SUPPORTING INFORMATION

Synthesis of Diarylmethylamines via Palladium-Catalyzed Regioselective Arylation of 1,1,3-Triaryl-2-Azaallyl Anions

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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 diethyl ether), dioxane, and 2-MeTHF 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. Note that in some cases, due to the large number of inequivalent aromatic carbons in the products, coincidental overlap of resonances prevented observation of all the expected resonances.

Preparation of Imines : Imines(**1a-1j**) were prepared according to literature procedures.[1]

Preparation of Aldimines : Aldimines (**1a'**, **1i'**, **1h'**, and **1l'** in Table 4) were prepared according to literature procedures.[2]

Preparation of Pd Dimer for 3rd Generation Pre-catalyst: Palladium μ-OMs dimer for 3rd generation pre-catalyst was prepared according to literature procedure.[3]

Procedure and Characterization for the Deprotonation/Benzylation of Benzophenone Imine

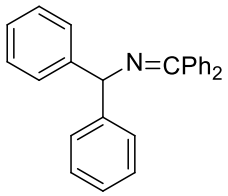
General Procedure A: An oven-dried microwave vial equipped with a stir bar was charged with imine **1a** (27.2 mg, 0.10 mmol) and $NaN(SiMe_3)_2$ (27.5 mg, 0.15 mmol) under a nitrogen atmosphere. Next, 1 mL of dry THF was added under nitrogen via syringe, the vial was sealed and benzyl chloride (13.8 μL, 0.12 mmol) was added to the reaction mixture via syringe through the rubber septum. The reaction mixture was next stirred for 12 h at 24 ℃, 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 assay yield was determined by ^1H NMR spectroscopy of the crude reaction mixture by integration using 1,4-dimethylbenzene as internal standard in accordance to literature procedures.[4]

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

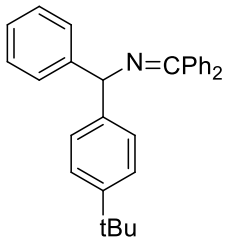
General Procedure B (Pd-Catalyzed Arylation of Ketimines): An oven-dried microwave vial equipped with a stir bar was charged with imine **1a** (54.3 mg, 0.20 mmol) under a nitrogen atmosphere. A stock solution of $Pd(OAc)_2$ (0.55 mg, 0.0025 mmol) and NiXantPhos (2.1 mg, 0.00375 mmol) under nitrogen in 0.5 mL dry CPME was taken up by syringe and added to the reaction vial. The vial was sealed, and 1-bromo-4-*tert*-butylbenzene (17.3 μL, 0.10 mmol) was added dropwise by syringe to this solution through the rubber septum. A solution of $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol) in 0.5 mL CPME was added portionwise by syringe at 0.1 mL/30 min at 24 ℃. The reaction mixture was stirred for 3 h at 24 ℃, 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.

General Procedure C (Pd-Catalyzed Arylation of Aldimines): An oven-dried microwave vial equipped with a stir bar was charged with aldimine **1a'** (54.3 mg, 0.20 mmol) under a nitrogen atmosphere. A stock solution of Buchwald's 3rd generation pre-catalyst Pd dimer (1.8 mg, 0.0025 mmol) and NiXantphos (2.8 mg, 0.0050 mmol) under nitrogen in 0.5 mL dry CPME was taken up by syringe and added to the reaction vial. The vial was sealed, and 1-bromo-4-*tert*-butylbenzene (17.3 μL, 0.10 mmol) was added dropwise by syringe to this solution through the rubber septum. A solution of $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol) in 0.5 mL CPME was added portionwise by syringe at 0.1 mL/30

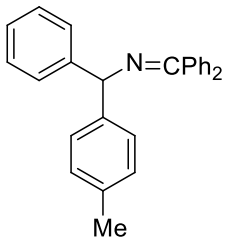
min at 60 °C. The reaction mixture was stirred for 12 h at 60 °C, opened to air, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in vacuo. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography.



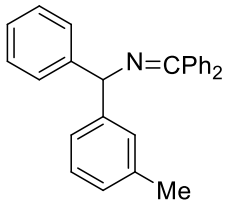
3aa – *N*-(diphenylmethylene)-1,1-diphenylmethanamine: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.2 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (31.3 mg, 90% yield) as a white solid. R_f = 0.70 (diethyl ether:hexanes = 1:5). The NMR spectral data match the previously published data.[5]



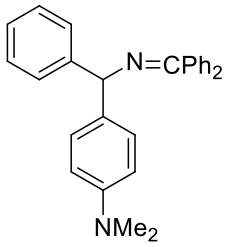
3ab – 1-(4-(*tert*-butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2b** (17.3 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (36.4 mg, 90% yield) as a white solid. Compound **3ab** was also synthesized following General Procedure C with aldimine **1a'** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol), aryl bromide (17.3 μL, 0.1 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 (37.9 mg, 94% yield) as a white solid. m.p. = 50–52 °C, R_f = 0.75 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77–7.74 (m, 2H), 7.44–7.41 (m, 3H), 7.37–7.31 (m, 5H), 7.29–7.23 (m, 6H), 7.20–7.17 (m, 1H), 7.10–7.07 (m, 2H), 5.53 (s, 1H), 1.27 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3): δ 166.8, 149.5, 145.2, 142.0, 140.1, 136.9, 130.1, 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.3, 126.8, 125.4, 69.8, 34.6, 31.6 ppm; IR (thin film): 3058, 2962, 1623, 1597, 1577, 1490, 1446, 1314, 1290, 1027, 779, 728, 700 cm^{-1}; HRMS calc'd for $C_{30}H_{30}N^+$ 403.2300, observed 404.2374 $[MH]^+$.



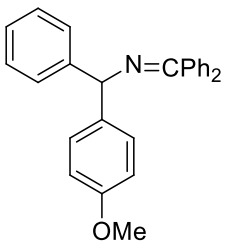
3ac – *N*-(diphenylmethylene)-1-phenyl-1-(*p*-tolyl)methanamine: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2c** (12.3 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (31.5 mg, 87% yield) as a white solid. Compound **3ac** was also synthesized following General Procedure B with ketamine **1b** (57.1 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 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 (32.2 mg, 89% yield) as a white solid. m.p. = 110–112 °C, R_f = 0.77 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.0 Hz, 2H), 7.43–7.42 (m, 3H), 7.37–7.31 (m, 5H), 7.27–7.24 (m, 2H), 7.21–7.16 (m, 3H), 7.08–7.07 (m, 4H), 5.52 (s, 1H), 2.29 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.9, 145.3, 142.1, 140.1, 137.0, 136.4, 130.2, 129.2, 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.7, 127.6, 126.8, 69.8, 21.2 ppm; IR (thin film): 3070, 1622, 1590, 1575, 1490, 1440, 1315, 1290, 1015, 780, 718, 700 cm^{-1}; HRMS calc'd for $C_{27}H_{24}N^+$ 361.1830, observed 362.1909 $[MH]^+$.



3ad – *N*-(diphenylmethylene)-1-phenyl-1-(*m*-tolyl)methanamine: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2d** (12.2 μL, 0.1 mmol) at 2.5 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 (30.1 mg, 83% yield) as a white solid. m.p. = 88–90 °C, R_f = 0.75 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.74 (m, 2H), 7.42–7.39 (m, 3H), 7.36–7.30 (m, 5H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20–7.11 (m, 4H), 7.07–7.06 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 5.52 (s, 1H), 2.28 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.9, 145.2, 145.0, 140.1, 138.0, 136.9, 130.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 126.8, 124.8, 70.1, 21.7 ppm; IR (thin film): 3058, 1622, 1598, 1578, 1490, 1446, 1314, 1289, 1000, 780, 723, 696 cm^{-1}; HRMS calc'd for $C_{27}H_{24}N^+$ 361.1830, observed 362.1908 $[MH]^+$.

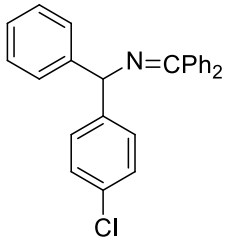


3ae – **4-(((diphenylmethylene)amino)(phenyl)methyl)-*N*,*N*-dimethylaniline**: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2e** (20.2 mg, 0.10 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:10) to give the product (30.4 mg, 78% yield) as a colorless oil. Compound **3ae** was also synthesized following General Procedure C with aldimine **1a'** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol), and aryl bromide **2e** (20.2 mg, 0.1 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 = 1:10) to give the product (31.2 mg, 80% yield) as a colorless oil. R_f = 0.44 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.43–7.40 (m, 3H), 7.35–7.29 (m, 5H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.17–7.14 (m, 3H), 7.10–7.08 (m, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 5.48 (s, 1H), 2.88 (s, 6H) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.3, 149.7, 145.7, 140.2, 137.1, 133.2, 130.1, 128.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.7, 126.5, 112.8, 69.5, 40.8 ppm; IR (thin film): 3058, 1611, 1577, 1518, 1490, 1445, 1315, 1276, 1028, 780, 717, 696 cm^{-1}; HRMS calc'd for $C_{28}H_{27}N_2^+$ 390.2096, observed 391.2177 $[MH]^+$, $C_{28}H_{26}N_2Na^+$ 413.1990 $[M+Na]^+$.

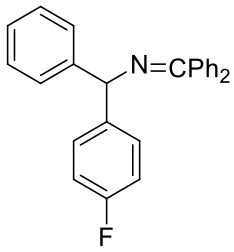


3af – ***N*-(diphenylmethylene)-1-(*p*-methoxyphenyl)-1-phenylmethanamine**: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2f** (12.5 μL, 0.1 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product (26.4 mg, 70% yield) as a thick oil. Compound **3af** was also synthesized following General Procedure B with ketamine **1d** (90.4 mg, 0.30 mmol), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol), aryl bromide **2a** (10.7 μL, 0.1 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 = 1:30) to give the product (26.8 mg, 71% yield). R_f = 0.55 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.42–7.39 (m, 3H), 7.37–7.30 (m, 5H),

7.27–7.20 (m, 4H), 7.18–7.15 (m, 1H), 7.08–7.06 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.51 (s, 1H), 3.74 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.8, 158.6, 145.4, 140.1, 137.4, 136.9, 130.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 127.9, 127.7, 126.8, 113.9, 69.4, 55.4 ppm; IR (thin film): 3059, 1609, 1578, 1508, 1490, 1445, 1314, 1276, 1030, 781, 725, 696 cm^{-1}; HRMS calc'd for $C_{27}H_{24}NO^+$ 377.1780, observed 378.1863 $[MH]^+$.



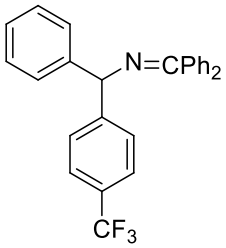
3ag – **1-(*p*-chlorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine**: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2g** (19.1 mg, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (34.3 mg, 90% yield) as a colorless oil. **3ag** was also synthesized following General Procedure B with ketamine **1f** (61.2 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 2.5 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 (34.0 mg, 89% yield) as a colorless oil. R_f = 0.78 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 7.5, 1.0 Hz, 2H)，7.42–7.40 (m, 3H), 7.37–7.31 (m, 3H), 7.29–7.22 (m, 8H), 7.20–7.17 (m, 1H), 7.05–7.04 (m, 2H), 5.51 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 167.5, 144.6, 143.6, 139.8, 136.7, 132.6, 130.4, 129.1, 128.9, 128.8, 128.69, 128.68, 128.65, 128.2, 127.8, 127.6, 127.1, 69.3 ppm; IR (thin film): 3060, 1622, 1598, 1576, 1488, 1446, 1315, 1282, 1014, 780, 715, 697 cm^{-1}; HRMS calc'd for $C_{26}H_{21}ClN^+$ 381.1284, observed 382.1350 $[MH]^+$.



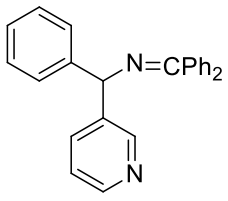
3ah – ***N*-(diphenylmethylene)-1-(*p*-fluorophenyl)-1-phenylmethanamine**: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2h** (11.0 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (31.4 mg, 86% yield) as a white solid. **3ah** was also synthesized following General Procedure B with ketamine **1e** (57.9 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 2.5 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 (30.3 mg, 83% yield) as a white solid. m.p. = 92–96 °C, R_f= 0.70 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.74 (m, 2H), 7.44–7.43 (m, 3H), 7.39–7.32 (m, 3H), 7.29–7.26 (m, 6H), 7.21–7.18 (m, 1H), 7.07–7.05 (m, 2H), 6.97–6.94 (m, 2H), 5.53 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.3, 161.8 (d, $^1J_{C\text{-}F}$= 243.3 Hz), 144.9, 140.8 (d, $^4J_{C\text{-}F}$= 3.1 Hz), 139.9, 136.8, 130.3, 129.2 (d, $^3J_{C\text{-}F}$= 7.9 Hz), 128.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.6, 127.0, 115.3 (d, $^2J_{C\text{-}F}$= 21.2 Hz), 69.3 ppm; IR (thin film): 3059, 1623, 1601, 1577, 1491, 1446, 1314, 1222, 1027, 779, 725, 696 cm^{-1}; HRMS calc'd for $C_{26}H_{21}FN^+$ 365.1580, observed 366.1656 [MH]$^+$.

3ai –*N*-(diphenylmethylene)-1-phenyl-1-(*p*-(trifluoromethyl)phenyl)methanamine: The

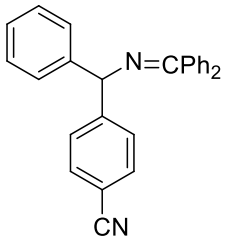


reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2i** (14.0 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (31.1 mg, 75% yield) as a colorless oil. R_f= 0.77 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76–7.74 (m, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.47–7.43 (m, 5H), 7.38–7.26 (m, 7H), 7.21–7.18 (m, 1H), 7.06–7.04 (m, 2H), 5.59 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.9, 149.0, 144.2, 139.7, 136.7, 130.5, 129.2, 129.0, 128.9, 128.7, 128.3, 128.0, 127.8, 127.7, 127.2, 125.5 (q, $J_{C\text{-}F}$= 3.8 Hz), 123.4 (q, $J_{C\text{-}F}$= 270.4 Hz), 69.7 ppm; IR (thin film): 3060, 1618, 1598, 1577, 1491, 1446, 1325, 1123, 1066, 1018, 779, 726, 697 cm^{-1}; HRMS calc'd for $C_{27}H_{23}F_3N^+$ 415.1548, observed 415.1627 [MH]$^+$.

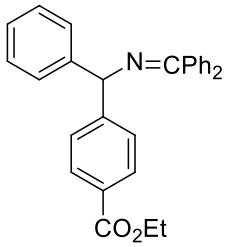


3aj – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2j** (9.6 μL, 0.1 mmol) at 5 mol % catalyst loading. The crude material was purified 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 (21.1 mg, 60% yield) as a white solid. **3aj** was also synthesized following General Procedure B with ketamine **1h** (54.5 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 5 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 (30.3 mg, 87% yield). Synthesis of **3aj** from aldimine was performed following General Procedure C with aldimine **1h'** (54.5 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 5 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 (26.8 mg, 77% yield) as a white solid. m.p. = 96–98 °C, R_f = 0.30 (diethyl ether:hexanes = 2.5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, *J* = 2.1 Hz, 1H), 8.44 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.75–7.73 (m, 2H), 7.71 (m, 1H), 7.45–7.40 (m, 3H), 7.39–7.36 (m, 1H), 7.34–7.31 (m, 4H), 7.29–7.26 (m, 2H), 7.21–7.17 (m, 2H), 7.06–7.04 (m, 2H), 5.59 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 168.0, 149.2, 148.3, 143.9, 140.4, 139.6, 136.5, 135.3, 130.5, 128.9, 128.8, 128.7, 128.6, 128.2, 127.6, 127.5, 127.2, 123.6, 67.7 ppm; IR (thin film): 3027, 1623, 1597, 1574, 1476, 1440, 1316, 1281, 1049, 782, 704, 695 cm^{-1}; HRMS calc'd for $C_{25}H_{21}N_2^+$ 348.1626, observed 349.1692 $[MH]^+$.

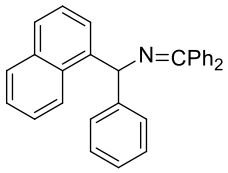


3ak – *p*-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2k** (18.2 mg, 0.1 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:50 to diethyl ether:hexanes = 1:10) to give the product (23.8 mg, 64% yield) as a colorless oil. R_f = 0.38 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–7.73 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46–7.32 (m, 8H), 7.27 (d, *J* = 4.0 Hz, 4H), 7.22–7.18 (m, 1H), 7.03–7.01 (m, 2H), 5.57 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$):168.3, 150.4, 143.7, 139.5, 136.5, 132.4, 130.6, 130.2, 128.9, 128.8, 128.7, 128.3, 128.2, 127.7, 127.6, 127.4, 119.1, 110.6, 69.6 ppm; IR (thin film): 3059, 2228, 1622, 1607, 1577, 1490, 1446, 1315, 1276, 1027, 781, 727, 697 cm^{-1}; HRMS calc'd for $C_{27}H_{21}N_2^+$ 372.1626, observed 373.1702 $[MH]^+$.

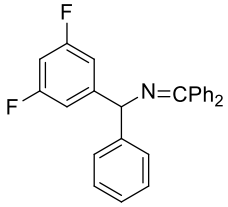


3al – Ethyl *p*-(((diphenylmethylene)amino)(phenyl)methyl)benzoate: The reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2l** (16.3 μL, 0.1 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:50 to

diethyl ether:hexanes = 1:20) to give the product (26.4 mg, 63% yield) as a colorless oil. R_f = 0.45 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.76–7.74 (m, 2H), 7.44–7.40 (m, 5H), 7.38–7.30 (m, 5H), 7.28–7.25 (m, 2H), 7.21–7.17 (m, 1H), 7.05–7.04 (m, 2H), 5.59 (s, 1H), 4.3 (q, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 167.8, 166.7, 150.1, 144.3, 139.8, 136.7, 130.4, 129.8, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.7, 127.6, 127.1, 69.8, 60.9, 14.5 ppm; IR (thin film): 3059, 1716, 1622, 1599, 1576, 1490, 1446, 1314, 1274, 1021, 780, 730, 698 cm^{-1}; HRMS calc'd for $C_{29}H_{26}NO_2^+$ 419.1885, observed 420.1944 [MH]$^+$.

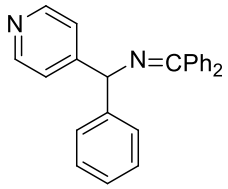


3ca – *N*-(diphenylmethylene)-1-(naphthalen-1-yl)-1-phenylmethanamine: The reaction was performed following General Procedure B with ketamine **1c** (64.3 mg, 0.20 mmol), LiO-*t*-Bu (24.0 mg, 0.30 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (28.3 mg, 71% yield) as a thick oil. We observed that grease co-elute with the product as only impurity shown in NMR spectra. Due to this reason, we hydrolyzed the product following the General Procedure of imine product hydrolysis to its ammonium salt **12** depicted below. Overall yield of arylation/hydrolysis was 68%. R_f = 0.71 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75–7.73 (m, 4H), 7.46–7.35 (m, 6H), 7.33–7.28 (m, 5H), 7.22–7.20 (m, 2H), 7.16–7.13 (m, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 6.26 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 167.2, 144.6, 140.2, 140.0, 137.8, 136.8, 134.3, 132.6, 131.2, 130.3, 130.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.2, 128.0, 127.8, 127.6, 126.7, 126.5, 125.8, 125.7, 125.4, 125.0, 67.2 ppm; IR (thin film): 3057, 1618, 1596, 1576, 1491, 1393, 1315, 1283, 1028, 798, 718, 696 cm^{-1}; HRMS calc'd for $C_{30}H_{24}N^+$ 397.1830, observed 398.1905 [MH]$^+$.

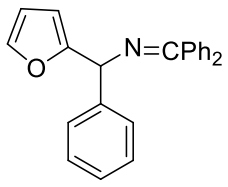


3ga – 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine: The reaction was performed following General Procedure B with ketamine **1g** (61.5 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 2.5 mol % catalyst loading. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product

(34.9 mg, 91% yield) as a white solid. m.p. = 106–108 °C, R_f = 0.80 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.73 (m, 2H), 7.45–7.41 (m, 3H), 7.39–7.32 (m, 3H), 7.28–7.25 (m, 4H), 7.23–7.19 (m, 1H), 7.05–7.03 (m, 2H), 6.91–6.87 (m, 2H), 6.61 (m, 1H), 5.48 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 168.1, 164.2 (d, $^1J_{C\text{-}F}$ = 247 Hz), 162.2 (d, $^1J_{C\text{-}F}$ = 247 Hz), 149.1 (t, $^3J_{C\text{-}F}$ = 8.5 Hz), 143.8, 139.6, 136.5, 130.6, 129.0, 128.9, 128.8(d, $^4J_{C\text{-}F}$ = 3.3 Hz), 128.3, 127.8, 127.7, 127.4, 110.5 (dd, $^2J_{C\text{-}F}$ = 20 Hz, $^3J_{C\text{-}F}$ = 5.9 Hz), 102.2 (t, $^2J_{C\text{-}F}$ = 25 Hz), 69.3 ppm; IR (thin film): 3435, 1622, 1597, 1491, 1446, 1313, 1290, 1115, 976, 780, 696 cm^{-1}; HRMS calc'd for $C_{26}H_{20}F_2N^+$ 383.1486, observed 384.1564 [MH]$^+$.

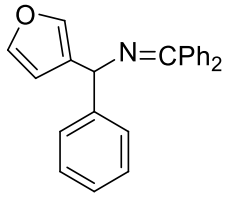


3ia – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine: The reaction was performed following General Procedure B with ketamine **1i** (54.4 mg, 0.20 mmol), $LiN(SiMe_3)_2$ (33.5 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 10 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:10 to diethyl ether:hexanes = 2:1) to give the product (31.4 mg, 90% yield) as a white solid. **3ia** was also synthesized following General Procedure C with aldimine **1i'** (54.4 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 5 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 (31.7 mg, 91% yield) as a white solid. m.p. = 118–120 °C, R_f = 0.33 (diethyl ether:hexanes = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.80–7.78 (m, 2H), 7.50–7.43 (m, 4H), 7.40–7.37 (m, 2H), 7.33–7.30 (m, 6H), 7.27–7.24 (m, 1H), 7.09–7.07 (m, 2H), 5.54 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 168.3, 153.4, 149.8, 143.3, 139.4, 136.3, 130.4, 128.8, 128.7, 128.6, 128.5, 128.1, 127.6, 127.5, 127.3, 122.5, 68.9 ppm; IR (thin film): 3026, 1623, 1593, 1560, 1490, 1446, 1316, 1280, 1027, 780, 727, 697 cm^{-1}; HRMS calc'd for $C_{25}H_{21}N_2^+$ 348.1626, observed 349.1694 [MH]$^+$.



3ja – *N*-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine: The reaction was performed following General Procedure B with ketamine **1j** (52.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7 μL, 0.1 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 (20.3 mg, 60% yield) as a white solid. m.p. = 90–92 °C, R_f = 0.70 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.44–7.43 (m, 3H), 7.38–7.36 (m, 3H), 7.33–7.29 (m, 5H), 7.25–7.23 (m, 1H), 7.16–7.15 (m, 2H), 6.28–6.27 (m, 1H), 6.09 (dd, *J* = 3.0, 0.5 Hz, 1H), 5.62 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 168.7, 156.8, 142.0, 141.9, 139.9, 136.6, 130.4, 129.0, 128.8, 128.6, 128.5, 128.2, 128.0, 127.9, 127.4, 110.2, 106.6, 64.7 ppm; IR (thin film): 3059, 1622, 1597, 1576, 1490, 1446, 1316, 1286, 1009, 779, 718, 696 cm^{-1}; HRMS calc'd for $C_{24}H_{20}NO^+$ 337.1467, observed 338.1550 [MH]$^+$.

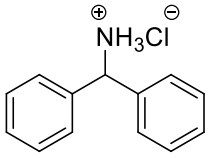


3la – *N*-(diphenylmethylene)-1-(furan-3-yl)-1-phenylmethanamine: The reaction was performed following General Procedure C with aldimine **1l'** (52.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.0 mg, 0.30 mmol), aryl bromide **2a** (10.7 μL, 0.1 mmol) at 5 mol % catalyst loading. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product (28.7 mg, 85% yield) as a white solid. m.p. = 64–66 °C, R_f= 0.70 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.41–7.40 (m, 3H), 7.34–7.26 (m, 9H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.11–7.09 (m, 2H), 6.25 (s, 1H), 5.49 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 167.4, 143.9, 143.1, 139.9, 139.4, 136.7, 130.3, 129.3, 128.9, 128.7, 128.6, 128.5, 128.2, 127.8, 127.6, 127.1, 109.9, 62.8 ppm; IR (thin film): 3059, 1622, 1597, 1576, 1490, 1446, 1315, 1285, 1018, 781, 716, 696 cm^{-1}; HRMS calc'd for $C_{24}H_{20}NO^+$ 337.1467, observed 338.1547 [MH]$^+$.

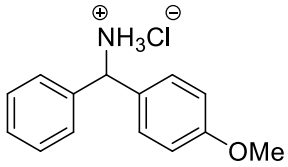
General Procedure D: Hydrolysis of Product Ketimines

A modified procedure from several literature reports[6] was used:

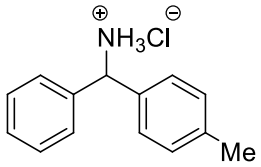
HCl 1N (1 mL) was added to the solution of imine **3ab** (40.4 mg 0.1 mmol) in THF (1 mL) at 0 °C. The solution was warmed to room temperature, stirred at room temperature and was monitored by TLC until all the imine was consumed. The THF was evaporated under vacuum. Another 1 mL HCl (1N) was added and a white precipitate was observed. The white solid was filtered and washed with cold Et_2O (1.0 mL×3). After drying under vacuum for 12 h, the hydrochloride salt was obtained as a white solid (25.4 mg, 92% yield).



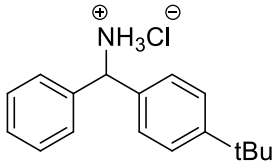
6 – diphenylmethanaminium chloride salt : The reaction was performed following General Procedure D with imine **3aa** (38.2 mg, 0.10 mmol) gave its ammonium salt **13** as white solid in 93% yield (20.4 mg). The NMR spectral data match the previously published data.[7]



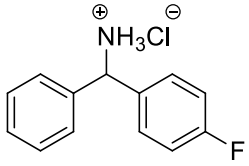
7 – (4-methoxyphenyl)(phenyl)methanaminium chloride salt : The reaction was performed following General Procedure D with imine **3af** (37.7 mg, 0.10 mmol) gave its ammonium salt **7** as white solid in 92% yield (22.9 mg). The NMR spectral data match the previously published data.[7]



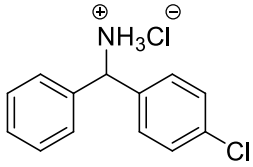
8 – phenyl(p-tolyl)methanaminium chloride salt : The reaction was performed following General Procedure D with imine **3ac** (36.1 mg, 0.10 mmol) gave its ammonium salt **8** as white solid in 96% yield (22.4 mg). The NMR spectral data match the previously published data.[7]



9 – (4-(*tert*-butyl)phenyl)(phenyl)methanamine ammounium salt : The reaction was performed following General Procedure D with imine **3ab** (40.3 mg, 0.10 mmol) gave its ammonium salt **9** as white solid in 92% yield (25.4 mg), m.p. = 272–274 ^{o}C; ^{1}H NMR (500 MHz, MeOD) δ 7.51–7.49 (m, 2H), 7.47–7.44 (m, 2H), 7.42–7.39 (m, 3H), 7.35–7.33 (m, 2H), 5.61 (s, 1H), 1.31 (s, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, MeOD): 153.5, 138.8, 135.7, 130.4, 130.1, 128.4, 128.2, 127.3, 59.2, 35.6, 31.7 ppm; IR (thin film): 3010, 2955, 1590, 1508, 1456, 1417, 1358, 1264, 1195, 1107, 1018, 784, 738, 698 cm^{-1}; HRMS calc'd for $C_{17}H_{20}^{+}$ 275.1441, observed 223.1480 [M-(NH_3Cl)]$^{+}$.

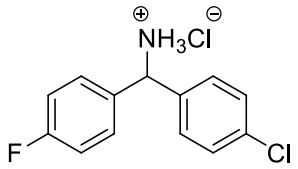


10 – (4-fluorophenyl)(phenyl)methanaminium chloride salt : The reaction was performed following General Procedure D with imine **3ah** (36.5 mg, 0.10 mmol) gave its ammonium salt **10** as white solid in 96% yield (22.8 mg). The NMR spectral data match the previously published data.[7]

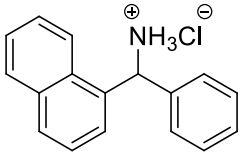


11 – (4-chlorophenyl)(phenyl)methanaminium chloride salt : The reaction was performed following General Procedure D with imine **3ag**

(38.2 mg, 0.10 mmol) gave its ammonium salt **11** as white solid in 93% yield (23.6 mg). The NMR spectral data match the previously published data.[7]



12 – (4-chlorophenyl)(4-fluorophenyl)methanaminium chloride salt : Arylation of **1f** and **2h** was conducted following General Procedure B on a 0.1 mmol scale using 1 equiv of **1f**, 2 equiv of $NaN(SiMe_3)_2$, and 2 equiv of **2h**. The crude material was purified by flash chromatography on deactivated silica gel (eluted with diethyl ether:hexanes = 1:100 to diethyl ether:hexanes = 1:50) to give the product (32.4 mg, 81% yield). After purification, product was hydrolyzed following General Procedure D gave its ammonium salt **12** as white solid in 79% overall yield (21.5 mg). m.p. = 268–270 ^{o}C; ^{1}H NMR (500 MHz, MeOD) δ 7.51–7.46 (m, 6H), 7.19 (t, J = 8.0 Hz, 2H), 5.73 (s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, MeOD): 164.3 (d, $^{1}J_{CF}$ = 246.3 Hz), 137.1, 135.9, 134.2 (d, $^{4}J_{CF}$ = 3.3 Hz), 130.8 (d, $^{3}J_{CF}$ = 8.5 Hz), 130.4, 130.1, 117.1 (d, $^{2}J_{CF}$ = 22.0 Hz), 58.0 ppm; IR (thin film): 2928, 1598, 1515, 1238, 1015, 829 cm^{-1}; HRMS calc'd for $C_{13}H_{13}Cl_2FN^{+}$ 272.0331, observed 219.0381 $[M-(NH_3Cl)]^{+}$.



13 – naphthalen-1-yl(phenyl)methanaminium chloride salt : As described in Section 2.6. Table 3, entry2. Imine **3ca** was hydrolyzed directly after purification. The reaction was performed following General Procedure D with imine **3ca** (28.3 mg, 0.071 mmol) gave its ammonium salt **13** as white solid in 95% yield, Overal 68% yield (18.1 mg). The NMR spectral data match the previously published data.[7]

Representative Microscale High-throughput Experimentation for Ligand Identification

General Experimental:

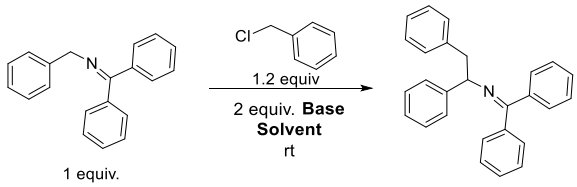
Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials was predosed with $Pd(OAc)_2$ (1 μmol) and the phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and $NaN(SiMe_3)_2$ (30 μmol) in THF was added to the ligand/catalyst mixture. The solvent was removed on the GeneVac and a parylene stir bar was then added to each reaction vial. Imine **1a** (10 μmol/reaction), bromobenzene (12 μmol) and 4,4′-di-*tert*-butylbiphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each reaction vial as a solution in THF (100 μL, 0.1 M). The 24-well plate was then sealed and stirred for 18 h at room temperature.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was added into each vial. The plate was covered again and the vials stirred for 10 min. to ensure good homogenization. Into a separate 24-well LC block was added 700 μL of acetonitrile, followed by 40 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

(1) Base and Solvent Screening for Deprotonation/Benzylation Studies:



Bases: $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, LiO^tBu, KO^tBu, NaO^tBu, NaH, LiOAc, KOAc, K_3PO_4, KOPh and Cs_2CO_3.

Well	Base	Solvent	Prod/IS[a]

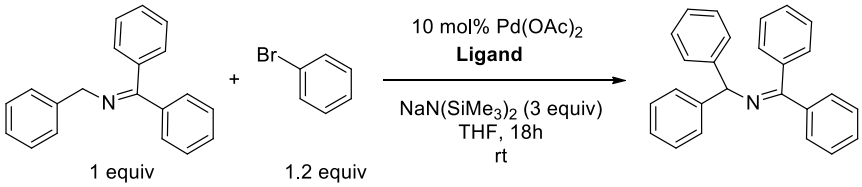
A01	LiO*t*Bu	CPME	0.00
B01		THF	0.16
A02	KO*t*Bu	CPME	5.22
B02		THF	5.79
A03	NaO*t*Bu	CPME	0.00
B03		THF	1.99
A04	$LiN(SiMe_3)_2$	CPME	0.16
B04		THF	3.59
A05	$NaN(SiMe_3)_2$	CPME	3.09
B05		THF	7.46
A06	$KN(SiMe_3)_2$	CPME	6.02
B06		THF	6.83
C01	NaH	CPME	0.10
D01		THF	0.89
C02	KOAc	CPME	0.00
D02		THF	0.00
C03	LiOAc	CPME	0.00
D03		THF	0.00
C04	K_3PO_4	CPME	0.00
D04		THF	0.00
C05	Cs_2CO_3	CPME	0.00

D05		THF	0.08
C06	KOPh	CPME	0.00
D06		THF	0.00

[a]Product/Internal standard ratio

The lead hit from the screening was **$NaN(SiMe_3)_2$** in **THF** (highest product/internal standard ratio). A scale-up reaction on a 0.1 mmol scale proved successful with isolation of the benzylation product in 95% yield.

(2) Ligand Screening:



$Pd(OAc)_2$ (10 mol %) was used to test 23 sterically and electronically diverse, mono- and bidentate phosphine ligands (ligands 1-23 from the Table below).

	Ligand libraries
1	2-(Di-*t*-butylphosphino)biphenyl (JohnPhos)
2	2-(Di-t-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl (RockPhos)
3	1,1'-Bis(di-*t*-butylphosphino)ferrocene (dtbpf)
4	2-Dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (SPhos)
5	Tri-*o*-tolylphosphine
6	2-(Di-1-adamantylphosphino)-*N*,*N*-dimethylaniline (Me-DalPhos)
7	1,1'-Bis(diisopropylphosphino)ferrocene (dippf)
8	5-(Di-*t*-butylphosphino)-1', 3', 5'-triphenyl-1'H-[1,4']bipyrazole (BippyPhos)
9	9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (XantPhos)

10 2-(Dicyclohexylphosphino)biphenyl (Cy-JohnPhos)

11 *N*-phenyl-2-(di-*t*-butylphosphino)pyrrole (cataCXium PtB)

12 *N*-phenyl-2-(dicyclohexylphosphino)pyrrole (cataCXium PCy)

13 racemic-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)

14 2-Dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl (DavePhos)

15 Butyldi-1-adamantylphosphine (cataCXium A)

16 Tricyclohexylphosphonium tetrafluoroborate

17 Tri-*t*-butylphosphonium tetrafluoroborate

18 1,2,3,4,5-Pentaphenyl-1'-(di-*t*-butylphosphino)ferrocene (QPhos)

19 2-Di-*tert*-butylphosphino-2',4',6'-triisopropylbiphenyl (*t*Bu-XPhos)

20 Dicyclohexyl-[3,6-dimethoxy-2-(2,4,6-triisopropylphenyl)phenyl]phosphane (BrettPhos)

21 1-[2-[Bis(*t*-butyl)phosphino]phenyl]-3,5-diphenyl-1H-pyrazole (TrippyPhos)

22 1,1'-Bis(diphenylphosphino)ferrocene (dppf)

23 4,6-Bis(diphenylphosphino)phenoxazine (NiXantPhos)

Well	**Ligand**	**Prod/IS**
A01	-	0.12
B01	JohnPhos	0.06
C01	RockPhos	0.07
D01	dtbpf	0.26

A02	SPhos	0.88
B02	*o*-Tolphosphine	0.37
C02	Me-DalPhos	0.12
D02	dippf	1.10
A03	BippyPhos	0.11
B03	XantPhos	0.77
C03	CyJohnPhos	0.54
D03	CataCXium PtB	0.10
A04	BINAP	0.14
B04	DavePhos	0.30
C04	CataCXium A	2.96
D04	CataCXium PCy	0.49
A05	PCy_3HBF_4	1.22
B05	*t*-Bu_3PHBF_4	0.60
C05	QPhos	0.20
D05	*t*-BuXPhos	0.07
A06	BrettPhos	0.14
B06	TrippyPhos	0.18
C06	dppf	0.47
D06	NIXANTPHOS	3.65

The lead hit from the screening was the combination of $Pd(OAc)_2$ (10 mol %) and **NIXANTPHOS** (10 mol %) (well D06). A scale-up reaction on a 0.1 mmol scale using the same procedure as HTE proved successful with product in 67% assay yield.

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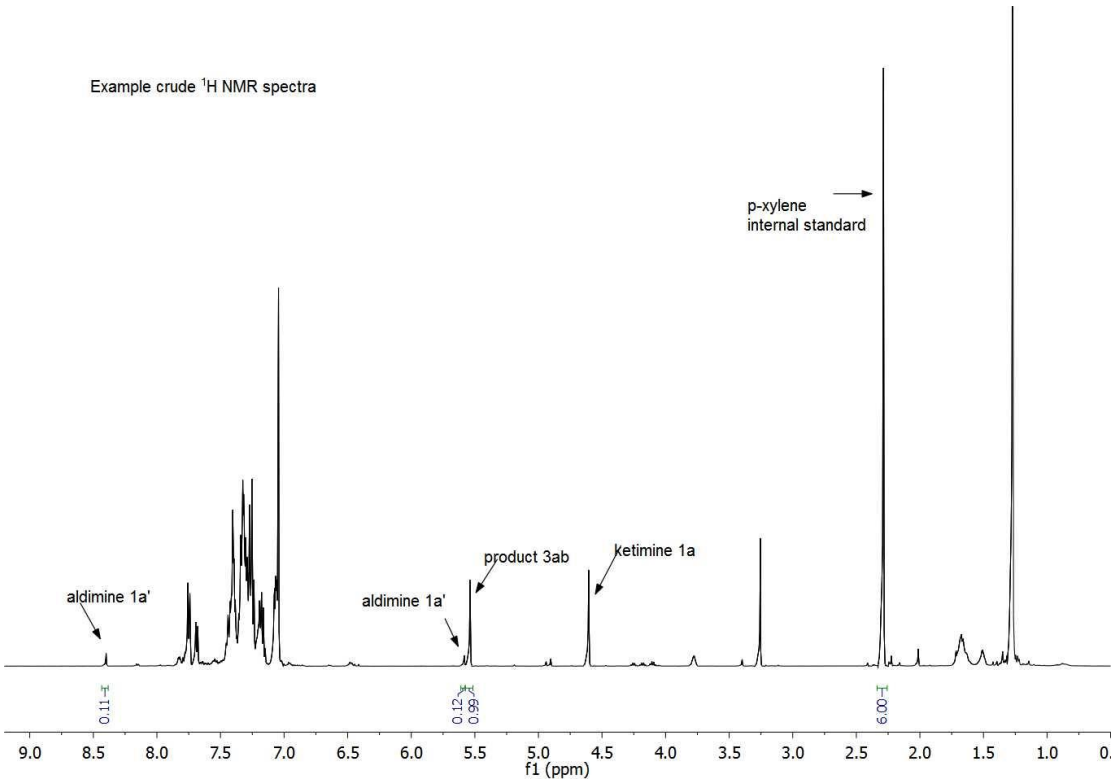
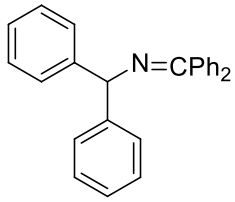
7. a) N. Plobeck, D. Powell, *Tetrahedron: Asymmetry* **2002**, *13*, 303-310; b) T. Niwa, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, *10*, 4689-4691.

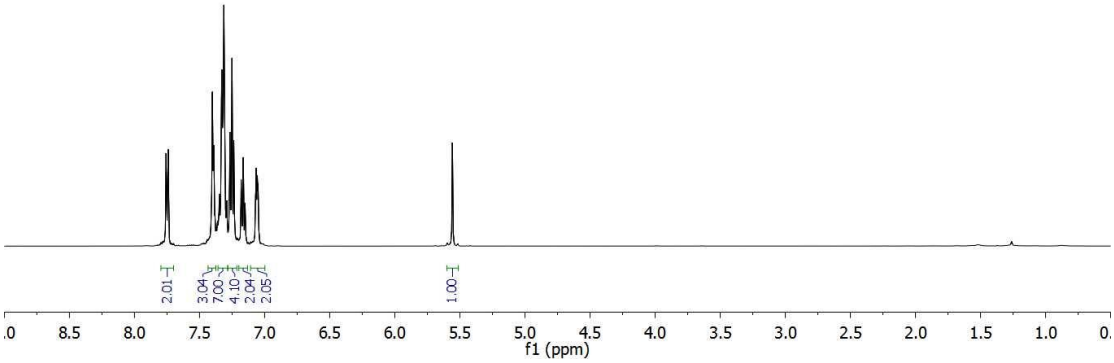
NMR Spectra.

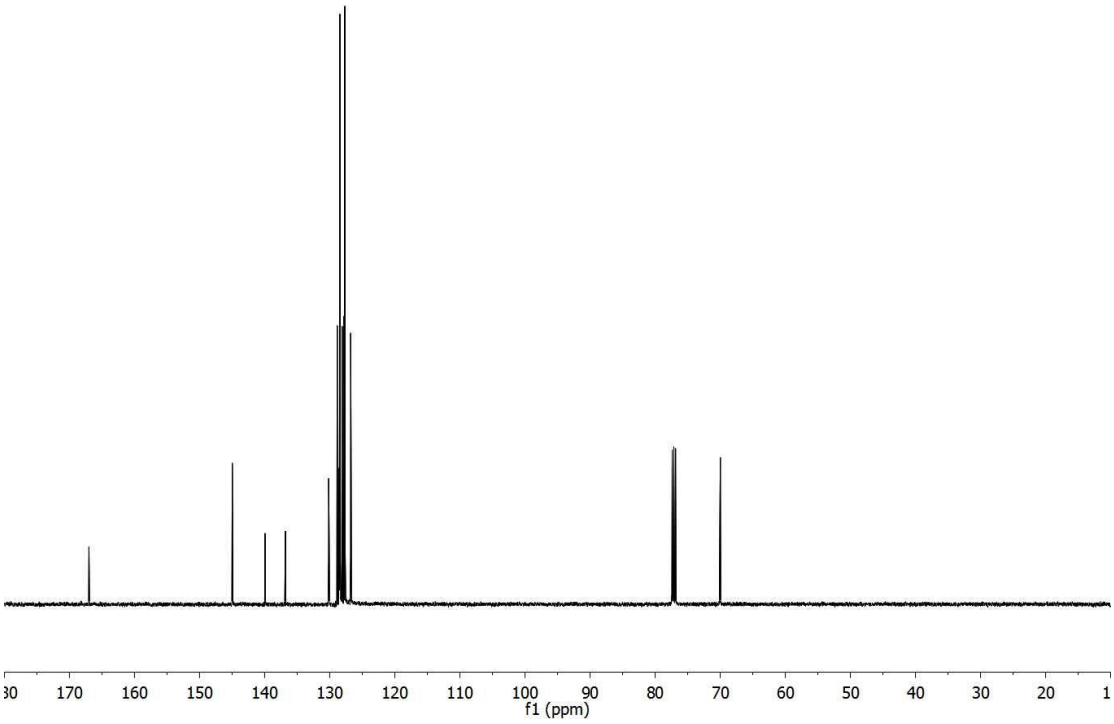
Example crude ^{1}H NMR spectra with 1,4-dimethylbenzene (*p*-xylene) as an internal standard



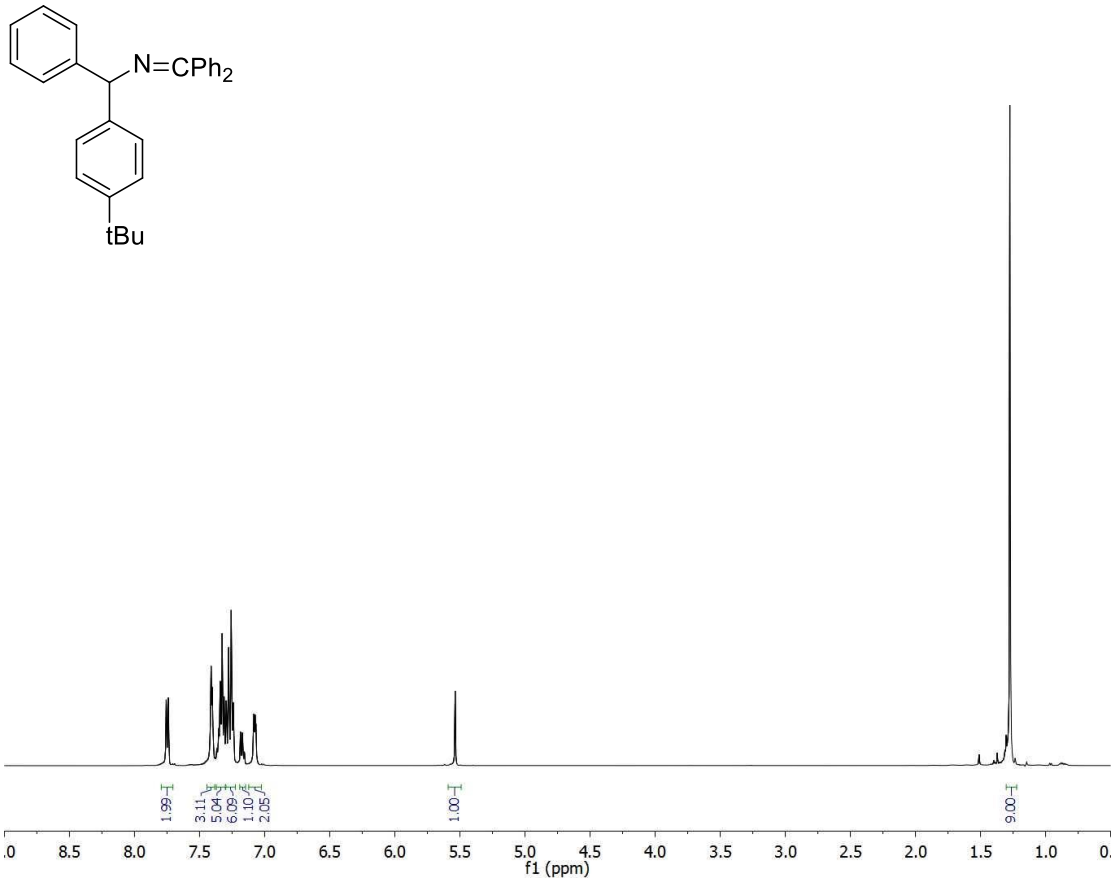
3aa – *N*-(diphenylmethylene)-1,1-diphenylmethanamine in $CDCl_3$

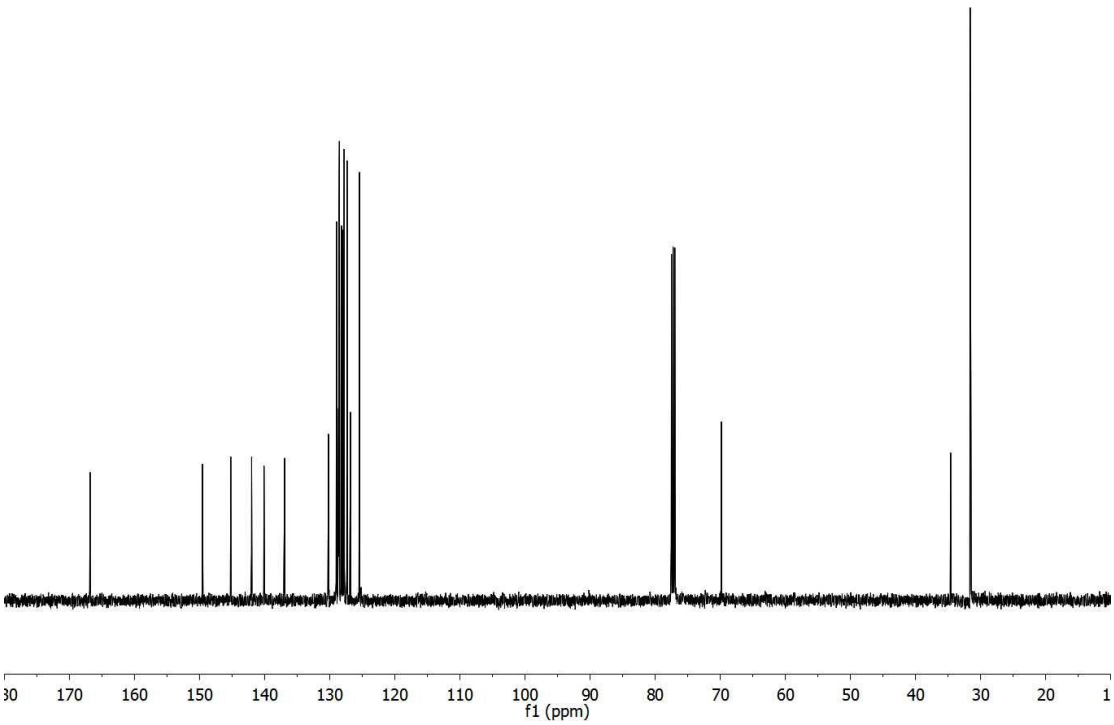




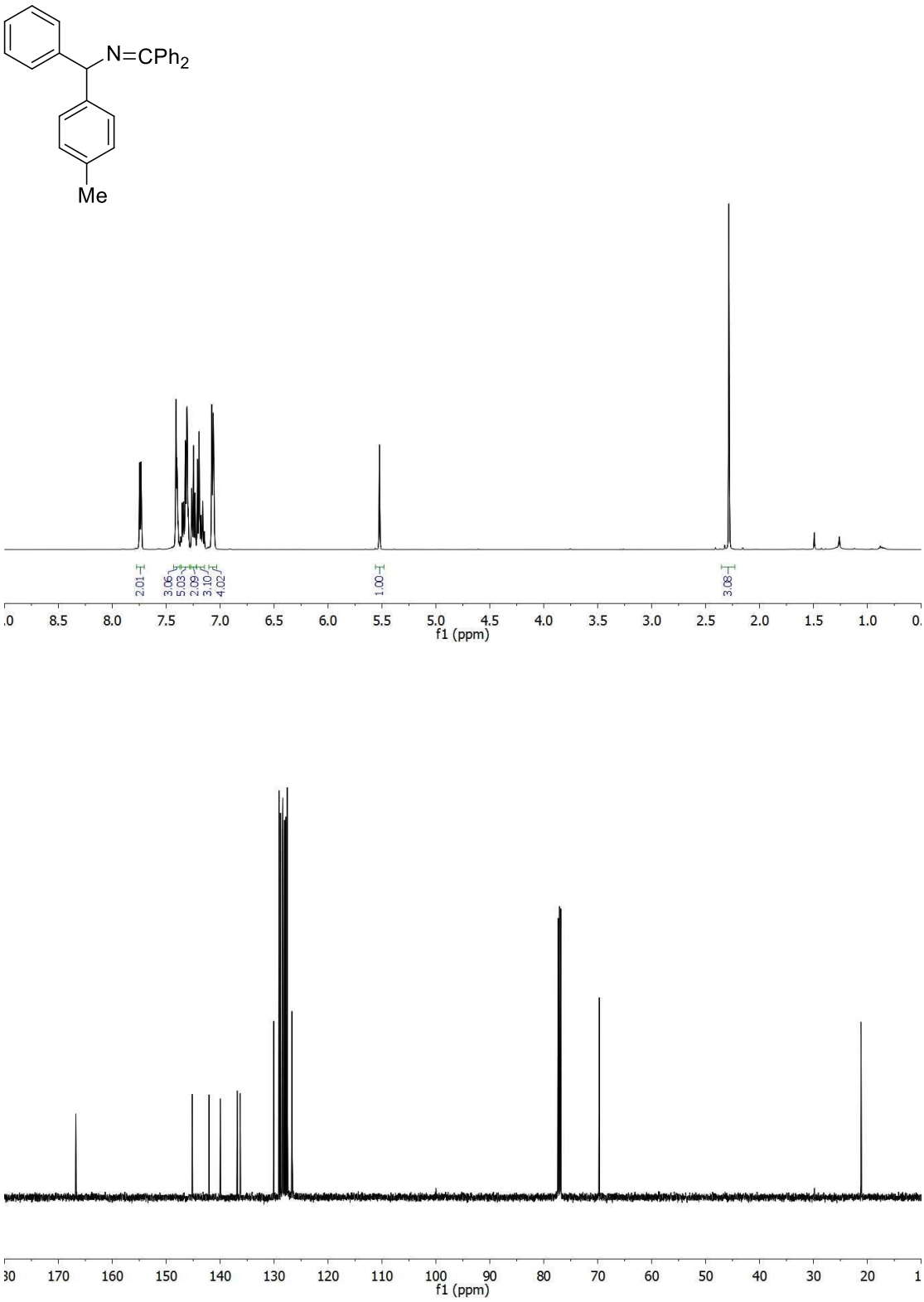


3ab – 1-(4-(*tert*-butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine in $CDCl_3$

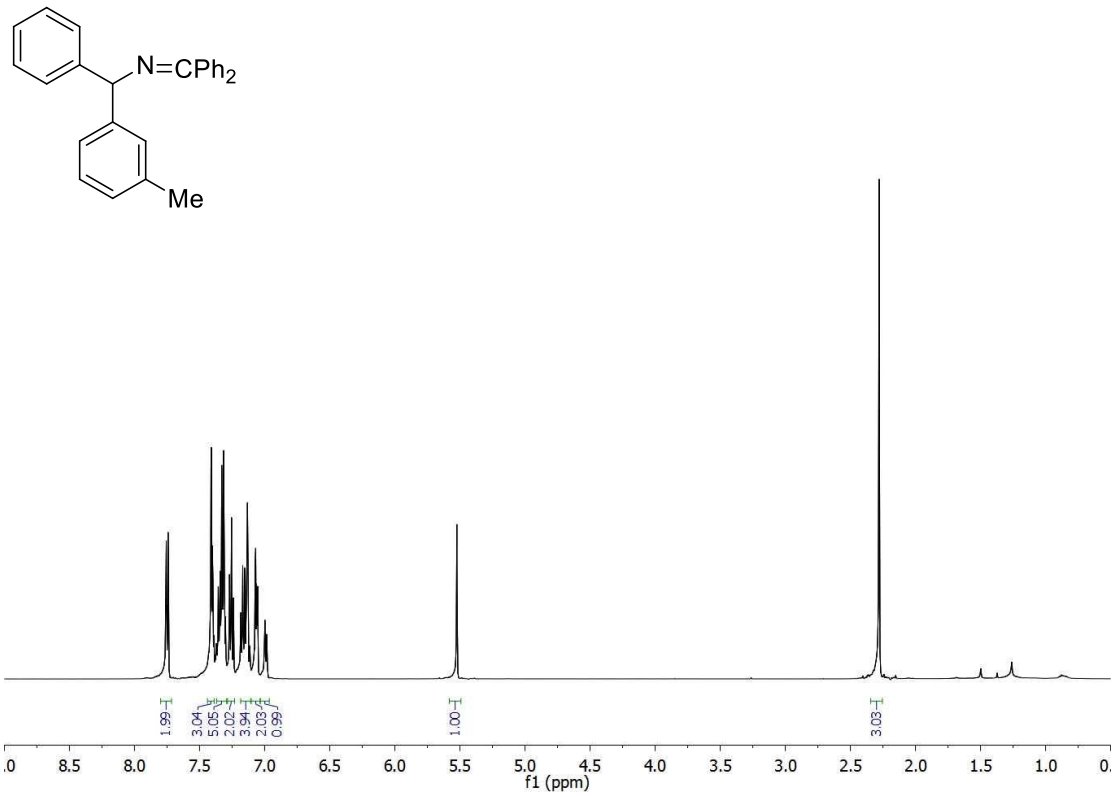


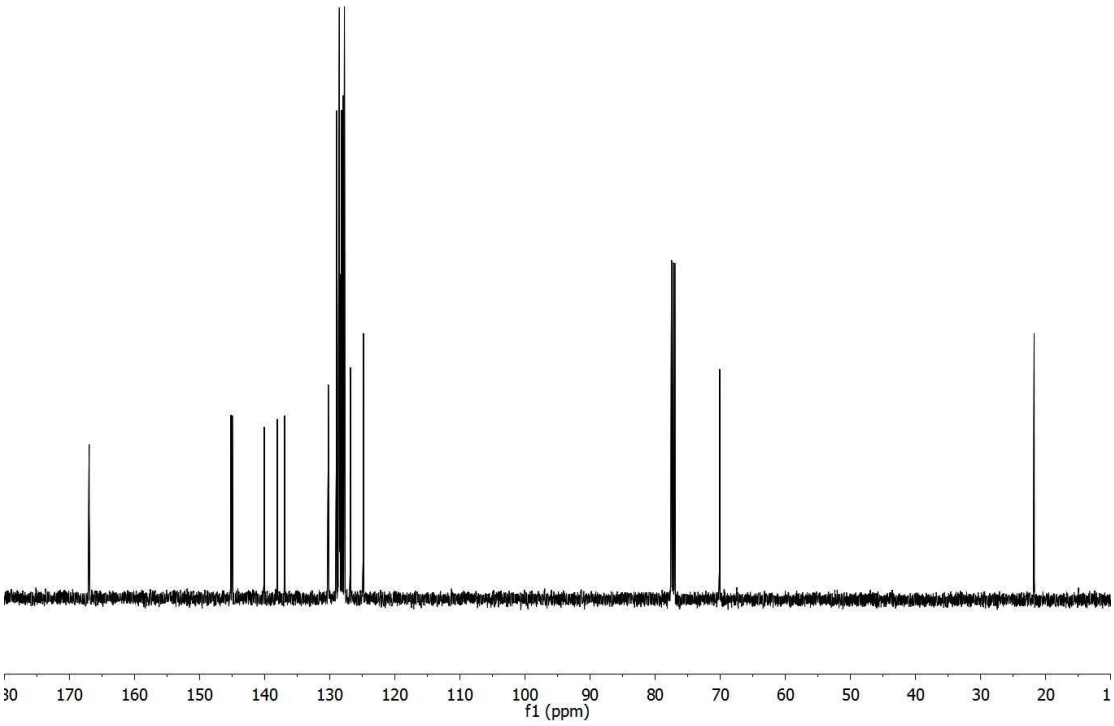


3ac – *N*-(diphenylmethylene)-1-phenyl-1-(*p*-tolyl)methanamine in $CDCl_3$

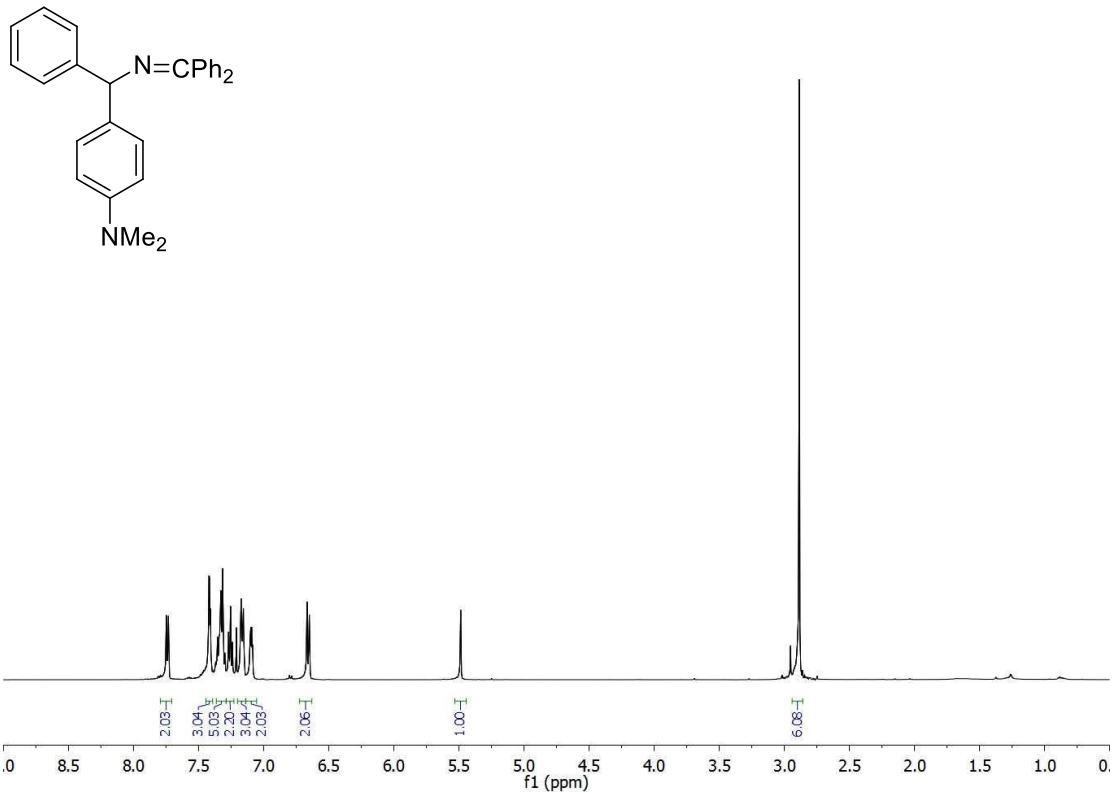


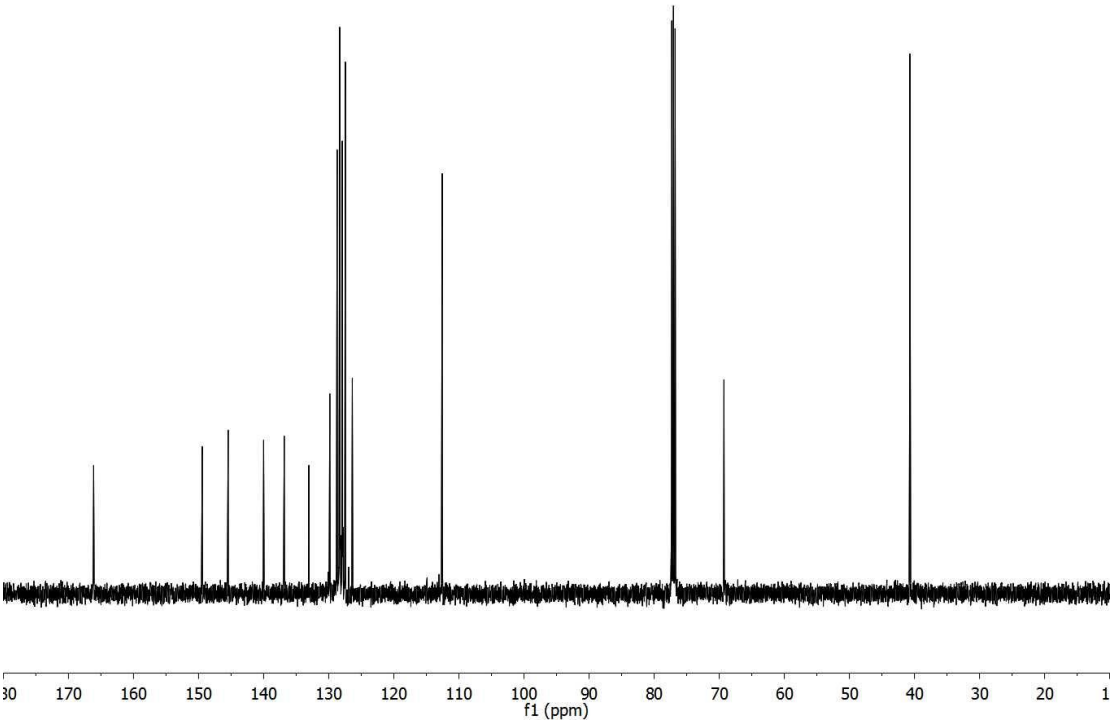
3ad – *N*-(diphenylmethylene)-1-phenyl-1-(*m*-tolyl)methanamine in $CDCl_3$



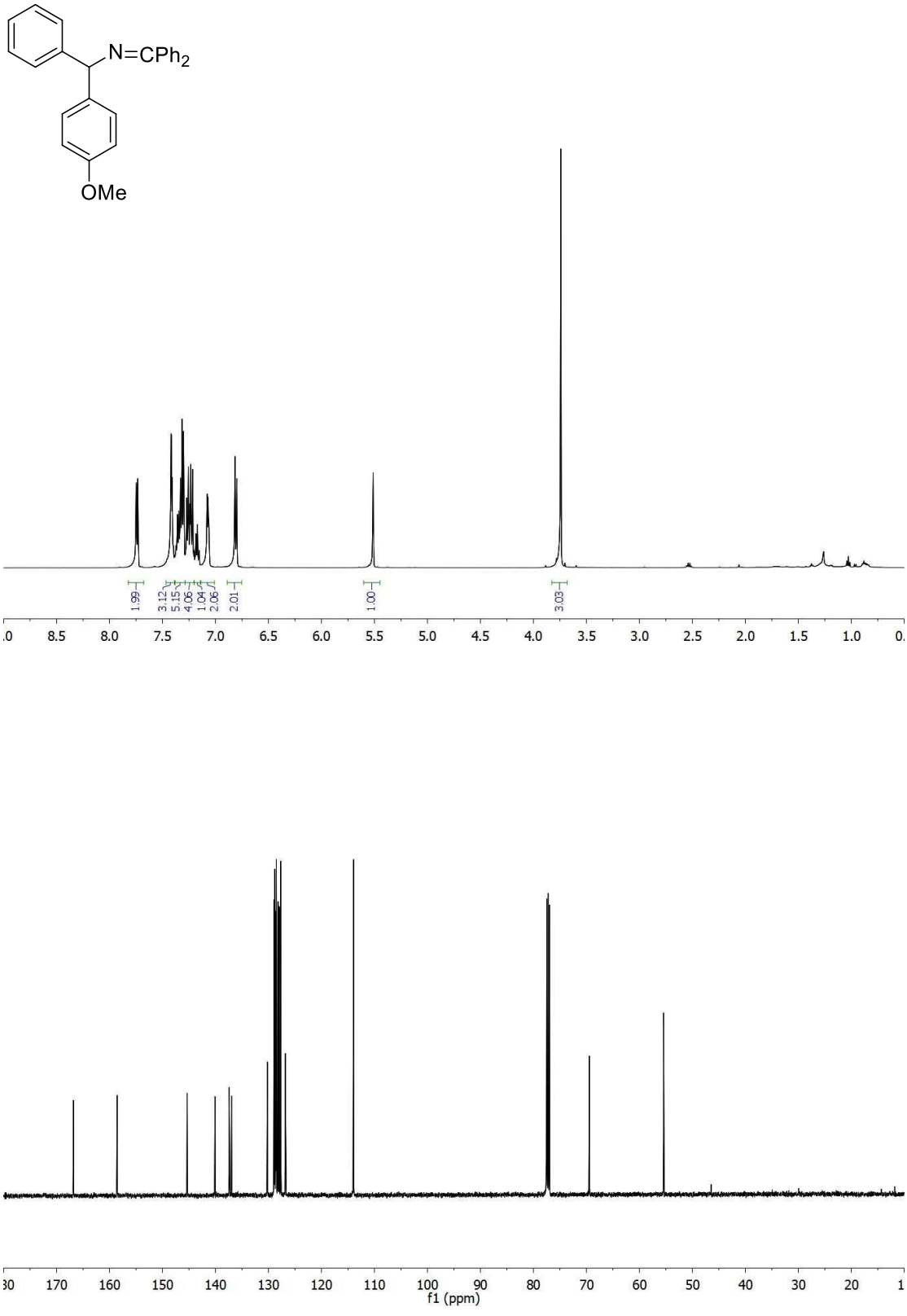


3ae – 4-(((diphenylmethylene)amino)(phenyl)methyl)-*N*,*N*-dimethylaniline in $CDCl_3$

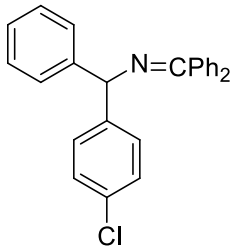


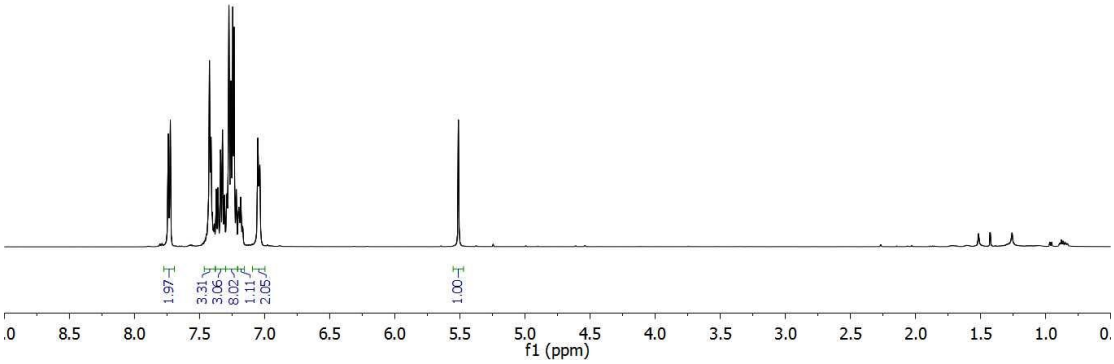


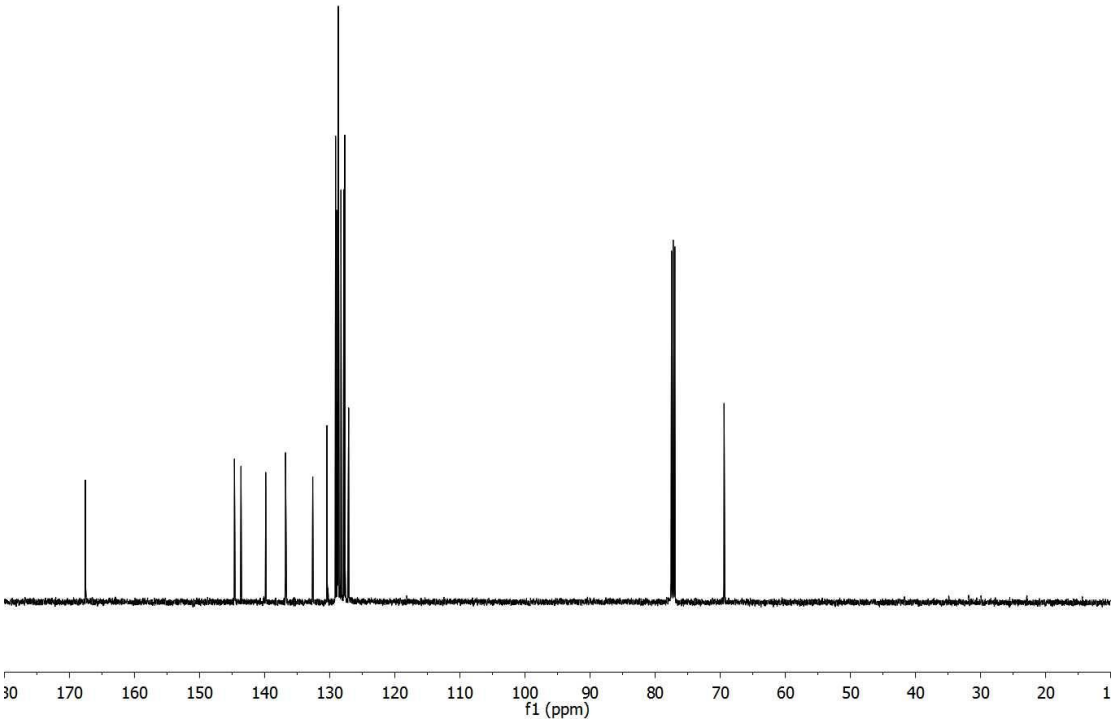
3af – *N*-(diphenylmethylene)-1-(*p*-methoxyphenyl)-1-phenylmethanamine in $CDCl_3$



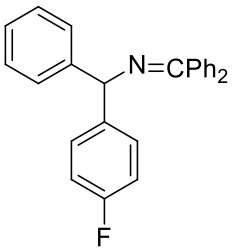
3ag – 1-(*p*-chlorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine in $CDCl_3$

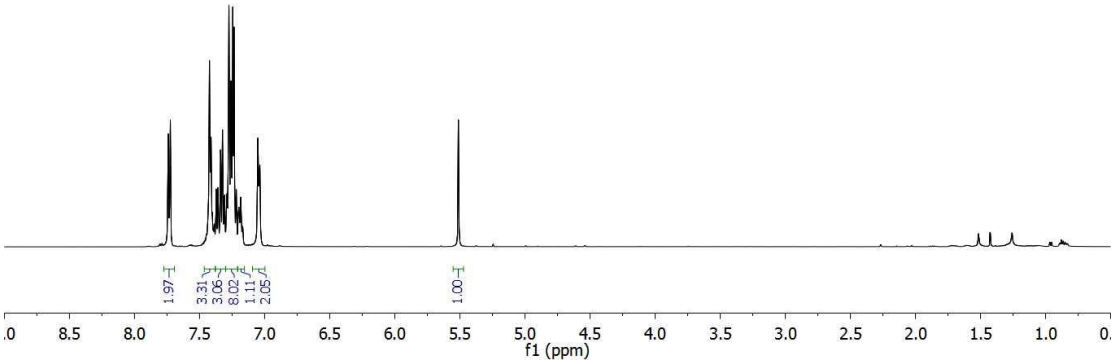


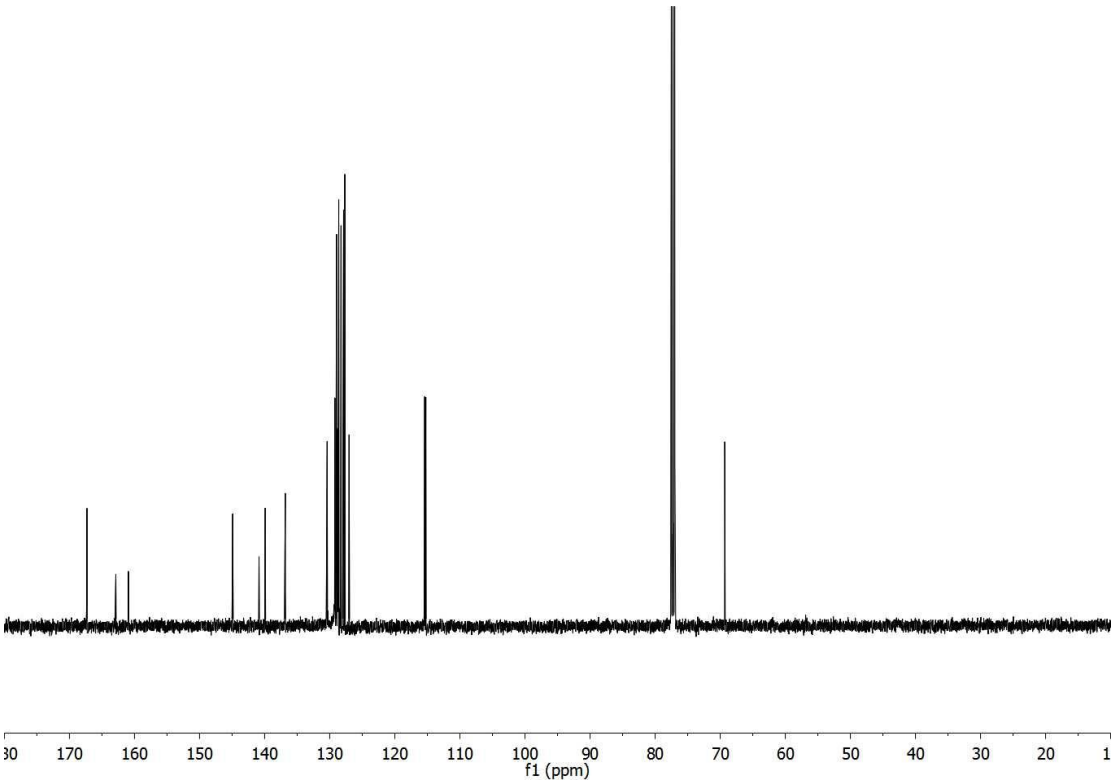




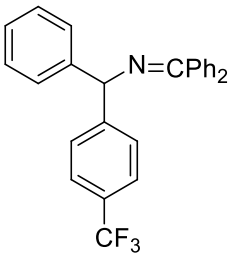
3ah – *N*-(diphenylmethylene)-1-(*p*-fluorophenyl)-1-phenylmethanamine in $CDCl_3$

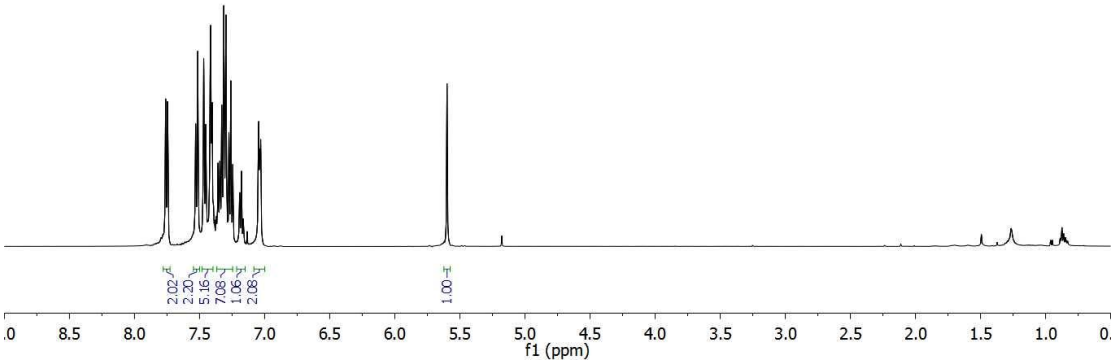


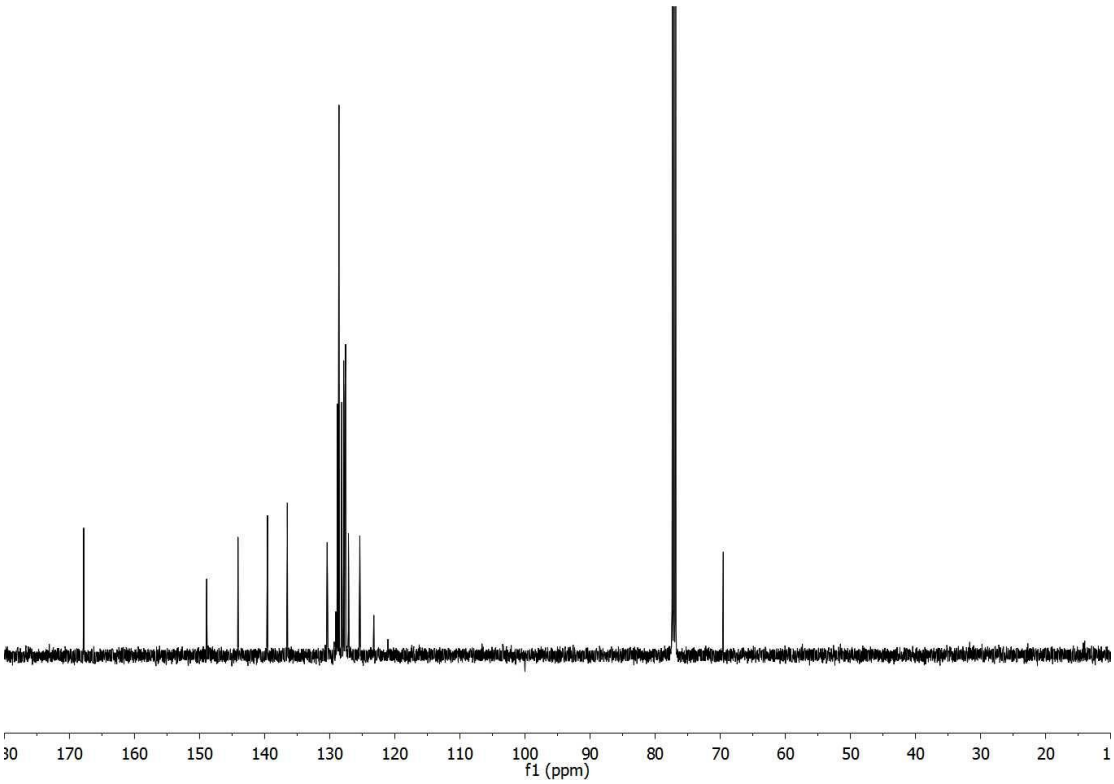




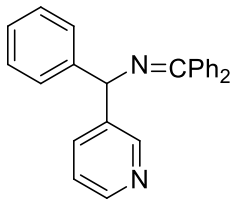
3ai –*N*-(diphenylmethylene)-1-phenyl-1-(*p*-(trifluoromethyl)phenyl)methanamine in $CDCl_3$

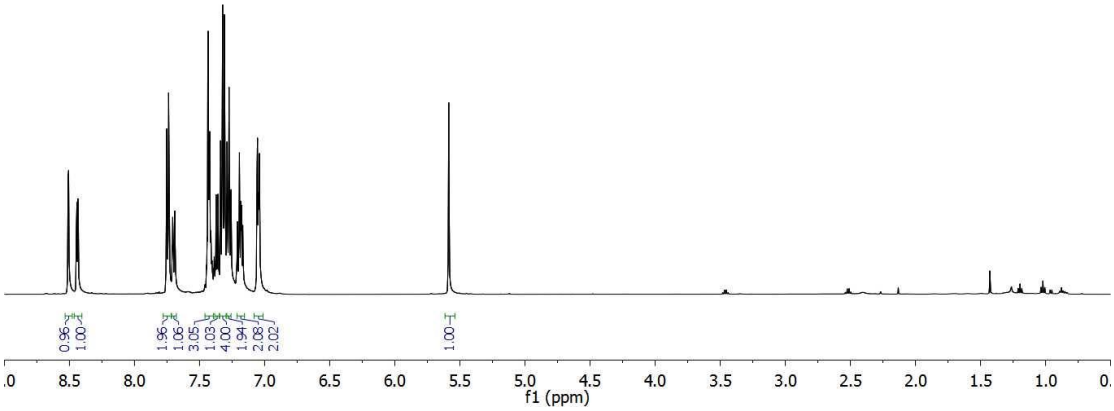


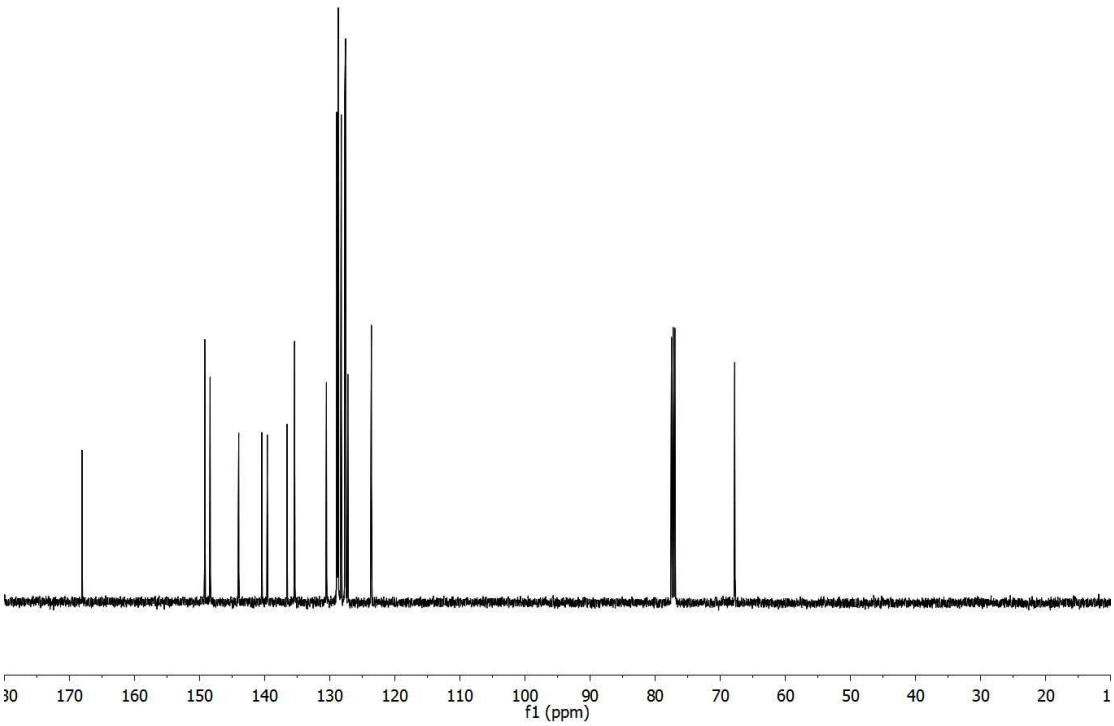




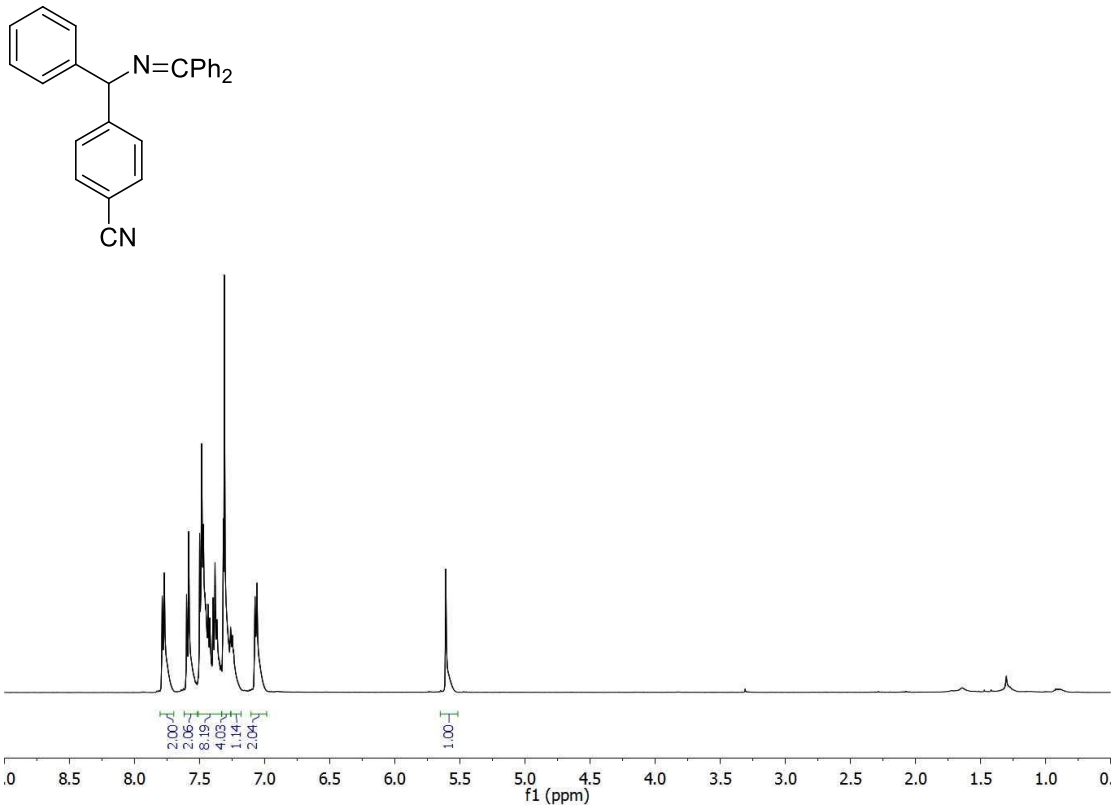
3aj – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine in $CDCl_3$

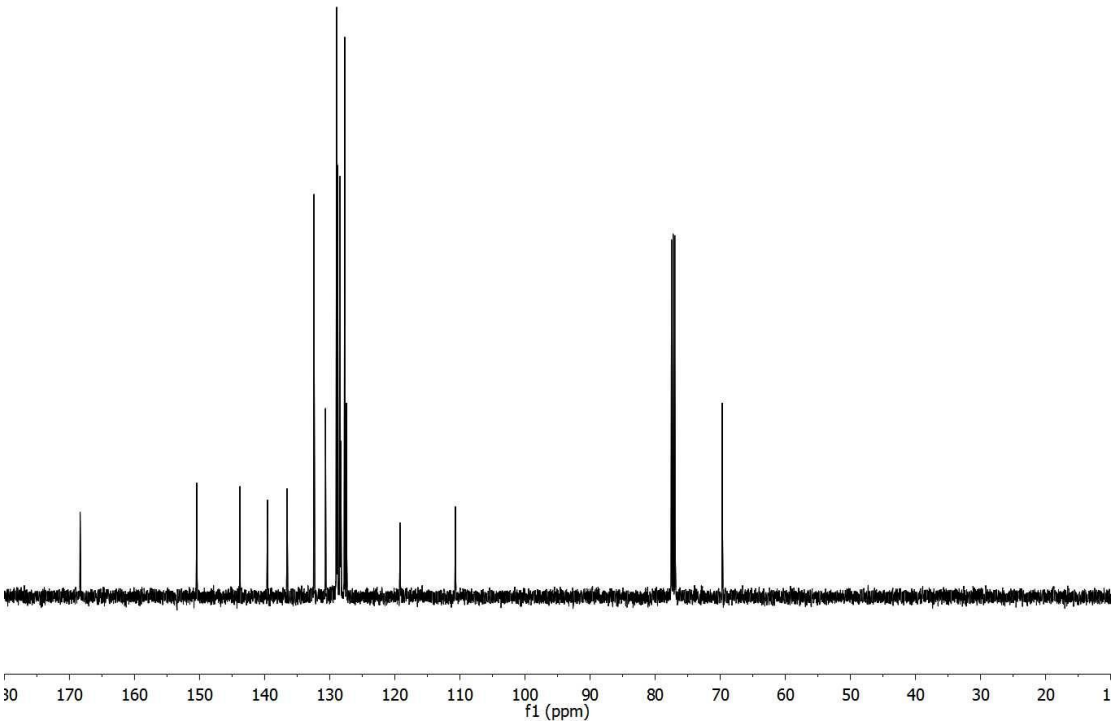




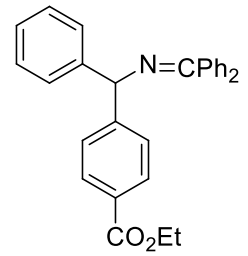


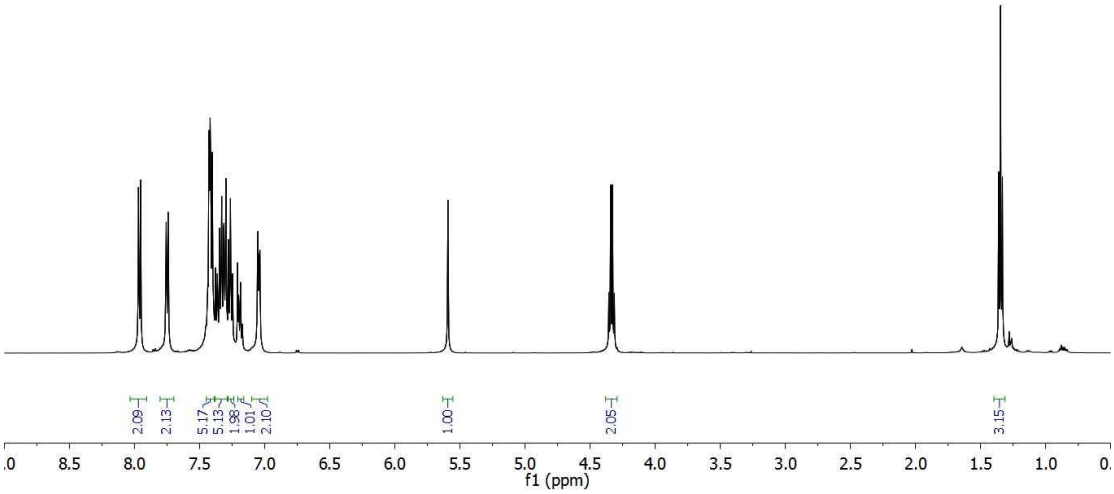
3ak – 4-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile in $CDCl_3$

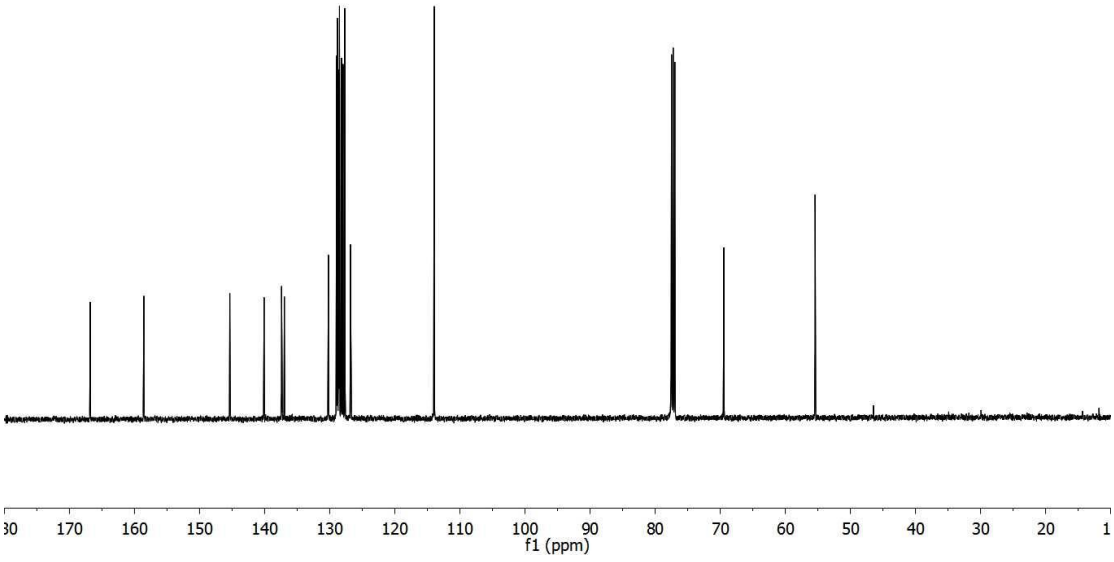




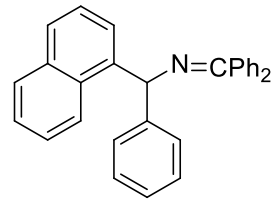
3al – Ethyl 4-(((diphenylmethylene)amino)(phenyl)methyl)benzoate in $CDCl_3$

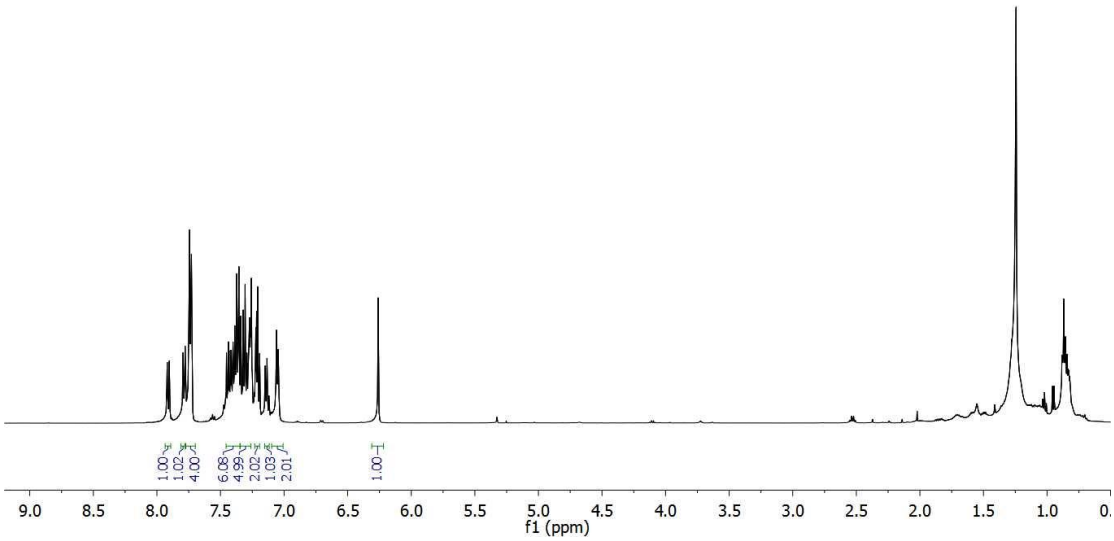


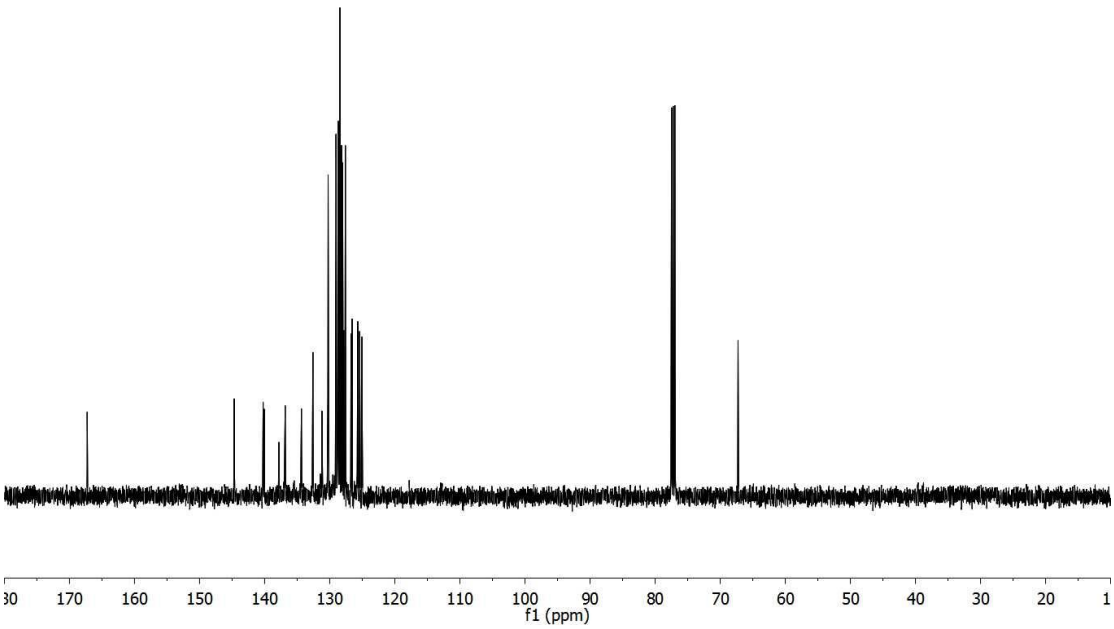




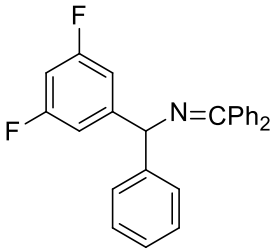
3ca – *N*-(diphenylmethylene)-1-(naphthalen-1-yl)-1-phenylmethanamine in $CDCl_3$

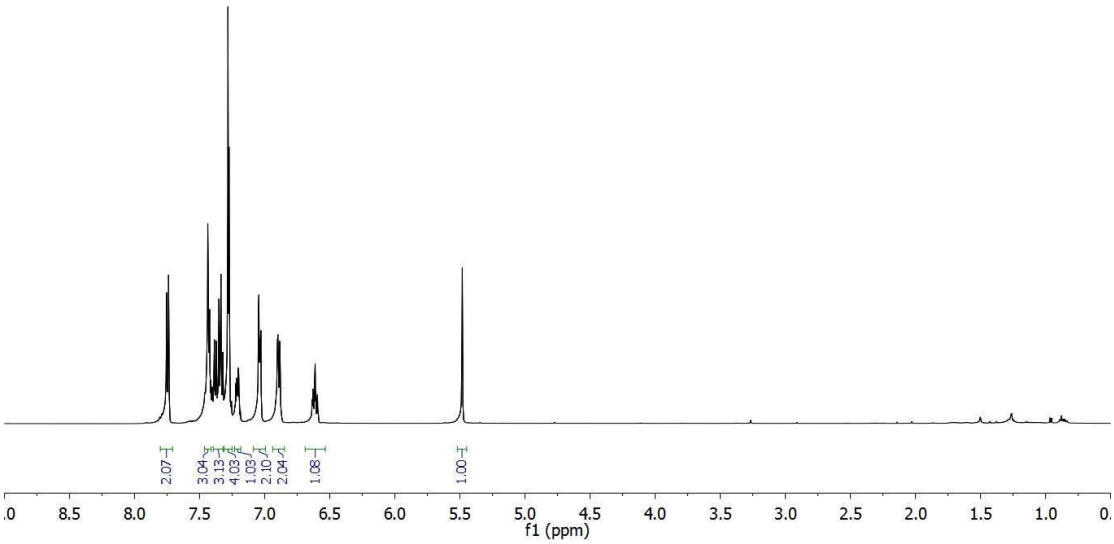


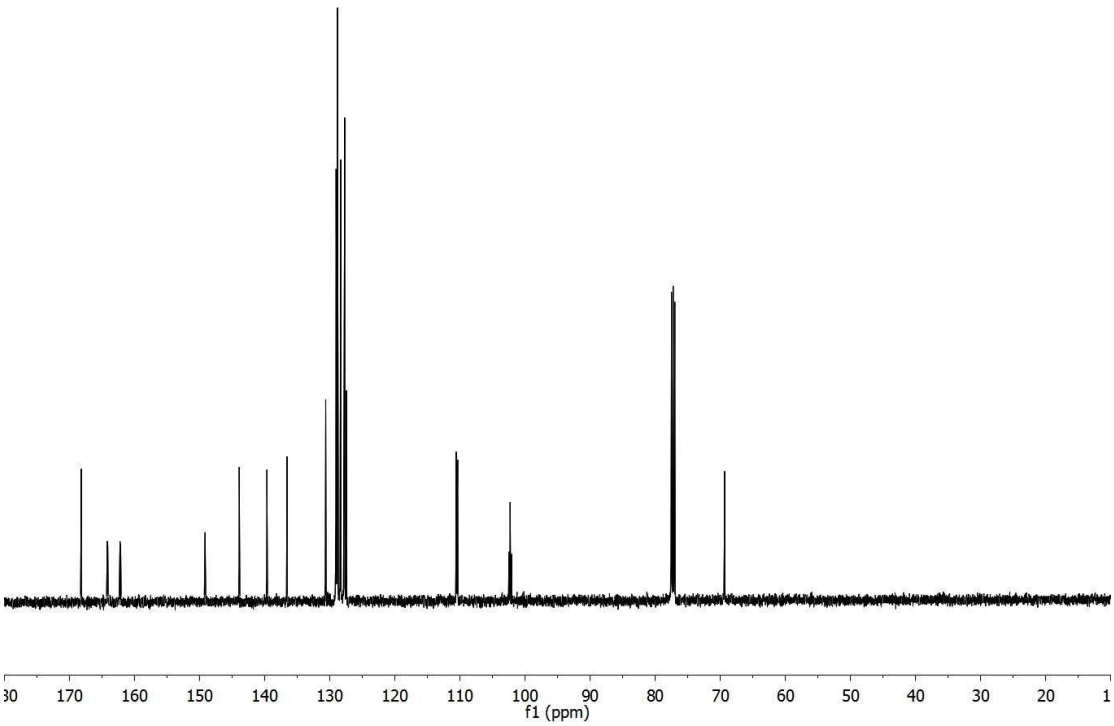




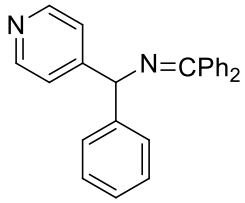
3ga – 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine in $CDCl_3$

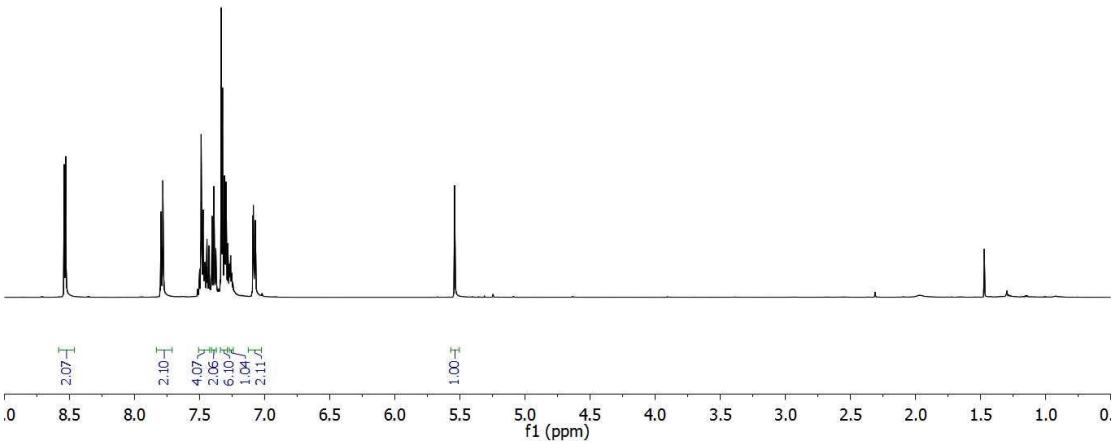


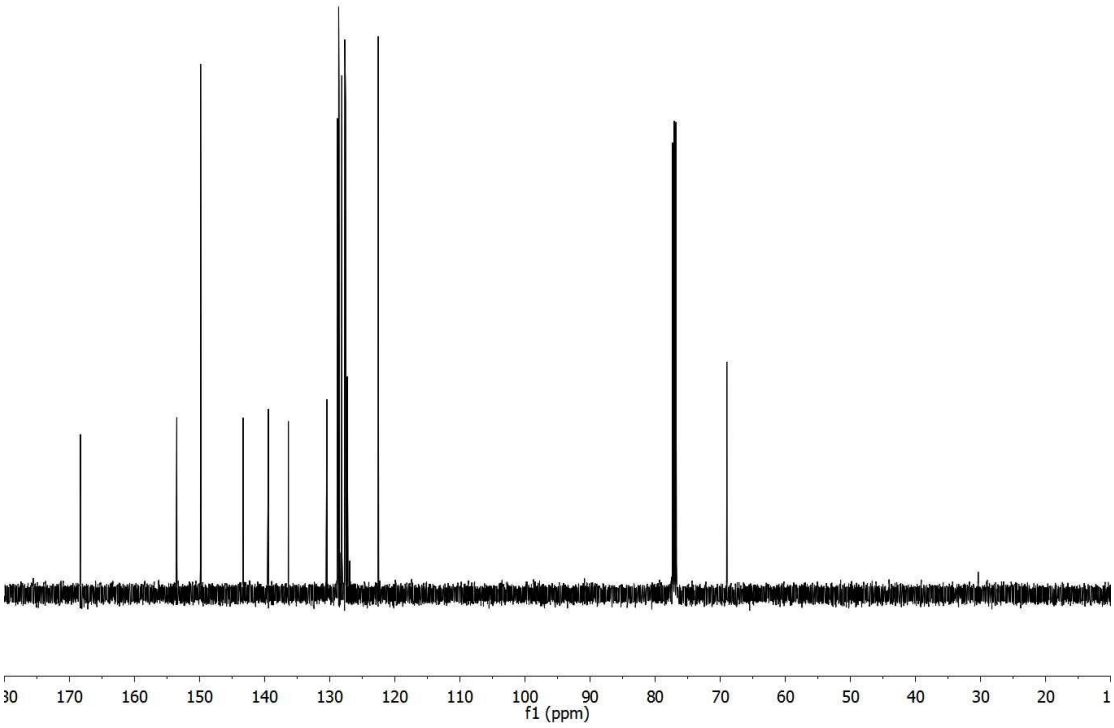




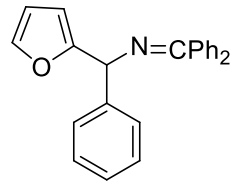
3ia – *N*-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine in $CDCl_3$

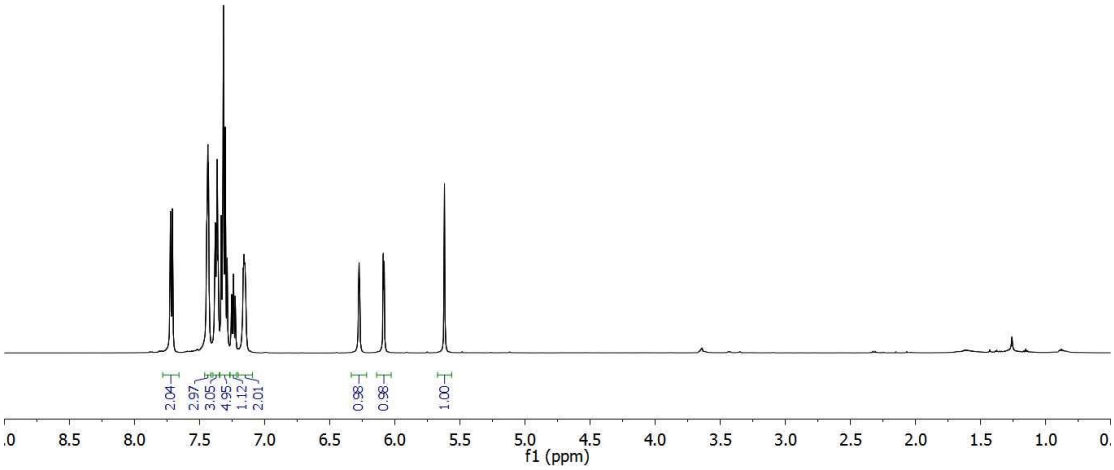


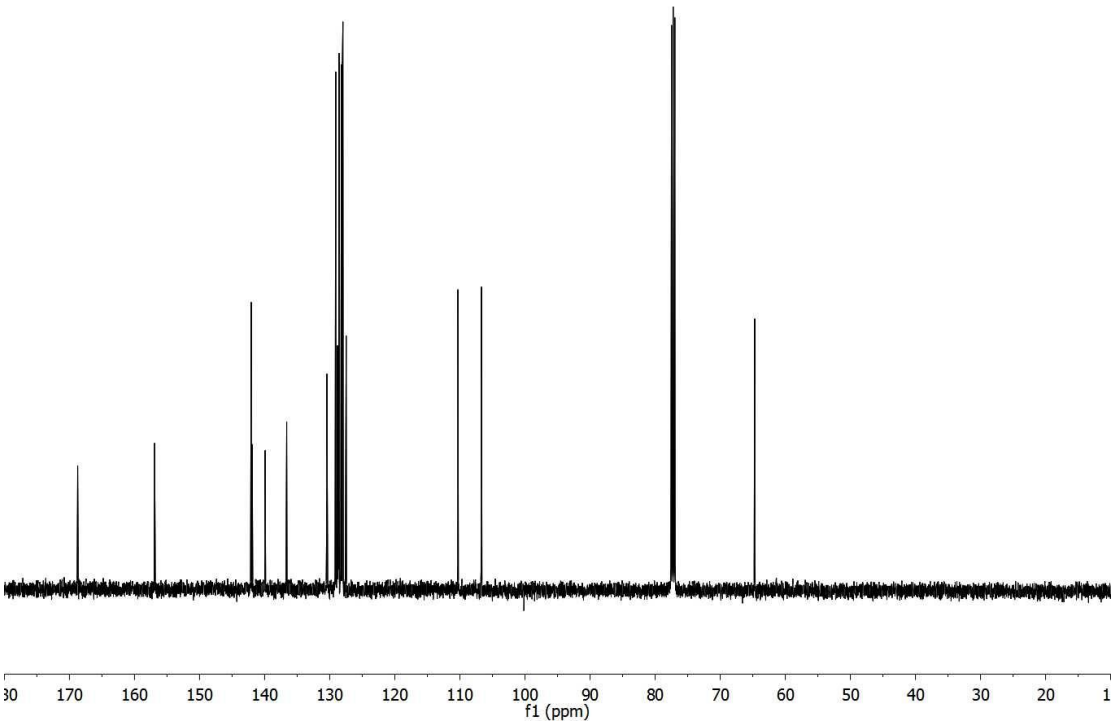




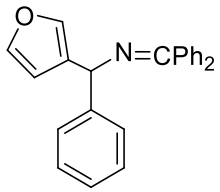
3ja – *N*-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine in $CDCl_3$

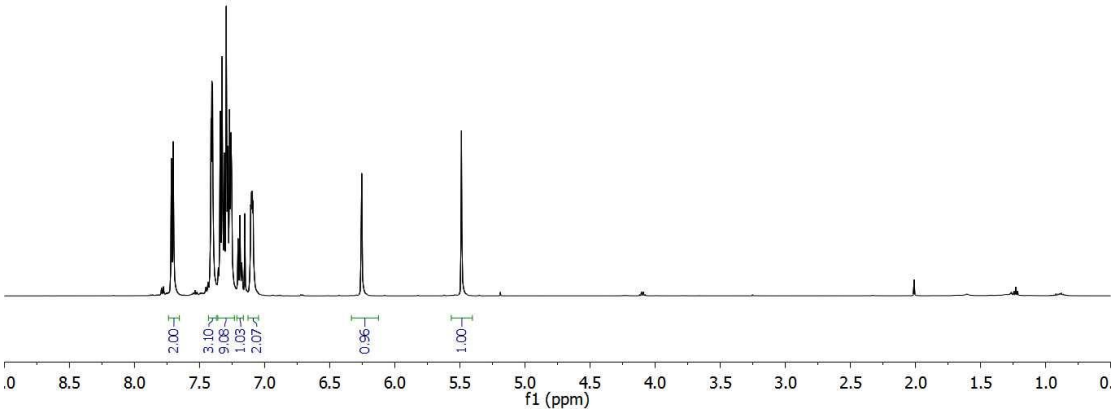


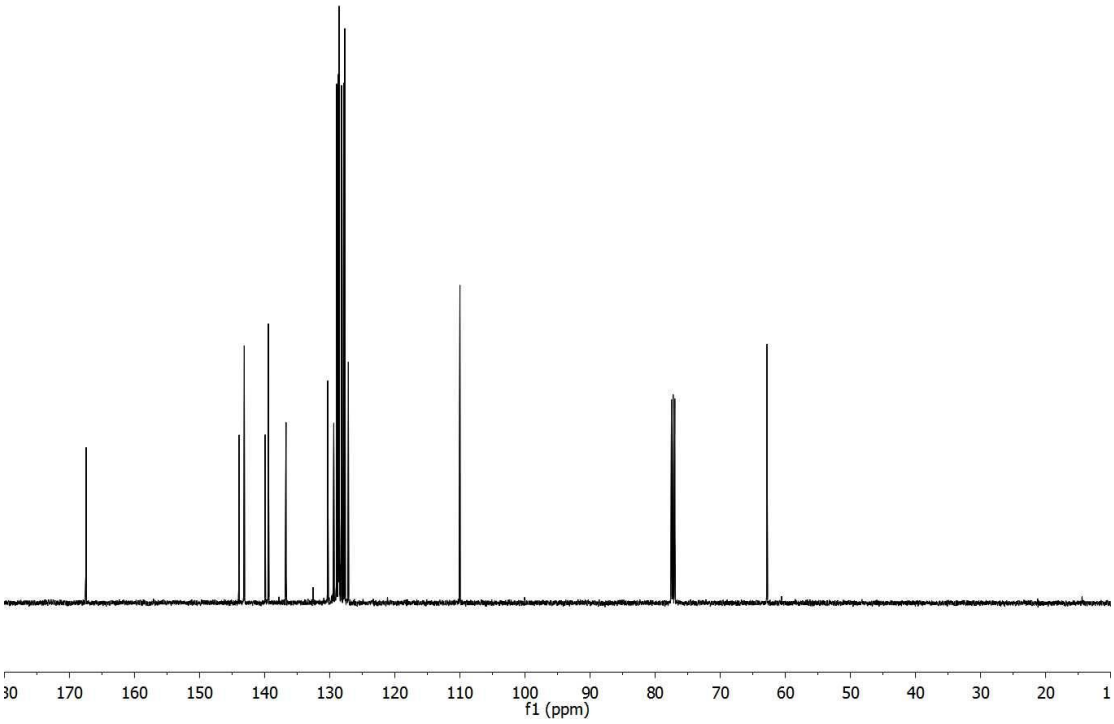




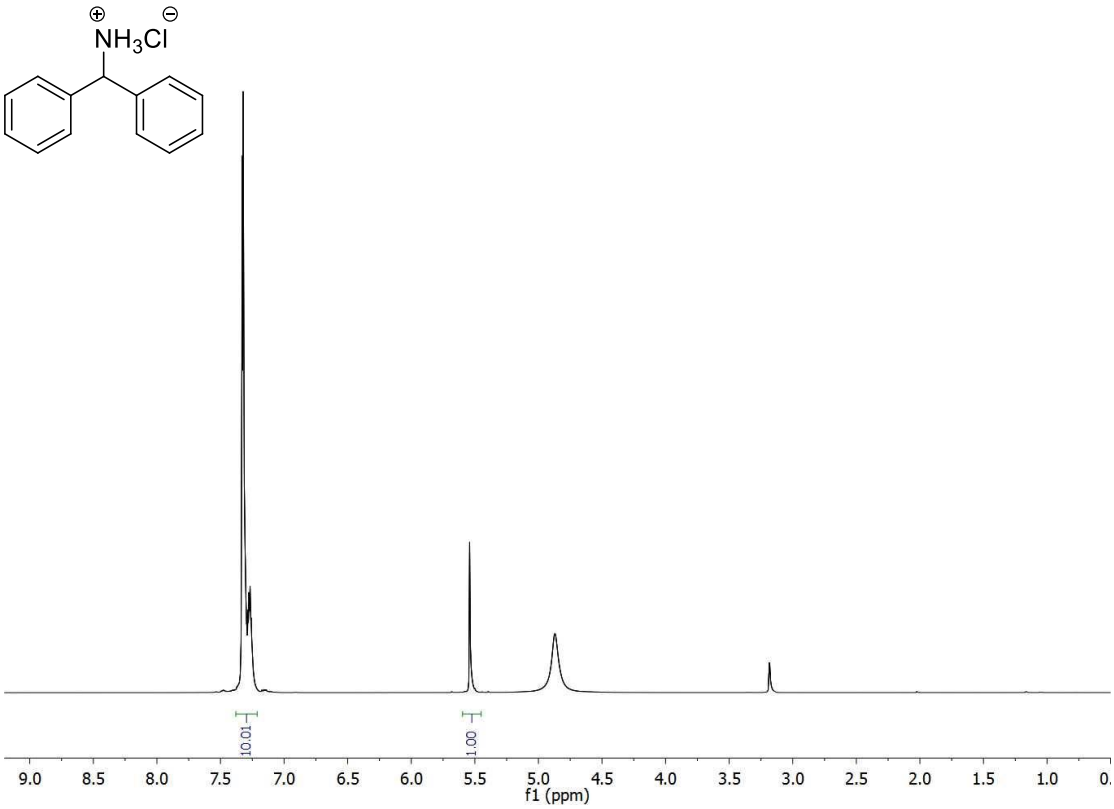
3la – *N*-(diphenylmethylene)-1-(furan-3-yl)-1-phenylmethanamine in $CDCl_3$

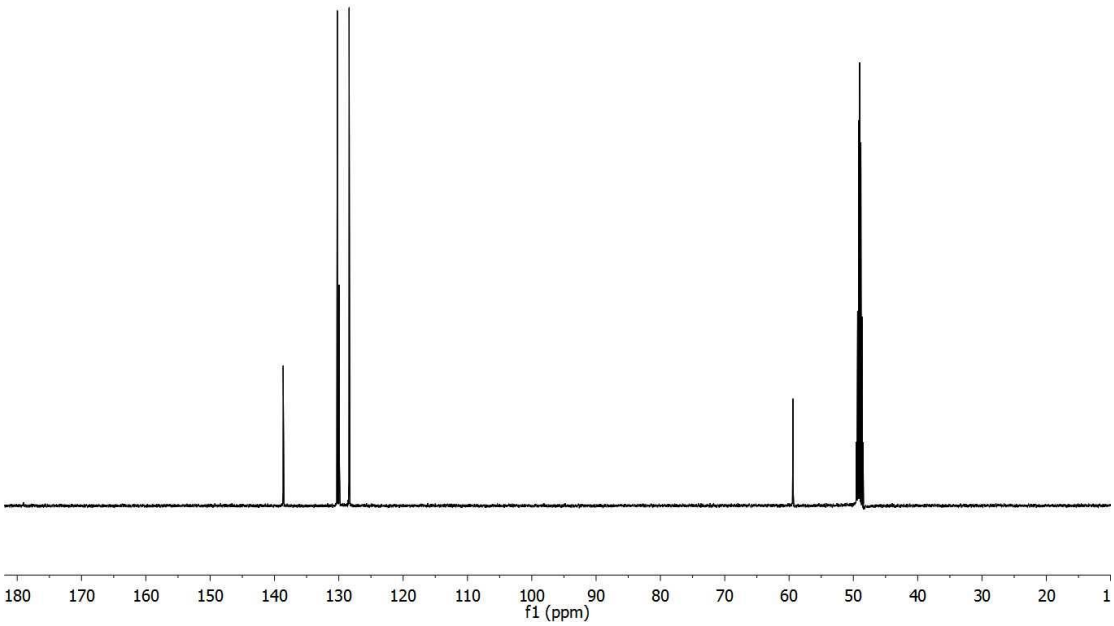




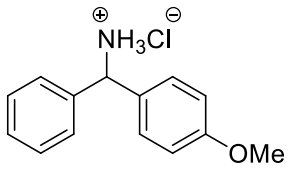


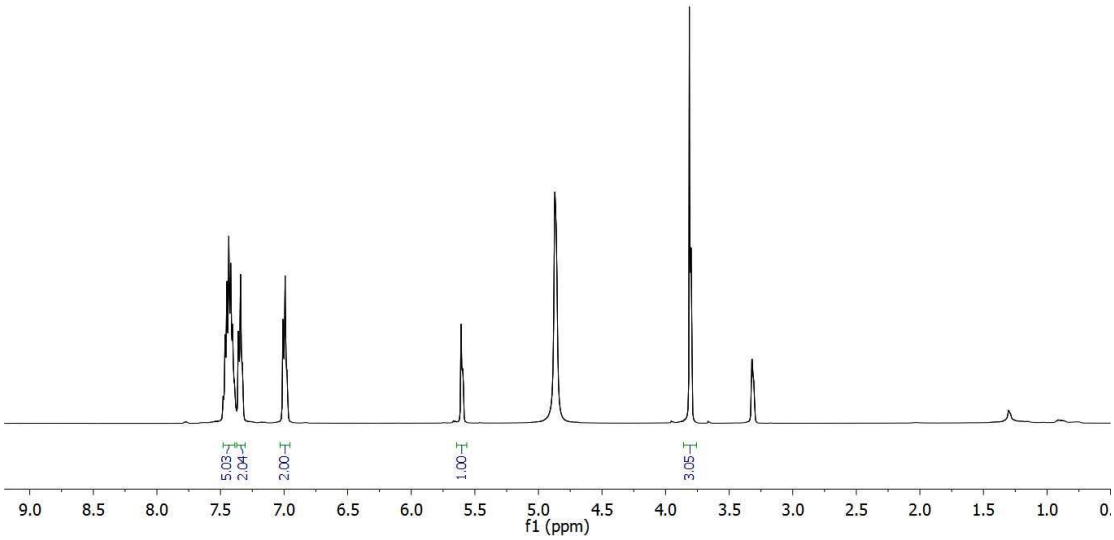
6 – diphenylmethanaminium chloride salt in Methanol-d_4

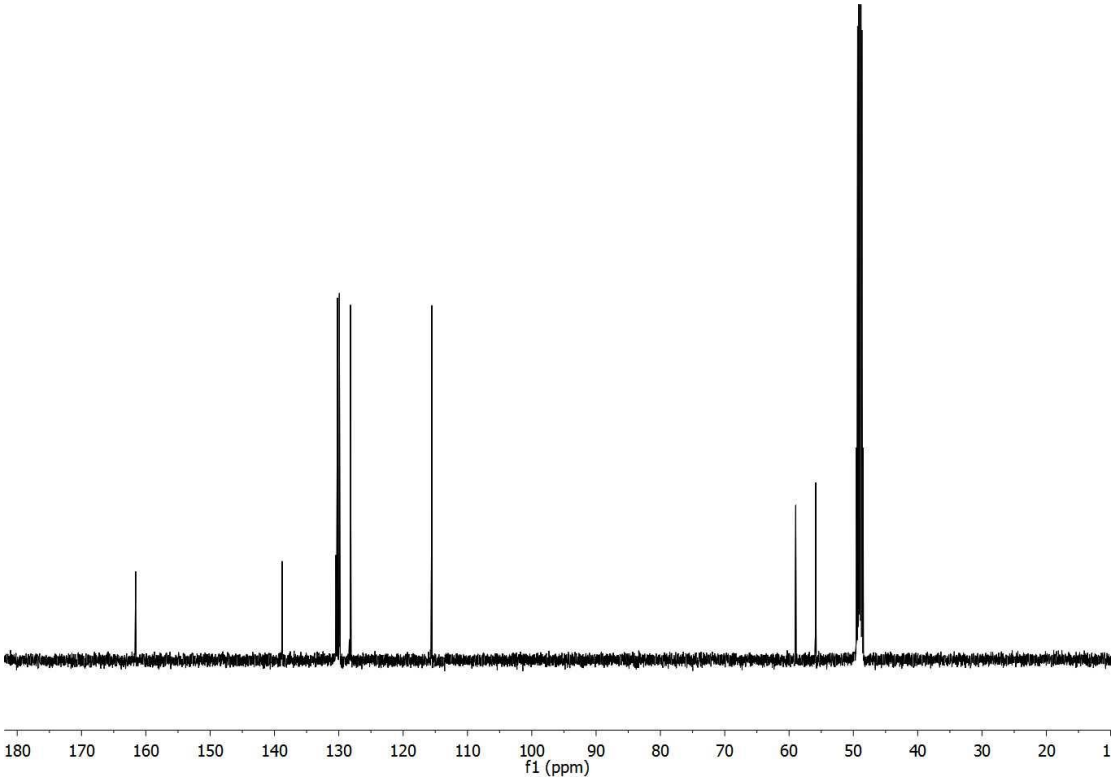




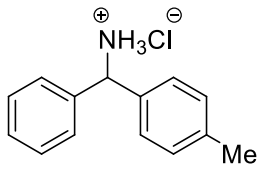
7 – (4-methoxyphenyl)(phenyl)methanaminium chloride salt in Methanol-d$_4$

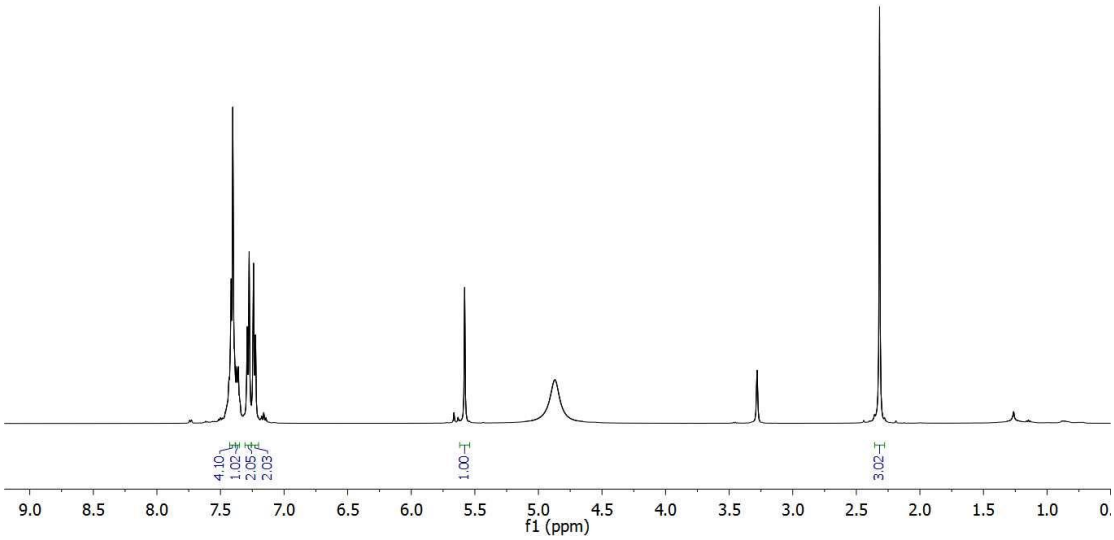


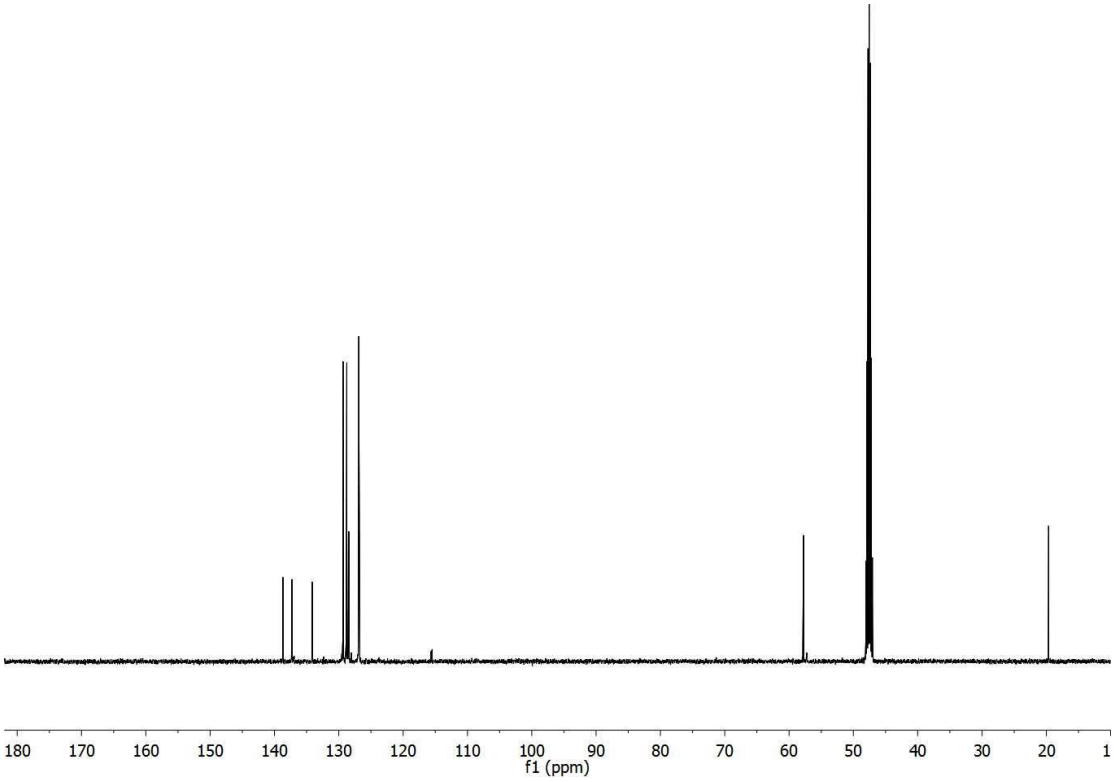




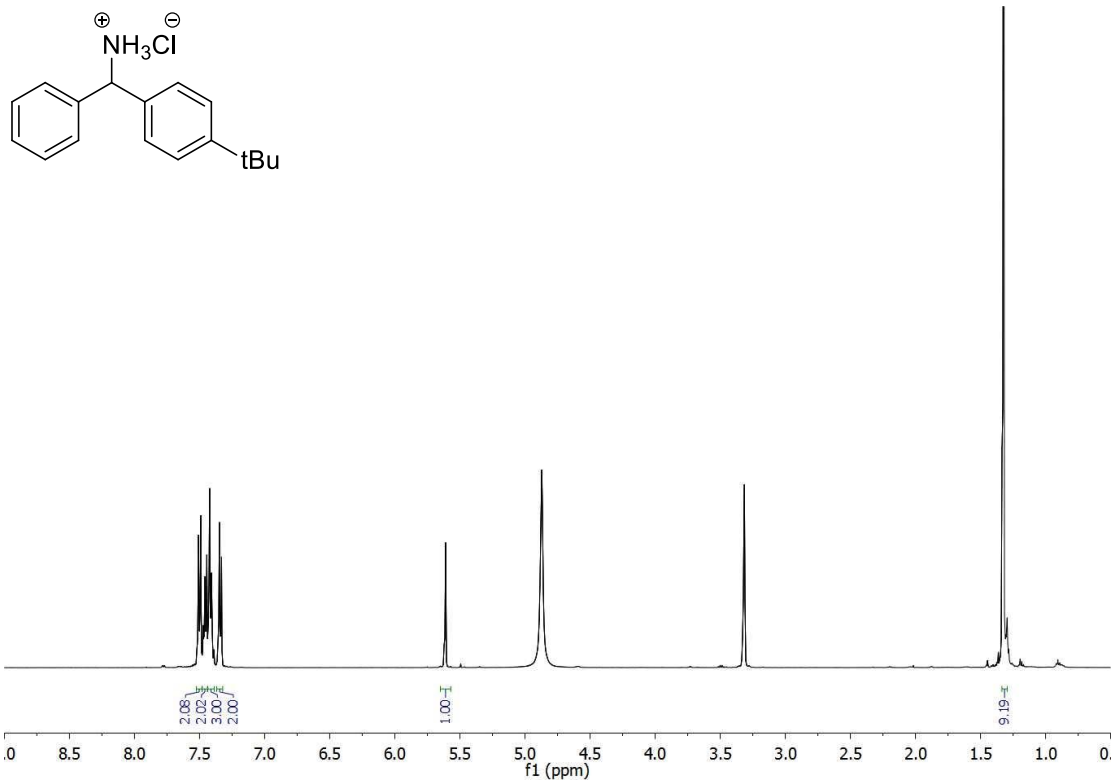
8 – phenyl(p-tolyl)methanaminium chloride salt in Methanol-d_4

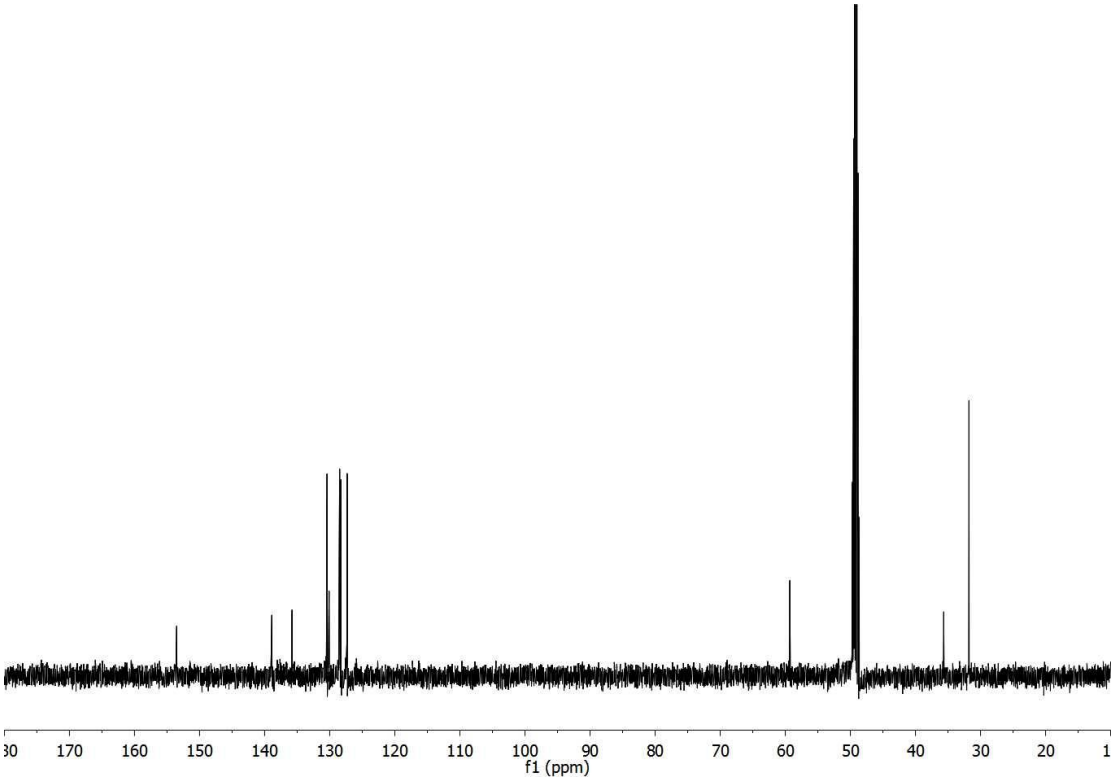




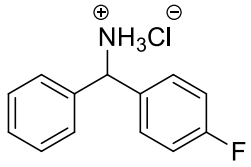


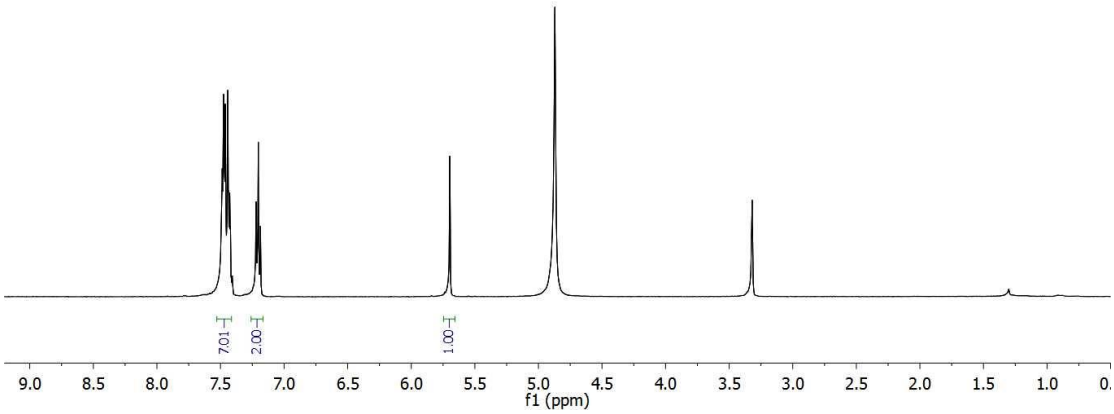
9 – (4-(*tert*-butyl)phenyl)(phenyl)methanamine ammounium salt in Methanol-d$_4$

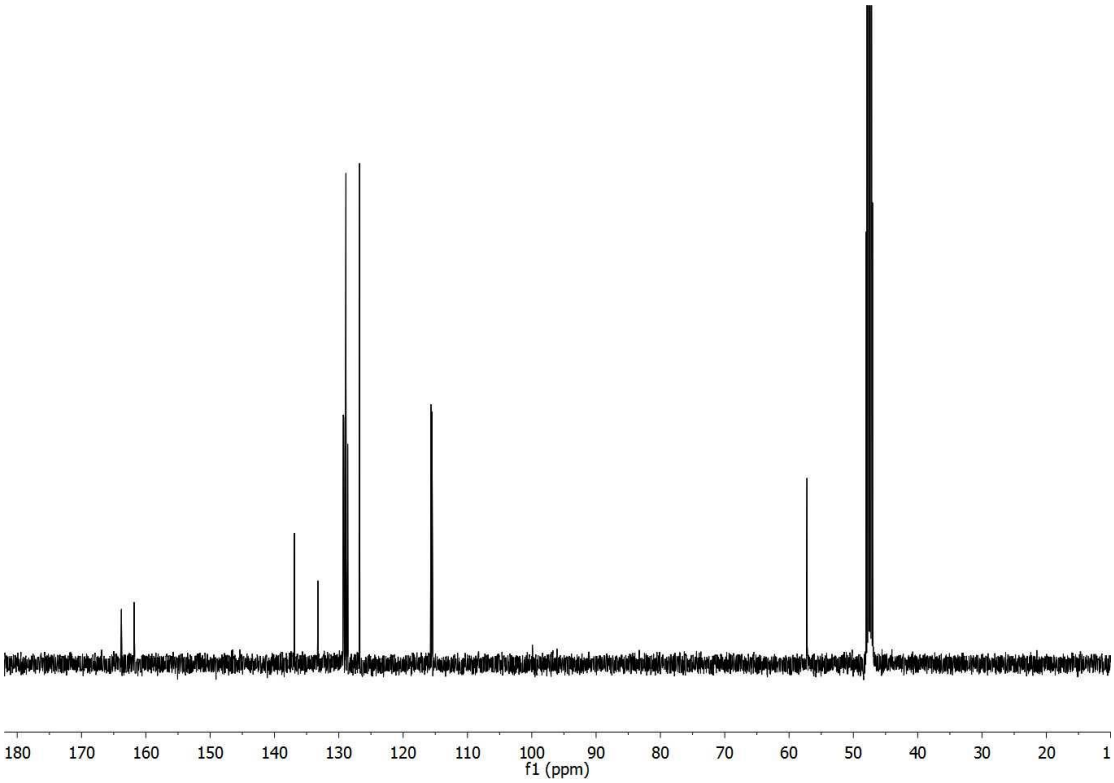




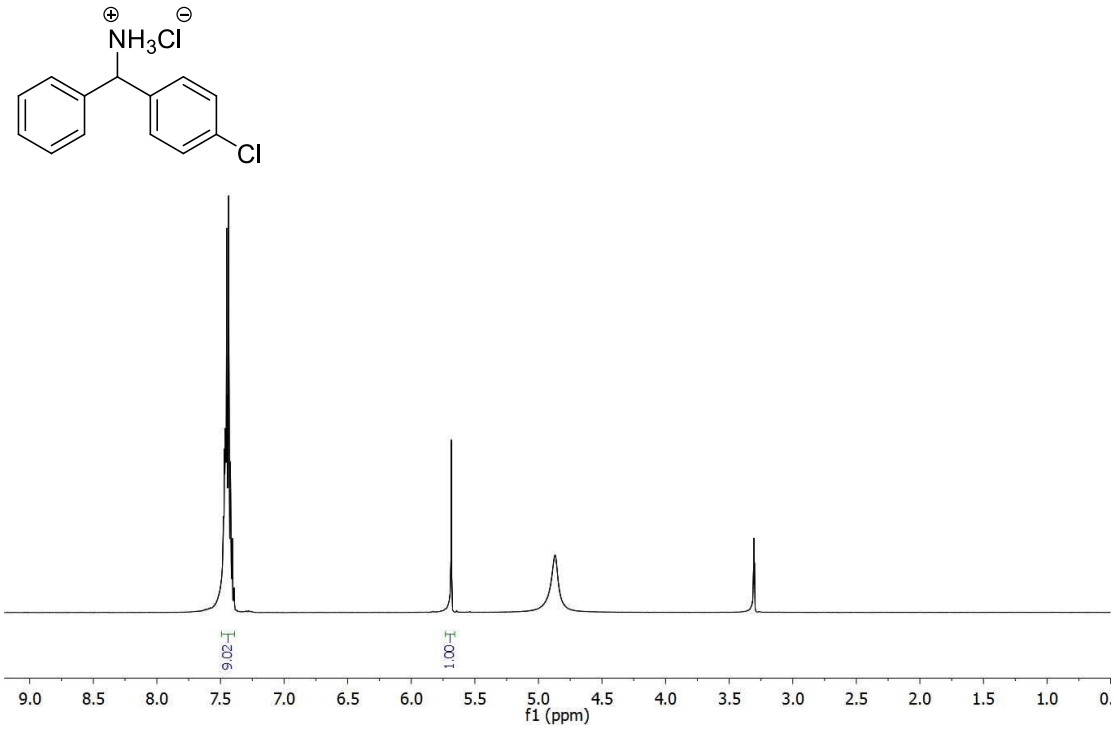
10 – (4-fluorophenyl)(phenyl)methanaminium chloride salt in Methanol-d_4

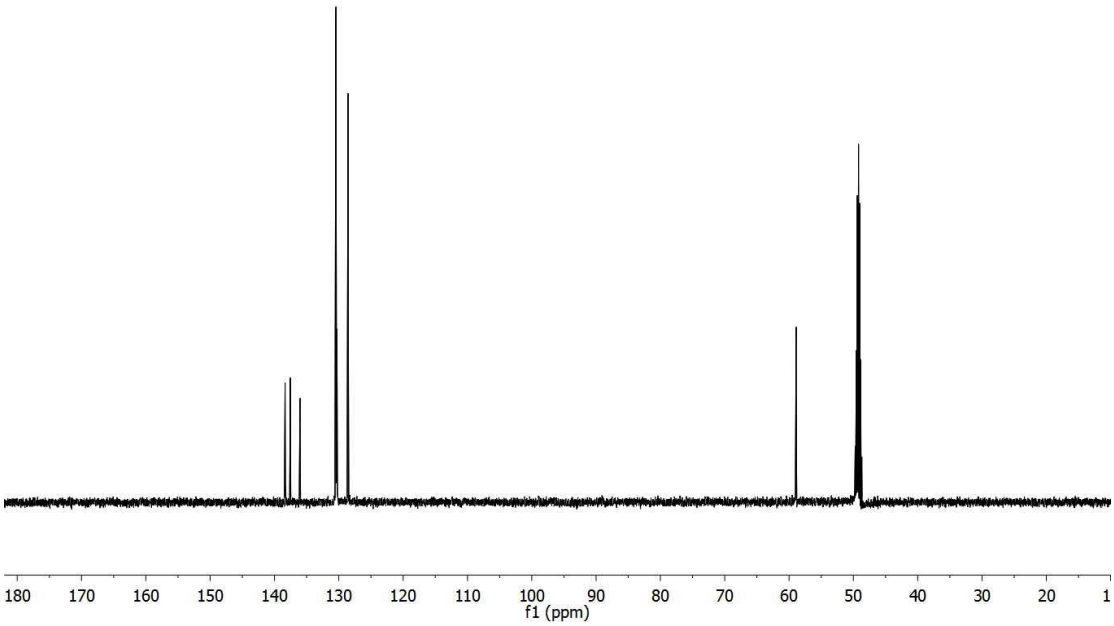




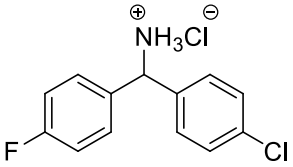


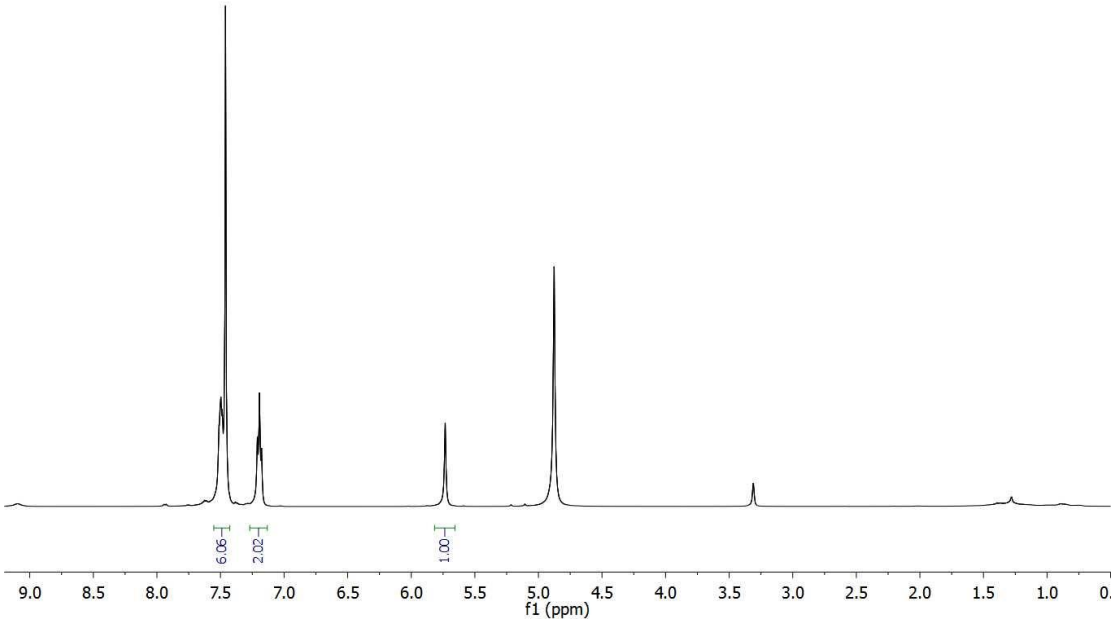
11 – (4-chlorophenyl)(phenyl)methanaminium chloride salt in Methanol-d_4

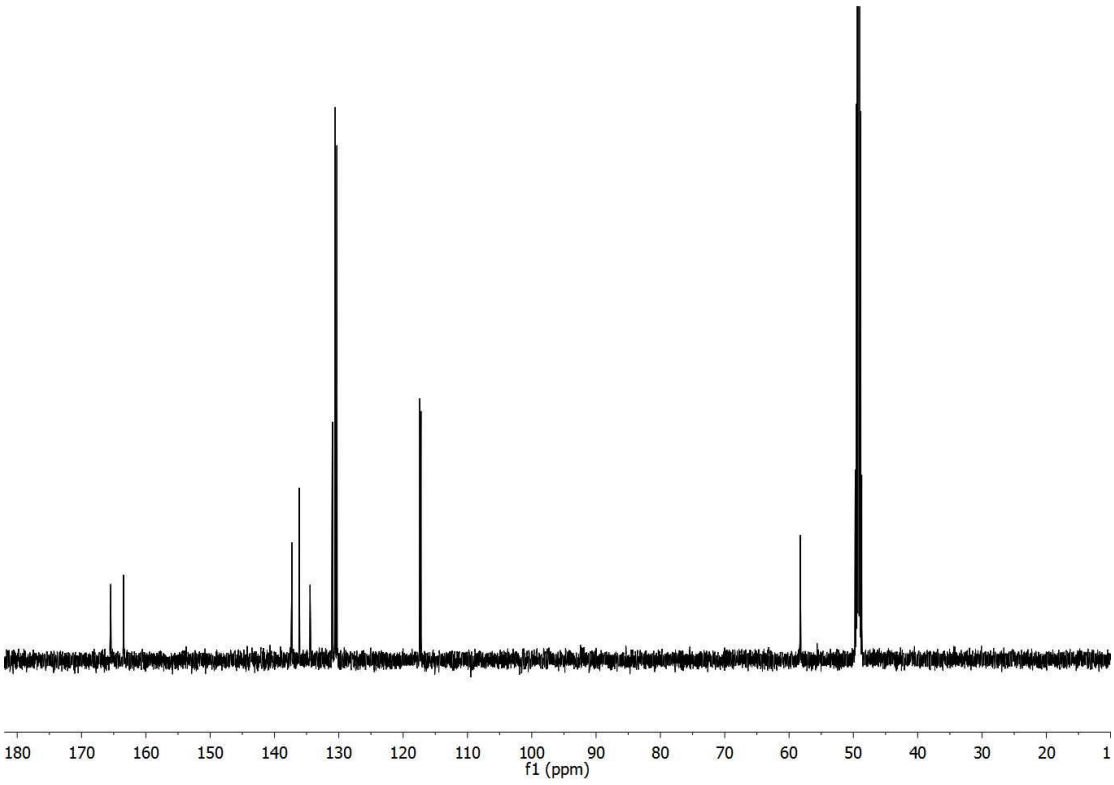




12 – (4-chlorophenyl)(4-fluorophenyl)methanaminium chloride salt in Methanol-d_4







13 – naphthalen-1-yl(phenyl)methanaminium chloride salt in Methanol-d_4