Supporting Information for

Beyond Classical Reactivity Patterns: Hydroformylation of Vinyl and Allyl Arenes to Valuable β- and γ-Aldehyde Intermediates using Supramolecular Catalysis

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Materials and Methods

General Procedures.

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. THF, pentane, hexane and diethyl ether were distilled from sodium benzophenone ketyl; CH_2Cl_2, isopropanol and methanol were distilled from CaH_2, toluene was distilled from sodium, and triethylamine was distilled from KOH pellets under nitrogen. NMR spectra were measured on a Bruker AMX 400 (400.1MHz, 100.6MHz and 162.0 for ^{1}H, ^{13}C and ^{31}P respectively). Infrared spectra were recorded on a Thermo Nicolet NEXUS 670 FT-IR. Elemental analyses were carried out on a Carlo Erba NCSO-analyzer. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. ESI-MS measurements were recorded on a Shimadzu LCMS-2010A liquid chromatography mass spectrometer by direct injection of the sample to the ESI probe. CD_2Cl_2, CD_3CN and DIPEA were dried over molecular sieves (3Å) and degassed by at least 3 freeze-pump-thaw cycles. If not stated otherwise, syngas refers to a 1 : 1 mixture of H_2 and CO, and the pressure refers to a sum pressure of both.

Materials.

All reagents were purchased from commercial suppliers and used without further purification, with the exception of a ligand building block – 1,1-bis-(-3-methyl-7-nitro-1*H*-indol-2-yl)-propane,[1] 1,1-bis-(-7-benzoylamino-3-methyl-1H-indol-2-yl)-propane (anion receptor **R1**),[1] 4-phenoxy-(R)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin (ligand **L8**),[2] which were synthesized according to the published procedures. The detailed synthesis procedures for ligands **L1**,[3] **L2**[4] and **L5**,[5] and substrates **5b-p**, **13**, **14**[5] were reported previously.

[1] P. Dydio, D.Lichosyt, T. Zieliński, J. Jurczak, *Chem. Eur. J.* **2012**, *18*, 13686–13701.
[2] V. E. Albrow, A. J. Blake, R. Fryatt, C. Wilson,S. Woodward, *Eur. J. Org. Chem.* **2006**, 2549–2557.
[3] P. Dydio, W. I. Dzik, M. Lutz, B. de Bruin, J. H. N. Reek, *Angew. Chem. Int. Ed.* **2011**, *50*, 396-400.
[4] P. Dydio, R. J. Detz, J. N. H. Reek, *J. Am. Chem. Soc.* **2013**, *135*, 10817–10828.
[5] P. Dydio, J. H. N. Reek, *Angew. Chem. Int. Ed.* **2013**, *52*, 3878-3882.

Synthesis of ligands and substrates

Synthesis of ligand L3

4-(Diphenylphosphino)phenylacetic acid: 4-Iodophenylacetic acid (2.91 g, 11.1 mmol), diphenylphosphine (1.93 ml, 11.1 mmol), triethylamine (3.13 ml) and palladium (II) acetate (4 mg), were dissolved in acetonitrile (50 ml) under argon, brought to reflux and continued overnight. The next day, the volatiles were evaporated under reduced pressure, and to the residue water (30 ml) and potassium hydroxide (1.49 g) were added. Then, the water phase was washed with diethyl ether (3·50 ml), acidified with 2M HCl to pH ~ 3, and extracted with ethyl acetate (150 ml and 2·50 ml). The combined organic layers were washed with water (25 ml), and then dried over $MgSO_4$, and the solvent was removed under vacuum. The solid residue was crystalized from hot ethyl acetate (20 ml), yielding 3.35 g (94%) of the product (which contains ~11% phosphine oxide).

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 12.40 (bs, 1H), 7.67-7.34 (m, 27), 7.32-7.16 (m, *7*H), 3.59 (s, 2H);

^{13}C NMR (100MHz, DMSO-d_6): δ = 172.3 (s), 136.8 (d, J_1 = 11.8 Hz), 136.0 (s), 134.6 (d, J_1 = 11.1 Hz), 133.3 (d, J_1 = 19.8 Hz), 133.1 (d, J_1 = 19.0 Hz), 129.8 (d, J_1 = 7.3 Hz), 128.9 (s), 128.7 (d, J_1 = 6.8 Hz), 40.4 (s);

^{31}P{^{1}H} NMR (162MHz, DMSO-d_6): δ = -7.27 (+ the phosphine oxide at 25.4);

HR MS (ESI): calcd. for $C_{20}H_{18}O_2P$ $[M+H]^+$: 321.1039, found: 321.1033.

Bis-(4-(diphenylphosphino)phenylacetamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane)) – ligand **L3**: 1,1-Bis-(-3-methyl-7-nitro-1*H*-indol-2-yl)propane (588 mg, 1.5 mmol) was suspended in methanol (25 ml) and 10% palladium on charcoal was added (0.12 g). The reaction mixture was flushed with hydrogen, and then vigorously stirred under a hydrogen atmosphere (balloon). The progress of the reaction was monitored by TLC, and after completion (~hour), the catalyst was filtered off over Celite®. The solvent was evaporated, and the crude diamine was immediately used in the subsequent reaction without further purification.

To the solution of crude diamine (1.5 mmol), 4-(diphenylphosphino)phenylacetic acid (1.2 g, 3.75 mmol), 4-dimethylaminopyridine (120 mg, 1 mmol) and 4-pyrrolidinopyridine (120 mg, 0.8 mmol) in dichloromethane (30 ml), N,N'-diisopropylcarbodiimide (1.88 ml, 12.1 mmol) was slowly added while stirring, and the mixture was allowed to continue stirring overnight. The solvent was evaporated and the solid residue was purified by column chromatography on silica gel (100 g), with a hexane : chloroform (2:1 → 1:2) mixture as an eluent. Fractions of the product were combined, and the solvent evaporated off, and pure product was obtained by recrystalliazation. The solid was dissolved in a minimum amount of dichloromethane and precipitated by the addition of hexane, followed by slow concentration under

vacuum (allowing to remove most of dichloromethane), and the powder was isolated by the filtration, yielding 0.95 g (66%) of **L3**·H_2O.

^{1}H NMR (400MHz, CD_2Cl_2): δ = 9.29 (s, 2H, NH-indole), 7.73 (s, 2H, NH-amide), 7.40-7.20 (m, 30H), 6.93 (dd, $J_1 = J_2$ = 7.6Hz, 2H), 6.79 (d, J_1 = 7.4Hz, 2H), 4.43 (t, J_1 = 8.0Hz, 1H, $CHCH_2CH_3$), 3.65 (s, 4H, CH_2CON), 2.26 (s, 6H, $ArCH_3$), 2.12 (m, 2H, $CHCH_2CH_3$), 0.95 (t, J = 7.2Hz, 3H, $CHCH_2CH_3$);

^{13}C{^{1}H} NMR (100MHz, CD_2Cl_2): δ = 169.7 (s), 137.5 (s(?)), 137.0 (s), 136.1 (s), 135.8 (s), 134.5 (d, J_1 = 19.3Hz), 134.1 (dd, J_1 = 19.6Hz, J_2 = 1.9Hz), 132.0 (s), 129.9 (d, J_1 = 7.0Hz), 129.2 (s), 129.0 (d, J_1 = 7.1Hz), 128.0 (s), 122.1 (s), 119.2 (s), 116.2 (s), 113.8 (s), 108.3 (s), 44.1 (s), 36.9 (s), 28.0 (s), 12.5 (s), 8.8 (s);

^{31}P{^{1}H} NMR (162MHz, CD_2Cl_2): δ = -6.05 (s).

Synthesis of ligand L4

3-(Diphenylphosphino)benzoic acid: 3-Iodobenzoic acid (4.56 g, 18.4 mmol), diphenylphosphine (3.33 ml, 19 mmol), triethylamine (5.23 ml) and palladium (II) acetate (9 mg), were dissolved in acetonitrile (60 ml) under argon, brought to reflux and continued overnight. The next day, the volatiles were evaporated under reduced pressure, and to the residue water (30 ml) and potassium hydroxide (2.4 g) were added. Then, the water phase was washed with diethyl ether (3·80ml), acidified with 2M HCl to pH ~ 3, and extracted with diethyl ether (3·70 ml). The combined organic layers were washed with water (60 ml), and then dried over $MgSO_4$, and the solvent was removed under vacuum. The solid residue was crystalized from a mixture of hot methanol (35 ml) and water (25 ml), yielding 4.8 g (88%) of the product, with the analytical data in agreement with the literature values.[6]

Bis-(3-(diphenylphosphino)benzamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane)) – ligand **L4**: 1,1-Bis-(-3-methyl-7-nitro-1*H*-indol-2-yl)propane (1.96 g, 5 mmol) was suspended in methanol (8 ml) and 10% palladium on charcoal was added (0.5 g). The reaction mixture was flushed with hydrogen, and then vigorously stirred under a hydrogen atmosphere (balloon). The progress of the reaction was monitored by TLC, and after completion (~hour), the catalyst was filtered off over Celite®. The solvent was evaporated, and the crude diamine was immediately used in the subsequent reaction without further purification.

To the solution of crude diamine (5 mmol), 3-(diphenylphosphino)benzoic acid (3.7 g, 12 mmol), 4-dimethylaminopyridine (300 mg, 2.5 mmol) and 4-pyrrolidinopyridine (300 mg, 2 mmol) in dichloromethane (100 ml), N,N'-diisopropylcarbodiimide (4.1 ml, 26 mmol) was slowly added while stirring, and the mixture was allowed to continue stirring overnight. The solvent was evaporated and the

[6] S. T. Kemme, Y. Schmidt, C. U. Grünanger, A. C. Laungani, C. Herber, B. Breit, *Synthesis* **2010**, *11*, 1924-1928.

solid residue was purified by column chromatography on silica gel (200 g), with a hexane : chloroform (1:1 → 0:1) mixture as an eluent. Fractions of the product were combined, and the solvent evaporated off, and pure product was obtained by recrystalliazation. The solid was dissolved in a mixture of dichloromethane (20 ml) and methanol (10 ml), precipitated by the addition of hexane, followed by slow concentration under vacuum, and the powder was isolated by the filtration, yielding 3.11 g (67%) of **L4**·$(H_2O)_{0.7}$·$(CH_3OH)_{0.3}$.

^{1}H NMR (400MHz, CD_2Cl_2): δ = 9.52 (s, 2H, NH-indole), 8.29 (s, 2H, NH-amide), 7.82 (d, J_1 = 8.0Hz, 2H), 7.70 (d, J_1 = 7.6Hz, 2H), 7.39-7.21 (m, 26H), 7.10 (dd, J_1 = J_2 = 7.7Hz, 2H), 6.94 (d, J_1 = 7.4Hz, 2H), 4.45 (t, J_1 = 8.0Hz, 1H, $CHCH_2CH_3$), 2.31 (s, 6H, $ArCH_3$), 2.14 (m, 2H, $CHCH_2CH_3$), 0.96 (t, J = 7.3Hz, 3H, $CHCH_2CH_3$);

^{13}C{^{1}H} NMR (100MHz, CD_2Cl_2): δ = 165.9 (s), 139.1 (d, J_1 = 14.0Hz), 137.0 (s), 136.9 (d, J_1 = 14.1Hz), 136.3 (s), 135.1 (d, J_1 = 7.7Hz), 134.2 (dd, J_1 = 20.3Hz, J_2 = 3.7Hz), 132.8 (d, J_1 = 25.9Hz), 132.3 (s), 129.5 (s), 129.2 (d, J_1 = 5.1Hz), 129.1 (d, J_1 = 7.1Hz), 127.2 (s), 122.2 (s), 119.2 (s), 116.3 (s), 114.1 (s), 108.2 (s), 36.9 (s), 27.8 (s), 12.5 (s), 8.9 (s);

^{31}P{^{1}H} NMR (162MHz, CD_2Cl_2): δ = -5.47 (s);

HR MS (ESI): calcd. for $C_{59}H_{51}N_4O_2P_2$ $[M+H]^+$: 909.3482, found: 909.3456;

Elemental analysis (%) calcd. for $C_{59}H_{50}N_4O_2P_2$·H_2O: C 76.44, H 5.65, N 6.64, P 6.68, found: C 76.27, H 6.43, N 5.22, P 6.41.

Synthesis of ligand L6

Phosphorochloridate of (4*S*,5*S*)-4,5-bis(diphenylhydroxymethyl)-2,2-dimethyldioxolane, (*S*,*S*)-taddol-PCl: All glassware was oven-dried or flame-dried under vacuum. All solvents and reagents were dry and degassed. (4*S*,5*S*)-4,5-bis(diphenylhydroxymethyl)-2,2-dimethyldioxolane – (*S*,*S*)-taddol was azeotropically dried prior to use, by co-evaporation with dry toluene. To a solution of TEA (0.56 ml, 4 mmol) in THF (10 mL) were added drop wise subsequently PCl_3 (0.20 ml, 2.3 mmol) and a solution of (*S*,*S*)-taddol (0.933 g, 2 mmol) in THF (10 ml) at -78°C. The reaction mixture was stirred for 30 minutes, then allowed to warm up to room temperature, and further stirred for 30 minutes at rt. Then, all volatiles were removed under vacuum, followed by addition of toluene (10 ml) and its evaporation. Next, the solid residue, being a mixture of the desired (*S*,*S*)-taddol-PCl and TEA*HCl salt, was dissolved/suspended in THF (20 ml) and used in the next step without further purification.

^{31}P{^{1}H} NMR (162MHz, THF-h_8): δ = 148.5

Ligand **L6** (bis-(4-((4*S*,5*S*)-2,2-dimethyl-α,α,α',α'-tetraphenyldioxolane-4,5-dimethanyl phosphito)-benzoamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane): All glassware was oven-dried or flame-dried under vacuum. All solvents and reagents were dry and degassed. Diol **4a**[5] was azeotropically

dried prior to use, by co-evaporation with dry toluene three times. To the solution of diol **4a** (572 mg, 1 mmol) and triethylamine (1.39 ml, 25 mmol) in THF (10 ml), the freshly-prepared solution of phosphorylchloride (2 mmol) in THF (20 ml) was added drop wise at -78°C. After 30 minutes the cooling bath was removed, and the mixture was allowed to continue stirring overnight. The reaction mixture was evaporated, to the solid residue THF (20 ml) were added, and the suspension was filtered through a plug of SiO_2 gel, which was subsequently washed with THF (20 ml). The combined organic fractions were concentrated, hexane (20 ml) was added, followed by evaporation of all volatiles to dryness, yielding 1.57 g (91%) of **L6**·THF·C_6H_{14}. NOTE: Ligand **L6** is sensitive, thus should be stored in inert conditions at low temperatures preferably.

^{1}H NMR (400 Mhz, CD_2Cl_2): δ = 9.48 (s, 2H), 8.08 (s, 1H), 8.06 (s, 1H), 7.59 – 7.13 (m, 50H), 7.04 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 6.98 – 6.09 (m, 2H), 6.42 (d, J_1 = 8.6 Hz, 4H), 5.68 (d, J_1 = 8.2 Hz, 2H), 5.06 (dd, J_1 = 8.3 Hz, J_2 = 1.6 Hz, 2H), 4.47 (t, J_1 = 7.8 Hz, 1H, C*H*CH_2CH_3), 2.30 (s, 6H, 2•ArC*H*$_3$), 2.20 (m, 2H, CHC*H*$_2CH_3$), 1.01 (t, J_1 = 7.3 Hz, 3H, $CHCH_2$C*H*$_3$), 0.95 (s, 6H), 0.57 (s, 6H);

^{13}C NMR (100MHz, CD_2Cl_2): δ = 165.2 (s), 155.6 (d, J_1 = 3.8 Hz), 155.5 (d, J_1 = 3.8 Hz), 146.4 (d, J_1 = 2.2 Hz), 146.2 (*p*dd, $J_1 \approx J_2$ = 2.5 Hz), 141.7 (s), 141.5 (d, J_1 < 2 Hz), 141.4 (d, J_1 = < 2 Hz), 136.2 (s), 132.3 (d, J_1 = 2.9 Hz), 129.5 (s), 129.4 (d, J_1 = 6.9 Hz), 129.0 (s), 128.8 (s), 128.5 (d, J_1 = 9.6 Hz), 128.2 (s), 128.0 (s), 127.9 (s), 127.79 (s), 127.76 (s), 127.69 (s), 127.5 (s), 127.4 (s), 125.8 (s), 122.4 (s), 119.6 (d, J_1 = 9.8 Hz), 119.3 (s), 116.1 (d, J_1 = 2.0 Hz), 113.9 (s), 113.6 (s), 108.2 (s), 87.4 (d, J_1 = 11.9 Hz), 85.8 (d, J_1 = 3.9 Hz), 85.7 (d, J_1 = 3.7 Hz), 82.8 (d, J_1 = 9.3 Hz), 80.7 (d, J_1 = 4.6 Hz), 37.2 (s), 30.5 (s), 27.5 (s), 27.1 (s), 26.2 (s), 12.5 (s), 8.9 (s);

^{31}P{^{1}H} NMR (162MHz, CD_2Cl_2): δ = 124.0.

Elemental analysis (%) calcd. for $C_{97}H_{86}N_4O_{12}P_2$·C_4H_8O: C 74.25, H 5.80, N 3.43, P 3.79, found: C 74.27, H 6.21, N 3.07, P 4.16.

Synthesis of ligand L7

Bis-(3-(benzyloxy)benzoamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane) (**3b**): 1,1-Bis-(-3-methyl-7-nitro-1H-indol-2-yl)propane[1] (1.96 g, 5 mmol) was suspended in methanol (80 ml) and 10% palladium on charcoal was added (0.4 g). The reaction mixture was flushed with hydrogen, and then vigorously stirred under a hydrogen atmosphere (balloon). The progress of the reaction was monitored by TLC, and after completion (~hour), the catalyst was filtered off over Celite®. The solvent was evaporated, and the crude diamine was immediately used in the subsequent reaction without further purification.

To the solution of crude diamine (5 mmol) and triethylamine (5.6 ml, 40 mmol) in dichloromethane (60 ml), the solution of 3-(benzyloxy)benzoyl chloride (3.1 g, 12.5 mmol) in dichloromethane (20 ml) was slowly added while stirring, and the mixture was allowed to continue stirring overnight. The reaction mixture was washed with the saturated water solution of NaHCO3 (2 • 50ml), water (50ml), then dried

with $MgSO_4$ and evaporated. The solid was dissolved/suspended in dichloromethane (100 ml) and hexane (100 ml), followed by the sonication (20 min), followed by concentration under vaccum (to ~80 ml), and the powder was isolated by the filtration of the solution, yielding 3.67 g (98%) of **3b**.

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 10.31 (bs, 2H), 10.09 (bs, 2H), 7.60 (s, 2H), 7.53 (d, J_1 = 7.5 Hz, 2H), 7.47 – 7.31 (m, 14H), 7.26 (d, J_1 = 7.9 Hz, 2H), 7.20 (dd, J_1 = 8.2 Hz, J_2 = 1.9 Hz, 2H), 6.97 (d, J_1 = J_2 = 7.8 Hz, 2H), 5.15 (s, 4H, PhCH_2), 4.50 (t, J = 8.0 Hz, 1H, CHCH$_2$CH$_3$), 2.23 (s, 6H, ArCH_3), 2.22 (m, 2H, CHCH_2CH$_3$), 0.91 (t, J = 7.3 Hz, 3H, CHCH$_2$CH_3);

^{13}C NMR (100MHz, DMSO-d_6): δ = 166.3, 158.3, 136.8, 136.5, 135.7, 130.4, 129.5, 128.5, 128.4, 127.9, 127.7, 122.7, 120.3, 118.3, 117.9, 115.0, 114.8, 114.1, 106.4, 36.1, 26.4, 12.2, 8.6.

HR MS (ESI): calcd. for $C_{49}H_{45}N_4O_4$ $[M+H]^+$: 753.3435, found: 753.3407;

Elemental analysis (%) calcd. for $(C_{49}H_{44}N_4O)_2 \cdot H_2O$: C 77.24, H 5.95, N 7.35, found: C 77.21, H 6.53, N 6.95.

Bis-(3-(hydroxy)benzoamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane) (**4b**): Diamide **3b** (3.39g, 4.5 mmol) was dissolved in a methanol: THF (1:3) mixture (80 ml) and 10% palladium on charcoal was added (1 g). The reaction mixture was flushed with hydrogen, and then vigorously stirred under a hydrogen atmosphere (balloon) at 40°C. The progress of the reaction was monitored by TLC, and after completion (~12 hours), the catalyst was filtered off over Celite®. The solvent was evaporated, and the pure product was obtained by recrystallization. The solid was dissolved/suspended in dichloromethane (~10ml) and precipitated by the addition of hexane (~200ml), followed by the sonication (15min), and the powder was isolated by the filtration of the solution, yielding 2.93 g (99%) of **4b**·DCM.

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 10.33 (bs, 2H), 9.98 (bs, 2H), 9.74 (bs, 2H), 7.42 (d, J_1 = 7.6 Hz, 2H), 7.38 (d, J_1 = 7.6 Hz, 2H), 7.34 (s, 2H), 7.29-7.23 (m, 4H), 7.00-6.93 (m, 4H), 4.49 (t, J_1 = 8.0 Hz, 1H, CHCH$_2$CH$_3$), 2.20 (m, 8H, ArCH_3 + CHCH_2CH$_3$), 0.91 (t, J_1 = 7.2 Hz, 3H, CHCH$_2$CH_3);

^{13}C NMR (100MHz, DMSO-d_6): δ = 165.8, 157.4, 136.6, 135.6, 130.4, 129.4, 128.1, 122.8, 118.5, 118.4, 118.3, 114.73, 114.66, 114.55, 106.4, 36.2, 26.4, 12.2, 8.6.

HR MS (ESI): calcd. for $C_{35}H_{33}N_4O_4$ $[M+H]^+$: 573.2496, found: 573.2482;

Elemental analysis (%) calcd. for $C_{35}H_{32}N_4O_4 \cdot CH_2Cl_2 \cdot$: C 65.75, H 5.21, N 8.52, found: C 66.20, H 5.43, N 8.30.

(*S*)-1,1'-Binaphthyl-2,2-diyl phosphorochloridate, (*S*)-binol-PCl: All glassware was oven-dried or flame-dried under vacuum. All solvents and reagents were dry and degassed. (*S*)-1,1'-Bi(2-naphthol) – (*S*)-binol was azeotropically dried prior to use, by co-evaporation with dry toluene. To a solution of TEA (1.1 ml, 8 mmol) in THF (20 mL) were added drop wise subsequently PCl_3 (0.40 ml, 4.6 mmol) and a solution of (*S*)-binol (1.14 g, 4 mmol) in THF (20 ml) at -78°C. The reaction mixture was stirred for 20 minutes, then

allowed to warm up to room temperature, and further stirred for 45 minutes at rt. Then, all volatiles were removed under vacuum, followed by addition of toluene (10 ml) and its evaporation. Next, the solid residue, being a mixture of the desired (S)-binol-PCl and TEA*HCl salt, was dissolved/suspended in THF (30 ml) and used in the next step without further purification.

$^{31}P\{^{1}H\}$ NMR (162MHz, THF-h_8): δ = 177.8

Ligand **L7** (bis-(3-((*S*)-1,1'-binaphthyl-2,2-diyl phosphito)benzoamide) of 1,1-bis-(-7-amino-3-methyl-1H-indol-2-yl)-propane): All glassware was oven-dried or flame-dried under vacuum. All solvents and reagents were dry and degassed. Diol **4b** (containing 4/3 mol of DCM per mol for **4b**) was azeotropically dried prior to use, by co-evaporation with dry toluene three times. To the solution of diol **4b** (2 mmol) and triethylamine (2.8 ml, 20 mmol) in THF (20 ml), the freshly-prepared solution of phosphorylchloride (4 mmol) in THF (20 ml) was added drop wise at -78°C. After 30 minutes the cooling bath was removed, and the mixture was allowed to continue stirring overnight. The reaction mixture was evaporated, to the solid residue THF (40 ml), and the suspension was filtered through a plug of SiO_2 gel, which was subsequently washed with THF (40 ml). The combined organic fractions were concentrated, hexane (30 ml) was added, followed by evaporation of all volatiles to dryness, yielding 2.48g (91%) of **L7**·THF·C_6H_{14}. NOTE: Ligand **L7** is sensitive, thus should be stored in inert conditions at low temperatures preferably.

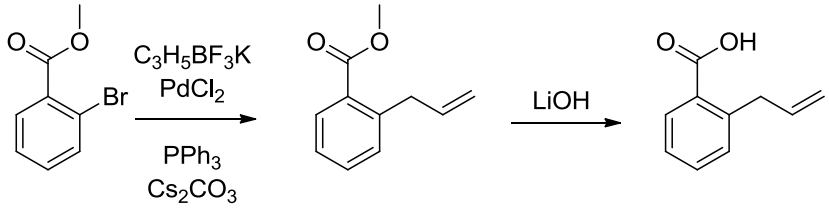
^{1}H NMR (400 Mhz, CD_2Cl_2): δ = 9.53 (*p*d, 2H), 8.27 (s, 1H), 8.22 (s, 1H), 8.04 – 7.80 (m, 8H), 7.58 – 7.15 (m, 26H), 7.02 – 6.79 (m, 4H), 4.49 (t, J_1 = 8.0 Hz, 1H, C*H*CH_2CH_3), 2.33 (*p*d, 6H, 2•ArCH_3), 2.16 (m, 2H, CHCH_2CH_3), 0.99 (t, J_1 = 7.2 Hz, 3H, $CHCH_2CH_3$);

^{13}C NMR (100MHz, CD_2Cl_2): δ = 165.2 (d, J_1 = 6.4 Hz), 152.2 (d, J_1 = 3.5 Hz), 152.1 (d, J_1 = 3.3 Hz), 147.8 (d, J_1 = 4.6 Hz), 147.21 (d, J_1 = 2.6 Hz), 147.17 (d, J_1 = 2.6 Hz), 136.7 (s), 136.4 (d, J_1 = 8.0 Hz), 133.2 (s), 132.9 (s), 132.3 (s), 132.2 (s), 131.7 (d, J_1 = 2.5 Hz), 131.1 (s), 130.5 (m), 128.8 (d, J_1 = 8.1 Hz), 128.2 (d, J_1 = 3.0 Hz), 127.2 (s), 127.1 (d, J_1 = 3.0 Hz), 126.9 (d, J_1 = 6.5 Hz), 125.7 (d, J_1 = 17.1 Hz), 124.6 (m), 124.0 (d, J_1 = 8.1 Hz), 123.7 (d, J_1 = 8.5 Hz), 123.4 (d, J_1 = 11.1 Hz), 123.2 (m), 122.2 (s), 121.9 (m), 119.9 (d, J_1 = 7.6 Hz), 119.7 (d, J_1 = 7.5 Hz), 119.3 (d, J_1 = 4.0 Hz), 116.4 (d, J_1 < 2.0 Hz), 114.1 (d, J_1 = 16.0 Hz), 108.2 (d, J_1 = 4.4 Hz), 36.8 (s), 26.0 (s), 12.6 (s), 8.9 (*p*d);

$^{31}P\{^{1}H\}$ NMR (162MHz, CD_2Cl_2): δ = 144.2 (s, 1P), 144.1 (s, 1P).

Elemental analysis (%) calcd. for $C_{75}H_{54}N_4O_8P_2$·C_4H_8O: C 74.52, H 4.91, N 4.40, P 4.87, found: C 73.13, H 5.34, N 4.14, P 4.82.

Synthesis of 2-allylbenzoic acid (15)



Methyl 2-allylbenzoate: The synthesis was performed according to the published procedures for analogical reactions with small modifications.[7] A 50 ml sealable Schlenk tube ('Schlenk bomb') was charged with methyl 2-bromobenzoate (0.63 ml, 4.5 mmol), potassium allyltrifluoroborate (1.0 g, 6.8 mmol), cesium carbonate (6 g), palladium (II) chloride (105 mg), triphenylphosphine (480 mg), THF (9 ml) and degassed water (1 ml), sealed with a Teflon screw cap and stirred at 85°C for ca. 40h. Then, the reaction mixture was diluted with DCM (50 ml) and water (30 ml), filtered over Celite, the organic layer was separated, and the water phase was extracted with DCM (2•50 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel, with a pentane : diethyl ether (95:5) mixture as an eluent. Fractions of the pure product were combined, and the solvent evaporated off, yielding 380 mg (48%) of product.

^{1}H NMR (400 Mhz, CD_2Cl_2): δ = 7.90 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 7.50 (ddd, $J_1 = J_2$ = 7.5 Hz, J_3 = 1.4 Hz, 1H), 7.36-7.31 (m, 2H), 6.10-6.00 (m, 1H, C*H*CH_2Ar), 5.10-5.03 (m, 2H, CH=CH_2), 3.91 (s, 3H, OCH_3), 3.79 (d, J_1 = 6.7 Hz, 2H, ArCH_2);

^{13}C NMR (100MHz, CD_2Cl_2): δ = 168.3, 141.9, 138.0, 132.3, 131.3, 130.8, 130.3, 126.6, 115.6, 52.2, 38.7;

HR MS (FAB): calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0916, found: 177.0908.

2-Allylbenzoic acid (**15**): A round-bottom flask was charged with methyl 2-allylbenzoate (360 mg, 2 mmol), lithium hydroxide (480 mg), a THF : methanol : water (4 : 1 : 1) mixture (10 ml), sealed and stirred at room temperature. The progress of the reaction was monitored by TLC, and after completion (overnight), the reaction mixture was diluted with water (20 ml), followed by evaporation of THF and methanol under reduced pressure (100 mbar, 40ºC). Then, the water phase residue was washed with DCM (20 ml), acidified with 1M HCl to pH ~ 3, and extracted with DCM (3•40 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum, yielding 296 mg (90%) of **15**.

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 12.85 (bs, 1H, COO*H*), 7.80 (d, J_1 = 7.5 Hz, 1H), 7.48 (ddd, $J_1 = J_2$ = 7.6 Hz, J_3 = 1.4 Hz, 1H), 7.33-7.27 (m, 2H), 6.01-5.90 (m, 1H, C*H*CH_2Ar), 5.03-4.95 (m, 2H, CH=CH_2), 3.71 (d, J_1 = 6.6 Hz, 2H, ArCH_2);

^{13}C NMR (100MHz, DMSO-d_6): δ = 169.2, 141.1, 138.2, 132.2, 131.2, 131.0, 130.7, 126.7, 116.0, 38.1;

HR MS (FAB): calcd. for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.0759, found: 163.0760.

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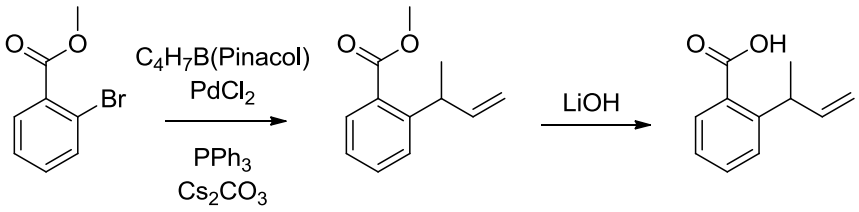
[7] G. A. Molander, A. R. Brown, J. Org. Chem, **2006**, *71*, 9681-9686.

Elemental analysis (%) calcd. for $C_{10}H_{10}O_2$: C 74.06, H 6.21, found: C 74.06, H 6.05.

Synthesis of 2-(but-3-en-2-yl)benzoic acid (16)



Methyl 2-(but-3-en-2-yl)benzoate: A 50 ml sealable Schlenk tube ('Schlenk bomb') was charged with methyl 2-bromobenzoate (0.51 ml, 3.66 mmol), trans-crotylboronic acid pinacol ester (1 g, 5.5 mmol), cesium carbonate (5 g), palladium (II) chloride (105 mg), triphenylphosphine (480 mg), THF (9 ml) and degassed water (1 ml), sealed with a Teflon screw cap and stirred at 85°C for ca. 36h.[8] Then, the reaction mixture was diluted with DCM (50 ml) and water (30 ml), filtered over Celite, the organic layer was separated, and the water phase was extracted with DCM (2•50 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel, with a pentane : diethyl ether (95:5) mixture as an eluent. Fractions of the product were combined, and the solvent evaporated off, yielding 810 mg of the mixture of the title product and (E)-methyl 2-(but-2-en-1-yl)benzoate (~89:11 ratio), containing some residual trans-crotylboronic acid pinacol ester, and the mixture was used in the next step without further purification.

^{1}H NMR (400 Mhz, CD_2Cl_2): δ = 7.73 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.45 (ddd, $J_1 \approx J_2$ = 7.7 Hz, J_3 = 1.5 Hz, 1H), 7.34 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.24 (ddd, $J_1 \approx J_2$ = 7.6 Hz, J_3 = 1.1 Hz, 1H), 6.08-5.98 (m, 1H, C*H*CH_2), 5.07 (ddd, J_1 = 7.6 Hz, $J_2 \approx J_3$ = 1.7 Hz, 1H, CHC*H*$_2$), 5.03 (d, J_1 = 1.6 Hz, 1H, CHC*H*$_2$), 4.39-4.30 (m, 1H, ArC*H*), 3.86 (s, 3H, OC*H*$_3$), 1.34 (d, J_1 = 7.0 Hz, 3H, CHC*H*$_3$);

^{13}C NMR (100MHz, CD_2Cl_2): δ = 168.8, 146.9, 143.3, 132.1, 130.5, 130.3, 128.2, 126.2, 113.4, 52.3, 38.6, 20.7;

HR MS (FAB): calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072, found: 191.1073.

2-(But-3-en-2-yl)benzoic acid (**16**): A round-bottom flask was charged with methyl 2-(but-3-en-2-yl)benzoate (796 mg, impure from previos step), lithium hydroxide (480 mg), a THF : methanol : water (4 : 1 : 1) mixture (10 ml), sealed and stirred at 50°C. The progress of the reaction was monitored by TLC, and after completion (overnight), the reaction mixture was diluted with water (20 ml), followed by evaporation of THF and methanol under reduced pressure (100 mbar, 40ºC). Then, the water phase residue was washed with DCM (20 ml), acidified with 1M HCl to pH ~ 3, and extracted with DCM (3•40

[8] For a recent study on regiodivergent Suzuki-Miyaura cross-coupling of allylboronates and aryl halides, see: Y. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **2013**, *135*, 10642–10645.

ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The solid residue was crystalized from a hot water : ethanol (20 : 5) mixture, yielding 543 mg (86% after 2 steps) of **16** (containing ~9% of (E)-methyl 2-(but-2-en-1-yl)benzoic acid).

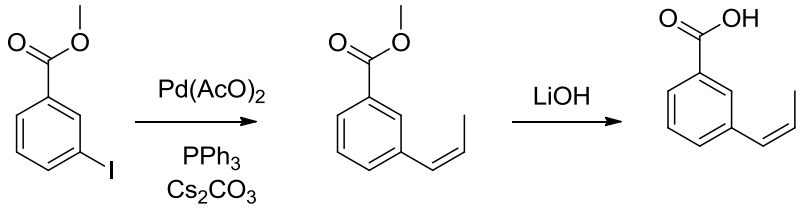
^{1}H NMR (400 Mhz, DMSO-d_6): δ = 12.93 (bs, 1H, COO*H*), 7.70 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 7.49 (ddd, $J_1 \approx J_2$ = 7.6 Hz, J_3 = 1.4 Hz, 1H), 7.34 (dd, J_1 = 7.9 Hz, J_2 < 1.0 Hz, 1H), 7.28 (ddd, $J_1 \approx J_2$ = 7.5 Hz, J_3 = 1.1 Hz, 1H), 6.08-5.98 (m, 1H, C*H*CH$_2$), 5.05 (s, 1H, CHC*H*$_2$), 5.01 (ddd, J_1 = 5.4 Hz, $J_2 \approx J_3$ = 1.5 Hz, 1H, CHC*H*$_2$), 4.43-4.35 (m, 1H, ArC*H*), 1.29 (d, J_1 = 6.9 Hz, 3H, CHC*H*$_3$);

^{13}C NMR (100MHz, DMSO-d_6): δ = 169.3, 145.5, 142.9, 131.5, 130.9, 129.6, 127.6, 125.9, 113.3, 37.5, 20.6;

HR MS (FAB): calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0916, found: 177.0917.

Elemental analysis (%) calcd. for $C_{11}H_{13}O_2$: C 74.49, H 6.86, found: C 75.01, H 6.80.

Synthesis of 3-[(1Z)-prop-1-en-1-yl]benzoic acid (17)



Methyl 3-[(1Z)-prop-1-en-1-yl]benzoate: A 50 ml sealable Schlenk tube (‘Schlenk bomb’) was charged with methyl 3-iodobenzoate (2.86 ml, 10.9 mmol), (1Z)-1-propenylboronic acid (2.5 g, 29 mmol), cesium carbonate (10 g), palladium (II) acetate (400 mg), triphenylphosphine (1.38 g), dimethoxyethane (25 ml) and degassed water (20 ml), sealed with a Teflon screw cap and stirred at 100°C for 4h. After cooling down, the reaction mixture was diluted with water (30 ml) and extracted with DCM (3•60 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel, with a hexane : diethyl ether (98:2) mixture as an eluent. Fractions of the product were combined, and the solvent evaporated off, yielding 1.77 g (92%) of product.

^{1}H NMR (400 Mhz, CD_2Cl_2): δ = 7.97 (s, 1H), 7.88 (d, J_1 = 7.7 Hz, 1H), 7.52 (d, J_1 = 7.7 Hz, 1H), 7.43 (dd, J_1 = J_2 = 7.7 Hz, 1H), 6.48 (d, J_1 = 11.6 Hz, 1H, C*H*Ar), 5.89 (dq, J_1 = 11.6 Hz, J_2 = 7.2 Hz, 1H, C*H*CH$_3$), 3.90 (s, 3H), 1.92 (dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H, CHC*H*$_3$);

^{13}C NMR (100MHz, CD_2Cl_2): δ = 167.3, 138.3, 133.5, 130.6, 130.1, 129.2, 128.6, 128.4, 127.8, 52.4, 14.8;

HR MS (EI): calcd. for $C_{11}H_{12}O_2$ $[M]^+$: 176.08373, found: 176.08341.

3-[(1Z)-Prop-1-en-1-yl]benzoic acid (**17**): A round-bottom flask was charged with methyl 3-[(1Z)-prop-1-en-1-yl]benzoate (1.75 g, 9.9 mmol), lithium hydroxide (960 mg), a THF : methanol : water (4 : 1 : 1) mixture (20 ml), sealed and stirred at 50ºC for 8h. Afterwards, the reaction mixture was diluted with water (40 ml), followed by evaporation of THF and methanol under reduced pressure (100 mbar, 40ºC). Then, the water phase residue was washed with DCM (40 ml), acidified with 1M HCl to pH ~ 3, and extracted with DCM (3•50 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum, yielding 1.53 g (95%) of **17**.

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 13.01 (bs, 1H, COO*H*), 7.87 (s, 1H), 7.81 (d, J_1 = 7.7 Hz, 1H), 7.54 (d, J_1 = 7.7 Hz, 1H), 7.48 (dd, J_1 = J_2 = 7.7 Hz, 1H), 6.49 (d, J_1 = 11.7 Hz, 1H, C*H*Ar), 5.85 (dq, J_1 = 11.7 Hz, J_2 = 7.2 Hz, 1H, C*H*CH_3), 1.86 (dd, J_1 = 7.3 Hz, J_2 = 1.9 Hz, 1H, CHC*H*$_3$);

^{13}C NMR (100MHz, DMSO-d_6): δ = 167.3, 137.3, 132.9, 130.8, 129.3, 128.8, 128.6, 127.7, 127.5, 14.5;

HR MS (EI): calcd. for $C_{10}H_{10}O_2$ $[M]^+$: 162.06806, found: 162.06719;

Elemental analysis (%) calcd. for $C_{10}H_{10}O_2$: C 74.06, H 6.21, found: C 74.28, H 6.12.

Coordination and titration studies

General comments.

All manipulations were conducted under inert atmosphere (argon or nitrogen) using oven-dried or flame dried glassware and pre-dried and degassed CD_2Cl_2 and CD_3CN as solvents. Commercially available tetrabutylammonium (TBA) salt was used as the source of benzoate anions. All NMR spectra, except where noted, were collected at 25ºC. If not stated otherwise, the IR spectra were collected at room temperature.

NMR complexation experiments

The anion titration experiments were conducted with a constant concentration of host protocol. An oven-dried vial equipped with a teflon stirring bar was charged with a ligand and, if necessary, with a rhodium precursor (1:1 ratio), followed by addition of an amount of CD_2Cl_2 to obtain a desired solution concentration. In case of preparation of a ligand – metal complex, the solution was stirred for a couple of minutes at room temperature. A quantitative formation of the desired [Rh(ligand)(acac)] complex was confirmed by the ^1H and ^{31}P NMR experiments of the solution. In another oven-dried vial a concentrated solution of tetrabutylammonium benzoate was prepared, by dissolving tetrabutylammonium benzoate salt in the previously prepared solution of the ligand or the [Rh(ligand)(acac)] complex (to keep constant the concentration of the ligand or the complex). Under inert atmosphere (a glove-box), aliquots (0.6-0.4ml) of the ligand/Rh-liagnd solution were transferred to NMR tubes, followed by addition of aliquots (0.0018-0.2ml) of the tetrabutylammonium benzoate in the ligand/Rh-ligand solution.

For the evaluation of the association constant for the [Rh(**L5**)(acac)] complex with benzoate anion, the chemical shift of ligand protons upon addition of different amount of the anion was observed. The highest changes were observed for both NH-indole and NH-amide protons, as expected, since they take part in hydrogen bond formation. Due to slow anion/receptor complex formation on the NMR timescale, there are two sets of NH signals observed between 0 and 1 equivalent of anion (some of other signals are significantly broaden, however, they sharpen above 1 equivalent of the anion), and their ratio depends on the amount of anion added (Figures S3-S4). When slightly more than a stoichiometric amount of anion is added (1.05 equiv.) all signals of the complex are sharpened, and further anion addition does not change the spectrum (Figures S3-S4). At this point the anion binding pocket is saturated. Similar observations were taken at $^{31}P\{^1H\}$ NMR spectra (Figure S5). Taking into account the total complex concentration ($C_{[Rh(\mathbf{L5})(acac)]}$= 0.001 M), the association constant can be easily estimated: $K_a = [CA]/([C]\cdot[A])$, with: [CA] ≡ the concentration of the anion-[Rh(**L5**)(acac)] complex, [C] ≡ the concentration of the free [Rh(**L5**)(acac)], [A] ≡ the concentration of the free anion. Based on analysis of the spectrum at 1.05

equivalents of anion: [CA] >> 0.95 · $C_{[Rh(\mathbf{L5})(acac)]}$, [C] << 0.05• $C_{[Rh(\mathbf{L5})(acac)]}$, so then [A] ~ 0.05•$C_{[Rh(\mathbf{L5})(acac)]}$. After rearrangement: K >> 380•$(C_{[Rh(\mathbf{L5})(acac)]})^{-1}$, so then $K_a >> 10^5$ [M^{-1}].

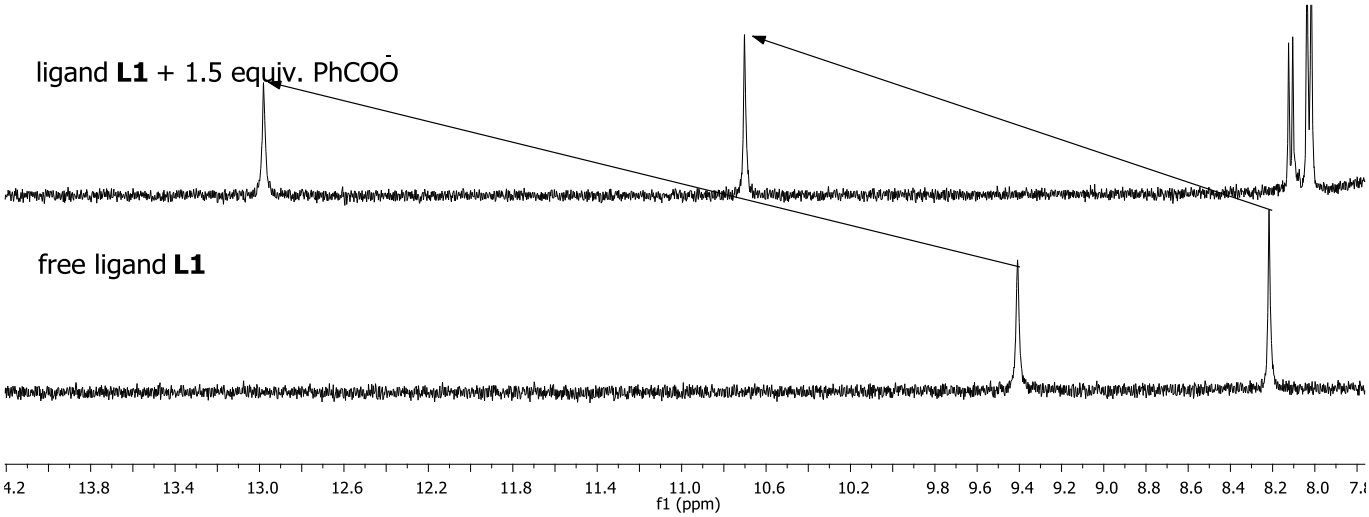


Figure S1. ^{1}H NMR (400MHz) titration of ligand **L1** (0.001 M solution) with TBA-$PhCO_2$ in CD_2Cl_2.

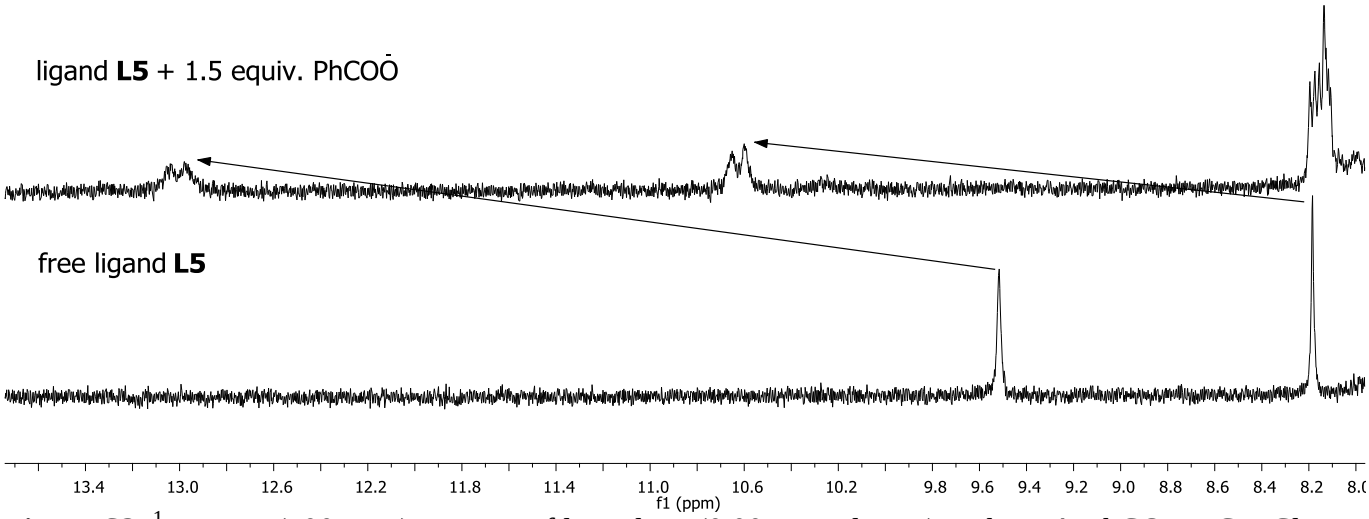


Figure S2. ^{1}H NMR (400MHz) titration of ligand **L5** (0.001 M solution) with TBA-$PhCO_2$ in CD_2Cl_2.

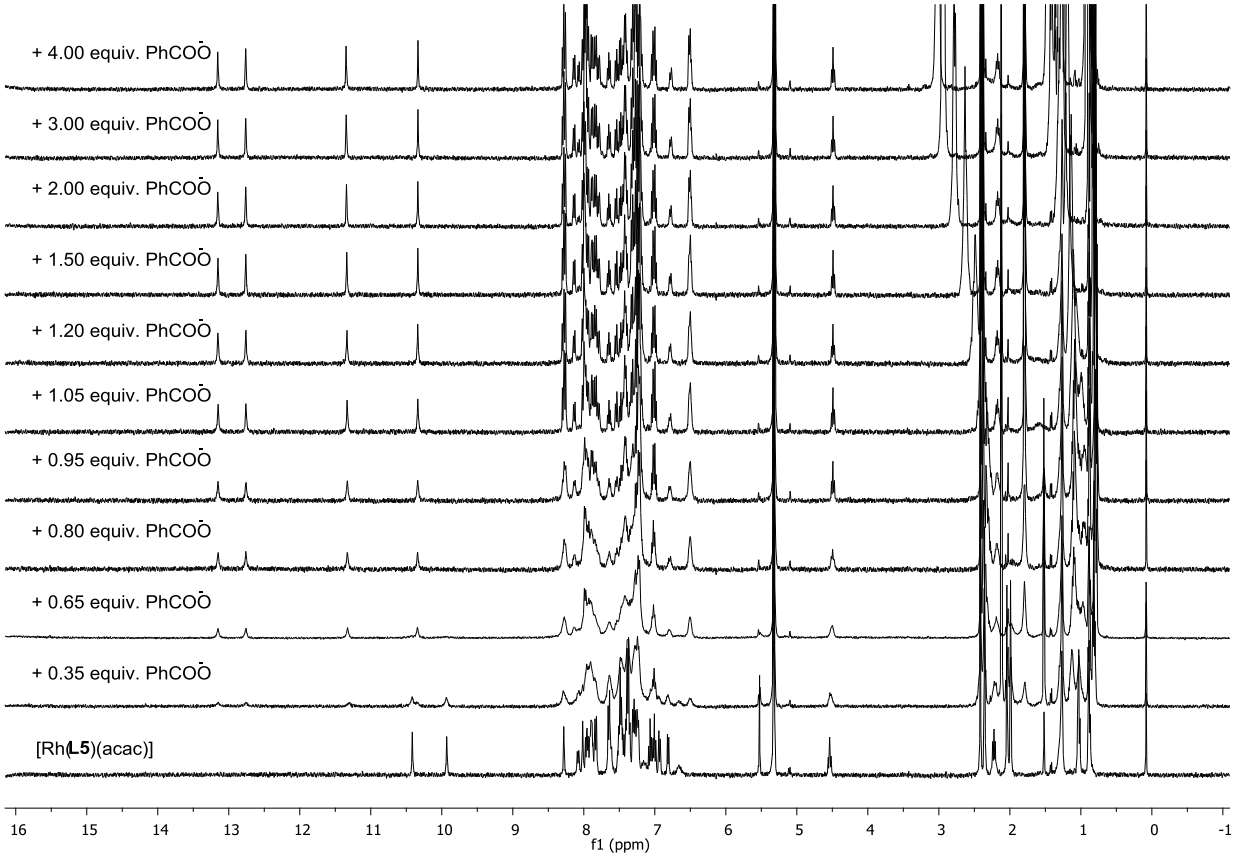


Figure S3. ^{1}H NMR (400MHz) titration of [Rh(**L5**)(acac)] (0.001 M solution) with TBA-$PhCO_2$ in CD_2Cl_2.

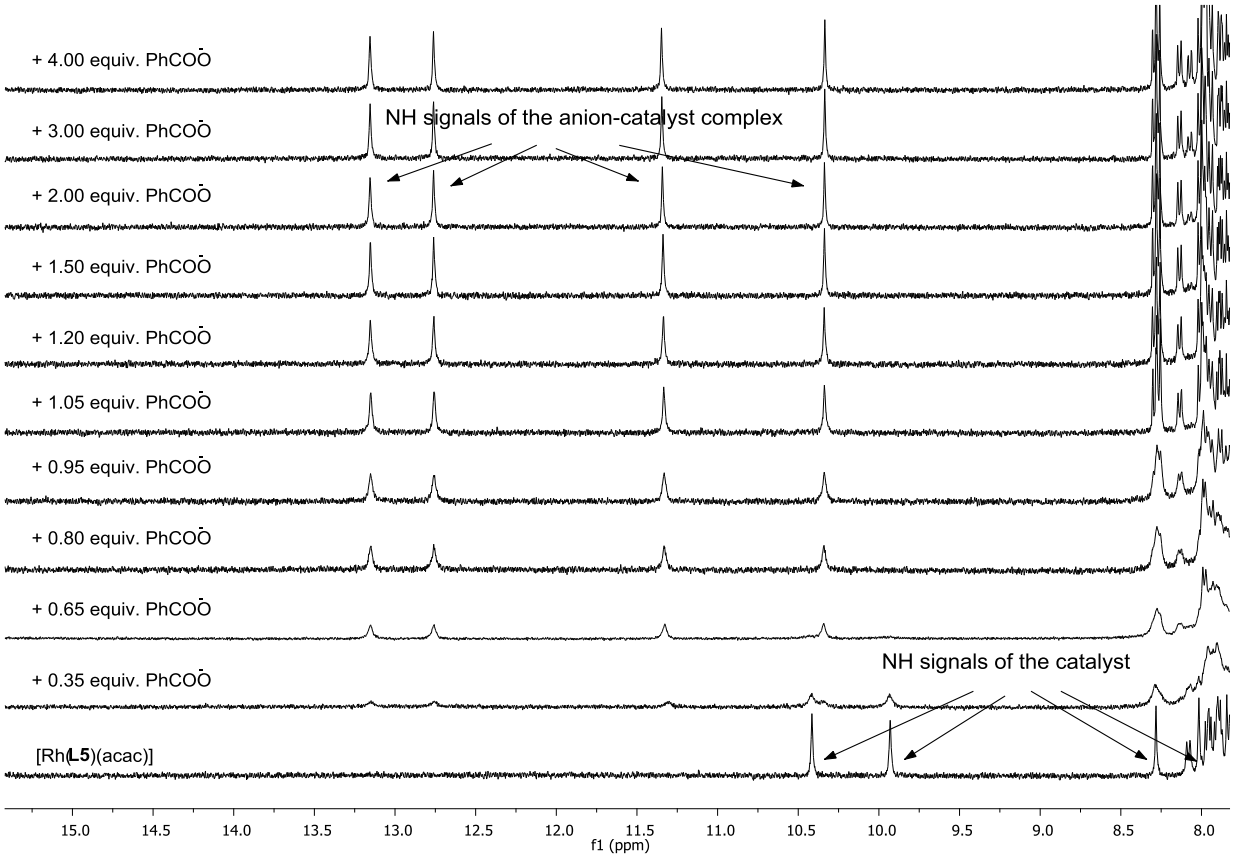


Figure S4. ^{1}H NMR (400MHz) titration of [Rh(**L5**)(acac)] (0.001 M solution) with TBA-$PhCO_2$ in CD_2Cl_2 - NH signals' region.

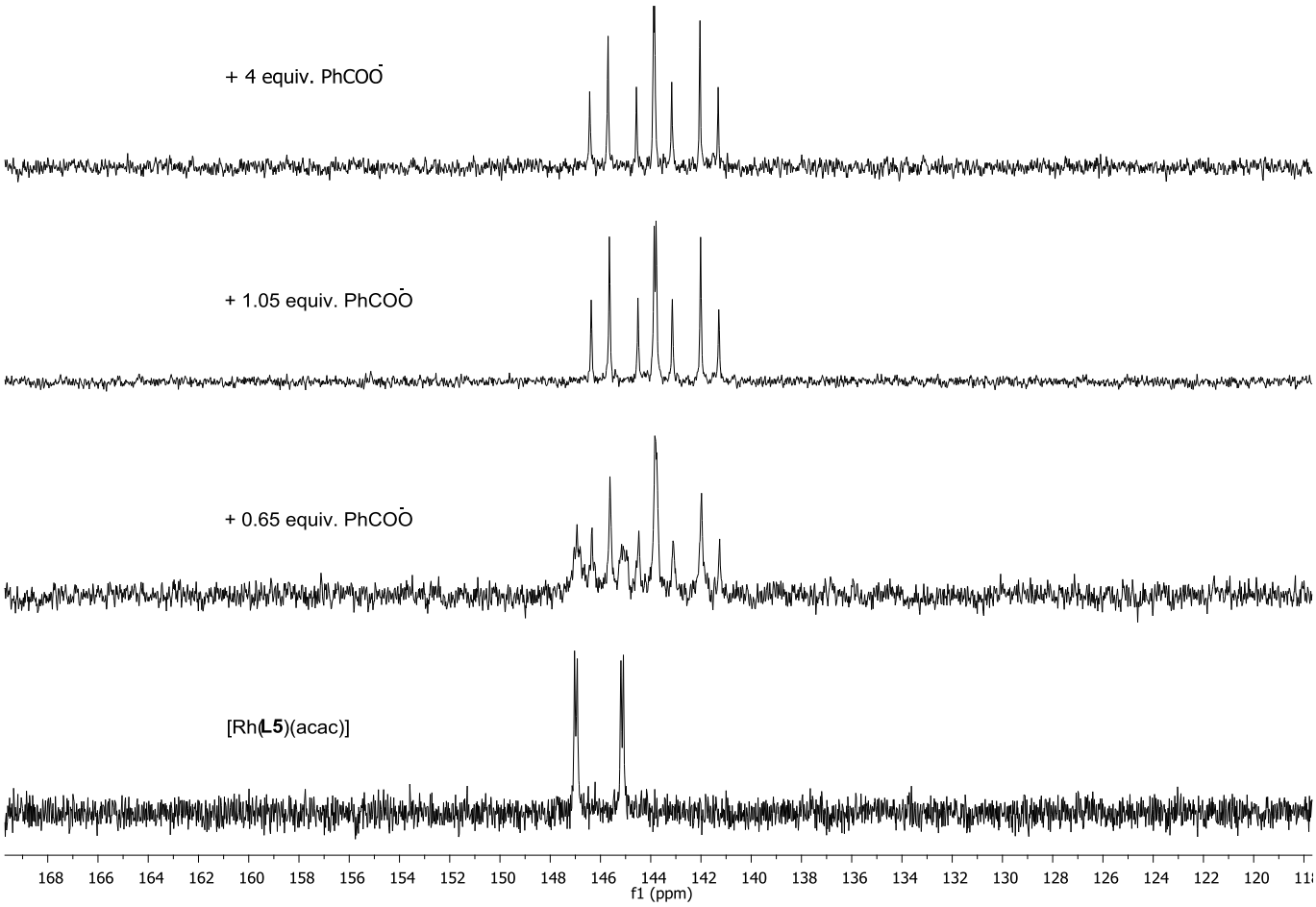


Figure S5. $^{31}P\{^{1}H\}$ NMR (162 MHz) titration of [Rh(**L5**)(acac)] (0.001 M solution) with TBA-$PhCO_2$ in CD_2Cl_2.

NMR complexation experiments under CO/H_2 pressure

A flame-dried Schlenk flask equipped with a teflon stirring bar was charged with a ligand and with $Rh(acac)(CO)_2$ (1:1 ratio), followed by addition of an appropriate amount of CD_2Cl_2 to obtain a desired concentration of the solution of a Rh-ligand complex. The solution was stirred for a few minutes at room temperature. Next, the solution was transferred to a high pressure NMR tube, which was then purged at least three times with 10 bar of syngas and subsequently pressurized with 5 bar of syngas. The tube was shaken occasionally and the conversion of the precatalyst was followed in time. In most cases, the pre-catalyst activation was conducted at room temperature, with the exception of the complex with **L2**. In this case, nearly no conversion was observed after 90 minutes, thus the activation was performed overnight at 50°C (full conversion). In case of complex with **L3**, the precipitation occurred shortly after preserusing, thus the activation was performed overnight at 40°C.

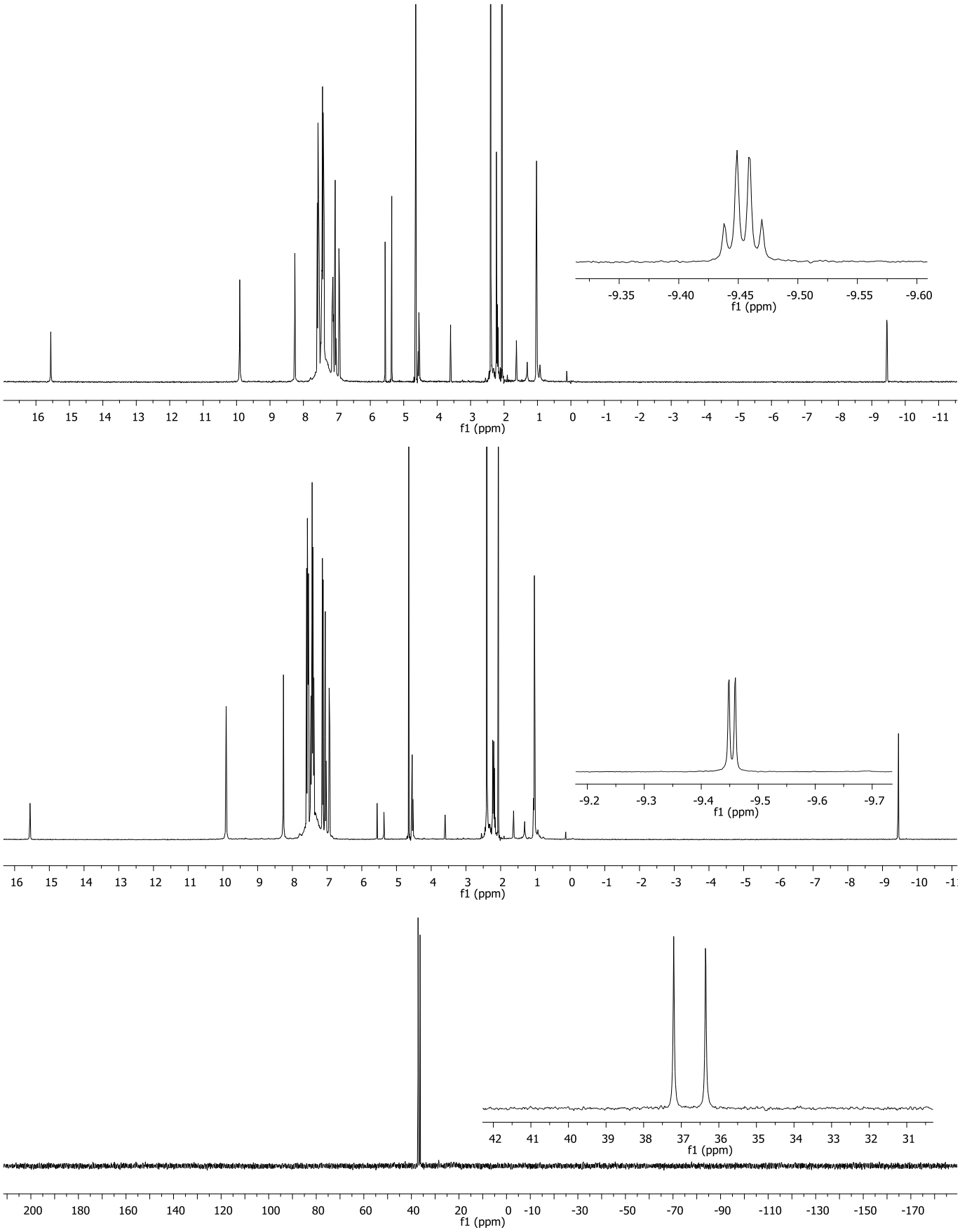
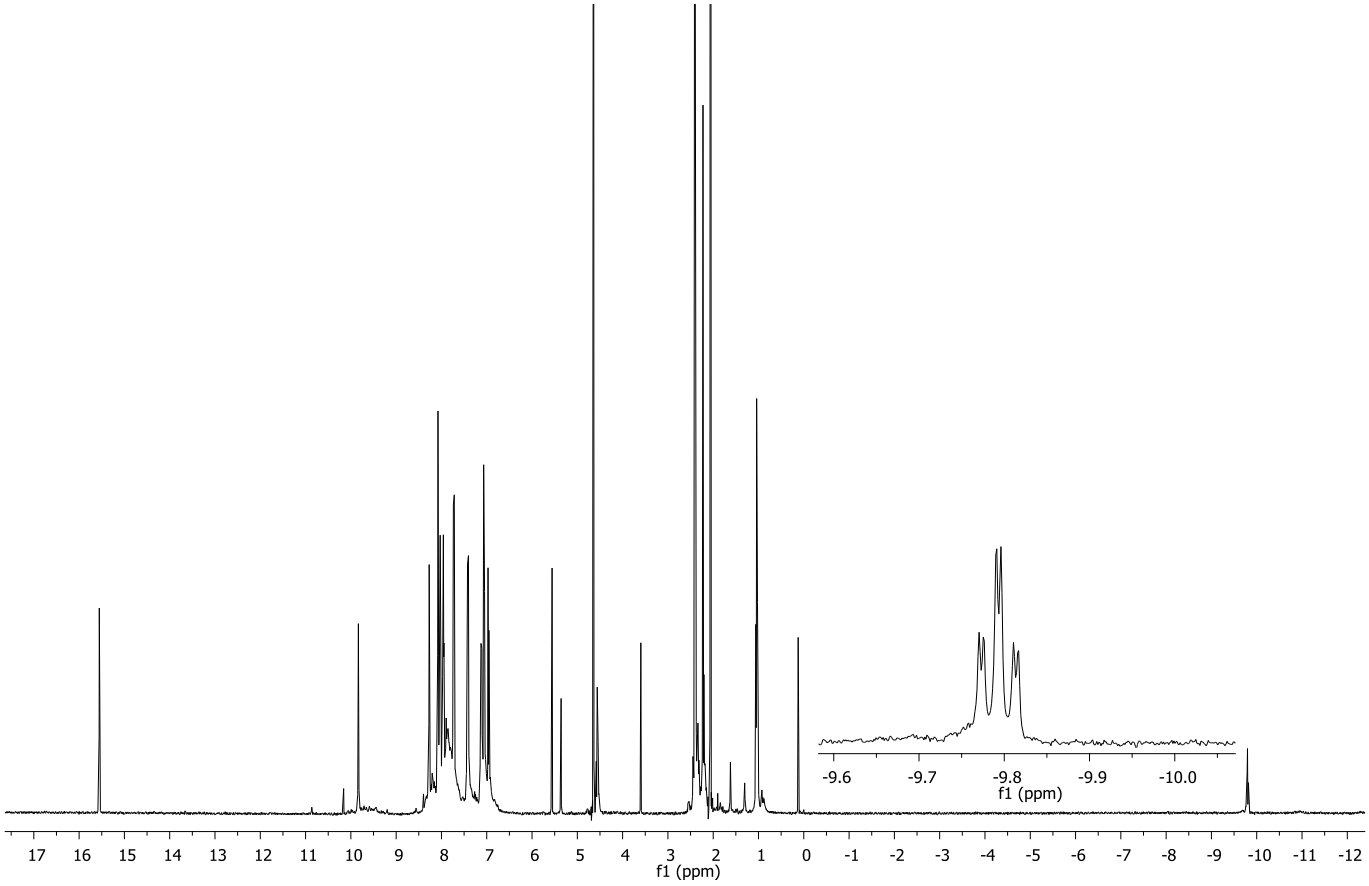


Figure S6. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L1**)$(CO)_2H$] complex (0.01 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.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-9.8
-9.9
-10.0
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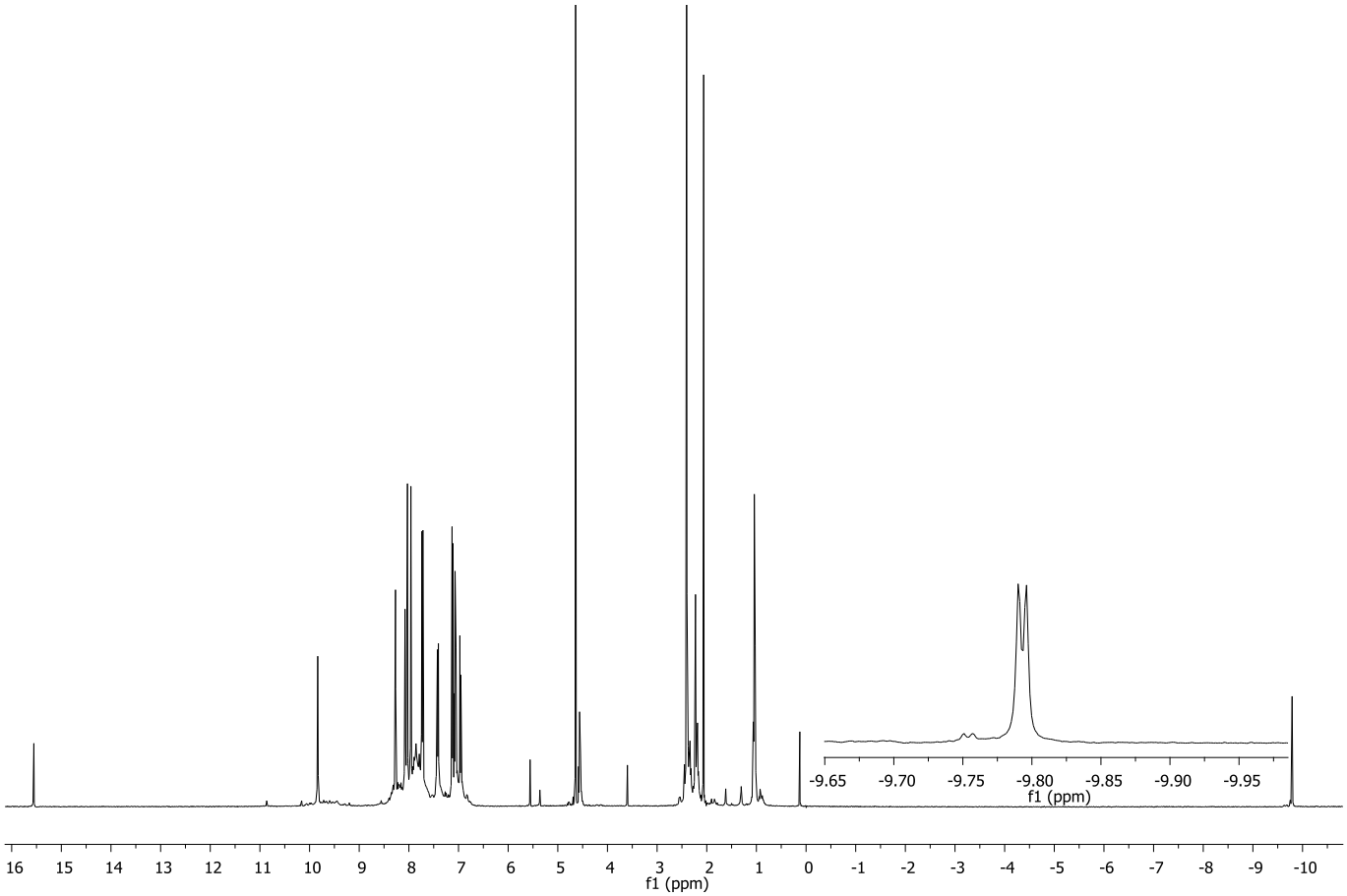
f1 (ppm)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-9.70
-9.75
-9.80
-9.85
-9.90
-9.95
f1 (ppm)
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f1 (ppm)

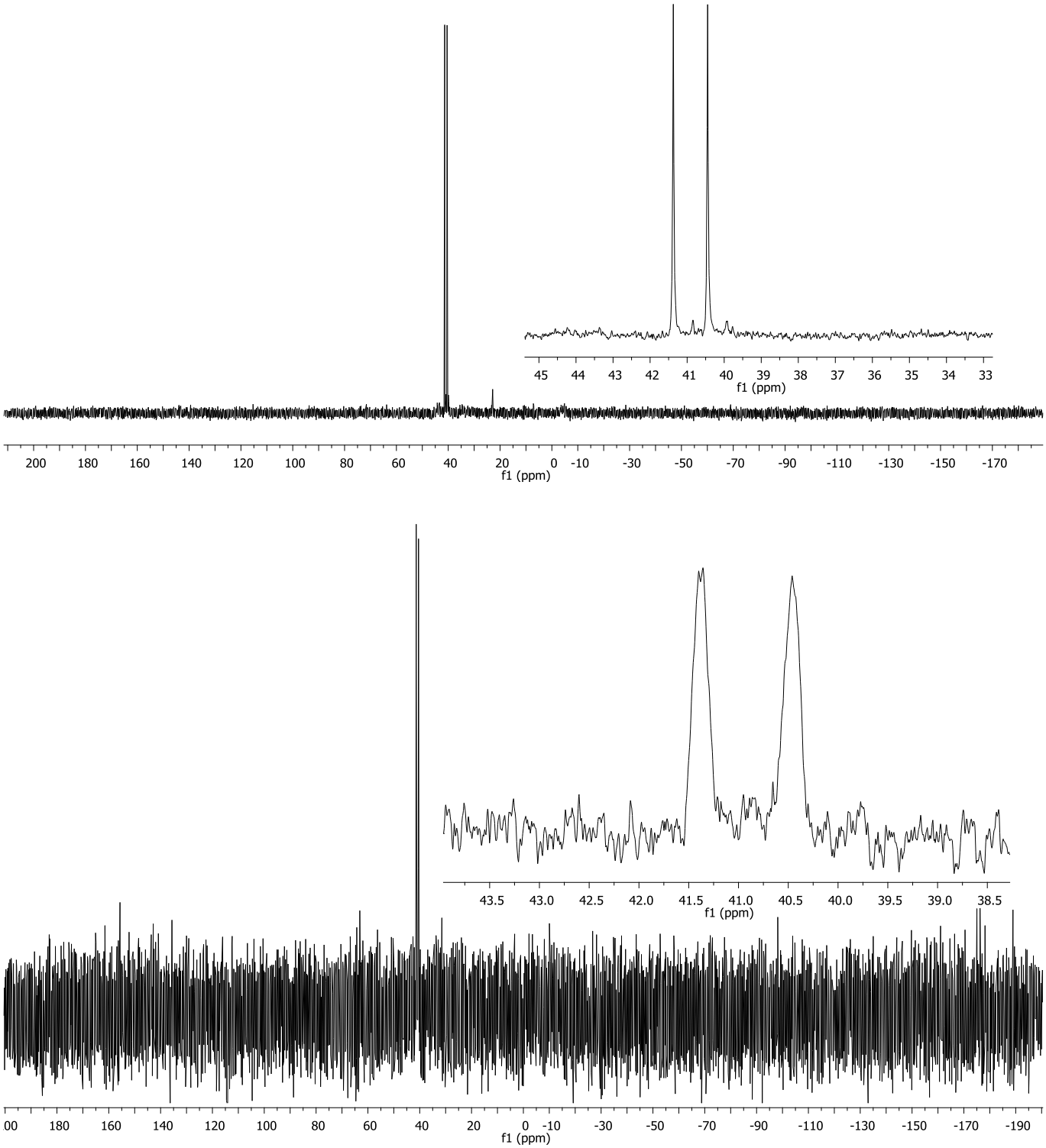


Figure S7. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle top), $^{31}P\{^{1}H\}$ (middle bottom) and ^{31}P (bottom) NMR spectra of [Rh(**L2**)$(CO)_2H$] complex (0.01 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

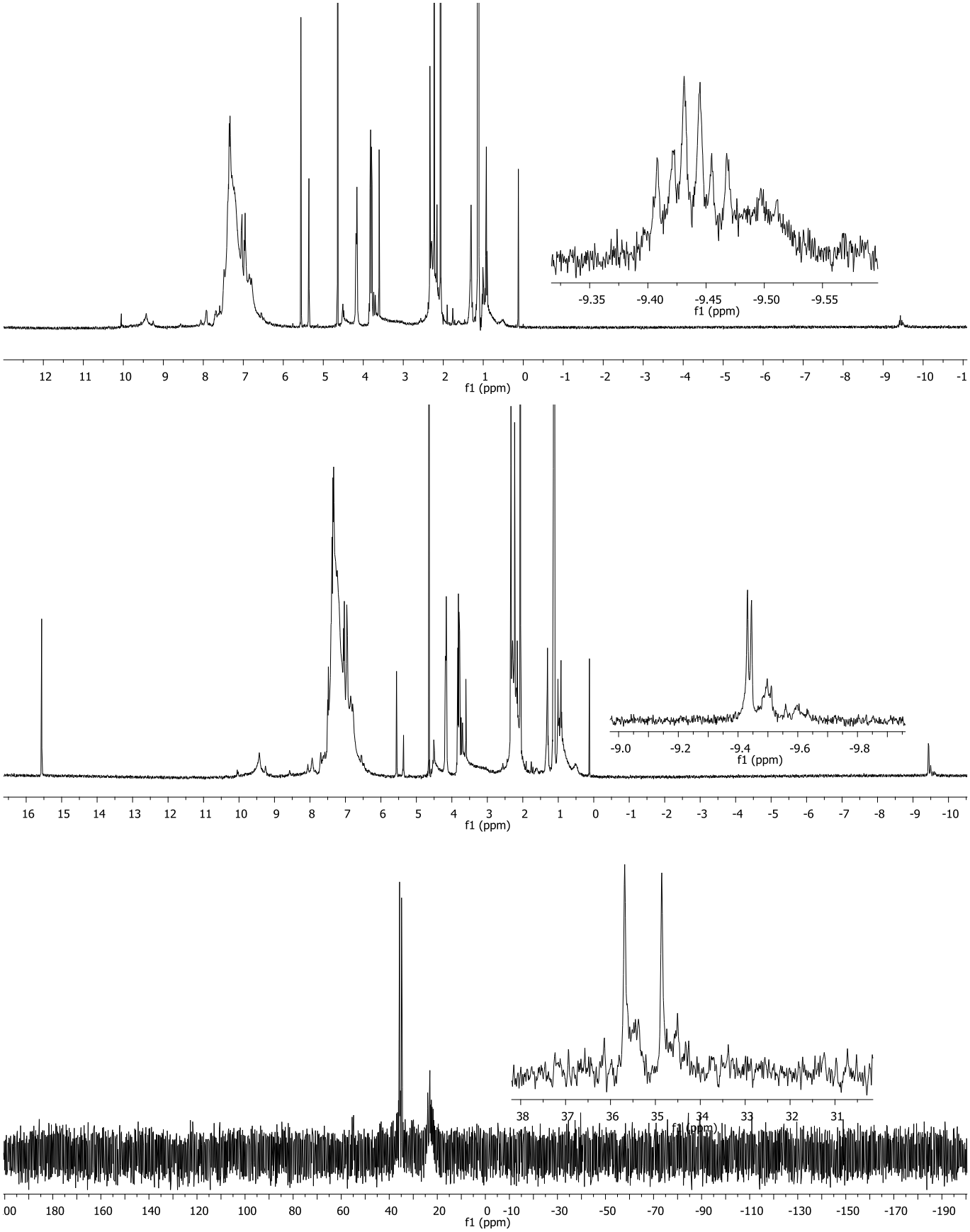


Figure S8. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L3**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

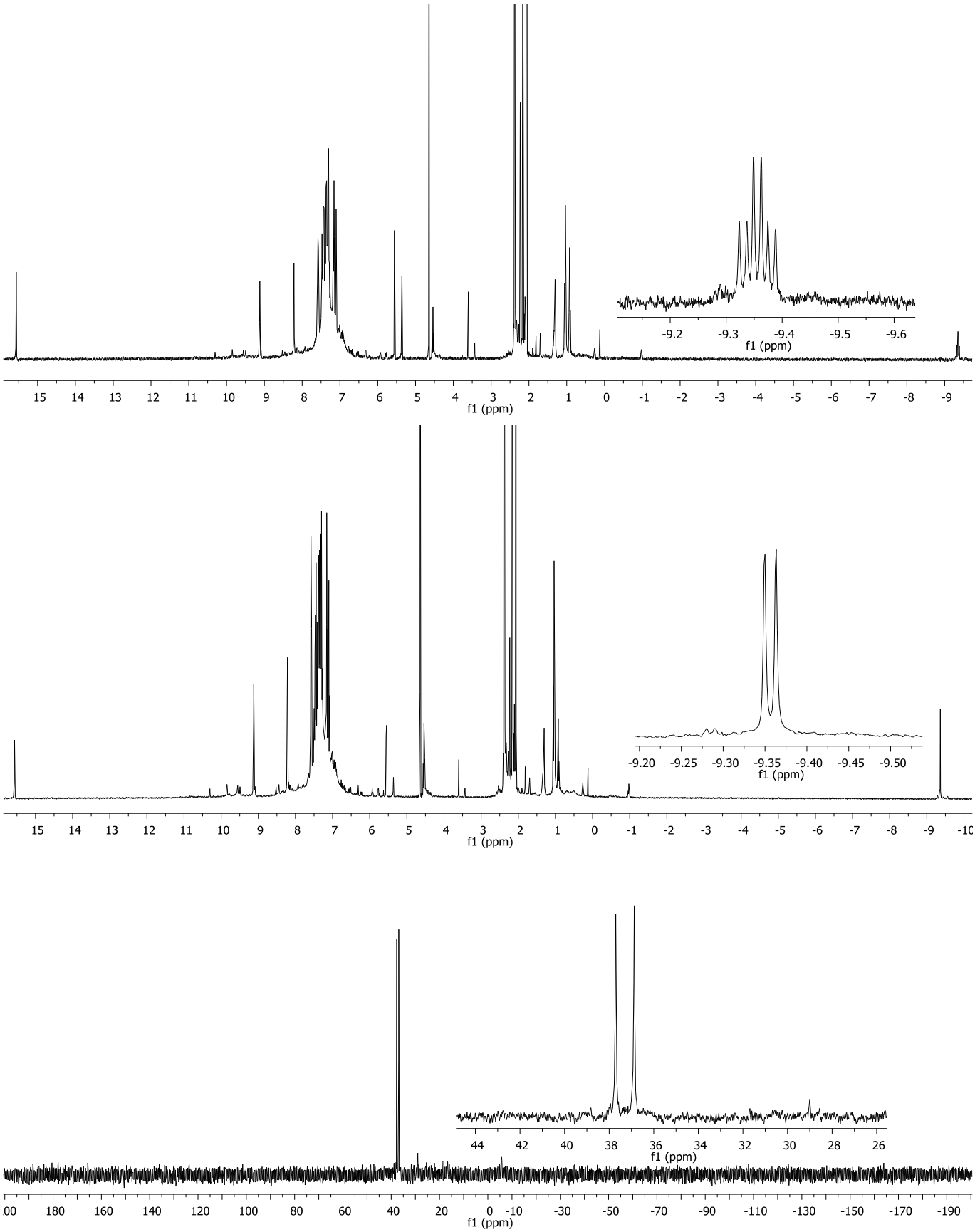


Figure S9. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L4**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

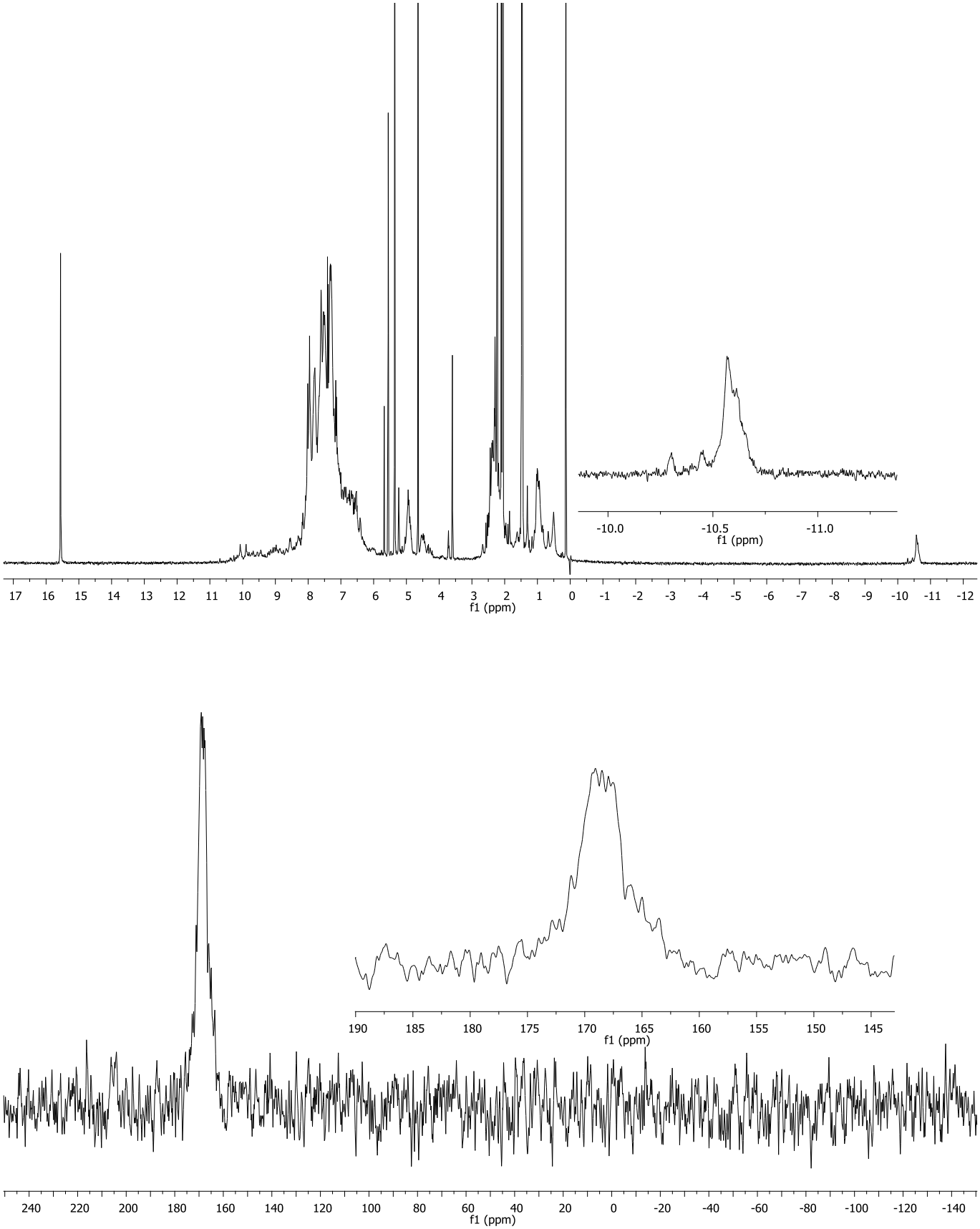
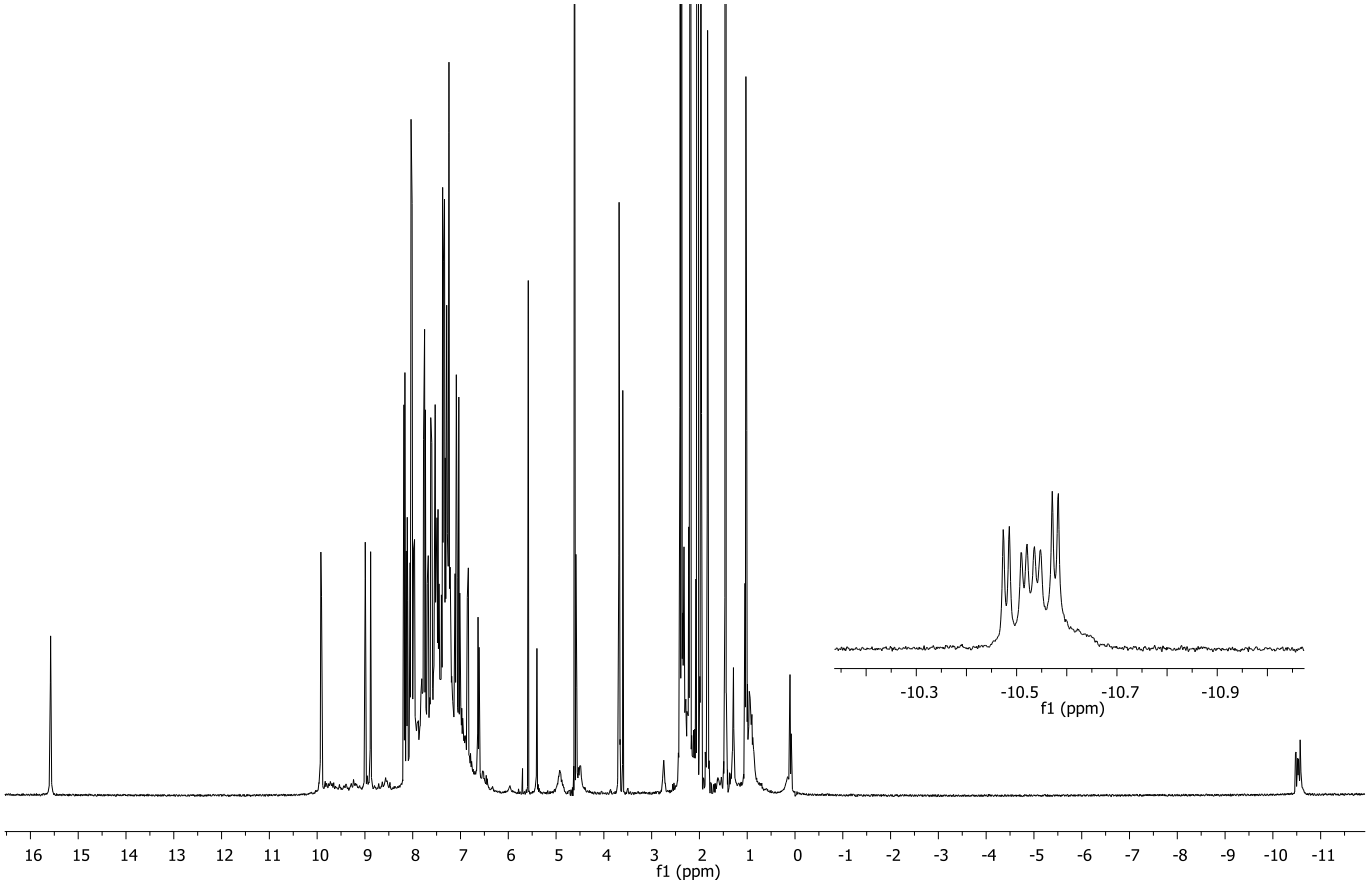


Figure S10. High pressure ^{1}H (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.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-10.5
-10.7
-10.9
f1 (ppm)
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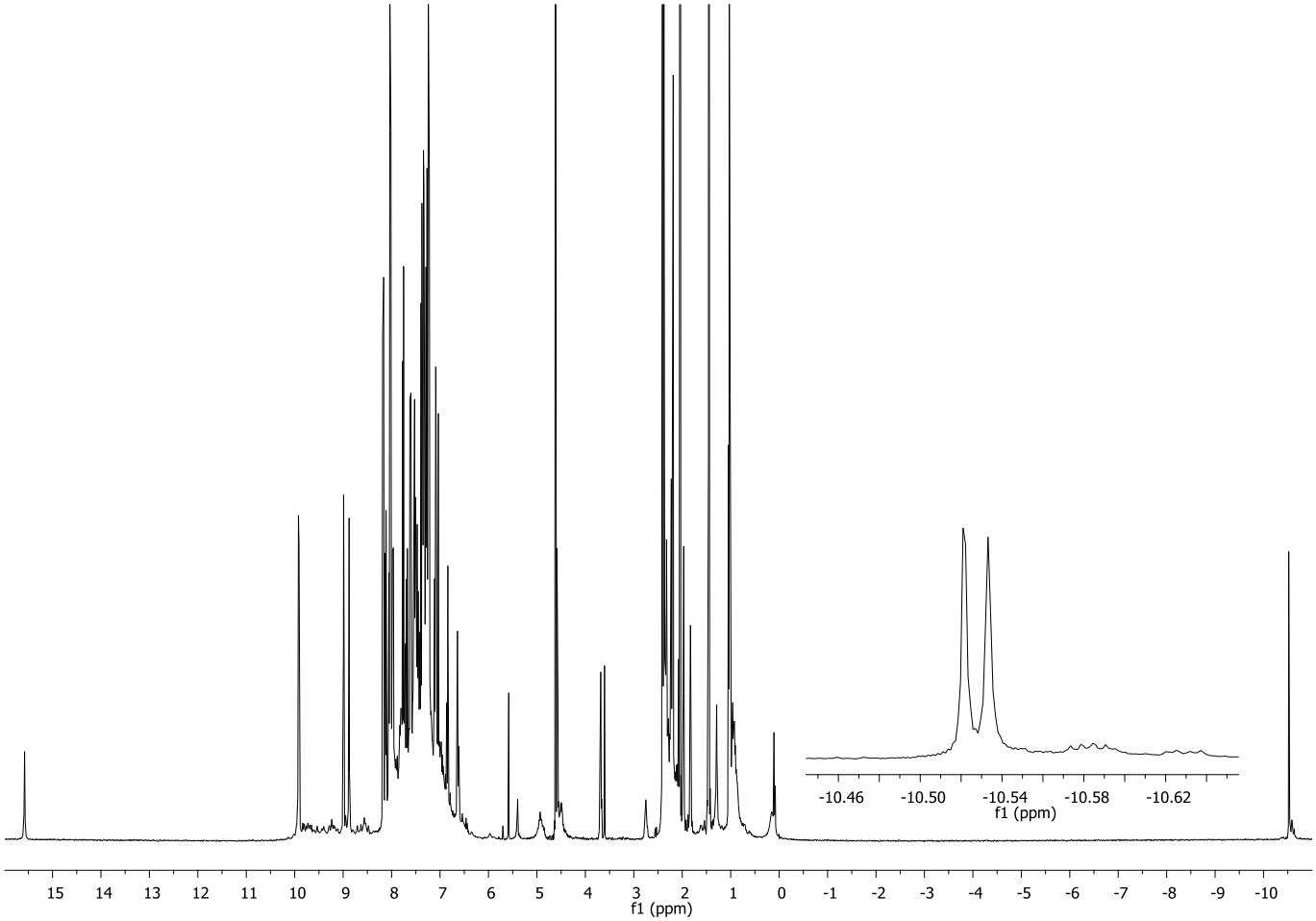
f1 (ppm)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-10.58
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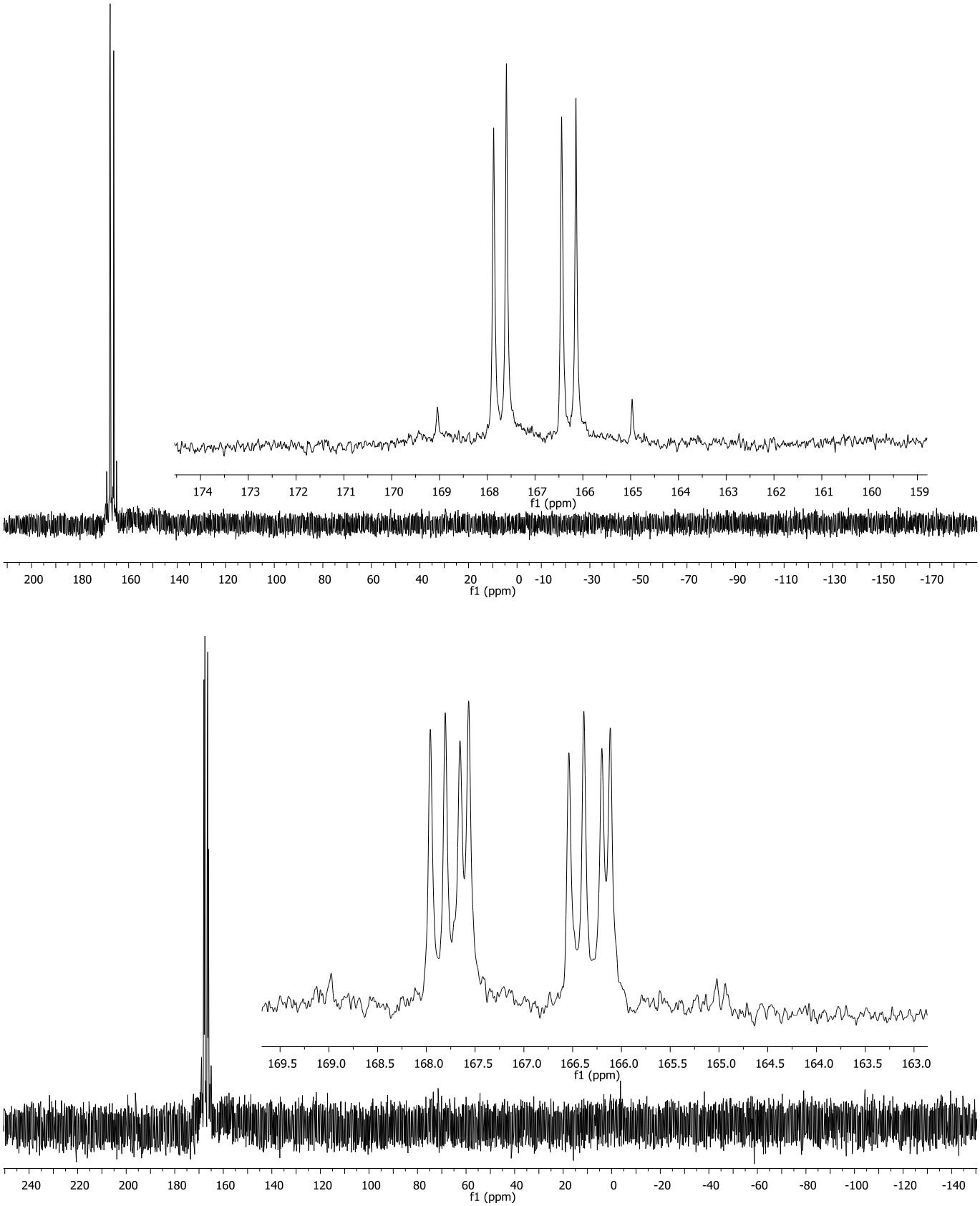
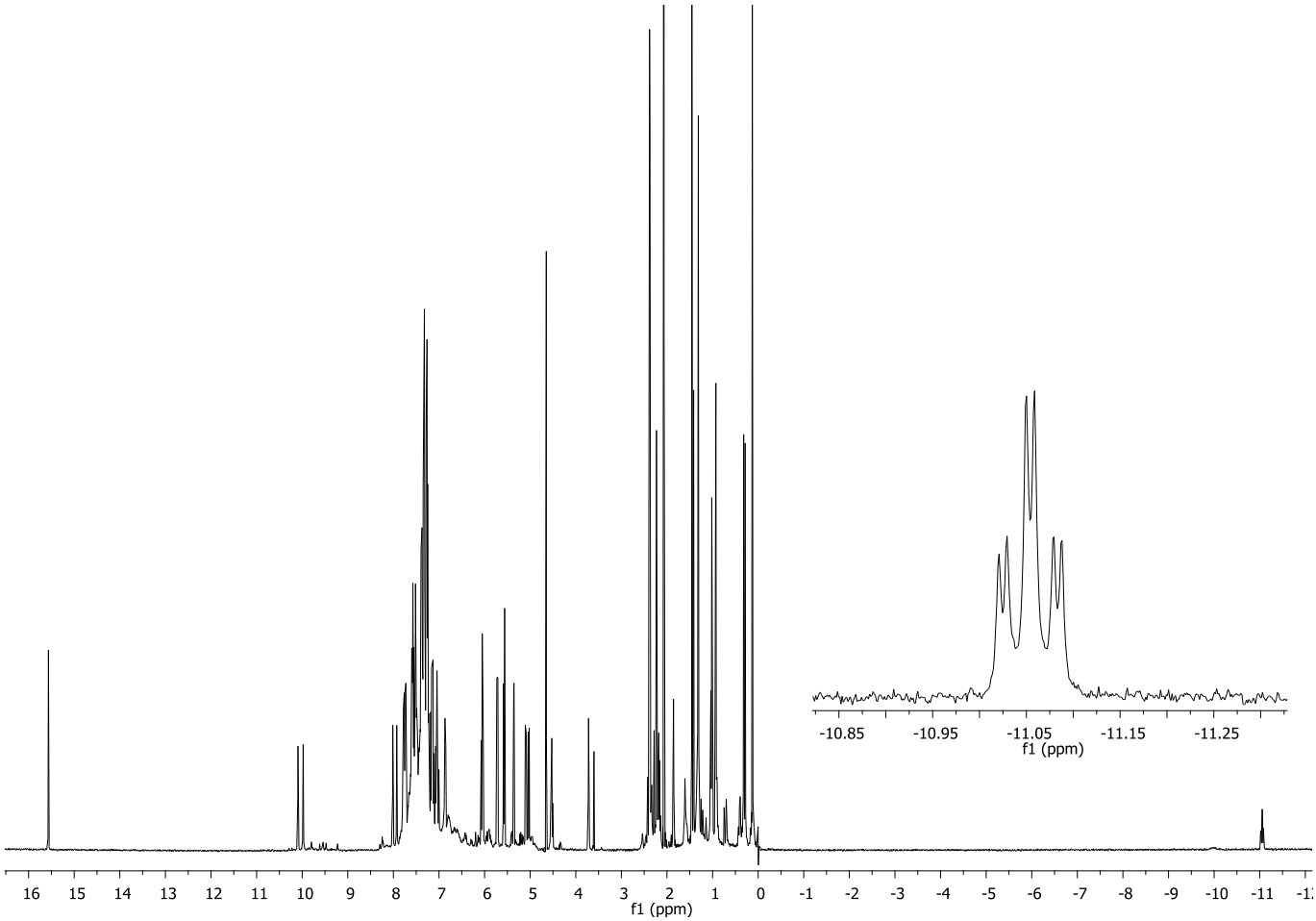


Figure S11. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle top), $^{31}P\{^{1}H\}$ (middle bottom) and ^{31}P (bottom) NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.02 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN + CD_2Cl_2 (1 : 1).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-11.15
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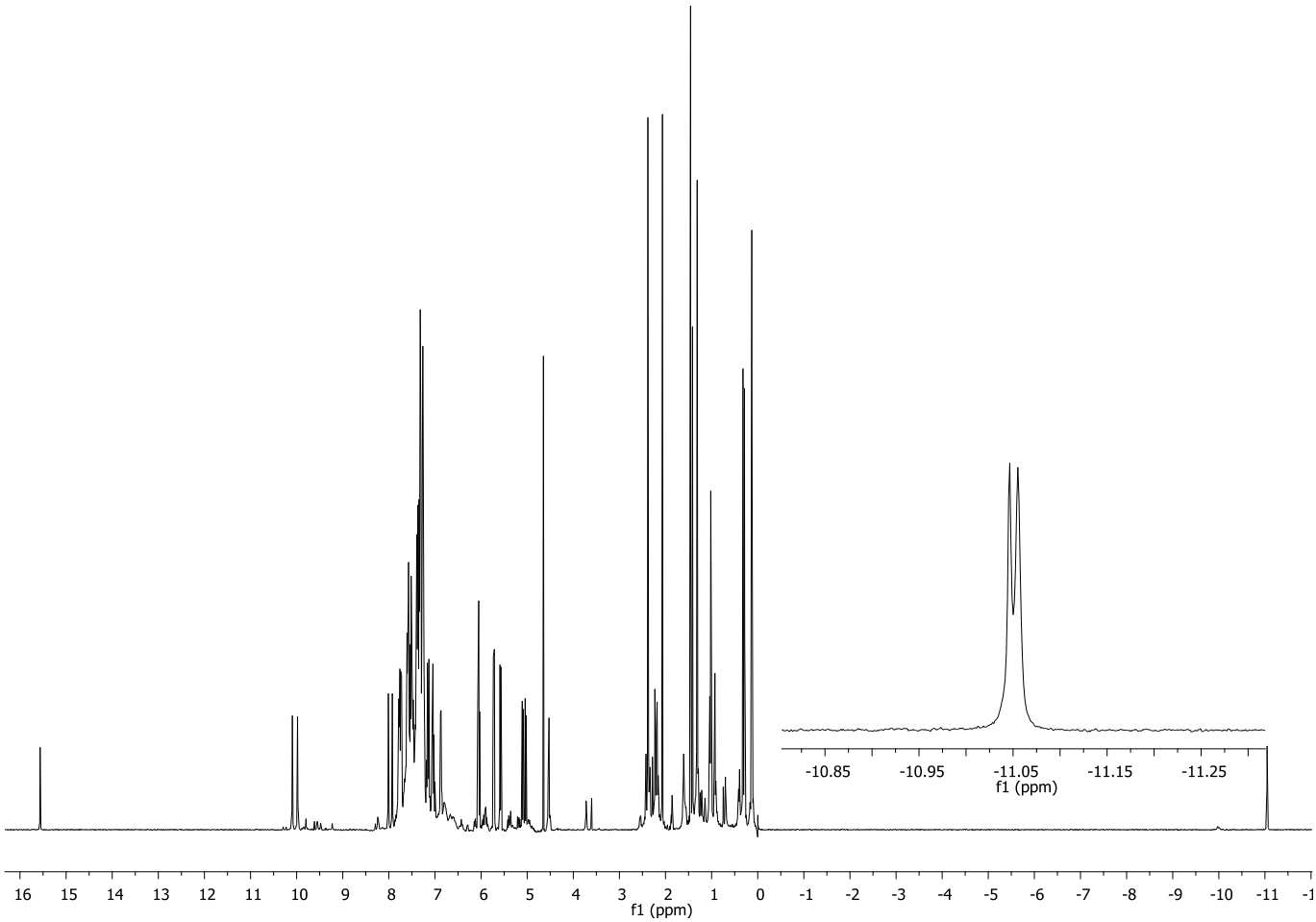
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f1 (ppm)

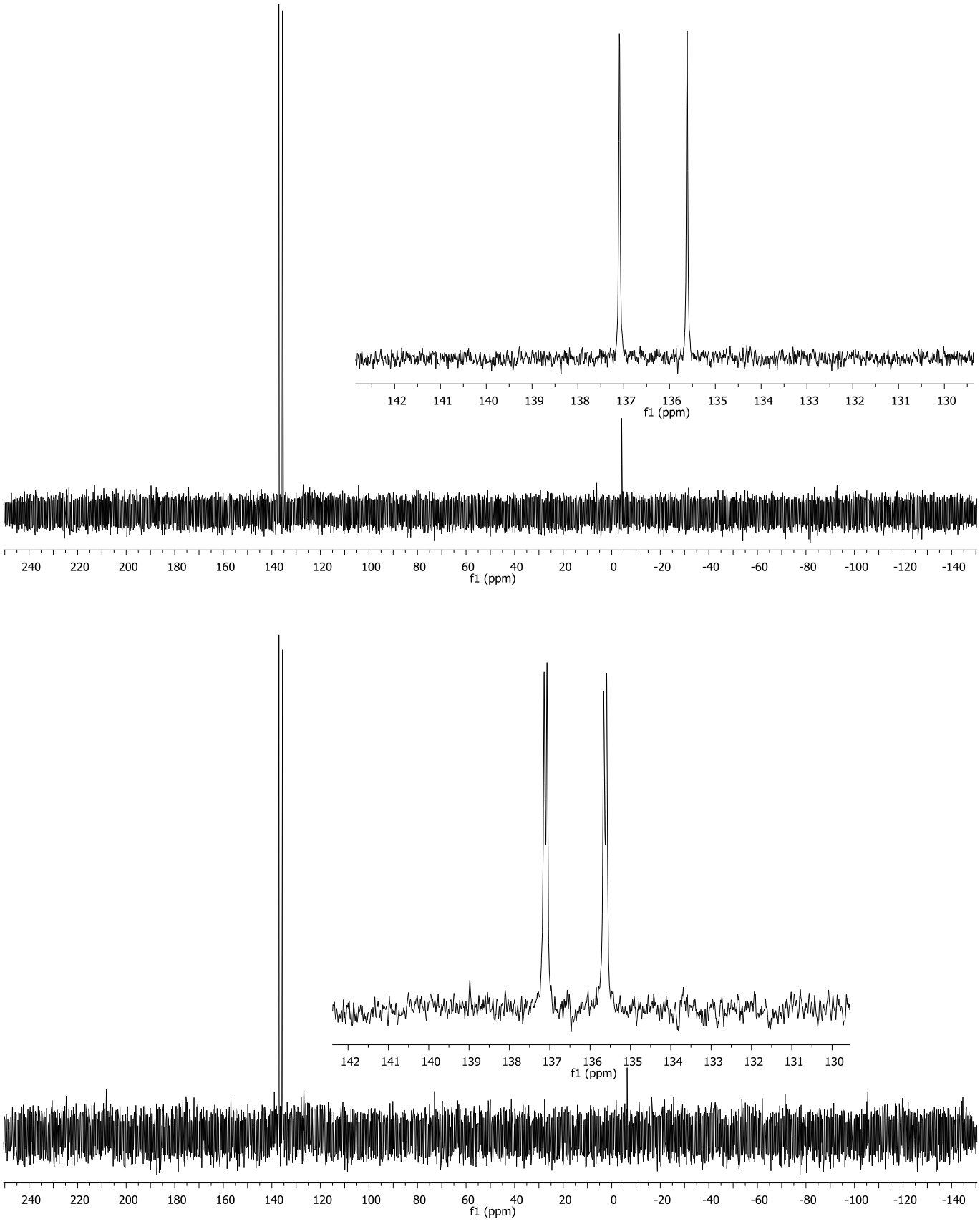


Figure S12. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle top), $^{31}P\{^{1}H\}$ (middle bottom) and ^{31}P (bottom) NMR spectra of [Rh(**L6**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN + CD_2Cl_2 (1 : 1).

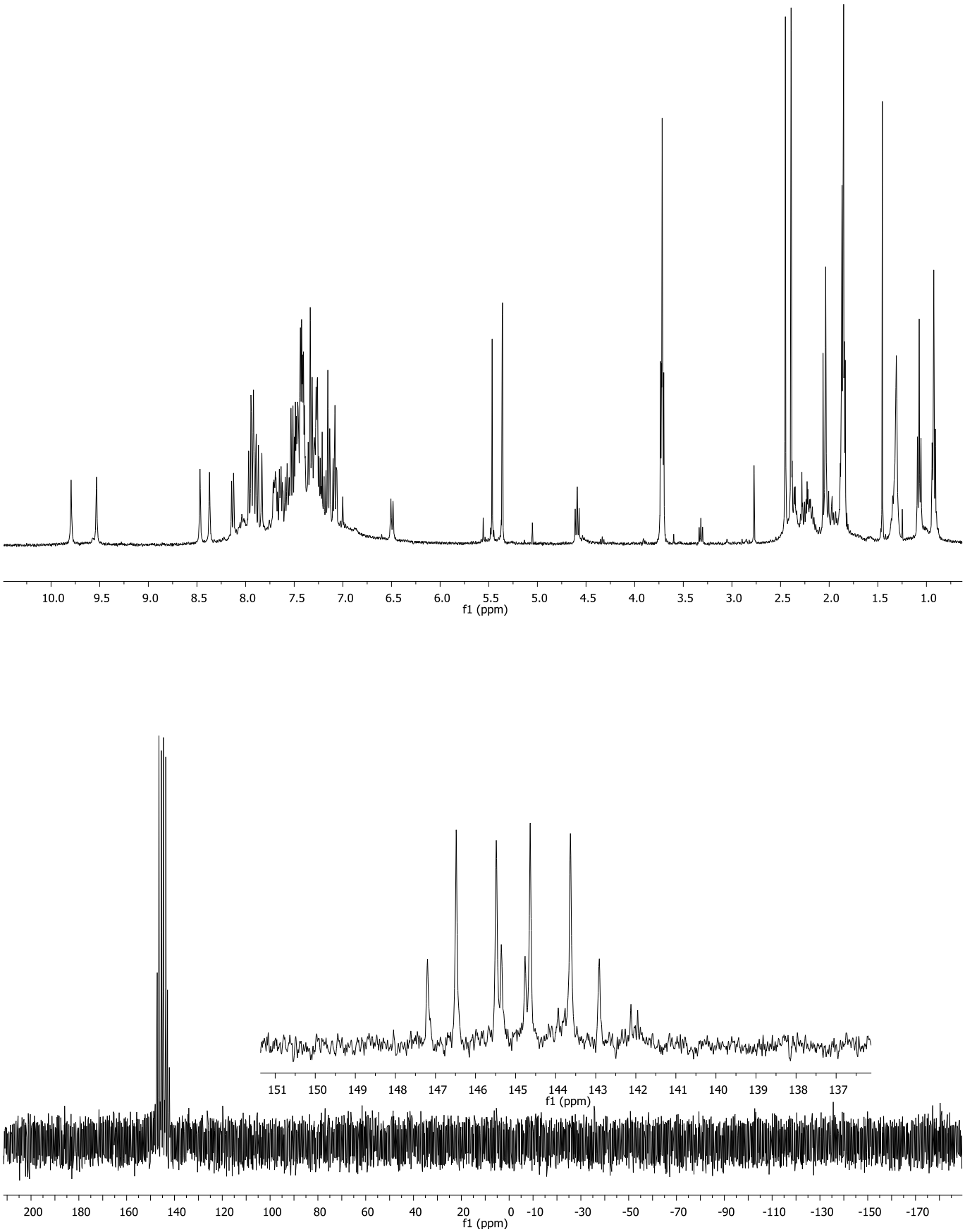


Figure S13. ^{1}H (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L7**)(acac)] complex (0.014 M solution), formed *in situ*, measured in CD_2Cl_2.

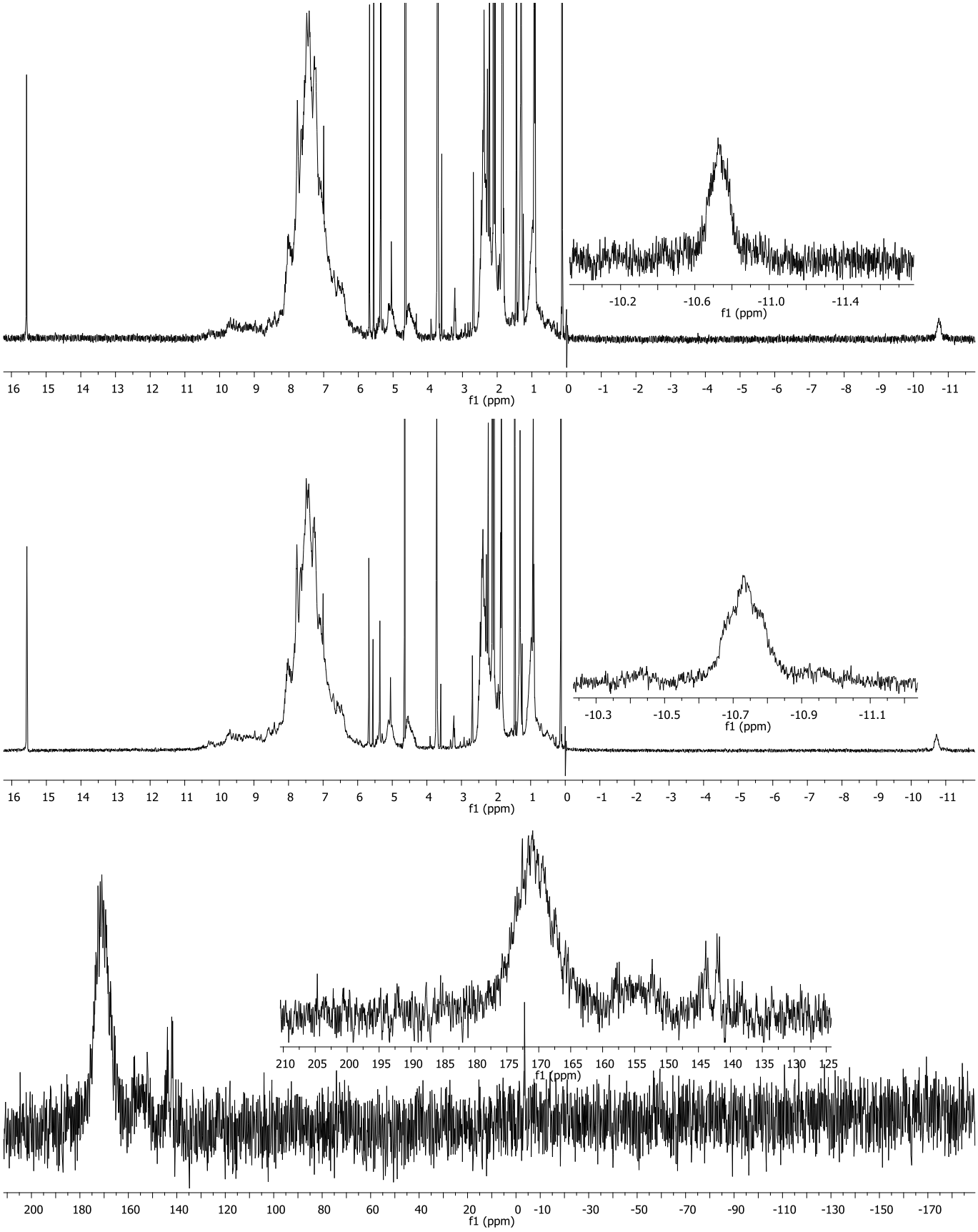


Figure S14. High pressure ^{1}H (top), $^{1}H\{^{31}P\}$ (middle) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of [Rh(**L7**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

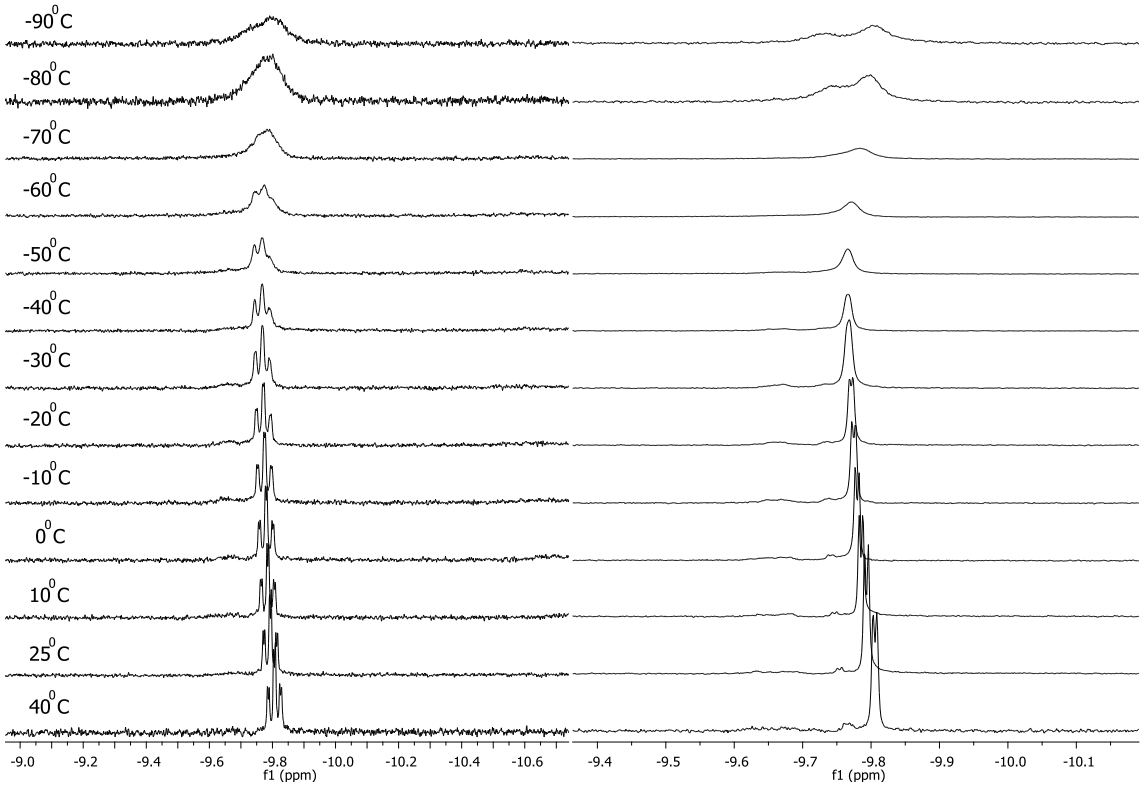


Figure S15. Variable temperature high pressure ^{1}H (left) and $^{1}H\{^{31}P\}$ (right) NMR spectra of [Rh(**L2**)$(CO)_2H$] complex (0.01 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

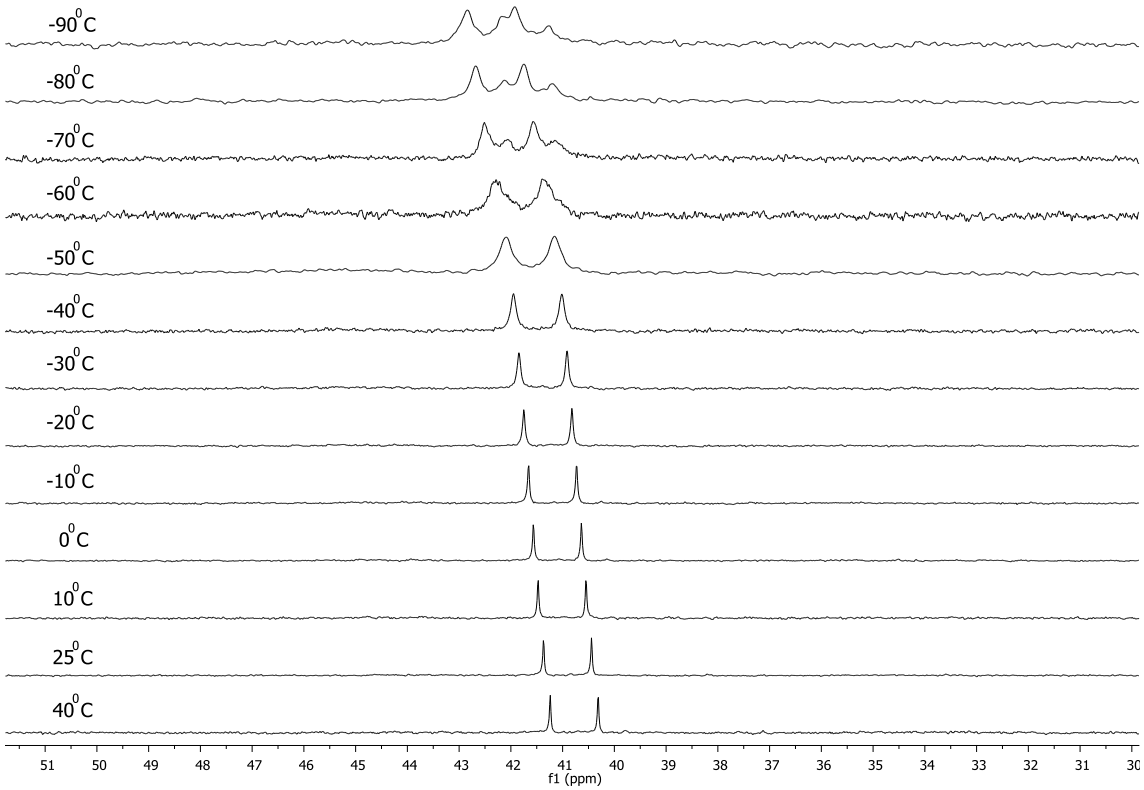


Figure S16. Variable temperature high pressure $^{31}P\{^{1}H\}$ NMR spectra of [Rh(**L2**)$(CO)_2H$] complex (0.01 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

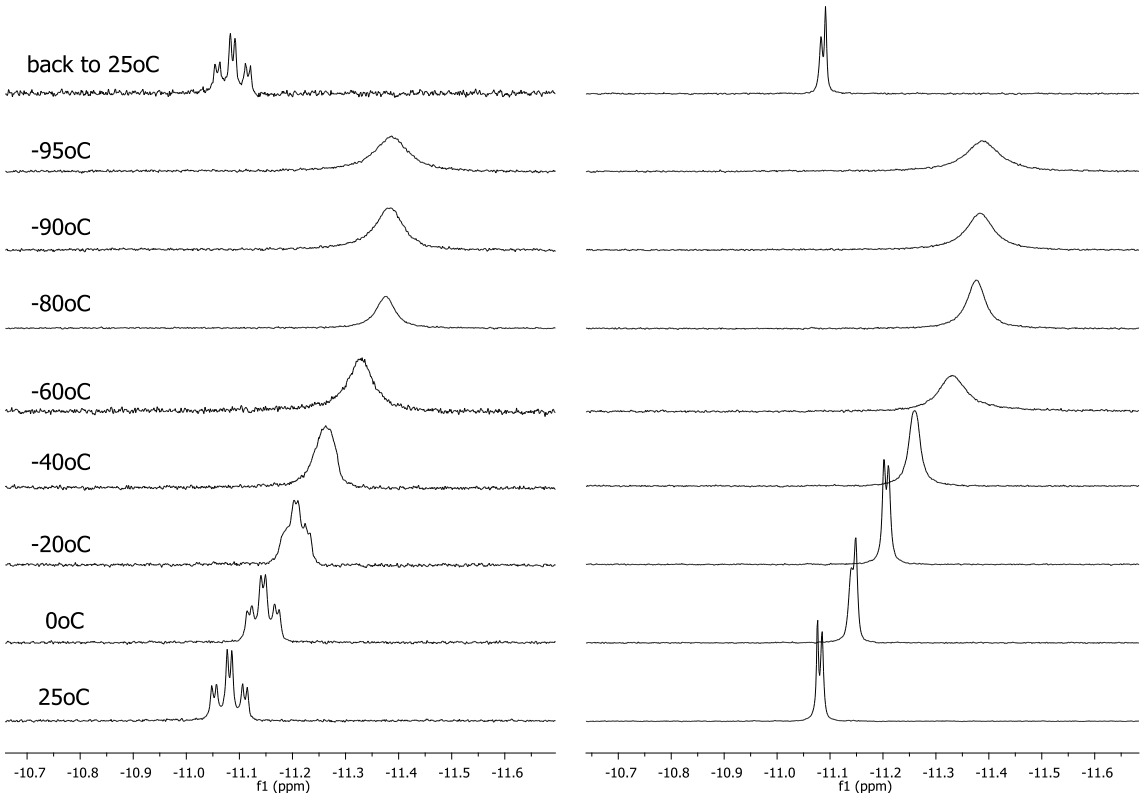


Figure S17. Variable temperature high pressure ^{1}H (left) and $^{1}H\{^{31}P\}$ (right) NMR spectra of [Rh(**L6**)$(CO)_2H$] complex (0.02 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

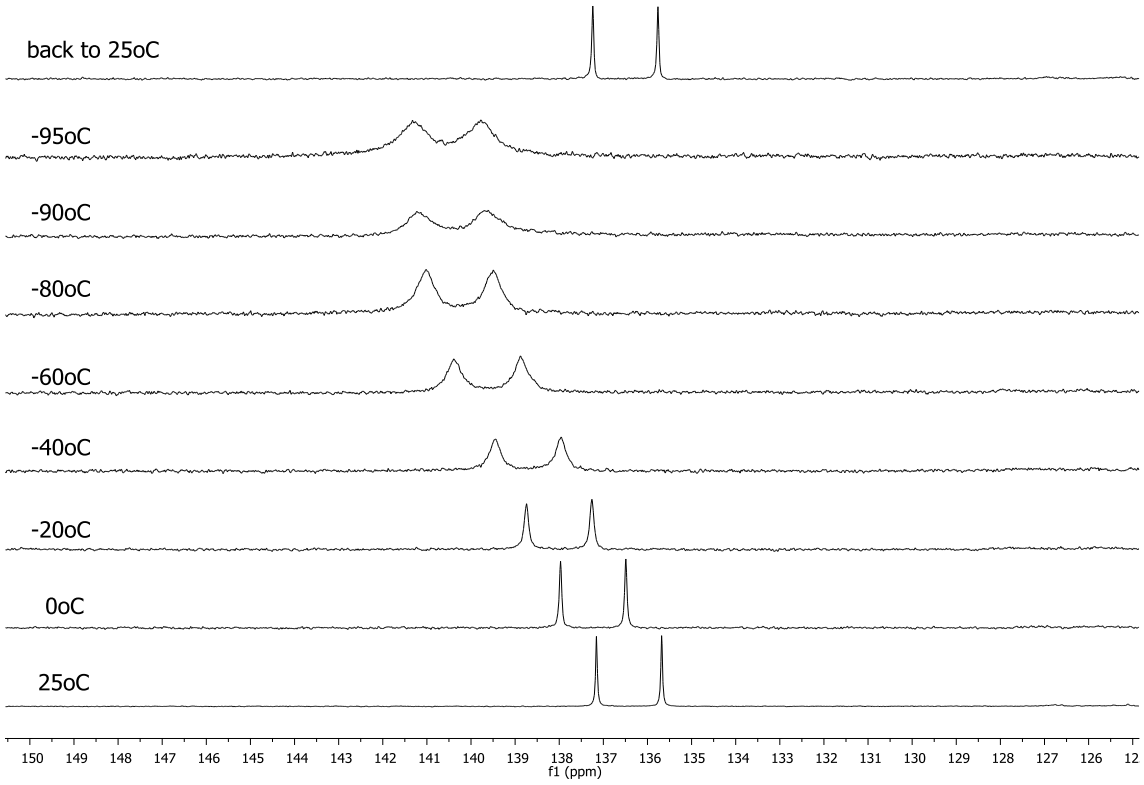


Figure S18. Variable temperature high pressure $^{31}P\{^{1}H\}$ NMR spectra of [Rh(**L6**)$(CO)_2H$] complex (0.02 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

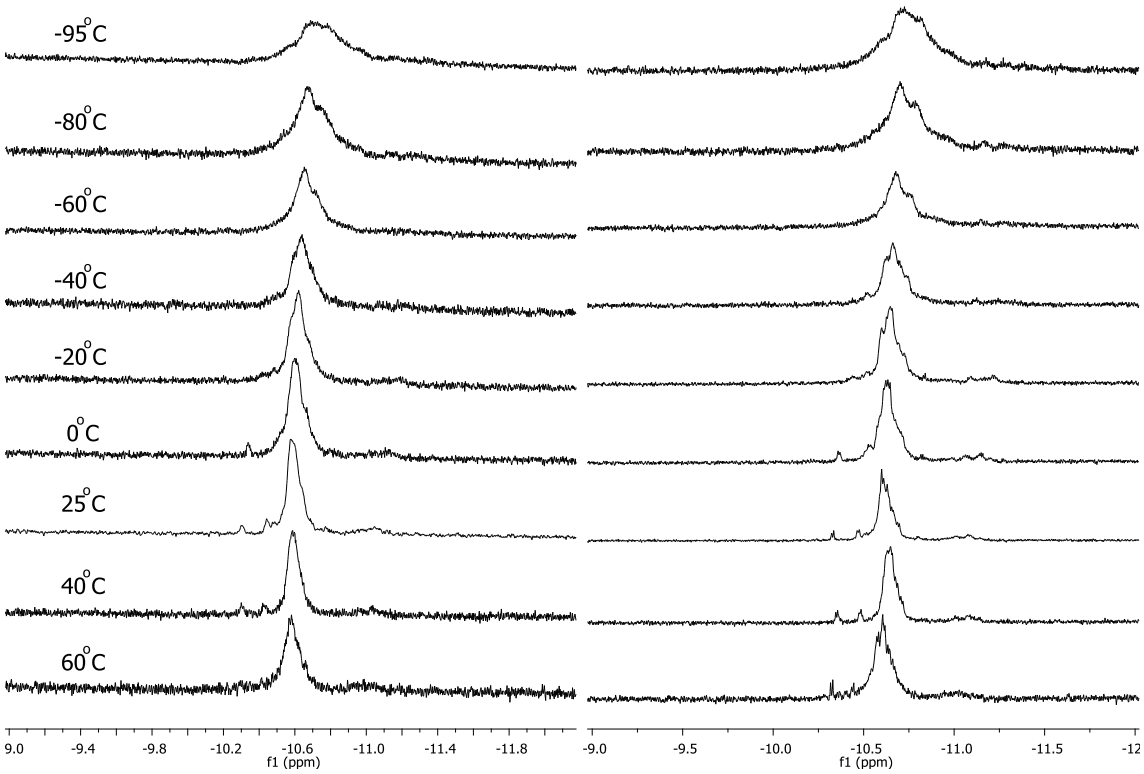


Figure S19. Variable temperature high pressure ^{1}H (left) and $^{1}H\{^{31}P\}$ (right) NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

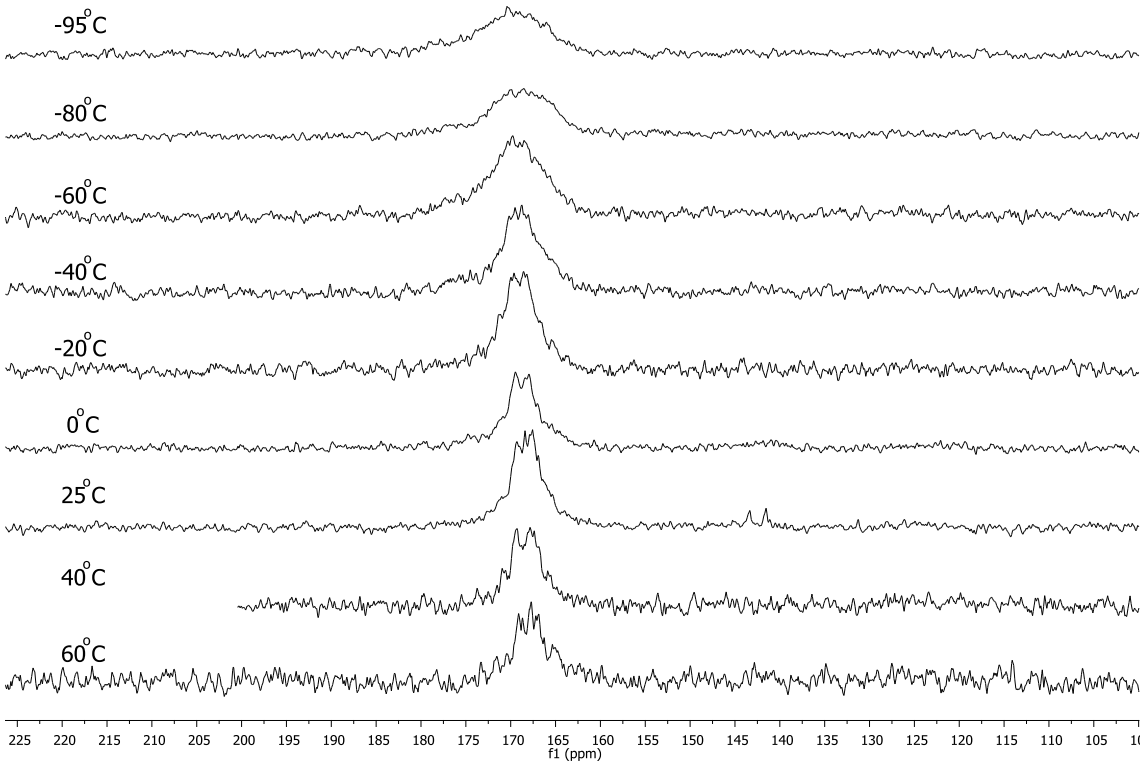


Figure S20. Variable temperature high pressure $^{31}P\{^{1}H\}$ NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.014 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_2Cl_2.

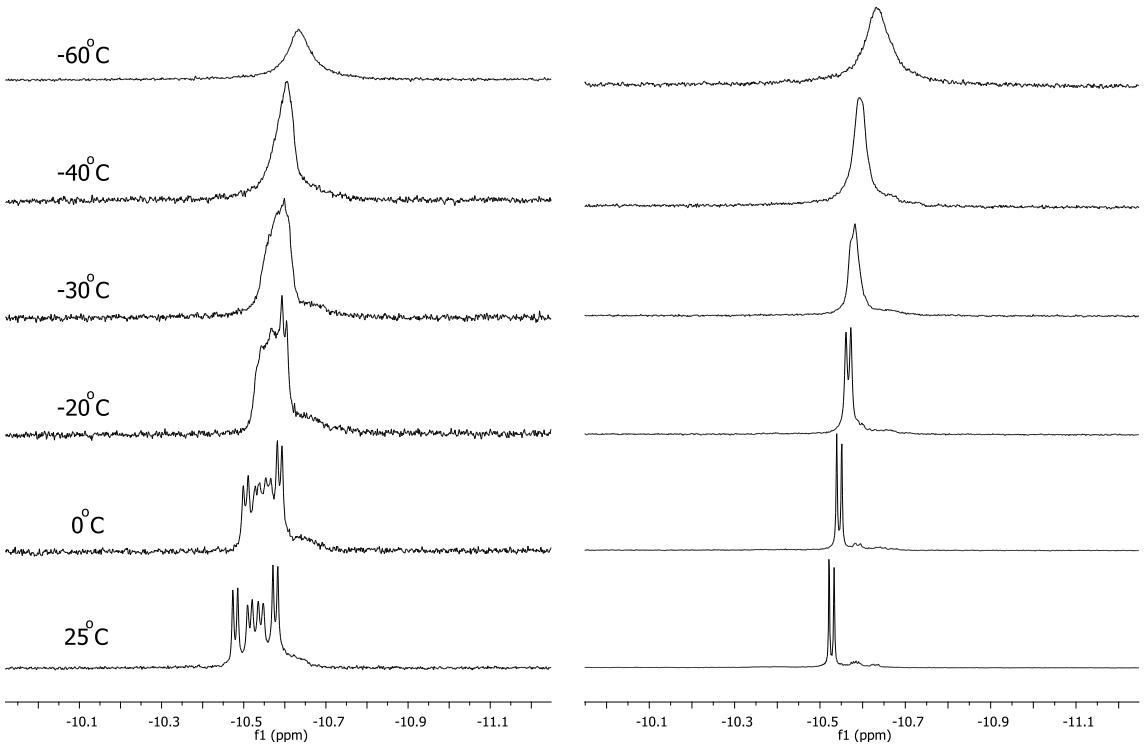


Figure S21. Variable temperature high pressure ^{1}H (left) and $^{1}H\{^{31}P\}$ (right) NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.02 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN + CD_2Cl_2 (1 : 1).

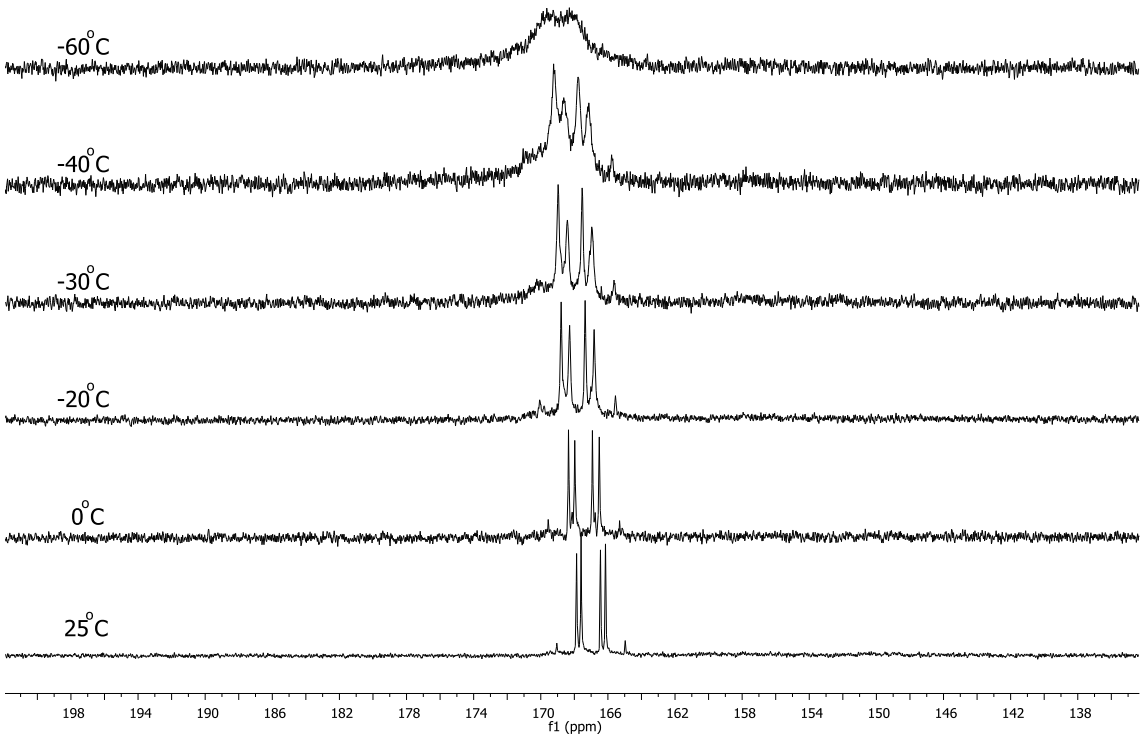


Figure S22. Variable temperature high pressure $^{31}P\{^{1}H\}$ NMR spectra of [Rh(**L5**)$(CO)_2H$] complex (0.02 M solution), formed *in situ*, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN + CD_2Cl_2 (1 : 1).

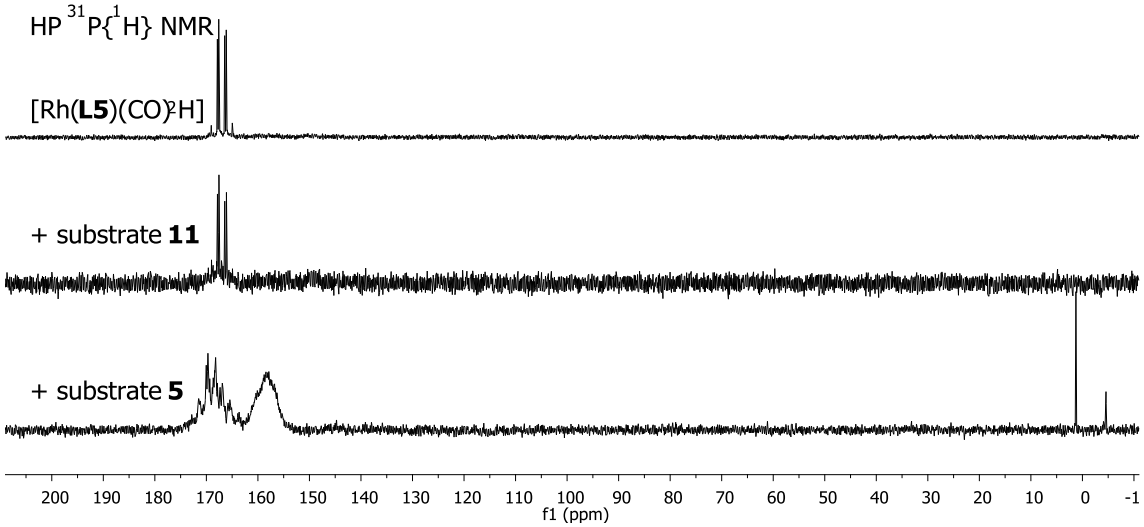


Figure S23. High pressure $^{31}P\{^{1}H\}$ NMR spectra of Rh(**L5**) complexes (0.01 M solution) in the absence (above) and in the presence of 10 equiv of substrate **11** (middle) or substrate **5** (below) and 15 equiv of TEA, formed in situ, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN + CD_2Cl_2 (1:1).

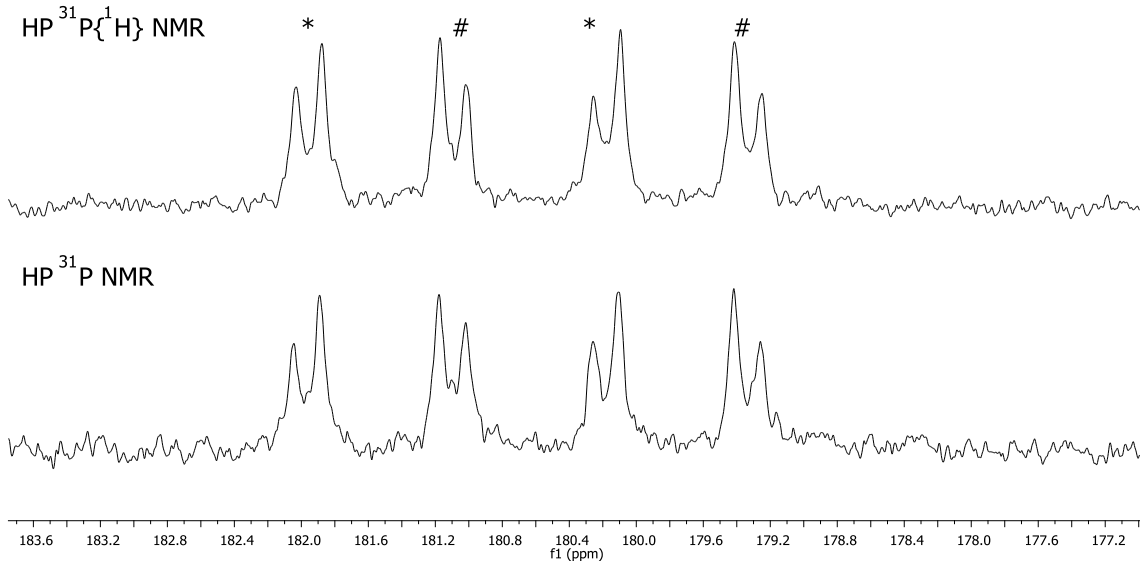


Figure S24. Fragments of high pressure $^{31}P\{^{1}H\}$ (above) and ^{31}P (below) NMR spectra of Rh(**L5**) complexes (0.01 M solution) in the presence of 10 equiv of product **8** and 15 equiv of TEA, formed in situ, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN; # and * denote signals of different phosphorus atoms.

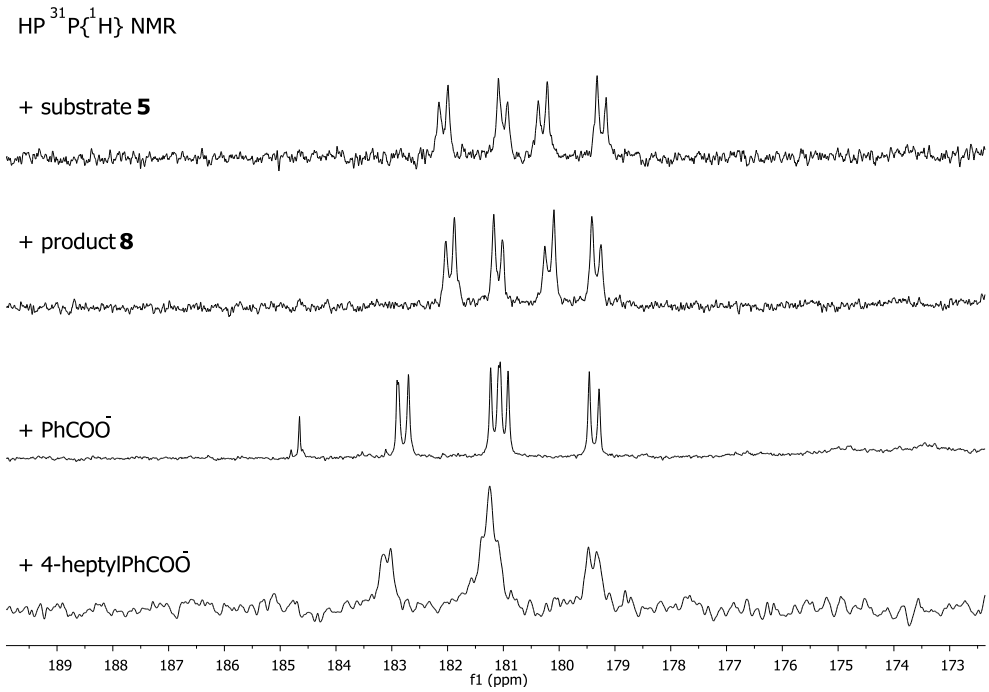


Figure S25. Fragments of high pressure $^{31}P\{^{1}H\}$ NMR spectra of Rh(**L5**) complexes (0.01 M solution) in the presence of 10 equiv of substrate **5** (top), product **8** (middle top), TBA-Benzoate (middle bottom) or 4-heptylbenzoic acid (bottom), with 15 equiv of TEA, formed in situ, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN.

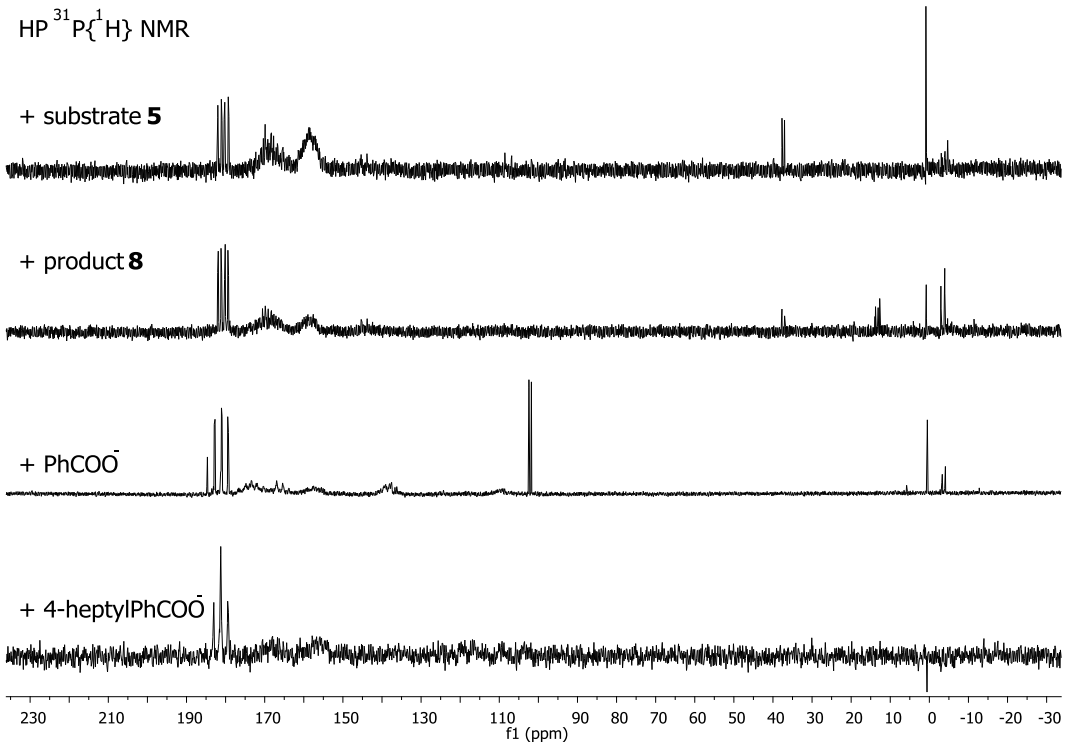


Figure S26. High pressure $^{31}P\{^{1}H\}$ NMR spectra of Rh(**L5**) complexes (0.01 M solution) in the presence of 10 equiv of substrate **5** (top), product **8** (middle top), TBA-Benzoate (middle bottom) or 4-heptylbenzoic acid (bottom), with 15 equiv of TEA, formed in situ, under 5 bar of syngas (CO/H_2, 1:1) measured in CD_3CN.

DOSY NMR experiments

The ^{1}H NMR spectra were measured using a Bruker AMX 400 MHz spectrometer: using Bruker's "ledbpgp2s" program with a diffusion delay of 180 ms and gradient length of 2 ms for each sample. The gradient strength was varied from 5 % to 95 %. The data were processed using the Bayesian DOSY Transform with the MestReNova 6.0.4 software package, with the processing parameters: the resolution factor of 1, one repetition, and 128 points in the diffusion dimension.

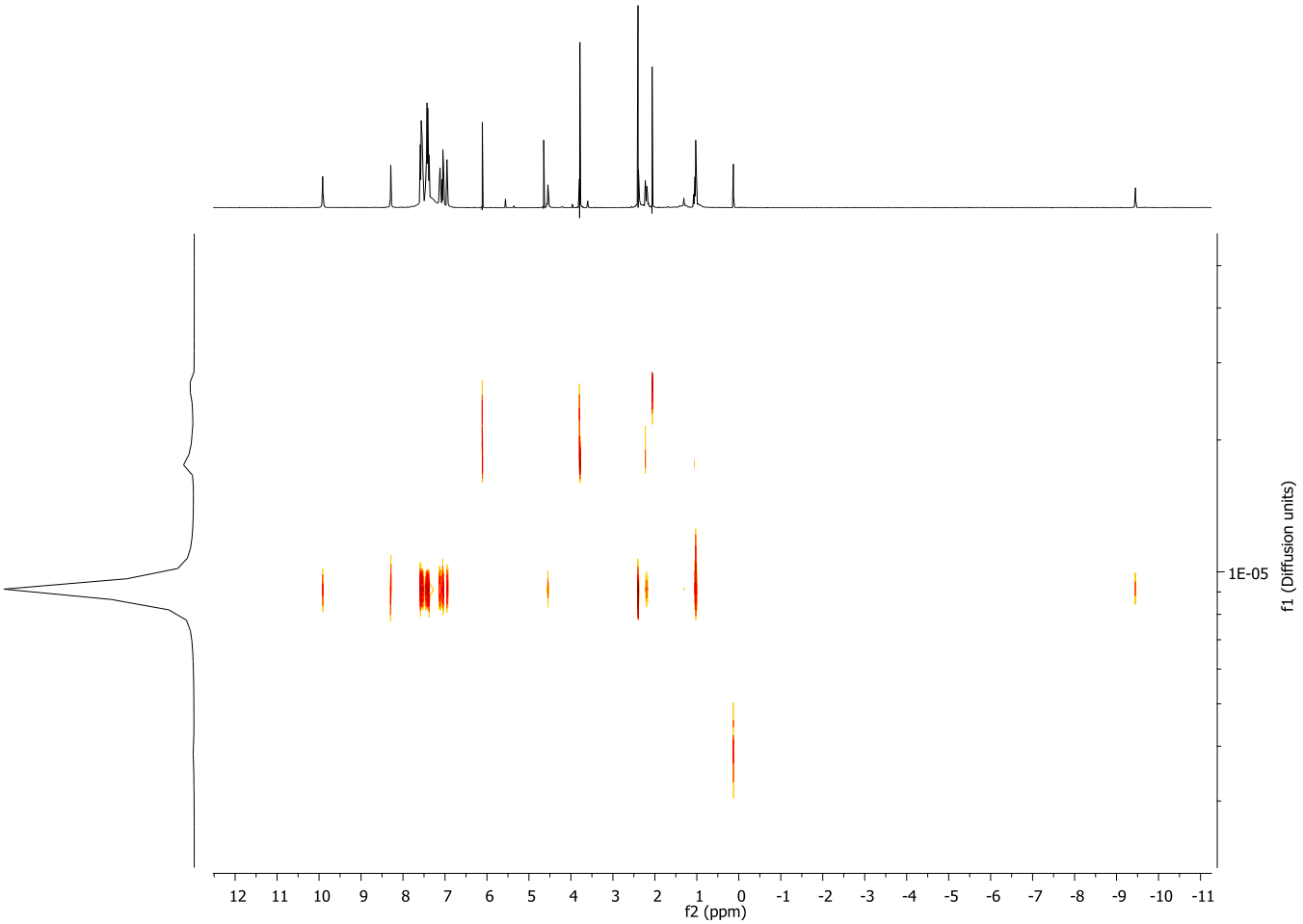


Figure S27. 2D DOSY HP ^{1}H NMR spectra of [Rh(**L1**)$(CO)_2$H] complex (0.02 M solution), formed *in situ* with 1,3,5-trimethoxybenzene as an internal standard, under 5 bar of syngas (CO/H_2, 1:1), measured in CD_2Cl_2.

Diffusion constant (D) for the complex = $9.15 \cdot 10^{-6}$ cm^2s^{-1} = $9.15 \cdot 10^{-10}$ m^2s^{-1}.

Using the Stokes–Einstein equation, $D = k \cdot T \cdot (6\pi \cdot \eta \cdot r_H)^{-1}$ (k = the Boltzmann constant, T = the absolute temperature, η = the fluid viscosity, r_H = the hydrodynamic radius), [9] the hydrodynamic radius of the complex can be estimated to $r_H = 5.55 \cdot 10^{-10}$ m.

[9] A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, *Chem. Soc. Rev*. **2008**, *37*, 479–489.

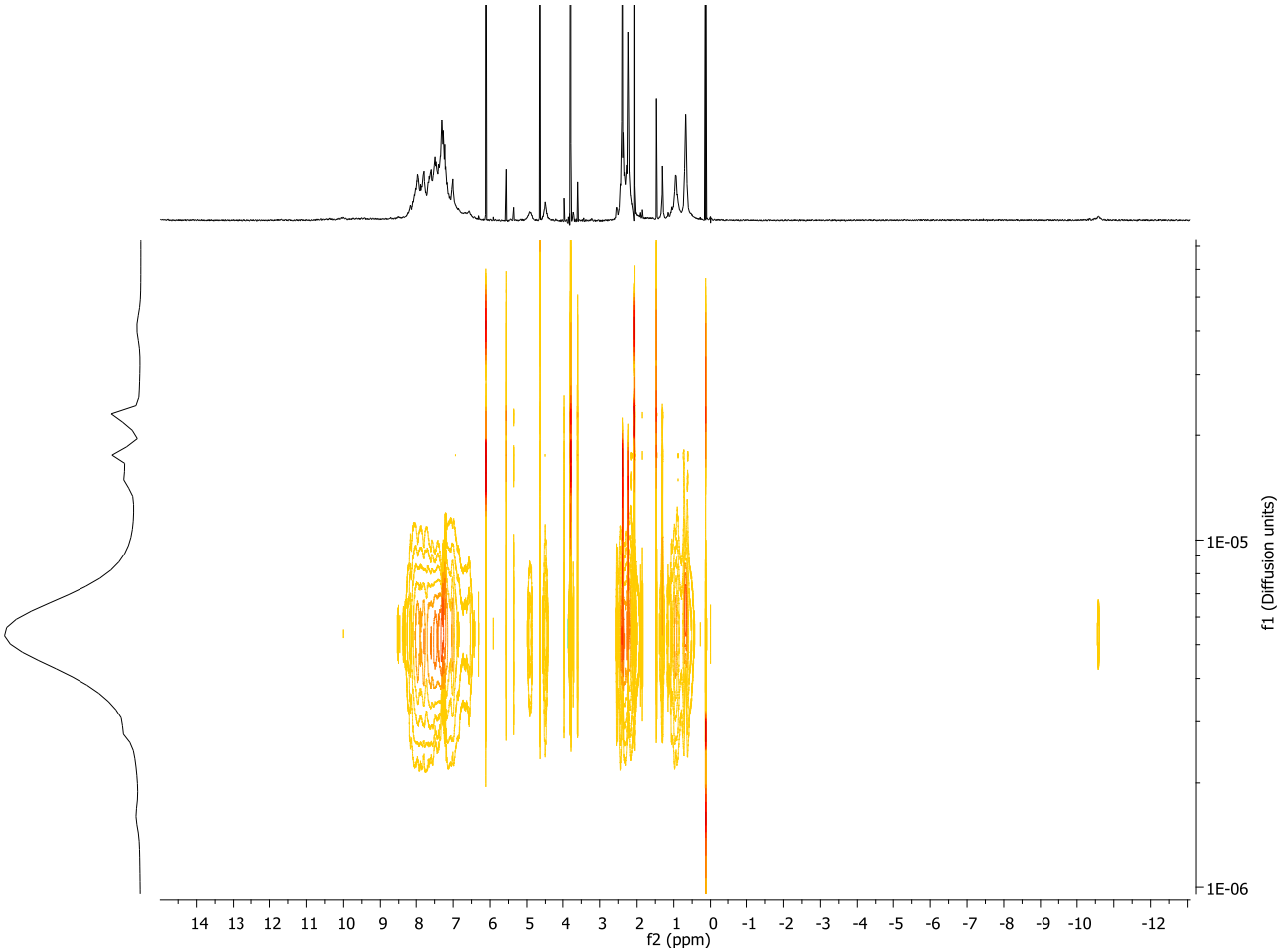


Figure S28. 2D DOSY HP ^{1}H NMR spectra of [Rh(**L5**)$(CO)_2$H] complex (0.02 M solution), formed *in situ*, with 1,3,5-trimethoxybenzene as an internal standard, under 5 bar of syngas (CO/H_2, 1:1), measured in CD_2Cl_2.

Diffusion constant (D) for the complex = $5.39 \cdot 10^{-6}$ cm^2s^{-1} = $5.39 \cdot 10^{-10}$ m^2s^{-1}

Using the Stokes–Einstein equation, $D = k \cdot T \cdot (6\pi \cdot \eta \cdot r_H)^{-1}$ (k = the Boltzmann constant, T = the absolute temperature, η = the fluid viscosity, r_H = the hydrodynamic radius),[9] the hydrodynamic radius of the complex can be estimated to $r_H = 9.42 \cdot 10^{-10}$ m.

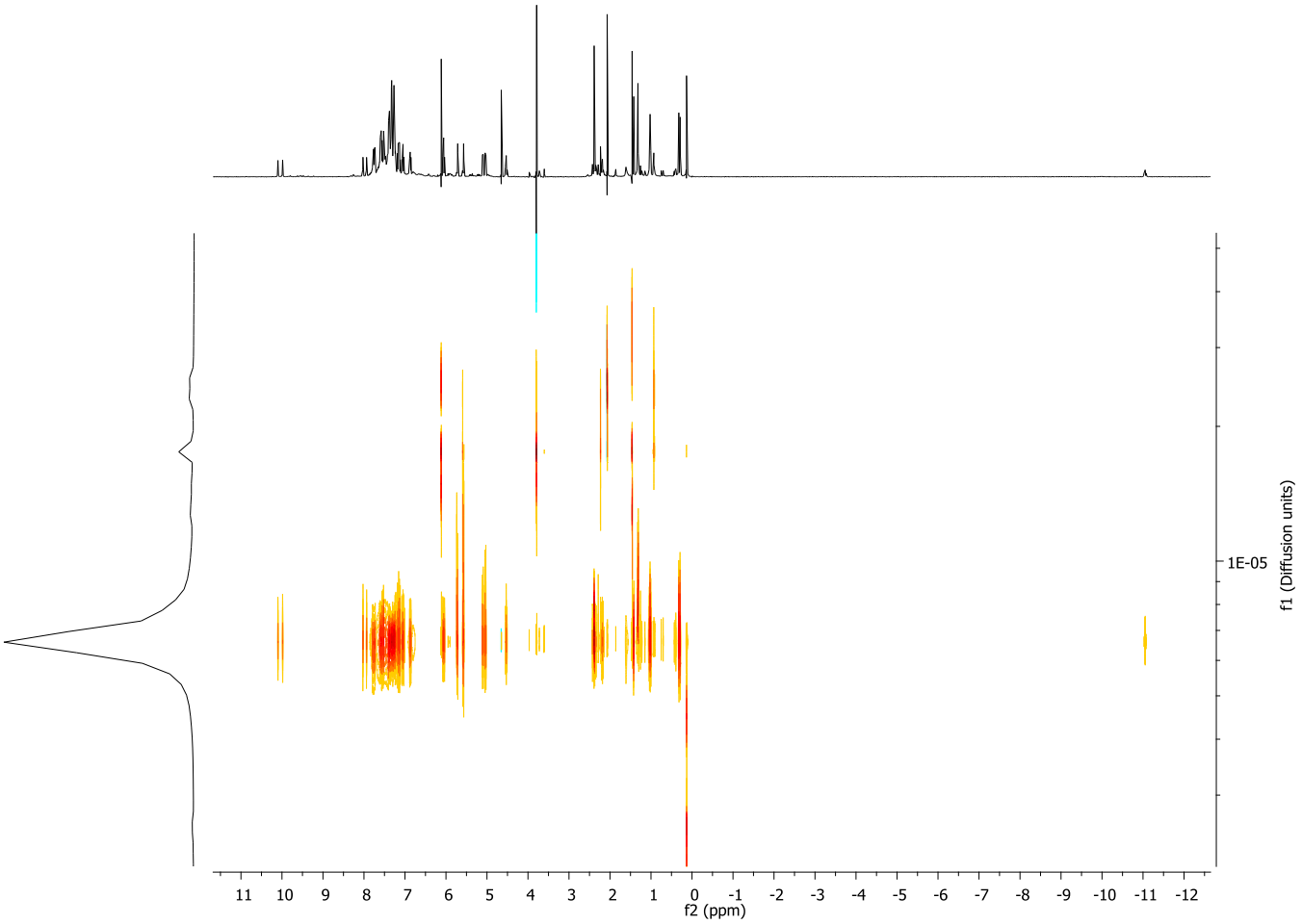


Figure S29. 2D DOSY HP ^{1}H NMR spectra of [Rh(**L6**)$(CO)_2$H] complex (0.02 M solution), formed *in situ*, with 1,3,5-trimethoxybenzene as an internal standard, under 5 bar of syngas (CO/H_2, 1:1), measured in CD_2Cl_2.

Diffusion constant (D) for the complex = $6.58 \cdot 10^{-6}$ cm^2s^{-1} = $6.58 \cdot 10^{-10}$ m^2s^{-1}

Using the Stokes–Einstein equation, $D = k \cdot T \cdot (6\pi \cdot \eta \cdot r_H)^{-1}$ (k = the Boltzmann constant, T = the absolute temperature, η = the fluid viscosity, r_H = the hydrodynamic radius),[9] the hydrodynamic radius of the complex can be estimated to $r_H = 7.71 \cdot 10^{-10}$ m.

High-pressure infrared (HP IR) studies under CO/H_2 pressure

These experiments were performed in a stainless steel (SS 316) 50 mL autoclave equipped with IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, 10 mm i.d., optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure transducer. The autoclave is equipped with a separately pressurized reservoir which allows for the addition of liquid to the main chamber, while it is pressurized.[10] If not stated otherwise, the HP IR experiments were performed at room temperature. All manipulations were conducted under inert atmosphere (argon or nitrogen).

In a flame-dried Schlenk flask equipped with a teflon stirring bar a solution of a ligand in DCM of desired concentration was prepared (the intial concentration is corrected for the dilution by the subsequent addition of the rhodium precursor solution; *vide infra*). In another flame-dried Schlenk flask, a solution of $Rh(CO)_2(acac)$ in DCM was prepared. Under inert atmosphere (via a syringe) the solution of the ligand (13.5 ml) was transferred to the main autoclave chamber, which was subsequently purged with 20bar of CO/H_2 and then pressurized at 20 bar of syngas. After full equilibration (~15 minutes), a background spectrum was collected, then the rhodium precursor solution (1.5 ml) was added (from the reservoir) and a series of kinetic measurements was started, following the development of the spectrum. For the rhodium deuteride studies, CO was used for the purging steps, followed by the pressurizng steps with D_2 (10 bar) and CO (additional 10 bar).

The IR experiments in the presence of an additive (the product or 4-heptylbenzoic acid) or with the substarte without the catalyst pre-formation were analogous to the above described coordination experiments, with the exception that the autoclave was initially charged with the solution of the ligand with the additive and TEA (of the desired ratio).

[10] P. C. J. Kamer, A. van Rooy, G. C. Schoemaker, P. W. N. M. van Leeuwen, *Coord. Chem. Rev.* **2004**, *248*, 2409-2424.

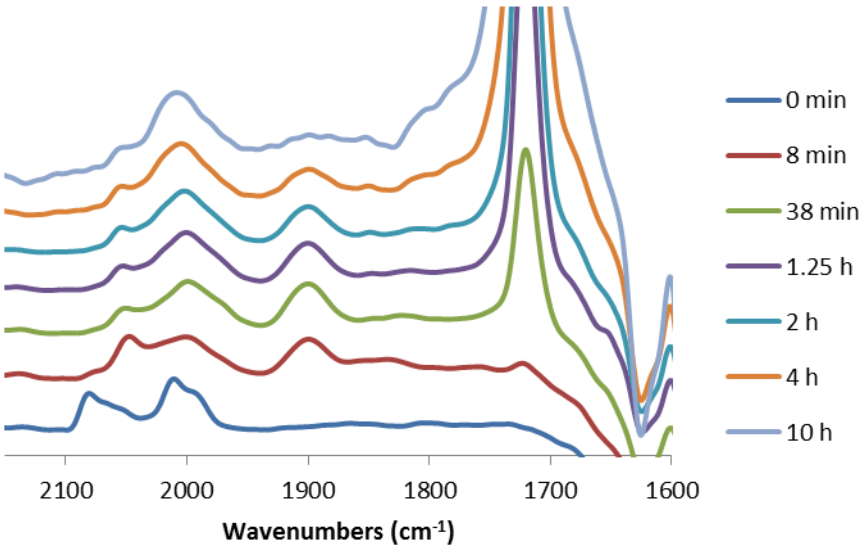


Figure S30. HP IR spectra of Rh(**L5**)$(CO)_2H$, formed in situ, in the presence of substrate **5** followed in time. Reagents and conditions: CO/H_2 = 1:1 (20 bar), CH_2Cl_2, 30°C, [substrate **5**] = 0.2 M, triethylamine (TEA, 1.5 equiv) was used as a base for anionic substrate generation, [$Rh(CO)_2(acac)$] (1 mol%), ligand **L5** (1.1 mol%). No incubation time for the catalyst pre-activation. "The 0 min spectrum" was collected immediately after the rhodium solution addition (no full pre-catalyst activation yet). Full conversion of the substrate reached before 10 h.

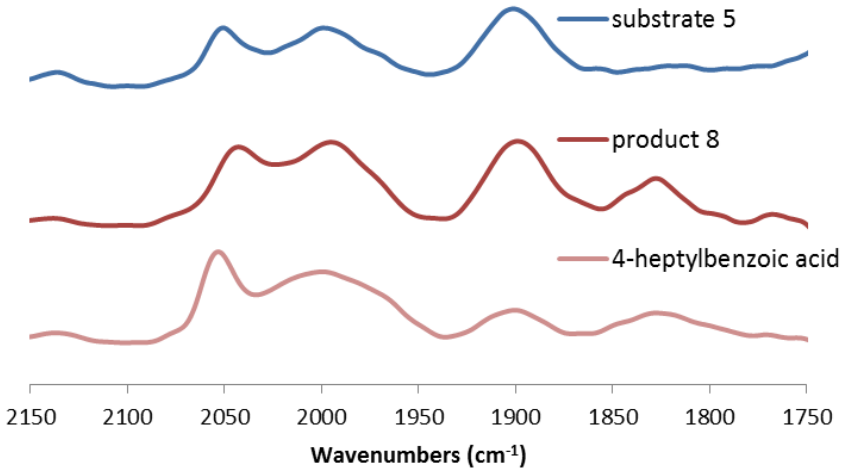


Figure S31. HP IR spectra of Rh(**L5**)$(CO)_2H$, formed in situ, in the presence of addtives: substrate **5**, product **8** or 4-heptylbenzoic acid, measure after 100 min of incubation. Reagents and conditions: CO/H_2 = 1:1 (20 bar), CH_2Cl_2, 22°C, [additive] = 0.2 M, triethylamine (TEA, 1.5 equiv) was used as a base for anionic additive generation, [$Rh(CO)_2(acac)$] (1 mol%), ligand **L5** (1.1 mol%).

Catalysis studies

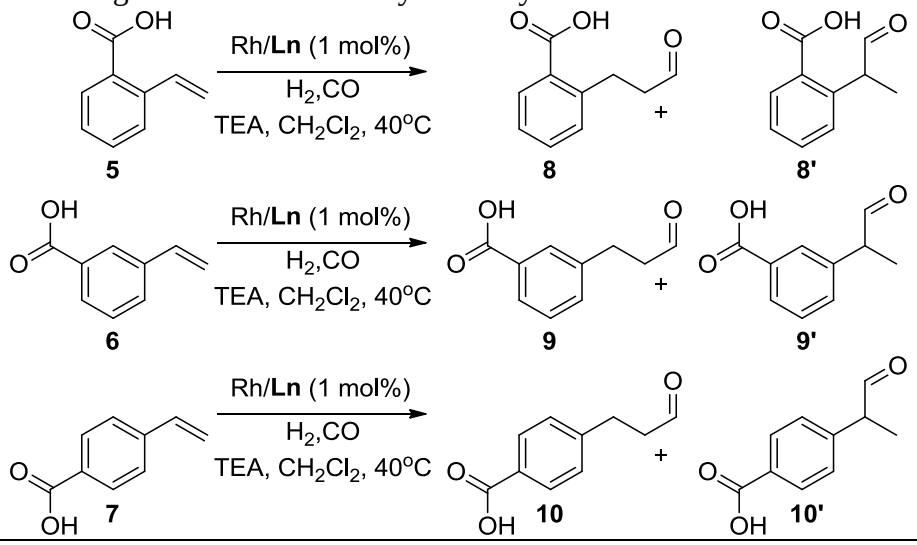
General procedure for the hydroformylation experiments

A stock solution for the hydroformylation experiments was prepared by charging a flame-dried Schlenk flask with $Rh(acac)(CO)_2$, ligand, base (if appropriate), internal standard (1,3,5-trimethoxybenzene) and appropriate solvent. The solution was stirred for 5 minutes and then transferred into 1.5ml reaction vessels equipped with mini teflon stir bars (under inert conditions), followed by substrate addition. The vessels were placed in a stainless steel autoclave (250 mL) charged with an insert suitable for 15 reaction vessels for conducting parallel reactions. Before starting the catalytic reactions, the charged autoclave was purged three times with 20 bar of syngas and then pressurized at 20 bar of syngas. The experiments at 1 bar of syngas were performed in an analogicall maner but in a standard Schlenk flask equipped with a gas ballon. The reaction mixtures were stirred at the appropriate temperature for the required reaction time, after which the pressure was released and the regioselectivity and the conversion were determined by NMR and/or GC. Additionally, in selected cases, the reaction mixtures were analyzed by electrospray ionization mass spectrometry (ESI MS).

For ^{1}H NMR analysis, small portions (~75 μl) of each reaction mixture were taken, from which the solvent was evaporated. Then, the residues were diluted to 0.7ml with DMSO-d_6 and ^{1}H NMR spectra were recorded and compared with a ^{1}H NMR spectrum of the initial reaction mixture (before the reaction). The ^{13}C NMR analysis was performed with analogic manner, but larger portions of (700 μl) of each reaction mixture were taken. No by-products (hydrogenation, double bond isomerisation) were observed (except where noted).

For GC analysis of reaction mixtures with carboxylic acid substrates, small portions (100 μl) of each reaction mixture were taken, from which the solvent was evaporated (100 mbar, 40ºC) and subsequently a pinch of $KHCO_3$ and DMF (0.3 ml) were added, followed by stirring for 5 minutes. Then, CH_3I (0.1 ml) was added and the stirring was continued for 1h. Then, samples were diluted with ethyl acetate (2ml) and water (1ml), the organic layers were separated and filtered via a HPLC syringe filter, and the GC spectra were recorded.

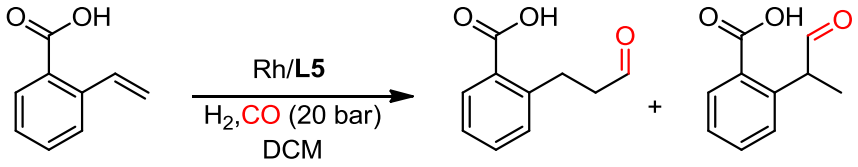
Table S1. Evaluation of ligands **L1**-**L7** for the hydroformylation of **5**-**7**.[a]



amount of TEA			1.5 equiv		1.0 equiv		0.5 equiv	
Entry	ligand	substrate	% conv.	% linear	% conv.	% linear	% conv.	% linear
1	**L1**	**5**	27	78	11	80	27	72
2	**L2**	**5**	58	87	22	85	64	85
3	**L3**	**5**	15	17	19	17	54	16
4	**L4**	**5**	33	55	50	57	81	56
5	**L5**	**5**	100	> 98	100	> 98	100	> 98
6	**L6**	**5**	76	> 98	100	> 98	100	> 98
7	**L7**	**5**	50	45	94	67	100	54
8	**L1**	**6**	93	19	52	16	63	14
9	**L2**	**6**	100	38	91	32	100	25
10	**L3**	**6**	40	9	41	8	56	6
11	**L4**	**6**	83	5	87	3	85	3
12	**L5**	**6**	100	75	100	73	100	67
13	**L6**	**6**	93	89	94	85	100	73
14	**L7**	**6**	96	18	80	17	100	18
15	**L1**	**7**	86	9	53	10	46	8
16	**L2**	**7**	100	14	88	18	95	21
17	**L3**	**7**	67	11	75	8	89	9
18	**L4**	**7**	66	15	74	11	87	10
19	**L5**	**7**	100	9	100	15	100	20
20	**L6**	**7**	45	39	61	24	96	28
21	**L7**	**7**	76	13	96	7	100	12

[a] Reagents and conditions: [substrate]=0.2M, TEA (0.5-1.5 equiv as specified), [$Rh(CO)_2(acac)$] (1 mol%), ligands **L1**-**L4** (1.5 mol%), ligands **L5**-**L7** (1.1 mol%), CO/H_2=1:1 (20 bar), 40°C, 24h. Conversion and regioselectivity determined by ^1H NMR analysis of the reaction mixture – '% linear' stands for yield of product **8**, **9** or **10**, for reactions woth **5**, **6** and **7**, respectively. No side products were observed for substrates **5** and **6**. Products of **7**, that is, aldehydes **10** and **10'** are reactive under the reaction conditions and tend to condensate, lowering the chemoselectivity.

Table S2. Hydroformylation of 2-vinylbenzoic acid **5** with the Rh(**L5**) – variation of reaction conditions.[a]

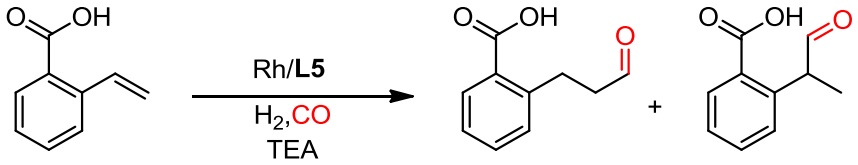


5 linear (**L**) branched (**B**)

Entry	[**5**] (M)	base	Rh (mol%)	temp. (°C)	time (h)	Regioselectivity L (%)	Regioselectivity B (%)	Side products[b]	Conversion (%)
1	**0.2**	**DIPEA 1.5 equiv.**	**1%**	**rt**	**24**	**>98**	**0**	**-**	**100%**
2	0.2	DIPEA 1.5 equiv.	0.25%	rt	24	>98	0	-	54%
3	0.2	DIPEA 1.5 equiv.	1%	40	24	>98	0	-	100%
4	0.2	TEA 1.5 equiv.	1%	40	24	>98	0	-	100%
5	**0.2**	**DIPEA 1.5 equiv.**	**0.25%**	**40**	**24**	**>98**	**0**	**-**	**100%**
6	0.2	DIPEA 1.5 equiv.	0.1%	40	24	>98	0	-	57%
7	1	DIPEA 1.5 equiv.	0.2%	40	24	>98	0	-	76%
8	1	DIPEA 1.5 equiv.	0.1%	40	24	>98	0	-	34%
9	0.2	DIPEA 1.5 equiv.	1%	60	24	>98	0	+	100%
10	**0.2**	**DIPEA 1.5 equiv.**	**0.1%**	**60**	**24**	**>98**	**0**	**+**	**100%**
11	1	DIPEA 1.5 equiv.	0.1%	60	24	>98	0	++	100%
12	0.2	DIPEA 1.5 equiv.	0.1%	80	24	>98	0	++	100%
13	1	DIPEA 1.5 equiv.	0.1%	80	24	>98	0	+++	100%
14	0.2	TEA 1.5 equiv.	0.25%	80	1	>98	0	+	100%
15	0.2	TEA 1 equiv.	0.25%	80	1	>98	0	+	100%
16	0.2	TEA 0.5 equiv.	0.25%	80	1	>98	0	-	100%
17	**0.2**	**TEA 0.5 equiv.**	**0.05%**	**80**	**1**	**>98**	**0**	**-**	**100%**
18	**0.2**	**TEA 0.5 equiv.**	**0.005%**	**80**	**1**	**>98**	**0**	**-**	**42%**
19	**0.2**	**TEA 0.5 equiv.**	**0.05%**	**100**	**1**	**>98**	**0**	**-**	**100%**
20	**0.2**	**TEA 0.5 equiv.**	**0.005%**	**100**	**1**	**>98**	**0**	**-**	**67%**
21	**0.2**	**TEA 0.5 equiv.**	**0.002%**	**100**	**1**	**>98**	**0**	**-**	**10%**
22	**0.2**	**TEA 0.5 equiv.**	**0.05%**	**120**	**1**	**>98**	**0**	**+**	**100%**

[a] Reagents and conditions: $Rh(CO)_2(acac)$ as a rhodium source, Rh : ligand **L5**, 1/1.1, CO/H_2 = 1/1 (20bar), CH_2Cl_2 as a solvent, regioselectivity and conversion were determined by ^1H NMR analysis of the crude reaction mixture; [b] The amount of side products, if present, was estimated by ^1H NMR analysis of the crude reaction mixture: (-) no (+) <5%, (++) 5-15%, (+++) > 15% of side products – ESI MS analysis reveals that these are products of the aldol condensation of the hydroformylation aldehyde product.

Table S3. Hydroformylation of 2-vinylbenzoic acid **5** with the Rh(**L5**) – variation of reaction conditions.[a]

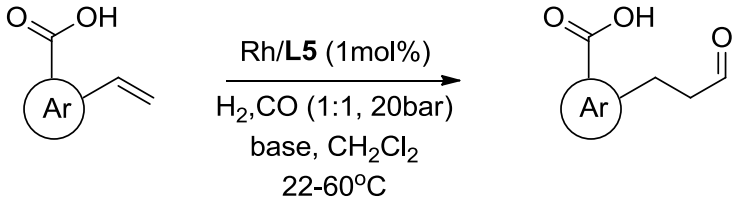


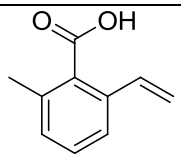
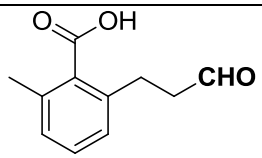
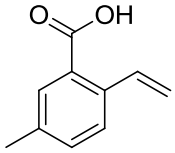
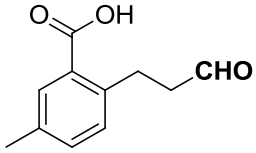
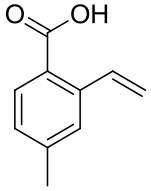
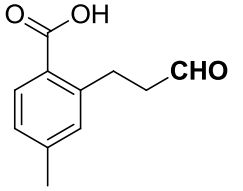
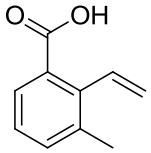
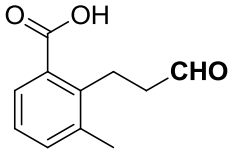
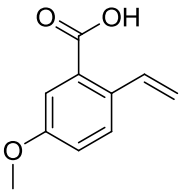
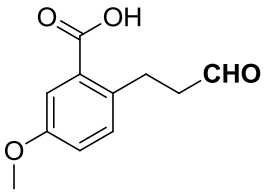
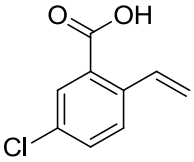
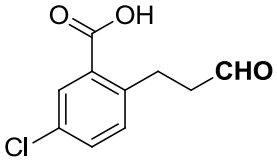
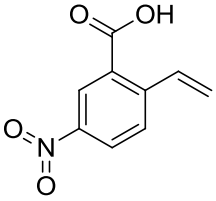
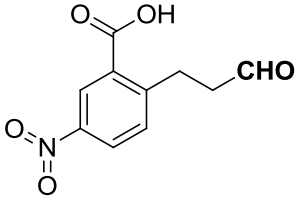
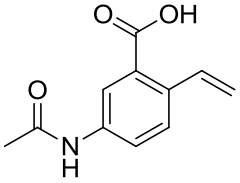
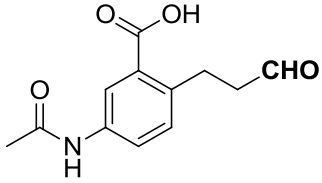
5 linear (**L**) branched (**B**)

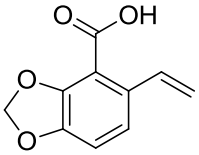
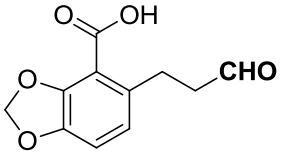
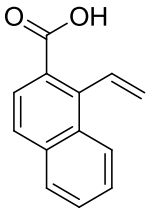
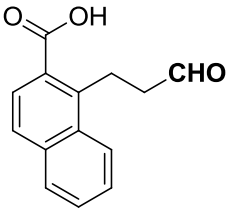
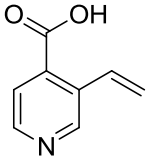
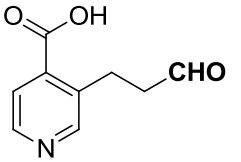
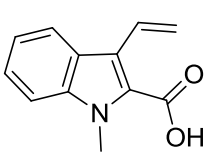
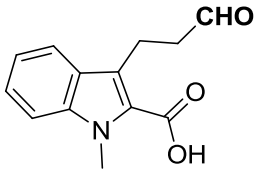
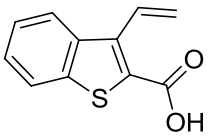
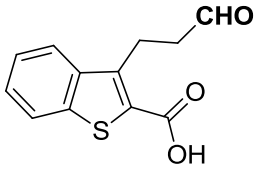
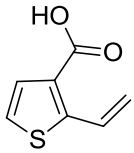
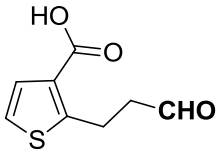
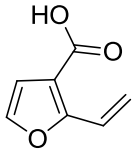
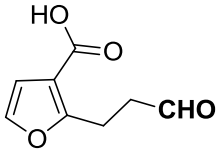
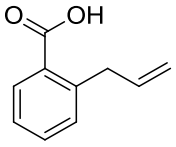
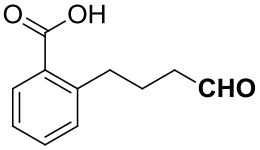
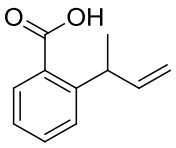
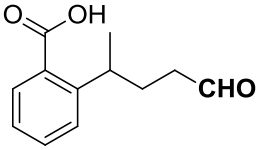
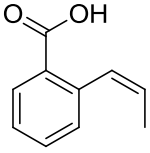
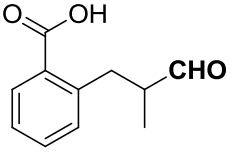
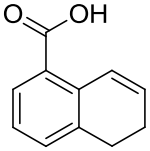
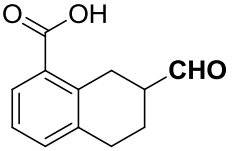
Entry	solvent	CO/H_2 pressure	temp. (°C)	Regioselectivity L (%)	Regioselectivity B (%)	Conversion (%)
1	CH_2Cl_2	1 bar	rt	>98	0	40%
2[b]	CH_2Cl_2	1 bar	35	>98	0	100%
3	toluene	20 bar	40	>98	0	100%
4	tetrahydrofurane	20 bar	40	>98	0	100%
5	acetonitrile	20 bar	40	>98	0	84%

[a] Reagents and conditions: $Rh(CO)_2(acac)$ as a rhodium source, [**5**] = 0.2 M, Rh : ligand **L5** : substrate **5** : TEA, 1/1.1/100/150, CO/H_2 = 1/1, 24h, regioselectivity and conversion were determined by ^1H NMR analysis of the crude reaction mixture; [b] 20h reaction time; no full conversion in some runs, presumably due to the catalyst sensitivity and lower control of the reaction conditions at 1 bar (a balloon-based setup).

Table S4. Hydroformylation of vinyl 2-carboxyarenes **5** with the Rh(**L5**) – substrate scope.[a]



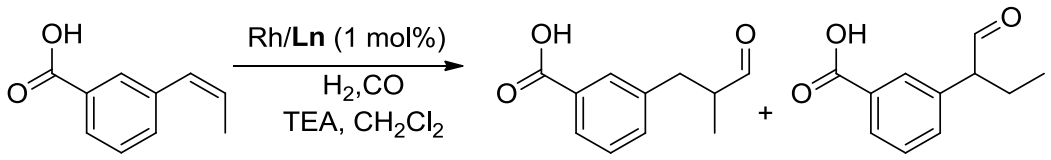
Entry	Substrate	Product	Temp.	Selectivity	Conversion
1			rt 40°C	>98% >98%	70% 100%
2			rt	>98%	100%
3			rt	>98%	100%
4			rt 40°C 40°C[b] 50°C[b,d]	>98% >98% >98% >98%	26% 70% 94% 100%
5			rt	>98%	100%
6			rt	>98%	100%
7			rt 40°C 40°C[b]	>98% >98% >98%	17% 80% 100%
8			rt	>98%	100%

9			rt 40°C	>98% >98%	64% 100%
10			rt 40°C 50°C[b] 60°C[b,d]	>98% >98% >98% >98%	2% 10% 80% 95%
11			rt 40°C	>98% >98%	86% 100%
12			rt 40°C	>98% >98%	85% 100%
13			rt 40°C	>98% >98%	73% 100%
14			rt	>98%	100%
15			rt	87%[c] (80%)[c]	100%
16			rt	>98%	100%
17			40°C[b]	>98%	100%
18			40°C[b,d]	>98%	100%
19			40°C[b,d] 60°C[b,d]	>98% >98%	38% 100%

[a] Reagents and conditions: $Rh(CO)_2(acac)$ as a rhodium source, [Rh] = 0.002 M, Rh : ligand **L5** : substrate : DIPEA, 1/1.1/100/150, CO/H_2 = 1/1 (20bar), 24h, CH_2Cl_2 as a solvent, regioselectivity and conversion was determined by ^1H and ^{13}C NMR analysis of the crude reaction mixture, no other isomers or side products were observed (except were noted), TEA

can be used instead of DIPEA; acac = acetylacetonate, DIPEA = N,N-diisopropylethylamine, TEA = triethylamine; [b] 72h reaction time; [c] regioselectivity and chemoselectivity towards aldehydes, respectively; [d] base : substrate 0.5/1.

Table S5. Hydroformylation of substrate **16** with the Rh(**L5**) and Rh(L6) catalysts – variation of reaction conditions.[a]



17 **22** **22'**

Entry	ligand	Temp.	TEA	Selectivity: % **22**	Conversion /%
1	**L5**	40°C	1.5 equiv.	-[b]	2
2	**L6**	40°C	1.5 equiv.	-[b]	1
3	**L5**	40°C	1.0 equiv.	44	4
4	**L6**	40°C	1.0 equiv.	-[b]	2
5	**L5**	60°C	1.5 equiv.	-[c]	36
6	**L6**	60°C	1.5 equiv.	-[c]	12
7	**L5**	60°C	1.0 equiv.	47	67
8	**L6**	60°C	1.0 equiv.	44	10
9	**L5**	60°C	0.9 equiv.	48	78
10	**L5**	**60°C**	**0.5 equiv.**	**48**	**85**
11	**L5**	70°C	1.0 equiv.	-[c]	100
12	**L5**	**70°C**	**0.5 equiv.**	**44**	**100**

[a] Reagents and conditions: $Rh(CO)_2(acac)$ as a rhodium source, [Rh] = 0.002 M, Rh : ligand: substrate, 1/1.1/100, CO/H_2 = 1/1 (20bar), 24h, CH_2Cl_2 as a solvent, regioselectivity and conversion was determined by ^1H NMR analysis of the crude reaction mixture, no side products were observed (hydrogentation, isomerization etc.), except were noted, and formation of the linear aldehyde product (**19**) could be detected (< 3%) at elevated temperatures; [b] regioselectivity not determined due to too low conversion; [c] regioselectivity not determined due to formation of side products – the aldol condensation of the hydroformylation aldehyde products.

The detailed analysis of reactions for substrates **5**, **5b-p**, **13-14** (including images of ^1H and ^{13}C NMR spectra for crude reaction mixtures, as well as of isolated products), and details concerning isolation and full characterization of products are provided in the communication of the preliminary results of the study.[5] Deatails concerning substrates **6-7** and **15-17** are provided below:

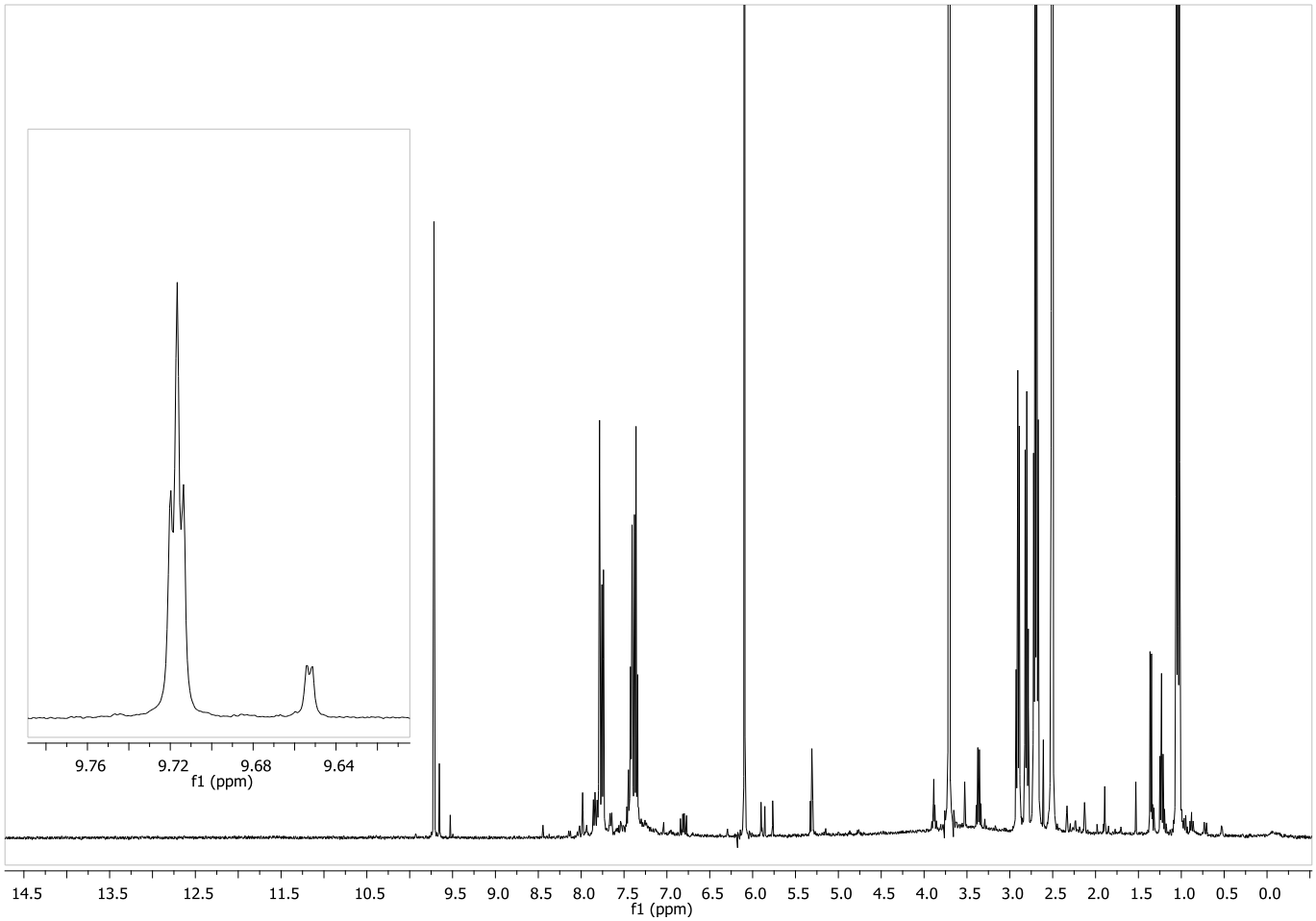


Figure S32. ^{1}H NMR (DMSO-d_6) spectrum of the crude reaction mixture for substarte **6** – Table S1, Entry 13 (1.5 equiv of TEA).

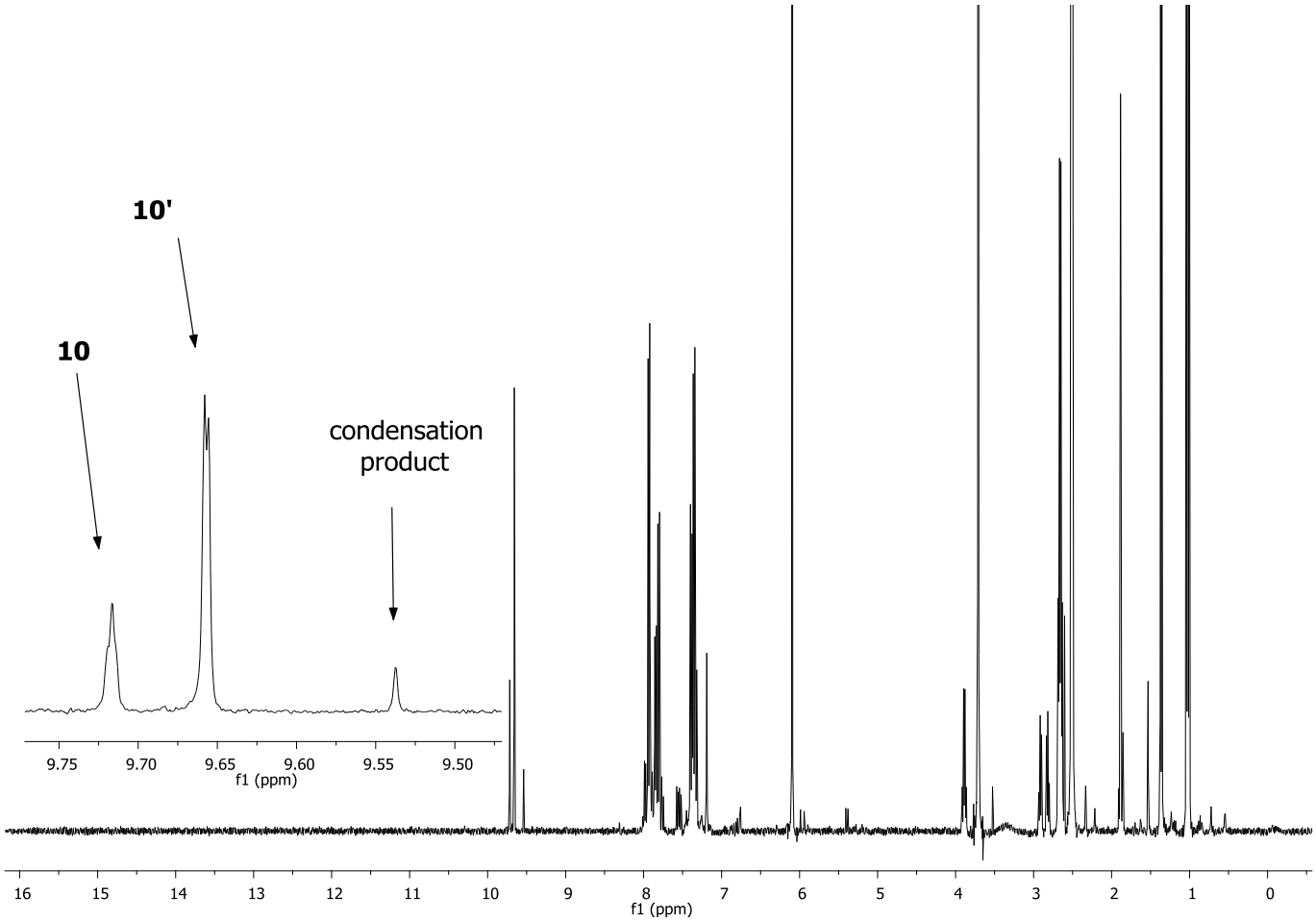


Figure S33. ^{1}H NMR (DMSO-d_6) spectrum of the crude reaction mixture for substarte **7** – Table S1, Entry 20 (0.5 equiv of TEA). "Condensation product", the aldol condensation products of the aldehyde formed, is continued to be formed also after stopping hydroformylation (in expense of products **10** and **10'**).

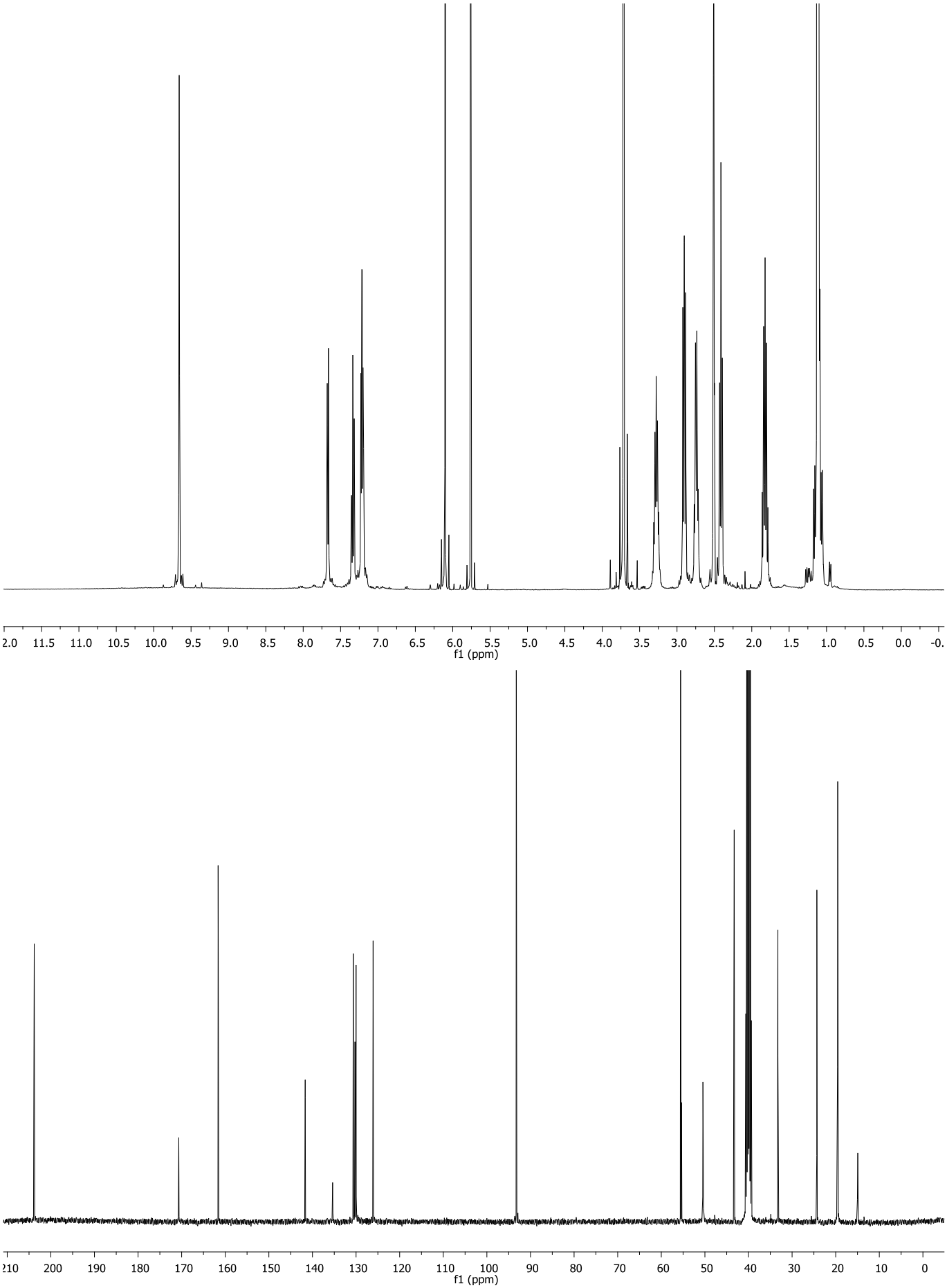


Figure S34. ^{1}H and ^{13}C NMR (DMSO-d_6) spectra of the crude reaction mixture for **15**.

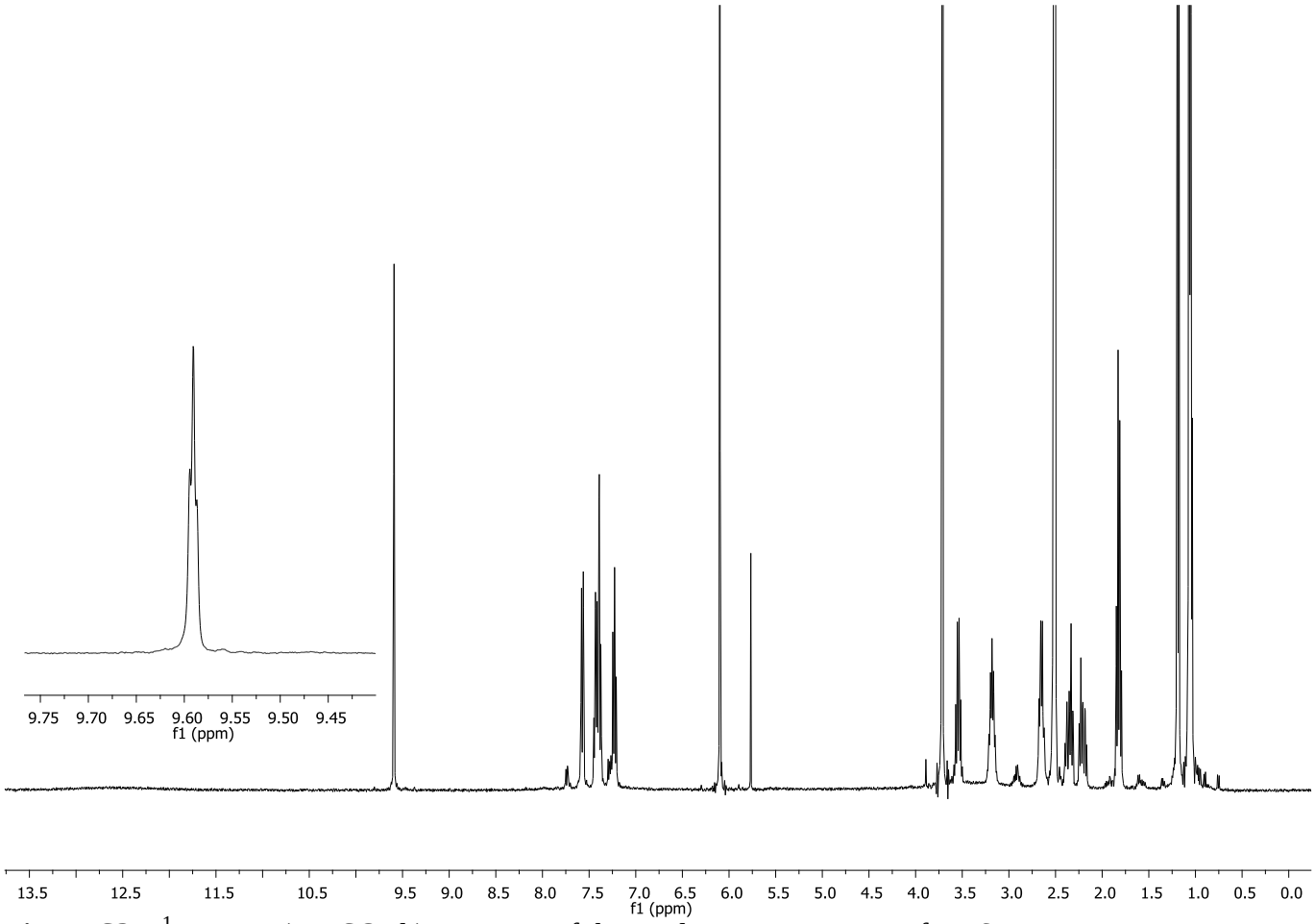


Figure S35. ^{1}H NMR (DMSO-d_6) spectrum of the crude reaction mixture for **16**.

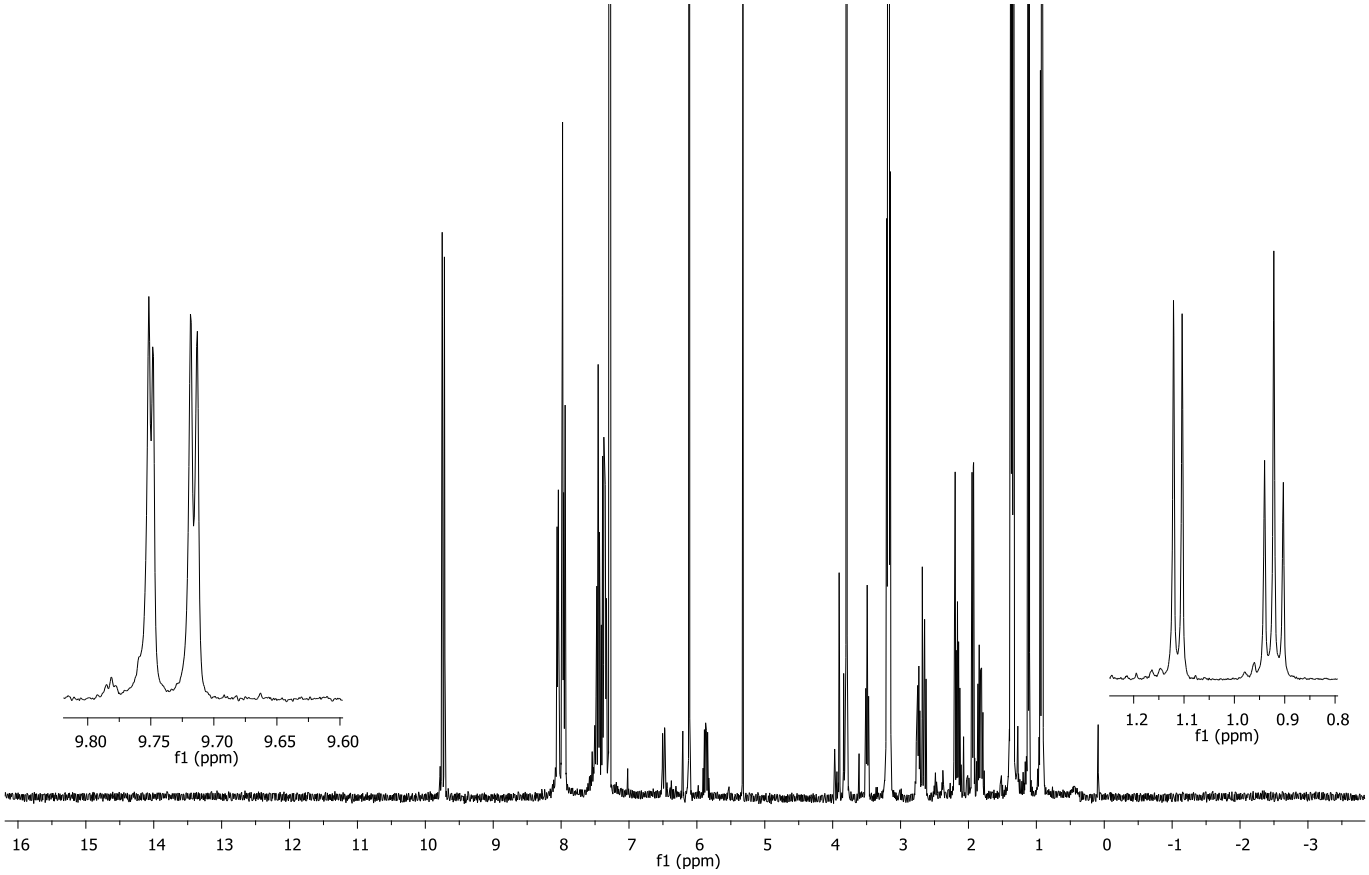


Figure S36. ^{1}H NMR ($CDCl_3$) spectrum of the crude reaction mixture for substarte **17** at 60°C – Table S5, Entry 10.

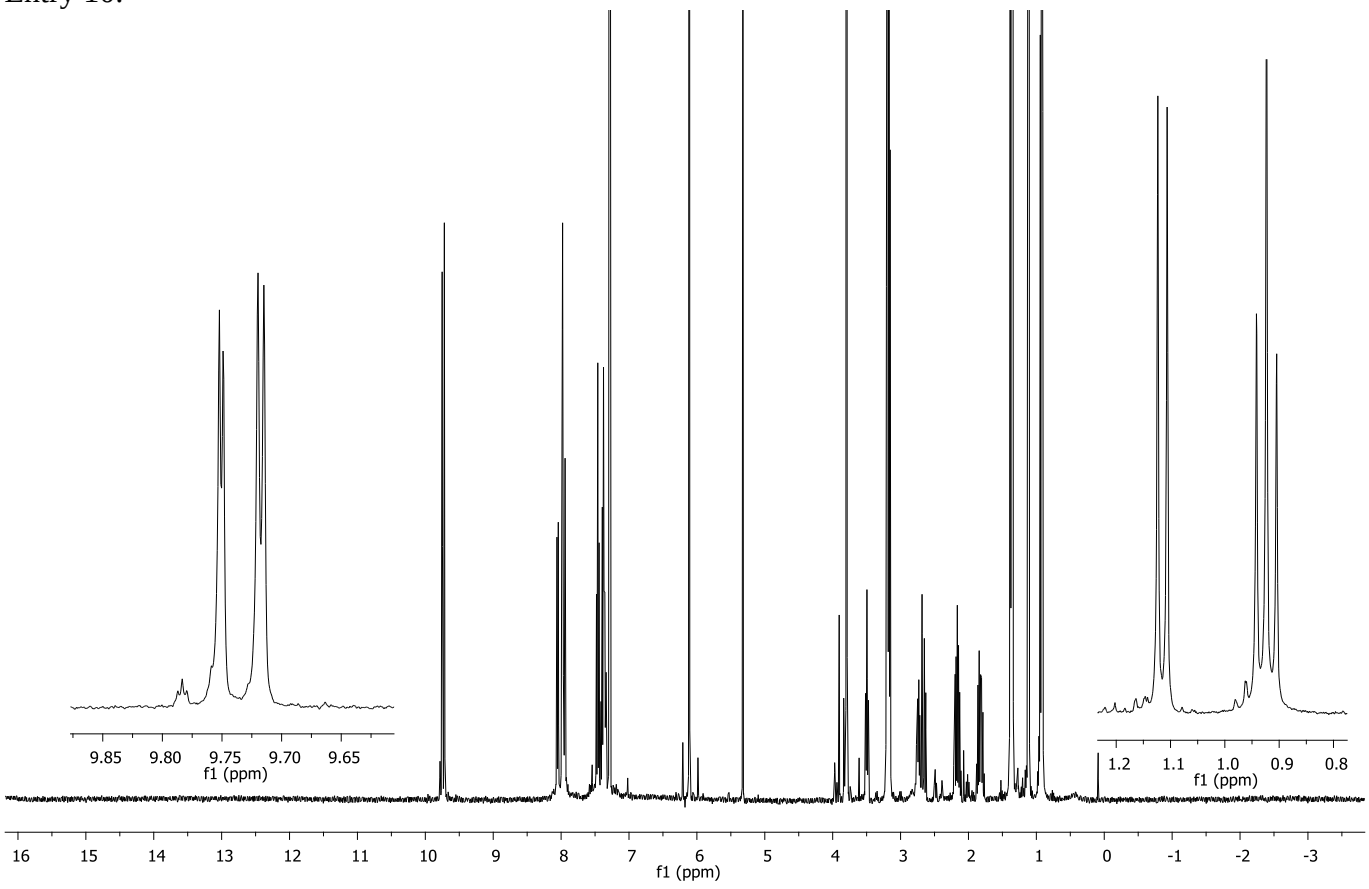
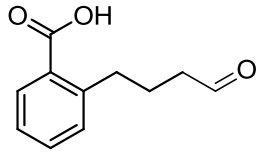


Figure S37. ^{1}H NMR ($CDCl_3$) spectrum of the crude reaction mixture for substarte **17** at 70°C – Table S5, Entry 12.

Isolation of 2-(4-oxobuty)-benzoic acid **20**:



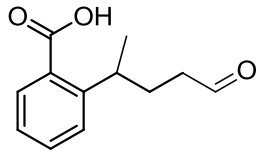
A stainless steel autoclave equipped with an oven-dried glass insert (15 mL) was charged with a solution of substrate **15** (97 mg, 0.6 mmol), dry triethylamine (1.5 equiv.), $Rh(CO)_2(acac)$ (1 mol%), ligand **L5** (1.1 mol%) in dry DCM (3 ml). The charged autoclave was carefully purged three times with 20 bar of syngas and then pressurized at 20 bar of syngas, followed by stirring at 40°C for 24. Afterwards the pressure was carefully released, the reaction mixture was diluted ethyl acetate to ~ 50 ml and the product was extracted with aqueous $NaHCO_{3\ (sat.)}$ (3·15ml). The combined aqueous layers were subsequently washed with ethyl acetate, then neutralized with 1M HCl and extracted with ethyl acetate (3·50ml). The organic layers were combined, dried over $MgSO_4$ and the solvent evaporated off, yielding 111 mg (96%) of **20** (containing ~2% of the alternative product : 3-(2-methyl-3-oxopropyl)benzoic acid; it can be easily removed by a column chromatography with SiO_2 and a hexane : diethyl ether : acetic acid mixture (200 : 100 :1) as an eluent).

^{1}H NMR (400 Mhz, DMSO-d_6): δ = 12.83 (bs, 1H, COO*H*), 9.65 (t, J_1 = 1.6 Hz, 1H, C*H*O), 7.79 (dd, J_1 = 8.1, J_2 = 1.5 Hz, 1H), 7.47 (ddd, J_1 = J_2 = 7.5, J_3 = 1.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 2.91 (t, J_1 = 7.6 Hz, 2H, ArCH_2), 2.43 (dt, J_1 = 7.3 Hz, J_2 = 1.6 Hz, 2H, CH_2CHO), 1.80 (tt, $J_1 \approx J_2$ = 7.5 Hz, 2H, CH_2CH_2CHO);

^{13}C NMR (100MHz, DMSO-d_6): δ = 203.3, 168.8, 142.7, 131.7, 130.9, 130.5, 130.3, 126.2, 44.7, 32.8, 23.8;

HR MS (EI): calcd. for $C_{11}H_{12}O_3$ $[M]^+$: 192.07864, found: 192.07828.

Isolation of 2-(5-oxopentan-2-yl)benzoic acid **21**:



A stainless steel autoclave equipped with an oven-dried glass insert (15 mL) was charged with a solution of substrate **16** (106 mg, 0.6 mmol; containing ~9% of the substrate isomer: (E)-methyl 2-(but-2-en-1-yl)benzoic acid), dry triethylamine (1.5 equiv.), $Rh(CO)_2(acac)$ (1 mol%), ligand **L5** (1.1 mol%) in dry DCM (3 ml). The charged autoclave was carefully purged three times with 20 bar of syngas and then pressurized at 20 bar of syngas, followed by stirring at 40°C for 72h. Afterwards the pressure was carefully released, the reaction mixture was diluted ethyl acetate to ~ 50 ml and the product was extracted with aqueous $NaHCO_{3\ (sat.)}$ (3·15ml). The combined aqueous layers were subsequently washed with ethyl

acetate, then neutralized with 1M HCl and extracted with ethyl acetate (3·50ml). The organic layers were combined, dried over $MgSO_4$ and the solvent evaporated off, giving 113 mg of **21** with ~9% of (E)-methyl 2-(but-2-en-1-yl)benzoic acid, which was purified by a column chromatography with SiO_2 (30 g) and a hexane : diethyl ether : acetic acid mixture (200 : 100 :1) as an eluent, yielding 100 mg of **21** (89% based on substrate **16**), and recovering 6 mg of (E)-methyl 2-(but-2-en-1-yl)benzoic acid.

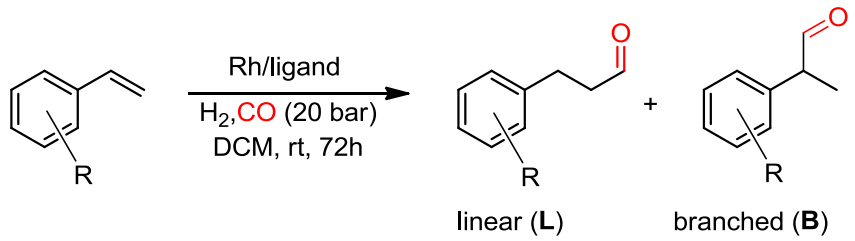
^{1}H NMR (400 Mhz, DMSO-d_6): δ = 12.95 (bs, 1H, COO*H*), 9.58 (t, J_1 = 1.5 Hz, 1H, C*H*O), 7.64 (dd, J_1 = 7.7, J_2 = 1.3 Hz, 1H), 7.49 (ddd, J_1 = J_2 = 7.6, J_3 = 1.3 Hz, 1H), 7.42 (dd, J_1 = 8.0, J_2 < 1.0 Hz, 1H), 7.23 (ddd, J_1 = J_2 = 7.5, J_3 = 1.3 Hz, 1H), 3.59-3.48 (m, 1H, ArC*H*), 2.39-2.16 (m, 2H, CH_2CHO), 1.88-1.77 (m, 2H, CH_2CH$_2$CHO), 1.19 (d, J_1 = 7.0 Hz, 3H);

^{13}C NMR (100MHz, DMSO-d_6): δ = 203.1, 169.6, 146.3, 131.8, 131.4, 129.1, 126.5, 125.8, 41.4, 33.5, 29.7, 22.0;

HR MS (ESI): calcd. for $C_{12}H_{14}O_3Na$ $[M+Na]^+$: 229.0835, found: 229.0835.

Control experiments

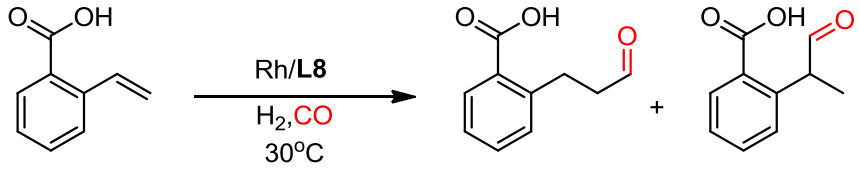
Table S6. Hydroformylation of styrene derivatives with the Rh(**L5**) and Rh(PPh_3) catalysts – control experiments.[a]

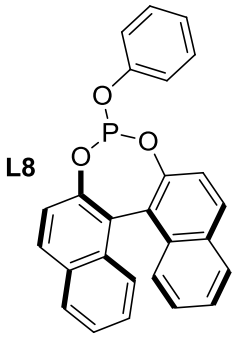


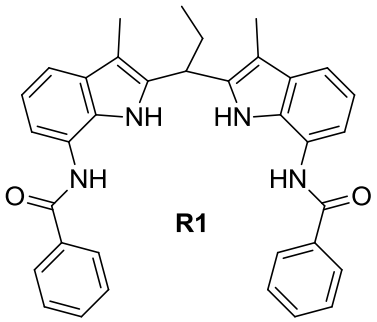
Entry	Substrate	Ligand	Regioselectivity		Conversion
			L (%)	B (%)	(%)
1	2-methylstyrene	**L5**	5	95	>99
2	2-methylstyrene	PPh_3	7	93	87
3	3-methylstyrene	**L5**	7	93	93
4	3-methylstyrene	PPh_3	4	96	89
5	2-methoxystyrene	**L5**	5	95	>99
6	2-methoxystyrene	PPh_3	9	81	>99
7	3-methoxystyrene	**L5**	6	94	92
8	3-methoxystyrene	PPh_3	2	98	94
9	styrene	**L5**	6	94	93
10	styrene	PPh_3	5	95	92
11	methyl 2-vinylbenzoate	**L5**	5	95	99
12	methyl 2-vinylbenzoate	PPh_3	5	95	84
13	methyl 3-vinylbenzoate	**L5**	5	95	97
14	methyl 3-vinylbenzoate	PPh_3	2	98	99
15[b]	2-(trifluoromethyl)styrene	**L5**	10	90	41
16	3-(trifluoromethyl)styrene	**L5**	4	96	92
17	3-(trifluoromethyl)styrene	PPh_3	1	99	100
18	4-(trifluoromethyl)styrene	**L5**	3	97	97
19	4-(trifluoromethyl)styrene	PPh_3	1	99	99

[a] Reagents and conditions: [substrate]=0.2M, $Rh(CO)_2(acac)$ (1mol%), ligand **L5** (1.1mol%) or PPh_3 (6%), CO/H_2 = 1:1 (20bar), CH_2Cl_2, 24h, at room temp.; [b] 24h reaction.

Table S7. Hydroformylation of 2-vinylbenzoic acid **5** – control experiments.[a]







Entry	TEA[b]	anion receptor **R1**[b]	Regioselectivity L (%)	Regioselectivity B (%)	Conversion (%)
1	-	-	-	-	0
2	-	+	-	-	0
3	+	-	-	-	0
4	+	+	-	-	0

[a] Reagents and conditions: $Rh(CO)_2(acac)$ as a rhodium source, [**5**] = 0.2 M, Rh : ligand **L8** : receptor **R1** : substrate **5** : TEA, 1/6/(2 or 0)/100/(150 or 0), CO/H_2 = 1/1 (20 bar), CH_2Cl_2, 24h, Conversion was determined by ^1H NMR analysis of the crude reaction mixture; [b] '+' and '-' denotes if the component was added to the reaction mixture.

Gas uptake experiments

The experiments were carried out in the AMTEC SPR16 equipment[11] consisting of 16 parallel reactors equipped with internal temperature and pressure sensors, and a mass flow controller. The apparatus is suited for monitoring gas uptake profiles during the catalytic reactions. Prior to catalytic experiments, the autoclaves were heated to 110°C and flushed with argon (22 bar) five times. The reactors were cooled to room temperature and flushed again with argon (22 bar) five times. Next, for experiments without the catalyst pre-incubation, the autoclaves were charged with solutions of the rhodium precursor [Rh(acac)$(CO)_2$], ligand, substrate, base (if necessary) and internal standard (1,3,5-trimethoxybenzene) in CH_2Cl_2 (8 ml). Then, the reactors were pressurized with syngas (CO/H_2, 1:1, desired reaction pressure) and heated up to appropriate temperature. Alternatively, for experiments with the catalyst pre-incubation, first the autocalves were charged with solutions of the rhodium precursor [Rh(acac)$(CO)_2$], ligand, additive (the product or 4-heptylbenzoic acid) and base (if necessary) in CH_2Cl_2 (4 ml). Then, the reactors were pressurized with syngas (CO/H_2, 1:1, 20 bar) and heated up to 30°C. After the incubation period (~ 20 h), the pressure was reduced to 2.0 bar, followed by subsequent addition of solutions of substrate, additive (the product or 4-heptylbenzoic acid) if desired, base and internal standard (1,3,5-trimethoxybenzene) in CH_2Cl_2 (4 ml), after which the pressure of syngas was increased immediately. For both protocols, the pressure of the reactive gas was kept constant during the reaction period, and the gas uptake was monitored and recorded for every reactor independently. After catalysis the pressure was reduced to 2.0 bar and samples were taken for further analysis (the NMR and/or GC analysis, as described in the previous section).

Conversions were determined by NMR analysis of the final reaction mixtures (in respect to the internal standard). Initially, the measured data of the gas consumption in time (attributed quantitatively to the conversion in time) were smoothed, to minimize the noise inherent in the integral measurements (to capture important patterns in the data, while leaving out noise),[12] with the Origin 8.0 software, applying the Boltzmann model or similar. To avoid artefacts, the correctness of the model used was evaluated and confirmed by the analysis of the regular residuals of the fitting. If a reaction went to completion, the most informative part of the data, that is, for the reaction period from 0 to ~98% conversion was used for analysis. The processed data were used to determine kinetic profiles reported in the main text (Figures 8-9). For final evaluation of the procedure, the initial data (without smoothing) was also analysied. The obtained results were compared with those obtained from the processed data, which revealed essentially the same kinetic profiles (see the following section), confirming the validity of the protocol.

[11] www.amtec-chemnitz.de
[12] D. G. Blackmond, *Angew. Chem. Int. Ed.* **2005**, *44*, 4302-4320.

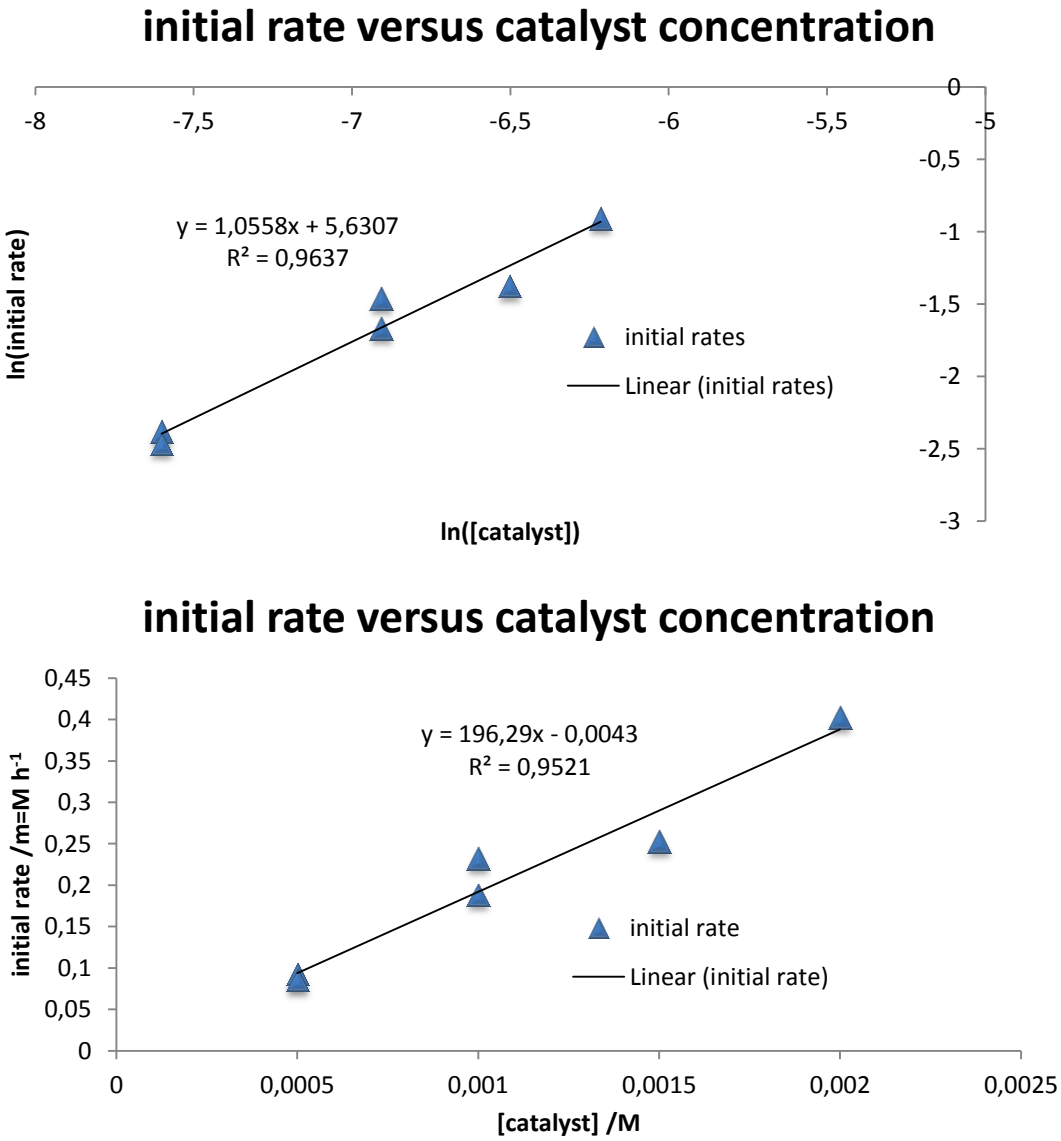


Figure S38. Dependence of the initial rate of the hydroformylation of **5** on the Rh(**L5**) catalyst concentration. Reagents and conditions: CO/H_2 = 1:1 (22 bar), 30°C, CH_2Cl_2, c(**5**) = 0.2 M, c(TEA) = 0.3 M, $[Rh(CO)_2(acac)]$/ligands **L5** = 1:1.1. Incubation time for the pre-catalyst activation = ca. 20h. For more details, see the detailed analysis provided in the following sections.

The plot of reaction rate versus catalyst concentration (below) clearly shows the linear dependence.

The plot of ln rate versus ln catalyst concentration (above) confirms the first order of reaction kinetics is in catalyst concentration.

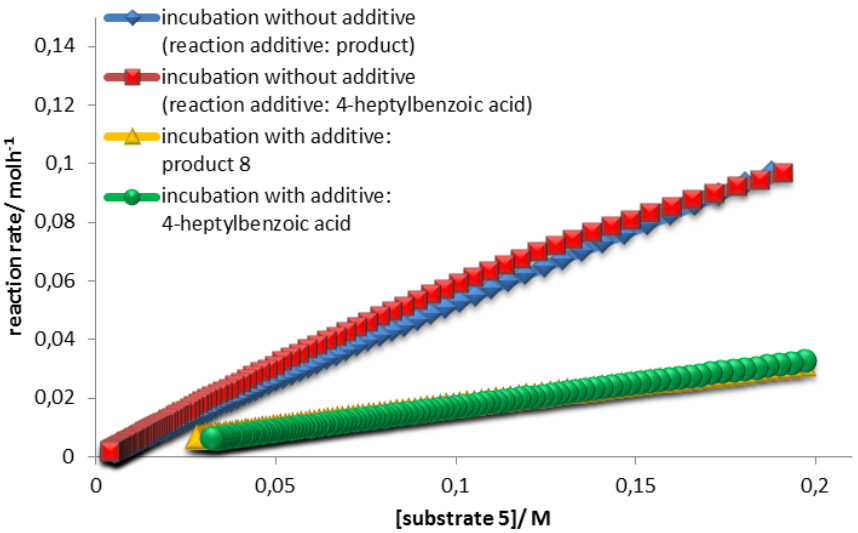


Figure S39. Graphical representation of the kinetic profiles: reaction rate versus substrate concentration plots from reaction with the pre-catalyst activation in the presence or absence of the product or 4-heptylbenzoic acid, for hydroformylation of **5** with the Rh/**L5** catalyst, determined by gas uptake methods. Reagents and conditions: 22 bar CO/H_2 (1:1), 30 °C, CH_2Cl_2, c(Rh) = 0.001 M, $[Rh(CO)_2(acac)]$/**L5** = 1:1.1; [**5**] = 0.2 M, [product **8**/4-heptylbenzoic acid] = 0.2 M; TEA (0.9 equiv of **5** + additive). Incubation time for the pre-catalyst activation = ca. 20h. For more details, see the detailed analysis provided in the following sections.

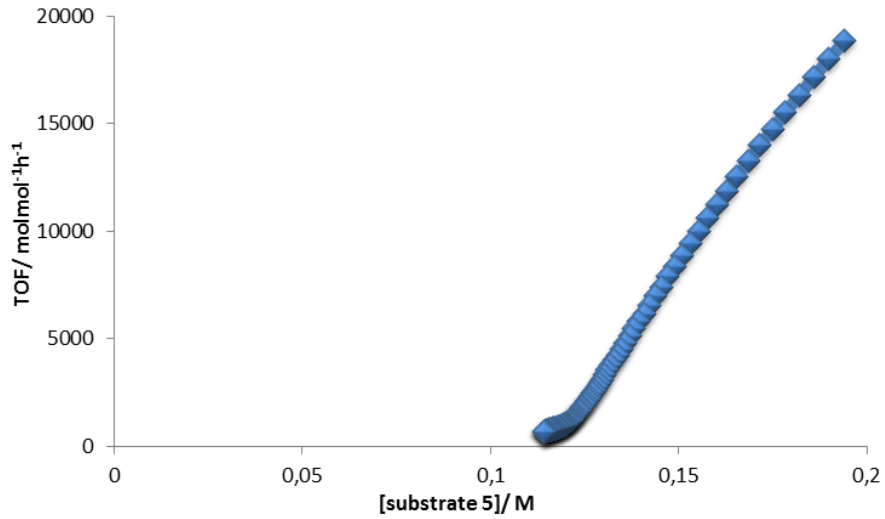
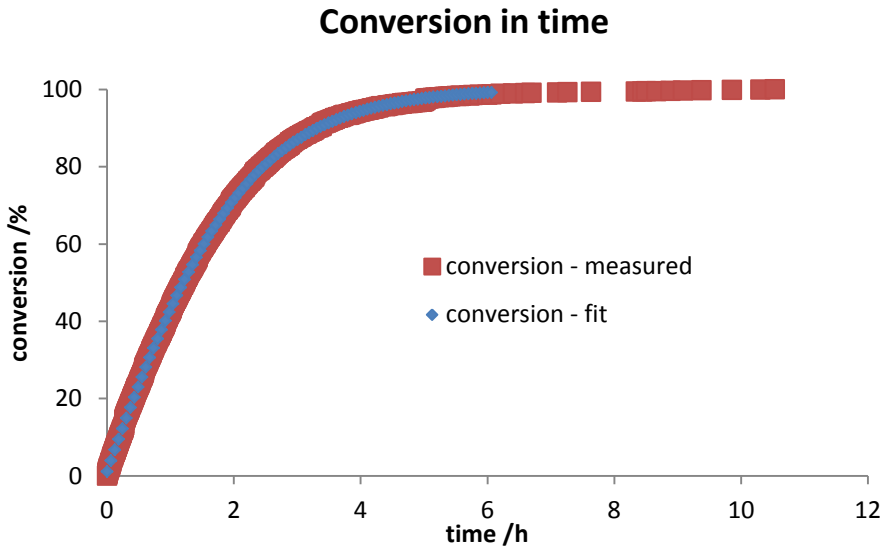
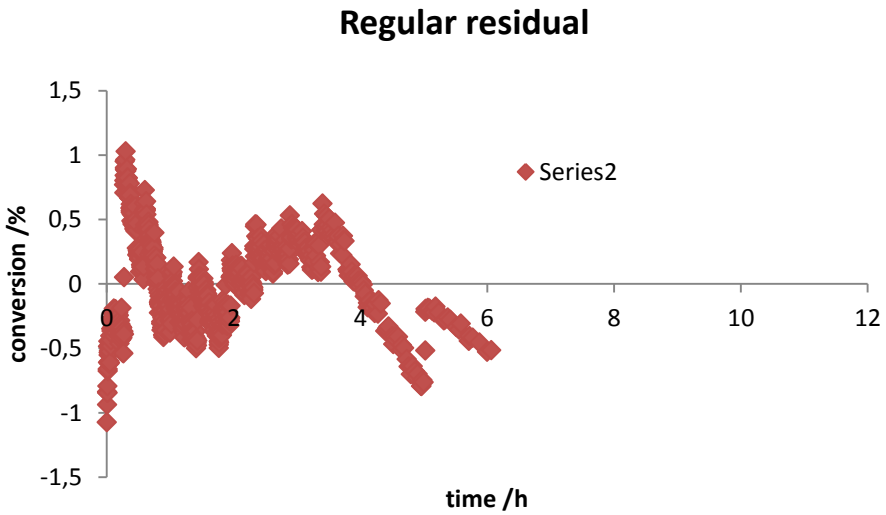


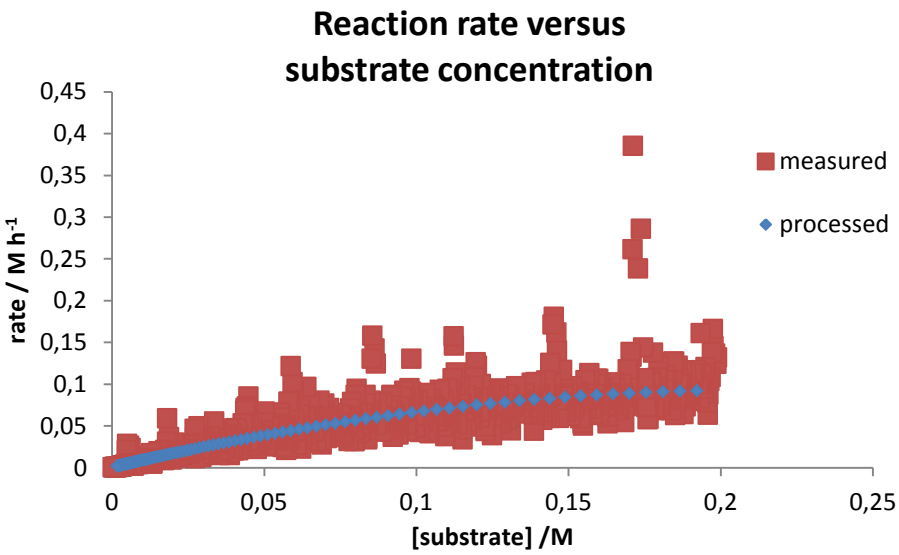
Figure S40. Turnover frequency versus substrate concentration for hydroformylation of **5** with the Rh/**L5** catalyst, at a very low catalyst loading, determined by gas uptake methods. Reagents and conditions: 20 bar CO/H_2 (1:1), CH_2Cl_2, 80 °C, [**5**] = 0.2 M, TEA (0.9 equiv), $[Rh(CO)_2(acac)]$ (0.001 mol%), **L5** (0.0011 mol%). No incubation time. For more details, see the detailed analysis provided in the following sections.

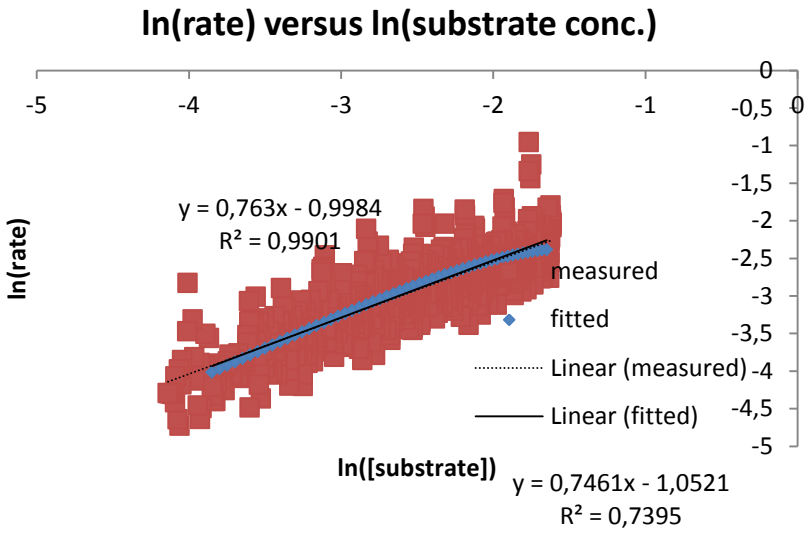
Hydroformylation of substrate 5 with the Rh(L5) catalysts, with the catalyst pre-incubation – different concentration of the catalyst or of the substrate:

1) Conditions: [**5**] = 0.2 M, [TEA] = 0.3 M, [Rh(acac)$(CO)_2$] = 0.0005 M, [**L5**] = 0.00055 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C.

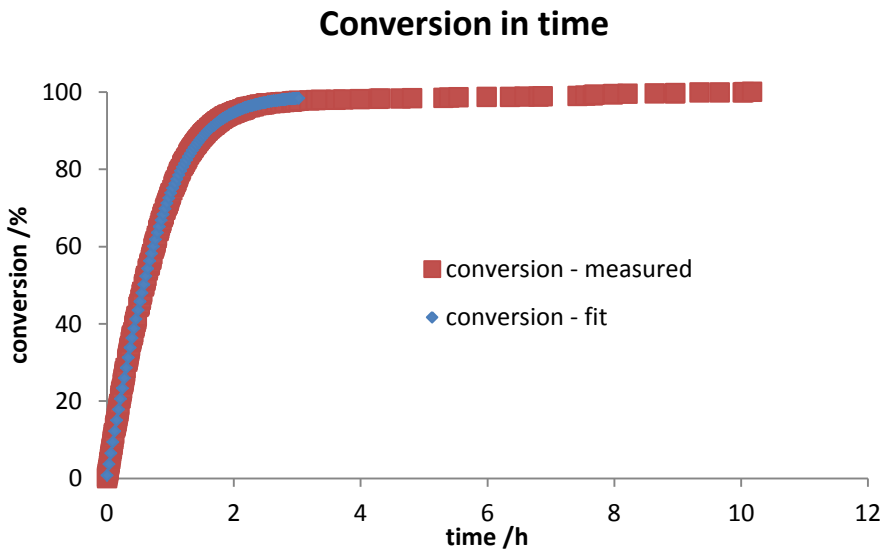


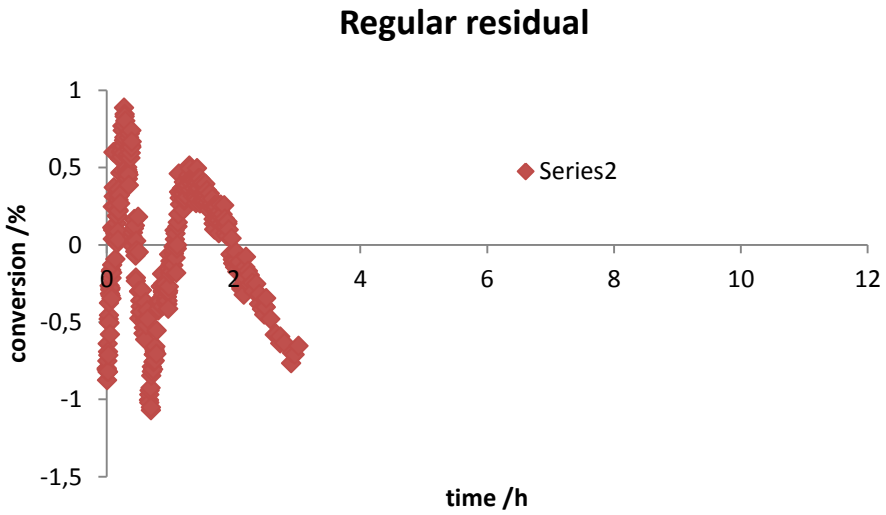


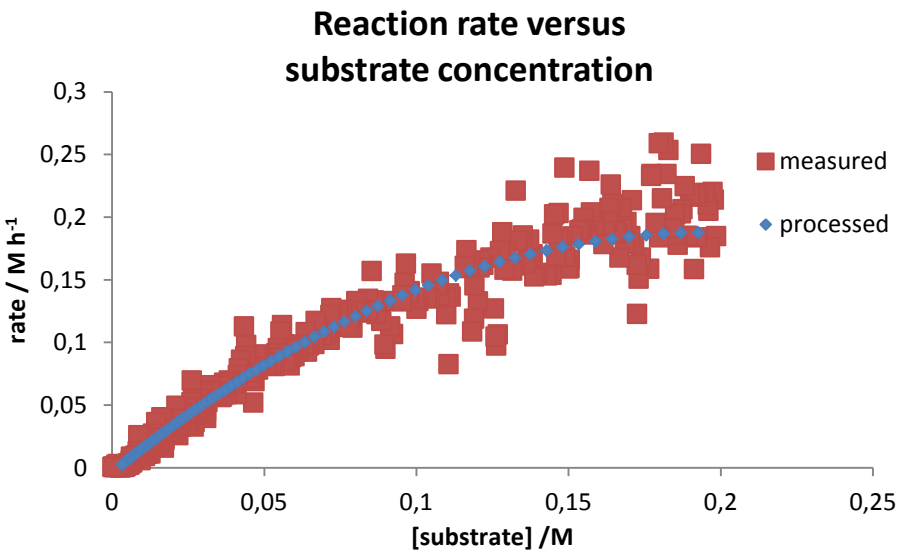

Reaction rate versus substrate concentration
rate / M h-1
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

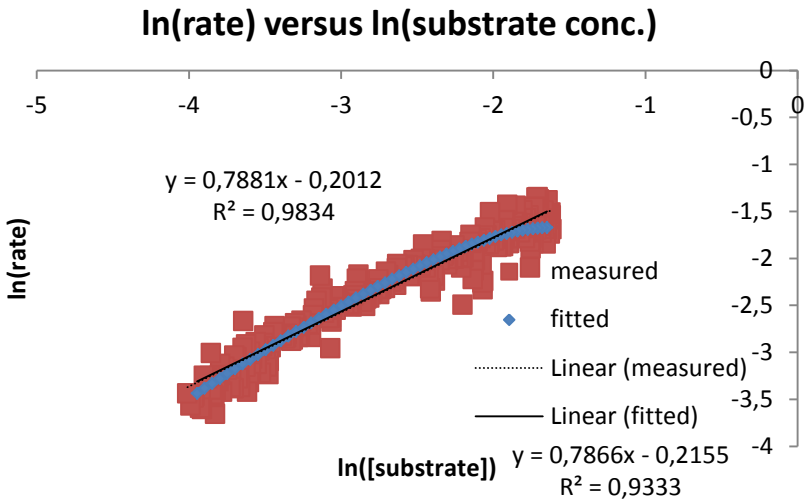

ln(rate) versus ln(substrate conc.)
ln(rate)
-5
-4
-3
-2
-1
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
-4,5
-5
y = 0,763x - 0,9984
R² = 0,9901
measured
fitted
Linear (measured)
Linear (fitted)
ln([substrate])
y = 0,7461x - 1,0521
R² = 0,7395

2) Conditions: [**5**] = 0.2 M, [TEA] = 0.3 M, [Rh(acac)$(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C.

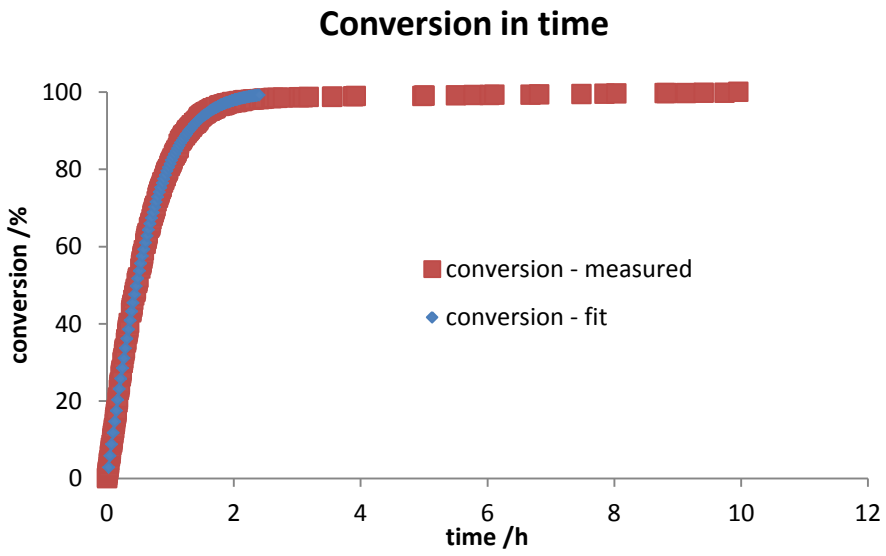


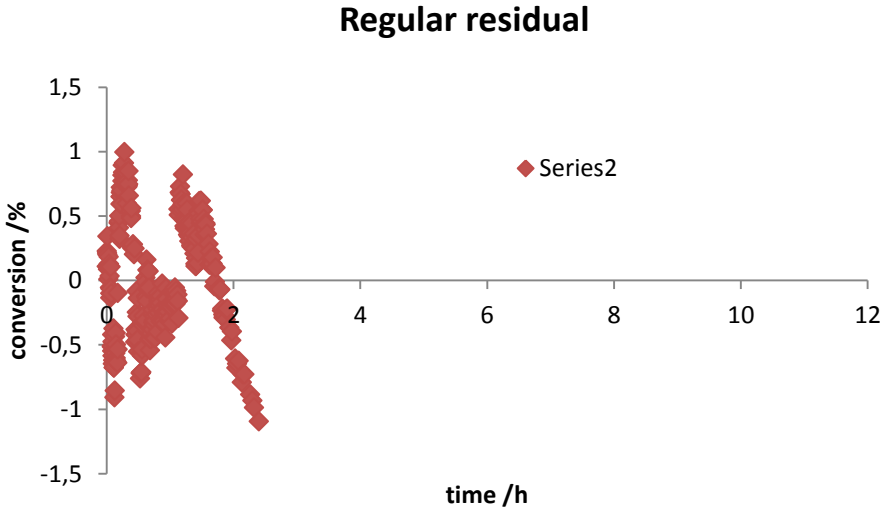


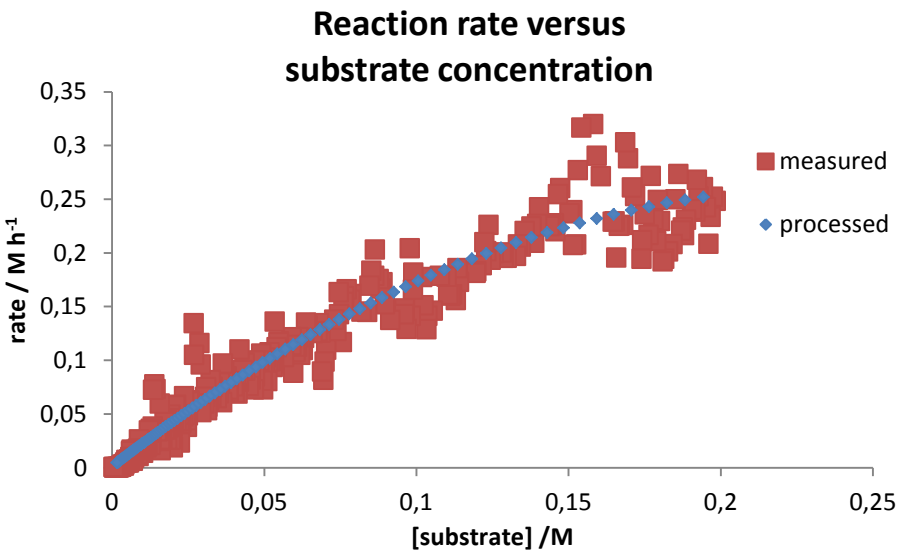

Reaction rate versus substrate concentration
rate / M h-1
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

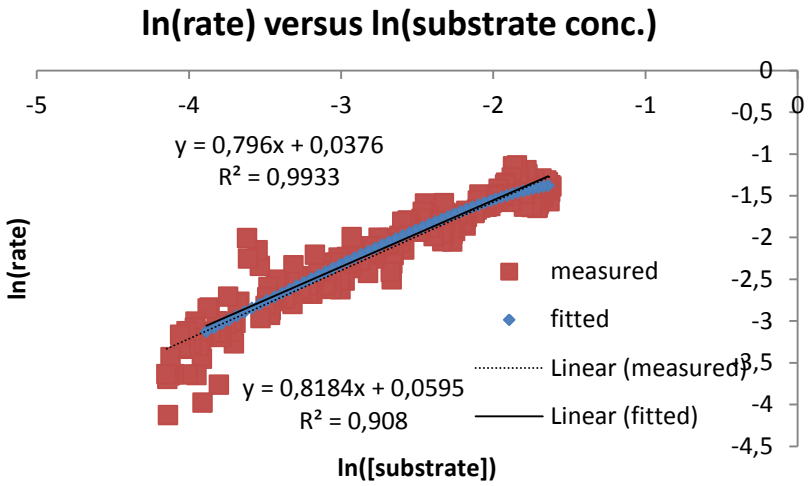

ln(rate) versus ln(substrate conc.)
y = 0,7881x - 0,2012
R² = 0,9834
ln(rate)
-5
-4
-3
-2
-1
0
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
ln([substrate])
measured
fitted
Linear (measured)
Linear (fitted)
y = 0,7866x - 0,2155
R² = 0,9333

3) Conditions: [**5**] = 0.2 M, [TEA] = 0.3 M, [Rh(acac)$(CO)_2$] = 0.0015 M, [**L5**] = 0.00165 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C.

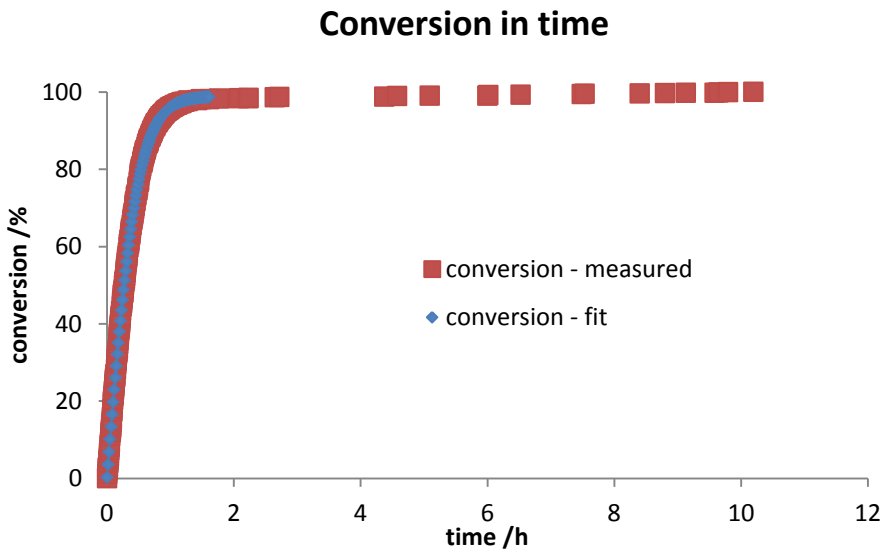


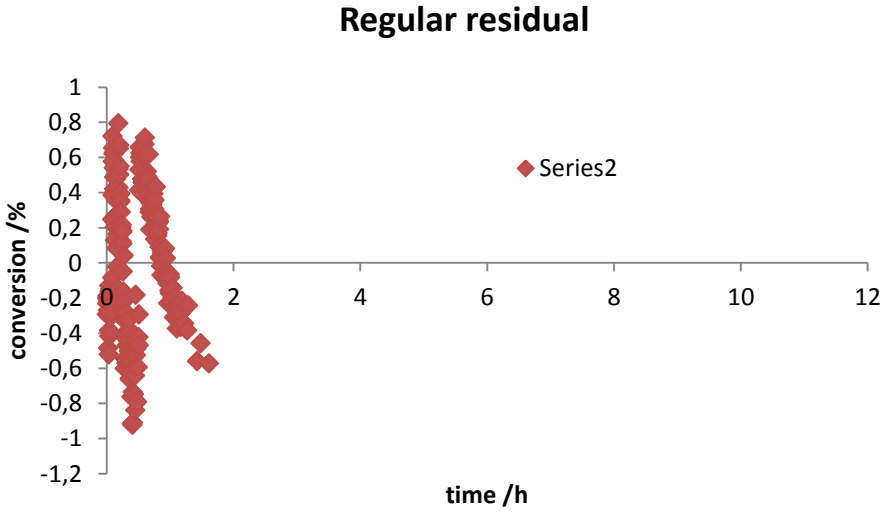


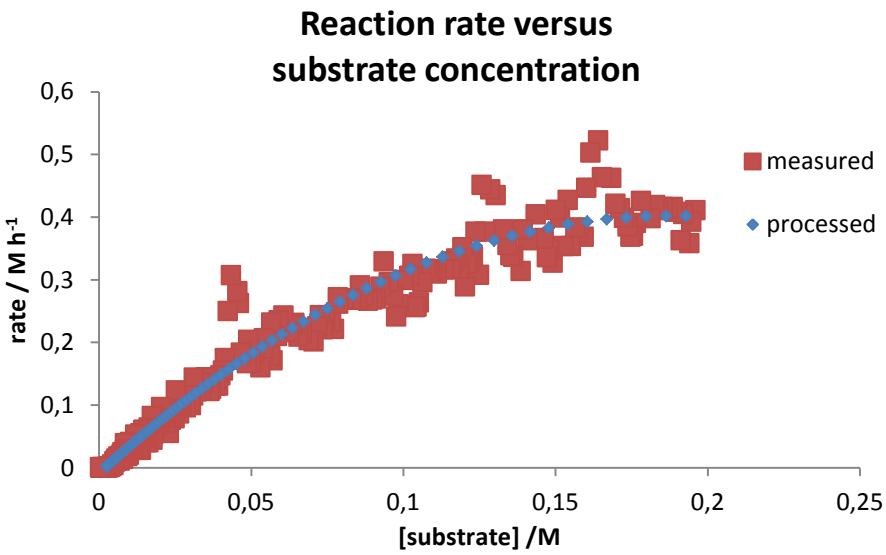

Reaction rate versus substrate concentration
rate / M h-1
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

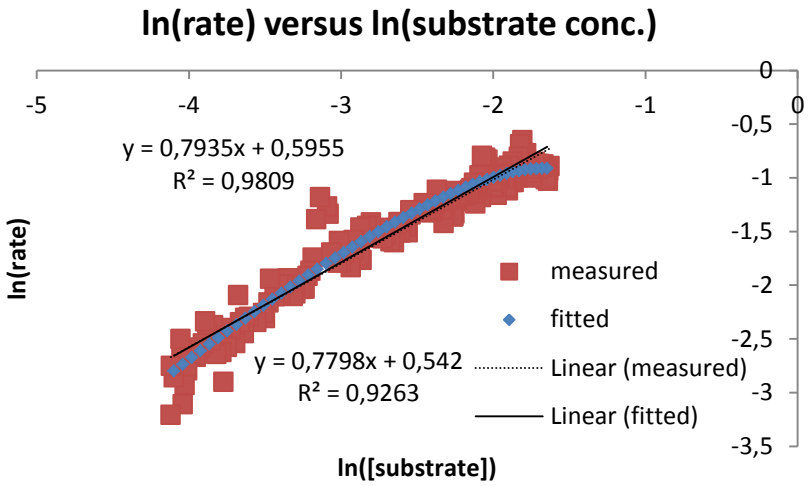

ln(rate) versus ln(substrate conc.)
y = 0,796x + 0,0376
R² = 0,9933
y = 0,8184x + 0,0595
R² = 0,908
ln(rate)
ln([substrate])
-5
-4
-3
-2
-1
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
-4,5
measured
fitted
Linear (measured)
Linear (fitted)

4) Conditions: [**5**] = 0.2 M, [TEA] = 0.3 M, [Rh(acac)$(CO)_2$] = 0.002 M, [**L5**] = 0.0022 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C.

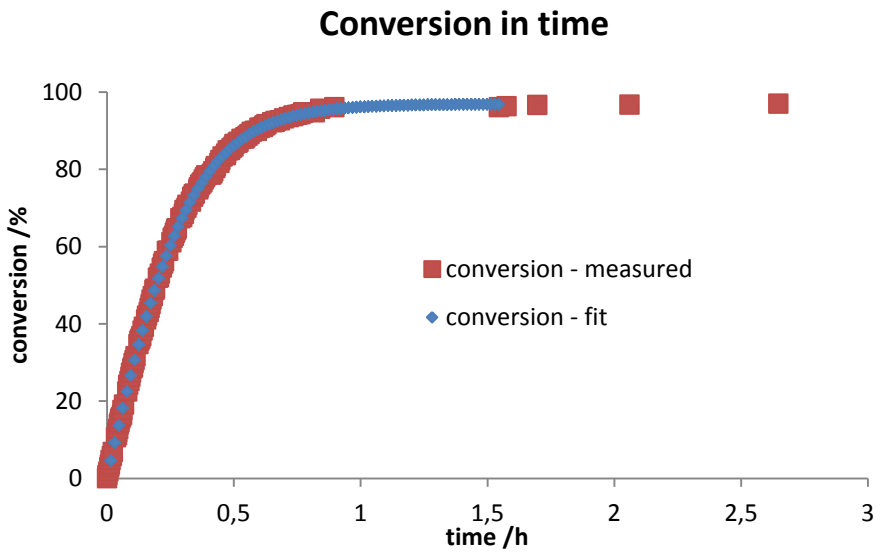


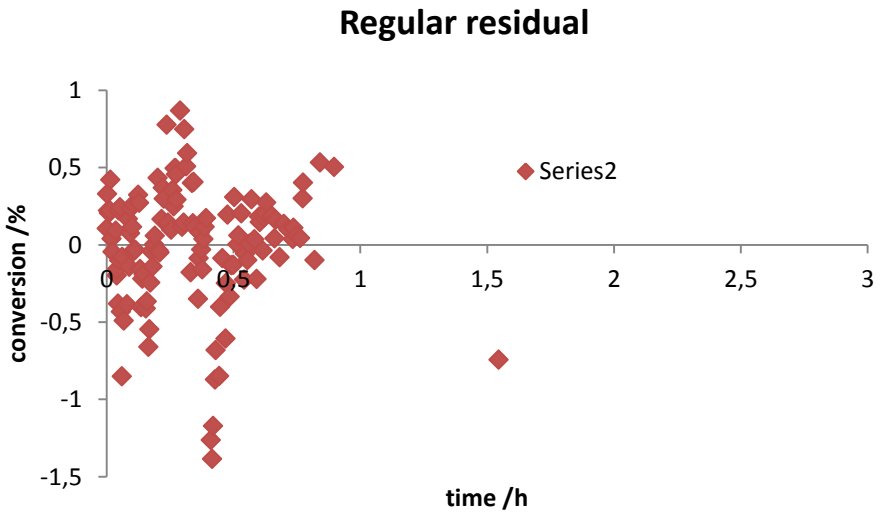


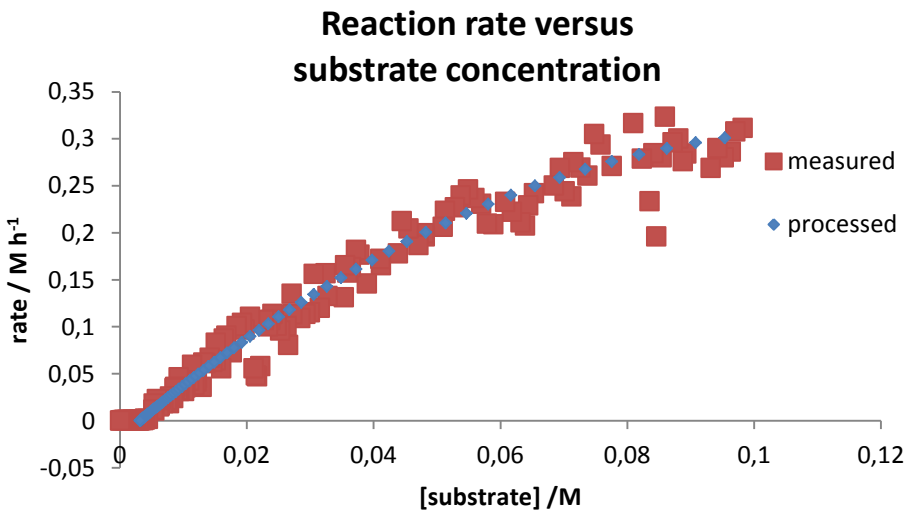

Reaction rate versus substrate concentration
rate / M h-1
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

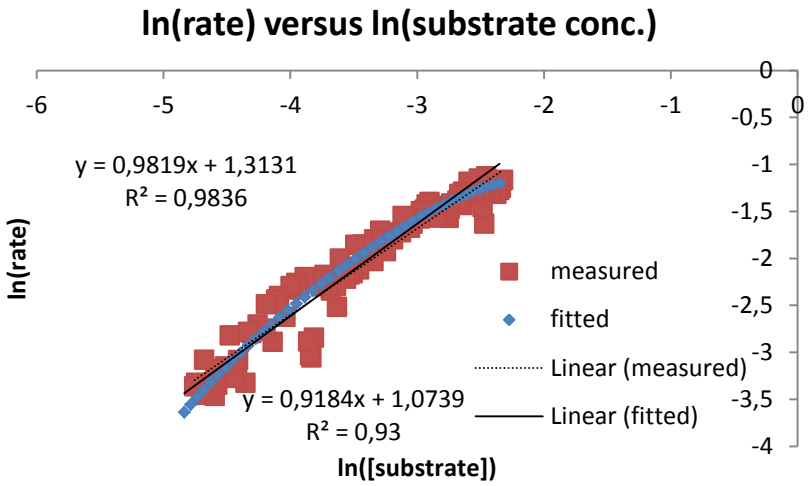

ln(rate) versus ln(substrate conc.)
y = 0,7935x + 0,5955
R² = 0,9809
y = 0,7798x + 0,542
R² = 0,9263
ln(rate)
ln([substrate])
-5
-4
-3
-2
-1
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
measured
fitted
Linear (measured)
Linear (fitted)

5) Conditions: [**5**] = 0.1 M, [TEA] = 0.15 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.

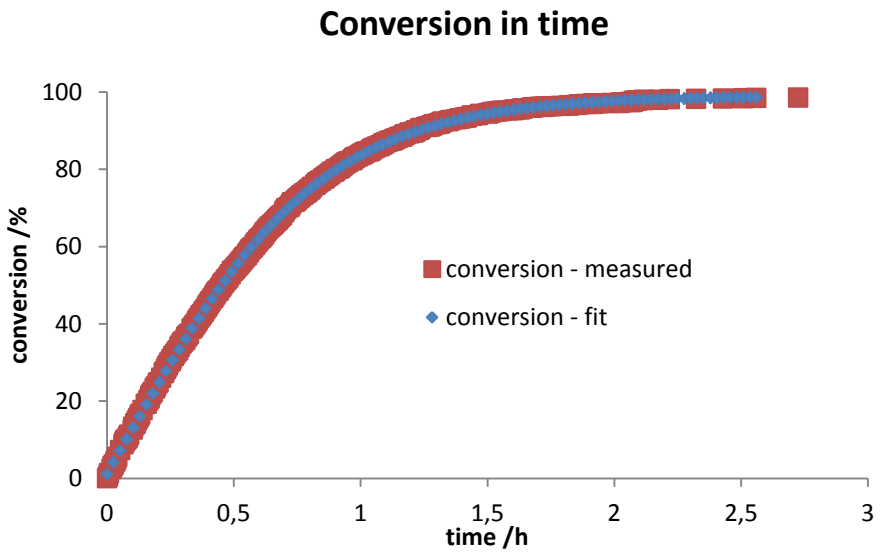


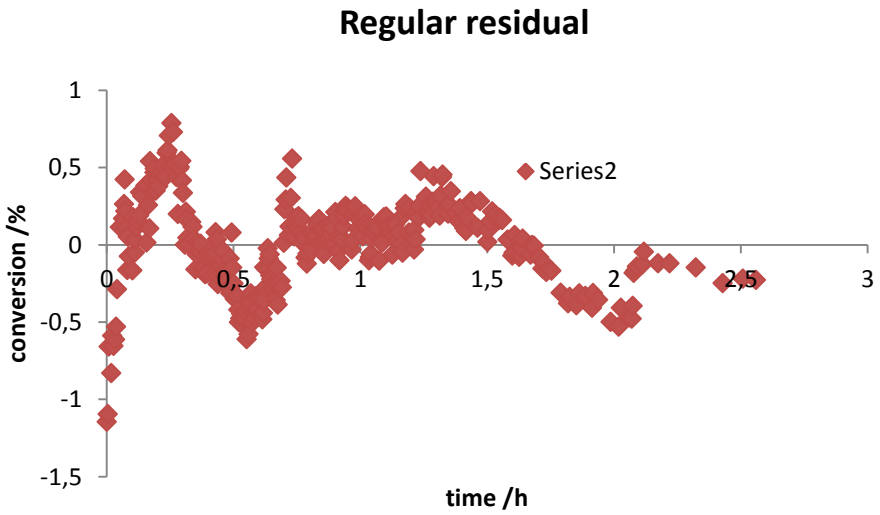


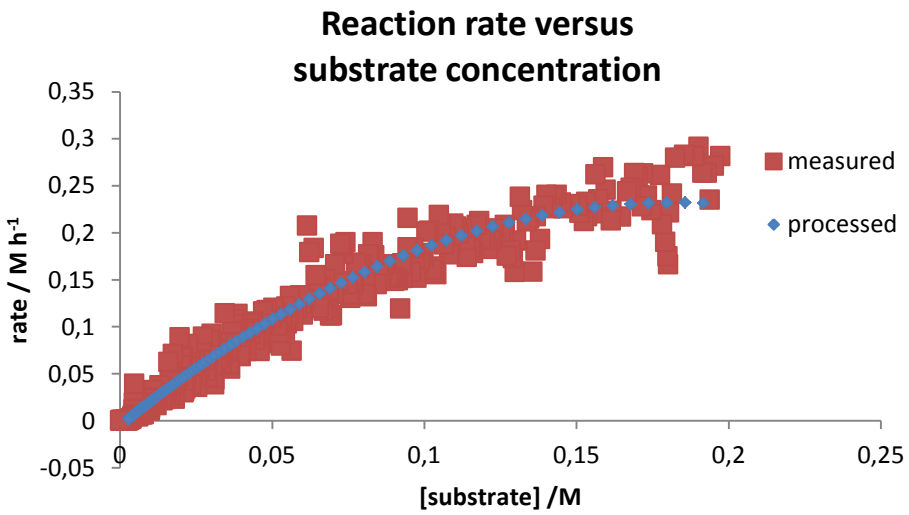

Reaction rate versus substrate concentration
rate / M h-1
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
-0,05
0
0,02
0,04
0,06
0,08
0,1
0,12
[substrate] /M
measured
processed

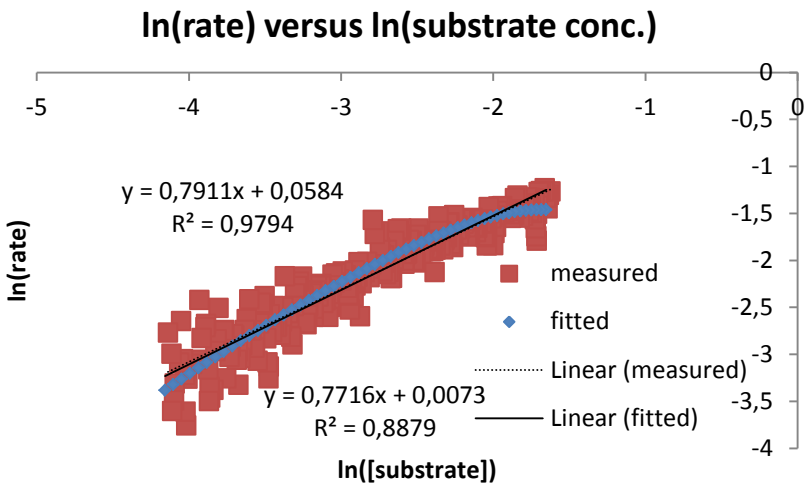

ln(rate) versus ln(substrate conc.)
y = 0,9819x + 1,3131
R² = 0,9836
y = 0,9184x + 1,0739
R² = 0,93
ln(rate)
ln([substrate])
-6
-5
-4
-3
-2
-1
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
measured
fitted
Linear (measured)
Linear (fitted)

6) Conditions: [**5**] = 0.2 M, [TEA] = 0.3 M, [Rh(acac)$(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C; (repetition of the experiment 2).

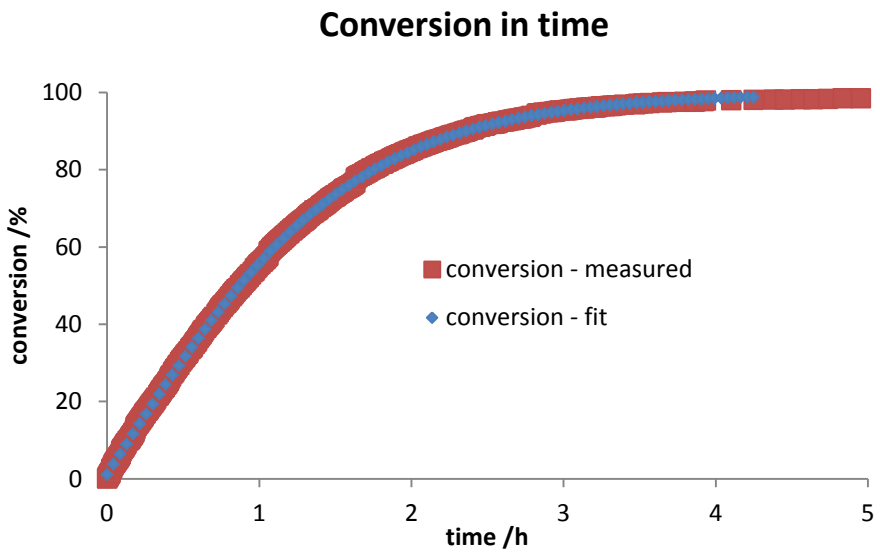


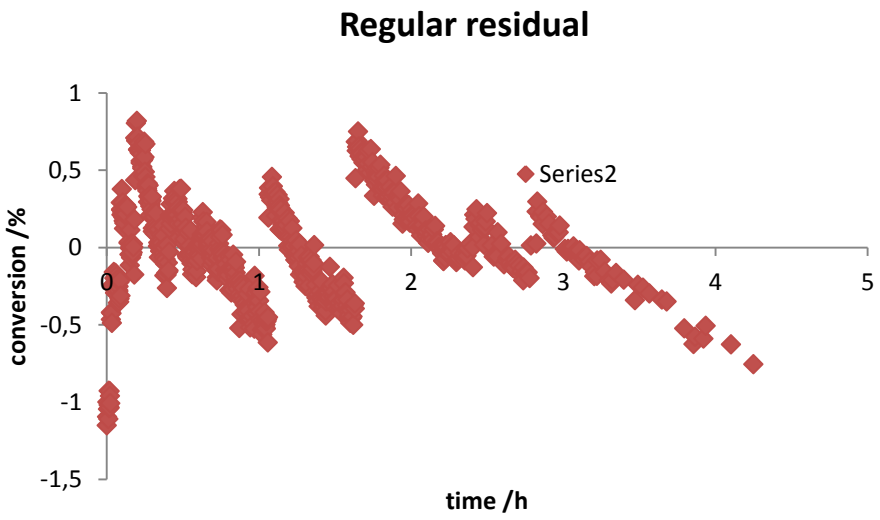


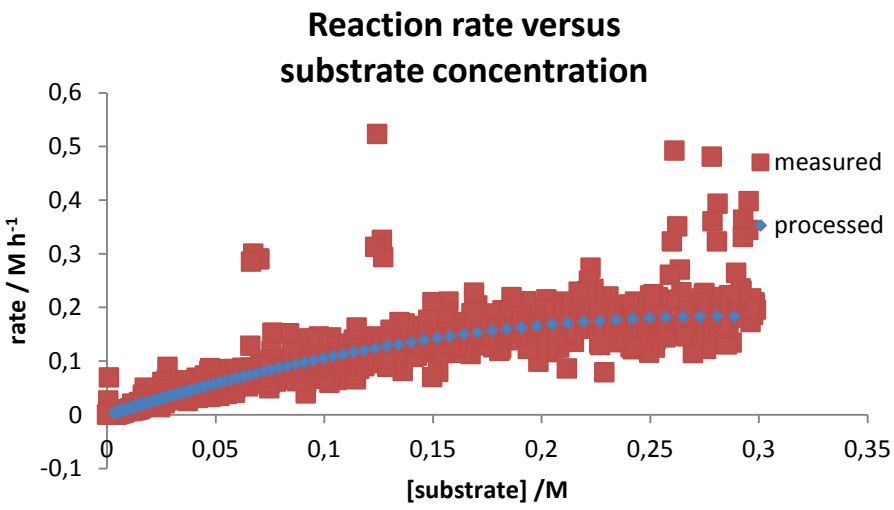

Reaction rate versus substrate concentration
rate / M h-1
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
-0,05
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

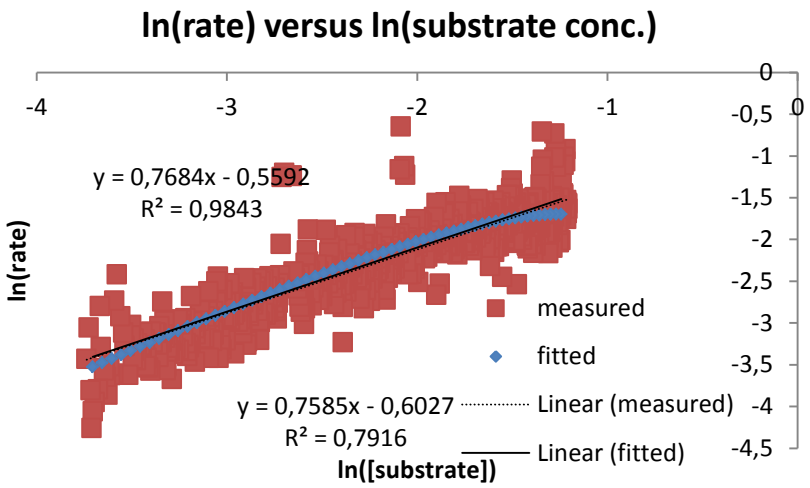

ln(rate) versus ln(substrate conc.)
ln(rate)
-5
-4
-3
-2
-1
0
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
y = 0,7911x + 0,0584
R² = 0,9794
y = 0,7716x + 0,0073
R² = 0,8879
ln([substrate])
measured
fitted
Linear (measured)
Linear (fitted)

7) Conditions: [**5**] = 0.3 M, [TEA] = 0.45 M, [Rh(acac)$(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with CO:H_2 (1:1) 20 bar at 30 °C.

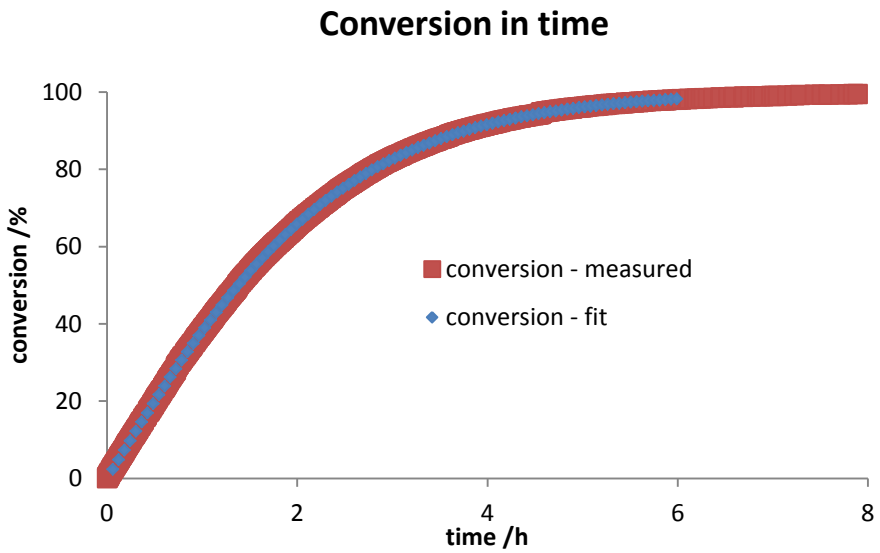


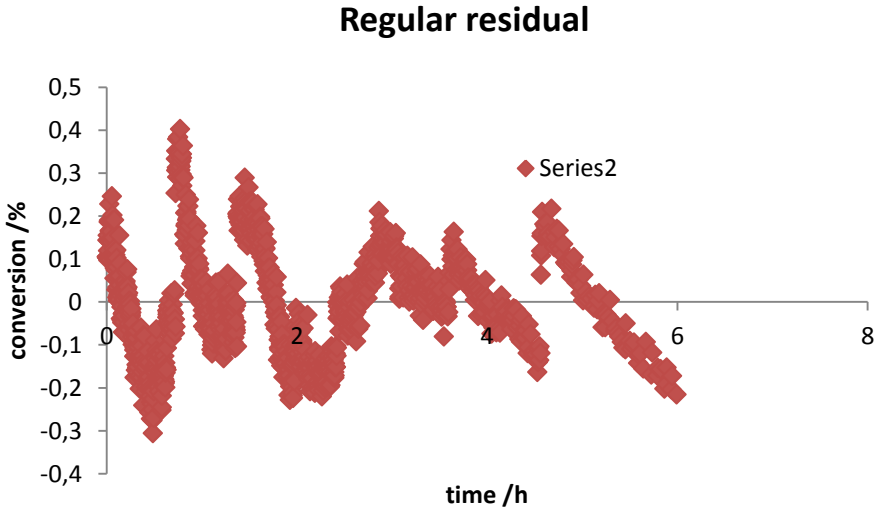


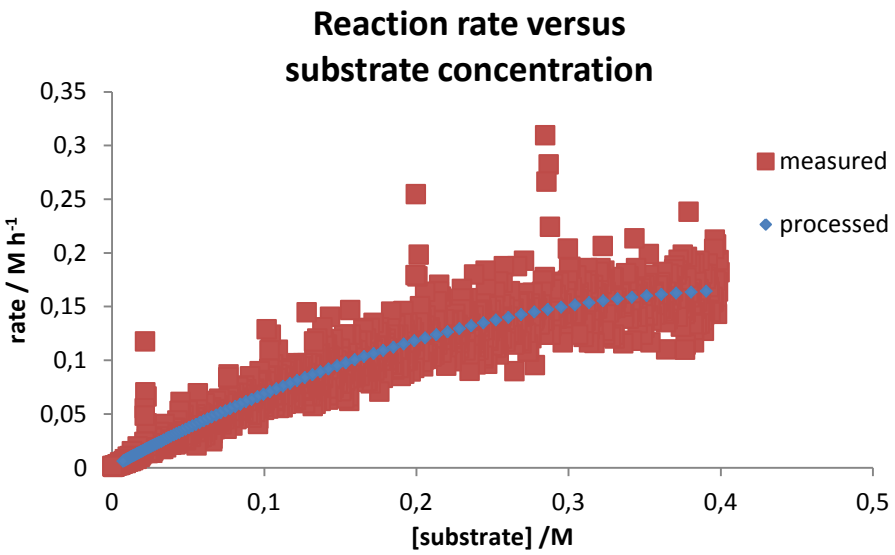


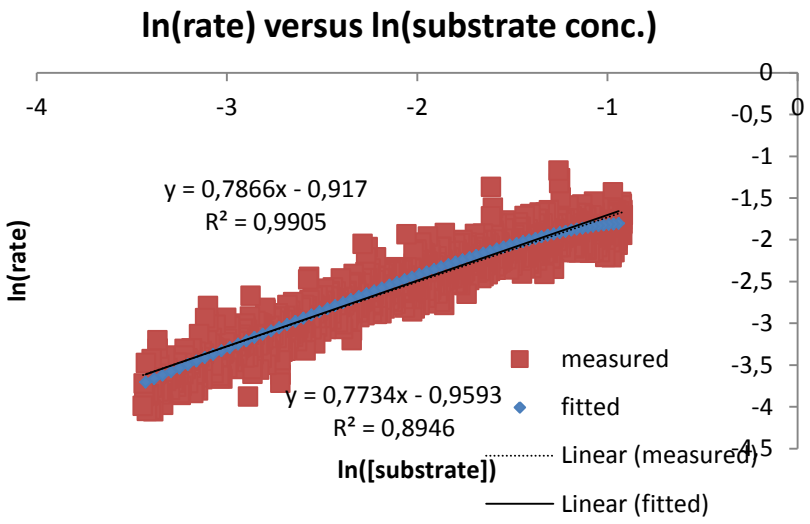

ln(rate) versus ln(substrate conc.)
y = 0,7684x - 0,5592
R² = 0,9843
y = 0,7585x - 0,6027
R² = 0,7916
ln(rate)
ln([substrate])
measured
fitted
Linear (measured)
Linear (fitted)
-4
-3
-2
-1
0
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
-4,5

8) Conditions: [**5**] = 0.4 M, [TEA] = 0.6 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.



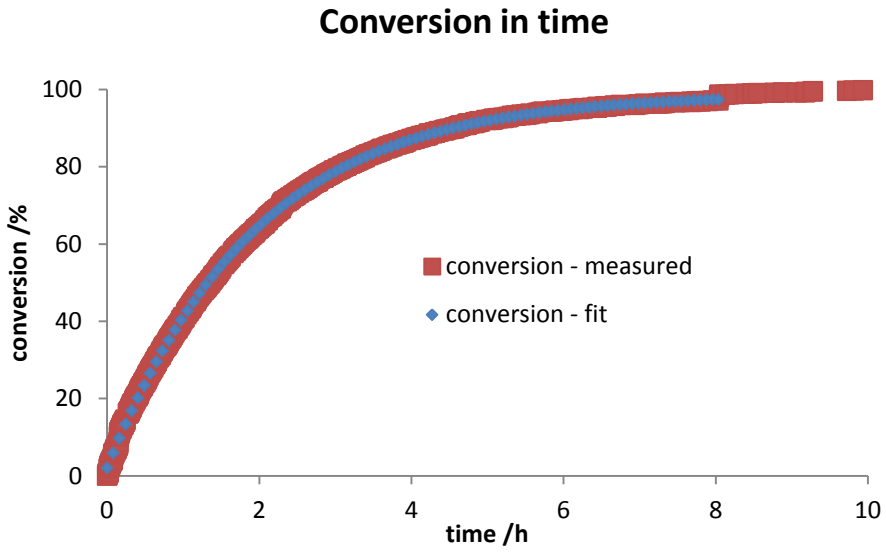


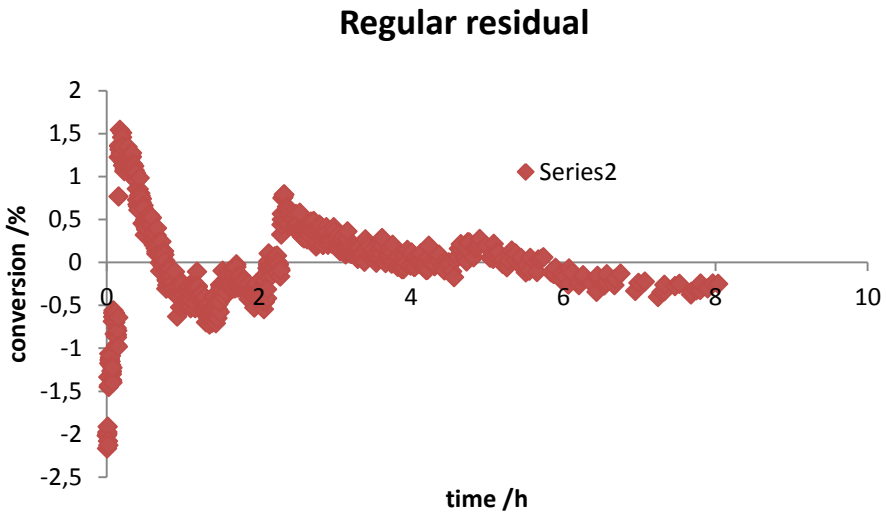

Reaction rate versus substrate concentration
rate / M h-1
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,1
0,2
0,3
0,4
0,5
[substrate] /M
measured
processed

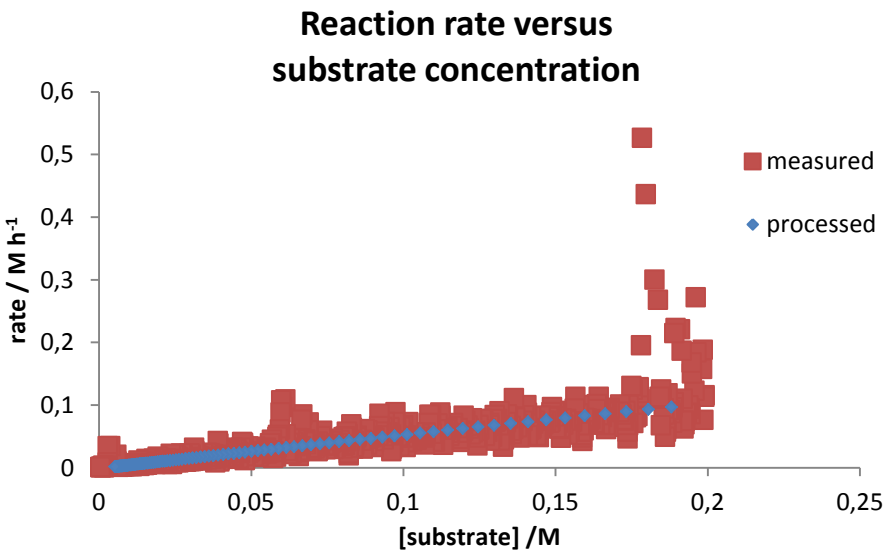

ln(rate) versus ln(substrate conc.)
ln(rate)
-4
-3
-2
-1
0
-0,5
-1
-1,5
-2
-2,5
-3
-3,5
-4
-4,5
y = 0,7866x - 0,917
R² = 0,9905
y = 0,7734x - 0,9593
R² = 0,8946
ln([substrate])
measured
fitted
Linear (measured)
Linear (fitted)

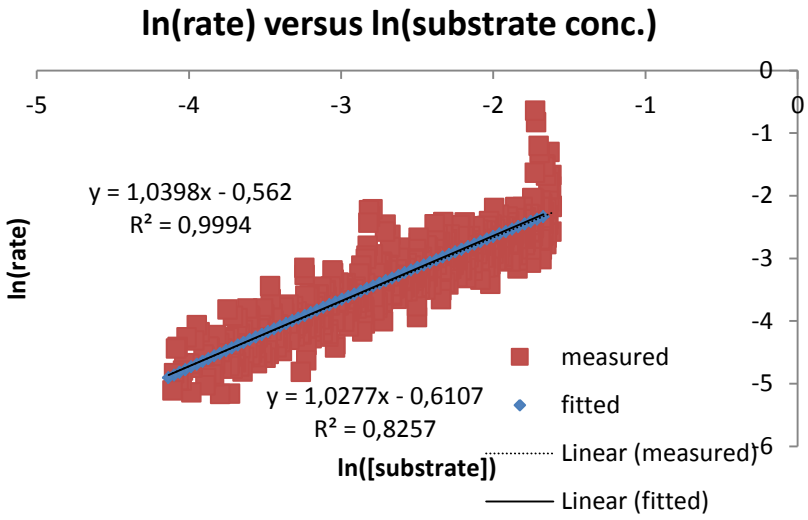
Hydroformylation of substrate 5 with the Rh(L5) catalysts, with the catalyst pre-incubation – influence of the additives on the catalyst activity and stabililty:

9) Conditions: [**5**] = 0.2 M, [product **8**] = 0.2 M, [TEA] = 0.6 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation in the absence of product **8**, for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.

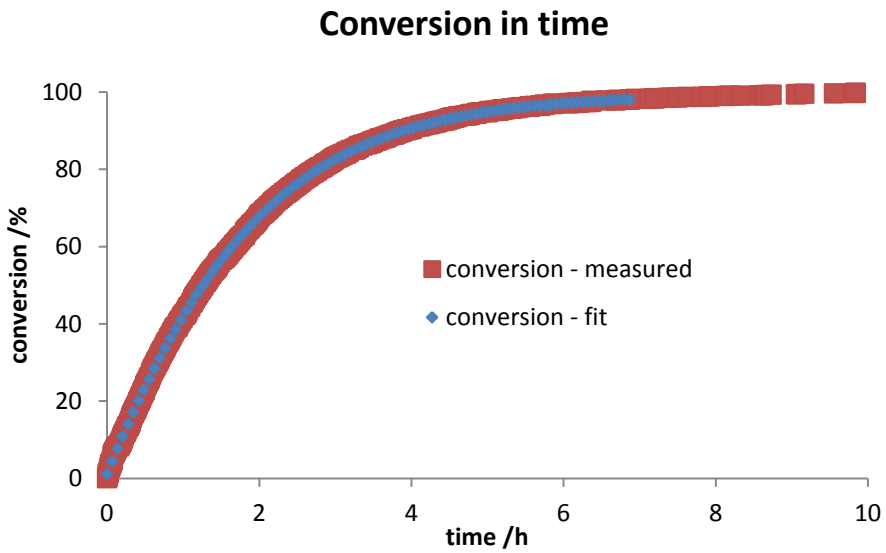


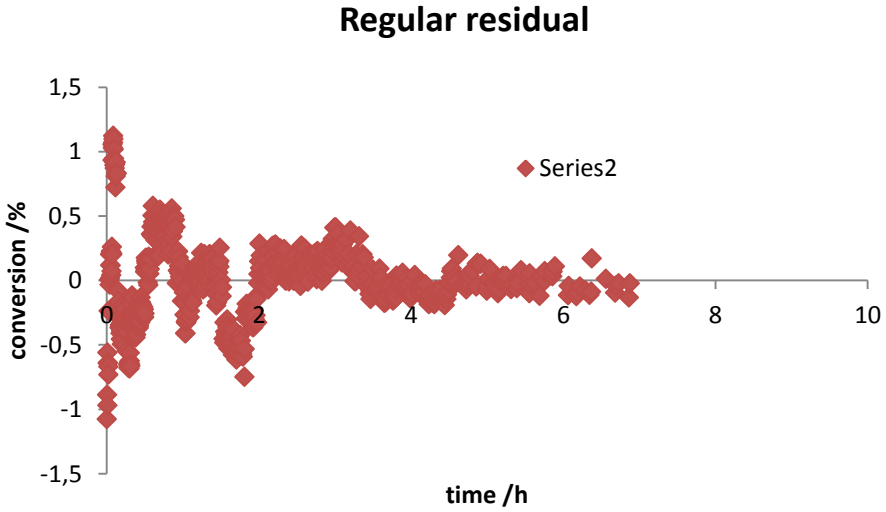


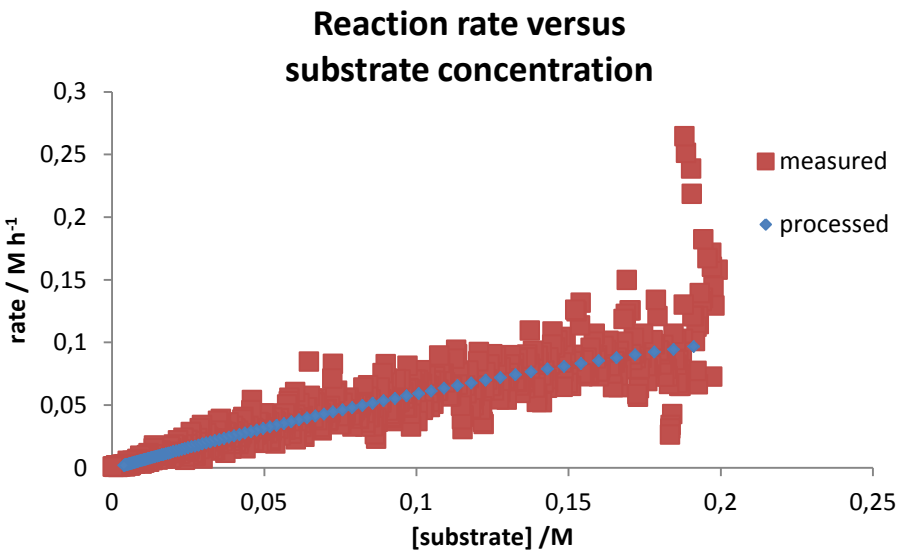

Reaction rate versus substrate concentration
rate / M h-1
0,6
0,5
0,4
0,3
0,2
0,1
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

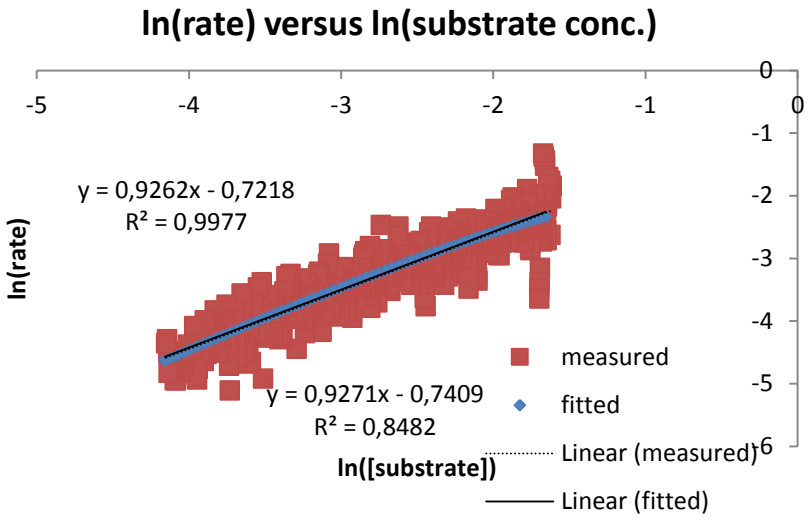

ln(rate) versus ln(substrate conc.)
ln(rate)
-5
-4
-3
-2
-1
0
-1
-2
-3
-4
-5
-6
y = 1,0398x - 0,562
R² = 0,9994
y = 1,0277x - 0,6107
R² = 0,8257
ln([substrate])
measured
fitted
Linear (measured)
Linear (fitted)

10) Conditions: [**5**] = 0.2 M, [4-heptylbenzoic acid] = 0.2 M, [TEA] = 0.6 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation in the absence of 4-heptylbenzoic acid, for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.

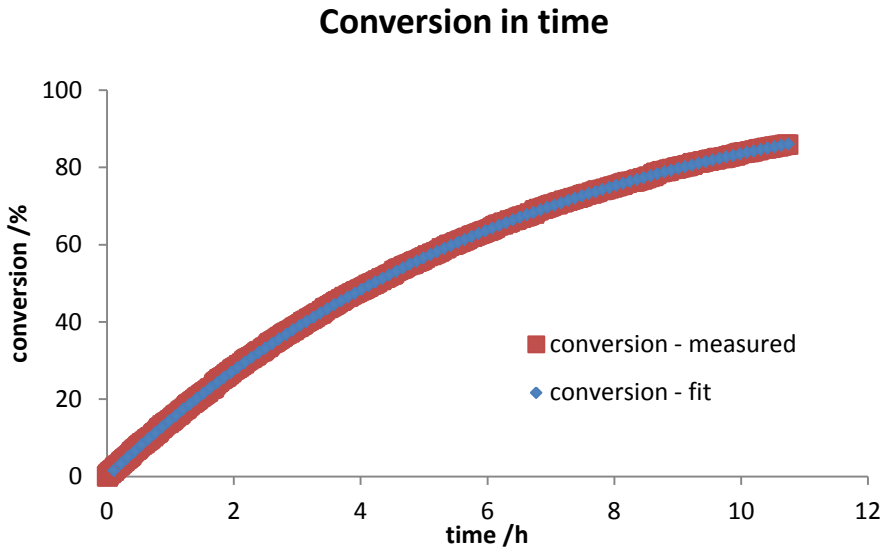


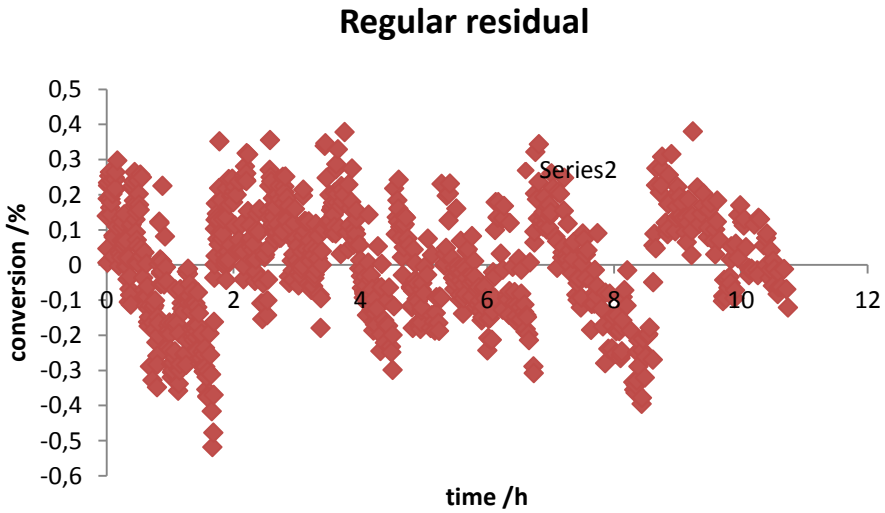


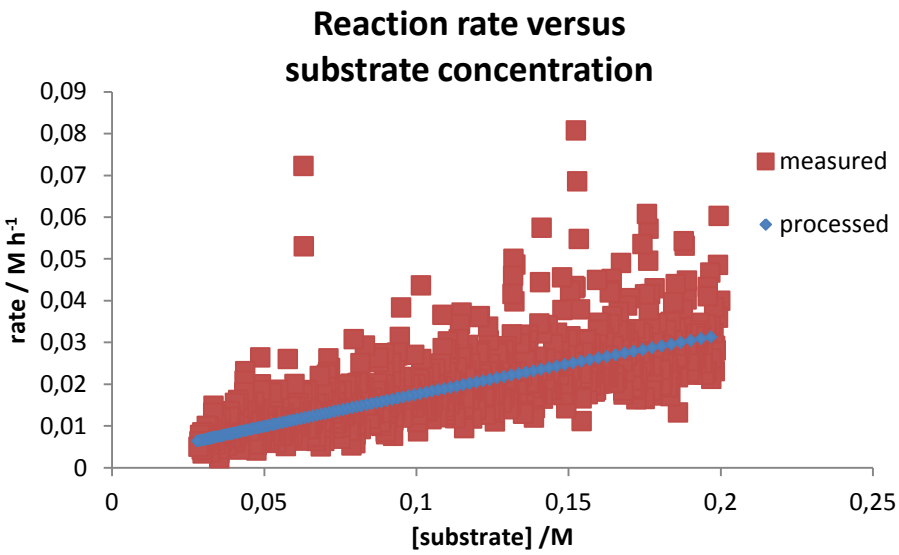

Reaction rate versus substrate concentration
rate / M h-1
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

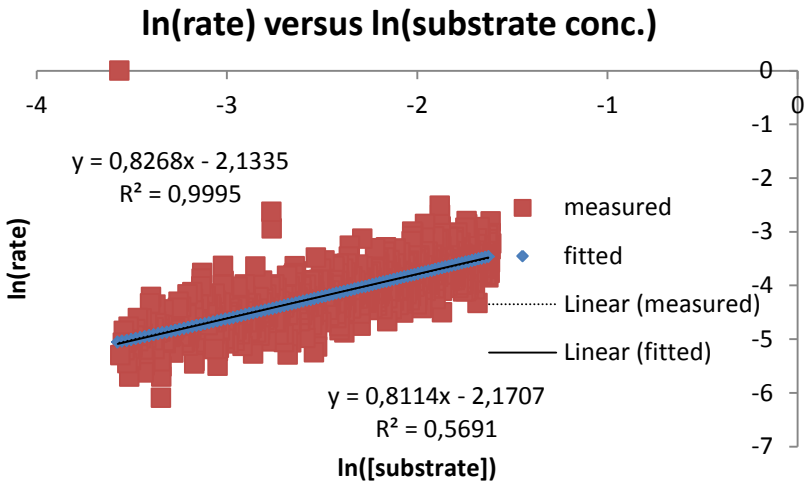

ln(rate) versus ln(substrate conc.)
y = 0,9262x - 0,7218
R² = 0,9977
y = 0,9271x - 0,7409
R² = 0,8482
ln(rate)
ln([substrate])
-5
-4
-3
-2
-1
0
-1
-2
-3
-4
-5
-6
measured
fitted
Linear (measured)
Linear (fitted)

11) Conditions: [**5**] = 0.2 M, [product **8**] = 0.2 M, [TEA] = 0.6 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation in the presence of product **8** (and the half of the final amount of TEA), for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.

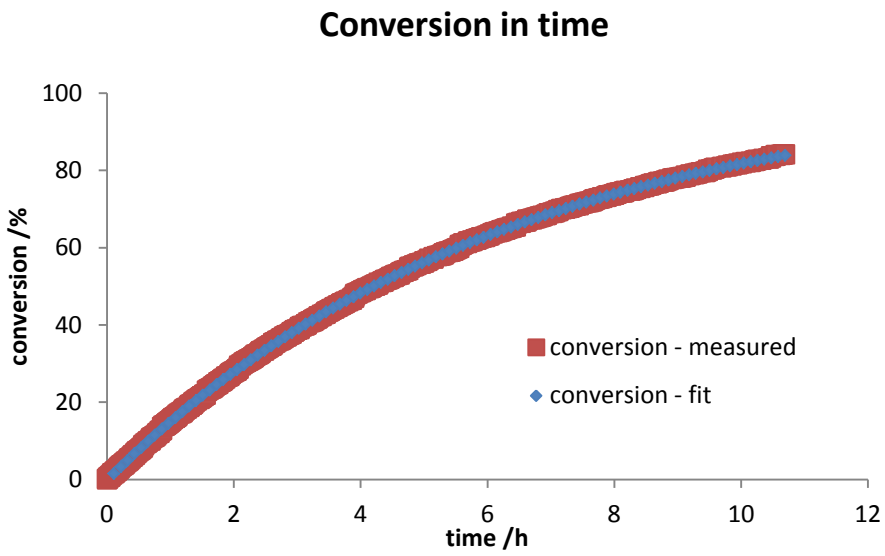


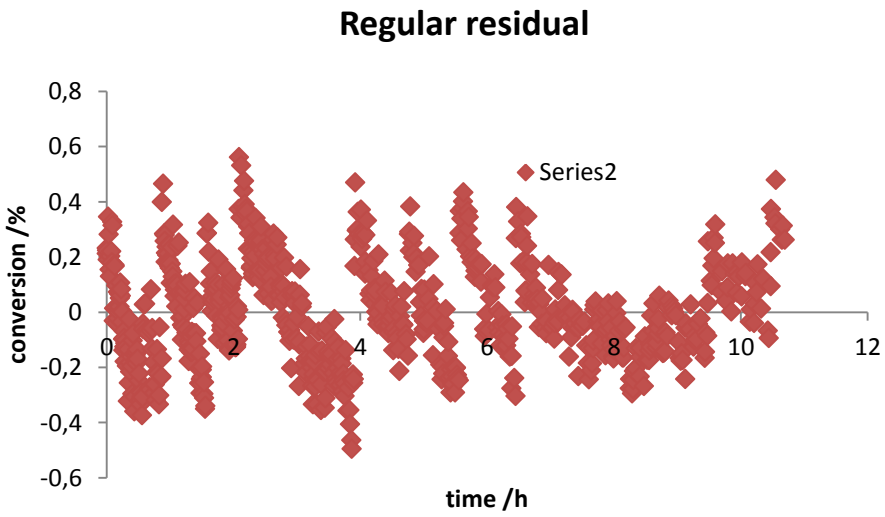


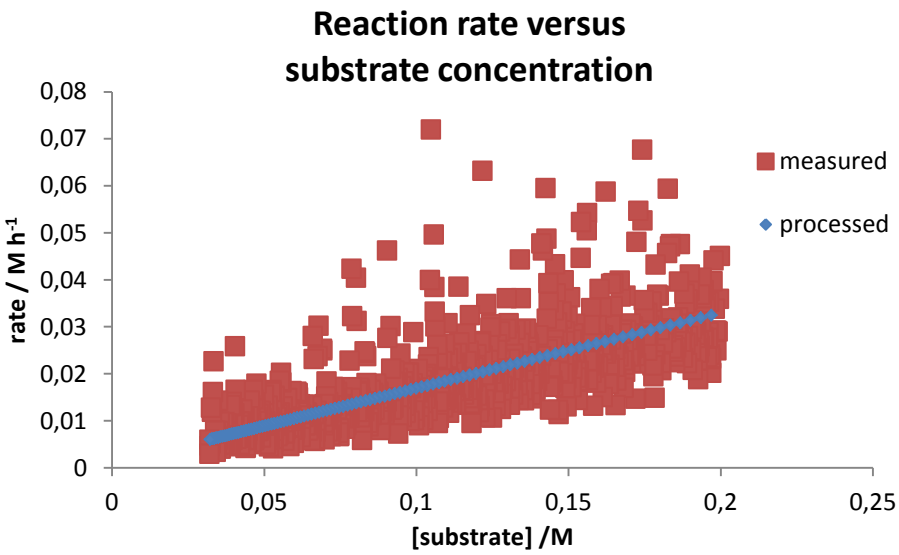

Reaction rate versus substrate concentration
rate / M h-1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

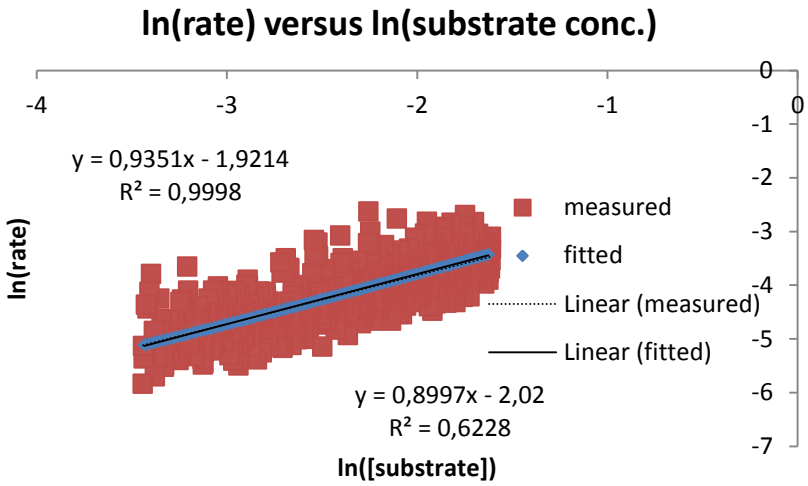

ln(rate) versus ln(substrate conc.)
y = 0,8268x - 2,1335
R² = 0,9995
y = 0,8114x - 2,1707
R² = 0,5691
ln(rate)
ln([substrate])
-4
-3
-2
-1
0
-1
-2
-3
-4
-5
-6
-7
measured
fitted
Linear (measured)
Linear (fitted)

12) Conditions: [**5**] = 0.2 M, [4-heptylbenzoic acid] = 0.2 M, [TEA] = 0.6 M, [$Rh(acac)(CO)_2$] = 0.001 M, [**L5**] = 0.0011 M in CH_2Cl_2 (8 ml), pressure $CO:H_2$ (1:1) 22 bar, 30 °C; the catalyst pre-incubation in the presence of 4-heptylbenzoic acid (and the half of the final amount of TEA), for ~ 20 h with $CO:H_2$ (1:1) 20 bar at 30 °C.



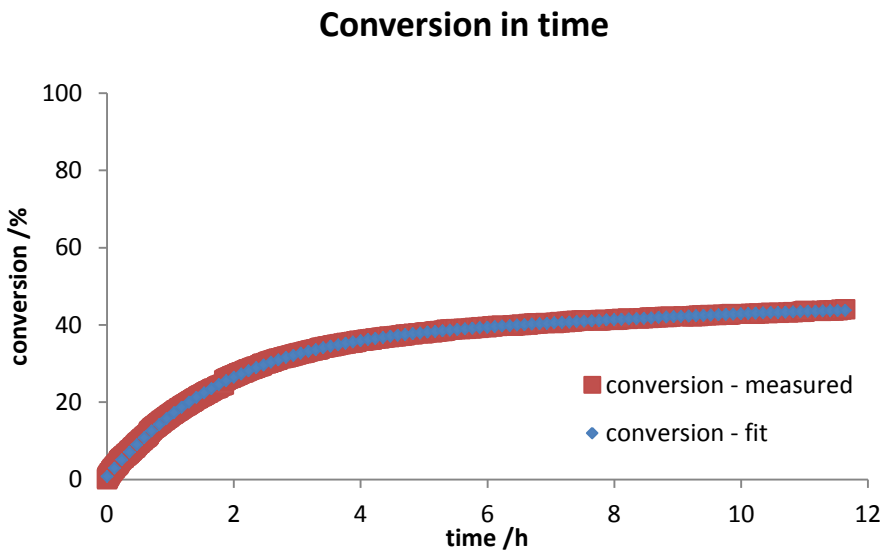


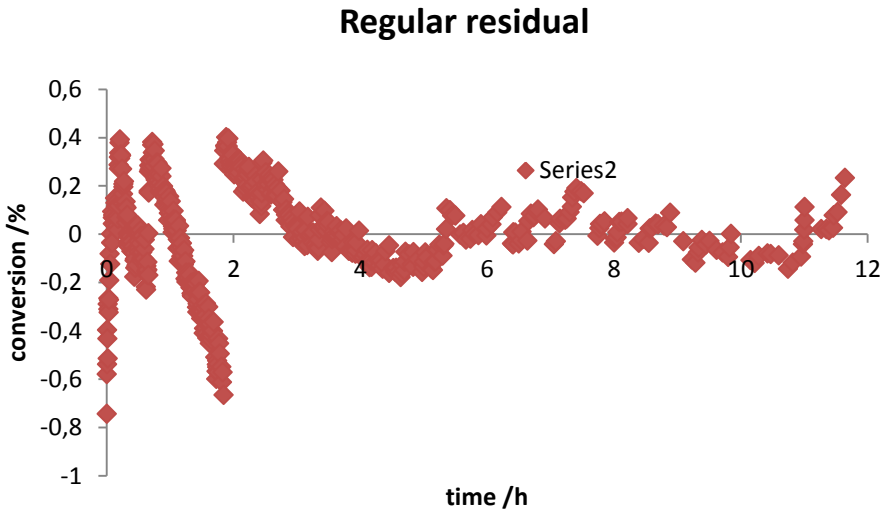

Reaction rate versus substrate concentration
rate / M h-1
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
0
0,05
0,1
0,15
0,2
0,25
[substrate] /M
measured
processed

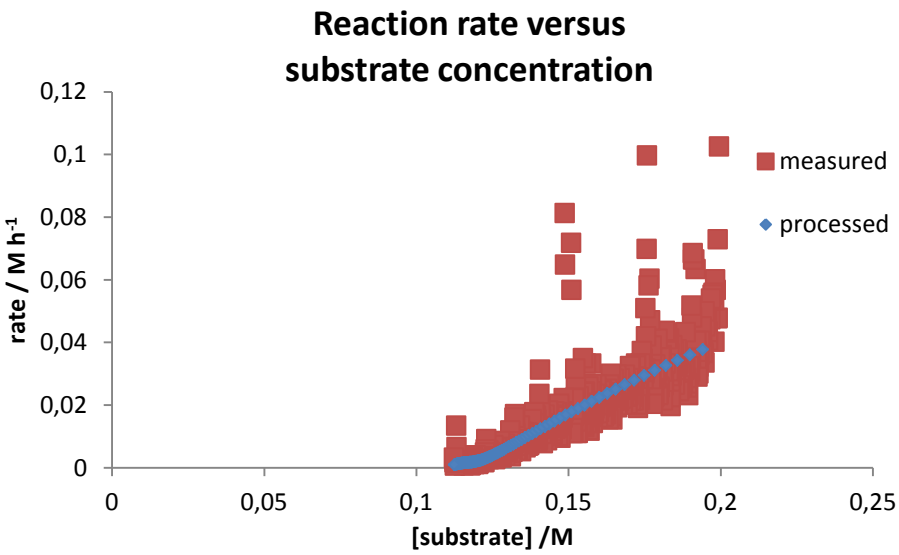

ln(rate) versus ln(substrate conc.)
y = 0,9351x - 1,9214
R² = 0,9998
y = 0,8997x - 2,02
R² = 0,6228
ln(rate)
ln([substrate])
-4
-3
-2
-1
0
-1
-2
-3
-4
-5
-6
-7
measured
fitted
Linear (measured)
Linear (fitted)

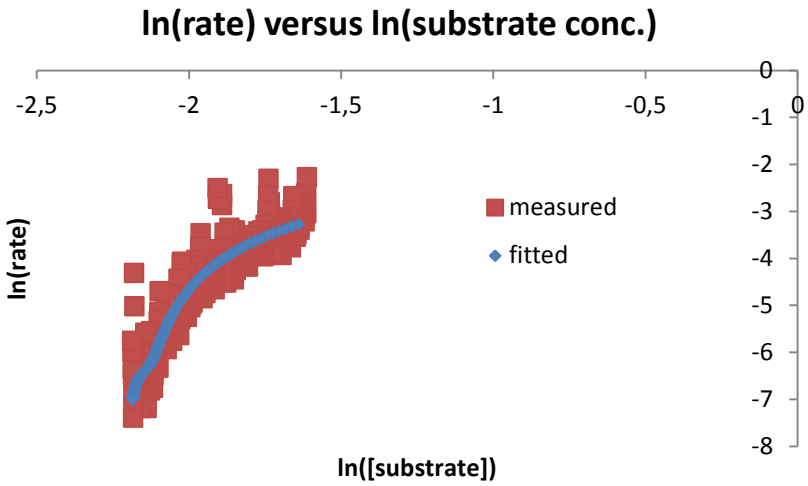
Hydroformylation of substrate 5 with the Rh(L5) catalysts, without the catalyst pre-incubation – at the very low catalyst loading (0.001 mol%):

Conditions: [**5**] = 0.2 M, [TEA] = 0.18 M, [Rh(acac)$(CO)_2$] = 0.000002 M, [**L5**] = 0.0000022 M in CH_2Cl_2 (8 ml), pressure CO:H_2 (1:1) 20 bar, 80 °C; no catalyst pre-incubation. Recorded 44% conversion.









The details of the other kinetic experiements, that is the hydroformylation of substrate **5** with different rhodium catalysts, evaluation of influence of the reaction temperature on the hydroformylation of **5** with the Rh(**L5**) catalyst, as well as, the hydroformylation of substrate **11** with the Rh(**L5**) catalyst are provided in the communication of the preliminary results of the study.[5]

NMR Spectra

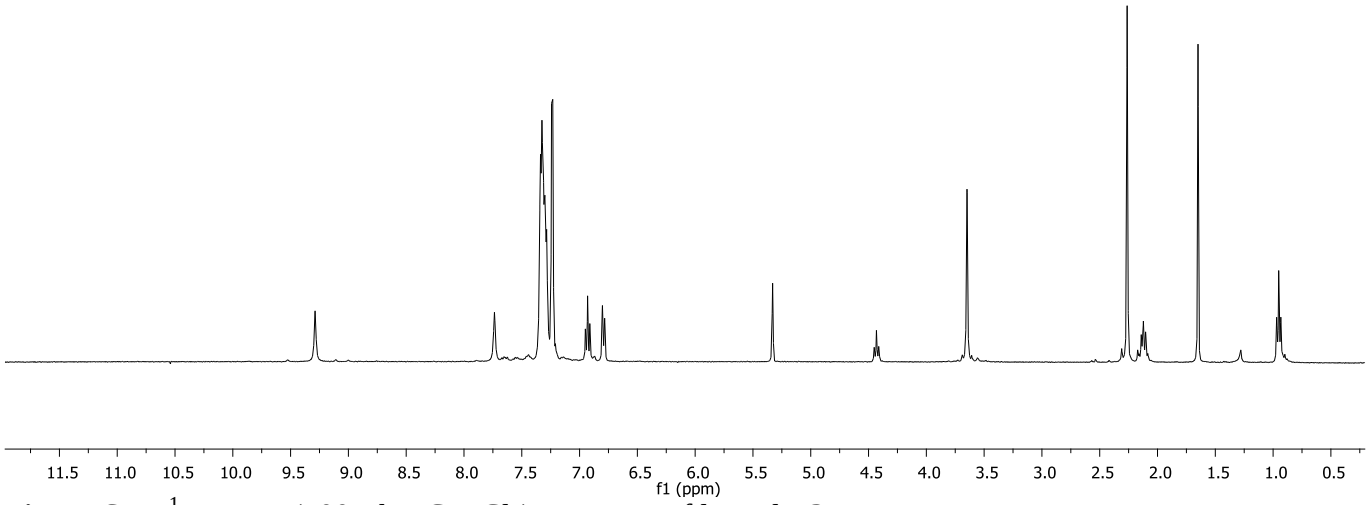


Figure S41. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of ligand **L3**.

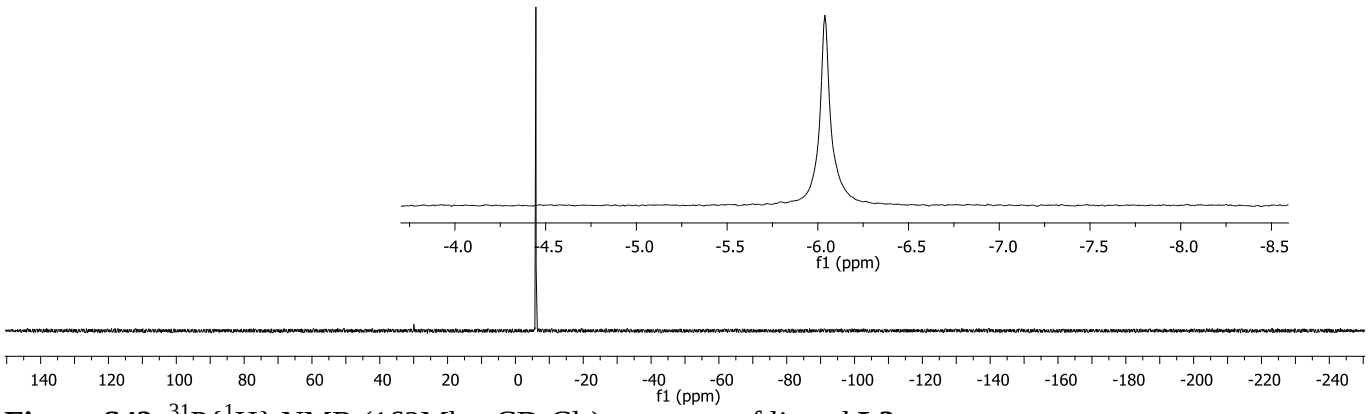


Figure S42. $^{31}P\{^{1}H\}$ NMR (162Mhz, CD_2Cl_2) spectrum of ligand **L3**.

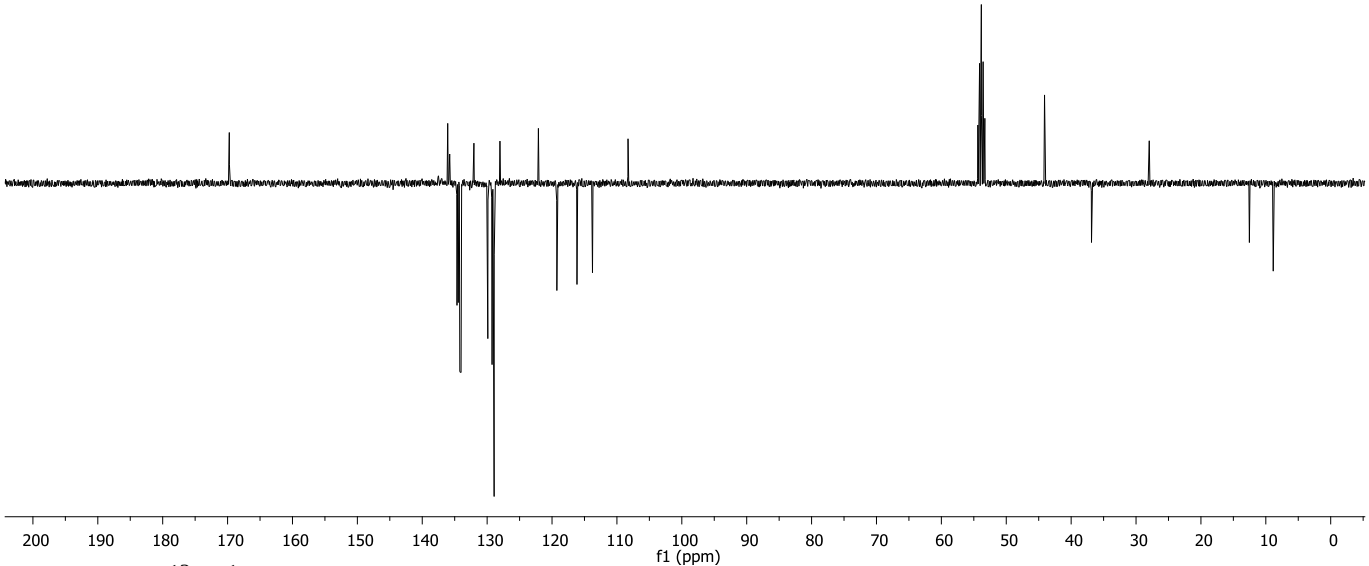


Figure S43. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L3**.

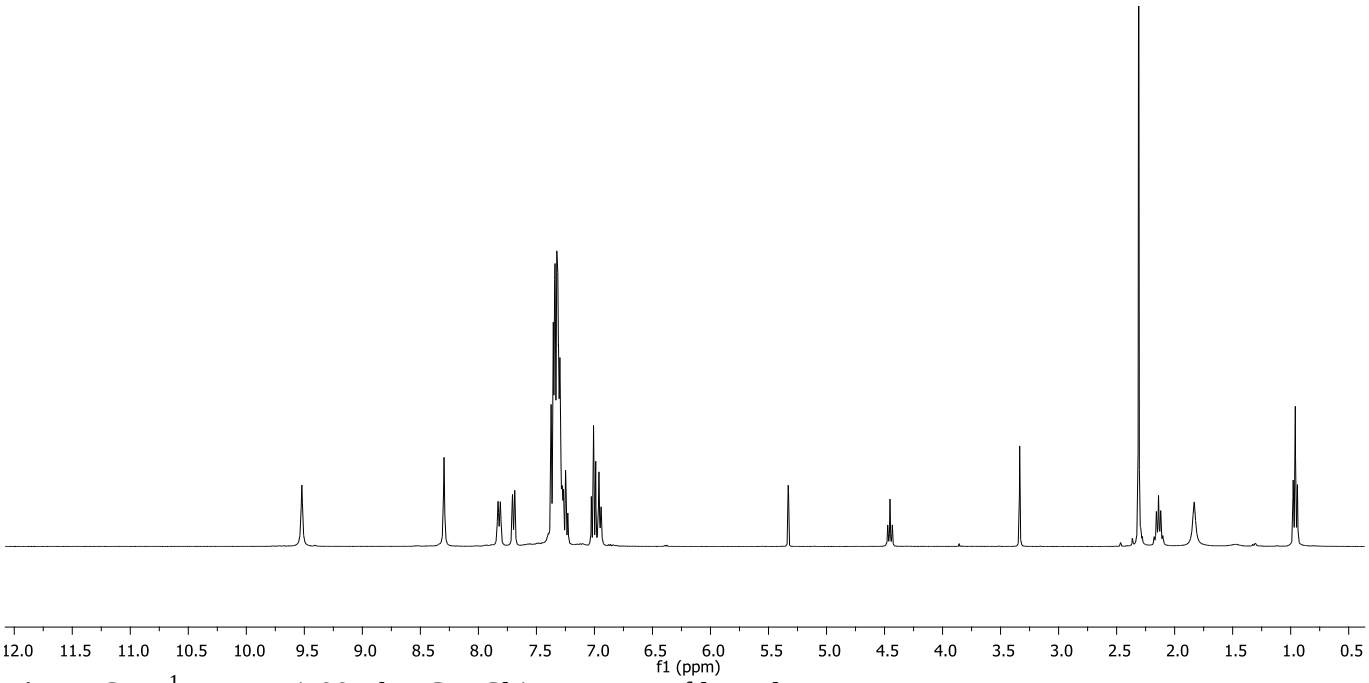


Figure S44. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of ligand **L4**.

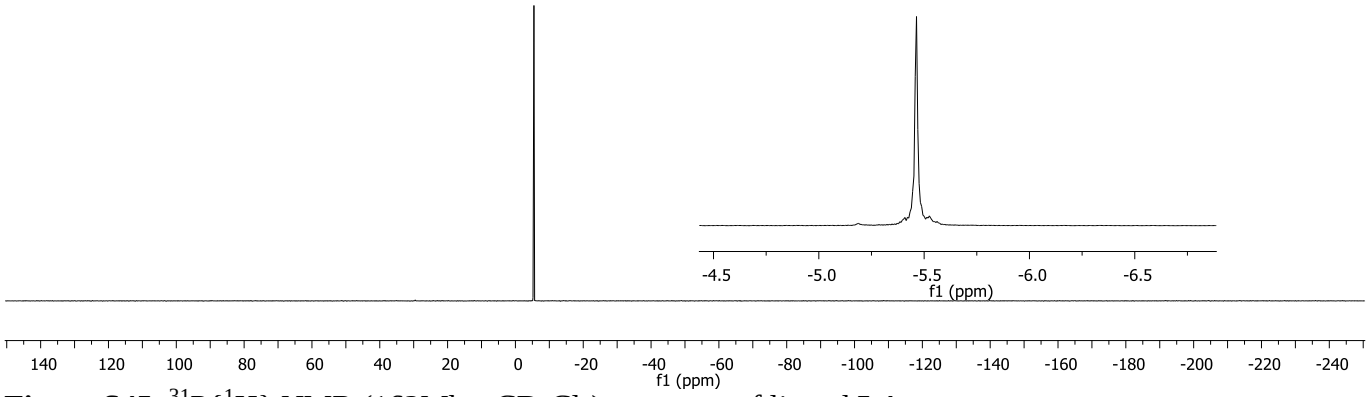


Figure S45. $^{31}P\{^{1}H\}$ NMR (162Mhz, CD_2Cl_2) spectrum of ligand **L4**.

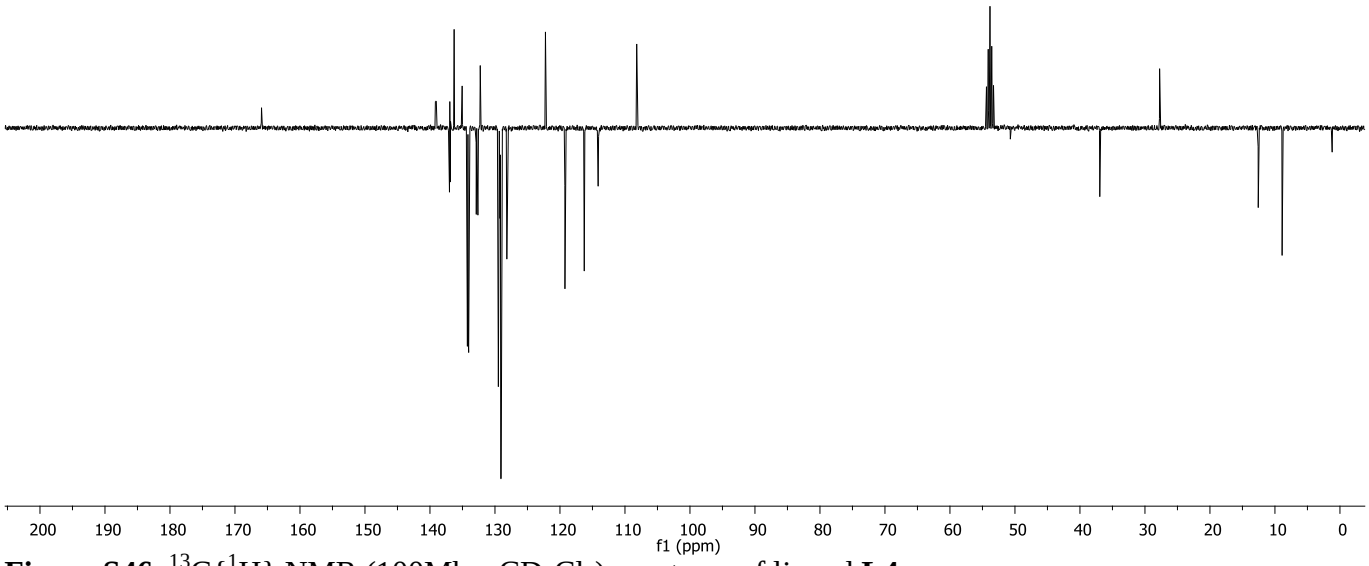


Figure S46. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L4**.

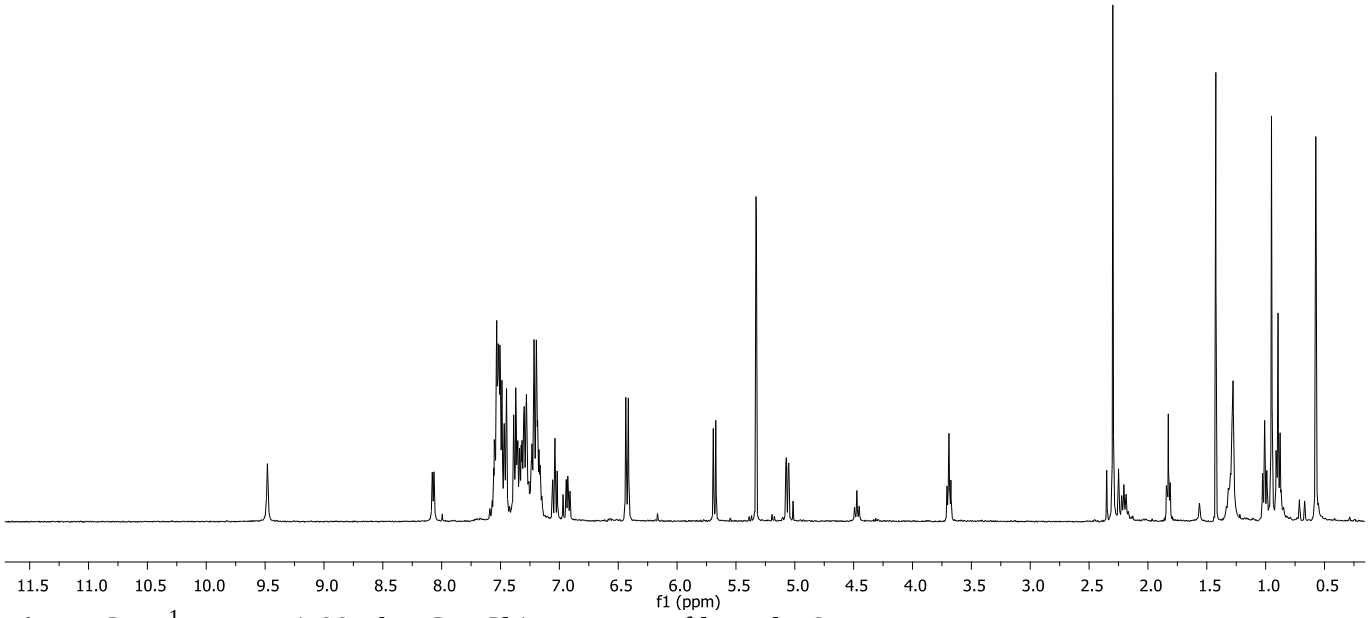


Figure S47. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of ligand **L6**.

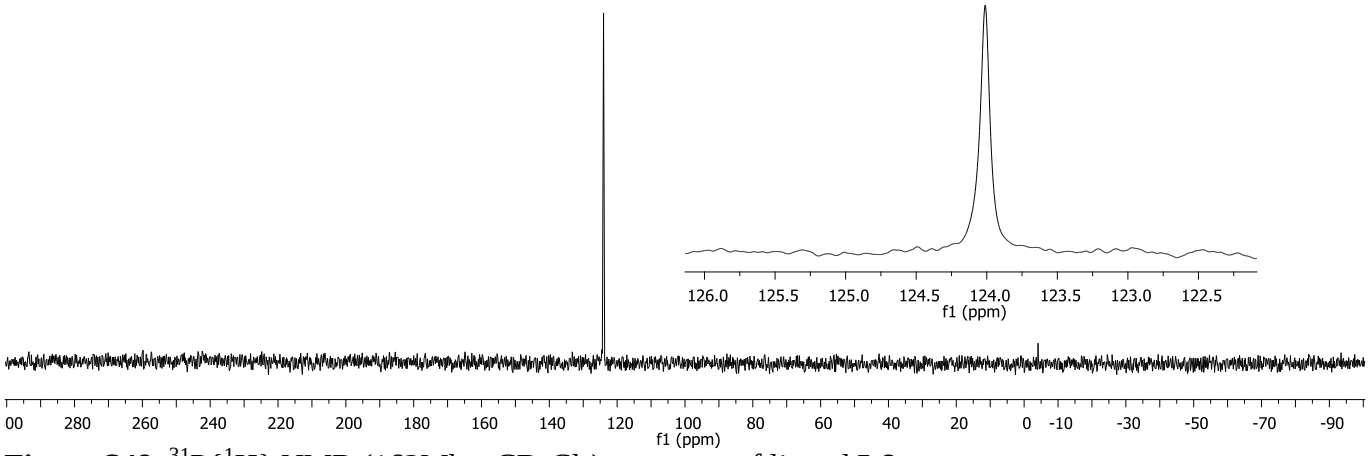


Figure S48. $^{31}P\{^{1}H\}$ NMR (162Mhz, CD_2Cl_2) spectrum of ligand **L6**.

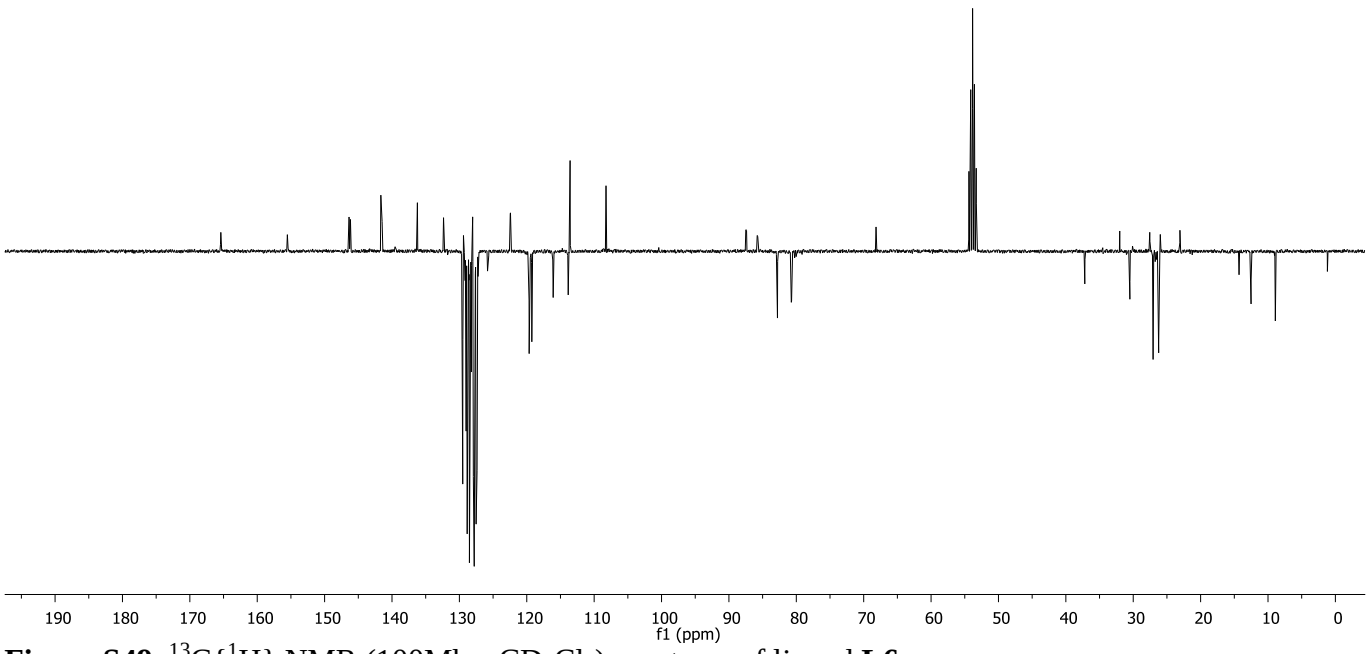


Figure S49. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L6**.

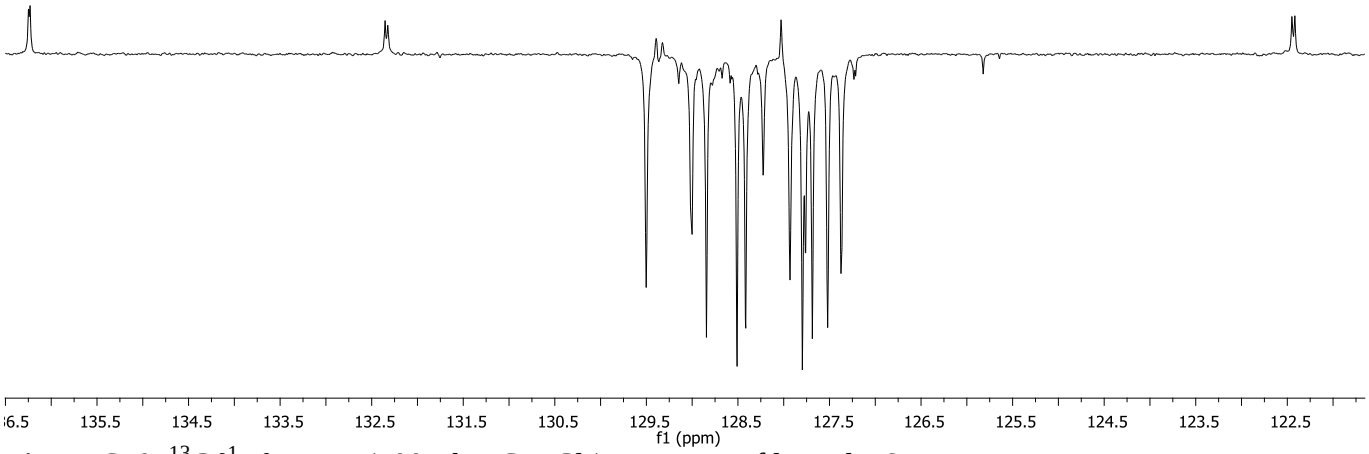


Figure S50. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L6 –** part.

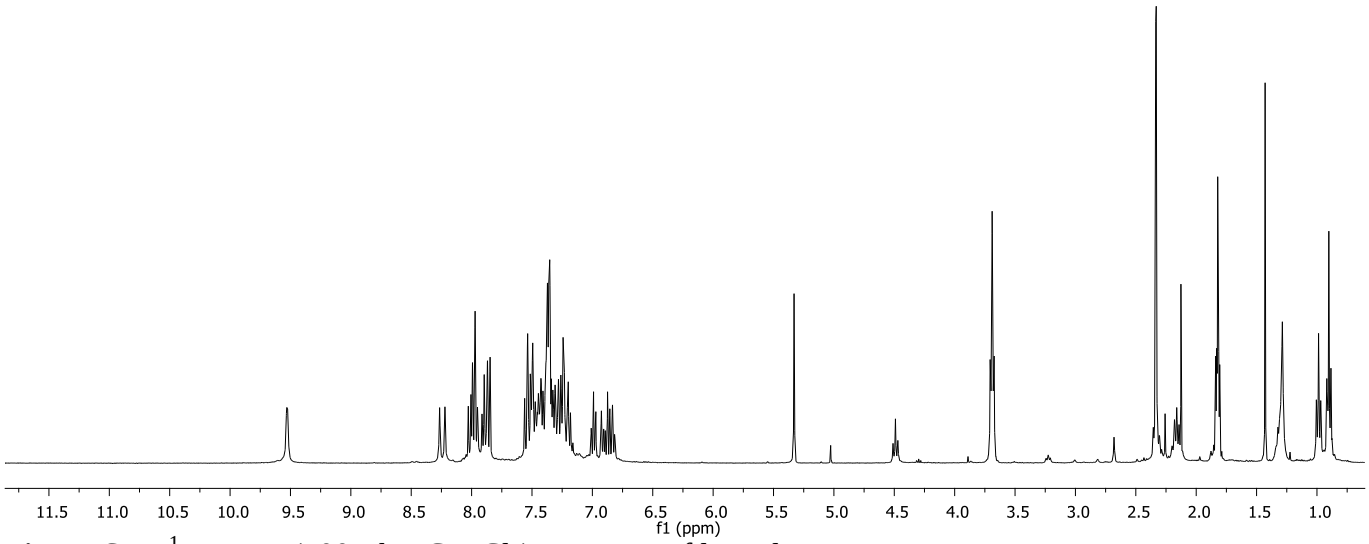


Figure S51. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of ligand **L7**.

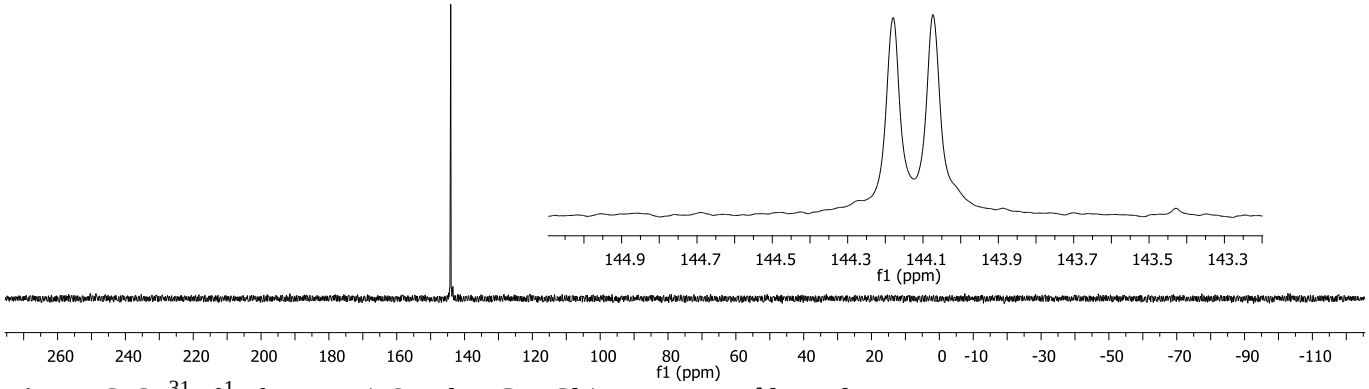


Figure S52. $^{31}P\{^{1}H\}$ NMR (162Mhz, CD_2Cl_2) spectrum of ligand **L7**.

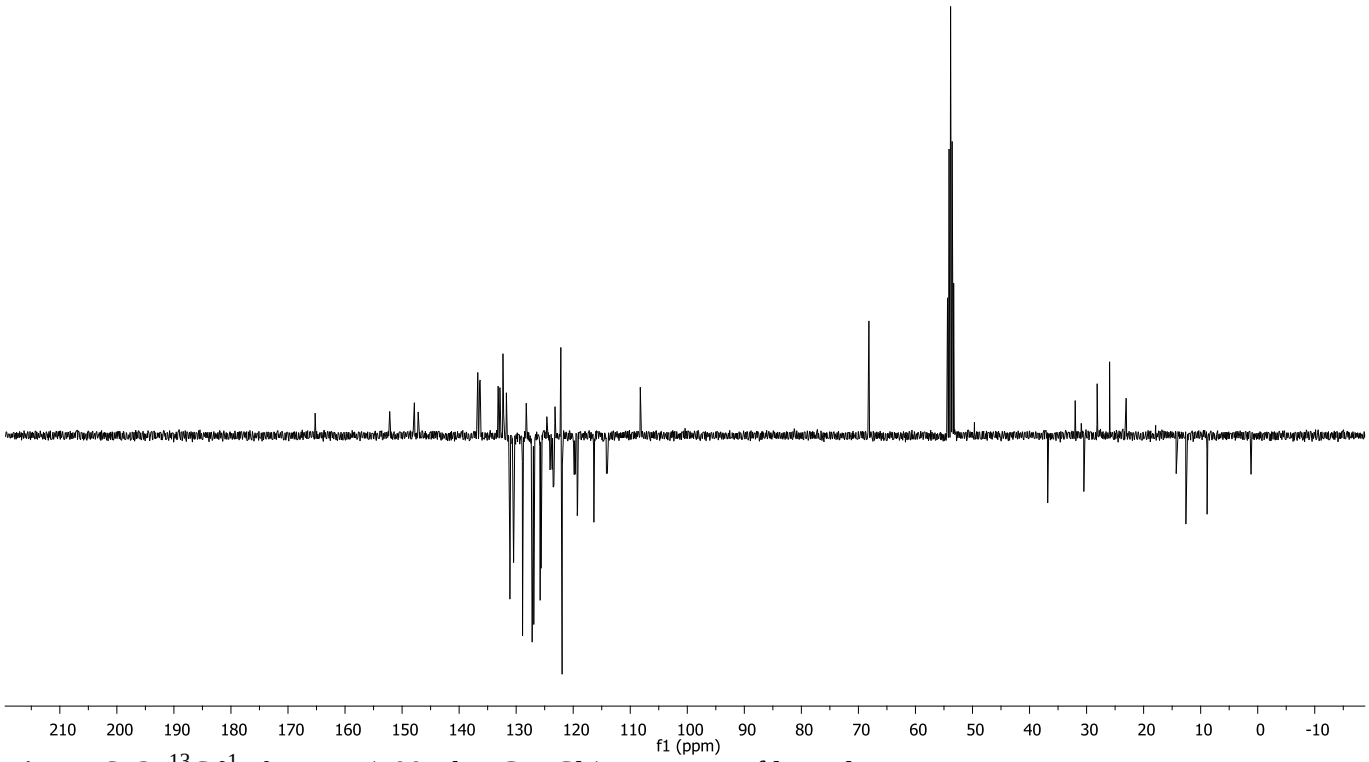


Figure S53. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L7**.

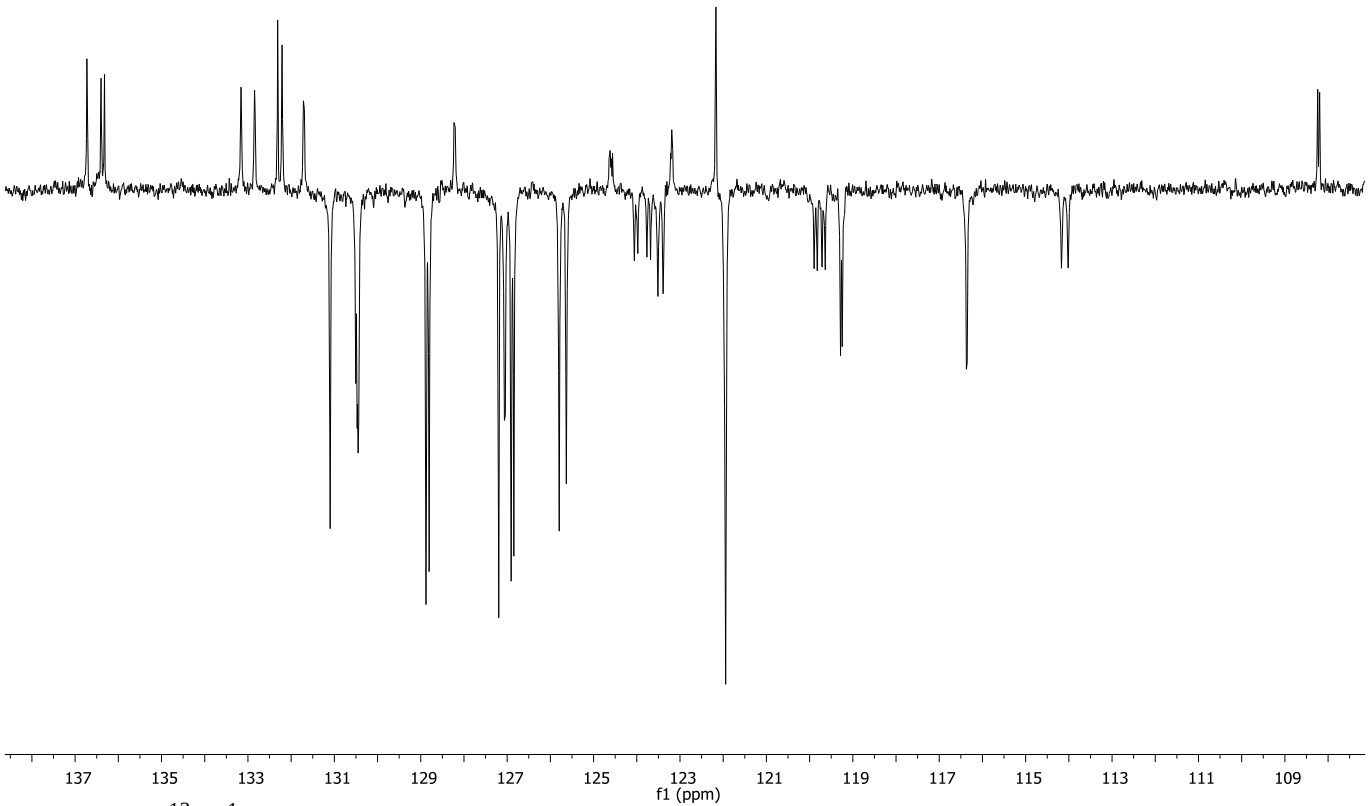


Figure S54. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of ligand **L7** – part.

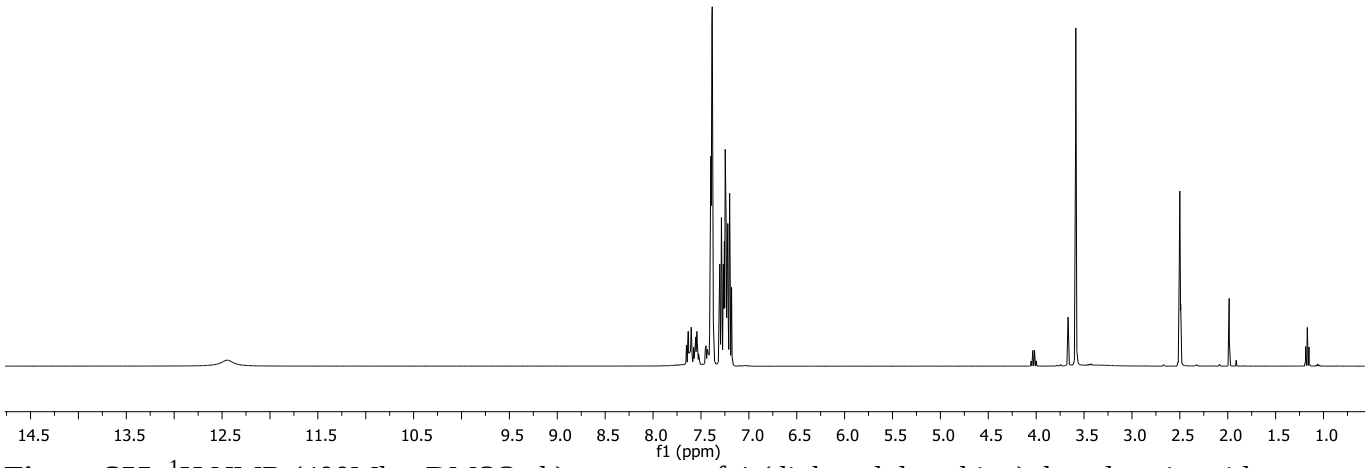


Figure S55. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of 4-(diphenylphosphino)phenylacetic acid.

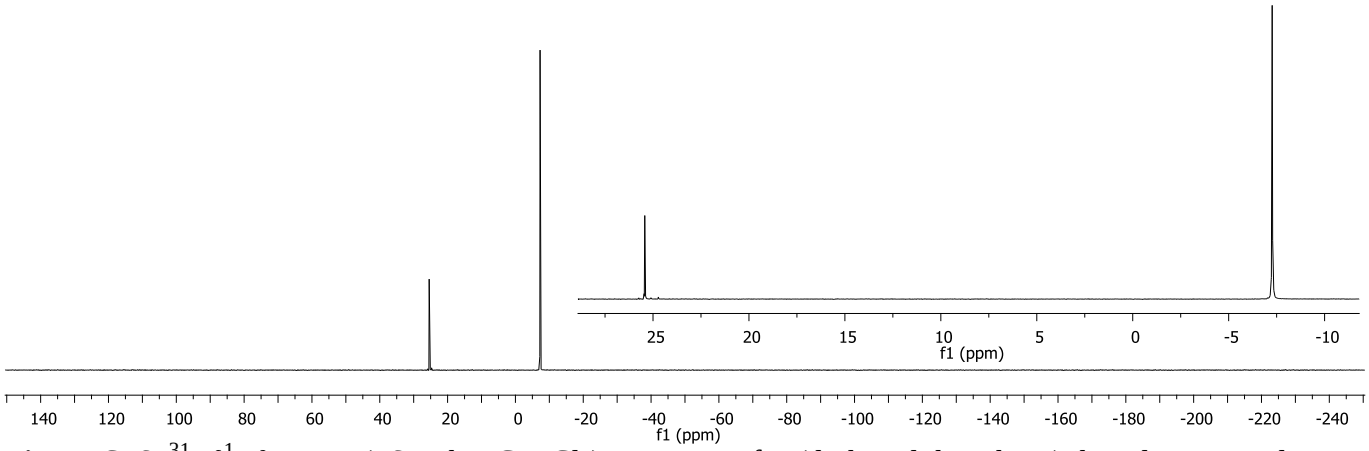


Figure S56. $^{31}P\{^{1}H\}$ NMR (162Mhz, CD_2Cl_2) spectrum of 4-(diphenylphosphino)phenylacetic acid.

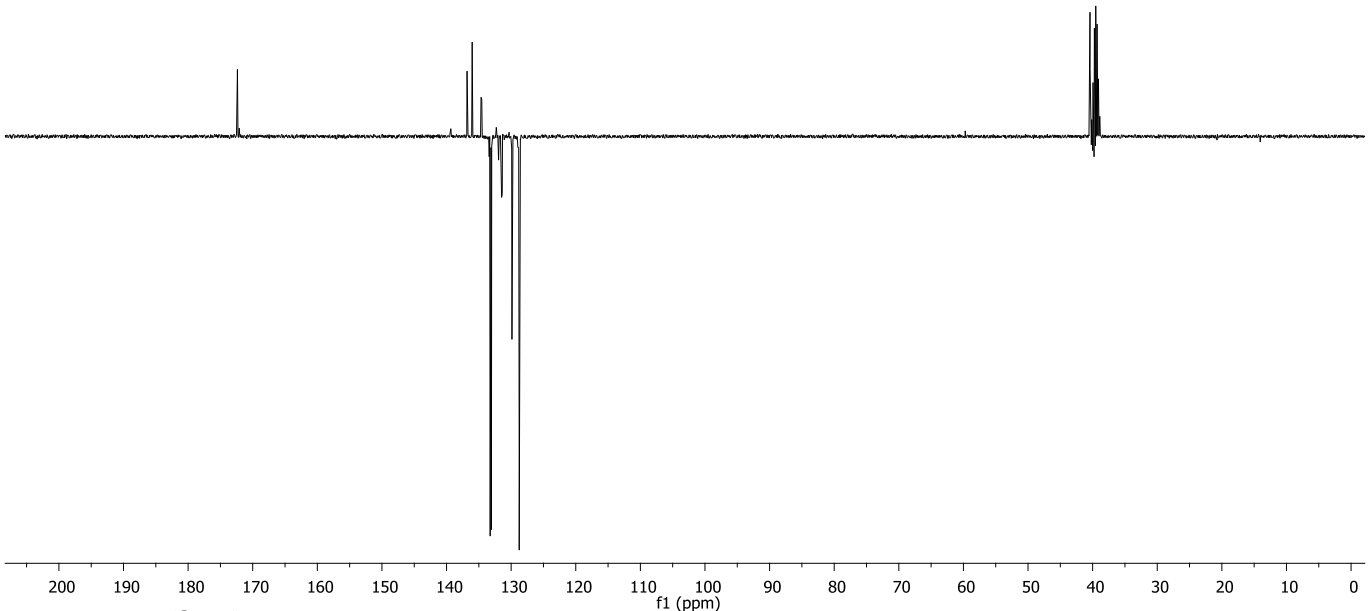


Figure S57. $^{13}C\{^{1}H\}$ NMR (100Mhz, DMSO-d_6) spectrum of 4-(diphenylphosphino)phenylacetic acid.

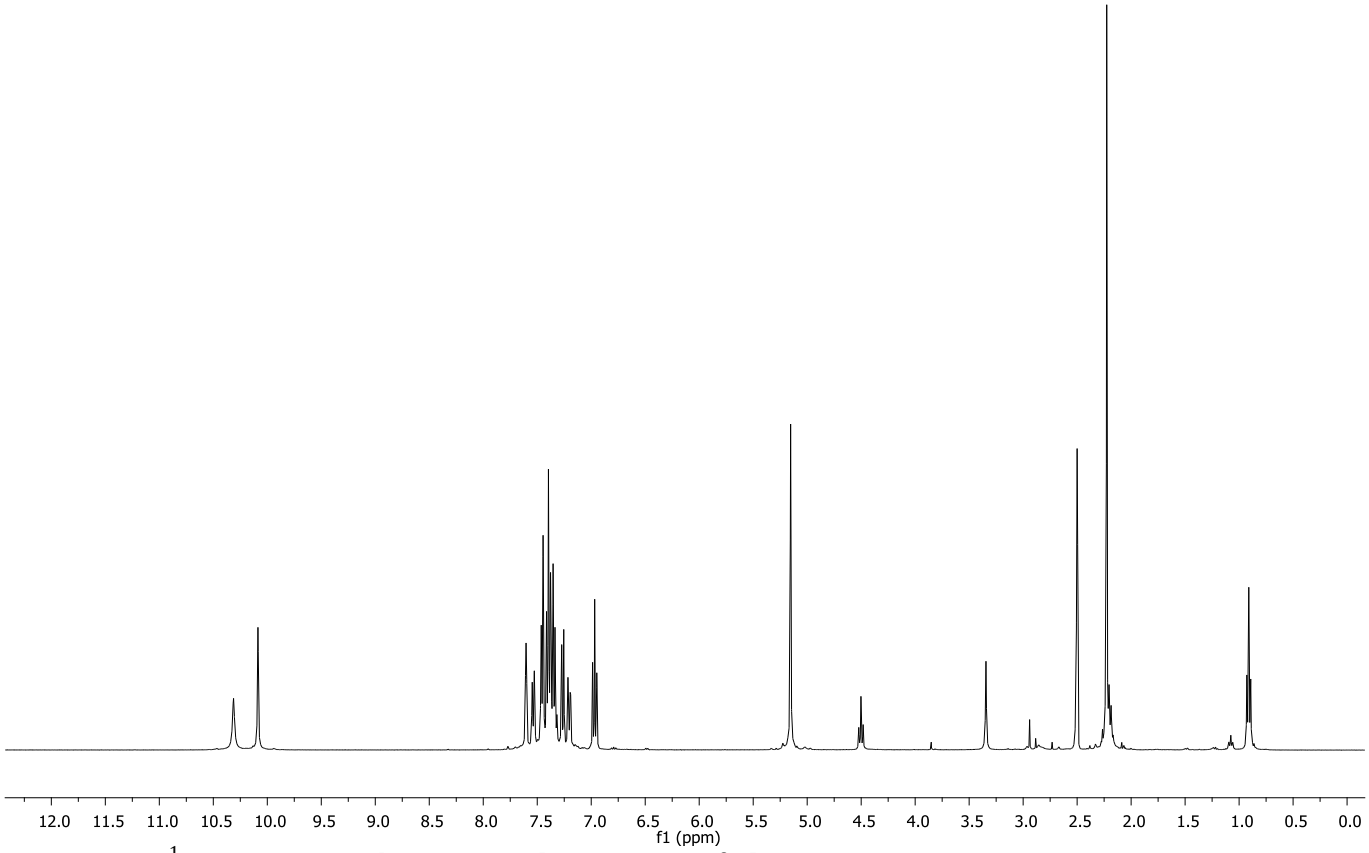


Figure S58. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **3b**.

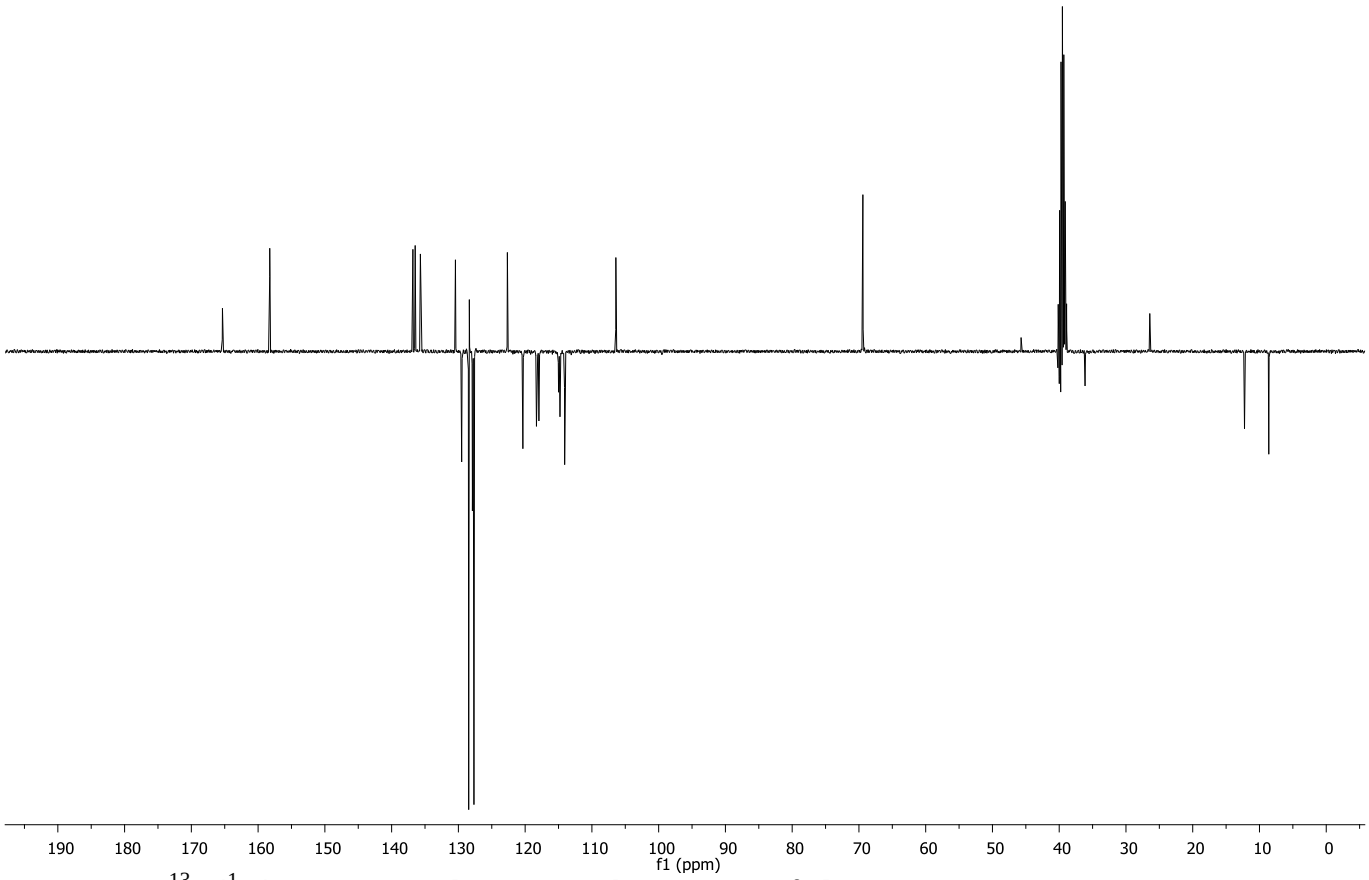


Figure S59. ^{13}C{^{1}H} NMR (100Mhz, DMSO-d_6) spectrum of **3b**.

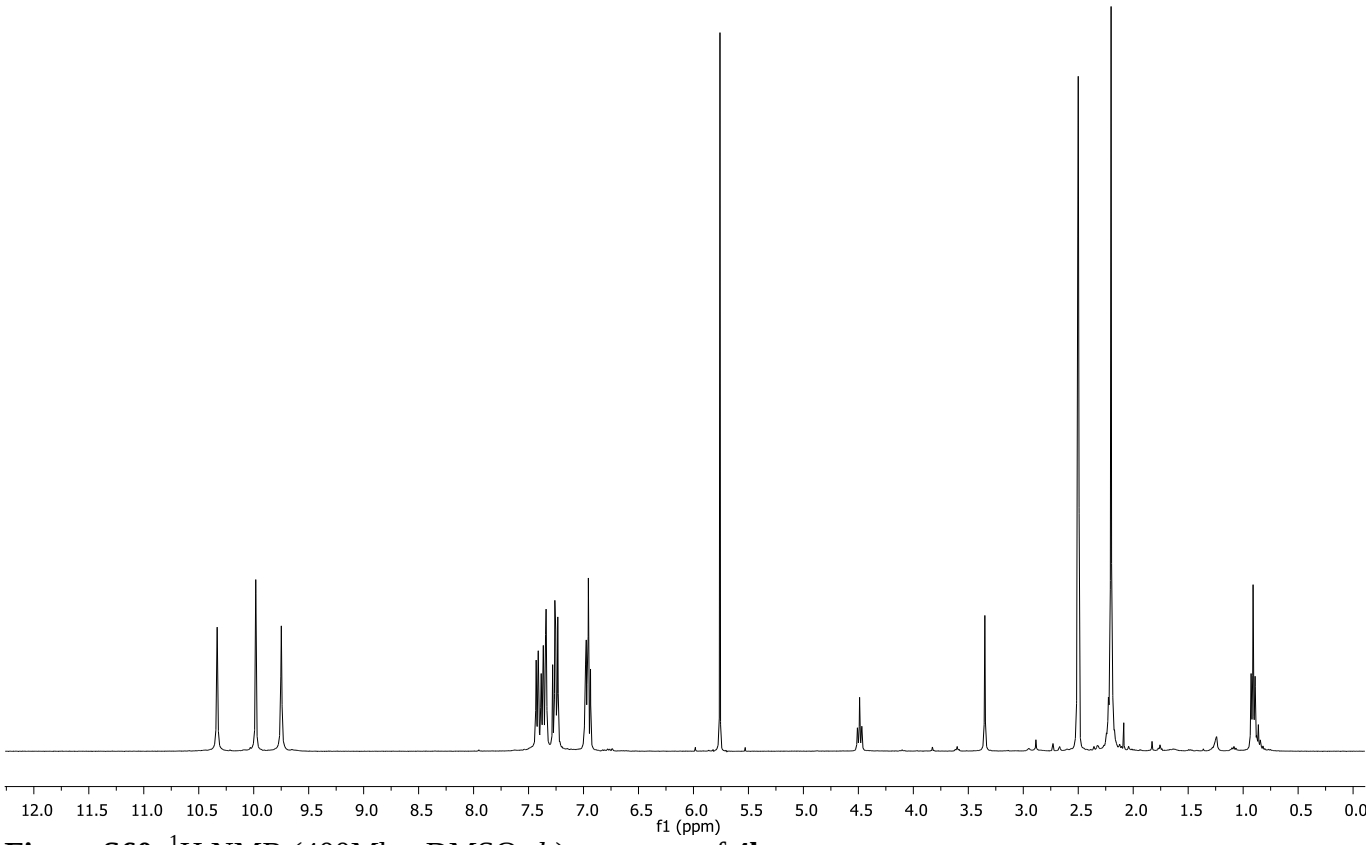


Figure S60. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **4b**.

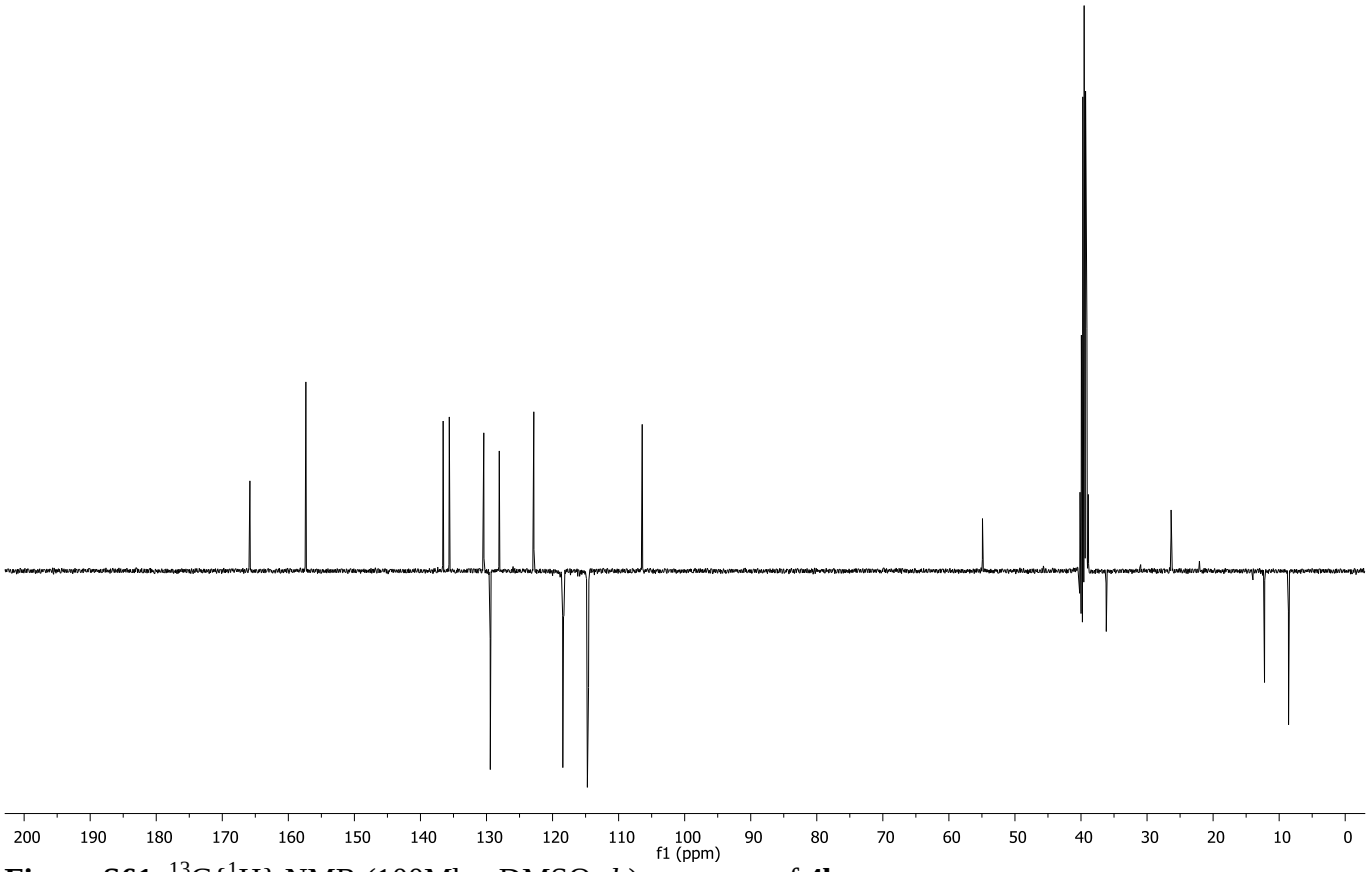


Figure S61. ^{13}C{^{1}H} NMR (100Mhz, DMSO-d_6) spectrum of **4b**.

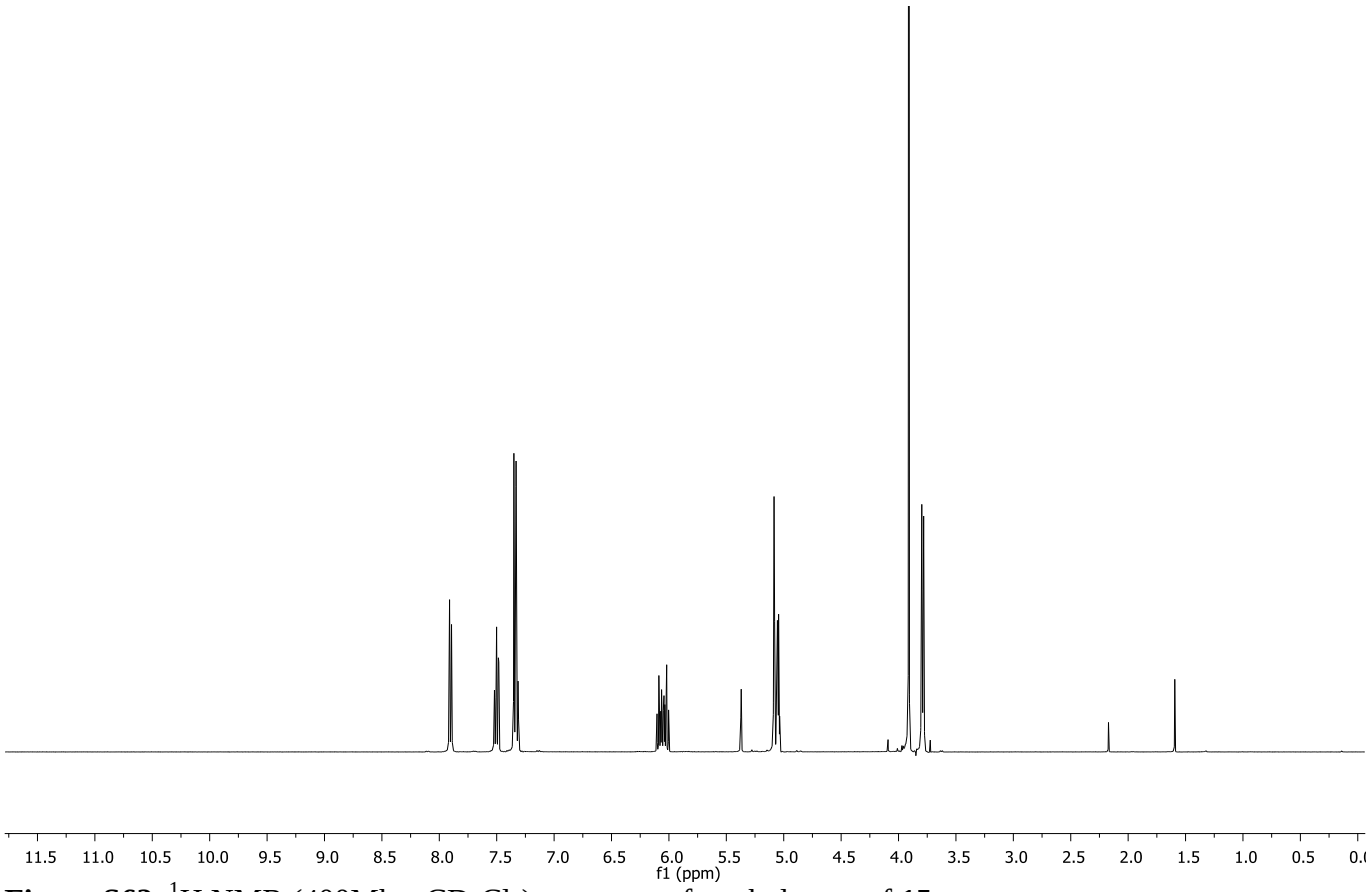


Figure S62. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of methyl ester of **15**.

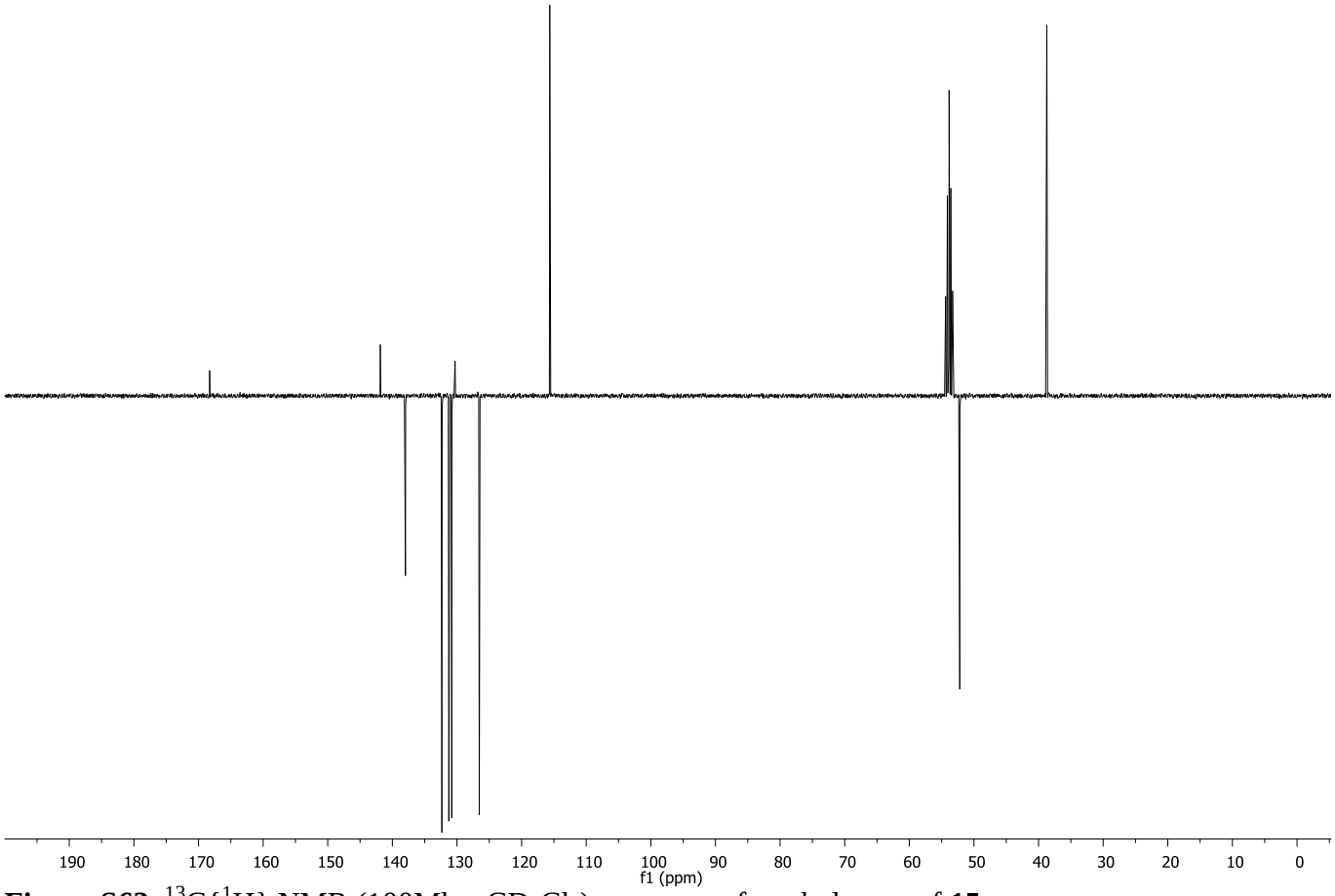


Figure S63. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of methyl ester of **15**.

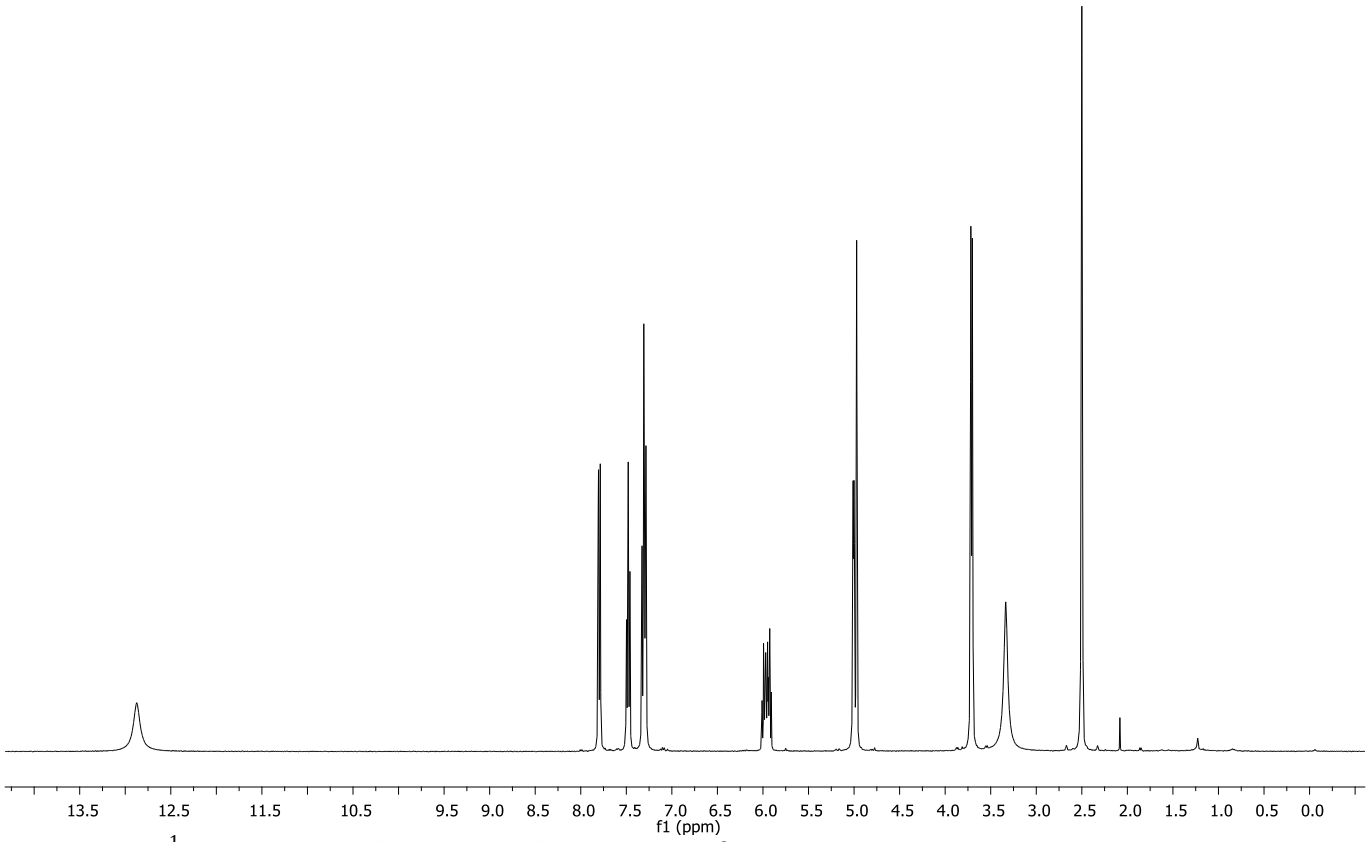


Figure S64. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **15**.

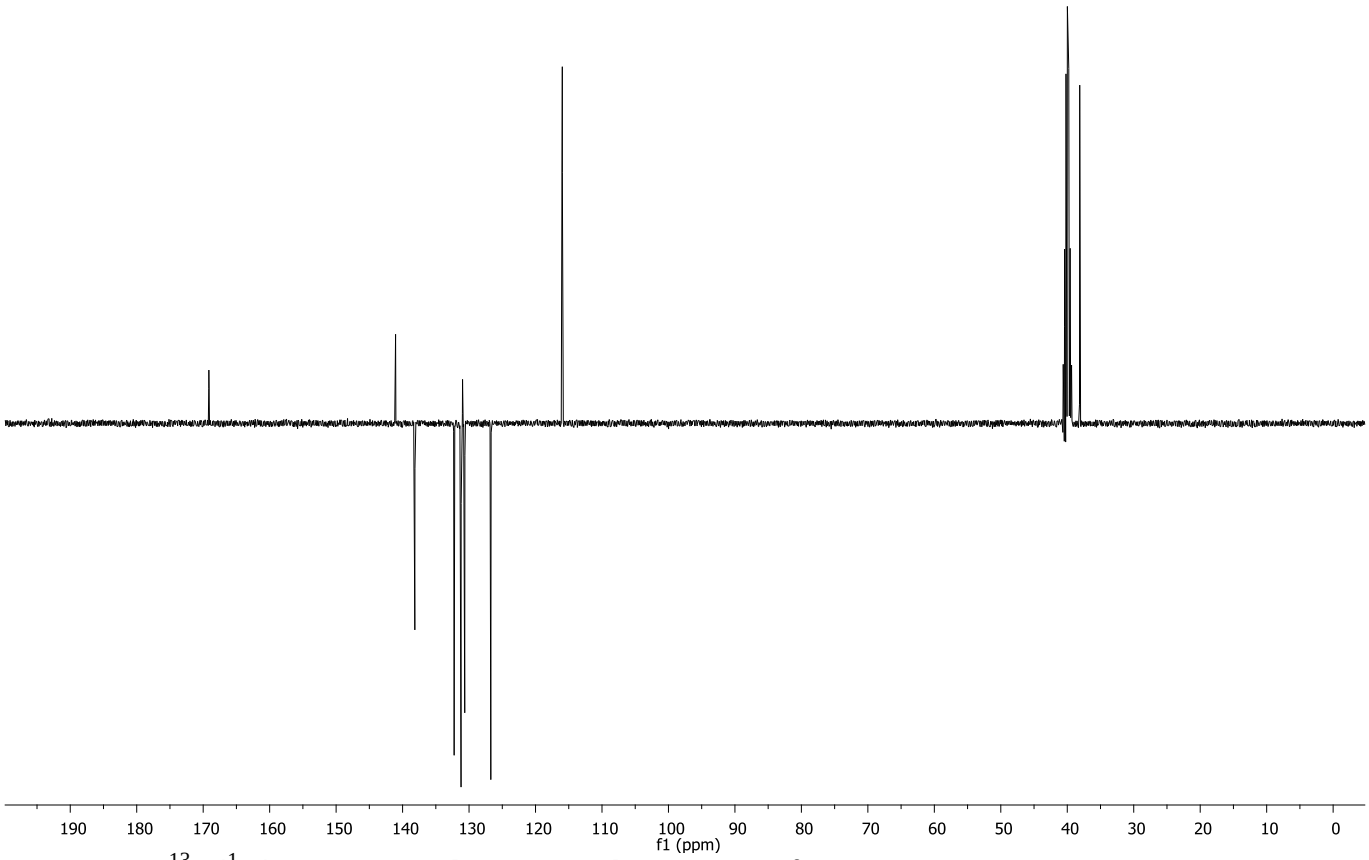


Figure S65. ^{13}C{^{1}H} NMR (100Mhz, DMSO-d_6) spectrum of **15**.

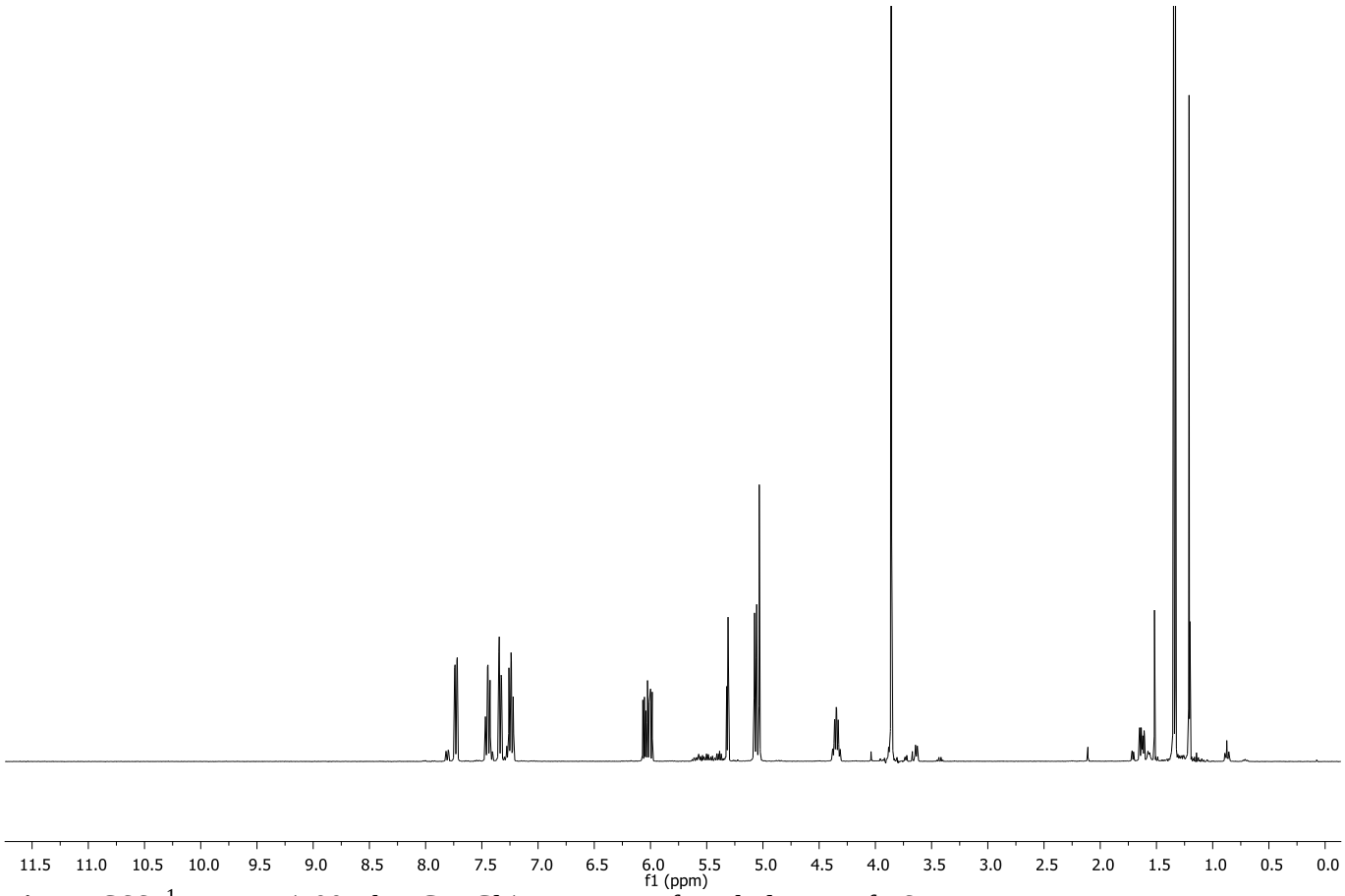


Figure S66. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of methyl ester of **16**.

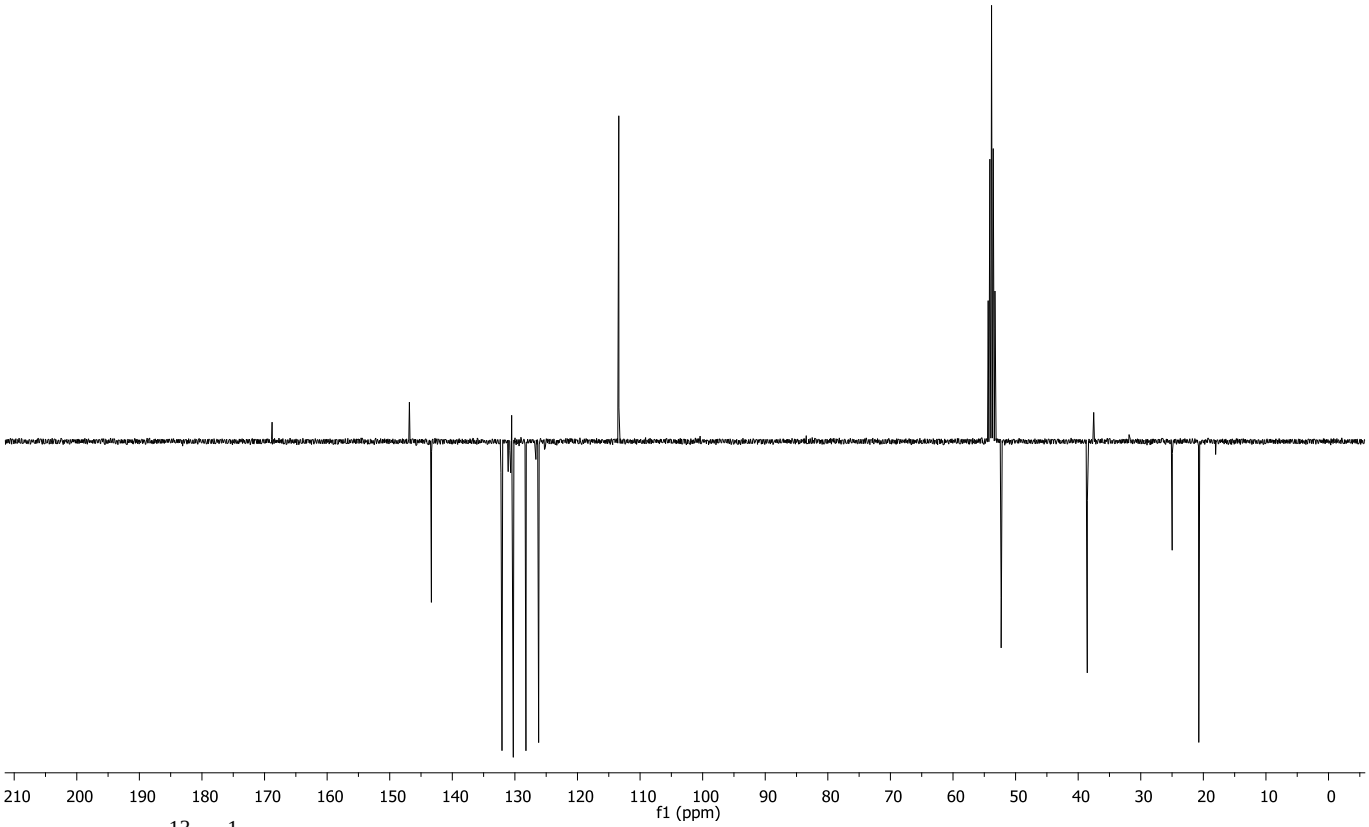


Figure S67. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of methyl ester of **16**.

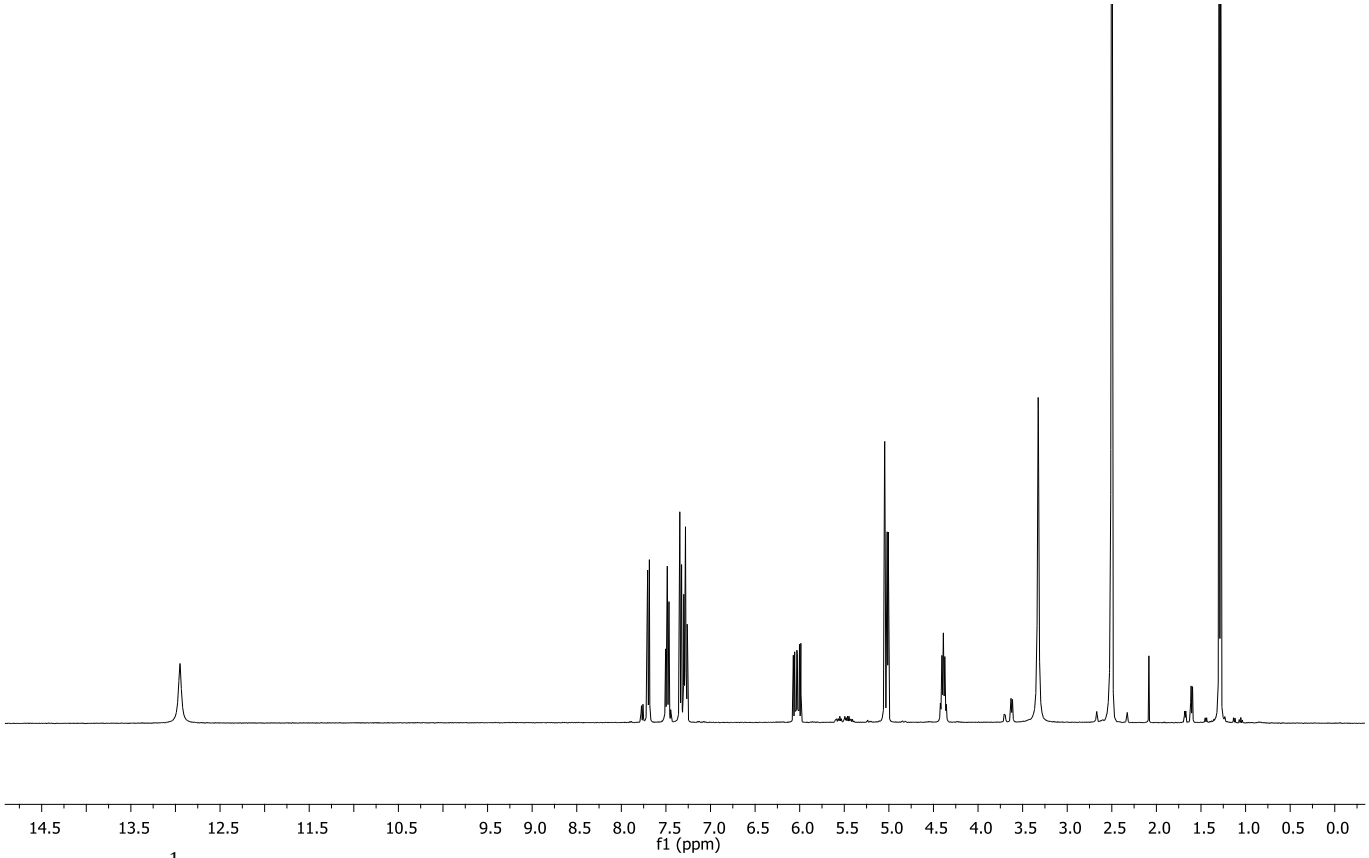


Figure S68. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **16**.

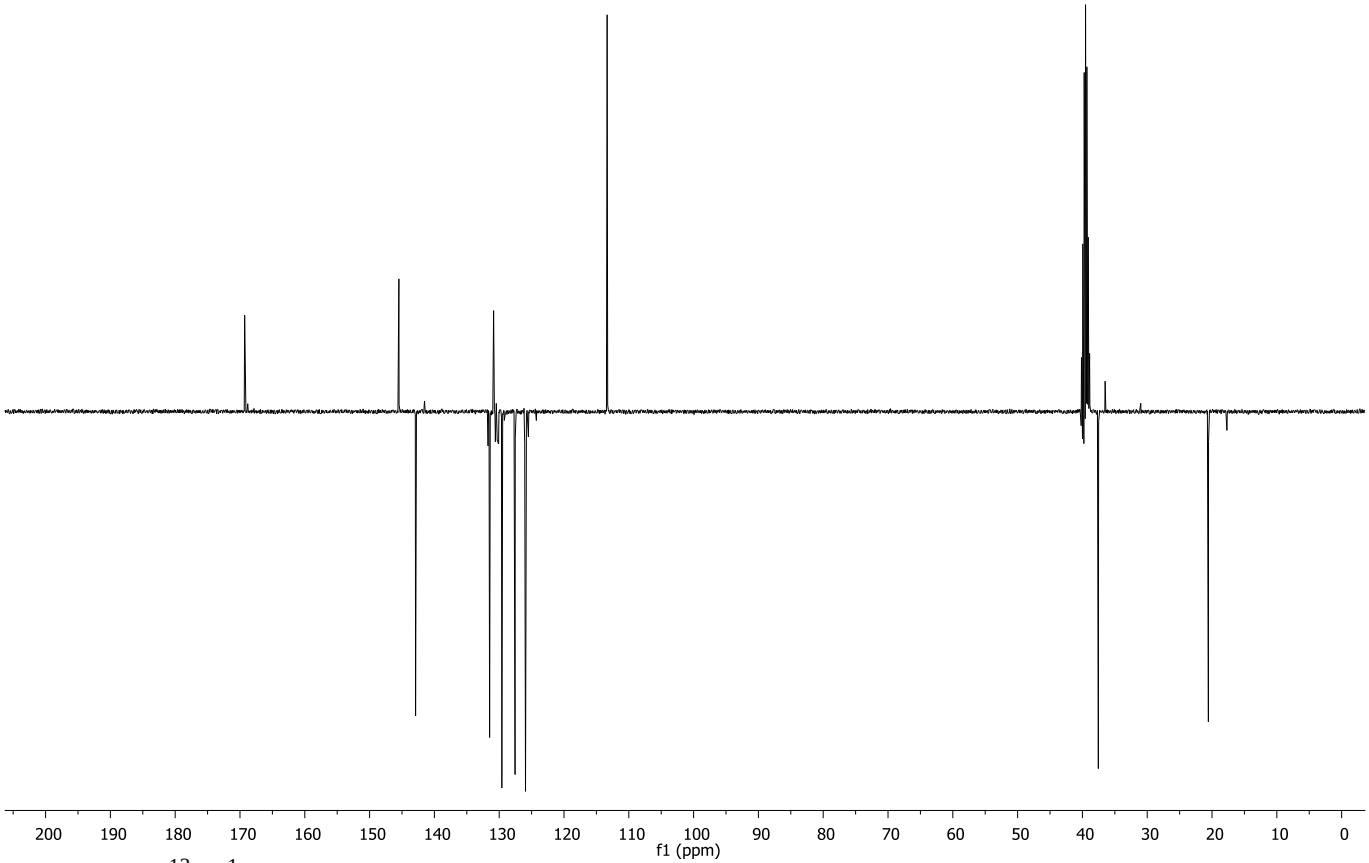


Figure S69. ^{13}C{^{1}H} NMR (100Mhz, DMSO-d_6) spectrum of **16**.

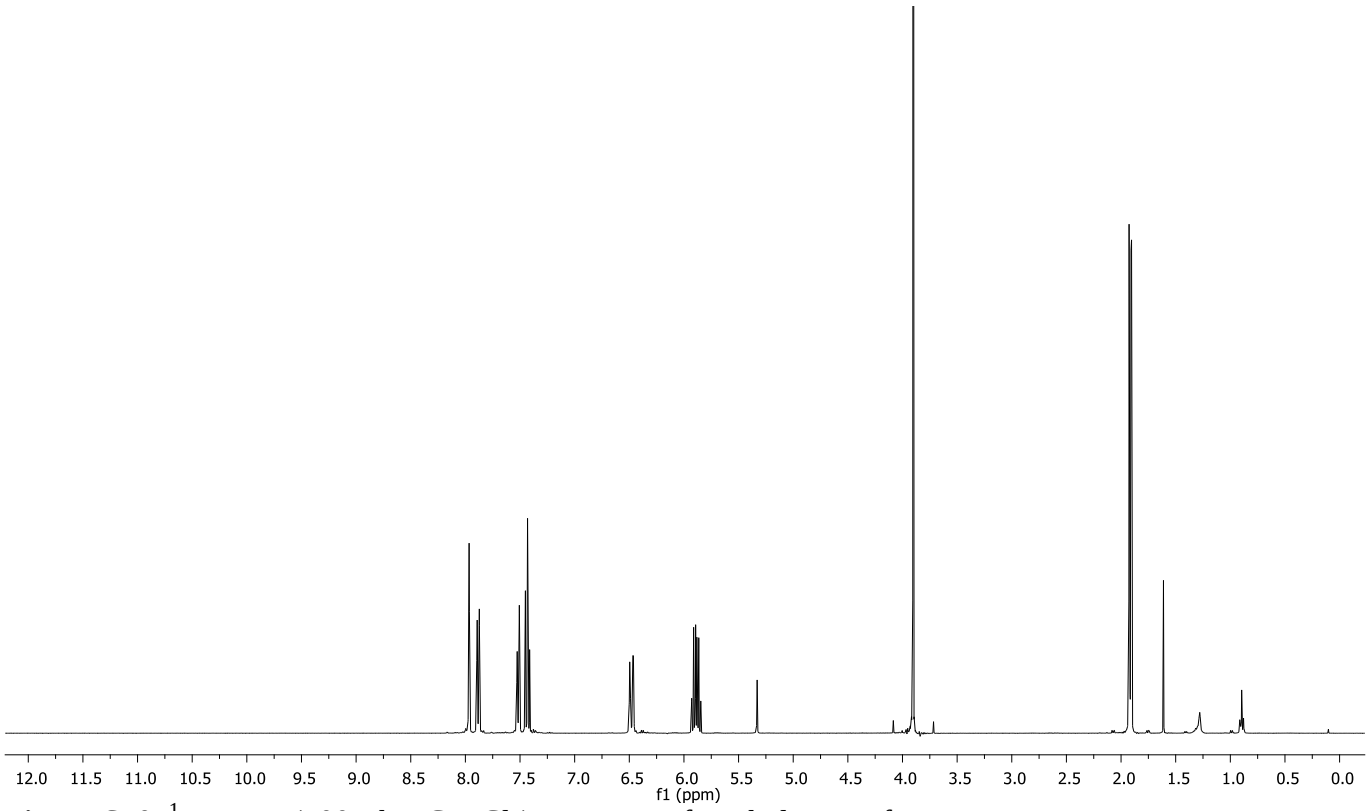


Figure S70. ^{1}H NMR (400Mhz, CD_2Cl_2) spectrum of methyl ester of **17**.

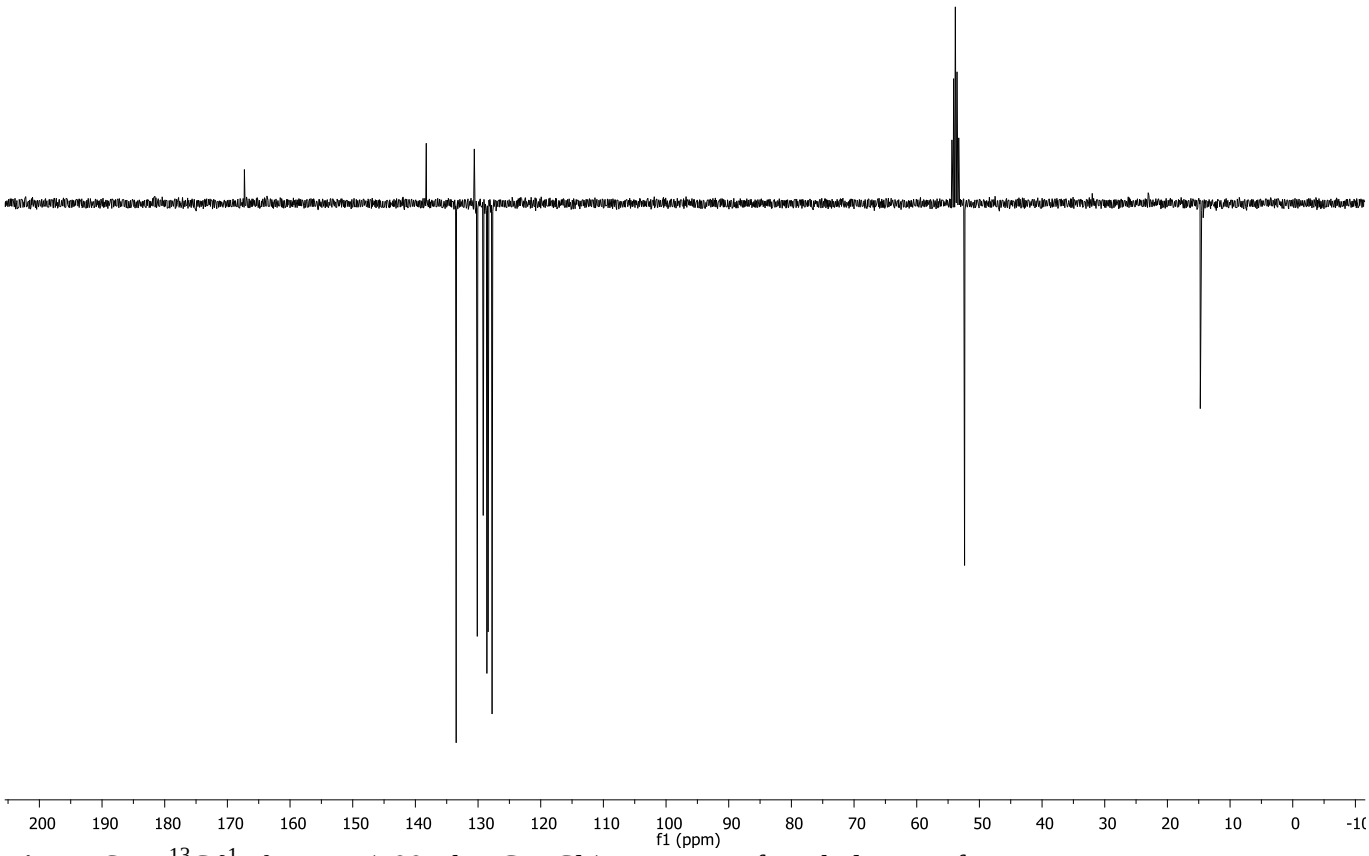


Figure S71. $^{13}C\{^{1}H\}$ NMR (100Mhz, CD_2Cl_2) spectrum of methyl ester of **17**.

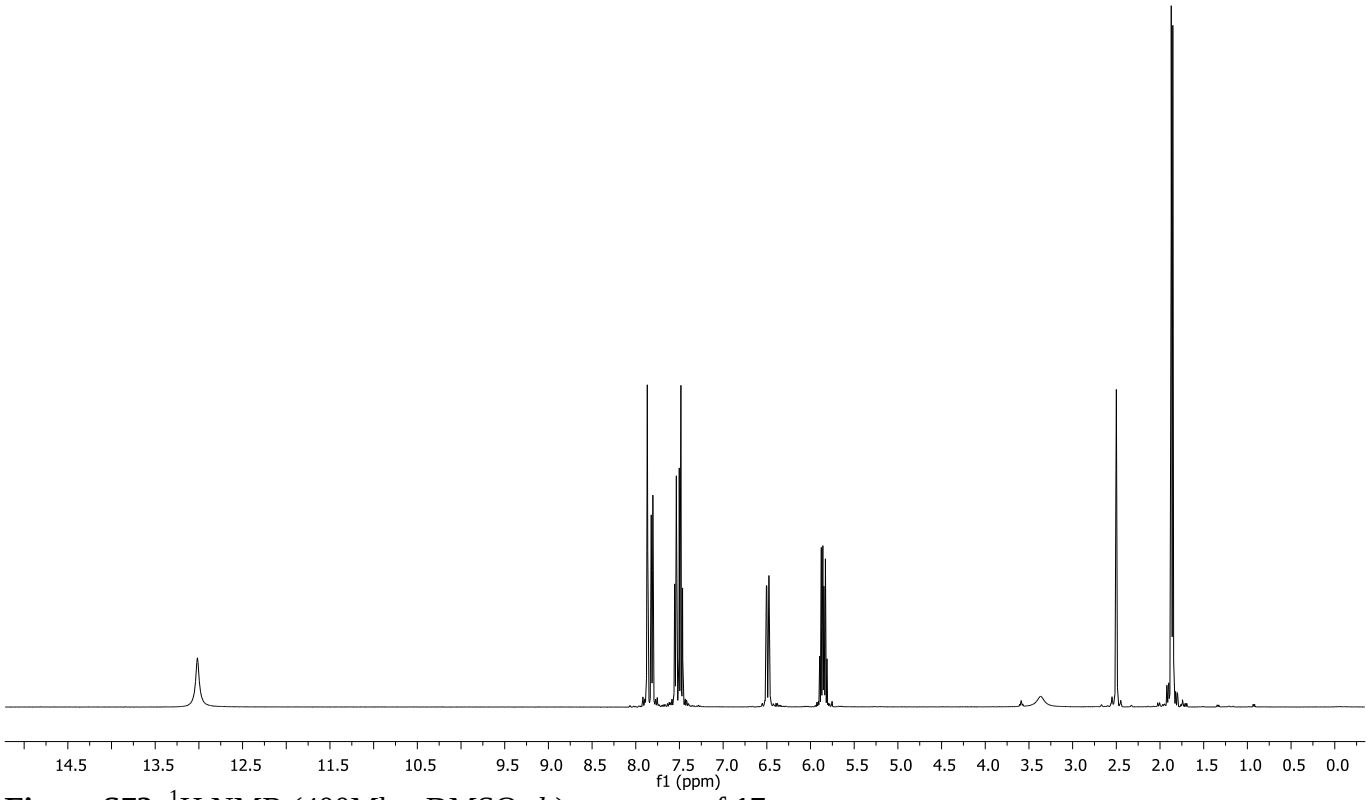


Figure S72. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **17**.

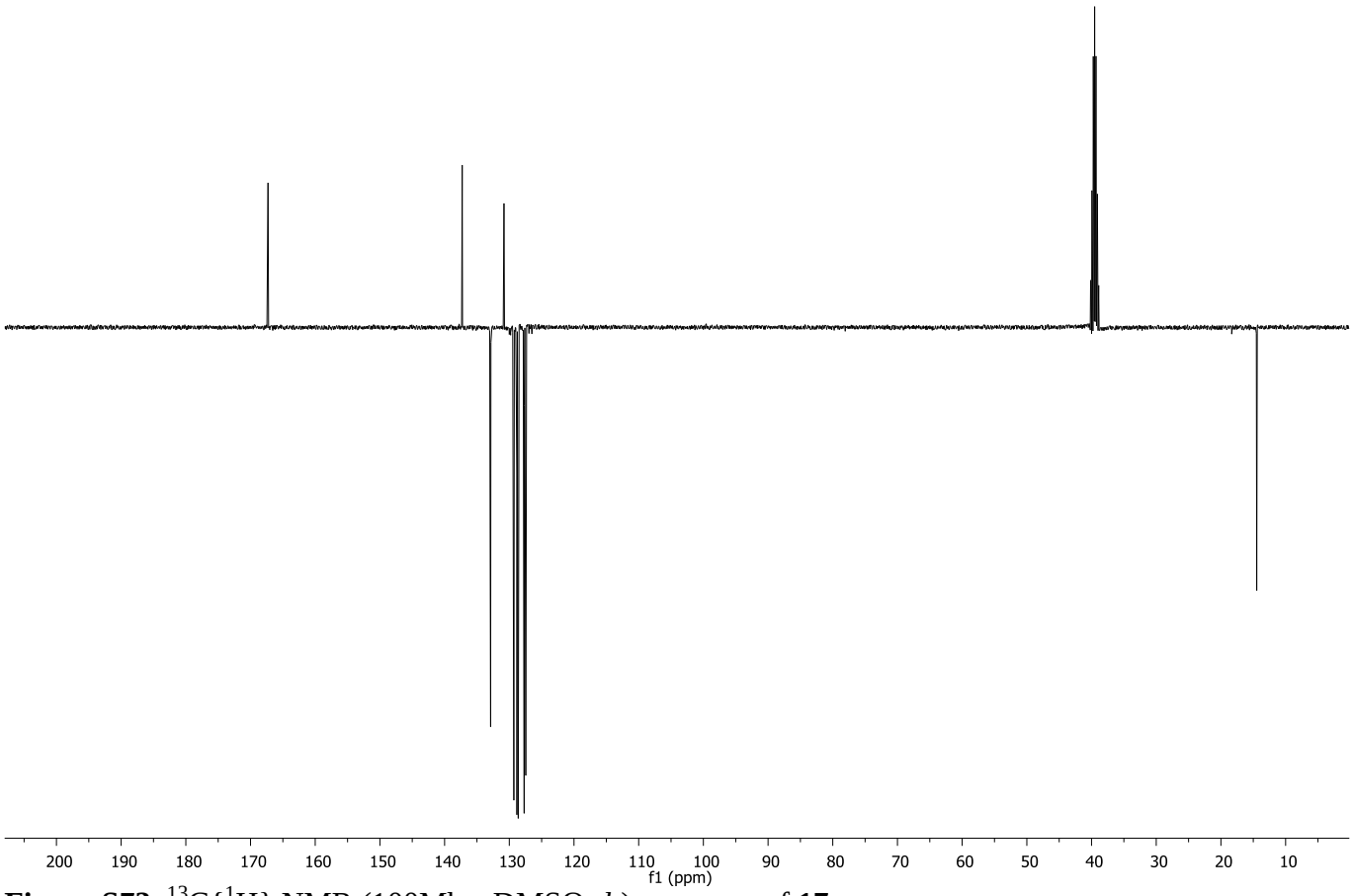


Figure S73. ^{13}C{^{1}H} NMR (100Mhz, DMSO-d_6) spectrum of **17**.

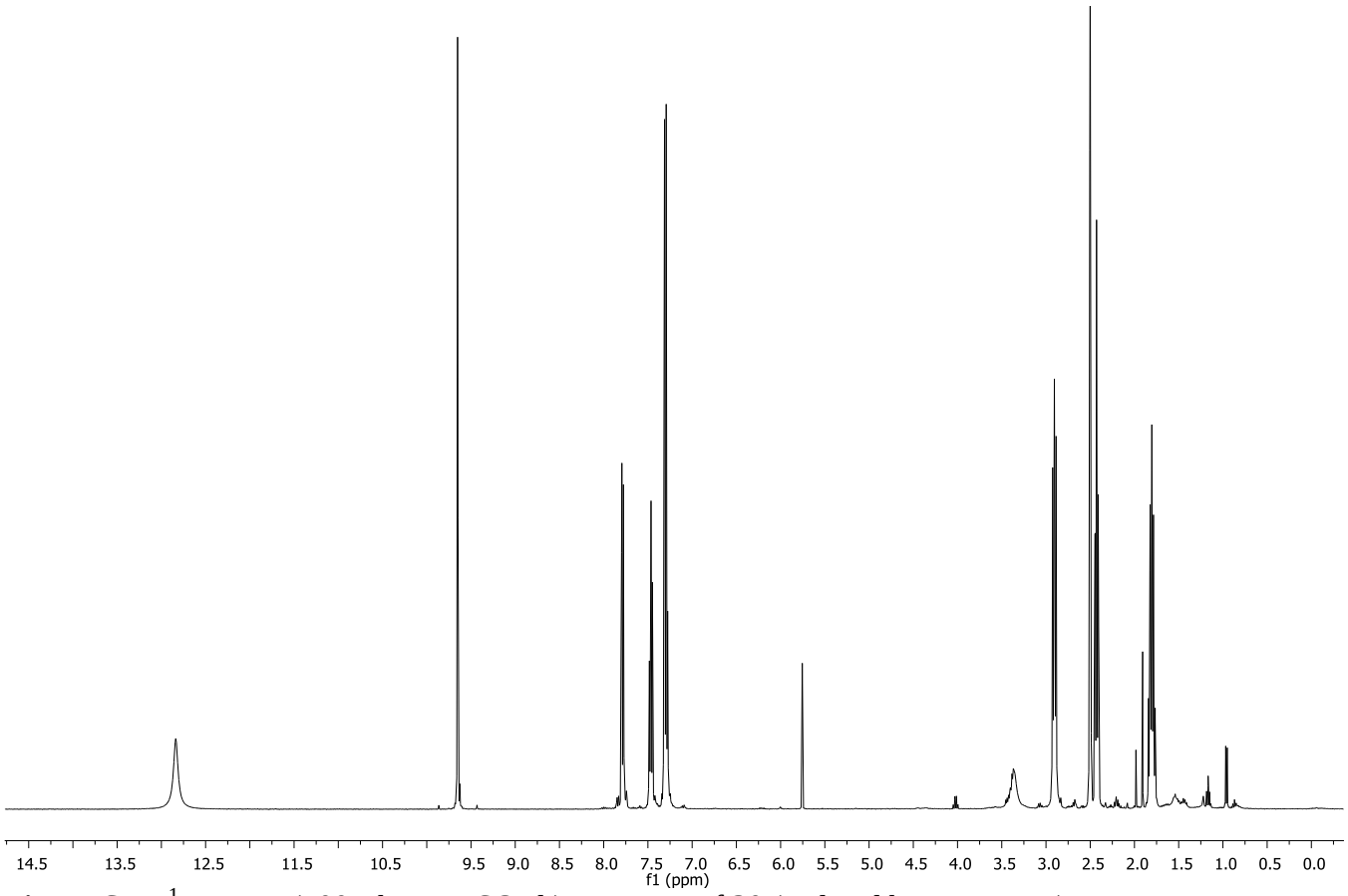


Figure S74. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **20** (isolated by extraction).

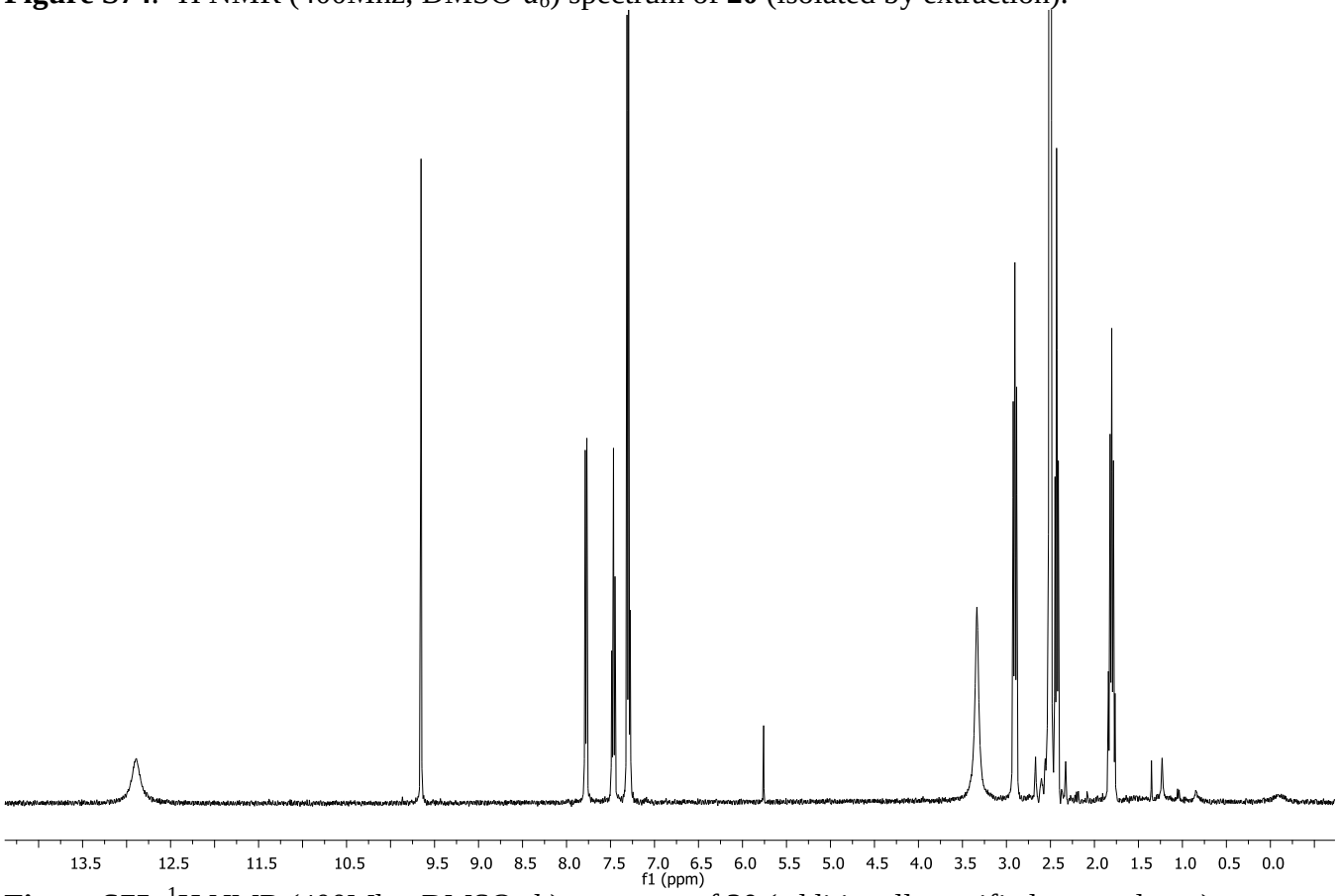


Figure S75. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **20** (additionally purified on a column).

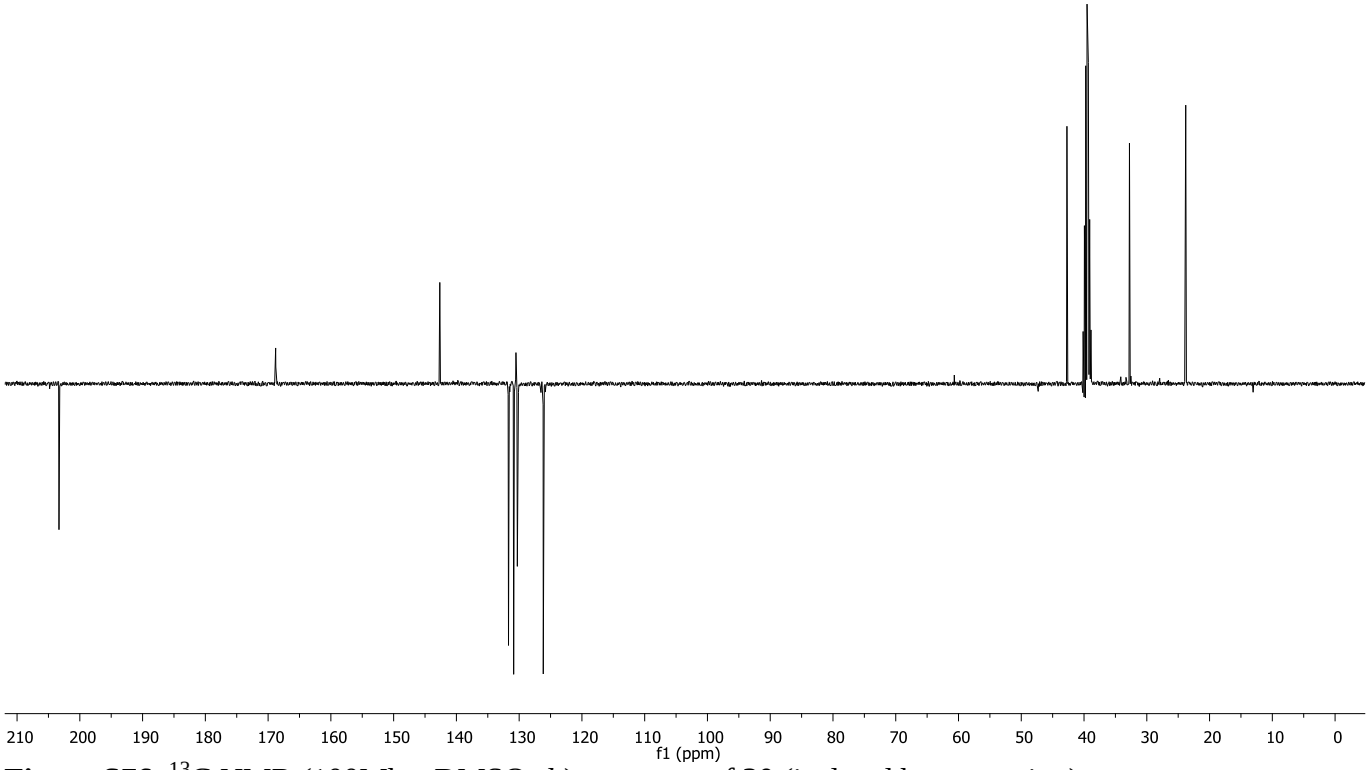


Figure S76. ^{13}C NMR (100Mhz, DMSO-d_6) spectrum of **20** (isolated by extraction).

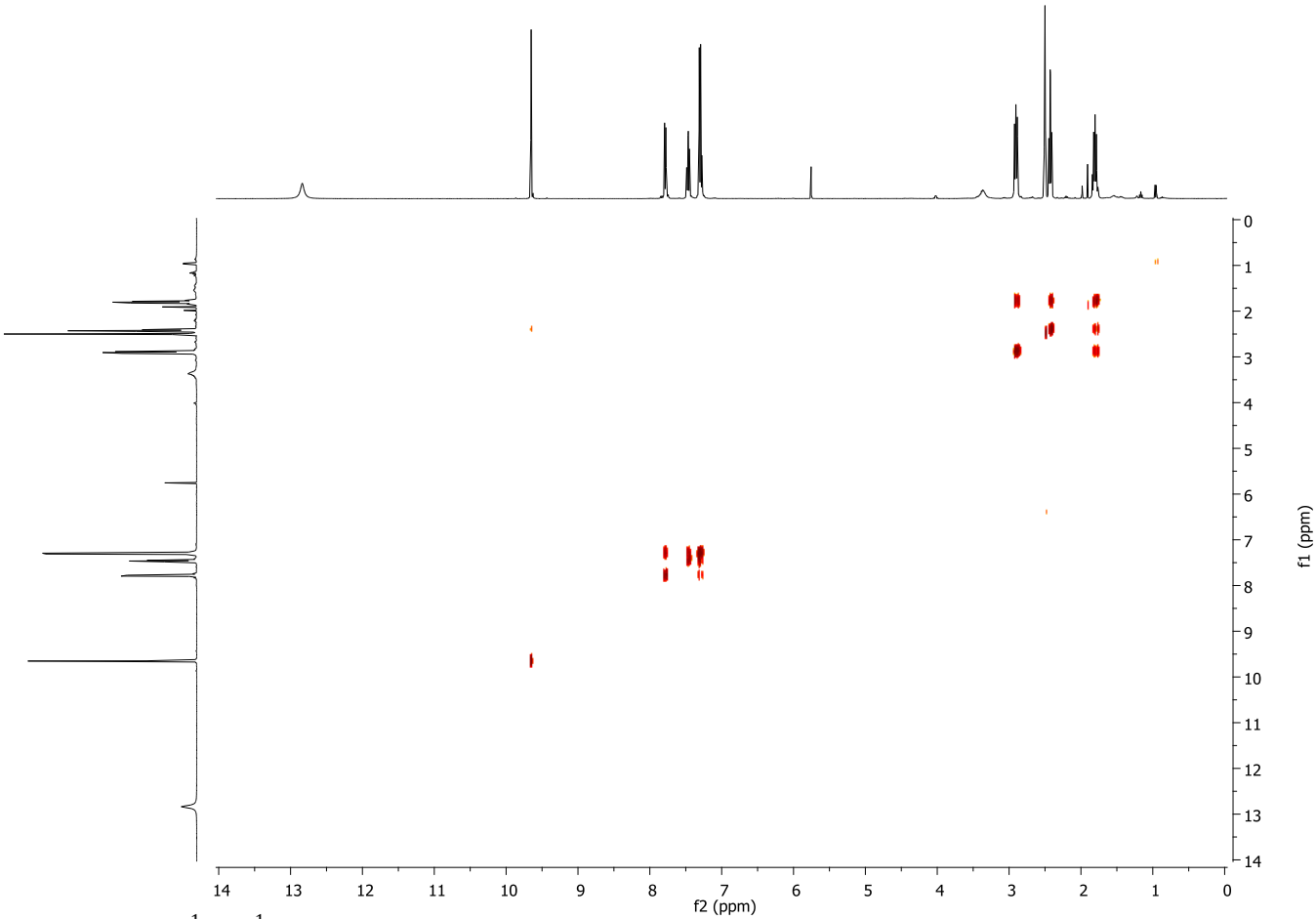


Figure S77. 2D ^{1}H – ^{1}H COSY NMR (400Mhz, DMSO-d_6) spectrum of of **20**.

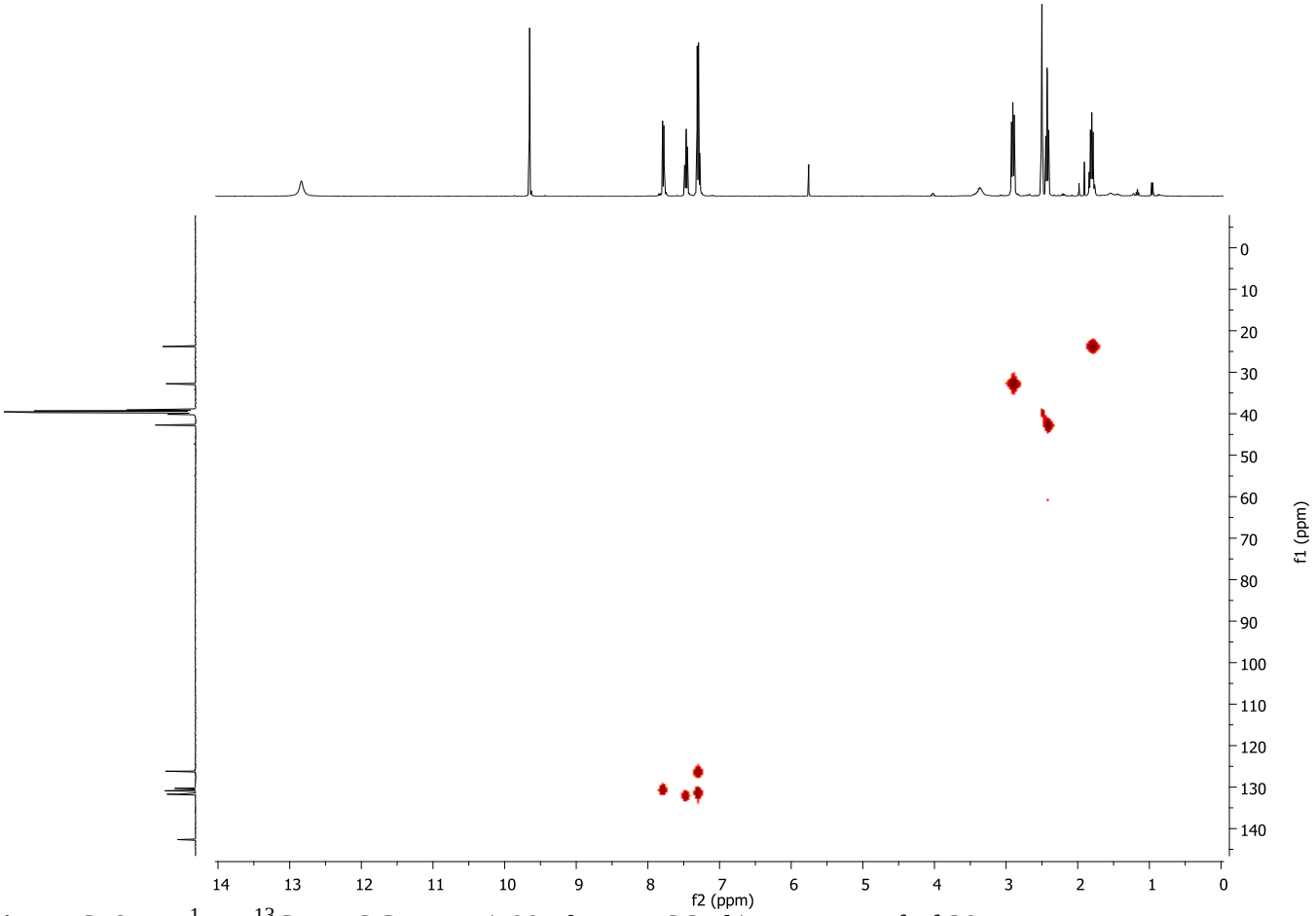


Figure S78. 2D ^{1}H – ^{13}C HMQC NMR (400Mhz, DMSO-d_6) spectrum of of **20**.

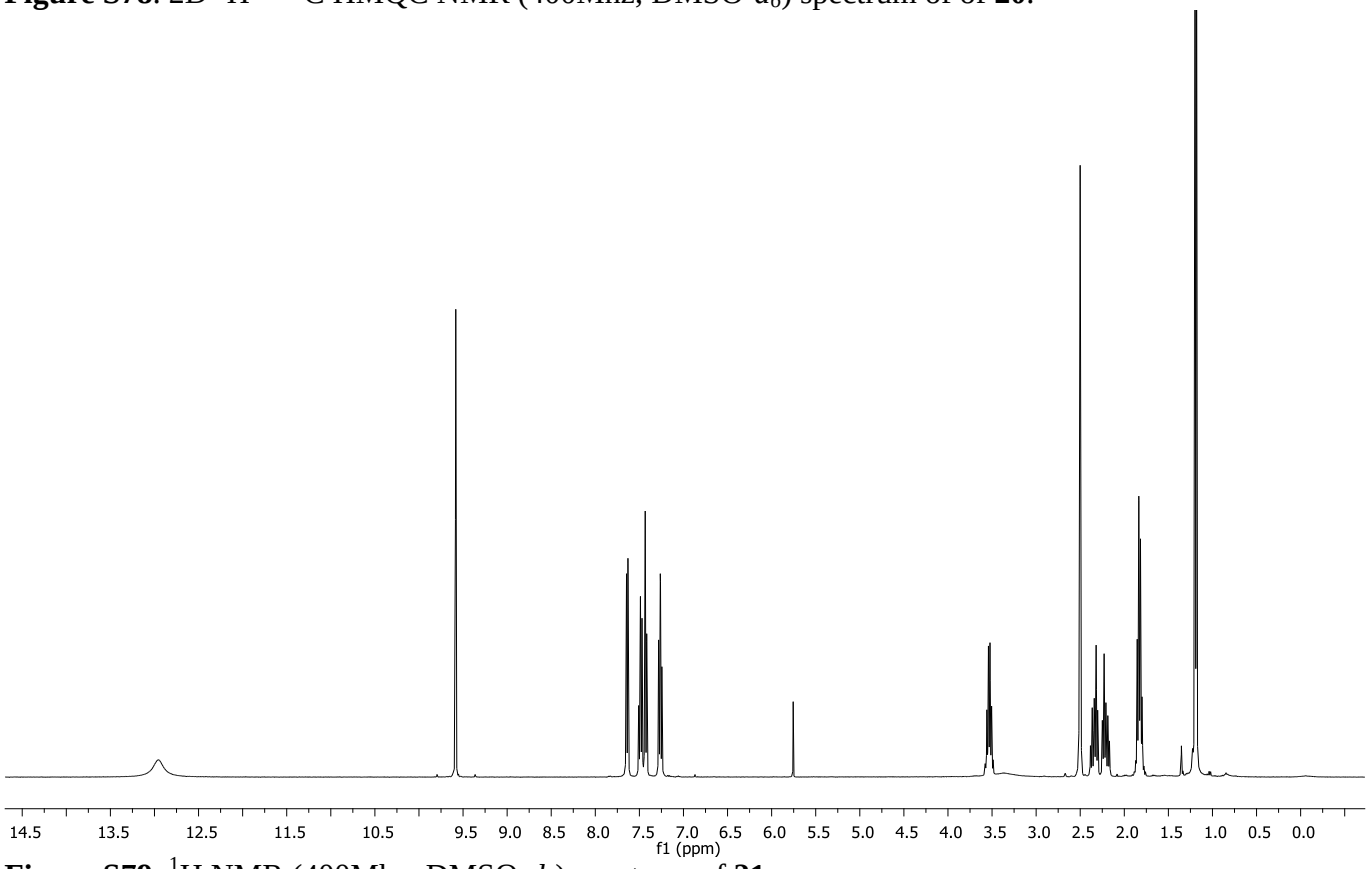


Figure S79. ^{1}H NMR (400Mhz, DMSO-d_6) spectrum of **21**.

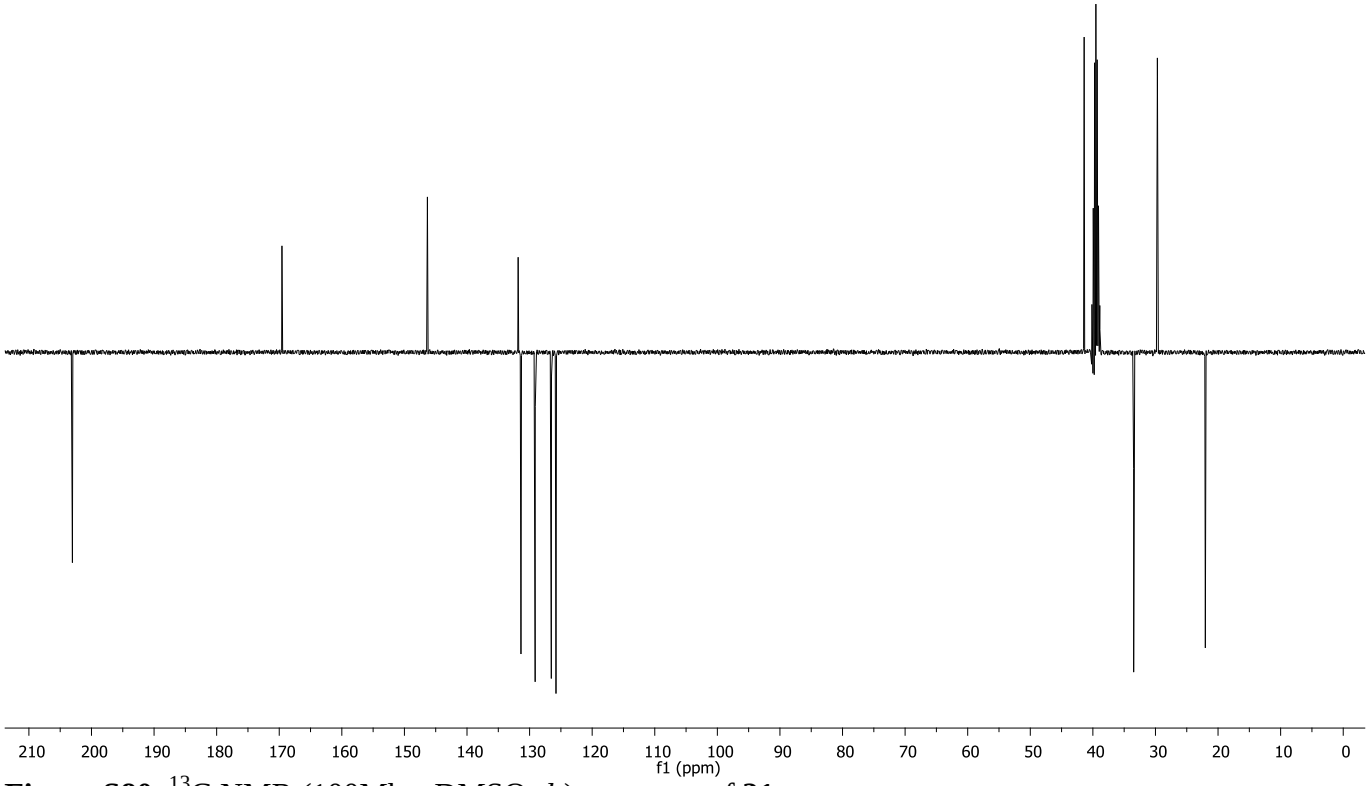


Figure S80. ^{13}C NMR (100Mhz, DMSO-d_6) spectrum of **21**.

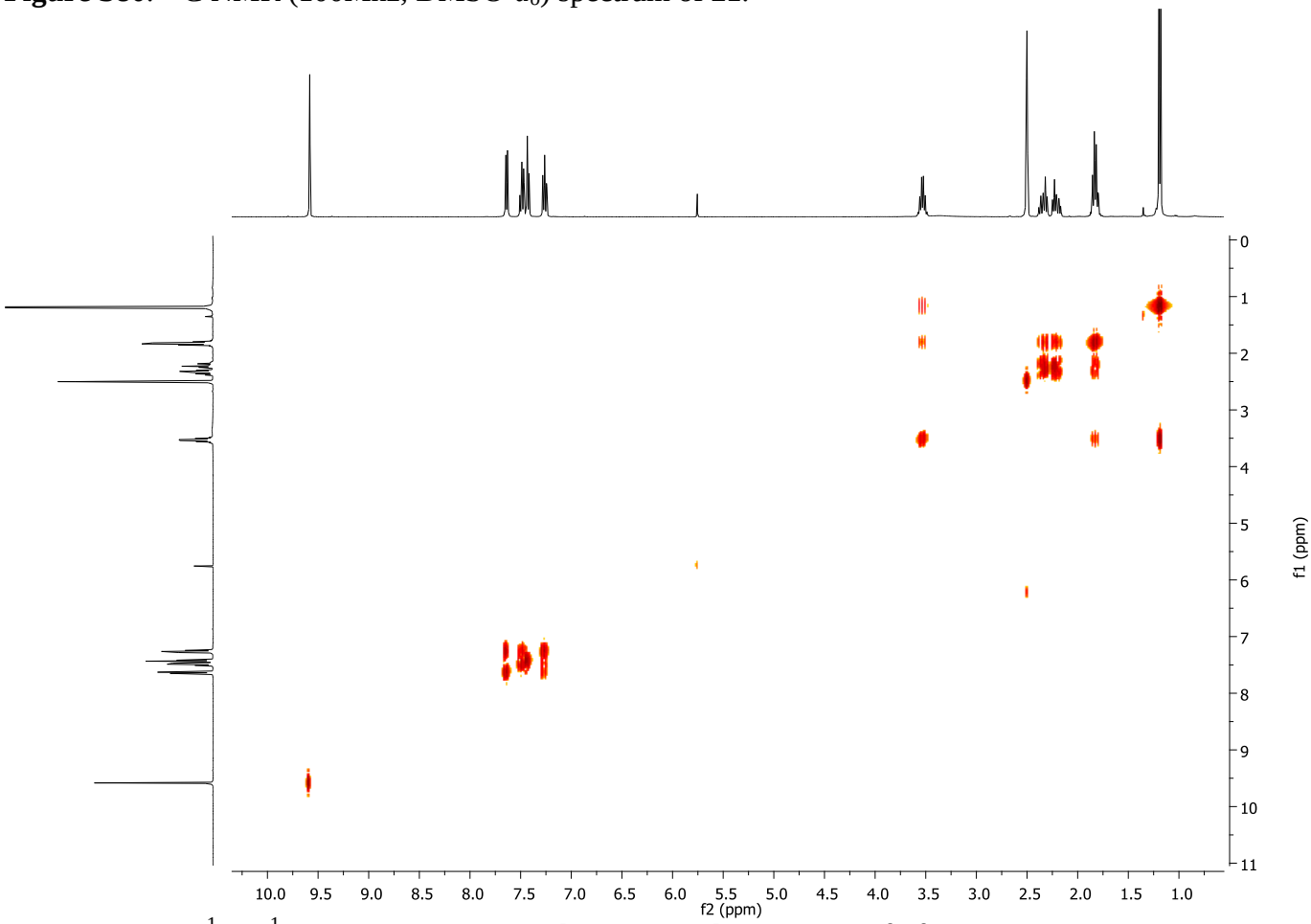


Figure S81. 2D ^{1}H – ^{1}H COSY NMR (400Mhz, DMSO-d_6) spectrum of of **21**.

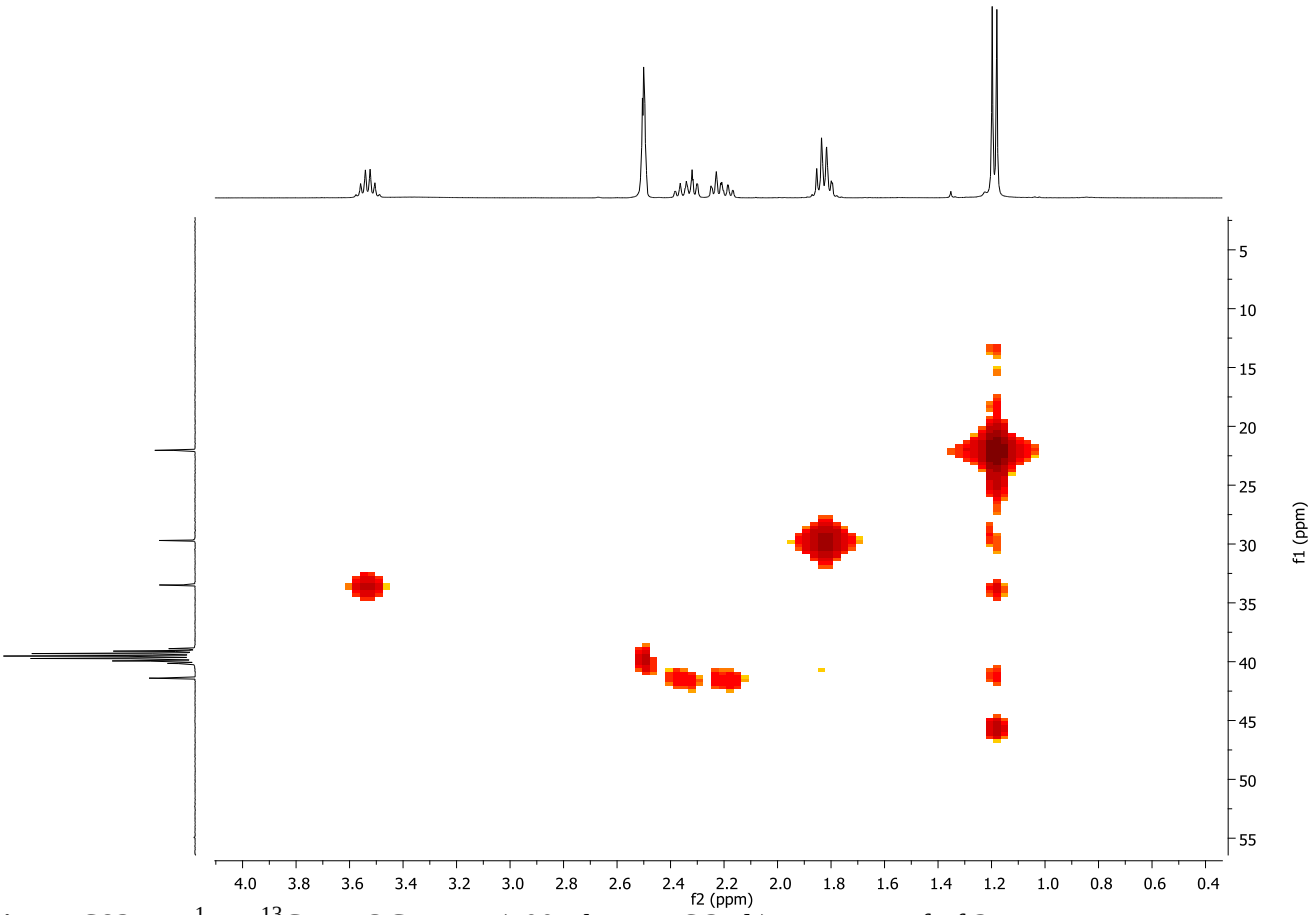


Figure S82. 2D ^{1}H – ^{13}C HMQC NMR (400Mhz, DMSO-d_6) spectrum of of **21** – part.

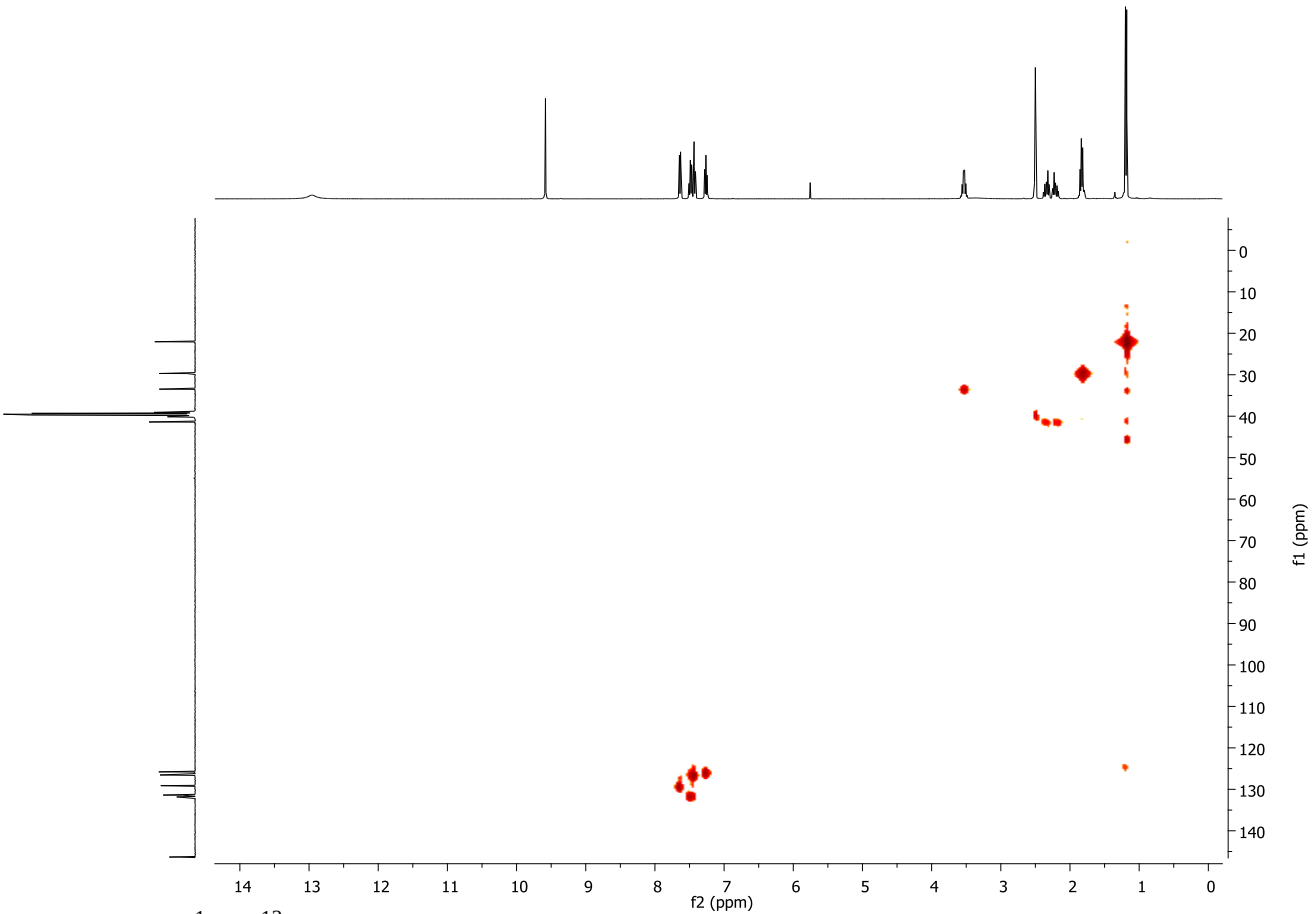


Figure S83. 2D ^{1}H – ^{13}C HMQC NMR (400Mhz, DMSO-d_6) spectrum of of **21**.