SUPPORTING INFORMATION

Transition-Metal-Free Radical C(sp^3)–C(sp^2) and C(sp^3)–C(sp^3) Coupling Enabled by 2-Azaallyls as Super-Electron-Donors and Coupling-Partners

Minyan Li,[1] Simon Berritt,[1] Lucas Matuszewski,[1] Guogang Deng,[2] Ana Pascual-Escudero,[3] Grace B. Panetti,[1] Michal Poznik,[4] Xiaodong Yang,[2] Jason J. Chruma[4] and Patrick J. Walsh*,[1]

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

[2]*Key Laboratory of Medicinal Chemistry for Natural Resource, School of Chemical Science and Technology, Yunnan University, Kunming, 650091, China.*

[3]*Dpto. Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain.*

[4]*Key Laboratory of Green Chemistry & Technology (MOE), College of Chemistry and Sino-British Materials Research Institute, College of Physical Science & Technology, Sichuan University, No. 29, Wangjiang Road, Chengdu, Sichuan, 610064, China.*

pwalsh@sas.upenn.edu

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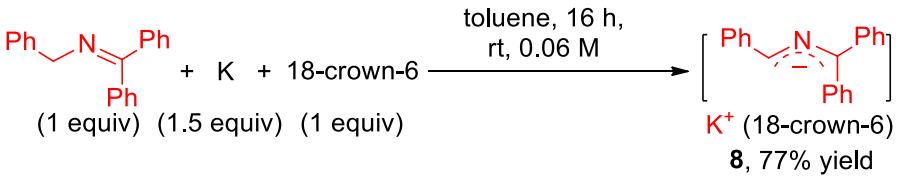
General Methods. All reactions were conducted under a nitrogen atmosphere of a glovebox with oven-dried glassware and standard Schlenk or vacuum line techniques.. All solutions were handled under nitrogen and transferred via "Eppendorf" brand pipetter. Anhydrous solvents, including CPME (cyclopentyl methyl ether) and MTBE (methyl *tert*-butyl ether), were purchased from Sigma-Aldrich and directly used. Unless otherwise stated, reagents were commercially available and used as purchased. 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. Reactions were performed in reaction slot of a Innova 2180 platform shaker and oven-dried glass beads were used instead of stir-bar. Flash chromatography was performed with silica gel (230–400 mesh, Silicycle). Deactivated silica gel was prepared by addition of 15 mL of Et_3N to 1 L of silica gel. ^1H and $^{13}C\{^1H\}$ 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.

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

Preparation of Azaallyl anion salt 8:



8, 77% yield

A scintillation vial was charged with a stir bar, 21 mg of potassium metal (0.555 mmol, 1.5 equiv) and 6 mL of toluene. To this stirring solution was added 100 mg of ketimine **1a** (0.369 mmol, 1 equiv) as a solid. The solution began to turn a light red-purple. 98 mg of solid 18-crown-6 (0.369 mmol, 1 equiv) was added portionwise. Upon addition the solution immediately turned dark purple. This solution was stirred 16 hours at room temperature and became a suspension. The mixture was heated to boiling and the liquid transferred to a fresh vial. The solution was slowly cooled to -30 ℃. The solid was collected over a medium sized fritted filter and washed with cold toluene before drying under vaccum for 6 hours. Yield: 163 mg, 0.284 mmol, 77%.

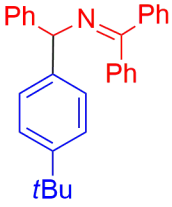
Preparation of Alkyl Halides 3c, 3d and Radical Clocks 2k, 2l, 3g:

Alkyl halides **3c**,[2a] **3d**[2b] and radical clocks **2k**,[2c] **2l**,[2d] **3g**[2e] were prepared according to literature procedures.[2]

Procedure and Characterization for the Arylation/Alkylation Reactions:

General procedure A for arylation: A brand-new oven-dried 4 mL glass vial equipped with two oven-dried glass beads was charged with ketimine **1a** (217.2 mg, 0.80 mmol) and 1-(*tert*-butyl)-4-iodobenzene **2a** (104.4 mg, 0.40 mmol) under a nitrogen atmosphere in a glove box. A solution of $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol) in 2.0 mL anhydrous DME was added by a pipetter to the reaction vial. The reaction mixture turned to a dark purple color. The vial was sealed with a cap, removed from the glove box and put in the reaction slot of a Innova 2180 platform shaker. The reaction mixture was shaken on the platform shaker for 4 h in total at 23 °C, opened to air, quenched with two drops of H_2O, diluted with 2 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 (3 x 2 mL), and the combined solutions were concentrated *in vacuo*. The entire crude material was loaded onto a deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (88.8 mg, 55% yield) as a white solid. From the flash chromatography, C3-arylated product **4aa'** was isolated in 25.8 mg, 16% yield as a colorless thick oil.

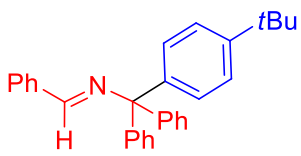
General procedure B for alkylation: A brand-new oven-dried 4 mL glass vial equipped with two oven-dried glass beads was charged with ketimine **1a** (54.3 mg, 0.20 mmol) and neopentyl iodide **3a** (19.8 mg, 0.10 mmol) under a nitrogen atmosphere in a glove box. A solution of $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol) in 1.0 mL anhydrous MTBE was added by a pipetter to the reaction vial. The reaction mixture turned to a dark purple color. The vial was sealed with a cap, removed from the glove box and put in the reaction slot of a Innova 2180 platform shaker. The reaction mixture was shaken on the platform shaker for 2 h in total at 23 °C, opened to air, quenched with two drops of H_2O, diluted with 2 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 (3 x 2 mL), and the combined solutions were concentrated *in vacuo*. The entire crude material was loaded onto a deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (32.4 mg, 95% yield) as a colorless thick oil.



4aa: 1-(4-(*tert*-Butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-(*tert*-butyl)-4-iodobenzene **2a** (104.4 mg, 0.40 mmol). 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 **4aa** (88.8 mg, 55% yield) as a white solid. The ^1H and $^{13}C\{^1H\}$ NMR data for this compound match the literature data.[3]

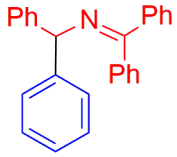
From the flash chromatography, C3-arylated product **4aa'** was isolated in 25.8 mg, 16% yield as colorless thick oil.



4aa': *N*-Benzylidene-1-(4-(*tert*-butyl)phenyl)-1,1-diphenylmethanamine

R_f = 0.85 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.86–7.83 (m, 2H), 7.83 (s, 1H), 7.43–7.41 (m, 3H), 7.30–7.29 (m, 10H), 7.25–7.24 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 1.31 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz,

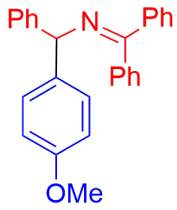
$CDCl_3$): δ 159.7, 149.7, 146.3, 142.7, 137.0, 130.8, 130.0, 129.6, 128.8, 128.7, 127.9, 126.8, 124.8, 78.2, 34.6, 31.5 ppm; IR (thin film): 2962, 1642, 1446, 1216, 830, 755 cm^{-1}; HRMS calc'd for $C_{30}H_{30}N^+$ 404.2378, observed 404.2403 $[M+H]^+$.



4ab: *N*-(Diphenylmethylene)-1,1-diphenylmethanamine

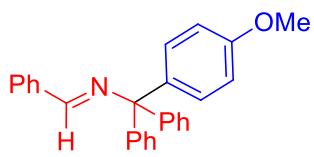
The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), iodobenzene **2b** (81.6 mg, 0.40 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (80.6 mg, 58% yield) as a white solid. The ^1H and $^{13}C\{^1H\}$ NMR data for this compound match the literature data.[3]

From the flash chromatography, C3-arylated product **4ab'** was isolated in 19.5 mg, 14% yield as colorless thick oil. ^1H and $^{13}C\{^1H\}$ NMR data for this compound match the literature data.[4]



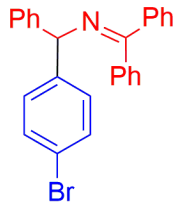
4ac: *N*-(Diphenylmethylene)-1-(4-methoxyphenyl)-1-phenylmethanamine The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-iodo-4-methoxybenzene **2c** (93.6 mg, 0.40 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product (75.5 mg, 50% yield) as a thick colorless oil. The ^1H and $^{13}C\{^1H\}$ NMR data for this compound match the literature data.[3]

From the flash chromatography, C3-arylated product **4ac'** was isolated in 19.6 mg, 13% yield as colorless thick oil.



4ac': *N*-Benzylidene-1-(4-methoxyphenyl)-1,1-diphenylmethanamine

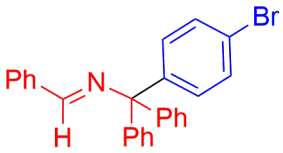
R_f = 0.61 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.86–7.84 (m, 2H), 7.83 (s, 1H), 7.43–7.41 (m, 3H), 7.30–7.29 (m, 7H), 7.25–7.23 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.6, 158.5, 146.4, 138.0, 136.9, 131.2, 130.9, 130.3, 129.9, 128.8, 128.7, 128.5, 127.95, 126.92, 113.2, 78.0, 55.4 ppm; IR (thin film): 3057, 2925, 1641, 1603, 1445, 1179, 998, 828, 755 cm^{-1}; HRMS calc'd for $C_{27}H_{24}NO^+$ 378.1858, observed 378.1875 $[M+H]^+$.



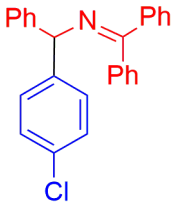
4ad: 1-(4-Bromophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-bromo-4-iodobenzene **2d** (113.2 mg, 0.40 mmol) in 9 h with MTBE as solvent. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (73.3 mg, 43% yield) as a thick colorless oil. R_f = 0.53 (diethyl ether:hexanes = 1:5);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.44–7.37 (m, 6H), 7.35–7.32 (m, 2H), 7.29–7.25 (m, 4H), 7.20 (d, *J* = 8.5 Hz, 3H), 7.06–7.04 (m, 2H), 5.49 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 167.6, 144.6, 144.2, 139.8, 136.8, 131.6, 130.4, 129.5, 128.9, 128.8, 128.7, 128.6, 128.3, 127.9, 127.7, 127.1, 120.8, 69.5 ppm; IR (thin film): 3061, 2876, 1622, 1485, 1446, 1216, 908, 758 cm^{-1}; HRMS calc'd for $C_{26}H_{21}BrN^+$ 426.0852, observed 426.0852 $[M+H]^+$.

From the flash chromatography, C3-arylated product **4ad'** was isolated in 23.9 mg, 14% yield as colorless thick oil.

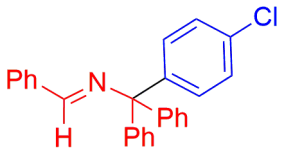


4ad': *N*-Benzylidene-1-(4-bromophenyl)-1,1-diphenylmethanamine
R_f= 0.78 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.83 (m, 2H), 7.79 (s, 1H), 7.44–7.41 (m, 5H), 7.32–7.23 (m, 12H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 160.1, 145.6, 145.3, 136.7, 131.7, 131.1, 131.0, 129.9, 128.85, 128.84, 128.1, 127.2, 121.1, 78.1 ppm; IR (thin film): 3058, 2924, 1642, 1580, 1446, 1217, 818, 698 cm^{-1}; HRMS calc'd for $C_{26}H_{21}NBr^+$ 426.0857, observed 426.0869 $[M+H]^+$.

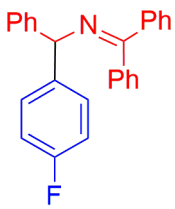


4ae: 1-(4-Chlorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-chloro-4-iodobenzene **2e** (95.6 mg, 0.40 mmol) in 9 h with MTBEas solvent. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (67.2 mg, 44% yield) as a thick colorless oil. The ^{1}H and $^{13}C\{^1H\}$ NMR data for this compound match the literature data.[3]

From the flash chromatography, C3-arylated product **4ae'** was isolated in 22.9 mg, 15% yield as colorless thick oil.



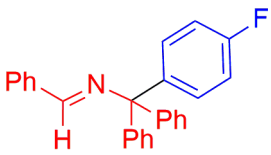
4ae': *N*-Benzylidene-1-(4-chlorophenyl)-1,1-diphenylmethanamine
R_f= 0.78 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.83 (m, 2H), 7.80 (s, 1H), 7.43–7.41 (m, 3H), 7.31–7.23 (m, 14H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 160.0, 145.4, 145.0, 136.7, 132.8, 131.3, 131.1, 129.9, 128.84, 128.83, 128.1, 127.2, 78.0 ppm; IR (thin film): 3059, 1642, 1489, 1217, 822, 697 cm^{-1}; HRMS calc'd for $C_{26}H_{21}NCl^+$ 382.1363, observed 382.1346 $[M+H]^+$.



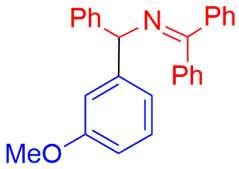
4af: *N*-(Diphenylmethylene)-1-(4-fluorophenyl)-1-phenylmethanamine The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-fluoro-4-iodobenzene **2f** (88.8 mg, 0.40 mmol) in 9 h. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (70.2 mg, 48% yield) as a

white solid. The ^{1}H and $^{13}C\{^{1}H\}$ NMR data for this compound match the literature data.[3]

From the flash chromatography, C3-arylated product **4af'** was isolated in 19.0 mg, 13% yield as colorless thick oil.

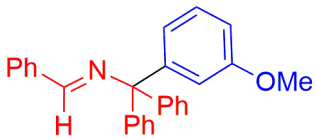


4af': *N*-Benzylidene-1-(4-fluorophenyl)-1,1-diphenylmethanamine
R_f= 0.78 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.84 (m, 2H), 7.81 (s, 1H), 7.44–7.42 (m, 3H), 7.32–7.25 (m, 12H), 6.99 (t, J = 6.5 Hz, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 161.8 (d, $J_{C\text{-}F}$ = 240.0 Hz) 159.9, 145.7, 142.0, 136.8, 131.6, 131.5, 131.0, 129.92, 128.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.0, 127.1, 114.7 (d, $J_{C\text{-}F}$ = 21.0 Hz), 78.0 ppm; IR (thin film): 3059, 1641, 1446, 1224, 755, 696 cm^{-1}; HRMS calc'd for $C_{26}H_{21}NF^{+}$ 366.1658, observed 166.1673 $[M+H]^{+}$.

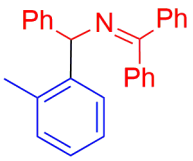


4ag: *N*-(Diphenylmethylene)-1-(3-methoxyphenyl)-1-phenylmethanamine The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-iodo-3-methoxybenzene **2g** (93.6 mg, 0.40 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:30) to give the product (71.0 mg, 47% yield) as a thick colorless oil. R_f= 0.45 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77–7.76 (m, 2H), 7.46–7.43 (m, 3H), 7.40–7.38 (m, 1H), 7.36–7.33 (m, 4H), 7.29–7.27 (m, 2H), 7.22–7.18 (m, 2H), 6.95 (t, J = 2.0 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.75 (ddd, J = 8.5, 2.0, 1.0 Hz, 1H), 5.54 (s, 1H) , 3.77 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 167.2, 159.8, 146.7, 144.9, 140.1, 136.9, 130.3, 129.5, 128.9, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8, 126.9, 120.2, 113.7, 112.1, 70.0, 55.4 ppm; IR (thin film): 3018, 2400, 1657, 1487, 1447, 1258, 908, 758 cm^{-1}; HRMS calc'd for $C_{27}H_{24}NO^{+}$ 378.1858, found 378.1841 $[M+H]^{+}$.

From the flash chromatography, C3-arylated product **4ag'** was isolated in 25.7 mg, 17% yield as colorless thick oil.

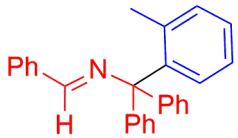


4ag': *N*-Benzylidene-1-(3-methoxyphenyl)-1,1-diphenylmethanamine
R_f= 0.60 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.84 (m, 2H), 7.83 (s, 1H), 7.44–7.42 (m, 3H), 7.30–7.29 (m, 8H), 7.26–7.24 (m, 3H), 6.91 (t, J = 2.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.80 (ddd, J = 8.5, 2.0, 1.0 Hz, 1H), 3.72 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 159.9, 159.3, 147.8, 145.8, 136.9, 130.9, 130.0, 128.84, 128.80, 128.7, 128.3, 128.1, 127.9, 127.0, 126.8, 122.6, 116.3, 111.8, 78.4, 55.3 ppm; IR (thin film): 3057, 1642, 1446, 755, 691 cm^{-1}; HRMS calc'd for $C_{27}H_{24}NO^{+}$ 378.1858, observed 378.1875 $[M+H]^{+}$.



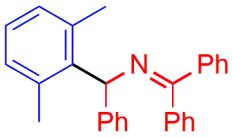
4ah: *N*-(Diphenylmethylene)-1-phenyl-1-(*o*-tolyl)methanamine The reaction was performed following the General Procedure A with with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 1-iodo-2-methylbenzene **2h** (87.2 mg, 0.40 mmol) in 9 h. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (66.5 mg, 46% yield) as a thick colorless oil. R_f= 0.67 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.42–7.38 (m, 3H), 7.36–7.29 (m, 3H), 7.26–7.16 (m, 6H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05–7.03 (m, 3H), 5.74 (s, 1H), 1.95 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.0, 144.2, 142.9, 140.0, 137.3, 135.6, 130.6, 130.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 126.8, 126.7, 126.3, 66.9, 19.7 ppm; IR (thin film): 3060, 2250, 1621, 1490, 1446, 1265, 908, 734 cm^{-1}; HRMS calc'd for $C_{27}H_{24}N^+$362.1909, found 362.1904 $[M+H]^+$.

From the flash chromatography, C3-arylated product **4ah'** was isolated in 21.7 mg, 15% yield as colorless thick oil.



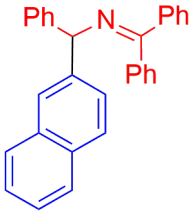
4ah': *N*-Benzylidene-1,1-diphenyl-1-(o-tolyl)methanamine

R_f= 0.71 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.89–7.86 (m, 2H), 7.43–7.41 (m, 3H), 7.33–7.32 (m, 4H), 7.29–7.26 (m, 4H), 7.25–7.21 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 1.72 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.8, 146.3, 143.5, 138.6, 137.1, 132.4, 132.2, 130.9, 129.1, 128.8, 128.1, 127.2, 126.7, 125.2, 79.3, 23.1 ppm; IR (thin film): 3058, 2924, 1638, 1490, 1217, 850, 697 cm^{-1}; HRMS calc'd for $C_{27}H_{24}N^+$ 362.1909, observed 362.1919 $[M+H]^+$.



4ai: 1-(2,6-Dimethylphenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine

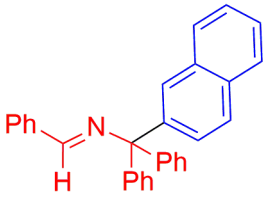
The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 2-iodo-1,3-dimethylbenzene **2i** (92.8 mg, 0.40 mmol) in 9 h. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (66.1 mg, 44% yield) as a thick colorless oil. R_f= 0.72 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.73 (m, 2H), 7.40–7.31 (m, 6H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.20–7.15 (m, 3H), 7.10–7.00 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.10 (s, 1H), 2.02 (s, 6H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 168.1, 144.2, 140.3, 140.2, 137.9, 137.3, 130.2, 129.1, 128.9, 128.8, 128.6, 128.3, 128.2, 127.8, 127.0, 126.6, 126.2, 64.6, 21.2 ppm; IR (thin film): 3018, 2400, 1623, 1491, 1468, 1216, 950, 754 cm^{-1}; HRMS calc'd for $C_{28}H_{26}N^+$376.2065, found 376.2072 $[M+H]^+$.



4aj: *N*-(Diphenylmethylene)-1-(naphthalen-2-yl)-1-phenylmethanamine

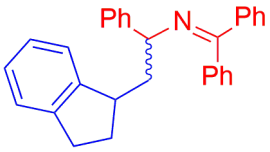
The reaction was performed following the General Procedure A with ketimine **1a** (217.2 mg, 0.80 mmol), $NaN(SiMe_3)_2$ (220.4 mg, 1.2 mmol), 2-iodonaphthalene **2i** (101.6 mg, 0.40 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (55.7 mg, 35% yield) as a thick colorless oil. R_f = 0.45 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79–7.73 (m, 6H), 7.48–7.34 (m, 11H), 7.30–7.25 (m, 2H), 7.22–7.17 (m, 1H), 7.11–7.09 (m, 2H), 5.73 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.5, 144.9, 142.6, 140.1, 137.0, 133.8, 132.9, 130.4, 130.3, 129.1, 129.0, 128.7, 128.6, 128.3, 128.2, 128.02, 127.96, 127.90, 127.1, 126.9, 126.8, 126.6, 126.5, 126.2, 126.1, 125.9, 125.7, 70.3 ppm; IR (thin film): 3025, 2875, 1621, 1491, 1278, 1216, 908, 720 cm^{-1}; HRMS calc'd for $C_{30}H_{24}N^+$398.1903, found 398.1906 $[M+H]^+$.

From the flash chromatography, C3-arylated product **4aj'** was isolated in 17.5 mg, 11% yield as colorless thick oil.



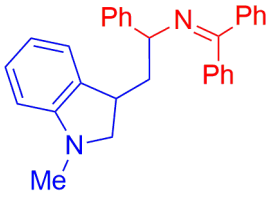
4aj': *N*-Benzylidene-1-(naphthalen-2-yl)-1,1-diphenylmethanamine

R_f = 0.73 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.88–7.86 (m, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 1.0 Hz, 1H), 7.49–7.41 (m, 6H), 7.36–7.27 (m, 10H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.2, 145.8, 143.6, 136.9, 133.0, 132.5, 131.0, 130.0, 128.88, 128.80, 128.6, 128.5, 128.0, 127.6, 127.4, 127.0, 126.2, 126.1, 78.6 ppm; IR (thin film): 3056, 1641, 1489, 1192, 817, 696 cm^{-1}; HRMS calc'd for $C_{30}H_{24}N^+$ 398.1909, observed 398.1918 $[M+H]^+$.



4ak: 2-(2,3-Dihydro-1H-inden-1-yl)-*N*-(diphenylmethylene)-1-phenylethanamine

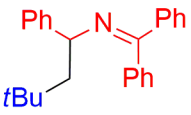
The reaction was performed following the General Procedure A with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-(but-3-en-1-yl)-2-iodobenzene **2k** (25.8 mg, 0.10 mmol) with Toluene as solvent in 6 h. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the **1:1** mixture of diastereomers of product **4ak** (38.5 mg, overall 96% yield) as a thick colorless oil. R_f = 0.62 (diethyl ether:hexanes = 1:5); HRMS calc'd for $C_{30}H_{28}N^+$ 402.2222, found 402.2222 $[M+H]^+$. Diastereomeric ratio was determined based on H^a (1H, ~ 4.6 ppm) and H^b (2H, ~ 7.7 ppm), see ^{1}H spectra (Page S42) for determination of diastereomeric ratio.



4al: *N*-(Diphenylmethylene)-2-(1-methylindolin-3-yl)-1-phenylethanamine

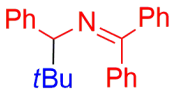
The reaction was performed following the General Procedure A with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), *N*-allyl-2-iodo-N-

methylaniline **2l** (27.3 mg, 0.10 mmol) with DME as solvent in 6 h. The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:10) to give the **1:1** mixture of diastereomers of product **4al** (36.7 mg, overall 88% yield) as a thick colorless oil. R_f= 0.40 (diethyl ether:hexanes = 1:5); HRMS calc'd for $C_{30}H_{29}N_2^+$ 417.2325, found 417.2325 $[M+H]^+$. Diastereomeric ratio was determined based on indoline methyl group (3H, ~ 2.6 ppm) and H^b (1H, ~ 6.6 ppm), see ^1H spectra (Page S43) for determination of diastereomeric ratio.



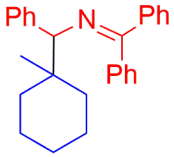
5aa: *N*-(Diphenylmethylene)-3,3-dimethyl-1-phenylbutan-1-amine

The reaction was performed following the General Procedure B with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), neopentyl iodide **3a** (19.8 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (32.4 mg, 95% yield) as a thick colorless oil. R_f= 0.73 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.69–7.67 (m, 2H), 7.44–7.41 (m, 3H), 7.37–7.32 (m, 3H), 7.30–7.25 (m, 4H), 7.21–7.18 (m, 1H), 7.04–7.02 (m, 2H), 4.52 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.12 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.80 (dd, *J* = 14.0, 4.0 Hz, 1H), 0.82 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.6, 147.2, 140.4, 137.5, 129.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.4, 126.5, 64.7, 53.9, 31.2, 30.5 ppm; IR (thin film): 3018, 2955, 2359, 1618, 1491, 1445, 1216, 909, 769 cm^{-1}; HRMS calc'd for $C_{25}H_{28}N^+$342.2222, found 342.2199 $[M+H]^+$.



5ab: *N*-(Diphenylmethylene)-2,2-dimethyl-1-phenylpropan-1-amine

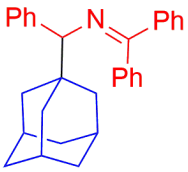
The reaction was performed following the General Procedure B with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 2-iodo-2-methylpropane **3b** (18.4 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (17.4 mg, 53% yield) as a thick colorless oil. R_f= 0.82 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.41–7.32 (m, 6H), 7.24–7.18 (m, 5H), 6.91 (d, *J* = 6.5 Hz, 2H), 3.99 (s, 1H), 0.91 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7, 143.0, 140.4, 137.2, 129.7, 129.1, 128.5, 128.04, 128.03, 127.95, 127.94, 127.4, 126.4, 75.6, 36.3, 26.9 ppm; IR (thin film): 3019, 2968, 1625, 1489, 1374, 1215, 761, 689 cm^{-1}; HRMS calc'd for $C_{24}H_{26}N^+$ 328.2065, found 328.2039 $[M+H]^+$.



5ac: *N*-(Diphenylmethylene)-1-(1-methylcyclohexyl)-1-phenylmethanamine

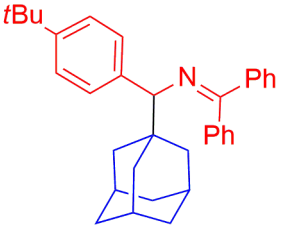
The reaction was performed following the General Procedure B with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodo-1-methylcyclohexane **3c** (22.4 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (15.1 mg, 41% yield) as a thick colorless oil. When 1-bromo-1-methylcyclohexane **3d** was used, following the same procedure, product was isolated in 13.6 mg, 37% yield. R_f= 0.78 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–

7.70 (m, 2H), 7.40–7.32 (m, 6H), 7.22–7.17 (m, 5H), 6.88 (d, J = 6.5 Hz, 2H), 4.00 (s, 1H), 1.54–1.51 (m, 1H), 1.32–1.44 (m, 6H), 1.25–1.19 (m, 1H), 1.16–1.06 (m, 2H), 1.03 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.0, 142.7, 140.6, 137.4, 129.9, 129.5, 128.7, 128.6, 128.24, 128.19, 128.18, 128.16, 127.5, 126.0, 126.5, 126.3, 76.1, 39.1, 35.3, 34.8, 26.6, 22.7, 22.2, 19.7 ppm; IR (thin film): 3019, 2975, 2400, 1625, 1489, 1215, 908, 769 cm^{-1}; HRMS calc'd for $C_{27}H_{30}N^+$368.2378, found 368.2368 $[M+H]^+$.



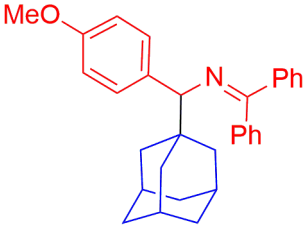
5ae: 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-phenylmethanamine

The reaction was performed following the General Procedure B with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (37.7 mg, 93% yield) as a thick colorless oil. When 1-bromoadamantane **3f** was used, following the same procedure with toluene as solvent, product was isolated in 24.7 mg, 61% yield. R_f = 0.72 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.40–7.33 (m, 6H), 7.25–7.18 (m, 5H), 6.91 (d, J = 6.5 Hz, 2H), 3.83 (s, 1H), 1.93 (s, 3H), 1.66–1.64 (m, 3H), 1.57 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.1, 142.0, 140.6, 137.4, 129.8, 129.4, 128.7, 128.22, 128.20, 128.16, 127.5, 126.5, 76.7, 39.5, 38.2, 37.4, 28.9 ppm; IR (thin film): 3019, 2400, 1730, 1600, 1215, 908, 756 cm^{-1}; HRMS calc'd for $C_{30}H_{32}N^+$406.2535, found 406.2543 $[M+H]^+$.



5be: 1-(Adamantan-1-yl)-1-(4-(*tert*-butyl)phenyl)-*N*-(diphenylmethylene)-methanamine

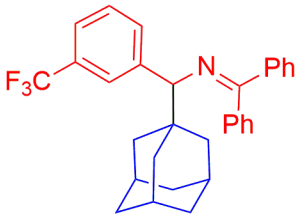
The reaction was performed following the General Procedure B with ketimine **1b** (65.4 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (26.8 mg, 58% yield) as a thick colorless oil. R_f = 0.78 (diethyl ether:hexanes = 1:5); ^1H NMR (500 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.37–7.30 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 6.5 Hz, 2H), 3.80 (s, 1H), 1.91 (s, 3H), 1.63–1.61 (m, 3H), 1.53–1.51 (m, 9H), 1.30 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.7, 149.1, 140.7, 138.8, 137.4, 129.7, 128.9, 128.7, 128.4, 128.2, 128.14, 128.12, 124.3, 76.5, 39.4, 38.3, 37.5, 34.6, 31.7, 28.9 ppm; IR (thin film): 3022, 2905, 2400, 1732, 1624, 1490, 1393, 1268, 908, 751 cm^{-1}; HRMS calc'd for $C_{34}H_{40}N^+$ 462.3161, found 462.3156 $[M+H]^+$.



5ce: 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(4-methoxyphenyl)-methanamine

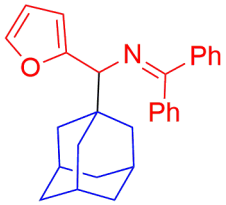
The reaction was performed following the General Procedure B with ketimine **1c** (60.2 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by

flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the product (29.6 mg, 68% yield) as a thick colorless oil. R_f = 0.63 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.37–7.30 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 6.5 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 1H), 1.90 (s, 3H), 1.64–1.61 (m, 3H), 1.56–1.53 (m, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.8, 158.3, 140.6, 137.4, 134.3, 130.3, 129.8, 128.7, 128.22, 128.20, 128.17, 128.15, 112.8, 76.0, 55.4, 39.4, 38.2, 37.5, 28.9 ppm; IR (thin film): 3019, 2399, 1626, 1508, 1217, 908, 773 cm^{-1}; HRMS calc'd for $C_{31}H_{34}NO^+$ 436.2640, found 436.2646 $[M+H]^+$.



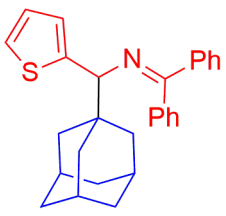
5de: 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(3-(trifluoromethyl)-phenyl)methanamine

The reaction was performed following the General Procedure B with ketimine **1d** (67.8 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (37.9 mg, 80% yield) as a thick colorless oil. R_f = 0.73 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.40–7.30 (m, 9H), 6.85 (d, *J* = 6.5 Hz, 2H), 3.86 (s, 1H), 1.93 (s, 3H), 1.65–1.62 (m, 3H), 1.56–1.52 (m, 9H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.1, 142.9, 140.2, 137.2, 132.8, 130.1, 128.8, 128.4, 128.3, 128.2, 127.98, 127.90, 126.0 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 76.4, 39.3, 38.8, 37.3, 28.8 ppm; IR (thin film): 3018, 2907, 1624, 1360, 1215, 908, 758 cm^{-1}; HRMS calc'd for $C_{31}H_{31}N_3F_3^+$ 474.2412, found 406.2535 $[M+H]^+$.



5ee: 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(furan-2-yl)methanamine

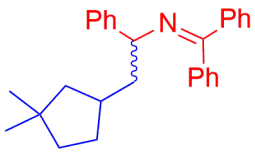
The reaction was performed following the General Procedure B with ketimine **1e** (52.2 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (23.7 mg, 60% yield) as a thick colorless oil. R_f = 0.74 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.40–7.30 (m, 7H), 6.97–6.95 (m, 2H), 6.29–6.28 (m, 1H), 6.06–6.05 (m, 1H), 3.98 (s, 1H), 1.94 (s, 3H), 1.67–1.59 (m, 12H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.9, 155.7, 140.9, 140.5, 137.1, 130.0, 128.9, 128.42, 128.38, 128.2, 109.9, 107.2, 70.9, 39.5, 38.6, 37.4, 28.9 ppm; IR (thin film): 3018, 2904, 2846, 1614, 1314, 1215, 942, 804 cm^{-1}; HRMS calc'd for $C_{28}H_{30}NO^+$ 396.2327, found 396.2349 $[M+H]^+$.



5fe: 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(thiophen-2-yl)methanamine

The reaction was performed following the General Procedure B with ketimine **1f** (55.4 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 1-iodoadamantane **3e** (26.2 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated

silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (35.0 mg, 85% yield) as a thick colorless oil. R_f= 0.85 (diethyl ether:hexanes = 1:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71–7.69 (m, 2H), 7.37–7.29 (m, 6H), 7.15 (d, *J* = 5.0 Hz, 1H), 6.95–6.94 (m, 2H), 6.91 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.68 (d, *J* = 3.5 Hz, 1H), 4.15 (s, 1H), 1.93 (s, 3H), 1.65–1.62 (m, 4H), 1.65–1.60 (m, 8H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.6, 144.6, 140.2, 136.8, 130.0, 128.8, 128.4, 128.3, 128.2, 128.1, 125.7, 124.3, 123.9, 72.7, 39.4, 38.2, 37.4, 28.9 ppm; IR (thin film): 3018, 2905, 1625, 1445, 1215, 815, 597 cm^{-1}; HRMS calc'd for $C_{28}H_{30}NS^+$ 412.2099, found 412.2073 $[M+H]^+$.



5ag: 2-(3,3-Dimethylcyclopentyl)-*N*-(diphenylmethylene)-1-phenylethanamine
The reaction was performed following the General Procedure B with ketimine **1a** (54.3 mg, 0.20 mmol), $NaN(SiMe_3)_2$ (55.1 mg, 0.3 mmol), 6-iodo-5,5-dimethylhex-1-ene **3g** (23.8 mg, 0.10 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:50) to give the **1:1** mixture of diastereomers of product **5ag** (36.2 mg, overall 95% yield) as a thick colorless oil. R_f= 0.68 (diethyl ether:hexanes = 1:5); HRMS calc'd for $C_{28}H_{32}N^+$ 382.2535, found 382.2559 $[M+H]^+$. Diastereomeric ratio was determined based on methyl group of the cyclopentane ring (3H, ~ 1.0 ppm and 3H, ~0.9 ppm), see ^{1}H spectra (Page S53) for determination of diastereomeric ratio.

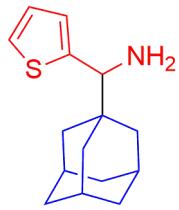
Gram Scale Sequential One-Pot Ketimine Synthesis/Alkylation Procedure:

An oven-dried 100 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). DCM (10 mL) was added under nitrogen via syringe through the rubber septum. 2-Thiophenemethylamine (1.13 g, 10.0 mmol) and benzophenone imine (1.81 g, 10.0 mmol) were added under nitrogen via syringe through the rubber septum. The reaction was stirred at 23 °C for 12 h, the solvent was completely removed in *vacuo* and the tube was filled with nitrogen. A solution (prepared in the glove box) of 1-iodoadamantane **3e** (1.31 g, 5.0 mmol) in 20 mL anhydrous MTBE was added to the Schlenk tube via syringe through the rubber septum. Next, a solution of $NaN(SiMe_3)_2$ (7.6 g, 15 mmol) in 30 mL anhydrous DME was added by syringe through the rubber septum. The reaction mixture was stirred for 6 h in total at 23 °C, 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 on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the product (1.69 g, 82% yield) as a thick colorless oil.

Product hydrolysis:

Hydrolysis of Product 5fe: An oven-dried microwave vial equipped with a stir bar was charged with **5fe** (41.2 mg 0.1 mmol). THF (1 mL) was added to the reaction vial via syringe and the reaction was cooled at 0 °C. HCl 1N (1 mL) was added to the reaction vial via syringe. The stirring solution was warmed to room temperature

and was monitored by TLC until **5fe** was consumed (reaction completed in 3 h). The reaction mixture was basified with 1N NaOH until the pH reached 14, transferred to a 30 mL seperatory funnel via pipette and was extracted with dichloromethane (3 x 2 mL). The combined organic layers were concentrated in *vacuo*, loaded onto a deactivated silica gel column via pipette and purified by flash chromatography on deactivated silica gel (eluted with hexanes to ethyl acetate:hexanes = 1:2) to give the amine product **6fe** as a yellow oil (24.5 mg, 99% yield).



6fe: Adamantan-1-yl(thiophen-2-yl)methanamine:

R_f = 0.12 (ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 5.0 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.85 (d, *J* = 3.5 Hz, 1H), 3.81 (s, 1H), 1.98 (s, 3H), 1.69–1.51 (m, 15H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 147.3, 126.1, 124.9, 123.5, 62.4, 38.9, 37.3, 36.7, 28.7 cm^{-1}; HRMS calc'd for $C_{15}H_{19}S$ 231.1207, observed 231.1190 $[M\text{-}NH_2]^+$.

Microscale High-throughput Experimentation:

(1) General Information. High-throughput Experimentation Screening was accomplished in a Vacuum Atmospheres glovebox with oxygen typically <5 ppm. The experimental design was accomplished using Accelrys Library Studio. Screening reactions were carried out in 1 mL vials (30 mm height×8 mm diameter) in 24-well plate aluminum reactor block. Liquid chemicals were dosed using multi-channel or single-channel pipettors. Solid chemicals were dosed manually as solutions or slurries in appropriate solvents. Undesired additional solvent was removed using a GeneVac system located inside the glovebox. The reactions were heated and stirred on a heating block with a tumble-stirrer (V&P Scientific) using 1.98 mm diameter×4.80 mm length parylene stir bars. The tumble stirring mechanism helped to insure uniform stirring throughout the 24-well plate. The reactions were sealed in the 24-well plate during reaction. Below each reactor vial in the aluminum 24-well plate was a 0.062 mm thick silicon-rubber gasket. Directly above the glass vial reactor tops was a Teflon perfluoroalkoxy copolymer resin sealing gasket and above that, two more 0.062 mm thick silicon-rubber gaskets. The entire assembly was compressed between an aluminum top and the reactor base with 9 evenly-placed screws.

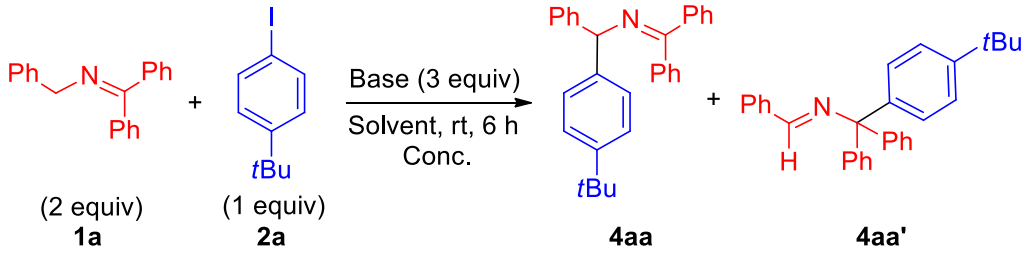
(2) Screening of base, solvent and concentration for transition metal-free arylation:

***Set up*:**

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials were firstly dosed with $NaN(SiMe_3)_2$ (30 μmol) and $LiN(SiMe_3)_2$ (30 μmol) in THF. The solvent was removed to dryness using a GeneVac. and a parylene stir bar was then added to each reaction vial. Ketimine **1a** (20 μmol/reaction) and 1-(*tert*-butyl)-4-iodobenzene **2a** (10 μmol) were then dosed together into each reaction vial as a solution in different solvents (50 μL, 0.2 M). For 0.1 M reactions, extra 50 μL solvent was added. The 24-well plate was then sealed with screws and stirred for 6 h at 23 °C.

***Work up*:**

Upon opening the plate to air, 500 µL of a solution of biphenyl (used as internal standard to measure UPLC yields) in acetonitrile (0.002 mol/L) was added into each vial. The plate was covered again and the vials stirred for 10 min. to ensure good homogenization. Into a separate 96-well LC block was added 700 µL of acetonitrile, followed by 25 µL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated UPLC instrument for analysis.



- Solvent: THF, CPME, DME, MTBE, Toluene, Cyclohexane
- Base: $LiN(SiMe_3)_2$ and $NaN(SiMe_3)_2$
- Concentration: 0.1 M and 0.2 M

Solvent	Base	Conc.	**4aa**/IS	**4aa'**/IS
THF	$LiN(SiMe_3)_2$	0.2	5.13	1.29
CPME	$LiN(SiMe_3)_2$	0.2	3.86	0.64
DME	$LiN(SiMe_3)_2$	0.2	7.01	1.72
MTBE	$LiN(SiMe_3)_2$	0.2	3.08	0.86
Tol	$LiN(SiMe_3)_2$	0.2	3.15	0.58
Cyclohexane	$LiN(SiMe_3)_2$	0.2	3.89	0.63
THF	$LiN(SiMe_3)_2$	0.1	5.32	1.10
CPME	$LiN(SiMe_3)_2$	0.1	3.02	0.48
DME	$LiN(SiMe_3)_2$	0.1	6.21	1.38
MTBE	$LiN(SiMe_3)_2$	0.1	4.17	0.87
Tol	$LiN(SiMe_3)_2$	0.1	2.07	0.34
Cyclohexane	$LiN(SiMe_3)_2$	0.1	3.15	0.41
THF	$NaN(SiMe_3)_2$	0.2	6.68	2.02
CPME	$NaN(SiMe_3)_2$	0.2	7.16	1.57
DME	**$NaN(SiMe_3)_2$**	**0.2**	**7.36**	**2.04**
MTBE	$NaN(SiMe_3)_2$	0.2	6.63	2.06
Tol	$NaN(SiMe_3)_2$	0.2	6.76	1.52
Cyclohexane	$NaN(SiMe_3)_2$	0.2	5.52	1.49
THF	$NaN(SiMe_3)_2$	0.1	6.05	1.36
CPME	$NaN(SiMe_3)_2$	0.1	5.87	1.08

DME	$NaN(SiMe_3)_2$	0.1	6.83	1.77
MTBE	$NaN(SiMe_3)_2$	0.1	6.13	1.70
Tol	$NaN(SiMe_3)_2$	0.1	5.33	1.02
Cyclohexane	$NaN(SiMe_3)_2$	0.1	5.33	1.31

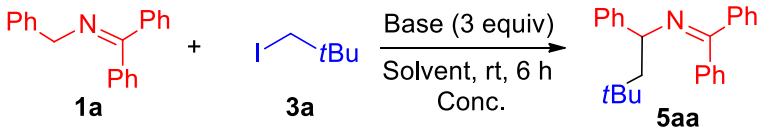
(3) Screening of base, solvent and concentration for transition metal-free alkylation:

***Set up*:**

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials were firstly dosed with $NaN(SiMe_3)_2$ (30 μmol) or $LiN(SiMe_3)_2$ (30 μmol) in THF. The solvent was removed to dryness using a GeneVac. and a parylene stir bar was then added to each reaction vial. Ketimine **1a** (20 μmol/reaction) and neopentyl iodide **3a** (10 μmol) were then dosed together into each reaction vial as a solution in different solvents (50 μL, 0.2 M). For 0.1 M reactions, extra 50 μL solvent was added. The 24-well plate was then sealed with screws and stirred for 6 h at 23 °C.

***Work up*:**

Upon opening the plate to air, 500 μL of a solution of biphenyl (used as internal standard to measure UPLC yields) in acetonitrile (0.002 mol/L) was added into each vial. The plate was covered again and the vials stirred for 10 min. to ensure good homogenization. Into a separate 96-well LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated UPLC instrument for analysis.



- Solvent: THF, CPME, DME, MTBE, Toluene, Cyclohexane
- Base: $LiN(SiMe_3)_2$ and $NaN(SiMe_3)_2$
- Concentration: 0.1 M and 0.2 M

Solvent	Base	Conc.	PDT/IS
THF	$LiN(SiMe_3)_2$	0.2	13.29
CPME	$LiN(SiMe_3)_2$	0.2	6.57
DME	$LiN(SiMe_3)_2$	0.2	13.02
MTBE	$LiN(SiMe_3)_2$	0.2	7.88
Tol	$LiN(SiMe_3)_2$	0.2	5.14
Cyclohexane	$LiN(SiMe_3)_2$	0.2	6.93
THF	$LiN(SiMe_3)_2$	0.1	13.05
CPME	$LiN(SiMe_3)_2$	0.1	5.95
DME	$LiN(SiMe_3)_2$	0.1	12.47

MTBE	$LiN(SiMe_3)_2$	0.1	6.77
Tol	$LiN(SiMe_3)_2$	0.1	5.43
Cyclohexane	$LiN(SiMe_3)_2$	0.1	5.94
THF	$NaN(SiMe_3)_2$	0.2	13.62
CPME	$NaN(SiMe_3)_2$	0.2	11.95
DME	$NaN(SiMe_3)_2$	0.2	13.99
MTBE	$NaN(SiMe_3)_2$	0.2	15.28
Tol	$NaN(SiMe_3)_2$	0.2	13.17
Cyclohexane	$NaN(SiMe_3)_2$	0.2	12.70
THF	$NaN(SiMe_3)_2$	0.1	12.22
CPME	$NaN(SiMe_3)_2$	0.1	11.70
DME	$NaN(SiMe_3)_2$	0.1	13.29
MTBE	**$NaN(SiMe_3)_2$**	**0.1**	**15.71**
Tol	$NaN(SiMe_3)_2$	0.1	12.73
Cyclohexane	$NaN(SiMe_3)_2$	0.1	11.79

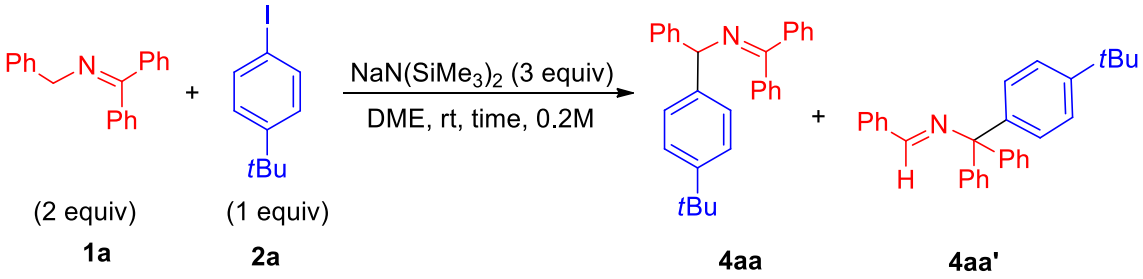
(4) Reaction Profile of Coupling between 1a and 2a.

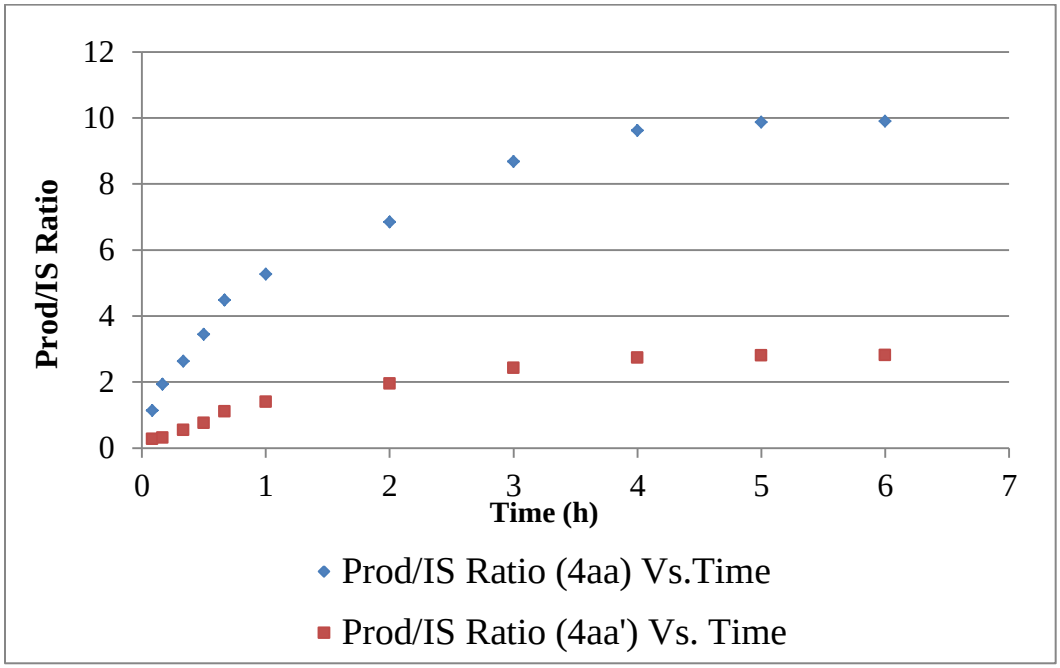
***Set up*:**

Experiments were set up inside a glovebox under a nitrogen atmosphere. 2 mL crimp top glass vials placed in a auto-sampler vial rack were firstly dosed with $NaN(SiMe_3)_2$ (60 μmol) in THF. The solvent was removed to dryness using a GeneVac. and a parylene stir bar was then added to each reaction vial. Ketimine **1a** (40 μmol/reaction) and 1-(*tert*-butyl)-4-iodobenzene **2a** (20 μmol) were dosed together into as a solution in DME (100 μL). Total volume of the reactions is 100 μL, 0.2 M. The vials were sealed with crimp caps, removed from the glovebox and stirred at 23 ^{o}C. Vials were sequentially quenched with 1 drop of water via syringe through the rubber septum at reaction time listed in the Supplementary Figure 1.

***Work up*:**

Upon opening the crimp cap with tweezers, 500 μL of a solution of biphenyl (used as internal standard to measure UPLC yields) in acetonitrile (0.002 mol/L) was added into each vial. The vials were stirred for 10 min. to ensure good homogenization. Into a separate 96-well LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated UPLC instrument for analysis.





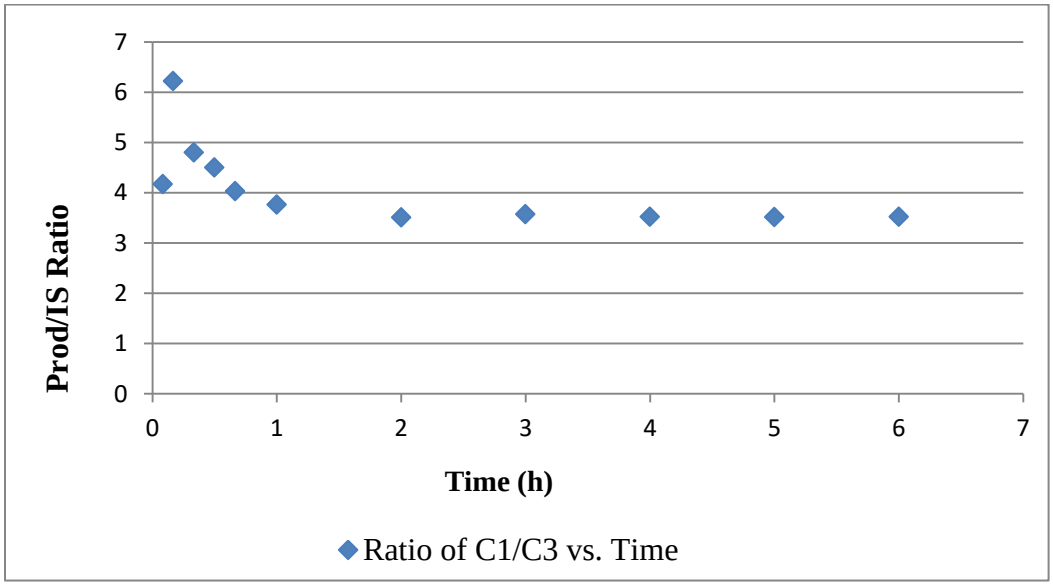


Figure S1. Reaction Profile of Coupling between **1a** and **2a**.

(4) Reaction Profile of Coupling between 1a and 3a.

***Set up*:**

Experiments were set up inside a glovebox under a nitrogen atmosphere. 2 mL crimp top glass vials were placed in a auto-sampler vial rack. A parylene stir bar was then added to each reaction vial. Ketimine **1a** (20 μmol/reaction) and neopentyl iodide **3a** (10 μmol) were dosed together into as a solution in MTBE (50 μL). $NaN(SiMe_3)_2$ (30 μmol/reaction) was then dosed into the vials as a solution in MTBE (50 μL). Total volume of the reactions is 100 μL, 0.1 M. The vials were sealed with crimp caps, removed from the glovebox and stirred at 23 °C. Vials were sequentially quenched with 1 drop of water via syringe through the rubber septum at reaction time listed in the Supplementary Figure 2.

***Work up*:**

Upon opening the crimp cap with tweezers, 500 μL of a solution of biphenyl (used as internal standard to measure UPLC yields) in acetonitrile (0.002 mol/L) was added into each vial. The vials stirred for 10 min. to ensure good homogenization. Into a separate 96-well LC block was added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat and mounted on an automated UPLC instrument for analysis.

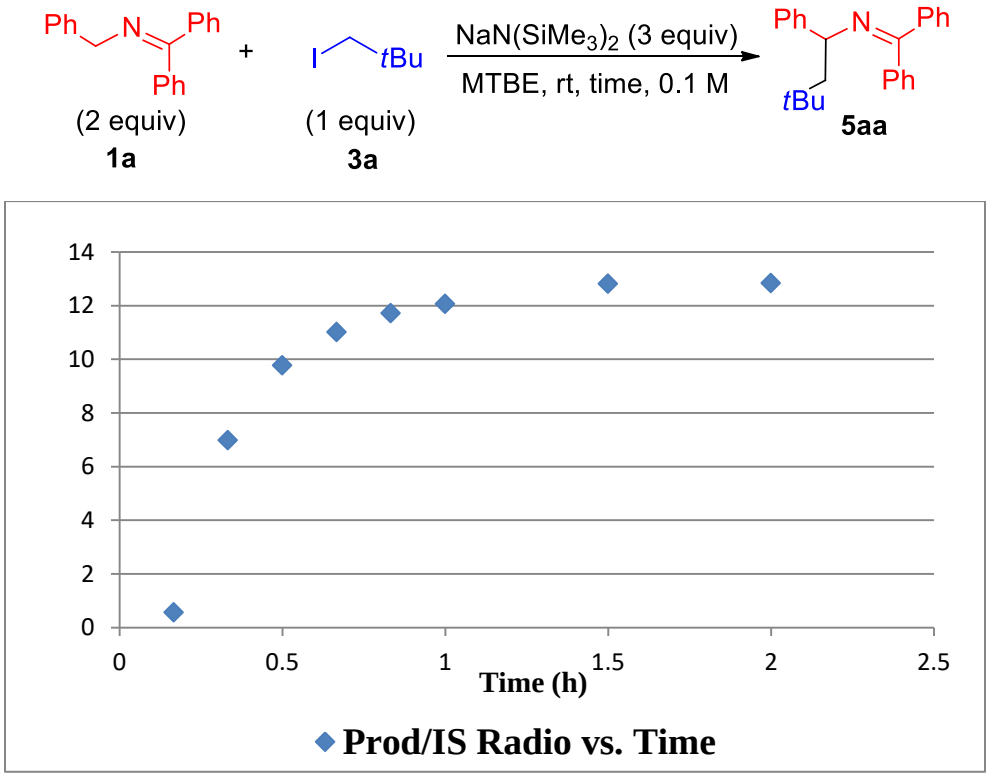
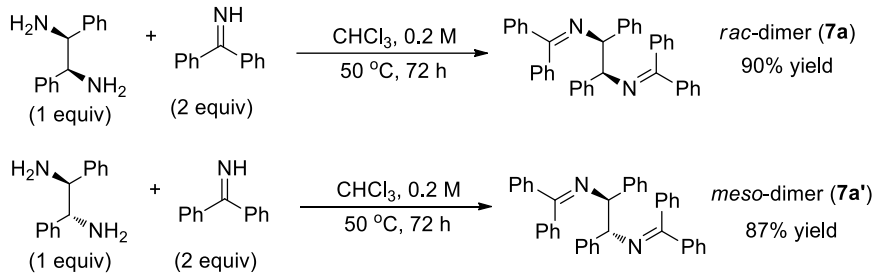


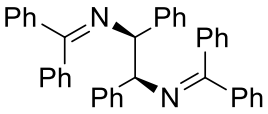
Figure S2. Reaction Profile of Coupling between **1a** and **3a**.

Study of Azaallyl Dimer 7a and 7a'

Rac- and *meso*-dimer product standards were prepared by condensation of the (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine and *meso*-1,2-diphenylethylenediamine with benzophenone imine following the procedure:



An oven-dried 8 mL microwave vial equipped with a stir bar was charged with diphenylethylenediamine (212.3 mg, 1 mmol) and benzophenone imine (362.4 mg, 2 mmol). $CHCl_3$ (5 mL) was added via syringe. The vial was then sealed with cap.The reaction mixture was stirred at 50 °C for 72 h. The reaction mixture was concentrated *in vacuo* till all solvent was removed. The entire crude material was loaded onto a deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:100) to give the *rac*-dimer **7a** (486.6 mg, 90% yield) and *meso*-dimer **7a'** (470.4 mg, 87% yield) as white solids. The ^{1}H NMR data for this compound match the literature data.[5]



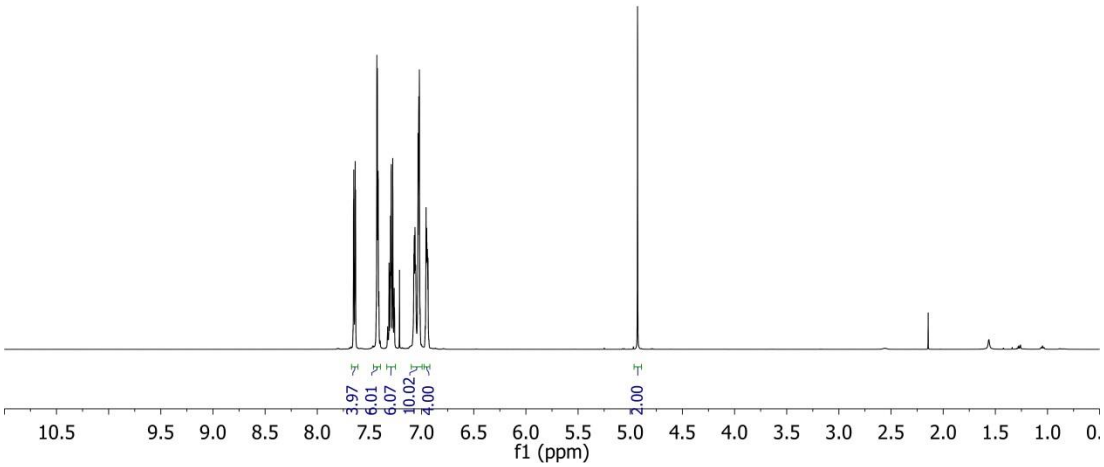


Figure S3. ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *rac*-dimer **7a**.

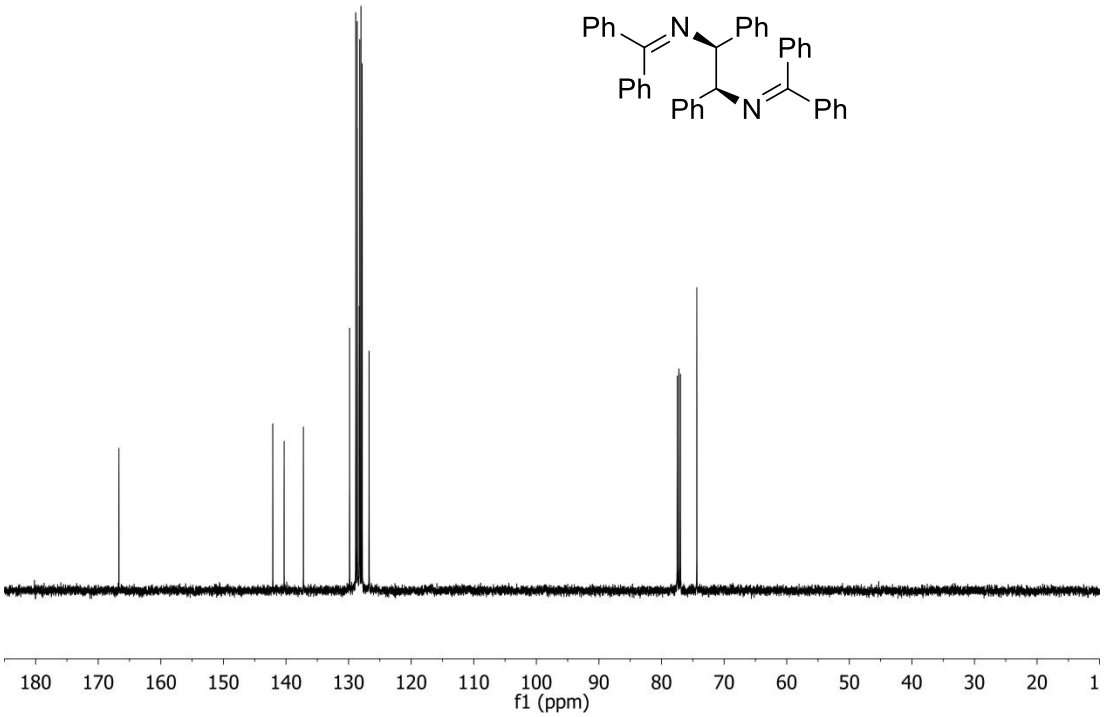


Figure S4. $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz) of *rac*-dimer **7a**.

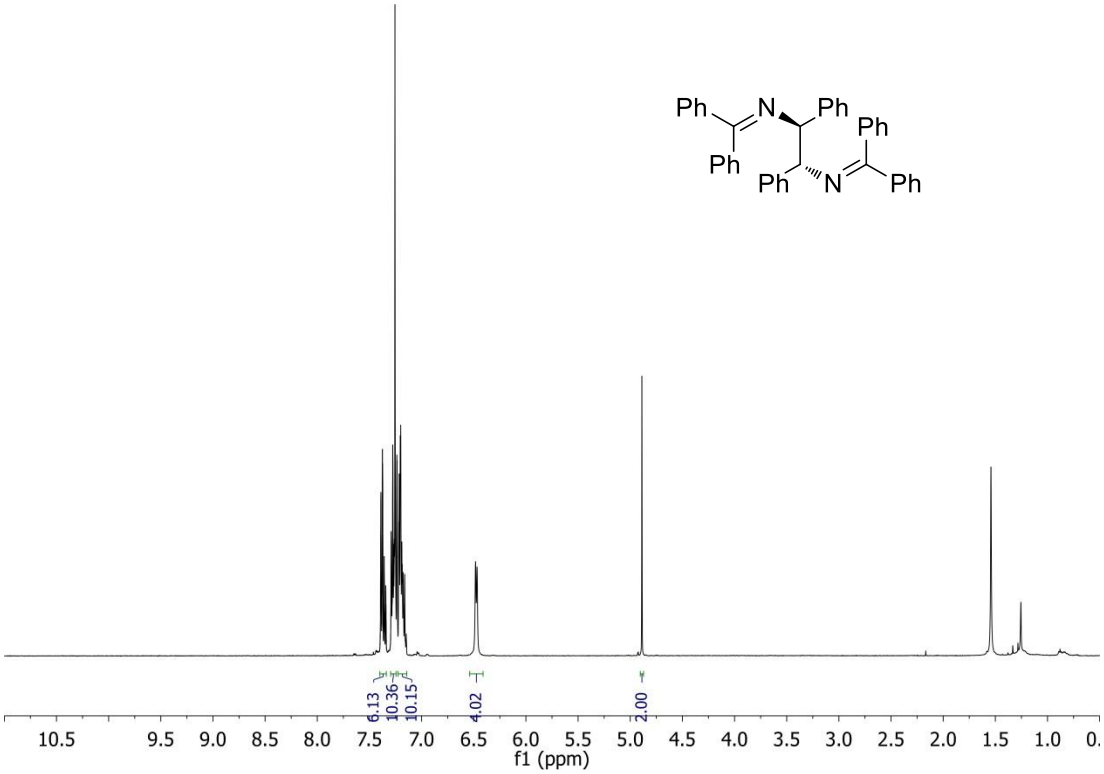


Figure S5. ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *meso*-dimer **7a'**.

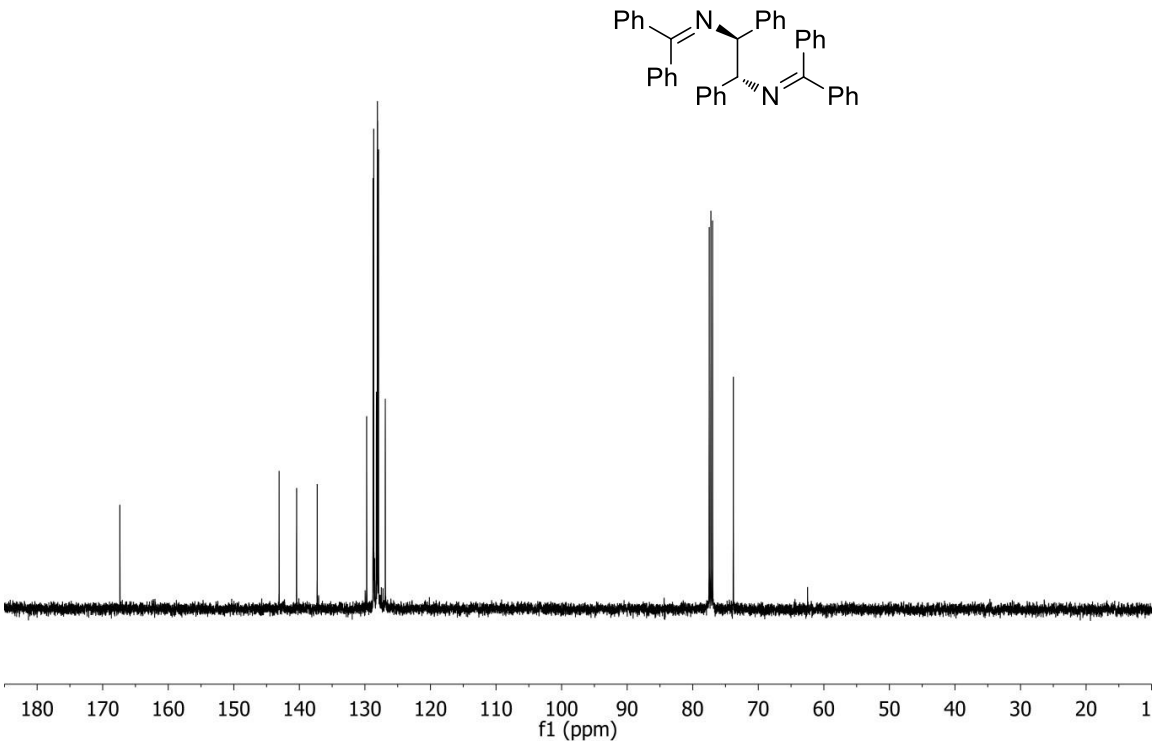


Figure S6. $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz) of *meso*-dimer **7a'**.

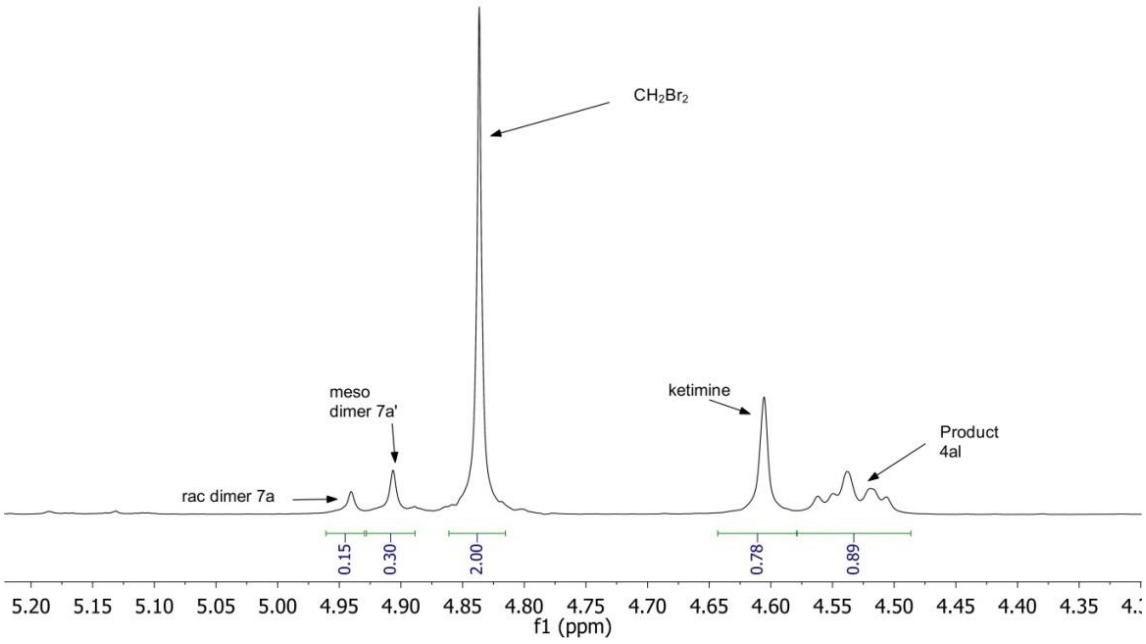


Figure S7. Crude ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of Coupling between **1a** and **2l**.

References

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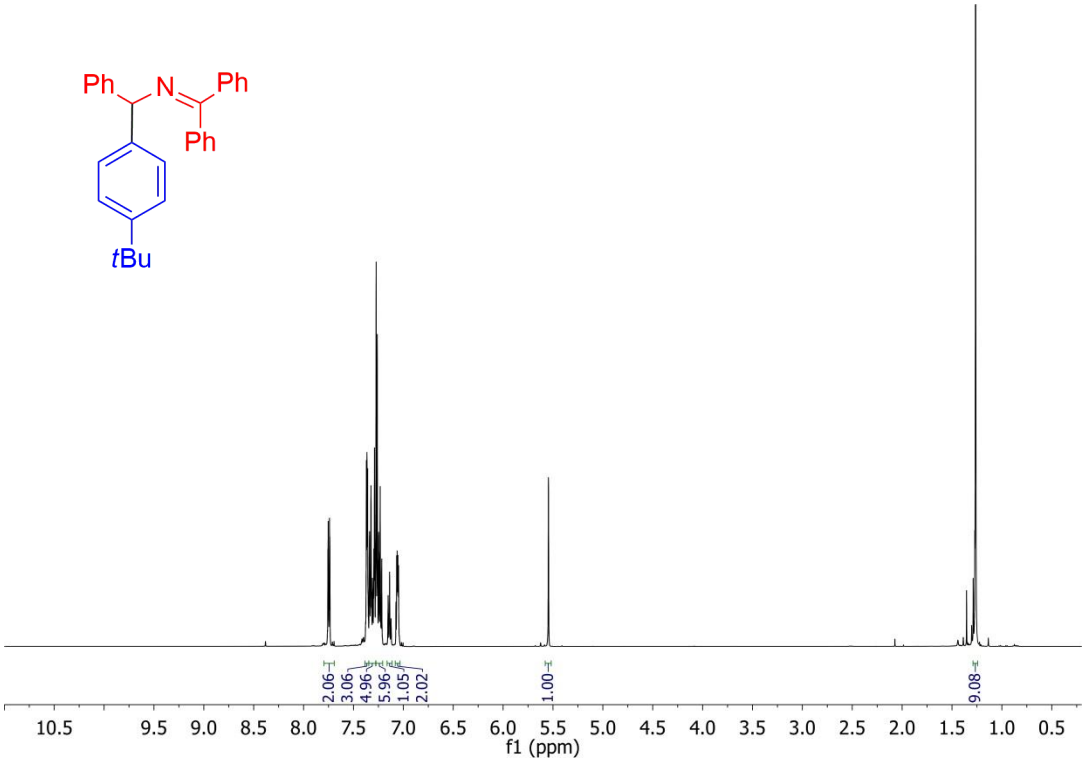
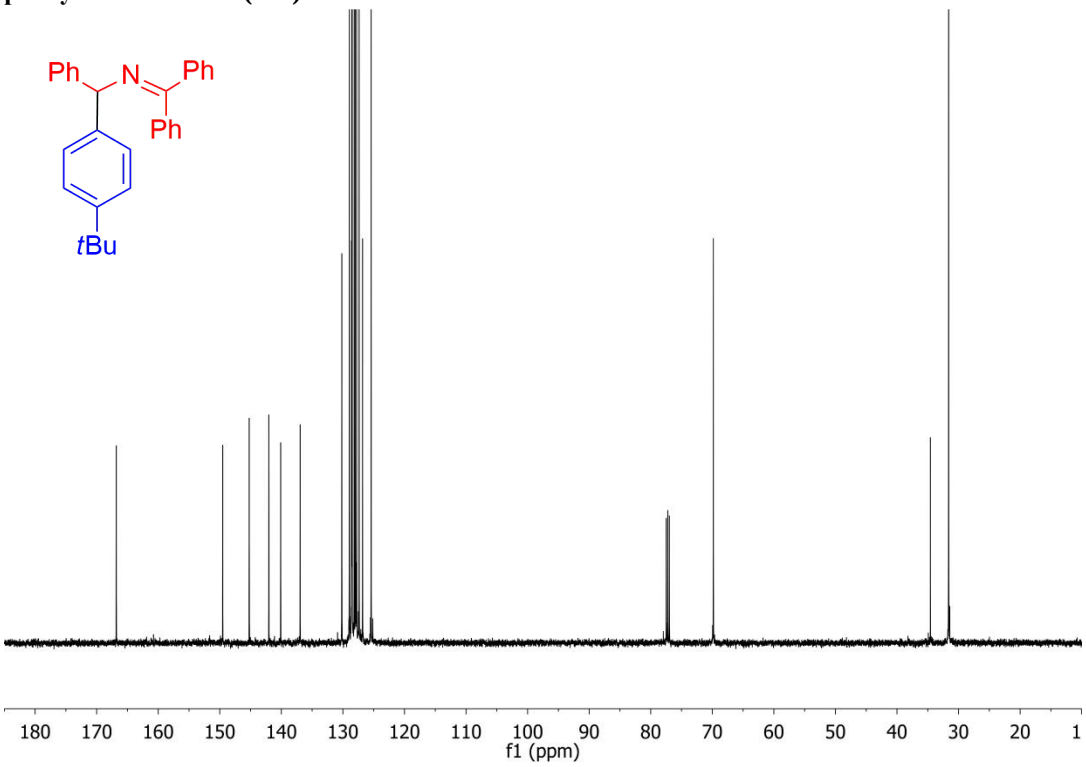
NMR Spectra

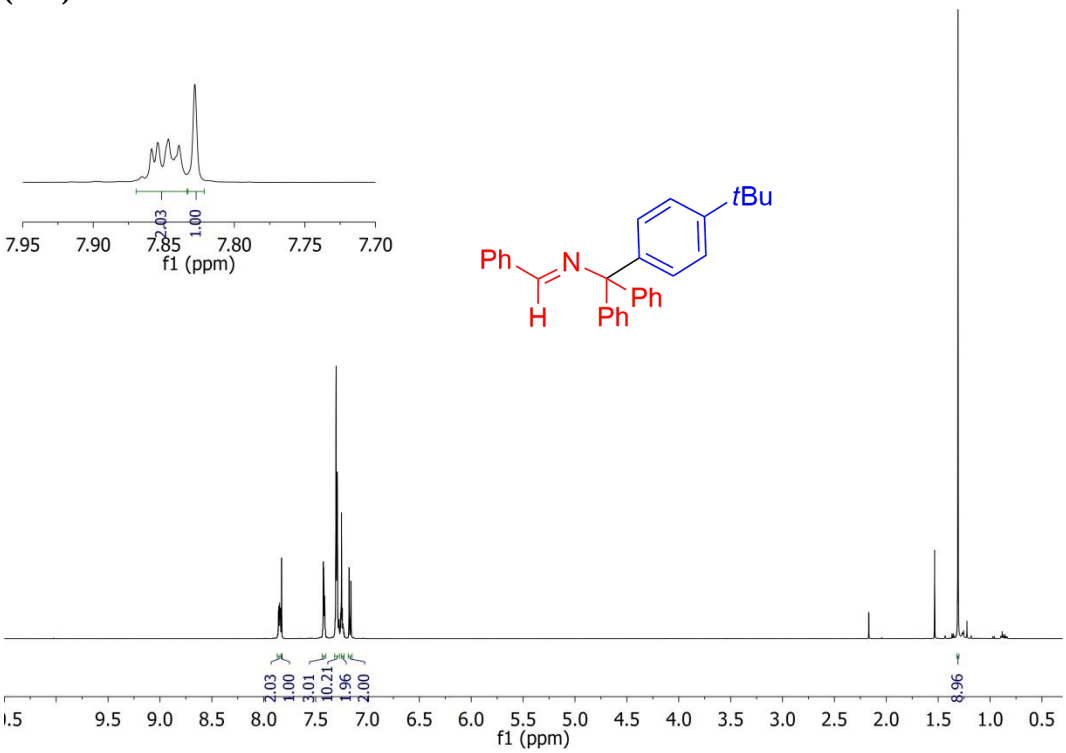
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(4-(*tert*-Butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine (4aa):



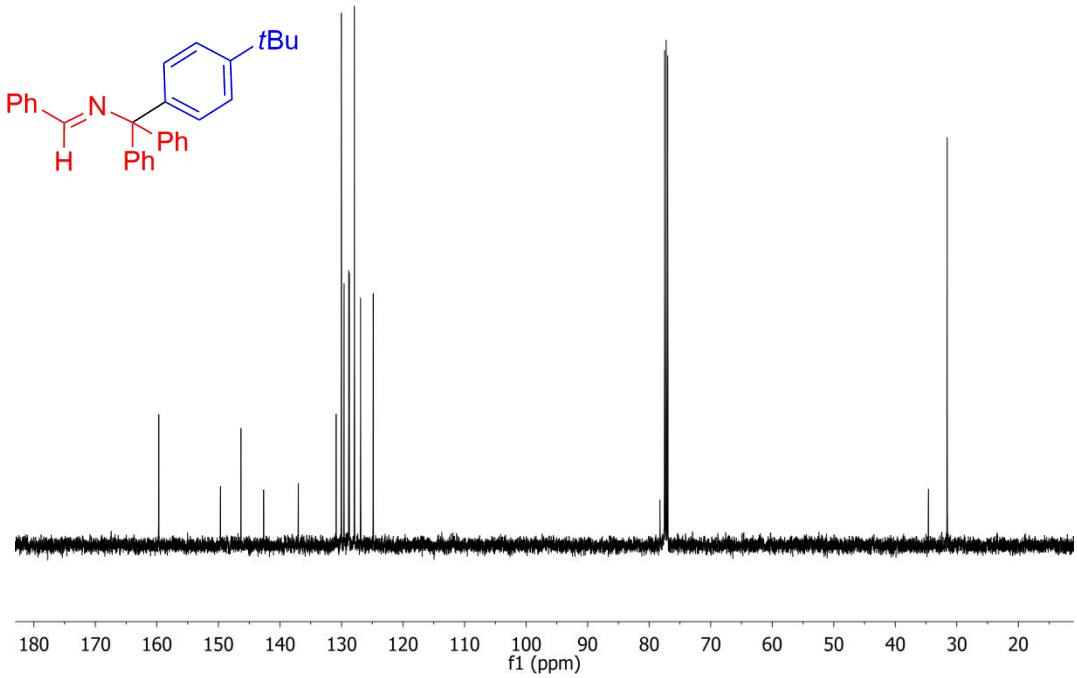
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(4-(*tert*-Butyl)phenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine (4aa):



^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(4-(*tert*-butyl)phenyl)-1,1-diphenylmethanamine (4aa'):



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1-(4-(*tert*-butyl)phenyl)-1,1-diphenylmethanamine (4aa'):



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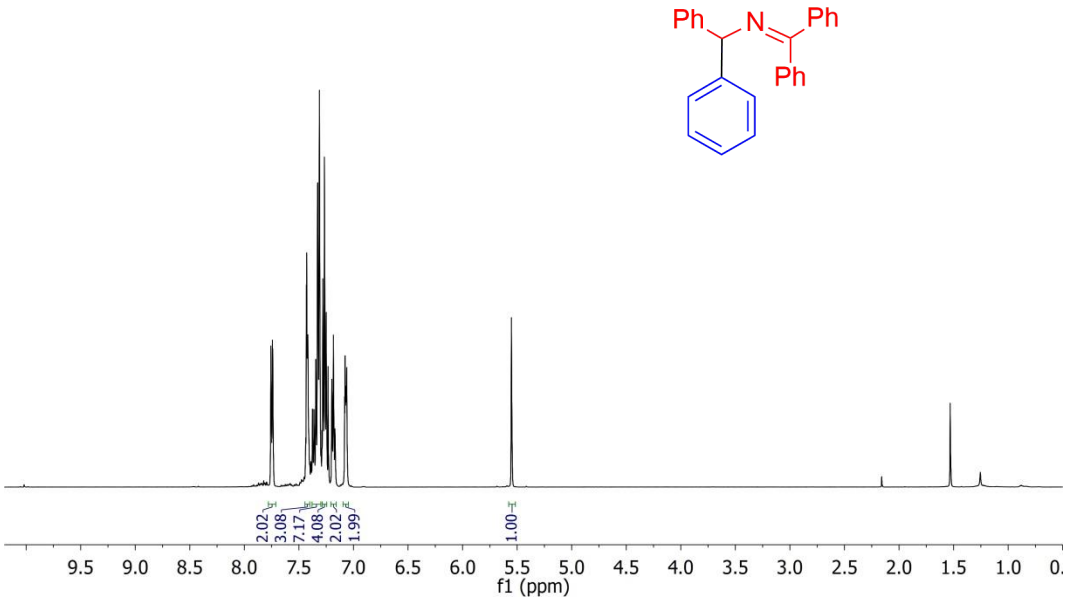
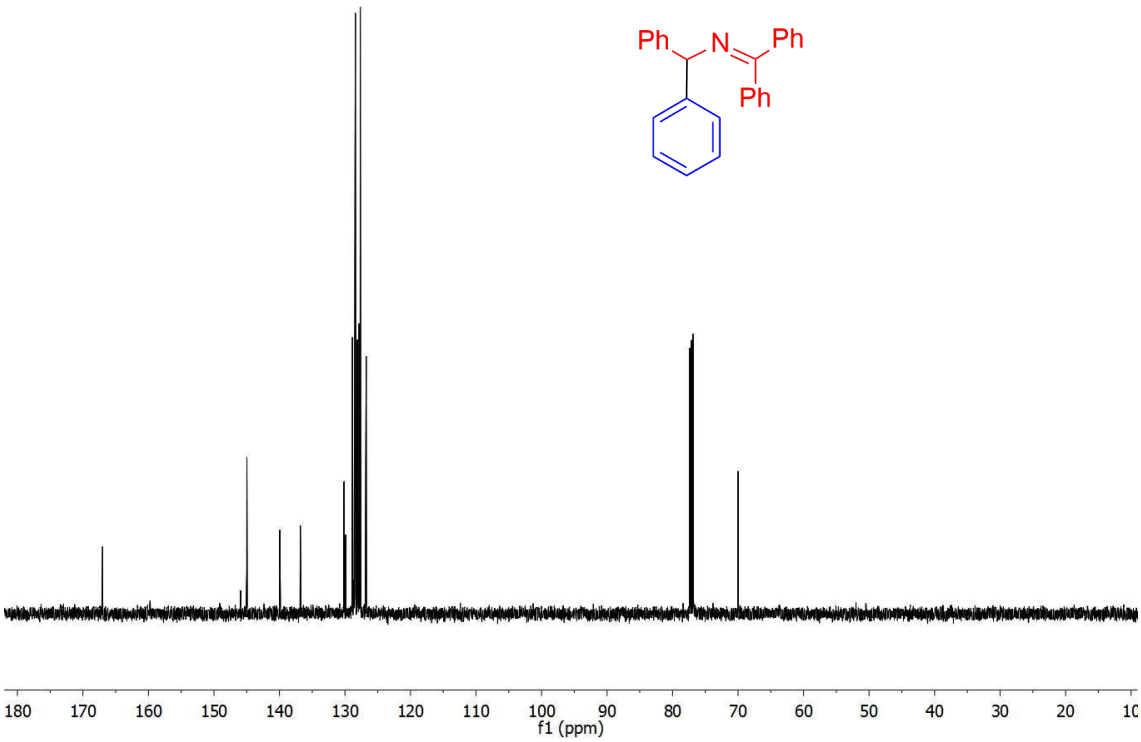
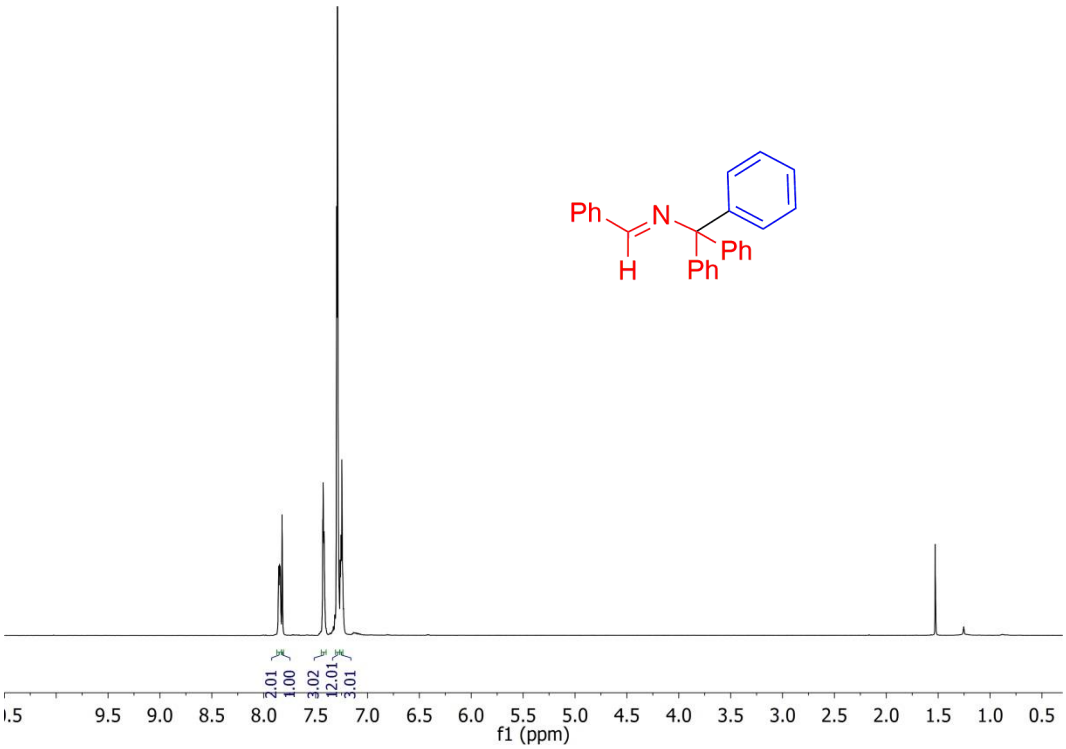


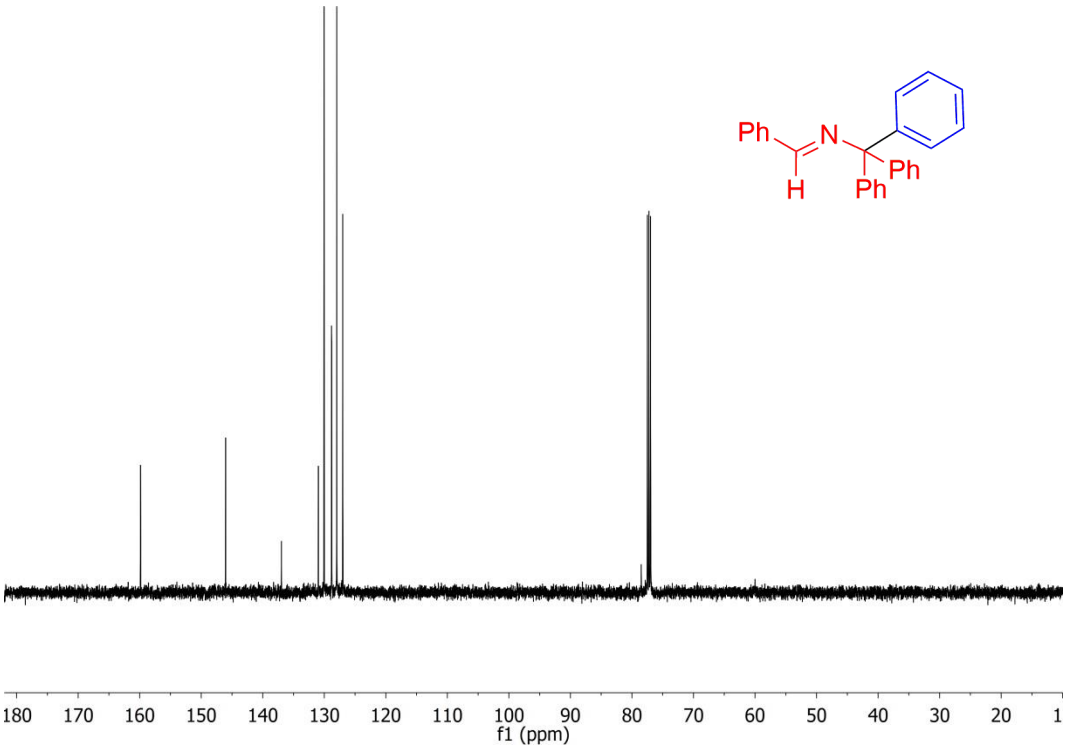
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-1,1-diphenylmethanamine (4ab):



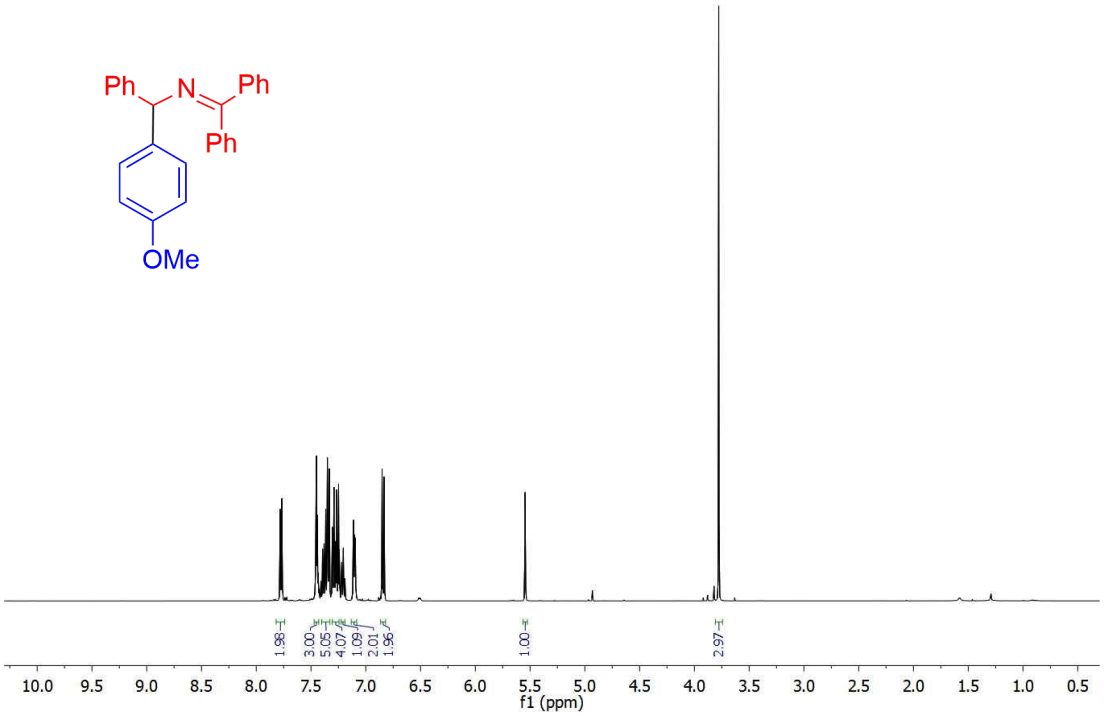
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1,1,1-triphenylmethanamine (4ab'):



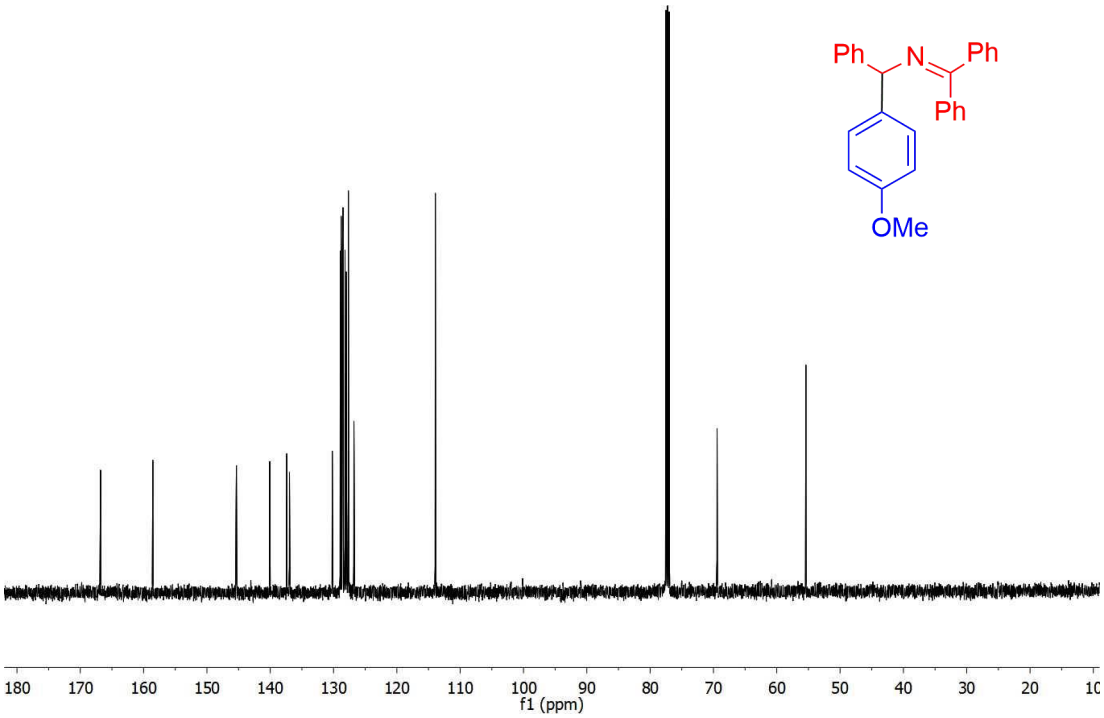
$^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1,1,1-triphenylmethanamine (4ab'):



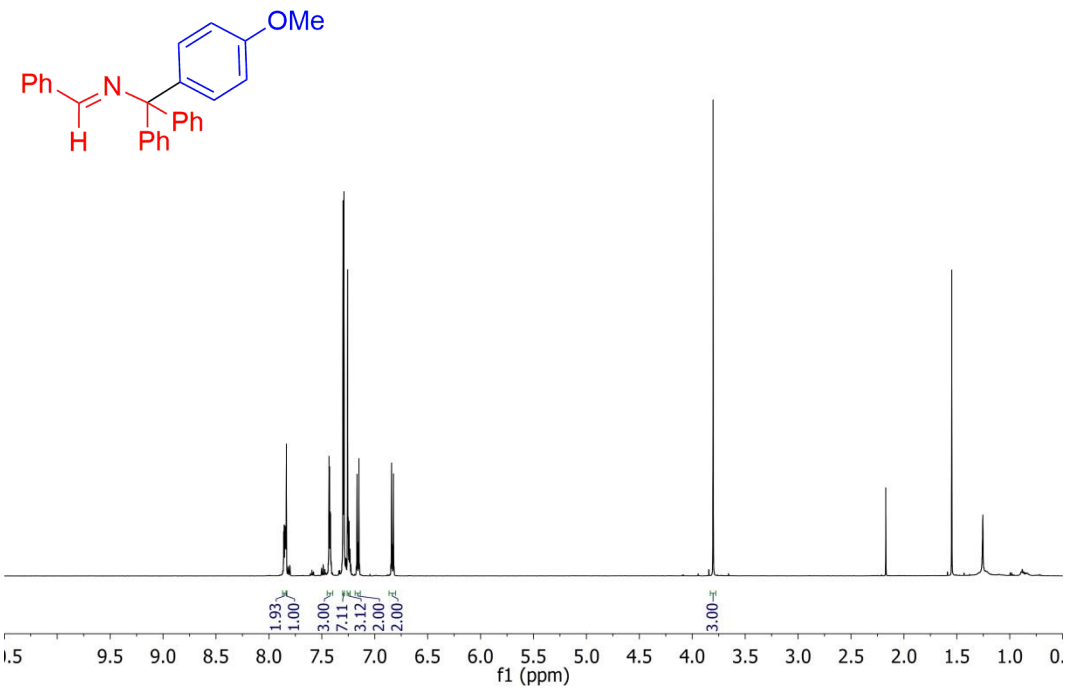
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-1-(4-methoxyphenyl)-1-phenylmethanamine (4ac):



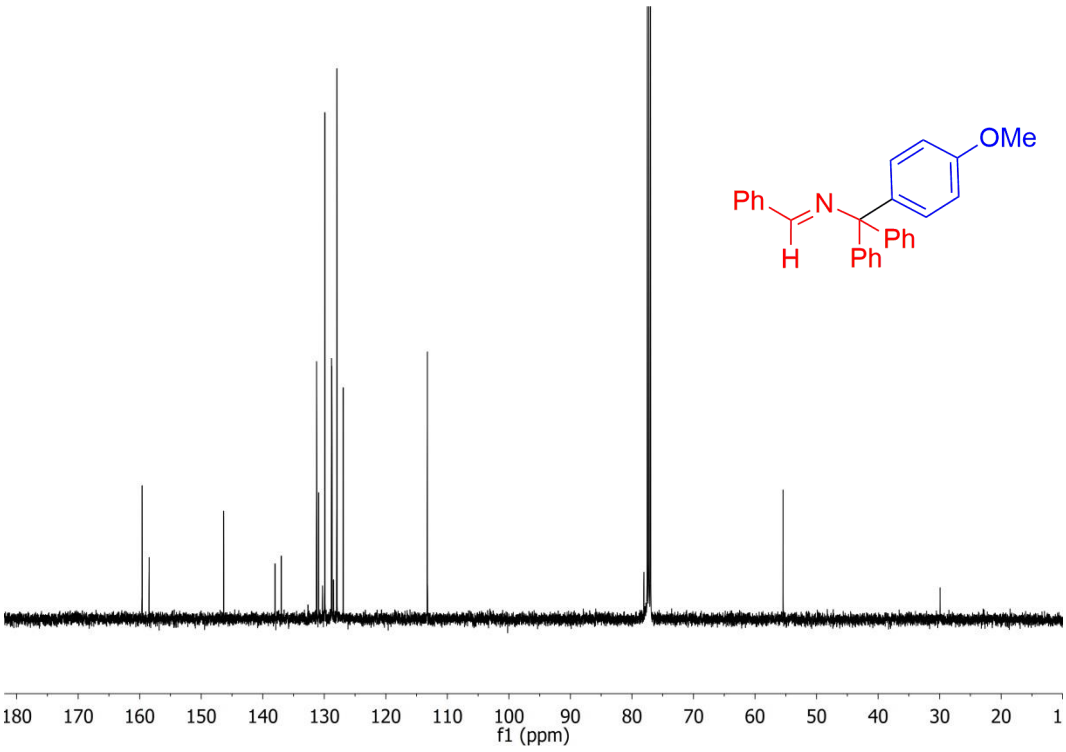
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-1-(4-methoxyphenyl)-1-phenylmethanamine (4ac):



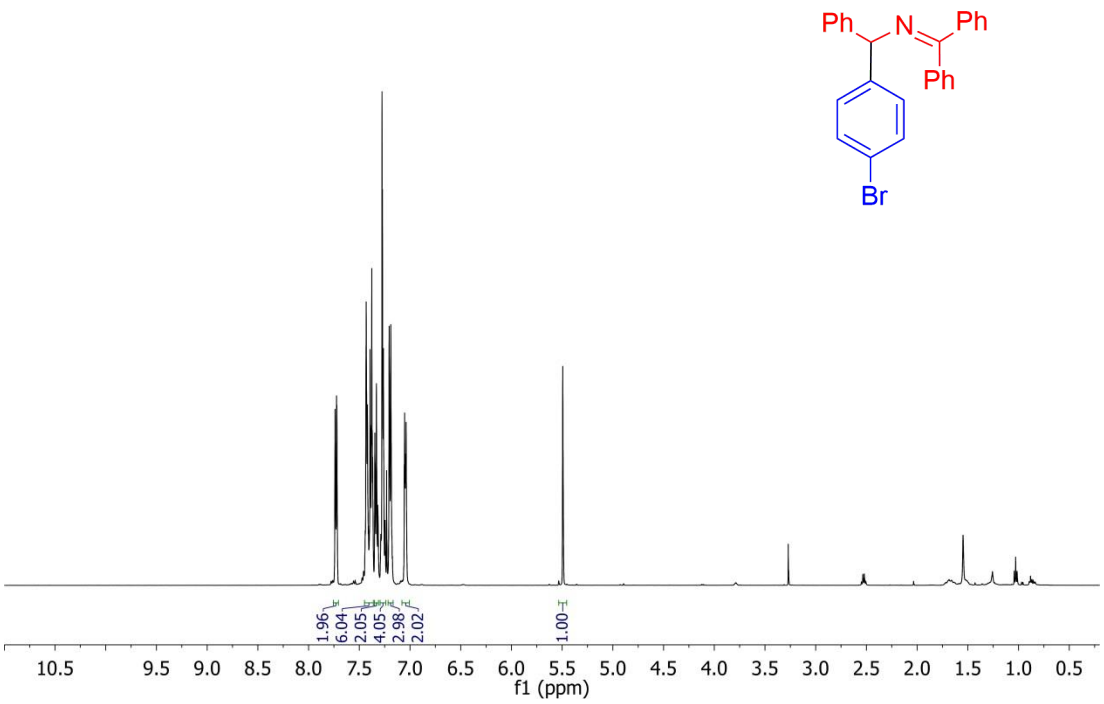
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(4-methoxyphenyl)-1,1-diphenylmethanamine(4ac'):



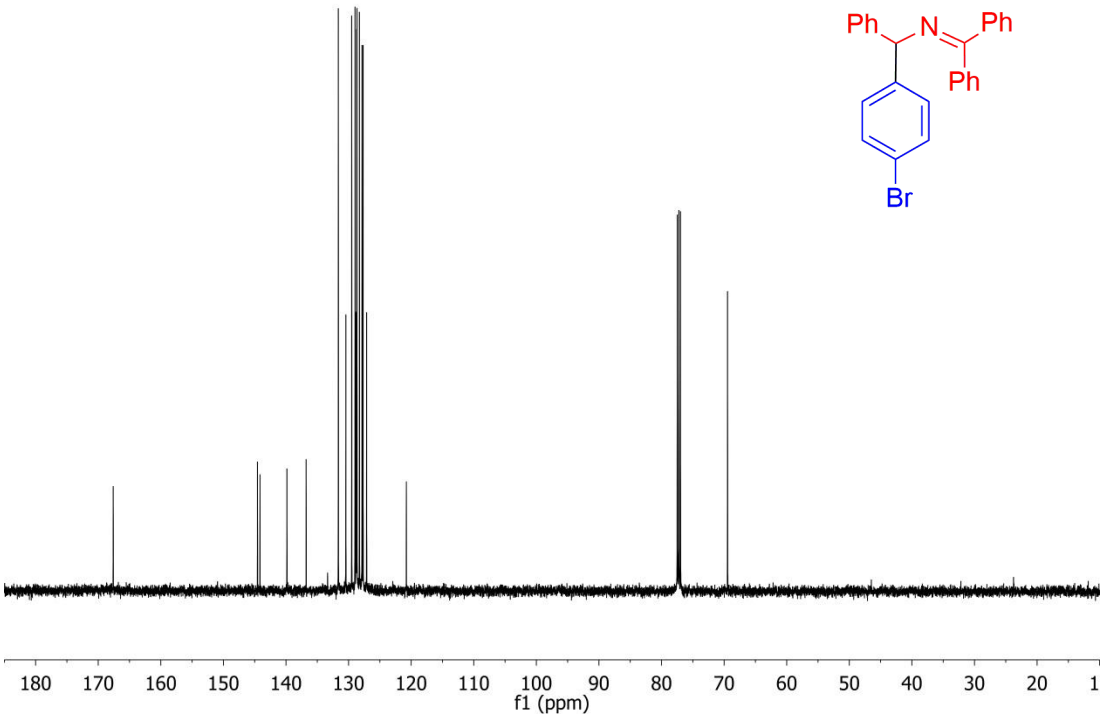
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1-(4-methoxyphenyl)-1,1-diphenylmethanamine (4ac'):



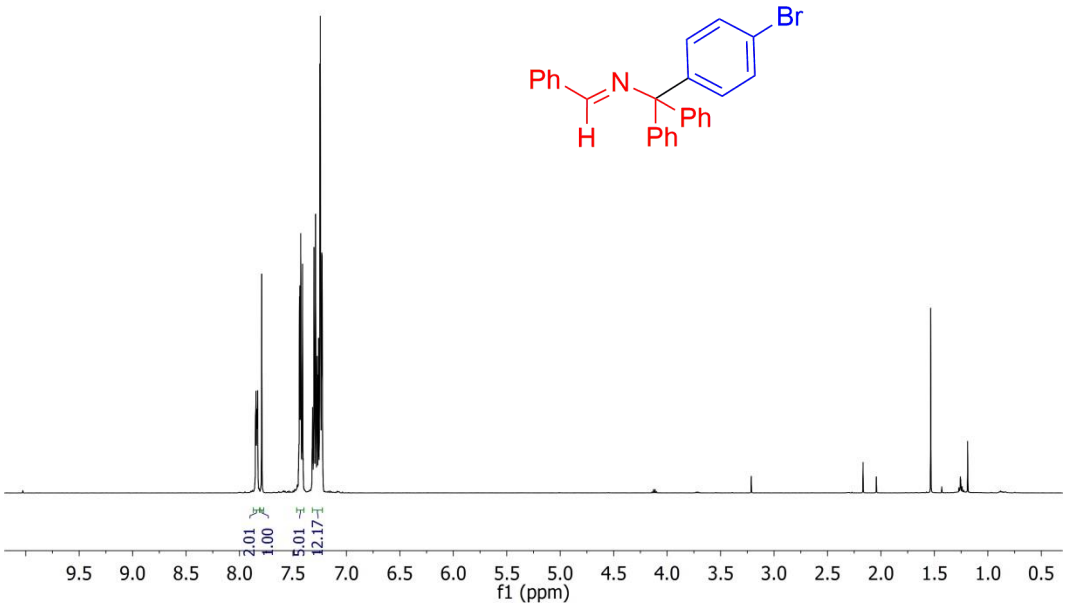
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(4-Bromophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine (4ad):



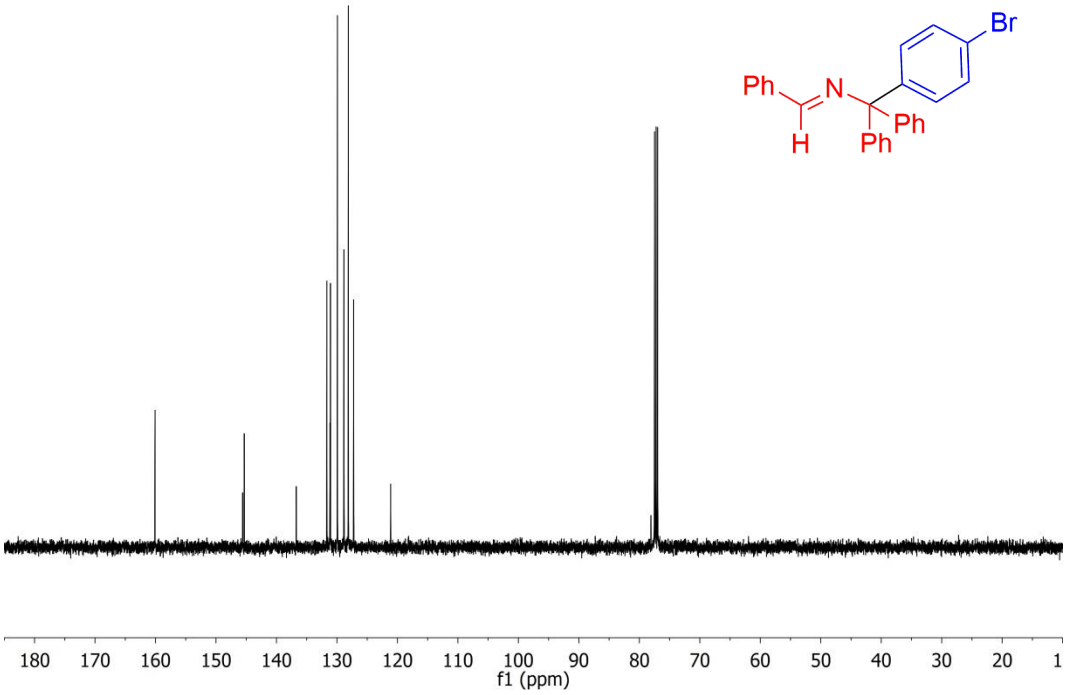
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(4-Bromophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine (4ad):



^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(4-bromophenyl)-1,1-diphenylmethanamine (4ad'):



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1-(4-bromophenyl)-1,1-diphenylmethanamine (4ad'):



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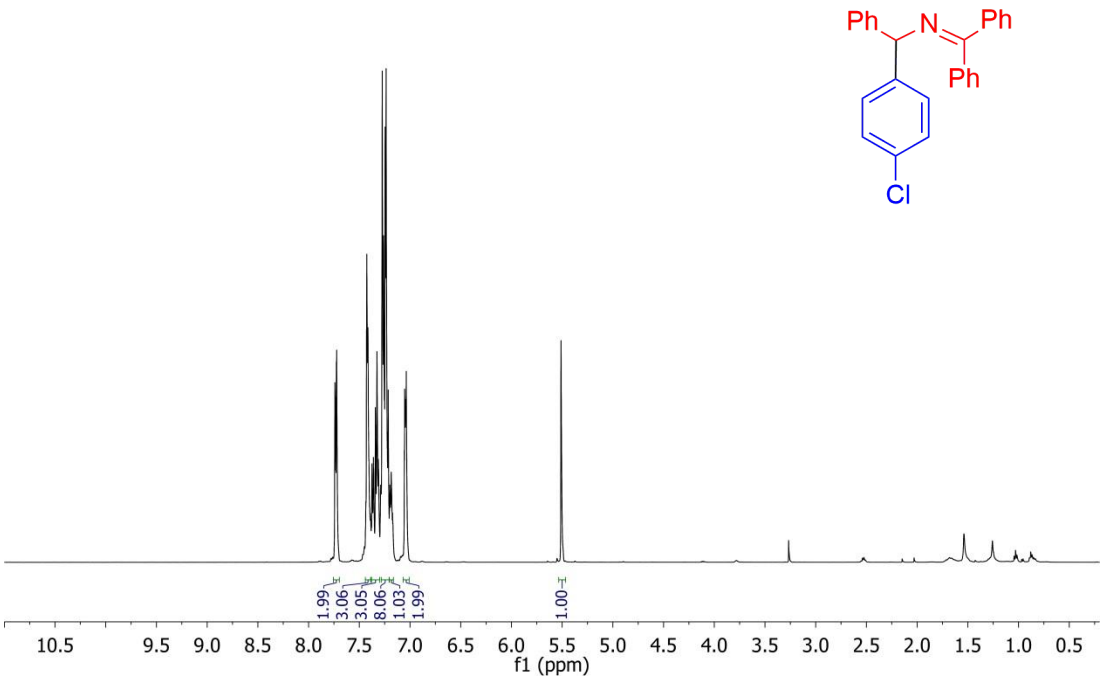

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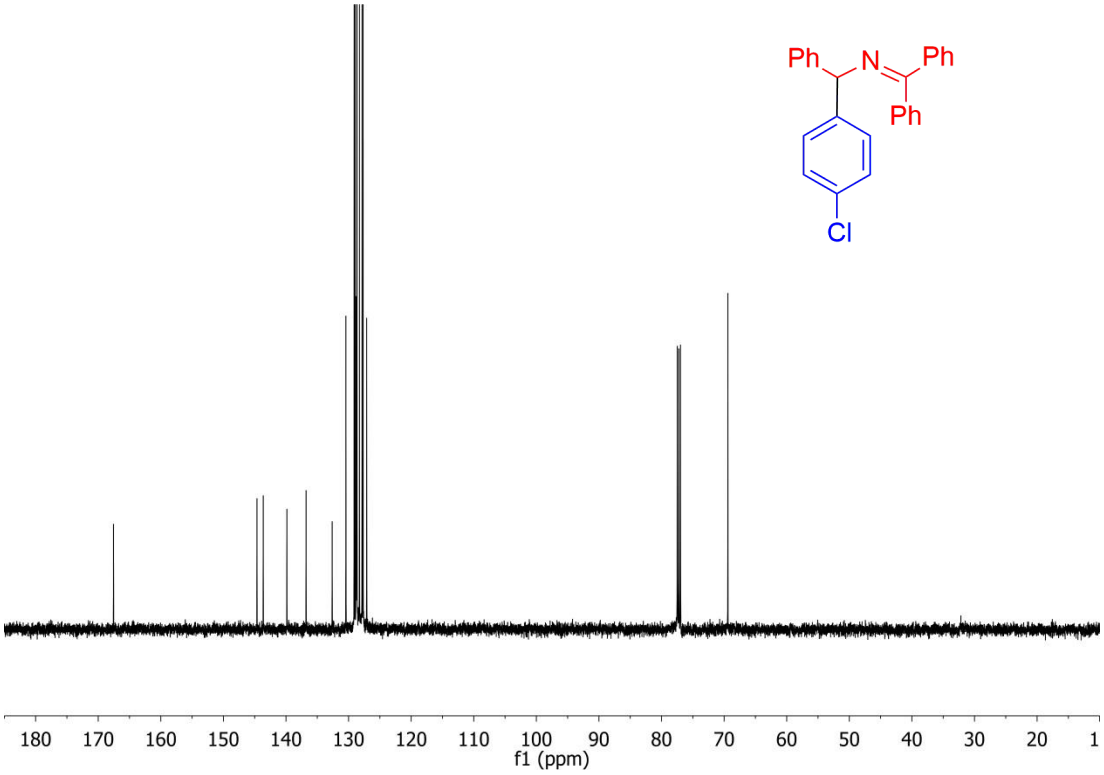
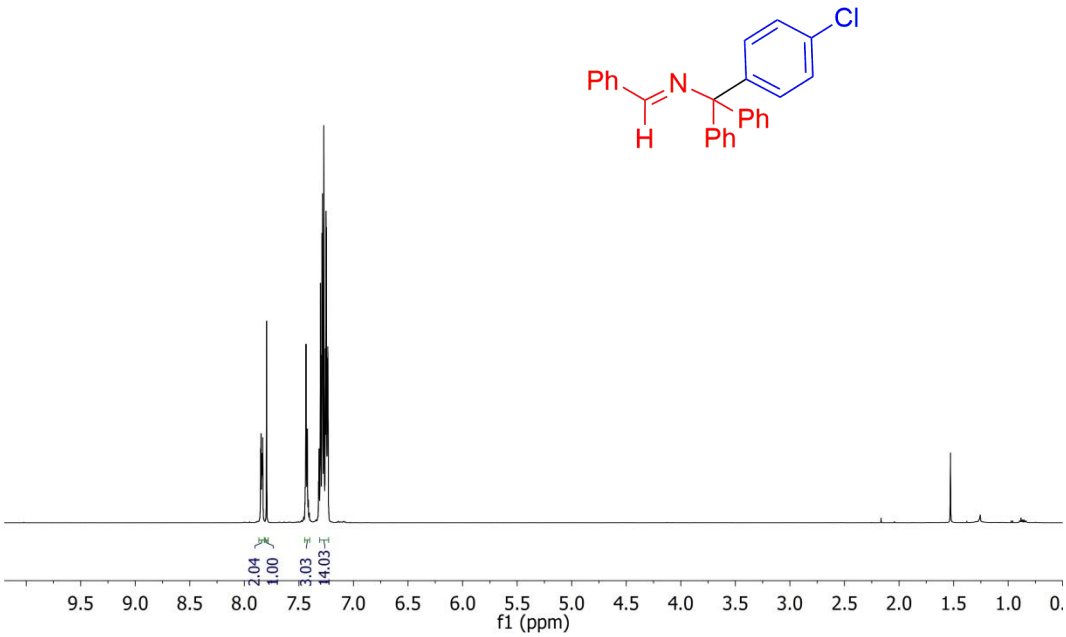


^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(4-chlorophenyl)-1,1-diphenylmethanamine (4ae')



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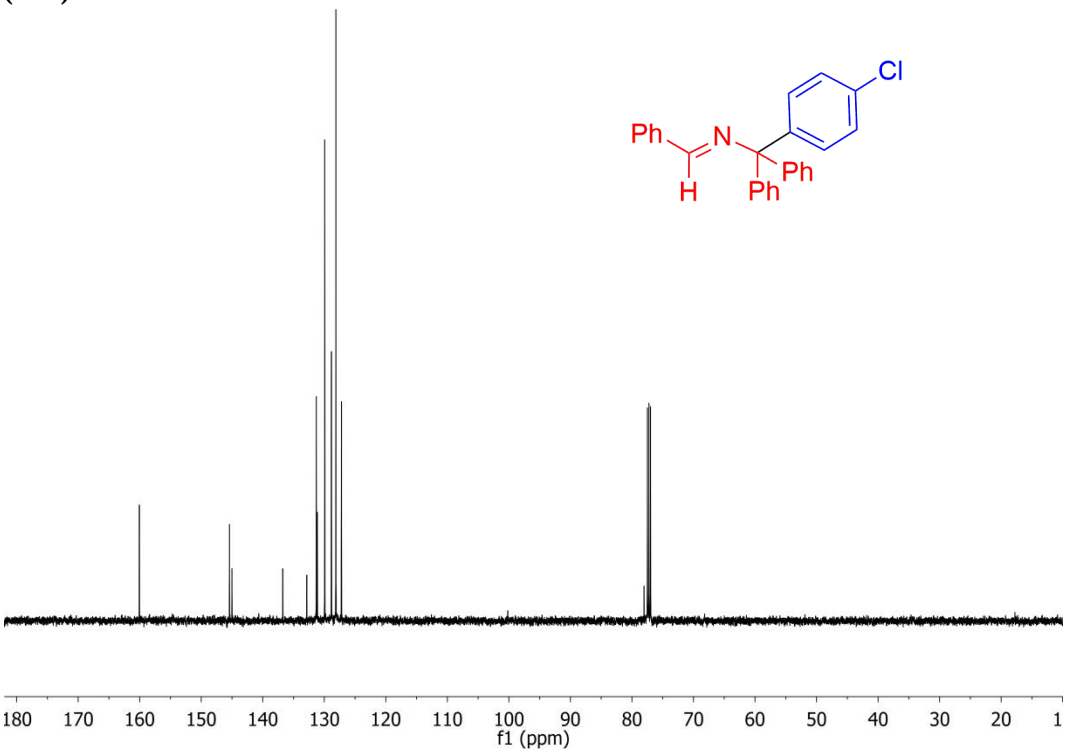

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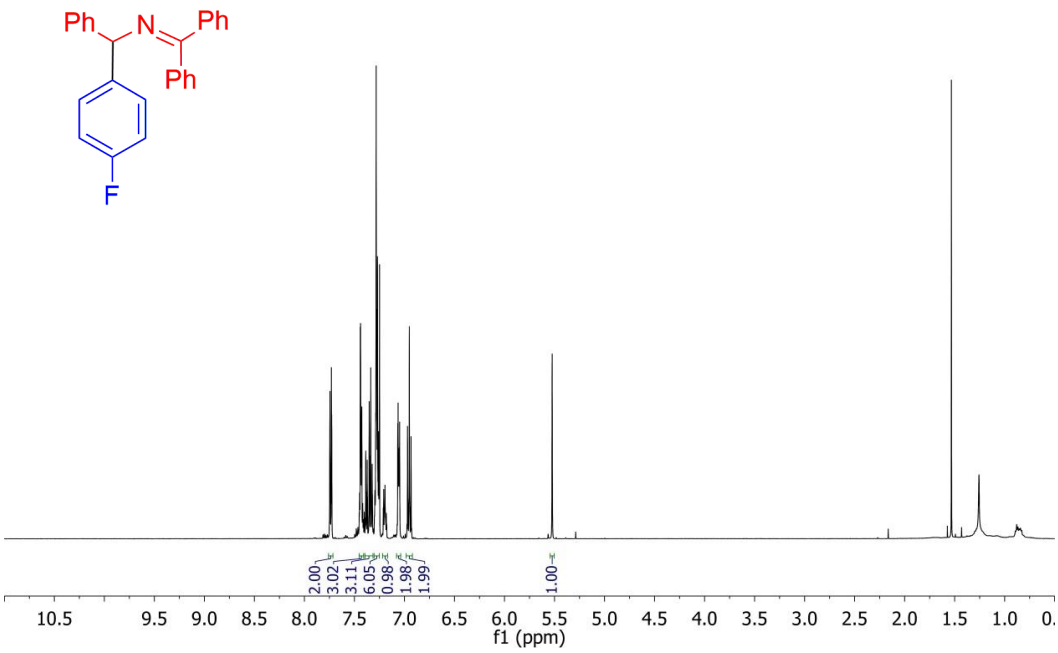

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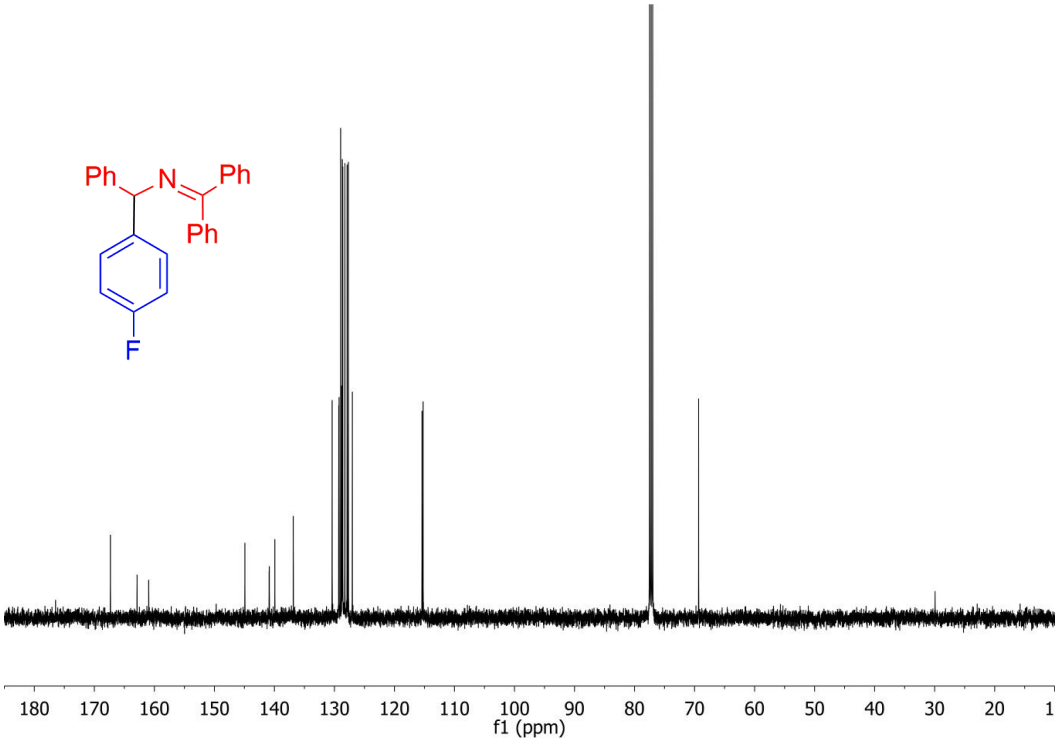

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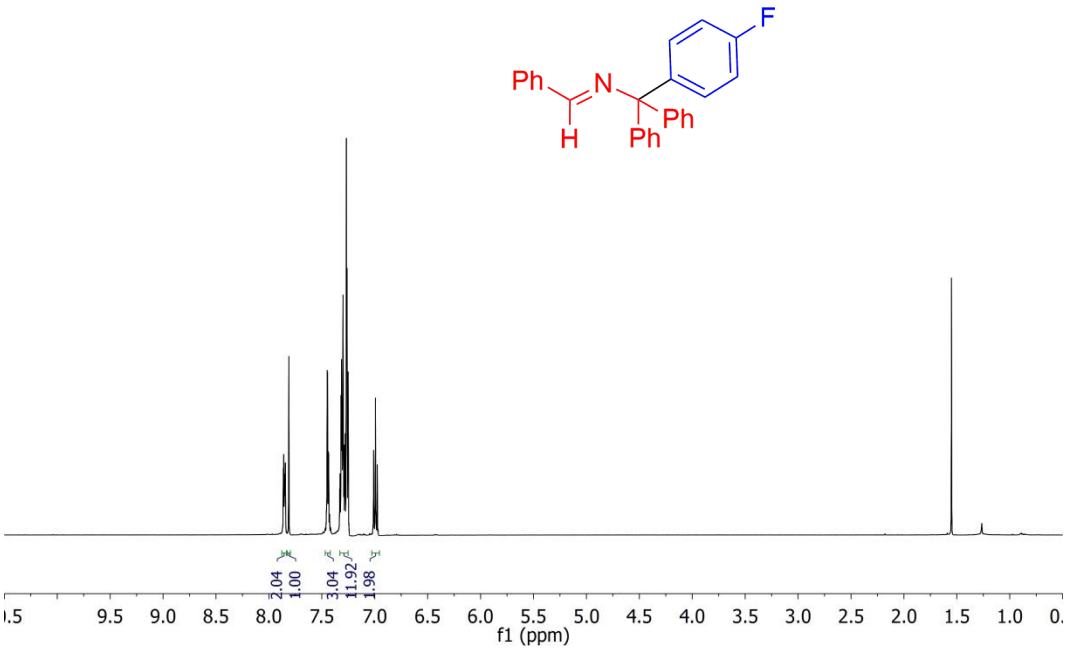

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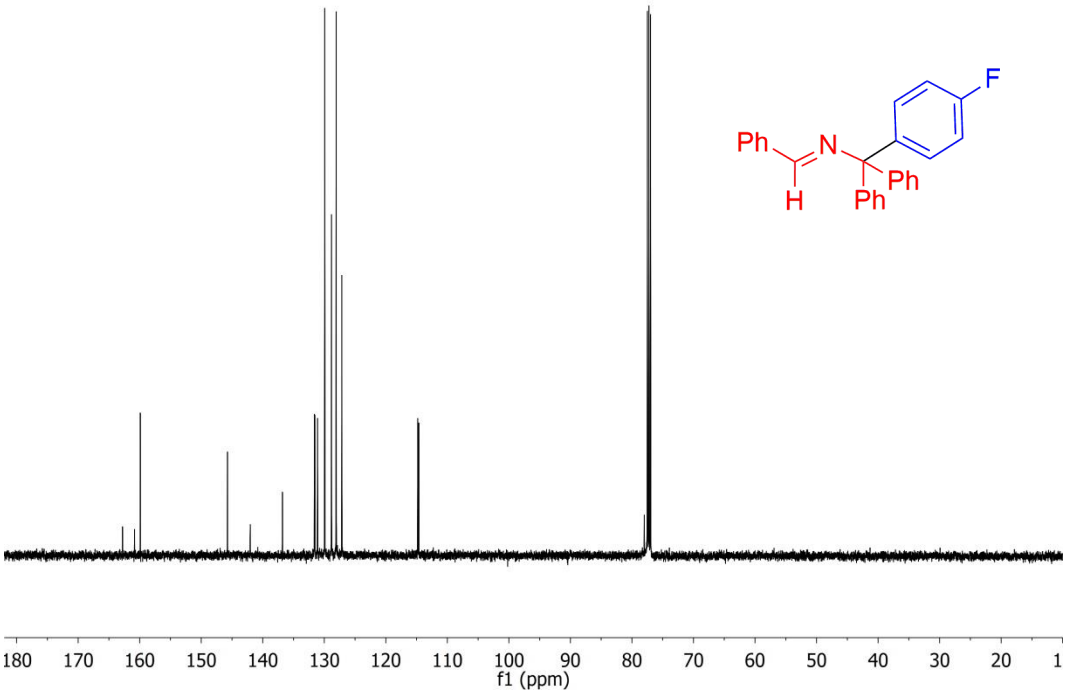
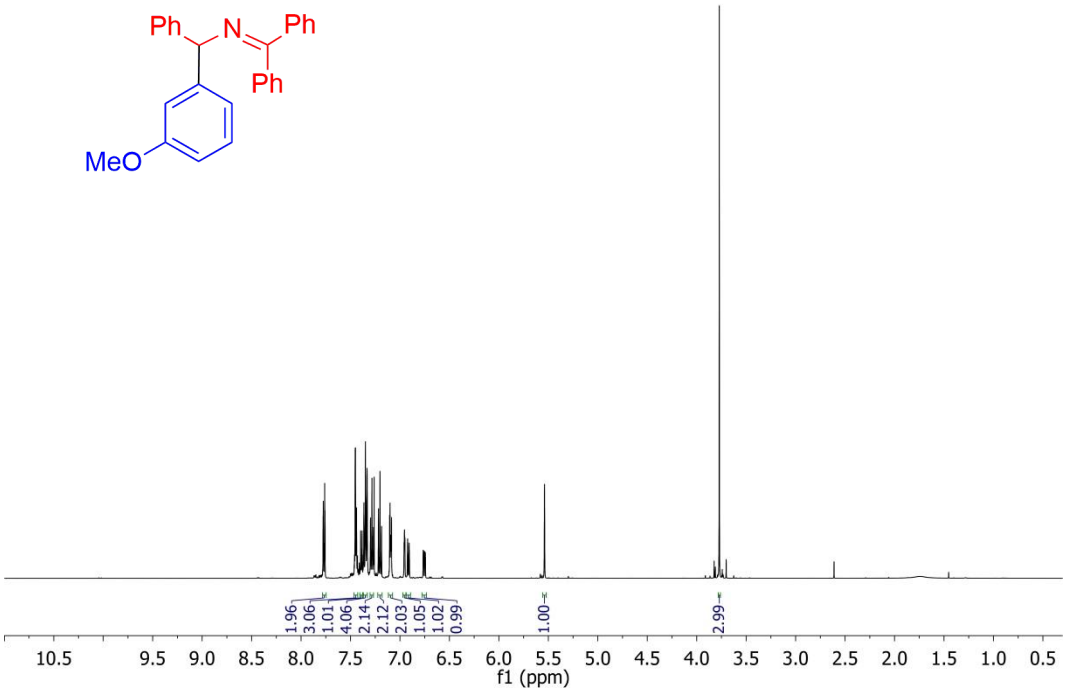
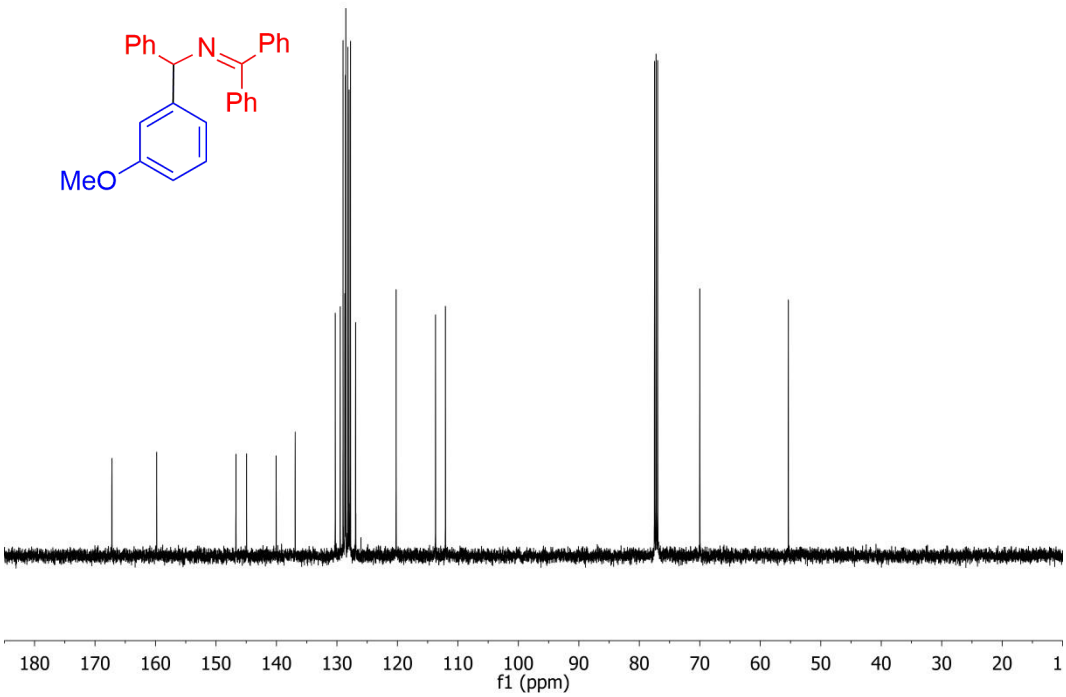


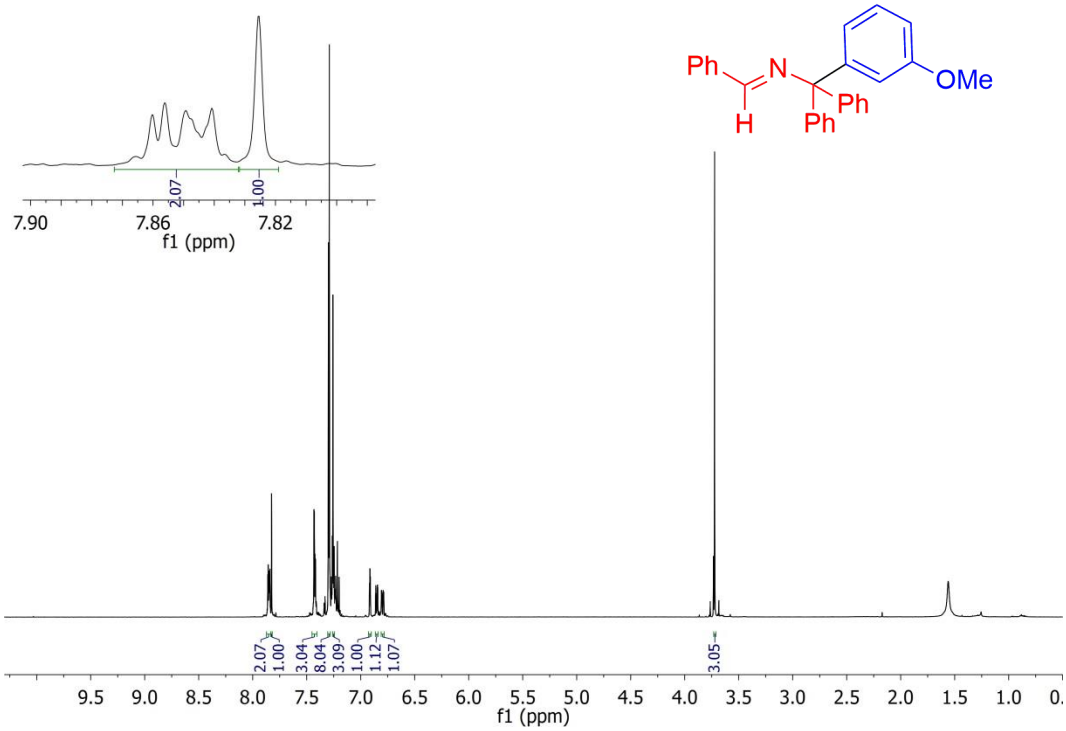
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-1-(3-methoxyphenyl)-1-phenylmethanamine (4ag):



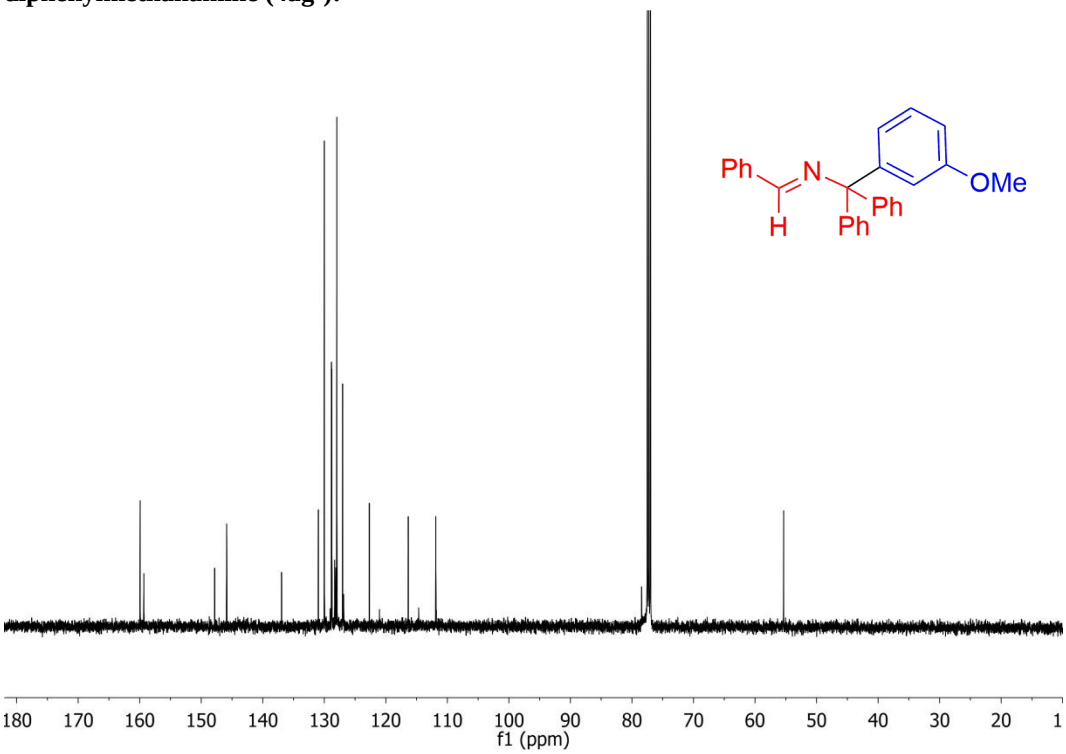
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-1-(3-methoxyphenyl)-1-phenylmethanamine (4ag):



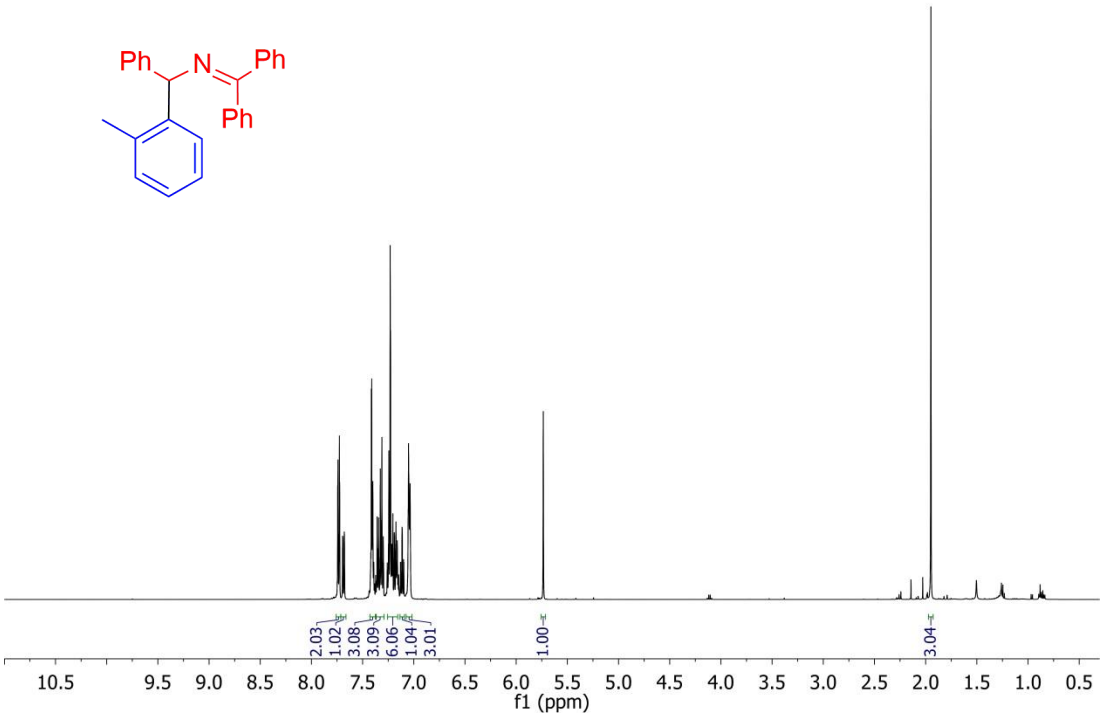
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(3-methoxyphenyl)-1,1-diphenylmethanamine (4ag'):



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1-(3-methoxyphenyl)-1,1-diphenylmethanamine (4ag'):



^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-1-phenyl-1-(*o*-tolyl)methanamine (4ah):



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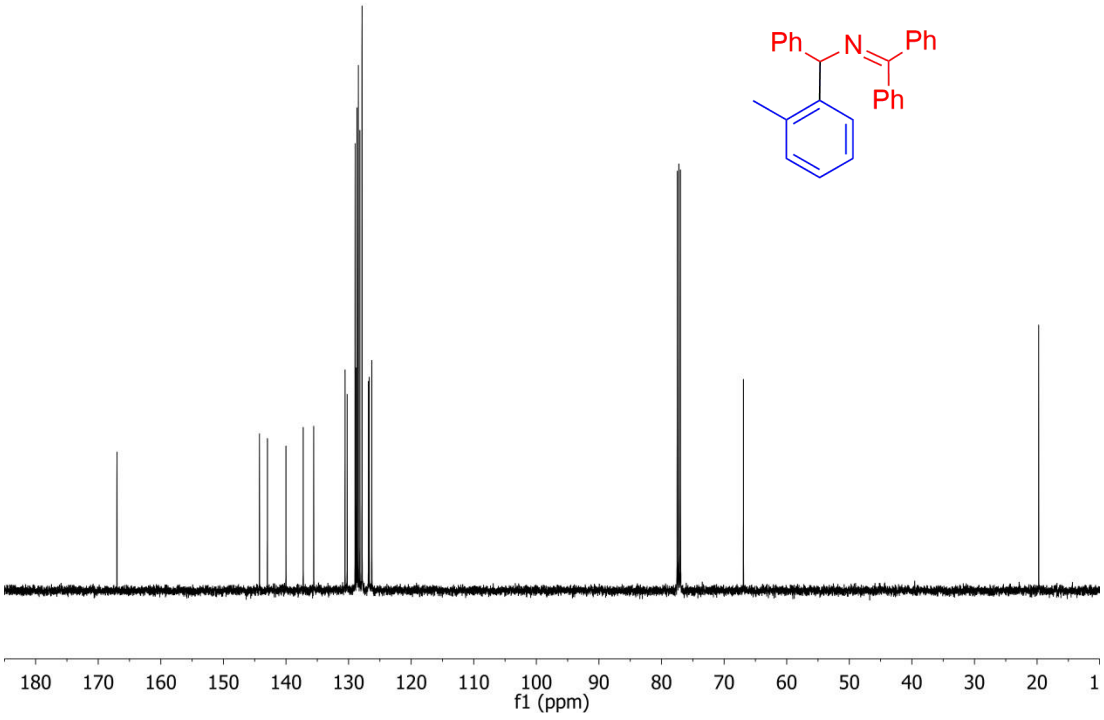

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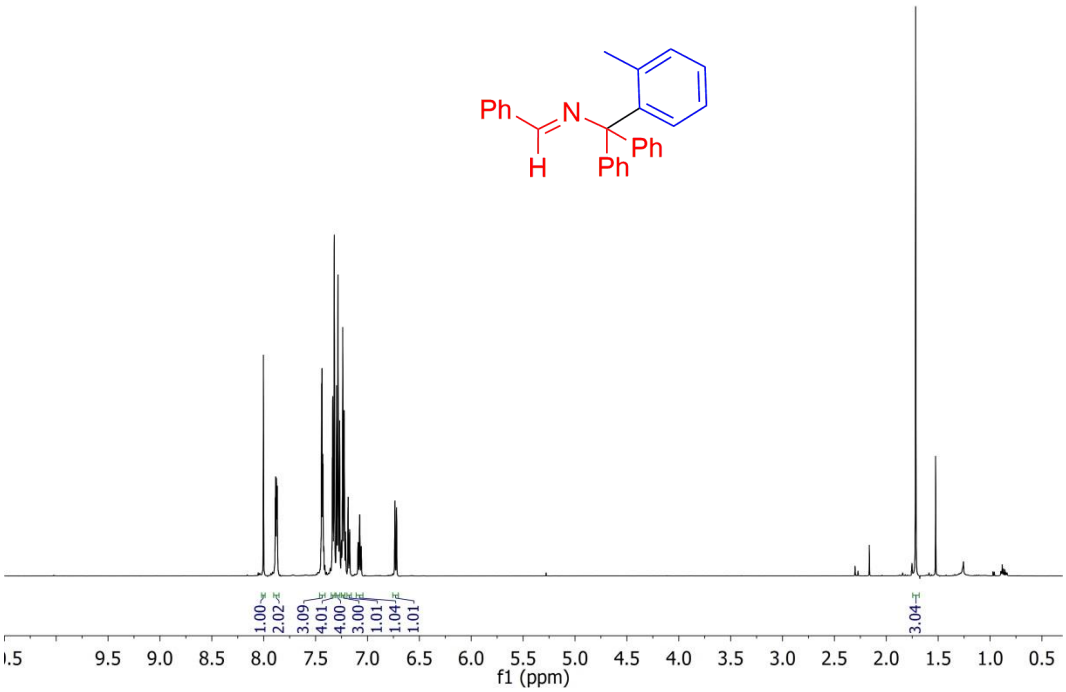
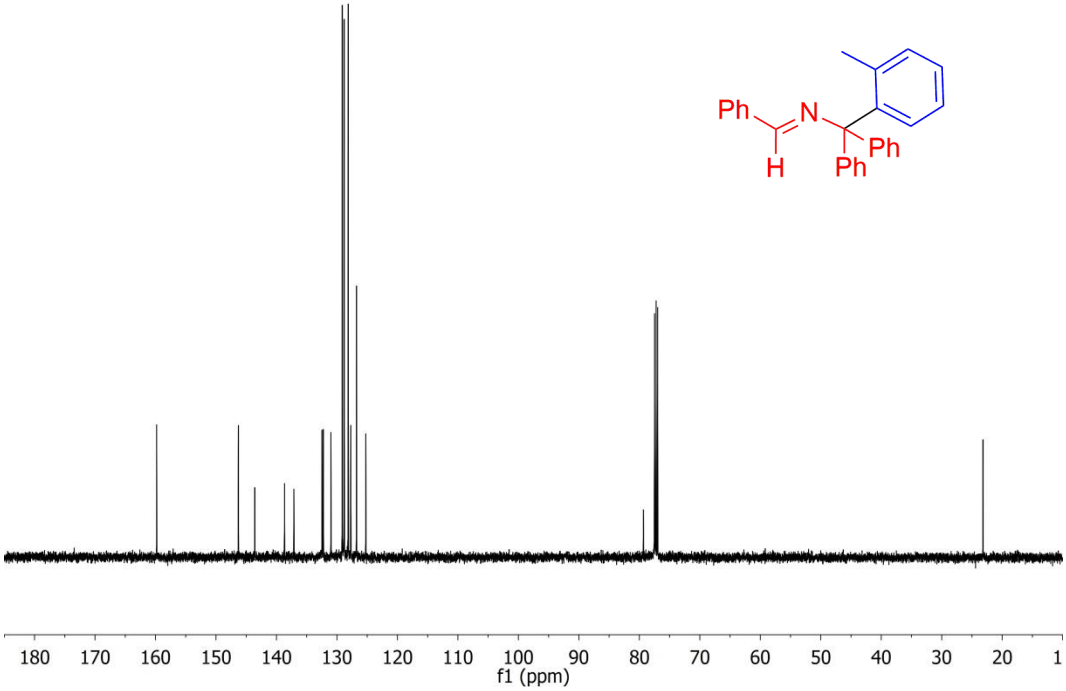


^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1,1-diphenyl-1-(o-tolyl)methanamine (4ah')



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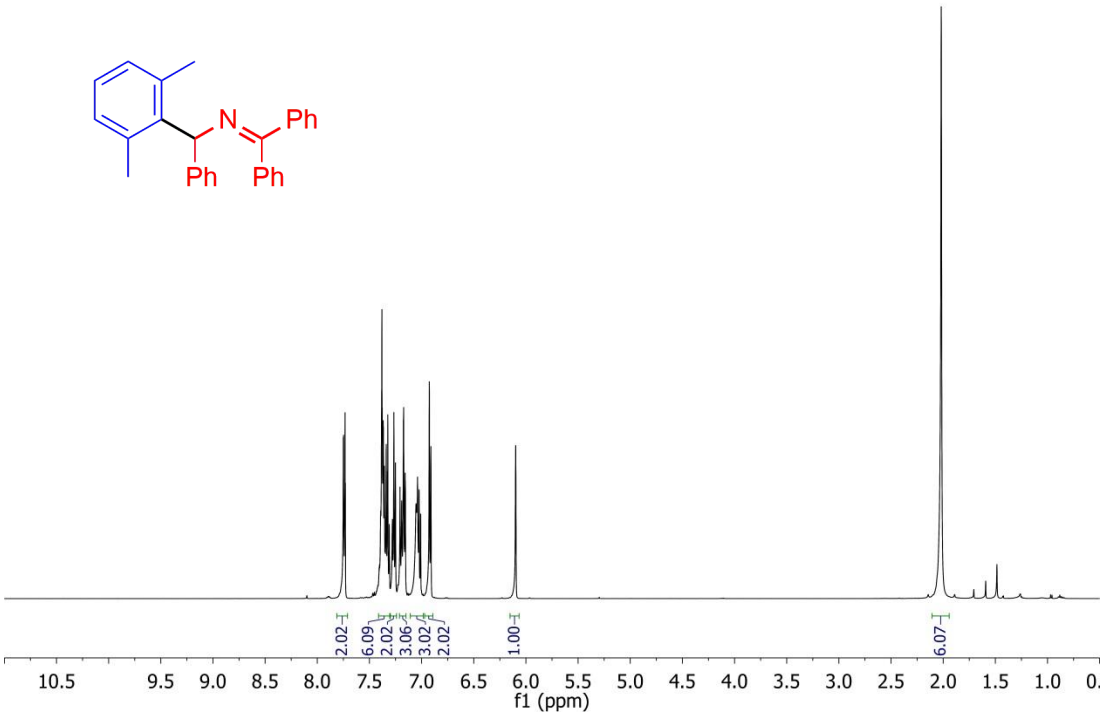

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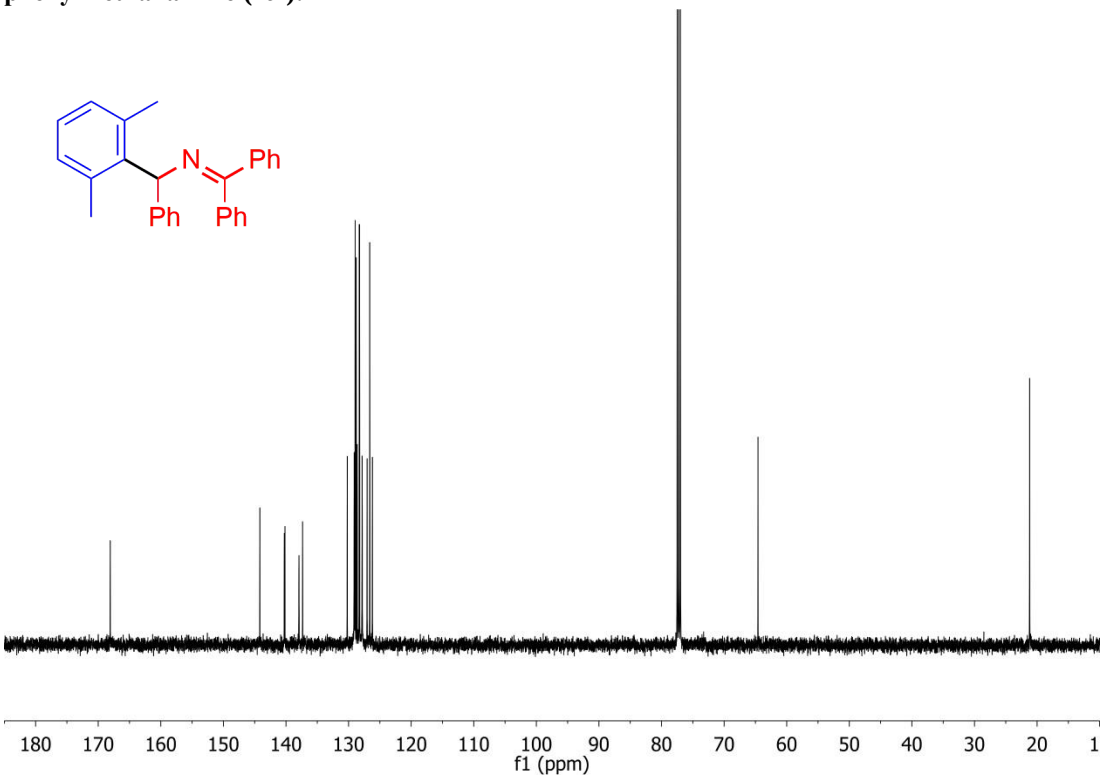
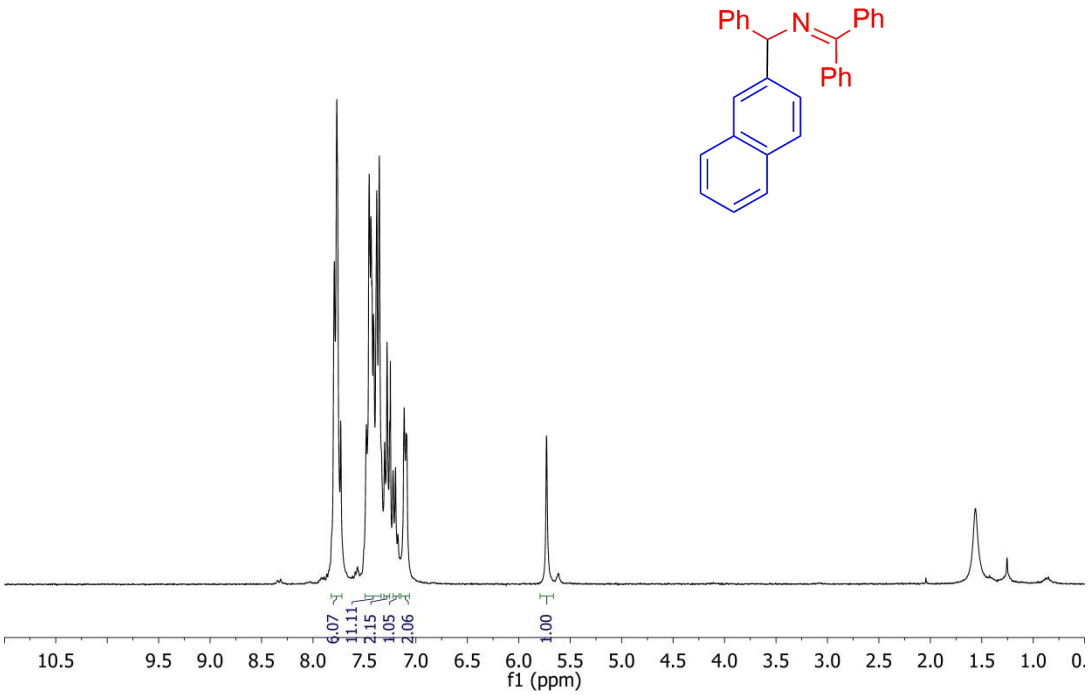


^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-1-(naphthalen-2-yl)-1-phenylmethanamine (4aj):



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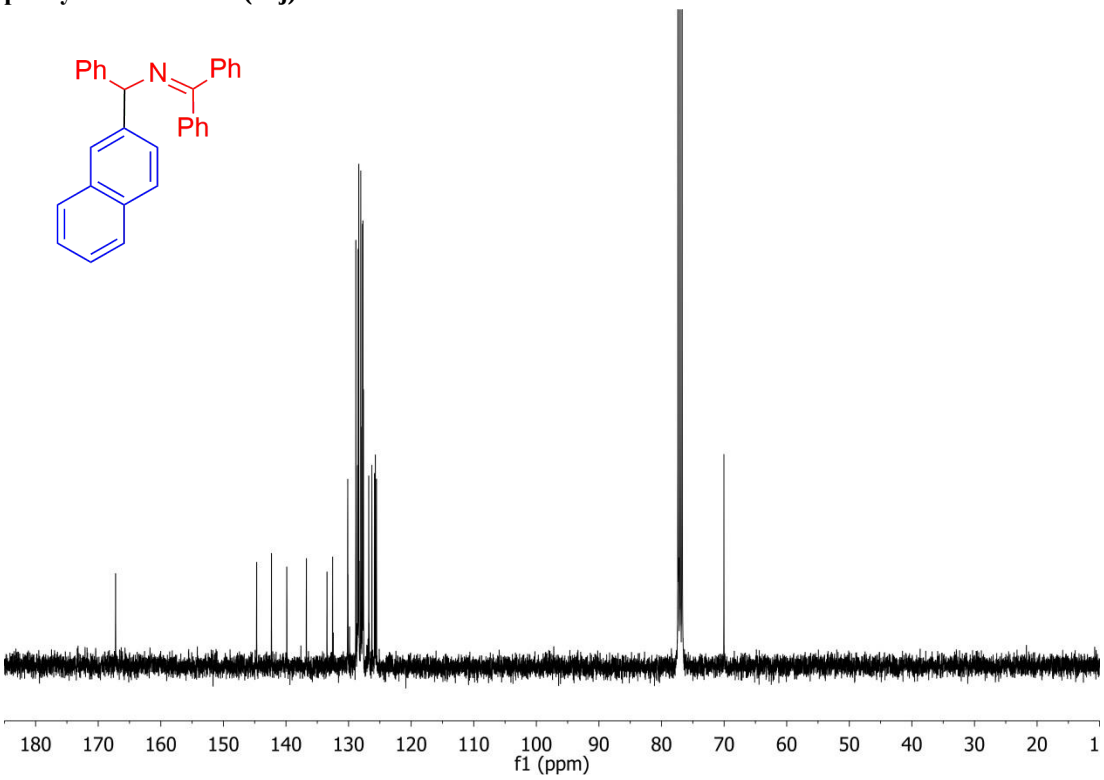
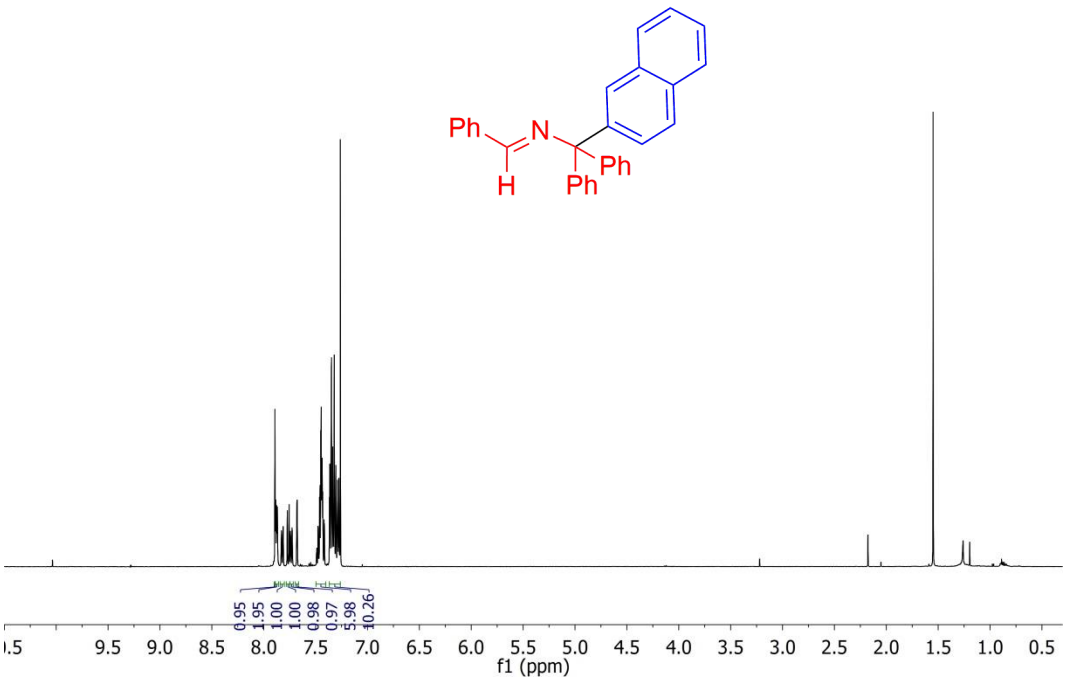
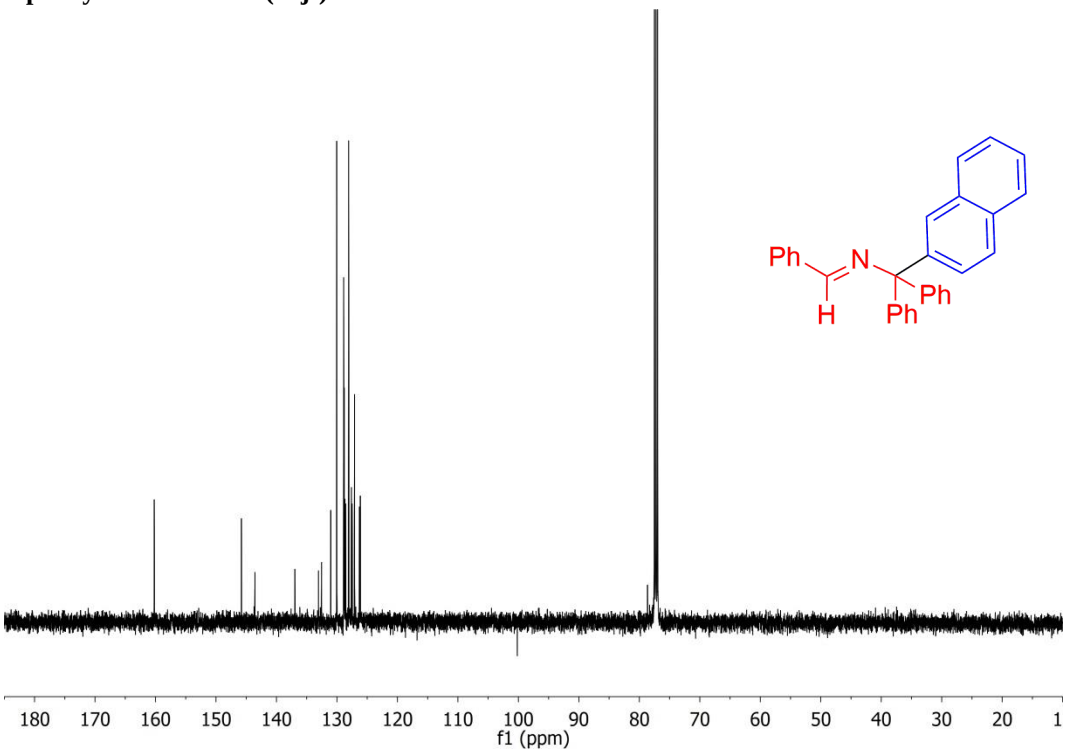


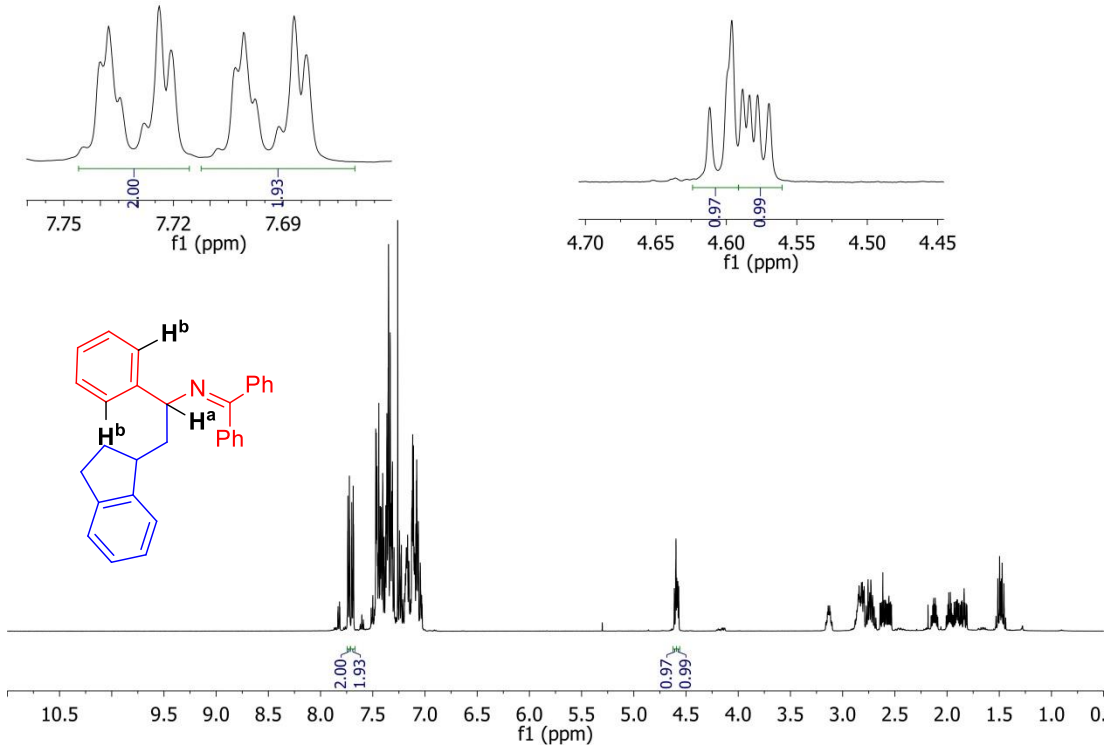
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-Benzylidene-1-(naphthalen-2-yl)-1,1-diphenylmethanamine (4aj'):



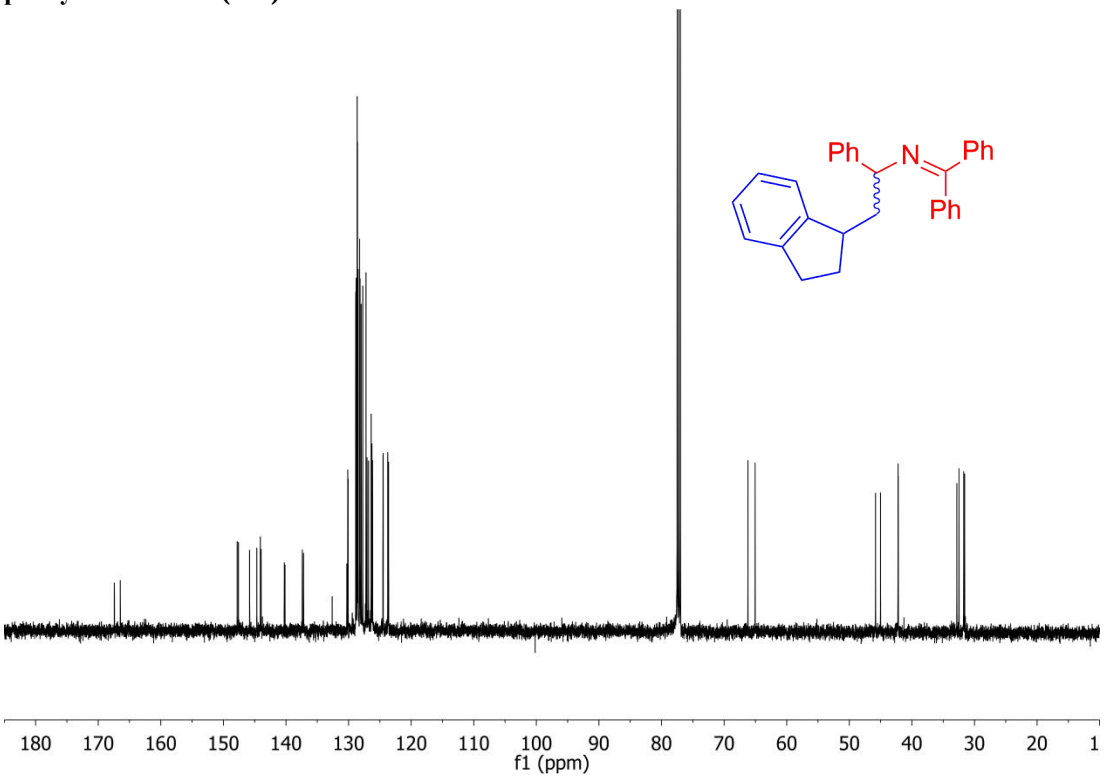
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-Benzylidene-1-(naphthalen-2-yl)-1,1-diphenylmethanamine (4aj'):



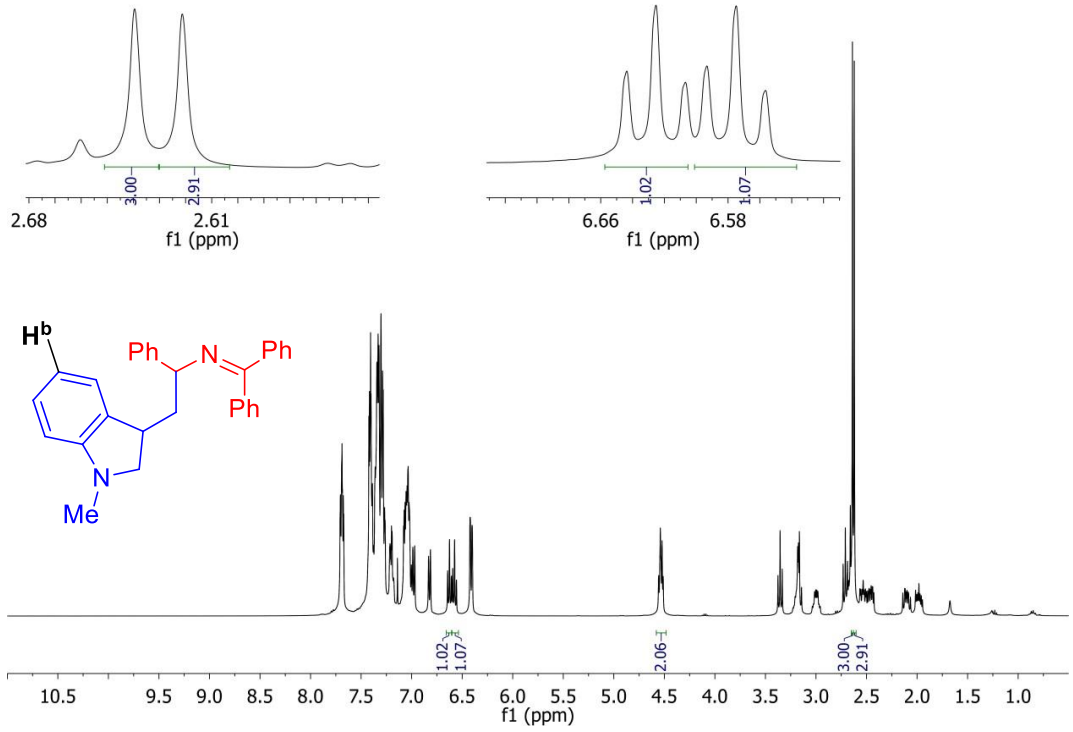
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(2,3-Dihydro-1H-inden-1-yl)-*N*-(diphenylmethylene)-1-phenylethanamine (4ak):



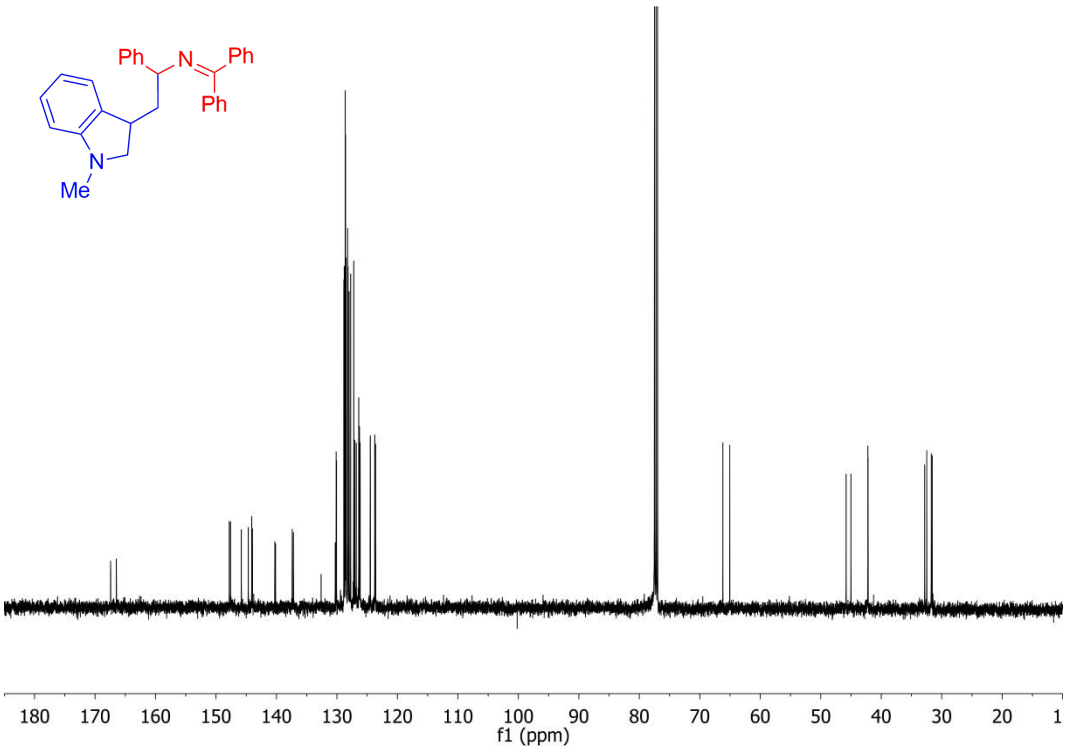
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(2,3-Dihydro-1H-inden-1-yl)-*N*-(diphenylmethylene)-1-phenylethanamine (4ak)



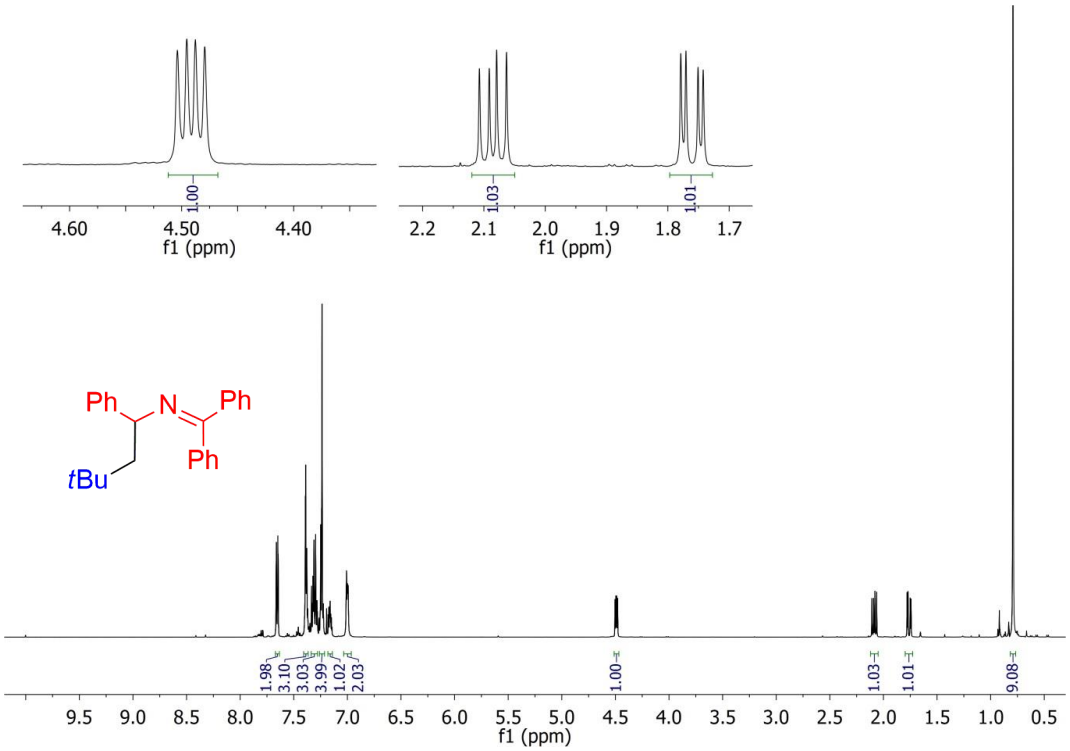
^{1}H NMR spectra ($CDCl_3$, 400 MHz) of *N*-(Diphenylmethylene)-2-(1-methylindolin-3-yl)-1-phenylethanamine (4al):



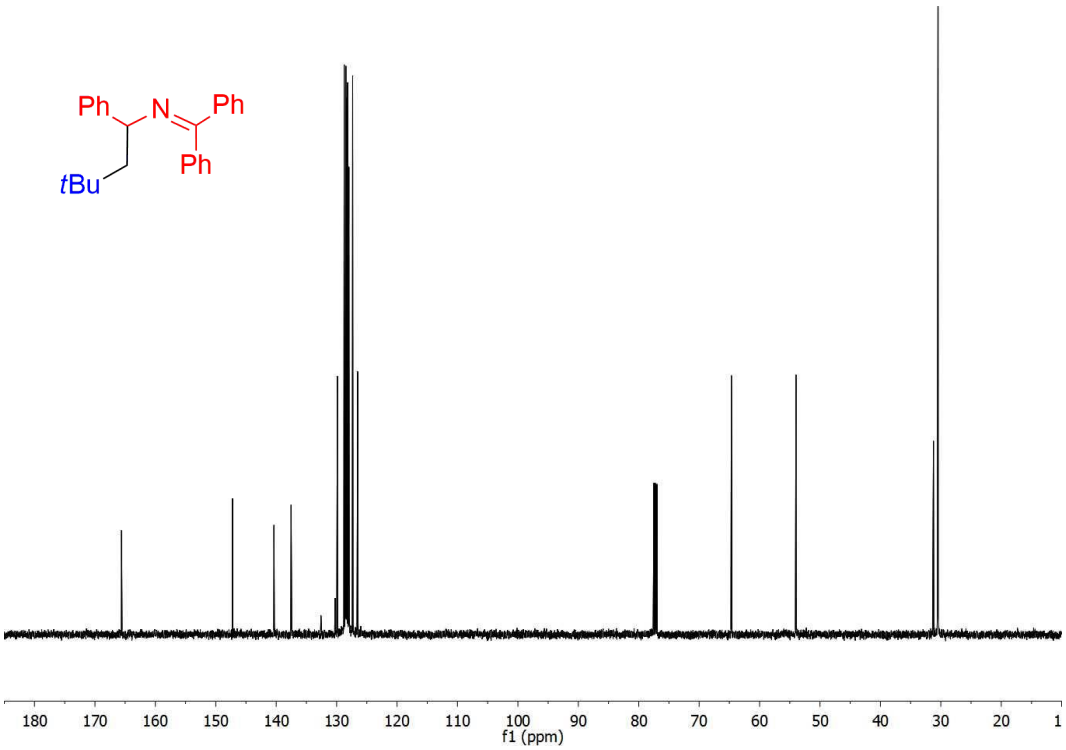
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 100 MHz) of *N*-(Diphenylmethylene)-2-(1-methylindolin-3-yl)-1-phenylethanamine (4al):



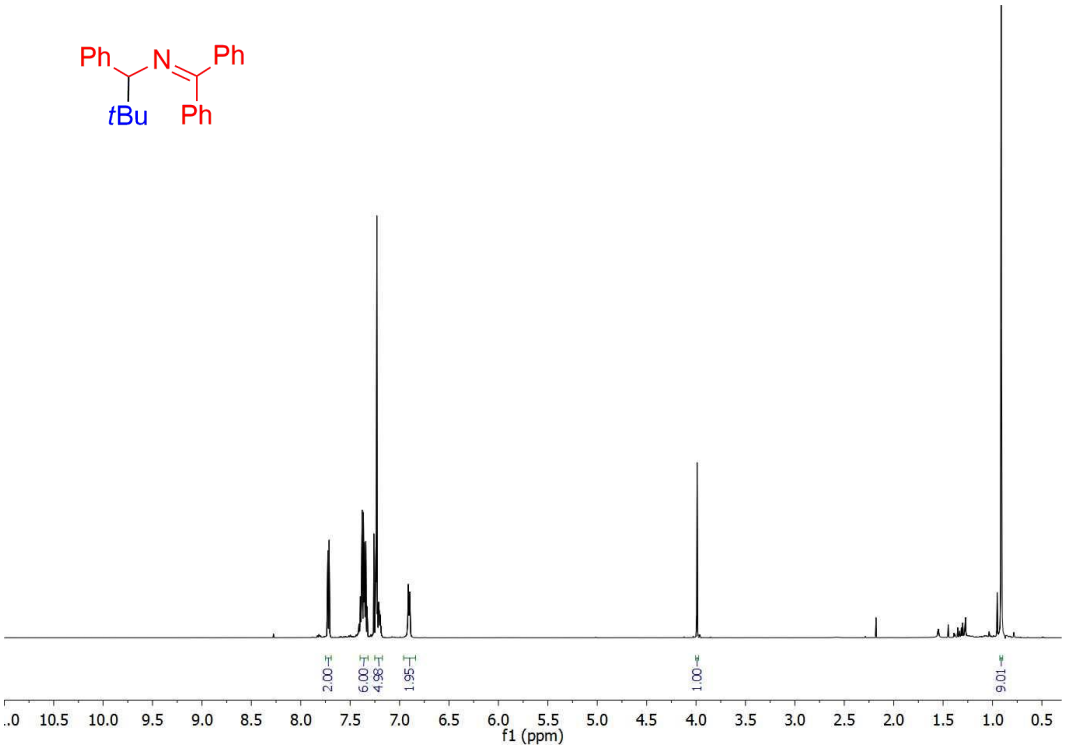
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-3,3-dimethyl-1-phenylbutan-1-amine (5aa):



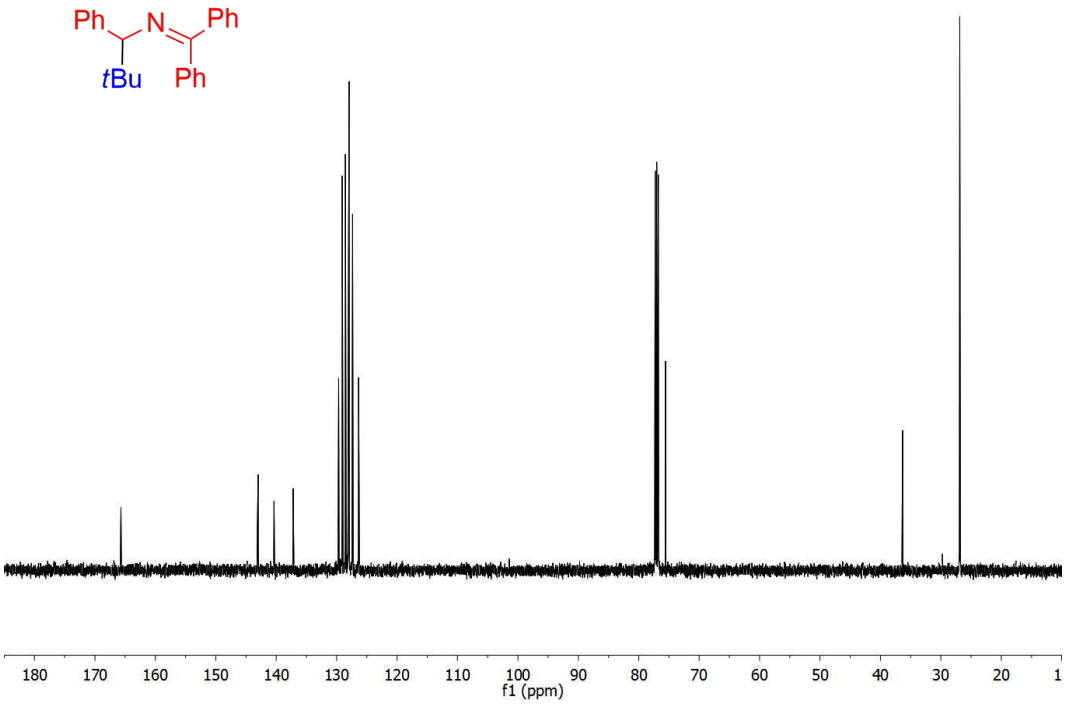
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-3,3-dimethyl-1-phenylbutan-1-amine (5aa):



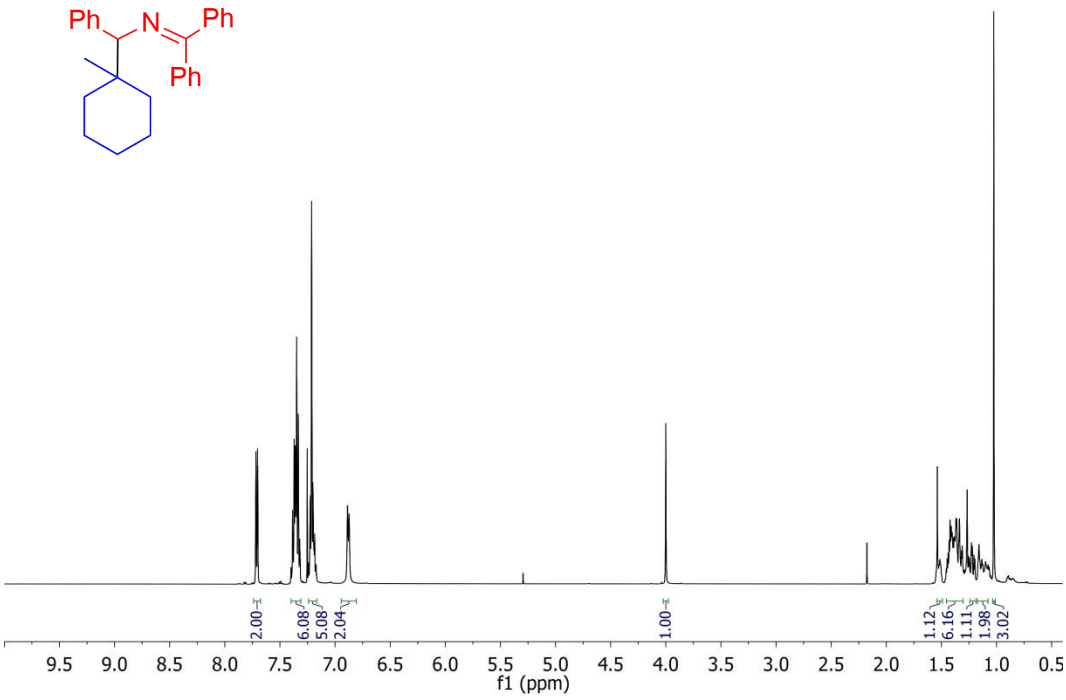
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-2,2-dimethyl-1-phenylpropan-1-amine (5ab):



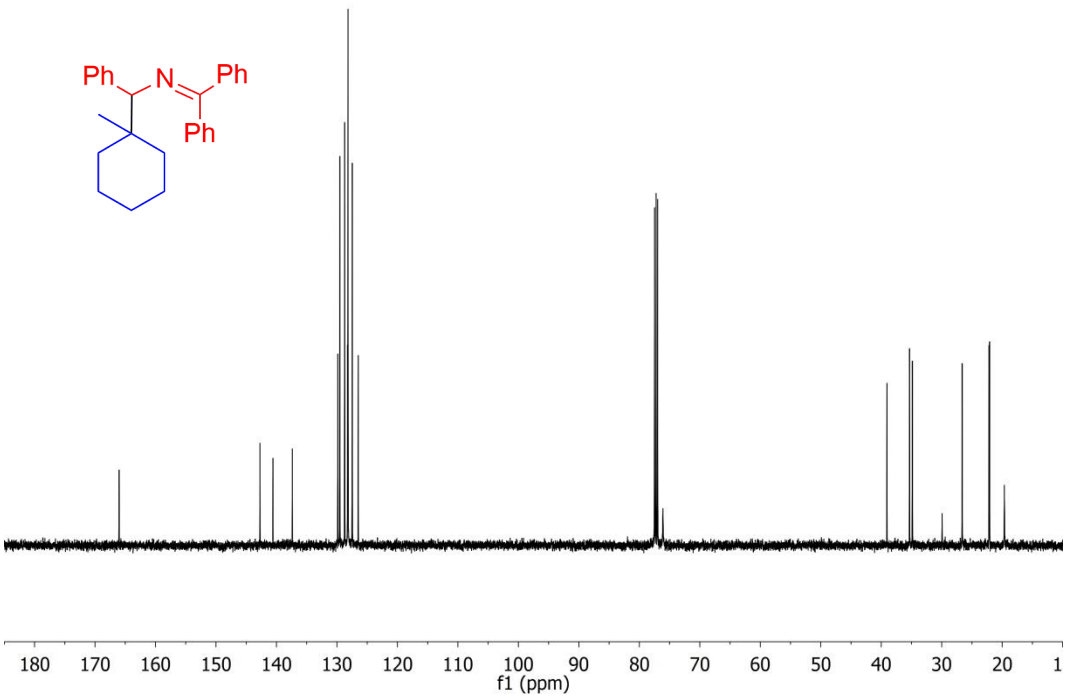
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-2,2-dimethyl-1-phenylpropan-1-amine (5ab):



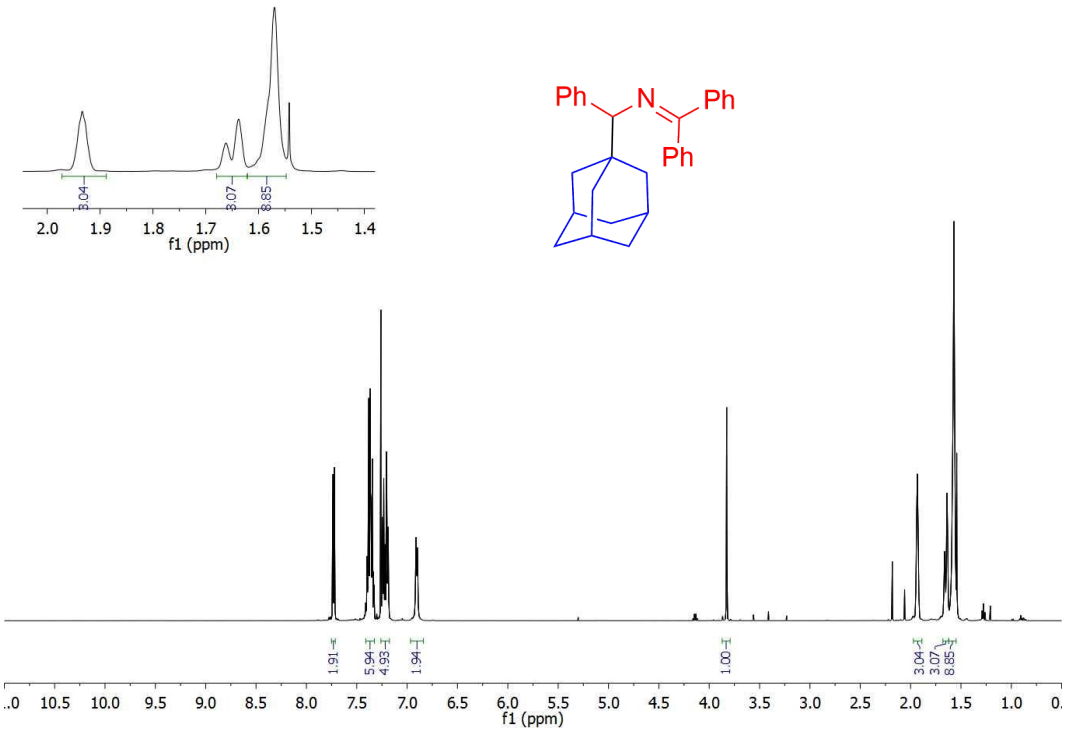
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of *N*-(Diphenylmethylene)-1-(1-methylcyclohexyl)-1-phenylmethanamine (5ac):



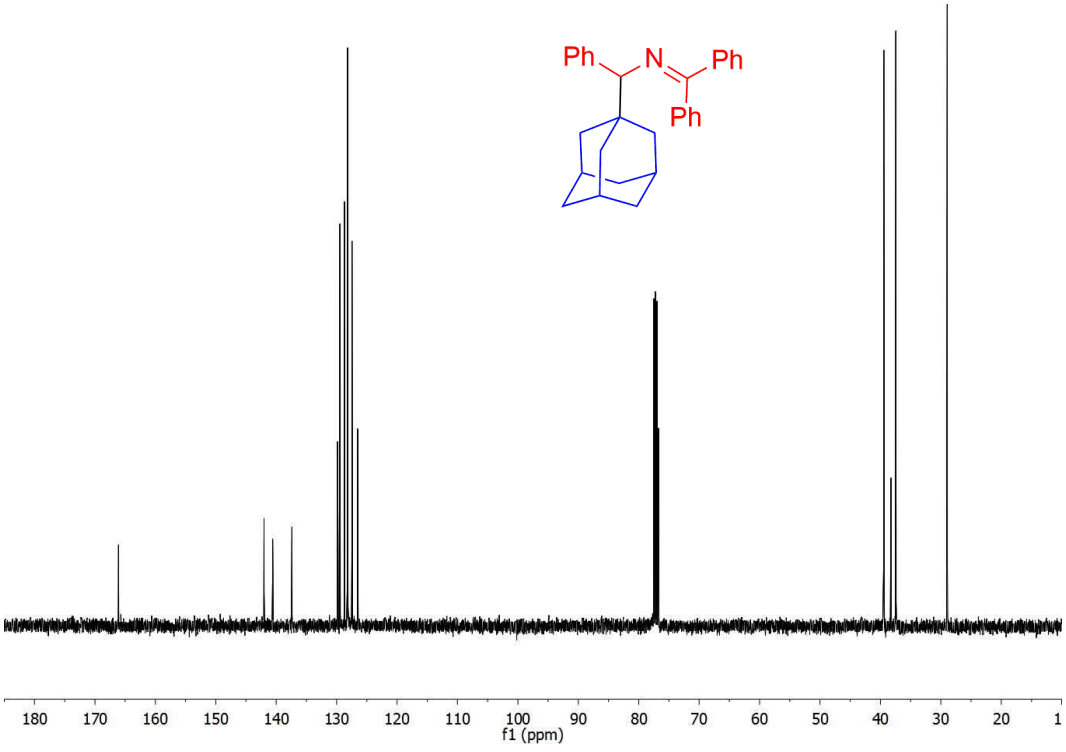
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of *N*-(Diphenylmethylene)-1-(1-methylcyclohexyl)-1-phenylmethanamine (5ac):



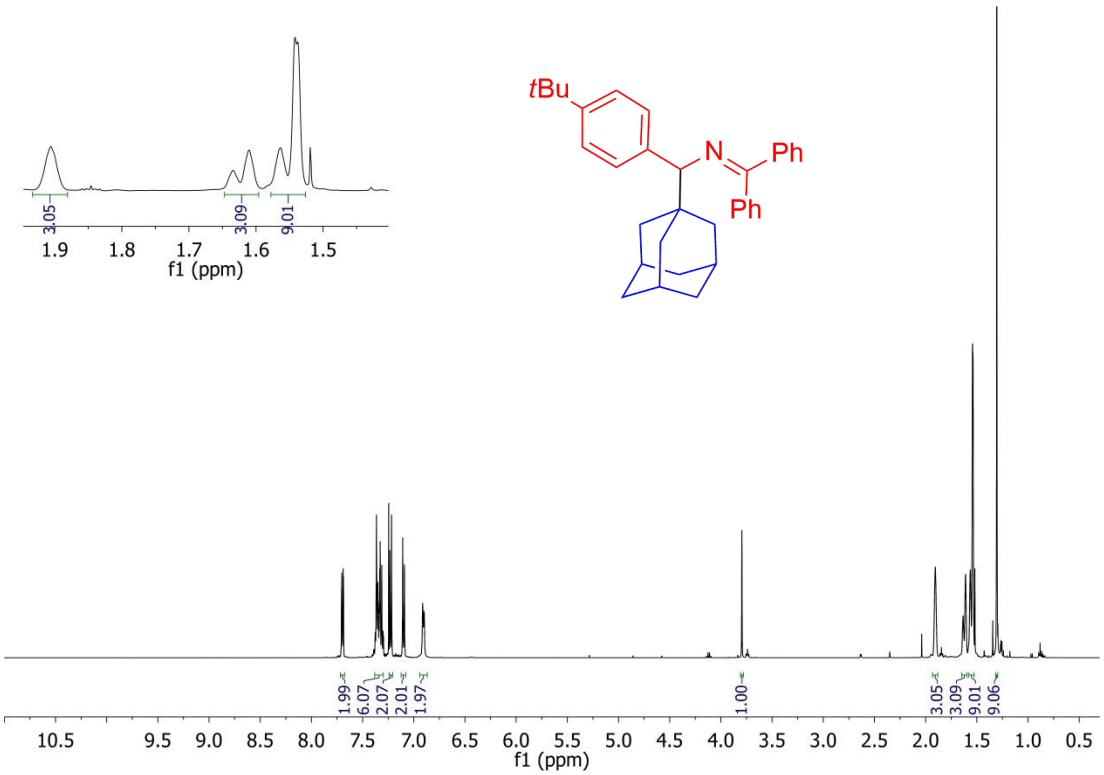
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-phenylmethanamine (5ae):



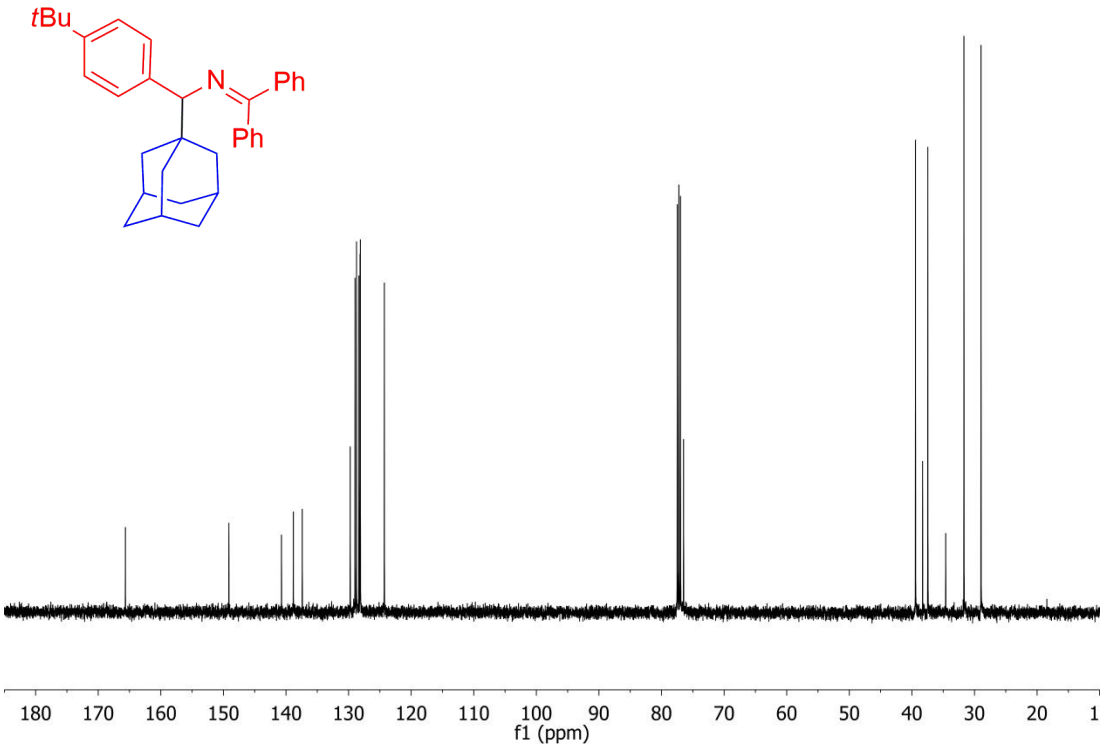
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-phenylmethanamine (5ae):



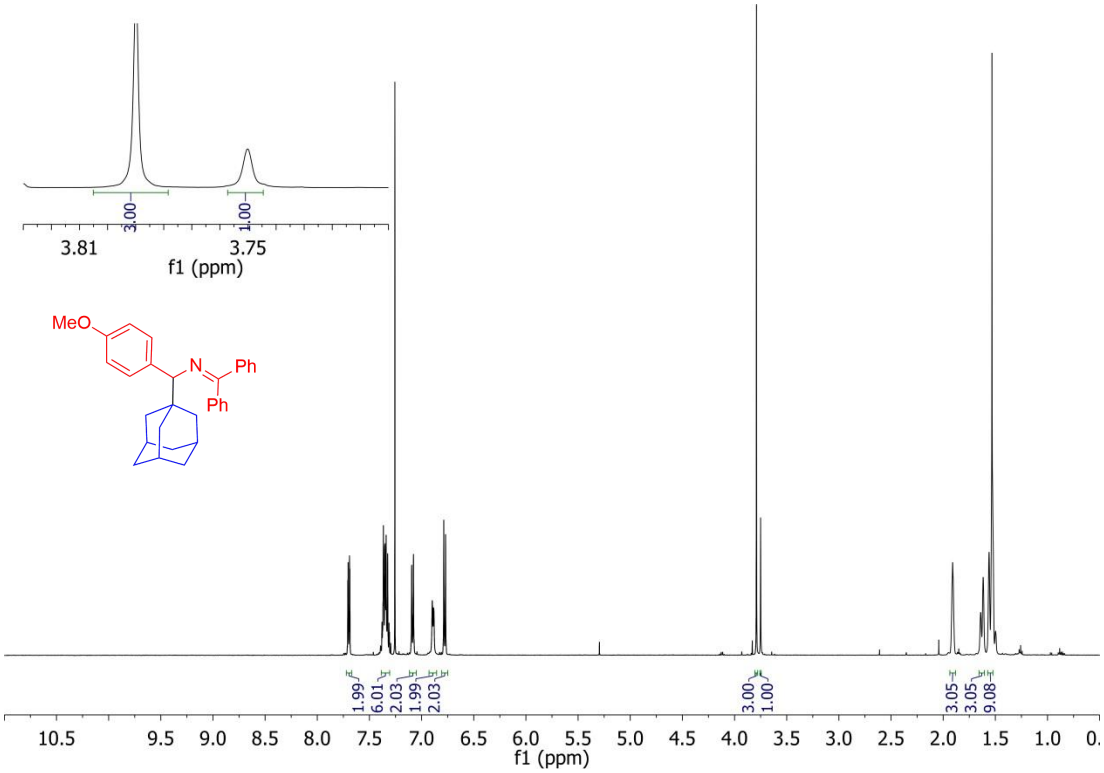
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-1-(4-(*tert*-butyl)phenyl)-*N*-(diphenylmethylene)methanamine (5be):



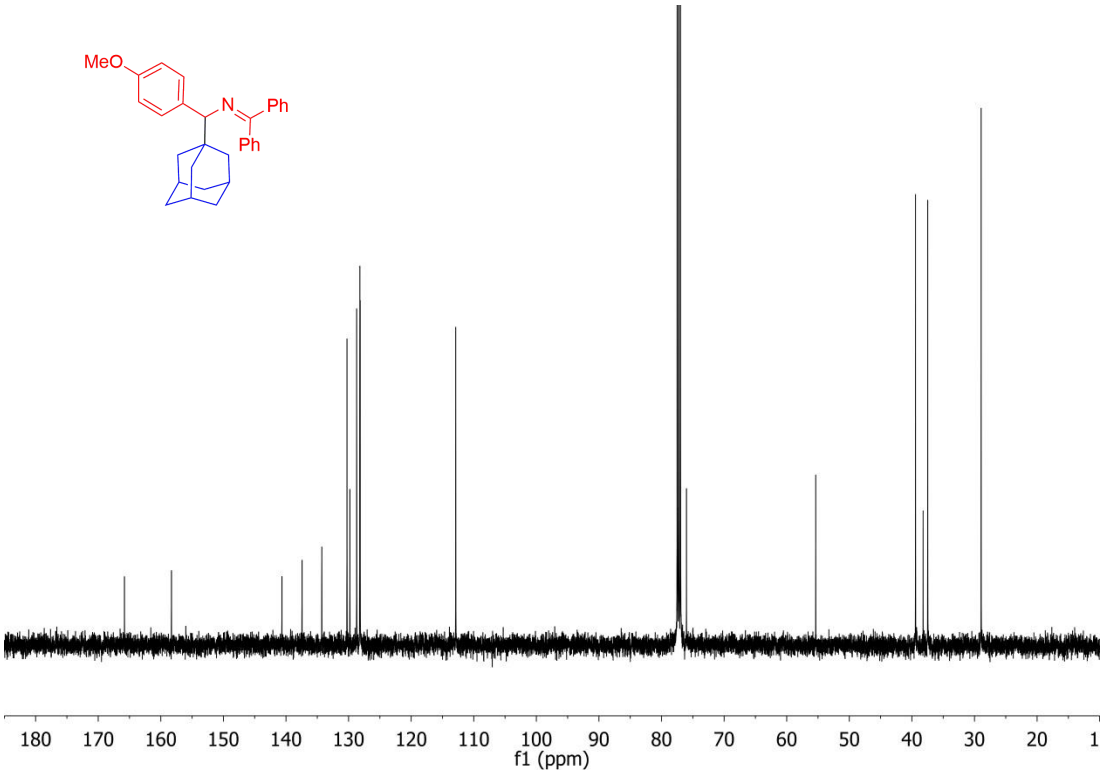
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-1-(4-(*tert*-butyl)phenyl)-*N*-(diphenylmethylene)methanamine (5be):



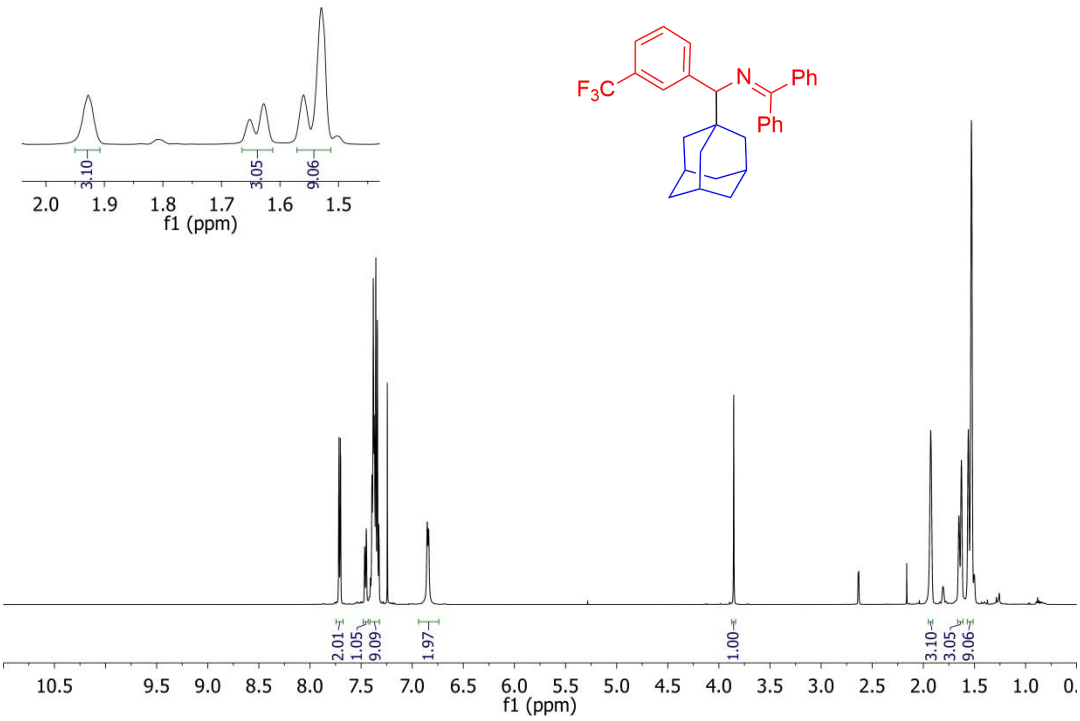
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(4-methoxyphenyl)methanamine (5ce):



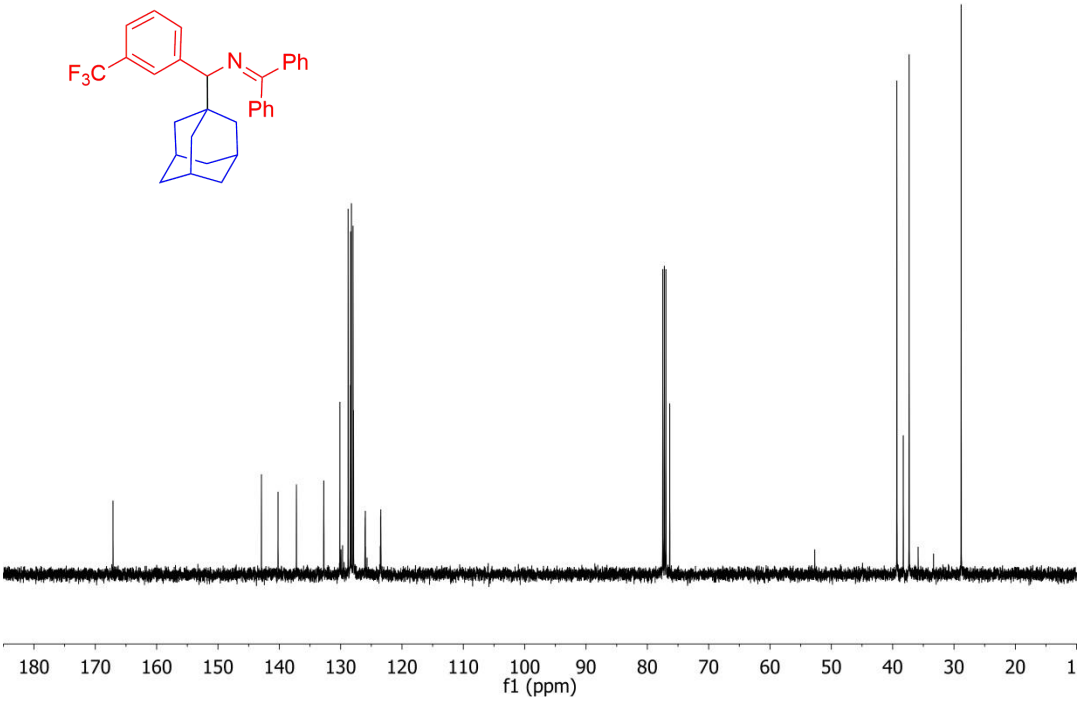
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(4-methoxyphenyl)methanamine (5ce):



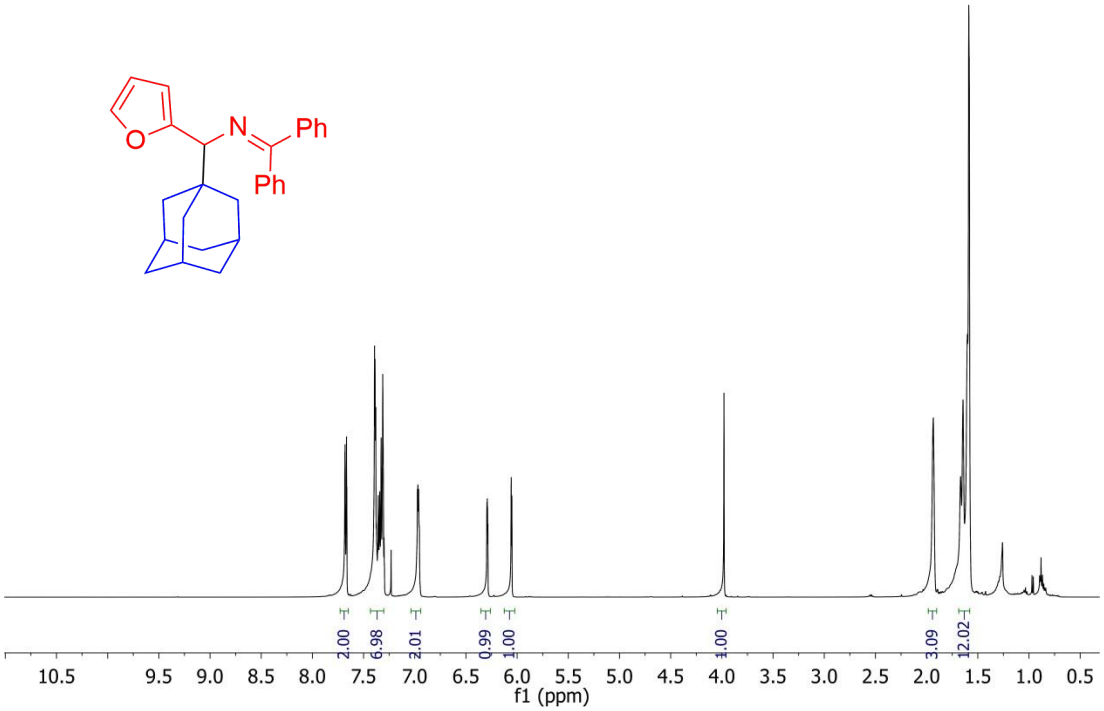
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(3-(trifluoromethyl)phenyl)methanamine (5de):



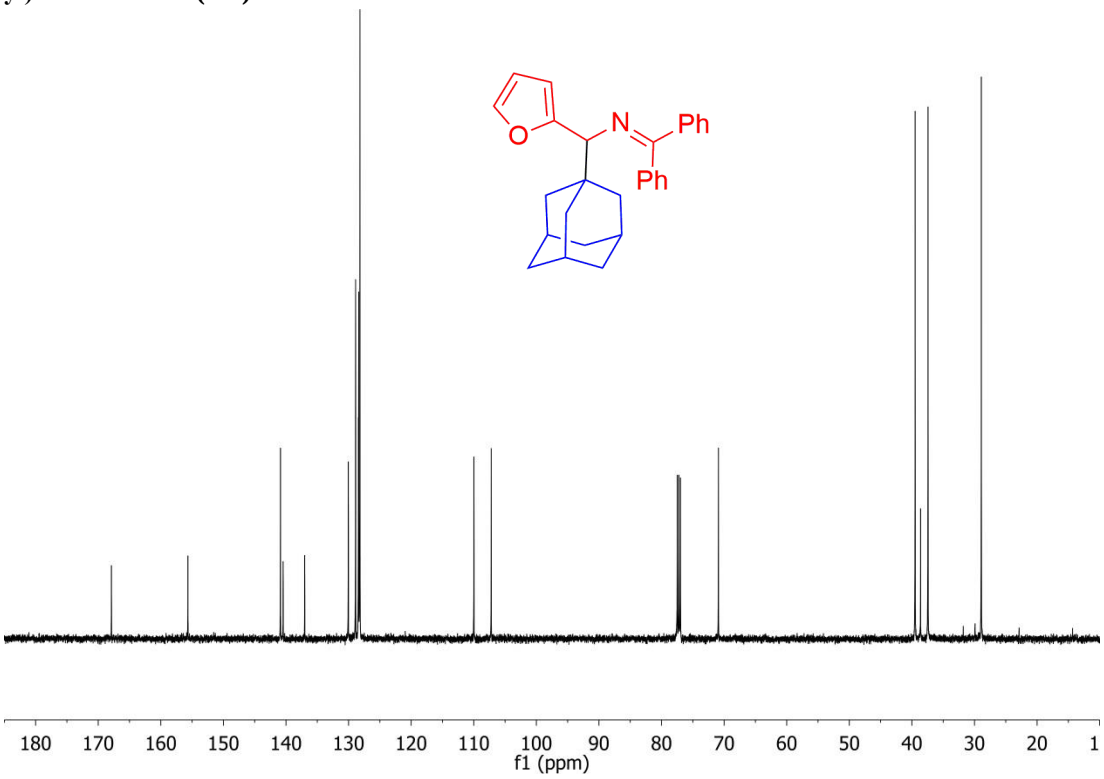
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(3-(trifluoromethyl)phenyl)methanamine (5de):



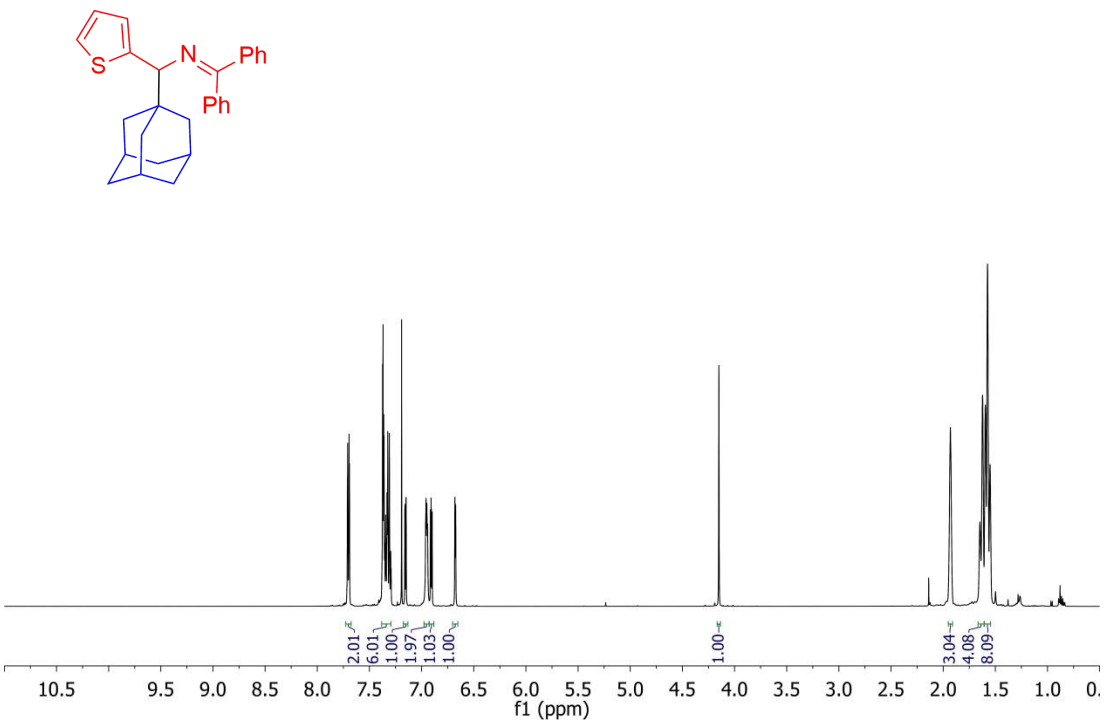
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(furan-2-yl)methanamine (5ee):



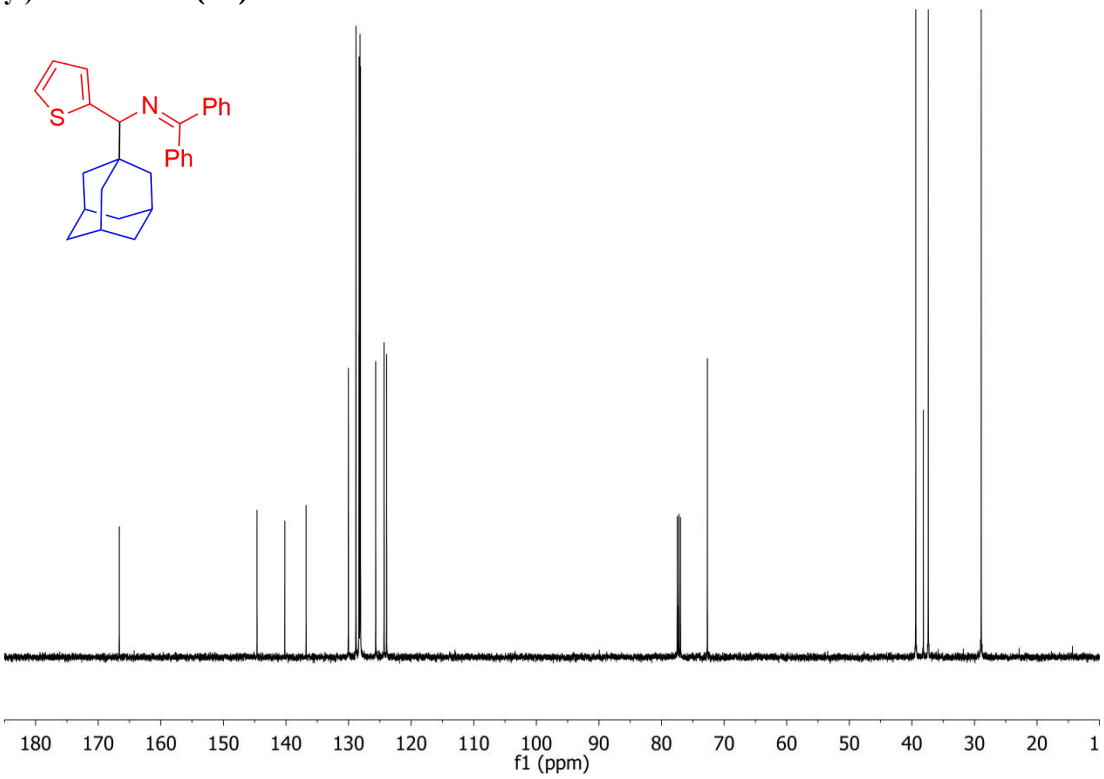
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(furan-2-yl)methanamine (5ee):



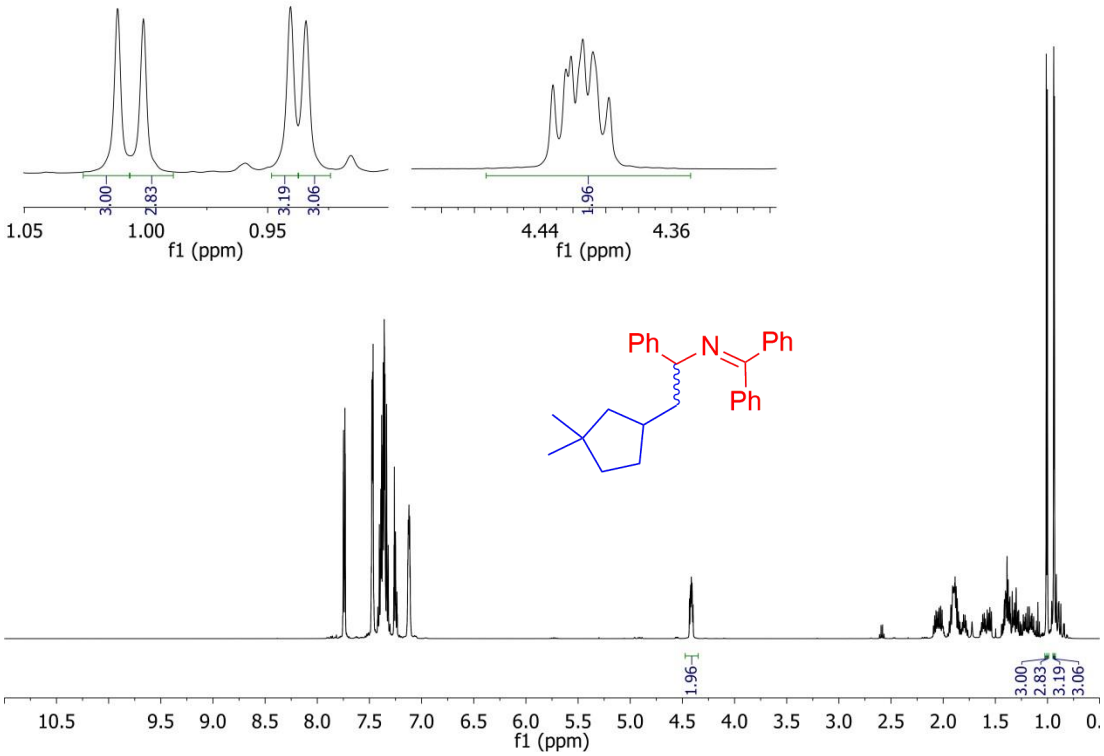
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(thiophen-2-yl)methanamine (5fe):



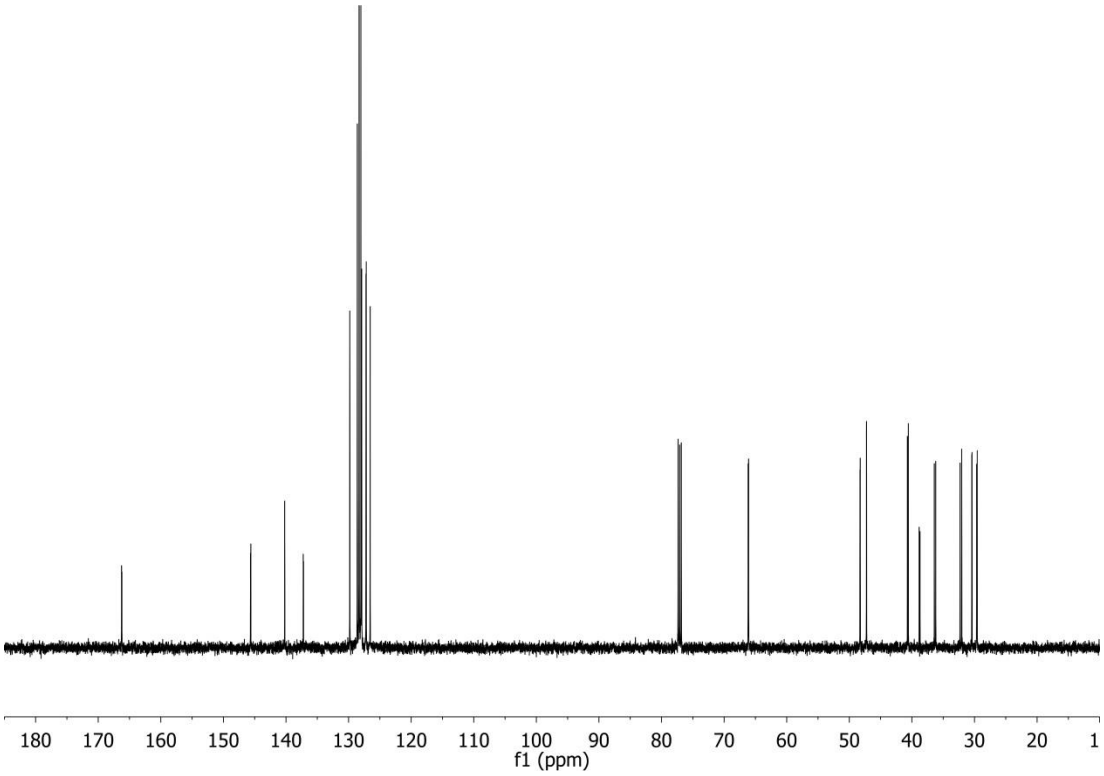
^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 1-(Adamantan-1-yl)-*N*-(diphenylmethylene)-1-(thiophen-2-yl)methanamine (5fe):



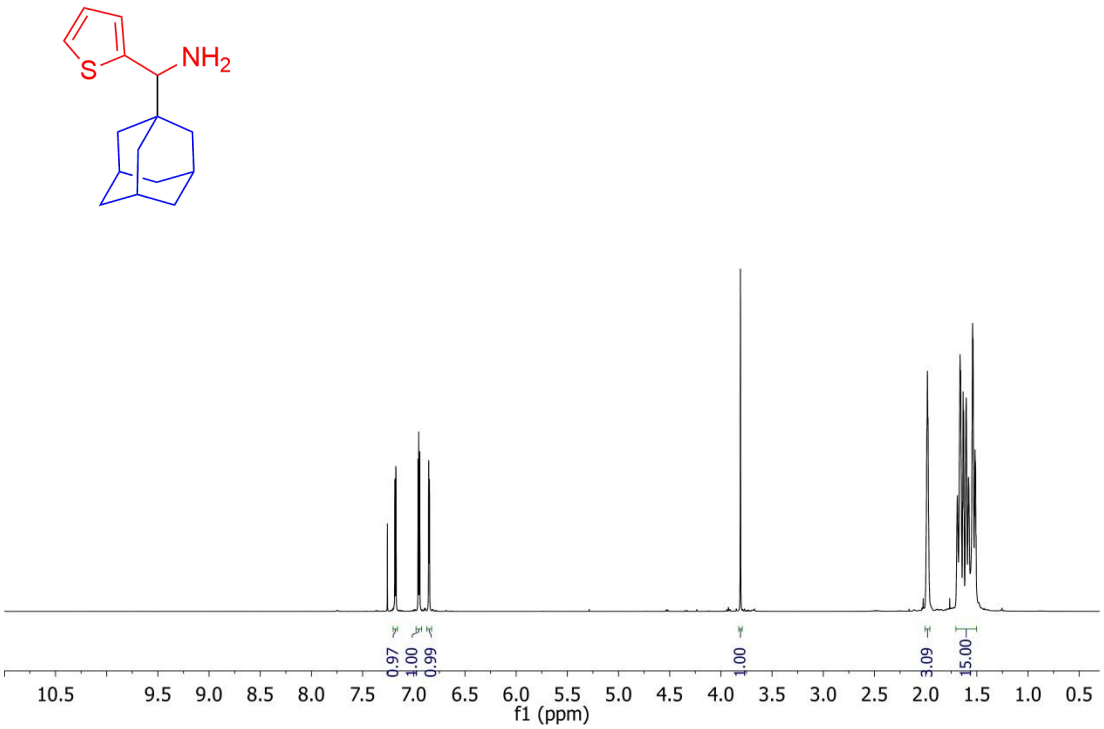
^{1}H NMR spectra ($CDCl_3$, 500 MHz) of 2-(3,3-Dimethylcyclopentyl)-*N*-(diphenylmethylene)-1-phenylethanamine (5ag):



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of 2-(3,3-Dimethylcyclopentyl)-*N*-(diphenylmethylene)-1-phenylethanamine (5ag):



^{1}H NMR spectra ($CDCl_3$, 500 MHz) of Adamantan-1-yl(thiophen-2-yl)methanamine (6fe):



^{13}C{^{1}H} NMR spectra ($CDCl_3$, 125 MHz) of Adamantan-1-yl(thiophen-2-yl)methanamine (6fe):