

EXPERIMENTAL SUPPORTING INFORMATION (PART 1)

A General and “*Universal*” Catalyst for the Base-Free Selective Mono-*N*-Alkylation of Amines with Alcohols. Insights into the Mechanism

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1. General

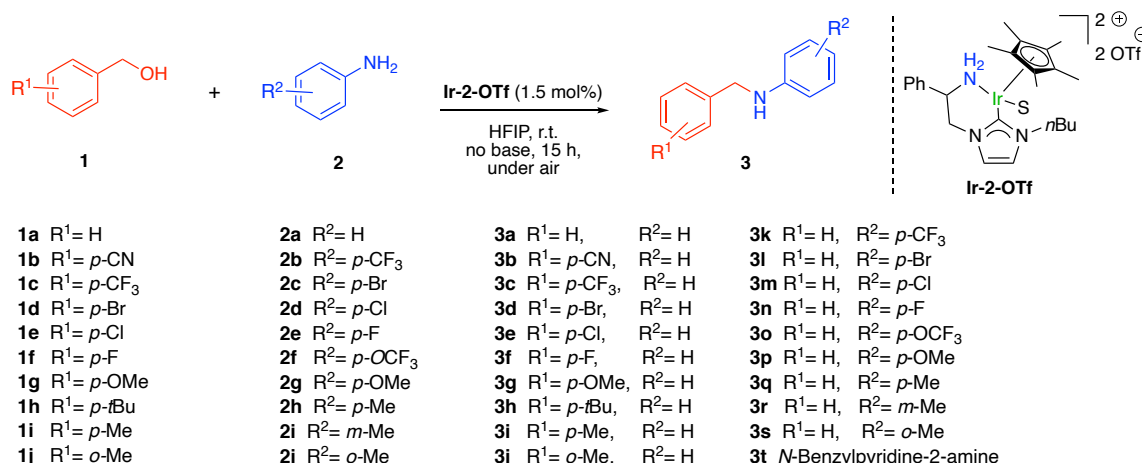
All reactions were carried out under an atmosphere of argon in oven-dried Biotage[®] microwave vials. Reagents were of analytical grade, obtained from commercial suppliers and used as purchased. Anhydrous dichloromethane and acetonitrile were obtained using a VAC solvent purification system. Flash chromatography was carried out on Davisil silica gel 60 (35-70 μm). Nuclear magnetic resonance (NMR) spectra were recorded at 400 or 500 MHz for ^1H NMR, and at 100 or 125 MHz for ^{13}C NMR, on a Bruker 400 and on a Bruker AV 500 spectrometer. ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm relative to the residual non-deuterated solvent peaks. Chloroform- d_3 : δH 7.26 (s) ppm, and δC 77.0 (t) ppm. Acetone- d_6 : δH 2.05 (quint) ppm, and δC 206.3 (m) and 29.9 (sept) ppm. Toluene- d_8 : δH 7.09 (m), 7.01 (s), 6.97 (m), 2.08 (quin) ppm, and δC 137.9 (s), 128.9 (t), 128.0 (1:1:1 t), 125.1 (1:1:1 t), 20.4 (sept) ppm. Methanol- d_4 : δH 4.78 (s), 3.31 (quin) ppm, and δC 49.0 (sept) ppm. Coupling constants (J) are given in Hz. ^1H NMR spectra were recorded using a relaxation delay $T_1 = 5$ s (important integral regions of spectra with $T_1 > 5$ s were equal to integral regions when $T_1 = 5$ s). High-resolution mass spectra (HRMS) were obtained on a Bruker MicroTOF ESI-TOF spectrometer.

2. General procedure for the *N*-alkylation of amines with alcohols

Iridium pre-catalyst **Ir-2-Cl** (2.4 mg, 0.004 mmol, 1 equiv.) and silver salt **AgOTf** (2.0 mg, 0.008 mmol, 2.1 equiv.) were suspended in anhydrous dichloromethane (1 mL), in a vial covered in aluminum foil. The reaction mixture was stirred at room temperature for 15 minutes. The mixture was filtered off through a pad of Celite® to remove the AgCl precipitated, and transferred to an oven dried pressure tube. The solvent was evaporated under vacuum and the active catalyst species used in-situ.

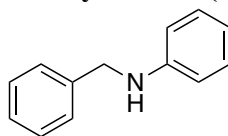
The pressure tube impregnated with the active iridium species **Ir-2-OTf** (0.004 mmol, 1.5 mol%) was loaded with dry HFIP (125 μ L), and the corresponding alcohol (0.25 mmol, 1 equiv.) and amine (0.25 mmol, 1 equiv.) were added. The mixture was stirred under the reaction conditions specified, and under air atmosphere (Scheme S1). After the reaction was complete, the yield was quantified by ¹H NMR spectroscopy using 1,2,4,5-tetrachloro-3-nitrobenzene as internal standard or by comparison with the unreacted starting material, and after purification by column chromatography using petroleum ether/EtOAc as eluent (95:5).

2.1. *N*-Alkylation of anilines with benzylic alcohols



Scheme S1. *N*-Alkylation of amines with alcohols catalyzed by **Ir-2-OTf**.

N-Benzylaniline (**3a**)



3a

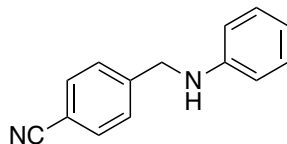
The general procedure was applied using aniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3a** (43 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc as eluent (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.40-7.29 (m, 5 H, Ar), 7.21-7.17 (m, 2 H, *o*-Ar), 6.76-6.74 (m, 1 H, *p*-Ar), 6.72-6.65 (m, 2 H, *m*-Ar), 4.35 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.1, 139.4, 129.3, 128.7, 127.6, 127.3, 117.7, 112.9, 48.4 ppm.

HRMS (ESI): calc. for C₁₃H₁₃N [M+H]⁺: 184.1121; found: 184.1124.

4-((Phenylamino)methyl)benzonitrile (**3b**)



3b

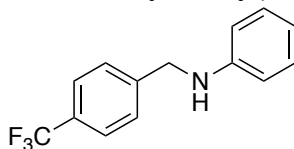
The general procedure was applied using aniline (0.25 mmol) and 4-(hydroxymethyl)benzonitrilealcohol (0.25 mmol, 1 equiv.). Reaction time was 36 h. Product **3b** (48 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.63-7.61 (m, 2 H, *m*-Bn), 7.49-7.47 (m, 2 H, *o*-Bn), 7.20 -7.16 (m, 2 H, *m*-Ar), 6.77-6.73 (m, 1 H, *p*-Ar), 6.60-6.57 (m, 2 H, *o*-Ar), 4.43 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.2, 145.4, 132.5, 139.4, 127.7, 118.9, 118.1, 112.9, 110.9, 47.8 ppm.

HRMS (ESI): calc. for C₁₄H₁₃N₂ [M+H]⁺: 209.1073; found: 209.1072.

N-(*p*-Trifluoromethylbenzyl)aniline (**3c**)



3c

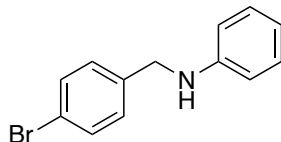
The general procedure was applied using aniline (0.25 mmol) and 4-trifluoromethylbenzyl alcohol (0.25 mmol, 1 equiv.). Reaction time was 36 h. Product **3c** (60 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁴

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.66-7.53 (m, 2 H, *m*-Bn), 7.51-7.26 (m, 2 H, *o*-Bn), 7.26 -7.21 (m, 2 H, *m*-Ar), 6.81-6.80 (m, 1 H, *p*-Ar), 6.68-6.64 (m, 2 H, *o*-Ar), 4.44 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.7, 143.8, 129.4 (q, *J*(¹³C, ¹⁹F) = 32.3 Hz), 127.6, 127.5, 125.6 (q, *J*(¹³C, ¹⁹F) = 3.7 Hz), 118.0, 113.0, 47.8 ppm.

HRMS (ESI): calc. for C₁₄H₁₃F₃N [M+H]⁺: 252.0995; found: 252.0999.

N-(*p*-Bromobenzyl)aniline (**3d**)



3d

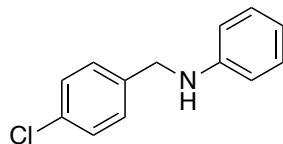
The general procedure was applied using aniline (0.25 mmol) and 4-bromobenzyl alcohol (0.25 mmol, 1 equiv.). Reaction time was 36 h. Product **3d** (60 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁴

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.48-7.45 (m, 2 H, *m*-Ar), 7.27-7.25 (m, 2 H, *m*-Bn), 7.21-7.17 (m, 2 H, *o*-Bn), 6.77-6.72 (m, 1 H, *p*-Ar), 6.63-6.61 (m, 2 H, *o*-Ar), 4.30 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.8, 138.5, 131.7, 129.3, 129.1, 121.0, 117.9, 113.0, 47.7 ppm.

HRMS (ESI): calc. for C₁₃H₁₃BrN [M+H]⁺: 262.0226; found: 262.0223.

***N*-(*p*-Chlorobenzyl)aniline (3e)**



3e

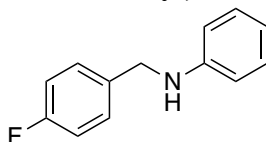
The general procedure was applied using aniline (0.25 mmol) and 4-chlorobenzyl alcohol (0.25 mmol, 1 equiv.). Reaction time was 36 h. Product **3e** (50 mg, 91% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.⁵

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.24 (s, 4 H, Bn), 7.23-7.20 (m, 2 H, *m*-Ar), 6.80-6.74 (m, 1 H, *p*-Ar), 6.67-6.64 (m, 2 H, *o*-Ar), 4.35 (s, 2 H, CH_2) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 147.7, 137.9, 132.9, 129.3, 128.8, 117.9, 113.0, 47.7 ppm.

HRMS (ESI): calc. for $\text{C}_{13}\text{H}_{13}\text{ClN}$ $[\text{M}+\text{H}]^+$: 218.0731; found: 218.0730.

***N*-(*p*-Fluorobenzyl)aniline (3f)**



3f

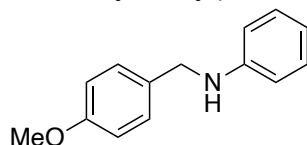
The general procedure was applied using aniline (0.25 mmol) and 4-fluorobenzyl alcohol (0.25 mmol, 1 equiv.). Reaction time was 36 h. Product **3f** (46 mg, 92% yield) was purified by column chromatography using petroleum ether/EtOAc as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.⁴

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.38-7.34 (m, 2 H, *m*-Ar), 7.23-7.22 (m, 2 H, *m*-Bn), 7.21-7.19 (m, 2 H, *o*-Bn), 7.08-7.03 (m, 1 H, *p*-Ar), 6.78-6.64 (m, 2 H, *o*-Ar), 4.32 (s, 2 H, CH_2) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 162.1 (d, J = 243 Hz), 148.0, 135.1 (d, J = 4.0 Hz), 129.3, 129.1, 129.0, 117.8, 115.4 (d, J = 21 Hz), 112.9, 47.7 ppm.

HRMS (ESI): calc. for $\text{C}_{13}\text{H}_{13}\text{FN}$ $[\text{M}+\text{H}]^+$: 202.1027; found: 202.1029.

***N*-(*p*-Methoxybenzyl)aniline (3g)**



3g

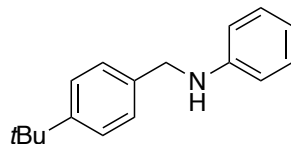
The general procedure was applied using aniline (0.25 mmol) and 4-methoxybenzyl alcohol (0.25 mmol, 1 equiv.). Product **3g** (50 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.³

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.31-7.26 (m, 2 H, *m*-Bn), 7.20-7.16 (m, 2 H, *o*-Bn), 6.89-6.87 (m, 2 H, *m*-Ar), 6.76-6.72 (m, 1 H, *p*-Ar), 6.68-6.65 (m, 2 H, *o*-Ar), 4.26 (s, 2 H, CH_2), 3.80 (s, 3 H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 158.9, 148.1, 131.3, 129.3, 128.9, 117.6, 114.0, 112.9, 55.3, 47.9 ppm.

HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 214.1226; found: 214.1225.

***N*-(4-(*tert*-butyl)benzyl)aniline (**3h**)**



3h

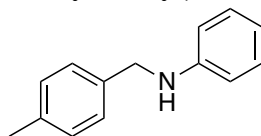
The general procedure was applied using aniline (0.25 mmol) and 4-*tert*-butylbenzyl alcohol (0.25 mmol, 1 equiv.). Product **3h** (57 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.⁵

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.44-7.35 (m, 4 H, *m*-Bn), 7.23-7.21 (m, 2 H, *m*-Ar), 6.77-6.70 (m, 1 H, *p*-Ar), 6.70-6.68 (m, 2 H, *o*-Ar), 4.33 (s, 2 H, CH_2), 1.38 (s, 9 H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 150.2, 148.3, 136.4, 129.3, 127.4, 125.6, 117.5, 112.8, 48.0, 34.5, 31.4 ppm.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$: 240.1747; found: 240.1750.

***N*-(*p*-Methylbenzyl)aniline (**3i**)**



3i

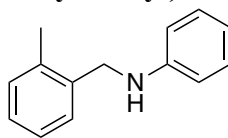
The general procedure was applied using aniline (0.25 mmol) and 4-methylbenzyl alcohol (0.25 mmol, 1 equiv.). Product **3i** (60 mg, 92% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.³

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.22-7.20 (m, 2 H, *m*-Ar), 7.19-7.17 (m, 4 H, Bn), 6.75-6.71 (m, 1 H, *p*-Ar), 6.71-6.64 (m, 2 H, *o*-Ar), 4.31 (s, 2H, CH_2), 2.37 (s, 3 H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 148.0, 136.9, 129.3, 127.6, 117.7, 113.0, 48.2, 21.1 ppm.

HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 198.1277; found: 198.1274.

***N*-(*o*-Methylbenzyl)aniline (**3j**)**



3j

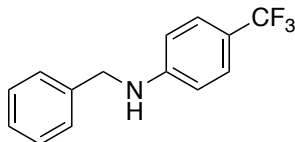
The general procedure was applied using aniline (0.25 mmol) and 2-methylbenzyl alcohol (0.25 mmol, 1 equiv.). Product **3j** (60 mg, 91% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ^1H and ^{13}C NMR spectroscopy data is in accordance with the one described in the literature.⁵

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.47-7.45 (m, 1 H, *o*-Ar), 7.35-7.28 (m, 5 H, Ar), 6.88-6.84 (t, J = 6.42 Hz, 1 H, Ar), 6.77-6.74 (d, J = 7.63 Hz, 2 H, Ar), 4.38 (s, 2 H, CH_2), 2.50 (s, 3 H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 148.4, 137.1, 136.4, 130.5, 129.4, 128.4, 127.5, 126.3, 117.6, 112.8, 46.5, 19.0 ppm.

HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$: 198.1277; found: 198.1275.

***N*-Benzyl-*p*-trifluoromethylaniline (3k)**



3k

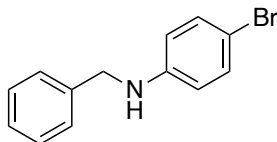
The general procedure was applied using 4-trifluoromethylaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3k** (60 mg, 89% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁶

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.38-7.29 (m, 5 H, Bn), 7.06-7.03 (m, 2 H, *m*-Ar), 6.61-6.59 (m, 2 H, *o*-Ar), 4.33 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 146.9, 140.6, 138.9, 128.8, 127.5, 127.4, 122.4, 122.0 (q, *J*(¹³C, ¹⁹F) = 255.2 Hz), 113.1, 48.5 ppm.

HRMS (ESI): calc. for C₁₄H₁₃F₃N [M+H]⁺: 252.0995; found: 252.0996.

***N*-Benzyl-*p*-bromoaniline (3l)**



3l

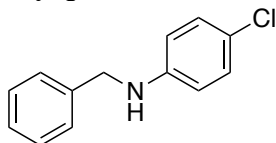
The general procedure was applied using 4-bromoaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3l** (58 mg, 88% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.35-7.28 (m, 5 H, Bn), 7.26-7.24 (m, 2 H, *m*-Ar), 6.54-6.49 (m, 2 H, *o*-Ar), 4.30 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 146.8, 138.7, 132.0, 128.7, 127.5, 127.4, 114.6, 48.4 ppm.

HRMS (ESI): calc. for C₁₃H₁₃BrN [M+H]⁺: 262.0226; found: 262.0225.

***N*-Benzyl-*p*-chloroaniline (3m)**



3m

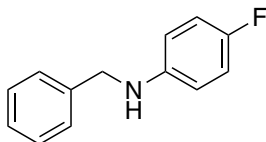
The general procedure was applied using 4-chloroaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3m** (60 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.43-7.36 (m, 5 H, Bn), 7.20-7.18 (m, 2 H, *m*-Ar), 6.61-6.59 (m, 2 H, *o*-Ar), 4.35 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 146.8, 139.0, 129.1, 128.8, 127.5, 127.4, 122.3, 122.1, 114.0, 48.4 ppm.

HRMS (ESI): calc. for C₁₃H₁₃ClN [M+H]⁺: 218.0731; found: 218.0733.

***N*-Benzyl-*p*-fluoroaniline (3n)**



3n

The general procedure was applied using 4-fluoroaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3n** (48 mg, 96% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

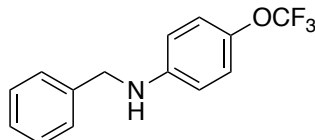
¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.42-7.32 (m, 5 H, Bn), 6.94-6.90 (m, 2 H, *m*-Ar), 6.62-6.58 (m, 2 H, *o*-Ar), 4.33 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 157.1, 154.7, 144.5, 139.3, 128.7, 127.5, 127.3, 115.8, 115.6, 113.7, 113.6 ppm.

¹⁹F NMR (376 MHz, CDCl₃, 298 K): δ = -127.9 ppm.

HRMS (ESI): calc. for C₁₃H₁₃FN [M+H]⁺: 202.1027; found: 202.1028.

***N*-Benzyl-*p*-trifluoromethoxyaniline (3o)**



3o

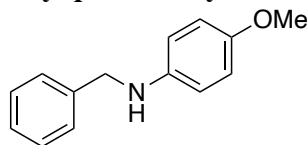
The general procedure was applied using 4-trifluoromethoxyaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3o** (60 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁷

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.37-7.29 (m, 5 H, Bn), 7.05-7.02 (m, 2 H, *m*-Ar), 6.61-6.57 (m, 2 H, *o*-Ar), 4.32 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 146.7, 140.7, 138.8, 128.7, 127.4, 122.4, 122.0, 119.5 (q, *J* = 250 Hz), 113.2, 48.5 ppm.

HRMS (ESI): calc. for C₁₄H₁₃F₃NO [M+H]⁺: 268.0944; found: 268.0945.

***N*-Benzyl-*p*-methoxyaniline (3p)**



3p

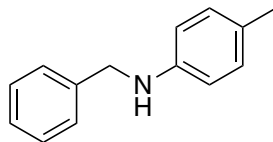
The general procedure was applied using 4-methoxyaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3p** (50 mg, 93% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.39-7.27 (m, 5 H, Bn), 6.79-6.77 (m, 2 H, *m*-Ar), 7.64-7.60 (m, 2 H, *o*-Ar), 4.29 (s, 2 H, CH₂), 3.75 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 152.3, 142.2, 139.5, 128.6, 127.6, 127.2, 114.8, 114.3, 55.8, 49.4 ppm.

HRMS (ESI): calc. for C₁₄H₁₆NO [M+H]⁺: 214.1226; found: 214.1226.

N-Benzyl-*p*-methylaniline (**3q**)



3q

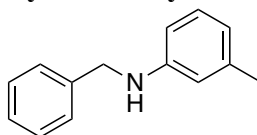
The general procedure was applied using 4-methylaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3q** (46 mg, 92% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.41-7.27 (m, 5 H, Bn), 7.00 (d, *J* = 8.0 Hz, 2 H, *m*-Ar), 6.59 (dt, *J* = 8.3, 2.3 Hz, 2 H, *o*-Ar), 4.33 (s, 2 H, CH₂), 2.26 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 145.8, 139.6, 129.8, 128.6, 127.5, 126.9, 125.7, 113.1, 48.7, 20.4 ppm.

HRMS (ESI): calc. for C₁₄H₁₆N [M+H]⁺: 198.1277; found: 198.1276.

N-Benzyl-*m*-methylaniline (**3r**)



3r

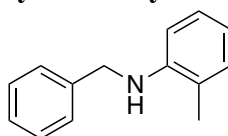
The general procedure was applied using 3-methylaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3r** (60 mg, 91% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.43-7.28 (m, 5 H, Bn), 7.119 (t, *J* = 7.6 Hz, 1 H, *m*-Ar), 6.60 (d, *J* = 7.5 Hz, 1 H, *p*-Ar), 6.59-6.49 (m, 2 H, *o*-Ar), 4.36 (s, 2 H, CH₂), 2.32 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.3, 139.6, 139.1, 129.2, 128.6, 127.6, 127.2, 118.6, 113.7, 110.0, 48.4, 21.7 ppm.

HRMS (ESI): calc. for C₁₄H₁₆N [M+H]⁺: 198.1277; found: 198.1275.

N-Benzyl-*o*-methylaniline (**3s**)



3s

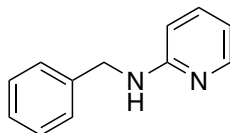
The general procedure was applied using *o*-methylaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3s** (61 mg, 92% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.47-7.20 (m, 5 H, Bn), 7.19-7.14 (m, 2 H), 6.75 (t, *J* = 7.6 Hz, 1 H, *p*-Ar), 6.70-6.68 (m, 1 H, *o*-Ar), 4.44 (s, 2 H, CH₂), 2.24 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 146.1, 139.6, 130.1, 128.7, 127.6, 127.2, 122.0, 117.2, 110.0, 48.4, 17.6 ppm.

HRMS (ESI): calc. for C₁₄H₁₆N [M+H]⁺: 198.1277; found: 198.1278.

N-Benzylpyridin-2-amine (**3t**)



3t

The general procedure was applied using pyridin-2-amine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3t** (39 mg, 84% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent.

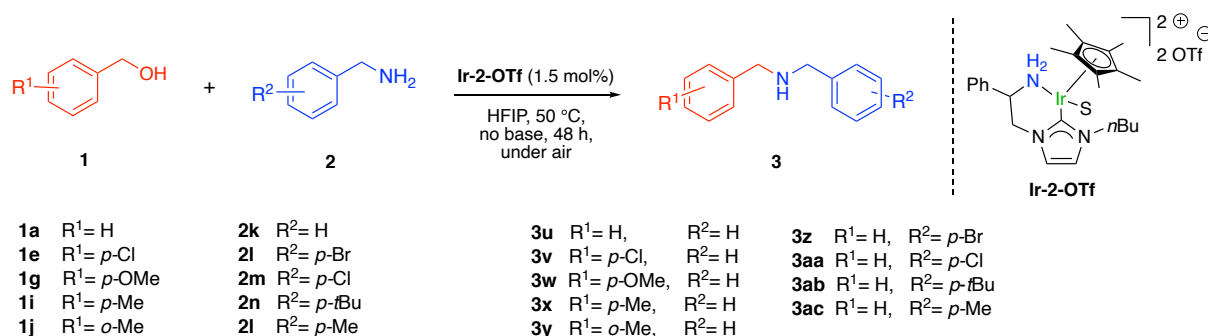
¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.10-8.08 (m, 1 H, pyr), 7.42-7.25 (m, 6 H, Ar-pyr), 6.60-6.57 (m, 1 H, pyr), 6.37 (d, *J* = 8.3 Hz, 1 H, pyr), 4.50 (d, *J* = 5.8 Hz, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 158.7, 148.2, 139.2, 137.5, 128.6, 127.4, 127.2, 113.1, 106.8, 46.3 ppm.

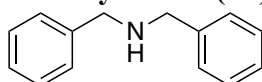
HRMS (ESI): calc. for C₁₂H₁₃N₂ [M+H]⁺: 185.1073; found: 185.1074.

2.2. *N*-Alkylation of benzylic amines with benzylic alcohols



Scheme S2. *N*-Alkylation of benzylic amines with benzylic alcohols catalyzed by **Ir-2-OTf**.

Dibenzylamine (**3u**)



3u

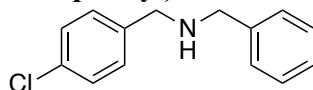
The general procedure was applied using benzylamine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3u** (46 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.⁹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.40-7.28 (m, 10 H, Ar), 3.84 (s, 4 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.2, 128.7, 128.4, 128.2, 128.2, 127.0, 126.8, 53.1 ppm.

HRMS (ESI): calc. for C₁₄H₁₆N [M+H]⁺: 198.1277; found: 198.1278.

***N*-Benzyl-1-(4-chlorophenyl)methanamine (3v and 3aa)**



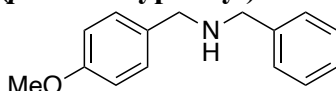
3v and 3aa

The general procedure was applied using benzylamine (0.25 mmol) and (4-chlorophenyl)methanol (0.25 mmol, 1 equiv.). Product **3v** (56 mg, 96% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. Same product was obtained using 4-chloroaniline (0.75 mmol) and benzyl alcohol (0.75 mmol, 1 equiv.) in 98% isolated yield (170 mg). Same product (**3aa**) was obtained using (4-chlorophenyl)methanamine (0.75 mmol) and benzyl alcohol (0.75 mmol, 1 equiv.) in 94% isolated yield (163 mg). ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁰

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.36-7.26 (m, 9 H, Ar), 3.83-3.76 (m, 4 H, CH₂) ppm.
¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.1, 138.8, 132.6, 129.5, 128.6, 128.5, 128.4, 128.2, 128.1, 127.0, 127.0, 53.1, 52.4 ppm.

HRMS (ESI): calc. for C₁₄H₁₅ClN [M+H]⁺: 232.0888; found: 232.0890.

***N*-Benzyl-1-(*p*-methoxyphenyl)methanamine (3w)**



3w

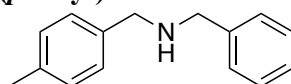
The general procedure was applied using benzylamine (0.25 mmol) and (4-methoxyphenyl)methanol (0.25 mmol, 1 equiv.). Product **3w** (54 mg, 95% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁰

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.35-7.26 (m, 7 H, Ar), 6.89-6.87 (m, 2 H, Ar), 3.81 (s, 3 H, CH₃), 3.81 (s, 2 H, CH₂), 3.76 (s, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 158.7, 140.4, 132.5, 129.3, 128.4, 128.2, 126.9, 113.7, 55.3, 53.1, 52.6 ppm.

HRMS (ESI): calc. for C₁₅H₁₈NO [M+H]⁺: 228.1383; found: 228.1386.

***N*-Benzyl-1-(*p*-tolyl)methanamine (3x and 3ac)**



3x and 3ac

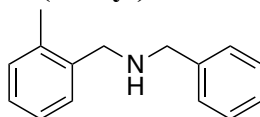
The general procedure was applied using benzylamine (0.25 mmol) and *p*-tolylmethanol (0.25 mmol, 1 equiv.). Product **3x** (49 mg, 93% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. Same product (**3ac**) was obtained using *p*-toluidine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.) in 95% isolated yield (50 mg). ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.35-7.14 (m, 9 H, Ar), 3.82-3.77 (m, 4 H, CH₂), 2.35 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.4, 137.3, 136.5, 136.5, 129.1, 129.1, 128.4, 128.4, 128.2, 128.1, 126.9, 53.1, 52.9, 21.1 ppm.

HRMS (ESI): calc. for C₁₅H₁₈N [M+H]⁺: 212.1434; found: 212.1435.

***N*-Benzyl-1-(*o*-tolyl)methanamine (3y)**



3y

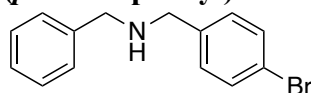
The general procedure was applied using benzylamine (0.25 mmol) and *o*-tolylmethanol (0.25 mmol, 1 equiv.). Product **3y** (48 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.36-7.15 (m, 9 H, Ar), 3.86 (s, 2 H, CH₂), 3.79 (s, 2 H, CH₂), 2.33 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.5, 138.3, 136.4, 130.3, 128.4, 128.1, 127.0, 126.9, 125.9, 53.6, 51.0, 18.9 ppm.

HRMS (ESI): calc. for C₁₅H₁₈N [M+H]⁺: 212.1434; found: 212.1436.

***N*-Benzyl-1-(*p*-bromophenyl)methanamine (3z)**



3z

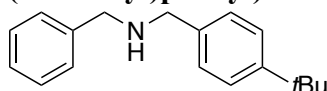
The general procedure was applied using 4-bromoaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3z** (64 mg, 93% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.46-7.22 (m, 9 H, Ar), 3.82-3.76 (m, 4 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.1, 139.4, 131.4, 129.8, 128.4, 128.1, 127.0, 120.7, 53.1, 52.4 ppm.

HRMS (ESI): calc. for C₁₄H₁₅BrN [M+H]⁺: 276.0382; found: 276.0383.

***N*-Benzyl-1-(4-(*tert*-butyl)phenyl)methanamine (3ab)**



3ab

The general procedure was applied using 4-(*tert*-butyl)aniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). Product **3ab** (61 mg, 93% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.

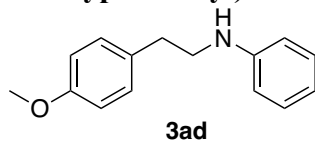
¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.38-7.26 (m, 9 H, Ar), 3.83 (s, 2 H, CH₂), 3.79 (s, 2 H, CH₂), 1.33-1.31 (m, 9 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 150.0, 140.0, 136.9, 128.4, 128.2, 127.9, 127.0, 125.4, 53.1, 52.7, 34.5, 31.4 ppm.

HRMS (ESI): calc. for C₁₈H₂₄N [M+H]⁺: 254.1903; found: 254.1903.

2.3. N-Alkylation of aliphatic and secondary alcohols with aniline

N-(4-Methoxyphenethyl)aniline (3ad)



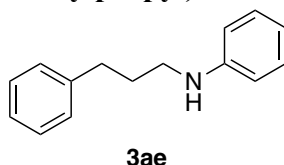
The general procedure was applied using aniline (0.25 mmol) and 2-(4-methoxyphenyl)ethanol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3ad** (49 mg, 85% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.21-7.14 (m, 4 H, Ar), 6.88-6.86 (m, 2 H, Ar), 6.74-6.70 (m, 1 H, *p*-Ar), 6.65-6.62 (m, 2 H, Ar), 3.81 (s, 3 H, CH₃), 3.39-3.35 (m, 2 H, CH₂), 2.89-2.86 (m, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 158.2, 148.1, 131.3, 129.7, 129.3, 117.4, 114.0, 113.0, 55.3, 45.2, 34.6 ppm.

HRMS (ESI): calc. for C₁₆H₂₀NO [M+H]⁺: 242.1539; found: 242.1539.

N-(3-Phenylpropyl)aniline (3ae)



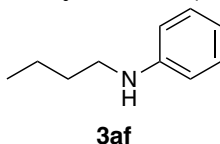
The general procedure was applied using aniline (0.25 mmol) and 3-phenylpropan-1-ol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3ae** (47 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹²

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.32-7.28 (m, 2 H, *m*-Ar), 7.22-7.15 (m, 5 H, Bn), 6.73-6.70 (m, 1 H, *p*-Ar), 6.70-6.59 (m, 2 H, *o*-Ar), 3.18-3.14 (m, 2 H, CH₂), 2.77-2.73 (m, 2 H, CH₂), 2.01-1.93 (m, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.3, 141.7, 129.2, 128.4, 128.4, 126.0, 117.3, 112.8, 43.44, 33.4, 31.1 ppm.

HRMS (ESI): calc. for C₁₅H₁₈N [M+H]⁺: 212.1434; found: 212.1434.

N-Butylaniline (3af)



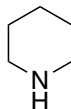
The general procedure was applied using hexan-1-amine (0.25 mmol) and butanol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3af** (44 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.19-7.15 (m, 2 H), 6.71-6.66 (m, 1 H), 6.61-6.59 (m, 2 H), 3.11 (t, *J* = 7.2 Hz, 2 H, CH₂CH₂CH₂CH₃), 1.65-1.57 (m, 2 H, CH₂CH₂CH₂CH₃), 1.48-1.39 (m, 2 H, CH₂CH₂CH₂CH₃), 0.96 (t, *J* = 7.3 Hz, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.9, 128.4, 128.2, 126.9, 54.0, 49.4, 31.8, 30.0, 27.0, 22.6, 14.0 ppm.

HRMS (ESI): calc. for C₁₀H₁₆N [M+H]⁺: 150.1277; found: 150.1278.

Piperidine (**3ag**)



3ag

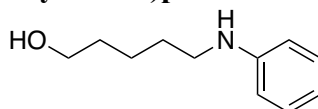
The general procedure was applied using 5-aminopentan-1-ol (0.25 mmol). The mixture was heated to 90 °C for 24 hours. Product **3ag** (20 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. This compound is commercially available.

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 2.72-2.70 (m, 4 H, CH₂), 1.48-1.40 (m, 6 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 47.4, 27.1, 25.1 ppm.

HRMS (ESI): calc. for C₅H₁₂N [M+H]⁺: 86.0964; found: 86.0966.

5-(Phenylamino)pentan-1-ol (**3ah**)



3ah

The general procedure was applied using aniline (0.25 mmol) and pentane-1,5-diol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3ah** (35 mg, 81% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁴

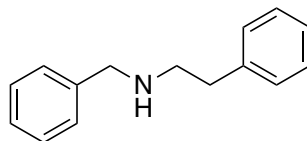
¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.20-7.18 (m, 2 H, *m*-Ar), 6.746-6.70 (m, 1 H, *p*-Ar), 6.64-6.62 (m, 2 H, *o*-Ar), 3.71-3.67 (m, 2 H, OHCH₂), 3.17-3.14 (m, 2 H, CH₂NH), 1.70-1.61 (m, 4 H, CH₂CH₂CH₂), 1.55-1.49 (m, 2 H, CH₂CH₂CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 188.4, 129.3, 117.2, 112.7, 62.8, 43.9, 32.5, 29.4, 23.4 ppm.

HRMS (ESI): calc. for C₁₁H₁₈NO [M+H]⁺: 180.1383; found: 180.1388.

2.4. *N*-Alkylation of aliphatic and secondary amines with benzyl alcohol

N-Benzyl-2-phenylethan-1-amine (**3ai**)



3ai

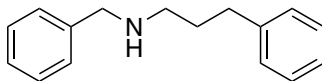
The general procedure was applied using 2-phenylethan-1-amine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3ai** (43 mg, 80% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁵

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.33-7.19 (m, 10 H, Ar), 3.81 (s, 2 H, PhCH₂), 2.94-2.90 (m, 2 H, NHCH₂), 2.86-2.82 (m, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.2, 140.0, 128.7, 128.5, 128.4, 128.1, 126.9, 126.2, 53.9, 50.5, 36.3 ppm.

HRMS (ESI): calc. for C₁₅H₁₈N [M+H]⁺: 212.1434; found: 212.1430.

***N*-Benzyl-3-phenylpropan-1-amine (3aj)**



3aj

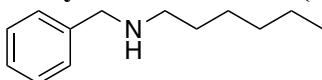
The general procedure was applied using 3-phenylpropan-1-amine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3aj** (33 mg, 57% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁶

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.33-7.16 (m, 10 H, Ar), 3.80 (s, 2 H, PhCH₂), 2.71-2.64 (m, 4 H, NHCH₂), 1.88-1.84 (m, 2 H, CH₂) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 142.0, 129.7, 128.8, 128.5, 128.3, 127.1, 126.2, 125.8, 53.8, 48.8, 33.6, 31.4 ppm.

HRMS (ESI): calc. for C₁₆H₂₀N [M+H]⁺: 226.1590; found: 226.1590.

***N*-Benzylhexan-1-amine (3ak)**



3ak

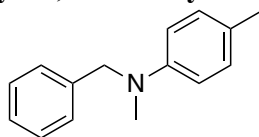
The general procedure was applied using hexylamine (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3ak** (25 mg, 90% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.34-7.25 (m, 5 H, *m*-Ar), 3.80 (m, 2 H, CH₂), 2.63 (t, *J* = 7.1 Hz, 2 H, CH₂), 1.54-1.48 (m, 2 H, CH₂), 1.34-1.25 (m, 6 H, CH₂) 0.90-0.86 (m, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.3, 128.4, 128.2, 126.9, 54.0, 49.4, 31.8, 30.0, 27.0, 22.6, 14.1 ppm.

HRMS (ESI): calc. for C₁₃H₂₂N [M+H]⁺: 192.1747; found: 192.1748.

***N*-Benzyl-*N*,4-dimethylaniline (3al)**



3al

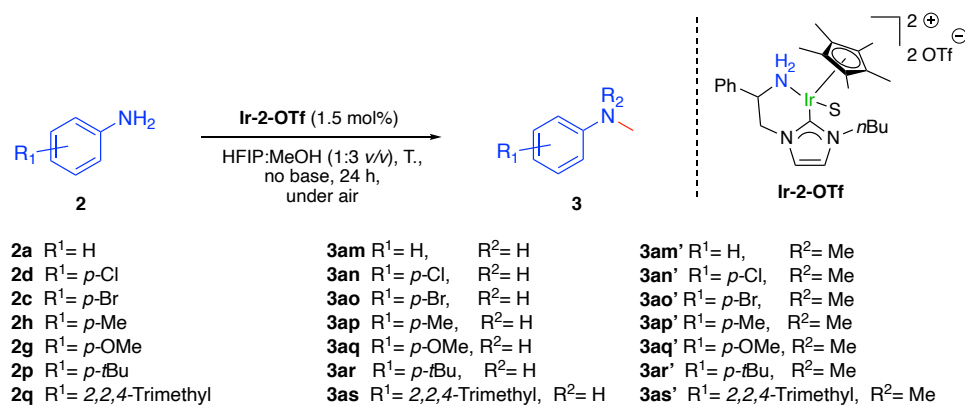
The general procedure was applied using *N*-4-dimethylaniline (0.25 mmol) and benzyl alcohol (0.25 mmol, 1 equiv.). The mixture was heated to 90 °C for 24 hours. Product **3al** (40 mg, 81% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁷

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.33-7.23 (m, 5 H, *m*-Bn), 7.05-7.02 (t, 2 H, *m*-Ar, *J* = 7.77 Hz), 6.70-6.68 (d, 2 H, *o*-Ar, *J* = 7.76 Hz), 4.49 (s, 2 H, PhCH₂), 2.97 (s, 3 H, NCH₃), 2.25 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.8, 139.3, 129.7, 128.5, 126.8, 126.8, 125.8, 112.7, 57.0, 38.6, 20.2 ppm.

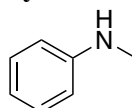
HRMS (ESI): calc. for C₁₅H₁₈N [M+H]⁺: 212.1434; found: 212.1432.

2.5. N-Methylation of anilines



Scheme S3. N-Alkylation of benzylamines with benzyl alcohols catalyzed by Ir-2-OTf.

N-Methylaniline (3am)



3am

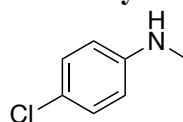
The general procedure was applied using aniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3am** (16 mg, 55% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.26-7.22 (m, 2 H, Ar), 6.81-6.76 (m, 1 H, Ar), 6.73-6.70 (m, 2 H, Ar), 2.88 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.8, 129.3, 117.9, 112.9, 30.9 ppm.

HRMS (ESI): calc. for C₇H₁₀N [M+H]⁺: 108.0808; found: 108.0810.

4-Chloro-N-Methylaniline (3an)



3an

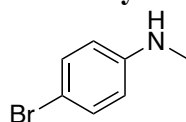
The general procedure was applied using 4-chloroaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **11ap** (26 mg, 71% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.17-7.13 (m, 2 H, Ar), 6.57-6.53 (m, 2 H, Ar), 2.84 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.9, 129.0, 121.8, 113.4, 30.8 ppm.

HRMS (ESI): calc. for C₇H₉ClN [M+H]⁺: 142.0418; found: 142.0420.

4-Bromo-*N*-Methylaniline (**3ao**)



3ao

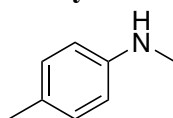
The general procedure was applied using 4-bromoaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3ao** (37 mg, 80% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.29-7.27 (m, 2 H, Ar), 6.52-6.50 (m, 2 H, Ar), 2.83 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.3, 131.9, 113.9, 108.8, 30.7 ppm.

HRMS (ESI): calc. for C₇H₉BrN [M+H]⁺: 185.9913; found: 185.9914.

N,4-Dimethylaniline (**3ap**)



3ap

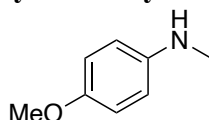
The general procedure was applied using 4-methylaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3ap** (24 mg, 78% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.06-7.03 (m, 2 H, Ar), 6.60-6.58 (m, 2 H, Ar), 2.85 (s, 3 H, CH₃), 2.29 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.2, 129.7, 126.5, 112.6, 31.1, 20.4 ppm.

HRMS (ESI): calc. for C₈H₁₂N [M+H]⁺: 122.0964; found: 122.0968.

4-Methoxy-*N*-methylaniline (**3aq**)



3aq

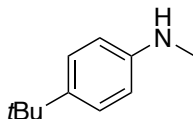
The general procedure was applied using 4-methoxyaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3aq** (23 mg, 70% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁸

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 6.85-6.81 (m, 2 H, Ar), 6.64-6.60 (m, 2 H, Ar), 3.78 (s, 3 H, CH₃), 2.83 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 152.1, 143.7, 114.9, 113.6, 55.9, 31.6 ppm.

HRMS (ESI): calc. for C₈H₁₂NO [M+H]⁺: 138.0913; found: 138.0910.

4-(*tert*-Butyl)-*N*-methylaniline (**3ar**)



3ar

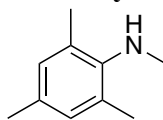
The general procedure was applied using 4-(*tert*-butyl)aniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3ar** (24 mg, 60% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.¹⁹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.27-7.23 (m, 2 H, Ar), 6.63-6.59 (m, 2 H, Ar), 2.85 (s, 3 H, CH₃), 1.31-1.30 (s, 9 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.0, 140.0, 125.9, 112.2, 33.8, 31.6, 31.0 ppm.

HRMS (ESI): calc. for C₁₁H₁₈N [M+H]⁺: 164.1434; found: 164.1428.

N-2,4,6-trimethylaniline (**3as**)



3as

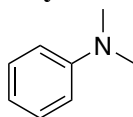
The general procedure was applied using *N*-2,4,6-trimethylaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 50 °C. Product **3as** (28 mg, 75% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²⁰

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 6.80 (s, 2 H, Ar), 2.24 (s, 3 H, CH₃), 2.20 (s, 3 H, CH₃), 2.19 (s, 6 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 140.2, 128.8, 127.1, 121.9, 30.9, 20.4, 17.6 ppm.

HRMS (ESI): calc. for C₁₀H₁₆N [M+H]⁺: 150.1277; found: 150.1282.

N,N-dimethylaniline (**3am'**)



3am'

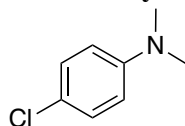
The general procedure was applied using aniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3am'** (28 mg, 68% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.32-7.28 (m, 2 H, Ar), 6.81-6.79 (m, 2 H, Ar), 6.78-6.76 (m, 1 H, Ar), 2.99 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 150.7, 129.1, 116.7, 112.7, 40.7 ppm.

HRMS (ESI): calc. for C₈H₁₂N [M+H]⁺: 122.0964; found: 122.0969.

4-Chloro-*N,N*-dimethylaniline (**3an'**)



3an'

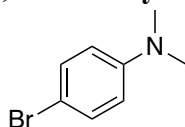
The general procedure was applied using 4-chloroaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3an'** (37 mg, 95% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.21-7.17 (m, 2 H, Ar), 6.68-6.64 (m, 2 H, Ar), 2.95 (s, 6 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 149.2, 128.8, 121.5, 113.7, 40.7 ppm.

HRMS (ESI): calc. for C₈H₁₁ClN [M+H]⁺: 156.0575; found: 156.0579.

4-Bromo-*N,N*-dimethylaniline (**3ao'**)



3ao'

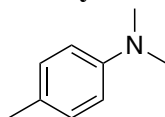
The general procedure was applied using 4-bromoaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3ao'** (47 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.34-7.30 (m, 2 H, Ar), 6.63-6.59 (m, 2 H, Ar), 2.95 (s, 6 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 149.5, 131.7, 114.1, 108.5, 40.6 ppm.

HRMS (ESI): calc. for C₈H₁₁BrN [M+H]⁺: 200.0069; found: 200.0075.

N,N,4-trimethylaniline (**3ap'**)



3ap'

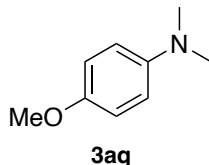
The general procedure was applied using 4-methylaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3ap'** (323 mg, 92% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²¹

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.10-7.07 (m, 2 H, Ar), 6.74-6.71 (m, 2 H, Ar), 2.93 (s, 6 H, CH₃), 2.29 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.9, 129.7, 129.6, 113.2, 41.1, 20.3 ppm.

HRMS (ESI): calc. for C₉H₁₄N [M+H]⁺: 136.1121; found: 136.1120.

4-Methoxy-*N,N*-dimethylaniline (**3aq**)



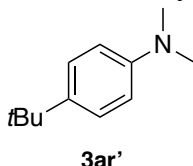
The general procedure was applied using 4-methoxyaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3aq** (36 mg, 95% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 6.89-6.85 (m, 2 H, Ar), 6.80-6.76 (m, 2 H, Ar), 3.79 (s, 3 H, CH₃), 2.89 (s, 6 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 152.1, 143.7, 114.9, 113.7, 55.9, 31.6 ppm.

HRMS (ESI): calc. for C₉H₁₄NO [M+H]⁺: 152.1070; found: 152.1079.

4-(*tert*-butyl)-*N,N*-dimethylaniline (**3ar**)



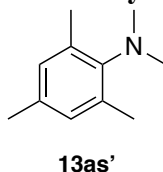
The general procedure was applied using 4-(*tert*-butyl)aniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3ar** (42 mg, 94% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²²

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.35-7.31 (m, 2 H, Ar), 6.80-6.76 (m, 2 H, Ar), 2.97 (s, 6 H, CH₃), 1.35 (s, 9 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 148.6, 139.4, 125.9, 112.7, 40.9, 33.8, 31.6 ppm.

HRMS (ESI): calc. for C₁₂H₂₀N [M+H]⁺: 178.1590; found: 178.1591.

N,N,2,4,6-pentamethylaniline (**3as**)



The general procedure was applied using 2,4,6-trimethylaniline (0.25 mmol) in a solvent mixture of HFIP/MeOH (1:3 v/v) at 90 °C. Product **3as** (36 mg, 88% yield) was purified by column chromatography using petroleum ether/EtOAc (95:5) as eluent. ¹H and ¹³C NMR spectroscopy data is in accordance with the one described in the literature.²³

¹H NMR (400 MHz, CDCl₃, 298 K): δ = 6.3 (s, 2 H, Ar), 2.82 (s, 6 H, CH₃), 2.28 (s, 6 H, CH₃), 2.26 (s, 3 H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 147.1, 137.0, 134.2, 129.4, 42.6, 20.7, 19.0 ppm.

HRMS (ESI): calc. for C₁₁H₁₈N [M+H]⁺: 164.1434; found: 164.1430.

3. Mechanistic elucidations

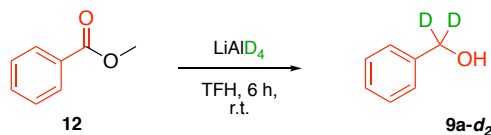
All reactions were carried out on pre-oven-dried glassware. Reagents were of analytical grade and used as purchased. ^1H NMR and ^{13}C NMR spectra were recorded at 125 MHz and 500 MHz, respectively, on a Bruker Avance spectrometer. The Chemical shifts reported are relative to the residual non-deuterated solvent peaks. All ^1H NMR spectra were quantitative: relaxation delay $T_1 = 5\text{ s}$. Quantitative ^{13}C NMR spectra were recorded with $T_1 = 10\text{ s}$ and no decoupling during acquisition.

All the mechanistic studies were carried out by performing independent reactions at room temperature. Each reaction consists of a vial impregnated with the active iridium species **Ir-2-OTf** (0.004 mmol) loaded with dry HFIP (250 μL), and the corresponding alcohol (0.25 mmol) and amine (0.25 mmol, 1 equiv.). These reactions were followed by ^1H NMR in the case of the deuterium-labelled studies (using an internal tube filled with D_2O) or stopped after a certain time in the case of the Hammett plot studies.

In the following kinetic plots (Figures S1, S2 and S4), product formation vs. time is plotted. The values were taken from the integrals corresponding to the product (benzylic protons) in time. No by-products were observed during the reaction in detectable amount (the total value of the integral of substrate at time 0 is equal to the sum of the integrals of product and substrate over time). Comparison of the integrals of the *ortho*- protons of the aniline and product were used to monitor the consumption of benzyl alcohol in the case of the kinetic isotope effect). In the Hammett studies, comparison of the integrals of the peaks corresponding to the benzylic protons of the amine product to those corresponding to the benzylic protons of the benzylic alcohol substrate allowed us to get the different rates.

3.1. Kinetic isotope effect investigations

Benzyl alcohol- α - d_2 (**1a-d₂**) was synthesized by reduction of methyl benzoate with lithium aluminum deuteride (Scheme 4.1).



Scheme S4. Synthesis of benzyl alcohol- α - d_2 (**1a-d₂**)

Parallel and independent reactions containing benzyl alcohol (**1a**) and benzyl alcohol- α - d_2 (**1a-d₂**), were carried out. To an NMR tube containing the active iridium species **Ir-2-OTf** (0.004 mmol) loaded with dry HFIP (200 μ L), the appropriate benzyl alcohol (0.25 mmol) and aniline (0.25 mmol) were added. An internal tube containing deuterated water (D_2O) was introduced in the reaction tube. The values used to plot formation of product over time were taken from comparison of the integrals of the peaks corresponding to the *ortho*- protons of aniline and product. A new acquisition was collected 180 seconds. The rates for each experiment with both benzyl alcohols (**1a**, **1a-d₂**) are given in Figure S1. The final measurement of the kinetic isotope effect for the *N*-alkylation of aniline with benzyl alcohol (**1a**) and benzyl alcohol- α - d_2 (**9a-d₂**) resulted in a KIE value of 1.9 ± 0.1 (Figure S4.1).

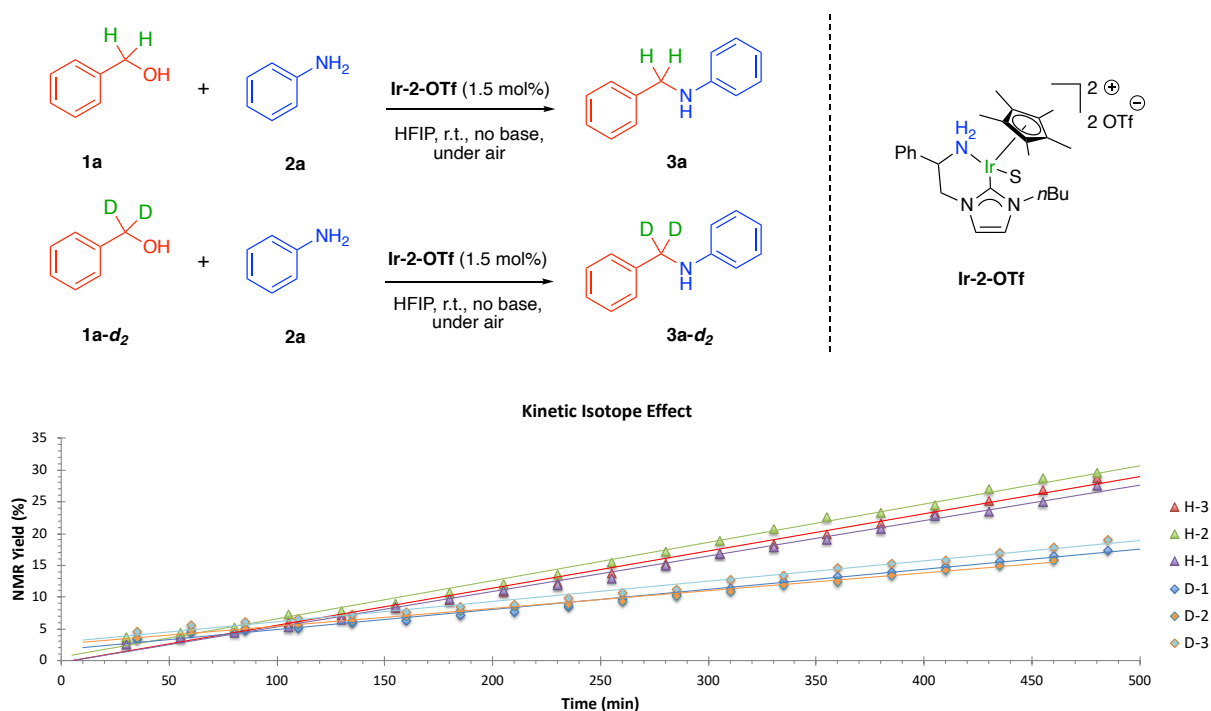
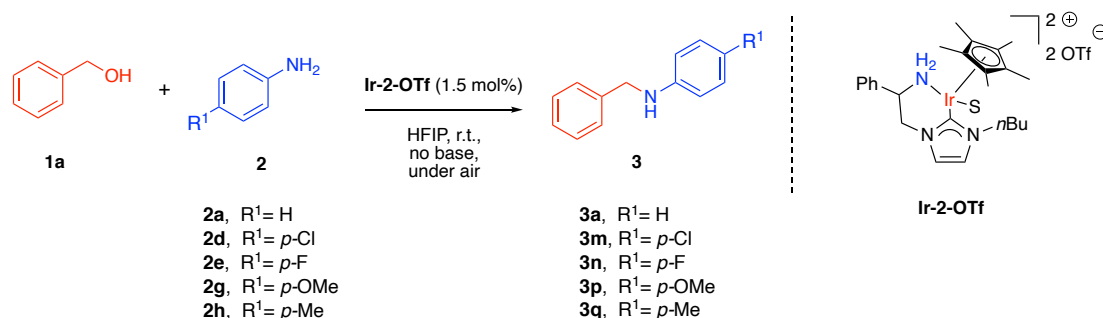


Figure S1. Initial rate plots showing formation of *N*-benzylaniline (**3a** or **3a-d₂**) over time for the reaction with benzyl alcohol (**1a**) or with deuterated benzyl alcohol (**1a-d₂**).

3.2. Hammett Studies

3.2.1 Hammett study of *para*-substituted anilines with benzyl alcohol



Scheme S6. Non-competition Hammett studies using benzyl alcohol **1a** and a series of anilines.

Parallel and independent reactions containing different substituted anilines (**2a**, **2d**, **2e**, **2g** and **2h**) were carried out. To a vial containing the active iridium species **Ir-2-OTf** (0.004 mmol) loaded with dry HFIP (250 μ L), the appropriate aniline (0.25 mmol) and benzyl alcohol (0.25 mmol) were added. The values used to plot formation of product over time are taken from comparing the integrals of the peaks corresponding to the benzylic protons of the amine product (**3**) to those corresponding to the benzylic protons of the substrate. Data was collected at 0, 60, 120 and 180 minutes. The rates for each experiment are given in Figure S2 and S3.

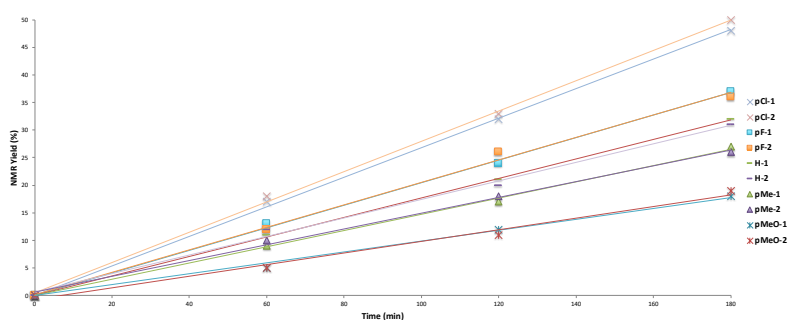


Figure S2. Initial rate plots using *para*-substituted anilines.

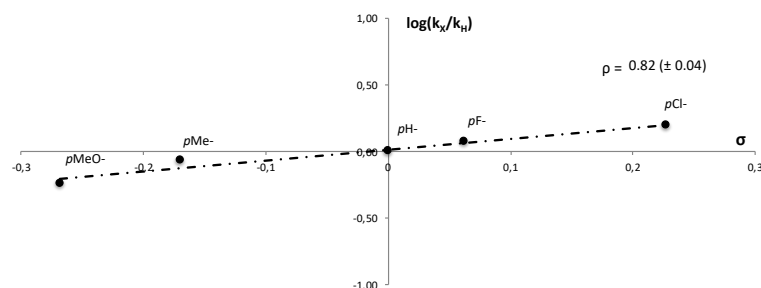
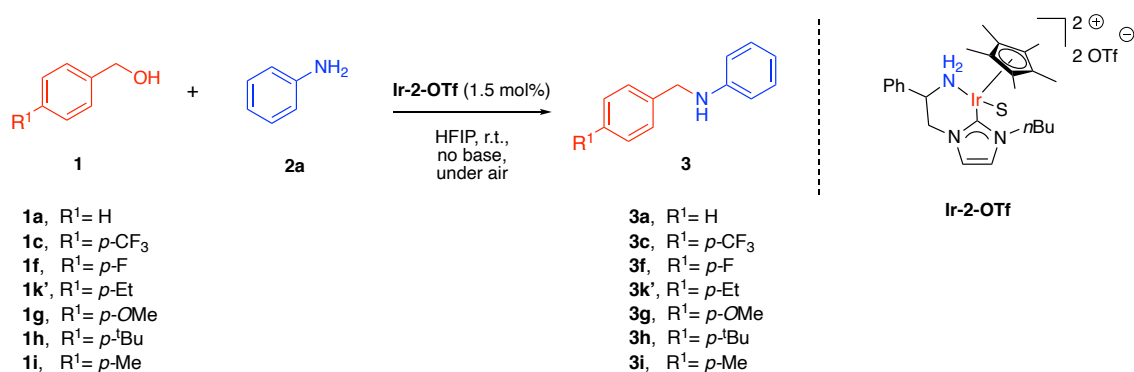


Figure S3. Hammett plot studies using *para*-substituted anilines.

3.2.2 Hammett study of *para*-substituted benzylic alcohols with aniline



Scheme S7. Non-competition Hammett studies using a series of benzylic alcohols and aniline **2a**.

Parallel and independent reactions containing different substituted benzylic alcohols were carried out. To a vial containing the active iridium species **Ir-2-OTf** (0.004 mmol) loaded with dry HFIP (250 μ L), the appropriate benzyl alcohol (0.25 mmol) and aniline (0.25 mmol) were added. The values used to plot formation of product over time are taken from comparing the integrals of the peaks corresponding to the benzylic protons of the amine product (**3**) to those corresponding to the benzylic protons of the substrate. Data was collected at 0, 30, 60 and 90 minutes. The rates for each experiment are shown in Figures S4 and S5.

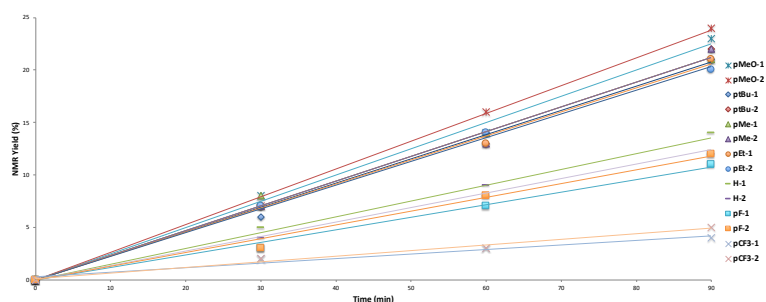


Figure S4. Initial rate plots using *para*-substituted benzylic alcohols.

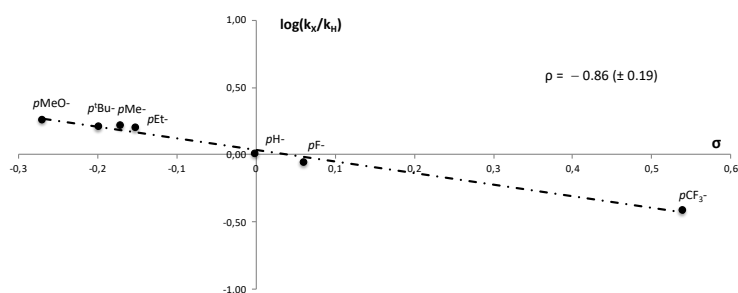


Figure S5. Hammett plot studies using *para*-substituted benzylic alcohols.

3.3 Reaction order studies

The study of the reaction orders of the different substrates and intermediates was conducted by following the reactions *via* ^1H NMR. Reactions were carried out in pre-oven-dried NMR tubes, equipped with an internal tube filled with deuterated water (D_2O).

3.3.1 The Variable Time Normalization Analysis (VTNA)

The Variable Time Normalization Analysis (VTNA) was applied in order to identify any possible catalyst poisoning or deactivation. We investigated how the reaction rate changes depending on the concentration of each species, and adjusted the corresponding parameter in the equation below described by Burés²⁴ to obtain the final reaction orders of each substrate, the catalyst and of the imine intermediate (eqn. (3.1)).

eqn. (3.1)

$$\Sigma [\text{A}]^\alpha [\text{B}]^\beta [\text{cat}]^\gamma \Delta t = \sum_{i=1}^n \left(\frac{[\text{A}]_i + [\text{A}]_{i-1}}{2} \right)^\alpha \left(\frac{[\text{B}]_i + [\text{B}]_{i-1}}{2} \right)^\beta [\text{cat}]^\gamma (t_i - t_{i-1})$$

This methodology consists of the independent study of each ingredient in the reaction. Concentration of one of the substrates or of the catalyst is changed while the others remain constant and the reaction is studied as it proceeds. The reaction order of that specific compound is then changed in a pre-treated excel sheet until the plot of product formation *vs* time converges for all different concentrations. The procedure is then repeated for all the other reagents, obtaining the correct reaction order and allowing us to identify the total order of the reaction.

3.3.2 Preparation of the stock solution of catalyst **Ir-2-OTf**

To an oven-dried vial containing iridium complex **Ir-2-Cl** (128 mg, 0.2 mmol) in 2 mL of dichloromethane, AgOTf (108 mg, 0.42 mmol, 1.2 equiv.) was added. The mixture is stirred for 15 minutes at room temperature and then filtered off through a pad of Celite® to remove the AgCl precipitate. The corresponding amount of this solution was then transferred to NMR tubes and the solvent was evaporated under vacuum. NMR tubes could then be stored in the freezer for several weeks. This procedure was repeated for every mechanistic study to ensure the same catalytic activity for each batch.

In the following plots, it is shown the increasing of the product concentration *vs.* time. Since no side products are observed, it is assumed that the sum of the integral of the product plus the integral of the substrate is equal to the integral of substrate at time 0. The concentration of the product was calculated comparison of the integration of the peaks corresponding to the *ortho*-protons of the aniline substrate **2a** and those corresponding to the amine product.

3.3.3 Reaction order studies with respect to benzyl alcohol substrate (**1a**)

A solution of aniline **2a** (0.15 mmol) and the corresponding amount of benzyl alcohol **1a** (0.65-0.25 mmol) in HFIP (250 μ L), was added to an NMR tube containing complex **Ir-2-OTf** (0.003 mmol). An internal tube containing D₂O is introduced in the NMR tube. The mixture was then placed in the NMR spectrometer and ¹H NMR acquisition was taken every 5 minutes.

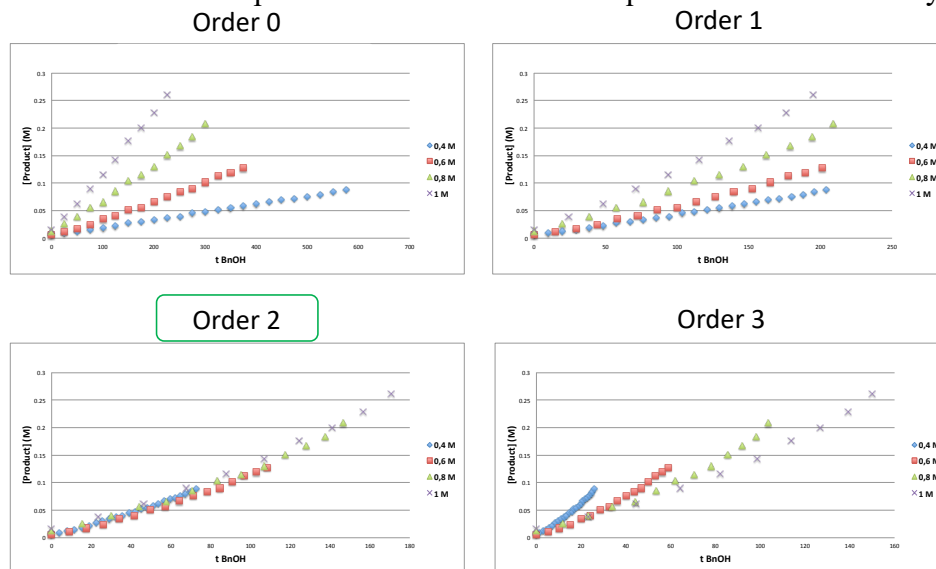


Figure S6. Determination of the reaction order of benzyl alcohol **1a**.

3.3.4 Reaction order studies with respect to aniline substrate (**2a**)

A solution of benzyl alcohol **1a** (0.15 mmol) and the corresponding amount of aniline **2a** (0.65-0.2 mmol) in HFIP (250 μ L), was added to an NMR tube containing complex **Ir-2-OTf** (0.003 mmol). An internal tube containing D₂O is introduced in the NMR tube. The mixture was then placed in the NMR spectrometer and ¹H NMR acquisition was taken every 5 minutes.

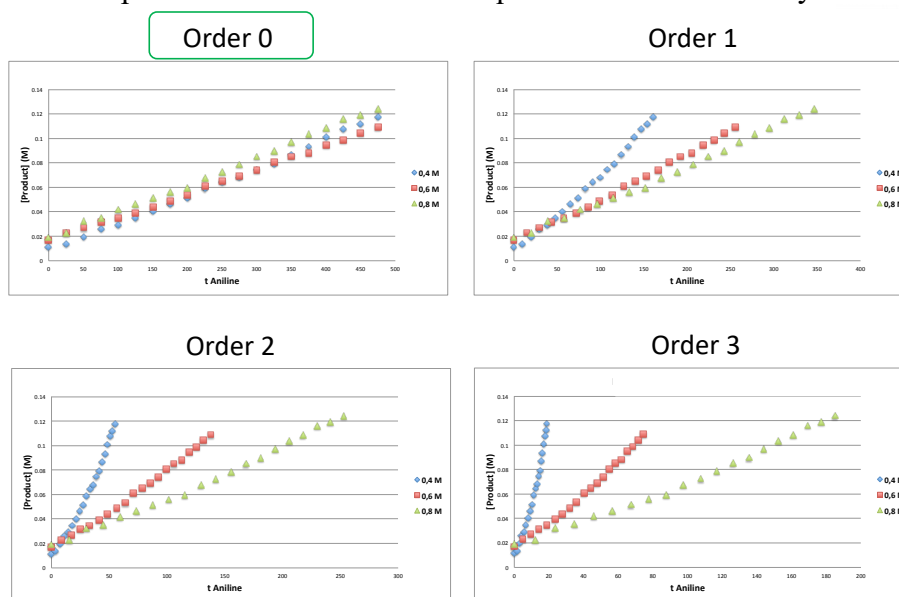


Figure S7. Determination of the reaction order of aniline **2a**.

3.3.5 Reaction order studies with respect to imine intermediate (**4a**)

A solution of benzyl alcohol **1a** (0.15 mmol), aniline **2a** (0.15 mmol) and imine **4a** (0.65-0.4 mmol) in HFIP (250 μ L), was added to and NMR tube containing complex **Ir-2-OTf** (0.003 mmol). An internal tube containing D₂O is introduced in the NMR tube. The mixture was then placed in the NMR spectrometer and ¹H NMR acquisition was taken every 5 minutes.

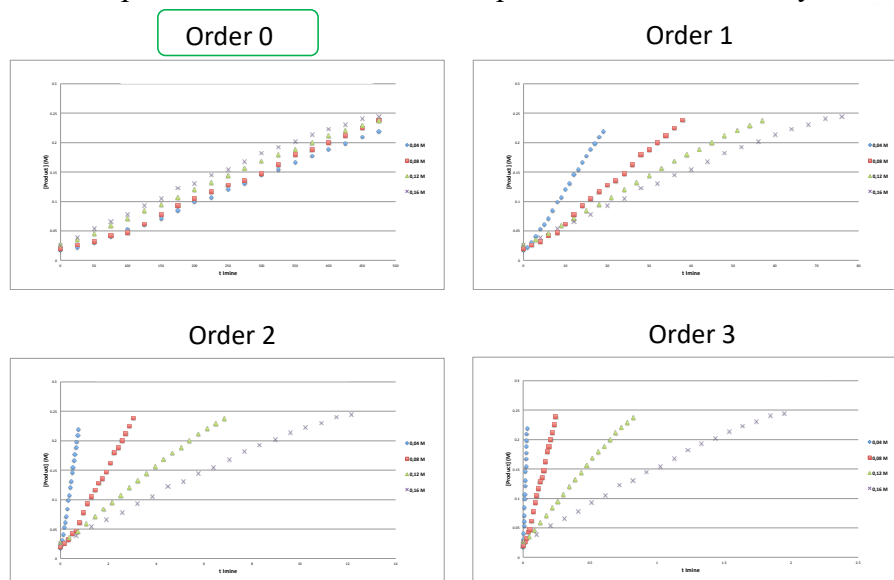


Figure S8. Determination of the reaction order of imine intermediate **4a**.

3.3.6 Reaction order studies with respect to Ir(III) catalyst (**Ir-2-OTf**)

A solution of benzyl alcohol **1a** (0.15 mmol) and aniline **2a** (0.15 mmol) in HFIP (250 μ L), was added to and NMR tube containing iridium complex **8** (0.0015-0.0125 mmol). An internal tube containing D₂O is introduced in the NMR tube. The mixture was then placed in the NMR spectrometer and ¹H NMR acquisition was taken every 5 minutes.

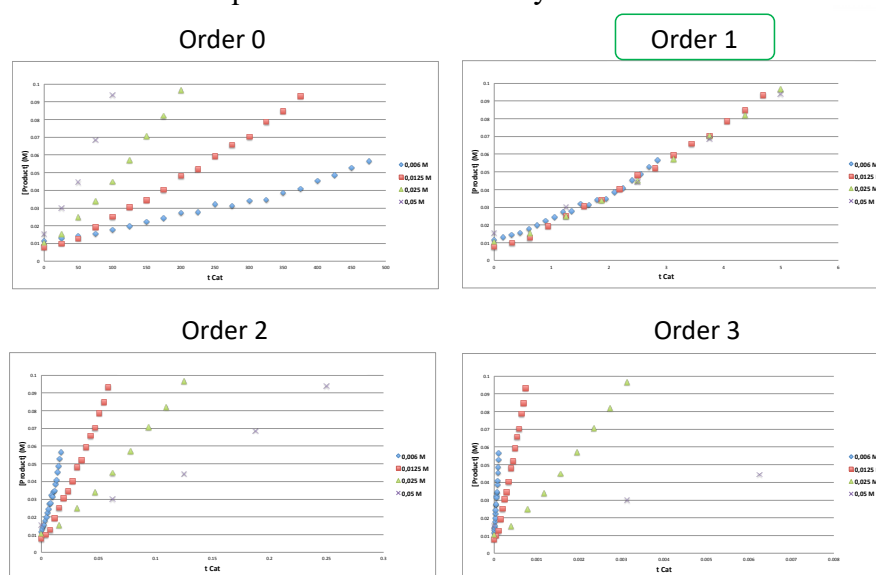
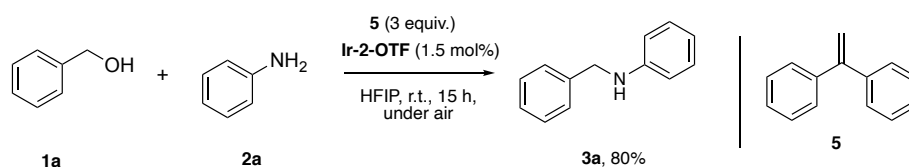


Figure S9. Determination of the reaction order of iridium(III) catalyst **Ir-2-OTf**.

3.4. Radical trapping experiments

Iridium pre-catalyst **Ir-2-Cl** (2.4 mg, 0.004 mmol, 1 equiv.) and silver salt **AgOTf** (2.0 mg, 0.008 mmol, 2.1 equiv.) were suspended in anhydrous dichloromethane (1 mL), in a vial covered in aluminum foil. The reaction mixture was stirred at room temperature for 15 minutes. The mixture was filtered off through a pad of Celite® to remove the AgCl precipitated, and transferred to an oven dried pressure tube. The solvent was evaporated under vacuum and the active catalyst species used in-situ.

The pressure tube impregnated with the active iridium species **Ir-2-OTf** (0.004 mmol, 1.5 mol%) was loaded with dry HFIP (125 μ L), and benzyl alcohol (**1a**) (0.25 mmol, 1 equiv.) aniline (**2a**) (0.25 mmol, 1 equiv.) and 1,1-diphenylethylene (**5**) (0.75 mmol, 3 equiv.) were added. The mixture was stirred under the reaction conditions specified, and under air atmosphere (Scheme S8). After the reaction was complete, the yield of product **3a** was quantified by ^1H NMR spectroscopy using 1,2,4,5-tetrachloro-3-nitrobenzene as internal standard.



Scheme S8. Radical trapping experiment using 1,1-diphenylethylene as radical scavenger.

3.5 Computational mechanistic study

3.5.1 Energies of starting complexes

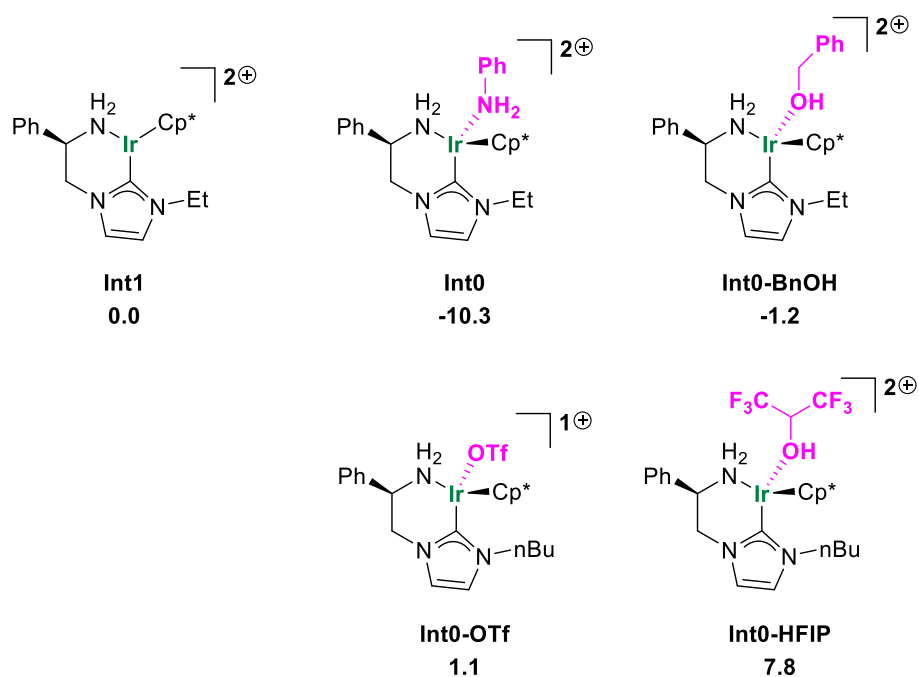


Figure S10. Relative energies (kcal/mol) of various complexes that can form between **Int1** and other species present in the reaction mixture.

3.5.2 Transition state of alcohol oxidation without a proton shuttle

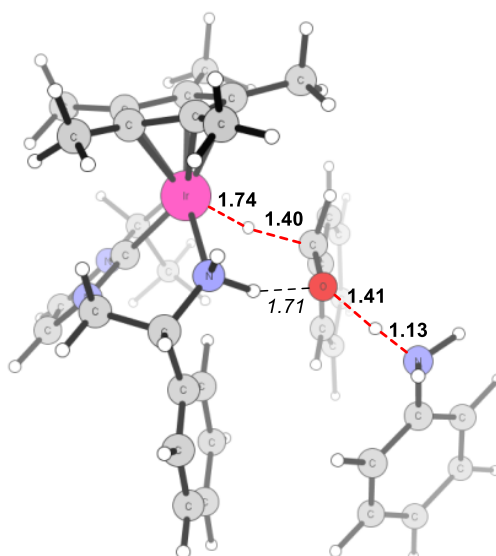


Figure S11. Optimized geometry of the alcohol oxidation TS without the involvement of an alcohol molecule as a proton shuttle.

3.5.3 Complexation of anilinium ion

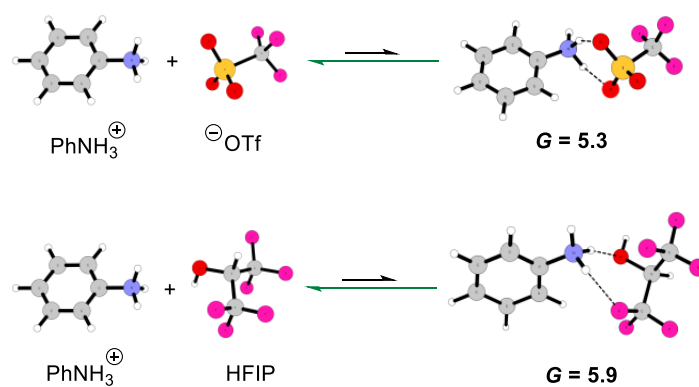


Figure S12. Calculated energies (kcal/mol) of the complexation of anilinium ion with either the OTf^- counterion or the HFIP solvent.

3.5.4 Inner-sphere mechanism for the alcohol oxidation

We have investigated the possibility of the alcohol oxidation to take place with an inner-sphere mechanism. This pathway involves a direct coordination of the alcohol substrate to the iridium metal center after decooordination of a molecule of aniline (**Int0-BnOH**). The calculated thermodynamics of all intermediates found resulted to be high in energy.

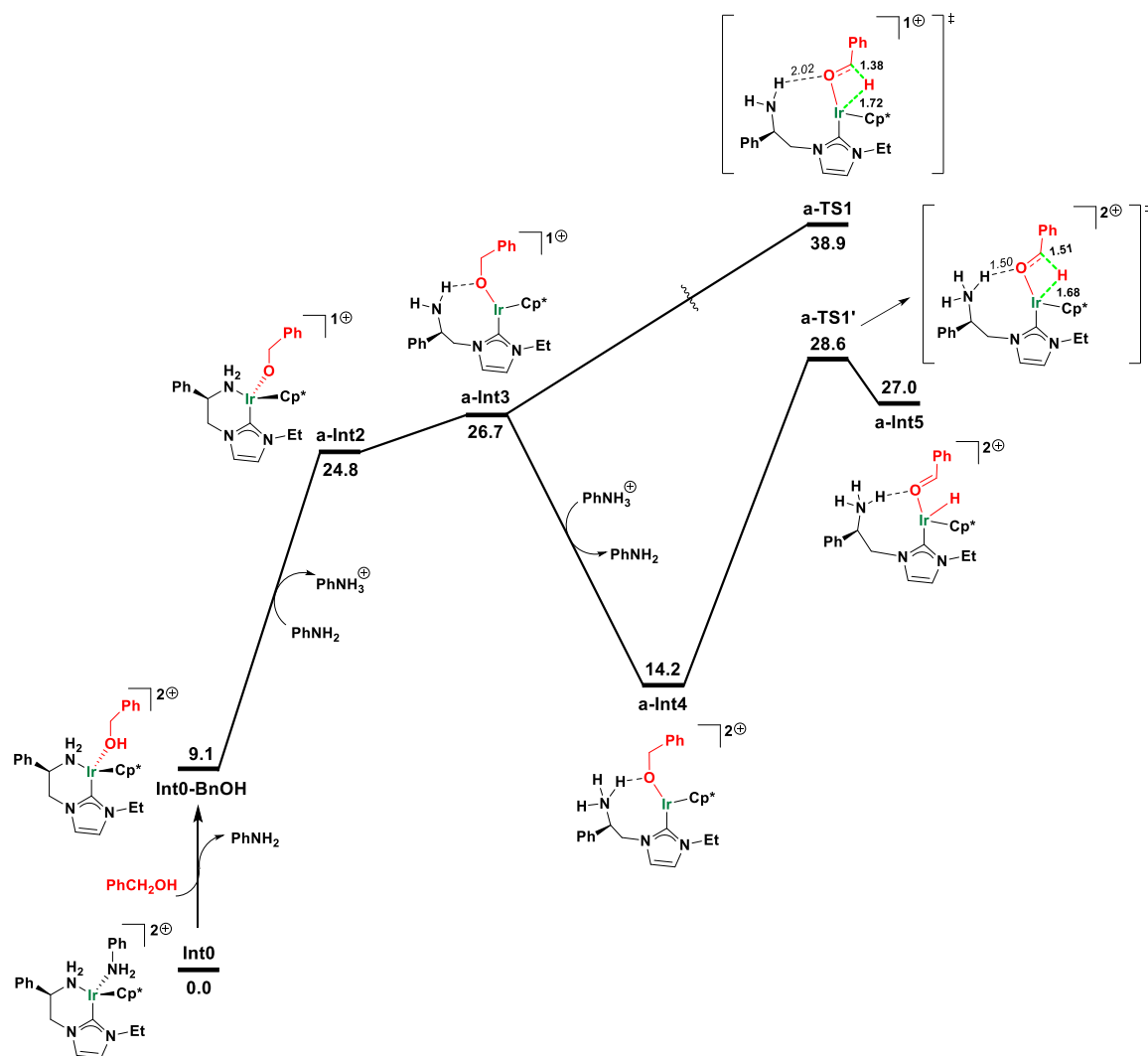


Figure S13. Calculated energy profile (kcal/mol) for the oxidation of the alcohol *via* an inner-sphere mechanism.

3.5.5 Mechanism of alcohol oxidation involving deprotonation of the amino group of the ligand

We have investigated the possibility of the alcohol oxidation taking place prior deprotonation of the amino group in the wingtip. In this deprotonation a molecule of aniline acts as base, forming **b-Int2**. From this intermediate, the thermodynamics of the resulting corresponding intermediates *via* inner- and outer-sphere pathway presented higher energy than the complexes proposed in the main mechanism.

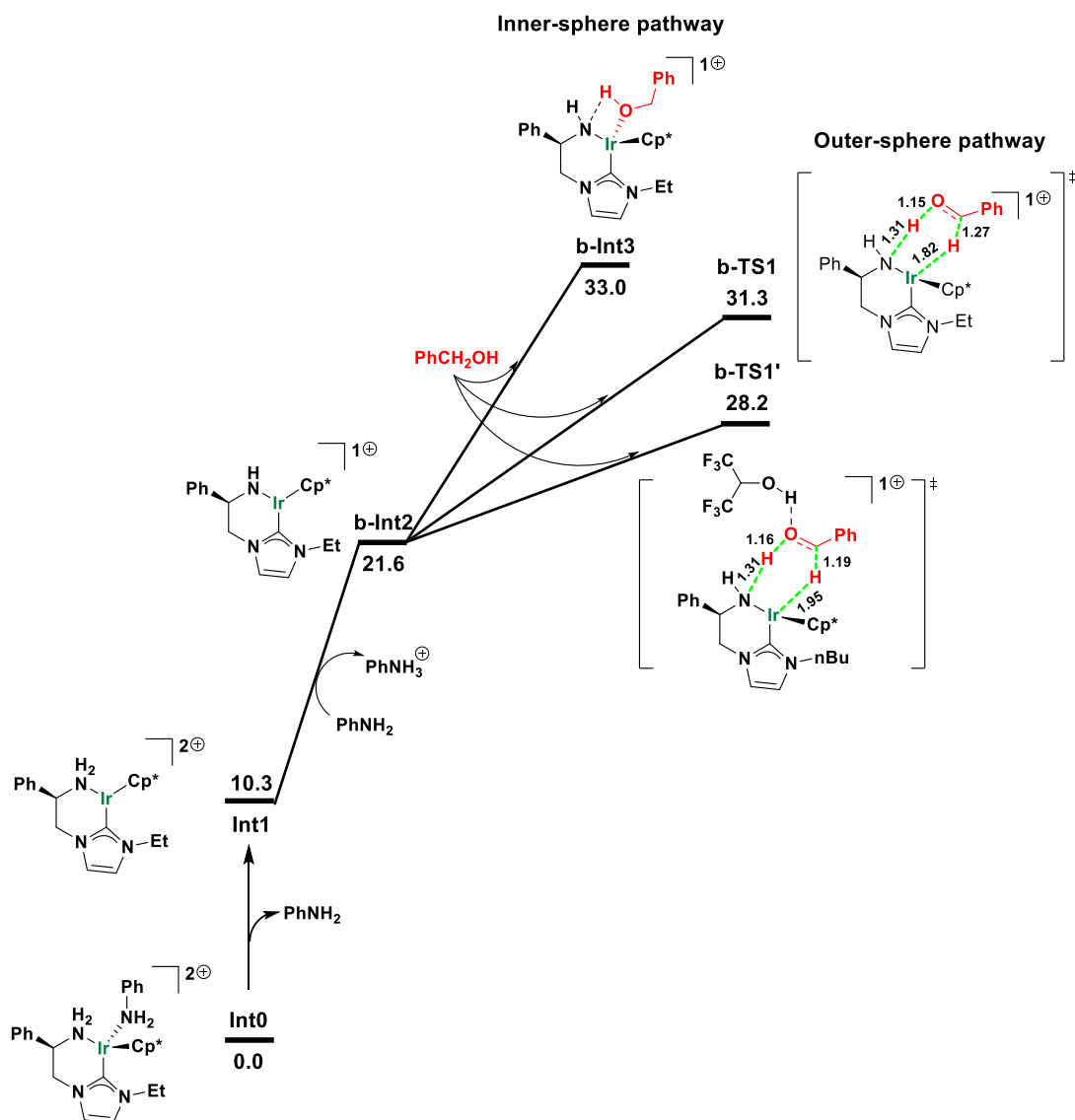


Figure S14. Oxidation of the alcohol after the deprotonation of the amino group in the wingtip of **Int1**.

3.5.6 HFIP-assisted iminium formation

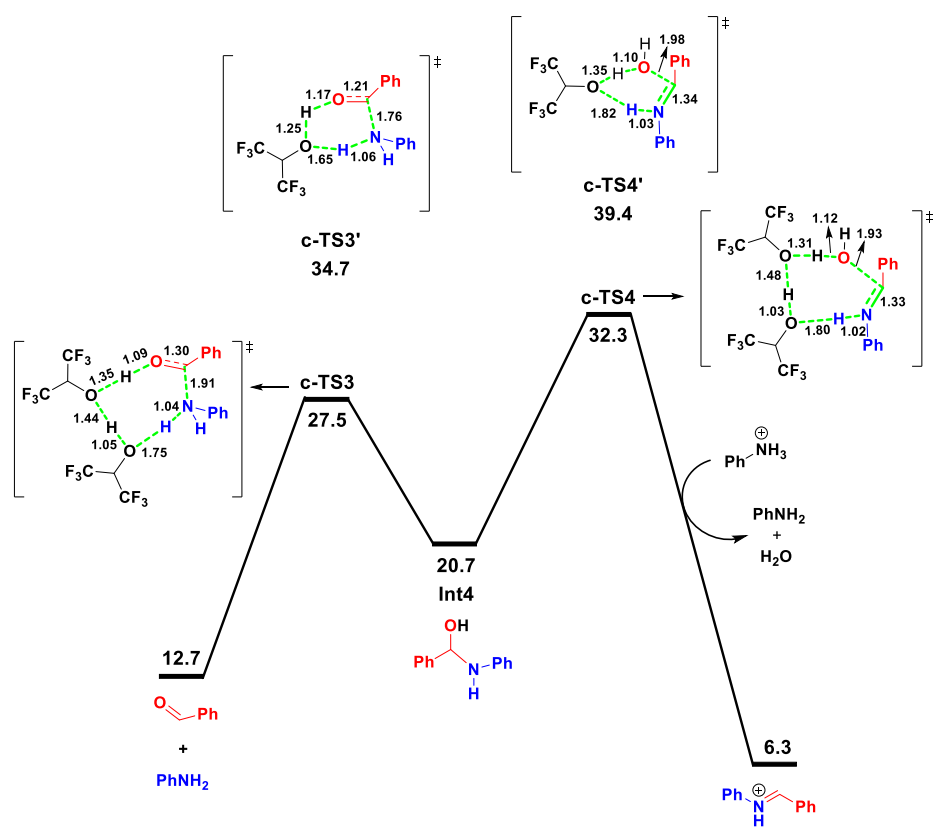


Figure S15. Calculated energy profile (kcal/mol) of the HFIP-assisted iminium formation pathway.

3.6 Extended X-ray absorption fine structure (EXAFS)

The pre-catalyst complex **Ir-2-Cl**, as well as the active species **Ir-2-OTf** were modelled. The EXAFS distances between atoms were compared and supported by the existing crystallographic data available.²⁵ The 1,2,3,4,5-pentamethylcyclopentadienyl ligand was modelled fixing the carbon atoms to an average interatomic distance to the iridium metal center according to the single crystal X-ray structure (Figure S16).

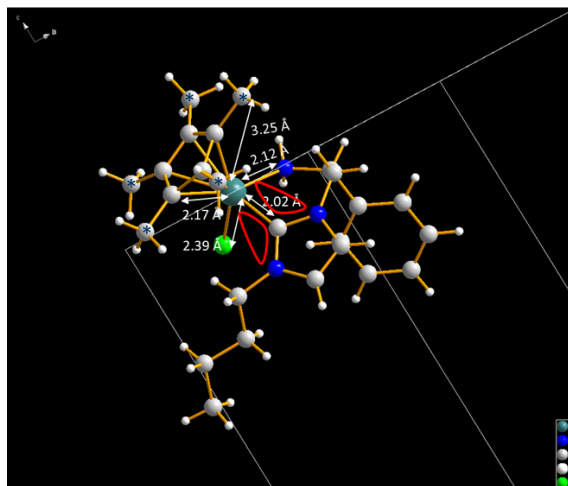


Figure S16. Single crystal structure of the inactive catalyst species **Ir-2-Cl**.

The lmfit module for Non-Linear Least-Squares Minimization and Curve-Fitting in Python3.0 was used to quantify the transitions in the XANES region.²⁶ Prior to data fitting, the raw EXAFS data were normalized using the algorithm available in EXAFSPAK. A composite model consisting of step and peak-fitting functions were minimized simultaneously.

The edge jump to continuum was modelled using a step function in the lmfit module in python. The various functions investigated from the built-in functions are listed below:

$$\begin{aligned} f(x; A, \mu, \sigma, \text{form}=\text{'linear'}) &= A_{\min}[1, \max(0, \alpha)] \\ f(x; A, \mu, \sigma, \text{form}=\text{'arctan'}) &= A[1/2 + \arctan(\alpha)/\pi] \\ f(x; A, \mu, \sigma, \text{form}=\text{'erf'}) &= A[1 + \text{erf}(\alpha)]/2 \end{aligned}$$

Where $\alpha = (x - \mu)/\sigma$

Amplitude (A), Center (μ) and Sigma (σ)

The best statistics were obtained using the arctangent function.

The transition to empty d-orbital were quantified using the peak fitting module from the lmfit library. The Lorentzian, Gaussian and PsuedoVoigt models were evaluated. Among them, the best statistics were obtained using the PsuedoVoigt model.

$$f(x; A, \mu, \sigma, \alpha) = \frac{(1-\alpha)}{\sigma_g \sqrt{2\pi}} e^{[-(x-\mu)^2/2\sigma_g^2]} + \frac{\alpha A}{\pi} \left[\frac{\sigma}{(x-\mu^2) + \sigma^2} \right]$$

Where $\sigma_g = \sigma/\sqrt{2\ln 2}$, the full width at half maximum of each component and of the sum is 2σ .

The best fit to XANES features were obtained using a composite model comprising of arctangent and PsuedoVoigt models.

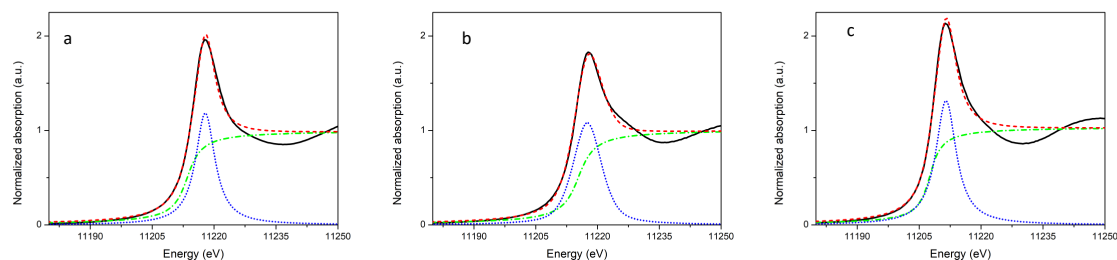


Figure S17. XANES fits to the white line using a Lorentzian and a step function of (a) reference $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3\text{SO}_4]$, (b) pre-catalyst **Ir-2-Cl** and (c) active catalyst **Ir-2-OTf**. (—) experimental data, (·····) fit, (---) arc-tangent function, (·····) PsuedoVoigt function.

Table S1. Summary of the arc tangent fit parameters in all samples.

	Lorentzian				Arctangent	
	Position (eV)	FWHM (eV)	Height	Area (FWHM x Height)	Position (eV)	FWHM (eV)
$[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3\text{SO}_4]$	11217.4	6.16	1.201	7.39	11213.2	2.49
Ir-2-Cl	11217.8	6.70	0.901	6.03	11213.1	2.53
Ir-2-OTf	11217.8	5.51	1.451	7.98	11212.9	2.41

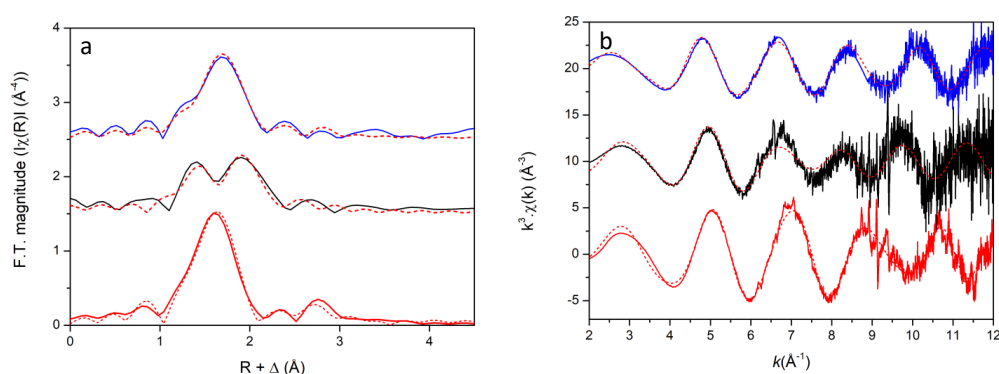


Figure S18. (a) FT spectra and (b) k^3 -weighted EXAFS data of the reference $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3\text{SO}_4]$, pre-catalyst **Ir-2-Cl** and active catalyst **Ir-2-OTf**. (—) $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3\text{SO}_4]$; (—) **Ir-2-Cl**; (—) **Ir-2-OTf**. The FT patterns are not phase corrected

Table S2. The structural model parameters at Ir-L_{III} edge. The error on co-ordination number and Debye-Waller factor are 25%. The parentheses values are standard deviations obtained from k^3 -weighted least-squares refinements of the EXAFS function $\chi(k)$ and do not include systematic errors of the measurement. The underscore values were optimized and fixed in each refinement. The multiple scattering paths indicated in * were refined with respect to Ir-C.

a) Ir-Cp*(SO ₄) S ₀ ² = 1 ΔE ₀ = -10.1 eV			
Scattering path	N	Radial distance (Å)	σ ² (Å ²)
Ir-Cp	5	2.132 (3)	0.0069 (4)
Ir-O	3	2.071 (6)	0.0051 (7)
Ir-CH ₃ (Cp*)	5	3.141 (9)	0.0068 (8)
b) Activated catalyst (AgOtf) S ₀ ² = 1 ΔE ₀ = -12.71 eV			
Scattering path	N	Radial distance (Å)	σ ² (Å ²)
Ir-Cp	5	2.187 (6)	0.00987 (6)
Ir-N	2	1.921 (9)	0.00630 (5)
Ir-C	1	2.101 (4)	0.00232 (2)
Ir-N-C*	4	3.168 (2)	0.00030 (6)
Ir-CH ₃ (Cp*)	5	3.389 (1)	0.01265 (5)
c) Inactivated catalyst S ₀ ² = 1 ΔE ₀ = -11.71 eV			
Scattering path	N	Radial distance (Å)	σ ² (Å ²)
Ir-Cp	5	2.207 (4)	0.00987 (4)
Ir-N	1	2.221 (3)	0.00630 (5)
Ir-C	1	2.035 (6)	0.00232 (7)
Ir-N-C*	4	3.198 (8)	0.00030 (8)
Ir-CH ₃ (Cp*)	5	3.396 (9)	0.00726 (9)
Ir-Cl	1	2.349 (2)	0.00365 (7)

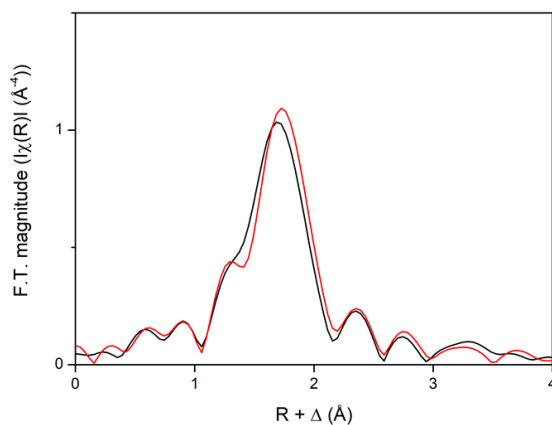


Figure S19. The phase uncorrected FT spectra of **Ir-2-OTf** in presence of aniline **2a** (red), and in absence of aniline **2a** (black). The FT patterns are not phase corrected.

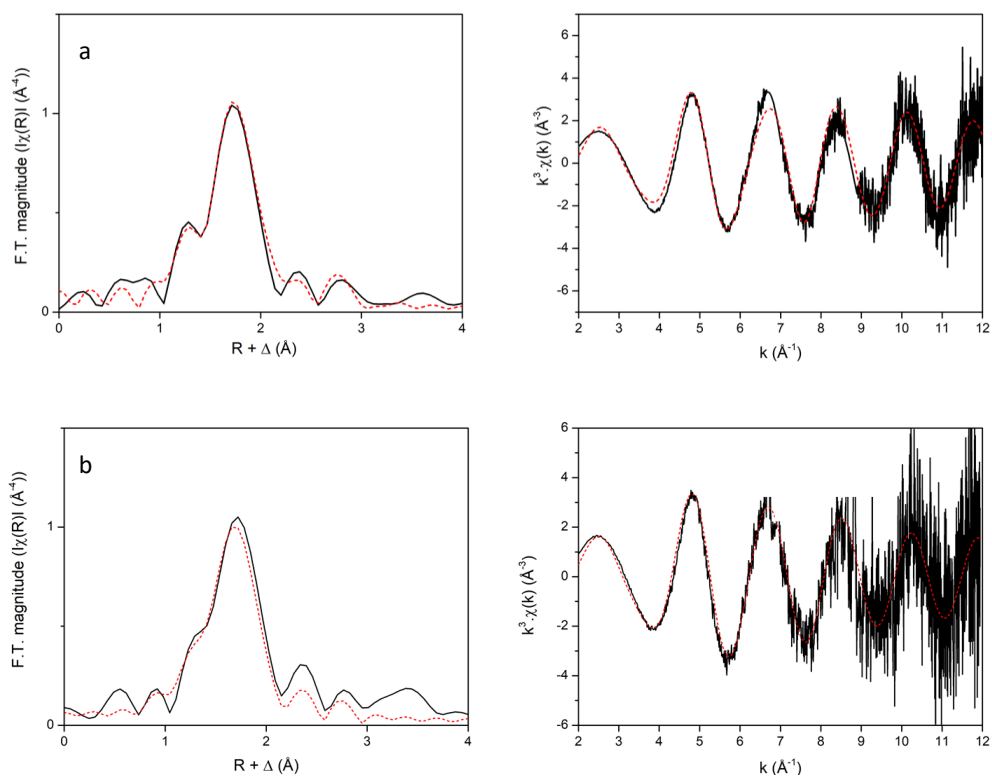


Figure S20. Top: *ex-situ* data and respective fits of control experiment of **Ir-2-OTf** in presence of aniline **2a**. FT spectra (left) and k^3 -weighted EXAFS data (right). Bottom: *ex-situ* data and respective fits of control experiment of **Ir-2-OTf** in absence of aniline **2a**. FT spectra (left) and k^3 -weighted EXAFS data (right). (—) experimental data; (.....) fit. The FT patterns are not phase corrected.

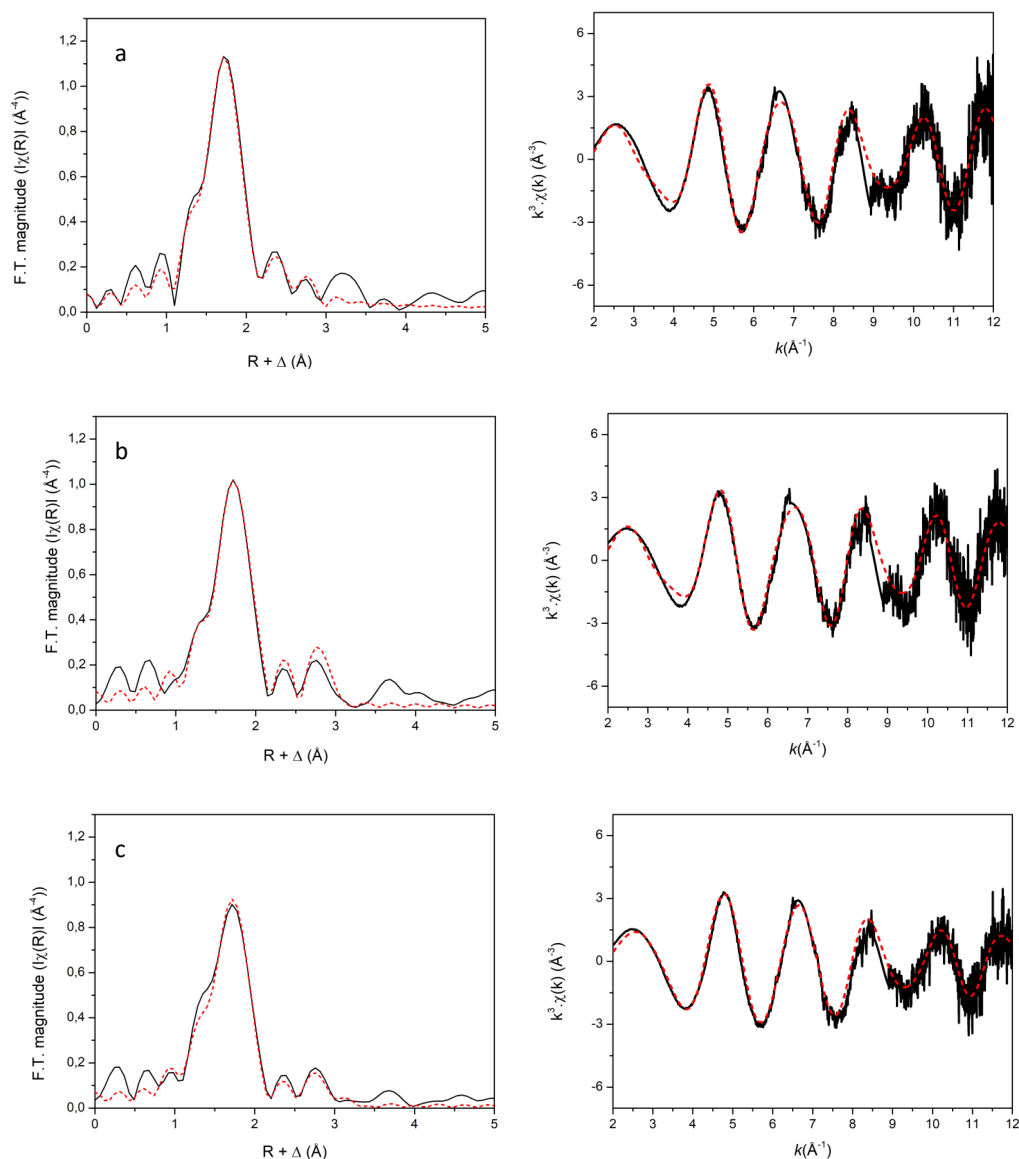


Figure S21. *Ex-situ* measurements. *N*-Alkylation of aniline **2a** with benzyl alcohol **1a** catalyzed by Ir-2-OTf. The phase uncorrected FT spectra and k^3 -weighted EXAFS data after (a) 5 hours, (b) 7 hours and (c) 10 hours reaction time.

(—) experimental data; (.....) fit, The FT patterns are not phase corrected

Time (min)	<u>N1</u> (Ir-Cp*)	<u>R1</u>	<u>σ_1^2</u>	<u>N2</u> (Ir-N)	<u>R2</u>	<u>σ_2^2</u>	<u>N3</u> (Ir-C)	<u>R3</u>	<u>σ_3^2</u>	<u>N4</u> (Ir-C-N)	<u>R4</u>	<u>σ_4^2</u>	<u>N5</u> (Ir-CH3)	<u>R5</u>	<u>σ_5^2</u>	<u>Eo</u>
4.8	5	2.204	0.0057	2.043	1.93	0.0017	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.7
9.6	5	2.204	0.0057	1.913	1.93	0.0015	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.1
14.4	5	2.204	0.0057	2.124	1.926	0.0024	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.03
19.2	5	2.204	0.0057	1.82	1.955	0.0027	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.82
33.6	5	2.204	0.0057	1.911	1.937	0.0018	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.47
43.2	5	2.204	0.0057	2.327	1.917	0.0024	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.32
48	5	2.204	0.0057	2.023	1.931	0.0021	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.22
62.4	5	2.204	0.0057	1.858	1.936	0.00072	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.83
67.2	5	2.204	0.0057	1.774	1.932	0.0007	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.42
72	5	2.204	0.0057	1.951	1.935	0.0023	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.52
76.8	5	2.204	0.0057	1.77	1.952	0.0025	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.64
81.6	5	2.204	0.0057	1.924	1.934	0.0025	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.91
86.4	5	2.204	0.0057	1.74	1.932	0.0012	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.50
96	5	2.204	0.0057	1.89	1.931	0.0033	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.79
100.8	5	2.204	0.0057	1.754	1.942	0.00091	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.20
105.6	5	2.204	0.0057	1.976	1.942	0.00083	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.97
110.4	5	2.204	0.0057	1.732	1.931	0.00053	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.85
115.2	5	2.204	0.0057	1.789	1.942	0.00085	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.24
120	5	2.204	0.0057	1.817	1.947	0.0021	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.75
129.6	5	2.204	0.0057	1.857	1.926	0.0022	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.19
139.2	5	2.204	0.0057	1.975	1.935	0.0049	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.17
148.8	5	2.204	0.0057	1.761	1.973	0.0058	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-11.82
158.4	5	2.204	0.0057	1.771	1.945	0.0005	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.69
168	5	2.204	0.0057	1.857	1.95	0.0054	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.20
172.8	5	2.204	0.0057	1.975	1.94	0.0055	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.58
177.6	5	2.204	0.0057	1.857	1.936	0.0006	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.54
182.4	5	2.204	0.0057	1.975	1.958	0.0084	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.62
187.2	5	2.204	0.0057	1.975	1.917	0.0079	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-15.33
192	5	2.204	0.0057	1.857	1.956	0.0064	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.91
196.8	5	2.204	0.0057	1.698	1.96	0.0057	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.91
201.6	5	2.204	0.0057	1.857	1.941	0.0041	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-13.2
206.4	5	2.204	0.0057	1.975	1.959	0.0082	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.12
211.2	5	2.204	0.0057	1.975	1.96	0.0021	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.88
240	5	2.204	0.0057	1.857	1.977	0.0024	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.93
249.6	5	2.204	0.0057	1.881	1.923	0.0065	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-14.46
254.4	5	2.204	0.0057	1.975	1.969	0.0122	1	2.108	0.0078	4	5	3.152	5	3.473	0.0109	-12.71

Table S3. Summary of refined and optimized parameters during the *in-situ* reaction from selected measurements. The underscore parameters were optimized during each individual refinement. The Ir–N single scattering parameters were varied in final refinement step. The Ir–C–N were optimized simultaneously with Ir–C single scattering path. *N* = mean number of neighbour distances, *R* = mean distances, *SS* = Debye Waller factor.

4. NMR Spectra of all compounds

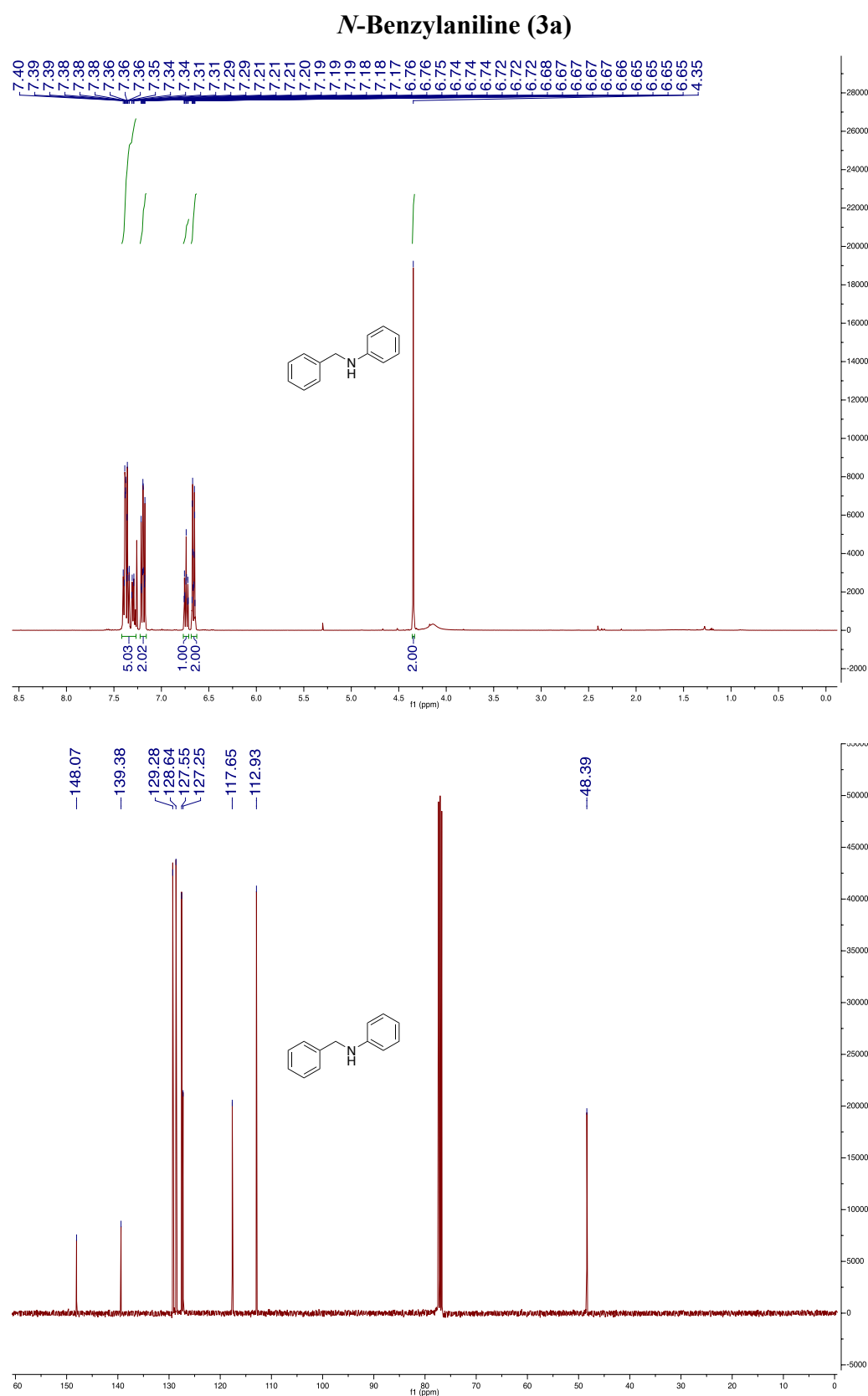


Figure S4.1. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3a** in CDCl_3 .

4-((Phenylamino)methyl)benzonitrile (**3b**)

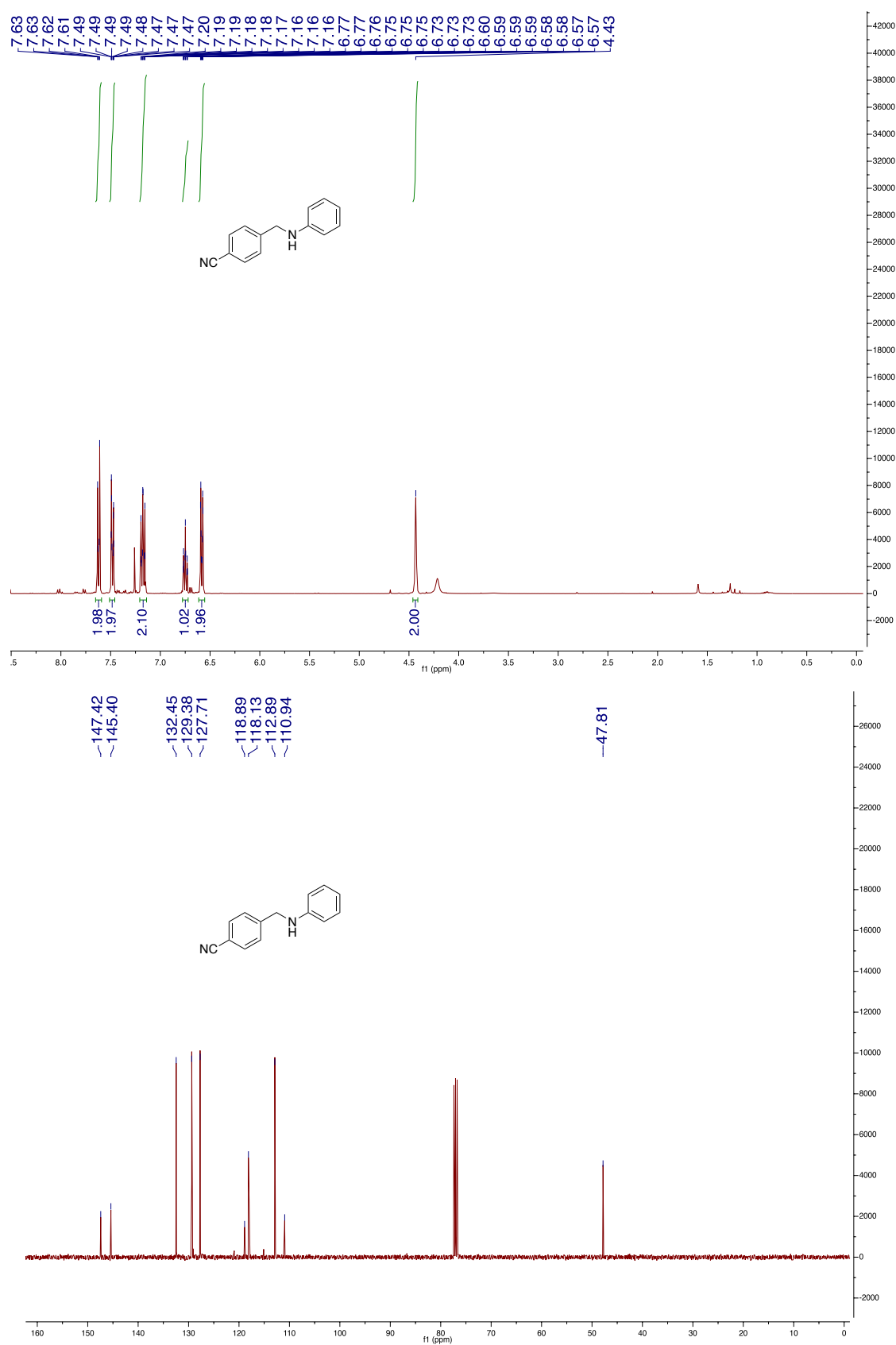


Figure S4.2. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3b** in CDCl₃.

***N*-(*p*-Trifluoromethylbenzyl)aniline (3c)**

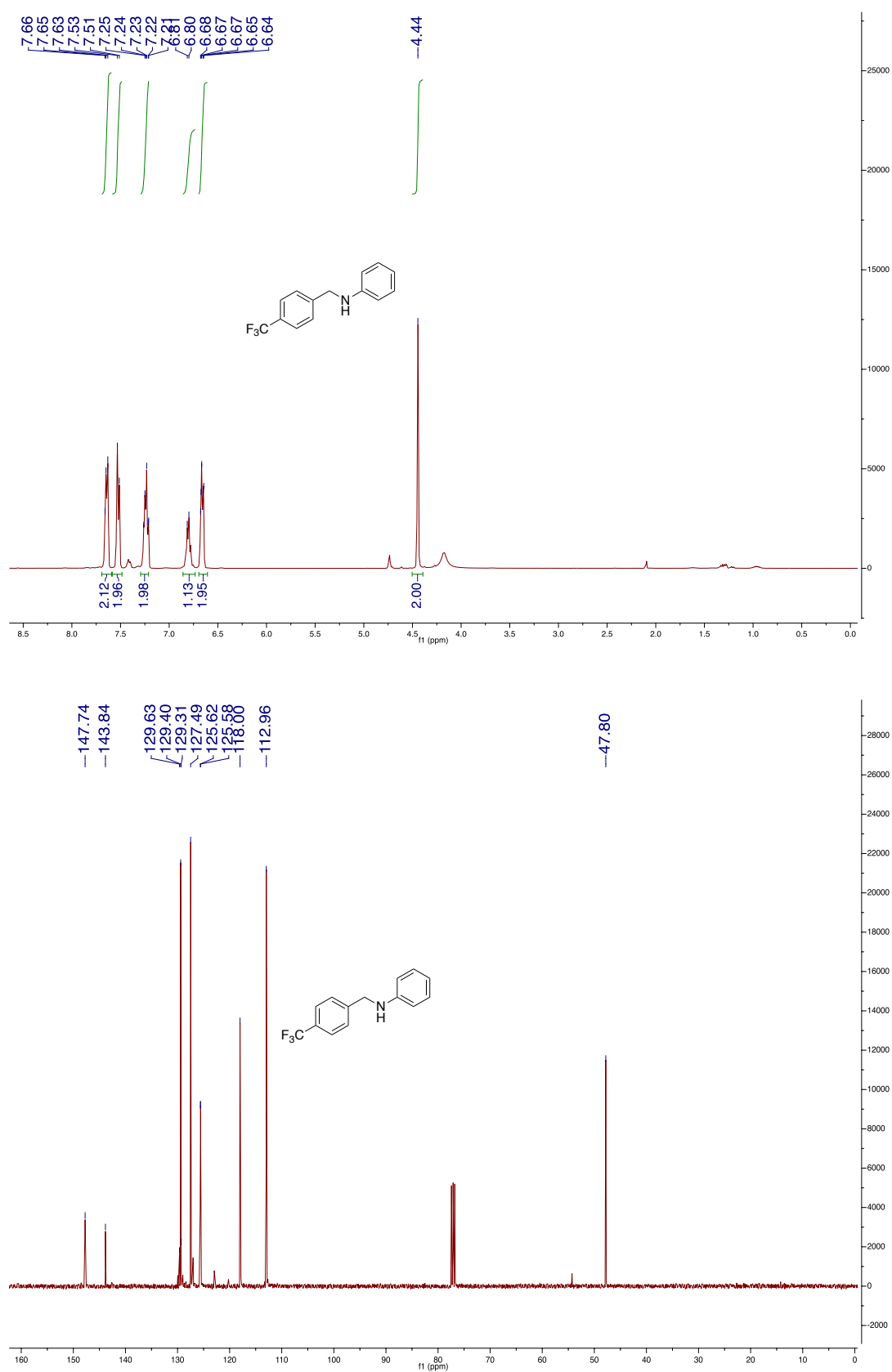


Figure S4.3. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3c** in CDCl₃.

***N*-(*p*-Bromobenzyl)aniline (3d)**

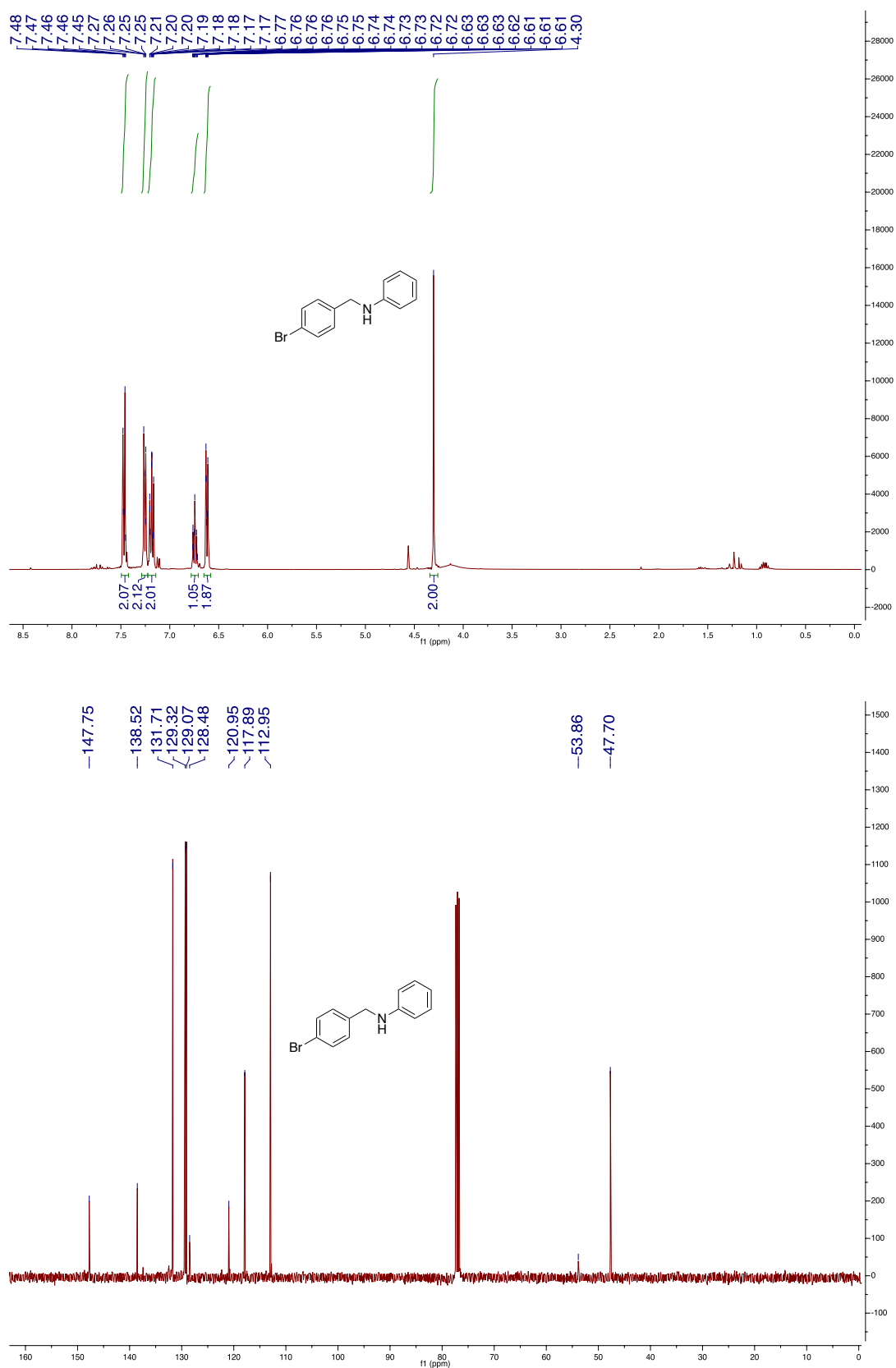


Figure S4.4. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3d** in CDCl₃.

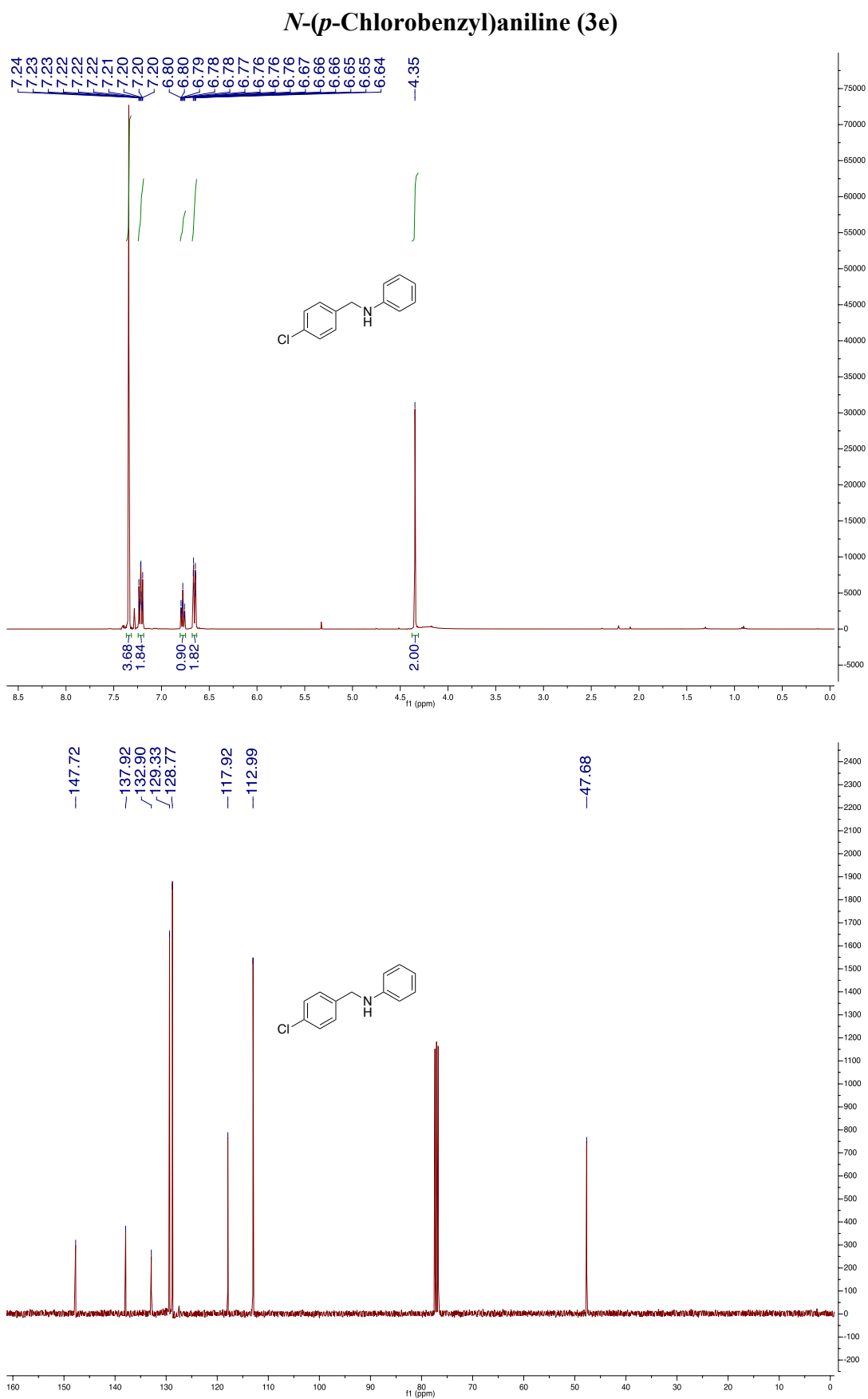


Figure S4.5. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3e** in CDCl₃.

***N*-(*p*-Fluorobenzyl)aniline (3f)**

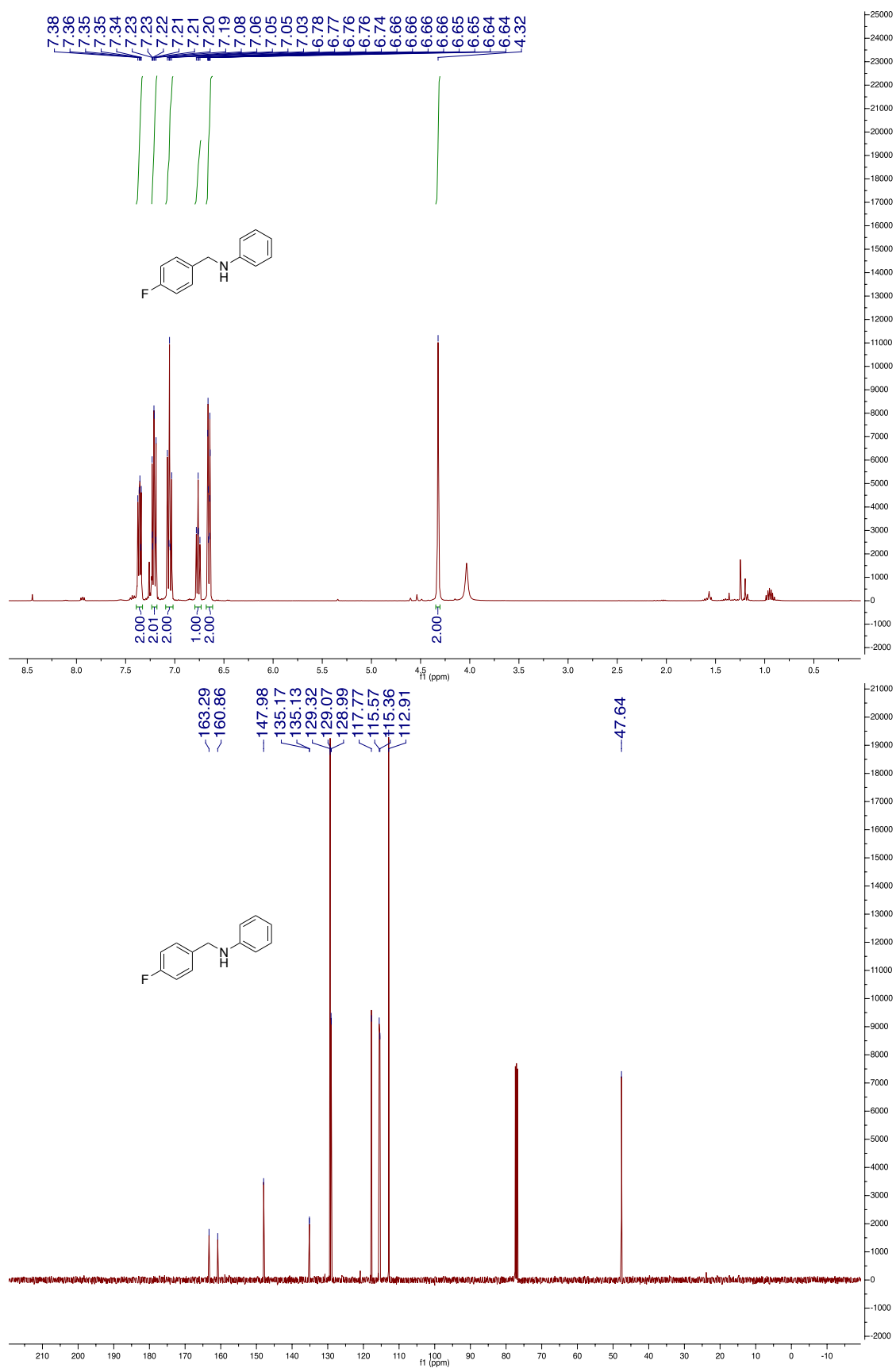


Figure S4.6. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3f** in CDCl₃.

***N*-(*p*-Methoxybenzyl)aniline (3g)**

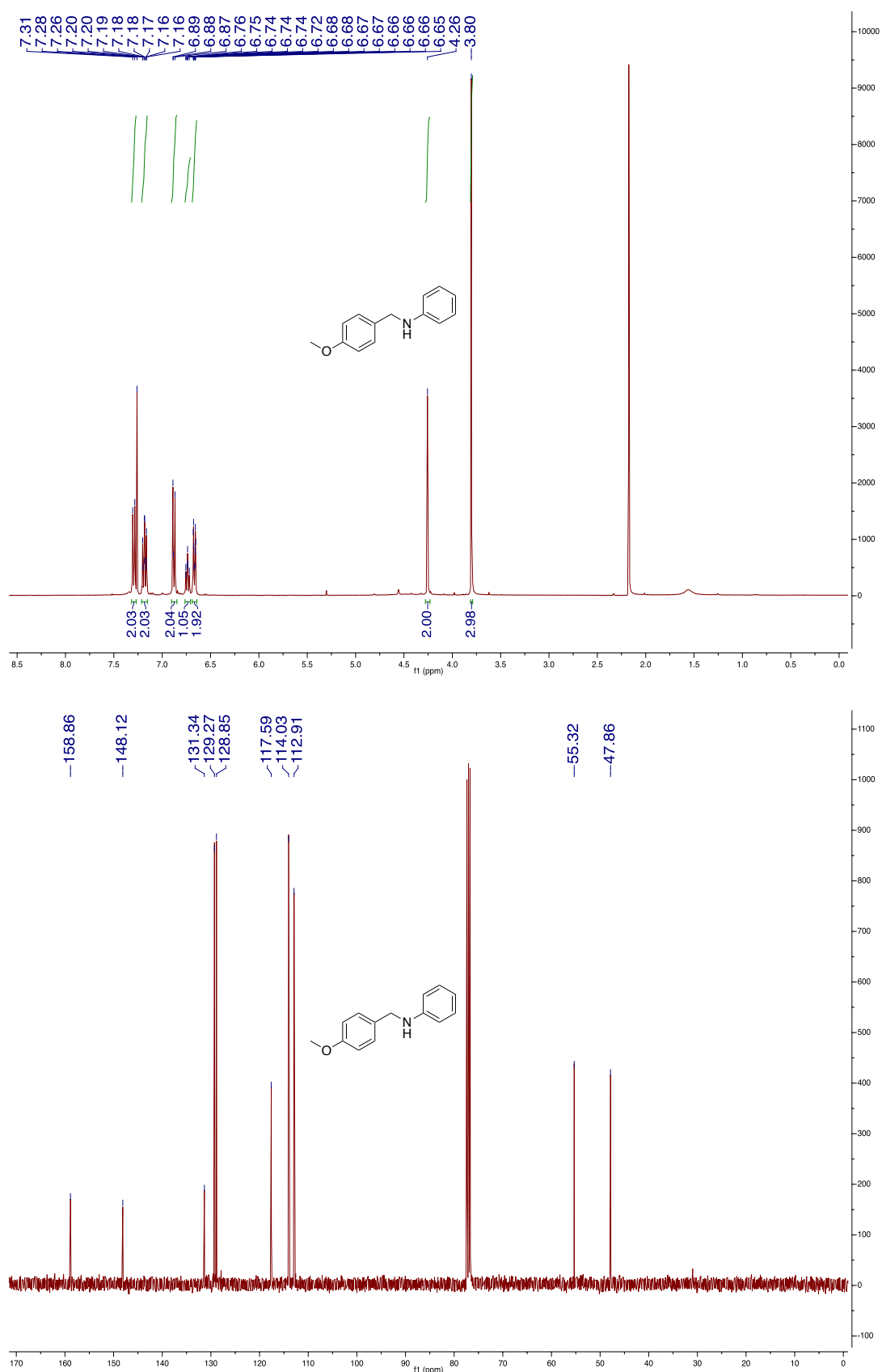


Figure S4.7. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3g** in CDCl₃.

***N*-(*p*-(*tert*-butyl)benzyl)aniline (**3h**)**

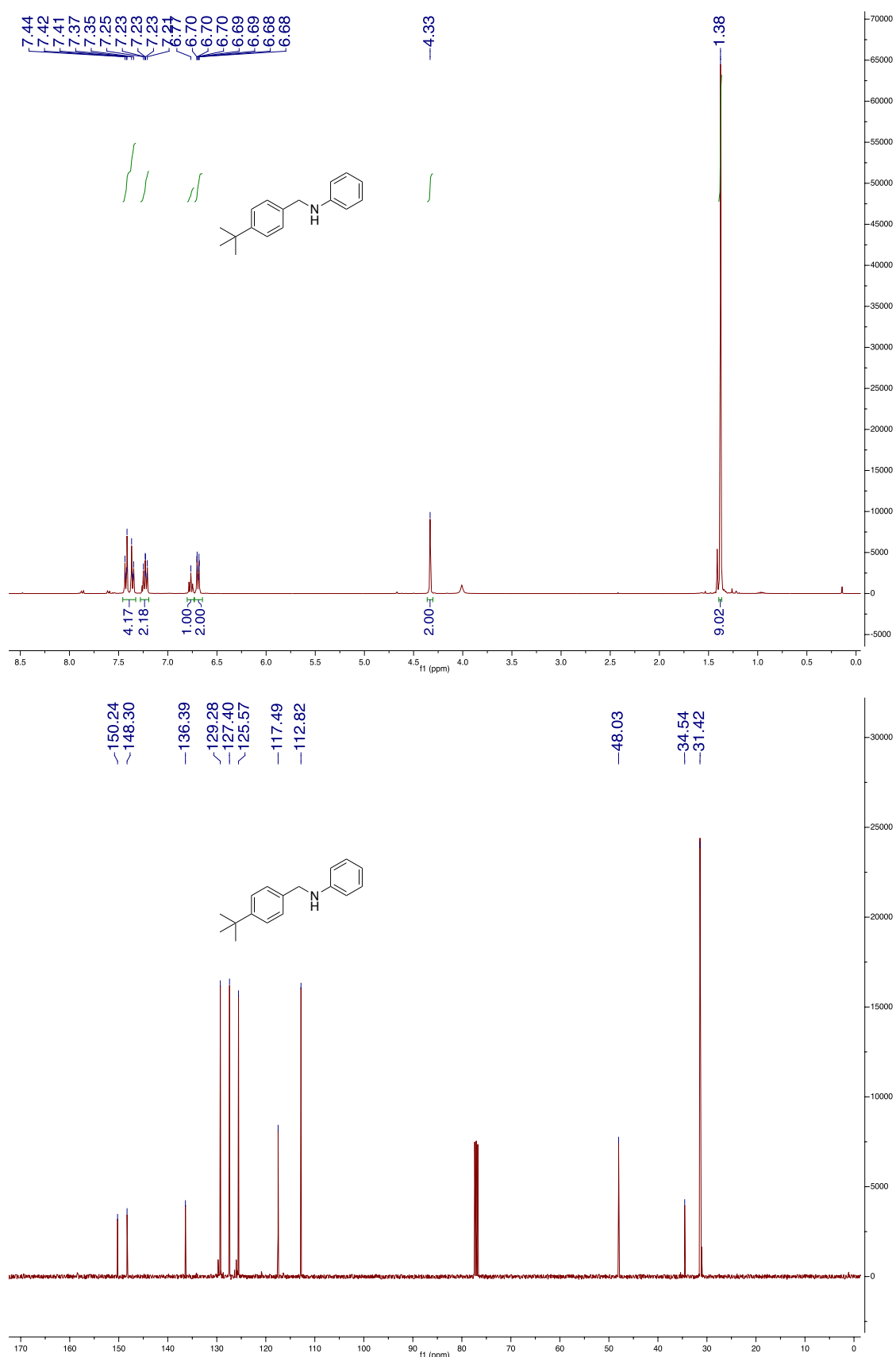


Figure S4.8. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3h** in CDCl_3 .

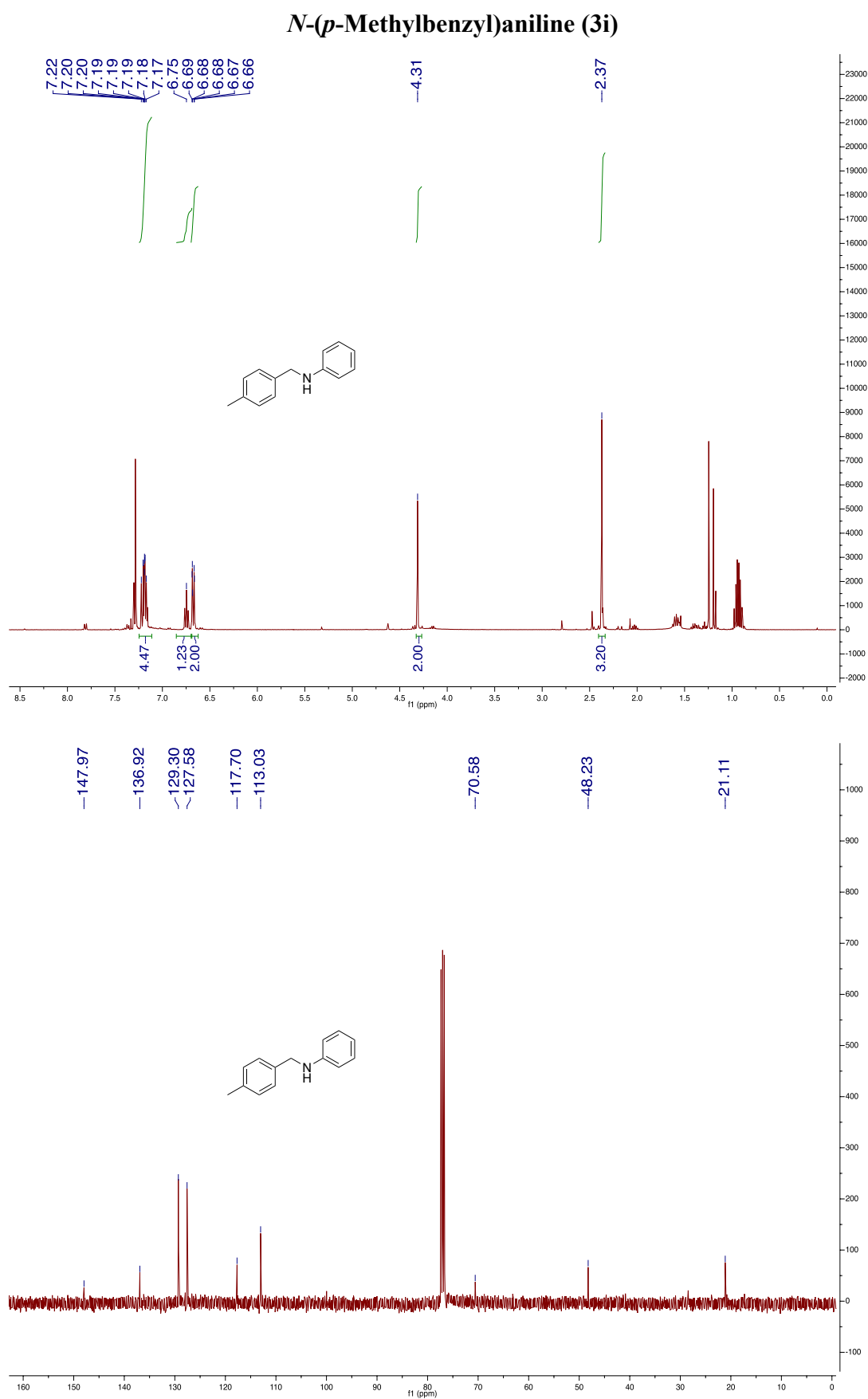


Figure S4.9. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3i** in CDCl_3 .

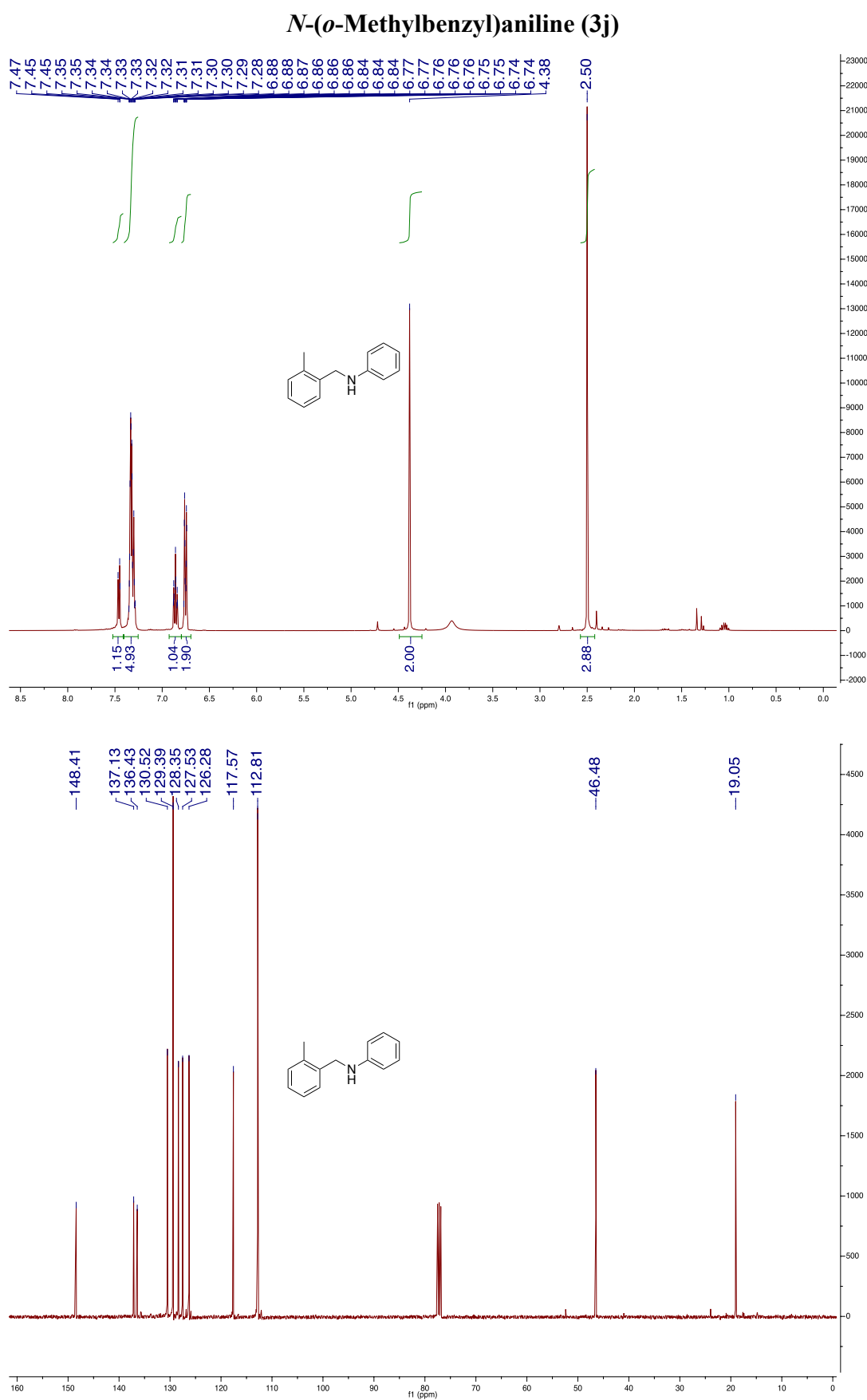


Figure S4.10. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3j** in CDCl_3 .

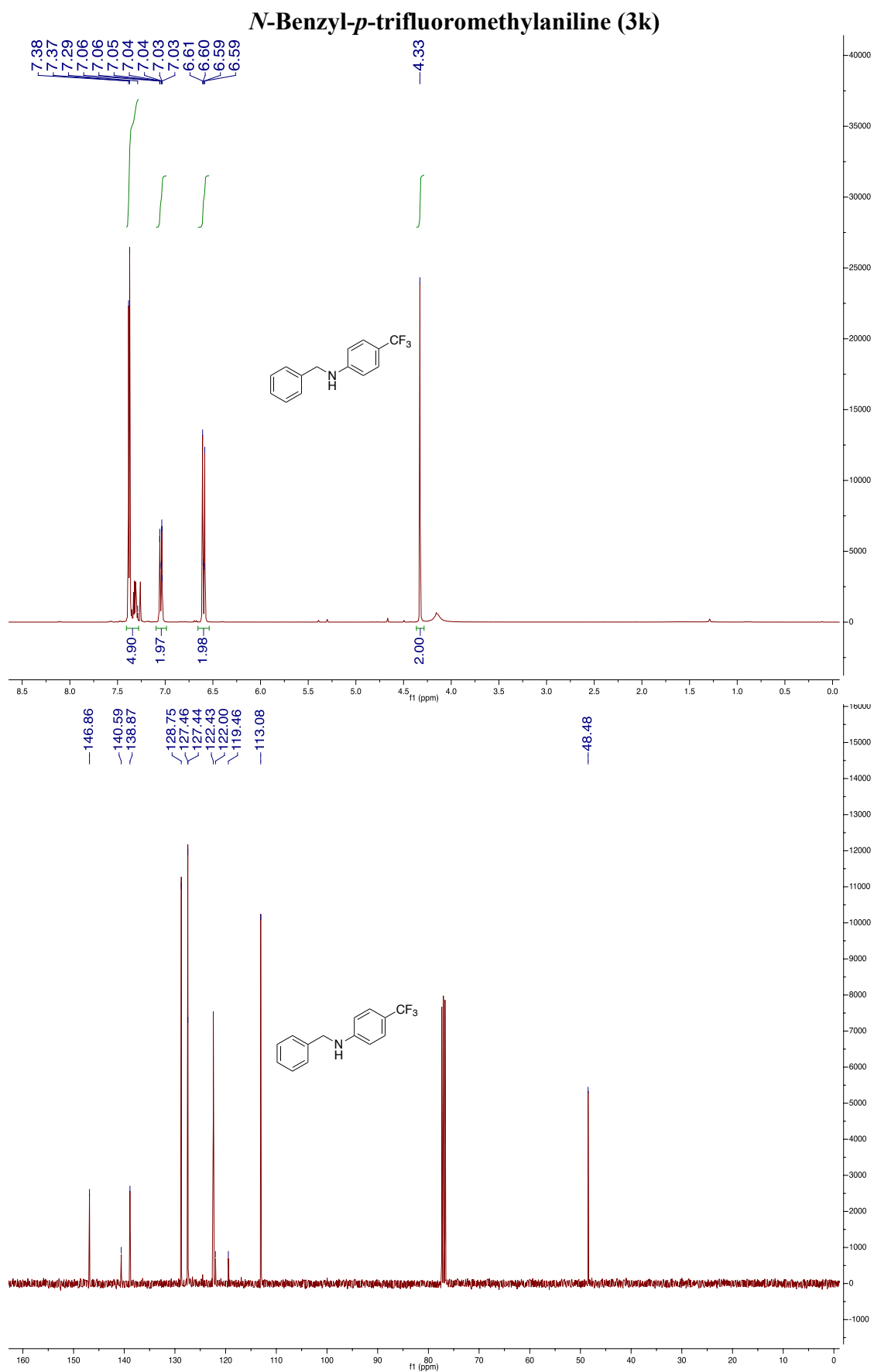


Figure S4.11. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3k** in CDCl₃.

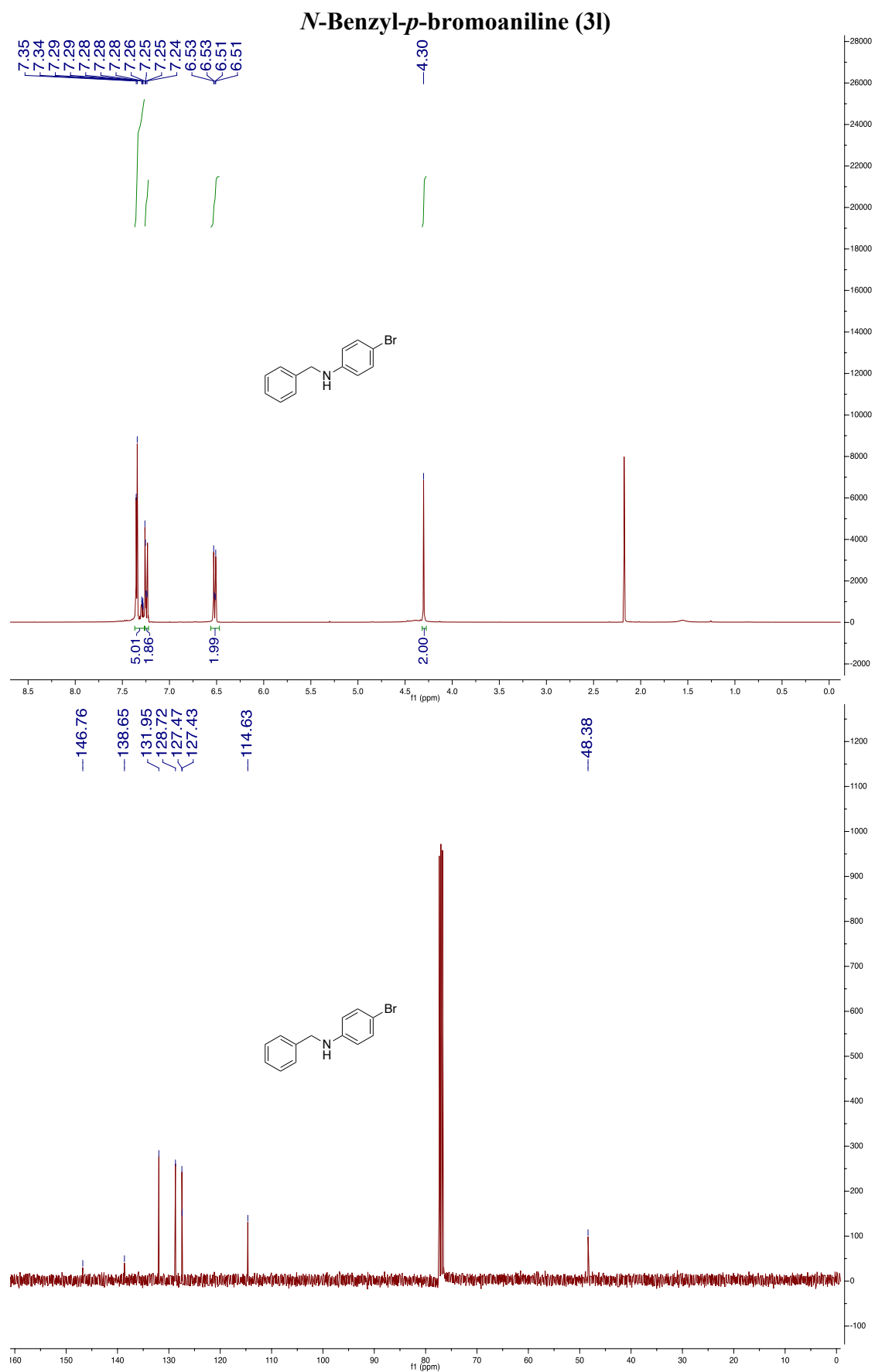


Figure S4.12. Top) ¹H NMR (400 MHz) and (bottom) ¹³C {¹H} NMR (100 MHz) spectra of **31** in CDCl₃.

***N*-Benzyl-*p*-chloroaniline (3m)**

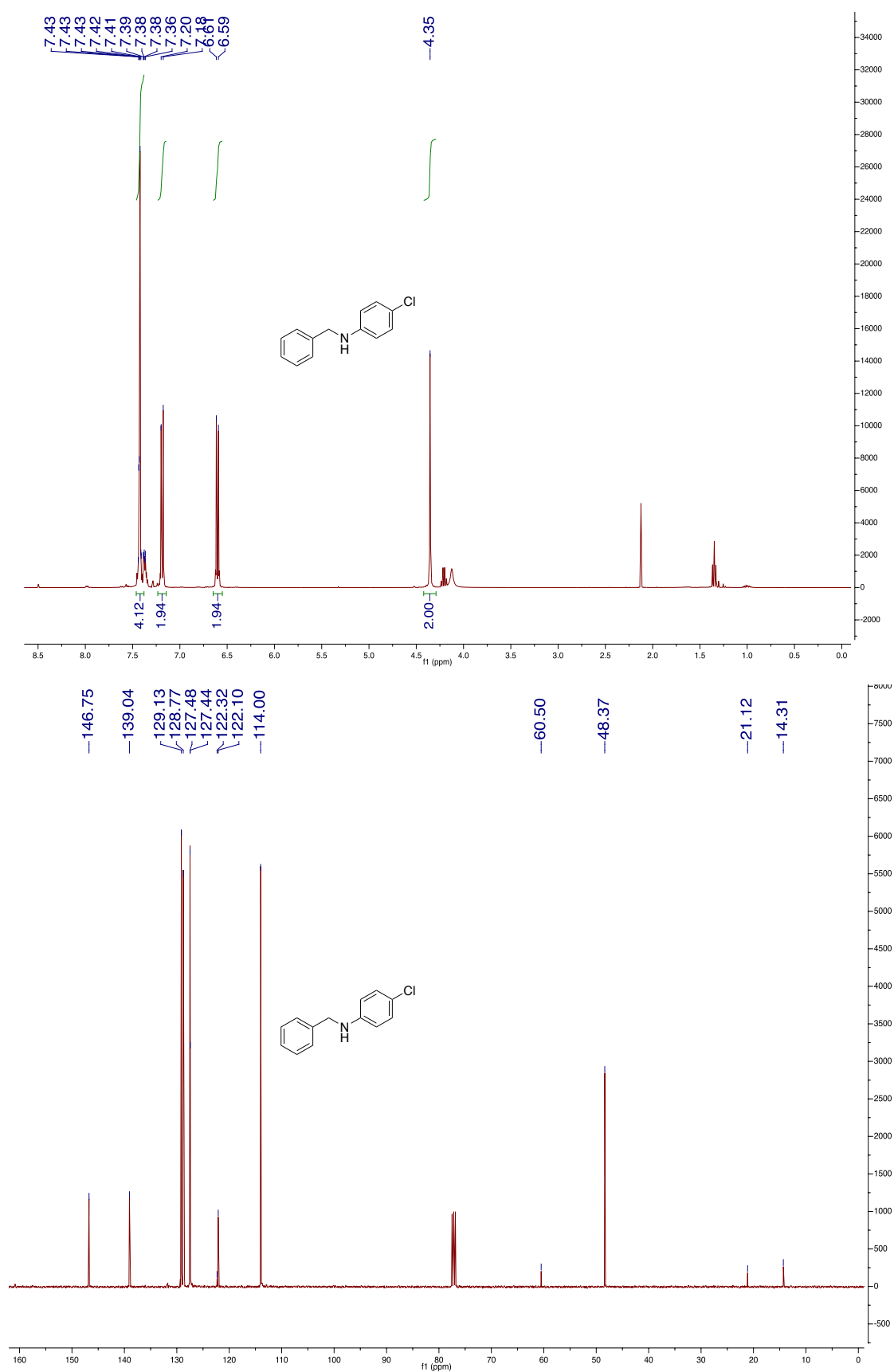


Figure S4.13. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3m** in CDCl_3 .

***N*-Benzyl-*p*-fluoroaniline (3n)**

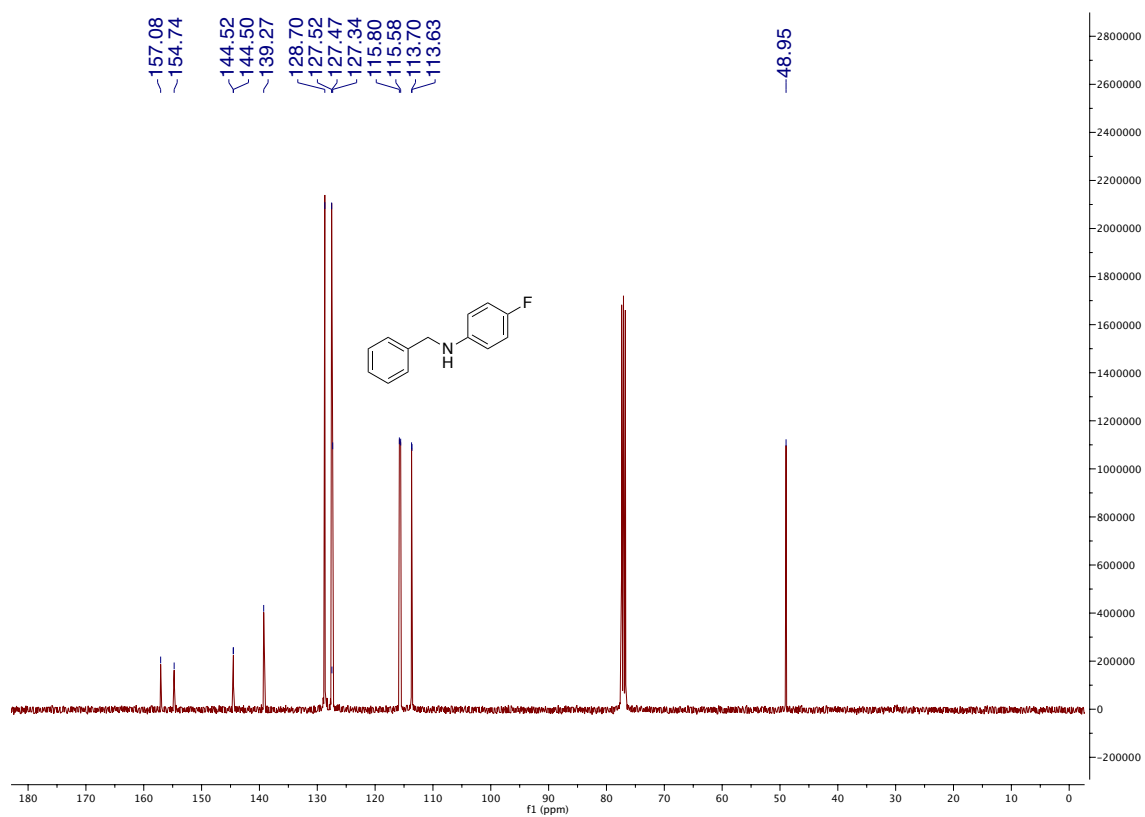
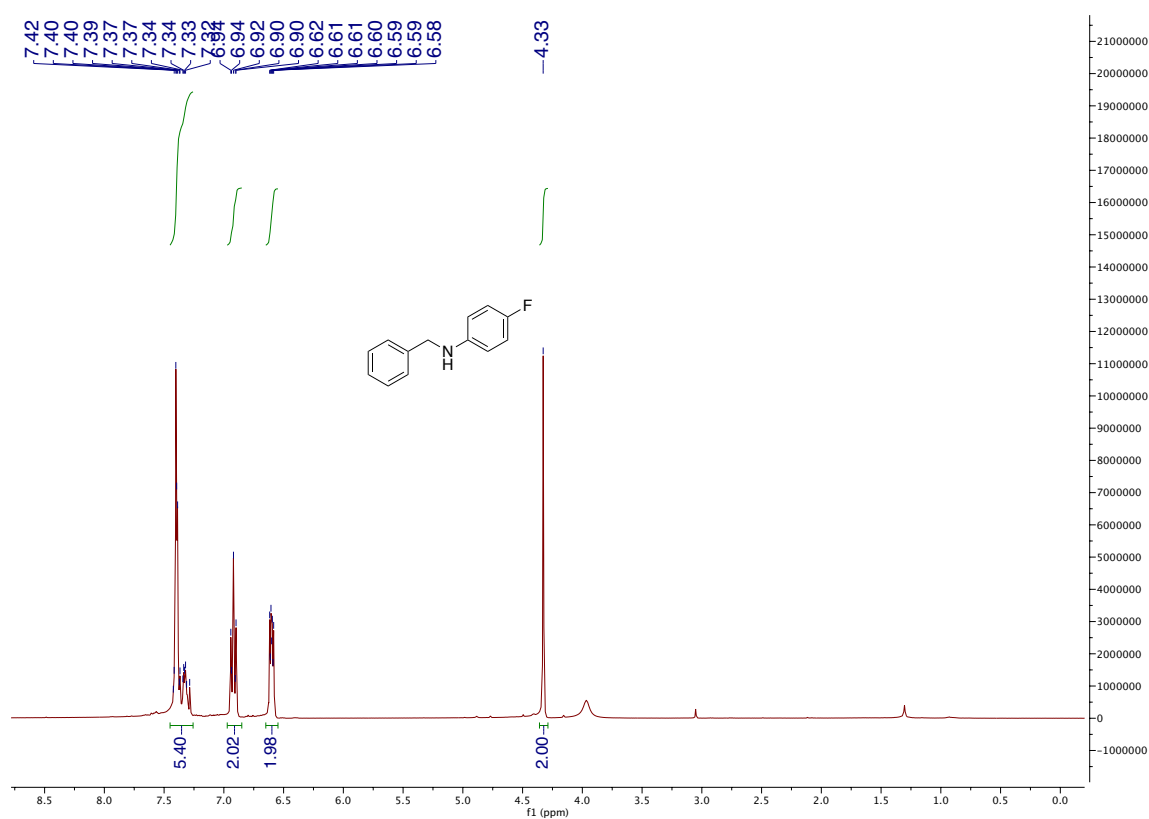


Figure S4.14. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3n** in CDCl₃.

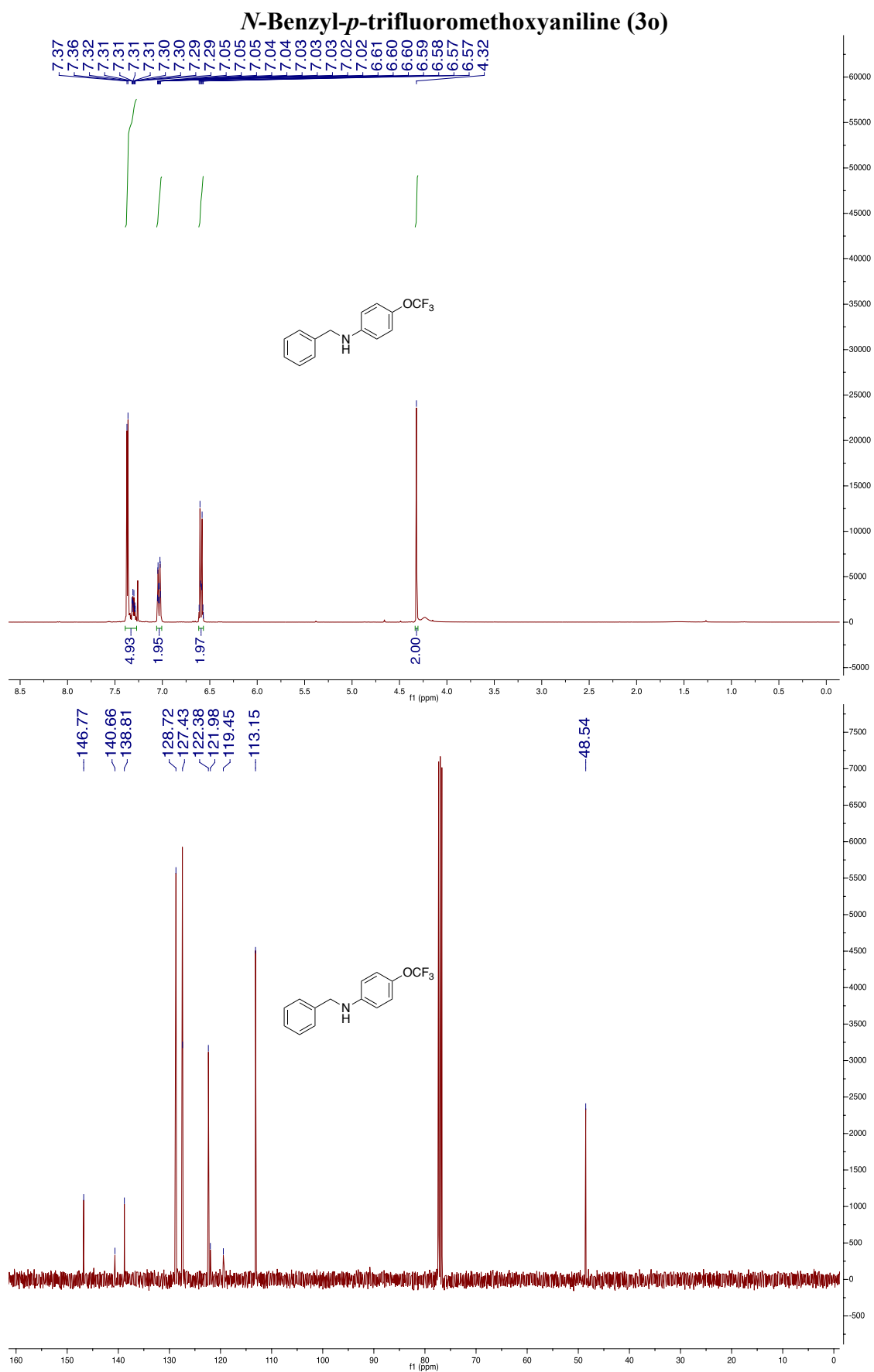


Figure S4.15. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C {¹H} NMR (100 MHz) spectra of **3o** in CDCl₃.

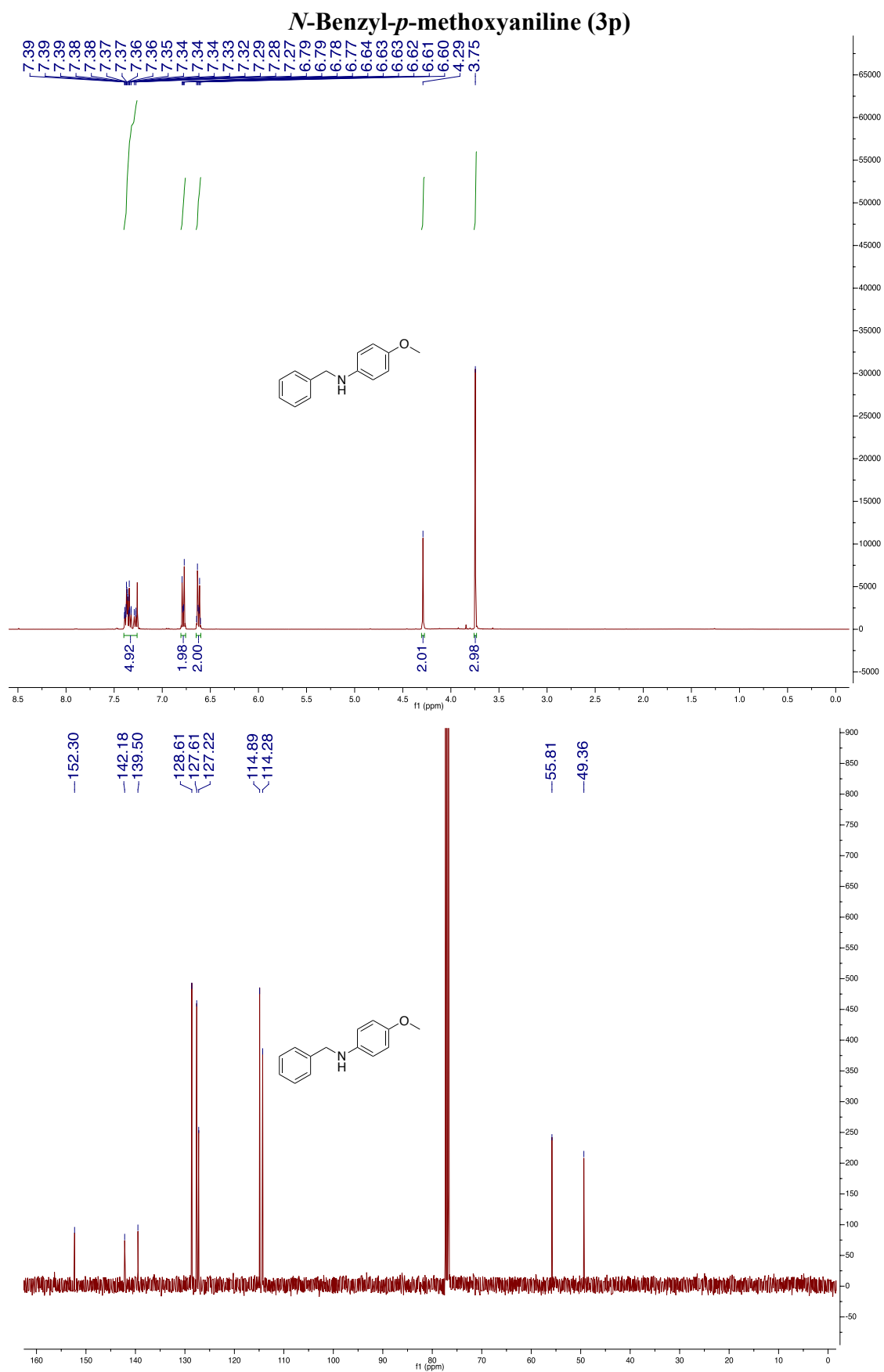


Figure S4.16. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3p** in CDCl_3 .

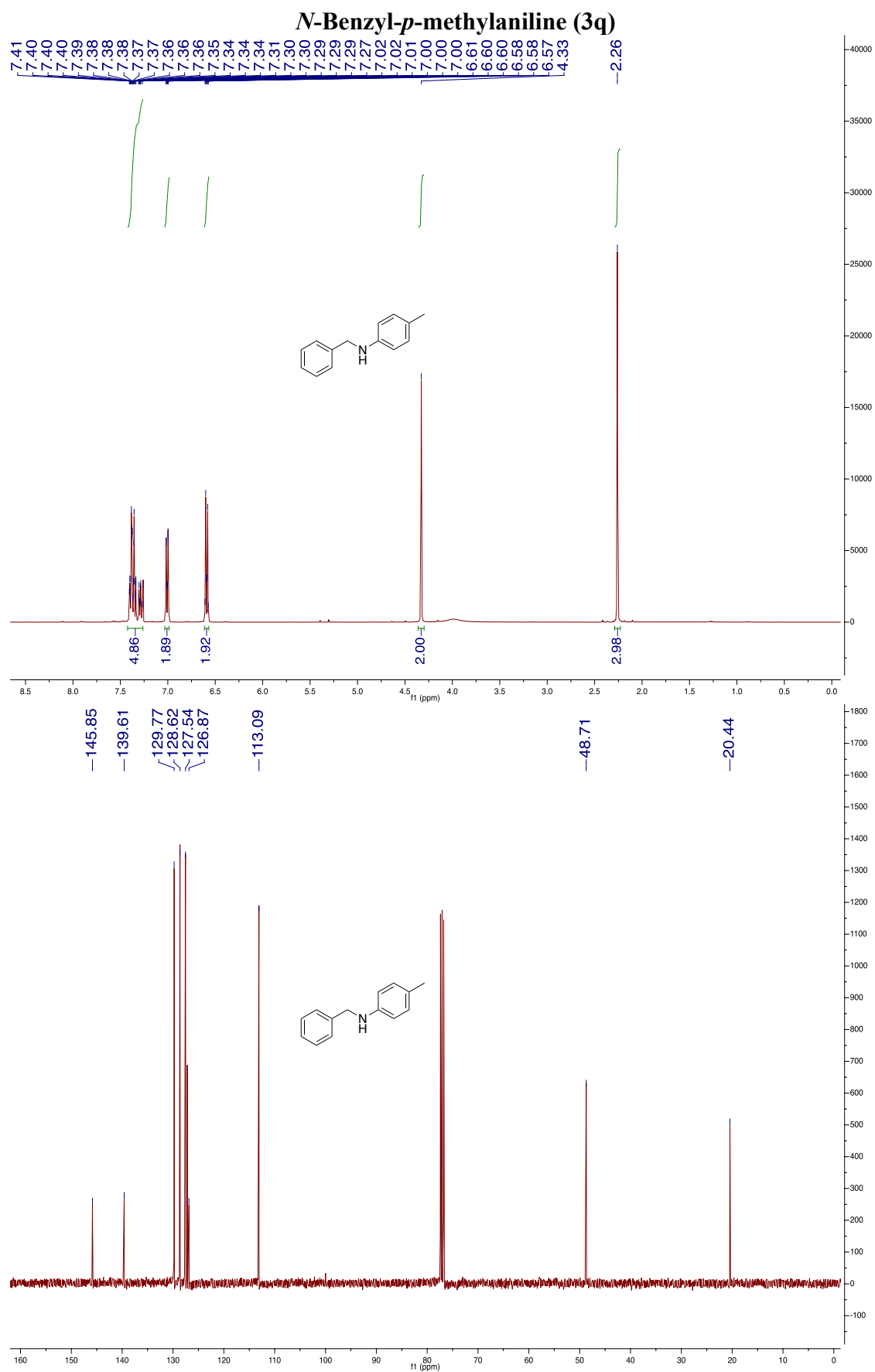


Figure S4.17. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3q** in CDCl_3 .

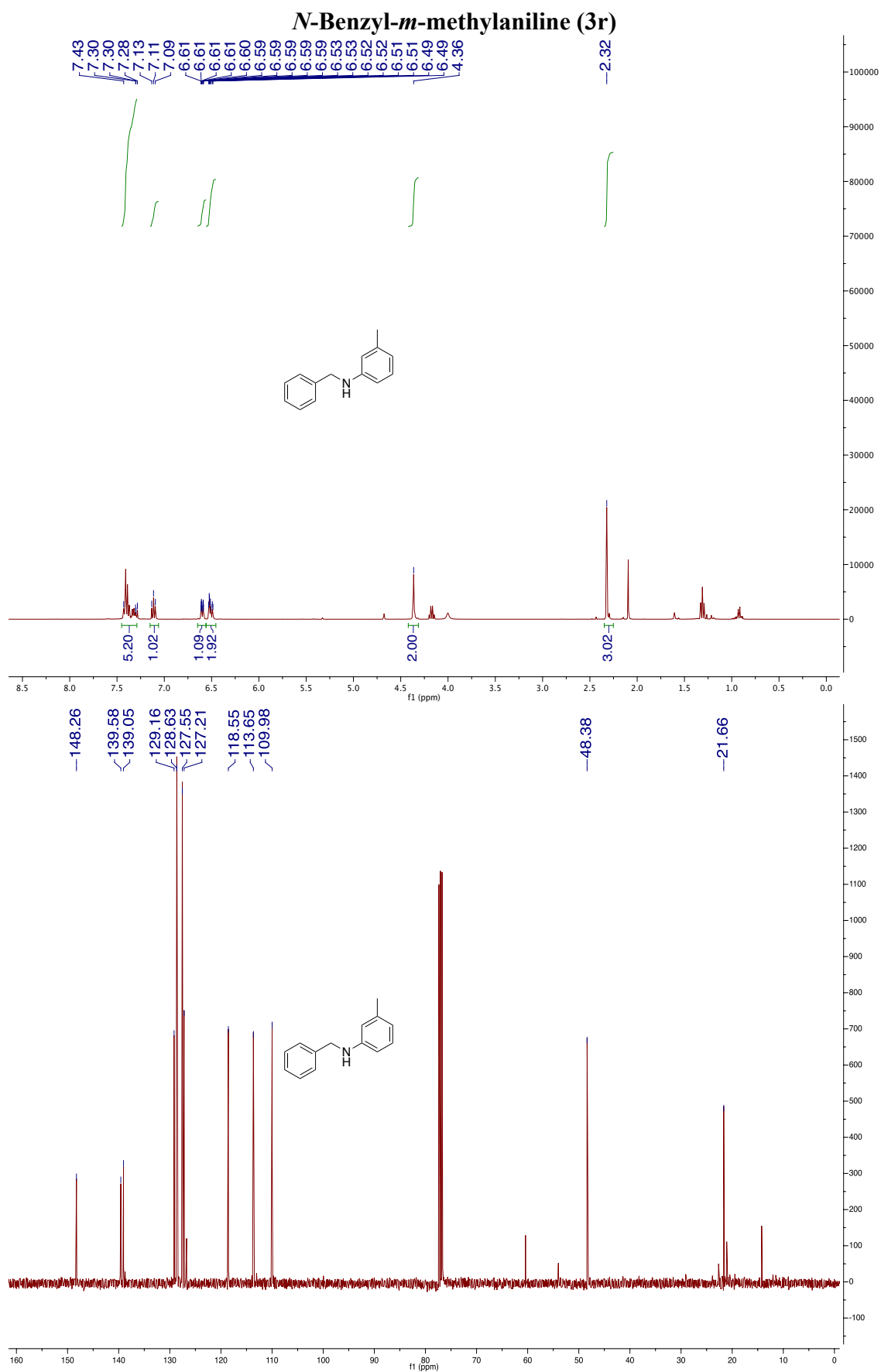


Figure S4.18. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3r** in CDCl_3 .

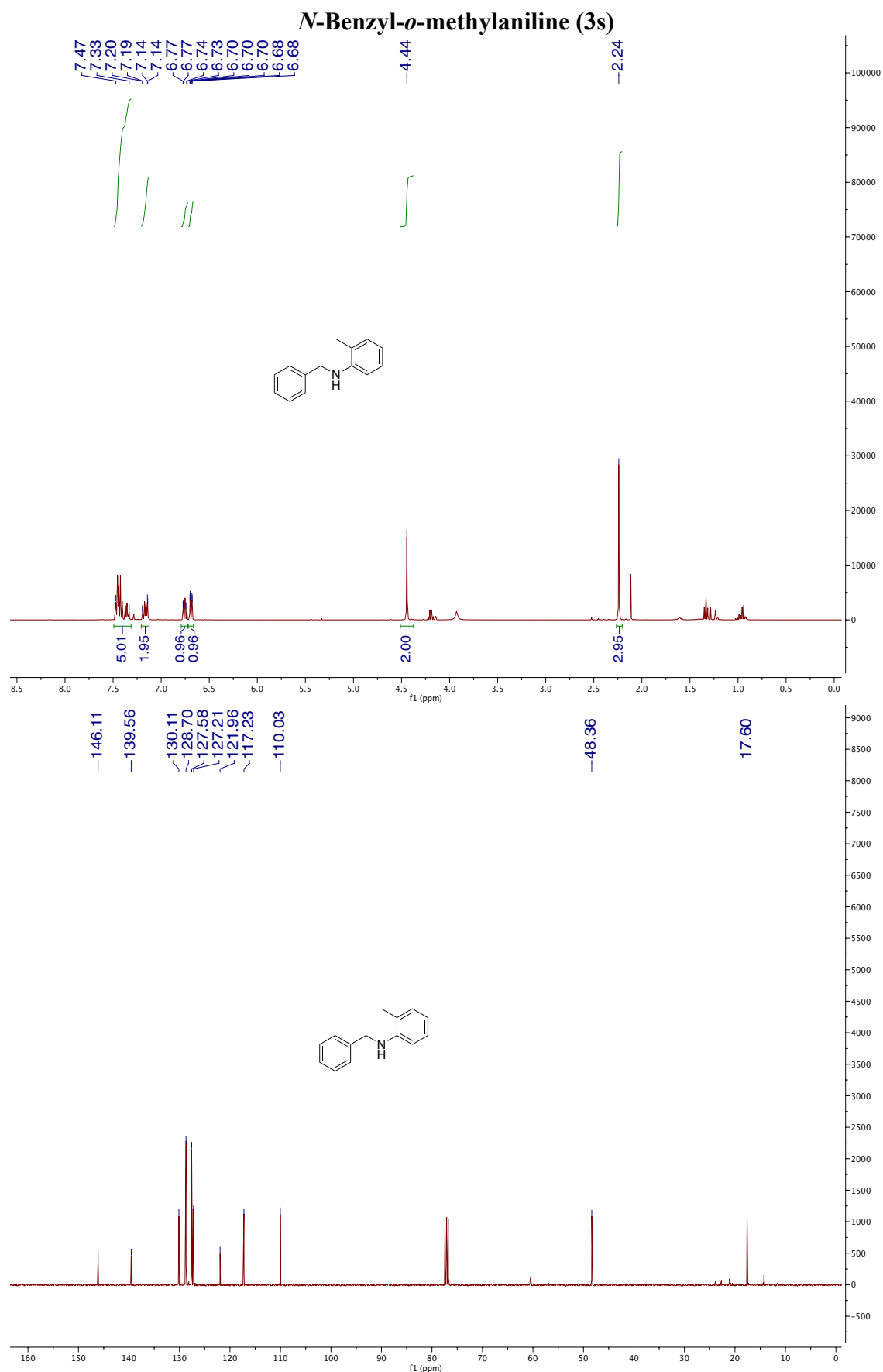


Figure S4.19. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3s** in CDCl₃.

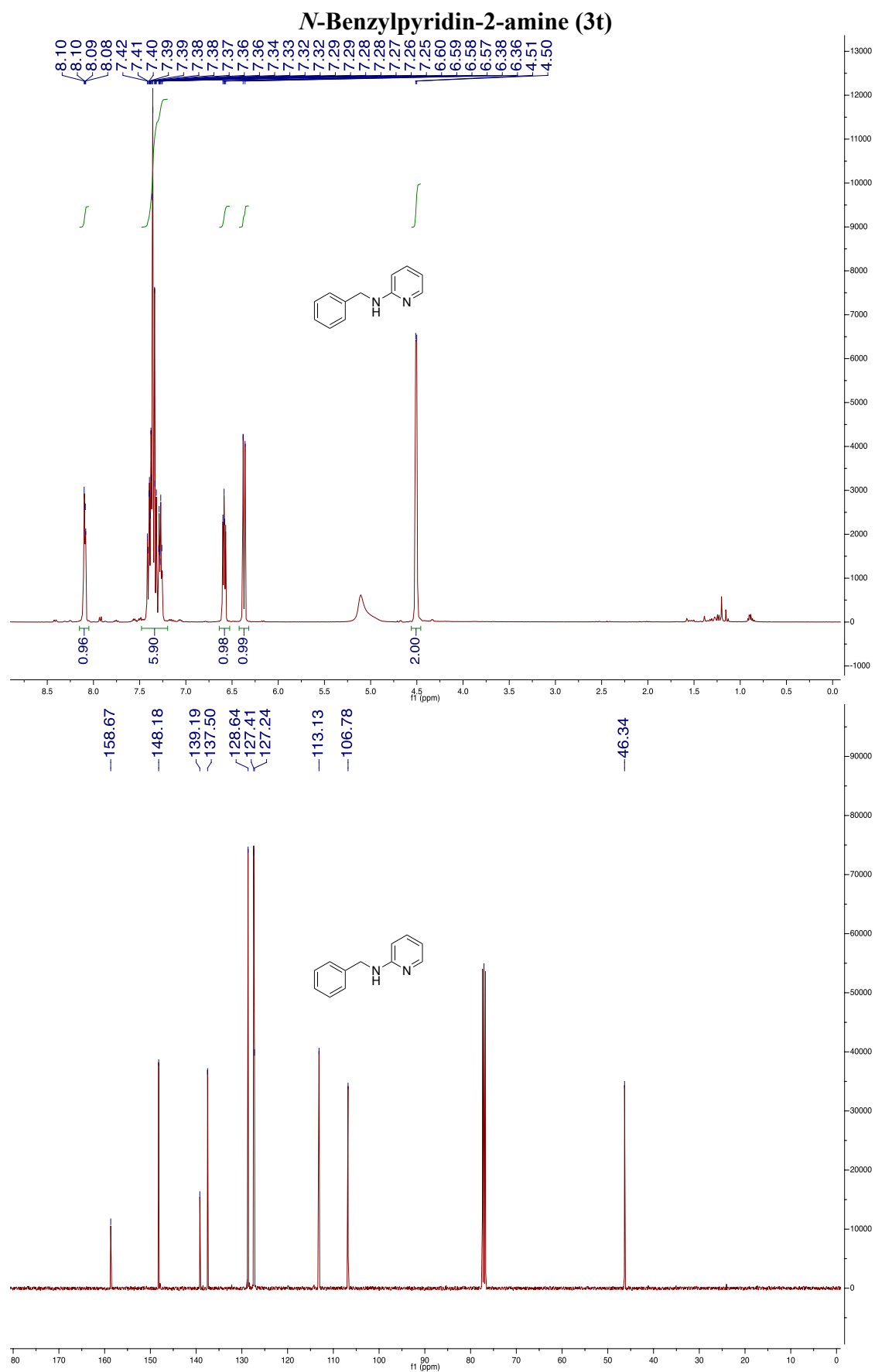


Figure S4.20. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3t** in CDCl_3 .

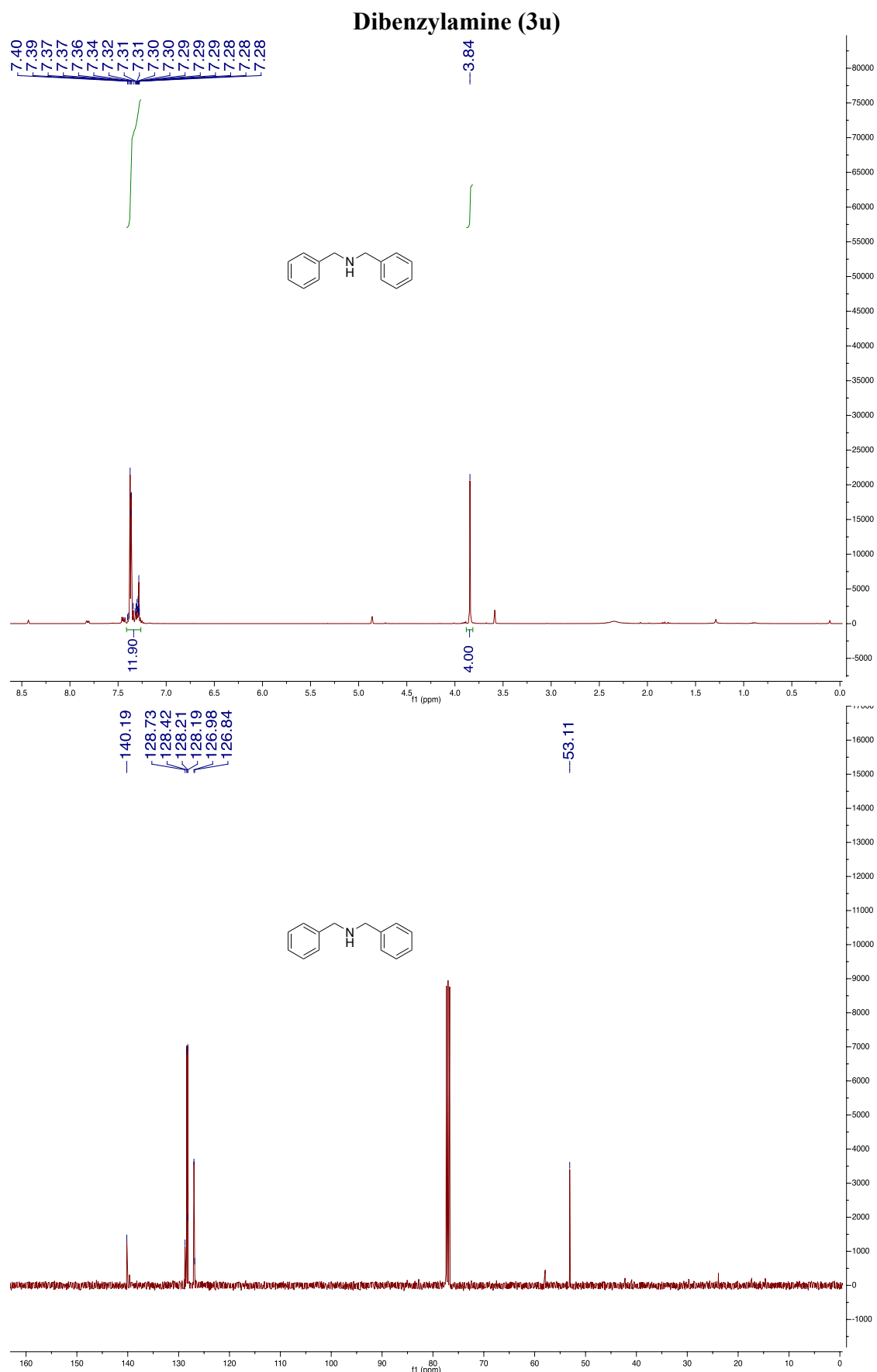


Figure S4.21. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3u** in CDCl_3 .

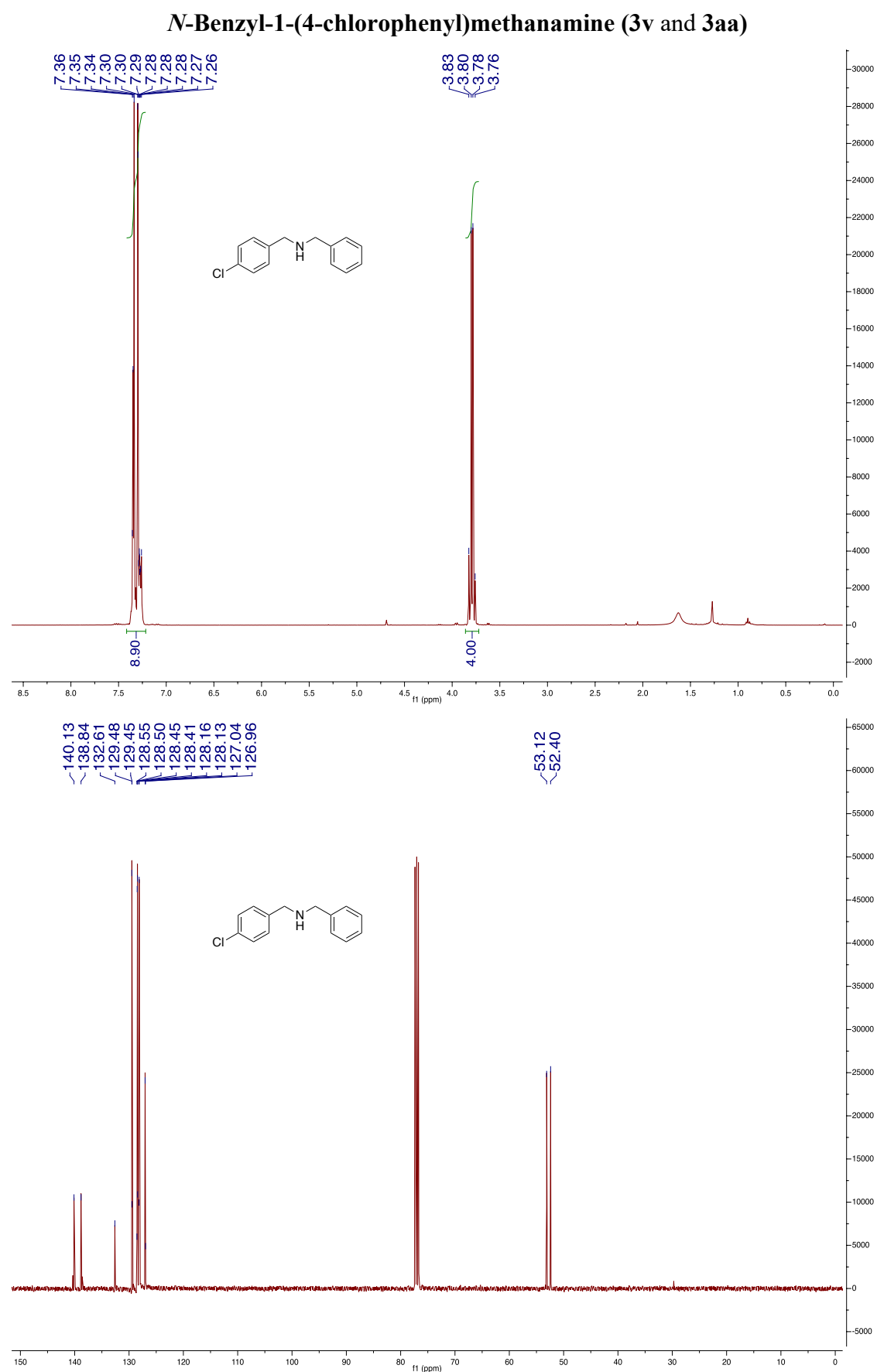


Figure S4.22. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3v/aa** in CDCl_3 .

***N*-Benzyl-1-(*p*-methoxyphenyl)methanamine (3w)**

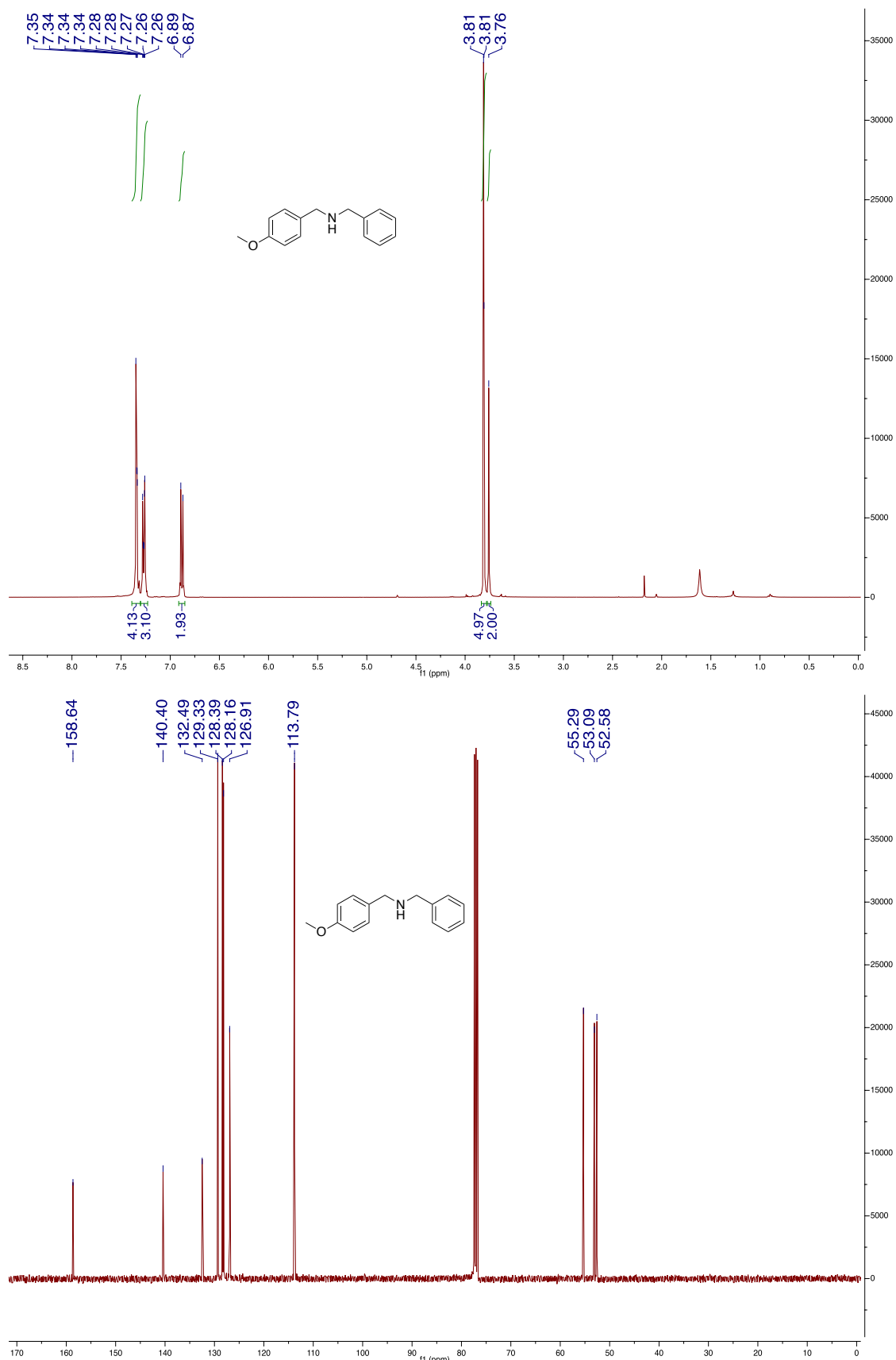


Figure S4.23. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3w** in CDCl_3 .

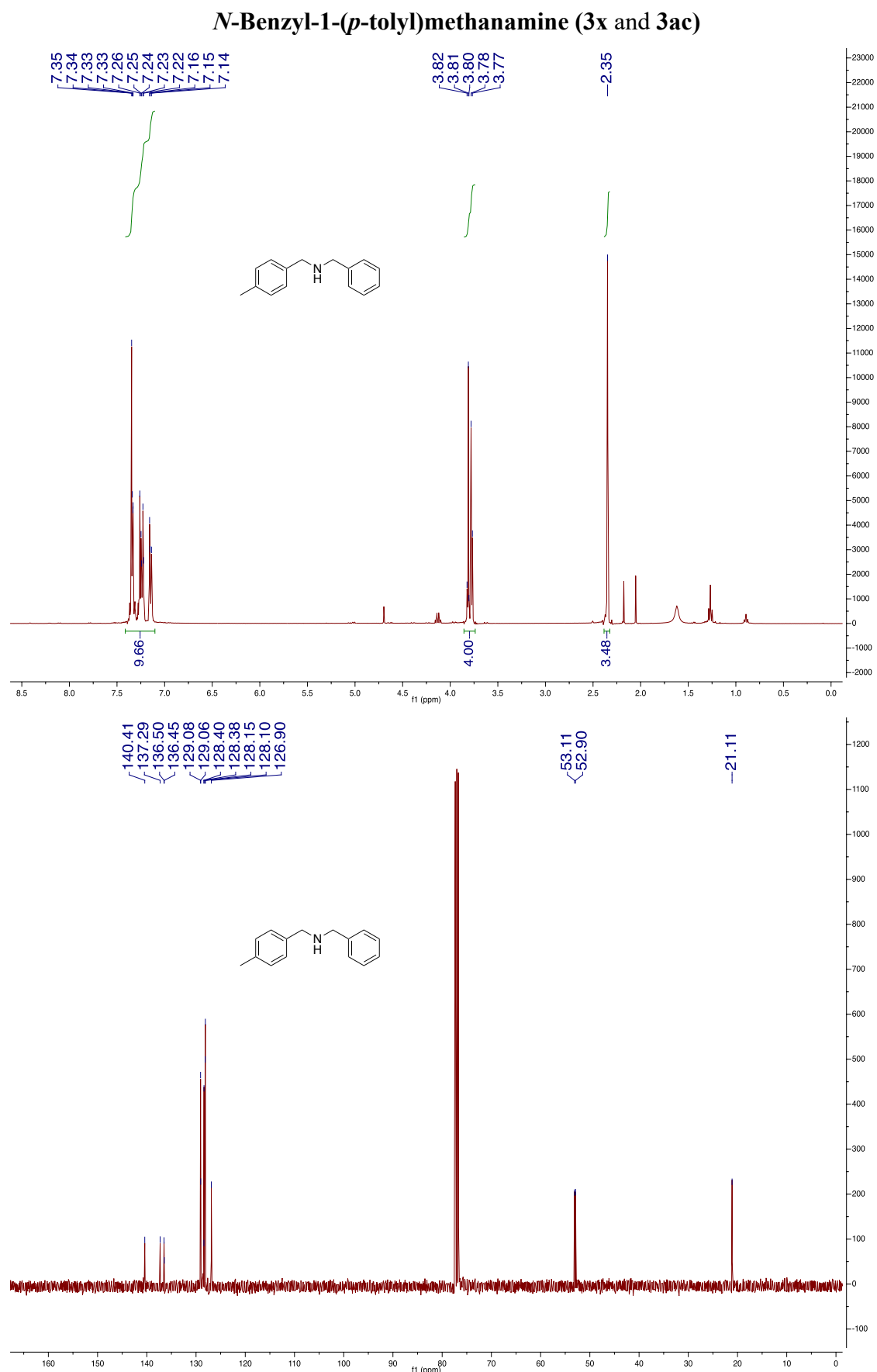


Figure S4.24. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C {¹H} NMR (100 MHz) spectra of 3x/ac in CDCl₃.

***N*-Benzyl-1-(*o*-tolyl)methanamine (3y)**

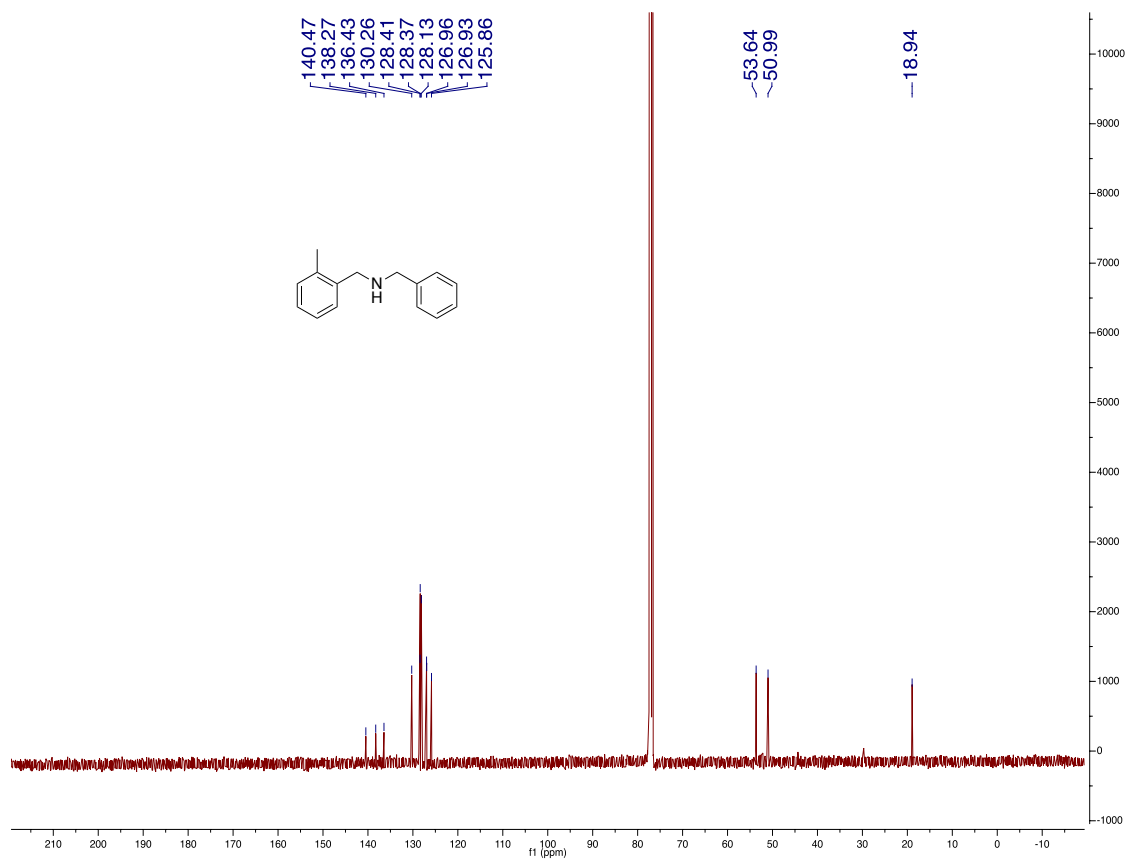
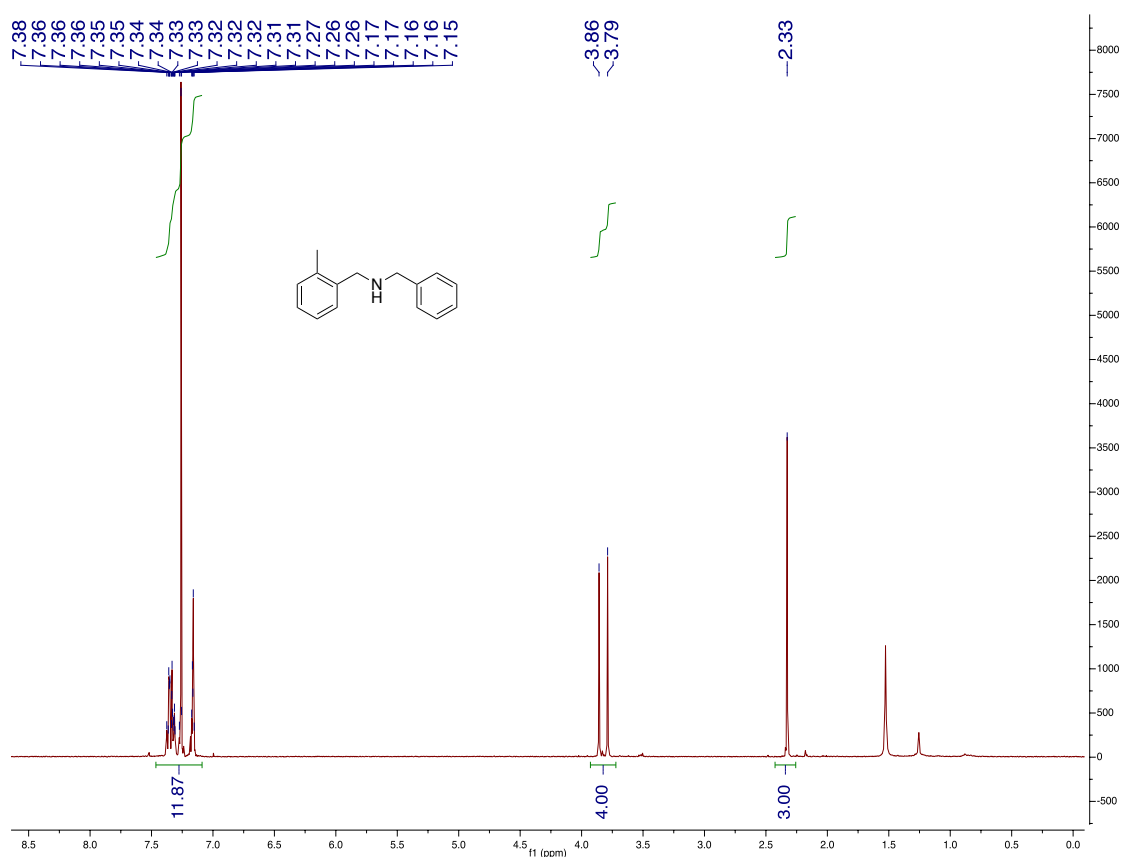


Figure S4.25. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C {¹H} NMR (100 MHz) spectra of **3y** in CDCl₃.

***N*-Benzyl-1-(*p*-bromophenyl)methanamine (**3z**)**

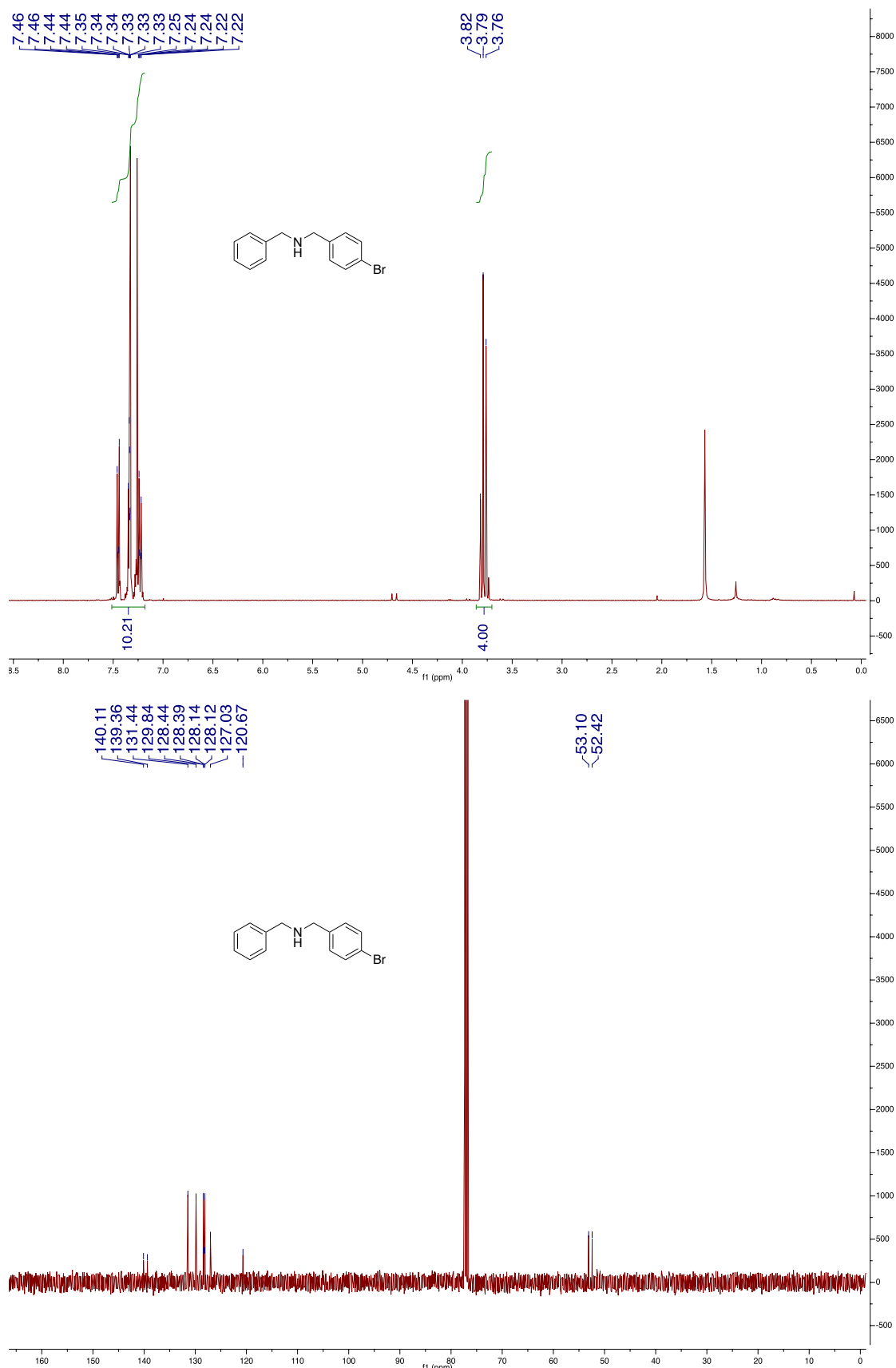


Figure S4.26. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C {¹H} NMR (100 MHz) spectra of **3z** in CDCl₃.

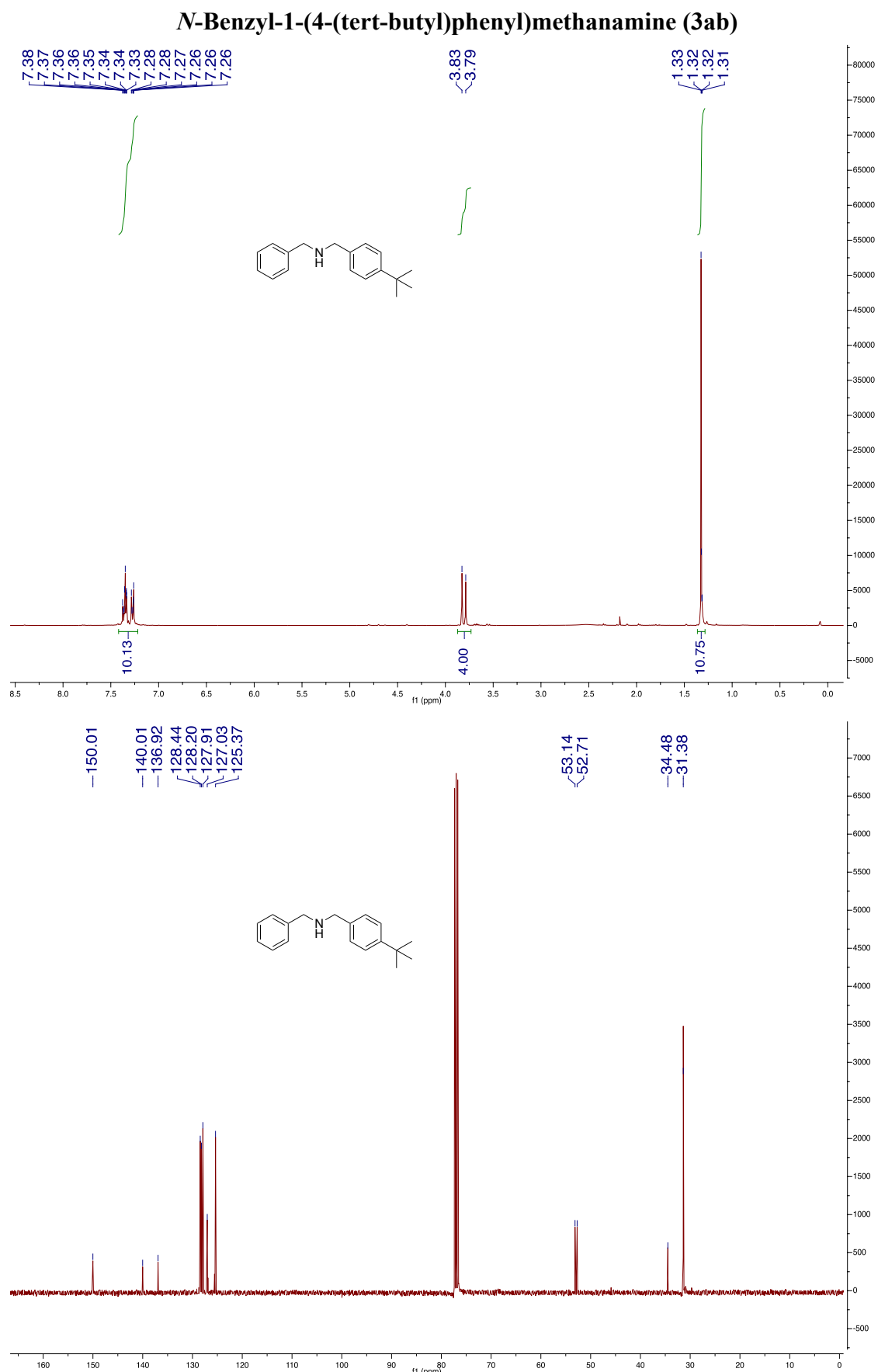


Figure S4.27. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ab** in CDCl₃.

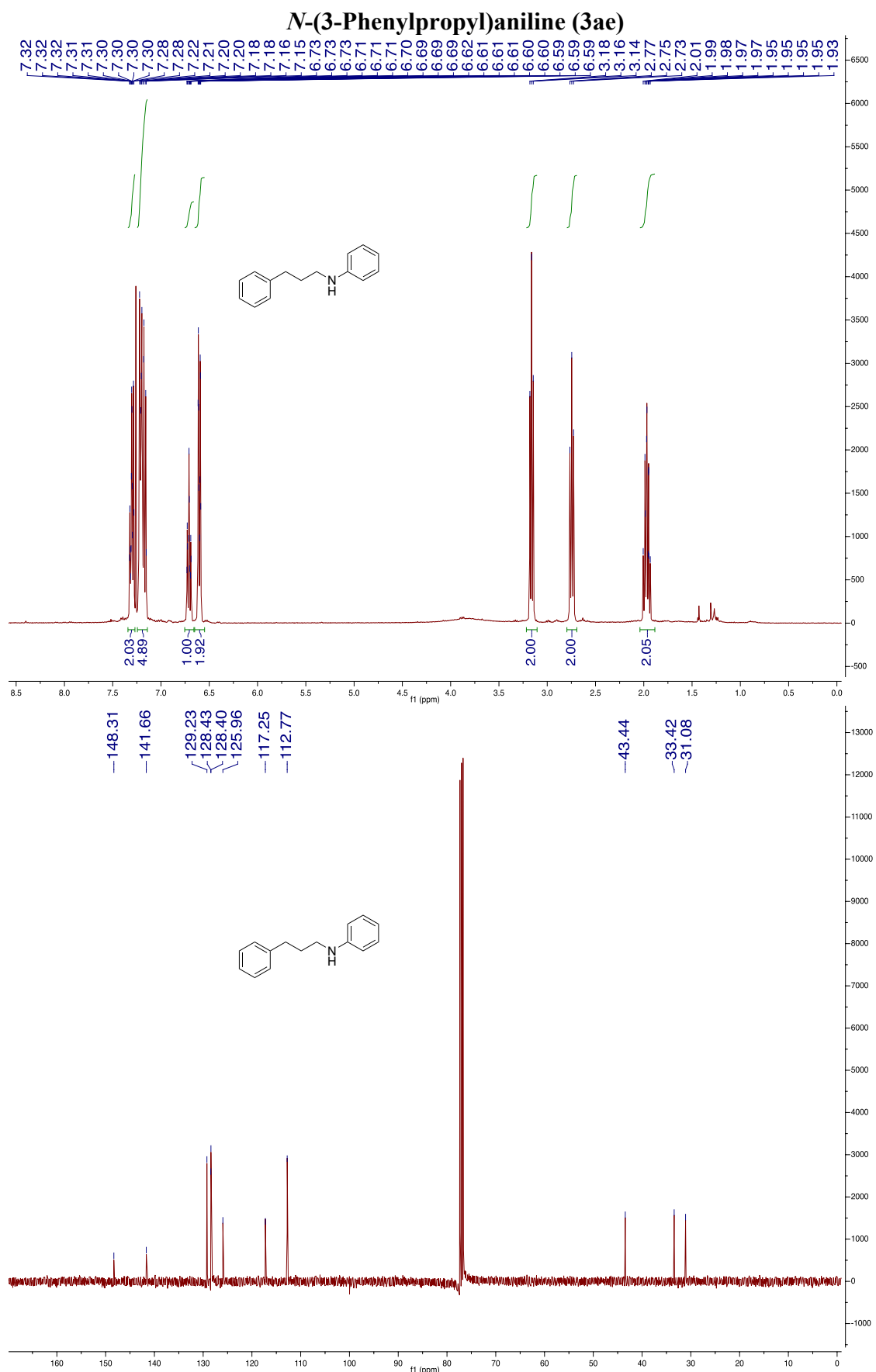


Figure S4.29. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ae** in CDCl₃.

***N*-Butylaniline (3af)**

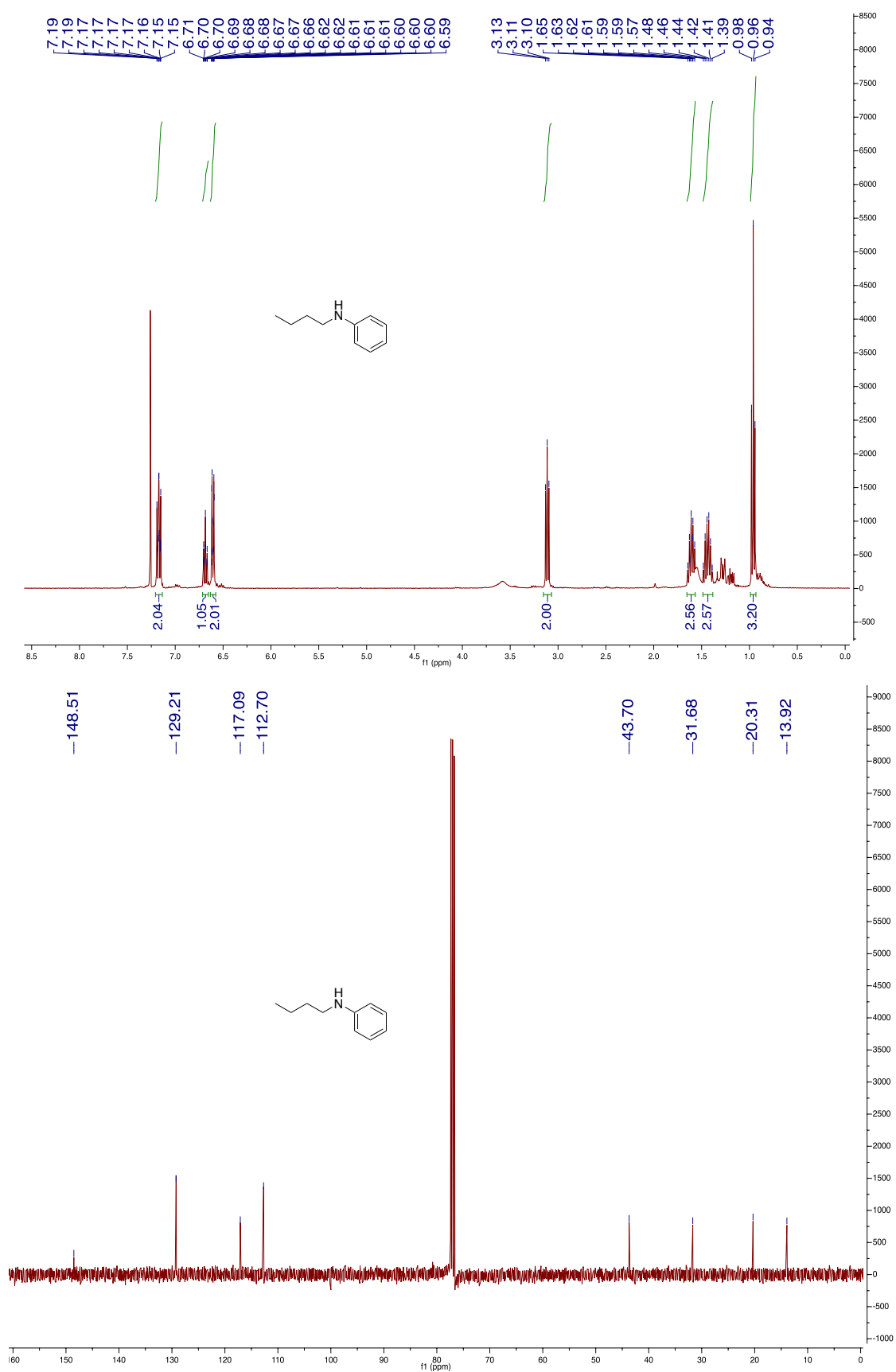


Figure S4.30. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3af** in CDCl₃.

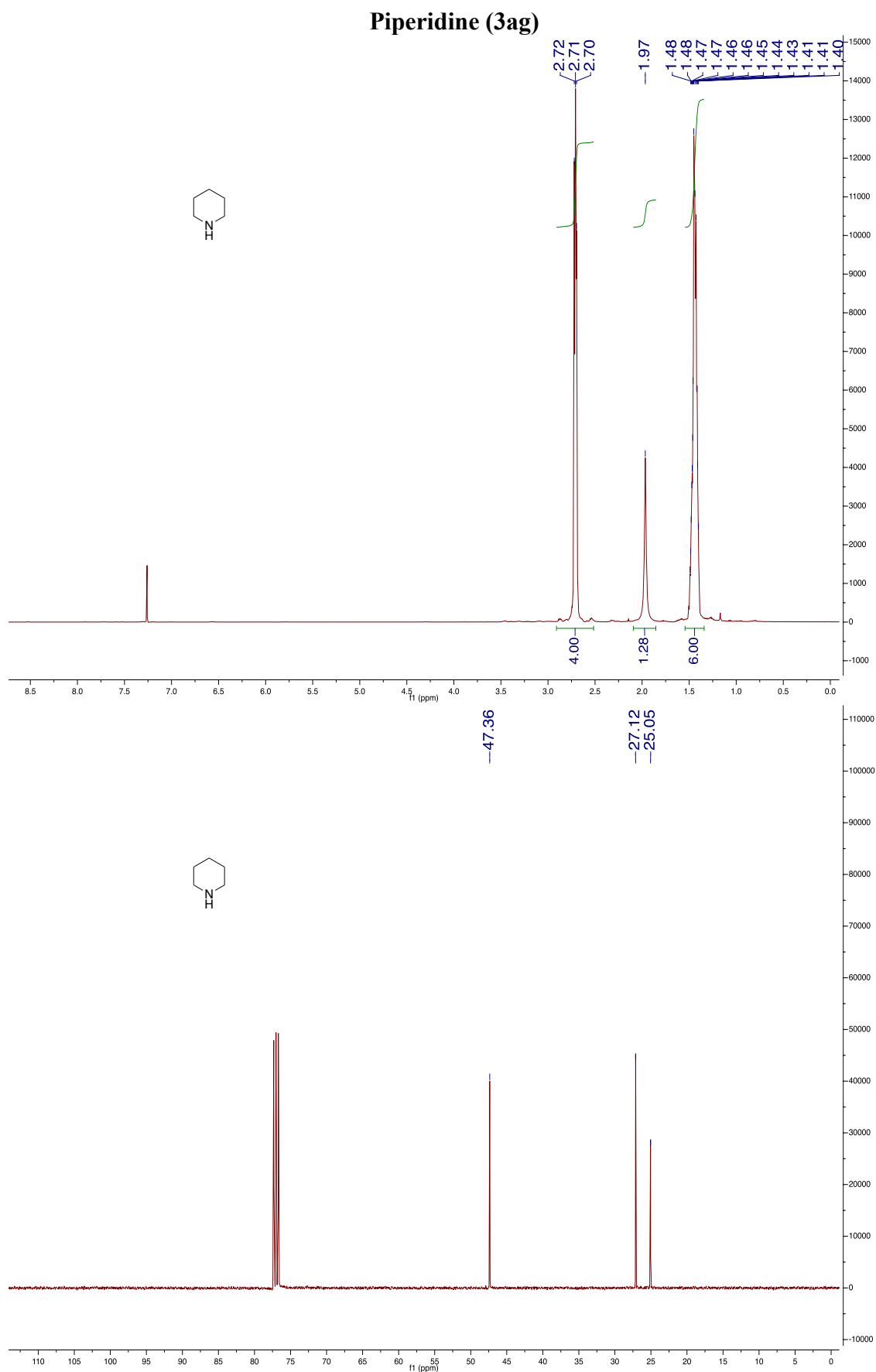


Figure S4.31. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ag** in CDCl₃.

5-(Phenylamino)pentan-1-ol (3ah)

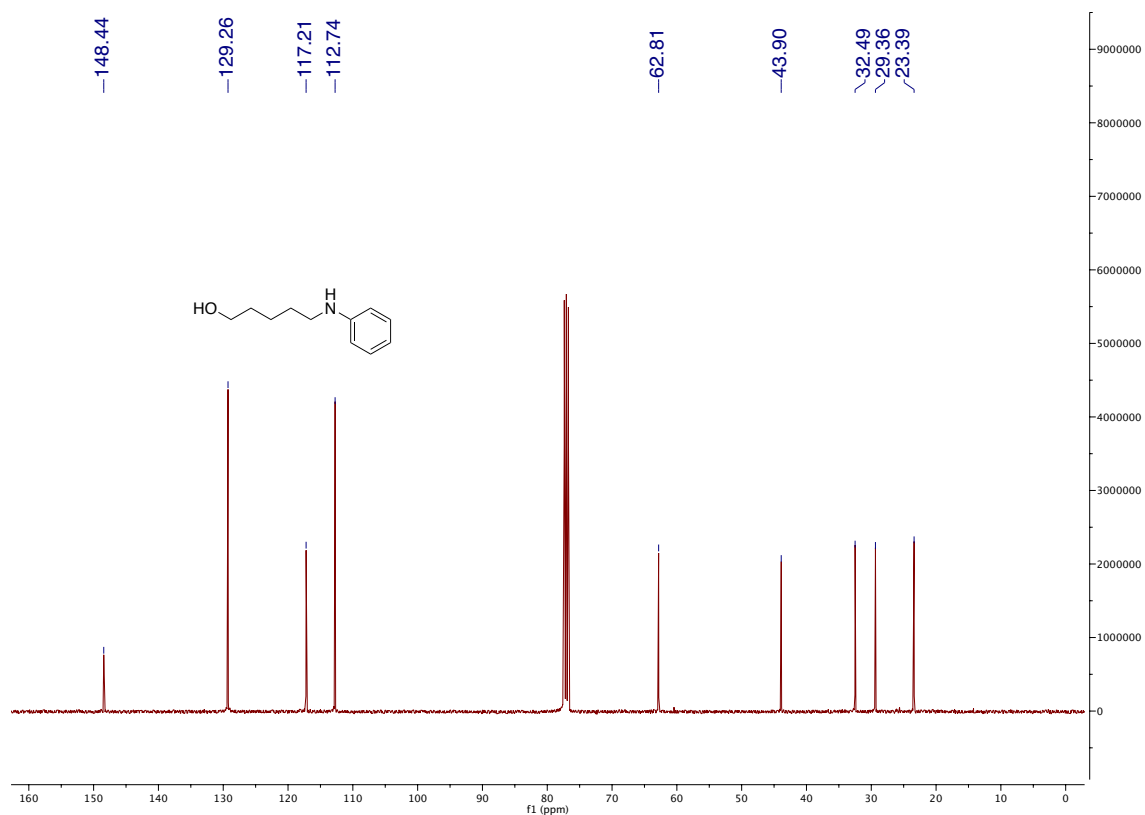
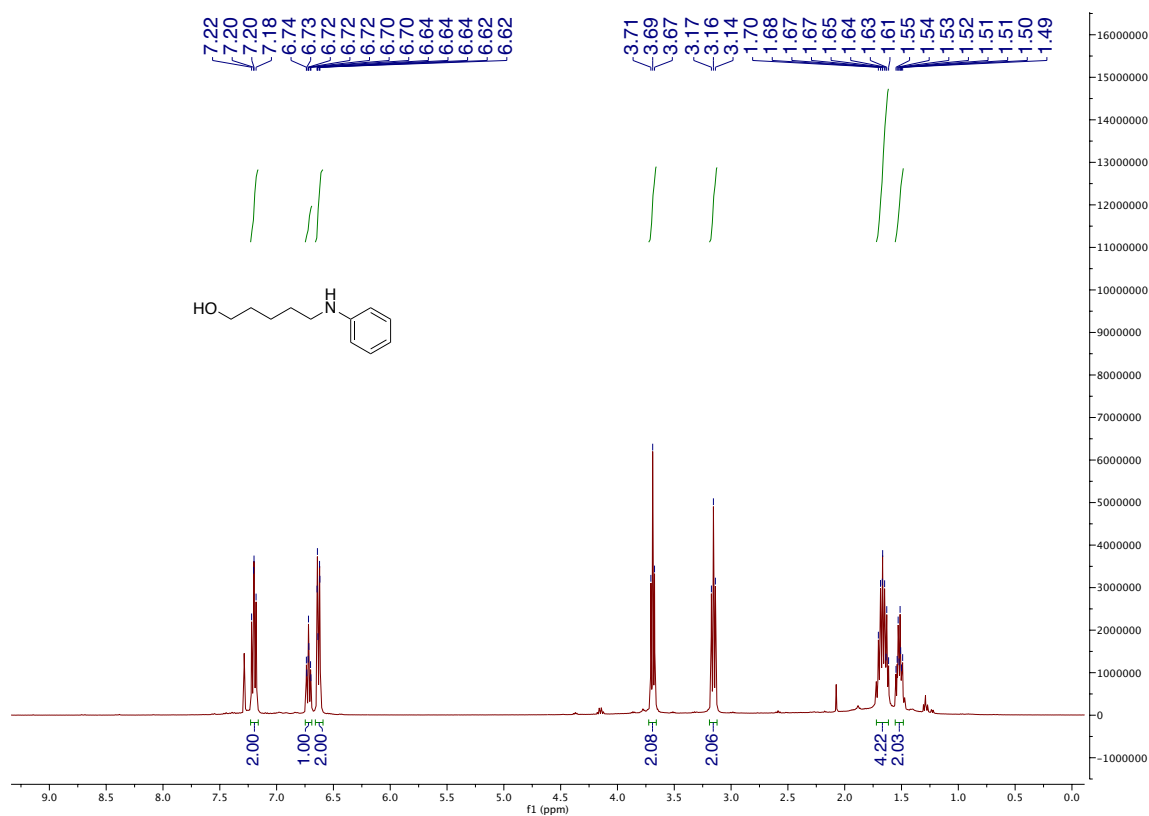


Figure S4.32. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ah** in CDCl₃.

***N*-Benzyl-2-phenylethan-1-amine (3ai)**

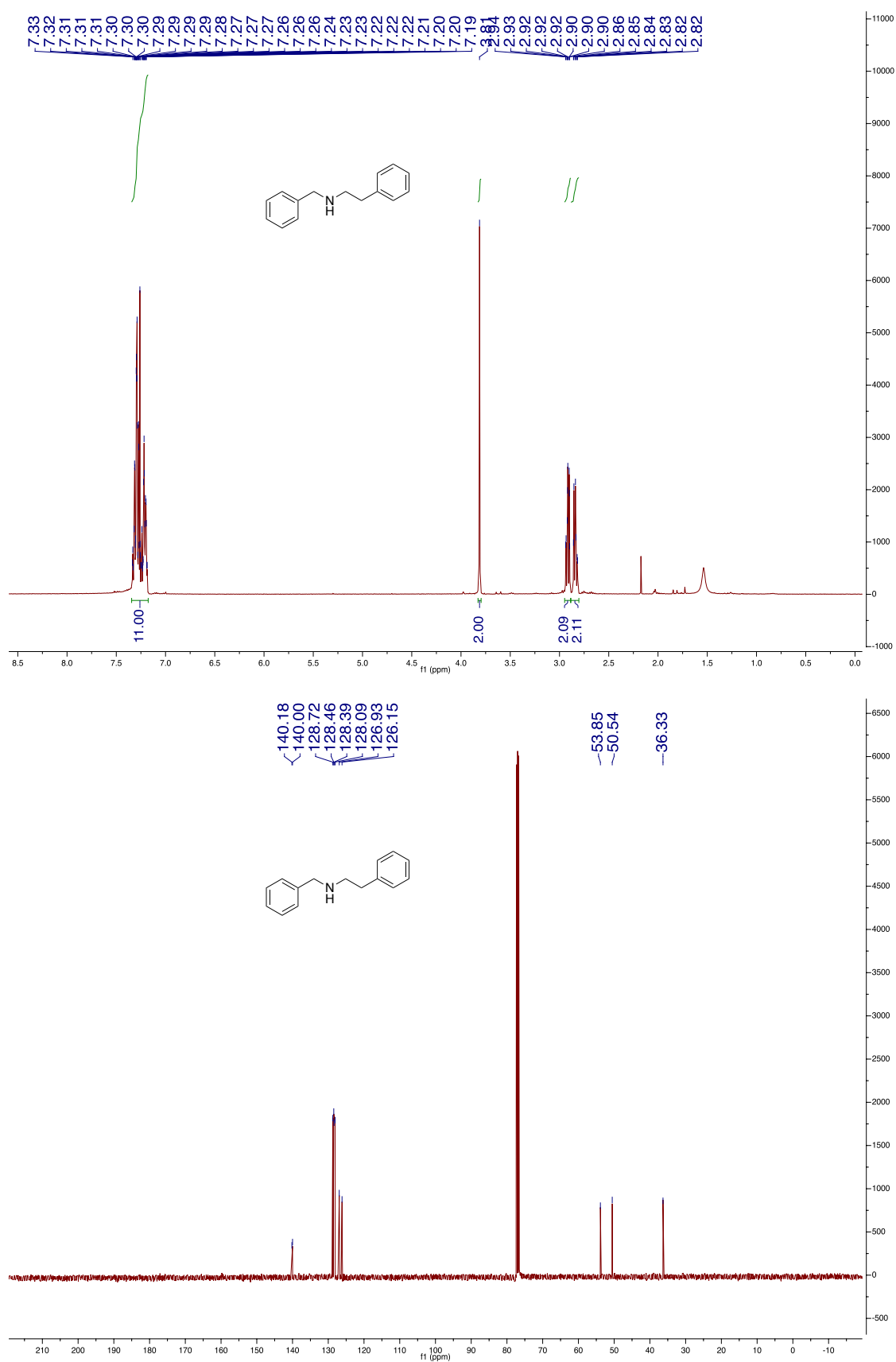


Figure S4.33. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ai** in CDCl₃.

***N*-Benzyl-3-phenylpropan-1-amine (3aj)**

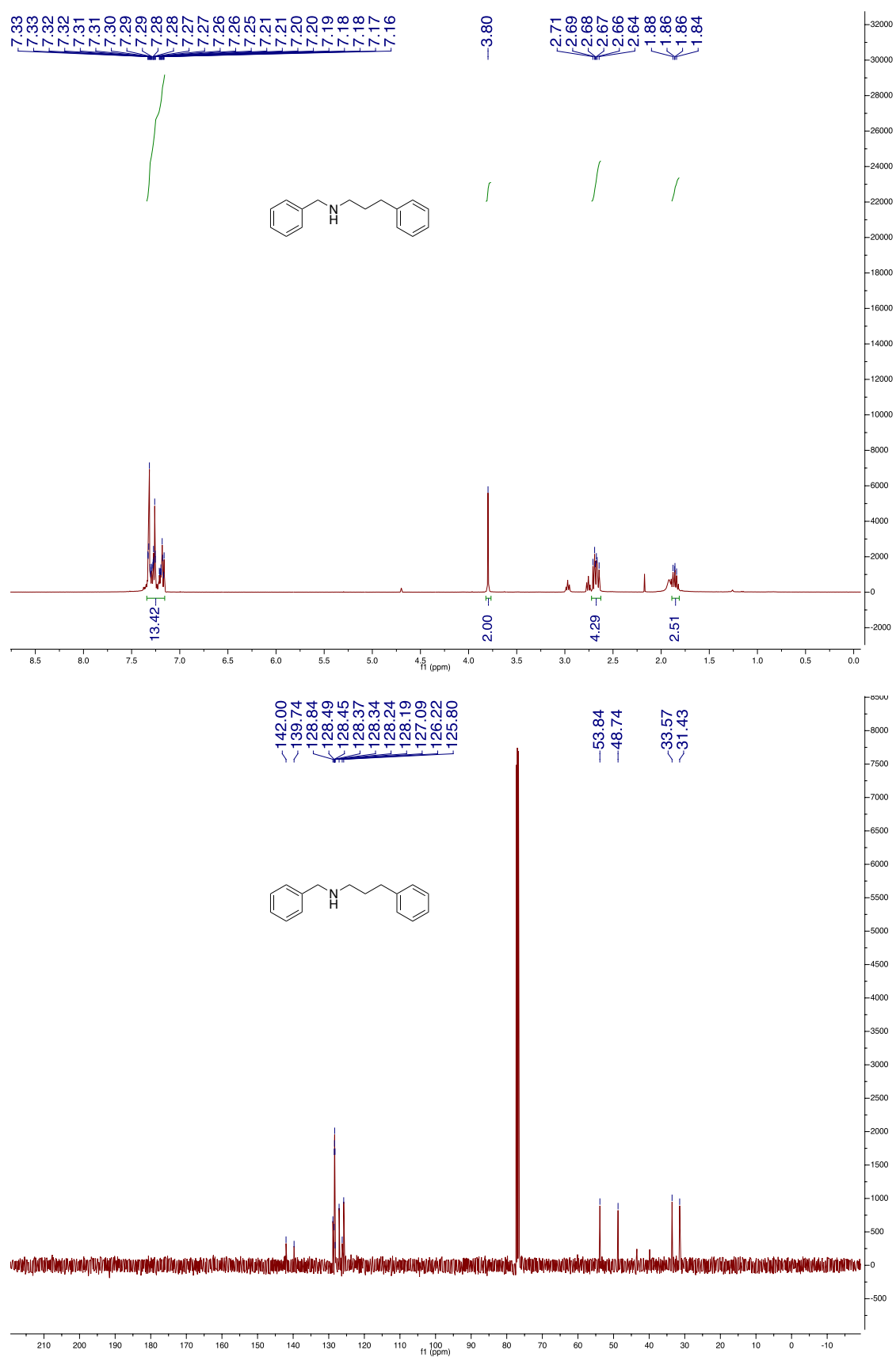


Figure S4.34. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3aj** in CDCl₃.

***N*-Benzylhexan-1-amine (3ak)**

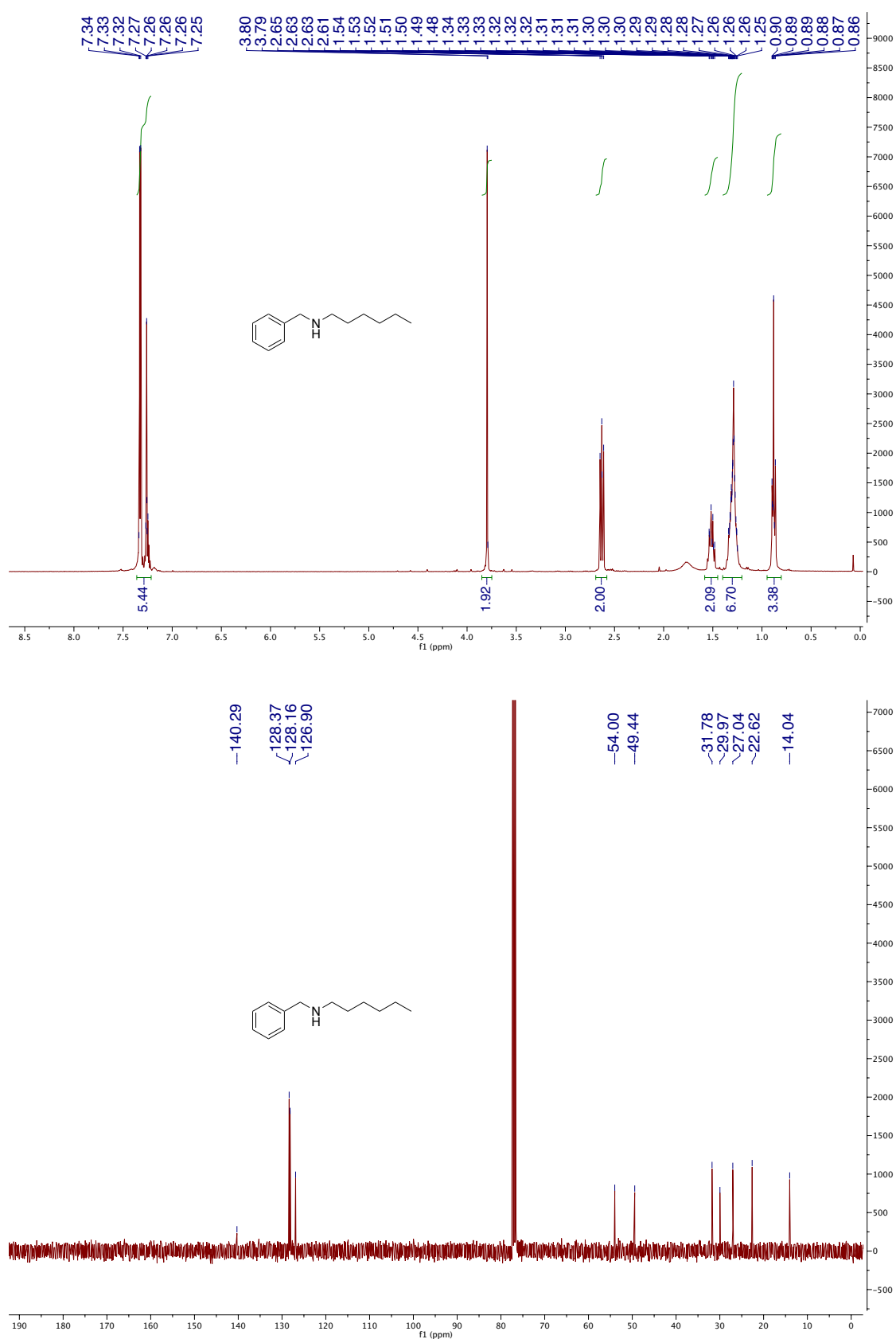


Figure S4.35. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ak** in CDCl₃.

***N*-Benzyl-*N*,4-dimethylaniline (3aI)**

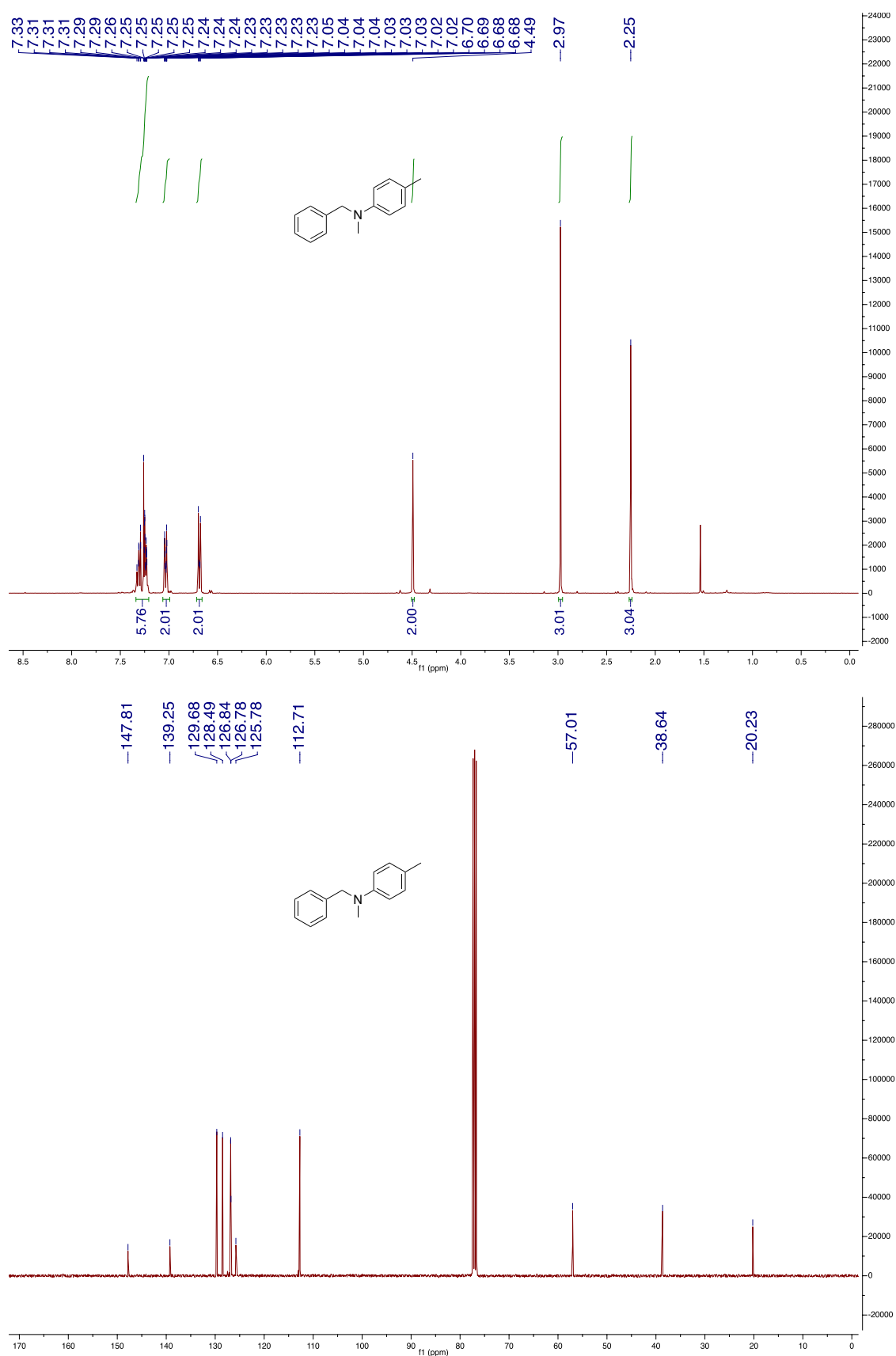


Figure S4.36. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3aI** in CDCl₃.

***N*-Methylaniline (3am)**

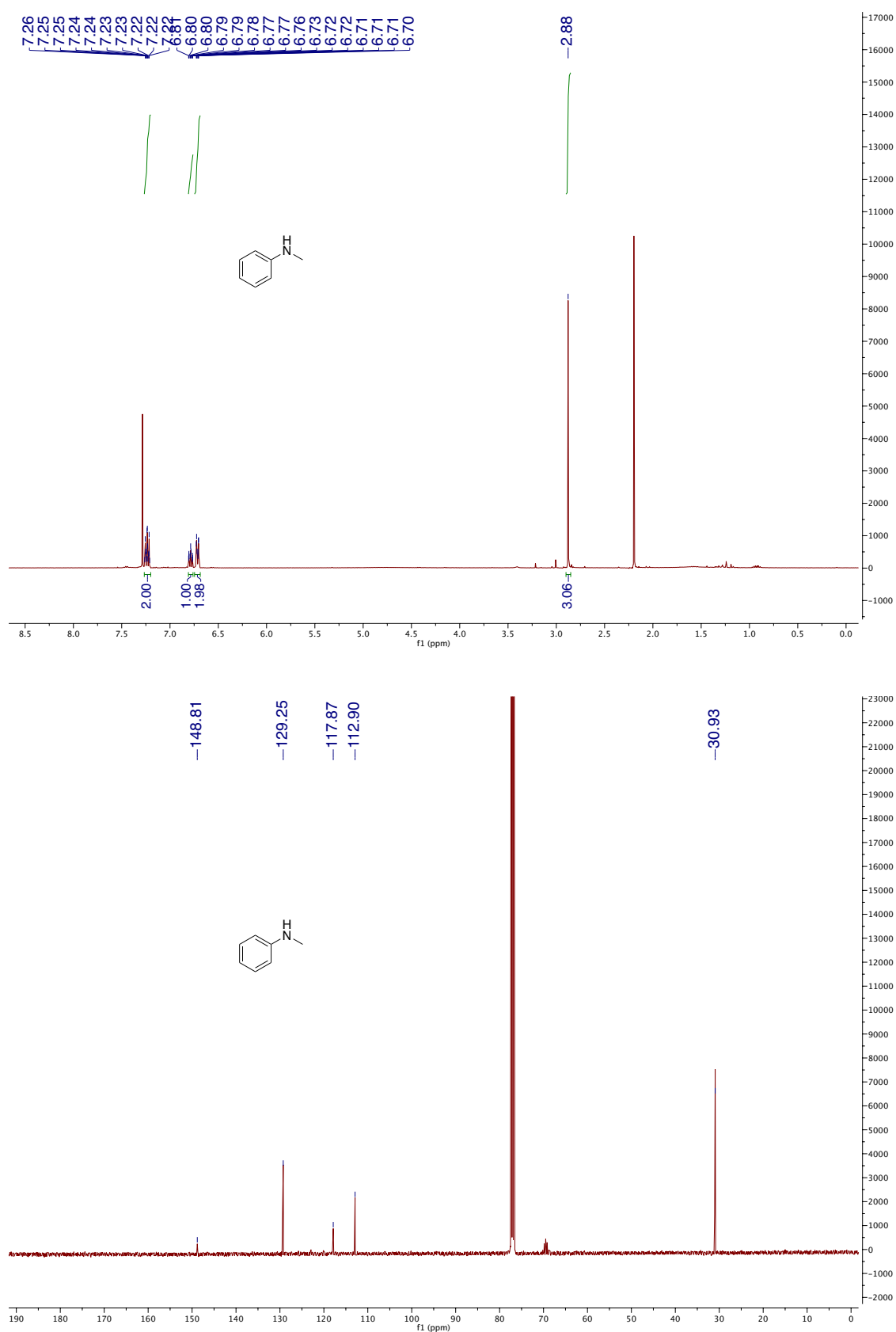


Figure S4.37. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3am** in CDCl₃.

4-Chloro-*N*-Methylaniline (3an)

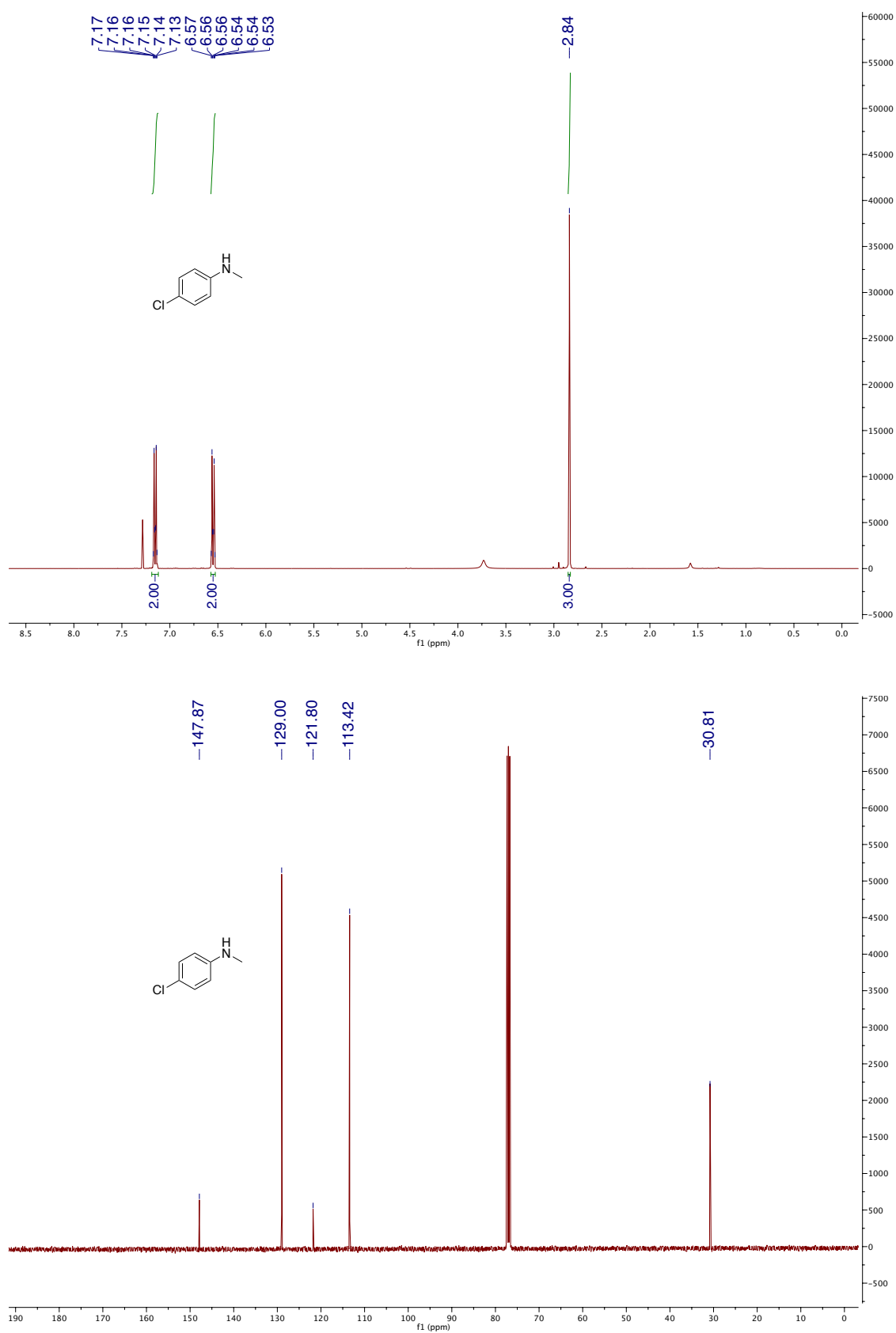


Figure S4.38. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3an** in CDCl₃.

4-Bromo-*N*-Methylaniline (3ao)

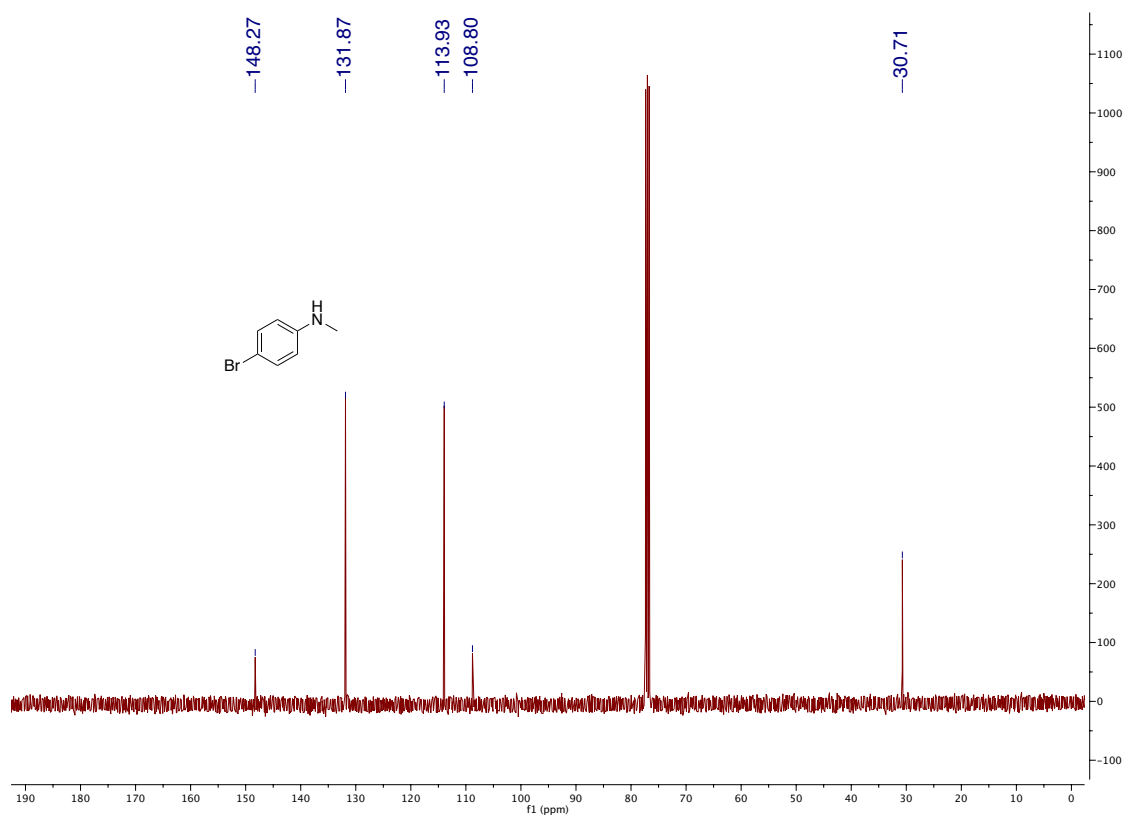
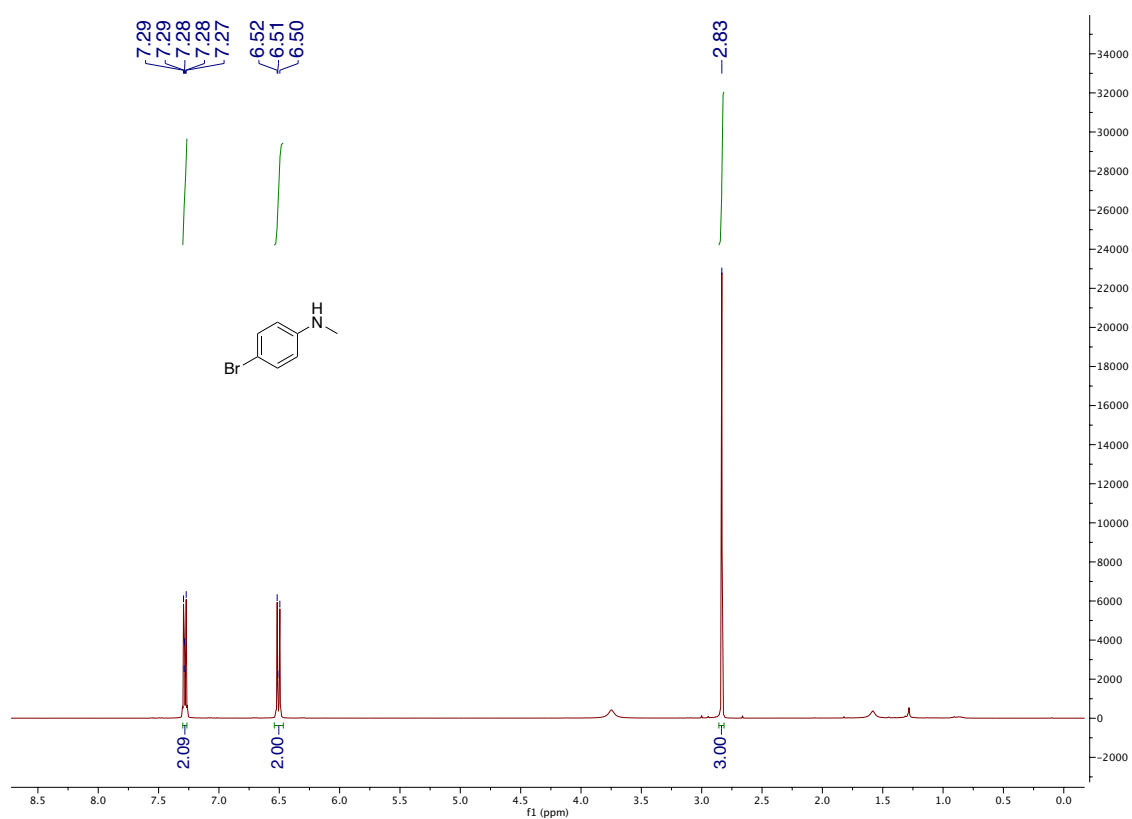


Figure S4.39. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ao** in CDCl₃.

***N*,4-Dimethylaniline (3ap)**

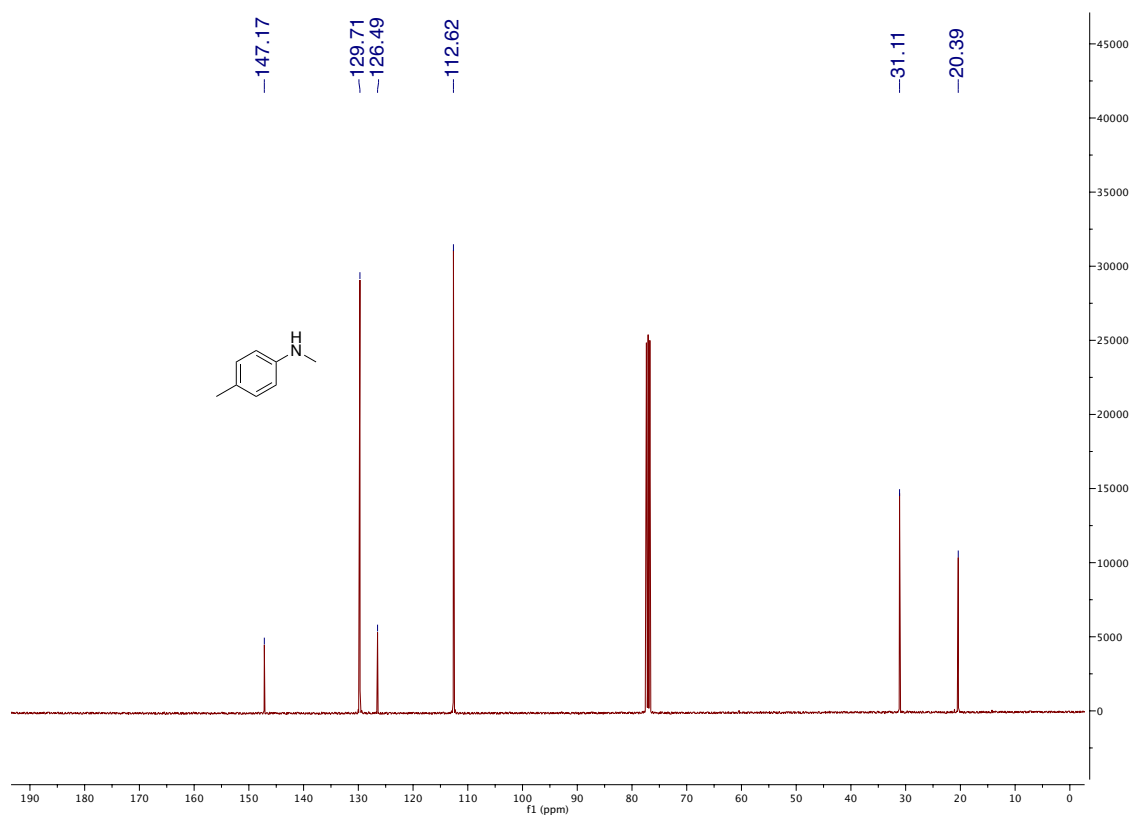
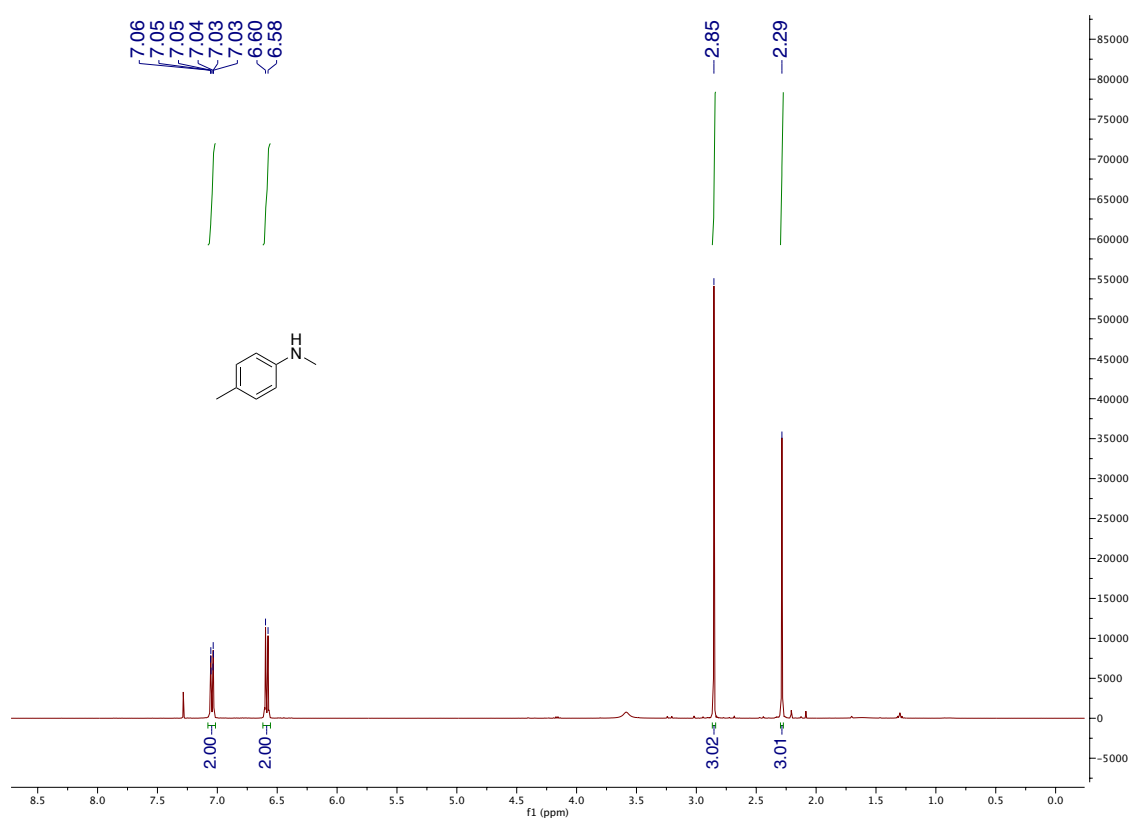


Figure S4.40. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ap** in CDCl₃.

4-Methoxy-*N*-methylaniline (3aq)

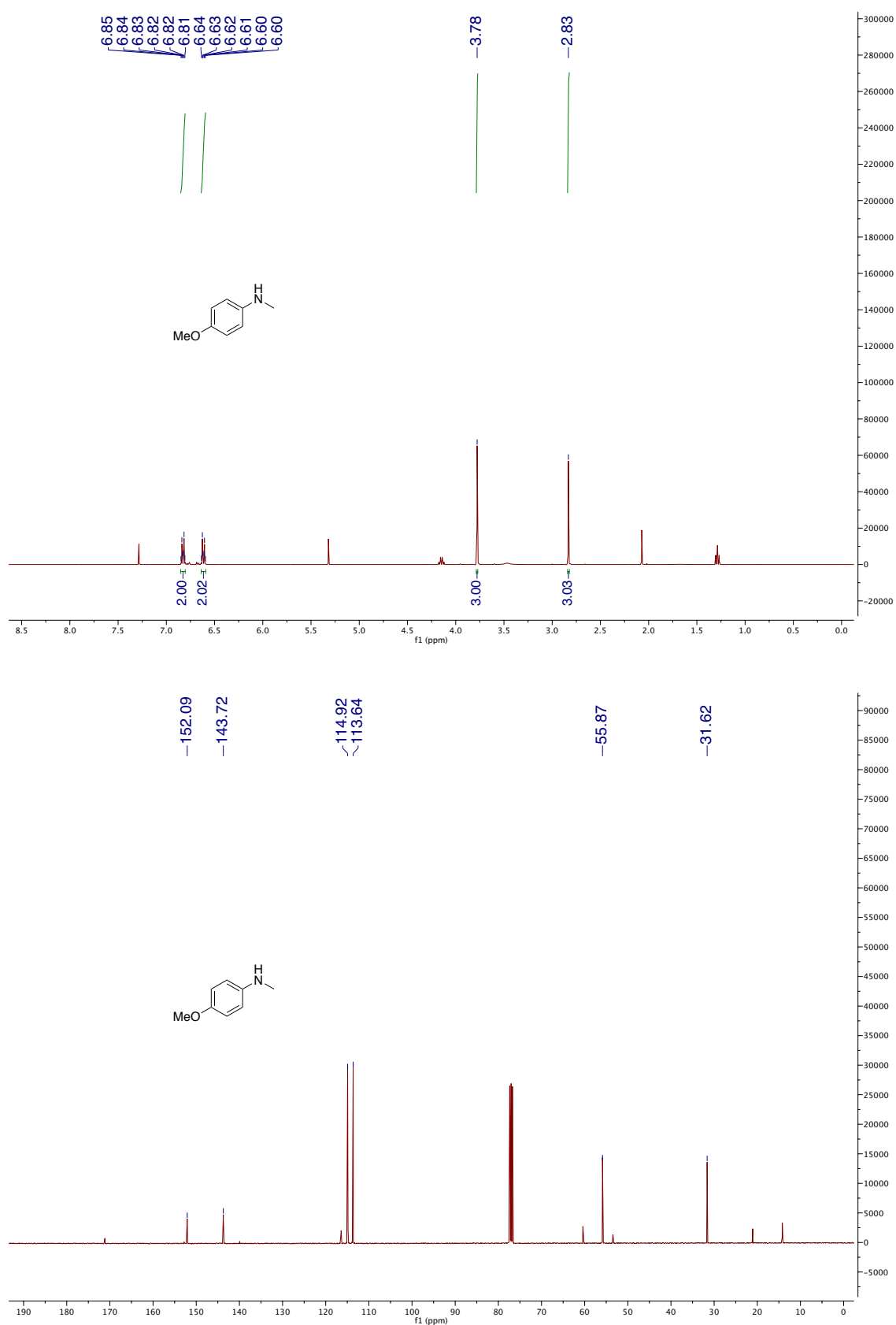


Figure S4.41. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3aq** in CDCl₃.

4-(*tert*-Butyl)-*N*-methylaniline (3ar)

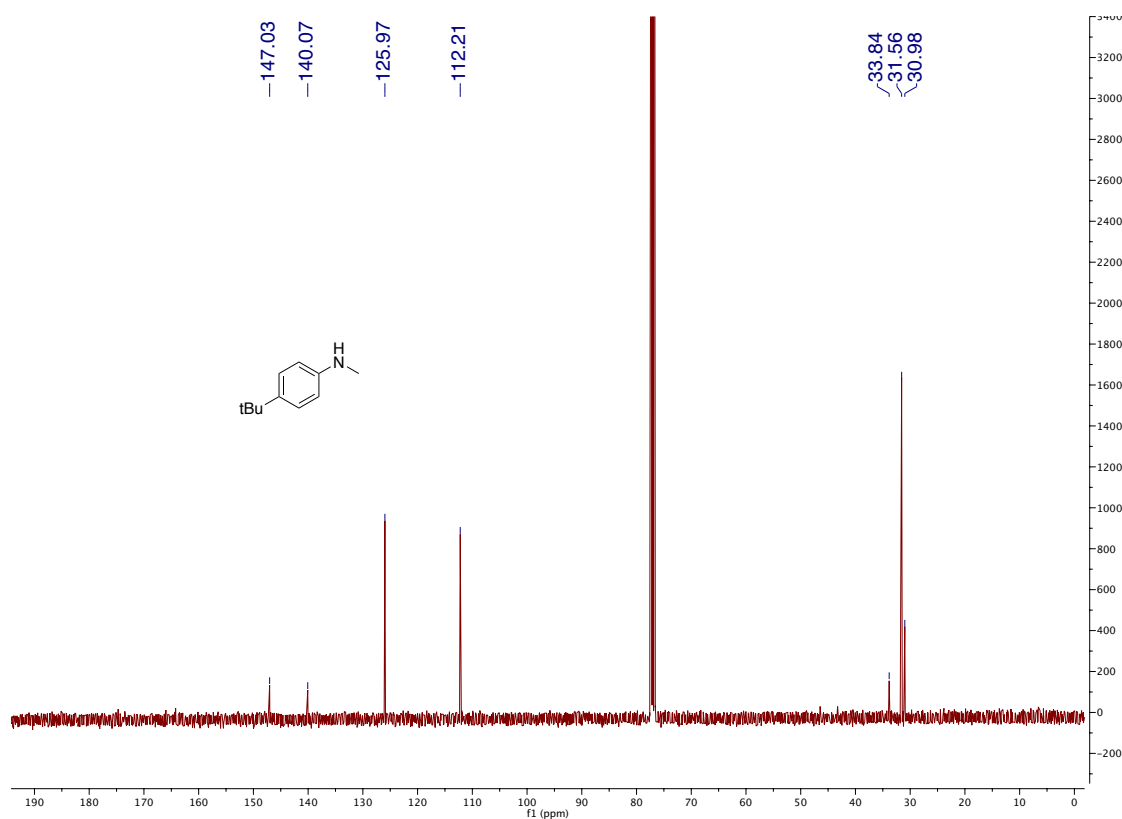
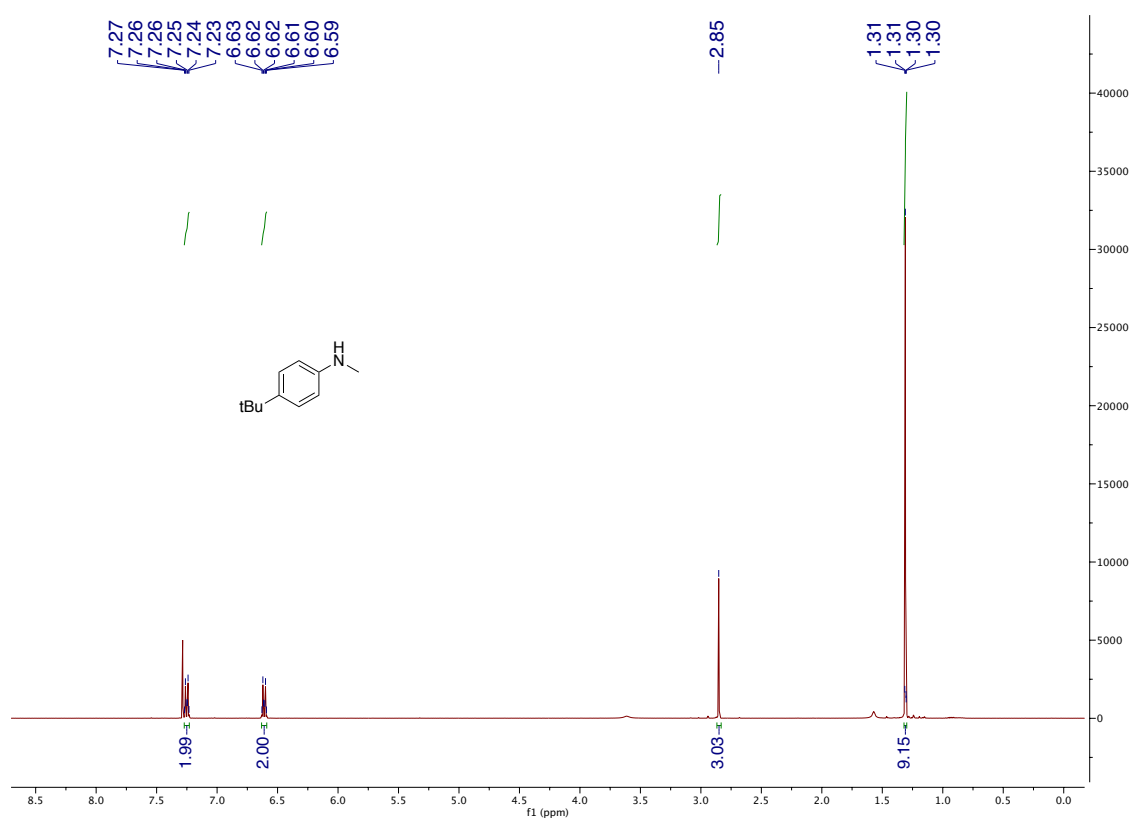


Figure S4.42. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ar** in CDCl₃.

***N*-2,4,6-tetramethylaniline (11au3as**

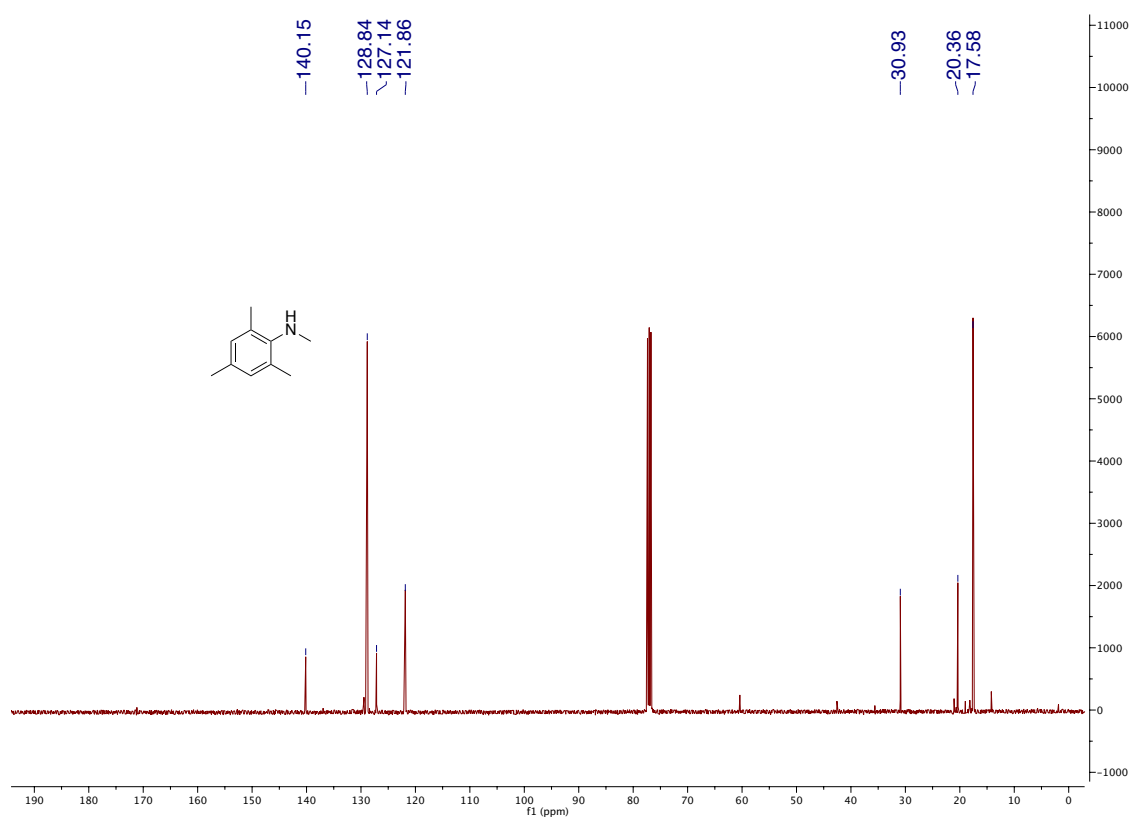
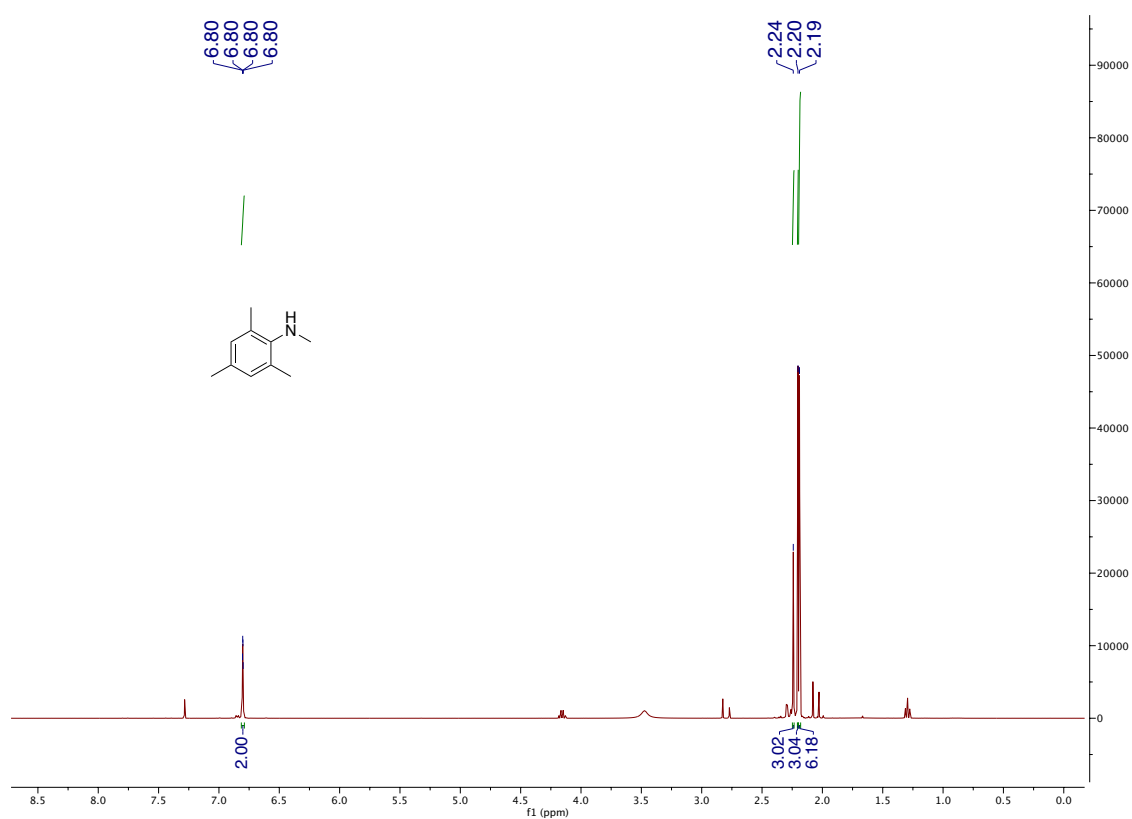


Figure S4.43. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3as** in CDCl₃.

***N,N*-dimethylaniline (3am')**

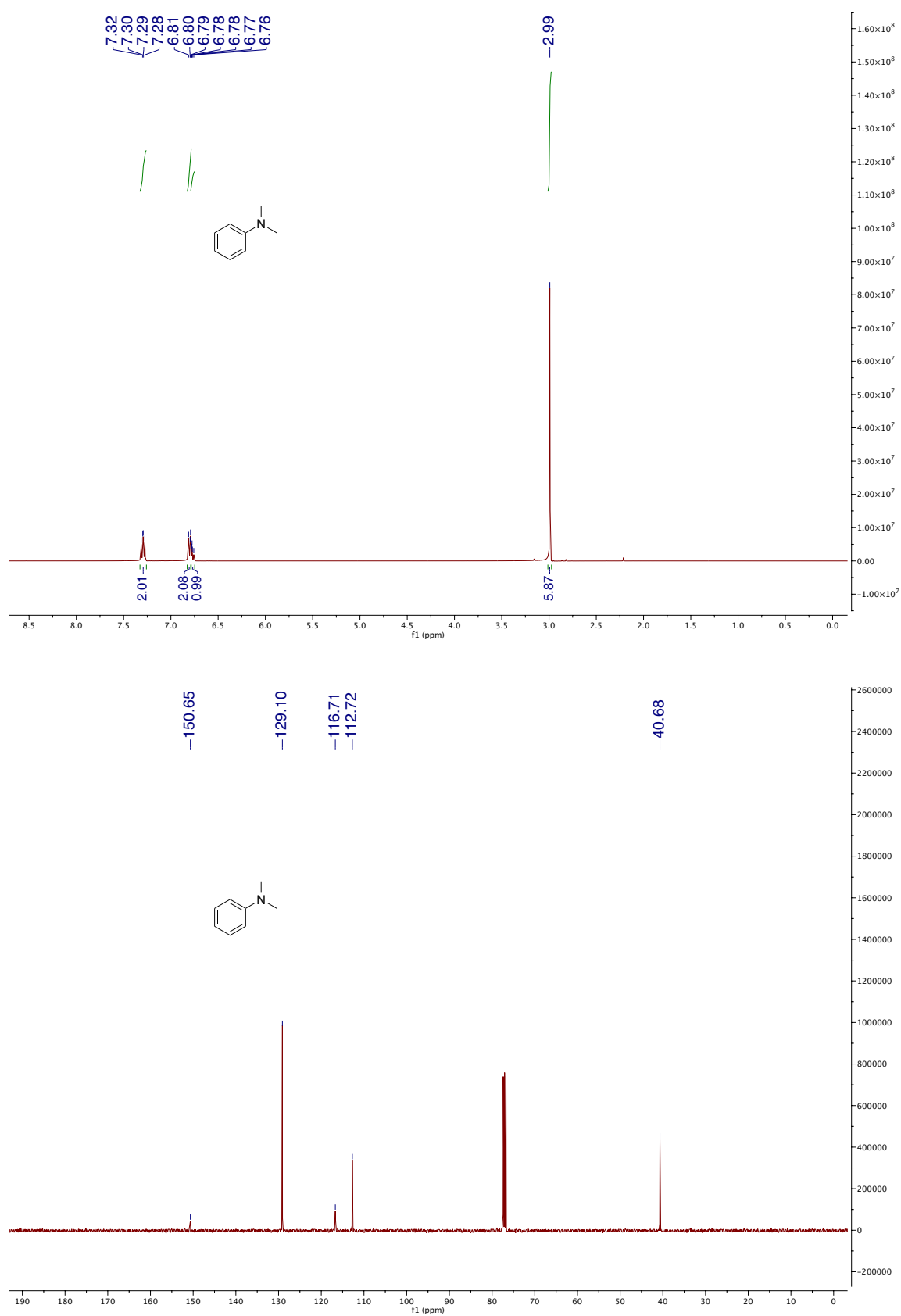


Figure S4.44. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3am'** in CDCl₃.

4-Chloro-*N,N*-dimethylaniline (3an')

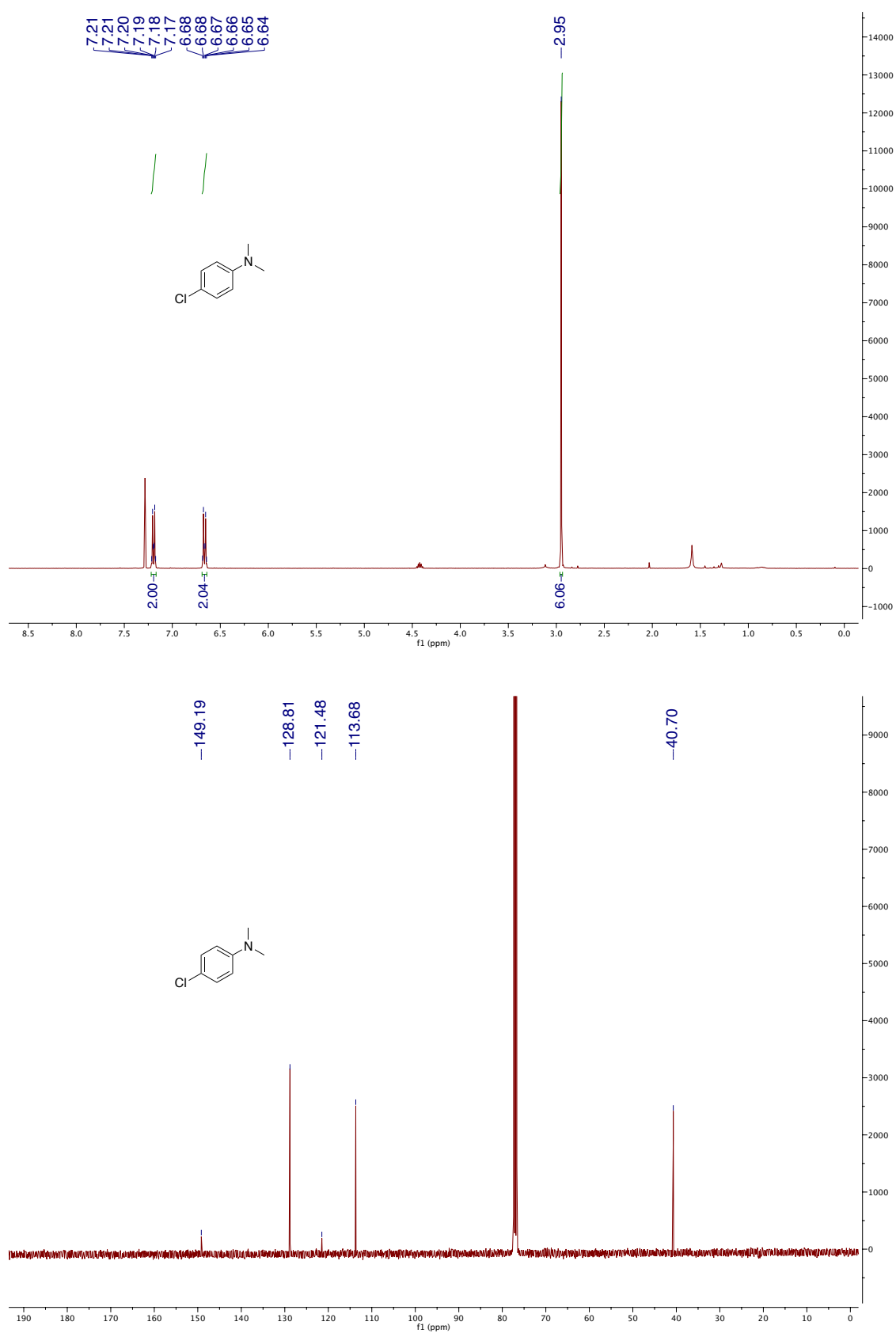


Figure S4.45. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3an'** in CDCl_3 .

4-Bromo-*N,N*-dimethylaniline (3ao')

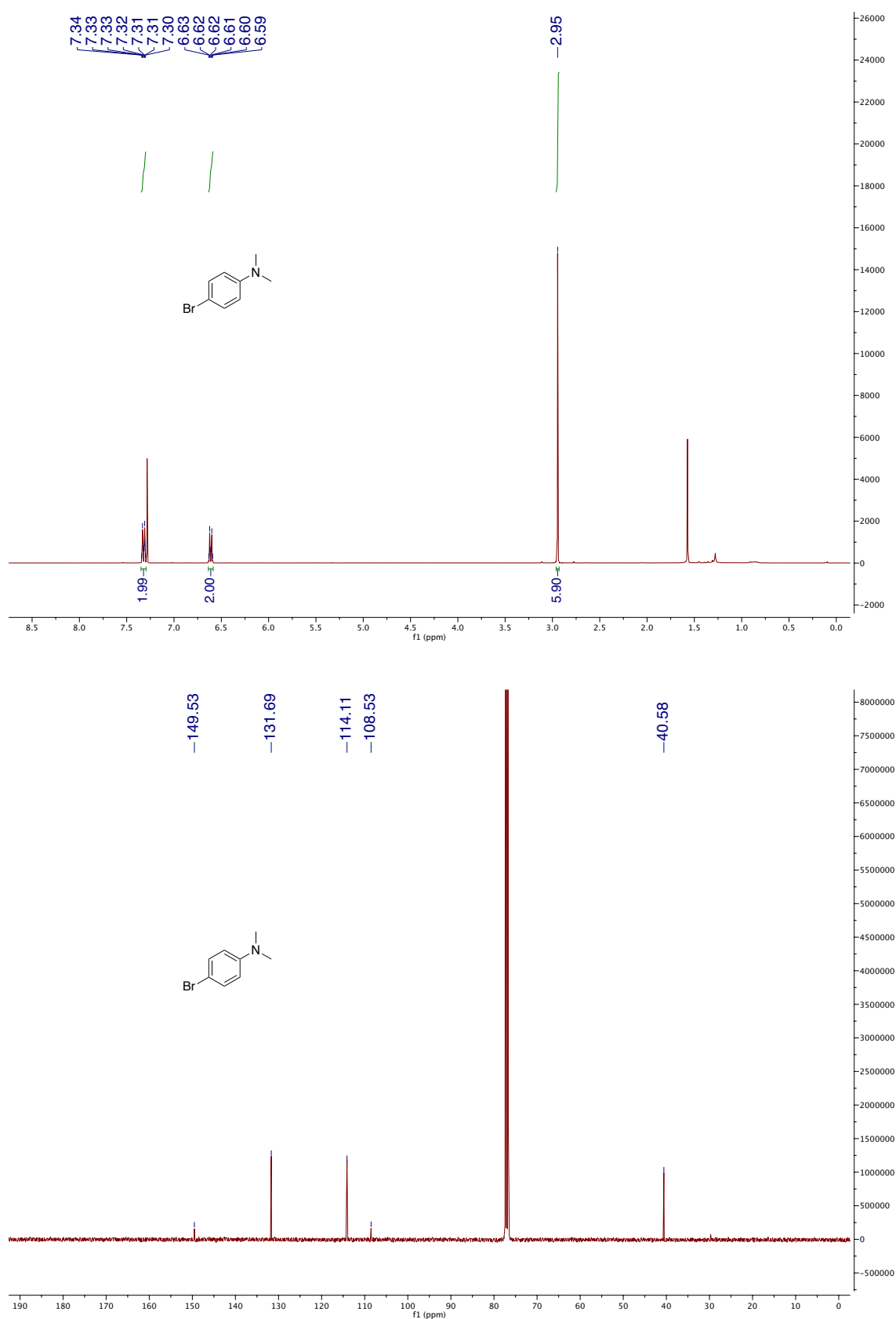


Figure S4.46. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ao'** in CDCl₃.

***N,N*,4-trimethylaniline (3ap')**

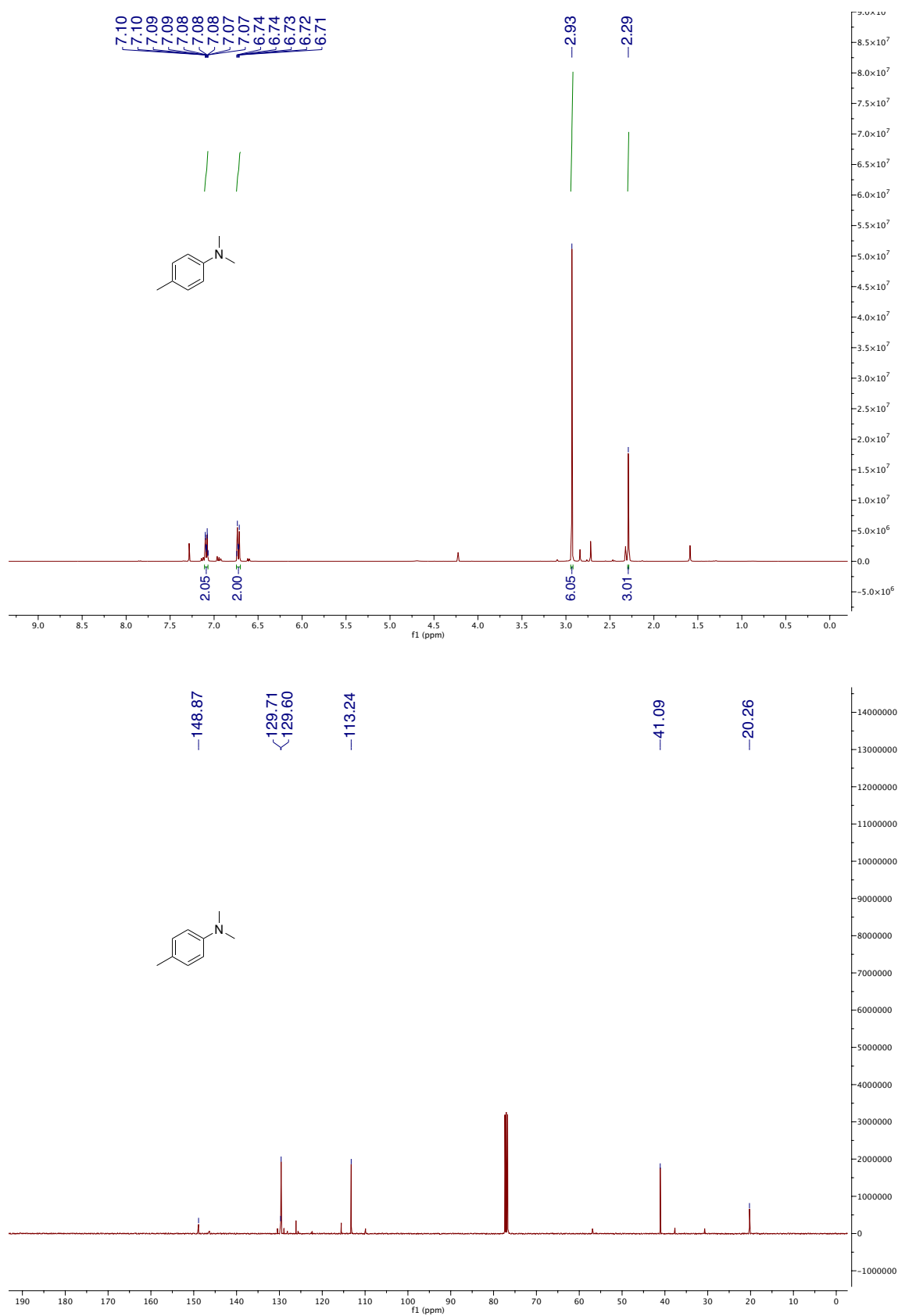


Figure S4.47. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3ap'** in CDCl_3 .

4-Methoxy-*N,N*-dimethylaniline (3aq')

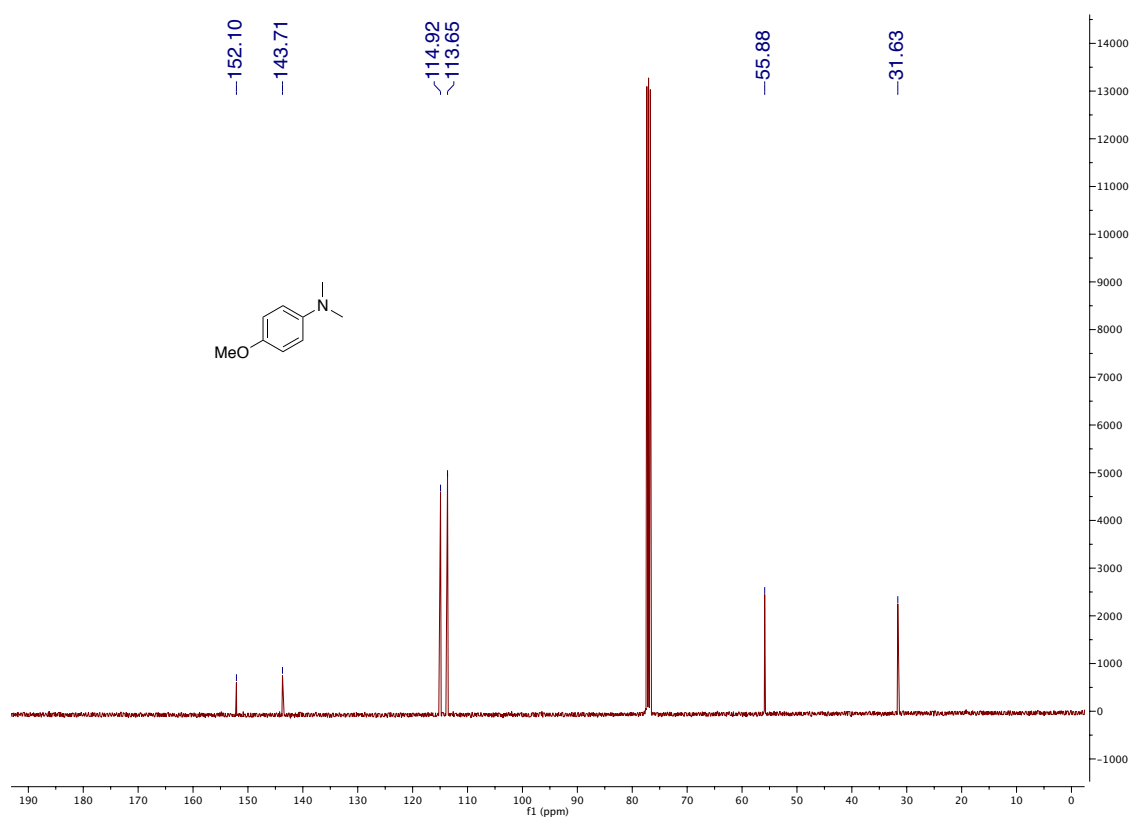
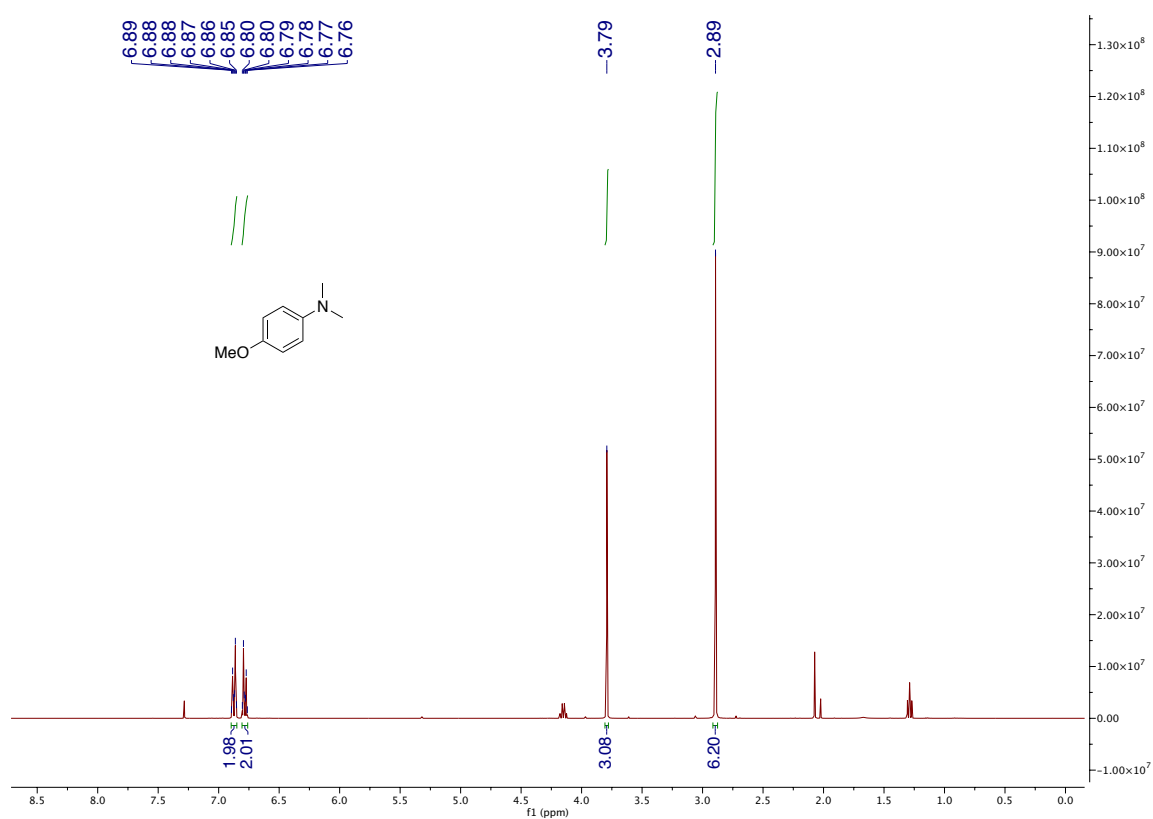


Figure S4.48. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3aq'** in CDCl₃.

4-(*tert*-Butyl)-*N,N*-dimethylaniline (3ar')

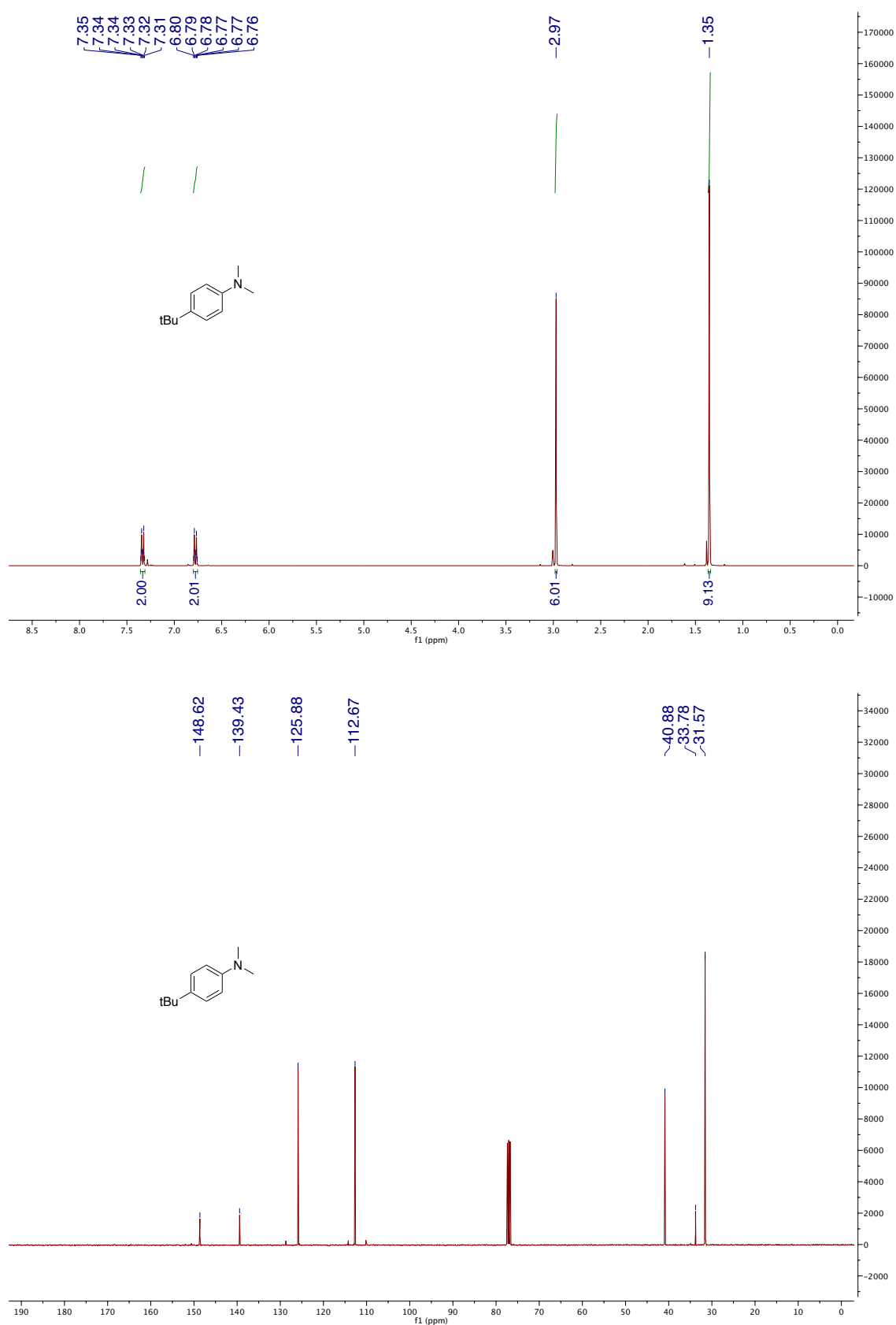


Figure S4.49. (Top) ¹H NMR (400 MHz) and (bottom) ¹³C{¹H} NMR (100 MHz) spectra of **3ar'** in CDCl₃.

***N,N*,2,4,6-pentamethylaniline (3as')**

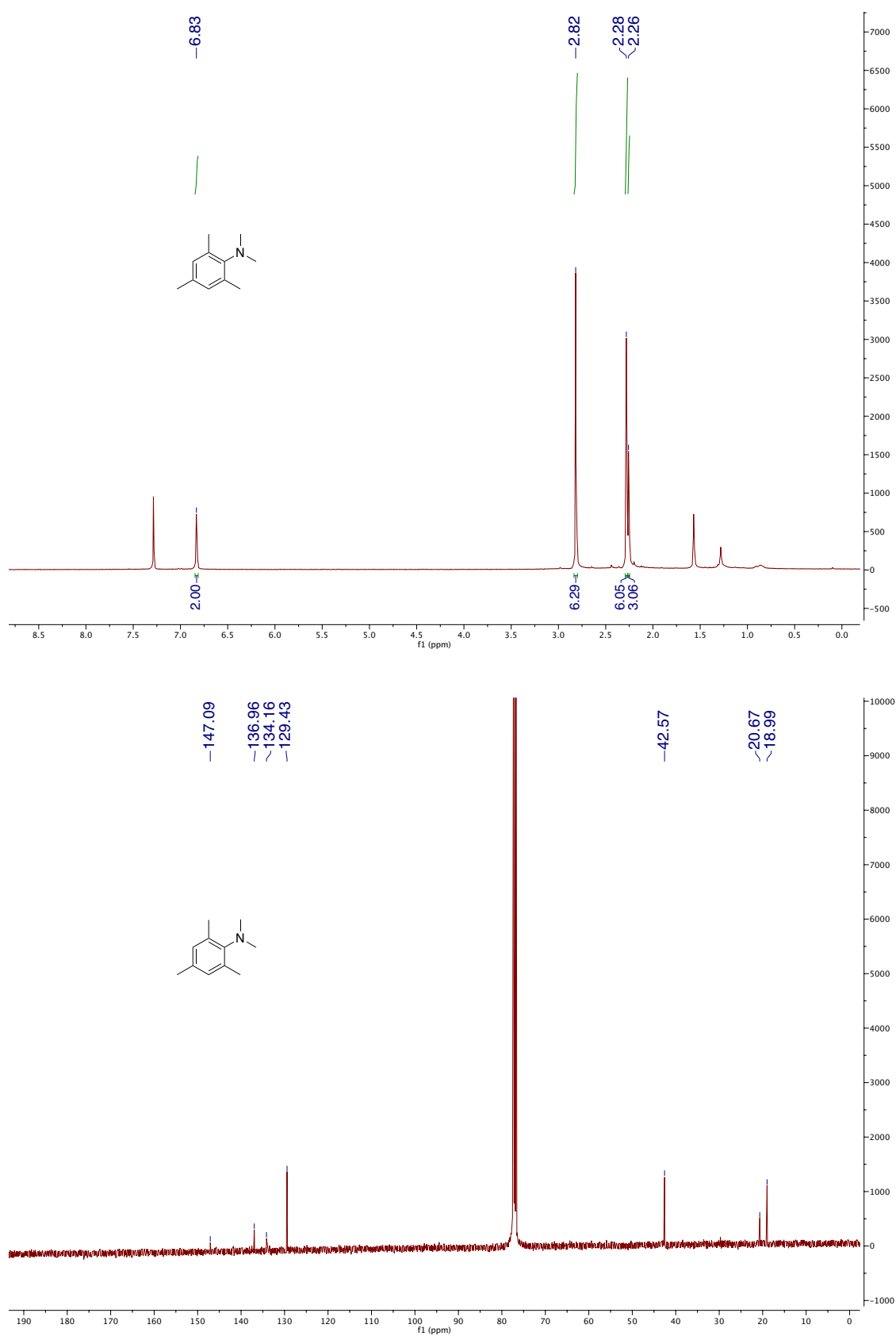


Figure S4.50. (Top) ^1H NMR (400 MHz) and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectra of **3as'** in CDCl_3 .

5. References

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