Supporting Information
For the Manuscript

Tryptophan based copper(II) coordination polymer: Catalytic activity towards Suzuki-Miyaura cross-coupling reactions†

Ahmad Husain,[a*] Pooja Rani,[b] Kuldeep Kaur Nar,[a] Amit Pratap Singh,[c] Rakesh Kumar,[d] K. K. Bhasin,[b] Girijesh Kumar[b*]

[a]*Department of Chemistry, DAV University, Jalandhar-144012, Punjab, India. [E-mail: Ahmad Husain: ahmad.husain@outlook.com]*
[b]*Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University Chandigarh, Chandigarh, India. [E-mail: gkumar@pu.ac.in]*
[c]*Department of Applied Sciences, National Institute of Technology, New Delhi-110040, India.*
[d] *Department of Chemistry, MCM DAV College, Kangra -176001, Himachal Pradesh, India.*

Table of content

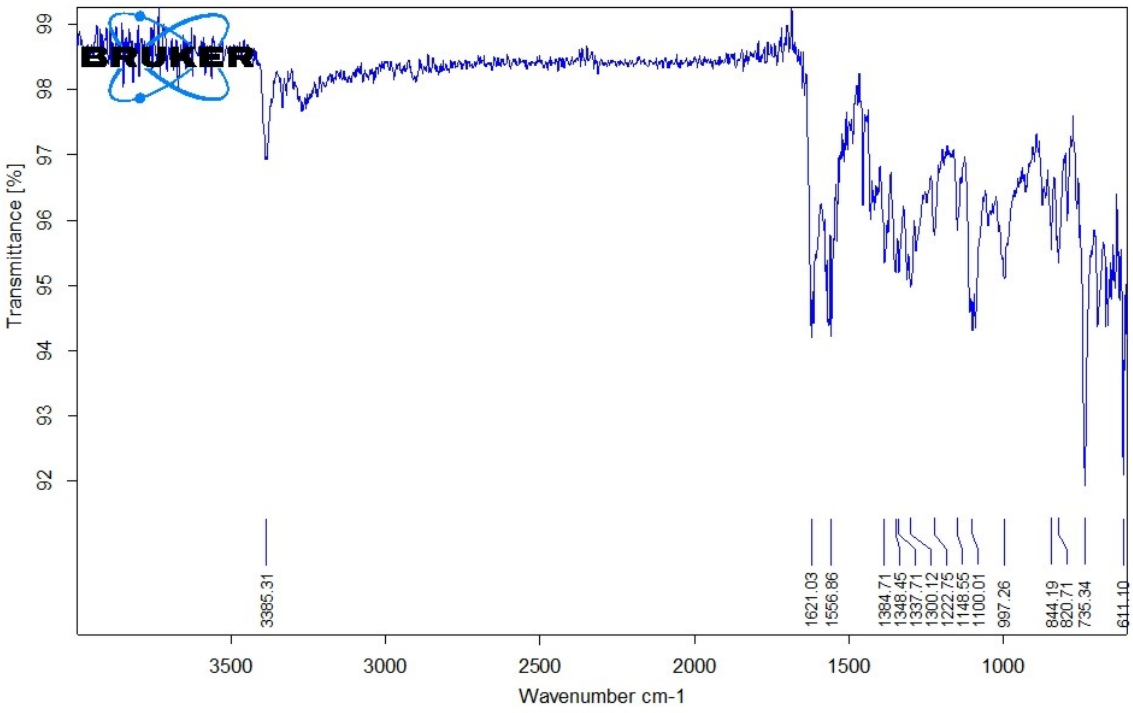
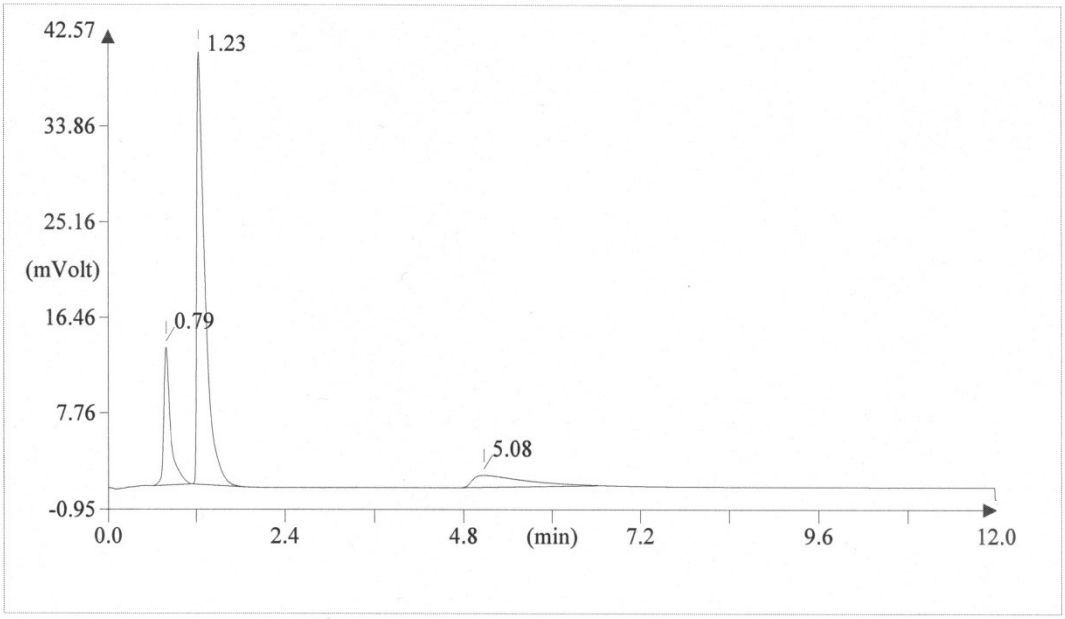


Fig. S1. IR spectrum of **CP1**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KK8 (# 82)
Analysis type:	UnkNown
Chromatogram filename:	UNK-03072018-12.dat
Sample weight:	1215



Element Name	Element %	Ret. Time
Nitrogen	15. 86	0. 79
Carbon	43. 75	1. 23
Hydrogen	3. 61	5. 08

Fig. S2. CHN data for **CP1**.

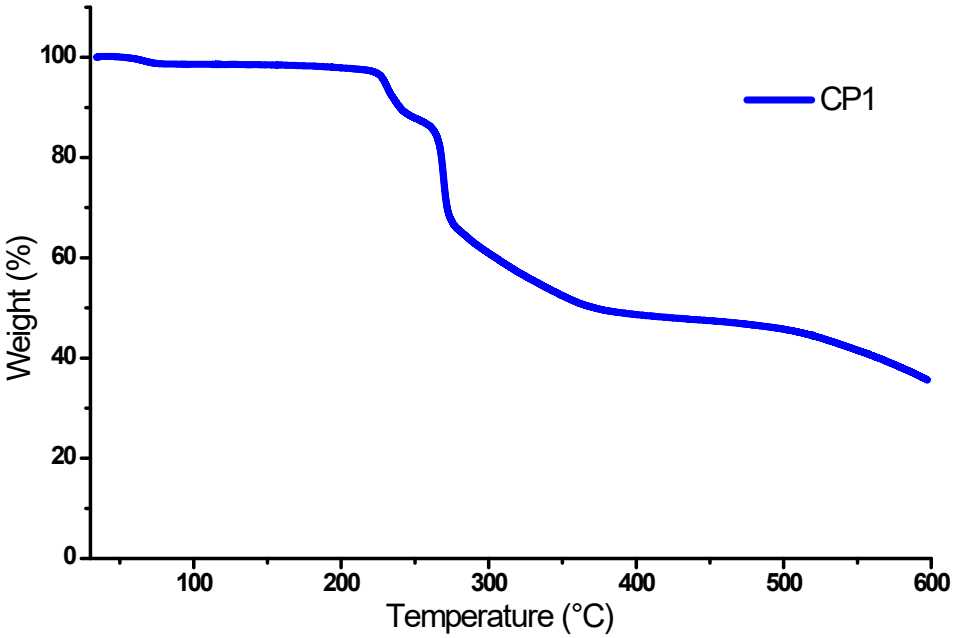


Fig. S3. TGA plot for **CP1**.

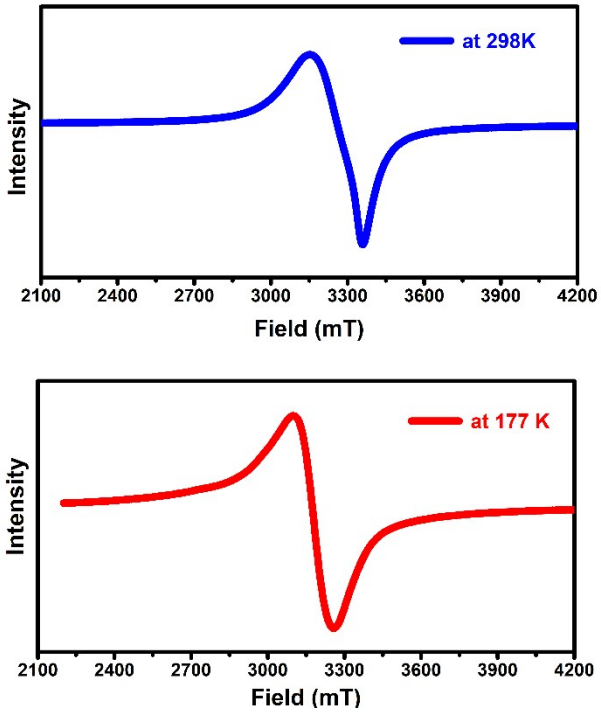


Fig. S4. X-band EPR spectrum of $[Cu(L\text{-}tryp)(azpy)_{1/2}(H_2O)(NO_3)]_{\infty}$ (**CP1**) at 298 K and at 177 K.

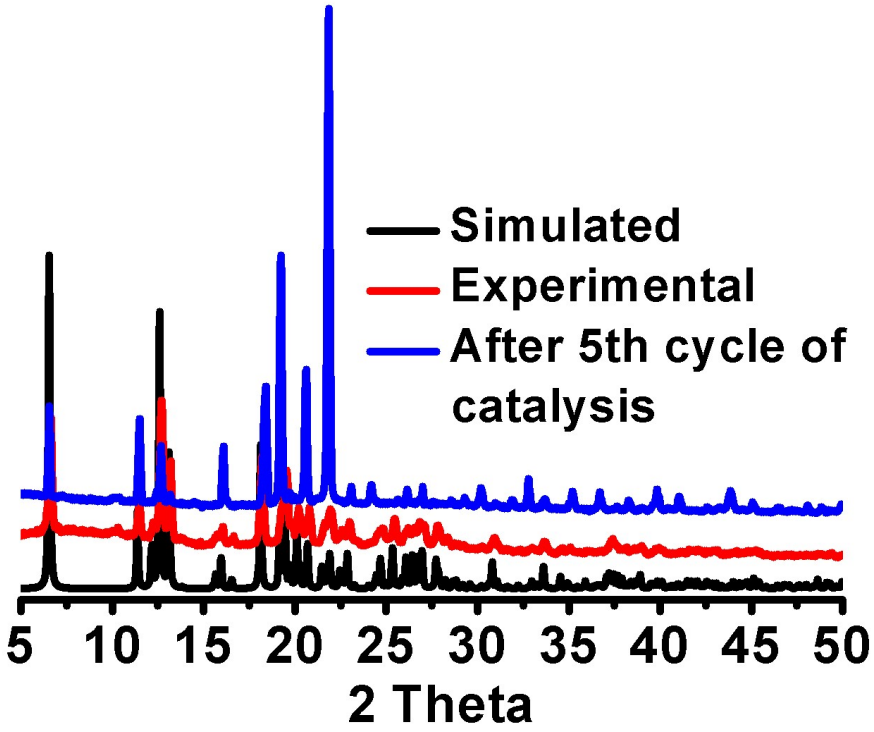


Fig. S5. PXRD pattern for coordination polymer **CP1**, before (red trace) and after Suzuki-Miyaura cross coupling reaction of phenylboronic acid with Iodobenzene (blue trace) and their comparison with the simulated pattern obtained from the single crystal structure analysis of **CP1** (black trace) using Mercury 4.0.

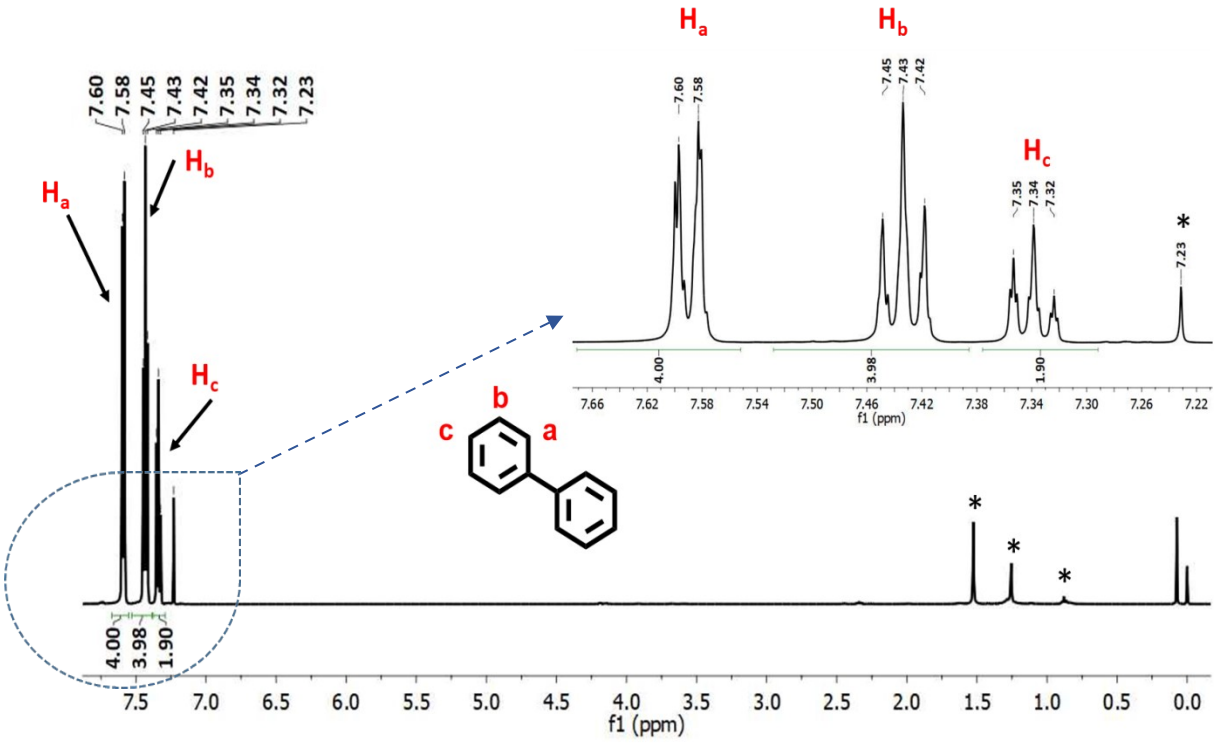


Fig. S6. ^{1}H NMR spectrum of biphenyl, a product of Suzuki coupling of benzeneboronic acid with Iodobenzene and bromobenzene using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 (dt, J = 8.1Hz, 1.6 Hz, 4H, H_a), 7.47 – 7.41 (m, 4H, H_b), 7.37 – 7.31 (m, 2H, H_c).

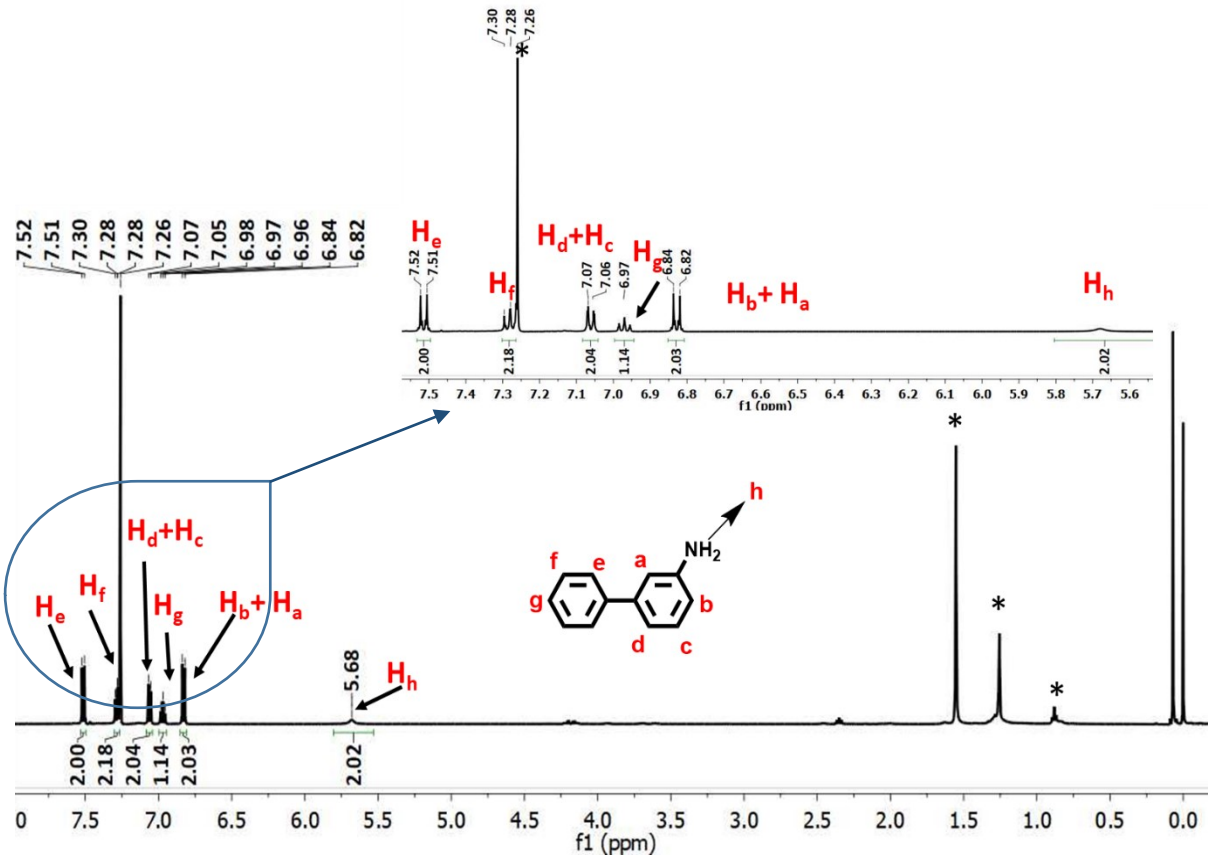


Fig. S7. ^{1}H NMR spectrum of [1,1'-biphenyl]-3-amine, a product of Suzuki coupling of benzeneboronic acid with 3-Iodoaniline using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 – 7.41 (m, 2H, H_e), 7.25 – 7.20 (m, 2H, H_f), 7.03 – 6.97 (m, 2H, H_d+H_c), 6.93 – 6.88 (m, 1H, H_g), 6.78 – 6.73 (m, 2H, H_b+H_a), 5.61 (s, 2H).

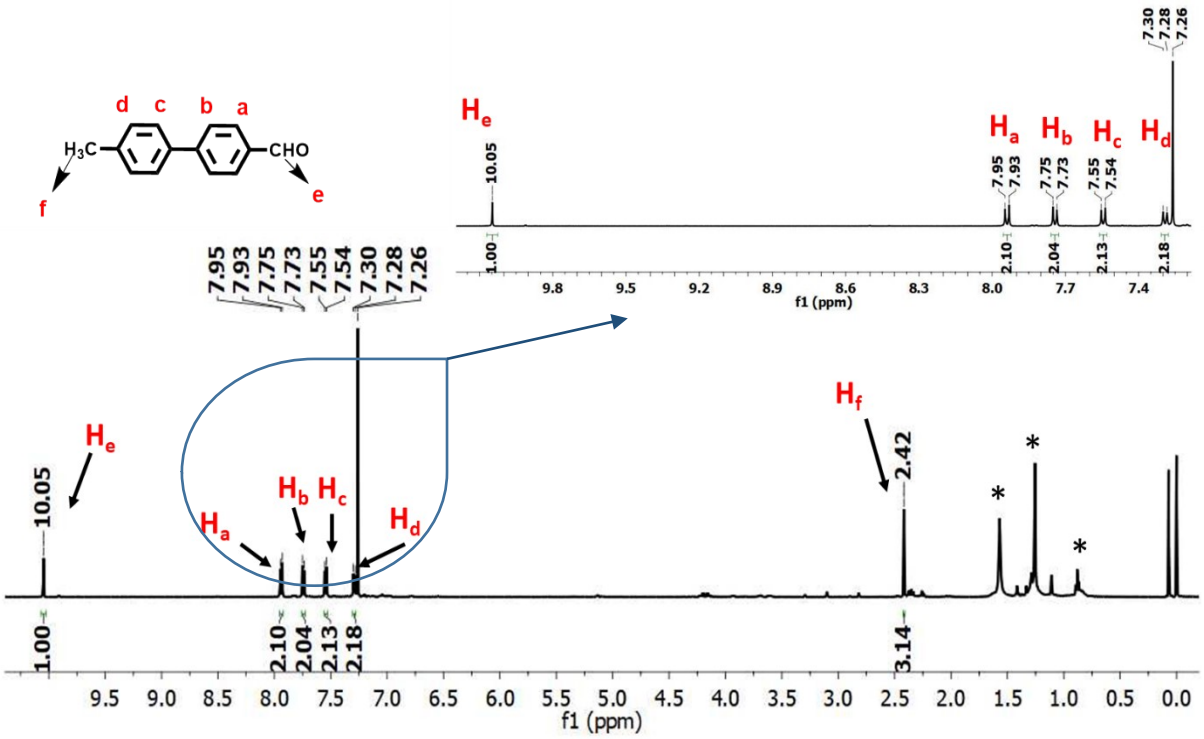


Fig. S8. ^{1}H NMR spectrum of 4'-methyl-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 4-Iodotoulene using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.05 (s, 1H, H_e), 7.94 (d, J = 8.4 Hz, 2H, H_a), 7.74 (d, J = 8.2 Hz, 2H, H_b), 7.54 (d, J = 8.2 Hz, 2H, H_c), 7.29 (d, J = 7.9 Hz, 2H, H_d), 2.42 (s, 3H, H_f).

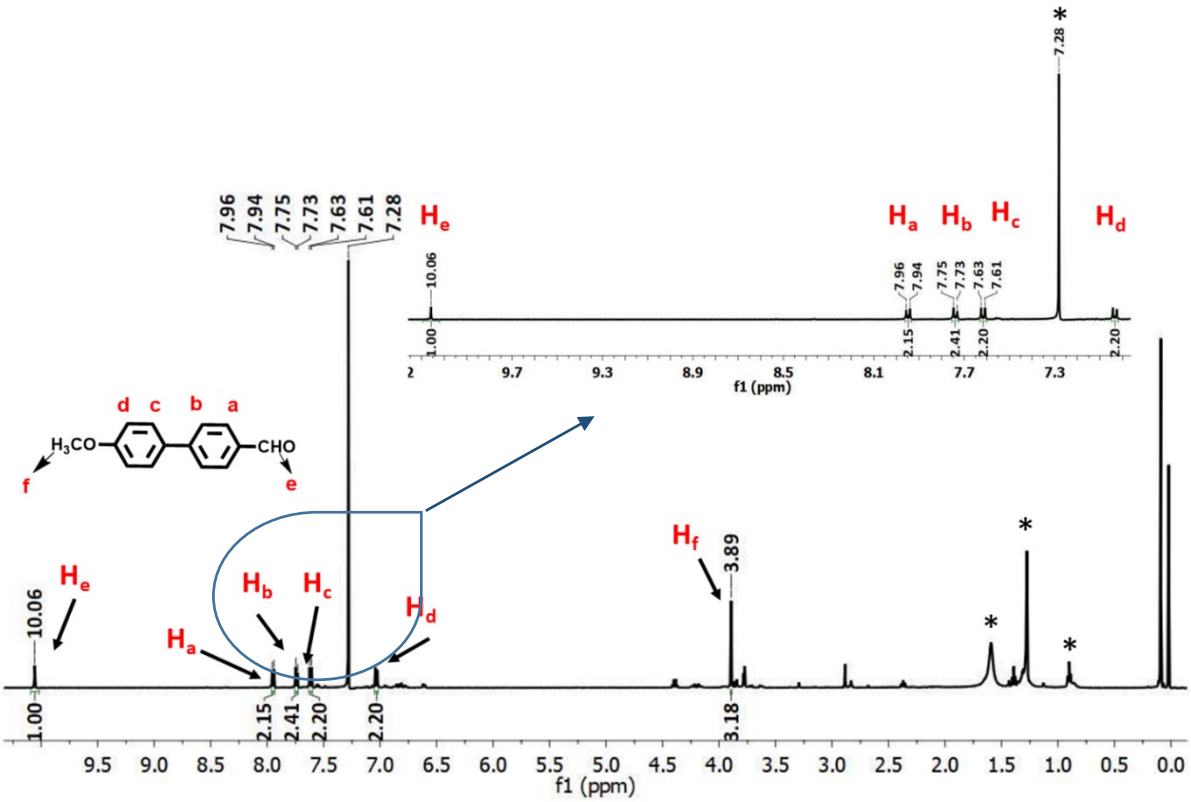


Fig. S9. ^{1}H NMR spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-Formylphenylboronic acid with 4-Iodoanisole using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.06 (s, 1H, H_e), 7.95 (d, J = 8.4 Hz, 2H, H_a), 7.74 (d, J = 8.2 Hz, 2H, H_b), 7.62 (d, J = 8.8 Hz, 2H, H_c), 7.08 – 6.99 (m, 3H, H_d), 3.89 (s, 3H, H_f).

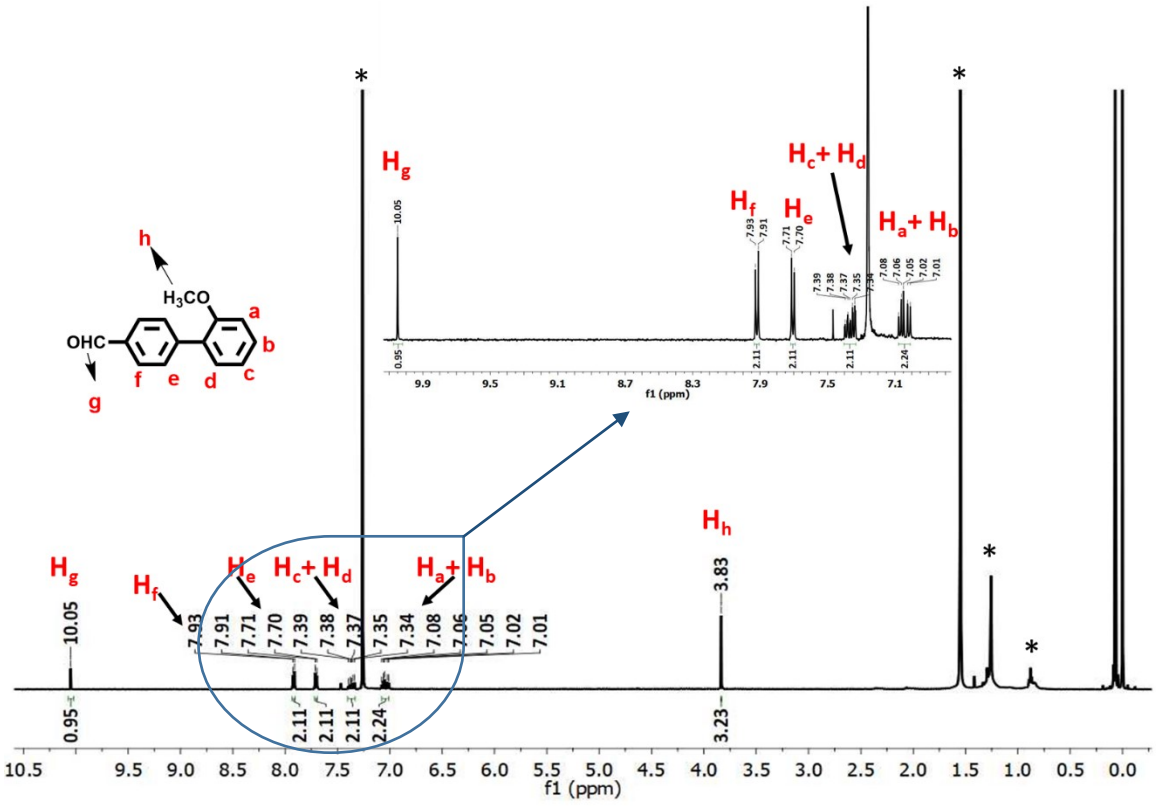


Fig. S10. ^{1}H NMR spectrum of 2'-methoxy-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 2-Iodoanisole using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H, H_g), 7.92 (d, J = 8.4 Hz, 2H, H_f), 7.71 (d, J = 8.2 Hz, 2H, H_e), 7.41 – 7.30 (m, 2H, H_c+H_d), 7.12 – 6.97 (m, 2H, H_a+H_b), 3.83 (s, 3H, H_h).

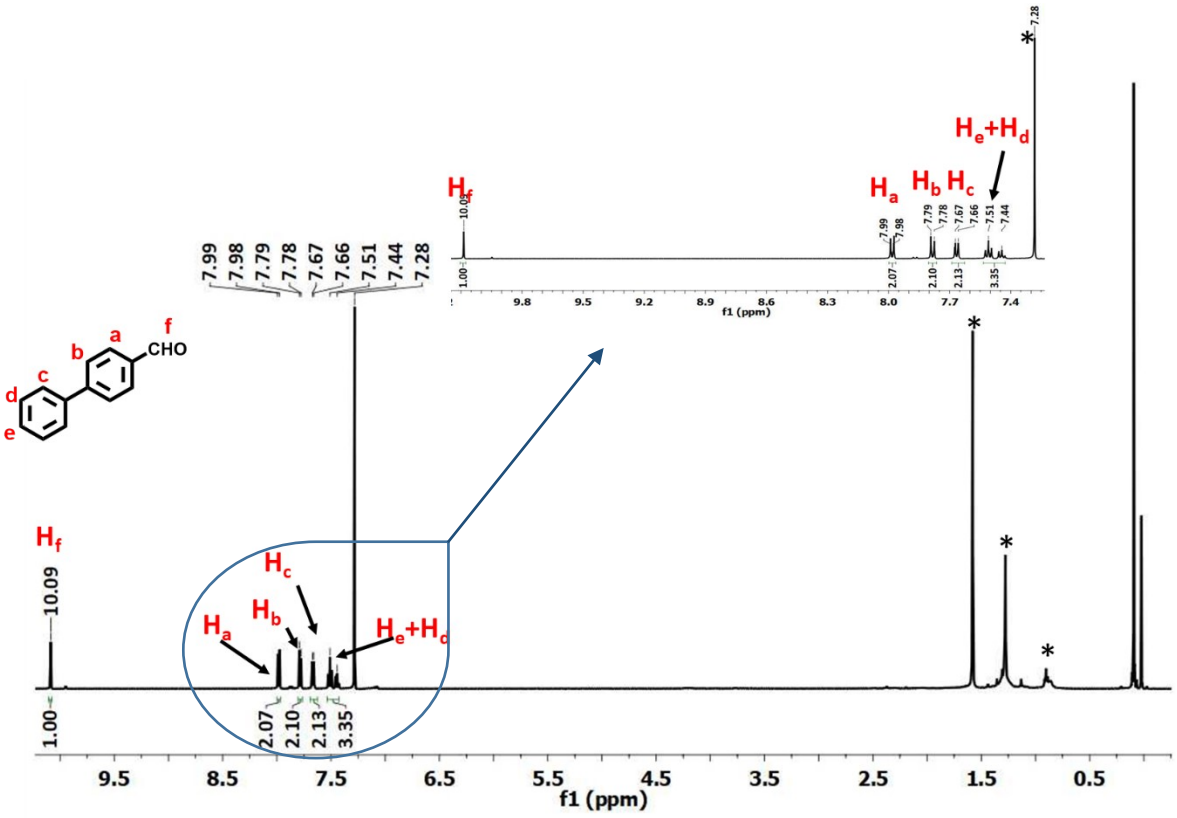


Fig. S11. ^{1}H NMR spectrum of [1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with Iodobenzene and bromobenzene using **CP1** as catalyst in $CDCl_3$. *Represents the solvent residual peak.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.09 (s, 1H, H_f), 7.99 (d, J = 8.1 Hz, 2H, H_a), 7.78 (d, J = 8.2 Hz, 2H, H_b), 7.67 (d, J = 7.0 Hz, 2H, H_c), 7.48 (m, 3H, H_d+H_e).

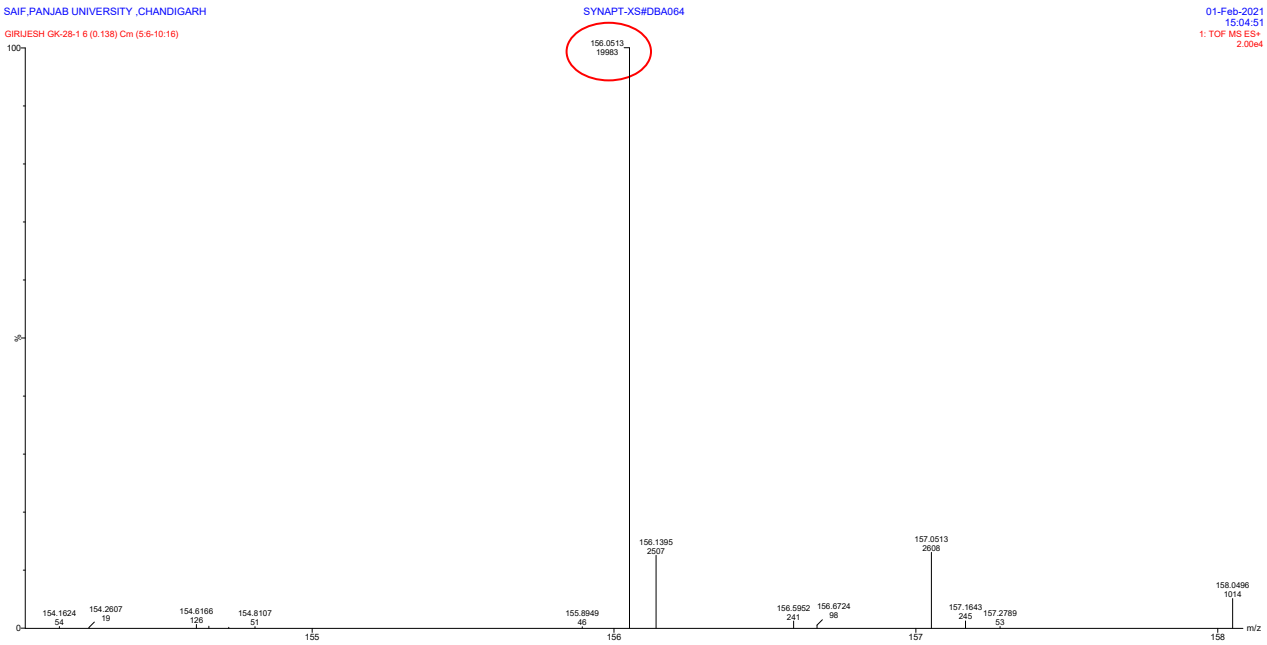


Fig. S12. HR mass spectrum of biphenyl, a product of Suzuki coupling of benzeneboronic acid with Iodobenzene and bromobenzene using **CP1** as catalyst. Calculated *m/z* is 154.0783, found *m/z* is [M+2] = 156.0513.

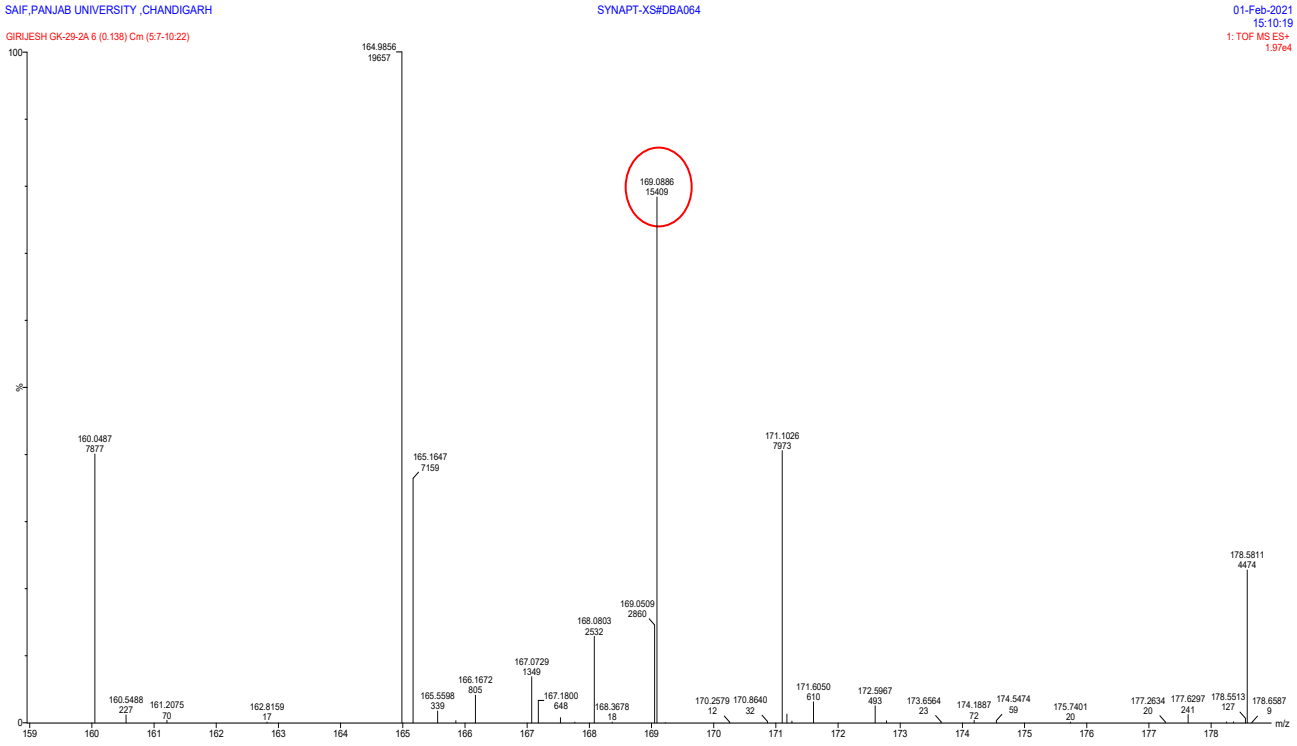


Fig. S13. HR mass spectrum of [1,1'-biphenyl]-3-amine, a product of Suzuki coupling of benzeneboronic acid with 3-Iodoaniline using **CP1** as catalyst. Calculated *m/z* is 169.0891, found *m/z* is 169.0886.

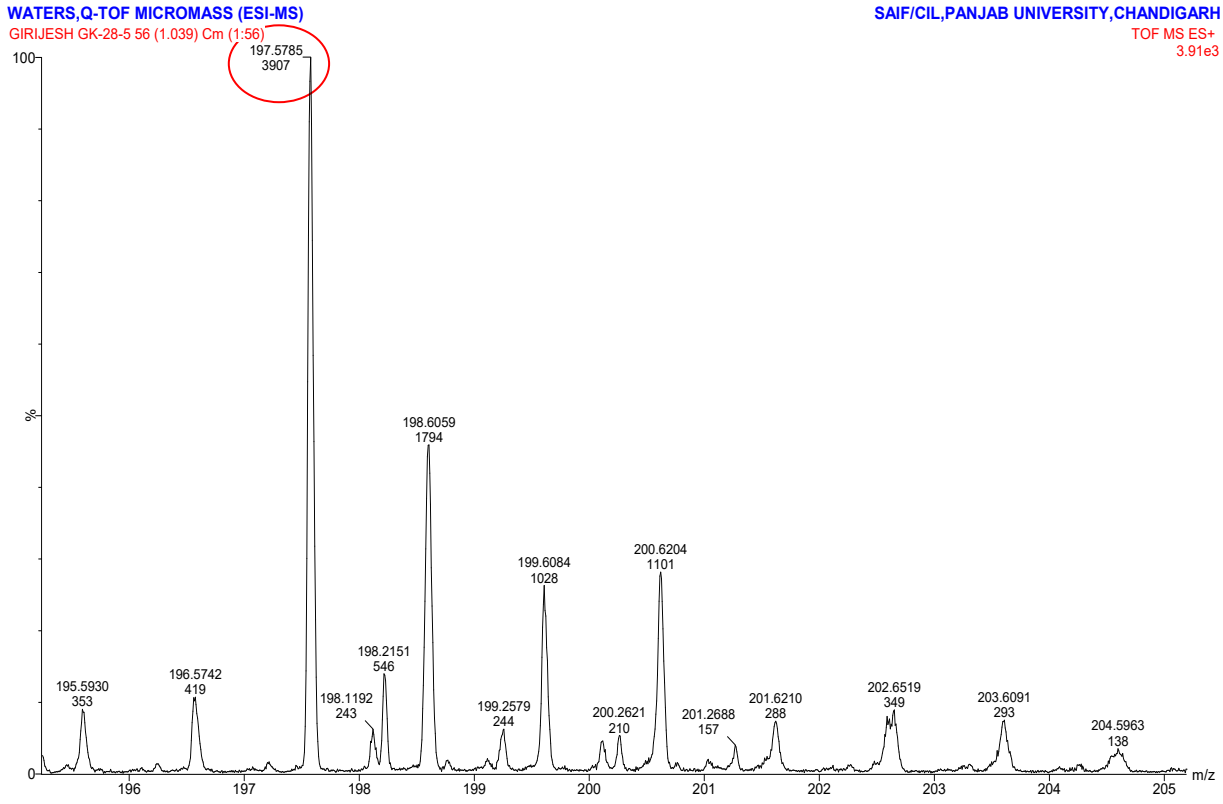


Fig. S14. HR mass spectrum of 4'-methyl-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 4-Iodotoulene using **CP1** as catalyst. Calculated *m/z* is 196.0888, found *m/z* is [M+1] = 197.5785.

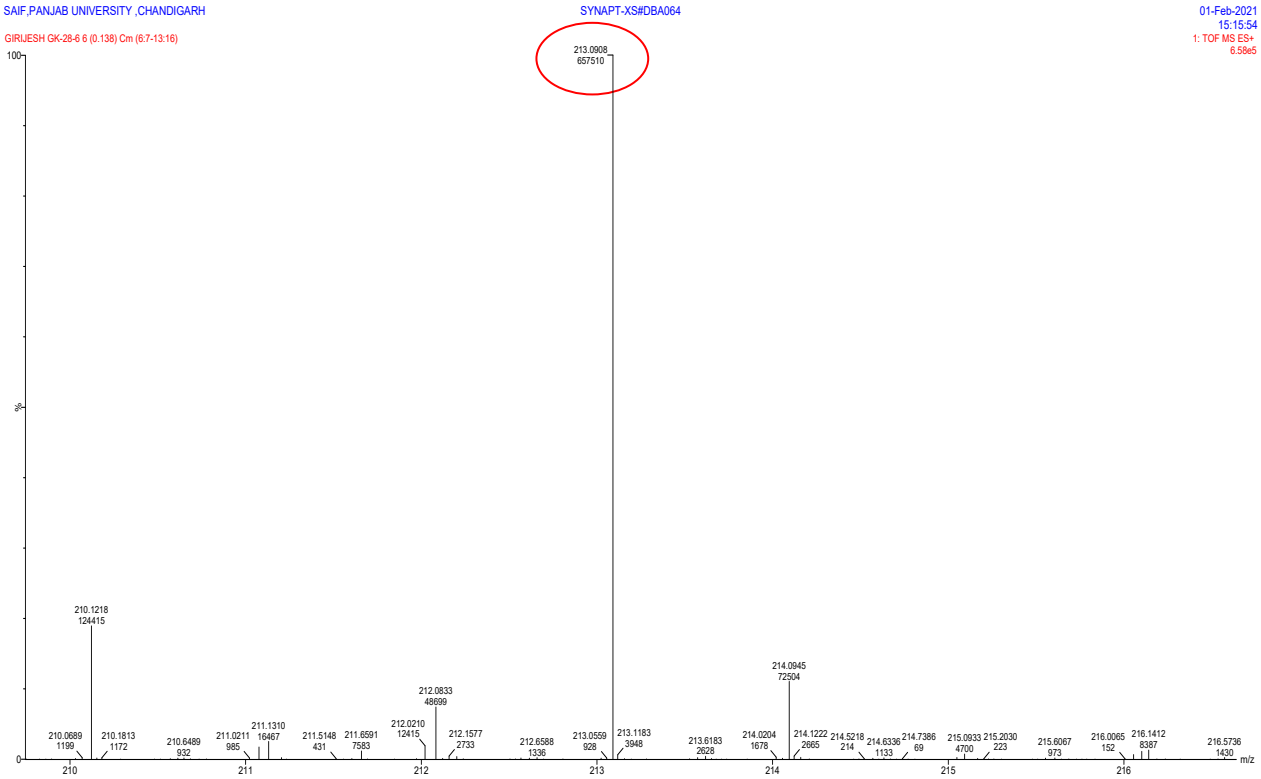


Fig. S15. HR mass spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 4-Iodoanisole using **CP1** as catalyst. Calculated *m/z* is 212.0837, found *m/z* is [M+1] = 213.0908.

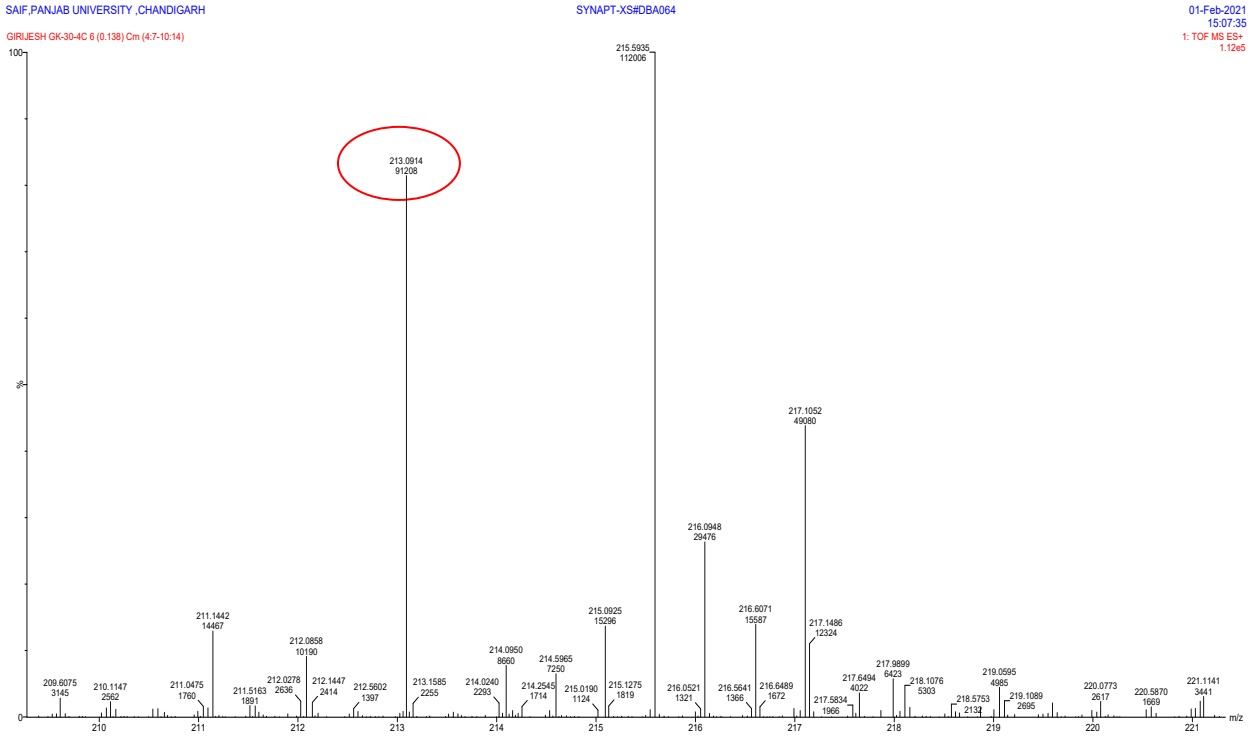


Fig. S16. HR mass spectrum of 2'-methoxy-[1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 2-Iodoanisole using **CP1** as catalyst. Calculated *m/z* is 212.0837, found *m/z* is [M+1] = 213.0914.

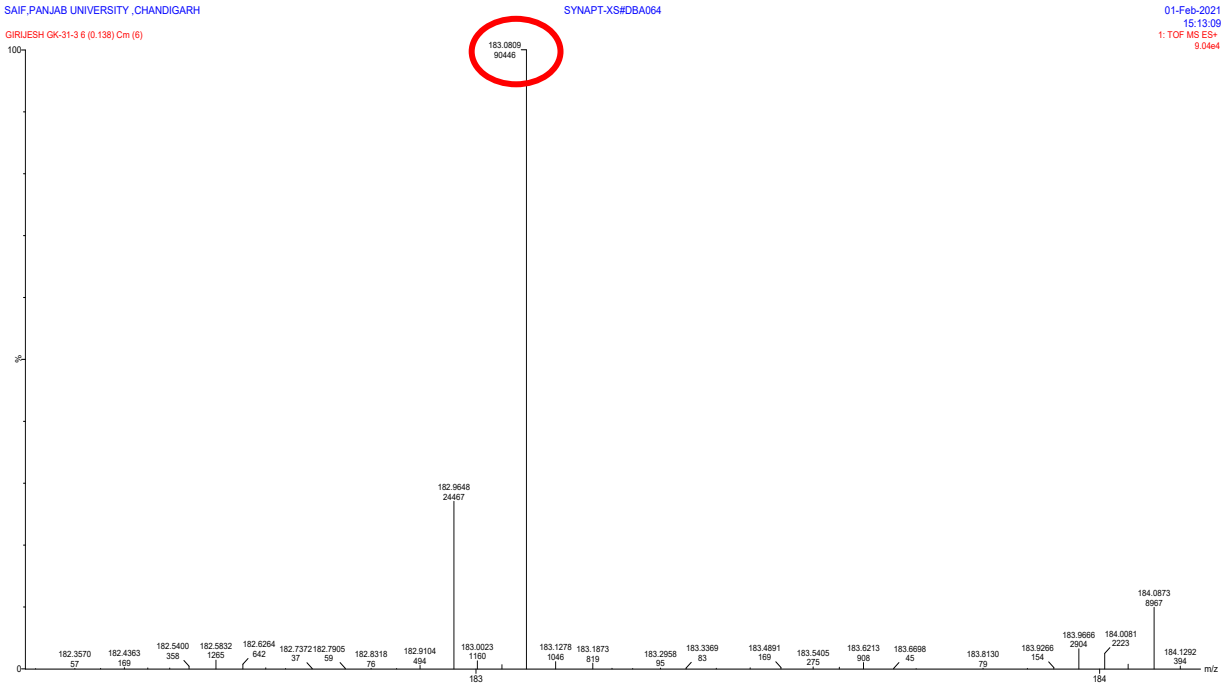


Fig. S17. HR mass spectrum of [1,1'-biphenyl]-4-carbaldehyde, a product of Suzuki coupling of 4-formylphenylboronic acid with 2-Iodoanisole using **CP1** as catalyst. Calculated *m/z* is 182.0732, found *m/z* is [M+1] = 183.0809.

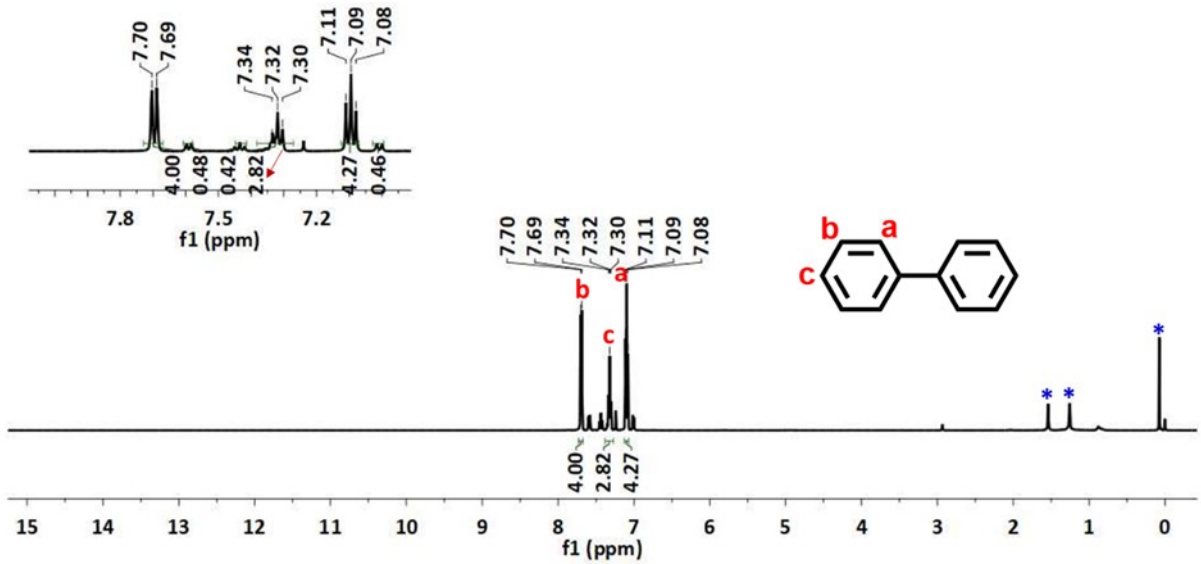


Fig. S18. ^{1}H NMR spectrum of supernatant solution recovered after the Suzuki-Miyaura cross-coupling reactions of iodobenzene and phenylboronic acid in $CDCl_3$ solvent (representative case). *Represents the solvent residual peaks. The traces seen in the spectrum are assigned to the unreacted substrate (i.e. iodobenzene) and phenyl boronic acid.

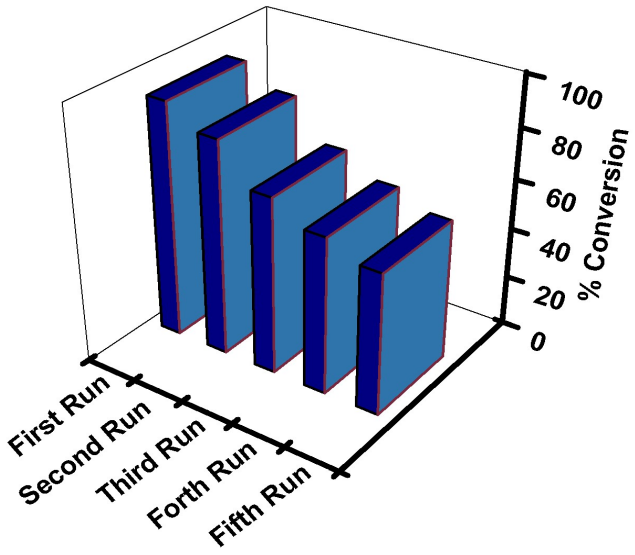


Fig. S19. Recyclability test of **CP1** for the cross-coupling reaction between iodobenzene and phenylboronic acid (representative case).

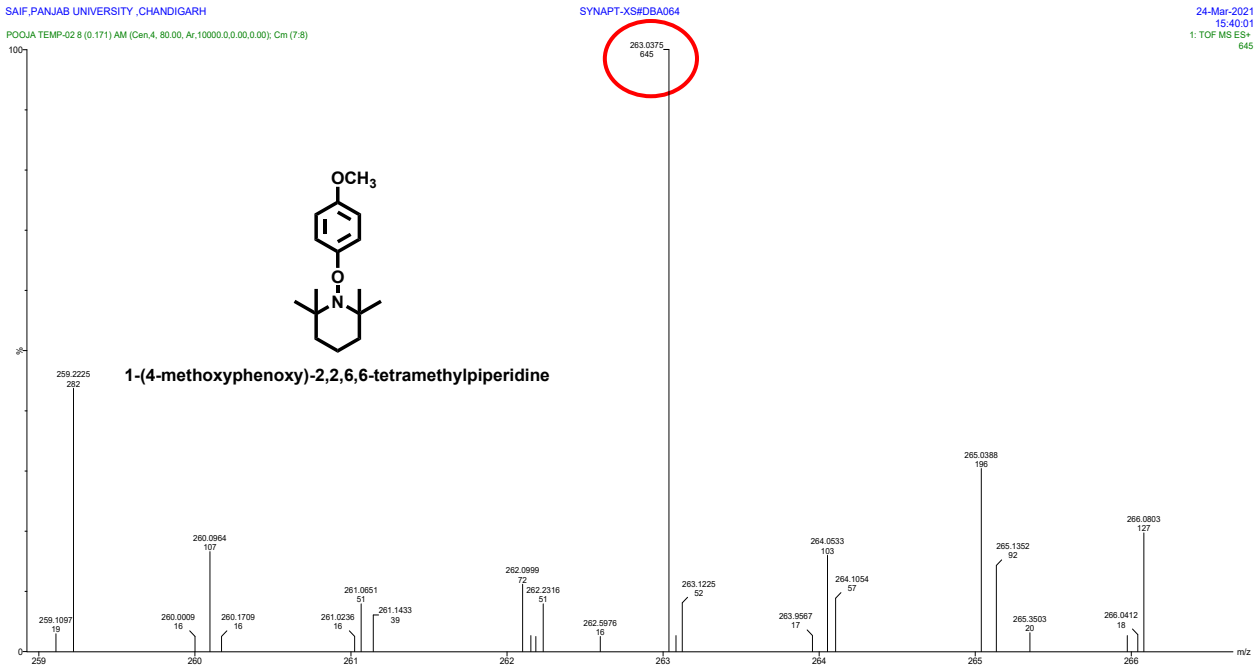


Fig. S20. HR mass spectrum of 1-(4-methoxyphenoxy)-2,2,6,6-tetramethylpiperidine, a radical adduct of 4-Iodoanisole using **CP1** as catalyst. Calculated *m/z* is 263.1885, found *m/z* is 263.0375.

Table S1. Hydrogen bonds for **CP1** [distances in Å; angles in degrees].

D–H···A [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N1–H1A···O5$^{\#1}$	2.25	3.09(1)	158.4
N1–H1B···O6$^{\#3}$	2.55	3.14(1)	124.5
O3–H3A···O5$^{\#5}$	2.06	2.87(1)	159.0
O3–H3B···O5$^{\#8}$	2.51	3.20(1)	138.2
O3–H3B···O4$^{\#8}$	2.38	3.11(1)	142.4
C5–H5···O6$^{\#1}$	2.57	3.46(2)	160.3

Symmetry transformations used to generate equivalent atoms: #1: 1-X, -0.5+Y, 0.5-Z; #3: 0.5+X, +Y, 0.5-Z; #5: -X, -0.5+Y, 0.5-Z; #8: 0.5-X, -0.5+Y, +Z; #11: -0.5+X, +Y, 0.5-Z;

Table S2. These molecular sizes of all the aryl halides are calculated with the help of Chem 3D program and using the literature protocol.[1–6]

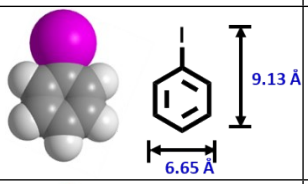
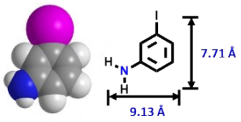
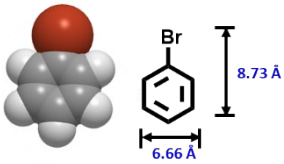
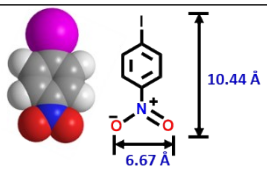
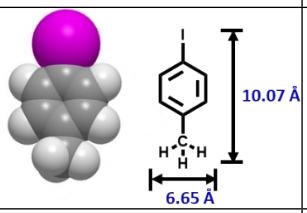
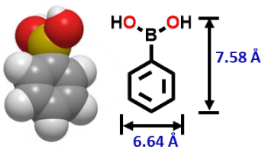
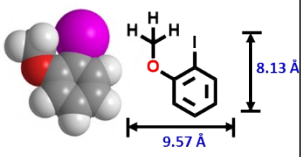
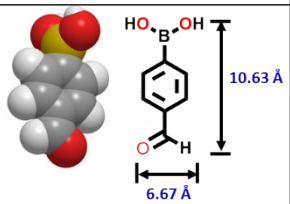
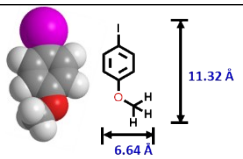
S.No.	Substrates/ reagents	Molecular size	S.No.	Substrates/ reagents	Molecular size
1.		6.65 × 9.13 Å^2	6.		7.71 × 9.13 Å^2
2.		6.66 × 8.73 Å^2	7.		6.67 × 10.44 Å^2
3.		6.65 × 10.07 Å^2	8.		6.64 × 7.58 Å^2
4.		8.13 × 9.57 Å^2	9.		6.67 × 10.63 Å^2
5.		6.64 × 11.32 Å^2			

Table S3. A comparative list of various transition metal based salts and their complexes including **CP1** that have been used for Suzuki-Miyaura cross coupling reactions.

Sr. No.	Complex	Catalyst loading (mol%)	Temperature (°C)	Base	Solvent	Time (h)	Yield (%)	Ref.
1.	[Cu(**L-tryp**)(azpy)$_{1/2}$(H_2O)NO_3]$_\infty$ **(1)**	2	80	NaOH	DMF	8	98	Present work
2.	$CuCl_2$ **(2)**	10	110	K_3PO_4	DMF	24	94	7
3.	PdNPs@Cu_2(BDC)$_2$DABCO **(3)**	0.01	25	K_2CO_3	H_2O/ EtOH	1	98	8
4.	Ni_2(^{i}Pr_2Im)$_4$(μ-COD) **(4)**	5	100	CsF	Toulene	18	95	9
5.	[Ni(Triaz^{NMe2}-iPr)Cl]Cl **(5)**	2	135	t-BuOK	Toulene	16	93	10
6.	[Co($COOCH_3$){C_6H_4-1-($NHPPh_2$)-3-($OPPh_2$)}] (**6a)** [Co($COOCH_3$){C_6H_5-1,3-$NHPPh_2)_2$}] (**6b)** [Co($COOCH_3)_2${C_5H_3N-2,6-($NHPPh_2)_2$}] (**6c)**	0.5/ 0.5/ 0.5	80	Cs_2CO_3	CH_3CN	16	50/ 54/ 56	11
7.	Cu-BIA-Si-Fe_3O_4 **(7)**	1.5	80	K_2CO_3	DMSO	2	95	12
8.	CuI **(8)**	10	80	LiO^{t}Bu	HMPA	48	90	13
9.	CuO-**L (9)**	20	130	K_2CO_3	DMF	48	87	14
10	CuI **(10)**	10	60	LiO^{t}Bu	DMF	12	87	15
11.	Ni powder **(11)**	10	110	K_2CO_3	PEG-400	10	99	16

Abbreviation: L-tryp = L-Tryptophan; azpy = 4,4'-azopyridine; BDC = 1,4-benzenedicarboxylate; DABCO = 1,4-diazabicyclo [2.2.2] octane; NP = Nanoparticles; ^{i}Pr_2Im = 1,3-bis(isopropyl)imidazolin-2-ylidene; COD = COD=1,5-cyclooctadiene; Triaz^{NMe2}-iPr = N,N'-Bis(diisopropylphosphino)-N''-dimethyl-2,4,6-triaminotriazine; BIA = 2-(1H-benzo[d]imidazol-2-yl)aniline; L = 2,2'-diamino-6,6'-dimethylbiphenyl.

References.

1. P. Rani, Gauri, A. Husain, K. K. Bhasin, and G. Kumar, *Cryst. Growth Des.,* 2020, **20**, 7141−7151.
2. G. Kumar and R. Gupta, *Inorg. Chem*., 2013, **52**, 10773−10787.
3. G. Kumar and R. Gupta, *Inorg. Chem*., 2012, **51**, 5497−5499.
4. J.-M. Gu, T.-H. Kwon, J.-H. Park and S. Huh, *Dalton Trans*., 2010, **39**, 5608–5610.
5. J.-M. Gu, W.-S. Kim and S. Huh, *Dalton Trans*., 2011, **40**, 10826–10829.
6. X.-M. Lin, T.-T. Li, L.-F. Chen, L. Zhang and C.-Y. Su, *Dalton Trans*., 2012, **41**, 10422–10429.
7. G. Ranjani and R. Nagarajan, *Org. Lett.,* 2017, **19**, 3974−3977.
8. S. Tahmasebi, J. Mokhtari, M. R. Naimi-Jamal, A. Khosravia and L. Panahi, *J. Org. Chem.,* 2017, **853**, 35-41.
9. J. Zhou, J. H. J. Berthel, M. W. Kuntze-Fechner, A. Friedrich, T. B. Marder and U. Radius*, J. Org. Chem.,* 2016, **81**, 5789−5794.
10. M. Mastalir, B. Stöger, E. Pittenauer, G. Allmaier and K. Kirchner, *Org. Lett.,* 2016, **18**, 3186−3189.
11. L. M. Kumar and B. R. Bhat, *J. Organomet. Chem.,* 2017, **827**, 41-48.
12. L. Danqing, J. Ming, L. Li and M. Mohammadnia, *Appl. Organomet. Chem.,* 2020, **34**, 5820.
13. P. Basnet, S. Thapa, D. A. Dickie and R. Giri, *Chem. Commun.,* 2016, **52**, 11072–11075.
14. Y.-M. Ye, B.-B. Wang, D. Ma, L.-X. Shao and J.-M. Lu, *Catal. Lett.*, 2010, **139**,141–144.
15. C.-T. Yang, Z.-Q. Zhang, Y.-C. Liu and L. Liu, *Angew. Chem. Int. Ed.,* 2011, **123**, 3990 –3993.
16. C. S. Cho and N. T. Tran, *Cat. Commun.,* 2009, **11**, 191–195.

****