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# 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 ether), 1,4-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). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>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<sub>3</sub>N 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.<sup>1</sup>

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

**Preparation of Buchwald's 3<sup>rd</sup> Generation Pre-catalyst:** Palladium μ-OMs dimer and 3<sup>rd</sup> generation precatalyst was prepared according to literature procedure.<sup>3</sup>

## 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<sub>3</sub>)<sub>2</sub> (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  $\mu$ L, 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 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> 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 <sup>1</sup>H NMR spectroscopy of the crude reaction mixture by integration using 1,4-dimethylbenzene as internal standard in accordance to literature procedures.<sup>4</sup>

#### 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)<sub>2</sub> (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  $\mu$ L, 0.10 mmol) was added dropwise by syringe to this solution through the rubber septum. A solution of NaN(SiMe<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol) in 0.5 mL CPME was added portionwise by syringe at 0.1 mL/30 min at 24 °C. The reaction mixture was stirred for 3 h at 24 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in vacuo. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography. (hexanes to diethyl ether:hexanes = 1:50).

**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  $3^{rd}$  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  $\mu$ L, 0.10 mmol) was added dropwise by syringe to this solution through the rubber septum. A solution of

NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol) in 0.5 mL CPME was added portionwise by syringe at 0.1 mL/30 min at 60  $\degree$ C. The reaction mixture was stirred for 12 h at 60  $\degree$ C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in vacuo. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography. (hexanes to diethyl ether:hexanes = 1:50).

#### General Procedure D: One-pot Ketimine Synthesis/Pd-Catalyzed arylation

An oven-dried microwave vial equipped with a stir bar was charged with benzylamine (32.1 mg, 0.30 mmol) and benzophenone imine (54.4 mg, 0.30 mmol) under a nitrogen atmosphere. Next, 1 mL of dry THF was added under nitrogen via syringe and the vial was sealed. The reaction was then placed in an oil bath at 50 °C. After the reaction mixture was stirred for 12 h at 50 °C, the solvent was completely removed in vacuo and the vial was refilled with nitrogen. 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 same reaction vial through the rubber septum. 1-Bromo-4-*tert*-butylbenzene (17.3  $\mu$ L, 0.10 mmol) was added dropwise. A solution of NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol) in 0.5 mL CPME was added portionwise at 0.1 mL/30 min at 24 °C. The reaction mixture was stirred for 3 h at 24 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated in vacuo. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography. (hexanes to diethyl ether:hexanes = 1:50).

**General Procedure E: One-pot Aldimine Synthesis/Pd-Catalyzed aryation**: An oven-dried microwave vial equipped with a stir bar was charged with benzaldehyde (21.2 mg, 0.20 mmol) and diphenylmethylamine (36.6 mg, 0.20 mmol) under a nitrogen atmosphere. Dry THF (1 mL) was then added under nitrogen via syringe and the vial was sealed. The reaction was then placed in an oil bath at 80 °C and stirred for 12 h. Next, the volatile materials were completely removed at rt and the remaining solid was dried under reduced pressure at 60 °C for 2 h. The vial was then backfilled with nitrogen and a stock solution of Buchwald's 3<sup>rd</sup> generation pre-catalyst Pd dimer (3.7 mg, 0.005 mmol)

and NIXANTPHOS (5.6 mg, 0.010 mmol) in 0.5 mL dry CPME was added by syringe through the rubber septum. Next, 1-bromo-4-*tert*-butylbenzene (17.3  $\mu$ L, 0.10 mmol) was added dropwise by syringe through the rubber septum. A solution of NaN(SiMe<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol) in 0.5 mL CPME was added portionwise at 0.05 mL/30 min at 60 °C. The reaction mixture was stirred for 6 h at 60 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> and silica. The pad was rinsed with an additional 6 mL of ethyl acetate, and the combined solutions were concentrated under reduced pressure. The crude material was loaded onto a silica gel column via pipette and purified by flash chromatography (hexanes to diethyl ether:hexanes = 1:50).



**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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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.<sup>5</sup>



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<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide (17.3  $\mu$ L, 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. The one pot synthesis of **3ab** was performed following General Procedure D with benzylamine (32.1 mg, 0.30 mmol), benzophenone imine (54.4 mg, 0.30 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide **2b** (17.3  $\mu$ L, 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 (37.1 mg, 92% yield) as a white solid. The one pot synthesis of **3ab** from aldimine was performed following General Procedure E with benzaldehyde (21.2 mg, 0.20 mmol) and diphenylmethanamine (36.6 mg, 0.20 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2b** (17.3  $\mu$ L, 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 (37.5 mg, 93% yield) as a white solid. m.p. = 50–52 °C, R/= 0.75 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS calc'd for C<sub>30</sub>H<sub>30</sub>N<sup>+</sup> 404.2378, observed 404.2374 [MH]<sup>+</sup>.



**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<sub>3</sub>)<sub>2</sub> (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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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 <sup>°</sup>C, R/= 0.77 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>24</sub>N+ 362.1909, observed 362.1909 [MH]<sup>+</sup>.



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<sub>3</sub>)<sub>2</sub> (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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>24</sub>N<sup>+</sup> 362.1909, observed 362.1908 [MH]<sup>+</sup>.

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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2e** (20.2 mg, 0.10 mmol) at 10 mol % catalyst loading. The crude material was

purified by flash chromatography on deactivated silica gel (eluted with hexanes to diethyl ether:hexanes = 1:10) to give the product (36.2 mg, 93% 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<sub>3</sub>)<sub>2</sub> (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. One pot synthesis of **3ae** was performed following General Procedure D with benzylamine (32.1 mg, 0.30 mmol), benzophenone imine (54.4 mg, 0.30 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), 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 (24.6 mg, 63% yield) as a colorless oil. The one pot synthesis of **3ae** from aldimine was performed following General Procedure E with benzaldehyde (21.2 mg, 0.20 mmol) and

diphenylmethanamine (36.6 mg, 0.20 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2e** (20.2 mg, 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 = 1:10) to give the product (28.5 mg, 73% yield) as a colorless oil.  $R_f$  = 0.44 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS calc'd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>+ 391.2174, observed 391.2177 [MH]+

# 3afN=CPh2N-(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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide 2f(12.5 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 (33.9 mg, 90% 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<sub>3</sub>)<sub>2</sub> (59.8 mg, 0.30 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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<sub>f</sub>= 0.55 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>24</sub>NO<sup>+</sup> 378.1858, observed 378.1863 [MH]<sup>+</sup>.

 3ag

 N=CPh2
 1-(p-chlorophenyl)-N-(diphenylmethylene)-1-phenylmethanamine:
 The

 S8

reaction was performed following General Procedure B with ketamine **1a** (54.3 mg, 0.20 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (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<sub>3</sub>)<sub>2</sub> (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. One pot synthesis of 3ag was performed following General Procedure D with benzylamine (32.1 mg, 0.30 mmol), benzophenone imine (54.4 mg, 0.30 mmol, 3 equiv), NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide 2g (19.1 mg, 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 (34.3 mg, 90% yield) as a colorless oil. R<sub>f</sub> = 0.78 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for  $C_{26}H_{21}ClN^+$ 382.1363, 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<sub>3</sub>)<sub>2</sub> (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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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. One pot synthesis of **3ah** was also performed following General Procedure E with benzaldehyde (21.2 mg, 0.20 mmol) and

diphenylmethanamine (36.6 mg, 0.20 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2h** (11.0 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 (30.0 mg, 82% yield) as a white solid. m.p. = 92–96 °C, R<sub>f</sub> = 0.70 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.3, 161.8 (d, <sup>1</sup>J<sub>C-F</sub>= 243.3 Hz), 144.9, 140.8 (d, <sup>4</sup>J<sub>C-F</sub>= 3.1 Hz), 139.9, 136.8, 130.3, 129.2 (d, <sup>3</sup>J<sub>C-F</sub>= 7.9 Hz), 128.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.6, 127.0, 115.3 (d, <sup>2</sup>J<sub>C-F</sub>= 21.2 Hz), 69.3 ppm; IR (thin film): 3059, 1623, 1601, 1577, 1491, 1446, 1314, 1222, 1027, 779, 725, 696 cm<sup>-1</sup>; HRMS calc'd for C<sub>26</sub>H<sub>21</sub>FN<sup>+</sup> 366.1655, observed 366.1656 [MH]<sup>+</sup>.

# 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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2i** (14.0  $\mu$ L, 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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>C-F</sub>*= 3.8 Hz), 123.4 (q, *J<sub>C-F</sub>*= 270.4 Hz), 69.7 ppm; IR (thin film): 3060, 1618, 1598, 1577, 1491, 1446, 1325, 1123, 1066, 1018, 779, 726, 697 cm<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>21</sub>F<sub>3</sub>N<sup>+</sup> 415.1626, observed 415.1627 [MH]<sup>+</sup>.



**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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2j** (9.6  $\mu$ L, 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<sub>3</sub>)<sub>2</sub>

(36.7 mg, 0.20 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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<sub>f</sub> = 0.30 (diethyl ether:hexanes = 2.5:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>+ 349.1705, observed 349.1692 [MH]\*.



N=CPh<sub>2</sub>

CO<sub>2</sub>Et

**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<sub>3</sub>)<sub>2</sub> (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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):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<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub>+ 373.1705, observed 373.1702 [MH]<sup>+</sup>.

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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide 2l

(16.3  $\mu$ L, 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<sub>f</sub> = 0.45 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>+ 420.1964, observed 420.1944 [MH]<sup>+</sup>.



**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  $\mu$ L, 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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>30</sub>H<sub>24</sub>N<sup>+</sup> 398.1909, observed 398.1905 [MH]<sup>+</sup>.

## 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<sub>3</sub>)<sub>2</sub> (36.7 mg, 0.20 mmol), aryl bromide **2a**  (10.7  $\mu$ L, 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<sub>f</sub>= 0.80 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 168.1, 164.2 (d, <sup>1</sup>*J*<sub>C-F</sub> = 247 Hz), 162.2 (d, <sup>1</sup>*J*<sub>C-F</sub> = 247 Hz), 149.1 (t, <sup>3</sup>*J*<sub>C-F</sub> = 8.5 Hz), 143.8, 139.6, 136.5, 130.6, 129.0, 128.9, 128.8(d, <sup>4</sup>*J*<sub>C-F</sub> = 3.3 Hz), 128.3, 127.8, 127.7, 127.4, 110.5 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 20 Hz, <sup>3</sup>*J*<sub>C-F</sub> = 5.9 Hz), 102.2 (t, <sup>2</sup>*J*<sub>C-F</sub> = 25 Hz), 69.3 ppm; IR (thin film): 3435, 1622, 1597, 1491, 1446, 1313, 1290, 1115, 976, 780, 696 cm<sup>-1</sup>; HRMS calc'd for C<sub>26</sub>H<sub>20</sub>F<sub>2</sub>N<sup>+</sup> 384.1564, observed 384.1564 [MH]<sup>+</sup>.



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<sub>3</sub>)<sub>2</sub> (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<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide **2a** (10.7  $\mu$ L, 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<sub>f</sub> = 0.33 (diethyl ether:hexanes = 2:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>\* 349.1705, observed 349.1694 [MH]\*.

N=CPh<sub>2</sub>
 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<sub>3</sub>)<sub>2</sub> (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); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>24</sub>H<sub>20</sub>NO<sup>+</sup> 338.1545, observed 338.1550 [MH]<sup>+</sup>.



**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<sub>3</sub>)<sub>2</sub> (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<sub>f</sub> = 0.70 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>; HRMS calc'd for C<sub>24</sub>H<sub>20</sub>NO<sup>+</sup> 338.1542, observed 338.1547 [MH]<sup>+</sup>.

# 3am



*N-(p-(((diphenylmethylene)amino)(phenyl)methyl)phenyl)acetamide:* 

The reaction was performed following General Procedure C with ketamine **1a** (54.3 mg, 0.20 mmol), NaN(SiMe<sub>3</sub>)<sub>2</sub> (55.0 mg, 0.30 mmol), aryl bromide **2m** (21.4 mg, 0.1 mmol) at 5 mol % Buchwald's 3<sup>rd</sup> generation pre-catalyst Pd

dimer (3.7 mg, 0.005 mmol) and 10 mol % NiXANTPHOS (5.6 mg, 0.010 mmol) 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 = 3:1) to give the product (30.4 mg, 75% yield) as a

white solid. R<sub>f</sub> = 0.33 (diethyl ether:hexanes = 2.5:1); m.p. = 80–82 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.14 (br s, 1H, NH), 7.72 (d, *J* = 8.0 Hz, 2H), 7.41–7.38 (m, 4H), 7.34–7.28 (m, 5H), 7.24–7.21 (m, 4H), 7.17–7.13 (m, 2H), 7.04–7.03 (m, 2H), 5.52 (s, 1H), 2.02 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 169.0, 167.1, 144.8, 140.8, 139.8, 136.7, 136.6, 130.2, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 127.7, 127.5, 126.8, 120.2, 69.4, 24.3 ppm; IR (thin film): 3300, 3059, 1665, 1601, 1577, 1491, 1446, 1371, 1276, 1028, 780, 718, 698 cm<sup>-1</sup>; HRMS calc'd for C<sub>28</sub>H<sub>25</sub>N<sub>2</sub>O<sup>+</sup> 405.1967, observed 405.1980 [MH]<sup>+</sup>.

 3an
 -N-(diphenylmethylene)-1-phenyl-1-(o-tolyl)methanamine:
 An

 N=CPh2
 oven-dried microwave vial equipped with a stir bar was charged with

 aldimine ketamine 1a (54.3 mg, 0.20 mmol), LiN(SiMe<sub>3</sub>)<sub>2</sub> (50.2 mg, 0.30 mmol)

 and Buchwald's 3<sup>rd</sup> generation pre-catalyst (9.3 mg, 0.010 mmol) under a

nitrogen atmosphere. The vial was sealed, and 1 mL dry CPME was taken up by syringe and added to the reaction vial. aryl bromide **2m** (12.0  $\mu$ L, 0.10 mmol)) was added dropwise by syringe to this solution through the rubber septum. The reaction mixture was stirred for 8 h at 60 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> 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 deactivated silica gel column via pipette and purified by flash chromatography (eluted with diethyl ether:hexanes = 1:100 to diethyl ether:hexanes = 1:50) to give the product (20.3 mg, 56% yield) as a colorless thick oil. R<sub>f</sub> = 0.71 (diethyl ether:hexanes = 1:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.74–7.72 (m, 2H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.41–7.39 (m, 3H), 7.35–7.29 (m, 3H), 7.24–7.14 (m, 6H), 7.11 (td, *J* = 7.0 Hz, 1.5 Hz 1H), 7.05–7.03 (m, 3H), 5.74 (s, 1H), 1.95 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 167.0, 144.3, 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): 3059, 3024, 1621, 1577, 1490, 1446, 1380, 1290, 1028, 778, 697 cm<sup>-1</sup>; HRMS calc'd for C<sub>27</sub>H<sub>24</sub>N<sup>+</sup> 362.1909, observed 362.1912 [MH]<sup>+</sup>.



# 3ij - N-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine:

An oven-dried microwave vial equipped with a stir bar was charged with aldimine ketamine **1i** (54.4 mg, 0.20 mmol) and Buchwald's 3<sup>rd</sup> generation pre-catalyst (9.3 mg, 0.010 mmol) under a nitrogen atmosphere. The vial was

sealed, and 0.5 mL dry CPME was taken up by syringe and added to the reaction vial. aryl bromide 2j (10.7  $\mu$ L, 0.1 mmol) was added dropwise by syringe to this solution through the rubber septum. A solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (50.2 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 4 h at 60 °C, opened to air, quenched with two drops of H<sub>2</sub>O, diluted with 3 mL of ethyl acetate, and filtered over a pad of MgSO<sub>4</sub> 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 deactivated silica gel column via pipette and purified by flash chromatography (eluted with Ethyl Acetate:Hexane = 1:5 to Ethyl Acetate:Methanol = 120:1) to give the product (31.4 mg, 90% yield) as a colorless thick oil.  $R_f = 0.31$ (Ethyl Acetate:Methanol = 100:5); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.53 (dd, *J* = 4.5 Hz, 2.0 Hz, 2H), 8.49 (dd, J = 4.5, 1.5 Hz, 1H), 8.47 (d, J = 2.0 Hz, 1H), 7.75-7.73 (m, 2H), 7.70-7.67 (m, 1H), 7.49-7.44 (m, 3H), 7.42–7.41 (m, 1H), 7.38–7.35 (m, 2H), 7.27–7.22 (m, 3H), 7.03 (dd, J = 7.0 Hz, 2.0 Hz, 2H), 5.54 (s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 169.5, 152.6, 150.2, 149.2, 149.0, 139.2, 139.0, 136.3, 135.5, 130.9, 129.2, 128.9, 128.9, 128.4, 127.5, 123.9, 122.5, 66.8 ppm; IR (thin film): 3027, 1622, 1595, 1575, 1445, 1317, 1282, 1024, 783, 704, 697 cm<sup>-1</sup>; HRMS calc'd for C<sub>24</sub>H<sub>20</sub>N<sub>3</sub>+ 350.1657, observed 350.1650 [MH]+.

#### **General Procedure F: Imine Product Hydrolysis**

A modified procedure from several literature reports<sup>6</sup> 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  $^{\circ}$ C. The solution was warmed to room temperature, stirred at room temperature and 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<sub>2</sub>O (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).



**8** – **diphenylmethanaminium chloride salt** : The reaction was performed following General Procedure F with imine **3aa** (38.2 mg, 0.10 mmol) gave its ammonium salt **8** as white solid in 93% yield (20.4 mg). The NMR spectral data

match the previously published data.7



9 - (4-methoxyphenyl)(phenyl)methanaminium chloride salt : The reaction was performed following General Procedure E with imine 3af (37.7 mg, 0.10 mmol) gave its ammonium salt 9 as white solid in 92%

yield (22.9 mg). The NMR spectral data match the previously published data.<sup>7</sup>



**10 – phenyl(p-tolyl)methanaminium chloride salt** : The reaction was performed following General Procedure F with imine **3ac** (36.1 mg, 0.10 mmol) gave its ammonium salt **10** as white solid in 96% yield (22.4 mg).

The NMR spectral data match the previously published data.7



11 - (4-(*tert*-butyl)phenyl)(phenyl)methanamine ammounium salt :
The reaction was performed following General Procedure F with imine
3ab (40.3 mg, 0.10 mmol) gave its ammonium salt 11 as white solid in

92% yield (25.4 mg), m.p. = 272–274 °C; <sup>1</sup>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; <sup>13</sup>C{<sup>1</sup>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<sup>-1</sup>; HRMS calc'd for C<sub>17</sub>H<sub>19</sub>+ 223.1487, observed 223.1480 [M-(NH<sub>2</sub>Cl)]<sup>+</sup>.



12 – (4-fluorophenyl)(phenyl)methanaminium chloride salt : The reaction was performed following General Procedure F with imine 3ah (36.5 mg, 0.10 mmol) gave its ammonium salt 12 as white solid in 96% yield (22.8

mg). The NMR spectral data match the previously published data.<sup>7</sup>



**13 - (4-chlorophenyl)(phenyl)methanaminium chloride salt** :
The reaction was performed following General Procedure F with imine **3ag** (38.2 mg, 0.10 mmol) gave its ammonium salt **13** as white solid in 93% yield

(23.6 mg). The NMR spectral data match the previously published data.<sup>7</sup>



14 - (4-chlorophenyl)(4-fluorophenyl)methanaminium chloridesalt : 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<sub>3</sub>)<sub>2</sub>, 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). Imine product was then hydrolyzed following General Procedure F gave its ammonium salt **14** as white solid in 79% overall yield (21.5 mg). m.p. = 268-270 °C; <sup>1</sup>H NMR (500 MHz, MeOD)  $\delta$  7.51–7.46 (m, 6H), 7.19 (t, *J* = 8.0 Hz, 2H), 5.73 (s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, MeOD): 164.3 (d, <sup>1</sup>*J*<sub>CF</sub> = 246.3 Hz), 137.1, 135.9, 134.2 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.3 Hz), 130.8 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.5 Hz), 130.4, 130.1, 117.1 (d, <sup>2</sup>*J*<sub>CF</sub> = 22.0 Hz), 58.0 ppm; IR (thin film): 2928, 1598, 1515, 1238, 1015, 829 cm<sup>-1</sup>; HRMS calc'd for C<sub>13</sub>H<sub>9</sub>ClF<sup>+</sup> 219.0377, observed 219.0381 [M-(NHz)]<sup>+</sup>.



**15** – 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 F

with imine **3ca** (28.3 mg, 0.071 mmol) gave its ammonium salt **15** as white solid in 95% yield, Overal 68% yield (18.1 mg). The NMR spectral data match the previously published data.<sup>7</sup>

#### **Functionalization of Diarylmethylamines**

Synthesis of acetamide 16

Acetamide **16** was synthesized following modified literature procedure<sup>8</sup>:

An oven-dried microwave vial equipped with a stir bar was charged with (4-fluorophenyl)(phenyl) methanaminium chloride salt (47.6 mg 0.2 mmol), acetyl chloride (18.8mg 0.24 mmol), pyridine (32.0 mg 0.8 mmol). 1 ml of DCM was taken up by syringe and added to the reaction vial. The vial was sealed and reaction mixture was stirred for 6 h at 24 °C. The reaction mixture was then diluted with DCM (2 mL) washed with sat. NaHCO<sub>3</sub> solution (5 ml) and 2M HCl (5ml). The organic layer were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to give the product **16** in 62% yield (30.2 mg) as white solid.

CH<sub>3</sub>

#### 16- N-((4-fluorophenyl)(phenyl)methyl)acetamide

The NMR spectral data match the previously published data.8

Synthesis of N-benzhydrylurea derivative 17:

N-benzhydrylurea derivatives 17 was synthesized following modified literature procedure<sup>9</sup>:

An oven-dried microwave vial equipped with a stir bar was charged with (4-chlorophenyl)(phenyl) methanaminium chloride salt (50.8 mg, 0.2 mmol), urea (72.1 mg, 1.2 mmol). 1 ml of water acidified with 0.1 ml Conc. HCl taken up by syringe and added to the reaction vial. The vial was sealed and the reaction mixture was stirred for 3 h at 135°C. After cooled to rt, the solid was filtered off and dried. Recrystallization from Ethanol/H<sub>2</sub>O gave product **17** in yield of 70% (36.5mg) as white solid.



# 17 - 1-((4-chlorophenyl)(phenyl)methyl)urea

m.p. = 154–156 °C, <sup>1</sup>H NMR (500 MHz, MeOD): δ 7.33–7.30 (m, 4H), 7.26–7.22 (m, 5H), 5.95 (s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): 161.1, 143.6, 143.1, 133.9, 129.9, 129.6, 129.5, 128.4, 58.3 ppm; HRMS

calc'd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>ONaCl<sup>+</sup> 283.0614, observed 283.0614 [M+Na]<sup>+</sup>. The NMR spectral data match the previously published data.<sup>9</sup>

#### 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)<sub>2</sub> (1  $\mu$ mol) and the phosphine ligands (2  $\mu$ mol for monodentate ligands and 1  $\mu$ mol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and NaN(SiMe<sub>3</sub>)<sub>2</sub> (30  $\mu$ mol) 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  $\mu$ mol/reaction), bromobenzene (12  $\mu$ mol) and 4,4'-di-*tert*-butylbiphenyl (1  $\mu$ mol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each reaction vial as a solution in THF (100  $\mu$ L, 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  $\mu$ L 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  $\mu$ L of acetonitrile, followed by 40  $\mu$ L 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<sub>3</sub>)<sub>2</sub>, NaN(SiMe<sub>3</sub>)<sub>2</sub>, KN(SiMe<sub>3</sub>)<sub>2</sub>, LiO'Bu, KO'Bu, NaO'Bu, NaH, LiOAc, KOAc, K<sub>3</sub>PO<sub>4</sub>, KOPh and Cs<sub>2</sub>CO<sub>3</sub>.

Well	Base	Solvent	Prod/IS <sup>a</sup>

A01	LiO <i>t</i> Bu	CPME	0.00
B01		THF	0.16
A02	KOtBu	CPME	5.22
B02		THF	5.79
A03		CPME	0.00
B03	NaOibu	THF	1.99
A04	LiN(SiMe <sub>3</sub> ) <sub>2</sub>	CPME	0.16
B04		THF	3.59
A05	NaN(SiMe <sub>3</sub> ) <sub>2</sub>	CPME	3.09
B05		THF	7.46
A06	KN(S:Ma)	CPME	6.02
B06	$\mathbf{KIN}(\mathbf{SIME}_3)_2$	THF	6.83
C01		CPME	0.10
D01	INall	THF	0.89
C02	KOAc	CPME	0.00
D02	KOAc	THF	0.00
C03	LiOAc	CPME	0.00
D03		THF	0.00
C04	K <sub>3</sub> PO <sub>4</sub>	CPME	0.00
D04		THF	0.00
C05	Cs <sub>2</sub> CO <sub>3</sub>	CPME	0.00

D05		THF	0.08
C06	KOPh	CPME	0.00
D06		THF	0.00

#### <sup>a</sup>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 <sub>3</sub> HBF <sub>4</sub>	1.22
B05	<i>t</i> -Bu <sub>3</sub> PHBF <sub>4</sub>	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)<sub>2</sub>(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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# NMR Spectra.

# Example crude <sup>1</sup>H NMR spectra with 1,4-dimethylbenzene (*p*-xylene) as an internal standard



3aa – N-(diphenylmethylene)-1,1-diphenylmethanamine in CDCl<sub>3</sub>



3ab - 1-(4-(tert-butyl)phenyl)-N-(diphenylmethylene)-1-phenylmethanamine in CDCl<sub>3</sub>



3ac - N-(diphenylmethylene)-1-phenyl-1-(p-tolyl)methanamine in CDCl<sub>3</sub>



3ad - N-(diphenylmethylene)-1-phenyl-1-(m-tolyl)methanamine in CDCl<sub>3</sub>



 $\label{eq:constraint} 3ae-4-(((diphenylmethylene)amino)(phenyl)methyl)-N, N-dimethylaniline in \ CDCl_3$ 



3af - N-(diphenylmethylene)-1-(p-methoxyphenyl)-1-phenylmethanamine in CDCl<sub>3</sub>



3ag - 1-(p-chlorophenyl)-N-(diphenylmethylene)-1-phenylmethanamine in CDCl<sub>3</sub>



3ah – N-(diphenylmethylene)-1-(p-fluorophenyl)-1-phenylmethanamine in CDCl<sub>3</sub>



3ai -N-(diphenylmethylene)-1-phenyl-1-(p-(trifluoromethyl)phenyl)methanamine in CDCl<sub>3</sub>





3aj - N-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine in CDCl<sub>3</sub>





N=CPh<sub>2</sub> ĊΝ 1.00-[ 0 5.5 5.0 4.5 f1 (ppm) 8.5 8.0 7.5 7.0 6.5 6.0 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0. 30 170 100 90 f1 (ppm) 1 160 150 140 130 120 110 80 70 60 50 40 30 20

3ak - 4-(((diphenylmethylene)amino)(phenyl)methyl)benzonitrile in CDCl<sub>3</sub>

3al - Ethyl 4-(((diphenylmethylene)amino)(phenyl)methyl)benzoate in CDCl<sub>3</sub>



3am - N-(4-(((diphenylmethylene)amino)(phenyl)methyl)phenyl)acetamide in CDCl<sub>3</sub>



3ca - N-(diphenylmethylene)-1-(naphthalen-1-yl)-1-phenylmethanamine in CDCl<sub>3</sub>





3ga - 1-(3,5-difluorophenyl)-*N*-(diphenylmethylene)-1-phenylmethanamine in CDCl<sub>3</sub>



3ia - N-(diphenylmethylene)-1-phenyl-1-(pyridin-4-yl)methanamine in CDCl<sub>3</sub>



3ja - N-(diphenylmethylene)-1-(furan-2-yl)-1-phenylmethanamine in CDCl<sub>3</sub>



3la - N-(diphenylmethylene)-1-(furan-3-yl)-1-phenylmethanamine in CDCl<sub>3</sub>



3am - N-(4-(((diphenylmethylene)amino)(phenyl)methyl)phenyl)acetamide in CDCl<sub>3</sub>



3an -N-(diphenylmethylene)-1-phenyl-1-(o-tolyl)methanamine in CDCl<sub>3</sub>





3ij - N-(diphenylmethylene)-1-phenyl-1-(pyridin-3-yl)methanamine in CDCl<sub>3</sub>



100 90 f1 (ppm) 





9 - (4-methoxyphenyl)(phenyl)methanaminium chloride salt in Methanol-d4



10 - phenyl(p-tolyl)methanaminium chloride salt in Methanol-d4





# 11 - (4-(tert-butyl)phenyl)(phenyl)methanamine ammounium salt in Methanol-d4

12 - (4-fluorophenyl)(phenyl)methanaminium chloride salt in Methanol-d4





# 13 - (4-chlorophenyl)(phenyl)methanaminium chloride salt in Methanol-d4



14 - (4-chlorophenyl)(4-fluorophenyl)methanaminium chloride salt in Methanol- $d_4$ 



S54

15 - naphthalen-1-yl(phenyl)methanaminium chloride salt in Methanol-d4



16 - N-((4-fluorophenyl)(phenyl)methyl)acetamide in CDCl<sub>3</sub>





# 17 - 1-((4-chlorophenyl)(phenyl)methyl)urea in Methanol-d<sub>4</sub>

