Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Protein – Inorganic Nano Hybrid Sheets of Pd Embedded BSA as Robust Catalyst in Water for Oxidase Mimic Activity and C-C Coupling Reactions, and as Sustainable Material for Micromolar Sensing of Dopamine

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Contents

SI01. TEM Images of Naked Pd_NPs, Pd_BSA$_1$ and Pd_BSA$_2$.

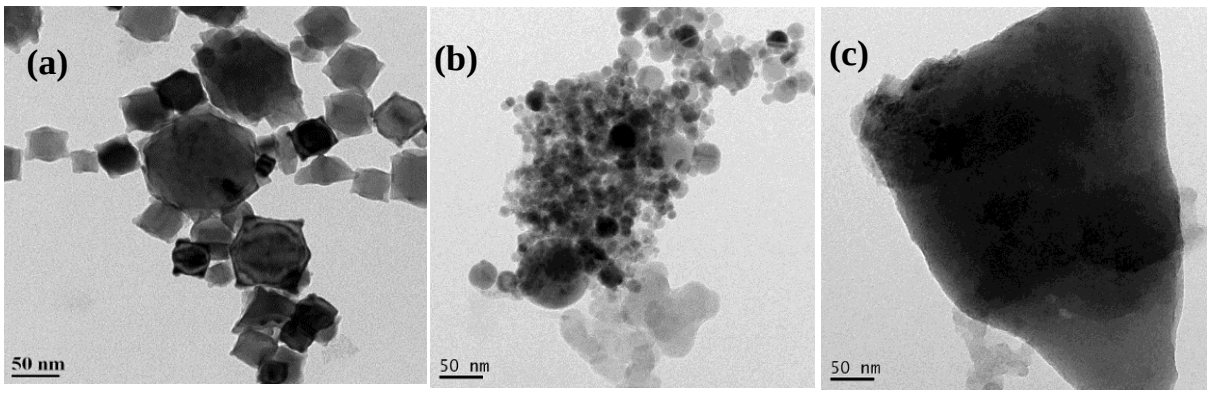


Figure S01. TEM images of (a) Naked Pd_NPs. (b) Spherical aggregates of Pd_BSA$_1$. (c) Initiation of smaller sheet formation in Pd_BSA$_2$.

SI02. TEM Images of Pd_NPs@BSA$_{sheet}$

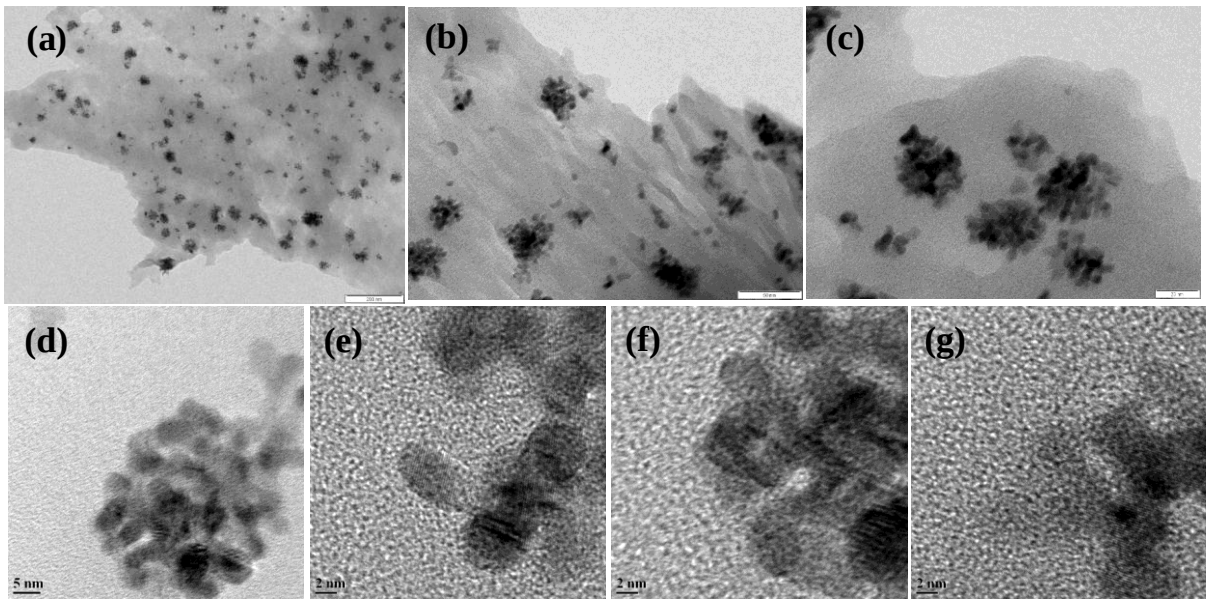
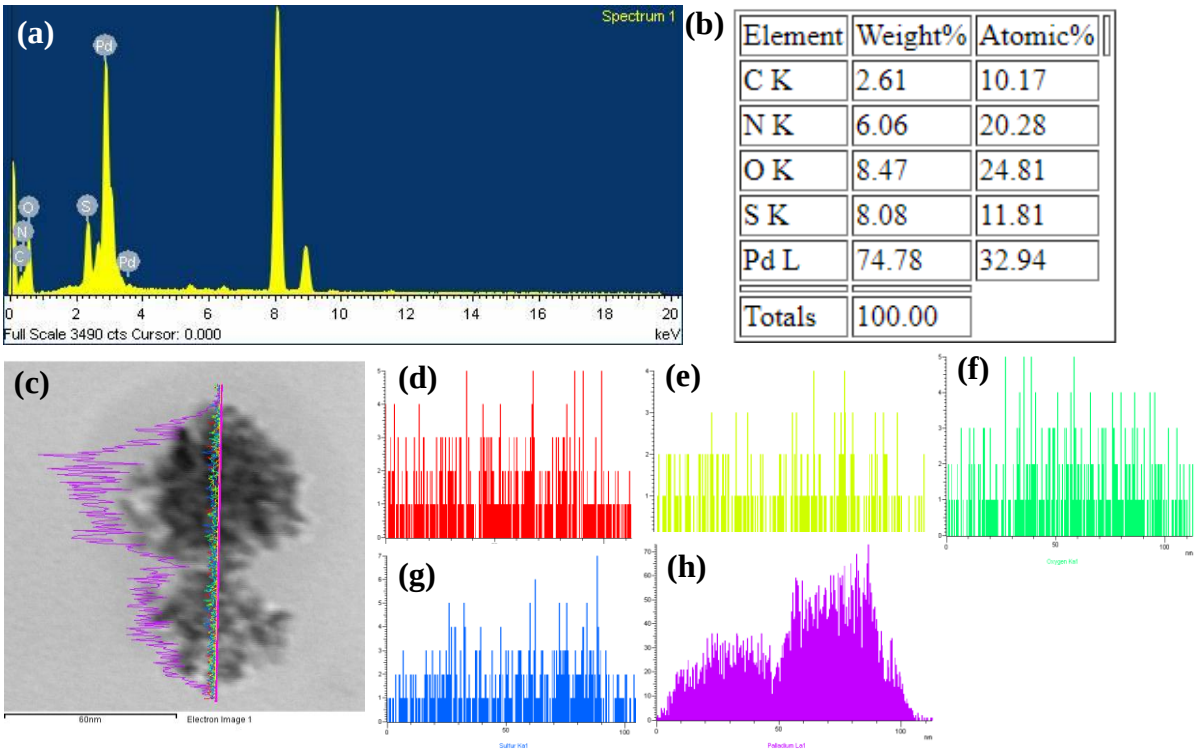


Figure S02. (a-c) are the TEM images of Pd_NPs@BSA$_{sheet}$ sheets. (d-g) HR-TEM of Pd_NPs embedded in Pd_NPs@BSA$_{sheet}$. Scale bar of (a) is (-200 nm), (b) is (-50 nm), (c) is (-20 nm), (d) is 5 nm, (e-g) is 2 nm.

SI03. EDS and Elemental Mapping of Pd_NPs@BSA$_{sheet}$.



Element	Weight%	Atomic%
C K	2.61	10.17
N K	6.06	20.28
O K	8.47	24.81
S K	8.08	11.81
Pd L	74.78	32.94
Totals	100.00	

Figure S03. (a) EDS of Pd_NPs@BSA$_{sheet}$. (b) Percentage element composition of Pd_NPs@BSA$_{sheet}$ from EDS. (c) Aggregate of Pd_NPs@BSA$_{sheet}$ area where line mapping is performed. Line mapping of (d) Carbon (red) (e) Nitrogen (yellow) (f) Oxygen (green) (g) Sulphur (blue) (h) Palladium (purple).

SI04. AFM and SEM Micrographs of Pd_NPs and Pd_NPs@BSA$_{sheet}$.

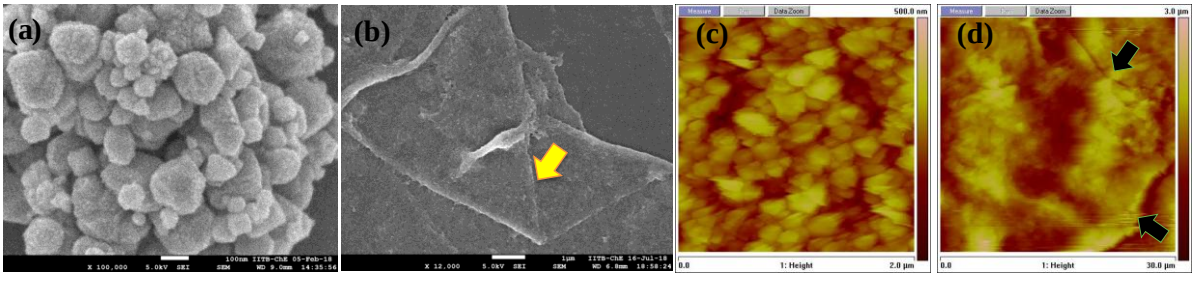


Figure S04. SEM images of (a) Naked Pd_NPs (scale bar -100 nm). (b) Hybrid Pd_NPs@BSA$_{sheet}$. Folds in the sheets are marked with yellow arrow. (scale bar – 1 µm). AFM images of (c) Naked Pd_NPs (scale bar – 2 µm). (d) Pd_NPs@BSA$_{sheet}$ where the edges are marked with black arrow. (scale bar – 30 µm).

SI05. Oxidase mimic activity of Pd_NPs@BSA$_{sheet}$ at pH 7.4 and enzyme kinetics

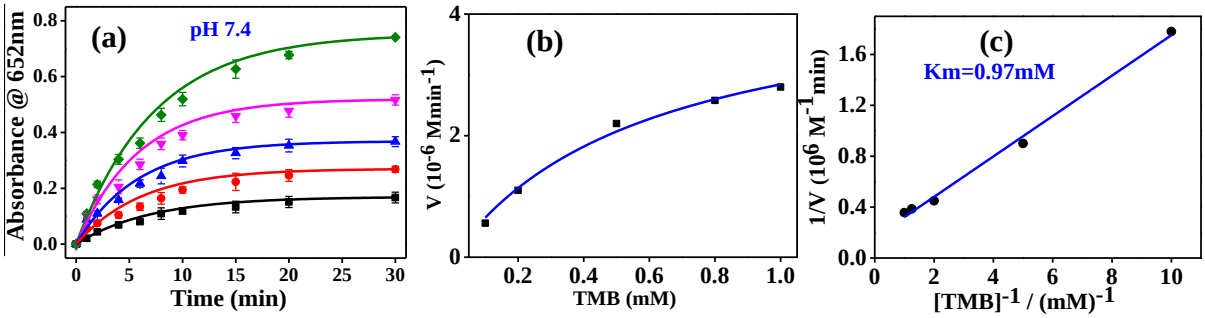


Figure S05. Oxidase activity of Pd_NPs@BSA$_{sheet}$ with varying substrate (TMB) concentrations at pH 7.4.[black – 0.1 mM, red – 0.3 mM, blue – 0.5 mM, magenta – 0.8 mM, green – 1 mM] using 100 µg/mL Pd_NPs@BSA$_{sheet}$ as catalyst at following time points: 1, 2, 4, 6, 8, 10, 15, 20, 30 minutes respectively. (b) steady state kinetics and (c) double reciprocal plots for calculation of K_m and V_{max} for oxidase activity of Pd_NPs@BSA$_{sheet}$ at pH 7.4.

SI06. Optimised Reaction Conditions for Suzuki Coupling.

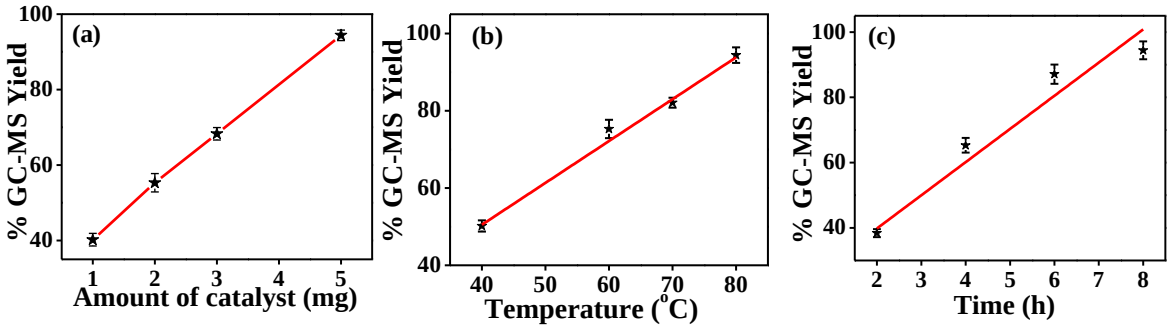


Figure S06. Optimised reaction conditions of Suzuki coupling for biphenyl product formation with varying conditions obtained from GC-MS yield (a) Amount of catalyst, (b) Temperature and (c) Time.

SI07. Substrate Scope of Pd_NPs@BSA$_{sheet}$ Catalyst in Suzuki Coupling Reactions.

Table S01. Suzuki coupling reactions of iodobenzene with derivatives of phenylboronic acid catalyzed by Pd_NPs@BSA$_{sheet}$.

Pd_NPs@BSA$_{sheet}$

Entry	Y	Z Product	% Con. /Sel.	TOF h^{-1}
1		1a	94.4/ 100	980
2		1b	98.5/ 100	1022
3		1c	93.6/ 99.5	972
4		1d	96.8/ 100	1005
5		1e	95.2/ 100	988
6		1f	92.7/ 90.5	962
7		1g	96.6/ 100	1003
8		1h	86.6/ 80.2[a]	899
9		1i	95.8/ 100	994
10		1j	96.8/ 77.6[b]	1005
11		1k	85.4/ 83.6[c]	886

Reaction conditions: A = iodobenzene (0.49 mmol) (1 equiv), B = phenylboronic acid (0.74 mmol), K_2CO_3 (0.98 mmol), Pd_NPs@BSA_{sheet} (5mg, 0.059 mol%), temperature (80 °C), time (8h). Major by-products: [a]2,2'-dimethoxy-1,1'-biphenyl, [b]3,3',5,5'-tetramethyl-1,1'-biphenyl, [c]3,3',4,4'-tetramethoxy-1,1'-biphenyl. Yield was calculated based on the GC-MS data. Turn over frequency calculated as (moles of product) / (moles of catalyst in terms of Pd × time in h)

SI08. Characterisation data of Suzuki Coupling Reaction Products.

Characterization Data of 1,1'-Biphenyl (1a). White solid; mp: 68–70°C, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, *J*= 8.5, 1.5 Hz, 4H), 7.45 (t, *J*= 8.0 Hz, 4H), 7.35(t, *J*= 7.5 Hz, 2H).

Characterization Data of 4-fluoro-1, 1'-Biphenyl (1b). White solid; mp: 75-79 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (dd, J= 6.0, 2.4 Hz, 3H), 7.76–7.72 (m, 1H), 7.22–7.16 (m, 4H), 7.12–7.06 (m, 1H).

Characterization Data of 4-Chloro-1, 1'-Biphenyl (1c). White solid; mp: 77-79°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50-7.46 (m, 4H), 7.42-7.39 (m, 5H).

Characterization Data of 4-methyl-1, 1'-biphenyl (1d). White solid; mp: 44-46 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H,), 7.25 (2H, d, *J* = 7.6 Hz), 2.40 (s, 3H).

Characterization Data of [[1, 1'-biphenyl]-4-carbaldehyde (1e). White solid; mp: 57-59 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.06 (s, 1H), 7.95 (dt, *J*= 8.0, 1.6 Hz, 2H), 7.75 (dd, *J*= 6.4, 1.6 Hz, 2H), 7.64 (dt, *J*= 7.2, 1.5 Hz, 2H), 7.5-7.40 (m, 3H).

Characterization Data of 1-{[1-1'biphenyl]-4-yl} ethane-1-one (1f). White solid; mp: 116–118°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03 (dt, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.69 (dt,

J = 8.5 Hz, 2 Hz, 2H), 7.63 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H,), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.42-7.39 (m, 1H), 2.64 (s, 3H).

Characterization Data of [1, 1'-biphenyl]-4-carbonitrile (1g). White solid; mp: 82-85 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.74–7.67 (m, 4H,), 7.59 (d, *J* = 8.0 Hz, 2H), 7.51–7.41 (m, 3H).

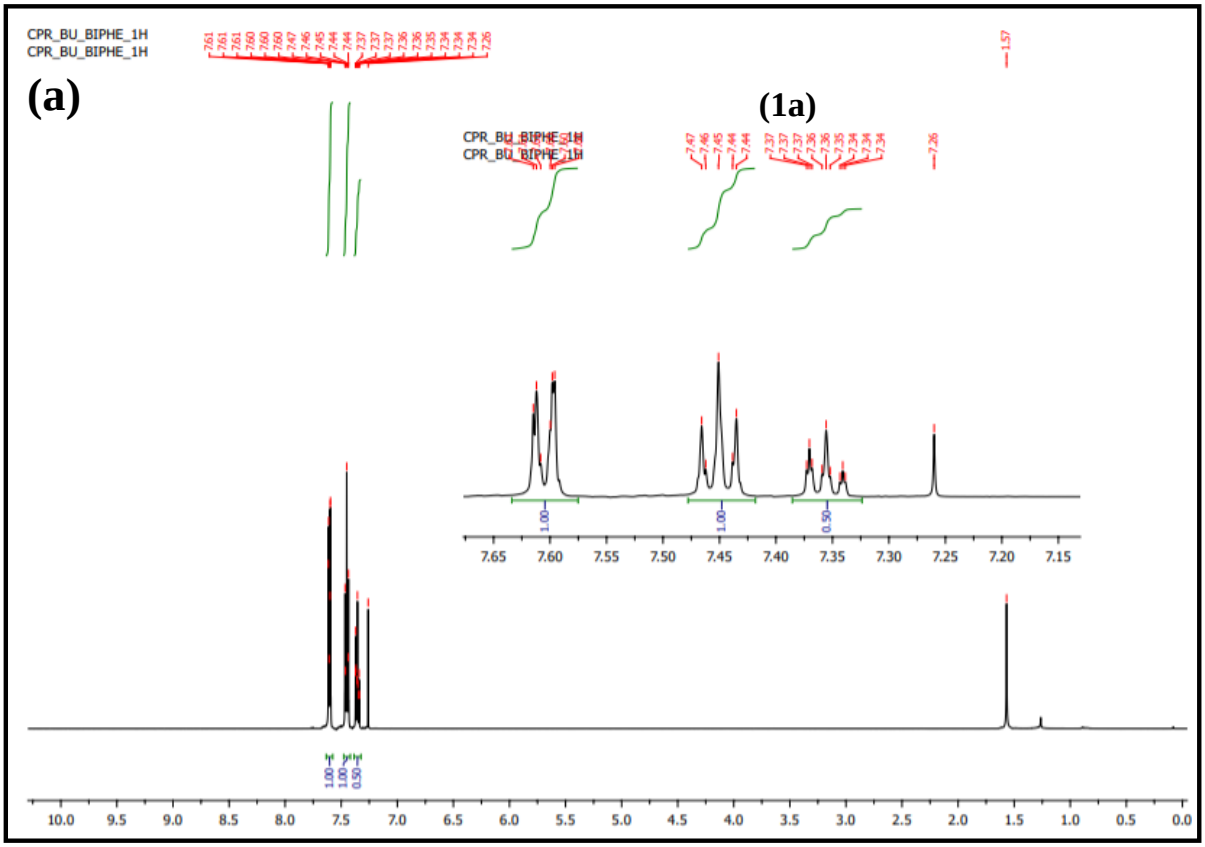
Characterization Data of 2-methoxy-1,1'-biphenyl (1h). White solid; mp 31-33°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.54 (d, *J* = 8.0, 2H,), 7.42 (t, *J* = 7.5, 2H), 7.35–7.32 (m, 3H), 7.04 (t, *J* = 7.0, 1H), 6.99 (d, *J* = 8.5, 1H,), 3.82 (3H, s).

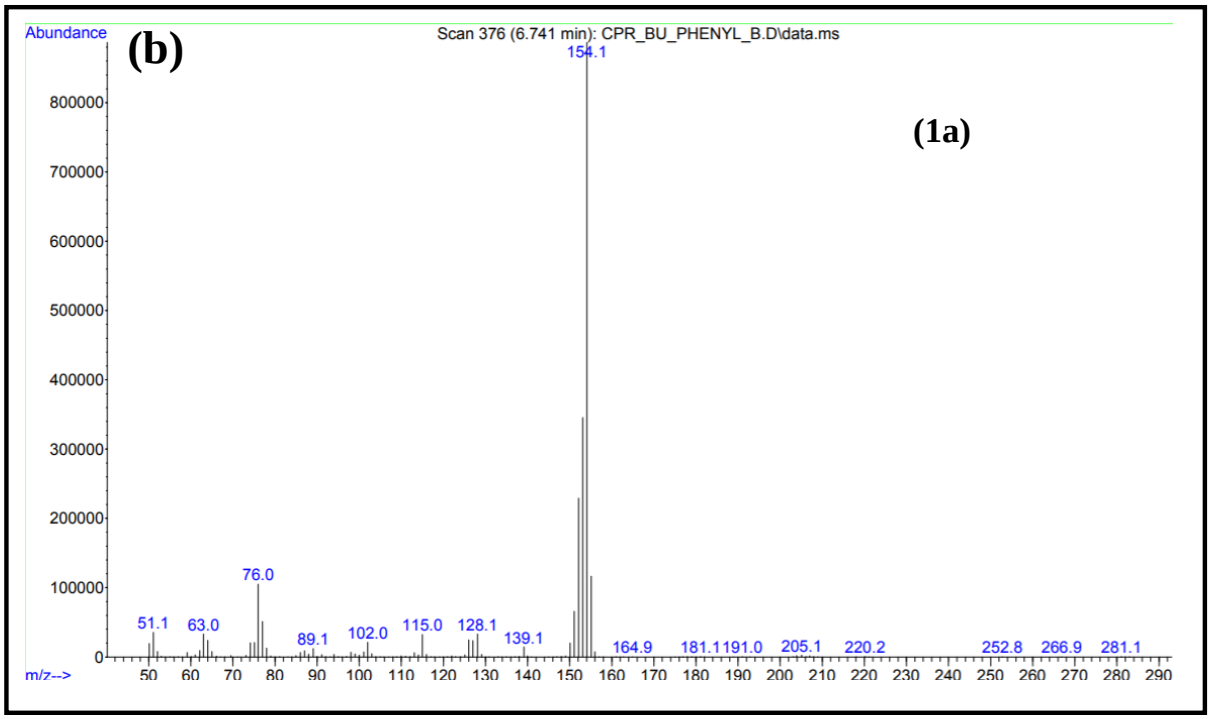
Characterization Data of 3-(trifluoromethyl)-1,1'-biphenyl (1i). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.42 (d, 1H,), 8.02 (s, 1H), 7.94-7.83 (m, 2H), 7.78-7.26 (m, 5H).

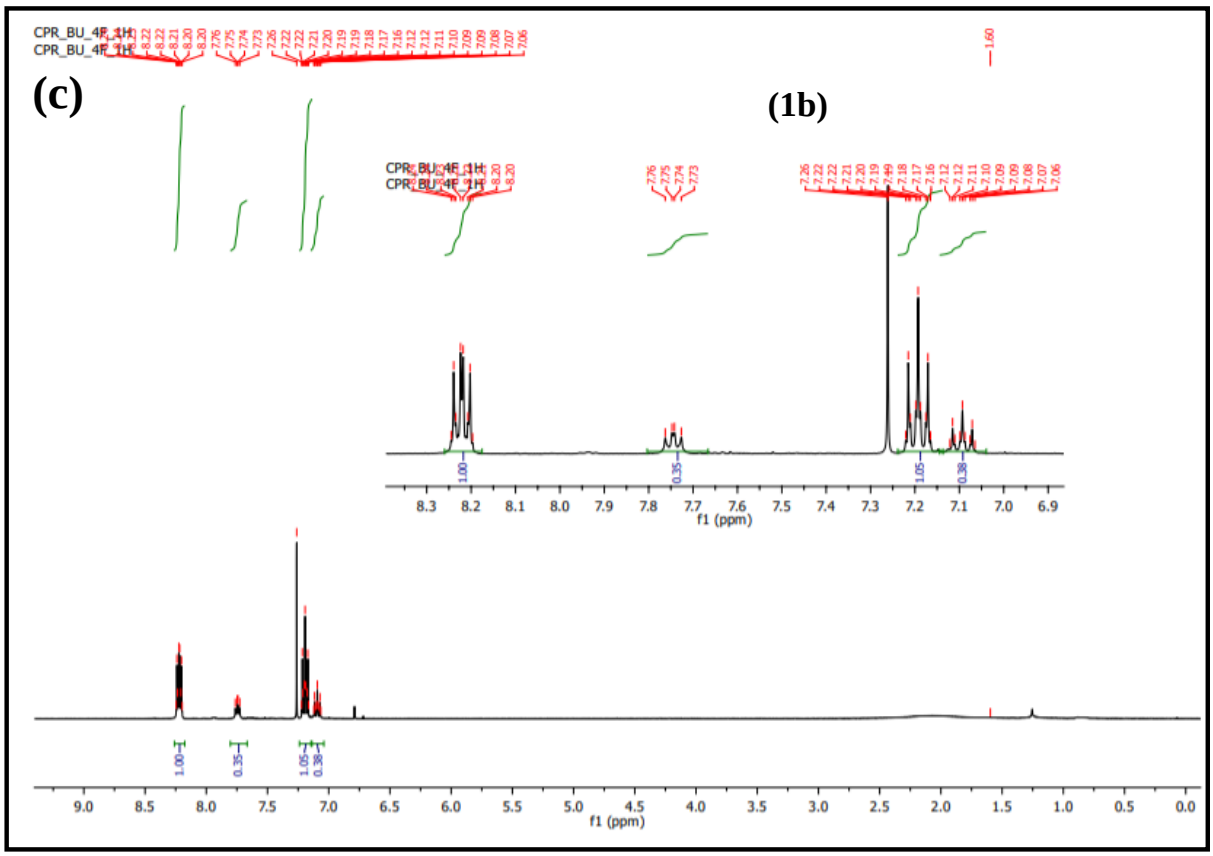
Characterization Data of 3, 5-dimethyl-1, 1'-biphenyl (1j). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J*= 7.2 Hz, 2H), 7.43 (t, *J*= 7.6 Hz, 2H), 7.35 (t, *J*= 7.2 Hz, 1H), 7.24 (s, 2H), 7.02 (s, 1H), 2.39 (s, 6H).

Characterization Data of 3, 4-dimethoxy-1, 1'-biphenyl (1k). White solid; mp: 43-46°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (dd, *J*= 8.0, 1.2 Hz , 2H), 7.43 (t, *J*= 7.2 Hz, 2H), 7.34-7.30 (m, 1H), 7.17-7.11 (m, 2H), 6.95 (d, *J*= 8.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H).

SI09. ^{1}H-NMR and GCMS Spectral Data of all the Cross Coupled Products.



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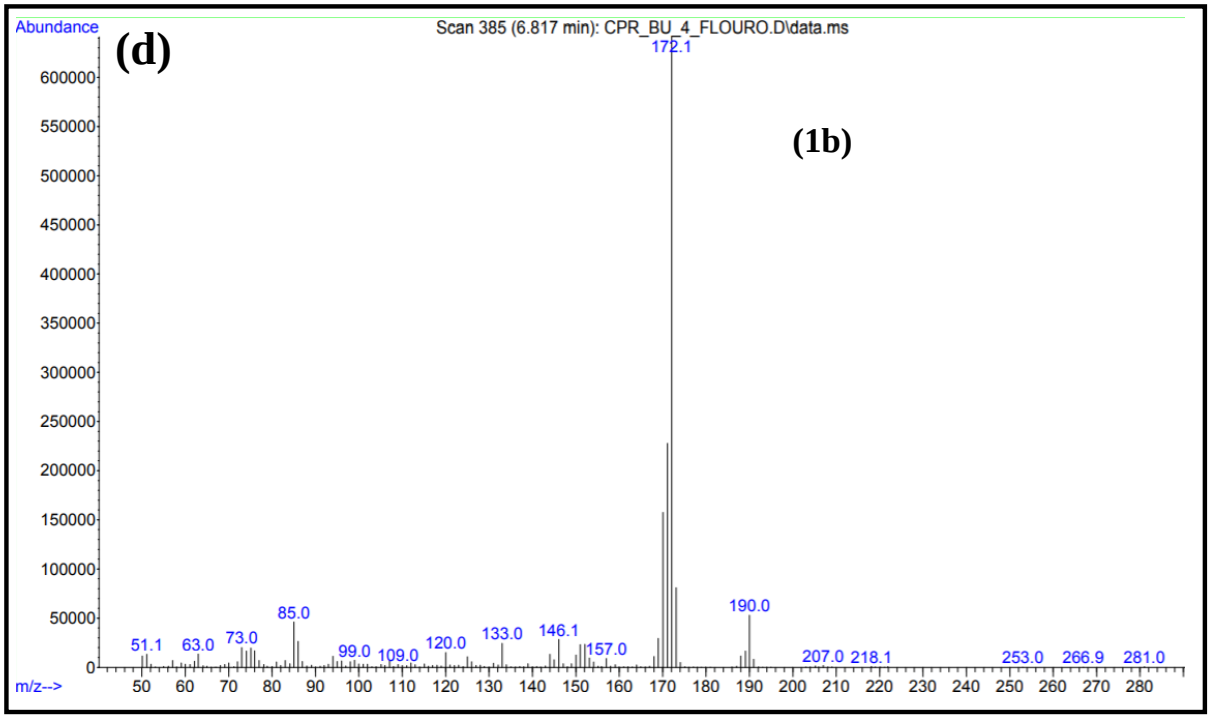
(1b)
f1 (ppm)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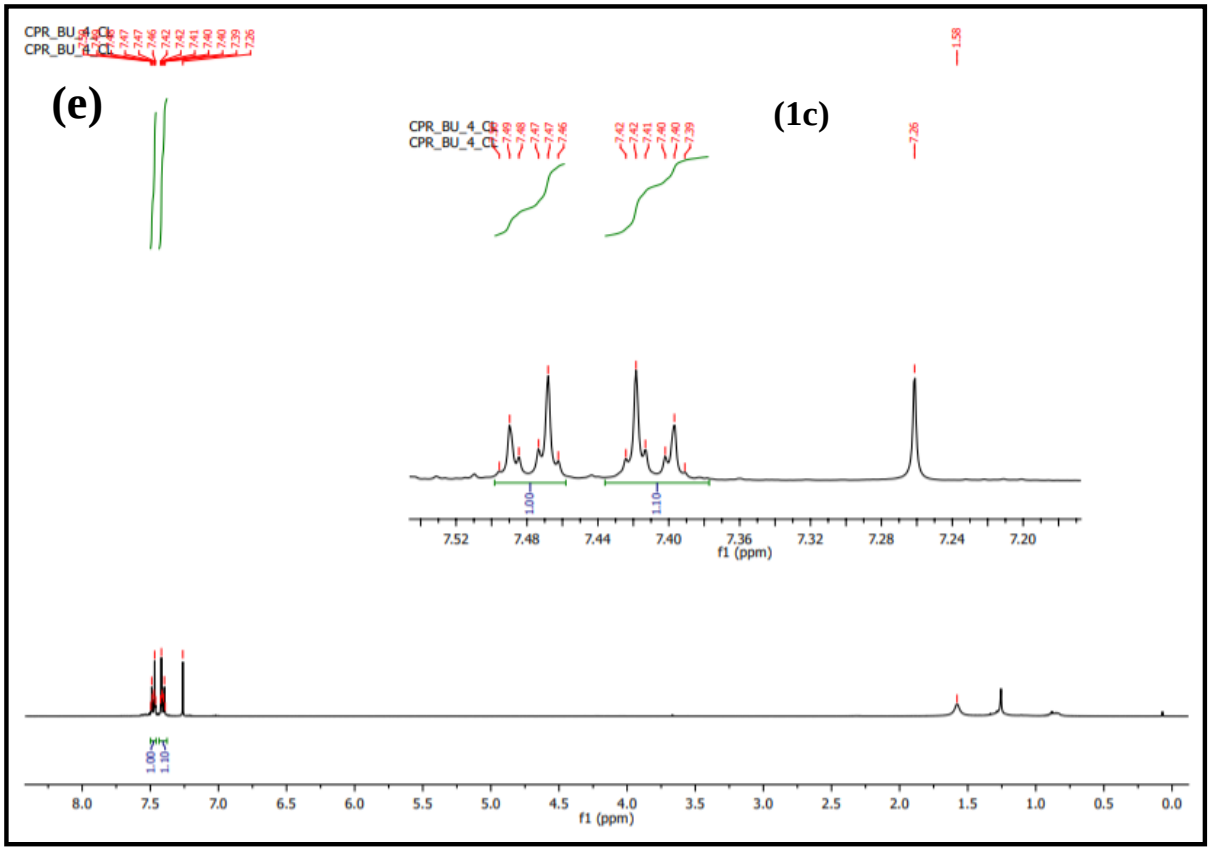
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(1c)
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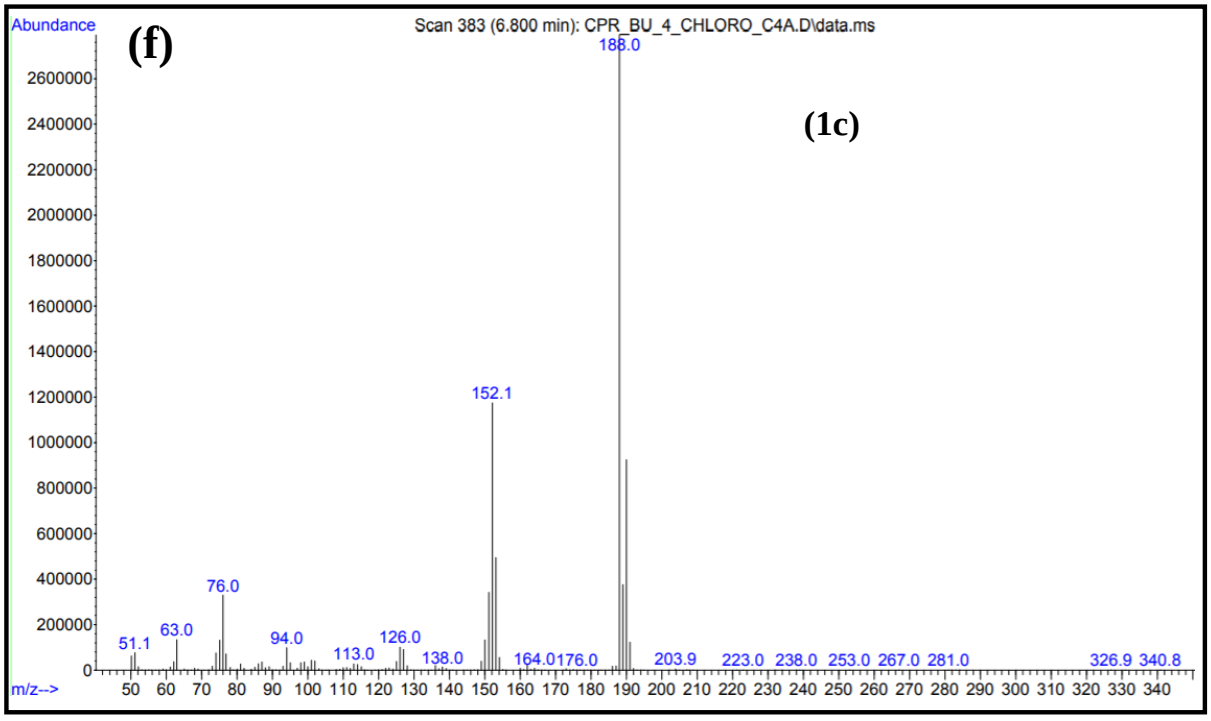
7.44
7.40
7.36
7.32
7.28
7.24
7.20
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


(f)
(1c)
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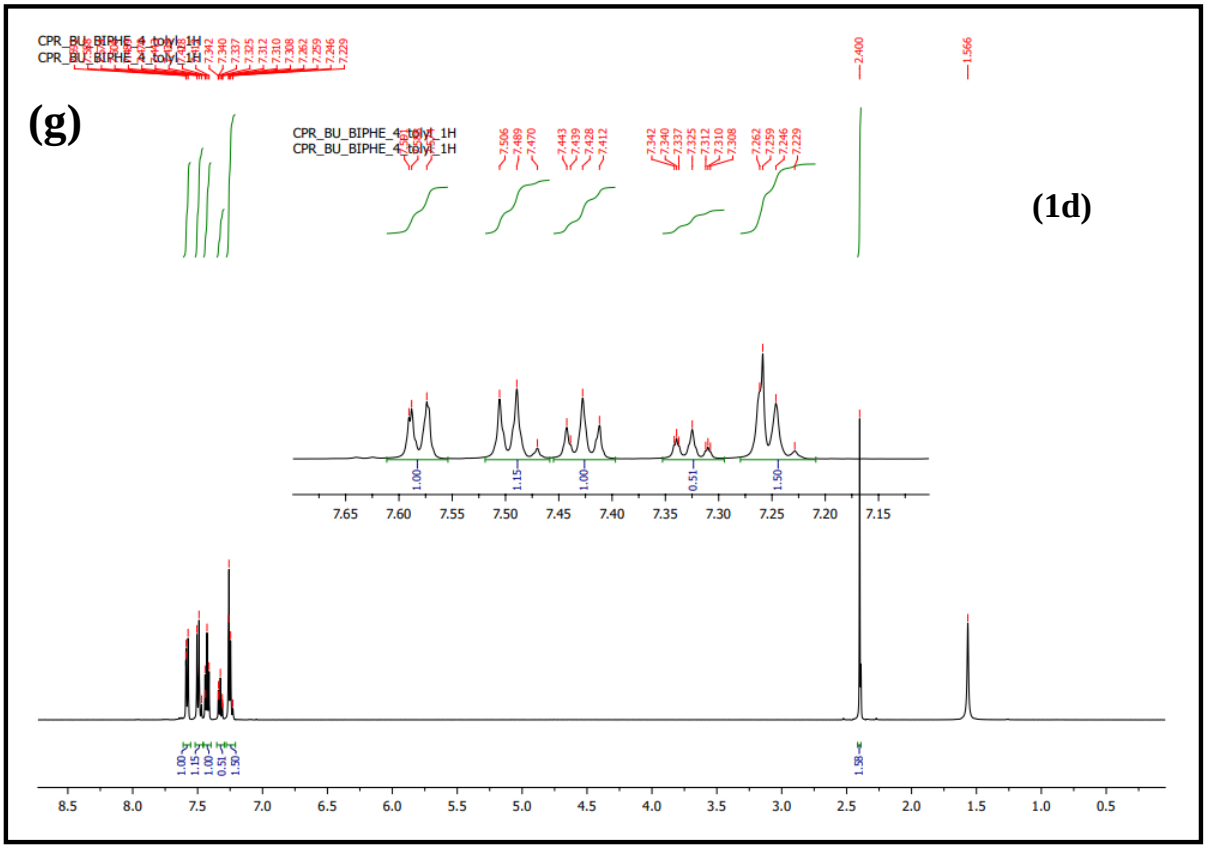
152.1
76.0
63.0
51.1
94.0
113.0
126.0
138.0
164.0
176.0
203.9
223.0
238.0
253.0
267.0
281.0
326.9
340.8
m/z-->


(g)
(1d)
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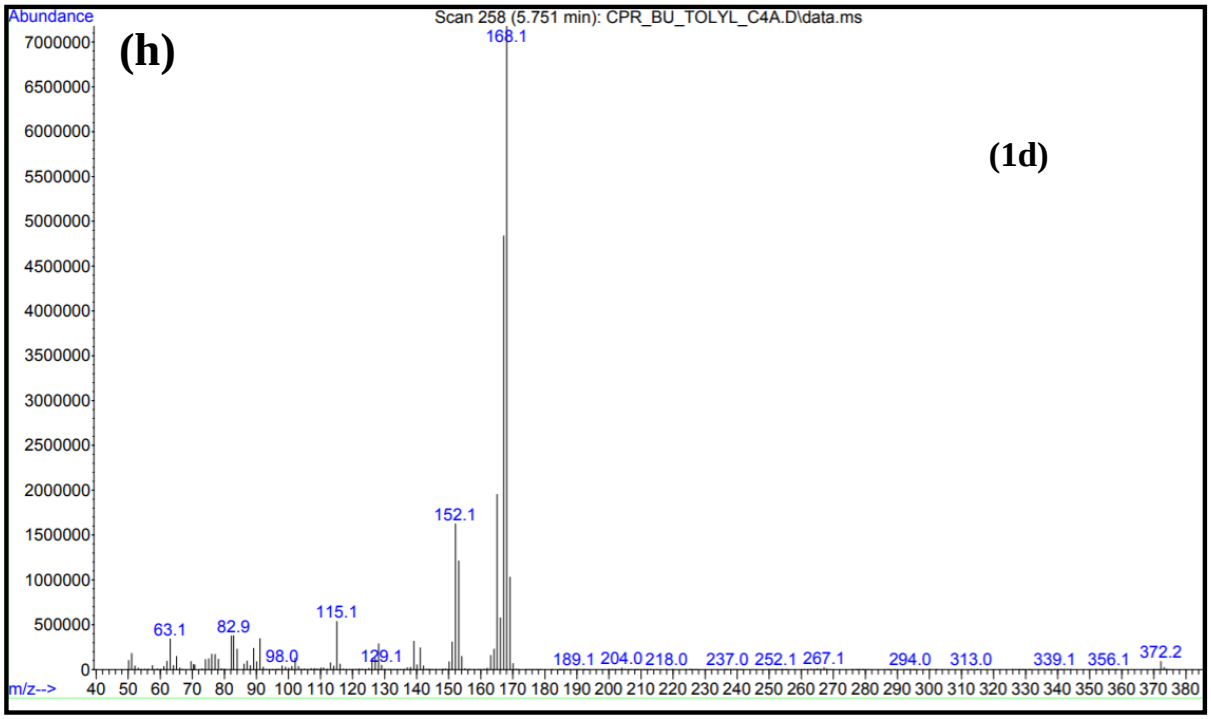
CPR_BU_BIPHE_4-tolyl_1H


(h)
(1d)
Abundance
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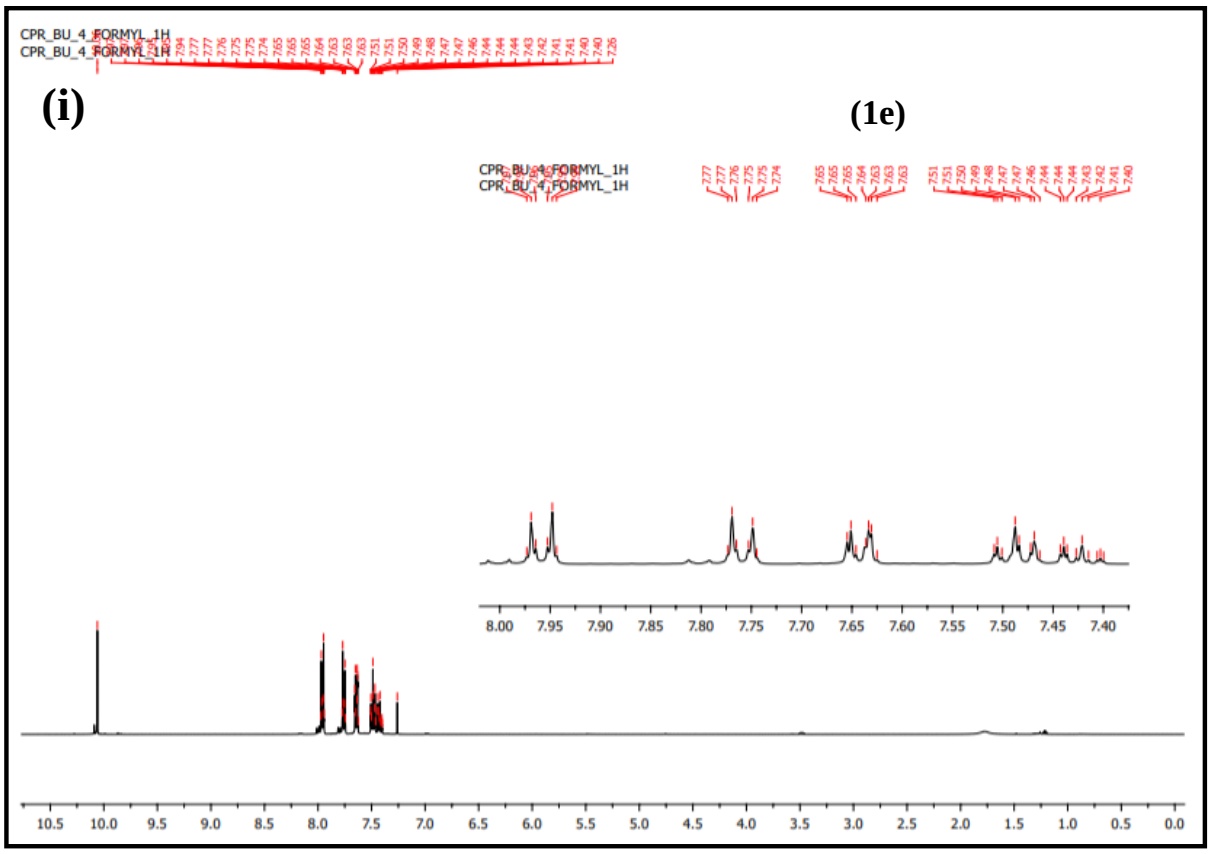
115.1
63.1
82.9
98.0
129.1
m/z-->


(i)
(1e)
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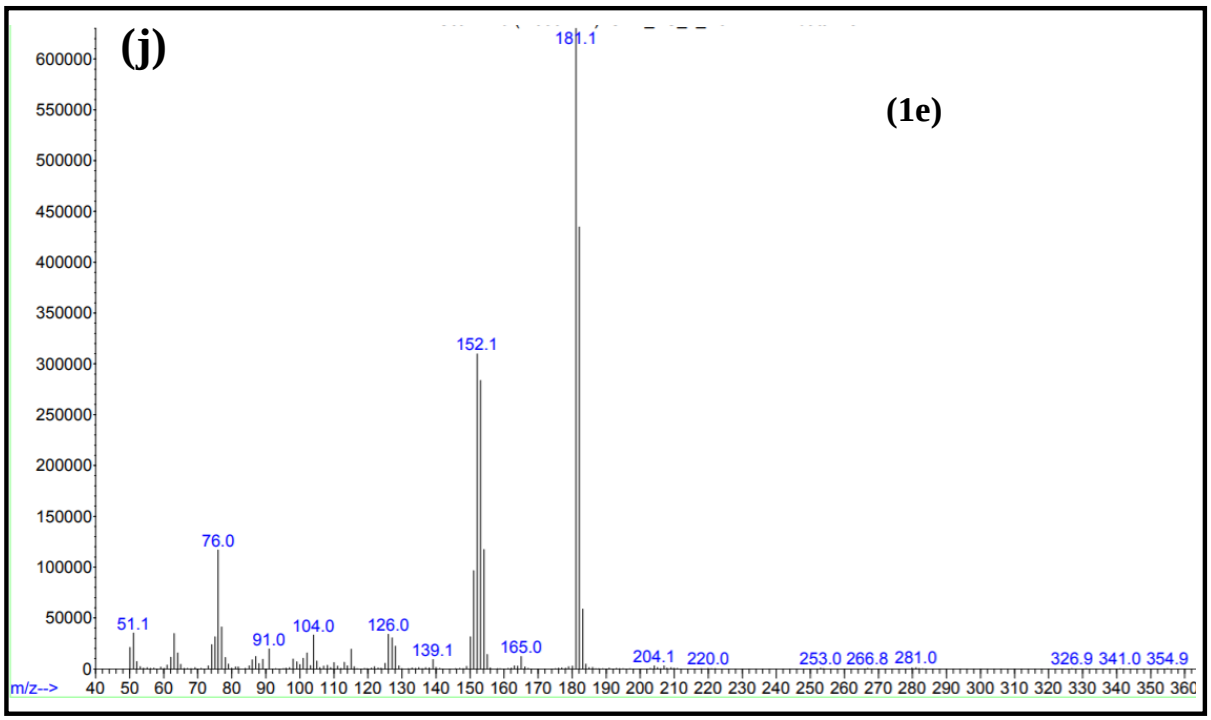
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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(1e)
181.1
152.1
76.0
51.1
91.0
104.0
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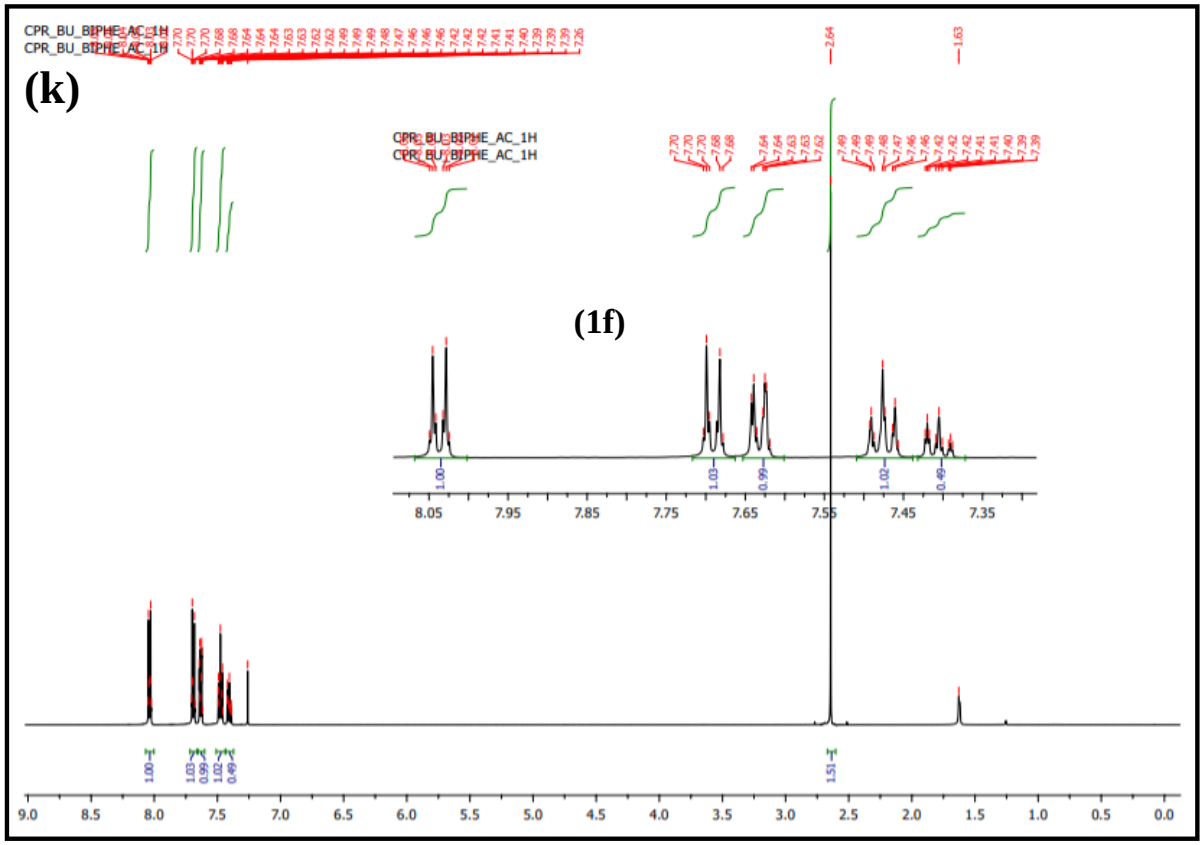
220.0
253.0
266.8
281.0
326.9
341.0
354.9
m/z-->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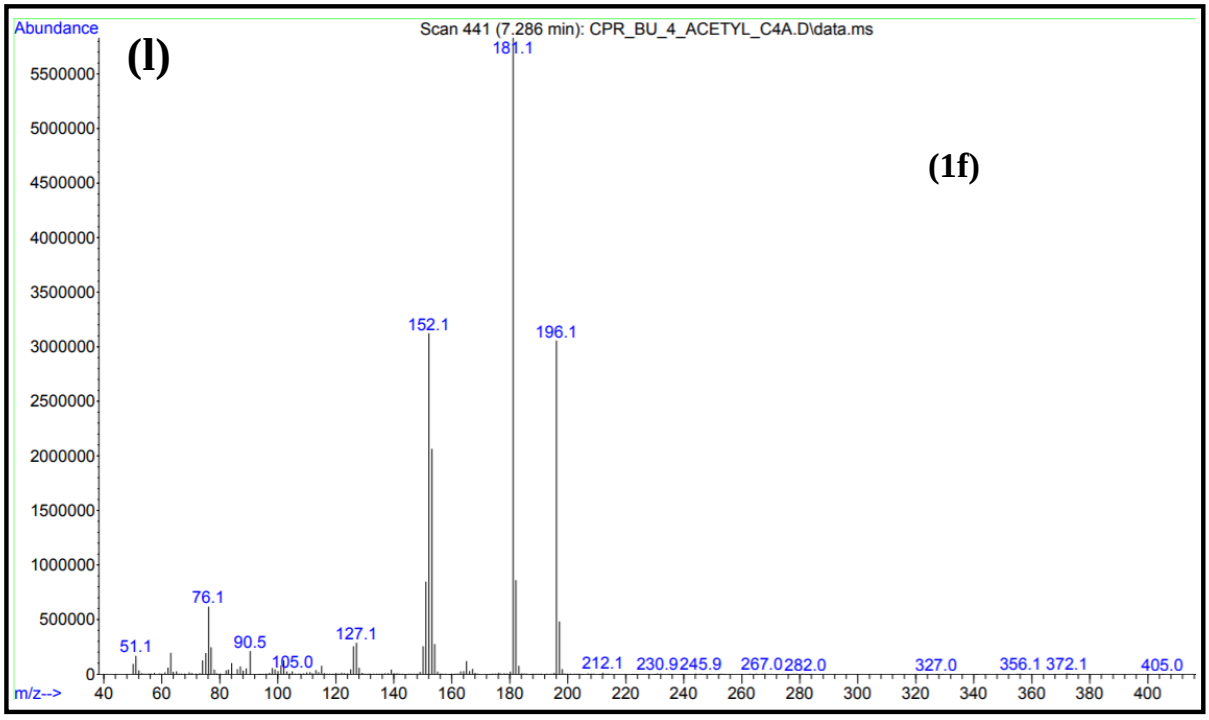
(1f)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(1f)
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51.1
90.5
105.0
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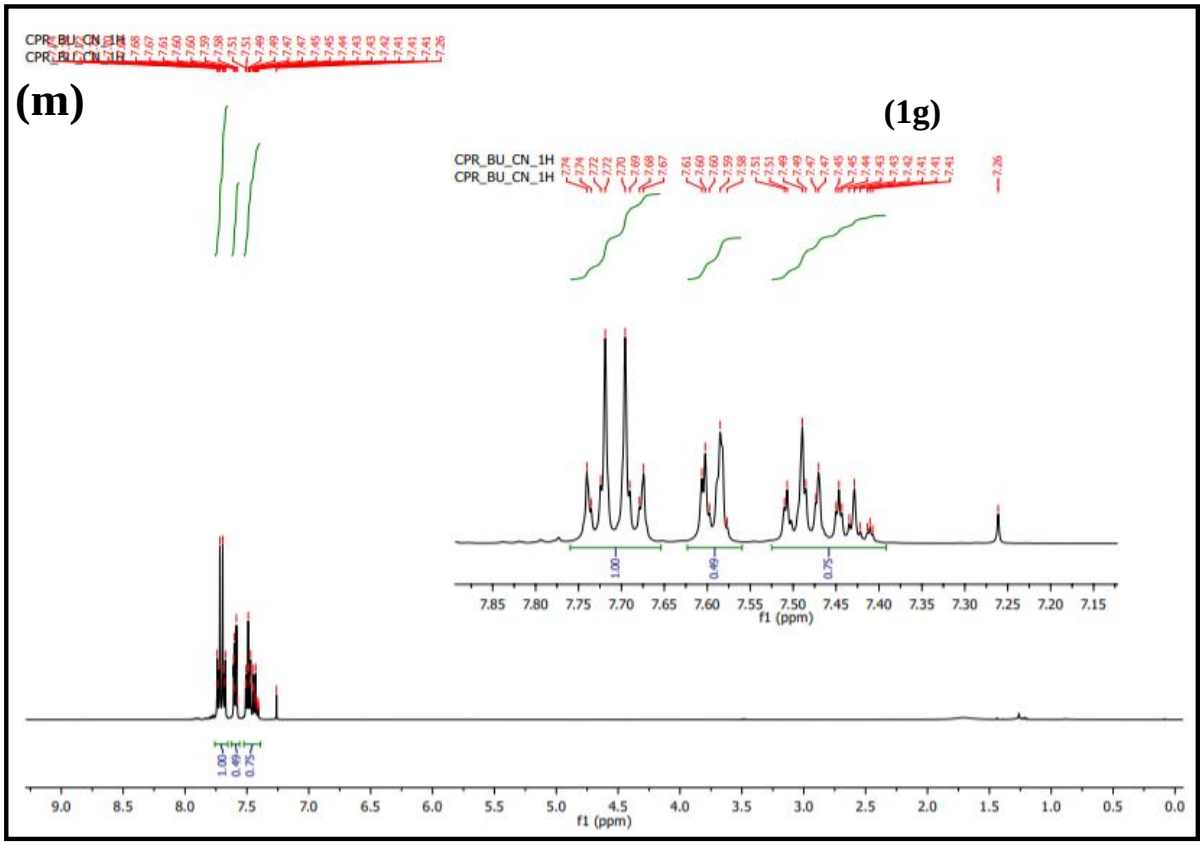
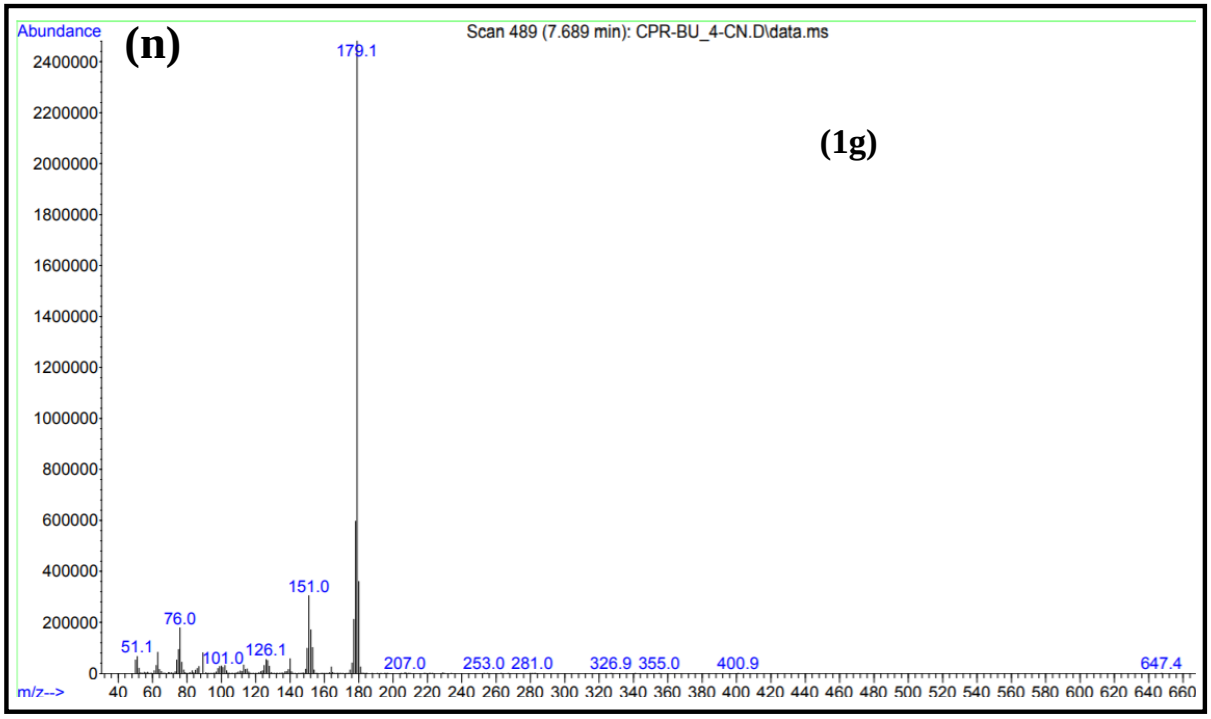
267.0
282.0
327.0
356.1
372.1
405.0
m/z-->


(m)
(1g)
CPR_BU_CN_1H
CPR_BU_CN_1H
f1 (ppm)


(n)
(1g)
Abundance
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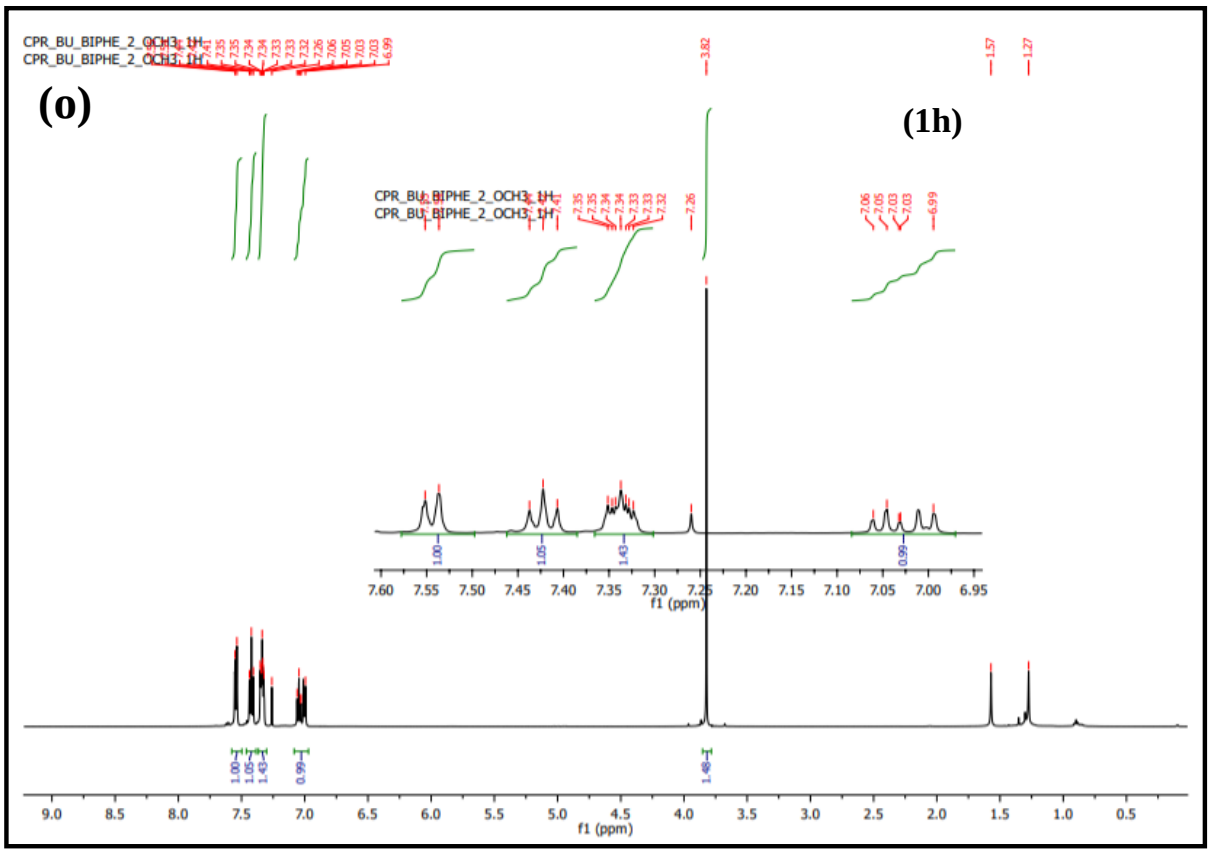
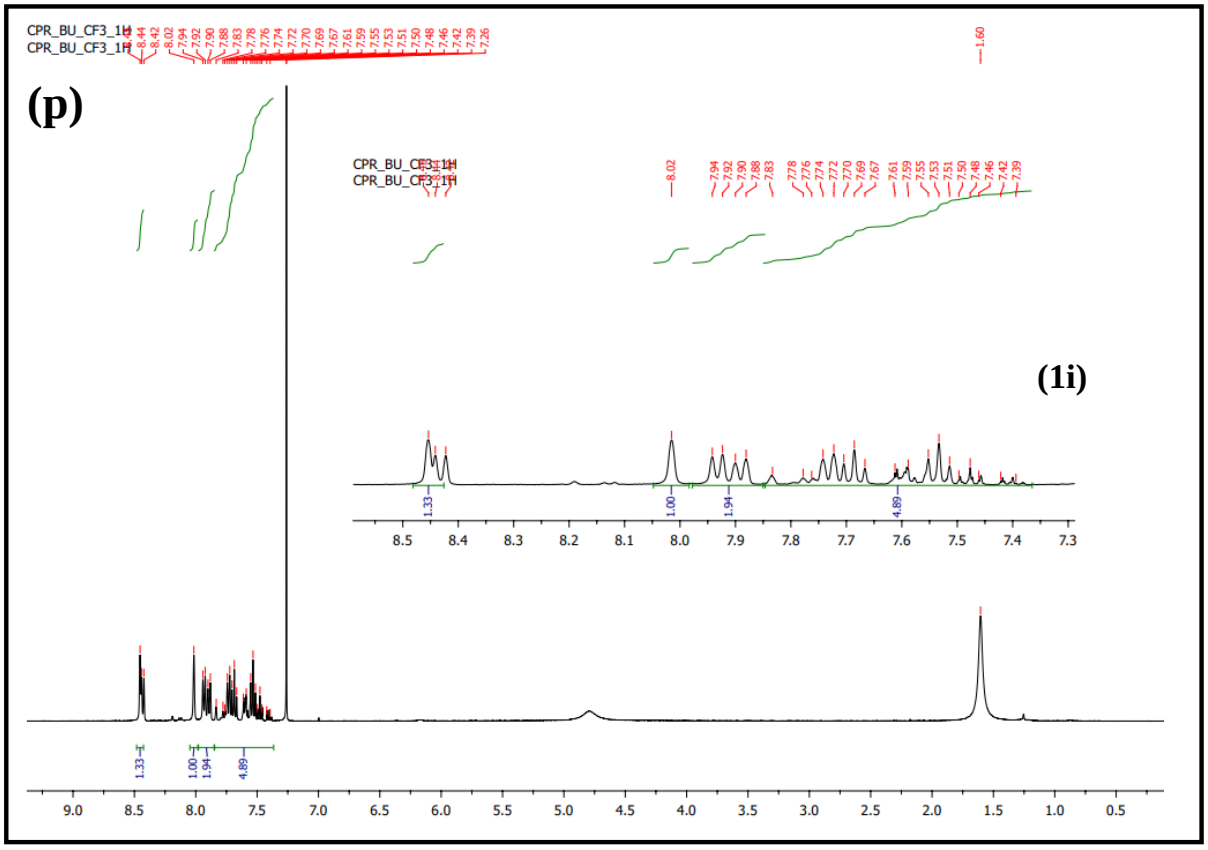
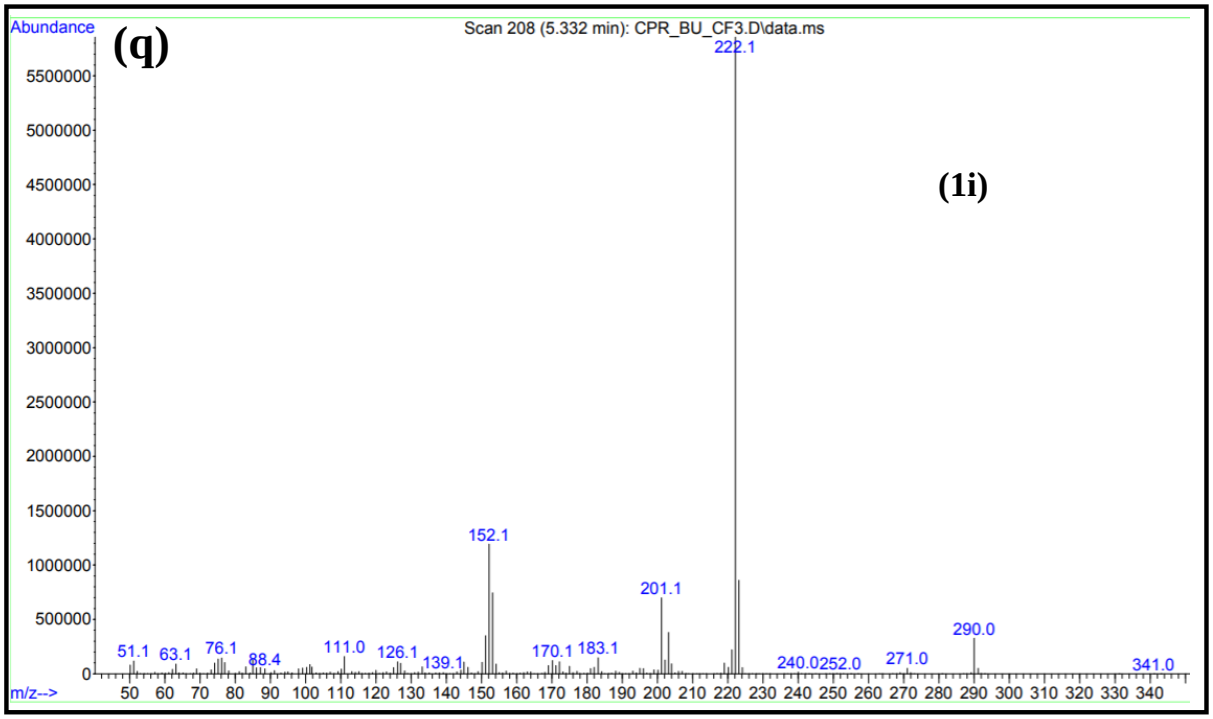
355.0
400.9
647.4
m/z-->


(o)
(1h)
f1 (ppm)


(p)
(1i)


(q)
Abundance
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(1i)
152.1
201.1
290.0
51.1
63.1
76.1
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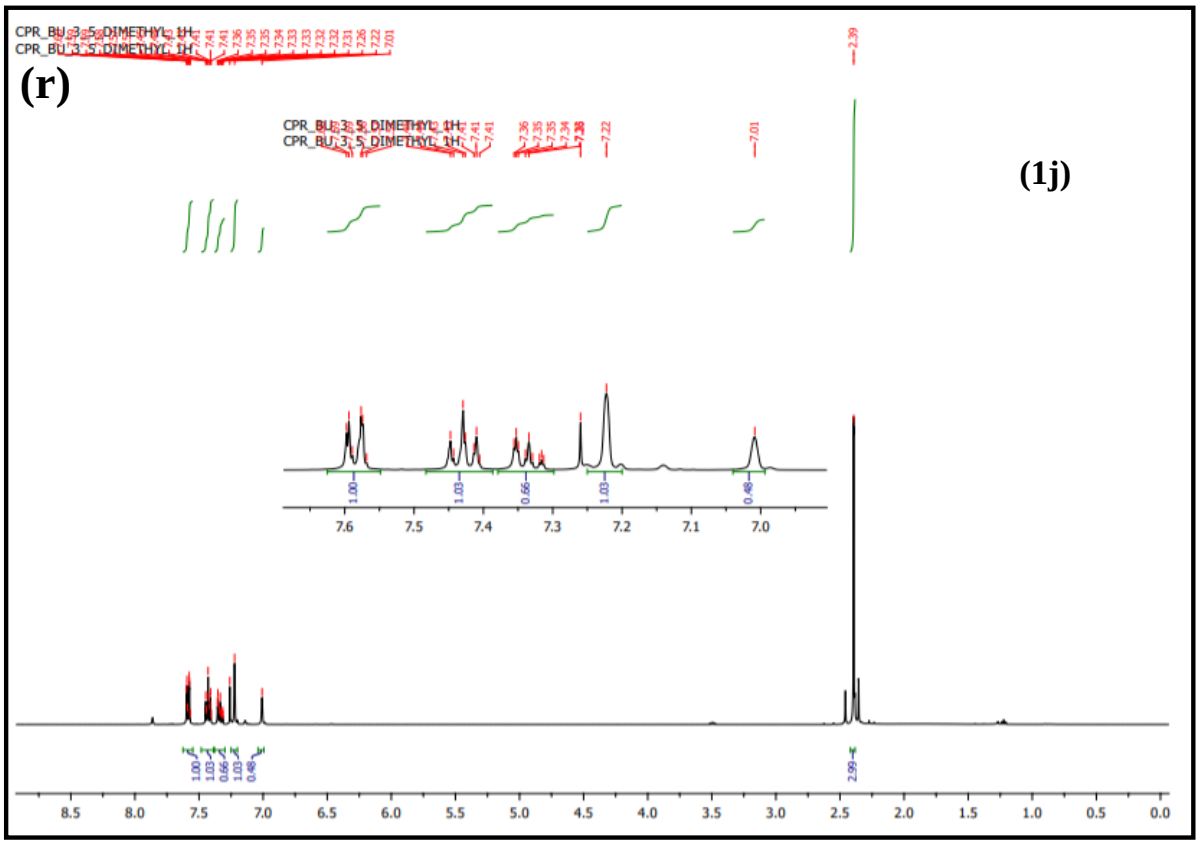
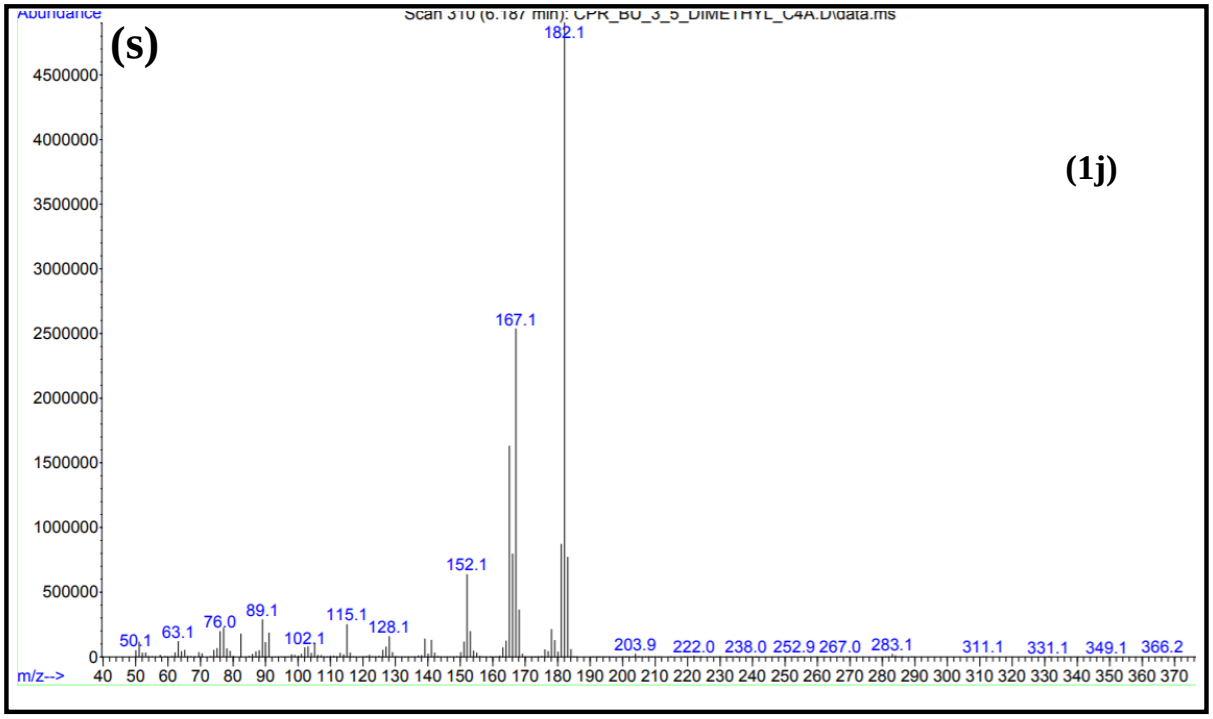
240.0
252.0
271.0
341.0
m/z-->


(r)
(1j)


(s)
(1j)
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89.1
76.0
115.1
128.1
63.1
50.1
102.1
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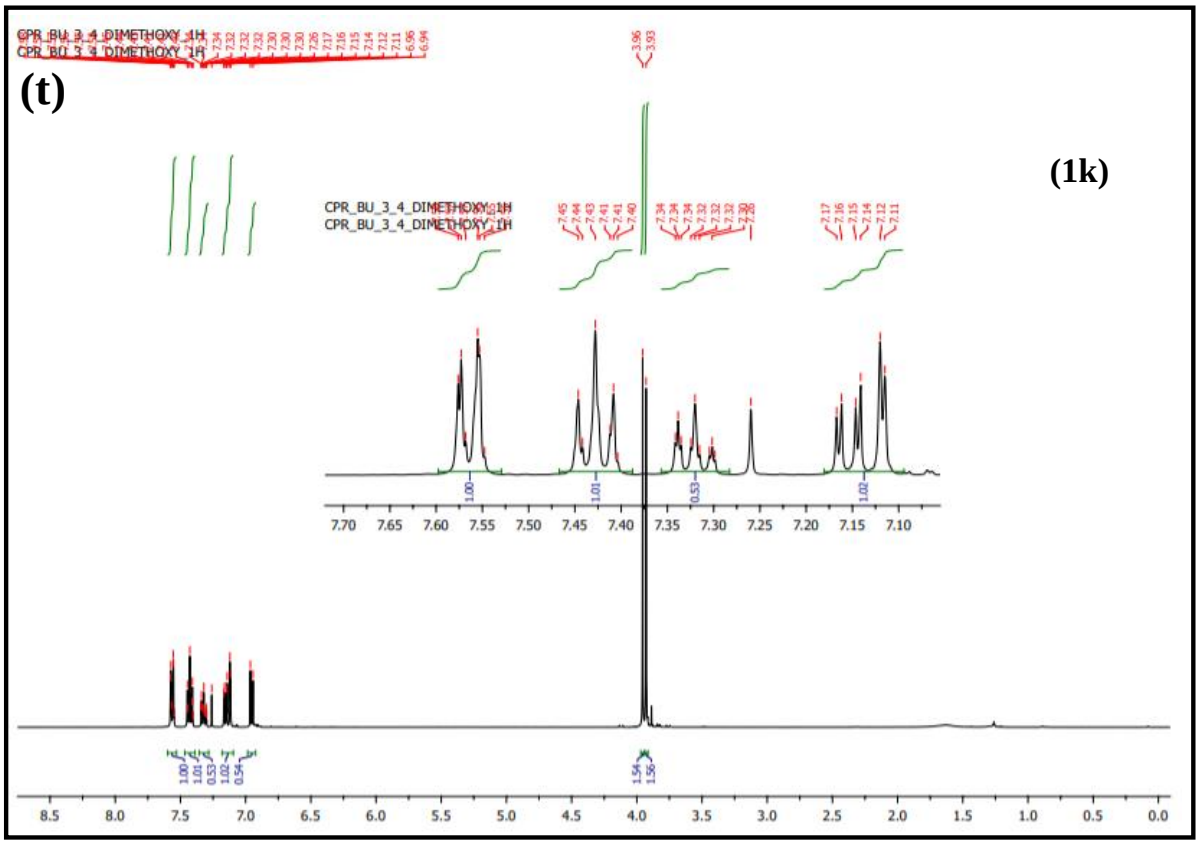
267.0
283.1
311.1
331.1
349.1
366.2
m/z-->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(1k)
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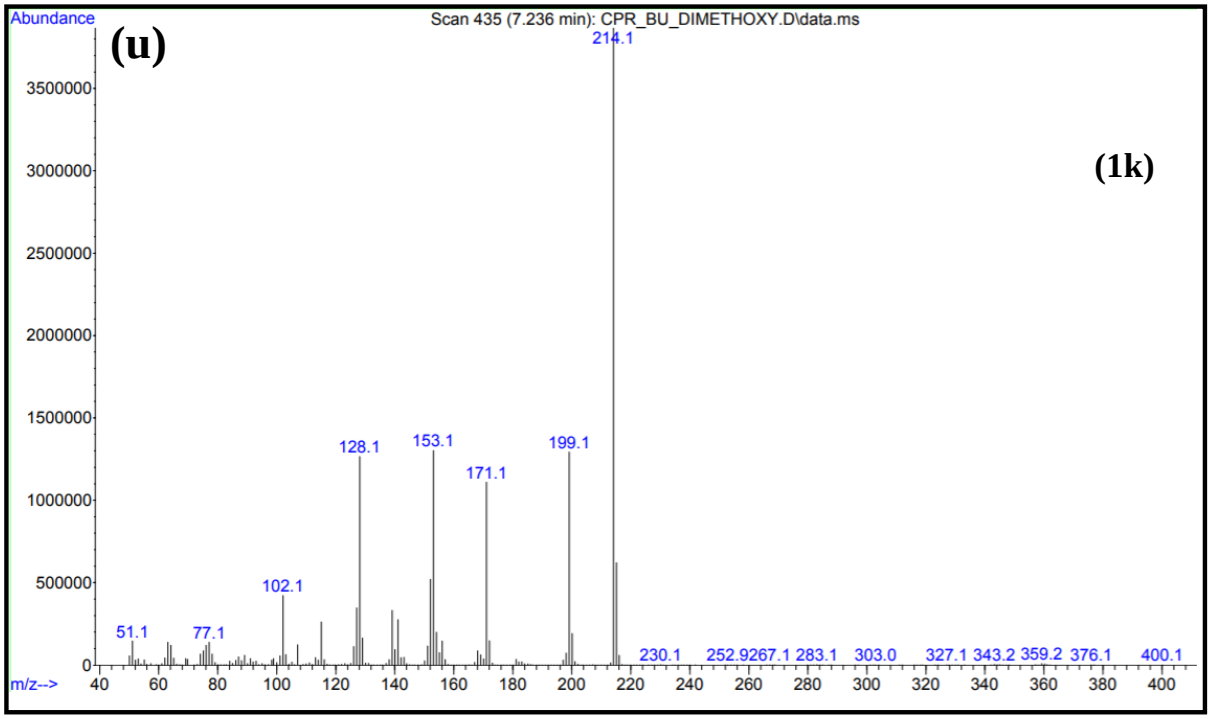

Figure S07. (a to u) are the ^{1}H spectra and GC-MS of Suzuki cross coupled products.