Supporting Information

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General Experimental

All reactions and manipulations were carried out using standard Schlenk techniques under inert atmosphere of purified argon or in an MBraun glovebox unless stated otherwise. All glassware was dried prior to use to remove traces of water. All chemicals were obtained from commercial suppliers and were used as received unless otherwise stated. Diethyl ether and THF were distilled from sodium/benzophenone and toluene was distilled from sodium. Extra dry 1,4 dioxane (99.8%), Me-THF (99+%), anisole (99+%) and dimethylcarbonate were purchased from Acros Organics, degassed and stored over 4 Å molecular sieves. DCM was distilled from calcium hydride. C_6D_6 was thoroughly degassed with Argon and stored over 4 Å molecular sieves. 1,1,1-tris(chloromethyl)ethane was degassed and dried over 3 Å molecular sieves. Novabiochem™ Merrifield resin (100-200 mesh, 1.23 mmol·g^{-1}, 1 % crosslinked) was obtained from EMD Millipore. JandaJel-Cl™ (50-100 mesh, 0.96 mmol·g^{-1}, 2 % crosslinked) was obtained from Sigma-Aldrich. ParaMax Merrifield resin (100-200 mesh, 1.2 mmol·g^{-1}, 4 % crosslinked) was obtained from Advanced Chemtech. Supported secondary phosphines **1a-d**[1,2] and [RuHCl(Triphos)CO] (**3**)[3] were synthesized according to literature.

NMR spectroscopic analysis was conducted using a Bruker FOURIER 300, an AVANCE II 400 or an AVANCE III 500. ^{1}H and ^{31}P NMR experiments were recorded using standard NMR techniques and the chemical shifts (δ) are reported relative to the solvent peak. Gel-phase ^{31}P NMR spectra of all resins were recorded unlocked and without additional shimming in dry THF as a solvent unless mentioned otherwise. Chemical shifts in ^{31}P NMR spectra are reported relative to 85 % H_3PO_4 in water. Solid-state NMR spectra were acquired using a Bruker Avance III spectrometer equipped with a 9.4 T widebore superconducting magnet. Samples were packed in 4.0 mm ZrO_2 rotors and rotated at MAS rates of 14 kHz (^{1}H, ^{31}P) and 12.5 kHz (^{13}C). Multiplicities are provided using the following abbreviations: s = singlet, m = multiplet and br = broad. NMR spectra were processed using TopSpin 3.2 or MestReNova 11.0. ATR-FTIR spectra were recorded on a Bruker Alpha FT-IR spectrometer. The Raman spectra were collected on a Renishaw inVia Raman microscope using a 633 nm laser with a laser power of 1.61 mW. The samples were mounted onto object slides and an objective with a magnification of 50x was applied. For the acquisition of each spectrum 10 scans with an irradiation time of at least 20 s per scan were applied. Elemental analyses were measured by Mikroanalytisches Laboratorium Kolbe in Oberhausen, Germany. GC-FID measurements were performed on a HP 6890 using an Agilent HP-5 column. ICP-OES analyses were measured using a Varian 715-ES.

General Procedure for the Preparation of Lithium Phosphides

A secondary phosphine (1.0 equiv.) was introduced into a dry Schlenk vessel, dissolved in dry THF and cooled to −78 °C. 1.0 equiv. of *n*-BuLi (1.6 M in hexanes) was added dropwise and upon addition the solution became bright yellow or orange. After 1 hour the cooling bath was removed, the reaction mixture was allowed to warm up to room temperature and was left for an additional amount of time until full conversion was confirmed by ^{31}P NMR. The lithium phosphides were directly used in subsequent reactions.

Lithium Diphenylphosphide

The lithium phosphide was obtained from diphenylphosphine (0.37 g, 2.01 mmol, 1.0 equiv.) and *n*-BuLi (1.25 mL, 1.6 M in hexanes, 1.0 equiv.) in dry THF (10 mL) as a bright orange solution (0.18 M).

^{31}P NMR (162 MHz, THF): δ = −22.1 (s) ppm.

Lithium Di(o-tolyl)phosphide

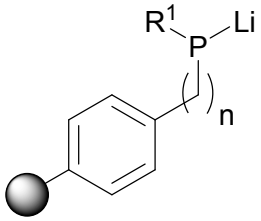
The lithium phosphide was obtained from di(*o*-tolyl)phosphine (0.22 g, 1.00 mmol, 1.0 equiv.) and *n*-BuLi (0.63 mL, 1.6 M in hexanes, 1.0 equiv.) in THF (5 mL) as a bright orange/red solution (0.15 M).

^{31}P NMR (162 MHz, THF): δ = −41.1 (s) ppm.

General Procedure for the Synthesis of Resin-Bound Phosphine Dichlorides 2a-d

Step 1

A resin-bound phosphine **1a** (851 mg, 0.96 mmol, 1.0 equiv.), **1b** (524 mg, 0.47 mmol, 1.0 equiv.), **1c** (535 mg, 0.59 mmol, 1.0 equiv.)[1] or **1d** (2.13 mmol·g^{-1}, 0.85 mmol, 1.0 equiv.)[2] was swollen in THF (15 mL). Next, LDA (2.0 M in THF/heptane/ethylbenzene, 10 equiv.) was added under gentle stirring to avoid mechanical abrasion of the resin. Upon addition, the resin turned dark red and was allowed to react for 3 hours. Next, the supernatant was removed and the resin was subsequently washed with three 10 mL portions of THF followed by three 10 mL portions of Et_2O. The product was used in the next step without additional purification.



Li·1a: MF (1% DVB), R^1 = Ph, n = 1

Li·1b: JJ, R^1 = Ph, n = 1

Li·1c: MF (4% DVB), R^1 = Ph, n = 1

Li·1d: PS, R^1 = ^{t}Bu, n = 0

Li·1a: Dark red resin; ^{31}P NMR (162 MHz, THF): δ = −39.1 (br s) ppm.

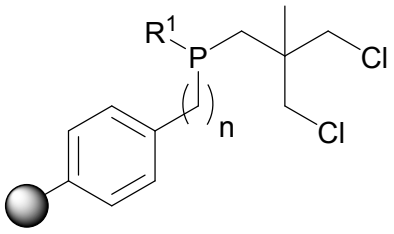
Li·1b: Dark red resin; ^{31}P NMR (162 MHz, THF): δ = −38.7 (br s) ppm.

Li·1c: Dark red resin; ^{31}P NMR (162 MHz, THF): δ = −40.3 (br s) ppm.

Li·1d: Dark red resin; ^{31}P NMR (162 MHz, THF): δ = −5.3 (br s) ppm.

Step 2

A lithiated resin-bound phosphine (**Li·1a**-**d**, 1.0 equiv.) synthesized in the previous step was swollen in THF (15 mL). 1,1,1-tris(chloromethyl)ethane (1.2 equiv., degassed and dried over 3 Å molecular sieves) was subsequently added to the resin at 0 °C under gentle stirring to avoid mechanical abrasion. After 1 hour the ice bath was removed and the reaction mixture was allowed to warm up to room temperature without stirring. When full conversion was observed using gel-phase ^{31}P NMR (generally within 3 hours), the supernatant was removed. The resin was subsequently washed with three 10 mL portions of THF and three 10 mL portions of Et_2O. The products were obtained as white resins. Supported phosphine dimethylenechlorides **2a-d** were directly used in the next step. **2a** was isolated and submitted for elemental analysis (yield for **2a** based on MF-Cl).



2a: MF (1% DVB), R^1 = Ph, n = 1

2b: JJ, R^1 = Ph, n = 1

2c: MF (4% DVB), R^1 = Ph, n = 1

2d: PS, R^1 = ^{t}Bu, n = 0

2a: Off-white resin (988.3 mg, 0.951 mmol, 99.1%); ^{31}P NMR (162 MHz, THF): δ = -30.3 (s) ppm; IR (solid): $\tilde{\nu}$ = 3058 (w), 3024 (w), 2919 (m), 2849 (w), 1600 (w), 1492 (m), 1451 (m), 1434 (w), 741 (m), 694 (s), 536 (m) cm^{-1}; Elemental analysis calcd (%) for **2a** (0.98 mmol·g^{-1}): P 3.15, Cl 7.22; found: P 3.19, Cl 7.70.

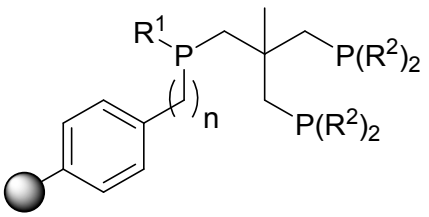
2b: Off-white resin (589.0 mg, 0.469 mmol, 99.8%); ^{31}P NMR (162 MHz, THF): δ = -29.8 (s) ppm.

2c: Off-white resin (612.4 mg, 0.585 mmol, 99.2%); ^{31}P NMR (162 MHz, THF): δ = -29.8 (br s) ppm.

2d: Yellow resin (501.2 mg, 0.823 mmol, 96.9%); ^{31}P NMR (162 MHz, THF): δ = -11.4 (br s) ppm.

General Procedure for the Synthesis of Resin-Bound Triphos ligands L_1-L_5

A resin-bound phosphine dichloride **2a** (**L_1**, 0.96 mmol, 1.0 equiv.; **L_5**, 0.29 mmol, 1.0 equiv.), **2b** (0.47 mmol, 1.0 equiv.), **2c** (0.59 mmol, 1.0 equiv.) or **2d** (0.85 mmol, 1.0 equiv.) synthesized in the last step was swollen in THF (10 mL). A freshly prepared secondary lithium phosphide solution (10-20 equiv.) in THF (15 mL) was added under gentle stirring to avoid mechanical abrasion of the resin. The reaction mixture was heated to 60 °C and was left overnight without stirring. The reaction was monitored using ^{31}P NMR and was allowed to react until full conversion was observed. If necessary, extra equivalents of lithium phosphide were added to drive the reaction to completion. Next, the supernatant was removed and the resin was subsequently washed with three 10 mL portions of THF followed by three 10 mL portions of Et_2O. The product was dried *in vacuo* yielding a white resin-bound Triphos ligand (**L_1**-**L_5**, yields based on starting resin).



L_1: MF (1% DVB), R^1 = R^2 = Ph, n = 1
L_2: JJ, R^1 = R^2 = Ph, n = 1
L_3: MF (4% DVB), R^1 = R^2 = Ph, n = 1
L_4: PS, R^1 = ^{t}Bu, R^2 = Ph, n = 0
L_5: MF (1% DVB), R^1 = Ph, R^2 = *o*-Tol, n = 1

L_1: White resin (1240.5 mg, 0.916 mmol, 95.4%); ^{31}P NMR (162 MHz, THF): δ = -25.4 (2P, s, -PPh_2), -28.1 (1P, s, -PPhBn) ppm; IR (solid): $\tilde{\nu}$ = 3056 (w), 3024 (w), 2919 (m), 2848

(w), 1600 (w), 1492 (m), 1451 (m), 1433 (m), 1025 (w), 838 (w) 737 (m), 693 (s), 441 (m) cm^{-1}; Elemental analysis calcd (%) for **L_1** (0.76 mmol·g^{-1}): P 7.05; found: P 7.39.

L_2: White resin (715.7 mg, 0.463 mmol, 98.5%); ^{31}P NMR (162 MHz, THF): δ = -25.5 (2P, s, -PPh_2), -28.1 (1P, s, -PPhBn) ppm; IR (solid): $\tilde{\nu}$ = 3056 (w), 3024 (w), 2918 (m), 2850 (w), 1600 (w), 1492 (m), 1451 (m), 1433 (m), 1086 (w), 1067 (w), 1026 (w), 738 (m), 694 (s), 430 (m) cm^{-1}; Elemental analysis calcd (%) for **L_2** (0.64 mmol·g^{-1}): P 5.98; found: P 5.80.

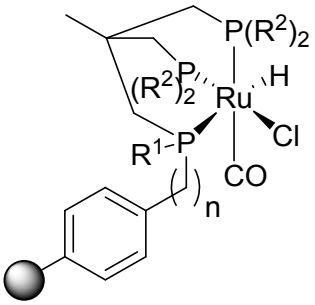
L_3: White resin (699.4 mg, 0.521 mmol, 88.3%); ^{31}P NMR (162 MHz, THF): δ = −25.4 (br s, -PPh_2), -27.8 (br s, -PPhBn) ppm (not possible to determine integrals due to peak overlap); IR (solid): $\tilde{\nu}$ = 3057 (w), 3024 (w), 2917 (m), 2849 (w), 1600 (w), 1492 (m), 1450 (m), 1433 (m), 1025 (w), 828 (w), 738 (m), 694 (s) cm^{-1}; Elemental analysis calcd (%) for **L_3** (0.78 mmol·g^{-1}): P 7.25; found: P 6.30.

L_4: Yellow resin (408.8 mg, 0.429 mmol, 50.5%); ^{31}P NMR (162 MHz, THF): δ = −8.8 (1P, br s, -P^{t}BuBn), -25.0 (1P, br s, -PPh_2), -25.8, (1P, br s, -PPh_2) ppm; IR (solid): $\tilde{\nu}$ = 3058 (w), 3025 (w), 2921 (m), 2857 (w), 1599 (w), 1493 (w), 1451 (m), 1433 (w), 1153 (w), 1124 (w), 1087 (w), 1070 (w), 823 (w), 746 (w), 696 (s), 428 (s) cm^{-1}; Elemental analysis calcd (%) for **L_4** (1.10 mmol·g^{-1}): P 10.23; found: P 8.06.

L_5: White resin (340.8 mg, 0.258 mmol, 89.1%); ^{31}P NMR (162 MHz, THF): δ = −28.3 (1P, br s, -PPhBn), -51.9 (1P, s, -P*o*-tol_2), -52.0, (1P, s, -P*o*-tol_2) ppm; IR (solid): $\tilde{\nu}$ = 3056 (w), 3024 (w), 2919 (m), 2849 (w), 1600 (w), 1492 (m), 1450 (m), 1373 (w), 1027 (w), 838 (w), 741 (m), 695 (s), 539 (m), 527 (m), 543 (m), 444 (m) cm^{-1}; Elemental analysis calcd (%) for **L_5** (0.78 mmol·g^{-1}): P 6.76; found: P 5.31.

General Procedure for the Synthesis of Resin-Bound Complexes C_1-C_5

A previously synthesized resin-bound Triphos ligand **L_1** (0.19 mmol, 1.0 equiv), **L_2** (0.10 mmol, 1.0 equiv.), **L_3** (0.13 mmol, 1.0 equiv.), **L_4** (0.20 mmol, 1.0 equiv.) or **L_5** (0.12 mmol, 1.0 equiv.) and [Ru(HCl(PPh_3)$_3$CO] (1.1 equiv.) were weighed into a Schlenk tube. The mixture was suspended in toluene (10 mL) and heated to 80 °C under gentle stirring. The reaction mixture was left at 80 °C with occasional stirring to avoid mechanical abrasion of the resin and the progress of the reaction was monitored by gel-phase ^{31}P NMR. Once full complexation of the resin-bound Triphos ligand was observed, the mixture was cooled to room temperature and the supernatant was removed. The resin-bound complex was washed with three 10 mL portions of THF, three 10 mL portions of DCM followed by three 10 mL portions of Et_2O. After drying *in vacuo* a yellow or orange resin-bound [RuHCl(Triphos)CO] complex (**C_1-C_5**) was obtained. (**C_1-C_5** yields based on ligands **L_1-L_5**).



C_1: MF (1% DVB), $R^1 = R^2$ = Ph, n = 1

C_2: JJ, $R^1 = R^2$ = Ph, n = 1

C_3: MF (4% DVB), $R^1 = R^2$ = Ph, n = 1

C_4: PS, $R^1 = {}^t$Bu, R^2 = Ph, n = 0

C_5: MF (1% DVB), R^1 = Ph, R^2 = *o*-Tol, n = 1

C_1: Yellow resin (273.0 mg, 0.18 mmol, 95.0%); ^{31}P NMR (121 MHz, THF:C_6D_6 6:1): δ = 49.8 and 41.8 (1P, br), 15.3 (1P, br), 1.2 (1P, br) ppm; ^{1}H MAS NMR (spinning rate 14 kHz,): δ = -5.80 (br, Ru–H) ppm; IR (solid): $\tilde{\nu}$ = 3055 (m), 3024 (w), 2918 (w), 2850 (w), 1968 (m, CO), 1922 (m, Ru–H), 1600 (w), 1492 (m), 1450 (m), 1433 (m), 1090 (w), 832 (m), 738 (m), 694 (s) cm^{-1}.

C_2: Yellow resin (161 mg, 0,12 mmol, 97.1 %): ^{31}P NMR (121 MHz, THF:C_6D_6 6:1): δ = 51.0 and 14.4 (1P, br), 0.8 (1P, br), 1.2 (1P, br) ppm; IR (solid): $\tilde{\nu}$ = 3055 (w), 3023 (w), 2917 (m), 2849 (w), 1975 (m, CO), 1925 (m, Ru–H), 1599 (w), 1580 (w), 1492 (m), 1450 (m), 1433 (m), 1090 (w), 841 (w), 739 (m), 694 (s) cm^{-1}.

C_3: Yellow resin (165 mg, 0,11 mmol, 91.2 %): ^{31}P MAS NMR (spinning rate 14 kHz,): δ = 51.8-5.7 (br, 3P) ppm; IR (solid): $\tilde{\nu}$ = 3056 (w), 3023 (w), 2917 (m), 2849 (w), 1970 (m, CO), 1920 (m, Ru–H), 1600 (w), 1582 (w), 1491 (m), 1450 (m), 1433 (m), 1090 (w), 840 (w), 739 (m), 693 (s) cm^{-1}.

C_4: Orange resin (141 mg, 0,13 mmol, 96.3 %): ^{31}P MAS NMR (spinning rate 14 kHz,): δ = 51.1-36.9 (m, 1P), 25.8-6.0 (m, 1P), -0.3--13.1 (m, 1P) ppm; ^{13}C MAS NMR (spinning rate 12.5 kHz,): δ = 146.0-128.1 (resin-Ar and P-Ar), 40.5 (resin-CH, P-CH_2, *C*CH_3, C*C*H_3), 32.7 (P-*C*$(CH_3)_3$), 28.4 (P-C(*C*$H_3)_3$) ppm, CO was not detected; IR (KBr): $\tilde{\nu}$ = 3024 (w), 2918 (m), 2854 (w), 1968 (m, CO), 1922 (m, Ru–H), 1595 (m), 1488 (w), 1432 (s), 1157 (w), 1089 (m), 1046 (w), 1019 (m), 822 (w), 743 (m), 694 (s) cm^{-1}.

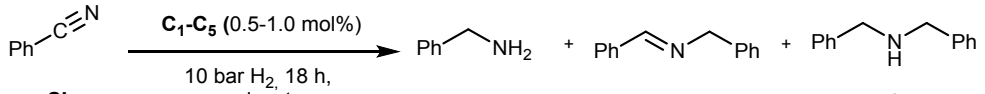
C_5: Yellow resin (171 mg, 0,11 mmol, 95.6 %): ^{31}P MAS NMR (spinning rate 14 kHz,): δ = 57.3--2.5 (br, 3P) ppm, ^{13}C MAS NMR (spinning rate 12.5 kHz,): δ = 140.6-128.4 (resin-Ar and P-Ar), 40.3 (resin-CH, P-CH_2, *C*CH_3, C*C*H_3), 22.7 (P-*o*-Tol-*C*H_3), ppm, CO was not detected; IR (solid): $\tilde{\nu}$ = 3054 (w), 3024 (w), 2918 (m), 2848 (w), 1968 (m, CO), 1920 (m, Ru–H), 1600 (w), 1492 (w), 1449 (m), 1434 (m), 1095 (w), 826 (w), 742 (m), 695 (s), 532 (m), 471 (m) cm^{-1}.

General Procedure for Nitrile Hydrogenation Experiments

The hydrogenation experiments were performed in a stainless steel autoclave charged with an insert suitable for up to 12 reaction vessels (1.5 mL) including Teflon mini stirring bars. Inside a glove box, a reaction vessel was charged with a resin-bound Ru-Triphos complex **C_1-C_5** or **3** (2.5-5.0 µmol, 0.5-1.0 mol%). Next, to the reaction vessel 1.0 mL of a stock solution of **S_1-S_{13}** (0.25-0.50 M) and the internal standard dodecane (50 mol%) dissolved in the desired solvent was added and the mixture was stirred gently for 5 minutes. Subsequently, the insert loaded with reaction vessels was transferred into the autoclave. The autoclave was purged three times with 10 bar of nitrogen gas followed by three purges with 10 bar of H_2 and then pressurized (10-30 bar) and heated to the desired temperature. The reaction mixtures were gently stirred at 450 rpm for 18-50 h. The autoclave was cooled to room temperature, depressurized and the conversion was determined by GC-FID measurements using the following column and conditions:

Agilent HP-5 column (30 m, 0.25 mm, 0.1 µm): T_0 = 80 °C, hold for 2 min then ΔT = 10 °C min^{-1} to 160 °C, then ΔT = 15 °C min^{-1} to 240 °C, then ΔT = 15 °C min^{-1} to 300 °C, then hold for 5 min.

Table S1 Full results of optimization in Ru-catalyzed hydrogenation of **S_1** using supported catalysts **C_1-C_5**.[a]



SI **A** **B** **C**

Entry	Catalyst [mol%]	Solvent	T [°C]	Time [h]	Conversion [%][b]	Selectivity [%][b]		
						A	**B**	**C**
1	**C_1** (0.5)	dioxane	100	18	>99	99	1	<1
2	**C_1** (0.5)	toluene	80	18	24	73	27	<1
3	**C_1** (0.5)	THF	80	18	37	97	3	<1
4	**C_1** (0.5)	Me-THF	80	18	18	86	6	<1
5	**C_1** (0.5)	Anisole	80	18	16	44	56	<1
6	**C_1** (0.5)	DMC	80	18	2	<1	2	<1
7	**C_2** (0.5)	dioxane	80	18	48	96	4	<1
8	**C_3** (1.0)	dioxane	100	50	>99	98	2	<1
9	**C_4** (0.5)	dioxane	80	18	44	97	3	<1
10	**C_5** (0.5)	dioxane	100	8	56	<1	>99	<1

[a] Conditions: substrate (0.5 mmol), 1,4-dioxane (1 mL), H_2 (10 bar). [b] Conversion and selecticvity determined by GC using dodecane as internal standard (IS).

General Procedure for Batch Recycling Experiments

The first nitrile hydrogenation cycle was performed as described above using **C_1** (5 µmol, 1.0 mol%), 1.0 mL of a stock solution of **S_1** in 1,4-dioxane (0.50 M) and dodecane as internal standard (50 mol%) at 100 °C and 10 bar H_2. After 2 hours, the autoclave was cooled and depressurized and the reaction vessel was removed. Keeping the catalyst under a H_2 atmosphere using a H_2-filled balloon, the supernatant was removed and the resin was washed with three 1 mL portions of THF. Next, new substrate stock solution (0.5 M, 1.0 mL) in 1,4-dioxane was added to the reaction vessel. The autoclave was then charged with the reaction vessel and a new reaction cycle was started. The supernatant was submitted for GC-FID and ICP-OES analysis.

Table S2 Batch recycling experiments using supported catalyst **C_1** in the hydrogenation of **S_1**.

Run	Conversion [%][b]	Selectivity [%][b]	
		A	**B**
1	17	>99	<1
2	26	>99	<1
3	34	99	1
4	39	99	1
5	36	97	3
6	31	97	3
7[c]	>99	95	5

[a] Conditions: substrate (0.5 mmol), catalyst (1.0 mol%), 1,4-dioxane (1 mL), 100 °C, H_2 (10 bar), 2 h. [b] Conversion and selectivity determined by GC using dodecane as internal standard (IS). [c] 18 h.

The amount of Ru leaching into the filtrates was analyzed by ICP-OES after each run. No ruthenium in solution was detected.

Continuous Flow Hydrogenation in Modular Microreaction System

Setup

Continuous flow reactions were performed using a customized Ehrfeld modular cartridge microreactor 240 (www.ehrfeld.com, Figure S1) equipped with a 63 x 10 mm cartridge (5 mL).[4] The stock solution containing substrate **S_1** in 1,4-dioxane (0.25 M) and 25 mol% of *n*-dodecane as internal standard was introduced by a Knauer K-501 HPLC pump (0.001-9.999 mL/min). H_2 was dosed by a Bronkhorst mass flow controller F211CV-050-AAD-33-V (www.bronkhorst.com). The stock solution and the hydrogen gas were mixed in a micromixer before the gas/liquid mixture entered the catalyst bed from the bottom of the reactor. After the micromixer, a pressure sensor was installed to monitor the inlet pressure of the reactor. Two temperature sensors installed before and after the reactor allowed to record the temperature of the reaction mixture. The system pressure was maintained by an Equilibar back pressure valve (www.equilibar.com).

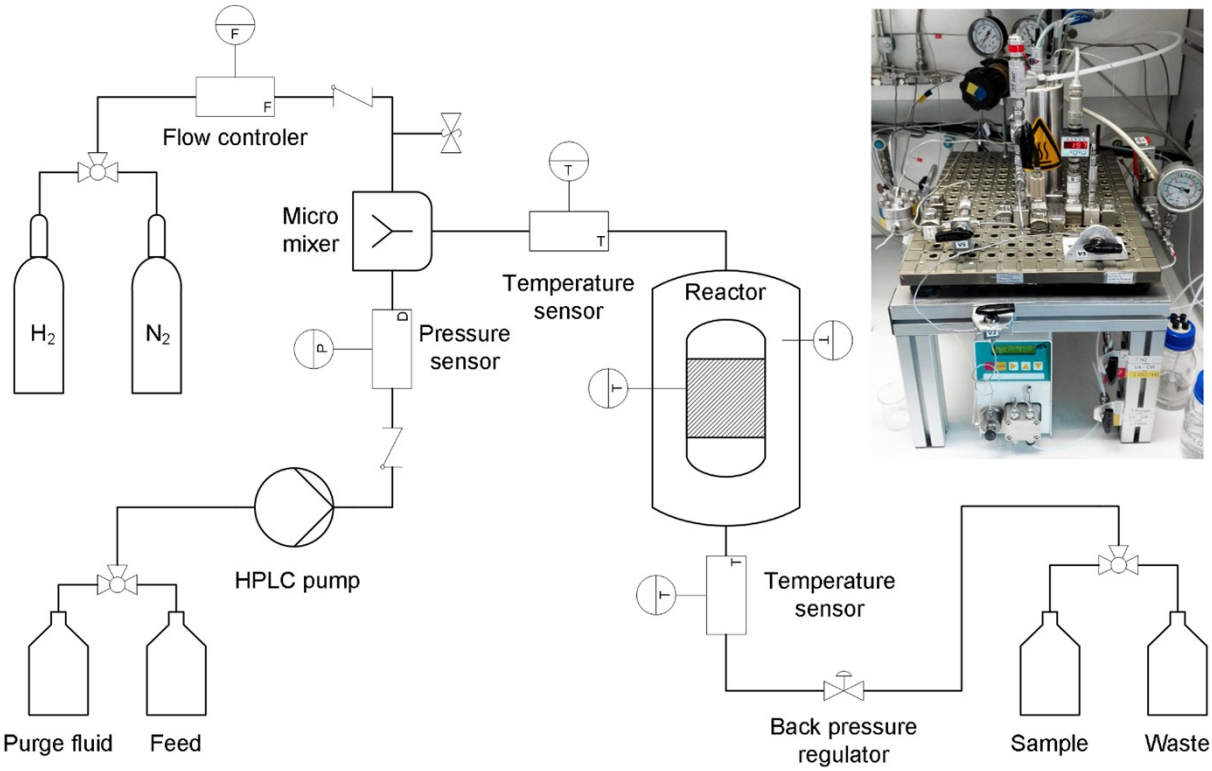


Figure S1 Flow scheme of modular microreactor setup for continuous flow hydrogenation reactions.

Procedure

200 mg of supported catalyst **C_1** (0.134 mmol) were charged into a Schlenk tube and swollen in 2 mL of 1,4-dioxane for 10 minutes. Under a flow of Argon, the cartridge layered with glass wool at the bottom was loaded with the suspension. After particle sedimentation and removal of the supernatant solvent, the catalyst bed (0.79 mL) was layered with glass wool, the

remaining volume of the reactor was filled with glass beads (0.25-0.50 mm) and topped with glass wool again. Next, the cartridge was sealed and inserted into the cartridge reactor under a gentle flow of N_2. At a system pressure of 10 bar the setup was purged with dioxane (0.2 mL·min^{-1}) and H_2 (2.5 mL·min^{-1}) until a constant inlet pressure was reached. After switching to the feed-stock solution at a rate of 0.2 mL·min^{-1}, the fluid inside the reactor was heated to 100 °C. During optimization, reaction conditions were varied throughout the experiment (Table S3, Figure S2). Samples of the product stream were collected downstream in vials and analyzed by GC-FID. Ru leaching into the product stream was analyzed by ICP-OES.

Table S3 Reaction conditions varied during continuous flow hydrogenation of **S_1** using supported catalyst **C_1**.

Setting	Time [min][a]	Flow rate [mL·min^{-1}]	H_2 flow [mL·min^{-1}]	*T* [°C]	*P* [bar]	TOF [h^{-1}][b]	Conv. [%][c,d]	Selectivity [%][d,e]
1	90	0.20	2.50	100	15	0	0	0
2	150	0.10	2.50	100	15	0.8	7	95
3	1360	0.05	2.50	100	17	4.7	83 (±6.5)	42 (±5.6)
4	1570	0.10	2.50	100	19	6.4	57 (±1.6)	39 (±1.9)
5	2740	0.10	2.50	100	29	9.0	80 (±2.5)	42 (±1.8)
6	2950	0.10	2.50	100	17	5.7	51 (±2.0)	45 (±3.4)
7	3070	0.10	1.25	100	17	5.5	49 (±0.9)	47 (±2.2)
8	4150	0.10	1.25	120	17	10.0	89 (±0.5)	67 (±2.4)
9	4330	0.10	1.25	135	17	11.0	98 (±1.3)	79 (±0.8)
10	4510	0.10	1.25	150	17	11.2	100 (±0.2)	84 (±0.6)
11	5560	0.05	1.25	150	17	5.6	100 (±0.0)	85 (±2.1)
12	5860	0.05	2.50	100	17	4.1	73 (±1.6)	73 (±1.8)

[a] Time until parameters were altered. [b] TOF (h^{-1}) calculated as flow rate (mL·min^{-1}) x concentration of stock solution (mmol·mL^{-1}) x conversion x 60 / n_{cat} (mmol). [c] Conversion of **S_1** determined by GC using dodecane as internal standard. [d] Conversion and selectivity are determined from samples taken every 30 to 60 minutes (values are averaged from at least 3 samples once stable conditions were obtained except for entry 1 and 2). Standard deviation in parenthesis. [e] Selectivity towards benzylamine (**A**).

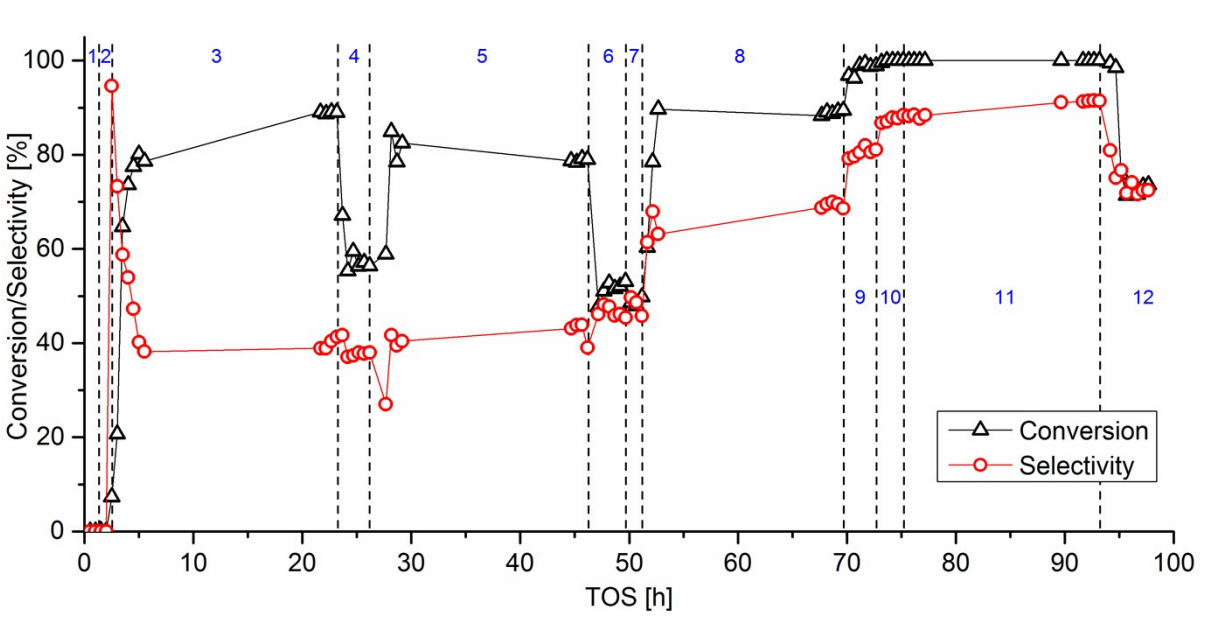


Figure S2 Continuous flow hydrogenation of $\mathbf{S_1}$ using $\mathbf{C_1}$. For conditions in settings 1-12 see Table S3. n_{Cat} = 0.134 mmol, 0,25 M solution of $\mathbf{S_1}$ in dioxane. Conversion determined by GC using dodecane as internal standard. Selectivity towards benzylamine (**A**).

The amount of Ru leaching into the filtrates was analyzed by ICP-OES after each run. No ruthenium in solution was detected.

Gel-Phase and Solid-State NMR spectra of Resin-Bound Ligands and Complexes

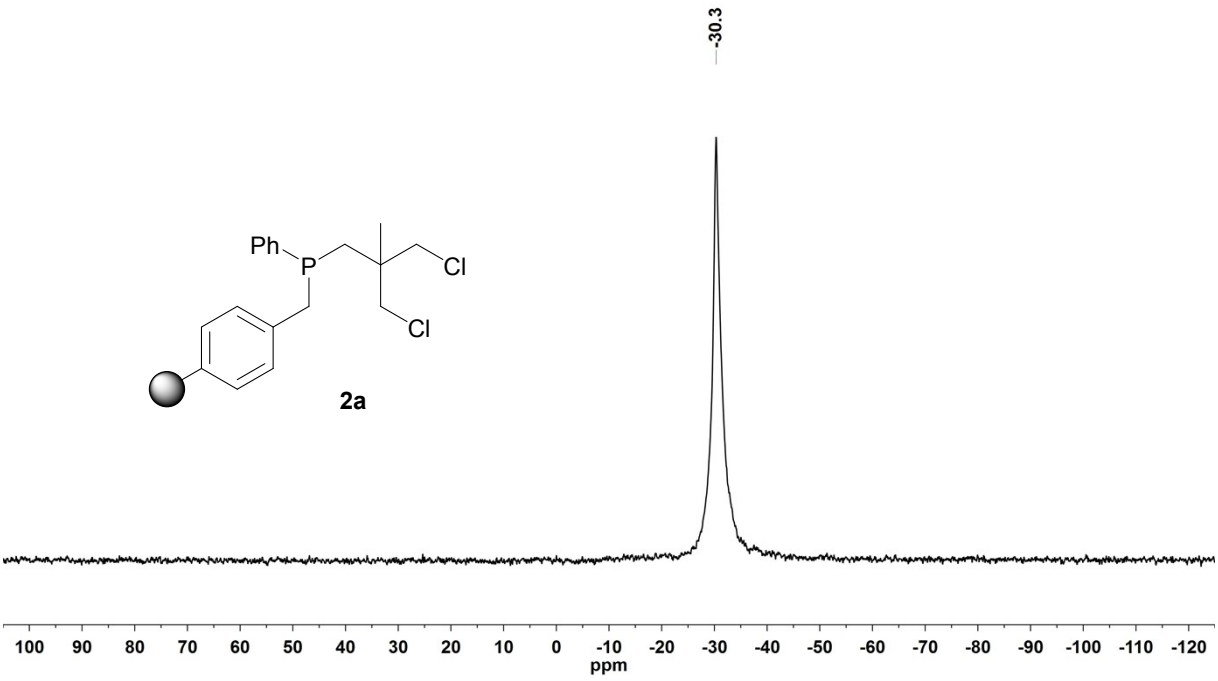


Figure S3 Representative gel-phase ^{31}P NMR spectrum of **2a** for resin-bound phosphine dichlorides (162 MHz, THF).

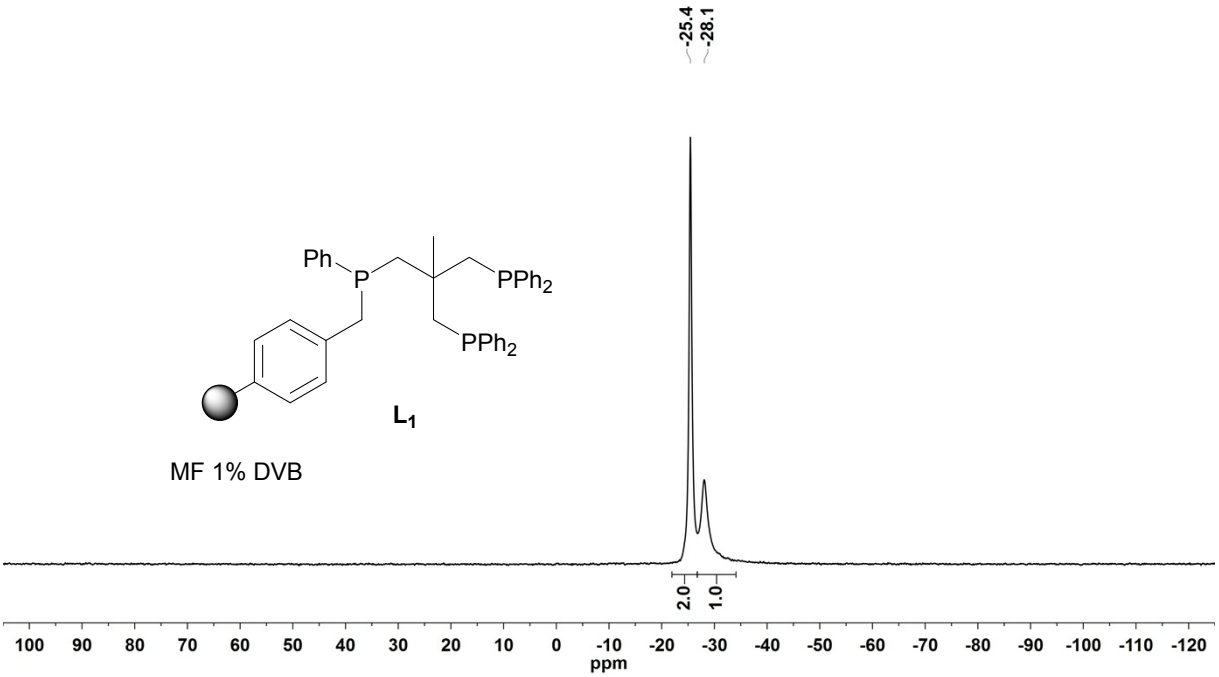


Figure S4 Gel-phase ^{31}P NMR spectrum of $\mathbf{L_1}$ (162 MHz, THF).

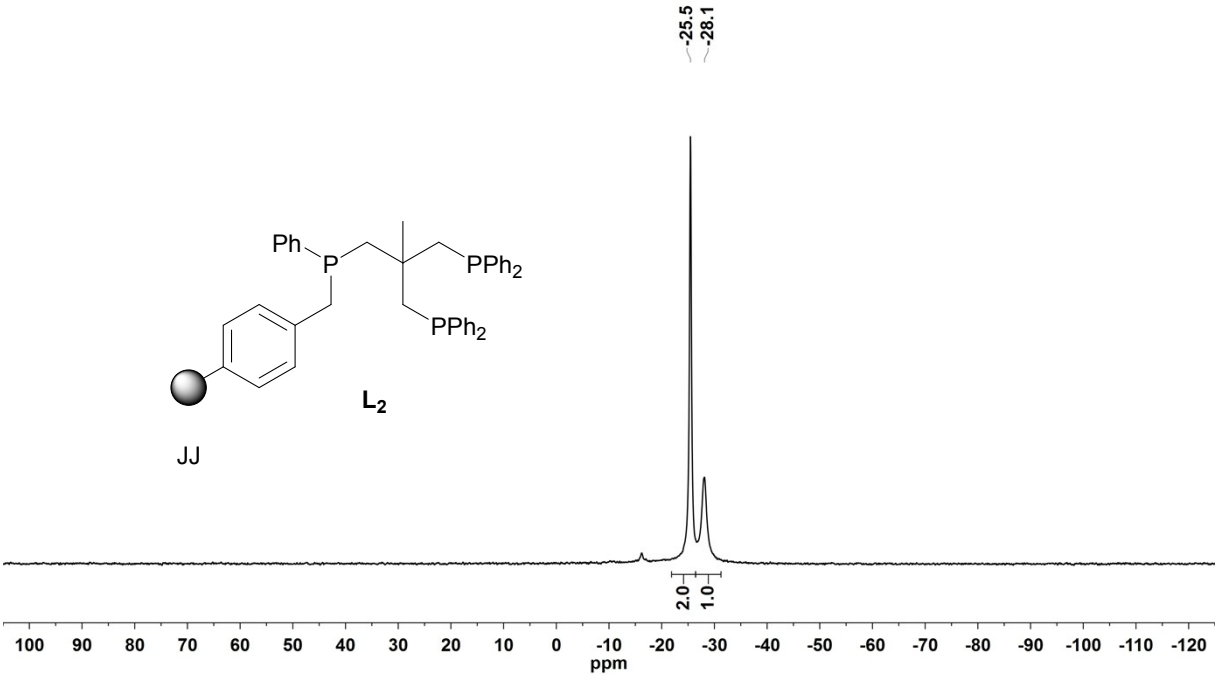


Figure S5 Gel-phase ^{31}P NMR spectrum of $\mathbf{L_2}$ (162 MHz, THF).

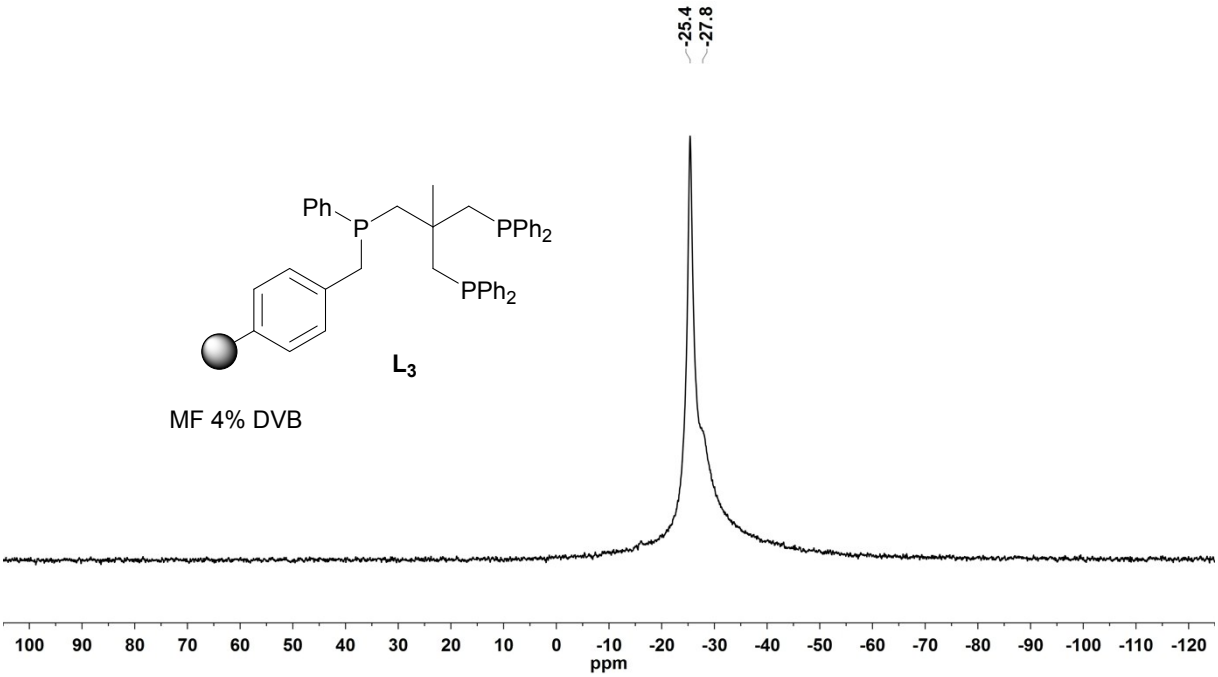


Figure S6 Gel-phase ^{31}P NMR spectrum of **L_3** (162 MHz, THF).

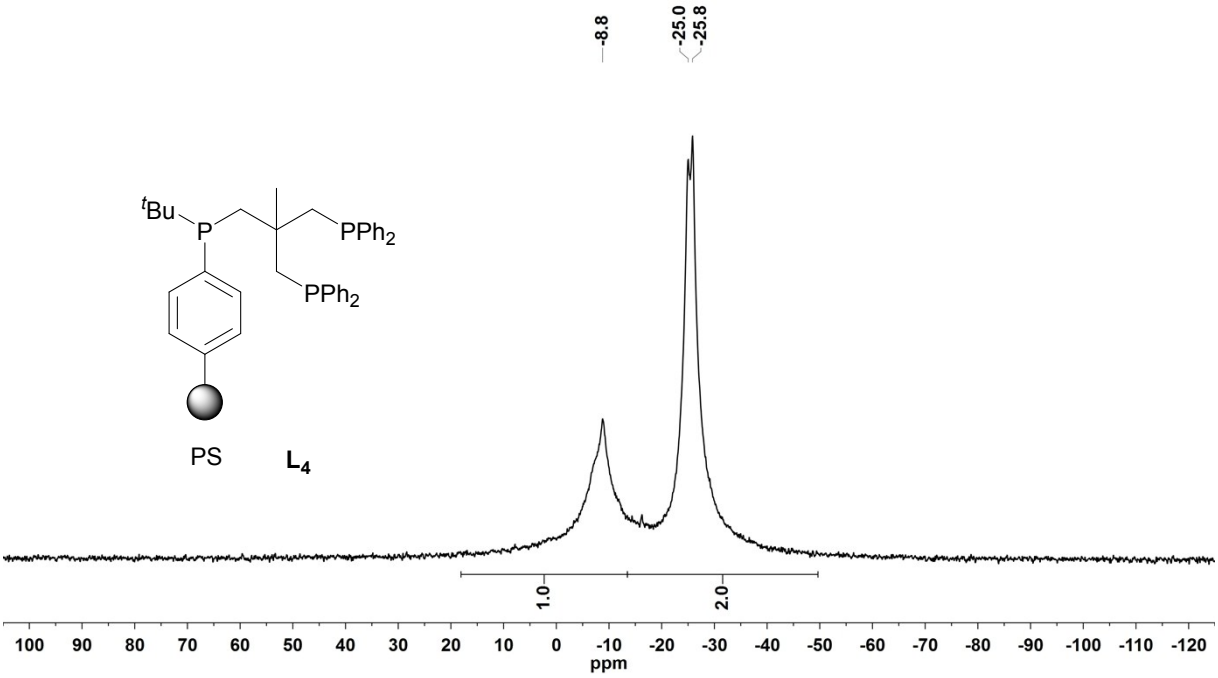


Figure S7 Gel-phase ^{31}P NMR spectrum of **L_4** (162 MHz, THF).

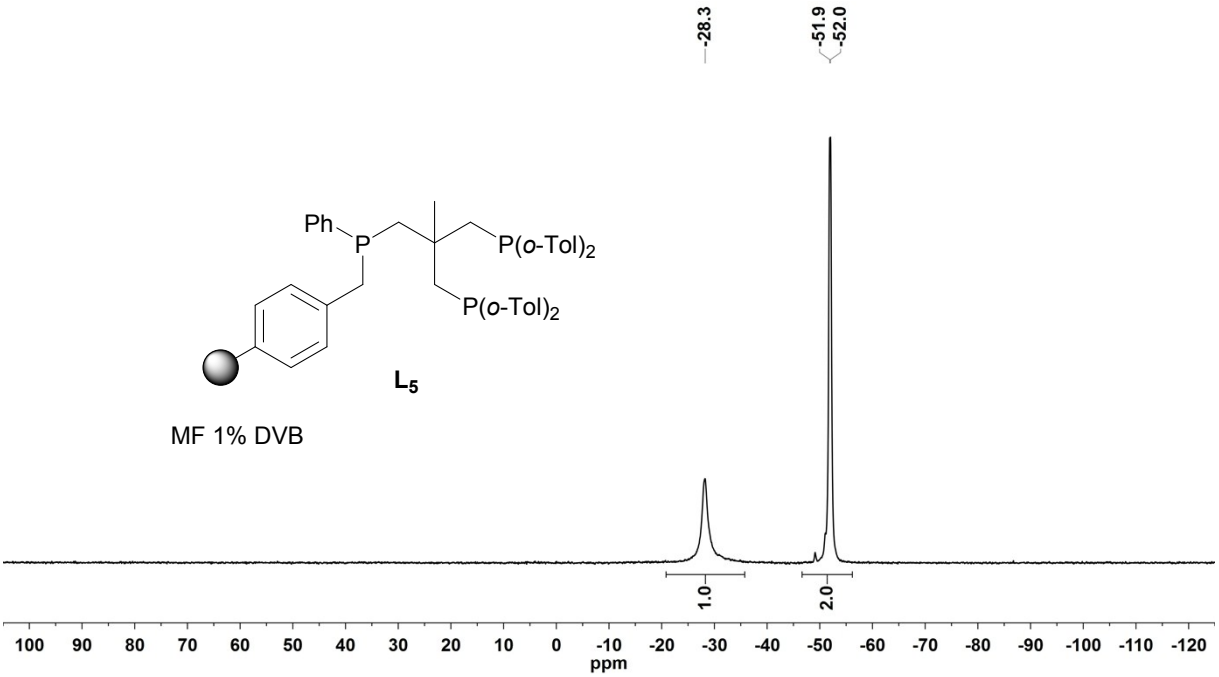


Figure S8 Gel-phase ^{31}P NMR spectrum of **L_5** (162 MHz, THF).

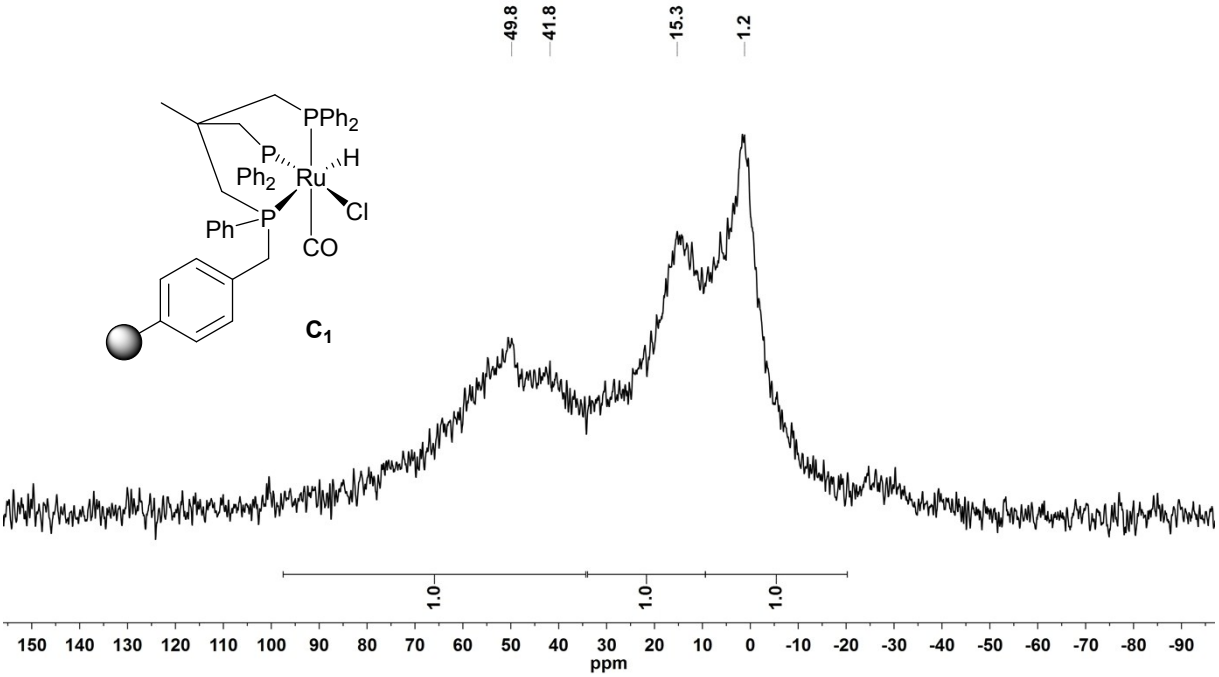


Figure S9 Gel-phase ^{31}P NMR spectrum of **C_1** (121 MHz, THF:C_6D_6 6:1).

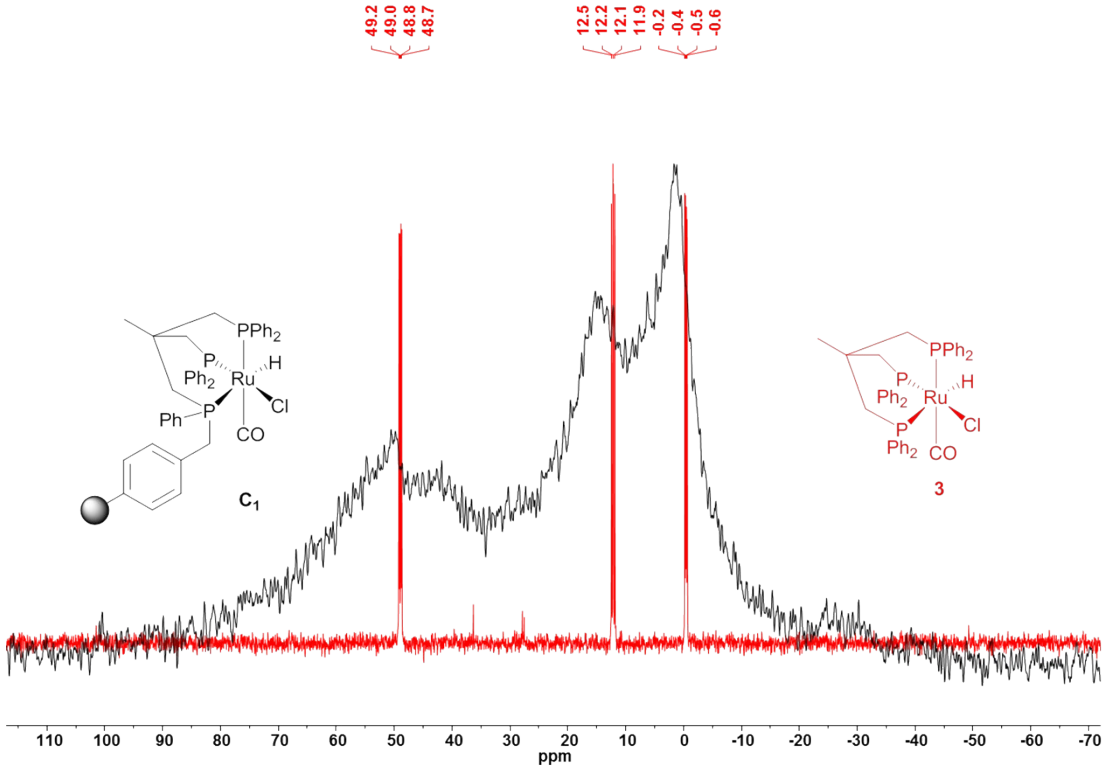


Figure S10 ^{31}P NMR spectra of supported Ru-Triphos complex $\mathbf{C_1}$ (black) and the solution-phase analogue **3** (red).

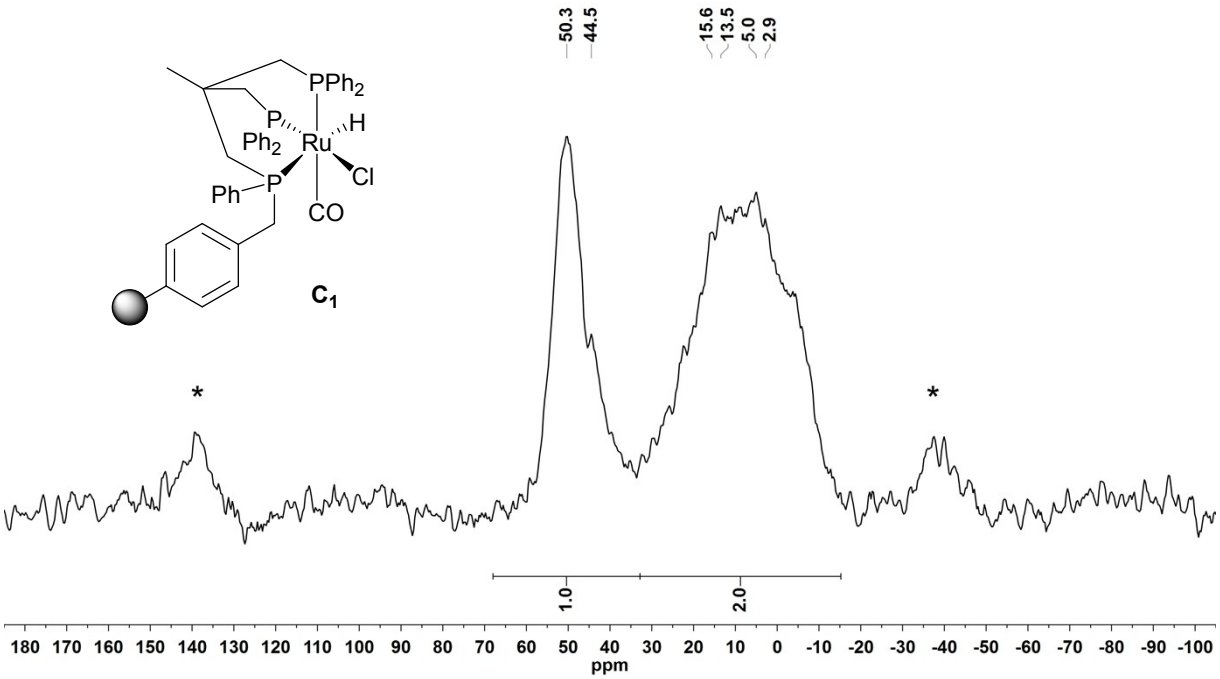


Figure S11 ^{31}P MAS NMR spectrum of $\mathbf{C_1}$ (spinning rate 14 kHz). Rotational sidebands are denoted by asterisks (*).

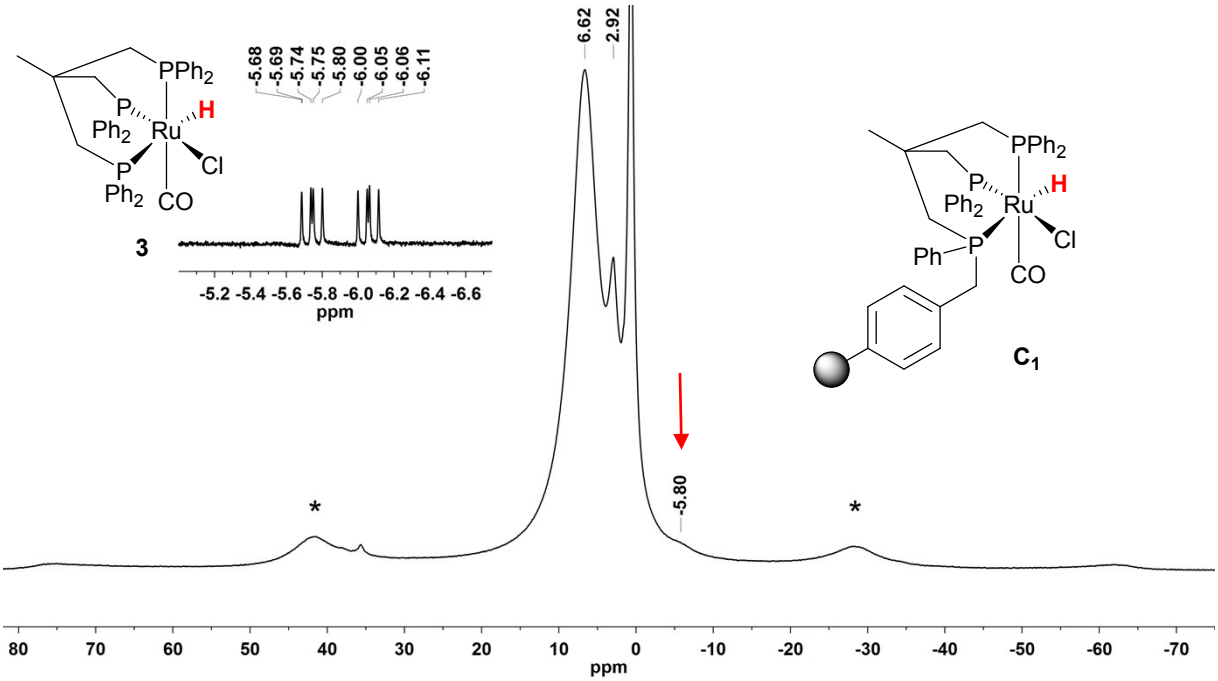


Figure S12 ^{1}H MAS NMR spectrum of $\mathbf{C_1}$ (spinning rate 14 kHz) and hydride region of solution phase ^{1}H NMR spectrum of **3** (top left). Rotational sidebands are denoted by asterisks (*).

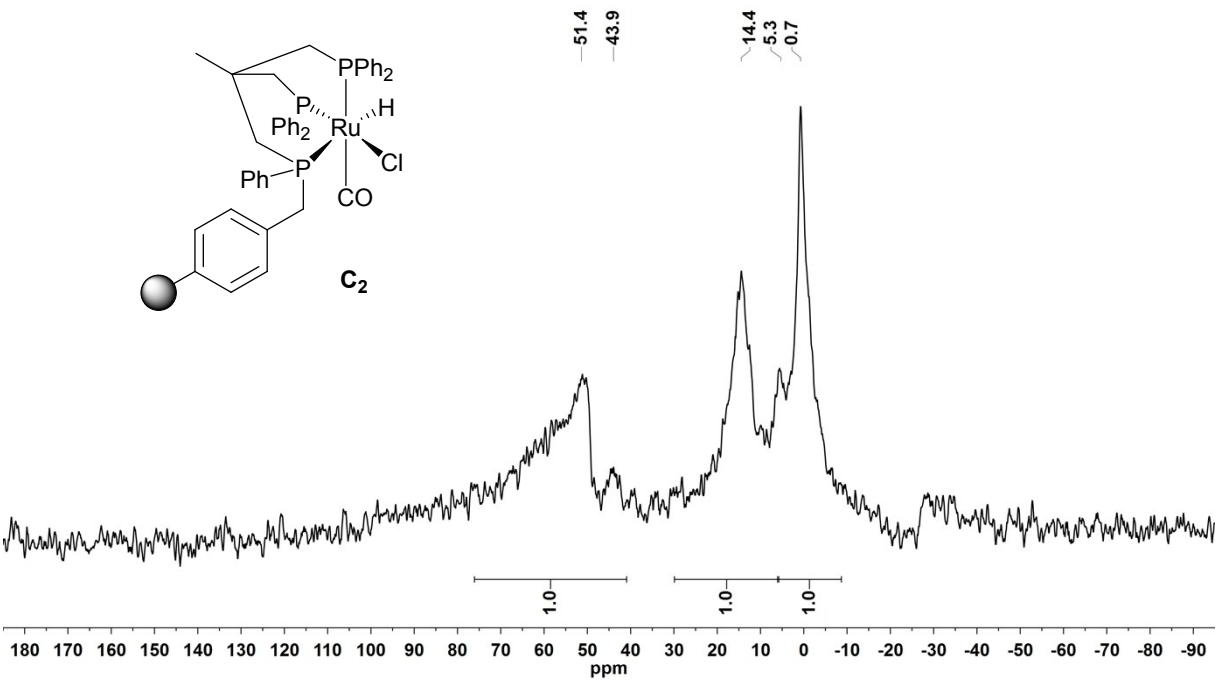


Figure S13 Gel-phase ^{31}P NMR spectrum of $\mathbf{C_2}$ (121 MHz, THF:C_6D_6 6:1).

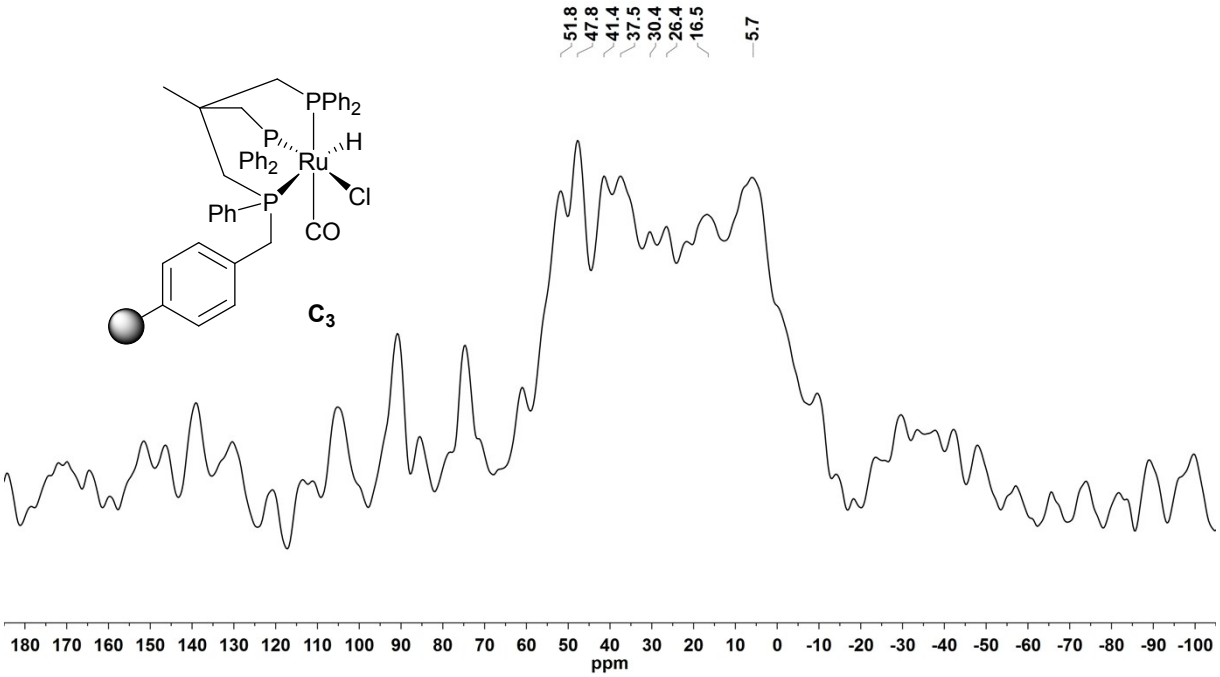


Figure S14 ^{31}P MAS NMR spectrum of $\mathbf{C_3}$ (spinning rate 14 kHz).

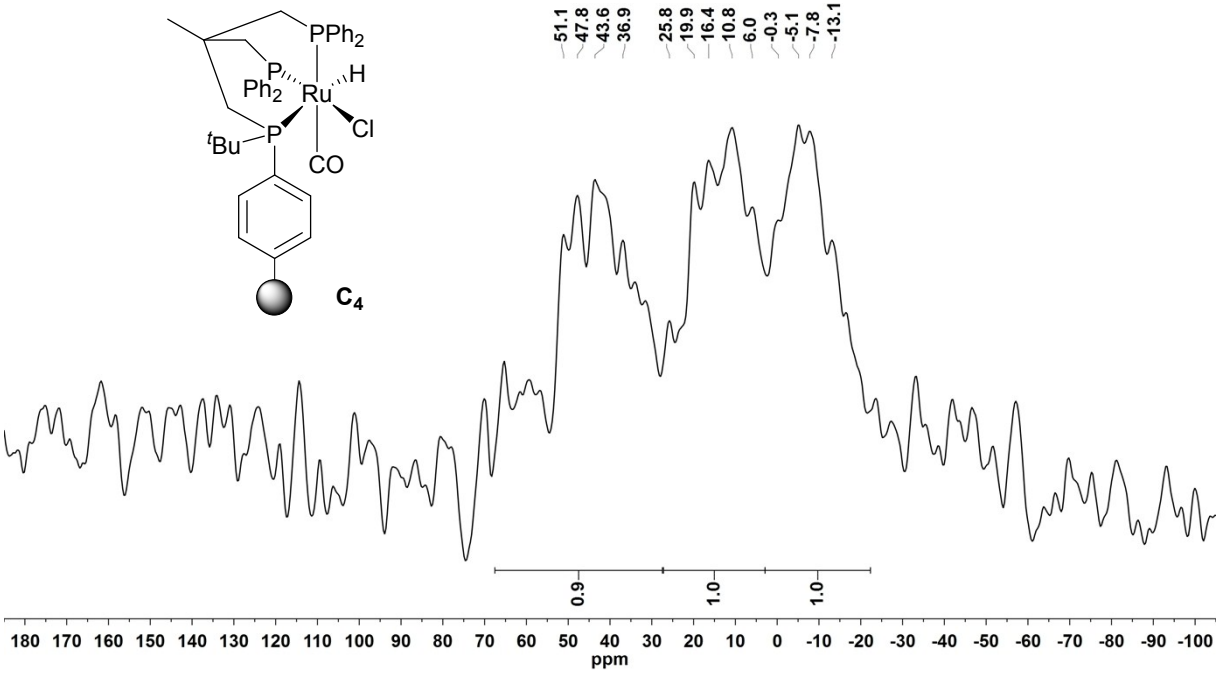


Figure S15 ^{31}P MAS NMR spectrum of $\mathbf{C_4}$ (spinning rate 14 kHz).

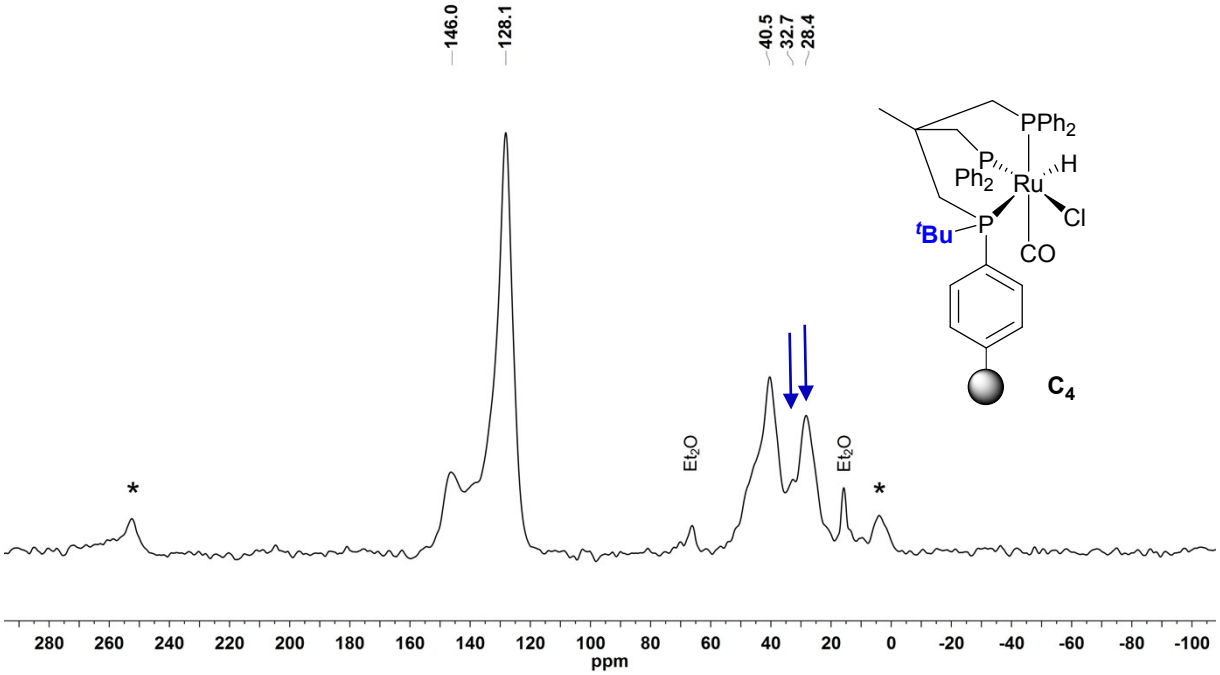


Figure S16 ^{13}C MAS NMR spectrum of $\mathbf{C_4}$ (spinning rate 12.5 kHz). Rotational sidebands are denoted by asterisks (*).

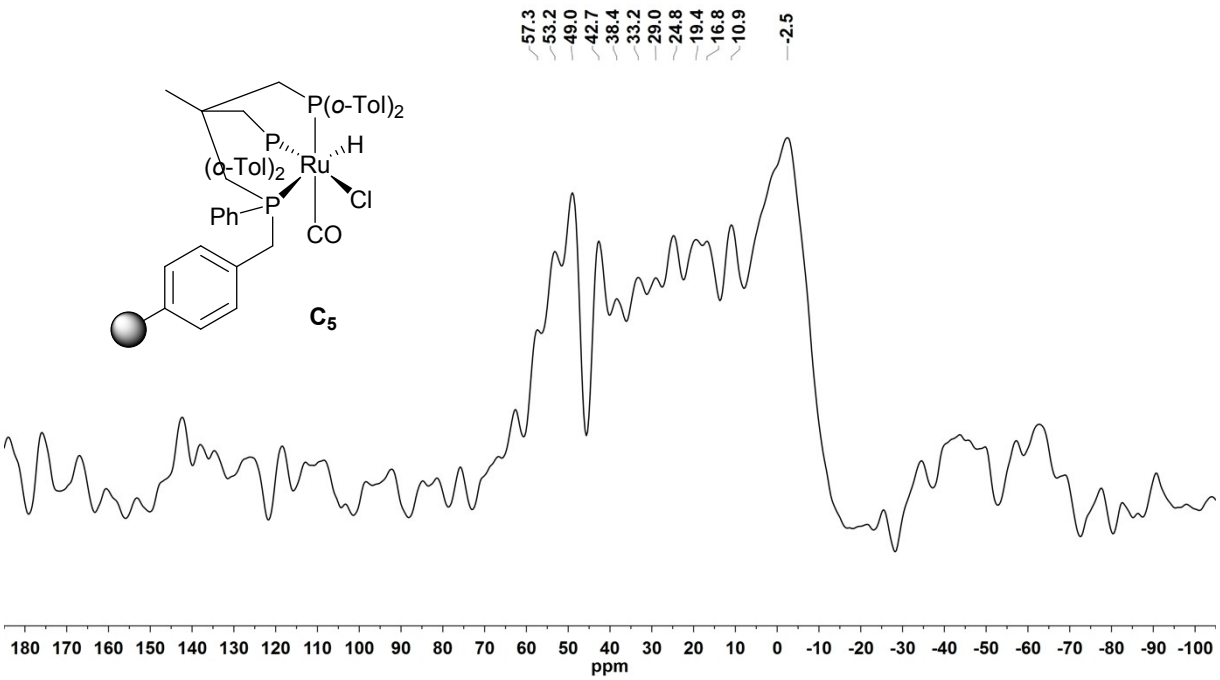


Figure S17 ^{31}P MAS NMR spectrum of $\mathbf{C_5}$ (spinning rate 14 kHz).

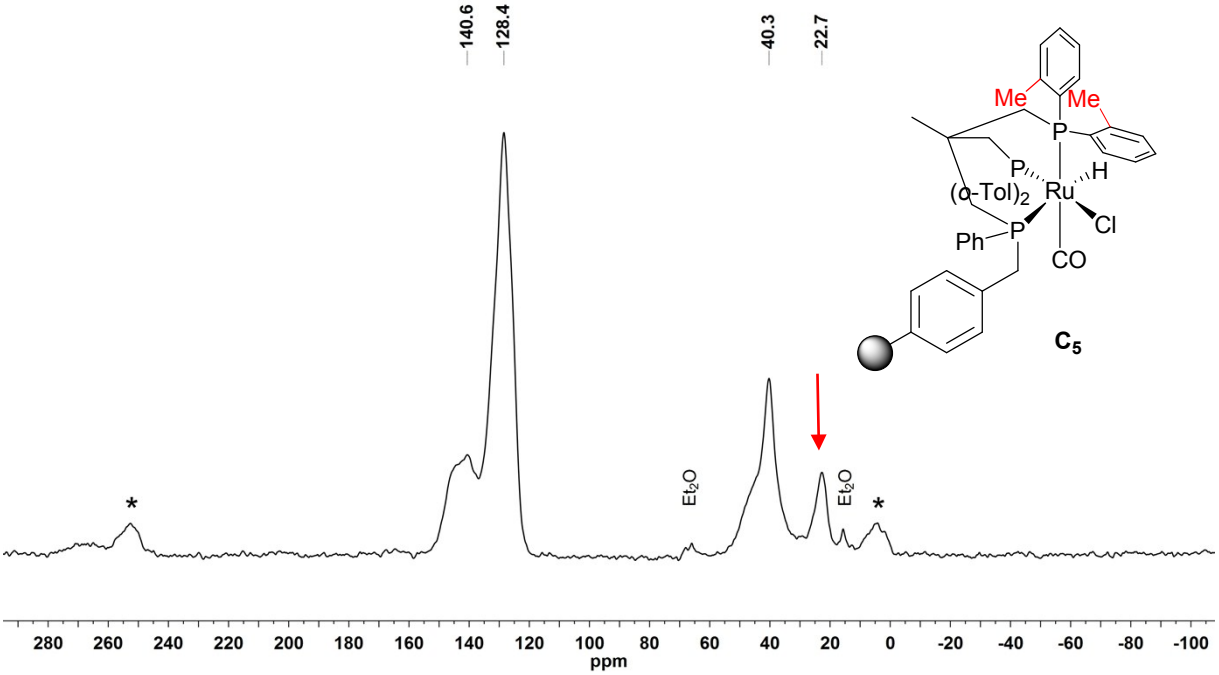


Figure S18 ^{13}C MAS NMR spectrum of $\mathbf{C_5}$ (spinning rate 12.5 kHz). Rotational sidebands are denoted by asterisks (*).

Representative FT-IR Spectra of Resin-Bound Triphos and Ru-Complex

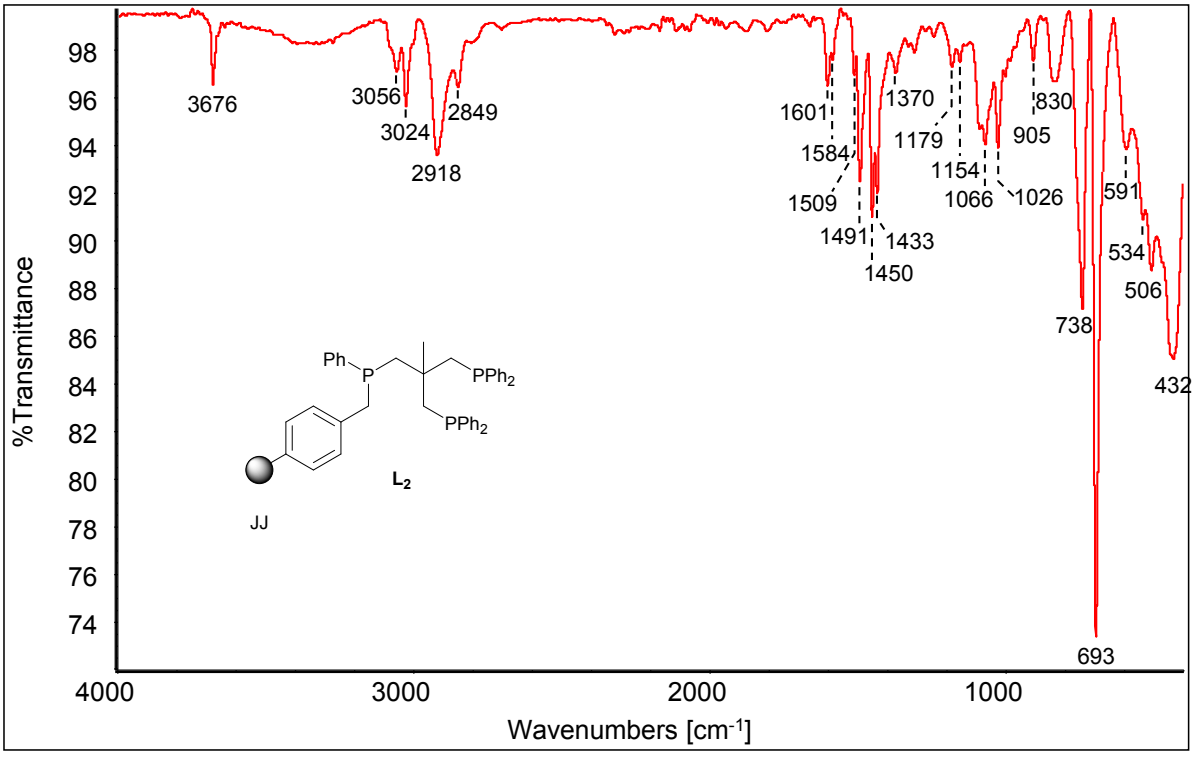


Figure S19 ATR-FTIR spectrum of JJ-bound Triphos ligand $\mathbf{L_2}$.

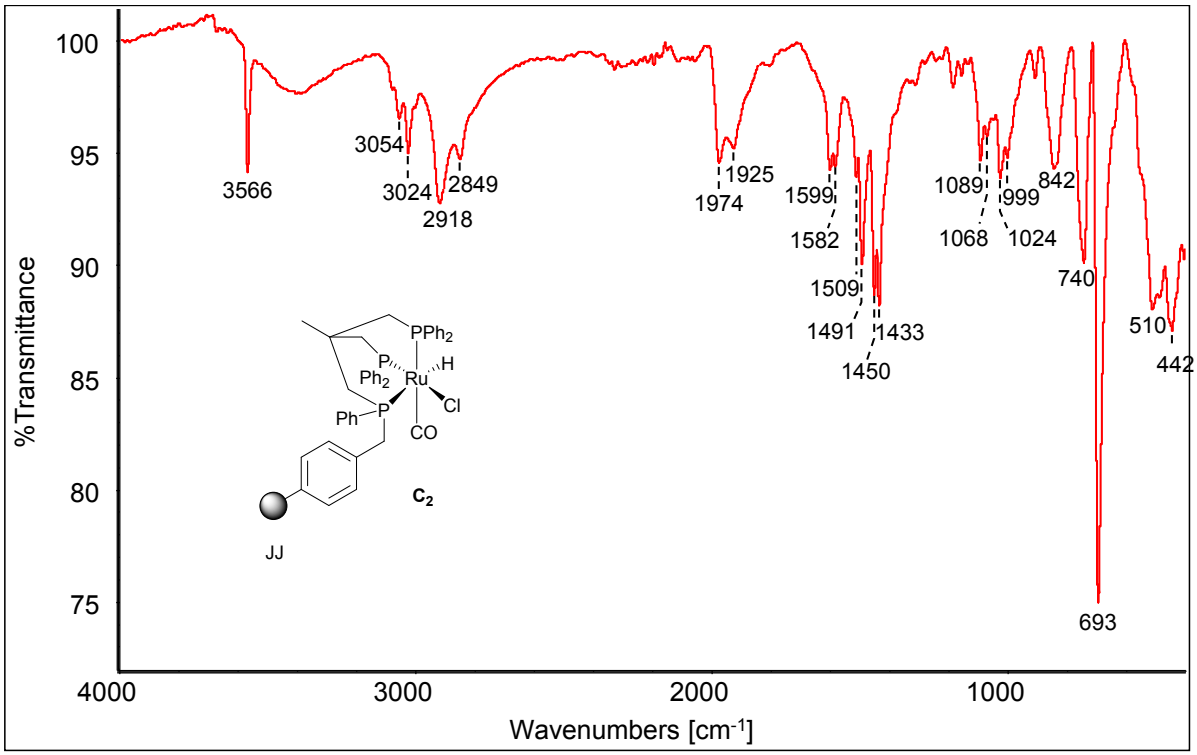


Figure S20 ATR-FTIR spectrum of JJ-bound Ru-Triphos complex **C_2**.

Representative Raman Spectra of L_2, C_2 and 3

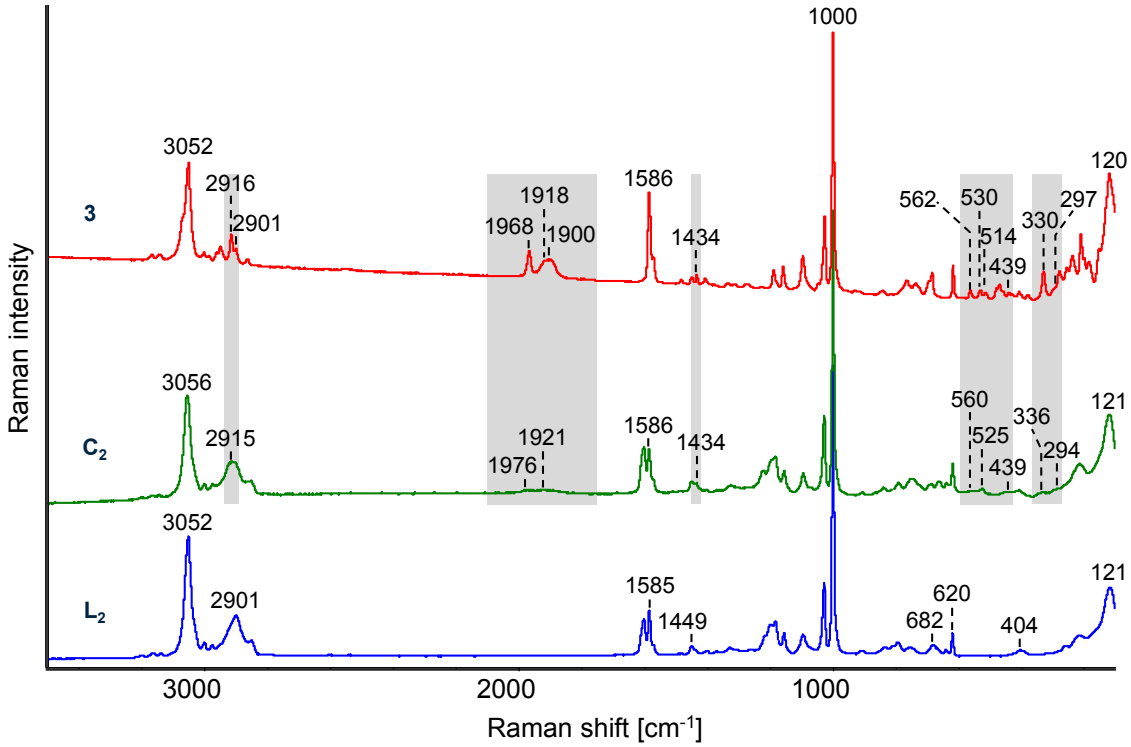


Figure S21 Stacked plot of Raman spectra of supported Triphos ligand **L_2** (blue spectrum), supported Ru-Triphos complex **C_2** (green spectrum) and homogeneous Ru-Triphos complex **3** (red spectrum) in the wavenumber range ν = 3500-100 cm^{-1}. Bands exclusively occurring in the spectra of **C_2** and **3** are highlighted in grey boxes.

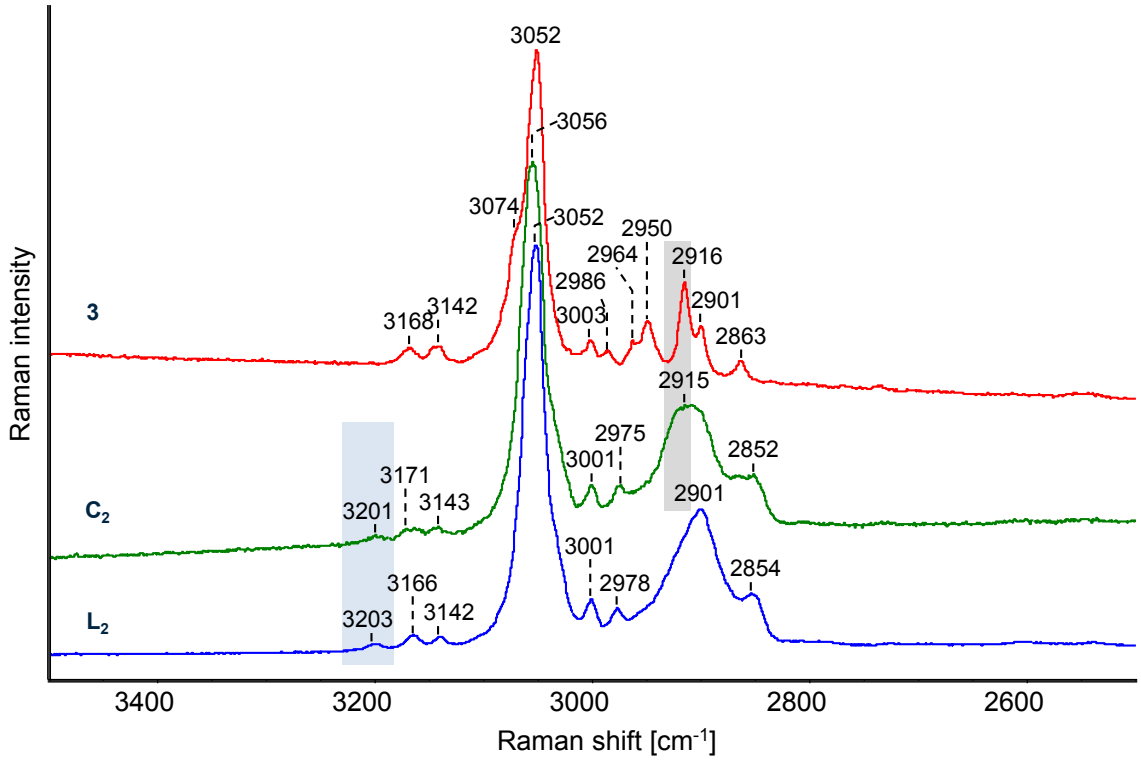


Figure S22 Stacked plot of Raman spectra of supported Triphos ligand $\mathbf{L_2}$ (blue spectrum), supported Ru-Triphos complex $\mathbf{C_2}$ (green spectrum) and homogeneous Ru-Triphos complex **3** (red spectrum) in the wavenumber range ν = 3500-2400 cm^{-1}. Bands exclusively occurring in the spectra of $\mathbf{C_2}$ and **3** are highlighted in grey boxes. Bands belonging to the polymeric support are highlighted in blue boxes.

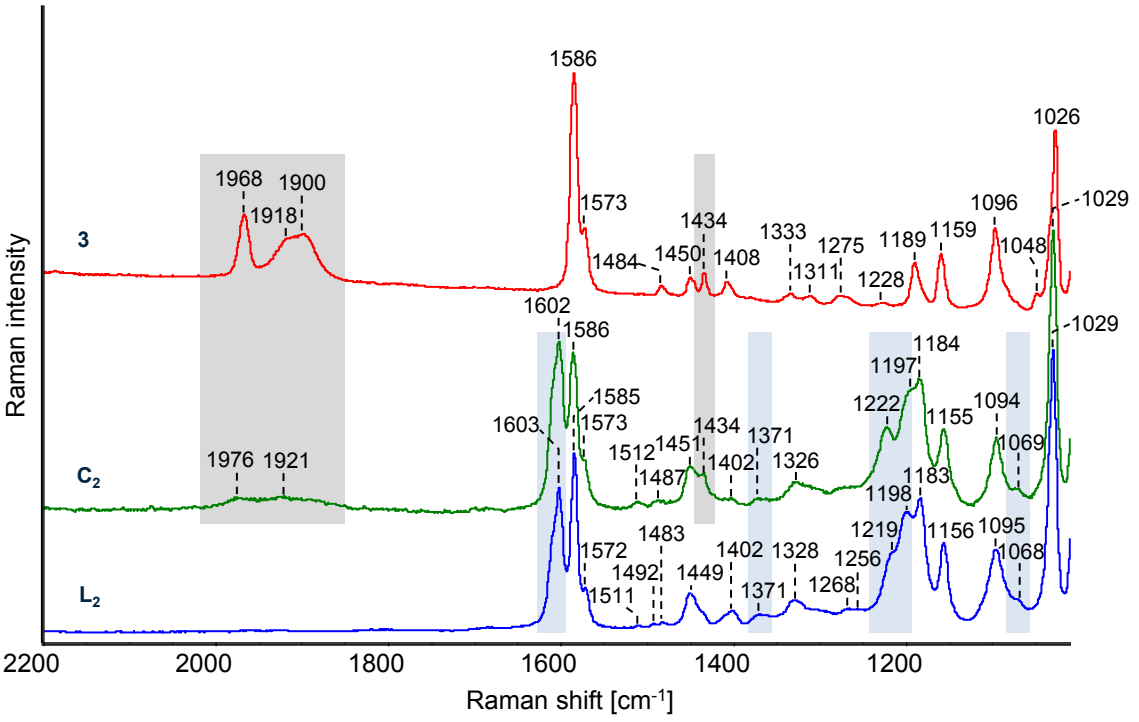


Figure S23 Stacked plot of Raman spectra of supported Triphos ligand $\mathbf{L_2}$ (blue spectrum), supported Ru-Triphos complex $\mathbf{C_2}$ (green spectrum) and homogeneous Ru-Triphos complex **3** (red spectrum) in the wavenumber range ν = 2200-1000 cm^{-1}. Bands exclusively occurring in the spectra of $\mathbf{C_2}$ and **3** are highlighted in grey boxes. Bands belonging to the polymeric support are highlighted in blue boxes.

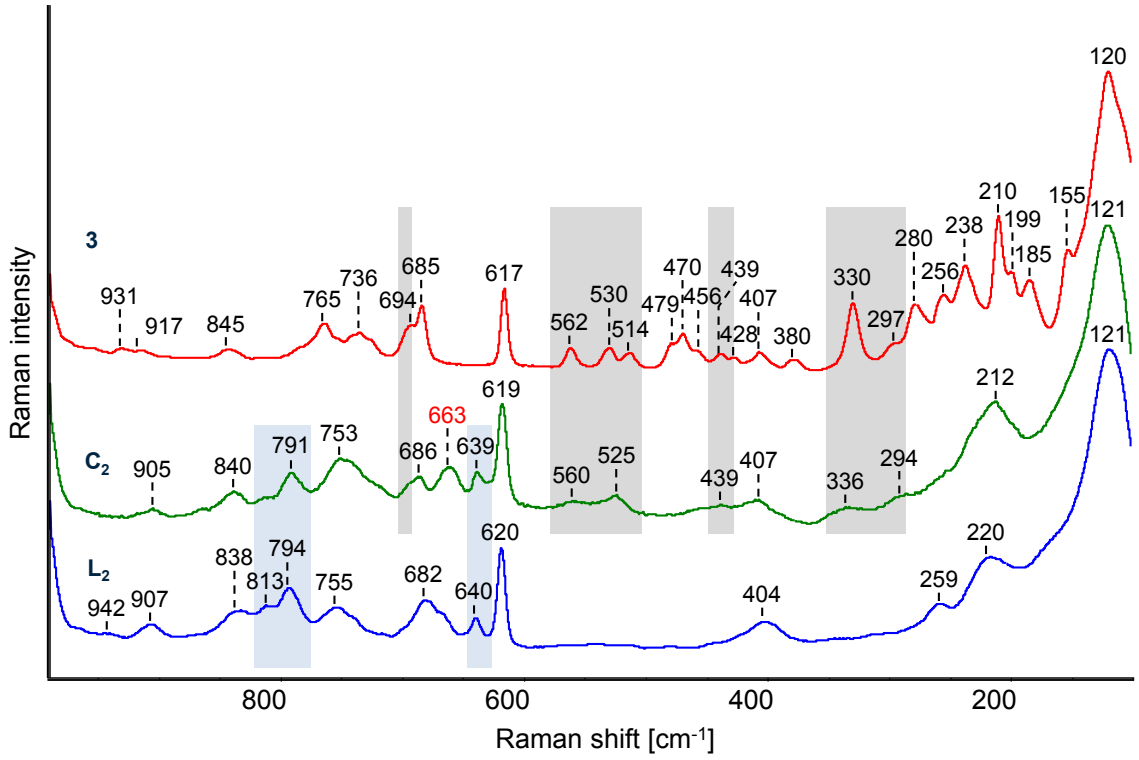


Figure S24 Stacked plot of Raman spectra of supported Triphos ligand $\mathbf{L_2}$ (blue spectrum), supported Ru-Triphos complex $\mathbf{C_2}$ (green spectrum) and homogeneous Ru-Triphos complex **3** (red spectrum) in the wavenumber range ν = 1000-100 cm^{-1}. Bands exclusively occurring in the spectra of $\mathbf{C_2}$ and **3** are highlighted in grey boxes. Bands belonging to the polymeric support are highlighted in blue boxes.

Representative GC Traces of Nitrile Hydrogenation Experiments

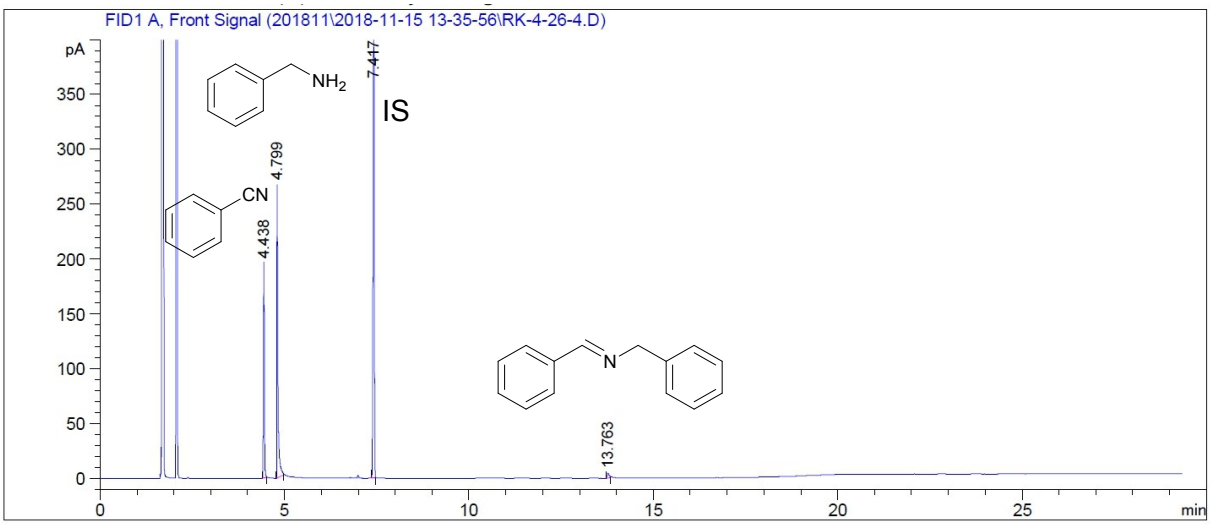


Figure S25 GC spectrum of hydrogenation of benzonitrile ($\mathbf{S_1}$).

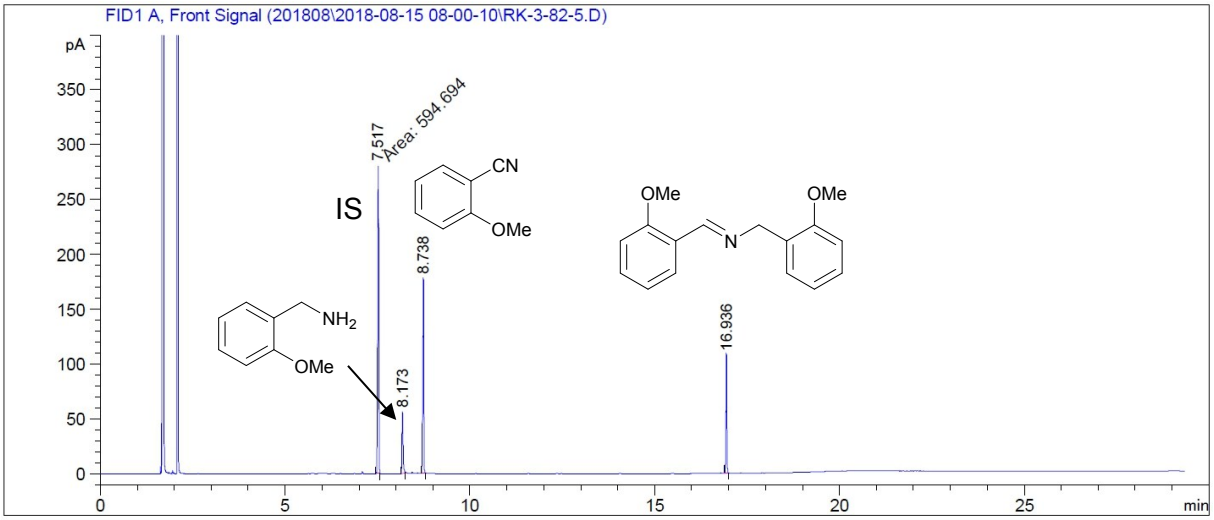


Figure S26 GC spectrum of hydrogenation of 2-methoxybenzonitrile (**S_7**).

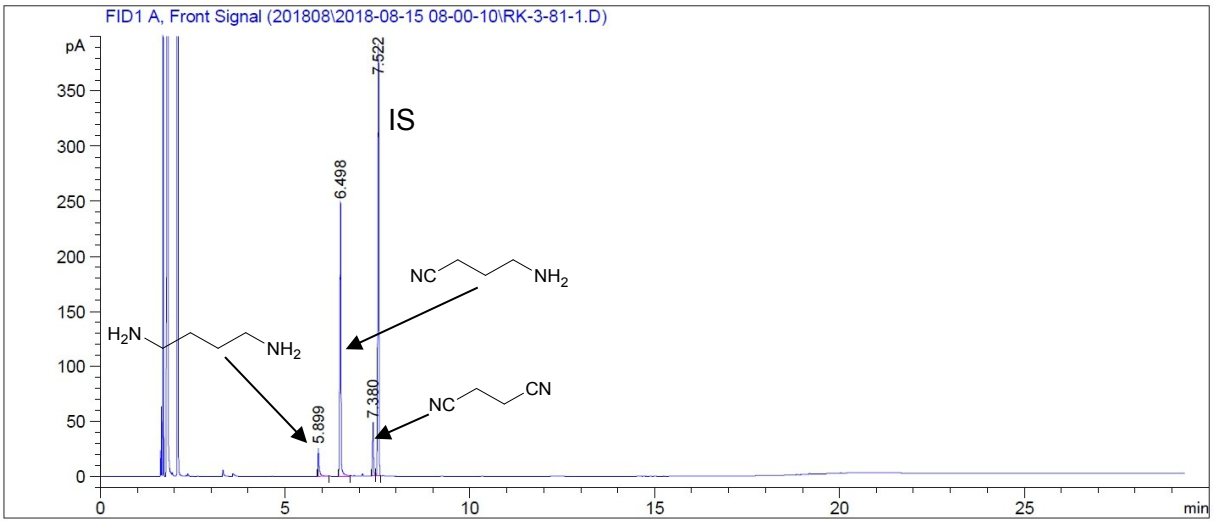


Figure S27 GC spectrum of hydrogenation of adiponitrile (**S_9**).

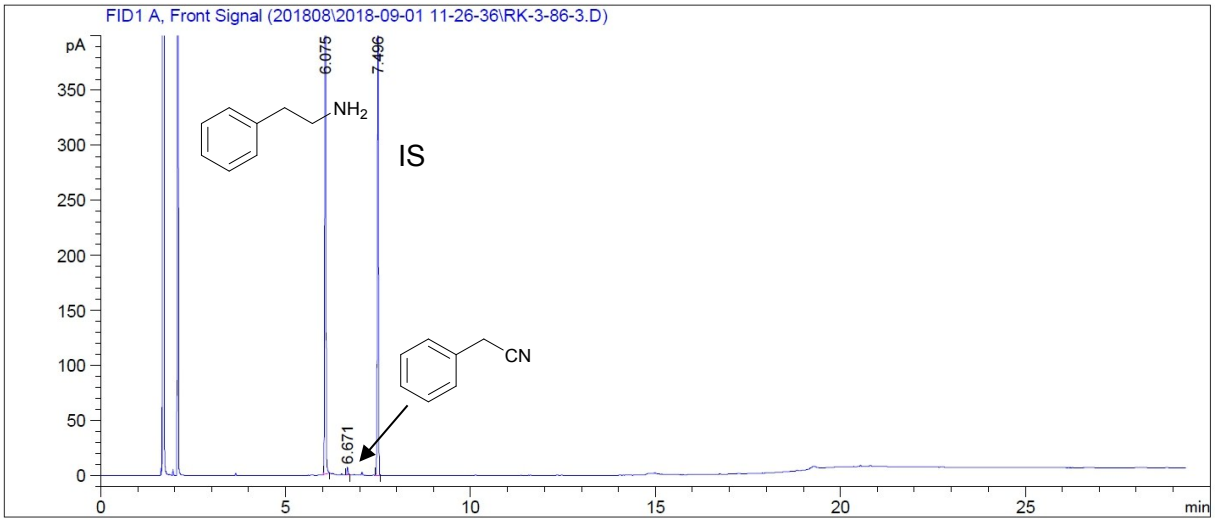


Figure S28 GC spectrum of hydrogenation of benzyl cyanide (**S_{12}**).

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1. F. J. L. Heutz, M. C. Samuels and P. C. J. Kamer, *Catal. Sci. Technol.*, 2015, **5**, 3296-3301.
2. M. C. Samuels, F. J. L. Heutz, A. Grabulosa and P. C. J. Kamer, *Top. Catal.*, 2016, **59**, 1793-1799.
3. K.-M. Sung, S. Huh and M.-J. Jun, *Polyhedron*, 1998, **18**, 469-479.
4. P. Loos, H. Alex, J. Hassfeld, K. Lovis, J. Platzek, N. Steinfeldt and S. Hübner, *Org. Process Res. Dev.*, 2015, **20**, 452-464.