Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Self-assembled Pd_6L_4 Cage and Pd_4L_4 Square using hydrazide based ligands: Synthesis, characterisation and catalytic activity in Suzuki-Miyaura Coupling Reaction

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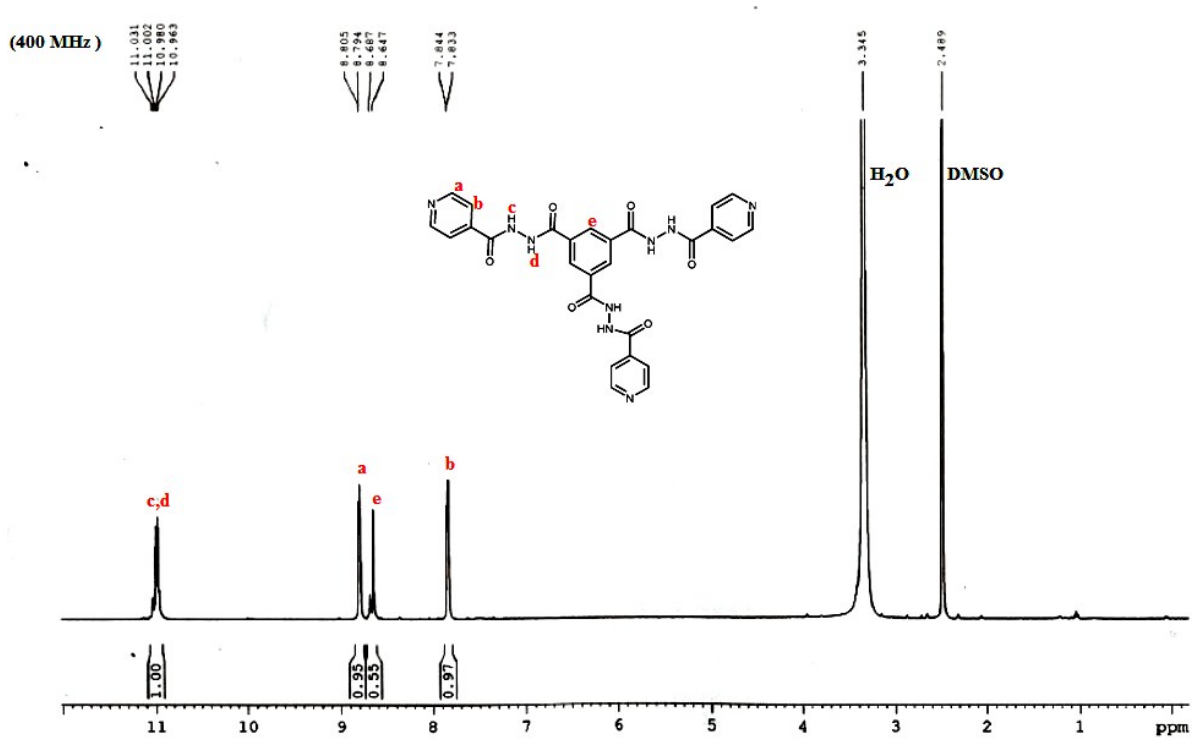


Fig. S1.[1]H NMR of ligand **L[1]** in DMSO-d_6 (400 MHz)

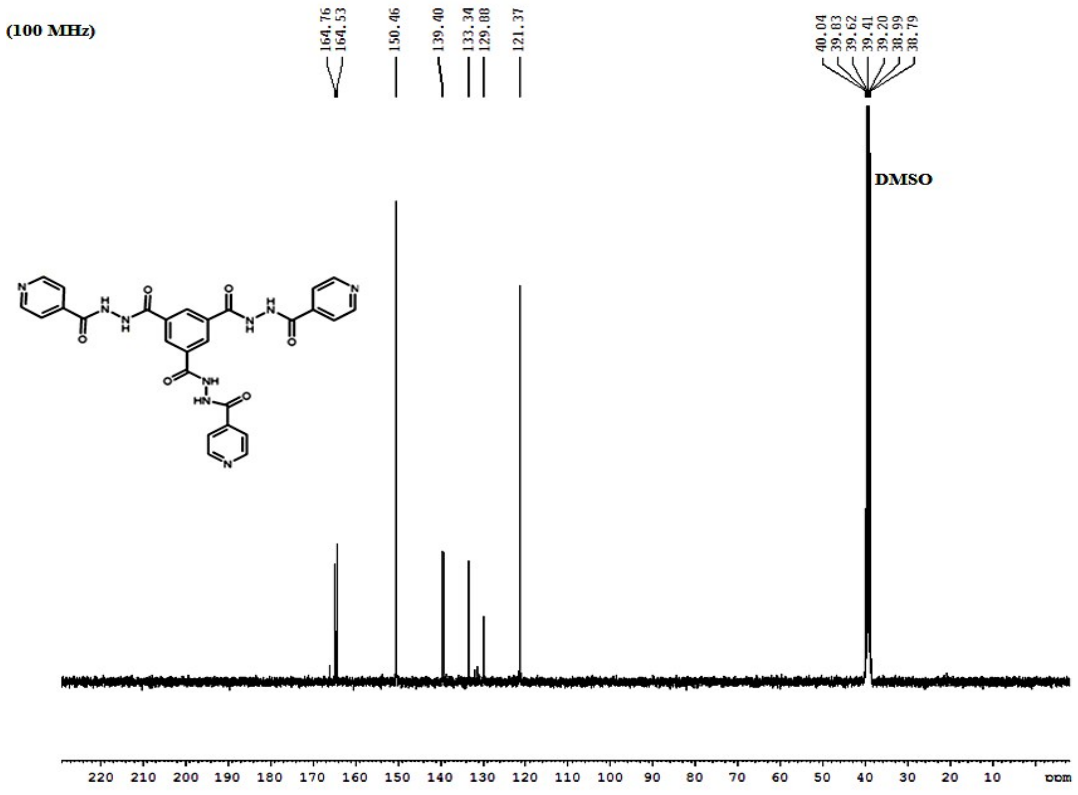


Fig. S2. [13]C-NMR spectrum of the ligand **L[1]** in DMSO-d_6 (100MHz)

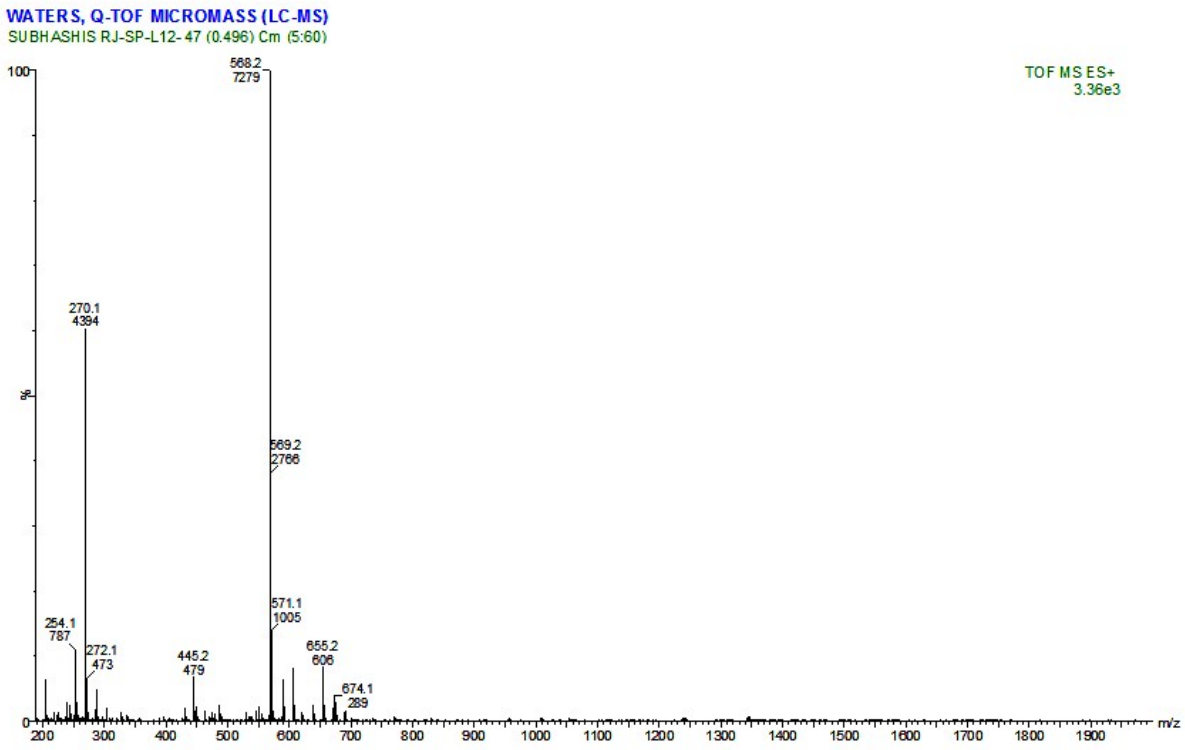


Fig. S3. ESI-MS of **L**[1] in DMSO

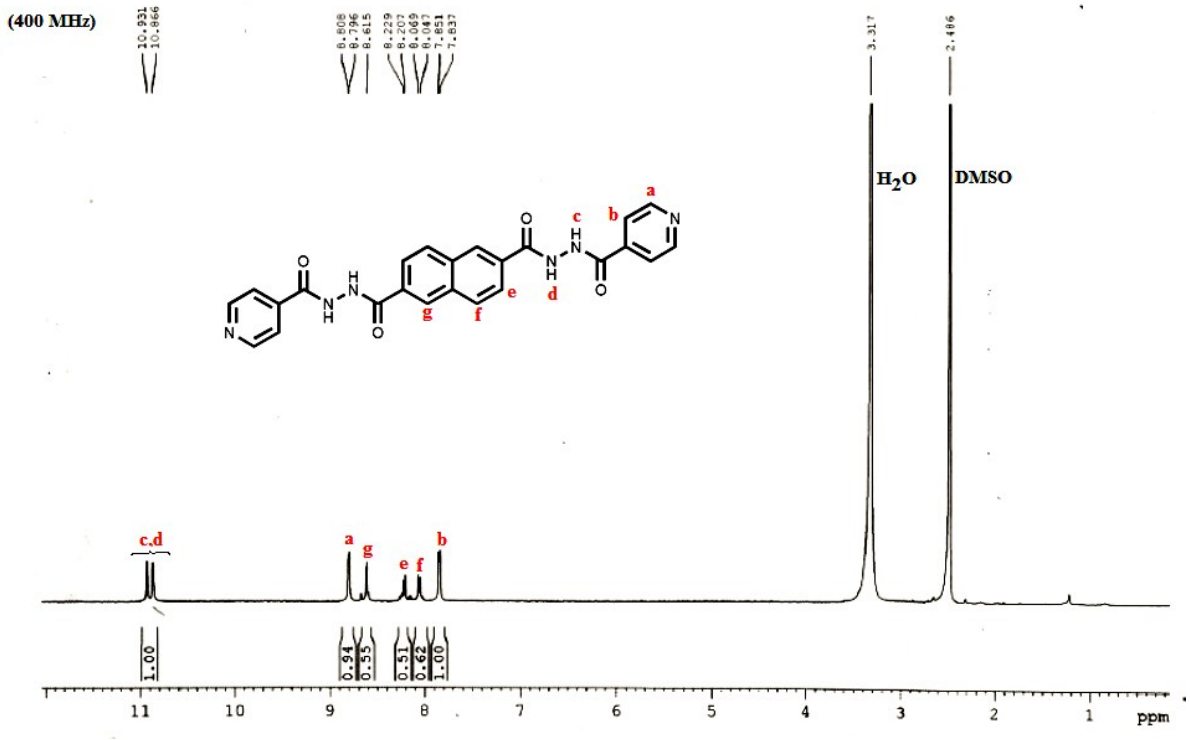


Fig. S4. [1]H NMR spectrum of **L**[2] in DMSO-d_6 (400 MHz)

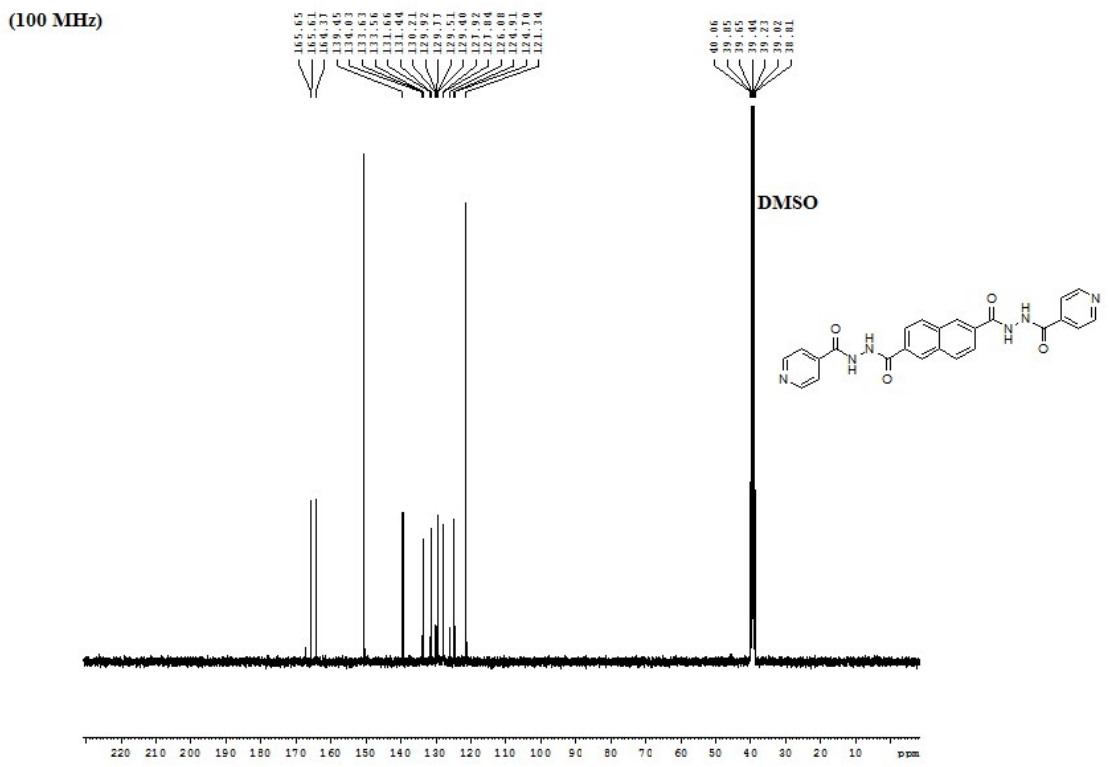


Fig. S5:^{13}C-NMR spectrum of the ligand **L²** in DMSO-d_6 (100 MHz)

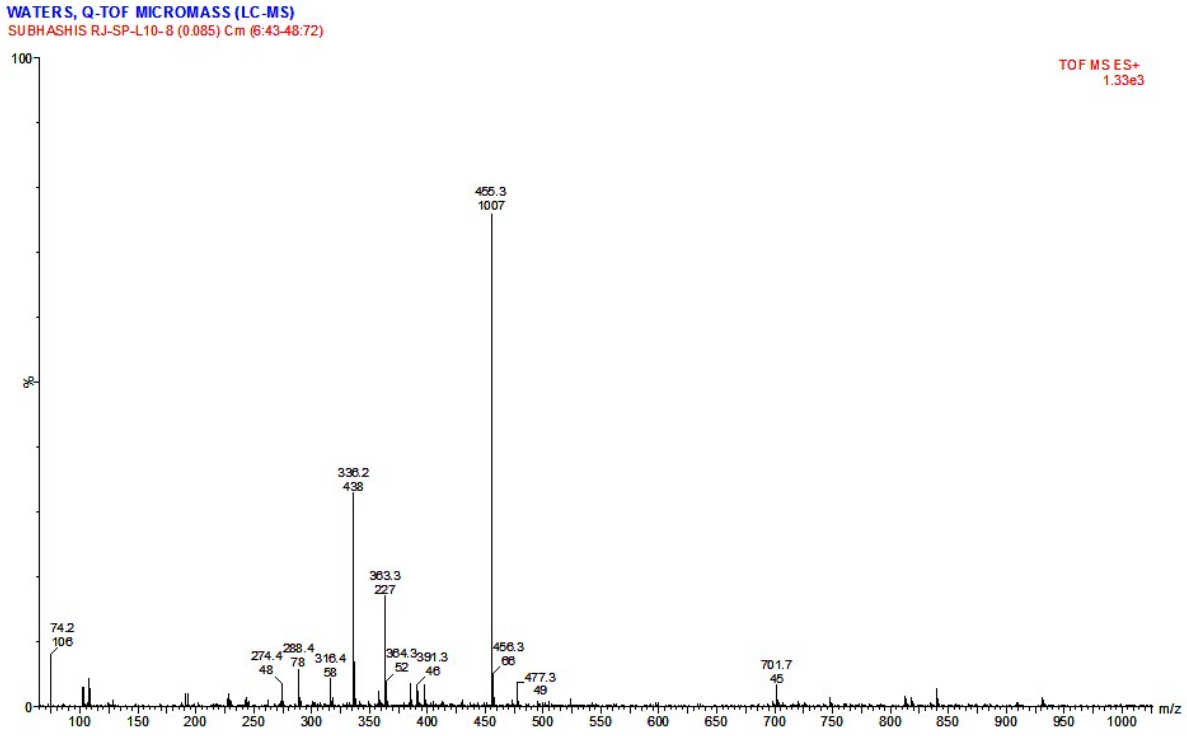


Fig.S6 ESI-MS of **L²** in DMSO

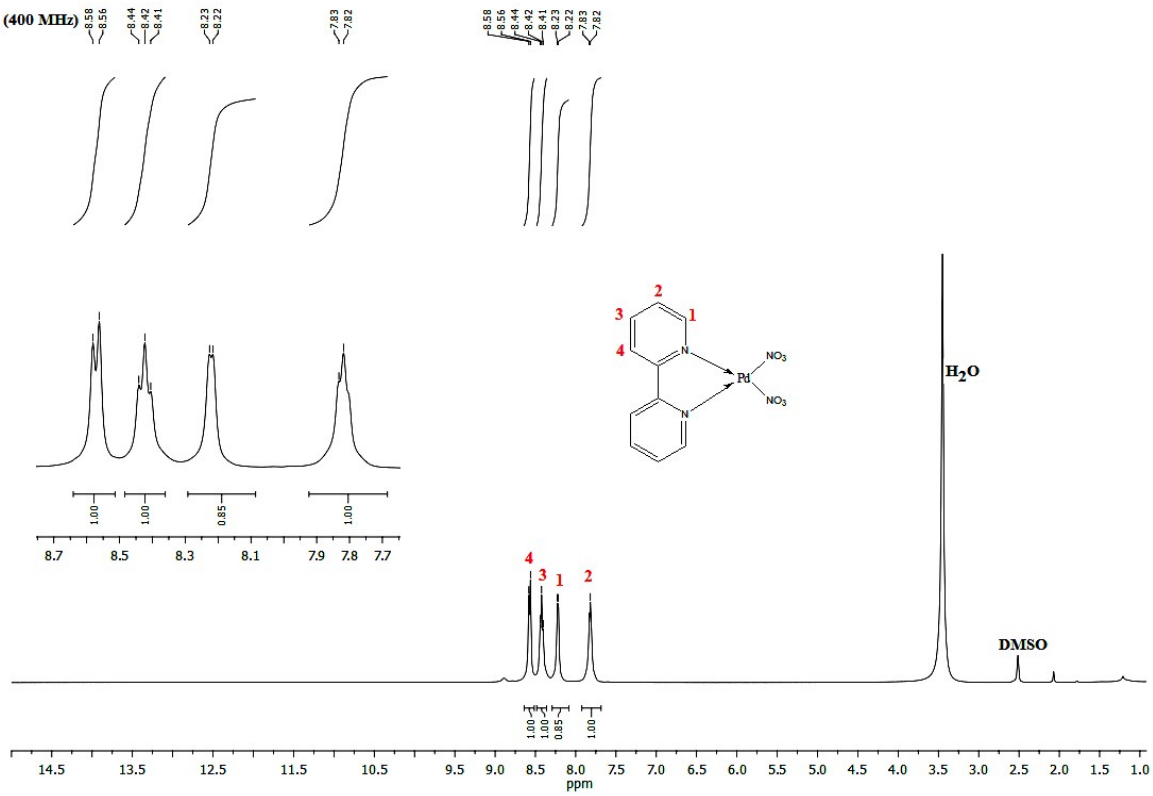


Fig. S7. ^{1}H NMR of $Pd^{II}(2,2'\text{-bipy})(NO_3)_2$ in DMSO-d_6 (400 MHz)

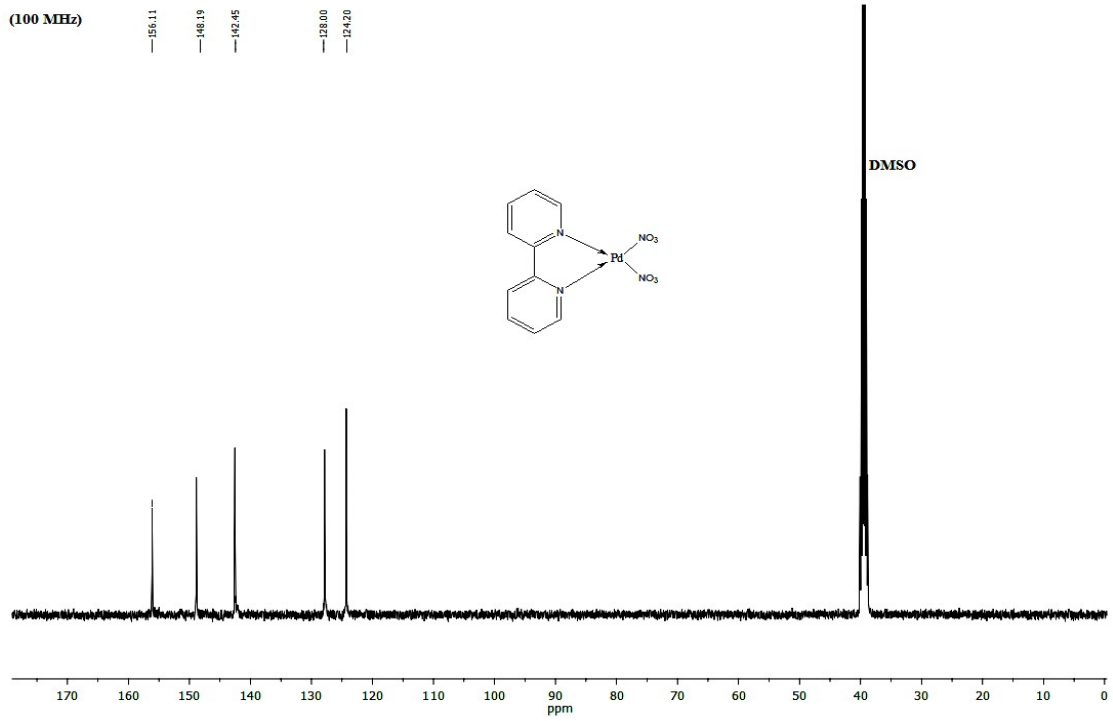


Fig. S8. ^{13}C NMR of $Pd^{II}(2,2'\text{-bipy})(NO_3)_2$ in DMSO-d_6 (100 MHz)

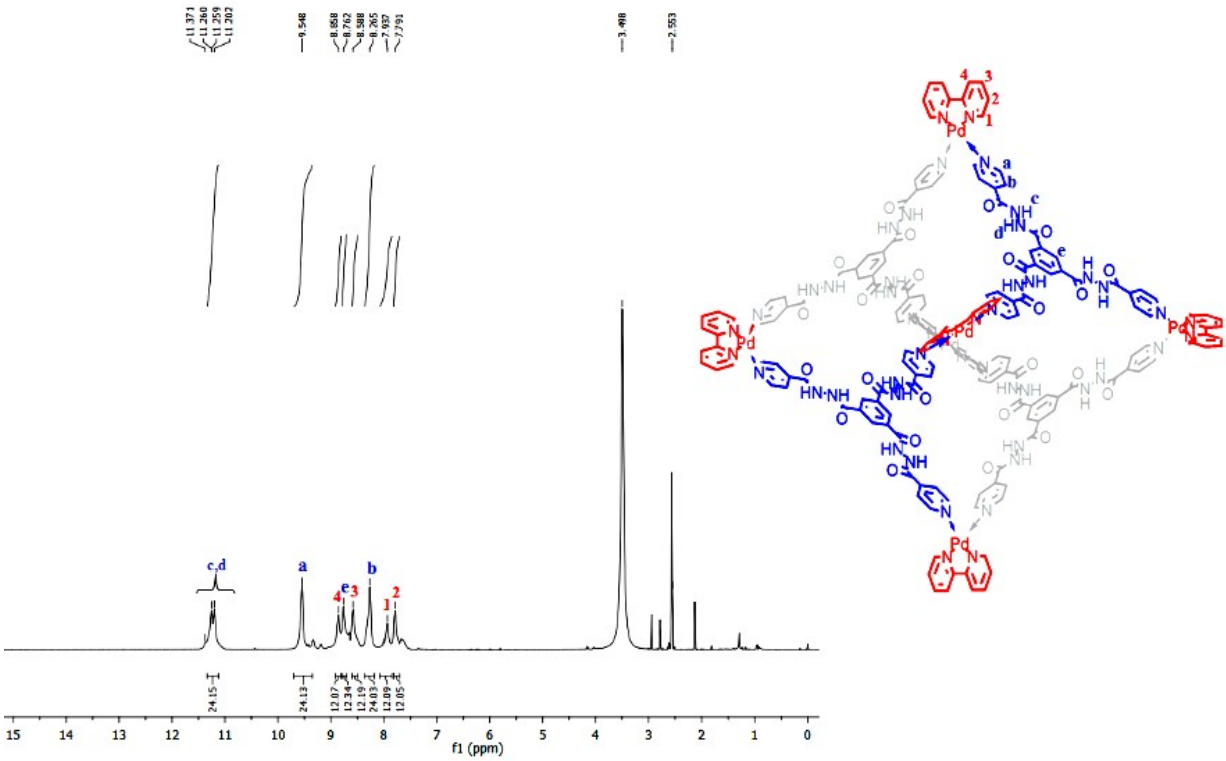


Fig. S9.[1]H NMR of cage **1** in DMSO-d_6 (400 MHz)

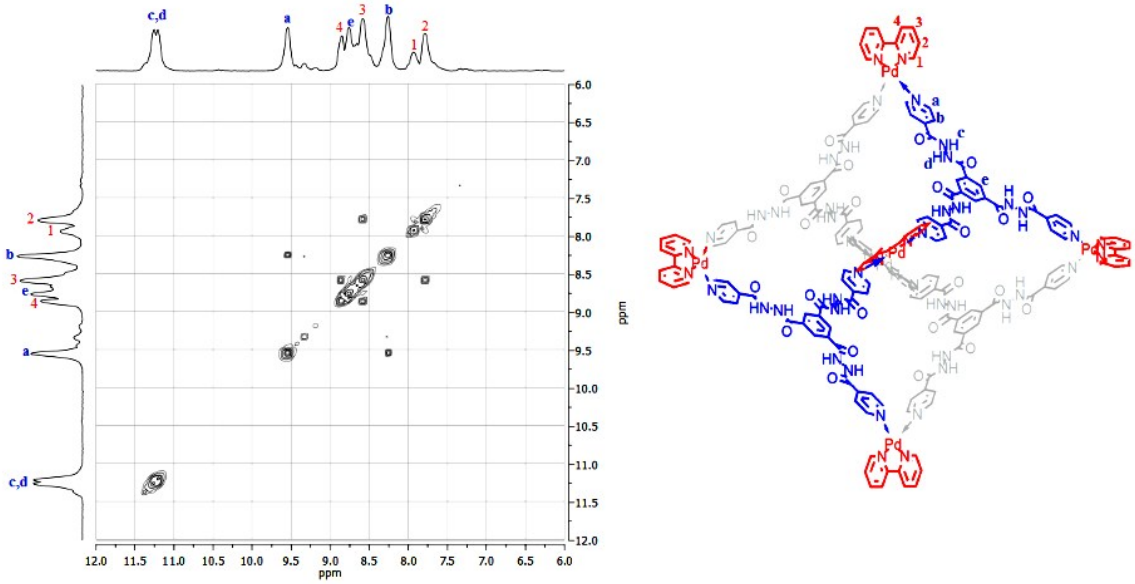


Fig. S10.[1]H-[1]H COSY spectrum of **1** in DMSO-d_6 (400 MHz)

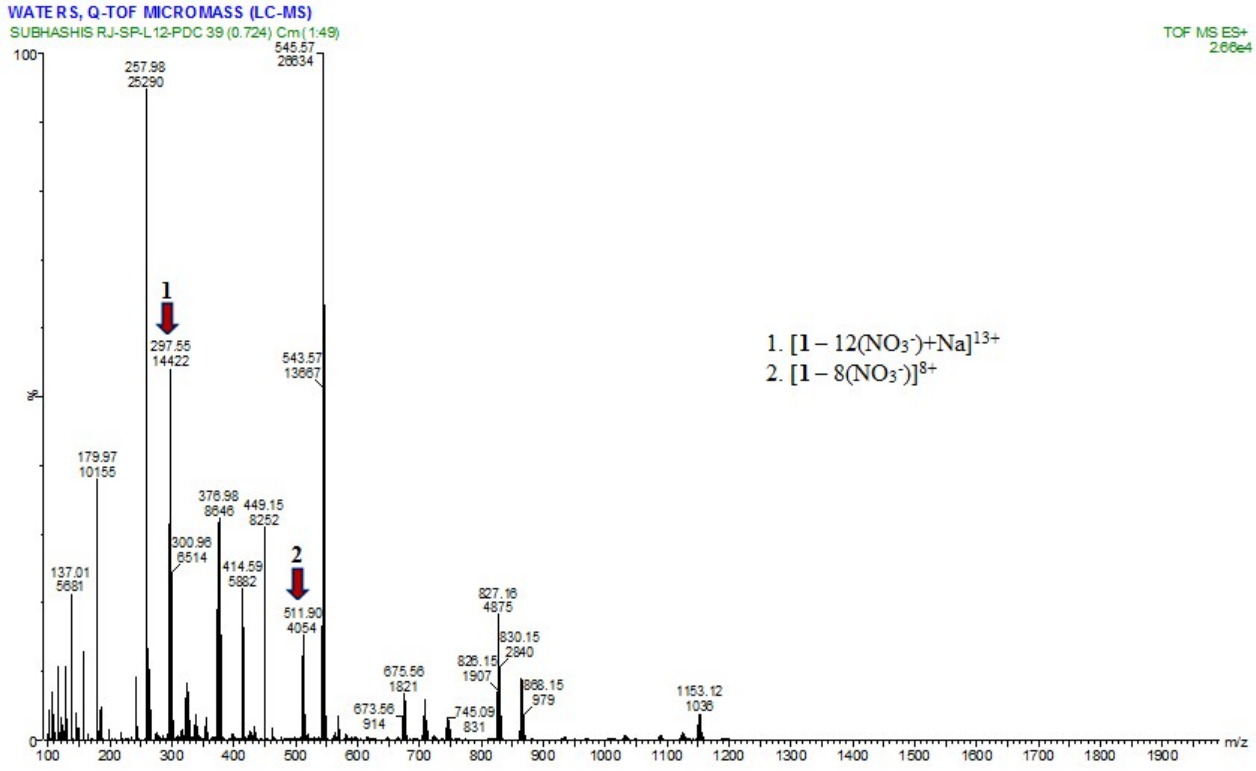


Fig.S11. ESI-MS of **1** in DMSO

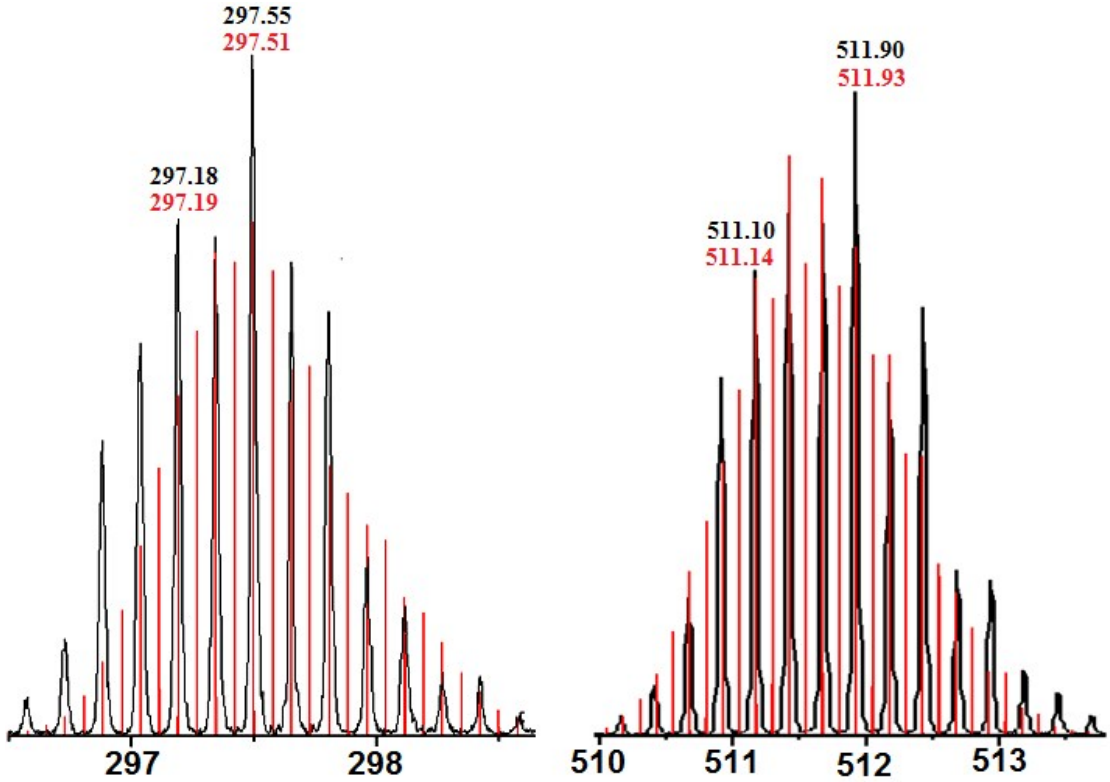


Fig. S12. ESI-MS spectra of [**1**-12NO_3^-+Na]$^{13+}$ (Left) and [**1**-8NO_3^-]$^{8+}$ (Right, Experimental in black and their simulated spectra in red).

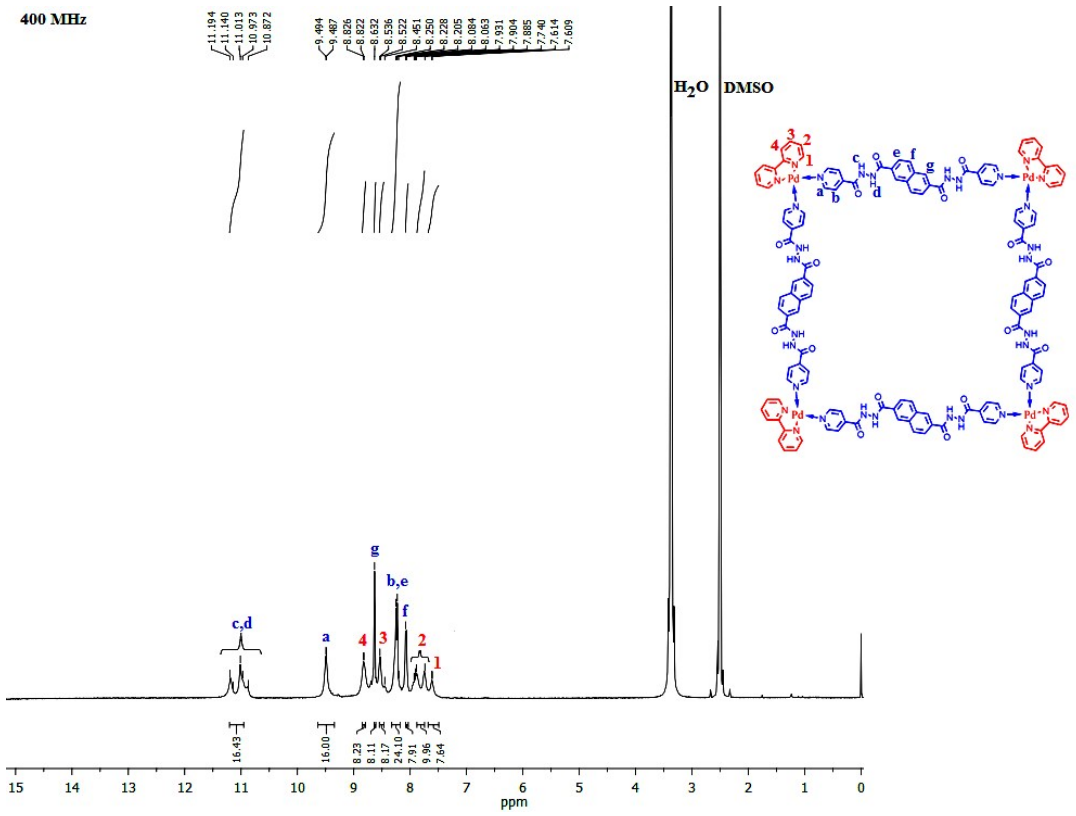


Fig.S13. ^{1}H NMR of square assembly **2** in DMSO-d_6 (400 MHz)

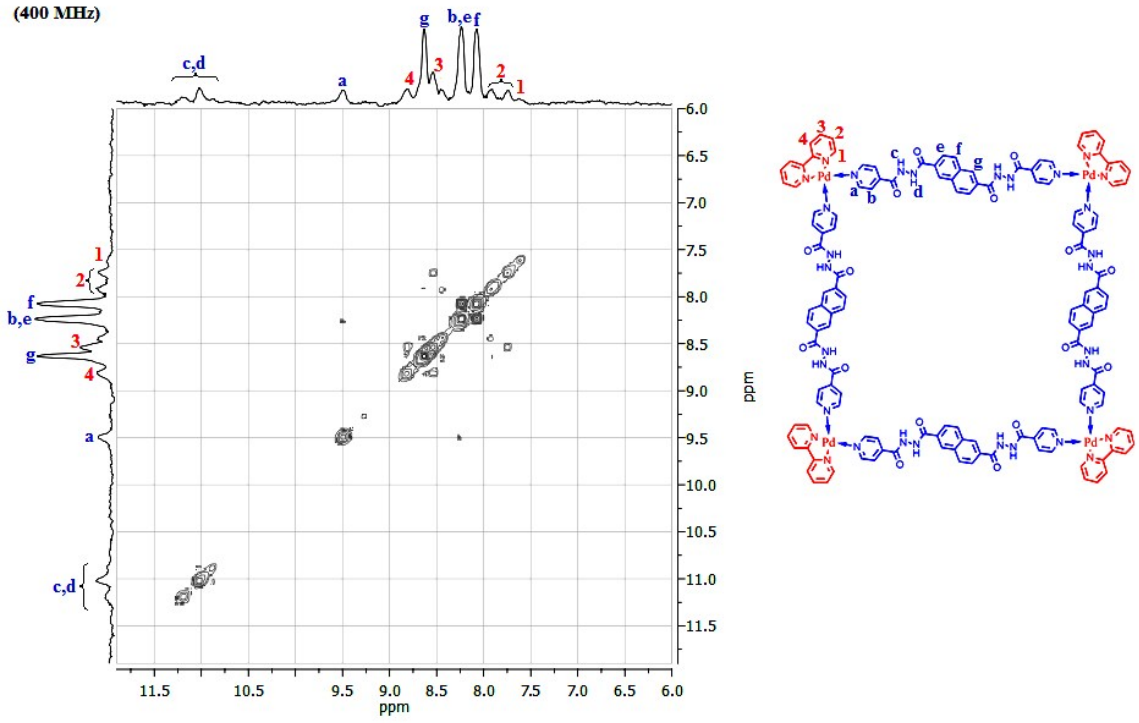


Fig. S14. ^{1}H-^{1}H COSY spectrum of square assembly **2** in DMSO-d_6 (400MHz)

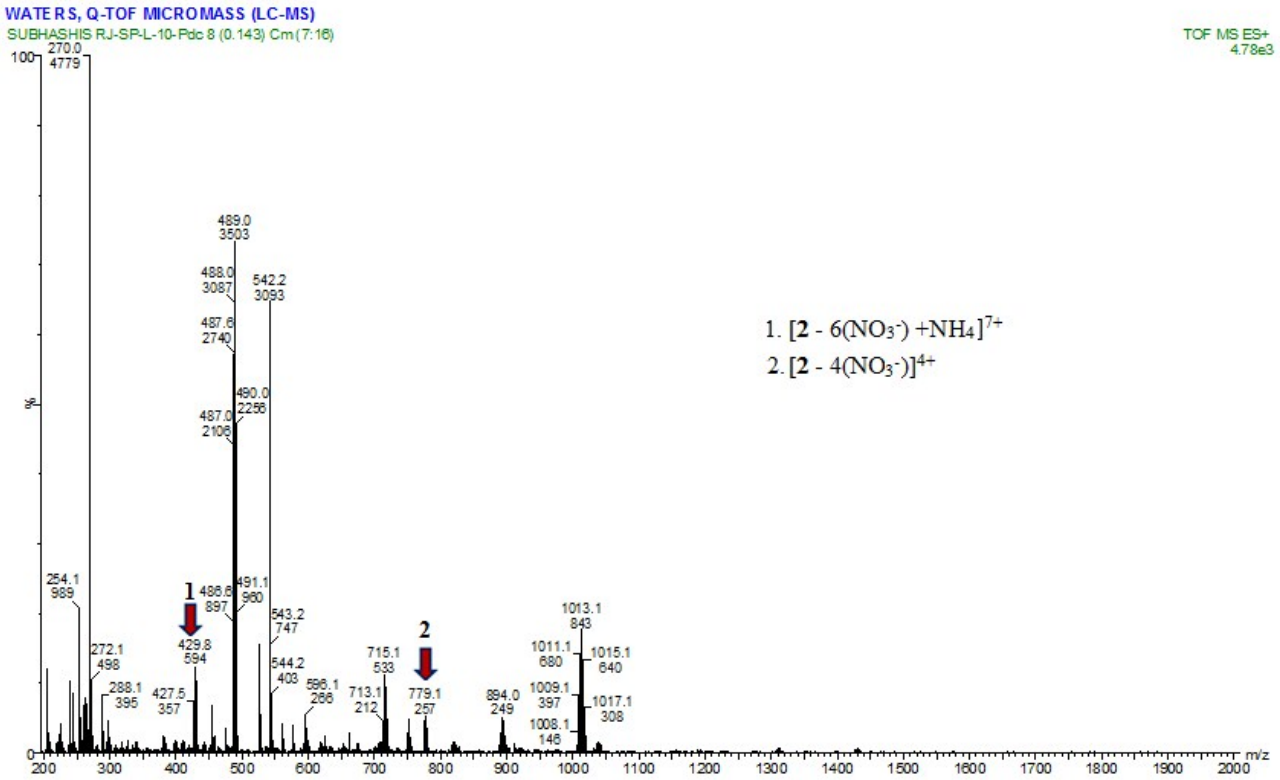


Fig. S15. ESI-MS of **2** in DMSO

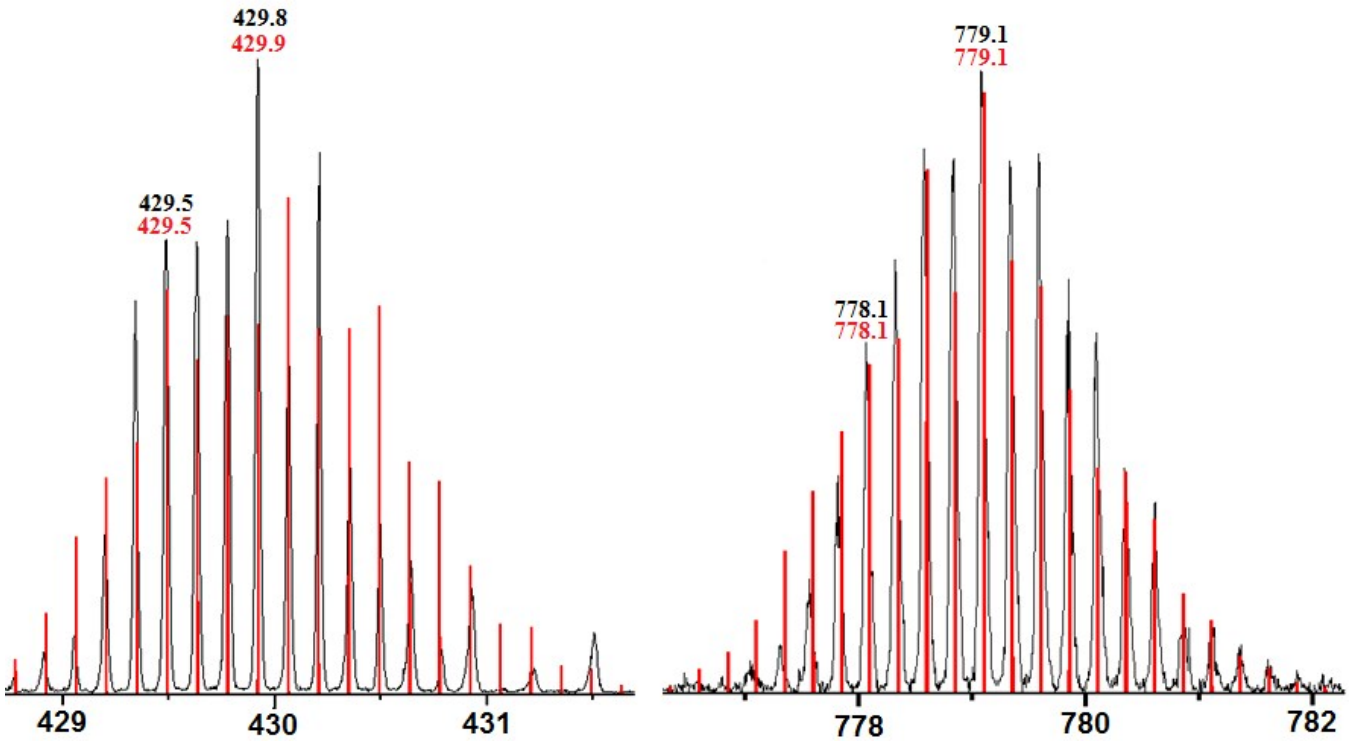


Fig. S16. ESI-MS spectra of [**2**-6NO_3^-+NH_4]$^{7+}$ (Left) and [**2**-4NO_3^-]$^{4+}$ (Right, Experimental in black and their simulated spectra in red).

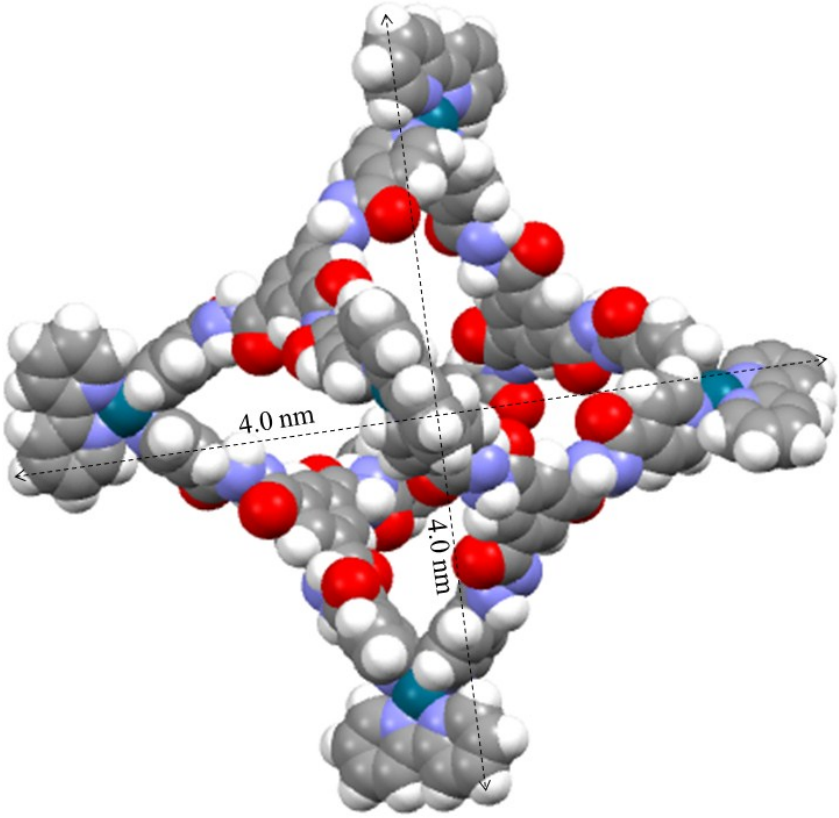


Figure S17. Optimised structure and dimensions of T_d-symmetric assembly **1**.

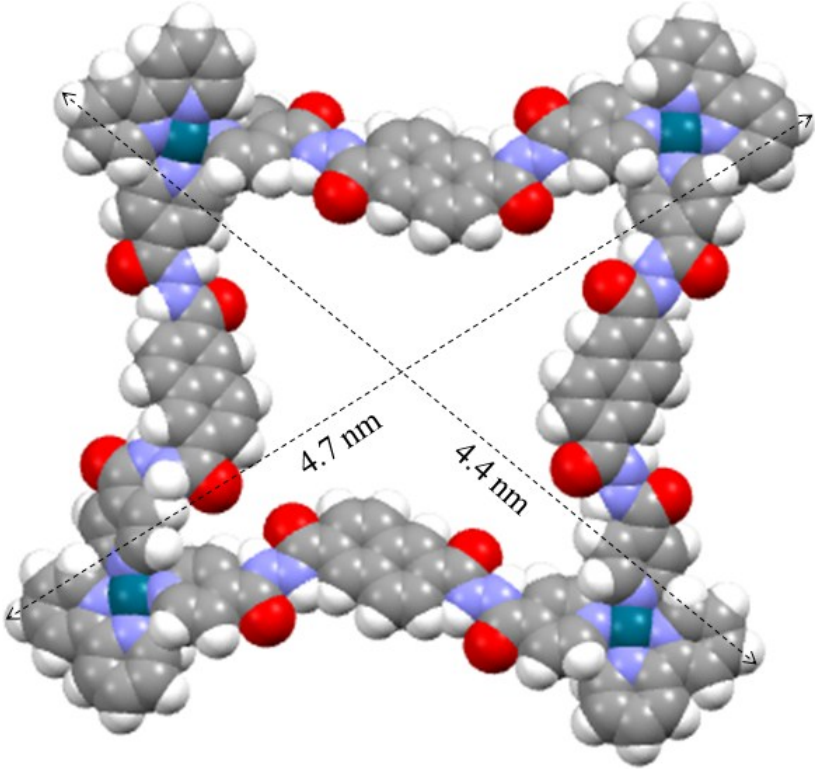
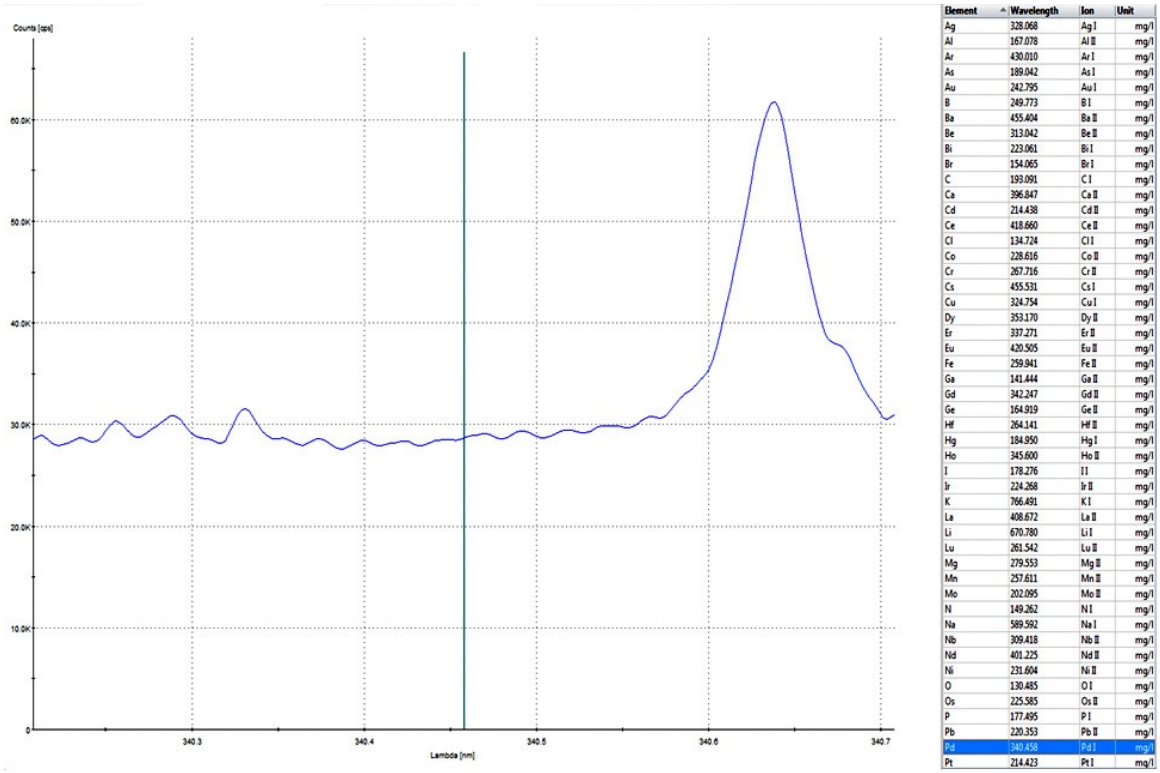
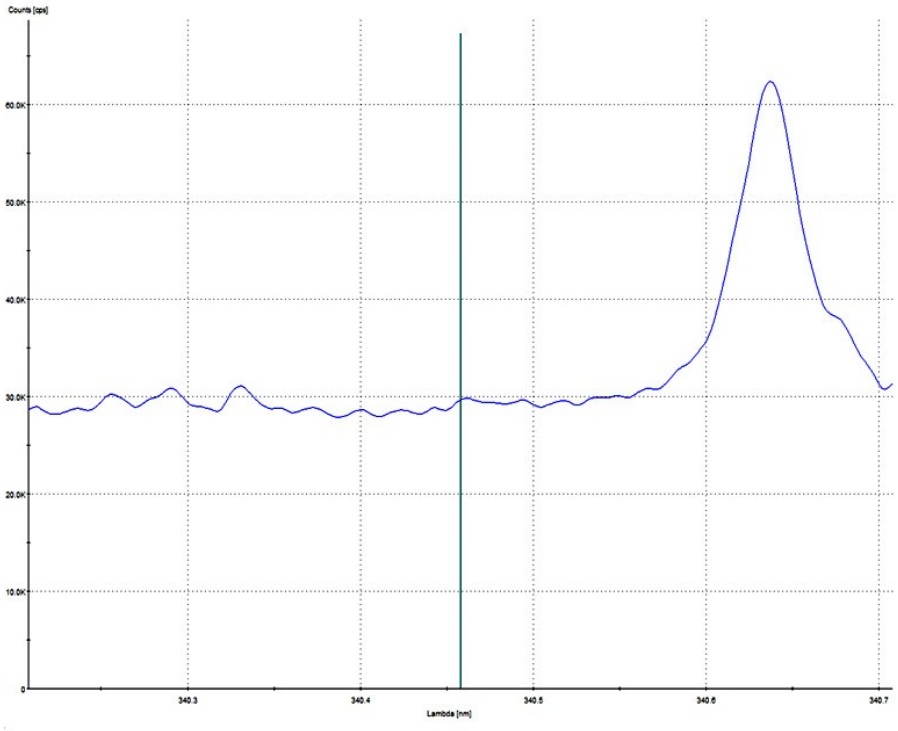


Figure S18. Optimised structure and dimensions of the square assembly **2**.



Element	Wavelength	Ion	Unit
Ag	328.068	Ag I	mg/l
Al	167.078	Al II	mg/l
Ar	430.010	Ar I	mg/l
As	189.042	As I	mg/l
Au	242.795	Au I	mg/l
B	249.773	B I	mg/l
Ba	455.404	Ba II	mg/l
Be	313.042	Be II	mg/l
Bi	223.061	Bi I	mg/l
Br	154.065	Br I	mg/l
C	193.091	C I	mg/l
Ca	396.847	Ca II	mg/l
Cd	214.438	Cd II	mg/l
Ce	418.660	Ce II	mg/l
Cl	134.724	Cl I	mg/l
Co	228.616	Co II	mg/l
Cr	267.716	Cr II	mg/l
Cs	455.531	Cs I	mg/l
Cu	324.754	Cu I	mg/l
Dy	353.170	Dy II	mg/l
Er	337.271	Er II	mg/l
Eu	420.505	Eu II	mg/l
Fe	259.941	Fe II	mg/l
Ga	141.444	Ga II	mg/l
Gd	342.247	Gd II	mg/l
Ge	164.919	Ge II	mg/l
Hf	264.141	Hf II	mg/l
Hg	184.950	Hg I	mg/l
Ho	345.600	Ho II	mg/l
I	178.276	I I	mg/l
Ir	224.268	Ir II	mg/l
K	766.491	K I	mg/l
La	408.672	La II	mg/l
Li	670.780	Li I	mg/l
Lu	261.542	Lu II	mg/l
Mg	279.553	Mg II	mg/l
Mn	257.611	Mn II	mg/l
Mo	202.095	Mo II	mg/l
N	149.262	N I	mg/l
Na	589.592	Na I	mg/l
Nb	309.418	Nb II	mg/l
Nd	401.225	Nd II	mg/l
Ni	231.604	Ni II	mg/l
O	130.485	O I	mg/l
Os	225.585	Os II	mg/l
P	177.495	P I	mg/l
Pb	220.353	Pb II	mg/l
Pd	340.458	Pd I	mg/l
Pt	214.423	Pt I	mg/l

Fig.S19a. ICP-AES of filtered reaction mixture of Suzuki coupling reactions catalysed by **1**



Element	Wavelength	Ion	Unit
Dy	353.170	Dy II	mg/l
Er	337.271	Er II	mg/l
Eu	420.505	Eu II	mg/l
Fe	259.941	Fe II	mg/l
Ga	141.444	Ga II	mg/l
Gd	342.247	Gd II	mg/l
Ge	164.919	Ge II	mg/l
Hf	264.141	Hf II	mg/l
Hg	184.950	Hg I	mg/l
Ho	345.600	Ho II	mg/l
I	178.276	I I	mg/l
Ir	224.268	Ir II	mg/l
K	766.491	K I	mg/l
La	408.672	La II	mg/l
Li	670.780	Li I	mg/l
Lu	261.542	Lu II	mg/l
Mg	279.553	Mg II	mg/l
Mn	257.611	Mn II	mg/l
Mo	202.095	Mo II	mg/l
N	149.262	N I	mg/l
Na	589.592	Na I	mg/l
Nb	309.418	Nb II	mg/l
Nd	401.225	Nd II	mg/l
Ni	231.604	Ni II	mg/l
O	130.485	O I	mg/l
Os	225.585	Os II	mg/l
P	177.495	P I	mg/l
Pb	220.353	Pb II	mg/l
Pd	340.458	Pd I	mg/l
Pt	214.423	Pt I	mg/l
Rb	420.185	Rb I	mg/l
Rh	343.489	Rh I	mg/l
Ru	240.272	Ru II	mg/l
S	180.731	S I	mg/l
Sb	206.833	Sb I	mg/l
Sc	361.384	Sc II	mg/l
Se	196.090	Se I	mg/l
Si	251.612	Si I	mg/l
Sm	359.260	Sm II	mg/l
Sn	189.991	Sn II	mg/l
Sr	407.771	Sr II	mg/l
Ta	240.063	Ta II	mg/l
Te	170.000	Te I	mg/l
Th	401.913	Th II	mg/l
Ti	334.941	Ti II	mg/l
Tl	190.864	Tl II	mg/l
Tm	313.126	Tm II	mg/l
U	385.958	U II	mg/l
V	292.464	V II	mg/l

Fig.S19b. ICP-AES of filtered reaction mixture of Suzuki coupling reactions catalysed by **2.**

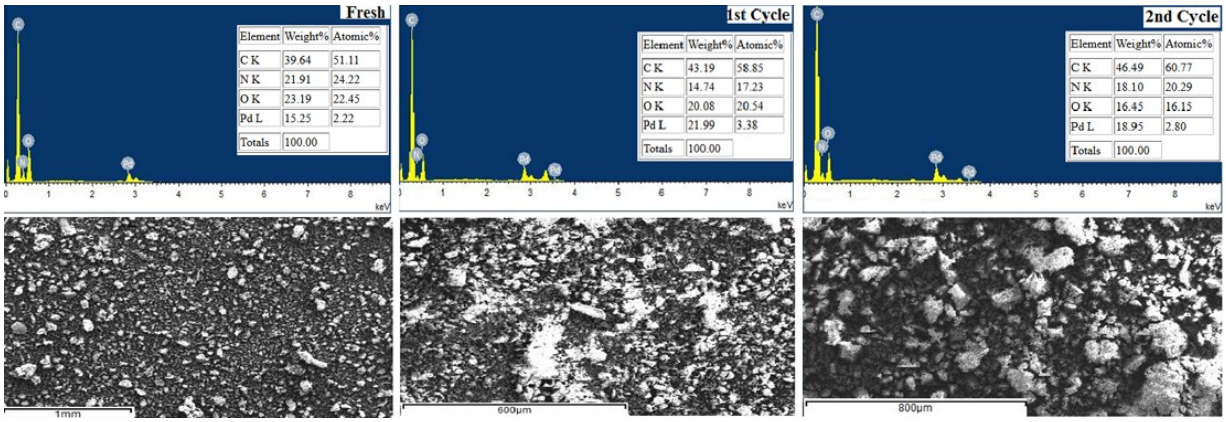


Fig.S20a. EDX spectra (top) and FE-SEM (bottom) images of **1** after each reaction cycle (up to 2nd cycle)

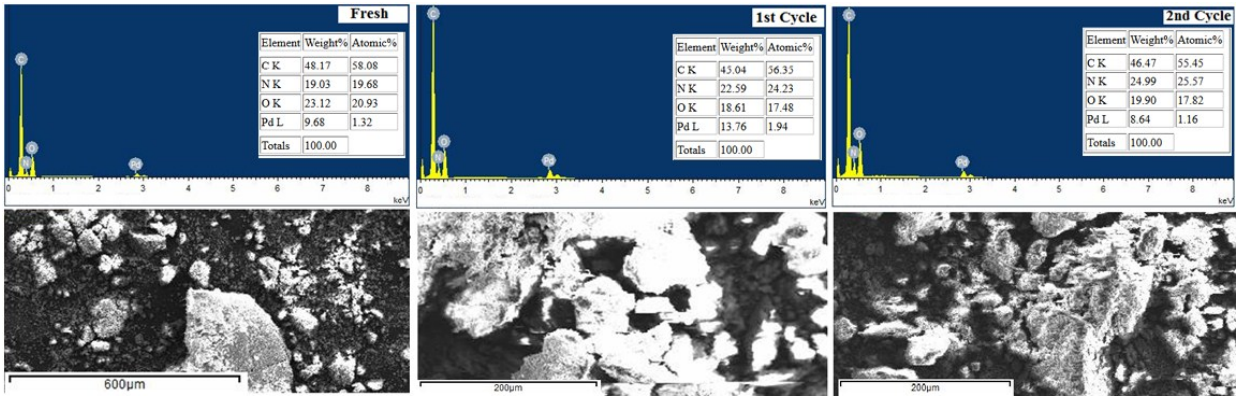


Fig.S20b. EDX (top) spectra and FE-SEM (bottom) images of **2** after each reaction cycle (up to 2nd cycle)

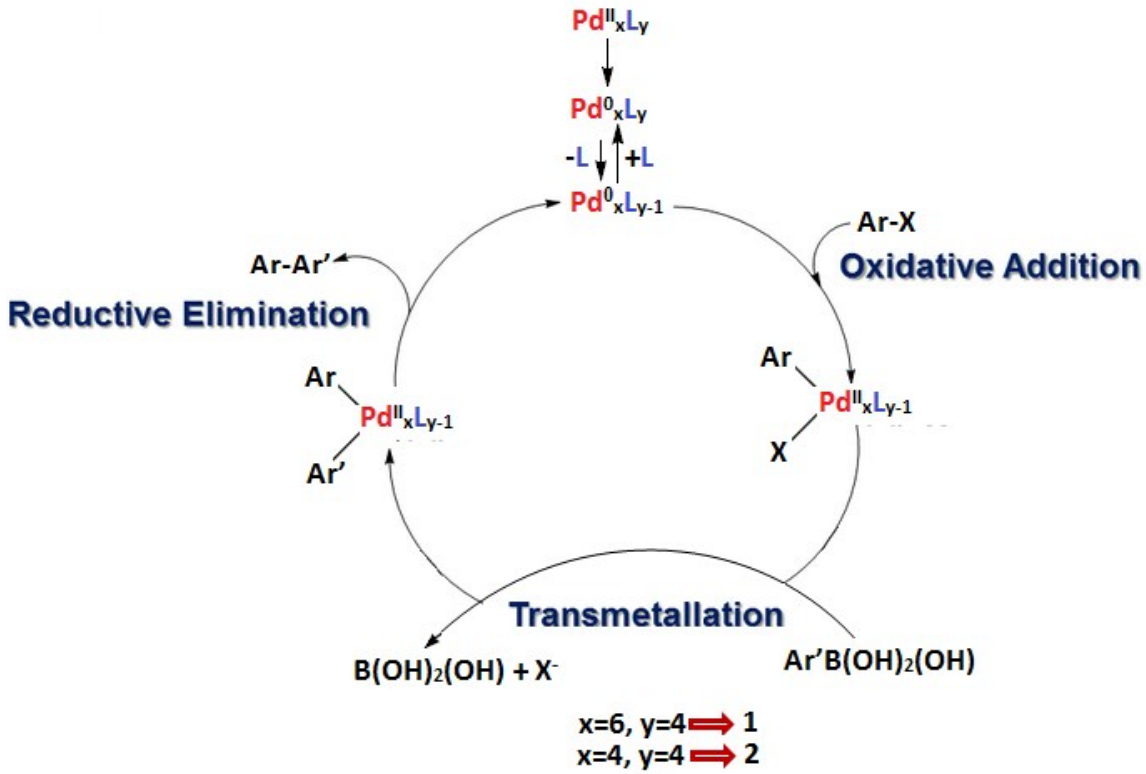
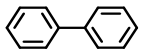
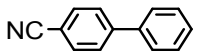


Figure 21. Suggested catalytic mechanism for the Suzuki-Miyaura cross-coupling reaction. [1, 2]

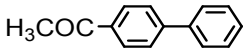
Products of Suzuki-Miyaura coupling and their characterization data:



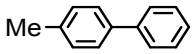
Biphenyl (1):[2] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.59 (d, J=7.08Hz, 4H), 7.44 (t, J=6Hz, 4H), 7.34 (t, J=8Hz, 2H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 141.21, 128.75, 127.25, 127.16.



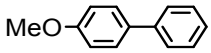
4-Cyanobiphenyl (2):[2] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.74 (d, J=6.4Hz, 2H), 7.69 (d, J=8.4Hz, 2H), 7.57 (d, J=8.4Hz, 2H), 7.49 (t, J=6.8Hz, 2H) 7.43 (t, J=4.8Hz, 1H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 145.70, 139.19, 132.63, 129.14, 128.68, 127.76, 127.26, 119.00, 110.90.



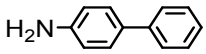
4-Acetylbiphenyl (3):[2] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 8.03 (d, J=8Hz, 2H), 7.68 (d, J=8Hz, 2H), 7.63 (d, J=7.7Hz, 2H), 7.47(t, J=7.6Hz, 2H), 7.40 (t, J=4Hz, 1H), 2.64(s, 3H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 197.86, 145.01, 139.88, 135.83, 128.99, 128.95, 128.27, 127.30, 127.26, 26.74.



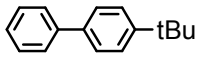
4-Methylbiphenyl (4):[3] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.57(d, J=8.4Hz, 2H), 7.49 (d, J=6.4Hz, 2H), 7.42 (t, J=7.6Hz, 2H), 7.32 (t, J=7.2Hz, 1H), 7.25(d, J=6.4Hz, 2H), 2.39(s, 3H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 141.22, 138.42, 137.11, 129.56, 128.79, 127.07, 127.06, 21.19.



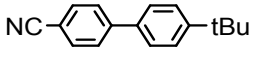
4-Methoxybiphenyl (5):[2] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.53 (t, J=8Hz, 4H), 7.41 (t, J=6.4Hz, 2H), 7.29 (t, J=7.6Hz, 1H), 6.98(d, J=6.4Hz, 2H), 3.84(s, 3H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 159.14, 140.84, 133.78, 128.76, 128.19, 126.77, 126.69, 114.21, 55.38.



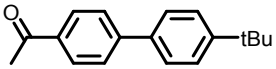
4-Aminobiphenyl (6):[3] White solid. Eluent: Petether/ethylacetate. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.53(d, J=5.2Hz, 2H), 7.43-7.36(m, 4H), 7.27(t, J=4.4Hz, 1H), 7.76(d, J=4.4Hz, 2H), 3.72(brs,2H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 145.80, 141.12, 131.56, 128.65, 128.00, 126.39, 126.24, 115.37.



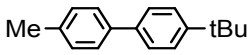
4-tert-Butyl-biphenyl (7):[4] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$ 25°C, TMS) 7.58 (d, J= 6Hz, 2H), 7.54 (d, J=6Hz, 2H), 7.48-7.40 (m, 4H), 7.32(t, J=8Hz, 1H), 1.36(s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 150.27, 141.08, 138.38, 128.72, 127.06, 127.01, 126.82, 125.74, 34.56, 31.40.



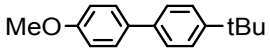
4'-tert-Butyl-biphenyl-4-carbonitrile (8):[4] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.69 (q, J=8Hz, 4H), 7.52 (q, J=8Hz, 4H), 1.36 (s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 151.97, 145.52, 136.23, 132.60, 127.52, 126.92, 126.12, 119.11, 110.55, 34.71, 31.30.



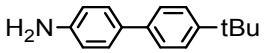
1-(4'-tert-Butyl-biphenyl-4-yl)-ethanone (9):[4] White solid. Eluent: Petether/ethyl acetate. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 8.02 (d, J=4.8Hz, 2H), 7.67 (d, J=5.2Hz, 2H), 7.57 (d, J=4.4Hz, 2H), 7.49(d, J=4.8Hz, 2H), 2.62(s, 3H), 1.36(s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 197.85, 151.48, 145.64, 136.92, 135.61, 128.95, 127.03, 126.96, 125.98, 34.67, 31.34, 26.71.



4'-tert-Butyl-4-methyl-biphenyl (10):[5] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.53-7.43(m, 6H), 7.23 (d, J=8Hz, 2H), 2.38 (s, 3H), 1.35(s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 149.96, 138.28, 138.20, 136.74, 129.46, 126.90, 126.63, 125.70, 34.54, 31.42, 21.15.



4'-tert-Butyl-4-methoxy-biphenyl(11):[4] White solid. Eluent: Petether/dichloromethane. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.51 (t, J=6.8Hz, 4H), 7.44 (d, J=6.6Hz, 2H), 6.96 (d, J=6.8Hz, 2H), 3.84(s, 3H), 1.36(s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 158.93, 149.63, 137.95, 133.64, 128.03, 126.39, 125.70, 114.14, 55.35, 34.50, 31.41.



4'-tert-Butyl-biphenyl-4-ylamine (12):[6] White solid. Eluent: Petether/ethylacetate. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C, TMS) 7.47(d, J=8.4, 2H), 7.43-7.39 (m, 4H), 6.74(d, J=6.4Hz, 2H), 3.73(brs, 2H), 1.34 (s, 9H).^{13}C-NMR (100 MHz, $CDCl_3$, 25°C, TMS) 149.19, 145.57, 138.29, 131.52, 127.90, 126.05, 125.62, 115.41, 34.46, 31.42.

REFERENCES:

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[2] Y. Dong, C. Zhao, J. Ma, Q. Liu, Y. Yu, P. Wang,Y. Li, *Green Chem.,* 2013, **15**, 3150
[3] Y.M.A. Yamada, S.M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.,* 2012**, 134**, 3190.
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^{1}H-NMR and ^{13}C-NMR spectra of the products of Suzuki coupling reactions in $CDCl_3$

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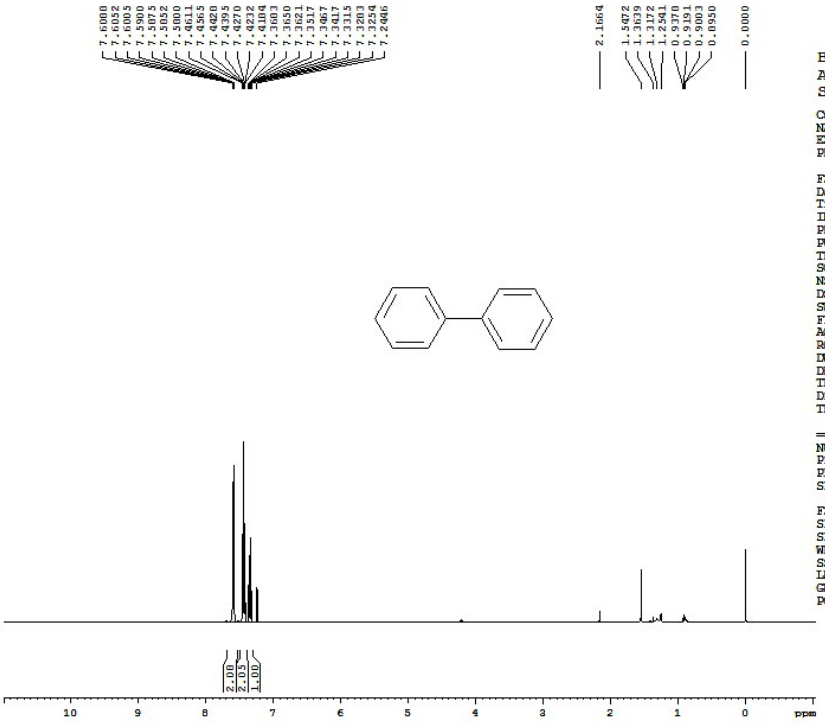

BRUKER
AVANCE II 400 NMR
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PROCNO 1

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TD 65536
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FIDRES 0.183399 Hz
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DE 6.00 usec
TE 292.5 K
D1 1.00000000 sec
TD0 1

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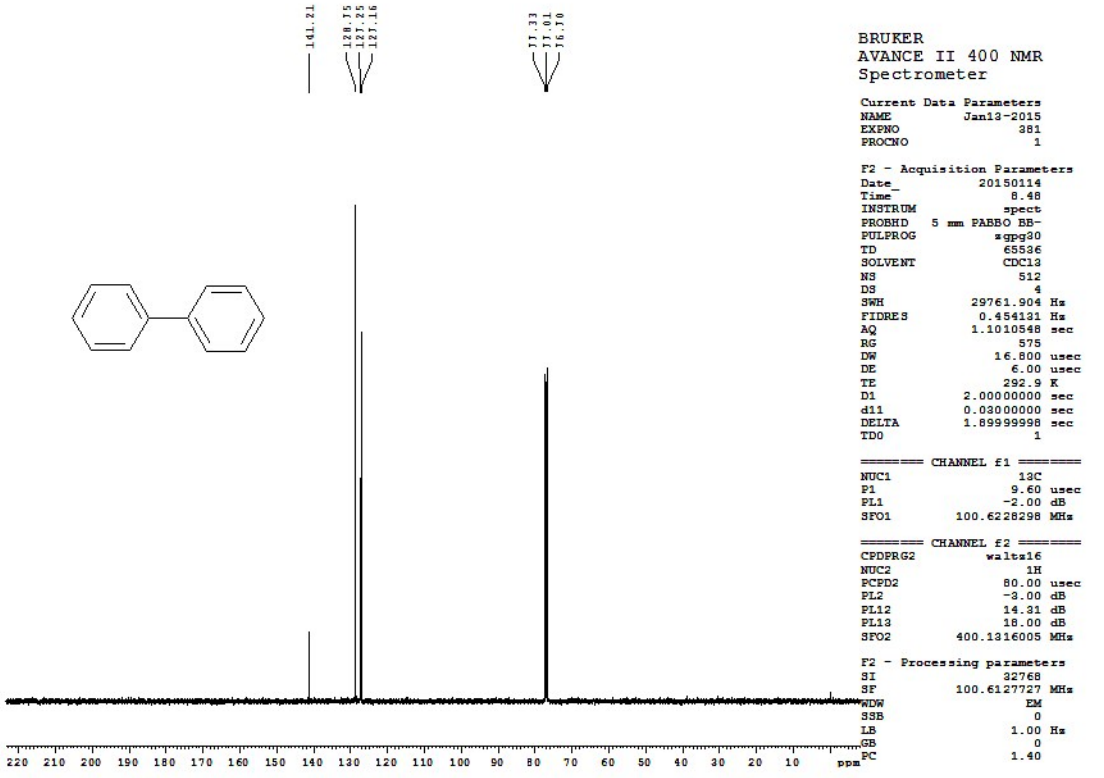

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TE 292.9 K
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d11 0.03000000 sec
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TD0 1

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PL1 -2.00 dB
SFO1 100.6228298 MHz

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PCPD2 80.00 usec
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PL12 14.31 dB
PL13 18.00 dB
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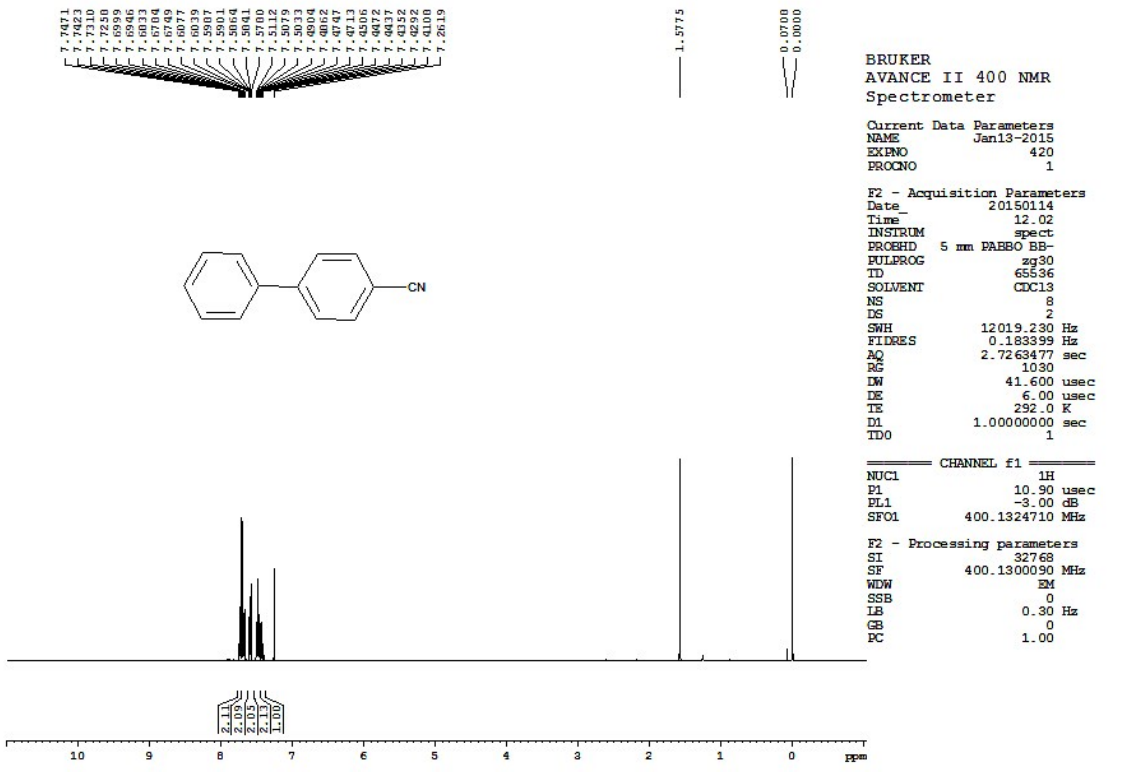

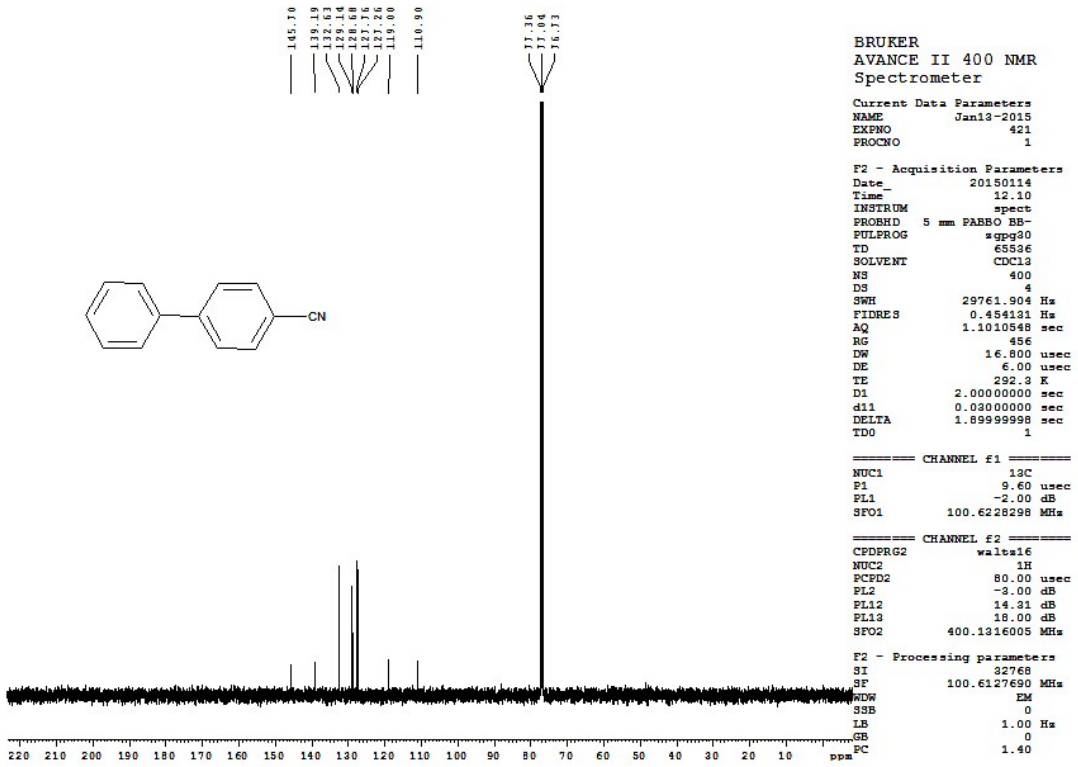

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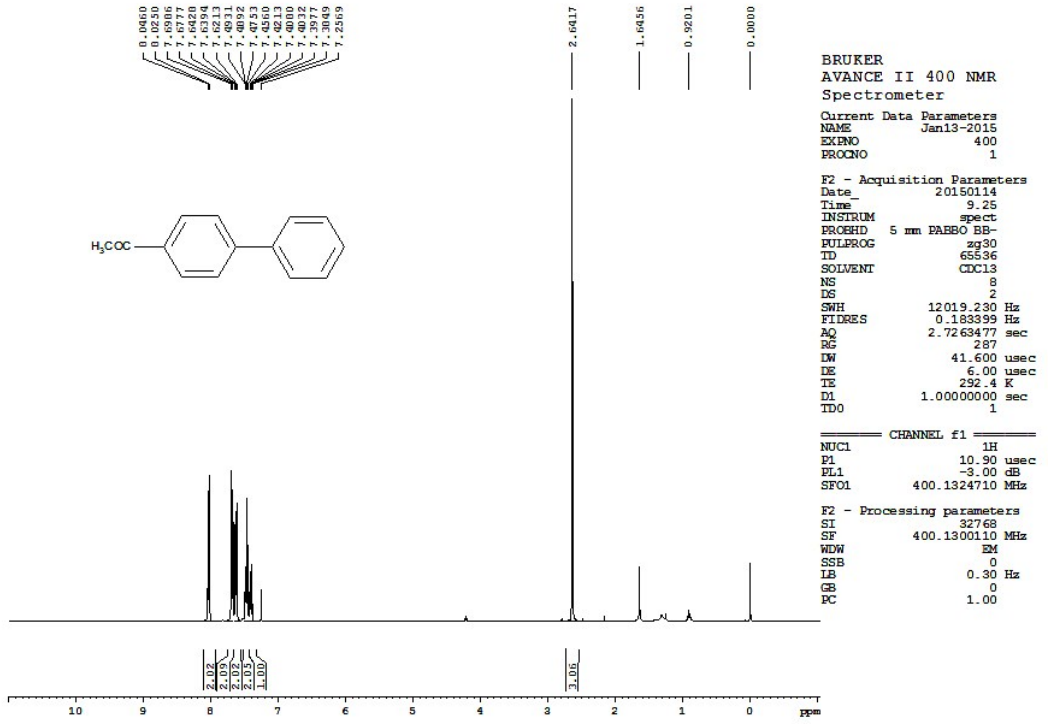

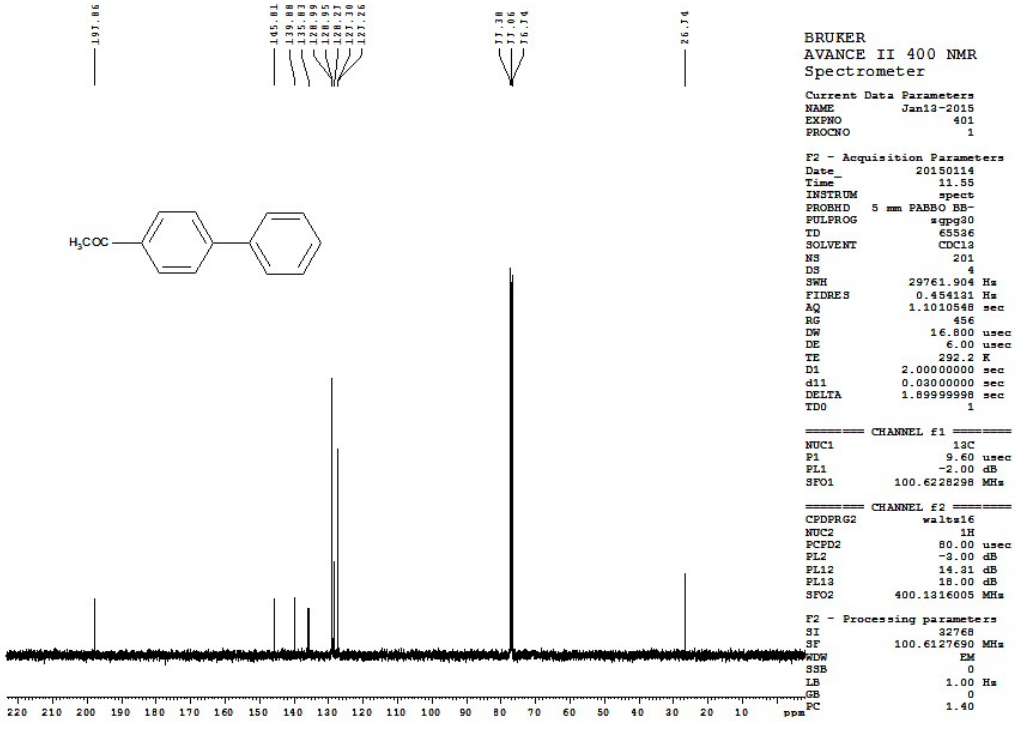

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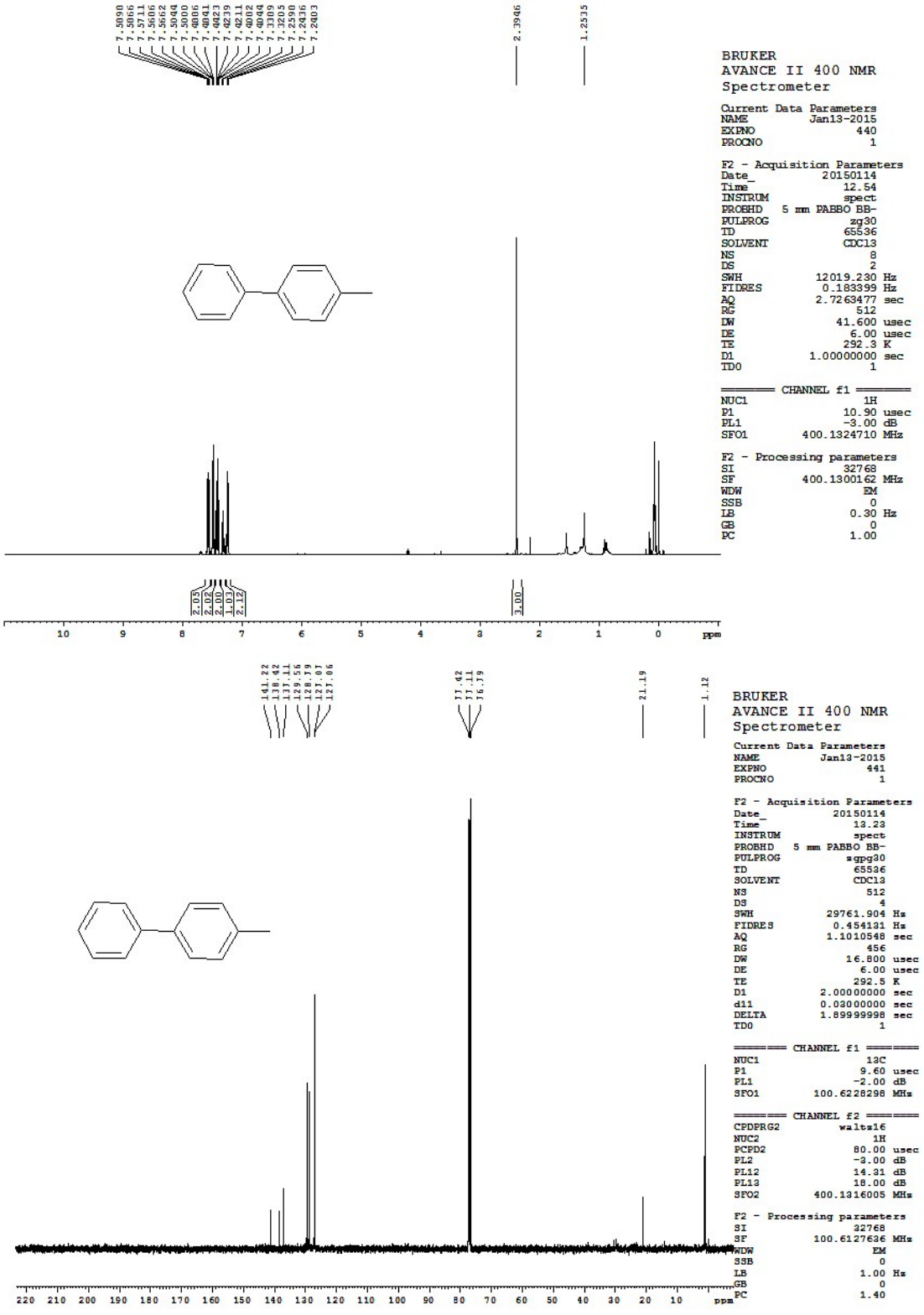

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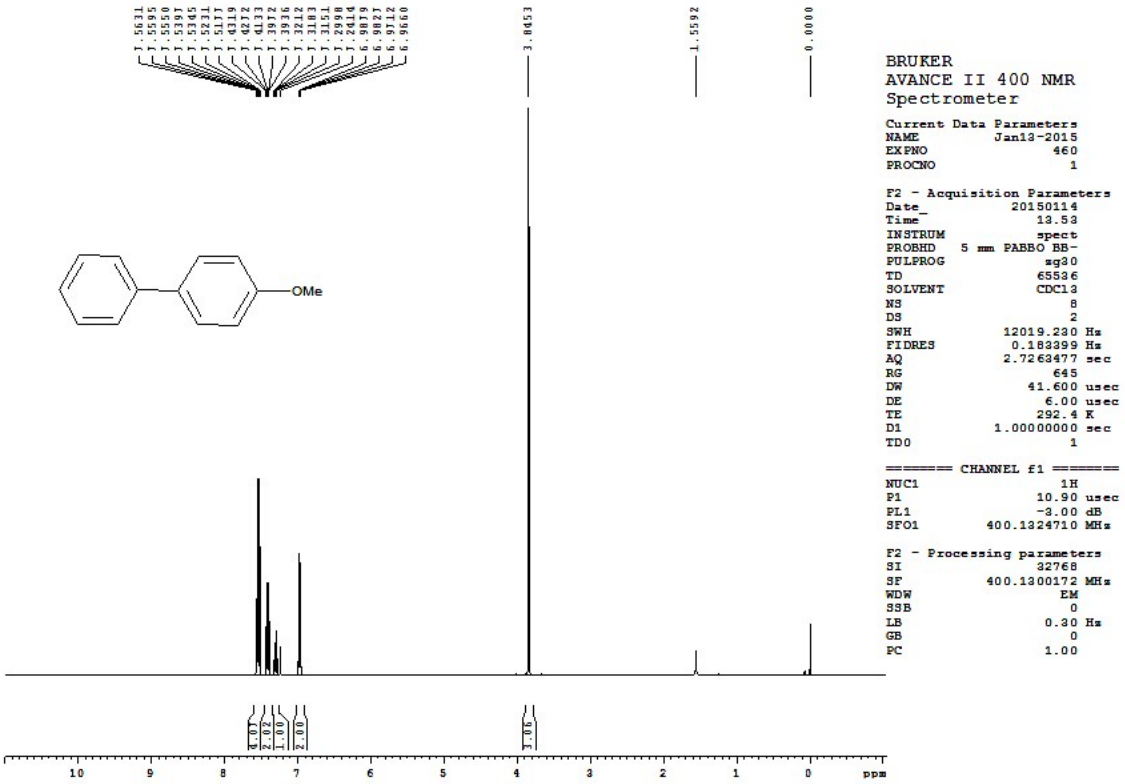

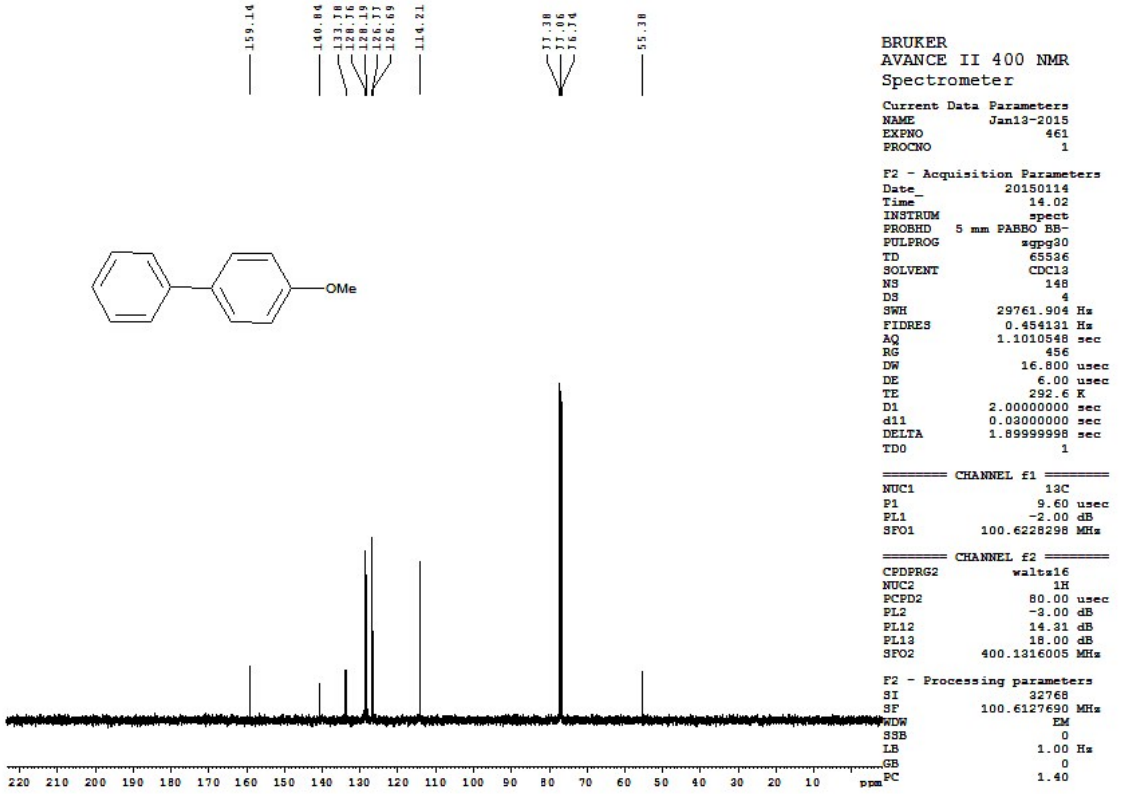

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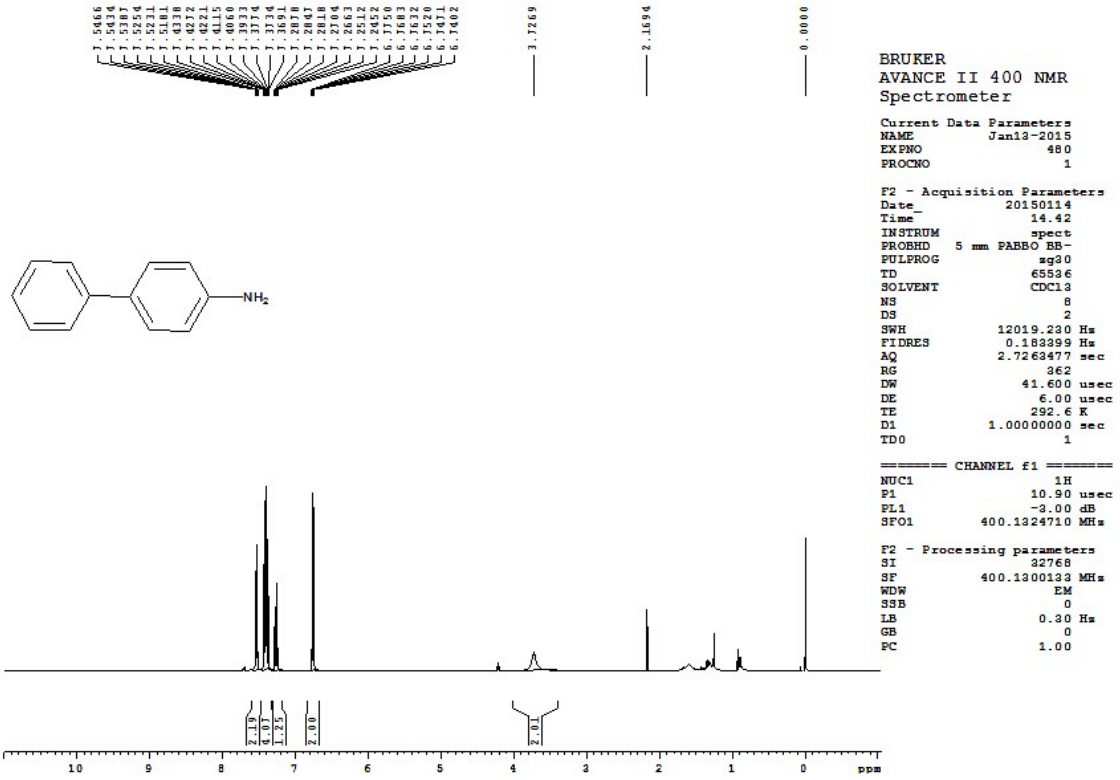

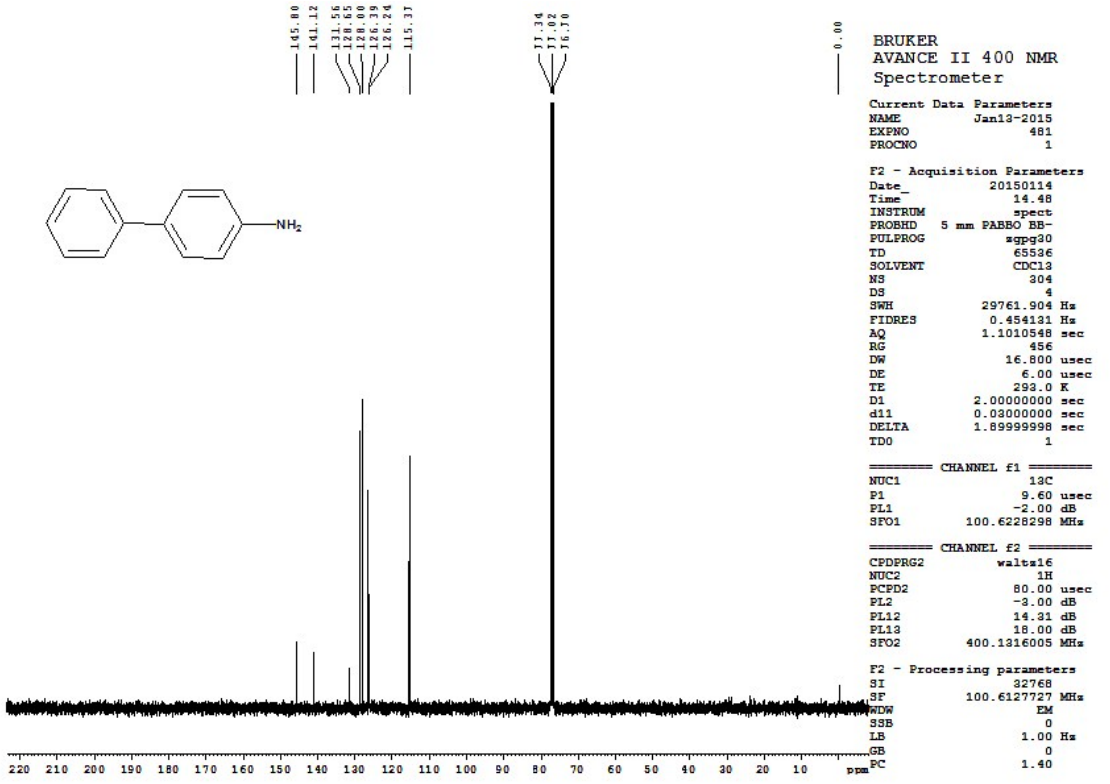

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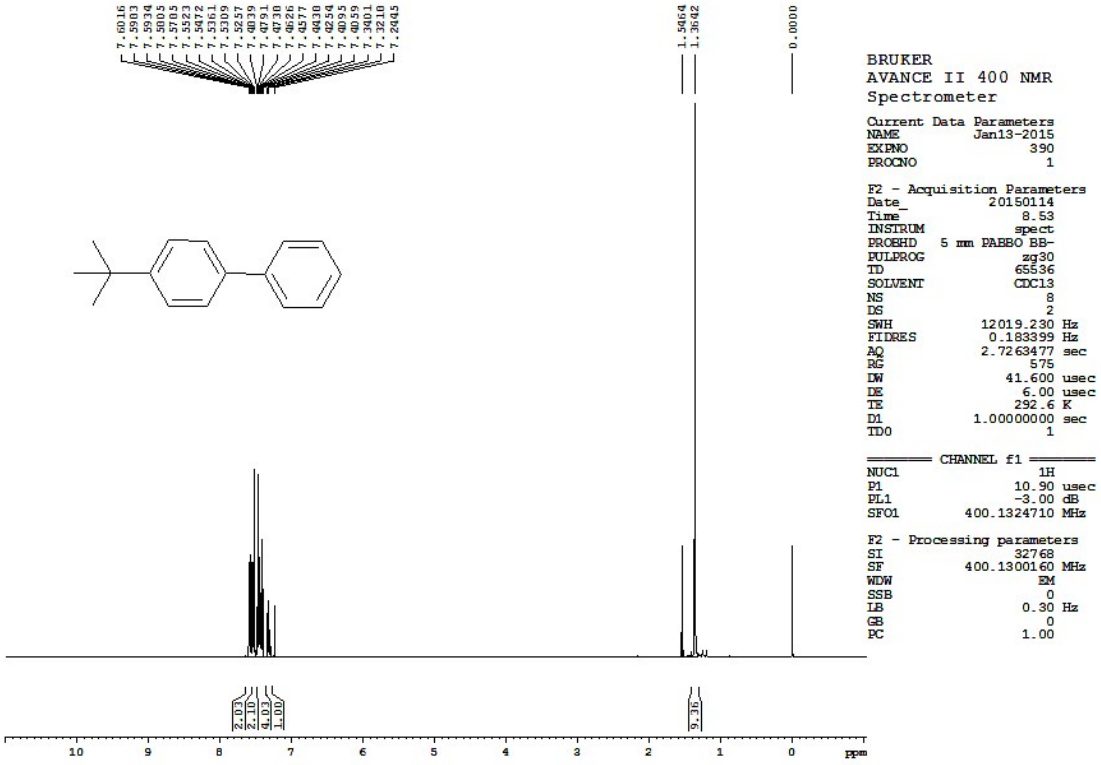

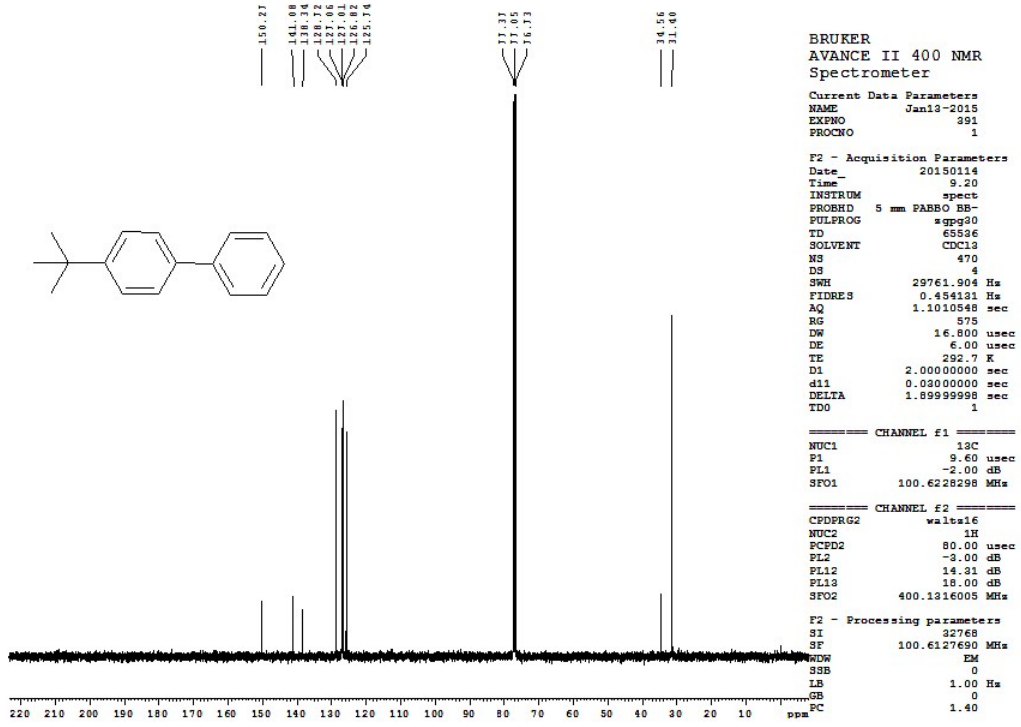

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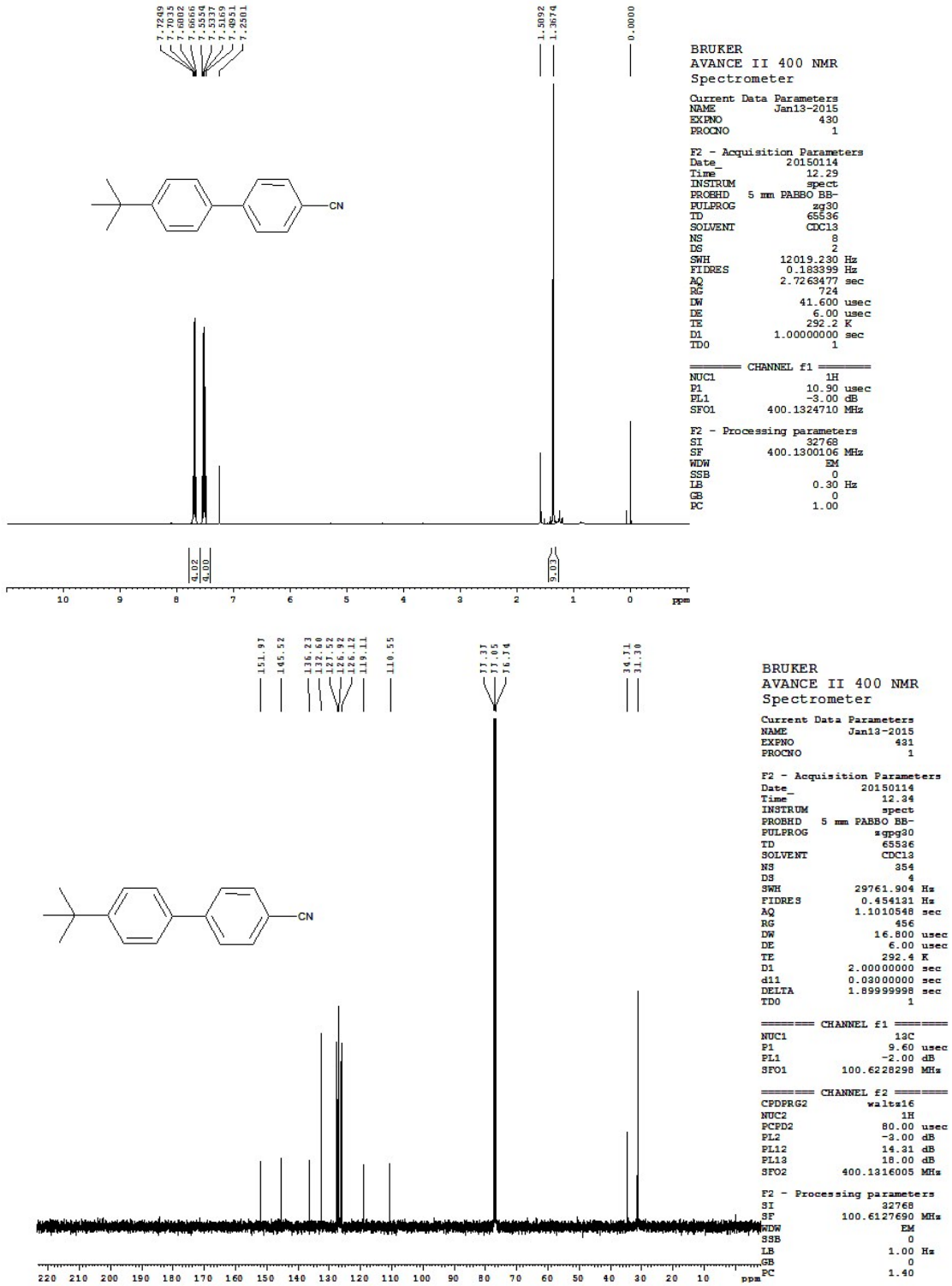

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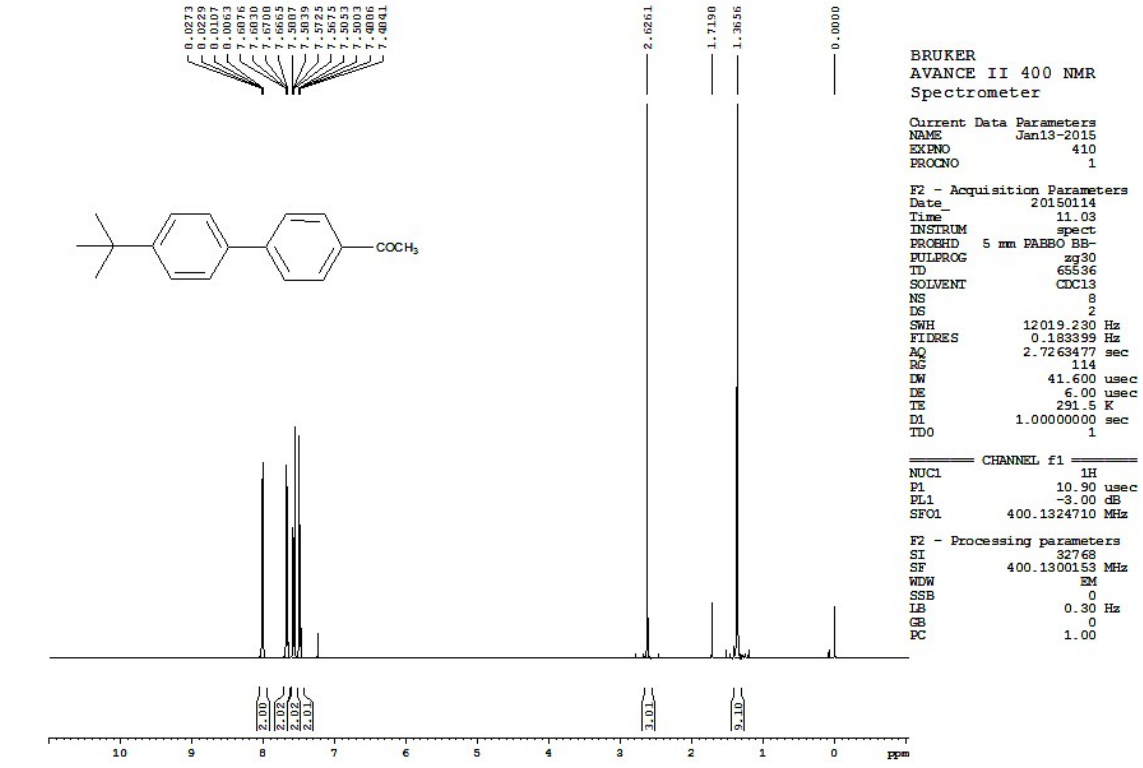

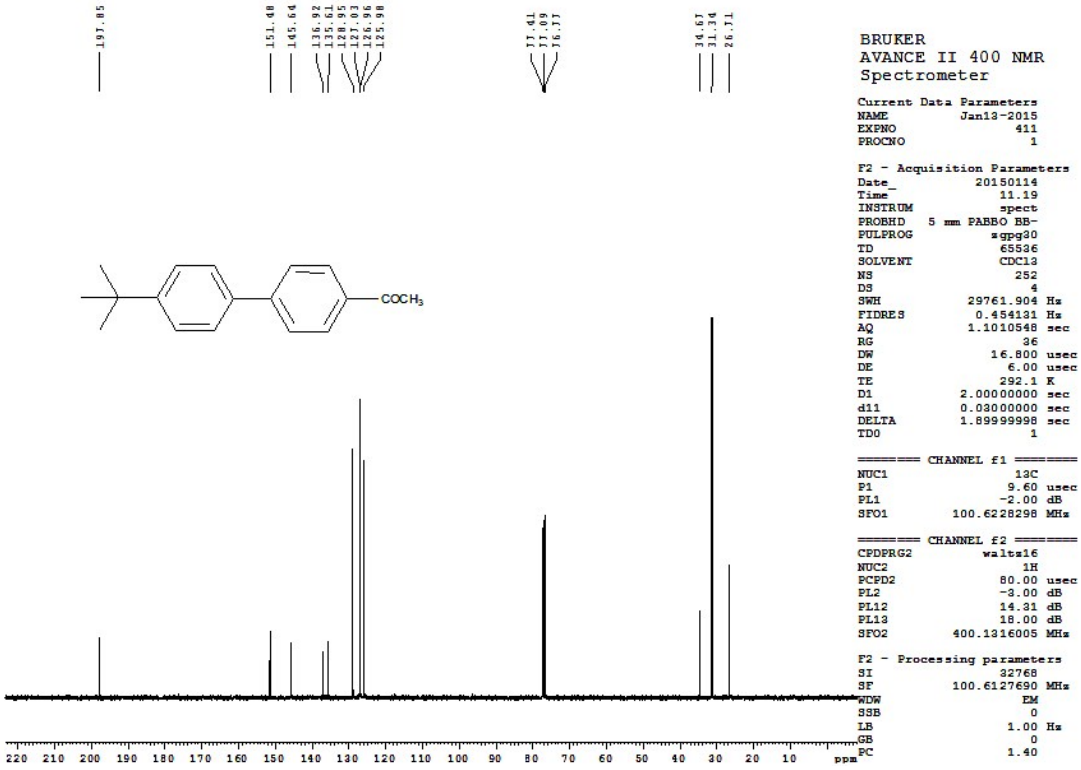

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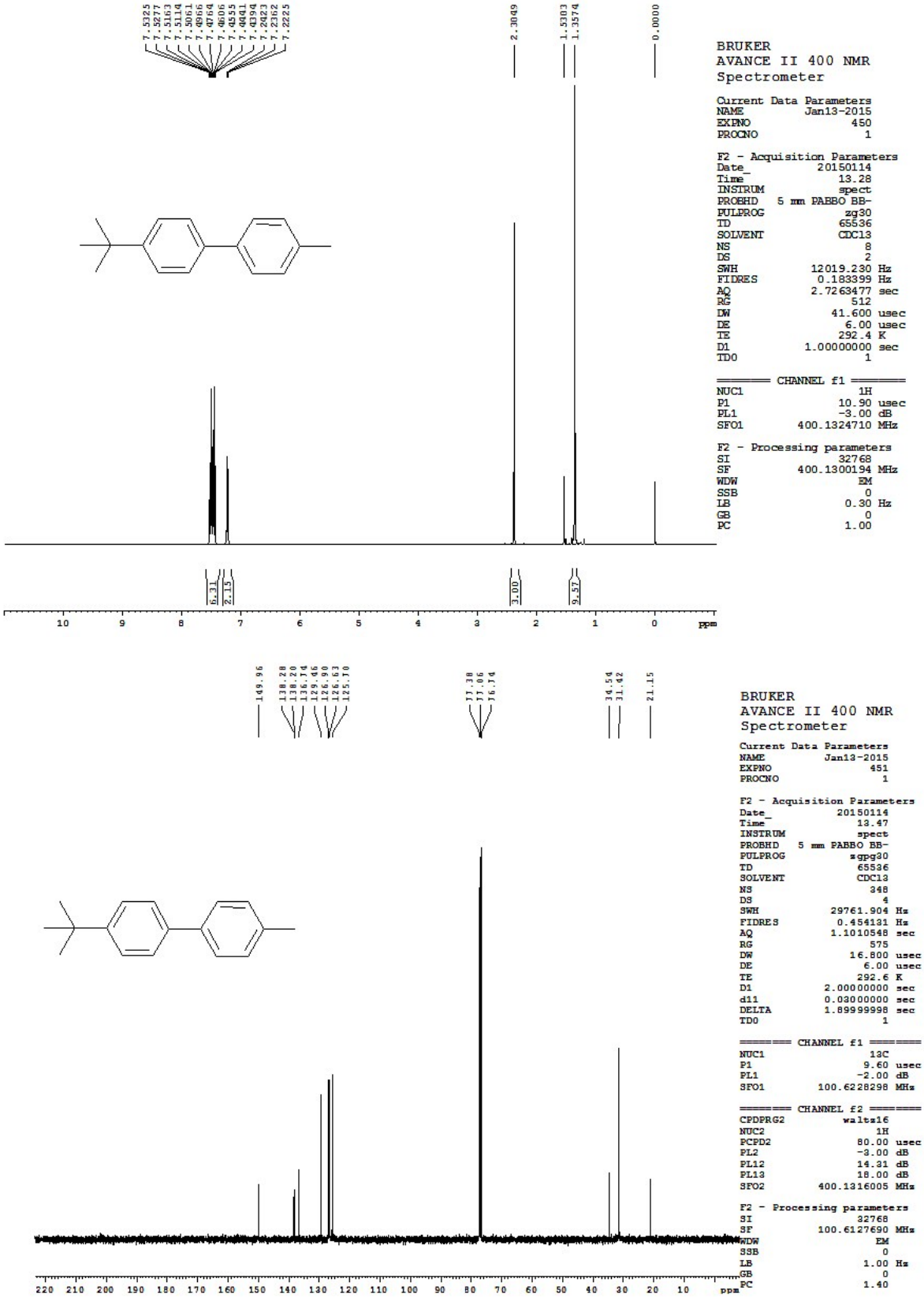


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PROCNO                 1

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TD0                    1

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NUC1                  1H
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PL1                -3.00 dB
SFO1          400.1324710 MHz

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BRUKER
AVANCE II 400 NMR
Spectrometer

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PROCNO                 1

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FIDRES         0.454131 Hz
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DW                16.800 usec
DE                 6.00 usec
TE                292.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.60 usec
PL1                -2.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
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PL2                -3.00 dB
PL12               14.31 dB
PL13               18.00 dB
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F2 - Processing parameters
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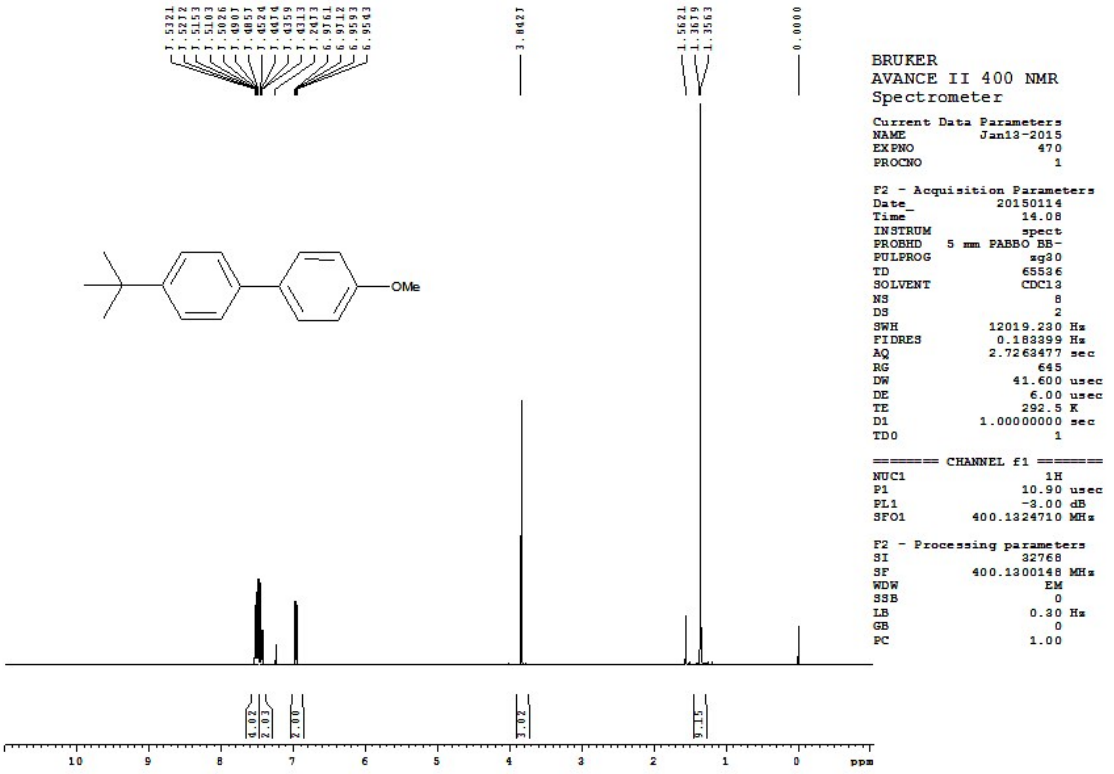

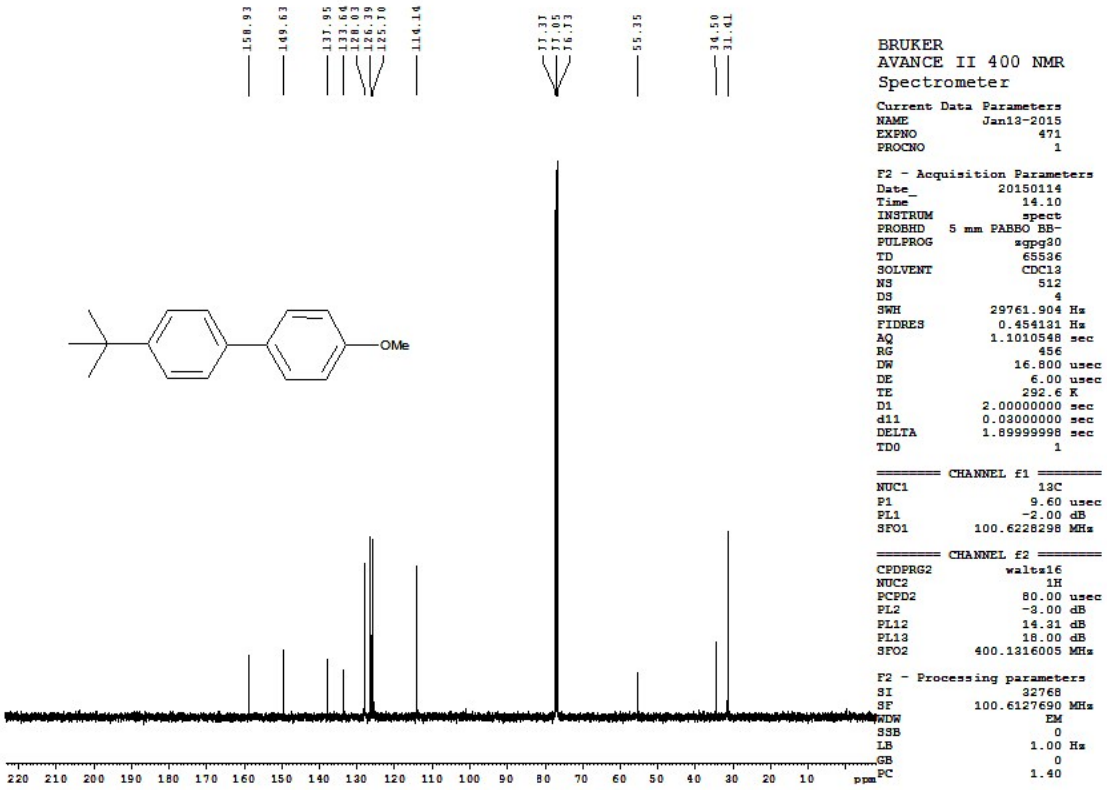

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