SUPPORTING INFORMATION

Palladium-catalyzed Regioselective Arylation of 1,1,3-Triaryl-2-azaallyl Anions with Aryl Chlorides

*Minyan Li, Simon Berritt, and Patrick J. Walsh**

Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, University of Pennsylvania, Department of Chemistry, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, USA.

pwalsh@sas.upenn.edu

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General Methods. All reactions were conducted under a nitrogen atmosphere with oven-dried glassware and standard Schlenk or vacuum line techniques. All solutions were handled under nitrogen and transferred via syringe. Anhydrous solvents, including CPME (cyclopentyl methyl ether) were purchased from Sigma-Aldrich and directly used without further purification. Toluene and THF were dried through activated alumina columns. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar or Matrix Scientific, and solvents were purchased from Fisher Scientific. Progress of reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with iodine or ceric ammonium molybdate (CAM) stain. Flash chromatography was performed with silica gel (230–400 mesh, Silicycle). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The infrared spectra were taken with KBr plates with a Perkin-Elmer Spectrum 100 Series spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and were uncorrected. Deactivated silica gel was prepared by addition of 15 mL of Et_3N to 1 L of silica gel.

Preparation of Ketimines : Ketimines were prepared according to literature procedures.[1]

Preparation of Aldimines : Aldimines were prepared according to literature procedures.[2]

Preparation of μ-OMs dimer 4 and NIXANTPHOS precatalyst 5: μ-OMs dimer **4** and NIXANTPHOS precatalyst **5** was prepared according to literature procedure.[3]

Procedure and Characterization for the Pd Catalyzed Arylation of Ketimines and Aldimines

General Procedure A: An oven-dried microwave vial equipped with a stir bar was charged with ketimine **1a** (54.3 mg, 0.20 mmol) under a nitrogen atmosphere in a glove box. A stock solution (prepared in the glove box) of μ-OMs dimer **4** (1.8 mg, 0.0025 mmol) and NIXANTPHOS (2.8 mg, 0.0050 mmol) in 0.5 mL anhydrous THF was added to the reaction vial via syringe. The vial was sealed with cap (with rubber septum)

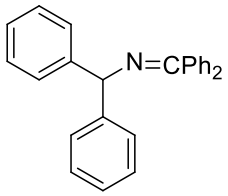
and removed from the glove box. 1-*tert*-Butyl-4-chlorobenzene **2b** (16.7 μL, 0.10 mmol)) was added dropwise by syringe to this solution through the rubber septum. While the reaction mixture was stirred at 60 °C in an oil bath, a solution of $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) in 0.5 mL anhydrous THF was added portionwise by syringe (0.05 mL every 30 min) through the rubber septum. The reaction mixture was stirred for 6 h in total, opened to air, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in *vacuo*. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography (hexanes to diethyl ether: hexanes = 1:50) to give the product (34.7 mg, 86% yield) as a white solid.

General Procedure B: An oven-dried microwave vial equipped with a stir bar was charged with ketimine **1a** (54.3 mg, 0.20 mmol) and NIXANTPHOS precatalyst **5** (9.3 mg, 0.010 mmol) under a nitrogen atmosphere in a glove box. Anhydrous THF (0.5 mL) was added to the reaction vial via syringe. The vial was sealed with cap (with rubber septum) and removed from the glove box. 1-*tert*-Butyl-4-chlorobenzene **2b** (16.7 μL, 0.10 mmol) was added dropwise by syringe to this solution through the rubber septum. While the reaction mixture was stirred at 23 °C, a solution of $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) in 0.5 mL anhydrous THF was added portionwise by syringe (0.1 mL every 30 min) through the rubber septum. The reaction mixture was stirred for 14 h in total, opened to air, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in *vacuo*. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography (hexanes to diethyl ether: hexanes = 1:50) to give the product (32.6 mg, 81% yield) as a white solid.

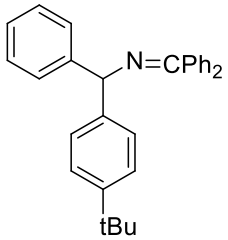
General Procedure C: Sequential One-Pot Ketimine Synthesis/Arylation

An oven-dried 50 mL Schlenk tube equipped with a stir bar was sealed with a rubber septum and was connected to a Schlenk line, evacuated, and refilled with nitrogen (repeated three times). Anhydrous THF (10 mL) was added under nitrogen via syringe through the rubber septum. 4-(Aminomethyl)pyridine (0.65 g, 6.0 mmol) and benzophenone imine (1.09 g, 6.0 mmol) were added under nitrogen via syringe through the rubber septum. The reaction was placed in an oil bath at 50 °C. After stirring for 12 h at 50 °C, the solvent was completely removed in *vacuo* and the tube was filled with nitrogen. A stock solution (prepared in the

glove box) of μ-OMs dimer **4** (27 mg, 0.0375 mmol) and NIXANTPHOS (42 mg, 0.0750 mmol) under nitrogen in 10 mL anhydrous THF was taken up by syringe and added to the Schlenk tube through the rubber septum. A stock solution (prepared in the glove box) of 6-chloroquinoline (0.49 g, 3 mmol) in 5 mL anhydrous THF was added to the Schlenk tube via syringe through the rubber septum. While the reaction mixture was stirred at 60 °C in an oil bath, a solution of $LiN(SiMe_3)_2$ (1.51 g, 9 mmol) in 15 mL anhydrous THF was added portionwise by syringe (3 mL every 30 min) through the rubber septum. The reaction mixture was stirred for 6 h in total, opened to air, and quenched with 10 mL of H_2O. The layers were separated and the aqueous layer was extracted with DCM (3X5 mL). The combined organic layers were concentrated in *vacuo*. The crude material was loaded onto a deactivated silica gel column via pipette and purified by flash chromatography (eluted with ethyl acetate: hexanes = 1:5 to ethyl acetate: methanol = 120:1) to give the product **3em** (1.02 g, 85% yield) as thick colorless oil.

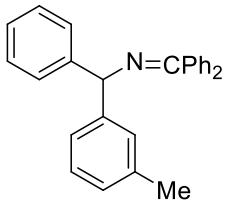


3aa – *N*-(diphenylmethylene)-1, 1-diphenylmethanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3aa** (31.3 mg, 90% yield, arylation of **1a**) or (33.0 mg, 95% yield, arylation of **1a'**) as a white solid. Room temperature synthesis of **3aa** was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3aa** (28.8 mg, 83% yield, arylation of **1a**) or (29.2 mg, 84% yield, arylation of **1a'**) as a white solid. R_f = 0.70 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]

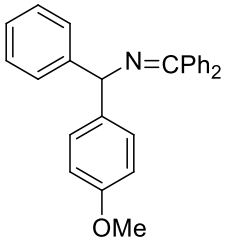


3ab – 1-(4-(*tert*-Butyl) phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2b** (16.7 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ab** (34.7 mg, 86% yield, arylation of **1a**) or

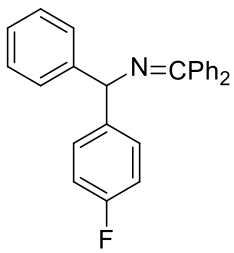
(36.7 mg, 91% yield, arylation of **1a'**) as a white solid. Room temperature synthesis of **3ab** was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2b** (16.7 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ab** (32.6 mg, 81% yield, arylation of **1a**) or (34.3 mg, 85% yield, arylation of **1a'**) as a white solid. R_f = 0.75 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]



3ac – *N*-(diphenylmethylene)-1-phenyl-1-(*m*-tolyl)methanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2c** (11.8 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ac** (27.8 mg, 77% yield) as a white solid. R_f = 0.75 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]



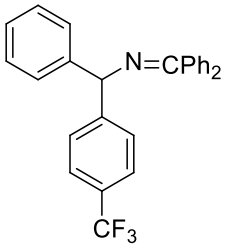
3ad – *N*-(diphenylmethylene)-1-(*p*-methoxyphenyl)-1-phenylmethanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.2 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2d** (12.3 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product **3ad** (22.6 mg, 60% yield) as a thick oil. R_f = 0.55 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]



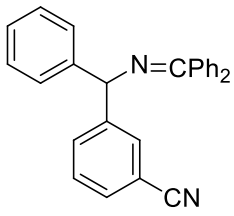
3ae – *N*-(diphenylmethylene)-1-(*p*-fluorophenyl)-1-phenylmethanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2e** (10.7 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ae** (28.1 mg, 77% yield, arylation of **1a**) or (30.7 mg, 84% yield, arylation of **1a'**) as a white solid. Room temperature synthesis of **3ae** was performed

following General Procedure B with ketamine **1a**, $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2e** (10.7 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ae** (25.9 mg, 71% yield) as a white solid. R_f = 0.70 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]

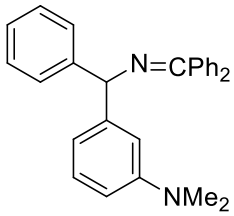
3af –*N*-(diphenylmethylene)-1-phenyl-1-(*p*-(trifluoromethyl)phenyl)methanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2f** (14.0 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3af** (36.1 mg, 87% yield, arylation of **1a**) or (35.2 mg, 85% yield, arylation of **1a'**) as a colorless oil. Room temperature synthesis of **3af** was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol) or aldimine **1a'** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2f** (14.0 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3af** (35.2 mg, 85% yield, arylation of **1a**) or (36.9 mg, 89% yield, arylation of **1a'**) as a colorless oil. R_f = 0.77 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]



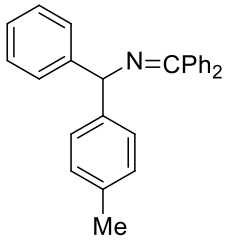
3ag –3-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2g** (13.8 mg, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:5) to give the product **3ag** (33.9 mg, 91% yield) as colorless oil. R_f = 0.39 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.73 (m, 2H), 7.67 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.48–7.39 (m, 5H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.29–7.27 (m, 4H), 7.23–7.10 (m, 1H), 7.03 (dd, *J* = 7.0, 1.5 Hz, 2H), 5.55 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 168.3, 146.6, 143.9, 139.5, 136.5, 132.2, 131.4, 130.7, 130.6, 129.3, 128.9, 128.8, 128.7, 128.3, 127.7, 127.6, 127.4, 119.3, 112.5, 69.3 ppm; IR (thin film): 3060, 2229, 1623, 1597, 1578, 1490, 1446, 1315, 1289, 1028, 781, 697 cm^{-1}; HRMS calc'd for $C_{27}H_{21}N_2^+$ 373.1705, observed 373.1701 $[MH]^+$.



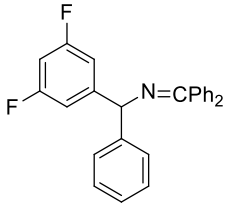
3ah–3-(((diphenylmethylene)amino)(phenyl)methyl)-*N*,*N*-dimethylaniline:



The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2h** (14.0 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:10) to give the product **3ah** (23.8 mg, 61% yield) as colorless oil. R_f = 0.42 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ7.75–7.74 (m, 2H), 7.41–7.39 (m, 3H), 7.35–7.30 (m, 5H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.17–7.13 (m, 2H), 7.10–7.08 (m, 2H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.51 (s, 1H), 2.87 (s, 6H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.8, 150.9, 145.8, 145.3, 140.2, 137.0, 130.1, 129.2, 129.0, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 126.7, 116.5, 112.3, 111.3, 70.5, 40.9 ppm; IR (thin film): 3058, 1600, 1577, 1492, 1445, 780, 696 cm^{-1}; HRMS calc'd for $C_{26}H_{26}N_2Na^+$ 391.2150, observed 391.2155 $[M+Na]^+$

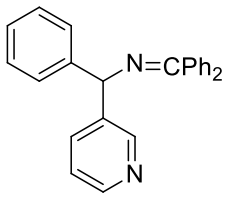


3ai – *N*-(diphenylmethylene)-1-phenyl-1-(*p*-tolyl)methanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2i** (11.8 μL, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ai** (31.1 mg, 86% yield) as a white solid. Compound **3ai** was also synthesized following General Procedure A with ketamine **1b** (57.1 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3ai** (31.1 mg, 86% yield) as a white solid. R_f = 0.77 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]

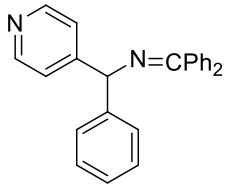


3aj – 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine: The reaction was performed following General Procedure A with ketamine **1a** (54.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2j** (11.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3aj** (31.1 mg, 81% yield) as a white solid. Compound **3aj** was also synthesized following General Procedure A

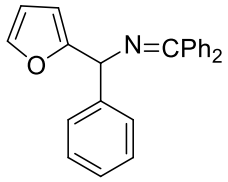
with ketamine **1c** (61.4 mg, 0.2 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product **3aj** (33.7 mg, 88% yield) as a white solid. R_f = 0.80 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]



3da – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine: The reaction was performed following General Procedure A with ketamine **1d** (54.5 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:10 to diethyl ether:hexanes = 2.5:1) to give the product **3da** (20.9 mg, 60% yield) as a white solid. R_f = 0.30 (diethyl ether:hexanes = 2.5:1). The NMR spectral data match the previously published data.[4]

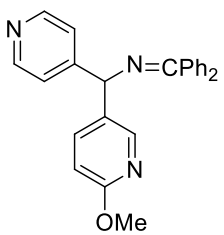


3ea – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine: The reaction was performed following General Procedure A with ketamine **1e** (54.5 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:10 to diethyl ether:hexanes = 2:1) to give the product **3ea** (31.7 mg, 91% yield) as a white solid. R_f = 0.33 (diethyl ether:hexanes = 2:1). The NMR spectral data match the previously published data.[4]

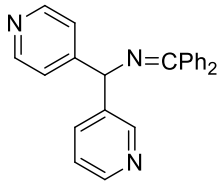


3fa – *N*-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine: The reaction was performed following General Procedure A with ketamine **1i** (52.3 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2a** (10.2 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product **3ia** (20.3 mg, 60% yield) as a white solid. R_f = 0.70 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[4]

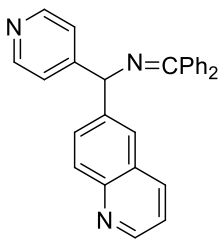
3ek –*N*-(diphenylmethylene)-1-(6-methoxypyridin-3-yl)-1-(pyridin-4-yl)methanamine: The reaction was performed following General Procedure A with ketamine **1e** (54.5 mg, 0.20 mmol) or aldimine **1e'** (54.5 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2k** (12.0 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude



material was purified by flash chromatography on deactivated silica gel (eluted with ethyl acetate: hexanes = 1:5 to ethyl acetate: methanol = 120:1) to give the product **3ek** (26.5 mg, 70% yield, arylation of **1e**) or (26.9 mg, 71% yield, arylation of **1e'**) as thick colorless oil. R_f = 0.26 (ethyl acetate:methanol = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (dd, *J* = 4.5, 1.5 Hz, 2H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.74–7.72 (m, 2H), 7.56 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.48–7.40 (m, 4H), 7.36 (t, *J* = 7.0 Hz, 3H), 7.26–7.24 (m, 2H), 7.07–7.04 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.47 (s, 1H), 3.91 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 168.9, 163.7, 153.1, 150.1, 145.6, 139.3, 138.6, 136.4, 131.9, 130.8, 129.1, 128.9, 128.4, 127.6, 122.5, 111.4, 66.2, 53.6 ppm; IR (thin film): 3021, 1604, 1571, 1490, 1291, 1026, 783, 696 cm^{-1}; HRMS calc'd for $C_{25}H_{22}N_3O^+$ 380.1763, observed 380.1769 $[MH]^+$.



3el –*N*-(diphenylmethylene)-1-(pyridin-3-yl)-1-(pyridin-4-yl)methanamine: The reaction was performed following General Procedure A with ketamine **1e** (54.5 mg, 0.20 mmol) or aldimine **1e'** (54.5 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2l** (9.6 μL, 0.10 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with ethyl acetate: hexanes = 1:5 to ethyl acetate:methanol = 120:1) to give the product **3el** (27.2 mg, 78% yield, arylation of **1e**) or (28.6 mg, 82% yield, arylation of **1e'**) as thick colorless oil. R_f = 0.31 (ethyl acetate:methanol = 20:1). The NMR spectral data match the previously published data.[4]



3em –*N*-(diphenylmethylene)-1-(pyridin-4-yl)-1-(quinolin-6-yl)methanamine: The reaction was performed following General Procedure A with ketamine **1e** (54.5 mg, 0.20 mmol) or aldimine **1e'** (54.5 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol), aryl chloride **2m** (16.4 mg, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with ethyl acetate: hexanes = 1:5 to ethyl acetate:methanol = 120:1) to give the product **3em** (35.9 mg, 90% yield, arylation of **1e**) or (35.9 mg, 90% yield, arylation of **1e'**) as thick colorless oil. Sequential One-Pot Synthesis of **3em** is described in General Procedure C. R_f = 0.38 (ethyl acetate:methanol = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (dd, *J* = 4.0, 1.5 Hz, 2H), 8.52 (d, *J* = 6.0 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.79–7.77 (m, 2H), 7.72 (s, 1H), 7.67 (dd, *J* = 9.0, 1.5 Hz, 1H),7.50–7.42 (m, 4H), 7.39–7.36 (m, 3H), 7.31 (d, *J* = 6.0 Hz, 2H), 7.06–7.05 (m, 2H), 5.70 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 169.0, 152.9, 150. 5, 150.0, 147.7, 141.5, 139.3, 136.3, 136.1, 130.7, 129.9, 129.5, 128.9, 128.8,

128.7, 128.3, 128.2, 127.5, 125.9, 122.6, 121.3, 68.8 ppm; IR (thin film): 3055, 1622, 1595, 1498, 1319, 1281, 697 cm^{-1}; HRMS calc'd for $C_{28}H_{22}N_3^+$ 400.1814, observed 400.1814 $[MH]^+$.

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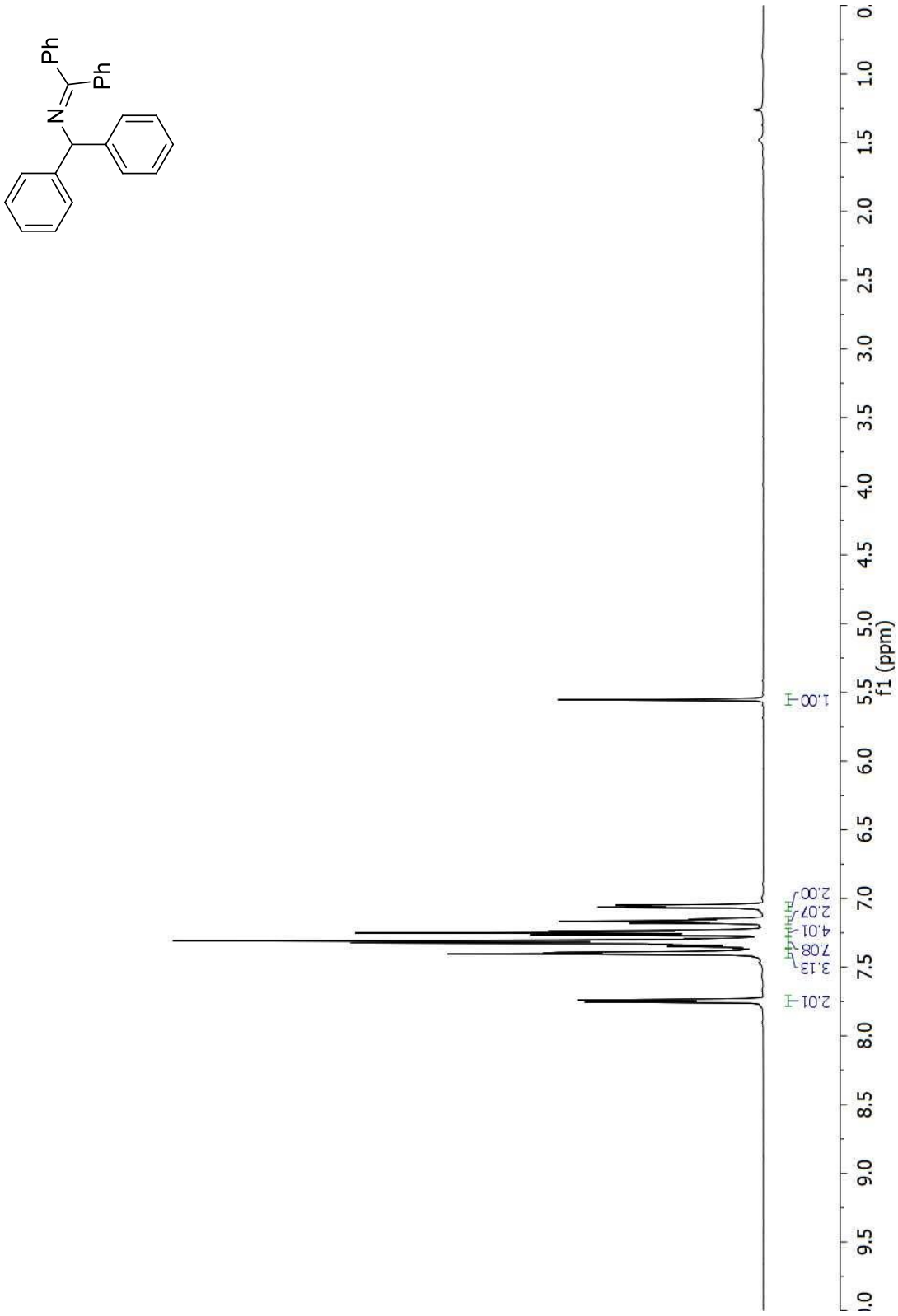
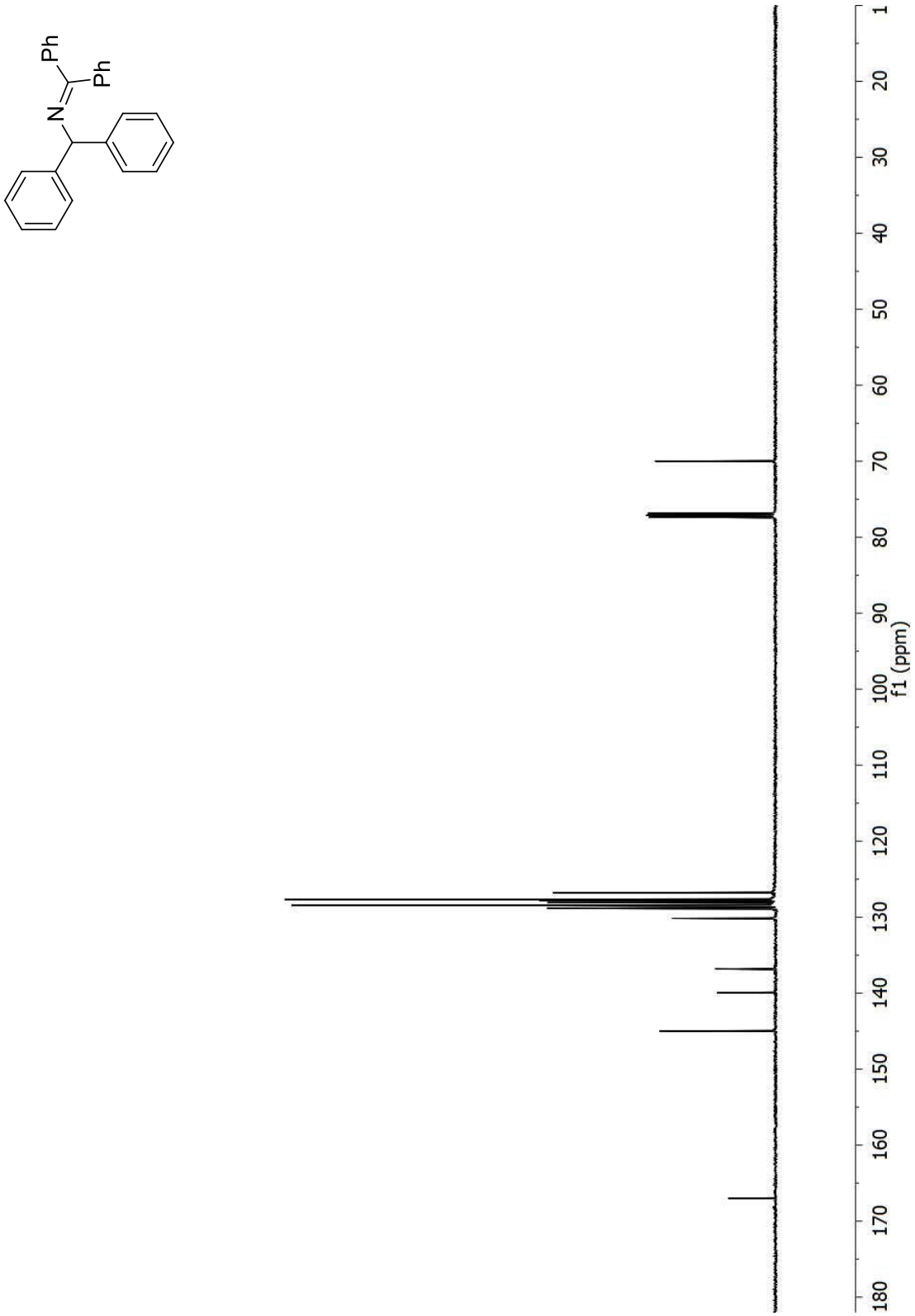
1. O'Donnell, J.; Bennett, W. D.; Bruder, W. A.; Jacobsen, W. N.; Knuth, K.; LeClef, B.; Polt, R. L.; Bordwell, F. G.; Mrozack, S. R.; Cripe, T. A. *J. Am. Chem. Soc.*, **1988**, *110*, 8520.
2. Hatano, M.; Hattori, Y.; Furuya, Y.; Ishihara, K. *Org. Lett.*, **2009**, *11*, 2321.
3. (a) Bruno, N. C.; Tudge, M. T.; Buchwald, S. L. *Chem. Sci*. **2013**, *4*, 916. (b) Zhang, J.; Bellomo, A.; Trongsiriwat, N.; Jia, T.; Carroll, P. J.; Dreher, S. D.; Tudge, M. T.; Yin, H.; Robinson, J. R.; Schelter, E. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 6276.
4. Li, M.; Yücel, B.; Adrio, J.; Bellomo, A.; Walsh, P. J. *Chemical Science* **2014**, *5*, 2383.

NMR Spectra

3aa – *N*-(diphenylmethylene)-1,1-diphenylmethanamine (^{1}H NMR, $CDCl_3$, 500 MHz)

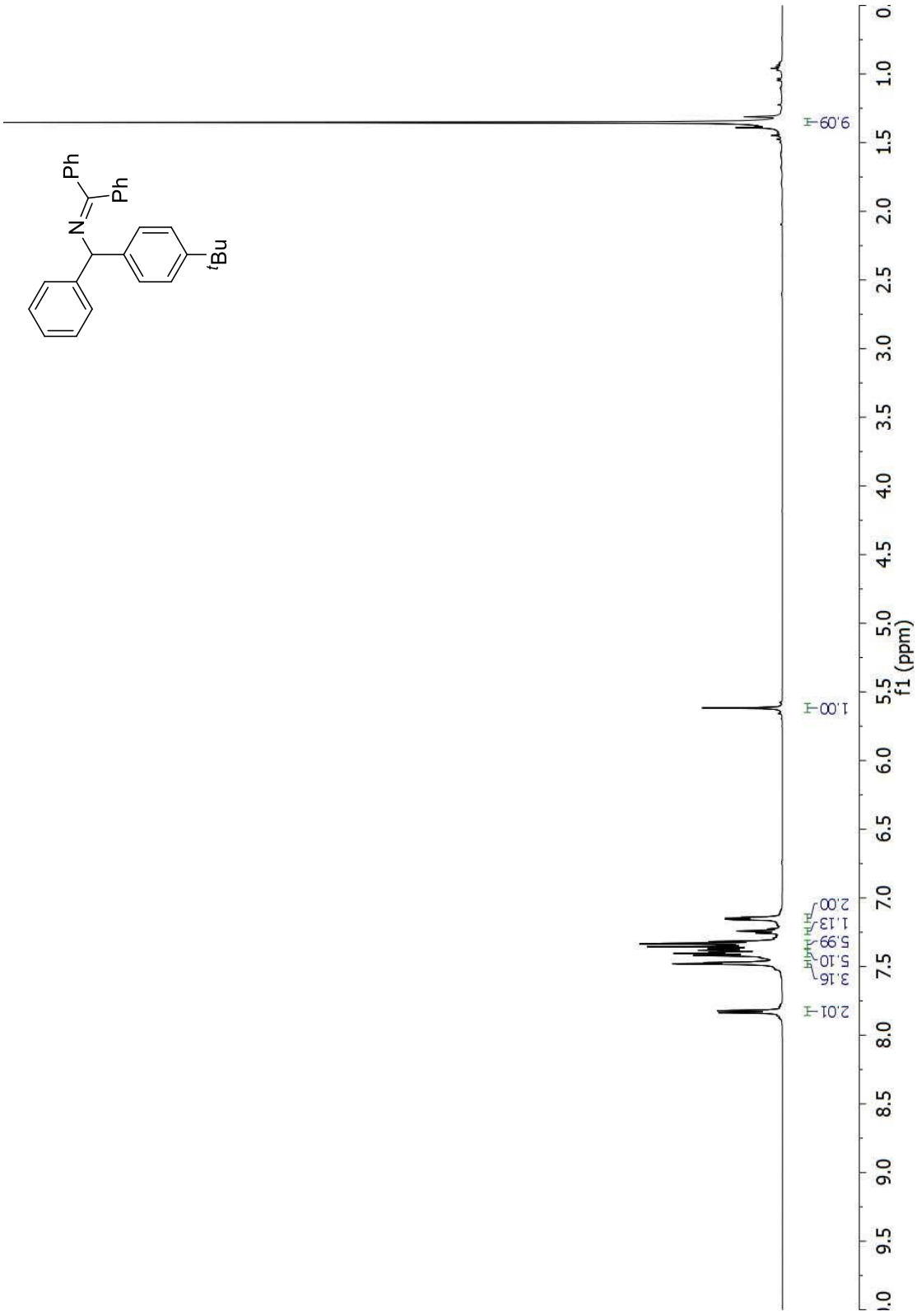


3aa – *N*-(diphenylmethylene)-1,1-diphenylmethanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



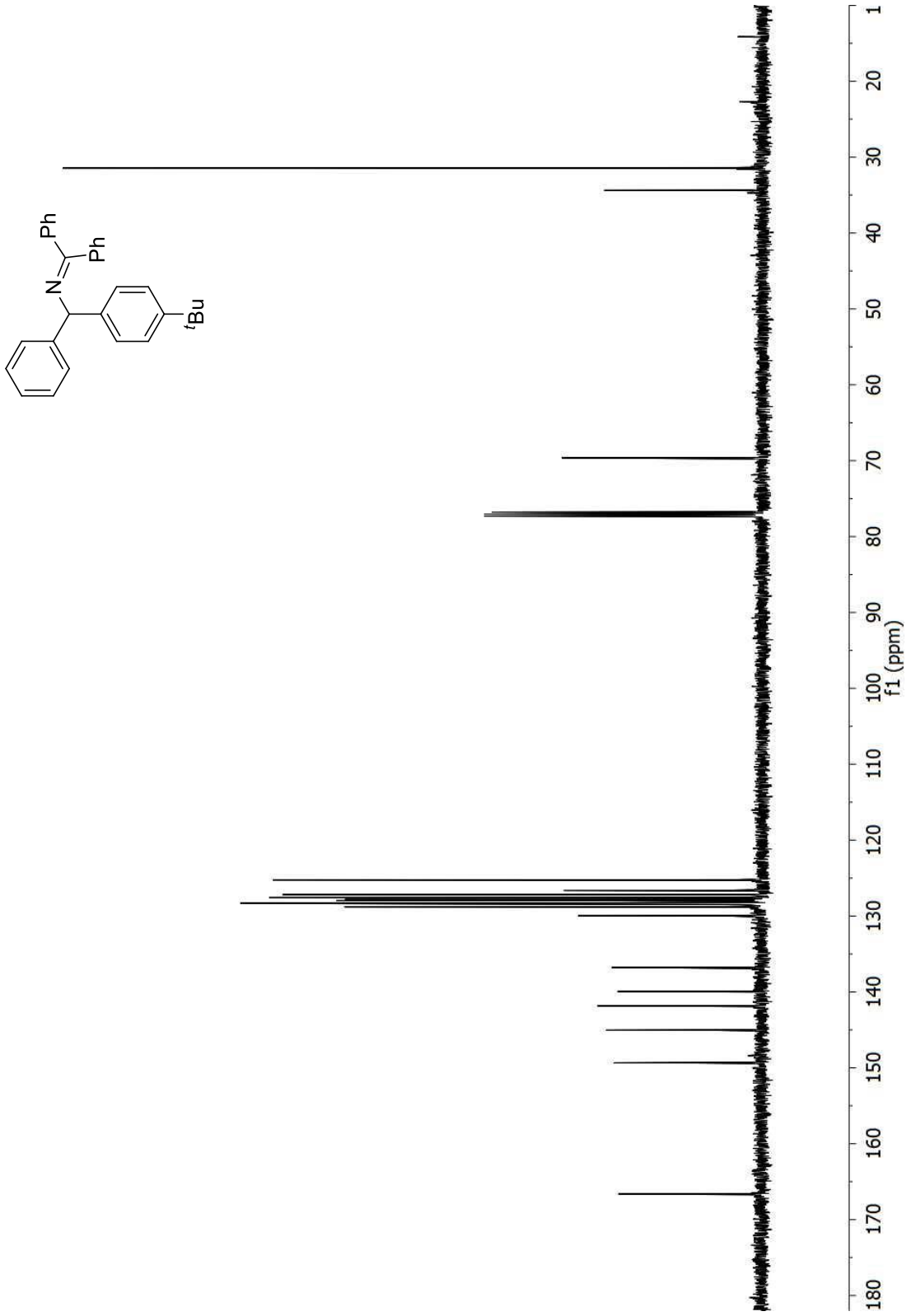
3ab – 1-(4-(*tert*-Butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)

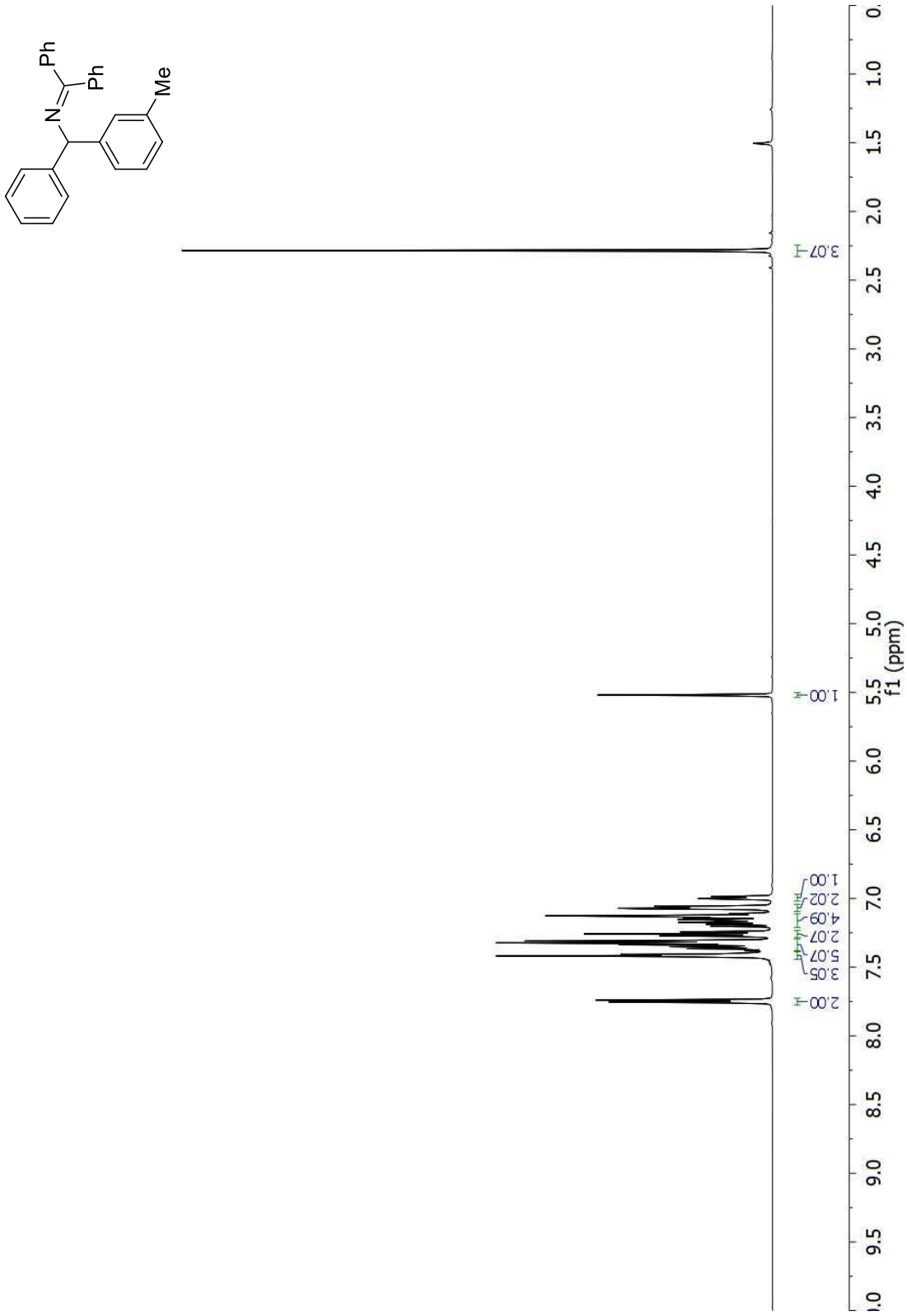


3ab – 1-(4-(*tert*-Butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

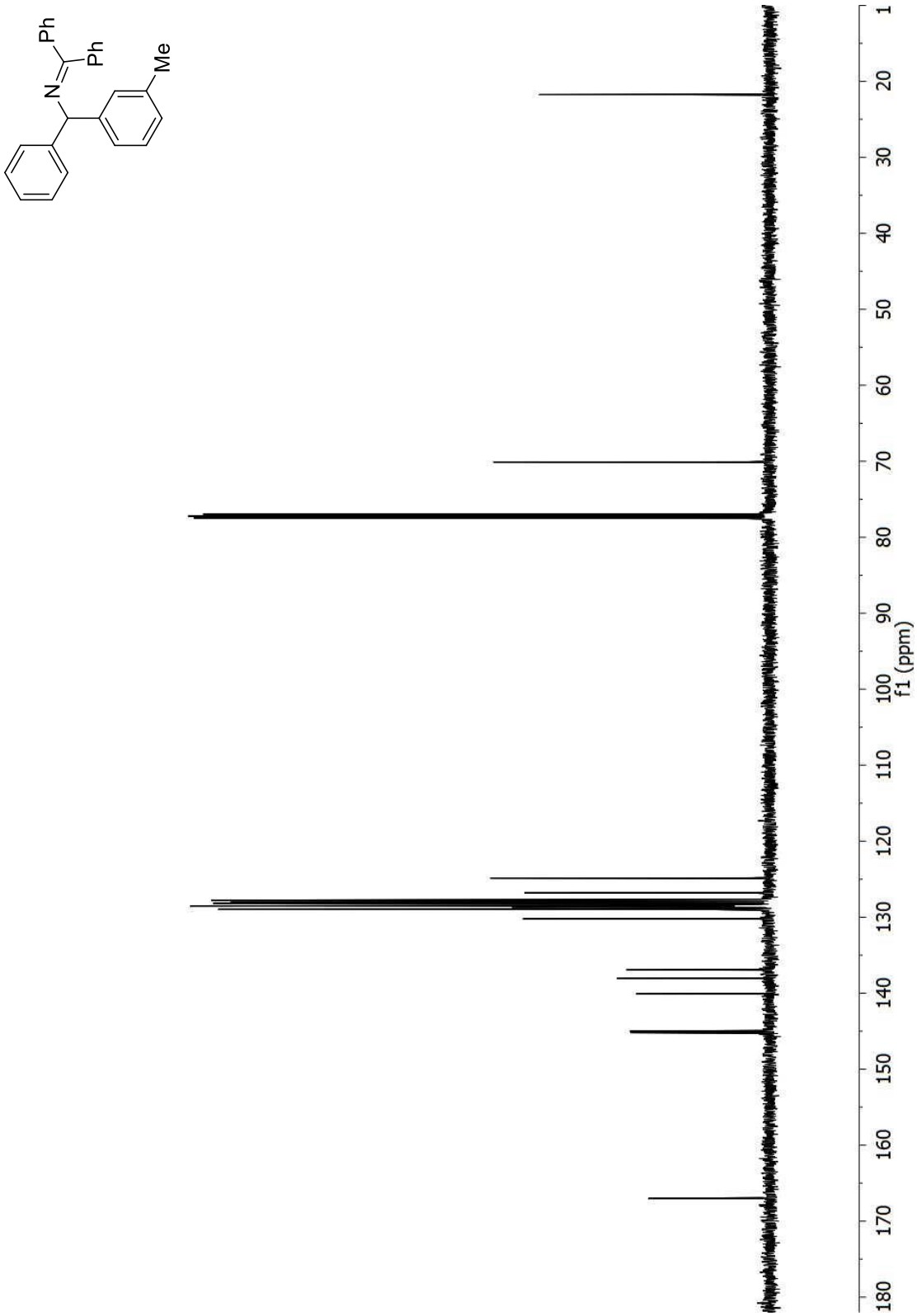
(^{13}C NMR, $CDCl_3$, 125 MHz)



3ac– *N*-(diphenylmethylene)-1-phenyl-1-(*m*-tolyl)methanamine (^{1}H NMR, $CDCl_3$, 500 MHz)

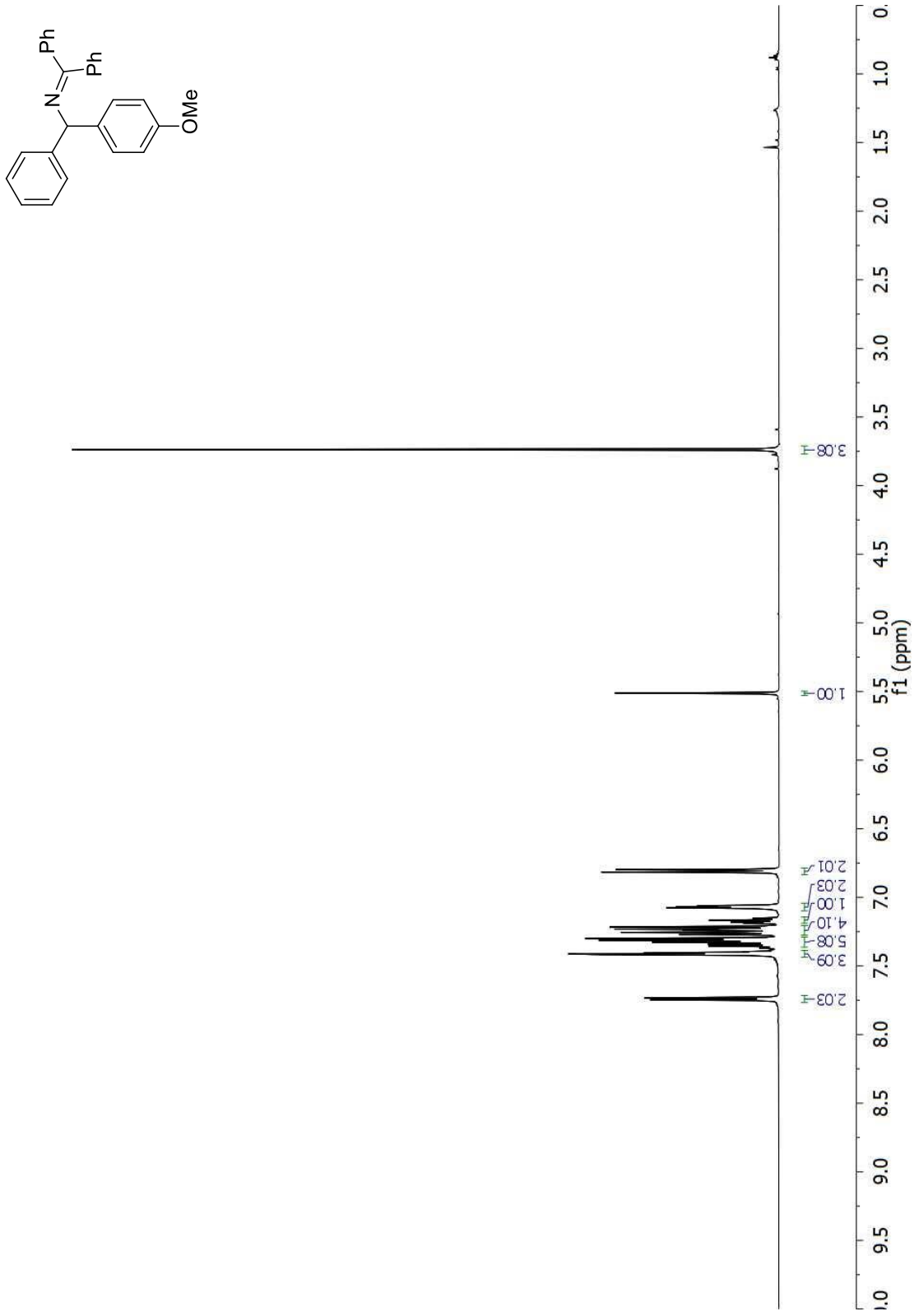


3ac– *N*-(diphenylmethylene)-1-phenyl-1-(*m*-tolyl)methanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



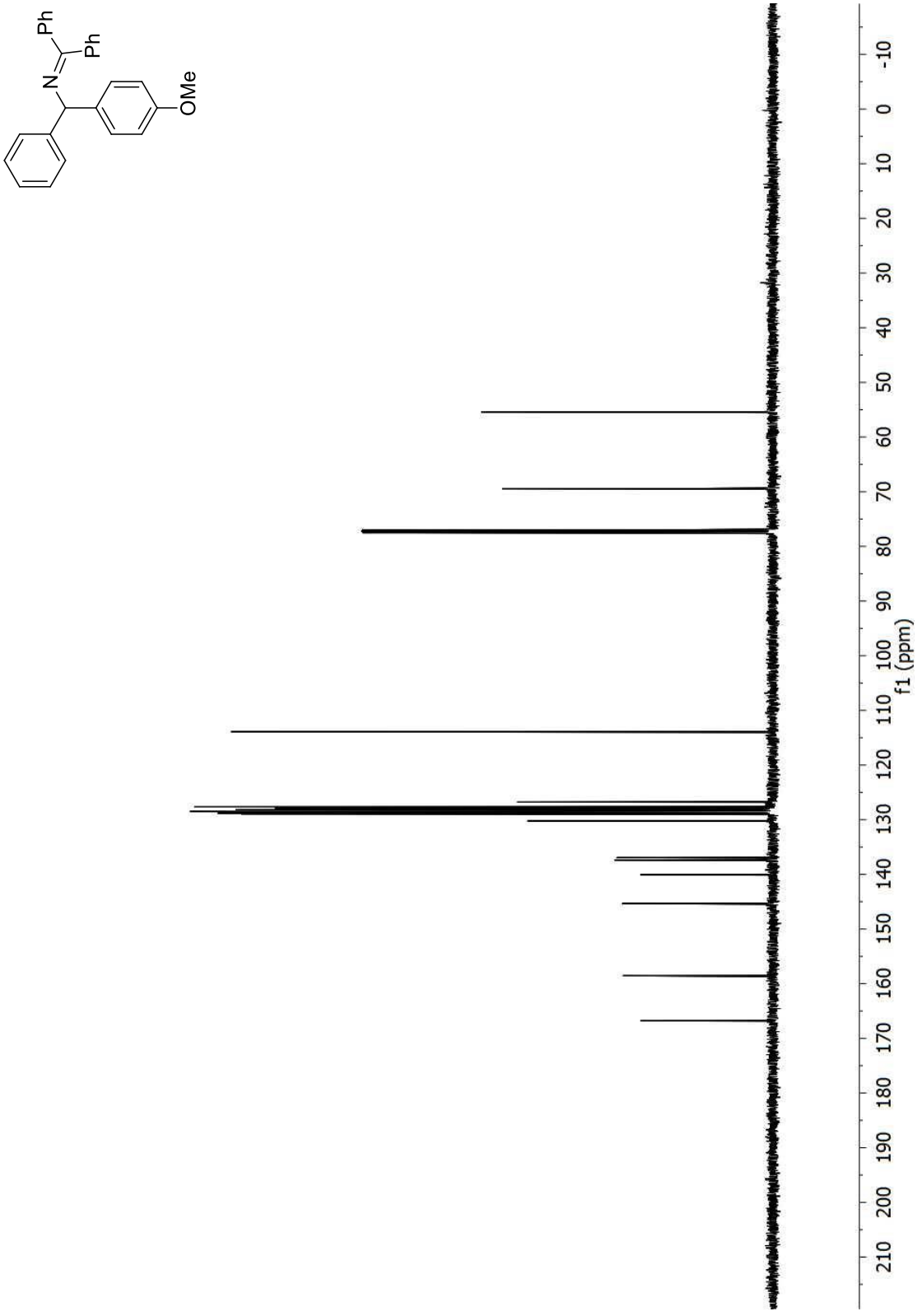
3ad – *N*-(diphenylmethylene)-1-(*p*-methoxyphenyl)-1-phenylmethanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)

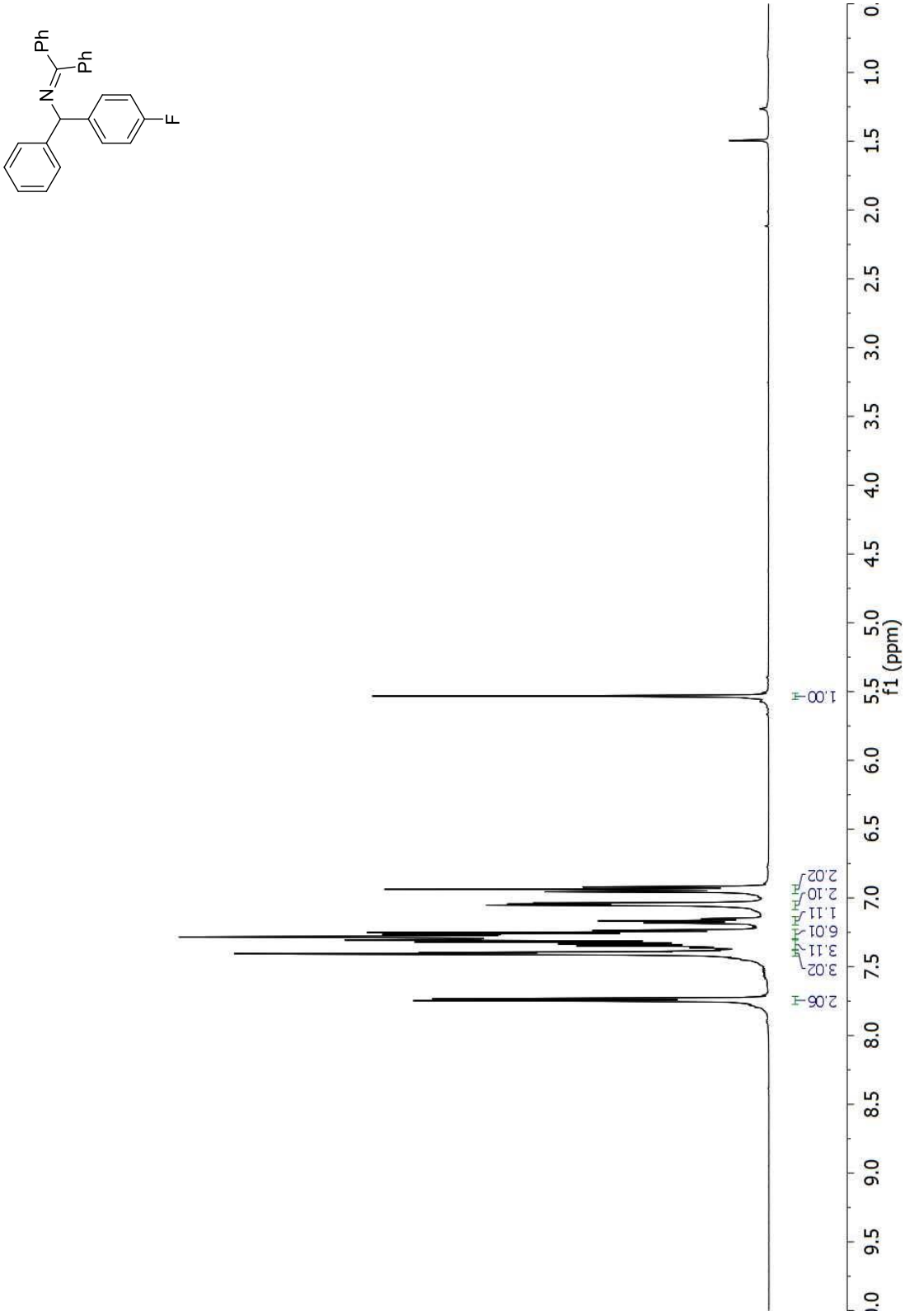


3ad – *N*-(diphenylmethylene)-1-(*p*-methoxyphenyl)-1-phenylmethanamine

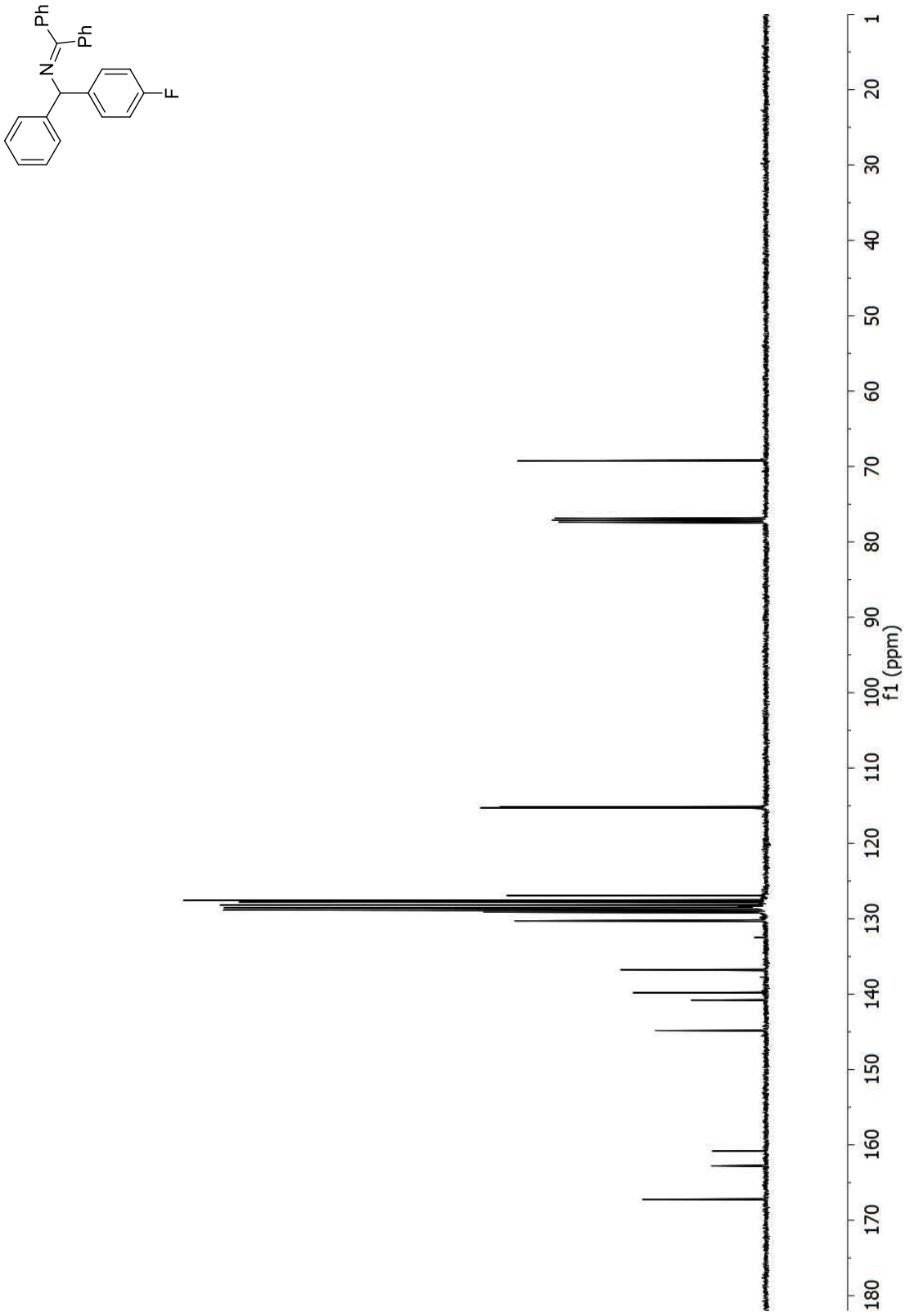
(^{13}C NMR, $CDCl_3$, 125 MHz)



3ae – *N*-(diphenylmethylene)-1-(*p*-fluorophenyl)-1-phenylmethanamine (^{1}H NMR, $CDCl_3$, 500 MHz)

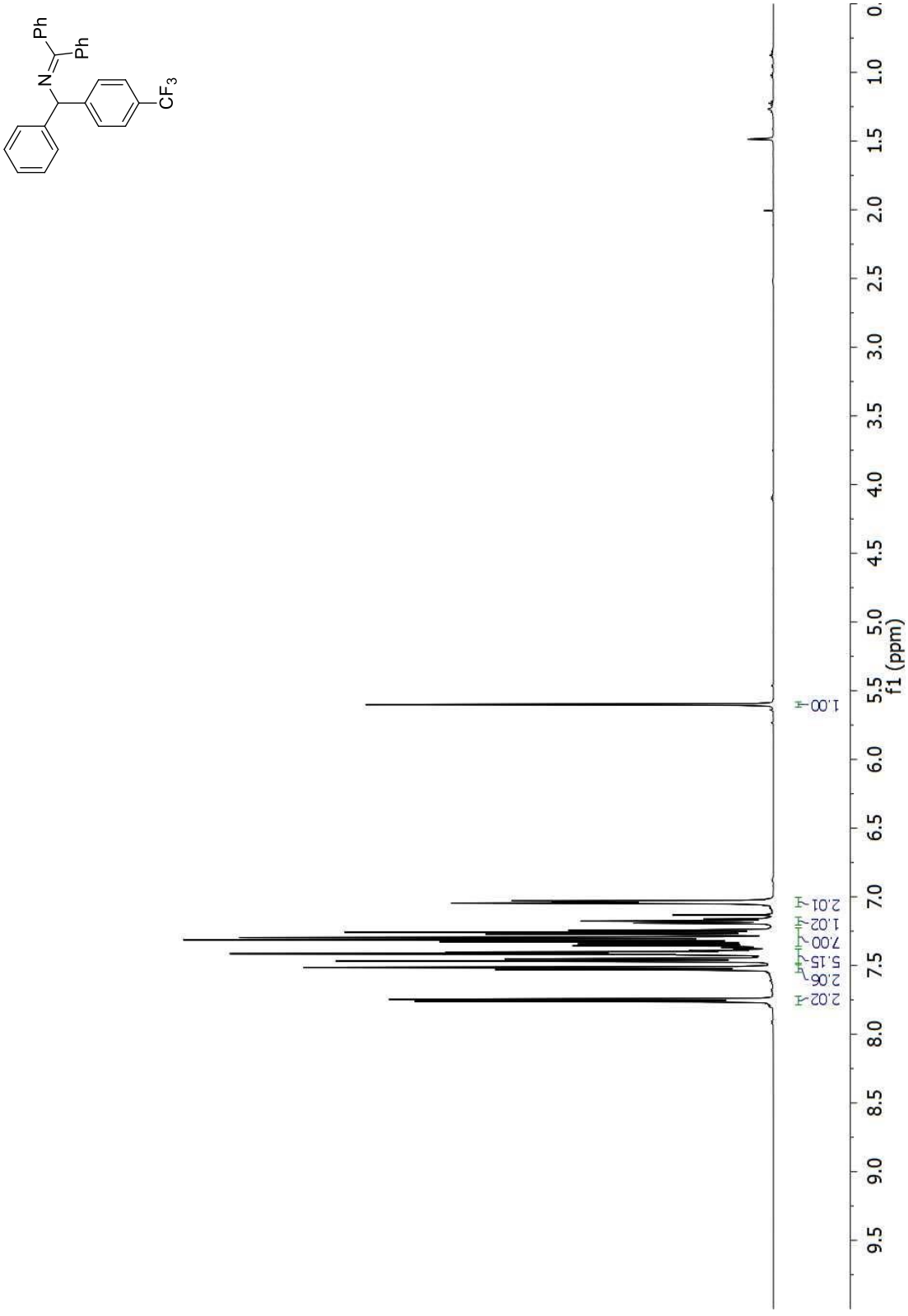


3ae – *N*-(diphenylmethylene)-1-(*p*-fluorophenyl)-1-phenylmethanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



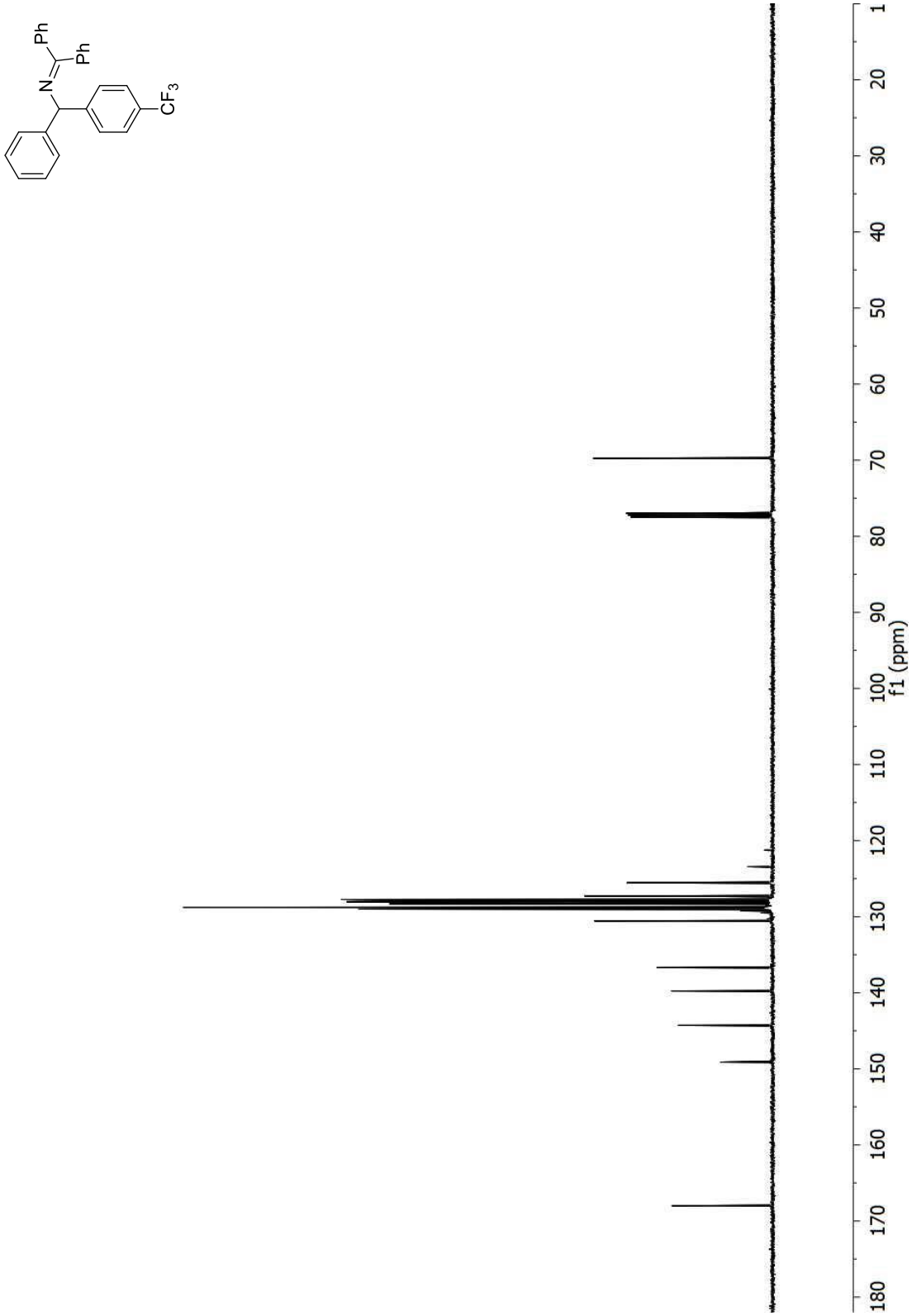
3af –*N*-(diphenylmethylene)-1-phenyl-1-(*p*-(trifluoromethyl)phenyl)methanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)

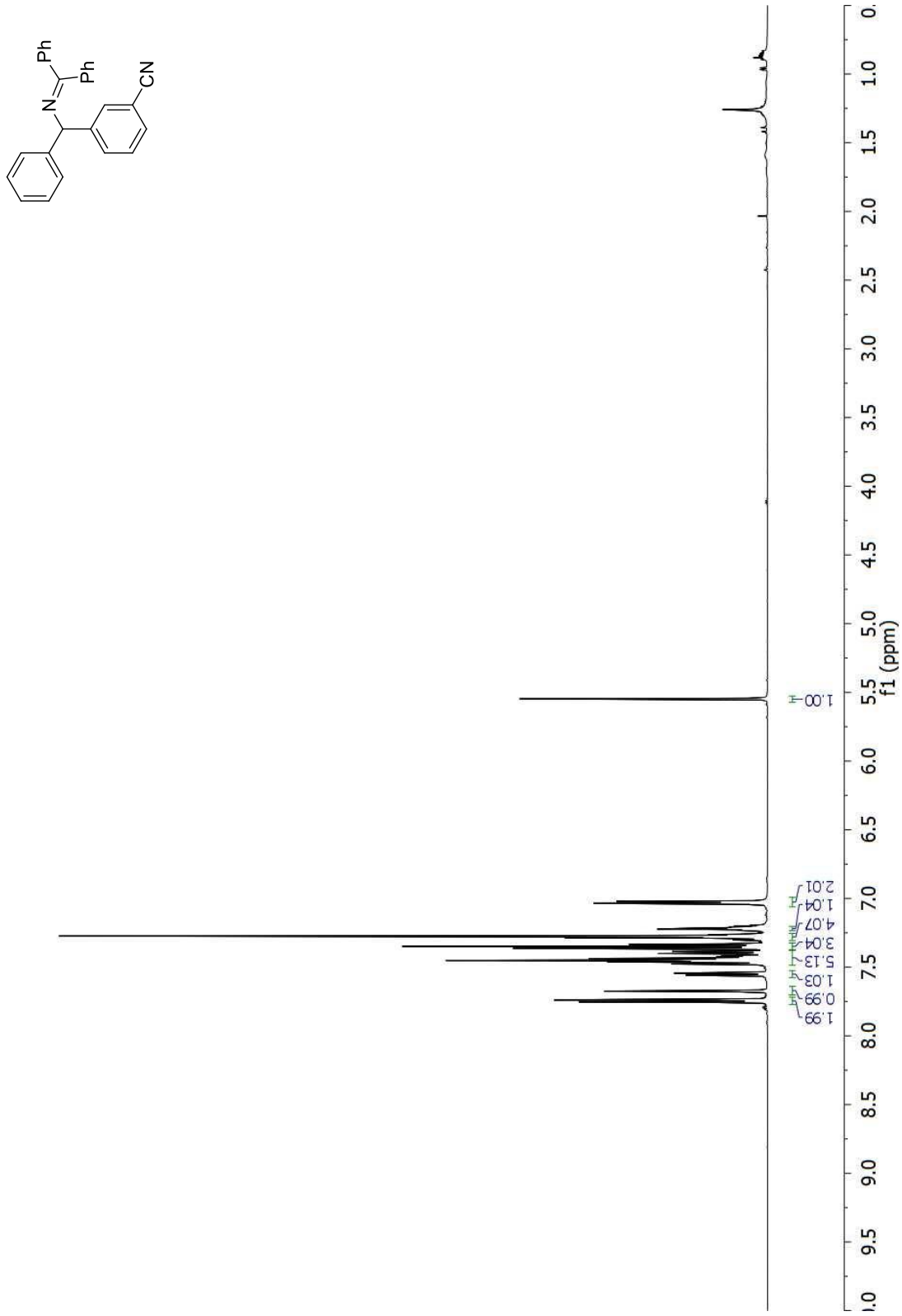


3af –*N*-(diphenylmethylene)-1-phenyl-1-(*p*-(trifluoromethyl)phenyl)methanamine

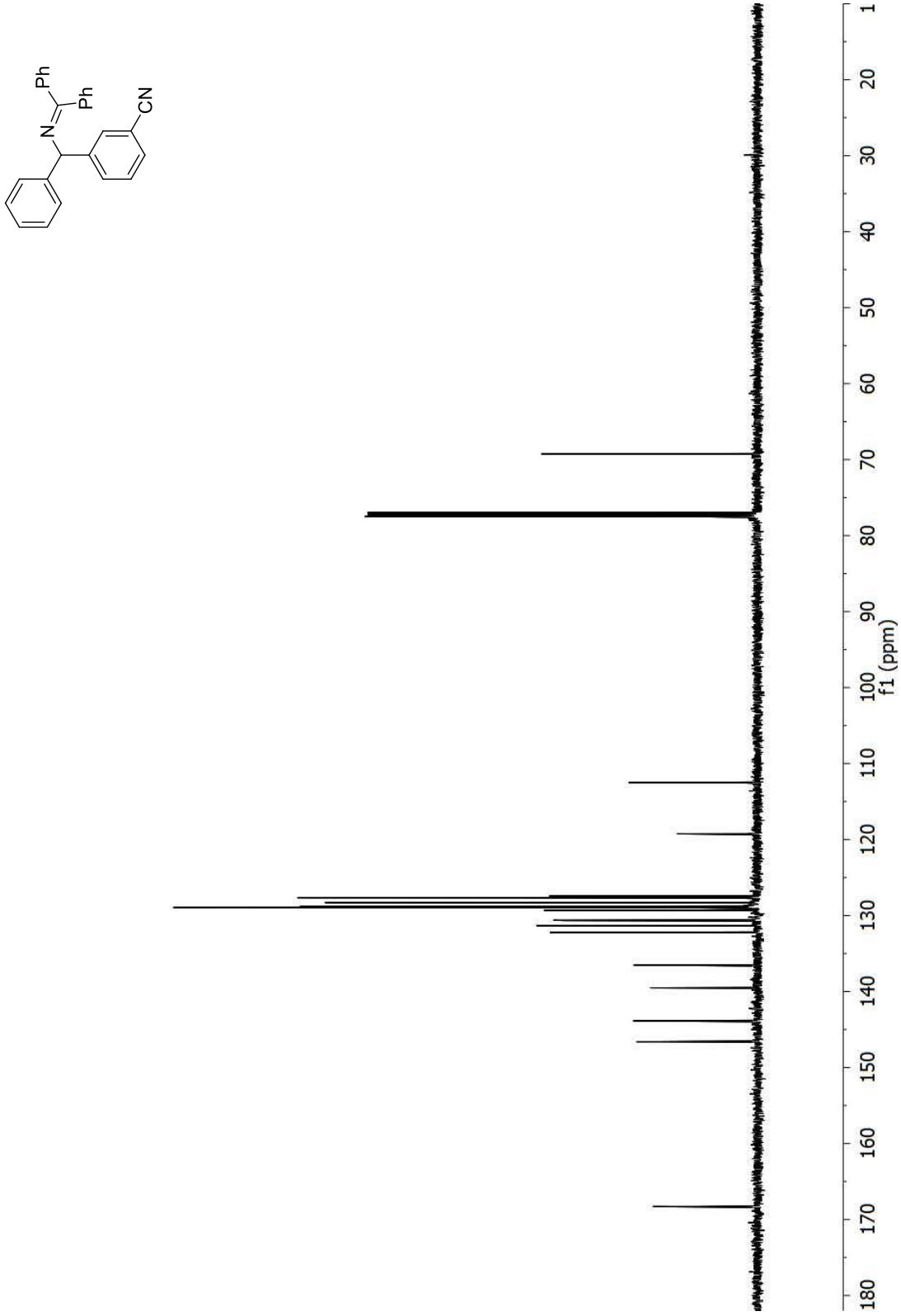
(^{13}C NMR, $CDCl_3$, 125 MHz)



3ag - 3-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile (^{1}H NMR, $CDCl_3$, 500 MHz)

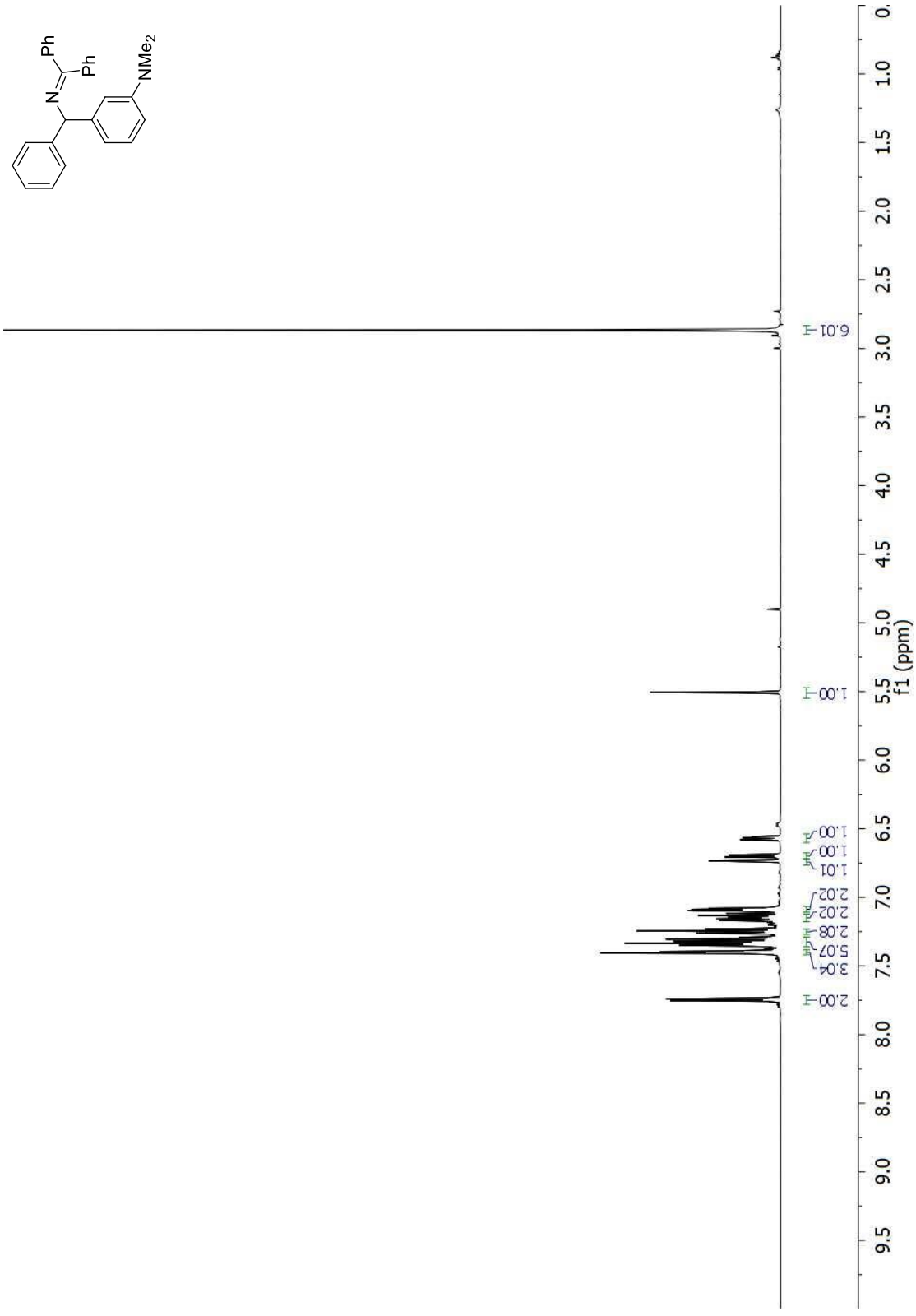


3ag - 3-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile (^{13}C NMR, $CDCl_3$, 125 MHz)



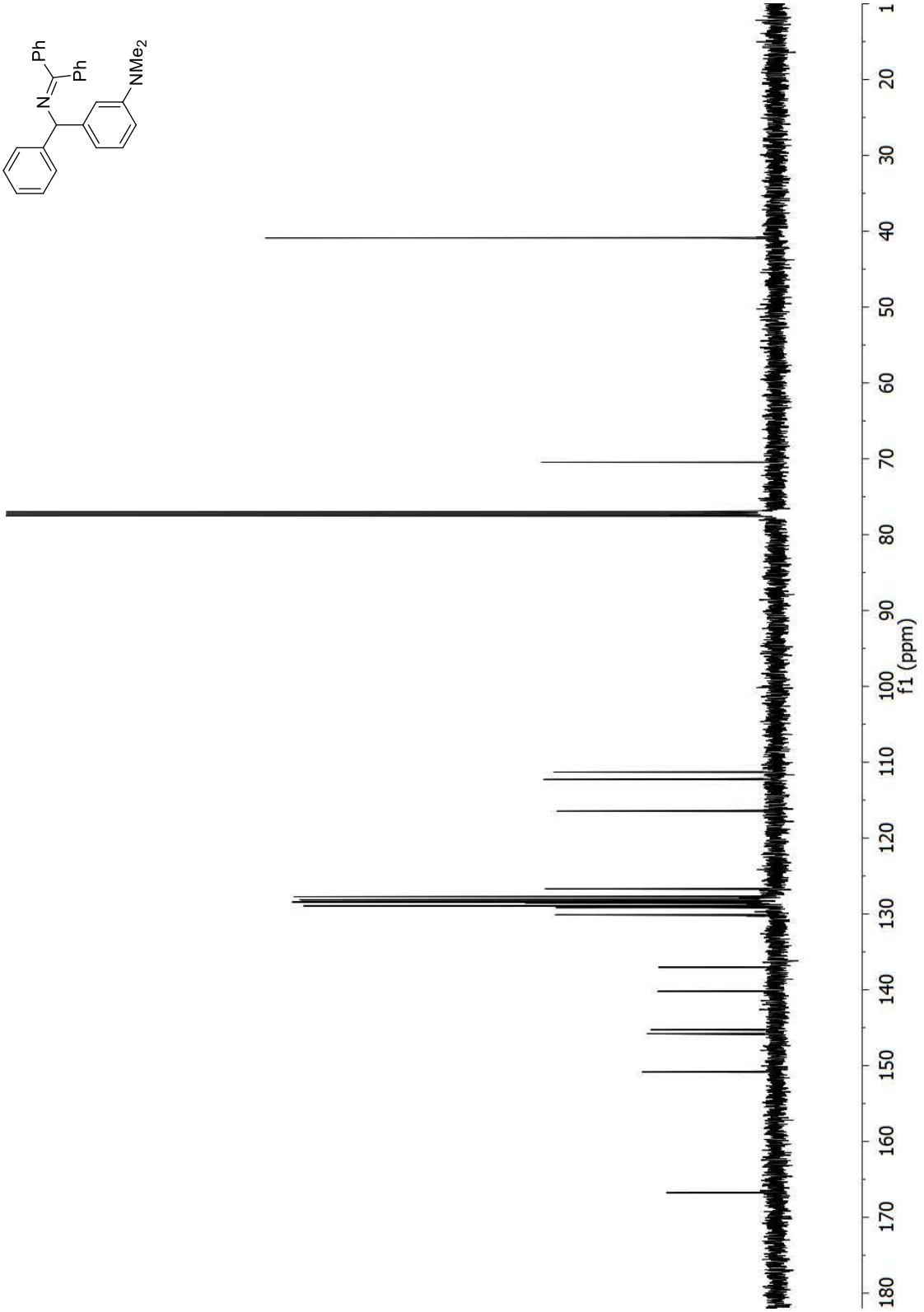
3ah – 3-(((diphenylmethylene)amino)(phenyl)methyl)-*N*,*N*-dimethylaniline

(^{1}H NMR, $CDCl_3$, 500 MHz)

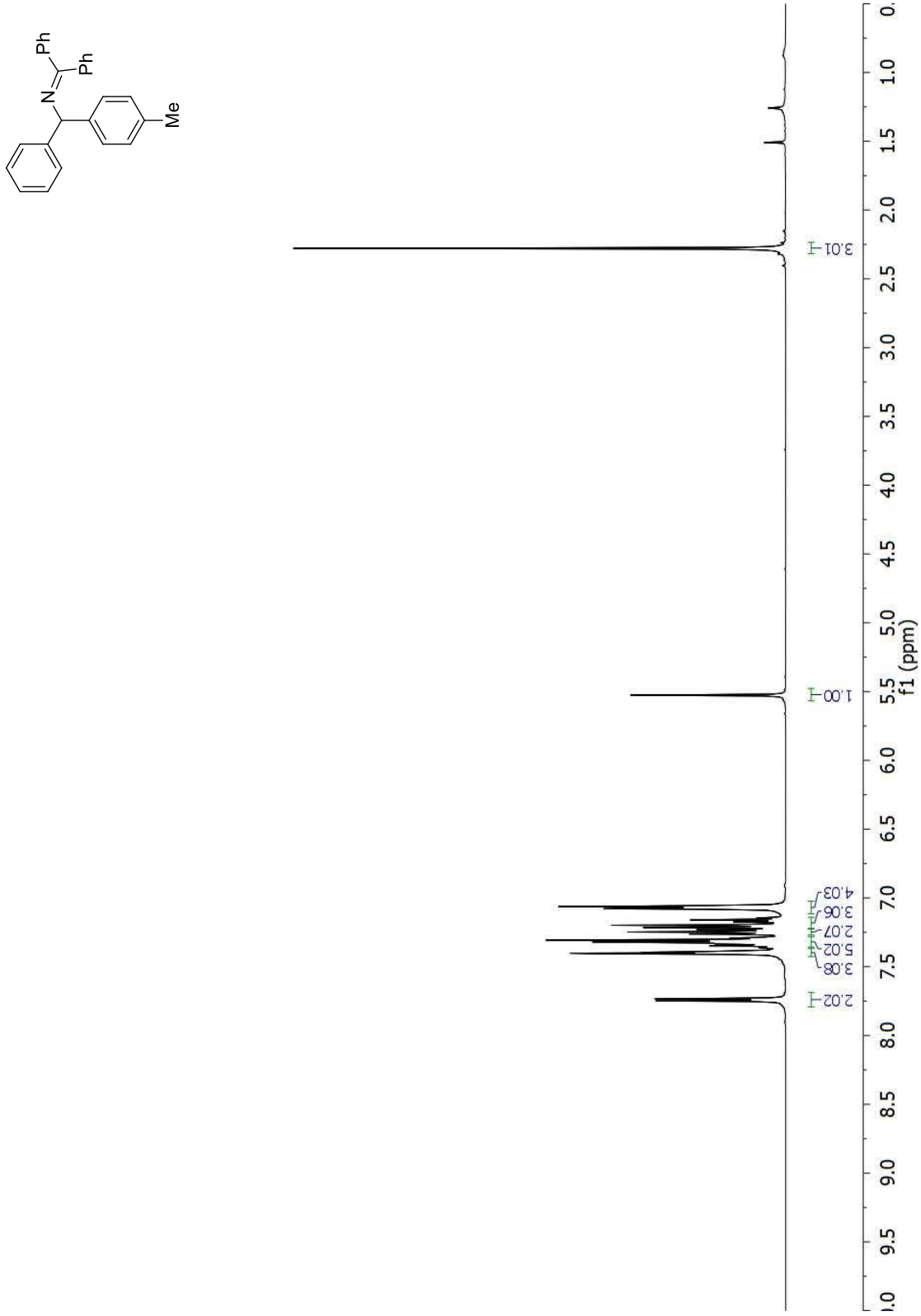


3ah – 3-(((diphenylmethylene)amino)(phenyl)methyl)-*N*,*N*-dimethylaniline

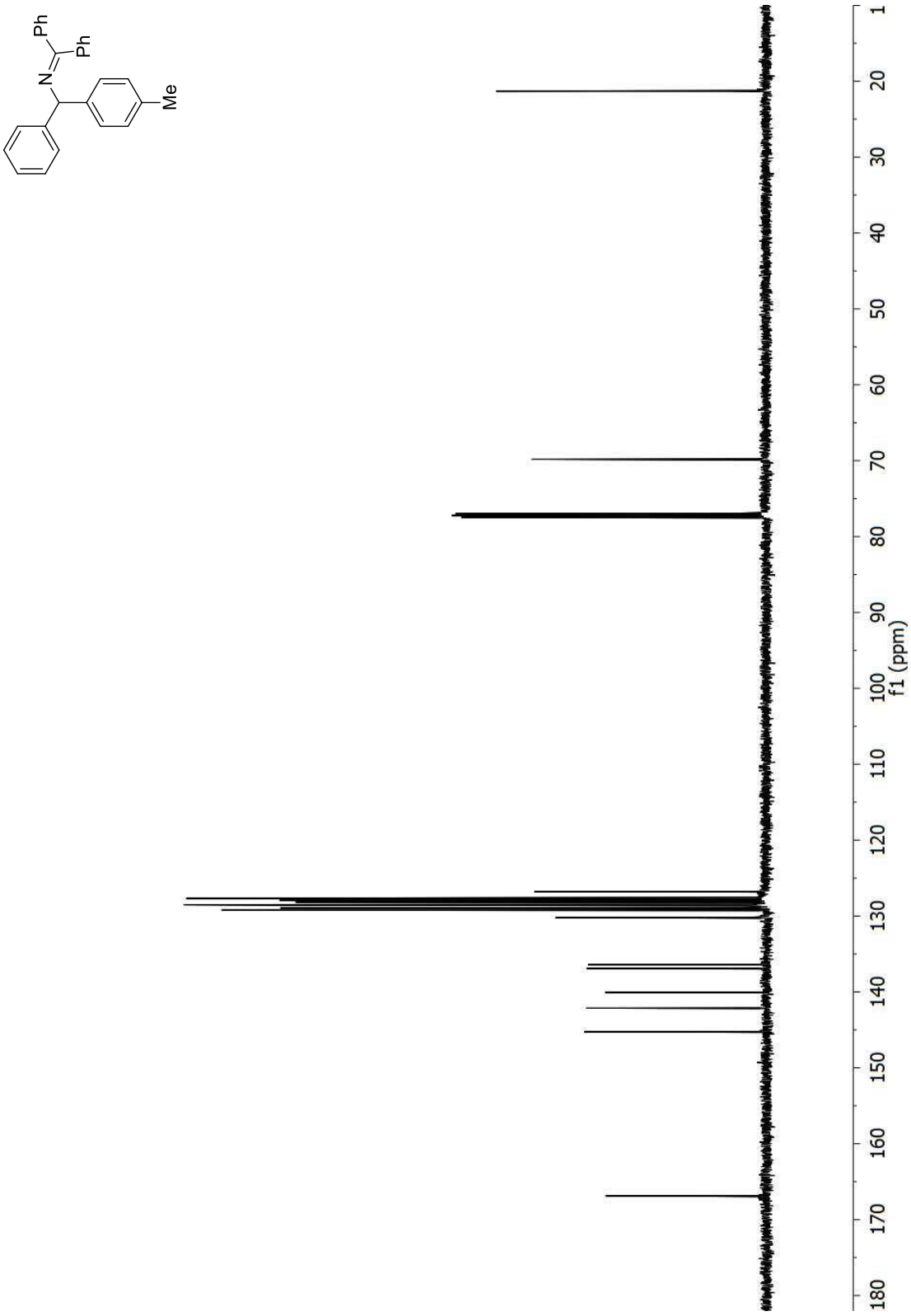
(^{13}C NMR, $CDCl_3$, 125 MHz)



3ai - *N*-(diphenylmethylene)-1-phenyl-1-(*p*-tolyl)methanamine (^{1}H NMR, $CDCl_3$, 500 MHz)

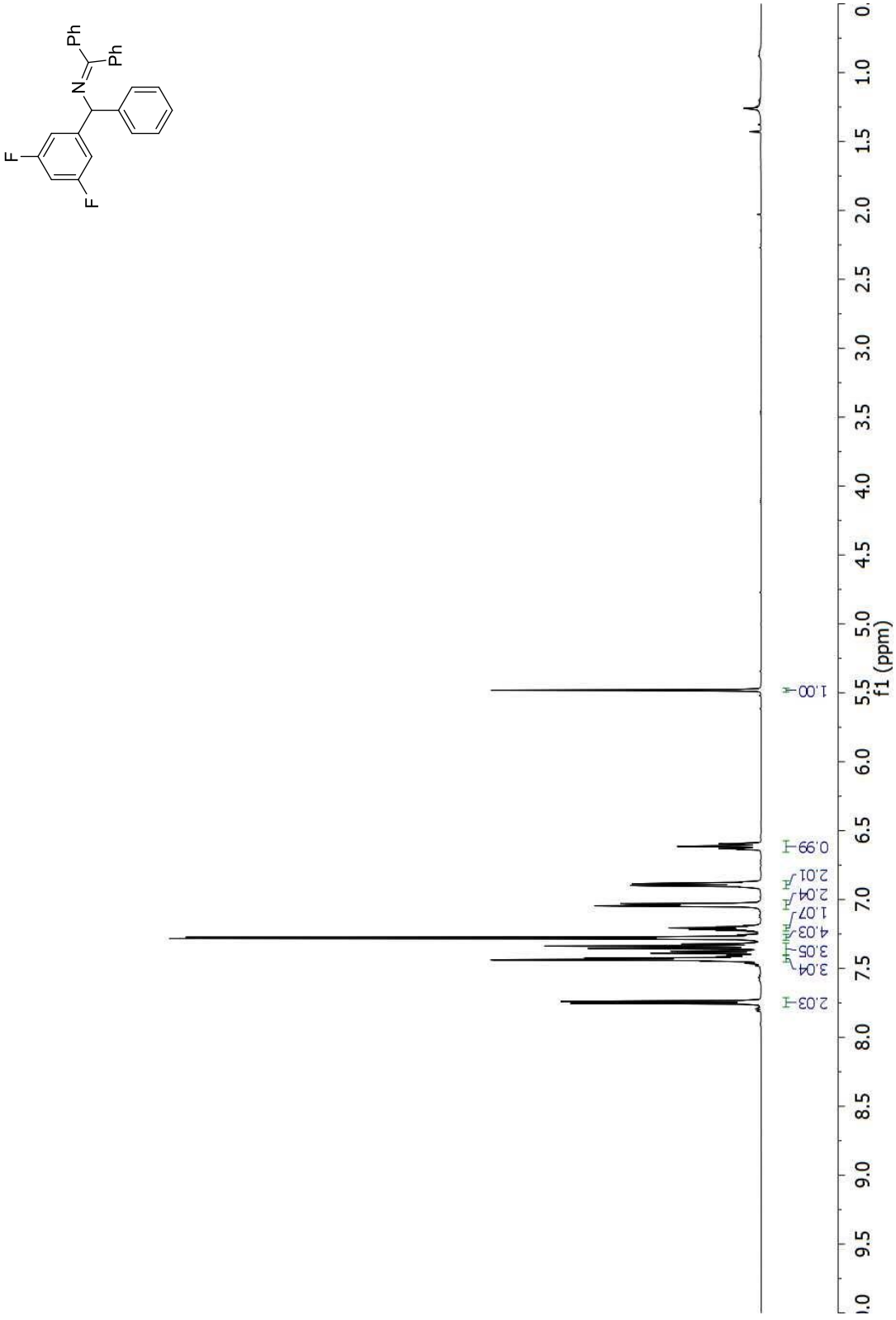


3ai - *N*-(diphenylmethylene)-1-phenyl-1-(*p*-tolyl)methanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



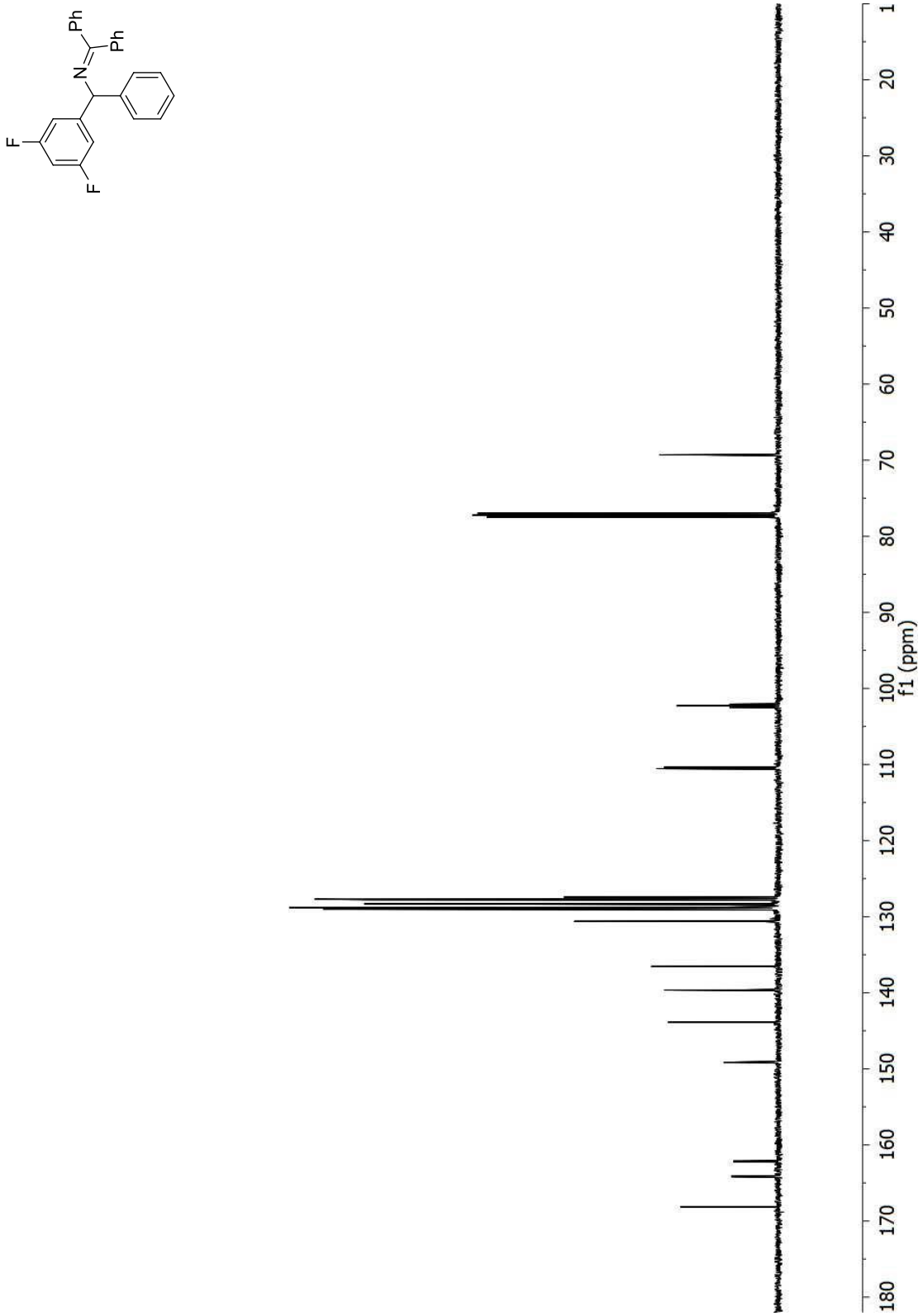
3aj - 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)

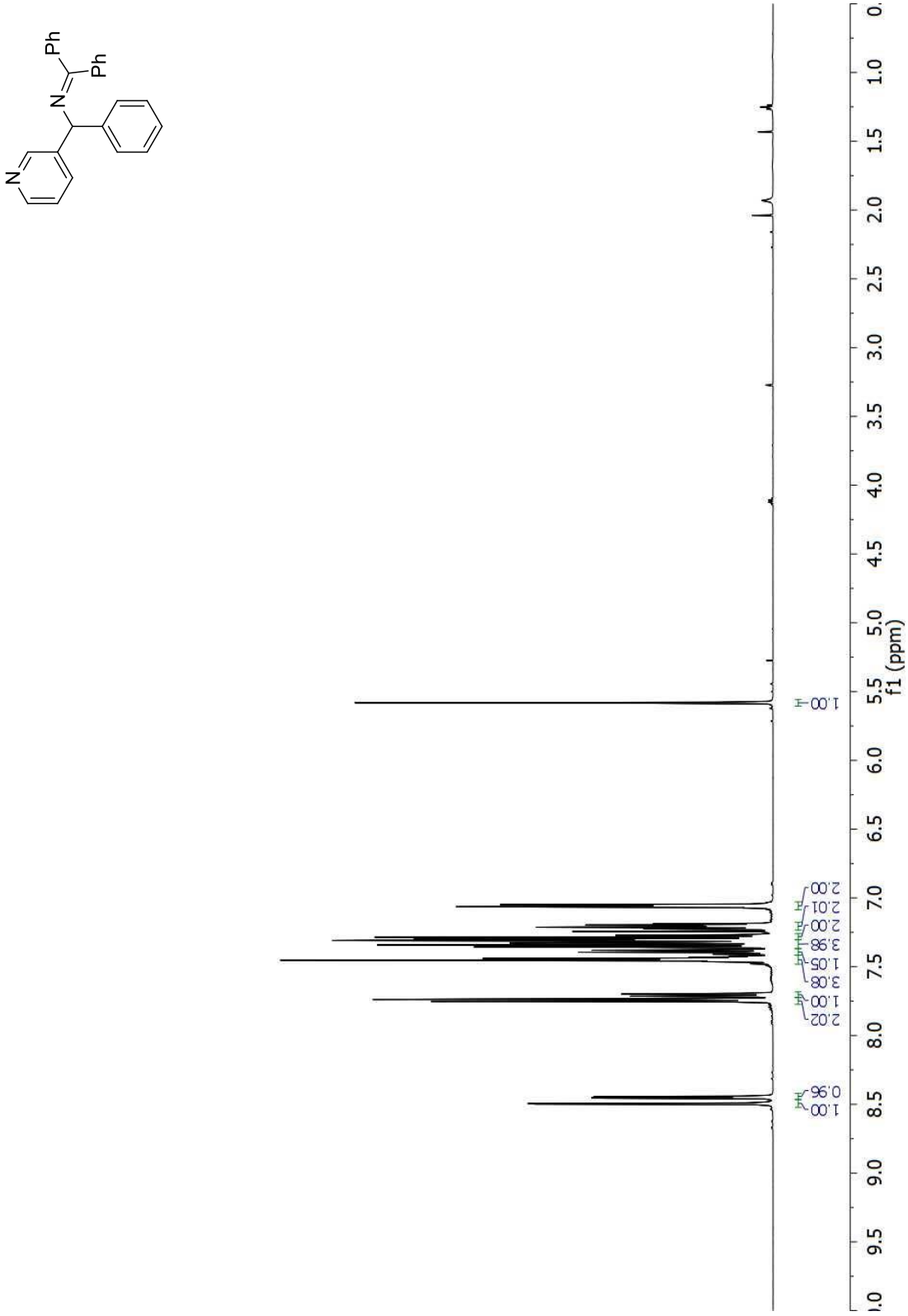


3aj - 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

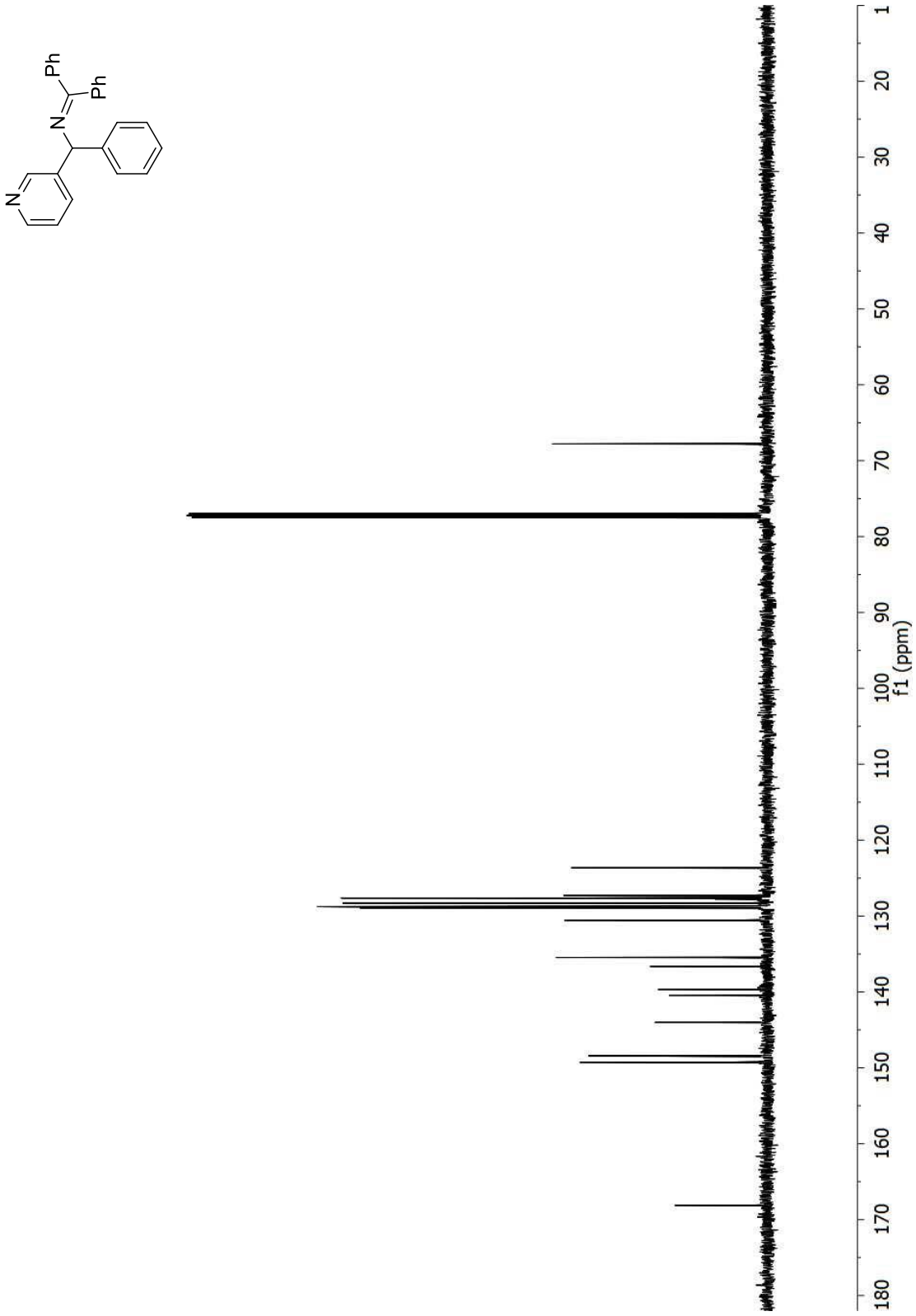
(^{13}C NMR, $CDCl_3$, 125 MHz)



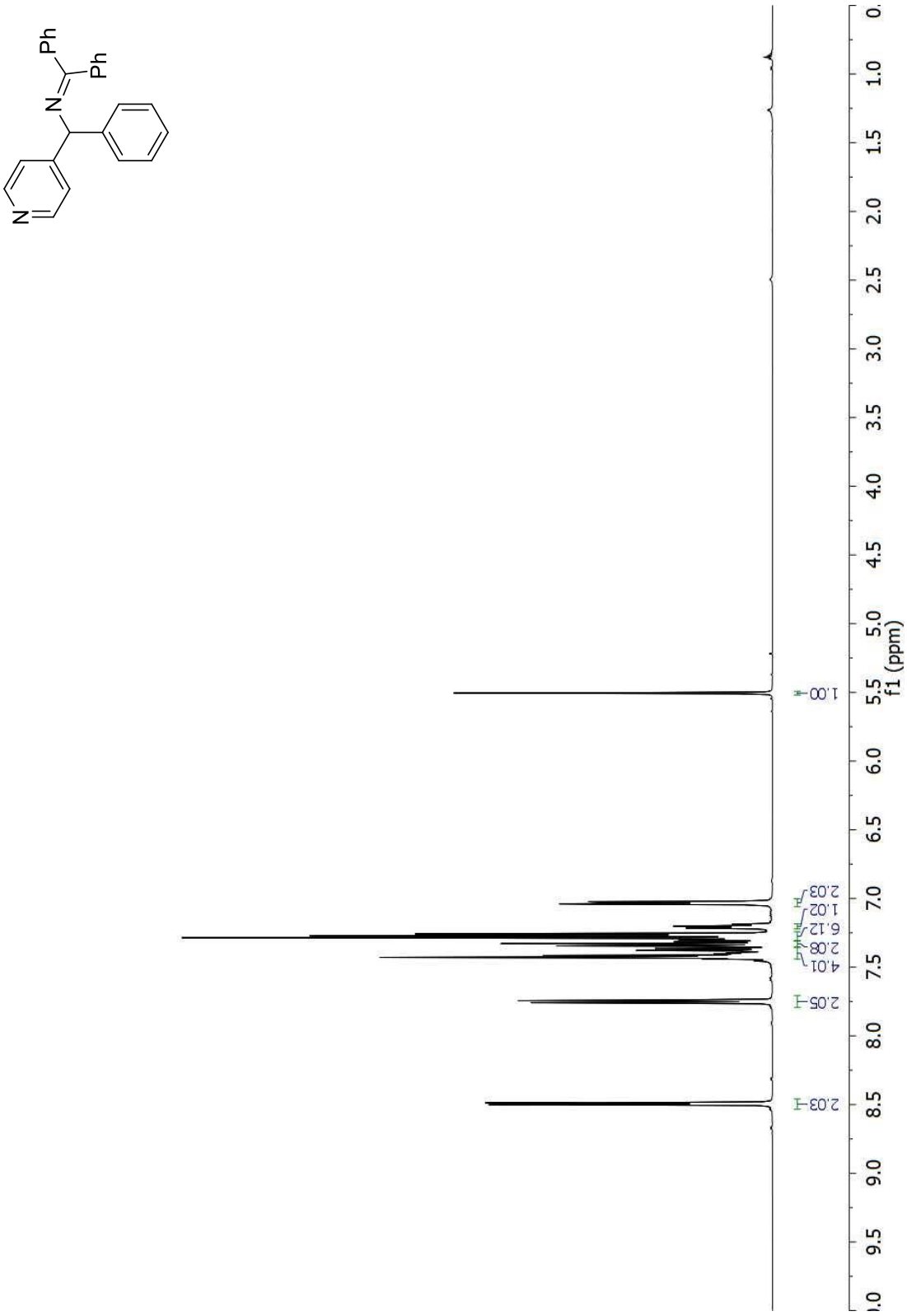
3da - *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine (^{1}H NMR, $CDCl_3$, 500 MHz)



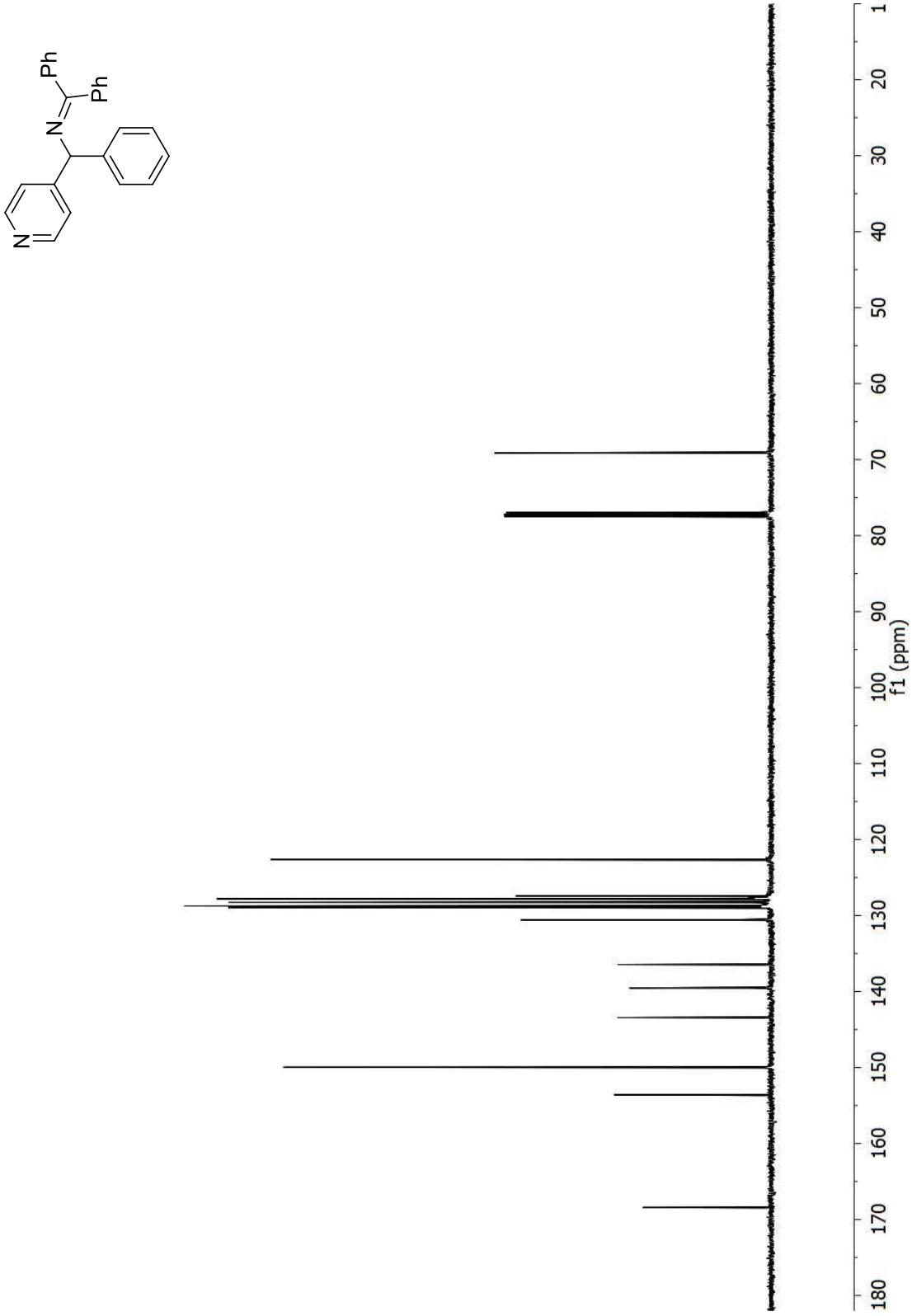
3da - *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



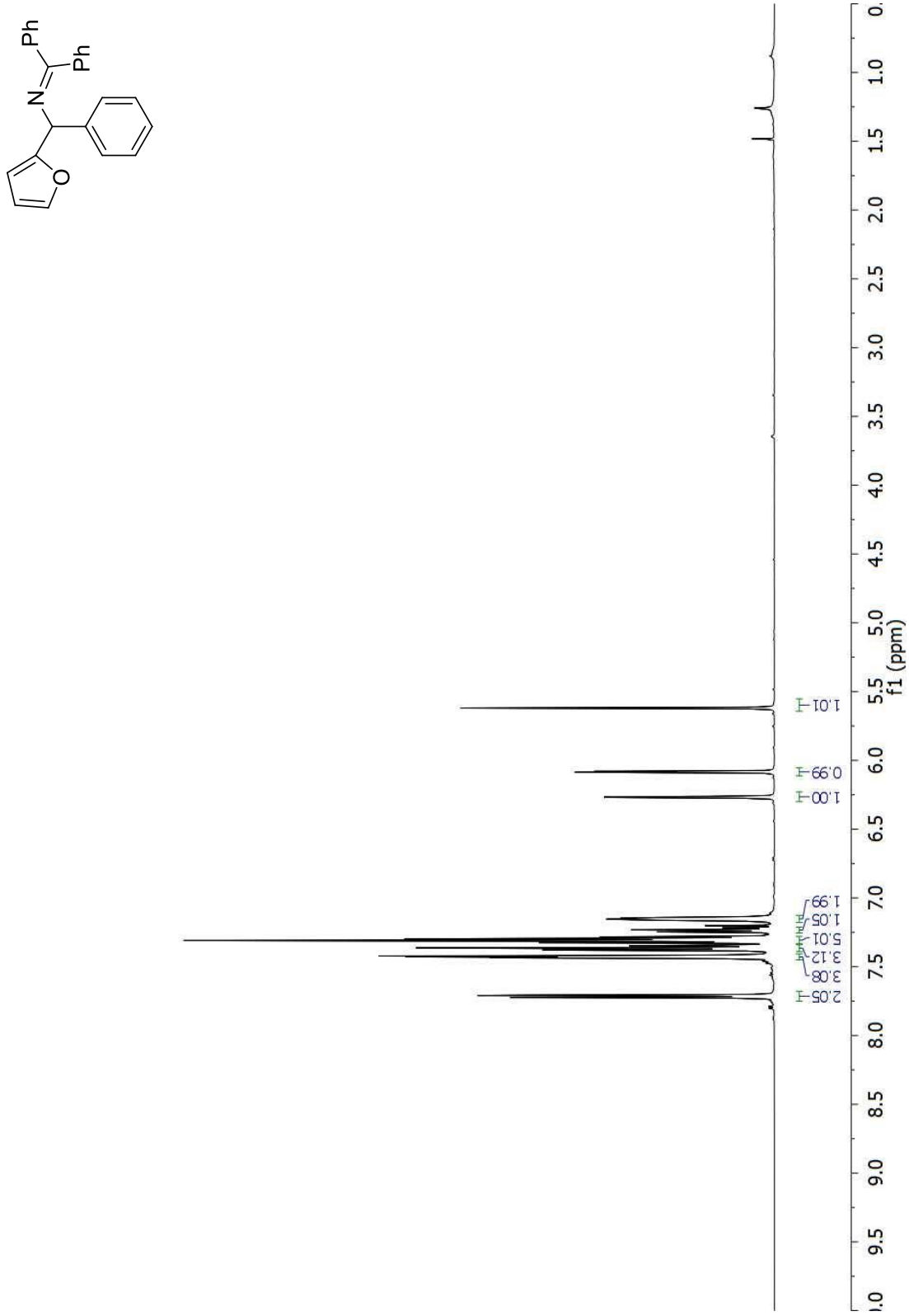
3ea - *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine (^{1}H NMR, $CDCl_3$, 500 MHz)



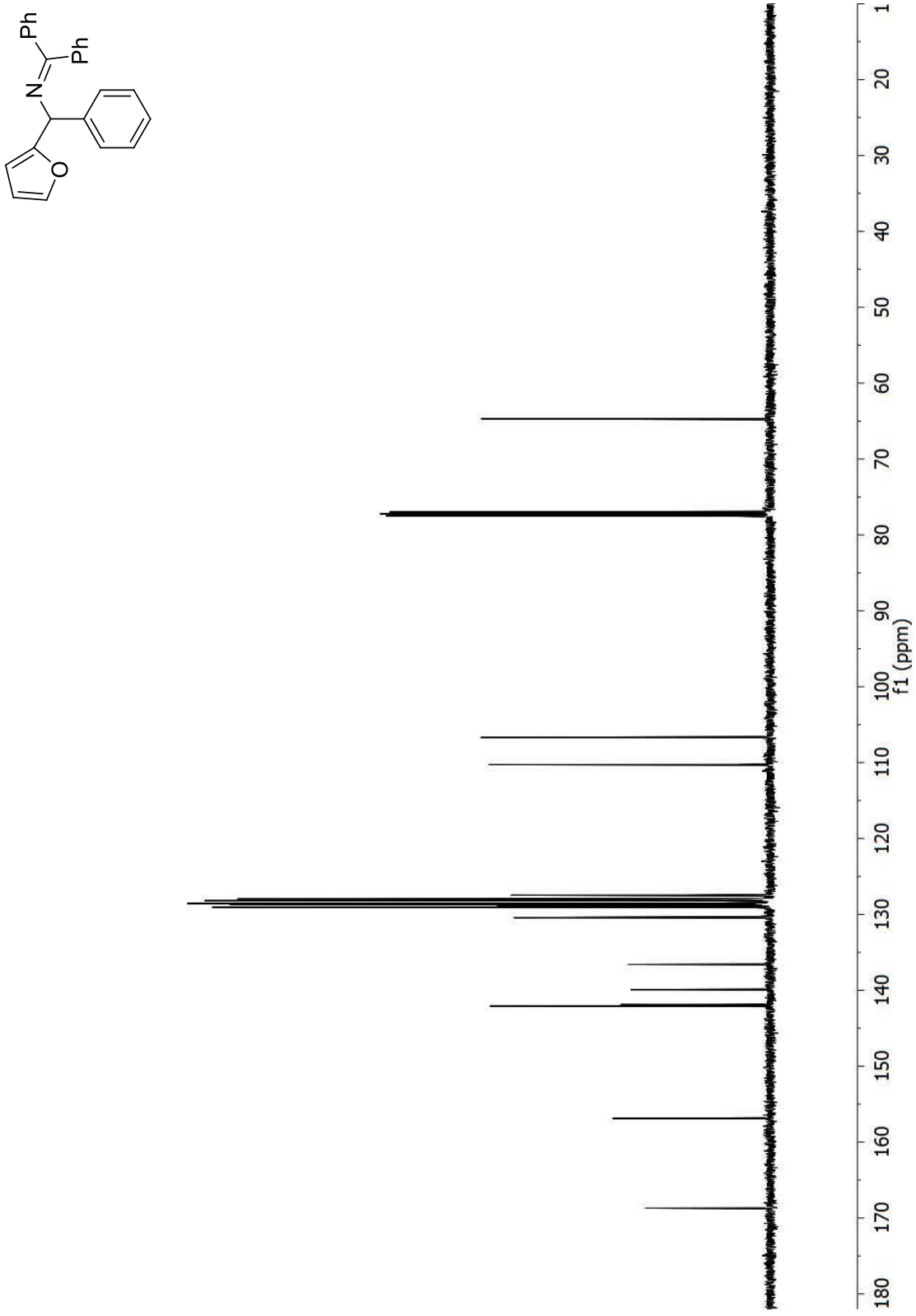
3ea - *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



3fa - *N*-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine (^{1}H NMR, $CDCl_3$, 500 MHz)

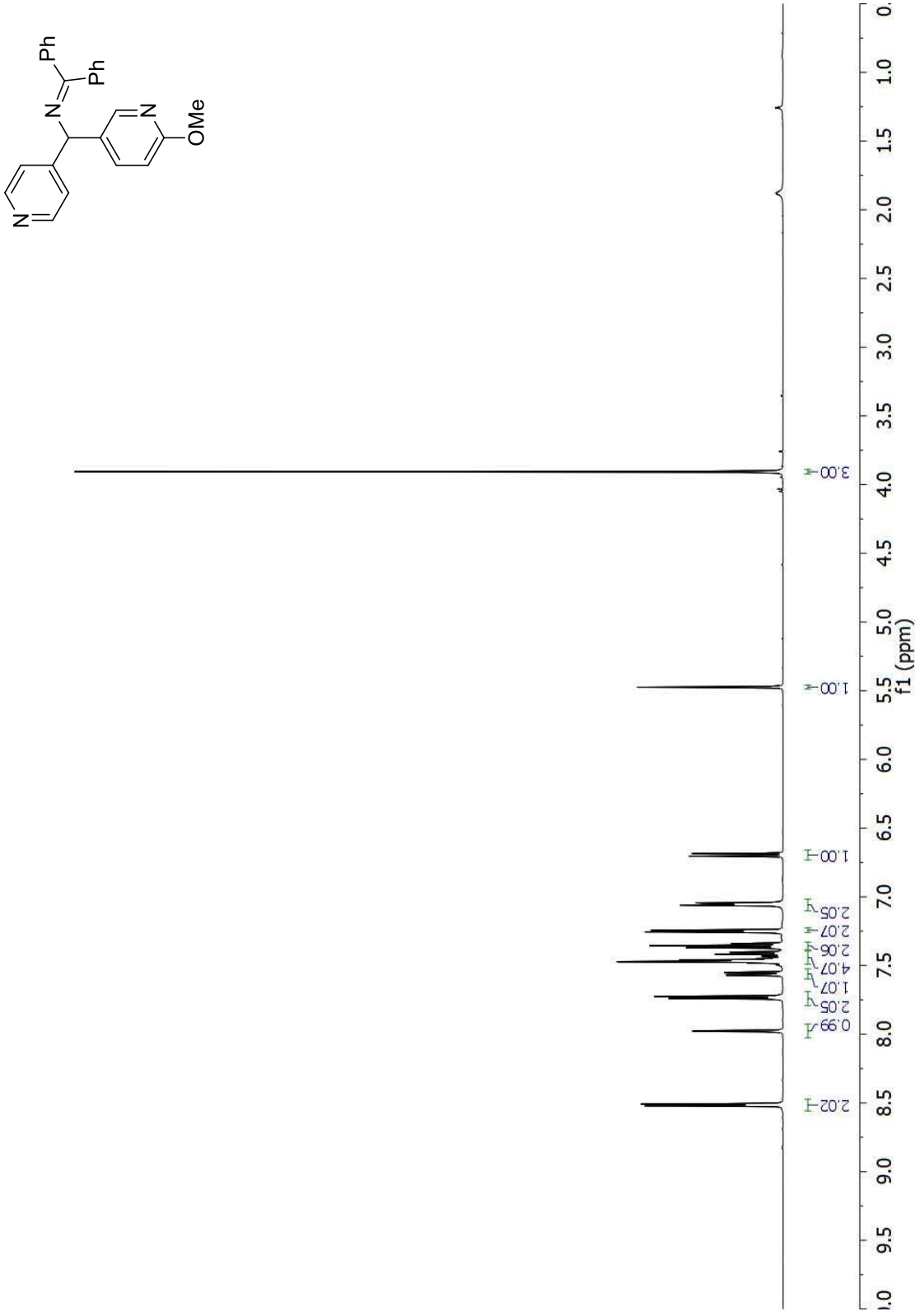


3fa - *N*-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine (^{13}C NMR, $CDCl_3$, 125 MHz)



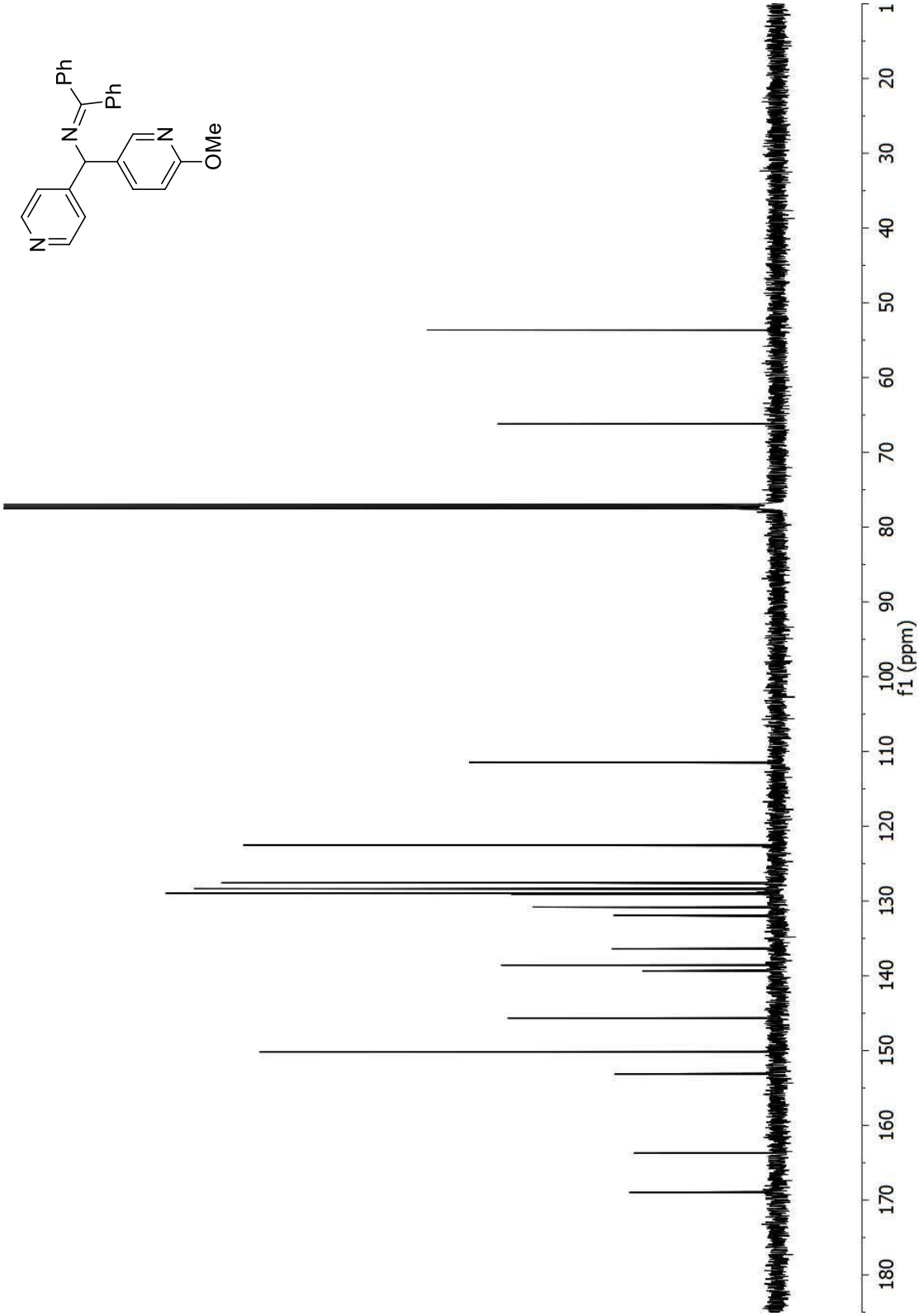
3ek - *N*-(diphenylmethylene)-1-(6-methoxypyridin-3-yl)-1-(pyridin-4-yl)methanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)



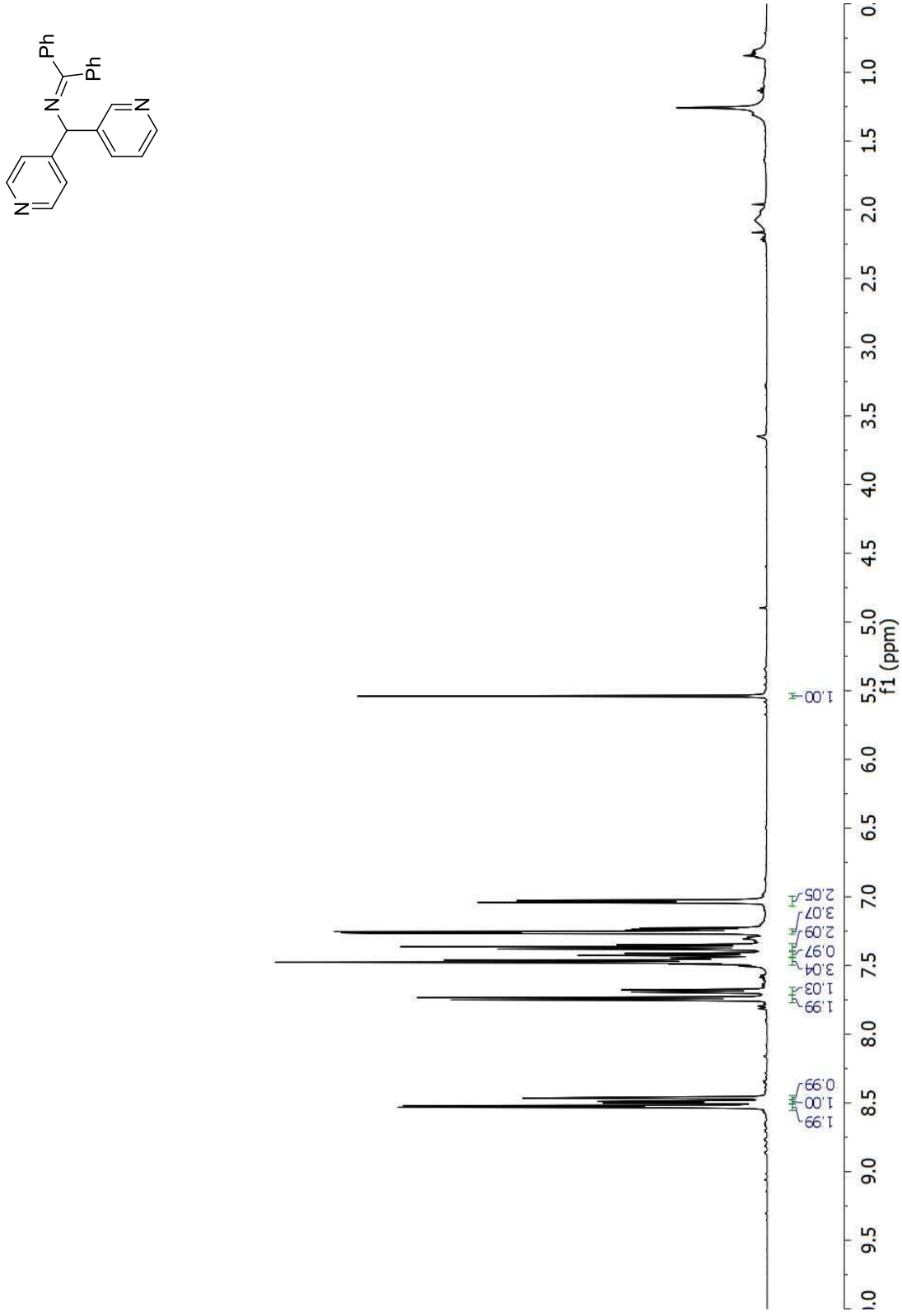
3ek - *N*-(diphenylmethylene)-1-(6-methoxypyridin-3-yl)-1-(pyridin-4-yl)methanamine

(^{13}C NMR, $CDCl_3$, 125 MHz)



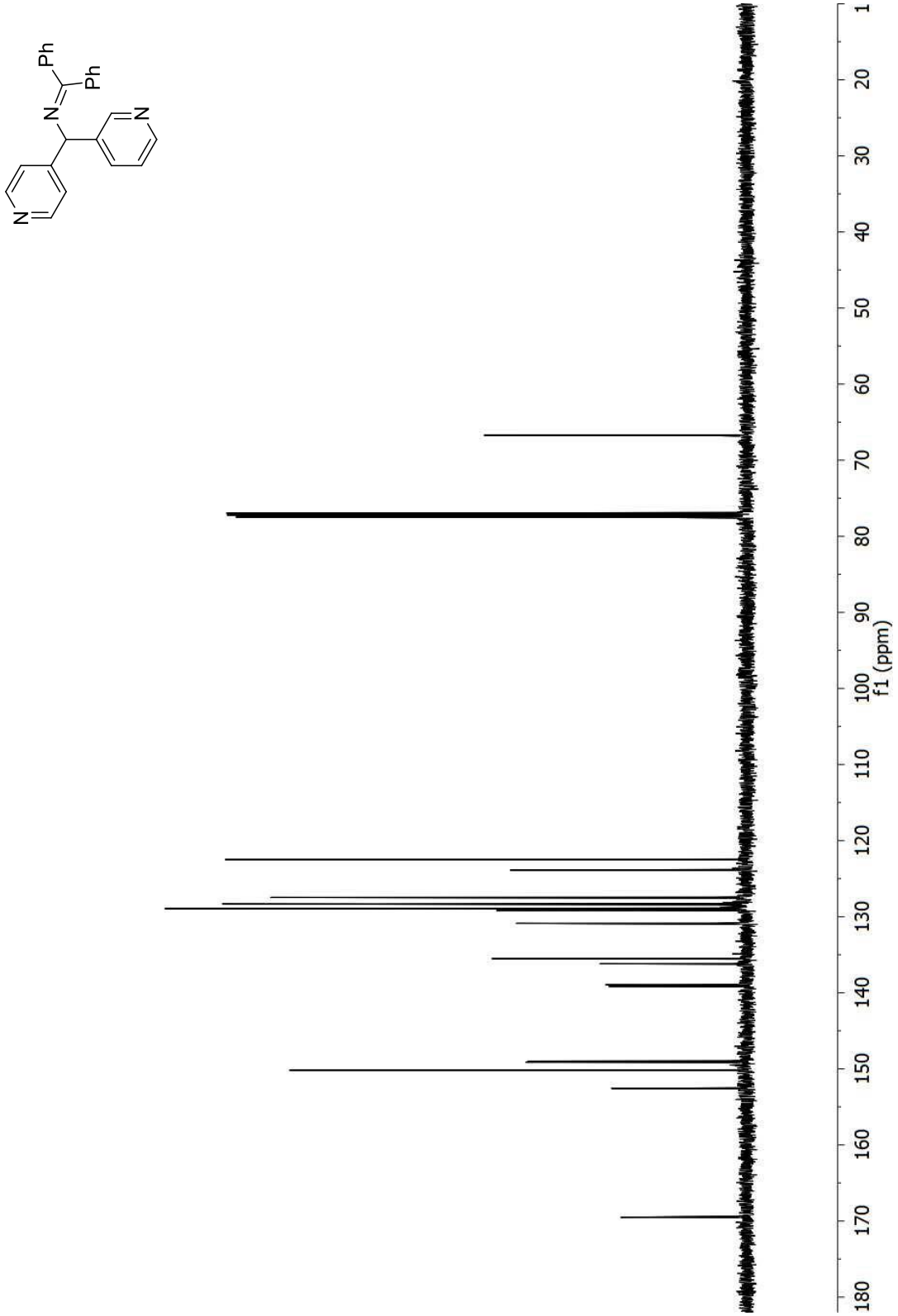
3el - *N*-(diphenylmethylene)-1-(pyridin-3-yl)-1-(pyridin-4-yl)methanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)



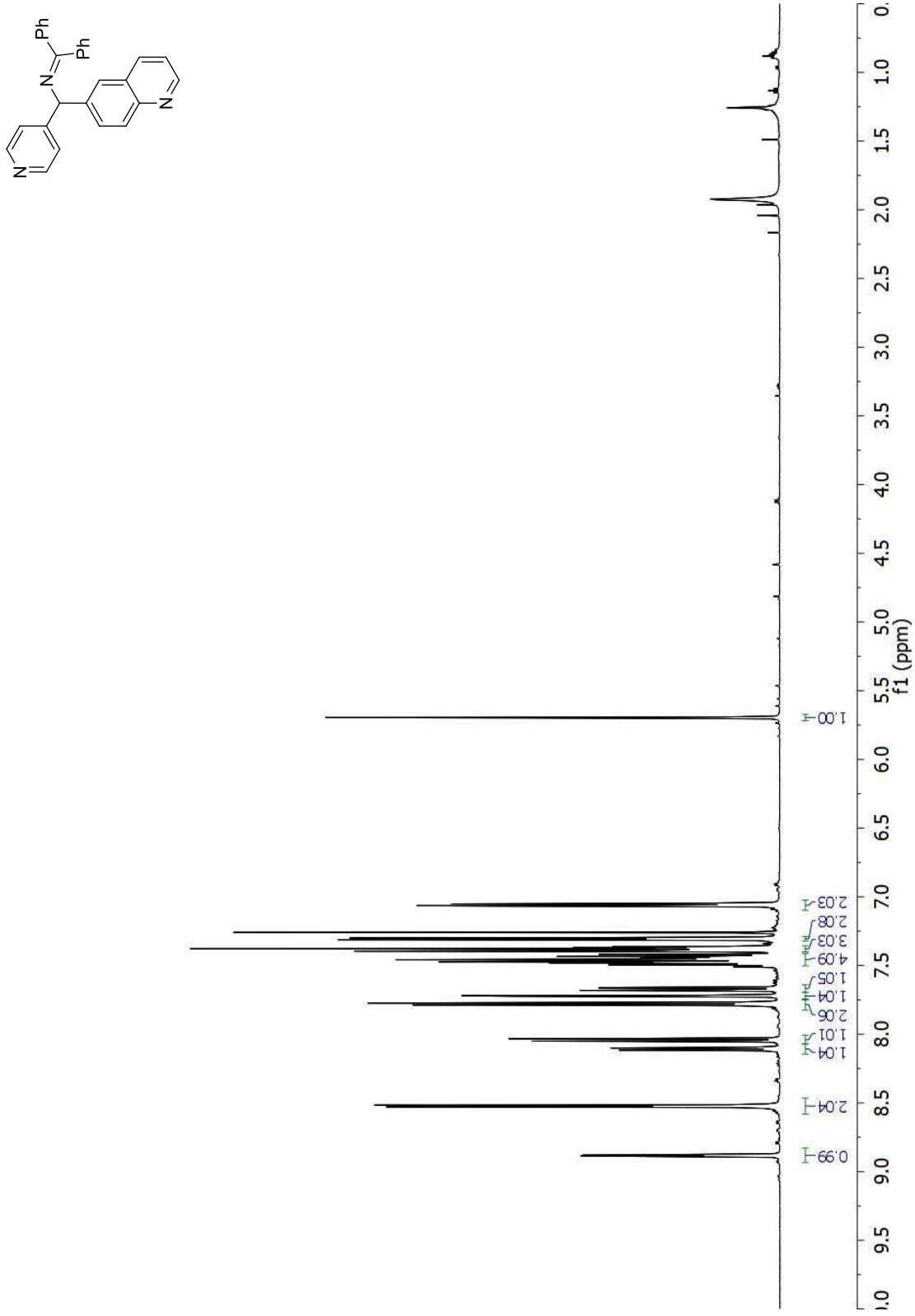
3el - *N*-(diphenylmethylene)-1-(pyridin-3-yl)-1-(pyridin-4-yl)methanamine

(^{13}C NMR, $CDCl_3$, 125 MHz)



3em - *N*-(diphenylmethylene)-1-(pyridin-4-yl)-1-(quinolin-6-yl)methanamine

(^{1}H NMR, $CDCl_3$, 500 MHz)



3em - *N*-(diphenylmethylene)-1-(pyridin-4-yl)-1-(quinolin-6-yl)methanamine

(^{13}C NMR, $CDCl_3$, 125 MHz)