

Supporting Information

Self-assembly of P-chiral supramolecular phosphine on rhodium and a direct evidence for Rh-catalyst-substrate

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1. Experiment section

All manipulations were carried out under an inert atmosphere using standard Schlenk line techniques or m-Braun glove box. Solvents were dried by standard procedure.¹ THF distilled from sodium/benzophenone under argon atmosphere. Acetonitrile and methylene chloride were distilled on calcium-hydride. [(COD)₂RhBF₄] and *N*-acetyldehydrophenylalanine were purchased from Sigma-Aldrich All other reagents/chemicals, solvents were purchased from local suppliers (Spectrochem Pvt. Ltd.; Avra Synthesis Pvt. Ltd.; Thomas Baker Pvt. Ltd. etc). The asymmetric hydrogenation was run in an Amar Equipment high pressure autoclave equipped with inlet/outlet and pressure regulators.

Solution NMR spectra were recorded on a Bruker Avance 400 and 500 MHz instruments at 298 K unless mentioned otherwise. Chemical shifts are referenced to external reference TMS (¹H and ¹³C). Coupling constants are given as absolute values. Multiplicities are given as follows s: singlet, d: doublet, t: triplet, m: multiplet, br: broad. FT-IR spectra were recorded on a Bruker α -T spectrophotometer in the range of 4000-400 cm⁻¹ by using CaF₂ pallets. Mass spectra were recorded on Thermo scientific Q-Exactive mass spectrometer. Synthesis of self-assembled Rh-complex according to our previous report.²

2. Demonstrating the self-assembly

2.1 Effect of concentration on H-bonding in L1:

In a NMR tube 0.0017 g (0.005 mmol) of **L1** was dissolved in 0.5 ml of CDCl₃ to make 10 mM solution of **L1**. The ¹H NMR of 10 mM solution was recorded at 25 °C and chemical shift of NH and NH₂ protons was identified. Next, in the same NMR tube another 0.0017 g (0.005 mmol) of **L1** (to make 20 mM solution of **L1**) was added and proton NMR was recorded. In similar manner, 30 mM, 40 mM, and 50 mM solution of **L1** was prepared and ¹H NMR was measured. Table S1 summarizes the change in chemical shift of NH and NH₂ protons of **L1** with increasing concentrations.

Table S1 : Monitoring the change in chemical shift of NH and NH₂ proton as a function of concentration of the **L1**.

Sr. no.	L1 (g)	L1 conc. (mM)	NH (ppm)	NH ₂ (ppm)
1	0.0017	10	6.43	4.59
2	0.0017 + 0.0017	20	6.55	4.62
3	0.0034 + 0.0017	30	6.66	4.65
4	0.0050 + 0.0017	40	6.76	4.68
5	0.0067 + 0.0017	50	6.85	4.70

2.2 Effect of concentration on H-bonding in C1:

Along the same lines, in a NMR tube 0.0048 g (0.005 mmol) of **C1** was dissolved in 0.5 ml of CDCl₃ to make 10 mM solution of **C1**. The ¹H NMR of 10 mM solution was recorded at 25 °C and chemical shift of NH₂ protons was recorded. Next, in the same NMR tube another 0.0048 g (0.005 mmol) of **C1** (to make 20 mM solution of **C1**) was added and proton NMR was recorded. In similar manner, 30 mM, 40 mM, and 50 mM solution of **C1** was prepared and ¹H NMR was measured. Table S2 summarizes the change in chemical shift of NH and NH₂ protons of **C1** with increasing concentrations.

Table S2 : Monitoring the change in chemical shift of NH₂ proton as a function of concentration of the **C1**.

Sr. no.	self-assembled Rh-complex (g)	C1 conc. (mM)	NH ₂ (ppm)
1	0.0048	10	5.15
2	0.0048 + 0.0048	20	5.16
3	0.0096 + 0.0048	30	5.17
4	0.0144 + 0.0048	40	5.18 [(5.26+5.11)/2]
5	0.0192 + 0.0048	50	5.19 [(5.28+5.09)/2]

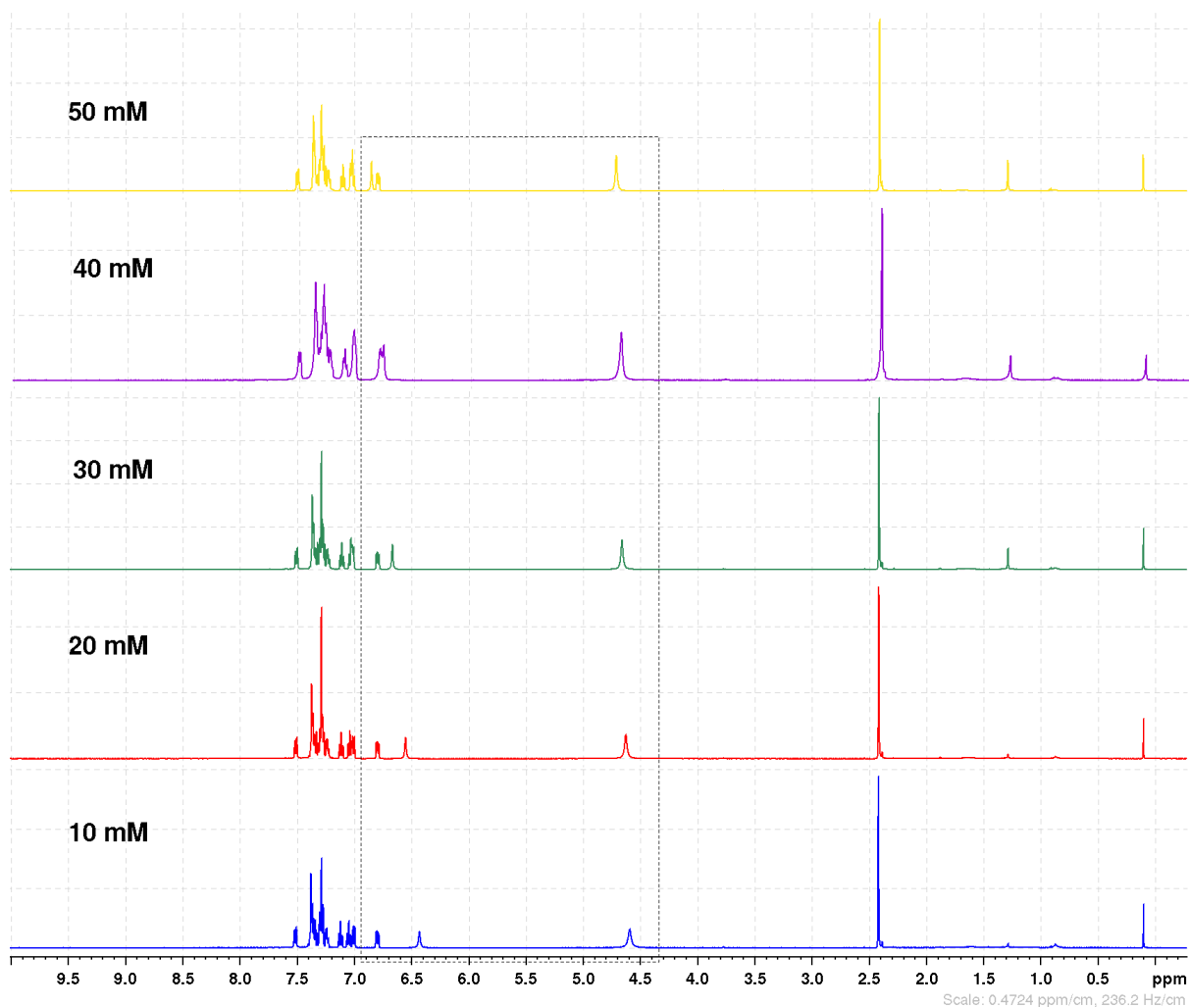


Fig. S1. ^1H NMR spectra of P-stereogenic supramolecular phosphine (**L1**) at different concentration.

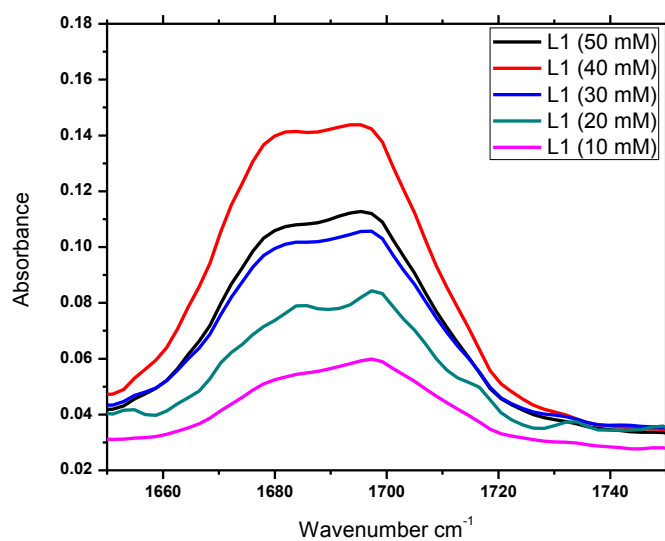


Fig. S2. IR spectra of P-stereogenic supramolecular phosphine (**L1**) at different concentration.

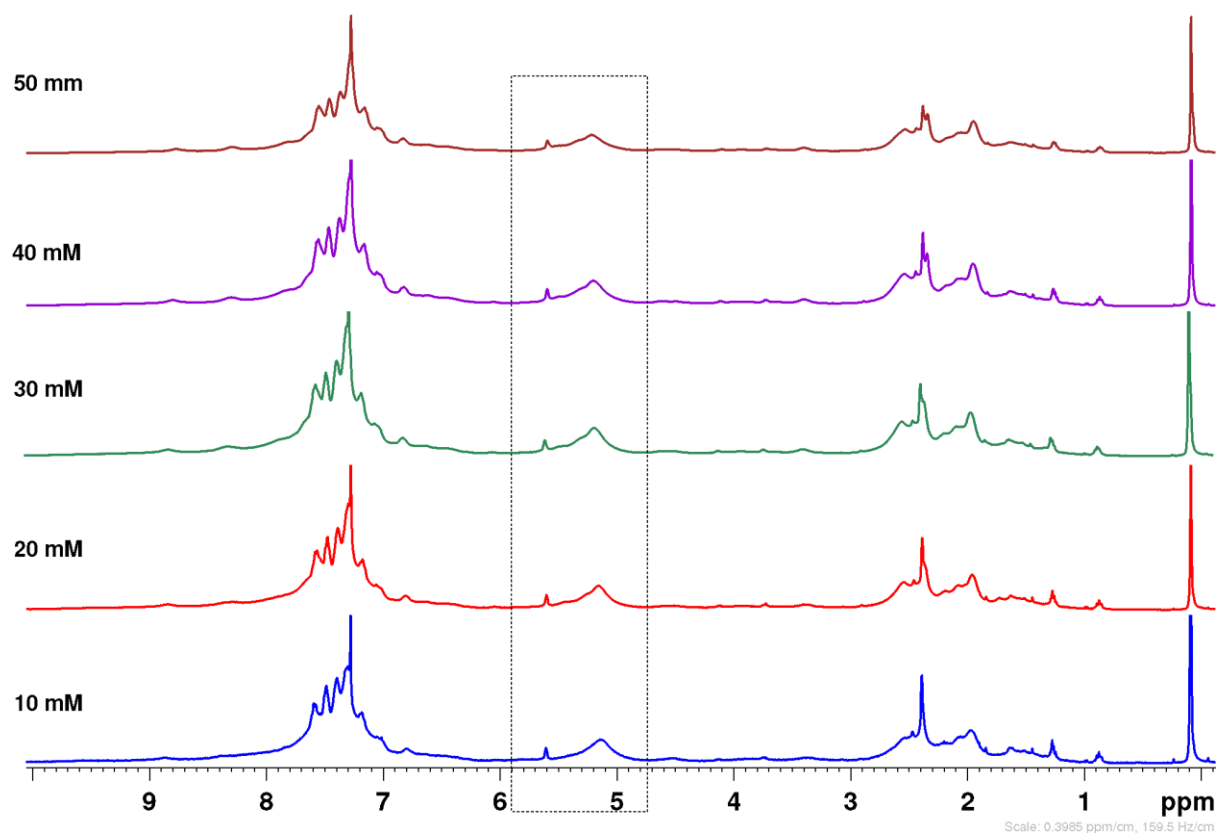


Fig. S3. ^1H NMR spectra of self-assembled Rh-complex (**C1**) at different concentration.

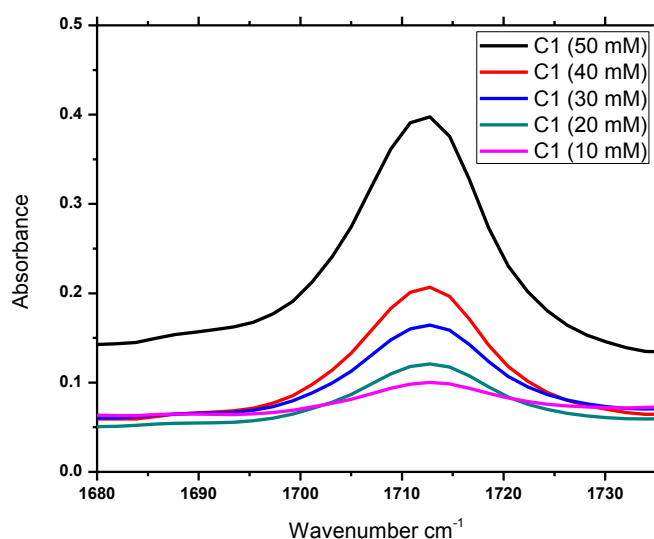


Fig. S4. IR spectra of **C1** at different concentration.

2.3 Effect of temperature on H-bonding in L1:

In the NMR tube 0.0017 g (0.005 mmol) of **L1** was dissolved in 0.5 ml of CDCl_3 to make 10 mM solution. The ^1H NMR was measured at different temperature starting from 298 K to 293K, 283 K, 273 K and 263 K. The change in chemical shift of the NH and NH_2 protons as a function of decreasing temperature is summarized in Table S3.

Table S3 : Monitoring the change in chemical shift of NH and NH_2 proton as a function of temperature of the **L1**.

Sr. no.	Temperature (K)	L1 conc. (mM)	NH (ppm)	NH_2 (ppm)
1	298	10	6.37	4.55
2	293	10	6.43	4.58
3	283	10	6.50	4.62
4 ^a	273	10	6.59	4.66
5 ^a	263	10	6.69	4.70

2.4 Effect of temperature on H-bonding in C1:

Similarly, 0.0048 g (0.005 mmol) of **C1** was charged to the NMR tube which was the dissolved in 0.5 ml of CDCl_3 to make a 10 mM solution of **C1**. The ^1H NMR of this 10 mM solution was recorded at different temperatures starting from 298 K to 293K, 283 K, 273 K and 263 K. There was hardly any change in the chemical shift of NH_2 proton as a function of decreasing temperature and Table S4 presents the change in chemical shift as a function of temperature.

Table S4 : Monitoring the change in chemical shift of NH and NH_2 proton as a function of temperature of the **C1**.

Sr. no.	C1 conc. (mM)	Temperature (K)	NH_2 (ppm)
1	10	298	5.12

2	10	293	5.13
3	10	283	5.14
4	10	273	5.18
5	10	263	5.19

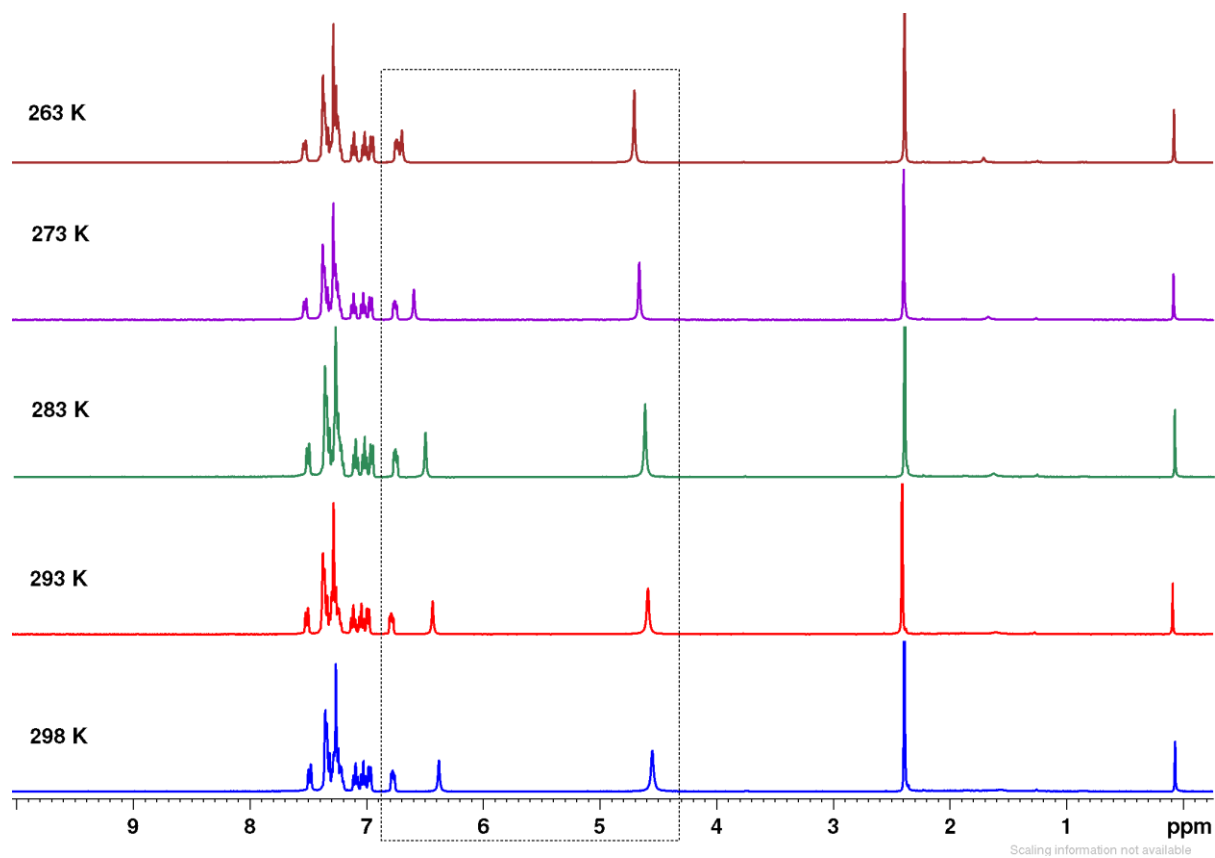


Fig S5. ^1H NMR spectra of **L1** at different temperature.

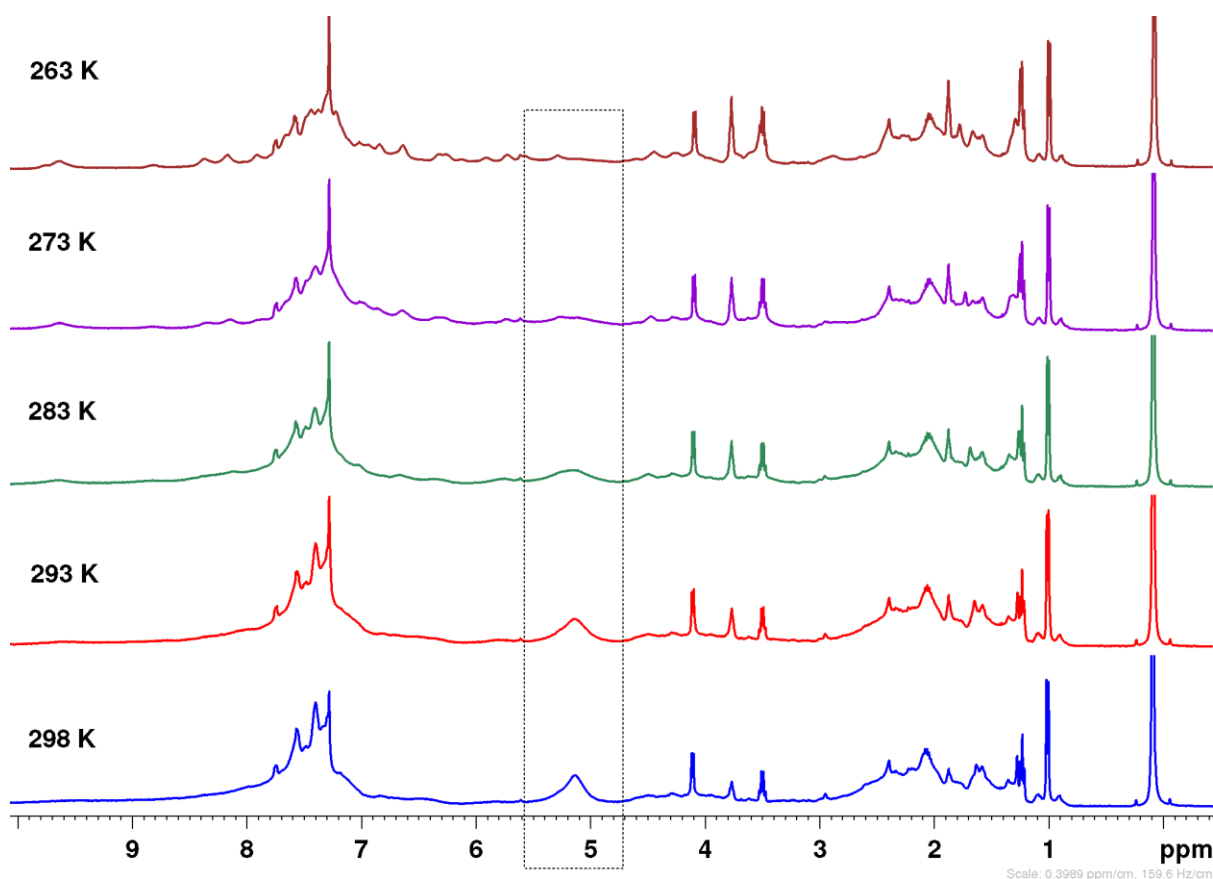
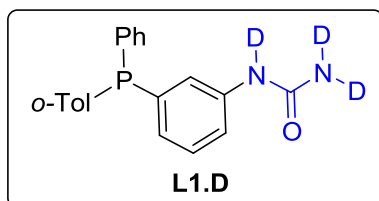


Fig S6. ^1H NMR spectra of **C1** at different temperature.

3. Synthesis of deuterated supramolecular phosphine ligand (L1.D)



In the 50 ml Schlenk flask 0.136 g (0.4 mmol) of ligand **L1** was dissolved in 2 ml CD_3OD . The above reaction solution was stirred for 2.5 hours at room temperature. The progress of their action was monitored by ^1H NMR spectroscopy. After the reaction was complete, volatiles were evaporated under vacuum. The residue was dried under high vacuum and ^1H NMR was recorded in CDCl_3 (Fig. S7-S10). ^2H NMR was recorded in 0.5 ml THF (THF- d_8 :THF, 0.1:0.4 ml). (ESI Fig. S7-S11).

^2H NMR (500 MHz, THF- d_8 , 298 K) δ = 7.87 (s, *ND*), 5.45 (s, *ND2*). ^1H NMR (500 MHz, CDCl_3 , 298 K) δ = 7.45 (d, J = 7.25 Hz, 1H, Ar), 7.33 (br. s., 3H, Ar), 7.16 - 7.30 (m, 5H, Ar), 7.04 - 7.14 (m, 2H, Ar), 6.97 (t, J = 6.87 Hz, 1H, Ar), 6.74 - 6.84 (m, 1H, Ar), 4.85 (d, J = 5.34 Hz, 0.80H, *NH*), 2.39 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3 , 298 K) δ = 156.6 (s, *CO*), 142.3 (s, Ar), 142.1 (s, Ar), 138.7 (t, J = 7.7Hz, Ar), 137.7 (d, J = 10.5 Hz, Ar), 135.9 (d, J = 10.4 Hz, Ar), 135.5 (d, J = 11.5

Hz, Ar), 133.5 (d, $J = 20.1$ Hz, Ar), 132.7 (s, Ar), 130.4 (s, Ar), 130.1 (d, $J = 4.8$ Hz, Ar), 129.4 (d, $J = 7.6$ Hz, Ar), 129.2 (d, $J = 18.2$ Hz, Ar), 128.8 (d, $J = 8.5$ Hz, Ar), 128.6 (d, $J = 6.6$ Hz, Ar), 126.0 (s, Ar) 125.4 (d, $J = 20.9$ Hz, Ar), 120.5 (d, $J = 20.4$ Hz, Ar), 21.10 (d, $J = 21.1$ Hz, CH_3). **ESI-MS** (+ve) (For $M = C_{20}H_{19}N_2OP$) $m/z = 335.13 [M+H]^+$.

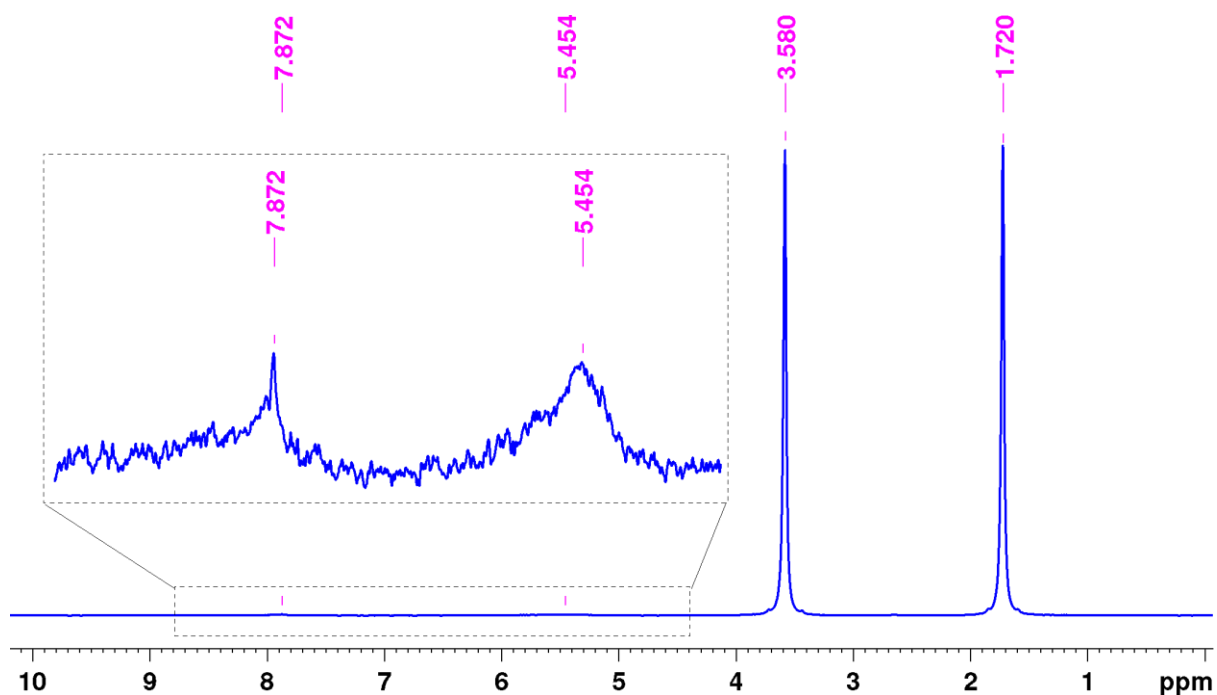


Fig. S7. 2H NMR spectrum of **L1.D** in THF- D_8 :THF (0.1:0.4 ml) solvent.

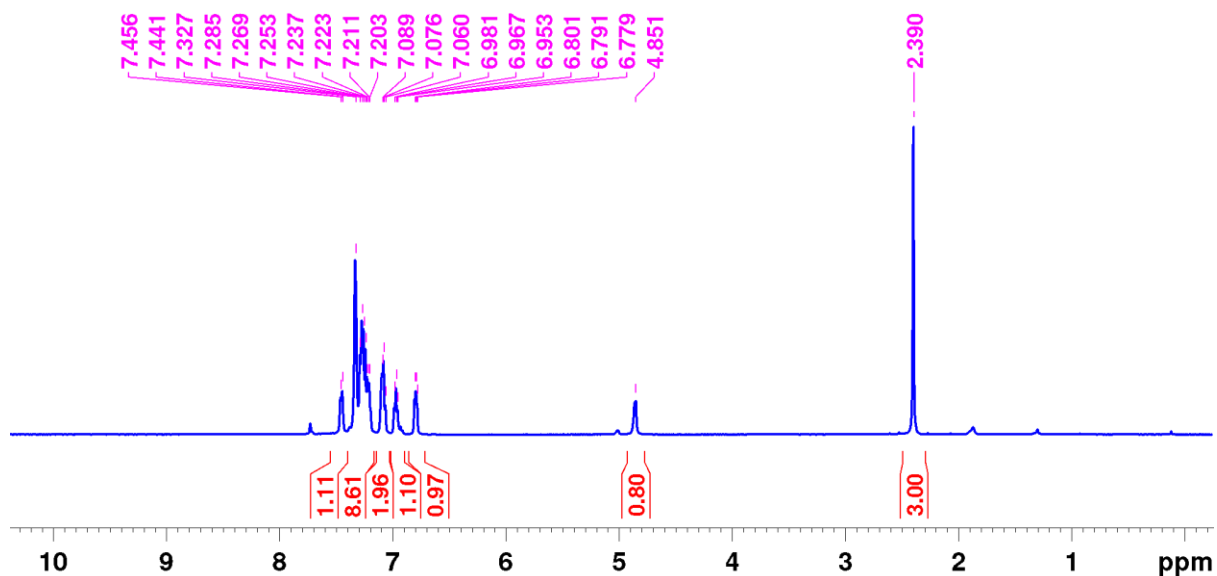


Fig. S8. 1H NMR spectrum of **L1.D** in $CDCl_3$.

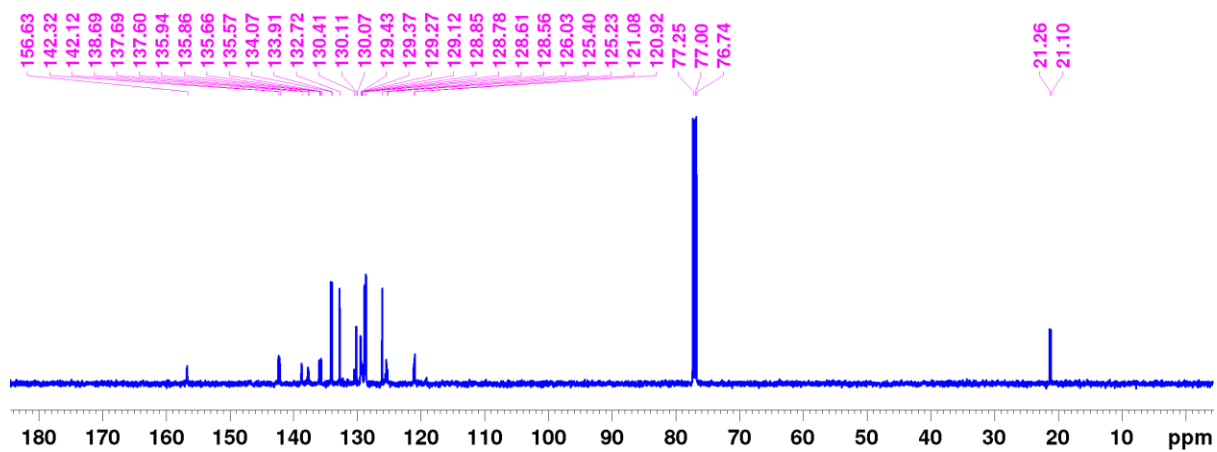


Fig. S9. ^{13}C NMR spectrum of **L1.D** in CDCl_3 .

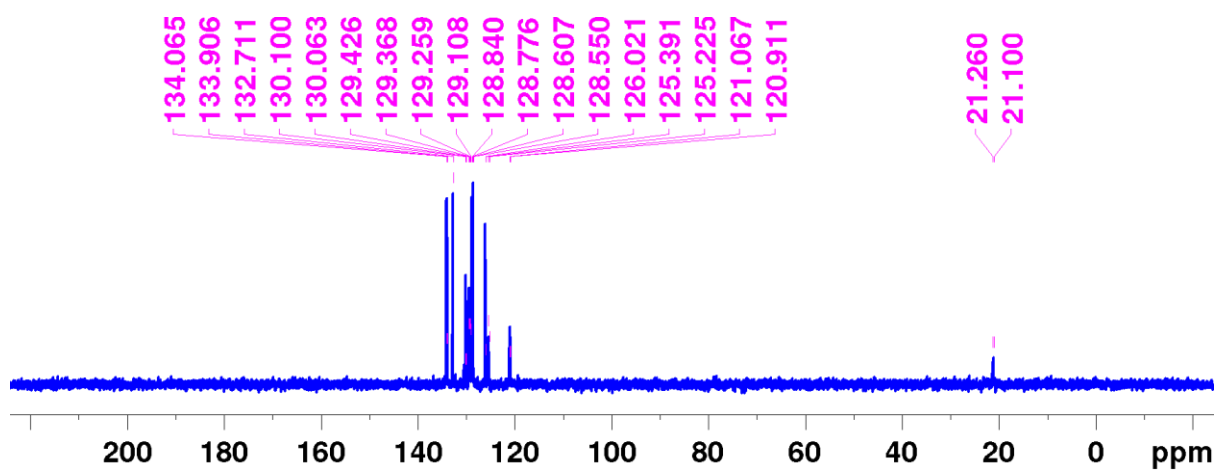


Fig. S10. ^{13}C NMR (DEPT) spectrum of **L1.D** in CDCl_3 .

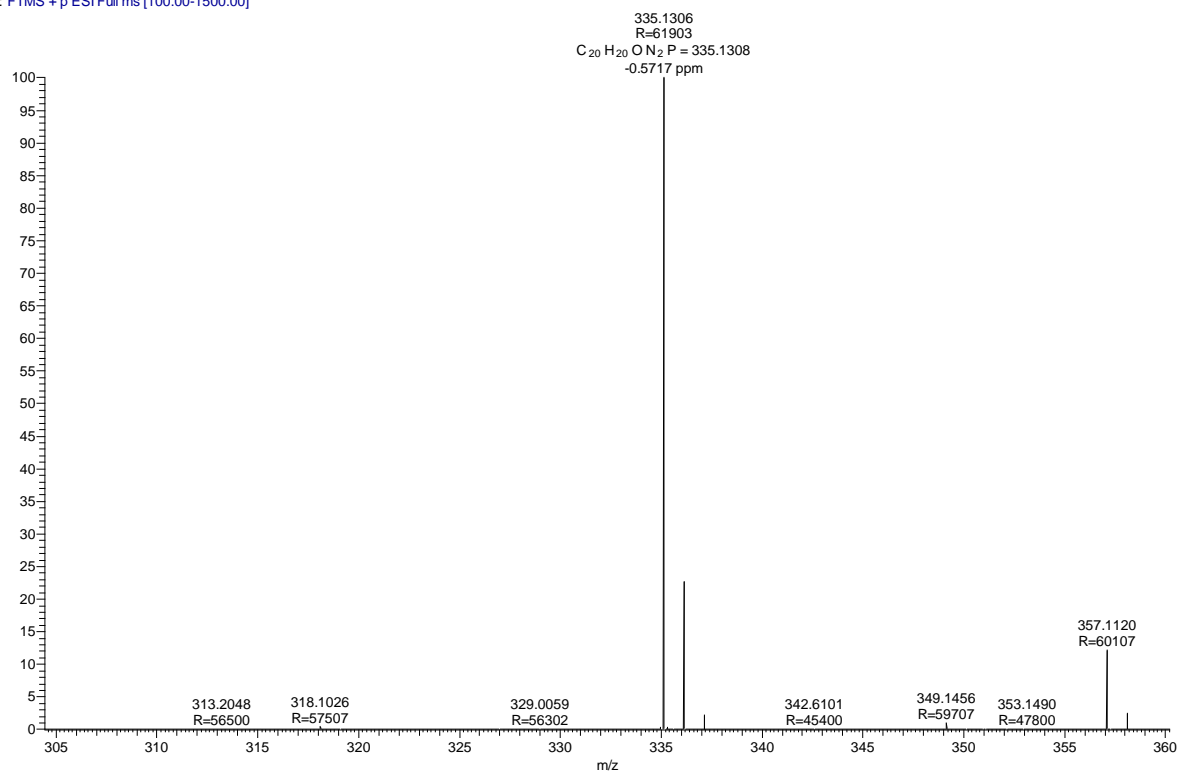
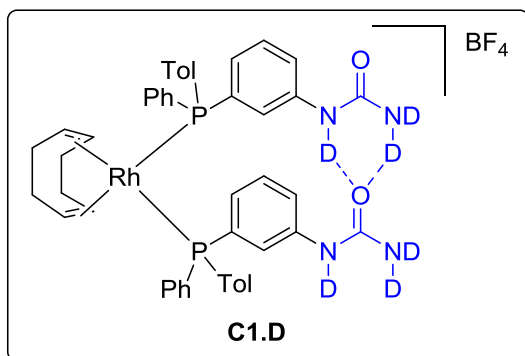


Fig. S11. ESIMS (+ve mode) spectrum of **L1.D**.

4. Synthesis of deuterated self-assembled Rh-complex (**C1.D**)



In a vacuum dried Schlenk flask $[\text{Rh}(\text{COD})_2\text{BF}_4]$ (1 eqv., 0.0985 mmol) and phosphine ligand **L1.D** (2 eq., 0.1974 mmol) was taken inside the glove box. The above mixture was dissolved in 8 ml DCM and reaction content was stirred for 2 hours at room temperature. After completion of

reaction, the reaction content was evaporated and concentrated to 2 ml. 20 ml diethyl ether was added to above content to obtain yellow coloured precipitate. The resultant solid was separated by cannula filtration, washed with diethyl ether (10 ml x 3 ml) and dried under vacuum. The resultant residue was identified as **C1.D** after complete characterization (see fig. ESI S12-S16).

^2H NMR (500 MHz, THF- d_8 , 298 K) δ = 8.29 (s, ND), 5.55 (s, ND2). ^1H NMR (400 MHz, CDCl_3 , 298 K) δ = 8.23-6.00 (m 26H, Ar), 5.75-4.95 (m, 5H, CH), 2.90-2.14 (m, 8H, CH_2), 2.14 (m, 6H, CH_3). ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ = 157.3 (s, CO), 156.8 (s, CO), 142.8 (s, Ar), 141.7 (s, Ar), 140.1 (s, Ar), 139.6 (s, Ar), 132.6 (s,

Ar), 132.2 (s, Ar), 131.7 (s, Ar), 131.6 (s, Ar), 130.5 (s, Ar), 130.0 (s, Ar), 128.6 (s, Ar), 126.0 (s, Ar), 125.6 (s, Ar), 125.4 (s, Ar), 123.0 (s, Ar), 121.6 (s, Ar), 118.7 (s, CH), 104.4 (s, CH), 65.7 (s, CH₂), 47.2 (s, CH₂), 32.6 (s, CH₂), 27.9 (s, CH₂), 23.5 (s, CH₃), 21.5 (s, CH₃). **ESI-MS** (+ve) (For M = C₄₈H₅₀N₄O₂P₂Rh) m/z = 879.24 [M]⁺.

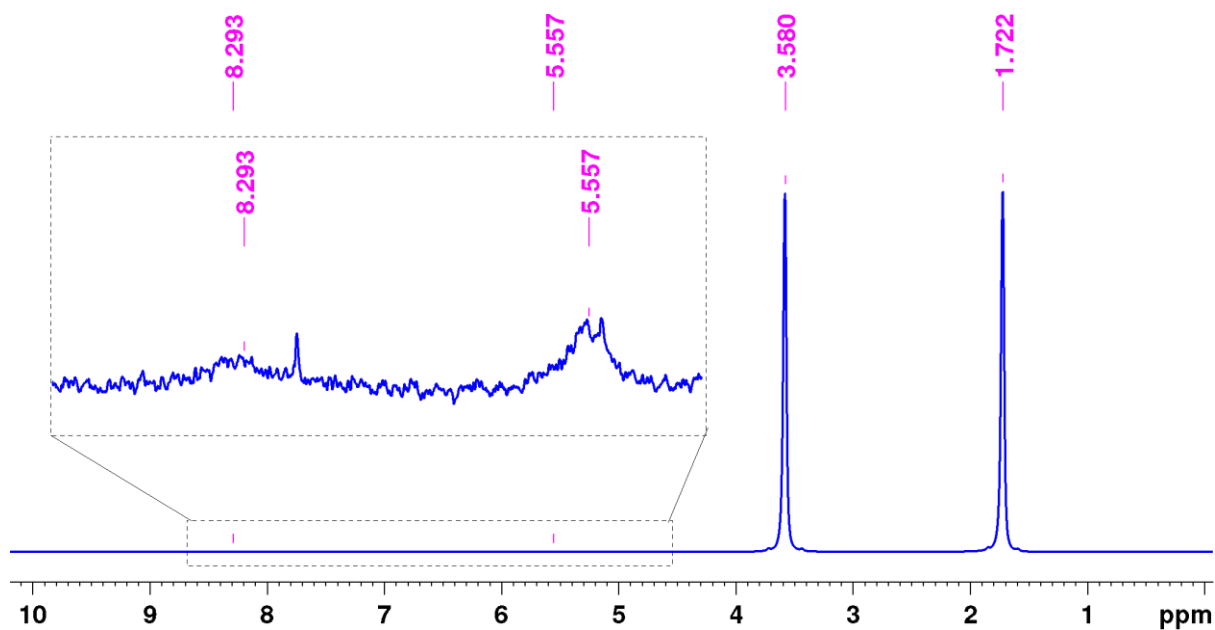


Fig. S12. ²H NMR spectrum of **C1.D** in THF-D₈:THF (0.1:0.4 ml) solvent.

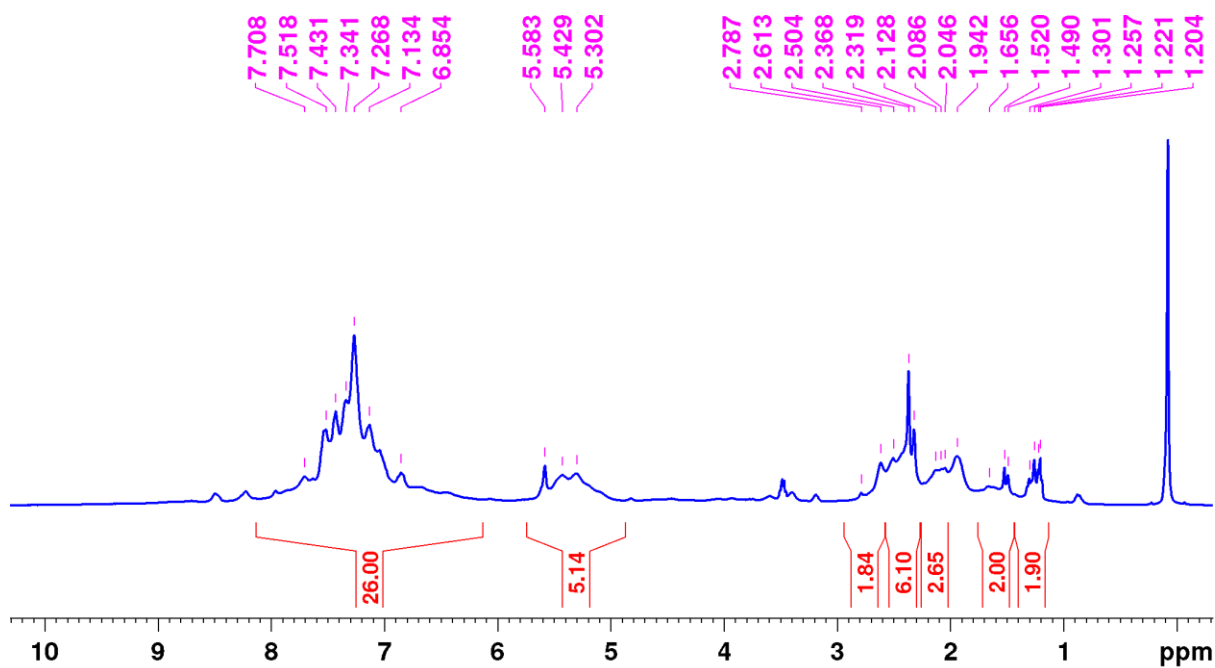


Fig. S13. ¹H NMR spectrum of **C1.D** in CDCl₃.

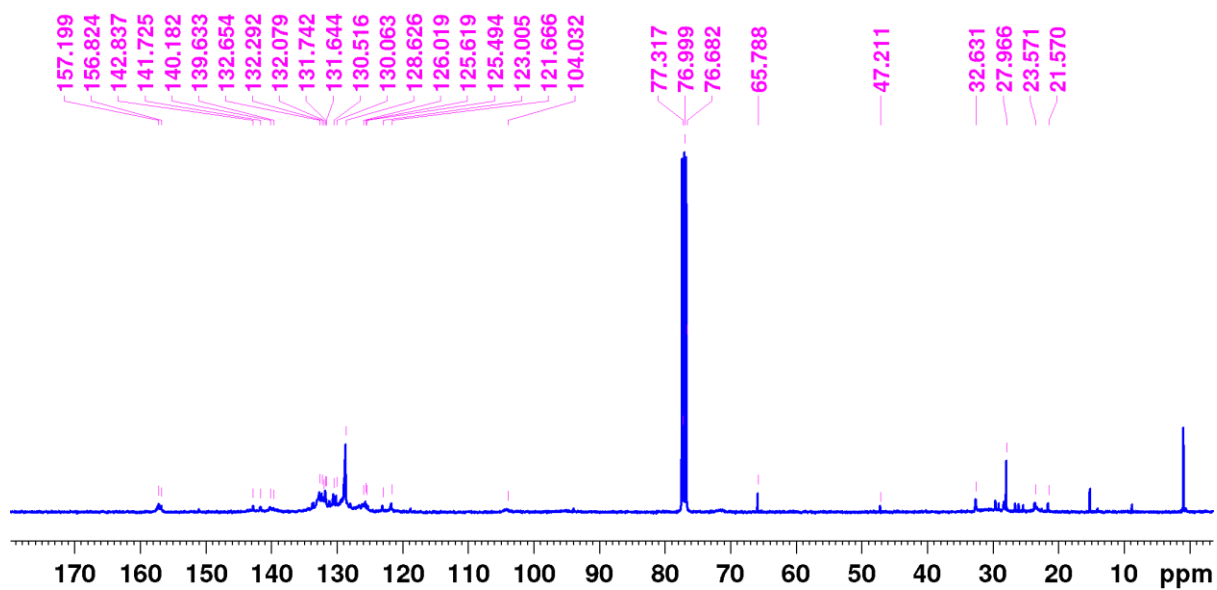


Fig. S14. ¹³C NMR spectrum of **C1.D** in CDCl₃.

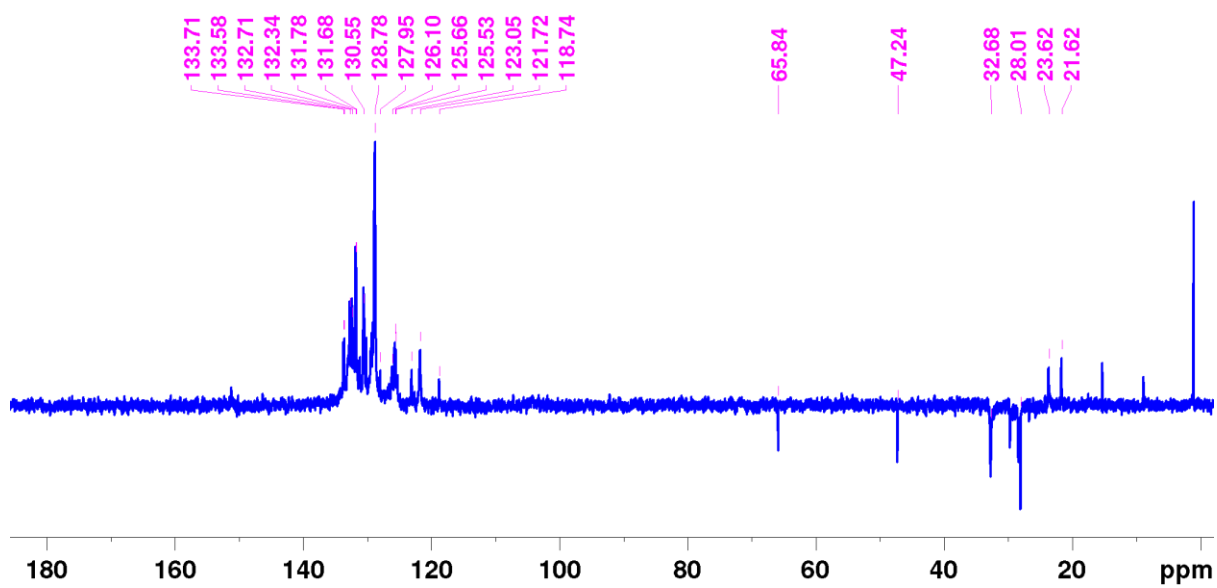


Fig. S15. ¹³C NMR (DEPT) spectrum of **C1.D** in CDCl₃.

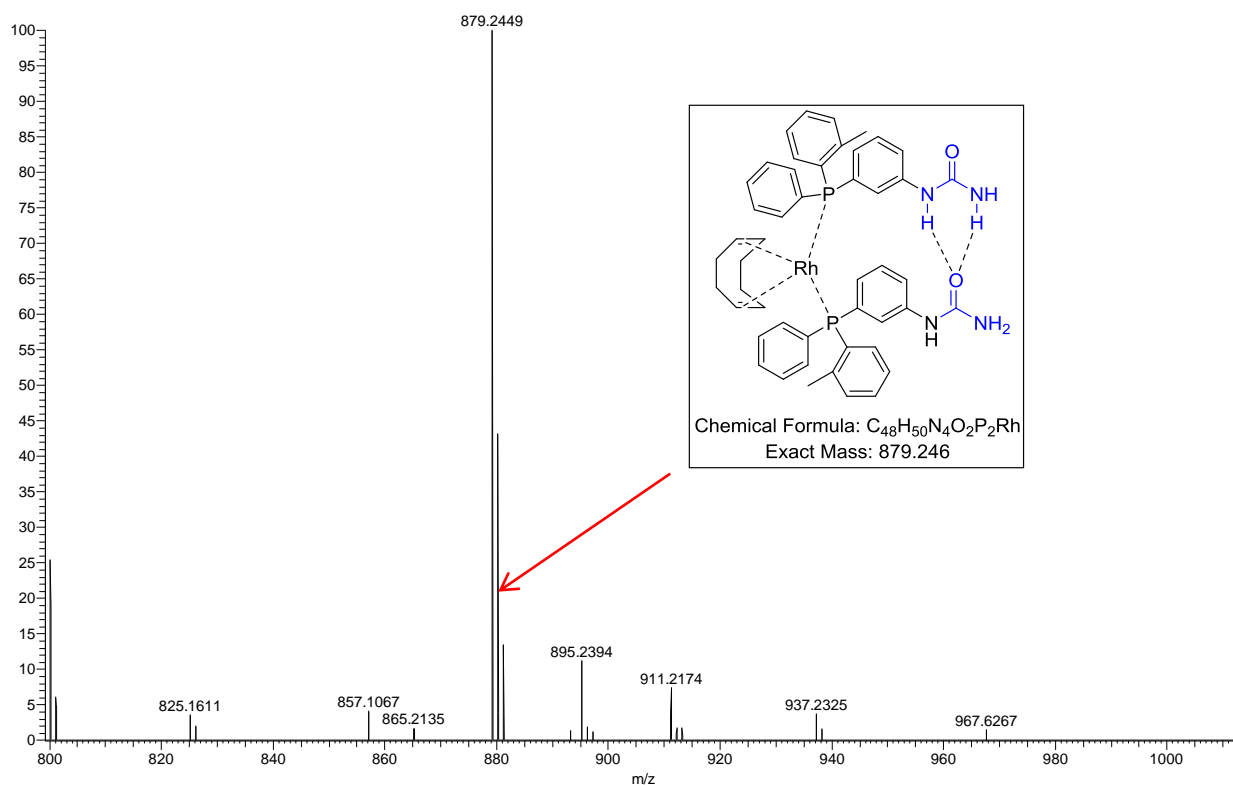
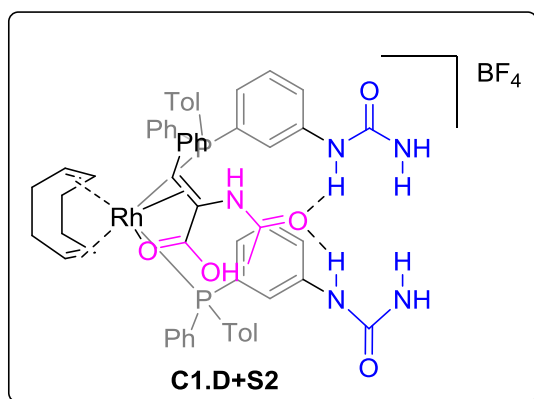


Fig. S16. ESIMS (+ve mode) spectrum of **C1.D**.

5. Stoichiometric study of self-assembled Rh-complex and **S2**



In the NMR tube **C1** 0.0048 g, 0.005 mmol was dissolved in CD_3CN to make 10 mM solution. The NH_2 proton chemical shift was confirmed by 1H NMR (ESI S17). In the same NMR tube **S2** 0.010 g, 0.005 mmol was added and 1H NMR was measured (see in ESI S18). Similar experiment was done with deuterium labeled self-assembled Rh-

complex (**C1.D**) and **S2**, and 2H NMR was recorded in THF- d_3 :THF (0.1:0.4 ml) solvent. For this experiment deuterium labeled self-assembled Rh-complex **C1.D** (0.0048 g, 0.005 mmol) was dissolved in THF- d_3 :THF (0.1:0.4 ml) to prepare 10 mM solution and 2H NMR was measured to confirm the chemical shift of ND and ND₂. After that **S2** (0.010 g, 0.005 mmol) was added in the same NMR tube and 2H NMR was recorded (see in ESI S17-S21).

^2H NMR (500 MHz, THF- d_8 , 298 K) δ = 8.45 (s, ND), 5.61 (s, ND_2). ^1H NMR (400 MHz, CD_3CN , 298 K) δ = 7.81-7.10 (m, 33H, Ar and NH), 5.10-4.10 (m, 9H, CH and NH_2), 2.41 (m, 4H, CH_2), 2.12 (m, 9H, CH_3), 1.53 (m, 2H, CH_2), 1.27 (m, 2H, CH_2). ESI-MS (+ve) (For $\text{C}_{59}\text{H}_{55}\text{D}_4\text{LiN}_5\text{NaO}_5\text{P}_2\text{Rh}$) m/z = 1116.24 $[\text{M}]^+$.

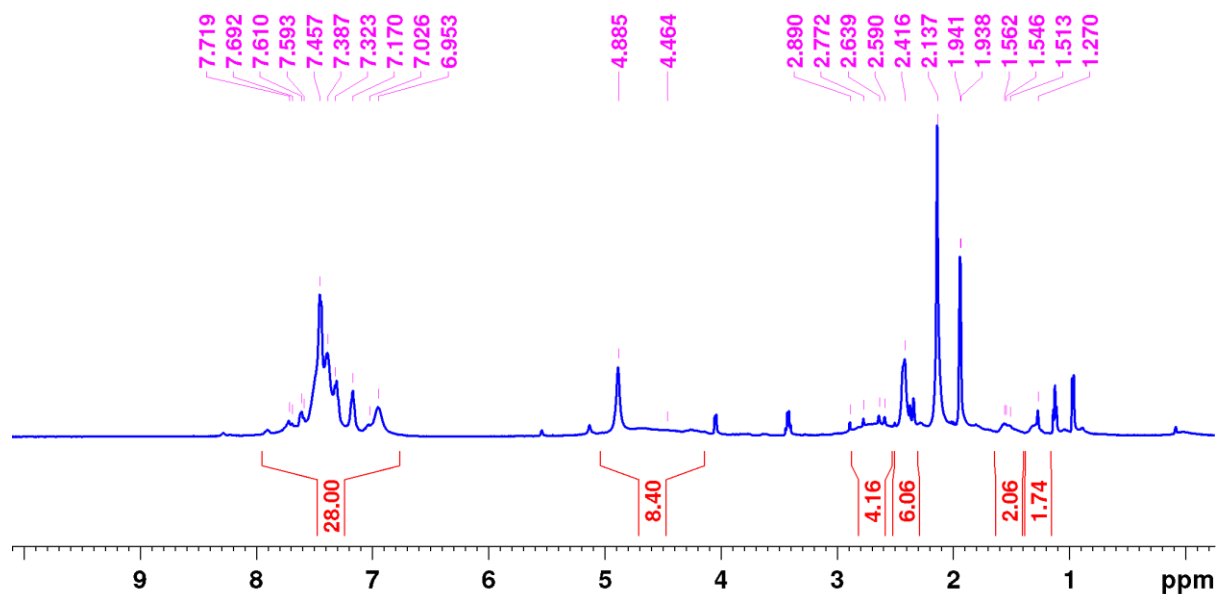


Fig. S17. ^1H NMR spectrum of **C1** in CD_3CN .

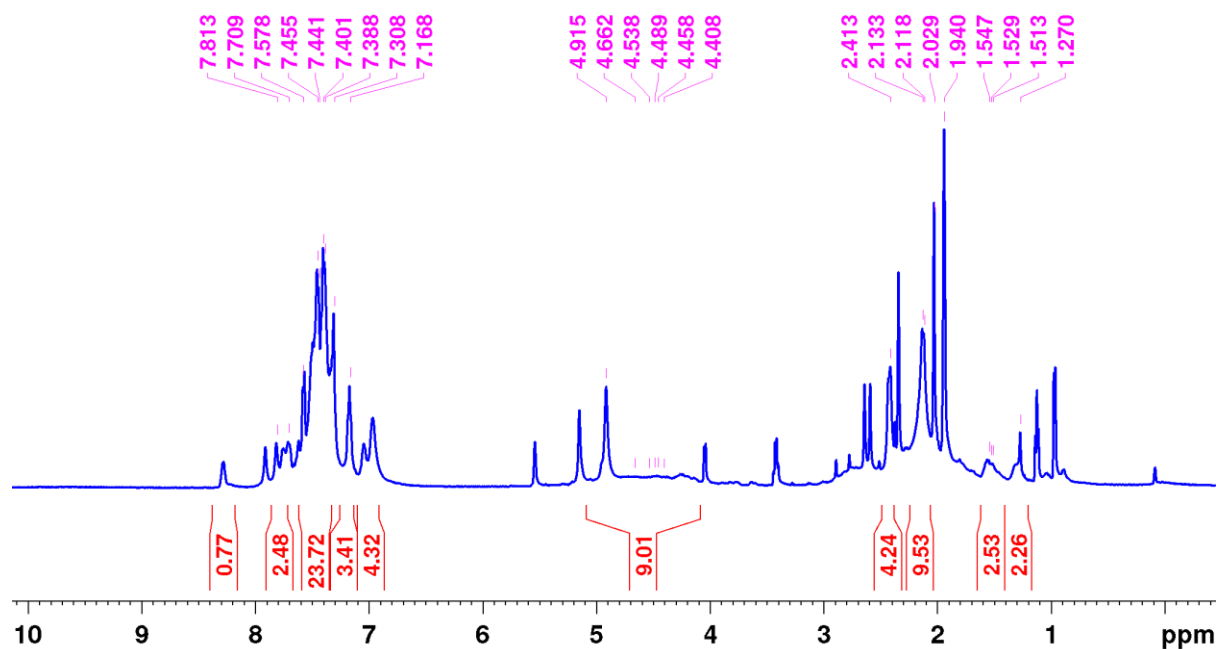


Fig. S18. ^1H NMR spectrum of self-assembled Rh-complex **C1+S2** in CD_3CN .

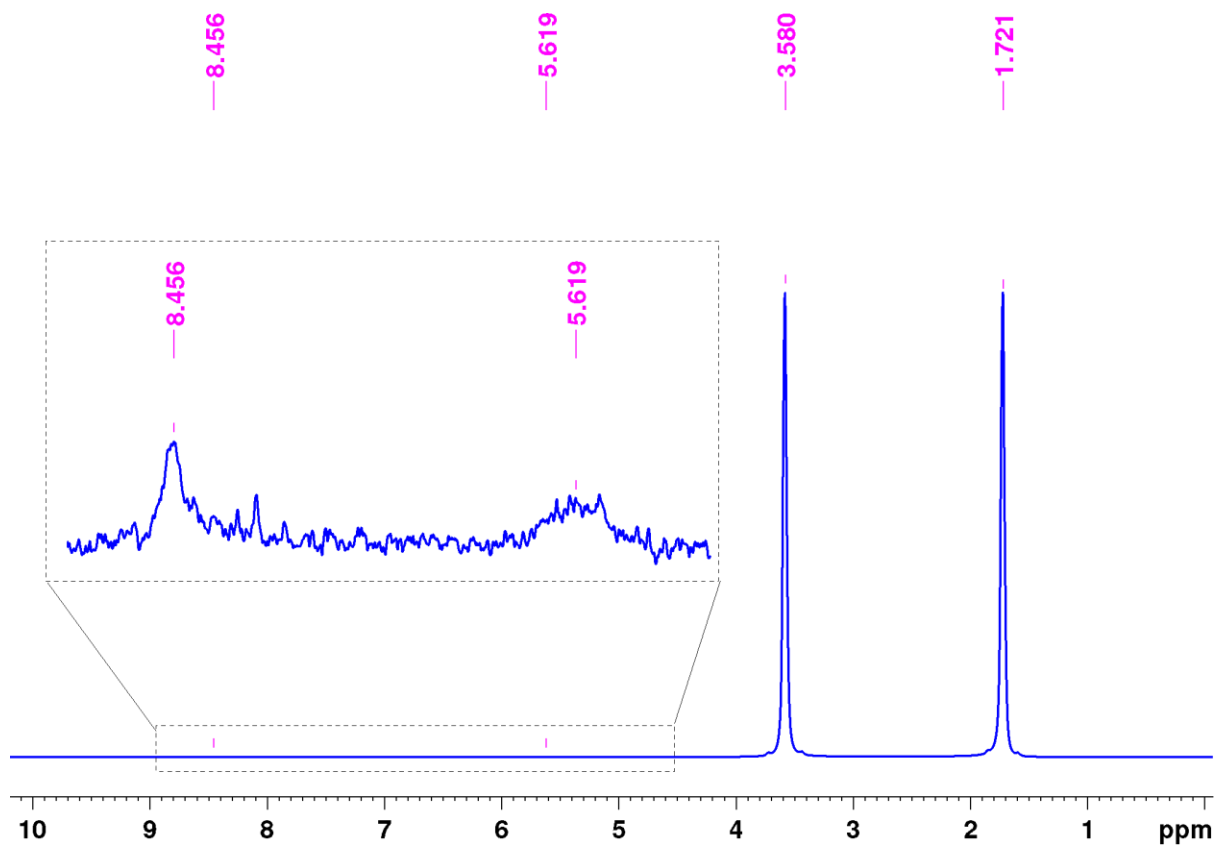


Fig. S19. ^2H NMR spectrum of **C1.D+S2** in $\text{THF-D}_8:\text{THF}$ (0.1:0.4 ml) solvent.

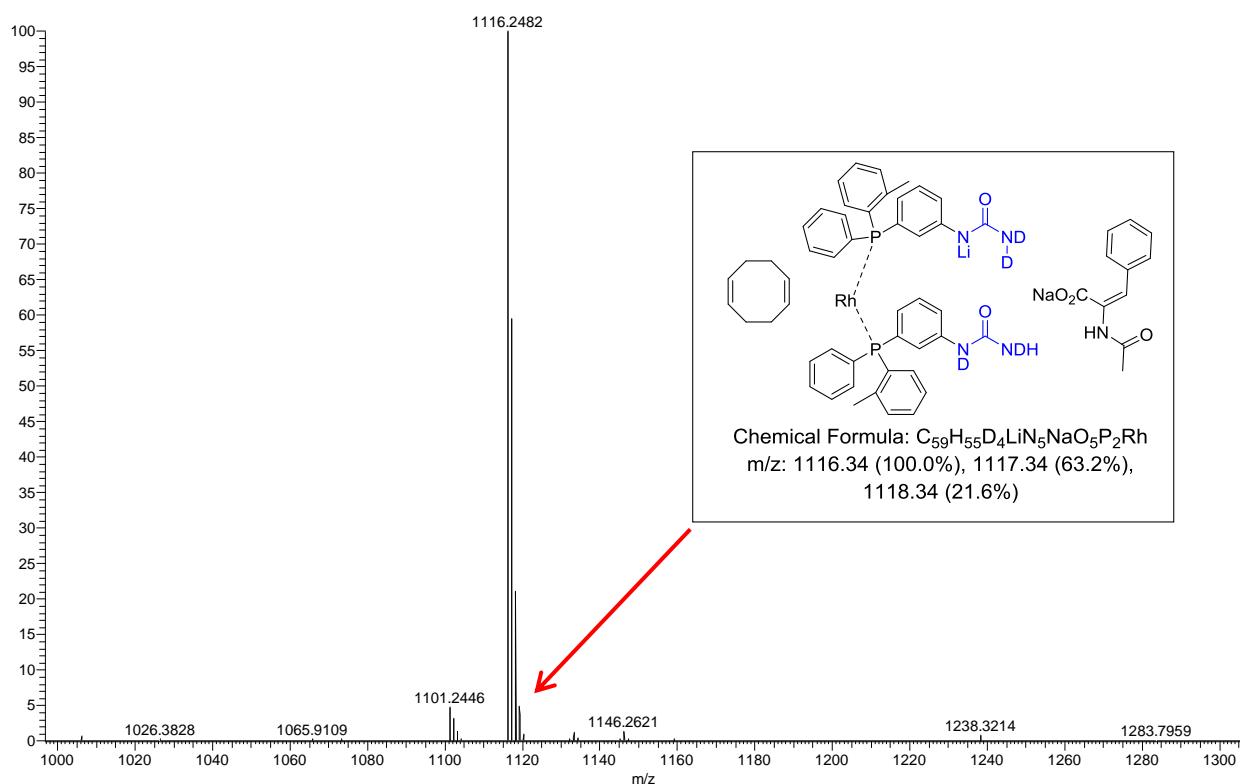


Fig. S20. ESI-MS (+ve mode) spectrum of C1.D+S2.

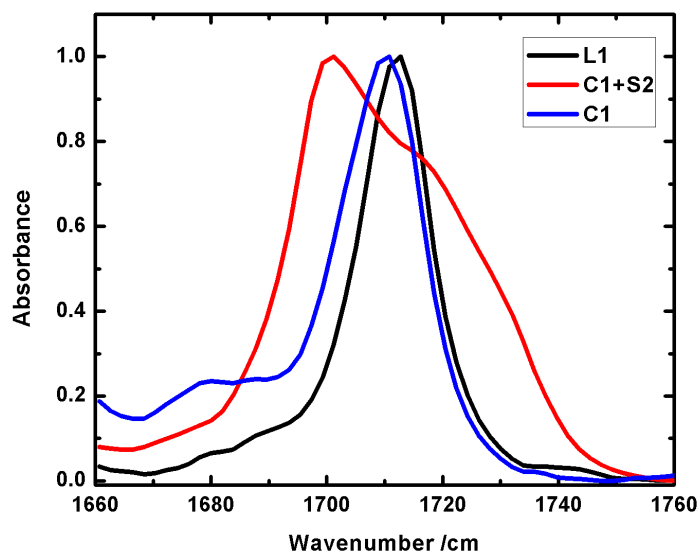
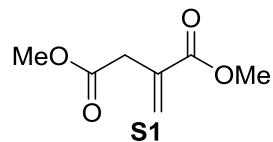
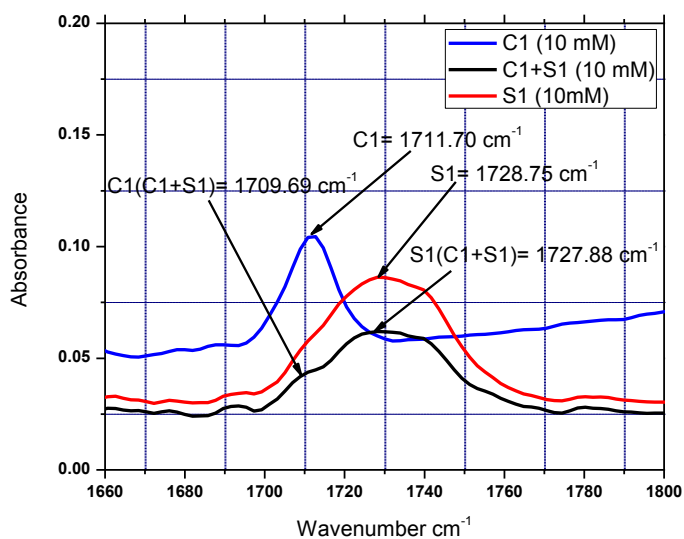


Fig. S21. Stacked IR spectra of ligand **L1** (black), self-assembled complex **C1** (blue) and complex **C1** + substrate **S2** (red).



22Fig. S22. IR spectrum of neat **C1**, neat **S1** and stoichiometric experiment of **C1+S1**.

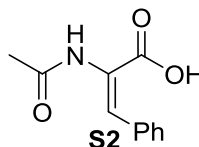
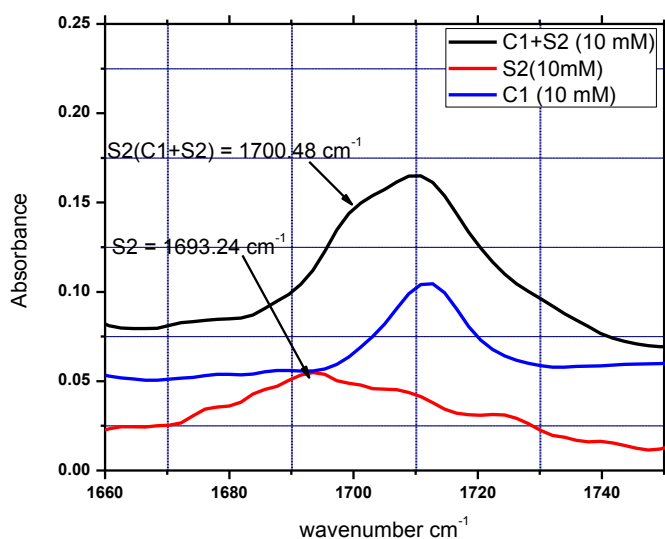


Fig. S23. IR spectrum of neat **C1**, neat **S2** and stoichiometric experiment of **C1+S2**.

6. References:

- 1) D. D. Perrin, W. L. Armarego, L. F. Willfred, Purification of Laboratory Chemicals, Pergamon, Oxford, 1988.
- 2) V. S. Koshti, N. R. Mote, S. Chikkali, *Organometallics*, 2015, **34**, 4802.