Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Chiral Bisphosphine Ligands based on Quinoline Oligoamide Foldamer: Application in Asymmetric Hydrogenation

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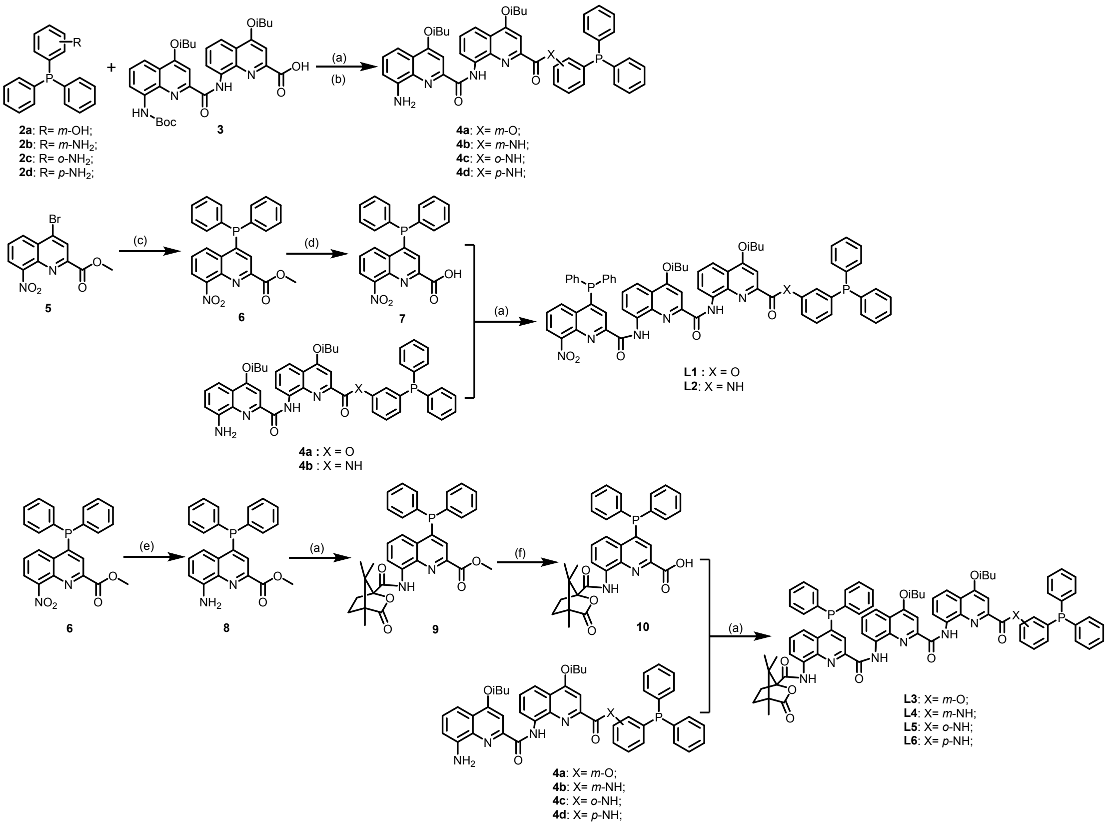
1. General Procedures and Materials.

All starting compounds and solvents were obtained from commercial suppliers and used as received unless otherwise indicated. Per-deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. Anhydrous dichloromethane (DCM) and toluene were dried by the solvent purification system. Compounds **1a-1g**,[1] **2a-2d**[2-4], **3**[5], **5**[6] were prepared according to the literatures and the NMR spectra of these compounds and the hydrogenation products of **1a-1g** are consistent with the literatures. Column chromatography was carried out on flash grade silica gel, using 0-20 psig pressure. Analytical TLC was carried out using tapered silica plates with a preadsorbent zone

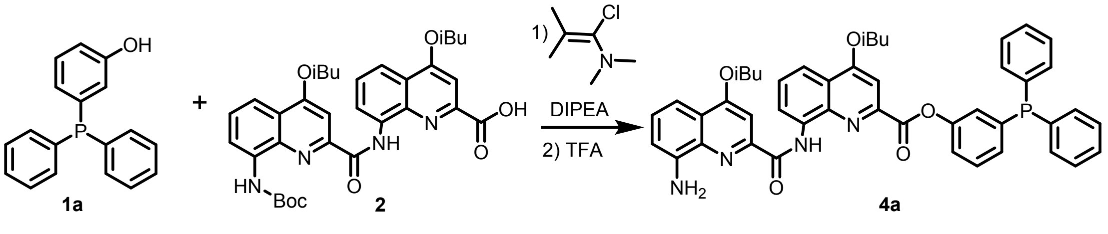
NMR spectra were obtained with JEOL Delta (600 MHz) using chloroform-*d* ($CDCl_3$) or DMSO-d_6 as the solvent. The chemical shift references were as follows: ^1H NMR: chloroform-*d*, 7.26 ppm; DMSO-d_6, 2.50 ppm; ^{13}C NMR: chloroform-*d*, 77.20 ppm; DMSO-d_6, 39.52 ppm. High-resolution mass spectra were recorded on Thermo Exactive or SCIEX TripleTOF 5600$^+$ System.

2. Synthesis of ligands L1-L6

Scheme S1. Synthesis of **L1-L6**.

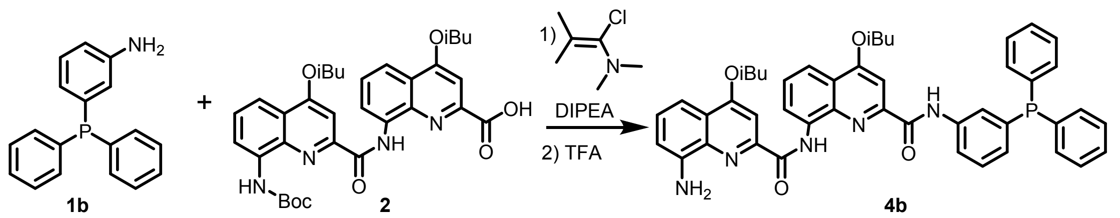


Conditions: (a) 1-chloro-N,N,2-trimethylprop-1-en-1-amine or oxalyl chloride (2.0 equiv.), compound **1** (0.90 equiv.), DIPEA (3 equiv.), DCM; (b) TFA, DCM, room temperature; (c) $HPPh_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (10%), TEA (2.0 equiv.), toluene, 80 °C; (d) NaOH (3.0 equiv.), THF/MeOH/H_2O, 40 °C; (e) Pd/C (10%), H_2, EA, room temperature; (f) NaOH (3 equiv.), dioxane.

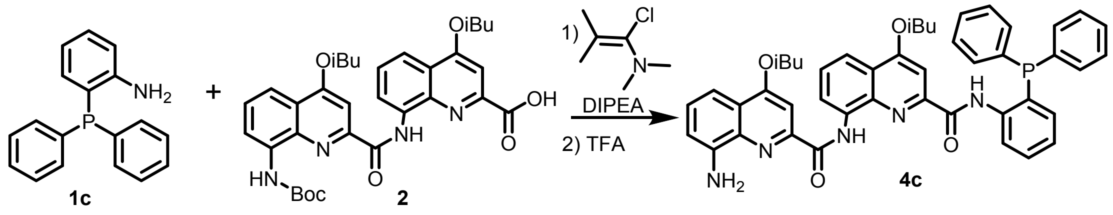


Compound 4a: Compound **2** (135 mg, 0.22 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution 1-chloro-N,N,2-trimethylprop-1-en-1-amine (60 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus 1-chloro-N,N,2-trimethylprop-1-en-1-amine were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 h and resolved in dry DCM. To the solution of compound **1a** (56 mg, 0.20 mmol, 0.90

equiv.) in DCM was slowly added DIPEA (0.12 mL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 h. The solution was removed and the residue was applied to a quick flash column chromatography to get product as a yellow solid. The solid was dissolved in DCM and TFA was added and the resulting mixture was stirred for another 1 h, and then the solvent and the excess TFA was removed under reduced pressure. The residue was purified by silica gel chromatography to gain compound **4a** as a yellow solid (99 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.60 (s, 1H), 9.11 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.76 (s, 1H), 7.73 – 7.67 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.42 – 7.31 (m, 14H), 6.74 (d, *J* = 7.1 Hz, 1H), 5.04 (br, 2H), 4.09 (t, *J* = 6.7 Hz, 4H), 2.31 (dp, *J* = 15.2, 8.6, 7.6 Hz, 2H), 1.16 (dd, *J* = 13.2, 6.7 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 163.4, 163.3, 151.5, 151.4, 148.3, 146.3, 144.8, 139.8, 137.4, 136.7, 136.6, 135.6, 134.1, 133.9, 132.0, 131.8, 123.0, 129.9, 129.3, 129.0, 128.9, 128.3, 126.9, 126.7, 123.2, 122.6, 117.7, 115.9, 110.7, 109.5, 101.9, 98.5, 75.5, 75.2, 29.9, 28.4, 28.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.42. HRMS (ESI) calculated for $C_{46}H_{44}N_4O_5P$ [M + H]$^+$: 763.3044, found 763.3024.

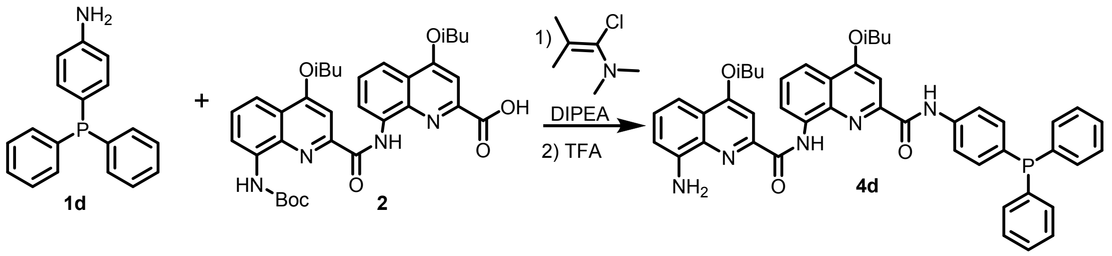


Compound **4b**: Compound **2** (171 mg, 0.28 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution 1-chloro-N,N,2-trimethylprop-1-en-1-amine (74 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus 1-chloro-N,N,2-trimethylprop-1-en-1-amine were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 h and resolved in dry DCM. To the solution of compound **1b** (58 mg, 0.26 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (0.15 mL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 h. The solution was removed and the residue was applied to a quick flash column chromatography to get product as a yellow solid. The solid was dissolved in DCM and TFA was added and the resulting mixture was stirred for another 1 h, and then the solvent and the excess TFA was removed under reduced pressure. The residue was purified by silica gel chromatography to gain compound **4a** as a yellow solid (110 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.96 (s, 1H), 9.83 (s, 1H), 8.94 (d, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 18.3, 12.9 Hz, 4H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.20 (m, 12H), 7.10 (t, *J* = 7.1 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 4.07 (d, *J* = 5.9 Hz, 4H), 2.28 (q, *J* = 10.3, 7.8 Hz, 2H), 1.14 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 163.6, 163.3, 163.2, 150.3, 148.6, 142.3, 138.5, 138.2, 138.0, 137.9, 137.5, 136.7, 136.6, 134.0, 133.9, 130.4, 130.3, 129.1, 128.8, 128.7, 128.2, 127.5, 126.5, 126.4, 122.8, 122.2, 122.1, 118.4, 116.5, 112.6, 111.4, 99.6, 98.5, 75.5, 75.1, 29.9, 28.3, 19.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.14. HRMS (ESI) calculated for $C_{46}H_{45}N_5O_4P$ $[M + H]^+$: 762.3209, found 762.3206.

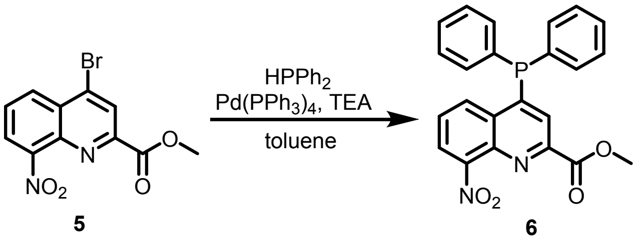


Compound **4c**: Compound **2** (145 mg, 0.24 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution 1-chloro-N,N,2-trimethylprop-1-en-1-amine (64 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus 1-chloro-N,N,2-trimethylprop-1-en-1-amine were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 h and resolved in dry DCM. To the solution of compound **1c** (60 mg, 0.22 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (0.13 mL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 h. The solution was removed and the residue was applied to a quick flash column chromatography to get product as a yellow solid. The solid was dissolved in DCM and TFA was added and the resulting mixture was stirred for another

1 h, and then the solvent and the excess TFA was removed under reduced pressure. The residue was purified by silica gel chromatography to gain compound **4a** as a yellow solid (18 mg, 15% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 12.16 (s, 1H), 10.60 (d, *J* = 6.3 Hz, 1H), 9.09 (d, *J* = 7.5 Hz, 1H), 8.22 (br, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.76 (s, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 10.1 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 5H), 6.82 (br, 1H), 6.75 (t, *J* = 7.4 Hz, 4H), 6.60 (d, *J* = 7.1 Hz, 1H), 4.09 (dd, *J* = 15.9, 6.3 Hz, 4H), 3.85 (s, 2H), 2.30 (dq, *J* = 14.5, 7.5, 6.9 Hz, 2H), 1.19 – 1.11 (m, 12H). 13C NMR (150 MHz,CHLOROFORM-D CDCl$_3$) δ 167.8, 150.1, 138.7, 133.7, 133.6, 133.5, 132.4, 131.0, 130.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.9, 125.5, 123.2, 122.7, 122.4, 99.3, 98.7, 75.4, 75.2, 65.7, 30.7, 29.8, 28.3, 27.3, 22.8 19.3, 19.2. ^{31}P NMR (243 MHz, CDCl$_3$) δ -19.32. HRMS (ESI) calculated for $C_{46}H_{45}N_5O_4P$ [M + H]$^+$: 762.3203, found 763.3201.

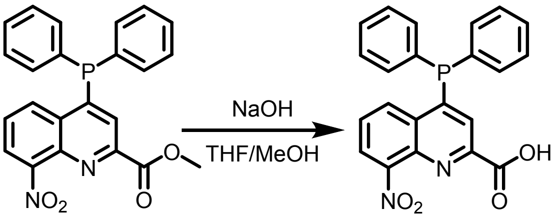


Compound **4d**: Compound **2** (145 mg, 0.24 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution 1-chloro-N,N,2-trimethylprop-1-en-1-amine (64 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus 1-chloro-N,N,2-trimethylprop-1-en-1-amine were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 h and resolved in dry DCM. To the solution of compound **1d** (60 mg, 0.22 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (0.13 mL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 h. The solution was removed and the residue was applied to a quick flash column chromatography to get product as a yellow solid. The solid was dissolved in DCM and TFA was added and the resulting mixture was stirred for another 1 h, and then the solvent and the excess TFA was removed under reduced pressure. The residue was purified by silica gel chromatography to gain compound **4a** as a yellow solid (80 mg, 53% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 11.99 (s, 1H), 10.14 (s, 1H), 8.91 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.78 (s, 1H), 7.72 (s, 1H), 7.70 – 7.61 (m, 4H), 7.40 (dd, *J* = 15.3, 7.6 Hz, 11H), 7.32 – 7.27 (m, 3H), 6.67 (d, *J* = 7.3 Hz, 1H), 4.12 (d, *J* = 6.4 Hz, 2H), 4.08 (d, *J* = 6.4 Hz, 2H), 2.31 (tt, *J* = 13.3, 6.6 Hz, 1H), 1.15 (dd, *J* = 11.7, 6.7 Hz, 12H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 163.9, 163.6, 163.5, 163.4, 150.1, 149.7, 148.8, 143.1, 141.9, 141.8, 138.7, 138.4, 137.4, 137.3, 137.2, 134.6, 134.5, 133.9, 133.8, 133.2, 133.1, 132.9, 132.4, 130.8, 130.0, 129.1, 129.0, 128.8, 128.4, 128.3, 127.8, 127.7, 123.0, 122.4, 120.9, 120.8, 120.7, 118.7, 118.5, 116.7, 116.6, 114.4, 112.1, 111.7, 110.9, 110.7, 99.5, 98.5, 75.6, 75.2, 28.4, 28.3, 19.4. ^{31}P NMR (243 MHz, CDCl$_3$) δ -4.90. HRMS (ESI) calculated for $C_{46}H_{45}N_5O_4$ [M + H]$^+$: 762.3204, found 762.3197.



Compound **6**: Compound **5** (300 mg, 0.96 mmol, 1.0 equiv.), HPPh$_2$ (200 mg, 1.08 mmol, 1.1 equiv.) and Pd(PPh$_3$)$_4$ (100 mg, 10%) was added to a two-neck flask with condenser and the flask was filled with Ar. TEA (0.27 mL, 2.0 eq.) and THF was added though syringe respectively. The resulting mixture was stirred at 80 °C for 16 h. The mixture was poured into water and extracted with DCM and purified with silica gel column to obtain compound **6** as a yellow solid (320 mg, 75% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.49 (d, *J* = 11.9 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.37 (m, 6H), 7.31 (t, *J* = 7.3 Hz, 4H), 3.95 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 165.5, 150.4, 150.3, 149.5, 149.2, 138.8, 134.6, 134.5, 133.2, 131.7, 131.5, 130.3, 130.2, 130.0, 129.5, 129.4, 127.3, 126.5, 124.3, 53.6, 53.4. ^{31}P NMR (243 MHz, CDCl$_3$) δ -14.76. HRMS (ESI) calculated for $C_{23}H_{17}N_2O_4P$ [M +

H]$^+$: 417.0999, found 417.0997.



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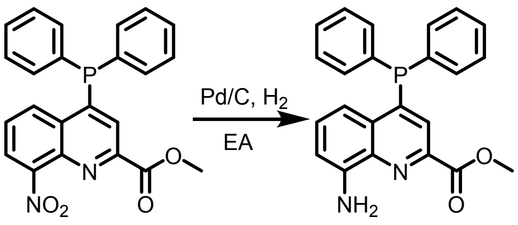
Compound **7**: Compound **6** (0.40 g, 0.96 mmol, 1.0 equiv.) was dissolved in a mixture of THF (8 mL), MeOH (2 mL) and H_2O (1 mL), NaOH (0.12 g, 2.88 mmol, 3.0 equiv.) was added and the mixture was stirred at 40 °C under Ar atmosphere. The progress of saponification was monitored by TLC. The solution was acidified with HCl (1 mol/L, aqueous), and then extracted with CH_2Cl_2. The solvent was evaporated and the residue was dried under vacuum and used directly without further purification. (0.38 g, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 12.0 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 3.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 4H), 7.32 (t, *J* = 7.9 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 149.4, 148.8, 148.7, 141.9, 141.2, 139.6, 133.3, 132.1, 131.6, 130.6, 129.8, 129.4, 129.3, 128.7, 127.1, 127.0, 124.8, 108.1, 107.8, 106.5, 104.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ -11.59. HRMS (ESI) calculated for $C_{22}H_{16}N_2O_4P$ [M + H]$^+$: 403.0842, found 403.0840.



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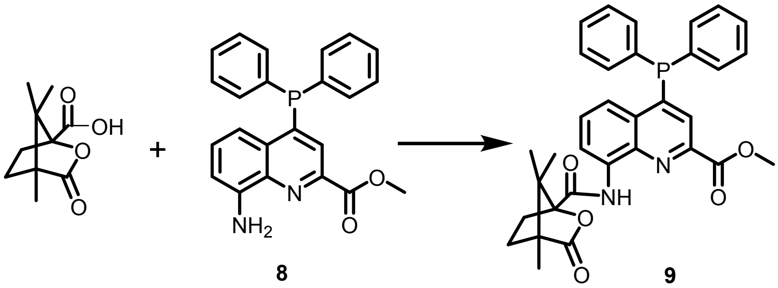
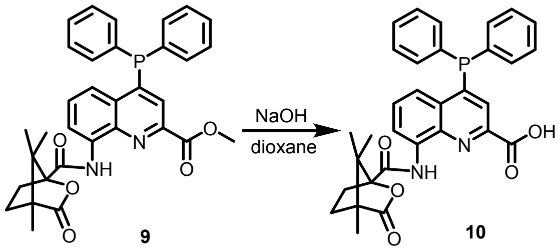
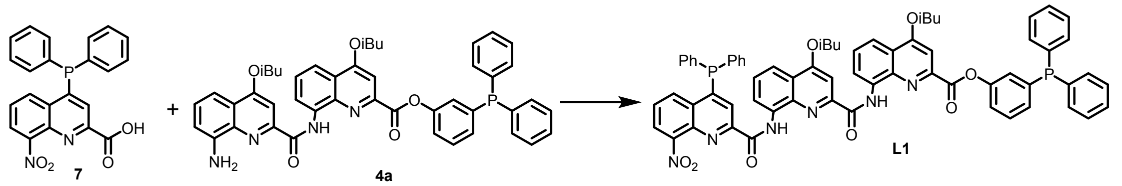
Compound **8**: Compound **6** (150 mg), ethyl acetate (25 mL) and Pd/C (10%) was added into a two-neck flask. The flask was filled with hydrogen and was stirred at room temperature for overnight under H_2 atmosphere. The reaction mixture was filtered and the filtrate was concentrated to obtain compound **8** with quantitative yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 4.2 Hz, 1H), 7.51 (dd, *J* = 8.3, 2.9 Hz, 1H), 7.37 (dt, *J* = 14.5, 7.4 Hz, 6H), 7.31 (q, *J* = 8.3, 7.8 Hz, 5H), 6.91 (d, *J* = 7.5 Hz, 1H), 5.21 (br, 2H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 148.0, 147.9, 145.9, 143.9, 134.6, 134.4, 132.7, 132.2, 132.1, 132.0, 131.8, 131.7, 130.2, 129.7, 129.1, 129.1, 125.3, 114.2, 114.0, 110.4, 52.8. ^{31}P NMR (243 MHz, $CDCl_3$) δ -12.85. HRMS (ESI) calculated for $C_{23}H_{20}N_2O_2P$ $[M + H]^+$: 387.1257, found 387.1257.



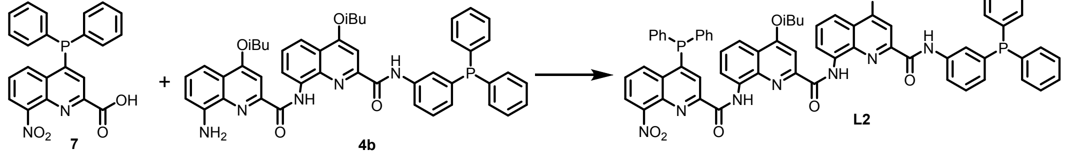
Compound **9**: (1*S*)-(-)-camphanyl acid (125 mg, 0.63 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (0.11 mL, 2.0 equiv.) and DMF (cat.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **8** (220 mg, 0.57 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (0.33 mL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 h. The solution was removed and the residue was applied to a flash column chromatography to get product as an off-white solid (290 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 8.71 (d, *J* = 7.7 Hz, 1H), 7.95 (dd, *J* = 8.5, 2.8 Hz, 1H), 7.68 (d, *J* = 3.8 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 1H), 7.39 (p, *J* = 6.7 Hz, 6H), 7.29 (d, *J* = 7.2 Hz, 4H), 4.01 (s, 3H), 2.68 (ddd, *J* = 14.1, 10.8, 4.2 Hz, 1H), 2.12 (ddd, *J* = 13.5, 9.3, 4.5 Hz, 1H), 2.02 (tt, *J* = 11.0, 4.5 Hz, 1H), 1.79 (ddd, *J* = 13.3, 9.3, 4.1 Hz, 1H), 1.19 (d, *J* = 5.0 Hz, 6H), 1.05 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 165.8, 165.7, 149.6, 149.4, 145.2, 137.3, 135.0, 134.5, 134.4, 133.9, 123.0, 129.6, 129.1, 125.3, 120.7, 120.6, 117.3, 92.9, 55.6, 54.5, 53.0, 30.4, 29.4, 16.9, 10.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.01. HRMS (ESI) calculated for $C_{33}H_{32}N_2O_5P$ [M + H]$^+$: 567.2043, found 567.2039.



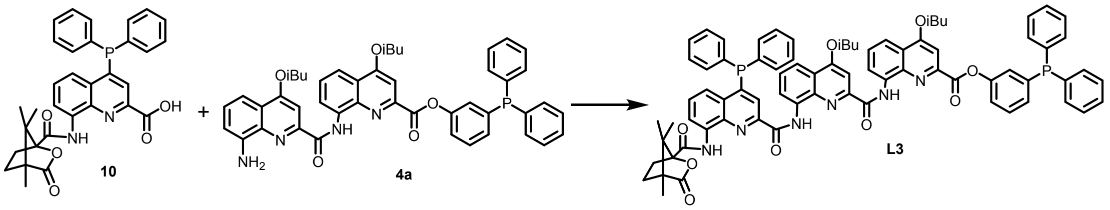
Compound **10**: Compound **6** (0.19 g, 0.34 mmol, 1.0 equiv.) was dissolved in dioxane (4 mL), NaOH (40 mg, 1.00 mmol, 3.0 equiv.) was added and the mixture was stirred at 40 °C under Ar amosphere. The progress of saponification was monitored by TLC. The solution was acidified with HCl (1 mol/L, aqueous) and extracted with CH_2Cl_2. The solvent was evaporated and the residue was dried under vacuum and was applied to a flash column chromatography to get product as an off-white solid (135 mg, 74% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.49 (s, 1H), 10.61 (s, 1H), 8.71 (d, J = 7.7 Hz, 1H), 7.88 (dd, J = 8.4, 2.8 Hz, 1H), 7.68 (t, J = 8.2 Hz, 1H), 7.57 (d, J = 3.9 Hz, 1H), 7.46 (d, J = 10.2 Hz, 6H), 7.31 (t, J = 7.6 Hz, 4H), 4.03 (q, J = 7.1 Hz, 1H), 2.05 (q, J = 10.5, 9.3 Hz, 2H), 1.71 – 1.62 (m, 1H), 1.12 (s, 3H), 1.07 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.1, 165.6, 165.4, 148.7, 148.5, 146.2, 136.6, 134.5, 134.2, 134.0, 133.3, 130.0, 129.8, 129.4, 129.2, 124.9, 120.1, 120.0, 117.2, 92.0, 54.8, 53.8, 39.5, 30.1, 28.4, 16.4, 16.3, 9.5. ^{31}P NMR (162 MHz, DMSO-d_6) δ -13.90. HRMS (ESI) calculated for $C_{32}H_{30}N_2O_5P$ [M + H]$^+$: 553.1887, found 553.1886.



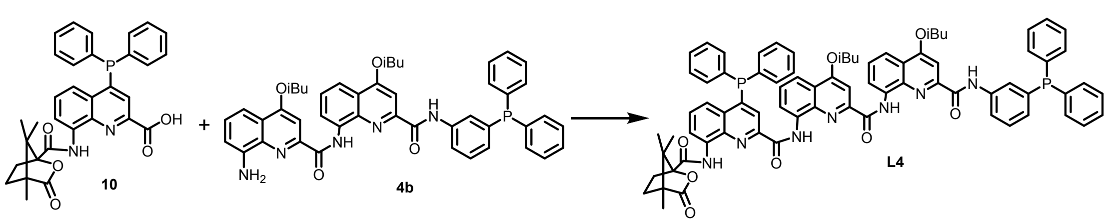
Compound **L1**: Compound **7** (30 mg, 0.073 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (16 μL, 2.5 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4a** (50 mg, 0.066 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (40 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 18 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (50 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.05 (s, 2H), 12.04 (s, 2H), 9.05 (d, *J* = 7.2 Hz, 1H), 8.92 (d, *J* = 12.2 Hz, 1H), 8.47 (dd, *J* = 8.9, 2.7 Hz, 1H), 8.02 (d, *J* = 10.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 4.2 Hz, 1H), 7.83 (s, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 6.2 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 10.6 Hz, 5H), 7.25 – 7.15 (m, 12H), 7.08 (t, *J* = 6.6 Hz, 1H), 6.93 (s, 1H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.86 (t, *J* = 6.6 Hz, 2H), 2.38 – 2.26 (m, 2H), 1.16 (t, *J* = 6.0 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 163.3, 162.7, 162.6, 162.2, 151.6, 151.2, 150.9, 150.8, 150.6, 146.8, 145.6, 140.3, 139.6, 139.5, 139.1, 137.8, 136.7, 135.9, 134.7, 134.6, 133.9, 133.8, 133.2, 131.6, 131.4, 131.0, 130.9, 130.8, 130.7, 130.1, 129.7, 129.6, 129.4, 129.3, 129.0, 128.9, 128.6, 127.7, 126.0, 125.8, 125.1, 124.3, 122.5, 122.2, 121.2, 118.4, 118.3, 100.7, 99.5, 75.5, 75.2, 28.3, 19.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.30, -10.85. HRMS (ESI) calculated for $C_{68}H_{57}N_6O_8P_2$ [M + H]$^+$: 1147.3708, found 1147.3694.



Compound **L2**: Compound **7** (36 mg, 0.090 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (20 μL, 2.5 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4a** (62 mg, 0.081 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (48 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 18 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (64 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.06 (s, 1H), 11.92 (s, 1H), 9.48 (s, 1H), 8.97 (d, *J* = 7.4 Hz, 1H), 8.76 (d, *J* = 7.6 Hz, 1H), 8.52 (dd, *J* = 8.5, 3.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 9.7 Hz, 1H), 7.92 (s, 1H), 7.75-7.71 (m, 2H), 7.54 – 7.40 (m, 15H), 7.31 – 7.20 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 3H), 7.04 (t, *J* = 7.0 Hz, 3H), 6.97 (t, *J* = 6.0 Hz, 1H), 6.92 (t, *J* = 6.6 Hz, 1H), 6.73 (d, *J* = 9.2 Hz, 1H), 4.22 (d, *J* = 6.1 Hz, 2H), 3.87 (d, *J* = 6.4 Hz, 2H), 2.38 (dt, *J* = 12.2, 6.6 Hz, 1H), 2.27 (dt, *J* = 13.0, 6.7 Hz, 1H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.15 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 163.4, 162.5, 161.3, 160.8, 151.4, 150.9, 150.8, 148.5, 146.3, 139.3, 139.0, 138.7, 138.6, 137.6, 137.4, 137.3, 137.0, 136.9, 135.0, 134.9, 134.7, 134.4, 133.9, 133.8, 133.7, 133.6, 131.8, 131.7, 131.6, 130.2, 129.4, 129.2, 129.1, 128.6, 128.4, 128.3, 128.2, 128.1, 125.7, 125.4, 124.3, 124.1, 123.9, 122.7, 122.1, 119.3, 118.9, 118.8, 116.9, 116.4, 99.4, 97.9, 75.7, 75.5, 29.9, 28.4, 28.3, 19.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.11, -10.64. HRMS (ESI) calculated for $C_{68}H_{58}N_7O_7P_2$ $[M + H]^+$: 1146.3867, found 1146.3860.

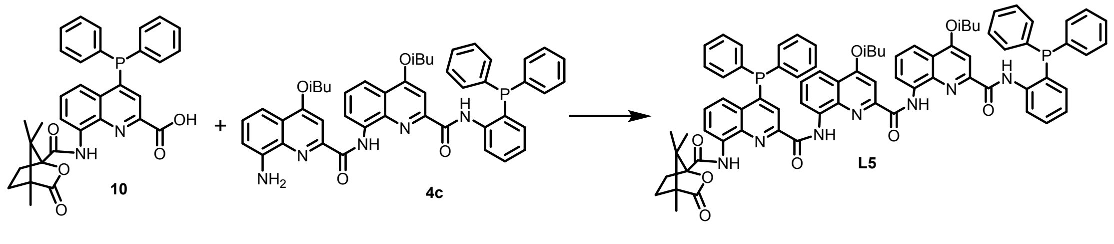


Compound **L3**: Compound **10** (47 mg, 0.087 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (16 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4a** (60 mg, 0.079 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (45 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (60 mg, 58% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.32 (s, 1H), 12.24 (s, 1H), 10.07 (s, 1H), 8.92 (d, *J* = 7.5 Hz, 1H), 8.77 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.77 (d, *J* = 4.0 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.38 (dt, *J* = 18.6, 6.1 Hz, 3H), 7.31 (dd, *J* = 10.1, 6.1 Hz, 8H), 7.16 (ddt, *J* = 36.1, 14.9, 8.1 Hz, 13H), 7.10 – 7.06 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 4.19 (d, *J* = 7.5 Hz, 1H), 4.19 (d, *J* = 7.5 Hz, 1H), 3.81 (dq, *J* = 15.2, 8.4 Hz, 2H), 2.32 (ddt, *J* = 24.5, 13.2, 5.9 Hz, 3H), 1.79 (td, *J* = 12.7, 4.3 Hz, 1H), 1.62 (t, *J* = 8.8 Hz, 1H), 1.17 (dt, *J* = 5.8, 3.3 Hz, 12H), 0.84 (d, *J* = 5.2 Hz, 6H), 0.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 165.1, 164.2, 163.8, 162.7, 162.5, 162.2, 151.0, 150.9, 150.5, 150.3, 148.9, 145.5, 139.3, 139.2, 138.9, 136.8, 136.0, 135.3, 134.8, 134.7, 134.6, 134.4, 134.0, 133.9, 133.8, 133.7, 133.6, 130.8, 130.7, 130.6, 130.4, 129.8, 129.7, 129.7, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.0, 127.6, 126.0, 125.8, 123.4, 122.5, 122.2, 121.4, 120.6, 120.5, 117.4, 116.8, 116.7, 116.1, 101.2, 99.2, 92.0, 75.4, 75.2, 55.0, 54.4, 29.9, 29.5, 29.0, 28.4, 22.9, 19.5, 19.4, 16.6, 16.5, 14.3, 9.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.28, -10.67. HRMS (ESI) calculated for $C_{78}H_{71}N_6O_9P_2$ $[M + H]^+$: 1297.4752, found 1297.4734.

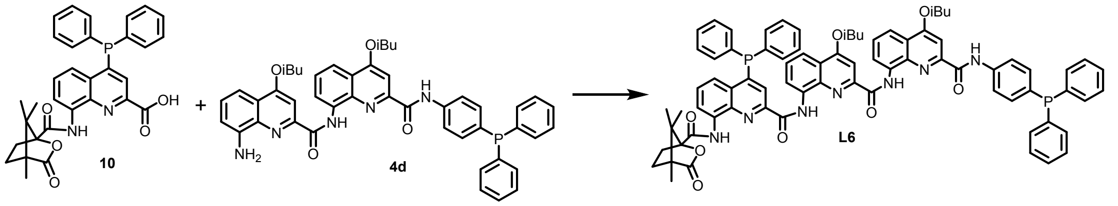


Compound **L4**: Compound **10** (60 mg, 0.109 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (20 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4b** (75 mg, 0.098 mmol, 0.90 equiv.) in DCM was slowly added DIPEA

(60 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (67 mg, 53% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.32 (s, 1H), 12.05 (s, 1H), 10.03 (s, 1H), 9.38 (s, 1H), 8.88 (d, *J* = 7.5 Hz, 1H), 8.59 (d, *J* = 7.3 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.74 (s, 1H), 7.73 – 7.59 (m, 6H), 7.57 – 7.43 (m, 5H), 7.31 (dt, *J* = 16.9, 8.5 Hz, 7H), 7.24 (d, *J* = 7.2 Hz, 7H), 7.12 (ddd, *J* = 28.7, 14.7, 7.4 Hz, 6H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.87 (s, 1H), 6.82 (t, *J* = 6.6 Hz, 1H), 6.66 (d, *J* = 9.2 Hz, 1H), 4.28 – 4.23 (m, 1H), 4.18 – 4.13 (m, 1H), 3.85 (dq, *J* = 15.3, 8.4 Hz, 2H), 2.43 – 2.20 (m, 4H), 2.17-2.10 (m, 1H), 1.81-1.77 (m, 1H), 1.67 – 1.58 (m, 2H), 1.24 – 1.15 (m, 12H), 0.83 (d, *J* = 8.2 Hz, 6H), 0.51 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 165.0, 164.2, 163.5, 163.3, 161.6, 160.1, 150.6, 148.6, 148.5, 138.9, 138.2, 137.6, 137.5, 137.3, 137.2, 137.0, 136.9, 135.8, 135.7, 135.5, 134.7, 134.5, 134.0, 133.9, 133.8, 133.7, 130.2, 129.7, 129.4, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 124.2, 124.0, 123.3, 122.6, 122.0, 121.1, 119.6, 118.0, 117.0, 116.8, 116.6, 99.3, 92.1, 75.6, 75.4, 55.1, 54.4, 32.1, 30.4, 29.9, 29.6, 29.0, 28.4, 19.4, 16.6, 16.5, 9.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ -4.17, -10.58. HRMS (ESI) calculated for $C_{78}H_{72}N_7O_8P_2$ $[M + H]^+$: 1296.4912, found 1296.4895.



Compound **L5**: Compound **10** (15 mg, 0.026 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (5 μL 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4c** (18 mg, 0.024 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (14 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (12 mg, 39% yield).^{1}H NMR (600 MHz, $CDCl_3$) δ 12.48 (s, 1H), 12.19 (s, 1H), 10.46 (d, *J* = 8.1 Hz, 1H), 10.01 (s, 1H), 8.95 (d, *J* = 7.3 Hz, 1H), 8.52 (d, *J* = 7.5 Hz, 1H), 8.07 – 7.83 (m, 8H), 7.70 – 7.58 (m, 7H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.36 (br, 7H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 12.2 Hz, 2H), 6.89 (t, *J* = 7.1 Hz, 5H), 6.81 (t, *J* = 6.5 Hz, 4H), 6.67 (s, 1H), 6.47 (s, 1H), 5.90 (s, 2H), 4.16 (br, 1H), 3.95 (br, 1H), 3.85 – 3.73 (m, 2H), 2.39 – 2.17 (m, 5H), 2.01 (br, 1H), 1.81 (br, 1H), 1.63 (br, 1H), 1.14 (d, *J* = 10.9 Hz, 12H), 0.86 (dd, *J* = 31.8, 14.7 Hz, 6H), 0.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 165.2, 164.5, 163.7, 163.1, 161.8, 159.8, 139.4, 139.3, 139.0, 138.1, 135.9, 134.6, 134.5, 133.9, 133.8, 133.6, 133.1, 133.0, 132.3, 131.1, 130.8, 130.7, 130.3, 129.7, 129.6, 129.5, 129.4, 129.1, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 124.7, 123.6, 122.8, 121.9, 121.1, 121.0, 120.9, 117.2, 116.9, 116.6, 116.4, 101.8, 99.3, 98.0, 92.1, 75.2, 55.0, 54.4, 32.1, 29.9, 29.6, 29.5, 29.0, 28.4, 27.4, 22.9, 19.6, 19.4, 16.6, 16.5, 14.3, 9.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ -10.88, -19.33. HRMS (ESI) calculated for $C_{78}H_{72}N_7O_8P_2$ $[M + H]^+$: 1296.4912, found 1296.4900.



Compound **L6**: Compound **10** (64 mg, 0.12 mmol, 1.0 equiv.) was dissolved in DCM under Ar and to this solution oxalyl chloride (22 μL, 2.0 equiv.) was added. The mixture was stirred for 2 hrs at room temperature and then the solvents and surplus oxalyl chloride were removed under reduced pressure to obtain the corresponding acyl chloride, which was dried for another 2 hrs and resolved in dry DCM. To the solution of compound **4d** (80 mg, 0.10 mmol, 0.90 equiv.) in DCM was slowly added DIPEA (63 μL, 3.00 equiv.), the acid chloride solution through a dry syringe in order. The resulting mixture was stirred at room temperature for another 16 hrs. The solution was removed and the residue was applied to a flash column chromatography to get product as a yellow solid (30 mg, 25% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.30 (s, 1H), 12.07 (s, 1H), 10.09 (s, 1H), 9.56 (s, 1H), 8.88 (s, 1H), 8.52 (s, 1H), 8.06 – 7.90 (m, 4H), 7.77 – 7.60 (m, 6H), 7.58 – 7.34 (m, 20H), 7.24 - 7.13 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.88 (s, 1H), 6.80 (d, *J* = 7.2 Hz, 2H), 4.28 – 4.19 (m, 1H), 4.10 (s, 1H), 3.94 – 3.84 (m, 2H), 2.83 (s, 1H), 2.43 – 2.14 (m, 6H), 2.02 (s, 1H), 1.83 (d, *J* = 13.0 Hz, 1H), 1.24 – 1.10 (m, 18H), 0.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 165.0, 164.1, 163.5, 163.4, 161.5, 159.8, 151.0, 150.7, 150.6, 148.6, 148.2, 138.6, 138.1, 137.9, 137.8, 137.4, 137.2, 135.8, 135.7, 135.6, 134.5, 134.4, 134.2, 134.1, 134.0, 133.4, 131.9, 131.8, 131.1, 130.8, 130.6, 130.3, 129.9, 129.6, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 127.8, 127.7, 123.3, 122.5, 122.0, 121.1, 121.0, 118.6, 118.5, 117.7, 117.1, 116.6, 116.6, 99.3, 98.2, 92.2, 75.5, 55.1, 30.4, 29.9, 29.0, 28.4, 19.5, 19.4, 16.7, 16.5, 9.9. ^{31}P NMR (243 MHz, $CDCl_3$) δ -5.31, -11.11. HRMS (ESI) calculated for $C_{78}H_{72}N_7O_8P_2$ $[M + H]^+$: 1296.4912, found 1296.4903.

3. ^{1}H NMR, ^{31}P NMR, MS and CD spectra for L[Rh] complexes

The procedure for the formation of L[Rh] complexes: One equivalent Rh(Cod)$_2$BF$_4$ was added to a solution of the bisphosphine ligand and the ^{1}H NMR, ^{31}P NMR, MS and CD spectra were conducted in a few minutes.

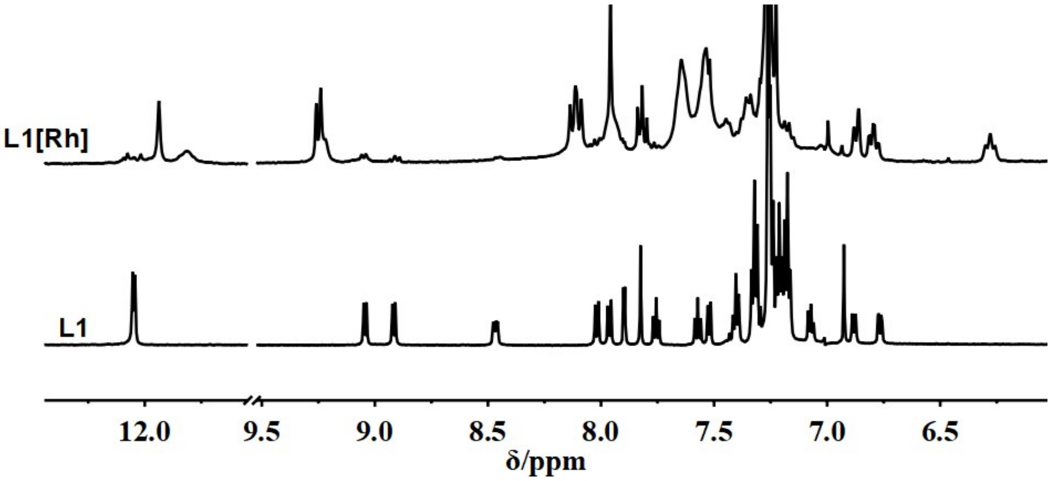


Fig. S1 ^{1}H NMR spectra of **L1** and the corresponding **L1**[Rh] in CDCl$_3$ at 298 K.

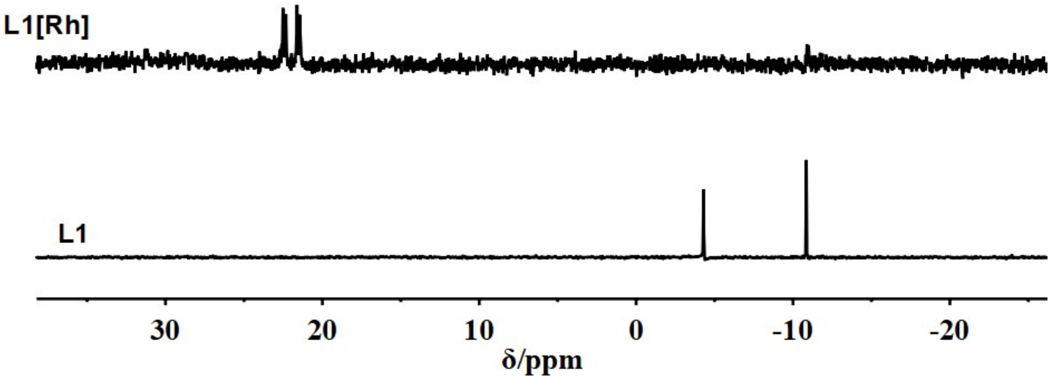


Fig. S2 ^{31}P NMR spectra of **L1** and the corresponding **L1**[Rh] (J = 43.74 Hz, 216.3 Hz) in CDCl$_3$ at 298 K.

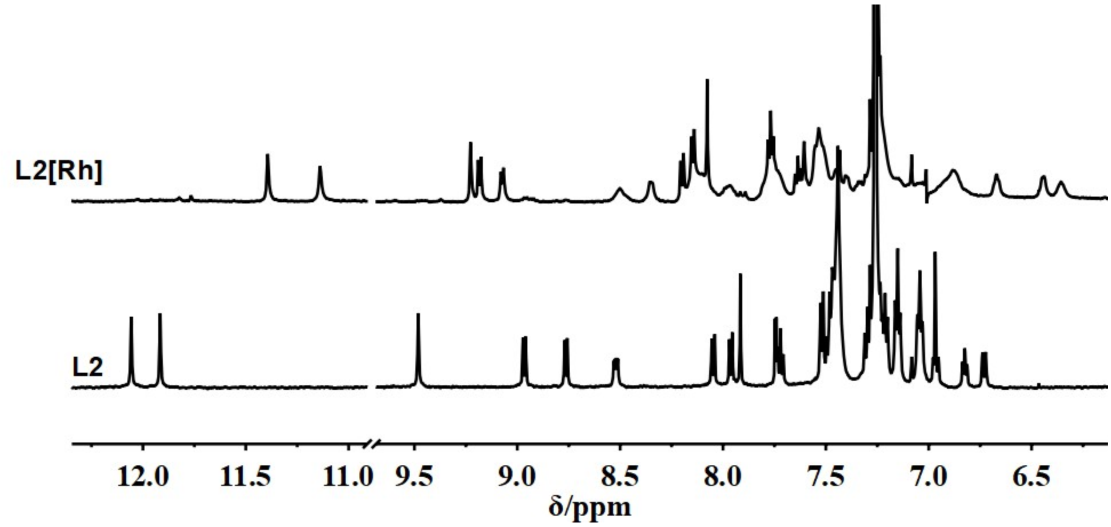


Fig. S3 ^{1}H NMR spectra of **L2** and the corresponding **L2**[Rh] in CDCl$_3$ at 298 K.

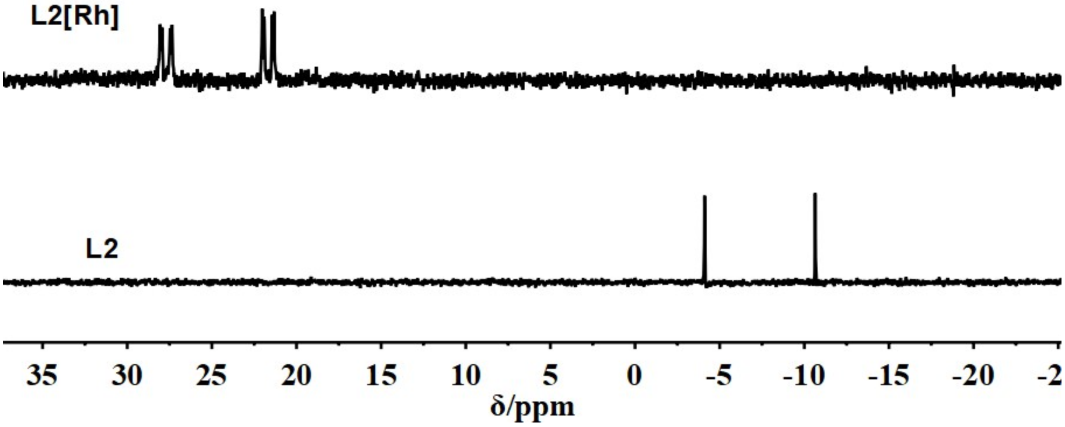


Fig. S4 ^{31}P NMR spectra of **L2** and the corresponding **L2**[Rh] ($J_{\text{P-P}}$=29.16 Hz, $J_{\text{P-Rh}}$ =140.9, 143.4 Hz) in CDCl$_3$ at 298 K.

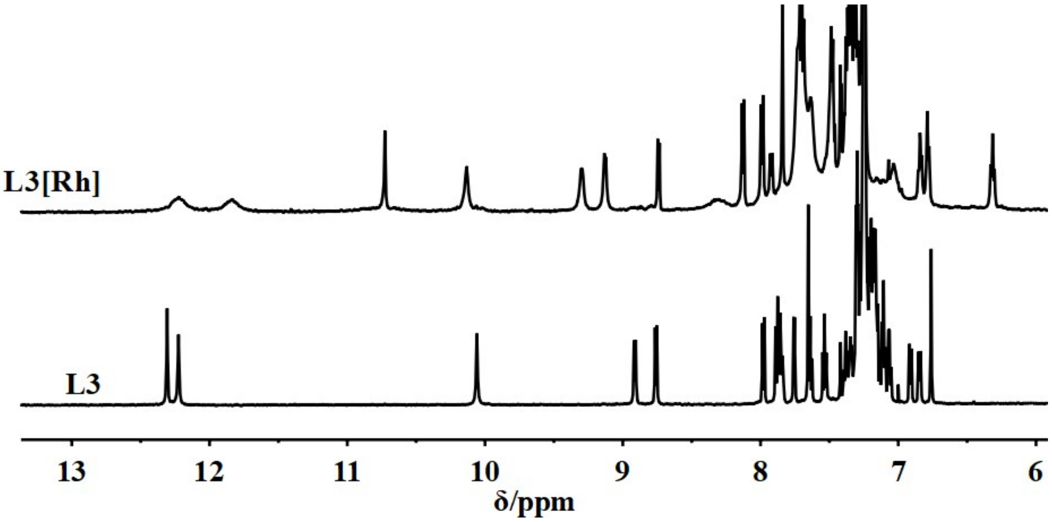


Fig. S5 ^{1}H NMR spectra of **L3** and the corresponding **L3**[Rh] in CDCl$_3$ at 298 K.

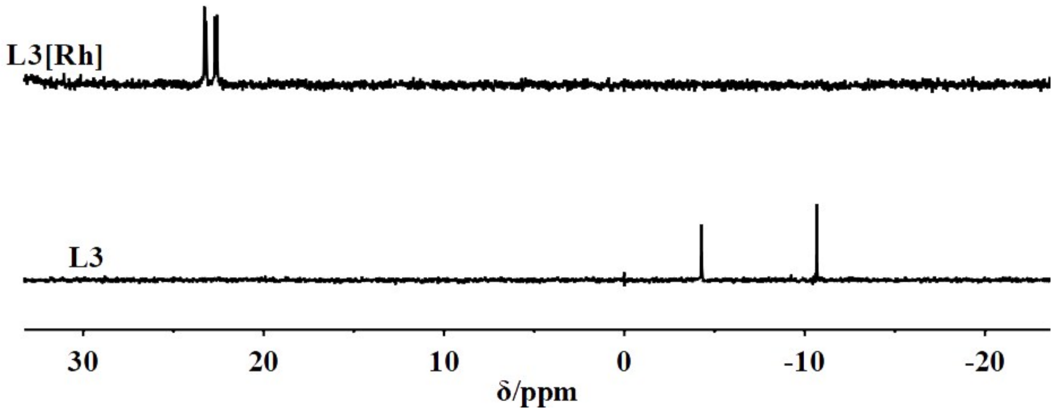


Fig. S6 ^{31}P NMR spectra of **L3** and the corresponding **L3**[Rh] (J = 26.7 Hz, 145.8 Hz) in $CDCl_3$ at 298 K.

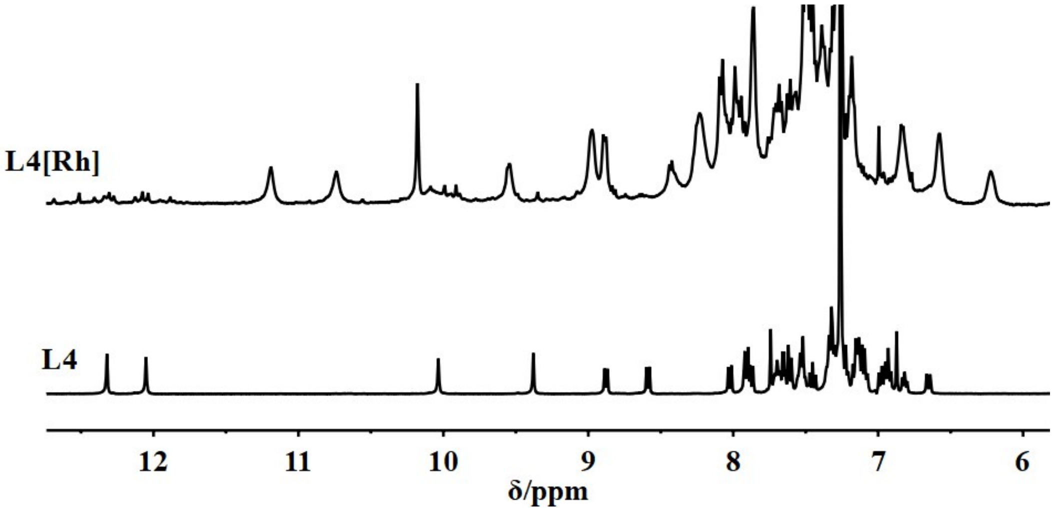


Fig. S7 ^{1}H NMR spectra of **L4** and the corresponding **L4**[Rh] in $CDCl_3$ at 298 K.

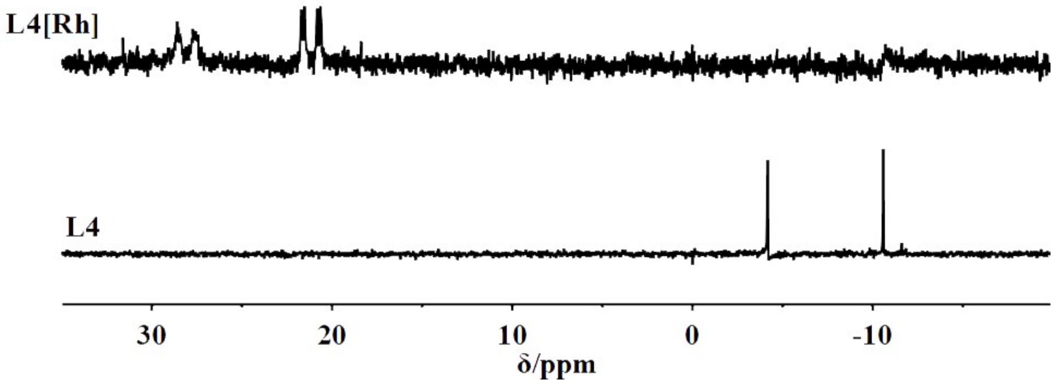


Fig. S8 ^{31}P NMR spectra of **L4** and the corresponding **L4**[Rh] ($J_{P\text{-}P}$=48.6 Hz, $J_{P\text{-}Rh}$ =172.5, 143.4 Hz) in $CDCl_3$ at 298 K.

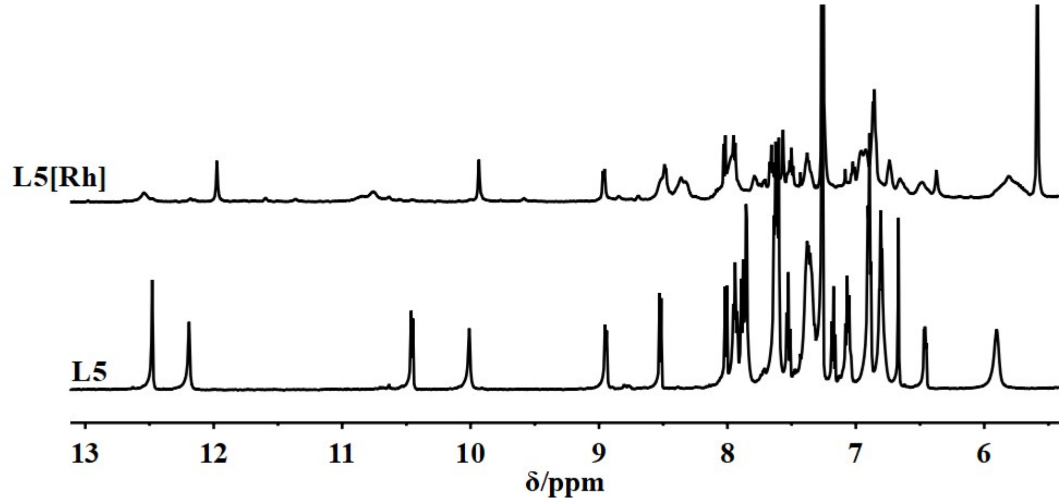


Fig. S9 ^{1}H NMR spectra of **L5** and the corresponding **L5**[Rh] in $CDCl_3$ at 298 K.

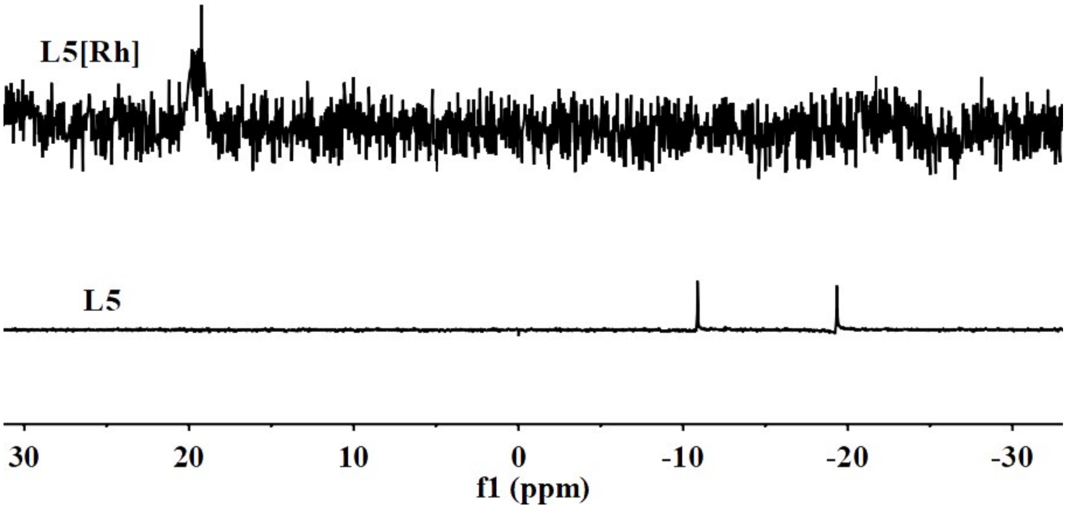


Fig. S10 ^{31}P NMR spectra of **L5** and the corresponding **L5**[Rh] in $CDCl_3$ at 298 K.

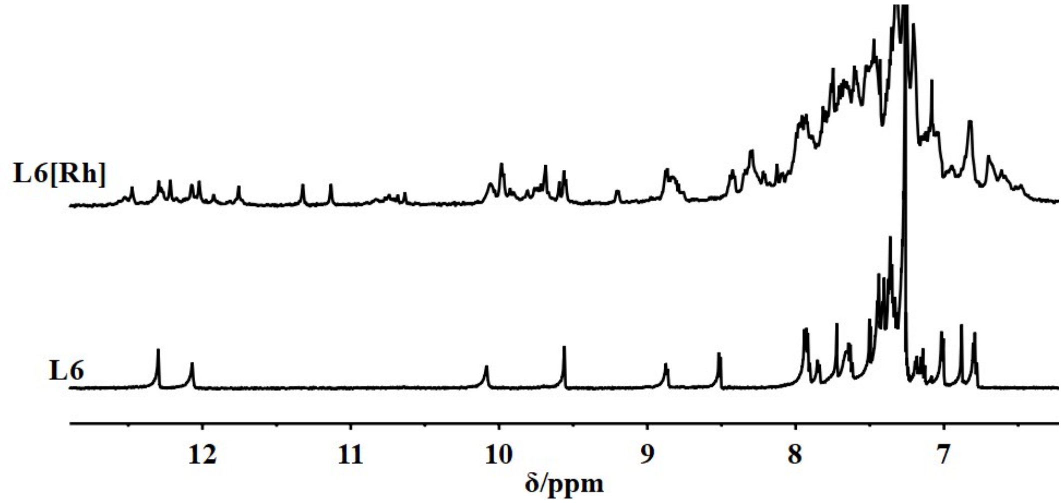


Fig.S11 ^{1}H NMR spectra of **L6** and the corresponding **L6**[Rh] in $CDCl_3$ at 298 K.

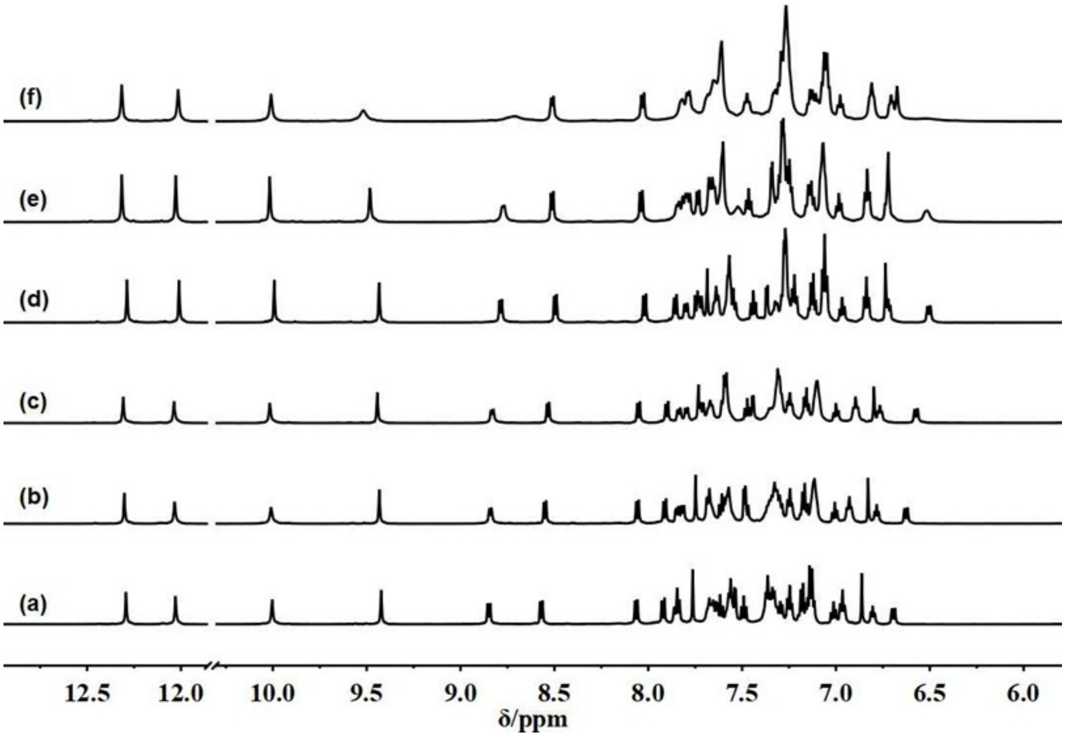


Fig. S12 Part of the variable temperature 600 MHz ^{1}H NMR spectra of **L4** at (a) 298 K, (b) 273 K, (c) 253 K, (d) 233 K, (e) 213 K and (f) 193 K in CD_2Cl_2.

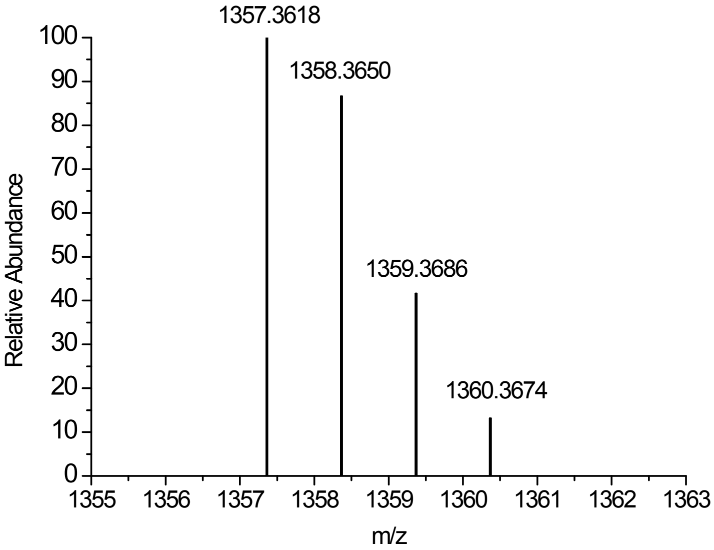


Fig. S13 ESI-Ms spectra of **L1**[Rh] calculated for $C_{76}H_{69}N_6O_8P_2Rh^+$: 1357.3629, found 1357.3618.

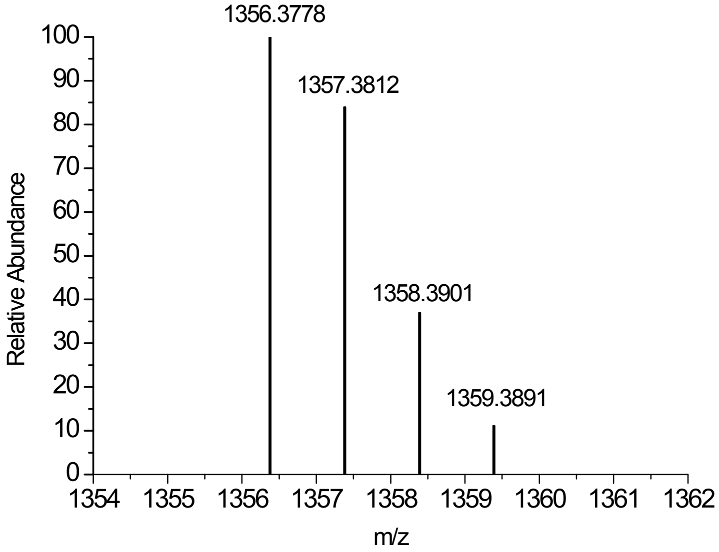


Fig. S14 ESI-Ms spectra of **L2**[Rh] calculated for $C_{76}H_{69}N_7O_7P_2Rh^+$: 1356.3789, found 1356.3778.

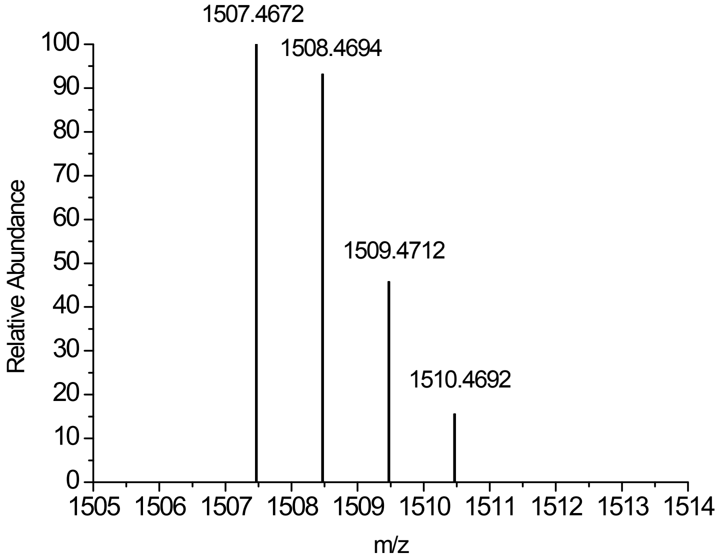


Fig. S15 ESI-Ms spectra of **L3**[Rh] calculated for $C_{86}H_{82}N_6O_9P_2Rh^+$: 1507.4674, found 1507.4672.

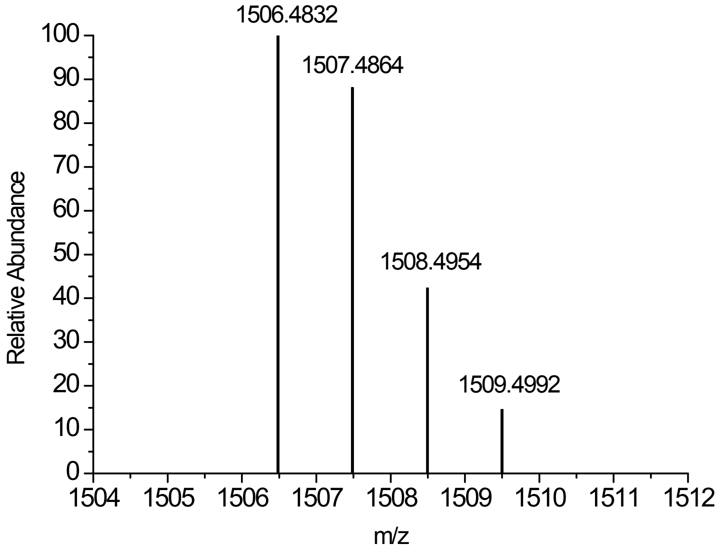


Fig. S16 ESI-Ms spectra of **L4**[Rh] calculated for $C_{86}H_{83}N_7O_8P_2Rh^+$: 1506.4828, found 1506.4832.

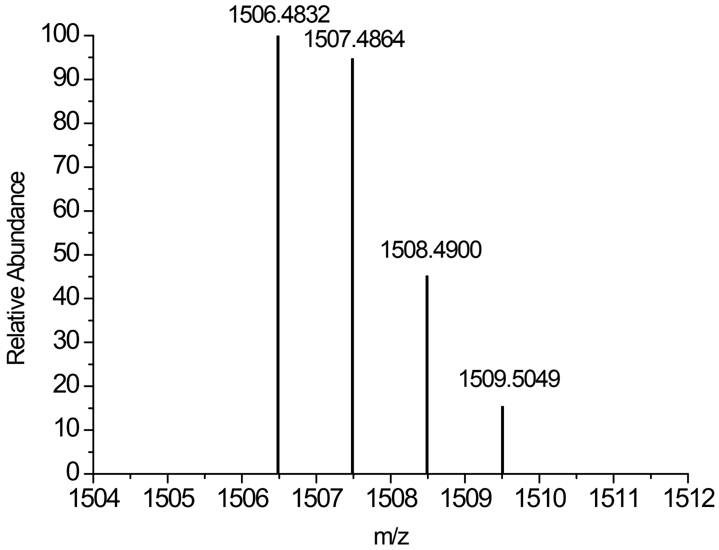


Fig. S17 ESI-Ms spectra of **L5**[Rh] calculated for $C_{86}H_{83}N_7O_8P_2Rh^+$: 1506.4828, found 1506.4832.

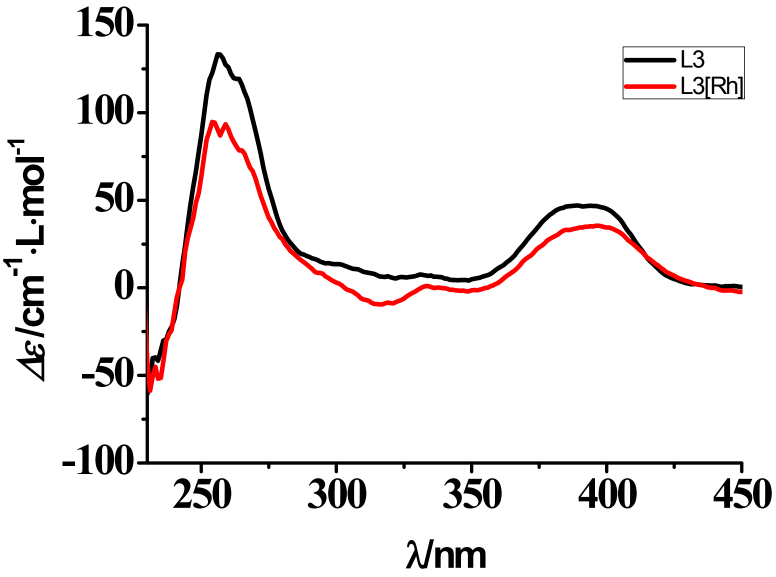


Fig. 18 CD spectra of **L3** and L3[Rh] in DCM at 298 K.

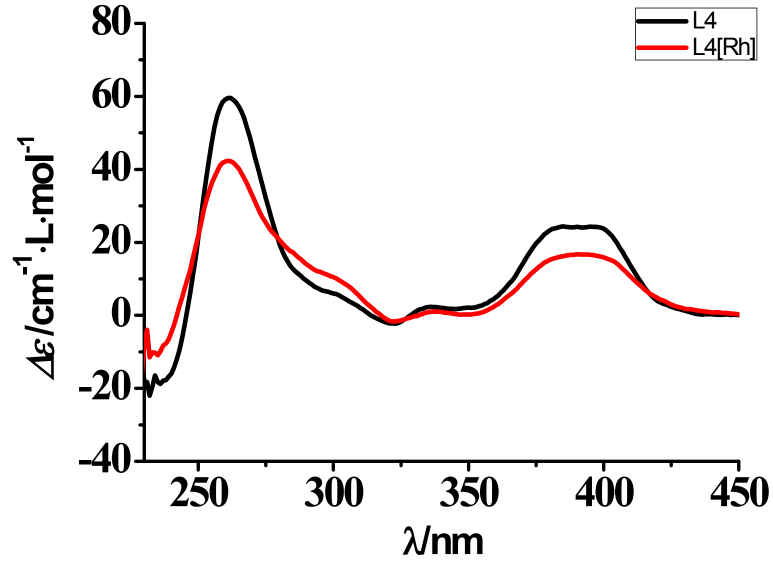


Fig. 19 CD pectra of **L4** and L4[Rh] in DCM at 298 K.

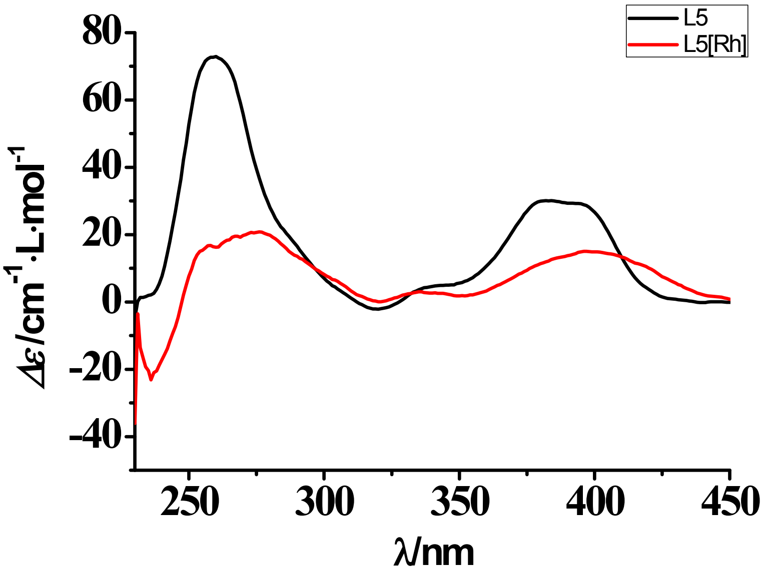


Fig. 20 CD spectra of **L5** and L5[Rh] in DCM at 298 K.

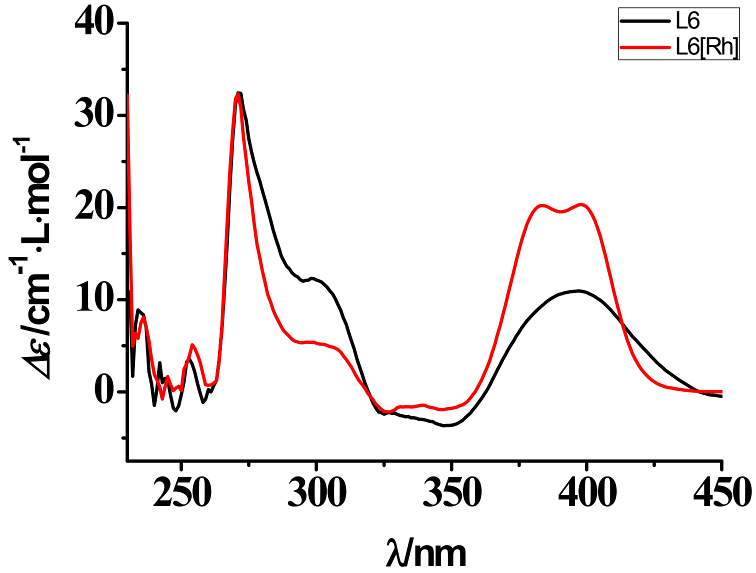
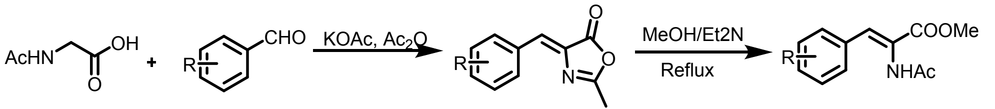


Fig. 21 CD spectra of **L6** and L6[Rh] in DCM at 298 K.

4. General procedure for the hydrogenation reaction

5.1 Synthesis of compound **1a-1g**

Compound **1a-1g** and their hydrogenation products are known compounds and were prepared according to the literature (*Angew. Chem. Int. Ed.*, 2015, **54**, 4334-4337). The ^{1}H NMR spectra are consistent with the literature



R=H, **1a**; 2-OMe, **1b**; R=3-OMe, **1c;**
R=4-OMe**, 1d**; R=3-Cl, **1e;** R=4-F, **1f**;
R=2-Me, **1g**

Compound **1a**: White solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.46 (d, *J* = 4.0 Hz, 2H), 7.39-7.35 (m, 3H), 3.85 (s, 3H), 2.14 (s, 3H).

Compound **1b**: Off-white solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.46 – 7.30 (m, 3H), 7.24 (br, 1H), 6.99 – 6.92 (m, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 2.07 (s, 3H).

Compound **1c**: White solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.38 – 7.27 (m, 2H), 7.11 – 6.84 (m, 4H), 3.85 (s, 3H), 3.80 (s, 3H), 2.14 (s, 3H).

Compound **1d**: White solid. ^{1}H NMR (600 MHz, CDCl$_3$-*d*) δ 7.42 (d, *J* = 22.5 Hz, 3H), 6.92 (d, *J* = 37.8 Hz, 3H), 3.84 (s, 6H), 2.16 (s, 3H).

Compound **1e**: White solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.44 (br, 1H), 7.31 (d, *J* = 10.7 Hz, 4H), 7.03 (br, 1H), 3.86 (s, 3H), 2.15 (s, 3H).

Compound **1f**: White solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.45 (br, 2H), 7.40 (br, 1H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.98 (br, 1H), 3.86 (s, 3H), 2.16 (s, 3H).

Compound **1g**: White solid. ^{1}H NMR (400 MHz, CDCl$_3$-*d*) δ 7.43 – 7.32 (m, 3H), 7.18 (d, J = 7.4 Hz, 2H), 6.92 (s, 1H), 3.84 (s, 3H), 2.36 (s, 3H), 2.15 (s, 3H).

5.2 Characterization Data of reduced products

Compound **1a –H**: ^{1}H NMR (600 MHz, CDCl$_3$-*d*) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 5.90 (s, 1H), 4.89 (q, *J* = 5.8 Hz, 1H), 3.73 (s, 3H), 3.17 – 3.07 (m, 2H), 1.99 (s, 3H).

Compound **1b–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.24 (td, *J* = 8.2, 1.6 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.92 – 6.85 (m, 2H), 6.22 (s, 1H), 4.74 (q, *J* = 6.7 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.10 (s, 2H), 1.93 (s, 3H).

Compound **1c–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 6.9 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 5.92 (s, 1H), 4.92 – 4.84 (m, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.09 (qd, *J* = 13.8, 5.7 Hz, 2H), 1.99 (s, 3H).

Compound **1d–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.00 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.88 (s, 1H), 4.84 (q, *J* = 5.7 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.06 (qd, *J* = 14.0, 5.6 Hz, 2H), 1.99 (s, 3H).

Compound **1e–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.22 (d, *J* = 5.8 Hz, 2H), 7.08 (s, 1H), 6.98 (d, *J* = 5.8 Hz, 1H), 5.96 (s, 1H), 4.87 (q, *J* = 5.9 Hz, 1H), 3.74 (s, 3H), 3.10 (ddd, *J* = 43.4, 13.9, 5.7 Hz, 2H), 2.00 (s, 3H).

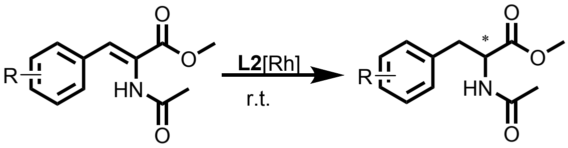
Compound **1f–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.08 – 7.02 (m, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 5.92 (s, 1H), 4.86 (q, *J* = 6.0 Hz, 1H), 3.72 (s, 3H), 3.16 – 3.03 (m, 2H), 1.99 (s, 3H).

Compound **1g–H**: ^{1}H NMR (600 MHz, $CDCl_3$-*d*) δ 7.09 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 5.93 – 5.82 (m, 1H), 4.91 – 4.80 (m, 1H), 3.73 (s, 3H), 3.08 (qd, *J* = 13.9, 5.7 Hz, 2H), 2.31 (s, 3H), 1.98 (s, 3H).

5.3 General procedure for the hydrogenation reaction

To a 5-mL vial containing a magnetic stirring bar was added the substrate (0.2 mmol) and the Rh(I)-complex in a solution under an argon atmosphere. The vial was purged three times with hydrogen and finally pressurized to 7 or 10 atm. The reaction mixture was stirred at room temperature for several hours. The residual hydrogen gas was released in a hood, and the conversion were determined by ^{1}H NMR analysis of the crude mixture. The reaction mixture was concentrated in vacuum, and the residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (10/1) as the eluent to afford the corresponding product as an off-white solid. The *ee* of the products were determined by GC using a Varian Chirasil-L-Val column CP7495 (25 m *0.25 mm). The ^{1}H NMR and GC spectra determining the conversions and *ee* values were shown blow. When 4% mol L2[Rh] or L1[Rh] was used as the catalyst, the conversions of the hydrogenation for **1a-1g** were over 98% in the solvents $CDCl_3$, toluene and THF and the ^1H NMR spectra were shown only once.

Table S1 Optimization for Hydrogenation of α-dehydroamino acid esters based on **L2**.



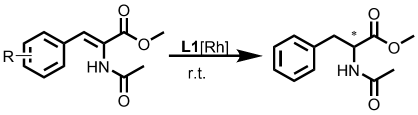
Entry	Substrate (R)	Conv. (%)[a]	Conv. (%)[b]	Conv. (%)[c]	Conv. (%)[d]	Conv. (%)[e]
1	**1a** (H)	30	94	>98	>98	>98
2	**1b** (2-OMe)	20	85	>98	>98	>98
3	**1c** (3-OMe)	15	84	>98	>98	>98
4	**1d** (4-OMe)	80	80	>98	>98	>98
5	**1e** (3-Cl)	80	72	>98	>98	>98
6	**1f** (4-F)	60	>98	>98	>98	>98
7	**1g** (2-Me)	65	>98	>98	>98	>98

Conditions: [a] 1 atm of H_2, **L2**/$Rh(Cod)_2BF_4$/substrate=2/2/100, $CDCl_3$;

[b] 10 atm of H_2, **L2**/$Rh(Cod)_2BF_4$/substrate=2/2/100, $CDCl_3$;

7 atm of H_2, **L2**/$Rh(Cod)_2BF_4$/substrate=4/4/100, 12 h, the solvent are [c]$CDCl_3$, [d]THF and [e]toluene; respectively; the conversions were determined by ^1H NMR spectra.

Table S2 Optimization for Hydrogenation of α-dehydroamino acid esters based on **L1**.



Entry	Substrate (R)	Conv. (%)[a]	Conv. (%)[b]	Conv. (%)[c]
1	**1a** (H)	>98	>98	>98
2	**1b** (2-OMe)	>98	>98	>98
3	**1c** (3-OMe)	>98	>98	>98
4	**1d** (4-OMe)	>98	>98	>98
5	**1e** (3-Cl)	>98	>98	>98
6	**1f** (4-F)	>98	>98	>98
7	**1g** (2-Me)	>98	>98	>98

Conditions: 7 atm of H_2, **L1**/$Rh(Cod)_2BF_4$/substrate=4/4/100, 12 h, and the conversions were determined by ^1H NMR spectra, the solvents are [a] $CDCl_3$, [b] THF and [c] toluene respectively.

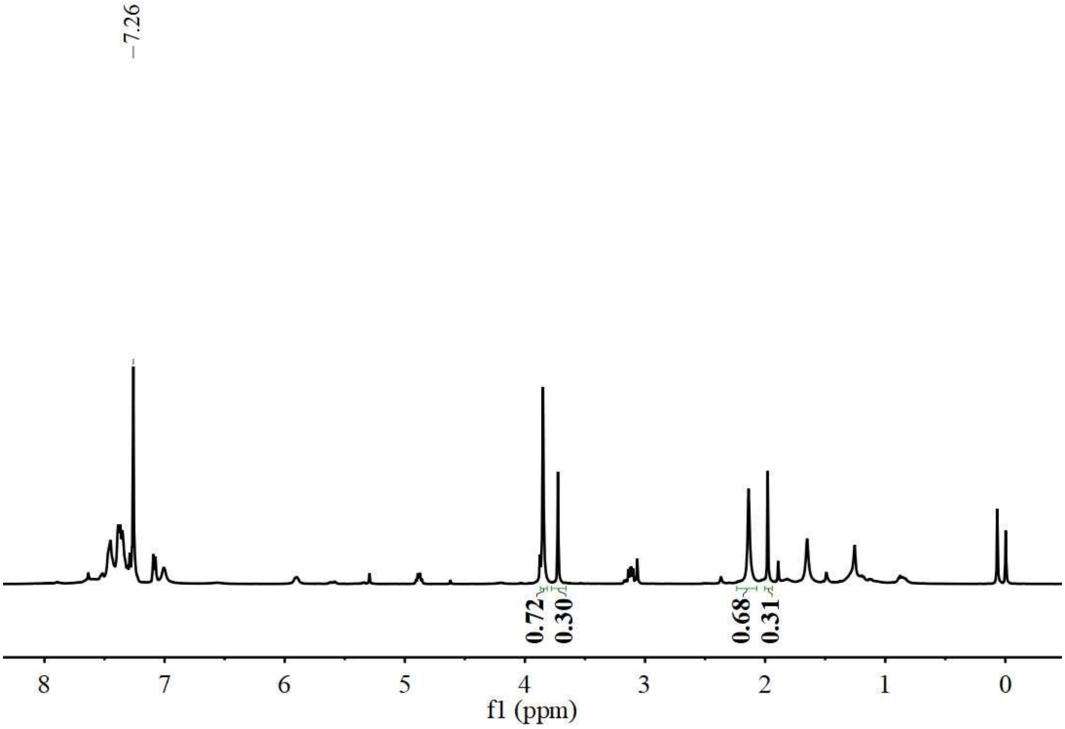


Fig. S22 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 30%.

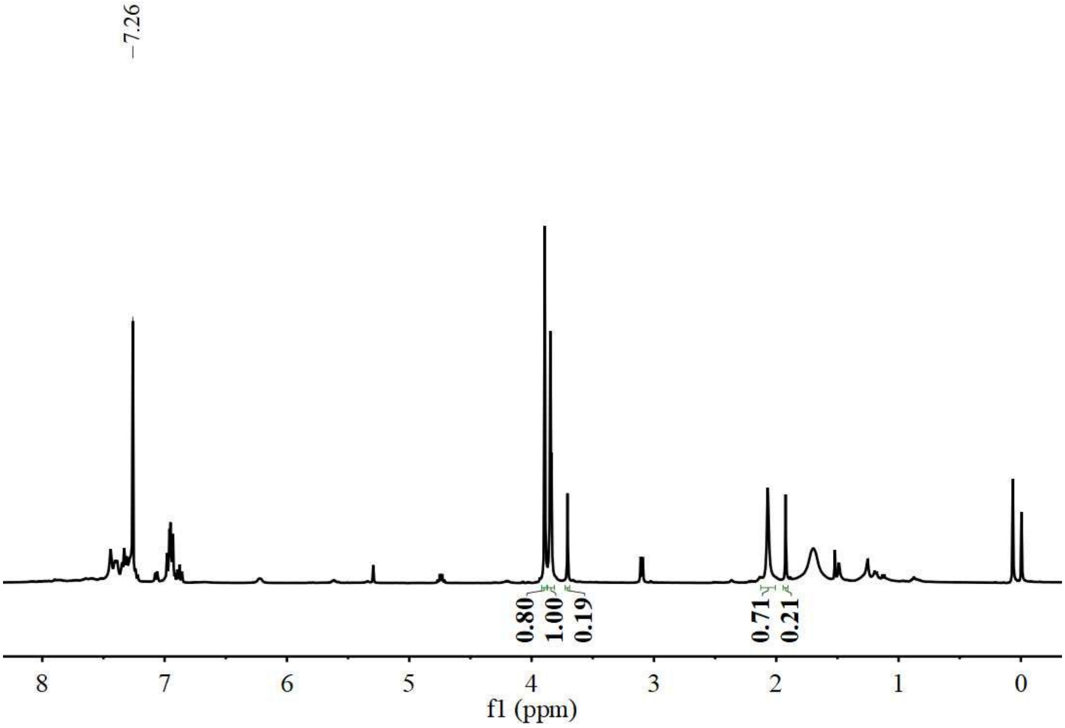


Fig. S23 The ^{1}H NMR spectrum of the hydrogenation of **1b** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 20%.

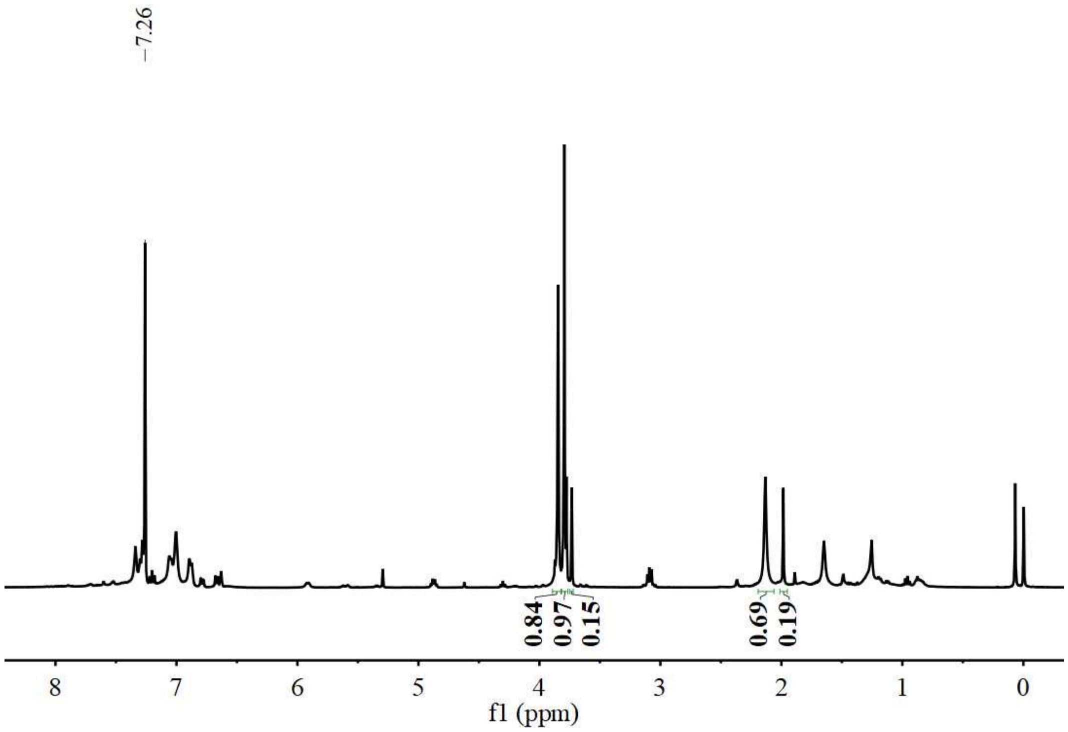


Fig. S24 The ^{1}H NMR spectrum of the hydrogenation of **1c** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 15%.

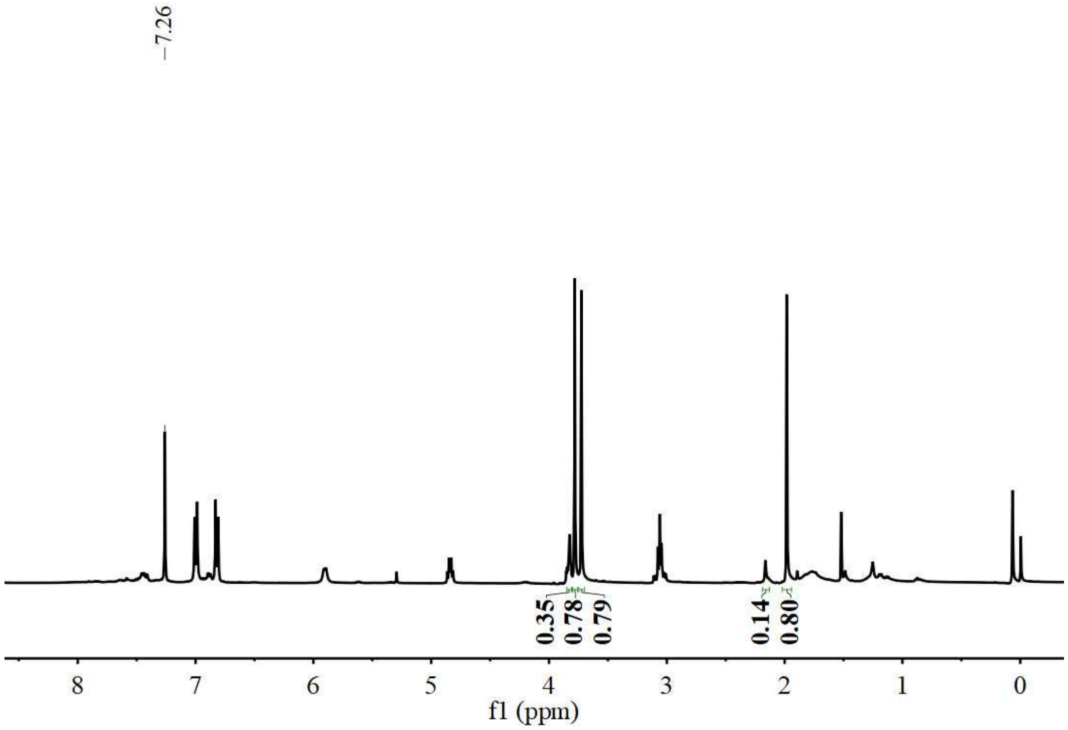


Fig. S25 The ^{1}H NMR spectrum of the hydrogenation of **1d** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 80%.

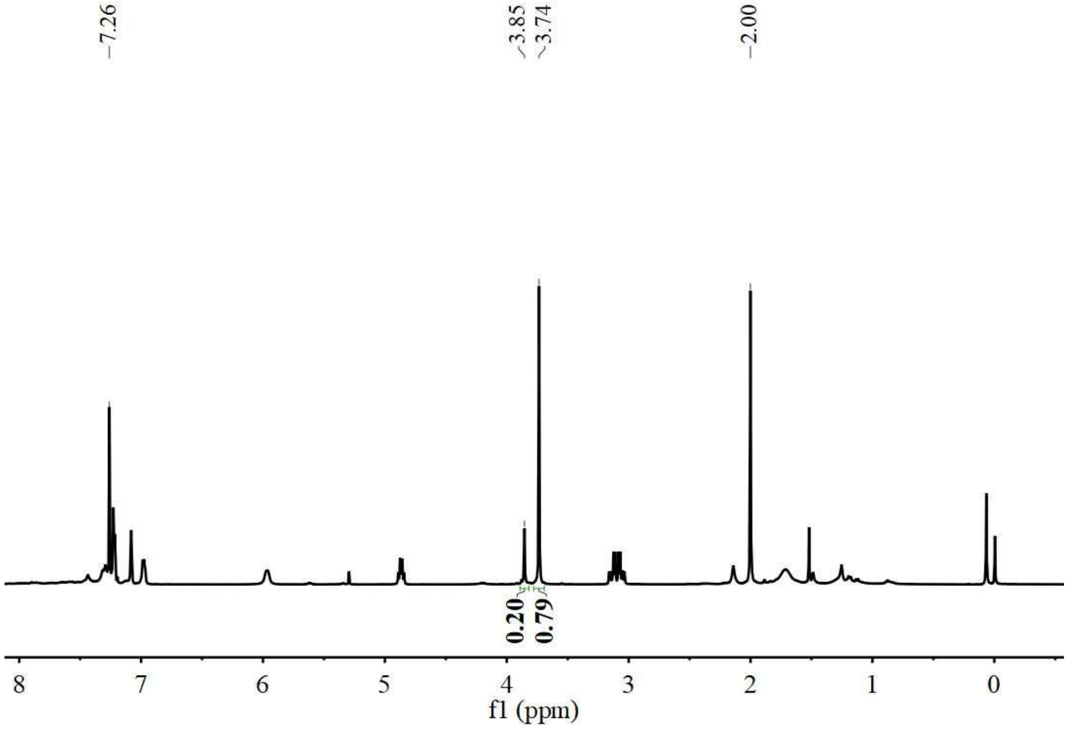


Fig. S26 The ^{1}H NMR spectrum of the hydrogenation of **1e** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 80%.

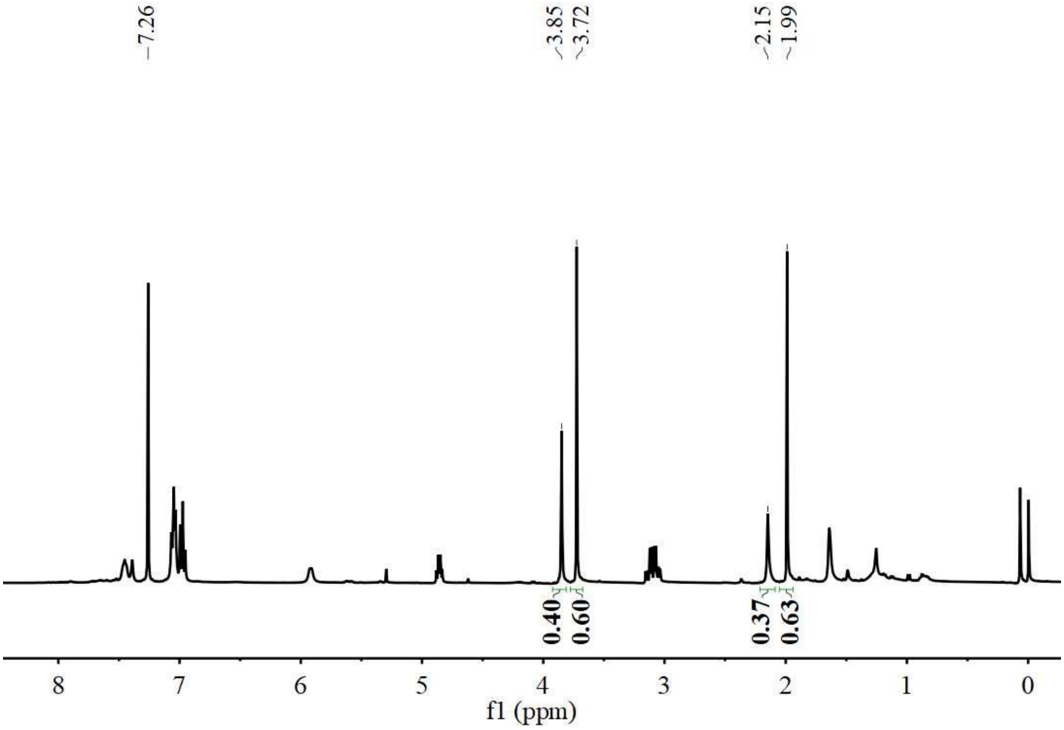


Fig. S27 The ^{1}H NMR spectrum of the hydrogenation of **1f** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 60%.

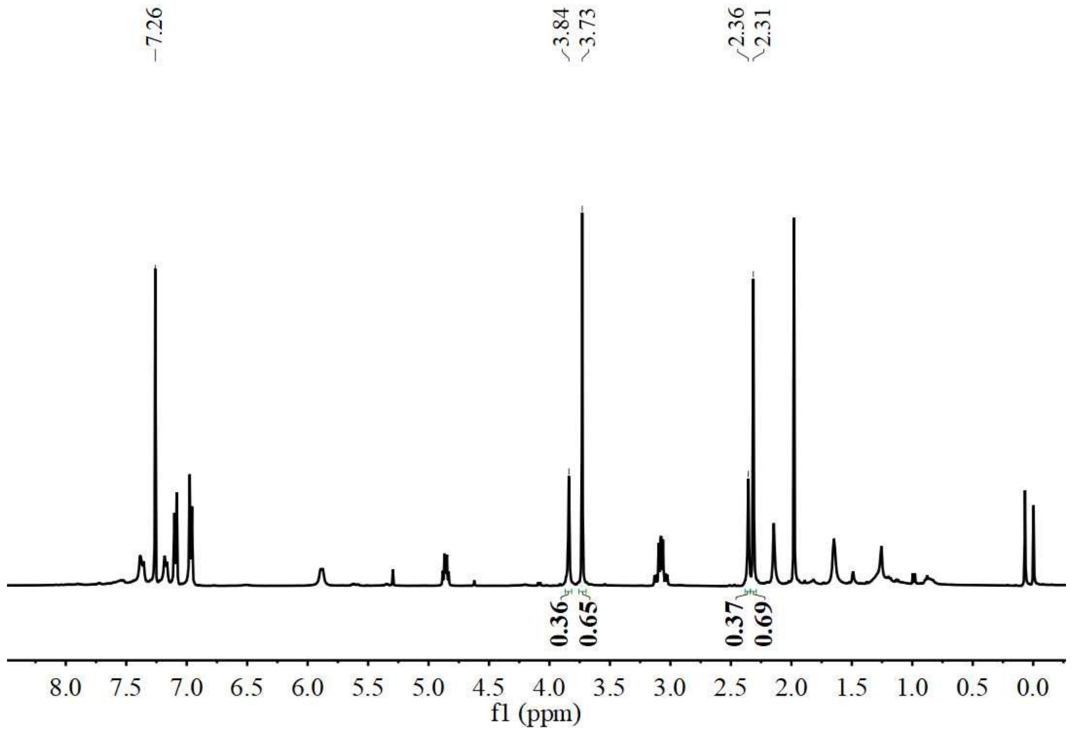


Fig. S28 The ^{1}H NMR spectrum of the hydrogenation of **1g** when 2% L2[Rh] and 1 atm of H_2 were used. The conversion of this reaction is 65%.

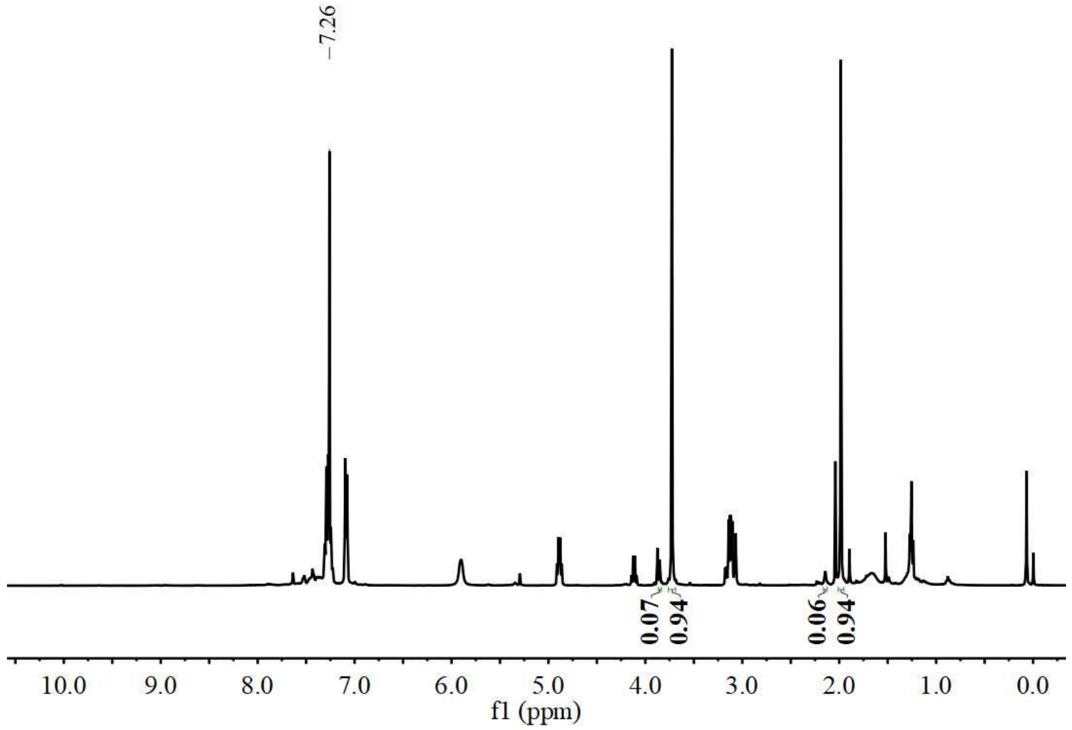


Fig. S29 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 94%.

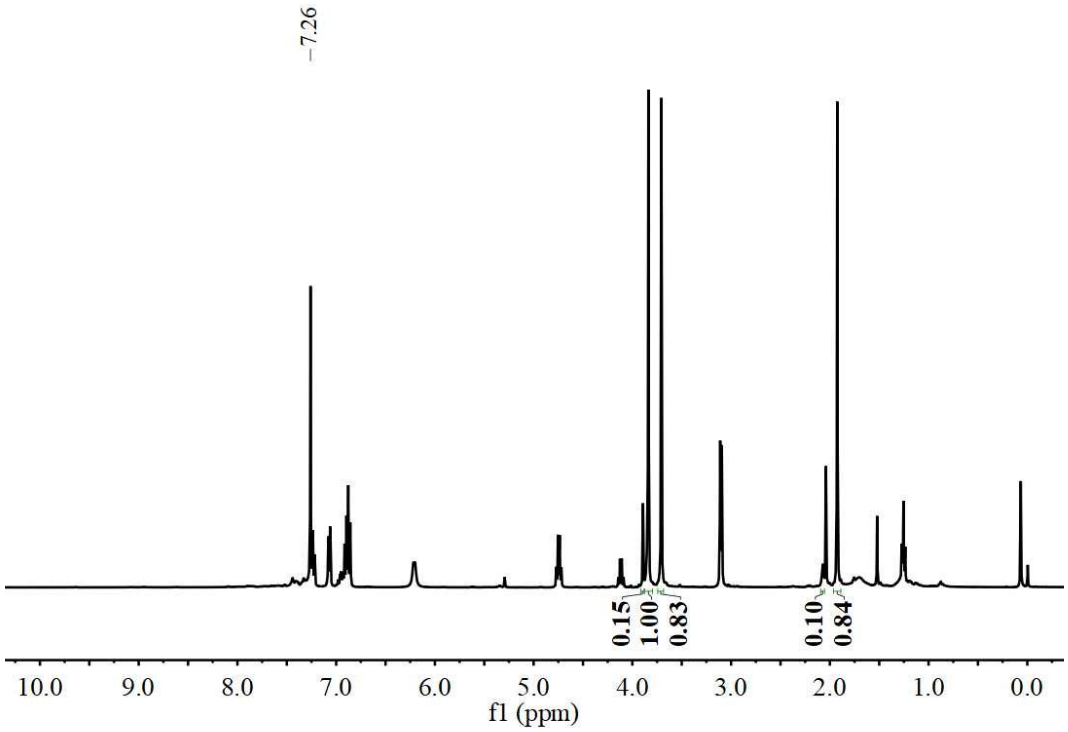


Fig. S30 The ^1H NMR spectrum of the hydrogenation of **1b** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 85%.

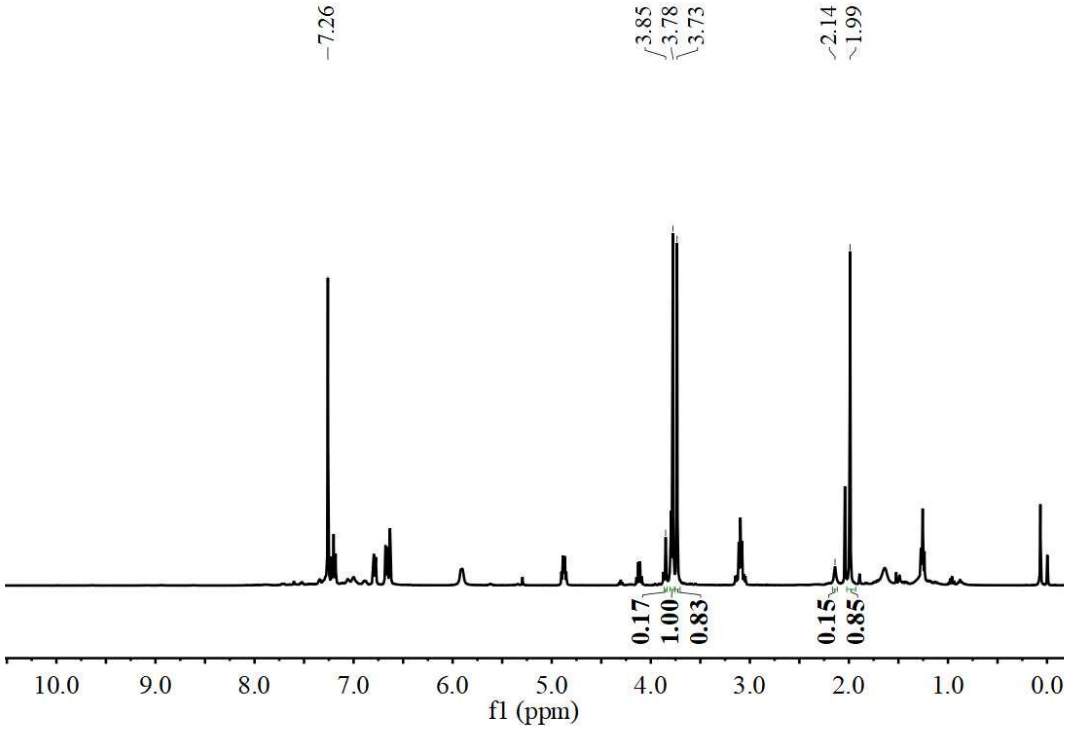


Fig. S31 The ^1H NMR spectrum of the hydrogenation of **1c** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 84%.

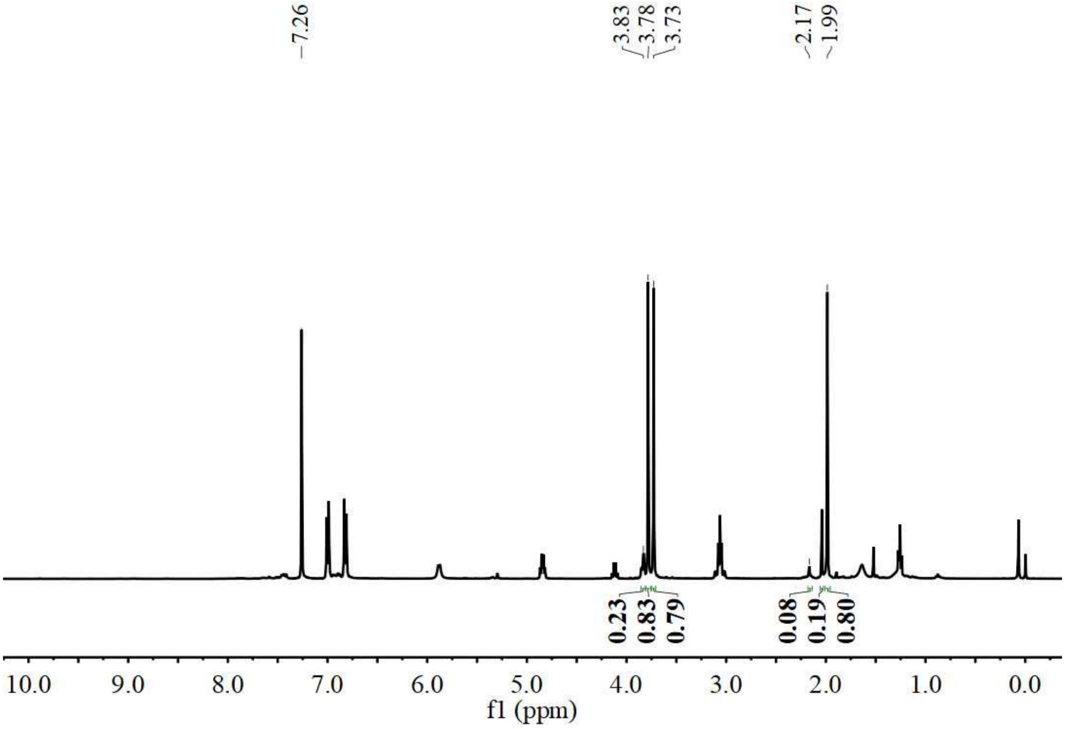


Fig. S32 The ^{1}H NMR spectrum of the hydrogenation of **1d**when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 80%.

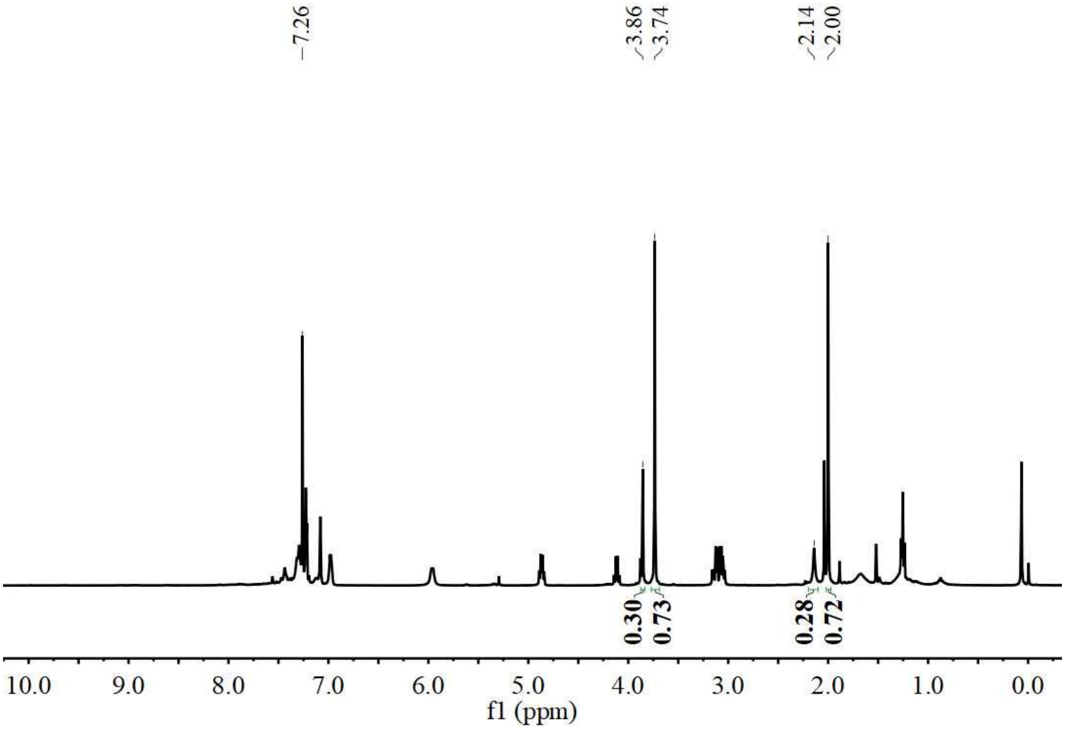


Fig. S33 The ^{1}H NMR spectrum of the hydrogenation of **1e** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 72%.

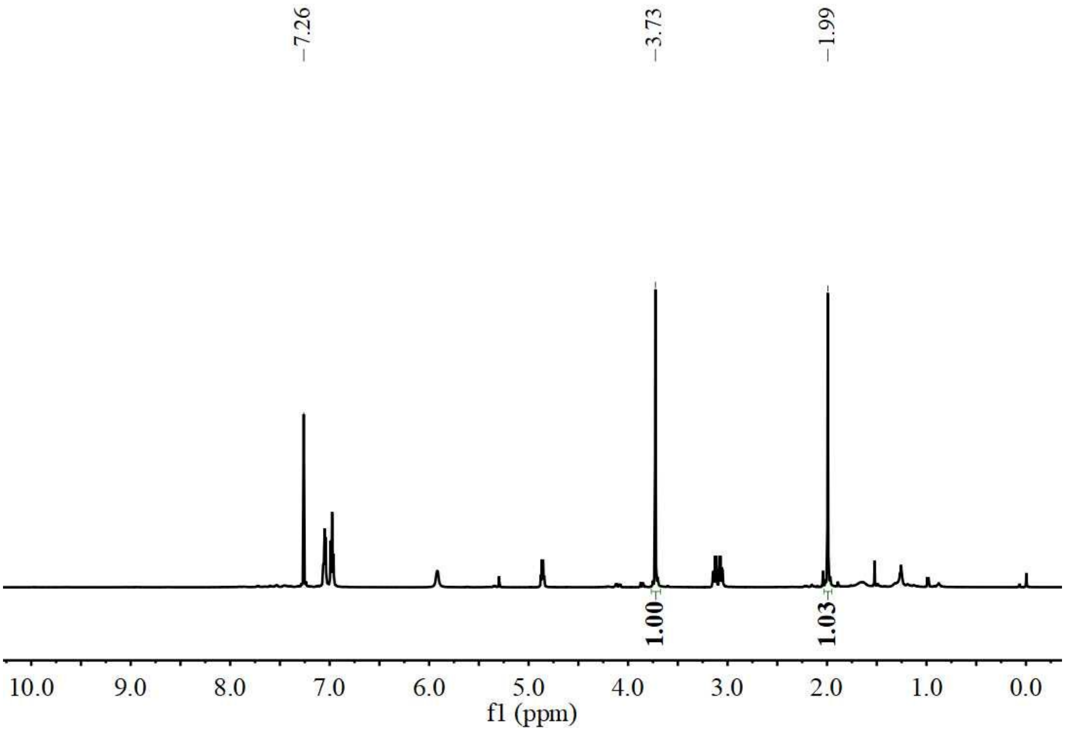


Figure S34. The ^{1}H NMR spectrum of the hydrogenation of **1f** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 98%.

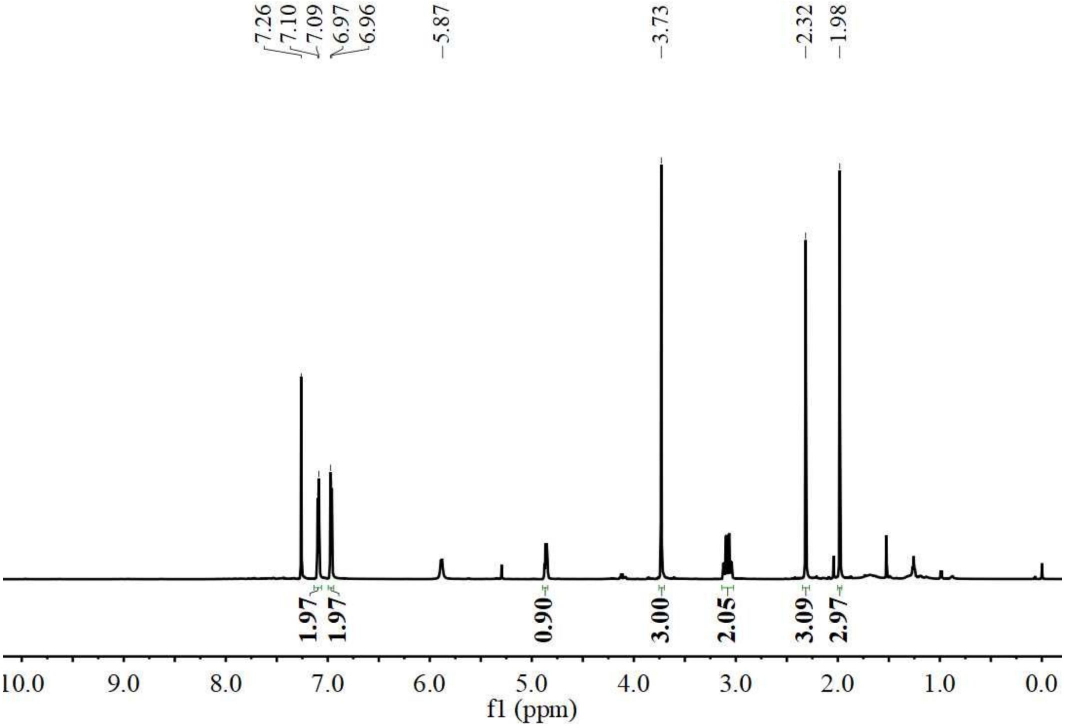


Fig. S35 The ^{1}H NMR spectrum of the hydrogenation of **1g** when 2% L2[Rh] and 10 atm of H_2 were used. The conversion of this reaction is 98%.

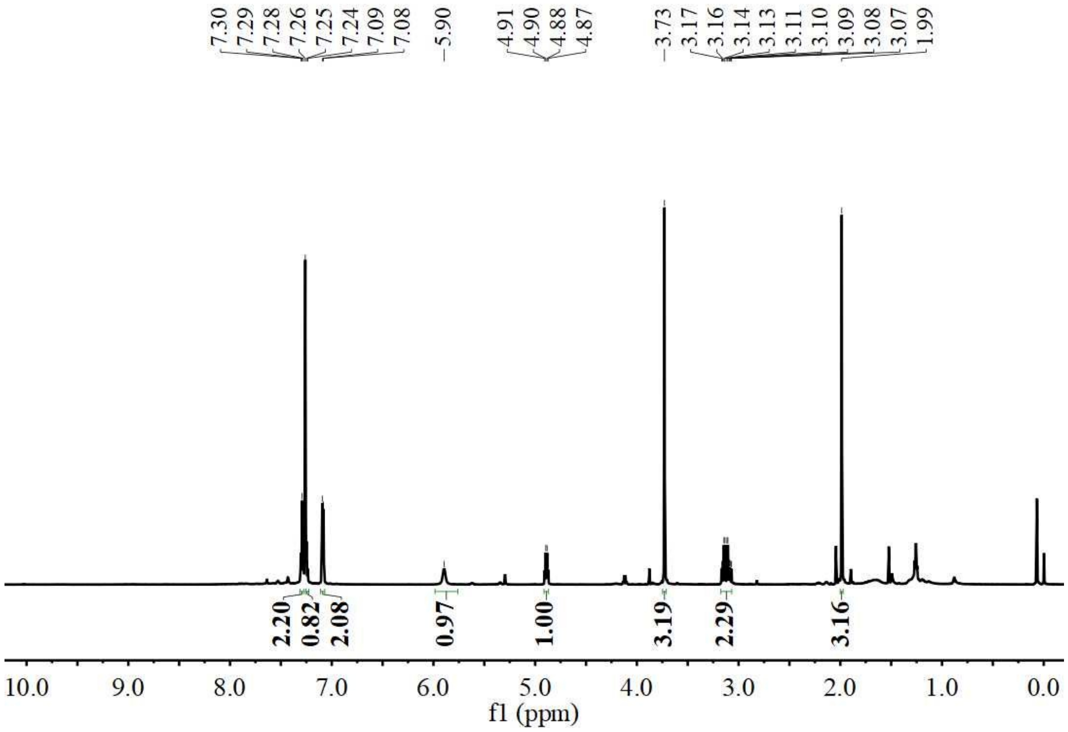


Fig. S36 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

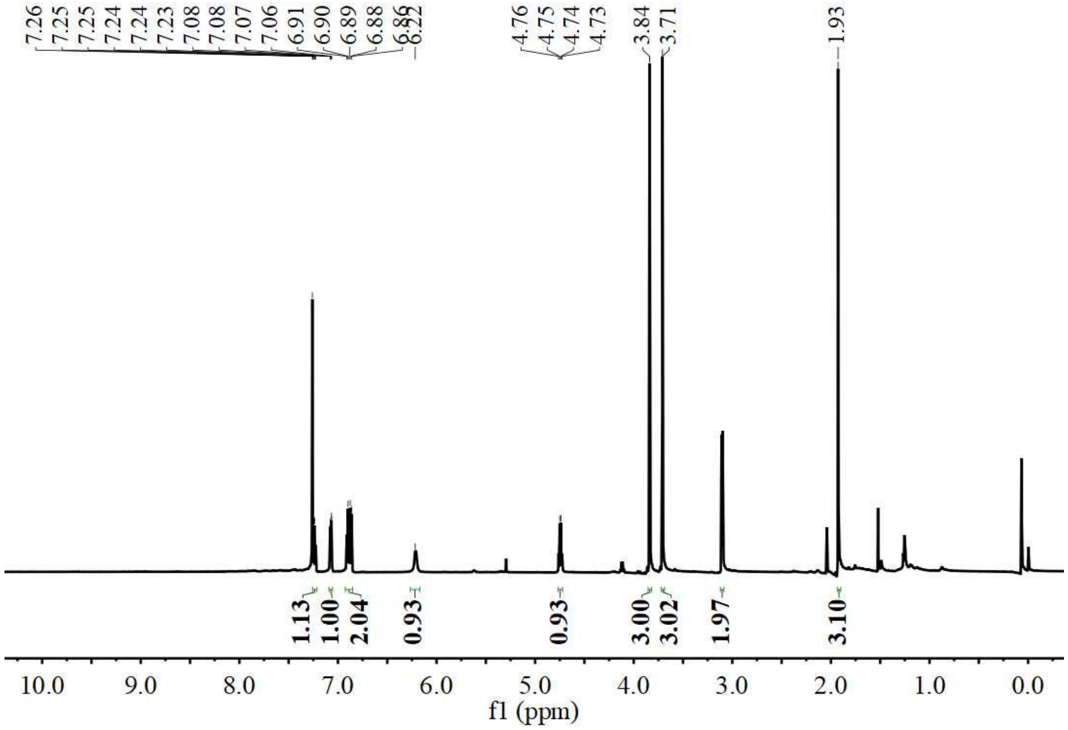


Fig. S37 The ^{1}H NMR spectrum of the hydrogenation of **1b** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

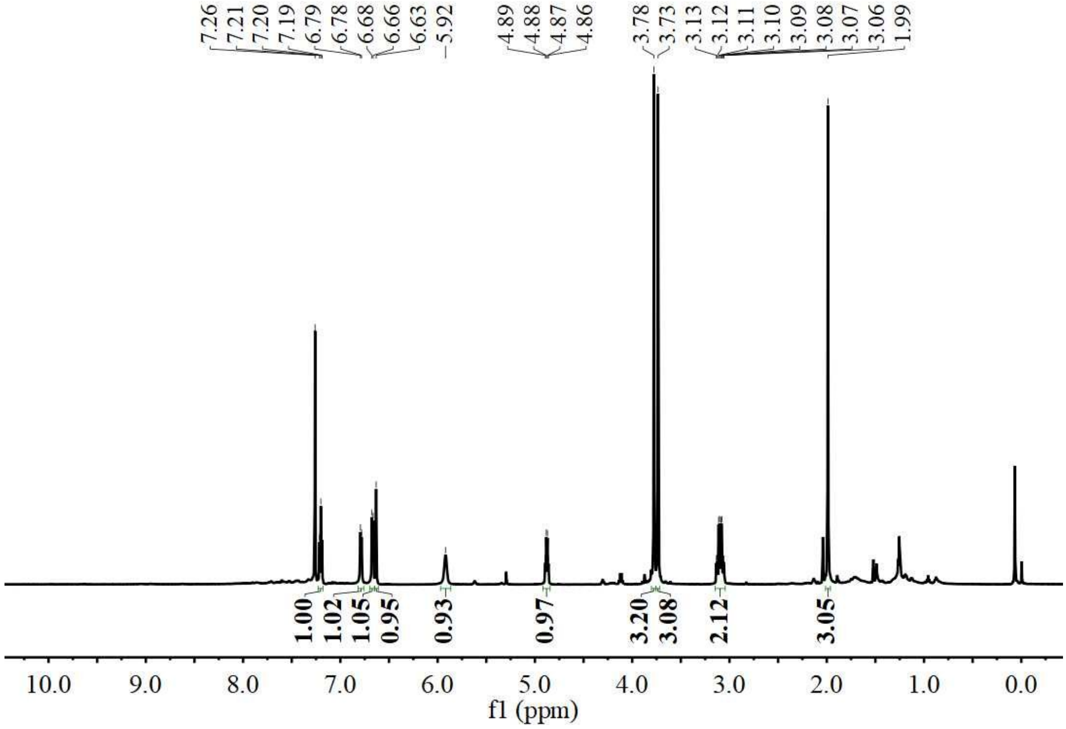


Fig. S38 The ^{1}H NMR spectrum of the hydrogenation of **1c** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

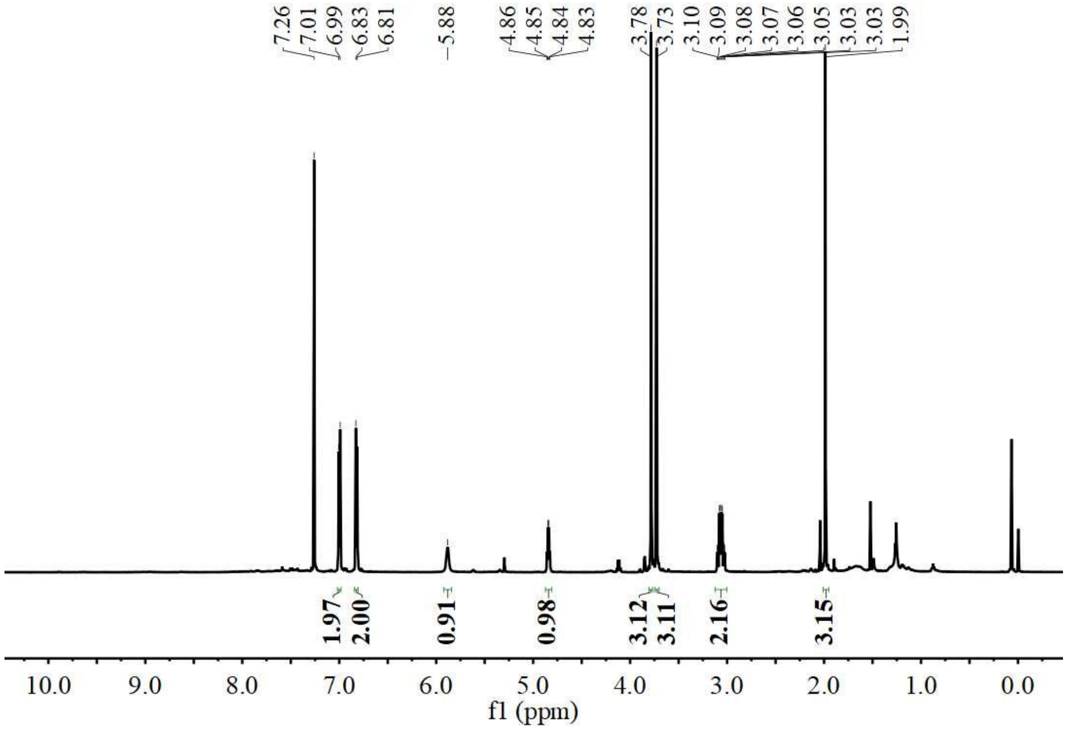


Fig. S39 The ^{1}H NMR spectrum of the hydrogenation of **1d** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

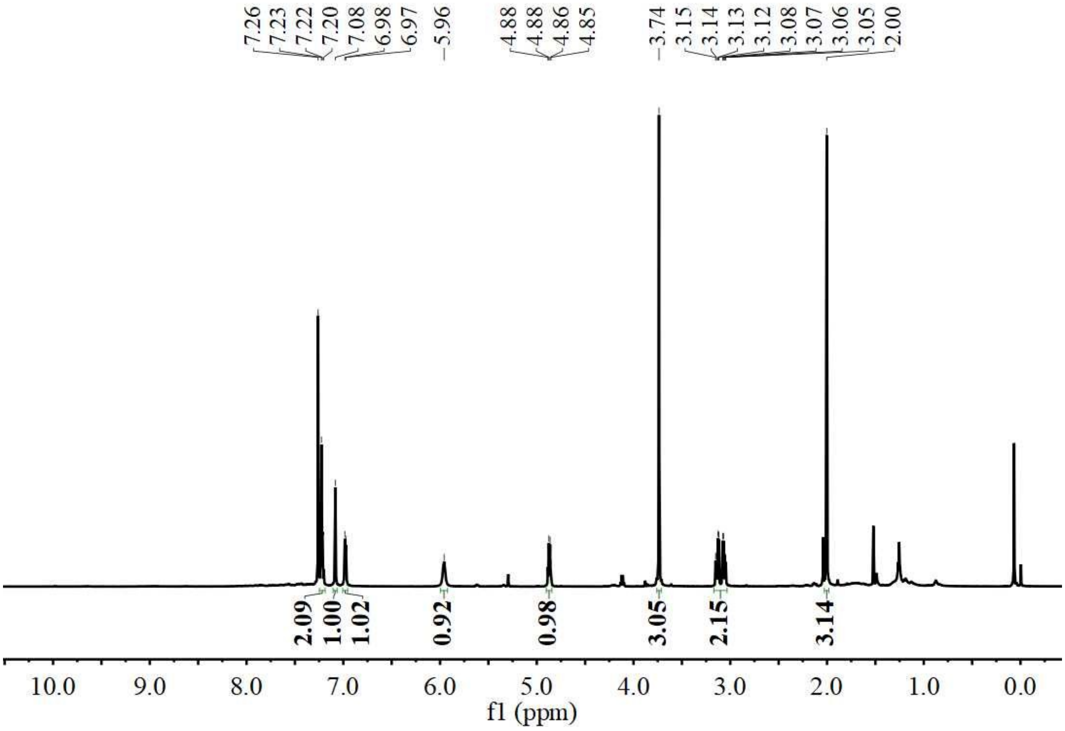


Fig. S40 The ^{1}H NMR spectrum of the hydrogenation of **1e** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

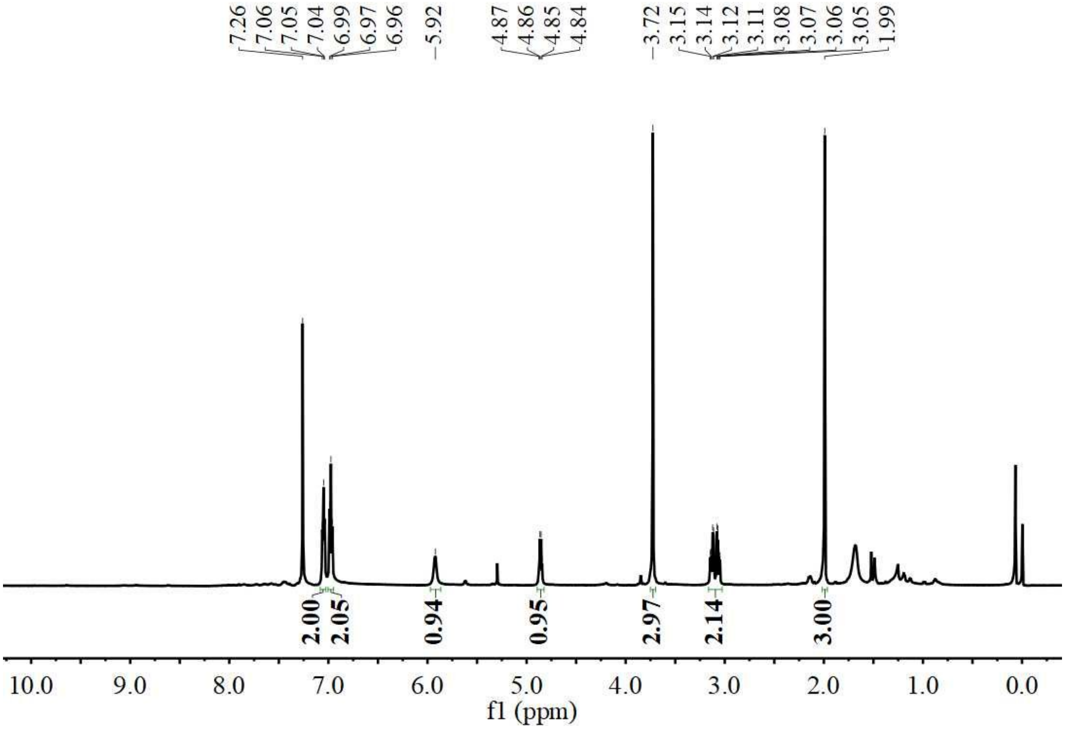


Fig. S41 The ^{1}H NMR spectrum of the hydrogenation of **1f** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

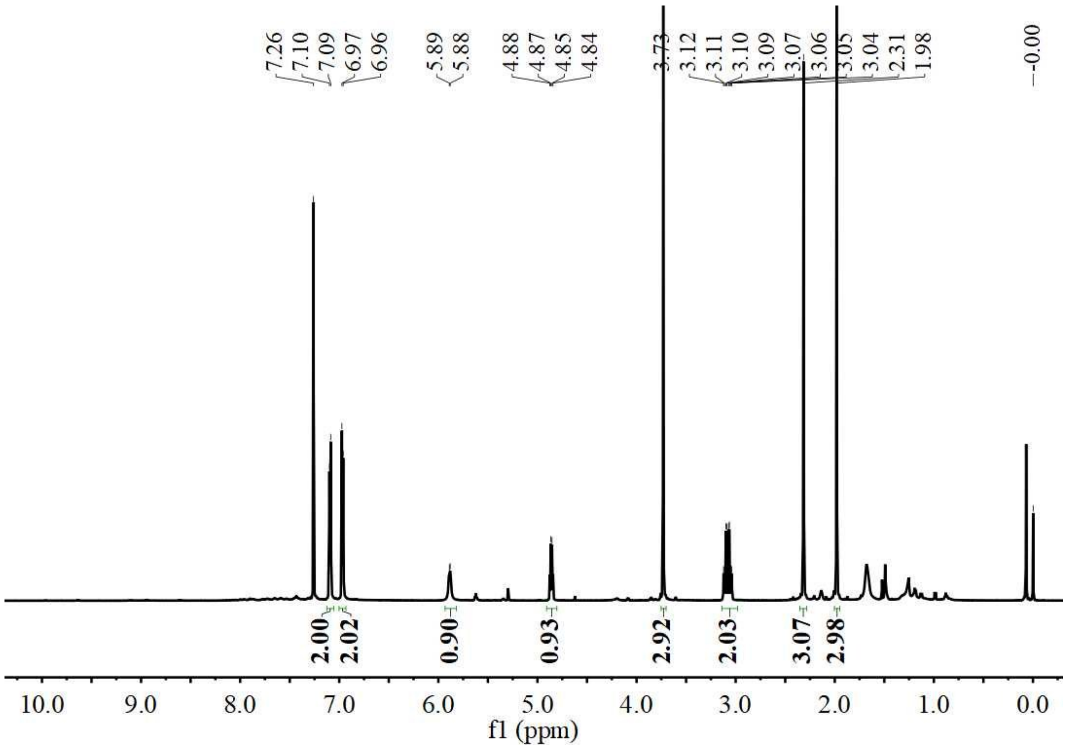


Fig. S42 The ^{1}H NMR spectrum of the hydrogenation of **1g** when 4% L2[Rh] or L1[Rh] was used. The conversion of these reactions are 98%.

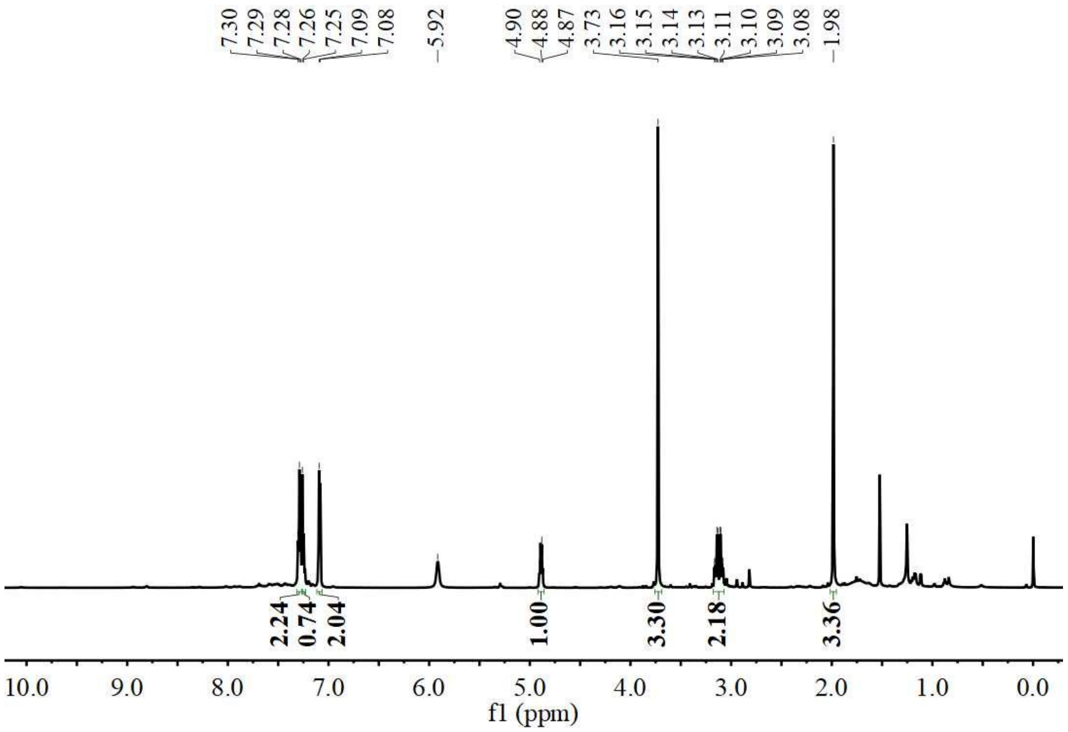
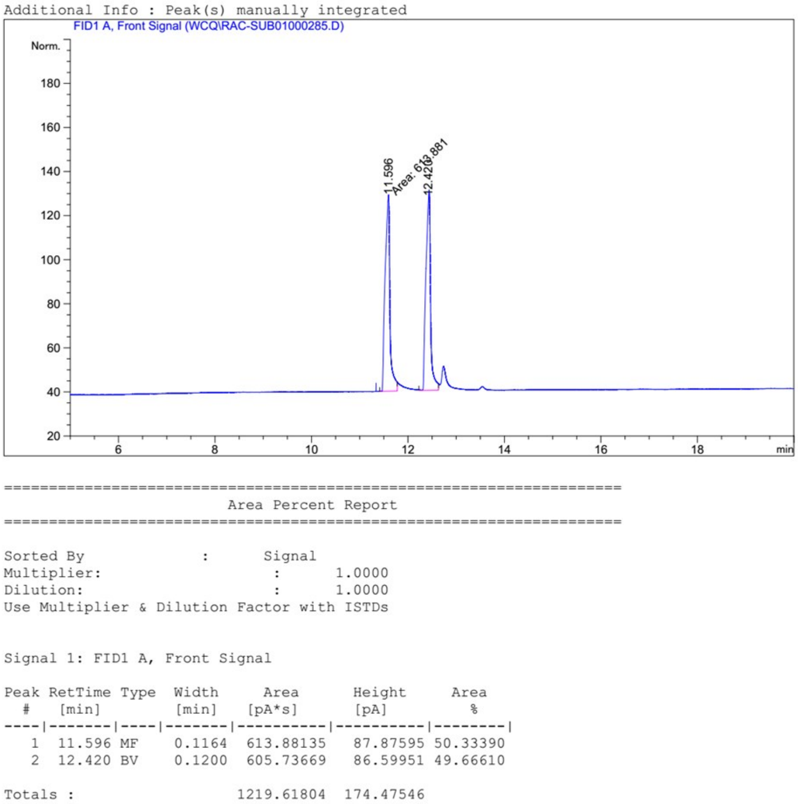


Fig. S43 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 4% L3[Rh] was used in $CDCl_3$, THF or toluene. The conversions of these reactions are 98%.



```
Additional Info : Peak(s) manually integrated

=====================================================================
                          Area Percent Report
=====================================================================

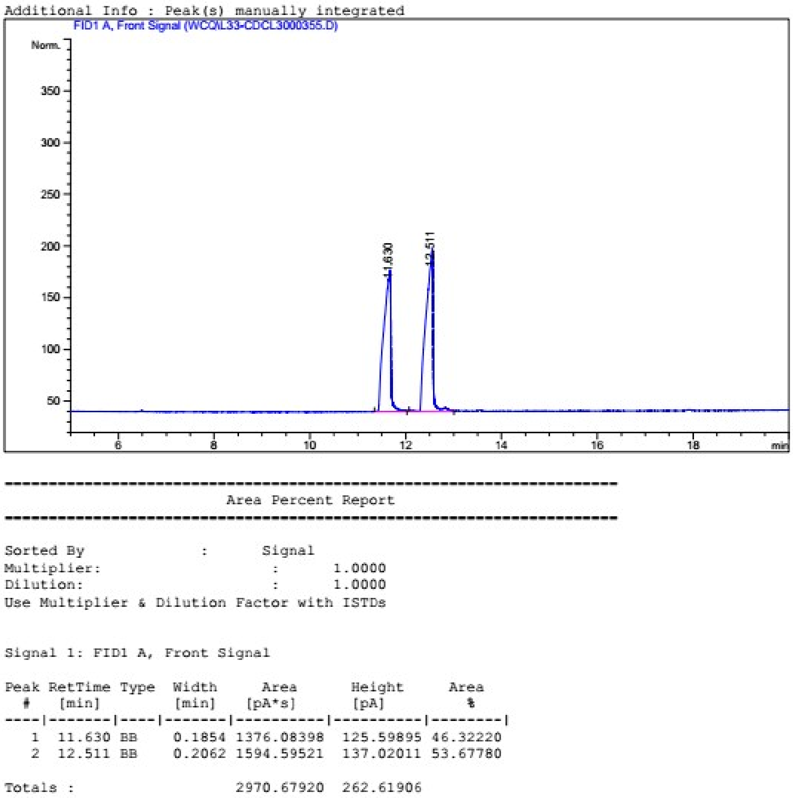
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  11.596 MF    0.1164  613.88135   87.87595 50.33390
   2  12.420 BV    0.1200  605.73669   86.59951 49.66610

Totals :                   1219.61804  174.47546
```

Fig. S44 The GC spectrum of the racemic hydrogenation product **1a-H**.



```
Additional Info : Peak(s) manually integrated

=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

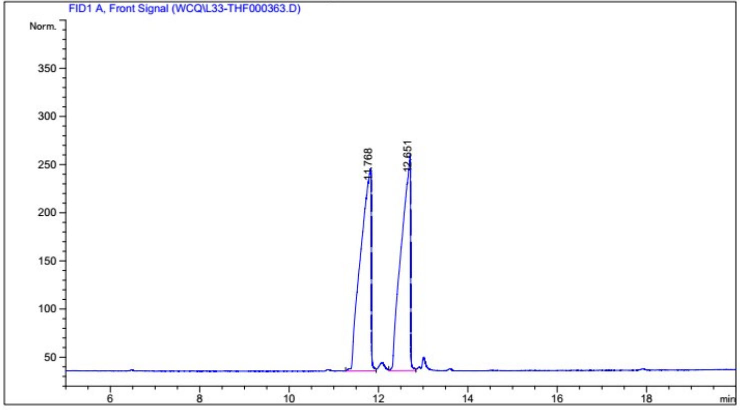

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  11.630 BB    0.1854 1376.08398  125.59895 46.32220
   2  12.511 BB    0.2062 1594.59521  137.02011 53.67780

Totals :                   2970.67920  262.61906
```

Fig. S45 The GC spectrum of the hydrogenation product **1a-H** when L3[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

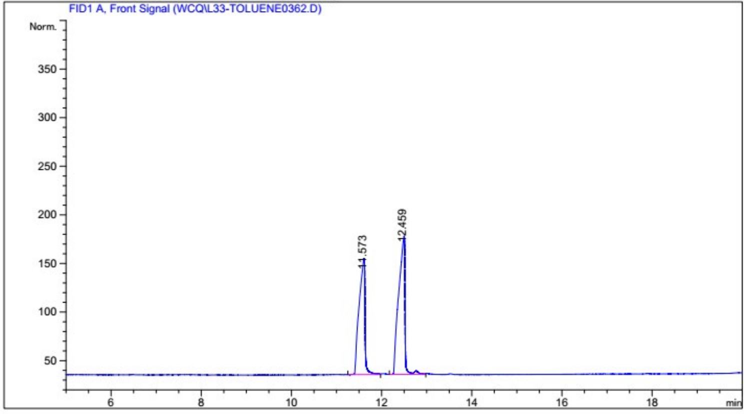

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.768 BV    0.2754 3405.53784  193.77072 51.79177
   2  12.651 VV    0.2342 3169.90405  202.05215 48.20823

Totals :                  6575.44189  395.82288
```

Fig. S46 The GC spectrum of the hydrogenation product **1a-H** when L3[Rh] was used as the catalyst and THF as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.573 BB    0.1782 1091.38135  105.62003 44.10622
   2  12.459 BB    0.1794 1383.05750  132.50343 55.89378

Totals :                  2474.43884  238.12347
```

Fig. S47 The GC spectrum of the hydrogenation product **1a-H** when L3[Rh] was used as the catalyst and toluene as the solvent.

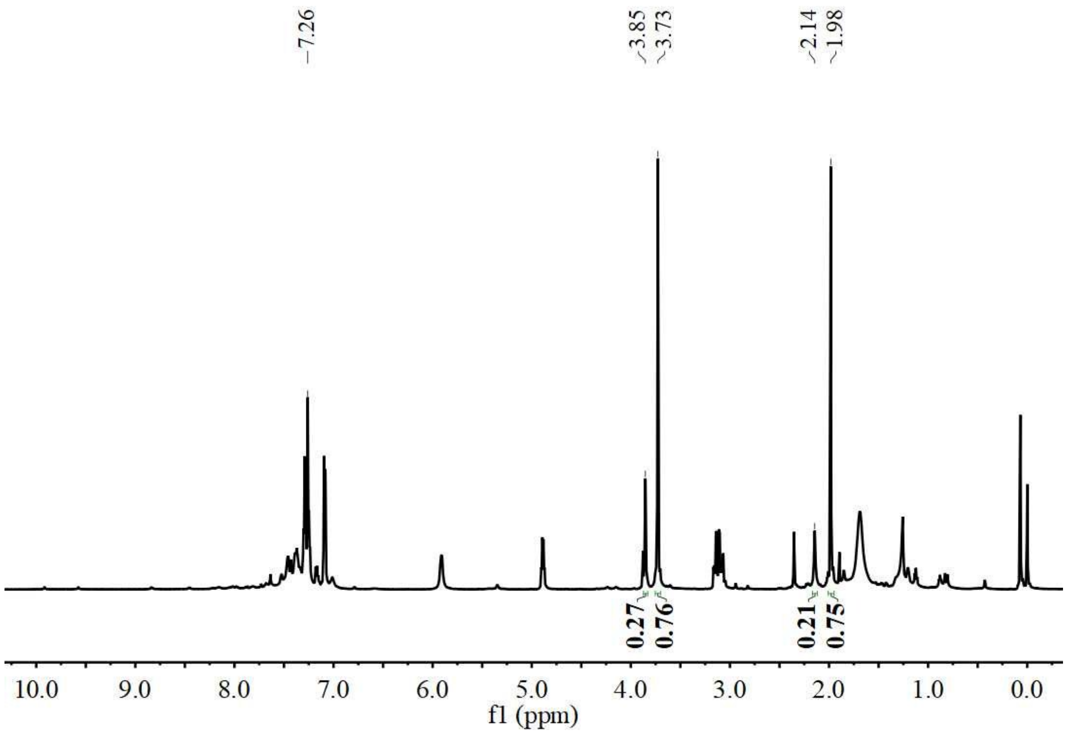
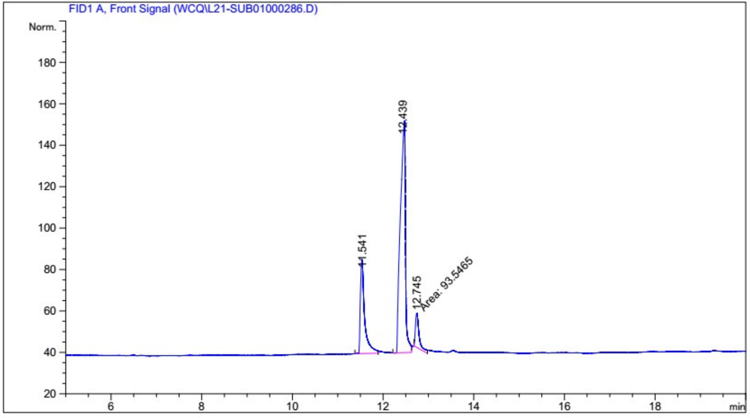


Fig. S48 The ^1H NMR spectrum of the hydrogenation of **1a** when 4% L4[Rh] was used in THF. The conversions of these reactions are 76%.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

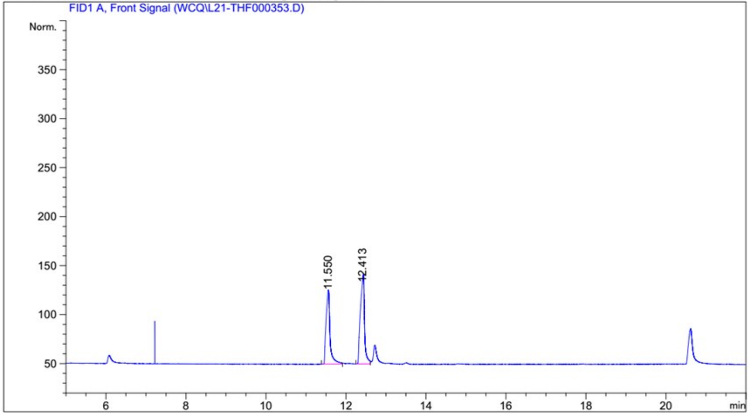

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.541 BB    0.1188  297.19080   39.93342 23.42865
   2  12.439 BV    0.1434  877.75562  103.81684 69.19673
   3  12.745 MM    0.0944   93.54654   16.52205  7.37462

Totals :                   1268.49295  160.27231
```

Fig. S49 The GC spectrum of the hydrogenation product **1a-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=================================================================
                     Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

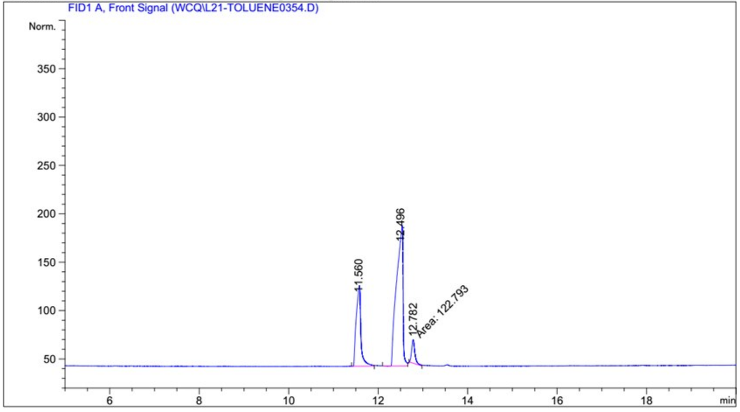

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #    [min]        [min]    [pA*s]     [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.550 BB    0.1163  525.30035   72.74097 44.31383
   2  12.413 BV    0.1348  660.10913   79.90623 55.68617

Totals :                 1185.40948  152.64720
```

Fig. S50 The GC spectrum of the hydrogenation product **1a-H** when L4[Rh] was used as the catalyst and THF as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=================================================================
                     Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #    [min]        [min]    [pA*s]     [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.560 BB    0.1348  604.63477   73.20419 27.61387
   2  12.496 BV    0.2002 1462.17725  125.20604 66.77812
   3  12.782 MM    0.0853  122.79314   23.99842  5.60800
```

Fig. S51 The GC spectrum of the hydrogenation product **1a-H** when L4[Rh] was used as the catalyst and toluene as the solvent.

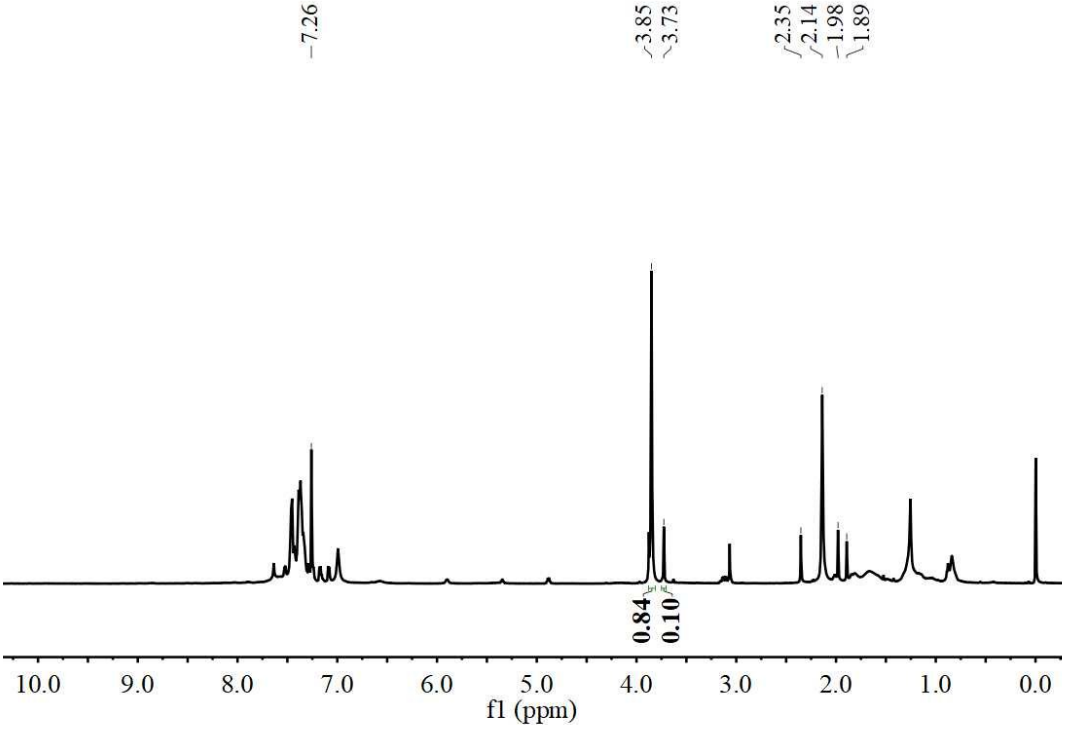


Fig. S52 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 4% L5[Rh] was used in $CDCl_3$. The conversions of these reactions are 10%.

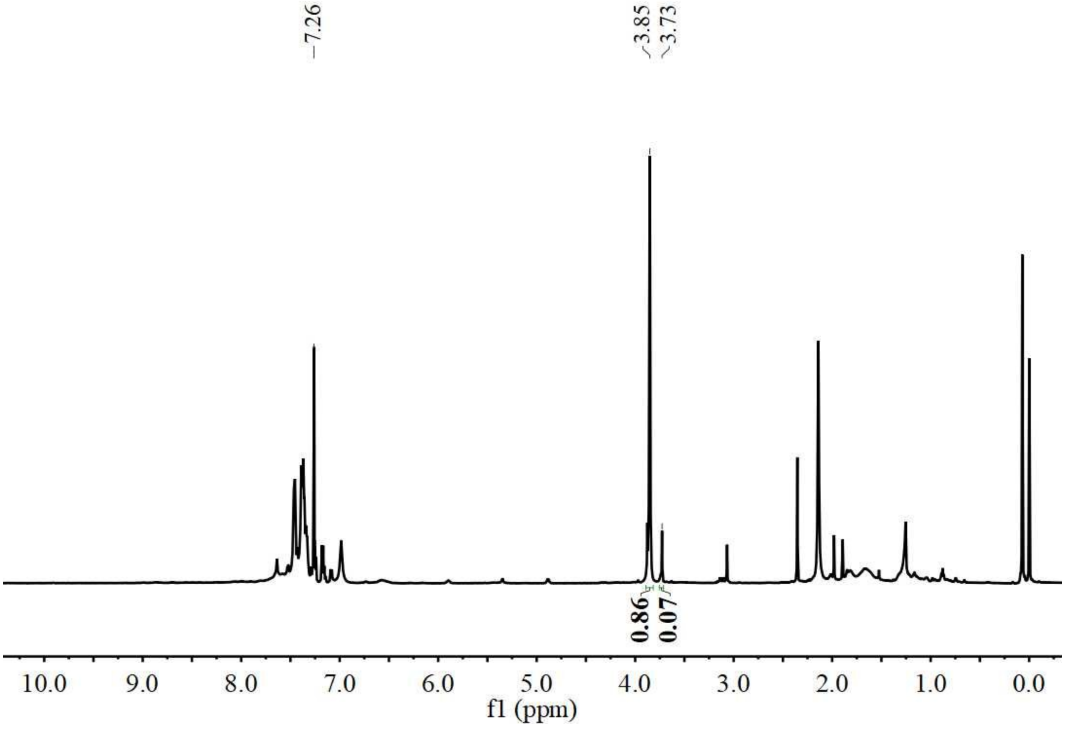


Fig. S53 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 4% L5[Rh] was used in THF. The conversions of these reactions are 6%.

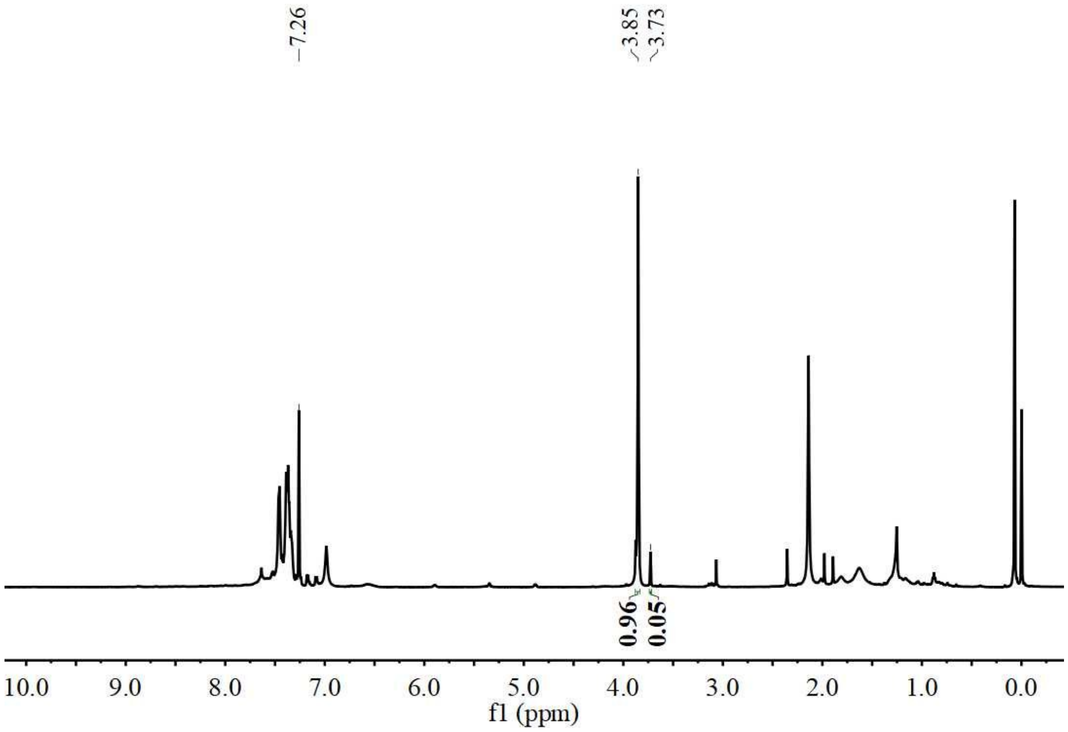
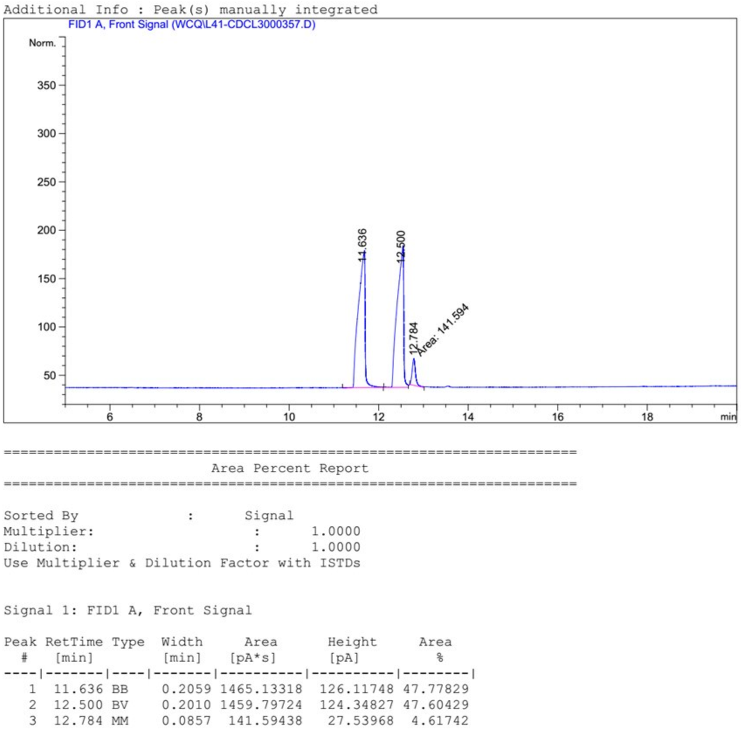


Fig. S54 The ^{1}H NMR spectrum of the hydrogenation of **1a** when 4% L5[Rh] was used in toluene. The conversions of these reactions are 5%.



```
Additional Info : Peak(s) manually integrated
FID1 A, Front Signal (WCQ\L41-CDCL3000357.D)
```

```
=====================================================================
                          Area Percent Report
=====================================================================

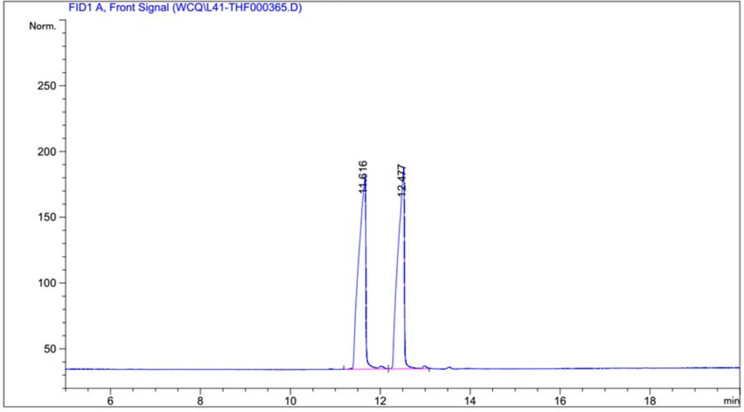
Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  11.636 BB    0.2059 1465.13318  126.11748 47.77829
   2  12.500 BV    0.2010 1459.79724  124.34827 47.60429
   3  12.784 MM    0.0857  141.59438   27.53968  4.61742
```

Fig. S55 The GC spectrum of the hydrogenation product **1a-H** when L6[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

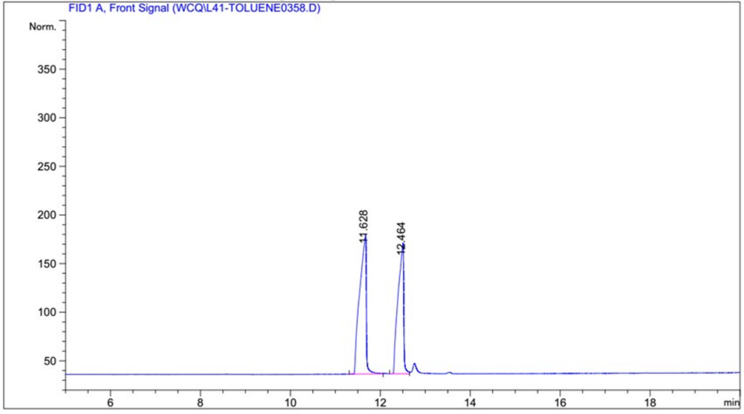

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.616 BV    0.2120 1585.65186  130.61369 51.43932
   2  12.477 VB    0.2004 1496.91602  128.02684 48.56068

Totals :                  3082.56787  258.64053
```

Fig. S56 The GC spectrum of the hydrogenation product **1a-H** when L6[Rh] was used as the catalyst and THF as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

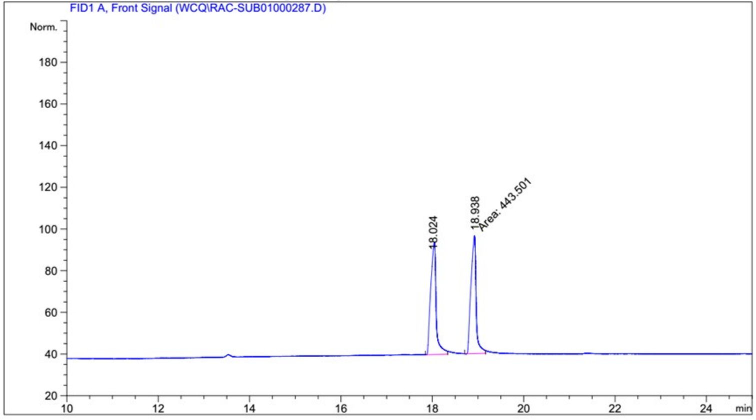

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.628 BB    0.1947 1465.17041  130.78236 55.47300
   2  12.464 BV    0.1673 1176.06128  118.19402 44.52700

Totals :                  2641.23169  248.97638
```

Fig. S57 The GC spectrum of the hydrogenation product **1a-H** when L6[Rh] was used as the catalyst and toluene as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

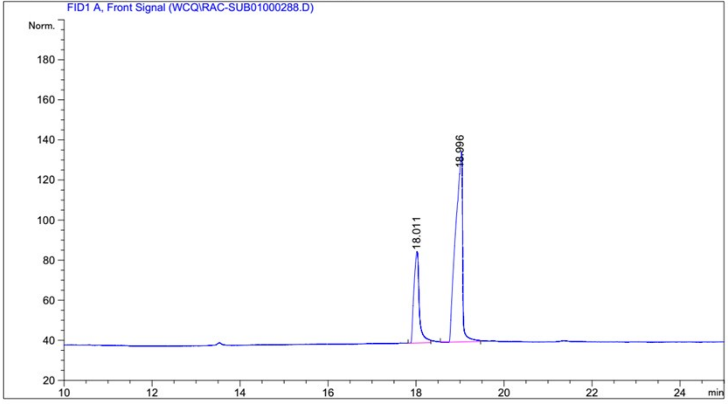

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  18.024 BB    0.1459  449.23239   48.76072 50.32102
   2  18.938 MF    0.1281  443.50067   57.70336 49.67898

Totals :                   892.73306  106.46408
```

Fig. S58 The GC spectrum of the racemic hydrogenation product **1b-H**.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                          Area Percent Report
=====================================================================

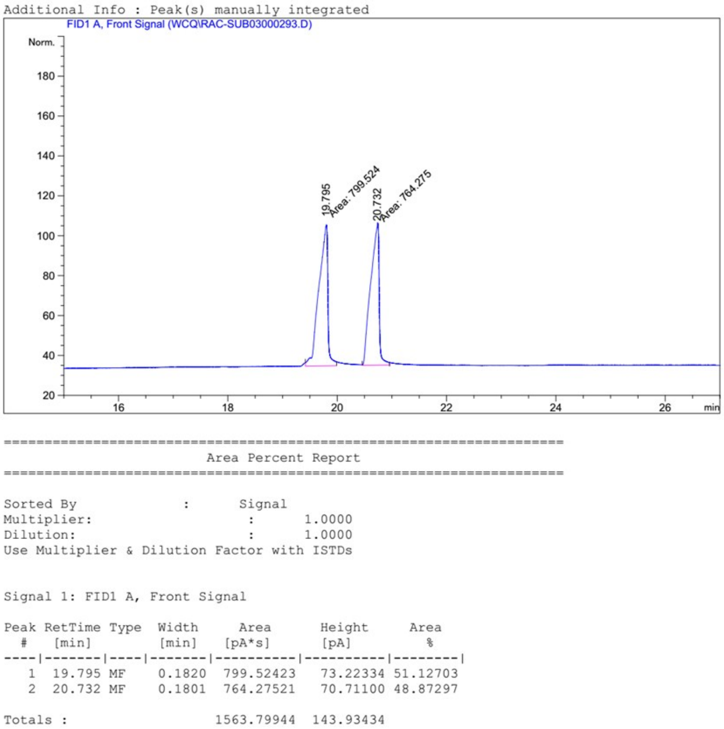
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  18.011 BB    0.1375  382.57422   45.05716 26.61527
   2  18.996 BB    0.2147 1054.84961   85.27907 73.38473

Totals :                  1437.42383  130.33622
```

Fig. S59 The GC spectrum of the hydrogenation product **1b-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.



```
Additional Info : Peak(s) manually integrated

=================================================================
                     Area Percent Report
=================================================================

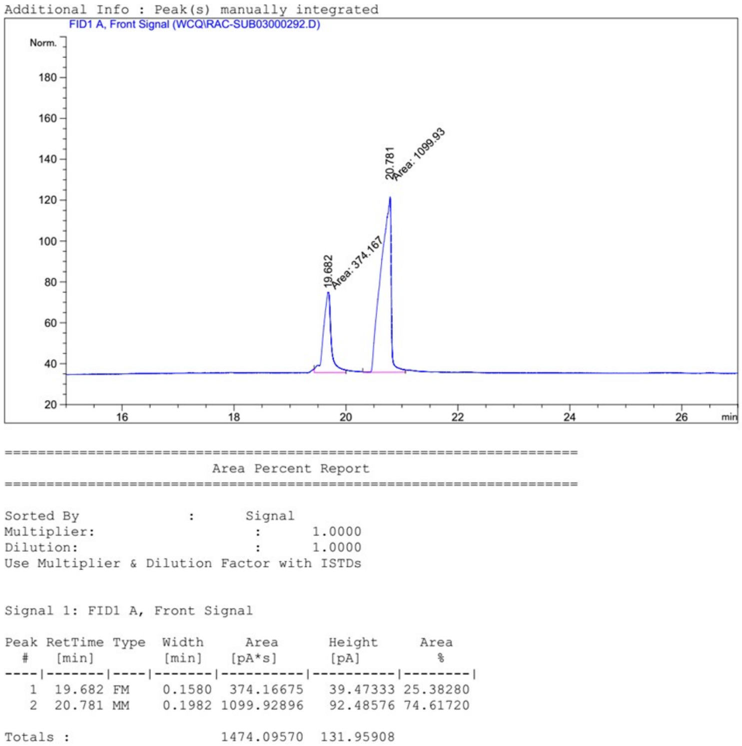
Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  19.795 MF    0.1820  799.52423   73.22334 51.12703
   2  20.732 MF    0.1801  764.27521   70.71100 48.87297

Totals :                  1563.79944  143.93434
```

Fig. S60 The GC spectrum of the racemic hydrogenation product **1c-H**.



```
Additional Info : Peak(s) manually integrated

=================================================================
                     Area Percent Report
=================================================================

Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

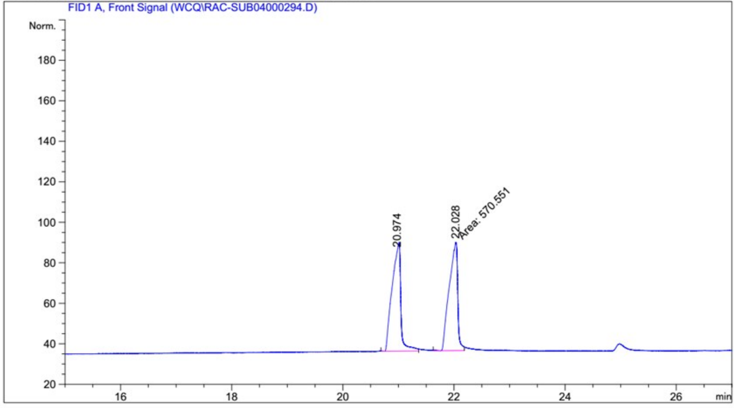

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  19.682 FM    0.1580  374.16675   39.47333 25.38280
   2  20.781 MM    0.1982 1099.92896   92.48576 74.61720

Totals :                  1474.09570  131.95908
```

Fig. S61 The GC spectrum of the hydrogenation product **1c-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

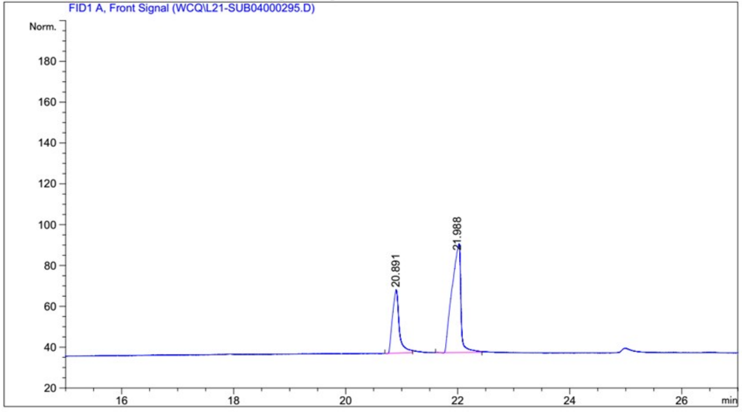

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  20.974 BB    0.1949  588.55048   49.99520 50.77643
   2  22.028 MF    0.1766  570.55121   53.86102 49.22357

Totals :                   1159.10168  103.85622
```

Fig. S62 The GC spectrum of the racemic hydrogenation product **1d-H**.

```
Additional Info : Peak(s) manually integrated
```



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==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

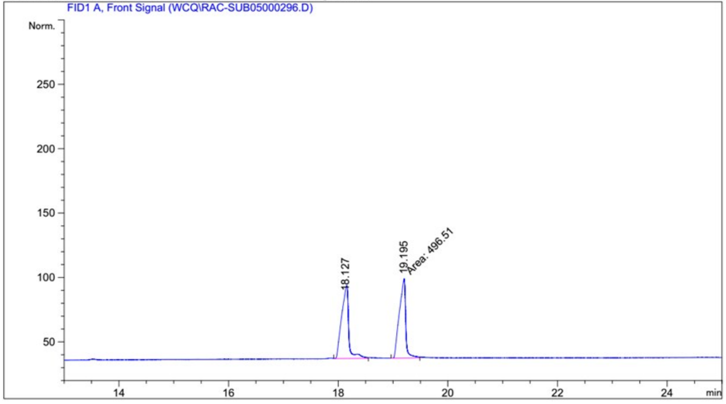

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  20.891 BB    0.1368  258.19464   30.60511 30.42178
   2  21.988 BB    0.2064  590.52167   48.39034 69.57822

Totals :                    848.71631   78.99545
```

Fig. S63 The GC spectrum of the hydrogenation product **1d-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

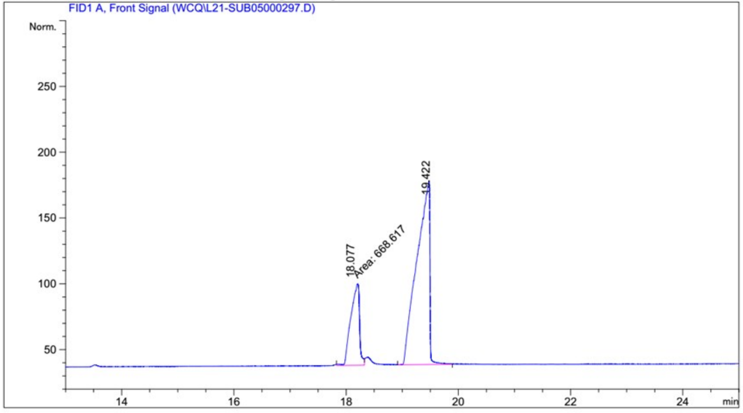

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  18.127 BB    0.1643  515.41370   50.30505 50.93404
   2  19.195 MM    0.1314  496.51010   62.98715 49.06596

Totals :                  1011.92380  113.29220
```

Fig. S64 The GC spectrum of the racemic hydrogenation product **1e-H**.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

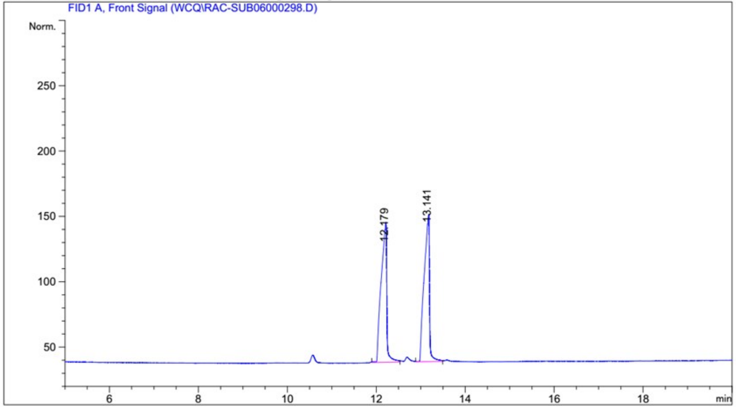

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  18.077 MF    0.1733  668.61743   64.29055 23.14959
   2  19.422 BB    0.2365 2219.63037  126.62242 76.85041

Totals :                  2888.24780  190.91297
```

Fig. S65 The GC spectrum of the hydrogenation product **1e-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

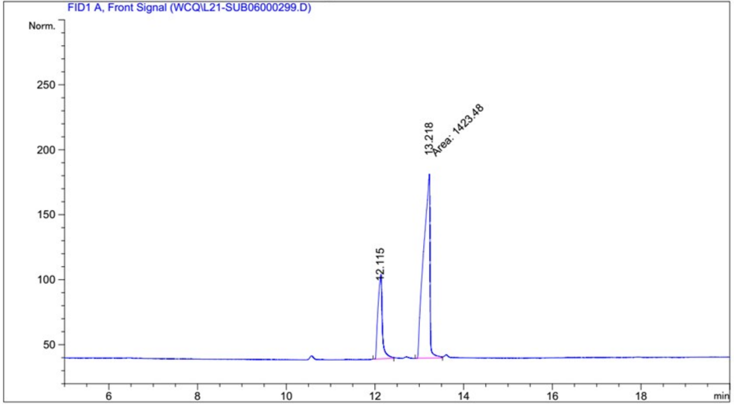

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.179 BB    0.1742  947.58563   89.90845 50.11402
   2  13.141 BB    0.1568  943.27374  104.24654 49.88598

Totals :                  1890.85938  194.15500
```

Fig. S66 The GC spectrum of the racemic hydrogenation product **1f-H**.

```
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

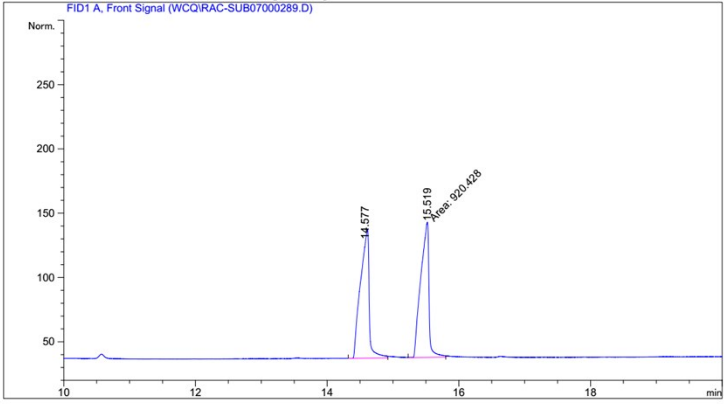

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.115 BB    0.1217  442.38098   57.53452 23.70927
   2  13.218 MM    0.1546 1423.47571  153.45425 76.29073

Totals :                  1865.85669  210.98877
```

Fig. S67 The GC spectrum of the hydrogenation product **1f-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

```
Additional Info : Peak(s) manually integrated
```



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

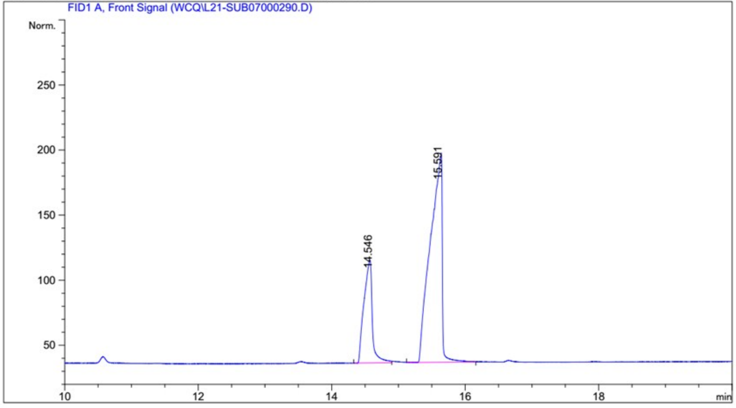

Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.577 BB    0.1709  924.63055   90.10077 50.11389
   2  15.519 MF    0.1477  920.42786  103.88194 49.88611

Totals :                  1845.05841  193.98271
```

Fig. S68 The GC spectrum of the racemic hydrogenation product **1g-H**.

```
Additional Info : Peak(s) manually integrated
```



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.546 BB    0.1593  691.92108   70.47344 25.88938
   2  15.591 BB    0.2507 1980.68518  137.97881 74.11062

Totals :                  2672.60626  208.45225
```

Fig. S69 The GC spectrum of the hydrogenation product **1g-H** when L4[Rh] was used as the catalyst and $CDCl_3$ as the solvent.

5. Crystal data

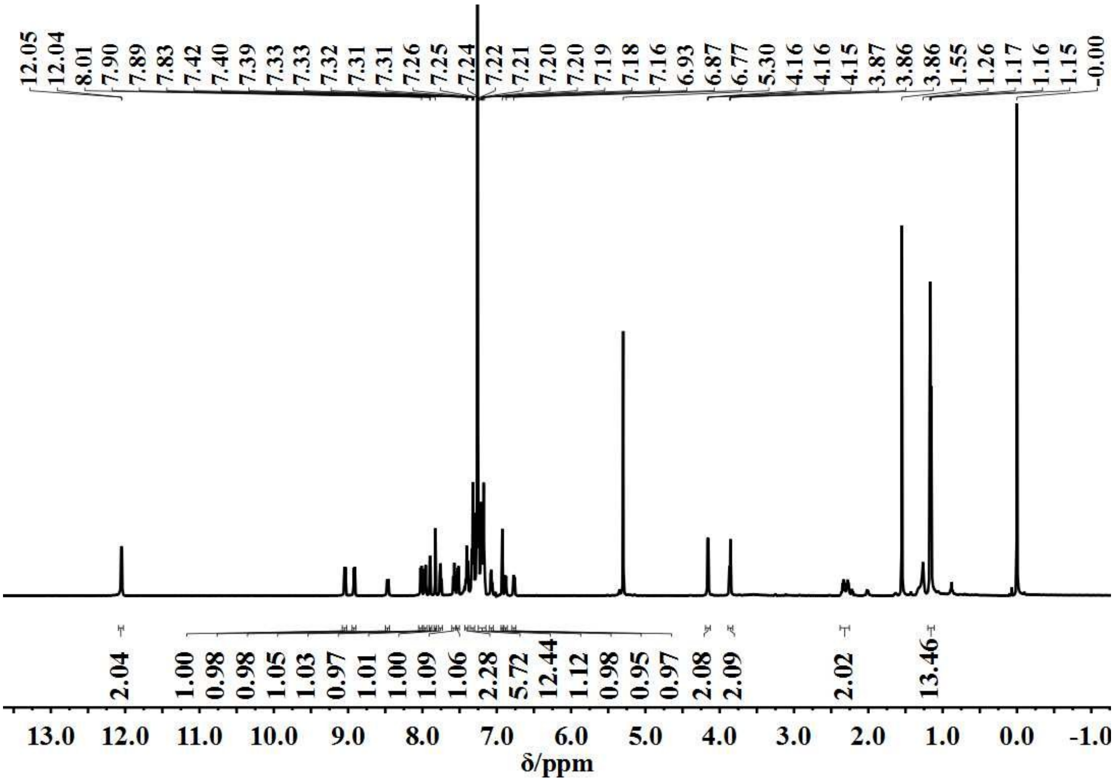
Table S3. Crystal data and structure refinement for **L1** and **L2**.

	L1	**L2**
Empirical formula	C68H56N6O8P2	C68H57N7O7P2·3CHCl3
Formula weight	1147.12	1504.25
Temperature (K)	100.01(10)	101
Crystal System	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a (Å)	13.6368(19)	19.2392(7)
b (Å)	14.139(2)	11.0026(5)
c (Å)	15.614(2)	33.5952(16)
α (deg)	104.059(13)	90
β (deg)	92.816(11)	101.948(4)
γ (deg)	92.523(13)	90
Volume (Å^3)	2911.9(8)	6957.4(5)
Z	2	4
ρcalcg (cm^3)	1.309	1.436
μ (mm^{-1})	1.194	4.236
Crystal size (mm^3)	0.3 × 0.25 × 0.1	0.2 × 0.15 × 0.05
F (000)	1202.0	3096.0
2Θ range for data	7.572 to 149.228	7.84 to 147.11
Index ranges	$-14 \le h \le 16$, $-17 \le k \le 11$, $-19 \le l \le 19$	$-21 \le h \le 23$, $-9 \le k \le 13$, $-39 \le l \le 41$
Reflections collected	19760	25470
Independent reflections	11269 [Rint = 0.1968, Rsigma = 0.2452]	13445 [Rint = 0.0946, Rsigma = 0.1093]
Data/restraints/parameters	11269/6/765	13445/66/888
Goodness-of-fit on F^2	1.074	0.999
Final R indexes [I>=2σ (I)]	R1 = 0.2092, wR2 = 0.4601	R1 = 0.1092, wR2 = 0.2783
Final R indexes [all data]	R1 = 0.3367 wR2 = 0.5528	R1 = 0.1436, wR2 = 0.2979
Largest diff. peak/hole (e·Å^{-3})	1.42/-0.71	0.97/-0.87
CCDC#	1939544	1939549

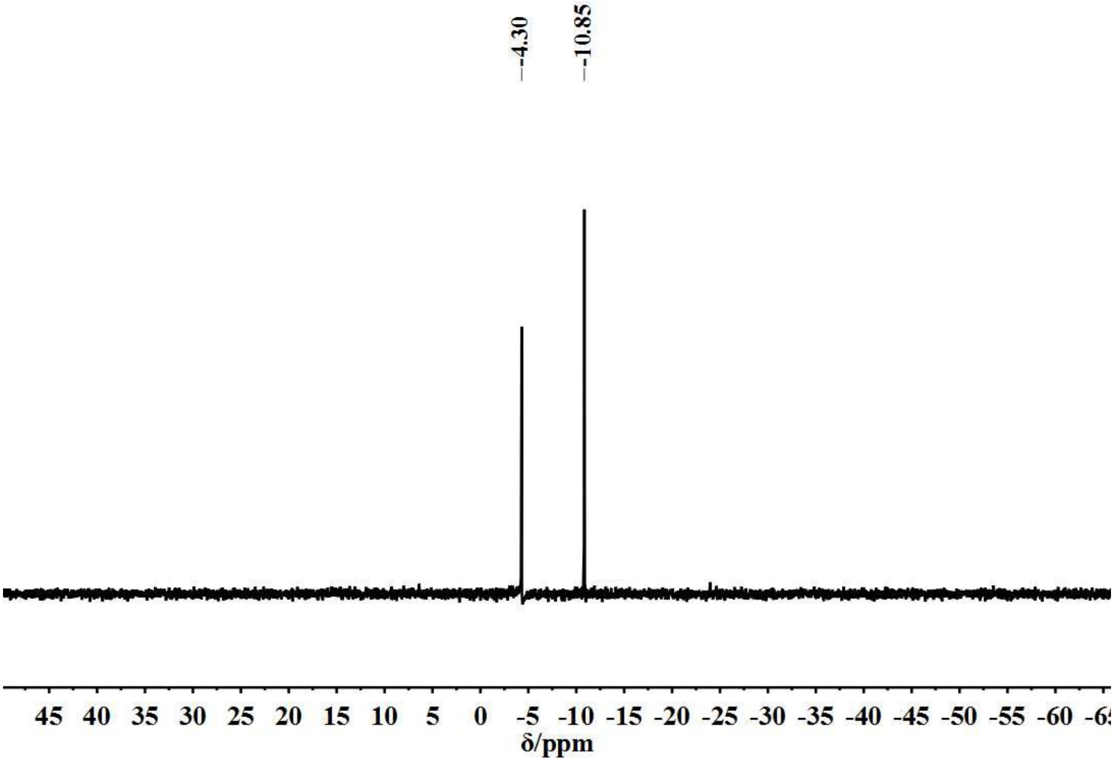
6. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra of new compounds

Compound **L1**

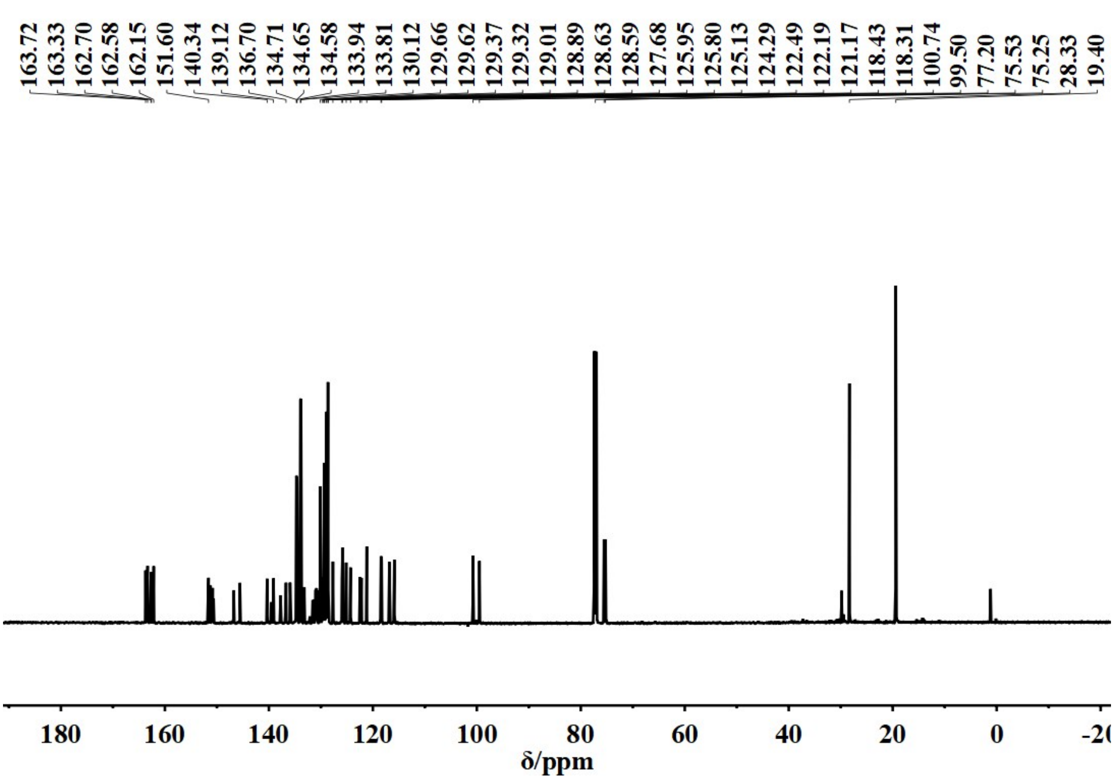
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

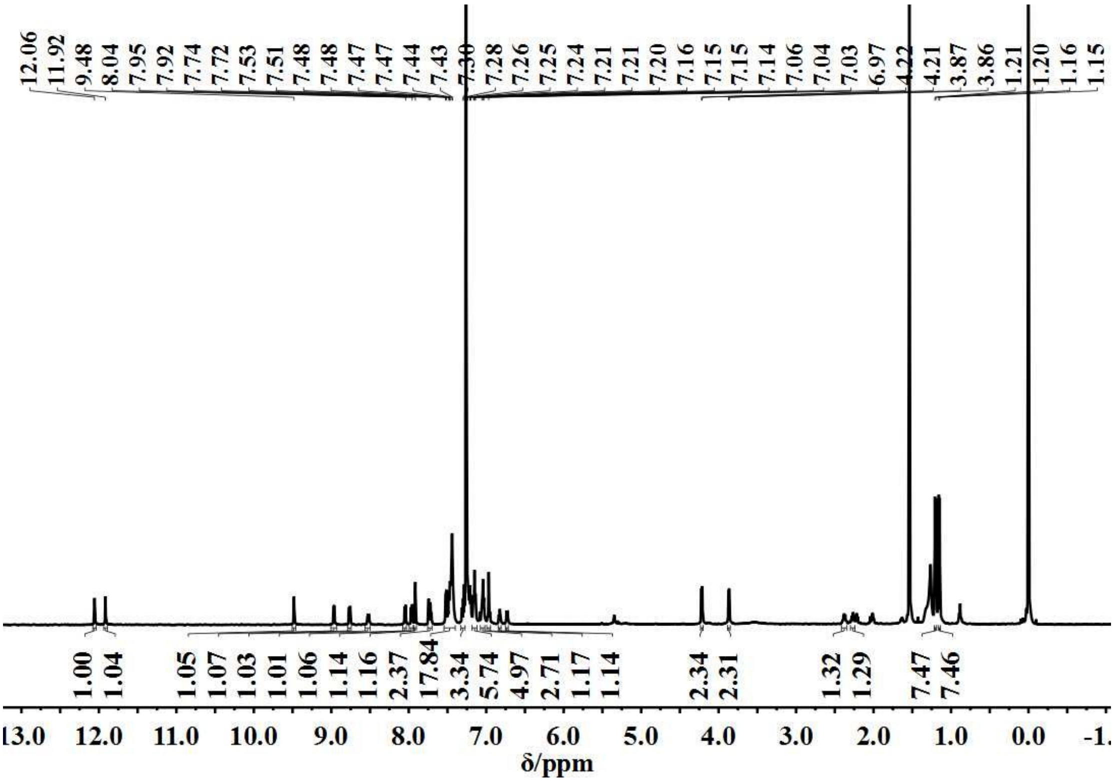


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

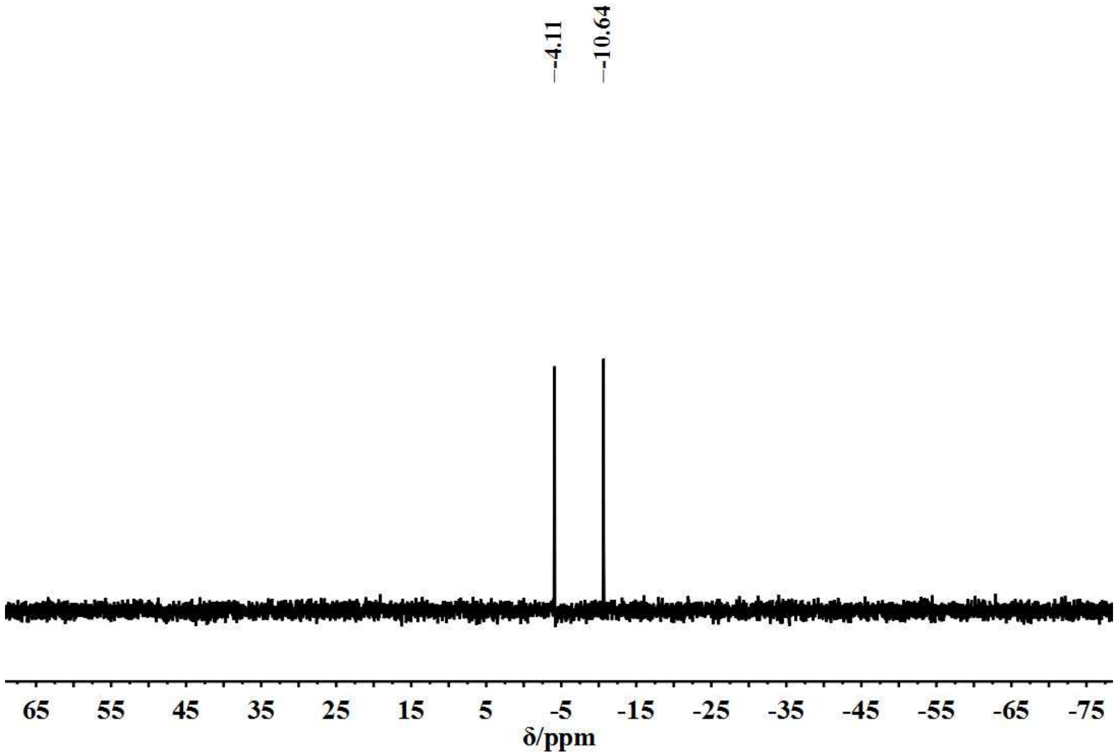


Compound **L2**

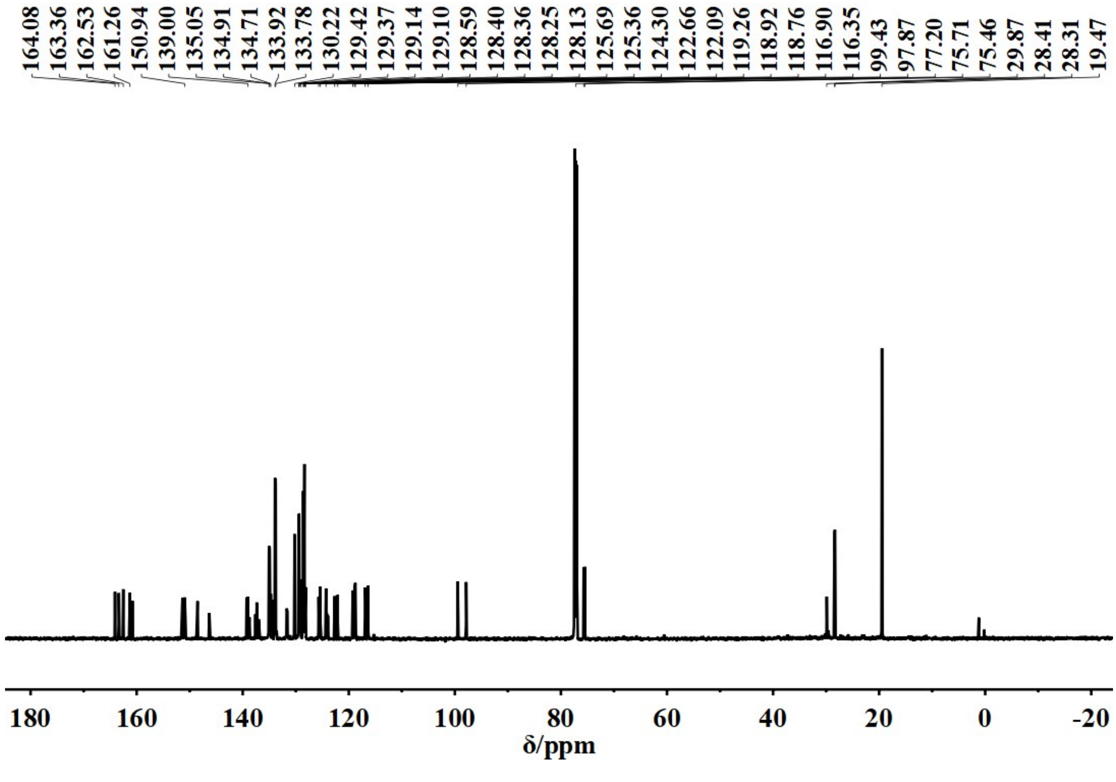
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

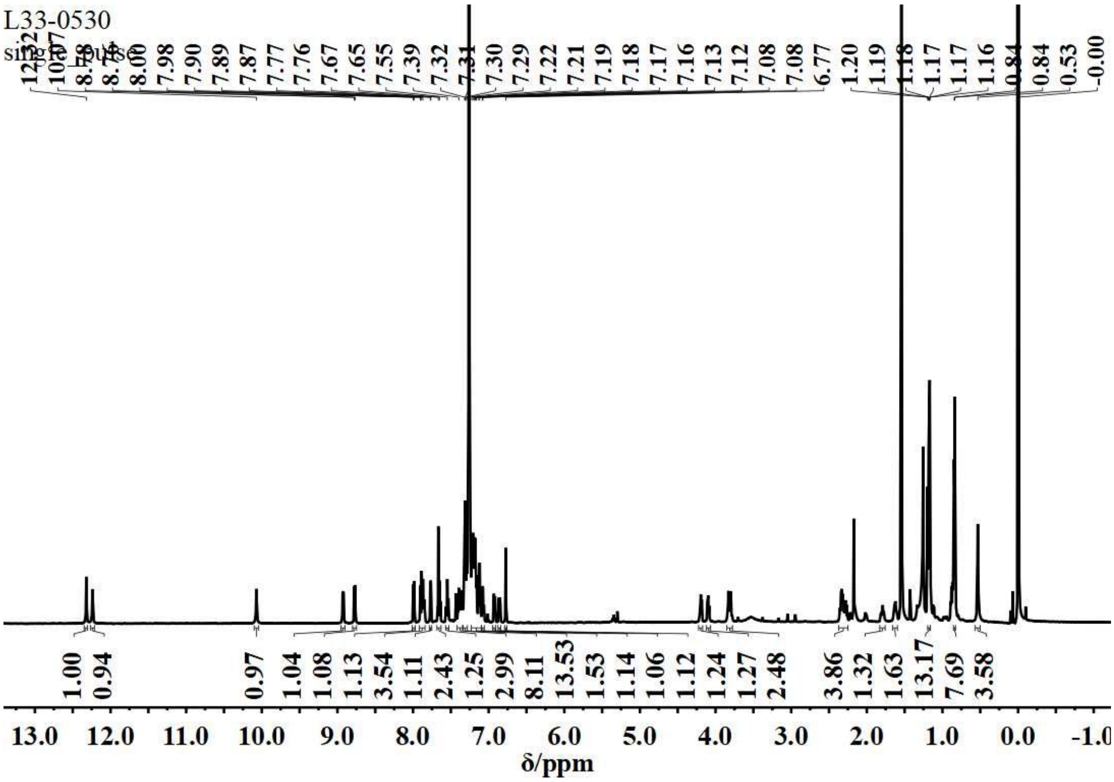


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

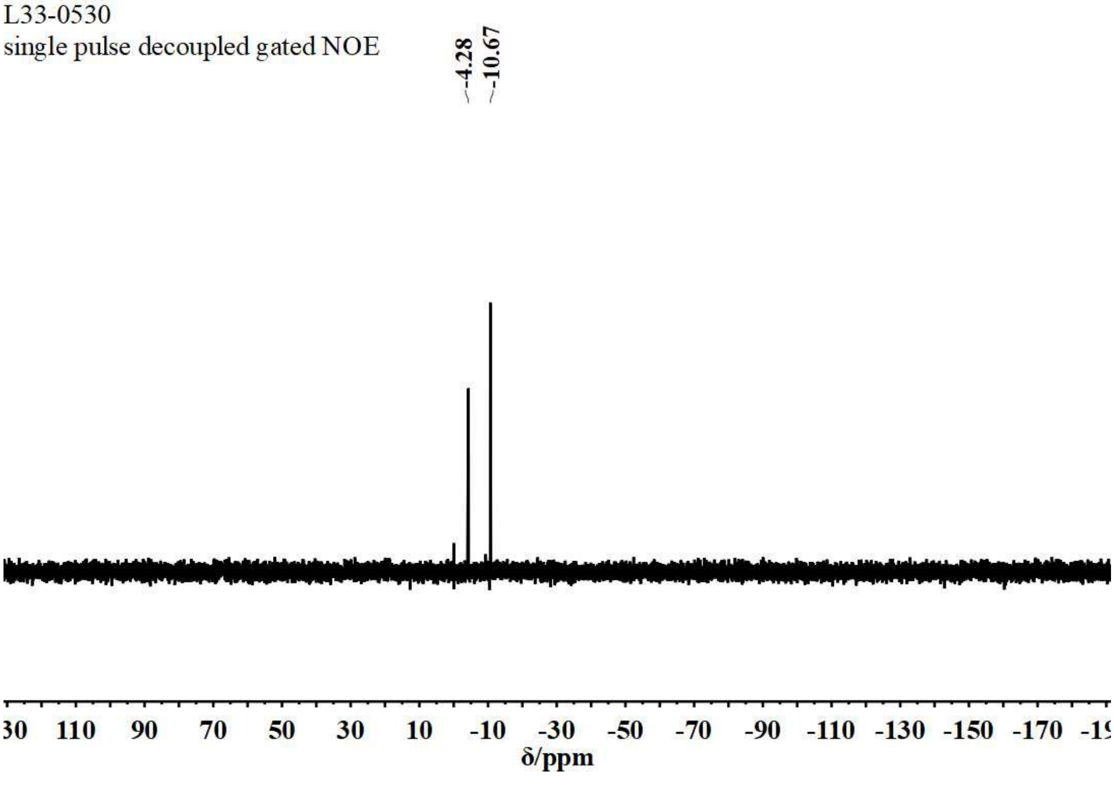


Compound **L3**

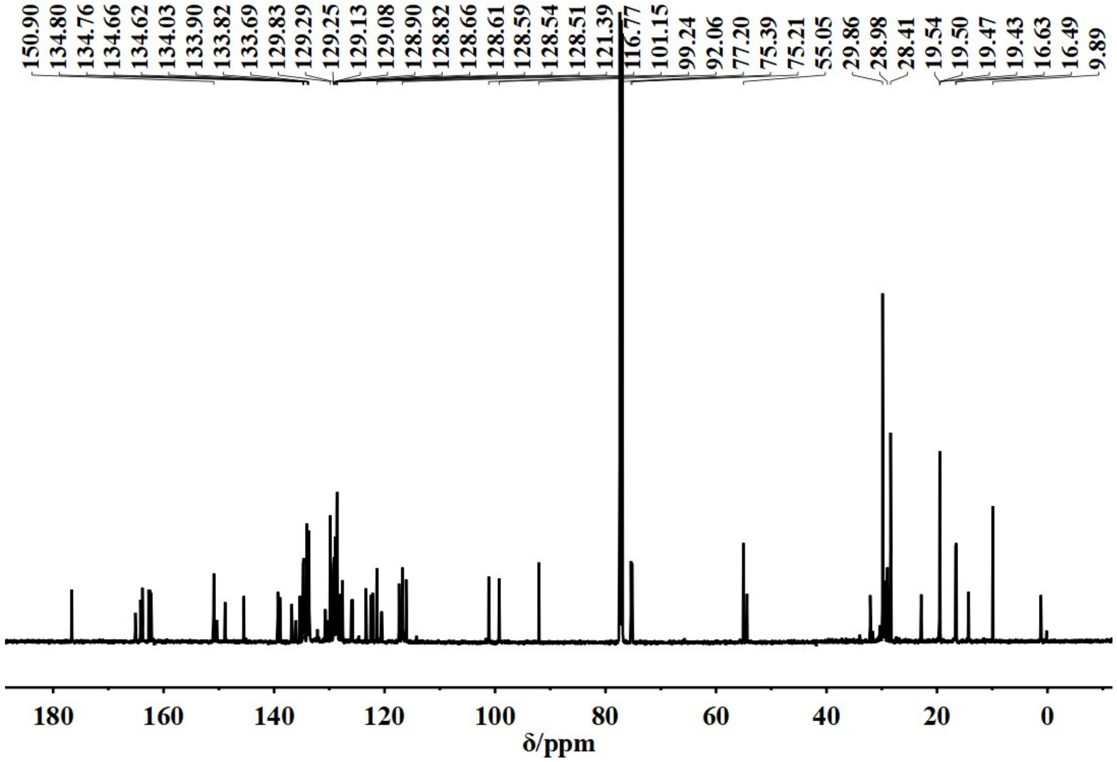
^{1}H NMR (600 MHz, 298 K, CDCl$_3$)



^{31}P NMR (243 MHz, 298 K, CDCl$_3$)

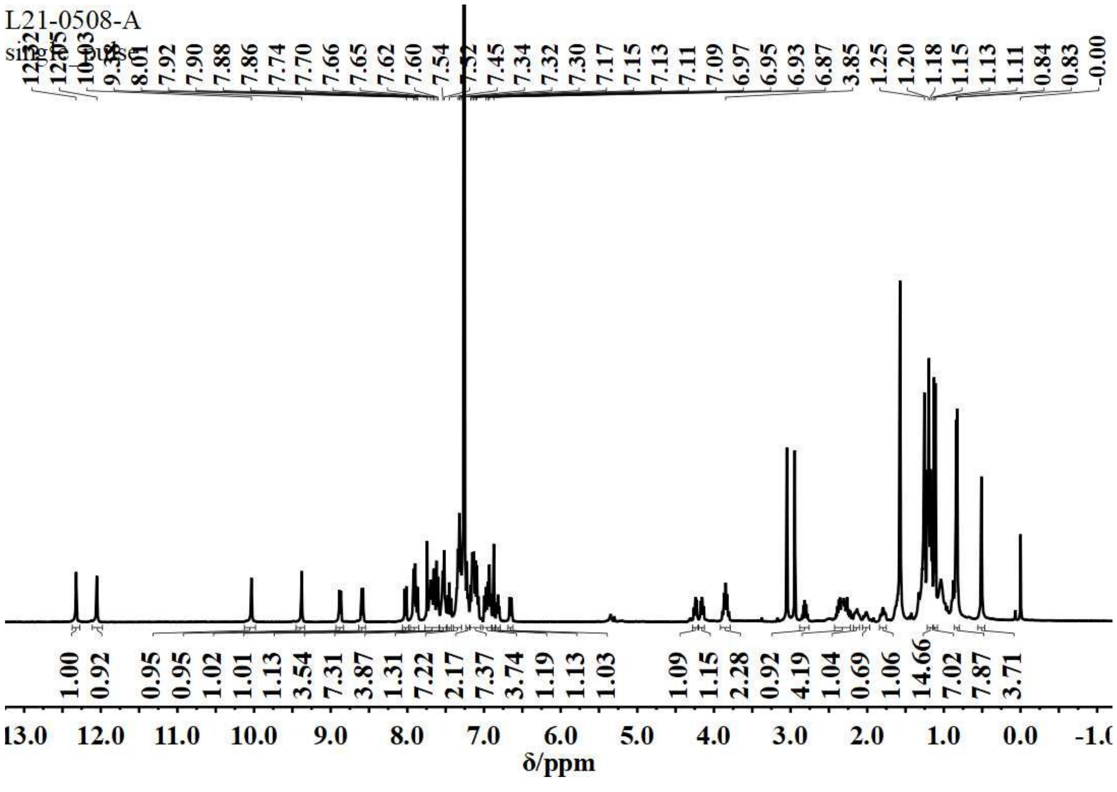


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

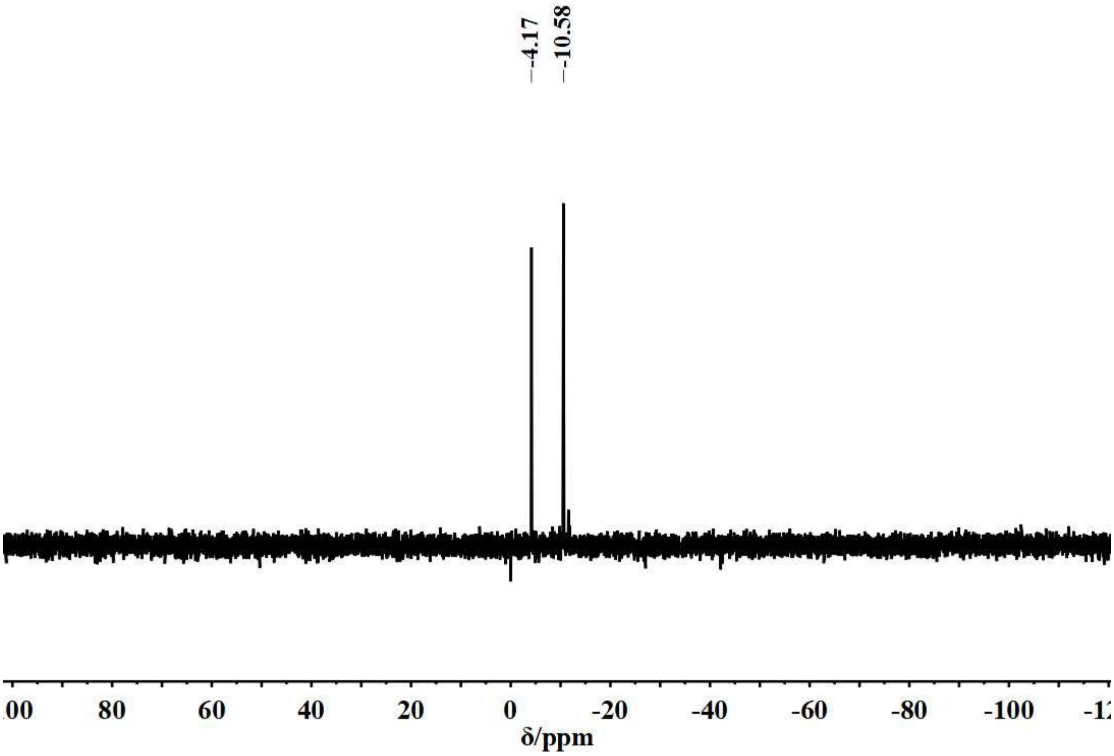


Compound **L4**

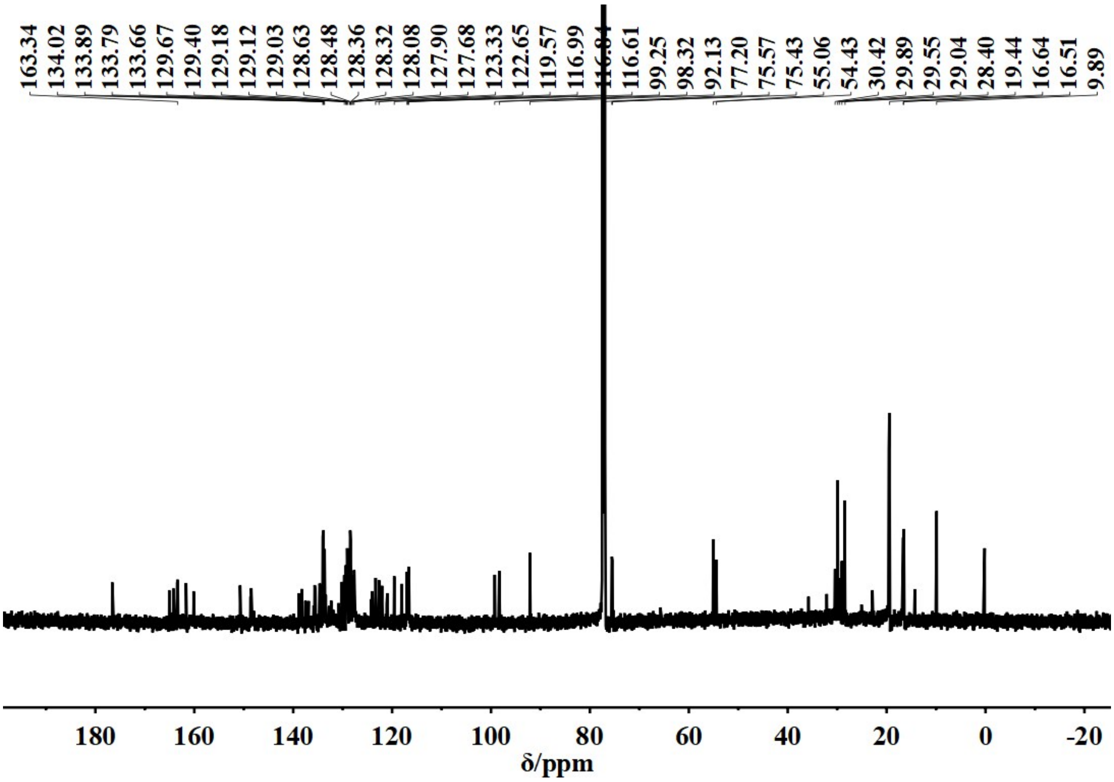
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

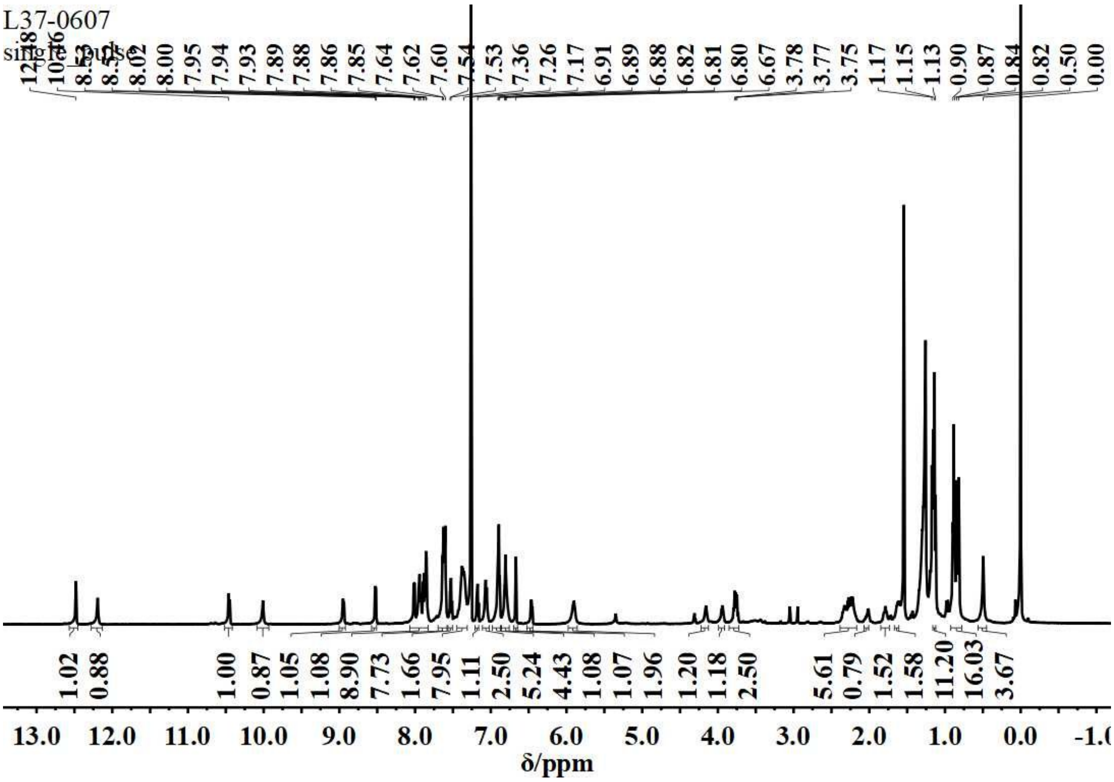


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

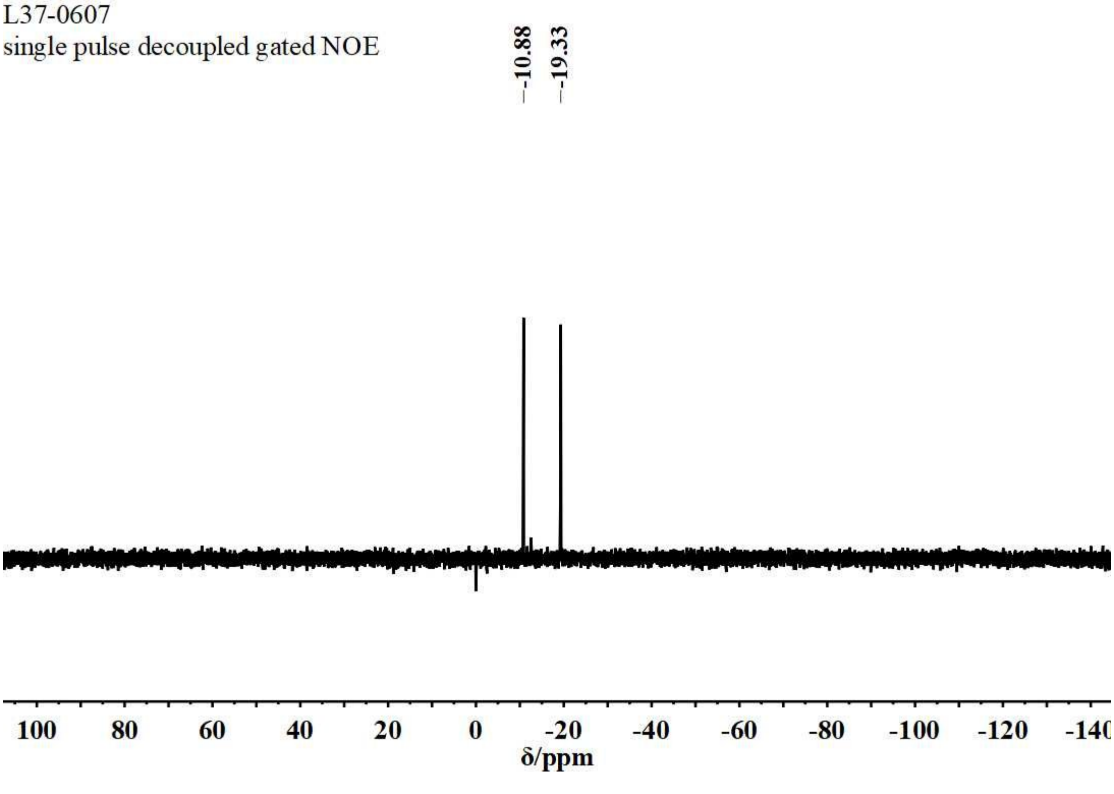


Compound **L5**

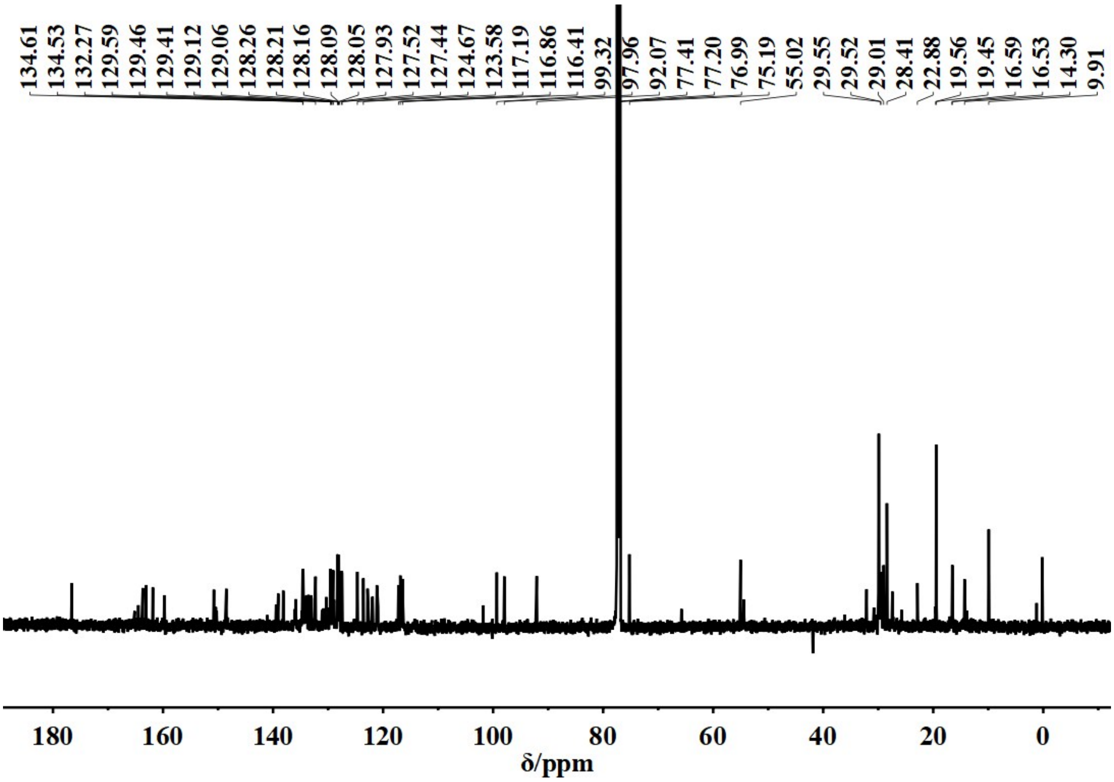
^{1}H NMR (600 MHz, 298 K, CDCl$_3$)



^{31}P NMR (243 MHz, 298 K, CDCl$_3$)

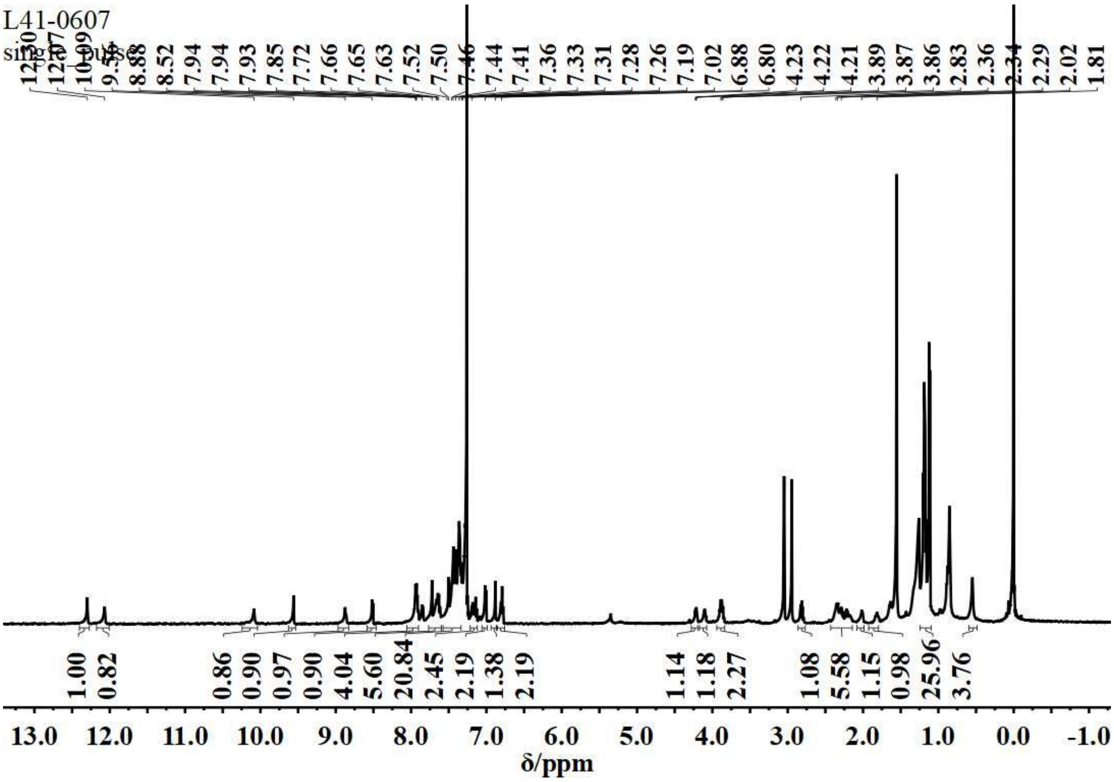


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)



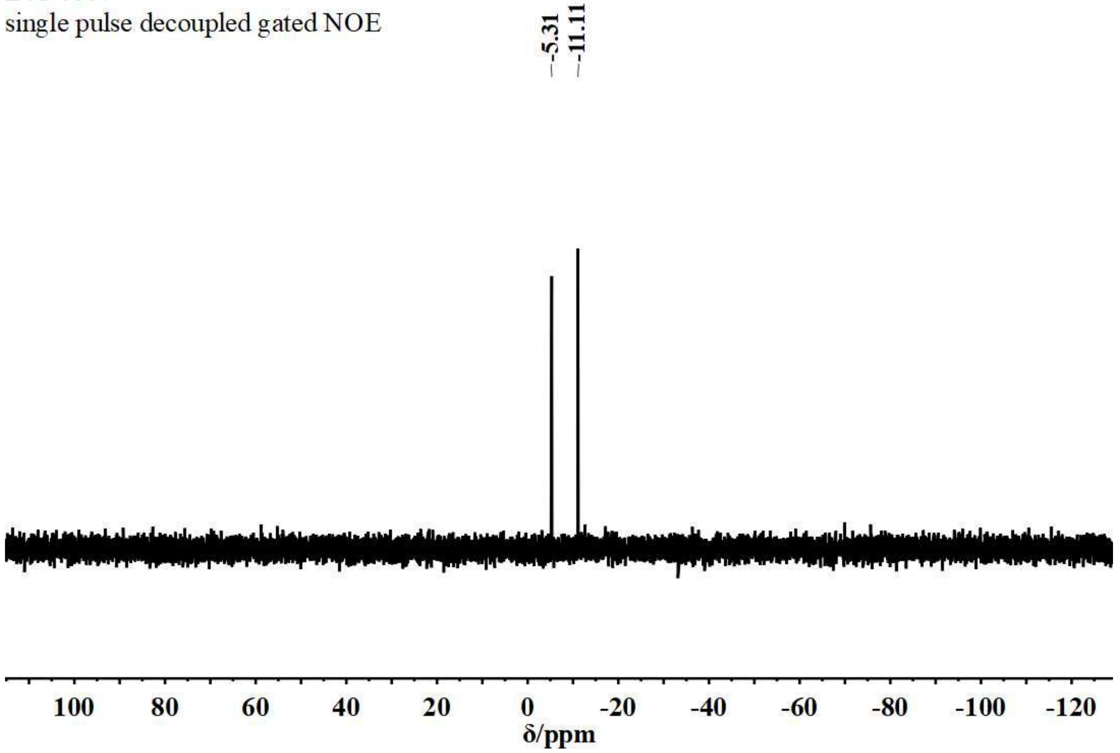
Compound **L6**

^{1}H NMR (600 MHz, 298 K, $CDCl_3$)

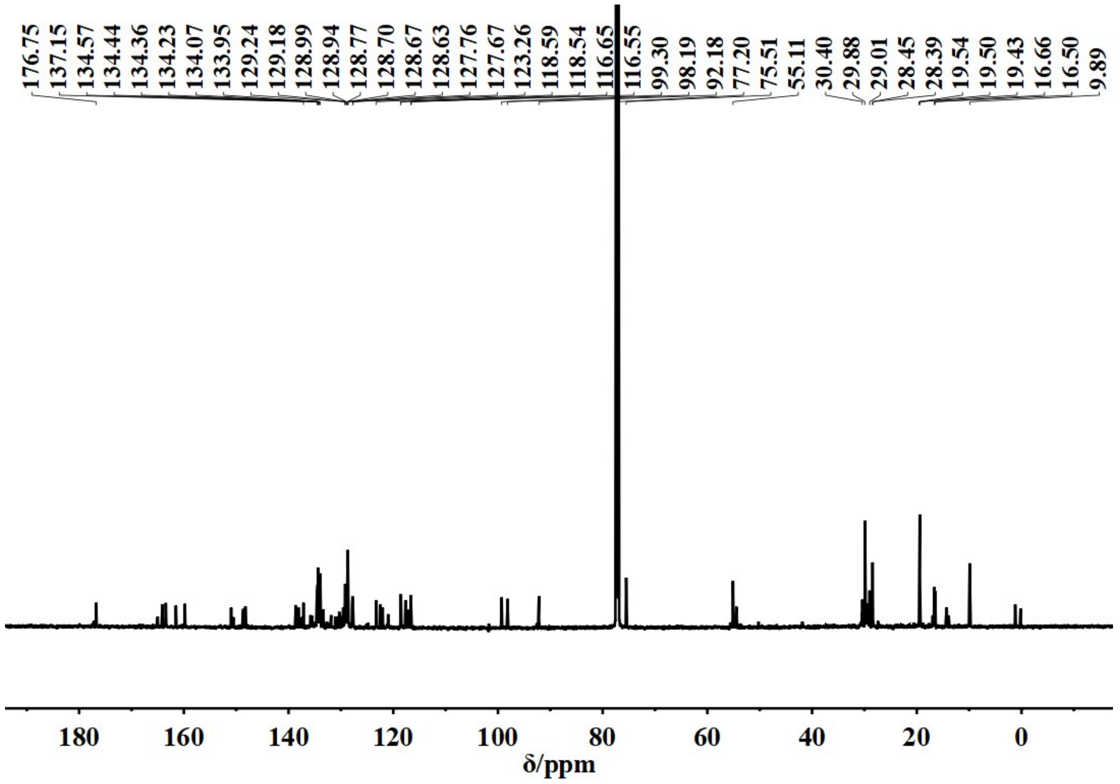


^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

L41-0607
single pulse decoupled gated NOE

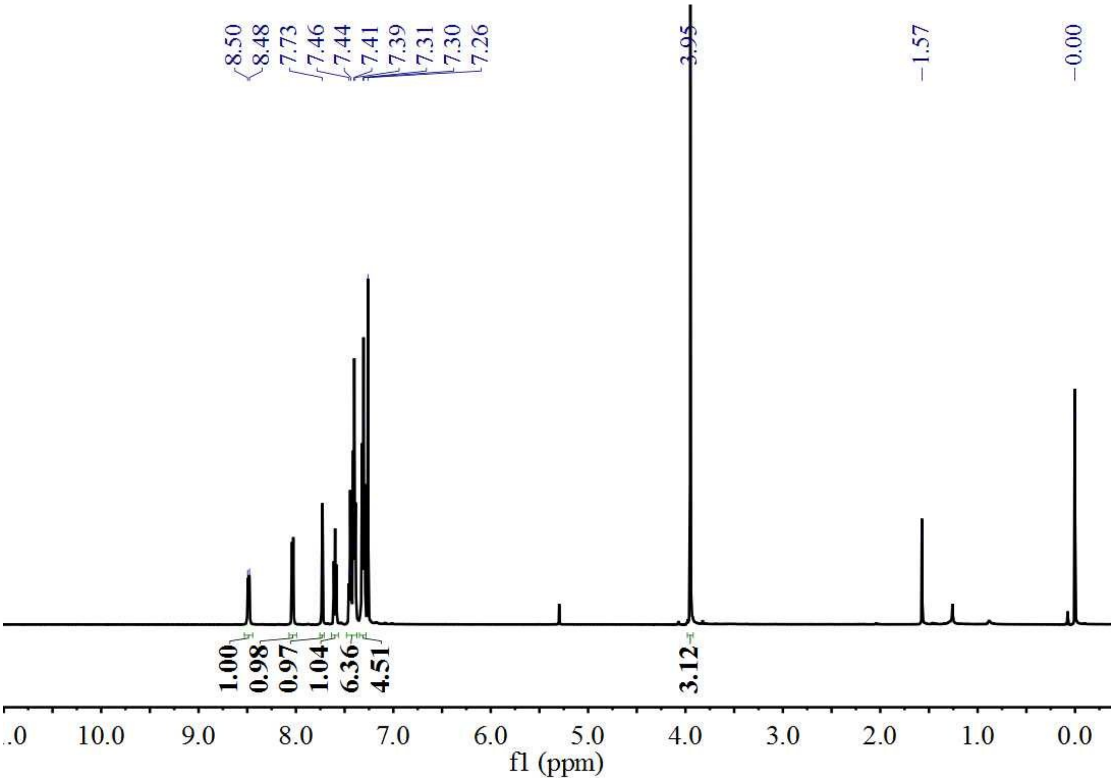


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

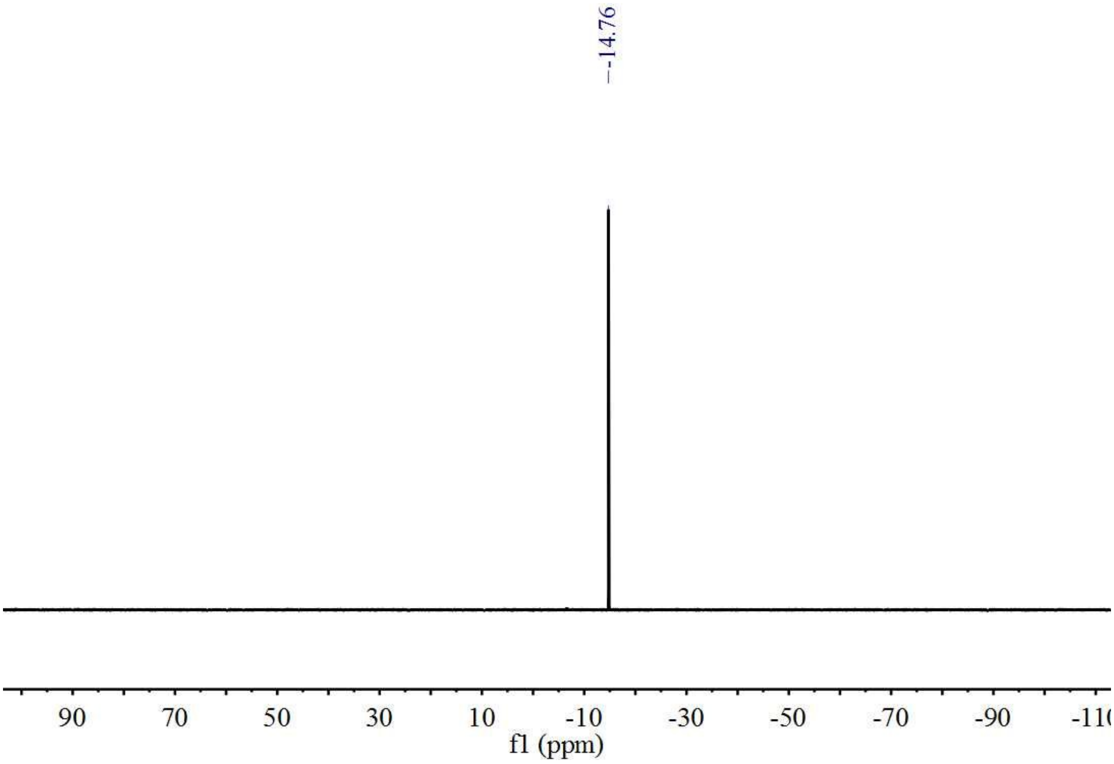


Compound **6**

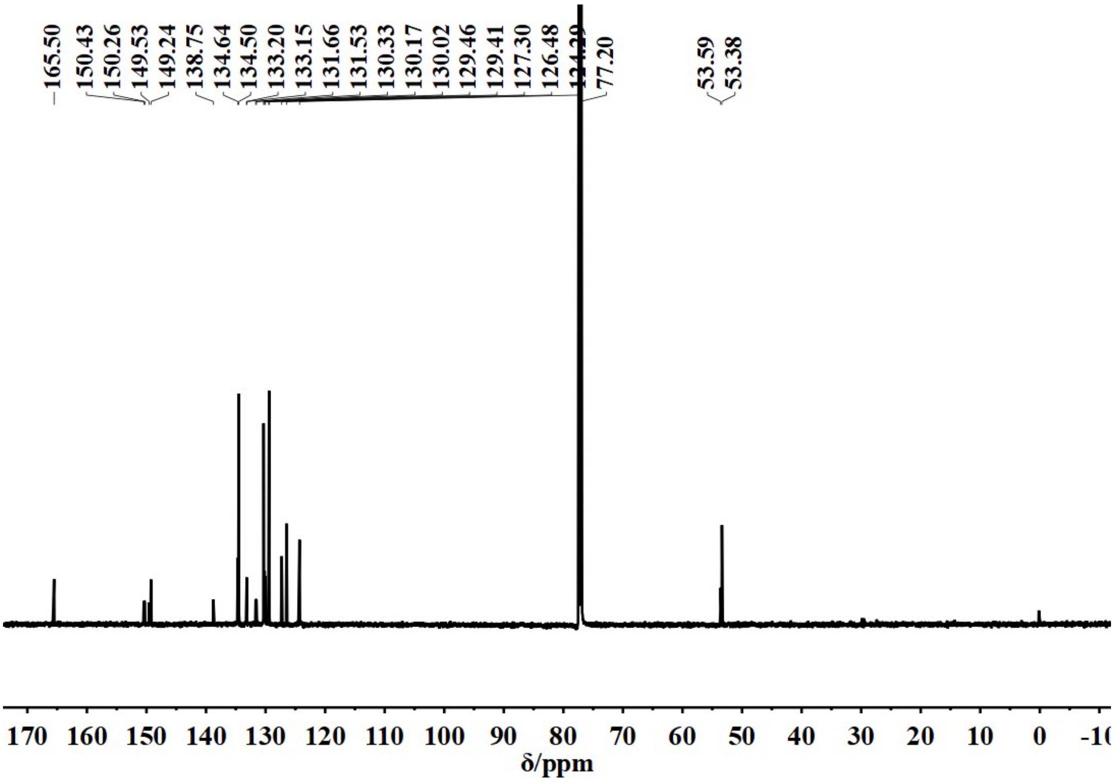
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

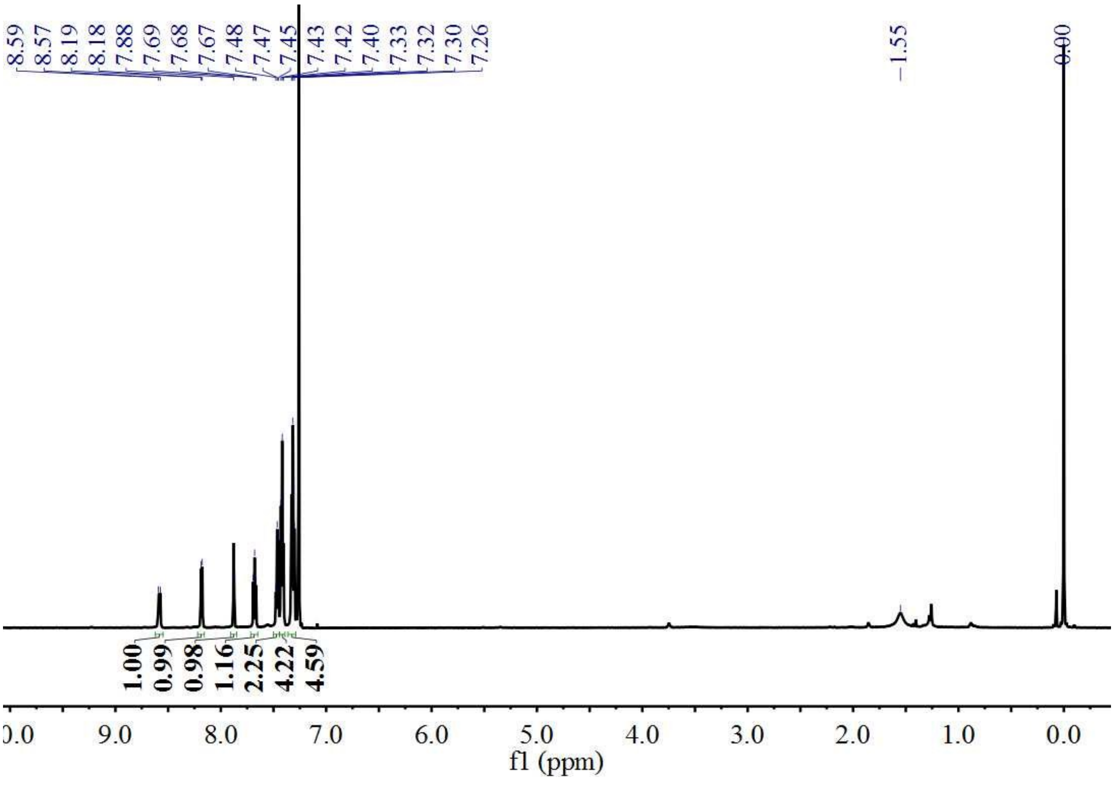


^{13}C NMR (150 MHz, 298 K, CDCl$_3$)

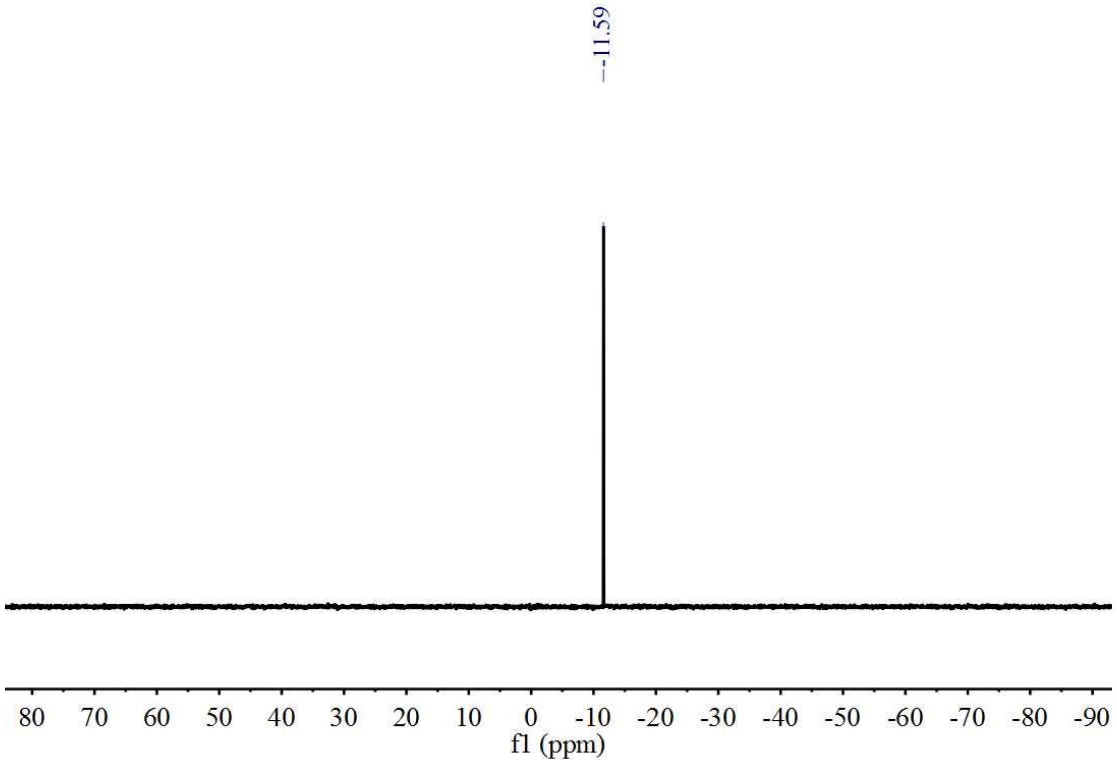


Compound **7**

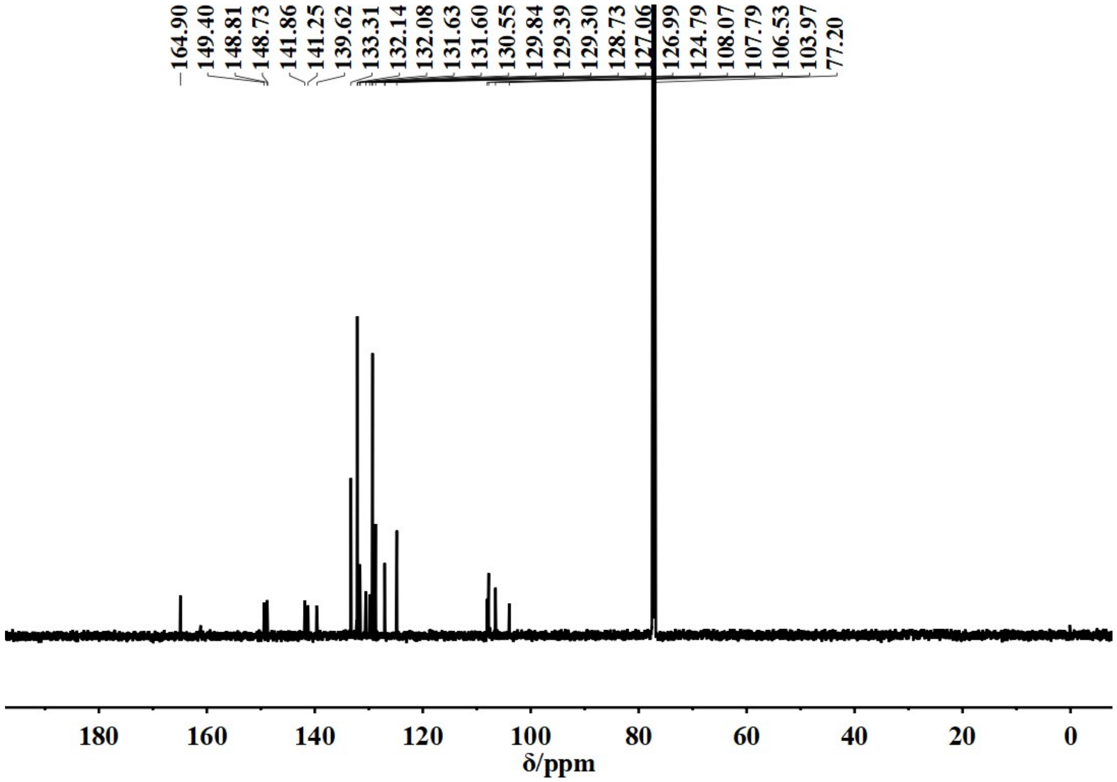
^{1}H NMR (600 MHz, 298 K, CDCl$_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

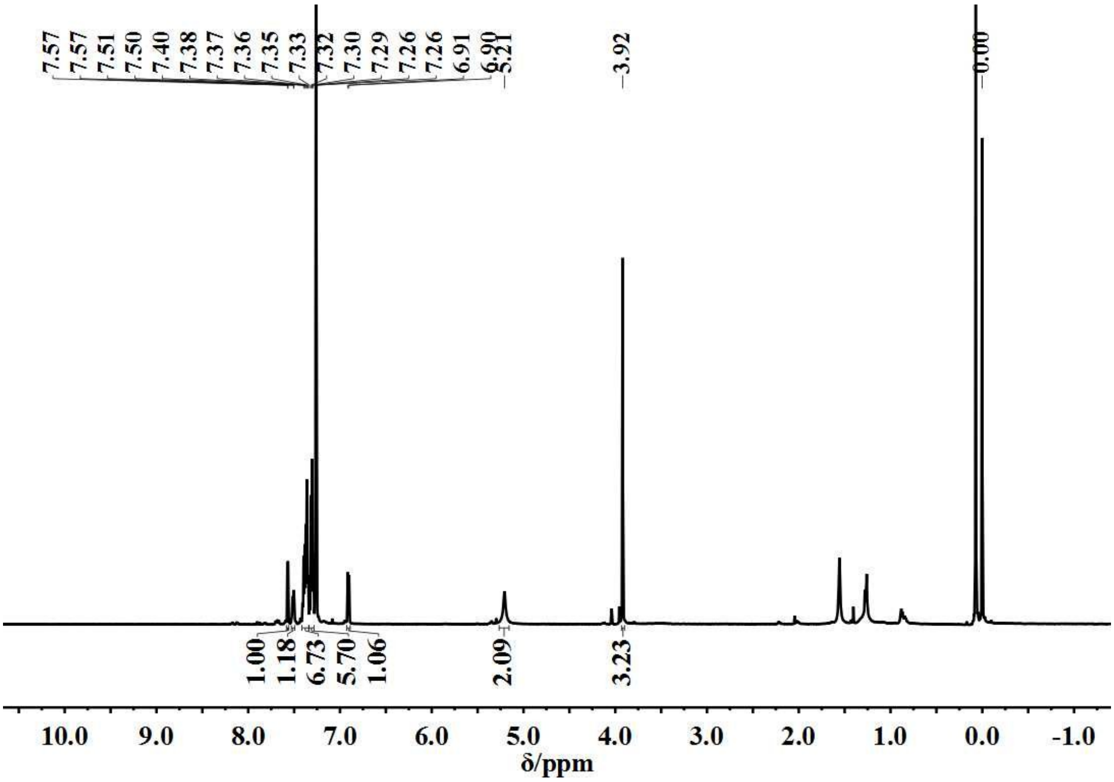


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

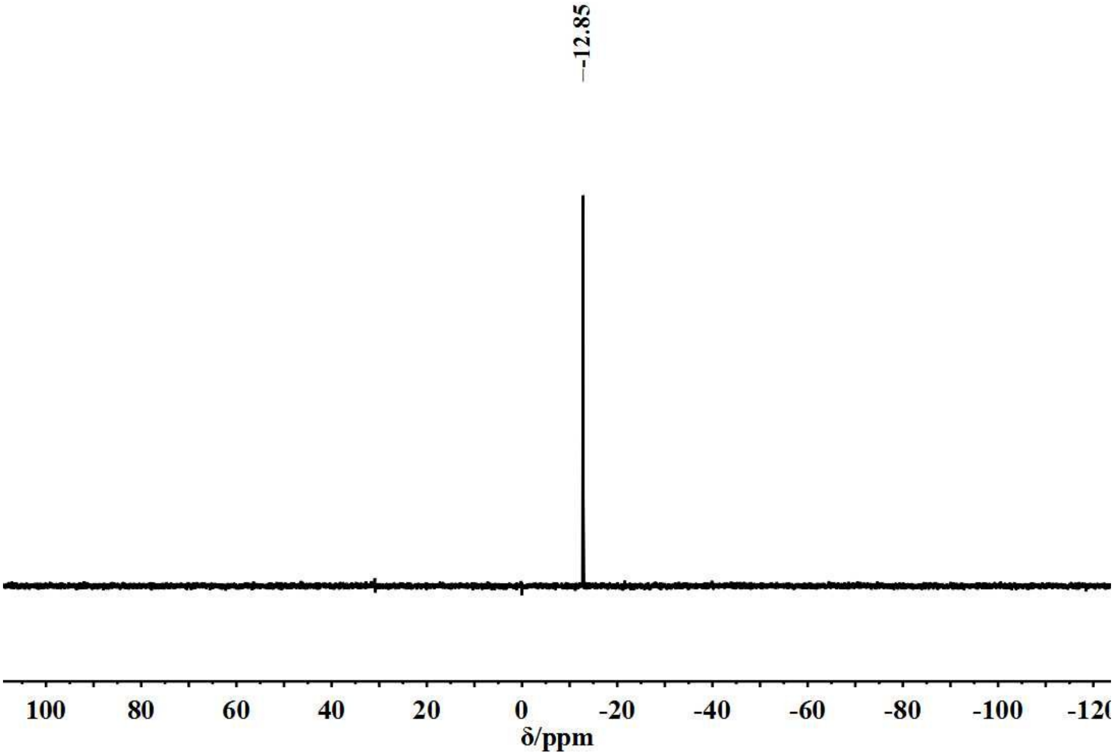


Compound **8**

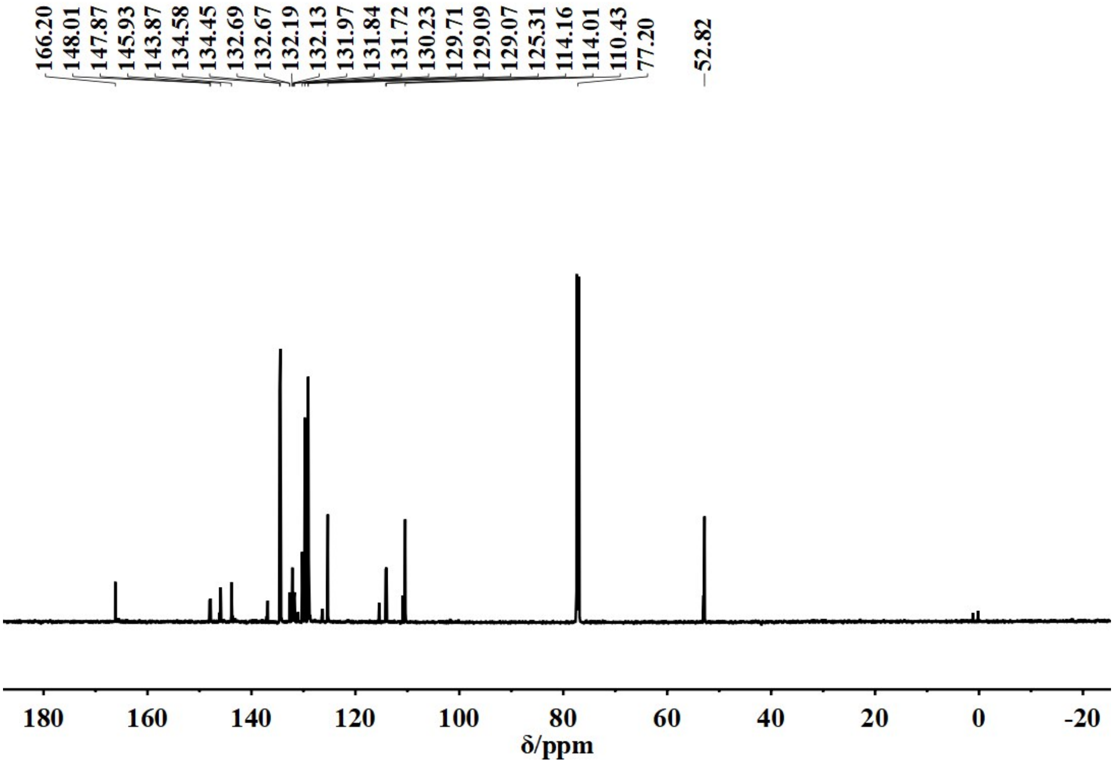
^{1}H NMR (600 MHz, 298 K, CDCl$_3$)



^{31}P NMR (243 MHz, 298 K, CDCl$_3$)

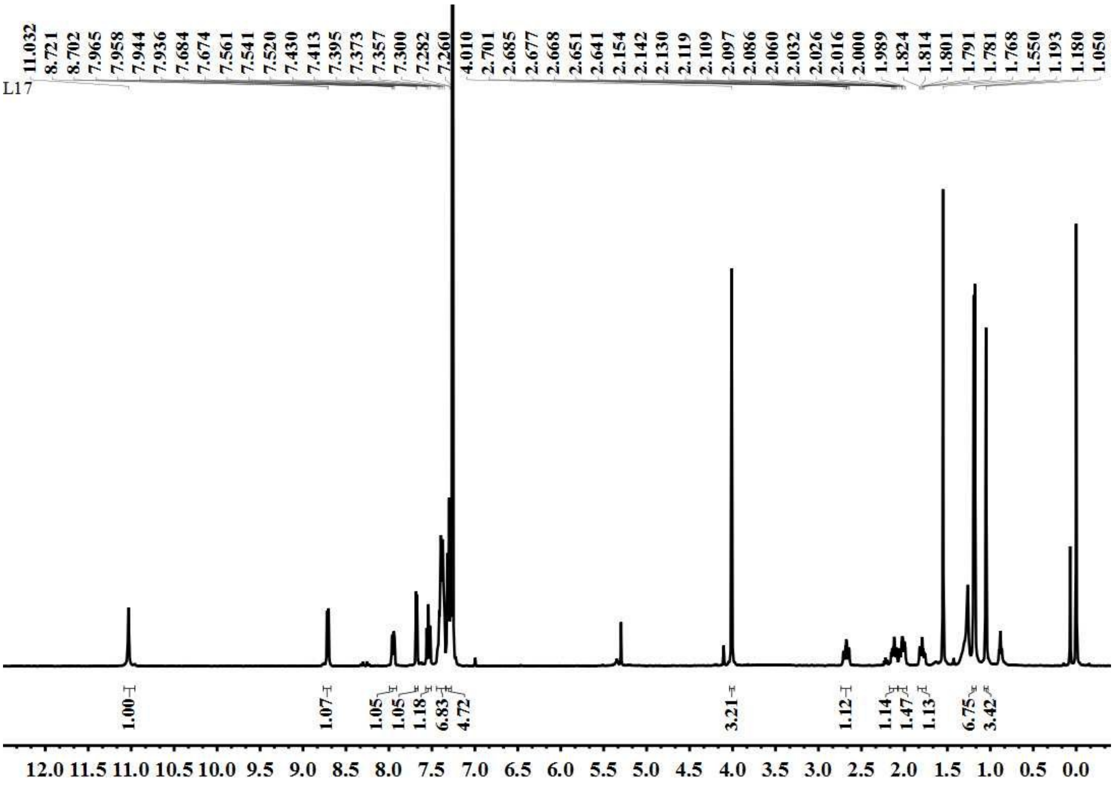


^{13}C NMR (150 MHz, 298 K, CDCl$_3$)

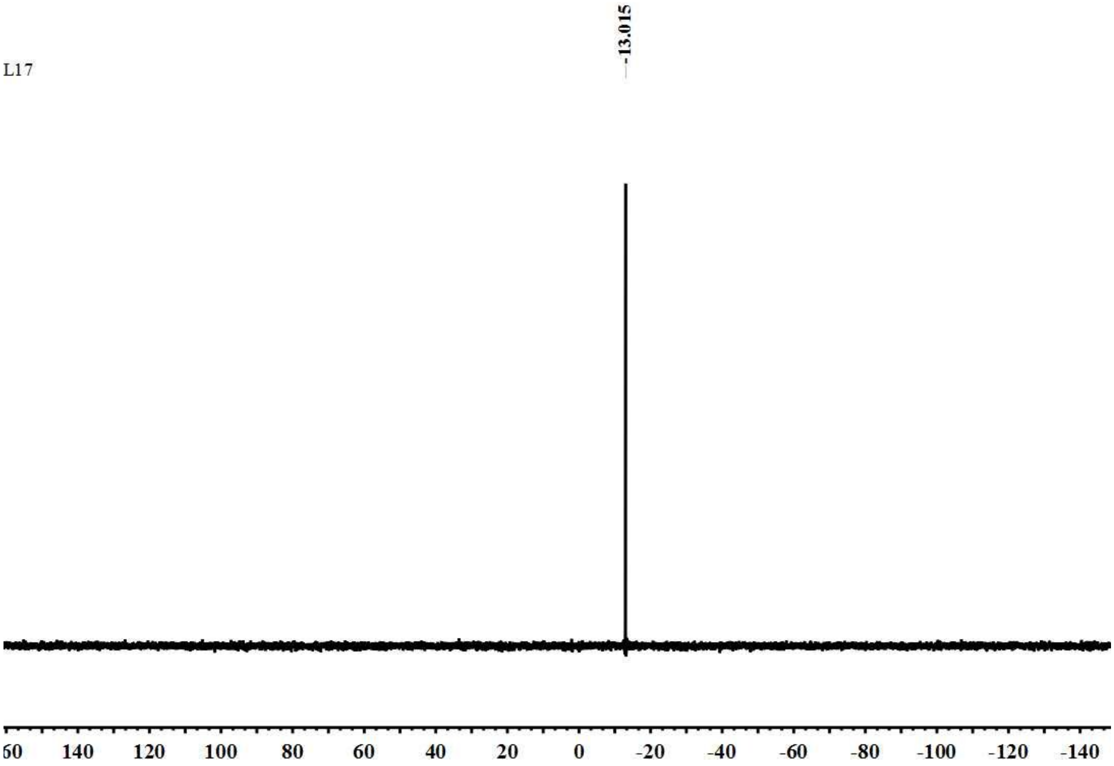


Compound **9**

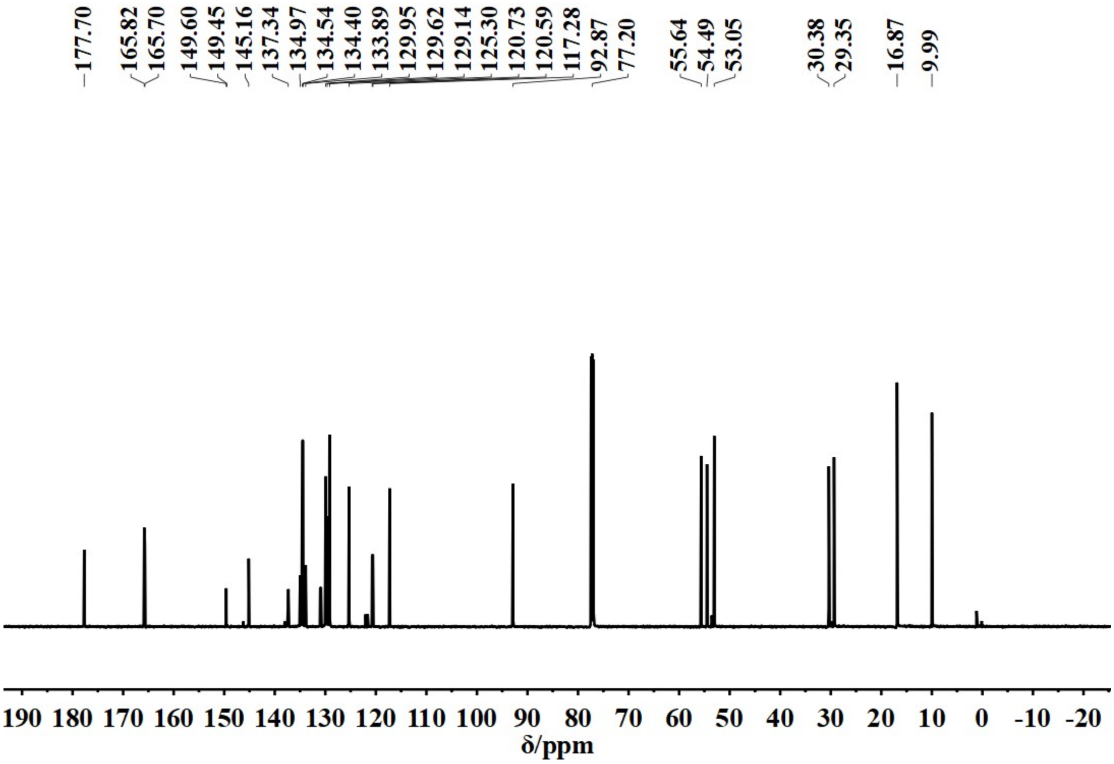
^{1}H NMR (400 MHz, 298 K, CDCl$_3$)



^{31}P NMR (162 MHz, 298 K, $CDCl_3$)

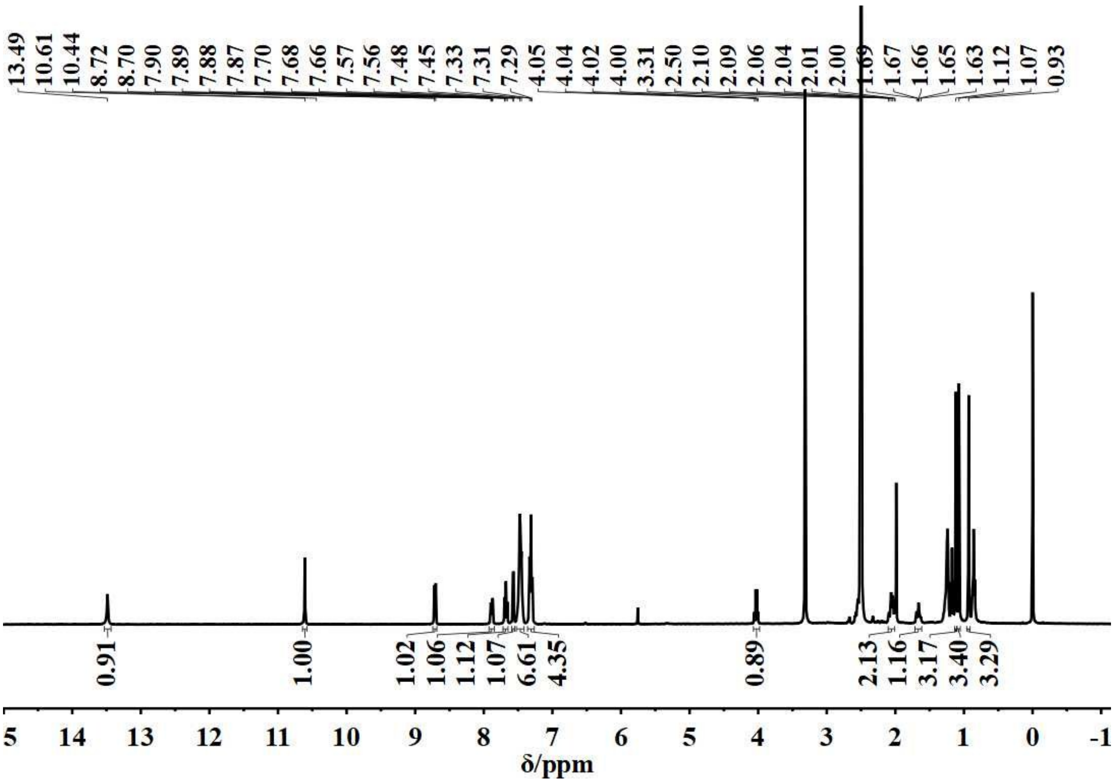


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

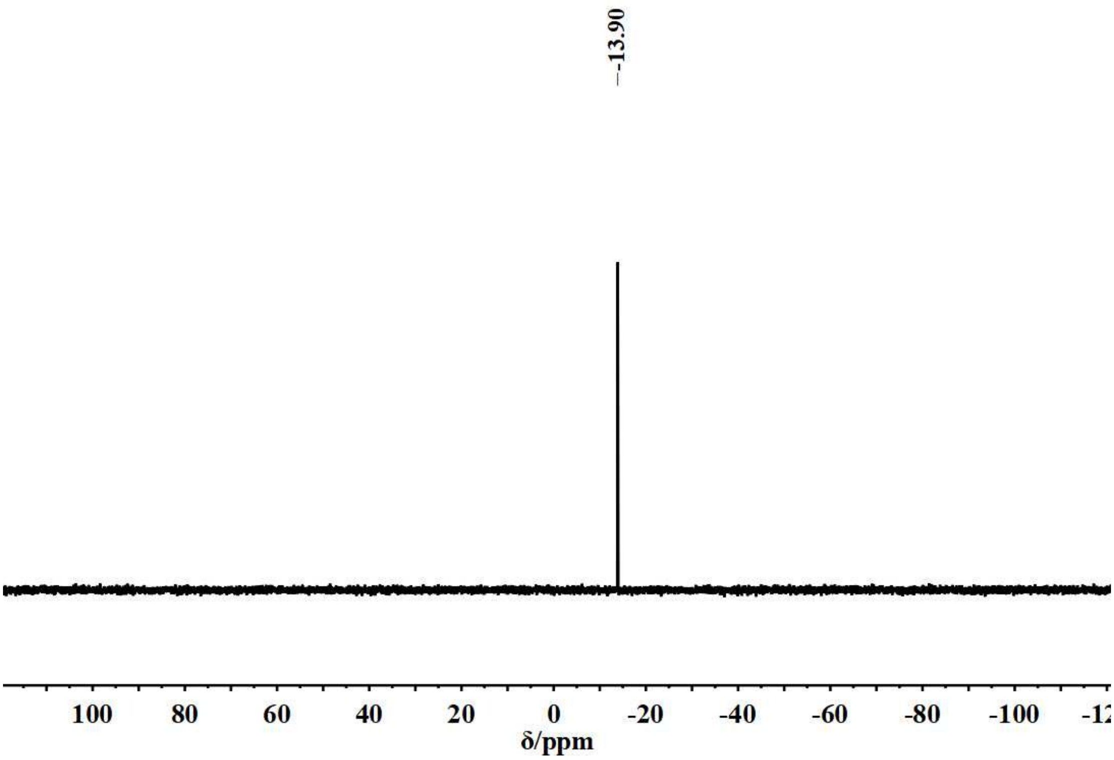


Compound **10**

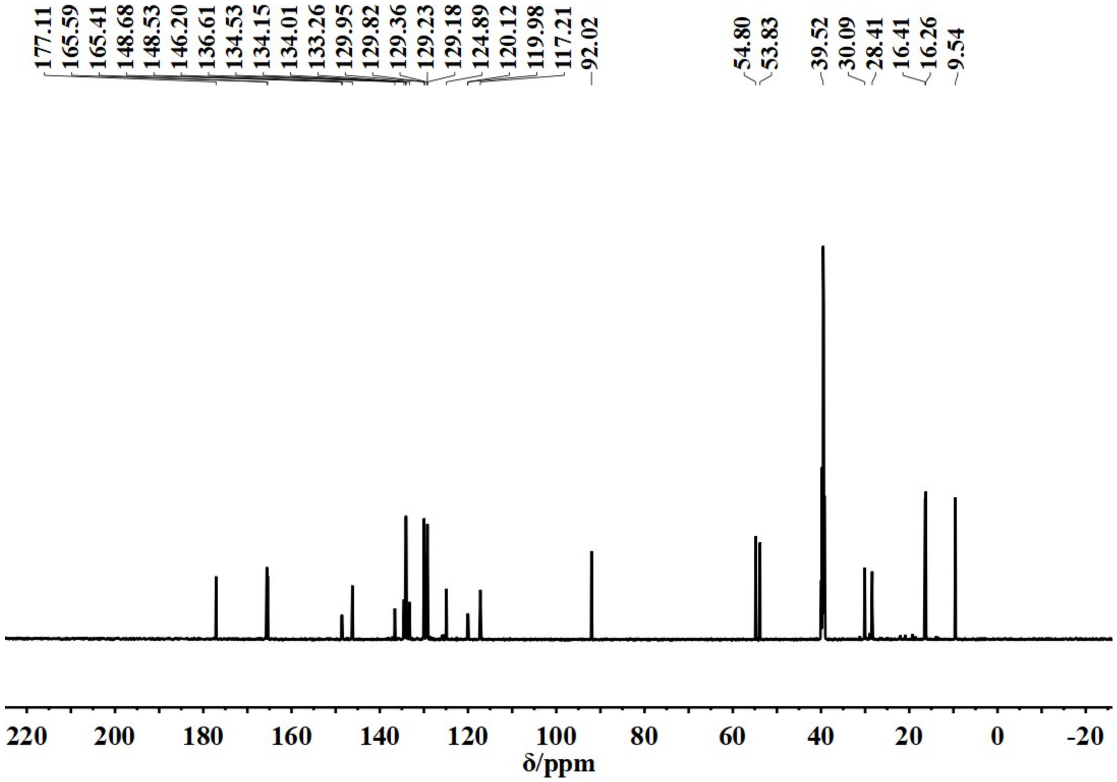
^{1}H NMR (400 MHz, 298 K, DMSO-d_6)



^{31}P NMR (162 MHz, 298 K, DMSO-d_6)

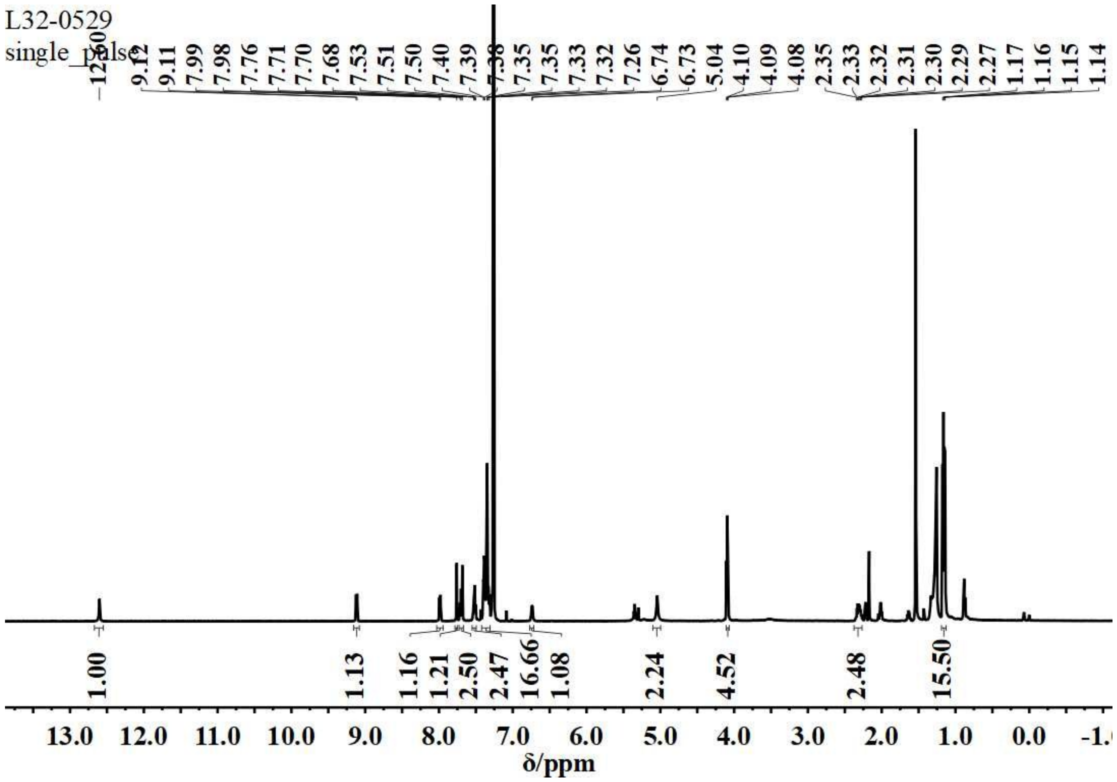


^{13}C NMR (150 MHz, 298 K, DMSO-d_6)



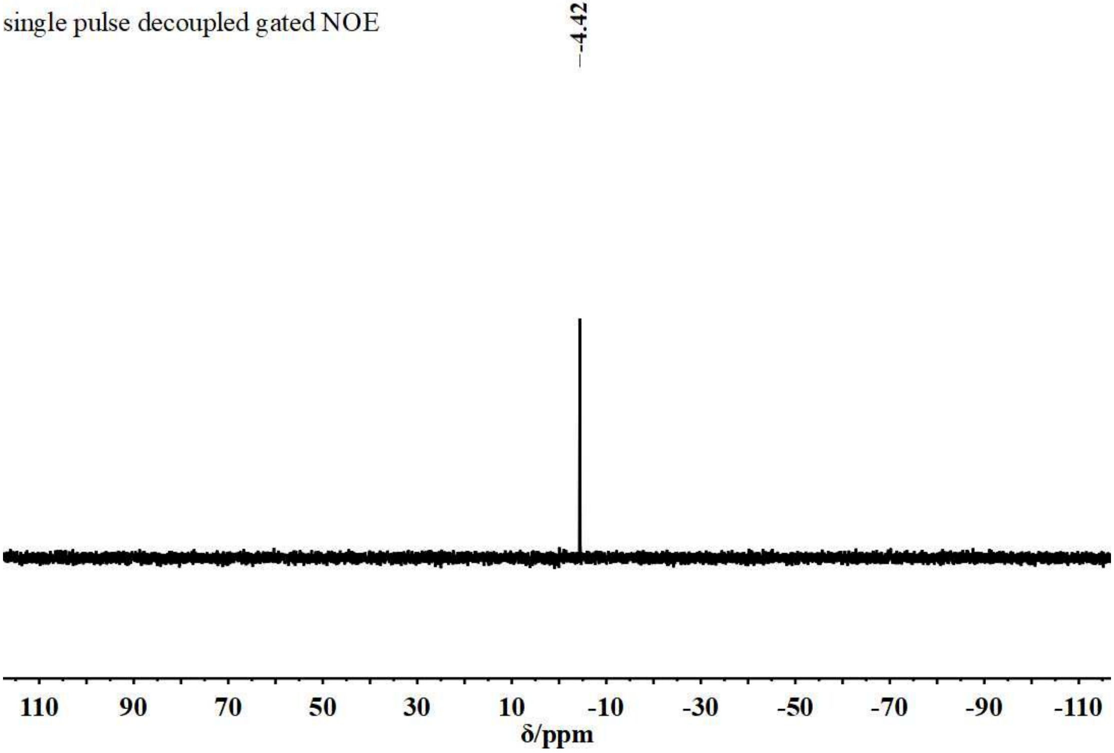
Compound **4a**

^{1}H NMR (600 MHz, 298 K, $CDCl_3$)

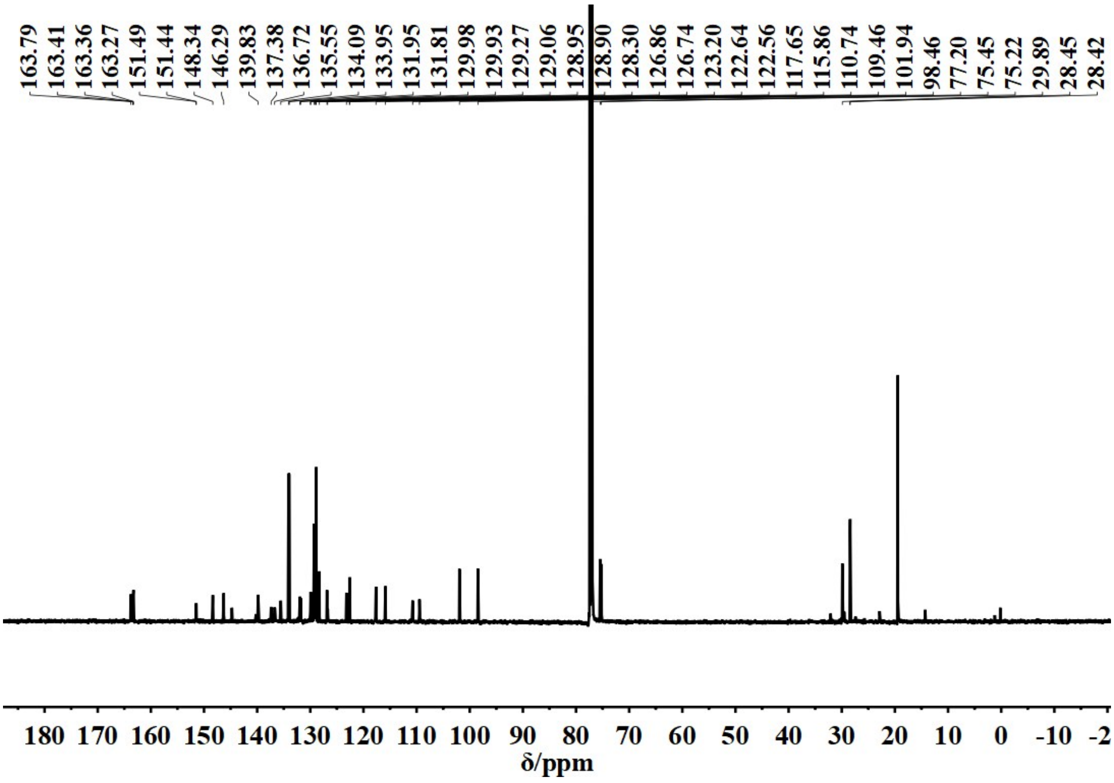


^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

L32-0529
single pulse decoupled gated NOE

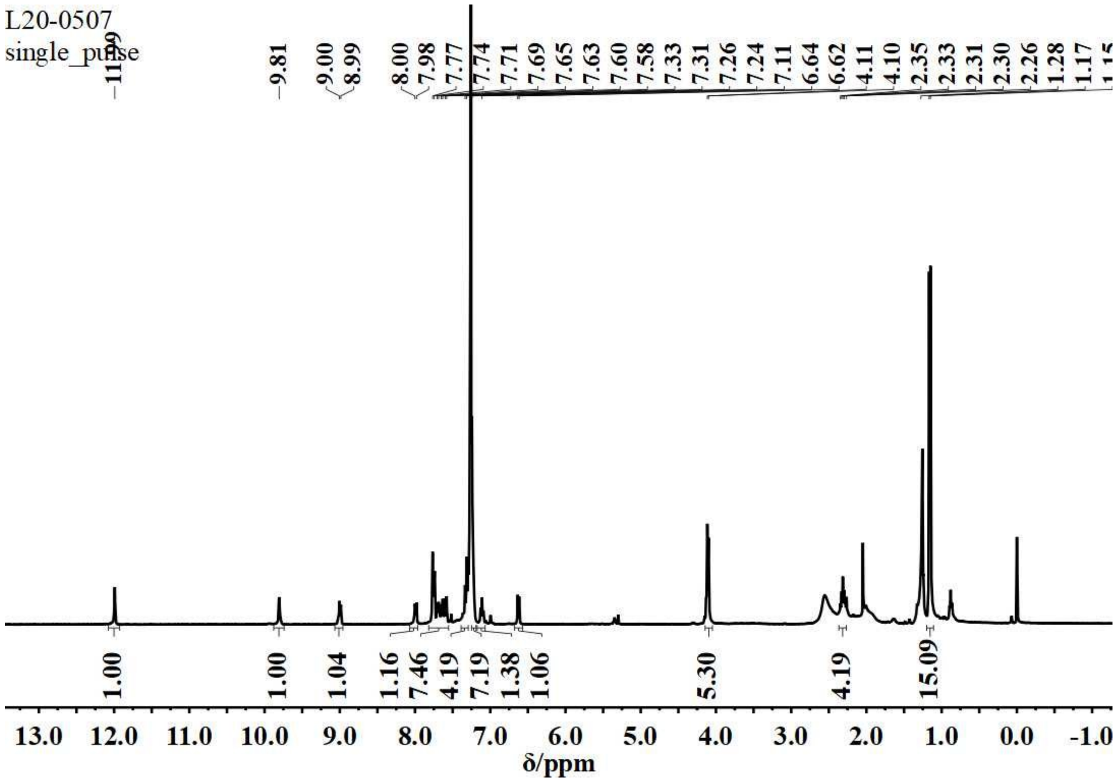


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

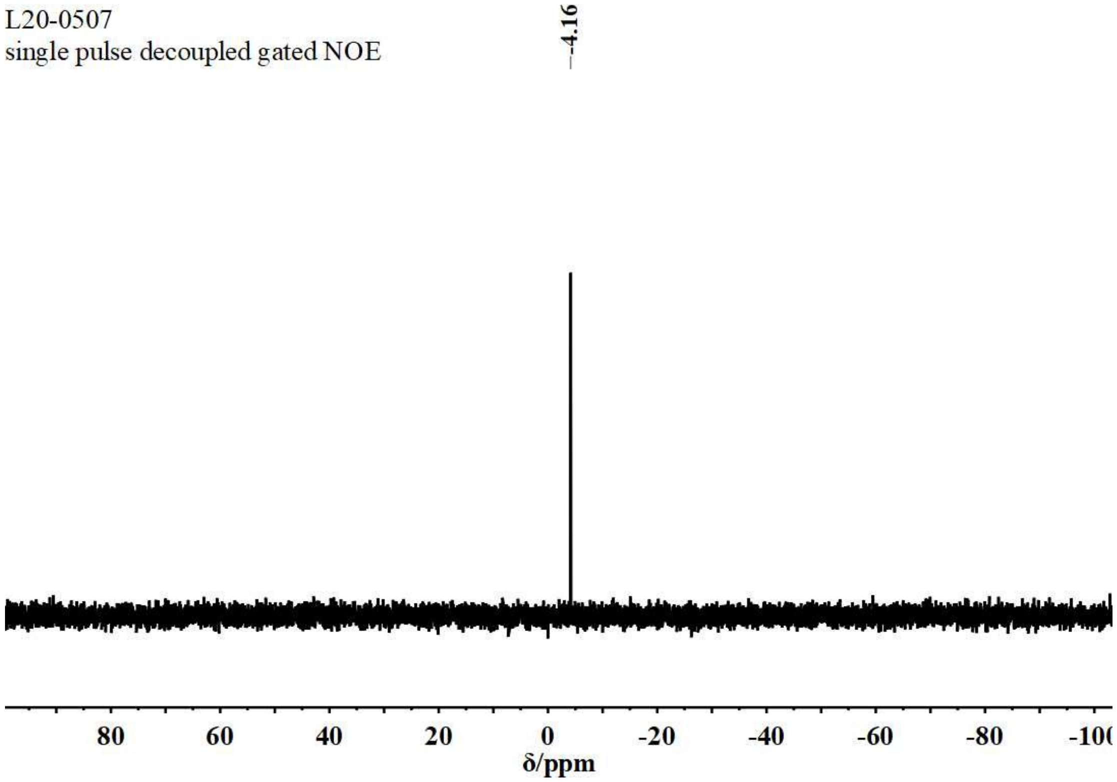


Compound **4b**

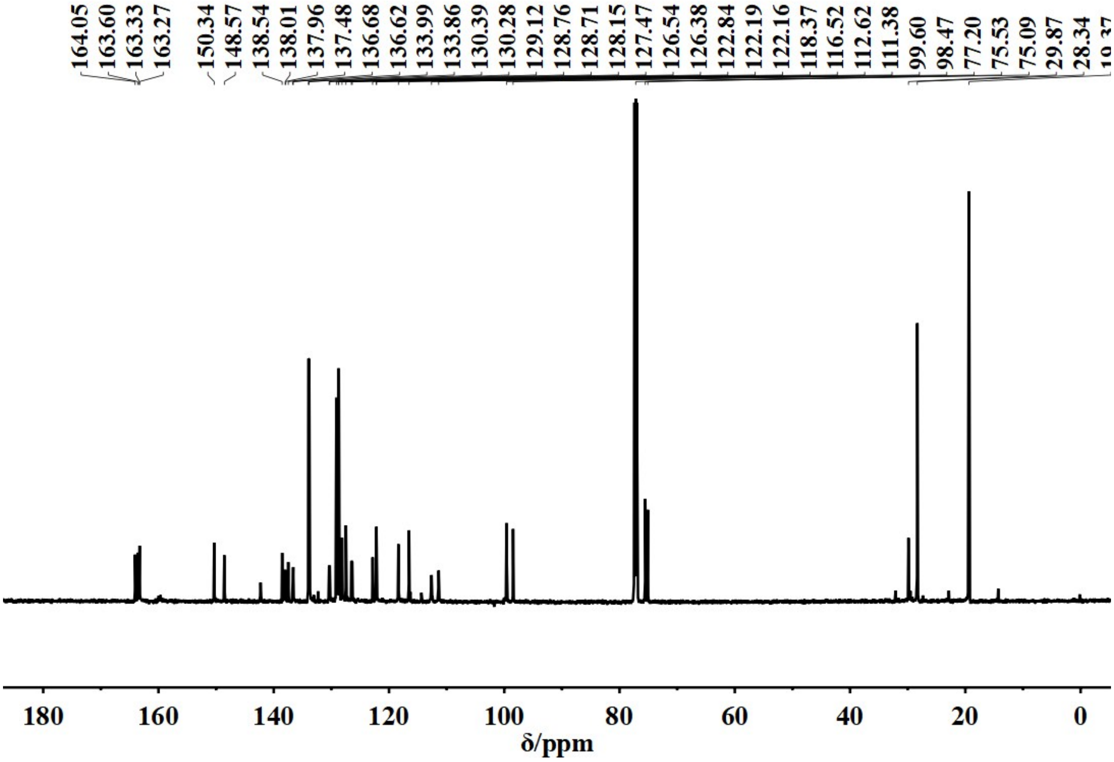
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

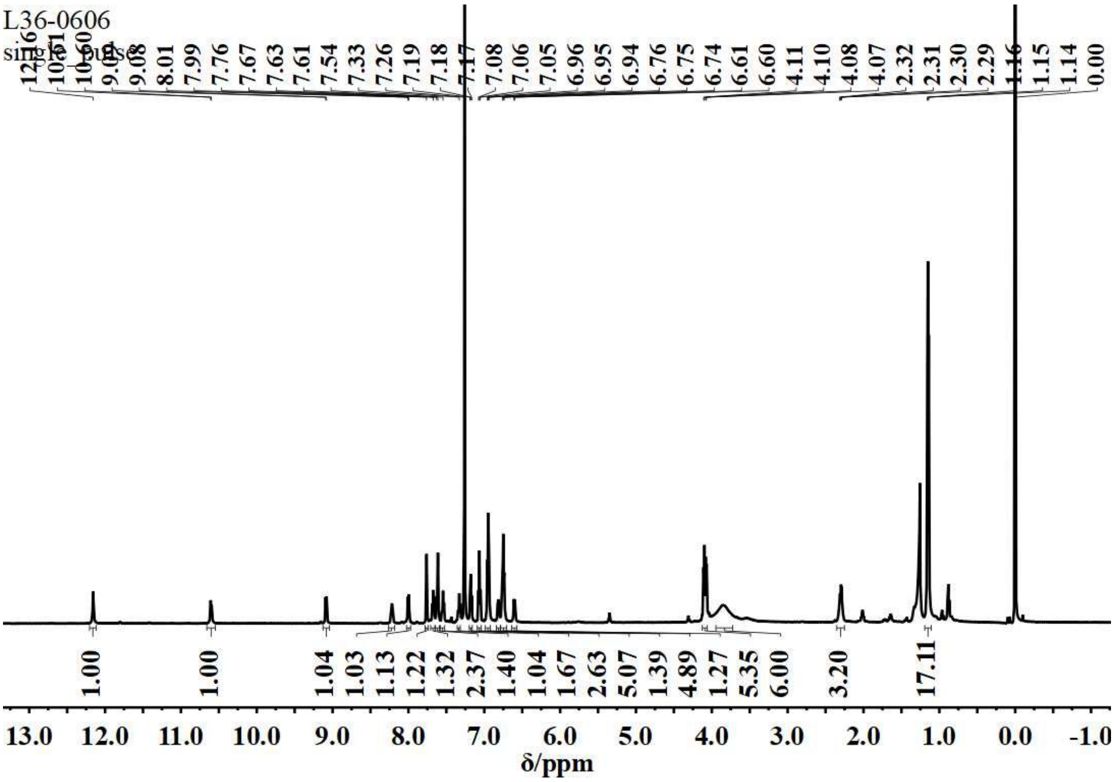


^{13}C NMR (150 MHz, 298 K, $CDCl_3$)

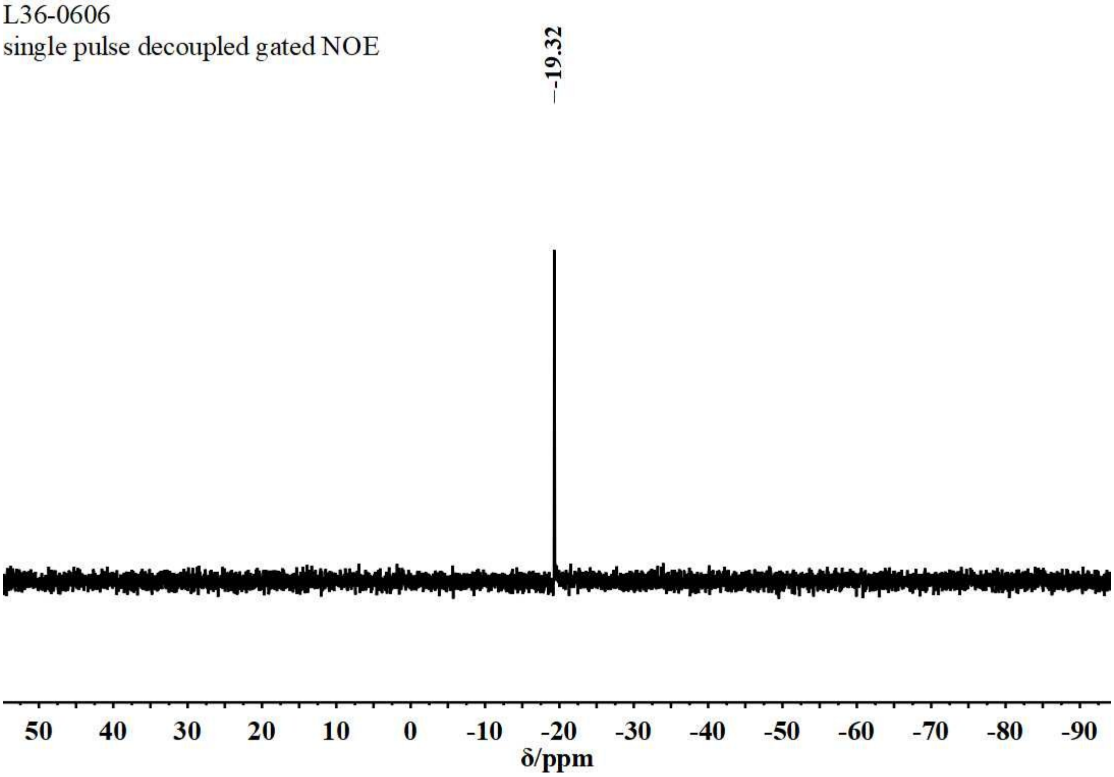


Compound **4c**

^1H NMR (600 MHz, 298 K, $CDCl_3$)

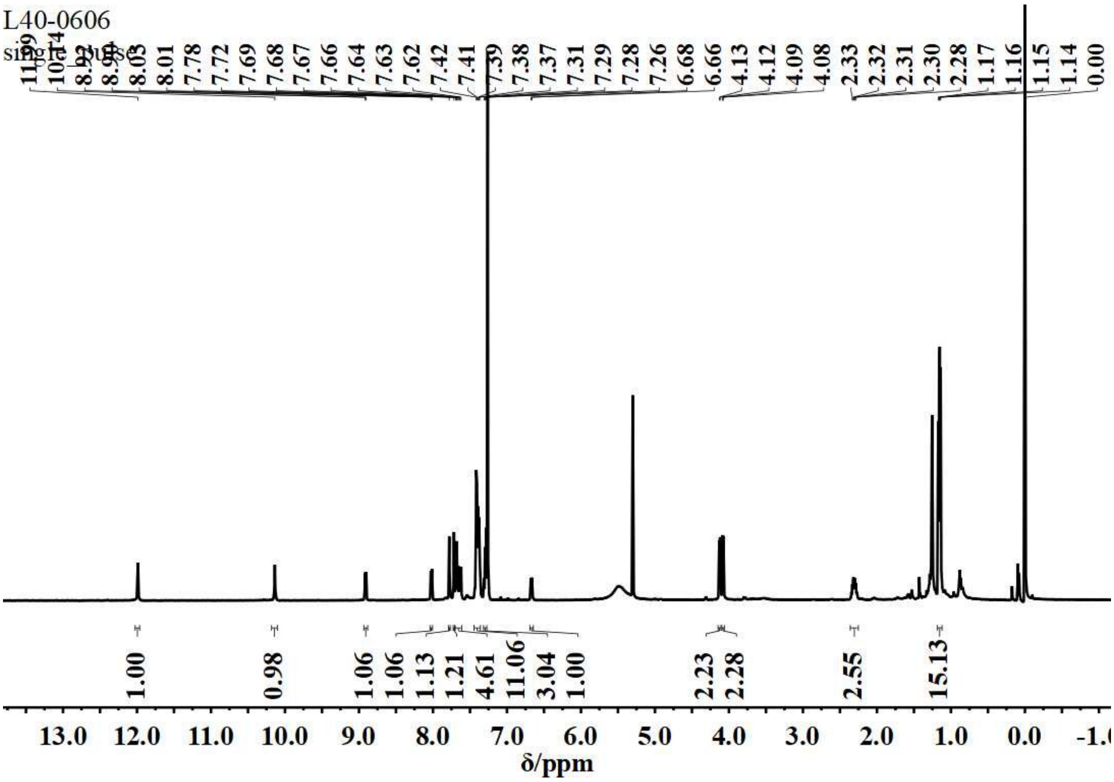


^{31}P NMR (243 MHz, 298 K, $CDCl_3$)

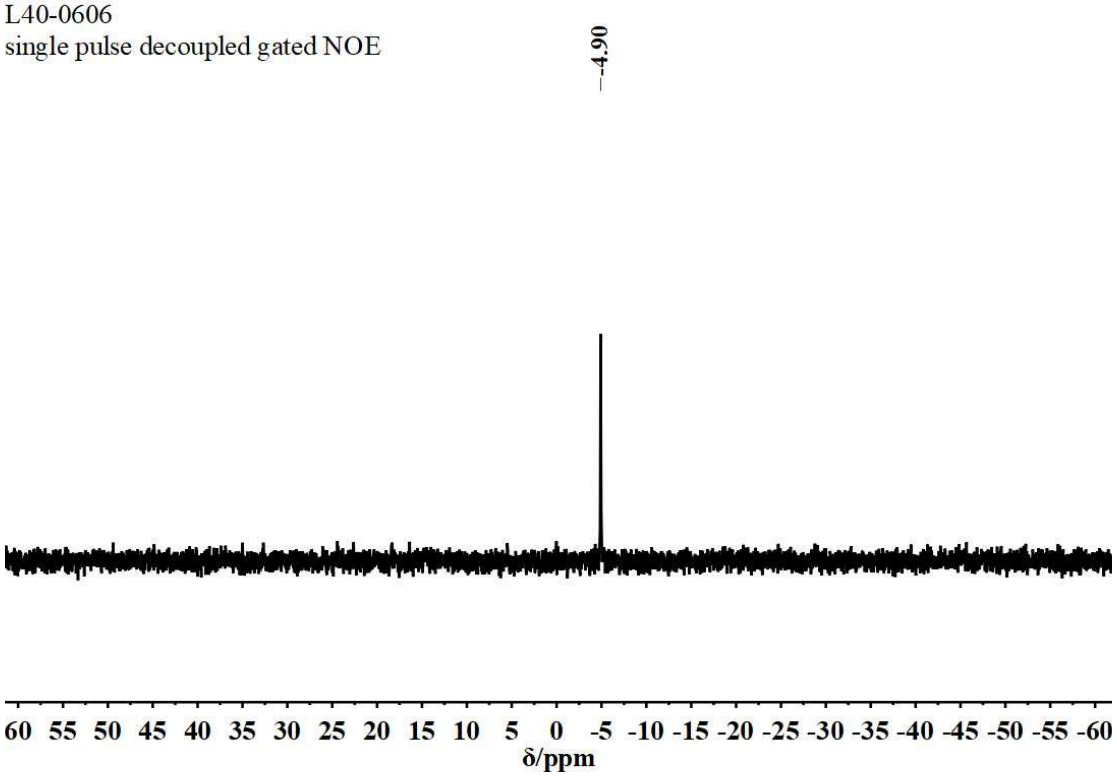


Compound **4d**

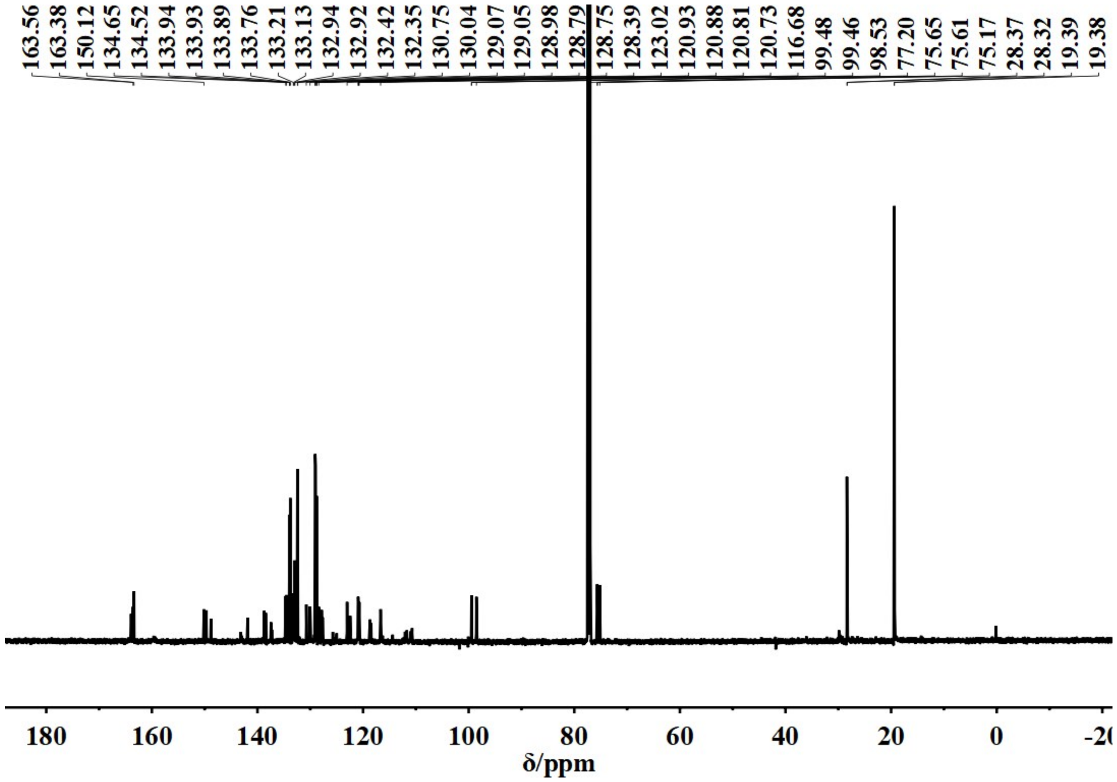
^{1}H NMR (600 MHz, 298 K, $CDCl_3$)



^{31}P NMR (243 MHz, 298 K, $CDCl_3$)



^{13}C NMR (150 MHz, 298 K, $CDCl_3$)



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2. R. Gramage-Doria, J. Hessels, S. H. Leenders, O. Troppner, M. Durr, I. Ivanovic-Burmazovic and J. N. Reek, *Angew. Chem. Int. Ed.*, 2014, **53**, 13380-13384.

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