Chiral Rh phosphine-phosphite catalysts immobilized on ionic resins for the enantioselective hydrogenation of olefins in water

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SUPPORTING INFORMATION

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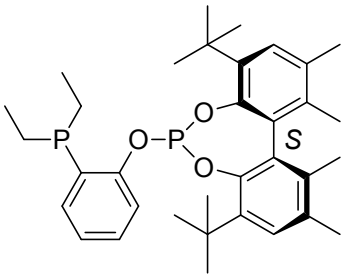
General Procedures

All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques unless stated otherwise. All organic solvents were distilled under nitrogen with the following desiccants: sodium-benzophenone-ketyl for diethyl ether, tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-Me-THF); sodium for hexanes and toluene; CaH_2 for dichloromethane, $Mg(OMe)_2$ for methanol. Water used for reactions was demineralized and deoxygenated. β-Aryl enamides were prepared by Erlenmeyer synthesis.[S1] Phosphine-phosphite (P-OP) ligands **1a**, **1d**, **1g** and **1h** and their [Rh(NBD)(P-OP)](BF_4) were prepared as described previously.[S2] All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on a Bruker DPX-300, DRX-400, or DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. All NMR measurements were carried out at 25 °C, unless otherwise stated. GC and HPLC analyses were performed by using a Hewlett-Packard Model HP 6890 and Waters 2695 chromatographs with Waters 996 PDA UV detector, respectively. HPLC analyses were performed at 30 ºC. Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter. ICP and HRMS analyses were carried out by the Microanalysis and Mass Spectrometry Services of Universidad de Sevilla at CITIUS, using Horiba Jobin Yvon, Ultima 2 spectrometer and JEOL JMS-SX 102A mass spectrometer, respectively.

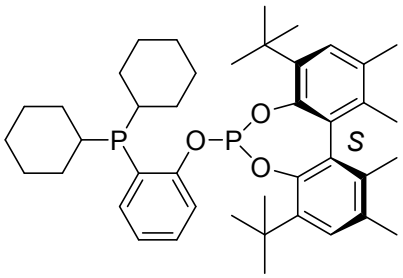
Synthesis and characterization of new phosphine-phosphite ligands

Ligand 1b



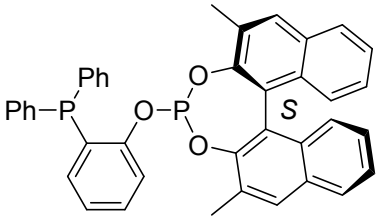
A solution of (*S*)-3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-2,2'-bisphenoxyphosphorus chloride (0.290 g, 0.69 mmol) and triethylamine (0.2 mL, 1.4 mmol) in toluene (15 mL) was dropwise added to a stirred solution of diethylphenolphosphine (0.122 g, 0.67 mmol) in toluene (10mL). The resulting mixture was left on stirring overnight, filtered and the solution obtained evaporated under vacuum. The oily residue residue produced was dissolved in diethyl ether (5 mL) and filtered through a short pad of neutral alumina. The solution obtained was evaporated under vacuum yielding compound **1b** as a white foamy solid (0.314 g, 83 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.35 (m, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 7.12 (m, 1H, Ar-H), 7.03 (m, 1H, Ar-H), 6.65 (m, 1H, Ar-H), 2.30 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.74-1.50 (m, 4H, $2CH_2$), 1.41 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 0.91 (m, 6H, $2CH_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 155.4 (d, *J*(C,P) = 12 Hz, OCq_{arom}), 154.3 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 145.0 (d, *J*(C,P) = 2 Hz, OCq_{arom}), 138.4 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 137.7 (s, Cq_{arom}), 135.2 (s, Cq_{arom}), 134.5 (s, Cq_{arom}), 133.3 (d, *J*(C,P) = 11 Hz, CH_{arom}), 132.7 (s, Cq_{arom}), 132.2 (d, *J*(C,P) = 5 Hz, Cq_{arom}), 131.8 (s, Cq_{arom}), 131.0 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 129.5 (s, CH_{arom}), 129.3 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 128.2 (s, CH_{arom}), 127.9 (s, CH_{arom}) , 123.5 (d, *J*(C,P) = 4 Hz, CH_{arom}), 120.5 (d, *J*(C,P) = 12 Hz, CH_{arom}), 34.9 (s, $C(CH_3)_3$), 34.7 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$), 31.3 (d, *J*(C,P) = 5 Hz, $C(CH_3)_3$), 20.6 (s, CH_3), 20.5 (s, CH_3), 18.8 (d, *J*(C,P) = 12 Hz, CH_2), 17.9 (d, *J*(C,P) = 11 Hz, CH_2), 16.9 (s, CH_3), 16.7 (s, CH_3), 10.2 (d, , *J*(C,P) = 15 Hz, CH_3), 10.0 (d, , *J*(C,P) = 13 Hz, CH_3). ^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$): δ = 130.2 (d, *J*(P,P) = 31 Hz, PO), -22.7 (d, *J*(P,P) = 31 Hz, P). HRMS (FAB): *m/z* 587.2814, $[M+Na]^+$ (calcd for: $C_{34}H_{46}NaO_3P_2$: 587.2820). $[\alpha]_D^{20}$= +379 (*c* 0.4, THF).

Ligand 1c



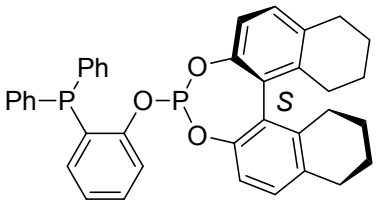
Compound **1c** was synthesized from dicyclohexylphenolphosphine and (*S*)-3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-2,2'-bisphenoxyphosphorus chloride following the procedure described for **1b**. White foamy solid (0.376 g, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (m, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 7.04 (m, 2H, Ar-H), 6.38 (m, 1H, Ar-H), 2.31 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.98-1.43 (m, 12H, cyclohexyl), 1.88 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.42 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.30-0.92 (m, 10H, cyclohexyl). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 156.1 (dd, *J*(C,P) = 18 Hz, *J*(C,P) = 4 Hz, OCq_{arom}), 145.6 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 145.1 (s, OCq_{arom}), 138.5 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 137.8 (s, Cq_{arom}), 135.2 (s, Cq_{arom}), 134.4 (s, Cq_{arom}), 134.0 (s, CH_{arom}), 132.6 (s, Cq_{arom}), 132.3 (d, *J*(C,P) = 6 Hz, Cq_{arom}), 131.7 (s, Cq_{arom}), 131.1 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 129.4 (s, CH_{arom}), 128.3 (s, CH_{arom}), 127.9 (s, CH_{arom}), 127.2 (dd, *J*(C,P) = 22 Hz, *J*(C,P) = 2 Hz, Cq_{arom}), 123.2 (s, CH_{arom}), 122.1 (d, *J*(C,P) = 9 Hz, CH_{arom}), 35.0 (s, $C(CH_3)_3$), 34.8 (s, $C(CH_3)_3$), 34.2 (d, *J*(C,P) = 15 Hz, PCH), 32.9 (d, *J*(C,P) = 13 Hz, PCH), 31.6 (s, $C(CH_3)_3$), 31.3 (d, *J*(C,P) = 5 Hz, $C(CH_3)_3$), 30.8 (d, *J*(C,P) = 17 Hz, CH_2), 30.3 (d, *J*(C,P) = 16 Hz, CH_2), 29.9 (d, *J*(C,P) = 11 Hz, CH_2), 28.9 (d, *J*(C,P) = 6 Hz, CH_2), 27.3 (m, $4CH_2$), 26.6 (d, J(C,P) = 2Hz, $2CH_2$), 20.6 (s, $2CH_3$), 16.9 (s, CH_3), 16.7 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 122.0 (d, *J*(P,P) = 42 Hz, PO), -14.4 (d, *J*(P,P) = 42 Hz, P). HRMS (EI): *m/z* 673.3950, $[M+H]^+$ (calcd for $C_{42}H_{59}O_3P_2$: 673.3939). $[\alpha]_D^{20}$= +381 (*c* 0.2, THF).

Ligand 1e



An ampoule was charged with (2-hydroxyphenyl)diphenylphosphonium bromide (0.120 g, 0.33 mmol), (*S*)-3,3'-di-methyl-2,2'-bisnaphtoxyphosphorus chloride (0.127 g, 0.33 mmol)[S3] and ScavengePore phenethyldiethylamine resin (Rapp Polymere, resin capacity 0.74mmol/g; 1.35 g, 1.0 mmol,). Dichloromethane was added (10 mL) and reaction mixture was shaken for 12 h using orbital stirrer. Solvent was removed under vacuum and residue was extracted with diethyl ether (5 x 5mL). Solution was concentrated and filtered through short pad of neutral alumina. Solvent was removed and ligand **1e** was isolated as a white foamy solid (0.175 g, 85% yield). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.60 (dd, *J*(H,H) = 8.0 Hz, 2.5Hz, 2H, Ar-H), 7.47-7.44 (m, 3H, Ar-H), 7.36 (m, 2H, Ar-H), 7.32-7.29 (m, 2H, Ar-H), 7.19-7.16 (m, 5H, Ar-H), 7.02-6.89 (m, 9H, Ar-H), 6.73 (t, *J*(H,H) = 7.4 Hz, 1H, Ar-H), 2.57(s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): *δ* = 154.7 (d, *J*(C,P) = 7 Hz, OCq_{arom}), 154.5 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 148.0 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 146.5 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 136.5 (d, *J*(C,P) = 7 Hz, Cq_{arom}), 136.4 (d, *J*(C,P) = 7 Hz, Cq_{arom}), 134.8 (s, CH_{arom}), 134.6 (s, CH_{arom}), 134.4 (s, CH_{arom}), 134.2 (s, CH_{arom}), 134.0 (s, CH_{arom}), 132.0 (m, Cq_{arom}), 131.6 (m, Cq_{arom}), 130.8 (s, Cq_{arom}), 130.7 (s, $2CH_{arom}$), 130.3 (s, CH_{arom}), 130.1 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 130.0 (s, CH_{arom}), 129.3 (s, CH_{arom}), 129.1 (s, CH_{arom}), 128.9 (s, $2CH_{arom}$), 128.8 (s, $2CH_{arom}$), 128.8 (s, Cq_{arom}), 128.0 (s, CH_{arom}), 127.9 (s, CH_{arom}), 127.1 (s, CH_{arom}), 127.0 (s, CH_{arom}), 125.7 (s, CH_{arom}), 125.6 (d, *J*(C,P) = 2 Hz, $2CH_{arom}$), 125.3 (s, CH_{arom}), 125.1 (s, CH_{arom}), 125.0 (d, *J*(C,P) = 6 Hz, Cq_{arom}), 122.9 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 120.1 (dd, *J*(C,P) = 12 Hz, 1 Hz, Cq_{arom}), 18.3 (d, *J*(C,P) = 4 Hz, *C*H_3), 17.7 (s, *C*H_3). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ = 139.5 (d, *J*(P, P) = 19 Hz, PO), -17.3 (d, *J*(P, P) = 19 Hz, PC). HRMS (ESI): *m/z* 621.1728, $[M+H]^+$ (calcd for $C_{40}H_{31}O_3P_2$: 621.1743). $[\alpha]_D^{20}$= +245 (*c* 0.7, THF).

Ligand 1f



A solution of (*S*)-5,5',6,6',7,7',8,8'-octahydro-2,2'-bisnaphtoxyphosphorus chloride (0.499 g, 1.39 mmol)[S3] and triethylamine (0.79 mL, 5.6 mmol) in methylene chloride (15 mL) was dropwise added to a stirred solution of (2-hydroxyphenyl)diphenylphosphonium bromide (0.500 g, 1.39 mmol) in methylene chloride (10 mL). Mixture was left stirring overnight. Solution was brought to dryness. Oily residue was extracted with diethyl ether (3 x 5 mL) and filtered through to another Schlenk tube. Solvent was removed under vacuum and oily product was washed with hexane (3 x 5mL). Oil residue was dissolved in diethyl ether (5 mL) and brought to dryness. Ligand **1f** was obtained as white foamy solid (0.409 g, 49% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.44-7.30 (m, 10H, Ar-H), 7.27-7.23 (m, 1H, Ar-H), 7.20-7.14 (m, 2H, Ar-H), 7.09-7.06 (m, 2H, Ar-H), 6.97-6.93 (m, 1H, Ar-H), 6.88-6.85 (m, 1H, Ar-H), 6.77-6.73 (m, 1H, Ar-H), 2.80 (m, 4H, CH_2), 2.62 (m, 2H, CH_2), 2.27-2.20 (m, 2H, CH_2), 1.79 (m, 5H, CH_2), 1.56 (m, 3H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 154.3 (dd, J(C,P) = 18, 8 Hz, OCq_{arom}), 146.1 (s, OCq_{arom}), 146.0 (d, J(C,P) = 6 Hz, OCq_{arom}), 139.0 (s, Cq_{arom}), 138.0 (s, Cq_{arom}), 136.4 (d, J(C,P) = 9 Hz, Cq_{arom}), 136.3 (d, J(C,P) = 9 Hz, Cq_{arom}), 135.6 (s, Cq_{arom}), 134.8 (s, Cq_{arom}), 134.7 (s, CH_{arom}), 134.6 (s, CH_{arom}), 134.5 (s, CH_{arom}), 134.4 (s, CH_{arom}), 134.3 (s, CH_{arom}), 133.9 (d, J(C,P) = 19 Hz, CH_{arom}), 130.7 (d, J(C,P) = 3 Hz, Cq_{arom}), 130.6 (s, CH_{arom}), 129.8 (s, CH_{arom}), 129.7 (d, J(C,P) = 5 Hz, Cq_{arom}), 129.6 (s, CH_{arom}), 129.4 (s, CH_{arom}), 129.0 (s, $2CH_{arom}$), 128.9 (s, $2CH_{arom}$), 128.1 (d, J(C,P) = 2 Hz, Cq_{arom}), 125.1 (s, CH_{arom}), 120.4 (d, J(C,P) = 10 Hz, CH_{arom}), 119.2 (s, $2CH_{arom}$), 29.5 (s, $2CH_2$), 28.2 (s, $2CH_2$), 23.1 (s, CH_2), 23.0 (s, CH_2), 22.9 (s, CH_2), 22.8 (s, CH_2). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 135.2 (d, J(P, P) = 14 Hz, PO), -17.0 (d, J(P, P) = 14 Hz, PC). HRMS (EI): *m/z* 601.2035, $[M+H]^+$ (calcd for $C_{38}H_{35}O_3P_2$: 601.2056). $[\alpha]_D^{20}$= +39 (*c* 0.6, THF).

Synthesis and characterization of [Rh(NBD)(P-OP)]BF_4 complexes

[Rh(NBD)(1b)](BF_4)

A solution of **1b** (0.220 g, 0.390 mmol) in methylene chloride (10 mL) was added dropwise to a stirred solution of [$Rh(NBD)_2$](BF_4) (0.145 g, 0.390 mmol) in methylene chloride (5 mL). A colour change from dark red to orange was observed in the solution. Reaction mixture was stirred for two hours, concentrated to 5mL and filtered. Solvent was partially evaporated and diethyl ether (25 mL) was added dropwise, producing an orange precipitate. The mixture was filtered, the solid collected, washed with diethyl ether (3 x 5mL) and dried under vacuum. Title product was isolated as orange powder (0.258 g, 77 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.48 (t, *J*(H,H) = 7.5 Hz, 1H, Ar-H), 7.43-7.35 (m, 2H, Ar-H), 7.33 (s, 1H, Ar-H), 7.32 (s, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 6.04 (brs, 1H, =CH NBD), 5.76 (brs, 1H, =CH NBD), 5.67 (brs, 1H, =CH NBD), 4.18 (brs, 1H, CH NBD), 3.98 (brs, 1H, CH NBD), 3.84 (brs, 1H, =CH NBD), 2.42-2.34 (m, 1H, PCH_2), 2.32 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.20-1.98 (m, 2H, CH_2), 1.86 (s, 3H, CH_3), 1.78 (s, 3H, CH_3),1.77 (m, 2H, CH_2 NBD), 1.72 (m, 1H, PCH_2), 1.50 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 1.18 (m, 6H, $2CH_2$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): *δ* = 155.1 (dd, *J*(C,Rh) = 9 Hz, *J*(C,P) = 4 Hz, OCq_{arom}), 144.9 (dd, *J*(C,Rh) = 14 Hz, *J*(C,P) = 1 Hz, OCq_{arom}), 143.6 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 137.8 (d, *J*(C,P) = 4 Hz, Cq_{arom}), 137.5 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 136.9 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 135.7 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 135.1 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 134.4 (d, *J*(C,P) = 4 Hz, Cq_{arom}), 133.8 (s, CH_{arom}), 130.9(s, CH_{arom}), 130.3 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 129.6 (d, *J*(C,P) = 2 Hz, CH_{arom}), 129.4 (d, *J*(C,P) = 1 Hz, CH_{arom}), 129.3 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 126.7 (dd, *J*(C,Rh) = 6 Hz, *J*(C,P) = 2 Hz, CH_{arom}) 123.2 (dd, *J*(C,Rh) = 4 Hz, *J*(C,P) = 2 Hz, CH_{arom}), 116.0 (dd, *J*(C,Rh) = 43 Hz, *J*(C,P) = 8 Hz, PCq_{arom}), 97.9 (dd, *J*(C,Rh) = 12 Hz, *J*(C,P) = 2 Hz, =CH NBD), 96.9 (dd, *J*(C,Rh) = 15 Hz, *J*(C,P) = 5 Hz, =CH NBD), 92.1 (td, *J*(C,Rh) = 7 Hz, *J*(C,P) = 2 Hz, =CH NBD), 79.8 (ddd, *J*(C,Rh) = 10 Hz, *J*(C,P) = 6 Hz, *J*(C,P) = 3 Hz, =CH NBD), 72.0 (m, CH_2 NBD), 56.0 (m, CH NBD), 55.4 (m, CH NBD), 35.5 (s, $C(CH_3)_3$), 35.3 (s, $C(CH_3)_3$), 31.9 (s, $C(CH_3)_3$), 32.0 (d, *J*(C,P) = 4 Hz, CH_2), 31.8 (s, $C(CH_3)_3$), 24.1 (d, *J*(C,P) = 30 Hz, PCH_2), 31.0 (d, *J*(C,P) = 6 Hz, CH_2), 20.6 (s, Ar-CH_3), 20.5 (s, Ar-CH_3), 16.8 (s, 2Ar-CH_3), 16.8 (s, CH_3), 15.6 (d, *J*(C,P) = 28 Hz, PCH_2), 9.7 (m, CH_3), 9.2 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 131.7 (dd, *J*(P, Rh) = 280 Hz, *J*(P, P) = 67 Hz, PO), 10.5 (dd, *J*(P, Rh) = 143 Hz, *J*(P, P) = 66 Hz, PC). Elemental analysis: calculated: C 58.17 %, H 6.43 %, found: C 58.45 %, H 6.49 %.

Complex [Rh(NBD)(1c)](BF$_4$)

This complex was obtained as an orange powder according procedure described above for [Rh(NBD)(**1b**)](BF$_4$) (0.282 g, 85% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.46 (t, *J*(H,H) = 7.5 Hz, 1H, Ar-H), 7.39-7.34 (m, 2H, Ar-H), 7.34 (s, 1H, Ar-H), 7.31 (s, 1H, Ar-H), 6.83 (m, 1H, Ar-H), 6.28 (brs, 1H, =CH NBD), 6.05 (brs, 1H, =CH NBD), 5.67 (brs, 1H, =CH NBD), 4.16 (brs, 1H, CH NBD), 3.95 (brs, 1H, CH NBD), 3.58 (brs, 1H, =CH NBD), 2.67 (m, 1H, PCH_2), 2.50 (m, 1H, CH_2 Cy), 2.32 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.28 (m, 1H, PCH), 1.97-1.66 (m, 10H, CH_2 Cy), 1.83 (s, 3H, CH_3), 1.79 (m, 2H, CH_2 NBD), 1.76 (s, 3H, CH_3), 1.50 (s, 9H, $C(CH_3)_3$), 1.45-1.20 (m, 6H, CH_2 Cy), 1.36 (s, 9H, $C(CH_3)_3$), 1.09-0.95 (m, 3H, $2CH_2$ Cy). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): *δ* = 155.1 (dd, *J*(C,Rh) = 9 Hz, *J*(C,P) = 4 Hz, OCq_{arom}), 144.9 (dd, *J*(C,Rh) = 14 Hz, *J*(C,P) = 1 Hz, OCq_{arom}), 143.7 (d, *J*(C,P) = 6 Hz, OCq_{arom}), 137.8 (d, *J*(C,P) = 4 Hz, Cq_{arom}), 137.5 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 137.0 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 135.8 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 135.2 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 134.5 (d, *J*(C,P) = 2 Hz, Cq_{arom}), 133.6 (s, CH_{arom}), 131.8 (s, CH_{arom}), 130.0 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 129.7 (d, *J*(C,P) = 2 Hz, CH_{arom}), 129.5 (d, *J*(C,P) = 1 Hz, CH_{arom}), 129.3 (d, *J*(C,P) = 3 Hz, Cq_{arom}), 126.4 (dd, *J*(C,Rh) = 5 Hz, *J*(C,P) = 2 Hz, CH_{arom}) 123.8 (dd, *J*(C,Rh) = 4 Hz, *J*(C,P) = 2 Hz, CH_{arom}), 114.9 (dd, *J*(C,Rh) = 37 Hz, *J*(C,P) = 8 Hz, PCq_{arom}), 99.4 (dd, *J*(C,Rh) = 14 Hz, *J*(C,P) = 4 Hz, =CH NBD), 96.2 (dd, *J*(C,Rh) = 13 Hz, *J*(C,P) = 5 Hz, =CH NBD), 89.7 (m, =CH NBD), 75.1 (ddd, *J*(C,Rh) = 11 Hz, *J*(C,P) = 6 Hz, *J*(C,P) = 2 Hz, =CH NBD), 71.9 (brs, CH_2 NBD), 55.5 (s, CH NBD), 55.0 (m, CH NBD), 38.7 (d, *J*(C,P) = 23 Hz, PCH), 35.5 (s, $C(CH_3)_3$), 35.3 (s, $C(CH_3)_3$), 32.8 (d, *J*(C,P) = 22 Hz, PCH), 32.4 (s, CH_2), 32.2 (s, $C(CH_3)_3$), 31.7 (s, $C(CH_3)_3$), 30.3 (d, *J*(C,P) = 4 Hz, CH_2), 28.8 (d, *J*(C,P) = 4 Hz, CH_2), 27.7 (d, *J*(C,P) = 14 Hz, CH_2), 27.2 (d, *J*(C,P) = 5 Hz, CH_2), 27.1 (d, *J*(C,P) = 7 Hz, CH_2), 26.9 (d, *J*(C,P) = 2 Hz, CH_2), 26.7 (d, *J*(C,P) = 4 Hz, CH_2), 26.4 (d, *J*(C,P) = 1 Hz, CH_2), 26.1 (d, *J*(C,P) = 1 Hz, CH_2), 20.6 (s, CH_3), 20.5 (s, CH_3), 16.8 (s, CH_3), 16.7 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 132.0 (dd, *J*(P, Rh) = 281 Hz, *J*(P, P) = 59 Hz, PO), 12.6 (dd, *J*(P, Rh) = 144 Hz, *J*(P, P) = 59 Hz, PC). Elemental analysis: calculated: C 61.64%, H 6.97%, found: C 61.74%, H 6.81%.

Complex [Rh(NBD)(1e)](BF$_4$)

This complex was obtained as an orange powder according procedure described above for [Rh(NBD)(**1b**)](BF$_4$) (0.173 g, 85 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H, Ar-H), 7.96-7.93 (m, 3H, Ar-H), 7.68-7.54 (m, 5H, Ar-H), 7.51-7.41 (m, 5H, Ar-H), 7.30-7.19 (m, 4H, Ar-H), 7.13 (d, *J*(H,H) = 8.2 Hz, 1H, Ar-H), 7.08 (m, 1H, Ar-H), 6.91 (m, 1H, Ar-H),

5.81 (brs, 2H, =CH NBD), 5.69 (brs, 1H, =CH NBD), 4.62 (brs, 1H, =CH NBD), 4.17 (brs, 1H, CH NBD), 4.14 (brs, 1H, CH NBD), 2.71 (s, 3H, Ar-CH_3), 2.46 (s, 3H, Ar-CH_3), 1.71 (m, 2H, CH_2 NBD). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 155.3 (d, *J*(C, P) = 11 Hz, OCq_{arom}), 146.9 (d, *J*(C, P) = 12 Hz, OCq_{arom}), 145.9 (d, *J*(C, P) = 6 Hz, OCq_{arom}), 134.9 (s, CH_{arom}), 133.9 (s, CH_{arom}), 133.9 (s, CH_{arom}), 133.8 (s, CH_{arom}), 133.6 (s, CH_{arom}), 133.5 (s, CH_{arom}), 132.8 (t, *J*(C, P) = 2 Hz, $2CH_{arom}$), 132.2 (s, $2Cq_{arom}$), 131.7 (dd, *J*(C, P) = 18, 2 Hz, $2Cq_{arom}$), 131.4 (s, CH_{arom}), 131.3 (s, CH_{arom}), 130.3 (dd, *J*(C, P) = 11, 3 Hz, $4CH_{arom}$), 129.5 (d, *J*(C, P) = 3Hz, Cq_{arom}), 129.2 (d, *J*(C, P) = 1 Hz, Cq_{arom}), 128.4 (s, CH_{arom}), 128.2 (s, CH_{arom}), 127.3 (s, CH_{arom}), 127.1 (d, *J*(C, P) = 9 Hz, Cq_{arom}), 127.0 (s, CH_{arom}), 126.7 (s, CH_{arom}), 126.6 (d, *J*(C, P) = 2 Hz, $2CH_{arom}$), 126.5 (s, Cq_{arom}), 126.4 (s, $2CH_{arom}$), 123.6 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 122.7 (t, *J*(C, P) = 4 Hz, CH_{arom}), 122.4 (d, *J*(C, P) = 3 Hz, Cq_{arom}), 116.3 (dd, *J*(C, P) = 52, 9 Hz, Cq_{arom}), 104.6 (brs, =CH NBD), 104.1 (brs, =CH NBD) 95.5 (brs, =CH NBD), 88.5 (brs, =CH NBD), 73.5 (s, CH_2 NBD), 56.5 (s, CH NBD), 56.1 (s, CH NBD), 19.0 (s, CH_3), 17.7 (s, CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ = 139.0 (dd, *J*(P, Rh) = 281 Hz, *J*(P, P) = 71Hz, PO), 16.7 (dd, *J*(P, Rh) = 142 Hz, *J*(P, P) = 71 Hz, PC). Elemental analysis: calculated: C 62.55%, H 4.24%, found: C 62.59%, H 4.05%.

Complex **[Rh(NBD)(1f)]BF_4**

This complex was obtained as an orange powder according procedure described above for [Rh(NBD)(**1b**)](BF_4) (0.521 g, 68% yield). ^1H NMR (500 MHz, CD_2Cl_2): δ = 7.65-7.57 (m, 9H, Ar-H), 7.38-7.36 (m, 1H, Ar-H), 7.32-7.29 (m, 2H, Ar-H), 7.21-7.16 (m, 2H, Ar-H), 7.05 (m, 1H, Ar-H), 6.89 (d, *J*(H, H) = 8.3 Hz, 1H, Ar-H), 5.74 (brs, 1H, =CH NBD), 5.65 (brs, 1H, =CH NBD), 5.55 (brs, 1H, =CH NBD), 4.78 (brs, 1H, =CH NBD), 4.13 (brs, 2H, CH NBD), 2.90-2.79 (m, 4H, CH_2), 2.69-2.58 (m, 2H, CH_2), 2.27 (m, 1H, CH_2), 2.15 (m, 1H, CH_2), 1.79 (m, 6H, CH_2), 1.79 (m, 2H, CH_2 NBD), 1.59-1.42 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 155.3 (d, *J*(C, P) = 11 Hz, OCq_{arom}), 145.7 (dd, *J*(C, P) = 12, 1 Hz, OCq_{arom}), 145.2 (d, *J*(C, P) = 5 Hz, OCq_{arom}), 140.1 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 139.1 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 137.4 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 136.7 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 134.8 (s, CH_{arom}), 134.7 (s, CH_{arom}), 134.6 (s, CH_{arom}), 133.5 (d, *J*(C, P) = 3 Hz, CH_{arom}), 133.3 (s, CH_{arom}), 133.2 (s, CH_{arom}), 133.1 (d, *J*(C, P) = 3 Hz, CH_{arom}), 132.4 (d, *J*(C, P) = 3 Hz, CH_{arom}), 130.5 (d, *J*(C, P) = 1 Hz, CH_{arom}), 130.4 (d, *J*(C, P) = 2 Hz, CH_{arom}), 130.2 (d, *J*(C, P) = 3 Hz, CH_{arom}), 130.1 (s, CH_{arom}), 130.1 (s, CH_{arom}), 130.0 (s, CH_{arom}), 127.7 (dd, *J*(C, Rh) = 53, 2 Hz, *J*(C, P) = 2 Hz, Cq_{arom}), 127.6 (d, *J*(C, P) = 2 Hz, Cq_{arom}), 126.8 (d, *J*(C, P) = 2

Hz,Cq_{arom}), 126.3 (d, *J*(C, P) = 49 Hz, Cq_{arom}), 126.2 (dd, *J*(C, P) = 7, 1 Hz, CH_{arom}), 122.5 (t, *J*(C, P) = 5 Hz, CH_{arom}), 119.1 (d, *J*(C, P) = 4 Hz, CH_{arom}), 118.3 (d, *J*(C, P) = 2 Hz, CH_{arom}), 116.9 (dd, *J*(C, Rh) = 52 Hz, *J*(C, P) = 9 Hz, Cq_{arom}), 103.5 (m, =CH NBD), 102.8 (m, =CH NBD), 93.8 (m, =CH NBD), 91.65 (m, =CH NBD), 73.1 (s, CH_2 NBD), 56.4 (s, CH NBD), 55.8 (s, CH NBD), 29.5 (s, CH_2), 29.4 (s, CH_2), 28.1 (s, CH_2), 28.0 (s, CH_2), 22.8 (s, CH_2), 22.7 (s, CH_2), 22.6 (s, CH_2), 22.6(s, CH_2).

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2): δ = 132.5 (dd, *J*(P, Rh) = 280 Hz, *J*(P, P) = 73 Hz, PO), 17.8 (dd, *J*(P, Rh) = 142 Hz, *J*(P, P) = 73 Hz, PC). Elemental analysis: calculated: C 61.25%, H 4.80%, found: C 61.20%, H 4.68%.

Preparation of supported complexes

Preparation of Li-resin

According to a previously described procedure,[S4] commercial Dowex® 50WX2-100 in its H^+ form (10 g) was washed with distilled water (10 x 50 mL). Washings initially orange became colourless. Resin was sequentially washed with methanol (5 x 50 mL), THF (3 x 50 mL), dichloromethane (2 x 50 mL), methanol (2 x 50 mL) and diethyl ether (3x50ml). Resin was finally dried using vacuum/argon cycles and left overnight under vacuum. Dry resin (9 g) was placed in a round-bottom flask and water was added (150 mL). Suspension was stirred for 5 minutes using orbital shaker, water was removed and 1 M solution of LiOH in water (360 mL) was slowly poured. The resulting mixture was left stirring for 15 minutes and supernatant removed by filtration. The resin was repeatedly washed with small portions of distilled water until neutral pH of washings was observed. Resin was then washed with methanol (5x50mL), diethyl ether (3x50mL), dried using vacuum/argon cycles and finally left under vacuum overnight. Product obtained as creamy white resin was stored in a glovebox.

General procedure for the immobilization of [Rh(diolefin)(P-OP)](BF_4) complexes

Supported complexes were prepared by interaction of solutions of title compounds with the Li-resin as exemplified below for **3a**. Li-resin (0.459 g, 2.21 mEq) was placed in a round-bottom Schlenk flask, degassed and methanol (10 mL) was added. Solution **3a** (0.063 g, 0.067 mmol) in methanol (5 mL) was added dropwise to a stirred suspension of the resin. Mixture

was stirred for 12 hours at room temperature and resin was filtered off using a thin cannula. Resin was washed with methanol (5 x 5mL), THF (3 x 5mL), diethyl ether (3 x 5 mL), dried using vacuum/argon cycles and left under vacuum overnight. Product **3a** was obtained as orange resin beads. ICP analysis of the mineralized resin (see mineralization procedure below) showed a rhodium content of 0.79 % w/w, what accounts for 61 % immobilization of the catalyst precursor. Corresponding data for other supported complexes are detailed below: **2d**, 1.10 % Rh, 83 % immobilization; **3b**, 0.92 % Rh, 68 % immobilization; **3c**, 0.87 % Rh, 66 % immobilization; **3e**, 1.16 % Rh, 87 % immobilization; **3f**, 1.09 % Rh, 81 % immobilization; **3g**, 1.06 % Rh, 80 % immobilization; **3h**, 0.91 % Rh, 74 % immobilization.

Procedures for asymmetric hydrogenation

Hydrogenations with supported catalyts performed in a parallel reactor

In a glovebox a suitable amount of supported catalyst (typically 5.0 mg) and corresponding amount of substrate **4a-4j** were placed in an HPLC vial. Small stirring bar was placed inside the vial and it was closed with a screw cap equipped with with PTFE septum. Vial was taken out of the glovebox and degassed water (1 mL) was injected into the vial. Vial was placed in a HEL CAT-18 reactor and small syringe needle was placed in the septum. The reactor was quickly closed and purged thoroughly with nitrogen, placed in an oil bath and heated to desired temperature. Reactor was then purged with hydrogen and pressurized at 4 bar of hydrogen and left magnetically stirred for suitable time. Then, the reactor was depressurized and the resulting suspension (or biphasic system composed by product and aqueous phases) or solution (reactions in MeOH) was separated from resin beads and brought to dryness. Conversion was determined by ^{1}H NMR analysis on the resulting residue. The latter was then dissolved in ethyl acetate/hexane 1:10 mixture and passed through a short pad of silica to remove catalyst impurities. The solution obtained was carefully evaporated and the residue obtained was analyzed by chiral chromatography to determine enantiomeric excess. Configuration for **5a** and **5b** was determined as described before.[S6] For products **5c-5j** configuration has been assigned by analogy to that observed in hydrogenations of **5a** and **5b**.

Hydrogenations with supported catalysts performed in a glass reactor (2-6 mL)

These reactions were run in a way similar to described above, with the exception that a Büchi miniclave 50 mL glass reactor was used.

Hydrogenations with supported catalysts performed in 2-Me-THF/H_2O (conditions A) or in Triton-X100/H_2O mixtures (conditions B)

These reactions were run in a way similar to described above either using a 2-Me-THF/H_2O (1:9) mixture or aqueous solutions of Triton-X100 of suitable concentration as solvents.

Hydrogenations with [Rh(NBD)(P-OP)](BF_4) complexes

In a glovebox suitable amount of catalyst (typically 1.0 mg) was placed in an HPLC vial as a solution in CH_2Cl_2. Solvent was evaporated under vacuum and the appropriate amount of substrate was added. Vial was closed and 1 mL of water was injected into the vial. Vial was placed in a HEL CAT-18 reactor and small syringe needle was placed in the septum. The reactor was closed and purged with nitrogen. Reactor was pressurized to 4 bar with hydrogen and left stirring for 24h. Reactor was depressurized; solution was brought to dryness and residue was analyzed in order to determine conversion and enantioselectivity.

Recycling experiments:

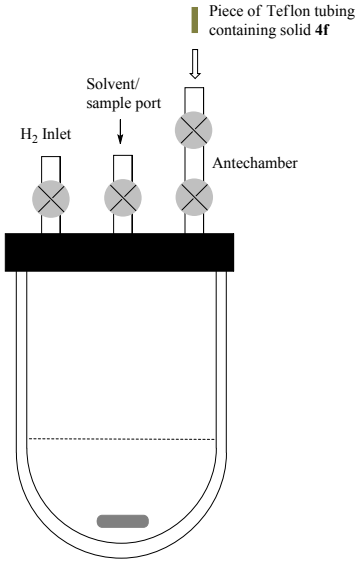
Catalyst recycling in hydrogenation of 4a

In a glove-box Büchi miniclave 50 mL glass reactor was charged with supported catalyst and substrate. Reactor was closed and taken out from the glovebox and suitable amount of solvent was injected through a port with a gas-tight syringe. Reactor was flushed with hydrogen with five pressurization (2 bar)/depressurization cycles and pressurized to 4bar. Reaction mixture was stirred for the desired time. Stirring was stopped and supernatant was separated from the catalyst using gas-tight syringe equipped with a long needle of bore diameter smaller than size of a resin bead. Reactor was fed with a solution of **4a**. Small pressure drop was observed due to manipulations so vessel was repressurized with hydrogen to 4 bars and stirring was started. Reaction mixture was again stirred over the time dependant on a length of the cycle.

Catalyst recycling in hydrogenation of 4f in water

These experiments were performed using the system schematically drawn in the following diagram. It is composed by a Büchi miniclave 50 mL glass reactor with ports for hydrogen

and introduction of solvent/extraction of reaction suspension and a third port including an antechamber for introduction of solid **4f**. The latter was packed inside a small piece of Teflon tubing (ca. 1.5 mm inner diameter). The procedure was analogous to that described above for **4a**, with the exception that substrate for the second and following cycles was added in solid form through the antechamber limited by two ball valves.



Determination of Rh leaching

For the determination of Rh leaching in reactions two procedures were used. First includes mineralization as follows. After hydrogenation, resin beads were separated from reaction mixture and the liquid phase obtained evaporated to dryness. An aliquot of the solid residue (typically 20 mg) was introduced in a microwave-heated digestión bomb and concentrated nitric acid (8 mL, 65 %) and H_2O_2 (1 mL, 30 %) were added, the mixture was heated at 200 ºC for 15 minutes, then cooled down to room temperature. Reactor was washed with distilled water, and solution finally diluted up to 25 mL with distilled water. The solution obtained was then analyzed by ICP. The experimentally determined detection limit for Rh using this procedure was 0.017 ppm. For reactions performed in water, samples for ICP analysis were alternatively prepared by taken part of the aqueous phase of the reaction mixture and diluted up to 5 mL with HNO_3 (65 %). For this procedure the detection limit experimentally determined was 0.047 ppm. In the case of reactions performed in 1-2 mL of water, supernatant was separated from resin beads and the latter washed with additional water finally obtaining 3.0 mL of solution. Of the resulting solution, a measured aliquot (1.5-2.5 mL) was

taken for ICP analysis. For reactions prepared with 6.0 mL of water (entries S14 and S15) the aliquot for analysis was obtained by taking 5.0 mL of the reaction mixture and concentrating it under reduced pressure down to 2 mL. For the recycling experiment (entries S16-S20) an aliquot of 1.0 mL was taken directly from the reaction mixture.

Table S1. Rh leaching values obtained in representative hydrogenation reactions

Entry	Entry/ Table[a]	Sample prep[b]	Rh total (mg)[c]	Rh leached (mg)	% Rh leached	[Rh] (ppm)
S1	1/1	**M**	0.039	0.0047	12.0	1.6
S2	7/1	**M**	0.055	0.0084	15.3	2.8
S3	1/2	**M**	0.039	0.0035	9.0	3.5
S4	2/2	**M**	0.055	0.0100	18.2	10.0
S5	13/3	**D**	0.035	<0.0003	<0.8	<0.3
S6	14/3	**D**	0.035	<0.0003	<0.8	<0.3
S7	3/4	**D**	0.058	<0.0005	<0.9	<0.2
S8	4/4	**D**	0.058	0.0014	2.4	0.7
S9	6/4	**D**	0.058	<0.0005	<0.9	<0.2
S10	7/4	**D**	0.058	<0.0005	<0.9	<0.2
S11	9/4	**D**	0.058	0.0012	2.0	0.6
S12	6/5	**D**	0.058	<0.0003	<0.5	<0.3
S14	10/5	**D**	0.058	<0.0003	<0.5	<0.05
S15	11/5	**D**	0.058	<0.0003	<0.5	<0.05
S16	22/6	**D**	0.070	<0.0014	<2.0	<0.2
S17	23/6	**D**	0.070	<0.0014	<2.0	<0.2
S18	24/6	**D**	0.070	<0.0014	<2.0	<0.2
S19	25/6	**D**	0.070	<0.0014	<2.0	<0.2

[a] Entry and Table in the main text. [b] Procedure used for the preparation of the ICP sample (D = dilution, M = mineralization). [c] Rh amount used in the reaction. [d] Calculated [Rh] (ppm) in the reaction medium.

Separation conditions for products 5a-5j

Racemic mixtures for HPLC analysis were obtained by hydrogenation of substrates **4a-4j** with achiral catalyst [Rh(COD)(DiPFc)](BF_4) [DiPFc = 1,1'-bis(diisopropylphosphino)ferrocene] in CH_2Cl_2. Below are detailed the separation conditions for **5a-5j**:

Methyl 2-acetamidopropanoate (5a):[S5] GC, , 150°C isotherm, β-dex 30m, 0.7mL/min, t_1 = 8.3 min (*R*), t_2 = 8.7 min (*S*).

Methyl 2-acetamido-3-phenylpropanoate (5b):[S5] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 10.1 min (*R*), t_2 = 12.6 min (*S*).

Methyl 2-acetamido-3-(p-tolyl)propanoate (5c):[S6] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 9.4 min (*R*), t_2 = 11.4 min (*S*).

Methyl 2-acetamido-3-(m-tolyl)propanoate (5d):[S7] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 11.9 min (*R*), t_2 = 14.5 min (*S*).

Methyl 2-acetamido-3-(4-methoxyphenyl)propanoate (5e):[S6] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 19.6 min (*R*), t_2 = 23.0 min (*S*).

Methyl 2-acetamido-3-(3-methoxyphenyl)propanoate (5f):[S8] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 16.8 min (*R*), t_2 = 21.0 min (*S*).

Methyl 2-acetamido-3-(3,4-dimethoxyphenyl)propanoate (5g):[S1a] HPLC, Chiralcel AD-H, 85:15 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 15.2 min (*R*), t_2 = 16.4 min (*S*).

Methyl 2-acetamido-3-(4-fluorophenyl)propanoate (5h):[S6] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 14.0 min (*R*), t_2 = 17.5 min (*S*).

Methyl 2-acetamido-3-(4-bromophenyl)propanoate (5i):[S8] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 14.5 min (*R*), t_2 = 19.6 min (*S*).

Methyl 2-acetamido-3-(3-bromophenyl)propanoate (5j):[S9] HPLC, Chiralcel OD-H, 90:10 *n*-hexane:^{i}PrOH, flow 1.0 mL/min, t_1 = 14.1 min (*R*), t_2 = 16.7 min (*S*).

Gel-phase NMR studies

Sample was prepared by placing **3g** (100 mg, 5.8 μmol Rh) in a heavy wall NMR Sample Tube equipped with a Teflon valve and slowly adding dry CD_3OD (1mL). Subsequent

hydrogenation was studied by pressurizing at 4 bar of H_2, while for the formation of enamide adducts the tube was depressurized and the proper amount of **4a** or **4b** was added under nitrogen. All $^{31}P\{^1H\}$ NMR spectra were acquired using standard pulse program.

References

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Figure S1. 1H NMR (CDCl3, 400 MHz) spectrum of 1b

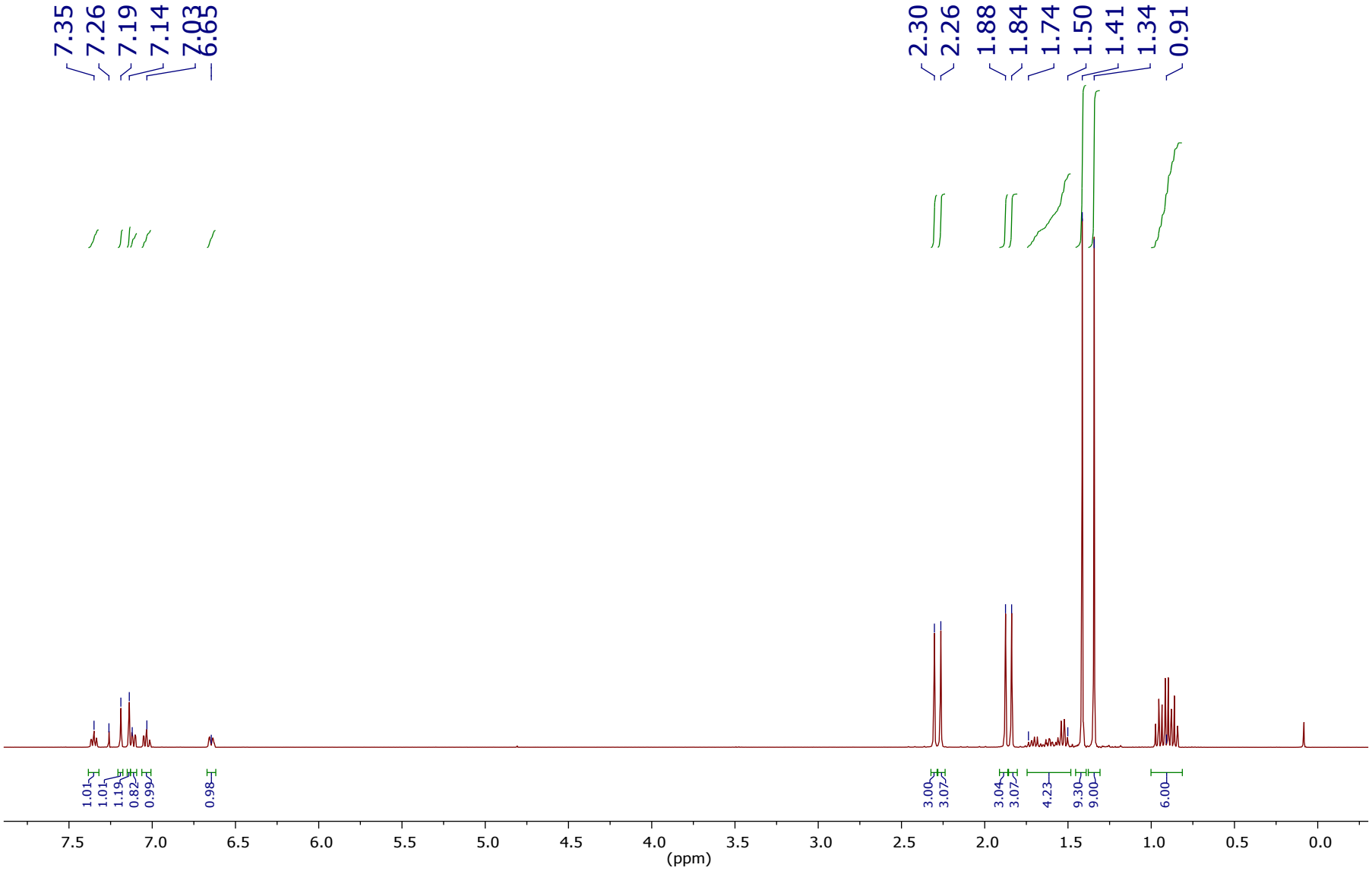


Figure S2. 13C{1H} NMR (CDCl3, 101 MHz) spectrum of 1b

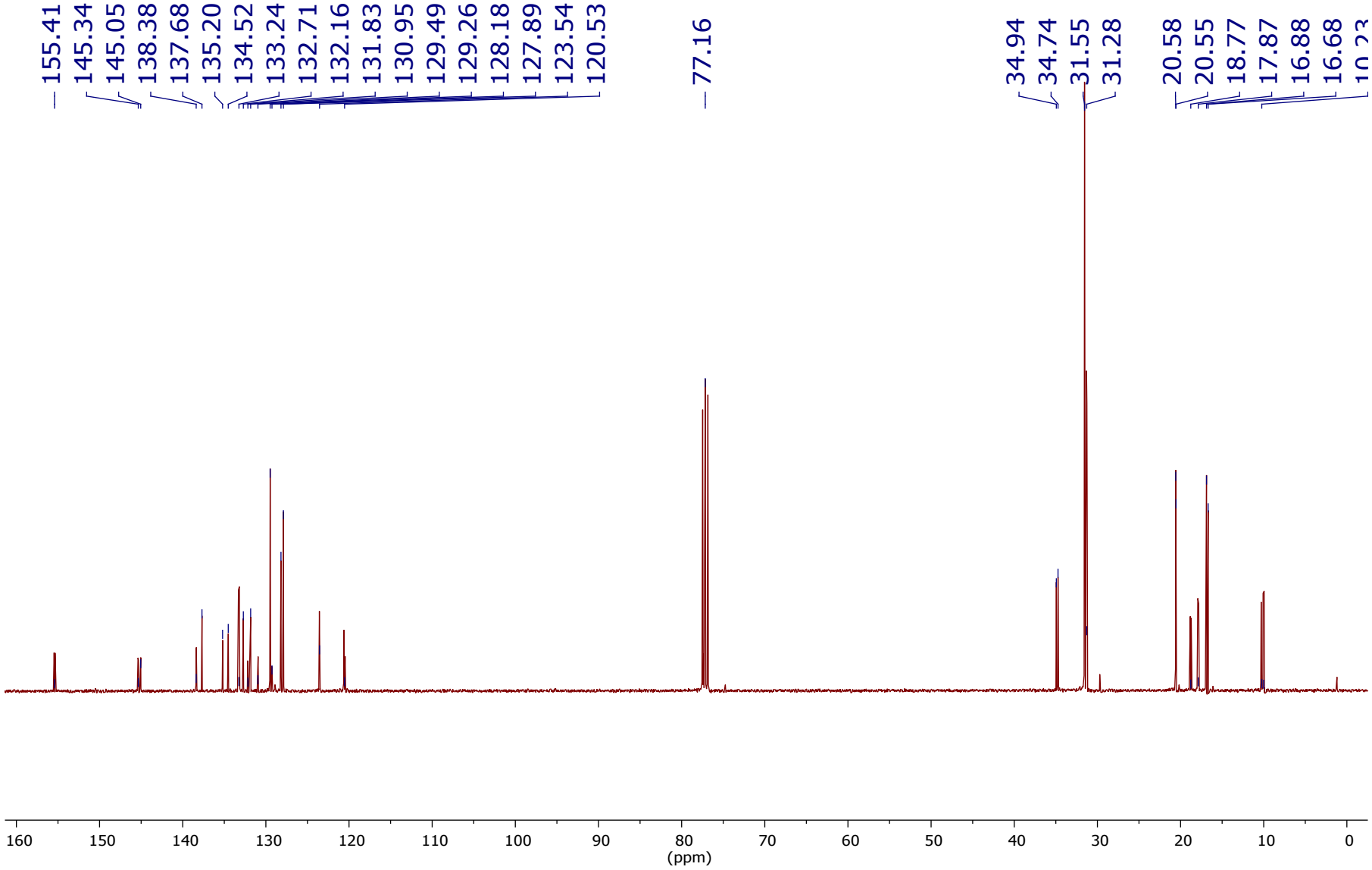


Figure S3. 31P{1H} NMR (CDCl3, 162 MHz) spectrum of 1b

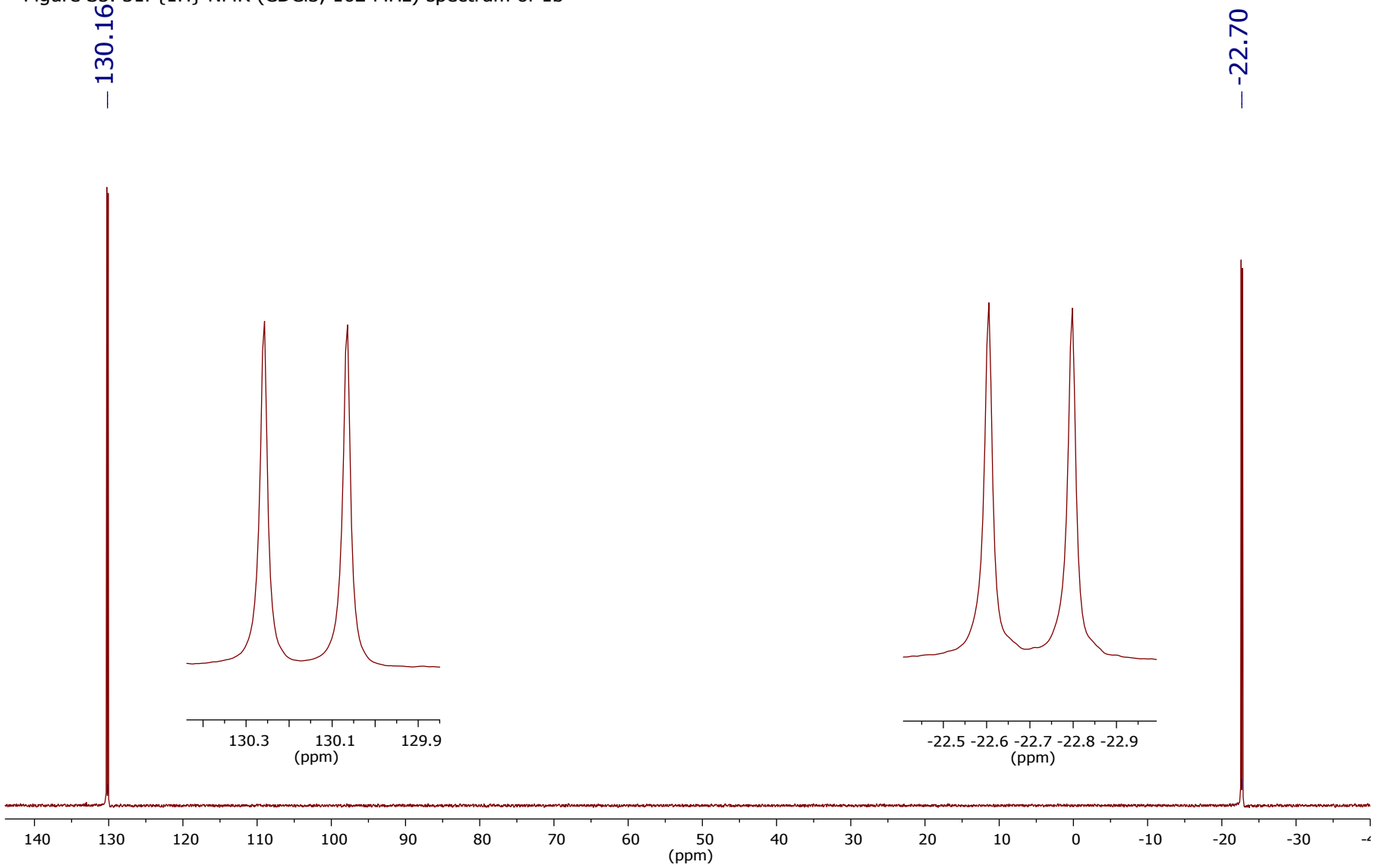


Figure S4. 1H NMR (CDCl3, 500 MHz) spectrum of 1c

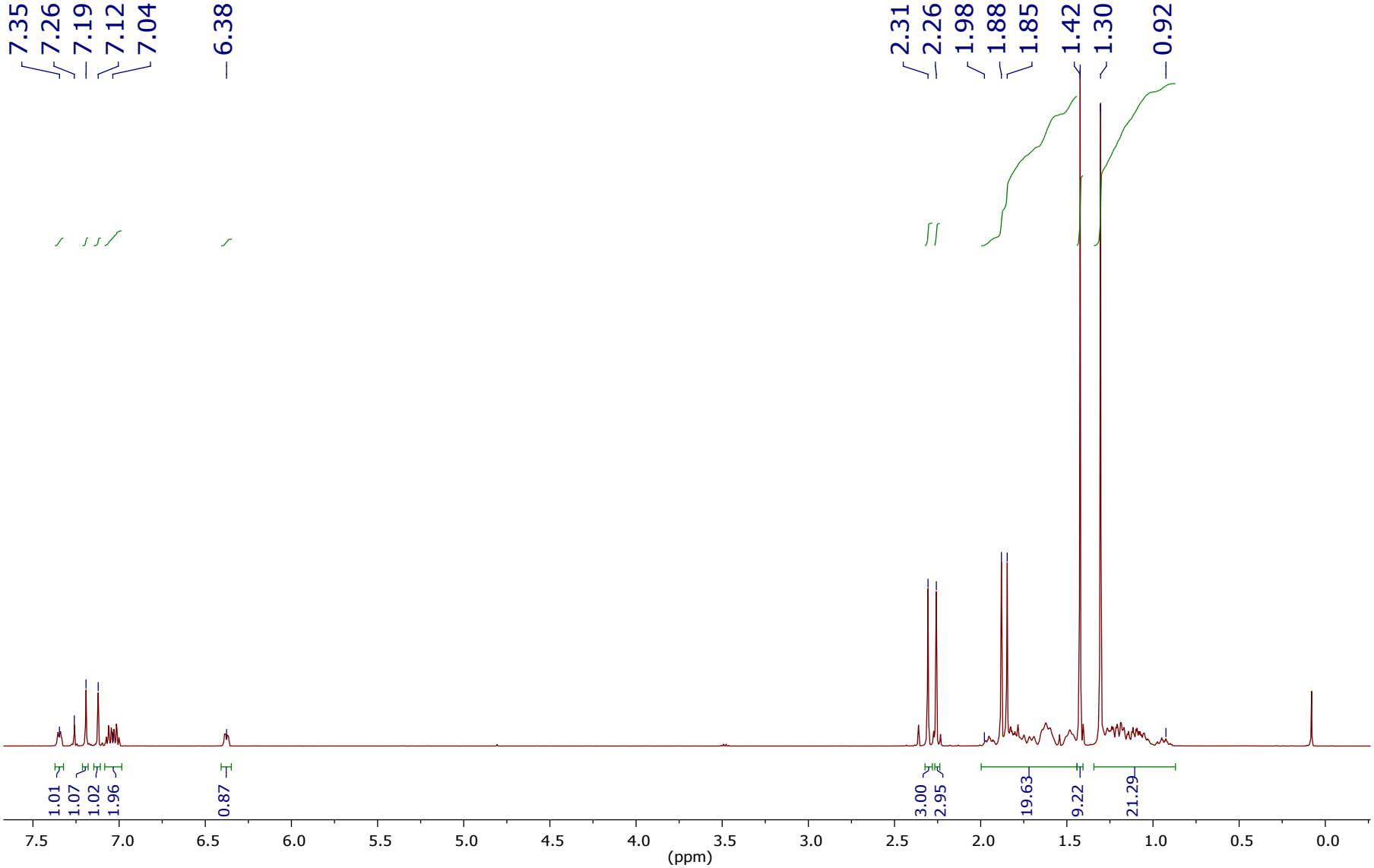


Figure S5. 13C{1H} NMR (CDCl3, 127 MHz) spectrum of 1c

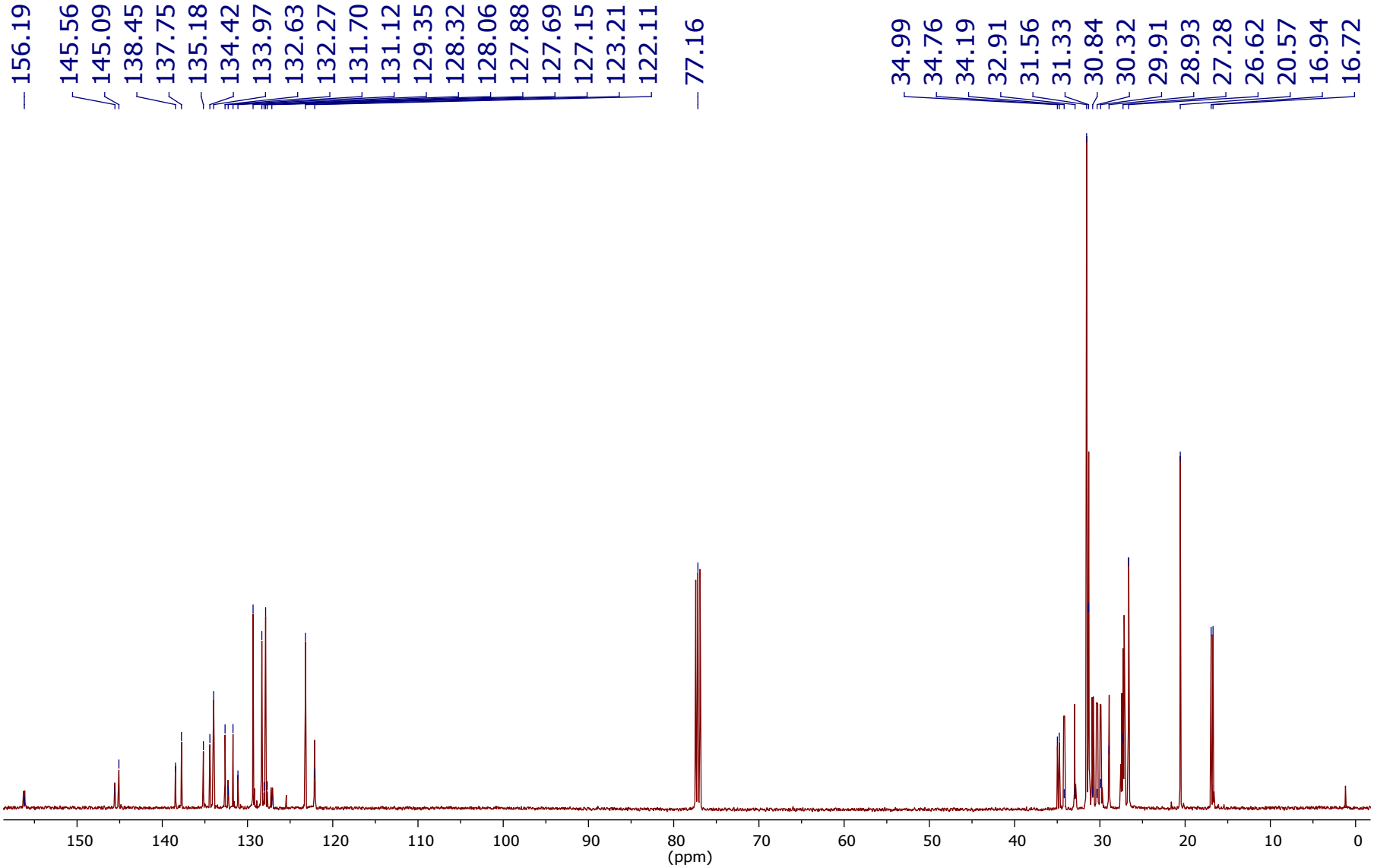


Figure S6. 31P{1H} NMR (CDCl3, 162 MHz) spectrum of 1c

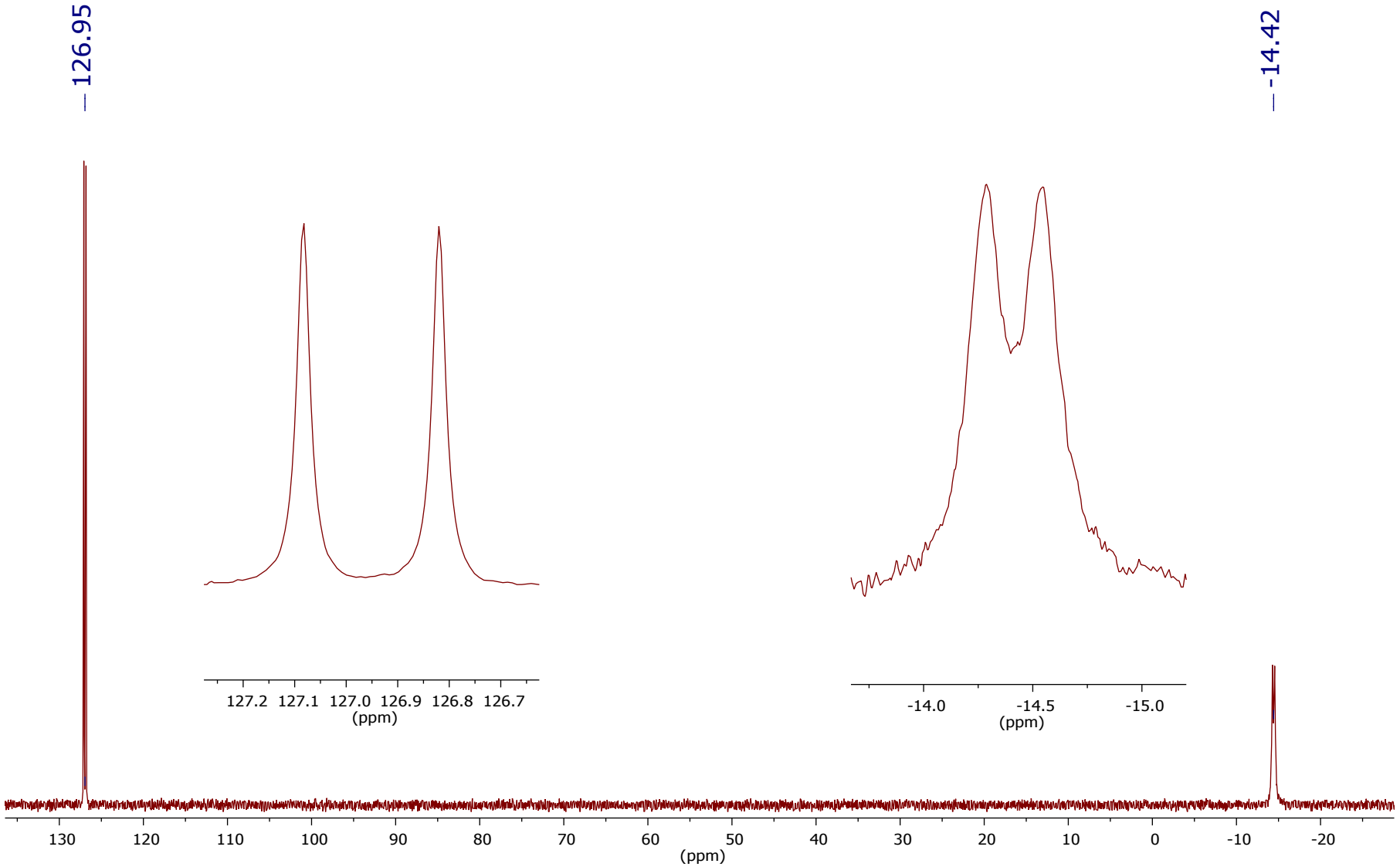


Figure S7. 1H NMR (CDCl3, 500 MHz) spectrum of 1d

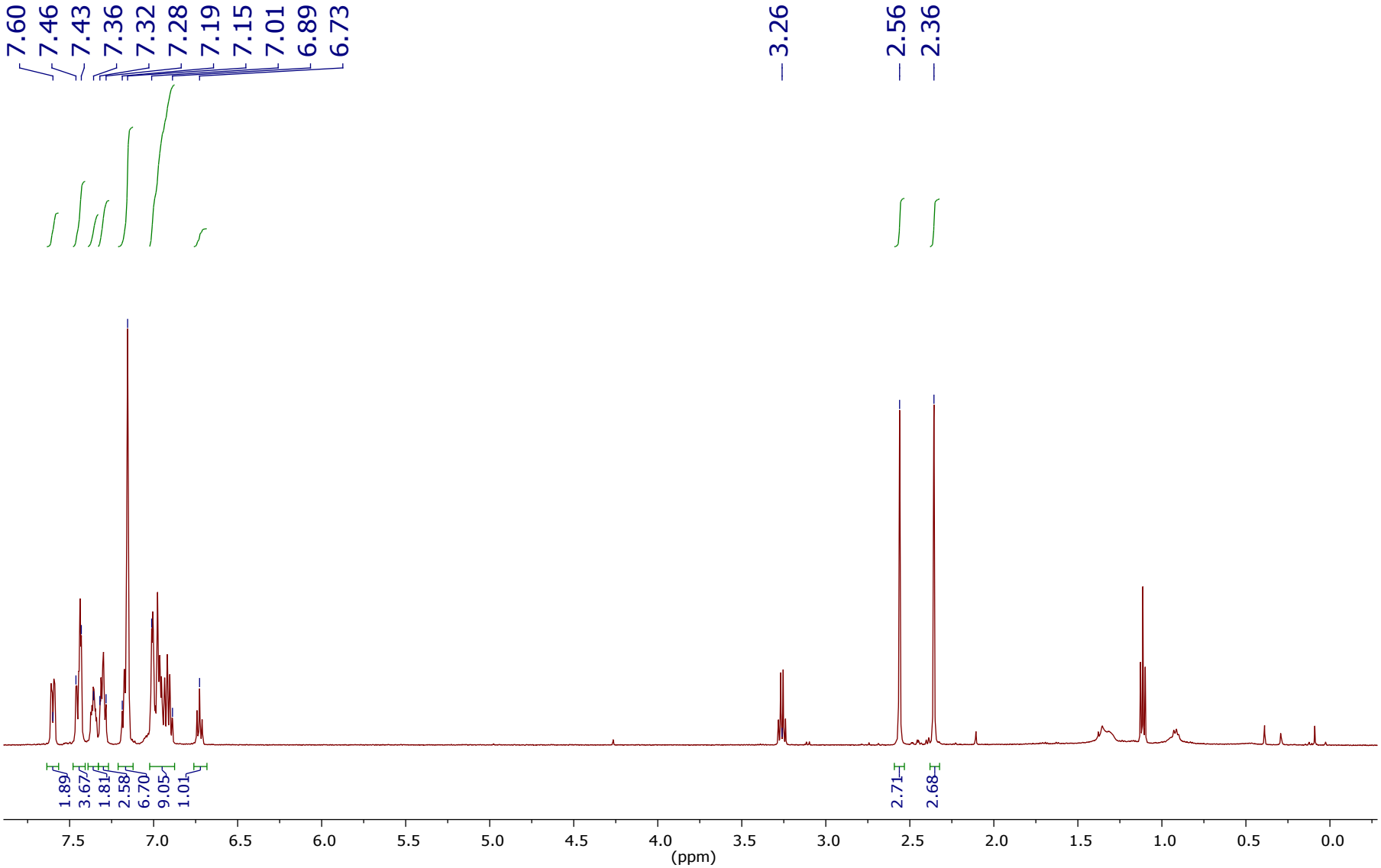


Figure S8. 13C{1H} NMR (CDCl3, 101 MHz) spectrum of 1d

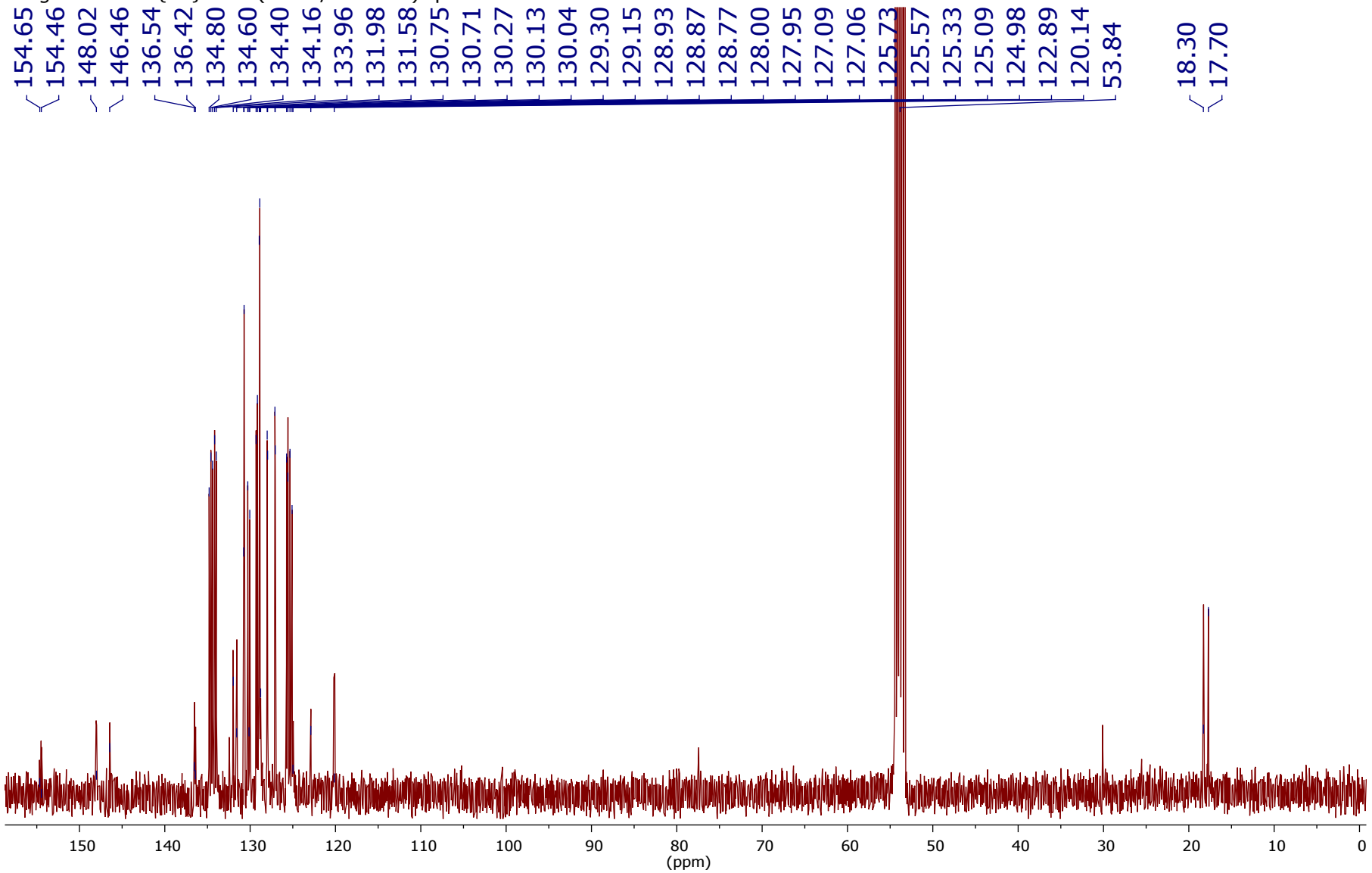


Figure S9. 31P{1H} NMR (CDCl3, 202 MHz) spectrum of 1d

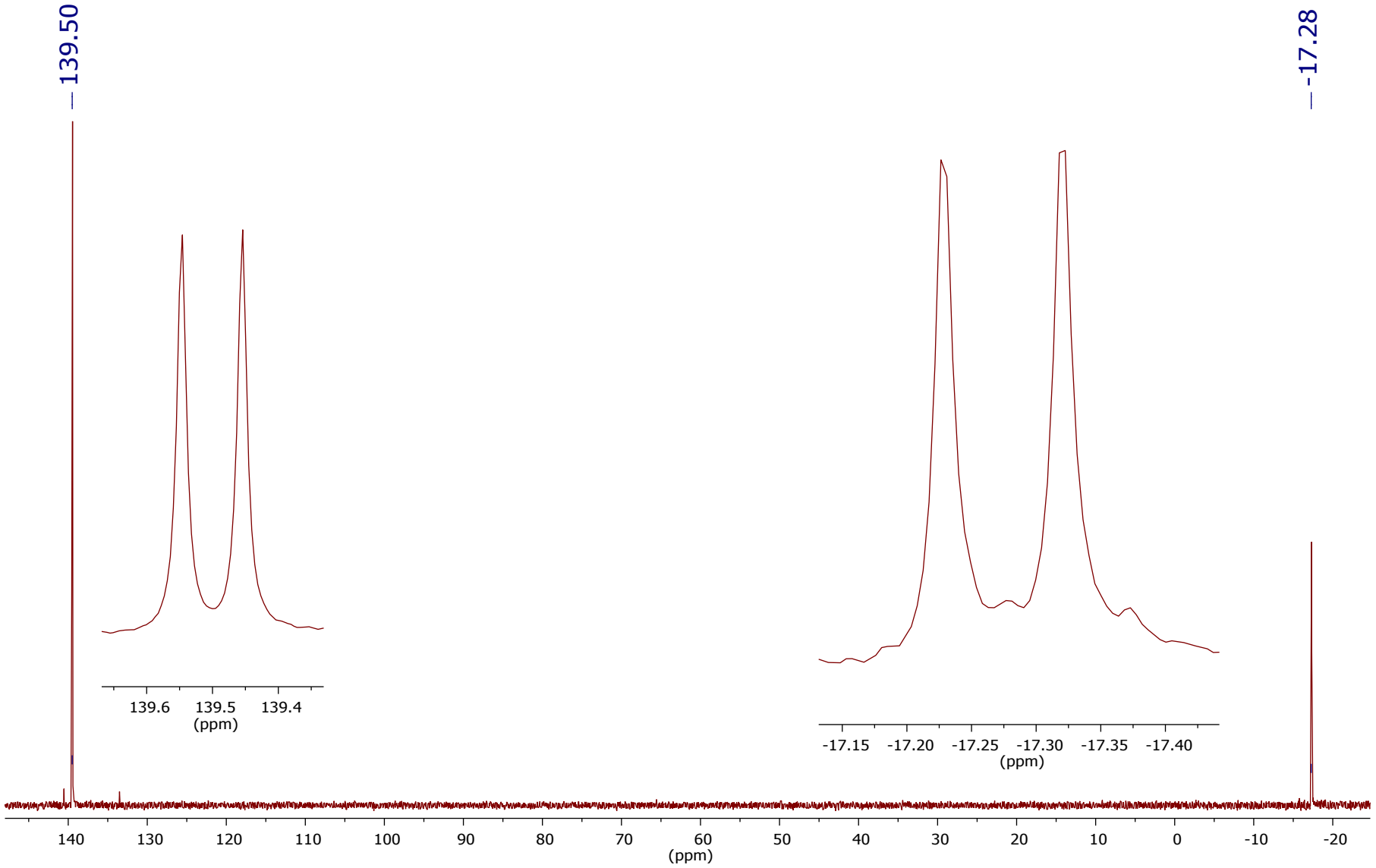


Figure S10. 1H NMR (CD2Cl2, 500 MHz) spectrum of 1f

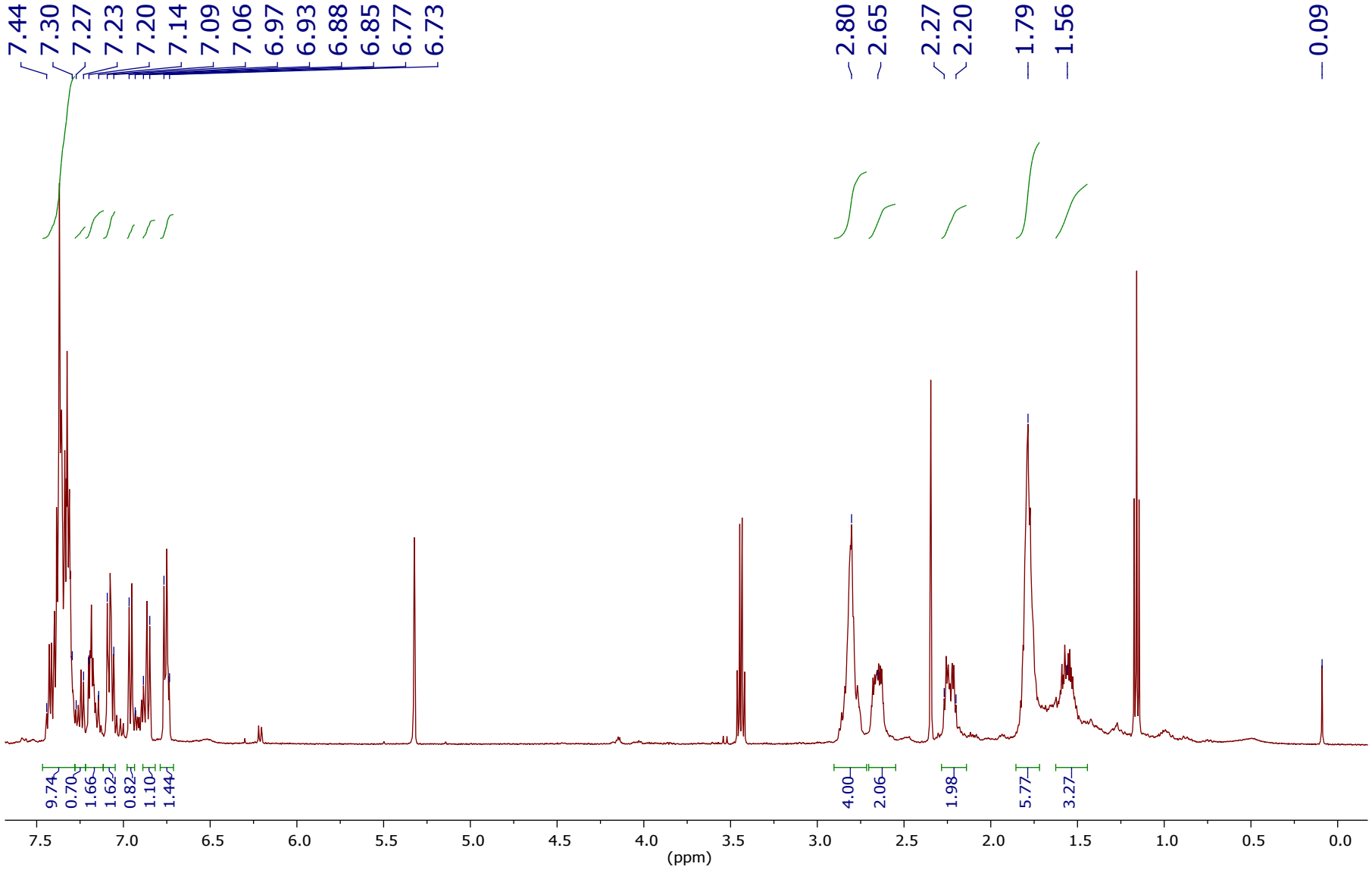


Figure S11. 13C{1H} NMR (CD2Cl2, 101 MHz) spectrum of 1f

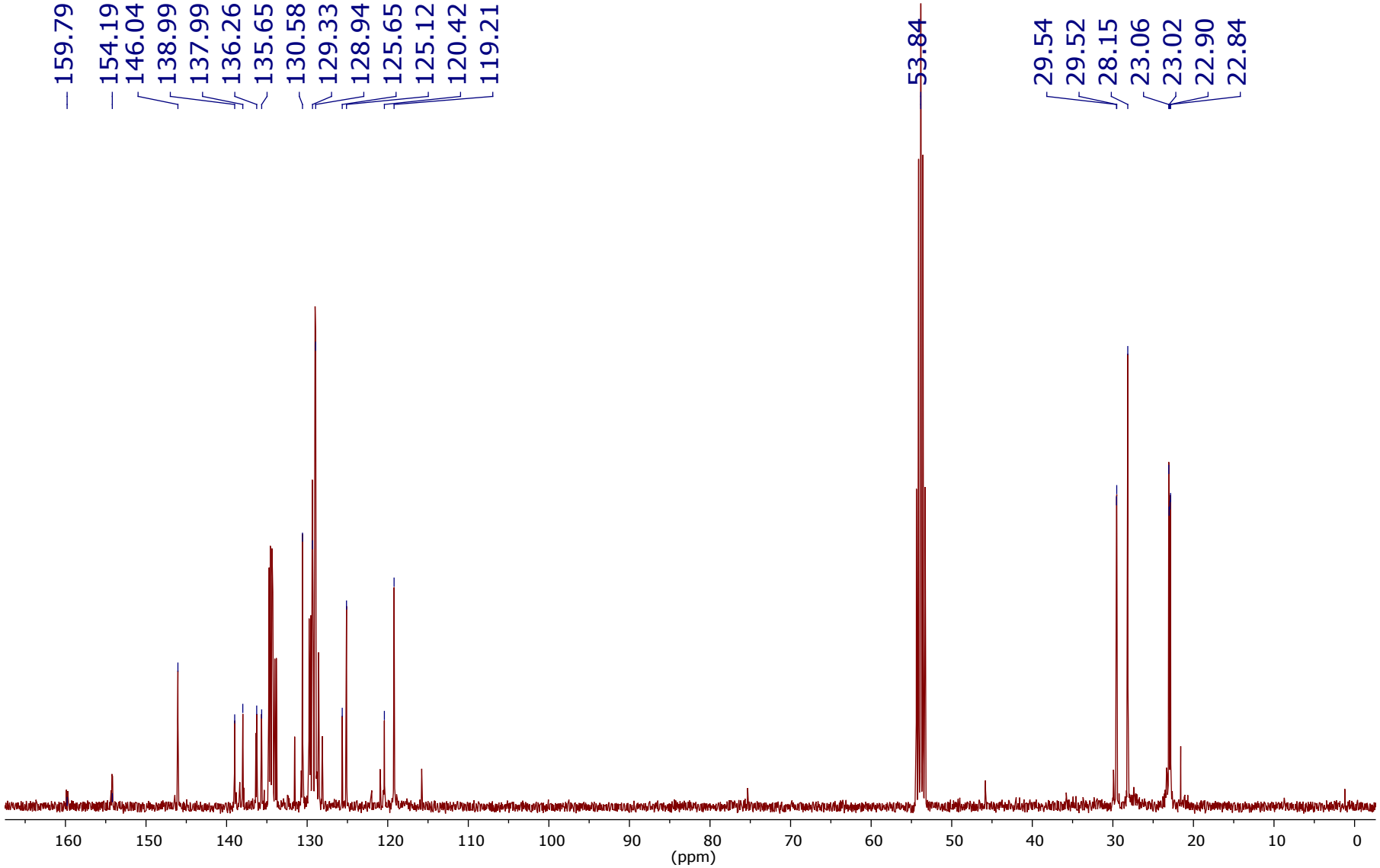


Figure S12. 31P{1H} NMR (CD2Cl2, 202 MHz) spectrum of 1f

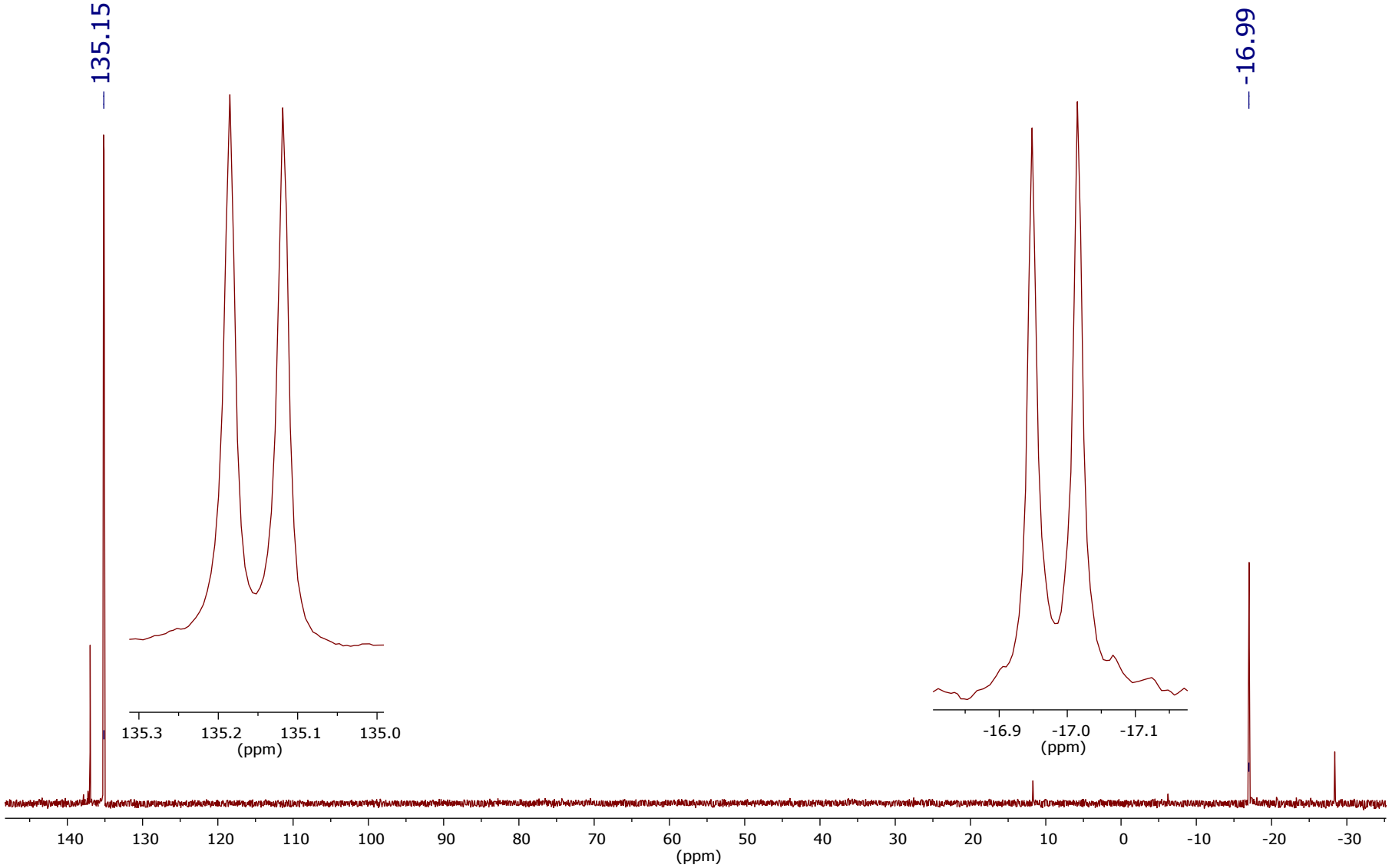


Figure S13. 1H NMR (CD2Cl2, 400 MHz) spectrum of [Rh(1b)(NBD)]BF4

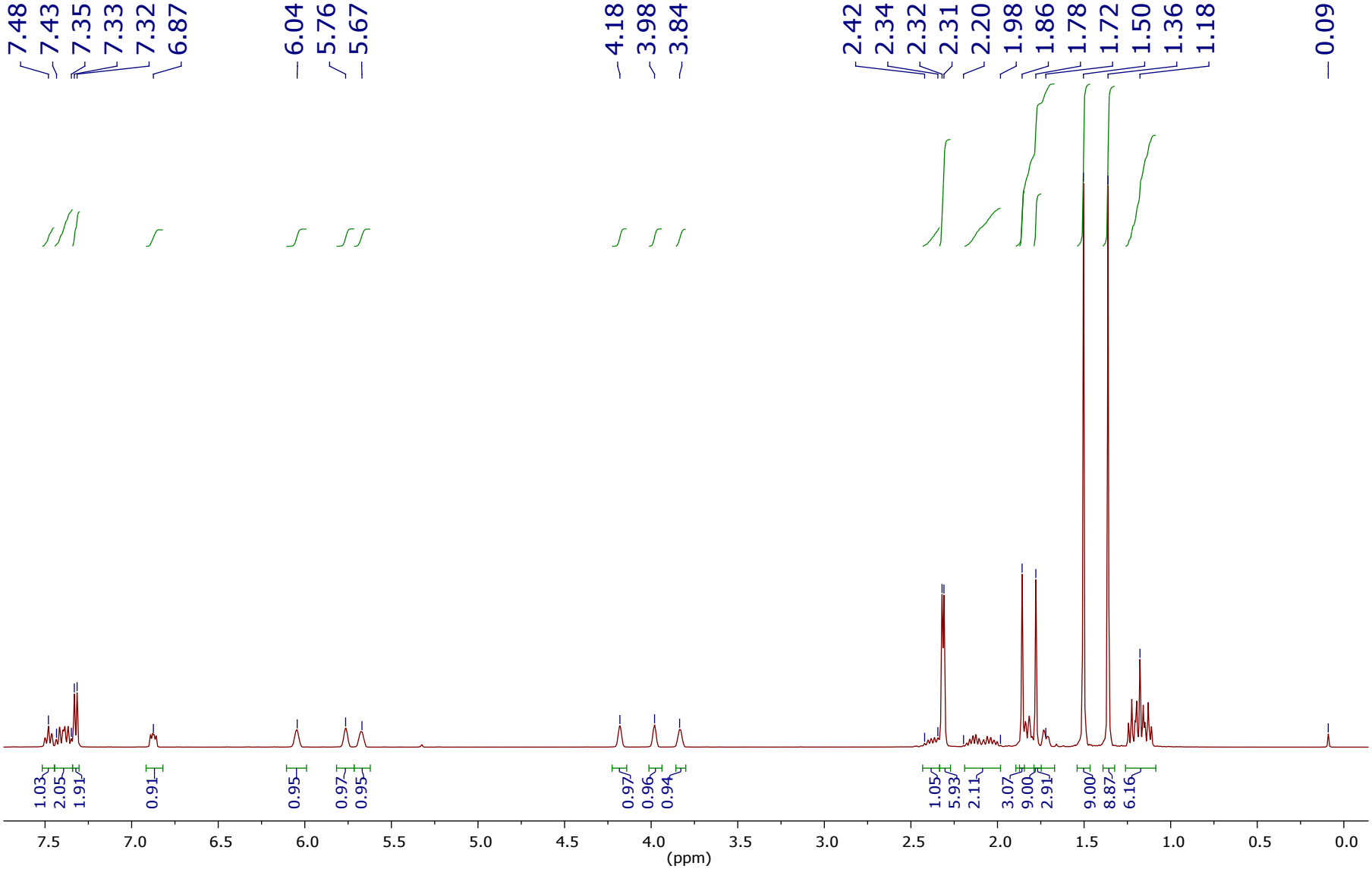


Figure S14. 13C{1H} NMR (CD2Cl2, 101 MHz) spectrum of [Rh(1b)(NBD)]BF4

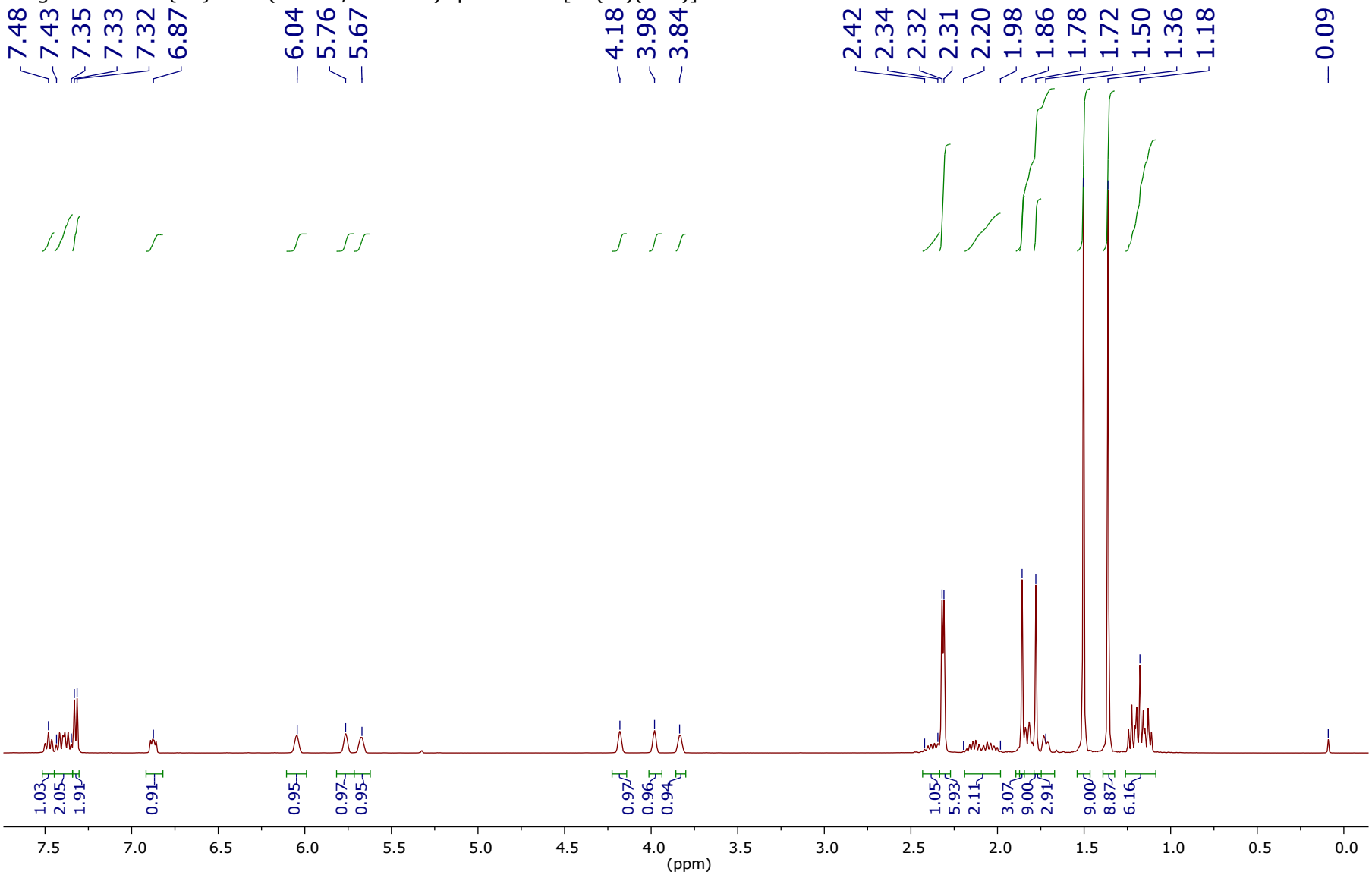


Figure S15. 31P{1H} NMR (CD2Cl2, 162 MHz) spectrum of [Rh(1b)(NBD)]BF4

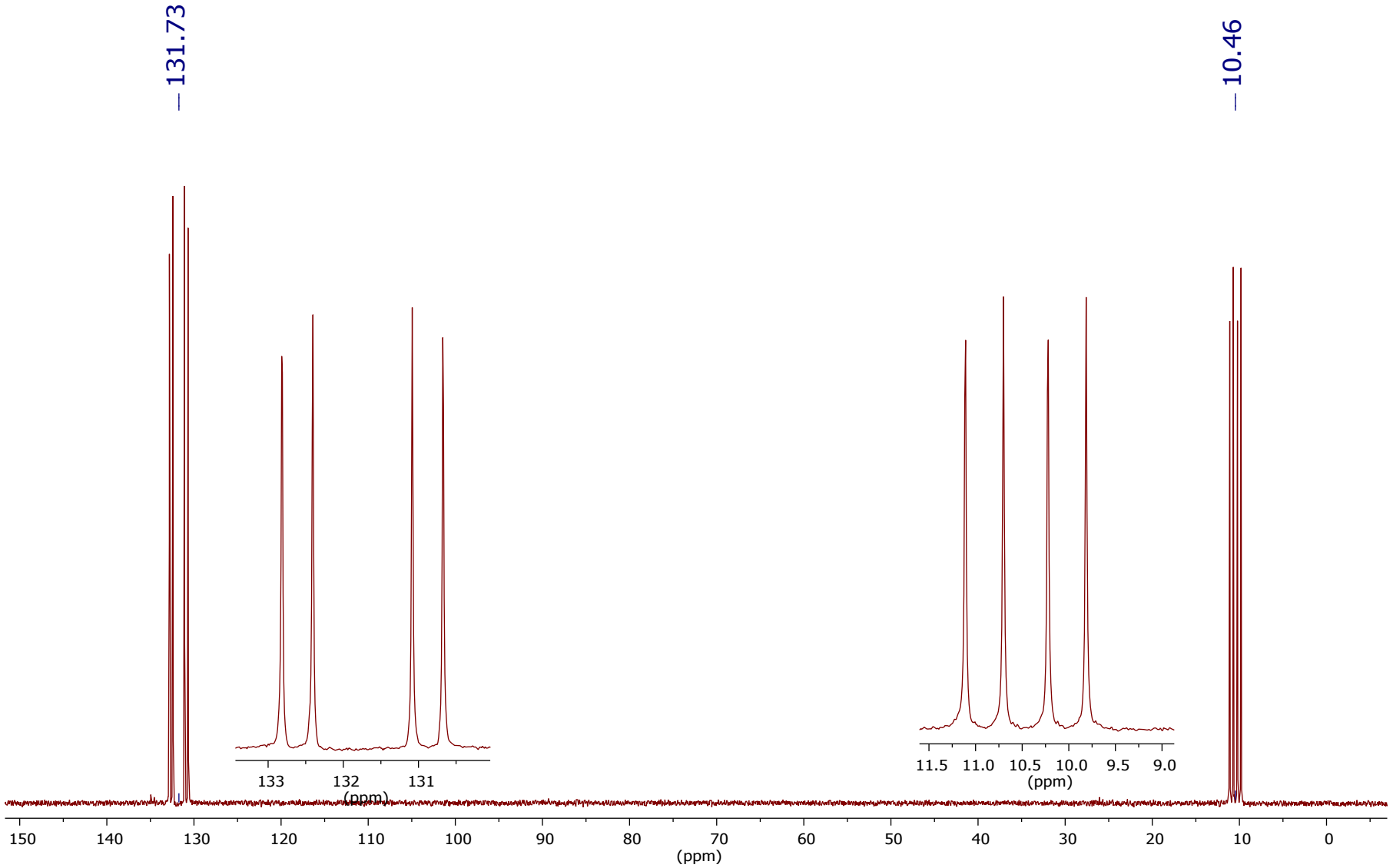


Figure S16. 1H NMR (CD2Cl2, 400 MHz) spectrum of [Rh(1c)(NBD)]BF4

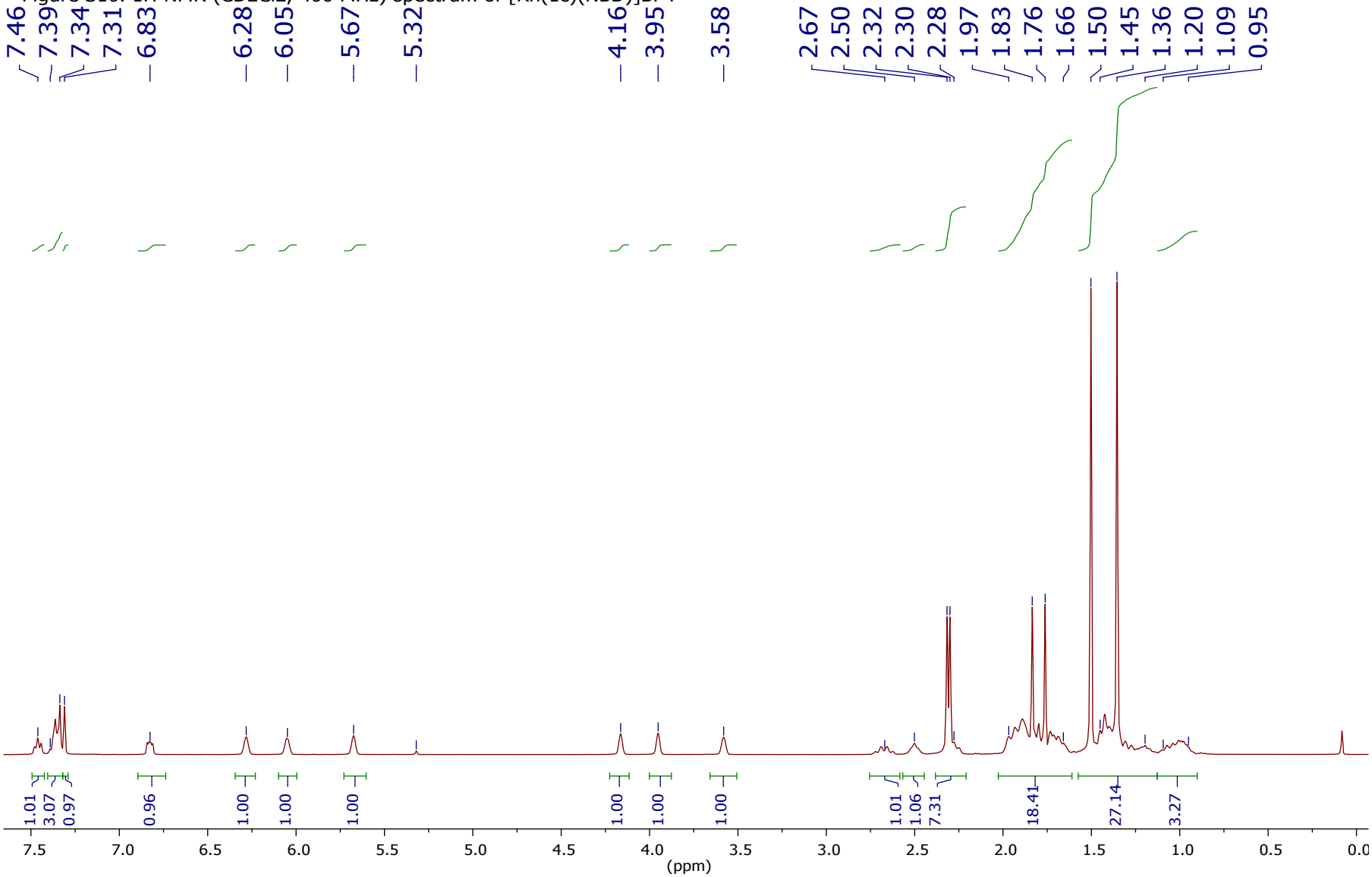


Figure S17. 13C{1H} NMR (CD2Cl2, 101 MHz) spectrum of [Rh(1c)(NBD)]BF4

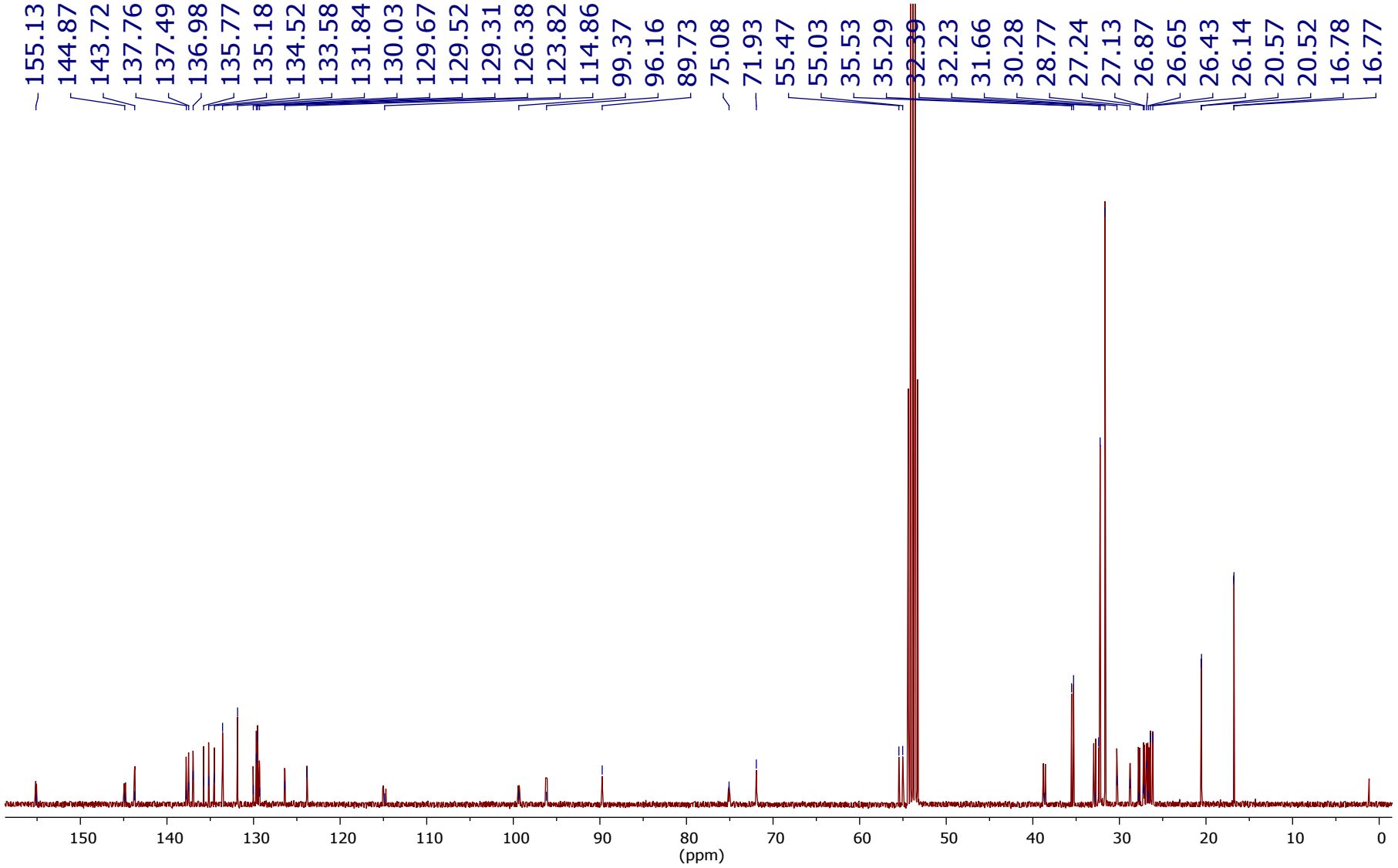


Figure S18. 31P{1H} NMR (CD2Cl2, 162 MHz) spectrum of [Rh(1c)(NBD)]BF4

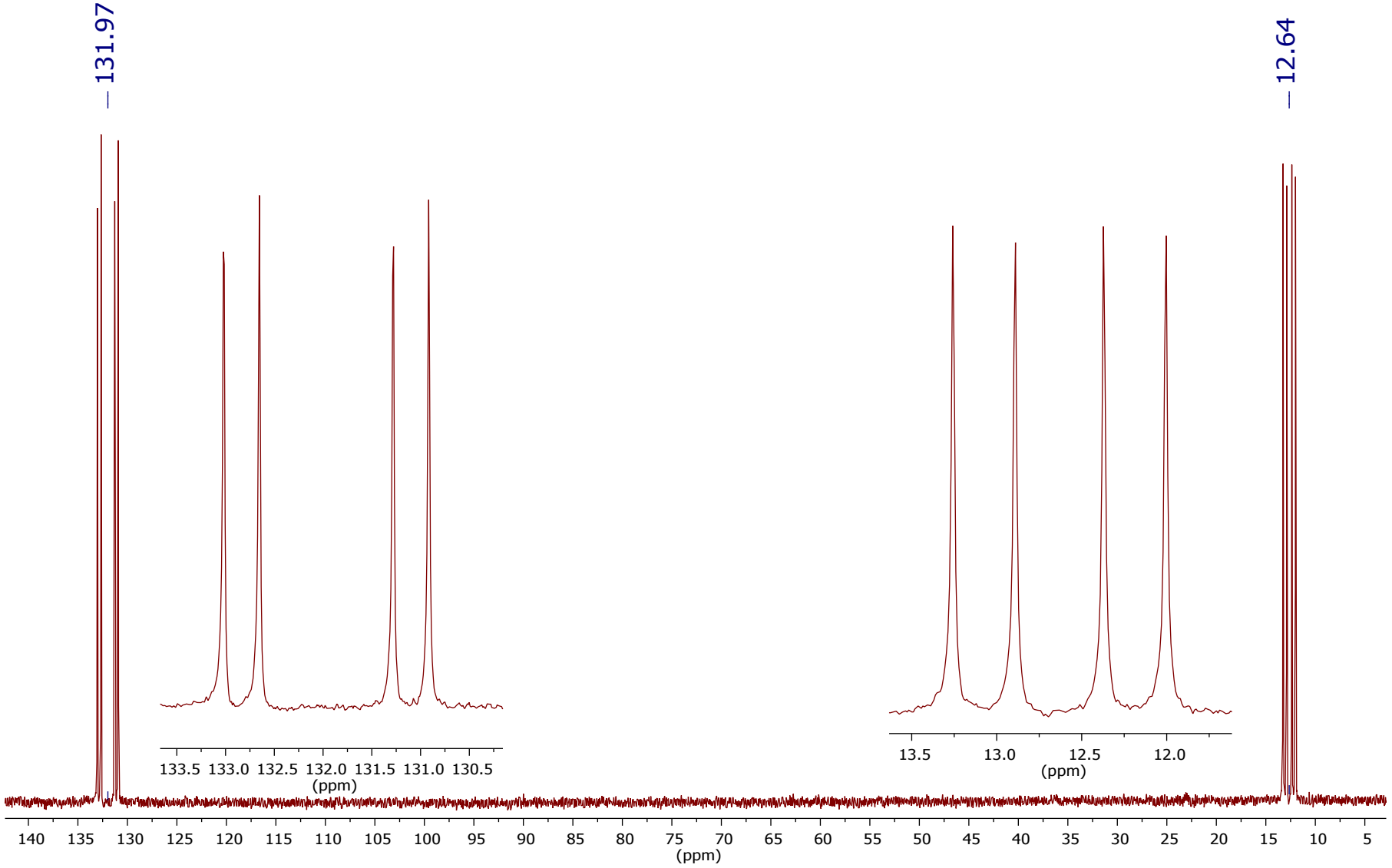


Figure S19. 1H NMR (CD2Cl2, 500 MHz) spectrum of [Rh(1e)(NBD)]BF4

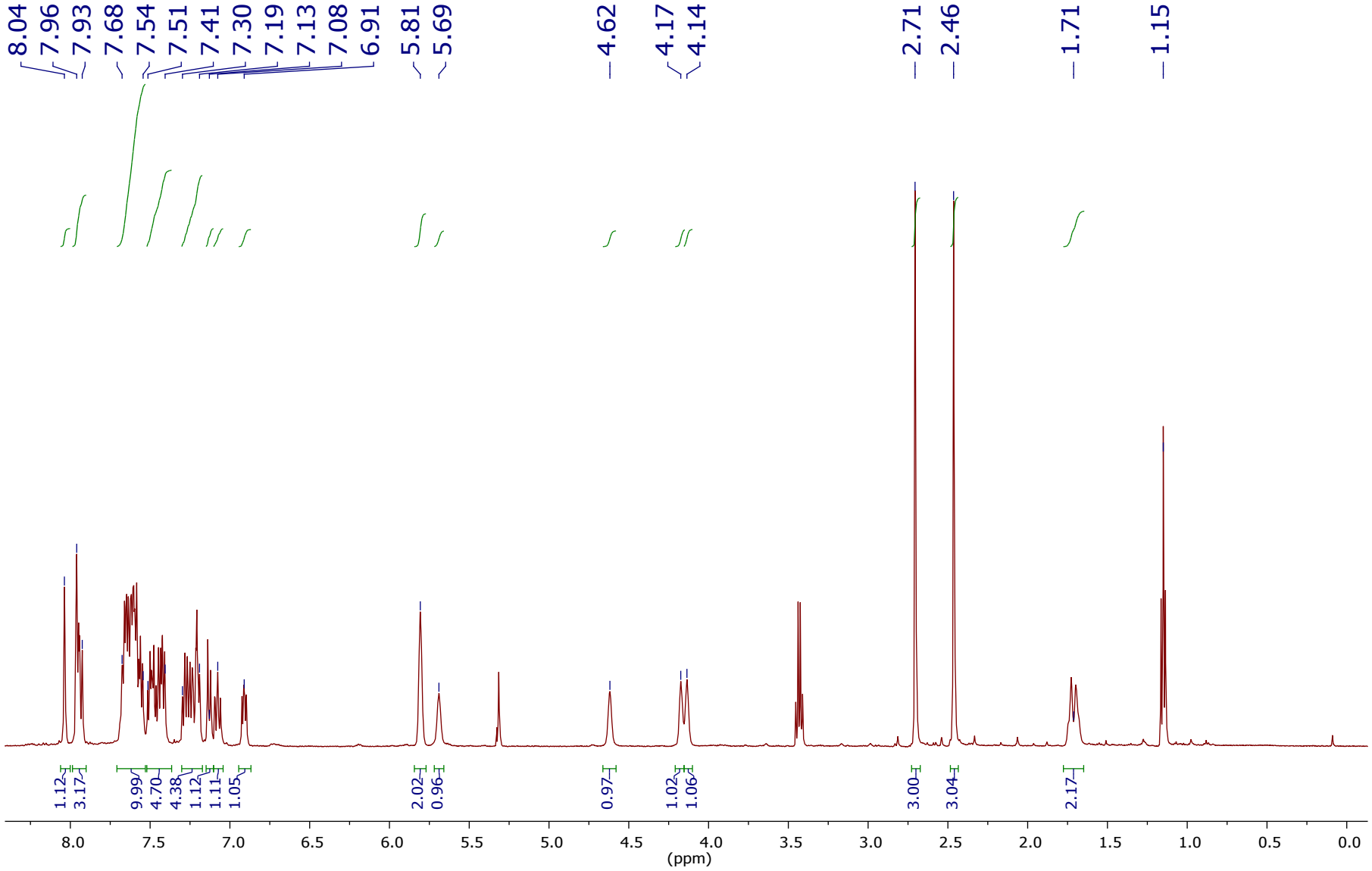


Figure S20. 13C{1H} NMR (CD2Cl2, 400 MHz) spectrum of [Rh(1e)(NBD)]BF4

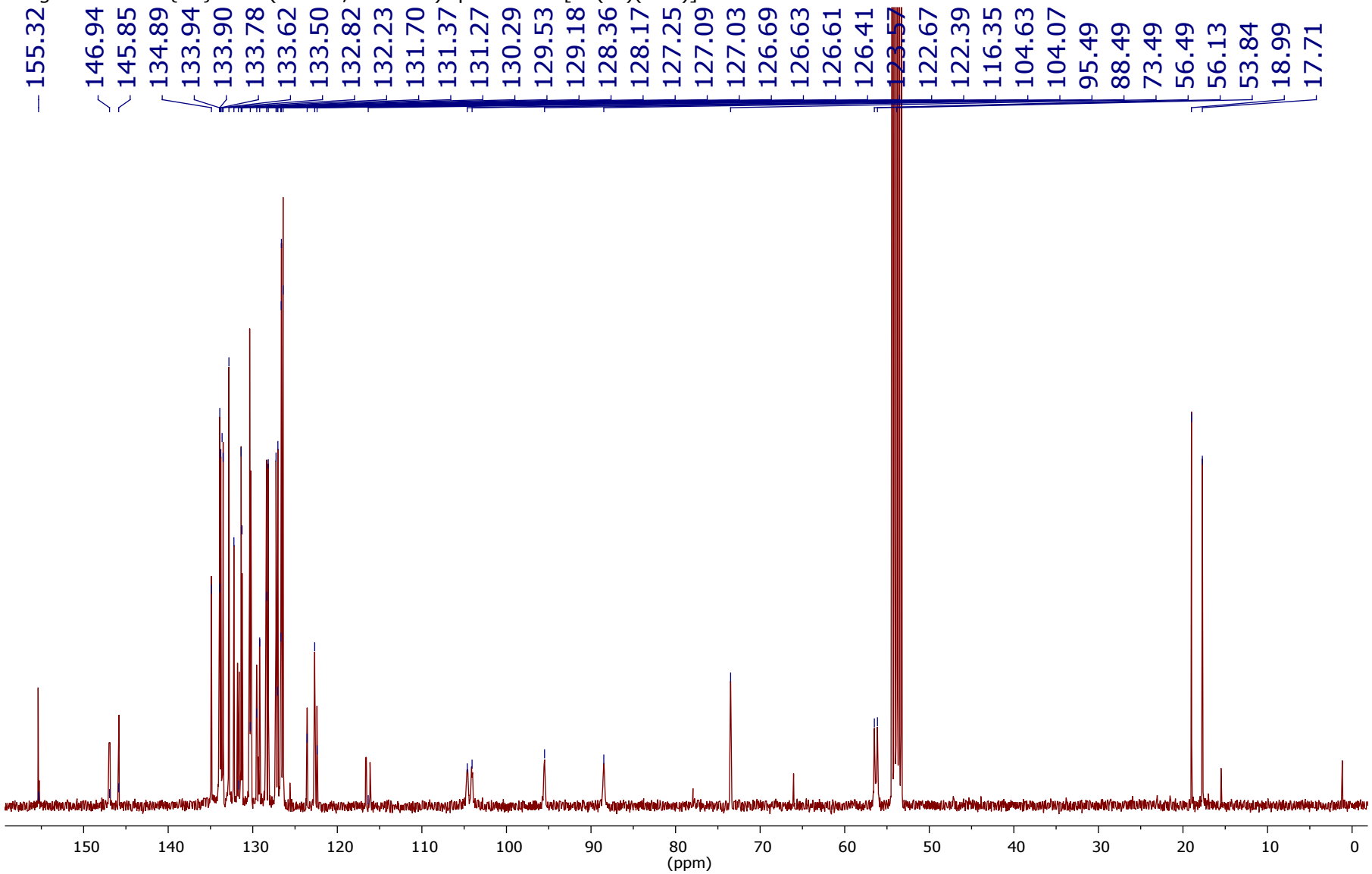


Figure S21. 31P{1H} NMR (CD2Cl2, 121.5 MHz) spectrum of [Rh(1e)(NBD)]BF4

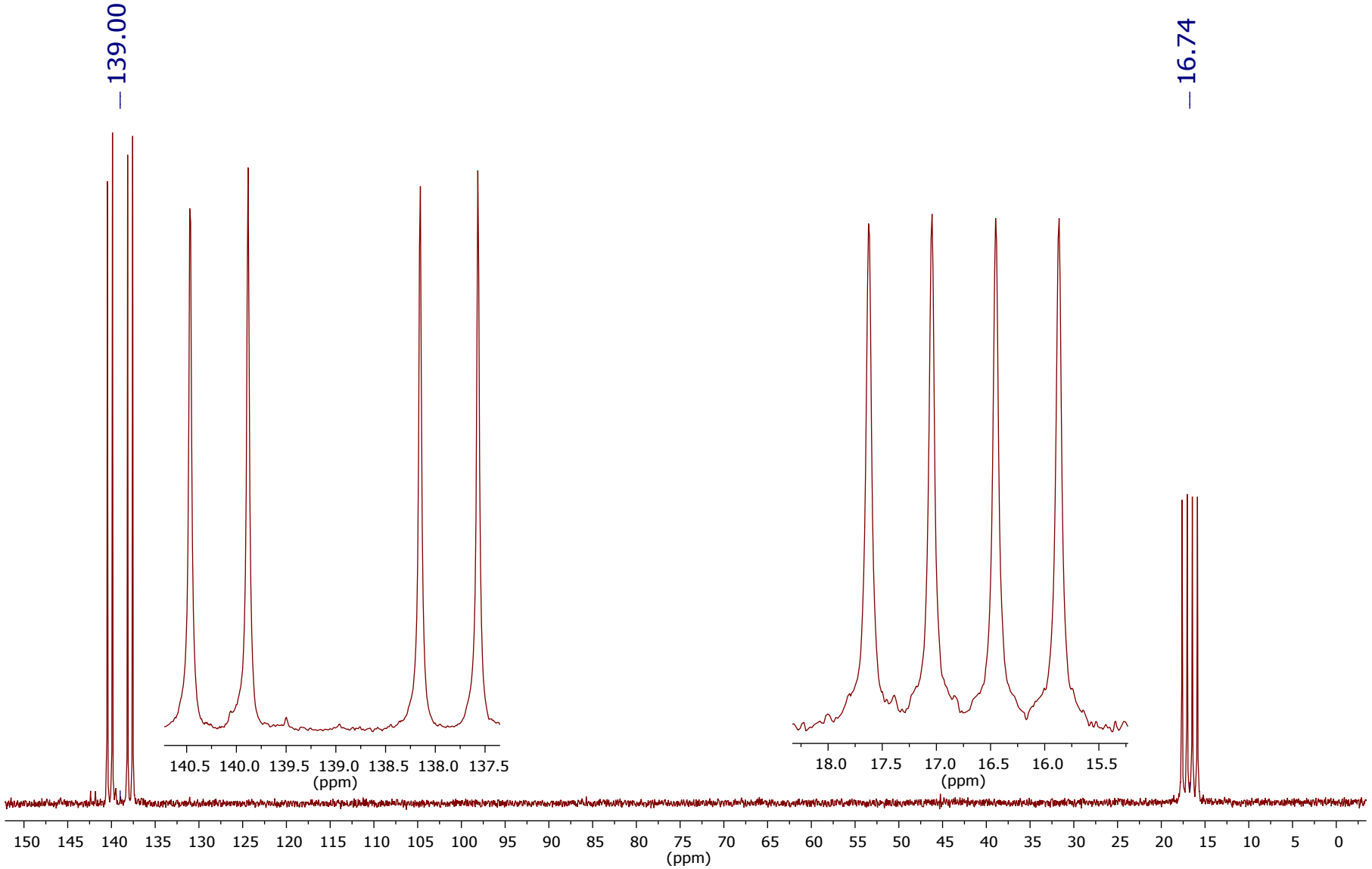


Figure S22. 1H NMR (CD2Cl2, 500 MHz) spectrum of [Rh(1f)(NBD)]BF4

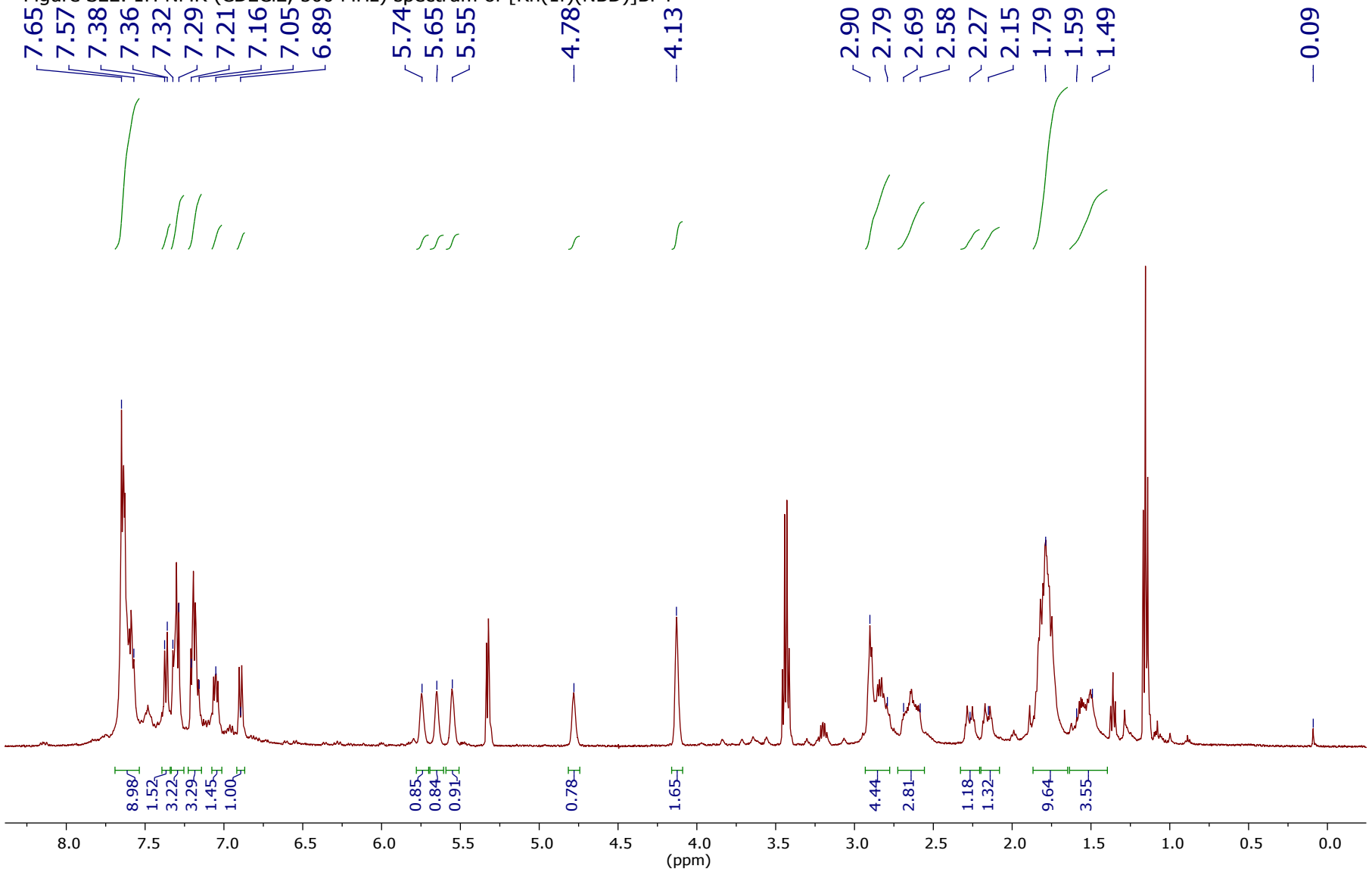


Figure S23. 13C{1H} NMR (CD2Cl2, 101 MHz) spectrum of [Rh(1f)(NBD)]BF4

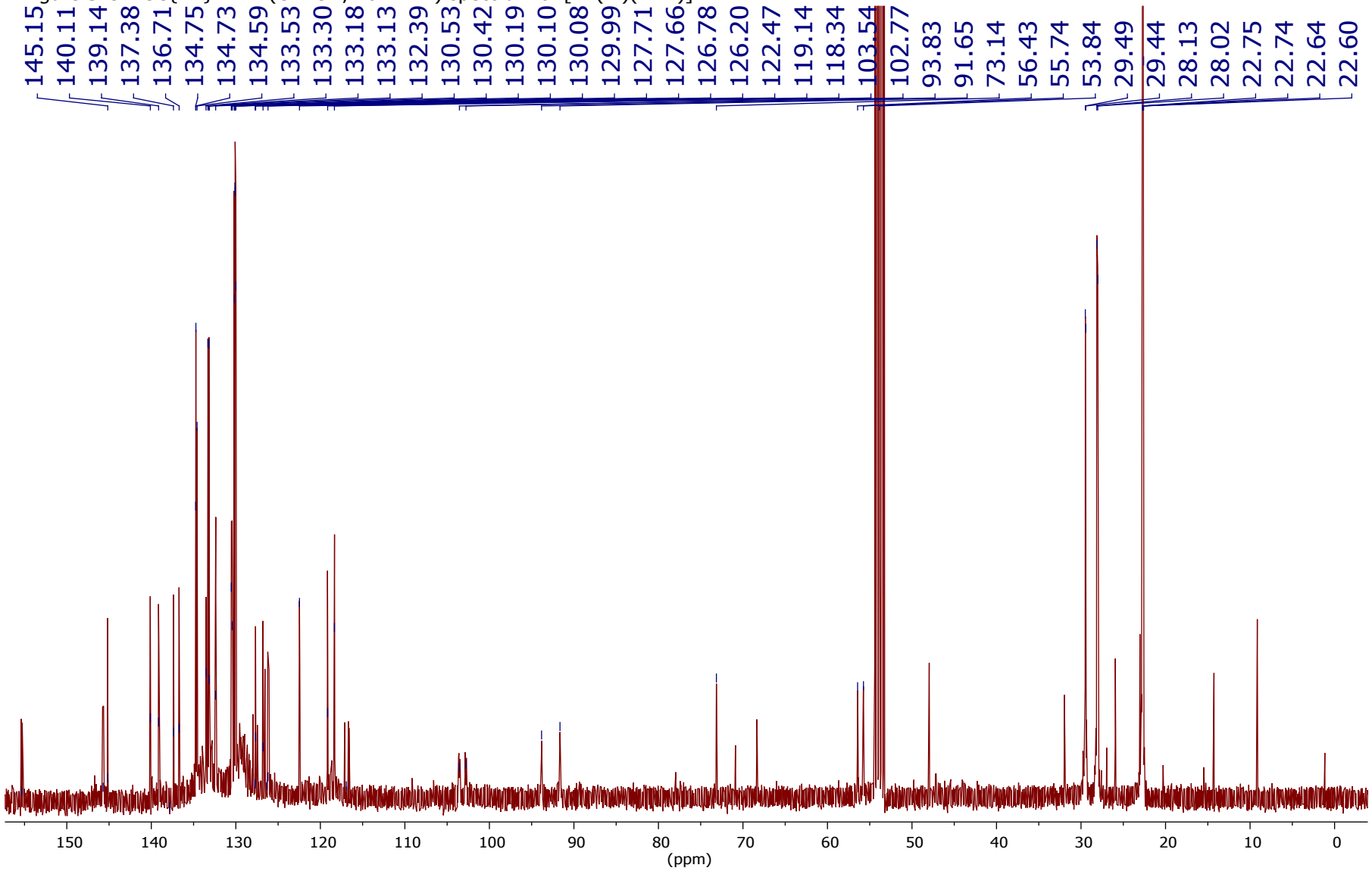


Figure S24. 31P{1H} NMR (CD2Cl2, 400 MHz) spectrum of [Rh(1f)(NBD)]BF4

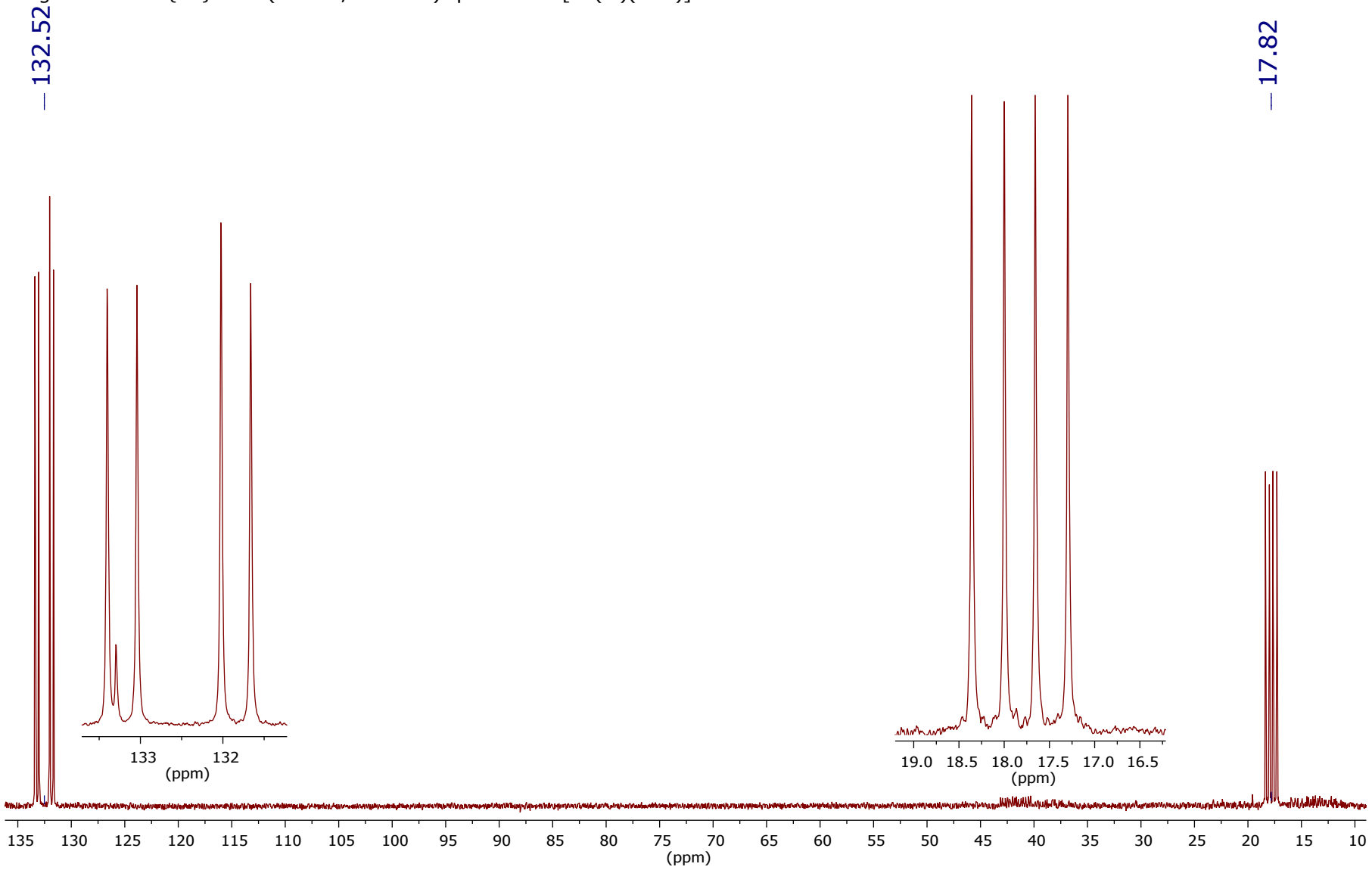


Figure S25. Gel-phase $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, CD_3OD) of complex **3g**

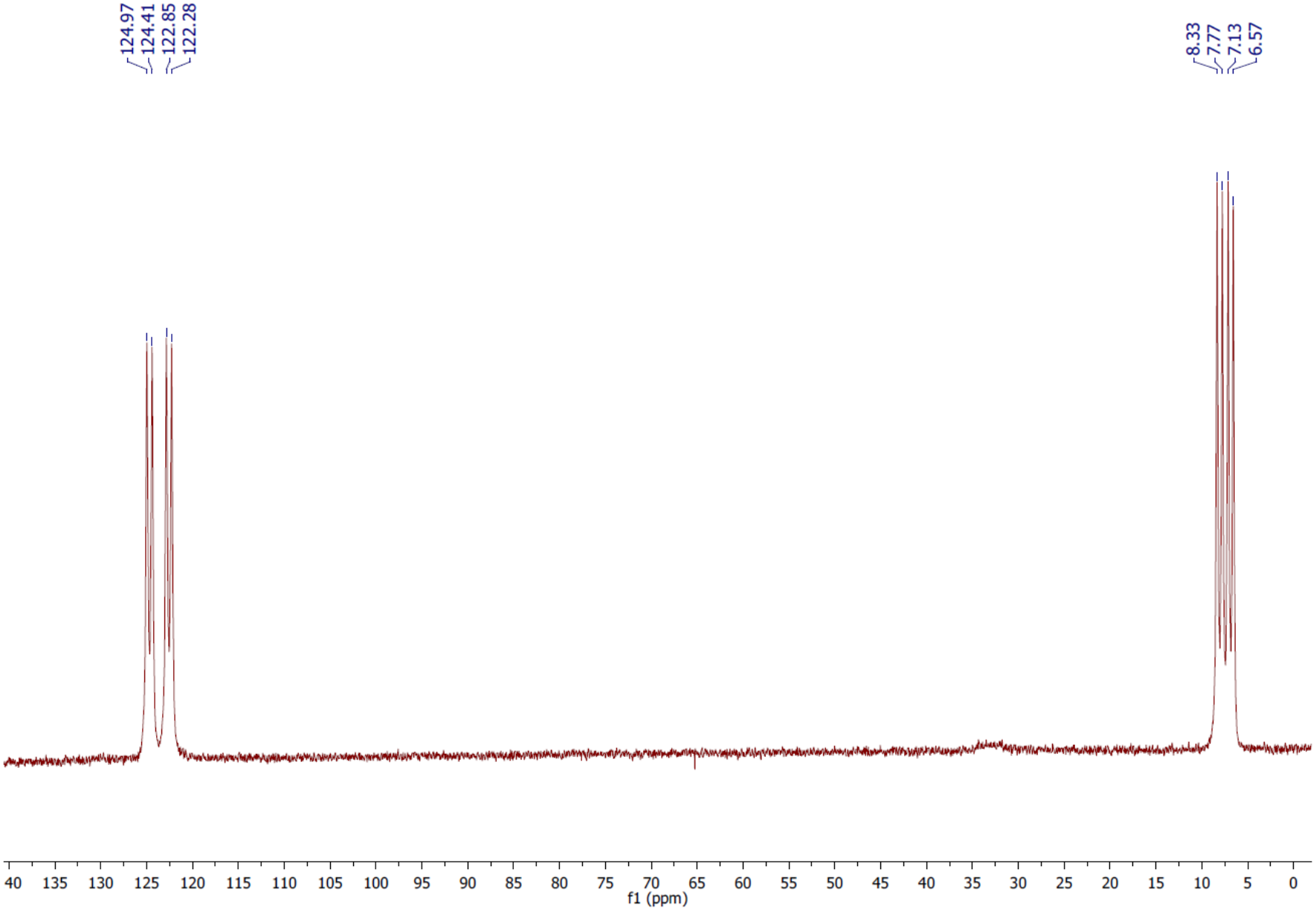


Figure S26. Gel-phase $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, CD_3OD) of complex **3g** pressurized under 4 bar H_2.

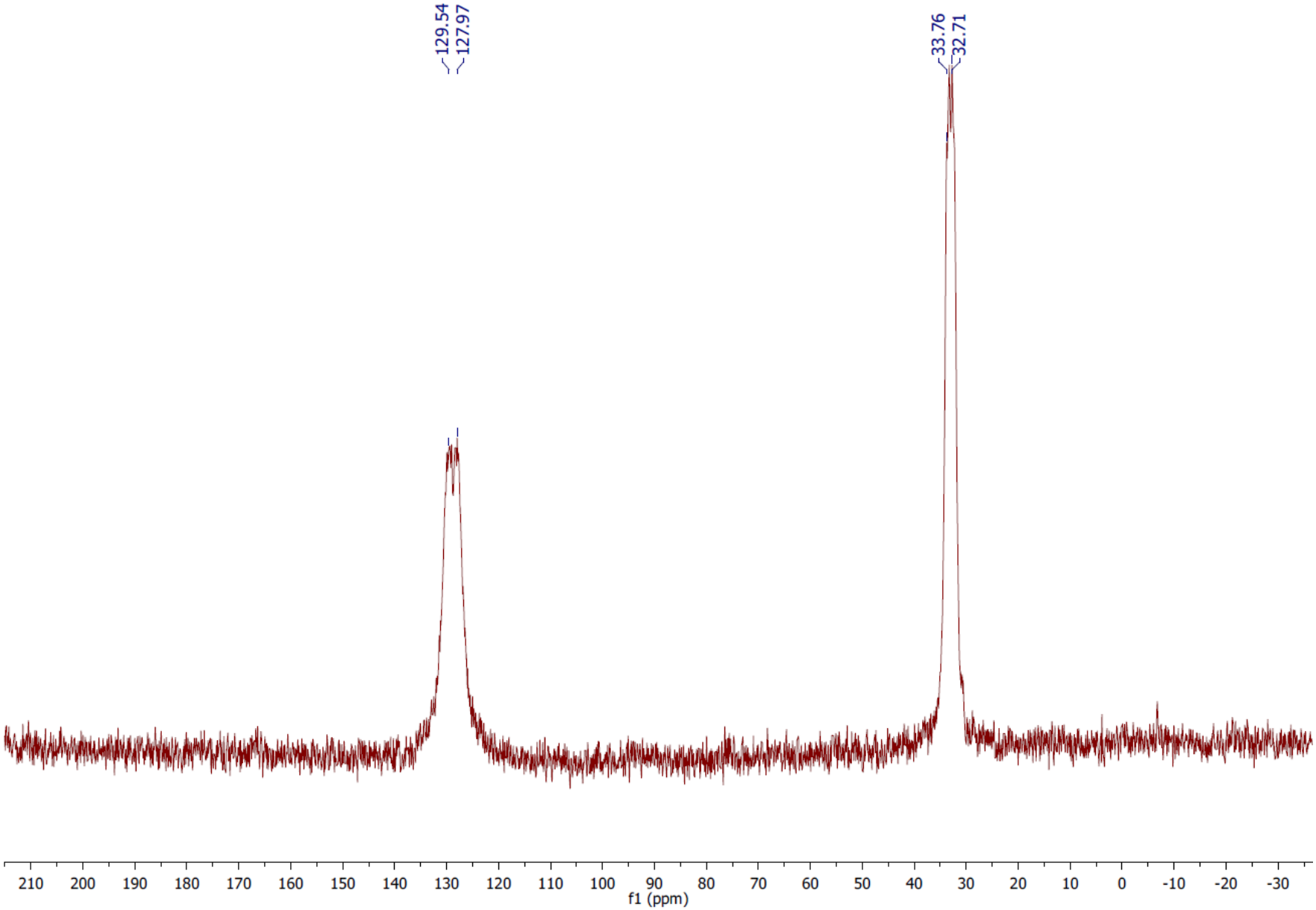


Figure S27. Gel-phase $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, CD_3OD) of complex **3g** after pressurizing with 4 bar H_2 and addition of 12 equiv. of **4b**

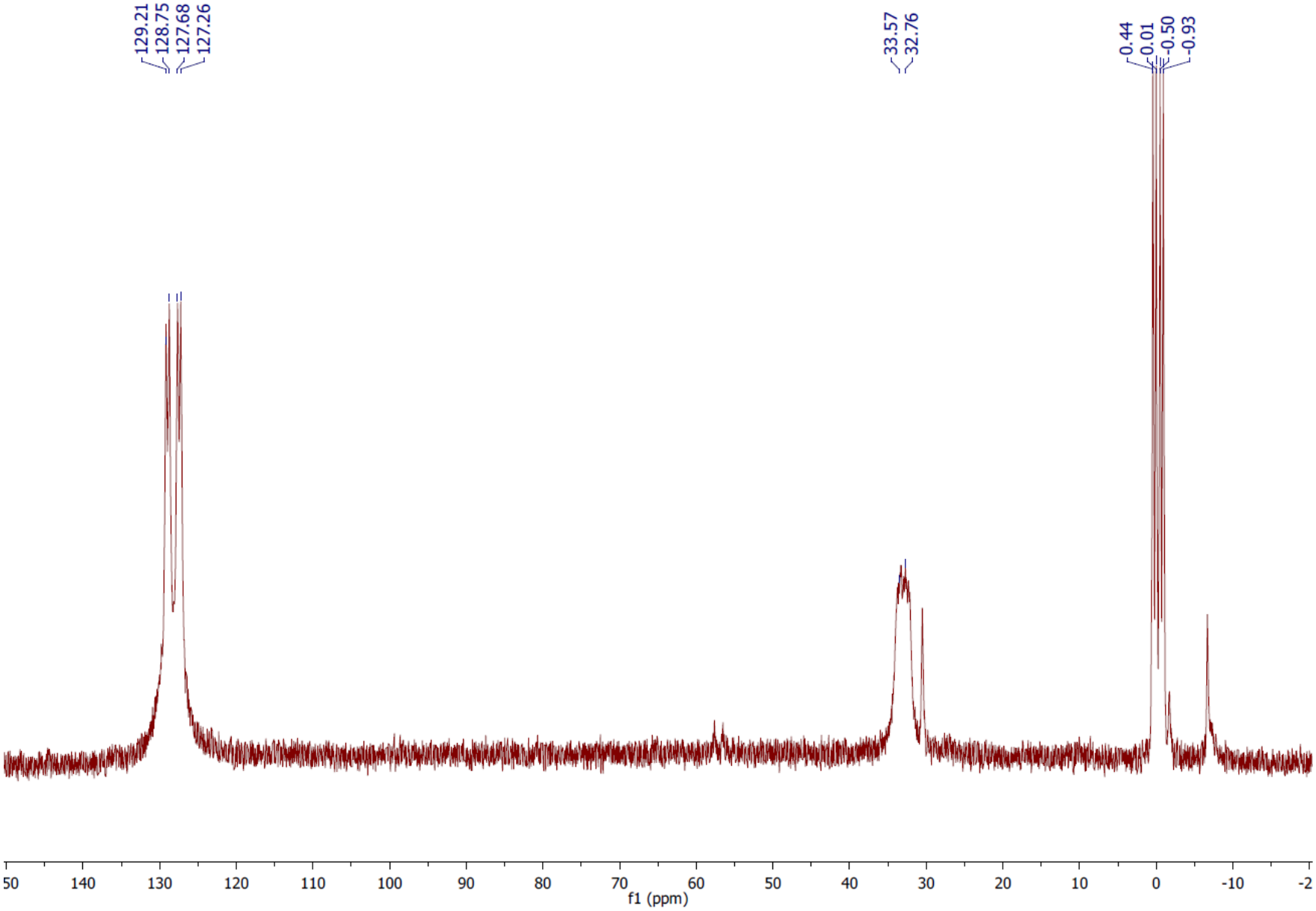
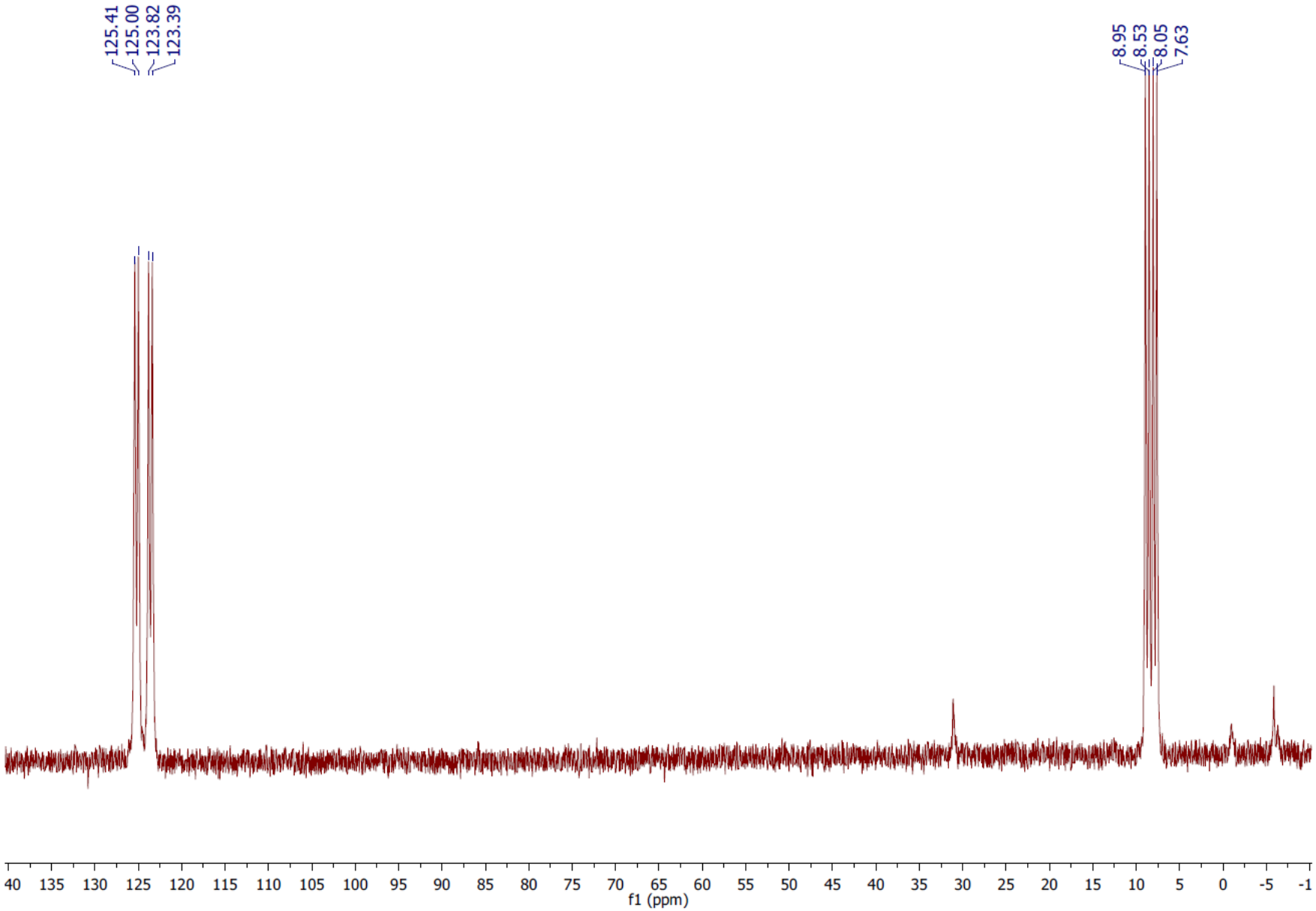
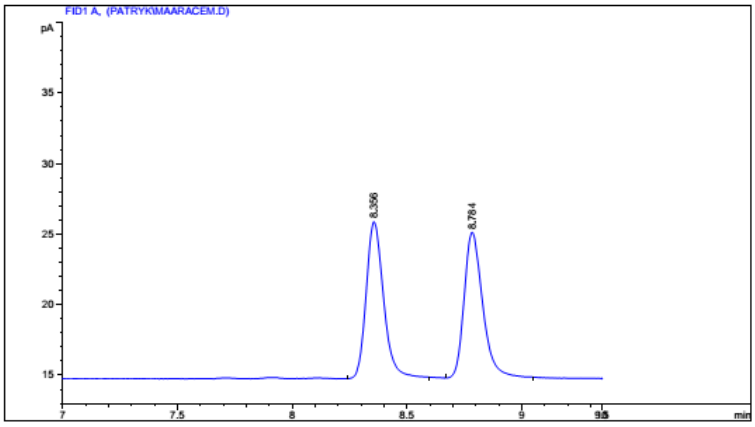


Figure S29. Gel-phase $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, CD_3OD) of complex **3g** regenerated after addition of NBD (12 equiv)



Enantiomeric excess determination of methyl 2-acetamidopropanoate **(5a)**

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 Results obtained with standard integrator!
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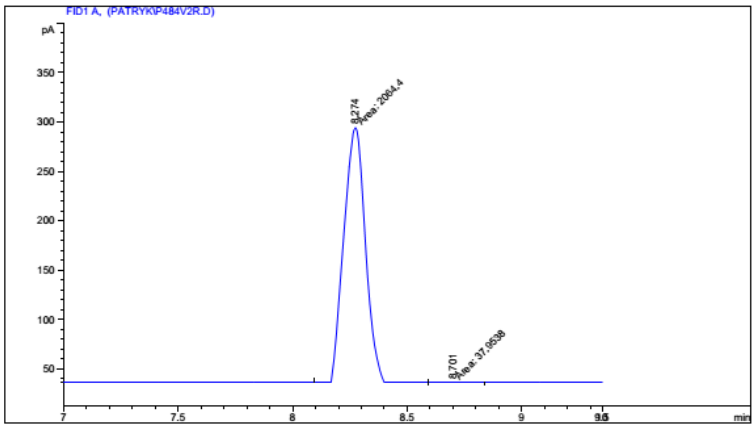
(*rac*)- (**5a**)

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 Results obtained with standard integrator!
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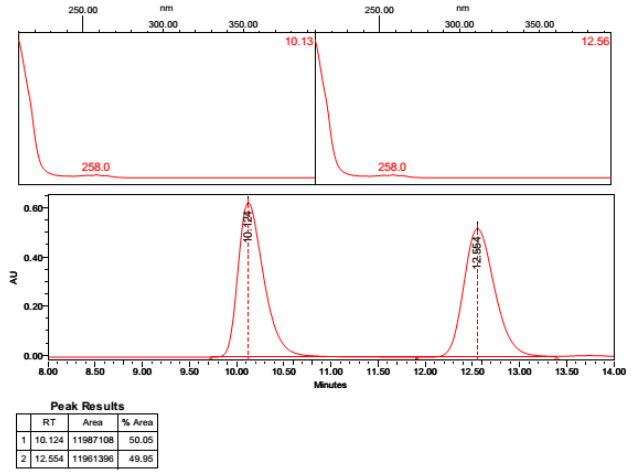
(*R*)- (**5a**)

Enantiomeric excess determination of methyl 2-acetamido-3-phenylpropanoate (**5b**)



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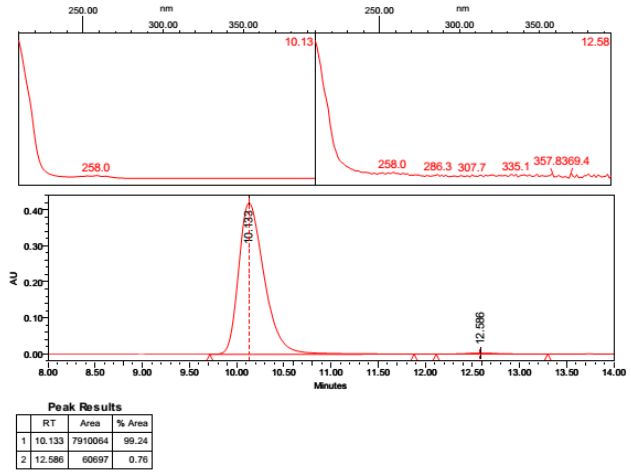
(*rac*)- (**5b**)



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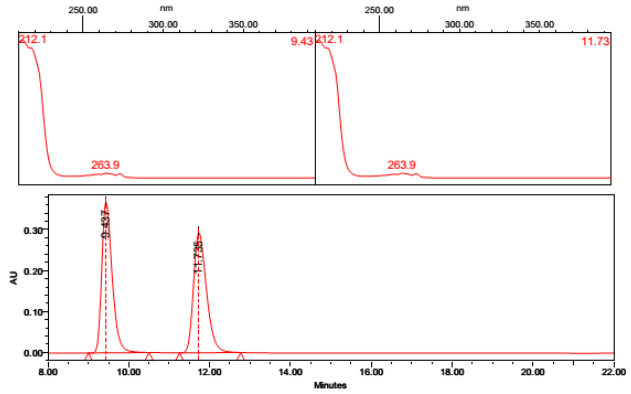
(*R*)- (**5b**)

Enantiomeric excess determination of methyl 2-acetamido-3-(4-methylphenyl)propanoate (**5c**)



Peak Results

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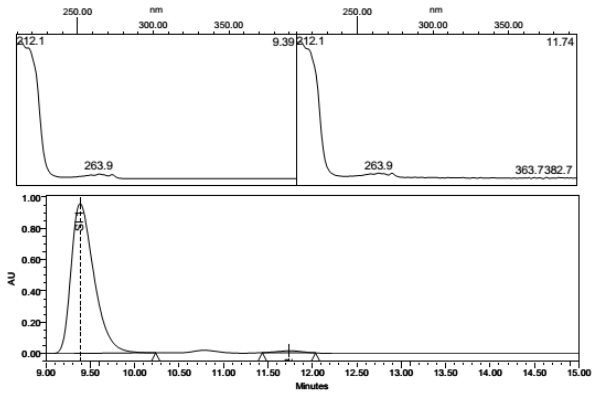
(*rac*)- (**5c**)



Peak Results

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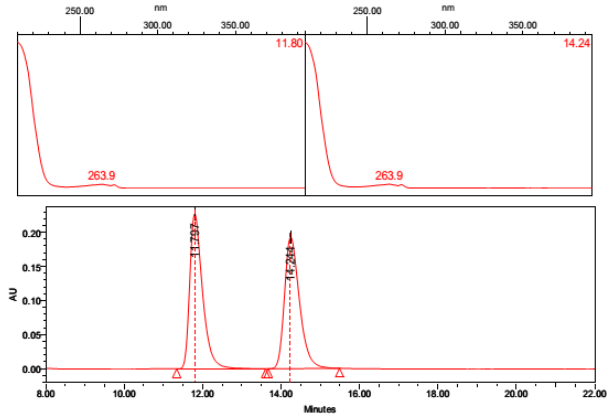
(*R*)- (**5c**)

Enantiomeric excess determination of methyl 2-acetamido-3-(3-methylphenyl)propanoate (**5d**)



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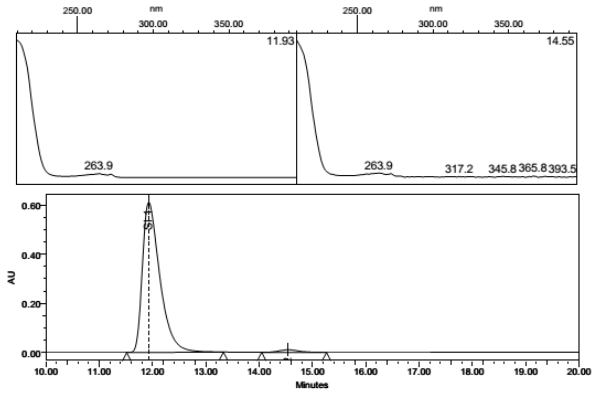
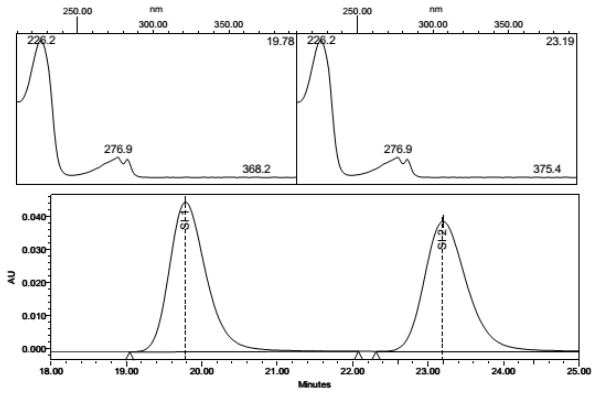


Peak Results

	Name	RT	% Area	Area	Height
1		11.930	98.02	13900328	610279
2		14.543	1.98	280604	10665

(*R*)- (**5d**)

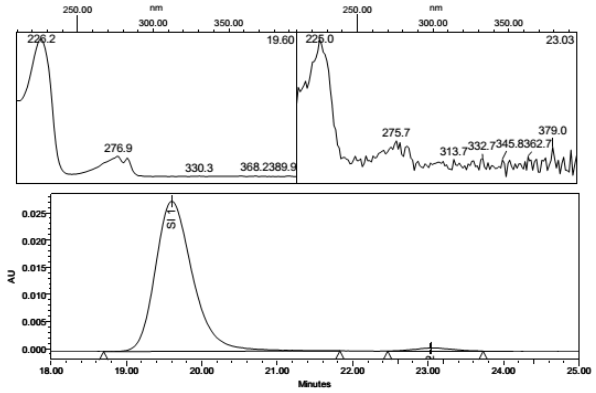
Enantiomeric excess determination of methyl 2-acetamido-3-(4-methoxyphenyl)propanoate (**5e**)



Peak Results

	Name	RT	% Area	Area	Height
1		19.782	50.00	1560861	45550
2		23.197	50.00	1560734	39550

(*rac*)- (**5e**)

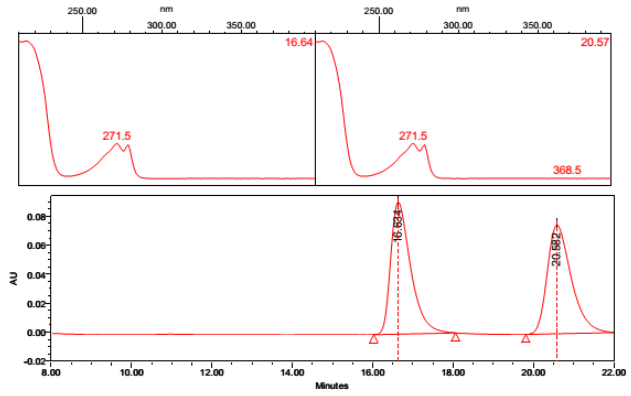


Peak Results

	Name	RT	% Area	Area	Height
1		19.600	97.79	947711	27630
2		23.036	2.21	21453	596

(*R*)- (**5e**)

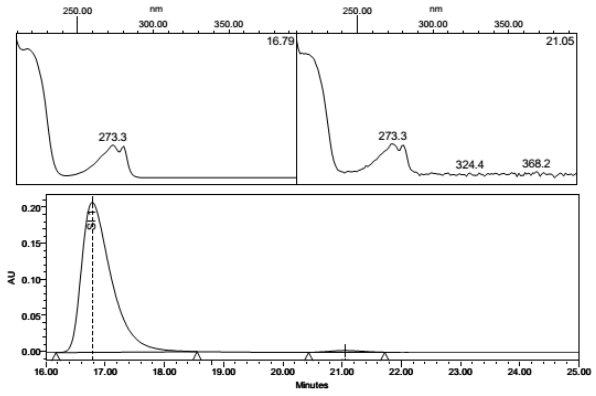
Enantiomeric excess determination of methyl 2-acetamido-3-(3-methoxyphenyl)propanoate (**5f**)



Peak Results

	RT	Area	% Area
1	16.634	3141637	50.20
2	20.582	3116017	49.80

(*rac*)- (**5f**)

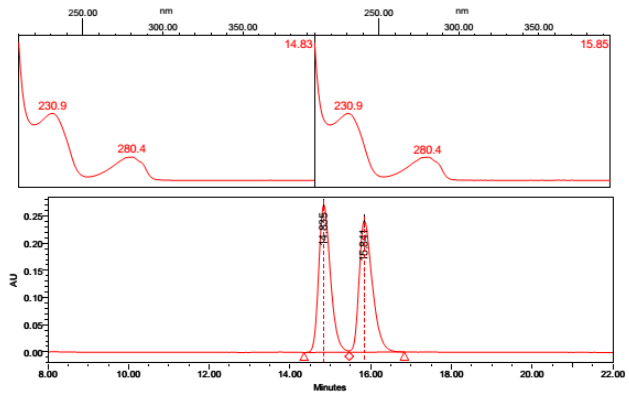


Peak Results

	Name	RT	% Area	Area	Height
1		16.783	98.68	7243462	208059
2		21.053	1.32	96666	2564

(*R*)- (**5f**)

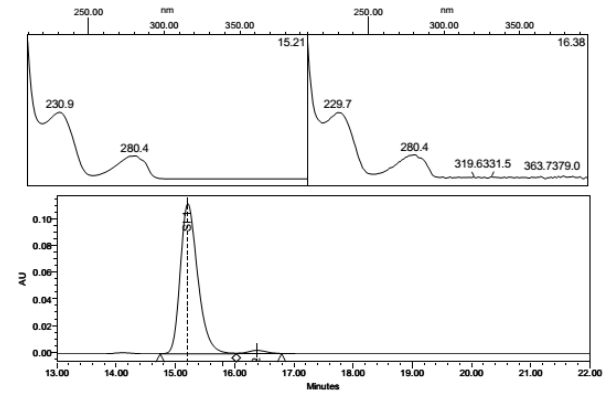
Enantiomeric excess determination of methyl 2-acetamido-3-(3,4-dimethoxyphenyl)propanoate (**5g**)



Peak Results

	RT	Area	% Area
1	14.835	5459450	49.88
2	15.841	5485972	50.12

(*rac*)- (**5g**)

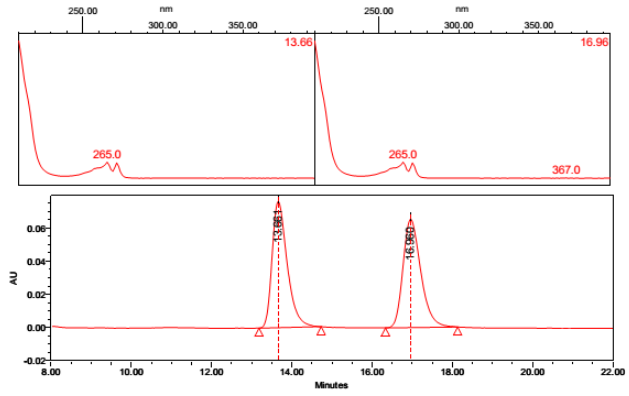


Peak Results

	Name	RT	% Area	Area	Height
1		15.210	97.78	2303080	112621
2		16.376	2.22	52360	2410

(*R*)- (**5g**)

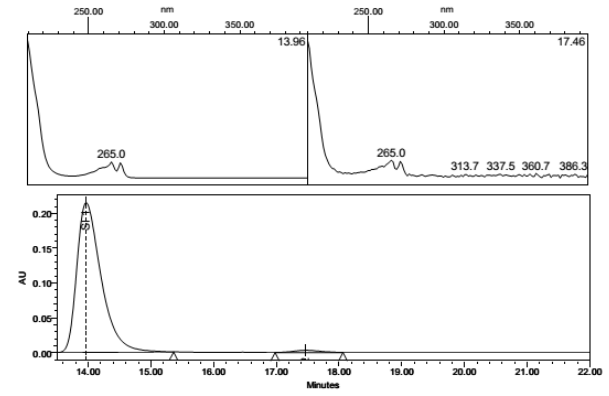
Enantiomeric excess determination of methyl 2-acetamido-3-(4-fluorophenyl)propanoate (**5h**)



Peak Results

	RT	Area	% Area
1	13.661	1991160	49.71
2	16.960	2014526	50.29

(*rac*)- (**5h**)

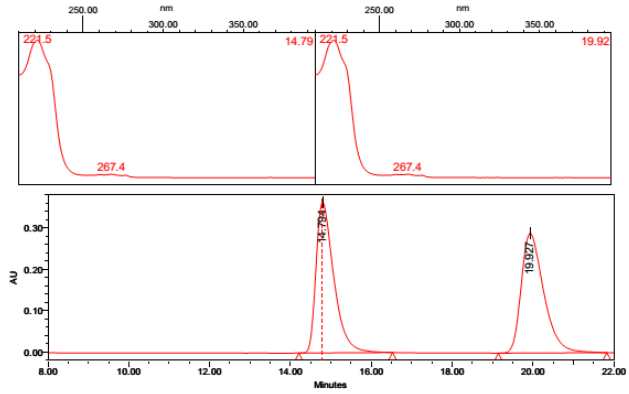


Peak Results

	Name	RT	% Area	Area	Height
1		13.966	98.38	5790447	215338
2		17.470	1.62	95623	3209

(*R*)- (**5h**)

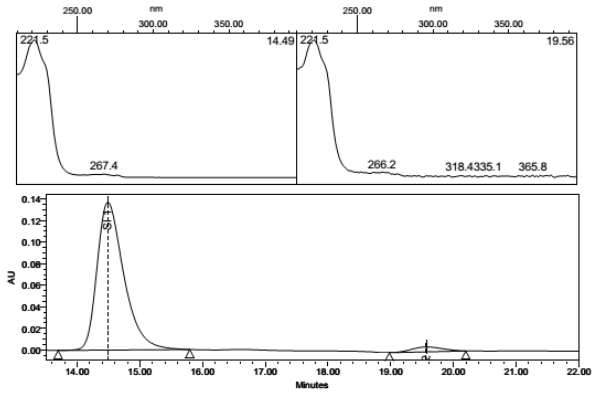
Enantiomeric excess determination of methyl 2-acetamido-3-(4-bromophenyl)propanoate (**5i**)



Peak Results

	RT	Area	% Area
1	14.794	11131941	49.92
2	19.927	11165836	50.08

(*rac*)- (**5i**)

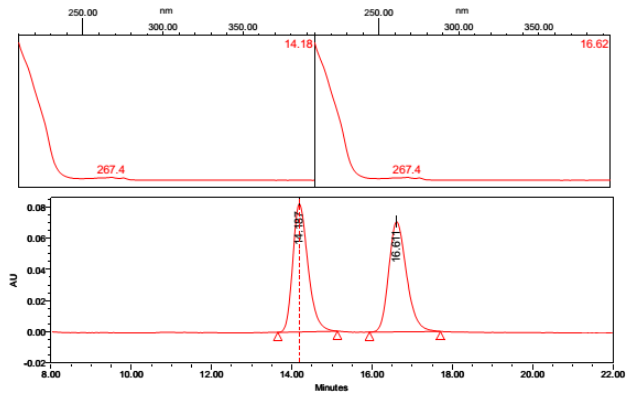


Peak Results

	Name	RT	% Area	Area	Height
1		14.488	96.31	4073963	137287
2		19.572	3.69	155884	4536

(*R*)- (**5i**)

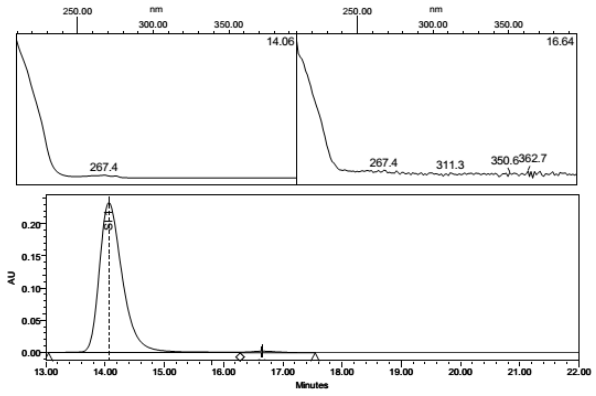
Enantiomeric excess determination of methyl 2-acetamido-3-(3-bromophenyl)propanoate (**5j**)



Peak Results

	RT	Area	% Area
1	14.187	2162404	49.81
2	16.611	2178958	50.19

(*rac*)- (**5j**)



Peak Results

	Name	RT	% Area	Area	Height
1		14.063	98.67	6382238	233463
2		16.652	1.33	85788	2516

(*R*)- (**5j**)