Supporting Information

Layered double hydroxides as bifunctional catalysts for the aryl borylation under ligand-free conditions

Lorenna C.L.L.F. Silva[1], Vinícius A. Neves[1], Vitor S. Ramos[2], Raphael S. F. Silva[3], José B. de Campos[2], Alexsandro A. da Silva[4], Luiz F. B. Malta[1,*] and Jaqueline D. Senra[1,4,*]

Table of Contents

S1 – Unit cell parameters for LDHs

Table S1: Unit cell parameters calculated using Rietveld refinement from XRD data for layered double hydroxides synthesized with or without sodium carbonate.

Condition applied	*Unit cell parameters LDH*				
	a(Å) ; b(Å)	**c(Å)**	α(°); β(°)	γ(°)	**Crystal system**
without carbonate	3.039204	26.920939	90	120	Rhombohedral
with carbonate	2.978894	22.519661	90	120	Rhombohedral

Table S2: Unit cell parameters calculated using Rietveld refinement from XRD data for layered double hydroxides synthesized pH=8 or 10.

Condition applied	*Unit cell parameters LDH*				
	a(Å) ; b(Å)	**c(Å)**	α(°); β(°)	γ(°)	**Crystal system**
pH=10	2.980682	22.576496	90	120	Rhombohedral
pH=8	2.978894	22.519661	90	120	Rhombohedral

Table S3: Unit cell parameters calculated using Rietveld refinement from XRD data for layered double hydroxides with post synthesis separation by filtration or centrifugation.

Condition applied	*Unit cell parameters LDH*				
	a(Å) ; b(Å)	**c(Å)**	α(°); β(°)	γ(°)	**Crystal system**
filtration	2.981242	22.576728	90	120	Rhombohedral
centrifugation	2.978894	22.519661	90	120	Rhombohedral

Table S4 : Unit cell parameters calculated using Rietveld refinement from XRD data for layered double hydroxides with or without post synthesis washing with ethanol/acetone.

Condition applied	*Unit cell parameters LDH*				
	a(Å) ; b(Å)	**c(Å)**	α(°); β(°)	γ(°)	**Crystal system**
washing	2.986764	22.497899	90	120	Rhombohedral
no washing	2.978894	22.519661	90	120	Rhombohedral

S2- General experimental details

All reagents and solvents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VNMRSYS-500 spectrometer at 25ºC. Chemical shift values are reported in δ (ppm) downfield from tetramethylsilane with reference to internal residual solvent. Multiplicities of signals are designated as follows: s = singlet; d = doublet; t = triplet; m

= multiplet; br = broad. The chemical shifts (δ) for ^{13}C are referenced relative to the signal from the carbon of the deuterated solvent. The yields were determined by GC-MS on a Shimadzu GC-2010 chromatograph with a DB-5 capillary column (30.0m x 0.25mm x 0.25μm) through corrected normalization of the peak areas.

General procedure for the borylation reaction: Under atmospheric condition, a 5 mL screw cap vial equipped with a magnetic stir bar was charged with bis(pinacolato)diboron (0.375 mmol, 1.5 equiv), aryl halide (0.25 mmol, 1.0 equiv), Na_2PdCl_4 solution, Cu/Al LDH and solvent (3 mL). The reaction vial was capped and stirred at 70ºC for 24h. The reaction mixture was diluted with 5 mL of dichloromethane, washed with water (2 x 15 mL), brine (1 x 15 mL), and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure to afford the crude product. The yields of the products were determined by GCMS analysis. All physical data of known compounds were in agreement with those reported in the literature.[8]

S3 – Spectroscopic data for the products 3, 4, 6, 7, 8, 9

Product 3: The NMR spectra of **3** agree with the literature data [8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, 2H), 7.97 (d, 2 H, ArH), 1.38 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 135.6, 122.4, 84.6, 24.8.

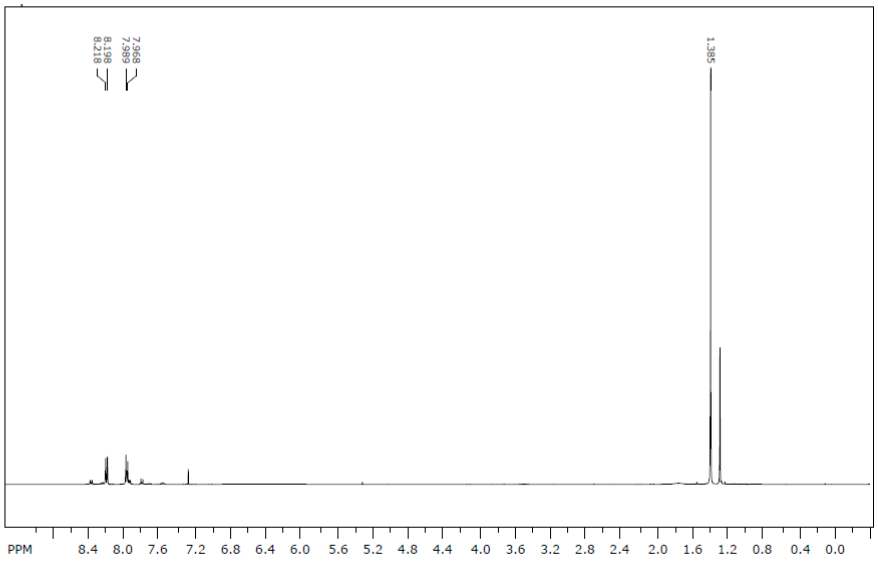


Figure S1: ^{1}H NMR of **3.**

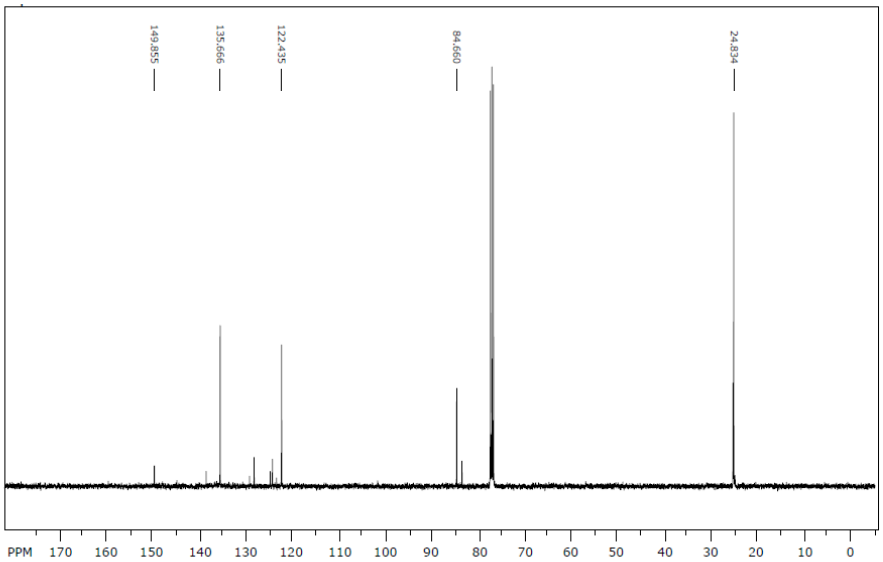


Figure S2: ^{13}C NMR of **3.**

Product 4: Reference [8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 2 H), 6.68 (d, 2 H), 3.70 (s, 2 H, NH_2) 1.29 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 136.4, 114.1, 79.4, 24.6.

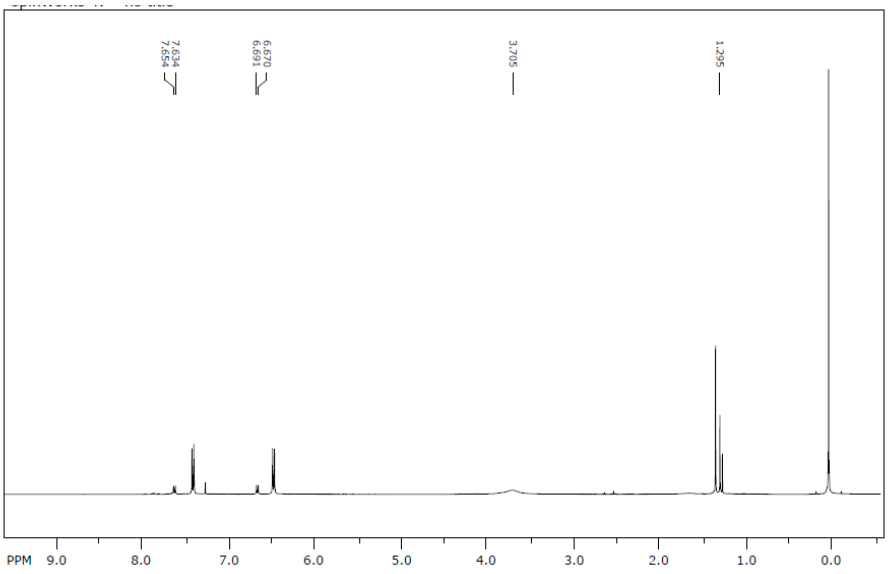


Figure S3: ^{1}H NMR of **4.**

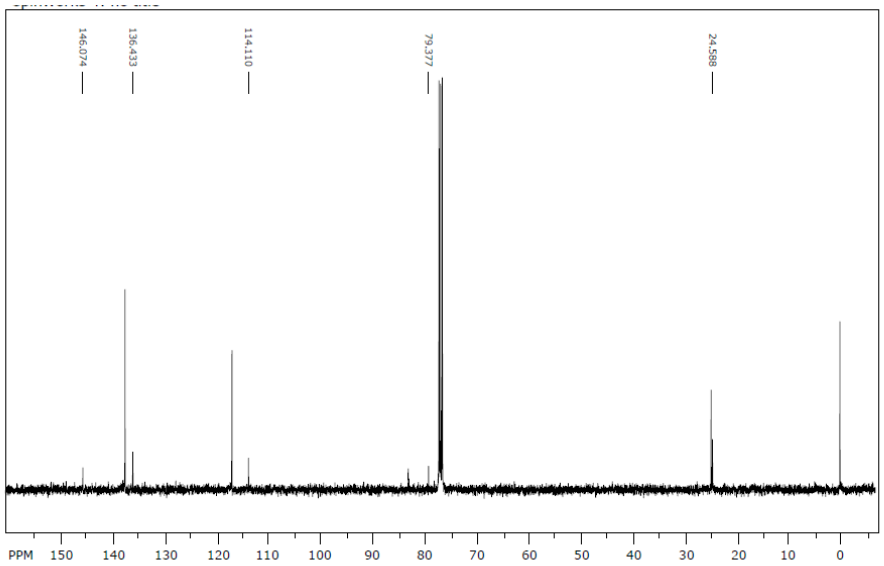


Figure S4: ^{13}C NMR of **4.**

Product 6: The NMR spectra of **6** agree with the literature data [8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, 2 H), 7.89 (d, 2 H), 2.57 (s, 3 H), 1.36 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 138.9, 134.9, 127.2, 84.3, 26.8, 25.0.

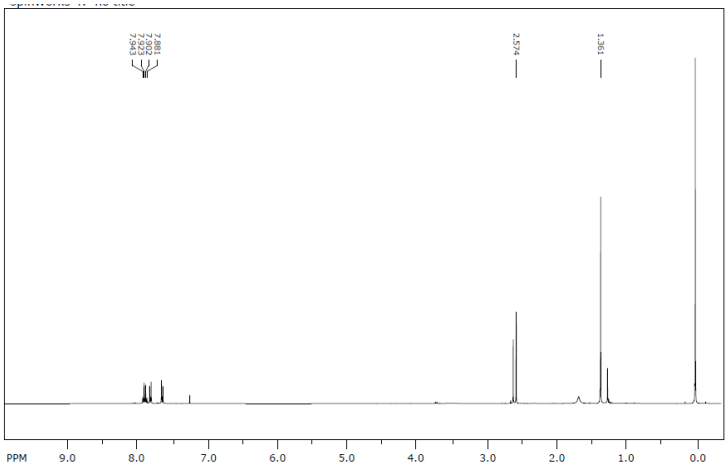


Figure S5: ^{1}H NMR of **6.**

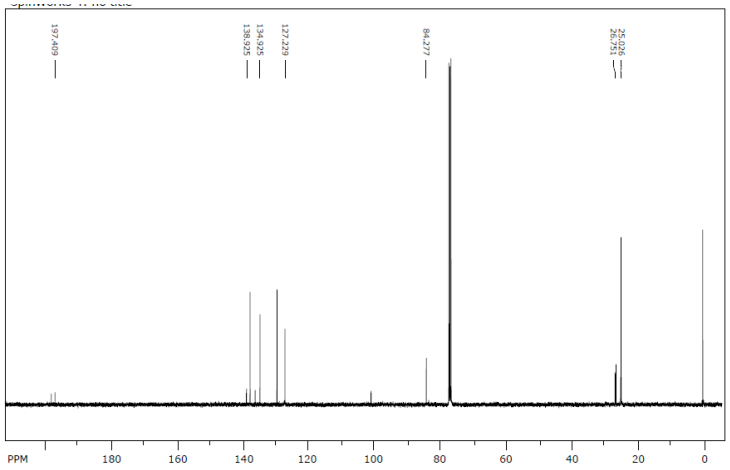


Figure S6: ^{13}C NMR of **6.**

Product 7: The NMR spectra of **7** agree with the literature data [8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4 (d, 2 H), 6.8 (d, 2 H), 3.8 (s, 3H), 1.36 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 133.3, 116.5, 113.0; 56.2, 24.6.

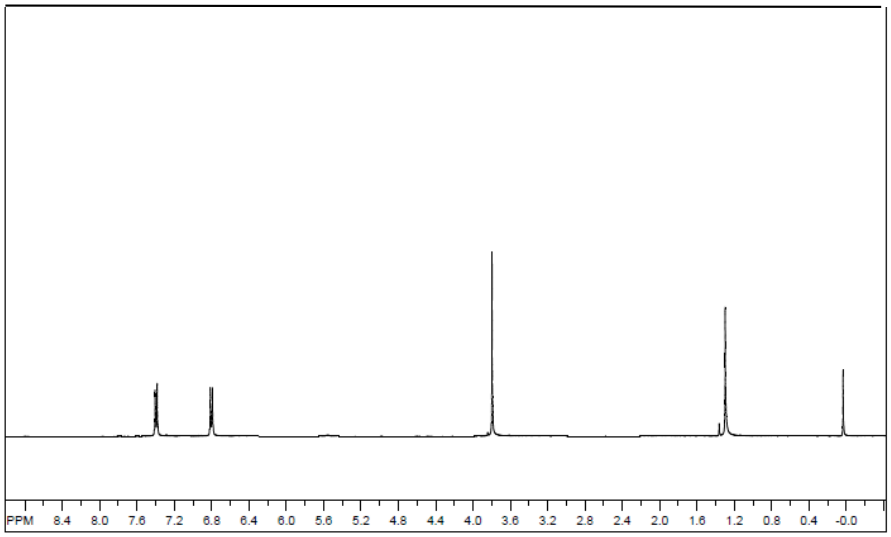


Figure S7: ^{1}H NMR of **7.**

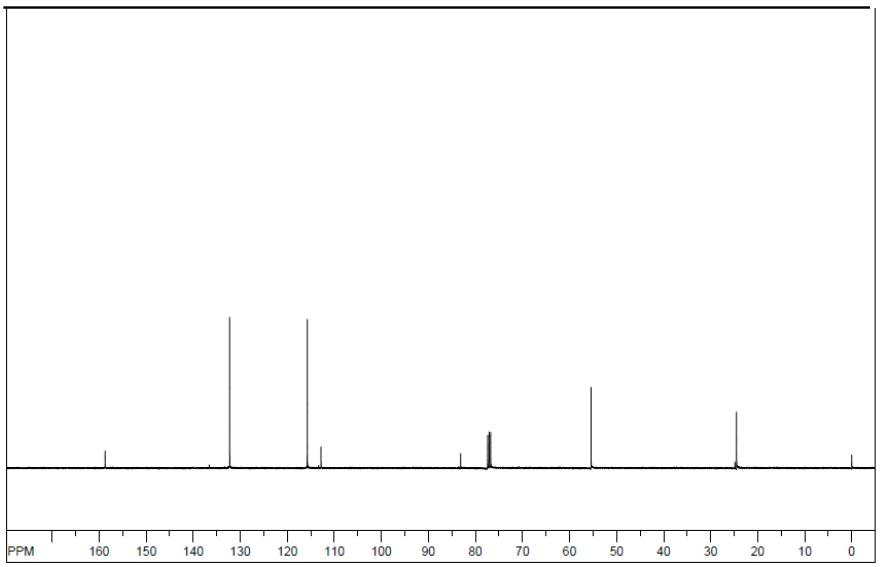


Figure S8: ^{13}C NMR of **7.**

Product 8: The NMR spectra of **8** agree with the literature data [8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 2 H), 7.51 (d, 2 H), 1.35 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 130.9, 126.2, 84.0, 24.8.

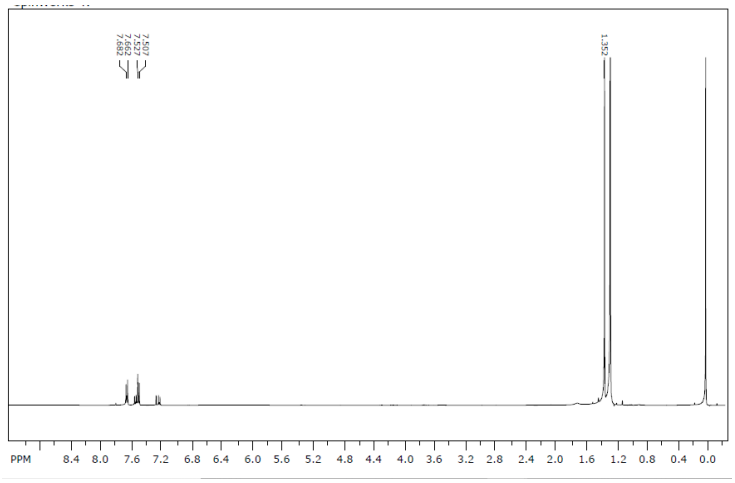


Figure S9: ^{1}H NMR of **8.**

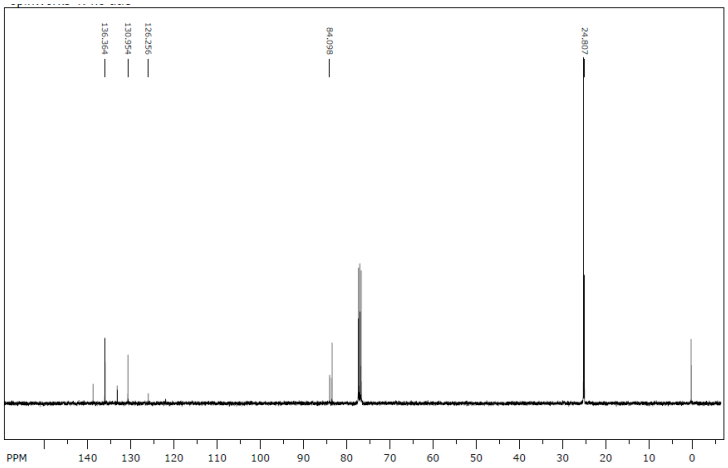


Figure S10: ^{13}C NMR of **8.**

Product 9. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3 (d, 1H), 7.9 – 7.7 (m, 2H), 7.67 – 7.45 (m, 2 H), 7.34 (dd, 2H), 1.36 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.3, 132.1, 131.6, 129.9, 127.9, 127.1, 126.3, 125.8, 122.9; 83.7, 25.2.

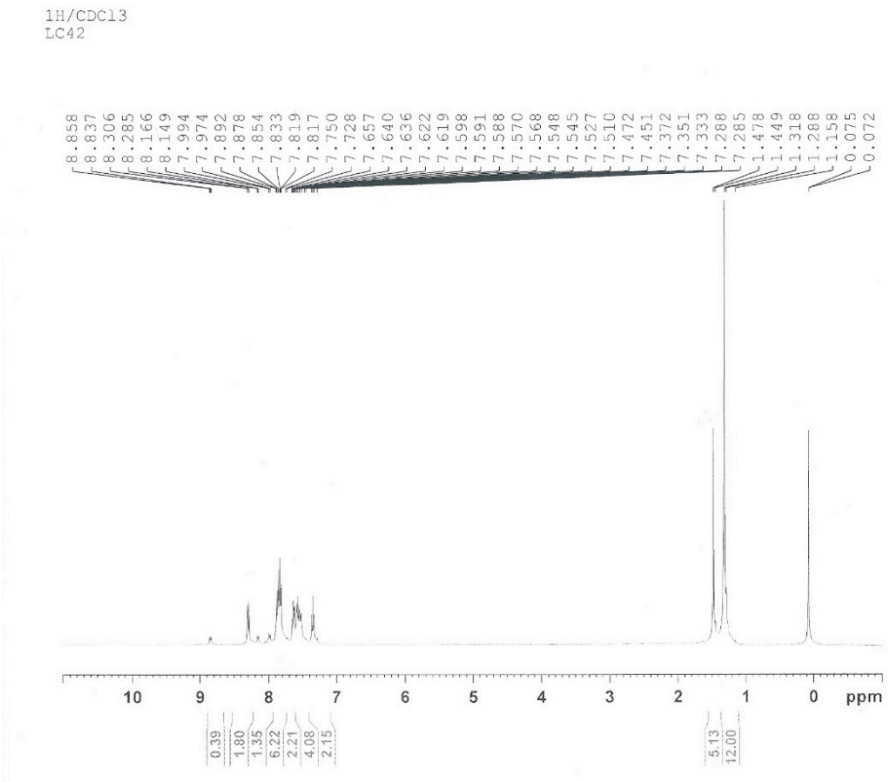
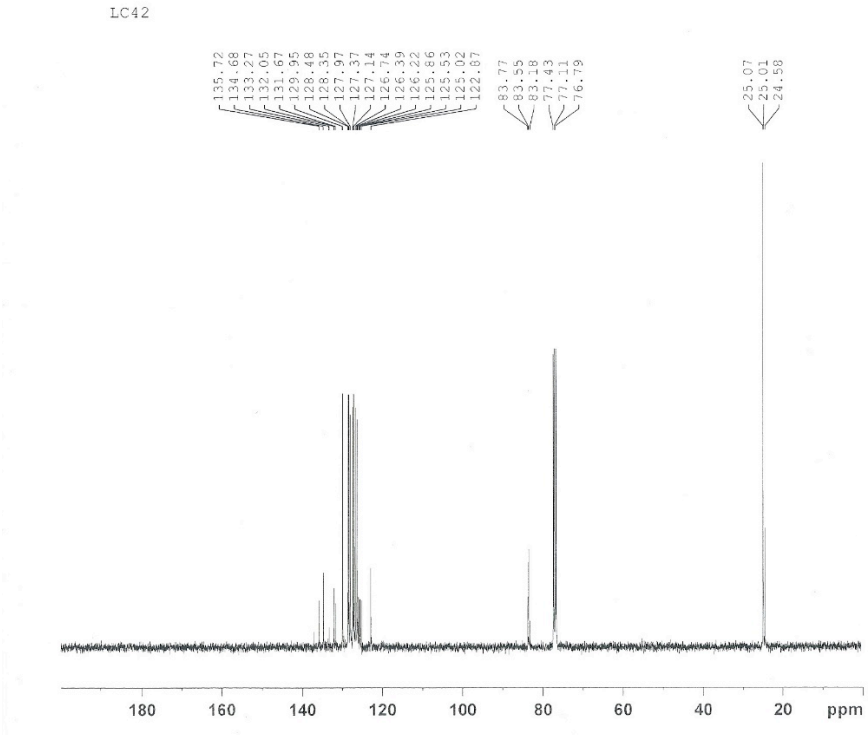


Figure S11: ^{1}H NMR of **9.**



3.

Figure S12: ^{13}C NMR of **9.**