.885350000
H	0.574139000	0.920327000	0.904297000
C	-3.313013000	4.594515000	0.963516000
F	-4.017425000	4.511454000	2.112152000
F	-4.198745000	4.408760000	-0.041587000
F	-2.863022000	5.860793000	0.867325000
C	1.553406000	3.385746000	1.199390000
F	2.207338000	3.309585000	0.014145000
F	1.720713000	4.640854000	1.653886000
F	2.216344000	2.562415000	2.045402000
C	-0.887927000	-1.335241000	1.169695000
C	-0.646613000	-1.168174000	2.544335000
H	-1.099830000	-0.331941000	3.069560000
C	0.188978000	-2.023401000	3.263634000
C	0.839792000	-3.079323000	2.628243000
H	1.497344000	-3.739320000	3.181689000
C	0.633464000	-3.254997000	1.264300000
C	-0.217285000	-2.401858000	0.557928000
H	-0.343606000	-2.560931000	-0.507362000
C	0.350194000	-1.834173000	4.745029000
F	0.320750000	-0.532665000	5.093858000
F	-0.637550000	-2.443520000	5.437112000
F	1.513923000	-2.344921000	5.198190000
C	1.388085000	-4.313737000	0.516575000
F	1.817249000	-5.306389000	1.319908000
F	0.640195000	-4.878266000	-0.455614000
F	2.486456000	-3.806304000	-0.094395000
C	5.552968000	0.610730000	-0.975012000
C	5.990524000	0.561269000	0.362045000
C	7.351026000	0.770222000	0.588681000
H	7.723198000	0.739017000	1.608561000
C	8.226168000	1.016348000	-0.465613000
H	9.281262000	1.176460000	-0.263982000
C	7.759083000	1.058983000	-1.776801000
H	8.447955000	1.252056000	-2.594130000
C	6.409898000	0.856930000	-2.064179000
C	5.881620000	0.899102000	-3.468779000
H	5.415874000	-0.052137000	-3.749434000
H	6.685565000	1.105082000	-4.178431000
H	5.117986000	1.676158000	-3.584835000
C	5.028278000	0.299806000	1.483296000
H	4.264783000	1.081791000	1.545959000
H	5.552731000	0.261467000	2.440193000
H	4.503532000	-0.651997000	1.346023000

TS3*:

Sum of electronic and zero-point Energies= -3259.843484

Sum of electronic and thermal Free Energies= -3259.947481

Au	1.973231000	-1.479841000	-0.849366000
P	0.396945000	-1.046834000	2.538456000
N	5.018606000	-0.816427000	-0.988839000
B	-1.883417000	-0.115033000	0.597835000
C	3.894160000	-1.126570000	-0.917617000
C	-0.768592000	-1.040289000	-0.012748000
C	-0.059214000	-1.639904000	-0.907333000
H	-0.543120000	-1.997204000	-1.817004000
C	-2.300875000	-0.440622000	2.131287000
C	-1.339322000	-0.814476000	3.094737000
C	-1.710343000	-1.005872000	4.434752000
H	-0.966805000	-1.307973000	5.169469000
C	-3.027270000	-0.827166000	4.844833000
H	-3.301770000	-0.980087000	5.885087000
C	-3.988282000	-0.455588000	3.906056000
H	-5.022368000	-0.314736000	4.210037000

C	-3.623492000	-0.270681000	2.575399000
H	-4.391740000	0.002942000	1.855509000
C	0.796488000	-2.805111000	3.109760000
H	0.946184000	-2.769735000	4.199118000
C	-0.354141000	-3.768202000	2.802044000
H	-0.579222000	-3.780379000	1.730156000
H	-1.269701000	-3.504114000	3.334876000
H	-0.072312000	-4.787169000	3.092764000
C	2.081531000	-3.313747000	2.445469000
H	2.342030000	-4.304539000	2.837097000
H	2.938911000	-2.656219000	2.607160000
H	1.938281000	-3.413227000	1.363393000
C	1.314578000	0.046477000	3.773639000
H	0.950988000	-0.237490000	4.771415000
C	0.952007000	1.512662000	3.524091000
H	1.403634000	2.144878000	4.297561000
H	-0.128334000	1.677429000	3.544587000
H	1.325867000	1.854365000	2.553795000
C	2.831319000	-0.148301000	3.741325000
H	3.232943000	0.004203000	2.732786000
H	3.133321000	-1.141047000	4.085820000
H	3.312686000	0.584527000	4.399592000
C	-3.029976000	-0.566376000	-0.507576000
C	-3.271565000	0.179225000	-1.669571000
H	-2.718658000	1.097811000	-1.840618000
C	-4.222357000	-0.224202000	-2.607795000
C	-4.953670000	-1.393383000	-2.416288000
H	-5.692573000	-1.706731000	-3.144375000
C	-4.716400000	-2.155279000	-1.274408000
C	-3.763114000	-1.751162000	-0.340363000
H	-3.590522000	-2.366001000	0.537912000
C	-4.405704000	0.576002000	-3.867529000
F	-4.286631000	1.898045000	-3.643734000
F	-3.478860000	0.252298000	-4.795862000
F	-5.612228000	0.366491000	-4.429330000
C	-5.529126000	-3.393879000	-1.018305000
F	-6.013314000	-3.924567000	-2.158566000
F	-6.588825000	-3.138163000	-0.222899000
F	-4.803259000	-4.349634000	-0.404933000
C	-1.443689000	1.456656000	0.441983000
C	-2.287021000	2.482152000	0.900887000
H	-3.243876000	2.229538000	1.348108000
C	-1.931348000	3.826553000	0.803063000
C	-0.702413000	4.200878000	0.258802000
H	-0.422766000	5.245309000	0.188584000
C	0.148343000	3.201558000	-0.196424000
C	-0.224587000	1.857748000	-0.112569000
H	0.464358000	1.106747000	-0.487184000
C	-2.844862000	4.884458000	1.356767000
F	-4.140884000	4.531834000	1.263290000
F	-2.596678000	5.120615000	2.663251000
F	-2.698447000	6.061210000	0.714586000
C	1.505297000	3.527960000	-0.744288000
F	2.492002000	3.075148000	0.075599000
F	1.704521000	4.847592000	-0.901401000
F	1.725309000	2.941860000	-1.942066000
C	6.327495000	-0.385523000	-1.085586000
C	7.351426000	-1.264204000	-0.685057000
C	8.661247000	-0.798660000	-0.790411000
H	9.477013000	-1.449745000	-0.490121000
C	8.930049000	0.479936000	-1.272386000
H	9.957963000	0.822413000	-1.346014000
C	7.892432000	1.322492000	-1.661980000
H	8.112115000	2.317314000	-2.038132000
C	6.561566000	0.912745000	-1.579640000
C	7.035494000	-2.638087000	-0.168637000
H	6.409442000	-2.593986000	0.729430000
H	7.951301000	-3.175771000	0.084725000
H	6.489951000	-3.229805000	-0.912016000
C	5.429386000	1.804068000	-1.999666000
H	4.748227000	2.022695000	-1.170815000
H	4.829250000	1.341414000	-2.790871000
H	5.809617000	2.754230000	-2.379790000

3b*:

Sum of electronic and zero-point Energies= -3259.891546

Sum of electronic and thermal Free Energies= -3259.996103

Au	-2.403724000	-1.006113000	0.274798000
P	0.277918000	-1.168426000	-2.500494000
N	-5.511001000	-0.592950000	0.537797000
B	2.060240000	-0.097945000	-0.611830000
C	-4.371468000	-0.844430000	0.434175000
C	0.535963000	-0.745151000	-0.770331000
C	-0.391187000	-0.863170000	0.211843000
H	0.033956000	-0.637218000	1.200253000
C	2.789137000	-0.420146000	-2.035111000
C	1.954024000	-0.863395000	-3.079821000
C	2.415548000	-1.096445000	-4.381836000
H	1.742067000	-1.437242000	-5.166174000
C	3.763053000	-0.904453000	-4.664397000
H	4.142486000	-1.079402000	-5.667083000
C	4.628643000	-0.504009000	-3.641531000
H	5.687159000	-0.377450000	-3.854660000
C	4.149872000	-0.270334000	-2.354594000
H	4.851409000	0.018941000	-1.575117000
C	-0.110106000	-2.965084000	-2.823352000
H	-0.305059000	-3.002079000	-3.905722000
C	1.107417000	-3.842827000	-2.506410000
H	1.370112000	-3.779754000	-1.445962000
H	1.985786000	-3.568511000	-3.094073000
H	0.861500000	-4.886980000	-2.725999000
C	-1.338347000	-3.484959000	-2.070439000
H	-1.533397000	-4.518034000	-2.379404000
H	-2.242861000	-2.902621000	-2.256296000
H	-1.156517000	-3.484104000	-0.992476000
C	-0.834413000	-0.110507000	-3.556975000
H	-0.460867000	-0.323585000	-4.570143000
C	-0.578982000	1.368252000	-3.248866000
H	-1.103207000	1.986445000	-3.985180000
H	0.483656000	1.621120000	-3.290446000
H	-0.947678000	1.636870000	-2.255284000
C	-2.324473000	-0.449923000	-3.508784000
H	-2.724020000	-0.348893000	-2.494025000
H	-2.536450000	-1.460473000	-3.868168000
H	-2.870836000	0.249077000	-4.152276000
C	2.820652000	-0.771305000	0.663137000
C	2.841455000	-0.183602000	1.936530000
H	2.393054000	0.795653000	2.079829000
C	3.440773000	-0.810715000	3.031596000
C	4.051506000	-2.052996000	2.890704000
H	4.516470000	-2.542358000	3.740746000
C	4.051647000	-2.654108000	1.633863000
C	3.449024000	-2.021611000	0.547122000
H	3.472355000	-2.516462000	-0.420439000
C	3.374514000	-0.154351000	4.381207000
F	3.572179000	1.175988000	4.303626000
F	2.167093000	-0.331667000	4.961636000
F	4.293360000	-0.647996000	5.234859000
C	4.741240000	-3.970707000	1.422877000
F	4.977616000	-4.618858000	2.580366000
F	5.933270000	-3.819752000	0.805956000
F	4.010249000	-4.798028000	0.643552000
C	1.903632000	1.540010000	-0.420181000
C	2.931350000	2.432583000	-0.773182000
H	3.851659000	2.050075000	-1.203458000
C	2.816785000	3.811867000	-0.594999000
C	1.656632000	4.368939000	-0.057486000
H	1.564112000	5.439949000	0.078207000
C	0.626548000	3.509441000	0.302705000
C	0.756119000	2.129884000	0.124815000

H	-0.081564000	1.499927000	0.407440000
C	3.922878000	4.717336000	-1.056758000
F	5.134986000	4.143128000	-0.931168000
F	3.783114000	5.047585000	-2.360373000
F	3.951160000	5.874777000	-0.365572000
C	-0.667892000	4.030160000	0.852607000
F	-1.704117000	3.747214000	0.023485000
F	-0.661788000	5.363701000	1.031039000
F	-0.976356000	3.466890000	2.039814000
C	-6.830784000	-0.205965000	0.677538000
C	-7.839520000	-1.094436000	0.262411000
C	-9.157711000	-0.665637000	0.403983000
H	-9.960569000	-1.324574000	0.091334000
C	-9.452186000	0.587256000	0.937504000
H	-10.489263000	0.898051000	1.043929000
C	-8.430167000	1.440965000	1.341728000
H	-8.668297000	2.415765000	1.757917000
C	-7.091105000	1.067469000	1.221260000
C	-7.497499000	-2.439999000	-0.309573000
H	-6.904705000	-2.344996000	-1.227289000
H	-8.404224000	-3.001118000	-0.549012000
H	-6.904938000	-3.035855000	0.395107000
C	-5.972797000	1.975673000	1.644733000
H	-5.336097000	2.253316000	0.793987000
H	-5.321691000	1.496171000	2.387767000
H	-6.367823000	2.895736000	2.083888000