Electronic supplementary information

Room Temperature *N*-Heterocyclic Carbene Manganese Catalyzed Selective *N*-Alkylation of Anilines with Alcohols

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I. General Information

Unless otherwise stated, all manipulations were carried out under dry argon using conventional Schlenk or glove box techniques. Non-halogenated solvents were dried over sodium benzophenone ketyl and halogenated solvents over CaH_2. 1-phenylimidazole[1] was prepared according to the literature procedure. All other reagents were purchased from commercial sources and used without further purification.

NMR spectra were recorded using a Bruker 400 MHz spectrometer, and chemical shifts are reported relative to TMS for ^{1}H and ^{13}C. ESI-MS spectra were taken on a Shimadzu LCMS-2010 instrument. GC analyses were recorded in a Shimadzu GC-2014C device equipped with a Wondacap 1 column.

II. Preparation of the Ligands and the Mn Complexs

M1 R^1 = Me
M2 R^1 = Ph

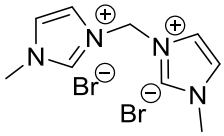
L1 R^1 = Me
L2 R^1 = Ph

Scheme S1. Synthesis of the Imidazolium Salts L1−L2.

General Method for the Preparation of Imidazolium Salts L1, and L2.[2]

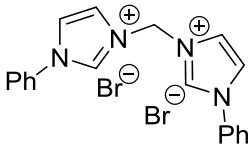
To a solution of the *N*-substituted imidazole (20 mmol) in 5 mL of THF in a sealed tube (15 mL) was added dibromomethane (10 mmol). The mixture is stirred at 130 ℃ for 48 hours, and the solid which precipitates is filtered and washed repeatedly with an excess amount of THF and CH_2Cl_2. The white solid was dried in vacuo, and **L1** or **L2** is obtained.

Synthesis of 3, 3'-methylenebis(1-methyl-1*H*-imidazol-3-ium) bromide (L1)



Following the general method using 1-methylimidazole (1.59 mL, 20 mmol) and dibromomethane (0.7 mL, 10 mmol) in 5 mL of THF, gave **L1** as a white solid.[2a] Yield: 2.84 g (85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (s, 2H), 8.11 (t, J = 1.8 Hz, 2H), 7.83 (t, J = 1.7 Hz, 2H), 6.79 (s, 2H), 3.91 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.01, 124.26, 121.89, 57.79, 36.24; MS (ESI) $[(M-2Br)]^{2+}$ 88.95.

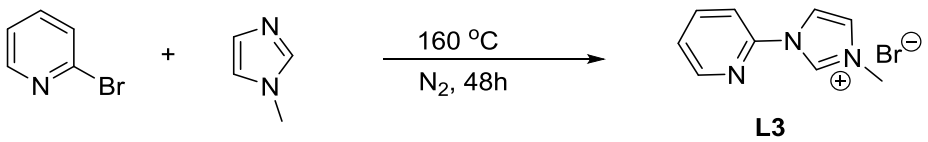
Synthesis of 3, 3'-methylenebis(1-phenyl-1*H*-imidazol-3-ium) bromide (L2)



Following the general method using 1-phenylimidazole (2.88 g, 20 mmol) and dibromomethane (0.7 mL, 10mmol) in 5 mL of THF, gave **L2** as a white solid.[3] Yield: 2.58 g (56%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 2H), 8.48 (s, 4H), 7.85 (d, J = 7.8 Hz, 4H), 7.71 (t, J = 7.6 Hz, 4H), 7.63 (t, J = 7.3 Hz, 2H), 6.98 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.33, 134.45, 130.27,

130.18, 123.03, 121.92, 121.52, 58.31; MS (ESI) $[(M-2Br)]^{2+}$ 150.95.

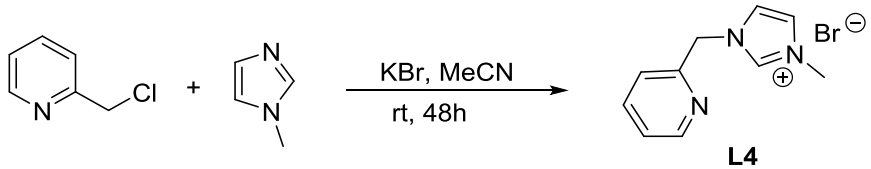
Synthesis of 3-methyl-1-(pyridin-2-yl)-1*H*-imidazol-3-ium bromide (L3)[4]



L3

A mixture of 2-bromopyridine (3.16 g, 20.0 mmol) and 1-methylimidazole (1.64 g, 20.0 mmol) was kept neat at 160 ℃ for 48 h. After cooling, the formed oily mixture was purified by column chromatography over silica gel (CH_2Cl_2/MeOH), yielding 2.39 g (20.0 mmol, 50%) of the desired product as a brownish hygroscopic solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.45 (d, *J* = 3.7 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.28 (s, 1H), 7.99-7.95 (m, 1H), 7.82 (s, 1H), 7.42-7.39 (m, 1H), 4.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.12, 145.97, 140.59, 135.79, 125.19, 124.33, 118.88, 114.80, 37.39; MS (ESI) $[M-Br]^+$ 160.19.

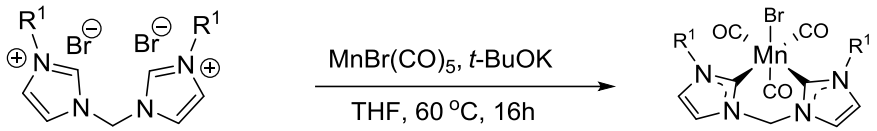
Synthesis of 3-methyl-1-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium bromide (L4)[5]



L4

To an anhydrous MeCN solution (70 mL) of 2.54 g (20.0 mmol) of 2-chloromethylpyridine (obtained by neutralization with Na_2CO_3 of the corresponding hydrochloride), 3.57 g (30.0 mmol) of KBr and 1.9 mL (21.6 mmol) of 1-methylimidazole were added under inert atmosphere (Ar). The red-orange mixture was stirred for 48 h and the solvent reduced to 3–4 mL under vacuum. An equivalent volume of CH_2Cl_2 (70 mL) was then added and the resulting suspension was filtered on a Celite filter. The clear solution was evaporated to dryness and the reddish sticky residue was re-dissolved in CH_2Cl_2 (15 mL) and precipitated with diethylether (40 mL). 4.04 g (yield 80%) of red hygroscopic solid **L4** was obtained. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.55 (d, *J* = 4.8 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.81 (s, 1H), 7.76 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 7.5, 4.9 Hz, 1H), 5.60 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.61, 149.53, 137.47, 137.25, 123.61, 123.04, 122.51, 52.90, 35.84; MS (ESI) $[M-Br]^+$ 173.80.

General Method for the Preparation of Mn Complexes Mn-1−Mn-4.[6]



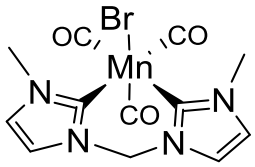
L1 R^1 = Me
L2 R^1 = Ph

Mn-1 R^1 = Me
Mn-2 R^1 = Ph

Scheme S2. Synthesis of the Mn Complexes Mn-1−Mn-2

To a suspended solution of $MnBr(CO)_5$ (0.35 g, 1.3 mmol) in 25 mL of THF in a sealed tube (150 mL) was added *t*-BuOK (0.26 g, 2.3 mmol) and the appropriate imidazolium salts (**L1**-**2**, 1 mmol). The mixture was stirred at 60 ℃ for 16 hours, and cooled to RT. All volatiles were removed under vacuum and the resulting residue was washed with Et_2O (80 mL) and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (100 mL), and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow solid.

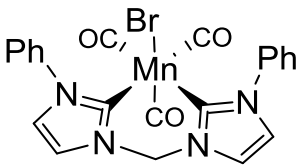
Synthesis of Mn-1



Mn-1

Following the general method using imidazolium salt (**L1**) (0.34 g, 1.0 mmol), gave **Mn-1** as a yellow solid.[6] Yield: 0.23 g (59%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 2H), 7.43 (s, 2H), 6.60 (d, J = 12.4 Hz, 1H), 6.01 (d, J = 13.0 Hz, 1H), 3.98 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 220.17, 190.32, 123.02, 121.19, 61.03, 36.88; IR (KBr): υ (CO) 2005 (s), 1913 (s), 1885 (s) cm^{-1}; MS (ESI) [M-Br]$^+$ 314.85.

Synthesis of Mn-2

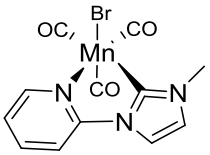


Mn-2

Following the general method using imidazolium salt (**L2**) (0.46 g, 1.0 mmol), gave **Mn-2** as a

yellow solid. Yield: 0.25 g (48%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (s, 2H), 7.58 – 7.47 (m, 12H), 6.80 (d, J = 11.7 Hz, 1H), 6.38 (d, J = 11.6 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 225.70, 218.83, 192.88, 139.51, 129.00, 128.62, 128.03, 124.09, 121.99, 61.26; IR (KBr): υ (CO) 2003 (s), 1918 (s), 1879 (s) cm^{-1}; MS (ESI) [M-Br]$^{+}$ 438.80.

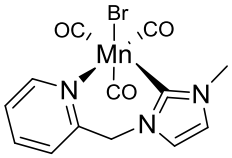
Synthesis of Mn-3[7]



Mn-3

To a suspended solution of the $MnBr(CO)_5$ (0.35 g, 1.3 mmol) in 20 mL of THF in a sealed tube (150 mL) was added *t*-BuOK (0.15 g, 1.3 mmol) and the imidazolium salt (**L3**, 0.26g, 1.1 mmol). The mixture was stirred at 60 ℃ for 16 hours, and cooled to RT. All volatiles were removed under vacuum and the resulting residue was washed with Et_2O (80 mL) and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (100 mL), and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow solid. Yield: 0.25 g (60 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.44-8.14 (m, 2H), 7.72-7.45 (m, 2H), 4.04(s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 225.47, 221.27, 217.16, 201.28, 153.29, 152.47, 126.60, 122.82, 116.81, 112.08, 37.57; IR (KBr): υ (CO) 2018 (s), 1923 (overlaped) cm^{-1}; MS (ESI) [M-Br]$^{+}$ 297.65.

Synthesis of Mn-4



Mn-4

To a suspended solution of the $MnBr(CO)_5$ (0.35 g, 1.3 mmol) in 20 mL of THF in a sealed tube (150 mL) was added *t*-BuOK (0.15 g, 1.3 mmol) and the imidazolium salt (**L4**, 0.28g, 1.1 mmol). The mixture was stirred at 60 ℃ for 16 hours, and cooled to RT. All volatiles were removed under vacuum and the resulting residue was washed with Et_2O (80 mL) and dissolved in dichloromethane (100 mL). The dichloromethane solution was washed with water (100 mL), and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness

under vacuum to yield a yellow solid. Yield: 0.26 g (61 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (d, J = 5.5 Hz, 1H), 8.00 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.52 – 7.49 (m, 1H), 7.47 (s, 1H), 5.78 (d, J = 17.9 Hz, 1H), 5.23 (d, J = 15.7 Hz, 1H), 4.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 224.91, 222.86, 215.38, 188.09, 157.78, 156.05, 139.06, 125.02, 123.98, 123.91, 122.10, 53.45, 37.62; IR (KBr): υ (CO) 2014 (s), 1927 (s), 1891 (s) cm^{-1}; MS (ESI) [M-Br]$^{+}$ 311.75.

III. *N*-alkylation of amines with alcohols

1, GC analysis method for the condition optimization.

GC analysis method:

Injector: Mode: Split; temp.: 330 ^{o}C; Gas: N_2 Pressure: 1.34 bar; Split ratio: 39:1; Split flow: 67.6 mL/min.

Column: Wondacap 1 column Capillary column (30 m x 0.25 mm); Nominal film thickness: 0.250 μm; Temperature program: Initial temperature 100 ℃, heat to 120 ℃ with 5 ℃/min, then heat to 200 ℃ with 50 ℃/min, hold for 5 min.

Initial Flow: 1.62 mL/min; Average velocity: 39.4 cm/sec, Pressure: 1.34 bar. Detector (FID): Temp.: 330 ^{o}C; Hydrogen flow: 40.0 mL/min; Air flow: 400.0 mL/min.

Preparation of GC sample:

Dilute the crude reaction mixture with 5 mL of EtOAc, filtered through the syringe filter and collected in GC vials for analysis.

Retention times: Benzaldehyde: 2.79 min; Aniline: 2.87 min; Benzyl alcohol: 3.33 min; *N*-1-diphenylmethanimine: 8.66 min; *N*, *N*-benzylphenylamine: 9.05 min.

2, *N*-alkylation of amines with alcohols catalyzed by Mn complex

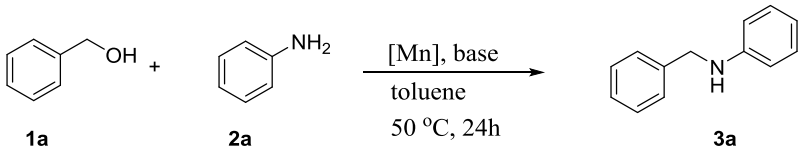
2.1, The condition optimization.

To a 15 mL reaction tube in a glovebox, was added aniline (0.5 mmol), benzylalcohol (0.5 mmol), base, **Mn-1**, and toluene (1 mL). Then the tube was closed with a rubber stopper and removed from the glovebox. The reaction mixture was stirred for 24 h at 50 ℃. After cooled to rt, the crude reaction mixture was diluted with 5 mL of EtOAc, filtered through a syringe filter and collected in GC vials for analysis.

To get the optimal reaction conditions, **Mn-1** was chosen for the further evaluation of different reaction parameters. The base has a great effect on the catalytic efficiency of **Mn-1**. It was found that the *t*-BuOK is an effective base to give the high yield. However, changing *t*-BuOK to other bases resulted in decreased product yields, and the weak bases such as K_2CO_3 and Na_2CO_3 even were ineffective (Table S1, entries 1-7). In addition, nearly 100 mol% *t*-BuOK is needed to obtain sufficient yields and avoid the presence of the imine as a byproduct. An attempt to lower the catalyst loading to 1 mol% resulted in a slight decrease of yield (Table S1, entry 8). However, when the catalyst loading was 0.5 mol%, the yield was only 44% (Table S1,

entry 9). Deficiently, the low yield was obtained when the reaction was performed under the air atmosphere (Table S1, entry 10). The control experiments show that the *N*-alkylation reaction did not proceed well in the absence of the catalyst or using a simple $MnBr(CO)_5$ as the catalyst (Table S1, entries 11 and 12). Importantly, the use of the simple combination of the $MnBr(CO)_5$ and **L1** and non-dried toluene also led to good conversions into the corresponding coupled product (Table S1, entries 13 and 14). To our delight, this transformation also occurred at room temperature, 85% and 98% yields were obtained in 24 h and 48 h, respectively (Table S1, entries 15 and 16). Finally, the optimal reaction conditions were performed in non-dried toluene at RT for 48h, with *t*-BuOK (1.0 equiv.) as the base and a loading of 1.5 mol% of the **Mn-1** (Table S1, entry 16).

Table S1. Optimization of the Reaction Parameters[a]

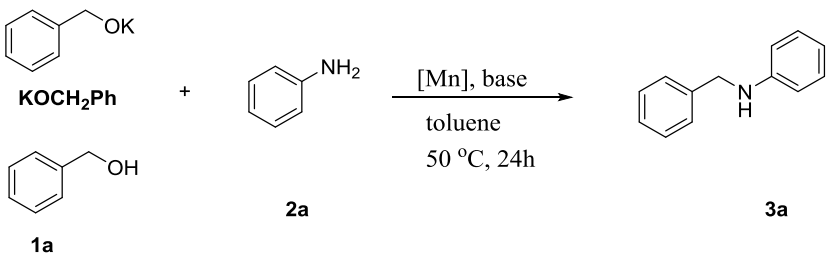


1a **2a** **3a**

entry	**Mn-1**. (mol%)	Base (mol%)	Yield. (%)[b]
1	1.5	*t*-BuOK (100)	98 (92)
2	1.5	*t*-BuOK (75)	77
3	1.5	*t*-BuOK (50)	61
4	1.5	KOH (100)	7
5	1.5	NaOH (100)	10
6	1.5	K_2CO_3 (100)	trace
7	1.5	Na_2CO_3 (100)	trace
8	1	*t*-BuOK (100)	88
9	0.5	*t*-BuOK (100)	44
10[c]	1.5	*t*-BuOK (100)	56
11	-	*t*-BuOK (100)	trace
12[d]	-	*t*-BuOK (100)	26
13[e]	-	*t*-BuOK (100)	90
14[f]	1.5	*t*-BuOK (100)	98 (91)
15[f,g]	1.5	*t*-BuOK (100)	85
16[f,h]	1.5	*t*-BuOK (100)	98 (91)

[a]*N*-alkylation reaction conditions: 0.5 mmol **1a**, 0.5 mmol **2a**, 1.5 mol% Mn, 1.0 mL toluene, 50 ℃, 24 h. [b]GC yield. (isolated yield in parentheses). [c]without N_2. [d]$MnBr(CO)_5$. [e]$MnBr(CO)_5$ and **L1**. [f]non-dried toluene. [g]RT, 0.25 mL toluene, 24 h. [h]RT, 0.25 mL toluene, 48 h.

Table S2. Screening of the Reaction Parameters with $KOCH_2Ph$[a]



entry	**Mn-1** (mol%)	**1a** (mmol)	$KOCH_2Ph$ (mmol)	**2a** (mmol)	Base (mol%)	Yield. (%)[a]
1[b]	1.5	/	0.5	0.5	*t*-BuOK (100)	12
2[b]	1.5	/	0.5	0.5	/	50
3[c]	1.5	/	0.5	0.5	*t*-BuOK (100)	8
4[b]	1.5	0.5	0.5	0.5	/	44
5[b]	1.5	0.25	0.25	0.5	*t*-BuOK (100)	75
6[b]	1.5	0.25	0.25	0.5	*t*-BuOK (50)	89
7[b]	1.5	0.25	0.25	0.5	/	trace
8[b]	1.5	0.5	0	0.5	*t*-BuOK (100)	98

[a]50 ℃, 24 h, GC yields. [b]1.0 mL toluene as solvent. [c]1.0 mL THF as the solvent.

And we have screened the reaction parameters of the *N*-alkylation of aniline with $KOCH_2Ph$ (Table S2). When the $KOCH_2Ph$ as the substrate, the yield is only 12% (Table S2, entry 1). However, without the *t*-BuOK, the yield could up to 50% (Table S2, entry 2). The reaction also did not proceed well in the THF (Table S2, entry 3) or **1a** as the substrate and $KOCH_2Ph$ as the base (Table S2, entry 4). To our surprise, when **1a** and $KOCH_2Ph$ were used as substrates, the yields is up to 75% (100% *t*-BuOK, Table S2, entry 5) and 89% (50% *t*-BuOK, Table S2, entry 6). However, without the *t*-BuOK, we couldn't observe the product (Table S2, entry 7). Those results indicated that the key roles of the *t*-BuOK and the alcohols in the *N*-alkylation of amines with alcohols.

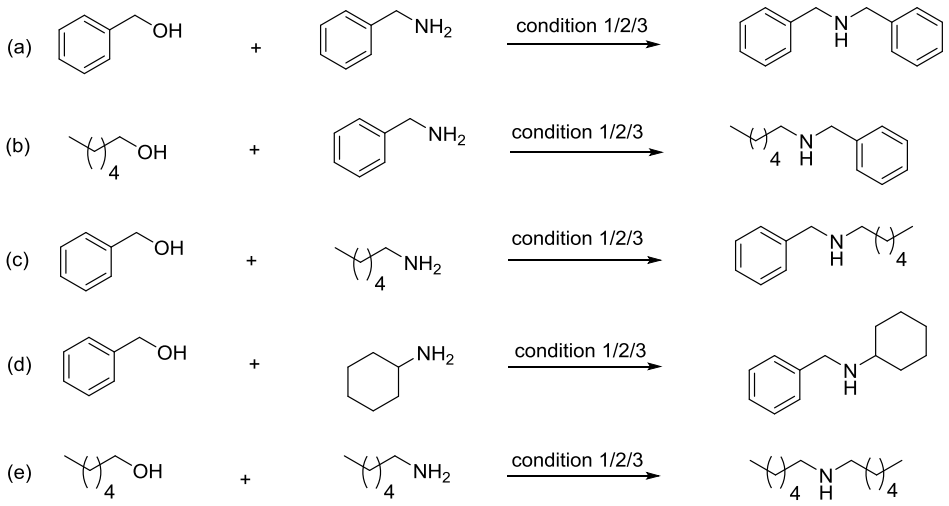
2.2, General method for the Substrate Screening

To a 15 mL reaction tube in a glovebox, was added amine (0.5 mmol), alcohol (0.5 mmol), **Mn-1** (0.0075 mmol), *t*-BuOK (0.5 mmol.) and toluene (0.25 mL). Then the tube was closed

with a rubber stopper and removed from the glovebox. The reaction mixture was stirred for 48 h at RT. After that, the crude reaction mixture was extracted with ethyl acetate. The solvent was evaporated to dryness and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/ petroleum ether). The yields were calculated based on isolated products.

2.21, The N-alkylation of aliphatic amines with alcohols by Mn-1

However, attempts at the alkylation of aliphatic amines (benzyl amine, *n*-hexylamine, and cyclohexylamine) with aliphatic alcohols (*n*-hexyl alcohol) or benzyl alcohol were unsuccessful, yielding only traces of products even at at relatively forcing reaction condition (by increasing the catalyst loading to 5.0 mol% and performing the reactions at 130 ℃).



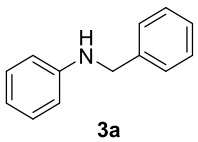
Condition 1: 0.5 mmol alcohol, 0.5 mmol amine, 0.25 mL toluene, **Mn-1** 1.5 mol%, rt, 48 h, Ar

Condition 2: 0.5 mmol alcohol, 0.5 mmol amine, 0.25 mL toluene, **Mn-1** 3 mol%, 100 ^{o}C, 24 h, Ar

Condition 3: 0.5 mmol alcohol, 0.5 mmol amine, 0.25 mL toluene, **Mn-1** 5 mol%,130 ^{o}C, 24 h, Ar

Scheme S3. The N-alkylation of aliphatic amines with alcohols by Mn-1

N-benzylaniline (**3a**).[8]

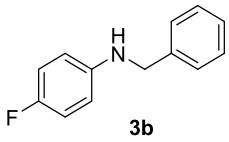


3a

The compound was prepared as described in the general method (colorless oil, 92% isolated yield, 84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.34 – 7.27 (m, 1H), 7.20 (t, J = 7.5 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.8 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101

MHz, $CDCl_3$) δ 148.27, 139.56, 129.37, 128.73, 127.61, 127.32, 117.67, 112.96, 48.42; MS (ESI) $[M+H]^+$ 183.65.

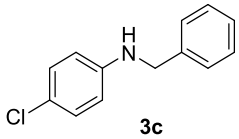
N-benzyl-4-fluoroaniline (**3b**).[9]



3b

The compound was prepared as described in the general method (colorless oil, 83% isolated yield, 83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 4H), 7.34 – 7.28 (m, 1H), 6.90 (t, *J* = 8.8 Hz, 2H), 6.62 – 6.54 (m, 2H), 4.31 (s, 2H), 3.94 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.00 (d, J_{C-F} = 236.3 Hz), 144.61, 139.36, 128.79, 127.60, 127.43, 115.78 (d, J_{C-F}= 22.2 Hz), 113.76 (d, J_{C-F}= 7.4 Hz), 49.05; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.91; MS (ESI) $[M+H]^+$ 201.60.

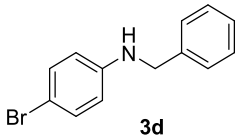
N-benzyl-4-chloroaniline (**3c**).[9]



3c

The compound was prepared as described in the general method (colorless oil, 87% isolated yield, 94 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.5 Hz, 4H), 7.30 (m, 1H), 7.15 – 7.08 (m, 2H), 6.59 – 6.53 (m, 2H), 4.31 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.77, 139.05, 129.18, 128.82, 127.53, 127.49, 122.21, 114.03 , 48.46; MS (ESI) $[M+H]^+$ 217.60.

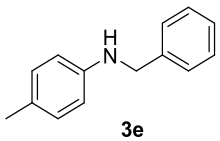
N-benzyl-4-bromoaniline (**3d**).[9]



3d

The compound was prepared as described in the general method (colorless oil, 90% isolated yield, 117 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 4H), 7.30 (m, 1H), 7.27 – 7.22 (m, 2H), 6.54 – 6.48 (m, 2H), 4.31 (d, *J* = 5.3 Hz, 2H), 4.09 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 138.9, 132.0, 128.8, 127.5, 127.4, 114.5, 109.2, 48.3; MS (ESI) $[M+H]^+$ 263.40.

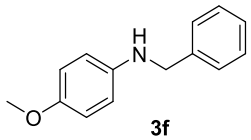
N-benzyl-4-methylaniline (**3e**).[10]



3e

The compound was prepared as described in the general method (colorless oil, 87% isolated yield, 86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 4H), 7.32 – 7.27 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.64 – 6.52 (m, 2H), 4.34 (s, 2H), 3.92 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.05, 139.79, 129.86, 128.71, 127.61, 127.26, 126.85, 113.11, 48.76, 20.52; MS (ESI) $[M+H]^+$ 197.65.

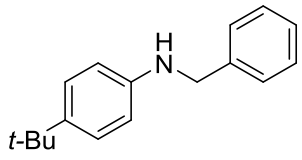
N-benzyl-4-methoxyaniline (**3f**).[10]



3f

The compound was prepared as described in the general method (colorless oil, 86% isolated yield, 91 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.32 (t, *J* = 6.8 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.67 – 6.61 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.25, 142.55, 139.79, 128.67, 127.62, 127.24, 114.99, 114.18, 55.8, 49.30; MS (ESI) $[M+H]^+$ 213.60.

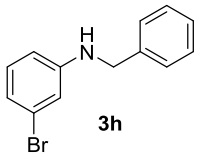
N-benzyl-4-(tert-butyl)aniline (**3g**).[11]



3g

The compound was prepared as described in the general method (colorless oil, 72% isolated yield, 86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 4.29 (s, 2H), 3.91 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.00, 140.47, 139.84, 128.72, 127.69, 127.30, 126.15, 112.70, 48.78, 34.00, 31.69; MS (ESI) $[M+H]^+$ 239.85.

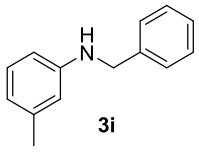
N-benzyl-3-bromoaniline (**3h**).[12]



3h

The compound was prepared as described in the general method (colorless oil, 75% isolated yield, 98 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.78 (t, *J* = 2.0 Hz, 1H), 6.53 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.31 (s, 2H), 4.11 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.50, 138.83, 130.64, 128.87, 127.61, 127.58, 123.41, 120.46, 115.54, 111.65, 48.23; MS (ESI) $[M+H]^+$ 263.40.

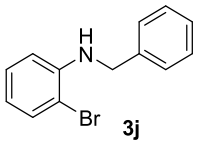
N-benzyl-3-methylaniline (**3i**).[13]



3i

The compound was prepared as described in the general method (colorless oil, 75% isolated yield, 79 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.48 (dd, *J* = 11.7, 3.7 Hz, 2H), 4.34 (s, 2H), 3.98 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.36, 139.69, 139.17, 129.28, 128.75, 127.66, 127.32, 118.67, 113.77, 110.10, 48.50, 21.76; MS (ESI) $[M+H]^+$ 198.65.

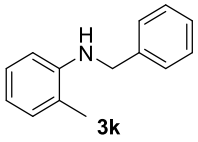
N-benzyl-2-bromoaniline (**3j**).[14]



3j

The compound was prepared as described in the general method (colorless oil, 67% isolated yield, 87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.36 – 7.28 (m, 1H), 7.20 – 7.12 (m, 1H), 6.65 – 6.59 (m, 2H), 4.80 (s, 1H), 4.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.91, 138.80, 132.50, 128.84, 128.60, 127.45, 127.34, 118.09, 111.74, 109.80, 48.11; MS (ESI) $[M+H]^+$ 263.40.

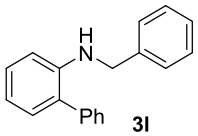
N-benzyl-2-methylaniline (**3k**).[12]



3k

The compound was prepared as described in the general method (colorless oil, 65% isolated yield, 64 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.31- 7.29 (m, 1H), 7.14 -7.09 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.40 (s, 2H), 3.82 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.19, 139.63, 130.20, 128.79, 127.67, 127.38, 127.29, 122.06, 117.31, 110.11, 48.45, 17.68; MS (ESI) $[M+H]^+$ 198.56.

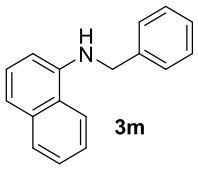
N-benzyl-[1,1'-biphenyl]-2-amine (**3l**).[10]



3l

The compound was prepared as described in the general method (colorless oil, 64% isolated yield, 83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.42 – 7.34 (m, 5H), 7.32 - 7.27 (m, 1H), 7.27 – 7.20 (m, 1H), 7.17 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 4.44 (s, 1H), 4.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.01, 139.60, 130.35, 129.51, 129.05, 128.83, 128.70, 127.80, 127.36, 127.15, 117.30, 110.88, 48.25; MS (ESI) $[M+H]^+$ 259.95.

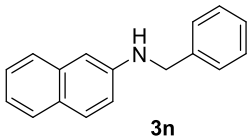
N-benzylnaphthalen-1-amine (**3m**).[15]



3m

The compound was prepared as described in the general method (yellow oil, 88% isolated yield, 103 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 7.0 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.43 – 7.32 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 4.71 (s, 1H), 4.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 139.22, 134.42, 128.86, 128.83, 127.87, 127.53, 126.74, 125.88, 124.88, 123.50, 120.02, 117.77, 104.88, 48.75; MS (ESI) $[M+H]^+$ 233.60.

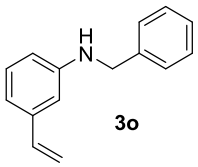
N-benzylnaphthalen-2-amine (**3n**).[16]



3n

The compound was prepared as described in the general method (yellow oil, 87% isolated yield, 101 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.57 (m, 3H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 3H), 7.33 (m, 1H), 7.22 (m, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 4.45 (s, 2H), 4.20 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 139.29, 135.30, 129.09, 128.82, 127.76, 127.74, 127.46, 126.45 , 126.12, 122.18, 117.98, 104.77, 48.49; MS (ESI) $[M+H]^+$ 233.60.

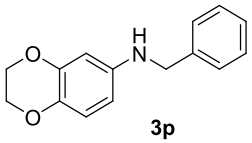
N-benzyl-3-vinylaniline (**3o**).[10]



3o

The compound was prepared as described in the general method (yellow oil, 85% isolated yield, 89 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.62 (m, 2H), 6.57 (dd, *J* = 8.0, 2.2 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 4.36 (s, 2H), 4.05 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.45, 139.49, 138.68, 137.39, 129.51, 128.76, 127.64, 127.38, 115.98, 113.61, 112.64, 110.71, 48.47; MS (ESI) $[M+H]^+$ 210.64.

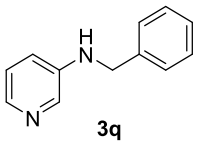
N-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (**3p**).[10]



3p

The compound was prepared as described in the general method (yellow oil, 45% isolated yield, 54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.22 – 6.16 (m, 2H), 4.26 (s, 2H), 4.24 – 4.20 (m, 2H), 4.20 – 4.15 (m, 2H), 3.77 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.17, 143.39, 139.70, 135.87, 128.73, 127.67, 127.31, 117.77, 106.89, 101.73, 64.90, 64.33, 49.20; MS (ESI) $[M+H]^+$ 241.87.

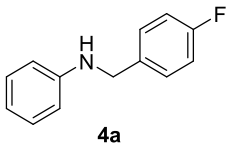
N-benzylpyridin-3-amine (**3q**).[10]



3q

The compound was prepared as described in the general method (yellow oil, 65% isolated yield, 60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.95 (d, *J* = 4.2 Hz, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.26 (m, 1H), 7.06 – 7.03 (m, 1H), 6.87 – 6.84 (m, 1H), 4.33 (d, *J* = 5.1 Hz, 2H), 4.22 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.15, 139.02, 138.64, 136.30, 128.86, 127.58, 127.50, 123.80, 118.64, 47.96; MS (ESI) $[M+H]^+$ 184.88

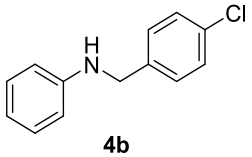
N-(4-fluorobenzyl)aniline (**4a**).[9]



4a

The compound was prepared as described in the general method (yellow oil, 85% isolated yield, 85mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.32 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.15 (d, J_{C-F} = 246.4Hz), 148.06, 135.23 (d, J_{C-F} = 2.9 Hz), 129.40, 129.10 (d, J_{C-F} = 8.0 Hz), 117.84, 115.54 (d, J_{C-F} = 21.2Hz), 112.99, 47.71; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.65; MS (ESI) $[M+H]^+$ 201.60.

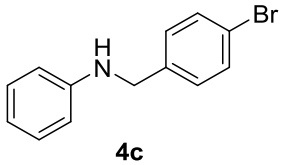
N-(4-chlorobenzyl)aniline (**4b**).[9]



4b

The compound was prepared as described in the general method (yellow oil, 91% isolated yield, 99mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 7.18 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.74 (m, 1H), 6.64 – 6.60 (m, 2H), 4.32 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 138.13, 132.99, 129.42, 128.87, 128.82, 117.93, 113.01, 47.74 ; MS (ESI) $[M+H]^+$ 217.50.

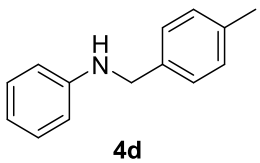
N-(4-bromobenzyl)aniline (**4c**).[9]



4c

The compound was prepared as described in the general method (yellow oil, 92% isolated yield, 120mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.18 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.30 (s, 2H), 4.08 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.92, 138.67, 131.82, 129.42, 129.16, 121.04, 117.94, 113.01, 47.78; MS (ESI) $[M+H]^+$ 263.30.

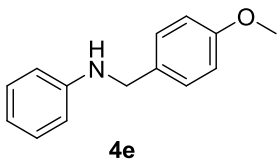
N-(4-methylbenzyl)aniline (**4d**).[9]



4d

The compound was prepared as described in the general method (yellow oil, 86 % isolated yield, 85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 11.3, 8.0 Hz, 4H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 2H), 3.98 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.35, 137.00, 136.48, 129.43, 129.37, 127.65, 117.61, 112.96, 48.21, 21.24; MS (ESI) $[M+H]^+$ 197.65.

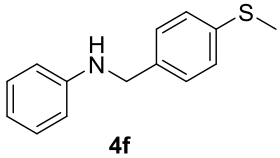
N-(4-methoxybenzyl)aniline (**4e**).[9]



4e

The compound was prepared as described in the general method (yellow oil, 82 % isolated yield, 87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.95 – 6.86 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.66 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.28 (s, 2H), 3.97 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.96, 148.32, 131.53, 129.36, 128.91, 117.60, 114.13, 112.95, 55.41, 47.90; MS (ESI) $[M+H]^+$ 213.60.

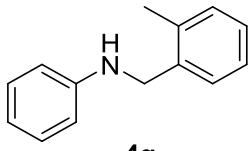
N-(4-(methylthio)benzyl)aniline (**4f**).[9]



4f

The compound was prepared as described in the general method (yellow oil, 89 % isolated yield, 102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 4H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 4.27 (s, 2H), 3.99 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.15, 137.27, 136.54, 129.37, 128.13, 127.13, 117.74, 112.98, 47.97, 16.16; MS (ESI) $[M+H]^+$ 230.90.

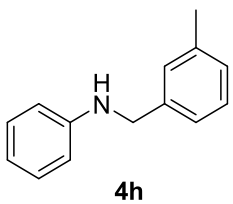
N-(2-methylbenzyl)aniline (**4g**).[17]



4g

The compound was prepared as described in the general method (yellow oil, 63 % isolated yield, 62 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 6.8 Hz, 1H), 7.21 -7.14 (m, 5H), 6.71 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 2H), 4.25 (s, 2H), 3.83 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41, 137.11, 136.45, 130.52, 129.39, 128.36, 127.53, 126.27, 117.57, 112.80, 46.49, 19.05; MS (ESI) $[M+H]^+$ 198.62.

N-(3-methylbenzyl)aniline (**4h**).[18]

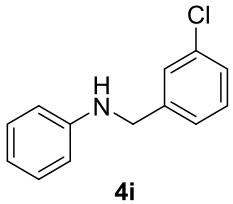


4h

The compound was prepared as described in the general method (yellow oil, 76 % isolated yield, 75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 5H), 7.08 (d, J = 7.4 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 2H), 4.26 (s, 2H), 3.95 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.36, 139.49, 138.41, 129.37, 128.65, 128.41, 128.10, 124.71, 117.62, 112.95, 48.47,

21.55; MS (ESI) $[M+H]^+$ 198.68.

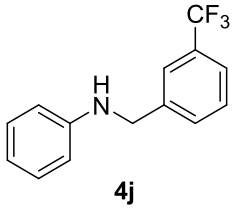
N-(3-chlorobenzyl)aniline (**4i**).[19]



4i

The compound was prepared as described in the general method (yellow oil, 74 % isolated yield, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.28 - 7.25 (m, 3H), 7.21 – 7.17 (m, 2H), 6.75 (t, J = 6.9 Hz, 1H), 6.64 – 6.61 (m, 2H), 4.33 (s, 2H), 4.09 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.90, 141.87, 134.65, 130.02, 129.44, 127.54, 127.49, 125.53, 117.98, 113.02, 47.90; MS (ESI) $[M+H]^+$ 218.56.

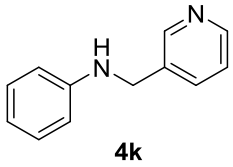
N-(3-(trifluoromethyl)benzyl)aniline (**4j**).[15]



4j

The compound was prepared as described in the general method (yellow oil, 84 % isolated yield, 105 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.59 – 7.55 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 2H), 4.41 (s, 2H), 4.12 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.87, 140.78, 130.76, 129.47, 129.21, 124.25, 124.22, 124.18, 124.15, 118.13, 113.07, 48.05; MS (ESI) $[M+Na]^+$ 274.03.

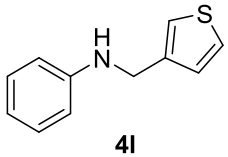
N-(pyridin-3-ylmethyl)aniline (**4k**).[20]



4k

The compound was prepared as described in the general method (yellow oil, 72 % isolated yield, 66 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.52 (d, *J* = 4.1 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 – 6.62 (m, 2H), 4.36 (s, 2H), 4.13 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.26, 148.80, 147.73, 135.19, 135.03, 129.44, 123.63, 118.13, 113.05, 45.89; MS (ESI) $[M+H]^+$ 184.81.

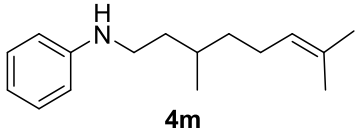
N-(thiophen-3-ylmethyl)aniline (**4l**).[20]



4l

The compound was prepared as described in the general method (yellow oil, 78 % isolated yield, 74 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 1H), 7.22 – 7.18 (m, 3H), 7.10 – 7.09 (m, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 2H), 3.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.17, 140.60, 129.40, 127.29, 126.27, 121.85, 117.84, 113.06, 43.91; MS (ESI) $[M+H]^+$ 189.75.

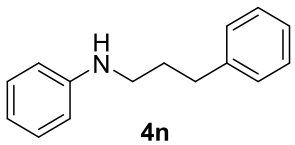
N-(3,7-dimethyloct-6-en-1-yl)aniline (**4m**).[8]



4m

The compound was prepared as described in the general method (yellow oil, 92 % isolated yield, 106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.4 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 5.12 (t, *J* = 6.9 Hz, 1H), 3.54 (s, 1H), 3.19 – 3.07 (m, 2H), 2.09 – 1.93 (m, 2H), 1.70 (s, 3H), 1.67 – 1.65 (m, 5H), 1.49 – 1.35 (m, 2H), 1.27 – 1.18 (m, 1H), 0.96 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.69, 131.46, 129.35, 124.80, 117.24, 112.84, 42.09, 37.24, 36.86, 30.58, 25.86, 25.62, 19.75, 17.82; MS (ESI) $[M+H]^+$ 231.99.

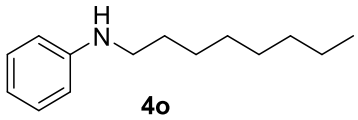
N-(3-phenylpropyl)aniline (**4n**).[21]



4n

The compound was prepared as described in the general method (yellow oil, 85 % isolated yield, 90 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.26 – 7.17 (m, 5H), 6.76 – 6.70 (m, 1H), 6.62 (d, *J* = 1.0 Hz, 1H), 6.60 (d, *J* = 0.9 Hz, 1H), 3.64 (d, *J* = 11.8 Hz, 1H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.82 – 2.71 (t, *J* = 7.0 Hz, 2H), 1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.47, 141.79, 129.35, 128.55, 128.52, 126.07, 117.34, 112.87, 43.54, 33.53, 31.19; MS (ESI) $[M+H]^+$ 211.60.

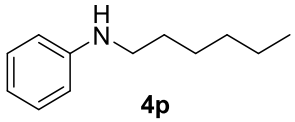
N-octylaniline (**4o**).[10]



4o

The compound was prepared as described in the general method (yellow oil, 85 % isolated yield, 87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.65 – 6.59 (m, 2H), 3.60 (s, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.67 -1.60 (m, 2H), 1.44 – 1.29 (m, 10H), 0.93 – 0.90 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 129.33, 117.19, 112.81, 44.14, 31.97, 29.73, 29.56, 29.41, 27.33, 22.80, 14.24; MS (ESI) $[M+H]^+$ 206.70.

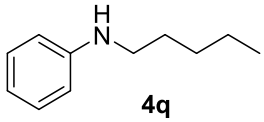
N-hexylaniline (**4p**).[10]



4p

The compound was prepared as described in the general method (yellow oil, 82 % isolated yield, 73 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.65 – 6.58 (m, 2H), 3.60 (s, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.46 – 1.31 (m, 6H), 0.94 – 0.91 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 129.33, 117.18, 112.81, 44.14, 31.79, 29.69, 27.00, 22.76, 14.17; MS (ESI) $[M+H]^+$ 178.51.

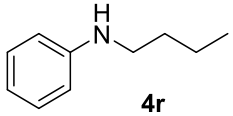
N-pentylaniline (**4q**).[10]



4q

The compound was prepared as described in the general method (yellow oil, 78 % isolated yield, 64 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.65 – 6.59 (m, 2H), 3.60 (s, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.68 -1.60 (m, 2H), 1.42 – 1.38 (m, 4H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 129.33, 117.19, 112.81, 44.11, 29.48, 29.42, 22.65, 14.18; MS (ESI) $[M+H]^+$ 164.54.

N-butylaniline (**4r**).[10]



4r

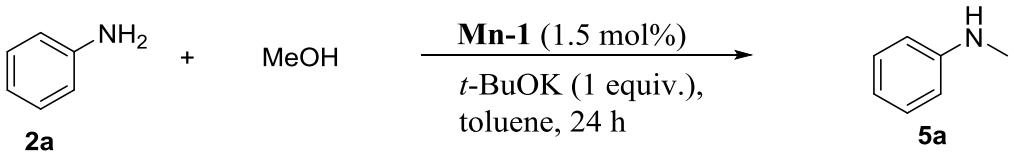
The compound was prepared as described in the general method (yellow oil, 75 % isolated yield, 56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.66 – 6.59 (m, 2H), 3.60 (s, 1H), 3.13 (t, J = 7.1 Hz, 2H), 1.69 – 1.53 (m, 2H), 1.50 – 1.43 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.67, 129.33, 117.19, 112.81, 43.80, 31.81, 20.43, 14.04; MS (ESI) $[M+H]^+$ 150.47.

2.3 *N*-methylation of Amines with Methanol Catalyzed by Mn-1

2.3.1 The reaction conditions optimization

Firstly, we conducted the methylation at 50 ^{o}C, however, the yield was only 17.5% (entry 1) and increasing the amount of the MeOH did not improve the conversion (entries 2-4). To our delight, at 100 ^{o}C, in the presence of excess MeOH (25 equiv.), the yield was up to 84.5% (entry 13). Increasing the temperature to 120 ^{o}C (entry 15) and the catalyst loading to 3 mol% (entry 16), has little effect on the conversion. Finally, the optimal conditions selected to probe the substrate scope of the reaction were **Mn-1** (1.5 mol%), *t*-BuOK (100 mol%), 100 ^{o}C, 24h (entry 13).

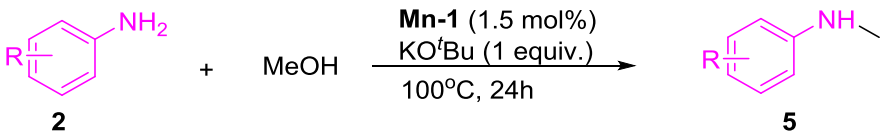
Table S3 Optimization of Reaction Conditions



Entry	MeOH (μL)	Temperature (°C)	Yield(%)
1	20 (1 equiv.)	50	17.5
2	40 (2 equiv.)	50	20.2
3	80 (4 equiv.)	50	19.3
4	160 (8 equiv.)	50	22.2
5	20 (1 equiv.)	80	20.4
6	40 (2 equiv.)	80	35.1
7	80 (4 equiv.)	80	43.3
8	160 (8 equiv.)	80	62.2
9	320 (16 equiv.)	80	63.0
10	500 (25 equiv.)	80	76.1
11	1000 (50 equiv.)	80	67.6
12[c]	1000 (50 equiv.)	80	51.8
13	500 (25 equiv.)	100	84.5
14	1000 (50 equiv.)	100	45.8
15	500 (25 equiv.)	120	77.3
16[d]	500 (25 equiv.)	100	85.9

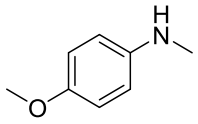
[a] General reaction conditions: 0.5 mmol aniline, x μL MeOH, 0.5 mmol *t*-BuOK, 1 mL toluene, 24 h, N_2. [b]Values given are yields with respect to unreacted amine, as determined by analysis of the GC. [c] without toluene, [d] Mn (3 mol%).

2.3.2 General Method for the *N*-methylation of Anilines with Methanol.



To a 15 mL sealing tube in a glovebox, was added amine (0.5 mmol), MeOH (500 μL), **Mn-1** (0.0075 mmol), *t*-BuOK (0.5 mmol.) and toluene (1 mL). Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred for 24 h at 100 °C. After cooled to RT, the mixture was diluted with ethyl acetate and filtered through a short pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the crude residue was purified by column chromatography (SiO2, petroleum ether/ethyl acetate as eluent).

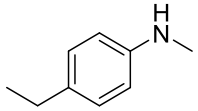
4-methoxy-N-methylaniline (**5b**).[10]



5b

The compound was prepared as described in the general method (yellow oil, 91 % isolated yield, 62 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.75 – 6.69 (m, 2H), 6.51 – 6.46 (m, 2H), 5.14 (s, 1H), 3.63 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.58, 144.32, 114.59, 112.57, 55.32, 30.53; MS (ESI) $[M+H]^+$ 138.34.

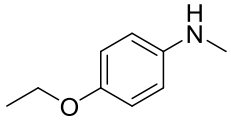
4-ethyl-N-methylaniline (**5c**).[10]



5c

The compound was prepared as described in the general method (yellow oil, 74% isolated yield, 50 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 2.84 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.47, 133.29, 128.64, 112.73, 31.18, 28.06, 16.14; MS (ESI) $[M+H]^+$ 136.36.

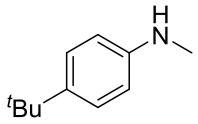
4-ethoxy-N-methylaniline (**5d**).[10]



5d

The compound was prepared as described in the general method (yellow oil, 70% isolated yield, 53 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.77 (m, 2H), 6.61 – 6.56 (m, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 2.81 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.44, 143.79, 115.92, 113.74, 64.30, 31.73, 15.15; MS (ESI) $[M+H]^+$ 152.36.

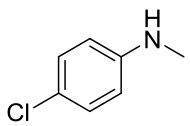
4-(tert-butyl)-N-methylaniline (**5e**).[10]



5e

The compound was prepared as described in the general method (yellow oil, 80% isolated yield, 65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.60 – 6.55 (m, 2H), 2.81 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.14, 140.18, 126.08, 112.34, 33.96, 31.69, 31.10; MS (ESI) $[M+H]^+$ 164.40.

4-chloro-N-methylaniline (**5f**).[22]

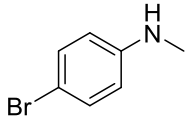


5f

The compound was prepared as described in the general method (yellow oil, 86% isolated yield,

61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 2H), 6.55 – 6.50 (m, 2H), 3.71 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.99, 129.13, 121.93, 113.55, 30.95; MS (ESI) $[M+H]^+$ 142.22.

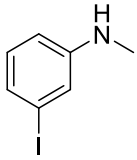
4-bromo-N-methylaniline (**5g**).[10]



5g

The compound was prepared as described in the general method (yellow oil, 91% isolated yield, 84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.49 – 6.44 (m, 2H), 3.71 (s, 1H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.37, 131.95, 114.03, 108.85, 30.81; MS (ESI) $[M+H]^+$ 186.25.

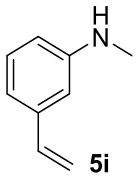
3-iodo-N-methylaniline (**5h**).[10]



5h

The compound was prepared as described in the general method (yellow oil, 90% isolated yield, 105 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 7.00 (m, 1H), 6.96 – 6.93 (m, 1H), 6.89 (t, *J* = 7.9 Hz, 1H), 6.57 – 6.54 (m, 1H), 3.72 (s, 1H), 2.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.53, 130.68, 126.05, 120.84, 111.90, 95.40, 30.56; MS (ESI) $[M+H]^+$ 234.11.

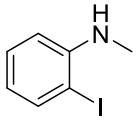
N-methyl-3-vinylaniline (**5i**).[10]



5i

The compound was prepared as described in the general method (yellow oil, 82% isolated yield, 55 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.74 – 6.65 (m, 2H), 6.55 (dd, *J* = 8.0, 1.8 Hz, 1H), 5.74 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.23 (dd, *J* = 10.9, 0.8 Hz, 1H), 2.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.61, 138.62, 137.47, 129.41, 115.68, 113.51, 112.34, 110.13, 30.86; MS (ESI) $[M+H]^+$ 134.19.

2-iodo-N-methylaniline (**5j**).[10]

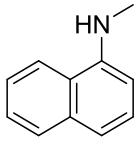


5j

The compound was prepared as described in the general method (yellow oil, 53% isolated yield, 62 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.56 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.44 (td, *J* = 7.6, 1.4 Hz, 1H), 4.19 (s, 1H), 2.88 (d, *J* = 4.6 Hz, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 148.33, 139.03, 129.61, 118.62, 110.15, 85.25, 31.11; MS (ESI) $[M+H]^+$ 234.11.

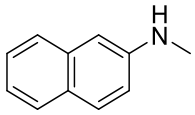
N-methylnaphthalen-1-amine (**5k**).[22]



5k

The compound was prepared as described in the general method (yellow oil, 85% isolated yield, 67 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.51 – 7.43 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 4.43 (s, 1H), 3.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.65, 134.35, 128.76, 126.80, 125.81, 124.78, 123.57, 119.91, 117.40, 103.88, 31.12; MS (ESI) $[M+H]^+$ 157.85.

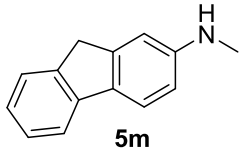
N-methylnaphthalen-2-amine (**5l**).[23]



5l

The compound was prepared as described in the general method (yellow oil, 86% isolated yield, 68 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 3H), 7.40 – 7.35 (m, 1H), 7.23 – 7.19 (m, 1H), 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 3.86 (s, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.11, 135.41, 128.92, 127.76, 127.59, 126.42, 126.05, 122.01, 118.01, 103.87, 30.88; MS (ESI) $[M+H]^+$ 157.85.

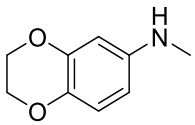
N-methyl-9H-fluoren-2-amine (**5m**).[10]



5m

The compound was prepared as described in the general method (yellow oil, 83% isolated yield, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 16.7, 7.9 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H), 6.65 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.84 (s, 2H), 2.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.05, 145.30, 142.53, 142.27, 131.89, 126.71, 124.86, 124.79, 120.69, 118.50, 111.74, 108.83, 37.07, 31.13; MS (ESI) $[M+H]^+$ 195.82.

N-methyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (**5n**).[10]

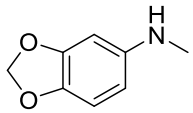


5n

The compound was prepared as described in the general method (yellow oil, 90% isolated yield, 74 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 – 6.68 (m, 1H), 6.18 – 6.14 (m, 2H), 4.24 – 4.22 (m, 2H), 4.19 – 4.17 (m, 2H), 2.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.62, 144.16, 135.65, 117.70,

106.54, 101.15, 64.89, 64.31, 31.55; MS (ESI) $[M+H]^+$ 166.29.

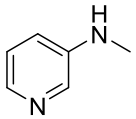
N-methylbenzo[d][1,3]dioxol-5-amine (**5o**).[22]



5o

The compound was prepared as described in the general method (yellow oil, 92% isolated yield, 69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, *J* = 8.3 Hz, 1H), 6.25 (d, *J* = 2.1 Hz, 1H), 6.05 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.85 (s, 2H), 3.51 (s, 1H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.45, 145.35, 139.64, 108.69, 103.90, 100.64, 95.70, 31.73; MS (ESI) $[M+H]^+$ 151.84.

N-methylpyridin-3-amine (**5p**).[10]

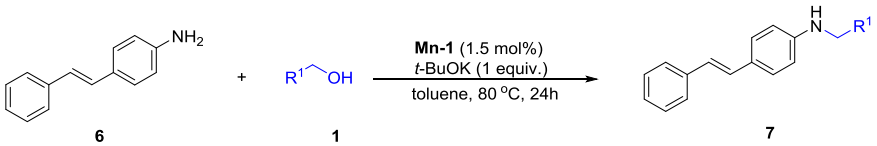


5p

The compound was prepared as described in the general method (yellow oil, 94% isolated yield, 51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.96 (d, *J* = 4.1 Hz, 1H), 7.10 (dd, *J* = 8.2, 4.5 Hz, 1H), 6.90 – 6.84 (m, 1H), 3.78 (s, 1H), 2.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.29, 138.71, 135.85, 123.85, 118.22, 30.44; MS (ESI) $[M+H]^+$ 109.10

2.4, *N*-alkylation of 4-aminostilbene with alcohols catalyzed by Mn-1

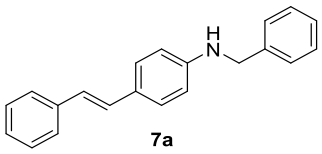
2.4.1 General method for the *N*-alkylation of 4-aminostilbene with alcohols.



6 **1** **7**

To a 15 mL sealing tube in a glovebox, was added 4-aminostilbene (0.5 mmol), alcohol (0.5 mmol), **Mn-1** (0.0075 mmol), *t*-BuOK (0.5 mmol.) and toluene (1 mL). Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred for 24 h at 80 °C. After cooled to RT, the crude reaction mixture was extracted with ethyl acetate. The solvent was evaporated to dryness and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/ petroleum ether). The yields were calculated based on isolated products.

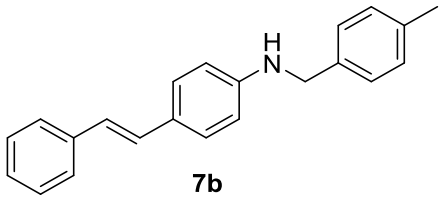
(E)-N-benzyl-4-styrylaniline (**7a**).[10]



7a

The compound was prepared as described in the general method (white solid, 90% isolated yield, 130 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.19 (m, 12H), 7.03 – 6.87 (m, 2H), 6.61 (d, *J* = 6.7 Hz, 2H), 4.34 (s, 2H), 4.13 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.94, 139.30, 138.21, 128.92, 128.80, 128.70, 127.90, 127.58, 127.43, 127.14, 126.88, 126.17, 124.73, 113.05, 48.32; MS (ESI) $[M+H]^+$ 285.90.

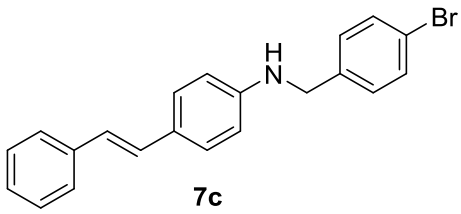
(E)-N-(4-methylbenzyl)-4-styrylaniline (**7b**).



7b

The compound was prepared as described in the general method (white solid, 84% isolated yield, 126 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.14 (m, 3H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.30 (s, 2H), 4.10 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.00, 138.24, 137.11, 136.21, 129.48, 128.96, 128.71, 127.90, 127.61, 127.10, 126.86, 126.17, 124.68, 113.06, 48.11, 21.25; MS (ESI) $[M+H]^+$ 299.97.

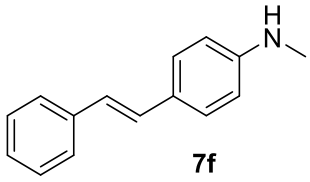
(E)-N-(4-bromobenzyl)-4-styrylaniline (**7c**).



7c

The compound was prepared as described in the general method (white solid, 80% isolated yield, 145 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 4H), 7.34 – 7.30 (m, 4H), 7.23 -7.17 (m, 3H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 2H), 4.30 (s, 2H), 4.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.56, 138.41, 138.14, 131.87, 129.13, 128.81, 128.72, 127.90, 127.42, 126.95, 126.19, 124.95, 121.15, 113.12, 47.66; MS (ESI) $[M+H]^+$ 363.80.

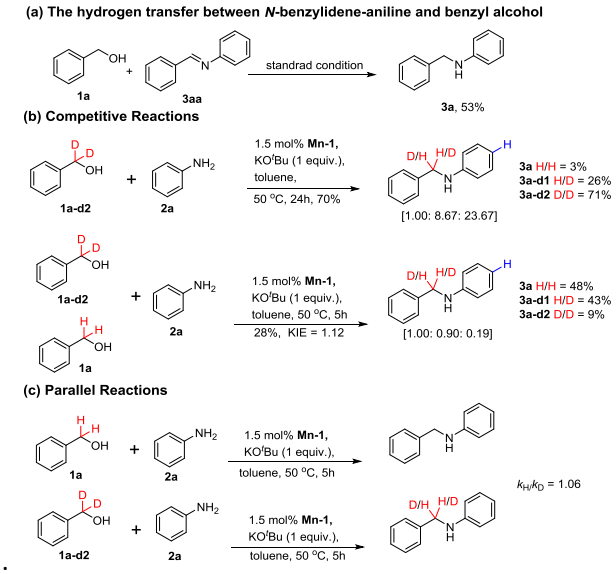
(E)-N-methyl-4-styrylaniline (**7d**).[24]



7f

The compound was prepared as described in the general method with 500 L MeOH as the alcohol and the temperature is 100 ^{o}C (white solid, 82% isolated yield, 86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 16.3 Hz, 1H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 1H), 2.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.14, 138.27, 129.02, 128.70, 127.86, 126.83, 126.79, 126.14, 124.52, 1^+ 209.90.

IV. Mechanism Details



Scheme S4. Preliminary mechanism studies.

1, Kinetic Isotope Effect (KIE) Studies

Intermolecular Competition Reactions

The kinetic isotope effect (KIE) studies were carried out to gain more information concerning the reaction pathway. The reaction of **1a-d2** (97% D) with **2a** under standard conditions gave a mixture of *N*-alkylated products **3a** (3%), **3a-d1** (26%) and **3a-d2** (71%) in 70% yield (Figure S1), which is indicative for the existence of D/H exchange in agreement with the literature.[8]

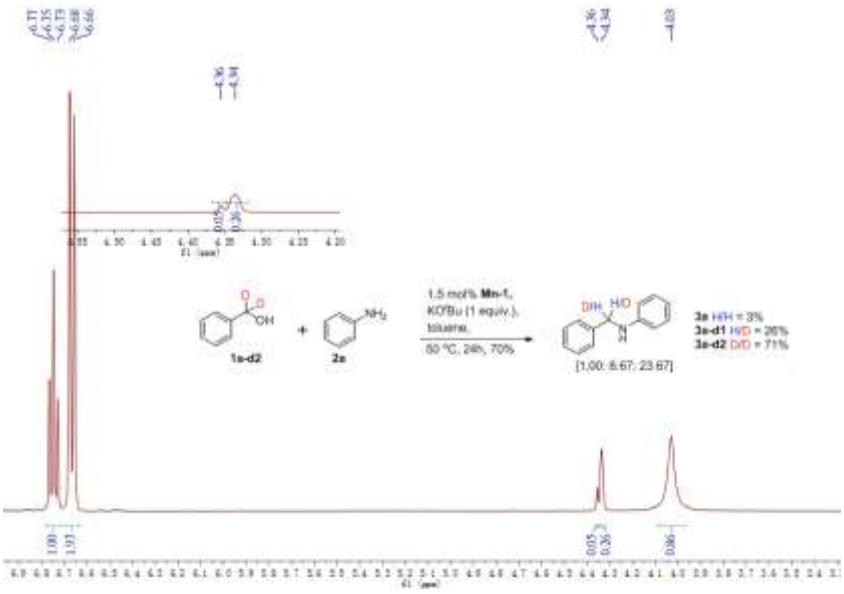


Figure S1. The ^{1}H NMR ($CDCl_3$) spectra of the products of the reaction of **1a-d2** with **2a** in the range of 3-7 ppm.

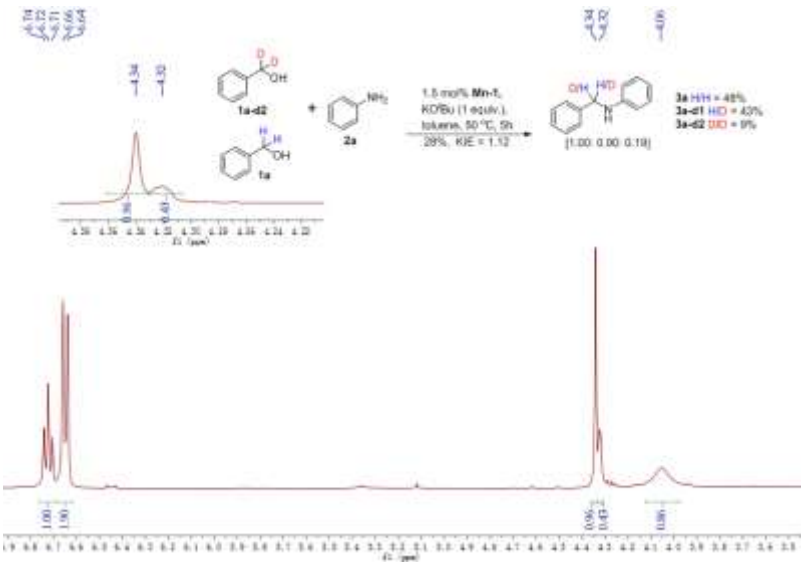


Figure S2. The ^{1}H NMR ($CDCl_3$) spectra of the products of intermolecular competition reactions in the range of 3-7 ppm.

Parallel Reactions

Two parallel reactions, one with benzyl alcohol (**1a**) and another with benzyl alcohol-*α*-d2 (**1a-d2**), were carried out. To a 15 mL reaction tube in a glovebox, was added aniline (0.5 mmol), appropriate benzyl alcohol (0.5 mmol), **Mn-1** (0.0075 mmol), *t*-BuOK (0.5 mmol.) and toluene (1 mL). Then the tube was closed with a rubber stopper and removed from the glovebox. The reaction mixture was stirred at 50 ℃, the aliquots were taken after 0, 1, 2, 3, 4 and 5h and the conversion of the aniline and yields of products were determined by GC. The calculated KIE (*k*H/kD) was 1.06 (Figure S3). Both the intermolecular competition and the parallel reactions of **1a** and **1a-d2** with **2a** showed low KIE value (KIE ≈ 1.1), suggesting that the alcohol oxidation step is not involved in the rate-determining step (rds) of the reaction.

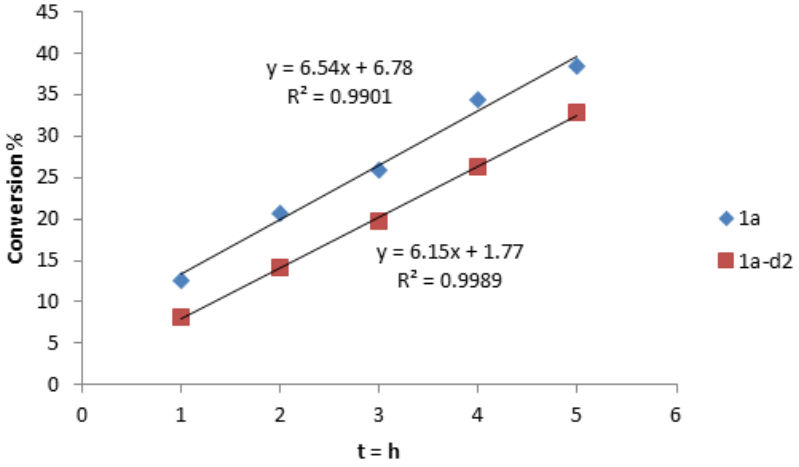


Figure S3. The plot of initial rates showing product yield over time for the reaction with benzyl alcohol (**1a**) or with deuterated benzyl alcohol (**1a-d2**).

2, NMR experiments for the mechanistic studies.

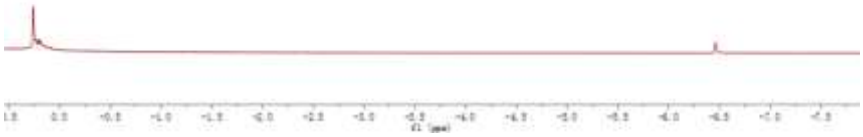


Figure S4. ^{1}H NMR (400 MHz, toluene-d_8) spectrum of reaction mixture for amination at 12 h of hydride region.

The reaction of **1a** (0.25 mmol) with **2a** (0.25 mmol) in the presence of **Mn-1** (30 mol%) and *t*-BuOK (100 mol%) in toluene-d_8 (0.5 ml) was conducted in an NMR tube. After the NMR tube kept at 50 ^{o}C for 12 h, a single hydrido signal at −6.46 ppm was observed (Figure S4), indicating the formation of **Mn-H** species.

3. In-situ IR Spectroscopy Study

In a 25 mL two-neck flask, **Mn-1** (60 mg, 0.075 mmol) and toluene (5 mL) were added firstly. The flask was connected to the infrared probe and purged three times and finally filled with N_2. After close the flask, the mixture was stirred at 80 ^{o}C, the three typical CO stretches at 1999, 1915 and 1875 cm^{-1} were observed in the spectrum (Figure S5, black). Then *t*-BuOK (140 mg, 1.25 mmol) was added, the new set of CO stretches (1973, 1891, 1868 cm^{-1}) were observed in the spectrum (Figure S5, red). After 1h, benzyl alcohol (130 μL, 1.25 mmol) was added (Figure S5, blue), the new set of CO stretches (1973, 1891, 1868 cm^{-1}) were also observed. Finally, the aniline (115 μL, 1.25 mmol) was added. The reaction was kept at 80 ^{o}C for 4h, and the CO stretches (Figure S5, purple) were kept unchanged. Therefore, there are mainly two sets of CO stretches (1999, 1915 and 1875 cm^{-1}) and (1973, 1891, 1868 cm^{-1}) in the reaction process. The former should belong to the **Mn-1,** and the latter is likely corresponding to new carbonyl Mn species.

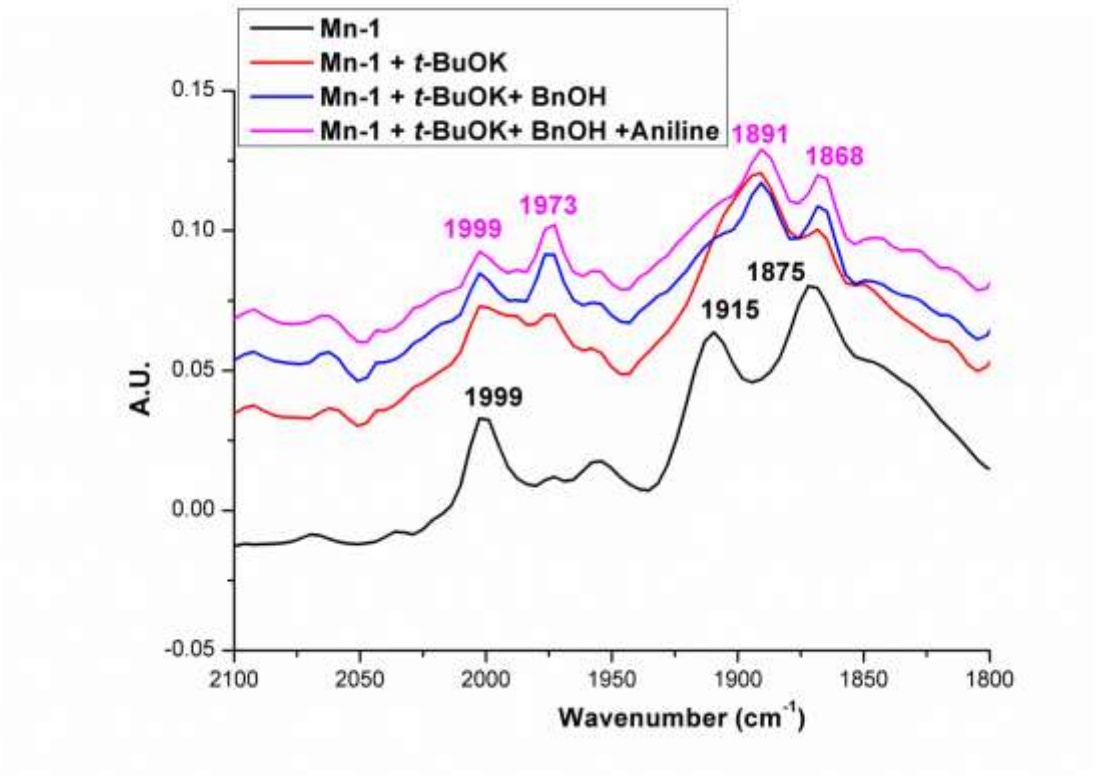


Figure S5. The in-situ IR spectroscopy of **Mn-1** catalyzed the *N*-alkylation of amines with alcohols.

Then, we employed DFT calculations (**Table S4**) to gain insight into the new carbonyl Mn species (**Figure S7**) involved in the reaction.[10] Firstly, the linear correlation of the experimental and DFT values (ν_{CO} (cm^{-1})) was corroborated by those results of **Mn-1**. With this linear regression equation, we could obtain the predicted values of the Mn species. And the predicted values of the **Mn-O*t*-Bu** and **Mn-OCH$_2$Ph** species have a good linear correlation with the new set of CO stretches (1973, 1891, 1868 cm^{-1}). Therefore, we assumed that the new carbonyl Mn species is likely the generated bis-NHC-Mn(OR)(CO)$_3$, suggesting Mn species with three coordinated carbonyls.

Table S4. **Experimental and DFT Calculated IR Spectra of the Proposed Manganese Species**

Species	DFT ν_{CO} (cm^{-1})	Experimental ν_{CO} (cm^{-1})	Predicted ν_{CO} (cm^{-1})
Mn-1	2069, 1997, 1963	1999, 1915, 1875	1986, 1922, 1882
Mn-O*t*-Bu	2055, 1980, 1943	1973, 1891, 1868	1973, 1901, 1865
Mn-OCH$_2$Ph	2056, 1980, 1943	1973, 1891, 1868	1974, 1901, 1865
Mn-H	2037, 1957, 1937	-	1956, 1879, 1860
Mn	2106, 2036, 2018	-	2022, 1955, 1937

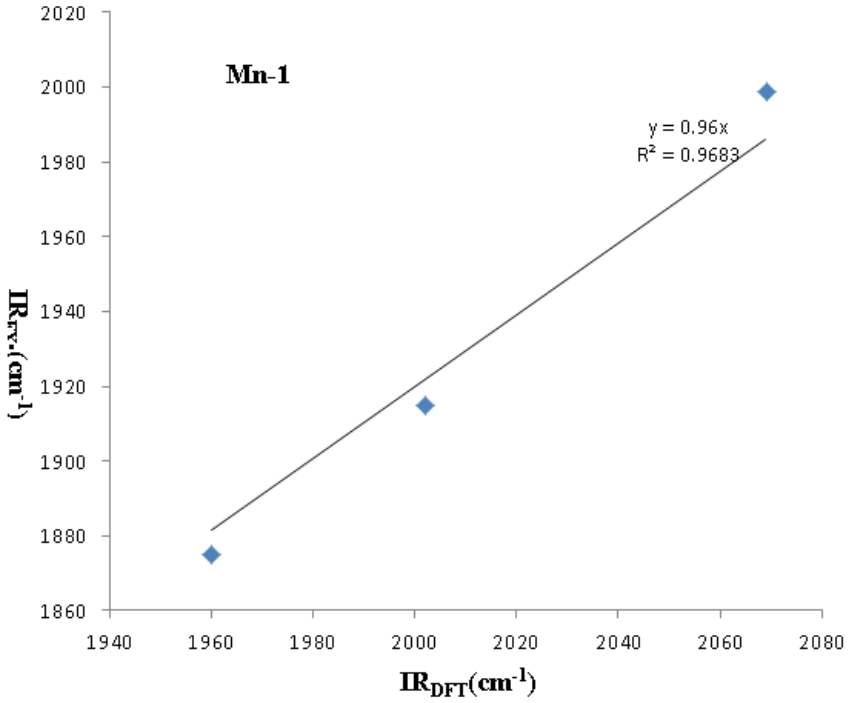


Figure S6 The linear correlation of the experimental and DFT values (ν_{CO} (cm^{-1})) of **Mn-1**.

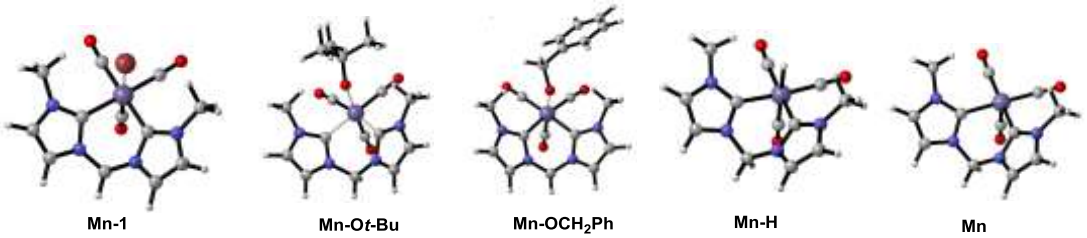


Figure S7 Optimized structures of the carbonyl Mn species.

4 Detection of hydrogen gas

To a 15 mL reaction tube in a glovebox, was added aniline (0.5 mmol), benzylalcohol (0.5 mmol), KO*t*Bu (0.5 mmol), **Mn-1** (1.5 mol%), and toluene (0.25 mL). Then the tube was closed with a rubber stopper and removed from the glovebox. After the reaction mixture was stirred for 48 h at room temperature, the head gas was collected by a gas-tight syringe and analyzed by GC. Hydrogen gas was detected.

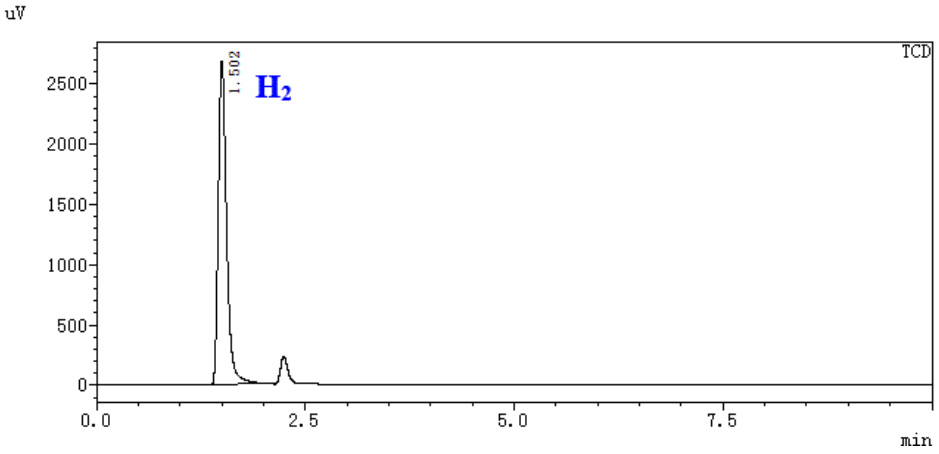
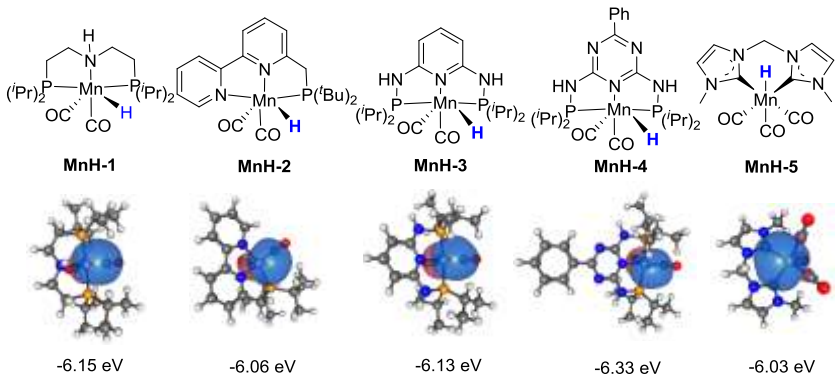


Figure S8 Detection of hydrogen gas by GC. GC parameters: injection temperature = 200 °C, column temperature = 60 °C, detector temperature = 150 °C. 5 Å molecular sieves column was used, and the carrier gas was N_2. The retention time for H_2 is 1.502 min.

Computational Section

Computational Details

1, DFT calculations on the M-H orbital energy of the Mn complexes



Scheme S5. The M-H orbital energy for the designed bis-NHC-Mn complex compared with those of typical phosphine-Mn complexes at the DFT level.

1, DFT calculations on IR Spectroscopy Study

All the structures were optimized by the density functional theory (DFT) at the B3LYP hybrid exchange-correlation functional[25] and the standard 6-31+g(d'p) 6d basis set for all atoms. The solvation effect of toluene was introduced in geometry optimizations through the SMD polarizable continuum model.[26] Dispersion effects were also included using the Grimme D3 correction.[27] All

the calculations were performed with the Gaussian 09 program.[28] The 3D optimized structures were displayed by CYLview visualization program.[29]

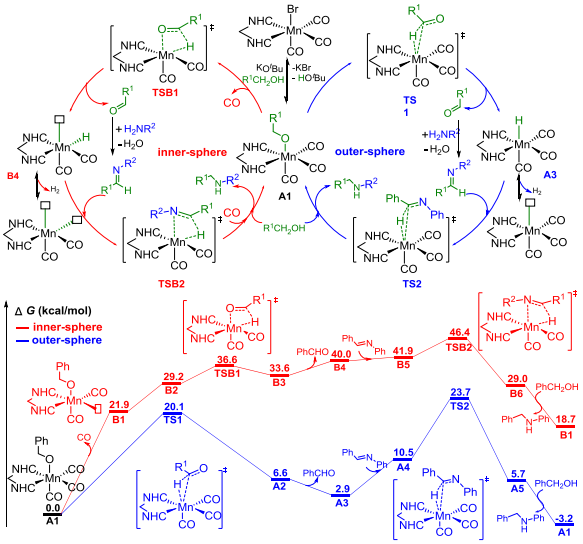
2, DFT calculations on reaction mechanism Study

All the structures were optimized by the density functional theory (DFT at the M06-L functional[30]) with basis sets I (def2svp basis set[31] for all atoms) in the gas phase. Frequency analysis calculations based on optimized structures were performed to characterize the structures to be minima (no imaginary frequency) or transition states (one imaginary frequency). IRC calculations were taken to confirm the connection between two minima for a transition state. Based on M06-L/BSI optimized geometries, the energy results were further refined by calculating the single point energy at the M06-L/BSII (SMD) level of theory (BSII designates def2svp basis set for all atoms), involved the bulky solvent effect of toluene (ε= 2.4). To reduce the overestimation of entropy, a scaling factor of 0.5 to the gas-phase entropic contributions (i.e., −TΔS) was applied.[32] The final free energy result of the species in the catalytic process was refined with this correction. The free energy of -2.9 kcal/mol for CO concentration correction at room temperature was further considered, which is derived from the free-energy change of the solubility of CO in toluene solvent (7.4 mmol, 298.15 K, 1 atm) to 1 M.[33] All the calculations were performed with the Gaussian 09 program. The 3D optimized structures were displayed by CYLview visualization program. NBO analysis was performed using NBO Version 3.1 as implemented in the Gaussian 09 package.[34] The molecular orbitals and natural bond orbitals were depicted by the IboView software.[35]

2.1, The inner-sphere mechanism

Different from the outer-sphere mechanism, the inner-sphere requires the dissociation of one carbonyl ligand to generate a vacant site for the β-H elimination to yield the metal-hydride intermediate, which then hydrogenates imine through an inner-sphere hydride insertion to furnish the N-alkylated product (Scheme S6). The inner-sphere pathway (**Fig S9**) initiates from **B1** (21.9 kcal/mol), which has a vacant site formed by the dissociation of one CO from **A1** (0.0 kcal/mol). From **B1**, the dehydrogenation of **1a** undergoes a *β*-H elimination transition state **TSB1** (36.6 kcal/mol), leading to intermediate **B3** (33.6 kcal/mol). After the dissociation of aldehyde, a Mn hydride intermediate **B4** (40.0 kcal/mol) was formed. The yielded aldehyde reacts with the amine in situ to give the imine for the subsequent hydrogenation step. Similar to the alcohol oxidation, the hydrogenation step involves an inner-sphere hydride transfer to the C=N bond via transition state **TSB2**

(46.4 kcal/mol), leading directly to **B6** (29.0 kcal/mol). The overall barrier is 46.4 kcal/mol, which indicates that the inner-sphere mechanism is not feasible.



Scheme S6. Proposed reaction mechanism based on experimental and DFT results.

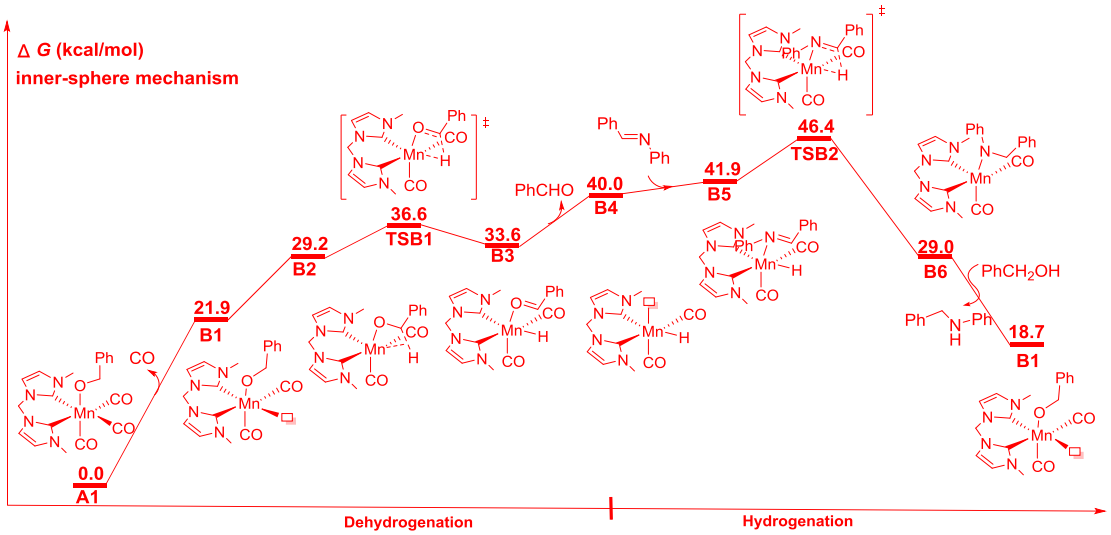


Figure S9. Calculated free-energy profile for the inner-sphere pathway. Free energies at the M06-L/BSII (SMD)// M06-L/BSI level of theory are given in kcal/mol.

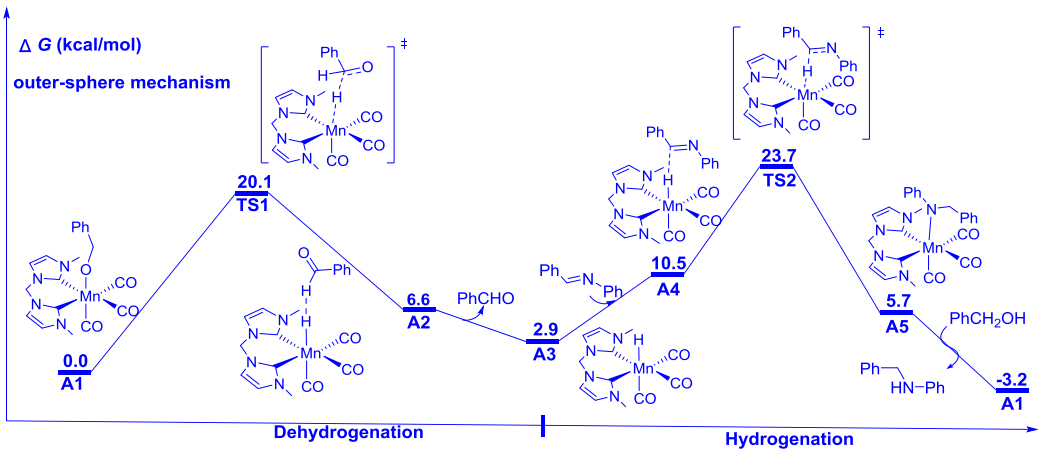


Figure S10. Calculated free-energy profile for the outer-sphere pathway. Free energies at the M06-L/BSII (SMD)// M06-L/BSI level of theory are given in kcal/mol.

In the outer-sphere pathway (**Fig S10**), starting from **A1** (0.0 kcal/mol), the dehydrogenation of **1a** undergoes via transition state **TS1** (20.1 kcal/mol), leading to a Mn hydride intermediate **A3** (2.9 kcal/mol). It should be noted that **TS1** was obtained at the BHandHLYP/BSI level of theory, because this transition state failed to be located with M06L functional, and the energy results were further refined by calculating the single point energy at the M06-L/BSII (SMD) level of theory. The yielded aldehyde reacts with the amine in situ to give the imine for the subsequent hydrogenation step. Similar to the alcohol oxidation, the hydrogenation step involves only a single step, through the direct hydride transfer transition state **TS2** (23.7 kcal/mol), leading directly to **A5** (5.7 kcal/mol). The overall barrier is 23.7 kcal/mol, which is 22.7 kcal/mol lower than that of the inner-sphere mechanism, mainly due to the unnecessity of carbonyl dissociation. The CO dissociation penalty is 21.9 kcal/mol (see **B1** in Figure S9).

Cartesian coordinates

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Mn-O*t*-Bu

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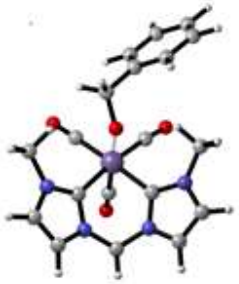
Mn-OCH$_2$Ph



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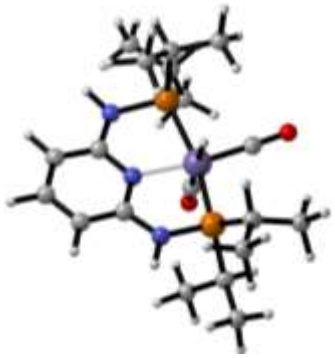

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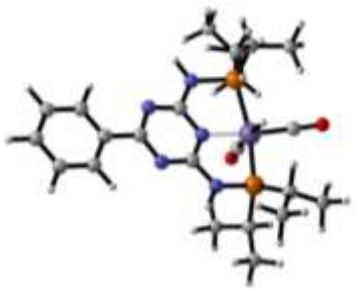
Mn-H-4



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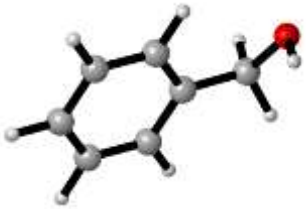

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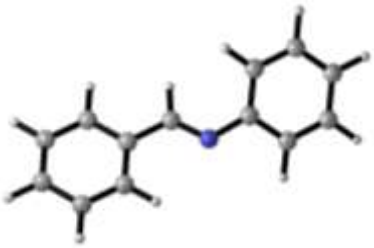

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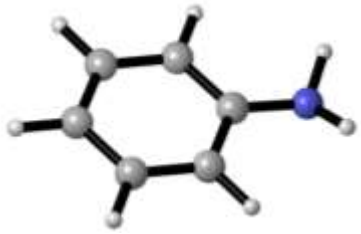

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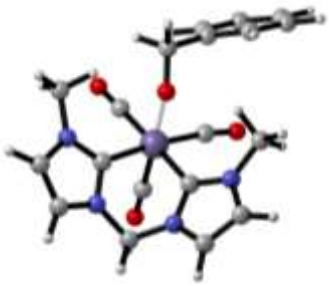

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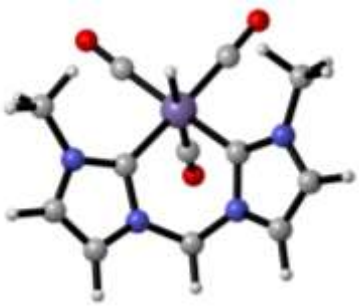

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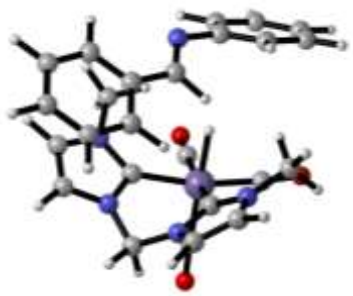

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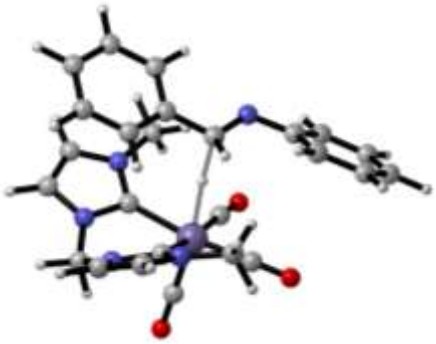

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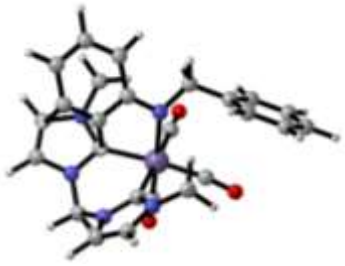
A5



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B1

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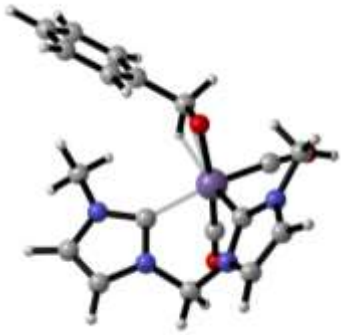

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B3

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B4

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B5

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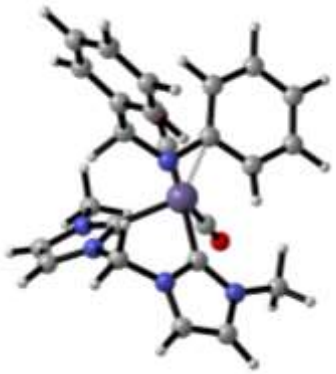
B6



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