Supporting Information

Alcohol Promoted N-methylation of Anilines with CO_2/H_2 over Cobalt Catalyst under Mild Conditions

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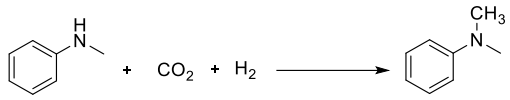
1. Analysis of reported catalytic systems of N-methylation of N-methylaniline with CO_2/H_2.

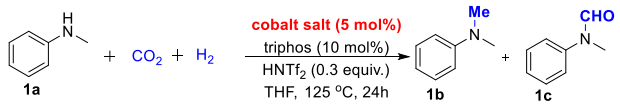
Table S1. Comparison of catalytic performance of $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$ to reported catalytic systems for N-methylation of N-methylaniline with CO_2/H_2.



Catalyst	Additive	Solvent	CO_2 (MPa)	H_2 (MPa)	T (°C)	t (h)	Yield (%)	TON	TOF	Ref
[Ru(triphos)(tmm)] (2.5 mol%)	$HNTf_2$ (5 mol%)	THF	2	6	140	22	97	38.8	1.76	[1]
$Ru(acac)_3$/triphos (1 mol%)	MSA (1.5 mol%)	THF	2	6	140	24	80	80	3.33	[2]
$Pd/CuZrO_x$ (0.75 mol%)	-	octane	1	2.5	150	30	71	94.7	3.16	[3]
$Pt\text{-}MoO_x/TiO_2$ (2 mol%)	-	none	1	4	200	24	85	42.5	1.77	[4]
$CuAlO_x$ (44 mol%)	-	hexane	3	7	160	24	86	1.95	0.08	[5]
Au/Al_2O_3 (0.5 mol%)	-	hexane	2	6	140	7	96	192	27.43	[6]
Re/TiO_2 (2 mol%)	-	dodecane	1	5	200	24	98	49	2.04	[7]
Cu/CeO_2 (3.9 mol%)	-	toluene	1	7	150	4	2.5	0.64	0.16	[8]
$Pd\text{-}ZnO/TiO_2$ (2.8 mol%)	-	toluene	1.5	4.5	180	24	87	31.07	1.29	[9]
$Co(OAc)_2{\cdot}4H_2O$/triphos (5 mol%)	$Sn(OTf)_2$ (30 mol%)	EtOH	2	7	125	24	82	16.4	0.68	This work

2. Reaction conditions optimization

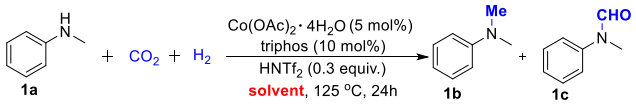
Table S2. Optimization of cobalt salts



Entry	Cobalt salt	Yield of **1b** (%)	Yield of **1c** (%)
1	-	<1	<1
2 [b]	$Co(OAc)_2{\cdot}4H_2O$	<1	<1
3	CoF_3	1	<1
4	$Co(acac)_3$	35	<1
5	$K_3[Co(CN)_6]$	<1	<1
6	CoF_2	2	2
7	$Co(ClO_4)_2{\cdot}6H_2O$	3	<1
8	$Co(BF_4)_2{\cdot}6H_2O$	19	<1
9	$Co(acac)_2{\cdot}2H_2O$	20	<1
10	$Co(OAc)_2{\cdot}4H_2O$	52	<1

Reaction condition: N-methylaniline (**1a**) (1.0 mmol), cobalt salt (5 mol %), triphos (10 mol %), $HNTf_2$ (0.3 equiv.), THF (2 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 125 °C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard. [b] no triphos.

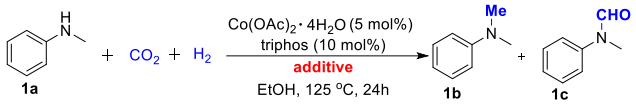
Table S3. Optimization of solvents



Entry	Solvent	Yield of **1b** (%)	Yield of **1c** (%)
1	*n*-heptane	12	<1
2	toluene	19	<1
3	1,4-dioxane	49	<1
4	EtOH	70	2
5	THF	52	<1
6	CH_3CN	2	<1
7	DMF	19	10

Reaction condition: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (5 mol %), triphos (10 mol %), $HNTf_2$ (0.3 equiv.), solvent (2 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 125 °C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

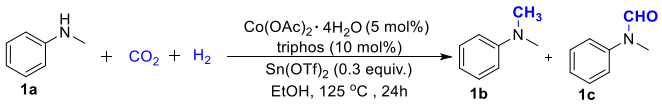
Table S4. Optimization of additive



Entry	Additive (equiv.)	Yield of **1b** (%)	Yield of **1c** (%)
1	-	<1	<1
2	MSA/0.3	6	3
3	TMA/0.3	58	3
4	$HNTf_2$/0.3	70	2
5	$Al(OTf)_2$/0.3	68	<1
6	$Yb(OTf)_2$/0.3	76	<1
7	$Sn(OTf)_2$/0.3	82	1
8	K_2CO_3/0.3	<1	<1
9	$Sn(OTf)_2$/0.1	37	<1
10	$Sn(OTf)_2$/0.2	70	5
11	$Sn(OTf)_2$/0.4	75	<1
13	$Sn(OTf)_2$/0.5	67	<1
14	$Sn(OTf)_2$/0.7	50	<1

Reaction condition: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), triphos (10 mol %), additive, EtOH (2.0 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 125 °C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

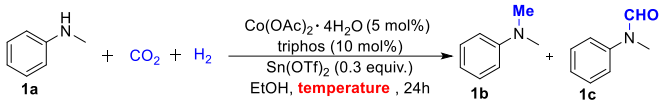
Table S5. Optimization of pressure



Entry	CO_2 (MPa)	H_2 (MPa)	Yield of **1b** (%)	Yield of **1c** (%)
1	2	7	82	1
2	1	7	40	<1
3	2	3	50	3

Reaction condition: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), triphos (10 mol %), $Sn(OTf)_2$ (0.3 equiv.), EtOH (2.0 mL), CO_2, H_2, 125 °C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

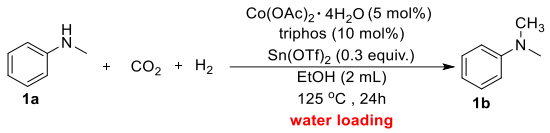
Table S6. Optimization of reaction temperature



Entry	temperature (°C)	Yield of **1b** (%)	Yield of **1c** (%)
1	95	18	8
2	105	31	7
3	115	51	6
4	125	82	1
5	135	76	<1
6	145	73	<1
7	155	59	<1
8	165	39	<1

Reaction condition: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), triphos (10 mol %), $Sn(OTf)_2$ (0.3 equiv.), EtOH (2.0 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 24 h. The yield of products was determined by GC, calibrated using n-dodecane as the internal standard.

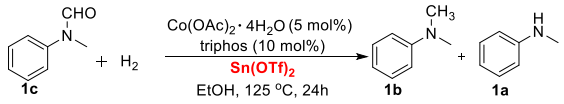
Table S7. The effect of water to the cobalt catalyzed N-methylation reduction



Entry	Water (equiv.)	Yield of **1b** (%)
1	500 mg 4Å	16
2	0	82
3	1	80
4	5	70

Reaction condition: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), triphos (10 mol %), $Sn(OTf)_2$ (0.3 equiv.), EtOH (2.0 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

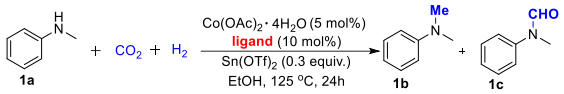
Table S8. The effect of $Sn(OTf)_2$ to the cobalt catalyzed N-formamide reduction reaction



Entry	$Sn(OTf)_2$ (equiv.)	Con. (%)	Yield of **1b** (%)
1	0	5	0.2
2	0.1	76	63
3	0.3	100	72
8	0.5	100	52

Reaction condition: **1c** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol %), triphos (10 mol %), $Sn(OTf)_2$, EtOH (2.0 mL), H_2 (7.0 MPa), 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

Table S9. Optimization of ligands



1a + CO_2 + H_2 → 1b + 1c

entry	ligand	Con. (%)	Yield of **1b** (%)
1	P*P*$_3$	0	0
2	Xantphos	0	0
3	PPh_3	0	0

Reaction condition: **1a** (1.0 mmol), cobalt salt (5 mol %), ligand (10 mol %), $Sn(OTf)_2$ (0.3 equiv.), EtOH (2 mL), CO_2 (2.0 MPa), H_2 (7.0 MPa), 125 °C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

3. The interaction of $Sn(OTf)_2$ and N-methyl formanilide.

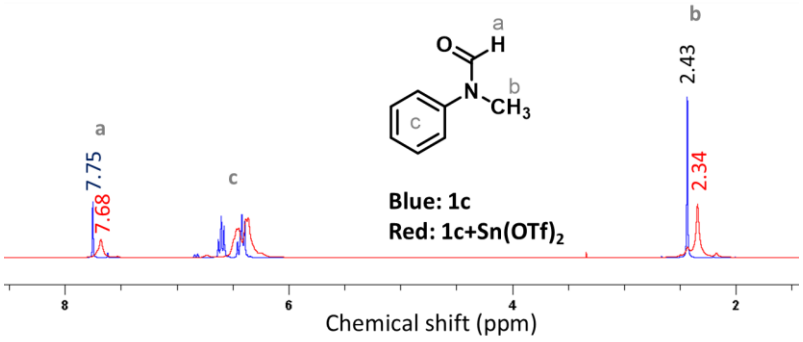


Figure S1. ^{1}H NMR spectra of **1c** and the mixture of $Sn(OTf)_2$ and **1c**.

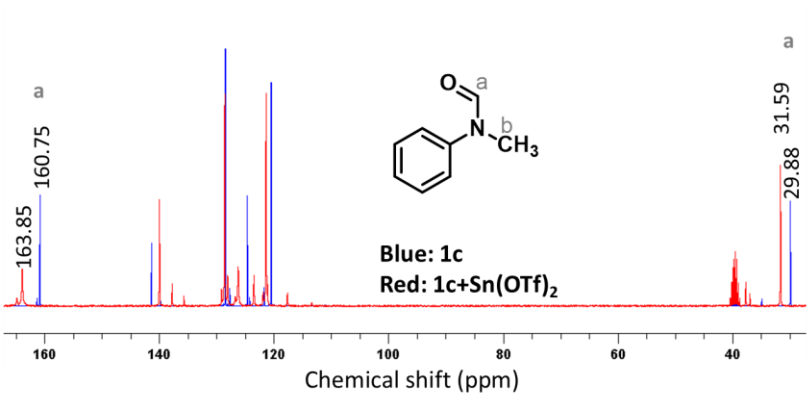


Figure S2. ^{13}C NMR spectra of **1c** and the mixture of $Sn(OTf)_2$ and **1c**.

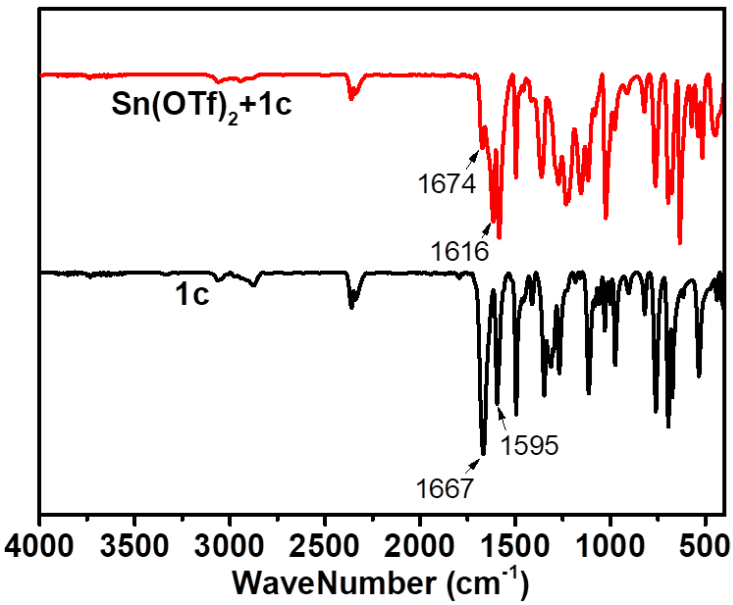


Figure S3. FTIR spectra of **1c** and the mixture of $Sn(OTf)_2$ and **1c**.

4. Mechanism investigation

4.1 ^{13}C isotope experiment of cobalt catalyzed hydrogenation of CO_2

Typical procedures: $Co(OAc)_2{\cdot}4H_2O$ (0.05 mmol), triphos (0.01 mmol), $Sn(OTf)_2$ (0.3 mmol), and EtOH (2 mL) were loaded into a stainless steel autoclave with a Teflon tube (16 mL inner volume) under N_2 atmosphere. The reactor was charged with $^{13}CO_2$ up to 1.0 MPa and then with H_2 until the total pressure reached 9.0 MPa at room temperature. The autoclave was moved to an oil bath of 125 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature, and the reaction product was analyzed by GC, GC-MS and NMR.

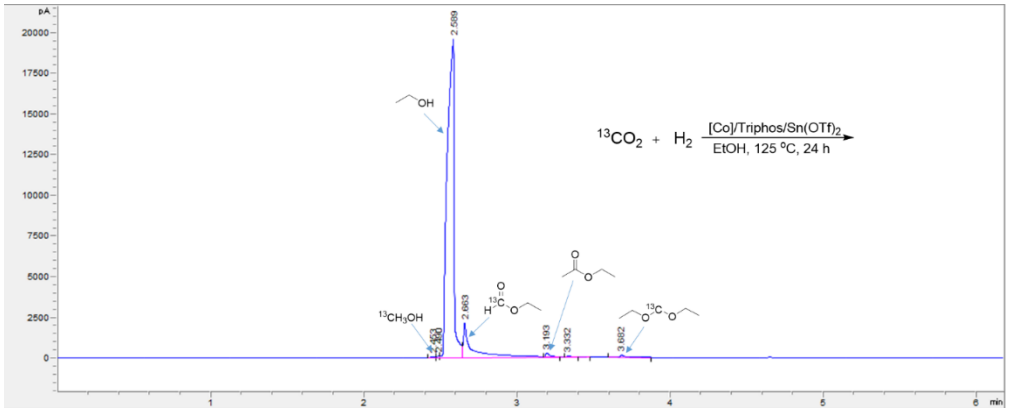


Figure S4. GC spectra of **reaction I, Scheme 2**.

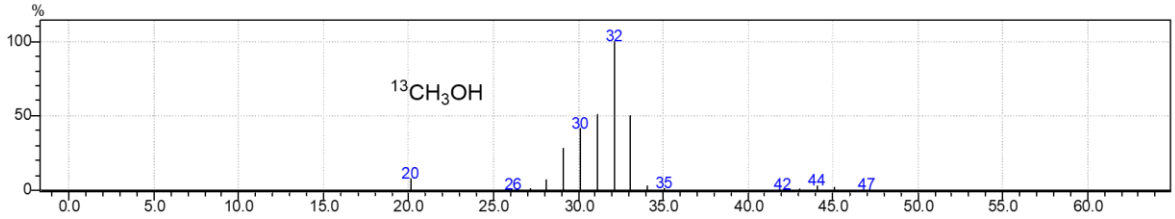


Figure S5. MS spectrum of $^{13}CH_3OH$ in **reaction I, Scheme 2.**

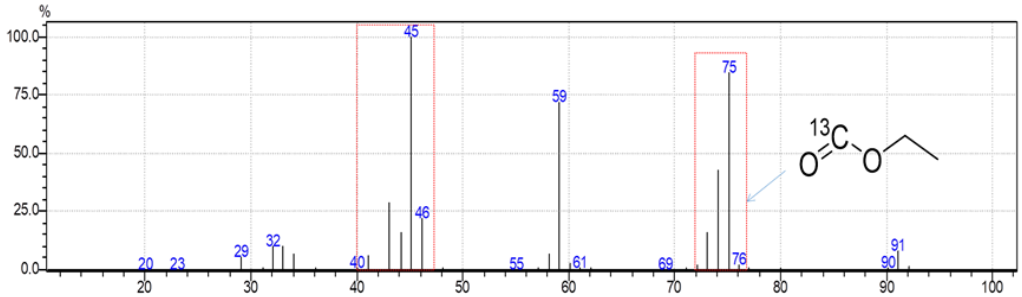


Figure S6. MS spectrum of $H^{13}COOEt$ in **reaction I, Scheme 2.**

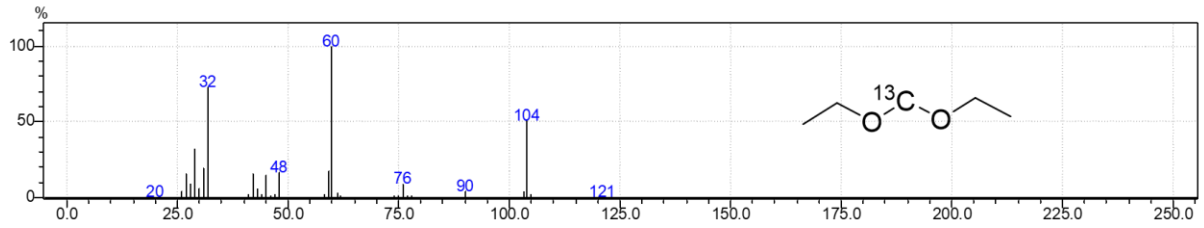


Figure S7. MS spectrum of $EtO^{13}CH_2OEt$ in **reaction I, Scheme 2.**

4.2 Cobalt catalyzed reductive coupling of 1a with various CO_2 hydrogenation products.

Table S8. Cobalt catalyzed reductive coupling of **1a** with various CO_2 hydrogenation products

Entry	CO_2 reduction level	Intermediates	Yield of **1b** (%)
1	2e reduction	HCOOH	53
2	2e reduction	HCOOEt	75
3	4e reduction	$EtOCH_2OEt$	3
4	4e reduction	HCHO	5
5	6e reduction	CH_3OH	2

Reaction conditions: [a] N-methylaniline (1.0 mmol), intermediate (10 mmol), $Co(OAc)_2{\cdot}4H_2O$ (5 mol %), triphos (10 mol %), $Sn(OTf)_2$ (0.3 equiv.), EtOH (2.0 mL), H_2 (7.0 MPa), 125 °C, 24h.

4.3 Cobalt catalyzed N-formamide reduction reaction

Typical procedures: **1c** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.05 mmol), Triphos (0.01 mmol), $Sn(OTf)_2$ (0.3 mmol), and EtOH (2 mL) were loaded into a stainless steel autoclave with a Teflon tube (16 mL inner volume) under N_2 atmosphere. The reactor was charged with H_2 up to 7.0 MPa at room temperature. The autoclave was moved to an oil bath of 125 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature, and the reaction product was analyzed by GC.

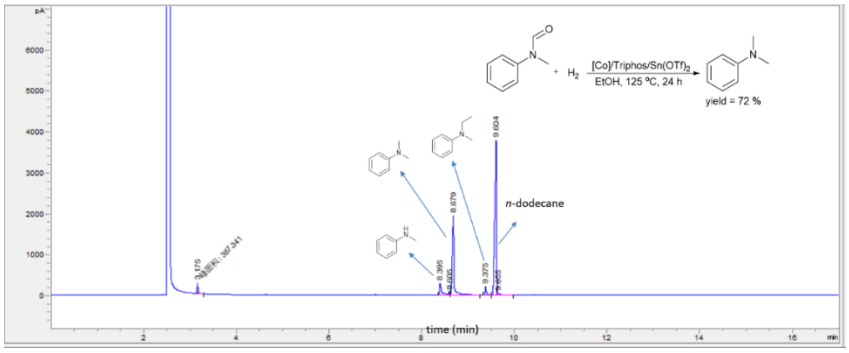


Figure S8. GC spectrum of cobalt catalyzed N-formamide reduction reaction.

4.4 ^{13}C isotope experiment of cobalt catalyzed N-methylation reaction

Typical procedures: **1a** (1.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.05 mmol), triphos (0.01 mmol), $Sn(OTf)_2$ (0.3 mmol), and EtOH (2 mL) were loaded into a stainless steel autoclave with a Teflon tube (16 mL inner volume) under N_2 atmosphere. The reactor was charged with $^{13}CO_2$ up to 1.0 MPa and then with H_2 until the total pressure reached 9.0 MPa at room temperature. The autoclave was moved to an oil bath of 125 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature, and the reaction product was analyzed by GC, GC-MS.

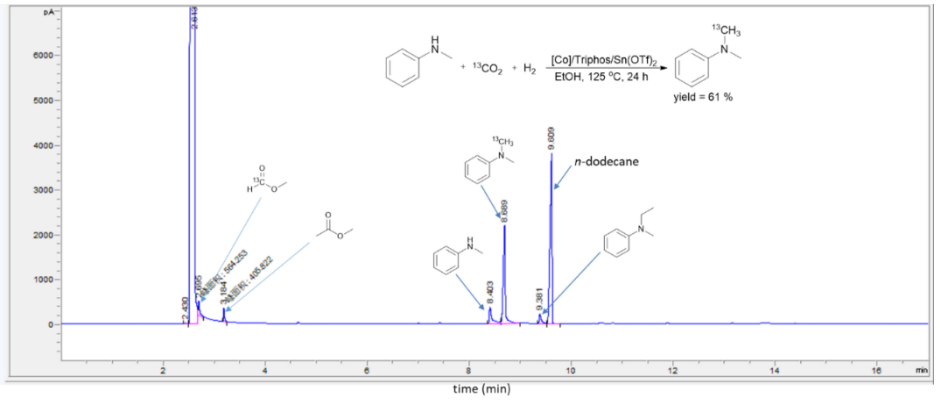


Figure S9. GC spectrum of ^{13}C isotope experiment of cobalt catalyzed N-methylation reaction.

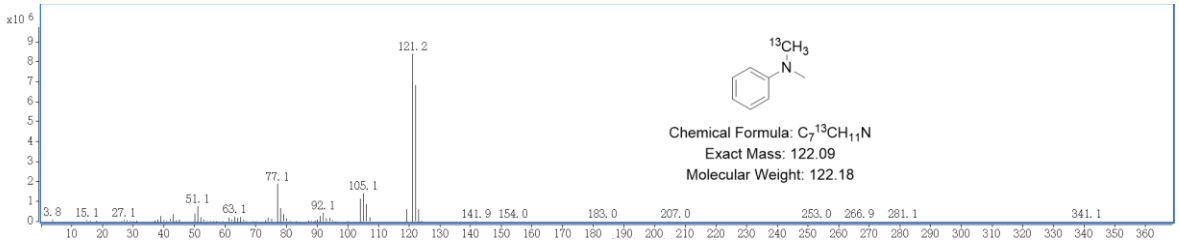
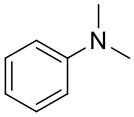
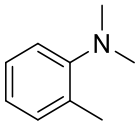


Figure S10. MS spectrum of ^{13}C isotope experiment of cobalt catalyzed N-methylation reaction.

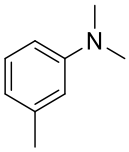
5. ^{1}H and ^{13}C NMR and HR-MS (ESI) data of products



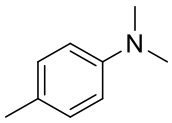
N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 - 7.28 (m, 2H), 6.87 - 6.77 (m, 3H), 3.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.78, 129.16, 116.76, 112.79, 77.48, 77.16, 76.84, 40.69. HR-MS (ESI) calculated for $C_8H_{12}N$ $[M+H]^+$: 122.0964, found: 122.0965.



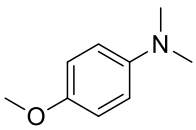
N,N,2-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 2H), 7.12 - 7.06 (m, 1H), 7.00 (m, 1H), 2.75 (s, 6H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.87, 132.25, 131.27, 126.55, 122.69, 118.49, 77.48, 77.16, 76.84, 44.35, 18.47. HR-MS (ESI) calculated for $C_9H_{14}N$ $[M+H]^+$: 136.1121, found: 136.1122.



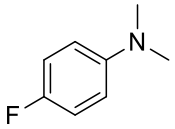
N,N,3-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.15 (m, 1H), 6.66 - 6.59 (m, 3H), 2.98 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.91, 138.81, 129.05, 117.81, 113.63, 110.10, 77.48, 77.16, 76.84, 44.79, 40.80, 22.00. HR-MS (ESI) calculated for $C_9H_{14}N$ $[M+H]^+$: 136.1121, found: 136.1122.



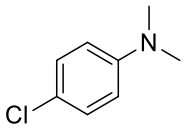
N,N,4-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, 2H), 6.80 - 6.69 (m, 2H), 2.94 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.97, 129.71, 126.26, 113.38, 77.48, 77.16, 76.84, 41.18, 20.36. HR-MS (ESI) calculated for $C_9H_{14}N$ $[M+H]^+$: 136.1121, found: 136.1122.



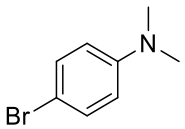
4-methoxy-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.87 - 6.80 (m, 2H), 6.79 - 6.70 (m, 2H), 3.75 (s, 3H), 2.85 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.17, 145.89, 115.04, 114.78, 77.48, 77.16, 76.84, 55.87, 41.93. HR-MS (ESI) calculated for $C_9H_{14}NO$ $[M+H]^+$: 152.1070, found: 152.1071.



4-fluoro-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 - 6.87 (m, 2H), 6.70 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (C-F, $J_{C\text{-}F}$ = 236.2 Hz), 147.7, 115.4 (C-F, $J_{C\text{-}F}$ = 22.1 Hz), 114.0 (C-F, $J_{C\text{-}F}$ = 7.4 Hz), 41.5. HR-MS (ESI) calculated for $C_8H_{11}FN$ $[M+H]^+$: 140.0870, found: 140.0871.



4-chloro-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.13 (m, 2H), 6.71 - 6.59 (m, 2H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.32, 128.94, 121.63, 113.82, 77.48, 77.16, 76.84, 40.80. HR-MS (ESI) calculated for $C_8H_{11}ClN$ $[M+H]^+$: 156.0575, found: 156.0575.



4-bromo-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.27 (m, 2H), 6.70 - 6.50 (m, 2H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.64, 131.81, 114.26, 108.68, 77.48, 77.16, 76.84, 40.68. HR-MS (ESI) calculated for $C_8H_{11}BrN$ $[M+H]^+$: 200.0069, found: 200.0071.

6. ^{1}H and ^{13}C NMR spectra of products

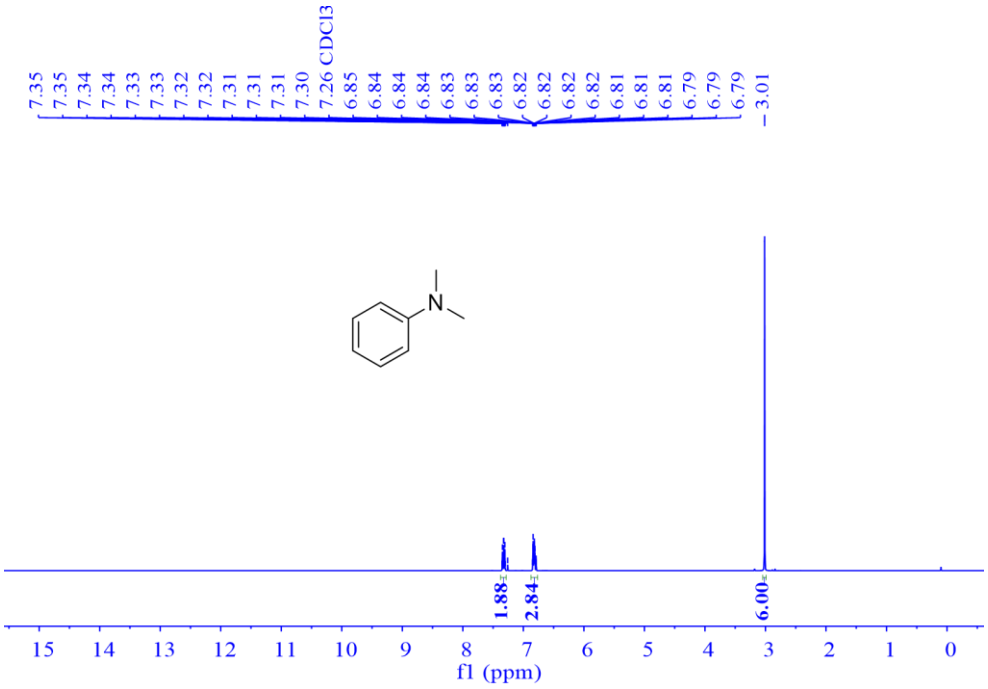


Figure S11. ^{1}H NMR of N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

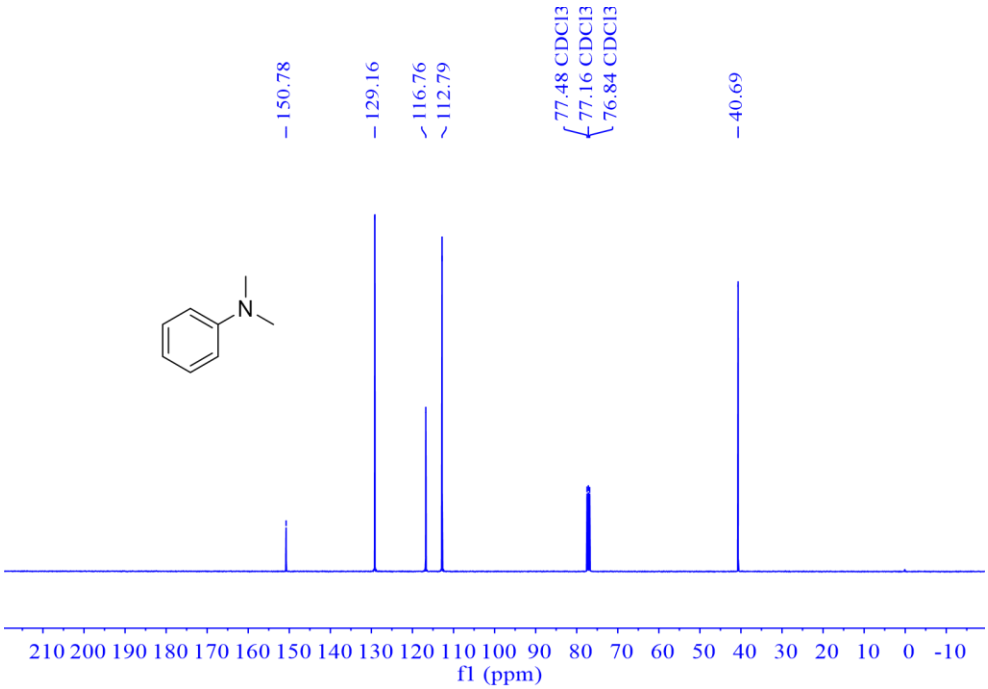


Figure S12. ^{13}C NMR of N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

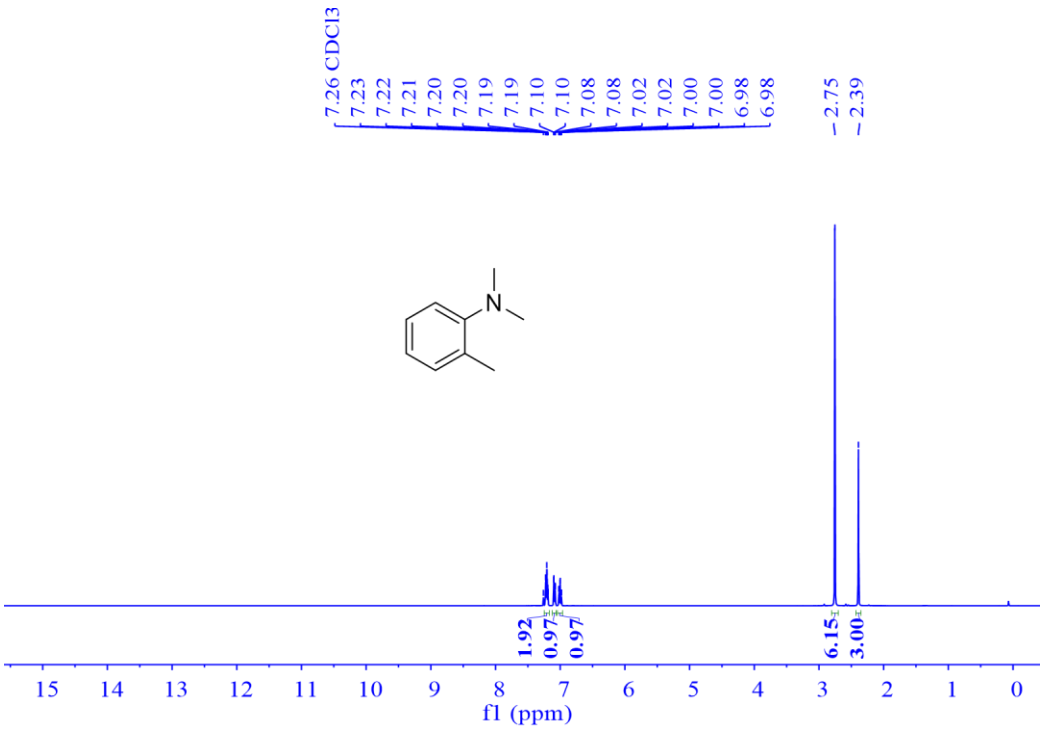


Figure S13. ^{1}H NMR of N,N,2-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

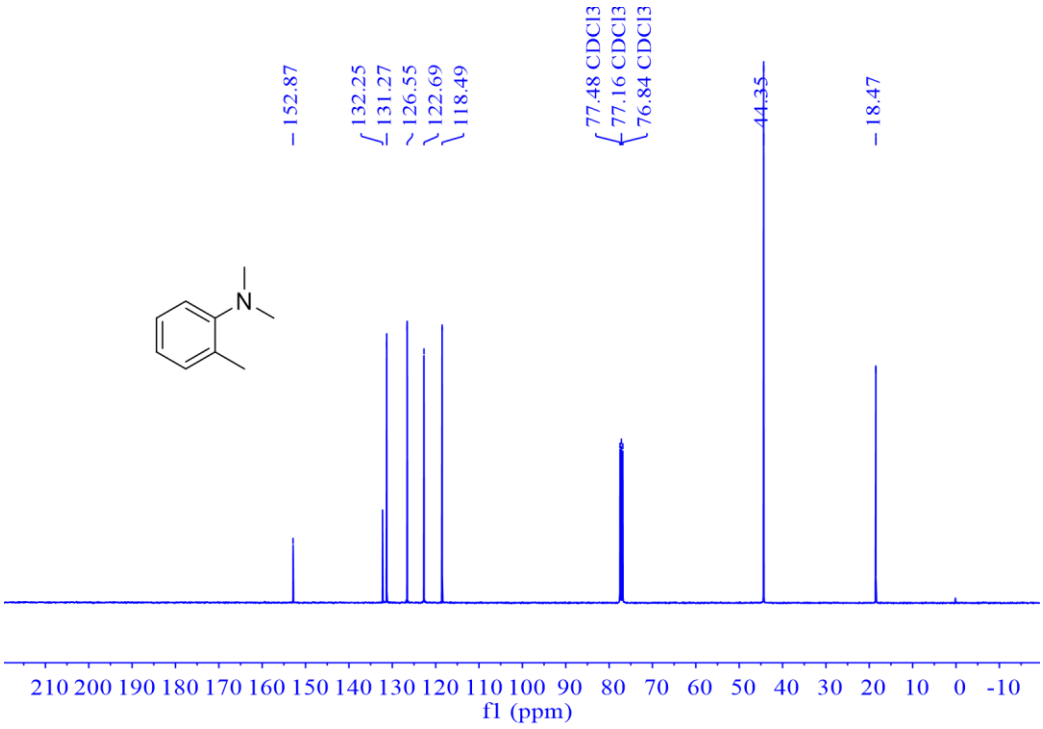


Figure S14. ^{13}C NMR of N,N,2-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

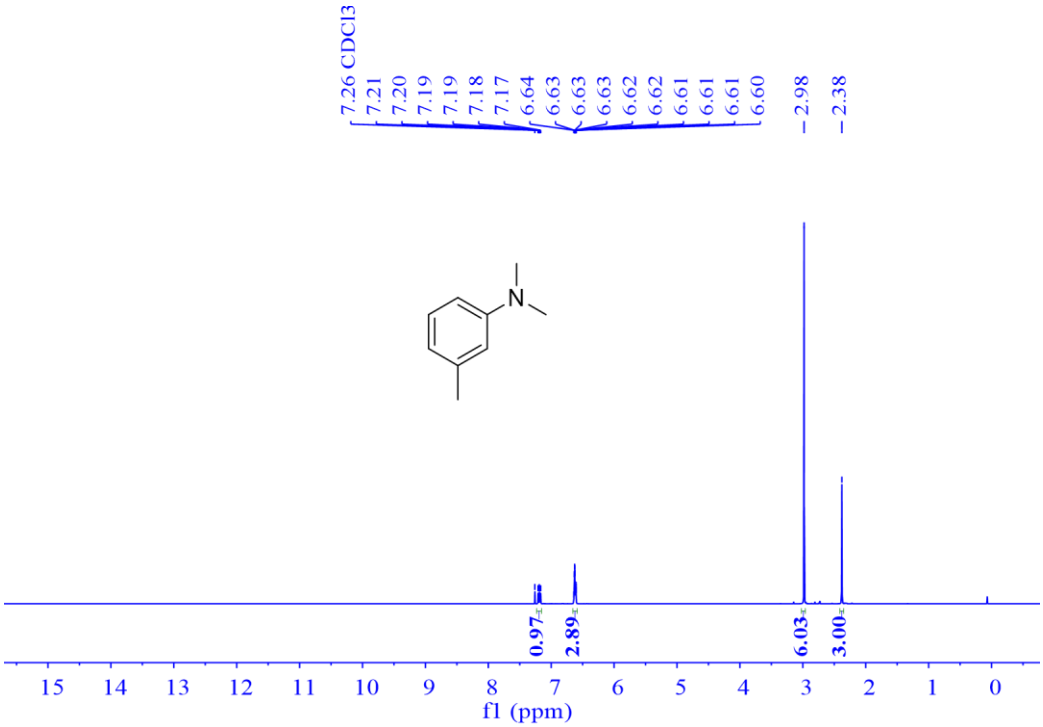


Figure S15. ^{1}H NMR of N,N,3-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

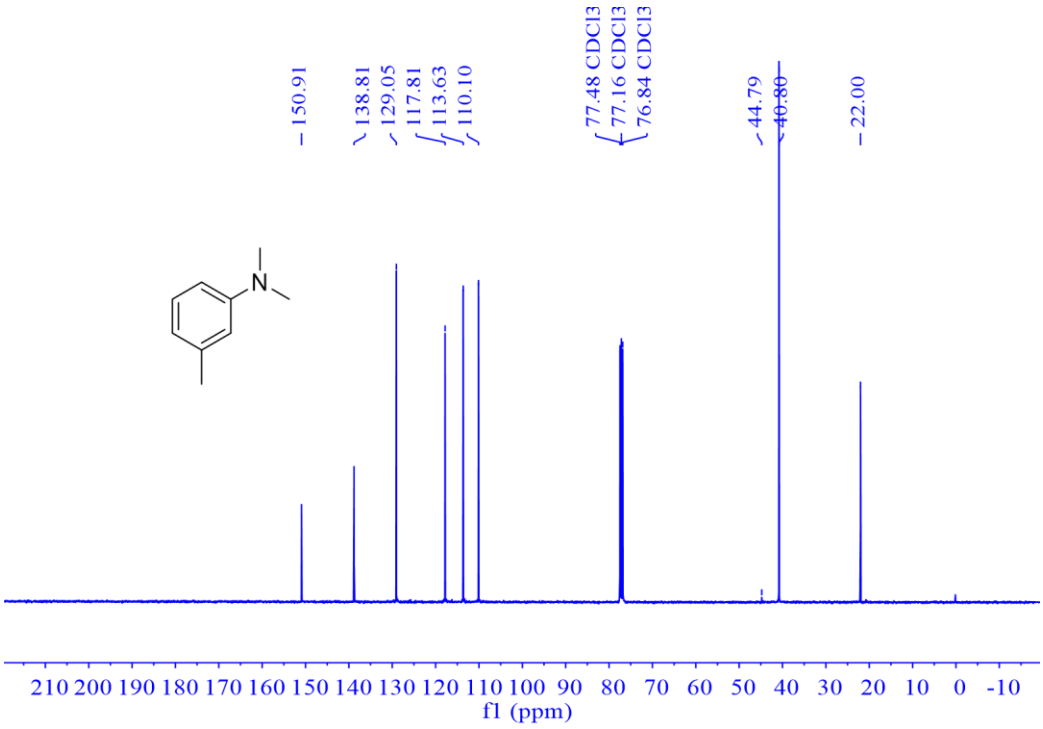


Figure S16. ^{13}C NMR of N,N,3-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

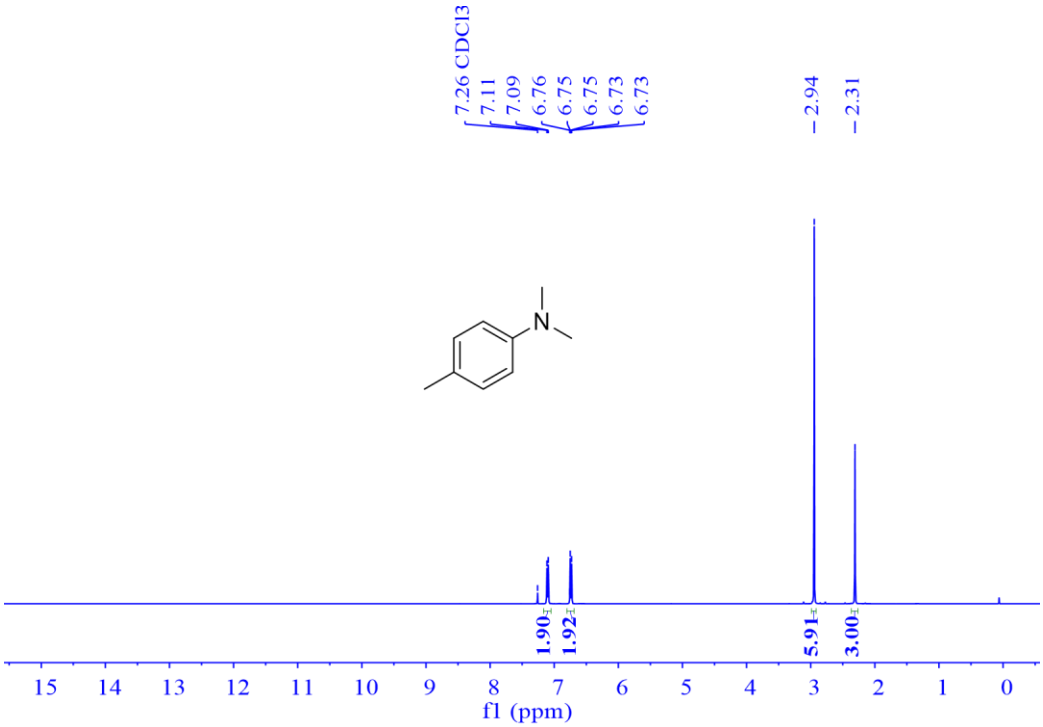


Figure S17. ^{1}H NMR of N,N,4-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

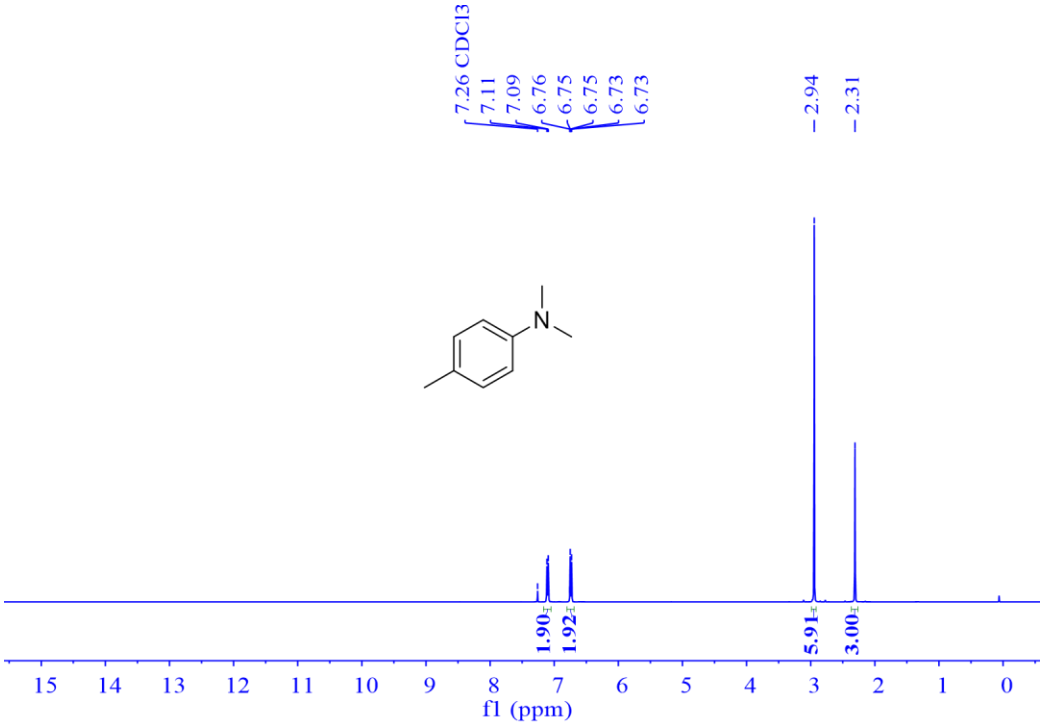


Figure S18. ^{13}C NMR of N,N,4-trimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

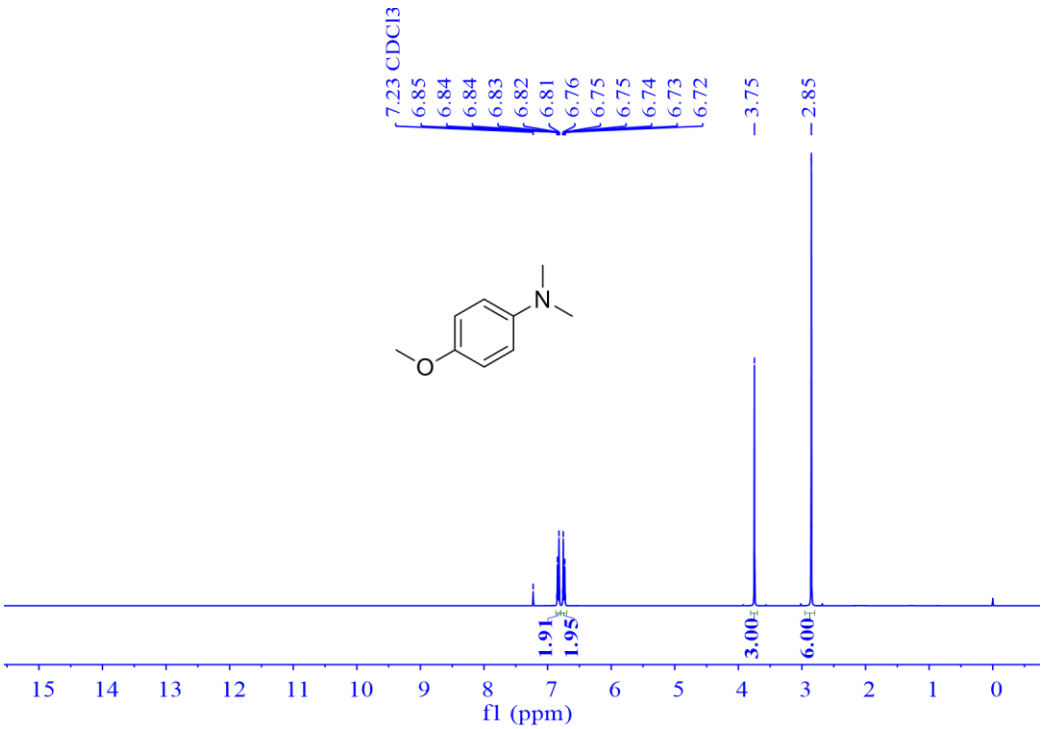


Figure S19. ^{1}H NMR of 4-methoxy-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

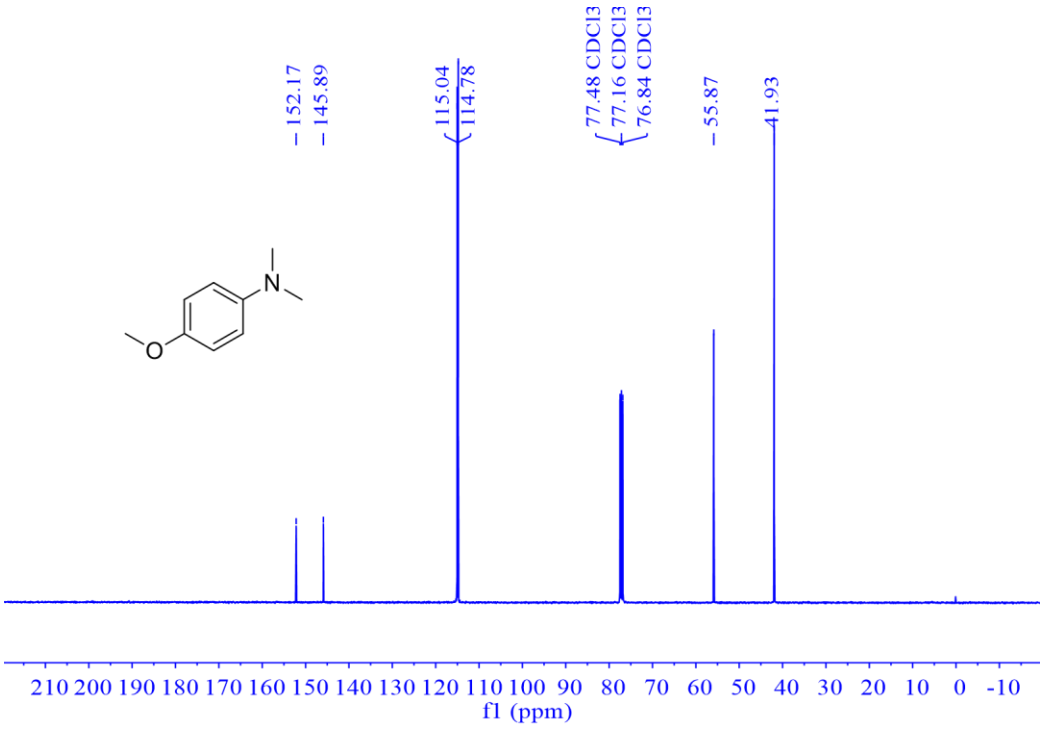


Figure S20. ^{13}C NMR of 4-methoxy-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

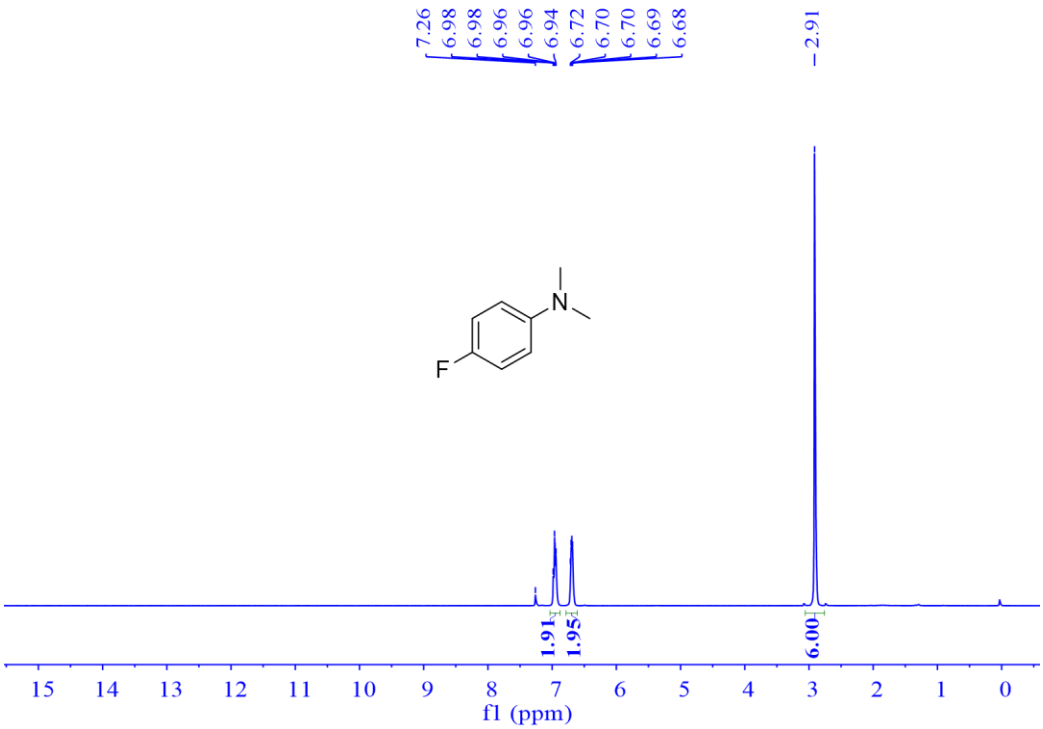


Figure S21. ^{1}H NMR of 4-fluoro-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

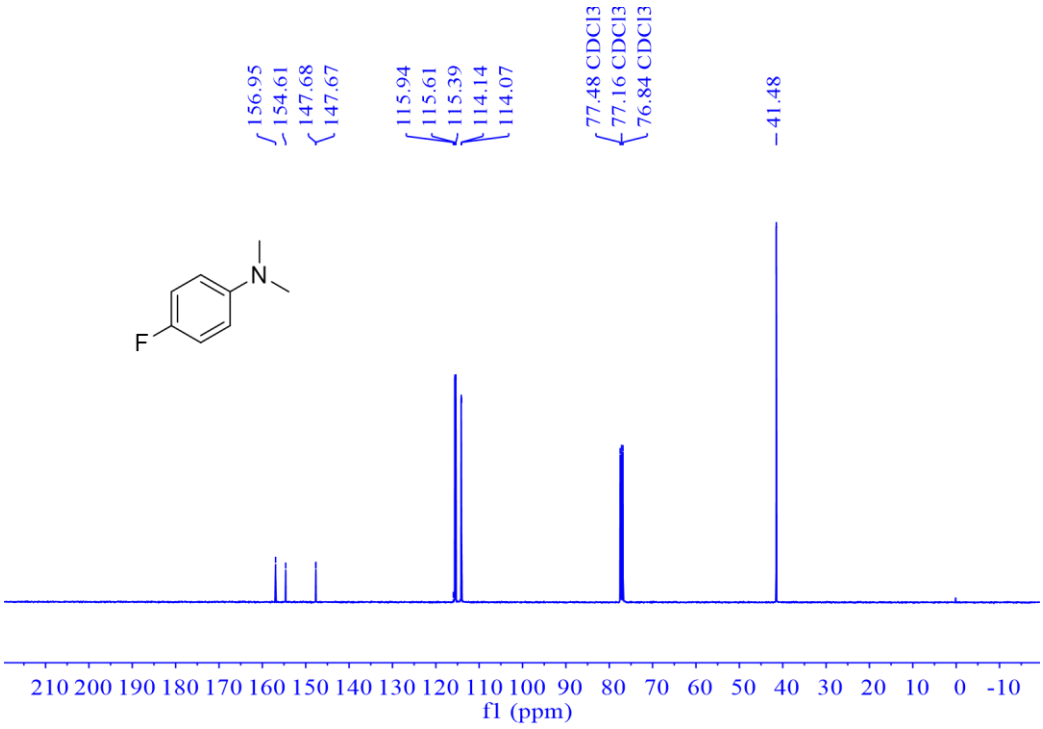


Figure S22. ^{13}C NMR of 4-fluoro-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

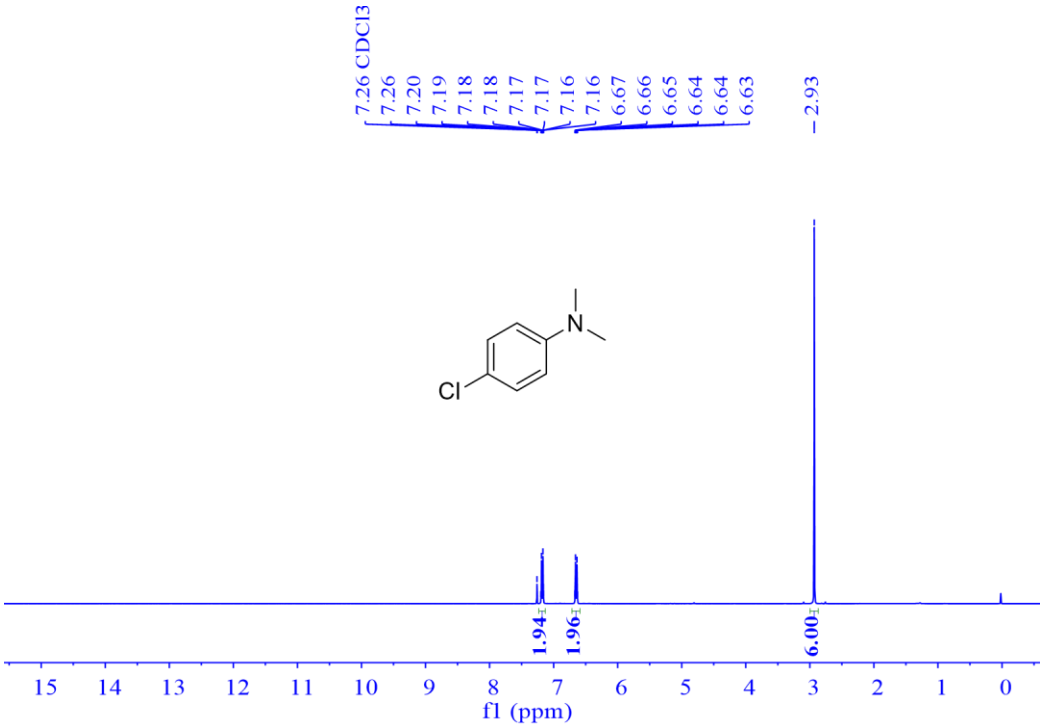


Figure S23. ^{1}H NMR of 4-chloro-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

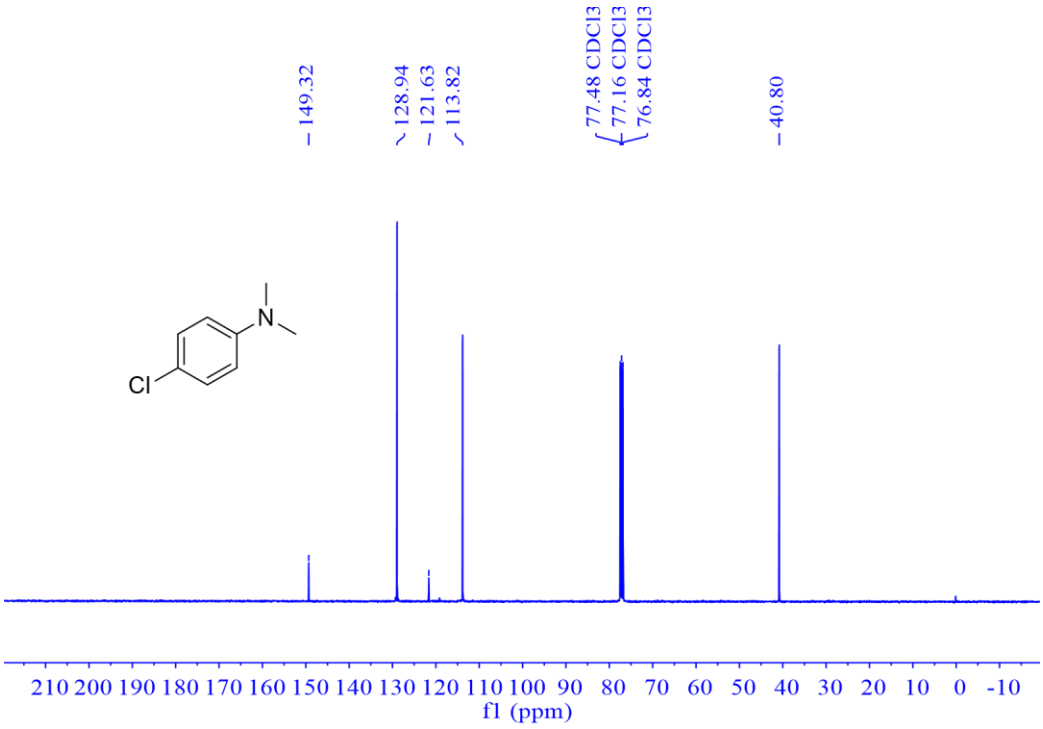


Figure S24. ^{13}C NMR of 4-chloro-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

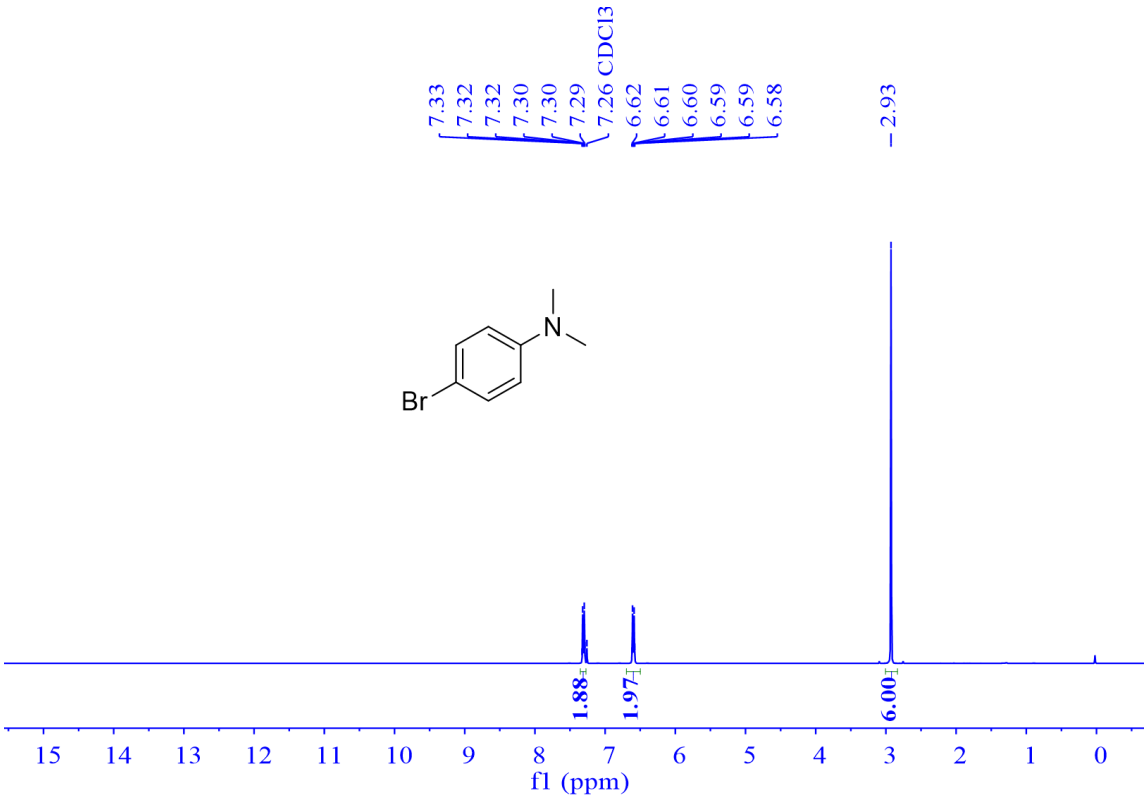


Figure S25. ^{1}H NMR of 4-bromo-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

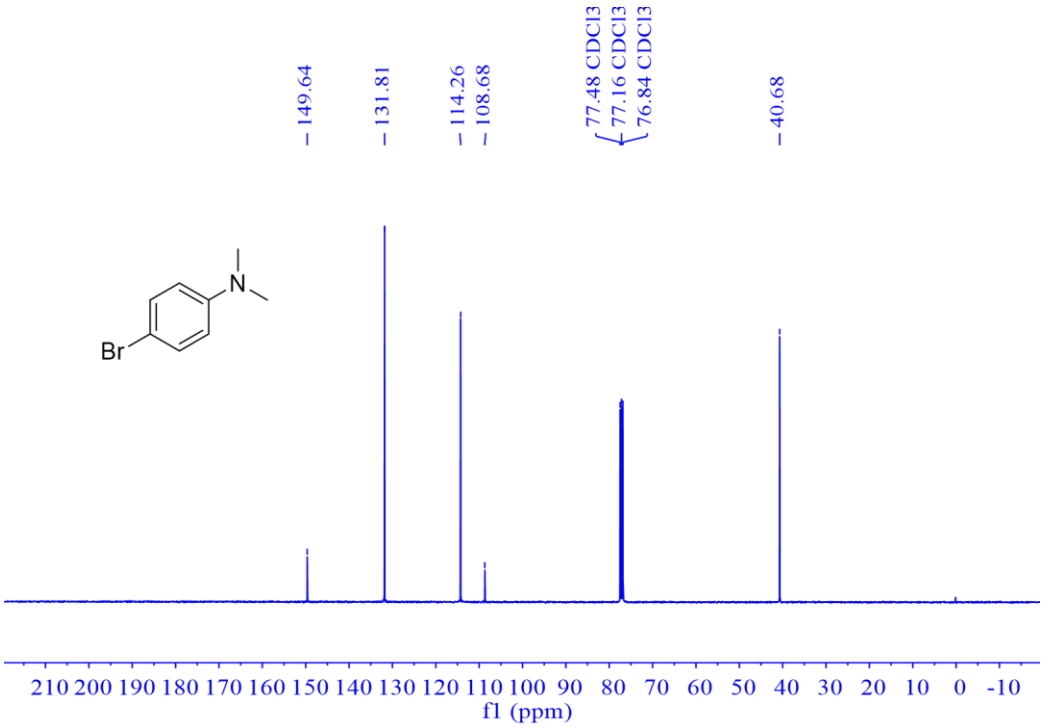


Figure S26. ^{13}C NMR of 4-bromo-N,N-dimethylaniline at 293.15 K in $CDCl_3$ (400 MHz).

7. GC-MS spectra of products

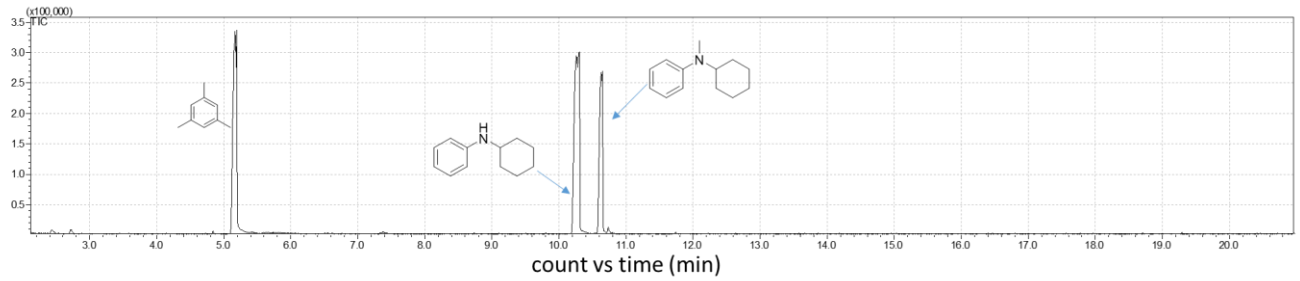


Figure S27. N-methylation of 4-aminothioanisole with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

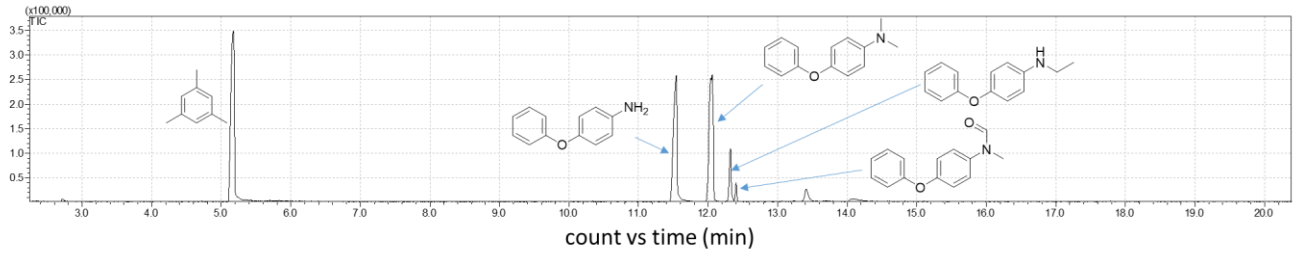


Figure S28. N-methylation of 4-phenoxyaniline with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

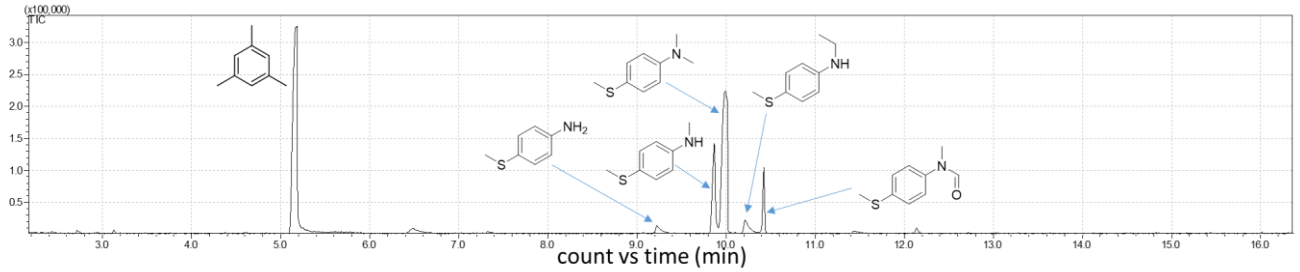


Figure S29. N-methylation of 4-aminothioanisole with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

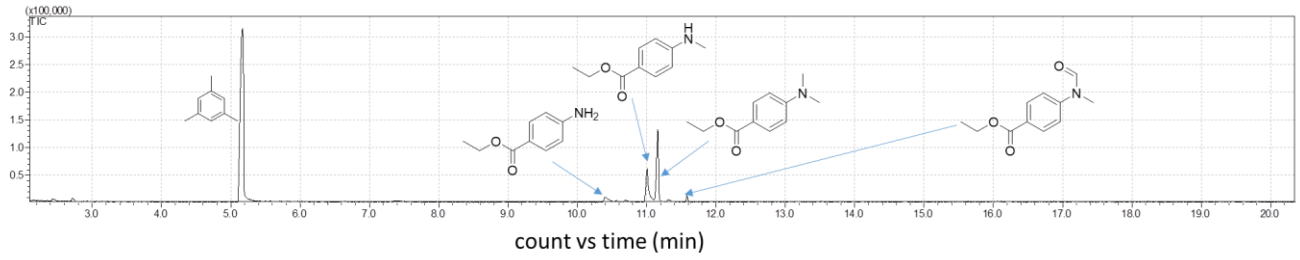


Figure S30. N-methylation of benzocaine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

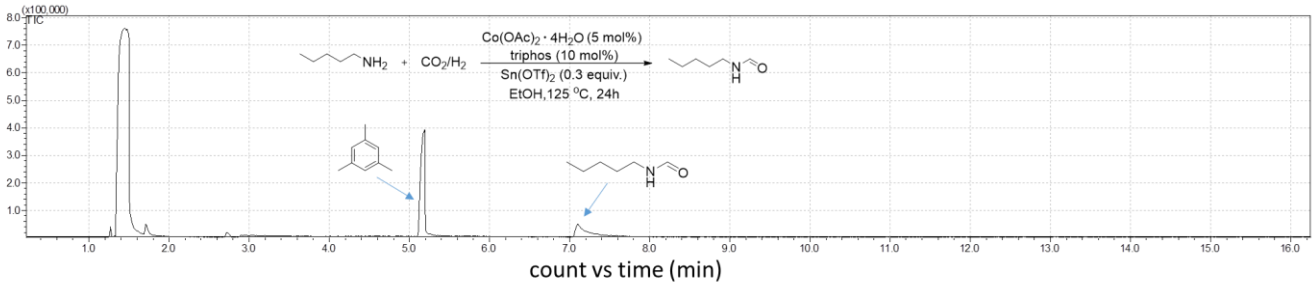


Figure S31. N-formylation of *n*-amylamine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

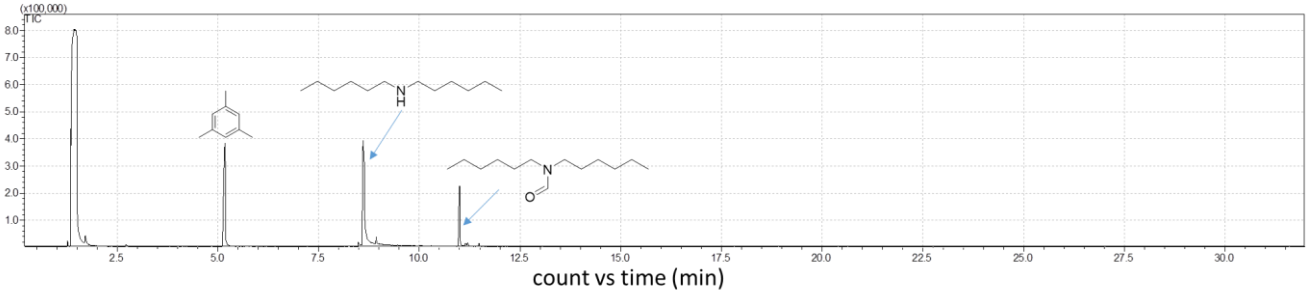


Figure S32. N-formylation of *n*-hexyl-1-hexanamine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

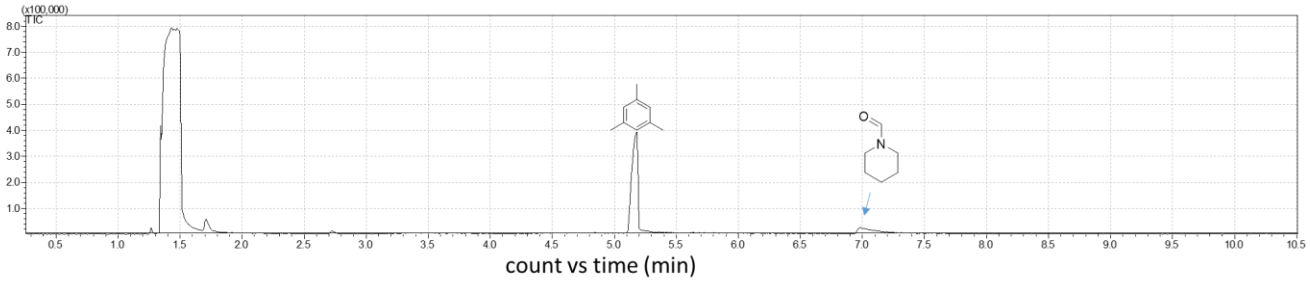


Figure S33. N-formylation of piperidine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

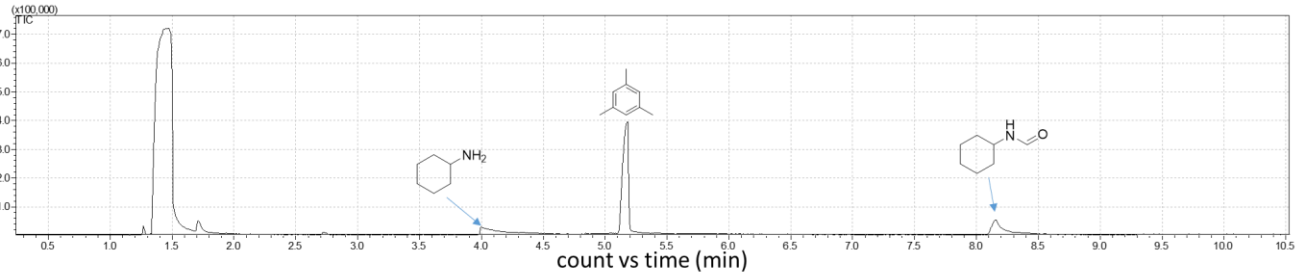


Figure S34. N-formylation of cyclohexylamine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

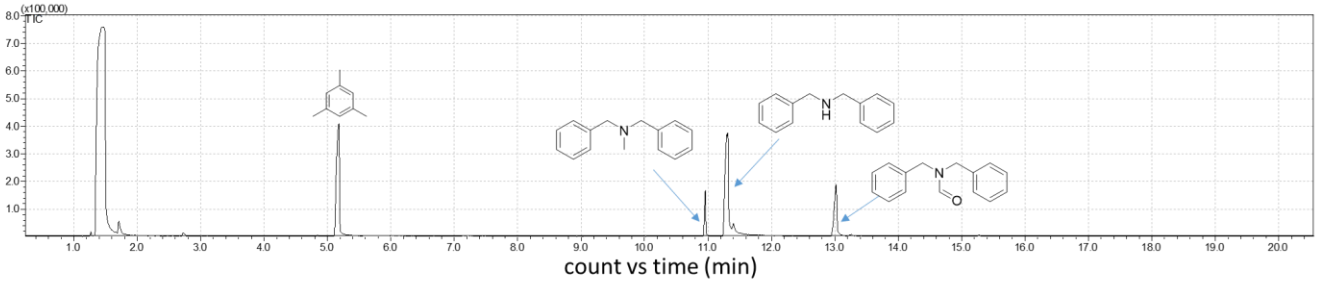


Figure S35. N-formylation of dibenzylamine with CO_2/H_2 over $Co(OAc)_2{\cdot}4H_2O$/triphos/$Sn(OTf)_2$

8. References

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