Supporting Information

Oxime-palladacycle complex Supported on Magnetic Nanoparticles: A Recyclable Catalyst for Suzuki-type decarbonylative cross-coupling of esters with aryl boronic acid

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Materials and Methods

The chemicals used are all reagent grade products. The sources of chemicals are as follows: Ferric chloride hexahydrate ($FeCl_3.6H_2O$) (Rankem, India), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) (SRLchem.com), tetraethyl orthosilicate (TEOS) (Rankem, India), 3-chloropropylethoxysilan (CPTES) (Aldrich, India), syn-2-Pyridinealdoxime (Aldrich, India), sodium hexafluorophosphate ($NaPF_6$) (Aldrich, India), palladium chloride ($PdCl_2$) (Spectrochem Pvt.Ltd., India.), lithium chloride (LiCl) (SRL Chemicals, India) and all the solvent employed

were obtained from (E. Merck, India). Organic substrates were purchased from Spectrochem Pvt.Ltd., India, SRL Chemicals, India and TCI chemicals and Aldrich, India.

All the FTIR spectra were recorded using a Perkin-Elmer spectrum 100 FTIR Spectrophotometer in the range 4000-400 cm^{-1} with samples as KBr pellets. CHN element analysis was done using the Perkin Elmer 2400 series II CHN analyzer. The surface area was measured at 77.3 K using the Brunauer-Emmett-Teller (BET) method on a standard module NOVA 1000E from Quantachrome Instruments. The pore size and pore volume were determined using the Barrett-Joyner-Halenda (BJH) model on a Quantachrome Instruments NOVA 1000E. The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku X-ray diffractometer (Minifiex, UK) in the 2θ range of 10–70º at 10º min^{-1} scanning rate with Cu Kα (k = 0.154 nm) radiation. The FESEM analysis was done using "JEOL, JSM Model 7200F" model. A JEOL JSM6390LV scanning electron micrograph attached with an energy-dispersive X-ray detector was used for SEM-EDX analysis. TEM analysis was done using "FEI COMPANY, USA, TECNAI G2 20 S-TWIN (200KV) in the resolution of 2.4Å. ICP-OES analysis of the compounds was performed with a Thermo Scientific™ iCAP™ 7600 inductively coupled plasma-optical emission spectrometer. Vibrating Sample Magnetometer (VSM) were recorded using "Lakeshore, Model:7410 series". Thermogravimetric analysis was performed on a SHIMADZU TGA-50 system utilising an aluminium pan under a N_2 atmosphere at a heating rate of 10 °C min^{-1}. The XPS analysis was performed on an X-ray photo spectrometer of a Thermo Fisher Scientific Instrument (model ESCALAB Xi+). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrophotometer using deuterated solvents.

1.1 Catalyst preparation:

1. Synthesis of Fe_3O_4 MNPs

Magnetic (Fe_3O_4) NPs were synthesized according to the previously reported methods (co-precipitation)[1,2] using $FeCl_3.6H_2O$ (1.29g, 8 mmol) and $FeSO_4.7H_2O$ (1.11g, 4 mmol) in deionized water (20 mL) under nitrogen atmosphere with continuous stirring for 30 min at 60 ° C. Then a black precipitate was formed by adding 10 mL ammonium hydroxide (25% in water v/v) and heated at 60 °C for 1hr. After cooling, the black precipitate was separated using a centrifuge and washed with deionized water and ethanol until it achieved a neutral pH reading. Then these magnetic nanoparticles were dried in a hot air oven and preserved for further use.

2. Synthesis of Fe_3O_4@TEOS

The MNPs (2g) obtained in the previous steps were dispersed in ethanol (20mL) by sonication for 20 min. To this solution, 10 mL of deionized water, TEOS (1.5 mL), and NH_3 (25%) were added and stirred for 24hr at room temperature. The resulting Fe_3O_4@TEOS were collected, washed with water and ethanol, and dried in an oven at 60 ° C.

3. Synthesis of Fe_3O_4@TEOS-CPTES

The Fe_3O_4@TEOS were functionalized with CPTES by refluxing CPTES (1.5 mL) to a suspension of silica-coated MNPs (1g) in anhydrous toluene for 12h at 110 °C. After cooling to room temperature, a brown precipitate was formed and collected by centrifugation and washed with acetone and dried.

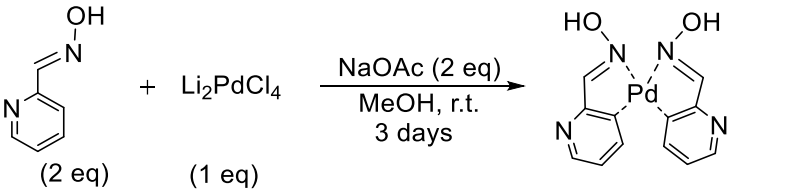
4. Synthesis of Fe_3O_4@TEOS-CPTES-oxime

For the synthesis of supported oxime ligand, an ethanolic suspension of Fe_3O_4@TEOS-CPTES (500mg) was added **to *syn* 2-pyridinealdoxime** (1g, 8mmol) and $NaPF_6$ (1.6g, 9.6mmol), and the mixture was stirred at 60 °C for 24h. The next day, the precipitate was separated by centrifugation washed with ethanol and dried for further use.

5. Synthesis of Fe_3O_4@TEOS-palladacycle

In the final step, to a solution of Li_2PdCl_4 (150mg, 0.57 mmol) in methanol (5mL), a methanolic solution of Fe_3O_4@TEOS-CPTES-oxime (500mg) and sodium acetate (65mg, 0.8 mmol) was added and stirred for 3 days at room temperature. Finally, the product Fe_3O_4@TEOS-Palladacycle was collected by an external magnet, washed with methanol and acetone, dried at 60 °C, and stored for further application in decarbonylative cross-coupling reactions.

Synthesis of bis oxime palladacycle:



2-pyridinealdoxime **Oxime palladacycle (A)**

Scheme S1: Synthesis of oxime palladacycle

In a round bottom flask, palladium chloride (100 mg, 0.56 mmol) and lithium chloride (48 mg, 1.12 mmol) were mixed in methanol (5 mL) and stirred for 5h. Complete conversion to Li2PdCl4 was confirmed by the change in colour of the reaction medium from brown to reddish brown. To this, a methanolic solution of syn 2-pyridinealdoxime (68 mg, 0.56 mmol) and sodium acetate (46 mg, 0.56 mmol) was added. The resultant reaction mixture was stirred for 3 days at room temperature. To this, water (10 mL) was added, and the corresponding oxime palladacycle complex precipitated and was filtered off. The residue was washed repeatedly with methanol and acetone, dried under oven at 60 °C, and stored for further use.[3]

ICP-OES Analysis

Sample preparation for ICP-OES (Metal digestion):

5 mg of Fe_3O_4@TEOS-palladacycle was taken in a beaker and acidify with aqua regia. The resultant reaction mixture was heated under a hot plate until complete dissolution of palladium

particle contained in the catalyst. Upon continued heating, the clear and transparent solution evaporates to dryness. After cooling to room temperature, the residue was dissolved in water and transferred to a 25 mL volumetric flask. Water was further added to makeup volume.

Characterization Data of the Catalyst

FTIR

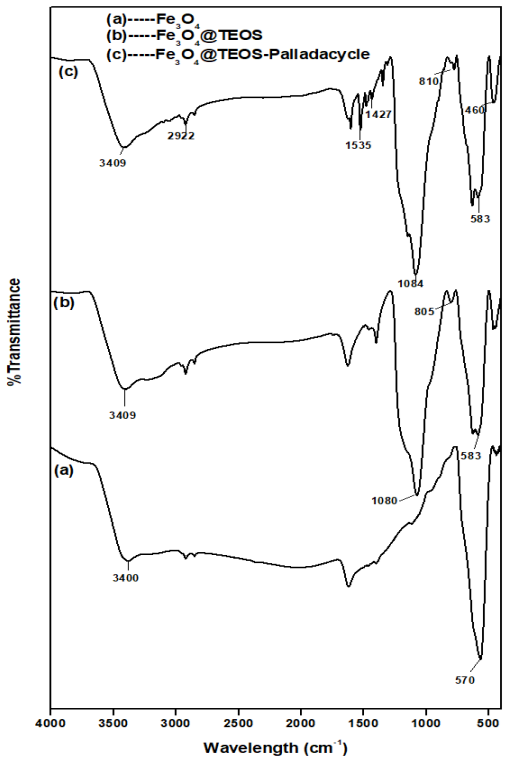


Fig. S1 FTIR spectra of (a) Fe_3O_4 (b) Fe_3O_4@TEOS (c) Fe_3O_4@TEOS-palladacycle

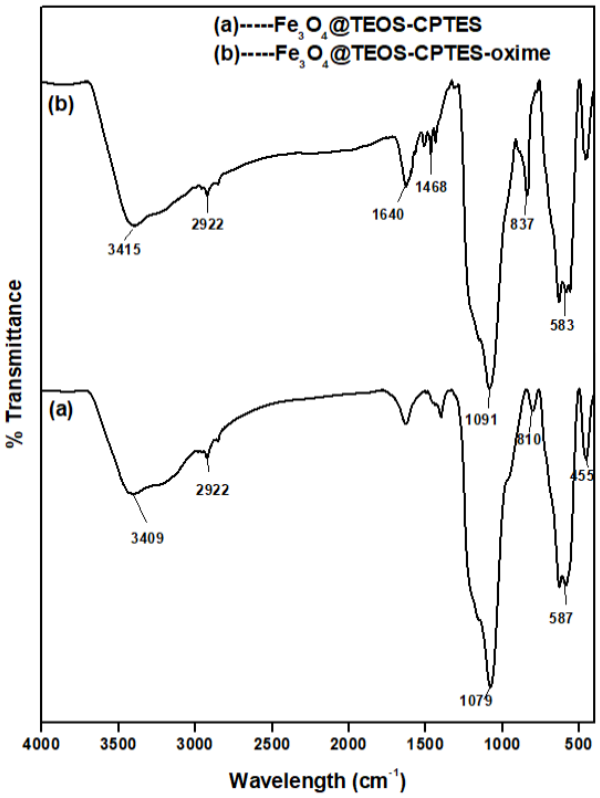
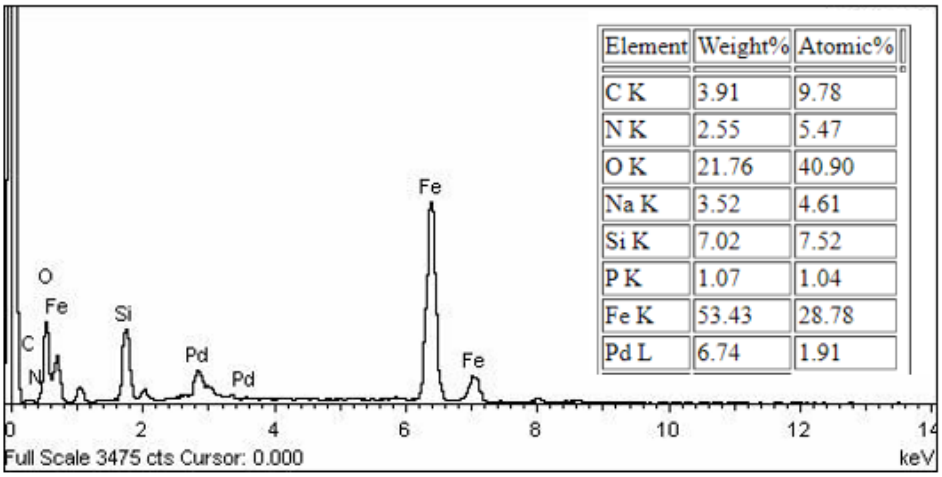


Fig. S2 FTIR spectra of (a) Fe_3O_4@TEOS-CPTES (b) Fe_3O_4@TEOS-CPTES-oxime

SEM-EDX:



Element	Weight%	Atomic%
C K	3.91	9.78
N K	2.55	5.47
O K	21.76	40.90
Na K	3.52	4.61
Si K	7.02	7.52
P K	1.07	1.04
Fe K	53.43	28.78
Pd L	6.74	1.91

Fig. S3 EDX spectra of Fe_3O_4@TEOS-palladacycle

FESEM:

(a) **(b)**

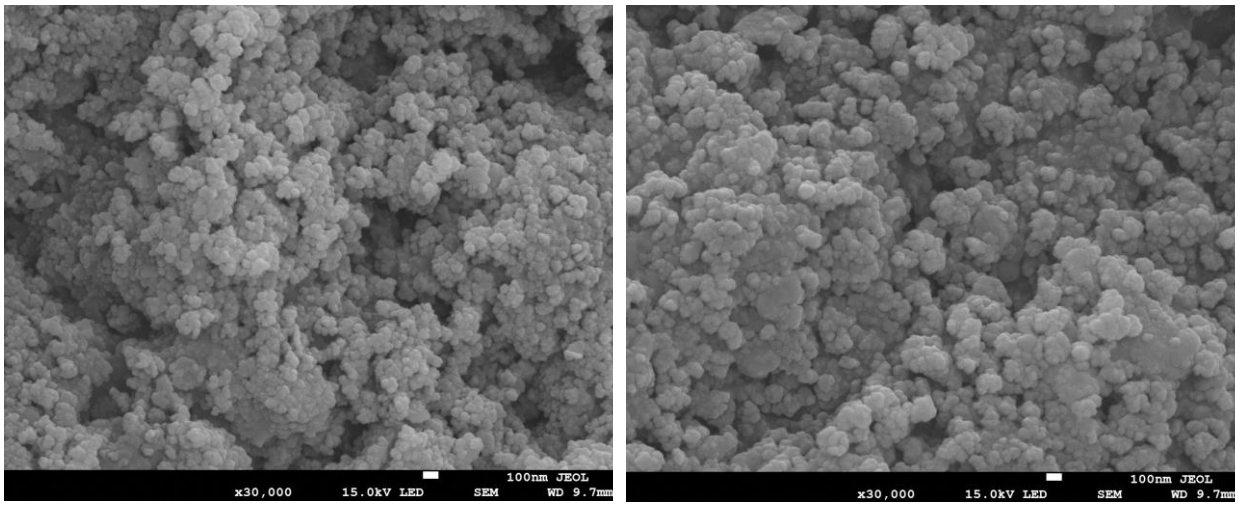


Fig. S4 FESEM images (a) Fe_3O_4 MNPs, (b) Fe_3O_4@TEOS-palladacycle

HRTEM:

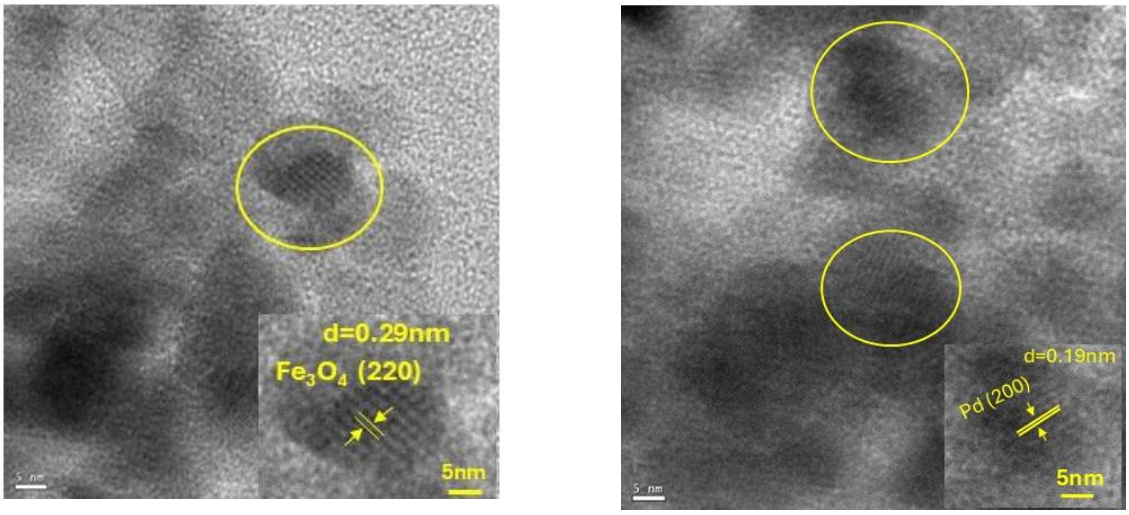


Fig. S5 HRTEM with lattice fringe of Fe_3O_4 and Fe_3O_4@TEOS-palladacycle

EDS elemental mapping

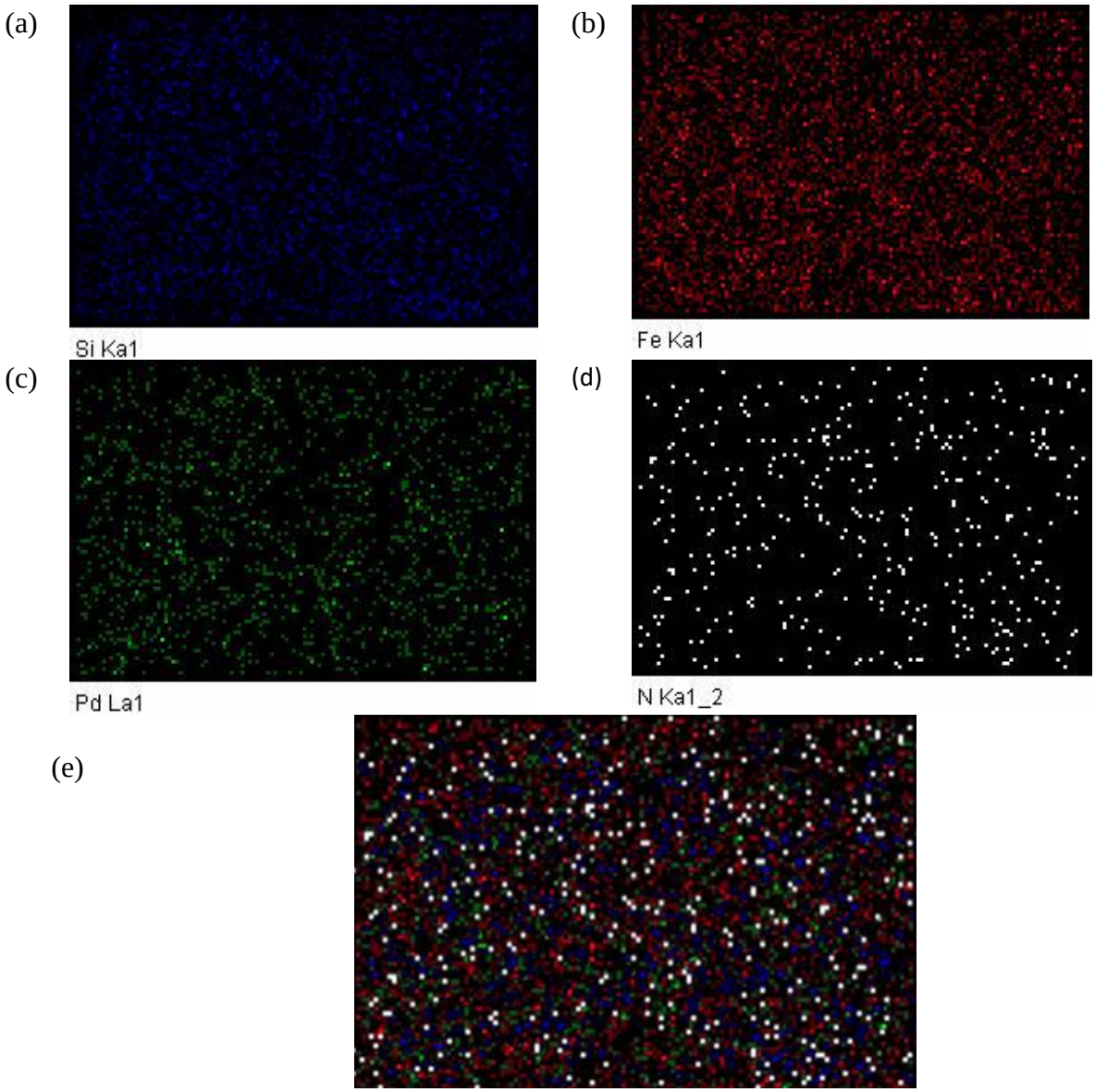


Fig. S6 EDS elemental mapping of (a) Si (b) Fe (c) Pd (d) N and (e) overlap image of Fe_3O_4@TEOS palladacycle

Magnetic property:

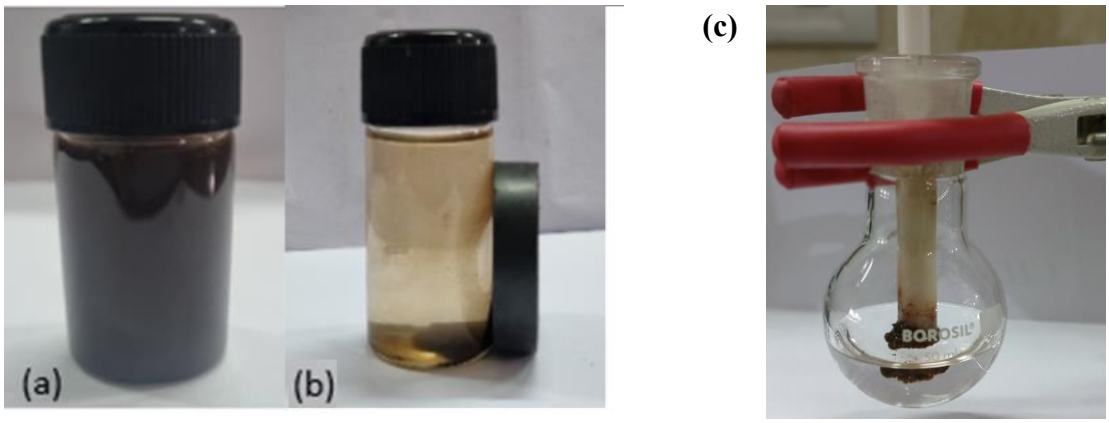


Fig. S7 (a) Uniform dispersion and (b, c) simple separation of the catalyst using an external magnetic field

XPS Analysis:

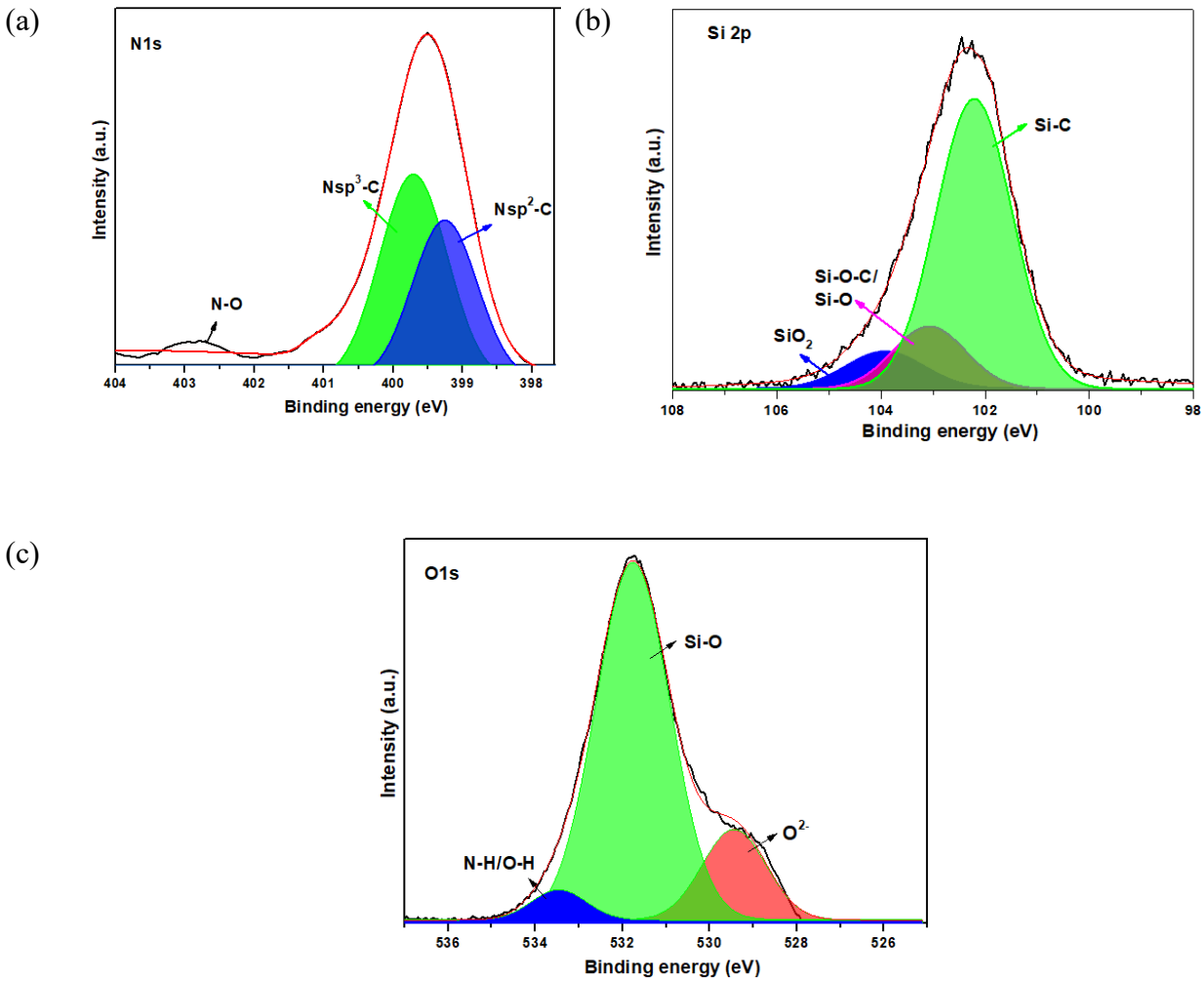


Fig. S8 XPS pattern of (a) N 1s (b) Si 2p (c) O 1s

Table S1: structural parameters of Fe_3O_4, Fe_3O_4@TEOS and Fe_3O_4@TEOS-palladacycle

Sample	Crystal structure	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)[a]	Magnetic particle size (nm)[b]
Fe_3O_4	Cubic	40.9	0.136	3	10.88
Fe_3O_4@TEOS-palladacycle	cubic	28.8	0.088	3.8	7.06

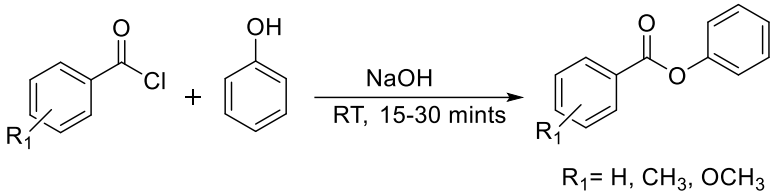
[a]Calculated by the BJH method. [b]Calculated by the Scherrer equation based on XRD patterns.

Preparation for Phenyl esters:

Representative Procedure of Esters

In a well-corked boiling tube or a small conical flask, mix 0.5 g phenol and 10 mL 5% NaOH. Benzoyl chloride (2mL) is added in little amounts at a time, and the mixture is vigorously stirred with occasionally cooling under running or cold water. After 15 minutes, the solid benzoate

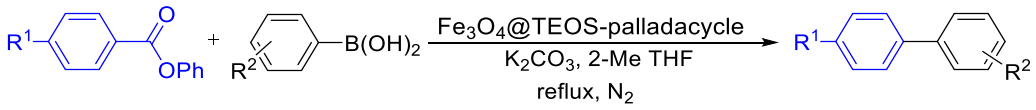
separates, and the solution should be alkaline at the end of the reaction; if it is not alkaline or oily, add another solid pellet of NaOH and shake. Collect the benzoate, wash it thoroughly with cold water, and then recrystallize it in ethanol.



Scheme S2: Synthesis of aryl esters

Pd-Catalyzed Decarbonylative Cross-Coupling

A 50-mL round bottom flask containing a magnetic stirring bar was dried with a heat gun *in vacuo* for 2 min and filled with N_2 after cooling to room temperature. The RB was charged with a mixture of aromatic ester **1** (1 mmol), arylboronic acid **2** (1.2 mmol), K_2CO_3 (2 mmol), catalyst (15 mg, 0.0171 mmol Pd) and 2Me-THF (4 mL). The reaction mixture was stirred at reflux in an oil bath for 12 h. After the reaction mixture had cooled to room temperature, it was diluted with EtOAc. The filtrate was concentrated *in vacuo* and the residue was purified by silica-gel column chromatography to afford biaryl **3**.



Reaction Optimization:

Effect of solvents on decarbonylative cross-coupling reactions of esters

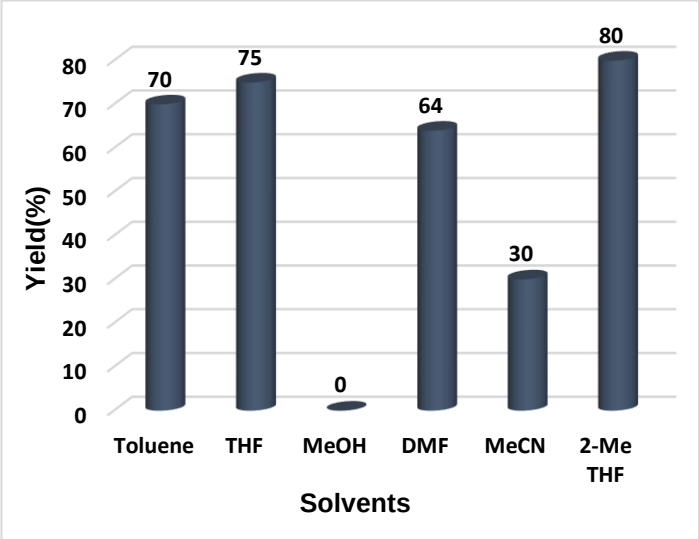


Fig. S9 Effect of solvents on decarbonylative cross-coupling reactions of esters

Effect of bases on decarbonylative cross-coupling reactions of esters

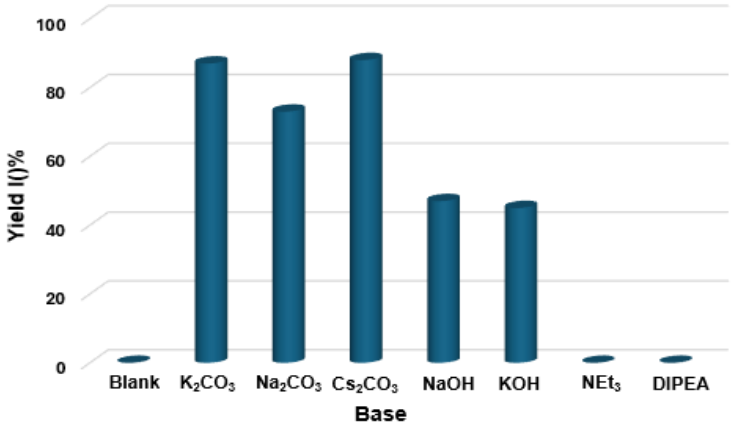
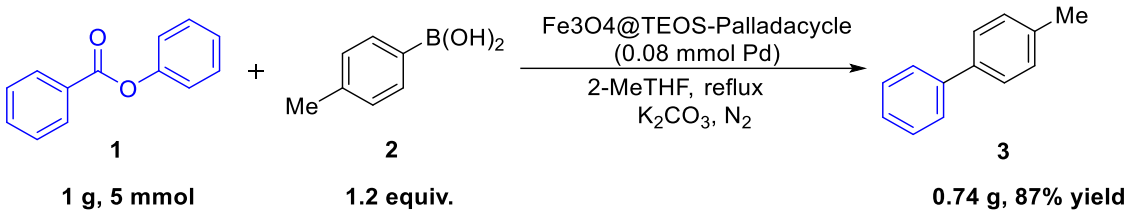


Fig. S10 Effect of bases on decarbonylative cross-coupling reactions of esters

General procedure for scale up synthesis:

A 250-mL round bottom flask containing a magnetic stirring bar was dried with a heat gun *in vacuo* for 2 min and filled with N_2 after cooling to room temperature. The RB was charged with a mixture of aromatic ester **1** (1g, 5 mmol), arylboronic acid **2** (0.8g, 6mmol), K_2CO_3 (1.3g,10 mmol), catalyst (75 mg, 0.08 mmol Pd) and 2Me-THF (20 mL). The reaction mixture was stirred at reflux in an oil bath for 12 h. After the reaction mixture had cooled to room temperature, it was diluted with EtOAc. The filtrate was concentrated *in vacuo* and the residue was purified by silica-gel column chromatography to afford biaryl **3** (0.74g, yield 87.2%).

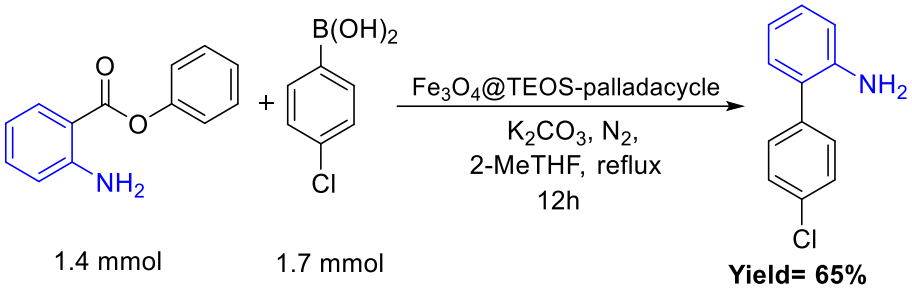
Scale-up synthesis of Cross-coupling product



Procedures for the total synthesis of Boscalid:

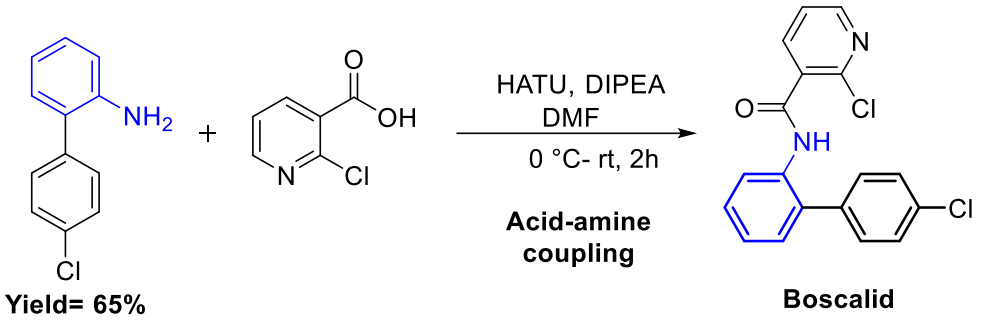
i) Procedure for Suzuki−Miyaura Coupling

A 100-mL round bottom flask containing a magnetic stirring bar was dried with a heat gun *in vacuo* for 2 min and filled with N_2 after cooling to room temperature. The RB was charged with phenyl 2-aminobenzoate (300mg, 1.4 mmol), 4-chloro boronic acid (262 mg, 1.7mmol), K_2CO_3 (2.8 mmol), catalyst (25 mg, 0.03 mmol Pd) and 2Me-THF (6 mL). The reaction mixture was stirred at reflux in an oil bath for 12 h. After the reaction mixture had cooled to room temperature, it was diluted with EtOAc. The filtrate was concentrated *in vacuo* and the residue was purified by silica-gel column chromatography to afford biaryl, 4'-chloro-[1,1'-biphenyl]-2-amine (187 mg, yield 65%).



ii) Procedure for acid-amine coupling for the synthesis of Boscalid:

To a stirred solution of 2-chloronicotinic acid (157 mg, 1 equiv.) in N,N-dimethylformamide (6 mL), N,N-diisopropylethylamine (390 mg, 3equiv.) and hexafluorophosphate azabenzotriazole tetramethyl uronium (HATU) (760 mg 3.0 equiv.) were added at 0°C and stirred for 10 minutes. Then, 4-chloro-[1,1'-biphenyl]-2-amine (245 mg, 1.2 equiv.) in N,N-dimethylformamide (2 mL) was added and reaction mixture was stirred at room temperature for 2 h. After completion of reaction, ice cold water was added to reaction mixture, and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure to get crude which was purified by silica gel column chromatography using ethyl acetate- hexane to afford Boscalid, off white solid. Yield: 160 mg, 73%.



Scheme S3 Synthesis of Boscalid

Hot filtration test and Reusability:

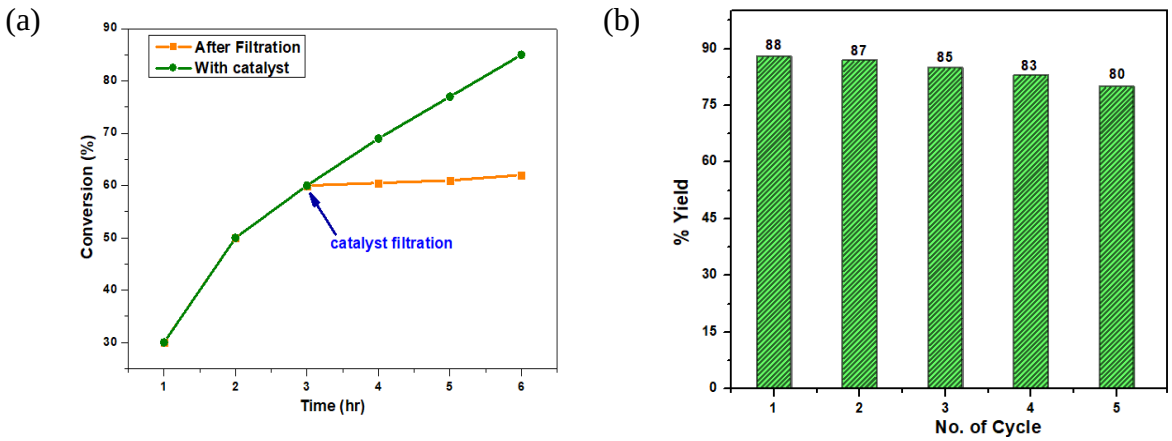
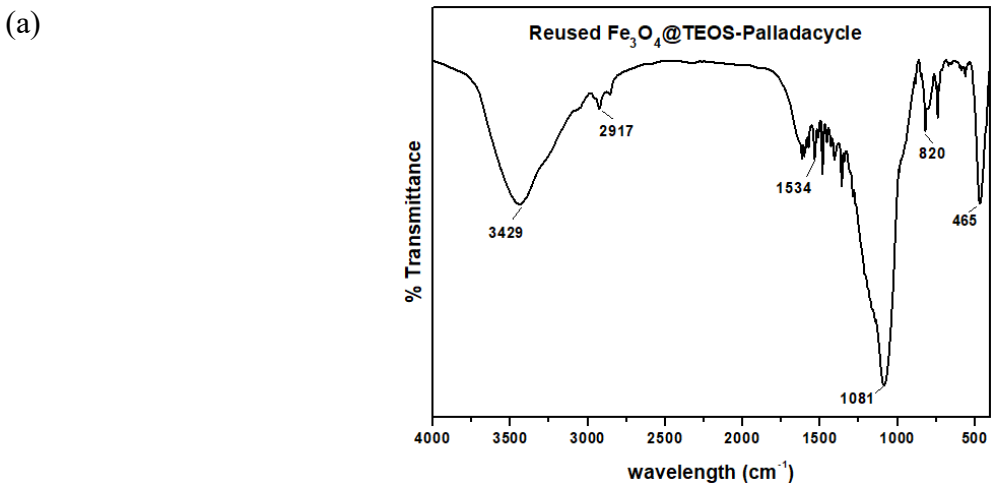


Fig. S11 (a) Hot filtration test; (b) Recyclability of the catalyst

Characterization of reused catalyst:



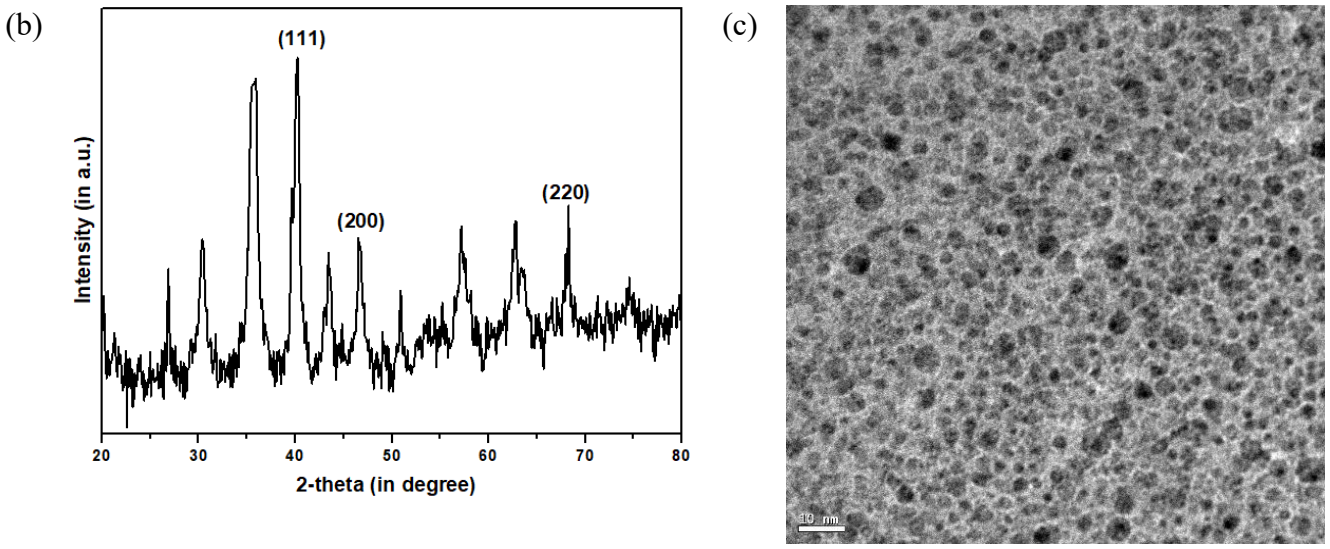


Fig. S12 (a) FTIR spectra (b) P-XRD pattern and (c) TEM images of the catalyst after 5th cycle

Test for elimination of CO gas

A phosphomolibdic acid (PMA)-PdCl2 test was performed to confirm that CO was removed from the reaction mixture (Figure S9, ESI). In this experiment, phosphomolybdic acid [$H_3PO_4(Mo^{VI}O_3)_{12}$] with catalytic amount of $PdCl_2$ oxidises the evolved CO gas into CO_2. This reaction reduces the yellow-colored phosphomolybdic acid to a blue-green-mixed valence heteropolymolybdate complex (Mo^{V} Mo^{VI}).[4]

Preparation of PMA-$PdCl_2$ solution: 50 mg $PdCl_2$ was dissolved in 2 drops of conc. HCl and was diluted with 5 mL of distilled water. Additionally, a cold saturated solution of phosphomolybdic acid (PMA) in water was prepared and then both the solution was mixed in a separate vial in 1:2 (PMA: $PdCl_2$) ratio. Now, this $PdCl_2$: PMA solution was applied some narrow piece of filter paper, which were then dried at room temperature for 1 hr. Then, one strip of the above dried filter paper was inserted into a 50 mL reaction RB using a septum as shown in the fig S9. The reaction mixture was heated at 100°C, as time passes, the yellow colour strip was changes to a dark-blue colour, suggesting the evolution of CO gas from the reaction mixture.

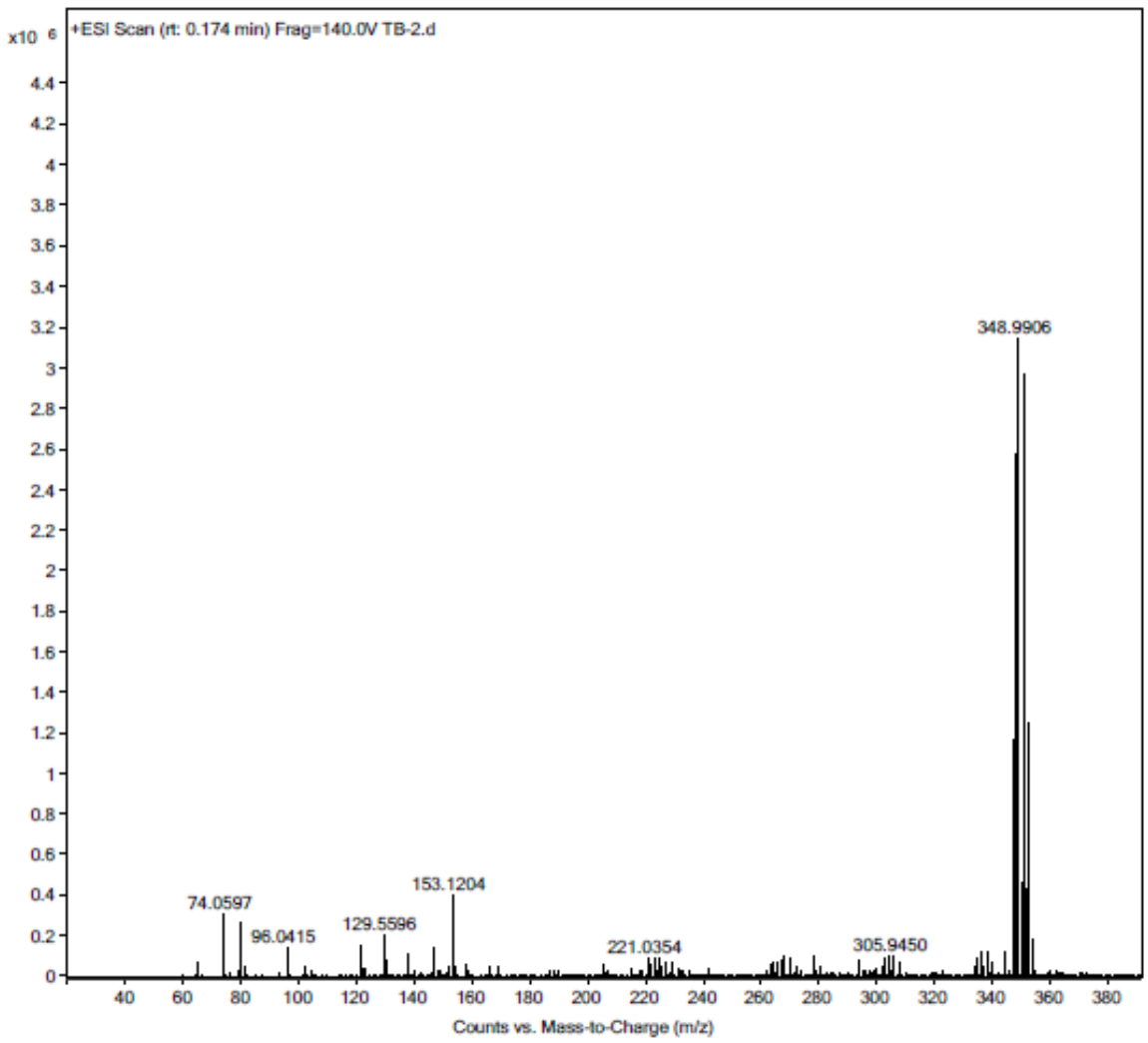
Fig. S13 Evolution of CO gas: Colour change of PMA-$PdCl_2$ strips before and after reaction

Comparison of the present catalytic system with other reported catalysts:

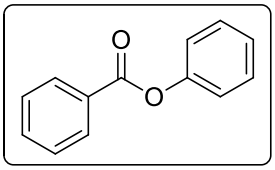
Table S2. Comparative Study of the present catalyst with earlier reported catalysts for the decarbonylative cross-coupling reaction of aryl boronic acid with different electrophiles to afford biaryl.

SL	Catalyst	Reaction condition	Coupling patners	Yield (%)	Re-usability	Ref.
1	$Ni(OAc)_2$ (5 mol%), $P(n\text{-}Bu)_3$ (20 mol%)	$ArB(OH)_2$, Na_2CO_3, toluene, 150 °C, 24 h	Aryl esters	99%	NA	5
2	$Ni(COD)_2$ (10 mol%,), PCy_3 (20 mol%)	$ArB(OH)_2$, Cs_2CO_3, toluene, 110 °C, 24h	Aryl esters	51%	NA	6
3	$Pd(OAc)_2$ (5 mol%), dcype (12 mol%)	$ArB(OH)_2$, Na_2CO_3, toluene, 130 °C, 12h	2-azinecarboxylate	92%	NA	7
4	$Ni(COD)_2$ (10 mol%,), PCy_3 (20 mol%)	$ArB(OH)_2$,t-BuOK, toluene, 120 °C, 20h	Ethyl Benzo[h]quinoline-10-carboxylate	81%	NA	8
5	$Pd(OAc)_2$ (5 mol%), dppb (10 mol%)	$ArB(OH)_2$, Et_3N, dioxane, 160 °C ,15 h	Carboxylic acids	95%	NA	9
6	[(1-*t*Bu-ind)PdCl]$_2$ (7.5 mol%), PPh_3 (30 mol%)	$ArB(OH)_2$, $NaHCO_3$,1,4-dioxane, 160 °C, 15 h	Aroyl Chlorides	92%	NA	10
7	$Pd(OAc)_2$ (5 mol%), 1,4-bis(diphenylphosphaneyl)butane (10 mol%)	$ArB(OH)_2$, Piv_2O, H_3BO_3 Et_3N, dioxane, 160 °C, 15 h.	Heterocyclic carboxylic acids	92%	NA	11
8	**Fe_3O_4@TEOS-palladacycle (1.71 mol% Pd)**	**$ArB(OH)_2$, K_2CO_3, 2-Me-THF, 100 °C, 10h**	**Aryl esters**	**91%**	**5 times**	**present work**

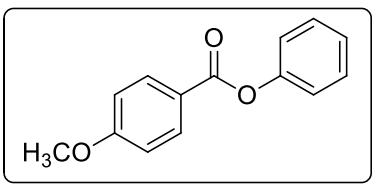
HR-MS data of oxime palladacycle:



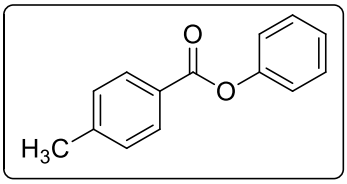
Characterization data of the starting materials of the Suzuki-type decarbonylative cross-coupling reaction



Phenyl benzoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 12.0 Hz, 2H), 7.64 (dd, 1H), 7.54 - 7.42 (m, 4H), 7.30 -7.22(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.31, 151.10, 133.71, 130.30, 129.71, 129.62, 128.70, 126.01, 121.85

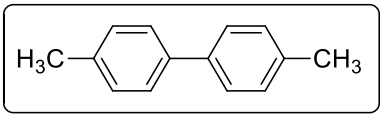


Phenyl 4-methoxybenzoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 12.0 Hz, 2H), 7.42 (dd, 2H), 7.26 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 163.98, 151.16, 132.39, 129.53, 125.82, 121.98, 121.90, 113.94, 54.76

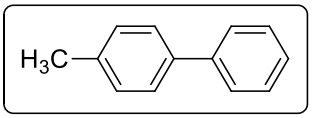


Phenyl 4-methylbenzoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.04 Hz, 2H), 7.48 – 7.35 (m, 2H), 7.37–7.15 (m, 5H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.36, 151.14, 144.50, 130.32, 129.55, 129.38, 126.93, 125.88, 121.86, 21.85

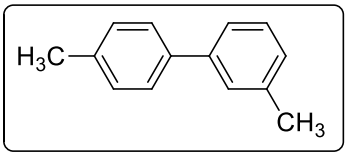
Characterization data of the product of the Suzuki-type decarbonylative cross-coupling reaction



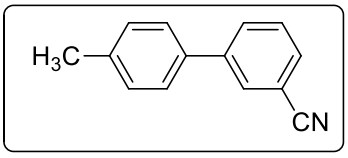
4,4'-dimethyl-1,1'-biphenyl (Table 2, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 2.39 (s, 6H)



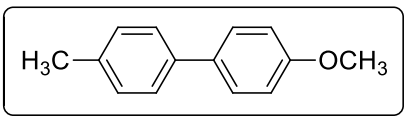
4-methyl-1,1'-biphenyl (Table 2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.51–7.41 (m, 3H), 7.35–7.31 (m, 3H), 7.27-7.23 (m, 2H), 2.40 (s, 3H).



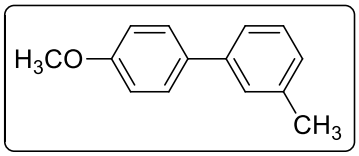
3,4'-dimethyl-1,1'-biphenyl (Table 2, entry 3): 1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (dd, J = 8.0, 1.8 Hz, 2H), 7.54-7.36 (m, 5H), 7.30-7.26 (m, 1H), 2.55 (s, *3*H), 2.52 (s, 3H)



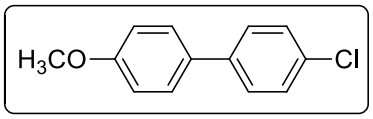
4'-methyl-[1,1'-biphenyl]-3-carbonitrile (Table 2, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.77 (m, 2H), 7.63-7.44 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H)



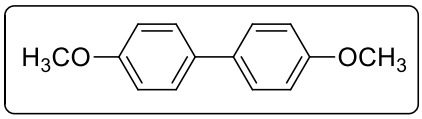
4-methoxy-4'-methyl-1,1'-biphenyl (Table 2, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.43 (m, 4H), 7.24 (dt, *J* = 7.8, 0.7 Hz, 2H), 6.98- 6.94 (m, 2H), 3.84 (s, 3H), 2.38 (s, 3H)



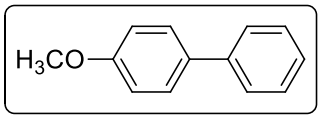
4'-methoxy-3-methyl-1,1'-biphenyl (Table 2, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.36- 7.33 (m, 4H), 7.11-6.95 (m, 2H), 3.84 (s, 3H), 2.41 (s, 3H)



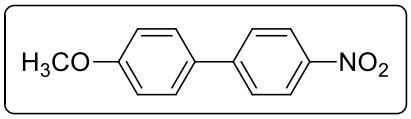
4-chloro-4'-methoxy-1,1'-biphenyl (Table 2, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50- 7.44 (m, 4H), 7.38-7.35 (m, 2H), 6.98-6.95 (m, 2H), 3.93 (d, *J* = 73.9 Hz, 3H).



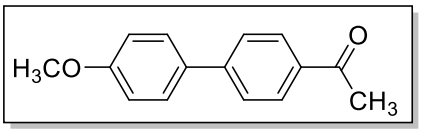
4,4'-dimethoxy-1,1'-biphenyl (Table 2, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.9 Hz, 4H), 6.95 (d, *J* = 8.9 Hz, 4H), 3.83 (s, 6H)



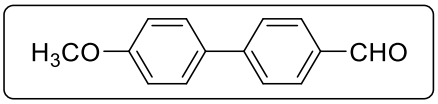
4-methoxy-1,1'-biphenyl (Table 2, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 4H), 7.43-7.39 (m, 3H), 7.29-6.96 (m, 2H), 3.84 (s, 3H)



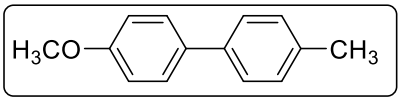
4-methoxy-4'-nitro-1,1'-biphenyl (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H)



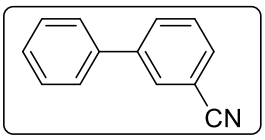
4-acetyl-4'-methoxybiphenyl (Table 2, entry 11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.60 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.92, 159.99, 145.47, 135.34, 132.33, 129.07, 128.48, 126.72, 114.49, 55.49, 26.77



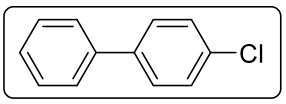
4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (Table 2, entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H)



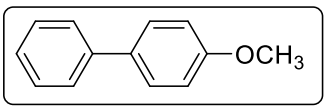
4-methoxy-4'-methyl-1,1'-biphenyl (Table 2, entry 13): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.46-7.43 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H)



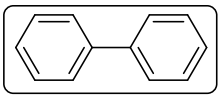
[1,1'-biphenyl]-3-carbonitrile (Table 2, entry 14): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.62-7.39 (m, 7H)



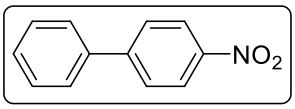
4-chloro-1,1'-biphenyl (Table 2, entry 15): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.4 Hz, 1H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.50 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.42 -7.35 (m, 3H)



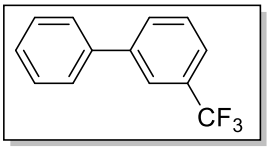
4-methoxy-1,1'-biphenyl (Table 2, entry 16): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 4H), 7.45-7.36 (m, 2H), 7.35-7.25 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H)



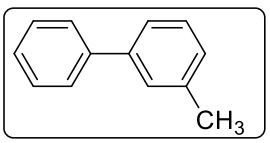
1,1'-biphenyl (Table 2, entry 17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 4H), 7.43-7.34 (m, 2H), 7.38-7.28 (m, 1H), 7.17-7.09 (m, 3H)



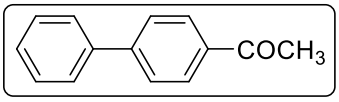
4-nitro-1,1'-biphenyl (Table 2, entry 18): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51-7.43 (m, 3H)



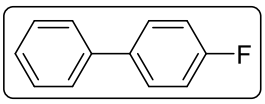
3-(trifluoromethyl)-1,1'-biphenyl (Table 2, entry 19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.78-7.63 (m, 1H), 7.64-7.56 (m, 4H), 7.56-7.42 (m, 3H)



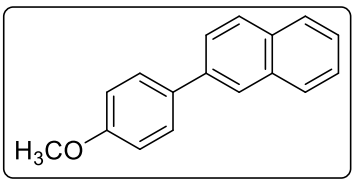
3-methyl-1,1'-biphenyl (Table 2, entry 20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.47-7.33 (m, 5H), 7.19-7.16 (m, 3H), 2.43 (s, 3H)



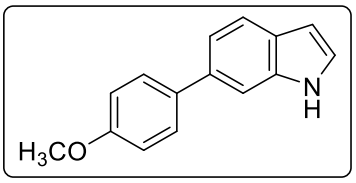
4-Acetylbiphenyl (Table 2, entry 21): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.70-7.61 (m, 4H), 7.48-7.37 (m, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.92, 145.90, 139.97, 135.93, 129.06, 129.02, 128.34, 127.38, 127.34, 26.79



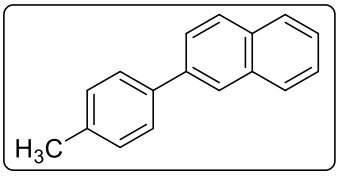
4-fluoro-1,1'-biphenyl (Table 2, entry 22): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56- 7.52 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 7.15-7.10 (m, 2H)



2-(4-methoxyphenyl) naphthalene (Table 2, entry 23): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.83 (m, 3H), 7.53-7.40 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H)

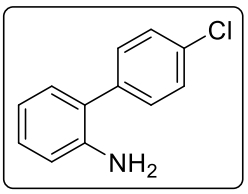


6-(4-methoxyphenyl)-1H-indole (Table 2, entry 25): ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.74 – 7.24 (m, 6H), 7.08 – 6.84 (m, 2H), 6.43 (t, *J* = 1.0 Hz, 1H), 3.74 (s, 3H)

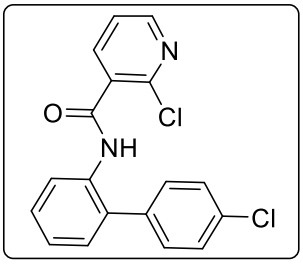


2-(p-tolyl) naphthalene (Table 2, entry 24): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 –7.87 (m, 3H), 7.57-7.33 (m, 8H), 2.50 (s, 3H)

Characterization data of the product (compound 6 and 7):

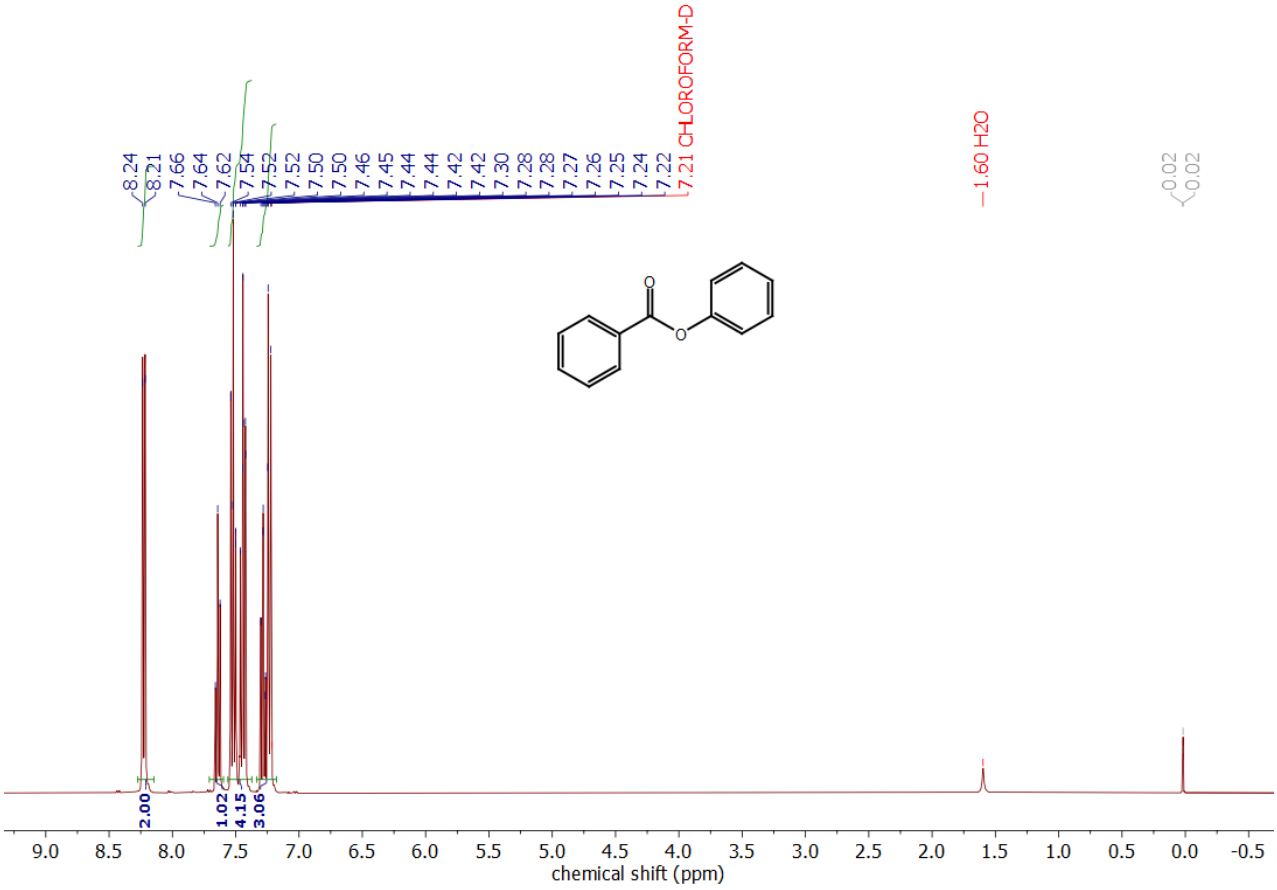


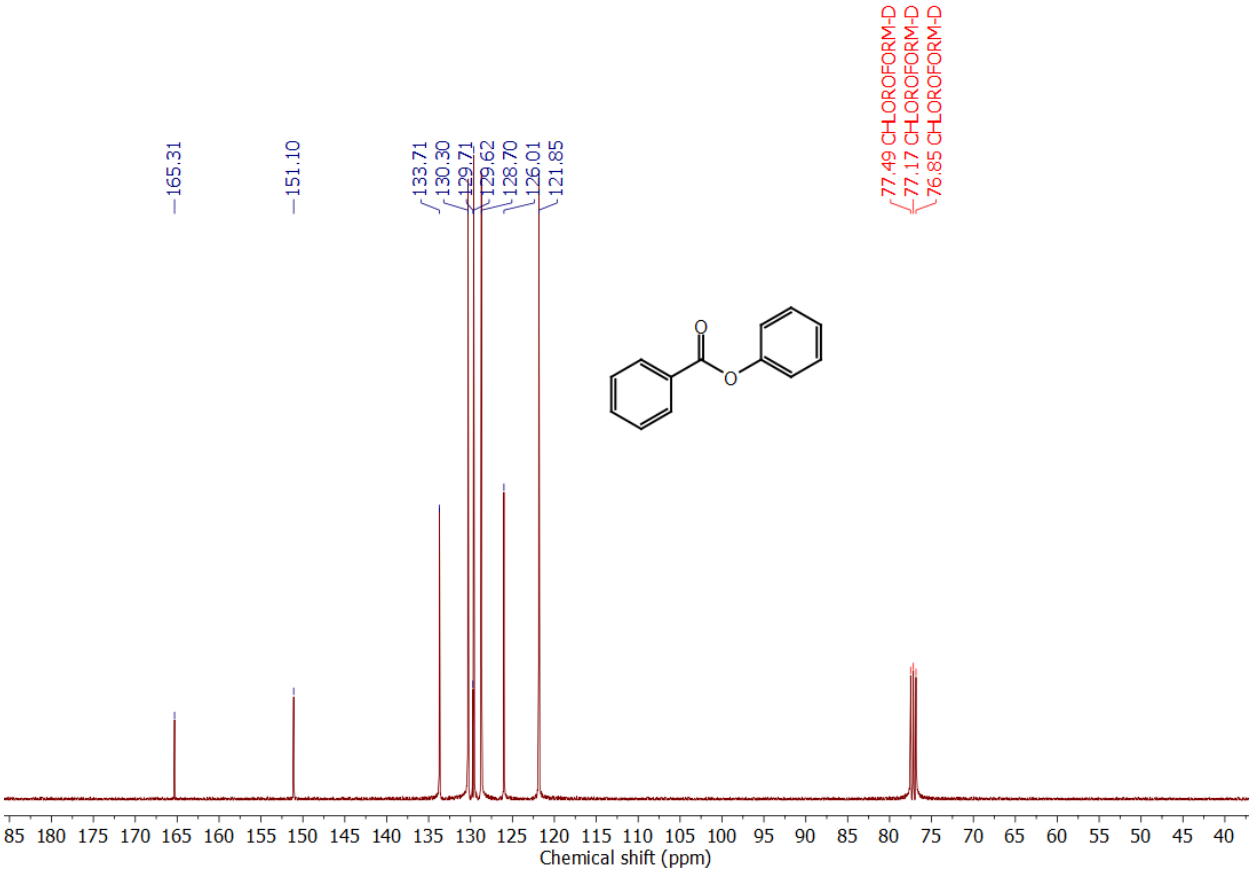
4'-chloro-[1,1'-biphenyl]-2-amine (compound 6):^{1}H NMR (400 MHz, DMSO-d6) δ 7.45-7.38 (m, 4H), 7.00 (d, *J*=8, 1H), 6.93 (d, *J*=8, 1H), 6.72 (d, *J*=8, 1H), 6.58 (d, *J*=8, 1H), 4.78 (s, 2H)

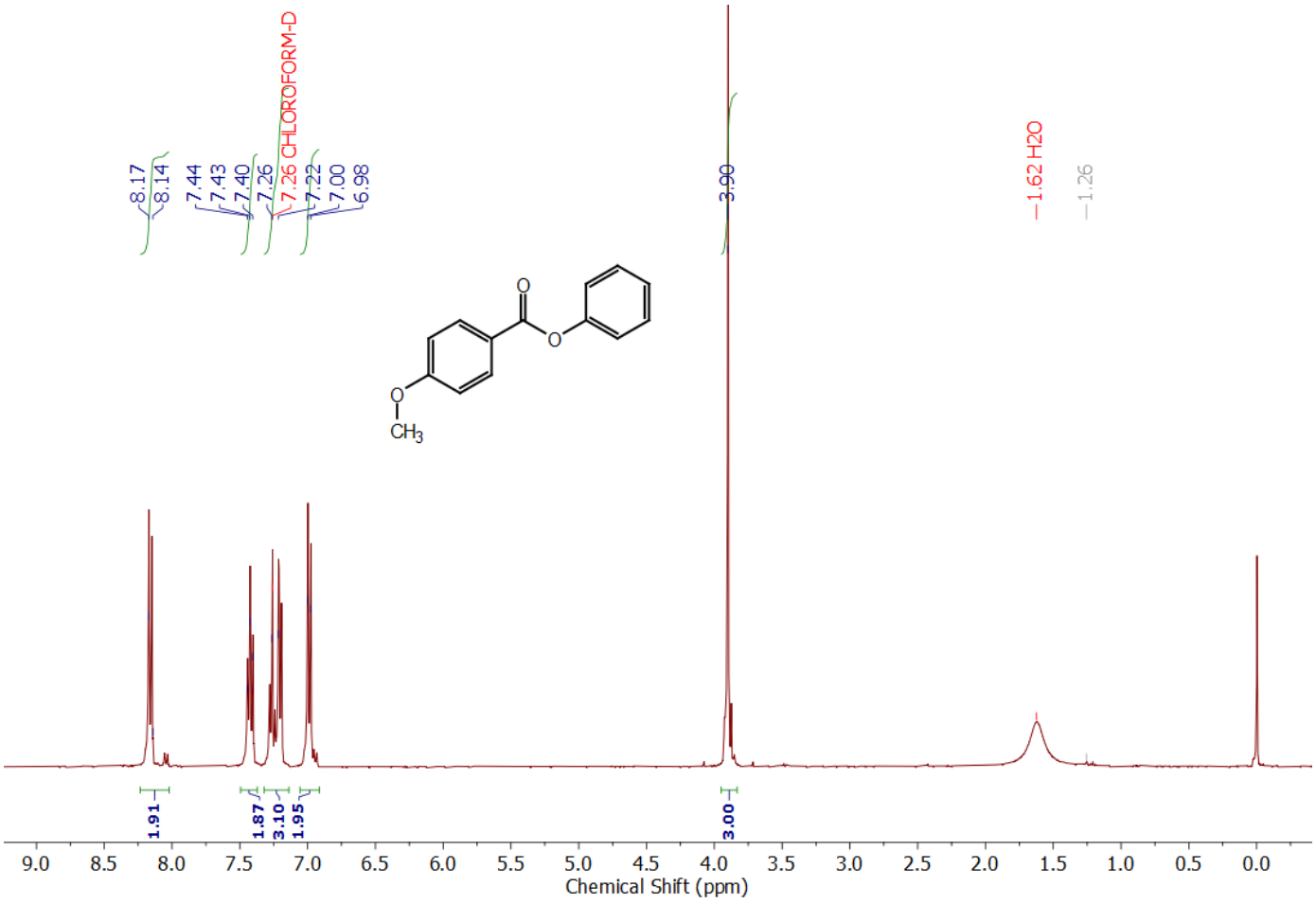


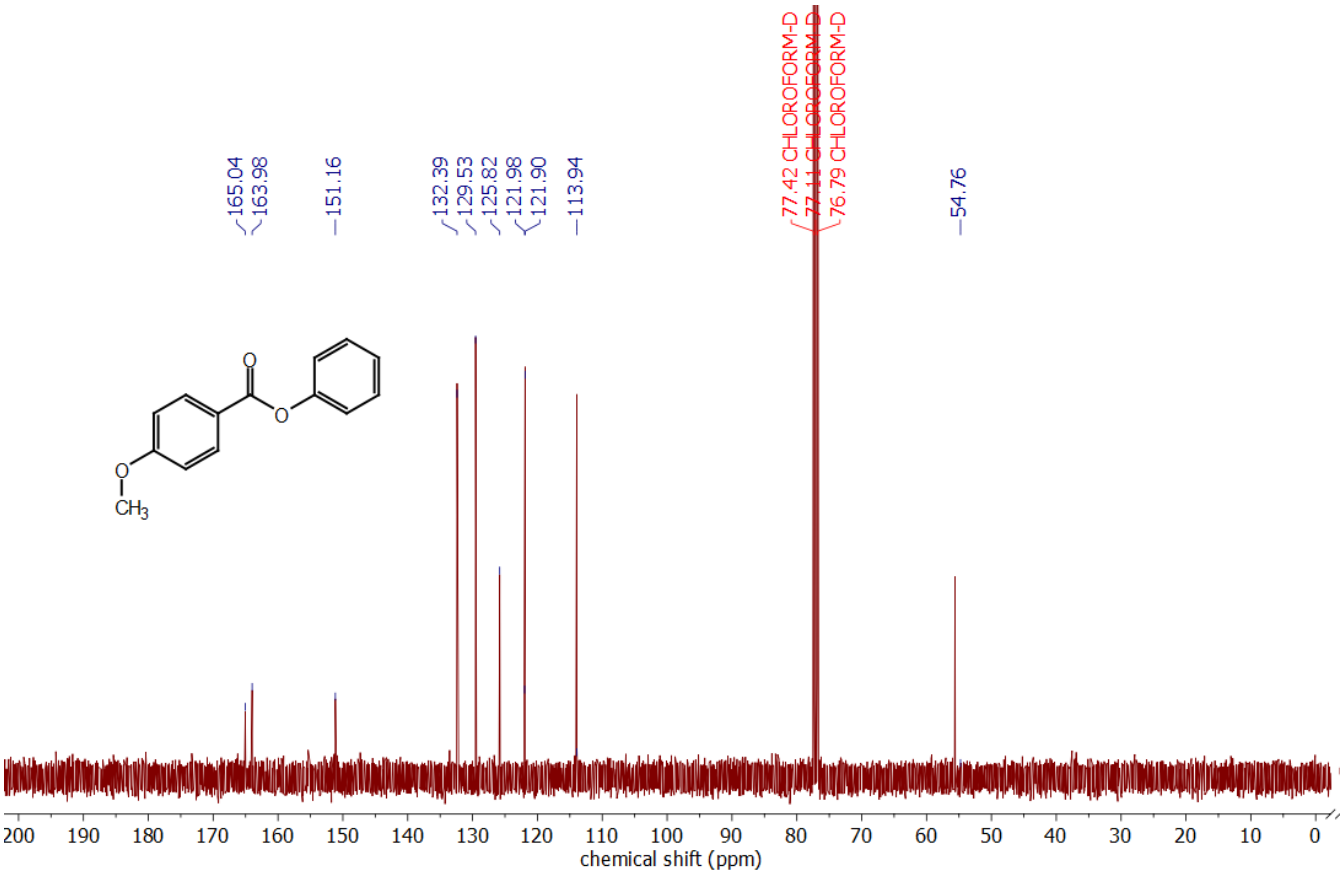
Boscalid (compound 7): ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 8.48 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.88 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.54-7.46 (m, 6H), 7.40-7.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.62, 151.43, 146.78, 140.25, 136.35, 134.54, 134.40, 132.37, 131.17, 130.90, 130.34, 129.41, 128.99, 125.45, 123.02, 122.23, 77.34.HR-MS: 343.039$[M+H]^+$

^{1}H (400 MHz, $CDCl_3$) **and ^{13}C** (100 MHz, $CDCl_3$): **NMR spectra of all the staring compounds.**


8.24
8.21
7.66
7.64
7.62
7.54
7.52
7.52
7.50
7.50
7.46
7.45
7.44
7.44
7.42
7.42
7.30
7.28
7.28
7.27
7.26
7.25
7.24
7.22
7.21 CHLOROFORM-D
1.60 H2O
0.02
0.02
O
O
2.00
1.02
4.15
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
chemical shift (ppm)


165.31
151.10
133.71
130.30
129.71
129.62
128.70
126.01
121.85
77.49 CHLOROFORM-D
77.17 CHLOROFORM-D
76.85 CHLOROFORM-D
O
O
85 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
Chemical shift (ppm)


8.17
8.14
7.44
7.43
7.40
7.26
7.26 CHLOROFORM-D
7.22
7.00
6.98
3.90
1.62 H2O
1.26
O
O
O
CH3
1.91
1.87
3.10
1.95
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


165.04
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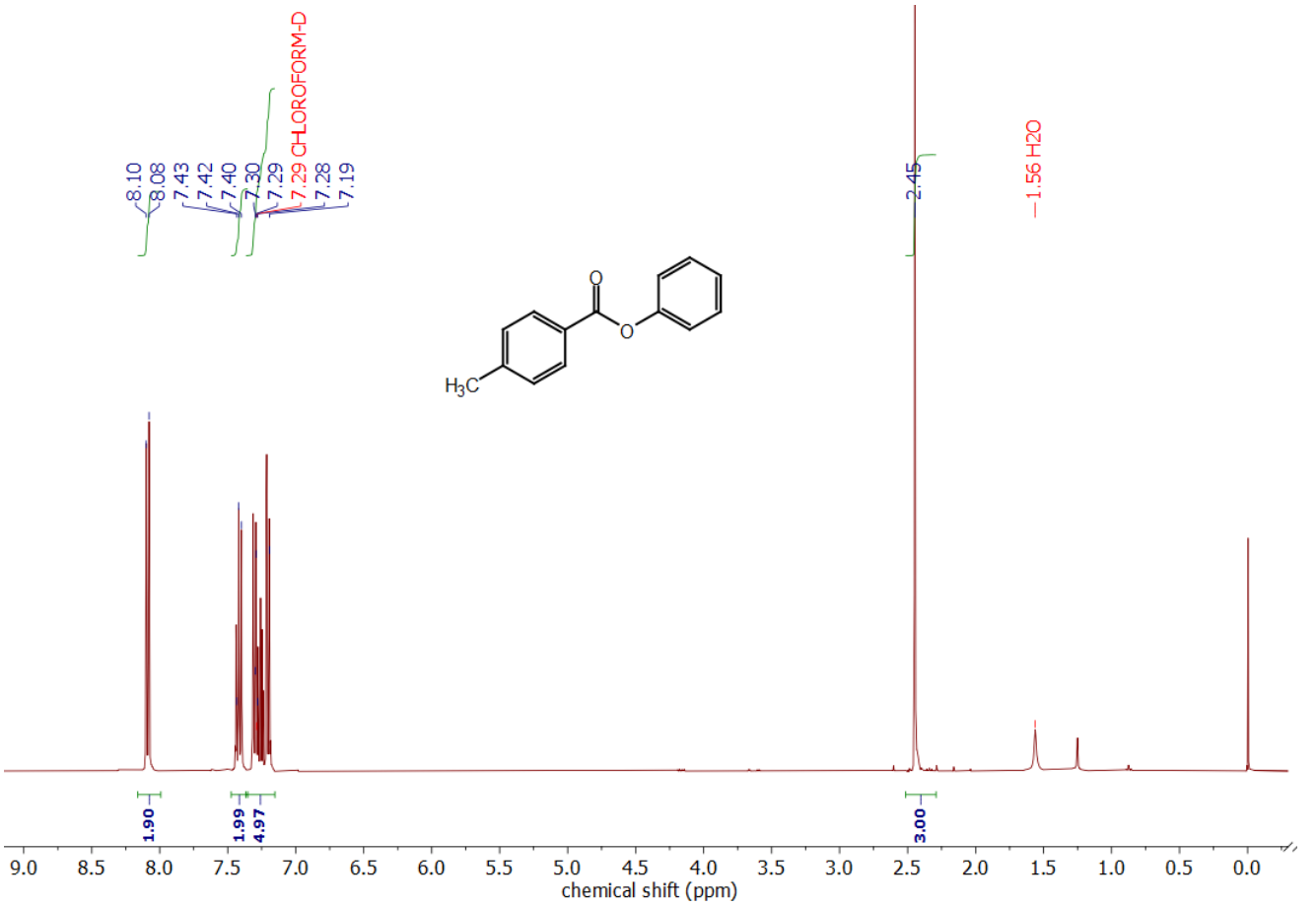
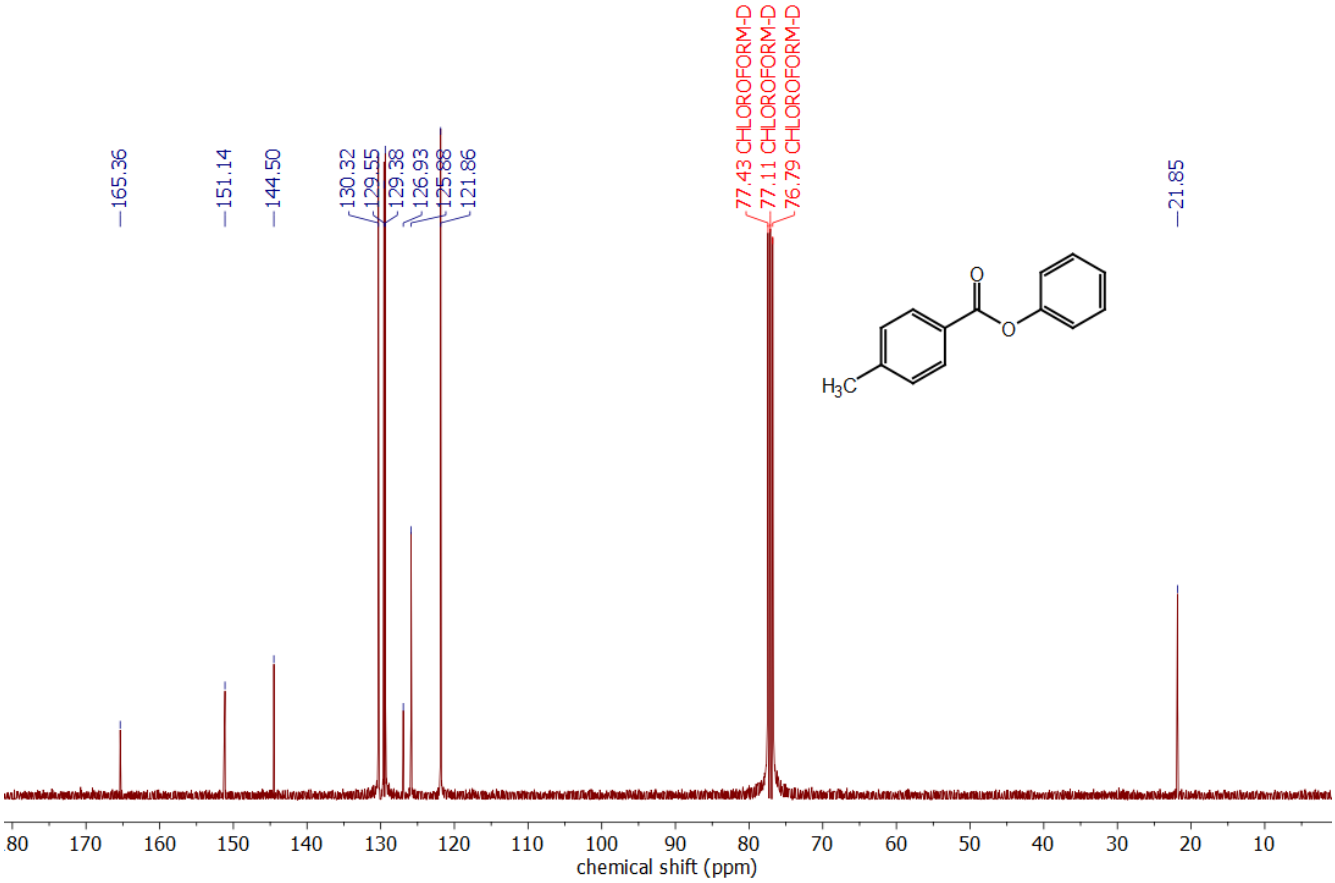
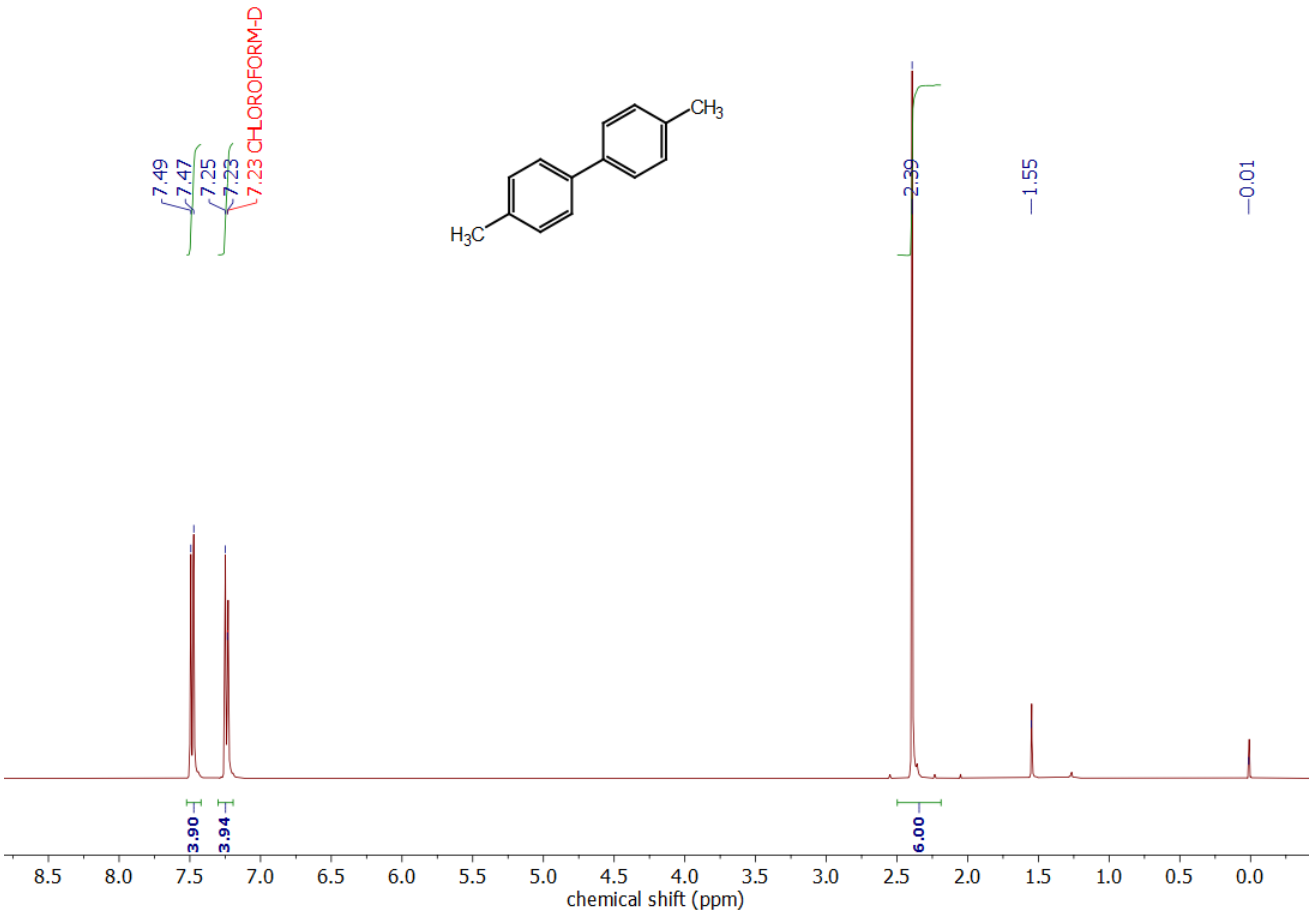
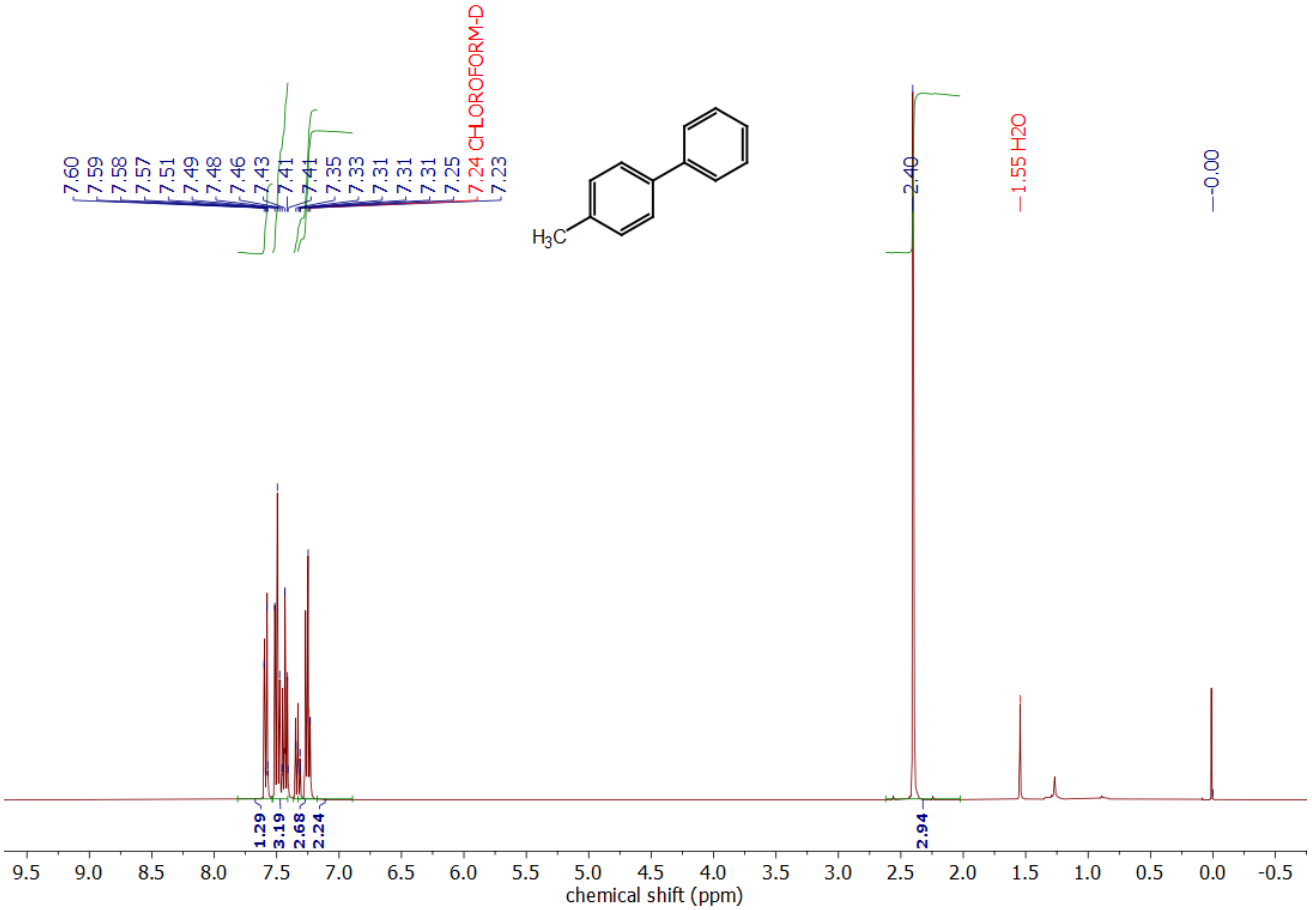
132.39
129.53
125.82
121.98
121.90
113.94
77.42 CHLOROFORM-D
77.11 CHLOROFORM-D
76.79 CHLOROFORM-D
54.76
O
O
O
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

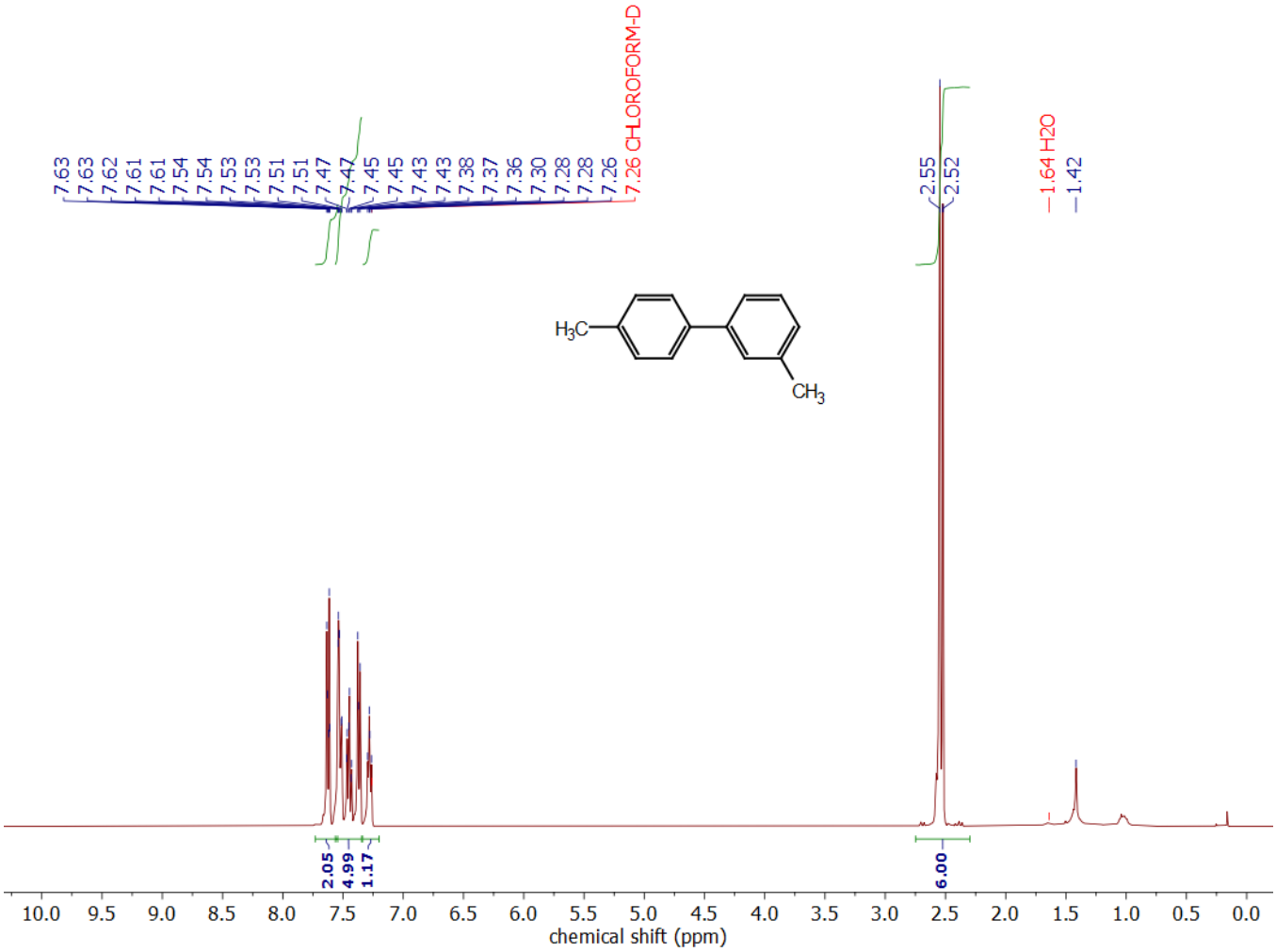


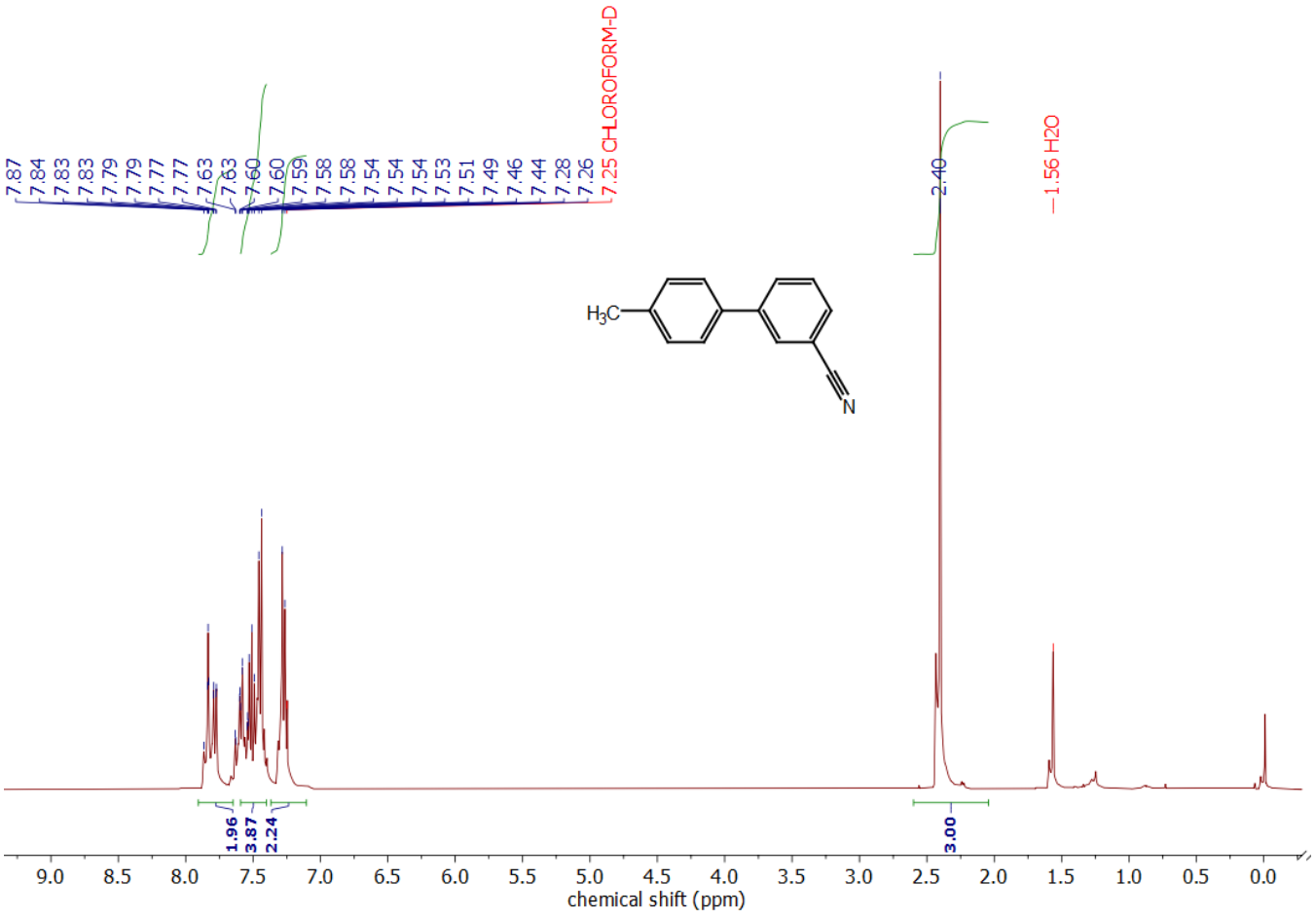


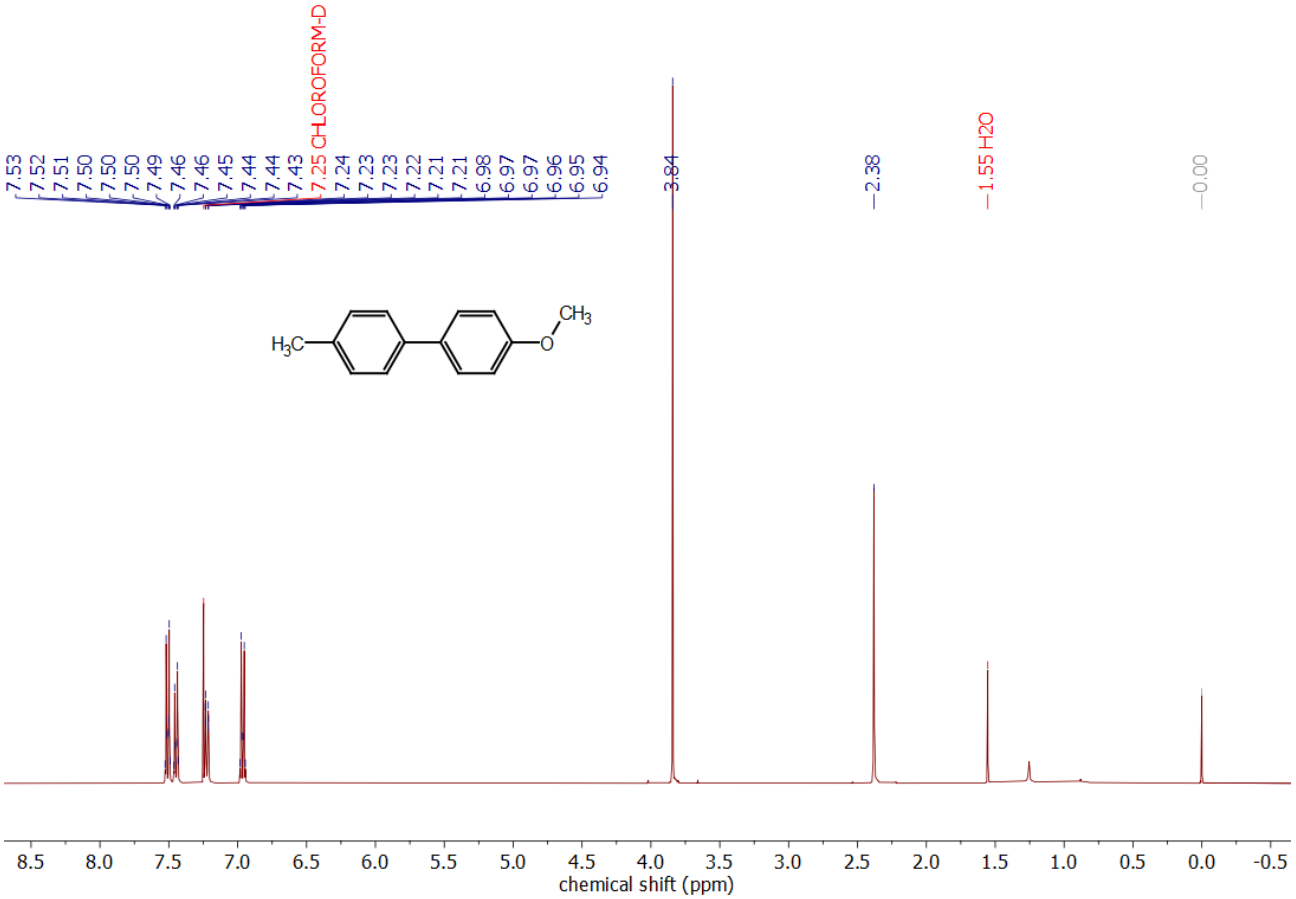
^{1}H and ^{13}C NMR of all the isolated cross-coupling compounds:

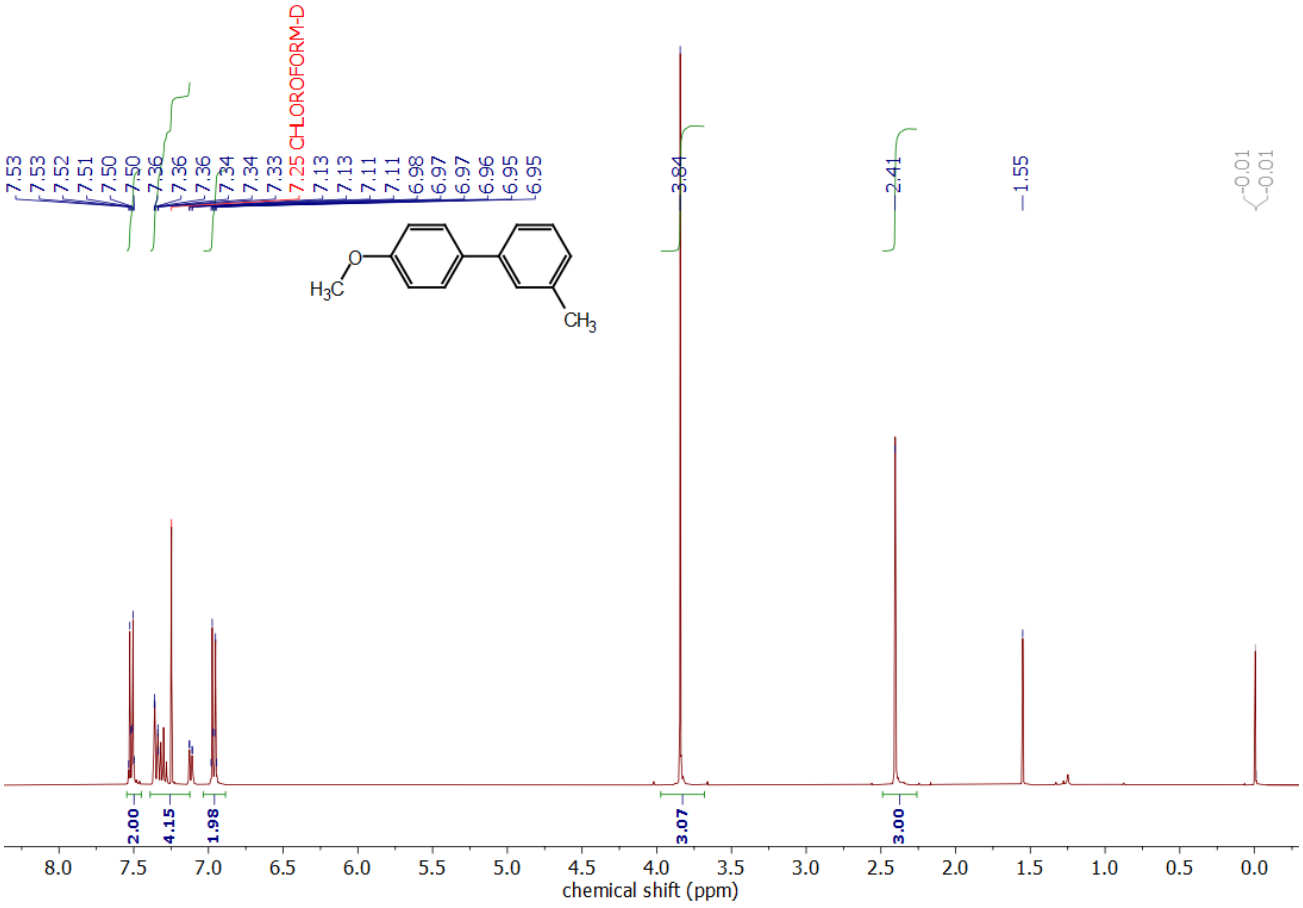

7.49
7.47
7.25
7.23
7.23 CHLOROFORM-D
CH3
H3C
2.39
1.55
0.01
3.90
3.94
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

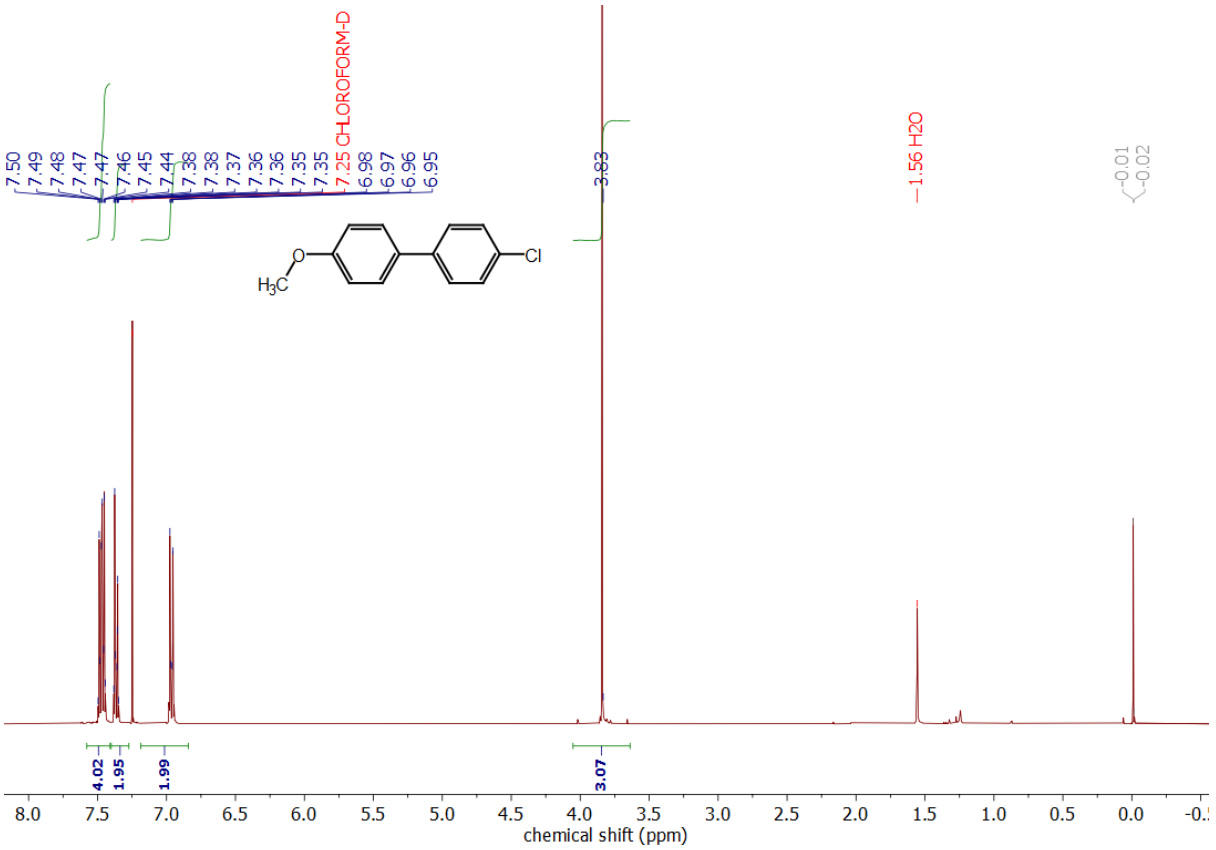

7.60
7.59
7.58
7.57
7.51
7.49
7.48
7.46
7.43
7.41
7.41
7.35
7.33
7.31
7.31
7.31
7.25
7.24 CHLOROFORM-D
7.23
H3C
2.40
1.55 H2O
0.00
1.29
3.19
2.68
2.24
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
chemical shift (ppm)

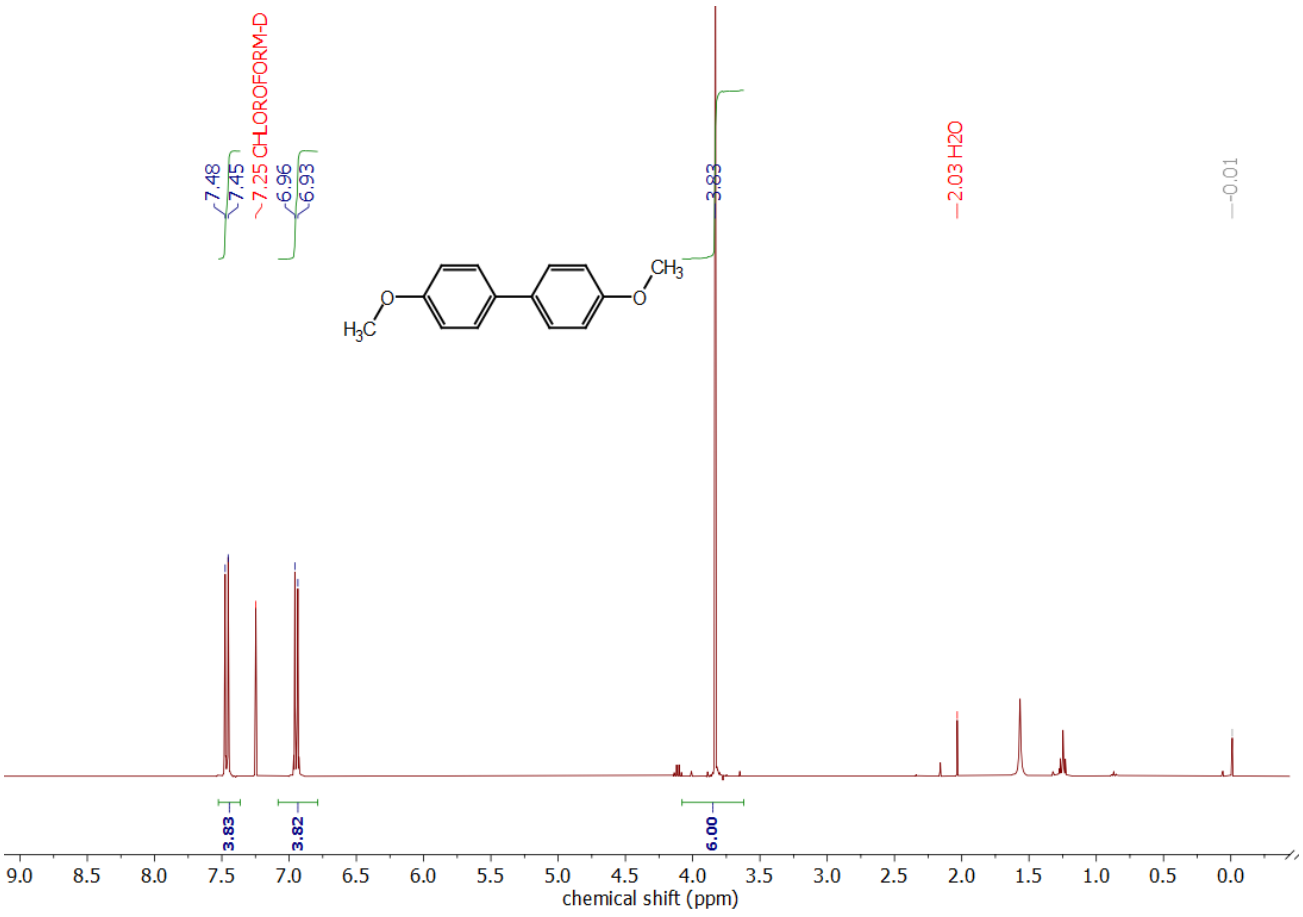

7.63
7.63
7.62
7.61
7.61
7.54
7.54
7.53
7.53
7.51
7.51
7.47
7.47
7.45
7.45
7.43
7.43
7.38
7.37
7.36
7.30
7.28
7.28
7.26
7.26 CHLOROFORM-D
2.55
2.52
1.64 H2O
1.42
H3C
CH3
2.05
4.99
1.17
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

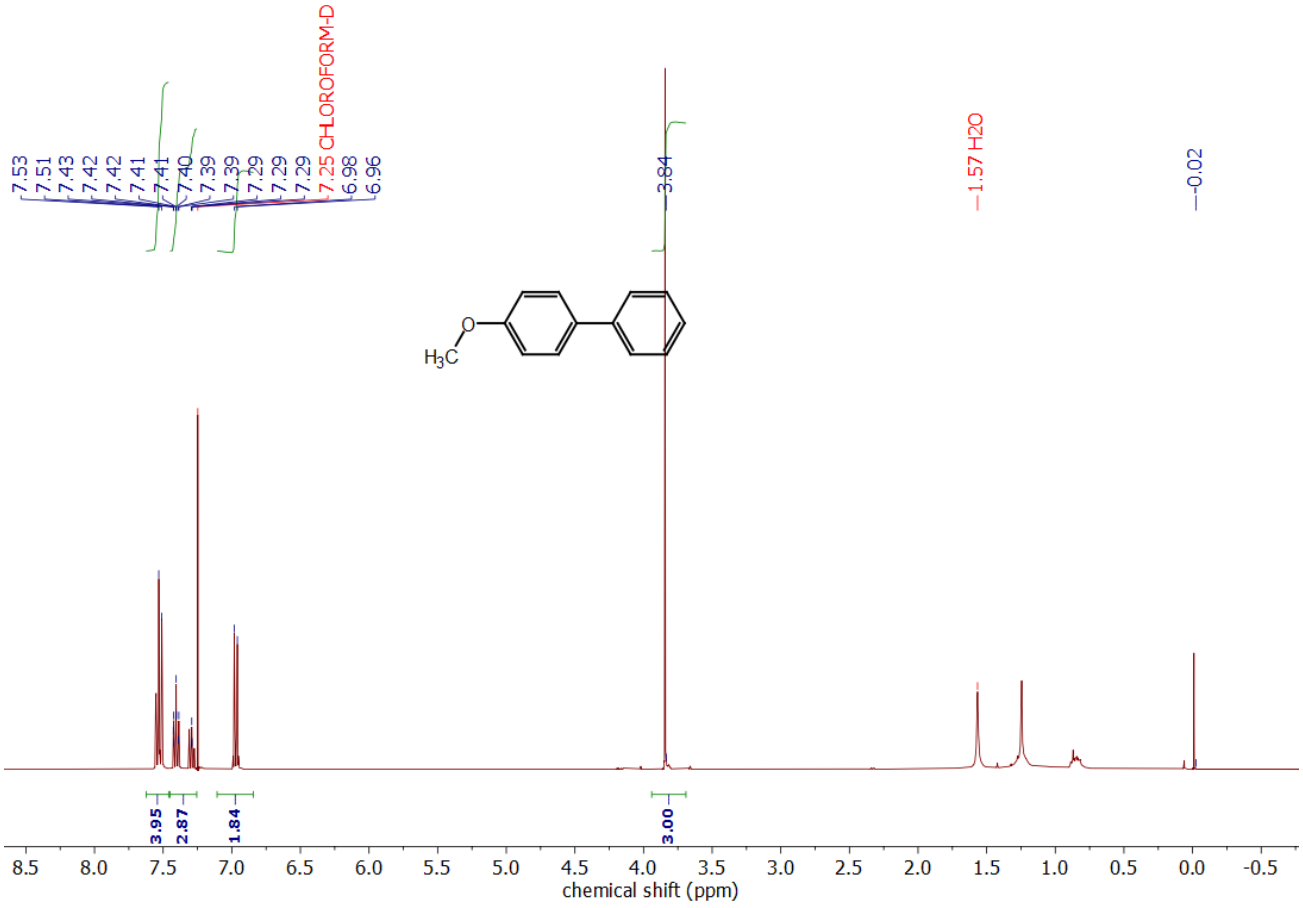

7.87
7.84
7.83
7.83
7.79
7.79
7.77
7.77
7.63
7.63
7.60
7.60
7.59
7.58
7.58
7.54
7.54
7.54
7.53
7.51
7.49
7.46
7.44
7.28
7.26
7.25 CHLOROFORM-D
2.40
1.56 H2O
H3C
N
1.96
3.87
2.24
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

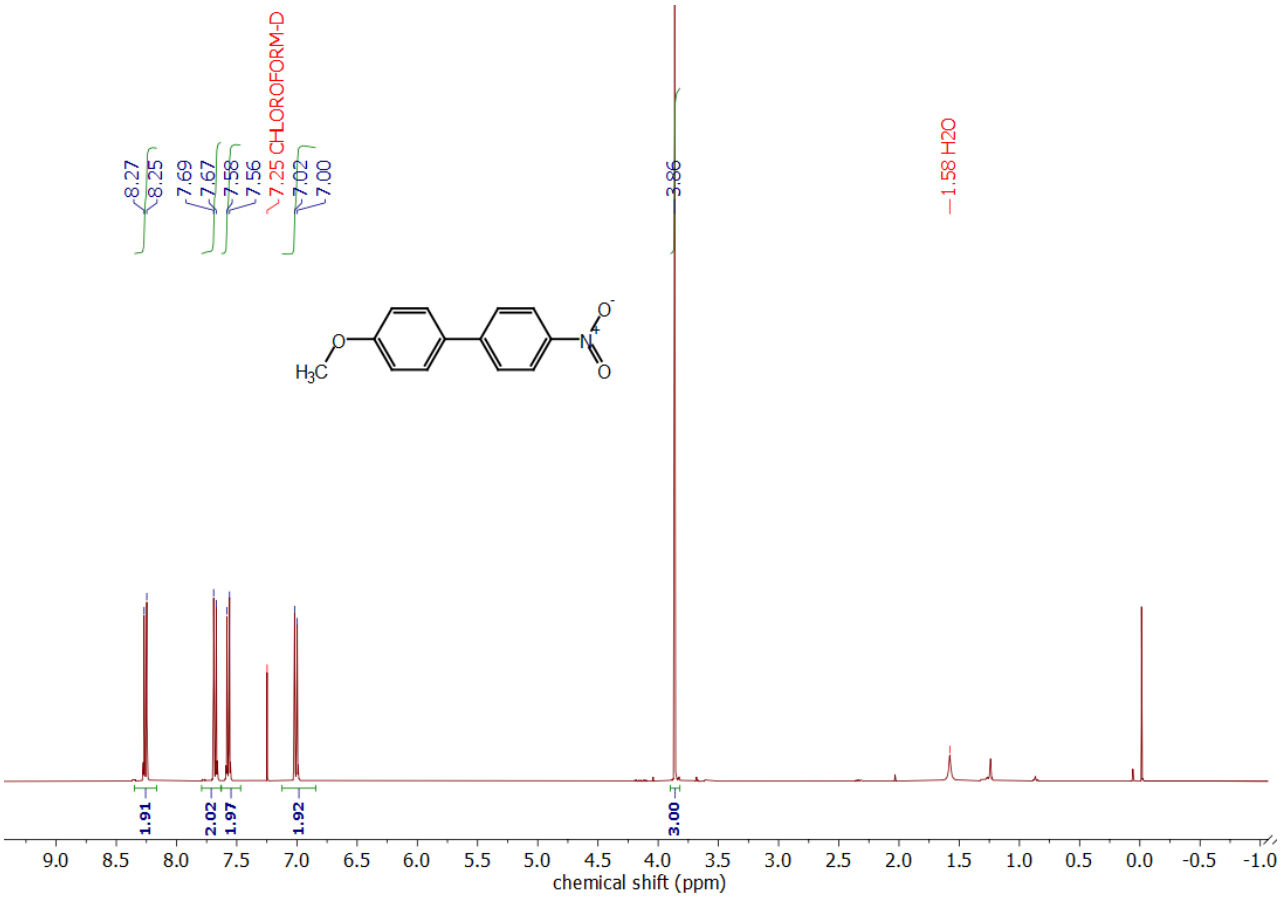

7.53
7.52
7.51
7.50
7.50
7.50
7.49
7.46
7.46
7.45
7.44
7.44
7.43
7.25 CHLOROFORM-D
7.24
7.23
7.23
7.22
7.21
7.21
6.98
6.97
6.97
6.96
6.95
6.94
3.84
2.38
1.55 H2O
0.00
H3C
O
CH3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
chemical shift (ppm)

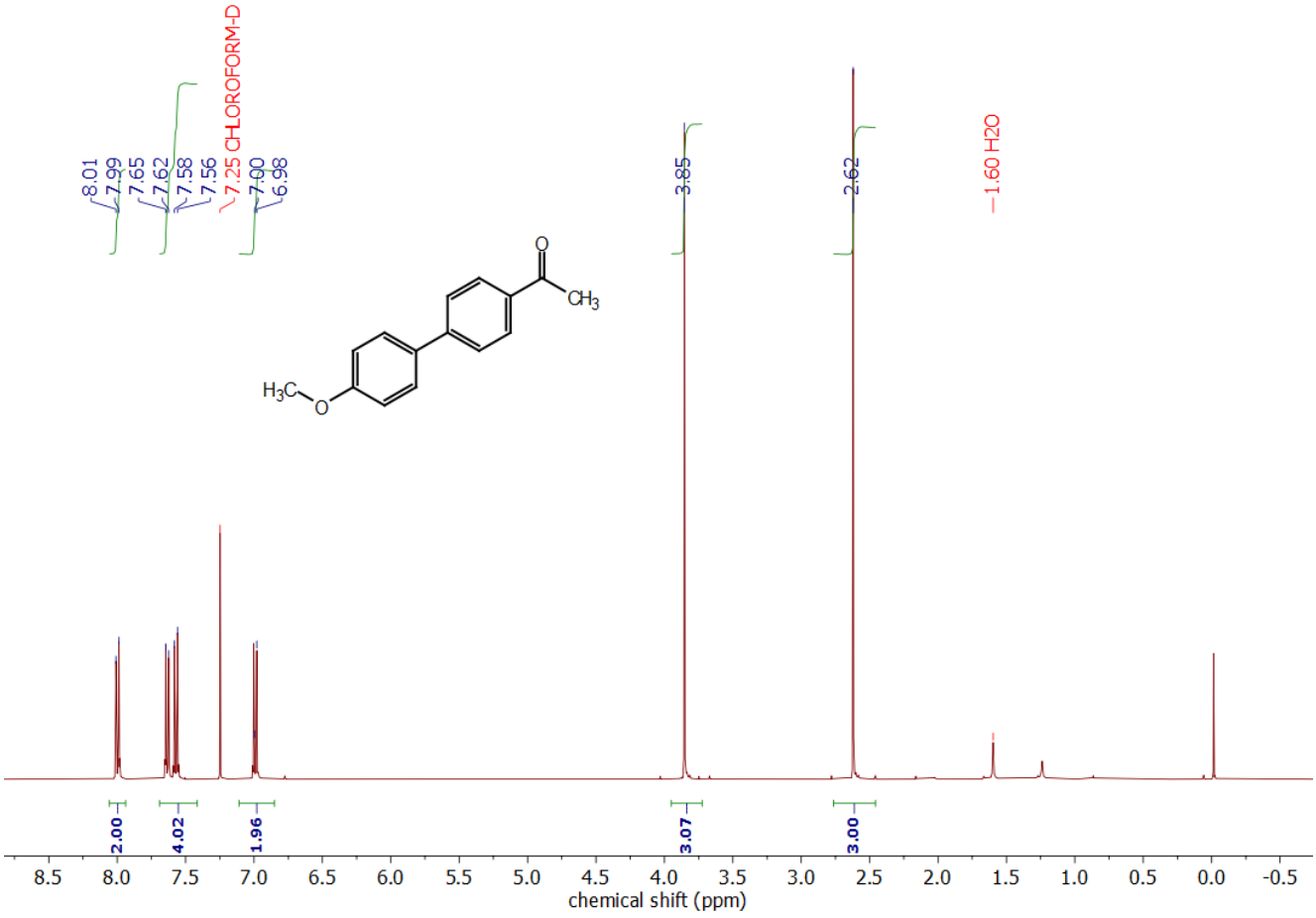

7.53
7.53
7.52
7.51
7.50
7.50
7.36
7.36
7.36
7.34
7.34
7.33
7.25 CHLOROFORM-D
7.13
7.13
7.11
7.11
6.98
6.97
6.97
6.96
6.95
6.95
3.84
2.41
1.55
0.01
0.01
O
H3C
CH3
2.00
4.15
1.98
3.07
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

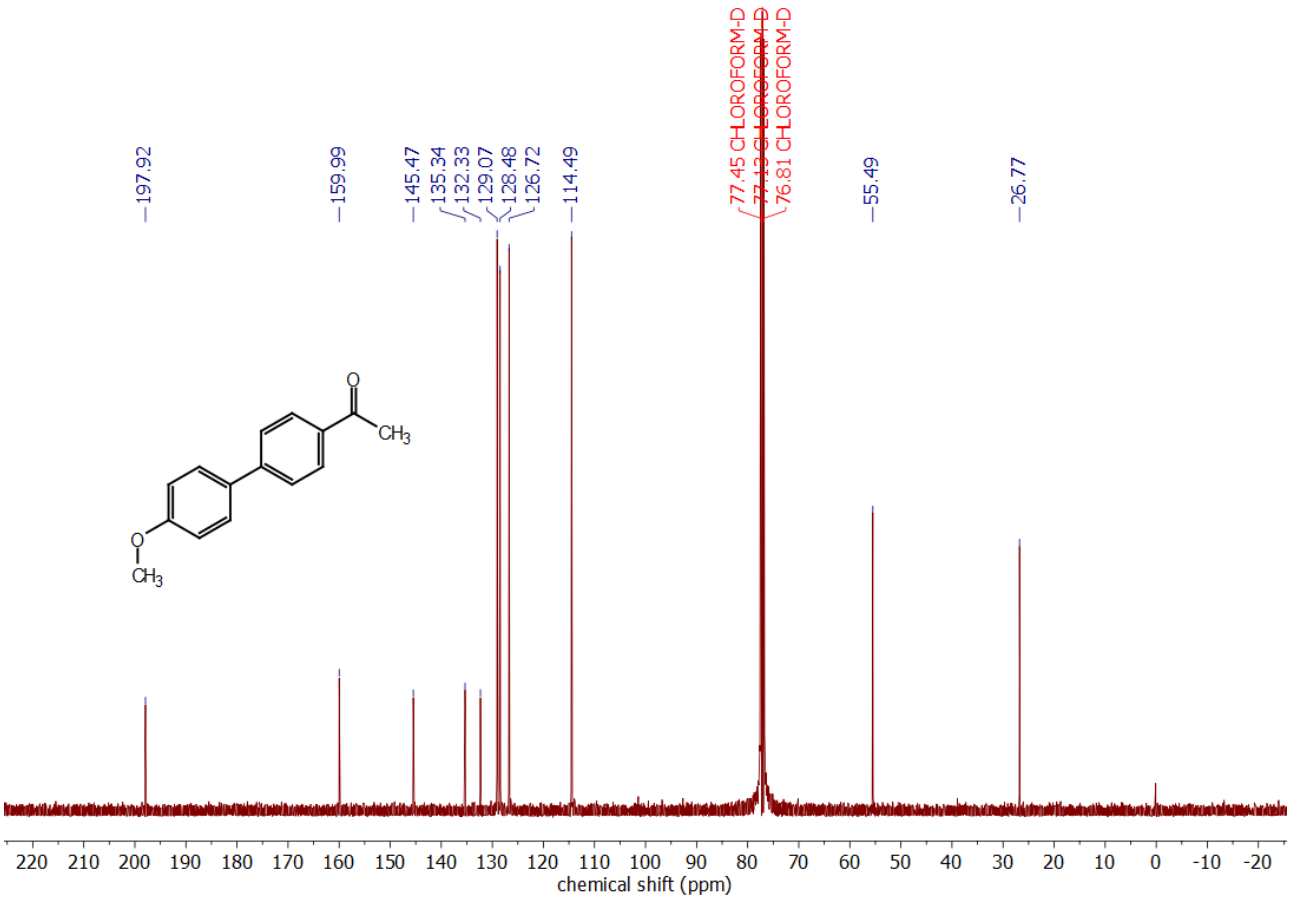

7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.25 CHLOROFORM-D
6.98
6.97
6.96
6.95
3.83
1.56 H2O
0.01
0.02
O
H3C
Cl
4.02
1.95
1.99
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

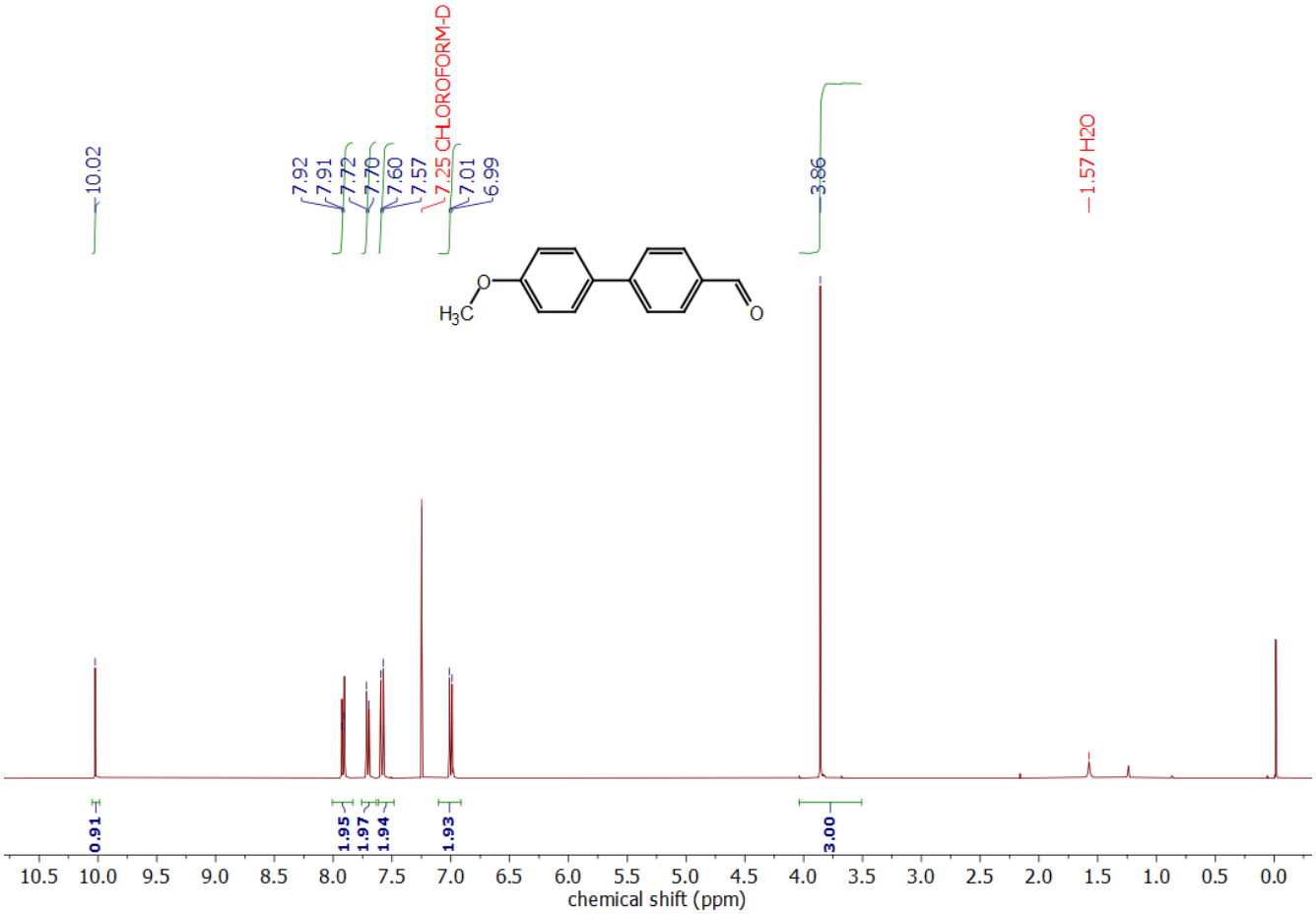

7.48
7.45
7.25 CHLOROFORM-D
6.96
6.93
3.83
2.03 H2O
0.01
O
H3C
CH3
O
3.83
3.82
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)

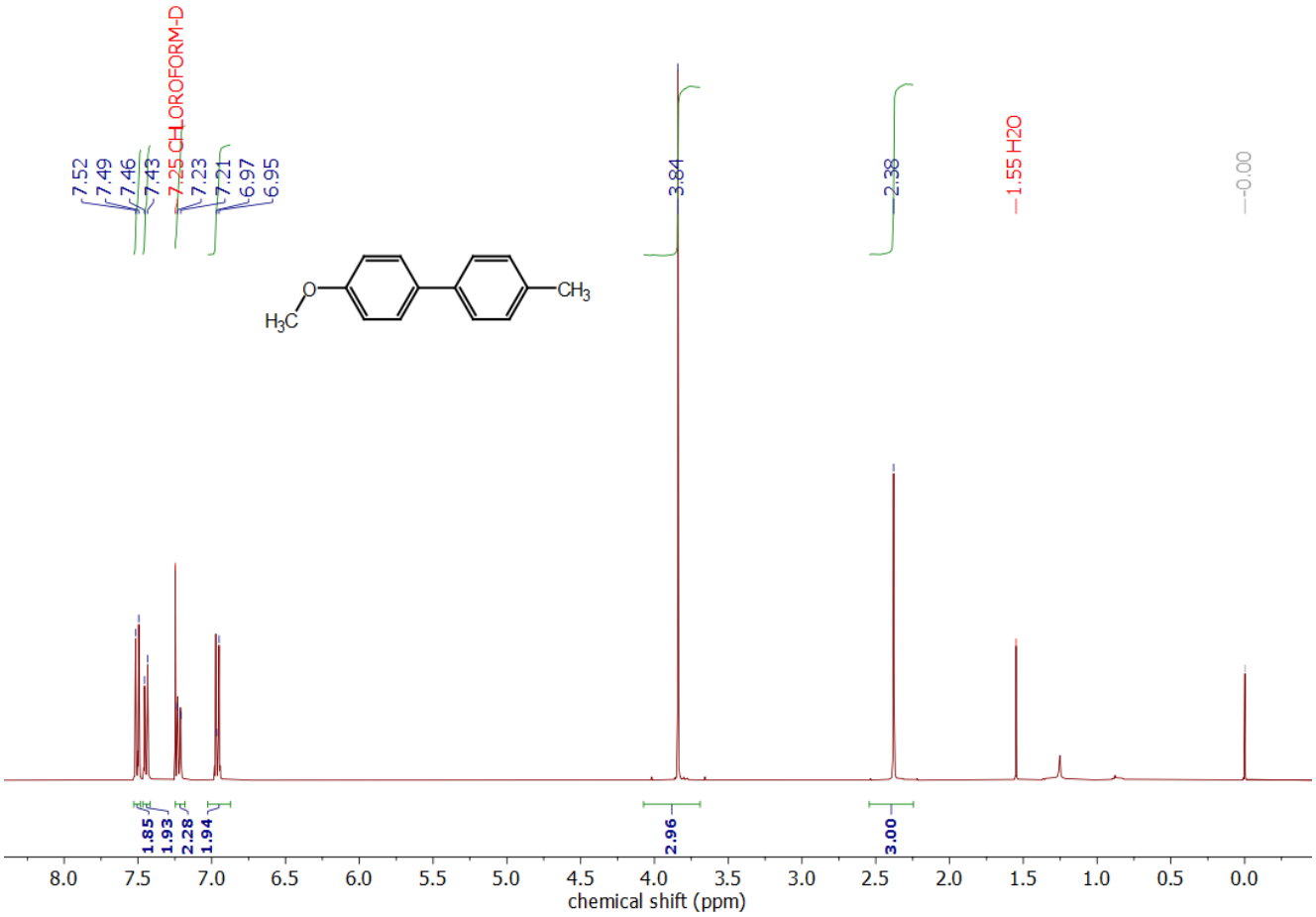

7.53
7.51
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.29
7.29
7.29
7.25 CHLOROFORM-D
6.98
6.96
3.84
1.57 H2O
0.02
O
H3C
3.95
2.87
1.84
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
chemical shift (ppm)

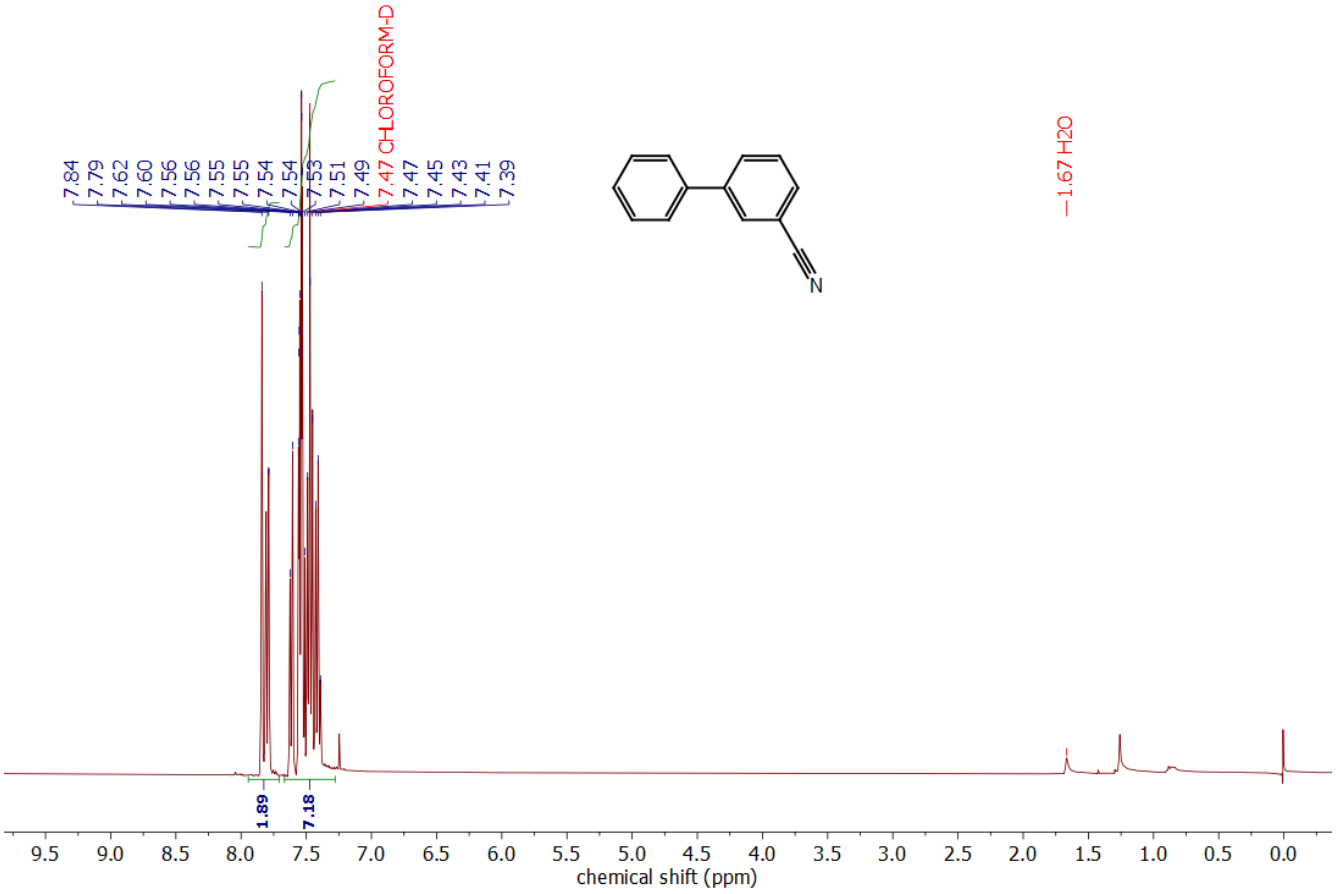

8.27
8.25
7.69
7.67
7.58
7.56
7.25 CHLOROFORM-D
7.02
7.00
3.86
1.58 H2O
O
H3C
O
N+
O-
1.91
2.02
1.97
1.92
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
chemical shift (ppm)

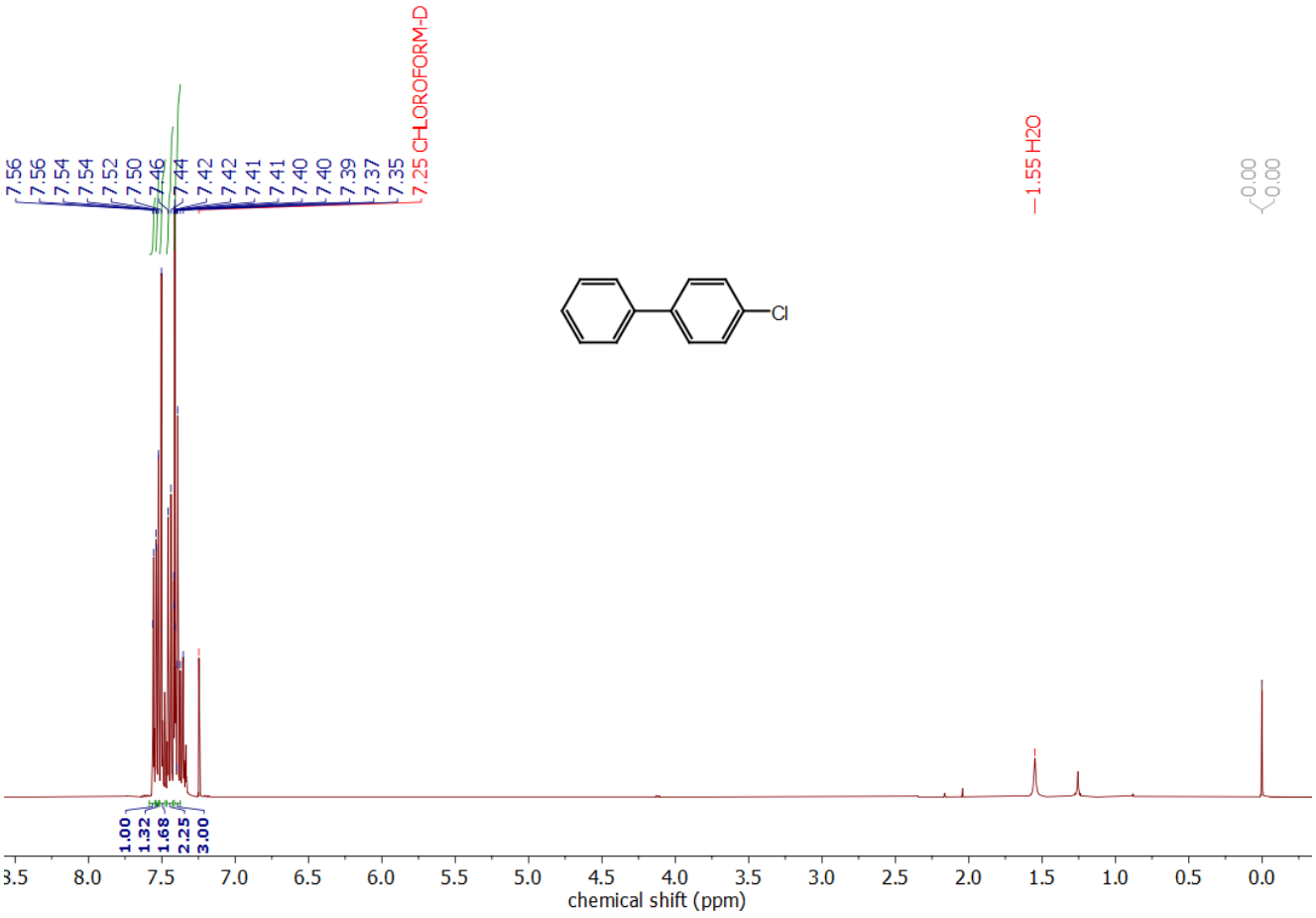

8.01
7.99
7.65
7.62
7.58
7.56
7.25 CHLOROFORM-D
7.00
6.98
3.85
2.62
1.60 H2O
O
CH3
H3C
O
2.00
4.02
1.96
3.07
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
chemical shift (ppm)


197.92
159.99
145.47
135.34
132.33
129.07
128.48
126.72
114.49
77.45 CHLOROFORM-D
77.13 CHLOROFORM-D
76.81 CHLOROFORM-D
55.49
26.77
O
CH3
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
chemical shift (ppm)


10.02
7.92
7.91
7.72
7.70
7.60
7.57
7.25 CHLOROFORM-D
7.01
6.99
3.86
1.57 H2O
O
H3C
O
0.91
1.95
1.97
1.94
1.93
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


7.52
7.49
7.46
7.43
7.25 CHLOROFORM-D
7.23
7.21
6.97
6.95
3.84
2.38
1.55 H2O
0.00
O
H3C
CH3
1.85
1.93
2.28
1.94
2.96
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


7.84
7.79
7.62
7.60
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.51
7.49
7.47 CHLOROFORM-D
7.47
7.45
7.43
7.41
7.39
1.67 H2O
N
1.89
7.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)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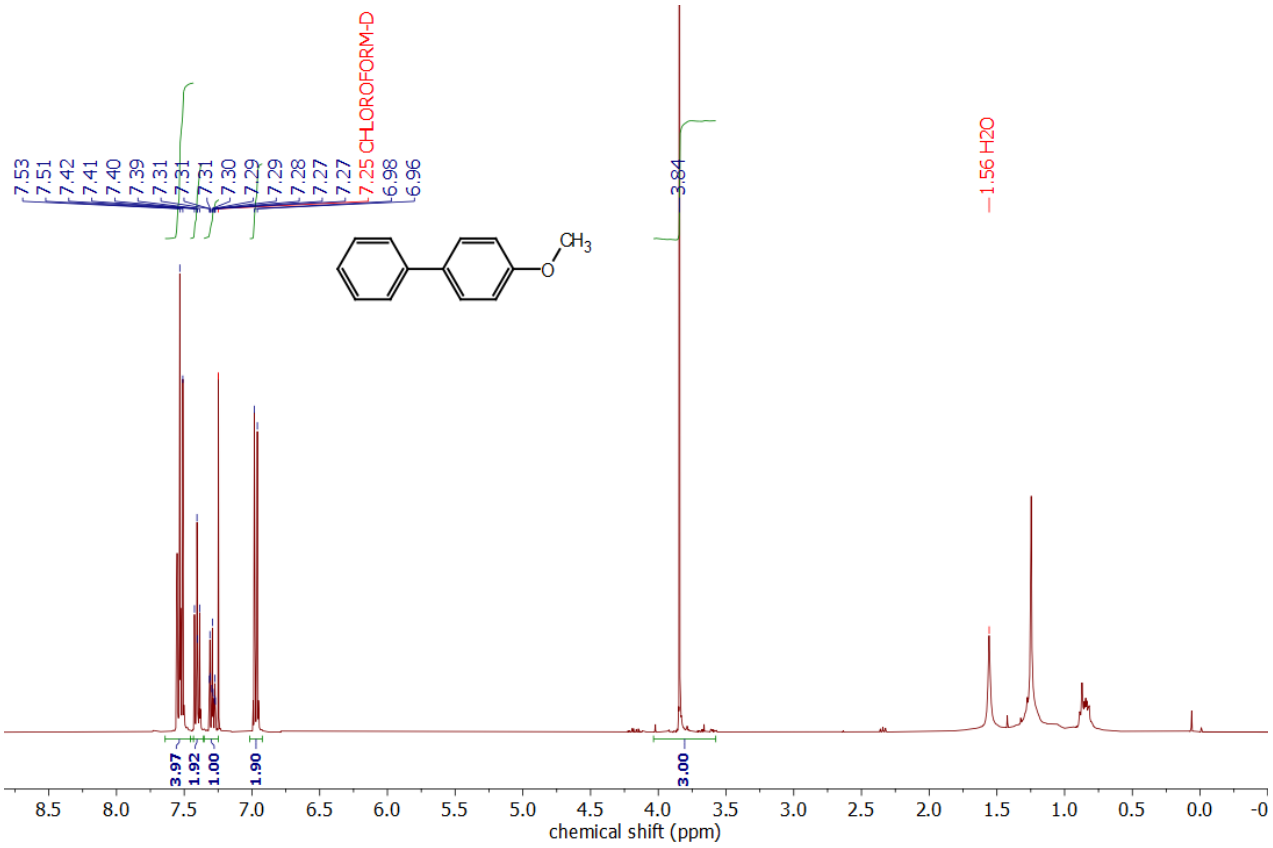
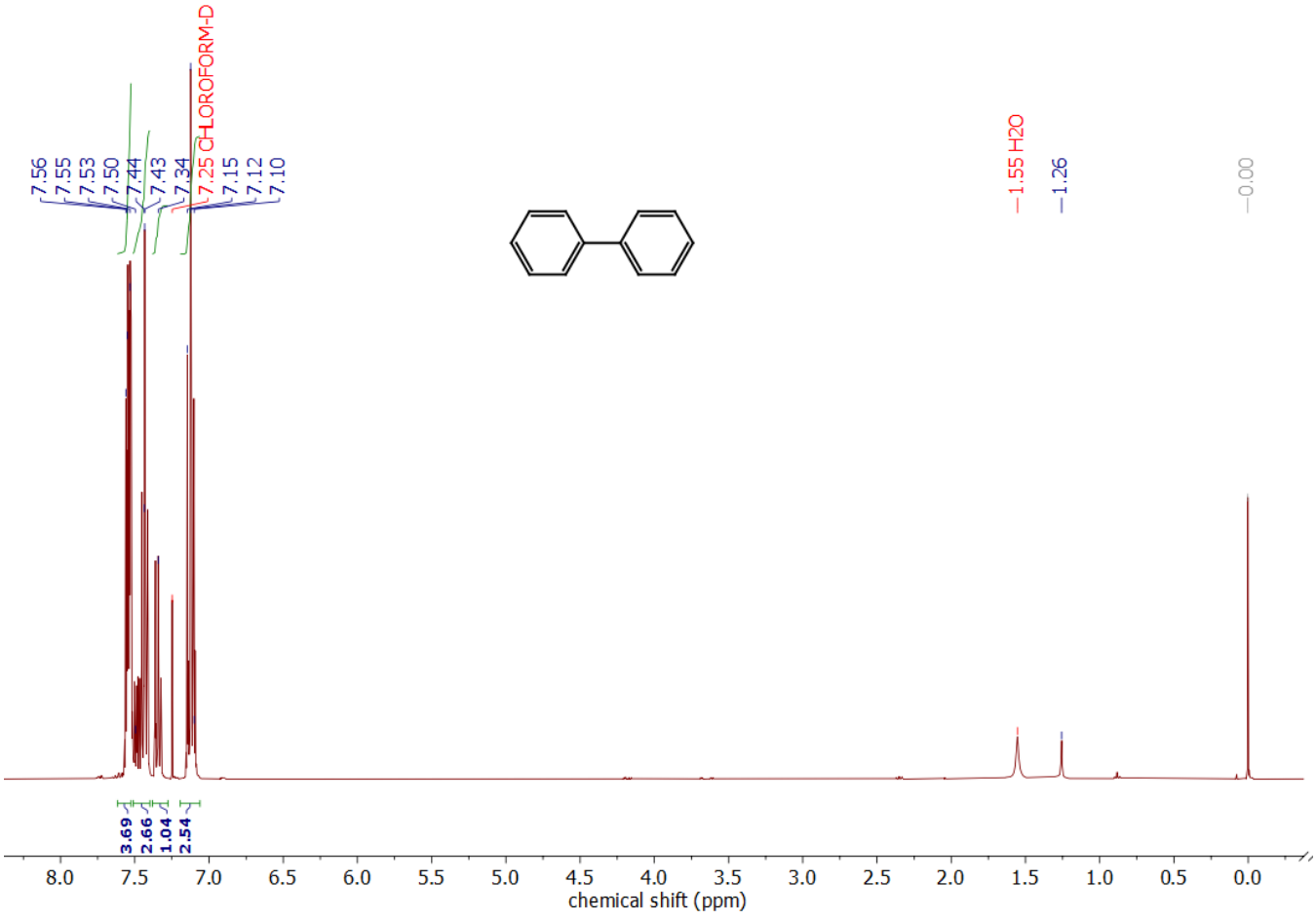
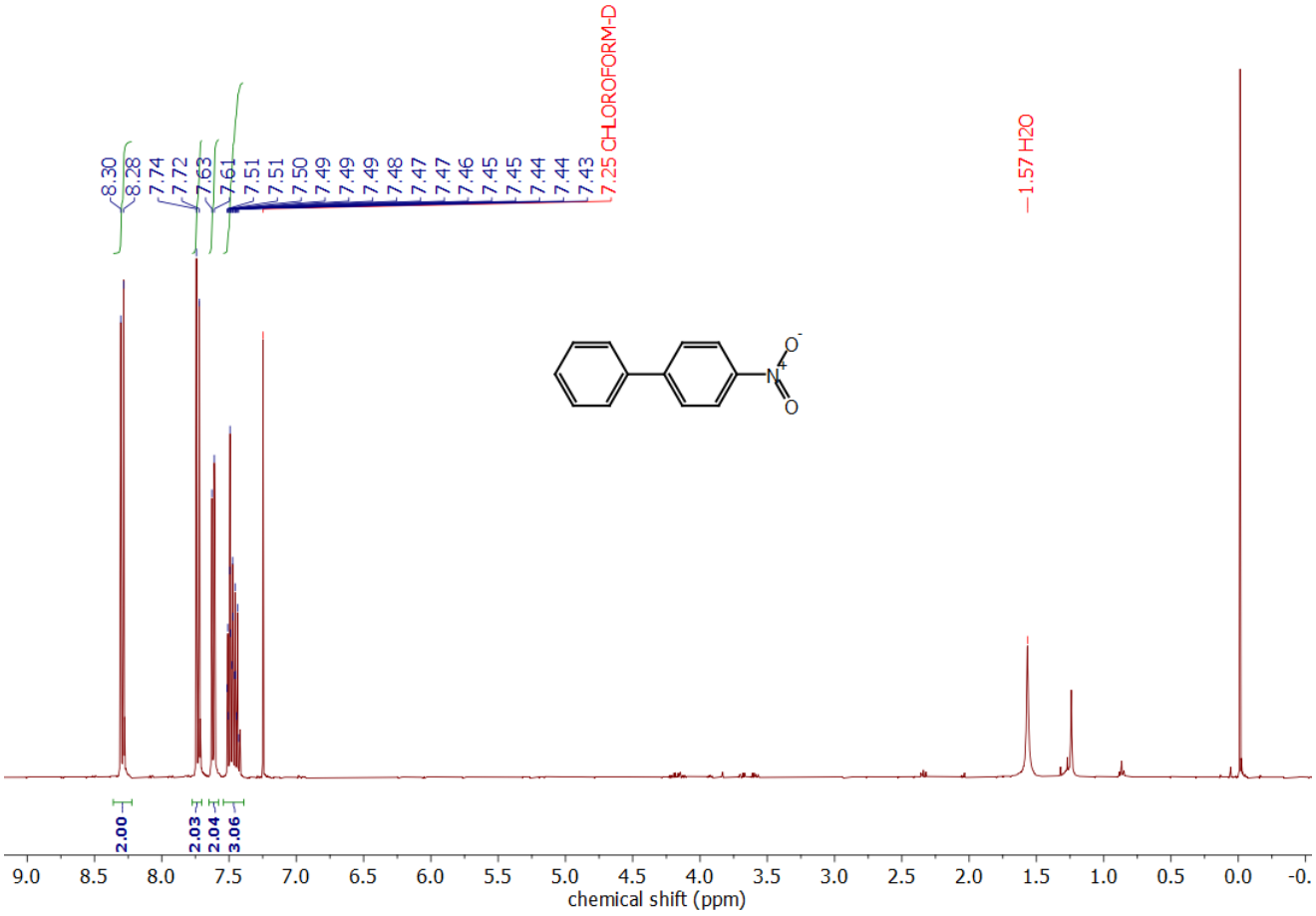
7.56
7.54
7.54
7.52
7.50
7.46
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.35
7.25 CHLOROFORM-D
1.55 H2O
0.00
0.00
Cl
1.00
1.32
1.68
2.25
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


7.53
7.51
7.42
7.41
7.40
7.39
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.25 CHLOROFORM-D
6.98
6.96
3.84
1.56 H2O
CH3
O
3.97
1.92
1.00
1.90
3.00
chemical shift (ppm)


7.56
7.55
7.53
7.50
7.44
7.43
7.34
7.25 CHLOROFORM-D
7.15
7.12
7.10
1.55 H2O
1.26
0.00
3.69
2.66
1.04
2.54
chemical shift (ppm)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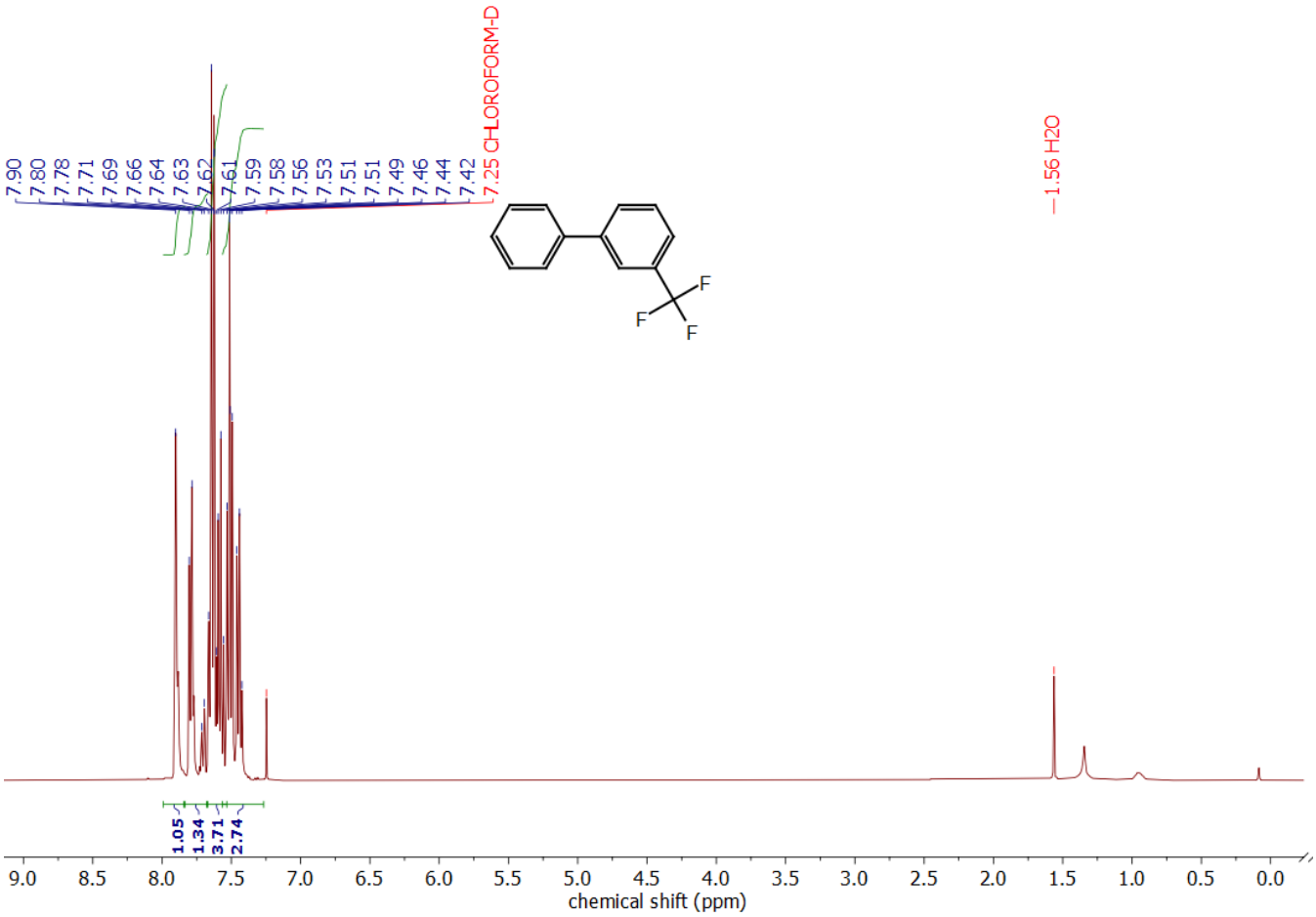
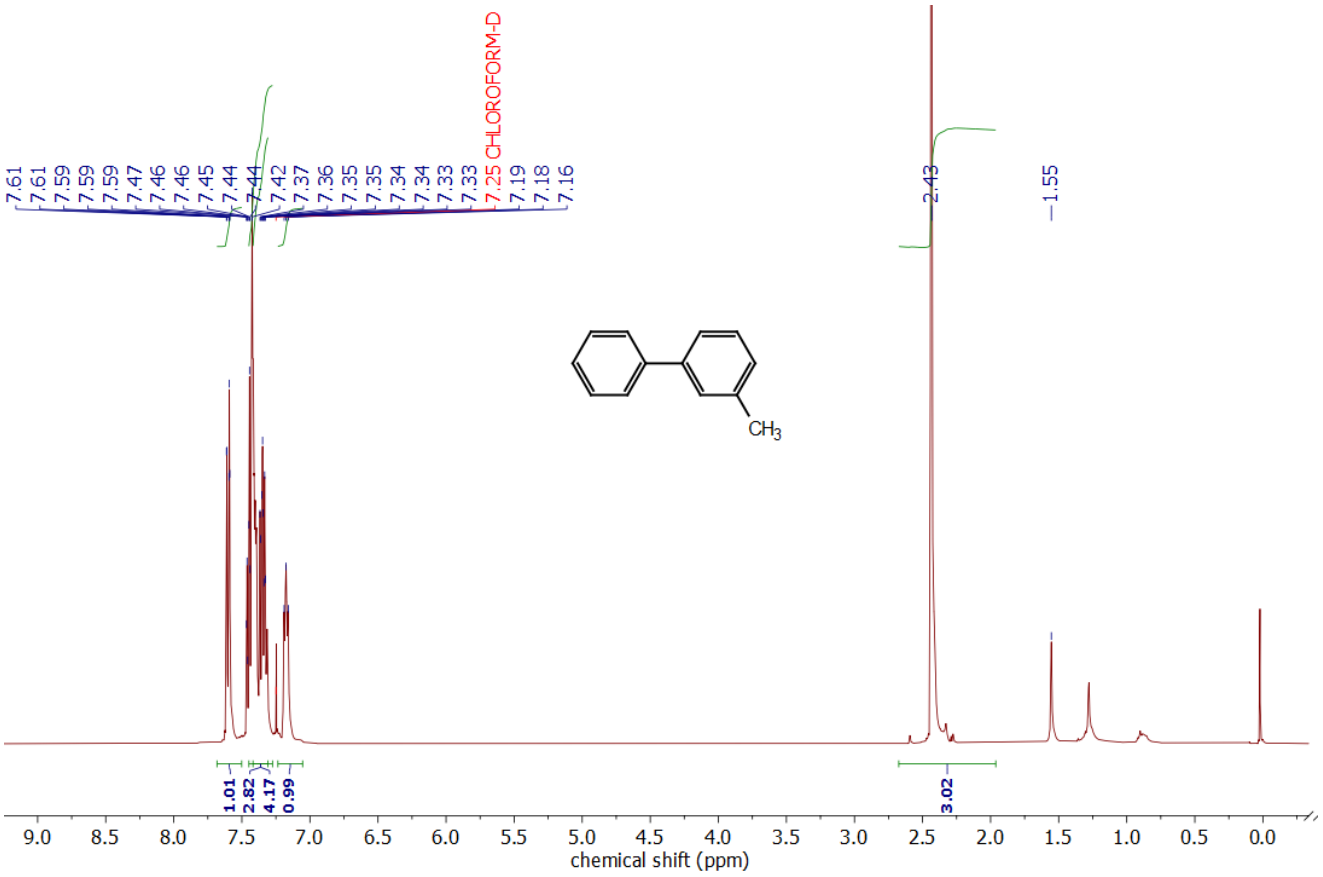
7.61
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.25 CHLOROFORM-D
1.57 H2O
2.00
2.03
2.04
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
chemical shift (ppm)


7.90
7.80
7.78
7.71
7.69
7.66
7.64
7.63
7.62
7.61
7.59
7.58
7.56
7.53
7.51
7.51
7.49
7.46
7.44
7.42
7.25 CHLOROFORM-D
1.56 H2O
F
F
F
1.05
1.34
3.71
2.74
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)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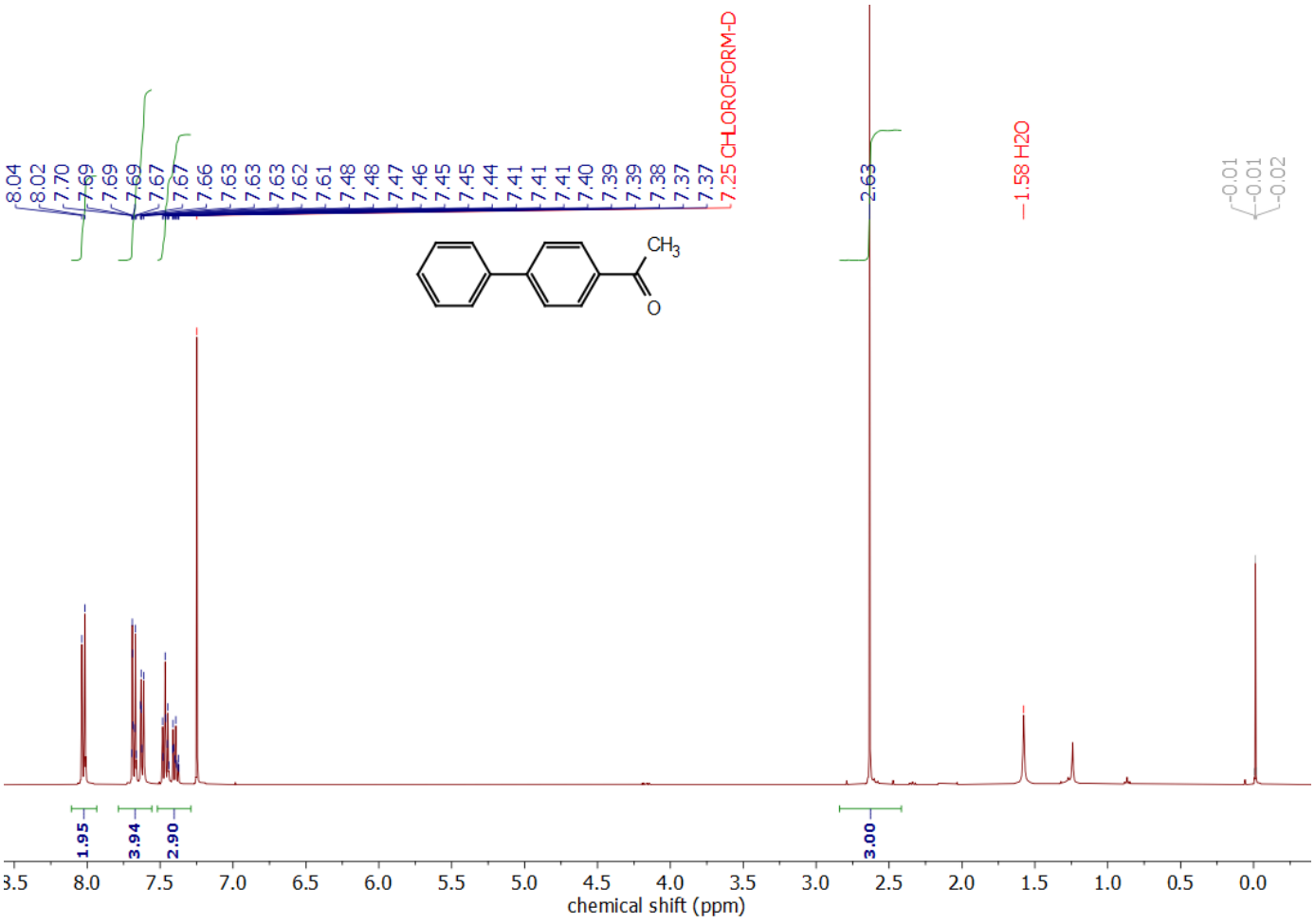
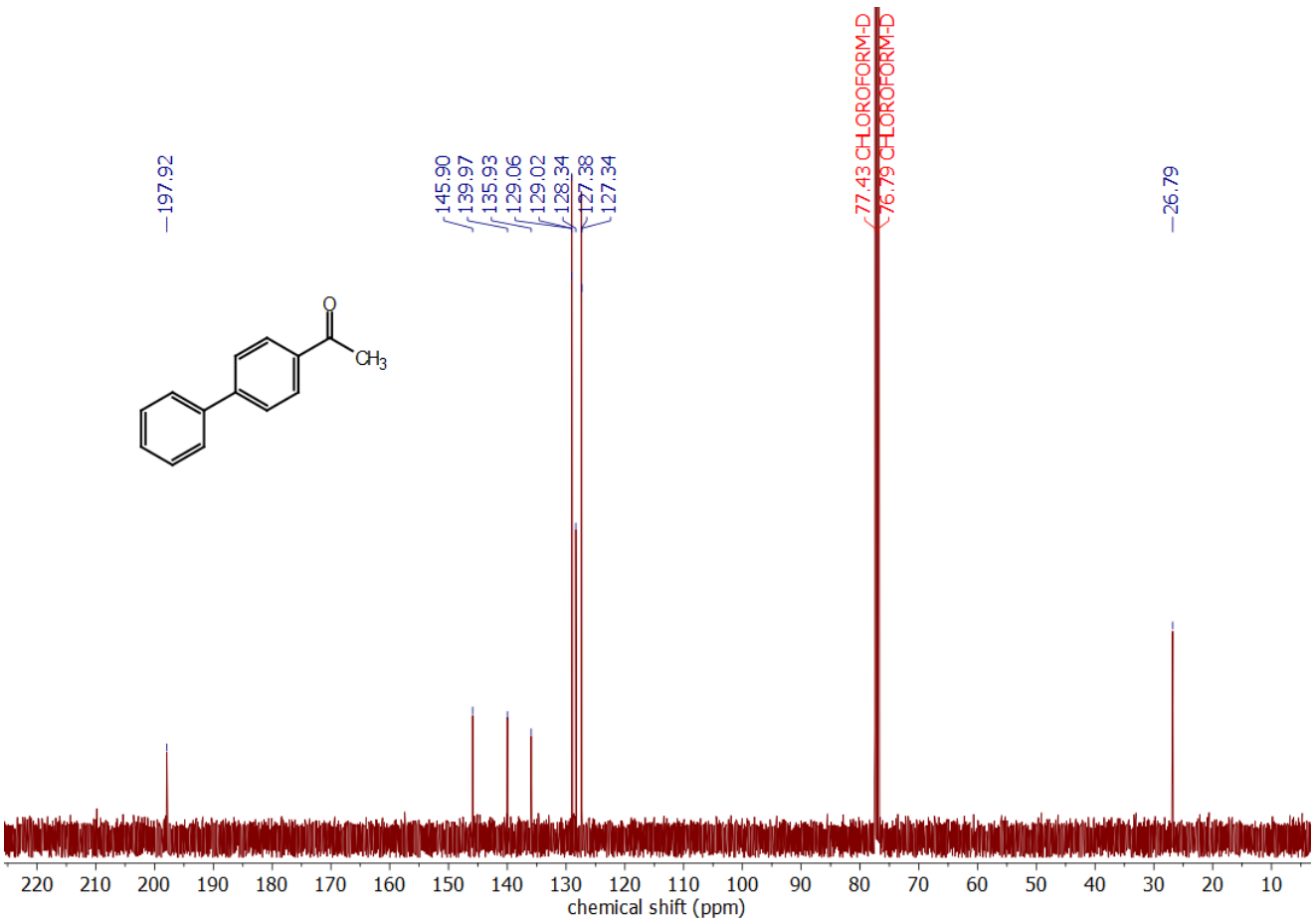
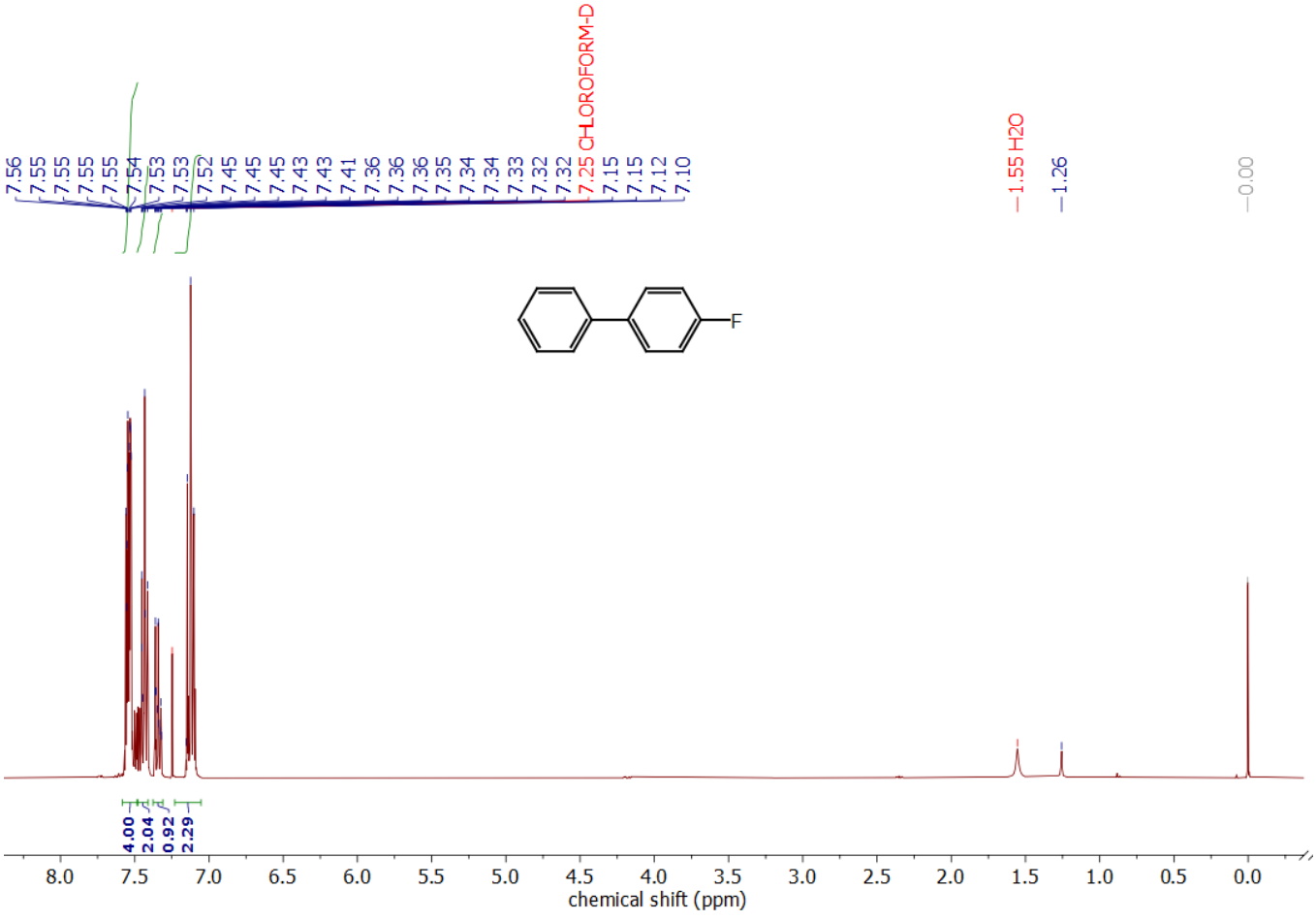
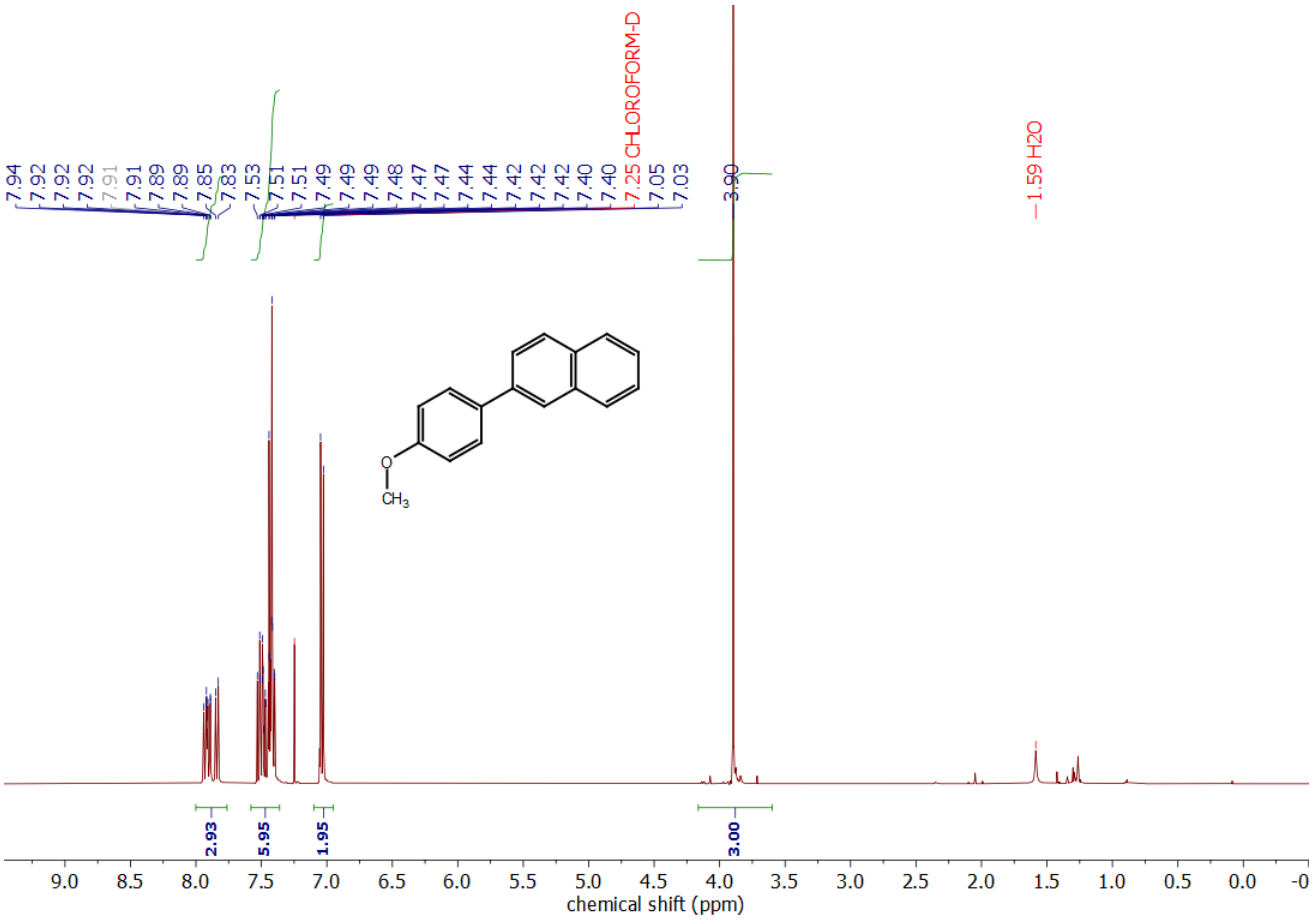
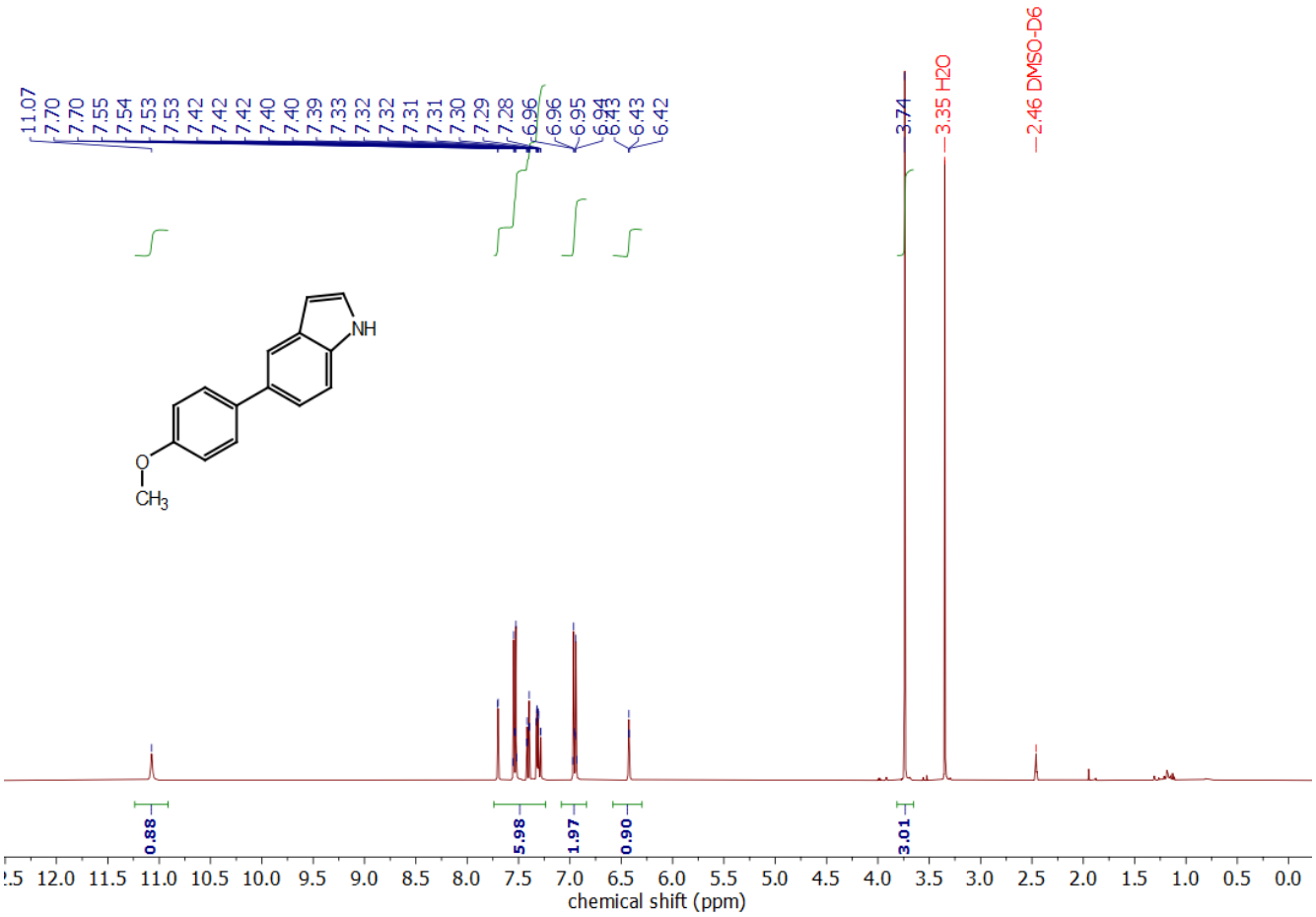
7.59
7.59
7.59
7.47
7.46
7.46
7.45
7.44
7.44
7.42
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.25 CHLOROFORM-D
7.19
7.18
7.16
2.43
1.55
CH3
1.01
2.82
4.17
0.99
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

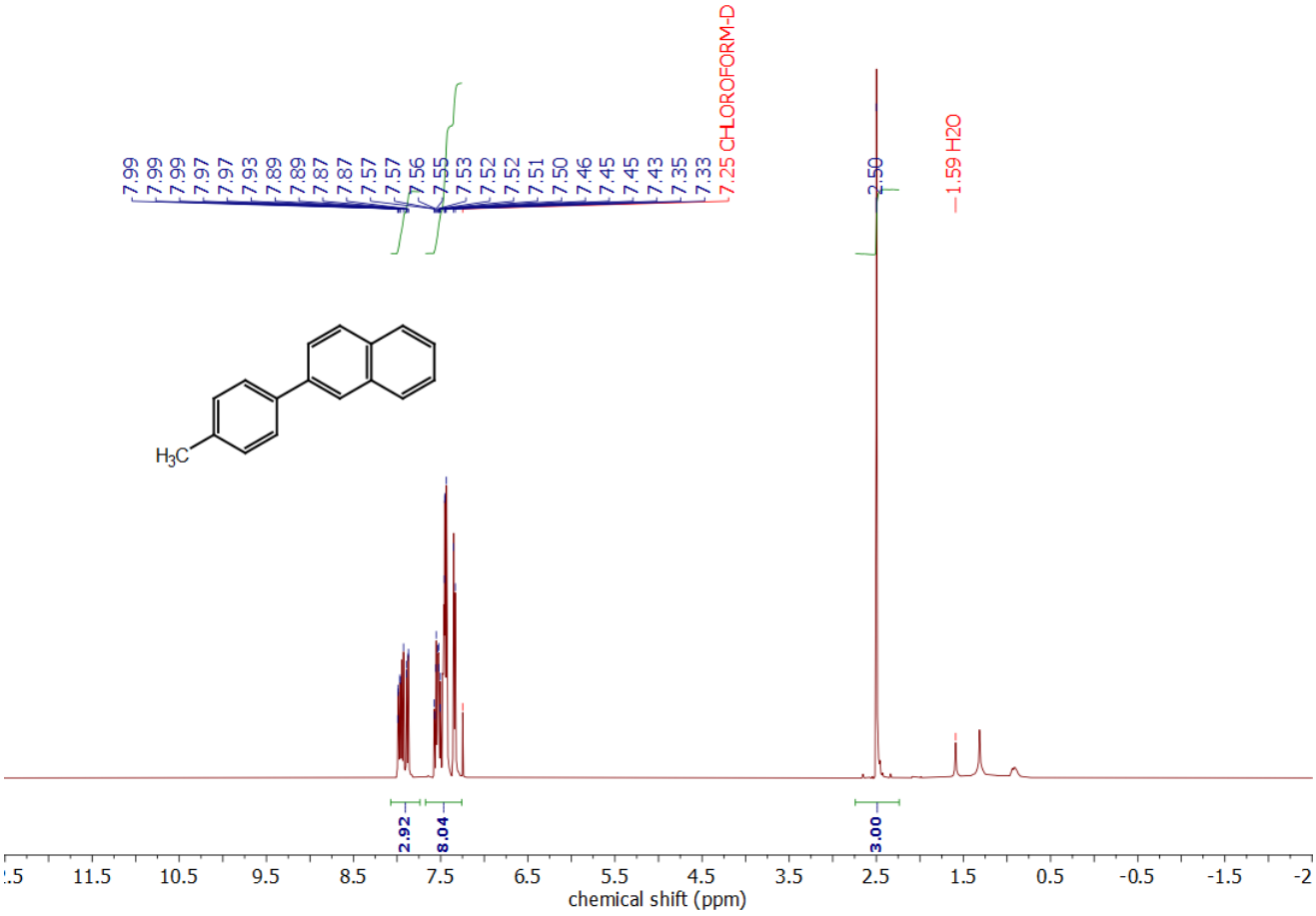

8.04
8.02
7.70
7.69
7.69
7.69
7.67
7.67
7.66
7.63
7.63
7.63
7.62
7.61
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.25 CHLOROFORM-D
2.63
1.58 H2O
0.01
0.01
0.02
CH3
O
1.95
3.94
2.90
3.00
3.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


197.92
145.90
139.97
135.93
129.06
129.02
128.34
127.38
127.34
77.43 CHLOROFORM-D
76.79 CHLOROFORM-D
26.79
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
chemical shift (ppm)

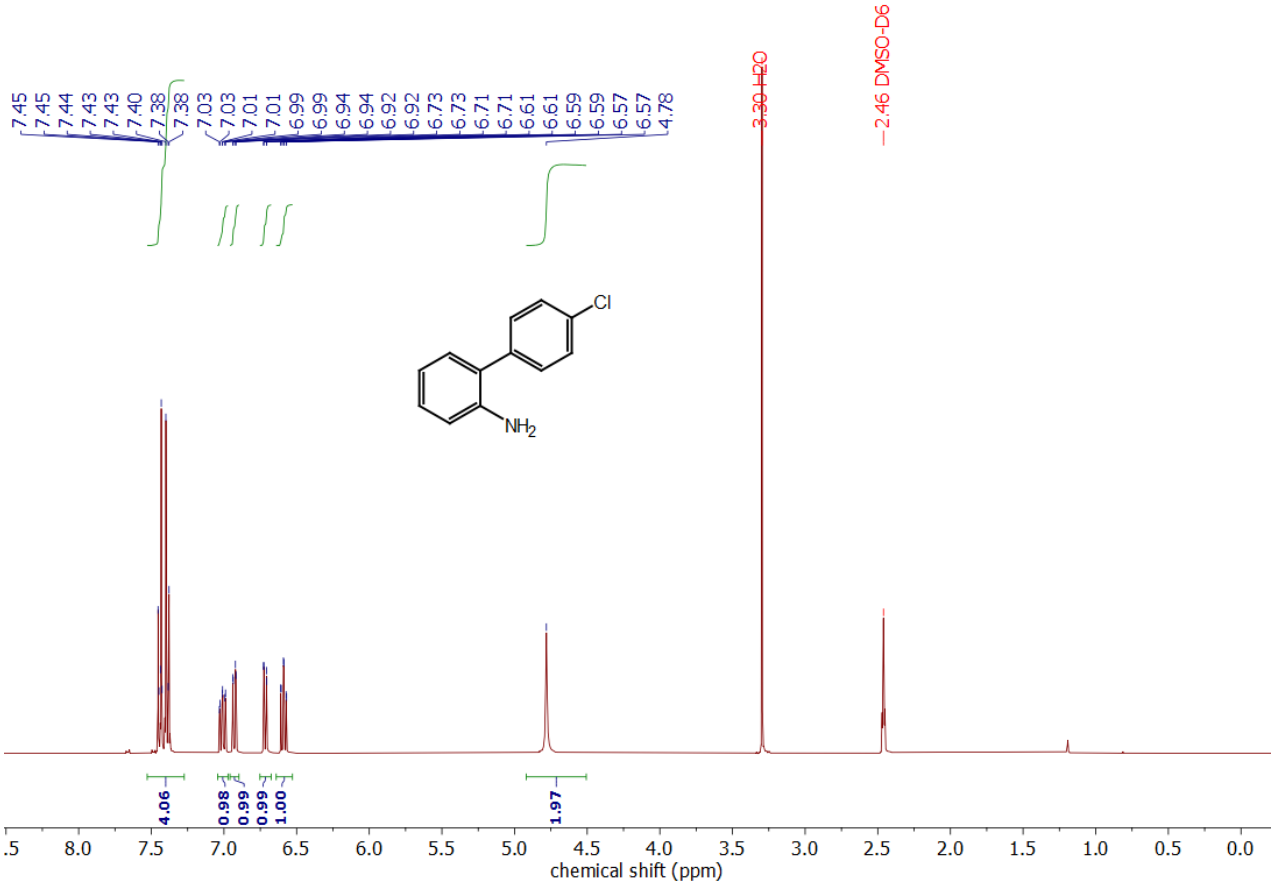

7.56 7.55 7.55 7.55 7.55 7.54 7.53 7.53 7.52 7.45 7.45 7.45 7.43 7.43 7.41 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32
7.25 CHLOROFORM-D
7.15 7.15 7.12 7.10
1.55 H2O
1.26
0.00
F
4.00
2.04
0.92
2.29
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

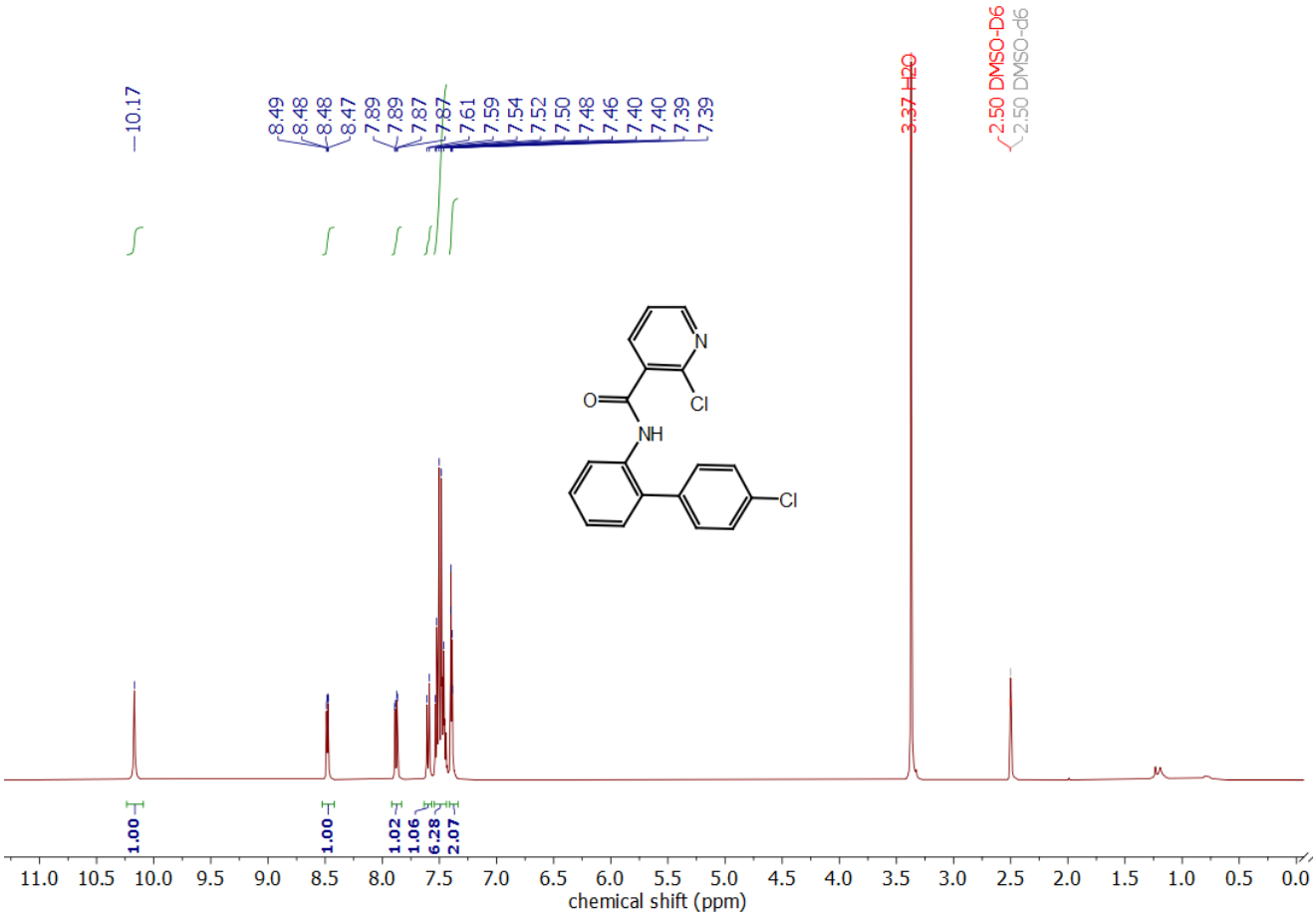

7.94
7.92
7.92
7.92
7.91
7.91
7.89
7.89
7.85
7.83
7.53
7.51
7.51
7.49
7.49
7.49
7.48
7.47
7.47
7.44
7.44
7.42
7.42
7.40
7.40
7.25 CHLOROFORM-D
7.05
7.03
3.90
1.59 H2O
O
CH3
2.93
5.95
1.95
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
chemical shift (ppm)

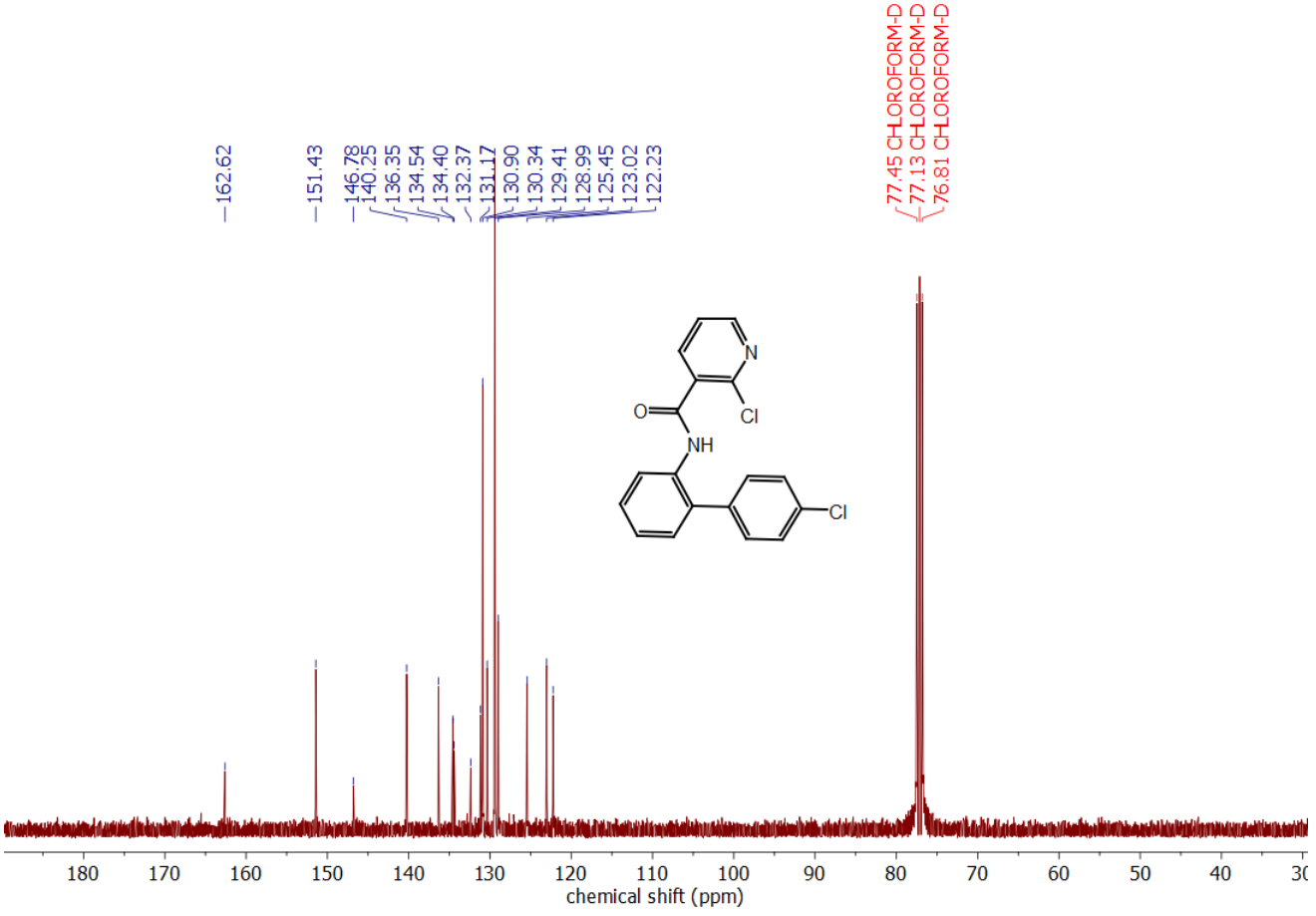

11.07
7.70
7.70
7.55
7.54
7.53
7.53
7.42
7.42
7.42
7.40
7.40
7.39
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
6.96
6.96
6.95
6.94
6.43
6.43
6.42
3.74
3.35 H2O
2.46 DMSO-D6
NH
O
CH3
0.88
5.98
1.97
0.90
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)



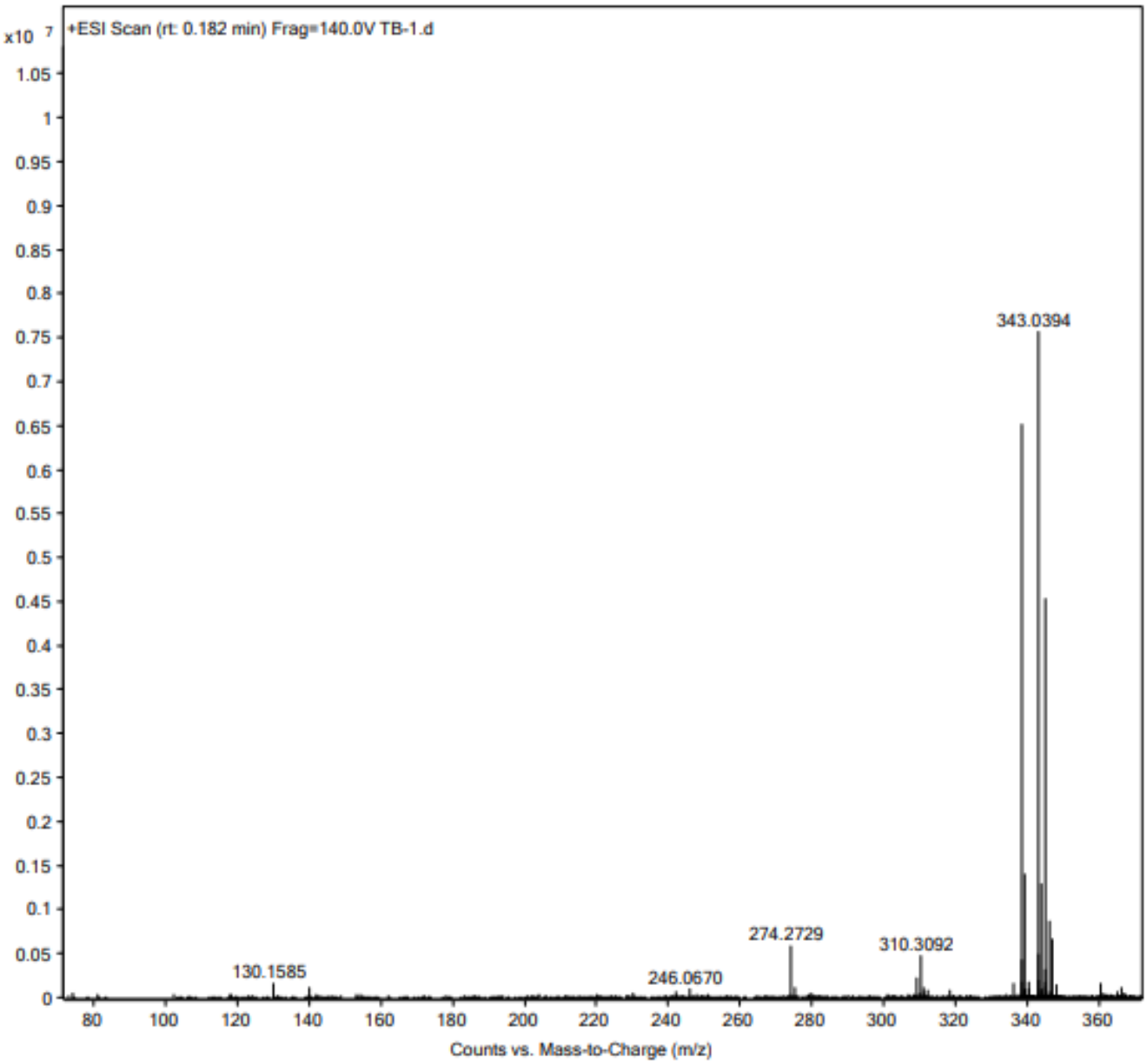
^{1}H (400 MHz, $CDCl_3$) **and ^{13}C** (100 MHz, DMSO-d_6) **NMR of Boscalid**[11]




10.17
8.49
8.48
8.48
8.47
7.89
7.89
7.87
7.87
7.61
7.59
7.54
7.52
7.50
7.48
7.46
7.40
7.40
7.39
7.39
3.37 H2O
2.50 DMSO-D6
2.50 DMSO-d6
N
Cl
O
NH
Cl
1.00
1.00
1.02
1.06
6.28
2.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)


162.62
151.43
146.78
140.25
136.35
134.54
134.40
132.37
131.17
130.90
130.34
129.41
128.99
125.45
123.02
122.23
77.45 CHLOROFORM-D
77.13 CHLOROFORM-D
76.81 CHLOROFORM-D
N
Cl
O
NH
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
chemical shift (ppm)

HR-MS data of Boscalid.



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