Facile Suzuki-Miyaura coupling of activated aryl halides using new CpNiBr(NHC) complexes

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Supplementary Information

*General synthesis for imidazolium bromide salts (**L1**, **L2**):*

To a slurry of imidazole (2.05 g, 30 mmol), KOH (3.38 g, 60 mmol), and K_2CO_3 (4.16 g, 30 mmol), in CH_3CN (20 mL) was added the benzyl/phenylethyl halide (RX, 30 mmol) and the resulting mixture was heated under reflux for 3 hours. The mixture was concentrated to dryness, extracted with DCM (20 mL), which was washed with H_2O (3 x 8 mL). The combined organic extracts was concentrated *in vacuo* to which the second aryl halide (R'X, 30 mmol) was added in CH_3CN (20 mL) and heated under reflux overnight. The resulting mixture was concentrated to dryness and washed several times with hexane (3 x 10 mL), Et_2O (3 x 10 mL), and EtOAc (3 x 10 mL) to give the precursor imidazolium salts in high yield (> 85%).

[*Im(Me)((CH₂)₂Ph)]Br* (***L1***): Yield: 87%. ^{1}H-NMR ($(CD_3)_2CO$, δ_H) 3.32 (t, $^3J_{HH}$ = 8 Hz, NC*H*$_2$CH$_2$, 2H), 4.04 (s, C*H*$_3$, 3H), 4.72 (t, $^3J_{HH}$ = 8 Hz, NCH$_2$C*H*$_2$, 2H), 7.18 – 7.30 (m, C$_6$*H*$_5$, 3H), 7.39 – 7.75 (m, C$_6$*H*$_5$, 2H), 7.76 (s, NC*H*, 1H), 7.92 (s, NC*H*, 1H), 10.16 (s, NC*H*N, 1H). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$, δ_C) 36.5 (s, *C*H$_2$), 37.0 (s, *C*H$_3$), 51.2 (s, *C*H$_2$), 123.4 (s, NC*C*H), 124.1 (s, s, NC*C*H), 127.6 (s, *C*$_6$H$_5$), 129.4 (s, *C*$_6$H$_5$), 129.9 (s, *C*$_6$H$_5$), 137.9 (s, *ipso*-*C*$_6$H$_5$), 138.4 (s, NC*C*N).

[*Im(Me)(4-NO₂Bn)]Br* (***L1***): Yield: 86%. ^{1}H-NMR ($(CD_3)_2CO$, δ_H) 3.75 (s, C*H*$_3$, 3H), 6.00 (s, C*H*$_2$, 2H), 6.96 (s, NC*H*, 1H), 7.09 (s, NC*H*, 1H), 7.99 (m, C$_6$*H*$_5$, 2H), 8.24 (m, C$_6$*H*$_5$, 2H), 10.34 (s, NC*H*N, 1H). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$, δ_C) 36.7 (s, *C*H$_3$), 51.9 (s, *C*H$_2$), 124.7 (s,

NCH), 124.8 (s, s, NCH), 128.5 (s, C_6H_4), 131.5 (s, C_6H_4), 136.5 (s, *ipso*-C_6H_5 *trans* to NO_2-group), 138.8 (s, *ipso*-C_6H_5 adjacent to NO_2-group), 143.0 (s, NCN).

Table 1: Crystal data and experimental parameters for compounds **L1, L2, 1, 2, 3, 4**.

Complex	**L1**	**L2**	**1**	**2**	**3**	**4**
Emp. formula	$C_{12}H_{15}BrN_2$	$C_{11}H_{12}BrN_3O_2$	$C_{22}H_{21}BrN_2Ni$	$C_{16}H_{17}BrN_2Ni$	$C_{20}H_{22}BrN_2Ni$	$C_{16}H_{16}BrN_3NiO_2$
Form. weight ($g.mol^{-1}$)	267.17	298.15	452.03	375.93	429.96	420.94
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	*Pnma*	*P*-1	*C*2/*c*	$P2_1/n$
Crystal descr.	colourless block	colourless rod	red fragment	red block	red block	red plate
a (Å)	7.537(2)	5.2343(2)	13.1389(6)	7.3271(5)	13.3223(9)	14.7447(1)
b (Å)	17.252(5)	24.6265(1)	17.3065(8)	9.1441(6)	12.7790(1)	28.446(3)
c (Å)	9.742(3)	19.0455(9)	8.3032(4)	11.4801(7)	22.2205(2)	9.0297(1)
α (°)	90.000	90.000	90.000	87.589(2)	90.000	90.000
β (°)	100.874(9)	94.7320(11)	90.000	82.321(2)	102.963(3)	120.885(2)
γ (°)	90.000	90.000	90.000	85.151(2)	90.000	90.000
Volume ($Å^3$)	1243.9(6)	2446.64(2)	1888.05(2)	759.17(9)	3686.5(5)	3250.3(6)
Z	4	8	4	2	8	8
Abs. coeff. ($m.mm^{-1}$)	3.276	4.553	3.151	3.900	3.223	3.664
F(000)	544.0	1200.0	920.0	380.0	1752.0	1696.0
Independent refl.	4967	4829	4734	12814	4098	7850
Completeness (%)	100	100	99	100	99	100
Data/Restr/Para	4967/0/196	4829/0/309	4734/0/167	12814/0/182	4098/0/218	7850/420/417
Goodness of fit on F^2	1.050	1.116	1.289	1.027	1.046	1.079
Final R_1 indices	0.0323	0.0436	0.0573	0.0476	0.0263	0.0622
wR_2 indices (all data)	0.0796	0.1099	0.1215	0.1060	0.0592	0.1718
Largest diffr. peak and hole ($e.Å^{-3}$)	1.19/-0.37	1.40/-0.48	1.95/-0.65	1.25/-0.53	0.69/-0.61	1.36/-0.77

Mass spectra for compounds **1** – **9:**

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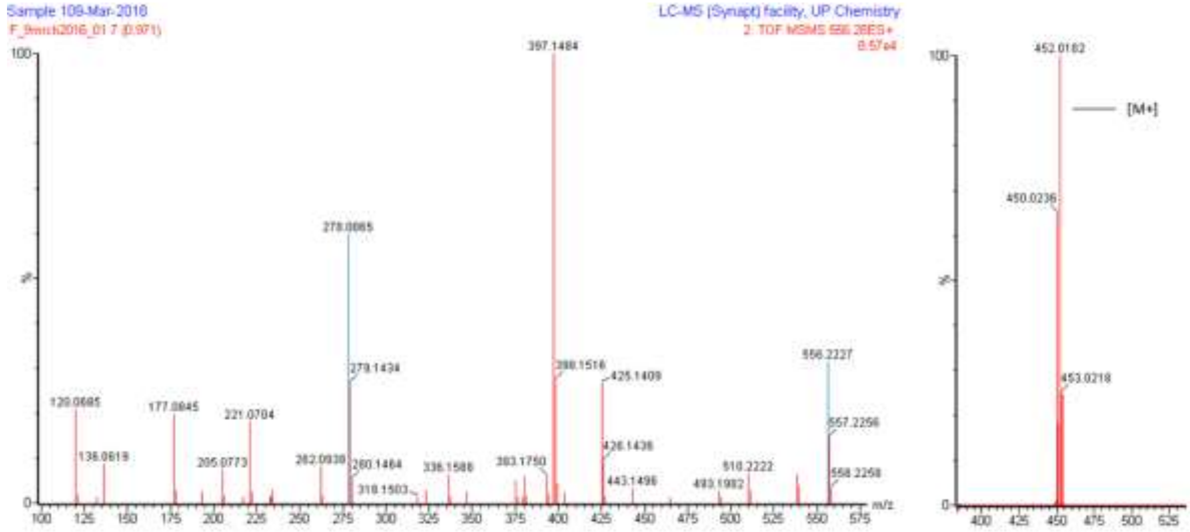
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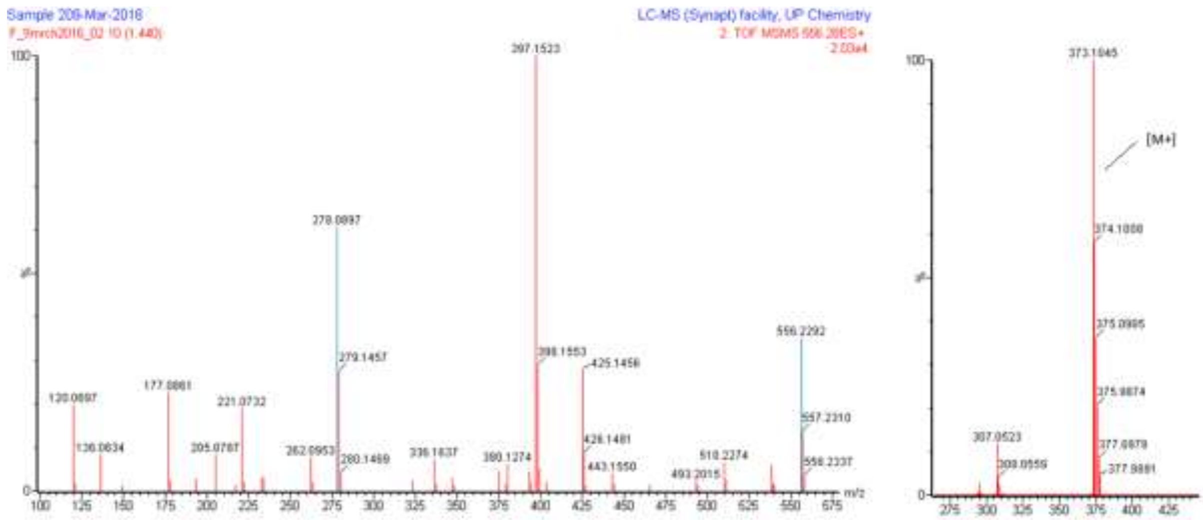
MS of **2**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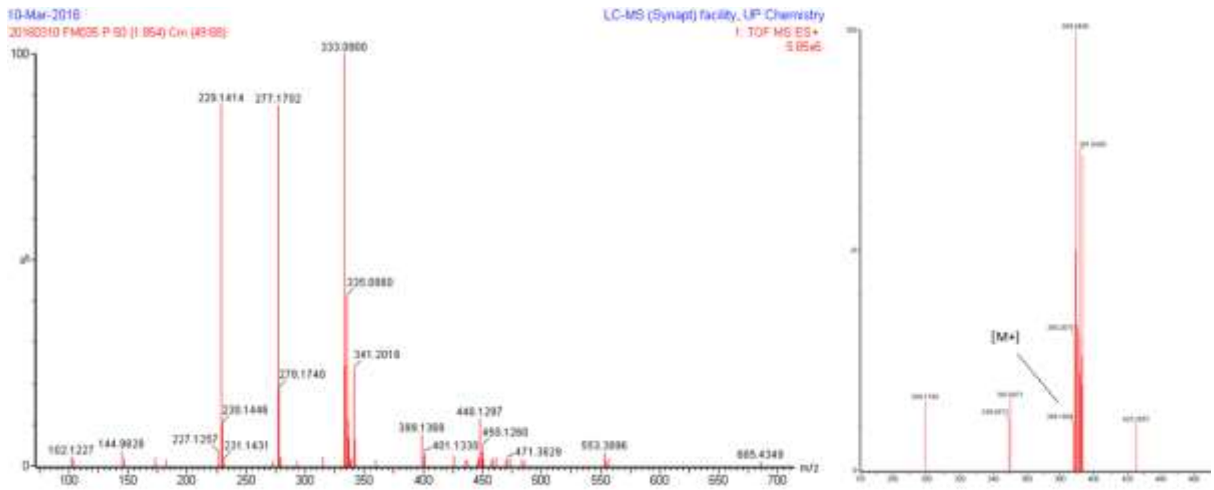
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m/z
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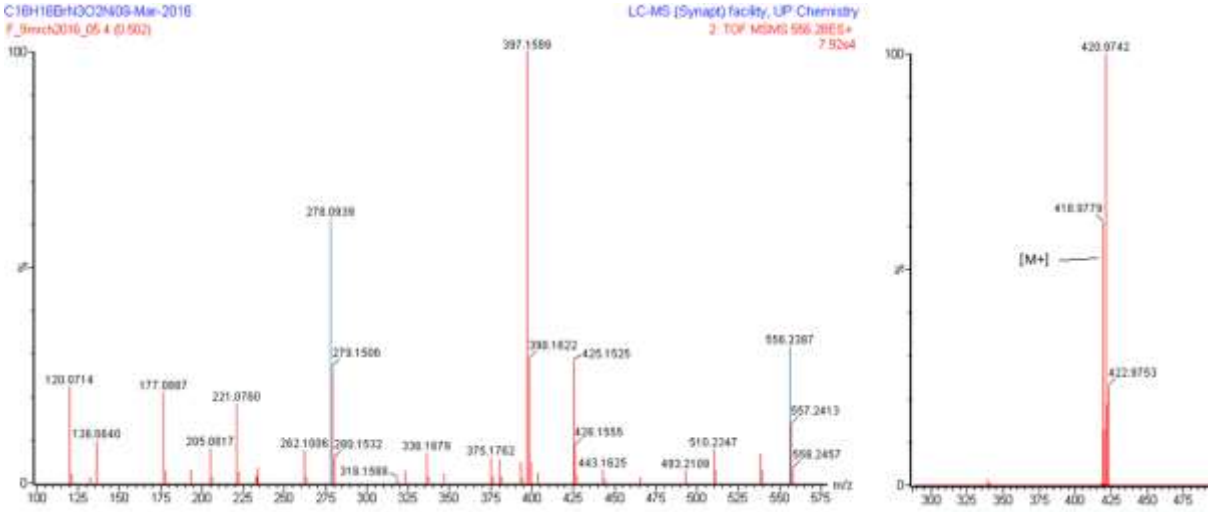

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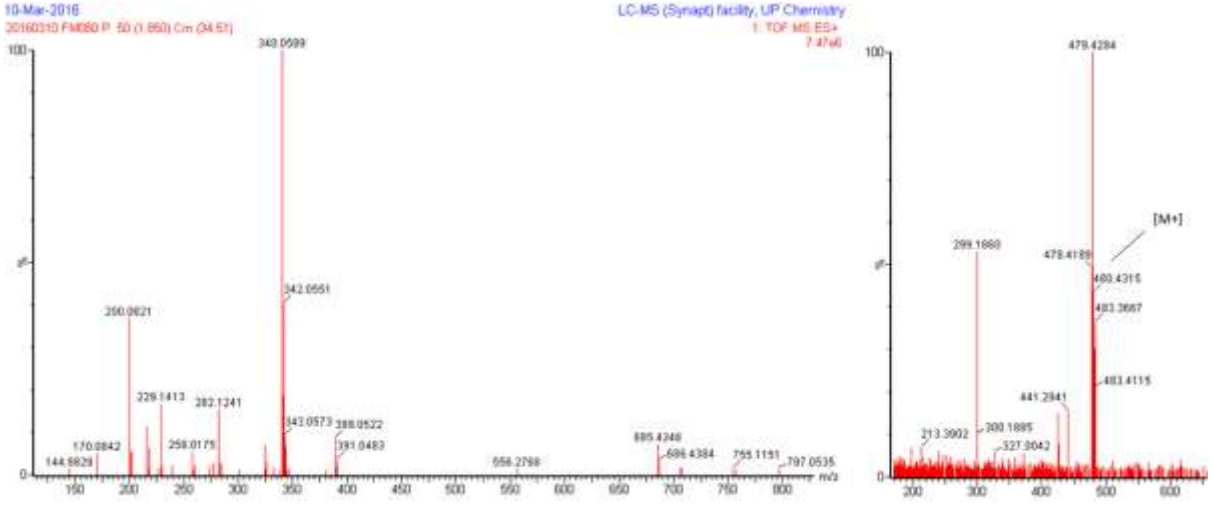

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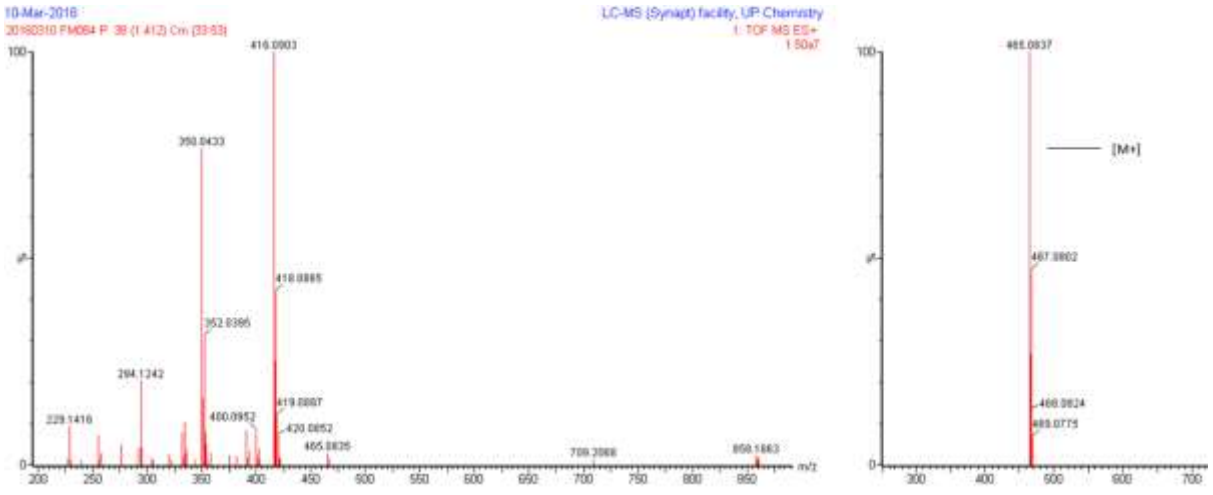

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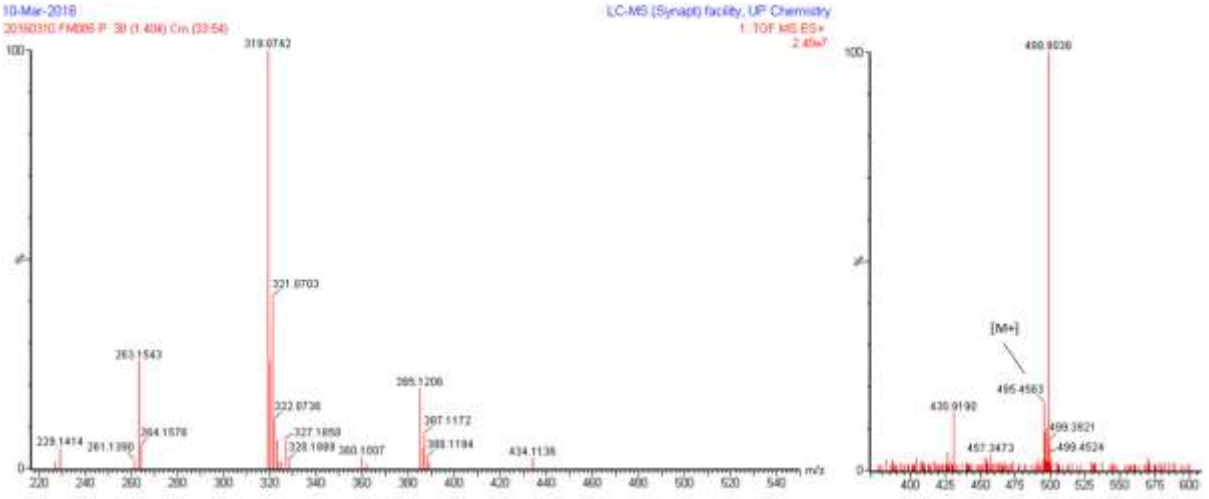

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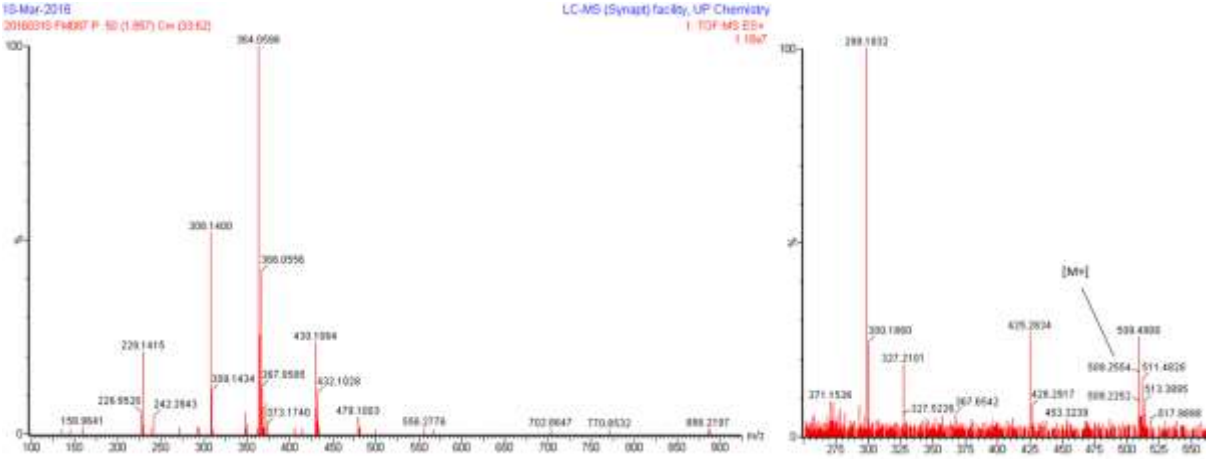

MS of **9**