Supporting Information

N-coordinated Ru(II) Catalyzed Solvent Free N-alkylation of Primary Amines with Alcohols through Borrowing Hydrogen Strategy

Bhavya P. Patel M.S.[1], Rishi Ranjan M.S.[2], Nimesh R. Chauhan M.S.[1], Suman Mukhopadhyay Ph.D.[2], Angshuman Roy Choudhury Ph.D.[3], Komal M. Vyas Ph.D.[1*]

[1] *Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120, India*

[2] *Department of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore-453552, India*

[3] *Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali, Sector 81, S. A. S. Nagar, Manauli PO, Mohali, Panjab 140306, India*

*Corresponding author: komal_vyas@spuvvn.edu

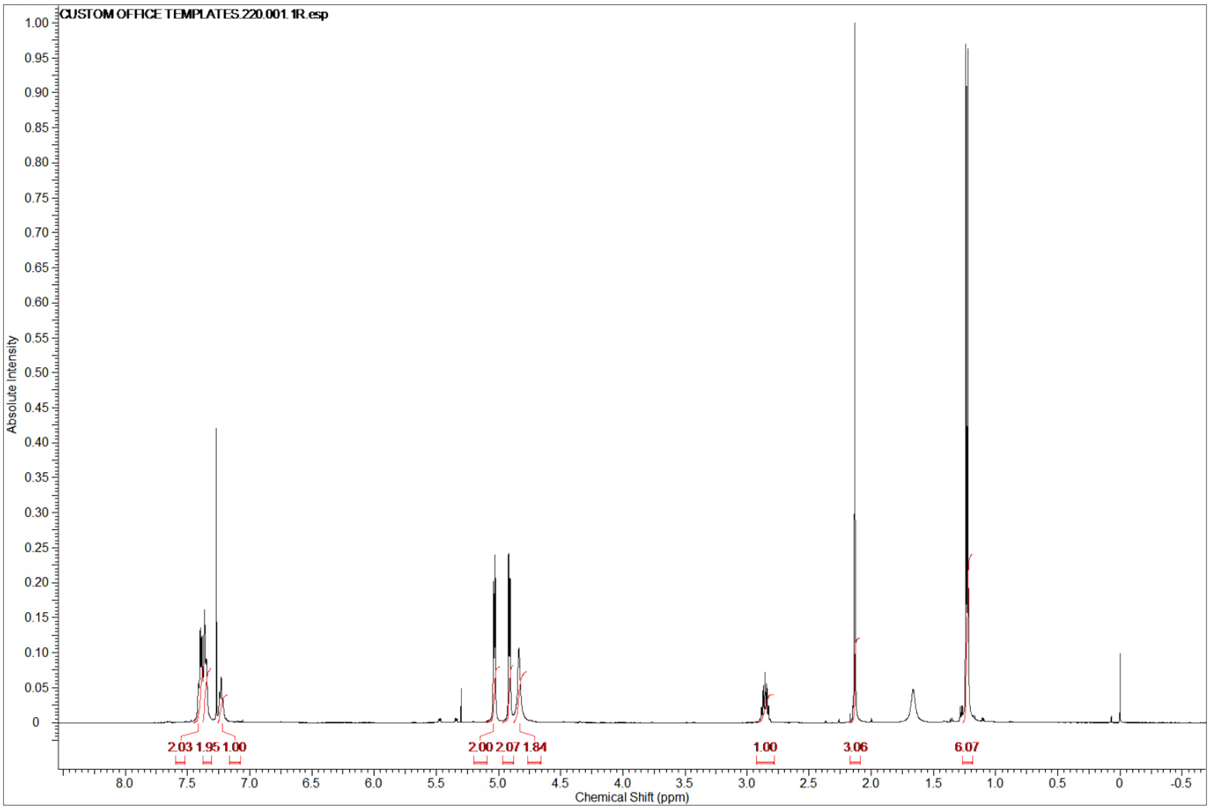


Fig. S1. ^{1}H NMR of **[Ru-3].**

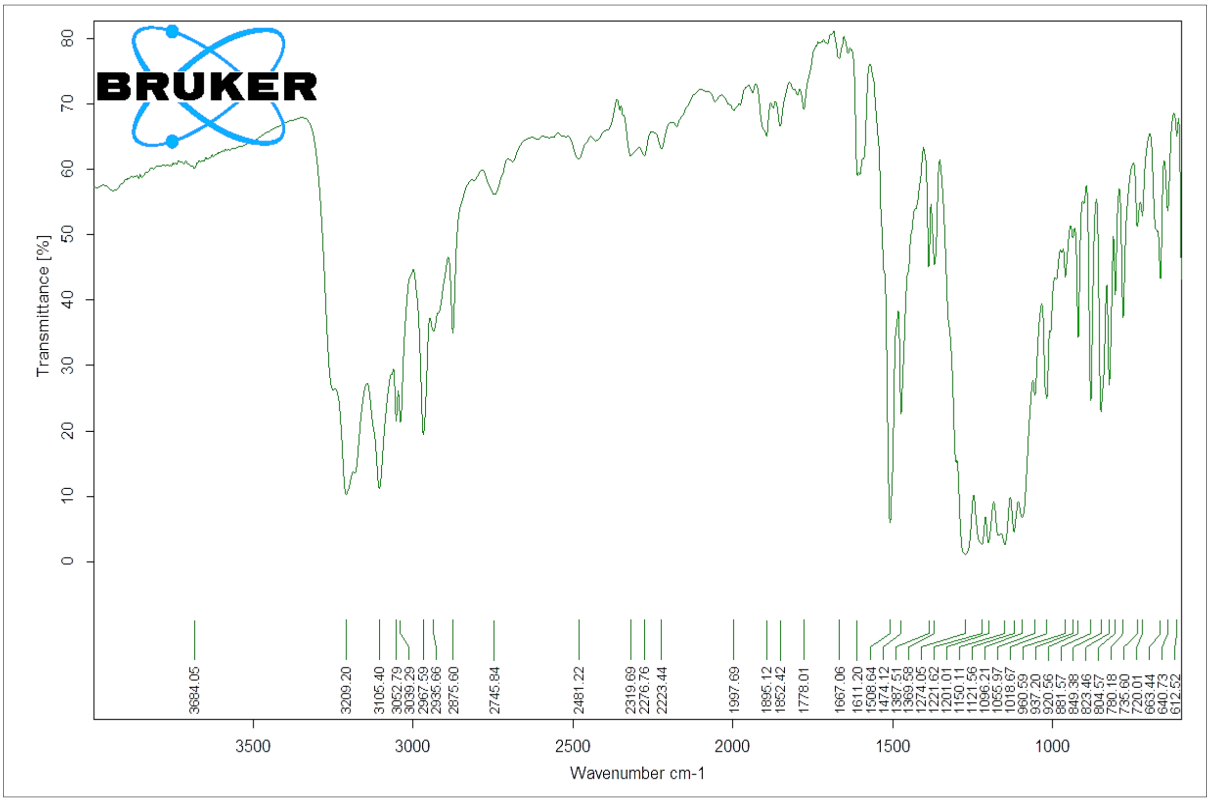


Fig. S2. FTIR spectrum of **[Ru-1]**

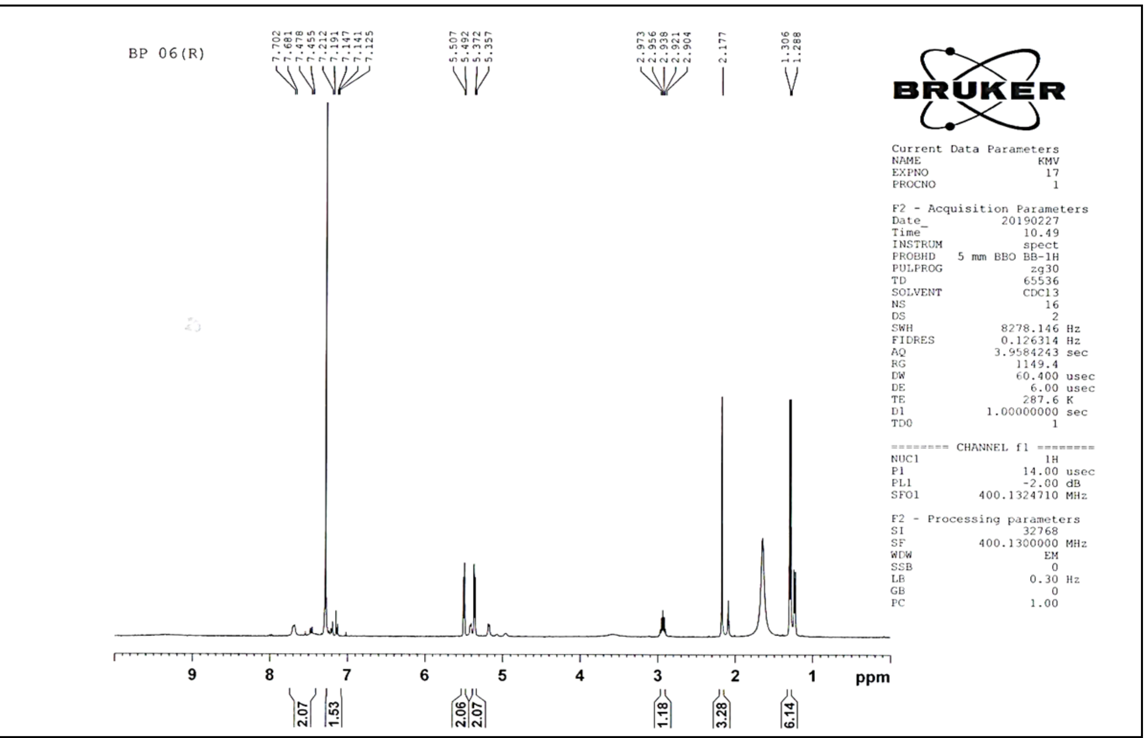


Fig. S3. ^{1}H NMR spectrum of **[Ru-1]**

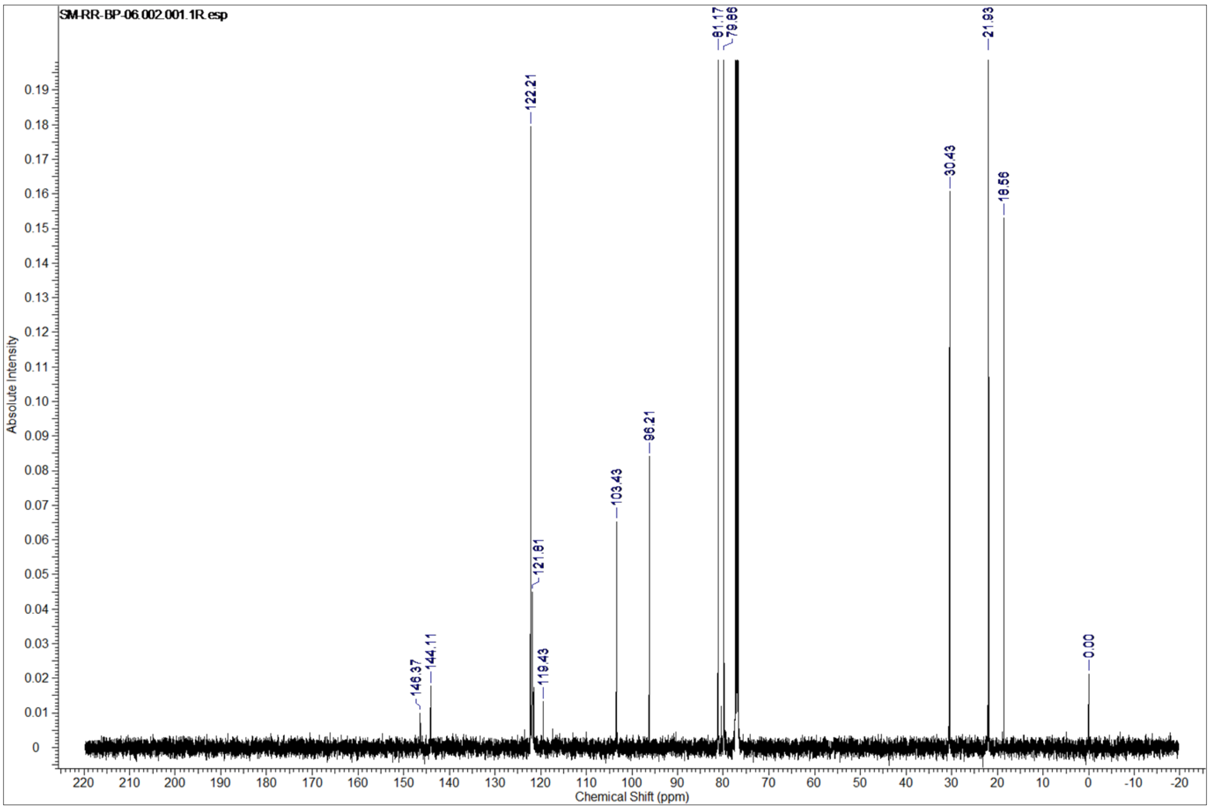


Fig. S4. ^{13}C NMR spectrum of **[Ru-1]**

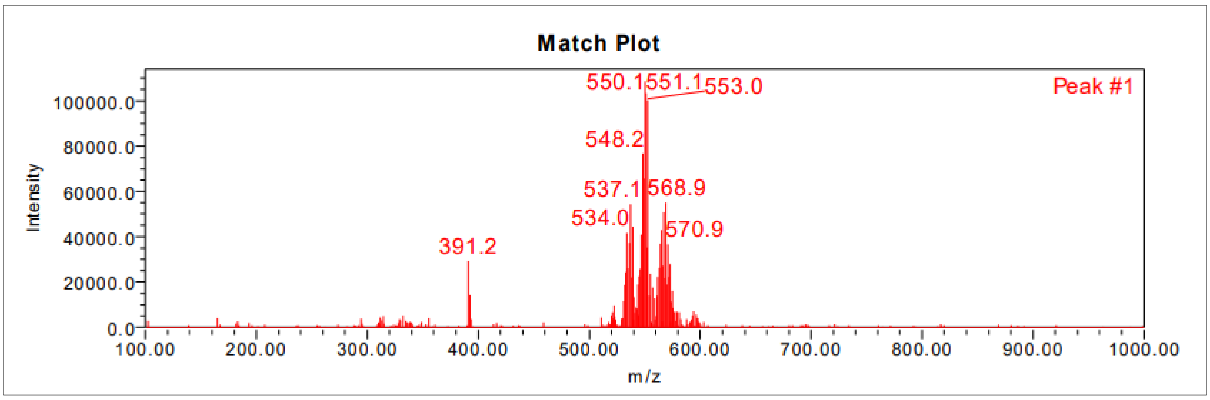
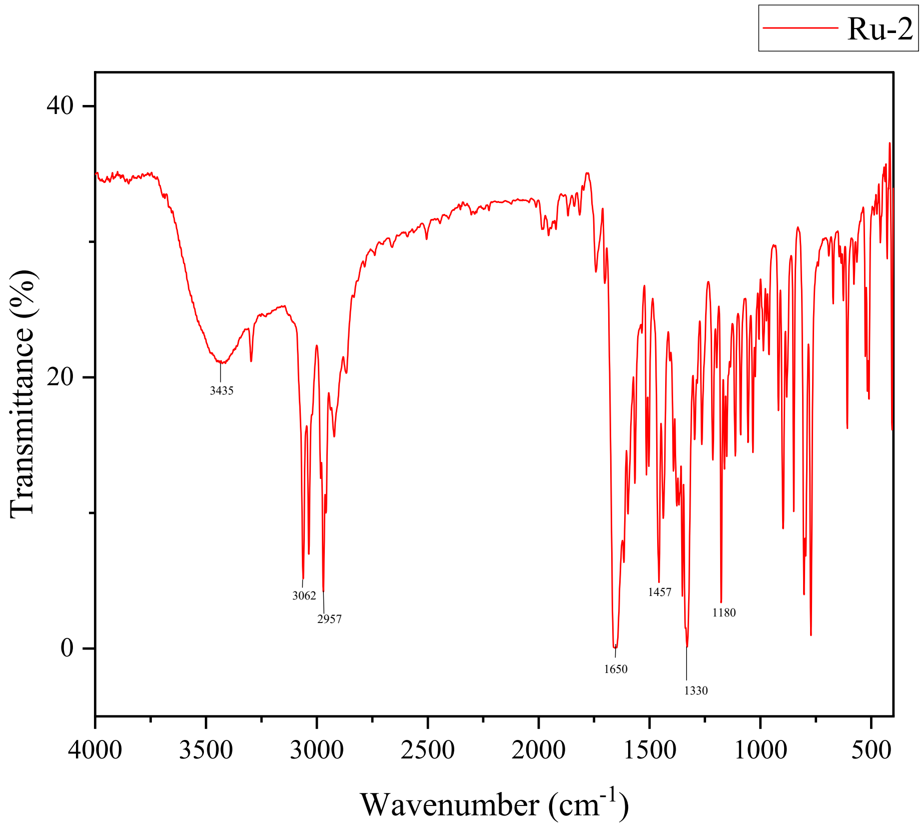


Fig. S5. Mass spectrum of **[Ru-1]**



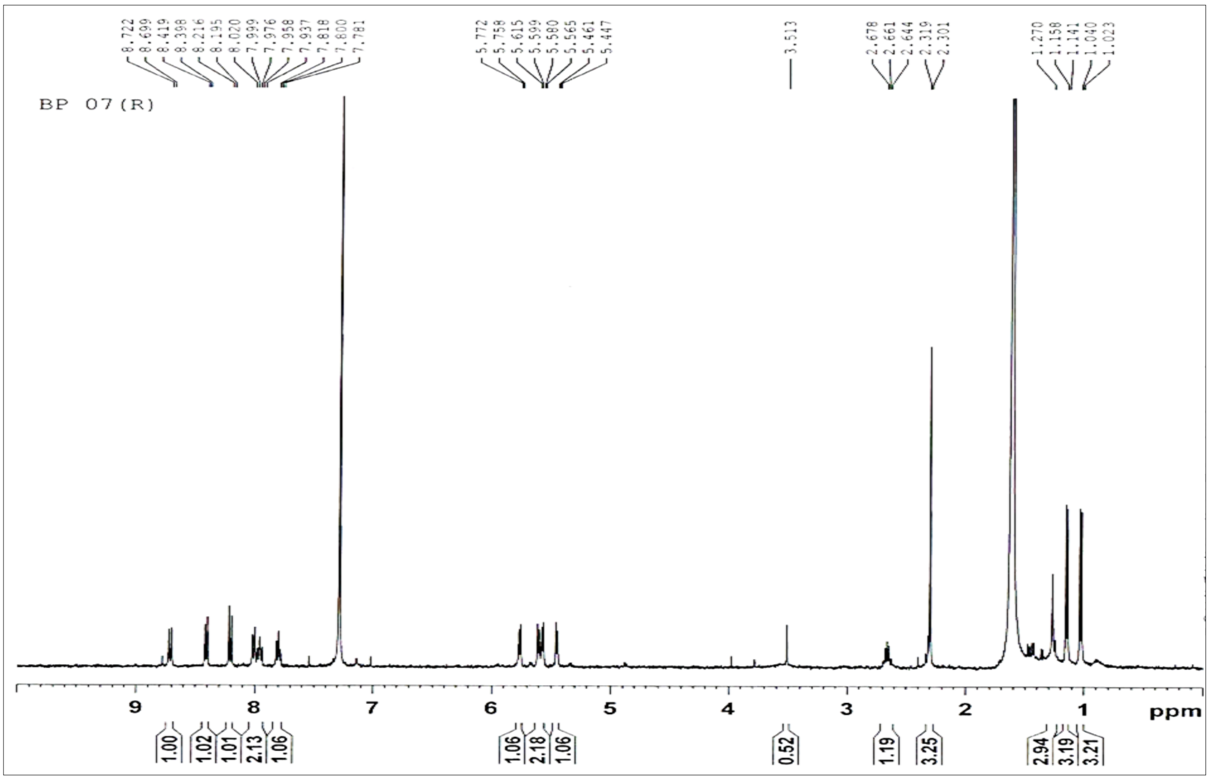


Fig. S6. FTIR spectrum of **[Ru-2]**

Fig. S7. ^{1}H NMR spectrum of **[Ru-2]**

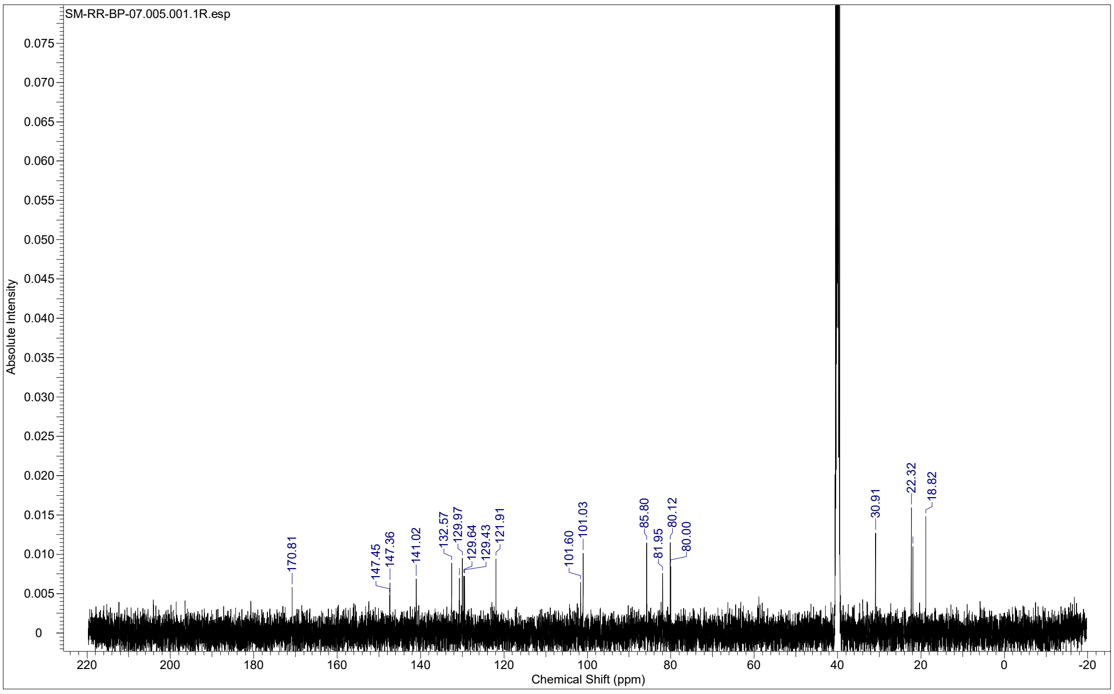


Fig. S8. ^{13}C NMR spectrum of **[Ru-2]**

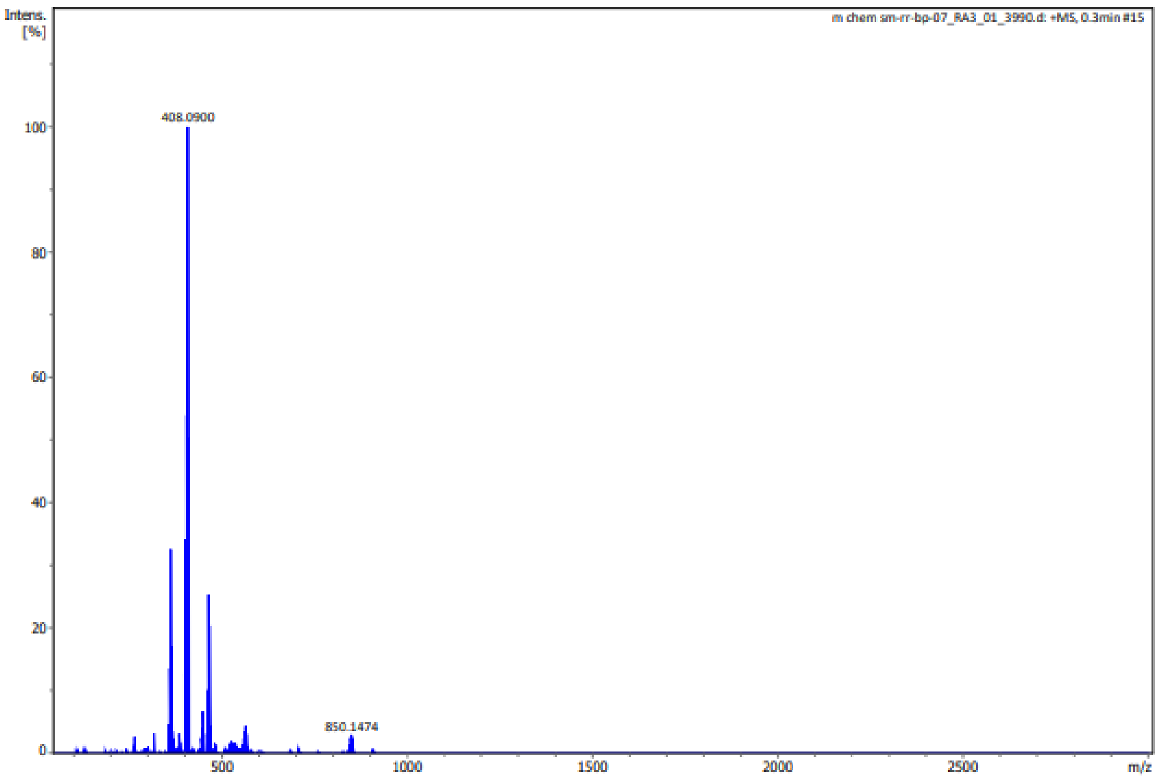


Fig. S9. Mass spectrum of **[Ru-2]**

Table S1. Bond lengths (in Å) of **[Ru-1]** and **[Ru-2].**

[Ru-1]		**[Ru-2]**	
Ru1 Cl2	2.4278(13)	Ru1 Cl1	2.4077(8)
Ru1 Cl1	2.4115(13)	Ru1 O1	2.0850(19)
Ru1 N1	2.184(4)	Ru1 N1	2.123(2)
Ru1 C13	2.209(5)	Ru1 C16	2.167(3)
Ru1 C9	2.219(5)	Ru1 C15	2.187(3)
Ru1 C12	2.220(5)	Ru1 C11	2.179(3)
Ru1 C11	2.188(5)	Ru1 C14	2.171(3)
Ru1 C8	2.155(5)	Ru1 C13	2.193(3)
Ru1 C10	2.156(5)	Ru1 C12	2.225(3)
N1 C1	1.439(7)	O1 C10	1.283(3)
C1 C6	1.392(7)	N1 C9	1.327(3)
C1 C2	1.373(8)	N1 C1	1.376(3)
C13 C12	1.443(8)	O2 C10	1.230(3)
C13 C8	1.420(8)	C16 C15	1.402(4)
C9 C8	1.476(9)	C16 C11	1.420(4)
C9 C10	1.416(8)	C9 C10	1.509(4)
C9 C15	1.465(9)	C9 C8	1.403(4)
C6 C5	1.377(9)	C15 C14	1.436(4)
C12 C11	1.414(8)	C15 C18	1.512(4)
C12 C14	1.485(8)	C1 C6	1.425(3)
C11 C10	1.435(9)	C1 C2	1.414(4)
O1 C4	1.420(9)	C11 C12	1.414(4)
O1 C7B	1.214(15)	C14 C13	1.399(4)
O1 C7A	1.214(15)	C6 C7	1.412(4)
C2 C3	1.400(9)	C6 C5	1.413(4)
F3A C7A	1.43(2)	C2 C3	1.366(4)
C5 C4	1.377(11)	C8 C7	1.359(4)
C4 C3	1.374(11)	C13 C12	1.419(5)
C15 C16	1.530(11)	C12 C17	1.511(5)
C15 C17	1.539(13)	C18 C20	1.518(5)
F2B C7B	1.43(2)	C18 C19	1.532(5)
F1A C7A	1.499(19)	C5 C4	1.354(4)
C7B F1B	1.33(2)	C3 C4	1.403(5)
C7B F3B	1.32(2)		
C7A F2A	1.268(16)		

Table S2. Bond angles (in °) of **[Ru-1]** and **[Ru-2].**

Ru-1		**Ru-2**	
Cl1 Ru1 Cl2	87.23(5)	O1 Ru1 Cl1	88.28(6)
N1 Ru1 Cl2	80.27(11)	O1 Ru1 N1	76.98(8)
N1 Ru1 Cl1	83.90(12)	O1 Ru1 C16	114.46(10)
N1 Ru1 C13	105.78(19)	O1 Ru1 C15	88.94(10)
N1 Ru1 C9	103.77(18)	O1 Ru1 C11	152.44(10)

N1 Ru1 C12	139.54(18)	O1 Ru1 C14	92.10(10)
N1 Ru1 C11	172.49(19)	O1 Ru1 C13	119.84(10)
C13 Ru1 Cl2	99.90(15)	O1 Ru1 C12	157.30(10)
C13 Ru1 Cl1	168.75(16)	N1 Ru1 Cl1	87.45(6)
C13 Ru1 C9	71.1(2)	N1 Ru1 C16	92.83(9)
C13 Ru1 C12	38.0(2)	N1 Ru1 C15	114.60(9)
C9 Ru1 Cl2	170.80(17)	N1 Ru1 C11	97.93(10)
C9 Ru1 Cl1	101.34(18)	N1 Ru1 C14	151.99(10)
C9 Ru1 C12	83.1(2)	N1 Ru1 C13	163.18(11)
C12 Ru1 Cl2	88.52(16)	N1 Ru1 C12	125.72(10)
C12 Ru1 Cl1	134.58(14)	C16 Ru1 Cl1	156.73(8)
C11 Ru1 Cl2	105.25(16)	C16 Ru1 C15	37.56(11)
C11 Ru1 Cl1	101.28(15)	C16 Ru1 C11	38.13(11)
C11 Ru1 C13	68.6(2)	C16 Ru1 C14	68.05(11)
C11 Ru1 C9	70.0(2)	C16 Ru1 C13	80.68(11)
C11 Ru1 C12	37.4(2)	C16 Ru1 C12	68.53(11)
C8 Ru1 Cl2	133.16(16)	C15 Ru1 Cl1	156.49(8)
C8 Ru1 Cl1	138.18(17)	C15 Ru1 C13	68.88(12)
C8 Ru1 N1	91.98(19)	C15 Ru1 C12	81.32(11)
C8 Ru1 C13	37.9(2)	C11 Ru1 Cl1	118.81(8)
C8 Ru1 C9	39.4(2)	C11 Ru1 C15	68.31(11)
C8 Ru1 C12	68.0(2)	C11 Ru1 C13	67.44(11)
C8 Ru1 C11	80.5(2)	C11 Ru1 C12	37.43(11)
C8 Ru1 C10	67.8(20)	C14 Ru1 Cl1	118.32(8)
C10 Ru1 Cl2	140.95(18)	C14 Ru1 C15	38.48(10)
C10 Ru1 Cl1	87.59(17)	C14 Ru1 C11	79.82(11)
C10 Ru1 N1	137.4(2)	C14 Ru1 C13	37.39(12)
C10 Ru1 C13	81.4(2)	C14 Ru1 C12	67.61(12)
C10 Ru1 C9	37.7(2)	C13 Ru1 Cl1	92.47(9)
C10 Ru1 C12	68.4(2)	C13 Ru1 C12	37.46(12)
C10 Ru1 C11	38.6(2)	C12 Ru1 Cl1	92.53(8)
C1 N1 Ru1	120.0(3)	C10 O1 Ru1	116.03(17)
C6 C1 N1	118.6(5)	C9 N1 Ru1	112.76(17)
C2 C1 N1	121.2(5)	C9 N1 C1	119.1(2)
C2 C1 C6	120.1(5)	C1 N1 Ru1	127.53(16)
C12 C13 Ru1	71.4(3)	C15 C16 Ru1	72.00(17)
C8 C13 Ru1	69.0(3)	C15 C16 C11	120.7(3)
C8 C13 C12	117.4(5)	C11 C16 Ru1	71.39(16)
C8 C9 Ru1	68.0(3)	N1 C9 C10	115.3(2)
C10 C9 Ru1	68.7(3)	N1 C9 C8	122.8(3)
C10 C9 C8	112.4(5)	C8 C9 C10	121.9(2)
C10 C9 C15	127.0(6)	C16 C15 Ru1	70.44(17)
C15 C9 Ru1	133.4(4)	C16 C15 C14	117.6(3)
C15 C9 C8	120.5(6)	C16 C15 C18	123.7(3)
C5 C6 C1	120.5(6)	C14 C15 Ru1	70.13(16)
C13 C12 Ru1	70.6(3)	C14 C15 C18	118.7(3)
C13 C12 C14	119.3(5)	C18 C15 Ru1	129.0(2)
C11 C12 Ru1	70.1(3)	N1 C1 C6	120.2(2)

C11 C12 C13	120.2(5)	N1 C1 C2	120.7(2)
C11 C12 C14	120.6(5)	C2 C1 C6	119.0(2)
C14 C12 Ru1	131.0(4)	C16 C11 Ru1	70.48(16)
C12 C11 Ru1	72.5(3)	C12 C11 Ru1	73.03(17)
C12 C11 C10	119.5(5)	C12 C11 C16	121.6(3)
C10 C11 Ru1	69.5(3)	C15 C14 Ru1	71.38(16)
C7B O1 C4	118.1(9)	C13 C14 Ru1	72.17(16)
C7A O1 C4	118.1(9)	C14 C13 Ru1	70.44(16)
C13 C8 Ru1	73.1(3)	O1 C10 C9	115.0(2)
C13 C8 C9	125.6(5)	O2 C10 O1	125.4(3)
C9 C8 Ru1	72.6(3)	O2 C10 C9	119.6(3)
C9 C10 Ru1	73.5(3)	C7 C8 C9	119.6(3)
C9 C10 C11	124.9(5)	C14 C13 C12	120.5(3)
		C12 C13 Ru1	72.48(16)
		C11 C12 Ru1	69.54(16)
		C13 C12 Ru1	70.05(16)
		C13 C12 C17	120.5(3)
		C17 C12 Ru1	129.6(2)

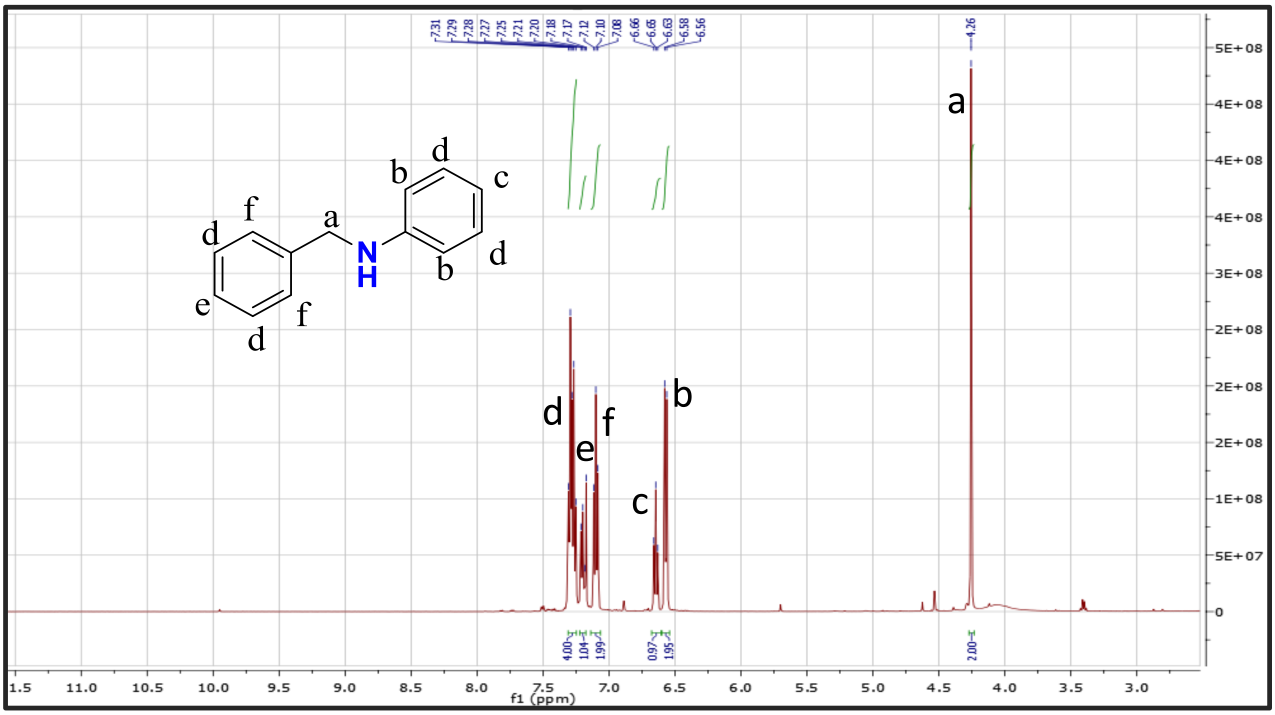


Fig. S10. [1]H NMR of N-benzyl aniline

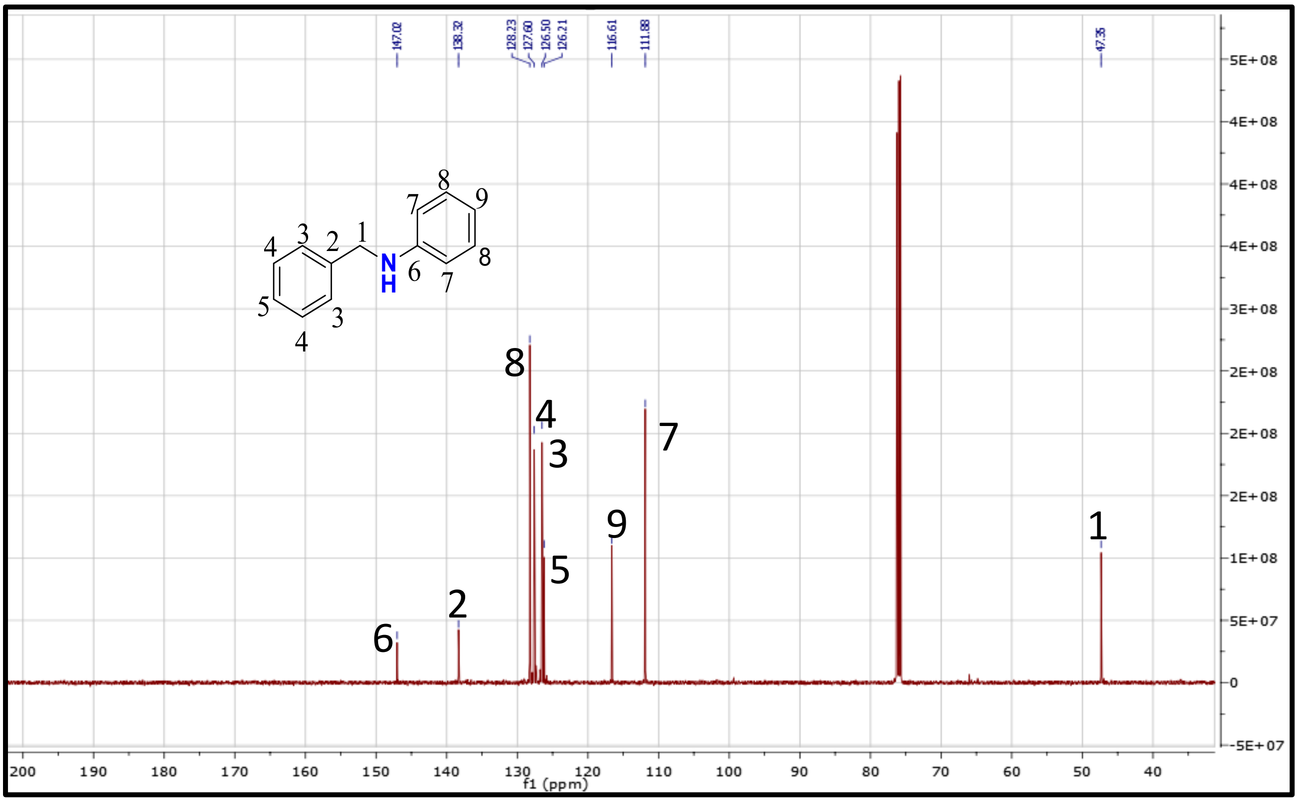


Fig. S11. ^{13}C NMR of N-benzylaniline

Detailed HPLC procedure

The Dionex HPLC-Ultimate 3000 pump was utilized to analyze products by injecting a 20 μL sample into a Diomex Acclaim® 120 C18 column (250 mm × 4.6 mm × 5 μm), flow rate was set at 1 mL min^{-1}. The analysis involved a linear gradient of 40% (v/v) acetonitrile in waterfor 35 min, which gradually increased to 100% (v/v) acetonitrile in water at 35 min, and was kept constant until 40 min. Thereafter the gradient decreased to 40% (v/v) acetonitrile in water at 42 min. Prior to injection, the samples were prepared by mixing 100 μL of crude reaction mixture in a 900 μL solution of acetonitrile-water (1:1) containing 0.1 % trifluoracetic acid. The samples were then filtered through a 0.45 μm syringe filter with a diameter of 13 mm and 2.7 pore size. The products were identified using Ultimate 3000 RS VWD, which operated at both 254 nm and 280 nm wavelengths.

HPLC yield calculation.

Conversion of benzyl alcohols, selectivity, and yield of aldehyde was calculated from the following formulas.

$$\% \text{ conversion} = (C_0 - C_R/C_0) \times 100\% \quad (1)$$

$$\% \text{ yield} = C_P/C_0 \times 100\% \quad (2)$$

$$\% \text{ selectivity} = C_P/(C_0 - C_P) \times 100\% \quad (3)$$

Where,

C_0 = Initial concentration of substrate

C_R = Final concentration of substrate

C_P = Final concentration of product

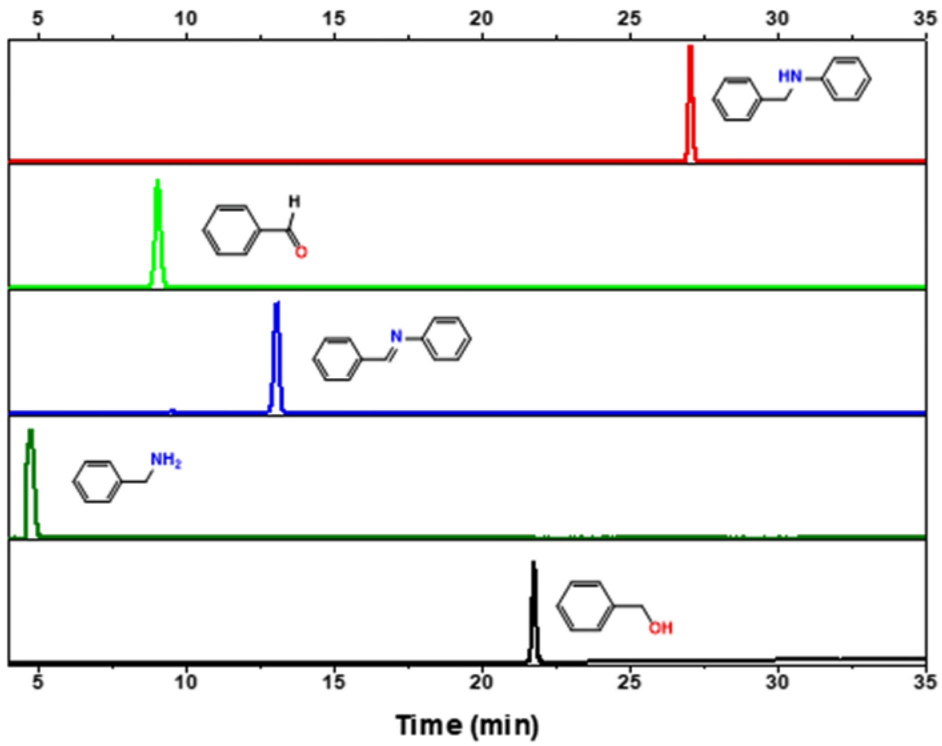


Fig. S12. HPLC chromatograms for N-alkylation of aniline with benzyl alcohol via borrowing hydrogen methodology

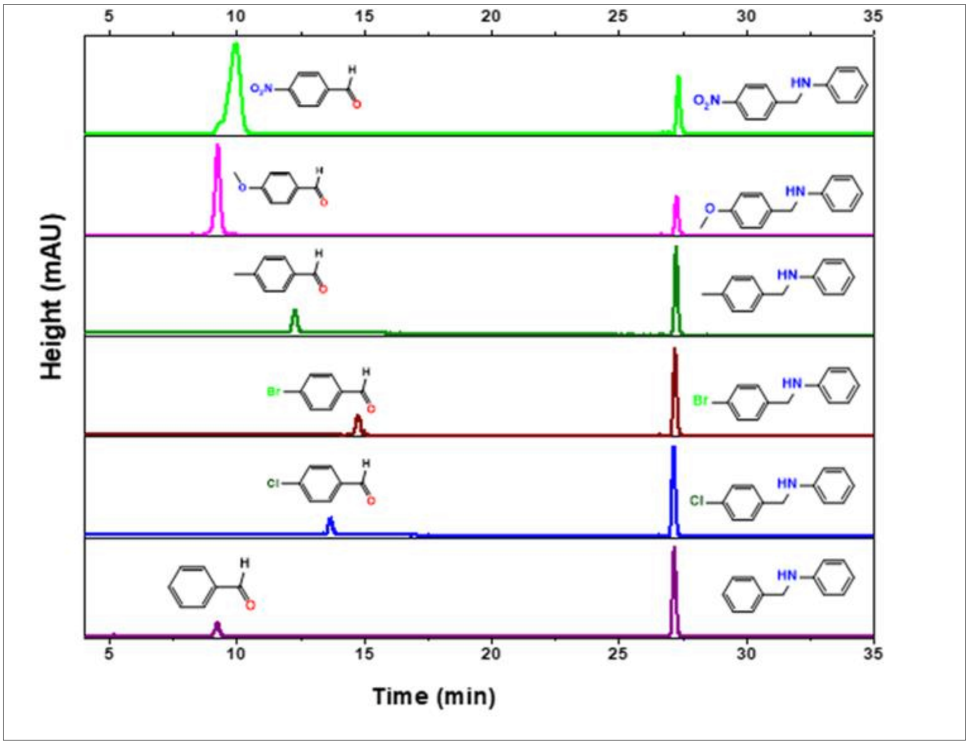


Fig. S13. HPLC Chromatograms of substrate scope for N-alkylation of aniline with substituted benzyl alcohols.

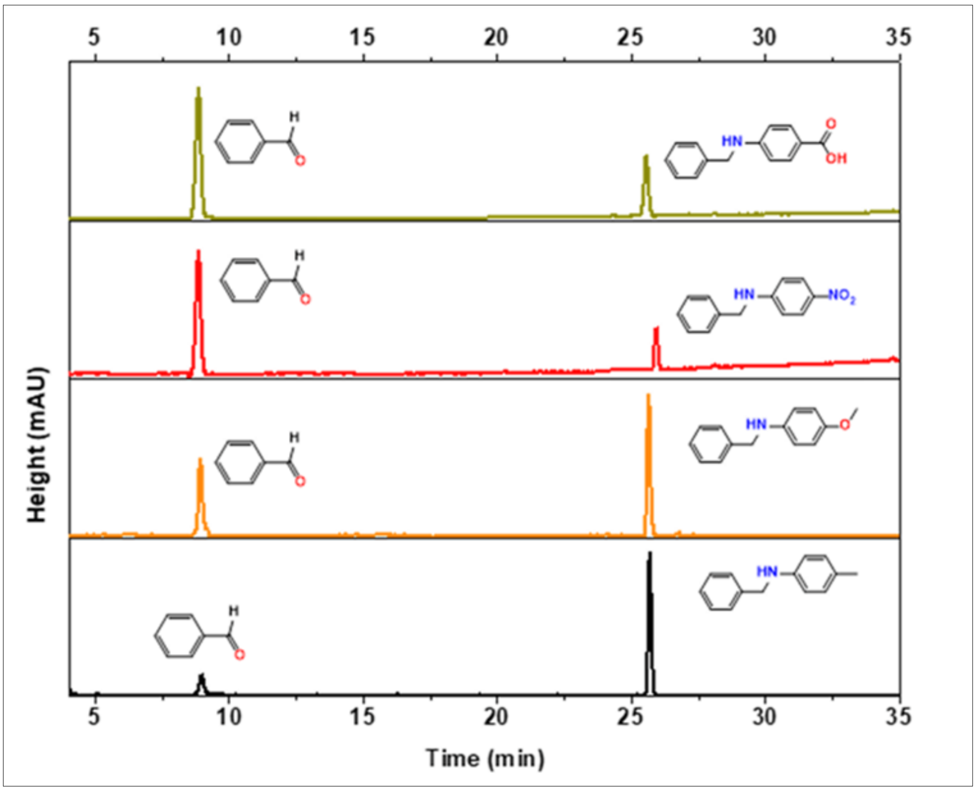


Fig. S14. HPLC Chromatograms of substrate scope for N-alkylation of anilines with benzyl alcohol.

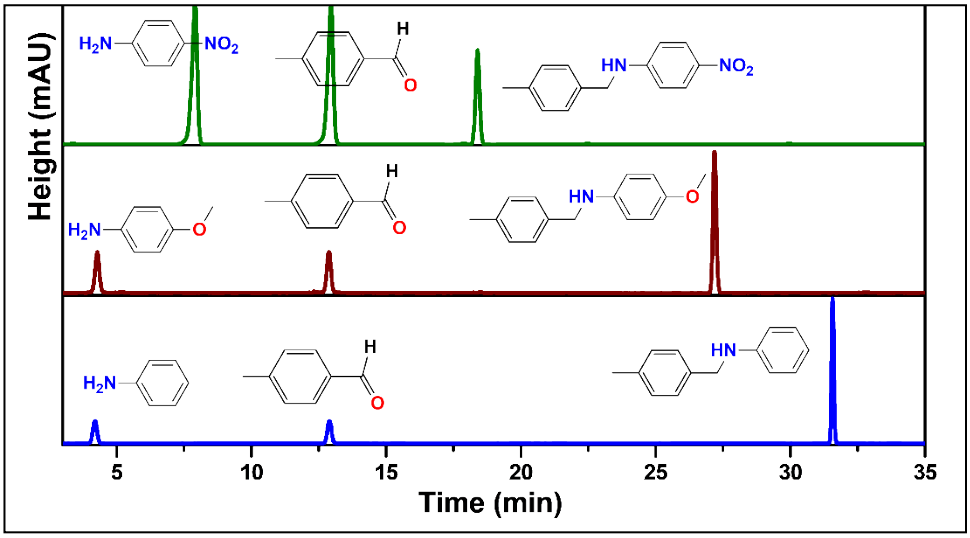


Fig. S15. HPLC Chromatograms of N-alkylation of anilines with *p*-CH_3 benzyl alcohol.

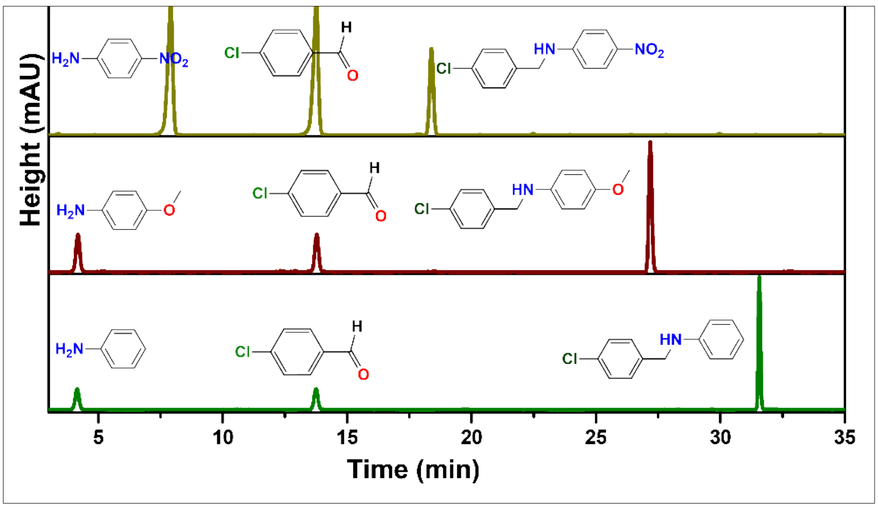


Fig. S16. HPLC Chromatograms of N-alkylation of anilines with *p*-Cl benzyl alcohol.

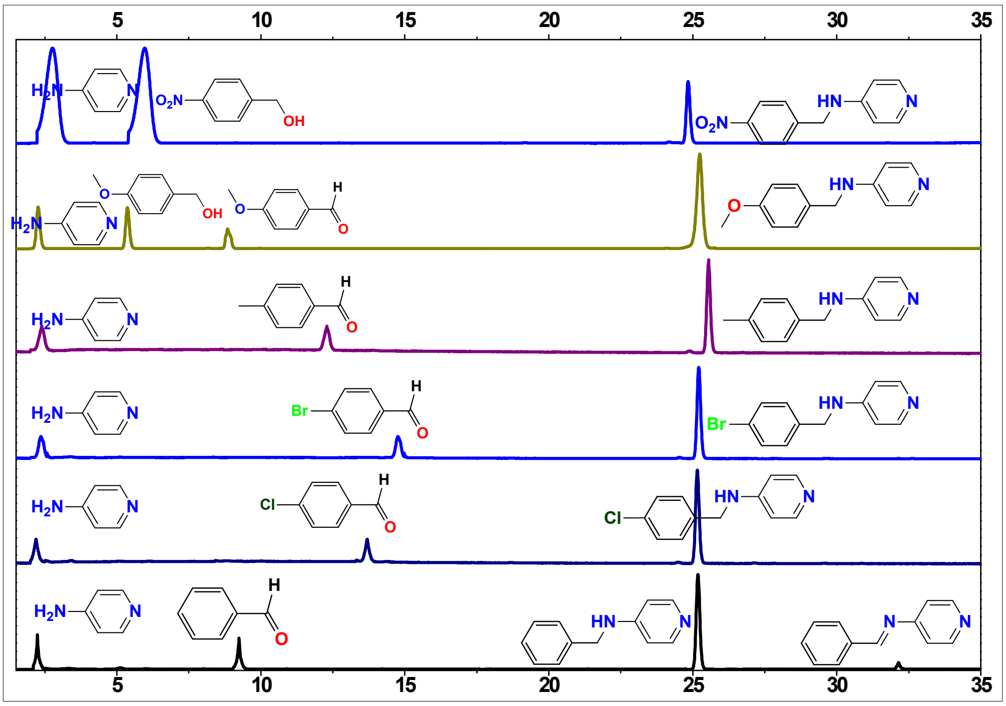


Fig. S17. HPLC Chromatograms of N-alkylation 4-aminopyridine with various benzyl alcohol.

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	14.614	2568693	24.87	612570	25.50	4.19	Benzenamine, N-(phenylmethylene)-
2	14.886	2302317	22.29	693810	28.88	3.32	Benzenemethanamine, N-phenyl-
3	14.950	1247037	12.07	526348	21.91	2.37	Benzenemethanamine, N-phenyl-
4	15.057	4212249	40.78	569576	23.71	7.40	Benzenemethanamine, N-phenyl-
		0330296	100.00	2402304	100.00		

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	14.621	408419	100.00	112914	100.00	3.62	Benzenamine, N-[(4-chlorophenyl)methyl]-
		408419	100.00	112914	100.00		

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	16.209	1022833	100.00	370934	100.00	2.76	Benzenamine, N-[(4-bromophenyl)methyl]-
		1022833	100.00	370934	100.00		

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	12.300	3421917	54.44	718886	56.24	4.76	Benzaldehyde, 4-nitro-
2	17.238	2863906	45.56	559358	43.76	5.12	Benzenamine, N-[(4-nitrophenyl)methyl]-
		6285823	100.00	1278244	100.00		

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	11.584	3823812	62.13	688456	57.24	5.55	Benzaldehyde, 4-methoxy-
2	16.356	2330575	37.87	514292	42.76	4.53	Benzenamine, N-[(4-methoxyphenyl)methyl]-
		6154387	100.00	1202748	100.00		

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	10.484	1314983	51.85	526409	58.39	2.50	Benzenemethanol, 4-methyl-
2	15.548	1221023	48.15	375138	41.61	3.25	Benzenamine, N-[(4-methylphenyl)methyl]-
		2536006	100.00	901547	100.00		

Fig. S18. GC-MS data of N-alkylation of anilines with benzyl alcohol