Supporting Information

Chemodivergent coupling of azoarenes with benzyl alcohols via borrowing hydrogen strategy using a well-defined nickel catalyst

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Contents

1.   General Experimental

All the manipulations were conducted under an argon atmosphere either in a glove box or using standard Schlenk techniques in pre-dried glasswares. The catalytic reactions were performed in oven-dried Schlenk tubes with magnetic bar. Solvents were dried over Na/benzophenone or Mg and distilled prior to use. Liquid reagents were flushed with argon prior to use. The ligand precursor 6-methoxy-2,2'-bipyridine[S1] and ligand 6-hydroxy-2,2'-bipyridine[S2] were prepared according to the previously described procedures. Deuterated benzyl alcohol was prepared following the literature procedure with 92.5% deuteration.[S3] All other chemicals were obtained from commercial sources and were used without further purification. High resolution mass spectrometry (HRMS) mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. NMR: (^{1}H and ^{13}C{^{1}H}) spectra were recorded at 200, 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C{^{1}H}), DEPT (distortionless enhancement by polarization transfer)}, respectively, in CDCl$_3$ solutions, if not otherwise specified; chemical shifts (δ) are given in ppm. The ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to residual solvent signals (CDCl$_3$: δ H = 7.26 ppm, δ C{^{1}H} = 77.2 ppm). The ^{1}H NMR yields were calculated using CH$_2$Br$_2$ as internal standard.

2.   Procedure for Synthesis of Nickel Complexes
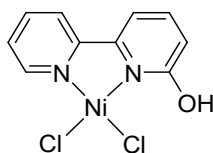
Synthesis and Characterization of Ni-1: A 50 mL Schlenk flask was charged with (DME)NiCl$_2$ (0.20 g, 0.91 mmol) and 6-hydroxy-2,2'-bipyridine (0.157 g, 0.91 mmol), and methanol (10 mL) was added into it under argon atmosphere. The reaction mixture was stirred at room temperature for 24 h, during which a green clear solution was formed. Methanol was evaporated under *vacuo* and the resulted green solid was washed with Et$_2$O (10 mL x 2). The solid compound was dried under *vacuo* to obtain **Ni-1** as green compound. Yield: 0.231 g (84%). Anal. Calcd for C$_{10}$H$_8$Cl$_2$N$_2$ONi.H$_2$O: C, 37.56; H, 3.15; N, 8.76. Found: C, 37.36; H, 2.93; N, 8.26. *Note: A molecule of H$_2$O might have incorporated into complex Ni-1 during the sample preparation.*
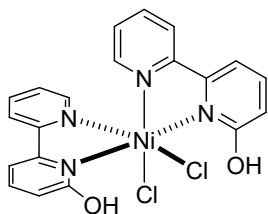
Synthesis and Characterization of Ni-2: A 50 mL Schlenk flask was charged with (DME)NiCl$_2$ (0.10 g, 0.455 mmol) and 6-hydroxy-2,2'-bipyridine (0.158 g, 0.92 mmol), and DCM (10 mL) was added into it under argon atmosphere. The reaction mixture was stirred at room temperature for 24 h, during which a green precipitate was formed. The reaction mixture was filtered and washed with CH$_2$Cl$_2$ (8 mL x 3). The solid was dried under vacuum to obtain compound **Ni-2**. Yield: 0.170 g (79%). Anal. Calcd for C$_{20}$H$_{16}$Cl$_2$N$_4$O$_2$Ni: C, 50.68; H, 3.40; N, 11.82. Found: C, 50.48; H, 3.43; N, 11.71. The molecular structure of **Ni-2** was established by X-ray crystallography.
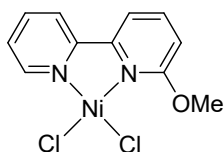
Synthesis and Characterization of Ni-3: A 50 mL Schlenk flask was charged with (DME)NiCl$_2$ (0.10 g, 0.455 mmol) and 6-methoxy-2,2'-bipyridine (0.085 g, 0.455 mmol), and methanol (10 mL) was added into it under argon atmosphere. The reaction mixture was stirred at room temperature for 24 h, during which a dark green clear solution was formed. Methanol was evaporated under *vacuo* and the resulted green solid was washed with Et$_2$O (10 mL x 2). The solid compound was dried under *vacuo* to obtain **Ni-3** as a dark green compound. Yield: 0.141 g (98%). Anal. Calcd for C$_{11}$H$_{10}$Cl$_2$N$_2$NiO.H$_2$O: C, 39.58; H, 3.62; N, 8.39; Found: C, 39.61; H, 3.90; N, 5.36. *Note: A molecule of H$_2$O might have incorporated into complex **Ni-3** during the sample preparation.*

3. Synthesis of 4,4'-dibutoxyazobenzene
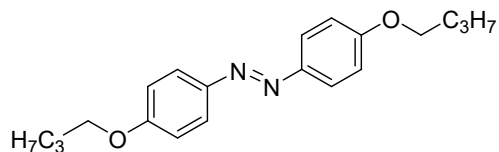
Synthesis of 4,4'-dibutoxyazobenzene (1r): To the mixture of 4-butoxyaniline (1.0 g, 6.05 mmol), CuBr (0.026 g, 0.182 mmol, 3 mol%) and pyridine (0.043 g, 0.545 mmol, 9 mol%) in a round bottom flask, toluene (8 mL) was added. The reaction mixture was stirred at 60 °C for 20 h. At ambient temperature, the volatiles were evaporated under *vacuo* and the crude product was subjected to the column chromatography on silica gel (petroleum ether/EtOAc:30/1) to yield **1r** (0.5 g, 51%) as an orange solid. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.86 (d, J = 9.0 Hz, 4H, Ar–H), 6.99 (d, J = 8.9 Hz, 4H, Ar–H), 4.04 (t, J = 6.5 Hz, 4H, CH$_2$), 1.84-1.77 (m, 4H, CH$_2$), 1.56-1.47 (m, 4H, CH$_2$), 0.99 (t, J = 7.4 Hz, 6H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 161.3 (2C, C$_q$), 147.1 (2C, C$_q$), 124.5 (4C, CH), 114.8 (4C, CH), 68.2 (2C, CH$_2$), 31.4 (2C, CH$_2$), 19.4 (2C, CH$_2$), 14.1 (2C, CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{20}$H$_{26}$N$_2$O$_2$ + H$^+$ [M + H]$^+$ 327.2073; Found 327.2065.

4. Detailed Optimization Study

Table S1. Optimization of Reaction Parameters [a]
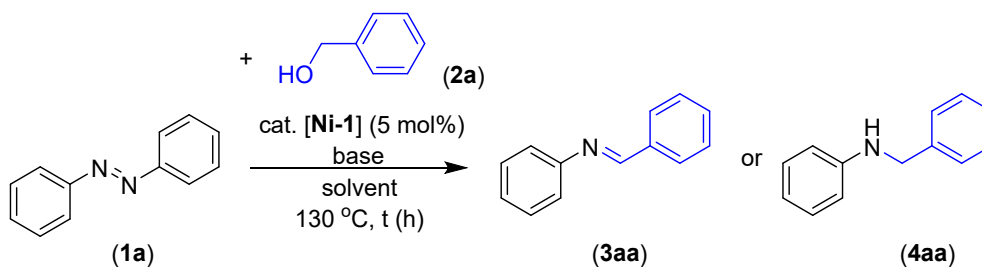
Entry	Equiv of 2a	Base	Equiv of base	Solvent (mL)	t (h)	3aa [b]	4aa [b]
1	2.0	KO^{t}Bu	0.4	--	12	17	--
2	2.0	KO^{t}Bu	0.4	toluene (0.2)	12	78	--
3	2.0	KO^{t}Bu	0.4	^{t}Bu-benzene (0.2)	12	19	--
4	2.0	KO^{t}Bu	0.4	mesitylene (0.2)	12	23	--
5	2.0	KO^{t}Bu	0.4	MeOH (0.2)	12	NR	--
6	2.0	KO^{t}Bu	0.4	EtOH (0.2)	12	NR	--
7	2.0	KO^{t}Bu	0.5	toluene (0.2)	12	63	15
8	2.0	KO^{t}Bu	0.3	toluene (0.2)	12	74	-
9	2.0	LiO^{t}Bu	0.4	toluene (0.2)	12	8	-
10	2.0	NaO^{t}Bu	0.4	toluene (0.2)	12	10	-
11	2.0	K$_2$CO$_3$	0.5	toluene (0.2)	12	68	-
12	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	12	72	-
13	2.0	**K$_2$CO$_3$**	**1.0**	**toluene (0.2)**	**20**	**88** (60)	-
14	2.0	K$_3$PO$_4$	1.0	toluene (0.2)	20	84	-
15	2.0	KOAc	1.0	toluene (0.2)	20	8	-
16	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	16	85	-
17 [c]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	16	-	-
18 [d]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	16	-	-
19 [e]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	16	35	-
20 [f]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	31	-
21 [g]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	9	-
22 [h]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	-	-
23 [i]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	4	-
24 [j]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	17	-
25 [k]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	3	-

26 [l]	2.0	K$_2$CO$_3$	1.0	toluene (0.2)	20	58	-
27	3.5	K$_2$CO$_3$	1.5	toluene (1.0)	24	78	-
28	2.0	KO^{t}Bu	1.0	toluene (0.2)	24	33	37
29	2.0	KO^{t}Bu	1.0	toluene (1.0)	24	15	42
30	3.5	KO^{t}Bu	1.0	toluene (1.0)	24	12	76
31	**3.5**	**KO^{t}Bu**	**1.5**	**toluene (1.0)**	**24**	**-**	**99 (95)**
32	3.5	KO^{t}Bu	1.3	toluene (1.0)	24	2	93
33 [c]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	-	88
34 [d]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	-	-
35 [e]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	9	90
36 [f]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	11	80
37 [g]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	42	53
38 [h]	3.5	KO^{t}Bu	1.5	toluene (1.0)	20	-	-
39 [j]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	42	58
40 [k]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	30	50
41 [l]	3.5	KO^{t}Bu	1.5	toluene (1.0)	24	9	76
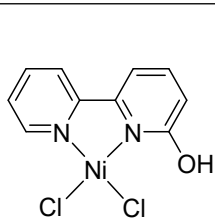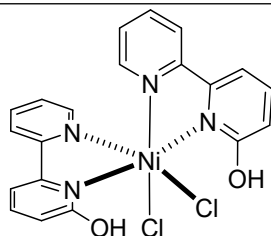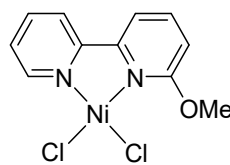
(Ni-1)   (Ni-2)   (Ni-3)

[a] Reaction Conditions: **1a** (0.037 g, 0.203 mmol), [**Ni-1**] (0.003 g, 0.01 mmol, 5 mol%) catalyst. [b] Yield by ^{1}H NMR, isolated yields are in parenthesis. [c] Reaction at 120 ^{o}C. [d] Reaction at 110 ^{o}C. [e] 3% of catalyst [**Ni-1**] was used. [f] Using catalyst [**Ni-2**], [g] Using catalyst [**Ni-3**]. [h] Without catalyst. [i] Using (DME)NiCl$_2$ as catalyst. [j] Using (DME)NiCl$_2$/bpy system. [k] Using (DME)NiCl$_2$/phen system. [l] Using (DME)NiCl$_2$/6-*OH*-bpy.

## 5. Representative Procedure for (De)hydrogenative Coupling

### Representative Procedure A (*Condition A*): Synthesis of Imine 3aa
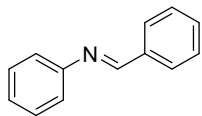
N*-Benzylideneaniline (3aa)**: An oven dried 25 mL Schlenk tube was charged with **1a** (0.037 g, 0.203 mmol), K_2CO_3 (0.028 g, 0.202 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a** (0.044 g, 0.406 mmol) and toluene (0.2 mL) inside the glove box. The tube was sealed by a glass stopper and the resultant reaction mixture in the tube was immersed in a preheated oil bath at 130 °C and stirred for 20 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. The volatiles were evaporated and compound was dried under *vacuo*. The crude product was dissolved in $CDCl_3$ (0.8 mL) and CH_2Br_2 (0.014 mL, 0.20 mmol) was added into it. The ^{1}H NMR yield of **3aa** was calculated to be 88%. Purification by column chromatography on neutral alumina (petroleum ether) yielded **3aa** (0.044 g, 60%) as light-yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1H, C*H)**, 7.97-7.95 (m, 2H, Ar–H), 7.53-7.52 (m, 3H, Ar–H), 7.47-7.43 (m, 2H, Ar–H), 7.30-7.26 (m, 3H, Ar–H). HRMS (ESI): *m/z* Calcd for $C_{13}H_{11}N$ + H^+ $[M + H]^+$ 182.0964; Found 182.0965. The ^{1}H NMR spectrum is consistent with the one reported in the literature.[S4]

Representative Procedure B (*Condition B*): Synthesis of Amine 4aa
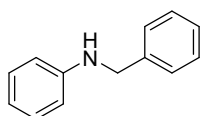
***N*-Benzylaniline (4aa)**: An oven dried 25 mL Schlenk tube was charged with **1a** (0.037 g, 0.203 mmol), KO^tBu (0.034 g, 0.303 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5.0 mol%), **2a** (0.077 g, 0.71 mmol) and toluene (1.0 mL) inside the glove box. The tube was closed with a glass stopper and immersed in a preheated oil bath at 130 °C and stirred for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. The volatiles were evaporated and compound was dried under *vacuo*. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **4aa** (0.071 g, 95%) as brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38-7.31 (m, 4H, Ar–H), 7.28-7.22 (m, 1H, Ar–H), 7.18-7.15 (m, 2H, Ar–H), 6.71 (t, *J* = 7.4 Hz, 1H, Ar–H), 6.63 (d, *J* = 8.1 Hz, 2H, Ar–H), 4.32 (s, 2H, C*H*$_2$), 4.00 (br s, 1H, N*H*). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 148.3 (C_q), 139.6 (C_q), 129.4 (2C, CH), 128.8 (2C, CH), 127.7 (2C, CH), 127.4 (CH), 117.7 (CH), 113.0 (2C, CH), 48.5 (CH_2). HRMS (ESI): *m/z* Calcd for $C_{13}H_{13}N$ + H^+ $[M + H]^+$ 184.1121;

Found 184.1120. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S4]
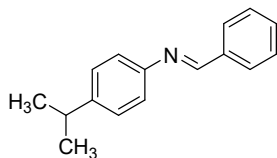
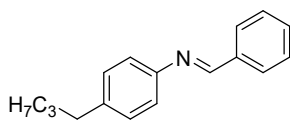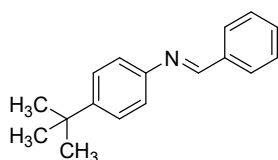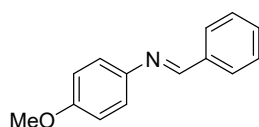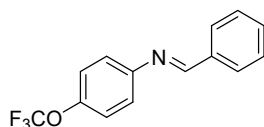## 6. Characterization Data for Imines
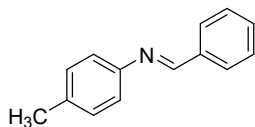
***N*-Benzylidene-4-methylaniline (3ba)**: The representative procedure **A** was followed, using substrate **1b** (0.042 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ba** was calculated to be 68% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]
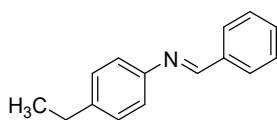
***N*-Benzylidene-4-ethylaniline (3ca)**: The representative procedure **A** was followed, using substrate **1c** (0.048 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ca** was calculated to be 65% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S6]

***N*-Benzylidene-4-isopropylaniline (3da)**: The representative procedure **A** was followed, using substrate **1d** (0.054 g, 0.203 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3da** was calculated to be 72% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S7]
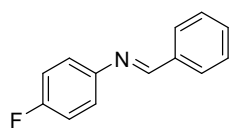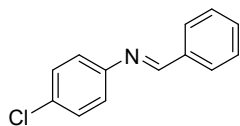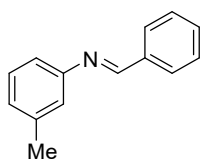

***N*-Benzylidene-4-butylaniline (3ea)**: The representative procedure **A** was followed, using substrate **1e** (0.059 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ea** was calculated to be 54% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S8]
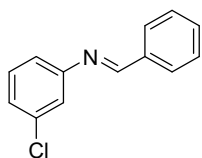
N-Benzylidene-4-tert-butylaniline (3fa): The representative procedure **A** was followed, using substrate **1f** (0.059 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3fa** was calculated to be 74% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S7]

N-Benzylidene-4-methoxyaniline (3ga): The representative procedure **A** was followed, using substrate **1g** (0.049 g, 0.202 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ga** was calculated to be 69% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S8]

N-Benzylidene-4-trifluoromethoxyaniline (3ha): The representative procedure **A** was followed, using substrate **1h** (0.070 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ha** was calculated to be 56% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S9]

N-Benzylidene-4-fluoroaniline (3ia): The representative procedure **A** was followed, using substrate **1i** (0.044 g, 0.202 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ia** was calculated to be 49% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S7]
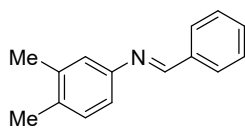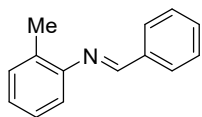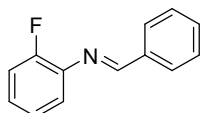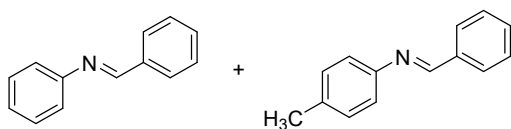
***N*-Benzylidene-4-chloroaniline (3ja)**: The representative procedure **A** was followed, using substrate **1j** (0.050 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ja** was calculated to be 50% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]
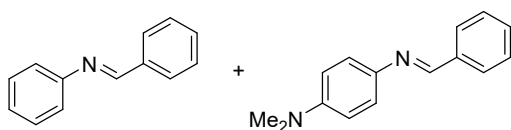

***N*-Benzylidene-3-methylaniline (3ka)**: The representative procedure **A** was followed, using substrate **1k** (0.042 g, 0.20 mmol) and **2a** (0.044 g, 0.406mmol). The ^{1}H NMR yield of **3ka** was calculated to be 68% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]
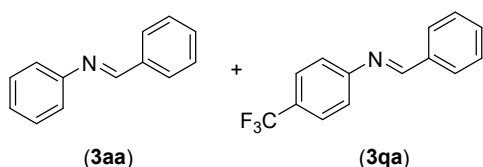

***N*-Benzylidene-3-chloroaniline (3la)**: The representative procedure **A** was followed, using substrate **1l** (0.050 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3la** was calculated to be 29% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]

***N*-Benzylidene-3,4-dimethylaniline (3ma)**: The representative procedure **A** was followed, using substrate **1m** (0.048 g, 0.201 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3ma** was calculated to be 66% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S10]
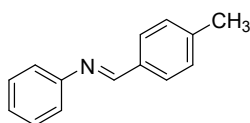
***N*-Benzylidene-2-methylaniline (3na)**: The representative procedure **A** was followed, using substrate **1n** (0.042 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3na** was calculated to be 50% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]

***N*-Benzylidene-2-fluoroaniline (3oa)**: The representative procedure **A** was followed, using substrate **1o** (0.044 g, 0.202 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3oa** was calculated to be 30% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S7]

***N*-Benzylideneaniline (3aa)** and ***N*-Benzylidene-4-methylaniline (3ba)**: The representative procedure **A** was followed, using substrate **1ab** (0.040 g, 0.204 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3aa** and **3ba** was calculated to be 43% and 41%, respectively, using CH_2Br_2 as an internal standard, respectively. The ^{1}H NMR spectrum is consistent with those reported in the literature.[S5]
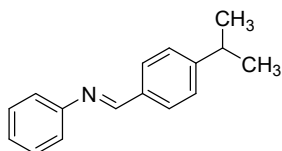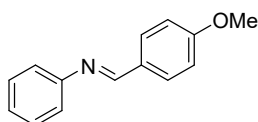

[*N*-Benzylideneaniline (3aa) and ***N*-Benzylidene-4-dimethylaminoaniline (3pa)]**: The representative procedure **A** was followed, using substrate **1ap** (0.025 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3aa** and **3pa** was calculated to be 39% and 37% using CH_2Br_2 as an internal standard, respectively. The ^{1}H NMR spectrum is consistent with the reported literature data. [S5,S11]

(3aa)   **(3qa)**

N-**Benzylideneaniline (3aa)** and *N*-**Benzylidene-4-trifluoromethylaniline (3qa)**: The representative procedure **A** was followed, using substrate **1aq** (0.050 g, 0.20 mmol) and **2a** (0.044 g, 0.406 mmol). The ^{1}H NMR yield of **3aa** was calculated to be 43% using CH_2Br_2 as an internal standard. The compound **3qa** was not formed. The ^{1}H NMR spectrum is consistent with the reported literature data.[S5]
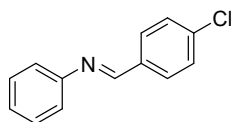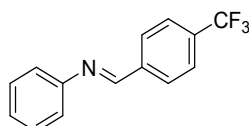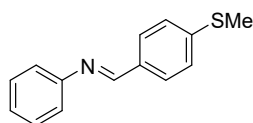

N-**(4-Methylbenzylidene)aniline (3ab)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2b** (0.050 g, 0.409 mmol). The ^{1}H NMR NMR yield of **3ab** was calculated to be 77% using CH_2Br_2 as an internal standard. The ^{1}H spectrum is consistent with the reported literature data.[S12]

N-**(4-Isopropylbenzylidene)aniline (3ac)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2c** (0.061 g, 0.406 mmol). The ^{1}H NMR yield of **3ac** was calculated to be 59% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S13]

N-**(4-Methoxybenzylidene)aniline (3ad)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2d** (0.056 g, 0.406 mmol). The ^{1}H NMR yield of **3ad** was calculated to be 81% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S12]
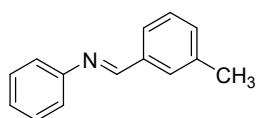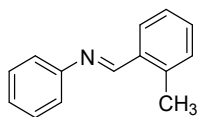
***N*-(4-Chlorobenzylidene)aniline (3ae)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2e** (0.058 g, 0.406 mmol). The ^{1}H NMR yield of **3ae** was calculated to be 55% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S14]

***N*-(4-Trifluoromethylbenzylidene)aniline (3af)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2f** (0.071 g, 0.403 mmol). The ^{1}H NMR yield of **3af** was calculated to be 29% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S15]
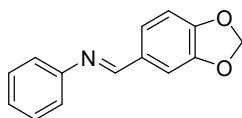

***N*-(4-Thiomethylbenzylidene)aniline (3ag)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2g** (0.063 g, 0.408 mmol). The ^{1}H NMR yield of **3ag** was calculated to be 42% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S16]

***N*-(3-Methylbenzylidene)aniline (3ah)**: The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2h** (0.050 g, 0.409 mmol). The ^{1}H NMR yield of **3ah** was calculated to be 64% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S17]

***N*-(2-Methylbenzylidene)aniline (3ai):** The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2i** (0.050 g, 0.409 mmol). The ^{1}H NMR yield of **3ai** was calculated to be 27% using CH_2Br_2 as an internal standard.[S17]


***N*-(benzo[d][1,3]dioxol-5-ylmethylene)aniline (3aj):** The representative procedure **A** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2j** (0.062 g, 0.407 mmol). The ^{1}H NMR yield of **3aj** was calculated to be 56% using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S18]

## 7.   Characterization Data for Amines
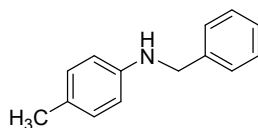
***N*-Benzyl-4-methylaniline (4ba):** The representative procedure **B** was followed, using substrate **1b** (0.042 g, 0.20 mmol) and **2a** (0.077 g, 0.71 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **4ba** (0.073 g, 93%) as colourless oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.42-7.37 (m, 4H, Ar–H), 7.33-7.30 (m, 1H, Ar–H), 7.04 (d, J = 7.9 Hz, 2H, Ar–H), 6.61 (d, J = 8.5 Hz, 2H, Ar–H), 4.35 (s, 2H, CH$_2$), 3.93 (br s, 1H, *NH*), 2.29 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 146.1 (C$_q$), 139.8 (C$_q$), 129.9 (2C, CH), 128.7 (2C, CH), 127.6 (2C, CH), 127.3 (CH), 126.9 (C$_q$), 113.1 (2C, CH), 48.8 (CH$_2$), 20.6 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$N + H$^+$ [M + H]$^+$ 198.1277; Found 198.1276. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
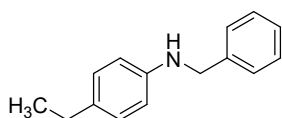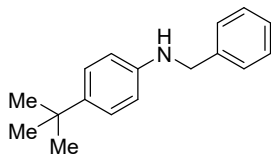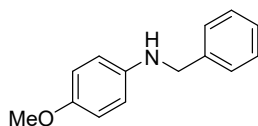

***N*-Benzyl-4-ethylaniline (4ca):** The representative procedure **B** was followed, using substrate **1c** (0.048 g, 0.20 mmol) and **2a** (0.076 g, 0.702 mmol). Purification by column chromatography

on silica gel (petroleum ether/EtOAc: 50/1) yielded **4ca** (0.075 g, 89%) as yellow liquid. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.46-7.39 (m, 4H, Ar–H), 7.36-7.32 (m, 1H, Ar–H), 7.09 (d, J = 8.5 Hz, 2H, Ar–H), 6.66 (t, J = 8.4 Hz, 2H, Ar–H), 4.37 (s, 2H, CH$_2$), 3.70 (br s, 1H, *NH*), 2.62 (q, J = 7.6 Hz, 2H, CH$_2$), 1.27 (t, J = 7.6 Hz, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 146.3 (C$_q$), 139.8 (C$_q$), 133.5 (C$_q$), 128.7 (2C, CH), 128.6 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 113.1 (2C, CH), 48.8 (CH$_2$), 28.1 (CH$_2$), 16.1 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{15}$H$_{17}$N + H$^+$ [M + H]$^+$ 212.1434; Found 212.1433. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
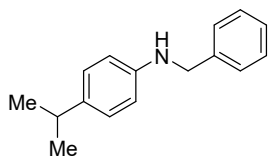
***N*-Benzyl-4-isopropylaniline (4da):** The representative procedure **B** was followed, using substrate **1d** (0.053 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4da** (0.073 g, 81%) as an orange oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.47-7.41 (m, 4H, Ar–H), 7.37-7.34 (m, 1H, Ar–H), 7.15 (d, J = 8.4 Hz, 2H, Ar–H), 6.68 (d, J = 8.5 Hz, 2H, Ar–H), 4.38 (s, 2H, CH$_2$), 3.90 (br s, 1H, *NH*), 2.91 (sept, J = 6.9 Hz, 1H, CH), 1.31 (d, J = 6.9 Hz, 6H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 146.4 (C$_q$), 139.9 (C$_q$), 138.2 (C$_q$), 128.7 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 127.2 (2C, CH), 113.0 (2C, CH), 48.8 (CH$_2$), 33.3 (CH), 24.4 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{16}$H$_{19}$N + H$^+$ [M + H]$^+$ 226.1590; Found 226.1589. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S20]
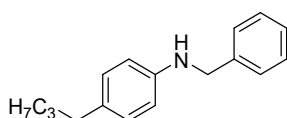
***N*-Benzyl-4-butylaniline (4ea):** The representative procedure **B** was followed, using substrate **1e** (0.059 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4ea** (0.083 g, 87%) as a brown oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.43-7.37 (m, 4H, Ar–H), 7.33-7.30 (m, 1H, Ar–H), 7.04 (d, J = 7.9 Hz, 2H, Ar–H), 6.62 (d, J = 8.0 Hz, 2H, Ar–H), 4.35 (s, 2H, CH$_2$), 3.90 (br s, 1H, *NH*), 2.55 (t, J = 7.6 Hz, 2H, CH$_2$), 1.62-1.56 (m, 2H, CH$_2$), 1.42-1.37 (m, 2H, CH$_2$), 0.97 (t, J = 7.4 Hz, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 146.3 (C$_q$), 139.9 (C$_q$), 132.2 (C$_q$), 129.3 (2C, CH), 128.8 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 113.07 (2C, CH), 48.8 (CH$_2$), 34.9

(CH$_2$), 34.1 (CH$_2$), 22.5 (CH$_2$), 14.2 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{17}$H$_{21}$N + H$^+$ [M + H]$^+$ 240.1752; Found 240.1742. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S21]

N-Benzyl-4-*tert*-butylaniline (4fa): The representative procedure **B** was followed, using substrate **1f** (0.059 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 40/1) yielded **4fa** (0.083 g, 87%) as an orange oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.37-7.31 (m, 4H, Ar–H), 7.27-7.24 (m, 1H, Ar–H), 7.22-7.18 (m, 2H, Ar–H), 6.60-6.56 (m, 2H, Ar–H), 4.29 (s, 2H, CH$_2$), 3.81 (br s, 1H, *NH*), 1.28 (s, 9H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 146.0 (C$_q$), 140.4 (C$_q$), 139.9 (C$_q$), 128.7 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 126.2 (2C, CH), 112.7 (2C, CH), 48.8 (CH$_2$), 34.0 (C$_q$), 31.7 (3C, CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{17}$H$_{21}$N + H$^+$ [M + H]$^+$ 240.1747; Found 240.1744. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
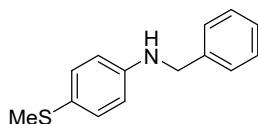

N-Benzyl-4-methoxyniline (4ga): The representative procedure **B** was followed, using substrate **1g** (0.049 g, 0.202 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1) yielded **4ga** (0.078 g, 91%) as a yellow oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.41-7.36 (m, 4H, Ar–H), 7.32-7.29 (m, 1H, Ar–H), 6.82 (d, *J* = 8.9 Hz, 2H, Ar–H), 6.64 (d, *J* = 8.9 Hz, 2H, Ar–H), 4.31 (s, 2H, CH$_2$), 3.77 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 152.3 (C$_q$), 142.6 (C$_q$), 139.8 (C$_q$), 128.7 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 115.0 (2C, CH), 114.2 (2C, CH), 55.9 (CH$_3$), 49.4 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$ON + H$^+$ [M + H]$^+$ 214.1226; Found 214.1226. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
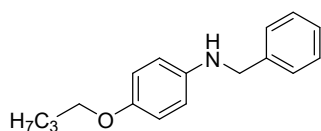
_N_-Benzyl-4-butoxyaniline (4ra): The representative procedure **B** was followed, using substrate **1r** (0.065 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **4ra** (0.065 g, 64%) as a brown oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.42-7.36 (m, 4H, Ar–H), 7.33-7.30 (m, 1H, Ar–H), 6.83 (d, J = 9.0 Hz, 2H, Ar–H), 6.64 (d, J = 8.9 Hz, 2H, Ar–H), 4.31 (s, 2H, CH$_2$), 3.93 (t, J = 6.5 Hz, 2H, CH$_2$), 3.51 (br s, 1H, _NH_), 1.81-1.74 (m, 2H, CH$_2$), 1.57-1.48 (m, 2H, CH$_2$), 1.02 (t, J = 7.4, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 151.9 (C$_q$), 142.5 (C$_q$), 139.9 (C$_q$), 128.7 (2C, CH), 127.7 (2C, CH), 127.3 (CH), 115.9 (2C, CH), 114.2 (2C, CH), 68.6 (CH$_2$), 49.4 (CH$_2$), 31.7 (CH$_2$), 19.4 (CH$_2$), 14.0 (CH$_3$). HRMS (ESI): m/z Calcd for C$_{17}$H$_{21}$ON + H$^+$ [M + H]$^+$ 256.1696; Found 256.1695.
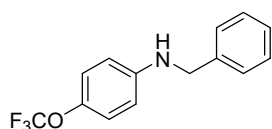
_N_-Benzyl-4-trifluoromethoxylaniline (4ha): The representative procedure **B** was followed, using substrate **1h** (0.070 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4ha** (0.031 g, 29%) as a yellow oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.37-7.34 (m, 4H, Ar–H), 7.32-7.29 (m, 1H, Ar–H), 7.04 (d, J = 8.4 Hz, 2H, Ar–H), 6.61-6.57 (m, 2H, Ar–H), 4.32 (s, 2H, CH$_2$), 4.14 (br s, 1H, _NH_). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 147.1 (C$_q$), 140.7 (C$_q$), 139.1 (C$_q$), 128.9 (2C, CH), 127.6 (3C, CH), 122.6 (2C, CH), 120.9 (q, $^1J_{C\text{-}F}$ = 255.2 Hz, CF$_3$), 113.2 (2C, CH), 48.6 (CH$_2$). HRMS (ESI): m/z Calcd for C$_{14}$H$_{12}$ONF$_3$ + H$^+$ [M + H]$^+$ 268.0944; Found 268.0941. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S22]
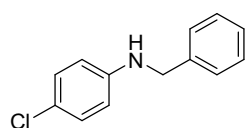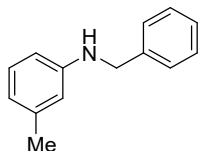

_N_-Benzyl-4-chlorolaniline (4ja): The representative procedure **B** was followed, using substrate **1j** (0.050 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4ja** (0.052 g, 60%) as yellow oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.38-7.34 (m, 4H, Ar–H), 7.33-7.27 (m, 1H, Ar–H), 7.12 (d, J = 8.9 Hz, 2H, Ar–H), 6.56 (d, J = 8.9 Hz, 2H, Ar–H), 4.31 (s, 2H, CH$_2$), 4.09

(br s, 1H, *NH*). $^{13}C\{^1H\}$-NMR (125 MHz, CDCl$_3$): δ = 146.8 (C$_q$), 139.1 (C$_q$), 129.2 (2C, CH), 128.9 (2C, CH), 127.6 (2C, CH), 127.5 (CH), 122.3 (C$_q$), 114.1 (2C, CH), 48.5 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{13}$H$_{12}$NCl + H$^+$ [M + H]$^+$ 218.0731; Found 218.0733. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]

N-Benzyl-4-thiomethylaniline (4sa): The representative procedure **B** was followed, using substrate **1s** (0.055 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 40/1) yielded **4sa** (0.066 g, 72%) as a yellow oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.35-7.31 (m, 4H, Ar–H), 7.29-7.26 (m, 1H, Ar–H), 7.22-7.18 (m, 2H, Ar–H), 6.59-6.56 (m, 2H, Ar–H), 4.30 (s, 2H, CH$_2$), 2.39 (s, 3H, CH$_3$). $^{13}C\{^1H\}$-NMR (100 MHz, CDCl$_3$): δ = 147.1 (C$_q$), 139.3 (C$_q$), 131.6 (2C, CH), 128.8 (2C, CH), 127.6 (2C, CH), 127.5 (CH), 124.6 (C$_q$), 113.6 (2C, CH), 48.5 (CH$_2$), 19.3 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$NS$^+$ [M]$^+$ 229.0920; Found 229.0909. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
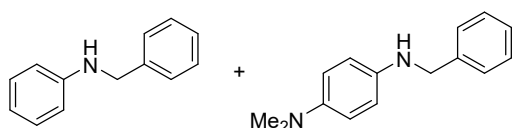

N-Benzyl-3-methylaniline (4ka): The representative procedure **B** was followed, using substrate **1k** (0.042 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **4ka** (0.069 g, 87%) as yellowish-brown oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.43-7.38 (m, 4H, Ar–H), 7.34-7.31 (m, 1H, Ar–H), 7.12 (t, *J* = 7.7 Hz, 1H, Ar–H), 6.61 (t, *J* = 7.5 Hz, 1H, Ar–H), 6.52-6.49 (m, 2H, Ar–H), 4.36 (s, 2H, CH$_2$), 3.99 (br s, 1H, *NH*), 2.33 (s, 3H, CH$_3$). $^{13}C\{^1H\}$-NMR (125 MHz, CDCl$_3$): δ = 148.4 (C$_q$), 139.7 (C$_q$), 139.2 (C$_q$), 129.3 (CH), 128.8 (2C, CH), 127.7 (2C, CH), 127.4 (CH), 118.7 (CH), 113.8 (CH), 110.1 (CH), 48.5 (CH$_2$), 21.8 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$N + H$^+$ [M + H]$^+$ 198.1277; Found 198.1278. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S23]
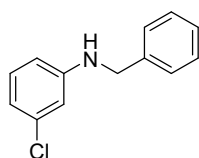
***N*-Benzyl-3-chloroaniline (4la):** The representative procedure **B** was followed, using substrate **1l** (0.050 g, 0.20 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 100/1) yielded **4la** (0.047 g, 54%) as pale yellow liquid. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.35-7.31 (m, 4H, Ar–H), 7.29-7.24 (m, 1H, Ar–H), 7.04 (t, J = 8.0 Hz, 1H, Ar–H), 6.66 (dd, J = 7.9, 1.9 Hz, 1H, Ar–H), 6.59 (t, J = 2.1 Hz, 1H, Ar–H), 6.46 (dd, J = 8.3, 2.3 Hz, 1H, Ar–H), 4.27 (s, 2H, CH$_2$), 4.07 (br s, 1H, *NH*). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 149.4 (C$_q$), 138.9 (C$_q$), 135.2 (C$_q$), 130.4 (CH), 128.9 (2C, CH), 127.6 (2C, CH), 127.5 (CH), 117.6 (CH), 112.7 (CH), 111.3 (CH), 48.2 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{13}$H$_{12}$ClN + H$^+$ [M + H]$^+$ 218.0737; Found 218.0622. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S24]
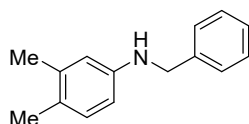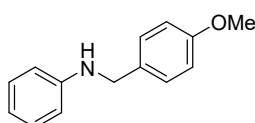

***N*-Benzyl-3,4-dimethylaniline (4ma):** The representative procedure **B** was followed, using substrate **1m** (0.048 g, 0.201 mmol) and **2a** (0.076 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4ma** (0.070 g, 82%) as colourless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.47-7.41 (m, 4H, Ar–H), 7.38-7.34 (m, 1H, Ar–H), 7.04 (d, J = 8.1, 1H, Ar–H), 6.58 (d, J = 2.1 Hz, 1H, Ar–H), 6.50 (dd, J = 8.0, 2.3 Hz, 1H, Ar–H), 4.38 (s, 2H, CH$_2$), 3.75 (br s, 1H, *NH*), 2.29 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 146.5 (C$_q$), 139.9 (C$_q$), 137.4 (C$_q$), 130.4 (CH), 128.7 (2C, CH), 127.6 (2C, CH), 127.2 (CH), 125.7 (C$_q$), 114.9 (CH), 110.4 (CH), 48.8 (CH$_2$), 20.2 (CH$_3$), 18.8 (CH$_3$). The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S24]
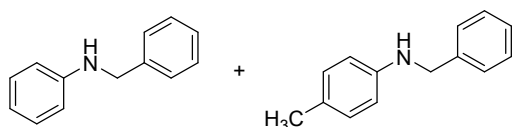
***N*-Benzylaniline (4aa) and *N*-Benzyl-4-methylaniline (4ba):** The representative procedure **B** was followed, using substrate **1ab** (0.040 g, 0.204 mmol) and **2a** (0.076 g, 0.703 mmol). The combine ^{1}H NMR yield of **4aa** and **4ba** was calculated to be 97% (peaks for both the products

are merging in ^{1}H NMR), using CH_2Br_2 as an internal standard. *(NOTE: Yield mentioned here is the combine yield for both compounds and they are inseparable by column chromatography)* HRMS (ESI): *m/z* Calcd for **4aa**, $C_{13}H_{13}N + H^+$ [M + H]$^+$ 184.1121; Found 184.1120 and for **4ba**, $C_{14}H_{15}N + H^+$ [M + H]$^+$ 198.1277; Found 198.1275. The ^{1}H NMR spectrum is consistent with the reported literature data.[S19]

***N*-Benzylaniline (4aa)** and ***N*-Benzyl-4-(dimethylamino)aniline (4pa)**: The representative procedure **B** was followed, using substrate **1ap** (0.046 g, 0.204 mmol) and **2a** (0.077 g, 0.71 mmol). The ^{1}H NMR yield of **4aa** and **4pa** was calculated to be 43% and 13%, respectively, using CH_2Br_2 as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S11,S25]
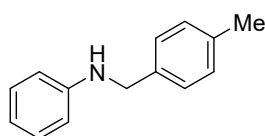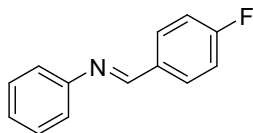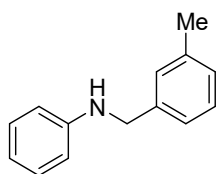

***N*-(4-Methylbenzyl)aniline (4ab)**: The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2b** (0.086 g, 0.704 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **4ab** (0.071 g, 89%) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 2H, Ar–H), 7.20-7.14 (m, 4H, Ar–H), 6.71 (t, *J* = 7.4 Hz, 1H, Ar–H), 6.64 (d, *J* = 7.6 Hz, 2H, Ar–H), 4.28 (s, 2H, CH_2), 3.97 (br s, 1H, *NH*), 2.35 (s, 3H, CH_3). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 148.4 (C_q), 137.0 (C_q), 136.5 (C_q), 129.5 (2C, CH), 129.4 (2C, CH), 127.7 (2C, CH), 117.7 (CH), 113.0 (2C, CH), 48.3 (CH_2), 21.3 (CH_3). HRMS (ESI): *m/z* Calcd for $C_{14}H_{15}N + H^+$ [M + H]$^+$ 198.1277; Found 198.1276. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
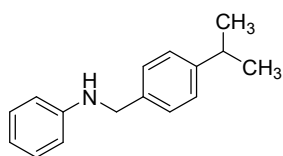
***N*-(4-isopropylbenzyl)aniline (4ac)**: The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and and **2c** (0.105 g, 0.70 mmol). Purification by column

chromatography on silica gel (petroleum ether/EtOAc: 70/1) yielded **4ac** (0.085 g, 93%) as an orange oil. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.26 (d, J = 8.0 Hz, 2H, Ar–H), 7.19-7.12 (m, 4H, Ar–H), 6.68 (t, J = 7.4 Hz, 1H, Ar–H), 6.60 (d, J = 7.6 Hz, 2H, Ar–H), 4.23 (s, 2H, CH$_2$), 3.88 (br s, 1H, *NH*), 2.93-2.83 (m, 1H, CH), 1.23 (d, J = 6.9 Hz, 6H, CH$_3$). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 148.4 (C$_q$), 148.0 (C$_q$), 136.9 (C$_q$), 129.4 (2C, CH), 127.7 (2C, CH), 126.8 (2C, CH), 117.6 (CH), 112.9 (2C, CH), 48.2 (CH$_2$), 33.9 (CH), 24.2 (2C, CH$_3$). HRMS (ESI): m/z Calcd for C$_{16}$H$_{19}$N + H$^+$ [M + H]$^+$ 226.1596; Found 226.1580. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S20]

N-(4-Methoxybenzyl)aniline (**4ad**): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2d** (0.097 g, 0.702 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **4ad** (0.075 g, 87%) as colourless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.33 (d, J = 8.6 Hz, 2H, Ar–H), 7.24-7.20 (m, 2H, Ar–H), 6.92 (d, J = 8.6 Hz, 2H, Ar–H), 6.76 (t, J = 7.3 Hz, 1H, Ar–H), 6.68 (d, J = 7.6 Hz, 2H, Ar–H), 4.28 (s, 2H, CH$_2$), 3.80 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 159.0 (C$_q$), 148.3 (C$_q$), 131.6 (C$_q$), 129.4 (2C, CH), 128.9 (2C, CH), 117.6 (CH), 114.1 (2C, CH), 113.0 (2C, CH), 55.4 (CH$_3$), 47.9 (CH$_2$). HRMS (ESI): m/z Calcd for C$_{14}$H$_{15}$NO + H$^+$ [M + H]$^+$ 214.1232; Found 214.1223. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
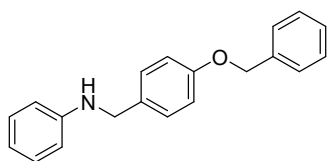
N-(4-Benzyloxybenzyl)aniline (**4ak**): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2k** (0.150 g, 0.70 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 50/1) yielded **4ak** (0.083 g, 71%) as light yellow solid. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.42-7.25 (m, 7H, Ar–H), 7.16 (t, J = 7.8 Hz, 2H, Ar–H), 6.94 (d, J = 8.5 Hz, 2H, Ar–H), 6.70 (t, J = 7.3 Hz, 1H, Ar–H), 6.61 (d, J = 8.0 Hz, 2H, Ar–H), 5.03 (s, 2H, CH$_2$), 4.22 (s, 2H, CH$_2$), 3.79 (br s, 1H, *NH*). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 158.2 (C$_q$), 148.4 (C$_q$), 137.2 (C$_q$), 131.2 (C$_q$), 129.4 (2C, CH), 129.0 (2C, CH), 128.7 (2C, CH), 128.1 (CH), 127.6 (2C, CH), 117.7 (CH), 115.1 (2C, CH), 113.0 (2C,

CH), 70.2 (CH$_2$), 47.9 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{20}$H$_{19}$NO + H$^+$ [M + H]$^+$ 290.1545; Found 290.1534. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S23]
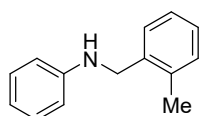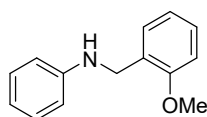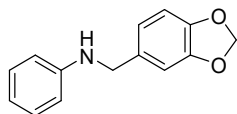

***N*-(4-Fluorobenzyl)aniline (4al)**: The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2l** (0.089 g, 0.704 mmol). The imine compounds **3aa** and **3al** were obtained as a mixture. The ^{1}H NMR yield of **3al+3aa** was calculated to be 34% using CH$_2$Br$_2$ as an internal standard. The ^{1}H spectrum is consistent with the reported literature data. *(NOTE: In this case, we obtained imine instead of amine)*. The ^{1}H NMR spectrum is consistent with the reported in the literature.[S12]

***N*-(3-Methylbenzyl)aniline (4ah)**: The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2h** (0.086 g, 0.704 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 20/1) yielded **4ah** (0.073 g, 91%) as colourless oil. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.23-7.14 (m, 5H, Ar–H), 7.07 (d, *J* = 7.4, 1H, Ar–H), 6.70 (t, *J* = 7.4 Hz, 1H, Ar–H), 6.61 (d, *J* = 8.5 Hz, 2H, Ar–H), 4.25 (s, 2H, CH$_2$), 3.91 (br s, 1H, *NH*), 2.33 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 148.4 (C$_q$), 139.5 (C$_q$), 138.4 (C$_q$), 129.4 (2C, CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 124.7 (CH), 117.7 (CH), 113.0 (2C, CH), 48.5 (CH$_2$), 21.6 (CH$_3$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$N + H$^+$ [M + H]$^+$ 198.1277; Found 198.1278. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S19]
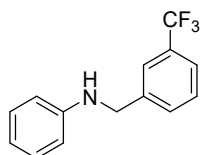
N-(3-Trifluoromethylbenzyl)aniline (4am): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2m** (0.123 g, 0.70 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 40/1) yielded **4am** (0.056 g, 56%) as yellow liquid. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.64 (s, 1H, Ar–H), 7.58-7.53 (m, 2H, Ar–H), 7.46 (t, J = 7.9 Hz, 1H, Ar–H), 7.19 (t, J = 7.9 Hz, 2H, Ar–H), 6.75 (t, J = 7.3 Hz, 1H, Ar–H), 6.63 (d, J = 7.9 Hz, 2H, Ar–H), 4.41 (s, 2H, CH$_2$), 4.14 (br s, 1H, *NH*). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 147.9 (C$_q$), 140.8 (C$_q$), 131.1 (q, $^2J_{C-F}$ = 32.7 Hz, C$_q$), 130.8 (CH), 129.5 (2C, CH), 129.3 (CH), 124.3 (q, $^1J_{C-F}$ = 272.5 Hz, CF$_3$), 124.2 (q, $^3J_{C-F}$ = 3.6 Hz, 2C, CH), 118.2 (CH), 113.1 (2C, CH), 48.1 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{12}$F$_3$N + H$^+$ [M + H]$^+$ 252.1000; Found 252.0992. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S23]

N-(2-Methylbenzyl)aniline (4ai): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2i** (0.087 g, 0.71 mmol). The ^{1}H NMR yield of **4ai** and **3ai** was calculated to be 44% and 27%, respectively, using CH$_2$Br$_2$ as an internal standard. The ^{1}H NMR spectrum is consistent with the reported literature data.[S17,S21]

N-(2-Methoxybenzyl)aniline (4an): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2n** (0.097 g, 0.702 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 40/1) yielded **4an** (0.069 g, 80%) as a yellow solid. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.31 (d, J = 7.5 Hz, 1H, Ar–H), 7.27-7.22 (m, 1H, Ar–H), 7.18-7.14 (m, 2H, Ar–H), 6.93-6.88 (m, 2H, Ar–H), 6.71-6.64 (m, 3H, Ar–H), 4.33 (s, 2H, CH$_2$), 3.86 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$): δ = 157.5 (C$_q$), 148.6 (C$_q$), 129.3 (2C, CH), 129.1 (CH), 128.5 (CH), 127.4 (C$_q$), 120.7 (CH), 117.5 (CH), 113.2 (2C, CH), 110.4 (CH), 55.5 (CH$_3$), 43.6 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{15}$NO + H$^+$ [M + H]$^+$

214.1232; Found 214.1210. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S21]

N-(Benzo[d][1,3]dioxol-5-ylmethyl)aniline (**4aj**): The representative procedure **B** was followed, using substrate **1a** (0.037 g, 0.203 mmol) and **2j** (0.107 g, 0.703 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc: 30/1) yielded **4aj** (0.049 g, 53%) as yellow solid. ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.22-7.18 (m, 2H, Ar–H), 6.89-6.79 (m, 3H, Ar–H), 6.74 (t, J = 7.3 Hz, 1H, Ar–H), 6.65 (d, J = 7.8 Hz, 2H, Ar–H), 5.95 (s, 2H, CH$_2$), 4.25 (s, 2H, CH$_2$), 4.00 (br s, 1H, *NH*). ^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$): δ = 148.2 (C$_q$), 148.0 (C$_q$), 146.9 (C$_q$), 133.5 (C$_q$), 129.4 (2C, CH), 120.7 (CH), 117.8 (CH), 113.0 (2C, CH), 108.4 (CH), 108.2 (CH), 101.1 (CH$_2$), 48.3 (CH$_2$). HRMS (ESI): *m/z* Calcd for C$_{14}$H$_{13}$NO$_2$ + H$^+$ [M + H]$^+$ 228.1025 ; Found 228.1018. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S23]

8. External Additive Experiments

Procedure for TEMPO/BHT Added Experiment (for 3aa Synthesis, *Conditions A*): An oven dried 25 mL Schlenk tube was charged with **1a** (0.037 g, 0.203 mmol), K$_2$CO$_3$ (0.028 g, 0.2 mmol), TEMPO (0.063 g, 0.403 mmol) [or BHT (0.089, 0.404 mmol)], **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a** (0.044 g, 0.406 mmol), and toluene (0.2 mL) inside the glove box. The tube was sealed by a glass stopper and the resultant reaction mixture in the tube was immersed in preheated oil bath at 130 ^{o}C and stirred for 20 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. Then, the volatiles were removed under *vacuo* and dried. *The ^{1}H NMR analysis indicated no formation of product in case of TEMPO and shows 20% of **3aa** in case of BHT.*

Procedure for TEMPO/Galvinoxyl/BHT Added Experiment (for 4aa Synthesis, *Conditions B*): An oven dried 25 mL Schlenk tube was charged with **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), TEMPO (0.063g, 0.403 mmol) [or Galvinoxyl (0.169 g, 0.401 mmol) or BHT (0.089, 0.404 mmol)], **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a** (0.077 g, 0.71 mmol), and toluene (1 mL) inside the glove box. The tube was sealed by a glass stopper and the resultant reaction mixture in the tube was immersed in preheated oil bath at 130 ^{o}C and

stirred for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. Then, the volatiles were removed under *vacuo* and dried. The ^{1}H NMR analysis indicated 54% formation of **3aa** in case of TEMPO and 23% of **3aa** in case of BHT and shows no product formation in case of galvinoxyl. *The formation of product **4aa** was not observed.*

Procedure for TEMPO Added Experiment (for Hydrogenation of 3aa): An oven dried 25 mL Schlenk tube was charged with **3aa** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), TEMPO (0.063 g, 0.403 mmol), **Ni-1** (0.003g, 0.01 mmol, 5 mol%), **2a** (0.077 g, 0.71 mmol), and toluene (1 mL) inside the glove box. The tube was sealed by a glass stopper and the resultant reaction mixture in the tube was immersed in preheated oil bath at 130 °C and stirred for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. Then, the volatiles were removed under *vacuo* and dried. The ^{1}H NMR analysis indicated no formation product **4aa** using CH_2Br_2 as an internal standard.

*Remark: Imine (**3aa**) hydrogenation is exclusively occurred via radical path.*

Procedure for TEMPO (Catalytic Amount) Added Experiment for 4aa Synthesis: An oven dried 25 mL Schlenk tube was charged with **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), TEMPO (0.003 g, 0.02 mmol, 10 mol%), **Ni-1** (0.003g, 0.01 mmol, 5 mol%), **2a** (0.077 g, 0.71 mmol), and toluene (1 mL) inside the glove box. The tube was sealed by a glass stopper and the resultant reaction mixture in the tube was immersed in preheated oil bath at 130 °C and stirred for 24 h. At ambient temperature, the reaction mixture was diluted with EtOAc and filtered through filter paper. Then, the volatiles were removed under vacuo and dried. The ^{1}H NMR analysis indicated 26% of **3aa** and 43% of **4aa** formation using CH_2Br_2 as an internal standard.

Remark: Organic radicals are involved during the catalytic process.

9. Controlled Experiments

(De)hydrogenative Coupling using Ni-3 (for 3aa; Condition A): The representative procedure **A** was followed using **1a** (0.037 g, 0.203 mmol), K_2CO_3 (0.028 g, 0.2 mmol), **Ni-3** (0.0031 g, 0.01 mmol, 5 mol%), **2a** (0.044 g, 0.406 mmol), and toluene (0.2 mL). The ^{1}H NMR analysis indicated 9% formation of **3aa** using CH_2Br_2 as an internal standard.

*Remark: Metal-Ligand cooperation plays crucial role for the formation of imine (**3aa**) while using K_2CO_3 base (Condition A)*

(De)hydrogenative Coupling using Ni-3 (for 4aa; Condition B): The representative procedure **B** was followed using **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-3** (0.0031 g, 0.01 mmol, 5 mol%) **2a** (0.077 g, 0.71 mmol), and toluene (1 mL). The ^{1}H NMR analysis indicated formation of **3aa** (43%) and **4aa** (53%) using CH$_2$Br$_2$ as an internal standard.

Remark: Formation of imine (3aa) or overall reaction is slow in the absence of Metal-Ligand cooperation; signifies the importance of complex Ni-1.

Hydrogenation of 3aa using Ni-3: The representative procedure **B** was followed using **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-3** (0.0031 g, 0.01 mmol, 5 mol%) **2a** (0.077 g, 0.71 mmol), and toluene (1 mL). The ^{1}H NMR analysis indicated formation of **4aa** in 95% using CH$_2$Br$_2$ as an internal standard.

Remark: Metal-Ligand cooperation has no role in the hydrogenation of imine (3aa) to amine (4aa).

Hydrogenation of 3aa using Ni-1: The representative procedure **B** was followed using **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a** (0.077 g, 0.71 mmol), and toluene (1 mL). *The ^{1}H NMR analysis indicated 85% of **4aa** formation* using CH$_2$Br$_2$ as an internal standard.

Attempted Dehydrogenation of 2a without 1a: The representative procedure **B** was followed using KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5 mol%) **2a** (0.077 g, 0.71 mmol), and toluene (1 mL). *The ^{1}H NMR analysis shows no dehydrogenation of **2a*** using CH$_2$Br$_2$ as an internal standard.

10. Deuterium Labelling Experiments

Dehydrogenative coupling using 2a-[D$_2$] (Condition B): The representative procedure **B** was followed using **1a** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a**-[D$_2$] (0.078 g, 0.71 mmol), and toluene (1 mL). The ^{1}H NMR analysis indicated 21% of **4aa**, 55% of **4aa**-[HD] and 24% of **4aa**-[DD] formation using CH$_2$Br$_2$ as an internal standard (Figure S1). HRMS (ESI): m/z Calcd for C$_{13}$H$_{13}$N + H$^+$ [M + H]$^+$ 184.1126; Found 184.1099, C$_{13}$H$_{12}$DN + H$^+$ [M + H]$^+$ 185.1189; Found 185.1181, C$_{13}$H$_{11}$D$_2$N + H$^+$ [M + H]$^+$ 186.1252; Found 186.1236. The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[S26]
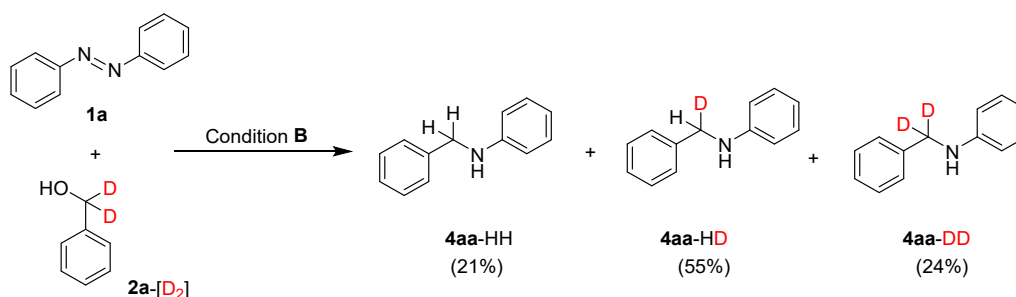
Conversion was calculated by ^{1}H NMR integration

	4aa or **4aa**-[D$_1$]	**4aa**-HH	**4aa**-HD	**4aa**-DD
Signal (δ)	6.71 [*para*-H, (1H)]	4.31 [benzyl-CH$_2$ (2H)]	4.29 [benzyl-H (1H)]	--
Integral value	1.00	0.42/2 = 0.21	0.55/1 = 0.55	--
Calculated ratio		21%	55%	24%
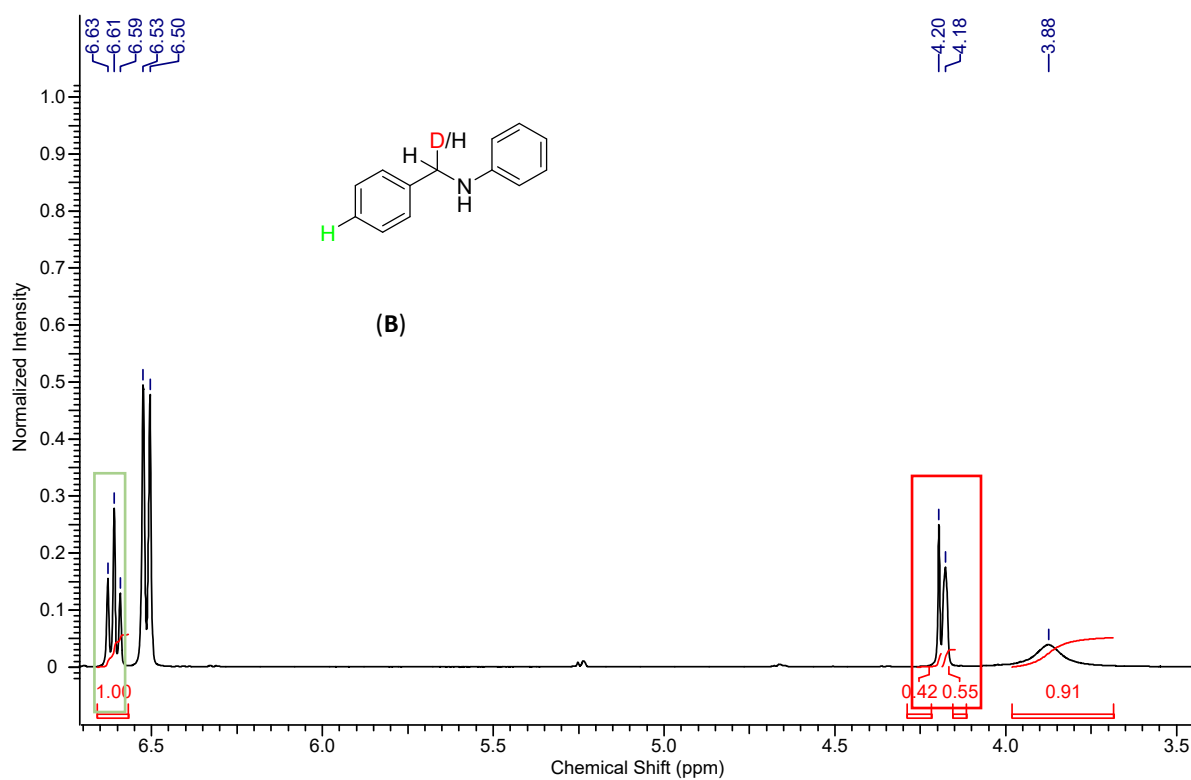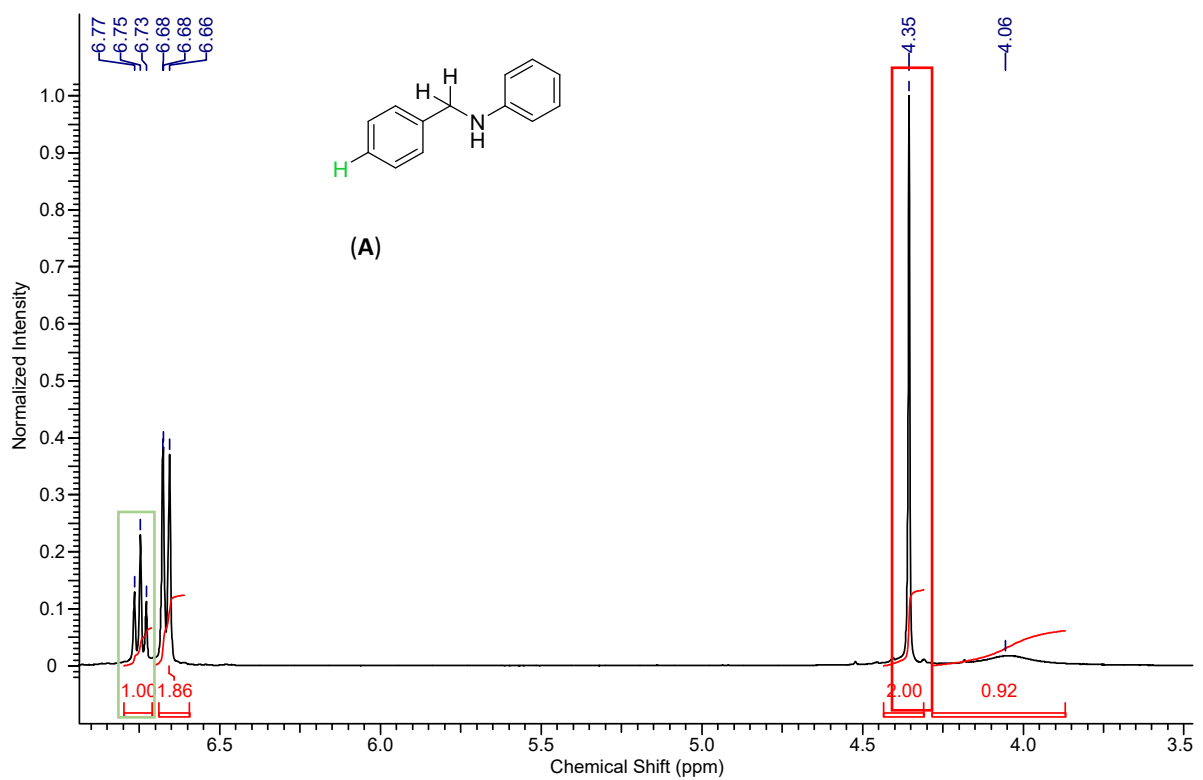
Figure S1. (A) ^{1}H NMR spectrum of **4aa**. (B) ^{1}H NMR spectrum of reaction mixture using **2a**-[D$_2$].

Procedure for Hydrogenation of 3aa using 2a-[D$_2$]: The representative procedure **B** was followed using **3aa** (0.037 g, 0.203 mmol), KO^{t}Bu (0.034 g, 0.304 mmol), **Ni-1** (0.003 g, 0.01 mmol, 5 mol%), **2a-[D2]** (0.078 g, 0.71 mmol), and toluene (1 mL). The ^{1}H NMR analysis indicated 46% of **4aa** and 54% of **4aa**-[HD] formation using CH$_2$Br$_2$ as an internal standard (Figure S2). HRMS (ESI): m/z Calcd for C$_{13}$H$_{13}$N + H$^+$ [M + H]$^+$ 184.1126; Found 184.1113, C$_{13}$H$_{12}$DN + H$^+$ [M + H]$^+$ 185.1189; Found 185.1177. The ^{1}H and ^{13}C spectra are consistent with those reported in the literature.[S26]

*Remarks: Formation of **4aa**-[DD] was not observed in this reaction, suggesting the irreversible hydrogenation process of **3aa**.*
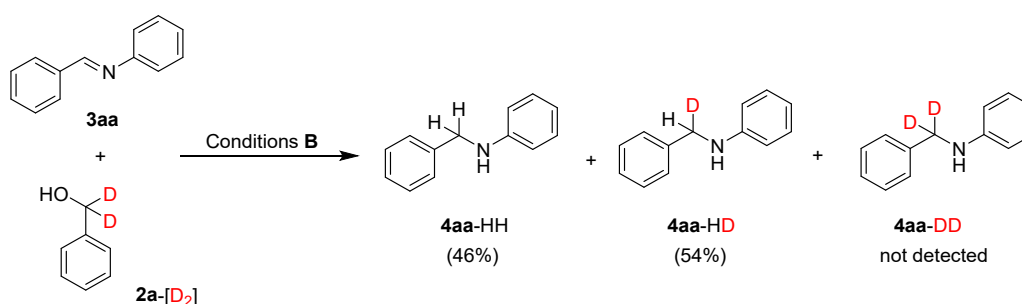
Conversion was calculated by ^{1}H NMR integration and HRMS peak ratio

	4aa or **4aa**-[D$_1$]	**4aa**-HH	**4aa**-HD	**4aa**-DD
Signal (δ)	6.71 [*para*-H, (1H)]	4.31 [benzyl-CH$_2$ (2H)]	4.29 [benzyl-H (1H)]	--
Integral value	1.00	0.92/2 = 0.46	0.54	--
Calculated ratio		46%	54%	--
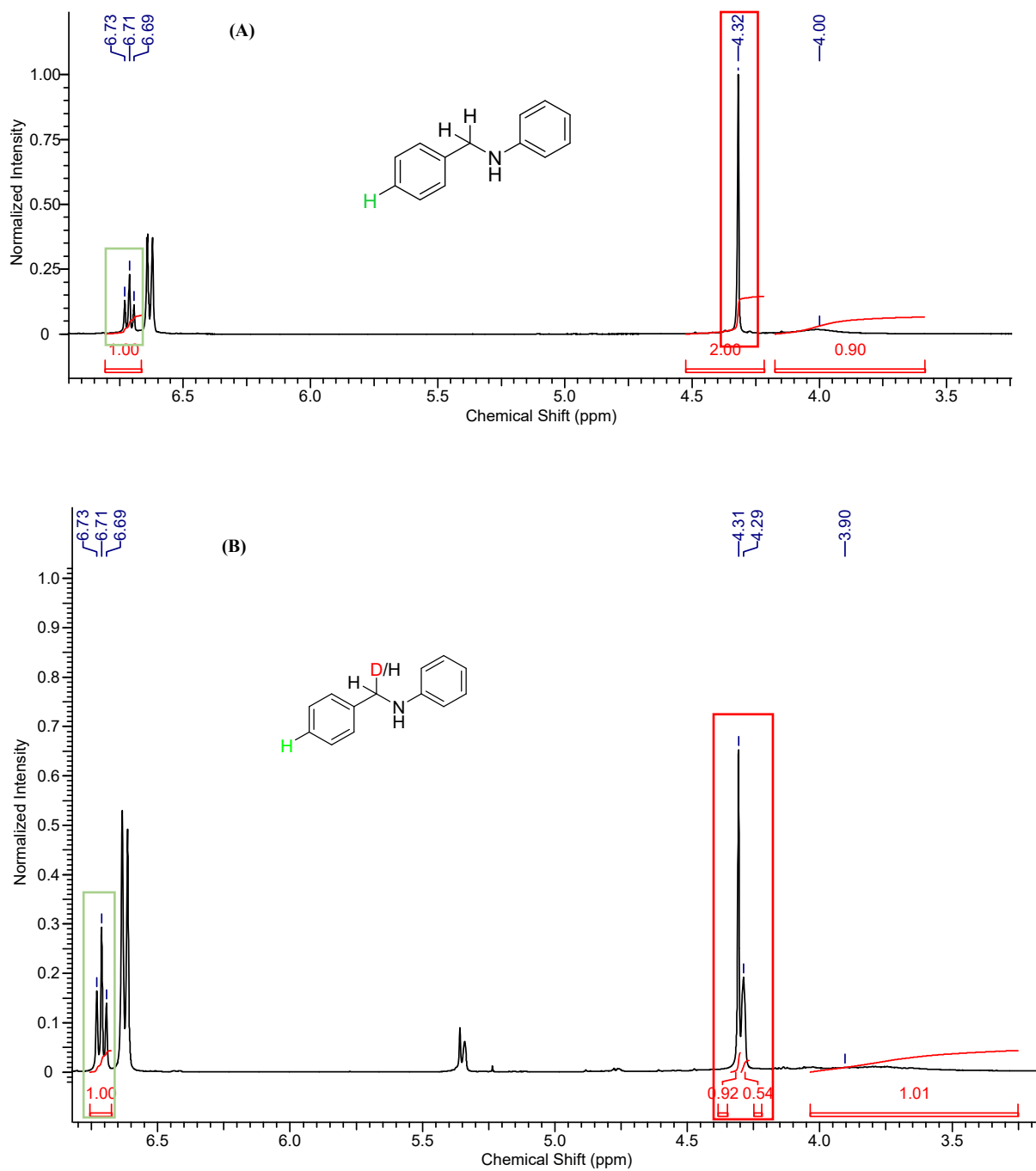
Figure S2. (A) ^{1}H NMR spectrum of **4aa**. (B) ^{1}H NMR spectrum of reaction mixture using **2a-**[D₂].

11. Cyclic Voltammetry Studies

Cyclic voltammetry was carried out using reference 3000 (Gamry instruments) electrochemical workstation in a standard 3 electrode setup. Glassy carbon electrode (2 mm diameter) as working, platinum wire as counter electrode and silver/silver chloride as reference electrode. All the electrodes were cleaned prior to each use. The reference electrode was stored in a 3 M KCl solution to maintain the equilibrium potential. The working electrode was cleaned by manual polishing with 0.05 micron alumina powder prior to experiment. All the experiments were carried out using 100 mM tetra-n-butylammonium perchlorate (TBAP) in dimethyl formamide (DMF) as supporting electrolyte. The concentration of all the analyte was maintained at 1 mM. Prior to experiments, the background signal without analyte was taken to optimize the potential window.

Electrochemical analysis was carried out using cyclic voltammetry to get the insight into the electrode potentials of various reaction components (Figure S3). From the cyclic voltammetry analysis, the E^0 values for **1a**, **3aa**, and KO^{t}Bu found to be –0.050 V, –0.254 V and –0.380 V, respectively. Since the E^0 value of KO^{t}Bu is more negative compared to **1a** and **3aa**, it can easily act as reducing agent for both of them, making the electron transfer feasible from KO^{t}Bu to **1a** and **3aa**. The electrode potential value of K_2CO_3 ($CO_3^{2-} \rightarrow CO_2 + O^{2-}$; E = –0.266 V)[S27] suggests that it can reduce the azobenzene (**1a**); however, reduction of imine (**3aa**) to amine (**4aa**) may not be feasible.

The electrode potential value of K^{t}OBu is reported as +0.1 V in the literature.[S28] Notably, the peak value was assigned by considering the peak; whereas in our case, we have assigned the electrode potential values for the onset potential by drawing the tangent, a more appropriate method. If one can assign the value of the cited paper via drawing a tangent, the potential will come close to our observed potential value. Therefore, the provided potential by us is consistent with the literature.

The additional peaks appear in the CV diagrams (ESI, Fig. S3(b-e)) are due to the DMF solvent. We have provided a CV diagram of DMF (Fig S3 (a)) for the reference, which has the same peaks.

Note: The electrode potential of K_2CO_3 could not be calculated because of its insolubility in DMF or DMSO solvent.
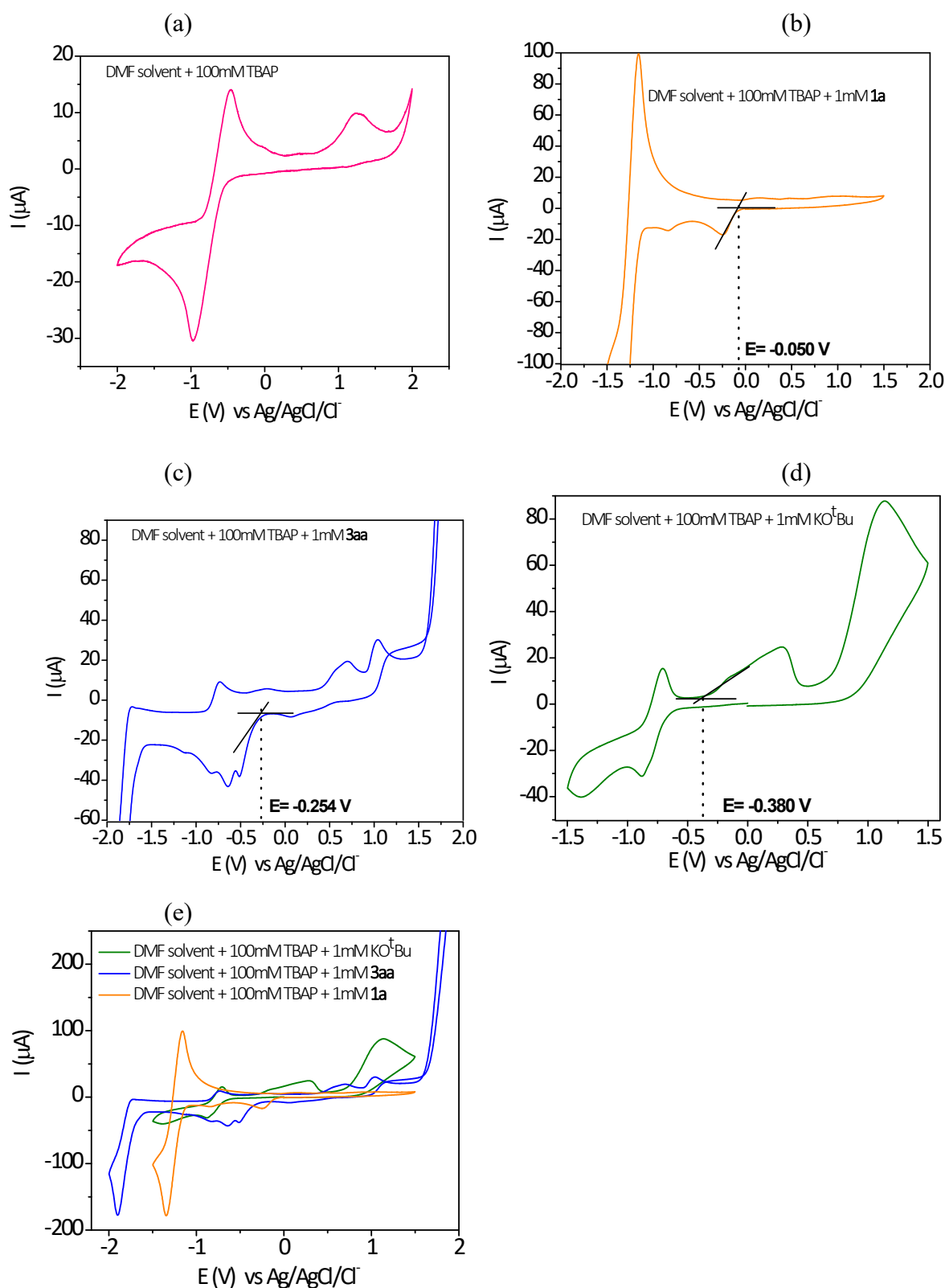
Figure S3. Cyclic voltammograms of (a) DMF, (b) 1 mM **1a**, (c) 1 mM **3aa**, (d) KO^{t}Bu (e) Combined data; at 100 mV/s scan rate. 100 mM TBAP was used a supporting electrolyte, with Glassy carbon as working electrode, Platinum wire as counter electrode and Ag/AgCl/Cl$^-$ as reference electrode.

12.   X-ray Structural Data

X-ray intensity data measurements of compound **Ni-2** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (MoK_α= 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three matrix sets of 36 frames (each matrix run consists of 12 frames). Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10-20 sec depending on the diffraction power of the crystals keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[S29] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[S30] structure solution program, using direct methods. The model was refined with a version of ShelXL-2018/3 (Sheldrick, 2015)[S31] using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP* III[S32] view of the compounds was drawn with 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii.

Table S2. Crystal data for **Ni-2**

	Ni-2
Formula	$C_{20}H_{16}Cl_2N_4NiO_2$, CH_2Cl_2
Molecular weight	558.90
Crystal Size, mm	$0.320 \times 0.290 \times 0.219$
Temp. (K)	100(2)
Wavelength (Å)	0.71073
Crystal Syst.	orthorhombic
Space Group	$Pna2_1$
a/Å	19.3515(14)
b/Å	10.4522(8)
c/Å	11.3070(9)
α/°	90
β/°	90
γ/°	90
V/Å^3	2287.0(3)
Z	4
D_{calc}/g cm^{-3}	1.623
μ/mm^{-1}	1.343
$F(000)$	1136
Ab. Correct.	multi-scan
T_{min}/ T_{max}	0.673/0.766
$2\theta_{max}$	61
Total reflns.	92687
Unique reflns.	6985
Obs. reflns.	6522
h, k, l (min, max)	(-27, 27), (-14, 14), (-16, 16)
R_{int} / R_{sig}	0.0.621/ 0.0293
No. of parameters	297
R1 [$I> 2\sigma(I)$]	0.0246
wR2[$I> 2\sigma(I)$]	0.0575
R1 [all data]	0.0296
wR2 [all data]	0.0610
goodness-of-fit	1.071
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.352, -0.645
CCDC	2211568

Table S3. Bond lengths (Å) for **Ni-2**.

Ni1-N3	2.059(2)	Ni1-N2	2.069(2)
Ni1-N4	2.128(2)	Ni1-N1	2.135(2)
Ni1-Cl2	2.4300(6)	Ni1-Cl1	2.4302(6)
O1-C1	1.334(3)	O1-H1	0.85(2)
O2-C20	1.334(3)	O2-H20	0.84(2)
N1-C1	1.339(3)	N1-C5	1.371(3)
N2-C10	1.338(3)	N2-C6	1.351(3)
N3-C11	1.339(3)	N3-C15	1.349(3)
N4-C20	1.339(3)	N4-C16	1.366(3)
C1-C2	1.400(3)	C2-C3	1.371(4)
C2-H2	0.95	C3-C4	1.390(4)
C3-H3	0.95	C4-C5	1.379(4)
C4-H4	0.95	C5-C6	1.482(4)
C6-C7	1.396(3)	C7-C8	1.390(4)
C7-H7	0.95	C8-C9	1.379(4)
C8-H8	0.95	C9-C10	1.391(4)
C9-H9	0.95	C10-H10	0.95
C11-C12	1.389(3)	C11-H11	0.95
C12-C13	1.384(4)	C12-H12	0.95
C13-C14	1.386(4)	C13-H13	0.95
C14-C15	1.396(3)	C14-H14	0.95
C15-C16	1.481(4)	C16-C17	1.382(4)
C17-C18	1.390(4)	C17-H17	0.95
C18-C19	1.375(4)	C18-H18	0.95
C19-C20	1.402(4)	C19-H19	0.95
Cl3-C21	1.760(3)	Cl4-C21	1.776(3)
C21-H21A	0.99	C21-H21B	0.99

Table S4. Bond angles (°) for **Ni-2.**

N3-Ni1-N2	89.89(8)	N3-Ni1-N4	79.25(8)
N2-Ni1-N4	94.15(8)	N3-Ni1-N1	94.89(8)
N2-Ni1-N1	79.06(8)	N4-Ni1-N1	171.11(8)
N3-Ni1-Cl2	88.28(6)	N2-Ni1-Cl2	177.78(6)
N4-Ni1-Cl2	86.74(6)	N1-Ni1-Cl2	99.85(6)
N3-Ni1-Cl1	178.81(6)	N2-Ni1-Cl1	89.87(6)
N4-Ni1-Cl1	99.61(6)	N1-Ni1-Cl1	86.21(6)
Cl2-Ni1-Cl1	91.98(2)	C1-O1-H1	116.(3)
C20-O2-H20	106.(3)	C1-N1-C5	117.2(2)
C1-N1-Ni1	129.35(17)	C5-N1-Ni1	112.97(17)
C10-N2-C6	118.8(2)	C10-N2-Ni1	125.54(18)
C6-N2-Ni1	115.68(17)	C11-N3-C15	119.4(2)
C11-N3-Ni1	124.94(17)	C15-N3-Ni1	115.65(16)
C20-N4-C16	117.7(2)	C20-N4-Ni1	129.35(17)
C16-N4-Ni1	112.89(16)	O1-C1-N1	120.2(2)
O1-C1-C2	116.3(2)	N1-C1-C2	123.4(2)
C3-C2-C1	118.4(3)	C3-C2-H2	120.8
C1-C2-H2	120.8	C2-C3-C4	119.4(2)
C2-C3-H3	120.3	C4-C3-H3	120.3
C5-C4-C3	119.3(2)	C5-C4-H4	120.3
C3-C4-H4	120.3	N1-C5-C4	122.2(2)
N1-C5-C6	115.6(2)	C4-C5-C6	122.2(2)
N2-C6-C7	121.6(2)	N2-C6-C5	116.3(2)
C7-C6-C5	122.1(2)	C8-C7-C6	118.8(3)
C8-C7-H7	120.6	C6-C7-H7	120.6
C9-C8-C7	119.6(2)	C9-C8-H8	120.2
C7-C8-H8	120.2	C8-C9-C10	118.4(3)
C8-C9-H9	120.8	C10-C9-H9	120.8
N2-C10-C9	122.9(3)	N2-C10-H10	118.5
C9-C10-H10	118.5	N3-C11-C12	122.5(2)
N3-C11-H11	118.8	C12-C11-H11	118.8
C13-C12-C11	118.6(3)	C13-C12-H12	120.7

C11-C12-H12	120.7	C12-C13-C14	119.2(2)
C12-C13-H13	120.4	C14-C13-H13	120.4
C13-C14-C15	119.4(3)	C13-C14-H14	120.3
C15-C14-H14	120.3	N3-C15-C14	121.0(2)
N3-C15-C16	116.2(2)	C14-C15-C16	122.8(2)
N4-C16-C17	122.4(2)	N4-C16-C15	115.8(2)
C17-C16-C15	121.8(2)	C16-C17-C18	118.9(3)
C16-C17-H17	120.6	C18-C17-H17	120.6
C19-C18-C17	119.6(3)	C19-C18-H18	120.2
C17-C18-H18	120.2	C18-C19-C20	118.4(3)
C18-C19-H19	120.8	C20-C19-H19	120.8
O2-C20-N4	120.1(2)	O2-C20-C19	117.0(2)
N4-C20-C19	122.9(2)	Cl3-C21-Cl4	110.56(17)
Cl3-C21-H21A	109.5	Cl4-C21-H21A	109.5
Cl3-C21-H21B	109.5	Cl4-C21-H21B	109.5
H21A-C21-H21B	108.1		

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14. ^{1}H and ^{13}C{^{1}H} NMR Spectra of 4,4'-Dibutoxyazobenzene

1q

(400 MHz, CDCl$_3$)

1q

(100 MHz, CDCl$_3$)
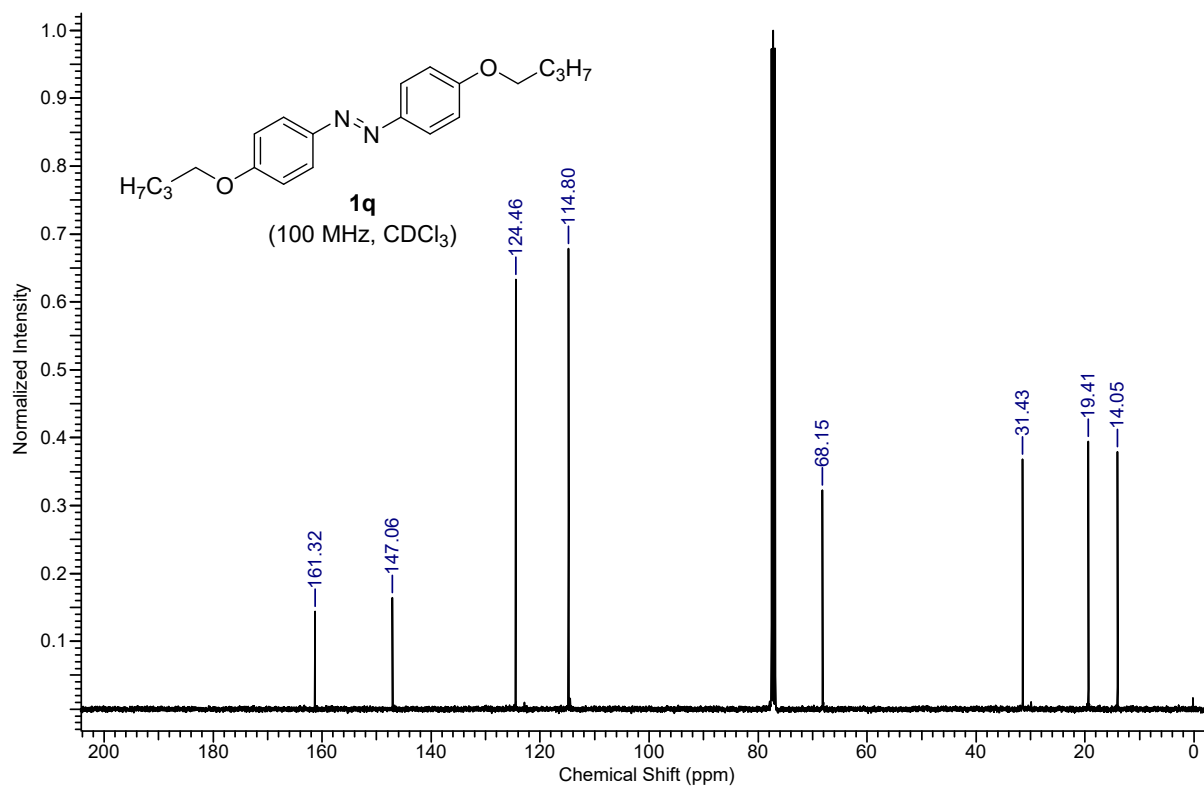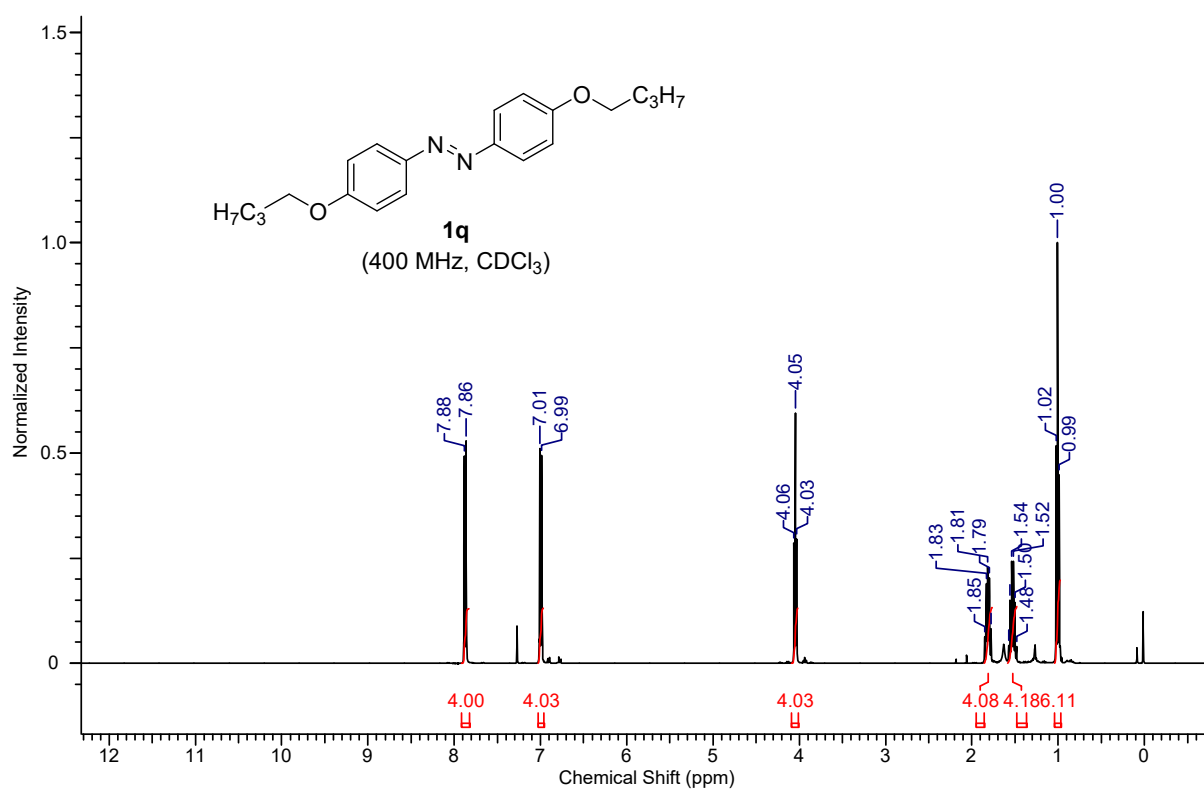
15. ^{1}H NMR Spectra of Imines
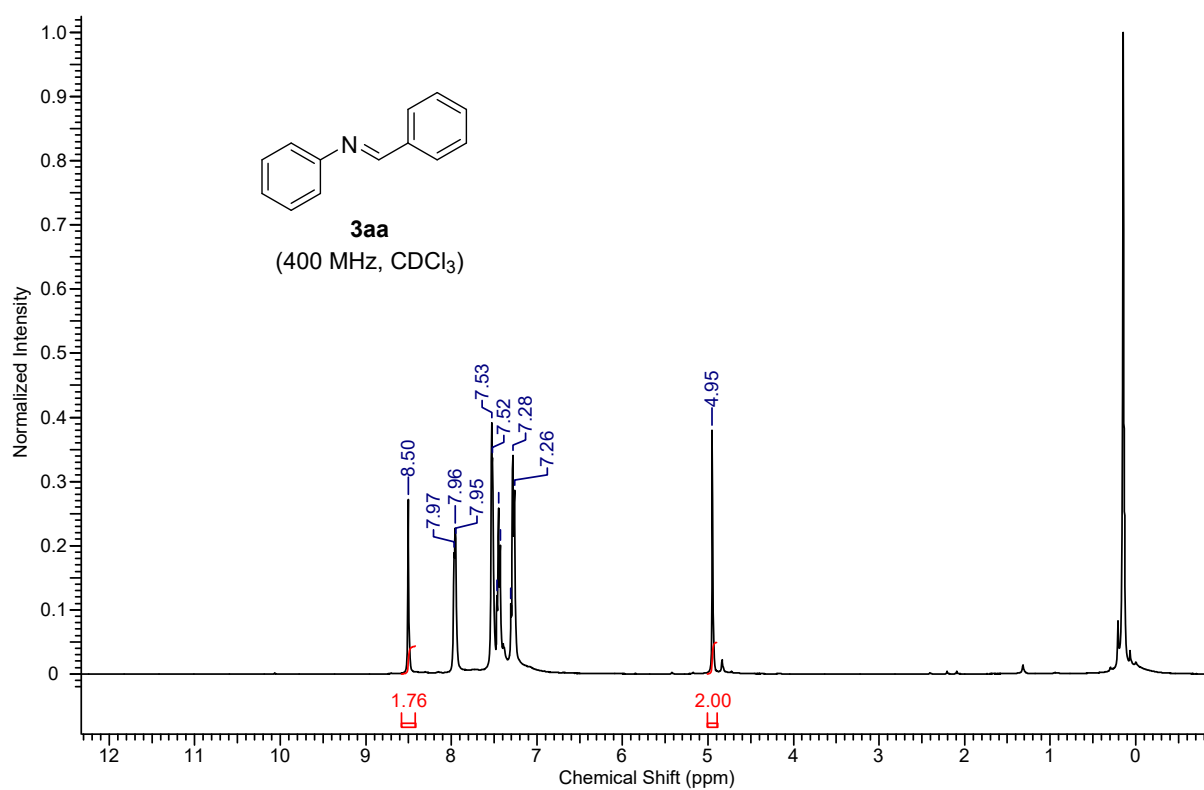
^{1}H-NMR spectrum of *N*-Benzylideneaniline (**3aa**) obtained from the crude reaction mixture
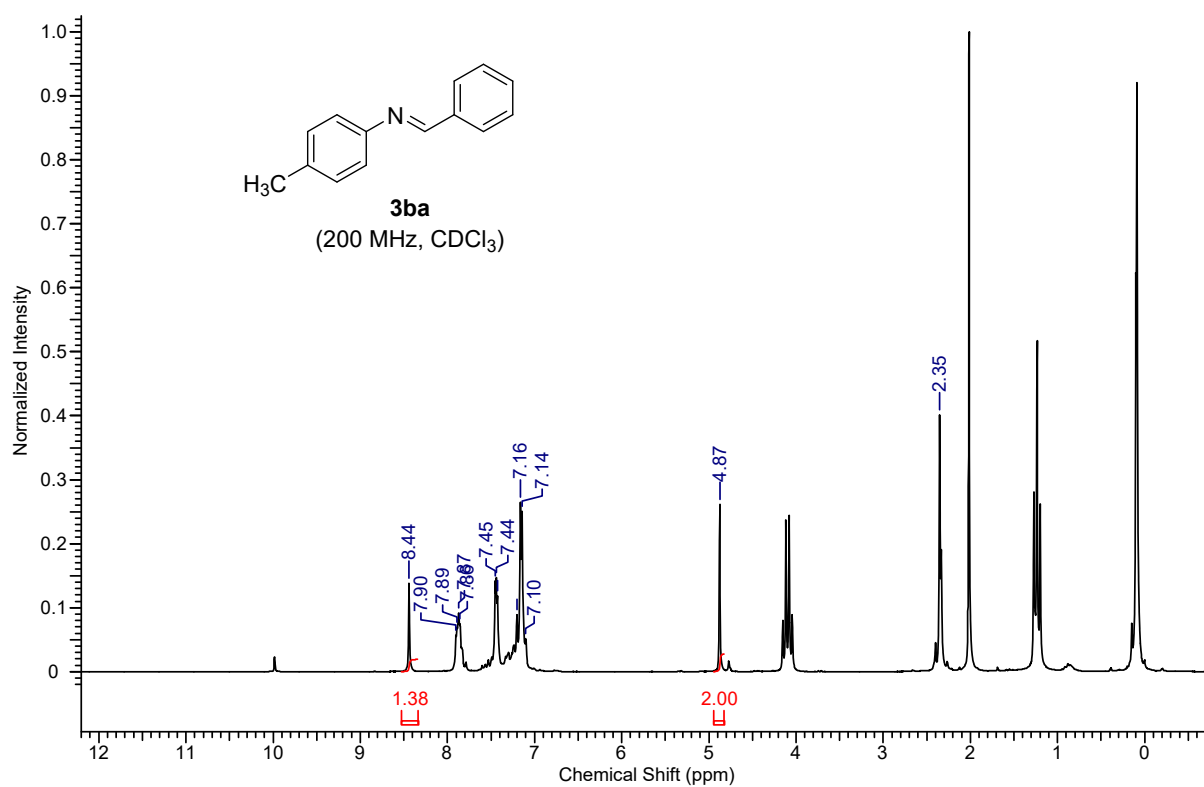
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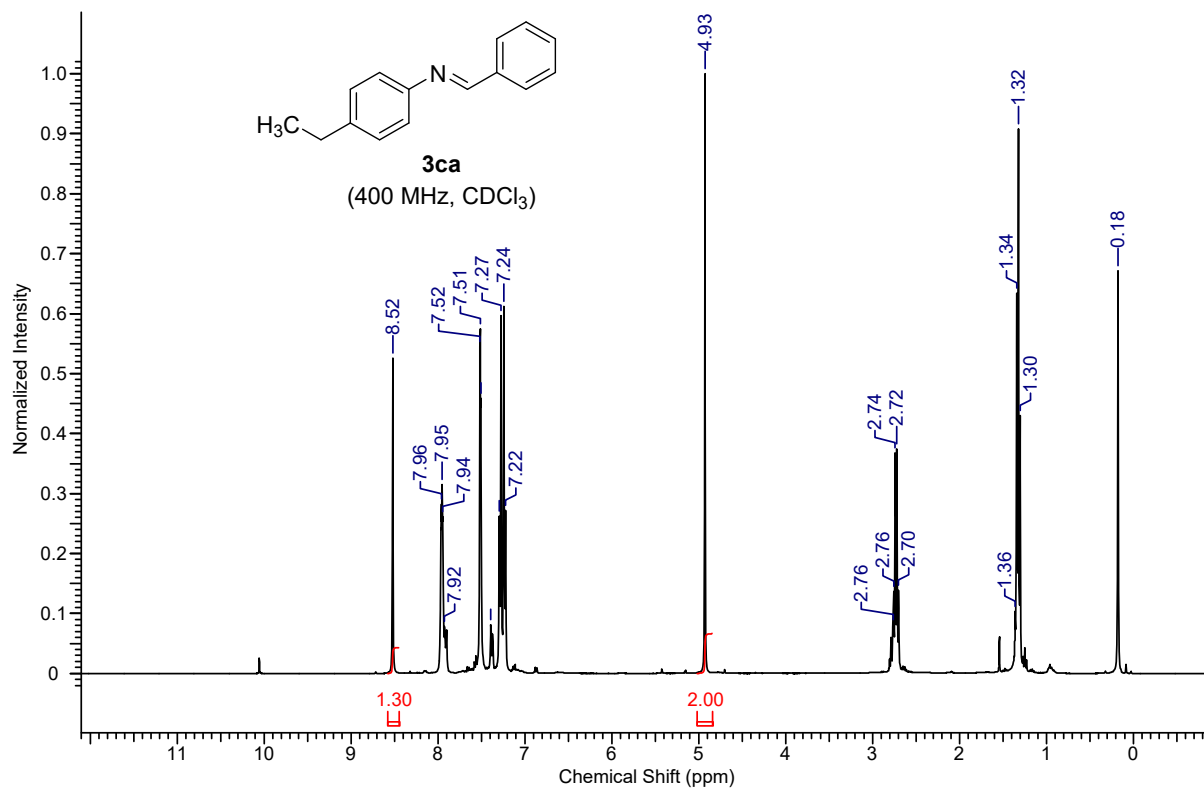
^{1}H-NMR spectrum of *N*-Benzylidene-4-ethylaniline (**3ca**) obtained from the crude reaction mixture
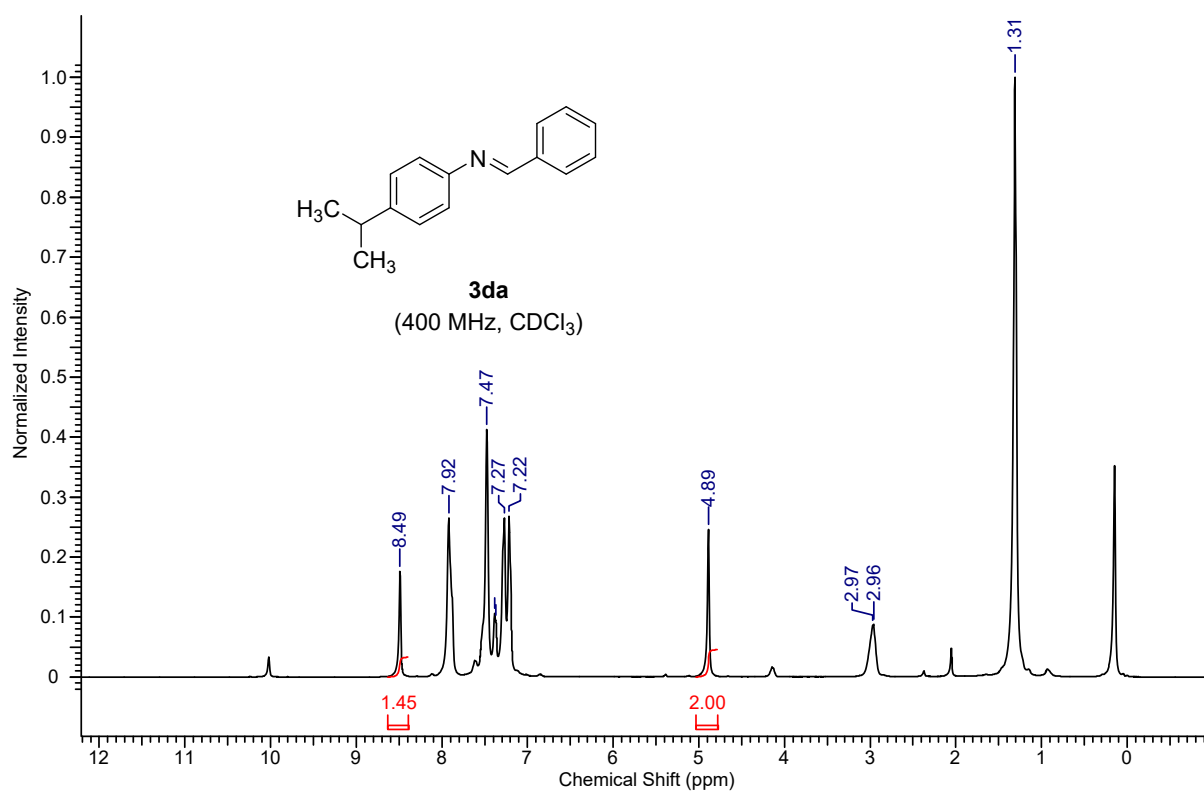
^{1}H-NMR spectrum of *N*-Benzylidene-4-isopropylaniline (**3da**) obtained from the crude reaction mixture
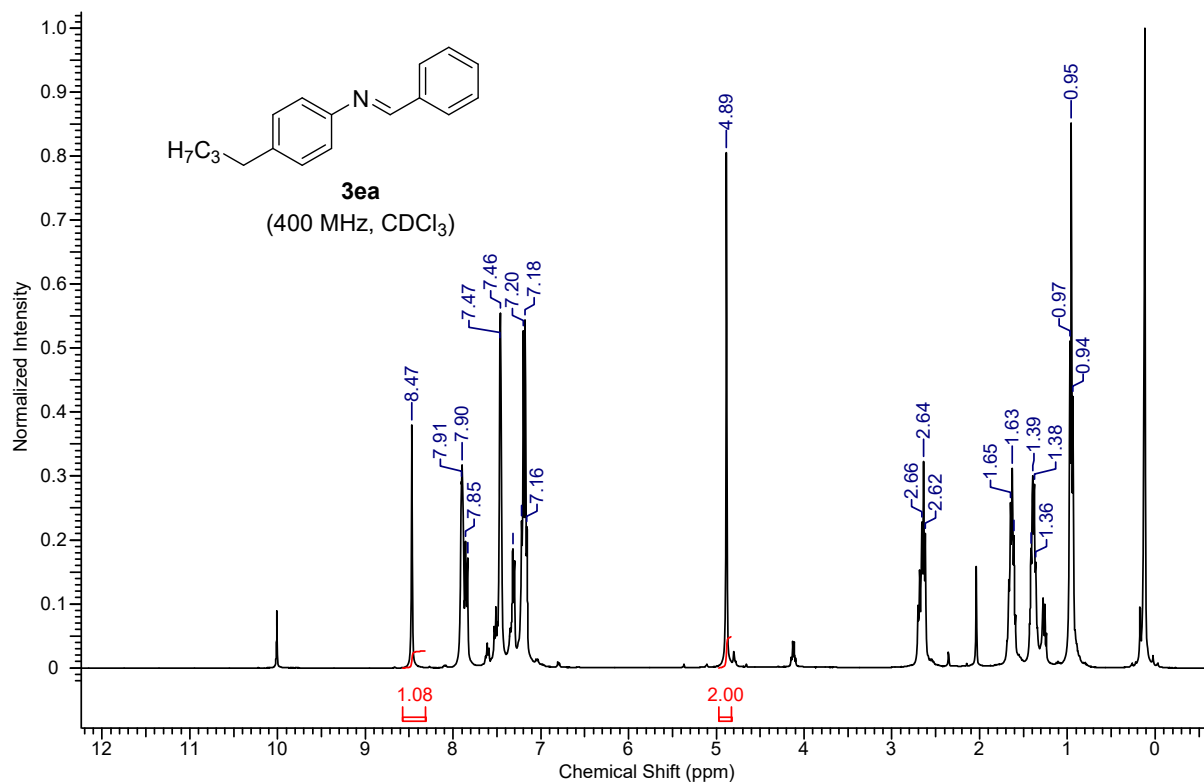
^{1}H-NMR spectrum of *N*-Benzylidene-4-butylaniline (**3ea**) obtained from the crude reaction mixture
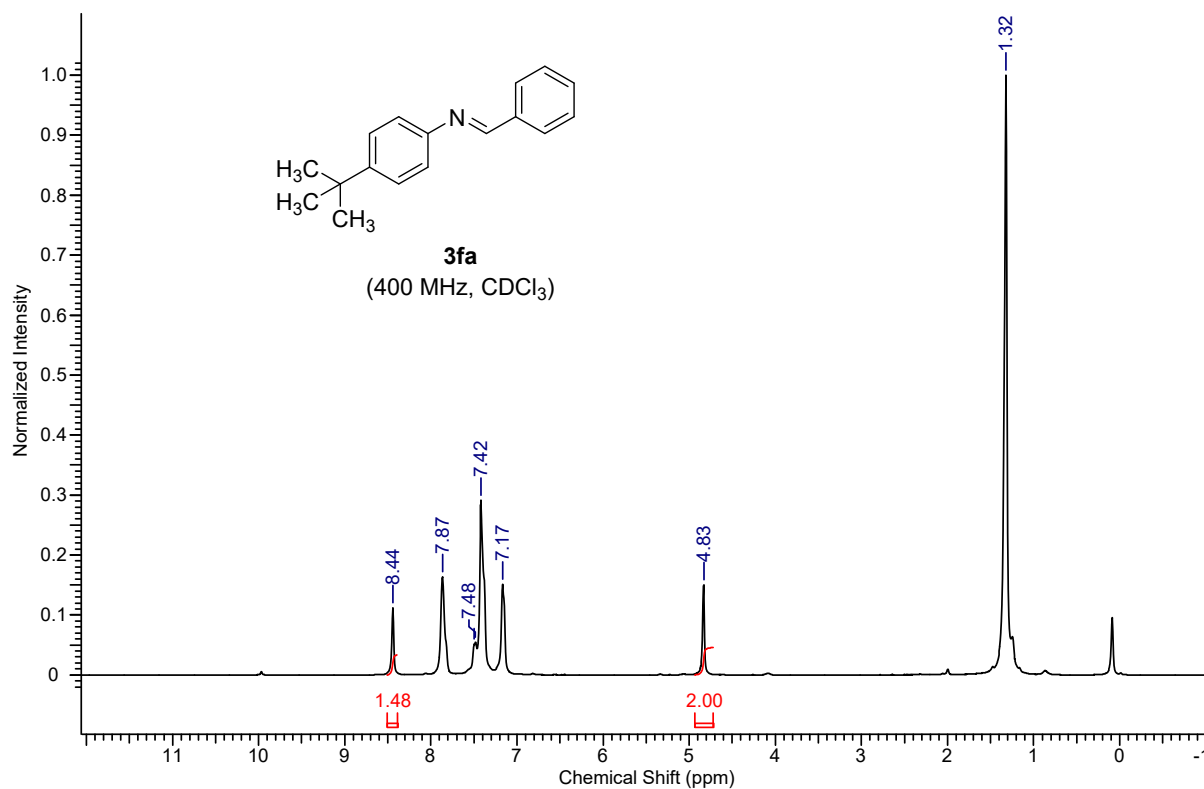
^{1}H-NMR spectrum of *N*-Benzylidene-4-*tert*-butylaniline (**3fa**) obtained from the crude reaction mixture
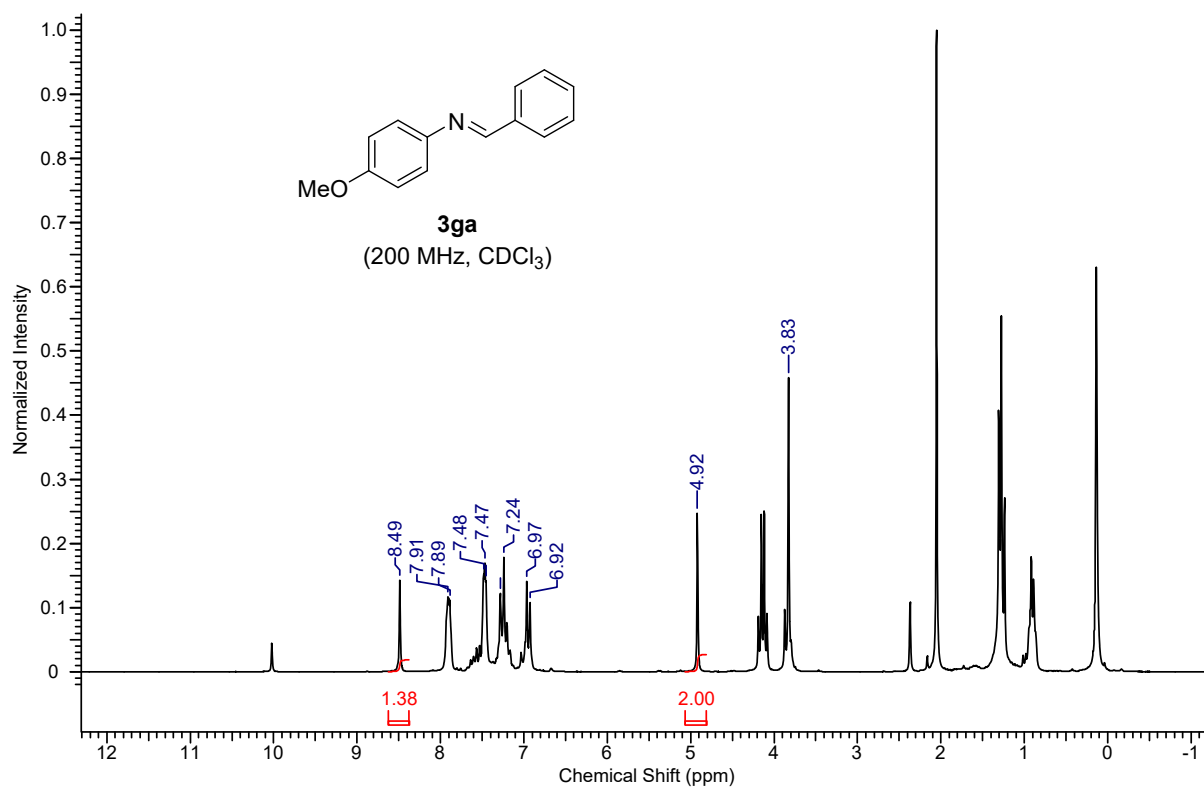
^{1}H-NMR spectrum of *N*-Benzylidene-4-methoxyaniline (**3ga**) obtained from the crude reaction mixture
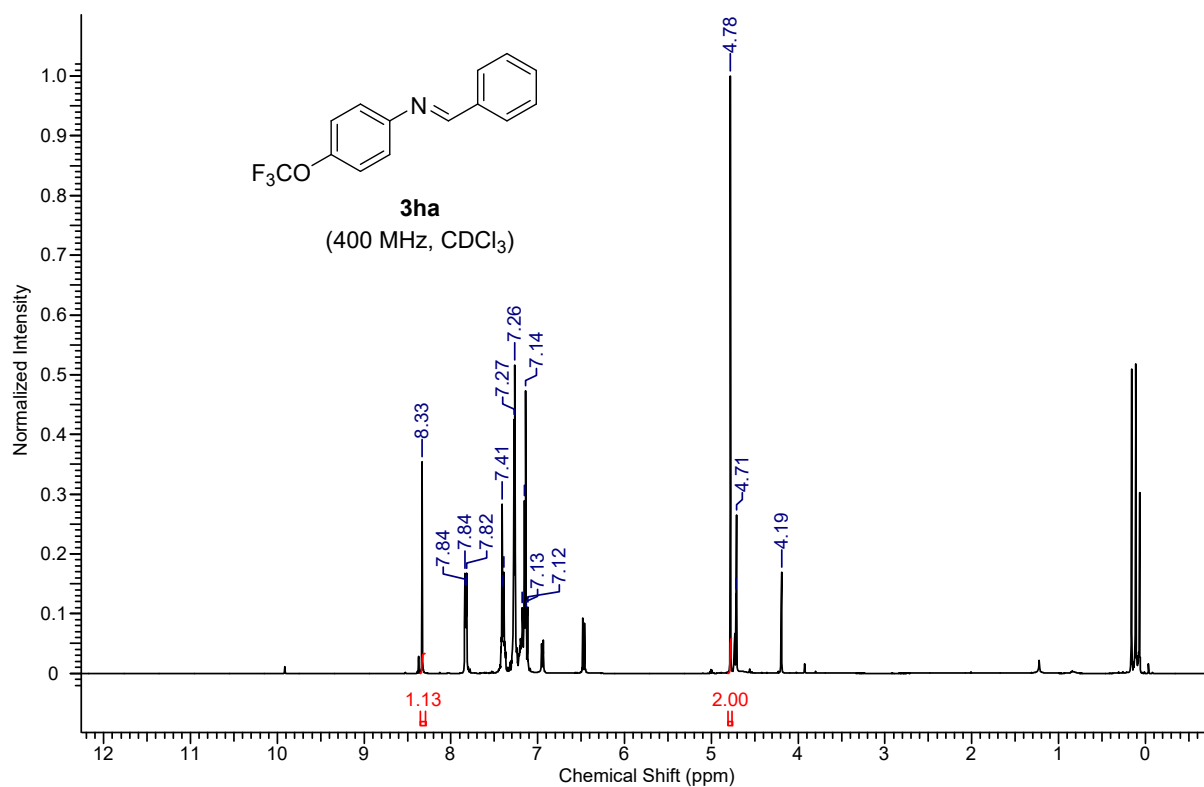
^{1}H-NMR spectrum of *N*-Benzylidene-4-trifluoromethoxyaniline (**3ha**) obtained from the crude reaction mixture
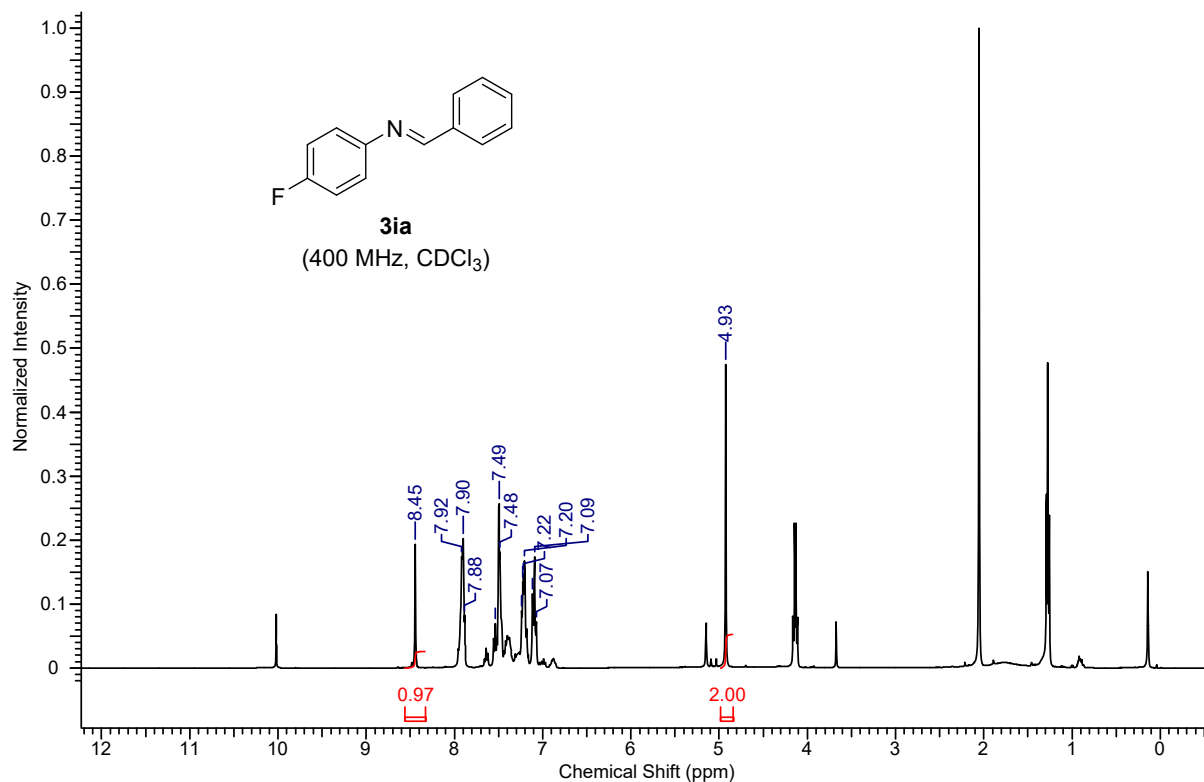
^{1}H-NMR spectrum of *N*-Benzylidene-4-fluoroaniline (**3ia**) obtained from the crude reaction mixture
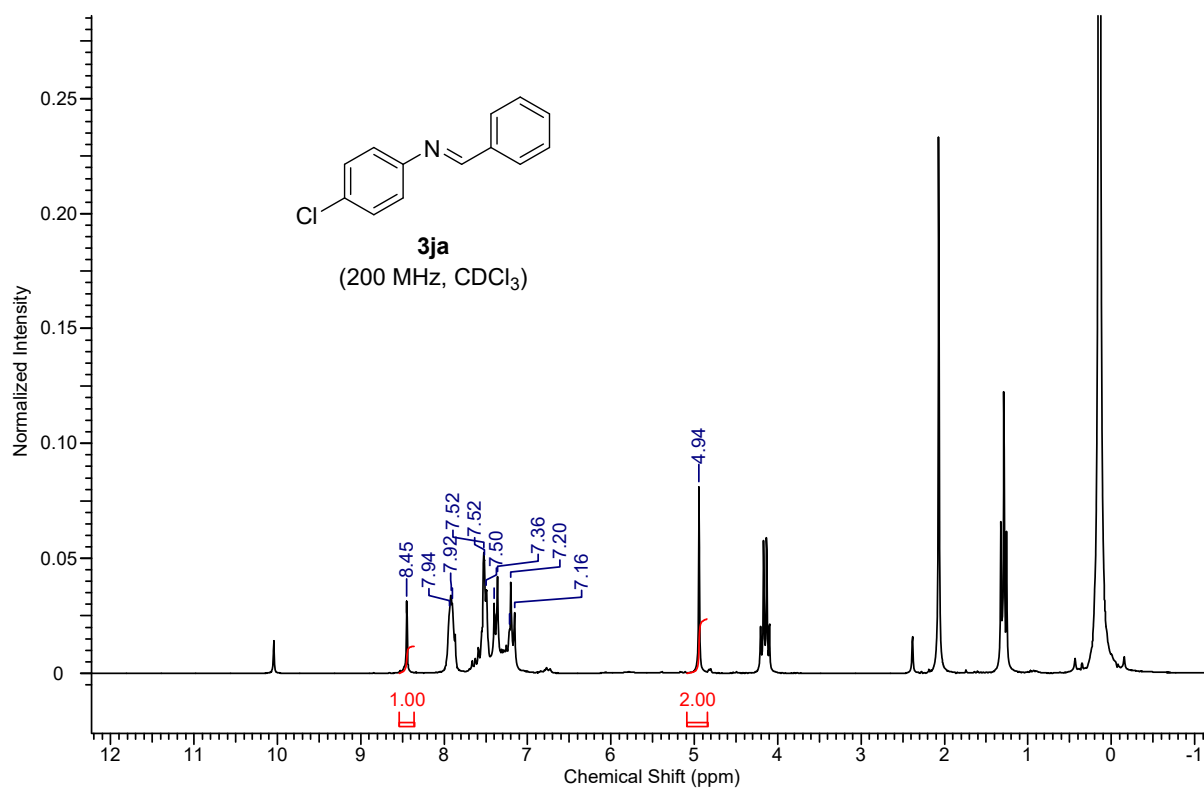
^{1}H-NMR spectrum of *N*-Benzylidene-4-chloroaniline (**3ja**) obtained from the crude reaction mixture
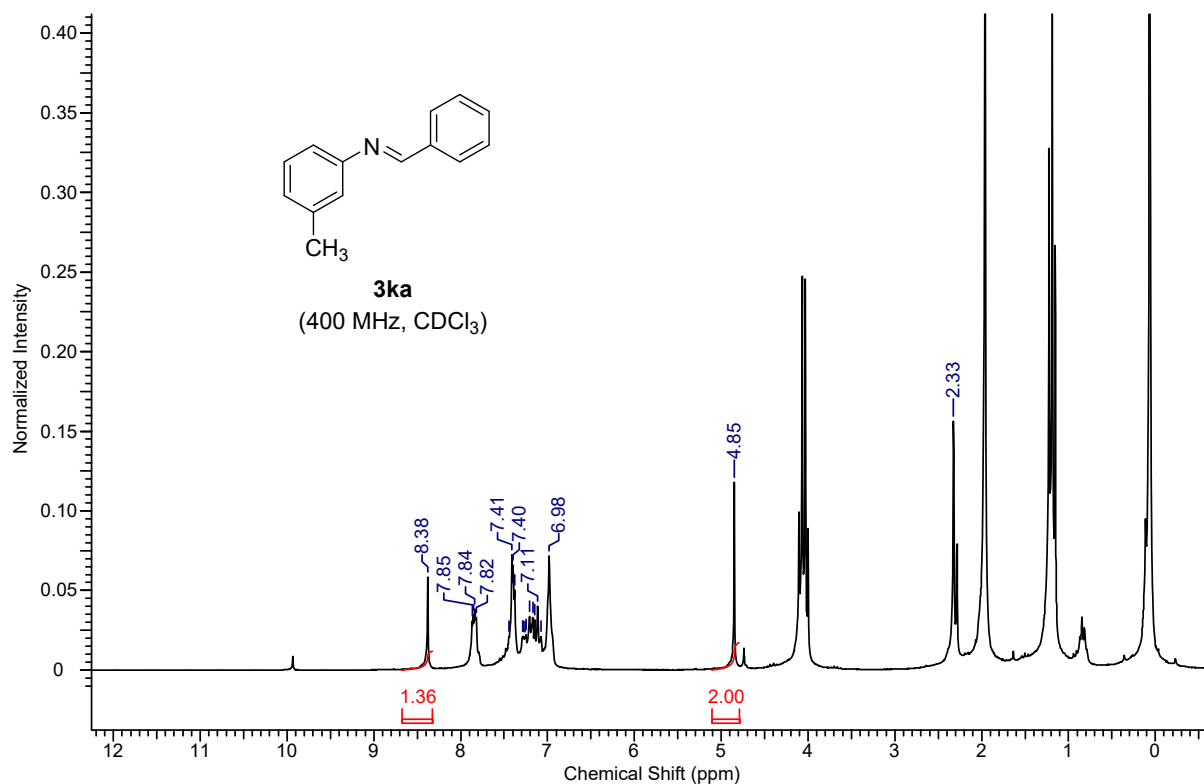
^{1}H-NMR spectrum of *N*-Benzylidene-3-methylaniline (**3ka**) obtained from the crude reaction mixture
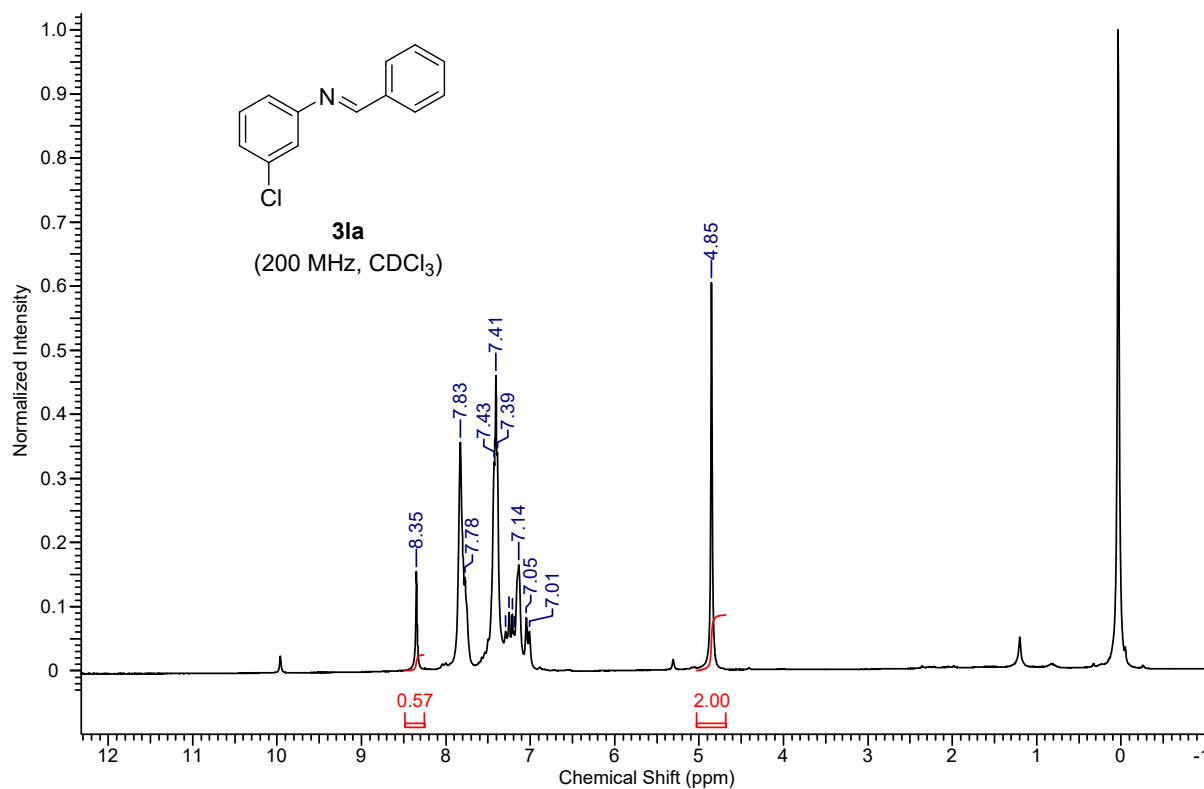
^{1}H-NMR spectrum of *N*-Benzylidene-3-chloroaniline (**3la**) obtained from the crude reaction mixture
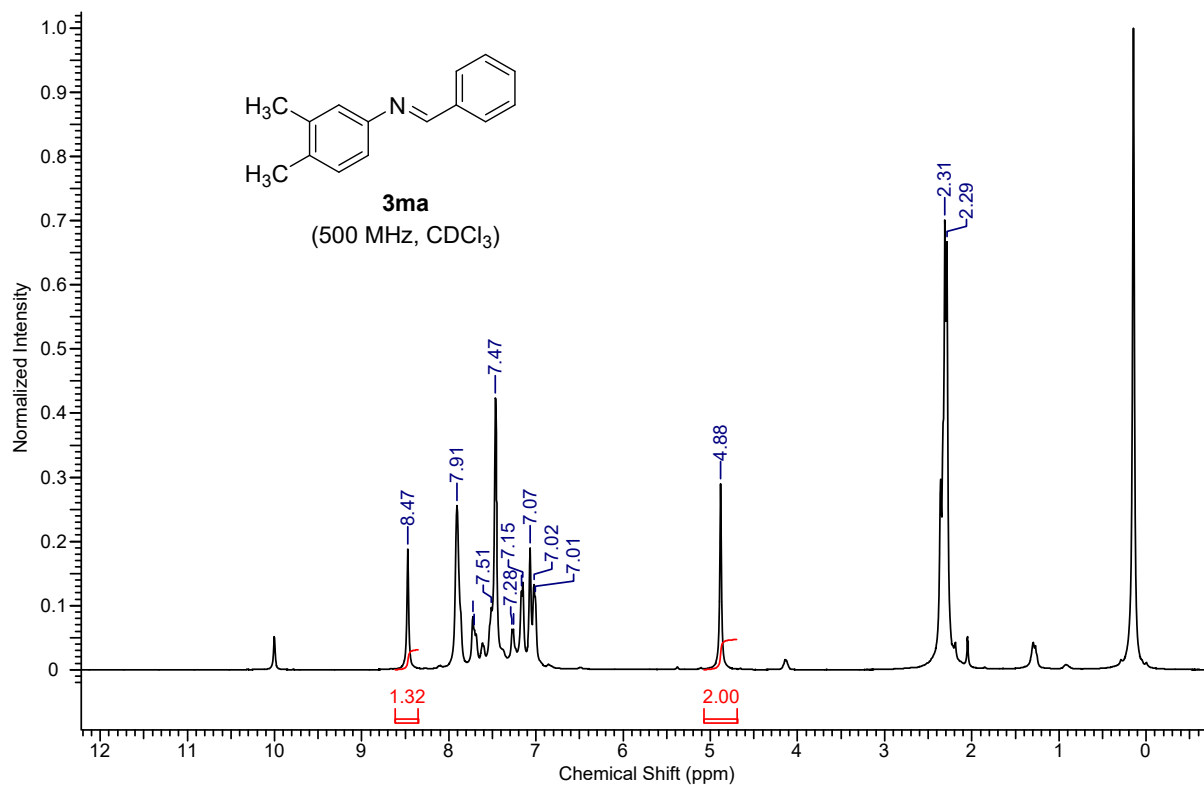
^{1}H-NMR spectrum of N-Benzylidene-3,4-dimethylaniline (**3ma**) obtained from the crude reaction mixture
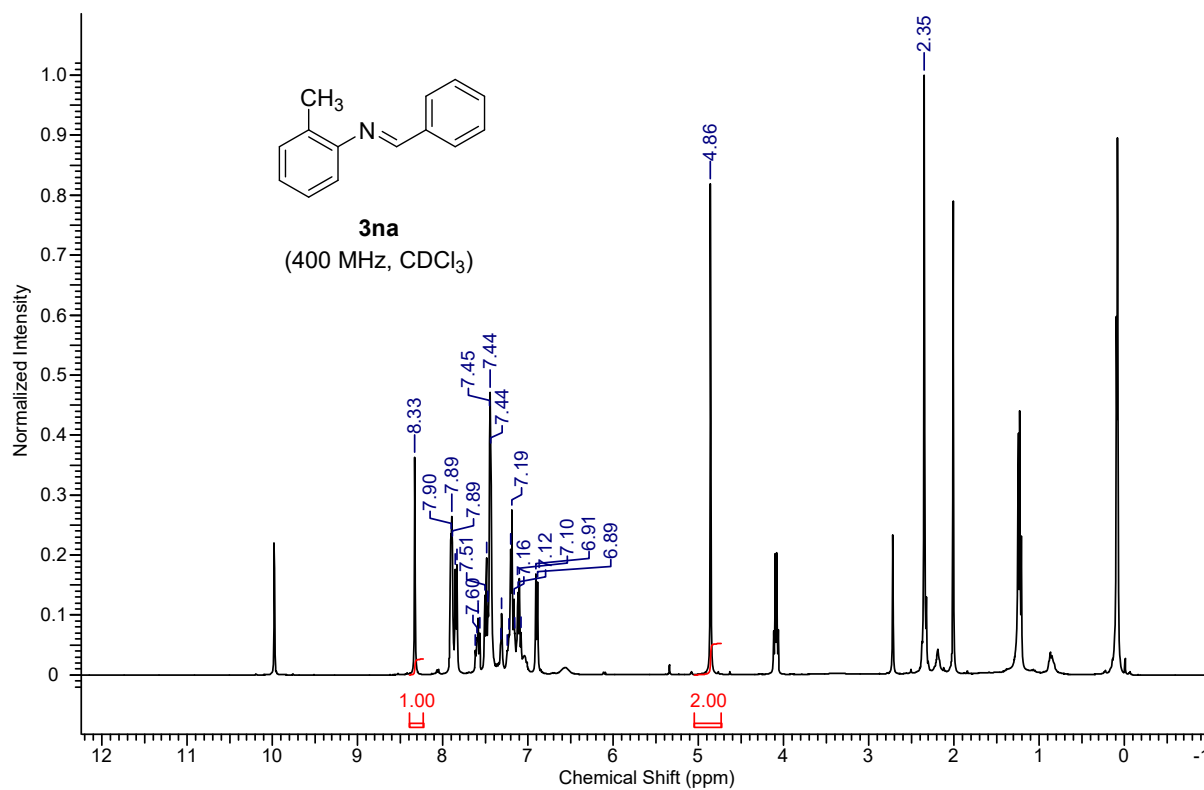
^{1}H-NMR spectrum of N-Benzylidene-2-methylaniline (**3na**) obtained from the crude reaction mixture
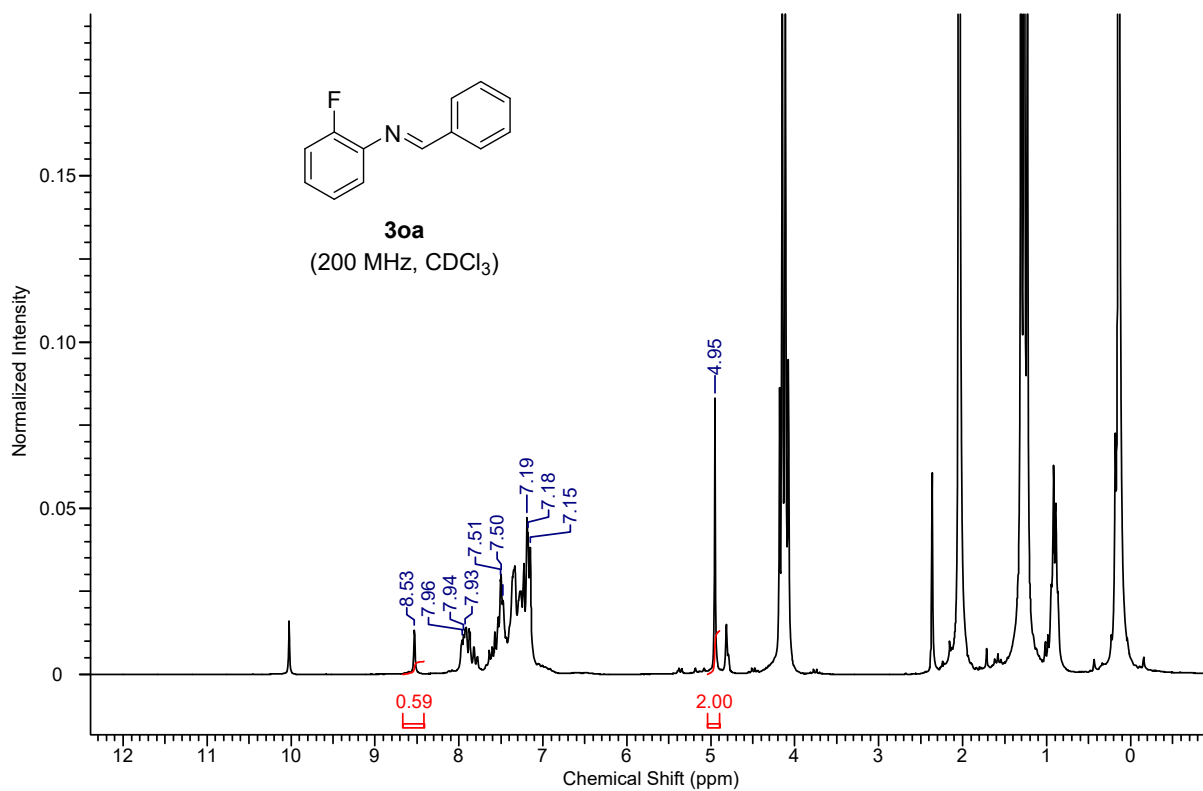
^{1}H-NMR spectrum of *N*-Benzylidene-2-fluoroaniline (**3oa**) obtained from the crude reaction mixture
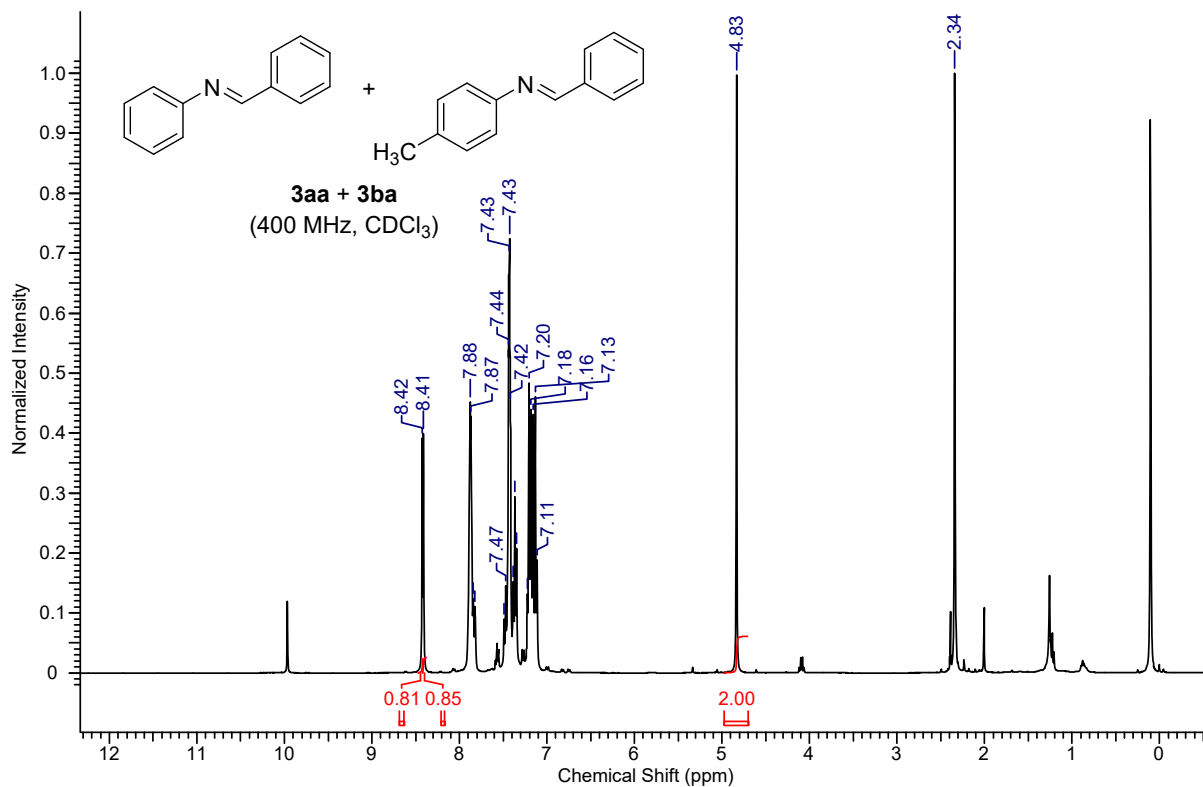
^{1}H-NMR spectrum of *N*-Benzylideneaniline (**3aa**) and N-Benzylidene-4-methylaniline (**3ba**) obtained from the crude reaction mixture
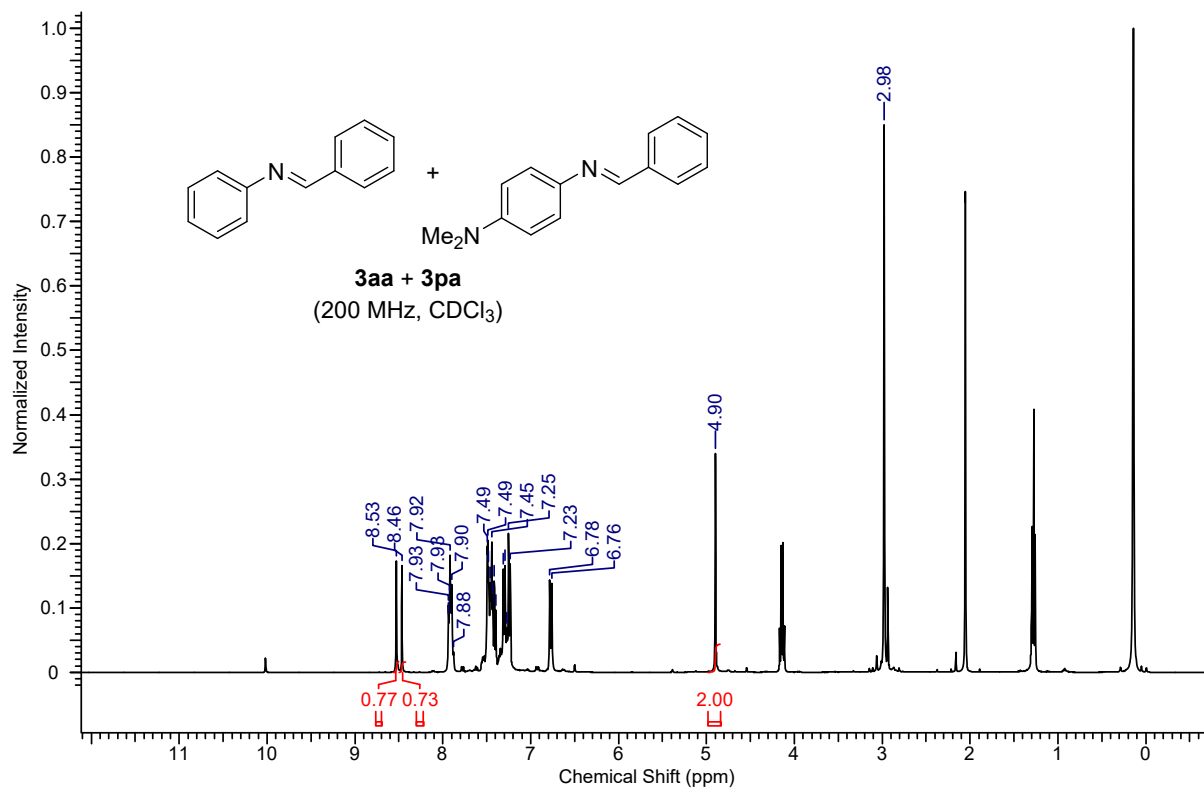
^{1}H-NMR spectrum of *N*-Benzylideneaniline (**3aa**) and *N*-Benzylidene-4-dimethylaminoaniline (**3pa**) obtained from the crude reaction mixture
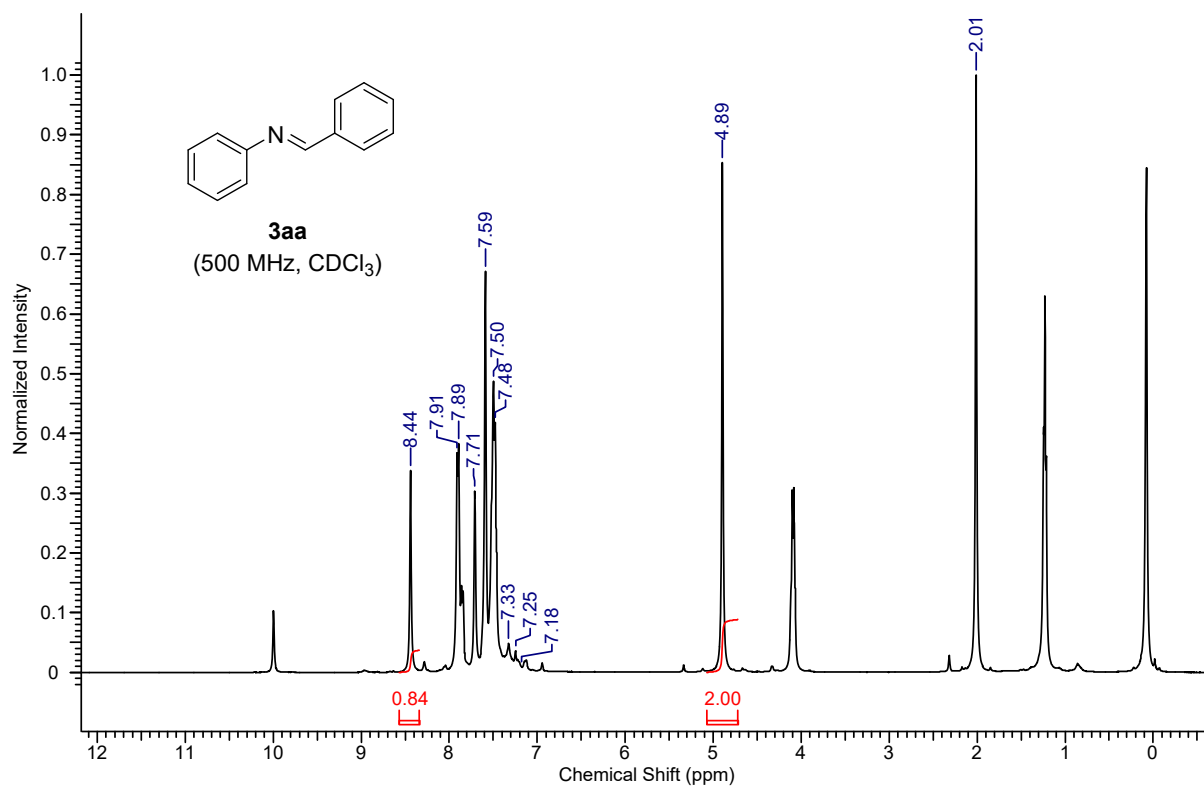
^{1}H-NMR spectrum of the reaction mixture of *N*-Benzylideneaniline (**3aa**) obtained from the crude reaction mixture
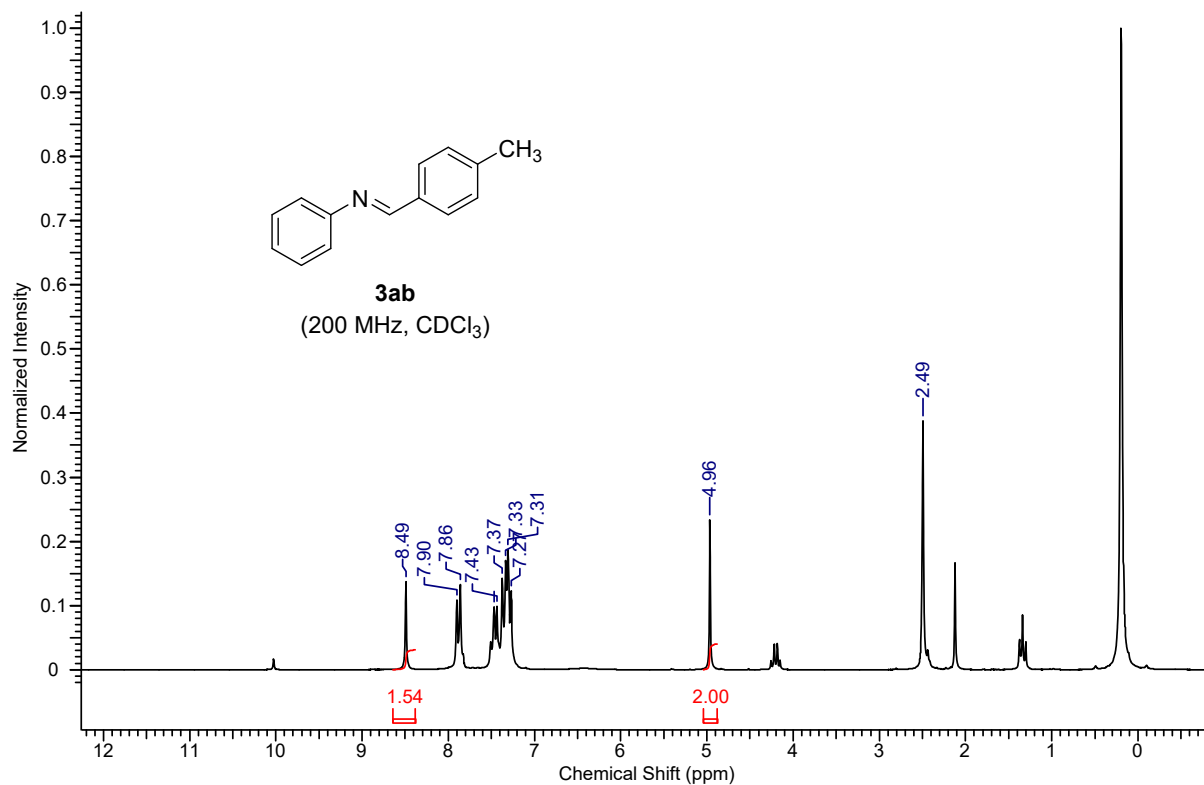
^{1}H-NMR spectrum of *N*-(4-methylbenzylidene)aniline (**3ab**) obtained from the crude reaction mixture
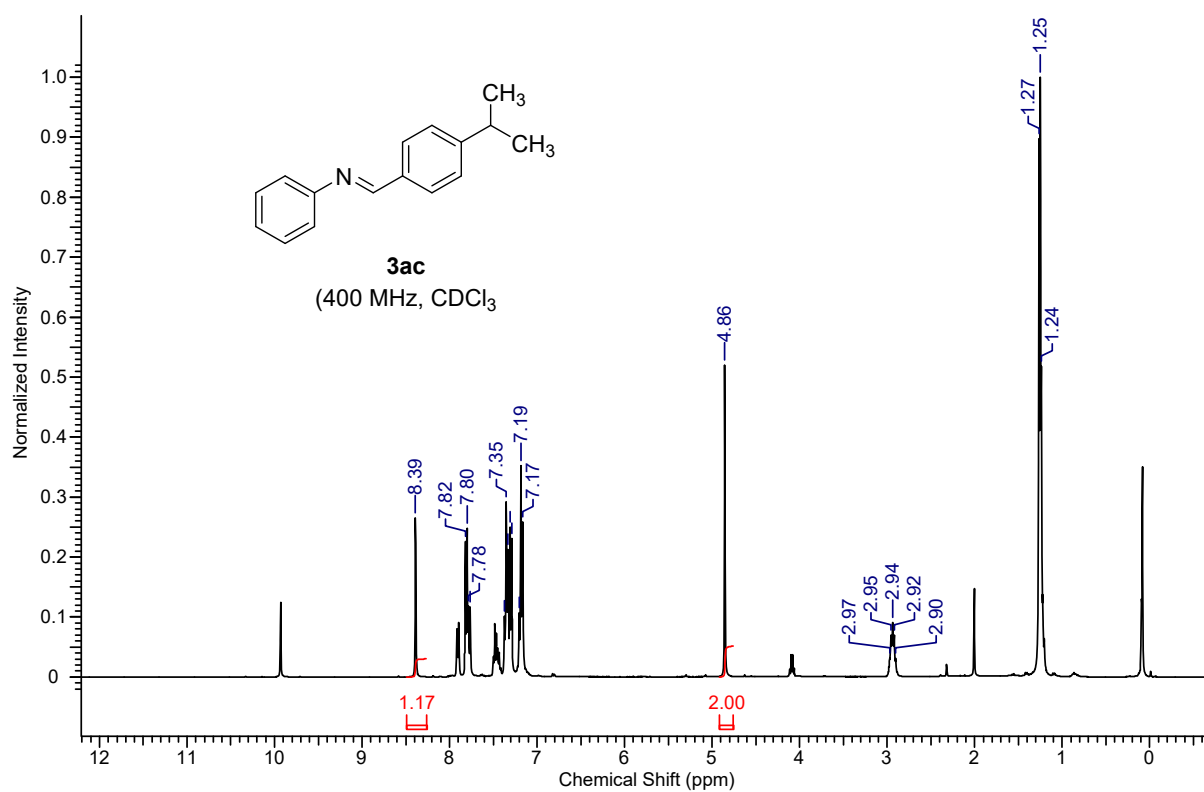
^{1}H-NMR spectrum of *N*-(4-isopropylbenzylidene)aniline (**3ac**) obtained from the crude reaction mixture
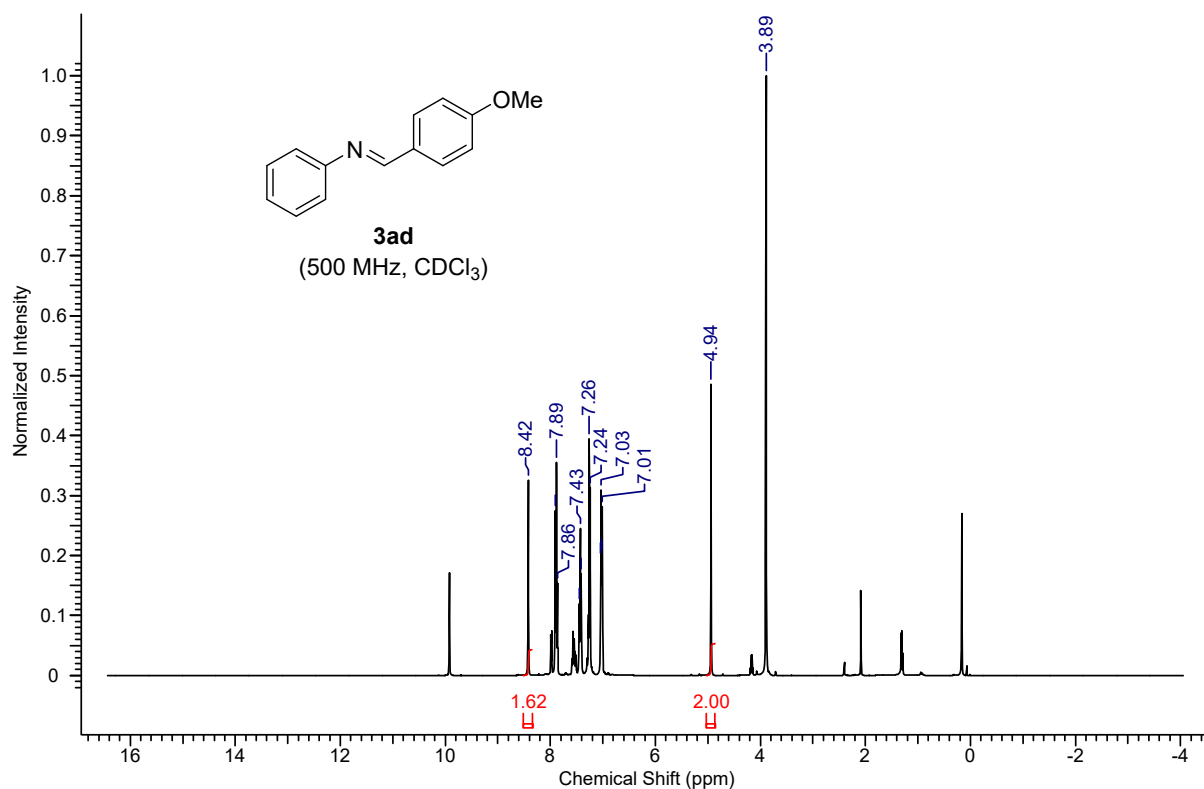
^{1}H-NMR spectrum of *N*-(4-methoxybenzylidene)aniline (**3ad**) obtained from the crude reaction mixture
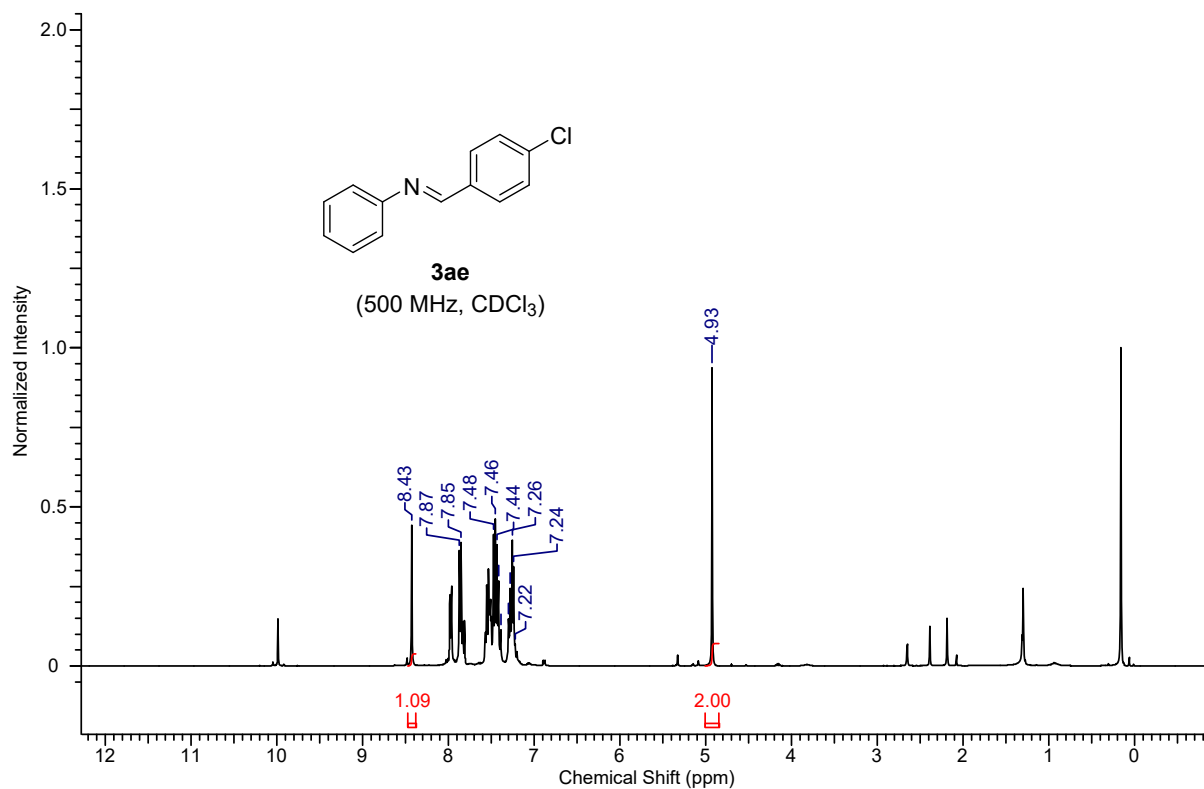
^{1}H-NMR spectrum of *N*-(4-chlorobenzylidene)aniline (**3ae**) obtained from the crude reaction mixture
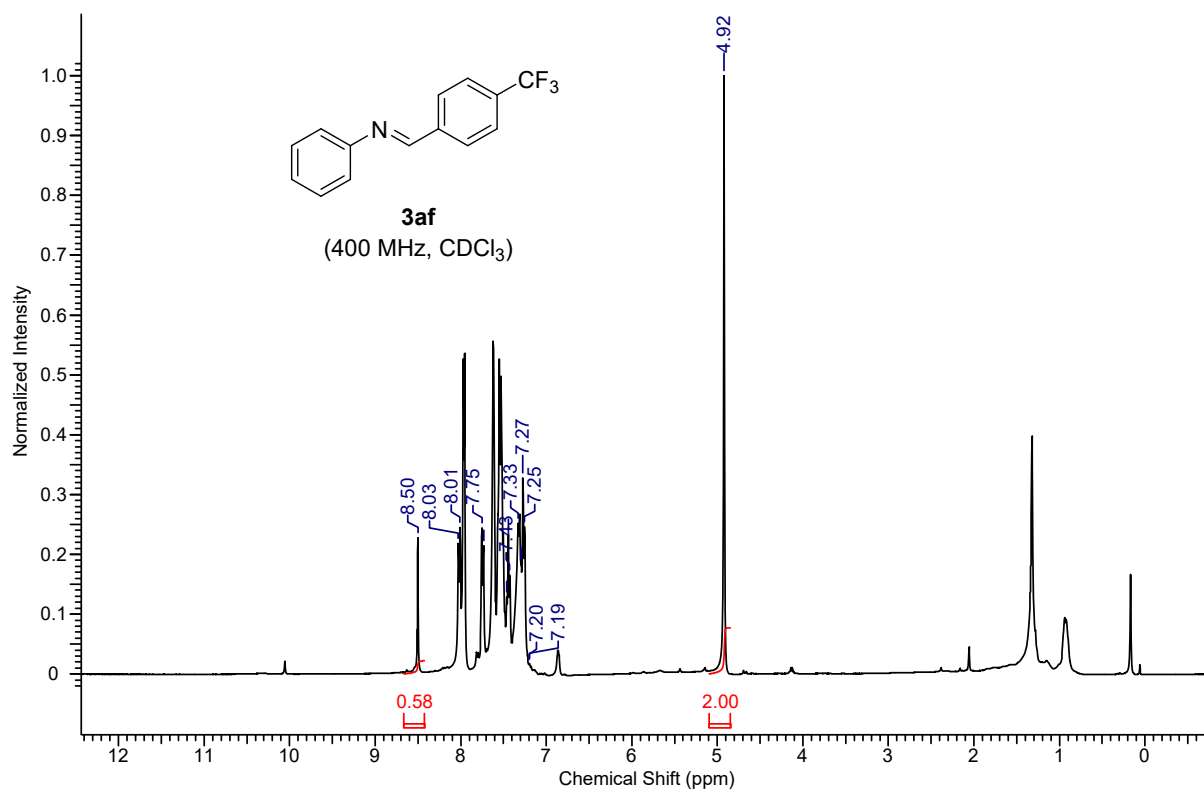
^{1}H-NMR spectrum of N-(4-trifluoromethoxybenzylidene)aniline (**3af**) obtained from the crude reaction mixture
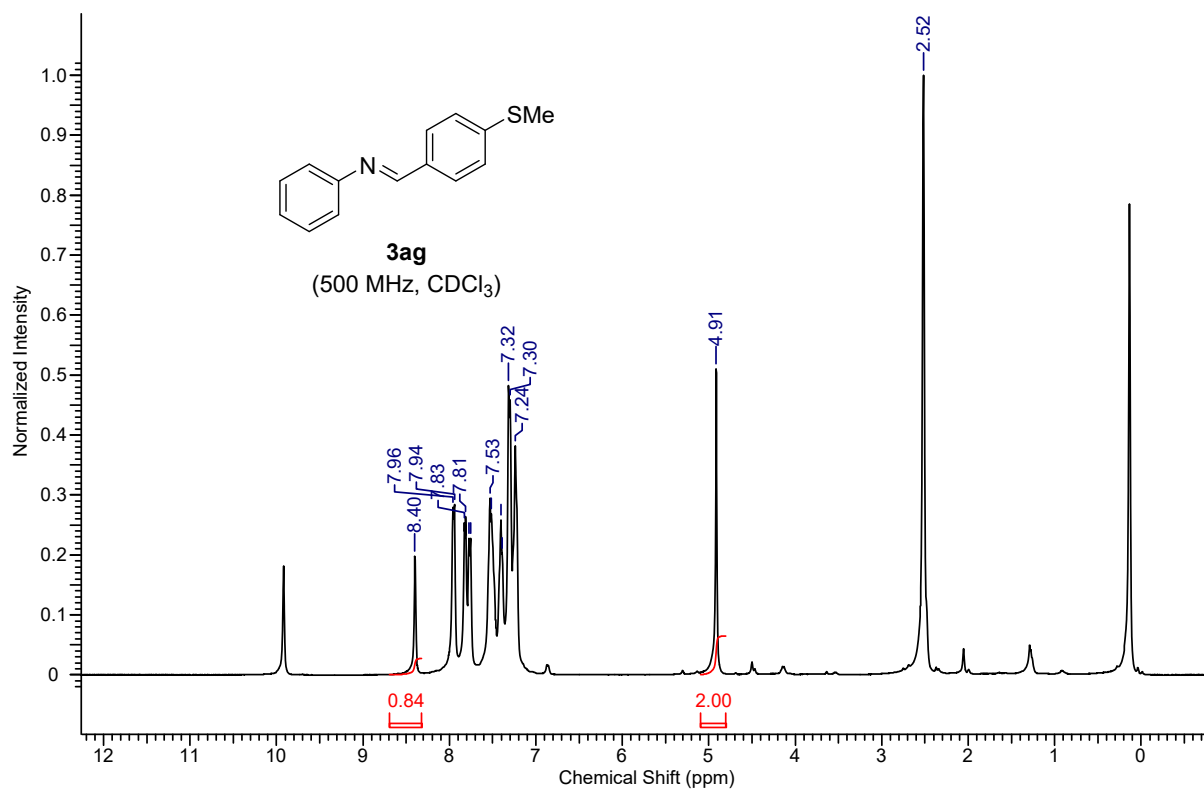
^{1}H-NMR spectrum of N-(4-thiomethylbenzylidene)aniline (**3ag**) obtained from the crude reaction mixture
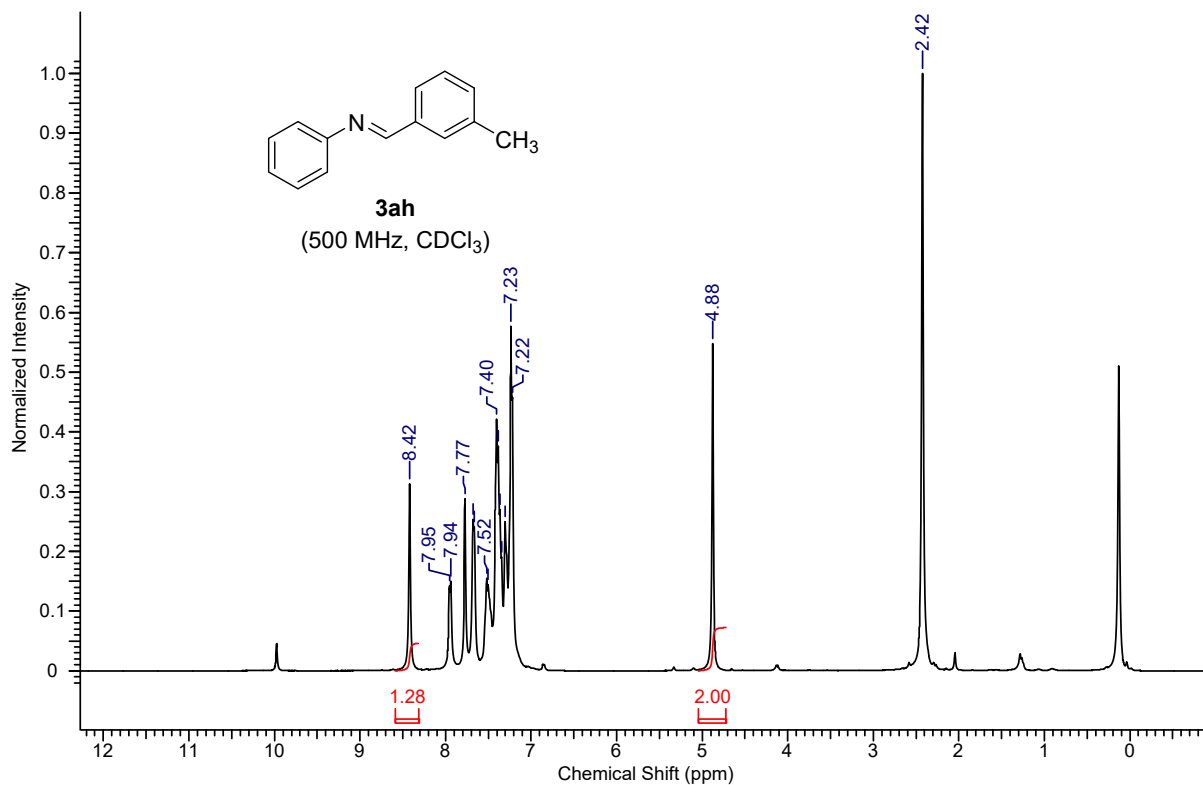
^{1}H-NMR spectrum of *N*-(3-methylbenzylidene)aniline (**3ah**) obtained from the crude reaction mixture
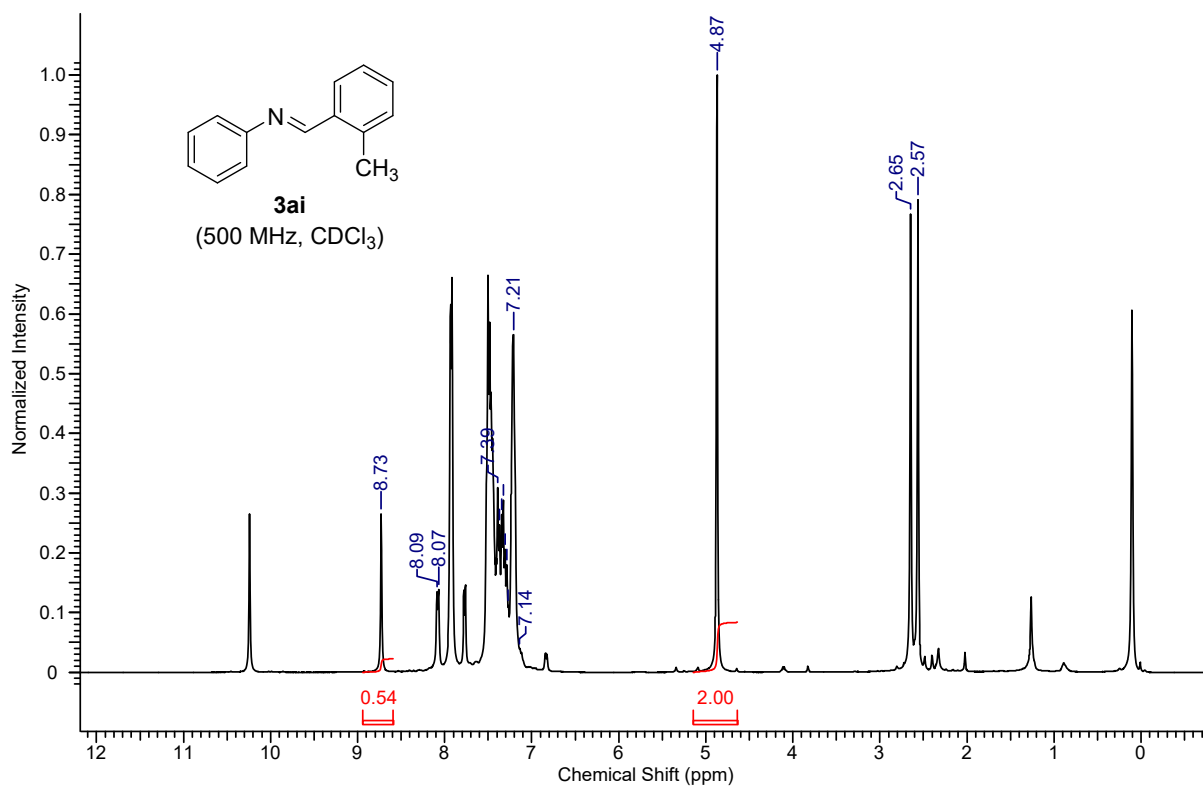
^{1}H-NMR spectrum of *N*-(2-methylbenzylidene)aniline (**3ai**) obtained from the crude reaction mixture
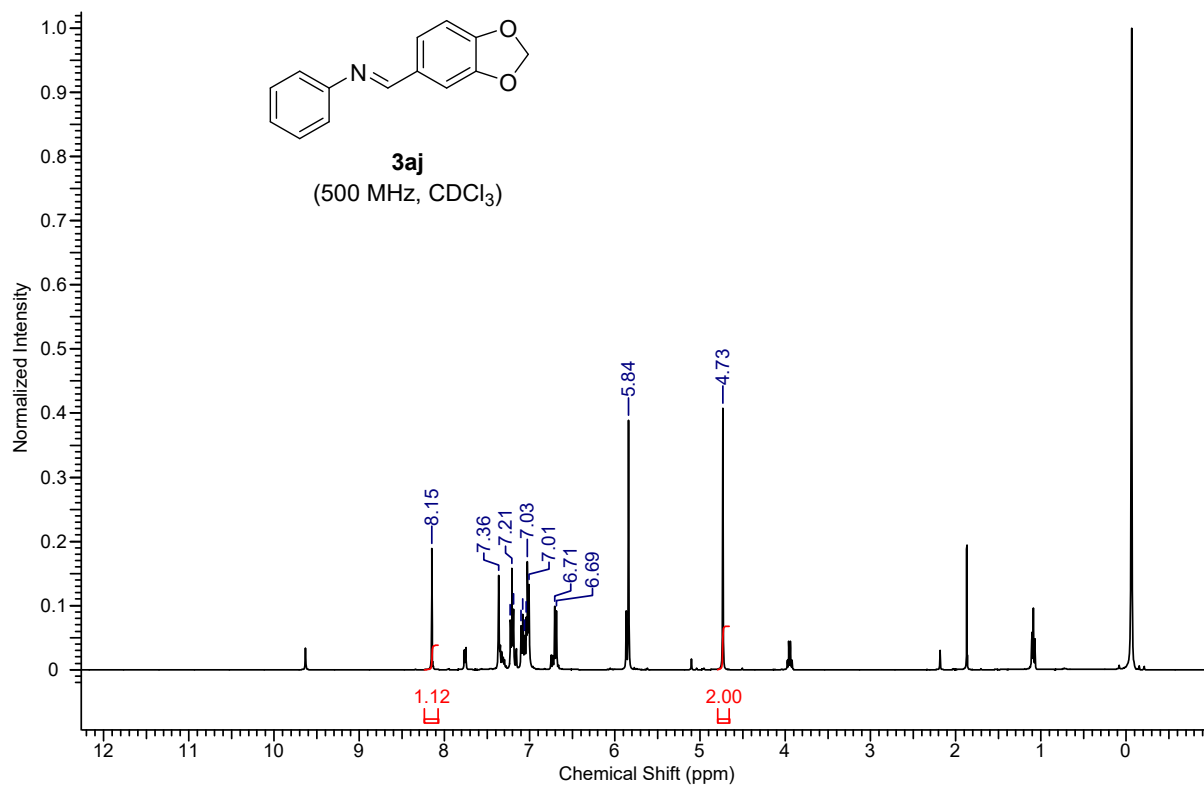
^{1}H-NMR spectrum of *N*-(benzo[d][1,3]dioxol-5-ylmethylene)aniline (**3aj**) obtained from the crude reaction mixture

16. ¹H and ¹³C{¹H} NMR Spectra of Amines
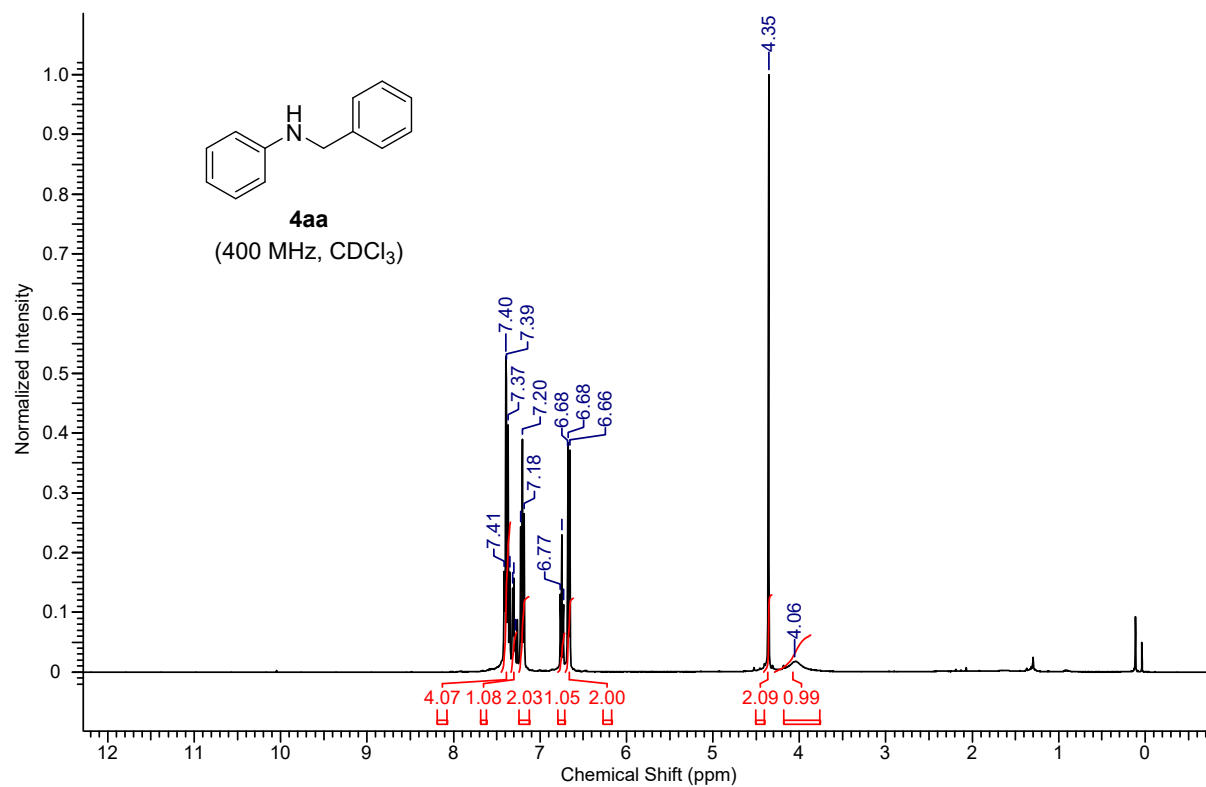
¹H-NMR spectrum of *N*-Benzylaniline (**4aa**)
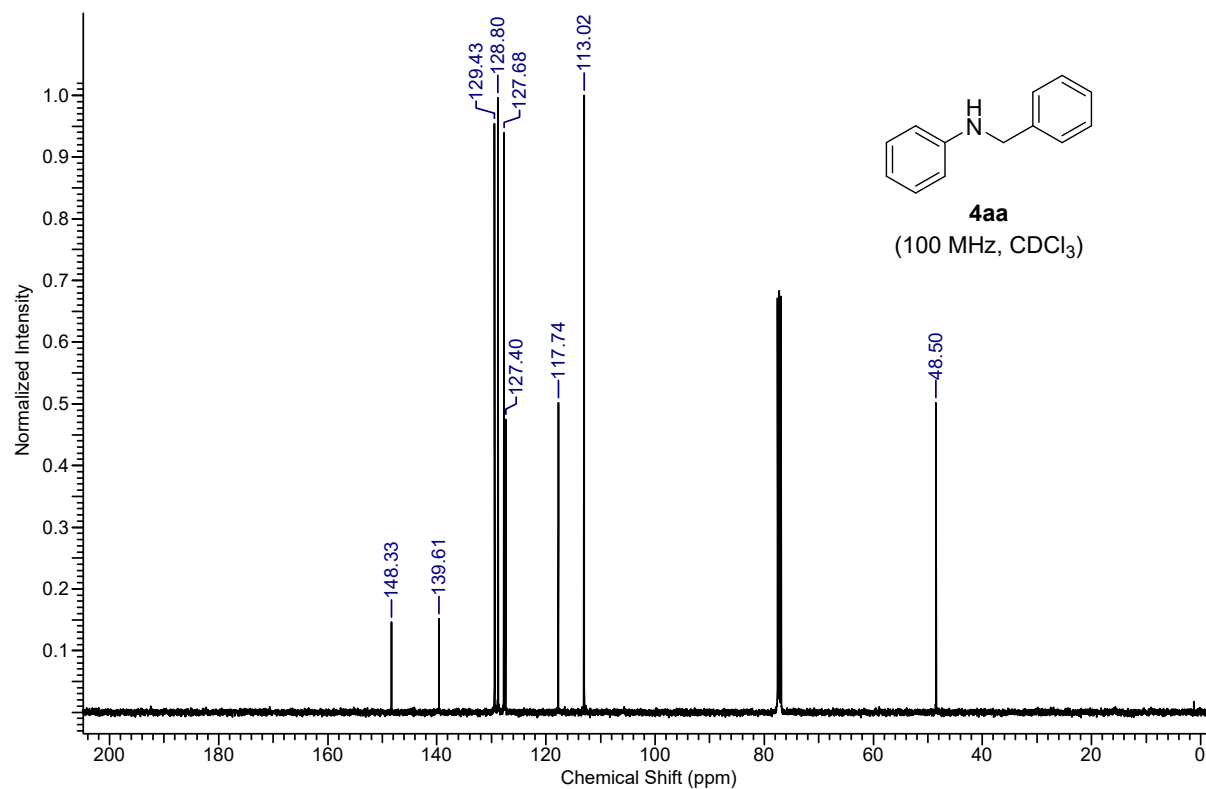
¹³C{¹H}-NMR spectrum of *N*-Benzylaniline (**4aa**)
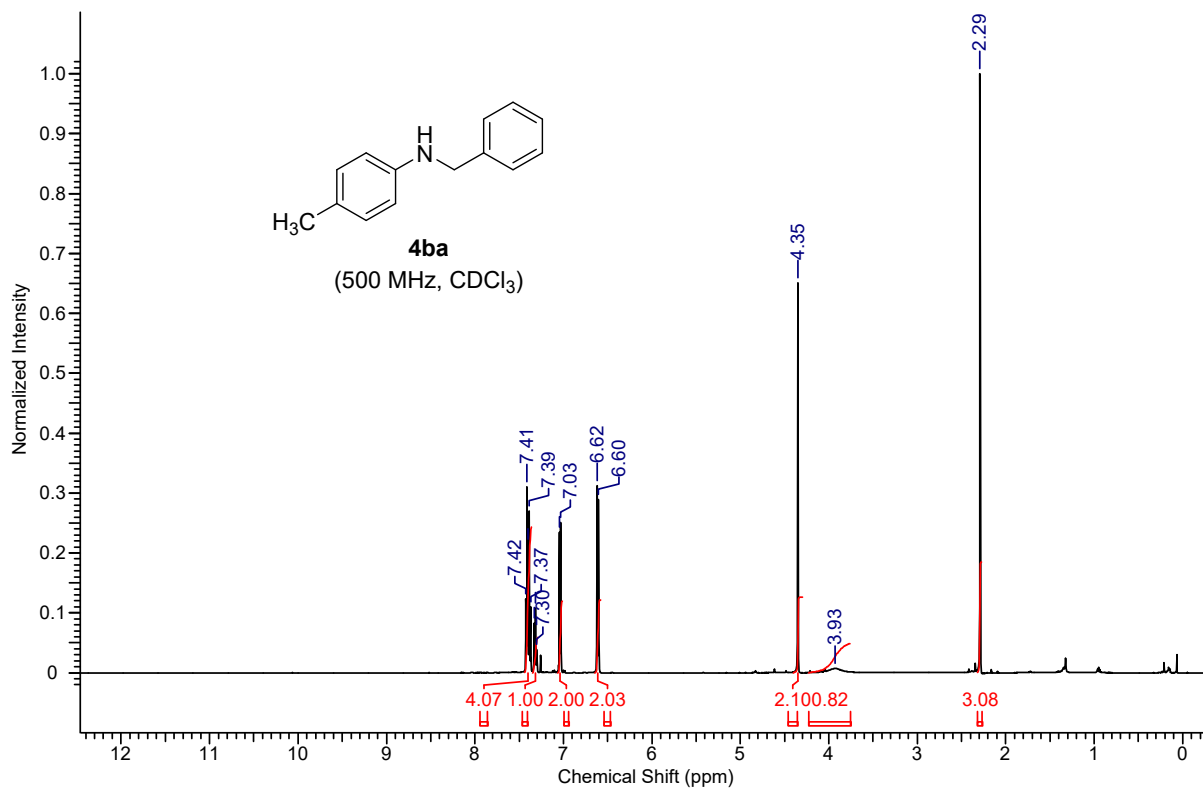
^{1}H-NMR spectrum of *N*-Benzyl-4-methylaniline (**4ba**)
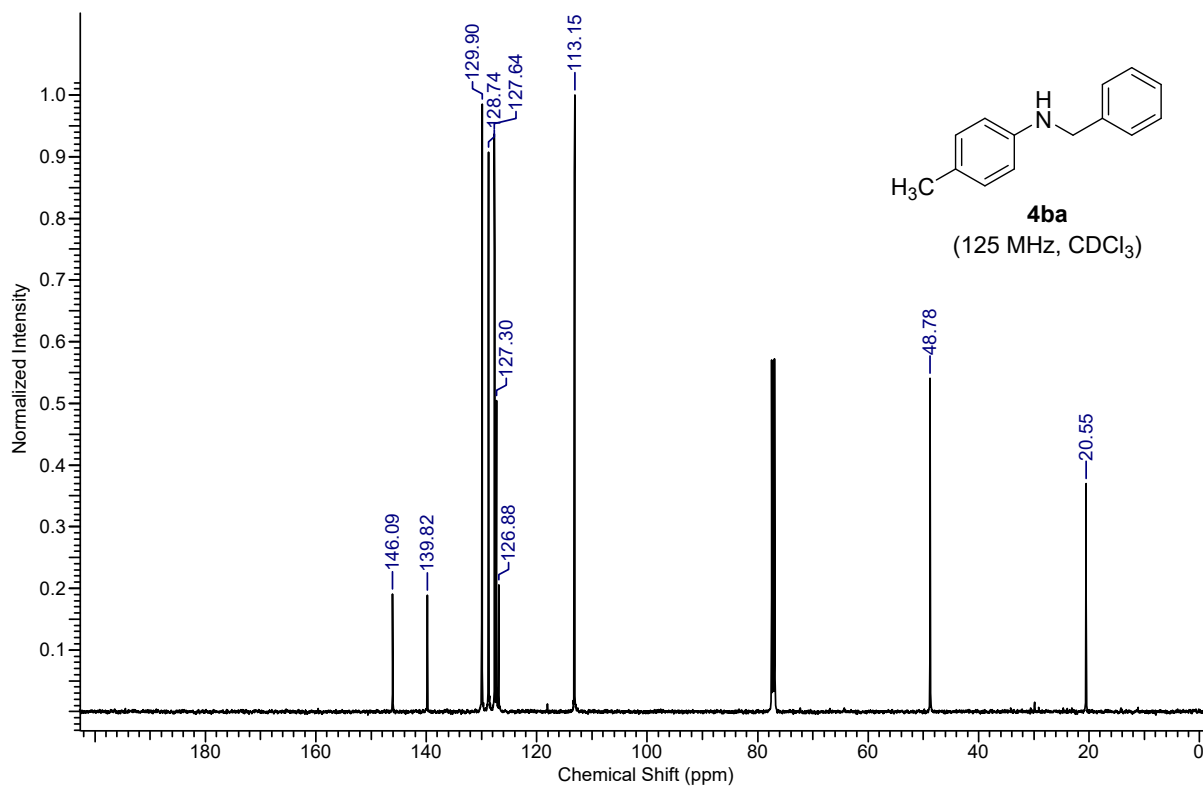
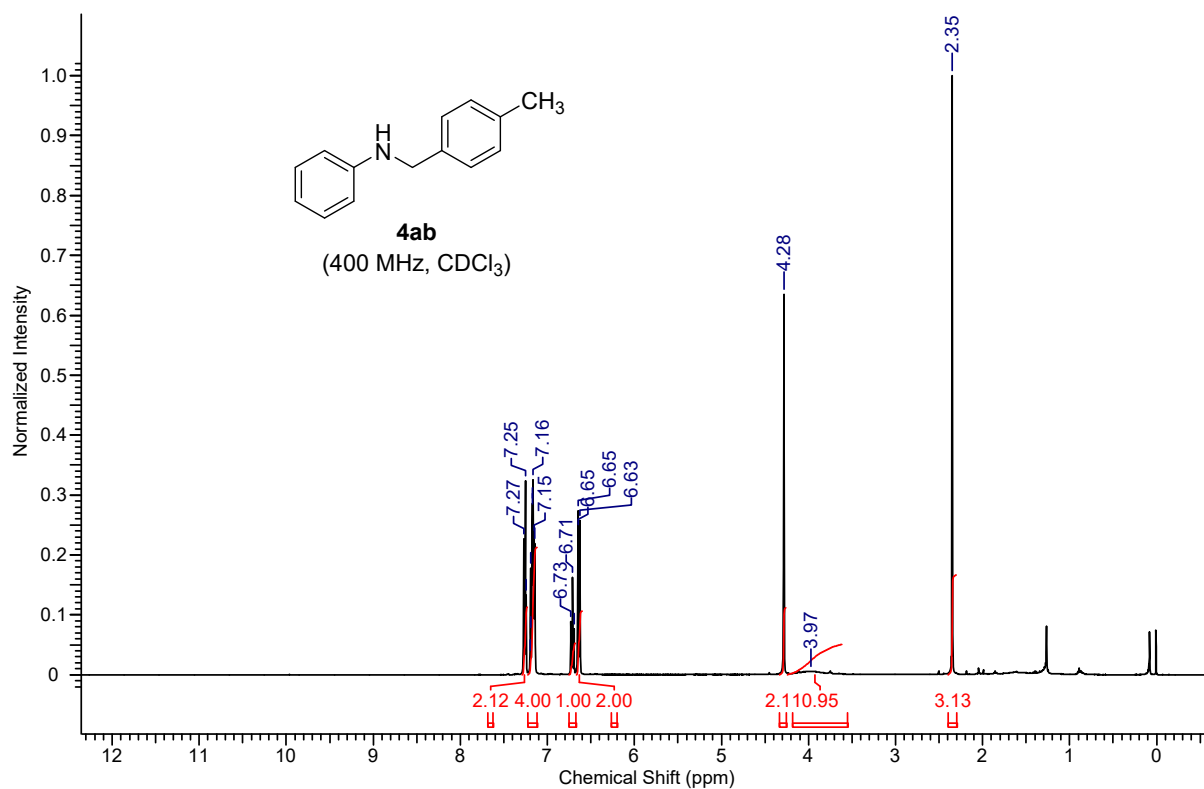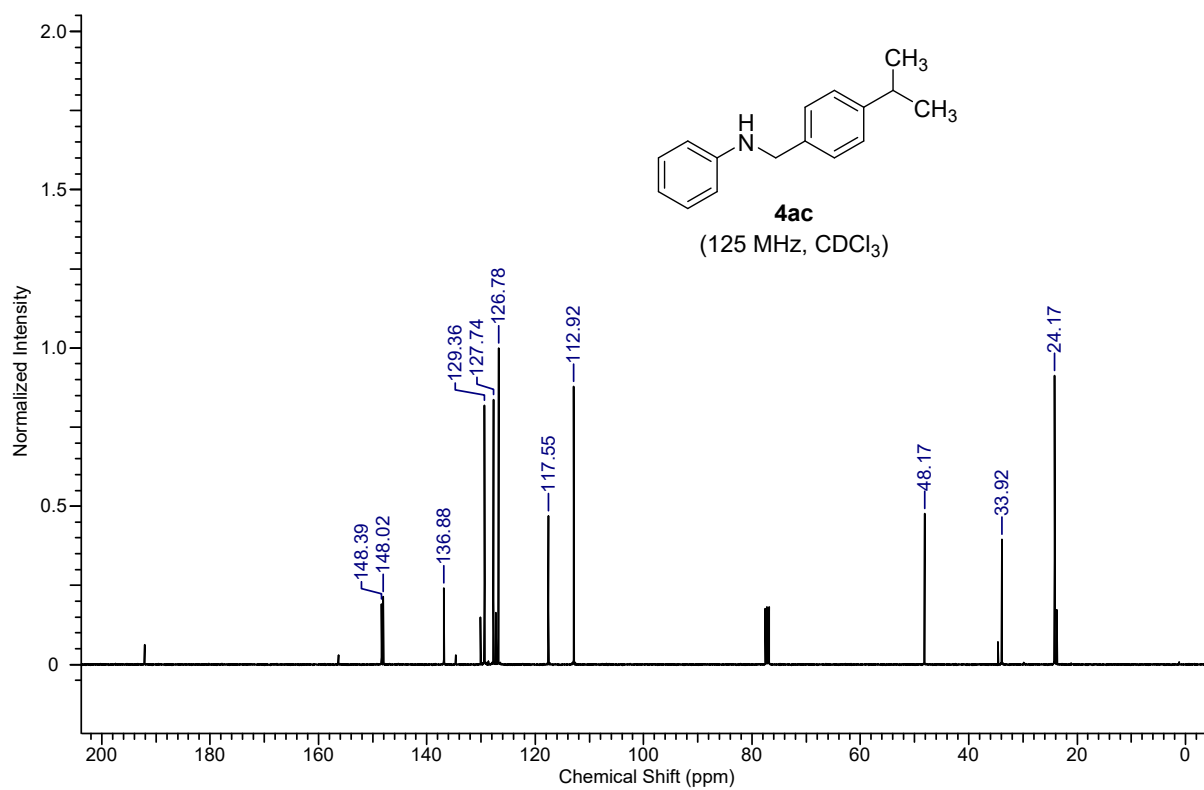^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-methylaniline (**4ba**)
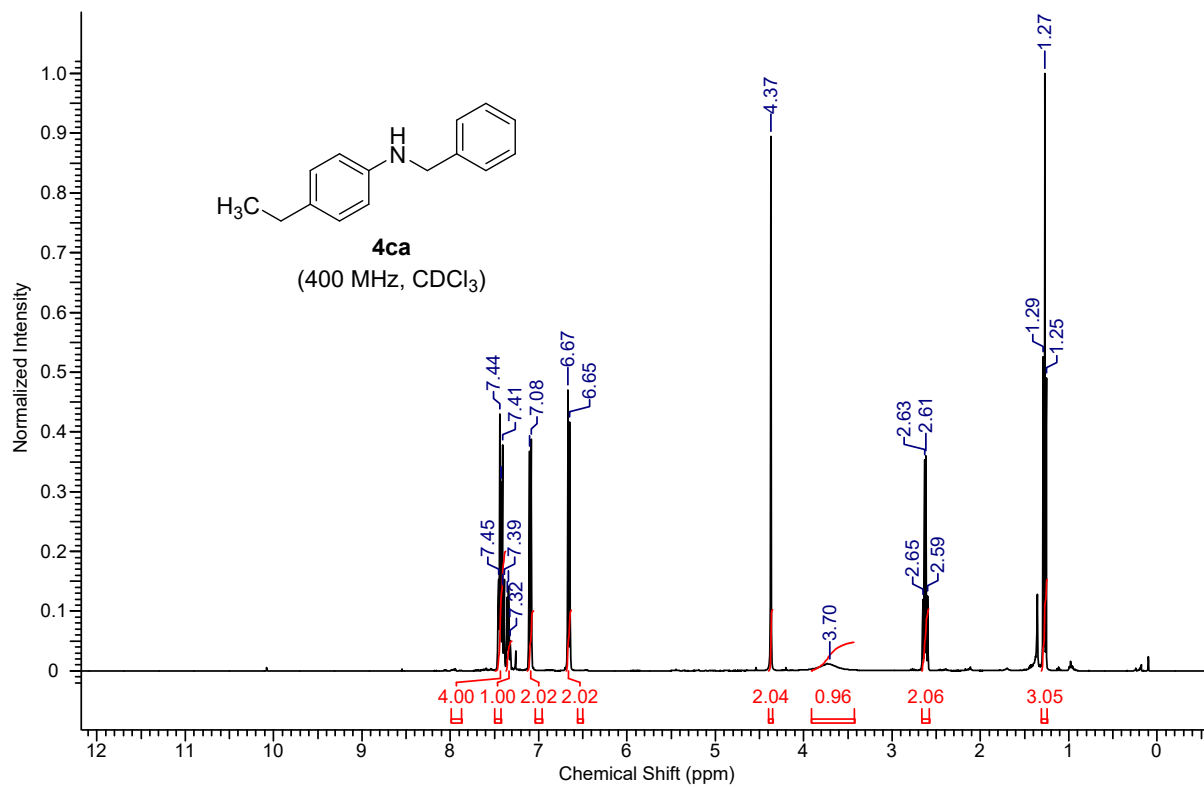
^{1}H-NMR spectrum of *N*-Benzyl-4-ethylaniline (**4ca**)
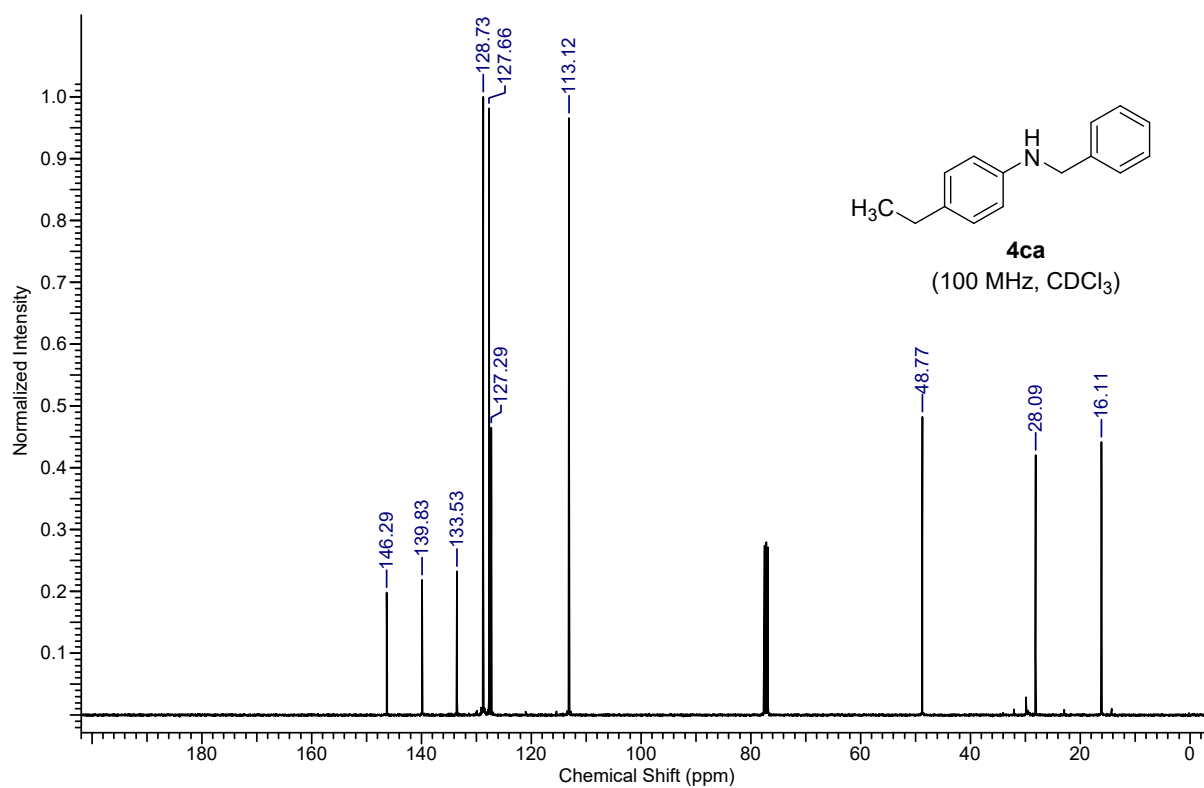
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-ethylaniline (**4ca**)
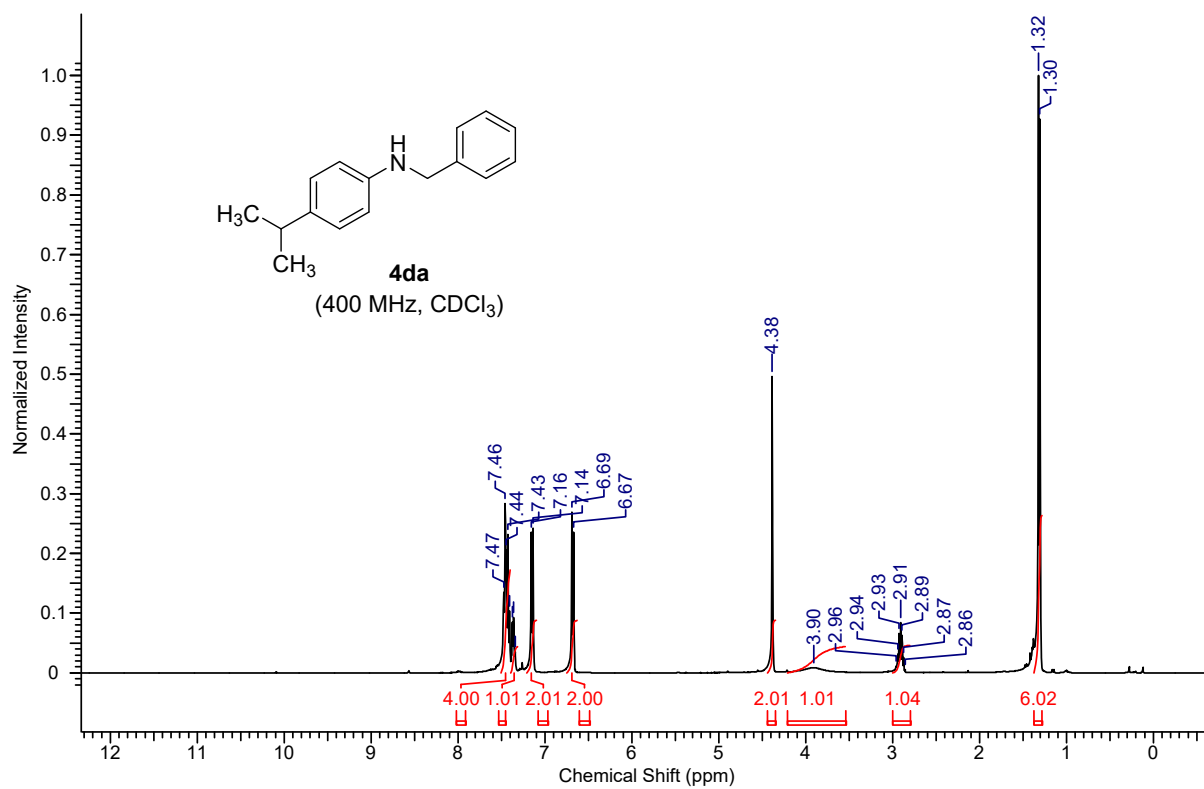
^{1}H-NMR spectrum of *N*-Benzyl-4-isopropylaniline (**4da**)
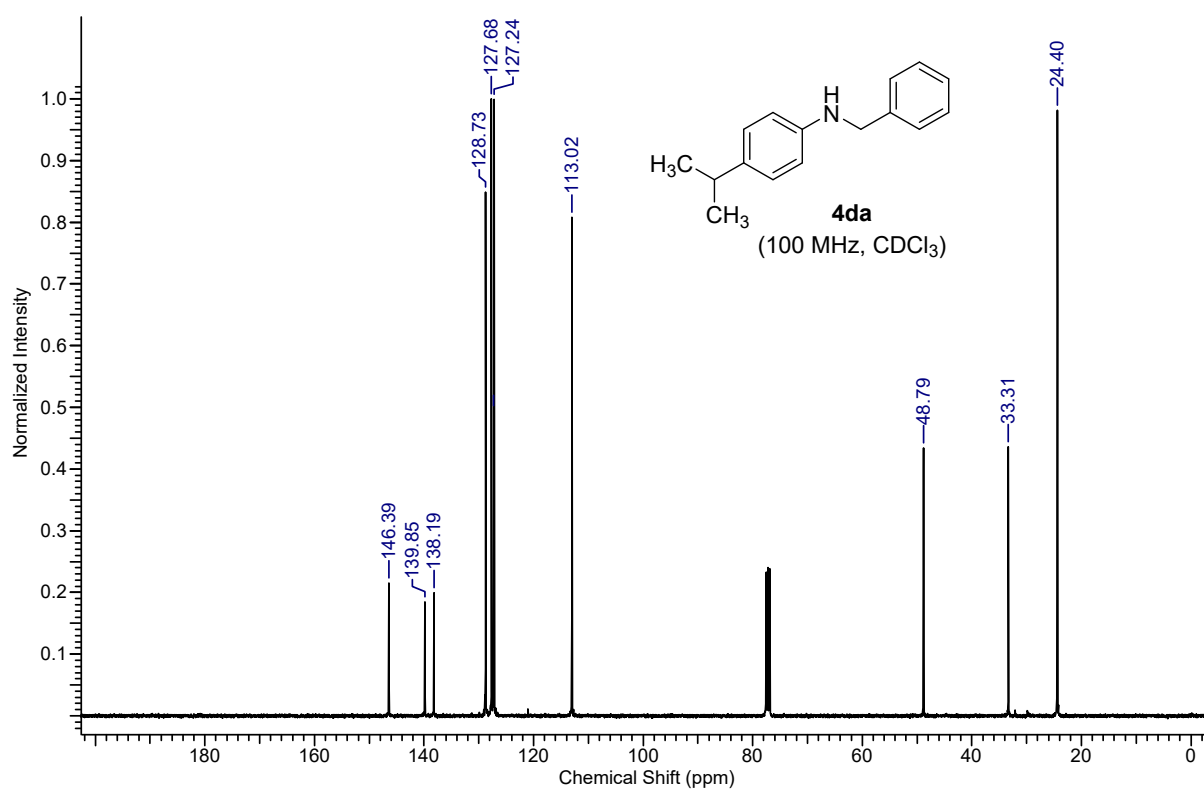
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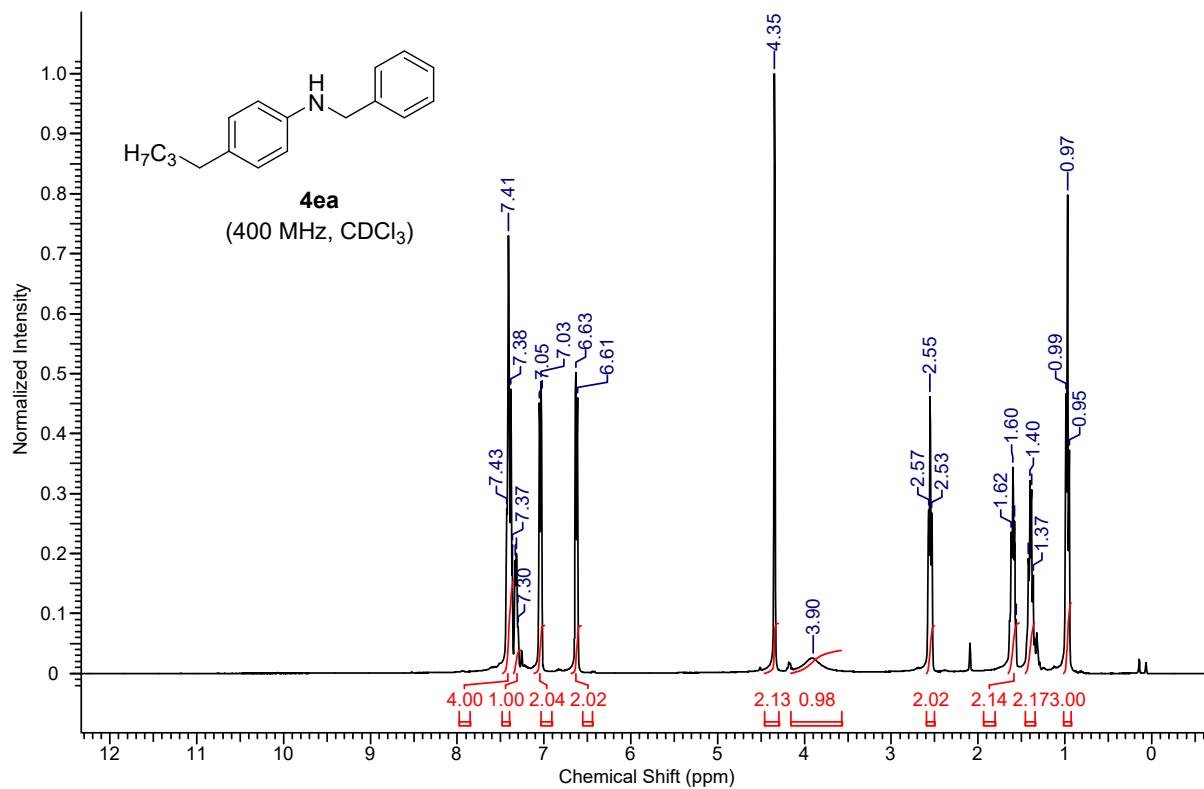
^{1}H-NMR spectrum of *N*-Benzyl-4-butylaniline (**4ea**)
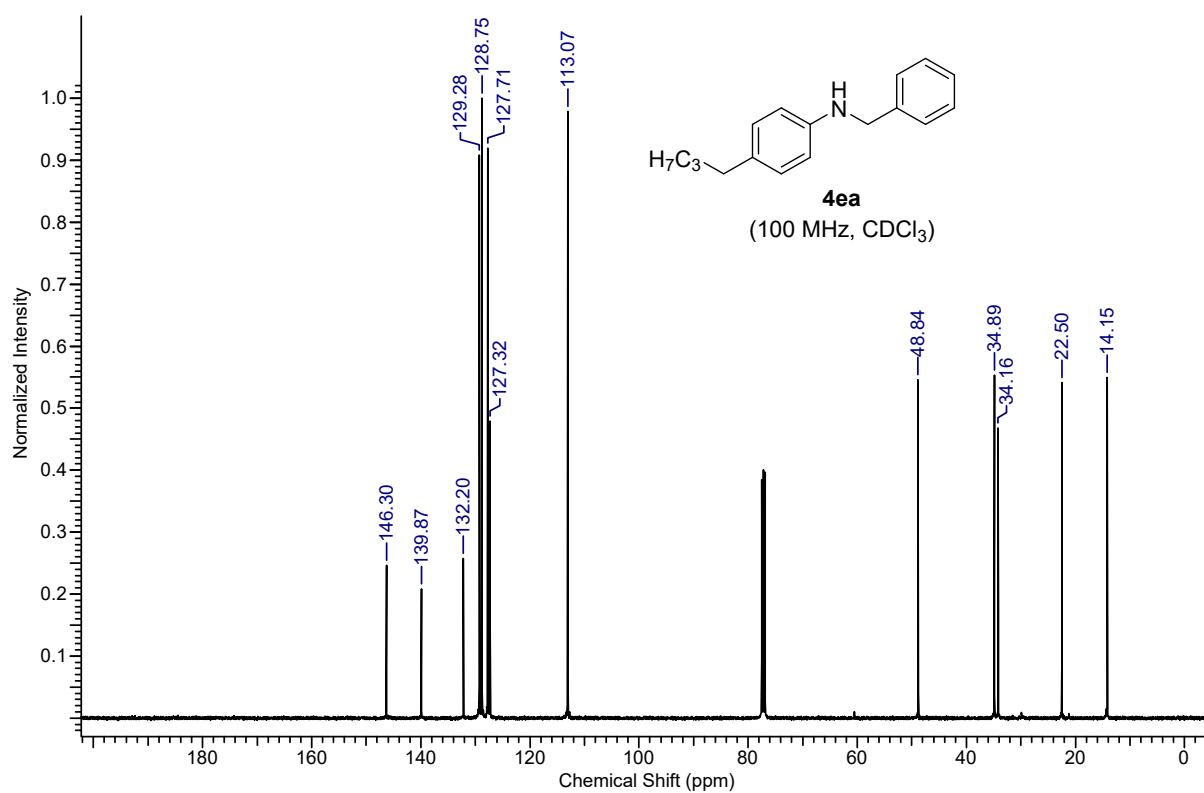
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-butylaniline (**4ea**)
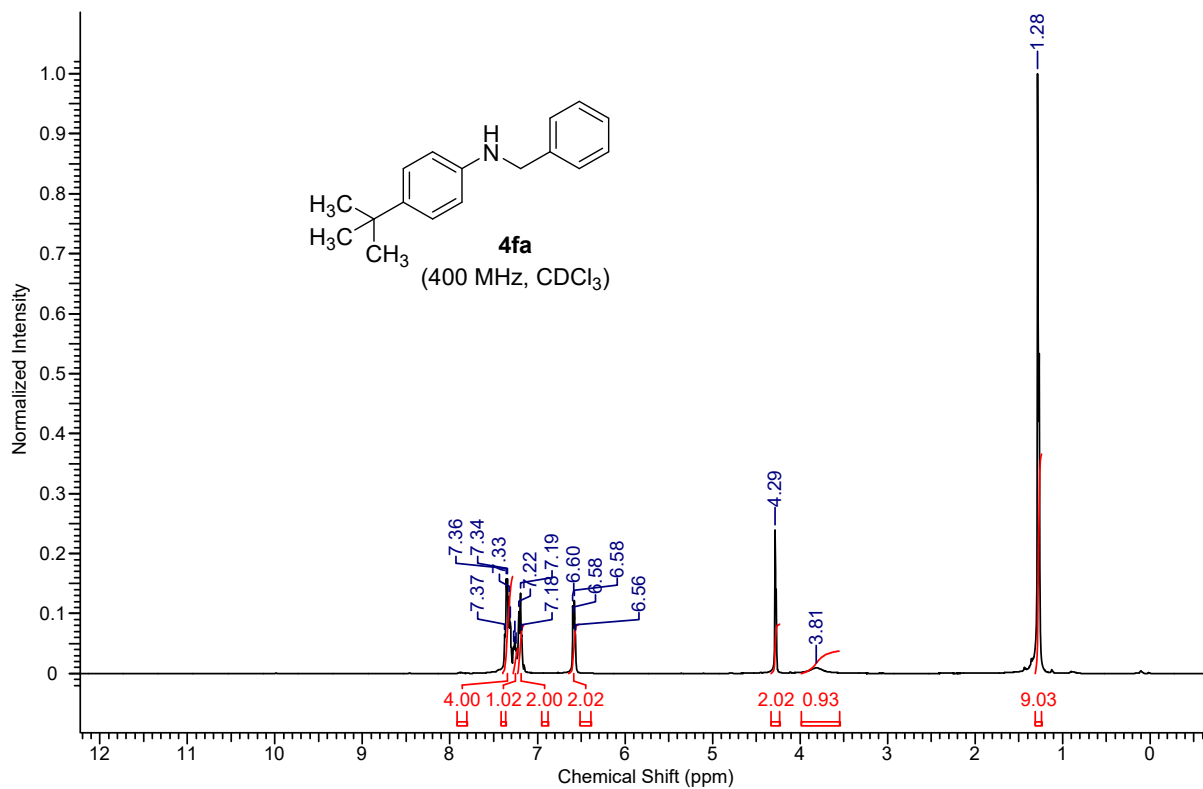
^{1}H-NMR spectrum of *N*-Benzyl-4-*tert*-butylaniline (**4fa**)
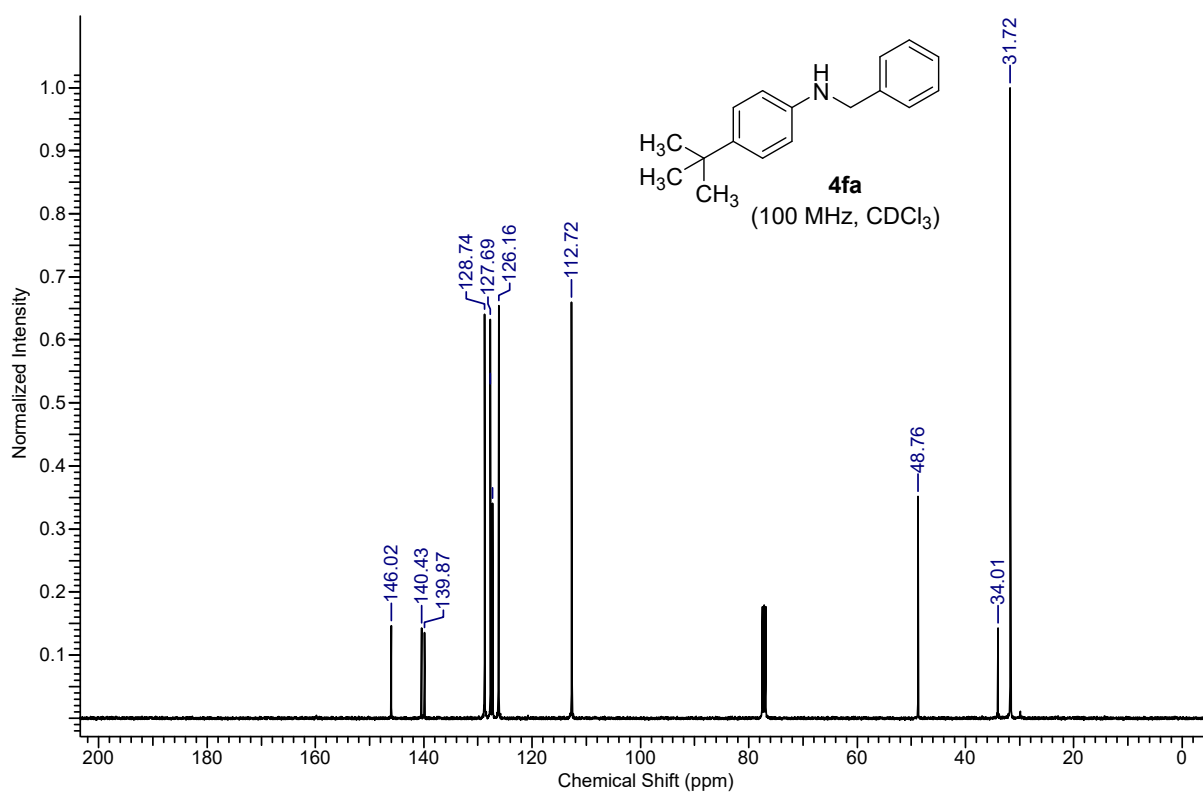
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-*tert*-butylaniline (**4fa**)
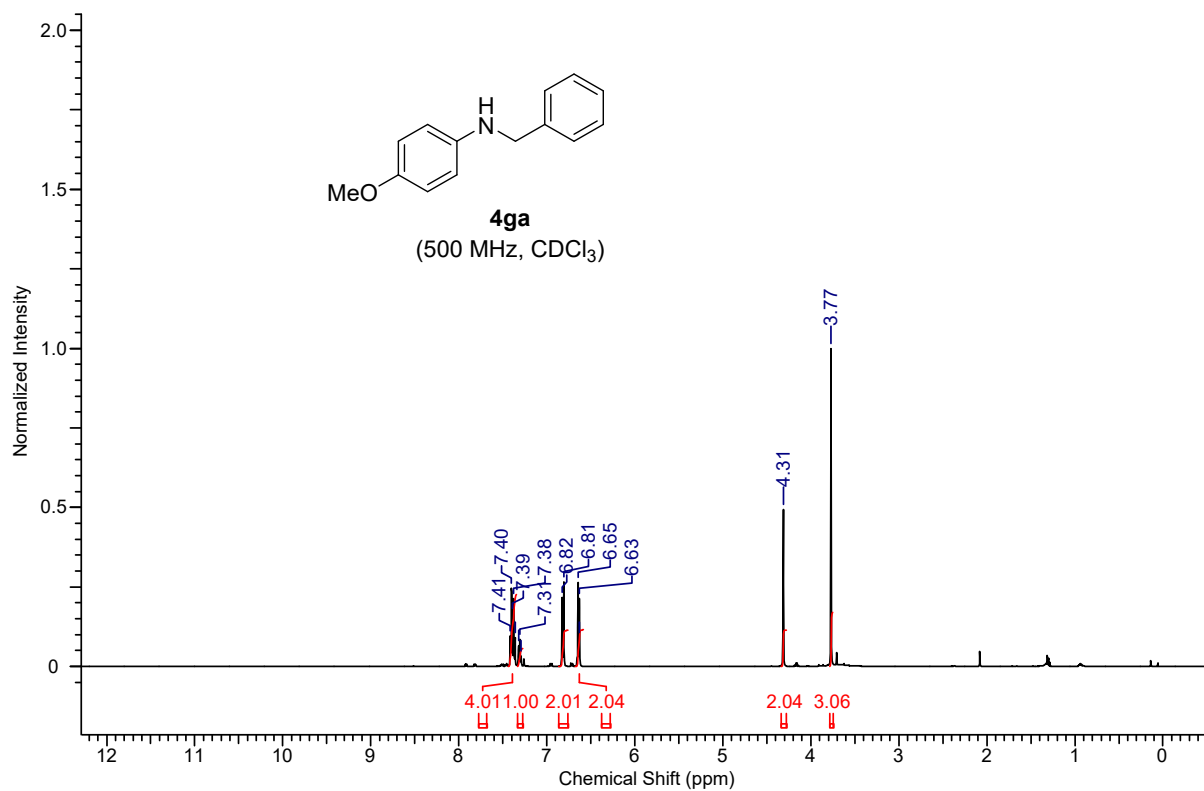
^{1}H-NMR spectrum of *N*-Benzyl-4-methoxyaniline (**4ga**)
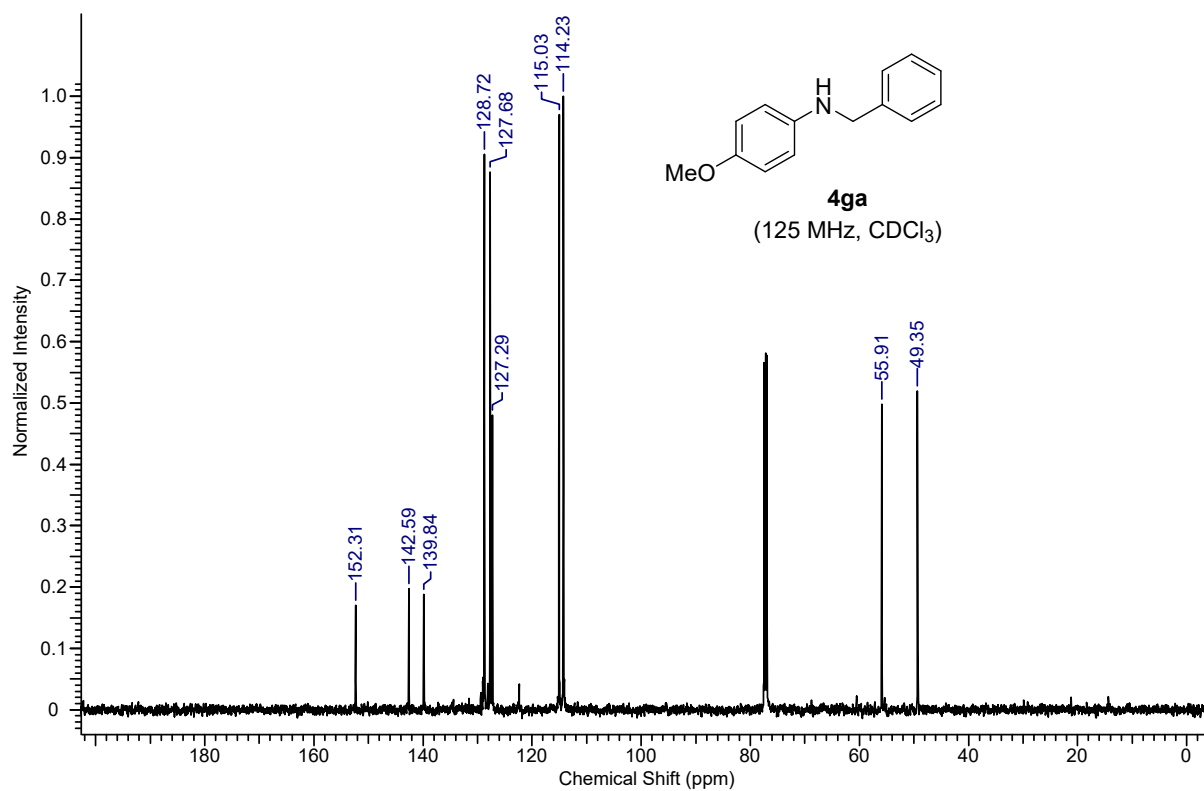
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-methoxyaniline (**4ga**)
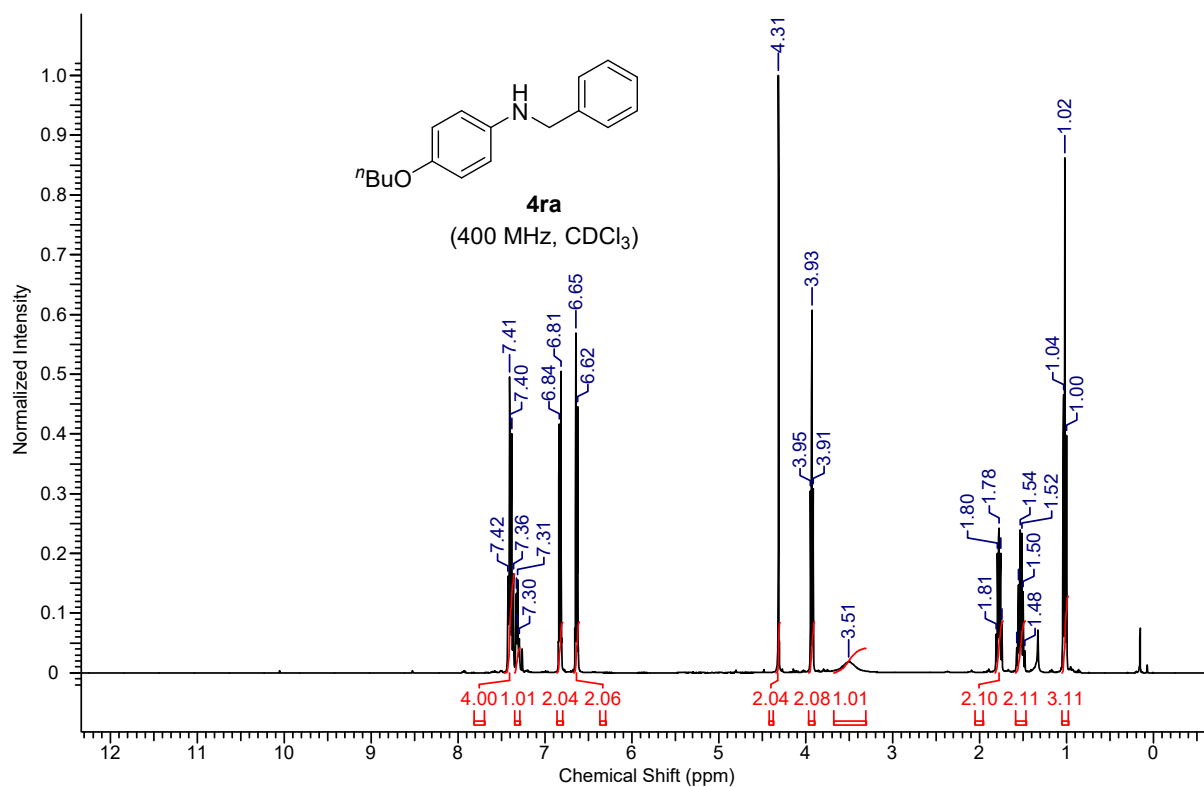
^{1}H-NMR spectrum of *N*-Benzyl-4-butoxyaniline (**4ra**)
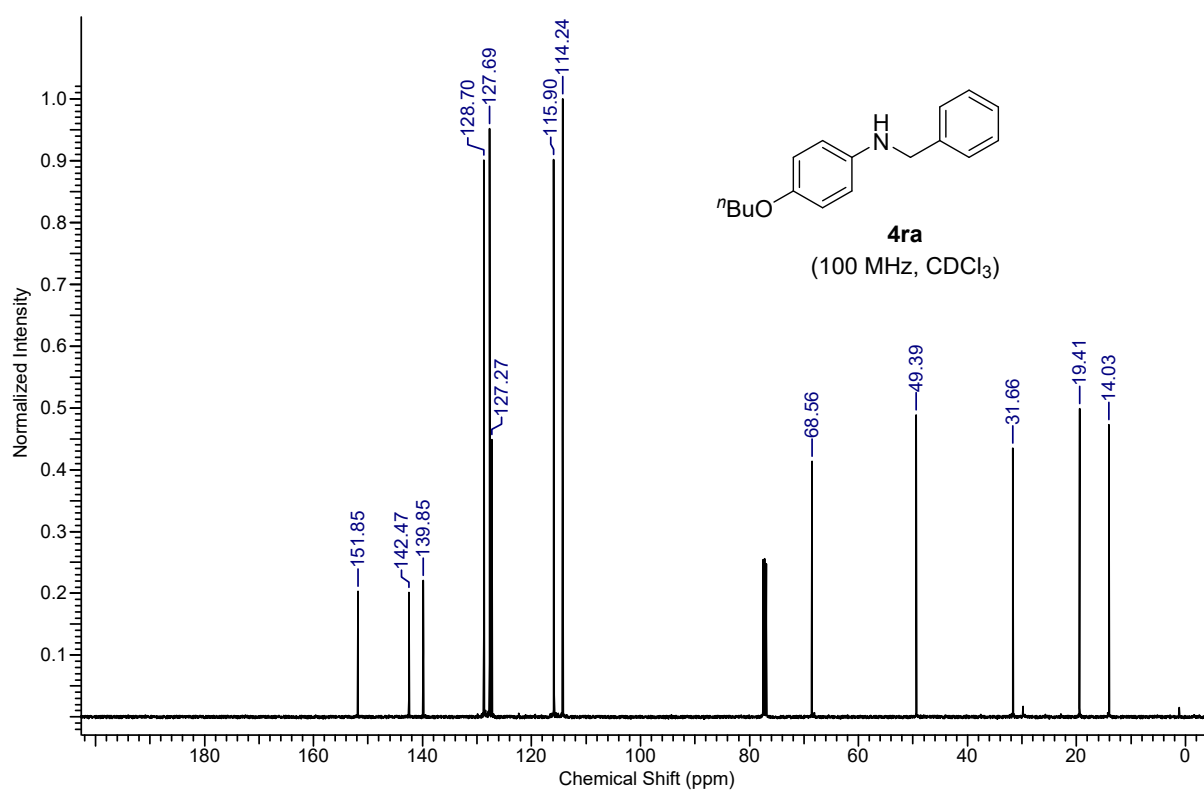
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-4-butoxyaniline (**4ra**)
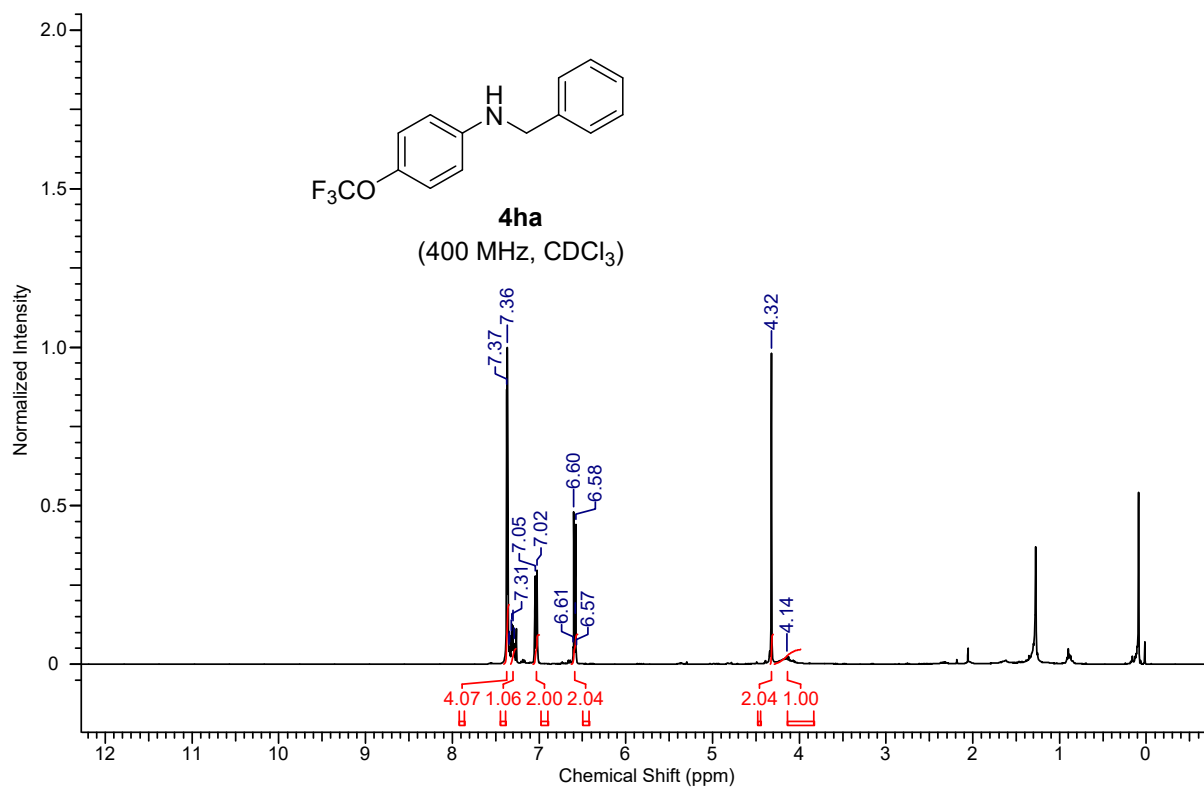
^{1}H-NMR spectrum of *N*-Benzyl-4-trifluoromethoxyaniline (**4ha**)
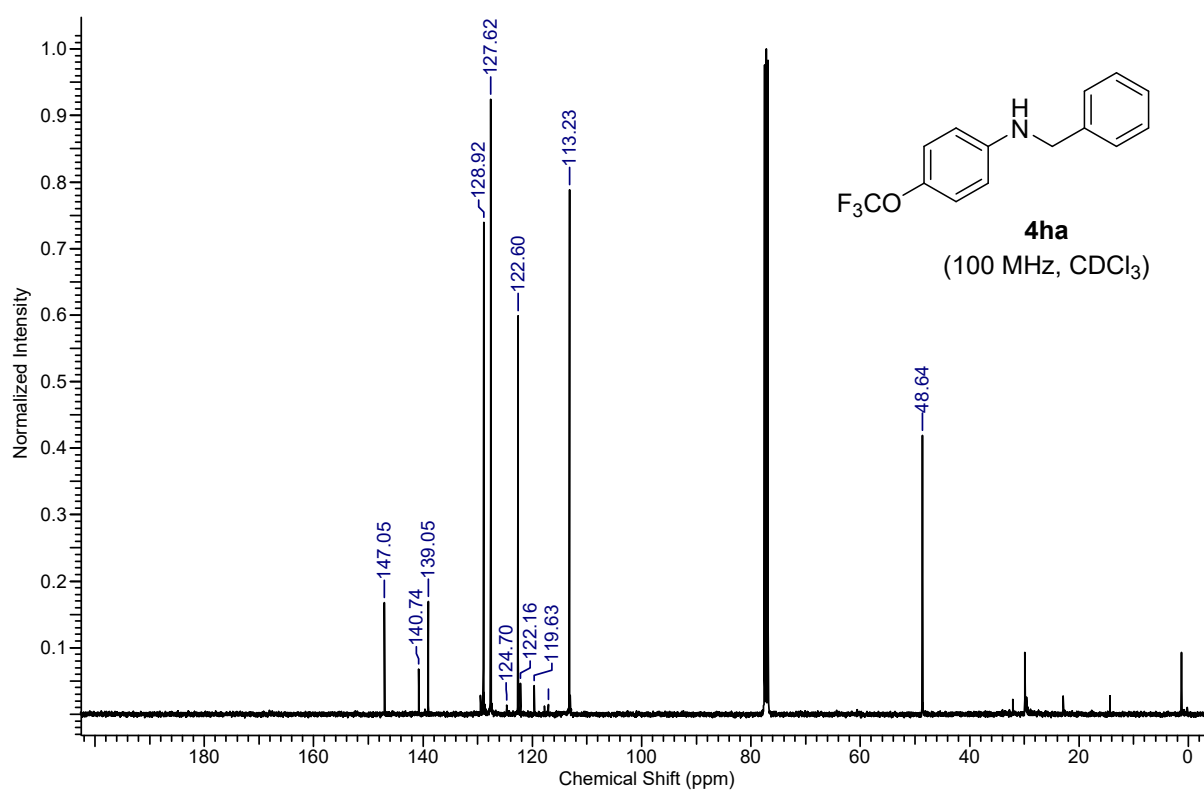
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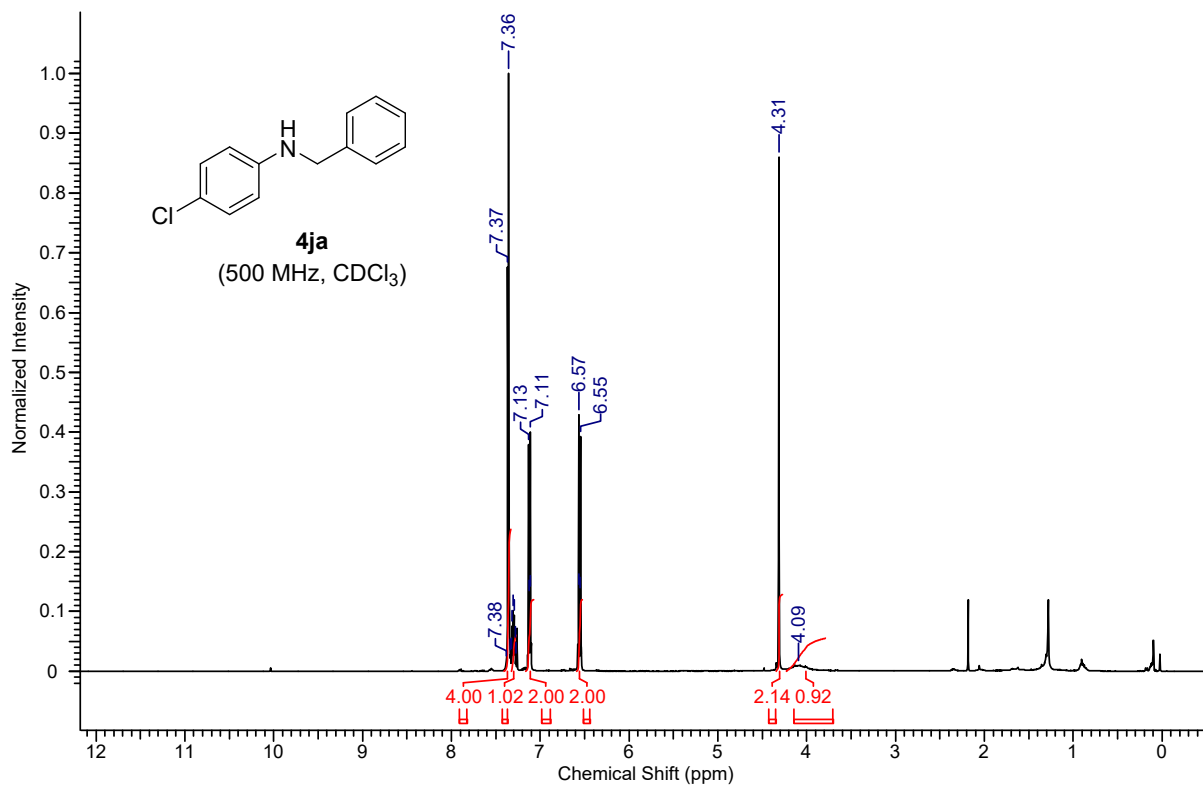
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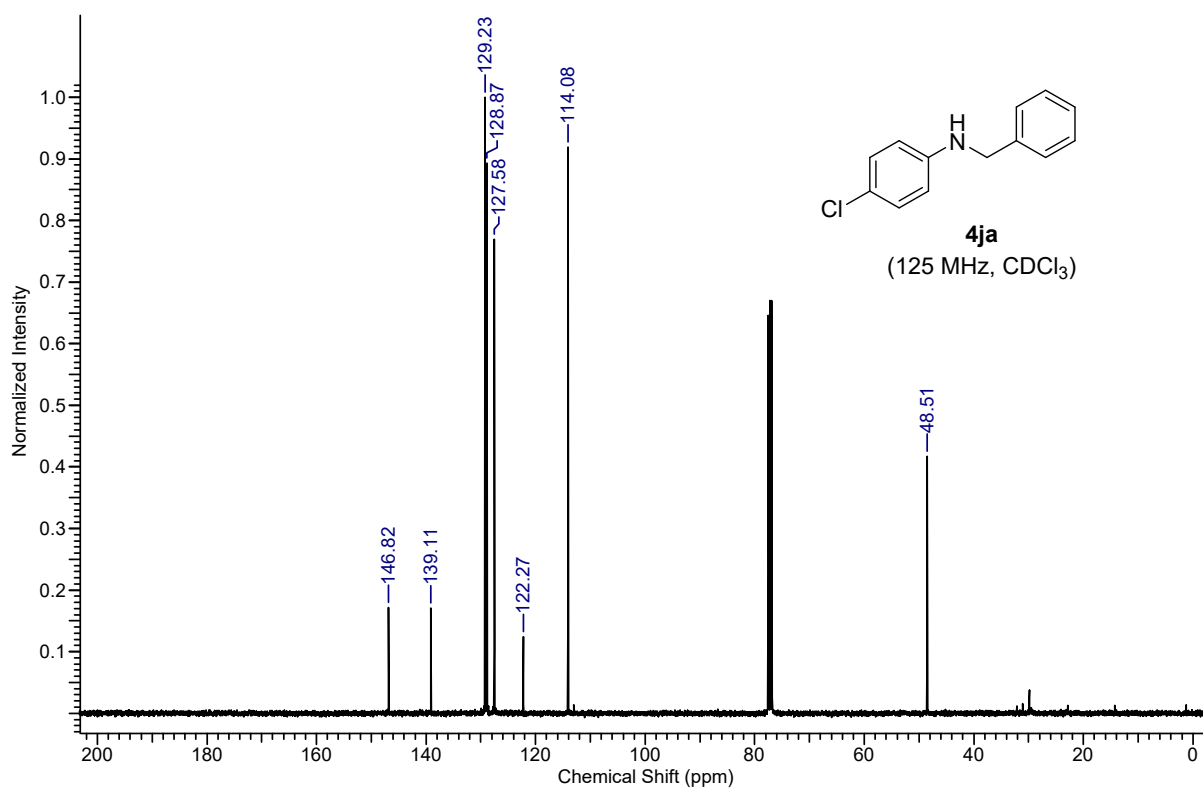
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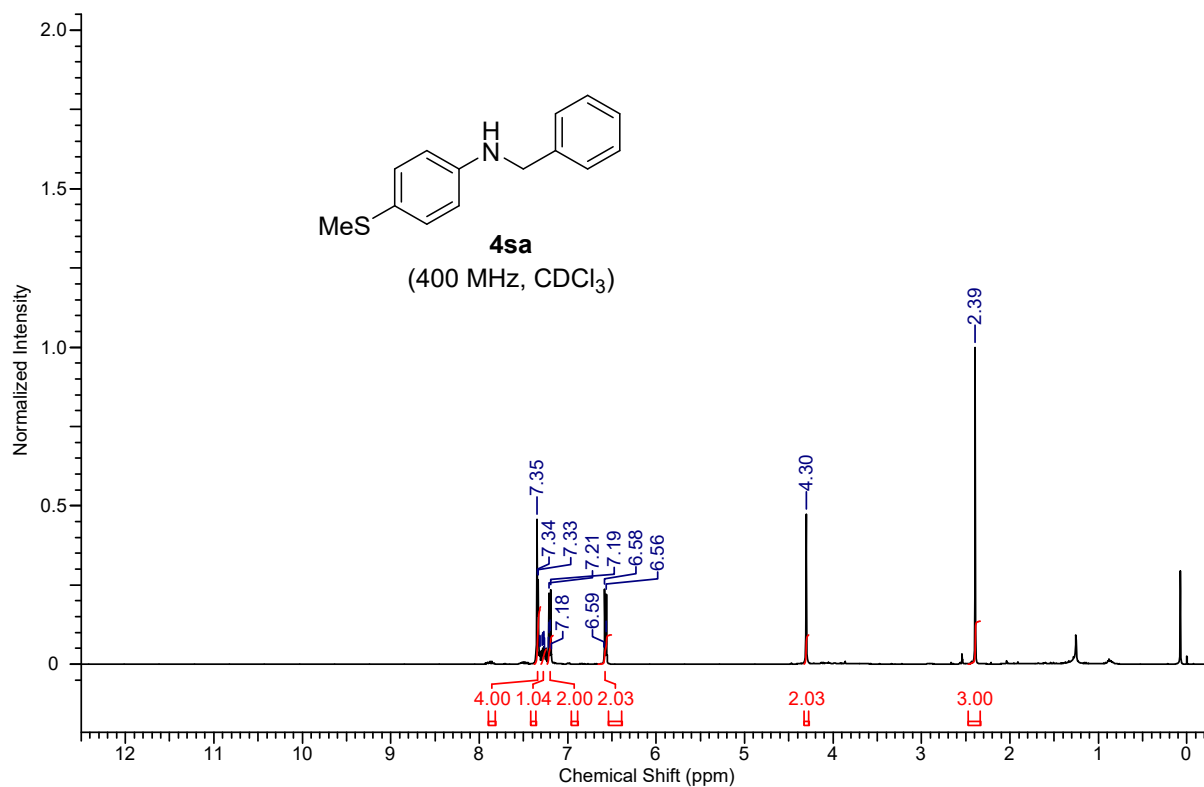
^{1}H-NMR spectrum of *N*-Benzyl-4-thiomethylaniline (**4sa**)
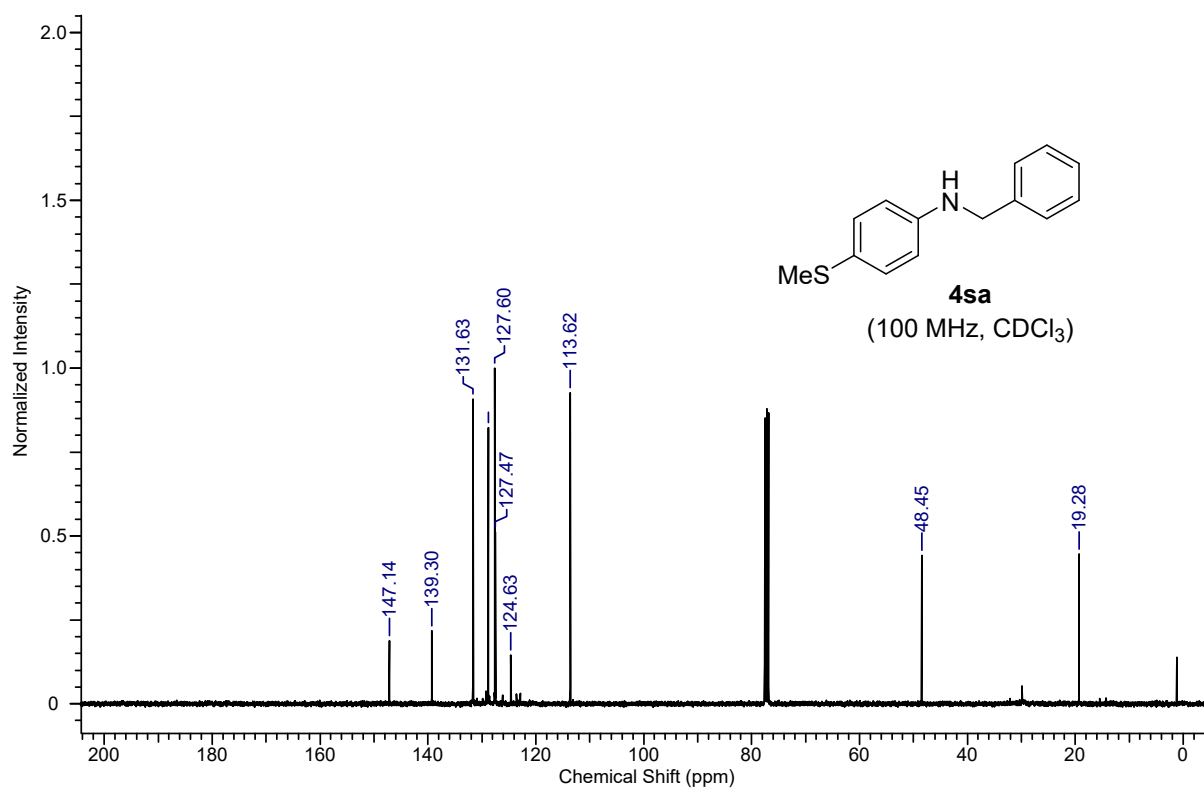
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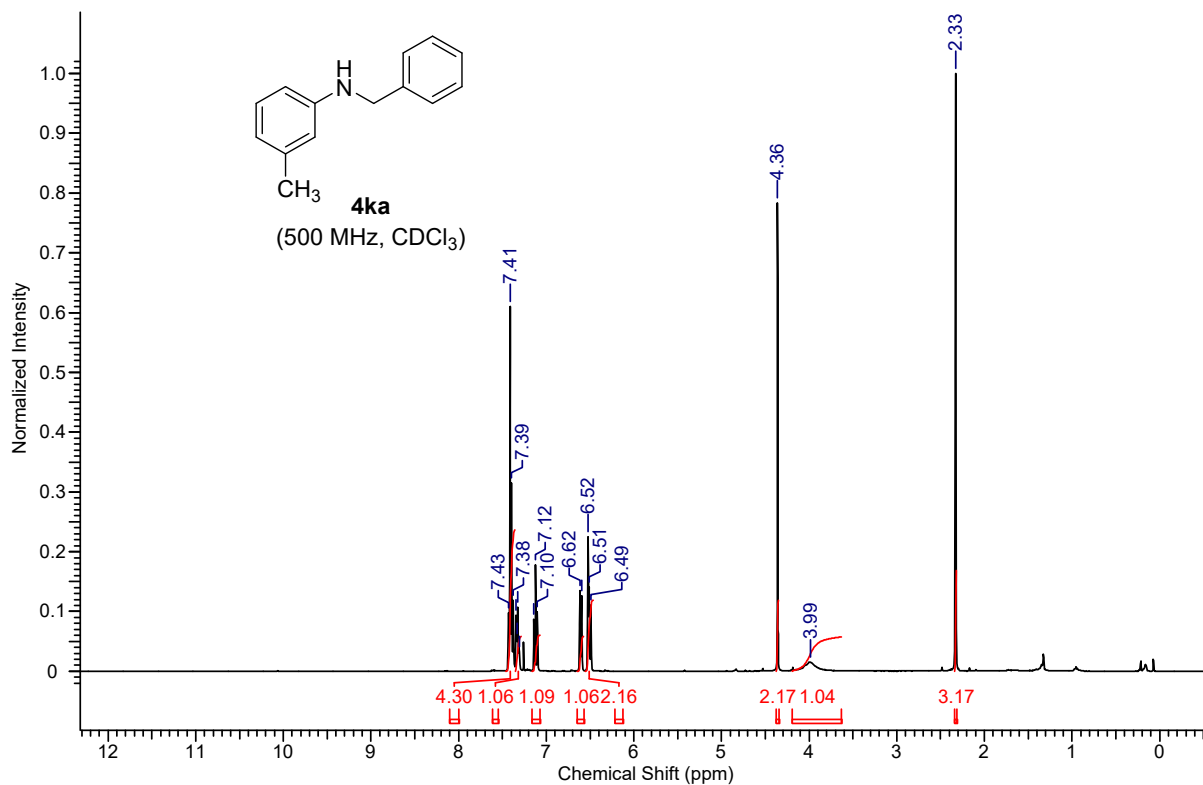
^{1}H-NMR spectrum of *N*-Benzyl-3-methylaniline (**4ka**)
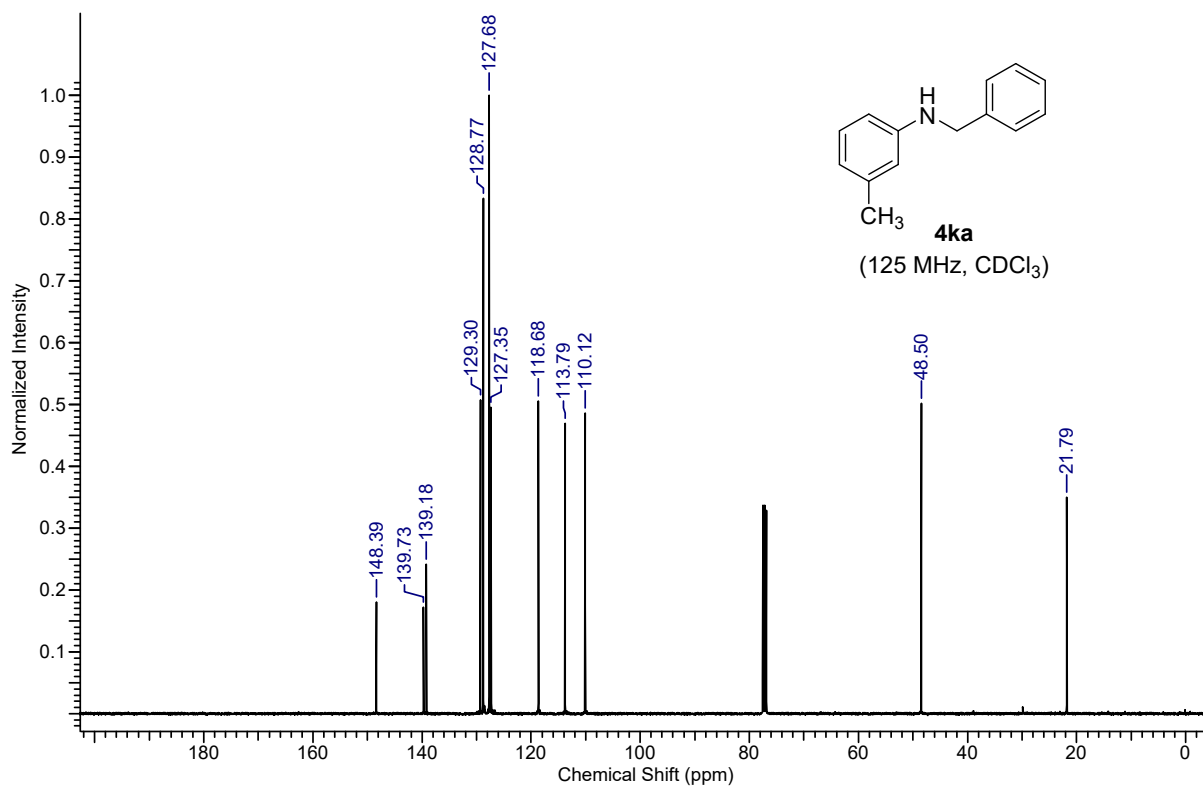
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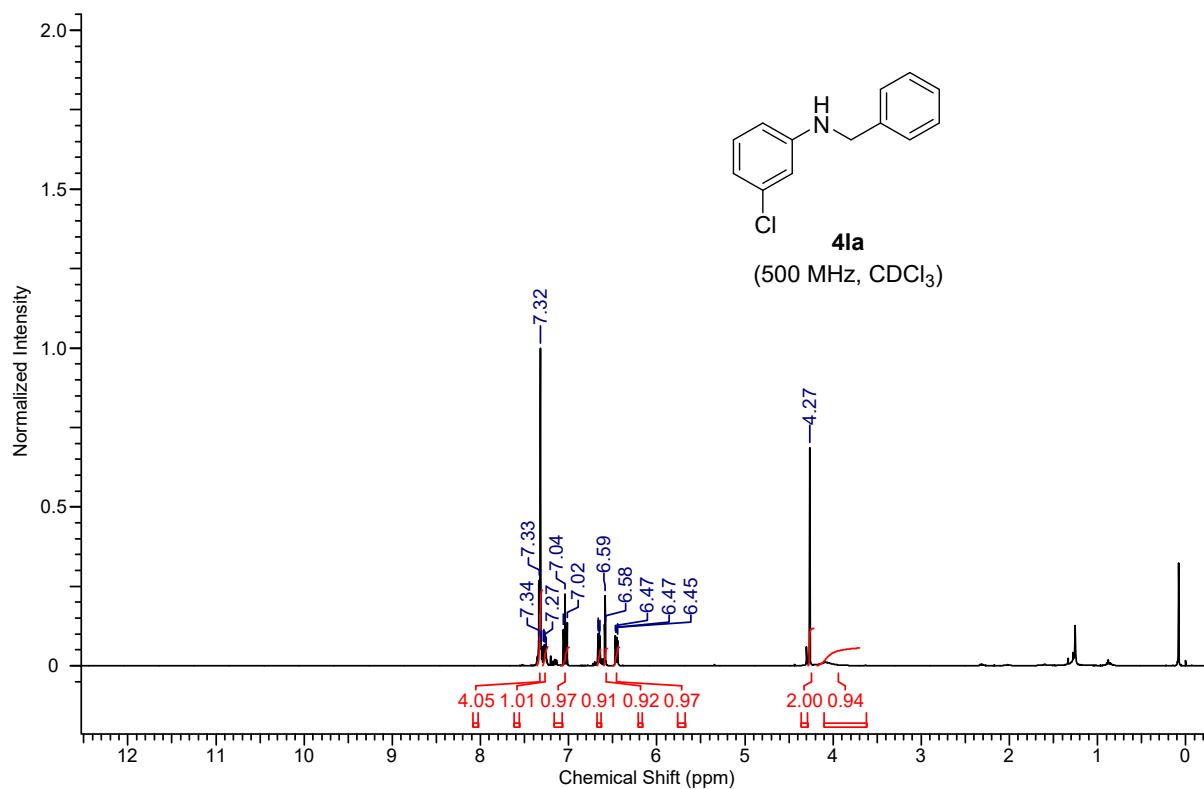
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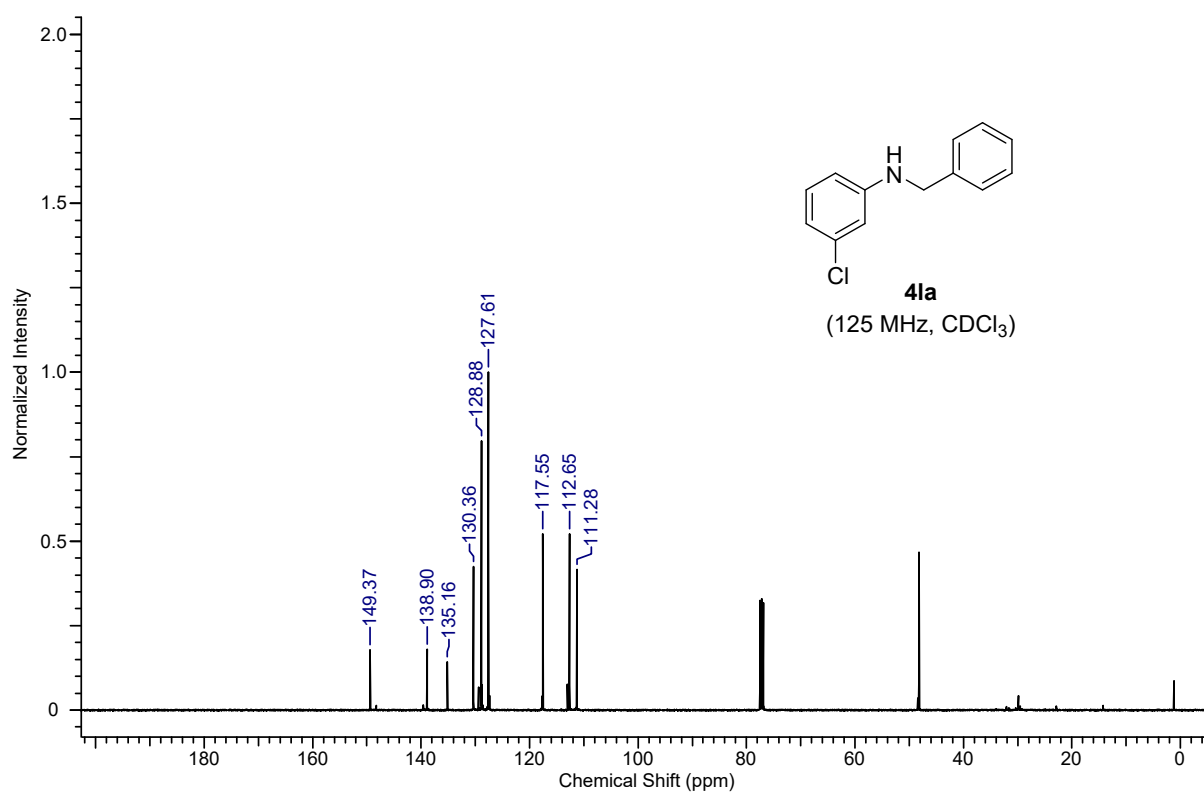
^{13}C{^{1}H}-NMR spectrum of *N*-Benzyl-3-chloroaniline (**4la**)
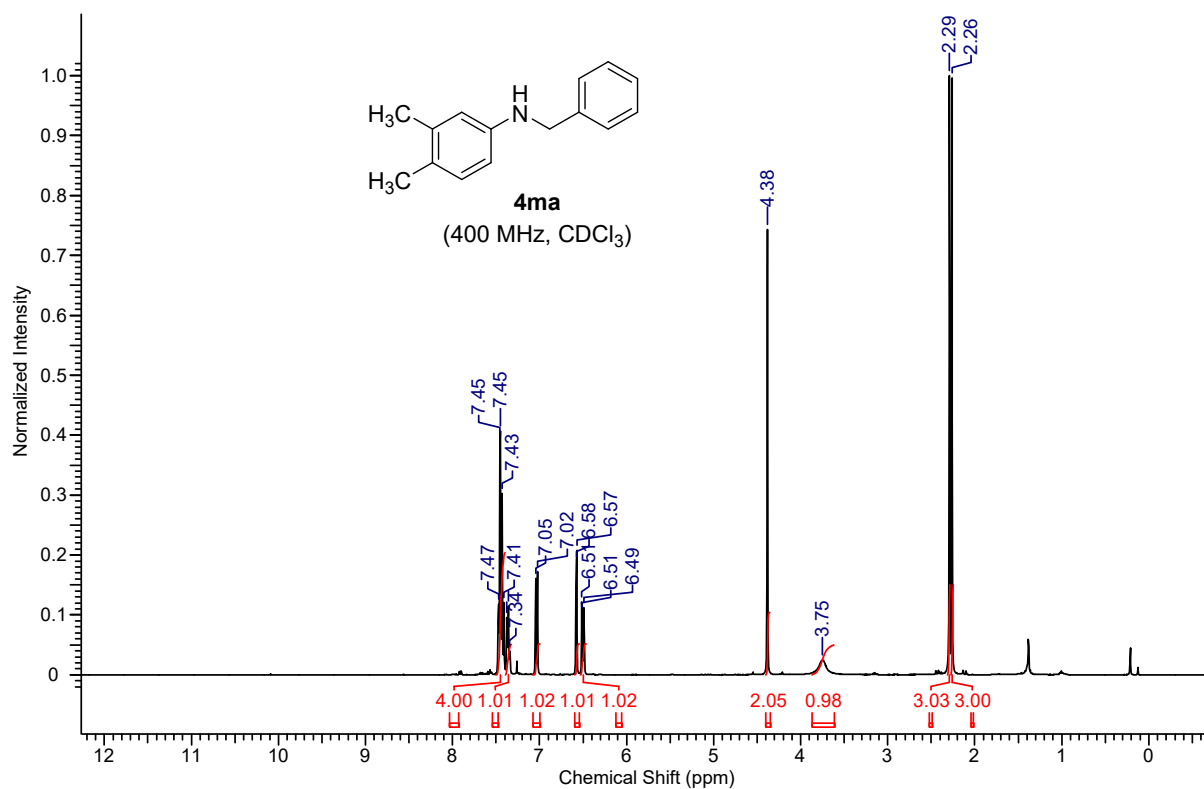
^{1}H-NMR spectrum of *N*-Benzyl-2,3-dimethylaniline (**4ma**)
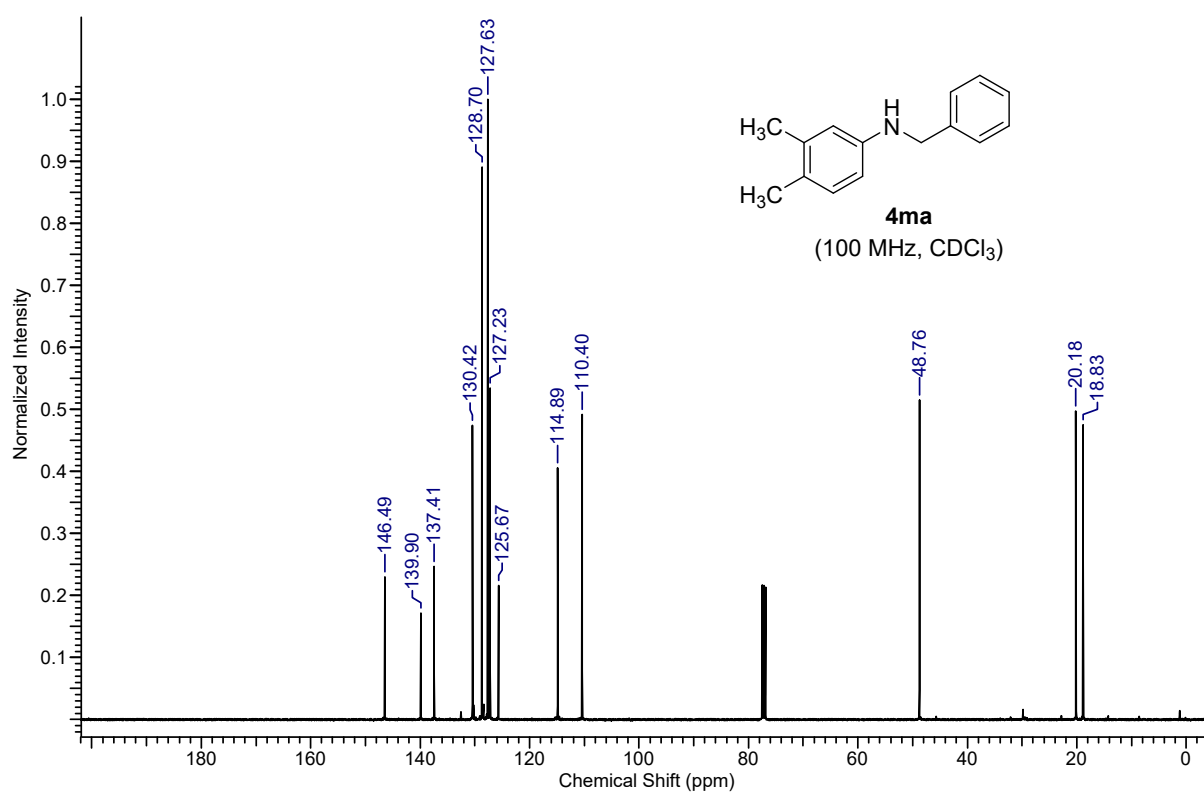
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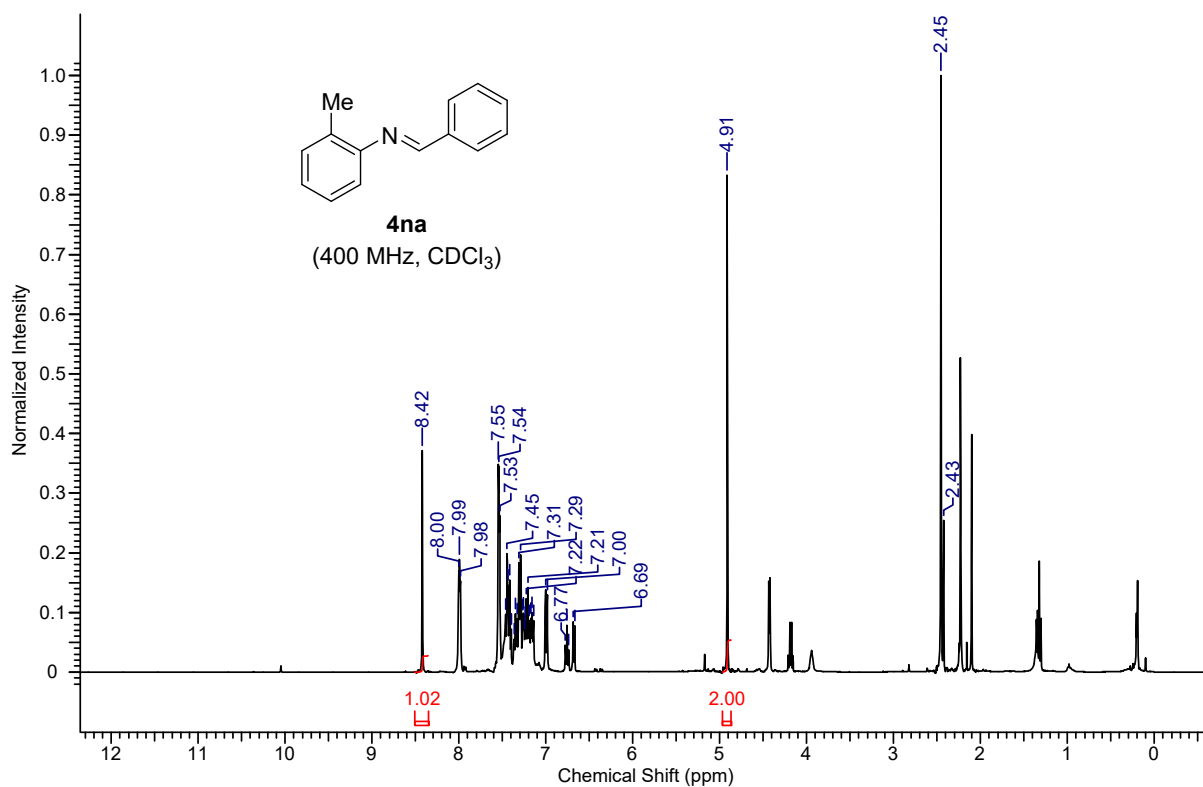
^{1}H-NMR spectrum of *N*-Benzyl-2-methylaniline (**4na**) obtained from the crude reaction mixture
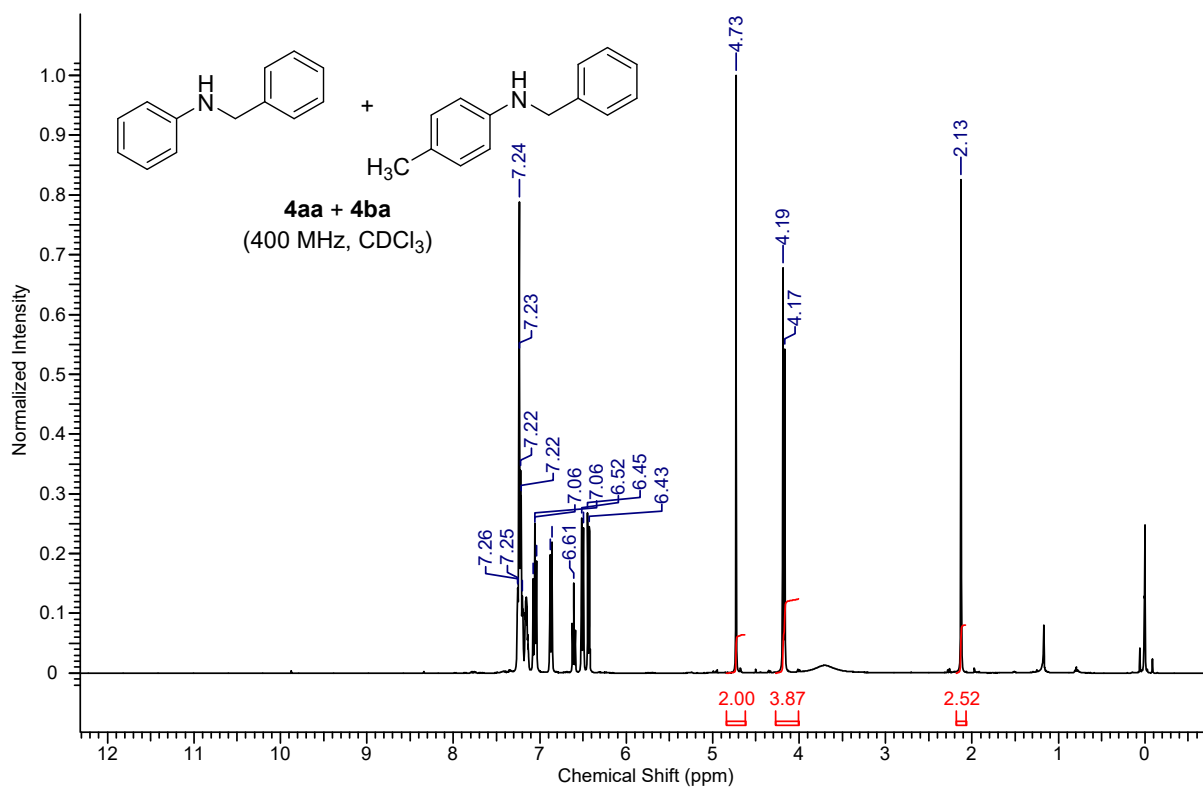
^{1}H-NMR spectrum of *N*-Benzylaniline (**4aa**) and *N*-Benzyl-4-methylaniline (**4ba**) obtained from the crude reaction mixture
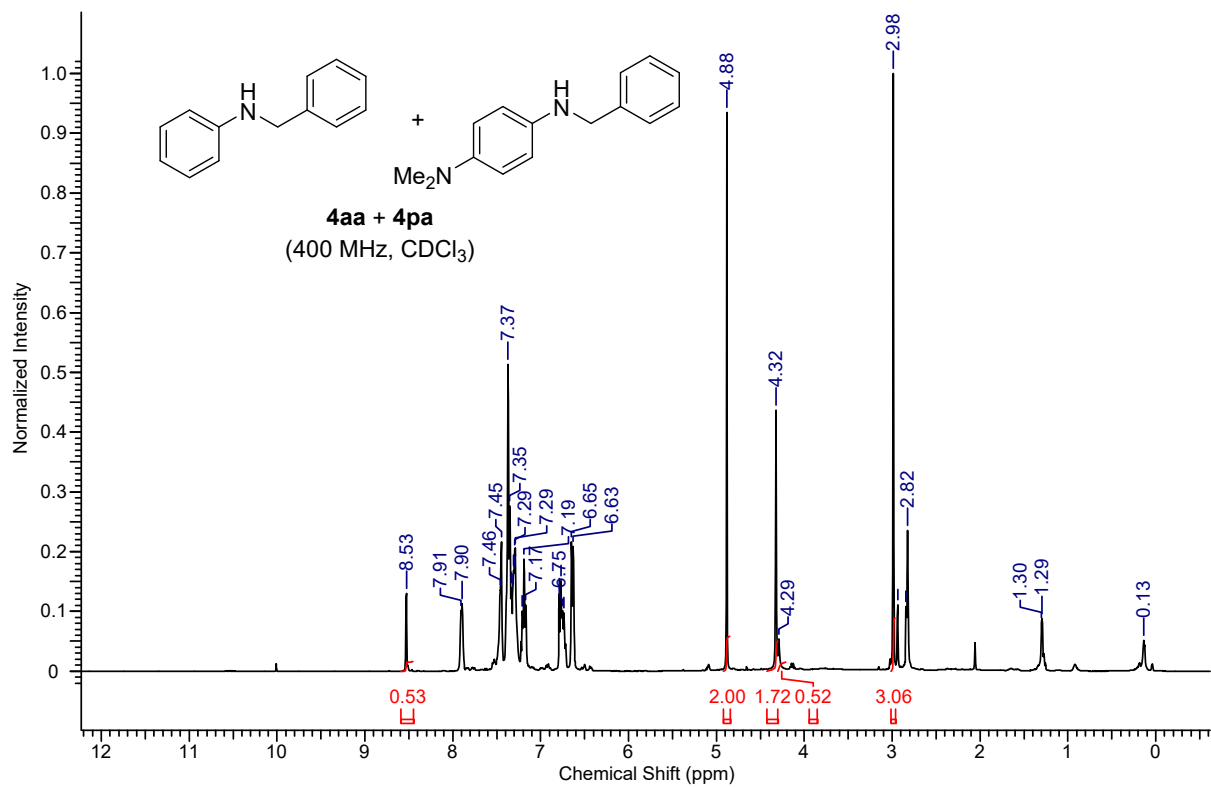
^{1}H-NMR spectrum of *N*-Benzylaniline (**4aa**) and *N*-Benzyl-4-(dimethylamino)aniline (**4pa**) obtained from the crude reaction mixture

^{1}H-NMR spectrum of *N*-(4-Methylbenzyl)aniline (**4ab**)
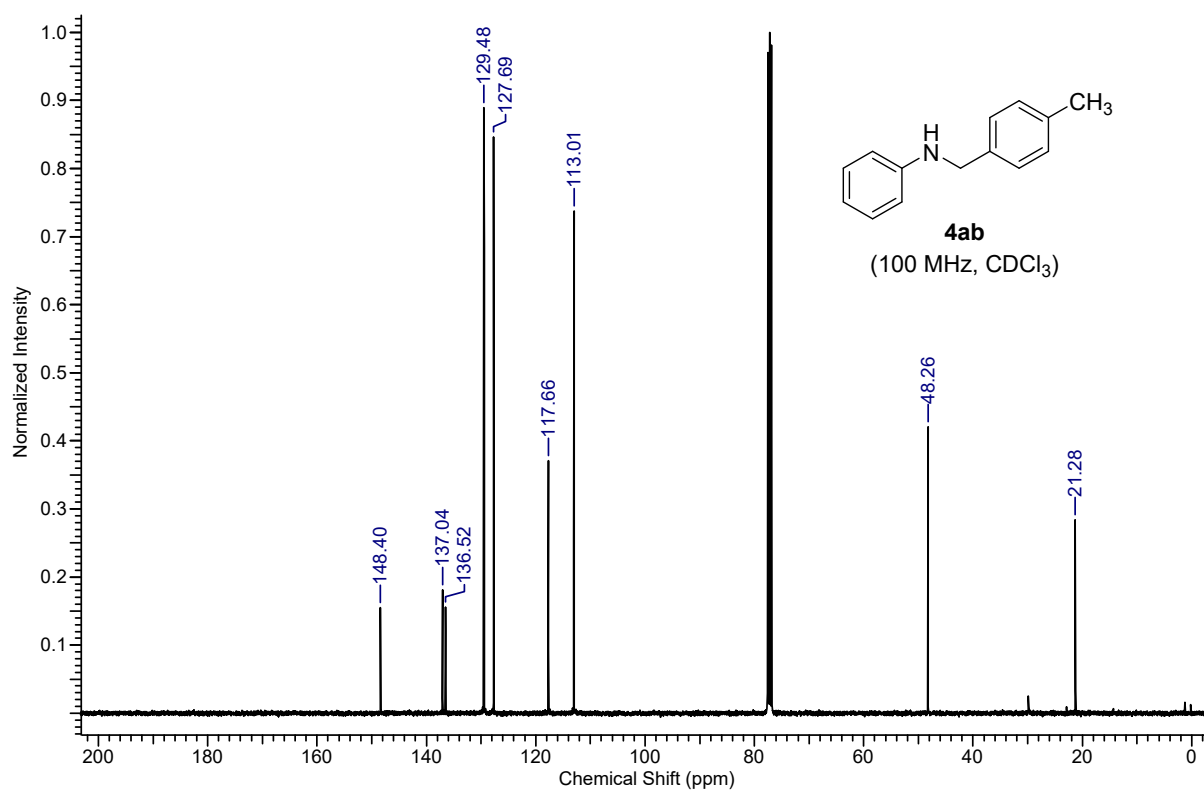
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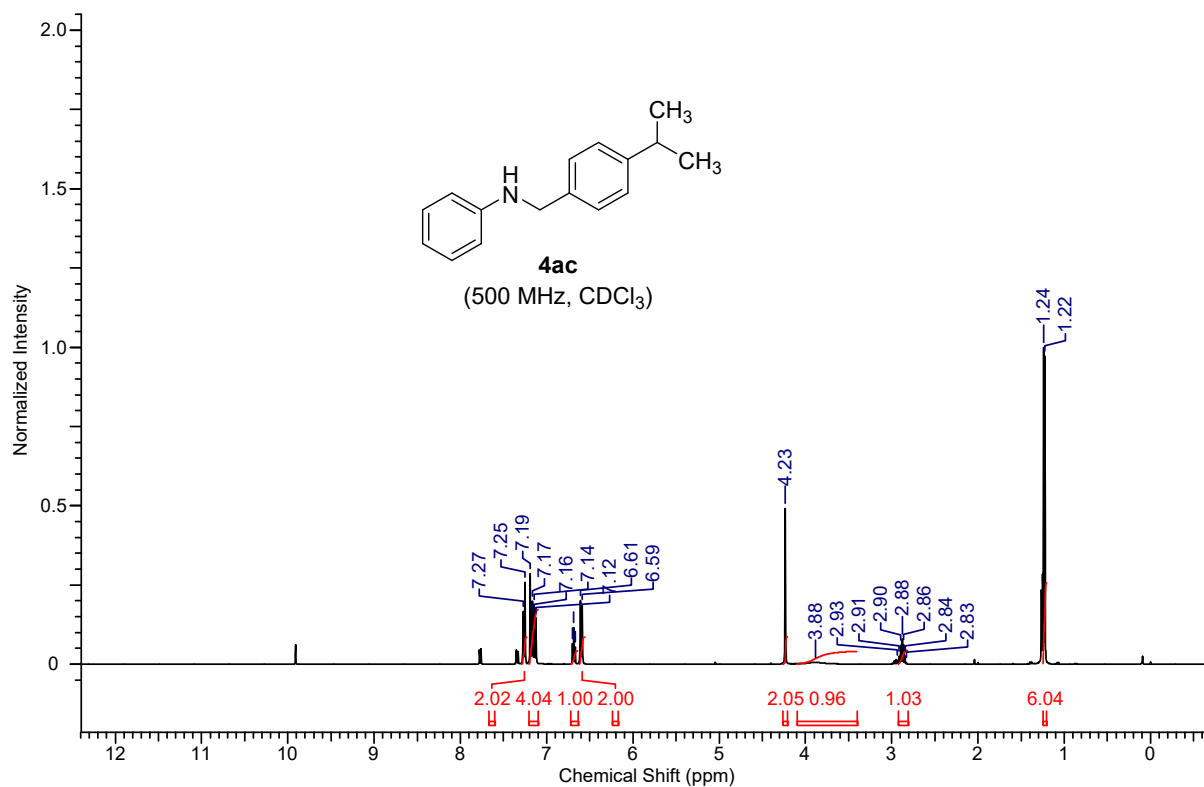
^{1}H-NMR spectrum of *N*-(4-isopropylbenzyl)aniline (**4ac**)

^{13}C{^{1}H}-NMR spectrum of *N*-(4-isopropylbenzyl)aniline (**4ac**)
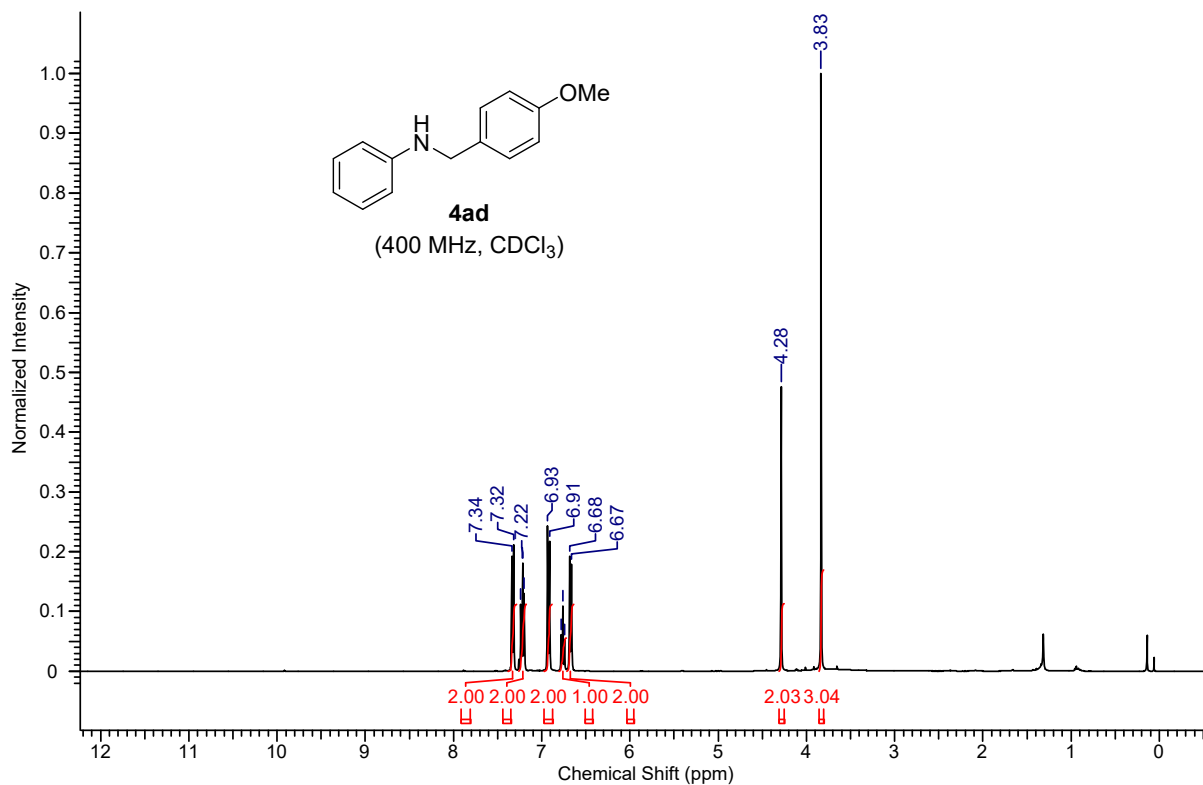
^{1}H-NMR spectrum of *N*-(4-methoxybenzyl)aniline (**4ad**)
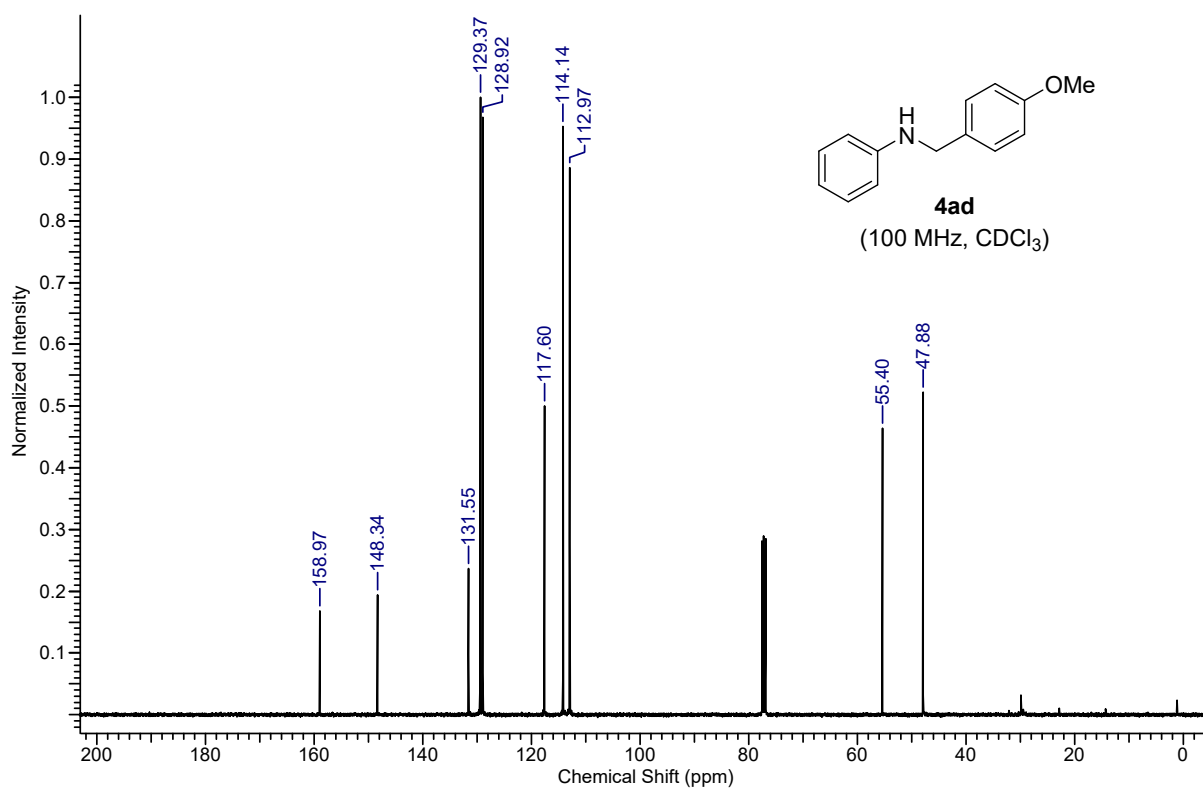
^{13}C{^{1}H}-NMR spectrum of *N*-(4-methoxybenzyl)aniline (**4ad**)
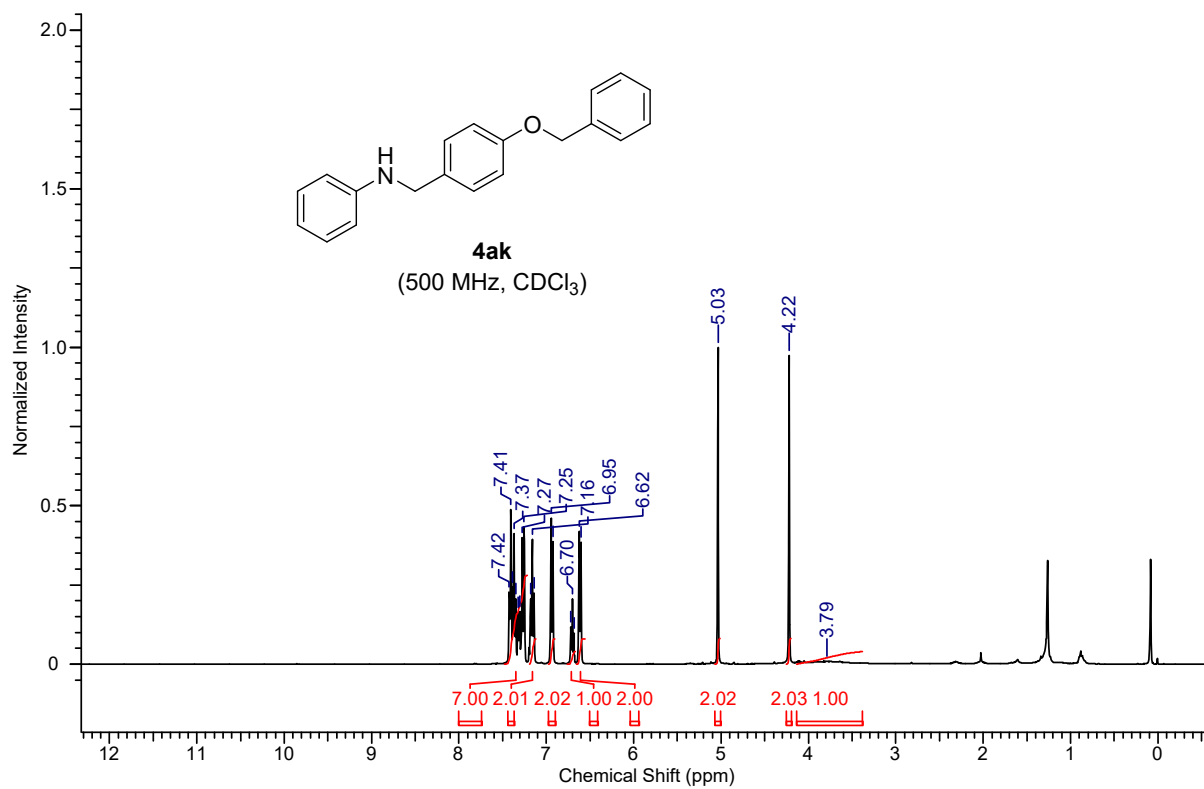
^{1}H-NMR spectrum of *N*-(4-benzyloxybenzyl)aniline (**4ak**)
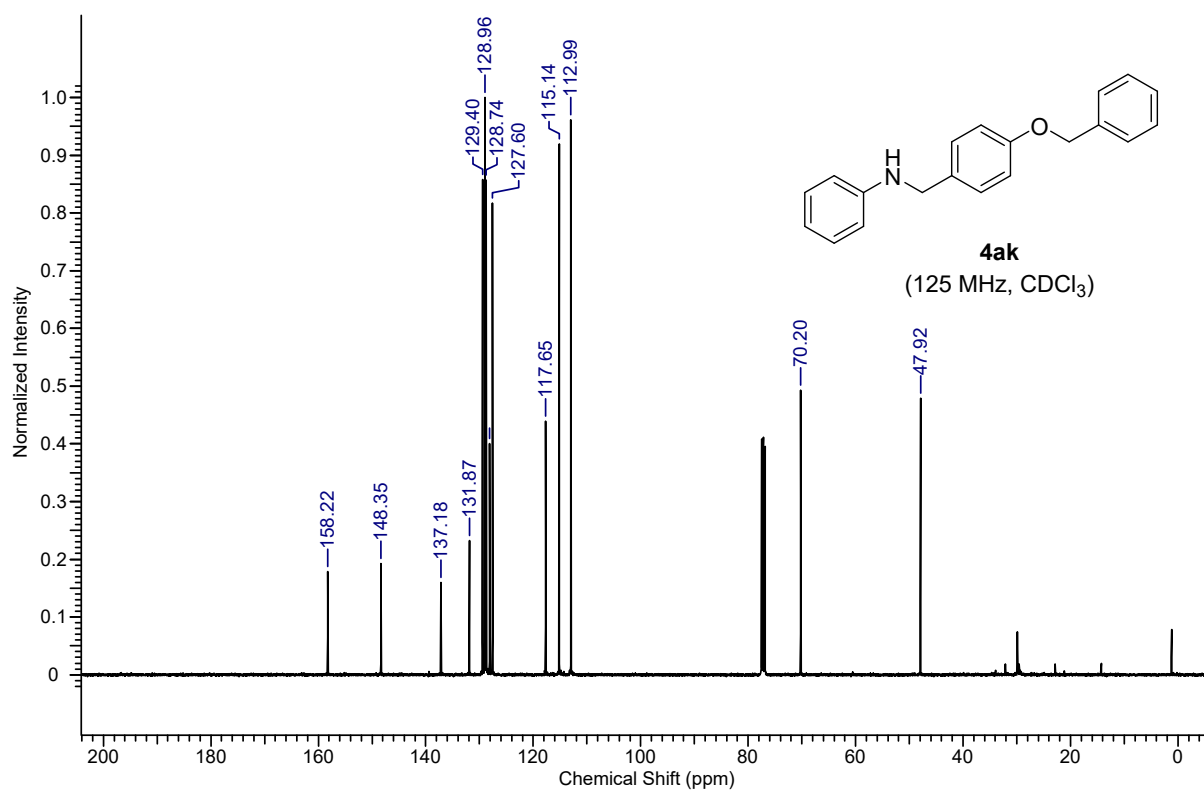
^{13}C{^{1}H}-NMR spectrum of *N*-(4-benzyloxybenzyl)aniline (**4ak**)
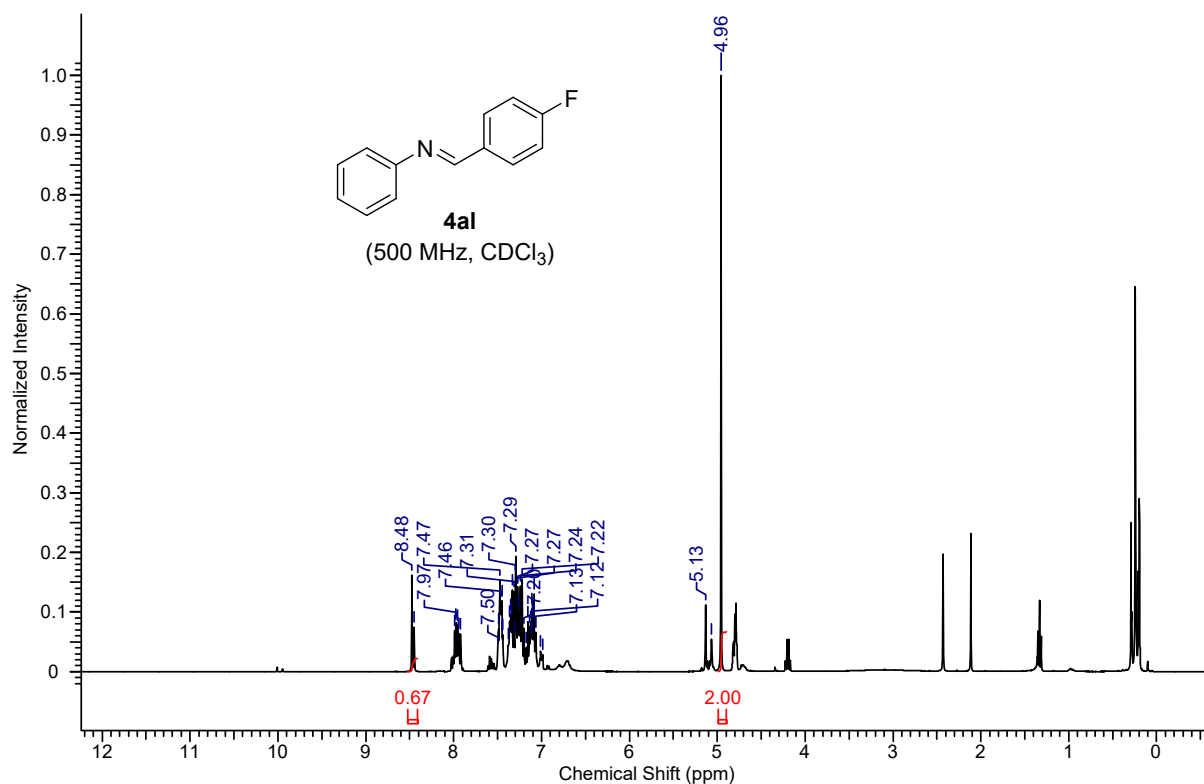
^{1}H-NMR spectrum of *N*-(4-fluorobenzylidene)aniline (**4al**) obtained from the crude reaction mixture
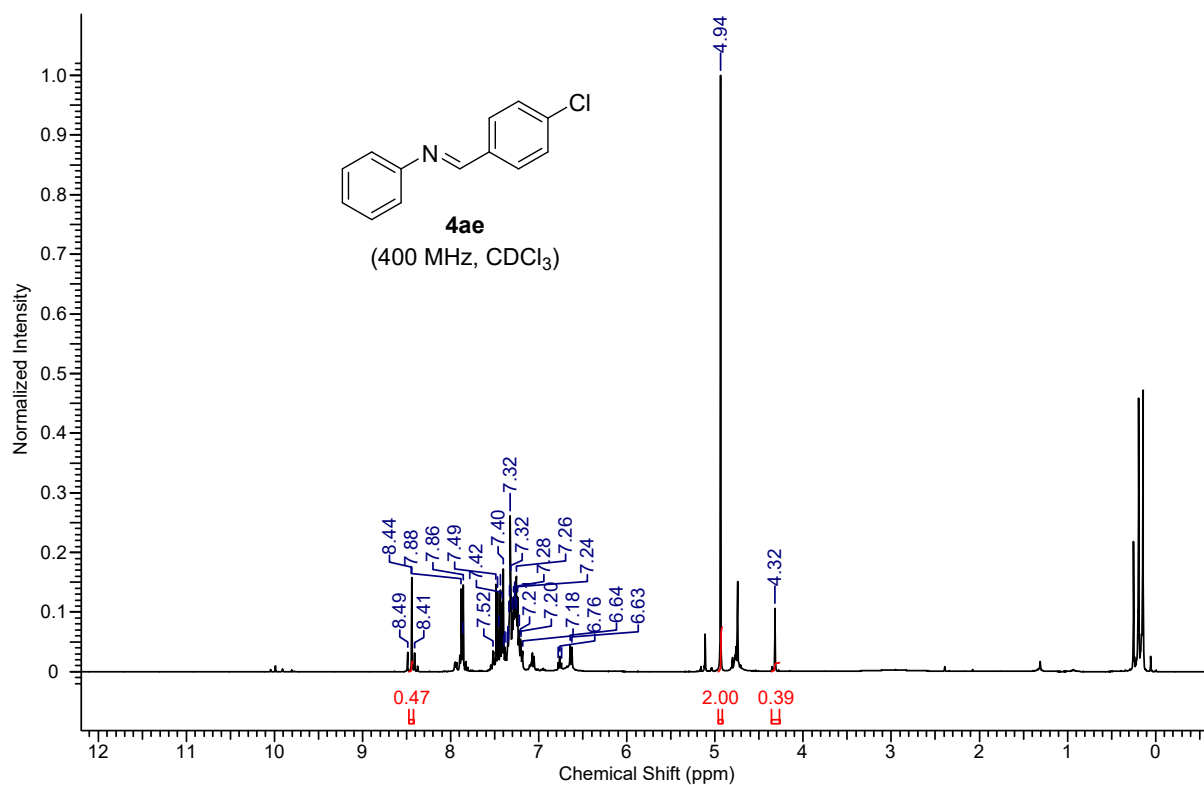
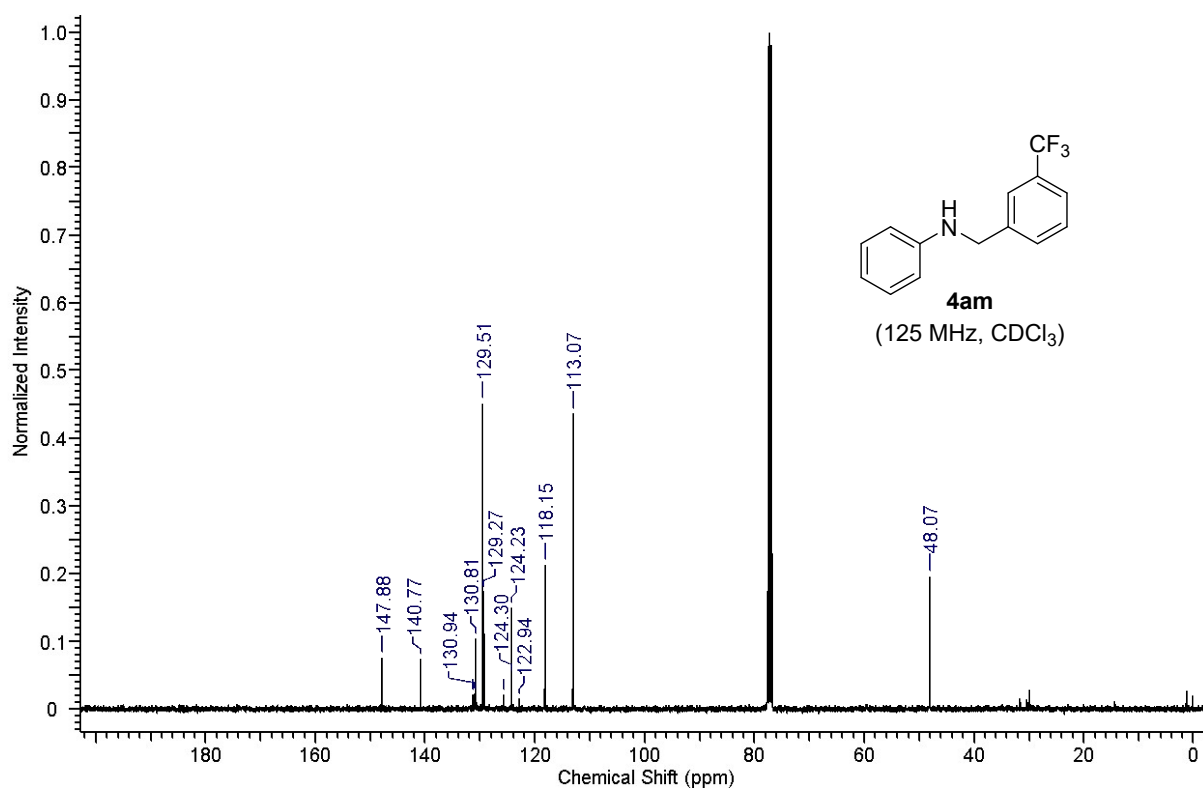^{1}H-NMR spectrum of *N*-(4-chlorobenzylidene)aniline (**4ae**) obtained from the crude reaction mixture
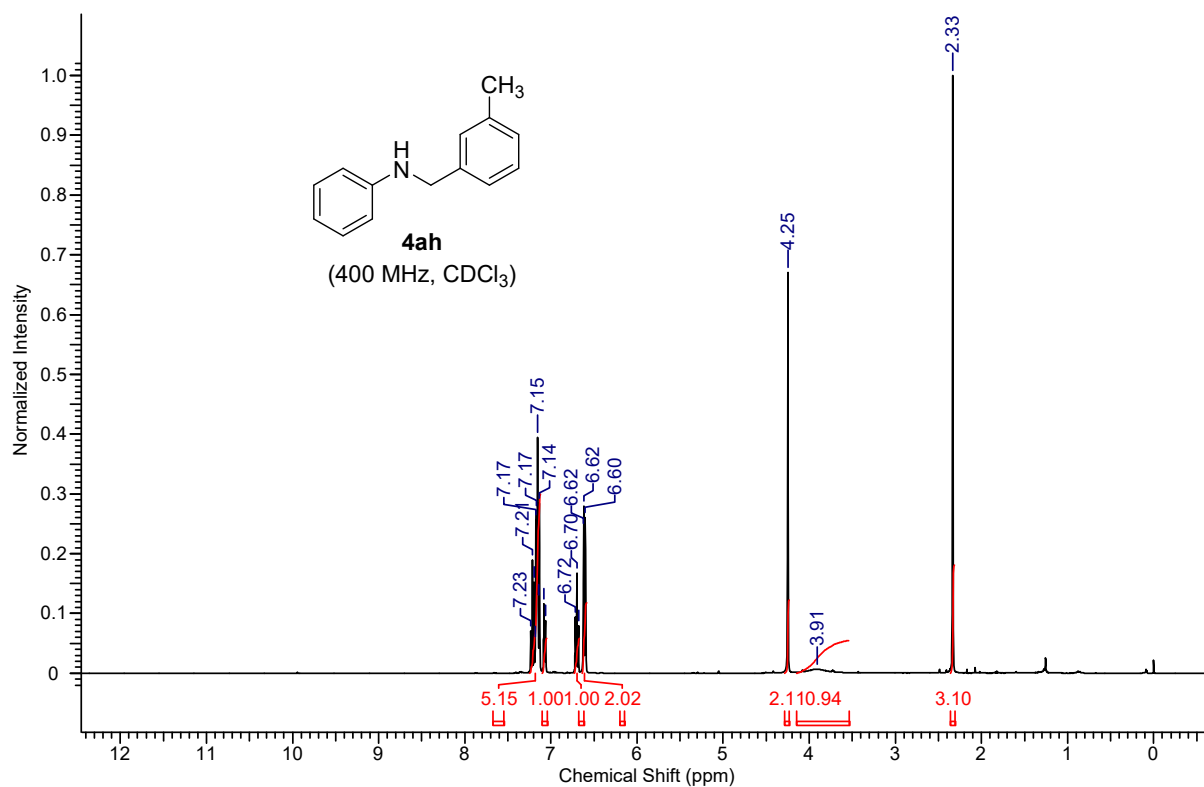
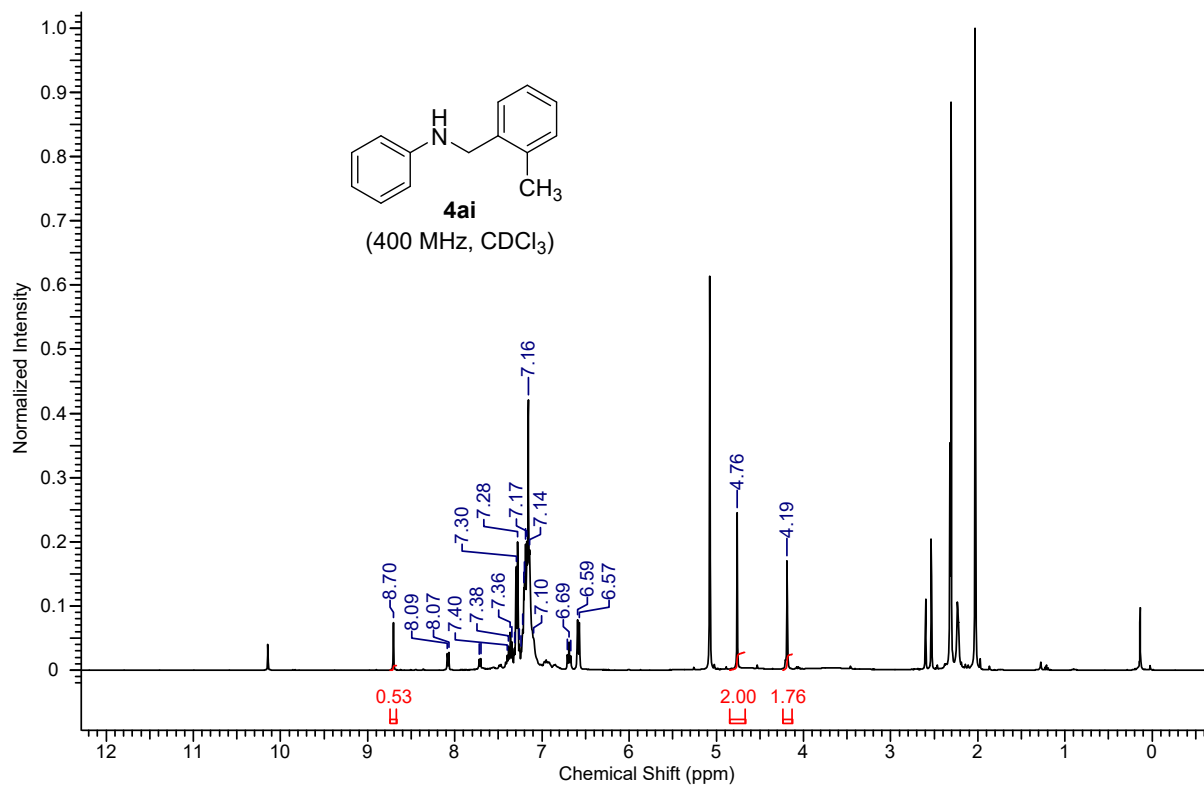^{1}H-NMR spectrum of *N*-(3-methylbenzyl)aniline (**4ah**)
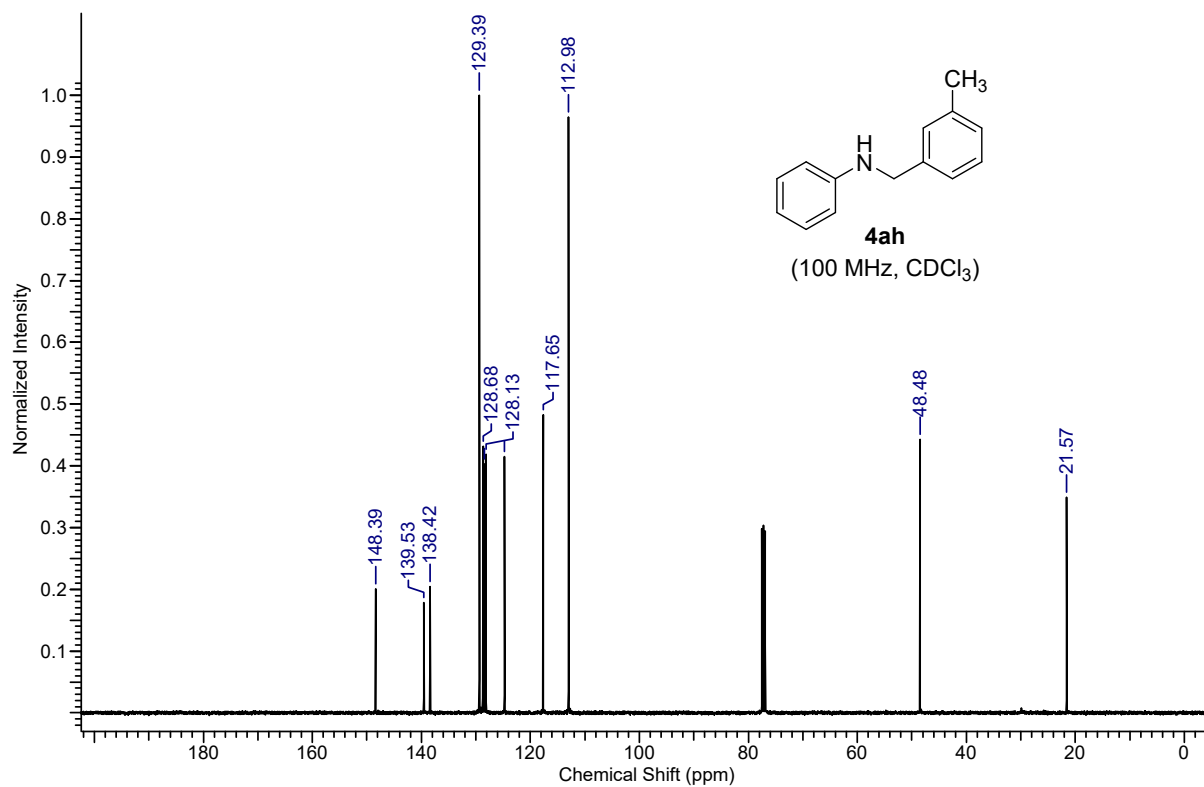
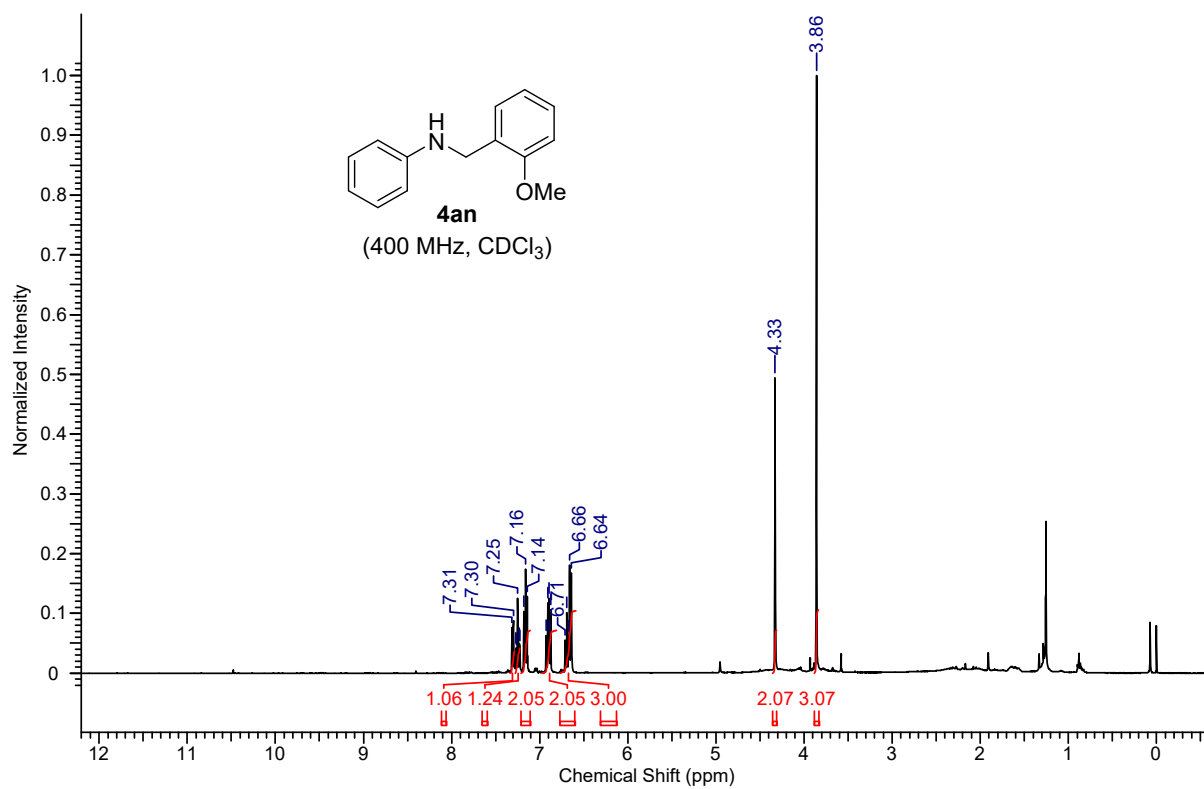^{13}C{^{1}H}-NMR spectrum of *N*-(3-methylbenzyl)aniline (**4ah**)
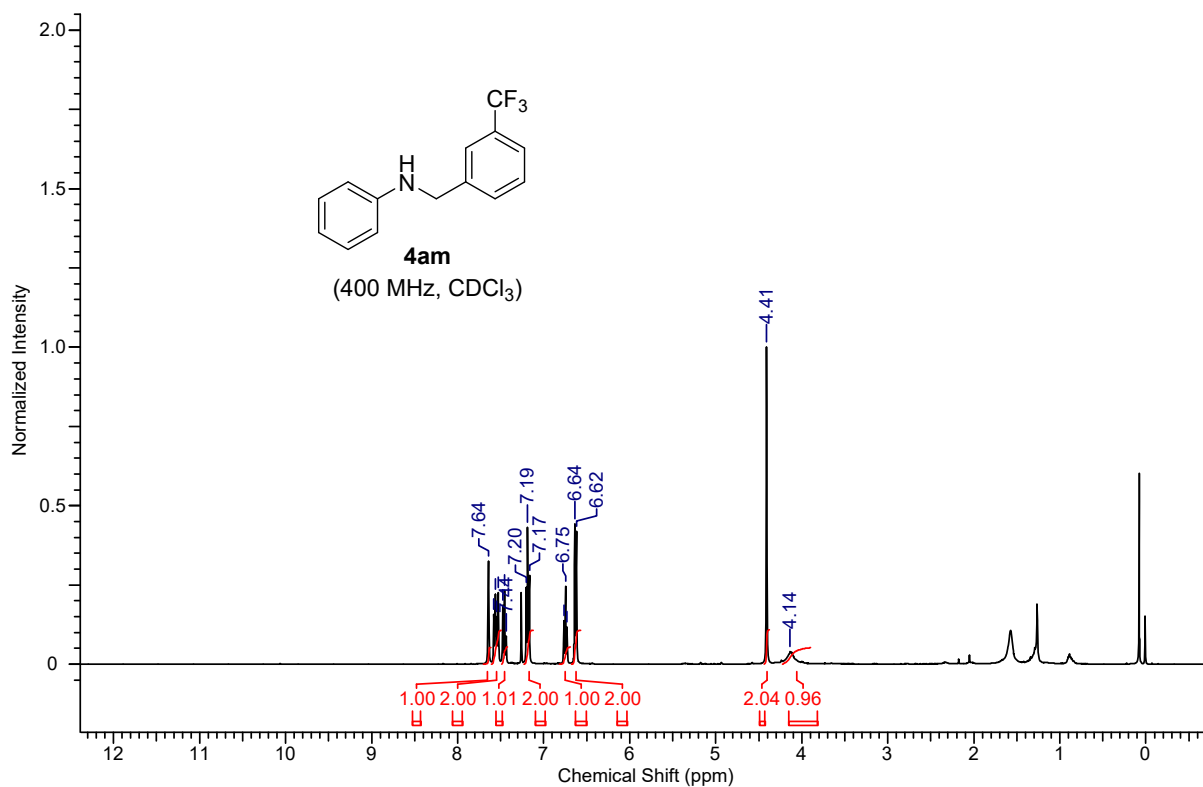
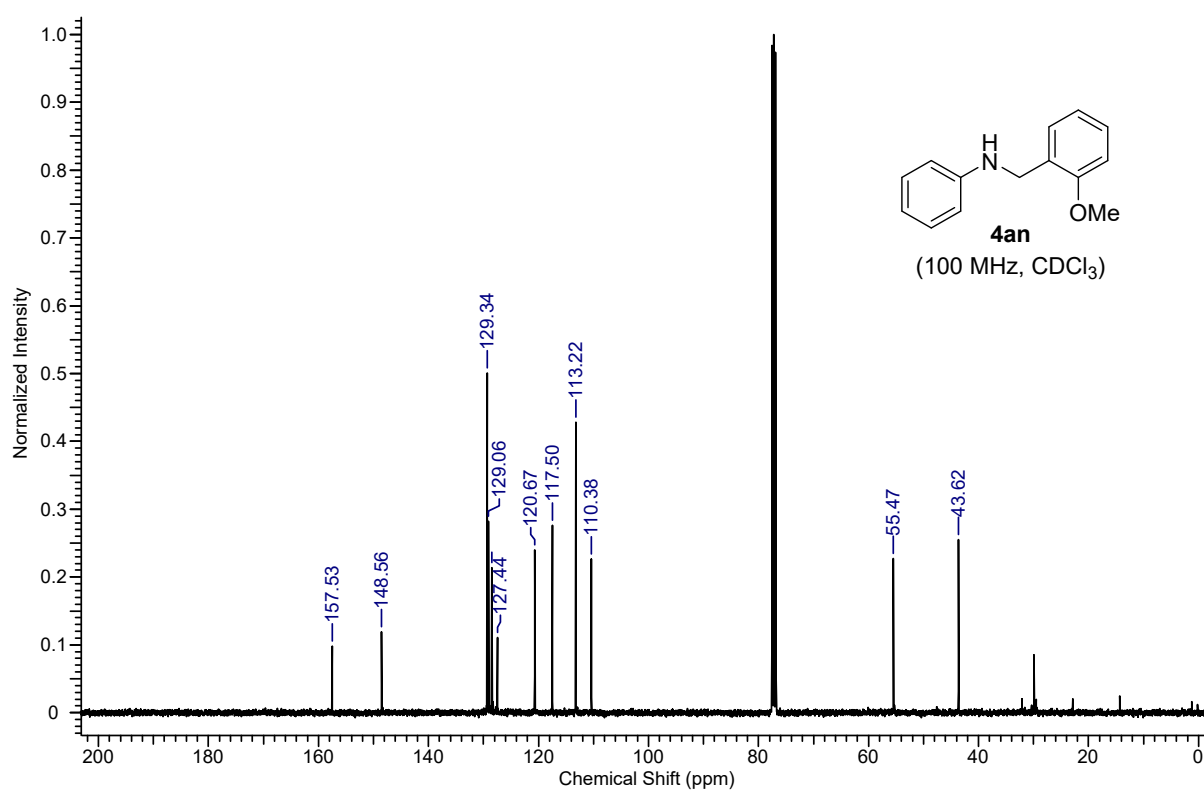^{1}H-NMR spectrum of *N*-(3-trifluoromethylbenzyl)aniline (**4am**)

^{13}C{^{1}H}-NMR spectrum of *N*-(3-trifluoromethylbenzyl)aniline (**4am**)
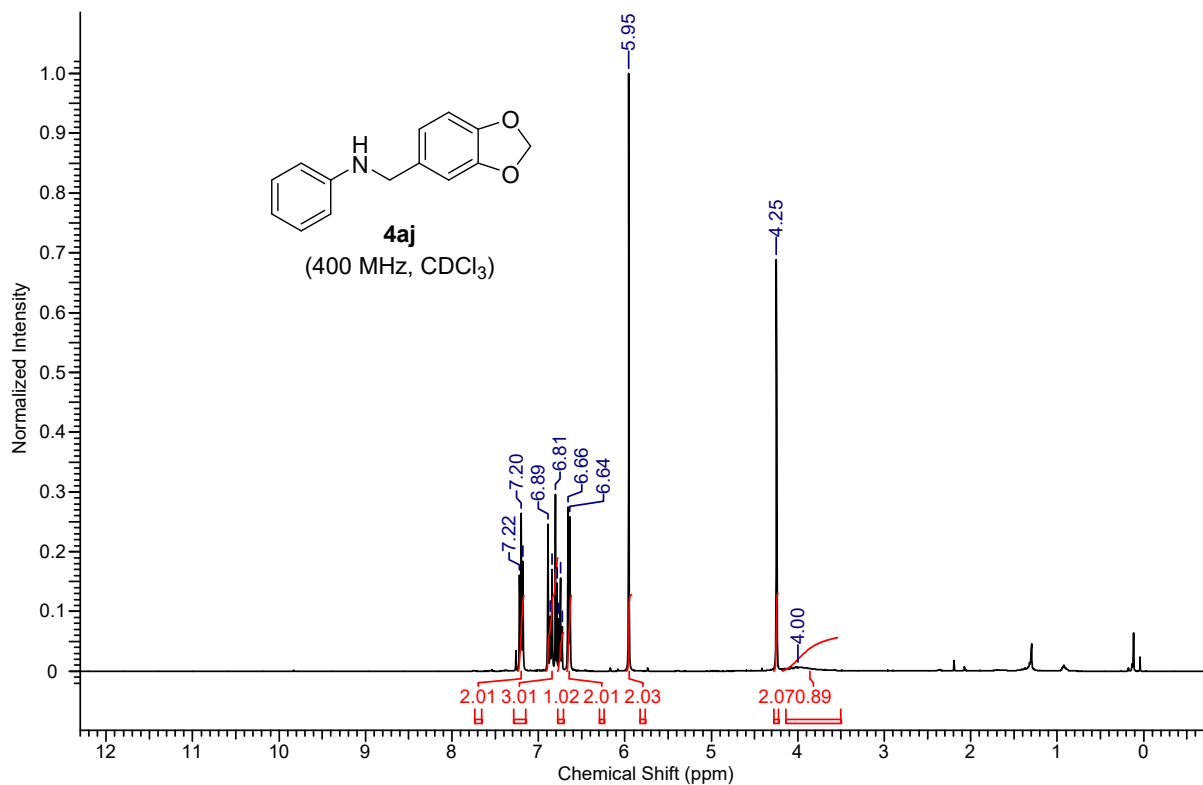
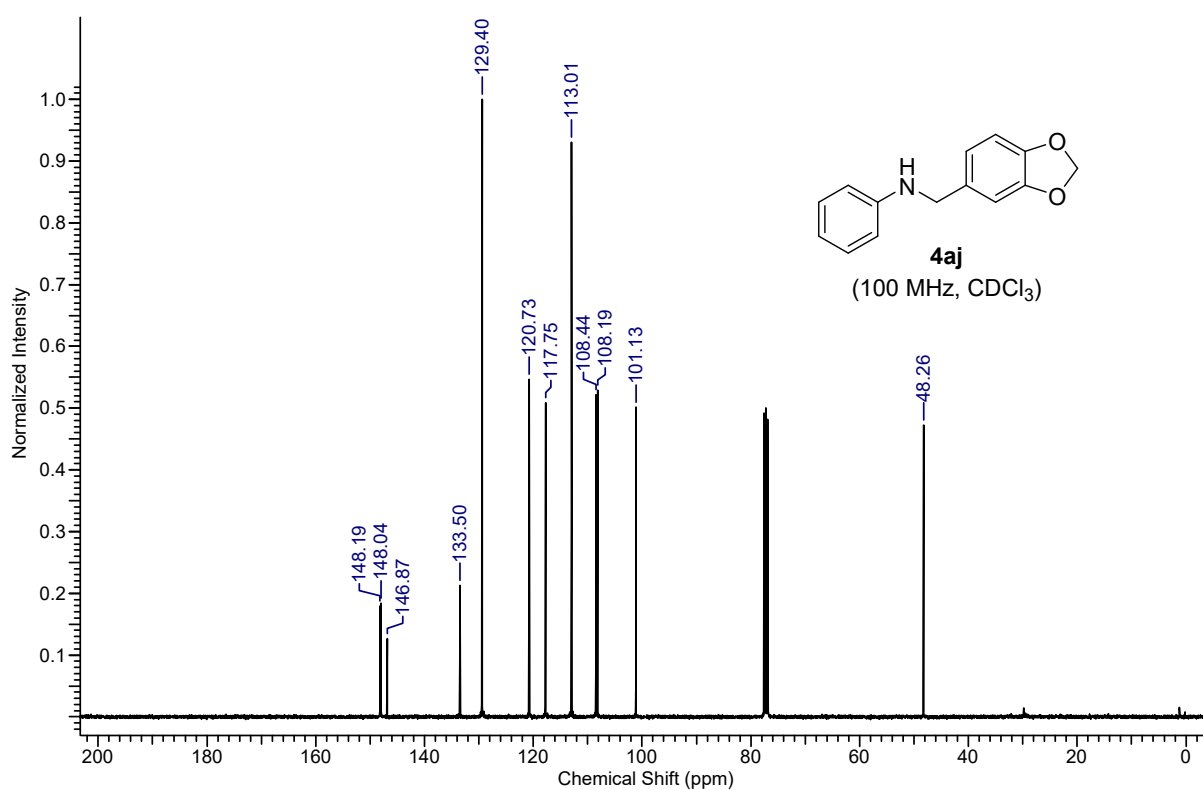^{1}H-NMR spectrum of *N*-(2-methylbenzyl)aniline (**4ai**) obtained from the crude reaction mixture

^{1}H-NMR spectrum of *N*-(2-methoxybenzyl)aniline (**4an**)

^{13}C{^{1}H}-NMR spectrum of *N*-(2-methoxybenzyl)aniline (**4an**)

^{1}H-NMR spectrum of N-(Benzo[d][1,3]dioxol-5-ylmethyl)aniline (**4aj**)

^{13}C{^{1}H}-NMR spectrum of N-(Benzo[d][1,3]dioxol-5-ylmethyl)aniline (**4aj**)