catalysts

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Supplementary Materials

Ferrocenylimine Palladium (II) Complexes: Synthesis, Characterization and Application in Mizoroki-Heck and Suzuki-Miyaura Cross-Coupling Reactions

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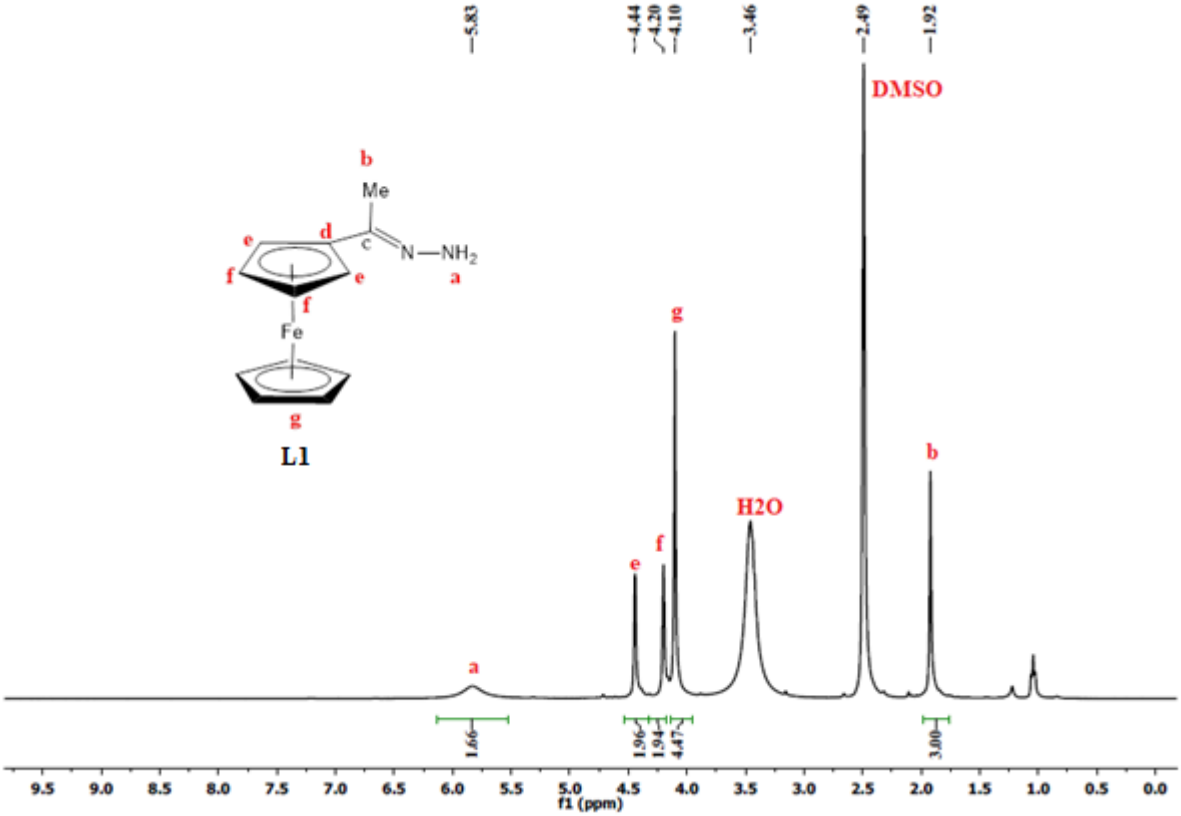


Figure S1: ^{1}H NMR spectrum of ferrocenyl hydrazone **L1**, recorded in DMSO-d_6 at 25 °C.

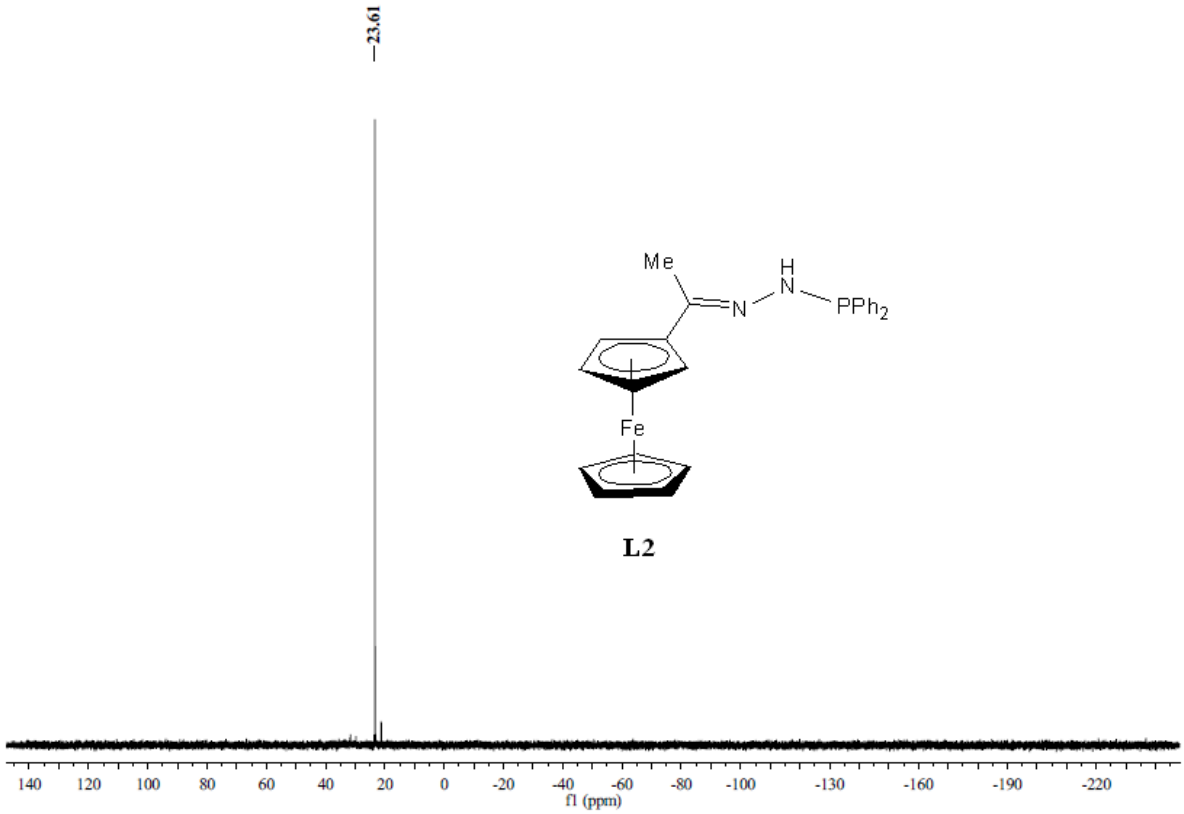


Figure S2: ^{31}P NMR spectrum of **L2**, recorded in $CDCl_3$ at 25 °C.

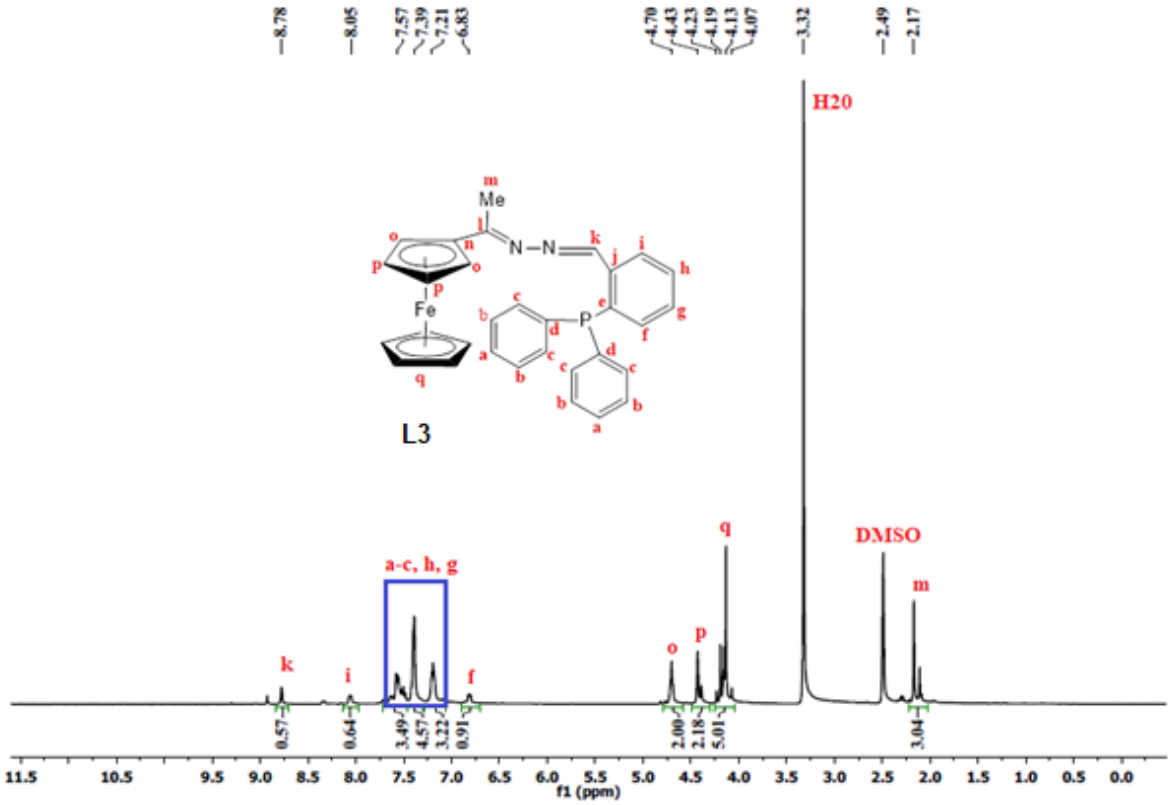


Figure S3: ^{1}H NMR spectrum of **L3**, recorded in DMSO-d$_6$ at 25 °C.

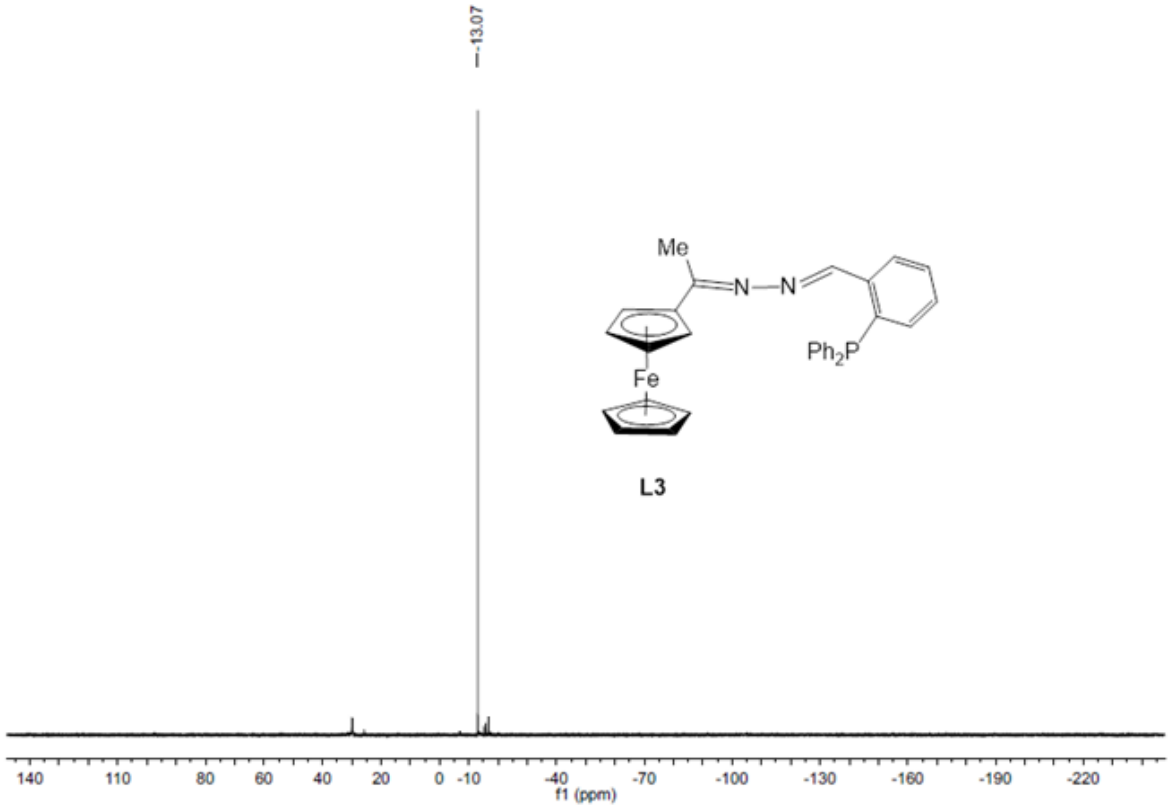


Figure S4: ^{1}P NMR spectrum of **L3**, recorded in DMSO-d$_6$ at 25 °C.

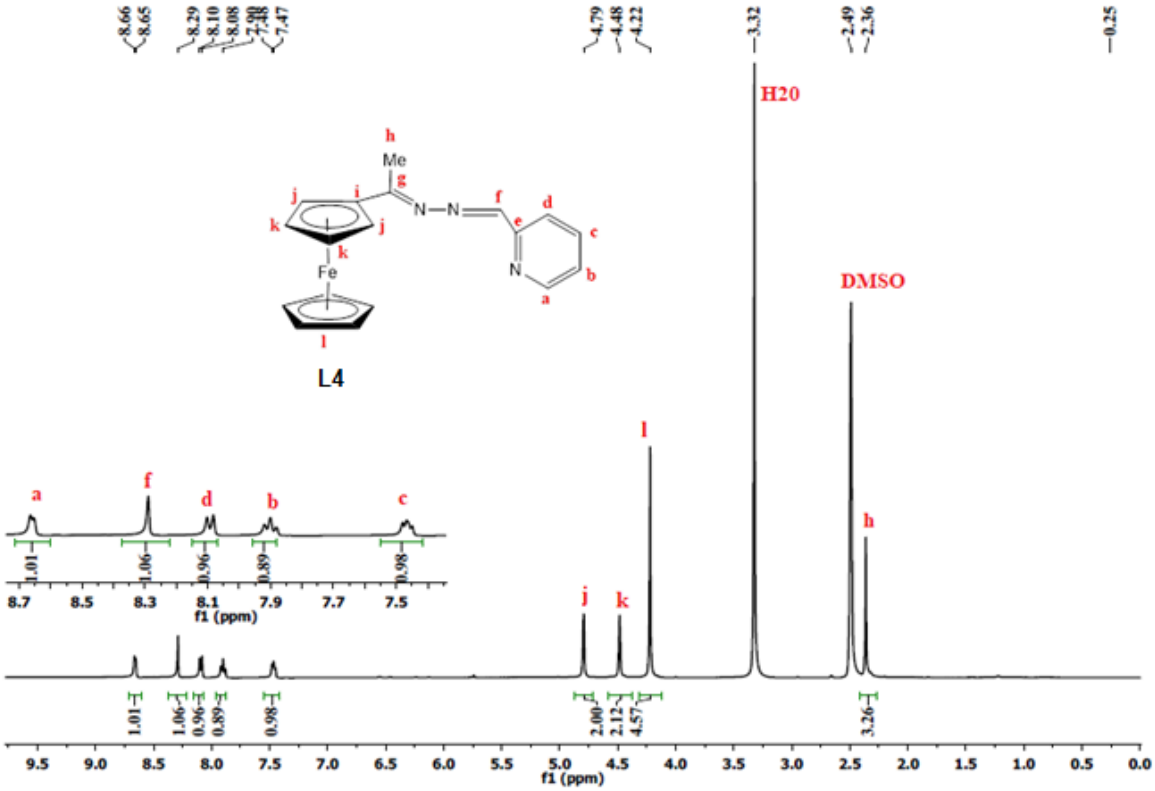
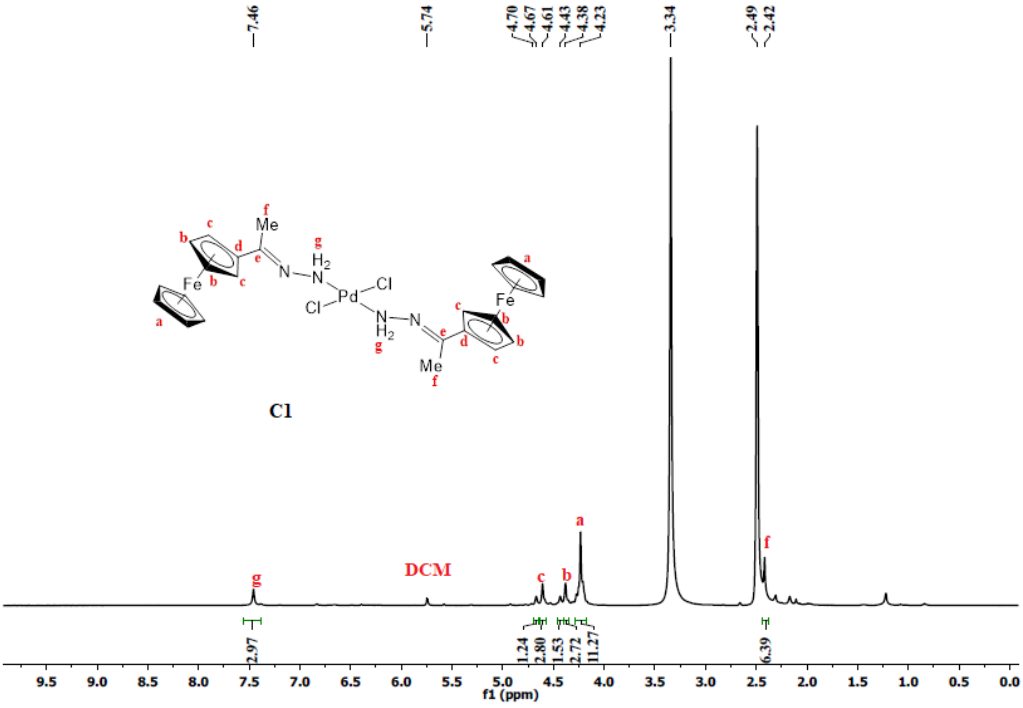
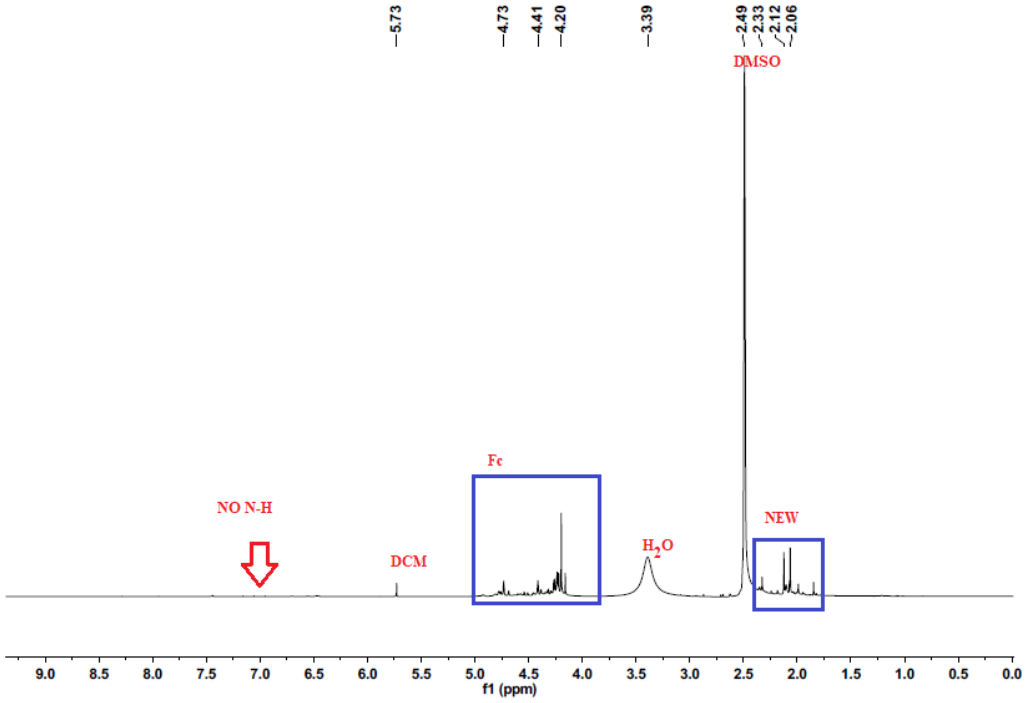


Figure S5: ^{1}H NMR spectrum of **L4**, recorded in DMSO-d_6 at 25 °C.



(a)



(b)

Figure S6: ^{1}H NMR spectrum of dichlorobis(ferrocenyliminehydrazone)palladium(II) complex **C1**, recorded in DMSO-d_6 at 25°C (**a**); ^{1}H NMR spectrum of **C1** after fours in room temperature, recorded in DMSO-d_6 at 25 °C (**b**).

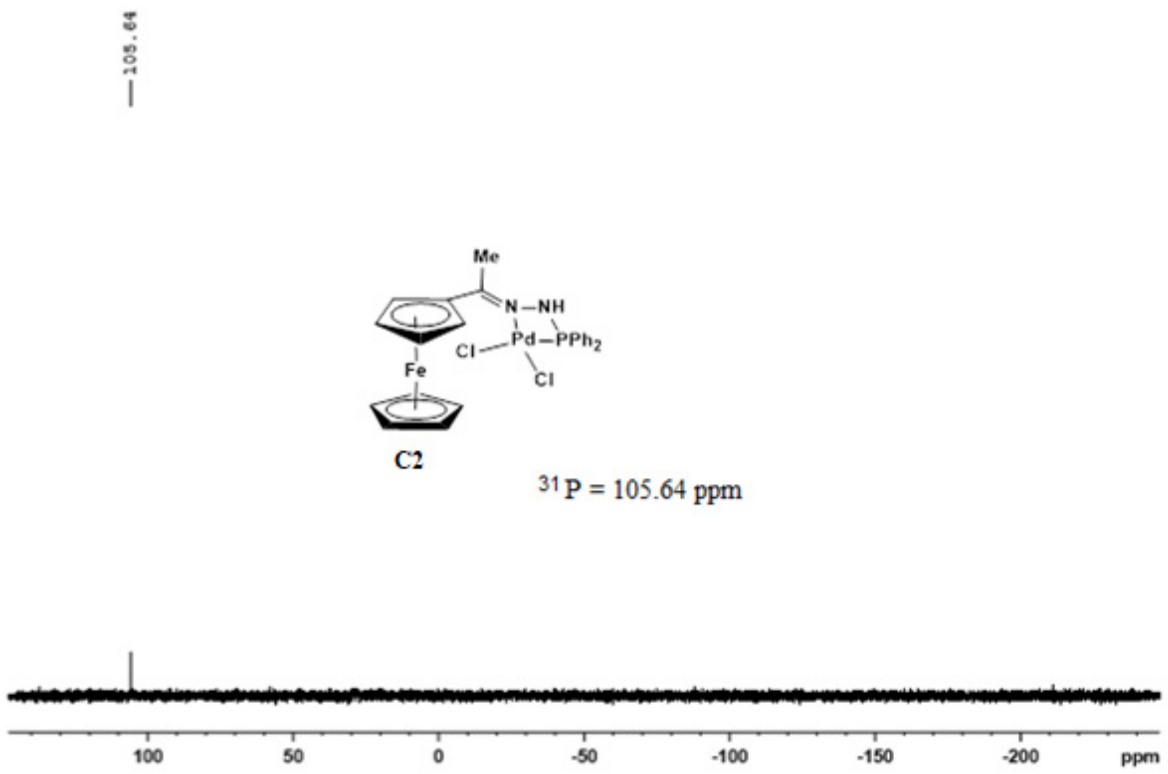


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of **C2**, recorded in DMSO-d_6 at 25 °C.

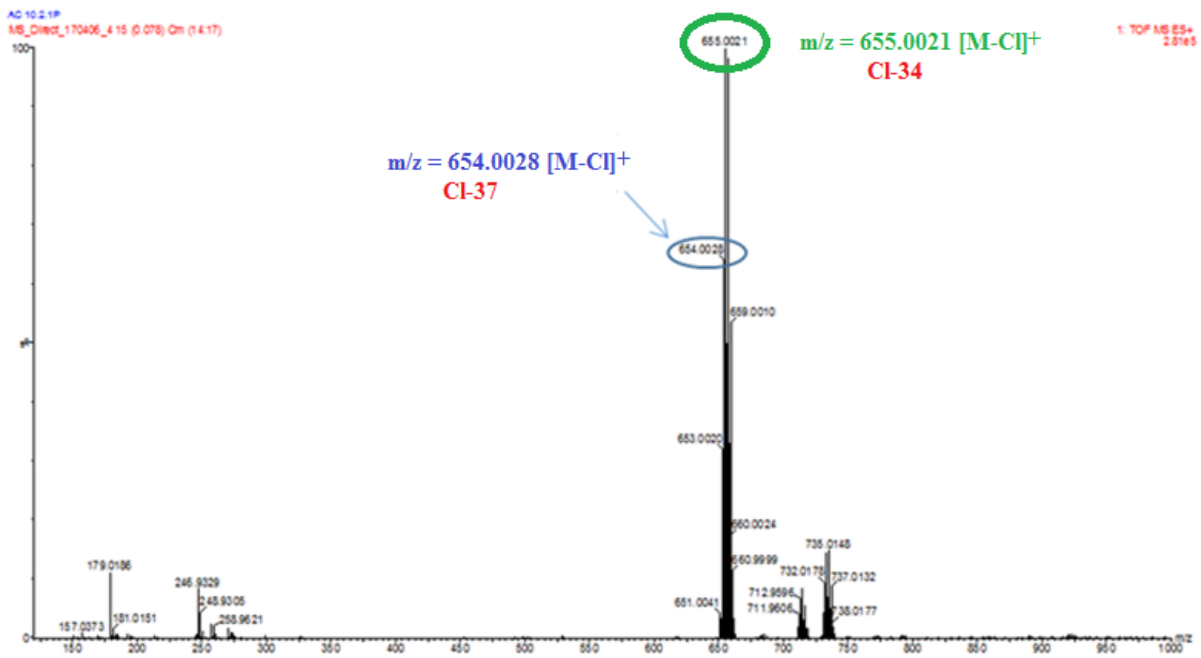


Figure S8: High resolution electrospray ionisation mass spectrum of **C3**, recorded in the positive mode.

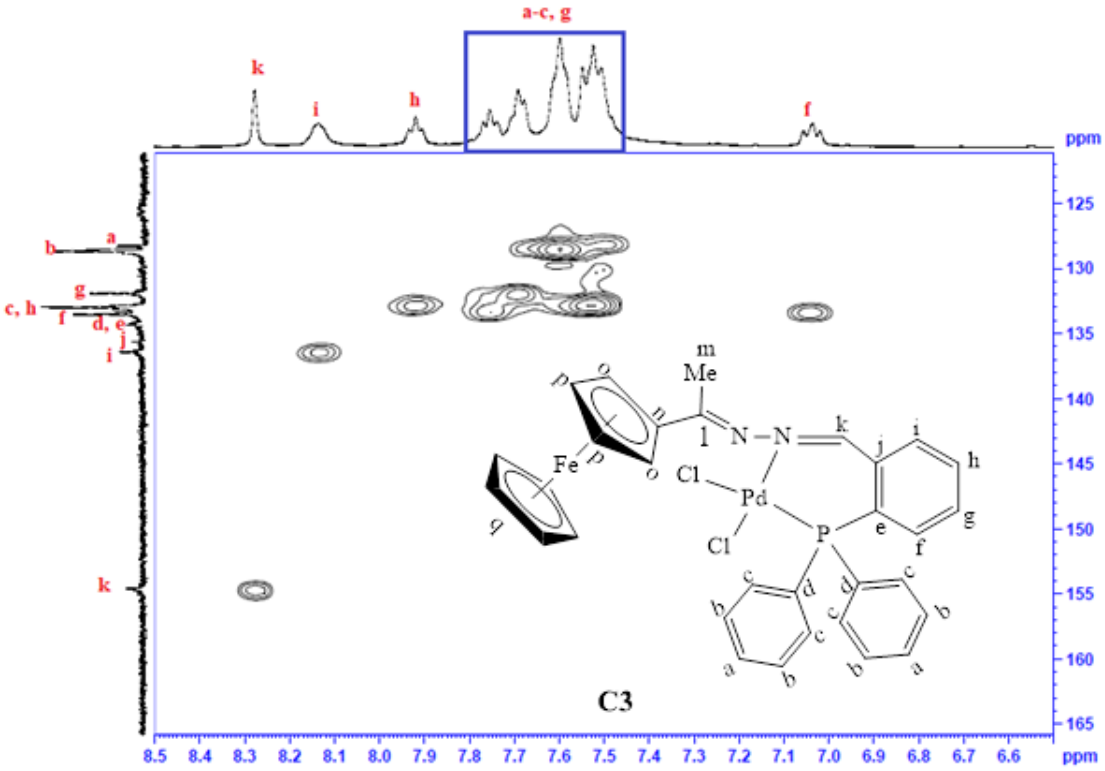


Figure S9: The HSQC 2D NMR of **C3** showing the region –***CHAr***P***Ph₂***, recorded in DMSO-d_6 at 25 ˚C.

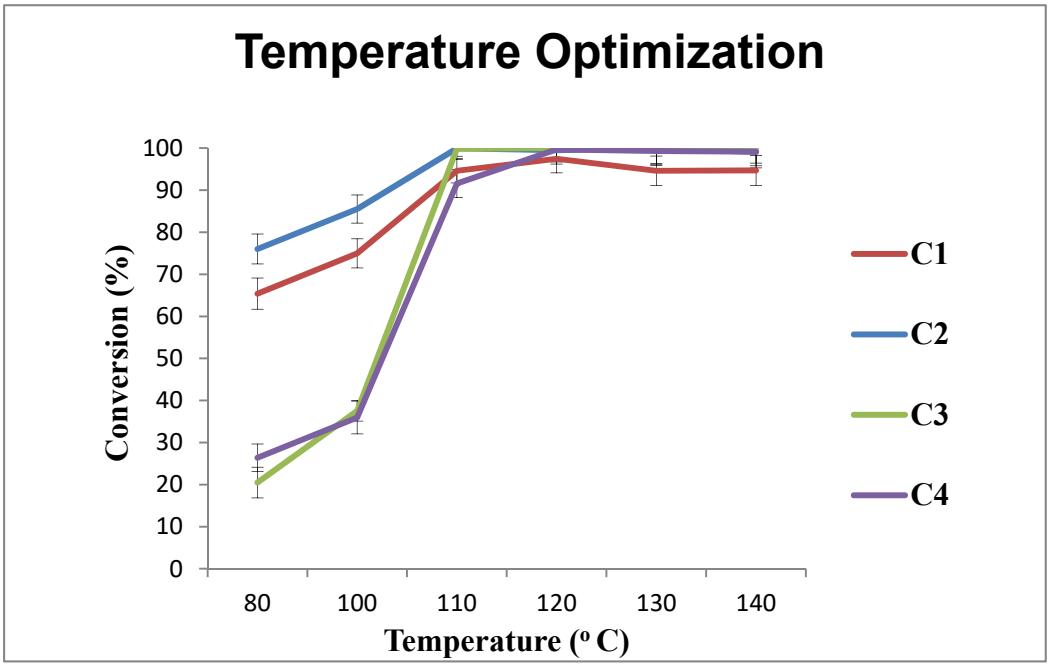


Figure S10: Temperature optimization in Mizoroki-Heck cross-coupling reactions carried out using **C1 – C4** as catalyst precursors. **Reaction conditions:** Temperature optimization. Reactions carried out in DMF (1.2 mL) with 0.66 mmol iodobenzene, 0.726 mmol of styrene, 1.32 mmol of Et_3N and 0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reactions were allowed to run for 4 hours.

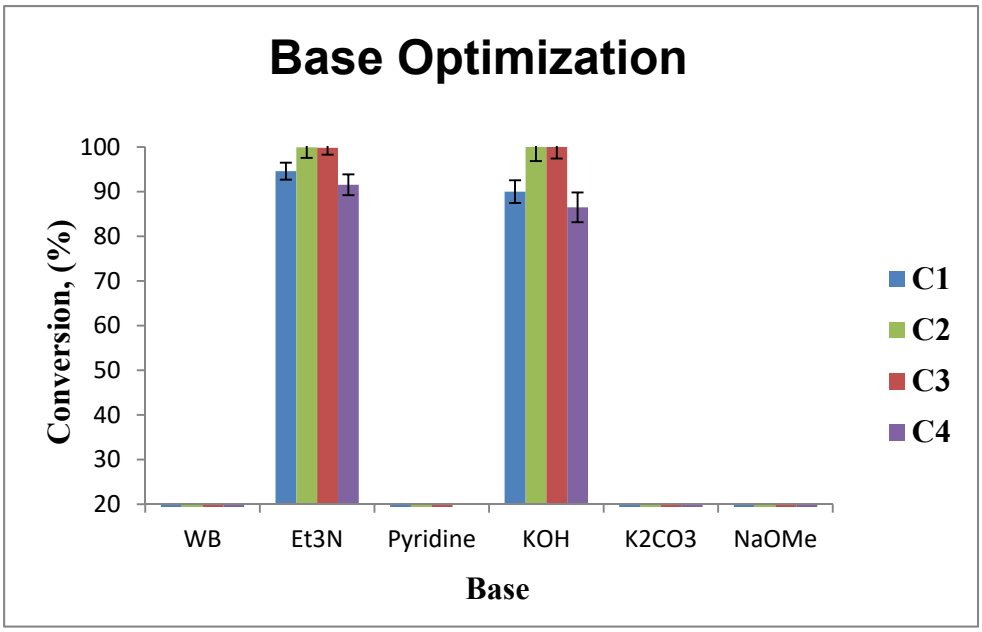


Figure S11: Base optimization in Mizoroki-Heck cross-coupling reactions carried out using (pre)catalysts **C1-C4**, **WB** = Without Base. **Reaction conditions:** Reactions carried out in DMF (1.2 mL) with 0.66 mmol iodobenzene, 0.726 mmol of styrene, 1.32 mmol of base and 0.5 mol % Pd catalyst loading (**C1 – C4**). The *n*-decane was used as internal standard and the reactions were allowed to run for 4 hours at 110 °C.

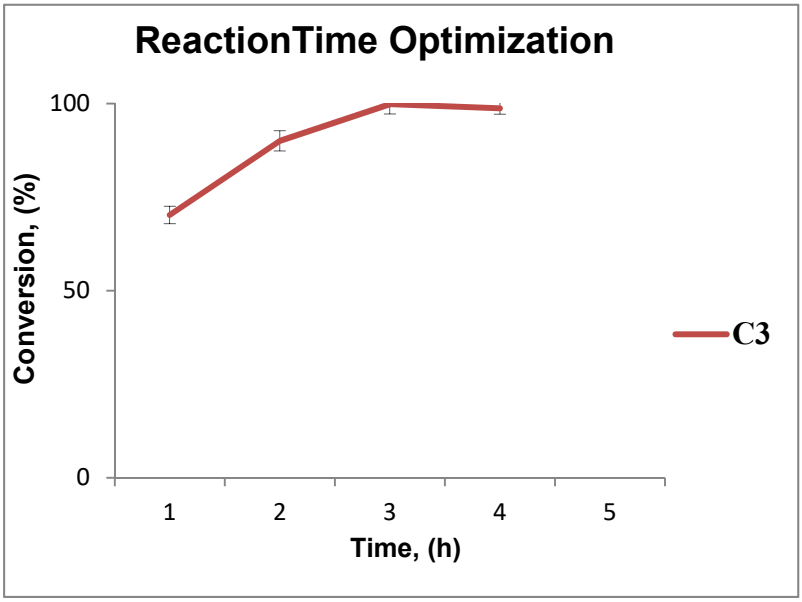


Figure S12: Time optimization in the Mizoroki-Heck cross-coupling reaction carried using (pre)catalyst **C3**, also includes effect of reaction time on TOF. **Reaction conditions**: Reaction time optimization using **C3**. Reactions carried out in DMF (1.2 mL) with 0.66 mmol iodobenzene, 0.726 mmol of styrene, 1.32 mmol of Et_3N and 0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reactions were allowed to run for 1-4 hours.

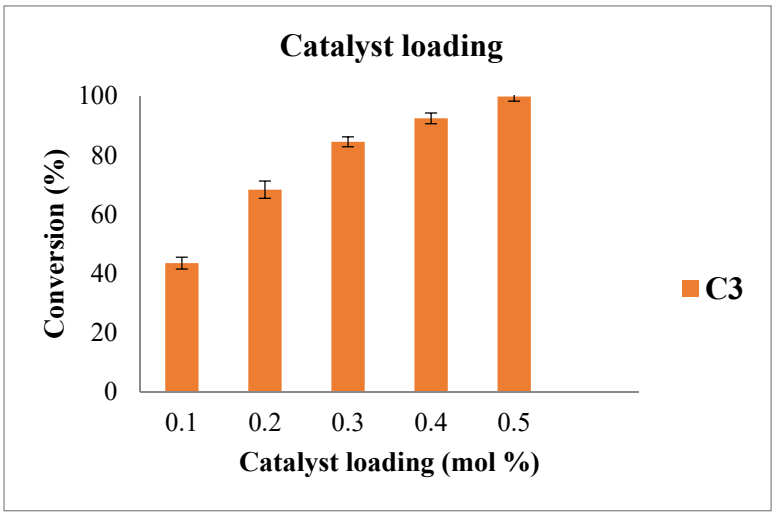


Figure S13: Optimization of catalyst loading in the Mizoroki-Heck cross-coupling reaction carried out (pre)catalyst **C3**. **Reaction conditions**: Catalyst loading optimization using **C3**. Reactions carried out in DMF (1.2 mL) with 0.66 mmol iodobenzene, 0.726 mmol of styrene, 1.32 mmol of Et_3N and 0.1-0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reactions were allowed to run for 3 hours at 110 ° C.

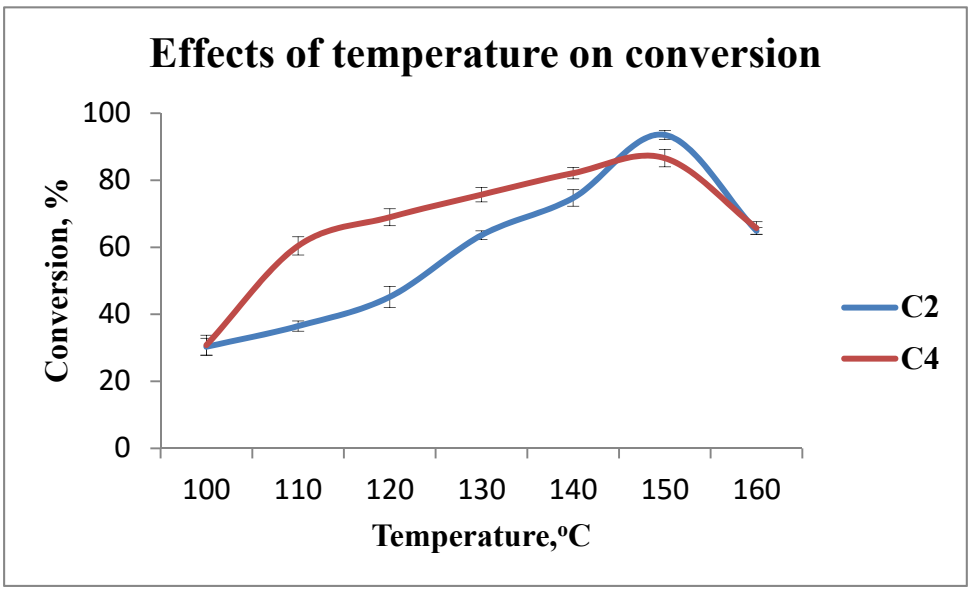


Figure S14: Temperature optimization in Suzuki-Miyaura cross-coupling reactions carried out using **C2** and **C4** as catalyst precursors. **Reaction conditions**: Reactions carried out in DMF (1.2 mL) with 0.67 mmol of bromobenzene, 1.06 mmol of phenylboronic acid, 1.33 mmol of KOH and 0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reaction was allowed to run for 3 hours at 150 °C.

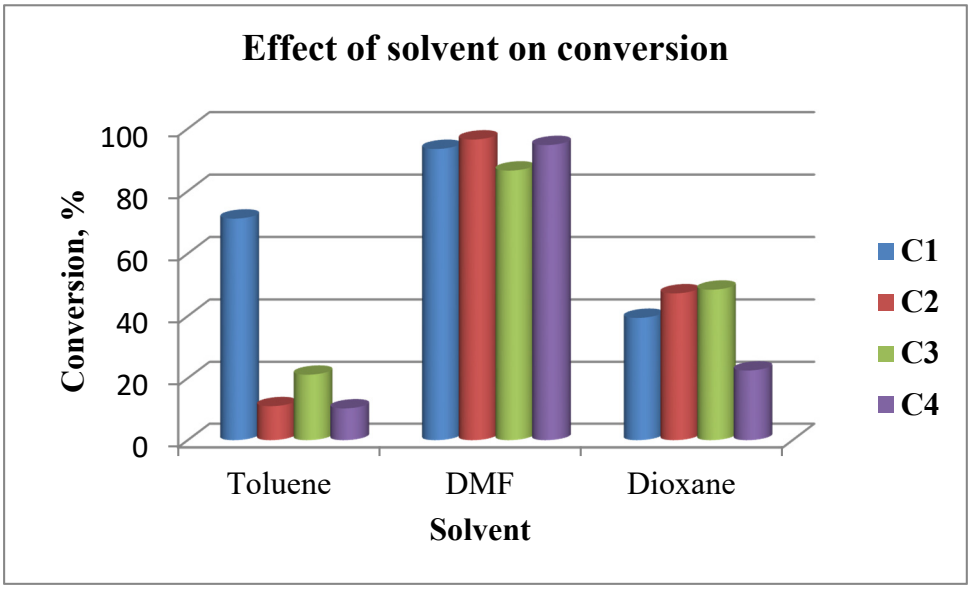


Figure S15: Solvent variation in Suzuki-Miyaura cross-coupling reactions carried out using pre-catalysts **C1 – C4**. **Reaction conditions**: Reactions carried out in 1.2 mL (DMF/ Dioxane/ Toluene) with 0.67 mmol of bromobenzene, 1.06 mmol of phenylboronic acid, 1.33 mmol of KOH and 0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reaction was allowed to run for 3 hours at 150 °C (**C1 – C4**).

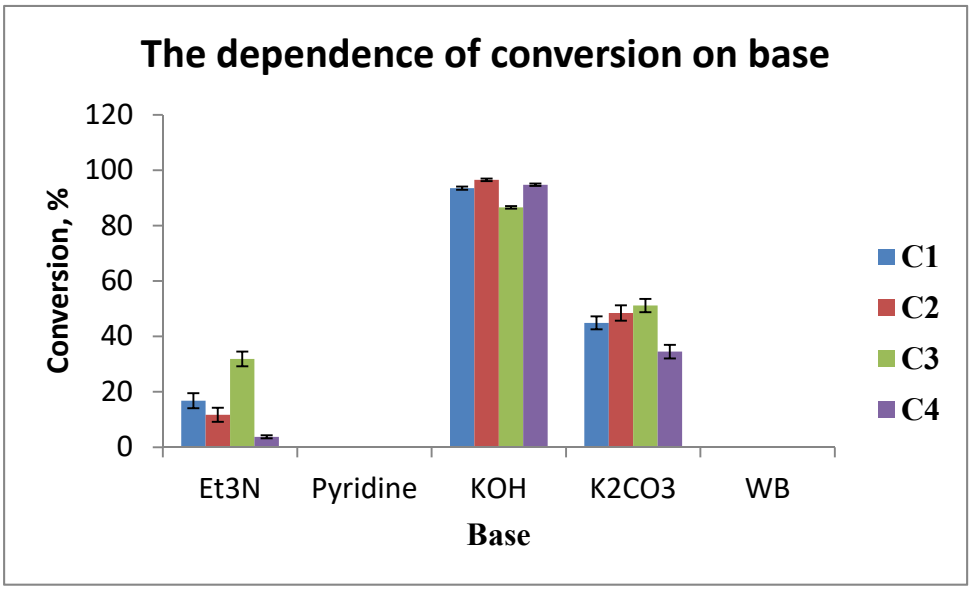
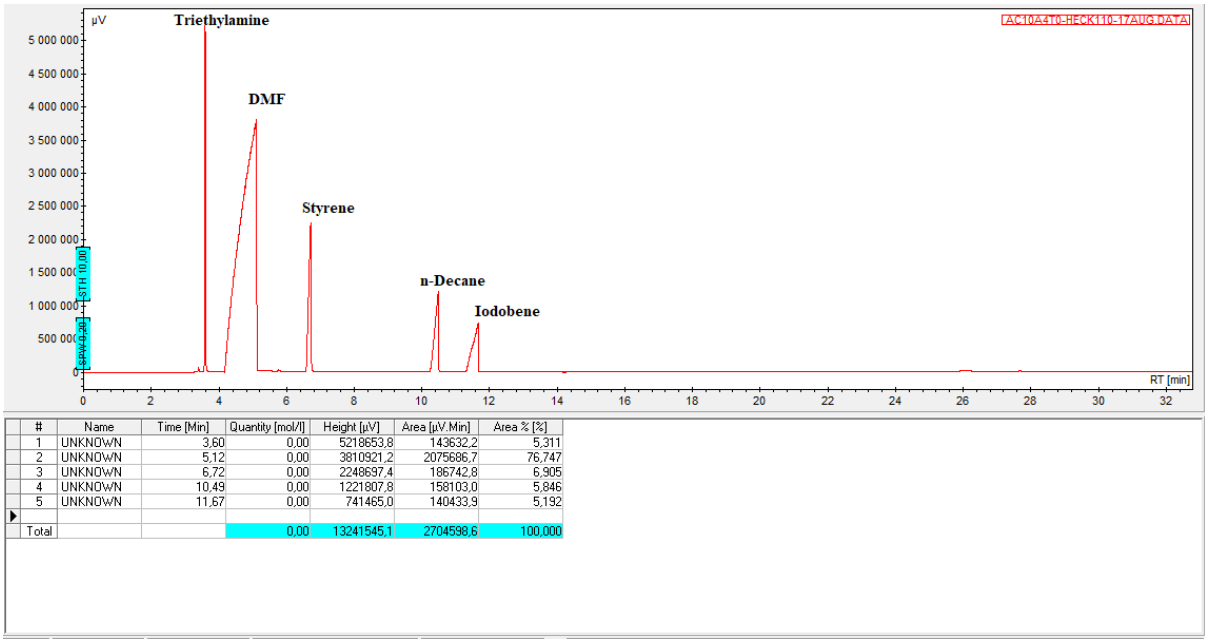
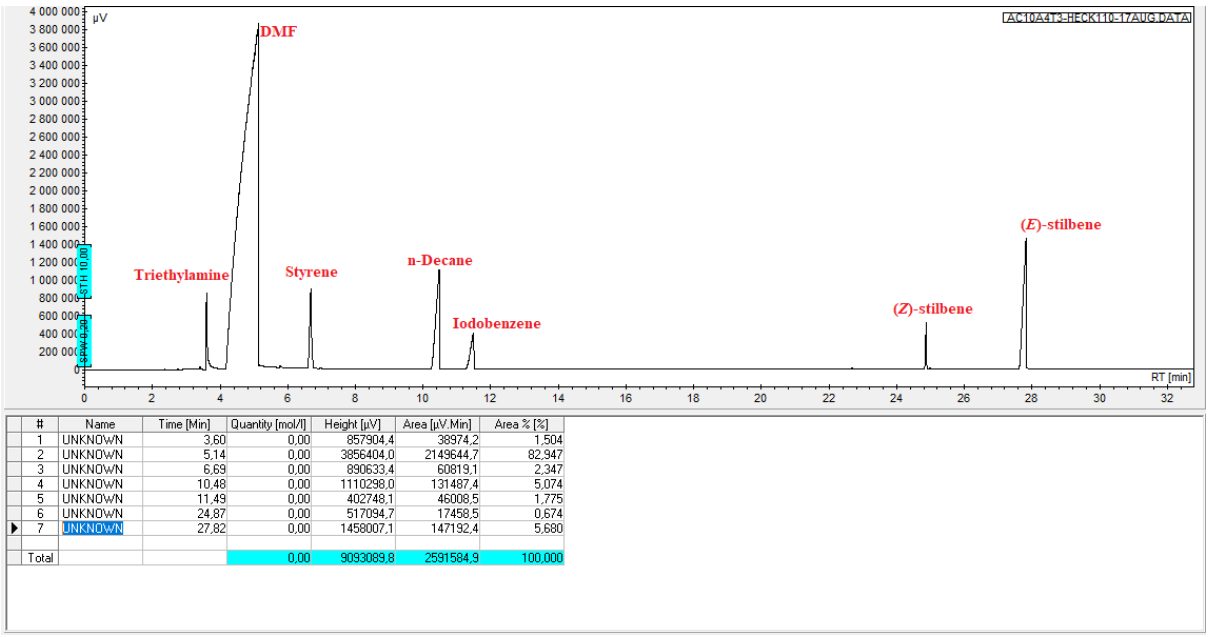


Figure S16: Base optimization in Suzuki-Miyaura cross-coupling reactions carried out using pre-catalysts **C1-C4**, **WB** = Without base. **Reaction conditions**: Reactions carried out in DMF (1.2 mL) with 0.67 mmol of bromobenzene, 1.06 mmol of phenylboronic acid, 1.33 mmol of (KOH/ pyridine/ KOH/ K2CO3) and 0.5 mol % Pd catalyst loading using *n*-decane as internal standard and the reaction was allowed to run for 3 hours at 150 °C (**C1 – C4**).



#	Name	Time [Min]	Quantity [mol/l]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	3,60	0,00	5218653,8	143632,2	5,311
2	UNKNOWN	5,12	0,00	3810921,2	2075686,7	76,747
3	UNKNOWN	6,72	0,00	2248697,4	186742,8	6,905
4	UNKNOWN	10,49	0,00	1221807,8	158103,0	5,846
5	UNKNOWN	11,67	0,00	741465,0	140433,9	5,192
Total			0,00	13241545,1	2704598,6	100,000

Figure S17: A representation of the gas chromatogram before the Mizoroki-Heck cross-coupling reaction of iodobenzene with styrene.



#	Name	Time [Min]	Quantity [mol/l]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	3,60	0,00	857904,4	38974,2	1,504
2	UNKNOWN	5,14	0,00	3856404,0	2149644,7	82,947
3	UNKNOWN	6,69	0,00	890633,4	60819,1	2,347
4	UNKNOWN	10,48	0,00	1110298,0	131487,4	5,074
5	UNKNOWN	11,49	0,00	402748,1	46008,5	1,775
6	UNKNOWN	24,87	0,00	517094,7	17458,5	0,674
7	UNKNOWN	27,82	0,00	1458007,1	147192,4	5,680
Total			0,00	9093089,8	2591584,9	100,000

Figure S18: A representation of the gas chromatogram after 3 hours of the Mizoroki-Heck cross-coupling reaction of iodobenzene with styrene.

CROSS-COUPLING PRODUCTS NMR

1. Mizoroki-Heck cross-coupling reactions product NMR spectra (^{1}H and ^{13}C{H})

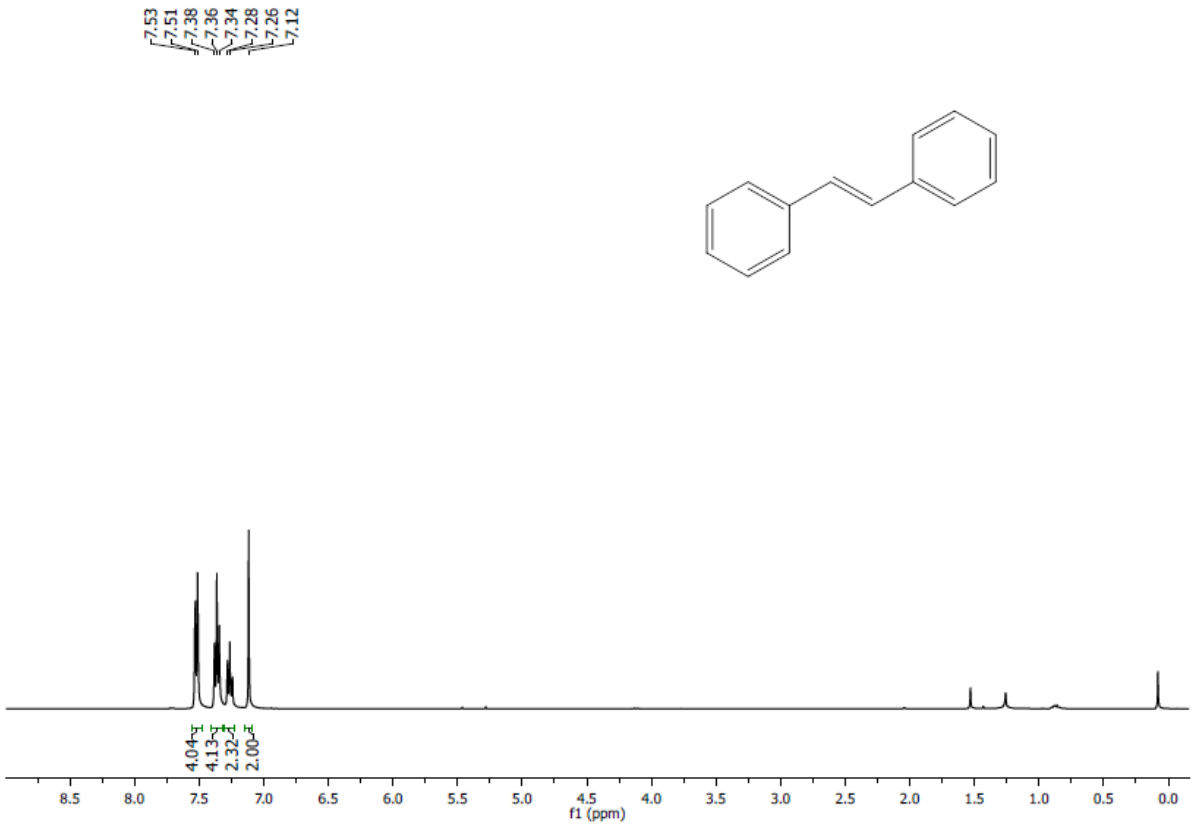


Figure S19: ^{1}H NMR spectrum of **stilbene**, recorded in $CDCl_3$ at 25 ˚C.

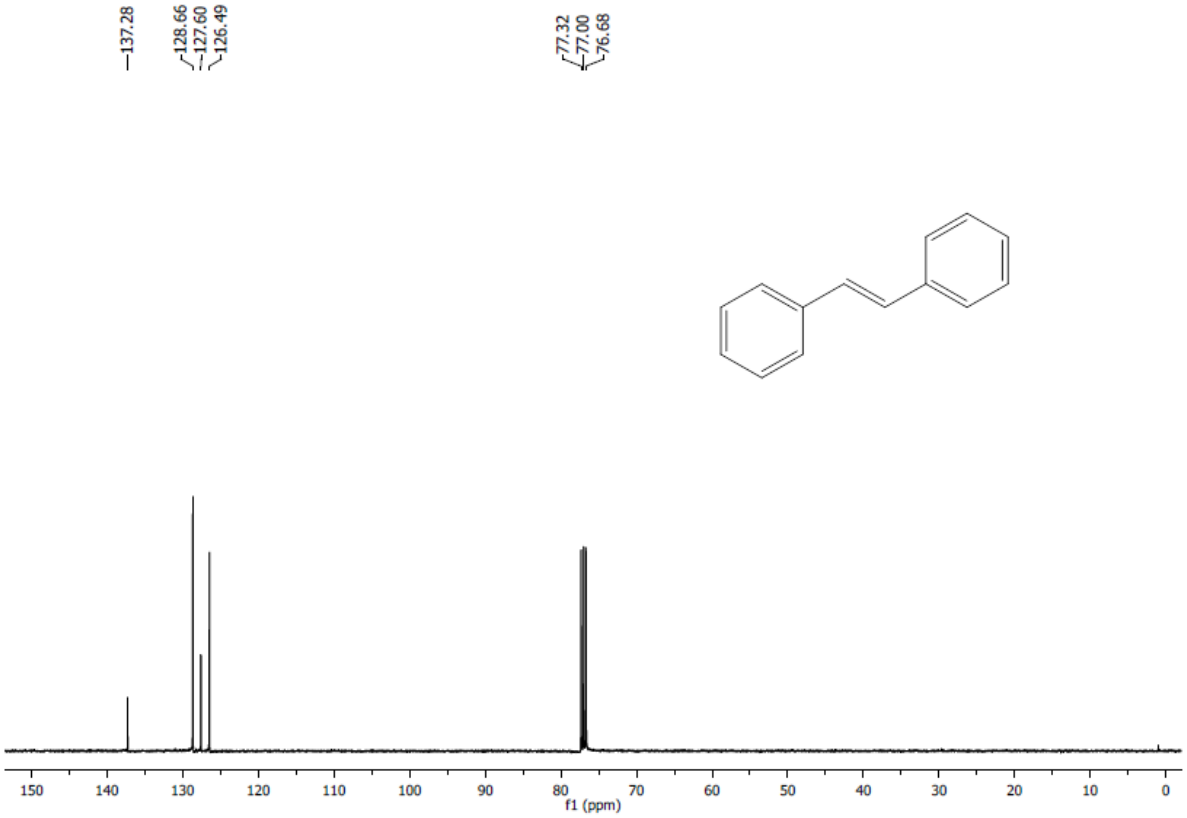


Figure S20: ^{13}C NMR spectrum of **stilbene**, recorded in CDCl3 at 25 °C.

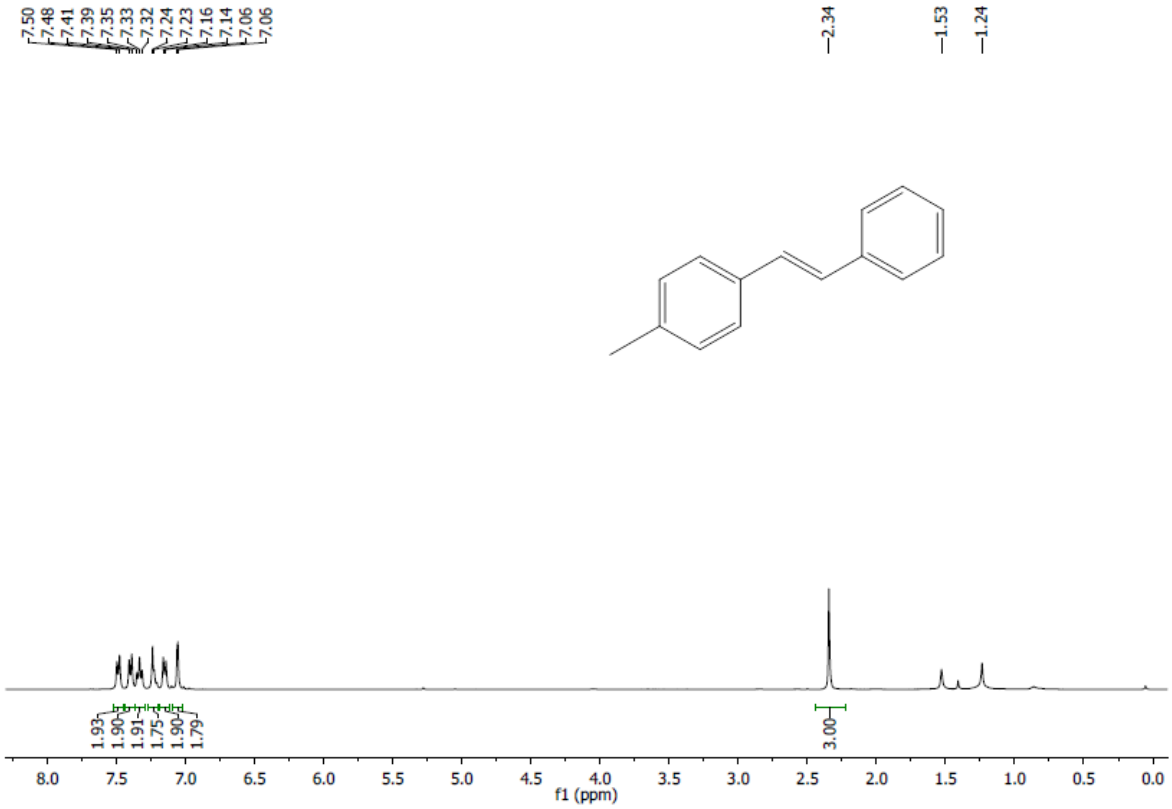


Figure S21: ^{1}H NMR spectrum of **4-methylstilbene**, recorded in CDCl3 at 25 °C.

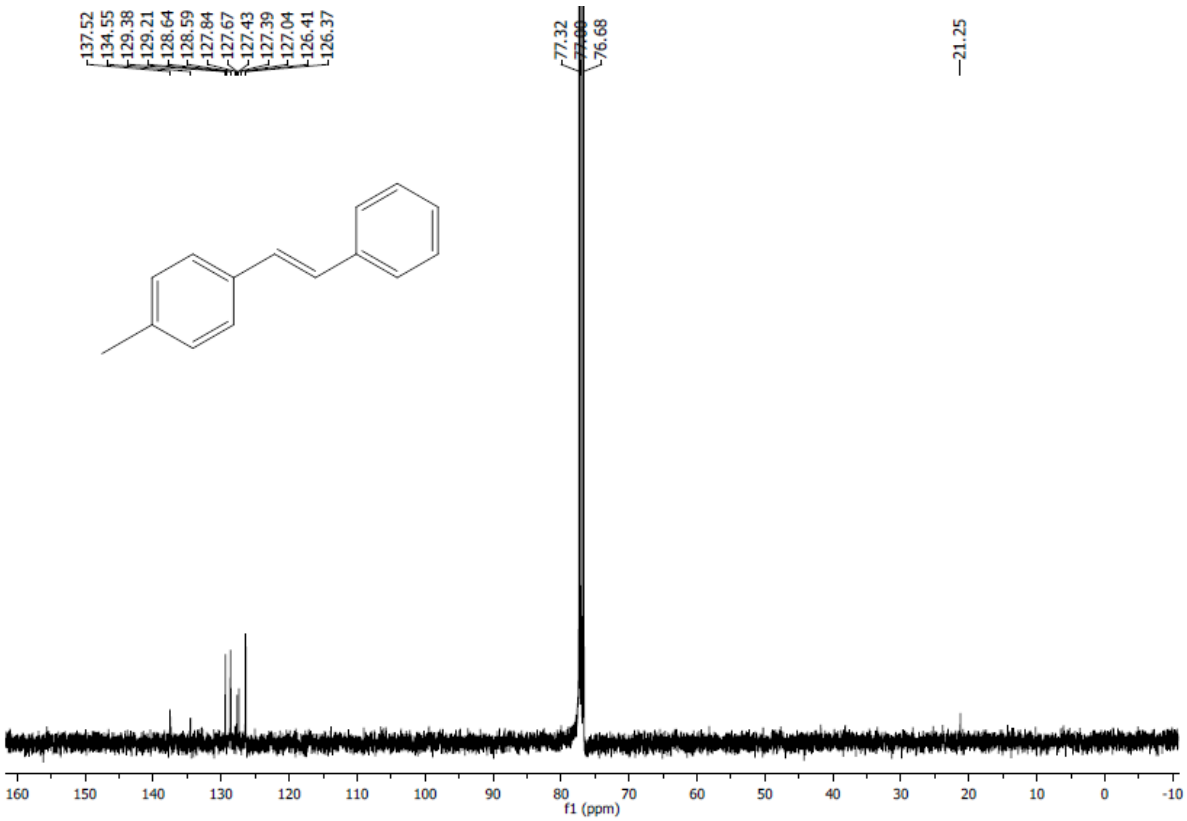


Figure S22: ^{13}C NMR spectrum of **4-methylstilbene**, recorded in CDCl3 at 25 ˚C.

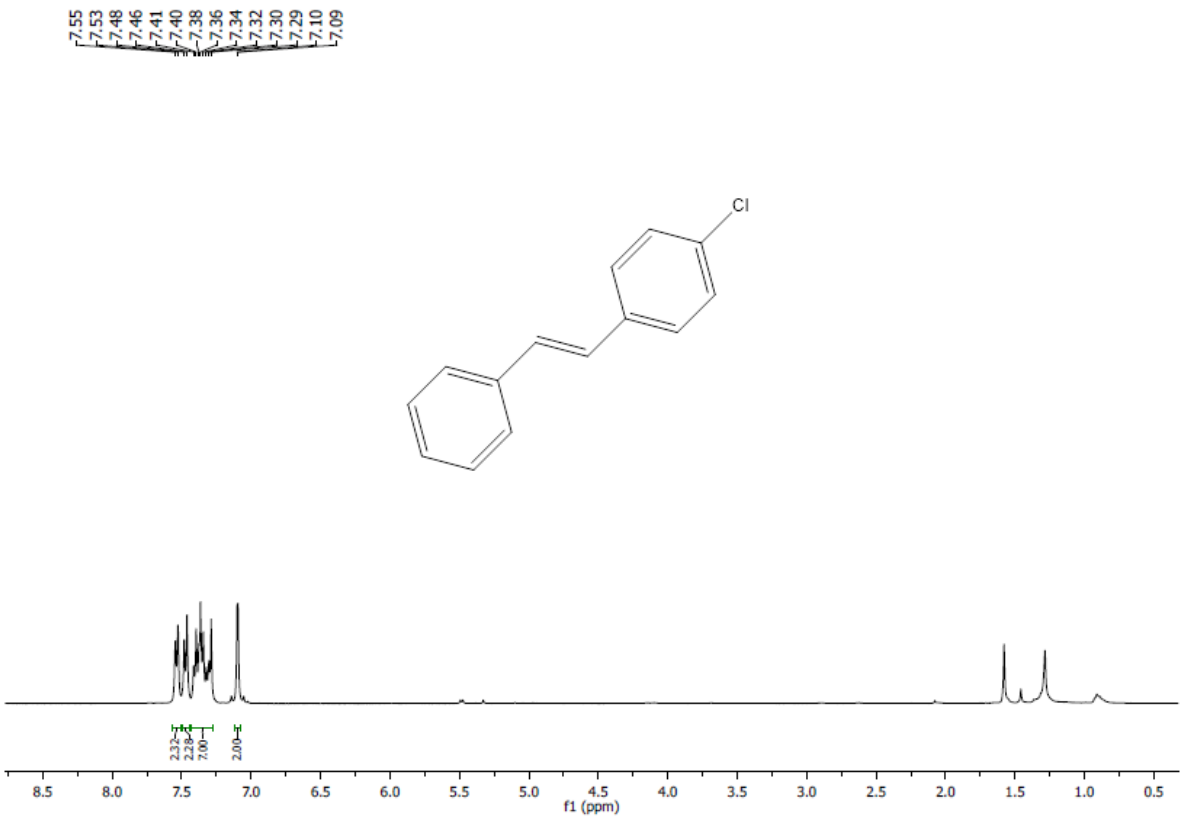


Figure S23 : ^{1}H NMR spectrum of **4-chlorostilbene**, recorded in CDCl3 at 25 ˚C.

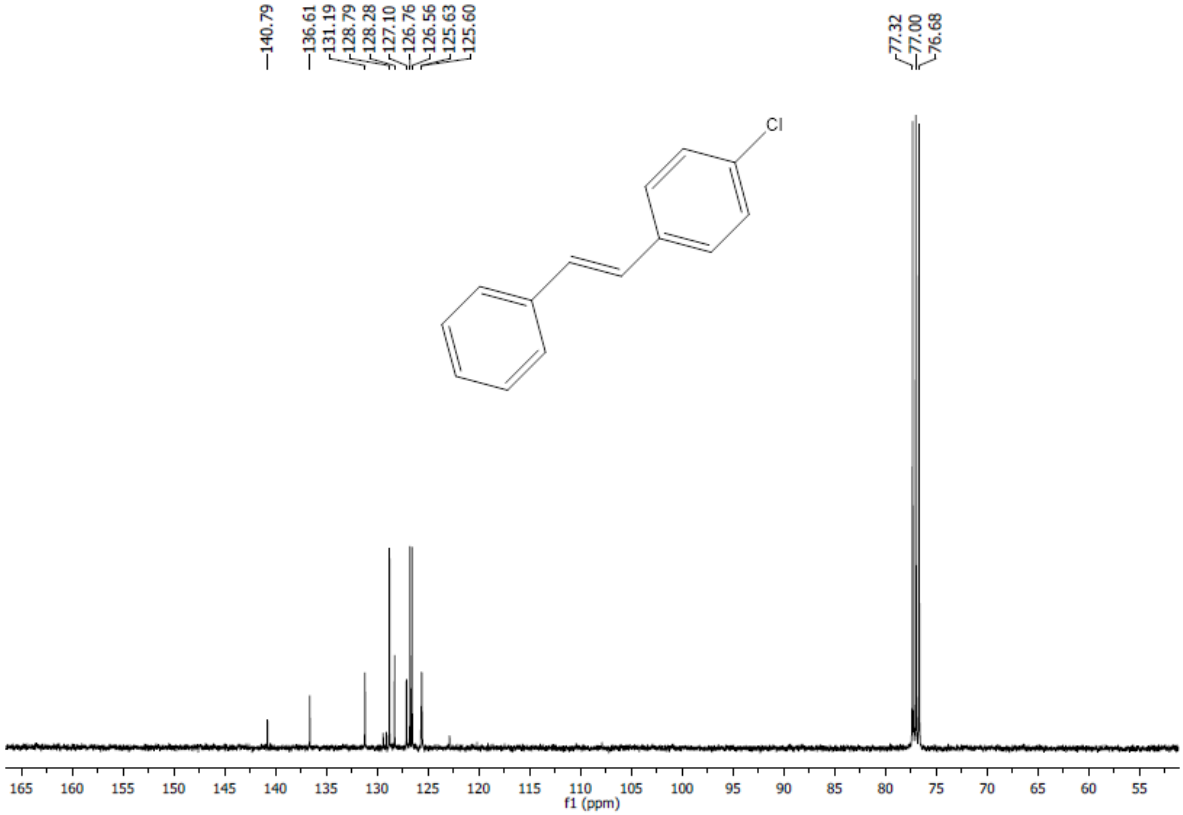


Figure S24 : ^{13}C NMR spectrum of **4-chlorostilbene**, recorded in CDCl3 at 25 ˚C.

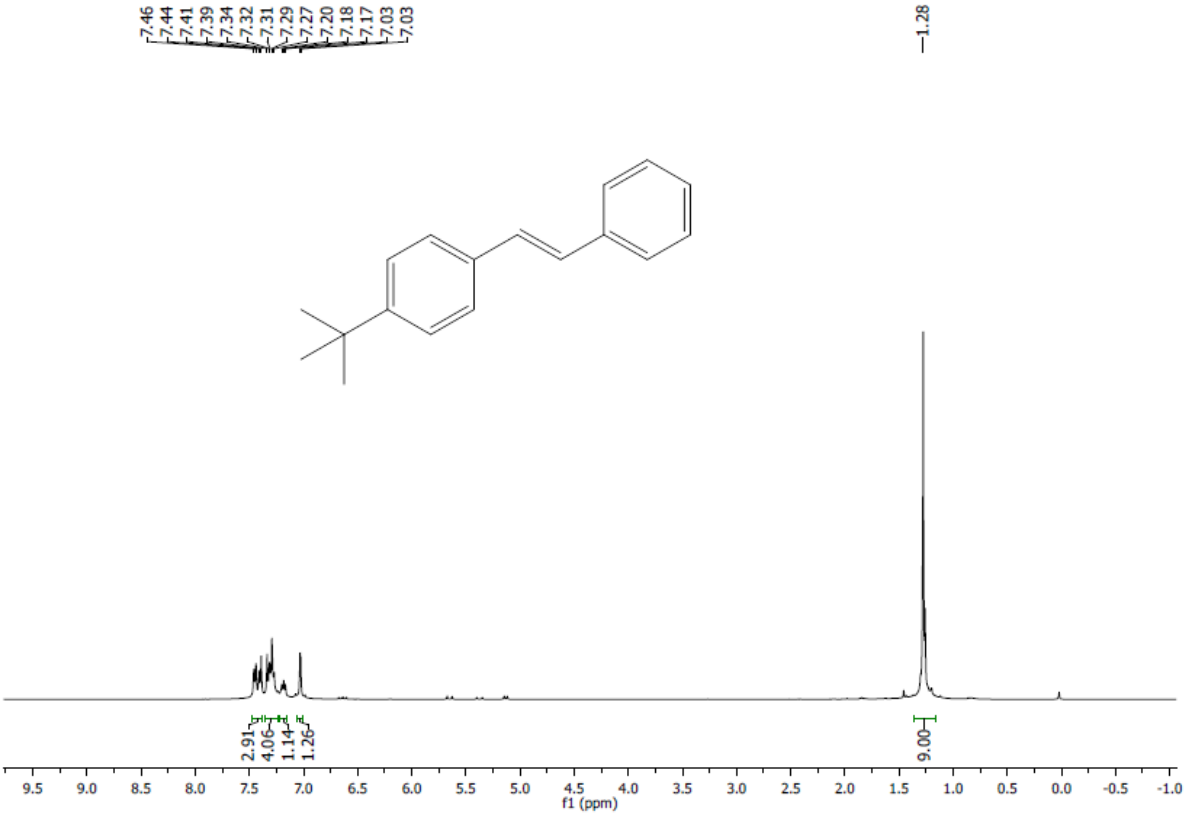


Figure S25: ^{1}H NMR spectrum of **4-tert-butylstilbene**, recorded in CDCl3 at 25 ˚C.

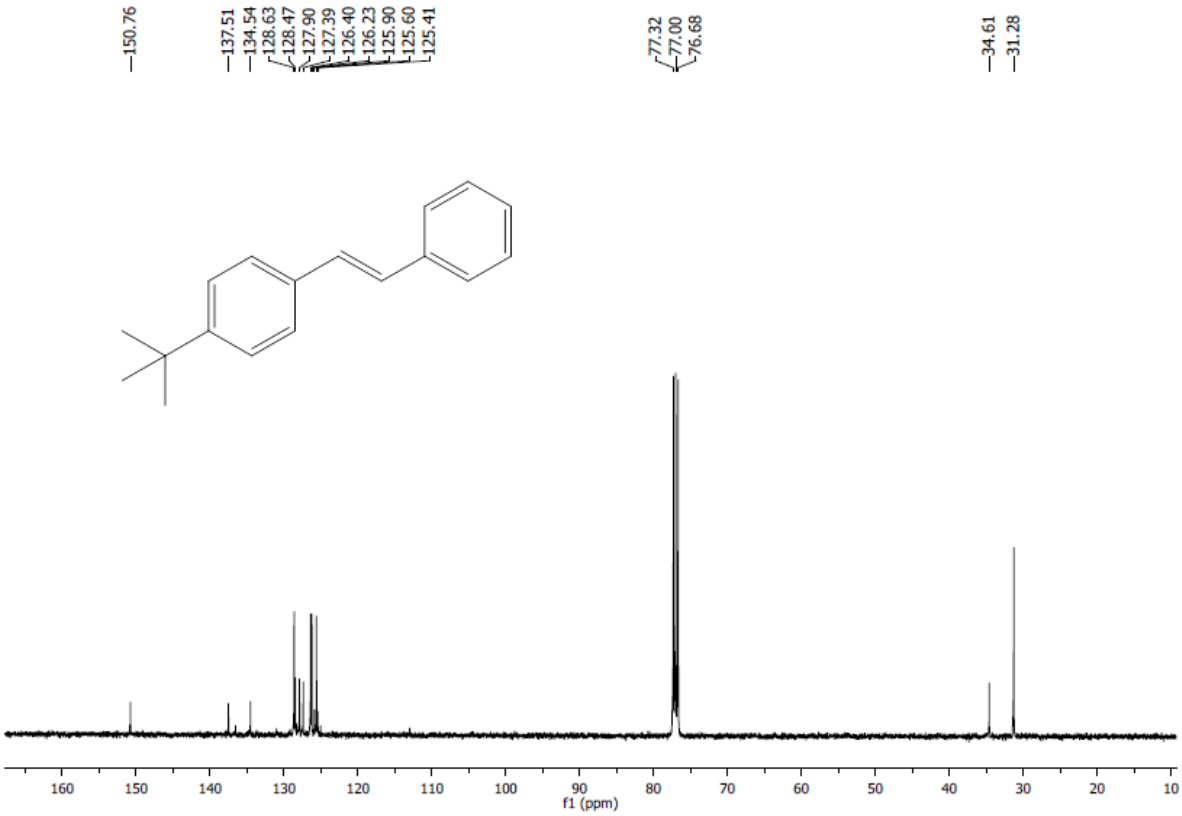


Figure S26: ^{13}C NMR spectrum of **4-tert-butylstilbene**, recorded in CDCl3 at 25 ˚C.

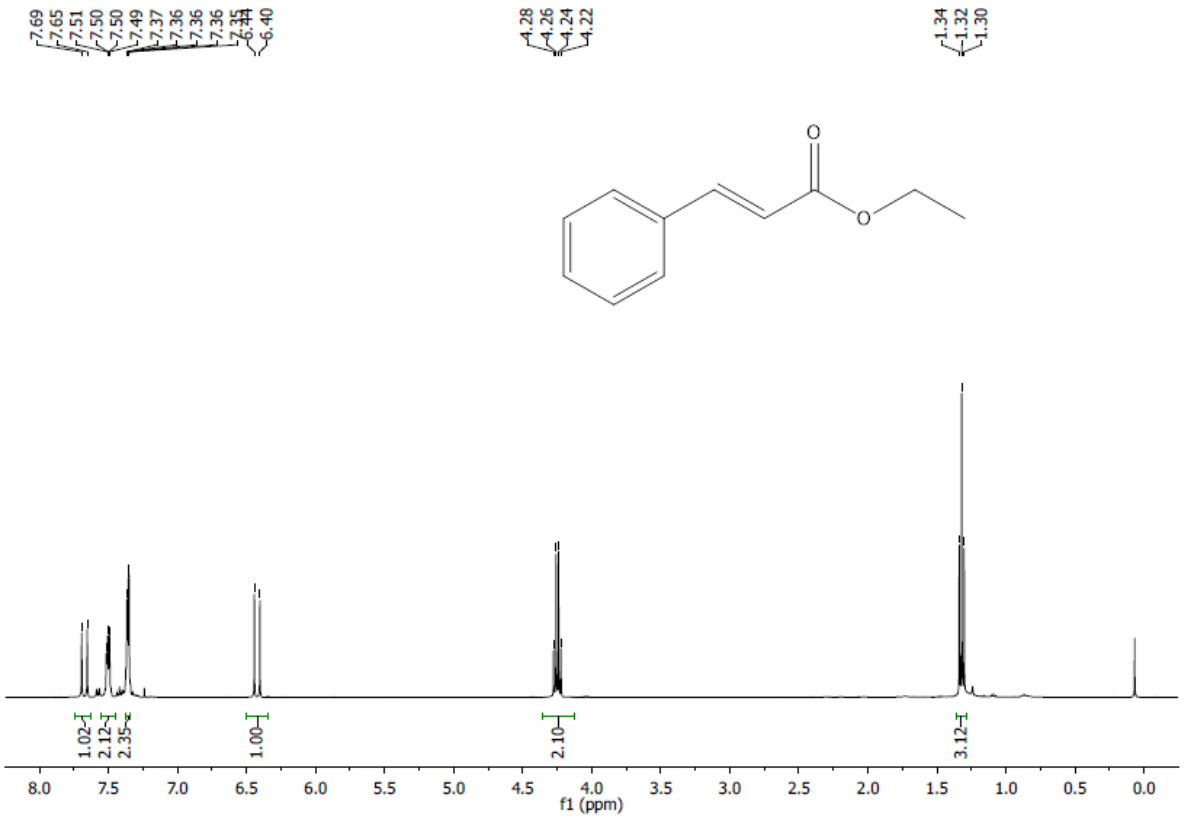


Figure S27: ^{1}H NMR spectrum of **styrene ethyl acrylate**, recorded in CDCl3 at 25 ˚C.

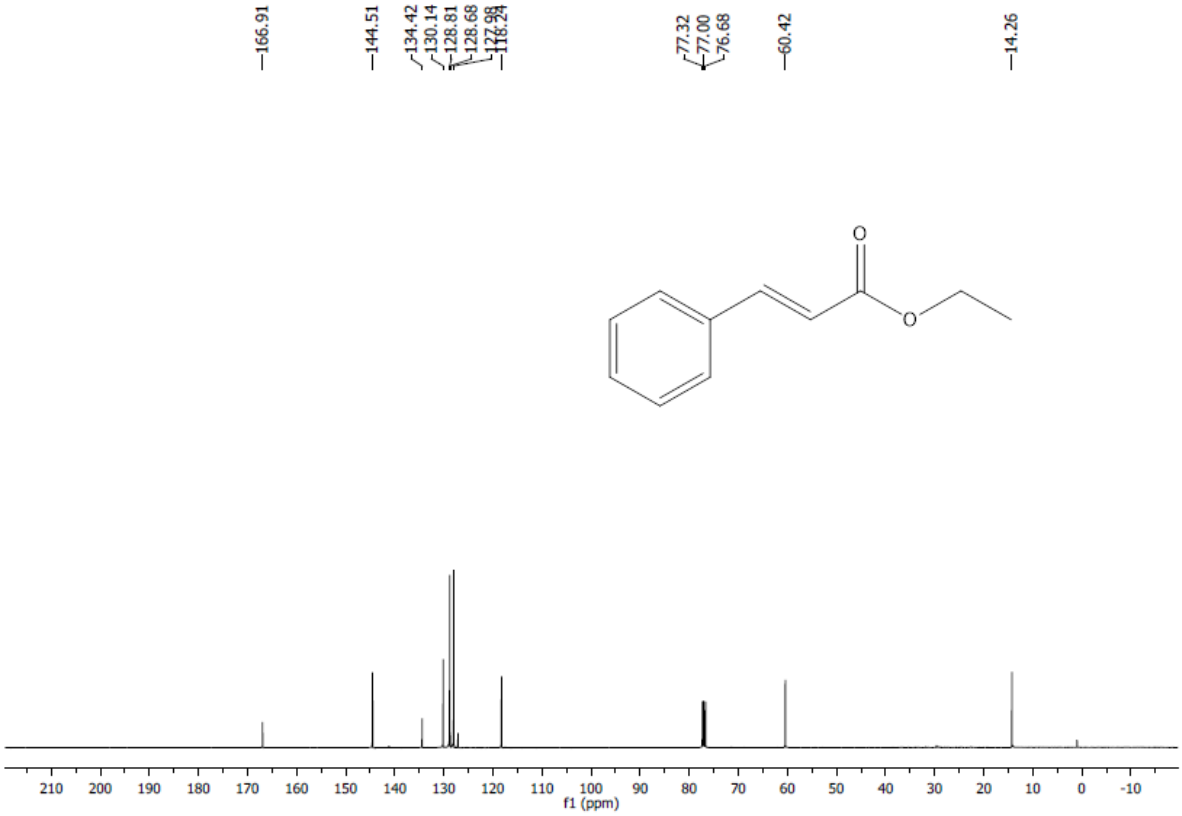


Figure S28: ^{13}C NMR spectrum of **styrene ethyl acrylate**, recorded in CDCl3 at 25 ˚C.

2. Suzuki-Miyaura cross-coupling reactions product NMR spectra (^{1}H and ^{13}C)

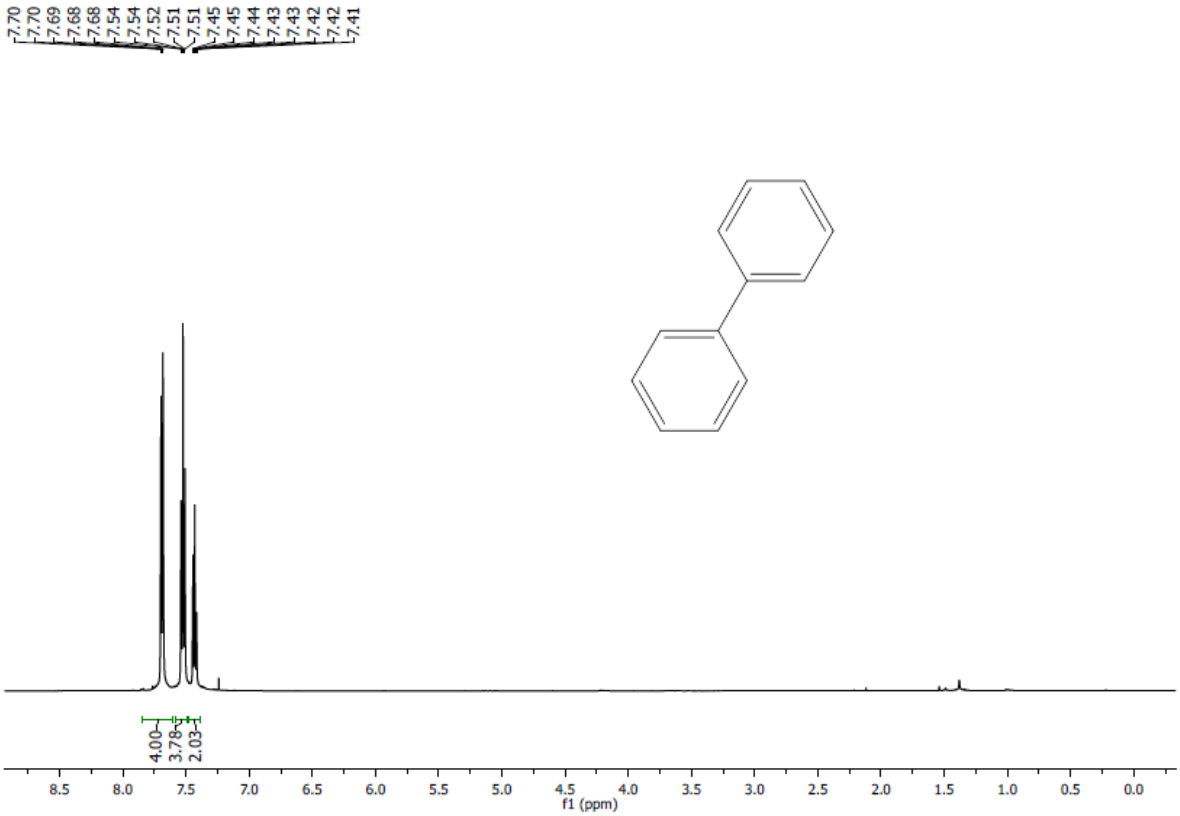


Figure S29: ^{1}H NMR spectrum of **biphenyl**, recorded in CDCl3 at 25 ˚C.

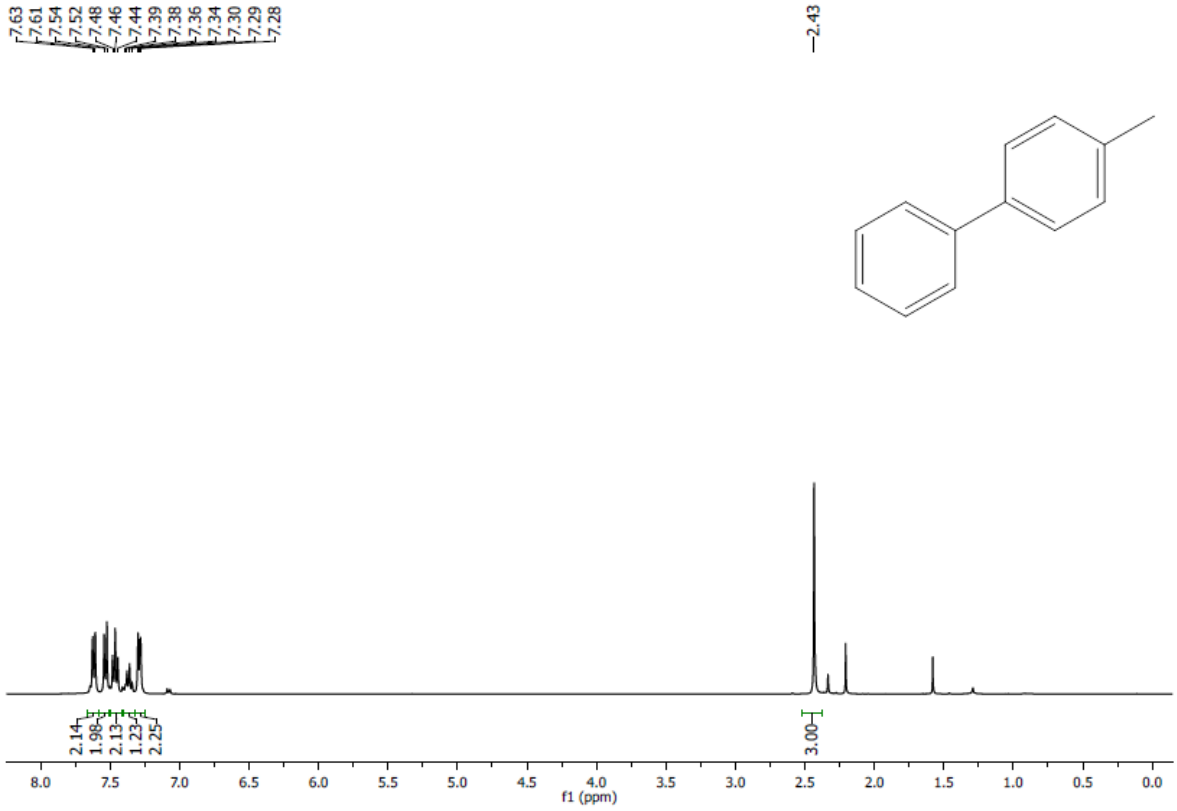


Figure S30: ^{1}H NMR spectrum of **4-methyl biphenyl**, recorded in CDCl3 at 25 ˚C.

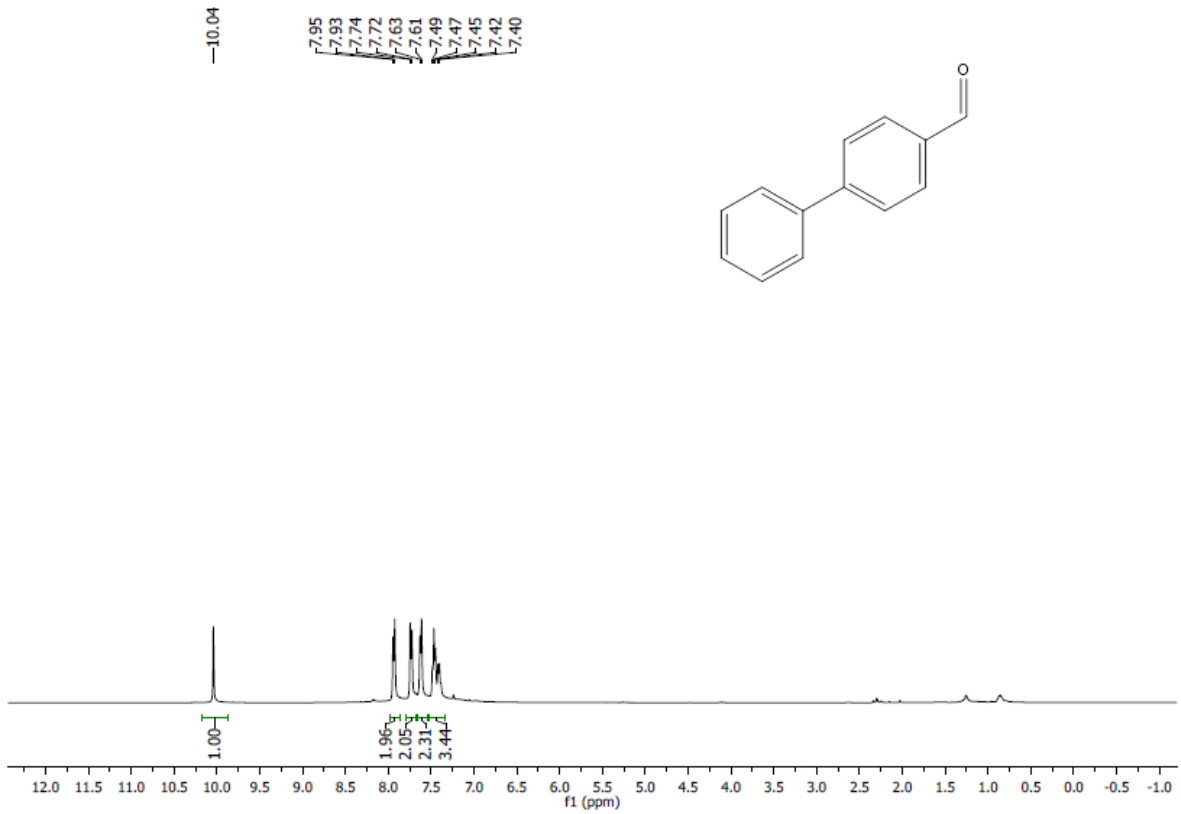


Figure S31: ^{1}H NMR spectrum of **biphenyl-4-carboxaldehyde**, recorded in CDCl3 at 25 ˚C.

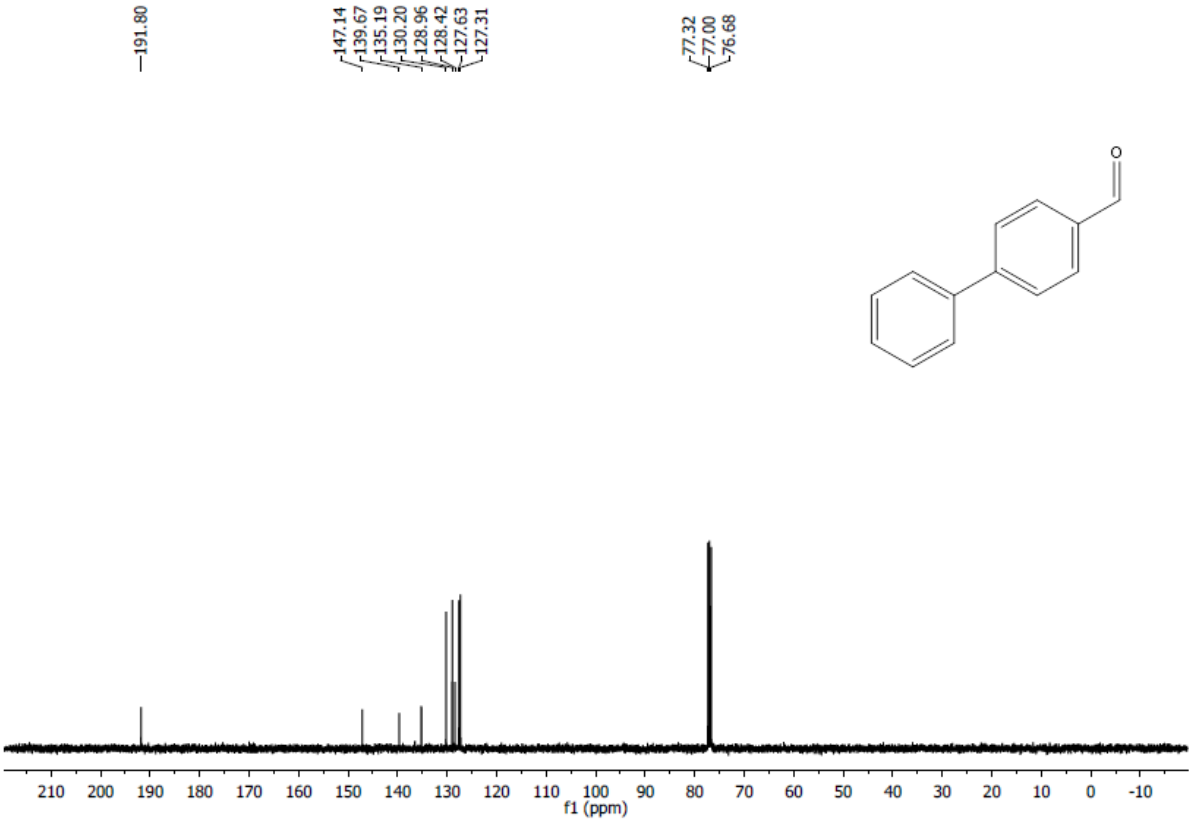


Figure S32: ^{13}C NMR spectrum of **biphenyl-4-carboxaldehyde**, recorded in CDCl3 at 25 ˚C.

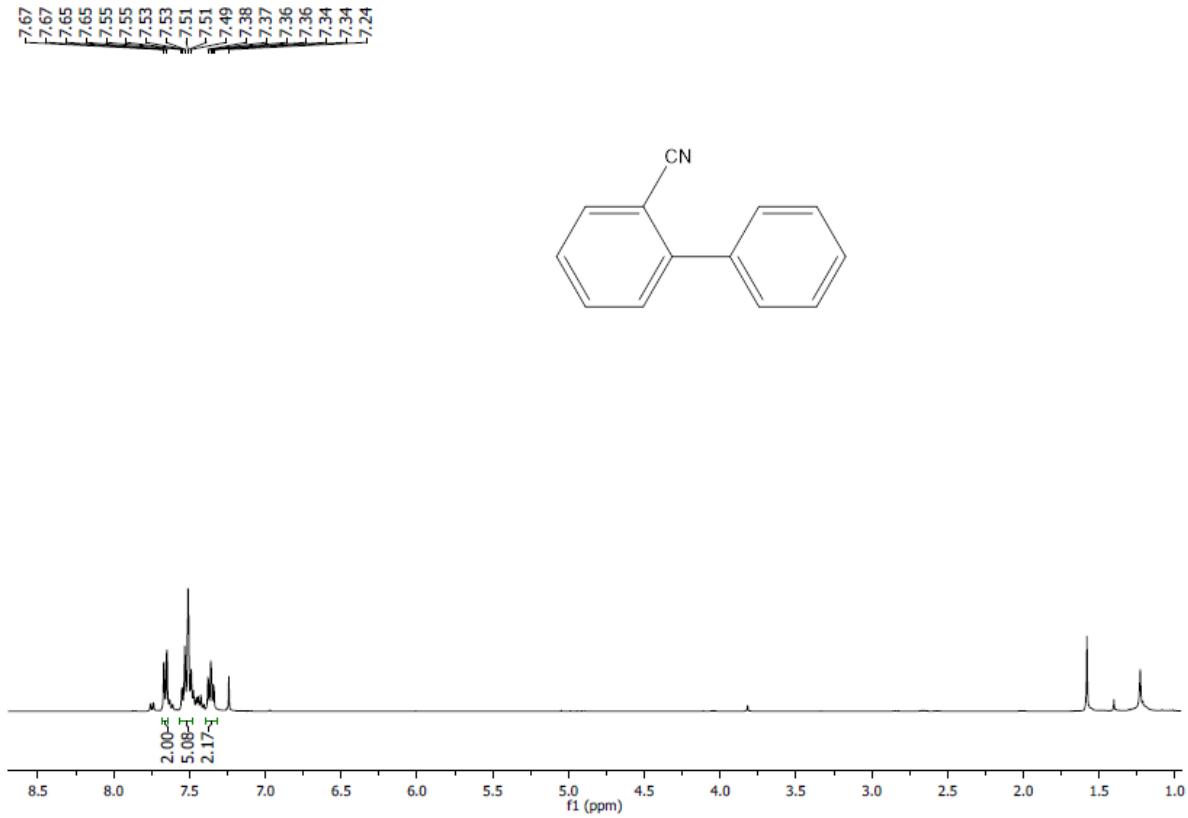


Figure S33: ^{1}H NMR spectrum of **2-cyanobiphenyl**, recorded in CDCl3 at 25 ˚C.

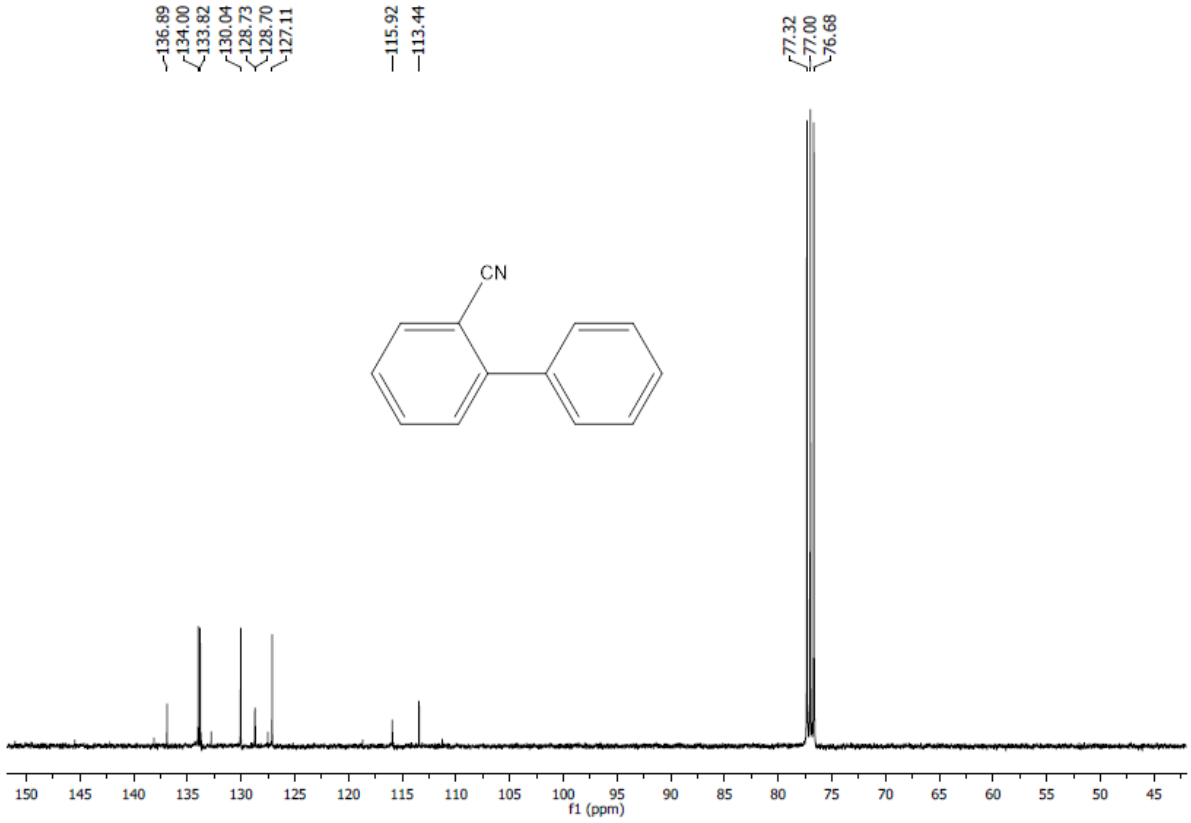


Figure S34: ^{13}C spectrum of **2-cyanobiphenyl**, recorded in CDCl3 at 25 ˚C.

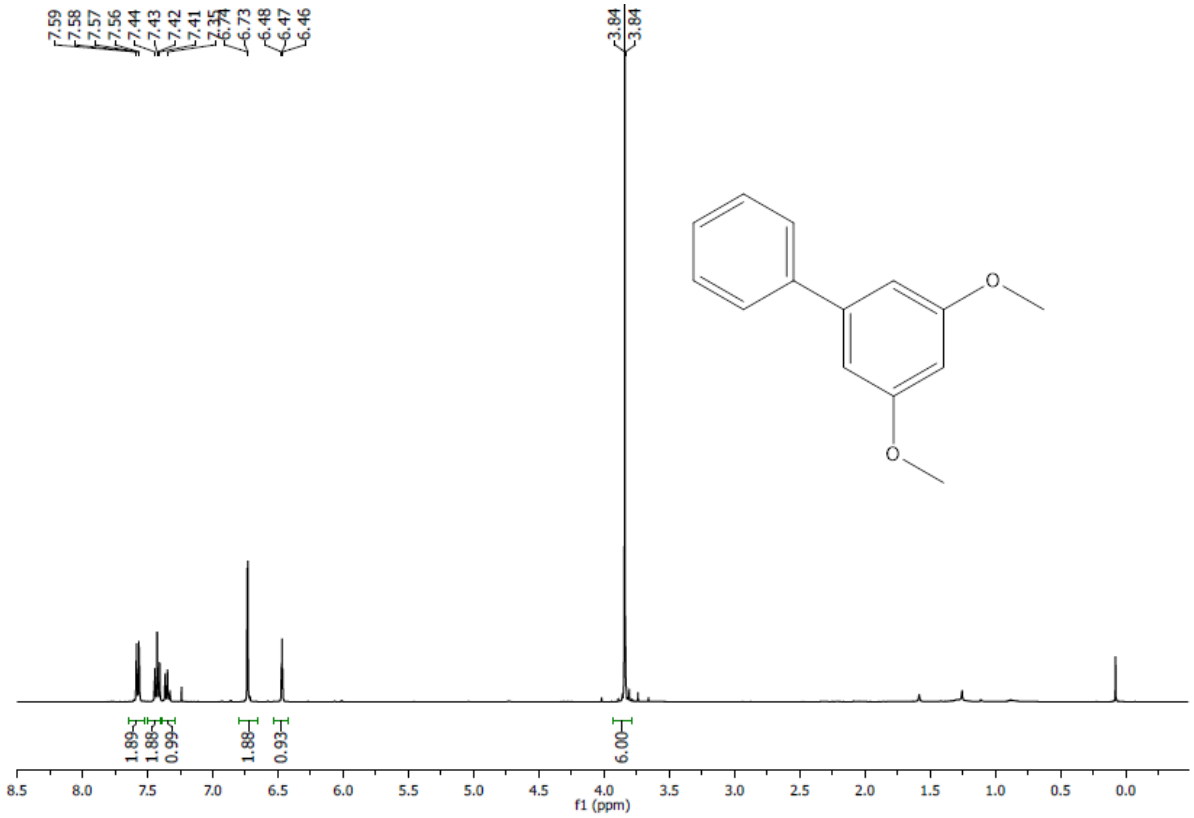


Figure S35: ^{1}H NMR spectrum of **3,5-dimethoxybiphenyl**, recorded in CDCl3 at 25 ˚C.

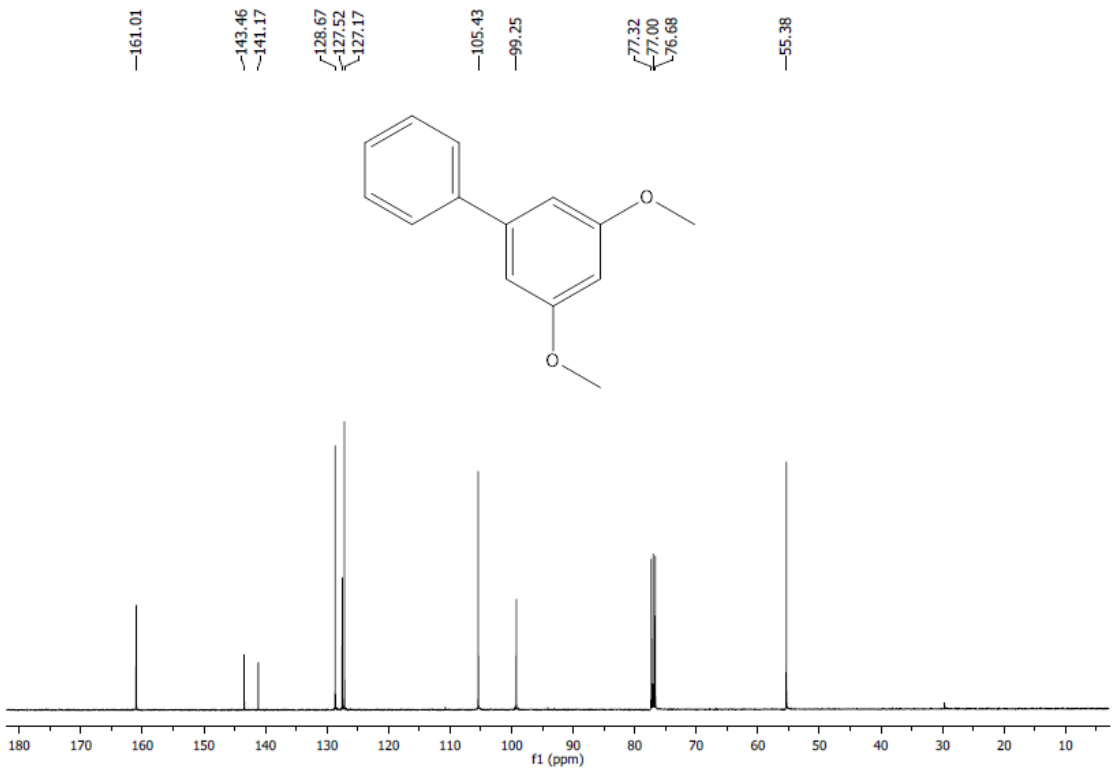


Figure S36: ^{13}C NMR spectrum of **3,5-dimethoxybiphenyl**, recorded in CDCl3 at 25 ˚C.

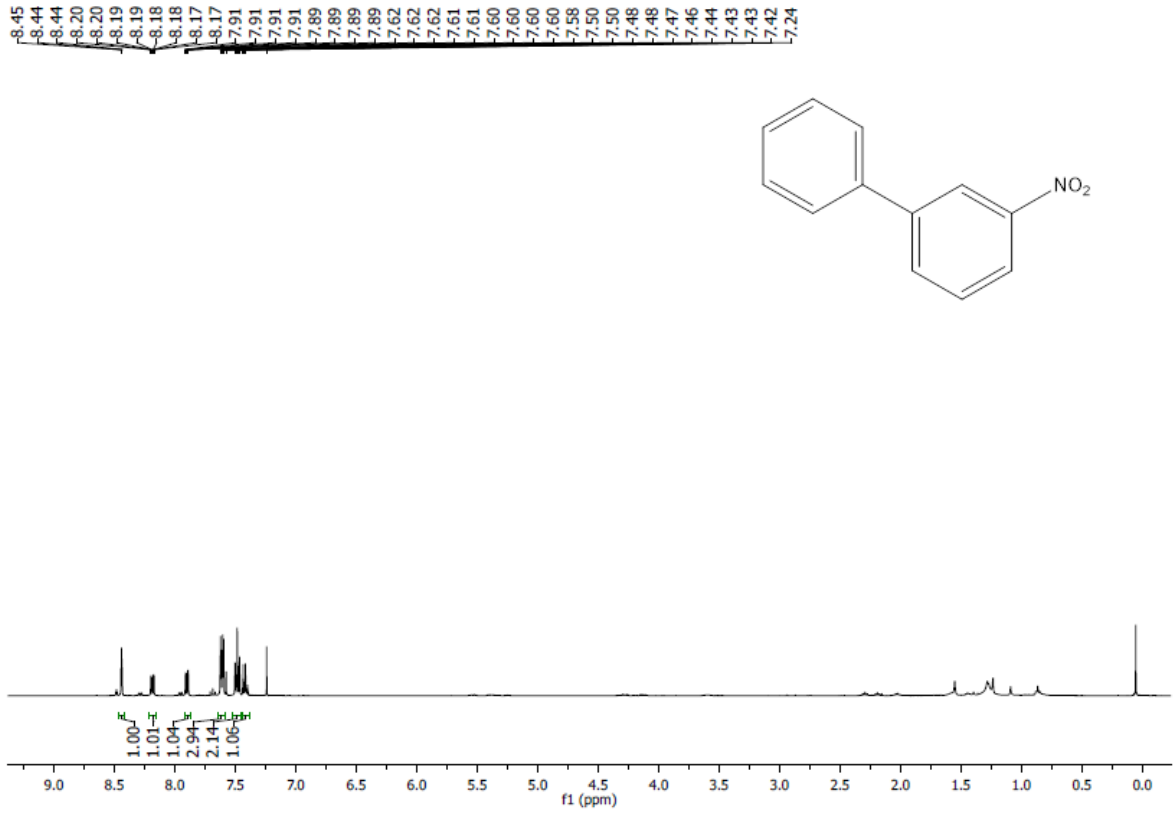


Figure S37: ^{1}H NMR spectrum of **3-nitrobiphenyl**, recorded in CDCl3 at 25 ˚C.

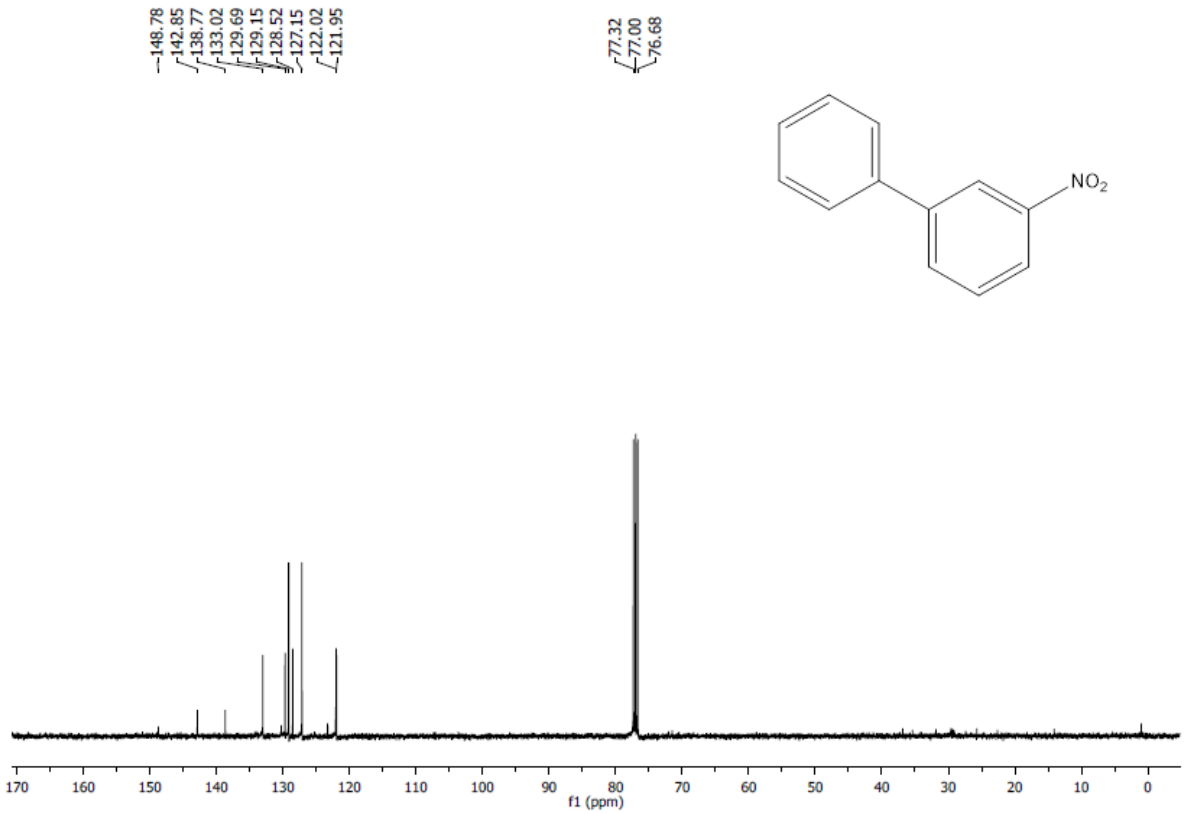


Figure S38: ^{13}C NMR spectrum of **3-nitrobiphenyl**, recorded in CDCl3 at 25 ˚C.