Supporting Information

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

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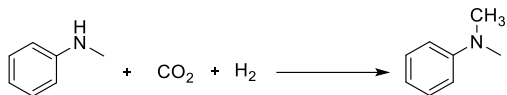b University of Chinese Academy of Sciences, Beijing 100049, China.

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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)$_2$·4H$_2$O/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-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$_2$O$_3$ (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-ZnO/TiO$_2$ (2.8 mol%)	-	toluene	1.5	4.5	180	24	87	31.07	1.29	[9]
Co(OAc)$_2$·4H$_2$O/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
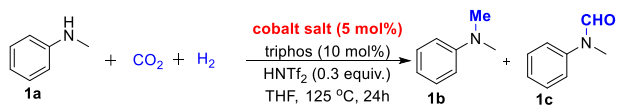
Entry	Cobalt salt	Yield of **1b** (%)	Yield of **1c** (%)
1	-	<1	<1
2 [b]	Co(OAc)$_2$·4H$_2$O	<1	<1
3	CoF$_3$	1	<1
4	Co(acac)$_3$	35	<1
5	K$_3$[Co(CN)$_6$]	<1	<1
6	CoF$_2$	2	2
7	Co(ClO$_4$)$_2$·6H$_2$O	3	<1
8	Co(BF$_4$)$_2$·6H$_2$O	19	<1
9	Co(acac)$_2$·2H$_2$O	20	<1
10	Co(OAc)$_2$·4H$_2$O	52	<1

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 ^{o}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
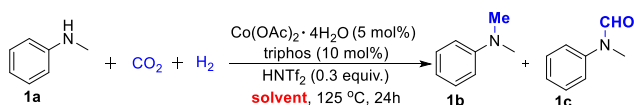
Entry	Solvent	Yield of **1b** (%)	Yield of **1c** (%)
1	*n*-heptane	12	<1
2	toluene	19	<1
3	1,4-dioxane	49	<1
4	EtOH	70	2
5	THF	52	<1
6	CH$_3$CN	2	<1
7	DMF	19	10

Reaction condition: **1a** (1.0 mmol), Co(OAc)$_2$·4H$_2$O (5 mol %), triphos (10 mol %), HNTf$_2$ (0.3 equiv.), solvent (2 mL), CO$_2$ (2.0 MPa), H$_2$ (7.0 MPa), 125 ^{o}C, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

Table S4. Optimization of additive
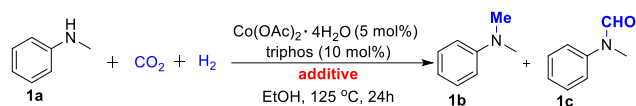
Entry	Additive (equiv.)	Yield of **1b** (%)	Yield of **1c** (%)
1	-	<1	<1
2	MSA/0.3	6	3
3	TMA/0.3	58	3
4	$HNTf_2$/0.3	70	2
5	$Al(OTf)_2$/0.3	68	<1
6	$Yb(OTf)_2$/0.3	76	<1
7	$Sn(OTf)_2$/0.3	82	1
8	K_2CO_3/0.3	<1	<1
9	$Sn(OTf)_2$/0.1	37	<1
10	$Sn(OTf)_2$/0.2	70	5
11	$Sn(OTf)_2$/0.4	75	<1
13	$Sn(OTf)_2$/0.5	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 ºC, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

Table S5. Optimization of pressure
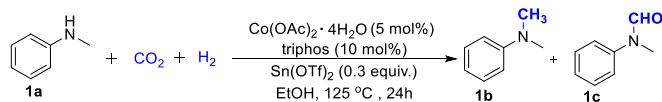
Entry	CO_2 (MPa)	H_2 (MPa)	Yield of **1b** (%)	Yield of **1c** (%)
1	2	7	82	1
2	1	7	40	<1
3	2	3	50	3

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 ºC, 24 h. The yield of products was determined by GC, calibrated using *n*-dodecane as the internal standard.

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Table S6. Optimization of reaction temperature
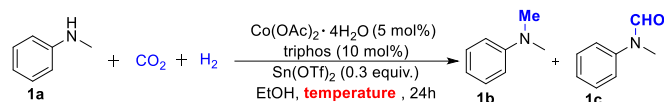
Entry	temperature (°C)	Yield of **1b** (%)	Yield of **1c** (%)
1	95	18	8
2	105	31	7
3	115	51	6
4	125	82	1
5	135	76	<1
6	145	73	<1
7	155	59	<1
8	165	39	<1

Reaction condition: **1a** (1.0 mmol), Co(OAc)$_2$·4H$_2$O (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
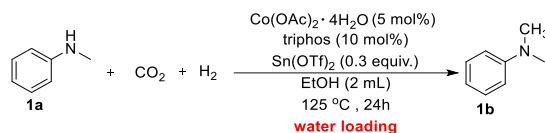
Entry	Water (equiv.)	Yield of **1b** (%)
1	500 mg 4Å	16
2	0	82
3	1	80
4	5	70

Reaction condition: **1a** (1.0 mmol), Co(OAc)$_2$·4H$_2$O (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
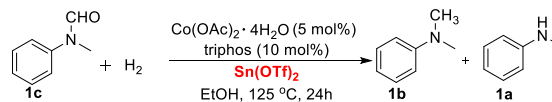
Entry	Sn(OTf)$_2$ (equiv.)	Con. (%)	Yield of **1b** (%)
1	0	5	0.2
2	0.1	76	63
3	0.3	100	72
8	0.5	100	52

Reaction condition: **1c** (1.0 mmol), Co(OAc)$_2$·4H$_2$O (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
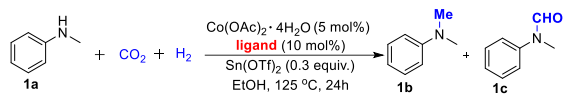
entry	ligand	Con. (%)	Yield of **1b** (%)
1	PP_3	0	0
2	Xantphos	0	0
3	PPh$_3$	0	0

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.
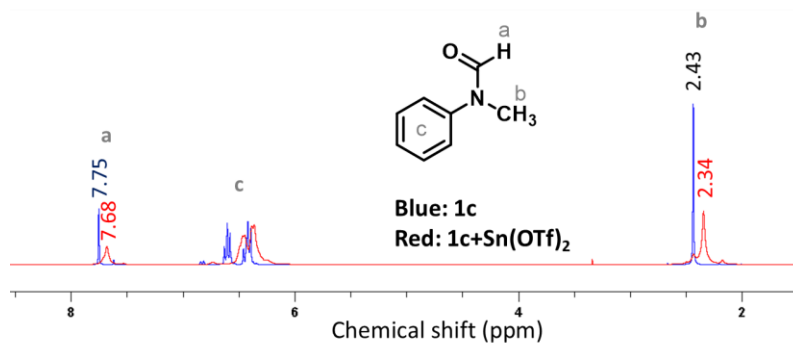
Figure S1. ¹H NMR spectra of **1c** and the mixture of Sn(OTf)₂ and **1c**.
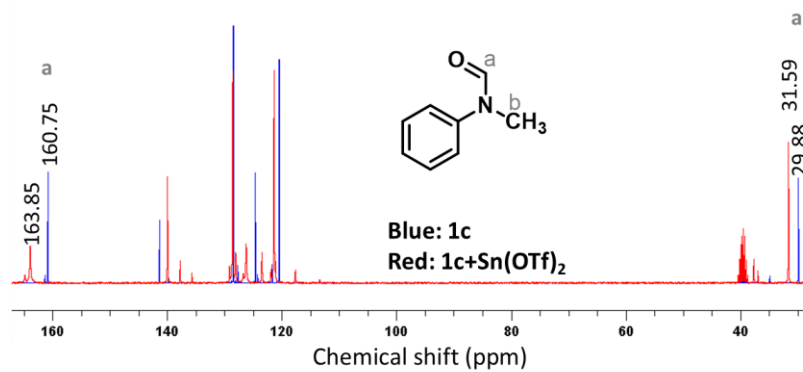
Figure S2. ¹³C NMR spectra of **1c** and the mixture of Sn(OTf)₂ and **1c**.
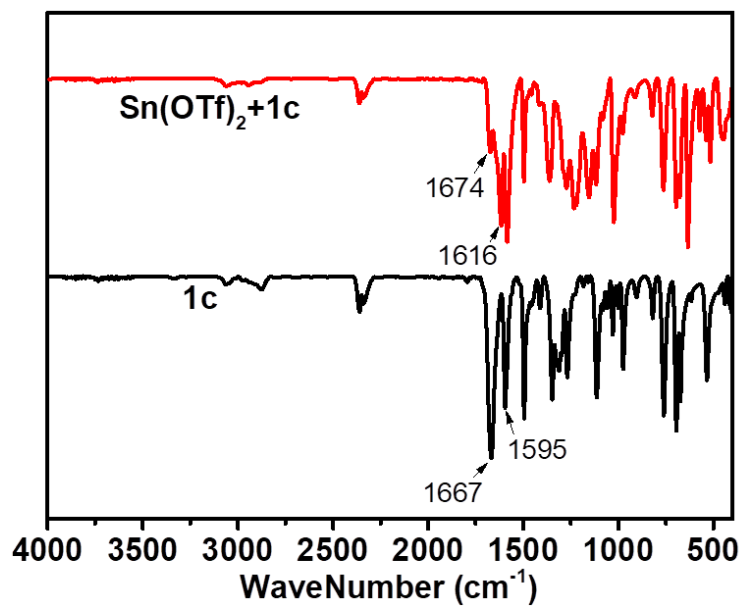
Figure S3. FTIR spectra of **1c** and the mixture of $Sn(OTf)_2$ and **1c**.

4. Mechanism investigation

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

Typical procedures: Co(OAc)$_2$·4H$_2$O (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.
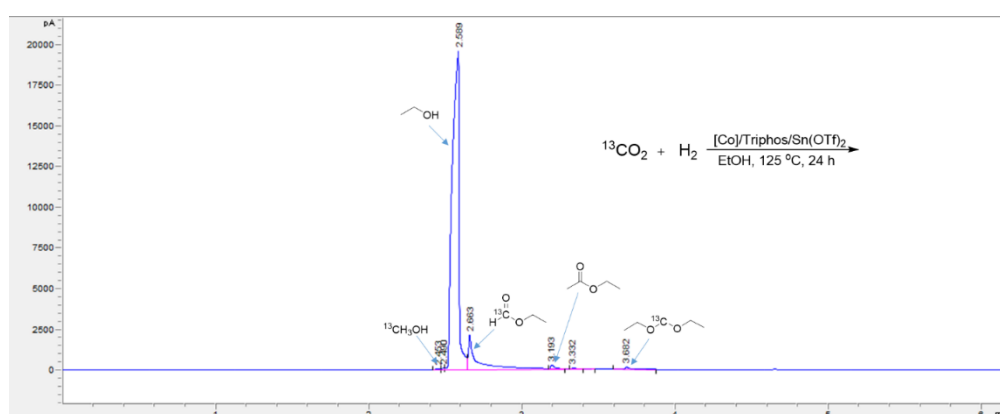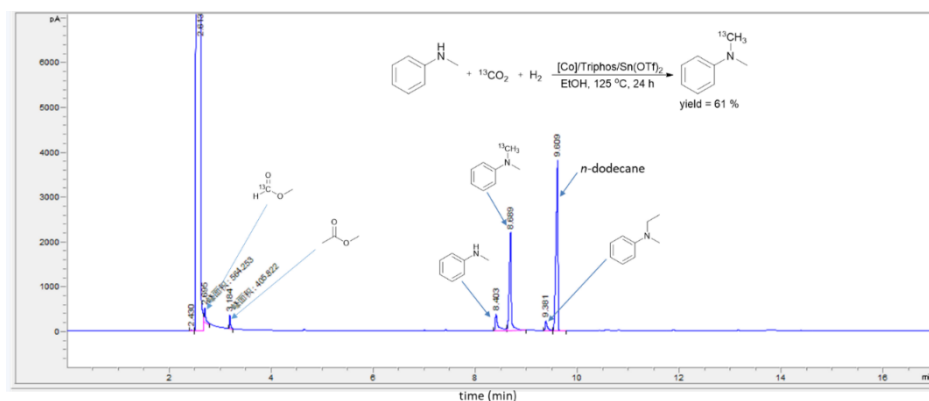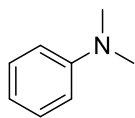

Figure S4. GC spectra of **reaction I, Scheme 2**.
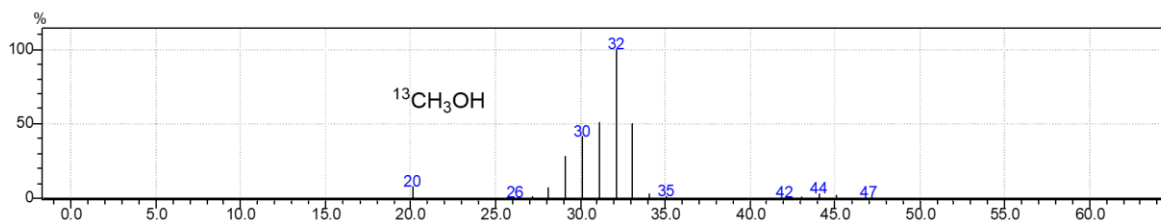
Figure S5. MS spectrum of ^{13}CH$_3$OH in **reaction I, Scheme 2**.
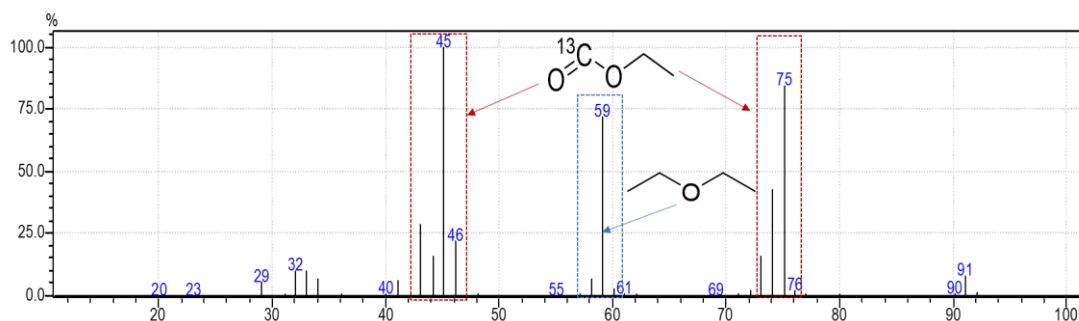
Figure S7. MS spectrum of EtO^{13}CH$_2$OEt in **reaction I, Scheme 2.**

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$_2$OEt	3
4	4e reduction	HCHO	5
5	6e reduction	CH$_3$OH	2

Reaction conditions: [a] N-methylaniline (1.0 mmol), intermediate (10 mmol), Co(OAc)$_2$·4H$_2$O (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)$_2$·4H$_2$O (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.
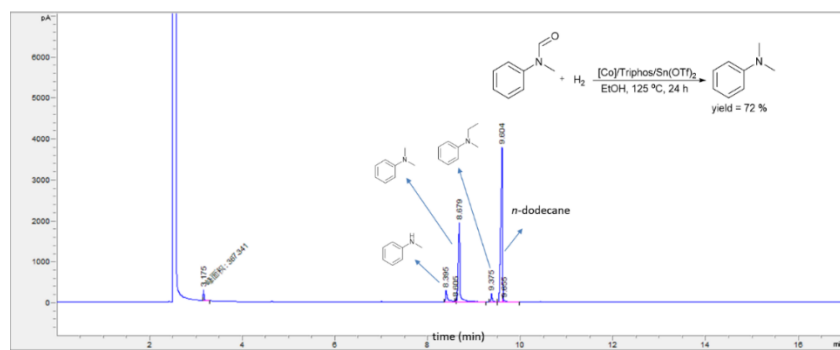
**Figure S8.** GC spectrum of cobalt catalyzed N-formamide reduction reaction.

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

Typical procedures: **1a** (1.0 mmol), Co(OAc)$_2$·4H$_2$O (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$_8$H$_{12}$N [M+H]$^+$: 122.0964, found: 122.0965.
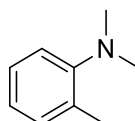
N,N,2-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 2H), 7.12 - 7.06 (m, 1H), 7.00 (m, 1H), 2.75 (s, 6H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.87, 132.25, 131.27, 126.55, 122.69, 118.49, 77.48, 77.16, 76.84, 44.35, 18.47. HR-MS (ESI) calculated for C$_9$H$_{14}$N [M+H]$^+$: 136.1121, found: 136.1122.
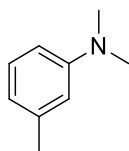
N,N,3-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.15 (m, 1H), 6.66 - 6.59 (m, 3H), 2.98 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.91, 138.81, 129.05, 117.81, 113.63, 110.10, 77.48, 77.16, 76.84, 44.79, 40.80, 22.00. HR-MS (ESI) calculated for C$_9$H$_{14}$N [M+H]$^+$: 136.1121, found: 136.1122.
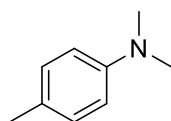
N,N,4-trimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, 2H), 6.80 - 6.69 (m, 2H), 2.94 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.97, 129.71, 126.26, 113.38, 77.48, 77.16, 76.84, 41.18, 20.36. HR-MS (ESI) calculated for C$_9$H$_{14}$N [M+H]$^+$: 136.1121, found: 136.1122.
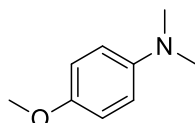
4-methoxy-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.87 - 6.80 (m, 2H), 6.79 - 6.70 (m, 2H), 3.75 (s, 3H), 2.85 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.17, 145.89, 115.04, 114.78, 77.48, 77.16, 76.84, 55.87, 41.93. HR-MS (ESI) calculated for C$_9$H$_{14}$NO [M+H]$^+$: 152.1070, found: 152.1071.
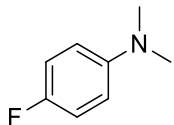
4-fluoro-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 - 6.87 (m, 2H), 6.70 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.6 (C-F, J_{C-F} = 236.2 Hz), 147.7, 115.4 (C-F, J_{C-F} = 22.1 Hz), 114.0 (C-F, J_{C-F} = 7.4 Hz), 41.5. HR-MS (ESI) calculated for C$_8$H$_{11}$FN [M+H]$^+$: 140.0870, found: 140.0871.
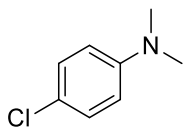
4-chloro-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.13 (m, 2H), 6.71 - 6.59 (m, 2H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.32, 128.94, 121.63, 113.82, 77.48, 77.16, 76.84, 40.80. HR-MS (ESI) calculated for C$_8$H$_{11}$ClN [M+H]$^+$: 156.0575, found: 156.0575.
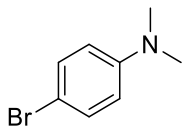
4-bromo-N,N-dimethylaniline. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.27 (m, 2H), 6.70 - 6.50 (m, 2H), 2.93 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.64, 131.81, 114.26, 108.68, 77.48, 77.16, 76.84, 40.68. HR-MS (ESI) calculated for C$_8$H$_{11}$BrN [M+H]$^+$: 200.0069, found: 200.0071.

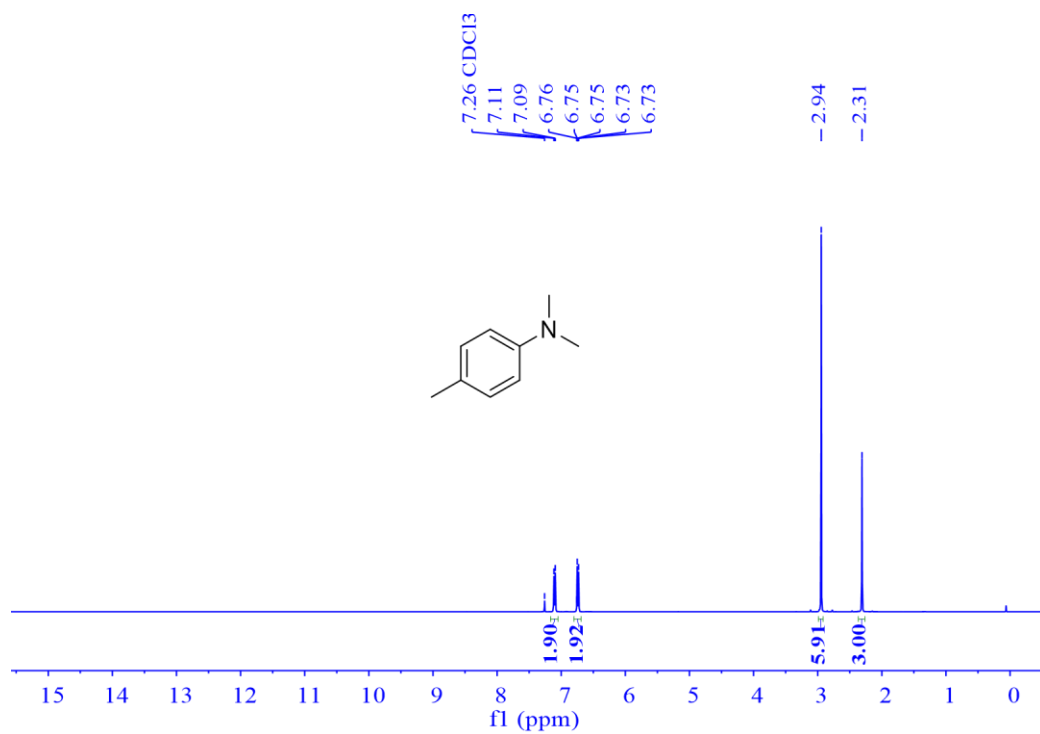## 6. ¹H and ¹³C NMR spectra of products
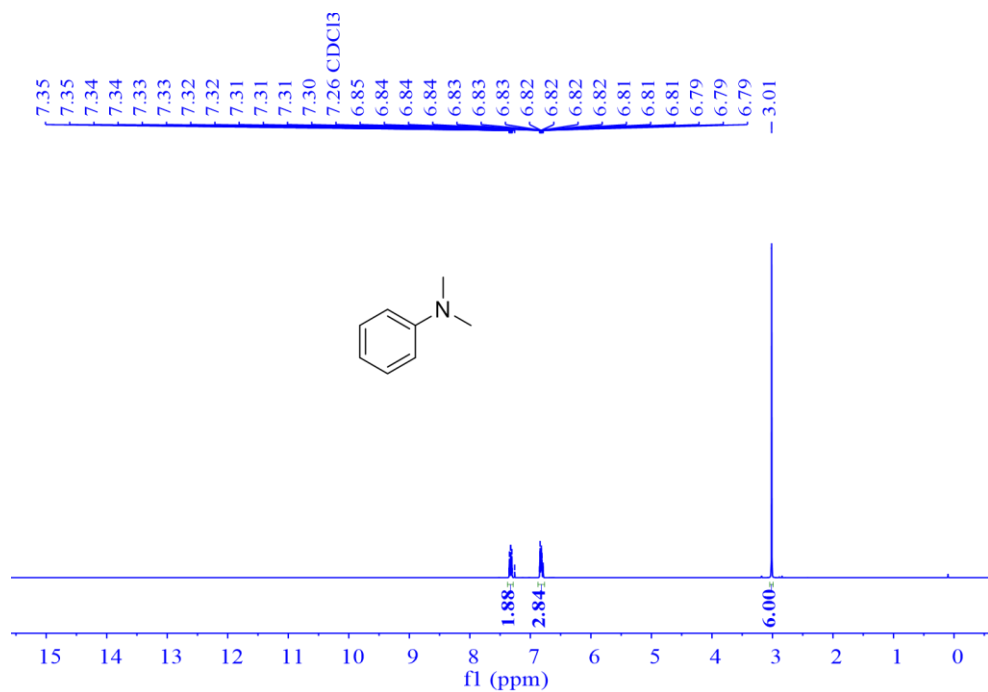
Figure S11. ¹H NMR of N,N-dimethylaniline at 293.15 K in CDCl₃ (400 MHz).
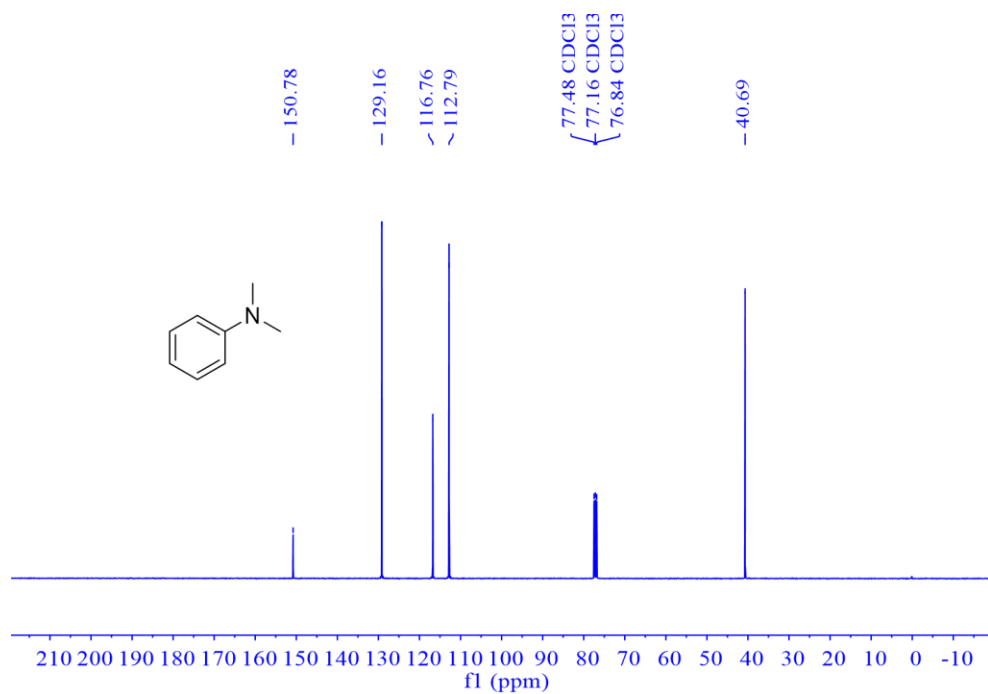
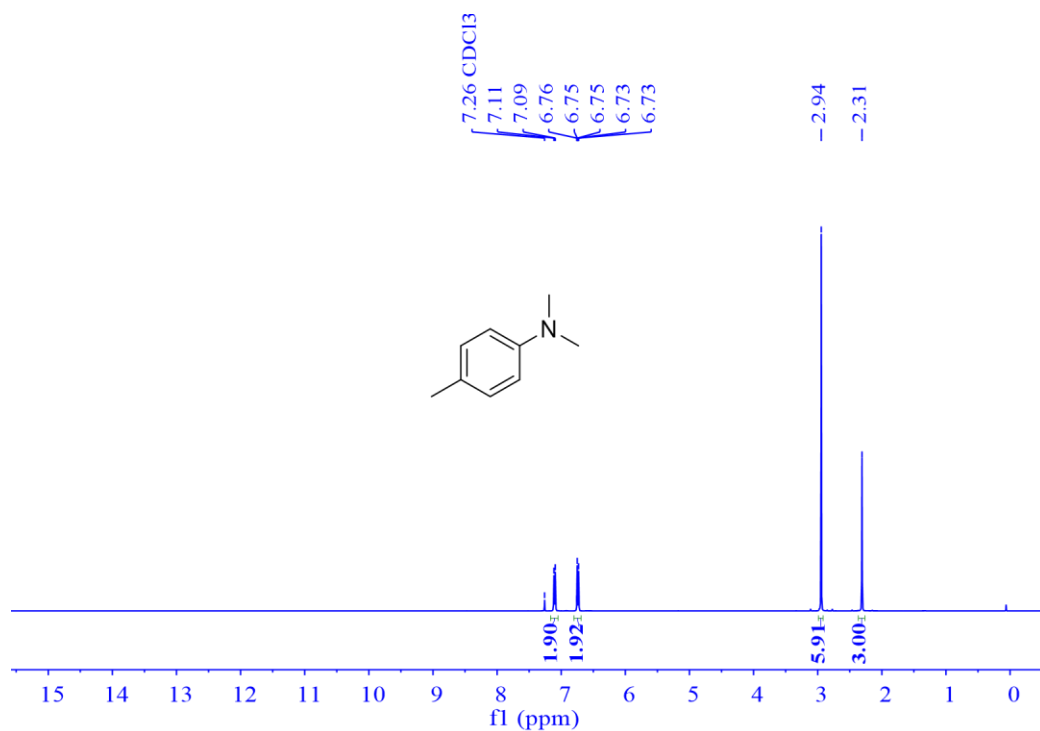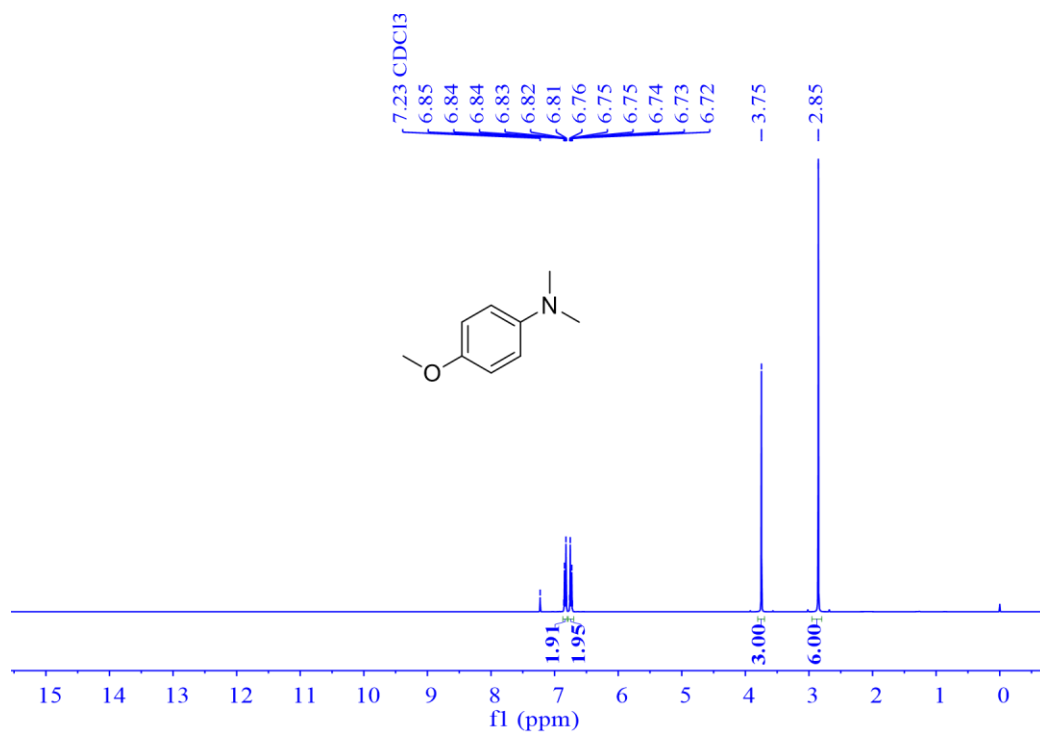**Figure S12.** ¹³C NMR of N,N-dimethylaniline at 293.15 K in CDCl₃ (400 MHz).
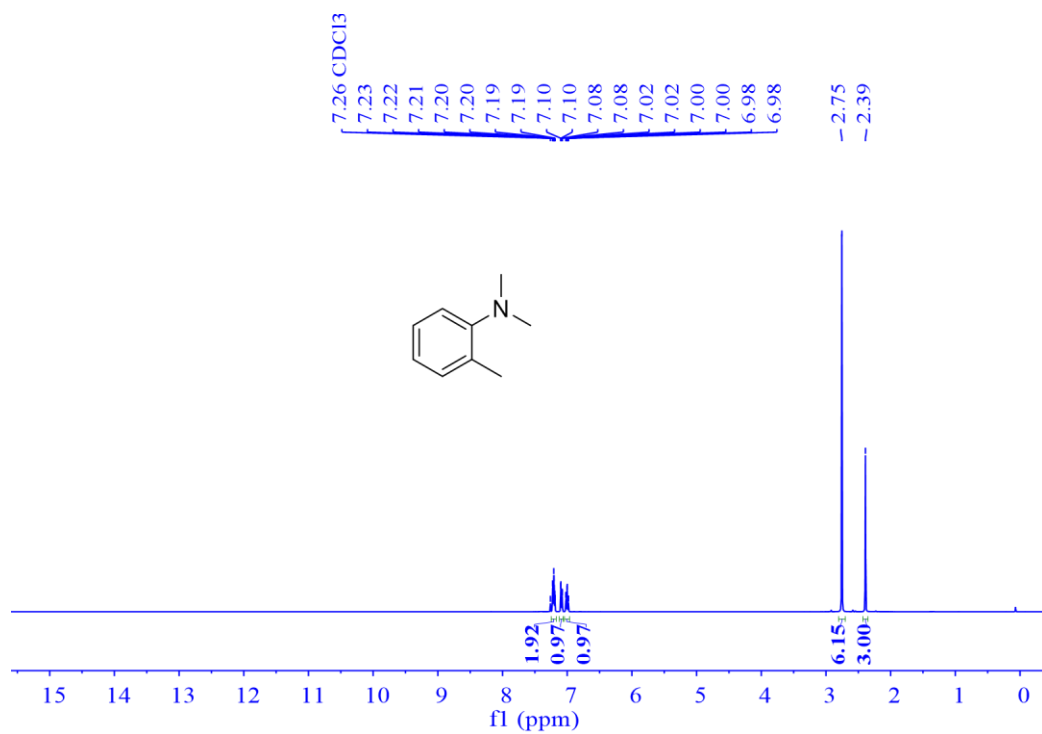
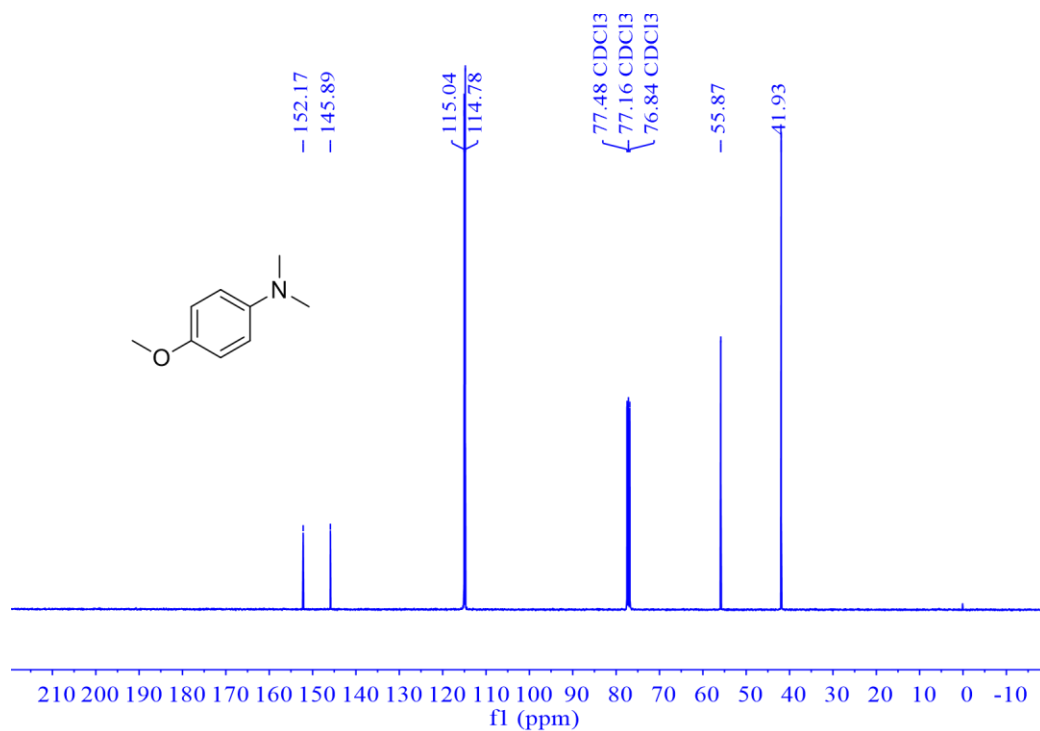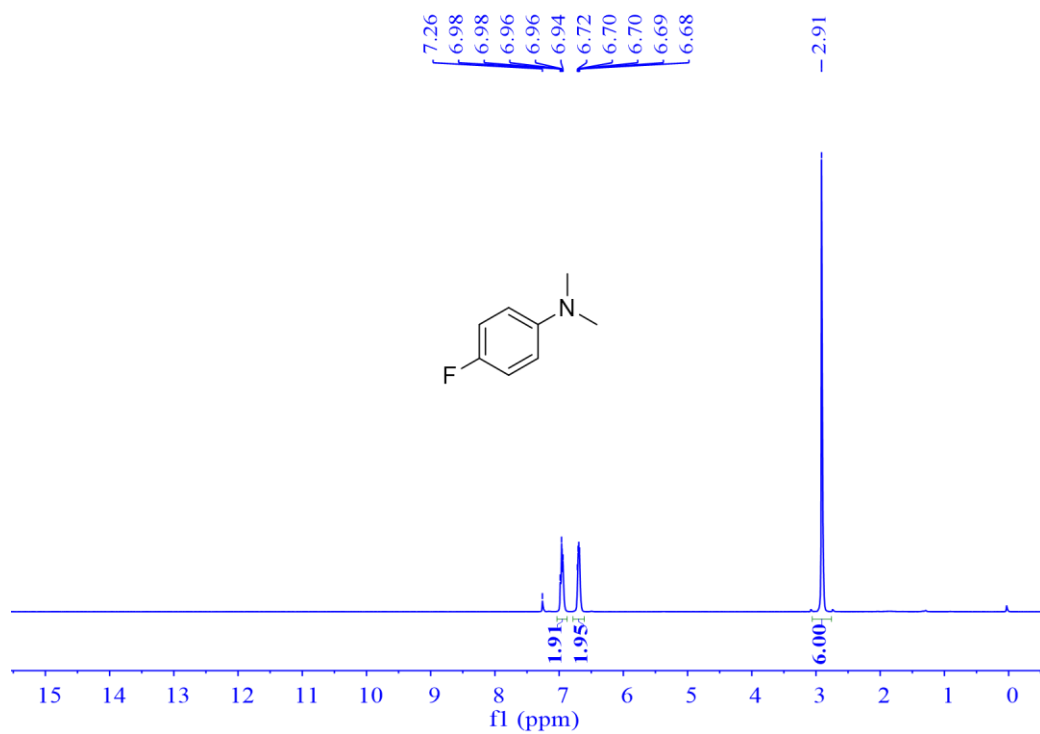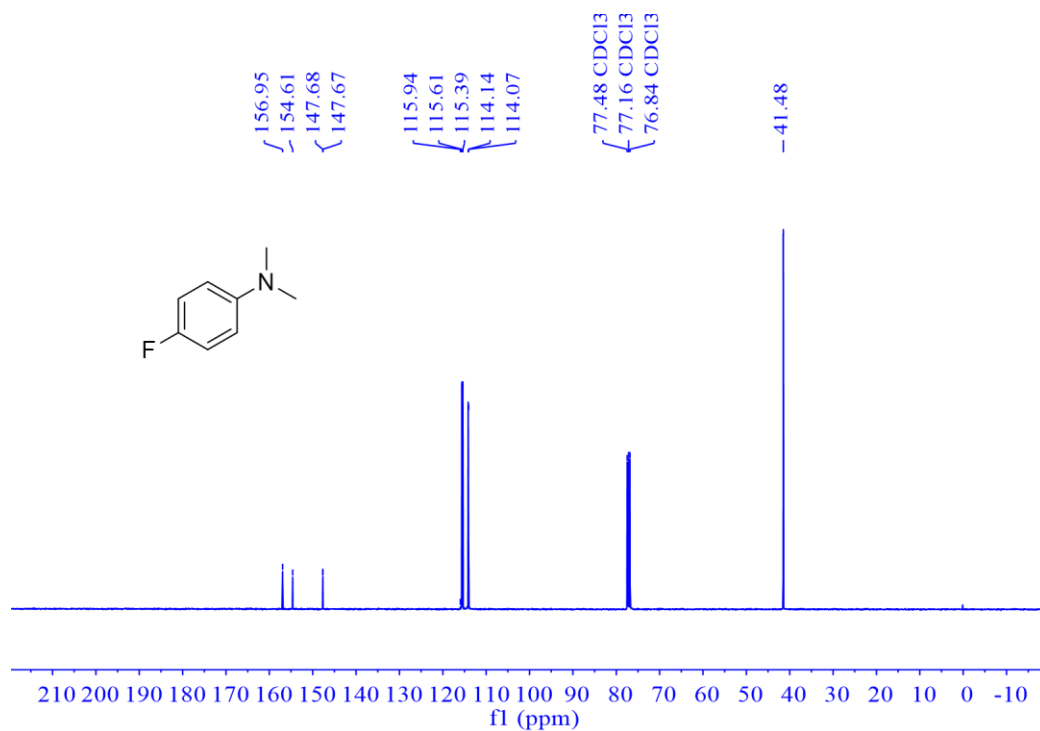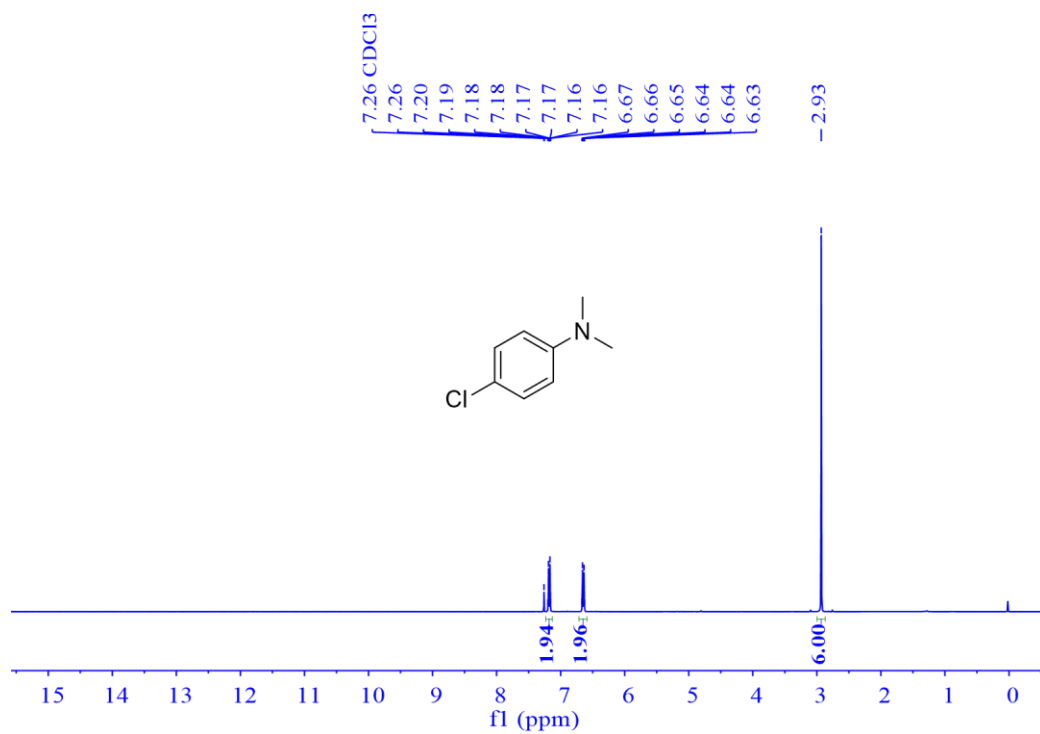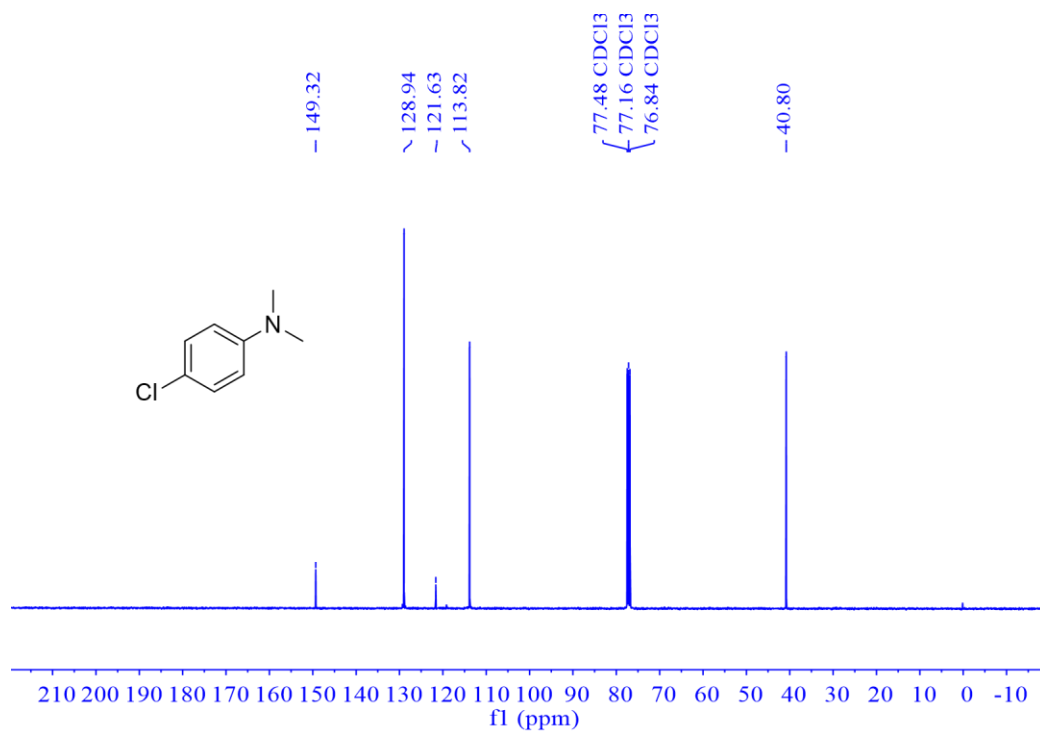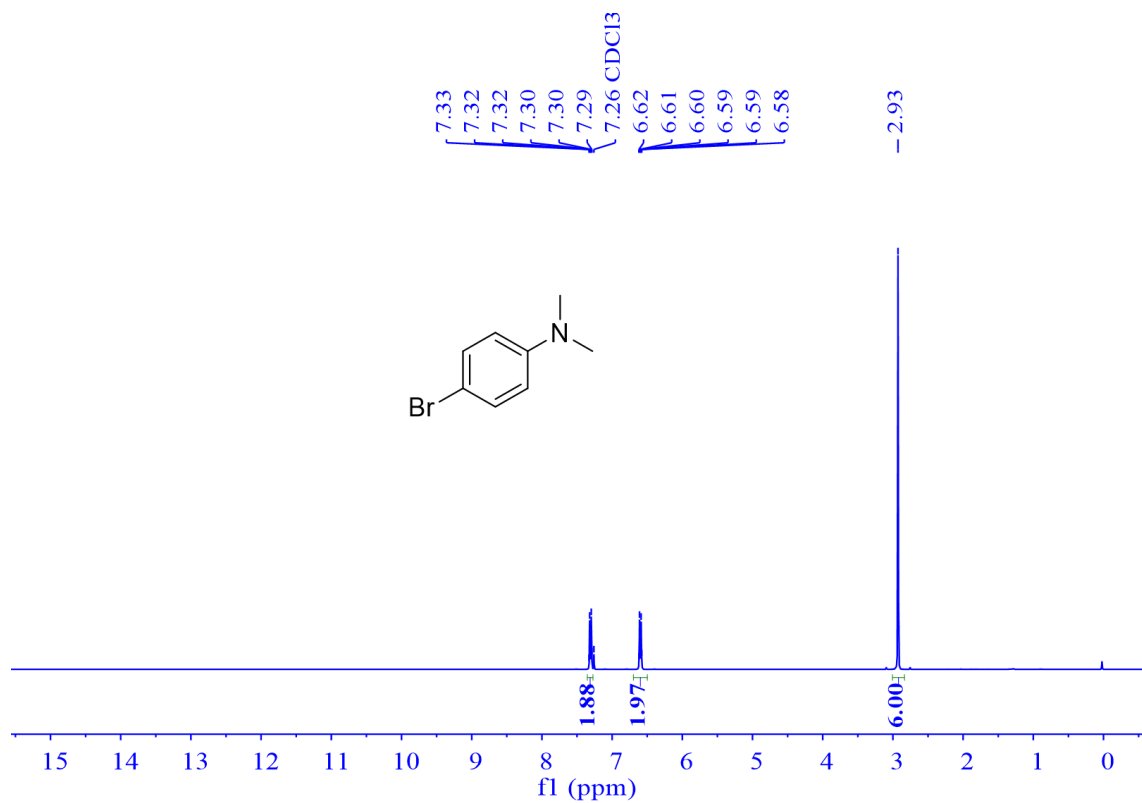**Figure S13.** ^{1}H NMR of N,N,2-trimethylaniline at 293.15 K in CDCl$_3$ (400 MHz).
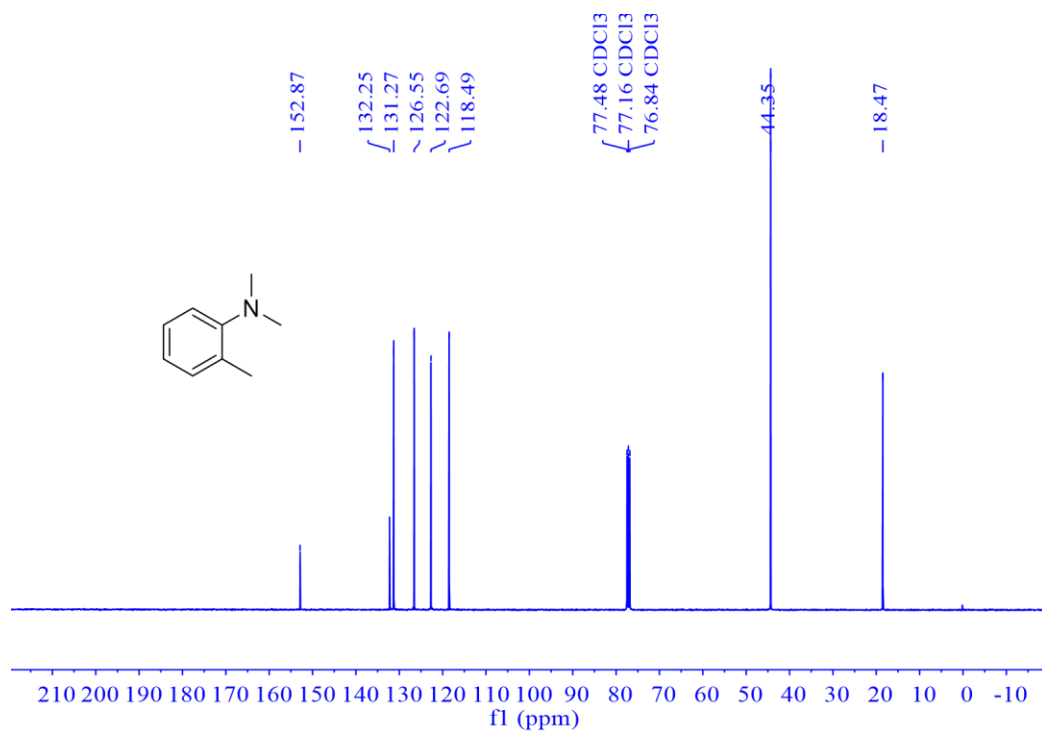
Figure S14. ^{13}C NMR of N,N,2-trimethylaniline at 293.15 K in CDCl$_3$ (400 MHz).
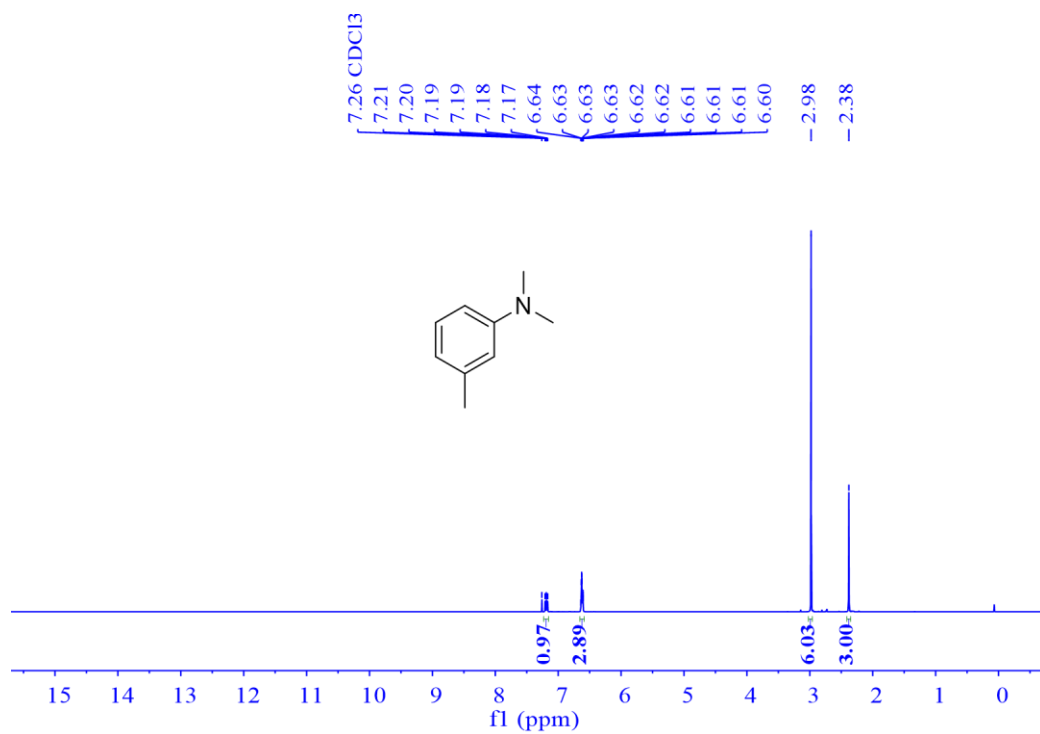
Figure S15. ^{1}H NMR of N,N,3-trimethylaniline at 293.15 K in CDCl$_3$ (400 MHz).
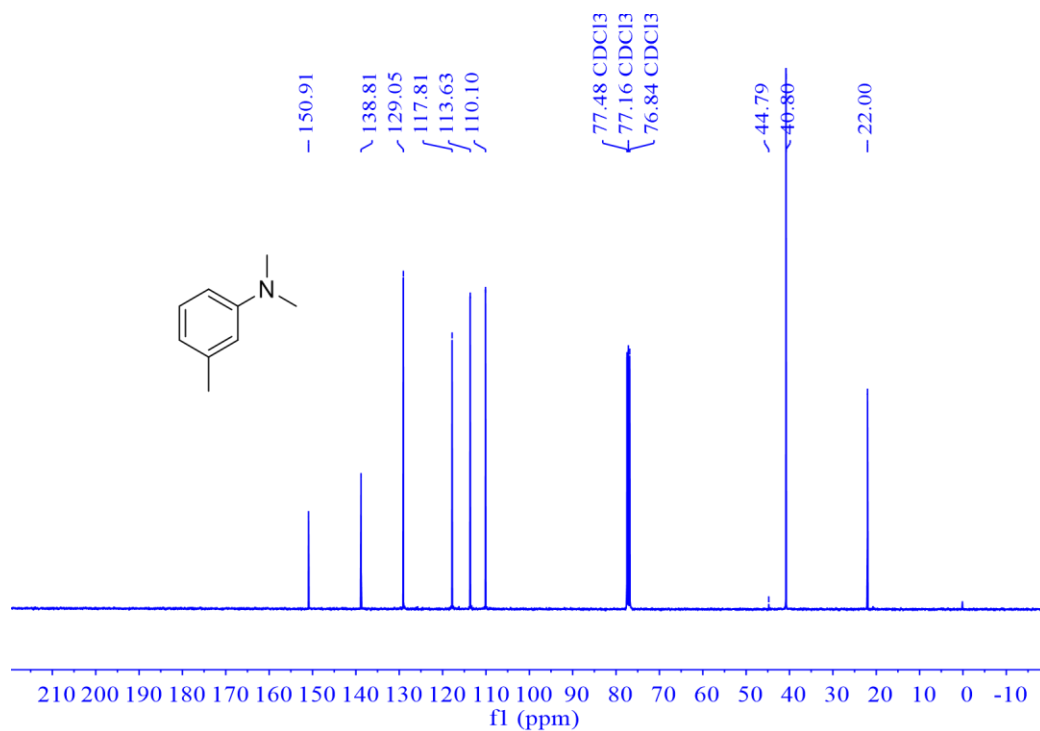
Figure S16. ^{13}C NMR of N,N,3-trimethylaniline at 293.15 K in CDCl$_3$ (400 MHz).

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. ^1H 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. ¹H NMR of 4-bromo-N,N-dimethylaniline at 293.15 K in CDCl₃ (400 MHz).
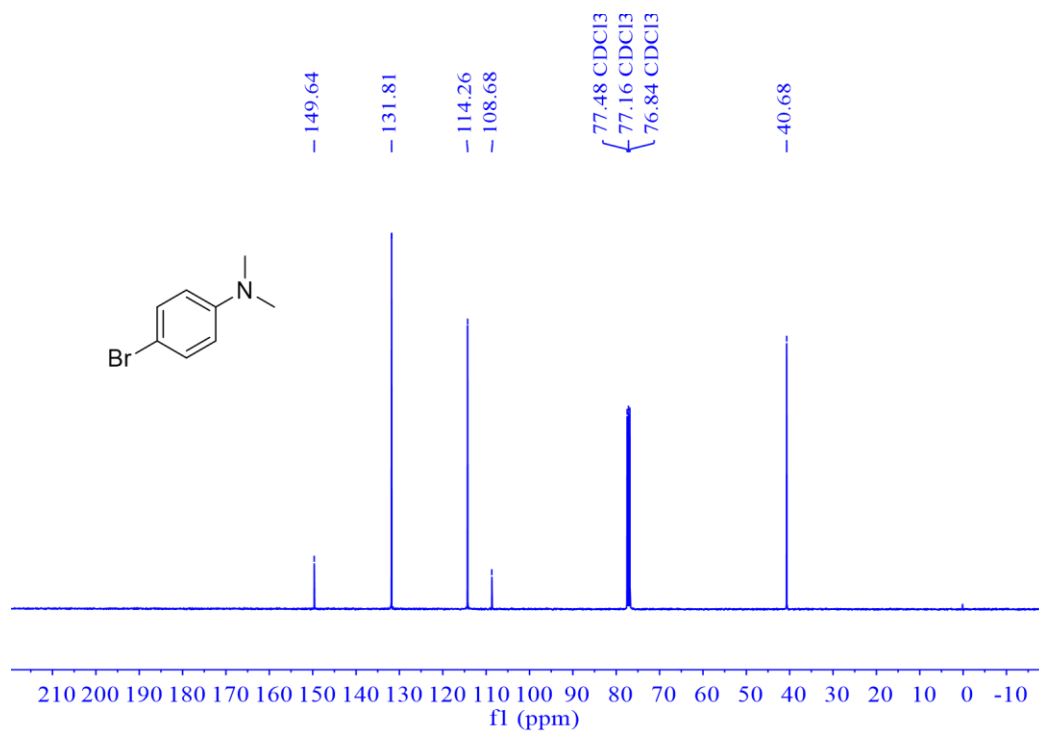
Figure S26. ¹³C NMR of 4-bromo-N,N-dimethylaniline at 293.15 K in CDCl₃ (400 MHz).

7. GC-MS spectra of products
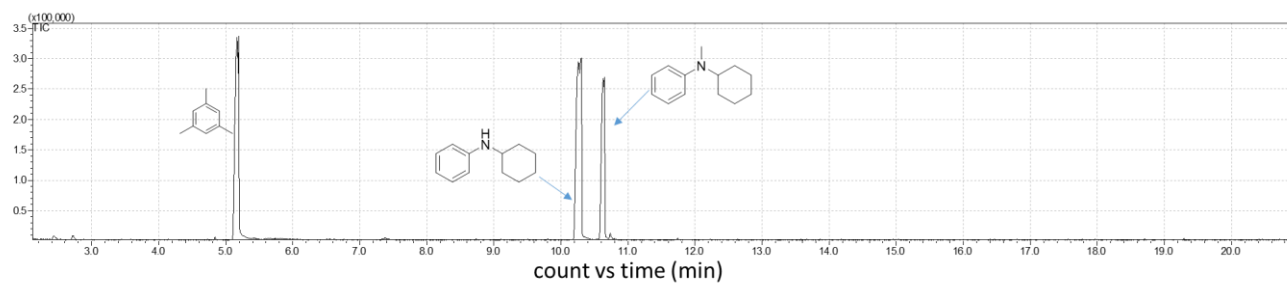
Figure S27. N-methylation of 4-aminothioanisole with CO_2/H_2 over Co(OAc)$_2$·4H$_2$O/triphos/Sn(OTf)$_2$
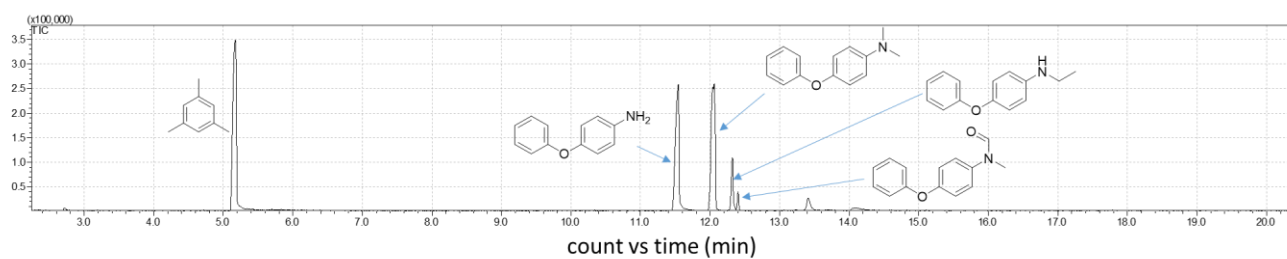
Figure S28. N-methylation of 4-phenoxyaniline with CO_2/H_2 over Co(OAc)$_2$·4H$_2$O/triphos/Sn(OTf)$_2$
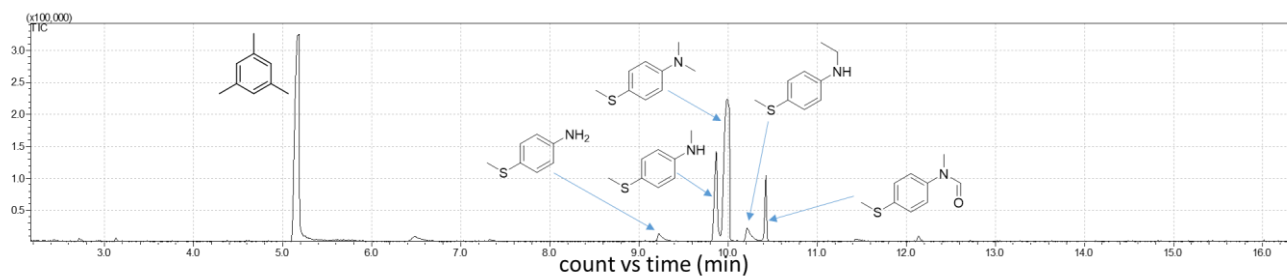
Figure S29. N-methylation of 4-aminothioanisole with CO_2/H_2 over Co(OAc)$_2$·4H$_2$O/triphos/Sn(OTf)$_2$
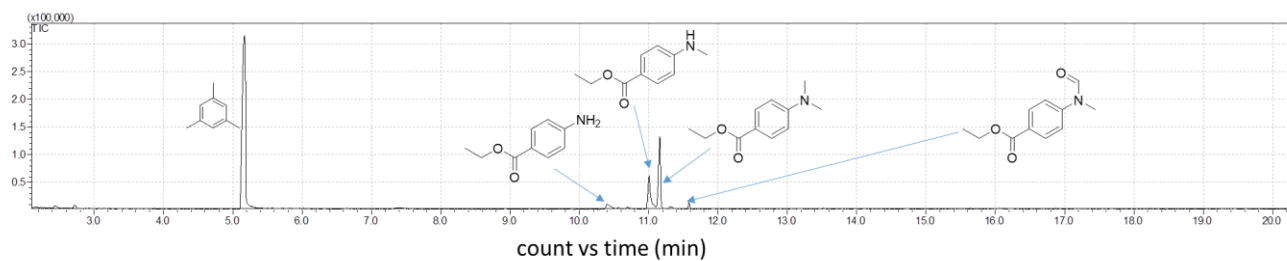
Figure S30. N-methylation of benzocaine with CO_2/H_2 over Co(OAc)$_2$·4H$_2$O/triphos/Sn(OTf)$_2$
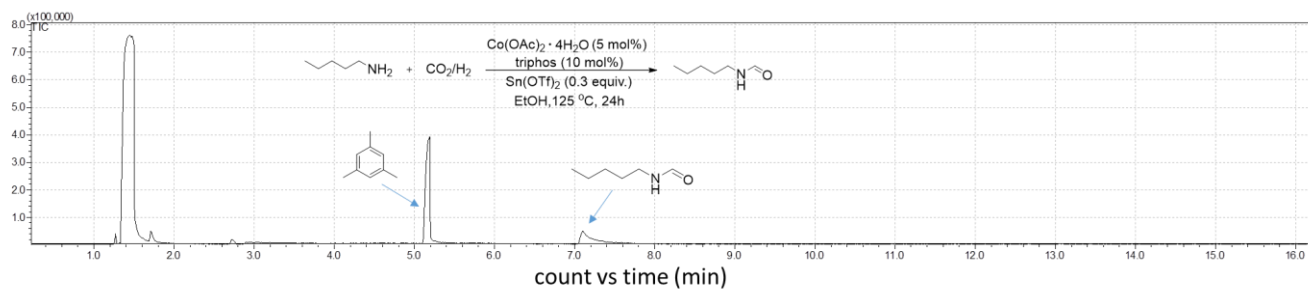
Figure S31. N-formylation of *n*-amylamine with CO_2/H_2 over $Co(OAc)_2 \cdot 4H_2O$/triphos/$Sn(OTf)_2$
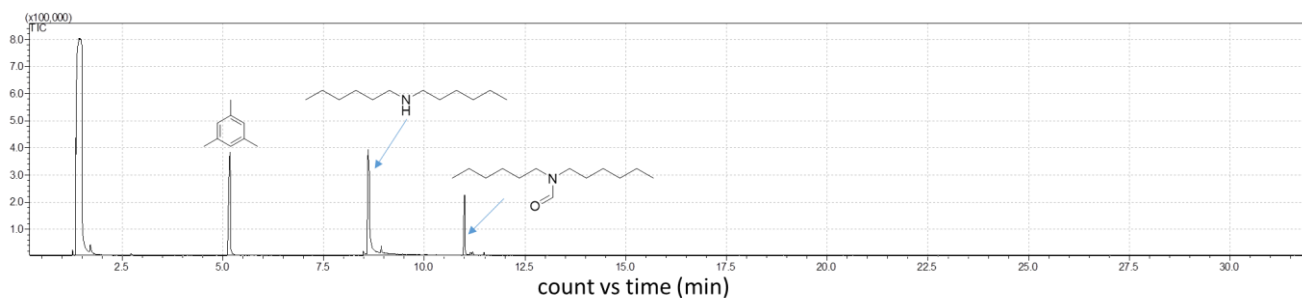
Figure S32. N-formylation of *n*-hexyl-1-hexanamine with CO_2/H_2 over $Co(OAc)_2 \cdot 4H_2O$/triphos/$Sn(OTf)_2$
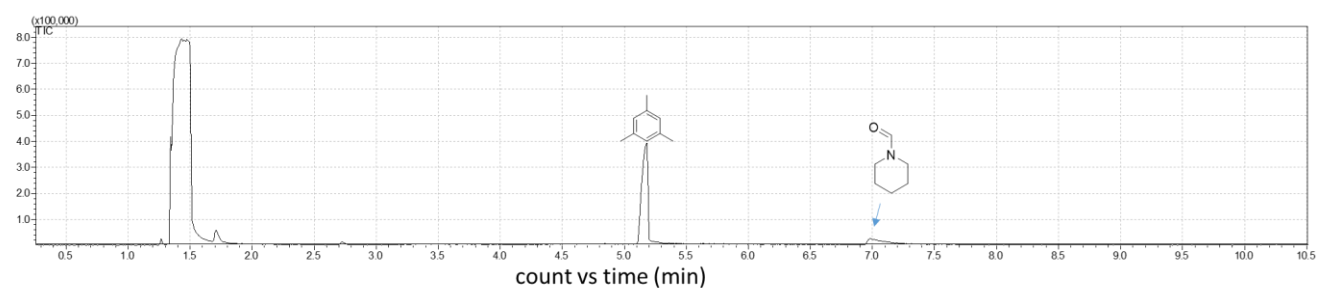
Figure S33. N-formylation of piperidine with CO_2/H_2 over $Co(OAc)_2 \cdot 4H_2O$/triphos/$Sn(OTf)_2$
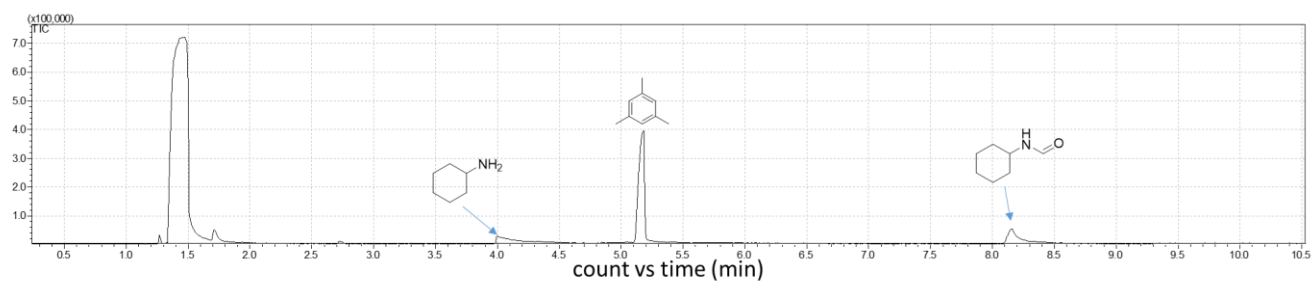
Figure S34. N-formylation of cyclohexylamine with CO_2/H_2 over $Co(OAc)_2 \cdot 4H_2O$/triphos/$Sn(OTf)_2$
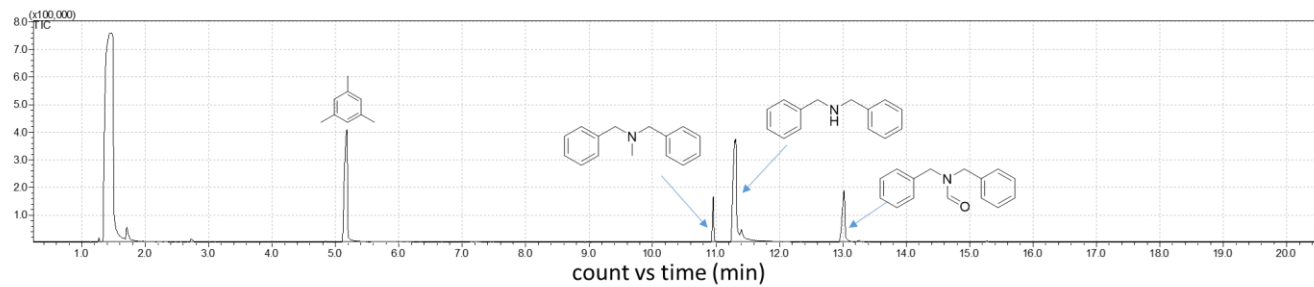
Figure S35. N-formylation of dibenzylamine with CO_2/H_2 over $Co(OAc)_2 \cdot 4H_2O$/triphos/$Sn(OTf)_2$

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