Supporting Information

A Ruthenium(II) Bis(Phosphinophosphinine) Complex as a Precatalyst for Transfer-Hydrogenation and Hydrogen-Borrowing Reactions

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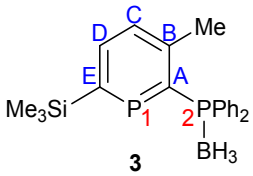
Experimental

General experimental details

All reactions were performed under an oxygen-free (H_2O, O_2 < 0.5 ppm) nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNIlab Plus glovebox unless otherwise noted. Anhydrous toluene was obtained from an MBRAUN SPS-800, 40-60 petroleum ether was distilled from sodium wire, chloroform (and $CDCl_3$) was distilled from calcium hydride, acetone-d_6 and isopropanol were dried over activated 4 Å molecular sieves. Methanol-d_4 was dried over activated 3 Å molecular sieves. Benzene-d_6 was dried over molten potassium and distilled. Anhydrous ethanol and methanol were purchased from Sigma-Aldrich. All anhydrous solvents were degassed before use and stored over activated molecular sieves, non-dry solvents were used as received from Fisher Scientific. Borane-dimethylsulfide, 1,4-diazabicyclo[2.2.2]octane (DABCO), diphenyl(1-prop-1-ynyl)phosphine and **4** were stored under nitrogen. NMR spectra were recorded on a Bruker AVIII300, AVI400, AVIII400, AV500, AV600 or Jeol ECS400 spectrometer using the internal protio resonance as a reference. 4,6-di(*tert*-butyl)-1,3,2-diazaphosphinine,[1] diphenyl(1-prop-1-ynyl)phosphine,[2] and *cis*-[$RuCl_2(dmso)_4$][3] were prepared according to literature methods. Electron ionisation mass spectrometry (EI-MS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh (compound **2**). Atmospheric-Pressure Solids Analysis Probe data was obtained on a Xevo G2-S instrument at the EPSRC UK National Mass Spectrometry Facility at Swansea University (compounds **3** and **4**). Elemental analyses were conducted using an Exeter CE-440 elemental analyser at Heriot-Watt University or by Mr Stephen Boyer at London Metropolitan University. Samples obtained from methanol/ethanol co-condensation experiments were analysed by GC-FID, using an Agilent 7820A GC, fitted with a DB-WAX capillary column, 30 m x 0.32 mm, I.D. 0.25 µm. Method: starting oven temp 50 °C, hold at 50 °C for 5 min, heat to 250 °C at 50 °C min^{-1}, hold at 250 °C for 5 min.

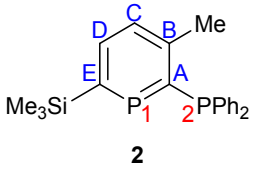


3

Compound 3

To a solution of diazaphosphinine (13.8 mmol) in 100 cm^3 toluene was added a dry and degassed toluene solution of diphenyl(1-prop-1-ynyl)phosphine (13.8 mmol, 1 equiv.) and the reaction was stirred at 85°C for 20 hours. After confirming consumption of the diazaphosphinine by ^{31}P NMR spectroscopy, trimethylsilylacetylene (2.0 cm^3, 14.4 mmol, 1.04 equivalents) was added and the reaction stirred at 85°C for 20 hours. Once the flask was cool, the contents were transferred to a round-bottomed flask and all solvent removed on a rotary evaporator. With vigorous stirring, the contents of the flask were extracted with 400 cm^3 of ether and the solution filtered through a sintered-glass funnel; this process was repeated two more times before all solvent was removed on a rotary evaporator. The resulting oil was eluted through a plug of silica with toluene until the eluent was colourless. All solvent was then removed on a rotary evaporator and the oil transferred to a Schlenk flask fitted with a stirrer bar. The oil was dissolved in 30 cm^3 of pentane and the flask was washed with a further 20 cm^3 which was added to the Schlenk flask. With vigorous stirring, borane-dimethylsulfide (1.4 cm^3, 14.8 mmol, 1.07 equiv.) was added via syringe. After a few seconds, a white precipitate formed and the heterogeneous mixture was stirred for 15 minutes then left to stand for 24 hours to ensure maximum precipitation. After cannula filtration and two subsequent 30 cm^3 pentane washes, the precipitate was dried under high-vacuum to give 3.64 g (9.57 mmol, 69%) of 2-diphenylphosphino-borane-3-methyl-6-trimethylsilyl phosphinine as a white solid. Crystals suitable for X-ray diffraction were grown from the pentane filtrate on standing at room temperature overnight.

^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.98 (m, 1H, H_D), 7.75-7.41 (m, 10H, PPh_2), 7.36 (m, 1H, H_C), 2.48 (s, 3H, C(CH_3)), 2.08-0.74 (bm, 3H, BH_3), 0.27 (s, 9H, Si(CH_3)$_3$); **^{31}P-NMR (162 MHz, 25 °C, $CDCl_3$):** δ = 255.42 (d, P_1, $^2J_{P1\text{-}P2}$ = 72.8 Hz), 22.65 (bs, P_2); **^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$):** δ = 167.31 (dd, C_E, $^2J_{CE\text{-}P1}$ = 80.3 Hz, $^2J_{CE\text{-}P2}$ = 5.9 Hz), 156.78 (dd, C_A, $^1J_{CA\text{-}P1}$ = 84.7 Hz, $^1J_{CA\text{-}P2}$ = 41.6 Hz), 150.40 (dd, C_B, $^2J_{CB\text{-}P1}$ = 12.2 Hz, $^2J_{CB\text{-}P2}$ = 12.0 Hz), 136.63 (dd, PPh_2), 132.69 (dd, C_C, $^3J_{CC\text{-}P1}$ = 19.3 Hz, $^3J_{CC\text{-}P2}$ = 8.9 Hz), 131.47 (s, PPh_2), 129.84 (dd, C_D, $^2J_{CD\text{-}P1}$ = 57.4 Hz, $^4J_{CD\text{-}P2}$ = 6.0 Hz) 128.94 (d, PPh_2), 26.26 (d, C-CH$_3$, $^3J_{C\text{-}P1}$ = 7.0 Hz), 0.09 (d, Si(CH$_3$)$_3$, $^3J_{C\text{-}P1}$ = 7.0 Hz); **^{11}B-NMR (96 MHz, 25 °C, $CDCl_3$):** δ = -35.8 (bs, BH$_3$); **^{29}Si-NMR (79 MHz, 25 °C, $CDCl_3$):** δ = -0.84 (dd, $^2J_{Si\text{-}P1}$ = 37.3 Hz, $^4J_{Si\text{-}P2}$ = 1.6 Hz); **HRMS** (ESI$^+$) *m/z*: ([M-H]$^+$) Calcd. for $C_{21}H_{27}BP_2Si$: 379.1376; Found: 379.1370; **Elemental Analysis:** Anal. Calcd. for $C_{21}H_{24}P_2Si$: C 66.33, H 7.16; Found: C 66.41, H 7.17.

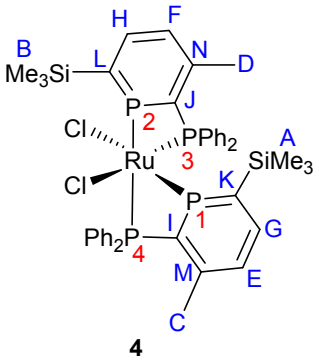


2

Compound 2

To a Schlenk flask containing 597 mg (1.57 mmol, 1 equiv.) of 2-diphenylphosphino-borane-3-methyl-6-trimethylsilylphosphinine **3** and 88.1 mg 1,4-diazabicyclo[2.2.2]octane (0.79 mmol, 0.5 equiv.) was added dry toluene (10 cm^3), and the pale yellow solution was allowed to stir for 18 hours. Cannula filtration of the reaction mixture removed insoluble DABCO(BH_3)$_2$ and all volatiles were then removed under high vacuum leaving a viscous oil which solidified over several hours. Under air, the resulting solid was transferred to a fritted filter funnel and extracted with 3 x 20 cm^3 portions of hexane. All solvent was then removed under vacuum leaving 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine **2** (558 mg, 1.52 mmol, 97%) as an almost colourless solid. Crystals of the product suitable for X-ray diffraction were grown from hexane solution at -25°C.

^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.92 (m, 1H, H_D), 7.44-7.28 (m, 11H, PPh_2 & H_C), 2.53 (s, 3H, (CH_3)C), 0.29 (s, 9H, Si(CH_3)$_3$); **^{31}P-NMR (162 MHz, 25 °C, $CDCl_3$):** δ = 249.84 (d, P_1, $^2J_{P1\text{-}P2}$ = 31.59 Hz), -7.50 (d, P_2, $^2J_{P2\text{-}P1}$ = 31.59 Hz); **^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$):** δ = 167.94 (d, C_E, $^1J_{CE\text{-}P1}$ = 80.7 Hz), 166.44 (dd, C_A, $^1J_{CA\text{-}P1}$ = 87.1 Hz, $^1J_{CA\text{-}P2}$ = 24.0 Hz), 148.11 (dd, C_B, $^2J_{CB\text{-}P1}$ = 23.2 Hz, $^2J_{CB\text{-}P2}$ = 12.0 Hz), 137.54 (d, PPh_2), 136.19 (m, C_C), 134.33 (dd, PPh_2), 130.48 (dd, C_D, $^2J_{CD\text{-}P1}$ = 20.8 Hz, $^4J_{CD\text{-}P2}$ = 4.0 Hz), 128.82 (s, PPh_2), 128.41 (d, PPh_2), 24.14 (d, CH$_3$, $^3J_{C\text{-}P1}$ = 24.8 Hz), -0.11 (d, Si(CH$_3$)$_3$, $^3J_{C\text{-}P1}$ = 6.4 Hz); **^{29}Si-NMR (79 MHz, 25 °C, $CDCl_3$):** δ = -1.56 (d, $^2J_{Si\text{-}P1}$ = 36.6 Hz); **EI** *m/z*: ([M]$^+$) 366.1; **Elemental Analysis:** Anal. Calcd. for $C_{21}H_{24}P_2Si$: C 68.83, H 6.60; Found: C 68.74, H 6.69.



4

Compound 4

To a Schlenk flask containing 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine **2** (558 mg, 1.52 mmol, 1 equiv.) and *cis*-[$RuCl_2(dmso)_4$] (361 mg, 0.75 mmol, 0.5 equiv) was added 10 cm^3 of anhydrous chloroform. The reaction mixture was heated to 55°C for 5 hours before the solvent was removed under reduced pressure. The contents of the flask were then heated to 70°C under high vacuum for 8 hours before being washed with 3 x 20 cm^3 portions of 40-60 pet. ether. The precipitate was dried under high vacuum, yielding **4** (583 mg, 0.64 mmol, 85%) as an air-sensitive bright orange powder. Crystals suitable for X-ray diffraction were grown from slow diffusion of 40-60 pet. ether into a benzene solution of **4**. Further purification (if DMSO remained) was achieved by recrystallisation from hot THF or slow diffusion of pet. ether into a DCM solution, which yielded the 1:1 DCM solvate.

^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 7.98 (ddd, 1H, H_H, $^3J_{HH\text{-}P2}$ = 22.4 Hz, $^3J_{HH\text{-}HF}$ = 8.5 Hz, $^5J_{HH\text{-}P3}$ = 5.4 Hz), 7.83 (dd, 2H, PPh_2), 7.67 (dd, 2H, PPh_2), 7.56-7.49 (m, 3H, PPh_2 & H_G), 7.34 (m, 1H, PPh_2), 7.29-7.21 (m, 3H, PPh_2), 7.19-7.11 (m, 4H, PPh_2), 7.07-7.04 (m, 3H, H_F & PPh_2), 6.92-6.86 (m, 5H, H_E & PPh_2), 2.16 (s, 3H, H_C), 1.62 (s, 3H, H_D), 0.50 (s, 9H, H_B), -0.01 (s, 9H, H_A); **^{31}P-NMR (202 MHz, 25 °C, $CDCl_3$):** δ = 235.19 (m, P_1), 229.9 (ddd, P_2, $^2J_{P2\text{-}P4}$ = 424.8 Hz), 2.34 (m, P_3), -2.43 (ddd, P_4, $^2J_{P4\text{-}P2}$ = 425.7 Hz); **^{13}C-NMR (126 MHz, 25 °C, $CDCl_3$):** δ = 166.75 (d, C_L, $^1J_{CL\text{-}P2}$ = 27.0 Hz), 160.86 (dd, C_K, $^1J_{CK\text{-}P1}$ = 24.7 Hz, $^3J_{CK\text{-}P4}$ = 5.4 Hz), 156.95 (ddd, C_J, $^1J_{CJ\text{-}P2}$ = 67.1 Hz, $^1J_{CJ\text{-}P3}$ = 20.0 Hz, $^3J_{CJ\text{-}P4}$ = 10.8 Hz), 149.91-148.85 (m, C_I & C_M, $^1J_{CI\text{-}P1}$ = 42.39 Hz, $^1J_{CI\text{-}P4}$ = 10.0 Hz), 147.18 (dd, C_N, $^2J_{CN\text{-}P2}$ = 11.6 Hz, $^2J_{CN\text{-}P3}$ = 6.9 Hz), 144.62 (d, C_G, $^2J_{CG\text{-}P1}$ = 18.5 Hz), 144.20 (dd, C_H, $^2J_{CH\text{-}P2}$ = 20.0 Hz, $^4J_{CH\text{-}P3}$ = 3.1 Hz), 134.13-127.62 (m, PPh_2), 126.78 (dd, C_F, $^3J_{CF\text{-}P2}$ = 35.5 Hz, $^3J_{CF\text{-}P3}$ = 6.9 Hz), 124.55 (dd, C_E, $^3J_{CE\text{-}P1}$ = 37.8 Hz, $^3J_{CE\text{-}P4}$ = 6.9 Hz), 23.31 (t, C_C, $^3J_{CC\text{-}P1}$ = 6.9 Hz), 21.53 (t, C_D, $^3J_{CD\text{-}P2}$ = 6.2 Hz), 0.59 (d, C_A, $^3J_{CA\text{-}P1}$ = 1.5 Hz), 0.1 (t, C_B, $^3J_{CB\text{-}P2}$ = 2.3 Hz), ; **^{29}Si-NMR (99 MHz, 25 °C, $CDCl_3$):** δ = -0.13 (dd, -*Si*$(CH_3)_3$, $^2J_{Si\text{-}P}$ = 21.8 Hz, $^4J_{Si\text{-}P}$ = 2.4 Hz), -0.95 (dd, -*Si*$(CH_3)_3$, $^2J_{Si\text{-}P}$ = 19.4 Hz, $^4J_{Si\text{-}P}$ = 3.0 Hz); **HRMS** (ESI$^+$) *m/z*: ([M-Cl]$^+$) Calcd. for $C_{42}H_{48}ClP_4RuSi_2$: 869.0985; Found: 869.0995; **Elemental Analysis:** Anal. Calcd. for $C_{42}H_{48}Cl_2P_4RuSi_2$: C 55.75, H 5.35; Found: C 55.91, H 5.40.

Reaction of 2 with alkoxide

To a vial containing **2** (10 mg, 0.03 mmol) was added 0.6 cm^3 $CDCl_3$ and 0.1 cm^3 ^{i}PrOH (1.31 mmol). The solution was pipetted into a vial containing KO^{t}Bu (3.4 mg, 0.03 mmol) before the reaction mixture was transferred to an NMR tube. The tube was shaken thoroughly and left for 2 hours, during which time the colour changed to a deep purple. ^{31}P NMR analysis showed complete conversion.

^{31}P-NMR (162 MHz, 25 °C, $CDCl_3$): 3.60 (d, $^2J_{P\text{-}P}$ = 56.7 Hz), -9.62 (d, $^2J_{P\text{-}P}$ = 56.7 Hz).

No reaction of 2 with alcohols

A solution of **2** (10 mg, 0.03 mmol) and 0.1 cm^3 of alcohol (methanol, ethanol, isopropanol) in 0.5 cm^3 $CDCl_3$ in an NMR tube fitted with a Teflon tap was left for 24 h at room temperature and the ^{31}P-NMR spectrum recorded. The solution was then heated to 82°C for 1 h and the ^{31}P-NMR spectrum re-recorded. No reaction was observed with any of the alcohols used.

No reaction of 4 with isopropanol

Under an atmosphere of nitrogen, an NMR tube was charged with **4** (20 mg, 0.02 mmol), $CDCl_3$ (0.5 cm^3) and isopropanol (0.2 cm^3). The tube was sealed with a Teflon tap and heated at 70°C for 48 h. ^{31}P-NMR spectroscopy revealed no reaction.

Reaction of 4 with KO^{t}Bu in ^{i}PrOH

To an NMR tube containing **4** (20 mg, 0.02 mmol) was added ^{i}PrOH (0.7 cm^3) to give a suspension. KO^{t}Bu (12.4 mg, 0.11 mmol, 5 equiv.) was added to give a dark orange solution. The tube was sealed with a Teflon tap and shaken thoroughly before the ^{31}P-

NMR spectrum was recorded (unlocked). Addition of acetophenone (26 µL, 0.22 mmol) to this mixture showed complete conversion to 1-phenylethanol by unlocked ^{1}H-NMR spectroscopy.

Investigation into catalyst activation

To a Schlenk flask containing **4** (20 mg, 0.02 mmol) and KO^{t}Bu (12.4 mg, 0.11 mmol, 5 equiv.) was added approximately 10 cm^3 ^{i}PrOH with strong stirring. The orange solution was stirred for five minutes before the solvent was removed *in vacuo*. The resulting oily residue was taken up in acetone-d_6 or methanol-d_4 and the ^{31}P-NMR spectrum recorded. These tests showed that the complex reacts rapidly with alkoxides in isopropanol, as expected. However, ^{31}P NMR spectroscopy indicated that multiple species were observed between 110 and -20 ppm. The ^{31}P-^{31}P COSY NMR spectrum of the reaction mixture was recorded over a 24 hour period, but only a few cross-peaks were observed due to low concentration of each individual species and the close proximity of many of the resonances. Addition of $CDCl_3$ to the strongly basic residue resulted in an immediate reaction with a colour change from orange to dark purple/black.

General procedure for NMR-scale reactions of 4 with alkoxides

Under an atmosphere of nitrogen, an NMR tube was charged with **4** (20 mg, 0.02 mmol), KO^{t}Bu/NaOMe (2 or 5 equiv.) and anhydrous C_6D_6/methanol-d_4. The tube was sealed with a Teflon tap and shaken thoroughly before the ^{31}P-NMR spectrum was recorded. These experiments showed that reaction of alkoxides with **4** in a non-protic solvent was considerably slower.

Experimental for the mass spectrometry studies of the activation of 4

Mass spectrometry studies of **4** + KO^{t}Bu in dry ^{i}PrOH comprised of electrospray (ESI) in positive and negative ion modes using a Waters Xevo G2-S instrument. Sample preparation involved dissolving KO^{t}Bu in 0.5 mL fresh, dry ^{i}PrOH in a screw-cap vial, and mixing by shaking for ~10 sec. The precatalyst **4** was then added and the vial shaken again for ~10 sec; this constitutes t = 0 time point to which sampling time points are relative. For the ESI analyses, the reactants were mixed as above using the 5.7:1 molar ratio for both polarities. A 20 µL aliquot of mixture solution was immediately introduced into the Xevo instrument via loop injection, into a continuous infusion of MeOH, flowing at a rate of 20 µL/min. The source temperature = 70°C and the desolvation temperature = 250°C. The capillary voltage = +2.5kV in positive mode and −3 kV in negative mode, and the cone voltage was +10 V in positive mode and −5 V in negative mode.

NMR and mass spectra of compounds 2 - 4

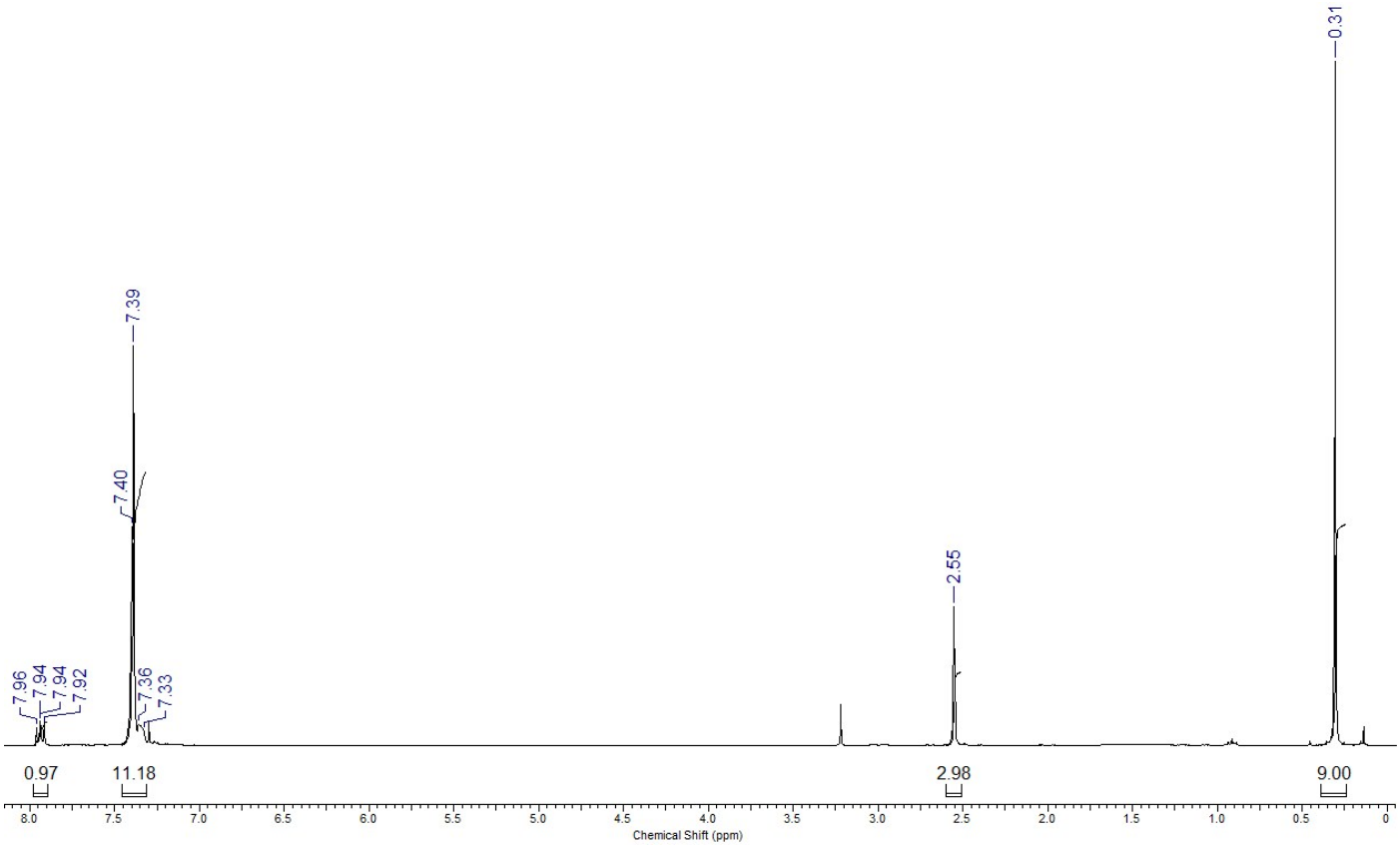


Figure S1. ^{1}H-NMR spectrum of **2**

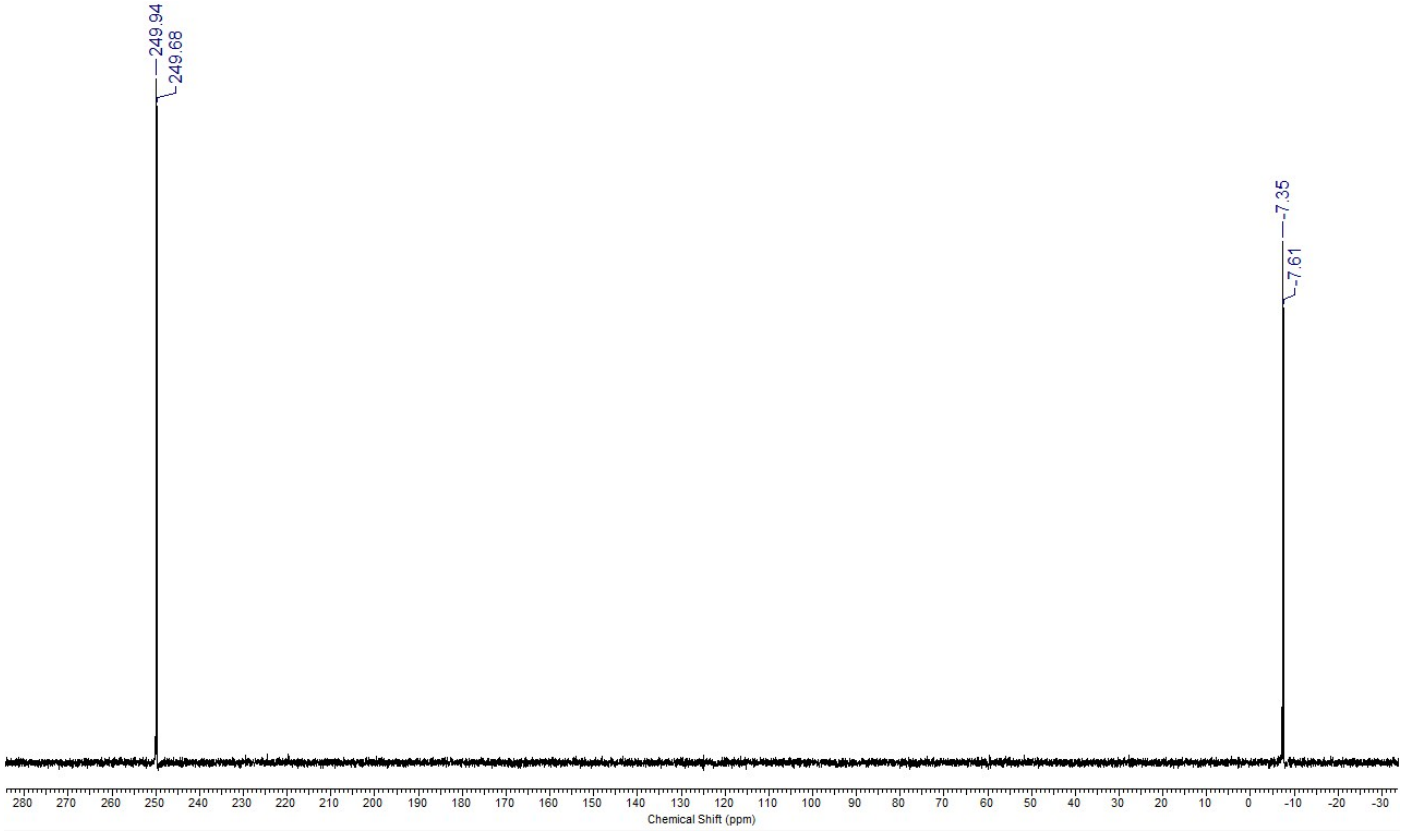


Figure S2. ^{31}P-NMR spectrum of **2**

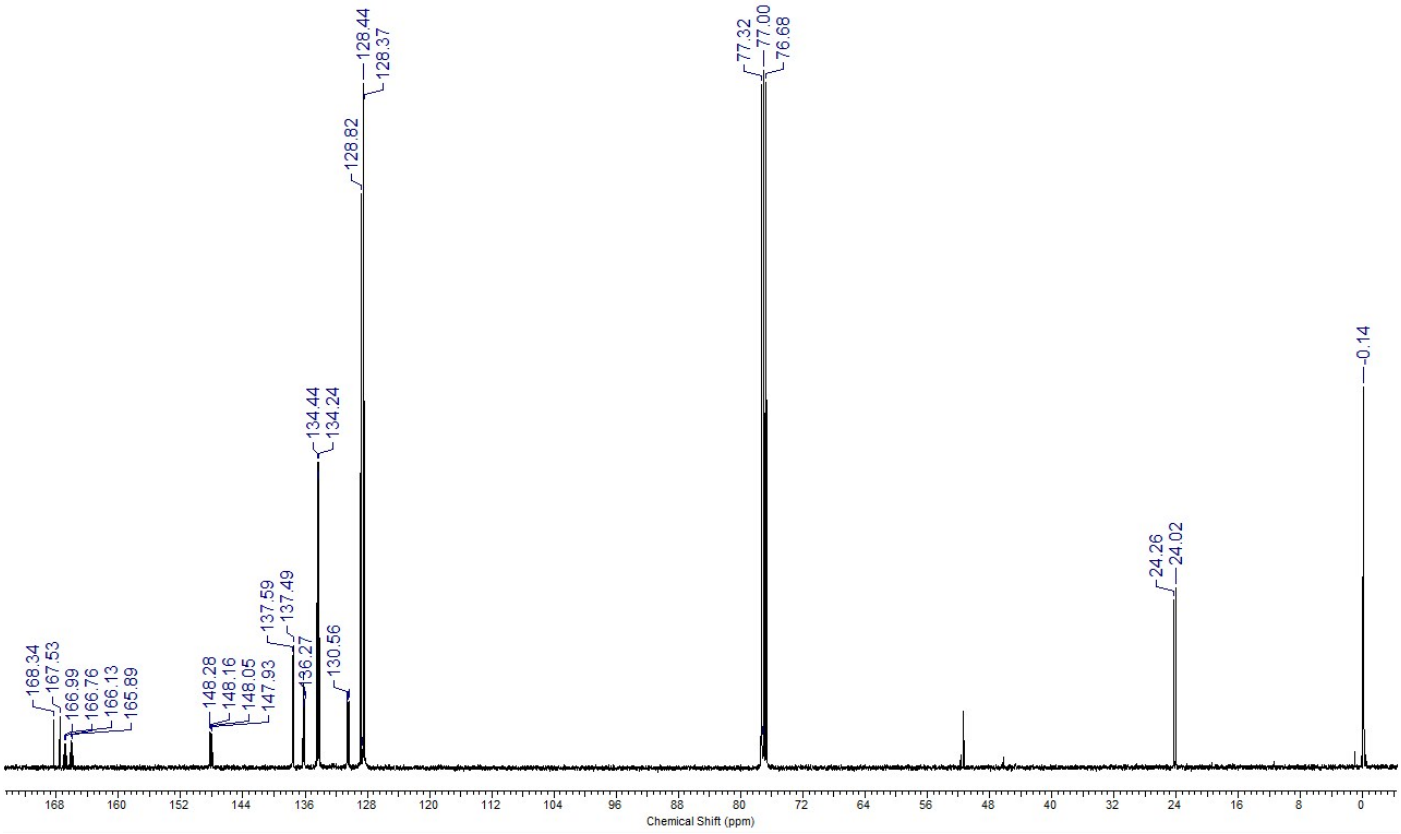


Figure S3. ^{13}C-NMR spectrum of **2**

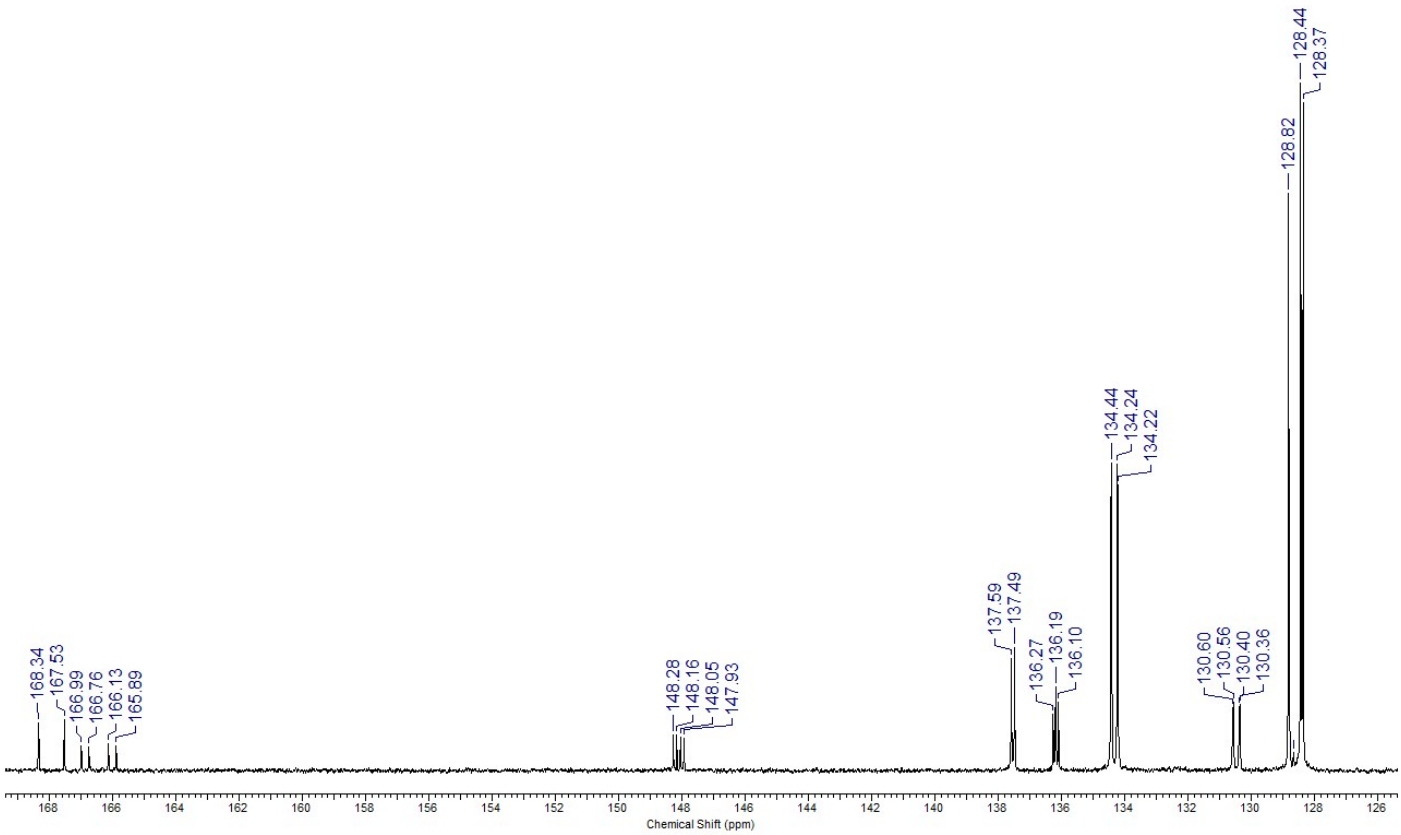


Figure S4. ^{13}C-NMR (aromatic region) spectrum of **2**

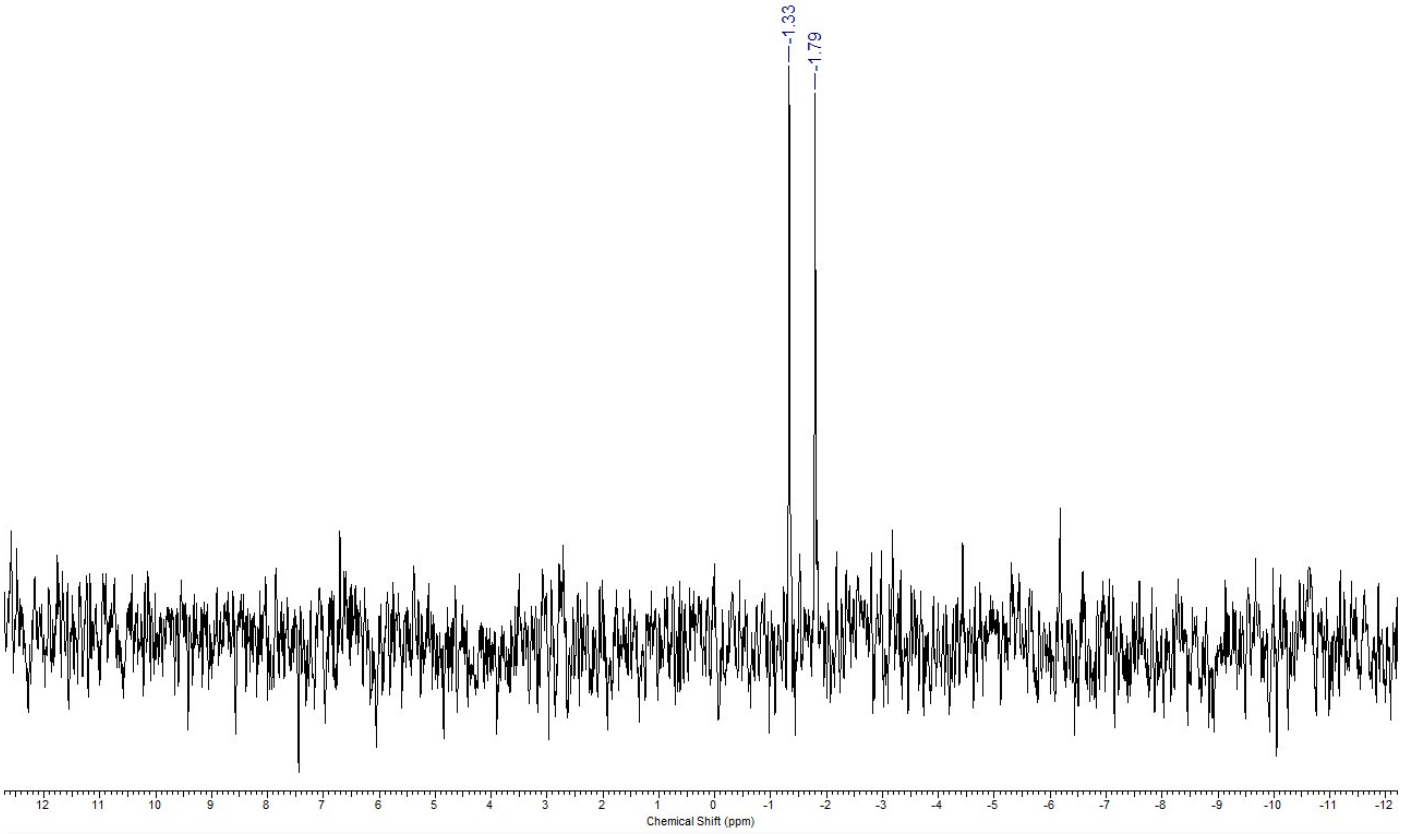


Figure S5. ^{29}Si-NMR spectrum of **2**

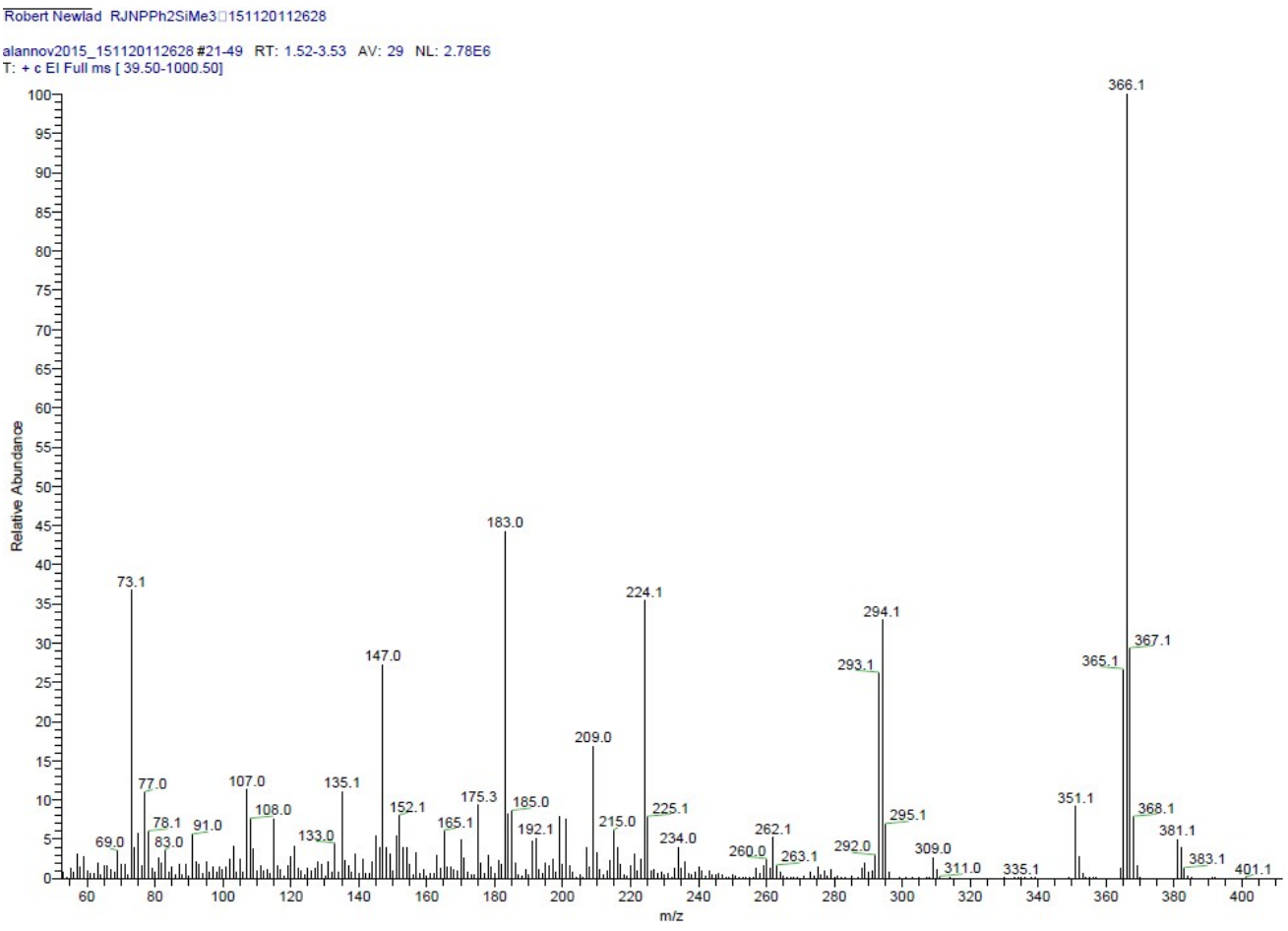


Figure S6. MS (EI) of **2**

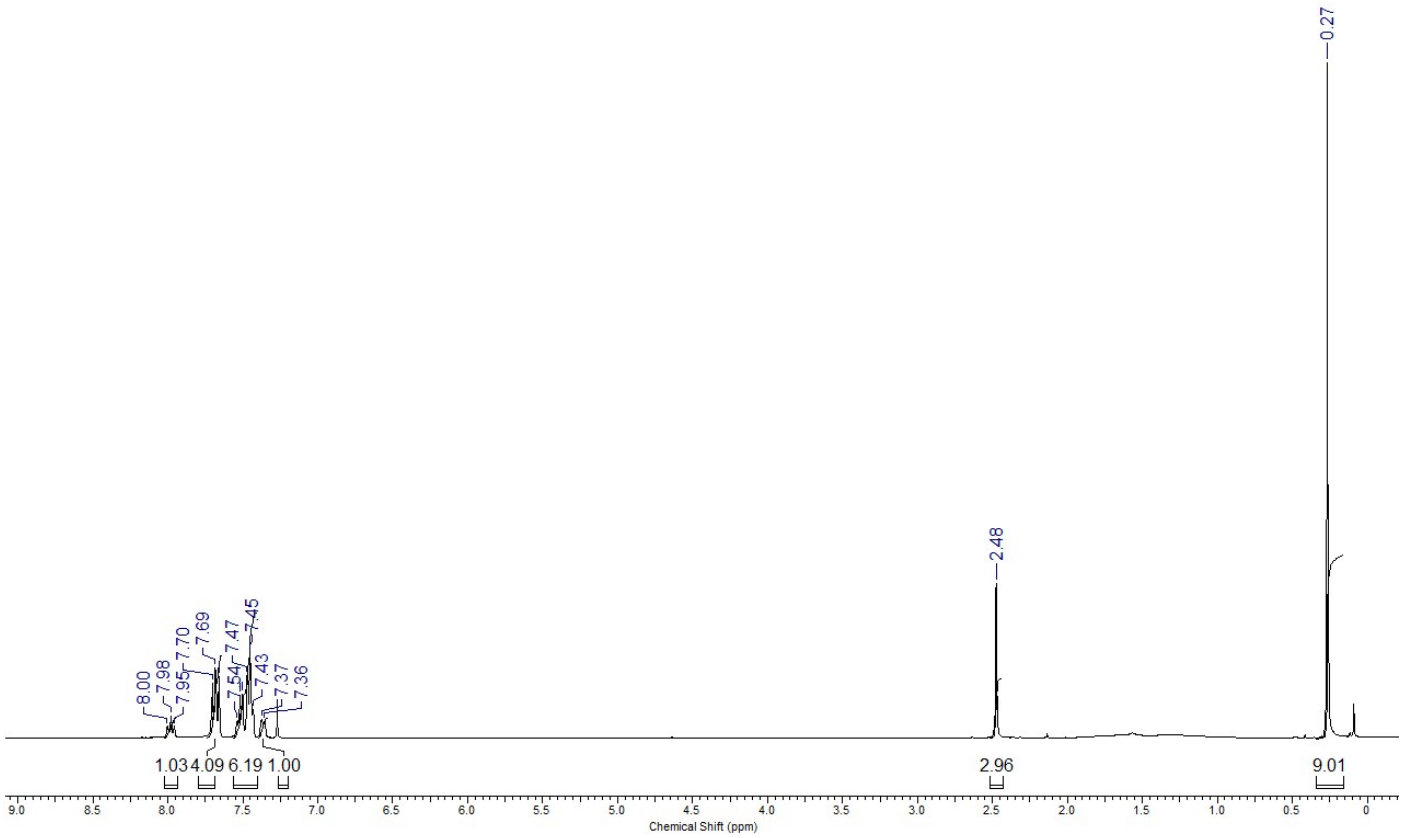


Figure S7. ^{1}H-NMR spectrum of **3**

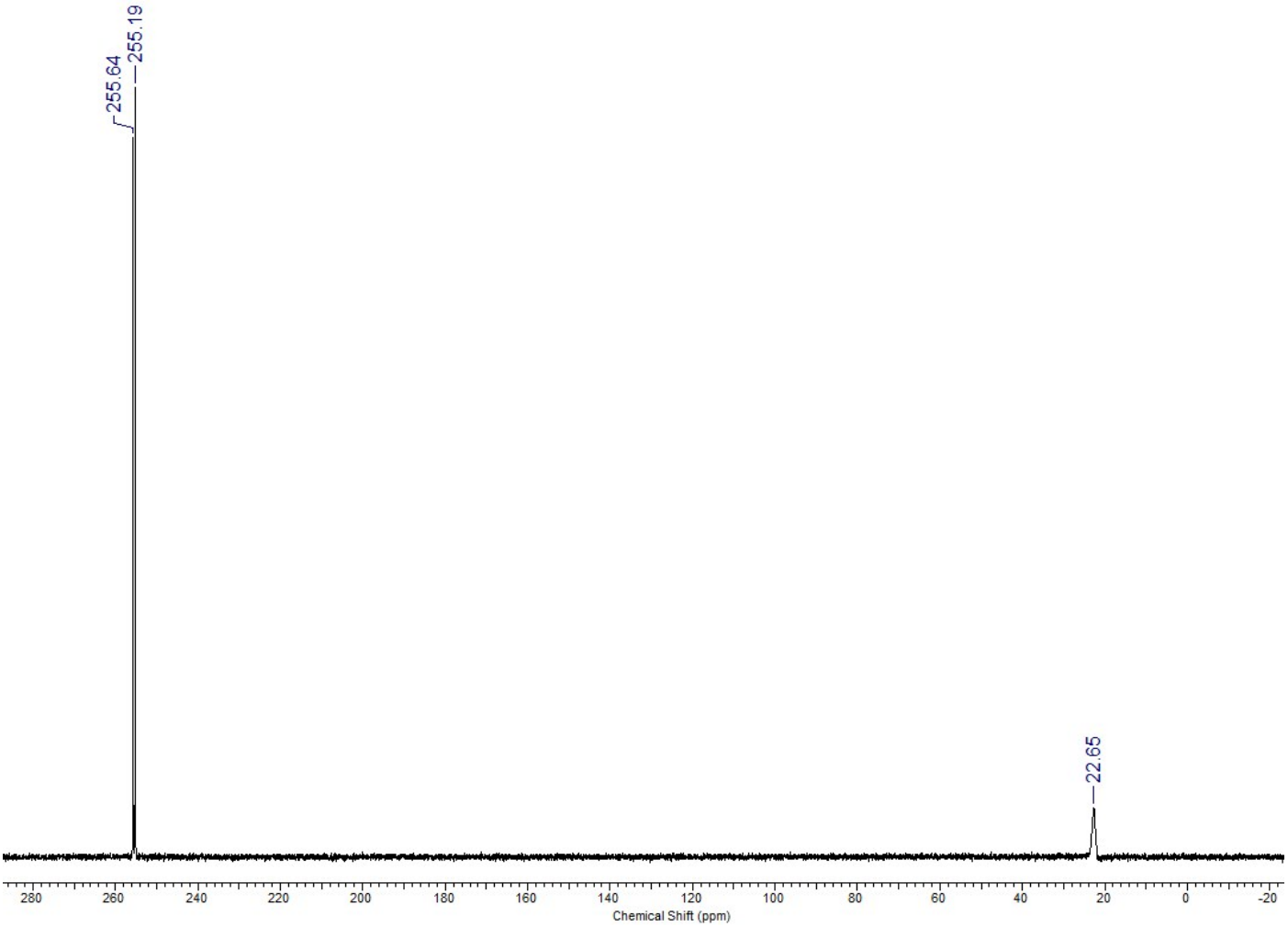


Figure S8. ^{31}P-NMR spectrum of **3**

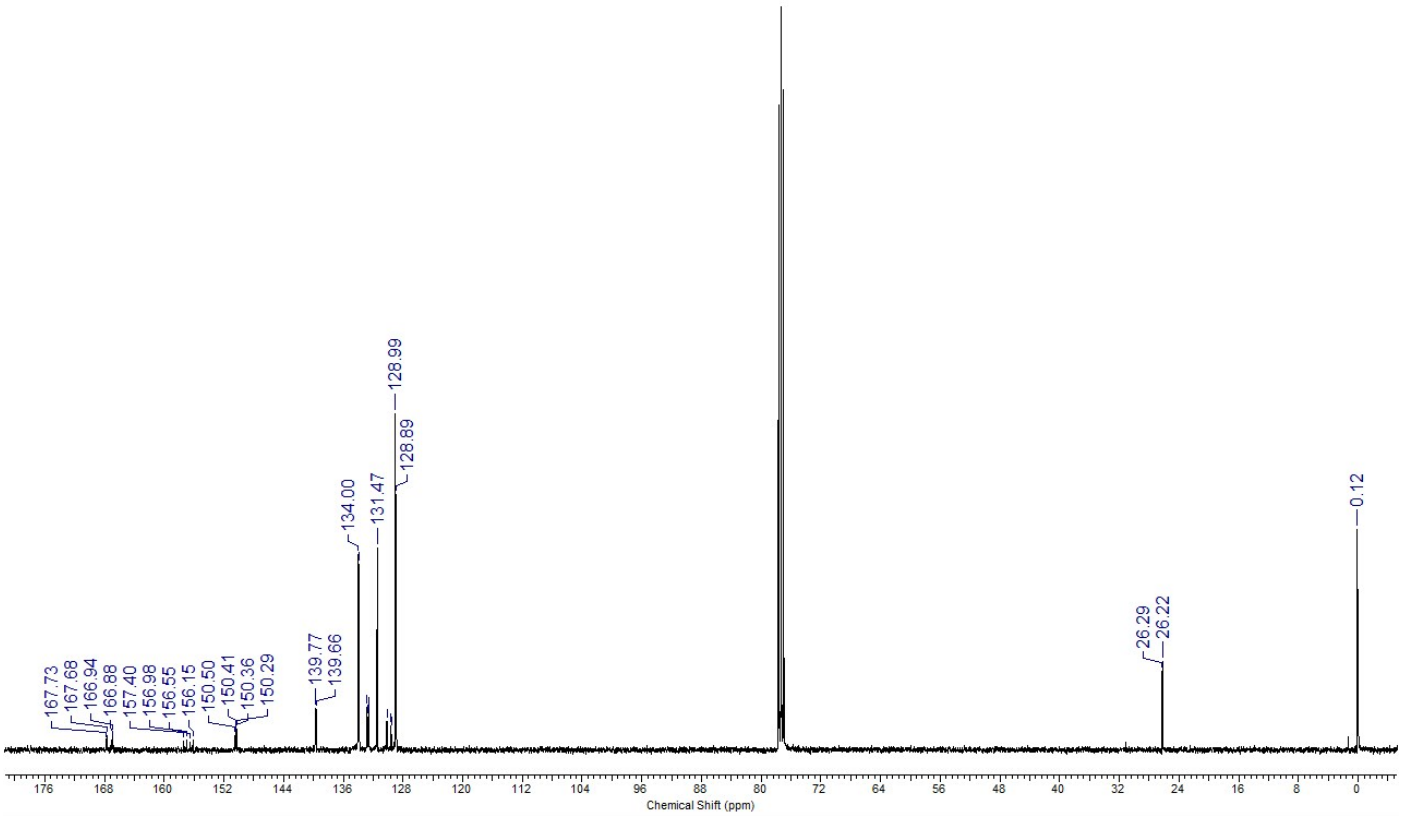


Figure S9. ^{13}C-NMR spectrum of **3**

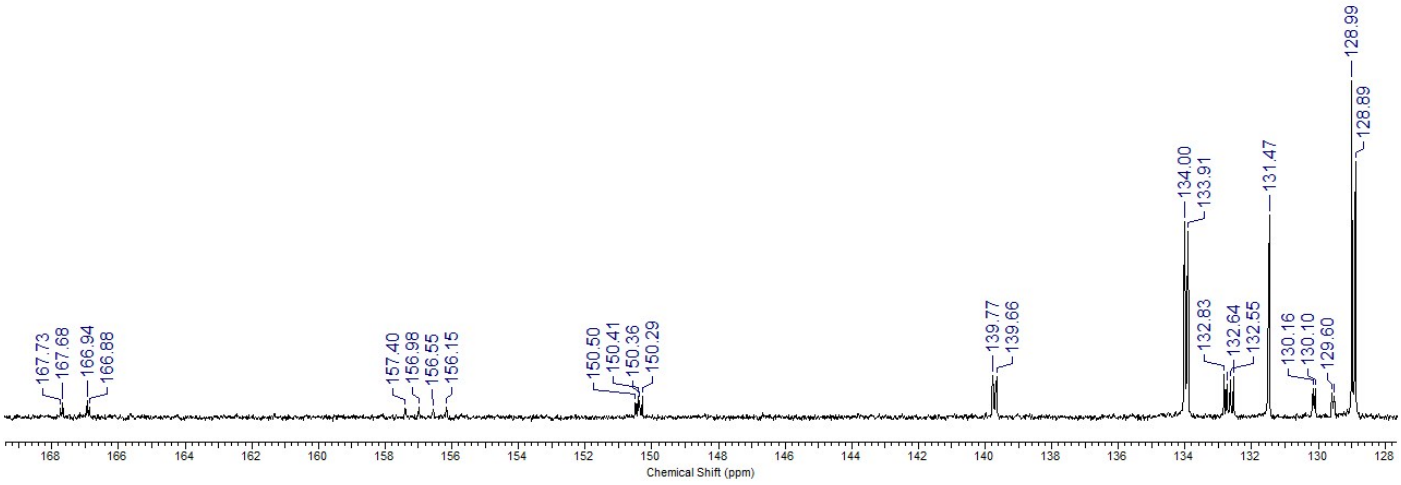


Figure S10. ^{13}C-NMR (aromatic region) spectrum of **3**

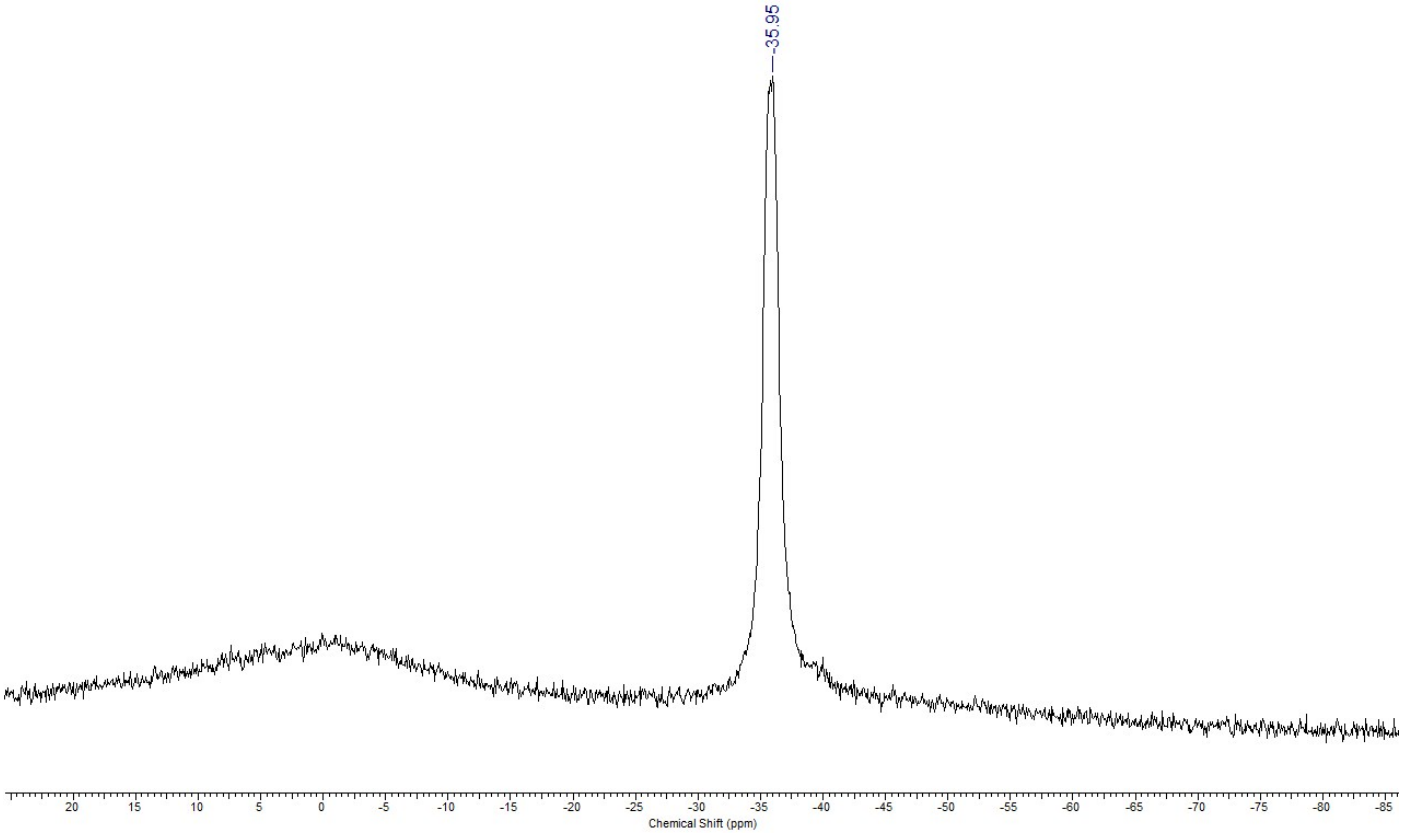


Figure S11. ^{11}B-NMR spectrum of **3**

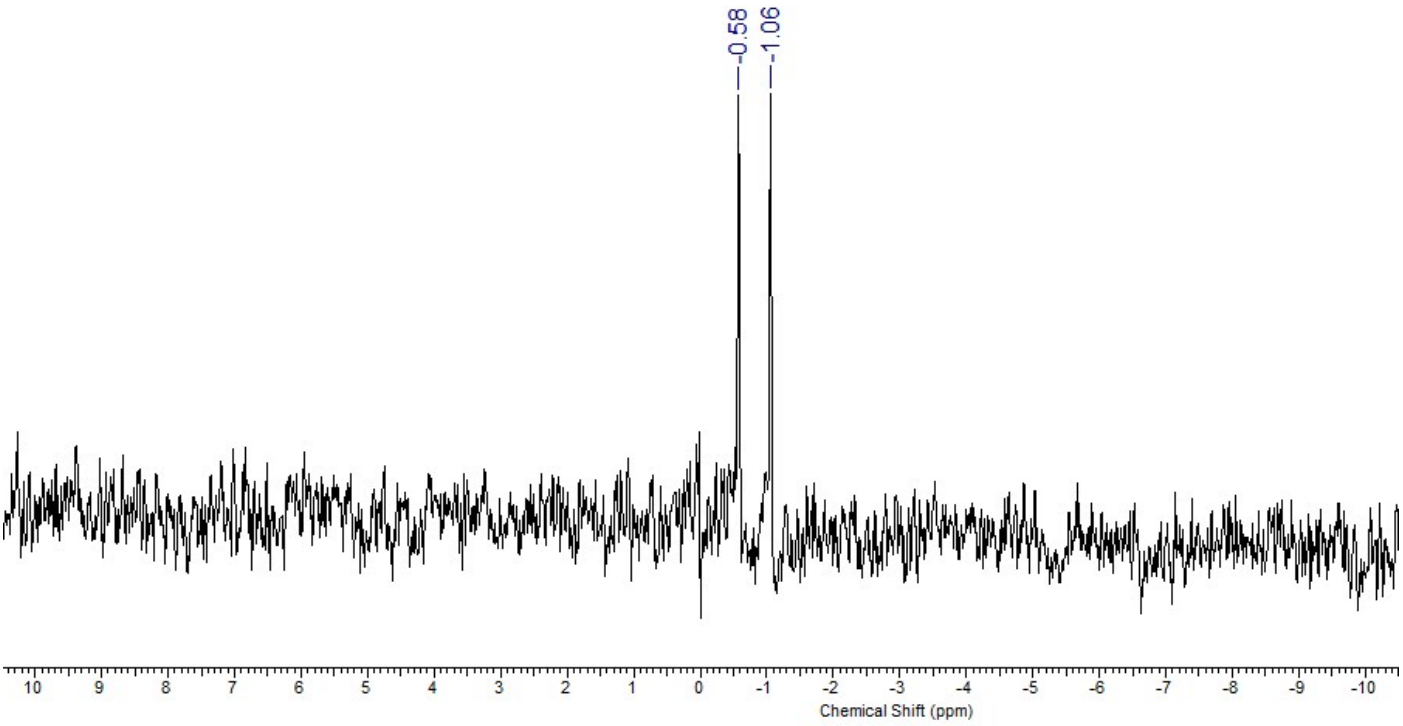


Figure S12. ^{29}Si-NMR spectrum of **3**

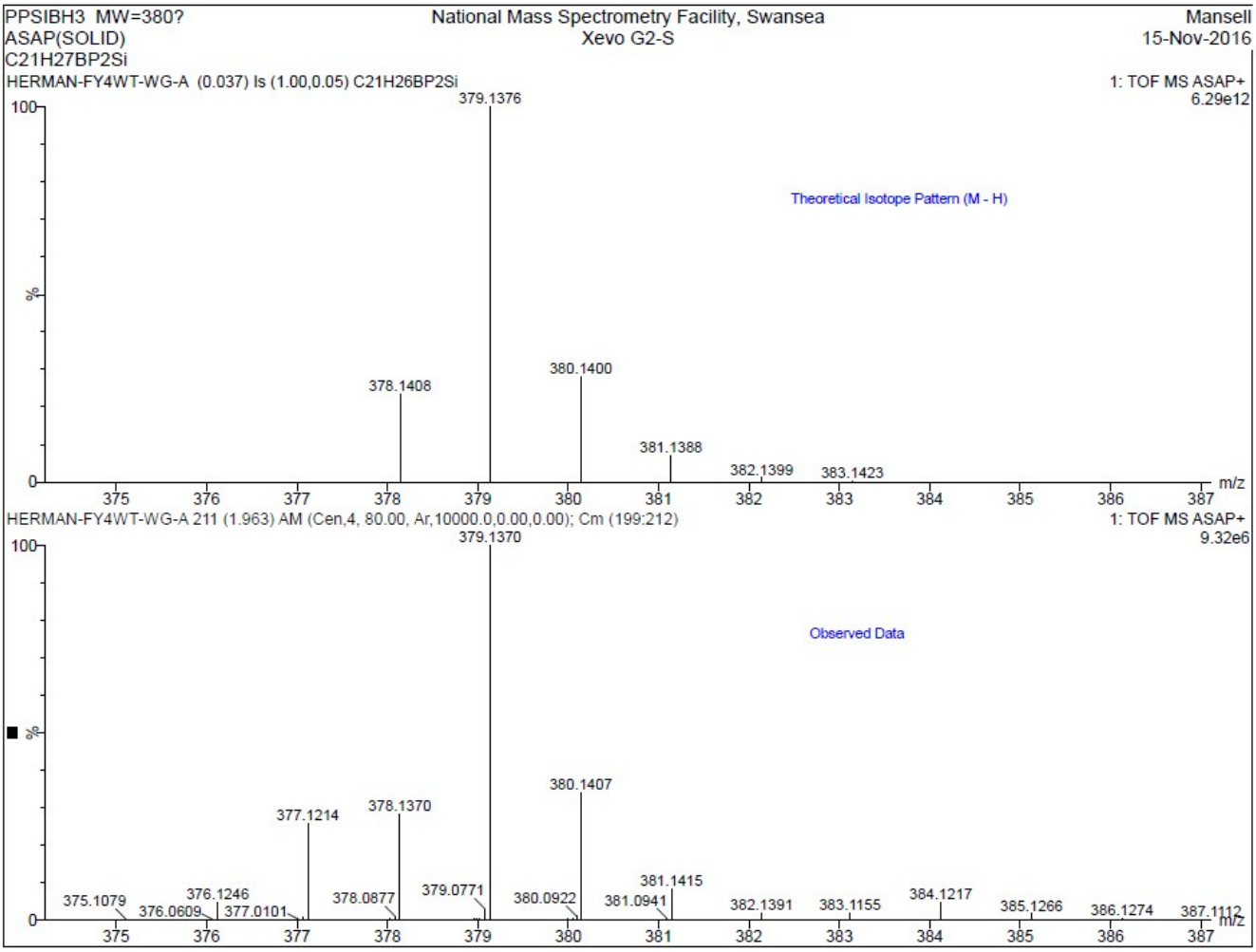


Figure S13. HRMS of **3**

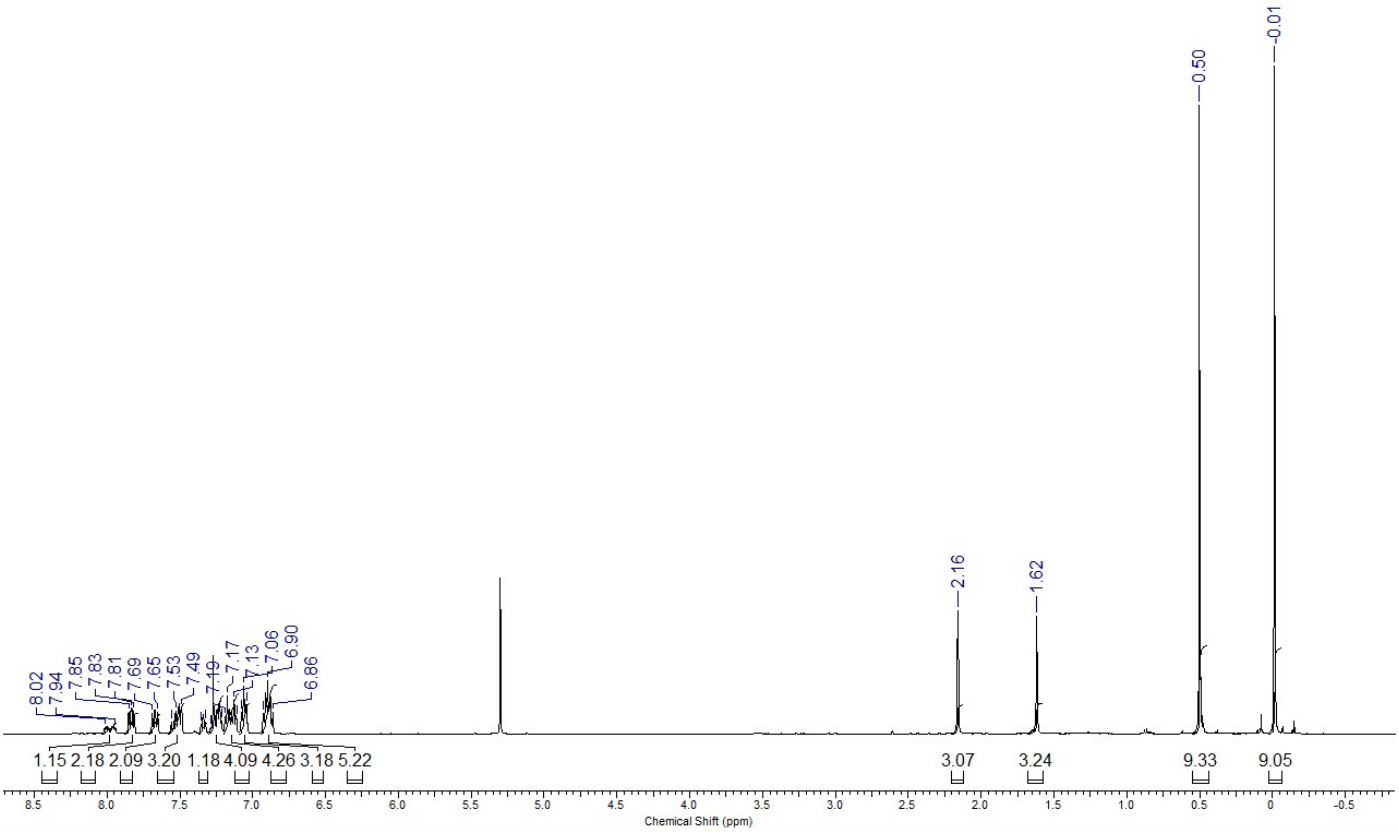


Figure S14. ^{1}H-NMR spectrum of **4**

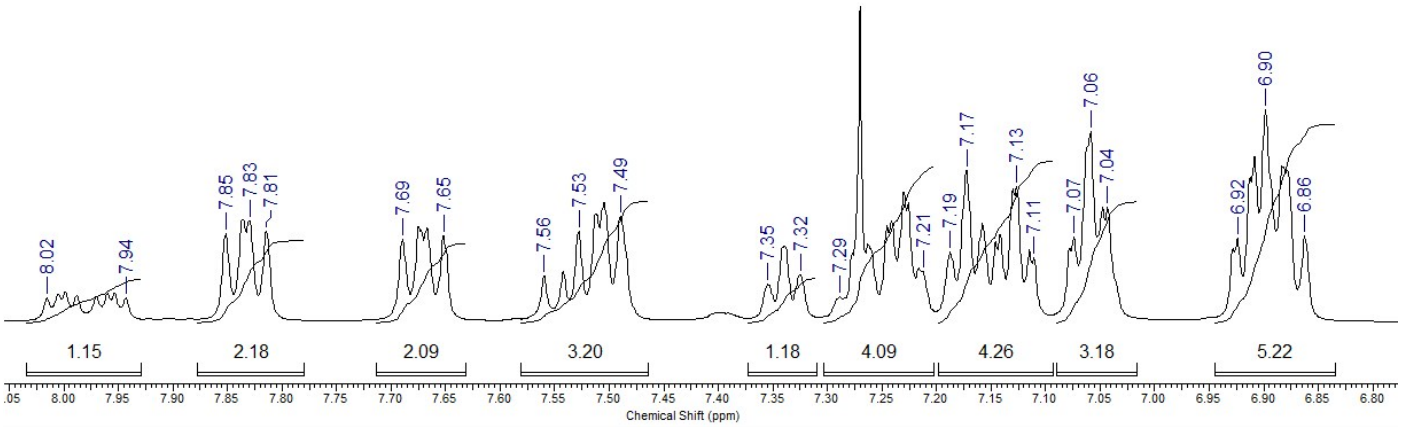


Figure S15. ^{1}H-NMR (aromatic region) spectrum of **4**

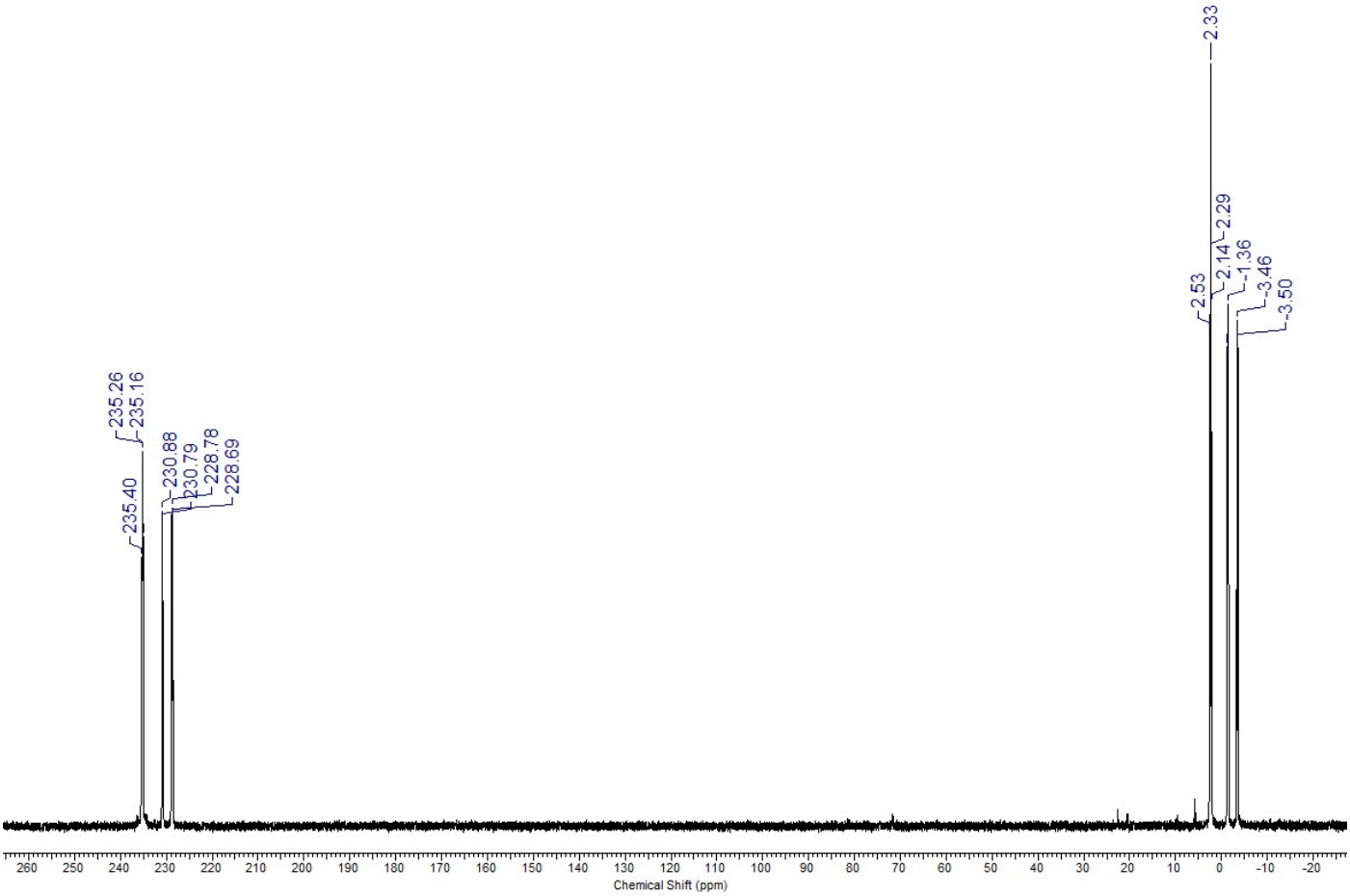


Figure S16. ^{31}P-NMR spectrum of **4**

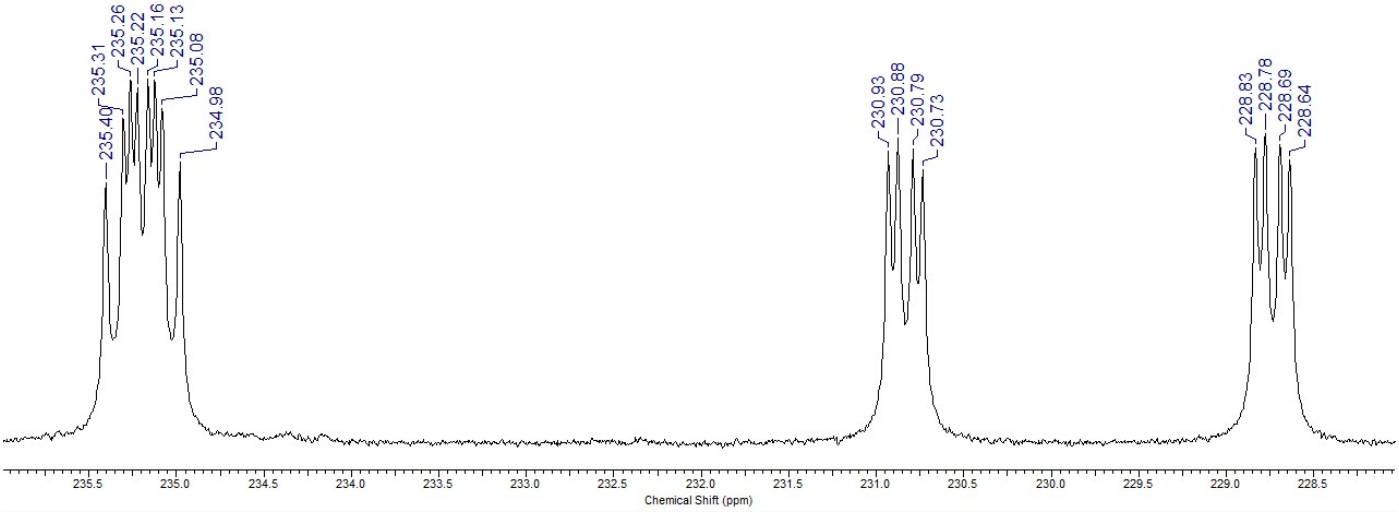


Figure S17. ^{31}P-NMR (phosphinine region) spectrum of **4**

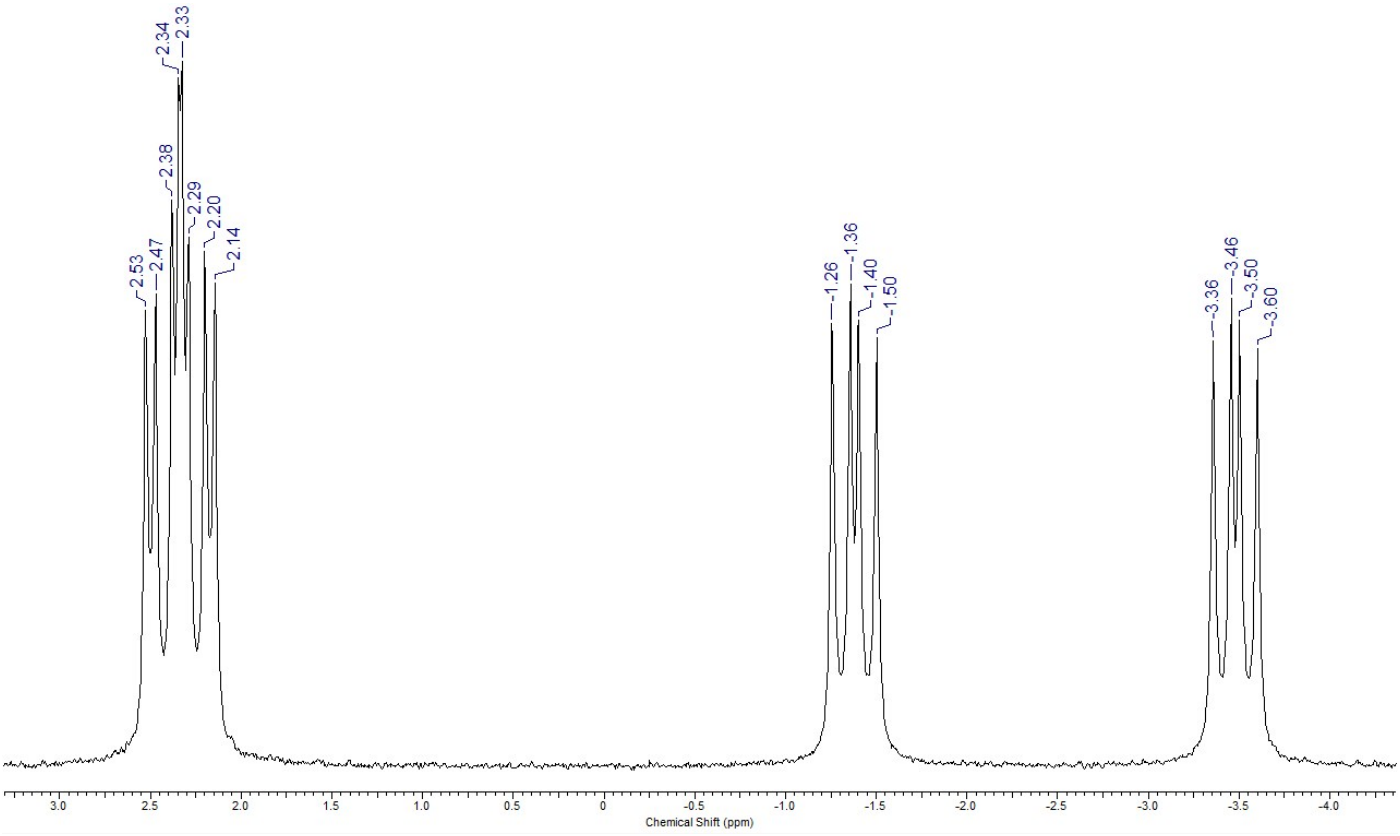


Figure S18. ^{31}P-NMR (phosphine region) spectrum of **4**

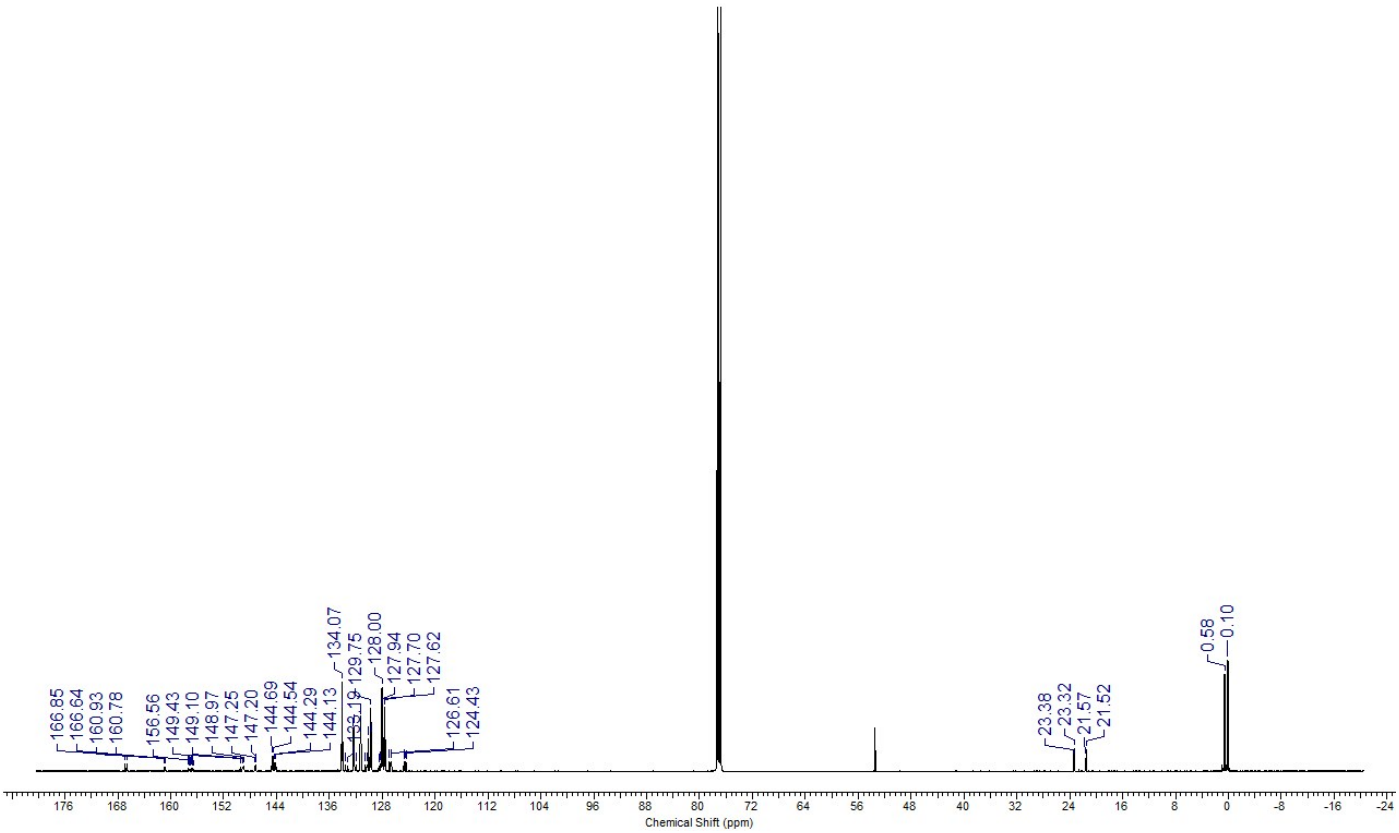


Figure S19. ^{13}C-NMR spectrum of **4**

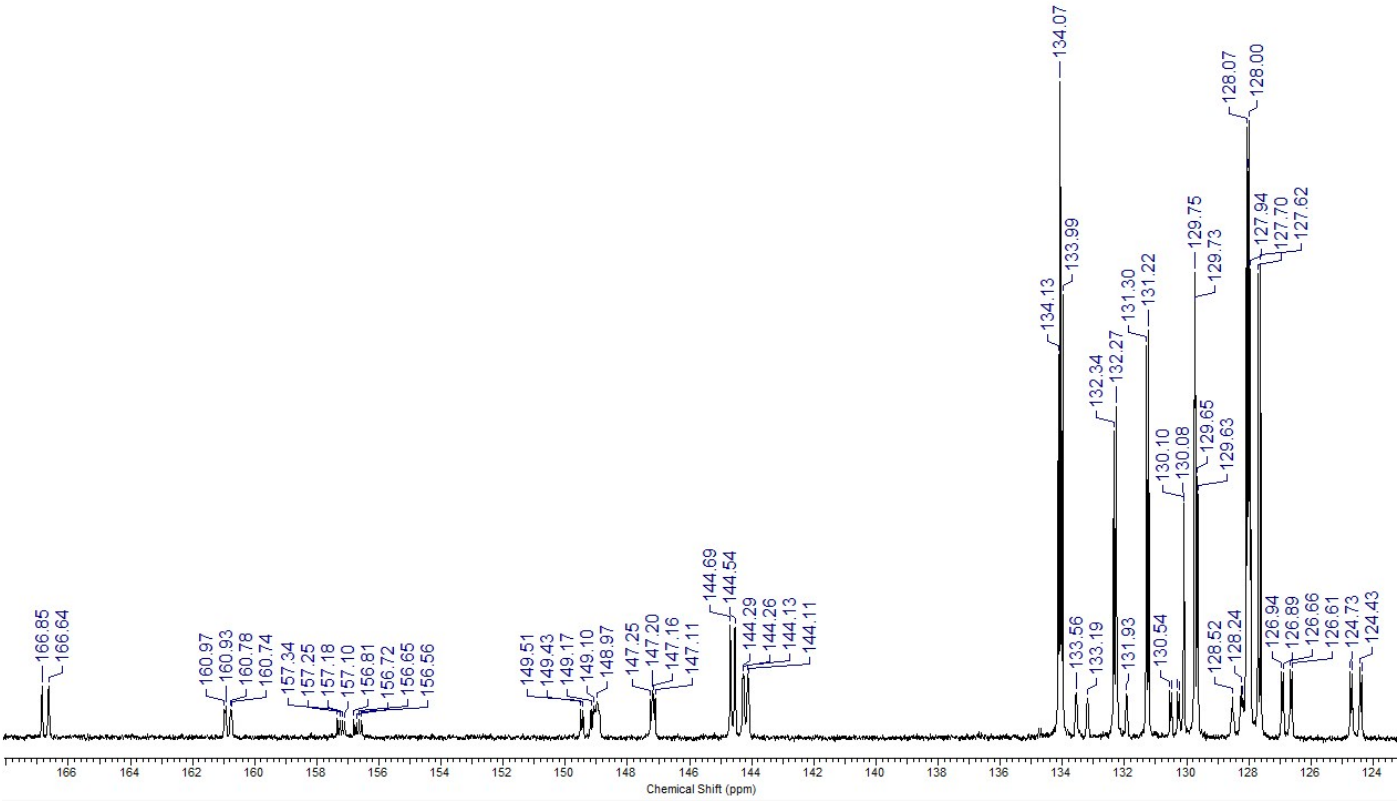


Figure S20. ^{13}C-NMR (aromatic region) spectrum of **4**

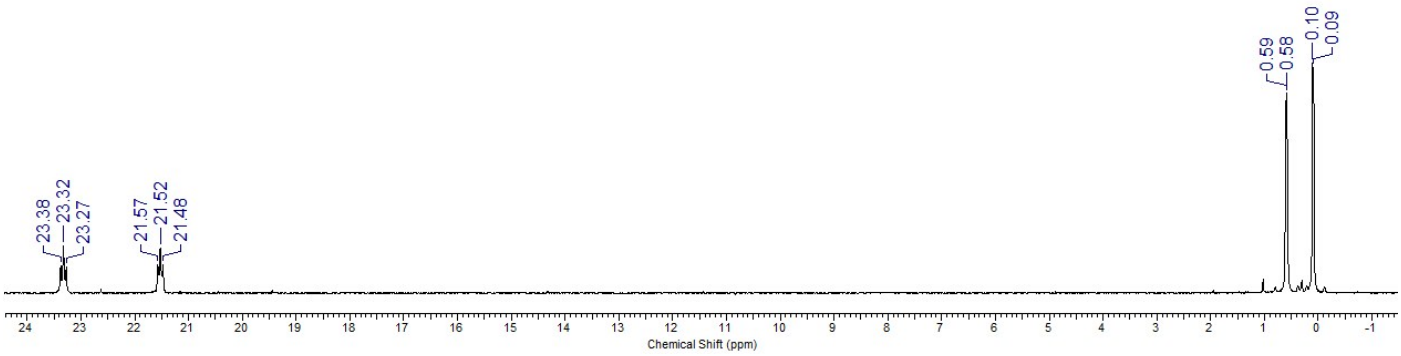


Figure S21. ^{13}C-NMR (alkyl region) spectrum of **4**

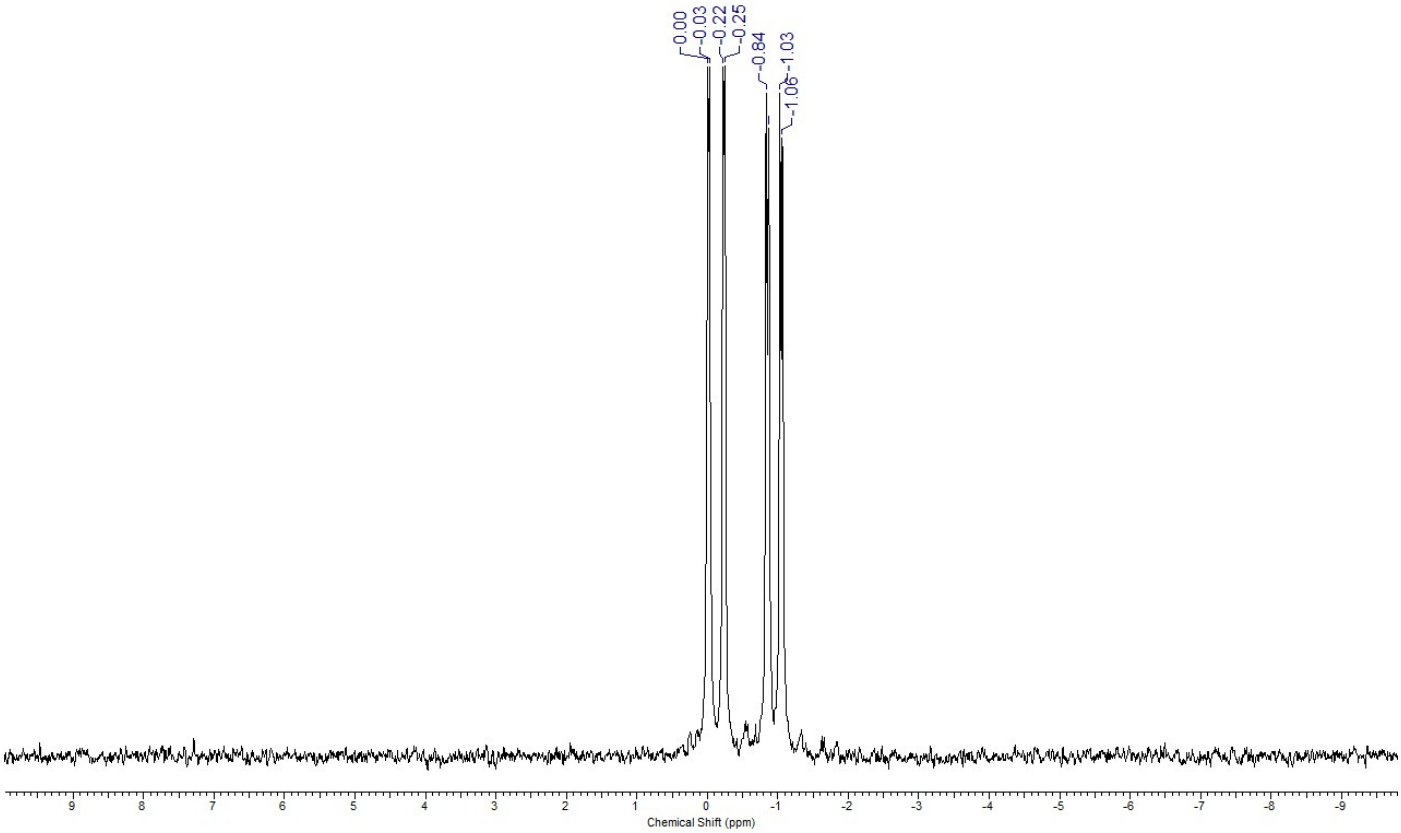


Figure S22. ^{29}Si-NMR spectrum of **4**

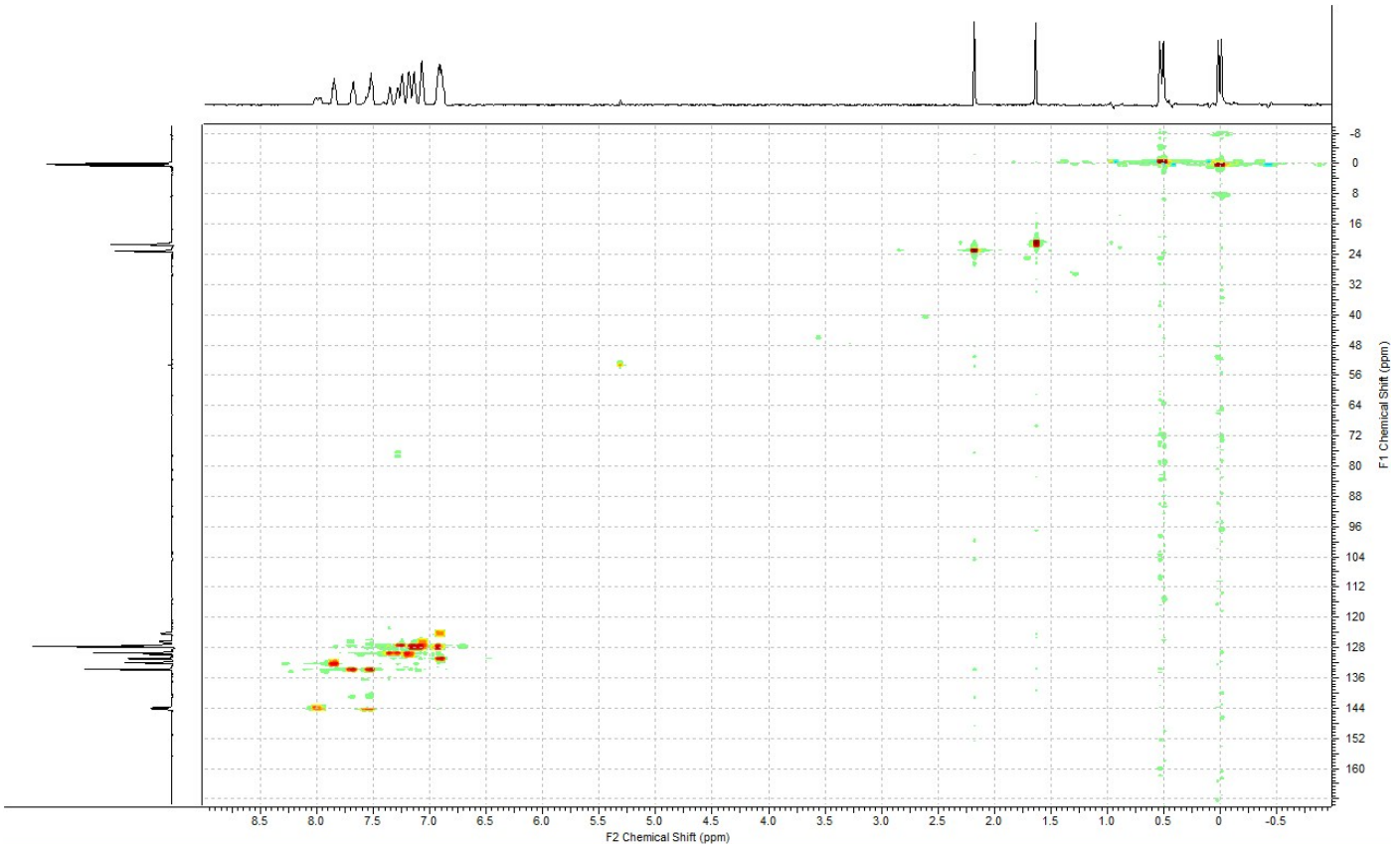


Figure S23. ^{1}H-^{13}C HSQC spectrum of **4**

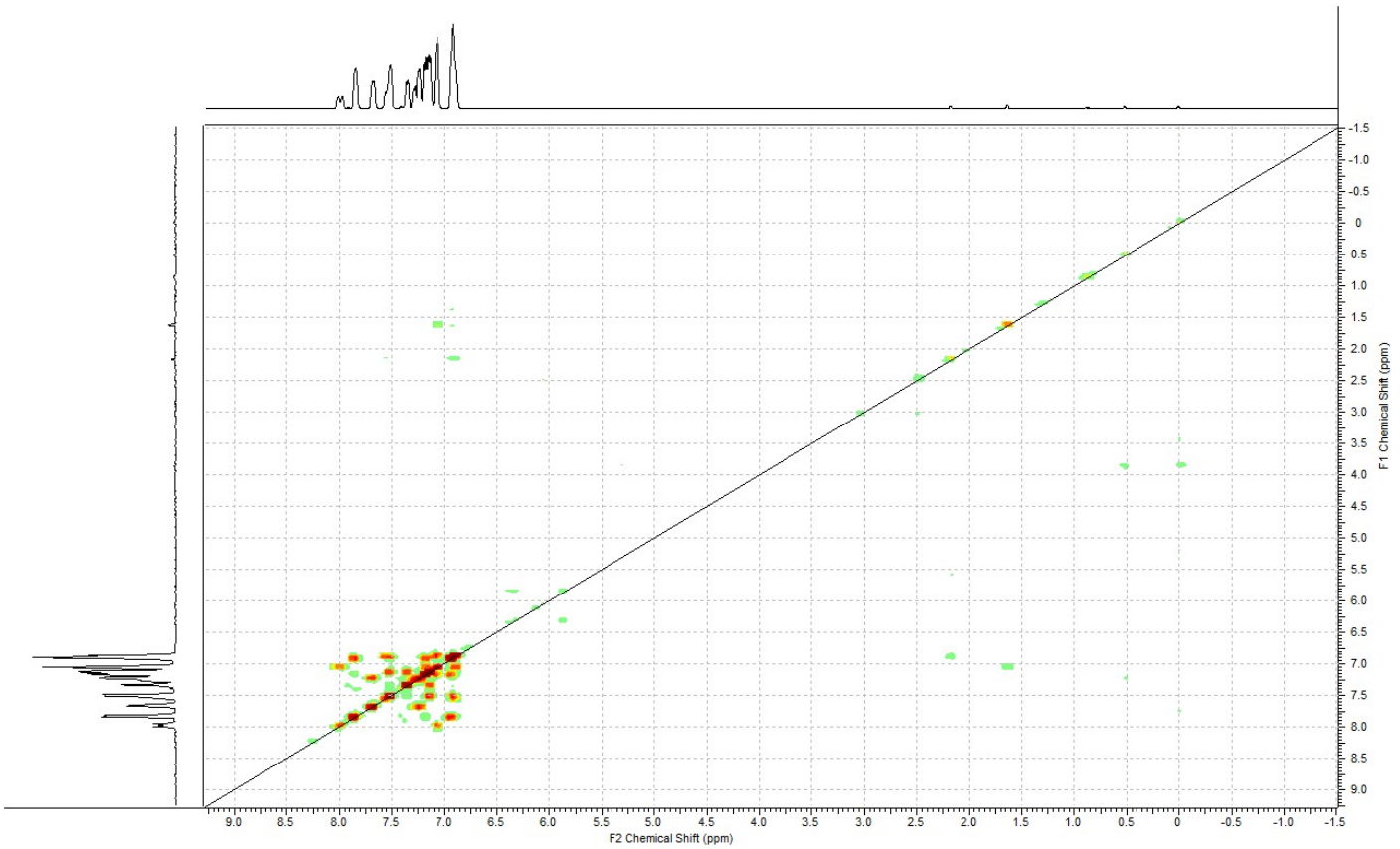


Figure S24. ^{1}H-^{1}H COSY spectrum of **4**

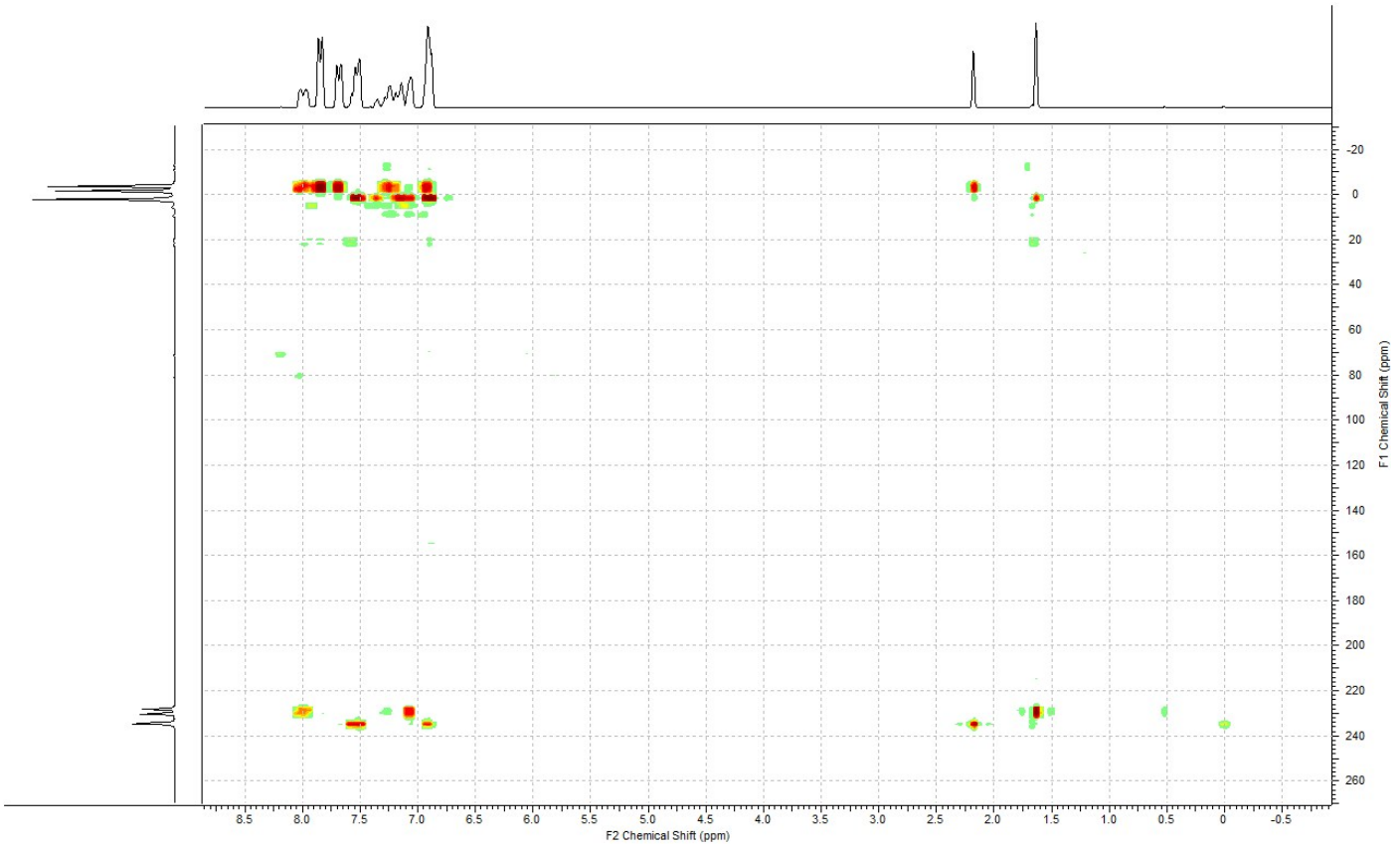


Figure S25. ^{1}H-^{31}P HMBC spectrum of **4**

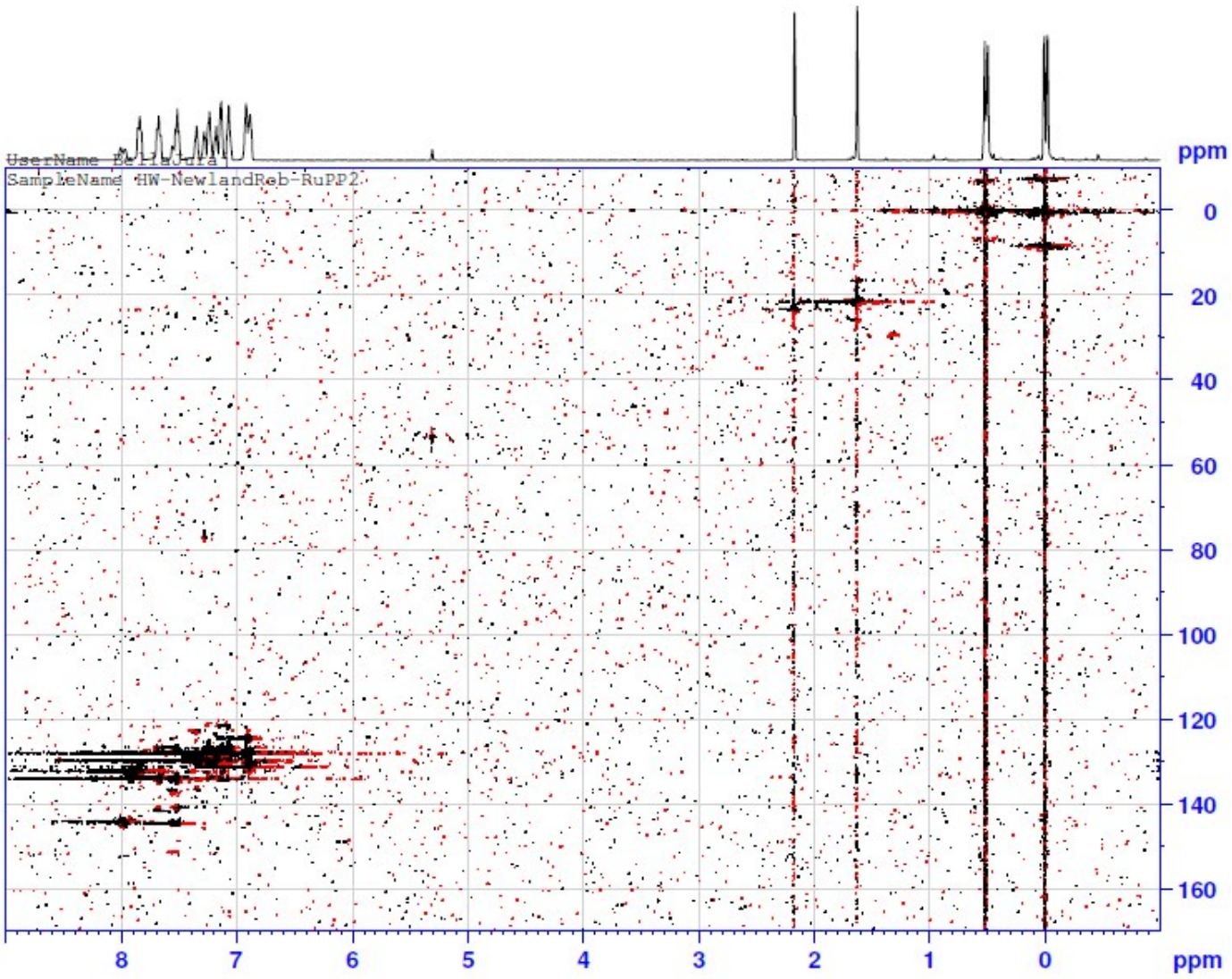


Figure S26. ^{1}H-^{13}C HMBC spectrum of **4**

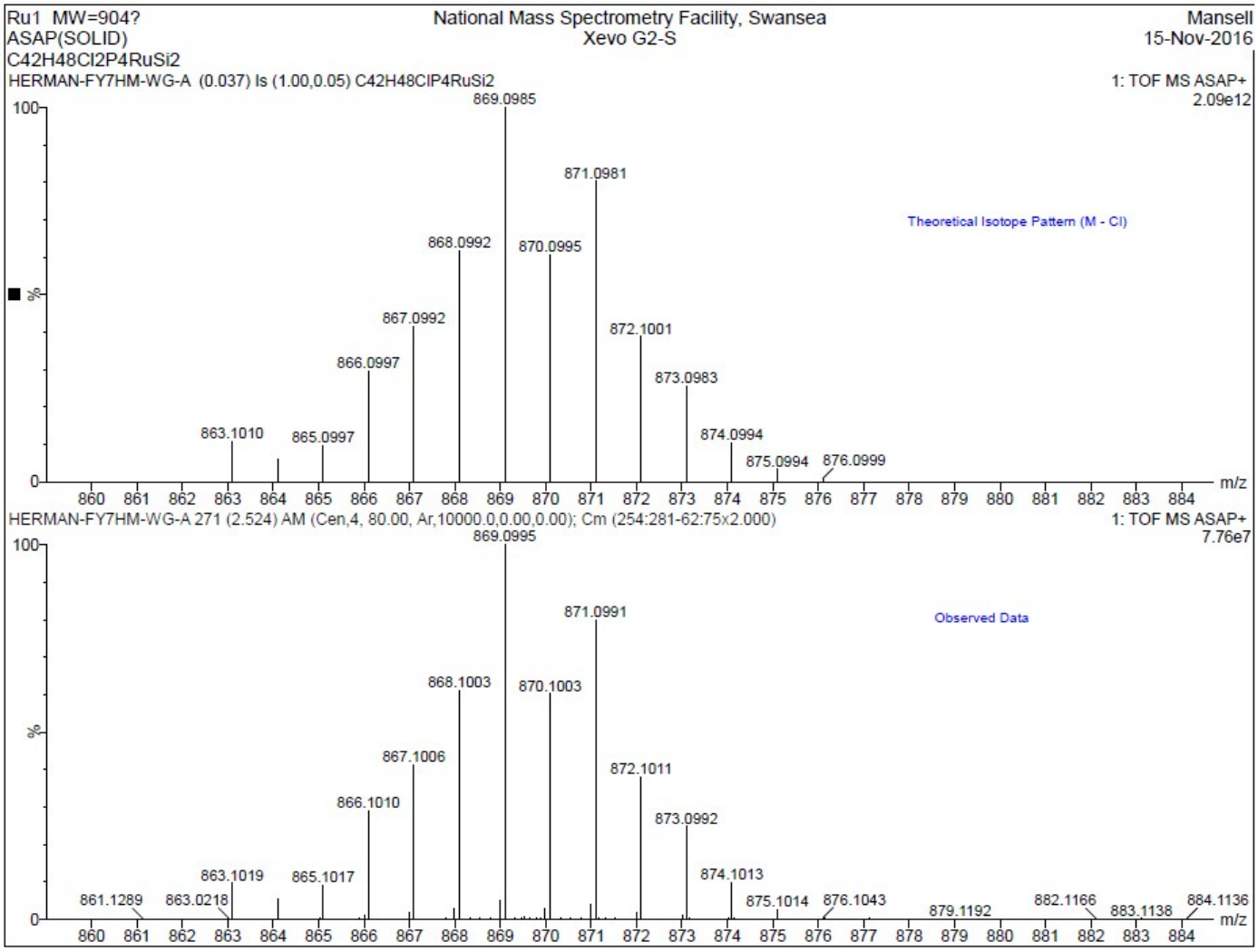


Figure S27. Accurate mass of [**4** - Cl]$^+$

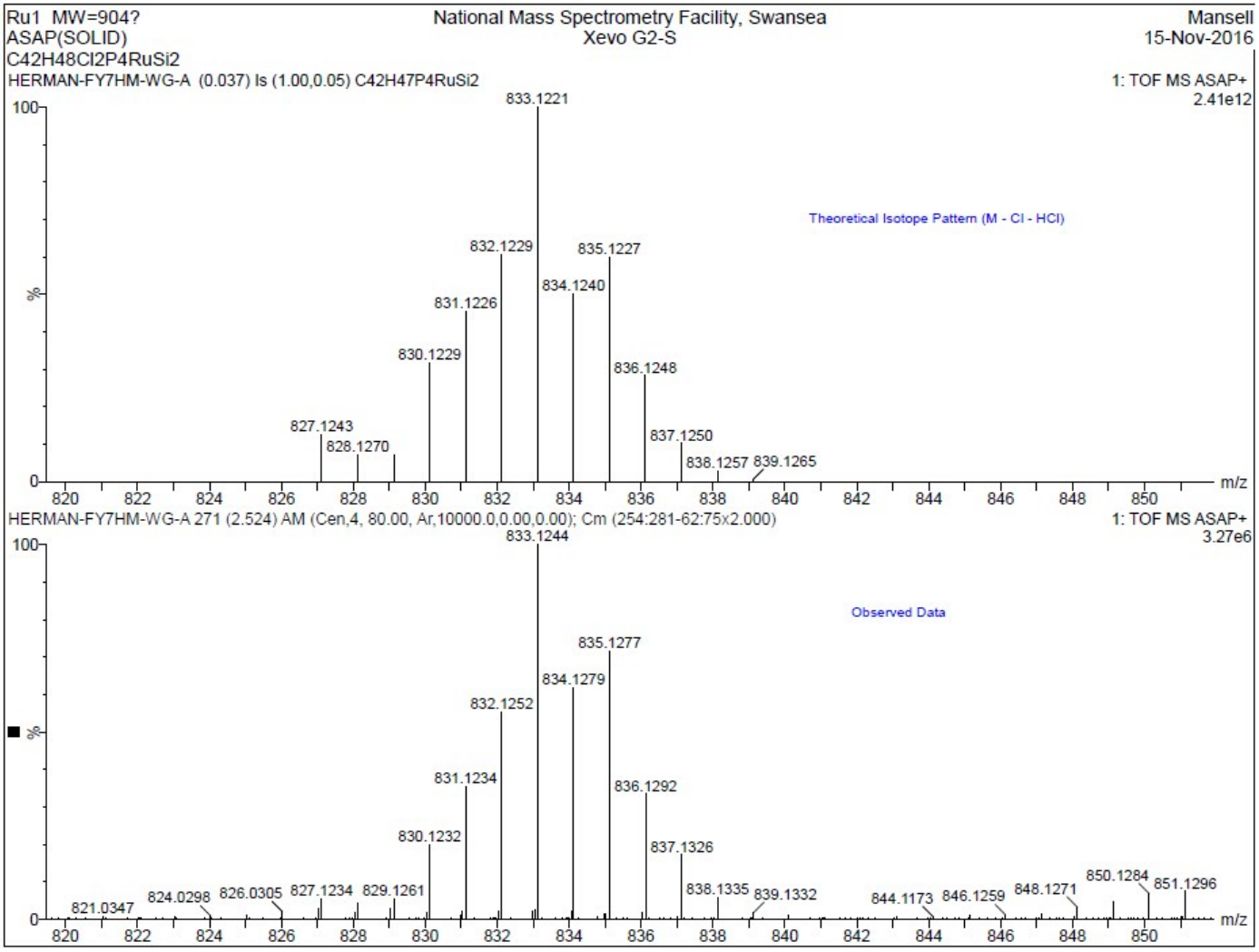


Figure 28. Accurate mass of [**4** - Cl - HCl]$^+$

NMR and mass spectra of reactions of 2 and 4 with MOR and/or ROH

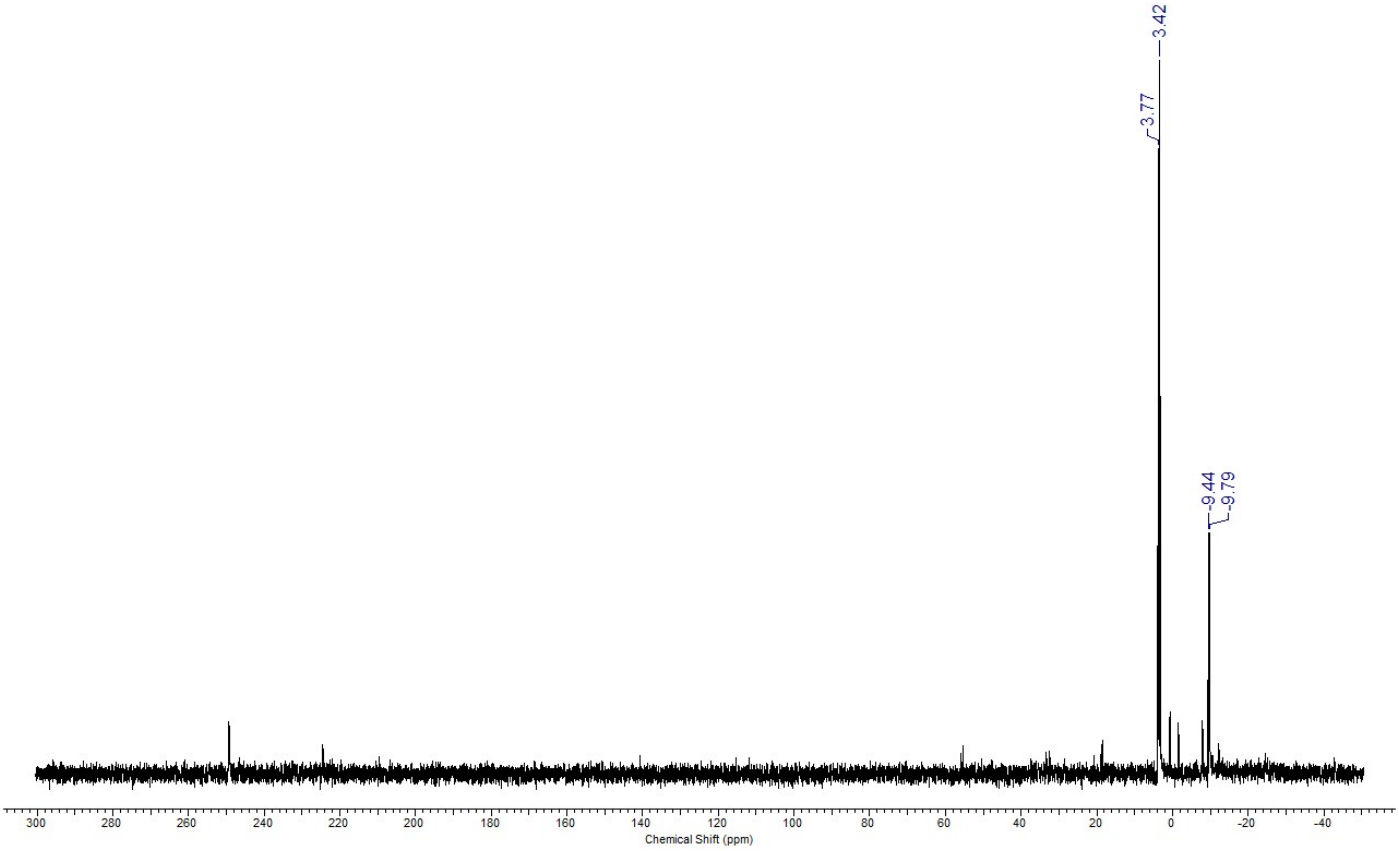


Figure S29. ^{31}P-NMR spectrum of the reaction between **2** and KO^{t}Bu in ^{i}PrOH/$CDCl_3$.

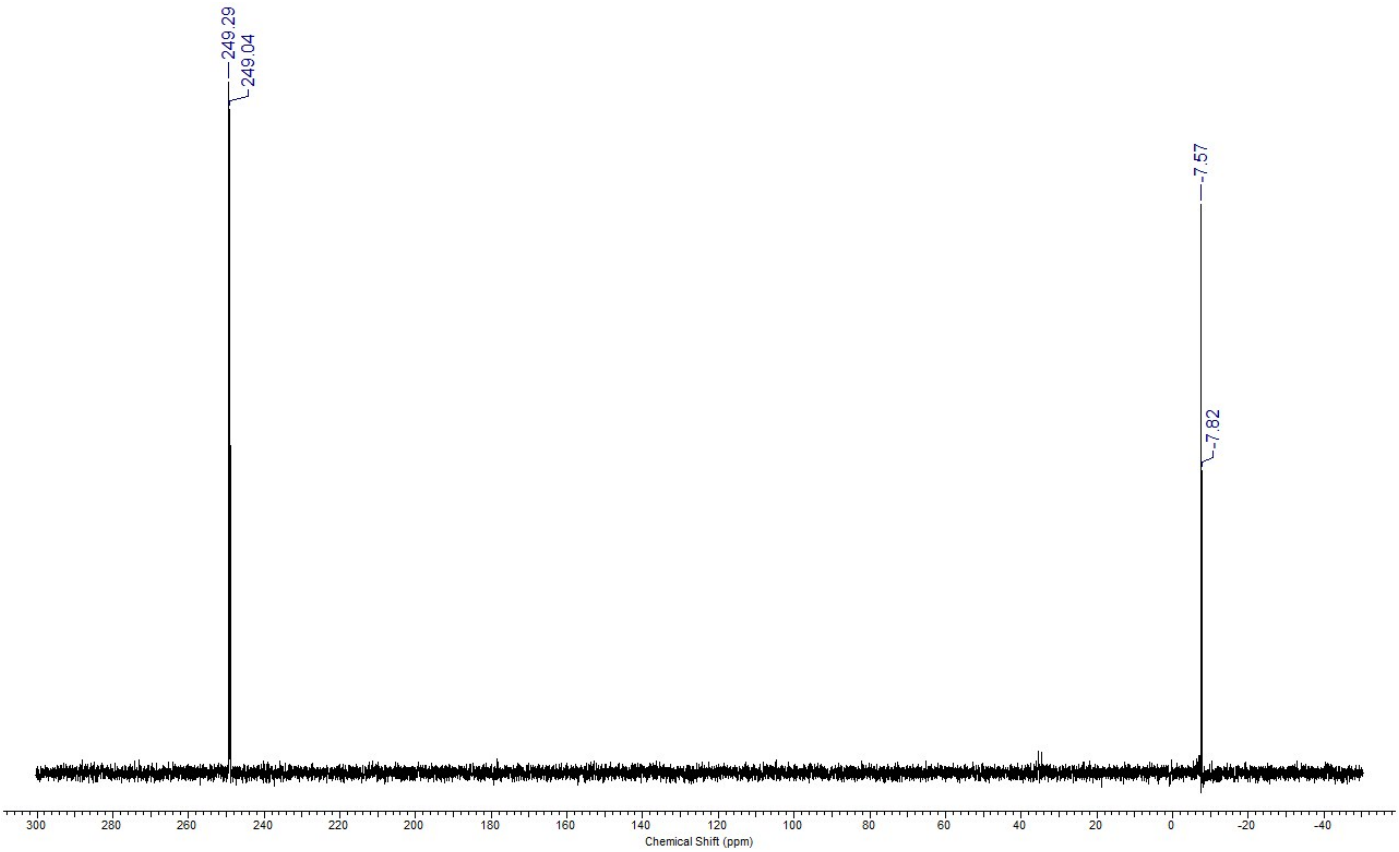


Figure S30. ^{31}P-NMR of **2** after 24h at 20°C and 1h at 82°C in $CDCl_3$ and excess MeOH indicating no reaction.

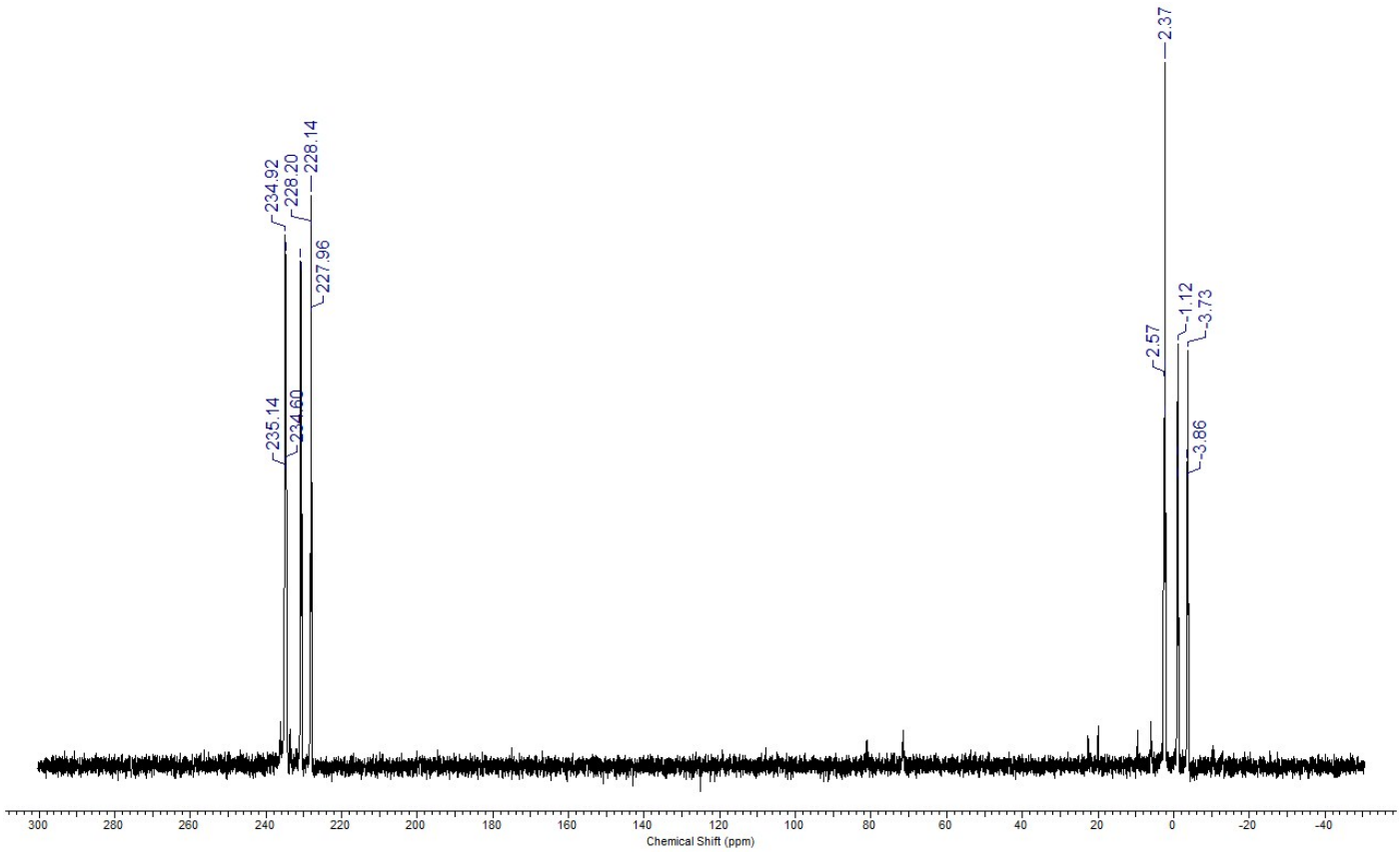


Figure S31. ^{31}P-NMR spectrum of **4** after 48h reflux in $CDCl_3$ and excess ^{i}PrOH indicating no reaction.

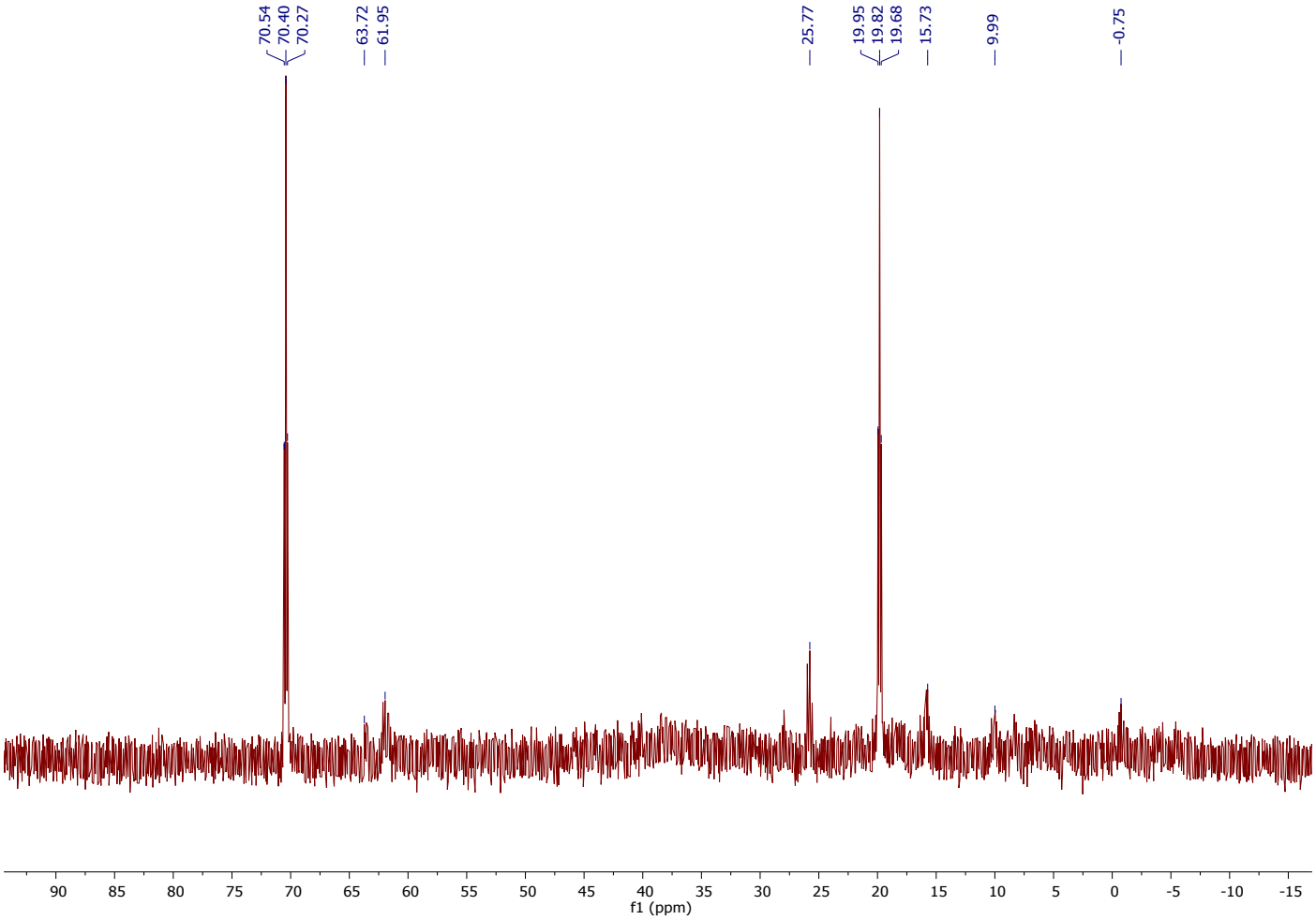


Figure S32. ^{31}P NMR spectrum of **4** + KO^{t}Bu in ^{i}PrOH (neat, unlocked) after reaction at room temperature.

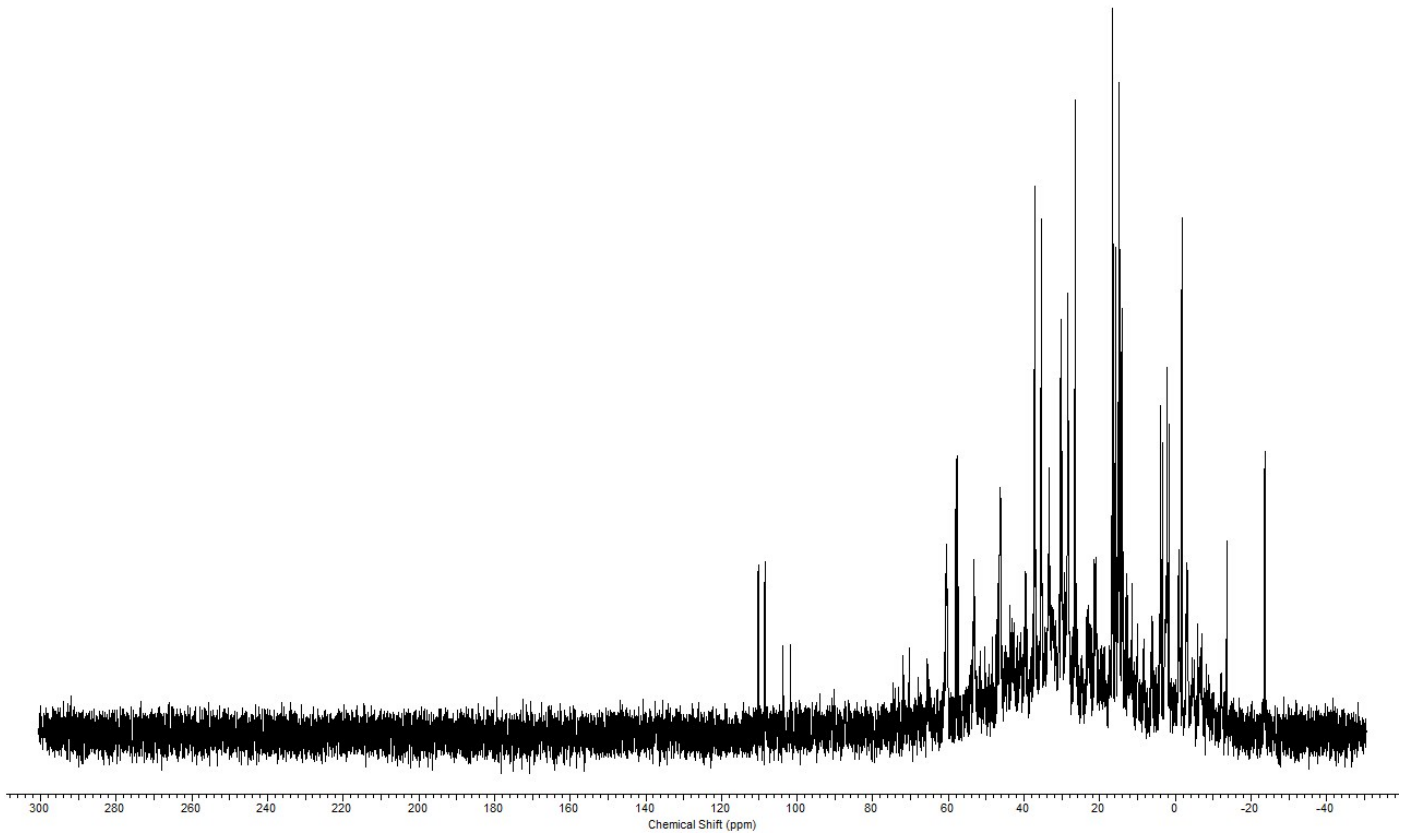


Figure S33. ^{31}P-NMR spectrum (acetone-d$_6$) of **4** after stirring with 5 equiv. KO^{t}Bu in ^{i}PrOH.

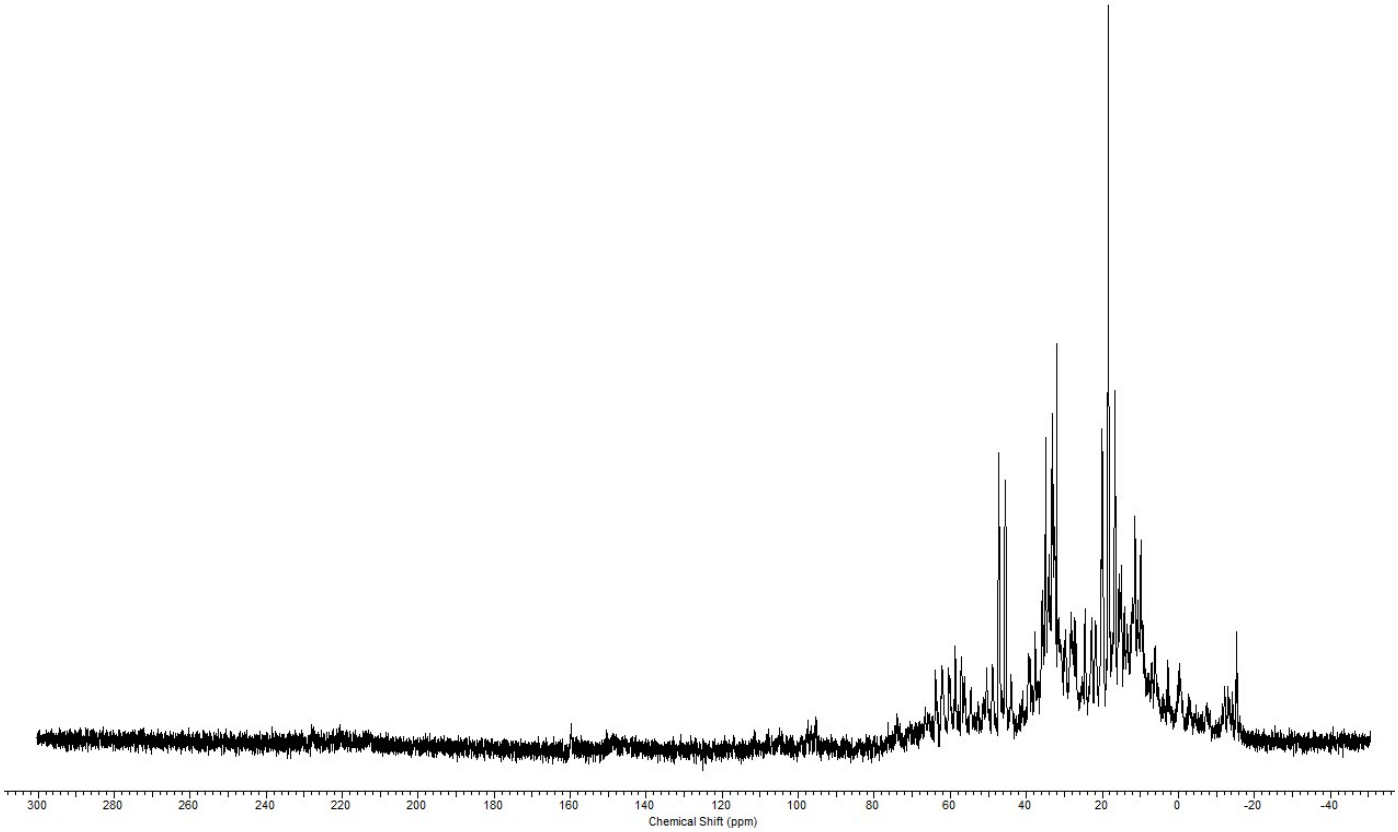


Figure S34. ^{31}P-NMR spectrum (methanol-d$_4$) of **4** after stirring with 5 equiv. KO^{t}Bu in ^{i}PrOH

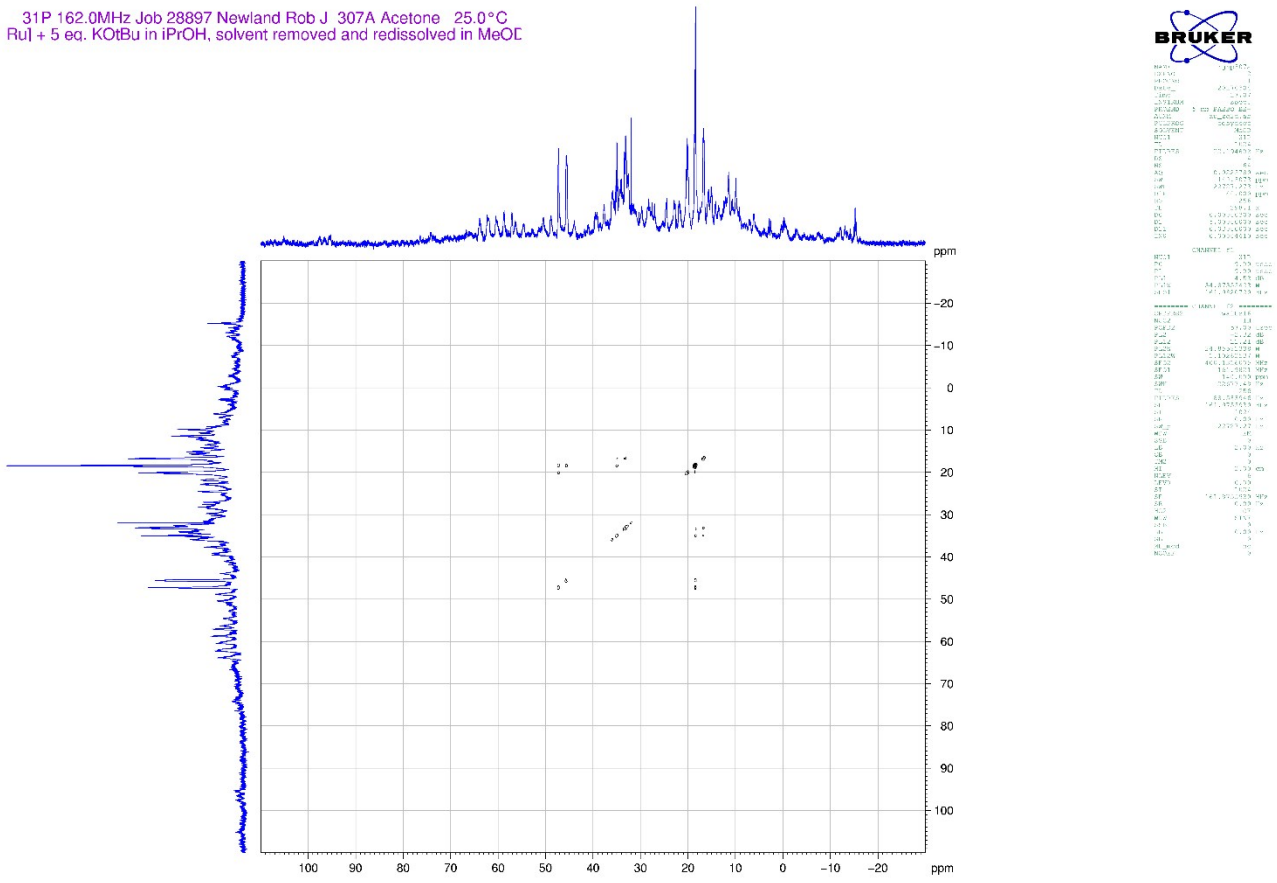


Figure S35. ^{31}P-^{31}P COSY NMR spectrum (methanol-d$_4$) of **4** after stirring with 5 equiv. KO^{t}Bu in ^{i}PrOH

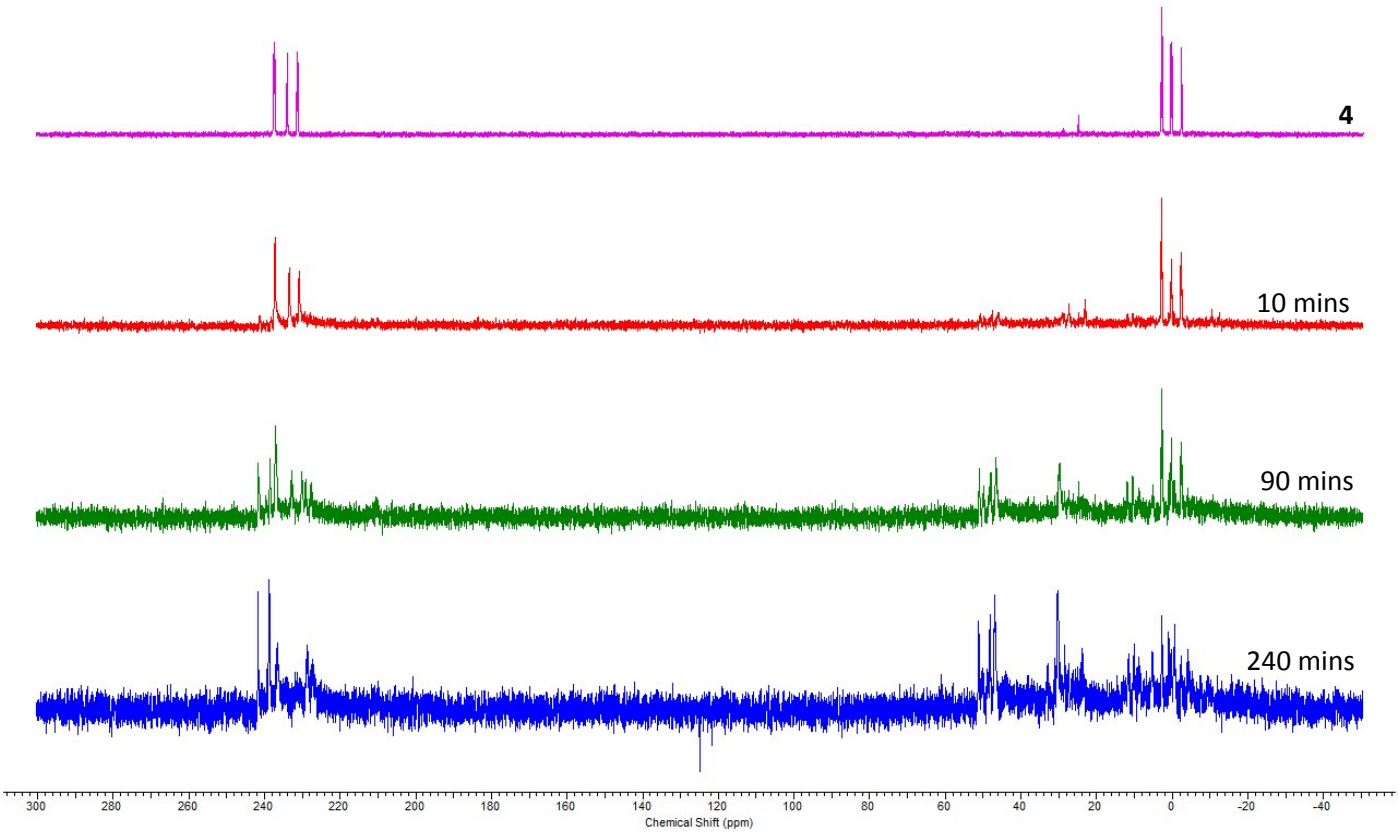


Figure S36. ^{31}P-NMR spectra of **4** with 5 equiv. KO^{t}Bu in C_6D_6. From top to bottom: starting complex, after 10 mins, after 90 mins, after 4 hours.

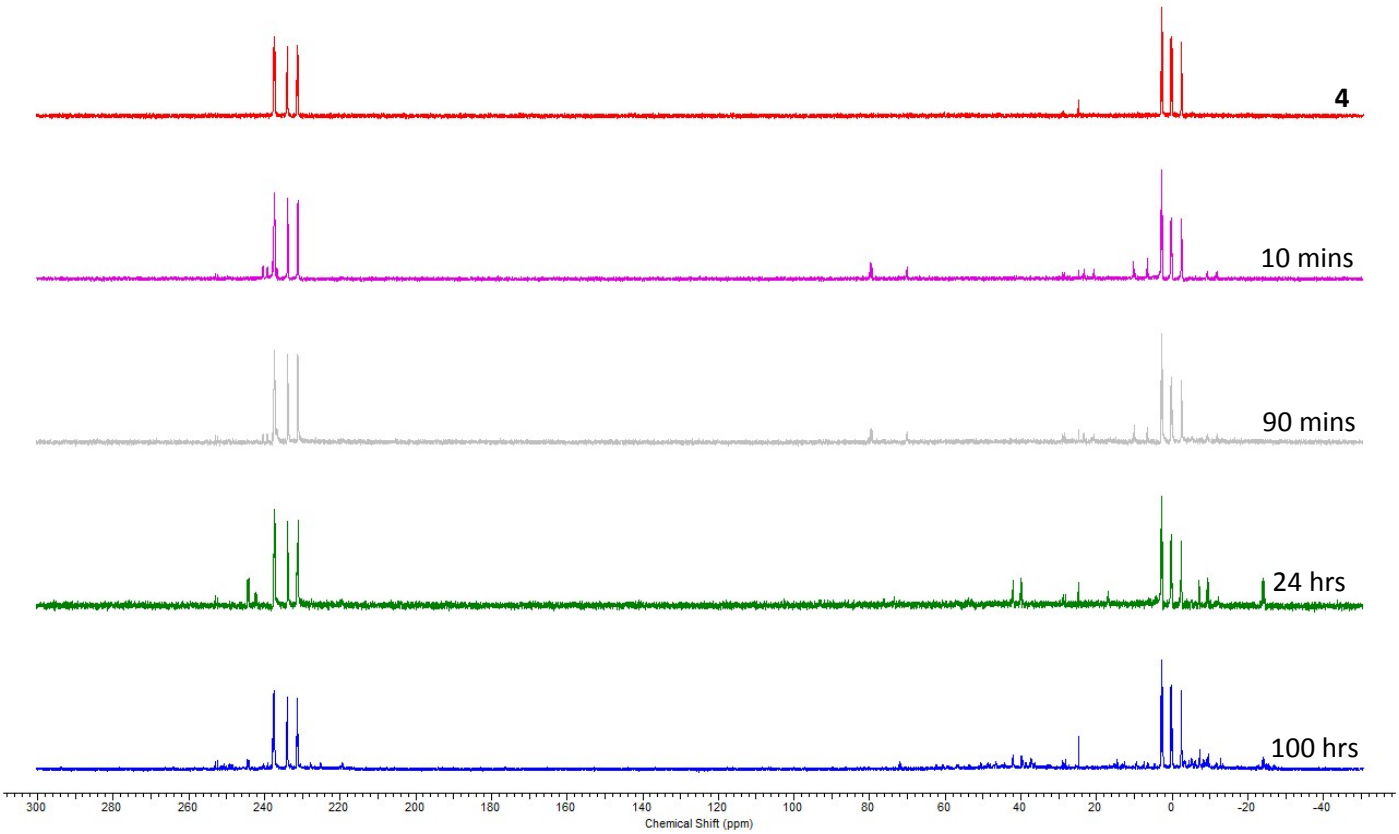


Figure S37. ^{31}P-NMR of **4** with 2 equiv. NaOMe in C_6D_6. From top to bottom: starting complex, after 10 mins, after 90 mins, after 24 hours, after 100 hours at 90°C.

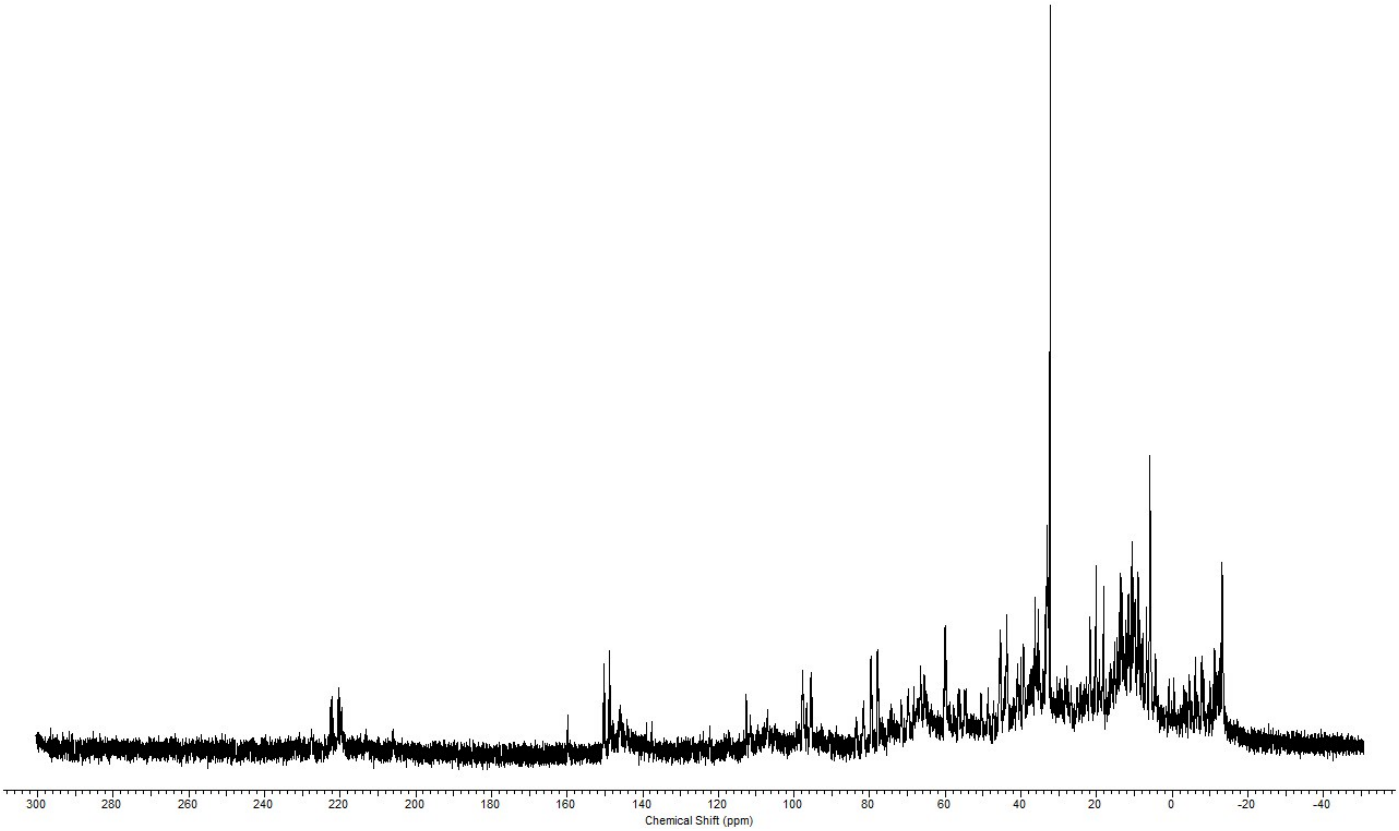


Figure S38. ^{31}P-NMR spectrum of **4** + 5 equiv. NaOMe in methanol-d_4

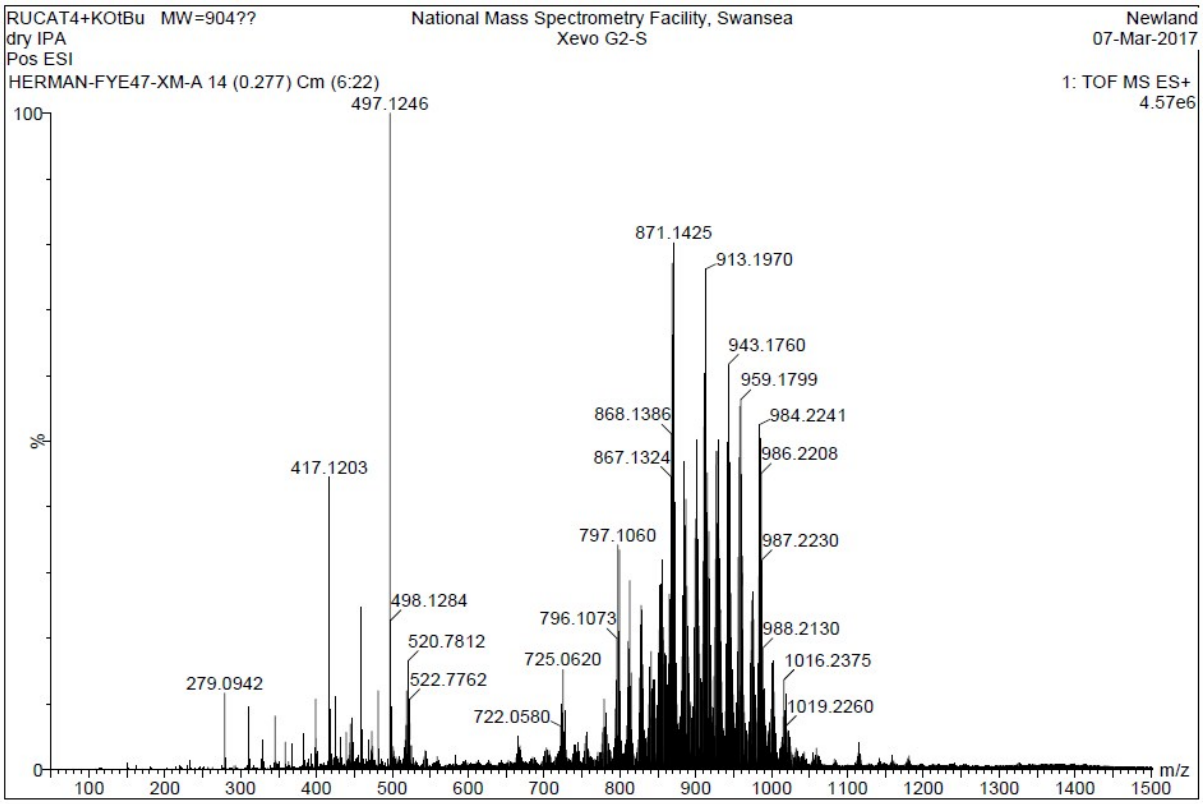


Figure S39. Mass spectrum from the reaction of **4** + KO^{t}Bu in ^{i}PrOH after 30 seconds (positive ion mode).

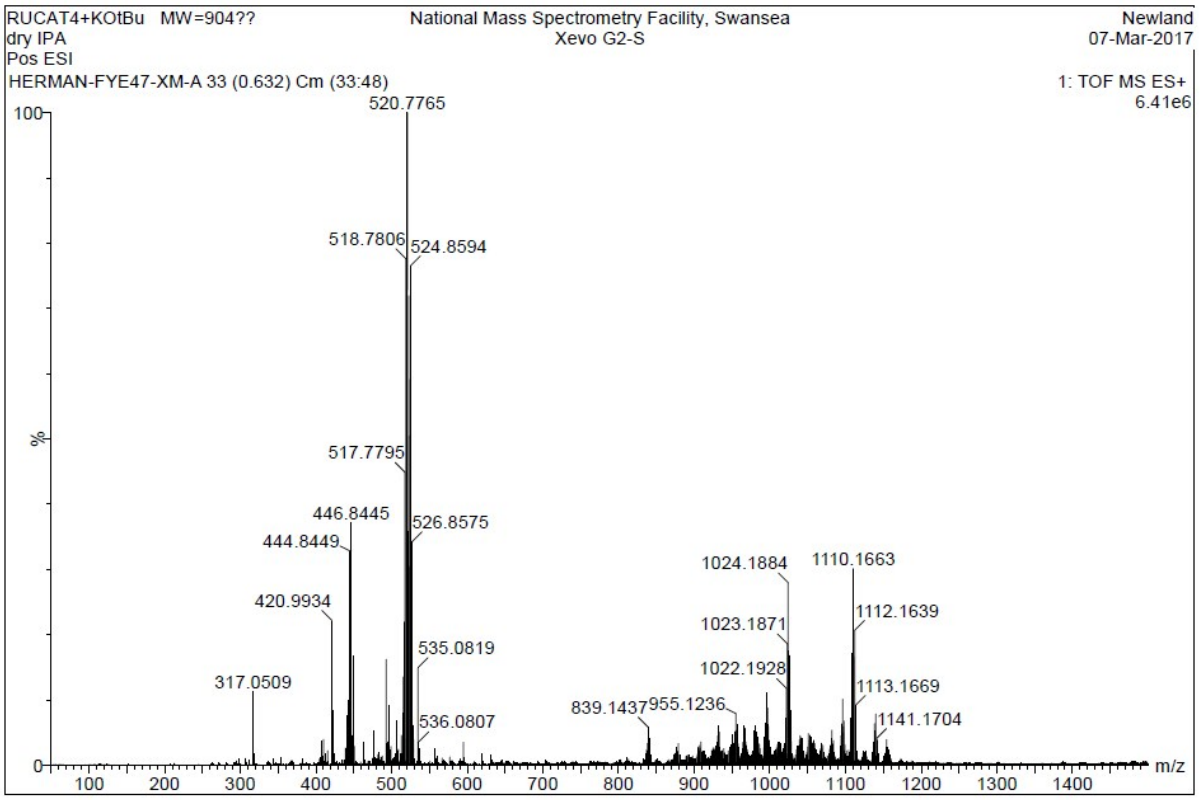


Figure S40. Mass spectrum from the reaction of **4** + KO^{t}Bu in ^{i}PrOH after 60 seconds (positive ion mode).

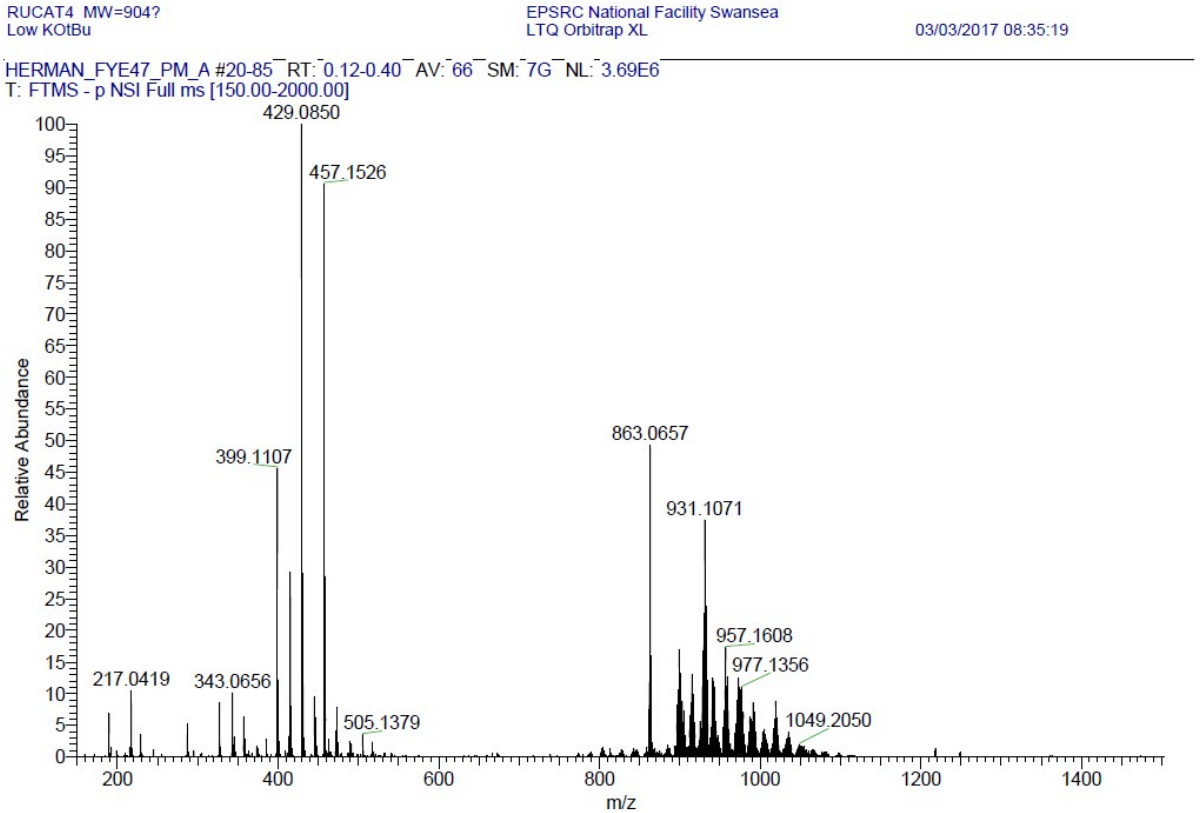


Figure S41. Mass spectrum from the reaction of **4** + KO^{t}Bu in ^{i}PrOH after 120 seconds (negative ion mode). Peak at 863 is from [B{3,5-$(CF_3)_2C_6H_3$}$_4$] impurity present as a contaminant in the mass spectrometer.

Crystallographic details

Single crystals of the samples were covered in inert oil and placed under the cold stream of a Bruker X8 APEXII four-circle diffractometer cooled to 100 K. Exposures were collected using Mo Kα radiation (λ = 0.71073). Indexing, data collection and absorption correction were performed using the APEXII suite of programs.[4] Structures were solved using direct methods (SHELXT)[5] and refined by full-matrix least-squares (SHELXL)[5] interfaced with the programme OLEX2[6] (Table S2).

Compound **4** had a poorly ordered benzene solvate molecule that was modelled at 100% occupancy with AFIX 66 used to force the six carbon atoms to form a regular hexagon. There were also additional solvent accessible voids identified in this structure. Although no other disordered solvent molecules could be identified and modelled, SQUEEZE revealed residual electron density in these voids, with the electron count pointing to probably two half molecules of disordered C_6H_6. SQUEEZE was therefore used and resulted in a small decrease in the R factors.

Table S1. Bond lengths (Å) and angles (°) for **2**, **3** and **4**

2	P(1)-C(1)	1.754(3)	P(1)-C(1)-C(2)	124.0(2)
	C(1)-C(2)	1.423(4)	C(1)-C(2)-C(3)	120.6(3)
	C(2)-C(3)	1.404(4)	C(2)-C(3)-C(4)	124.9(2)
	C(3)-C(4)	1.393(4)	C(3)-C(4)-C(5)	125.5(2)
	C(4)-C(5)	1.396(4)	C(4)-C(5)-P(1)	121.0(2)
	C(5)-P(1)	1.749(3)	C(5)-P(1)-C(1)	103.6(1)
	C(1)-P(2)	1.847(3)	P(1)-C(1)-P(2)	119.9(1)
3	P(1)-C(1)	1.754(1)	P(1)-C(1)-C(2)	124.2(1)
	C(1)-C(2)	1.407(2)	C(1)-C(2)-C(3)	120.5(1)
	C(2)-C(3)	1.405(2)	C(2)-C(3)-C(4)	125.1(1)
	C(3)-C(4)	1.385(2)	C(3)-C(4)-C(5)	124.2(1)
	C(4)-C(5)	1.399(2)	C(4)-C(5)-P(1)	121.2(1)
	C(5)-P(1)	1.734(1)	C(5)-P(1)-C(1)	103.7(1)
	C(1)-P(2)	1.827(1)	P(1)-C(1)-P(2)	114.5(1)
	P(2)-B(1)	1.928(2)		
4	P(1)-C(1)	1.710(7)	P(1)-C(1)-C(2)	115.8(6)
	C(1)-C(2)	1.398(9)	C(1)-C(2)-C(3)	128.1(7)
	C(2)-C(3)	1.384(11)	C(2)-C(3)-C(4)	126.5(6)
	C(3)-C(4)	1.409(11)	C(3)-C(4)-C(5)	116.5(7)
	C(4)-C(5)	1.405(8)	C(4)-C(5)-P(1)	125.5(5)
	C(5)-P(1)	1.714(7)	C(5)-P(1)-C(1)	107.6(3)
	C(5)-P(2)	1.826(7)	P(1)-C(5)-P(2)	97.6(3)
	P(3)-C(22)	1.732(6)	P(3)-C(22)-C(23)	125.5(4)
	C(22)-C(23)	1.391(8)	C(22)-C(23)-C(24)	118.0(5)
	C(23)-C(24)	1.387(8)	C(23)-C(24)-C(25)	125.4(5)
	C(24)-C(25)	1.397(8)	C(24)-C(25)-C(26)	128.8(6)
	C(25)-C(26)	1.413(8)	C(25)-C(26)-P(3)	115.2(5)
	C(26)-P(3)	1.718(6)	C(26)-P(3)-C(22)	107.0(3)
	C(22)-P(4)	1.836(6)	P(3)-C(22)-P(4)	96.2(3)
	P(1)-Ru(1)	2.310(2)	P(1)-Ru(1)-P(2)	69.89(6)
	P(2)-Ru(1)	2.342(2)	P(3)-Ru(1)-P(4)	70.32(5)
	P(3)-Ru(1)	2.241(2)		
	P(4)-Ru(1)	2.369(2)		
	Ru(1)-Cl(1)	2.430(2)		
	Ru(1)-Cl(2)	2.477(2)		

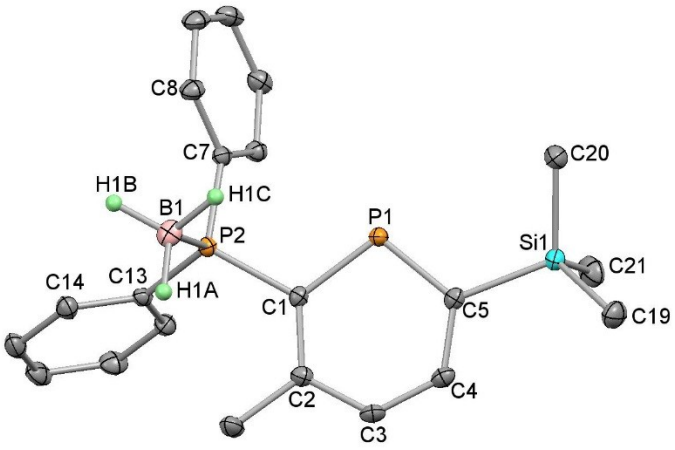


Figure S42. Molecular structure of compound **3** (thermal ellipsoids at 50% probability). All H-atoms except for those attached to B have been omitted for clarity.

Table S2. Crystallographic data for compounds **2**, **3** and **4**

Identification code	**2**	**3**	**4**
Empirical formula	$C_{21}H_{24}P_2Si$	$C_{21}H_{27}BP_2Si$	$C_{48}H_{54}Cl_2P_4RuSi_2$
Formula weight	366.43	380.26	982.94
Temperature/K	100.0	100.0	100.0
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	16.815(4)	10.1934(5)	19.2383(11)
b/Å	5.8402(15)	9.3080(4)	25.4095(17)
c/Å	21.487(5)	22.7635(9)	10.8916(6)
α/°	90	90	90
β/°	104.221(10)	102.195(2)	105.042(3)
γ/°	90	90	90
Volume/Å^3	2045.5(9)	2111.07(16)	5141.8(5)
Z	4	4	4
ρ_{calc}g/cm^3	1.190	1.196	1.270
μ/mm^1	0.271	0.264	0.610
F(000)	776.0	808.0	2032.0
Crystal size/mm^3	0.37 × 0.1 × 0.04	0.45 × 0.20 × 0.20	0.60 × 0.30 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.998 to 54.814	4.744 to 61.188	3.884 to 49.554
Index ranges	-21 ≤ h ≤ 19, -7 ≤ k ≤ 7, -21 ≤ l ≤ 27	-14 ≤ h ≤ 14, -13 ≤ k ≤ 13, -32 ≤ l ≤ 32	-22 ≤ h ≤ 22, -29 ≤ k ≤ 26, -12 ≤ l ≤ 12
Reflections collected	15927	59456	46318
Independent reflections	4534 [R_{int} = 0.0525, R_{sigma} = 0.0596]	6461 [R_{int} = 0.0548, R_{sigma} = 0.0357]	8777 [R_{int} = 0.1045, R_{sigma} = 0.1060]
Data/restraints/parameters	4534/0/221	6461/0/239	8777/36/516
Goodness-of-fit on F^2	1.080	1.035	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1623	R_1 = 0.0361, wR_2 = 0.0821	R_1 = 0.0624, wR_2 = 0.1271
Final R indexes [all data]	R_1 = 0.0850, wR_2 = 0.1779	R_1 = 0.0505, wR_2 = 0.0886	R_1 = 0.1197, wR_2 = 0.1476
Largest diff. peak/hole / e Å^{-3}	0.85/-0.52	0.41/-0.31	0.85/-0.61

Transfer Hydrogenation

Experimental Procedure

To a dry Schlenk flask, under N_2, fitted with a stirrer bar containing an a known amount of 1,3,5-trimethoxybenzene, ^{i}PrOH and substrate (1 mmol) were added stock solutions of **4** (0.1 mol%) and KO^{t}Bu (0.5 mol%) in ^{i}PrOH, to a total solvent volume of 2.3 cm^3. After 1 hour, 0.1 cm^3 was removed by syringe and the ^{1}H-NMR spectrum ($CDCl_3$) recorded, the reaction was then quenched by admission of air into the flask. Reactions at 82°C were run in a 50 cm^3 Schlenk flask fitted with a Teflon tap.

Blank Reactions

The transfer hydrogenation of acetophenone was repeated, with either **4** or KO^{t}Bu removed. The reactions were run at 20°C for 1 hour, then at 70°C for another hour.

Reagent Removed	% Product (20°C, 1 hour)	% Product (70°C, 1 hour)
4	Not detected	Not detected
KO^{t}Bu	Not detected	Not detected

Crude Product NMR Spectra

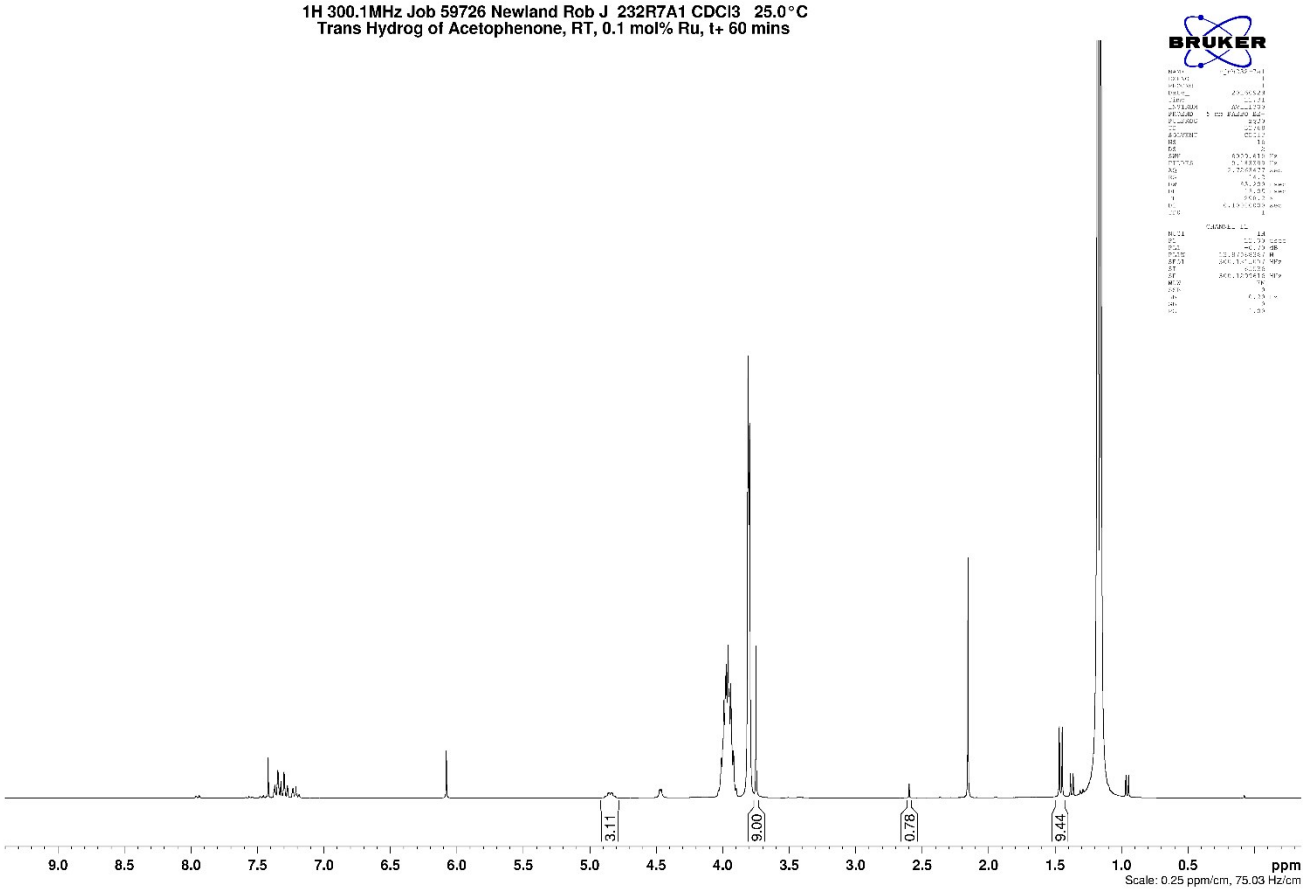


Figure S43. Transfer hydrogenation of acetophenone, 20°C, 1 hour

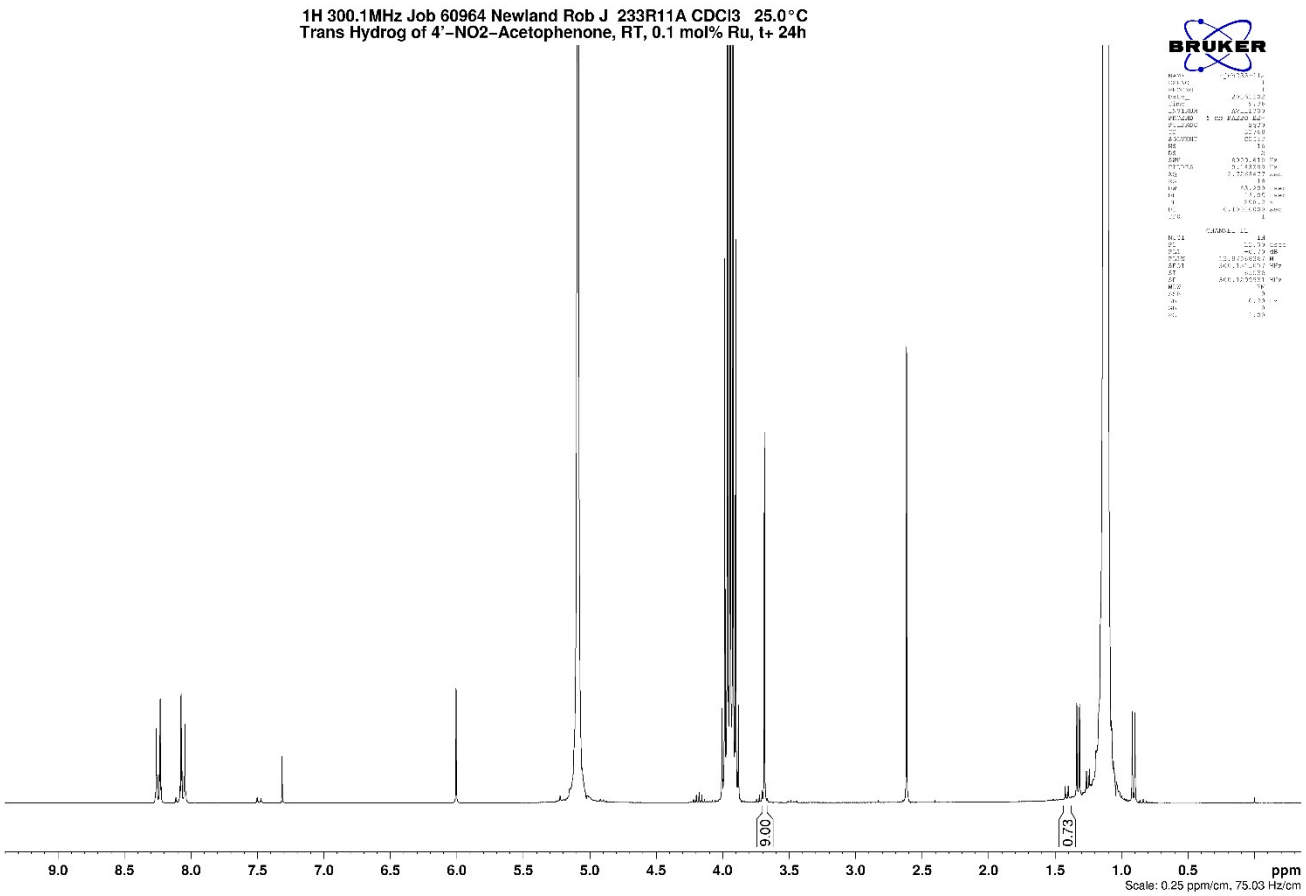


Figure S44. Transfer hydrogenation of 4'-nitroacetophenone, 20°C, 24 hours

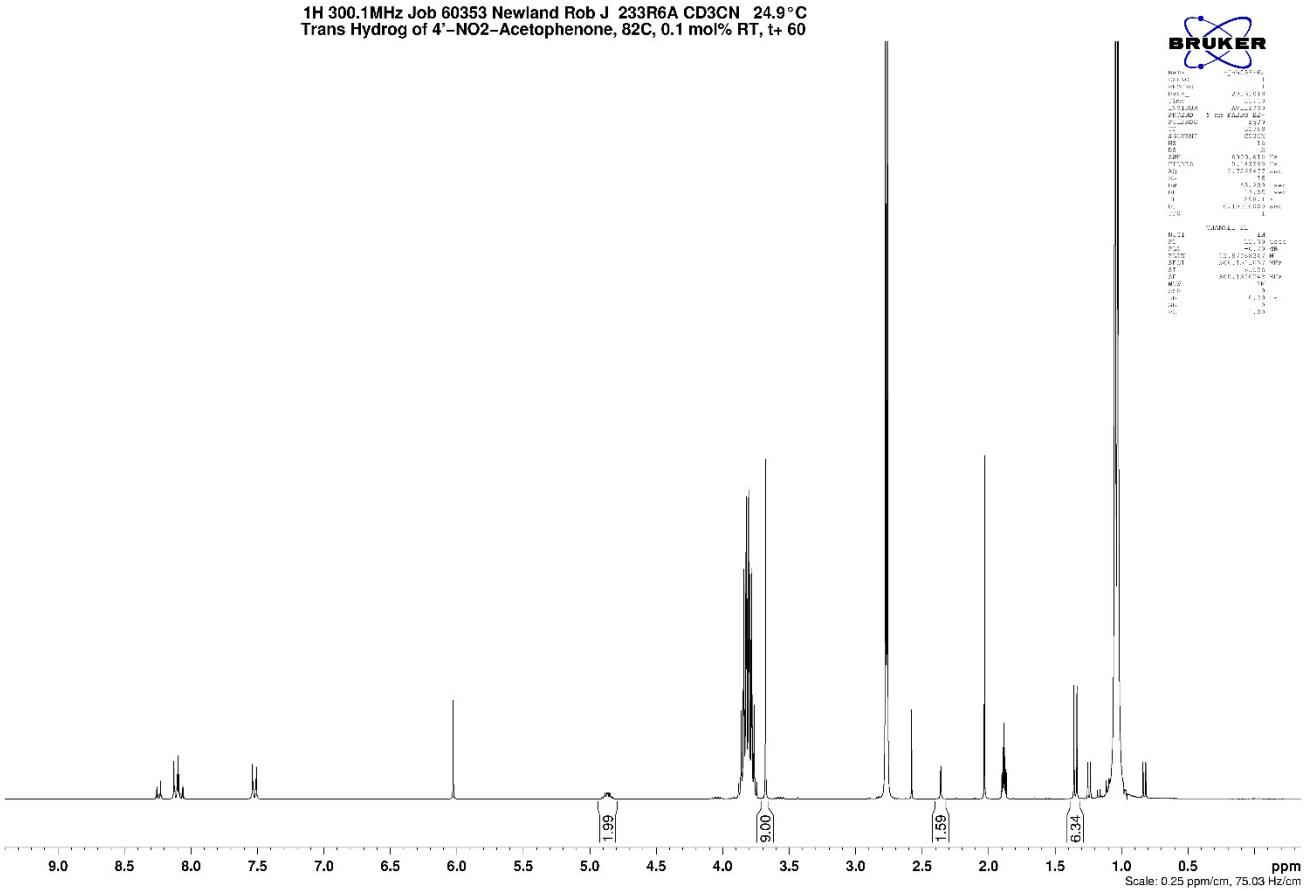


Figure S45. Transfer hydrogenation of 4'-nitroacetophenone, 82°C, 1 hour

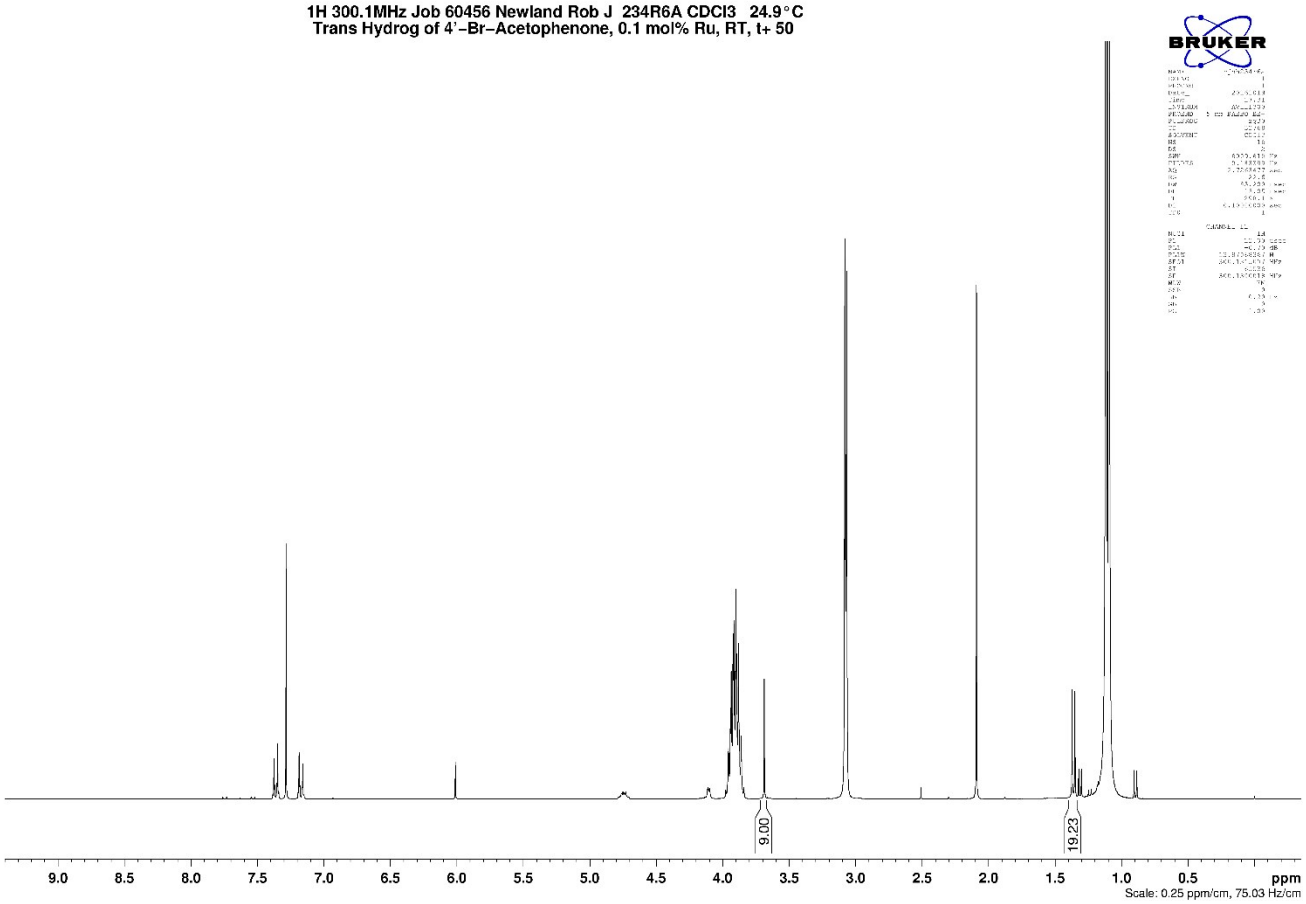


Figure S46. Transfer hydrogenation of 4'-bromoacetophenone, 20°C, 1 hour

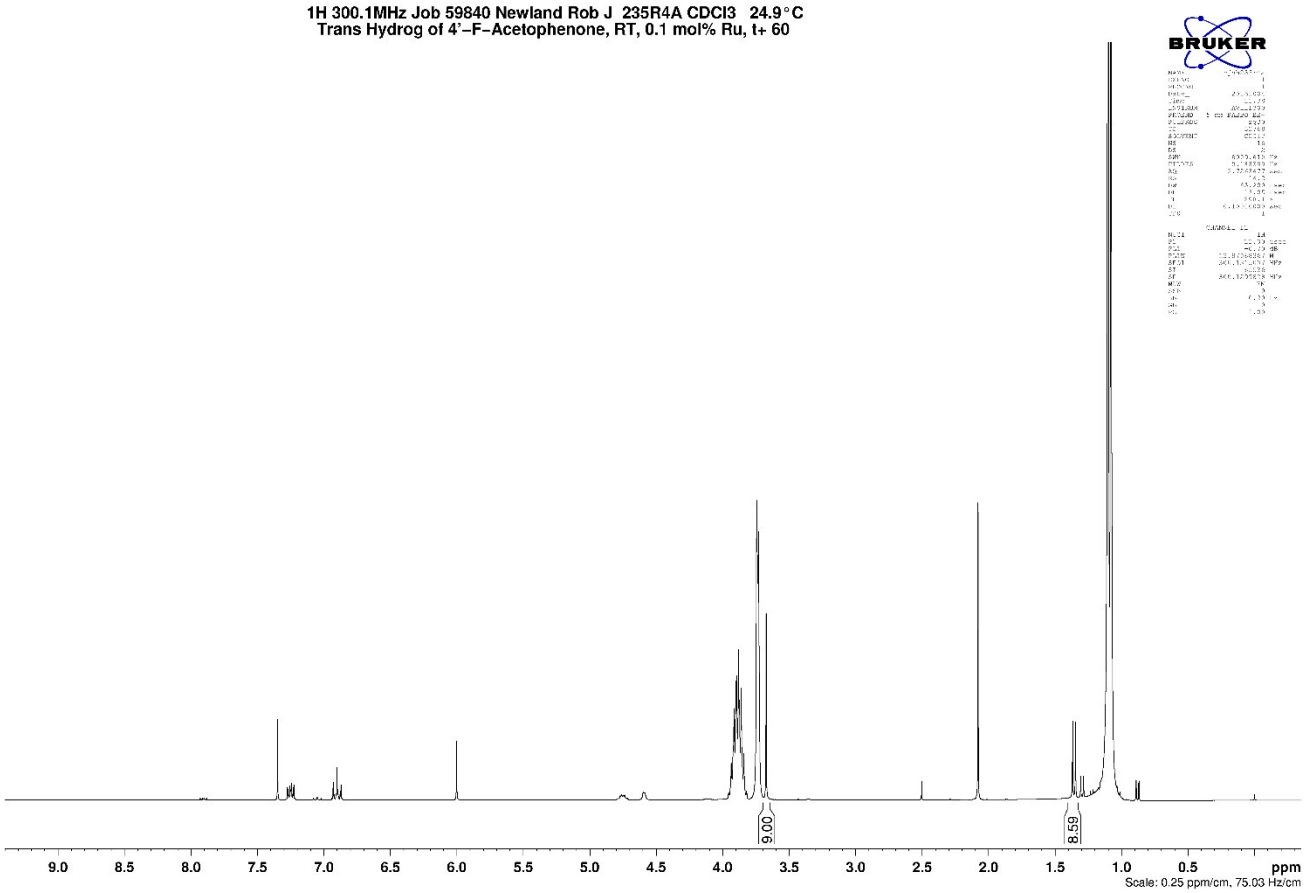


Figure S47. Transfer hydrogenation of 4'-bromoacetophenone, 20°C, 1 hour

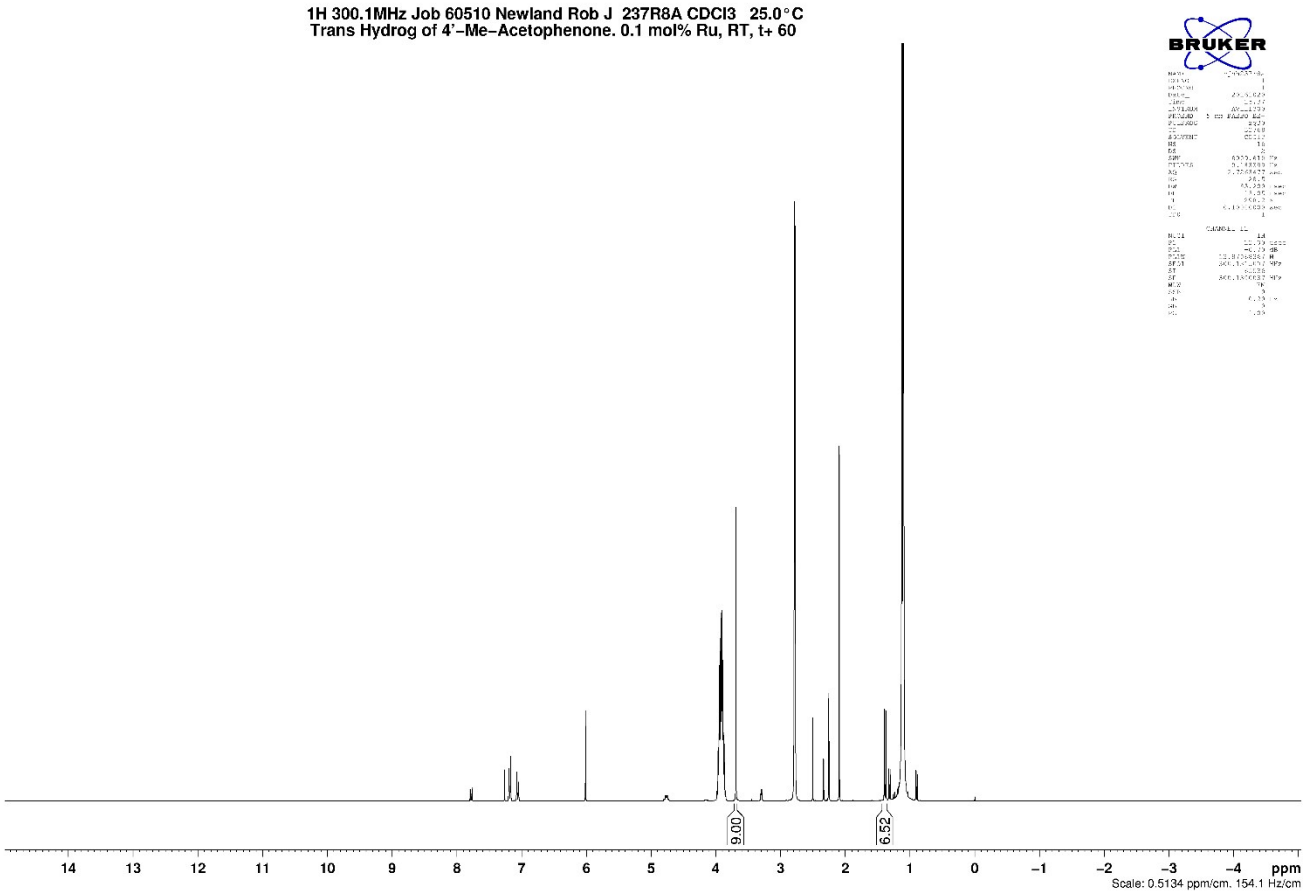


Figure S48. Transfer hydrogenation of 4'-methylacetophenone, 20°C, 1 hour

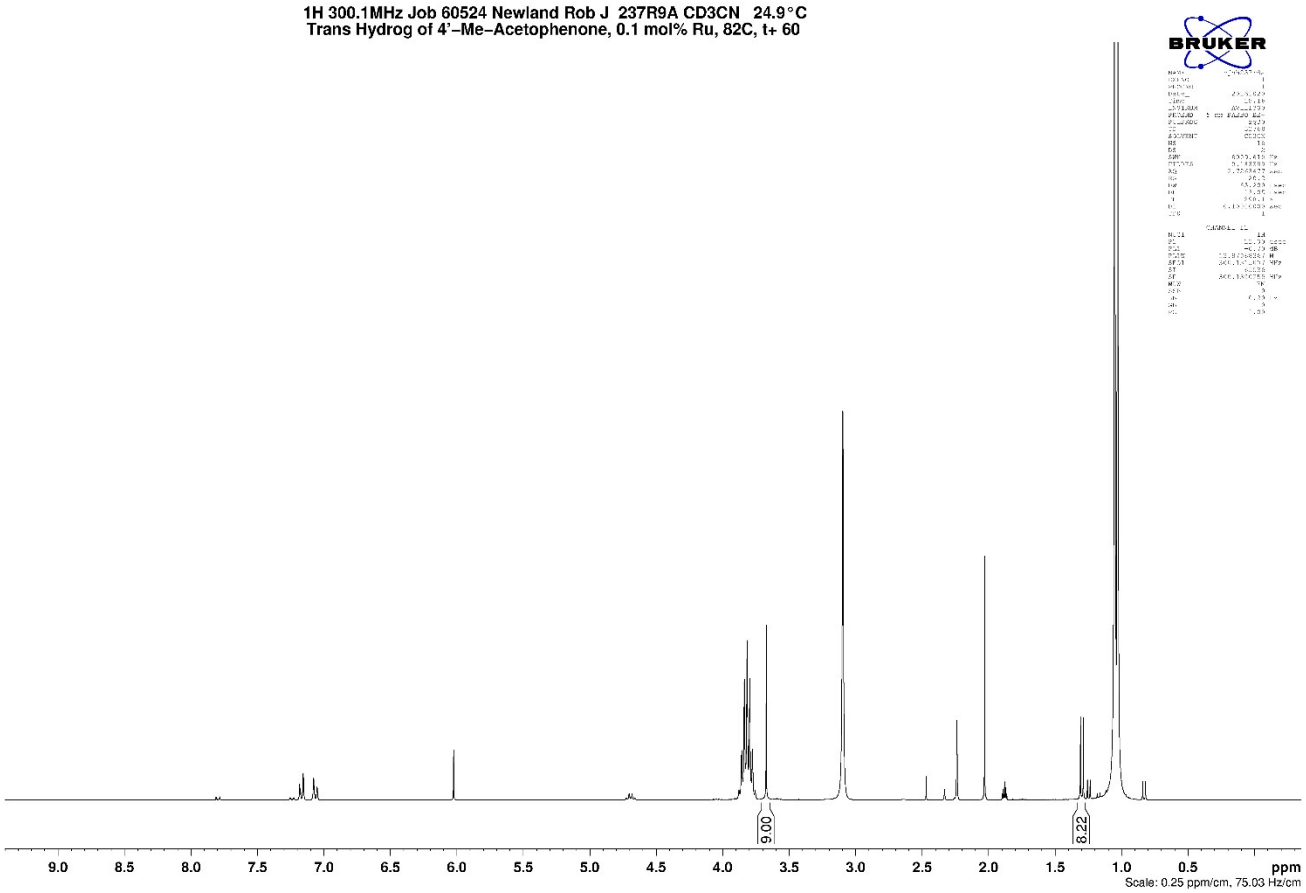


Figure S49. Transfer hydrogenation of 4'-methylacetophenone, 82°C, 1 hour

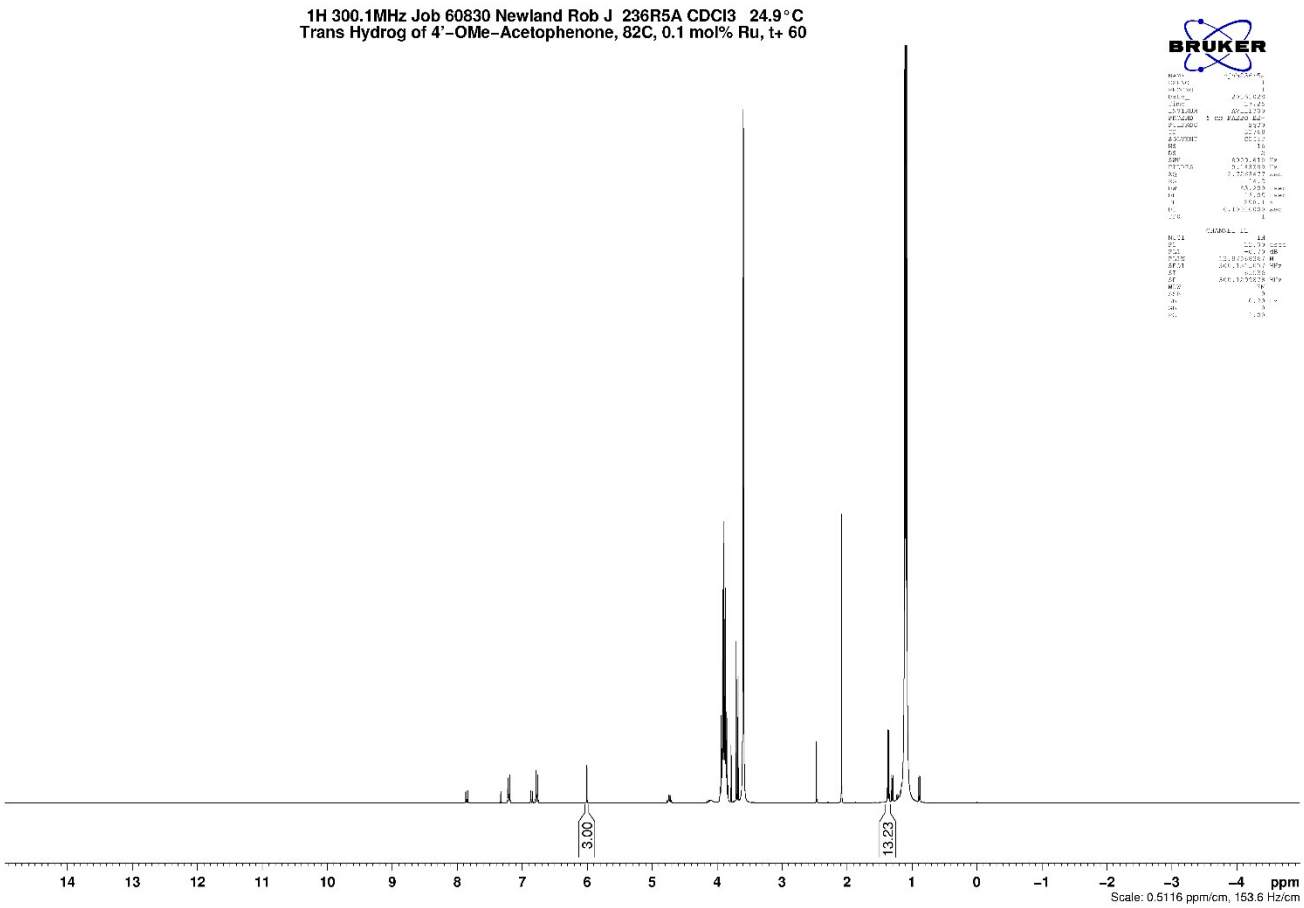


Figure S50. Transfer hydrogenation of 4'-methoxyacetophenone, 82°C, 1 hour

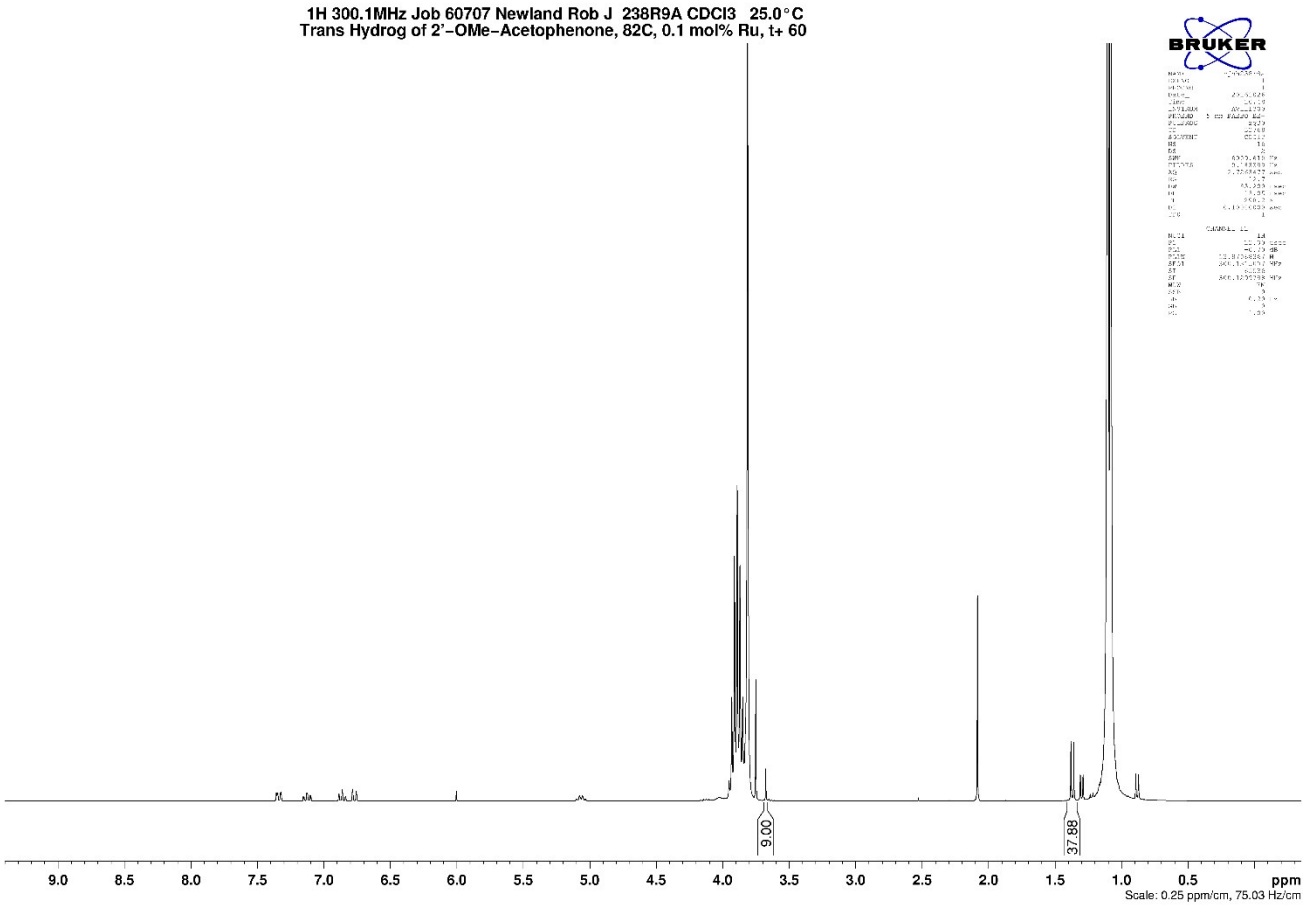


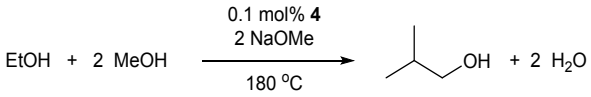
Figure S51. Transfer hydrogenation of 2'-methoxyacetophenone, 82°C, 1 hour

Co-condensation of methanol and ethanol to isobutanol

Experimental Procedure

4 (0.015 g, 0.017 mmol, 0.1 mol%), and NaOMe (1.85 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert inside a glove box. The insert was sealed within a 100 cm^3 Parr stainless steel autoclave which was then transferred to a N_2/vacuum manifold. Methanol (10 cm^3) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 cm^3, 17.13 mmol). The autoclave was sealed and placed into a pre-heated (180 °C) aluminium heating mantle. After the reaction run time (2 or 20h), the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 µL of sample, 25 µL of hexadecane standard, 1.7 cm^3 Et_2O – sample refiltered through a glass filter paper to remove insoluble salts).

Table S3. Ruthenium catalysed conversion of methanol and ethanol to isobutanol



Run[a]	Run Time/h	EtOH Conversion[b]	TON[c](Selectivity)[d][Yield]		
			Isobutanol	*n*-Propanol	*n*-Butanol
1	2	43.4	381(87.7)[38.1]	53(12.3)[5.3]	-
2	20	52.2	495(96.0)[49.5]	19(3.7)[1.9]	4(0.3)[0.4]

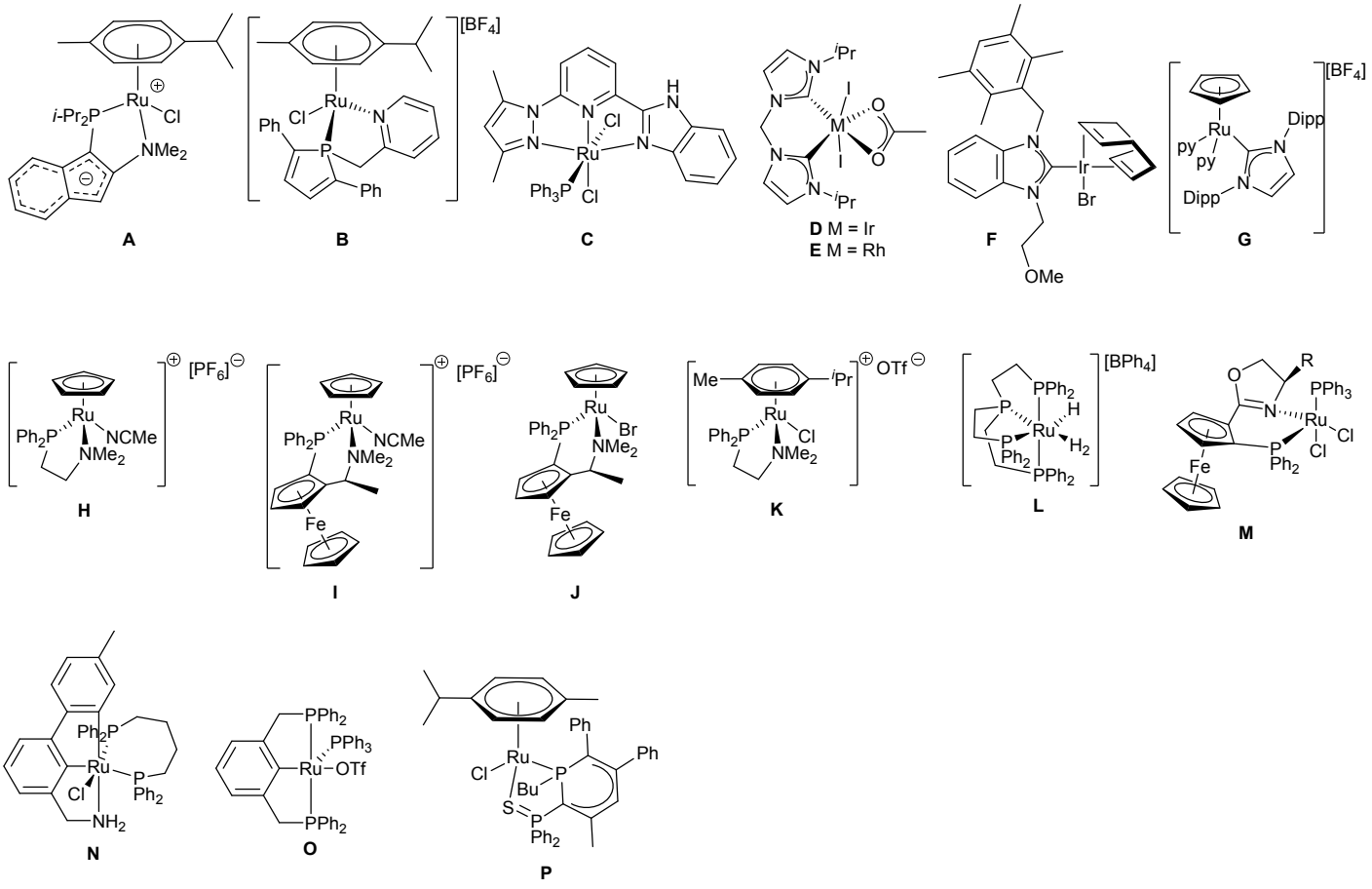
[a] Conditions: 1 cm^3 ethanol, 10 cm^3 methanol, 0.1 mol% catalyst, 200 mol% NaOMe, 180 °C. [b] Total conversion of ethanol to liquid products, isobutanol, *n*-propanol and *n*-butanol. [c] TON based on mmol of substrate converted to products per mmol of Ru. [d] Total selectivity to products in the liquid fraction determined by GC. % based on ethanol.

Comparison of the activities of acetophenone transfer hydrogenation catalysts

Catalyst	Catalyst loading	Temperature/°C	Time	Conversion/%	Reference
4	0.1 mol%	20	1 h	94	-
[Ru(mes)(TsDPEN)Cl]	0.5 mol%	Room temp.	15 h	95	7
$[RuCl_2(C_6H_6)]_2$ + 5 equiv. $HOC_2H_4NH_2$	0.5 mol%	28	5 h	93	8
$[RuCl_2(PPh_3)_3]$	0.1 mol%	82	6 h	75%	Ref 36 in paper
A	0.05 mol%	82 (reflux)	5 min	99	9
B	0.000005 mol%	90	15 h	100	10
C	0.2 mol%	25	1 min	95	11
D	0.1 mol%	70	2 h	>98	12
E	0.1 mol%	82 (reflux)	10 h	>98	13
F	0.5 mol%	80	1.5 h	99	14
G	0.05 mol%	80	1 h 20 min	82	15
H	0.5 mol%	25	24 h	> 99	16
I	0.5 mol%	25	24 h	No reaction	16
J	0.5 mol%	82	48 h	> 99	16
K	0.5 mol%	25	24 h	< 5	16
L*	0.4 mol%	60	5 h	96	17
M	0.5 mol%	Room temp.	2 h	94	18
N	0.005 mol%	82 (reflux)	5 min	98	19
O	0.1 mol%	82	30 min	90	20
P	0.5 mol%	80	2.5 days	98	Ref 6 in paper
$Ru(H)_2(PPh_3)_4$*	0.5 mol%	85	3 h	93	21

Table S4. Comparison of catalyst activity for the transfer hydrogenation of acetophenone.

Mes = mesityl, TsDPEN = N-tosyl-1,2-diphenyl-1,2-diaminoethane, * = No base used. Entries in blue are at room temperature, the entry in green is the most active catalyst at room temperature that we are aware of.



References

1. N. Avarvari, P. Le Floch and F. Mathey, *J. Am. Chem. Soc.*, 1996, **118**, 11978.
2. W. Hewertson, I. C. Taylor and S. Trippett, *J. Chem. Soc. C*, 1970, 1835.
3. E. A. I. Bratsos, M. E. Ringenberg and T. B. Rauchfuss, in *Inorg. Synth.*, John Wiley & Sons, Inc., 2010, pp. 148-152.
4. Bruker AXS Inc., Madison,Wisconsin, USA, 2009.
5. G. M. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
7. S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, **1995**, 117, 7562.
8. R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, **1997**, 30, 97
9. R. J. Lundgren, M. A. Rankin, R. McDonald, G. Schatte and M. Stradiotto, *Angew. Chem. Int. Ed.*, **2007**, 46, 4732.
10. C. Thoumazet , M. Melaimi , L. Ricard , F. Mathey and P. Le Floch, *Organometallics*, **2003**, 22, 1580.
11. M. Zhao, Z. Yu, S. Yan and Y. Li, *Tetrahedron Lett.*, **2009**, 50, 4624.
12. M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller and R. H. Crabtree, *Organometallics*, **2002**, 21, 3596.
13. M. Albrecht, R. H. Crabtree, J. Mata and E. Peris, *Chem. Commun.*, **2002**, 32.
14. H. Türkmen, T. Pape, F. E. Hahn and B. Çetinkaya, *Eur. J. Inorg. Chem*. **2008**, 5418.
15. V. H. Mai and G. I. Nikonov, *Organometallics*, **2016**, 35, 943.
16. C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao and W. Weissensteiner, *J. Chem. Soc. Dalton Trans.,* 2001, 2989.
17. C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini and A. Polo, *Organometallics*, **1993**,12, 3753.
18. Y. Nishibayashi, I. Takei, S. Uemura and M. Hidai, *Organometallics*, **1999**, 18, 2291.
19. W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando and P. Rigo, *Angew. Chem. Int. Ed.*, **2005**, 44, 6214.
20. P. Dani, T. Karlen, R. A. Gossage, S. Gladiali and G. van Koten, *Angew. Chem. Int. Ed*. **2000**, 39, 743.
21. E. Mizushima, M. Yamaguchi and T. Yamagishi, *J. Mol. Catal. A: Chem.*, **1999**, 148, 69