Rhodacarborane complexes with a triphenylphosphonium substituent as efficient catalysts for on-water transfer hydrogenation of carbonyl compounds

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SUPPORTING INFORMATION

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Experimental Section

General Considerations

Unless otherwise stated, all reactions were carried out under an argon atmosphere (if not considered separately) using standard Schlenk techniques with subsequent work-up in air. All solvents were purified and degassed by standard procedures. Starting materials 1,2-$(Bn)_2$-1,2-$C_2B_{10}H_{10}$,[1] $(PPh_3)_2NiCl_2$[2] and $[(cod)RhCl]_2$[3] were prepared as described in the literature. NMR spectra were obtained using Bruker Avance 300, Avance 400, Avance IIIHD 500 and Avance II 600 NMR spectrometers. Chemical shifts (δ) are given in ppm relative to solvent residual signals for $CDCl_3$ (^{1}H: δ = 7.27 ppm; $^{13}C\{^1H\}$: δ = 77.16 ppm), acetone-d_6 (^{1}H: δ = 2.05 ppm), DMSO-d_6 (^{1}H: δ = 2.50 ppm; $^{13}C\{^1H\}$: δ = 39.52 ppm), CH_3OH (^{1}H: δ = 3.31 ppm; $^{13}C\{^1H\}$: δ = 49.00 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; multiplet, br, broad. High-resolution mass spectra were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in positive ion mode; samples were dissolved in acetonitrile and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage 4.0 kV; mass scanning range: m/z 150–2000; external calibration with solution NaI in $MeOH/H_2O$; drying and heating gases (nitrogen) (each 10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: 250 C; flow rate 100% acetonitrile 0.4 mL/min. Molecular ions in the spectra were analyzed and matched with the appropriately calculated *m*/*z* and isotopic profiles in the LabSolutions v.5.114 program.

[7,8-(Bn)$_2$-7,8-nido-$C_2B_9H_{10}$]Tl (1) and [7,8-(Bn)$_2$-7,8-nido-$C_2B_9H_9$]Tl_2 (2):

A mixture of 1,2-$(Bn)_2$-1,2-$C_2B_{10}H_{10}$ (830 mg, 2.56 mmol) and KOH (800 mg, 14.3 mmol) in ethanol (15 ml) was refluxed for 16 hours, after which the solvent was removed *in vacuo.* The residue was dissolved in degased water (30 ml). Half of the solution was neutralized to pH~7 by the addition of acetic acid. Following the addition of a solution of $TlNO_3$ (350 mg, 1.32 mmol) in water (10 ml), [7,8-$(Bn)_2$-7,8-*nido*-$C_2B_9H_{10}$]Tl precipitated as a white solid. The colorless precipitate, was filtered, washed with water and dried over P_2O_5 *in vacuo.*

To the remaining half of alkaline carborane solution, a solution of $TlNO_3$ (800 mg, 3.00 mmol) in water (20 ml) was added. The mixture was heated at 60 °C for 3 hours. The yellow precipitate of **2** was filtered off, washed with water, acetone and dried over P_2O_5 *in vacuo.*

1: yield 628 mg (95%). ^{1}H NMR (400 MHz, acetone-d_6) *δ*: 7.21−7.15 (m, 8H, C_6H_5), 7.08−7.05 (m, 2H, C_6H_5), 3.14 (d, J = 15.5 Hz, 2H, CH_2), 3.01 (d, J = 15.5 Hz, 2H, CH_2), −2.43 (br, 1H, BHB). $^{11}B\{^1H\}$ NMR (128 MHz, acetone-d_6) *δ*: −9.2 (2B), −10.6 (1B), −17.3 (2B), −18.4 (2B), −33.7 (1B), −36.4 (1B). Anal. Calcd for $C_{16}H_{24}B_9Tl$: C, 37.10; H, 4.67%. Found: C, 37.64; H, 4.86%.

2: yield 600 mg (65%). Insoluble in organic solvents. Although the containment of carbon in the sample was less than theoretical it was used in the next step as is. Anal. Calcd for $C_{16}H_{23}B_9Tl_2$: C, 26.64; H, 3.21%. Found: C, 24.87; H, 3.08%.

9-PPh$_3$-7,8-(Bn)$_2$-7,8-nido-C$_2$B$_9$H$_9$ (3):

To a stirred solution of **1** (156 mg, 301 μmol) and PPh_3 (158 mg, 602 μmol) in acetone (5 ml), $[NH_4]_2[Ce(NO_3)_6]$ (330 mg, 602 μmol) was added in one portion. After stirring for 1 hour at RT, the insoluble material was filtered off, washed with acetone and solvent was removed *in vacuo.* The residue was chromatographed on SiO_2 using a CH_2Cl_2 − petroleum ether (1:1) mixture as the eluent. After solvent removal *in vacuo,* and the product was crystallized from a CH_2Cl_2 – EtOH mixture. The yield was 43 mg (25%).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70−7.66 (m, 6H, C_6H_5), 7.62−7.59 (m, 3H, C_6H_5), 7.51− 7.48 (m, 8H, C_6H_5), 7.42− 7.39 (m, 2H, C_6H_5), 7.32− 7.29 (m, 1H, C_6H_5), 7.04− 7.00 (m, 3H, C_6H_5), 6.61−6.69 (m, 1H, C_6H_5), 3.41 (d, 1H, J = 16 Hz, CH_2), 3.25 (d, 1H, J = 15.5 Hz, CH_2), 2.86−2.80 (m, 2H, CH_2), −2.30 (br, 1H, BHB). ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$) δ: −3.8 (1B), −5.7 (1B), −11.6 (1B), −12.8 (d, $^1J_{BP}$ = 142 Hz, 1B), −14.258 (1B), −19.4 (1B), −23.6 (1B), −27.3 (1B), −34.3 (1B). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 141.15 (s), 140.65 (s), 134.58 (d, J = 9.2 Hz), 132.47 (d, J = 2.7 Hz), 129.58 (s), 129.39 (s), 129.16 (s), 129.07 (s), 128.30 (s), 127.77 (s), 126.21 (d, J = 2.5 Hz), 125.21 (d, J = 69.7 Hz, CP), 61.98 (br s, C-cage), 41.11 (s, CH_2), 39.07 (d, J = 3.6 Hz, CH_2). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ: 7.11 (q, J = 146 Hz). Anal. Calcd for $C_{34}H_{38}B_9P$: C, 71.03; H, 6.66%. Found: C, 70.63; H, 6.79%.

10-PPh$_3$-7,8-(Bn)$_2$-7,8-nido-C$_2$B$_9$H$_9$ (4):

A mixture of 2 (117 mg, 162 μmol) and $(PPh_3)_2NiCl_2$ (106 mg, 162 μmol) in 1,2-dichloroethane (3 ml) was heated at 80 °C for 1 hour. Acetic acid was then added and reaction mixture heated for an additional hour at the same temperature. After cooling to RT and filtering, the solvent was removed *in vacuo.* The residue was then chromatographed on SiO_2 using a mixture of CH_2Cl_2 − petroleum ether (1:1) as the eluent. After solvent removal *in vacuo,* the product was crystallized from a CH_2Cl_2 – EtOH mixture. The yield was 24 mg (26%).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67−7.60 (m, 9H, C_6H_5), 7.54−7.52 (m, 6H, C_6H_5), 7.24−7.18 (m, 10H, C_6H_5), 3.36 (d, 2H, J = 15.5 Hz, CH_2), 3.21 (d, 2H, J = 15.5 Hz, CH_2), −1.34 (br, 1H, BHB). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ: −7.9 (1B), −10.0 (2B), −15.5 (4B), −33.1 (d, J = 145 Hz, 1B), −35.4 (1B). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 141.54 (s), 134.28 (d, J = 9.5 Hz), 132.78 (d, J = 2.7 Hz), 129.63 (s), 129.25 (d, J = 11.6 Hz) , 127.93(s), 125.85 (s), 124.15 (d, J = 71.4 Hz, CP), 66.65 (s, C-cage), 53.58 (s, C-cage), 41.49 (s). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ: 6.31 (q, J = 163 Hz). Anal. Calcd for $C_{34}H_{38}B_9P$: C, 71.03; H, 6.66%. Found: C, 70.58; H, 6.75%.

Synthesis of cyclooctadiene rhodium complexes

A solution of carborane **3** or **4** (71 mg, 123 μmol) in THF (5 ml) was carefully added to sodium hydride (caution: hydrogen evoluation) and heated at 60 °C for 2 hours. The clear solution was decantated from the exess of NaH and added to $[(cod)RhCl]_2$ (31 mg, 61.7 μmol). After stirring the reaction mixture at 60 °C for 2 hours, the solution was evaporated *in vacuo* to drines. The residue was chromatographed on SiO_2 using a mixture of ethyl acetate and petroleum ether (1:3) as the eluent. The product was obtained as the yellow solids by crystallization from a CH_2Cl_2 − petroleum ether mixture.

1,8-Bn$_2$-2,2-(cod)-7-PPh$_3$-2,1,8-closo-RhC$_2$B$_9$H$_8$ (5): yield 57 mg (59%). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.65 (br, 2H, C_6H_5), 7.89 (br, 2H, C_6H_5), 7.80−7.58 (m, 6H, C_6H_5), 7.55−7.33 (m, 5H, C_6H_5), 7.24−7.10 (m, 8H, C_6H_5), 6.62−6.60 (m, 2H, o-$C_6H_5CH_2$), 4.79 (br, H, cod CH), 4.74 (br, H, cod CH), 4.39 (br, H, cod CH), 3.85 (br, H, cod CH), 3.82 (d, 1H, J = 14.1 Hz, CH_2Ph), 3.72 (d, 1H, J = 14.1 Hz, CH_2Ph), 3.00 (d, 1H, J = 13.4 Hz, CH_2Ph), 2.71 (d, 1H, J = 13.4 Hz, CH_2Ph), 2.46 (br, 1H, cod CH_2), 2.32 (br, 1H, cod CH_2), 2.20−2.03 (m, 4H, cod CH_2), 1.79 (br, 1H, cod CH_2), 1.47 (br, 1H, cod CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ: −4.8 (br), −11.4 (br), −16.5 (br), −19.7 (br). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 140.80 (s, $CH_2C_6H_5$), 138.7 (s, $CH_2C_6H_5$), 136.31 (d, J = 8.6 Hz), 134.73 (s), 134.65 (br), 133.28 (d, J = 2.0 Hz, PPh_3), 132.70 (d, J = 1.9 Hz, PPh_3), 131.62 (d, J = 1.8 Hz, PPh_3), 130.32 (s, $CH_2C_6H_5$), 129.64 (s, $CH_2C_6H_5$), 129.47 (d, J = 10.8 Hz, PPh_3), 128.59 (d, J = 10.5 Hz, PPh_3), 128.27 (d, J = 11.3 Hz, PPh_3), 127.85 (s), 127.66 (d, J = 56.7 Hz, PPh_3), 127.61 (s), 126.60 (s), 125.87 (s), 125.05 (d, J = 75.7 Hz, PPh_3), 123.88 (d, J = 65.1 Hz, PPh_3), 83.95 (d, J = 9.0 Hz, cod CH), 82.24 (d, J = 10.8 Hz, cod CH), 81.29 (d, J = 8.8 Hz, cod CH), 79.52−79.42 (m, cod CH), 64.65 (br, cage C), 50.24 (s, cage C), 47.40 (s, CH_2Ph), 43.43 (d, J = 6.5 Hz, CH_2Ph), 32.48 (s, cod CH_2), 32.22 (s, cod CH_2), 31.31 (s, cod CH_2), 30.97 (s, cod CH_2). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ: 1.1 ÷ −2.1 (m). Anal. Calcd for $C_{42}H_{49}B_9PRh$: C, 64.26; H, 6.29%. Found: C, 64.25; H, 6.34%.

1,2-Bn$_2$-3,3-(cod)-8-PPh$_3$-3,1,2-closo-RhC$_2$B$_9$H$_8$ (6): yield 87 mg (90%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88−7.72 (m, 6H, C_6H_5), 7.62−7.41 (m, 9H, C_6H_5), 7.31−7.15 (m, 10H, C_6H_5), 4.32 (d, 2H, J = 14.5 Hz, CH_2Ph), 4.17 (d, 2H, J = 14.5 Hz, CH_2Ph), 4.02 (s, 4H, cod CH), 1.871 (br, cod CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ: −5.3, −6.3, −11.8, −18.0. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 139.64 (s), 134.67 (d, J = 8.0 Hz, PPh_3), 131.75 (s), 130.94 (s), 128.43 (d, J = 10.7 Hz, PPh_3), 127.90 (s), 127.81 (br d, J = 65.2 Hz, PPh_3), 126.60 (s), 78.83 (d, J = 13.9 Hz, cod CH), 67.27 (s, C-cage), 44.978 (s, CH_2Ph), 31.58 (s, cod CH_2), 31.02 (s, cod CH_2). $^{31}P\{^1H\}$ NMR (162

MHz, $CDCl_3$) δ: 9.2−5.9 (m). Anal. Calcd for $C_{34}H_{38}B_9P$: C, 71.03; H, 6.66%. Found: C, 70.58; H, 6.75%. Anal. Calcd for $C_{42}H_{49}B_9PRh$: C, 64.26; H, 6.29%. Found: C, 64.19; H, 6.25%.

Thermal isomerization of 6 to 1,8-Bn$_2$-2,2-(cod)-11-PPh$_3$-2,1,8-closo-RhC$_2$B$_9$H$_8$ (7):

A solution of **6** (94 mg) in *o*-xylene (5 ml) was heated at 120 °C for 4 hours. The solvent was removed *in vacuo,* and the residue was chromatographed on SiO_2 using a mixture ethyl acetate – petroleum ether (1:6) as the eluent. The major mobile yellow band was collected, the solvent was removed *in vacuo* to give a solid, which was further crystallized from a CH_2Cl_2 – petroleum ether mixture. The yield was 66 mg (70%).

^1H NMR (400 MHz, $CDCl_3$) δ: 7.88−7.73 (m, 6H, C_6H_5), 7.61−7.44 (m, 9H, C_6H_5), 7.33−6.98 (m, 10H, C_6H_5), 4.73 (br, 1H, cod CH), 4.53 (br, 1H, cod CH), 4.09 (br, 1H, cod CH), 3.91 (d, 1H, *J* = 14.1 Hz, CH_2Ph), 3.69 (br, 1H, cod CH), 3.35 (d, 1H, *J* = 14.1 Hz, CH_2Ph), 2.95−2.87 (m, 2H, CH_2Ph), 2.50 (br, 2H, cod CH_2), 2.16 (br, 2H, cod CH_2), 2.05 (br, 1H, cod CH_2), 1.89 (br, 2H, cod CH_2), 1.57 (br, 1H, cod CH_2). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ: −4.69 (br), −7.50 (br), −11.59 (br), −13.99 (br), −14.86 (br), −16.88 (br), −20.98 (br). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 141.08 (s), 139.49 (s), 134.77 (d, *J* = 8.2 Hz, PPh_3), 131.94 (d, *J* = 2.0 Hz, PPh_3), 130.41 (s), 130.21 (s), 128.35 (d, *J* = 11.3 Hz, PPh_3), 127.64 (s), 127.54 (s), 126.89 (br d, *J* = 66.4 Hz, PPh_3), 126.24 (s), 125.97 (s), 87.96 (d, *J* = 8.3 Hz, cod CH), 83.57 (d, *J* = 7.8 Hz, cod CH), 79.04 (d, *J* = 12.0 Hz, cod CH), 78.25 (d, *J* = 12.0 Hz, cod CH), 63.78 (br, cage C), 52.18 (d, *J* = 5.3 Hz, cage C), 47.43 (s, CH_2Ph), 46.05 (s, CH_2Ph), 33.89 (s, cod CH_2), 33.14 (s, cod CH_2), 31.64 (s, cod CH_2), 29.23 (s, cod CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ: 6.31 (q, *J* = 148 Hz). Anal. Calcd for $C_{42}H_{49}B_9PRh$: C, 64.26; H, 6.29%. Found: C, 64.36; H, 6.31%.

Chloride complexes:

To a suspension of complex **5** or **7** (40 mg) in an AcOH/Ac_2O (1:3, 2 ml) mixture, hydrochloric acid was added dropwise (0.2 ml), and resulting orange mixture stirred at 100 °C for 1 hour. After cooling, the reaction mixture was diluted with water to a final volume of 10 ml. The product was filtered off, washed with water and dried. The complex chloride was then obtained as an orange solid after recrystallization from a chloroform – petroleum ether mixture and dried *in vacuo* at 100 °C.

8: yield 35 mg (92%). ^1H NMR (600 MHz, DMSO-d_6) δ: 8.37−8.34 (m, 1H, Ph), 8.23−8.19 (m, 3H, Ph), 7.77−7.72 (m, 2H, Ph), 7.69−7.66 (m, 5H, Ph), 7.52−7.47 (m, 2H, Ph), 7.42 (t, *J* = 6.5 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.25−7.19 (m, 3H), 7.17−7.15 (m, 4H), 7.11−7.09 (d, *J* = 7.0 Hz, 2H), 6.72−6.68 (m, 2H), 3.58 (d, *J* = 14.1 Hz, 1H, CH_2Ph), 3.28 (d, *J* = 13.8 Hz, 1H, CH_2Ph), 2.77 (d, *J* = 13.8 Hz, 1H, CH_2Ph). $^{11}B\{^1H\}$ NMR (192 MHz, DMSO-d_6) δ: 20.3 (br), 6.2 (br), −4.4 (br), −14.6

(br), −19.4 (br). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ: 141.45, 140.68, 139.60, 138.60, 138.47, 137.02, 134.24 (d, J_{CP} = 10.3 Hz), 133.53 (d, J_{CP} = 9.2 Hz), 133.23, 132.85, 132.47, 130.82 (d, J_{CP} = 12.3 Hz), 130.06, 129.61, 129.52, 129.44, 129.37, 128.09, 127.76, 127.09, 126.23, 125.18 (d, J_{CP} = 10.5 Hz), 124.90, 124.36, 122.38, 121.86, 57.37 (br, cage C), 46.60 (s, cage C), 43.11 (d, J_{CP} = 6.0 Hz, CH_2Ph), 41.82 (s, CH_2Ph). $^{31}P\{^1H\}$ NMR (202 MHz, DMSO-d_6) δ: 16.8−13.6 (q, $^1J_{BP}$ = 157.8 Hz). HRMS (ESI) *m/z*: calcd for $[C_{34}H_{36}B_9PRh]^+$ 676.2500, found 676.2496. Anal. Calcd for $C_{34}H_{37}B_9PCl_2Rh$: C, 54.61; H, 4.99 %. Found: C, 54.36; H, 5.31%.

9: yield 35 mg (87%). ^1H NMR (500 MHz, DMSO-d_6) δ: 7.75−7.64 (m, 9H, Ph), 7.58−7.51 (m, 6H, Ph), 7.38−7.31 (m, 3H, Ph), 7.27−7.24 (m, 2H, Ph), 7.21−7.18 (m, 1H, Ph), 7.11 (d, J = 7.0 Hz, 2H, Ph), 7.06 (d, J = 7.2 Hz, 2H, Ph), 3.60 (d, J = 15.0 Hz, 1H, CH_2Ph), 3.19 (d, J = 15.0 Hz, 1H, CH_2Ph), 3.27 (s, 2H, CH_2Ph). $^{11}B\{^1H\}$ NMR (160 MHz, DMSO-d_6) δ: −4.0 (br), −4.9 (br). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ: 138.48 (s), 137.50 (s), 134.91 (d, J_{CP} = 8.8 Hz), 132.45 (s), 130.41 (s), 129.91 (s), 128.59 (d, J_{CP} = 12.5 Hz), 128.16 (s), 127.87 (s), 127.23 (s), 126.62 (s), 123.82 (s, J_{CP} = 72.7 Hz, PPh_3), 69.34 (d, J_{CRh} = 14.7 Hz, cage C), 62.31 (s, cage C), 44.05 (s, CH_2Ph), 42.50 (s, CH_2Ph). $^{31}P\{^1H\}$ NMR (202 MHz, DMSO-d_6) δ: 8.97 (q, J_{PB} = 157.8 Hz). HRMS (ESI) *m/z*: calcd for $[C_{34}H_{36}B_9PRh]^+$ 676.2500, found 676.2499. Anal. Calcd for $C_{34}H_{37}B_9PCl_2Rh$: C, 54.61; H, 4.99 %. Found: C, 54.07; H, 5.25%.

(S)-proline complex 10*:*

A mixture of **8** (40 mg, 53.5 μmol), (*S*)-proline (7 mg, 60.8 μmol) and K_2CO_3 (18 mg, 130.4 μmol) in CH_3CN (3 ml) was stirred for 24 h. The solvent was removed from resulting yellow suspension *in vacuo* and the product was extracted with two 2 ml portions of 1,2-dichloroethane. The resulting solution was filtered, evaporated *in vacuo* to ~2 ml, vial with the solution was placed in the flask with Et_2O and allowed it stand at 6 °C for 24 hours. The yellow needles of **10** were filtered off, washed with Et_2O, and dried. The yield was 10 mg (47 %).

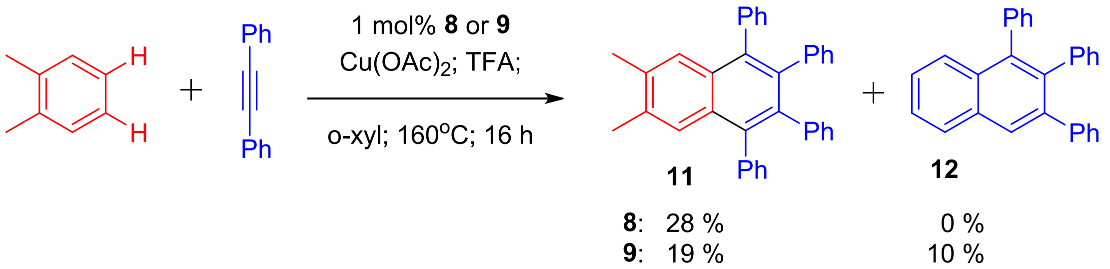
^1H NMR (600 MHz, CD_3OD) δ: 8.25−8.22 (m, 2H), 7.81−7.78 (m, 1H), 7.76−7.73 (m, 3H), 7.63−7.59 (m, 4H), 7.47−7.42 (m, 4H), 7.27−7.21 (m, 3H), 7.18−7.11 (m, 6H), 6.69 (d, J = 6.8 Hz, 2H), 4.04 (t, J = 8.3 Hz, 1H, CHC(O)O), 3.63 (d, J = 14.0 Hz, 1H), 3.62 (d, J = 13.6 Hz, 1H), 3.35 (d, J = 14.0 Hz, 1H), 2.921 (d, J = 13.6 Hz, 1H), 2.18−2.13 (m, 1H, proline CH), 2.04−1.97 (m, 1H, proline CH), 1.724−1.65 (m, 1H, proline CH), 1.64−57 (m, 1H, proline CH), 1.41−1.31 (m, 1H, proline CH), 1.28−1.21 (m, 1H, proline CH). $^{11}B\{^1H\}$ NMR (192 MHz, CD_3OD) δ: 8.0 (br), −2.2 (br), −5.0 (br), −6.4 (br), −7.3 (br), −14.5 (br), −20.8 (br). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ: 184.50 (s, C(O)O), 140.19, 138.56, 135.20, 135.16, 135.09, 134.92, 134.67, 134.21, 132.50 (d, J_{CP} = 11.2 Hz) , 131.67, 131.17 (d, J_{CP} = 11.2 Hz), 130.73, 130.52 (d, J_{CP} = 10.4 Hz), 129.15, 128.78, 128.31, 127.66, 126.48 (d, J_{CP} = 10.1 Hz), 126.06, 124.47, 124.04, 63.99 (s, cage C), 58.051 (br, cage C), 52.490 (s, proline), 46.13 (br, CH_2Ph), 45.44 (d, J_{CP} = 6.0 Hz, CH_2Ph), 43.85 (s, proline), 31.93 (s, proline C), 27.64 (s, proline). $^{31}P\{^1H\}$ NMR (202 MHz, DMSO-d_6) δ: 8.97 (q, J_{PB} = 165.8 Hz). Anal. Calcd for $C_{39}H_{44}B_9NO_2PRh$: C, 59.30; H, 5.61 %. Found: C, 59.21; H, 5.48%.

Preparation of enantiopure complex 8:*

To a stirred suspension of (*S*)-proline complex **10** (15 mg) in CH_3OH (1 ml) hydrochloric acid (20 µl) was added, and the mixture was stirred for 30 min. The reaction mixture was diluted with water to a final volume of 10 ml and the product was filtered off, washed with water and dried. The yield was 13 mg (92%). The NMR spectra of the product were identical to those of **8** prepared from cyclooctadiene complex **5**.

Catalytic investigations

Oxidative coupling of o-xylene with diphenylacetylene



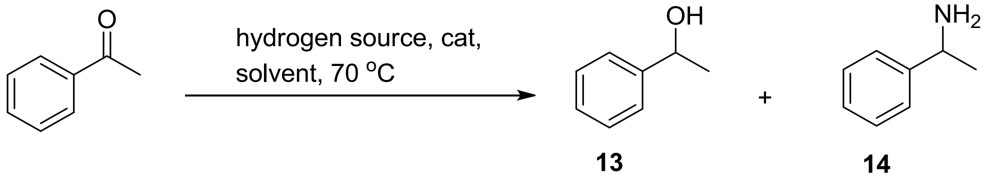
Complexes **8** or **9** (2 mol% based on rhodium) of, $Cu(OAc)_2 \cdot H_2O$ (110 mg, 0.58 mmol), diphenylacetylene (0.5 mmol) and of *o*-xylene (2 ml) were placed in a tube equipped with a stirbar, without inert atmosphere. TFA (34.2 mg, 0.3 mmol) was then added, and the reaction mixture was stirred at 160 °C for 16 h. After the reaction was cooled, the precipitate was centrifuged off. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (1 × 15 cm). The first colorless band, containing unreacted alkyne, was eluted with PE. The second band was eluted with a mixture of PE−CH_2Cl_2 (7:1) to give the target product.

For **8**: the yield of target target naphthalene is 32 mg (28%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 2H), 7.18 − 7.26 (m, 10H), 6.80 − 6.87 (m, 10H), 2.30 (s, 6H) (cf.[4])

For **9**: the yield of target naphthalene is 22 mg (19%); triphenylnaphtalene (9 mg, 10%) was isolated as a by-product. Eluent PE−CH_2Cl_2 (9:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.95 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.29 – 7.17 (m, 10H), 6.99 – 6.94 (m, 3H), 6.87 – 6.90 (m, 2H) (cf.[4]).

Data are in consistent with literature.

***General procedure for the optimization reactions*:**



A heavy-walled Schlenk tube with a Teflon plug valve and an internal volume of 12 ml was equipped with a magnetic stir bar, $HCOONH_4$, rhodium complex (1 mol% based on rhodium), and the tube was filled with argon. The solvent (0.4 ml) and acetophenone (37 μl, 316 μmol) were added to the mixture, and the Schlenk tube was closed. The reaction was heated with stirring fo the appropriate time in a silicone bath preheated to 70 °C (the silicone oil covered the entire volume of the reactor). After cooling the reaction mixture to RT, the solvent was removed *in vacuo.* The residue was extracted with CH_2Cl_2, and *p*-dinitrobenzene (11 mg, 101 μmol) was added to the extract as an internal standard and stirred until dissolved. The solvent was removed *in vacuo,* a the residue was dissolved in $CDCl_3$ for concentration measurement by ^{1}H NMR.

Optimized procedure:

A heavy walled Schlenk tube with a Teflon plug valve and internal volume of 12 ml was equipped with a magnetic stir bar, substrate (0.79 μmol), $HCOONH_4$ (100 mg, 1.59 mmol), complex **8** (1.2 mg, 0.2 mol%), and filled with argon. Water (100 μl) was added to the mixture and the Schlenk tube closed. The reaction mixture was heated with stirring for the appropriate time in a preheated silicone bath (the silicone oil covered the entire volume of the reactor). After cooling to RT, the reaction mixture was extracted 3 × 3 ml of Et_2O, extracts dried with Na_2SO_4 and solvent removed *in vacuo*. The residue was purified by column chromatography on SiO_2.

1-Phenylethanol (15a): yield 86 mg (90%). Eluent PE−AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39−7.380 (m, 4H, Ph), 7.340−7.29 (m, 1H, Ph), 4.895−4.847 (m, 1H, CH), 2.57 (br, 1H, OH) 1.50 (d, J = 6.5 Hz, 3H, CH_3) (cf.[5]). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25 %. Found: C, 78.25; H, 8.12%. HPLC: Chiralpak IA3 column, heptane/*i*-PrOH 99:1, 1.0 ml/min; tR(*R*-isomer) = 14.9 min, tR(*S*-isomer, major) = 15.7 min.[6]

1-(4-chlorophenyl)ethanol (15b)**:** yield 117 mg (95%). Eluent PE−AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34−7.24 (m, 4H, C_6H_4), 4.79 (q, J = 6.5 Hz, 1H, CH), 3.10 (br, 1H, OH) , 1.42 (d, J = 6.5 Hz, 3H, CH_3) (cf.[5]). Anal. Calcd for C_8H_9OCl: C, 61.35; H, 5.79%. Found: C, 61.19; H, 5.89%.

1-Phenyl-1-propanol (15c): yield 80 mg (75%). Reaction was preceded at 100 °C. Eluent PE−AcOEt (5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40−7.28 (m, 5H, Ph), 4.57 (t, J = 6.4 Hz, 1H, CH), 2.48 (br, 1H, OH), 1.88−1.68 (m, 2H, CH_2), 0.931 (t, *J* = 8.6 Hz, 3H, CH_3) (cf.[7]). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%. Found: C, 79.05; H, 8,56%.

1-indanol (15d): yield 91 mg (86%). Reaction was preceded at 100 °C. Eluent PE−AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.44−7.38 (m, 1H, C_6H_4), 7.33−7.25 (m, 3H, C_6H_4), 5.22 (t, J = 6.0 Hz, 1H, CH), 3.114−3.02 (m, 1H, CH_2), 2.88−2.78 (m, 2H, CH_2, OH), 2.53−2.42 (m, 1H, CH_2), 1.99−1.88 (m, 1H, CH_2) (cf.[5]). Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51 %. Found: C, 80.31; H, 7.38%.

1-(Pyridin-2-yl)ethanol (15e): yield 62 mg (64%). Reaction was preceded at 100 °C for 24 h in presence of 2 eqv. HCOOH. Eluent PE−AcOEt−^{i}PrOH (3:1:0.4). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.52 (d, J = 4.9 Hz, 1H, Py), 7.70 (t, J = 8.3 Hz, 1H, Py), 7.33 (d, J = 8.0 Hz, 1H, Py), 7.22−7.180, (m, 1H, Py), 4.92 (q, J = 6.6 Hz, 1H, CH), 4.43 (br, 1H, OH), 1.52 (d, J = 6.6 Hz, 3H, CH_3) (cf.[5]). Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37 %. N, 11.37. Found: C, 67.89; H, 7.15%.

4-Phenylbutan-2-ol (15f): yield 102 mg (86%). Eluent PE−AcOEt (4:1). ^{1}H NMR ($CDCl_3$) *δ*: 7.34−7.29 (m, 2H, Ph), 7.24−7.20 (m, 3H, Ph), 3.88−3.84 (m, 1H, CH), 2.83− 2.66 (m, 2H, CH_2), 1.84−1.77 (m, 2H, CH_2), 1.45 (br, 1H, OH), 1.26 (d, J = 6.2 Hz, 3H, CH_3) (cf.[5]). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39 %. Found: C, 79.59; H, 9.31%. HPLC: Chiralpak IB3 column, heptane/*i*-PrOH 90:10, 1.0 ml/min; tR(*S*-isomer, major) = 3.41 min, tR(*R*-isomer) = 3.94 min.

2-phenylpropan-1-ol (15g): yield 80 mg (75%). Eluent PE−AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H, Ph), 7.28−7.27 (m, 2H, Ph), 3.71 (d, J = 7.0 Hz, 2H, CH_2), 3.01−2.93 (m, 1H, CH), 1.74 (br, 1H, OH), 1.31 (d, J = 7.0 Hz, 3H, CH_3) (cf.[8]).Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%. Found: C, 79.10; H, 8.61%.

4-methylbenzyl alcohol (15h)**:** yield 75 mg (80%). Eluent PE−AcOEt (1:1). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.27 (d, J = 8.0 Hz, 2H, C_6H_4), 7.20 (d, J = 8.0 Hz, 2H, C_6H_4), 4.63 (s, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.34 (s, 1H, OH) (cf.[9]). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25 %. Found: C, 78.45; H, 8.12%.

4-methoxybenzyl alcohol (15i)**:** yield 89 mg (82%). Eluent PE−AcOEt (1:1). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.25 (d, J = 8.6 Hz, 2H, C_6H_4), 6.88 (d, J = 8.6 Hz, 2H, C_6H_4), 4.55 (s, 2H, CH_2), 3.80 (s, 3H, CH_3), 2.72 (s, 1H, OH) (cf.[7]). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30 %. Found: C, 69.38; H, 7.58%.

3-nitrobenzyl alcohol (15j)**:** yield 92 mg (77%). Eluent PE−AcOEt (2:1). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.16 (s, 1H, C_6H_4), 8.06 (d, J = 8.1 Hz, 1H, C_6H_4), 7.65 (d, J = 8.6 Hz, 1H, C_6H_4), 7.481 (t, J = 7.9 Hz, 1H, C_6H_4), 4.760 (s, 2H, CH_2), 3.276 (br, 1H, OH) (cf.[7]). Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61 %. Found: C, 55.26; H, 4.75%.

Data are in consistent with literature.

Catalytic oxidation of (±)-1-phenylethanol with acetone:

A heavy-walled Schlenk tube with a Teflon plug valve and internal volume of 12 ml was equipped with a magnetic stir bar, complex **8** (1.6 mg, 0.25 mol% based on rhodium), K_2CO_3 (10 mg, 72.4 μmol), and the tube was filled with argon. The acetone (1 ml) and (±)-1-phenylethanol (100 μl, 835 μmol) were added to the mixture and Schlenk tube closed. The reaction mixture was heated for 24 hours in a silicone bath preheated to 80 °C (the silicone oil covered the entire volume of the reactor). The solvent was removed *in vacuo,* and the residue dissolved in $CDCl_3$. Analysis by ^1H NMR spectroscopy indicated complete conversion of (±)-1-phenylethanol to acetophenone.

The isotopic exchange reaction of hydrogen to deuterium in complex 8:

A heavy walled Schlenk tube with a Teflon plug valve and internal volume of 12 ml was equipped with a magnetic stir bar, complex **8** (2.2 mg), K_2CO_3 (10 mg), and the tube was filled with argon. Acetone (0.25 ml) and either isopropanol-d_8 or isopropanol (0.25 ml) were added to the mixture and Schlenk tube was closed. The reaction was heated for 24 hours in a silicone bath preheated to 80 °C (the silicone oil covered the entire volume of the reactor). The resulting solution was decanted from precipitate, acidified with 10 μl of concentrated HCl and evaporated to dryness *in vacuo*. The residue was then analyzed by HRMS method.

NMR Spectra

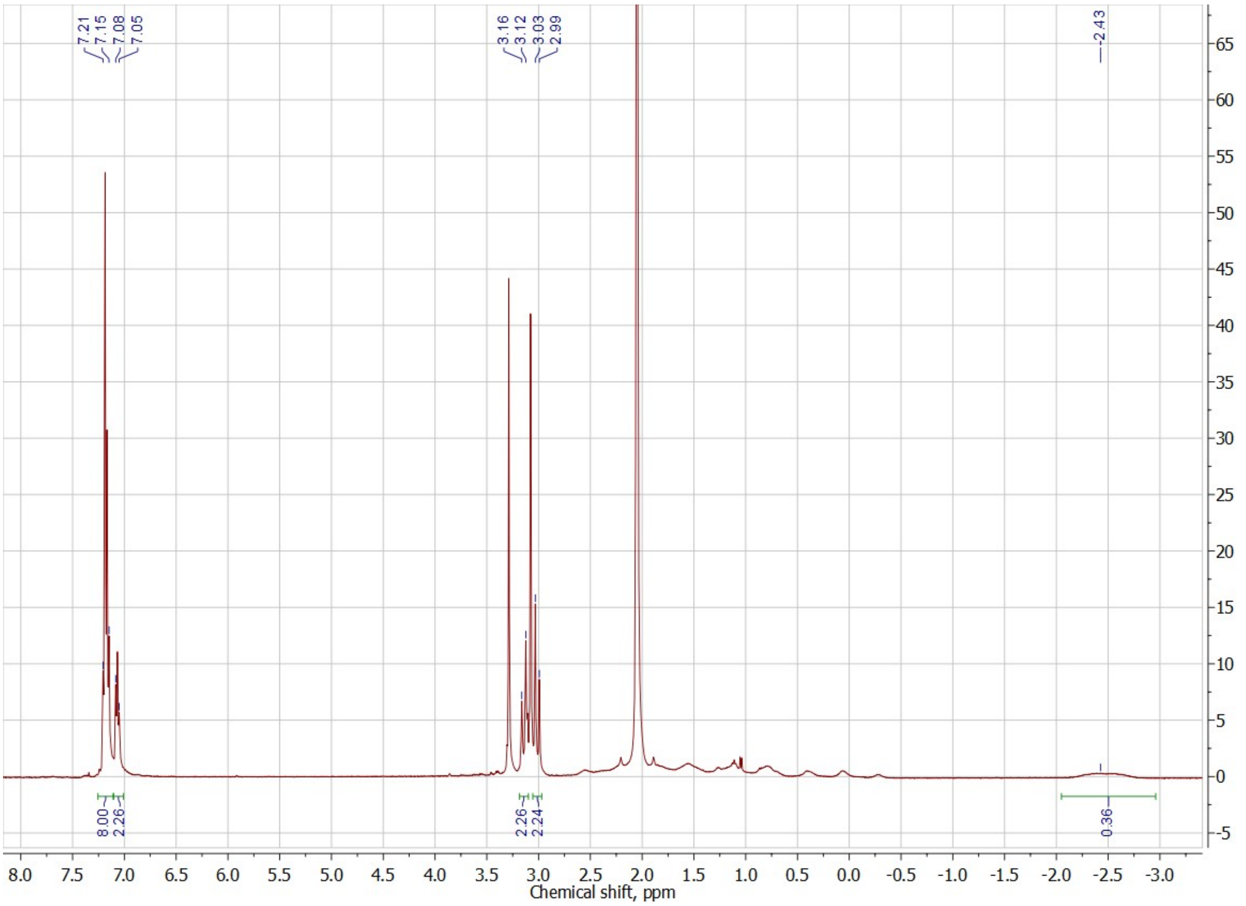


Figure S1. ^{1}H NMR spectrum of **1** in acetone-d$_6$.

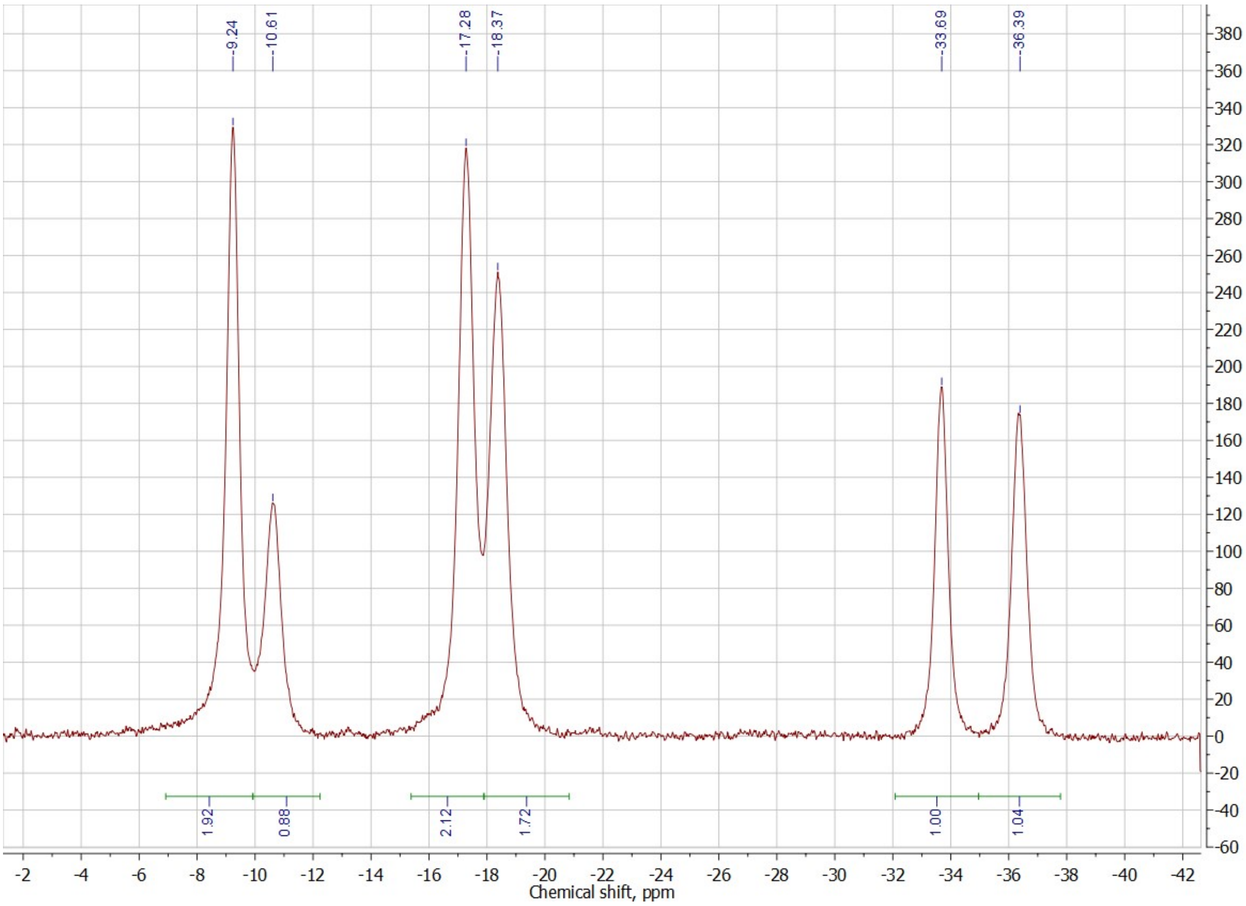


Figure S2. ^{11}B{^{1}H} NMR spectrum of **1** in acetone-d$_6$.

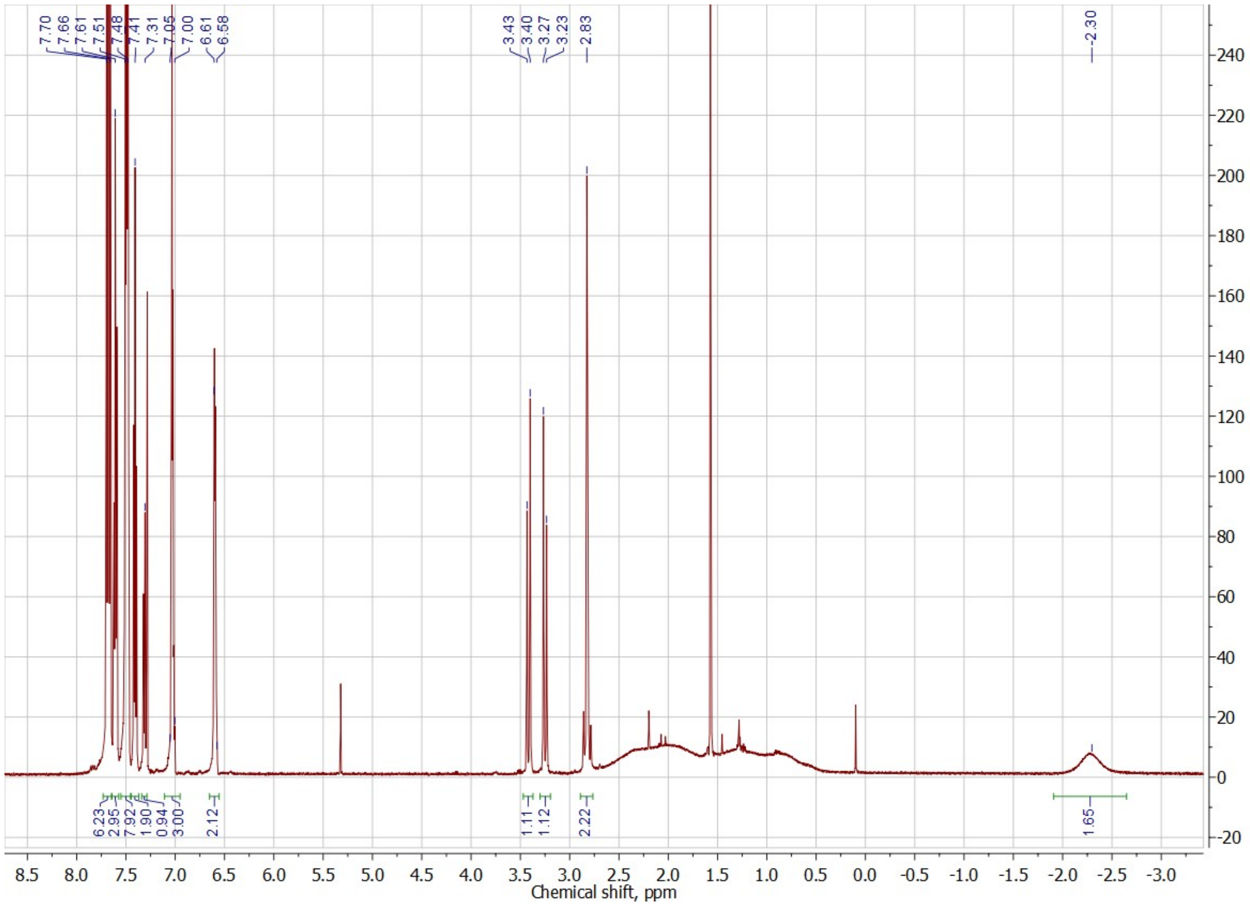


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$.

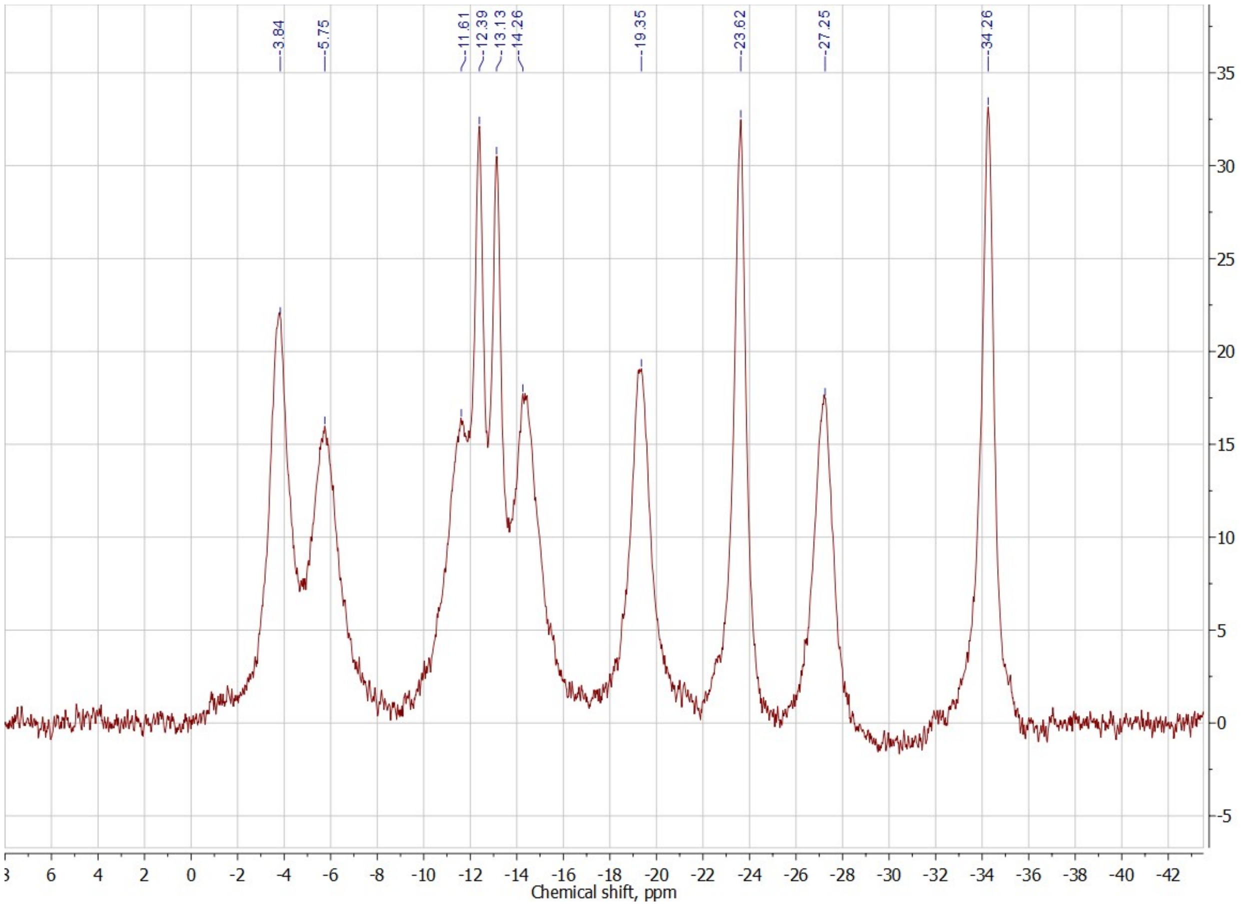


Figure S4. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

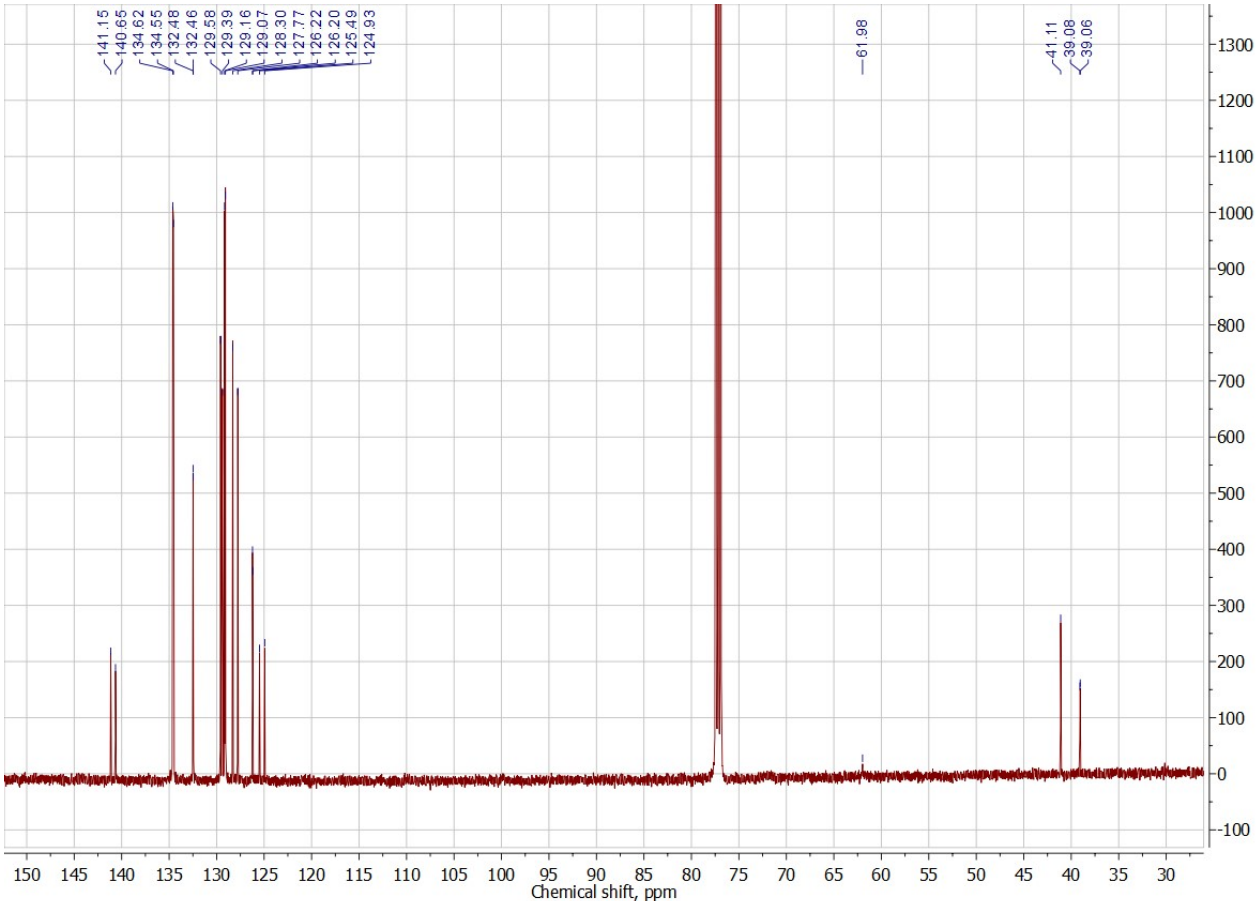


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

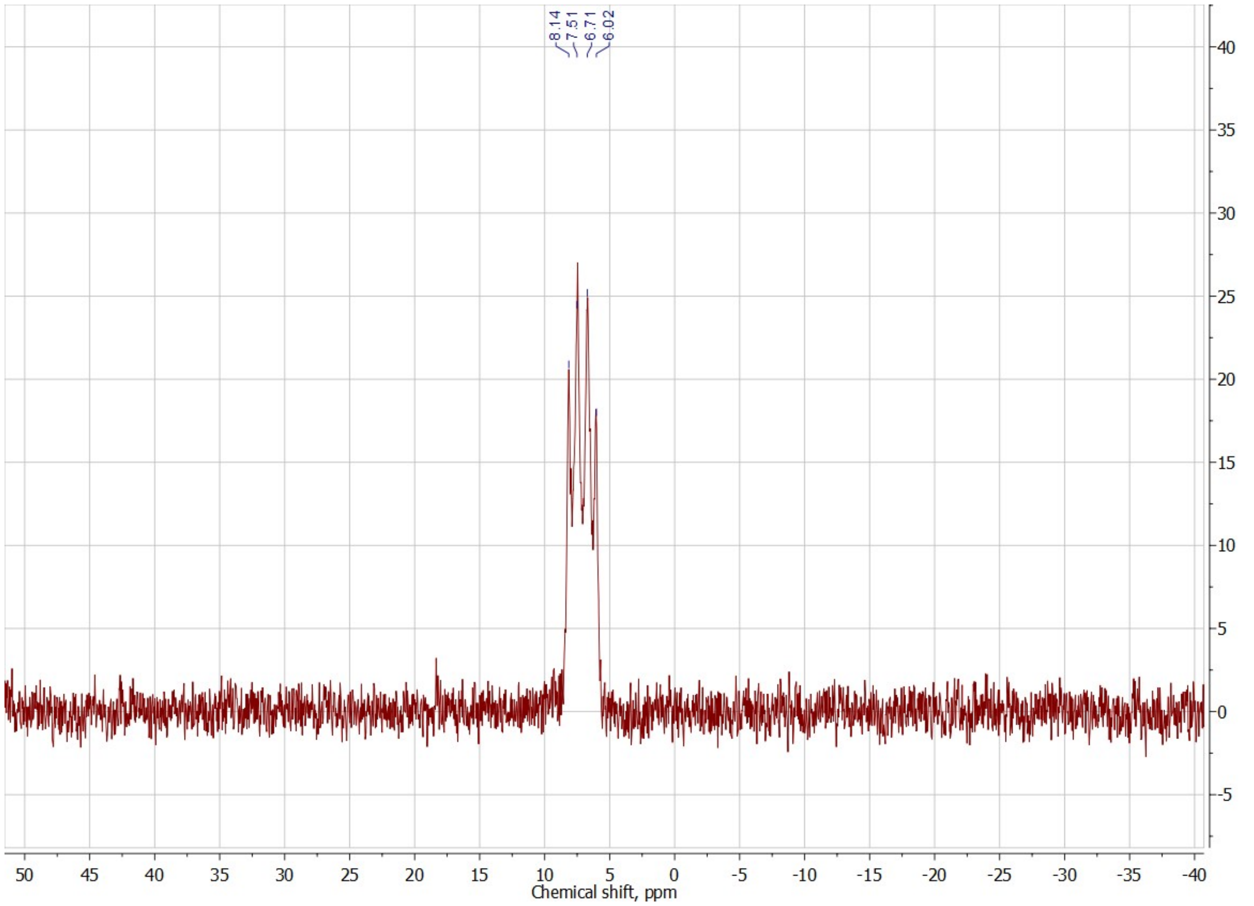


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

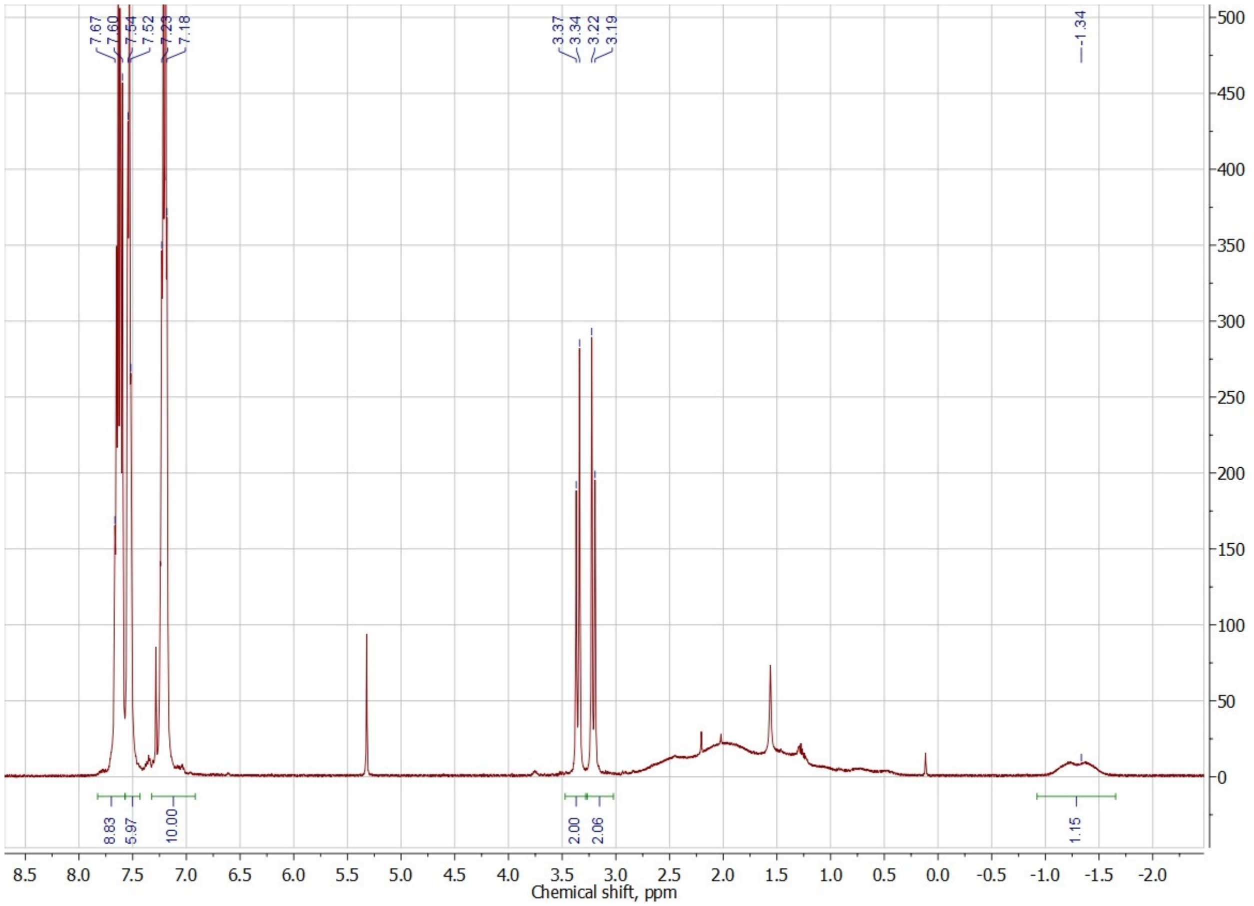


Figure S7. ^{1}H NMR spectrum of **4** in $CDCl_3$.

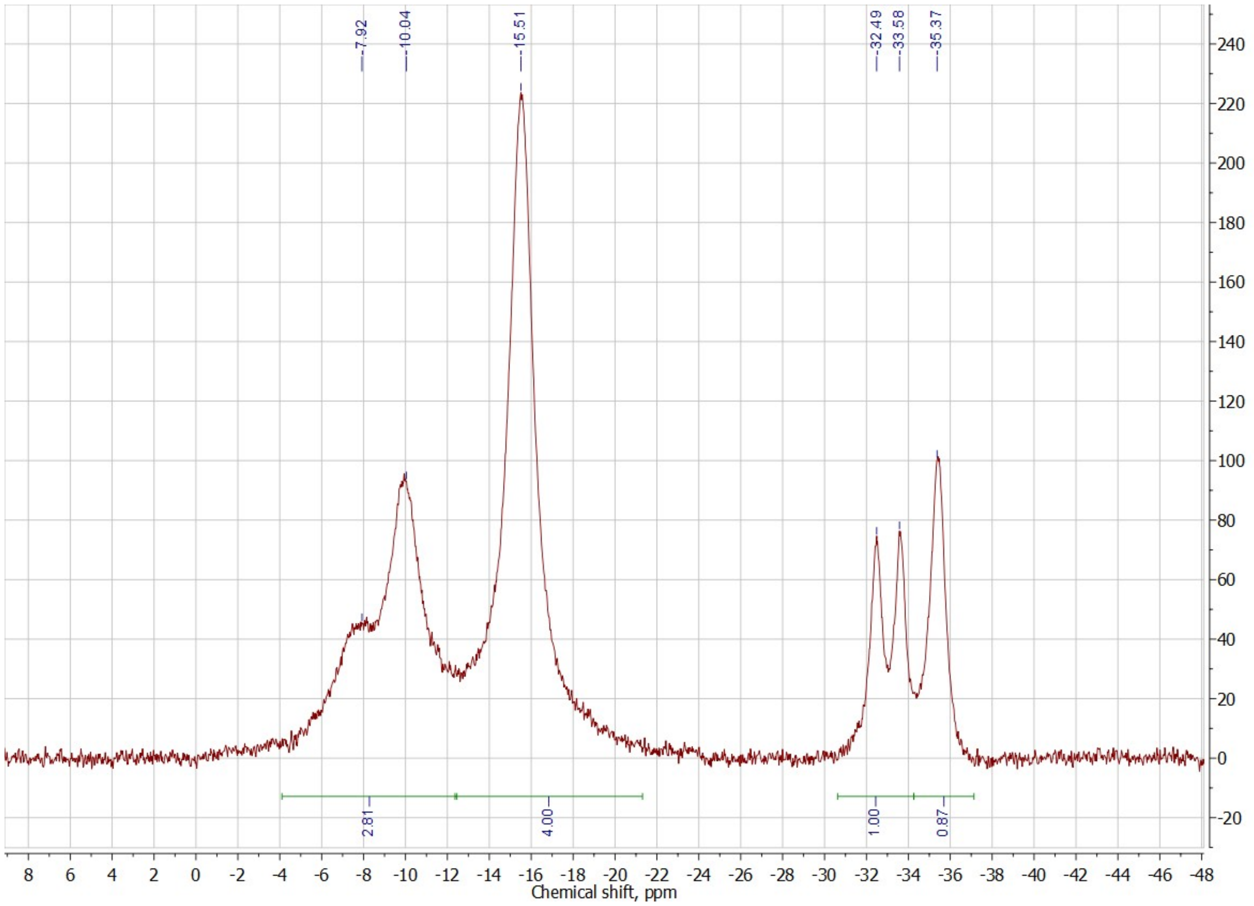


Figure S8. ^{11}B{^{1}H} NMR spectrum of **4** in $CDCl_3$.

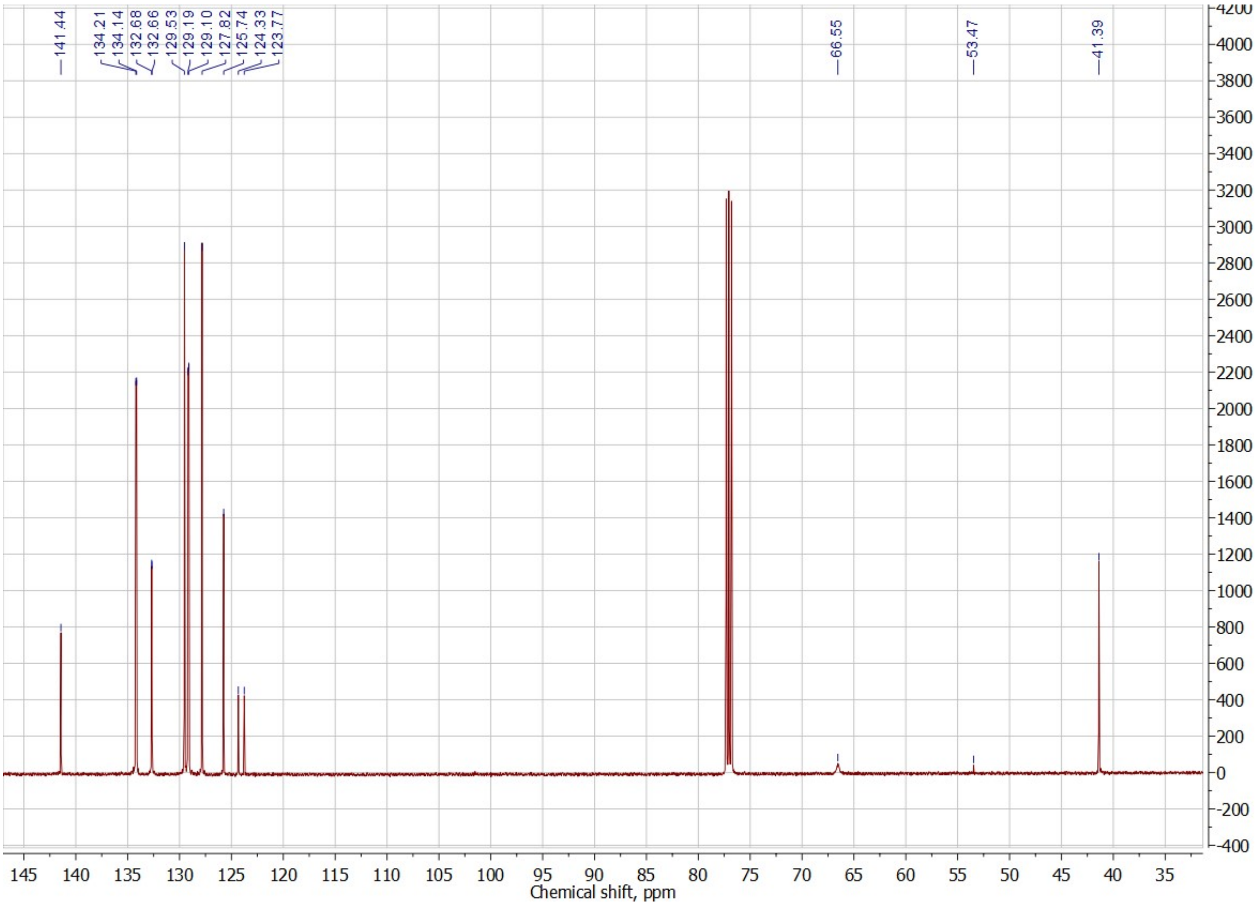


Figure S9. $^{13}C\{^1H\}$ NMR spectrum of **4** in $CDCl_3$.

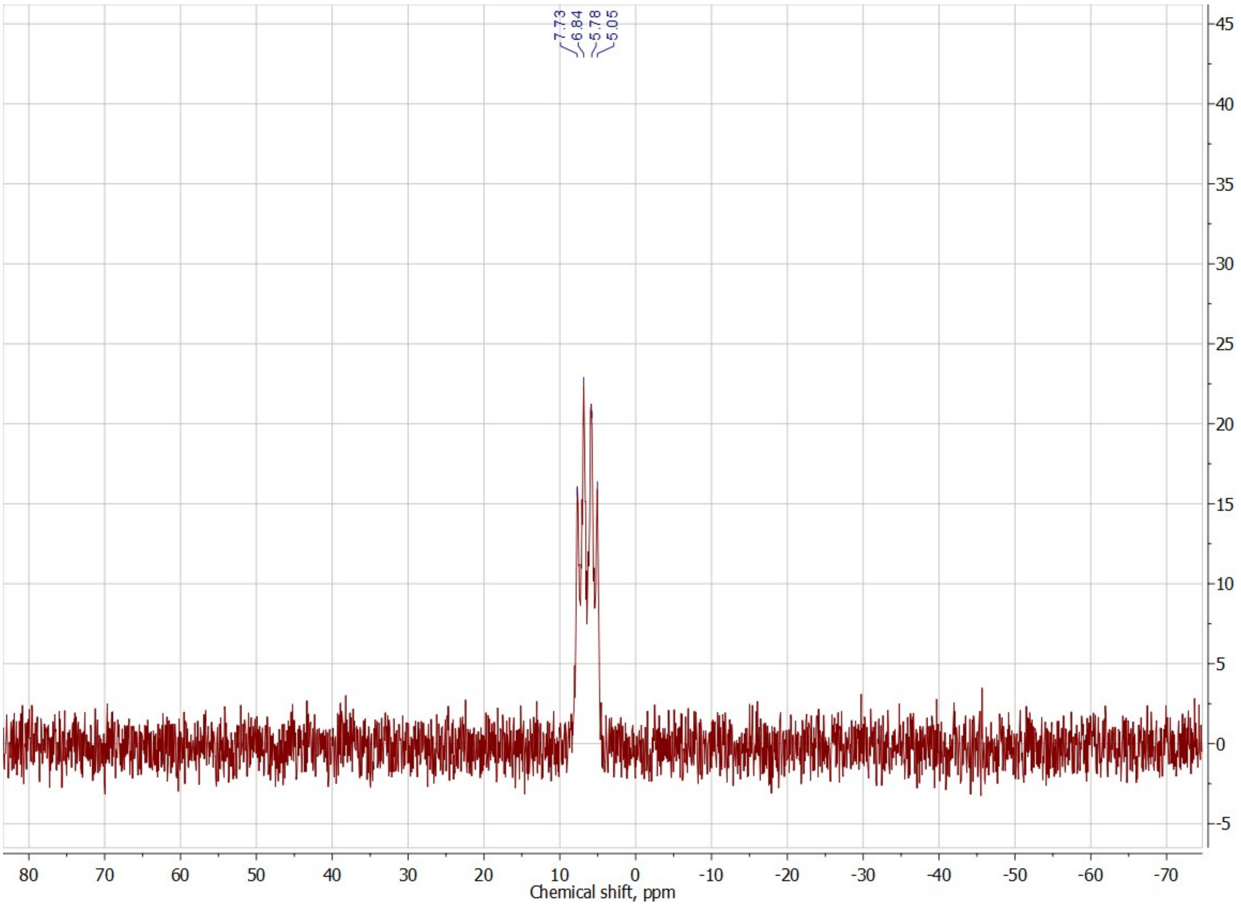


Figure S10. $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$.

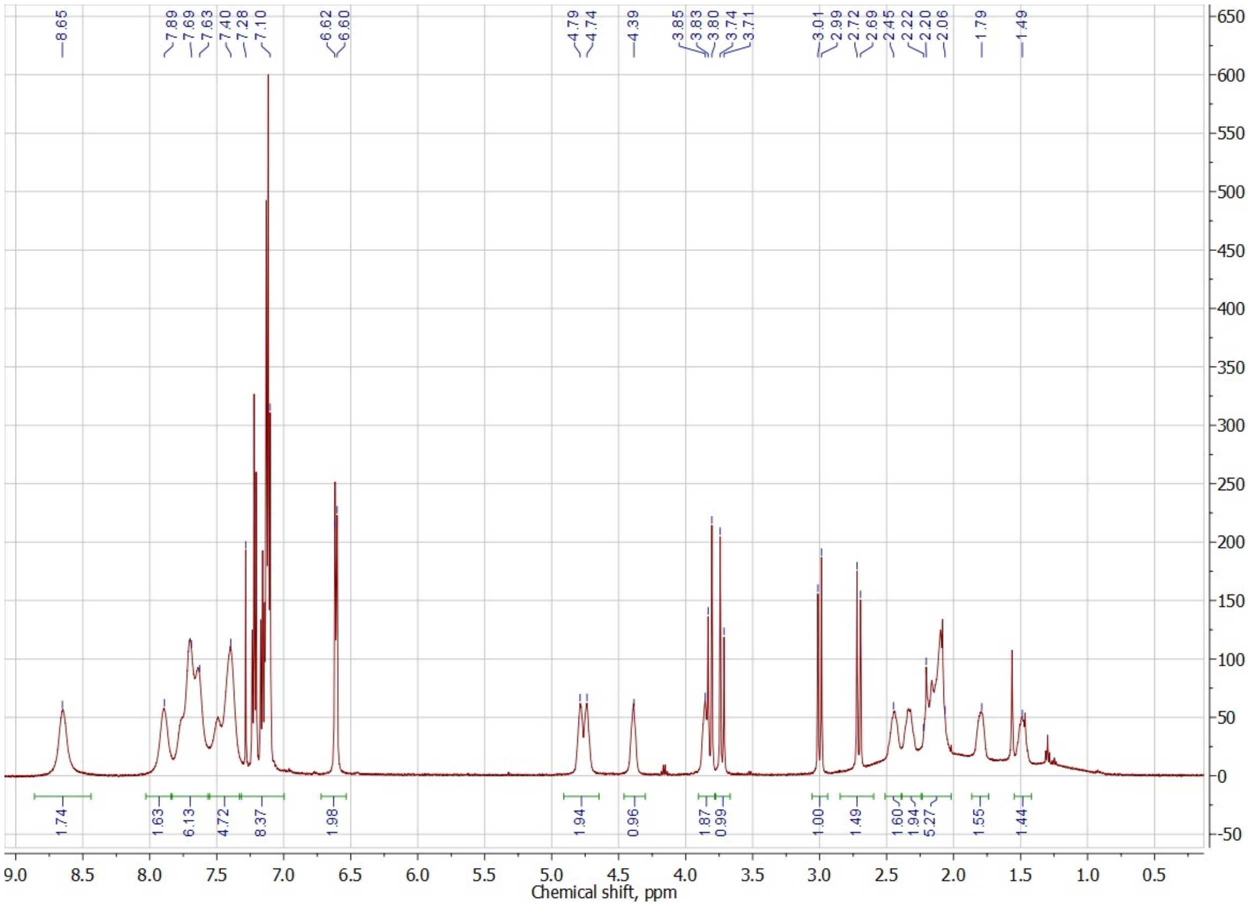


Figure S11. ^{1}H NMR spectrum of **5** in CDCl$_3$ at 25 °C.

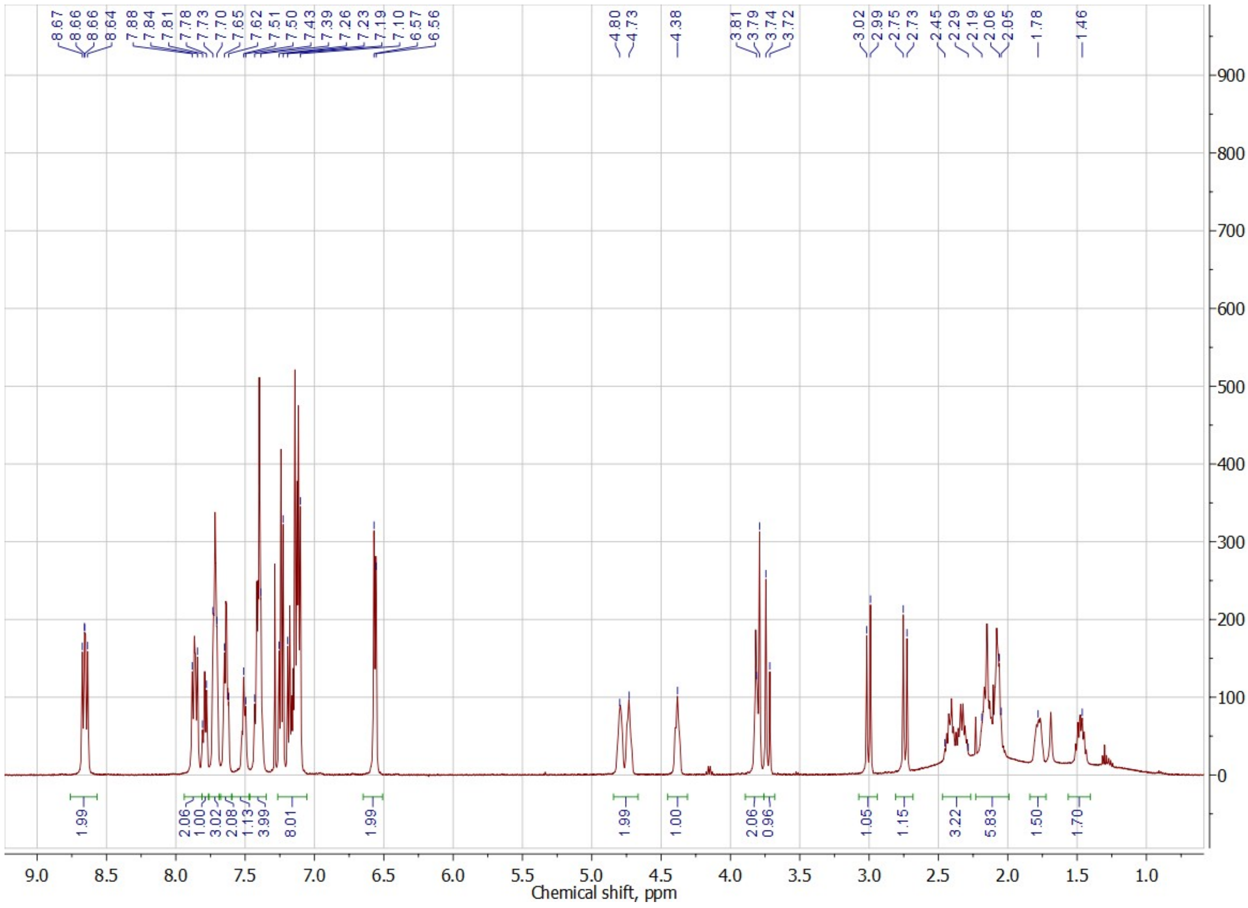


Figure S12. ^{1}H{^{31}P} NMR spectrum of **5** in CDCl$_3$ at –22 °C.

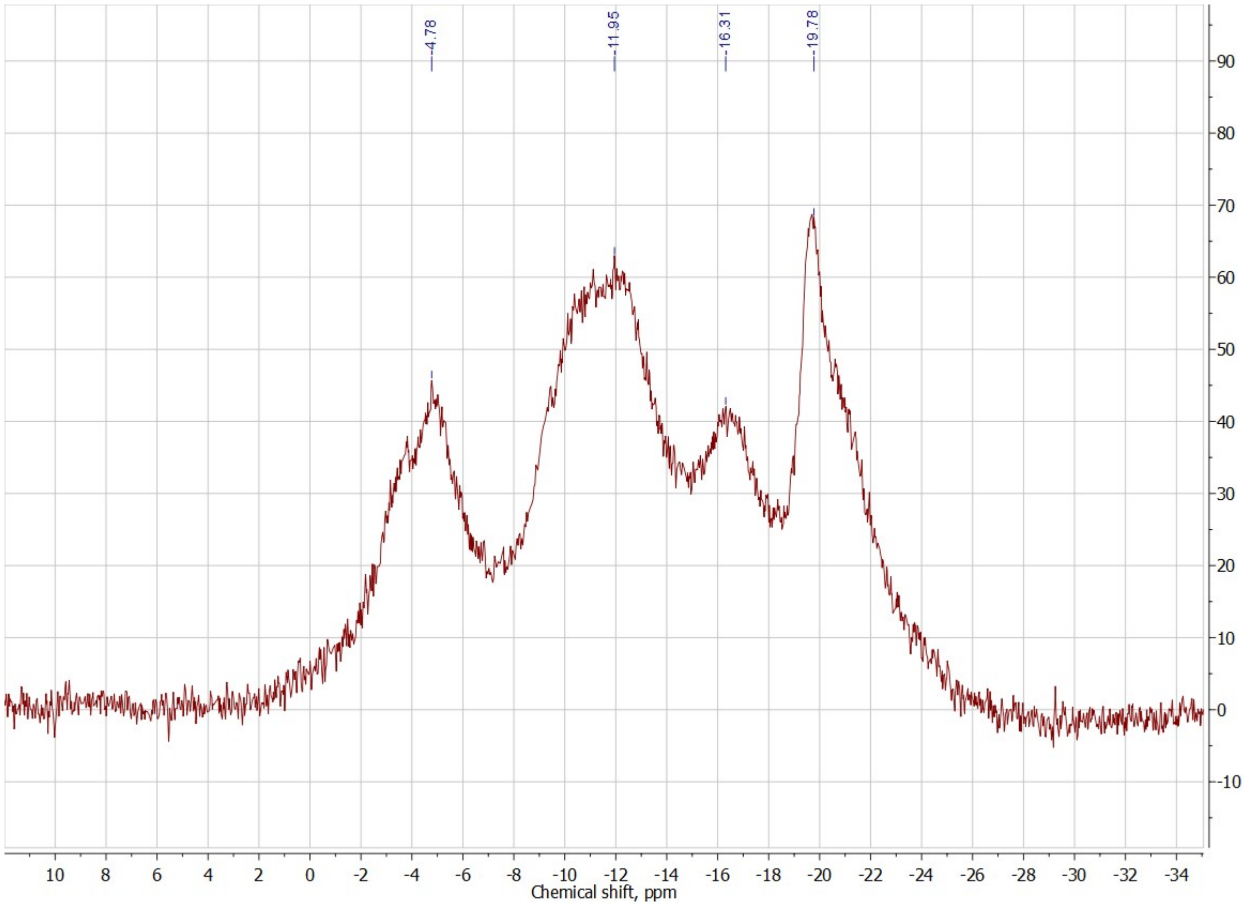


Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

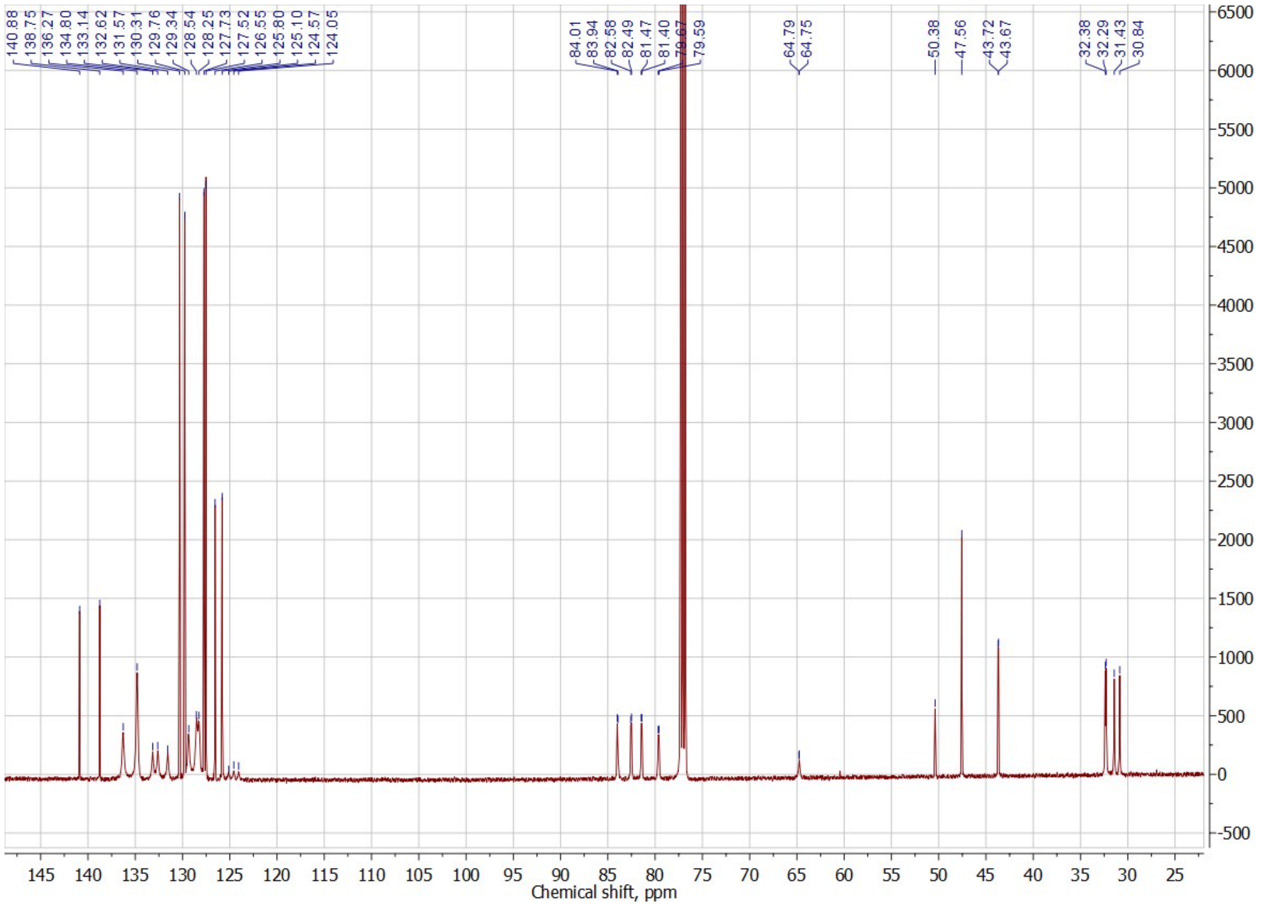


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ at 25 °C.

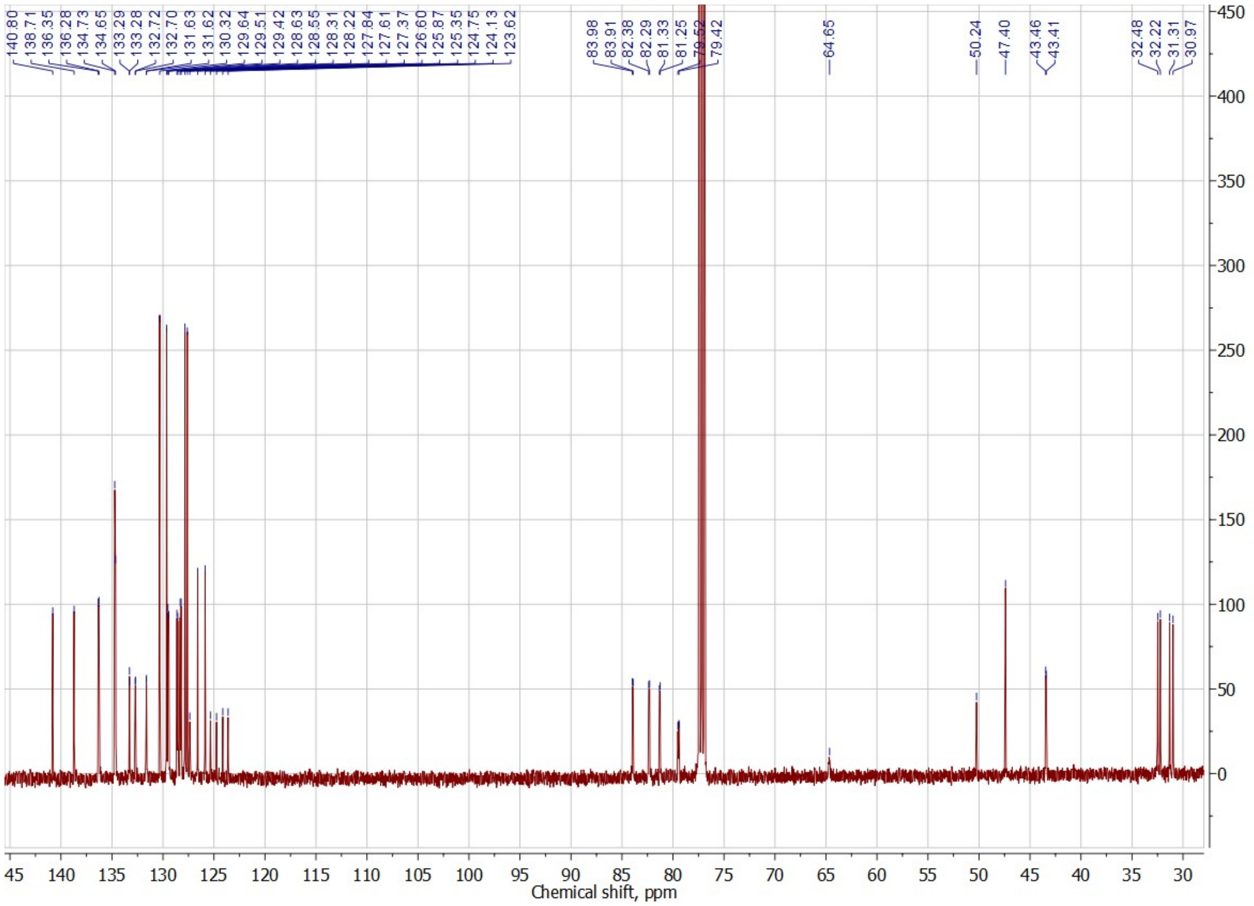


Figure S15. $^{13}C\{^1H\}$ NMR spectrum of **5** in $CDCl_3$ at –22 °C.

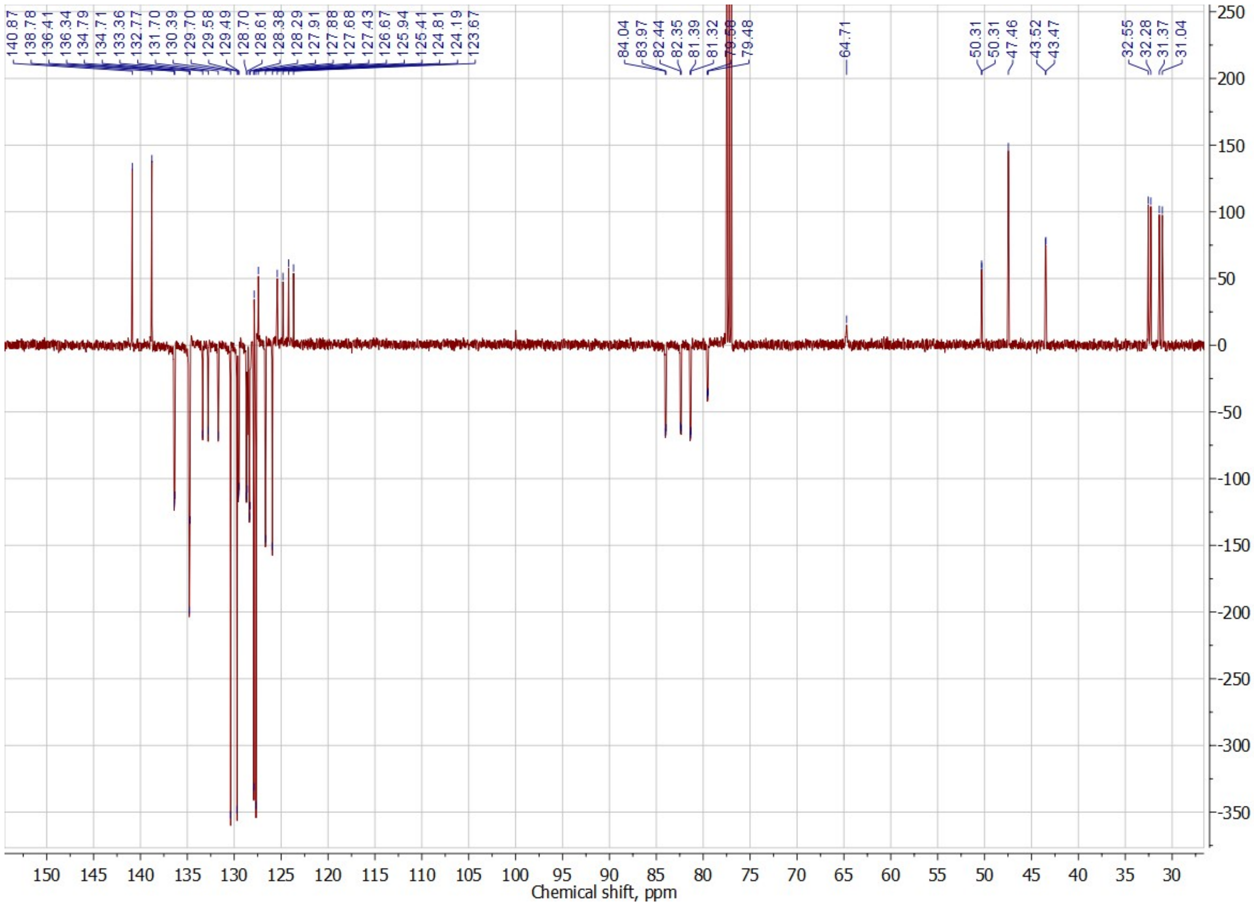


Figure S16. $^{13}C\{^1H\}$ JMOD spectrum of **5** in $CDCl_3$ at –22 °C.

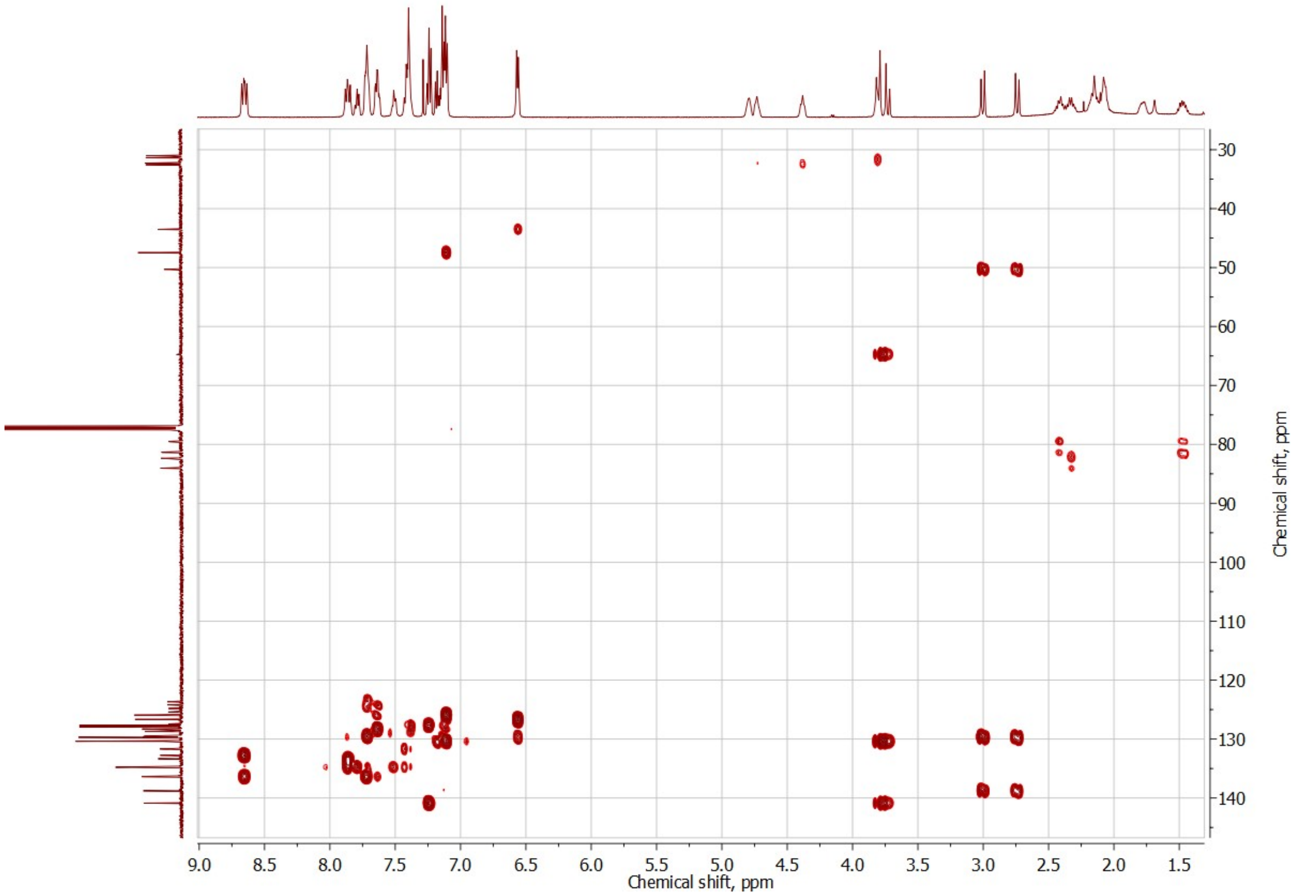


Figure S17. $^{1}H^{13}C$ HMBC NMR spectrum of **5** in $CDCl_3$ at –22 °C.

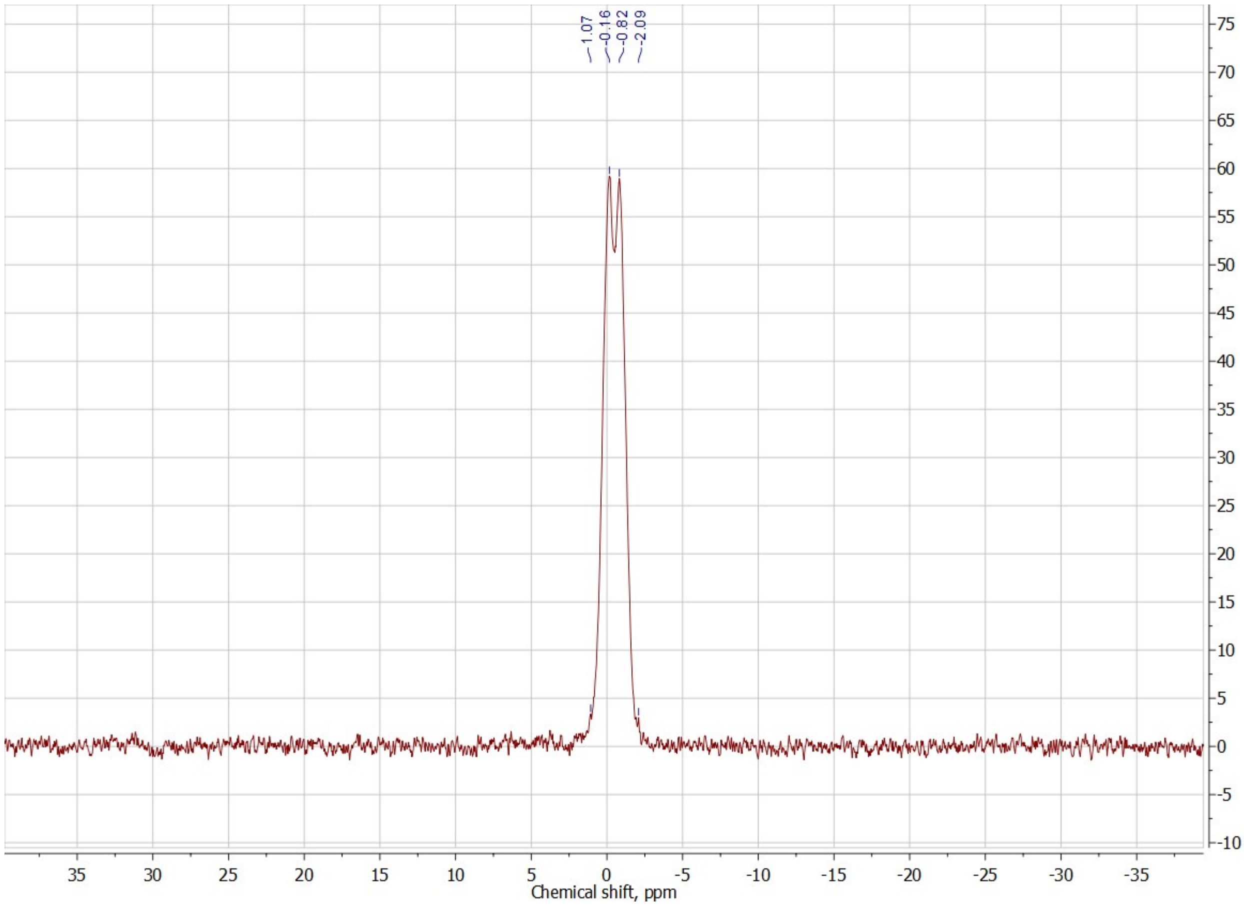


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

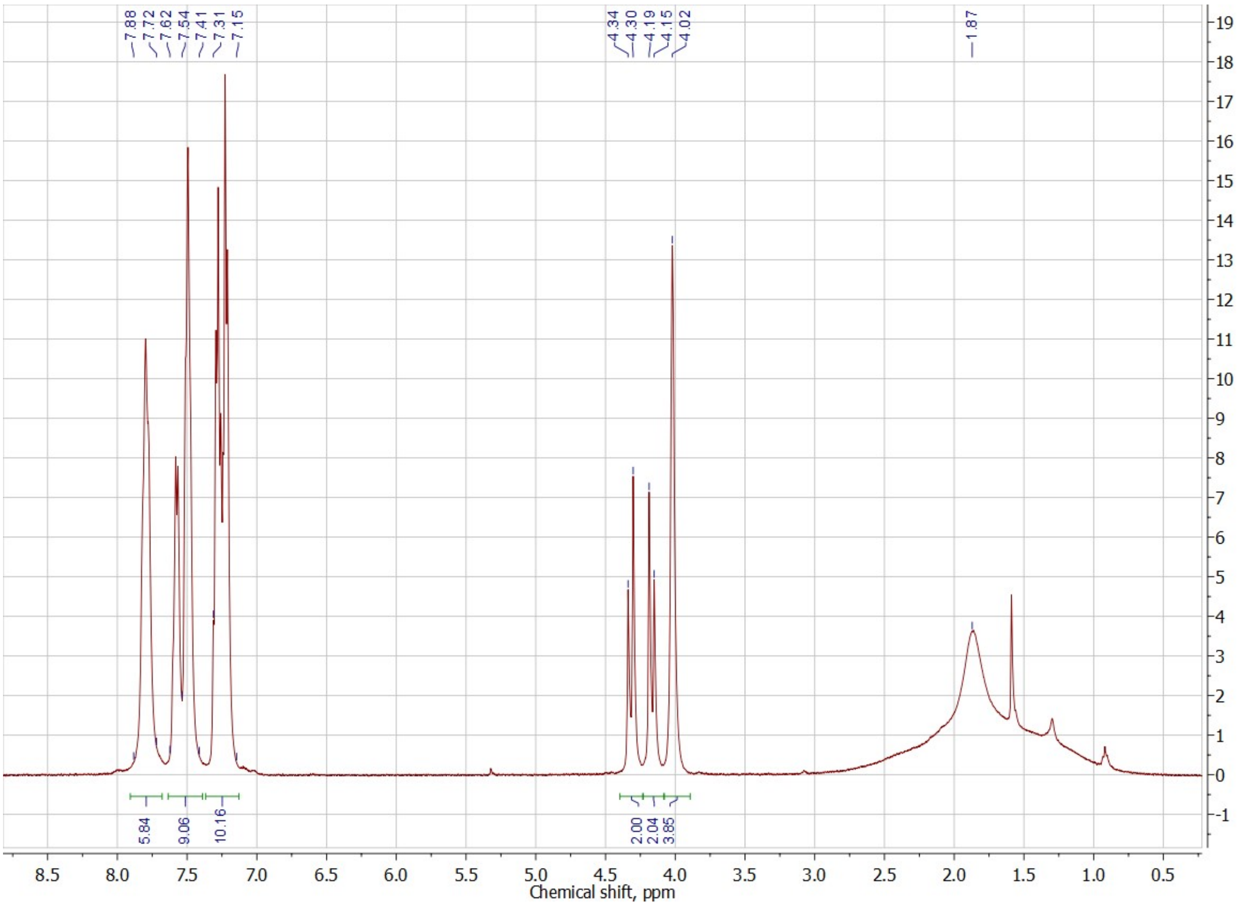


Figure S19. ^{1}H NMR spectrum of **6** in $CDCl_3$.

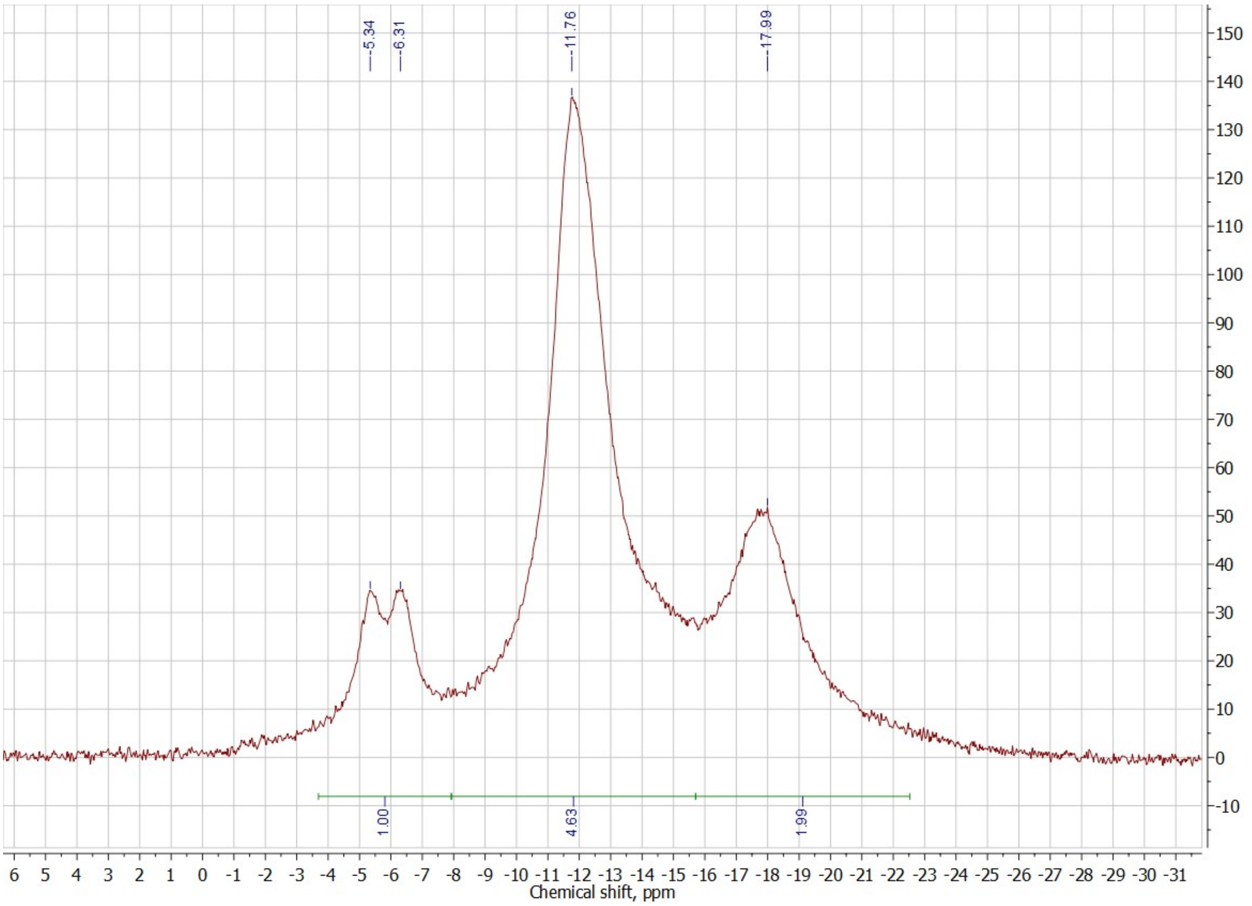


Figure S20. $^{11}B\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

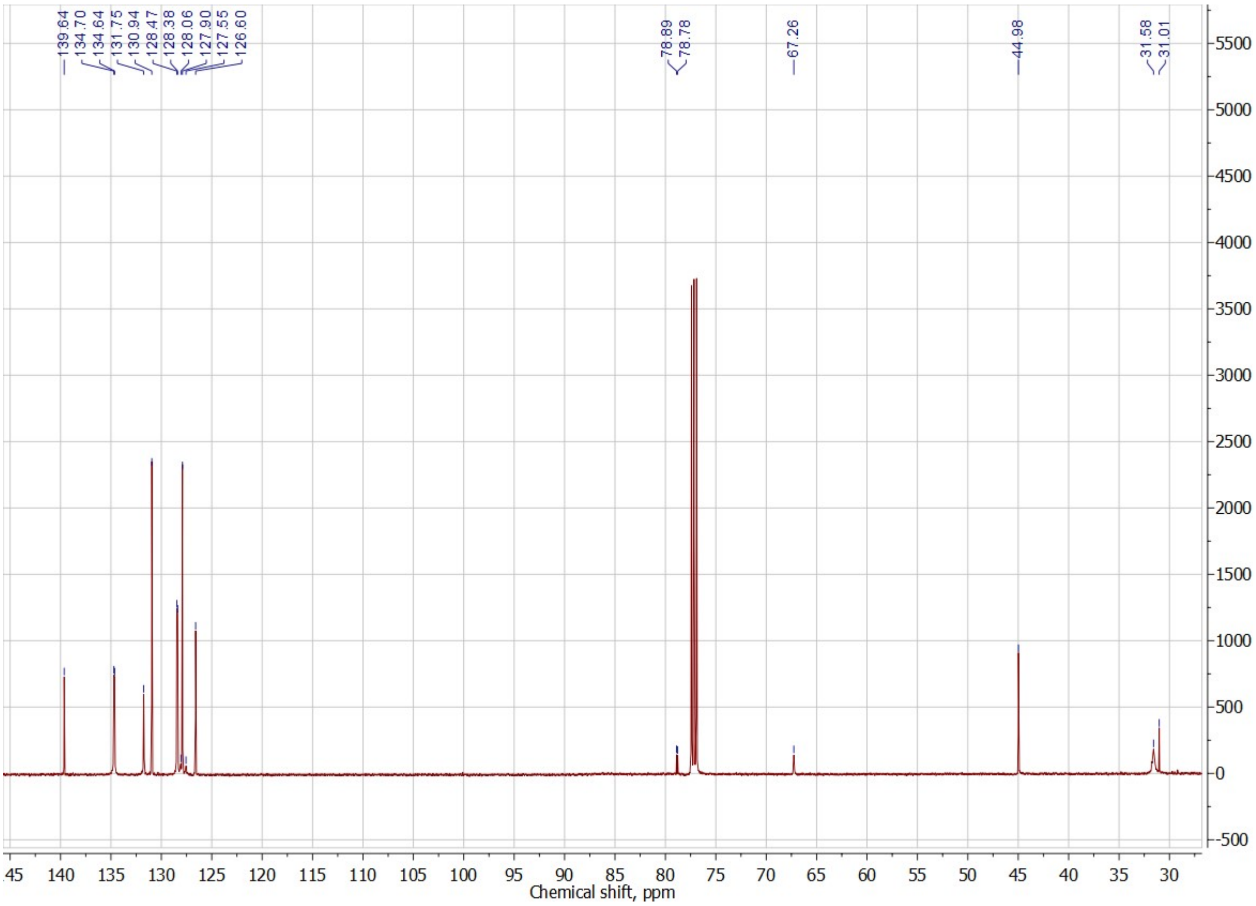


Figure S21. $^{13}C\{^1H\}$ NMR spectrum of **6** in $CDCl_3$.

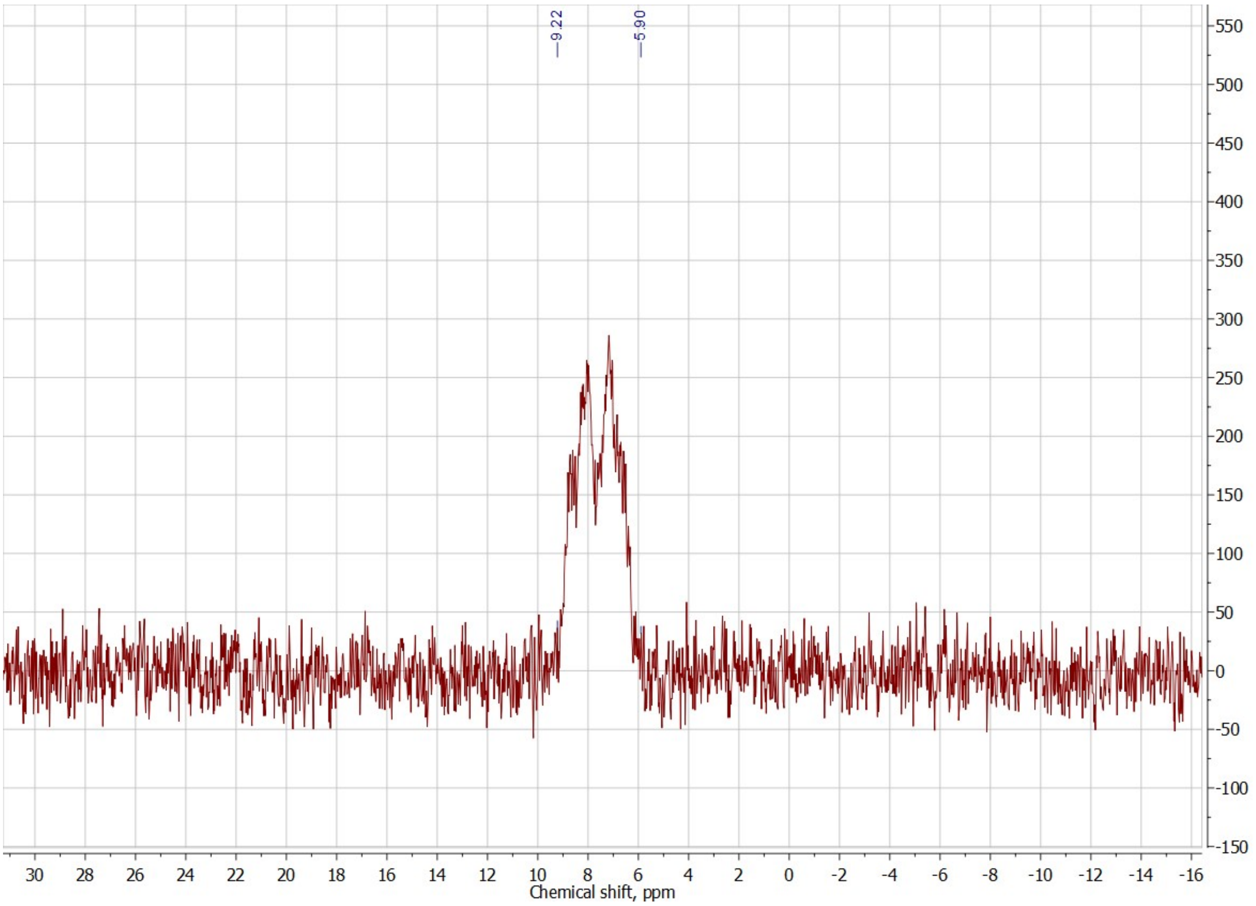


Figure 22. $^{31}P\{^1H\}$ NMR spectrum of **6** in $CDCl_3$.

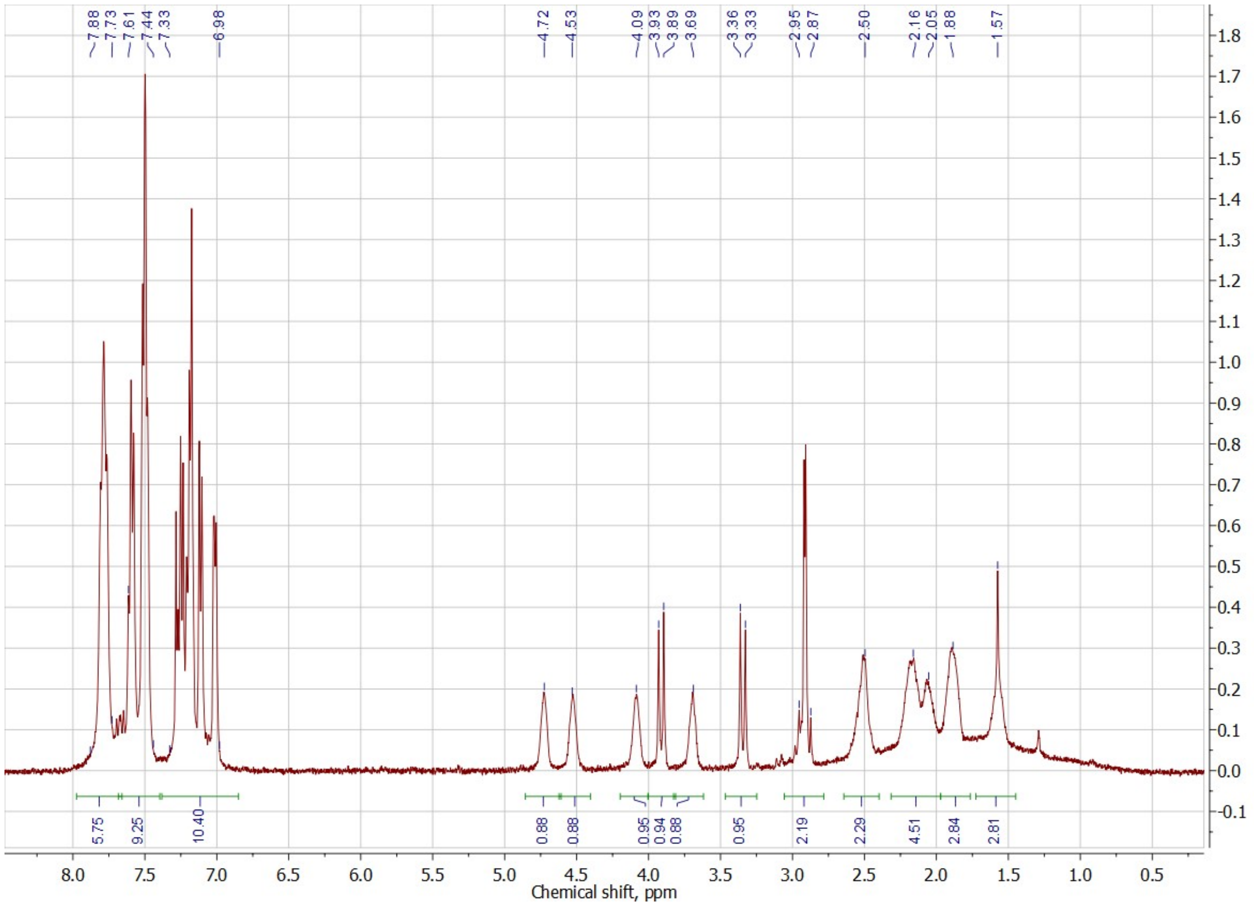


Figure S23. ^{1}H NMR spectrum of **7** in CDCl$_3$.

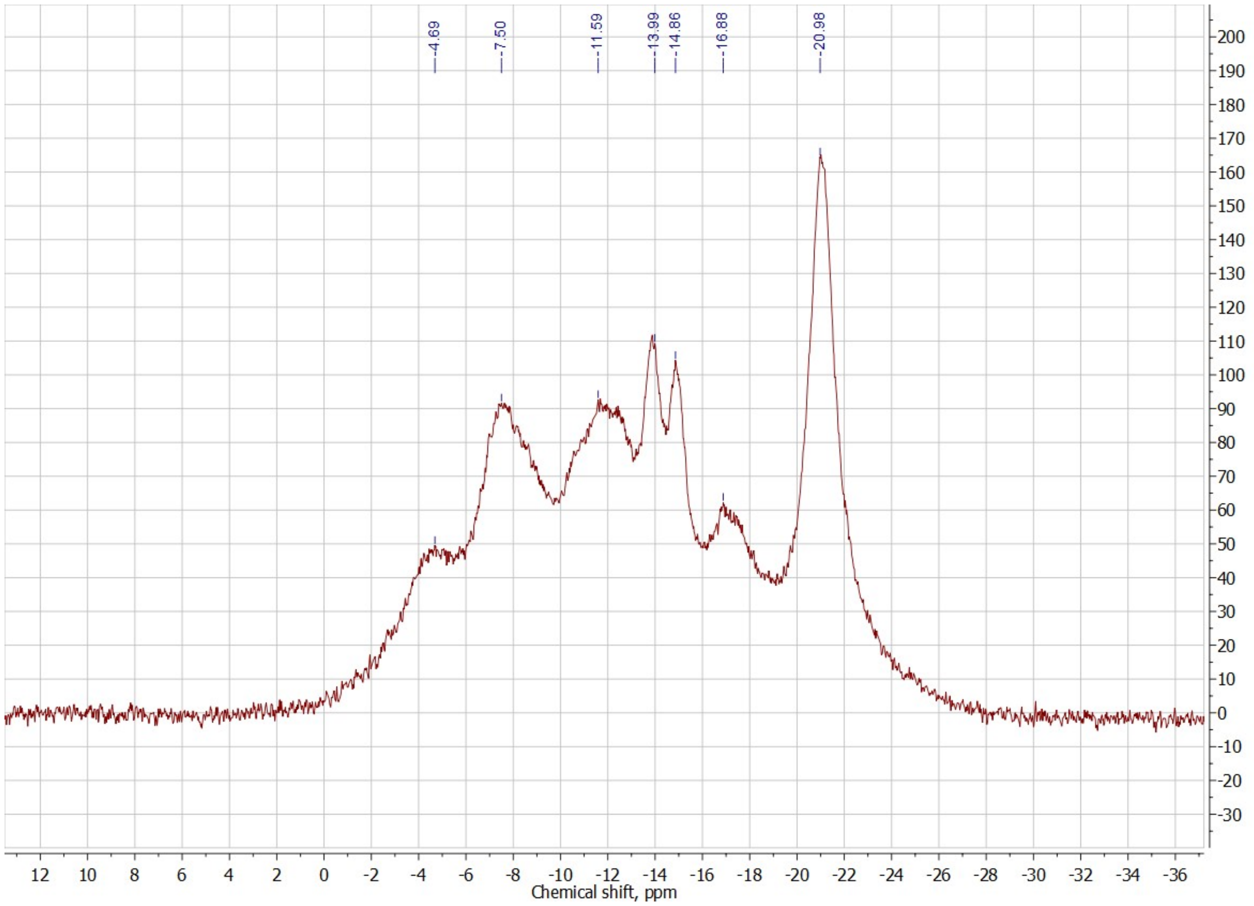


Figure S24. ^{11}B{^{1}H} NMR spectrum of **7** in CDCl$_3$.

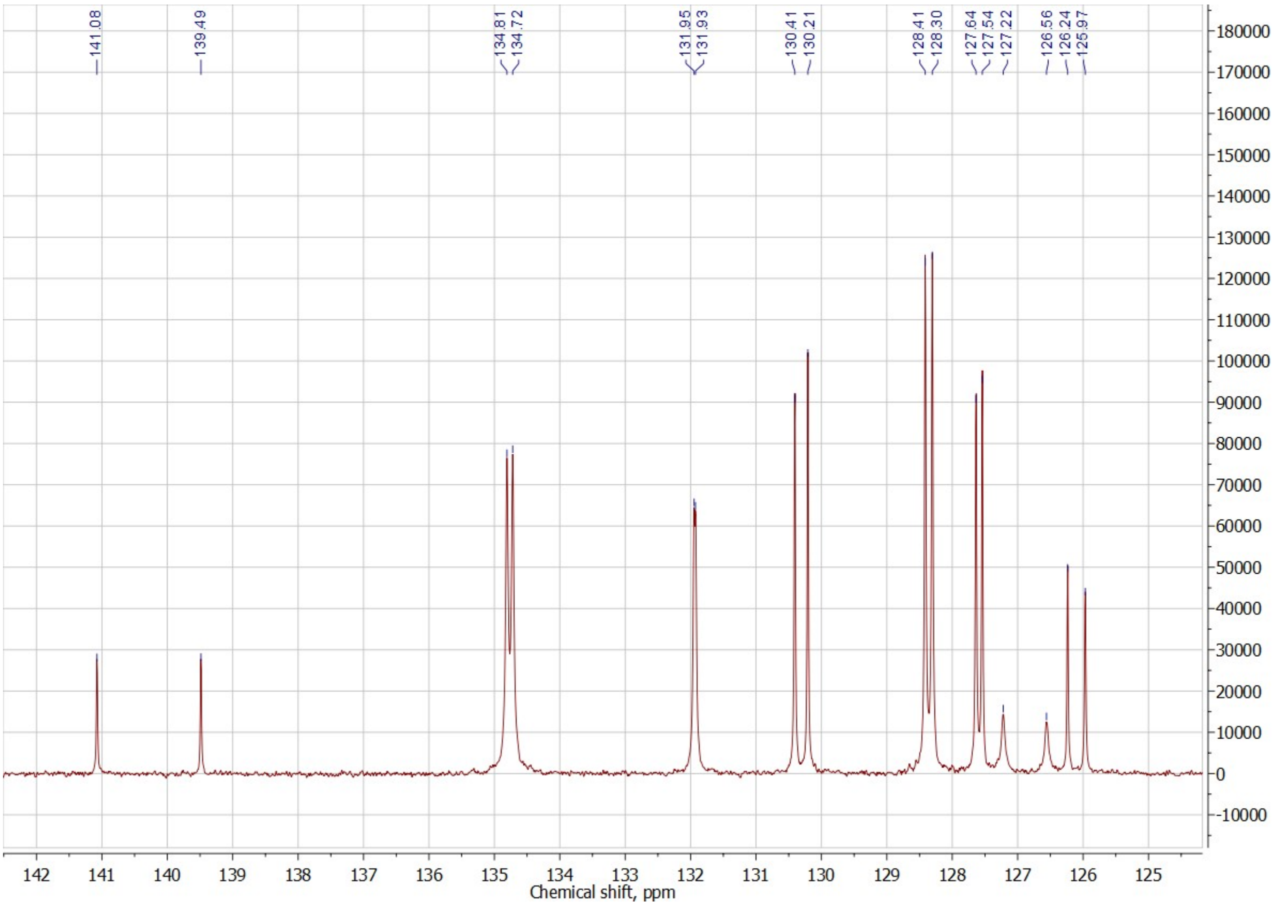


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

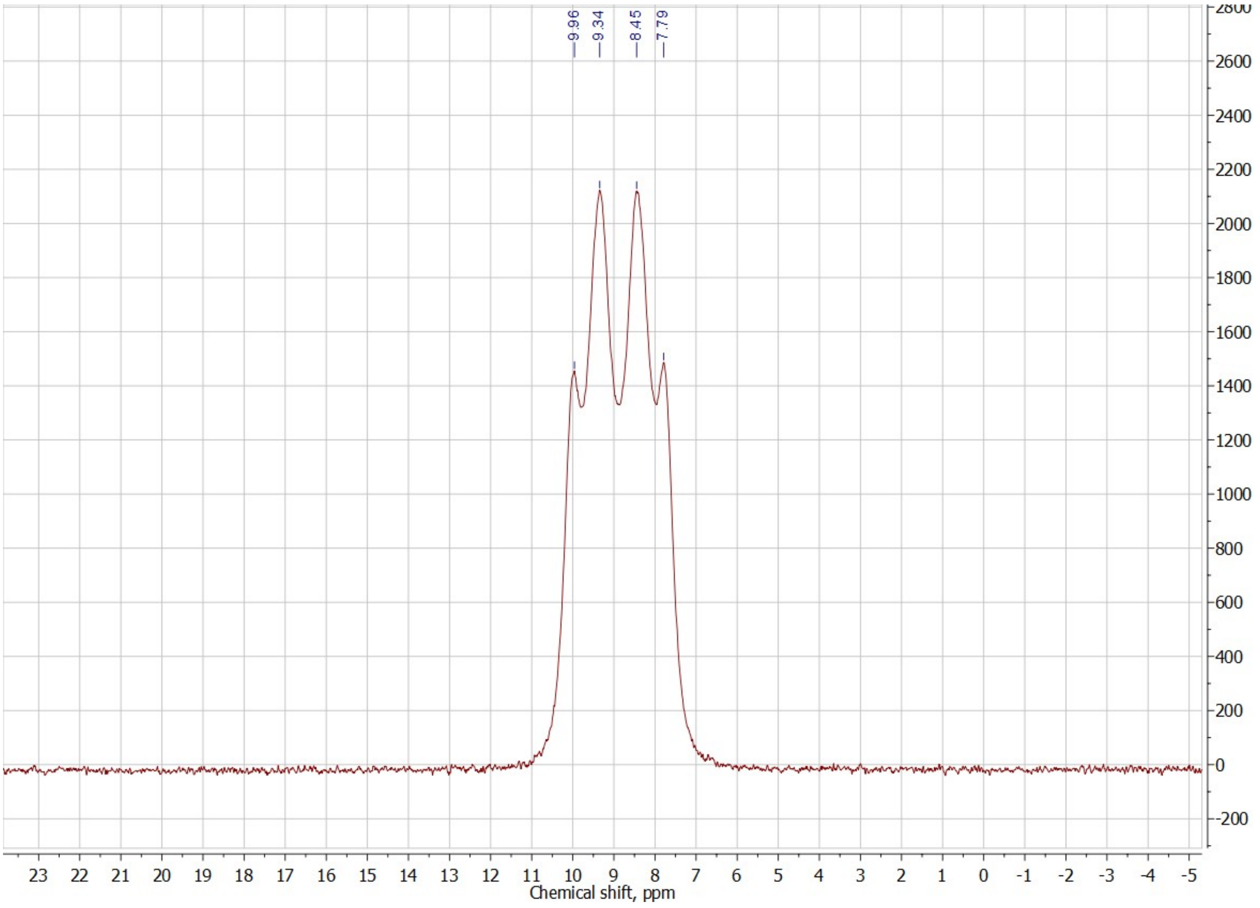


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

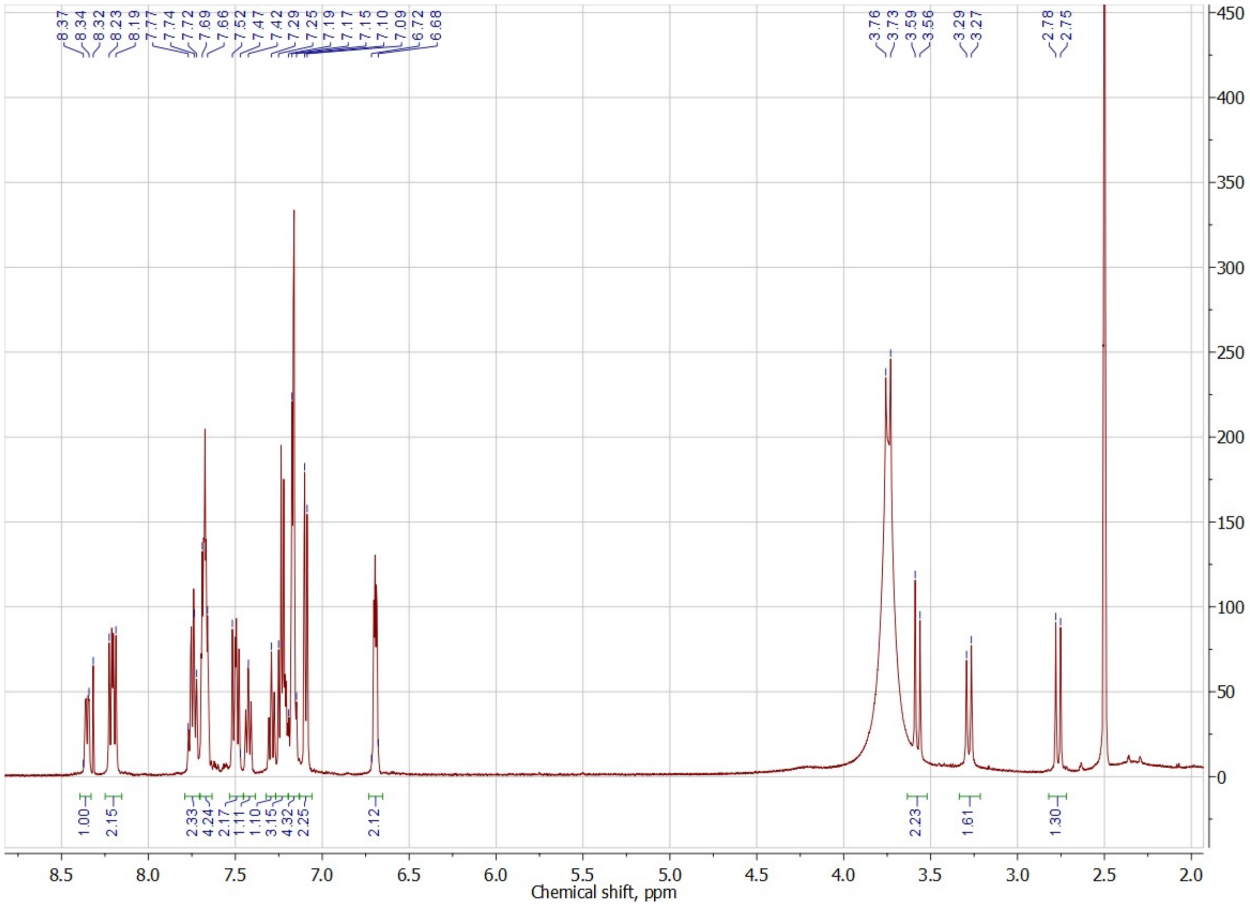


Figure S27. ^{1}H NMR spectrum of **8** in DMSO-d$_6$.

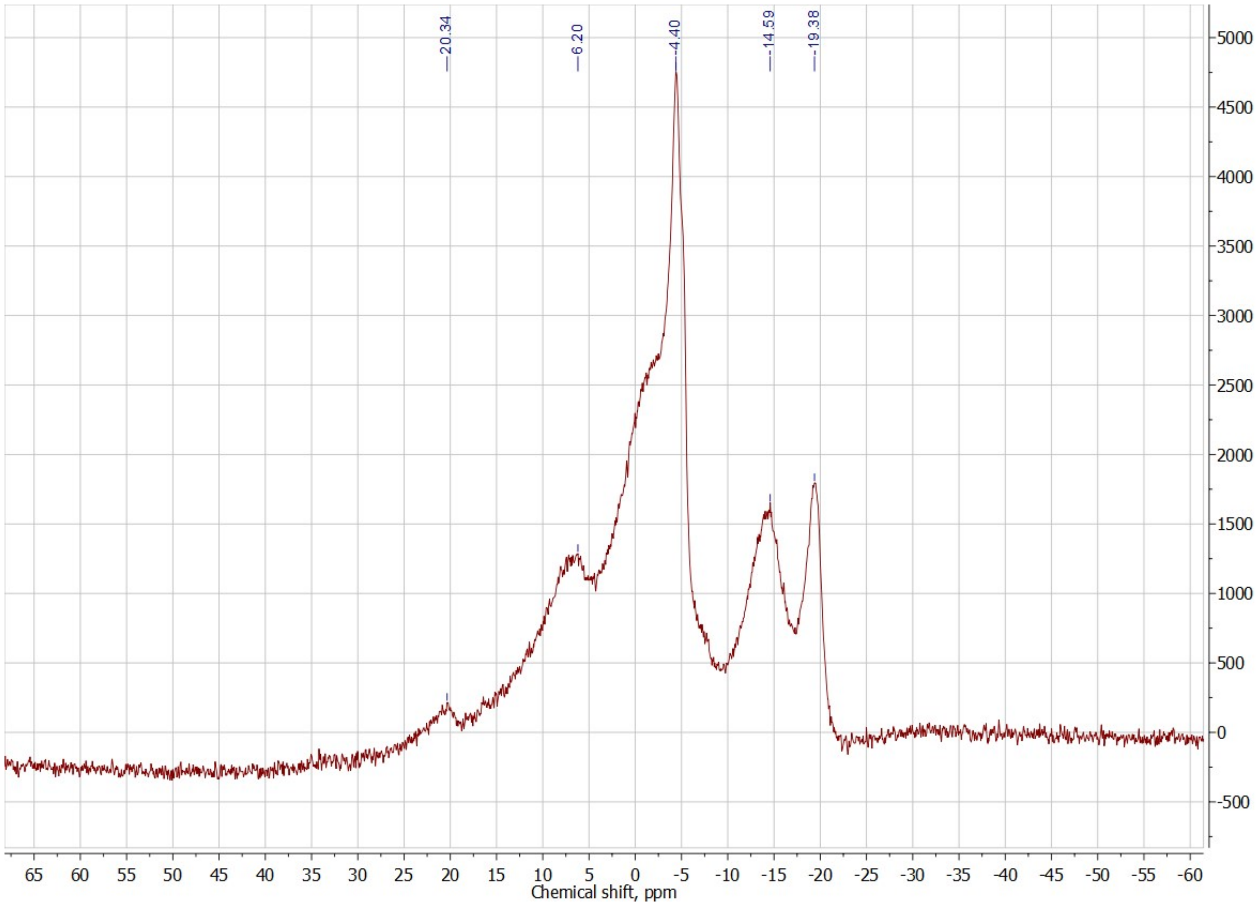


Figure S28. ^{11}B{^{1}H} NMR spectrum of **8** in DMSO-d$_6$.

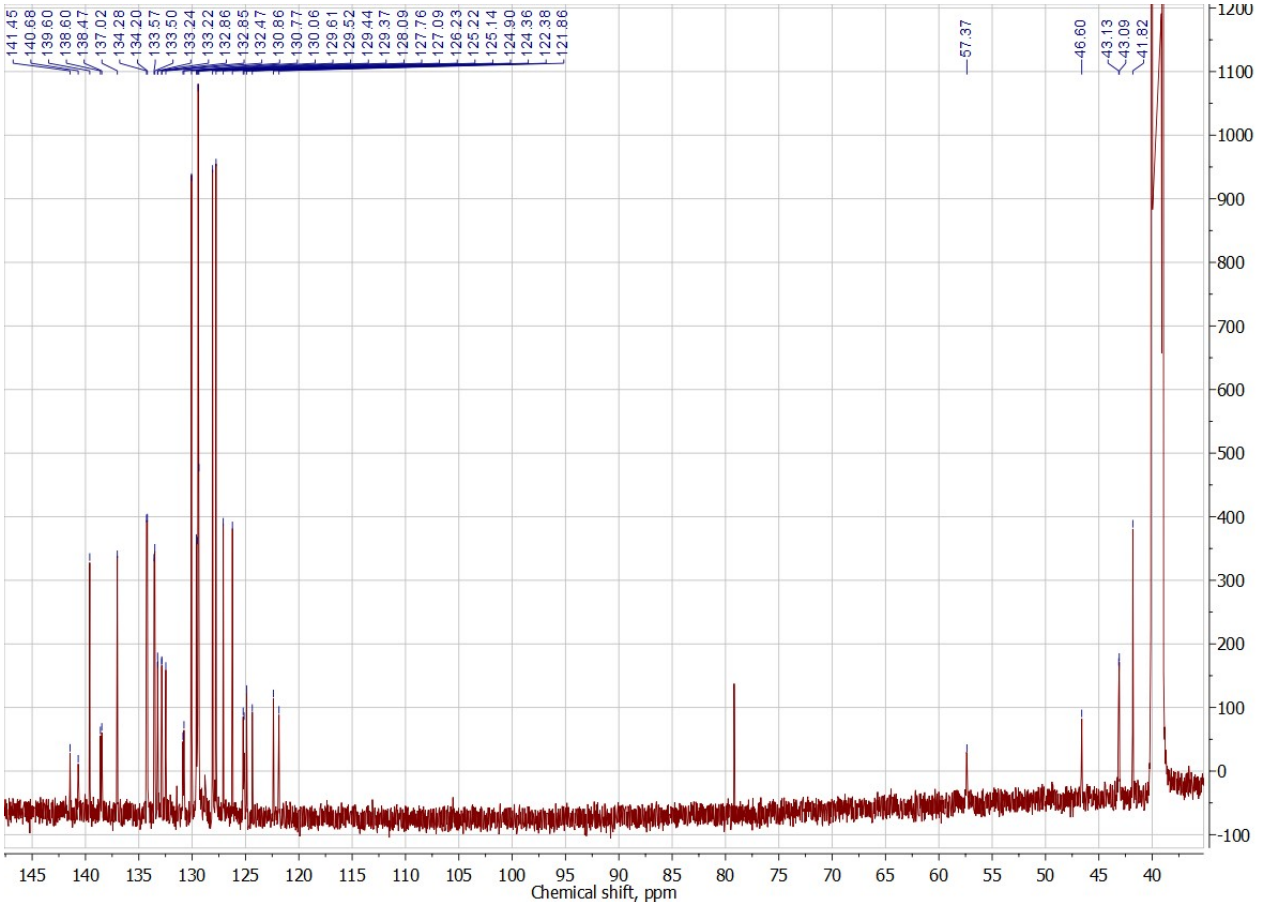


Figure S29. $^{13}C\{^1H\}$ NMR spectrum of **8** in DMSO-d$_6$.

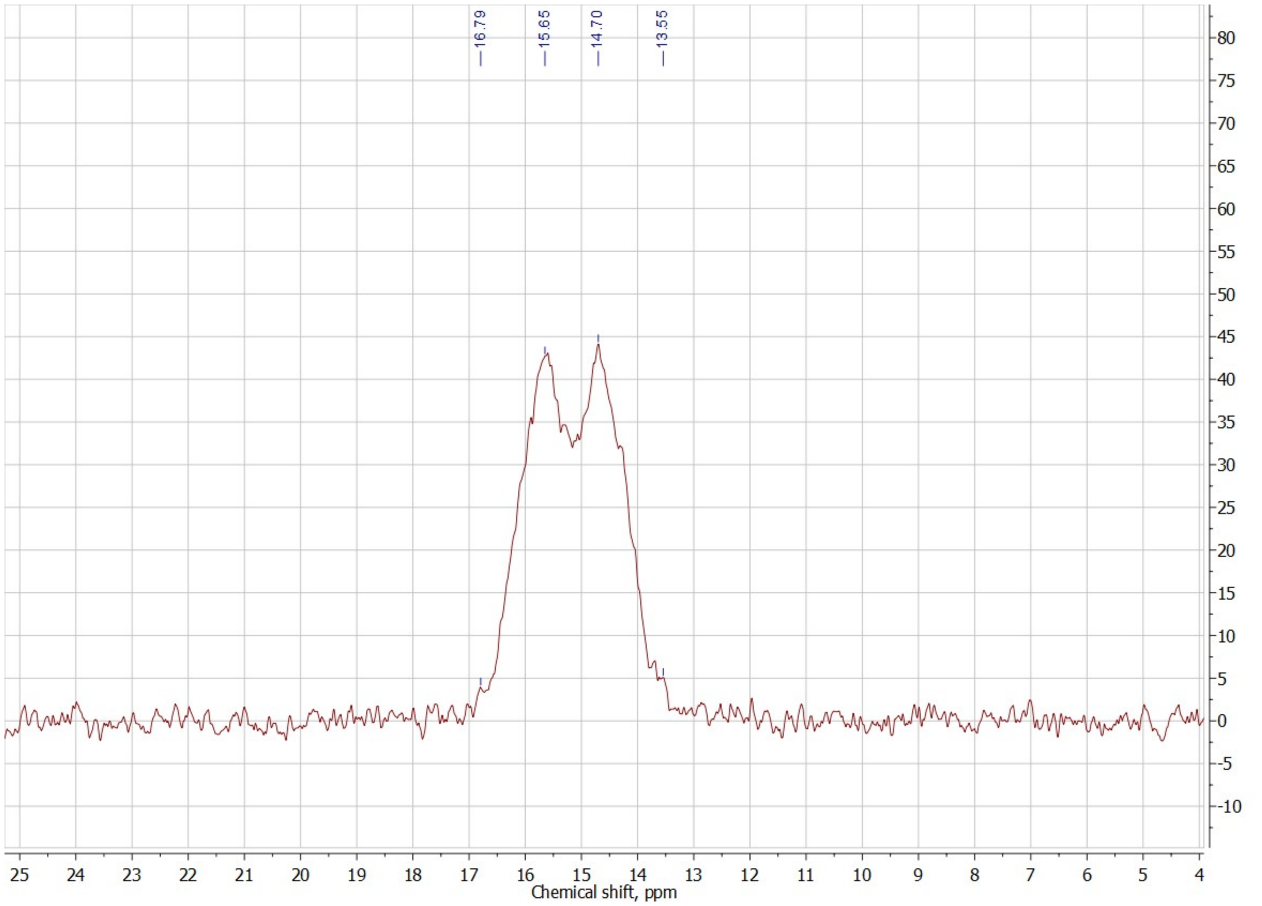


Figure S30. $^{31}P\{^1H\}$ NMR spectrum of **8** in DMSO-d$_6$.

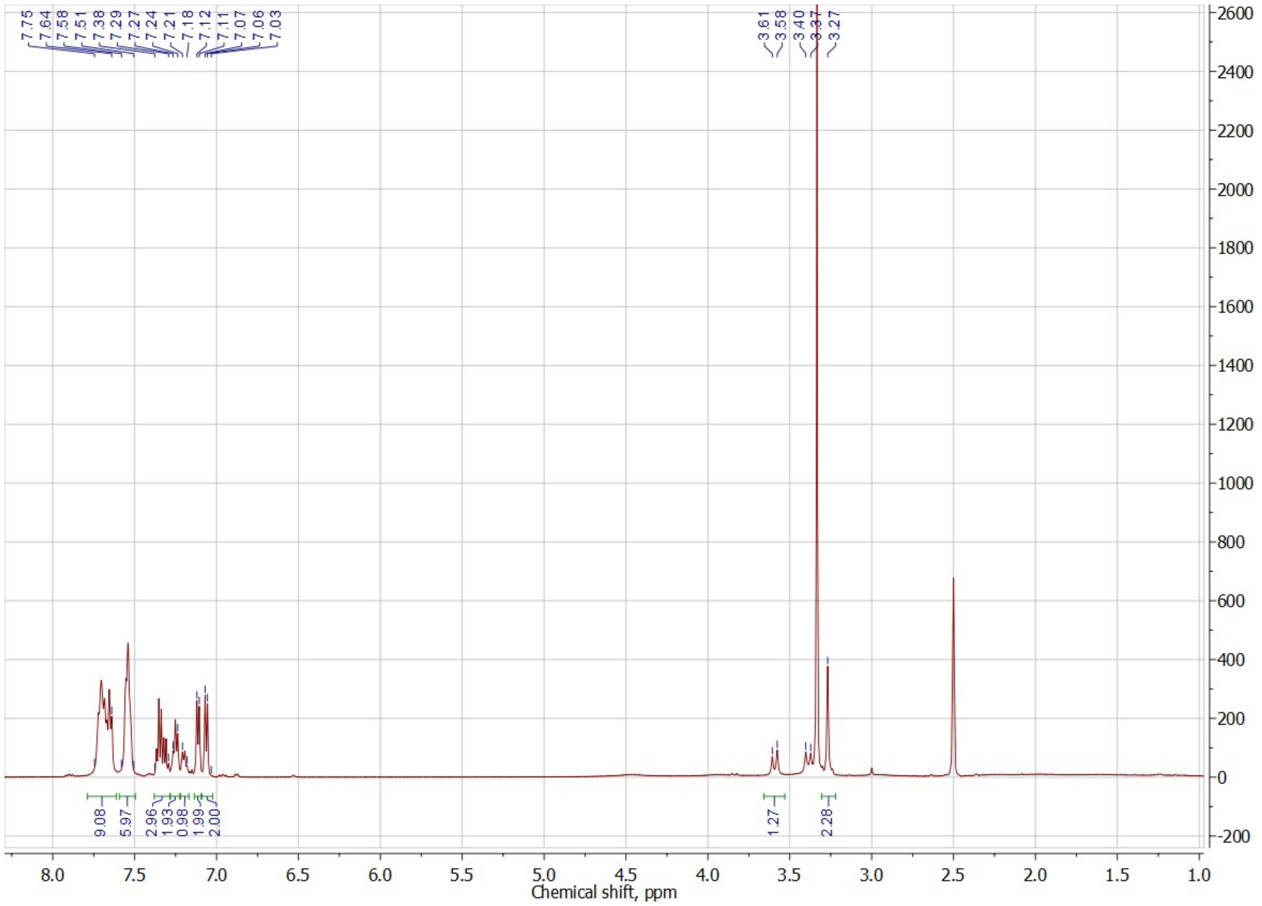


Figure S31. ^{1}H NMR spectrum of **9** in DMSO-d$_6$.

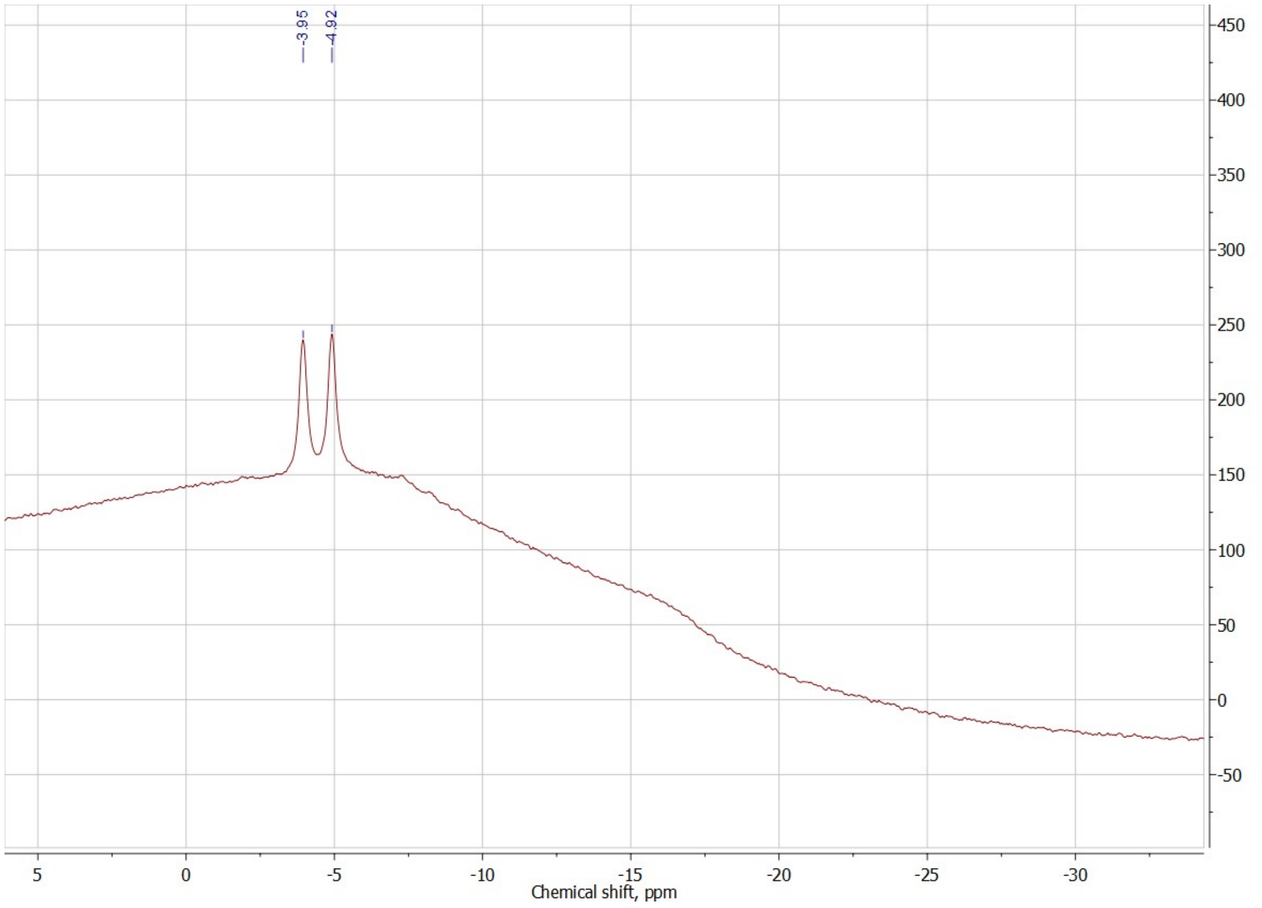


Figure S32. ^{11}B{^{1}H} NMR spectrum of **9** in DMSO-d$_6$.

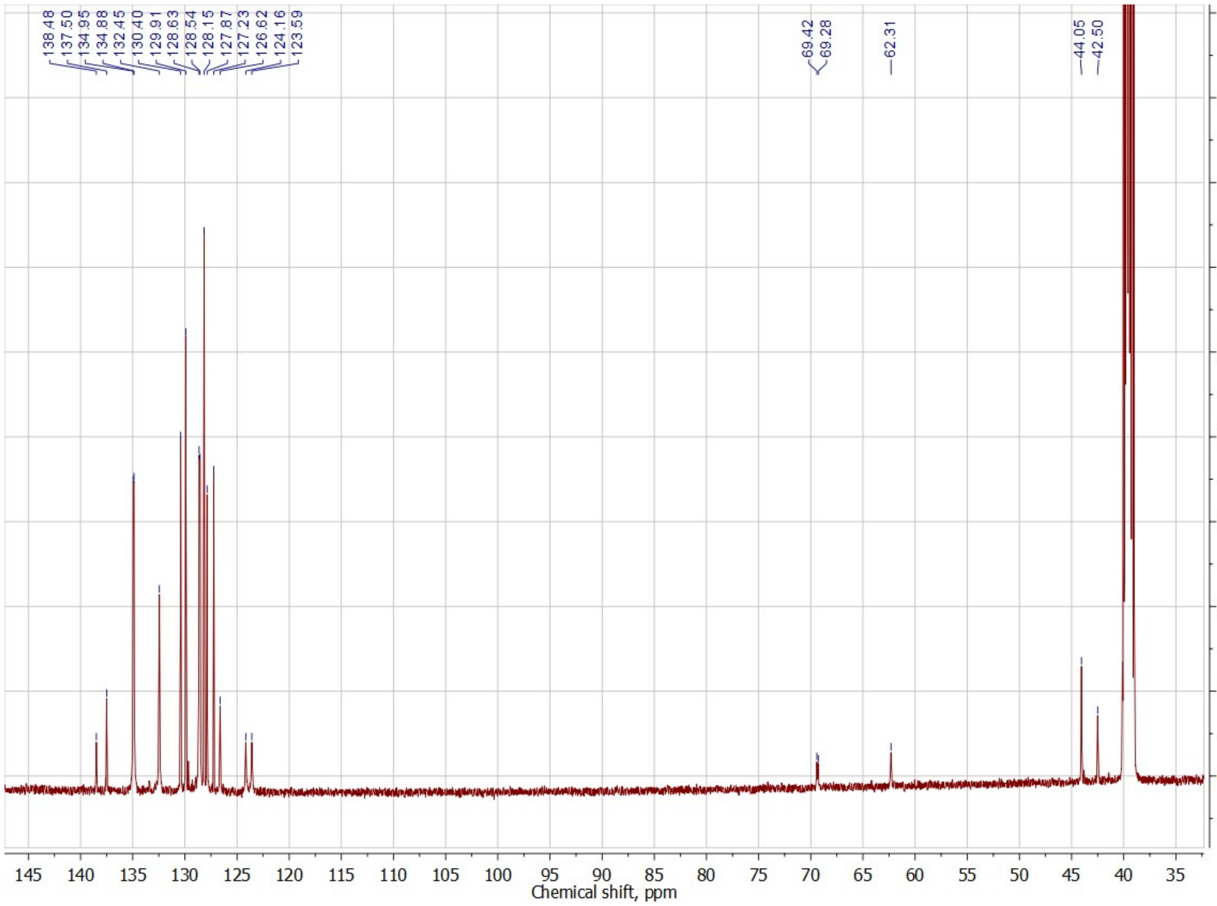


Figure S33. $^{13}C\{^1H\}$ NMR spectrum of **9** in DMSO-d$_6$.

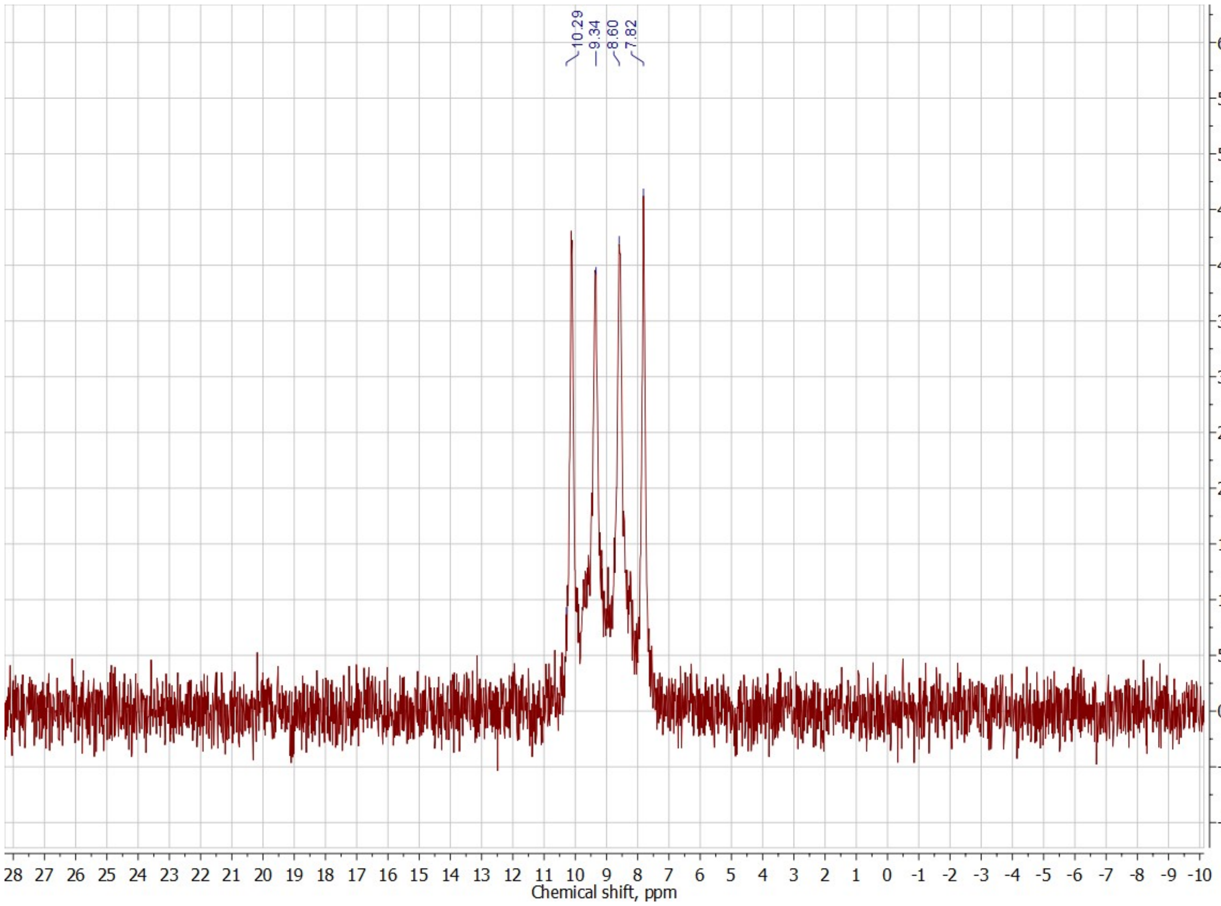


Figure S34. $^{31}P\{^1H\}$ NMR spectrum of **9** in DMSO-d$_6$.

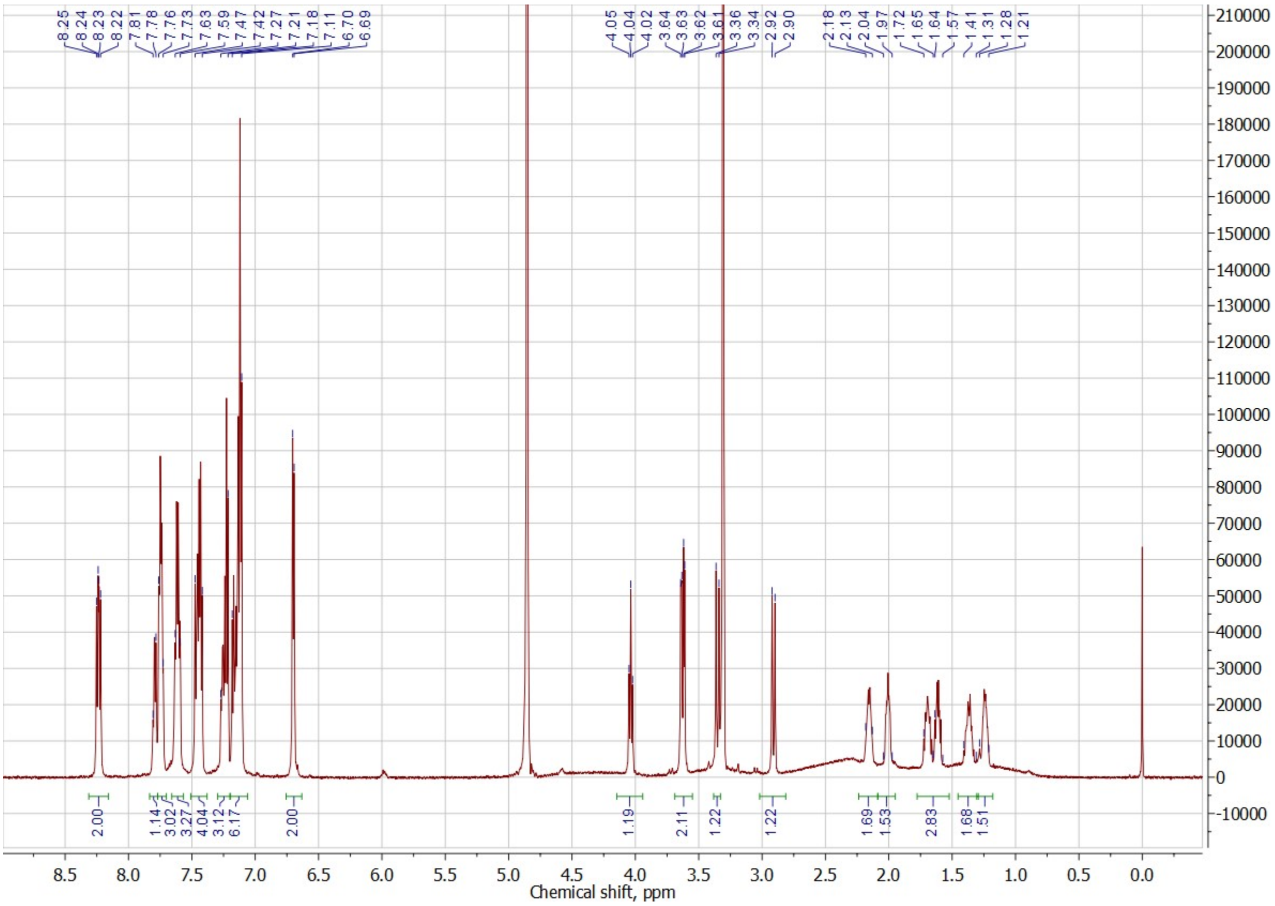


Figure S35. ^{1}H NMR spectrum of **10** in CD_3OD.

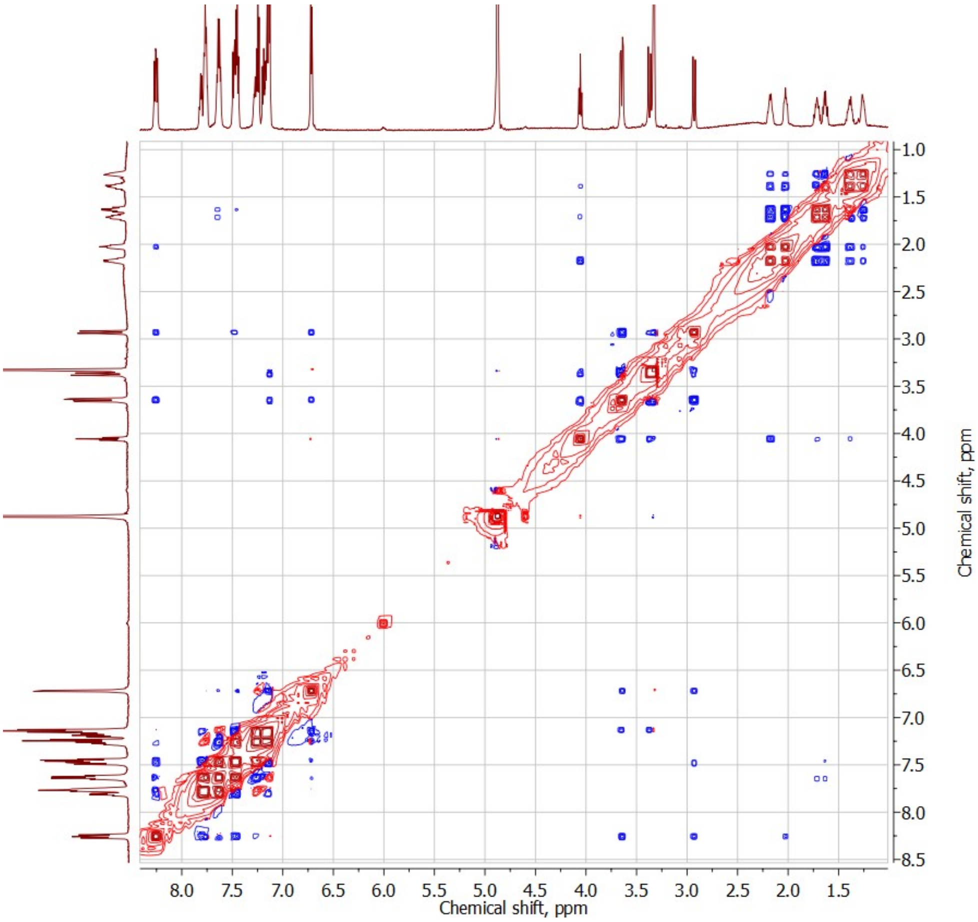


Figure S36. ^{1}H^{1}H NOESY NMR spectrum of **10** in CD_3OD.

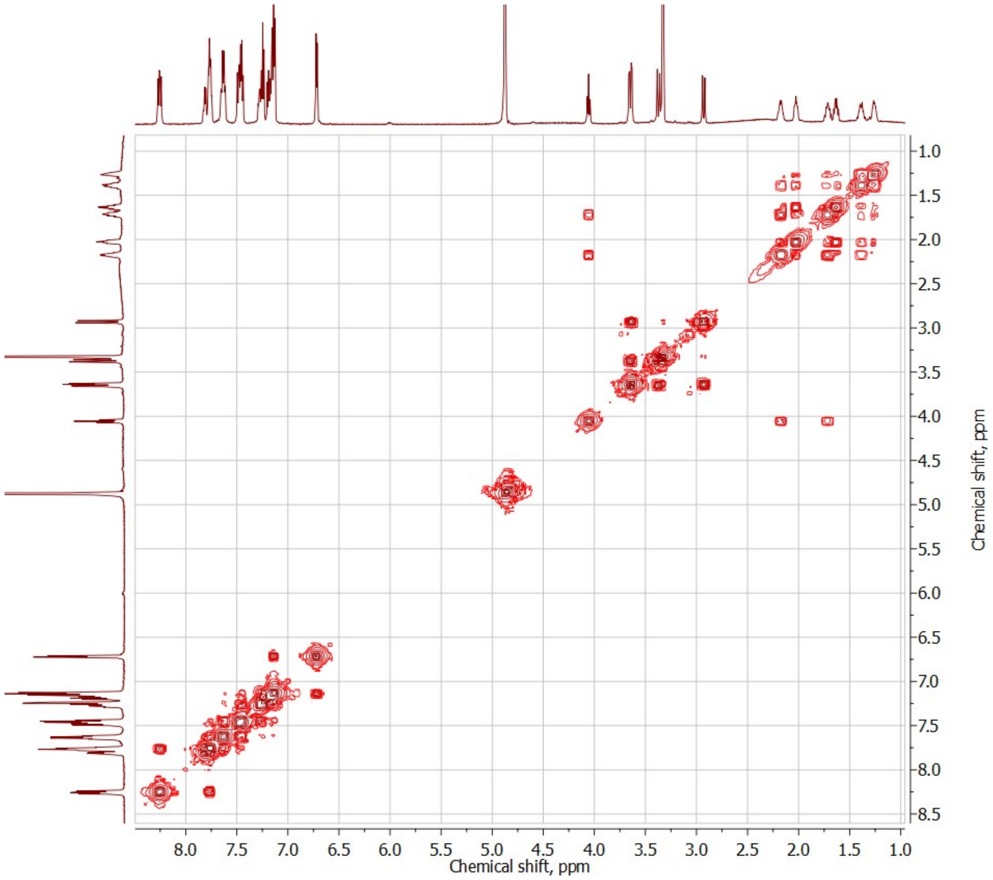


Figure S37. $^1H^1H$ COSY NMR spectrum of **10** in CD_3OD.

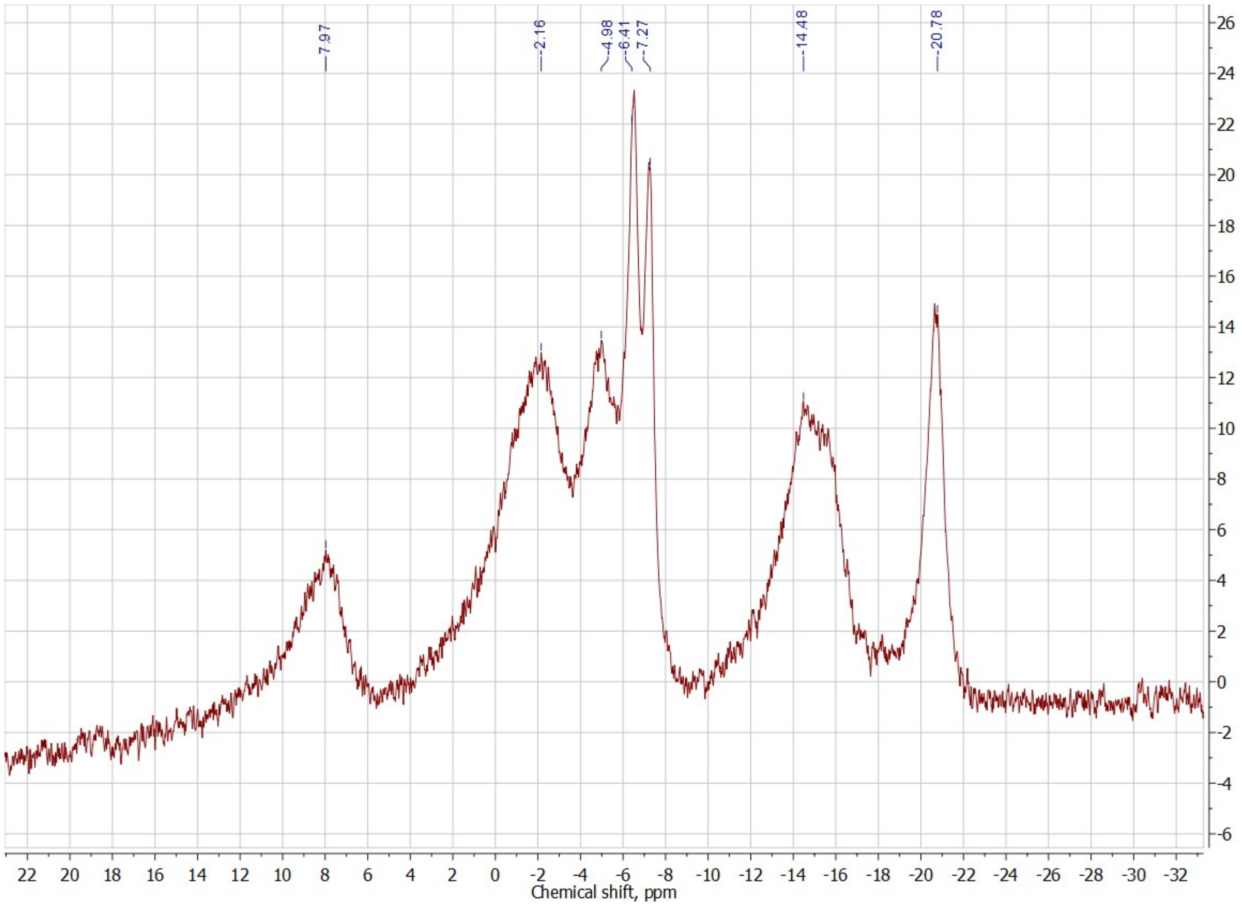


Figure S38. $^{11}B\{^1H\}$ NMR spectrum of **10** in CD_3OD.

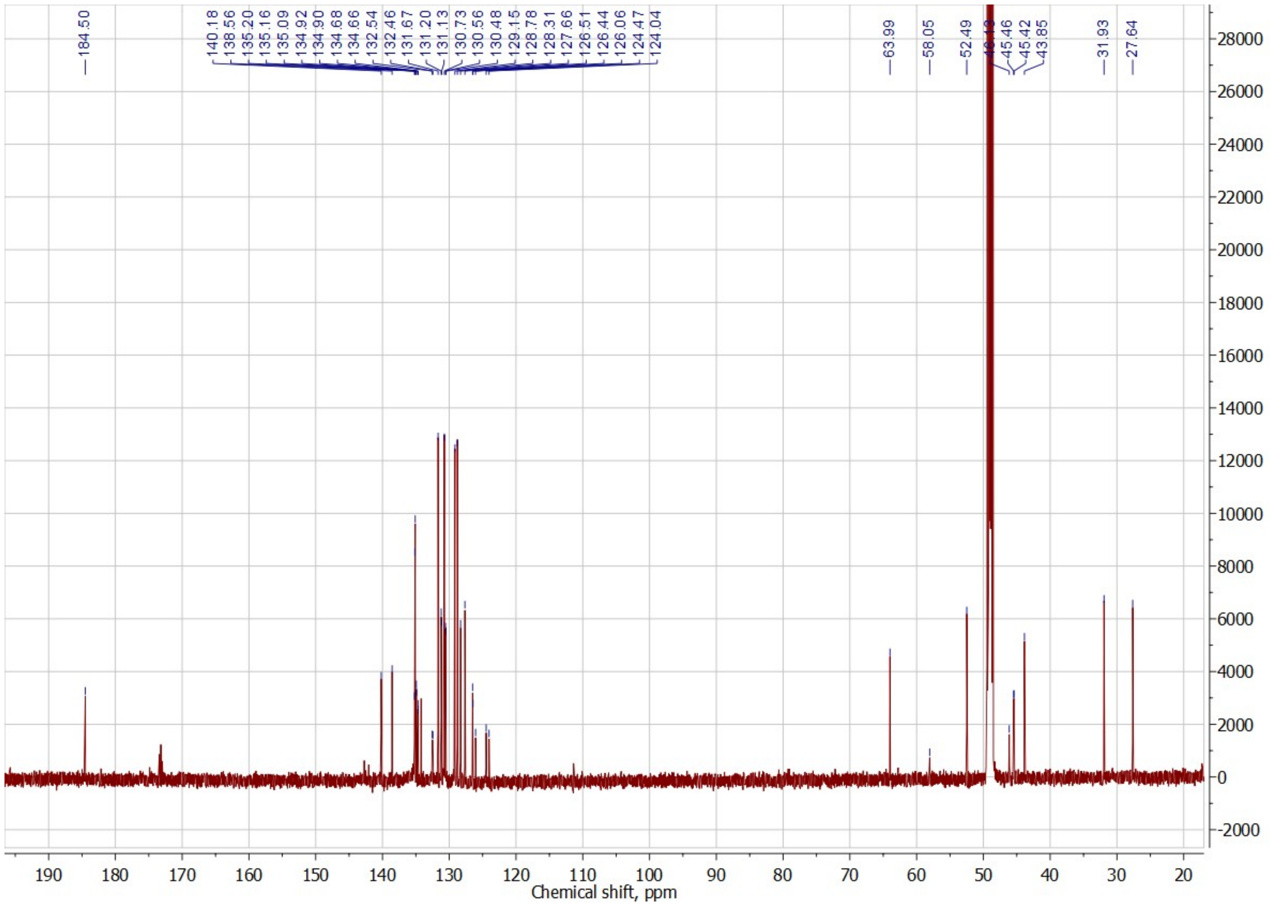


Figure S39. $^{13}C\{^1H\}$ NMR spectrum of **10** in CD_3OD.

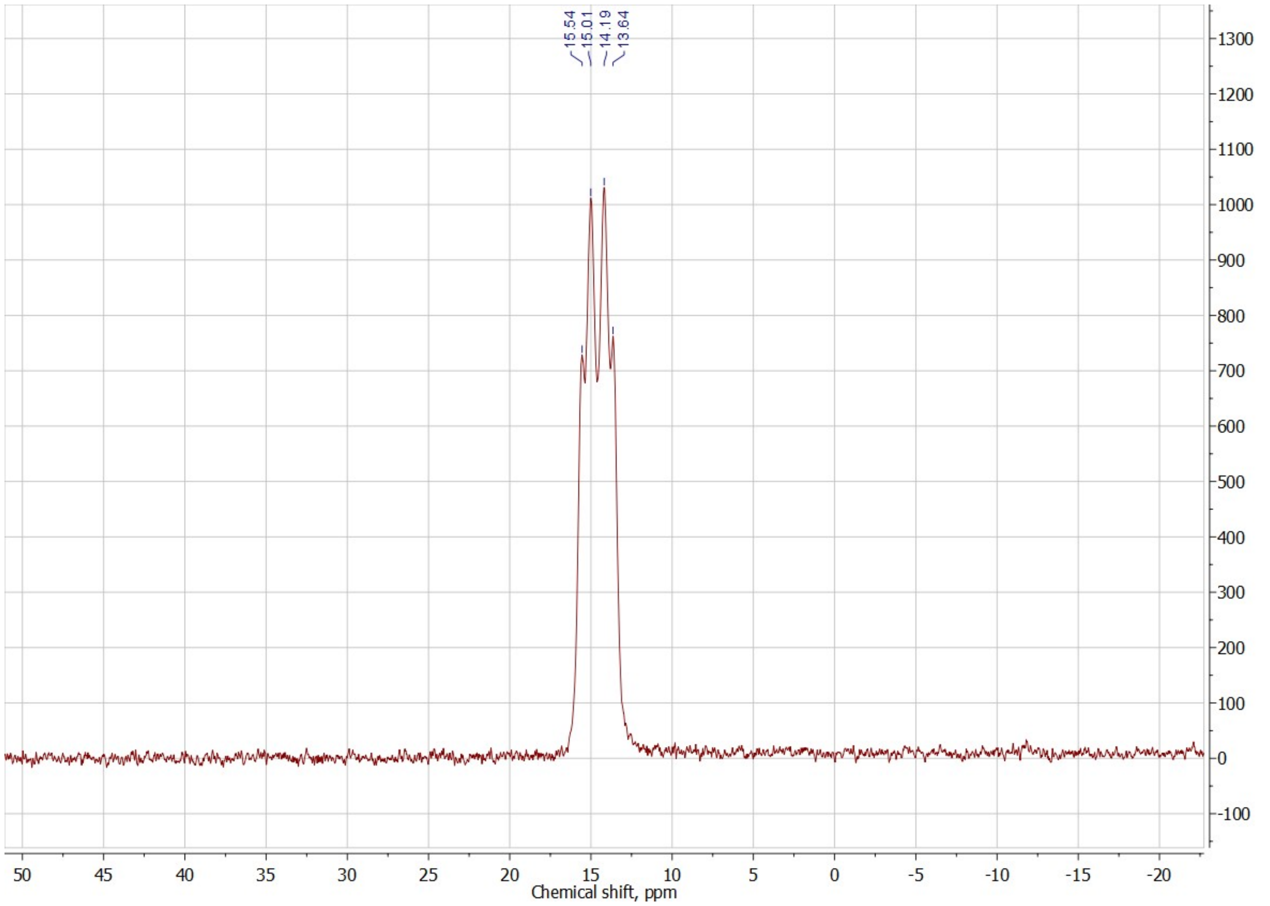


Figure S40. $^{31}P\{^1H\}$ NMR spectrum of **10** in CD_3OD.

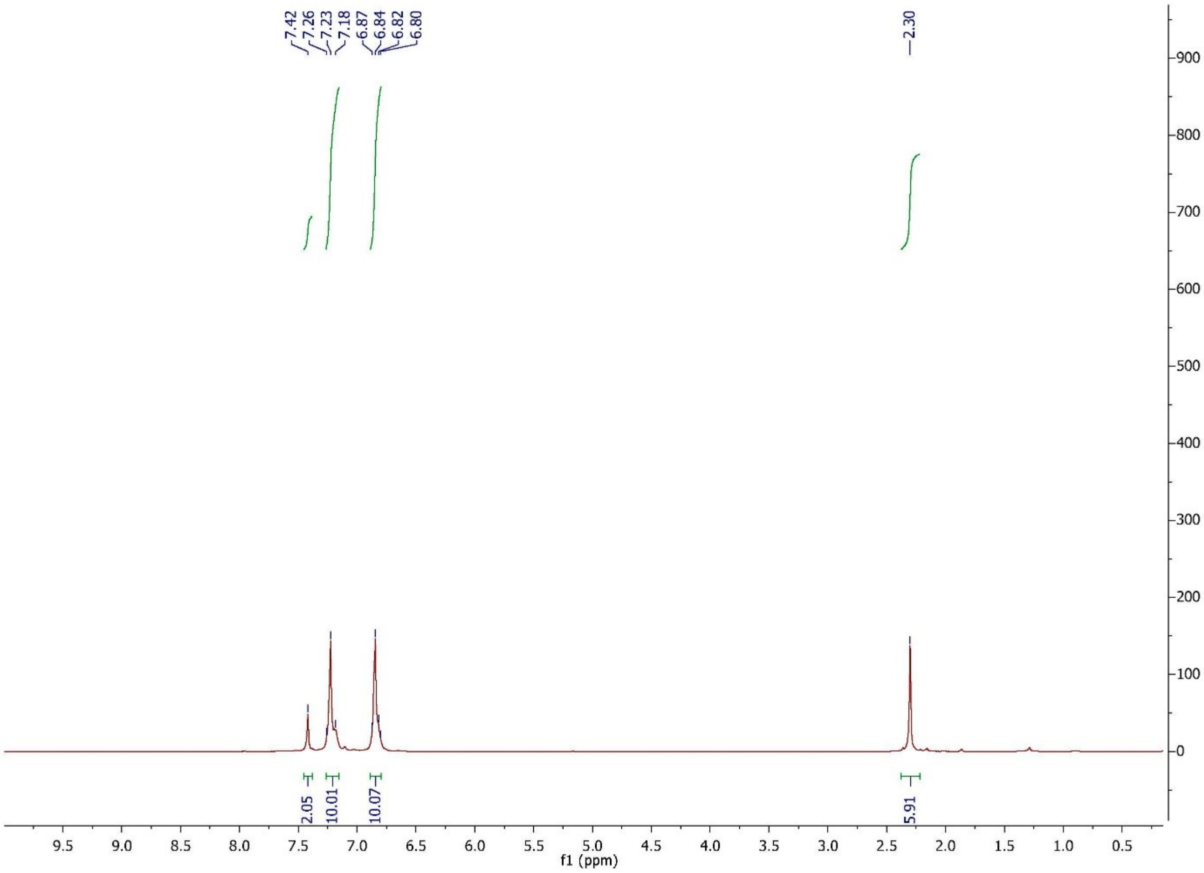


Figure S41. ^{1}H NMR spectrum of **11** in $CDCl_3$.

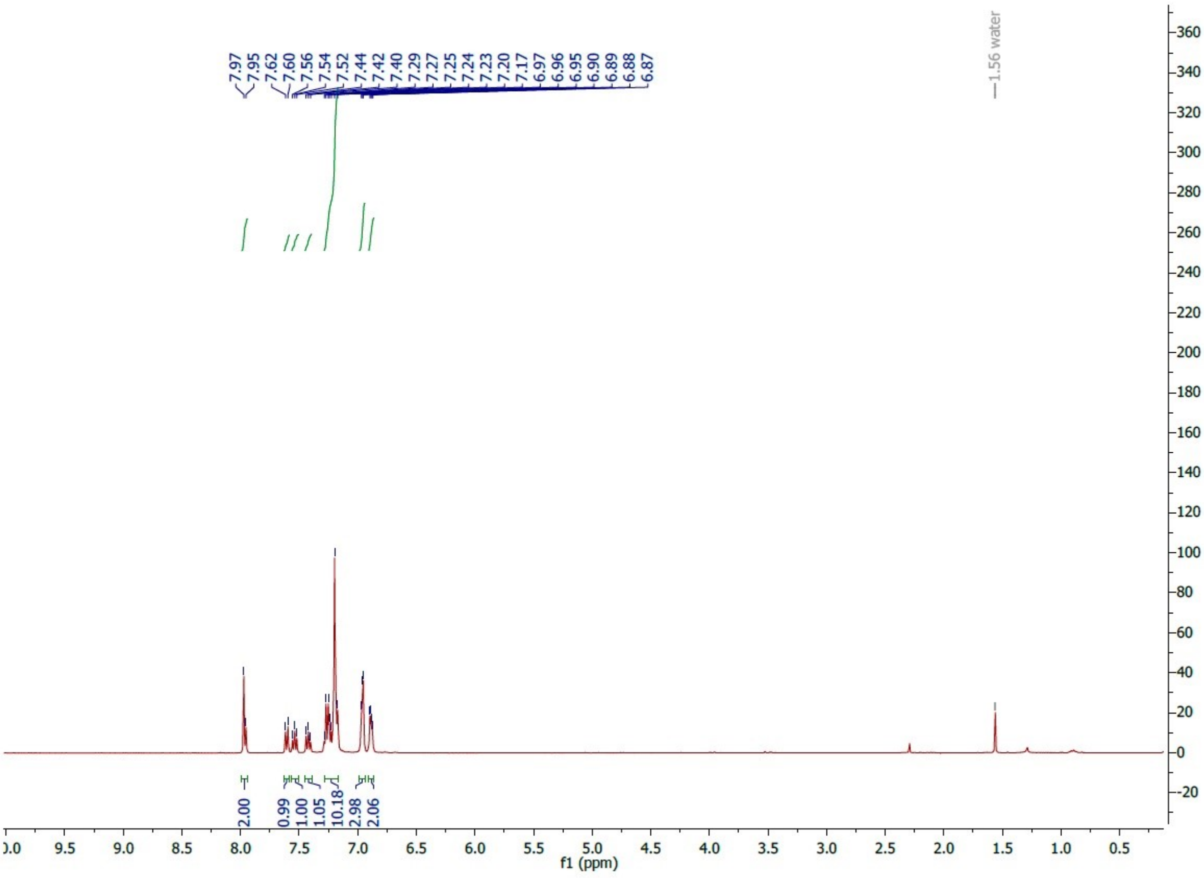


Figure S42. ^{1}H NMR spectrum of **12** in $CDCl_3$.

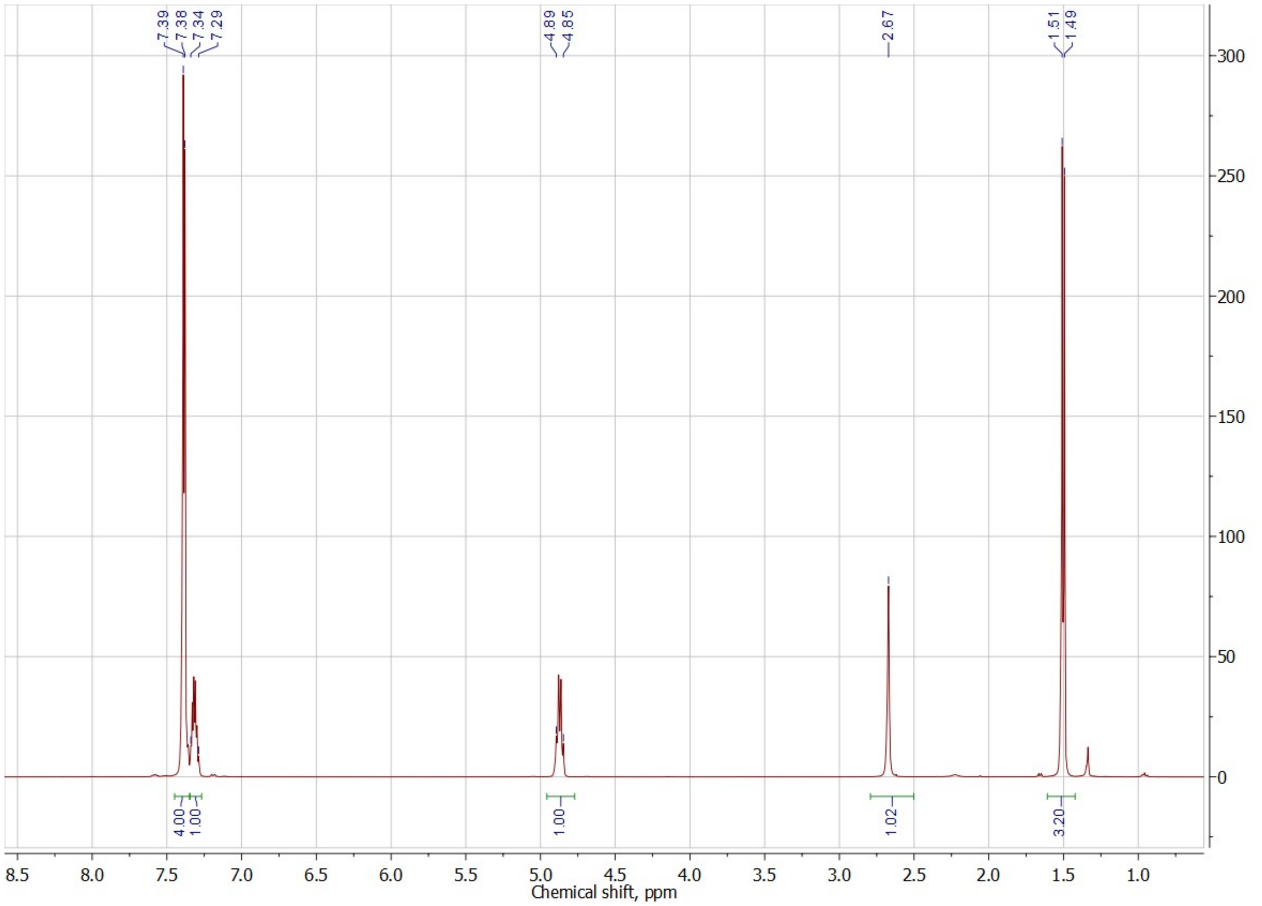


Figure S43. ^{1}H NMR spectrum of 1-phenylethanol (**15a**) in $CDCl_3$.

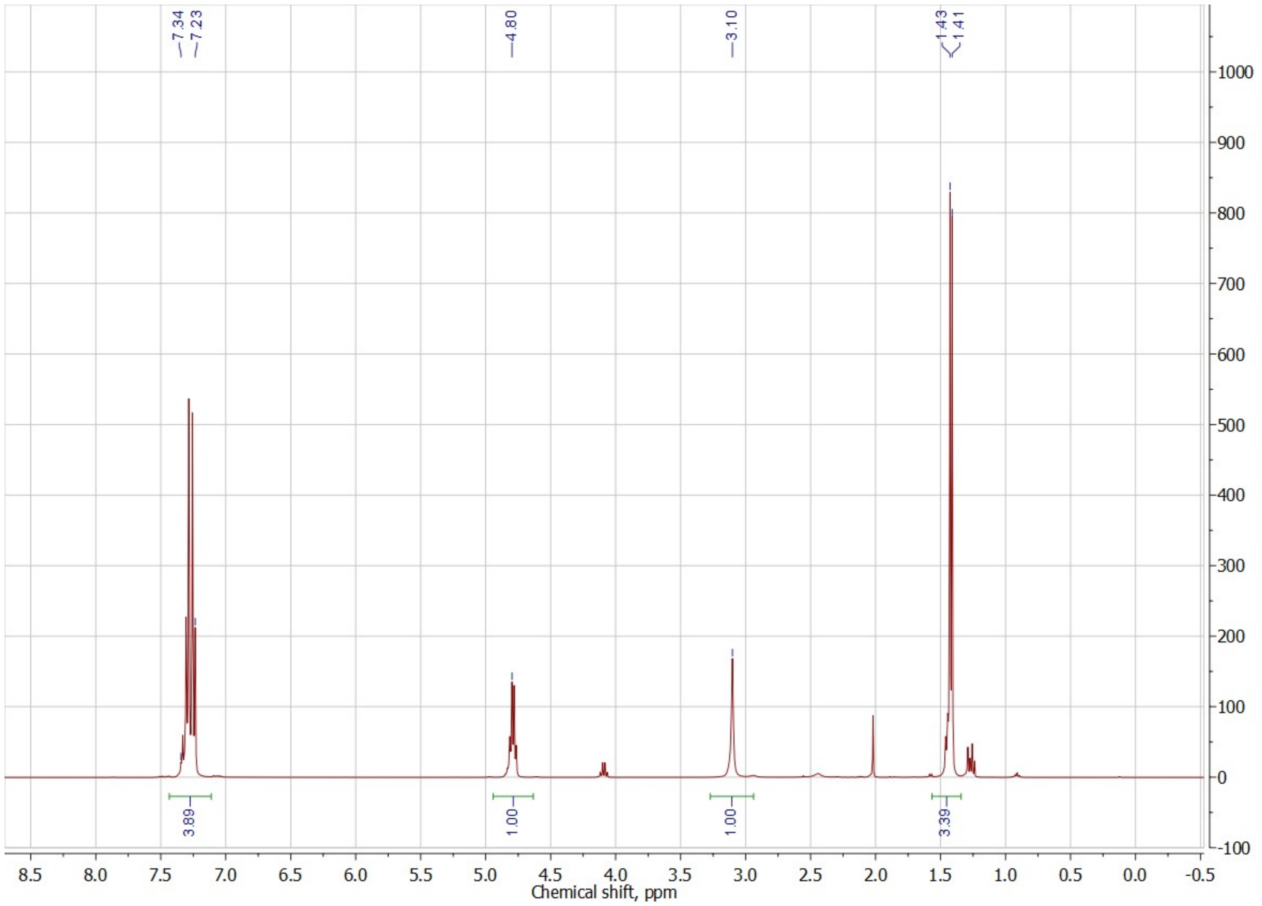


Figure S44. ^{1}H NMR spectrum of 1-(4-chlorophenyl)ethanol (**15b**) in $CDCl_3$.

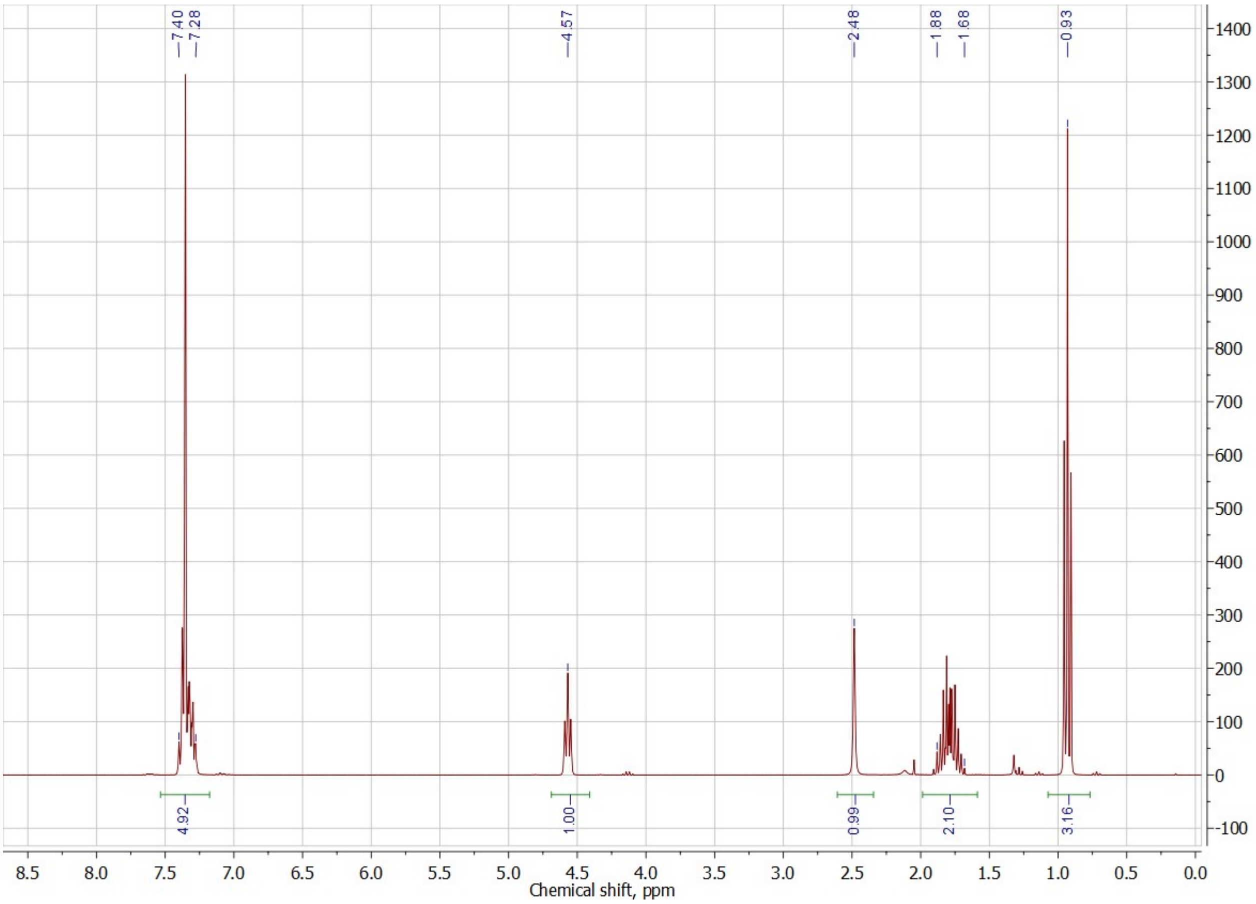


Figure S45. ^{1}H NMR spectrum of 1-Phenyl-1-propanol (**15c**) in CDCl$_3$.

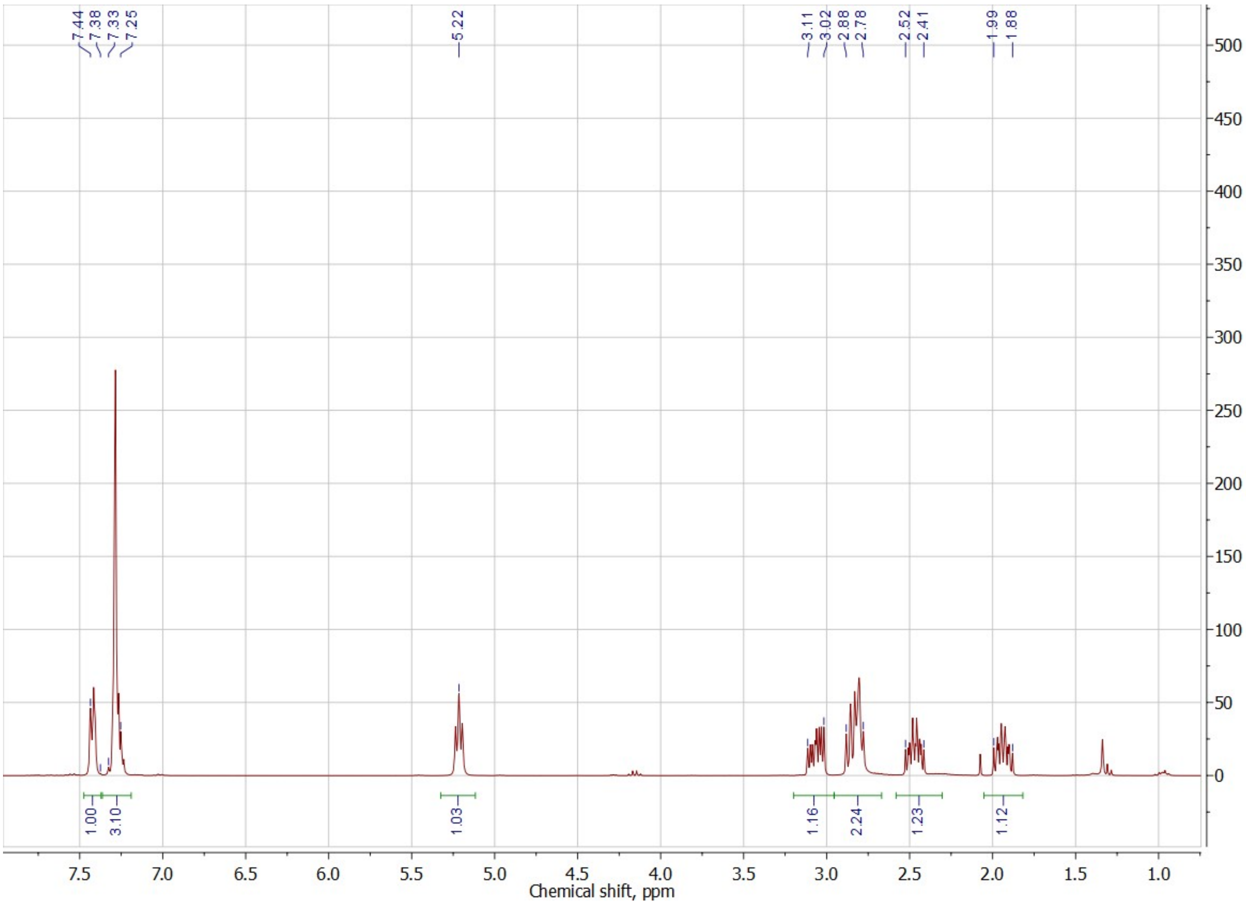


Figure S46. ^{1}H NMR spectrum of 1-indanol(**15d**) in CDCl$_3$.

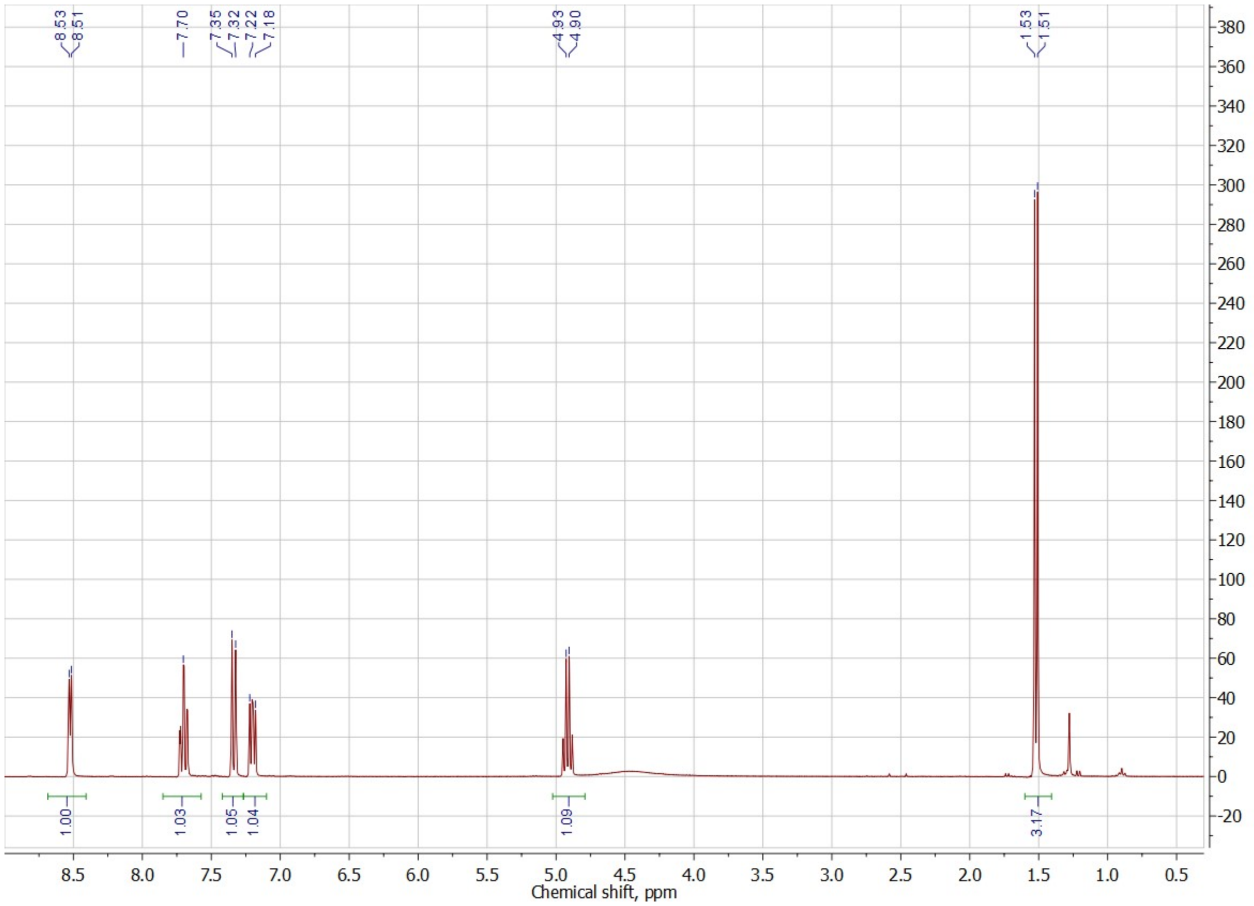


Figure S47. ^{1}H NMR spectrum of 1-(Pyridin-2-yl)ethanol (**15e**) in $CDCl_3$.

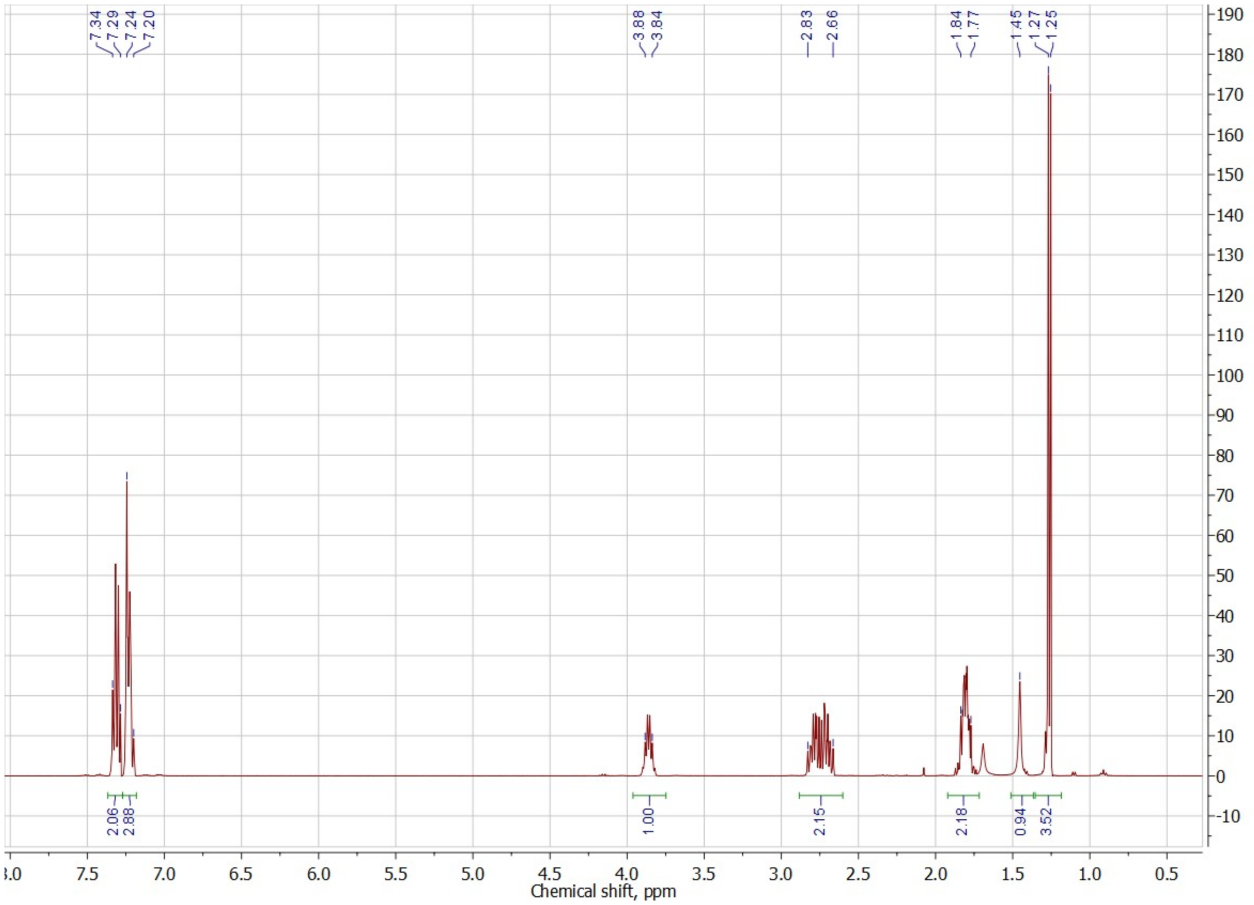


Figure S48. ^{1}H NMR spectrum of 4-Phenylbutan-2-ol (**15f**) in $CDCl_3$.

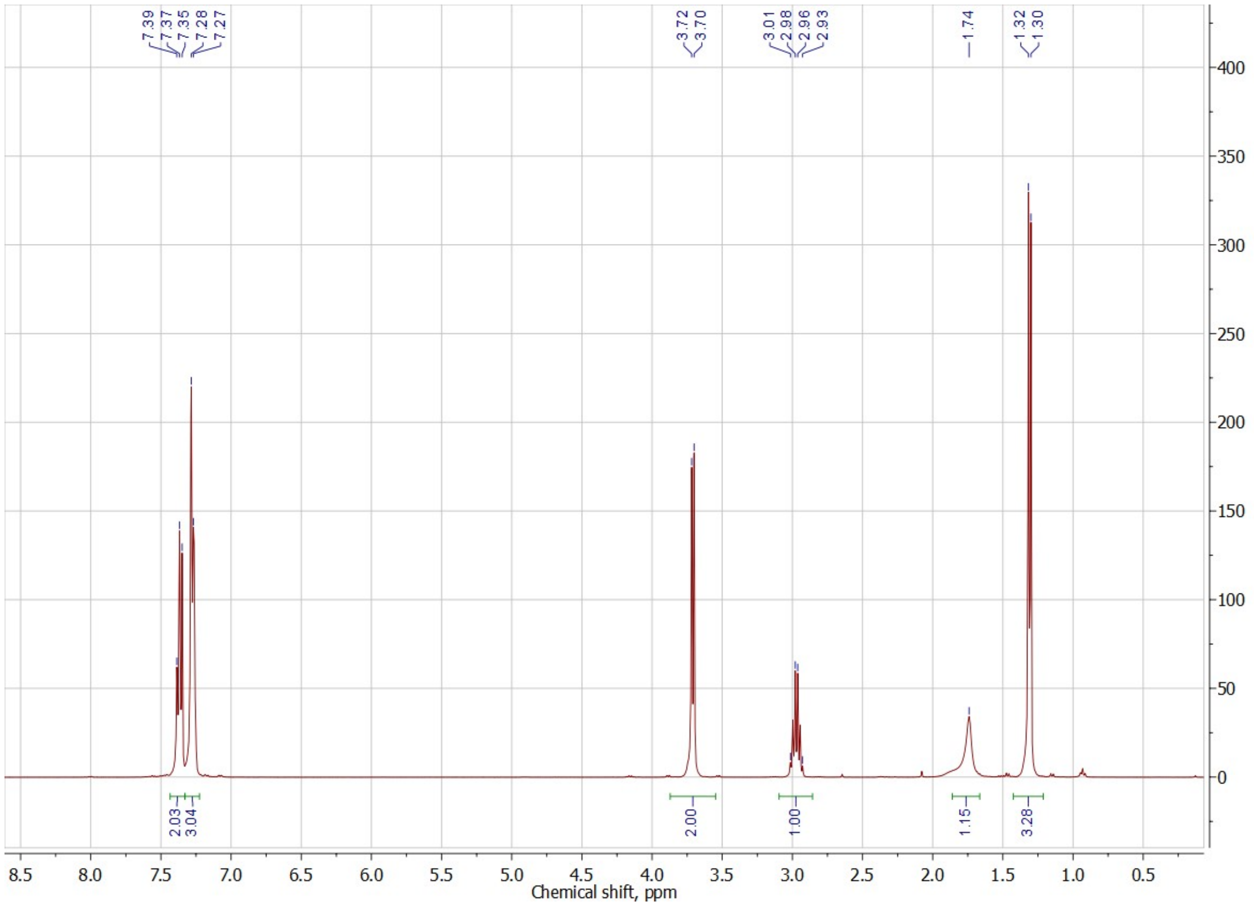


Figure S49. ^{1}H NMR spectrum of 2-phenylpropan-1-ol (**15g**) in $CDCl_3$.

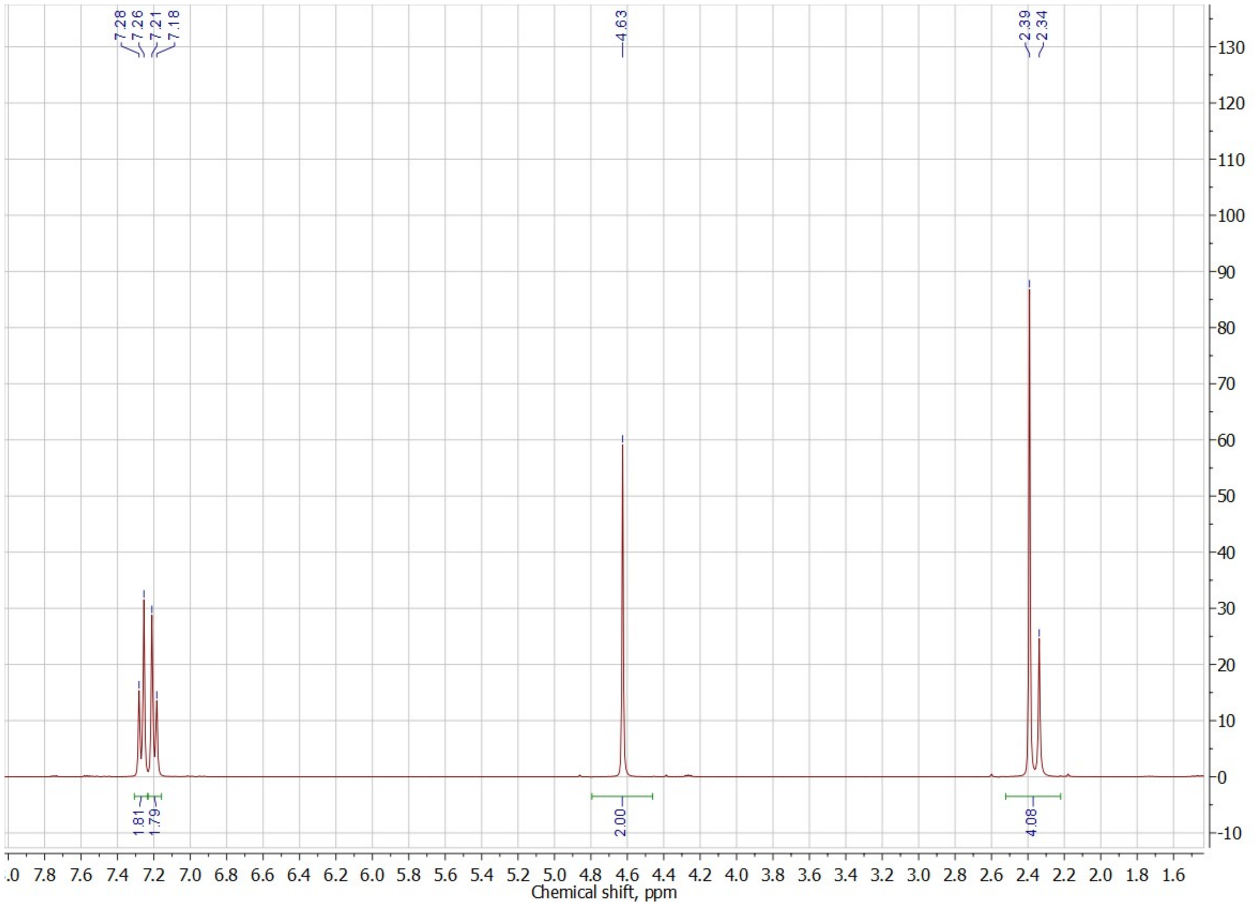


Figure S50. ^{1}H NMR spectrum of 4-methylbenzyl alcohol (**15h**) in $CDCl_3$.

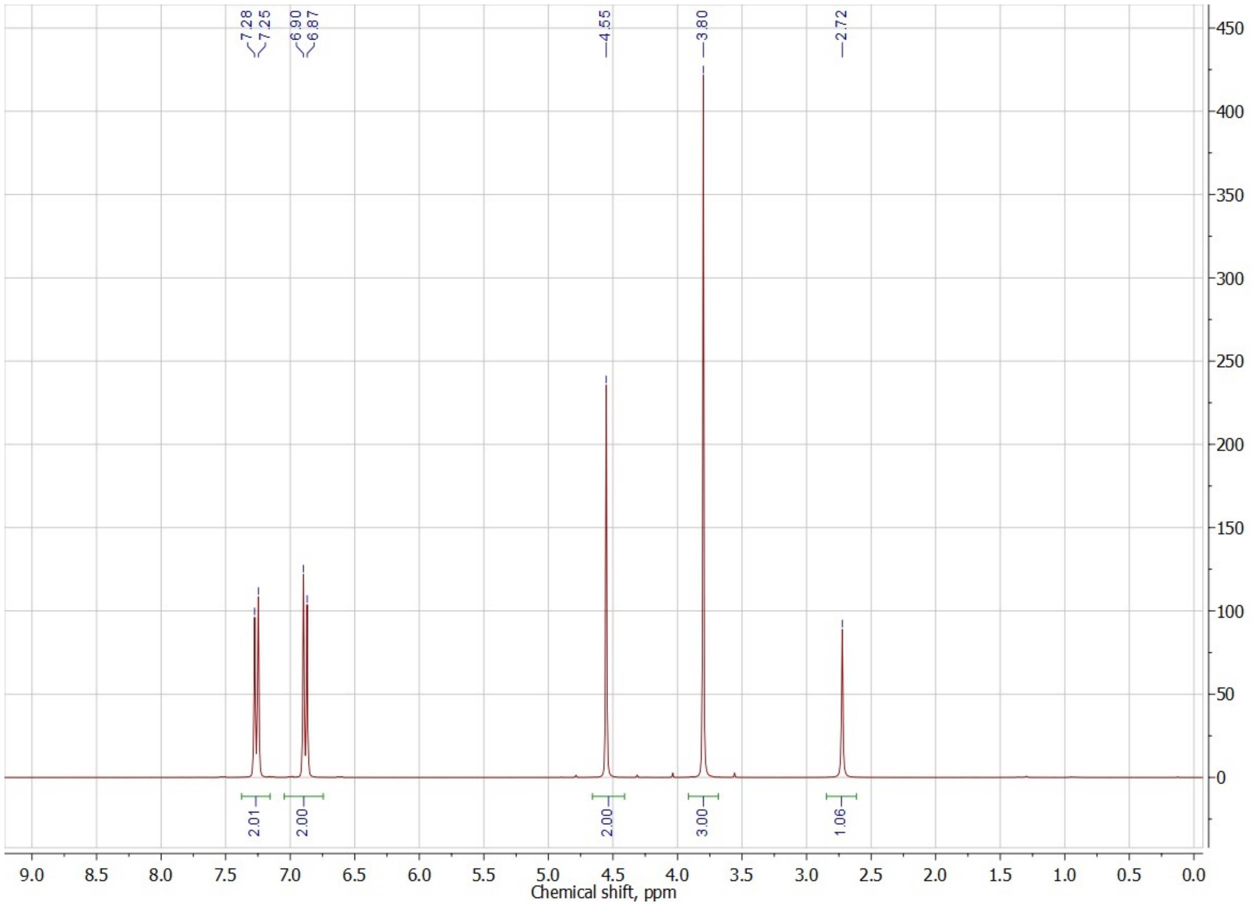


Figure S51. ^{1}H NMR spectrum of 4-methoxybenzyl alcohol (**15i**) in CDCl$_3$.

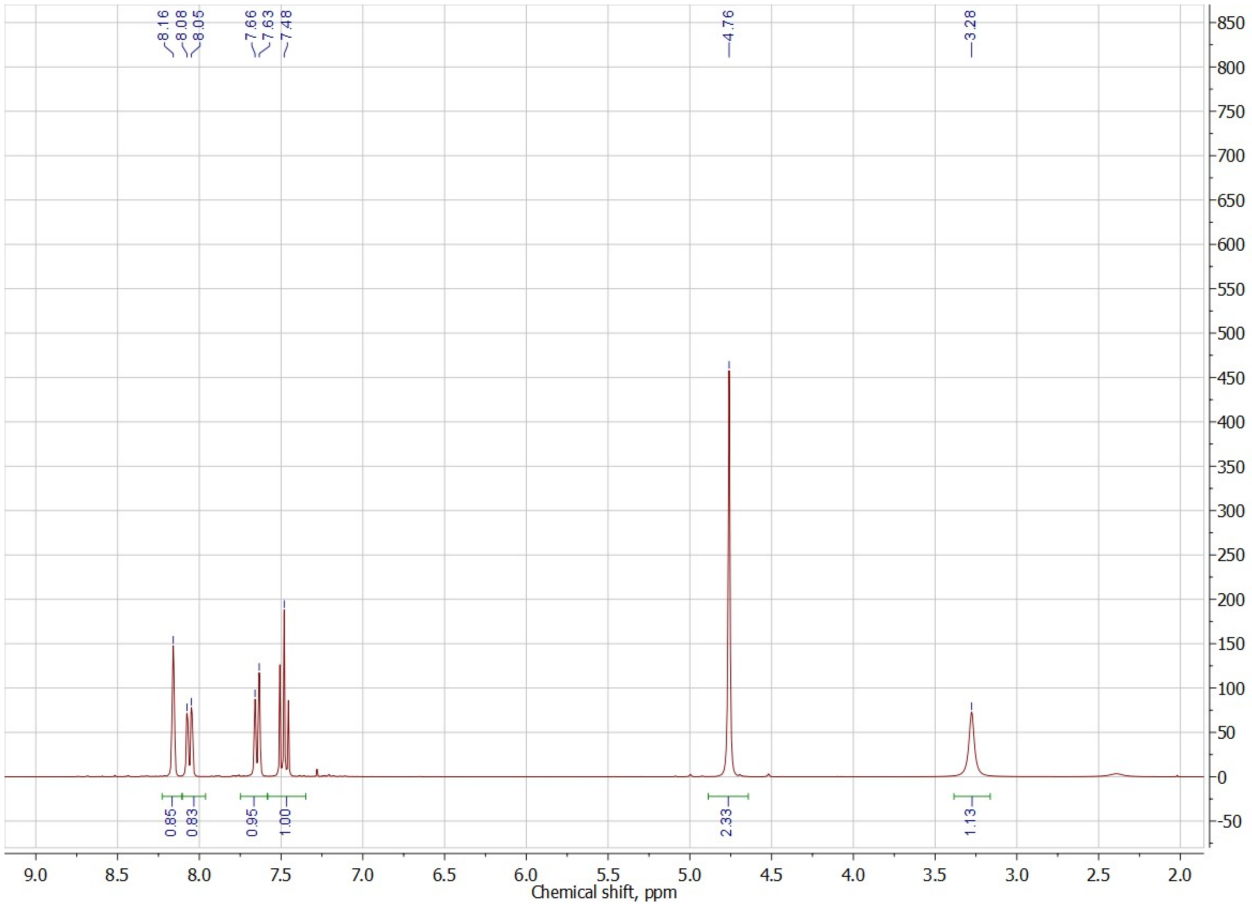


Figure S52. ^{1}H NMR spectrum of 4-nitrobenzyl alcohol (**15j**) in CDCl$_3$.

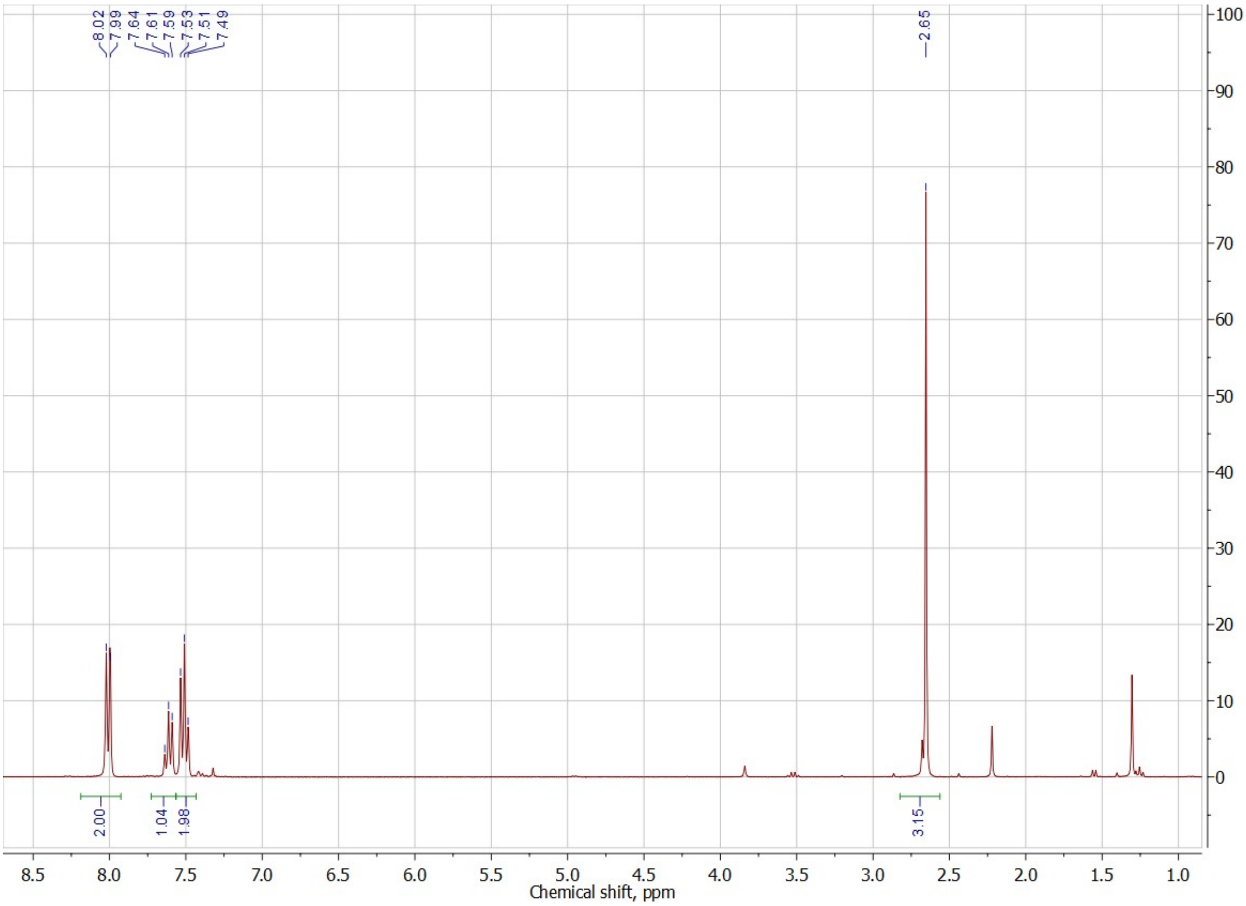


Figure S53. ^{1}H NMR spectrum of the reaction mixture after oxidation of (±)-1-phenylethanol with acetone catalyzed by complex **8** ($CDCl_3$).

HRMS (ESI +) Spectra

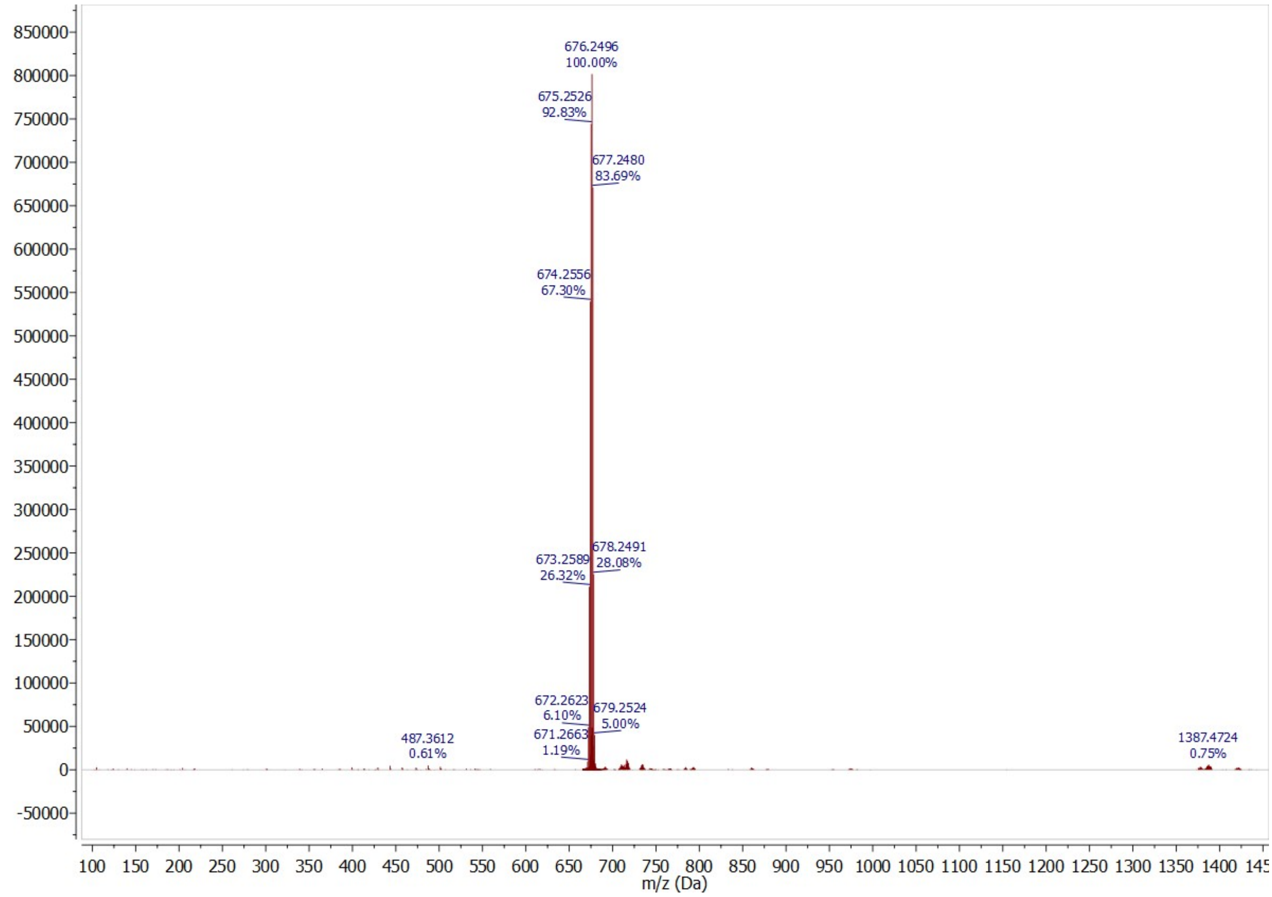


Figure S54. The HRMS (ESI +) spectrum of complex **8**.

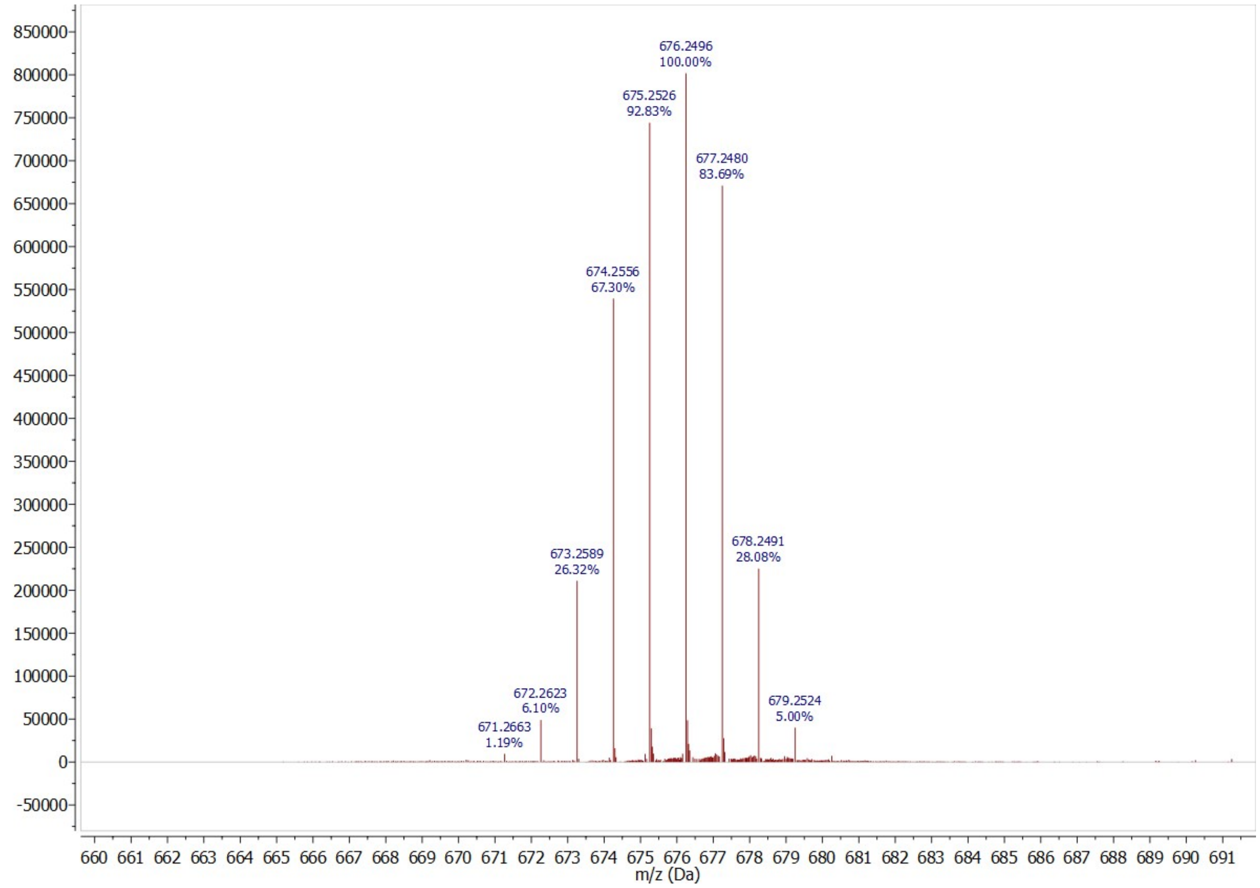


Figure S55. The HRMS (ESI +) spectrum of complex **8**.

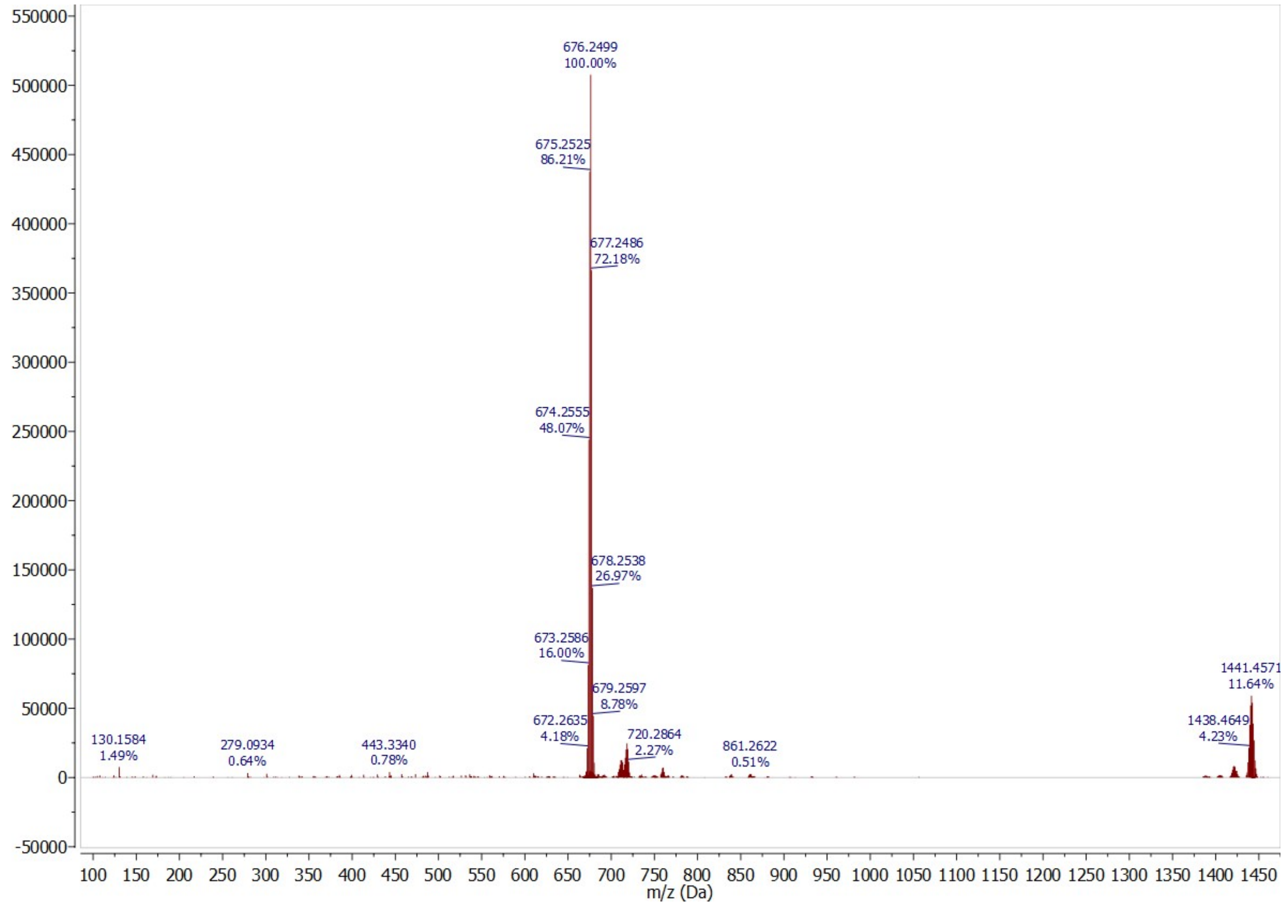


Figure S56. The HRMS (ESI +) spectrum of complex **9**.

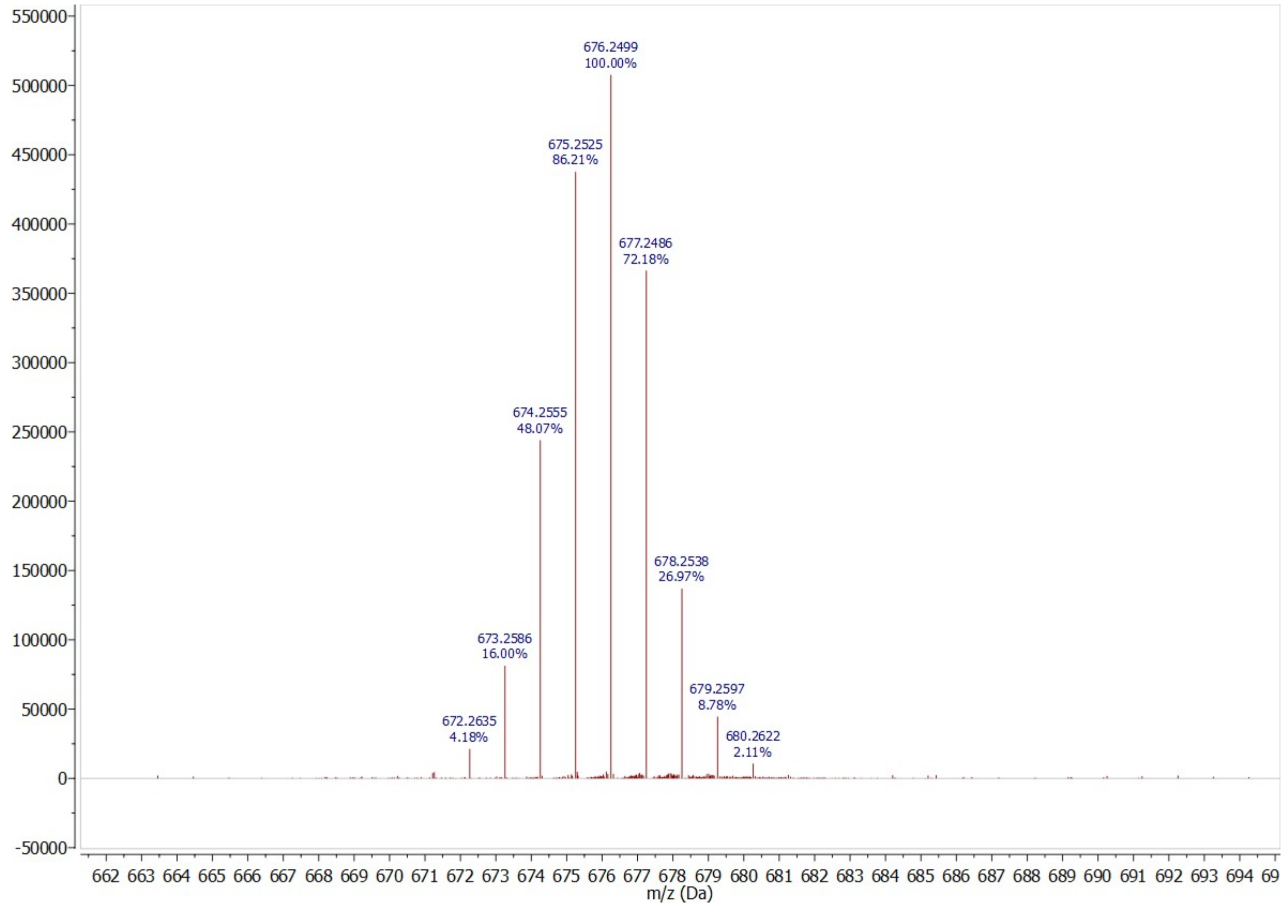


Figure S57. The HRMS (ESI +) spectrum of complex **9**.

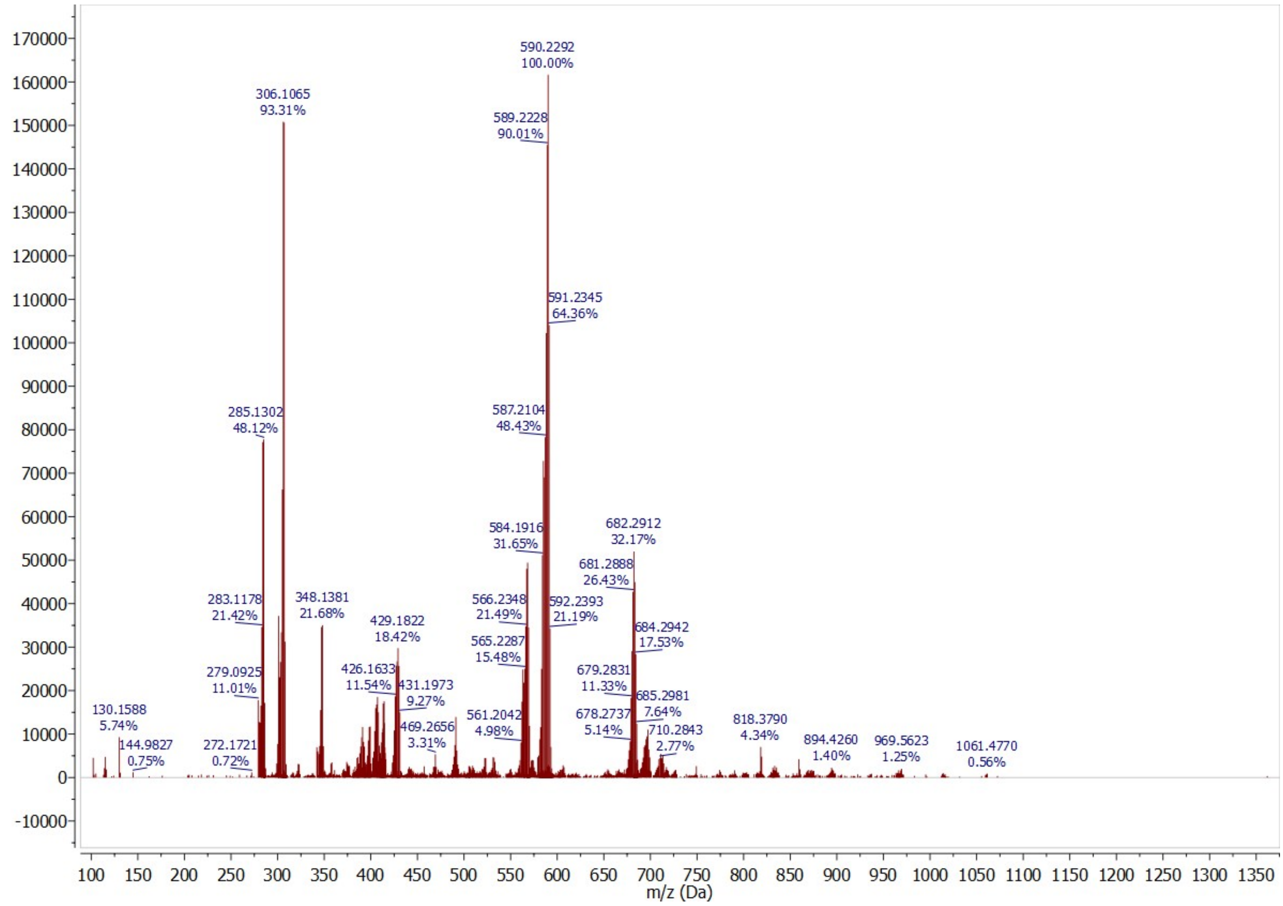


Figure S58. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol-d_8.

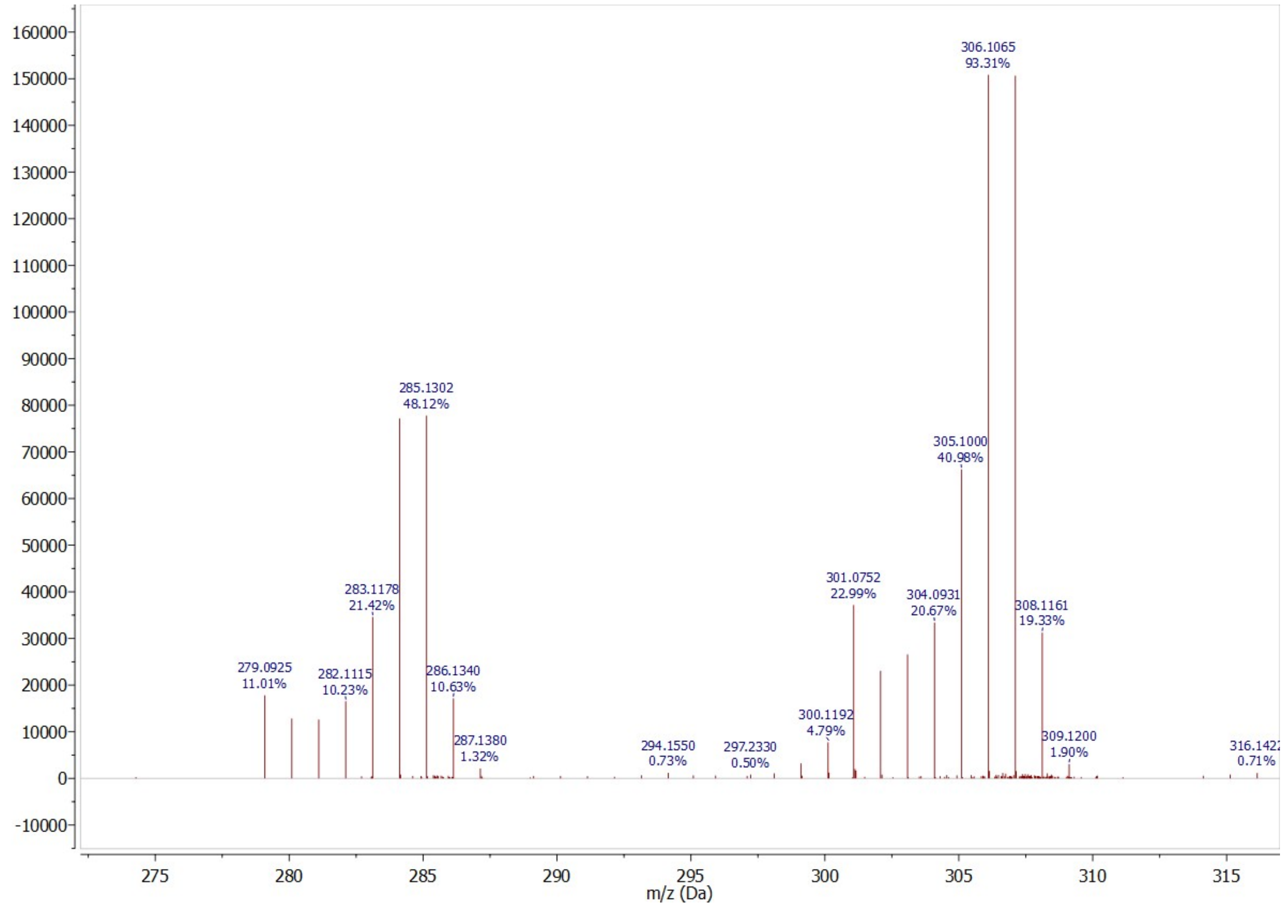


Figure S59. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol-d_8.

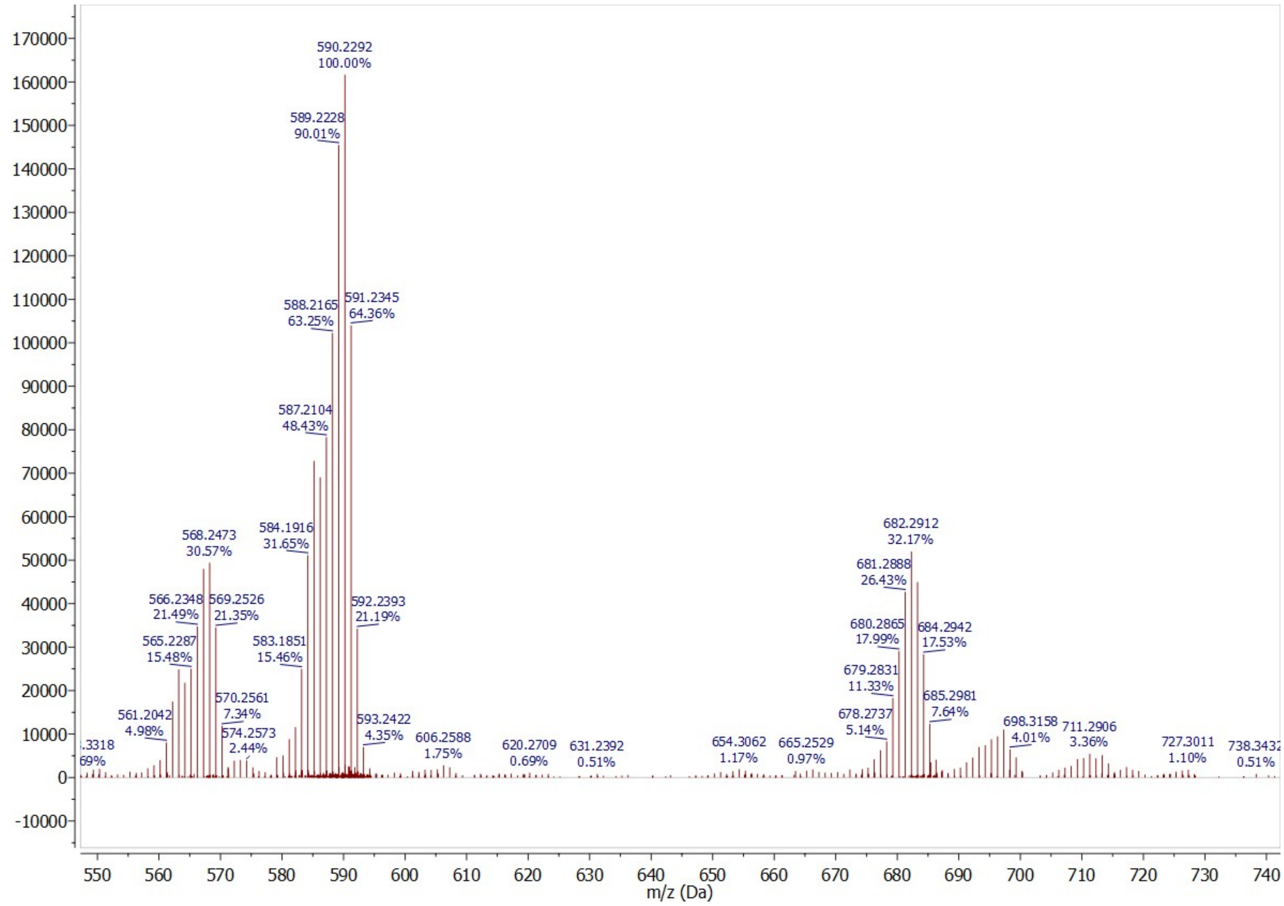


Figure S60. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol-d_8.

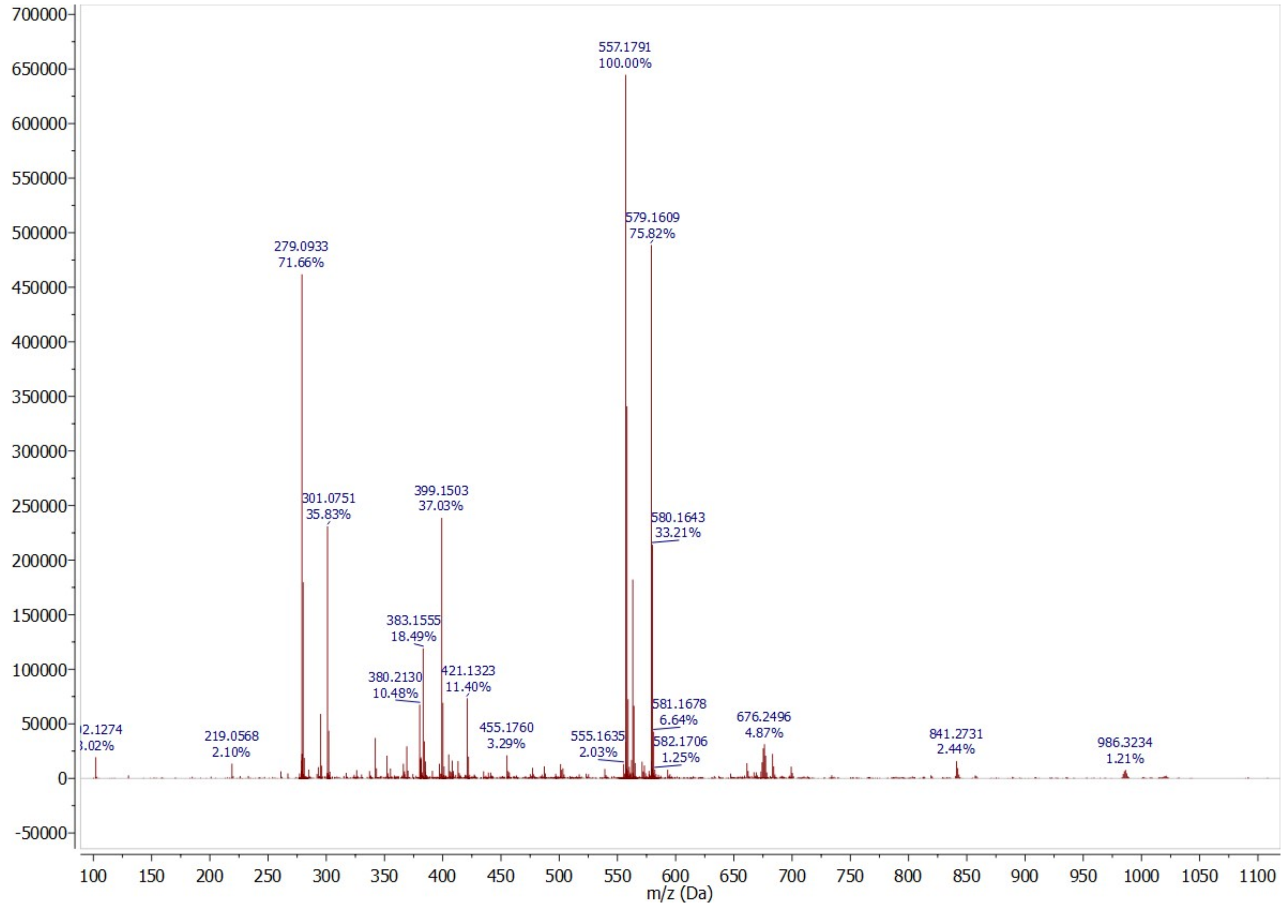


Figure S61. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol.

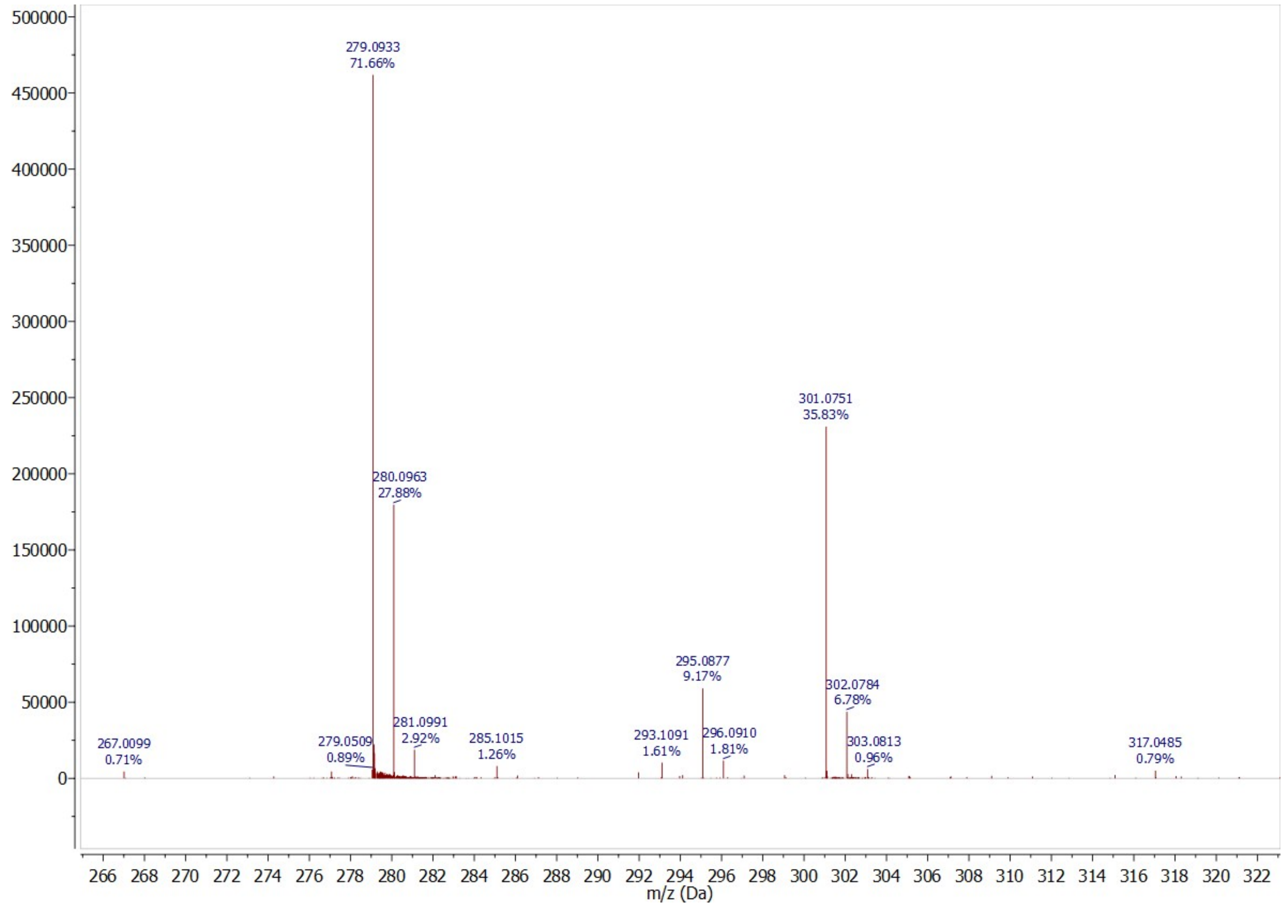


Figure S62. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol.

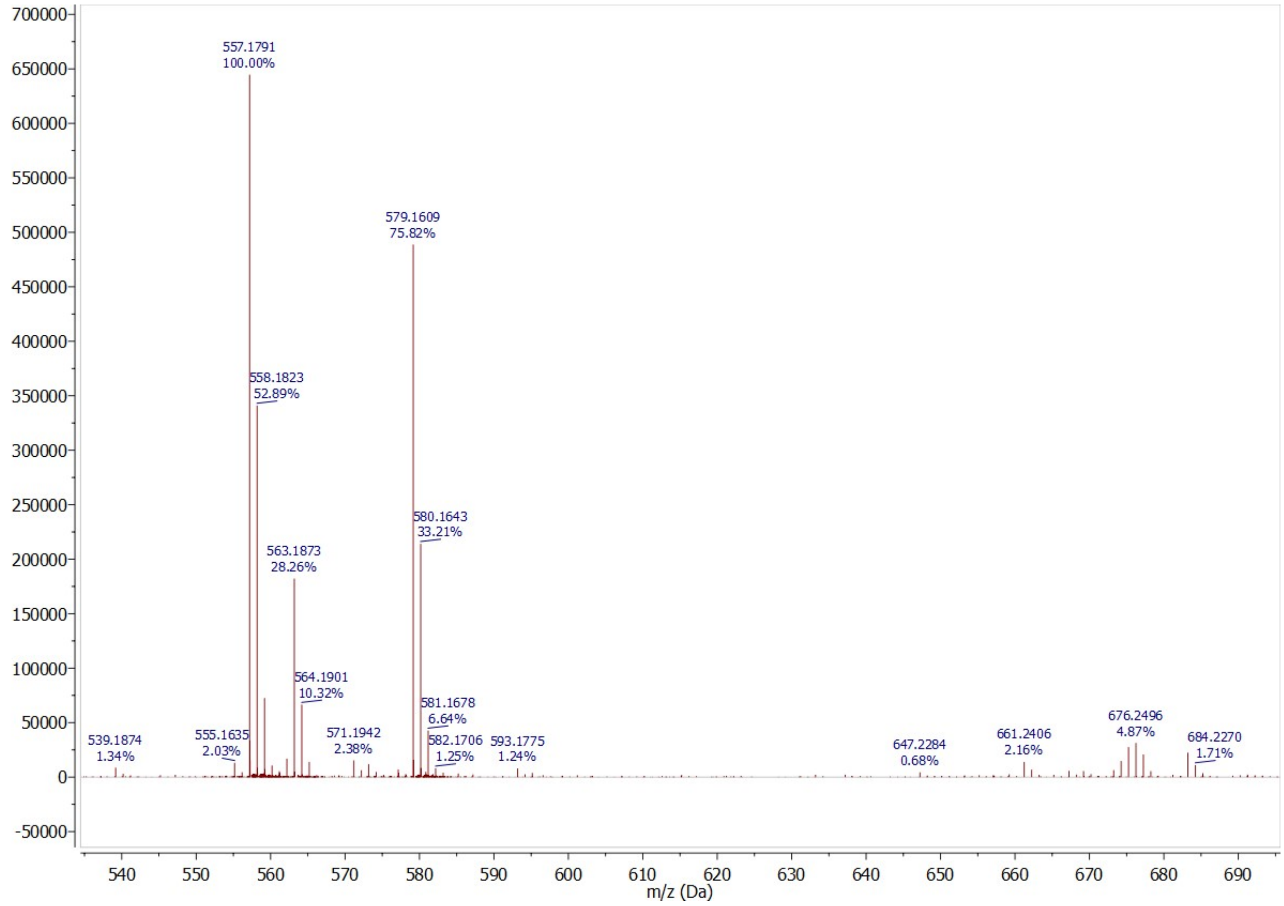
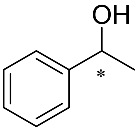
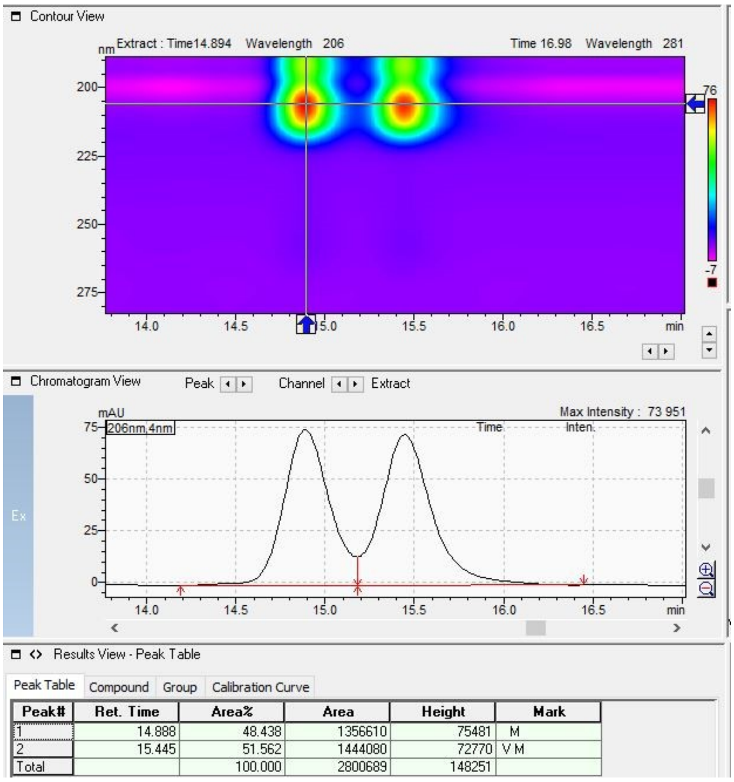


Figure S63. The HRMS (ESI +) spectrum of exchange reaction in acetone/isopropanol.

Chiral Chromatography





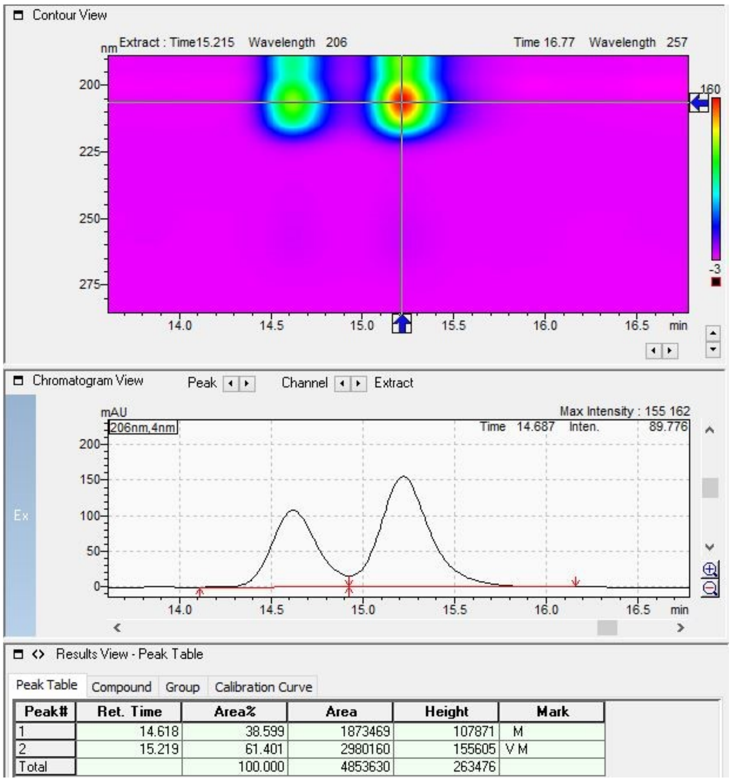
Extract : Time14.894 Wavelength 206

Time 16.98 Wavelength 281

Max Intensity : 73 951

Peak#	Ret. Time	Area%	Area	Height	Mark
1	14.888	48.438	1356610	75481	M
2	15.445	51.562	1444080	72770	V M
Total		100.000	2800689	148251	

Fig. S64. VM-1 rac Column IA-3 hept-IPA 99-1, 1 ml min, tR(1) = 14.89 min, tR(2) = 15.45 min



Extract : Time15.215 Wavelength 206

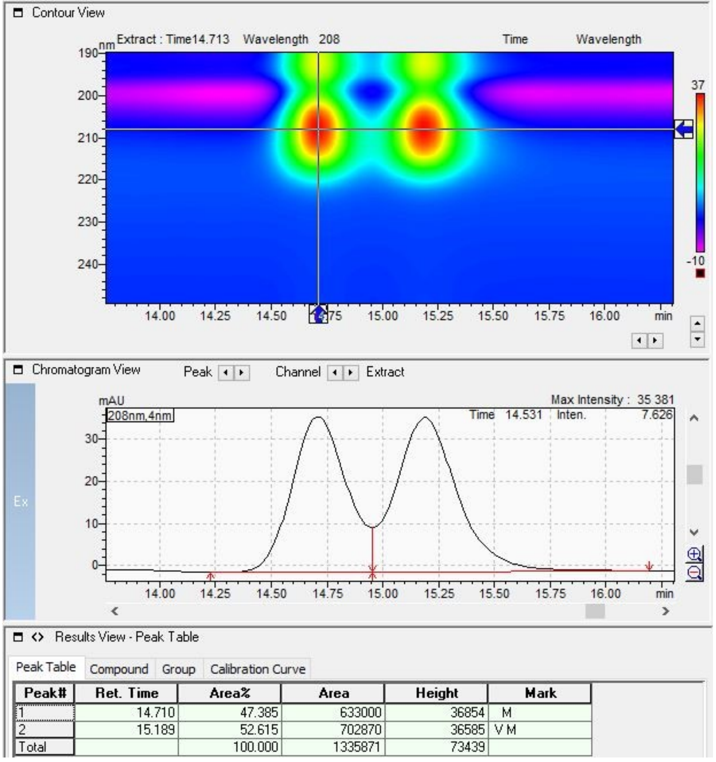
Time 16.77 Wavelength 257

Max Intensity : 155 162

Time 14.687 Inten. 89.776

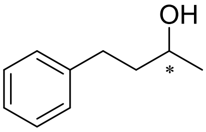
Peak#	Ret. Time	Area%	Area	Height	Mark
1	14.618	38.599	1873469	107871	M
2	15.219	61.401	2980160	155605	V M
Total		100.000	4853630	263476	

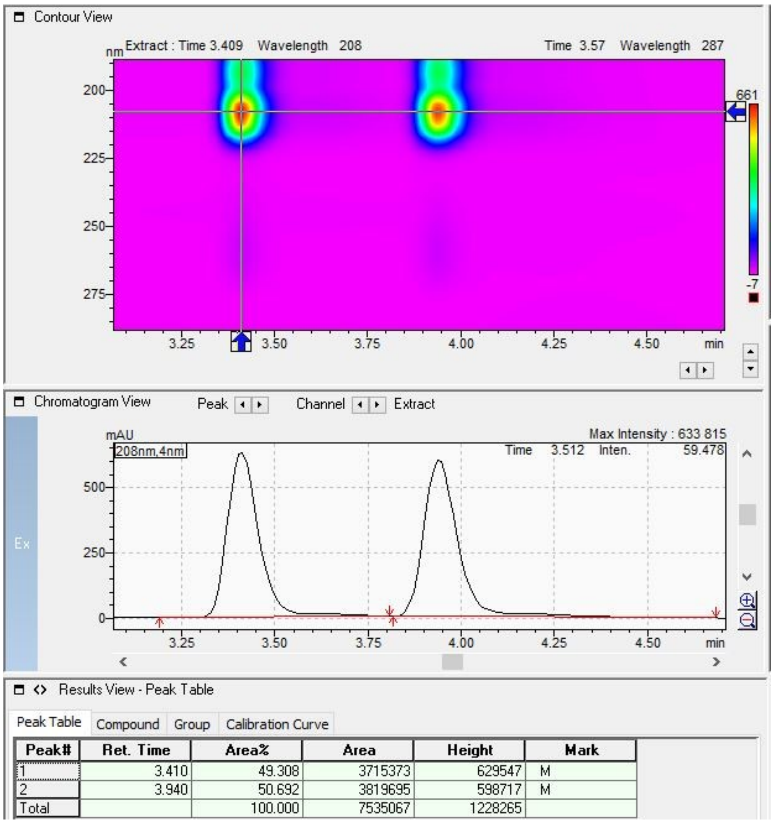
Fig. S65. VM-2 chiral Column IA-3 hept-IPA 99-1, 1 ml min, ee 23%



Peak#	Ret. Time	Area%	Area	Height	Mark
1	14.710	47.385	633000	36854	M
2	15.189	52.615	702870	36585	V M
Total		100.000	1335871	73439	

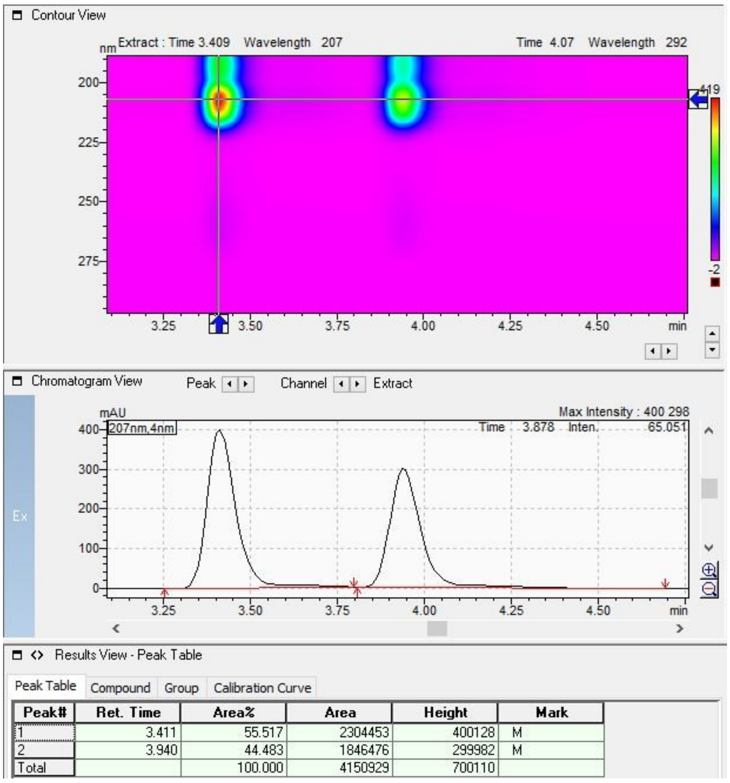
Fig. S66. VM-6 chiral Column IA-3 hept-IPA 99-1, 1 ml min, ee 5%





Peak#	Ret. Time	Area%	Area	Height	Mark
1	3.410	49.308	3715373	629547	M
2	3.940	50.692	3819695	598717	M
Total		100.000	7535067	1228265	

Fig. S67. VM-4 rac Column IA-B hept-IPA 90-10, 1 ml min, tR(1) = 3.41 min, tR(2) = 3.94 min



Peak#	Ret. Time	Area%	Area	Height	Mark
1	3.411	55.517	2304453	400128	M
2	3.940	44.483	1846476	299982	M
Total		100.000	4150929	700110	

Fig. S68. VM-5 chiral Column IA-B hept-IPA 90-10, 1 ml min, ee 11%

Single Crystal XRD (SC-XRD)

Crystals of **5** and **6** were grown by slow diffusion of petroleum ether into a solution of complexes in CH_2Cl_2, and those of **10**•0.5Et_2O, by slow gas phase diffusion of Et_2O into a solution of complex in CH_3OH. X-ray diffraction data were collected at 100 K with a Bruker Quest D8 CMOS diffractometer using graphite-monochromated Mo-Kα radiation (lλ = 0.71073 Å, ω-scans). Using Olex2,[10] the structures were solved with the ShelXT[11] structure solution program using Intrinsic Phasing and refined with the XL[12] refinement package using Least-Squares minimisation. Hydrogen atoms of the BH groups in **5**, **6** and **10**•0.5Et_2O and of the NH groups in **10**•0.5Et_2O were found in difference Fourier synthesis while the positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model. The severely disordered molecule of lattice diethyl ether in **10**•0.5Et_2O was treated as a diffuse contribution to the total scattering without specific atom positions using the Mask option of OLEX2. Crystallographic data and structure refinement parameters are given in Table S1. CCDC 2526352, 2526353 and 2526354 contain the supplementary crystallographic data for **5**, **6** and **10**•0.5Et_2O, respectively.

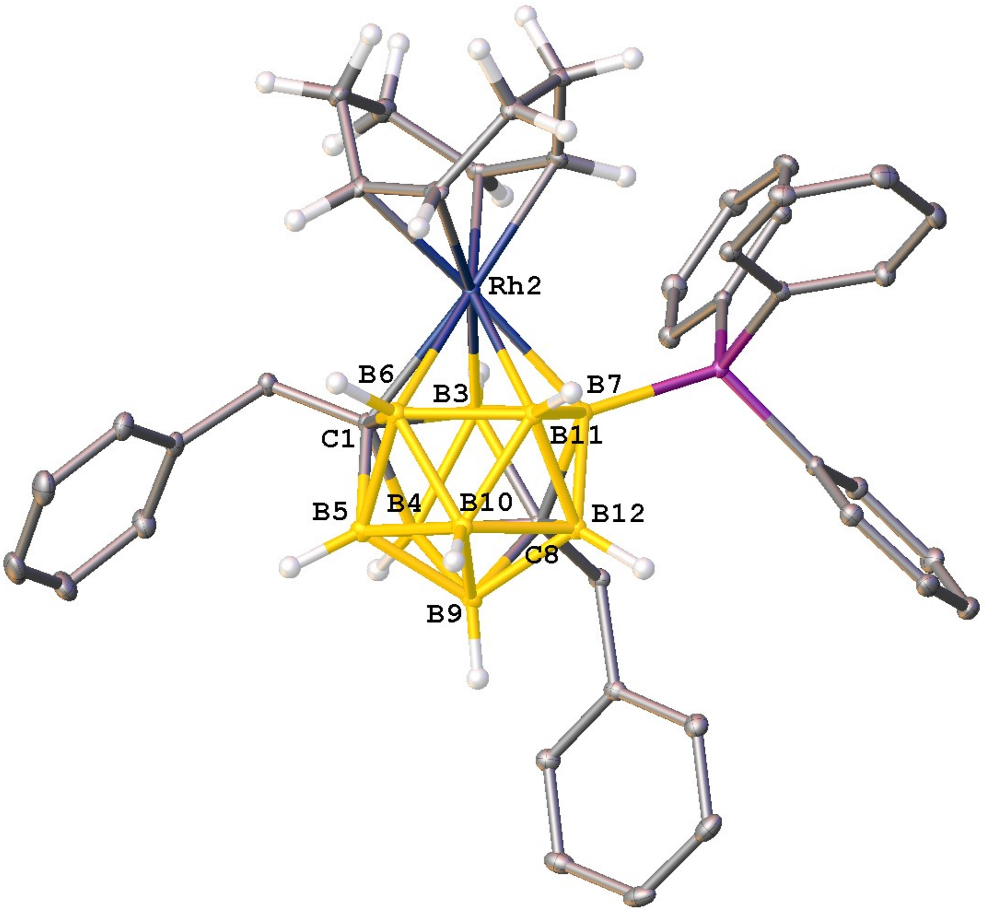


Figure S69. General view of **5.** Hereinafter, hydrogen atoms except those of the BH and NH groups or at COD moieties are omitted, other atoms are shown as thermal ellipsoids (p = 30%) and only atoms of the metallacarborane core are labeled.

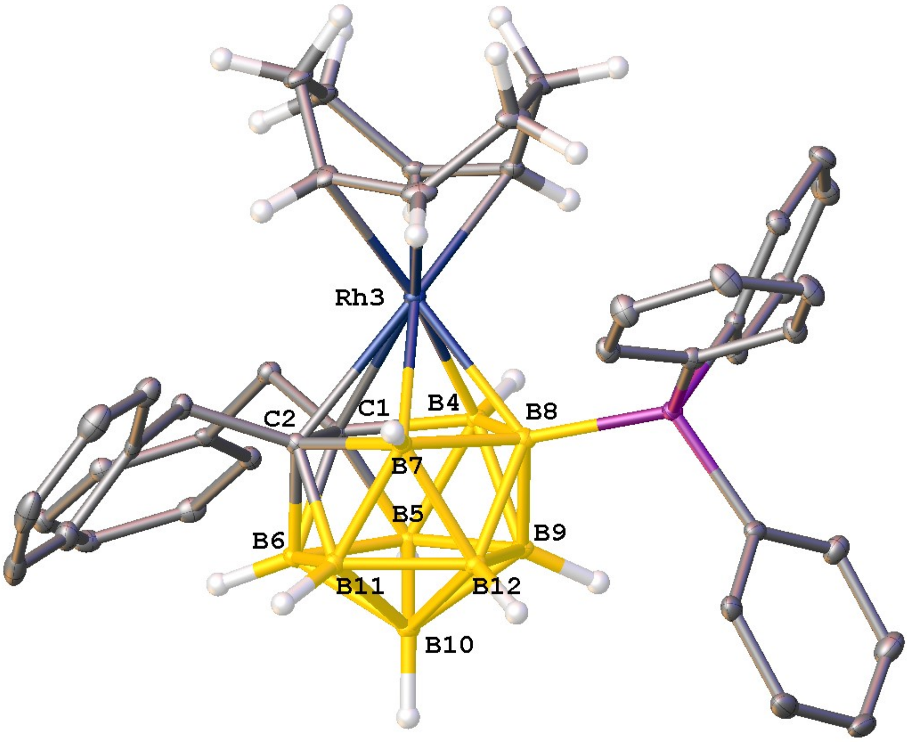


Figure S70. General view of **6**. The second symmetry-independent molecule is omitted.

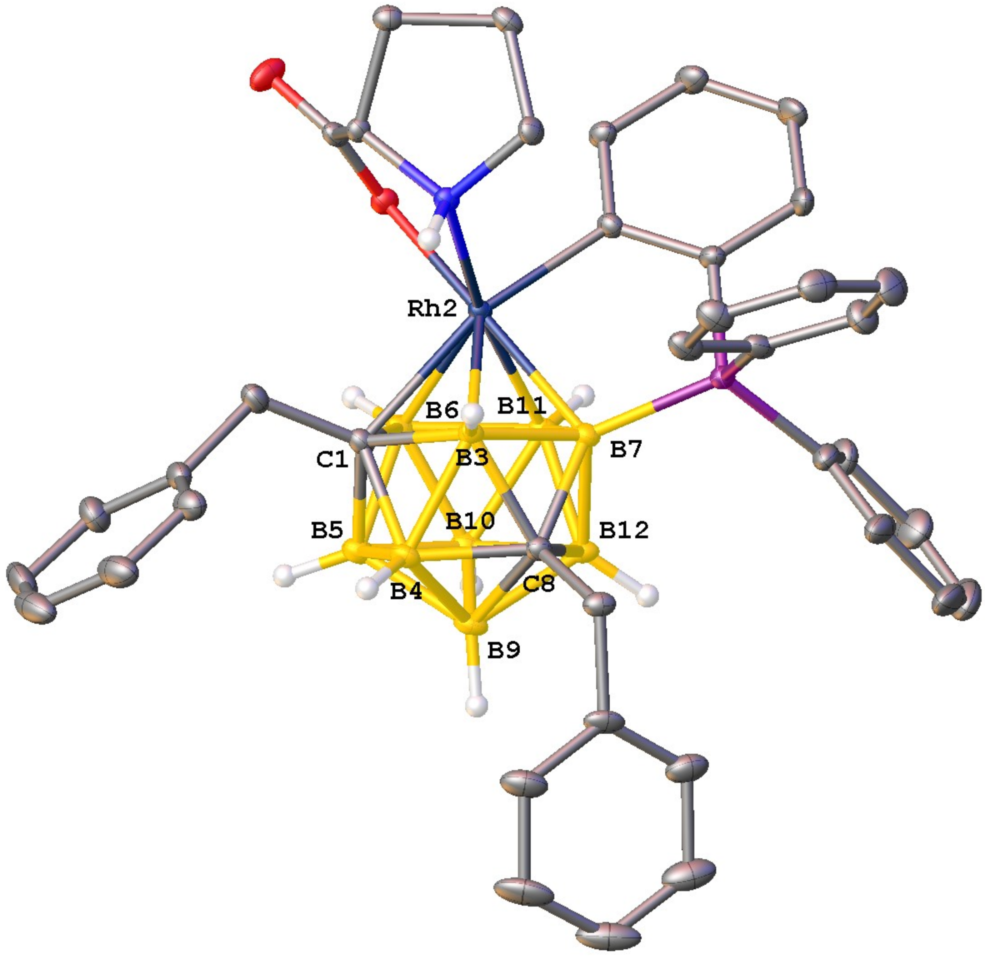


Figure S71. General view of **10**•0.5Et_2O. The second symmetry-independent molecule, disordered lattice solvent and minor components of the disordered phenyl groups are omitted.

Table S1. Crystallographic data and structure refinement parameters for **5**, **6** and **10**•0.5Et_2O.

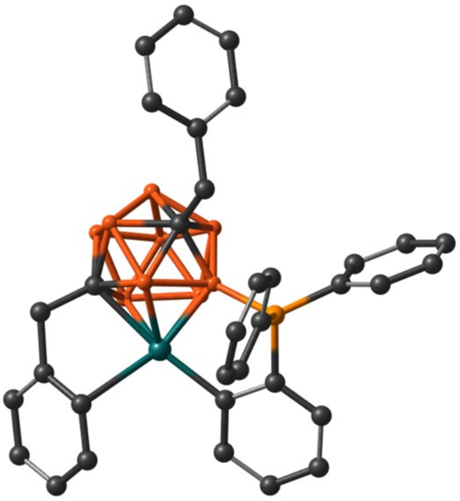
Compound	**5**	**6**	**10**•0.5Et_2O
Empirical formula	$C_{42}H_{49}B_9PRh$	$C_{42}H_{49}B_9PRh$	$C_{41}H_{49}B_9NO_{2.5}PRh$
Formula weight	784.98	784.98	826.98
T, K	100	100	100
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	*P-1*	$P2_1/c$	$P2_12_12_1$
Z	2	8	8
a (Å)	12.2842(2)	10.5003(2)	18.6491(3)
b (Å)	12.8919(2)	19.6990(3)	21.7922(4)
c (Å)	13.3696(2)	36.9753(5)	22.7209(4)
α (°)	104.9050(10)	90	90
β (°)	109.6550(10)	92.3190(10)	90
γ (°)	95.2440(10)	90	90
V (Å^3)	1889.66(5)	7641.9(2)	9233.9(3)

D_{calc} (g cm^{-3})	1.380	1.365	1.190
Linear absorption, μ (cm^{-3})	5.26	5.21	4.39
F(000)	812	3248	3416
$2\theta_{max}$, °	56	56	56
Reflections measured	23774	94179	217202
Independent reflections	9108	18433	22265
Observed reflections ($I > 2\sigma(I)$)	7971	14452	21099
Parameters	510	1051	940
$R1$ (on F for obs. refls)	0.0313	0.0385	0.0278
$wR2$ (on F^2 for all refls)	0.0686	0.0823	0.0700
Goodness-of-fit	1.010	1.027	1.042
Largest diff. peak and hole (e $Å^{-3}$)	0.446 and -0.412	0.441 and -0.581	0.547 and -0.334
CCDC	2526352	2526353	2526354

Computational Details

The calculated thermodynamic parameters for the target complexes were obtained by DFT methodologies using Orca programm (version 5.0.3)[13,14] on PBE0/def2-TZVP[15,16] level on all atoms with ECP on rhodium atom. The geometry optimizations were carried out without symmetry constraints, analytical hessians were computed and verified to have no negative frequencies. The Orca's output offers Gibbs free energy at 298.15 K temperature under 1 atm pressure. The ChemCraft program[17] was used for molecular modeling and visualization.

$[\mathbf{CarbPPh_2(\mathit{o}\text{-}C_6H_4\text{-}\kappa C)Rh}]^+$



G = -1990.83537343 Eh

45	-1.616111000	9.464204000	4.088608000
15	0.565325000	7.165351000	4.673693000
6	1.699827000	7.294185000	3.268371000
6	2.252680000	5.114492000	5.546356000
1	2.983991000	5.484302000	4.838359000
6	-3.174312000	8.958831000	2.568695000
6	-0.132241000	9.671612000	5.438688000
6	-3.375601000	3.147630000	-0.040203000
1	-3.745152000	3.146007000	-1.058925000
6	-2.842505000	11.406661000	2.331627000
6	2.004545000	6.186739000	2.474510000
1	1.603379000	5.209285000	2.712080000
6	-2.095046000	6.529700000	2.895633000
5	-3.691276000	8.995694000	4.173766000
6	-2.132397000	4.233444000	1.719782000
6	-3.381959000	10.169138000	1.663458000
1	-2.874208000	9.999628000	0.710018000
1	-4.443343000	10.290394000	1.442233000
6	0.991044000	5.703601000	5.635139000
6	-1.314565000	5.390484000	2.223429000
1	-0.736565000	5.820028000	1.402329000
1	-0.598666000	5.008351000	2.954310000
6	3.085055000	8.667264000	1.852680000
1	3.513755000	9.634182000	1.617789000
6	0.765878000	8.623056000	5.694119000
6	3.380011000	7.564930000	1.065577000
1	4.036811000	7.668478000	0.209966000
5	-3.796331000	6.347569000	3.165294000
6	2.578810000	4.052775000	6.375605000
1	3.559198000	3.597378000	6.303283000
6	-2.616768000	4.215008000	0.415937000
1	-2.394853000	5.039324000	-0.253567000
6	-2.404438000	3.151287000	2.552077000
1	-2.021084000	3.145158000	3.567432000
5	-2.656204000	6.335261000	4.499559000
6	0.070149000	5.232143000	6.572941000
1	-0.903075000	5.697782000	6.666184000
6	1.655406000	3.577882000	7.295190000
1	1.912993000	2.745790000	7.939784000
6	0.404563000	4.170863000	7.396494000
1	-0.314259000	3.807477000	8.120954000
6	-3.679137000	12.437587000	2.733624000
1	-4.740667000	12.377188000	2.521828000
6	-0.003301000	10.828888000	6.209538000

1	-0.675874000	11.666791000	6.055400000
6	1.758647000	8.721819000	6.665746000
1	2.439131000	7.896295000	6.845181000
5	-3.187593000	7.417916000	1.915134000
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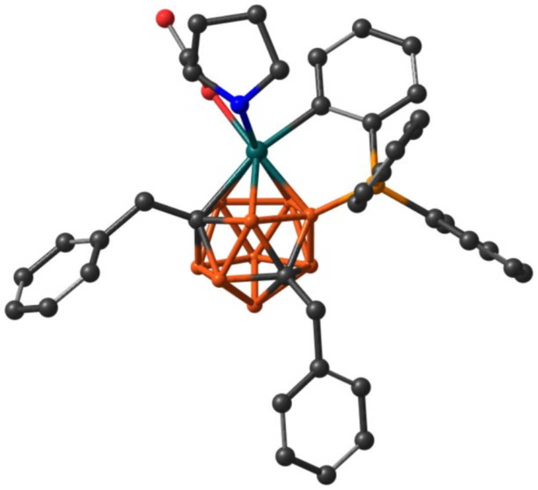

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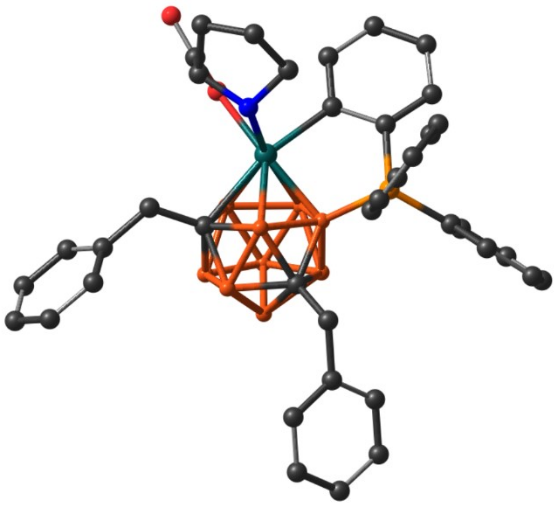

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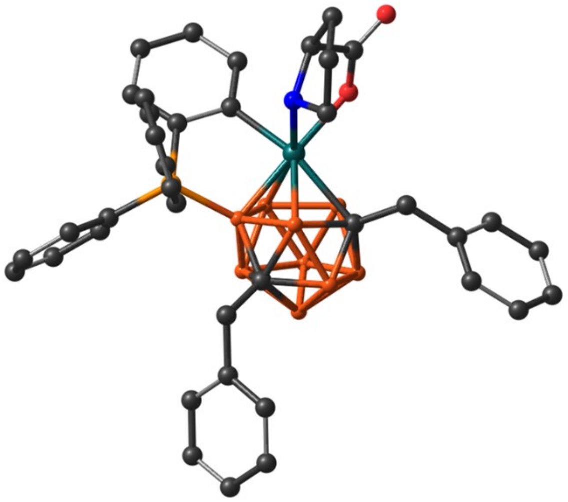

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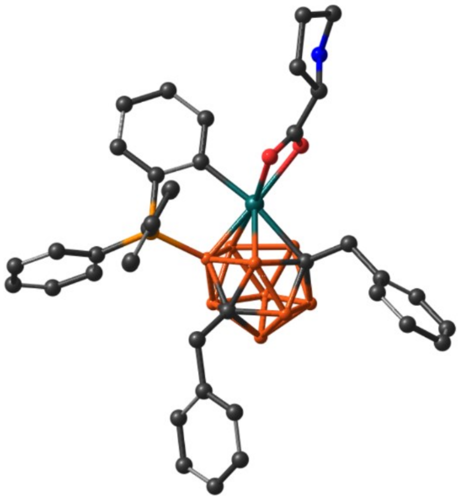

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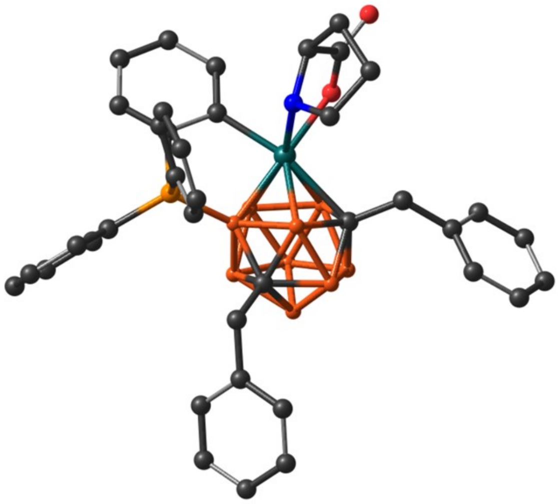

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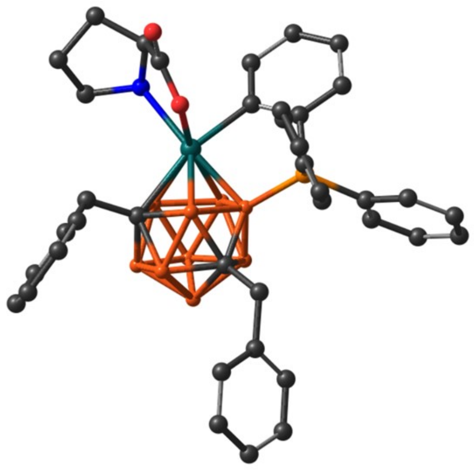

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