



Supporting Information

for

Synthesis of 2-benzyl *N*-substituted anilines via imine condensation–isoaromatization of (*E*)-2-arylidene-3-cyclohexenones and primary amines

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Beilstein J. Org. Chem. **2024**, *20*, 1468–1475. doi:10.3762/bjoc.20.130

Experimental procedures, characterization data, and copies of NMR spectra of all new compounds

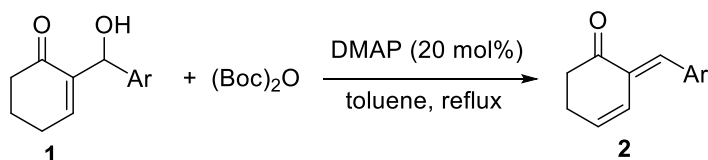
Table of Contents

I.	General information.....	S1
II.	Synthesis and characterization data of (<i>E</i>)-2-methylene-3-cyclohexenones 2	S1–S2
III.	Synthesis and characterization data of product 4 and 5f/5o	S2–S13
IV.	Gram-scale synthesis of 4aa	S13
V.	Successive one-pot synthesis of 4aa	S13
VI.	Derivation of the products	S13–S14
VII.	References	S14
VIII.	Copies of ¹ H and ¹³ C NMR spectra of new compounds	S15–S61

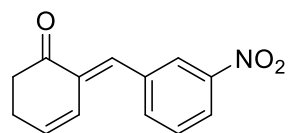
I. General information

Melting points were measured using a micro-melting point tester (Model FX-RD-X5E). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard and CDCl_3 or $\text{DMSO}-d_6$ as a solvent. The chemical shifts (δ) were expressed in parts per million (ppm) and the coupling constants (J) were in Hz. Reactions were detected by thin-layer chromatography (TLC) with pre-coated G254 silica gel. All solvents and chemical reagents unless otherwise noted were used as commercially available without further purification. Starting materials of (*E*)-2-methylene-3-cyclohexenones **2a–p** were synthesized according to the literature procedures^[1].

II. Synthesis and characterization data of (*E*)-2-methylene-3-cyclohexenones **2**

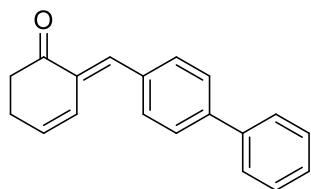


According to the reported literature^[1], to a solution of MBH alcohol **1** (13.2 mmol) in toluene (50 mL) was added $(\text{Boc})_2\text{O}$ (3.16 g, 14.5 mmol) and DMAP (0.32 g, 2.6 mmol), and the resulting solution was stirred at reflux temperature for 12 h. After completion of the reaction monitored by TLC analysis, the solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford the pure (*E*)-2-methylene-3-cyclohexenones **2**. (*E*)-2-methylene-3-cyclohexenones **2** bearing a C_6H_5 (**2a**)^[1], $2\text{-BrC}_6\text{H}_4$ (**2b**)^[2], $2\text{-MeC}_6\text{H}_4$ (**2c**)^[2], $3\text{-ClC}_6\text{H}_4$ (**2d**)^[2], $3\text{-MeOC}_6\text{H}_4$ (**2e**)^[1], $4\text{-BrC}_6\text{H}_4$ (**2g**)^[2], $4\text{-ClC}_6\text{H}_4$ (**2h**)^[1], $4\text{-MeC}_6\text{H}_4$ (**2i**)^[1], 2-furyl (**2m**)^[1], 2-thienyl (**2n**)^[2], $4\text{-MeOC}_6\text{H}_4$ (**2p**)^[1] are known compounds.



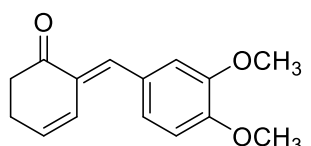
2-(3-Nitrobenzylidene)cyclohex-3-en-1-one (**2f**)

Yellow solid; 44% yield; m. p. 52–56 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.52–7.48 (m, 1H), 7.30 (s, 1H), 6.77 (d, $J = 12.0$ Hz, 1H), 6.24–6.20 (m, 1H), 2.65–2.62 (m, 2H), 2.59–2.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 148.5, 137.3, 135.8, 133.7, 133.1, 129.6, 128.7, 124.3, 124.2, 123.1, 38.2, 24.8. IR (KBr): ν 1589, 1535, 1354, 1259, 732 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{13}\text{H}_{11}\text{NO}_3 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 252.0637, found 252.0638.



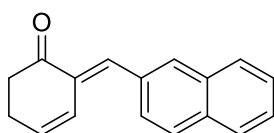
2-([1,1'-Biphenyl]-4-ylmethylene)cyclohex-3-en-1-one (2j)

Yellow solid; 47% yield; m. p. 107-109 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.60 (m, 4H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.46-7.43 (m, 3H), 7.38-7.34 (m, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.20-6.15 (m, 1H), 2.70-2.67 (m, 2H), 2.62-2.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.3, 141.5, 140.4, 134.6, 131.7, 131.2, 131.2, 130.7, 128.9, 127.8, 127.2, 127.1, 125.4, 38.4, 24.7. IR (KBr): ν 1599, 1484, 1353, 1270, 1004 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{19}\text{H}_{16}\text{O}+\text{Na}$ $[\text{M}+\text{Na}]^+$ 283.1099, found 283.1096.



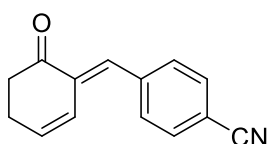
2-(3,4-Dimethoxybenzylidene)cyclohex-3-en-1-one (2k)

Yellow solid; 62% yield; m. p. 70-72 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.98-6.95 (m, 2H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.17-6.12 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.66-2.65 (m, 2H), 2.61-2.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 149.8, 148.9, 132.3, 130.5, 129.9, 128.4, 125.5, 123.8, 113.3, 111.2, 56.1, 38.3, 24.6. IR (KBr): ν 1680, 1570, 1515, 1255, 1133, 1025 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_3+\text{H}$ $[\text{M}+\text{H}]^+$ 245.1178, found 245.1180.



2-(Naphthalen-2-ylmethylene)cyclohex-3-en-1-one (2l)

Yellow solid; 57% yield; m. p. 81-83 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.85-7.83 (m, 3H), 7.59 (s, 1H), 7.55-7.53 (m, 1H), 7.52-7.49 (m, 2H), 7.04 (d, $J = 8.0$ Hz, 1H), 6.23-6.18 (m, 1H), 2.73-2.70 (m, 2H), 2.65-2.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 133.3, 133.3, 133.1, 132.3, 131.5, 131.4, 130.0, 128.5, 128.2, 127.8, 127.4, 126.6, 125.5, 38.4, 24.8. IR (KBr): ν 1684, 1560, 1442, 1229, 1123 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{17}\text{H}_{14}\text{O}+\text{H}$ $[\text{M}+\text{H}]^+$ 235.1123, found 235.1125.



4-((6-Oxocyclohex-2-en-1-ylidene)methyl)benzonitrile (2o)

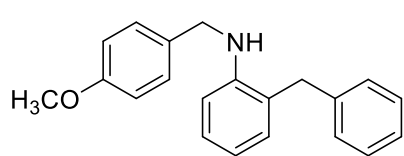
Pale yellow solid; 42% yield; m. p. 98-100 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.23 (s, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.19-6.16 (m, 1H), 2.59-2.58 (m, 2H), 2.55-2.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 140.0, 133.5, 132.9, 132.0, 128.9, 124.2, 118.4, 111.5, 37.9, 24.6. IR (KBr): ν 2231, 1687, 1583, 1266, 1137, 875 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}+\text{H}$ $[\text{M}+\text{H}]^+$ 210.0919, found 210.0916.

III. Synthesis and characterization data of products 4 and 5f/5o

In a vial containing a magnetic stirrer was placed (*E*)-2-methylene-3-cyclohexenone **2** (0.2 mmol), primary aliphatic amine **3** (2.0 mmol) and DME (2 mL). The reaction mixture was stirred at 60 °C and the reaction process was monitored by TLC analysis. After completion, the solvent was concentrated under reduced

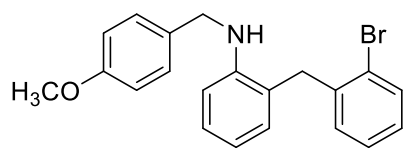
pressure and the residue was purified by column chromatography on silica gel to give product **4**. In the case of reaction with a *meta*-nitro bearing (*E*)-2-methylene-3-cyclohexenone **2f**, 2-benzylphenol **5f** was partially obtained together with normal product **4fa**. A *para*-cyano substituted 3-cyclohexenone **2o** generated 2-benzylphenol **5o** exclusively.

Product **4ab** is a known compound, and the spectroscopic data were consistent with that reported in cited reference^[3].



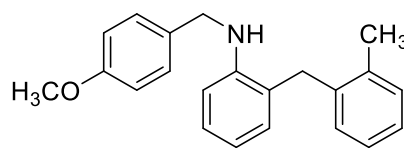
2-Benzyl-N-(4-methoxybenzyl)aniline (4aa)

White solid; 82% yield; m. p. 102-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.25 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.16-7.13 (m, 3H), 7.07 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.73-6.70 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 2H), 3.89 (s, 2H), 3.81 (br.s, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 146.2, 139.5, 131.4, 130.7, 128.8, 128.7, 128.6, 128.0, 126.5, 124.8, 117.3, 114.0, 111.0, 55.4, 47.7, 38.4. IR (KBr): ν 1599, 1364, 1239, 1068 cm⁻¹. ESI HRMS: calcd. for C₂₁H₂₁NO+Na [M+Na]⁺ 326.1521, found 326.1523.



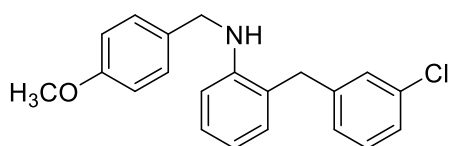
2-(2-Bromobenzyl)-N-(4-methoxybenzyl)aniline (4ba)

Pale yellow solid; 28% yield; m. p. 99-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.15-7.09 (m, 2H), 7.07-7.01 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.65-6.61 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 2H), 3.88 (s, 2H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 146.0, 138.6, 132.9, 131.4, 130.6, 130.4, 128.6, 128.2, 128.1, 127.7, 125.2, 123.4, 117.4, 111.0, 55.4, 47.6, 38.0. IR (KBr): ν 1604, 1513, 1360, 1247, 1174 cm⁻¹. ESI HRMS: calcd. for C₂₁H₂₀BrNO+H [M+H]⁺ 382.0807, found 382.0805.



N-(4-Methoxybenzyl)-2-(2-methylbenzyl)aniline (4ca)

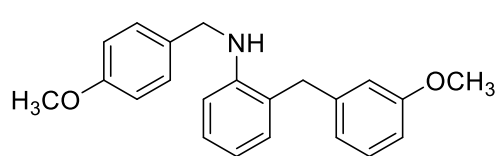
Pale yellow solid; 38% yield; m. p. 118-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.17-7.09 (m, 6H), 6.98 (d, *J* = 4.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 12.0 Hz, 2H), 6.70-6.66 (m, 2H), 4.23 (s, 2H), 3.79 (s, 2H), 3.78 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 146.1, 137.2, 136.9, 131.5, 130.4, 130.0, 129.0, 128.7, 127.7, 126.7, 126.3, 124.2, 117.5, 114.1, 110.8, 55.4, 47.8, 35.3, 19.7. IR (KBr): ν 1601, 1510, 1354, 1242, 1173 cm⁻¹. ESI HRMS: calcd. for C₂₂H₂₃NO+Na [M+Na]⁺ 340.1677, found 340.1674.



2-(3-Chlorobenzyl)-N-(4-methoxybenzyl)aniline (4da)

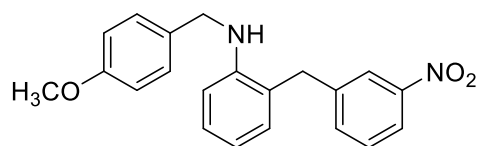
Yellow oil; 65% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.06 (m, 4H),

6.96-6.94 (m, 4H), 6.73 (d, $J = 8.0$ Hz, 2H), 6.66-6.63 (m, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 4.10 (s, 2H), 3.77 (s, 2H), 3.70 (s, 3H), 3.64 (br.s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 146.0, 141.7, 134.7, 131.3, 130.8, 130.0, 128.8, 128.6, 128.3, 126.9, 126.8, 123.8, 117.4, 114.1, 111.2, 55.4, 47.7, 38.0. IR (neat): ν 1596, 1513, 1364, 1249, 1175 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{ClNO} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 360.1131, found 360.1134.



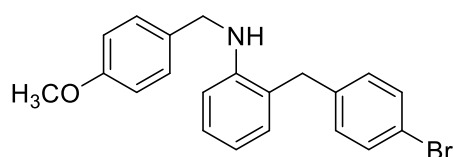
2-(3-Methoxybenzyl)-N-(4-methoxybenzyl)aniline (4ea)

Pale yellow oil; 52% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.13-7.04 (m, 2H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.72-6.62 (m, 6H), 6.54 (d, $J = 8.0$ Hz, 1H), 4.09 (s, 2H), 3.78 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 158.8, 146.2, 141.2, 131.4, 130.7, 129.8, 128.6, 128.0, 124.6, 121.1, 117.3, 114.3, 112.0, 111.0, 55.4, 55.2, 47.6, 38.5. IR (neat): ν 1599, 1355, 1261, 1090, 799 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{23}\text{NO}_2 + \text{H}$ $[\text{M} + \text{H}]^+$ 334.1807, found 334.1806.



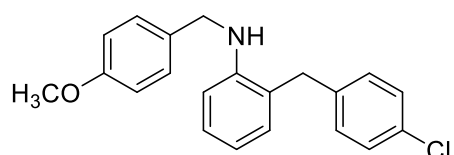
N-(4-Methoxybenzyl)-2-(3-nitrobenzyl)aniline (4fa)

Yellow solid; 23% yield; m. p. 96-98 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 1H), 7.95 (s, 1H), 7.41-7.34 (m, 2H), 7.14-7.11 (m, 1H), 7.00-6.96 (m, 3H), 6.73 (d, $J = 8.0$ Hz, 2H), 6.69-6.66 (m, 1H), 6.62 (d, $J = 8.0$ Hz, 1H), 4.12 (s, 2H), 3.89 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 148.7, 145.9, 141.8, 134.8, 131.1, 130.7, 129.6, 128.7, 128.7, 123.6, 123.1, 121.7, 117.7, 114.2, 111.4, 55.4, 47.8, 37.8. IR (KBr): ν 1602, 1527, 1353, 1246 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 371.1372, found 371.1376.



2-(4-Bromobenzyl)-N-(4-methoxybenzyl)aniline (4ga)

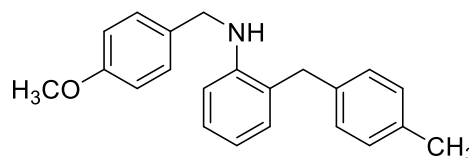
Yellow oil; 76% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.0$ Hz, 2H), 7.09-7.05 (m, 1H), 6.93-6.90 (m, 5H), 6.72 (d, $J = 12.0$ Hz, 2H), 6.64-6.61 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 4.06 (s, 2H), 3.71 (s, 2H), 3.68 (s, 3H), 3.60 (br.s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 146.0, 138.6, 131.8, 131.2, 130.7, 130.4, 128.7, 128.2, 124.0, 120.3, 117.4, 114.1, 111.1, 55.4, 47.7, 37.7. IR (neat): ν 1603, 1513, 1362, 1248, 748 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{BrNO} + \text{H}$ $[\text{M} + \text{H}]^+$ 382.0807, found 382.0805.



2-(4-Chlorobenzyl)-N-(4-methoxybenzyl)aniline (4ha)

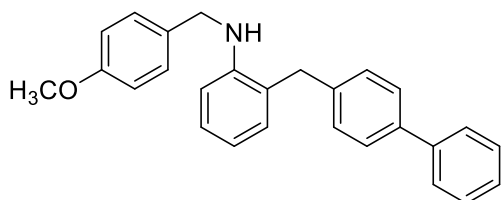
Yellow solid; 78% yield, m. p. 46-49 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 8.0$ Hz, 2H), 7.09-7.05 (m, 1H), 6.99-6.92 (m, 5H), 6.72 (d,

$J = 8.0$ Hz, 2H), 6.65-6.61 (m, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 4.07 (s, 2H), 3.74 (s, 2H), 3.69 (s, 3H), 3.61 (br.s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 146.0, 138.0, 132.3, 131.3, 130.7, 130.0, 128.9, 128.7, 128.2, 124.1, 117.4, 114.1, 111.1, 55.4, 47.7, 37.6. IR (neat): ν 1602, 1513, 1364, 1248, 747 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{ClNO} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 360.1131, found 360.1133.



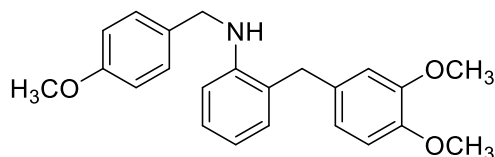
***N*-(4-Methoxybenzyl)-2-(4-methylbenzyl)aniline (4ia)**

Pale yellow oil; 77% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.11 (m, 1H), 7.08-7.02 (m, 5H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.72-6.68 (m, 1H), 6.61 (d, $J = 8.0$ Hz, 1H), 4.16 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 146.2, 136.3, 136.0, 131.5, 130.6, 129.5, 128.6, 127.9, 125.0, 117.3, 114.0, 111.0, 55.4, 47.6, 38.0, 21.2. IR (neat): ν 1603, 1514, 1360, 1248, 1175, 748 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{23}\text{NO} + \text{H}$ $[\text{M} + \text{H}]^+$ 318.1858, found 318.1856.



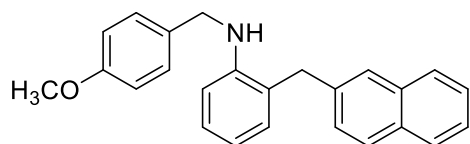
2-([1,1'-Biphenyl]-4-ylmethyl)-*N*-(4-methoxybenzyl)aniline (4ja)

Yellow solid; 75% yield; m. p. 75-77 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.35-7.31 (m, 2H), 7.25-7.21 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.10-7.06 (m, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.67-6.63 (m, 3H), 6.56 (d, $J = 8.0$ Hz, 1H), 4.08 (s, 2H), 3.83 (s, 2H), 3.74 (br.s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 146.2, 141.0, 139.4, 138.6, 131.3, 130.7, 129.1, 128.9, 128.6, 128.0, 127.5, 127.3, 127.1, 124.6, 117.3, 114.0, 111.0, 55.3, 47.7, 38.0. IR (KBr): ν 1599, 1511, 1365, 1250, 747 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{27}\text{H}_{25}\text{NO} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 402.1834, found 402.1838.



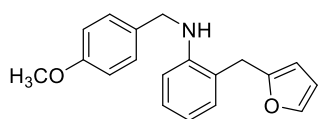
2-(3,4-Dimethoxybenzyl)-*N*-(4-methoxybenzyl)aniline (4ka)

Pale yellow solid; 63% yield; m. p. 102-105 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.16 (m, 1H), 7.10-7.06 (m, 3H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.73-6.70 (m, 2H), 6.67 (d, $J = 8.0$ Hz, 1H), 4.19 (s, 2H), 3.88 (s, 3H), 3.85 (s, 2H), 3.80 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 149.2, 147.7, 146.2, 131.9, 131.4, 130.4, 128.7, 127.9, 125.0, 120.6, 117.3, 114.0, 111.9, 111.5, 110.9, 56.0, 55.8, 55.3, 47.7, 38.0. IR (KBr): ν 1598, 1365, 1136, 777 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_3 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 386.1732, found 386.1736.



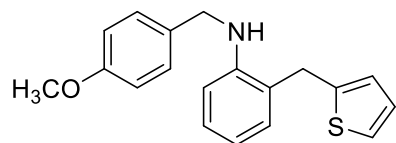
***N*-(4-Methoxybenzyl)-2-(naphthalen-2-ylmethyl)aniline (4la)**

Pale yellow solid; 76% yield; m. p. 89-91 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.70 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.47 (s, 1H), 7.36-7.34 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.11-7.07 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.68-6.64 (m, 1H), 6.56-6.52 (m, 3H), 4.02 (s, 2H), 3.95 (s, 2H), 3.79 (br.s, 1H), 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 146.3, 137.0, 133.8, 132.4, 131.3, 128.5, 128.1, 127.8, 127.7, 127.2, 127.0, 126.2, 125.6, 124.5, 117.3, 113.9, 111.0, 55.3, 47.6, 38.7. IR (KBr): ν 1599, 1511, 1356, 1247 cm⁻¹. ESI HRMS: calcd. for C₂₅H₂₃NO +H [M+H]⁺ 354.1858, found 354.1857.



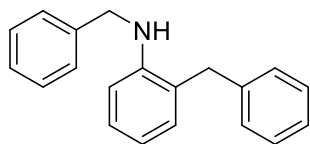
2-(Furan-2-ylmethyl)-*N*-(4-methoxybenzyl)aniline (4ma)

Yellow solid; 42% yield; m. p. 98-100 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.65-6.61 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 4.0 Hz, 1H), 5.91 (d, *J* = 4.0 Hz, 1H), 4.16 (s, 2H), 3.79 (s, 2H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 153.4, 146.2, 141.7, 131.4, 130.3, 128.8, 128.3, 122.5, 117.5, 114.1, 111.2, 110.5, 106.5, 55.4, 47.7, 31.2. IR (KBr): ν 1600, 1513, 1354, 1244 cm⁻¹. ESI HRMS: calcd. for C₁₉H₁₉NO₂ +H [M+H]⁺ 294.1494, found 294.1496.



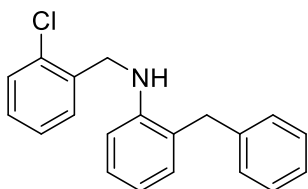
***N*-(4-Methoxybenzyl)-2-(thiophen-2-ylmethyl)aniline (4na)**

Pale yellow solid; 73% yield; m. p. 113-115 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.02 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.83-6.81 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 4.0 Hz, 1H), 6.65-6.61 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.11 (s, 2H), 3.96 (s, 2H), 3.86 (br.s, 1H), 3.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 146.1, 143.0, 131.3, 130.1, 128.6, 128.3, 127.0, 125.3, 124.5, 124.2, 117.4, 114.1, 111.3, 55.4, 47.7, 32.8. IR (KBr): ν 1599, 1510, 1353, 1241, 1172, cm⁻¹. ESI HRMS: calcd. for C₁₉H₁₉NOS +H [M+H]⁺ 310.1266, found 310.1268.



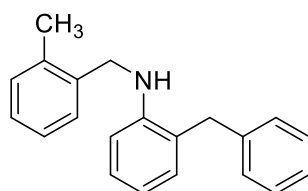
***N*,2-Dibenzylaniline (4ab)**

Yellow solid; 73% yield; m. p. 50-52 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.12 (m, 6H), 7.09 (d, *J* = 4.0 Hz, 2H), 7.05 (d, *J* = 4.0 Hz, 1H), 7.01-6.98 (m, 3H), 6.66-6.62 (m, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 2H), 3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 139.5, 139.4, 130.8, 128.8, 128.7, 128.6, 128.0, 127.3, 127.2, 126.5, 124.8, 117.4, 111.0, 48.1, 38.4. IR (KBr): ν 1602, 1509, 1450, 1360, 1122 cm⁻¹. ESI HRMS: calcd. for C₂₀H₁₉N +Na [M+Na]⁺ 296.1415, found 296.1418.



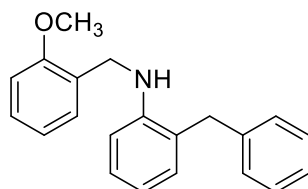
2-Benzyl-N-(2-chlorobenzyl)aniline (4ac)

Yellow oil; 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.18 (m, 3H), 7.15-7.10 (m, 3H), 7.08-6.98 (m, 4H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.66-6.63 (m, 1H), 6.46 (d, $J = 12.0$ Hz, 1H), 4.28 (s, 2H), 3.95 (br.s, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 139.4, 136.7, 133.3, 130.9, 129.5, 128.8, 128.7, 128.6, 128.3, 128.0, 126.9, 126.6, 124.8, 117.6, 111.1, 45.5, 38.4. IR (neat): ν 1604, 1514, 1357, 1266 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{18}\text{ClN} + \text{H}$ $[\text{M}+\text{H}]^+$ 308.1206, found 308.1208.



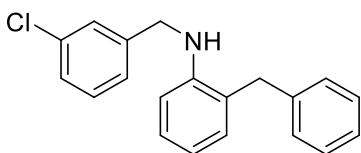
2-Benzyl-N-(2-methylbenzyl)aniline (4ad)

Pale yellow solid; 80% yield; m. p. 72-74 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.14 (m, 2H), 7.13-7.10 (m, 2H), 7.07-7.05 (m, 4H), 7.03-7.00 (m, 2H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.67-6.64 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 4.10 (s, 2H), 3.80 (s, 2H), 3.64 (br.s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 139.5, 136.9, 136.31, 130.8, 130.4, 128.8, 128.7, 128.0, 127.4, 126.5, 126.2, 124.7, 117.3, 110.7, 46.2, 38.4, 18.8. IR (KBr): ν 1599, 1509, 1355, 1264 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{N} + \text{Na}$ $[\text{M}+\text{Na}]^+$ 310.1572, found 310.1576.



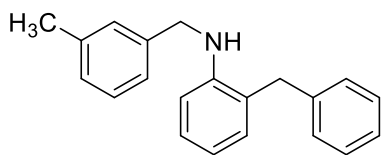
2-Benzyl-N-(2-methoxybenzyl)aniline (4ae)

Yellow oil; 75% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.15 (m, 2H), 7.11-7.06 (m, 5H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.74-6.69 (m, 2H), 6.62-6.57 (m, 2H), 4.18 (s, 2H), 3.93 (br.s, 1H), 3.80 (s, 2H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4, 146.4, 139.6, 130.7, 128.7, 128.7, 128.2, 127.9, 127.3, 126.4, 124.8, 120.5, 117.2, 111.2, 110.2, 55.2, 43.3, 38.2. IR (neat): ν 1512, 1461, 1354, 1242 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{NO} + \text{H}$ $[\text{M}+\text{H}]^+$ 304.1701, found 304.1705.



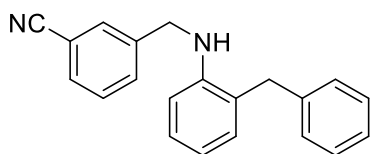
2-Benzyl-N-(3-chlorobenzyl)aniline (4af)

Yellow oil; 52% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.18 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.09-7.05 (m, 4H), 7.03-6.99 (m, 2H), 6.96 (s, 1H), 6.86 (d, $J = 4.0$ Hz, 1H), 6.66-6.62 (m, 1H), 6.44 (d, $J = 8.0$ Hz, 1H), 4.11 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 141.7, 139.3, 134.5, 130.9, 129.9, 128.9, 128.6, 128.0, 127.3, 127.2, 126.7, 125.3, 124.8, 117.6, 111.0, 47.5, 38.5. IR (neat): ν 1599, 1514, 1352, 1268, 1076 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{18}\text{ClN} + \text{Na}$ $[\text{M}+\text{Na}]^+$ 330.1025, found 330.1028.



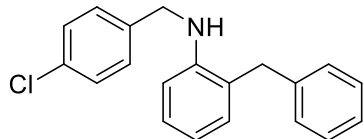
2-Benzyl-N-(3-methylbenzyl)aniline (4ag)

Yellow oil; 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.18 (m, 2H), 7.16-7.14 (m, 1H), 7.11-7.05 (m, 4H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.83-6.79 (m, 2H), 6.66-6.63 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 4.12 (s, 2H), 3.83 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 139.5, 139.3, 138.3, 130.8, 128.8, 128.7, 128.5, 128.0, 128.0, 127.9, 126.6, 124.7, 124.5, 117.3, 111.0, 48.3, 38.4, 21.5. IR (neat): ν 1603, 1513, 1453, 1353, 1266 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{N} + \text{H}$ $[\text{M} + \text{H}]^+$ 288.1752, found 288.1750.



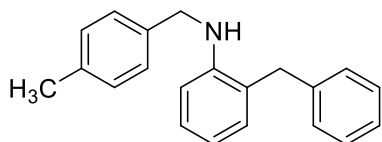
3-(((2-Benzylphenyl)amino)methyl)benzonitrile (4ah)

Yellow solid; 57% yield; m. p. 92-94 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.0$ Hz, 1H), 7.26-7.16 (m, 6H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.05-7.01 (m, 2H), 6.68-6.65 (m, 1H), 6.38 (d, $J = 8.0$ Hz, 1H), 4.18 (s, 2H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 141.1, 139.3, 131.5, 131.1, 130.9, 130.4, 129.3, 128.9, 128.5, 128.0, 126.9, 124.9, 118.9, 117.9, 112.7, 110.9, 47.0, 38.5. IR (KBr): ν 2230, 1599, 1364, 1268, 1070 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{18}\text{N}_2 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 321.1368, found 321.1366.



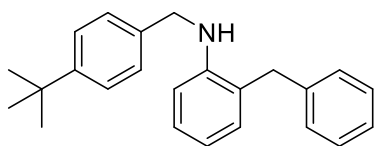
2-Benzyl-N-(4-chlorobenzyl)aniline (4ai)

Pale yellow solid; 66% yield; m. p. 74-75 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.19 (m, 2H), 7.15 (d, $J = 4.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.10-7.08 (m, 2H), 7.05-7.01 (m, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 6.68-6.64 (m, 1H), 6.47 (d, $J = 8.0$ Hz, 1H), 4.13 (s, 2H), 3.84 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.7, 139.4, 138.0, 132.8, 130.9, 128.9, 128.8, 128.6, 128.5, 128.0, 126.6, 124.8, 117.6, 111.1, 47.4, 38.5. IR (KBr): ν 1604, 1513, 1453, 1269, 1091, 811 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{18}\text{ClN} + \text{H}$ $[\text{M} + \text{H}]^+$ 308.1206, found 308.1209.



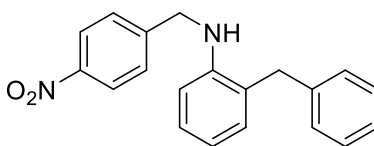
2-Benzyl-N-(4-methylbenzyl)aniline (4aj)

Yellow oil; 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.18 (m, 2H), 7.15 (d, $J = 4.0$ Hz, 1H), 7.09 (d, $J = 4.0$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.99-6.97 (m, 3H), 6.89 (d, $J = 8.0$ Hz, 2H), 6.65-6.62 (m, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 4.12 (s, 2H), 3.82 (s, 2H), 3.78 (br.s, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 139.5, 136.8, 136.3, 130.7, 129.3, 128.8, 128.7, 128.0, 127.3, 126.5, 124.7, 117.3, 111.0, 47.9, 38.4, 21.2. IR (neat): ν 1604, 1513, 1453, 1354, 802 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{N} + \text{H}$ $[\text{M} + \text{H}]^+$ 288.1752, found 288.1750.



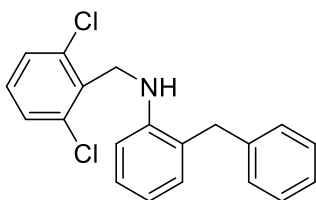
2-Benzyl-N-(4-(*tert*-butyl)benzyl)aniline (4ak)

Yellow oil; 66% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.20 (m, 4H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.11-7.06 (m, 3H), 7.00-6.96 (m, 3H), 6.67-6.63 (m, 1H), 6.58 (d, $J = 8.0$ Hz, 1H), 4.15 (s, 2H), 3.83 (s, 2H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 146.2, 139.5, 136.3, 130.7, 128.8, 128.8, 128.0, 127.1, 126.5, 125.6, 124.8, 117.3, 111.0, 47.9, 38.3, 34.6, 31.5. IR (neat): ν 1603, 1513, 1364, 1266, 746 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{27}\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 352.2041, found 352.2045.



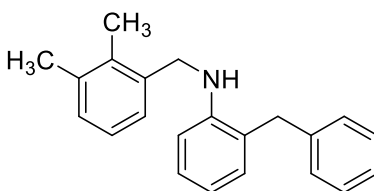
2-Benzyl-N-(4-nitrobenzyl)aniline (4al)

Yellow solid; 76% yield; m. p. 97-99 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 12.0$ Hz, 2H), 7.32-7.28 (m, 2H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.20-7.16 (m, 4H), 7.13 (d, $J = 4.0$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 6.77-6.73 (m, 1H), 6.44 (d, $J = 8.0$ Hz, 1H), 4.35 (s, 2H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 147.1, 145.1, 139.3, 131.2, 128.9, 128.6, 128.0, 127.6, 126.7, 124.9, 123.8, 118.0, 111.0, 47.2, 38.5. IR (KBr): ν 1602, 1519, 1453, 1343, 1264, 759 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2 + \text{H}$ $[\text{M} + \text{H}]^+$ 319.1447, found 319.1445.



2-Benzyl-N-(2,6-dichlorobenzyl)aniline (4am)

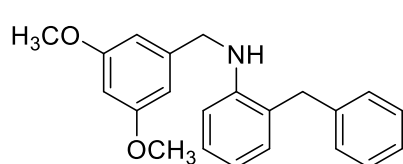
Pale yellow oil; 57% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.17-7.12 (m, 5H), 7.10-7.07 (m, 1H), 7.05-7.01 (m, 3H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.68-6.65 (m, 1H), 4.41 (s, 2H), 3.80 (br.s, 1H), 3.76 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.7, 139.4, 138.0, 132.8, 130.9, 128.9, 128.8, 128.6, 128.5, 128.0, 126.6, 124.8, 117.6, 111.1, 47.4, 38.5. IR (neat): ν 1602, 1436, 1353, 1255, 1189 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 364.0636, found 364.0638.



2-Benzyl-N-(2,3-dimethylbenzyl)aniline (4an)

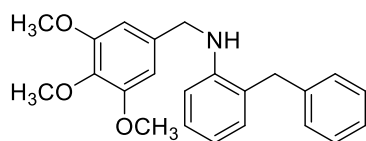
Pale yellow oil; 77% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.17-7.08 (m, 4H), 7.04 (d, $J = 4.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.93-6.89 (m, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.66-6.63 (m, 1H), 6.58 (d, $J = 8.0$ Hz, 1H), 4.09 (s, 2H), 3.76 (s, 2H), 3.57 (br.s, 1H), 2.17 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 139.5, 137.1, 136.8, 135.1, 130.7, 129.2, 128.7, 128.7, 128.0, 126.5, 126.4, 125.6, 124.7, 117.2, 110.7, 47.0, 38.3, 20.5, 14.5. IR (neat): ν 1603, 1513, 1453, 1354, 1264 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{23}\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 324.1728,

found 324.1726.



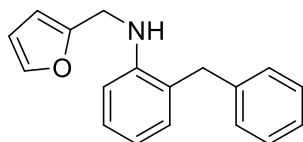
2-Benzyl-N-(3,5-dimethoxybenzyl)aniline (4ao)

Yellow oil; 55% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.18 (m, 2H), 7.14-7.10 (m, 3H), 7.08-7.04 (m, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.66-6.63 (m, 1H), 6.52 (d, $J = 8.0$ Hz, 1H), 6.25 (s, 3H), 4.12 (s, 2H), 3.84 (s, 2H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 146.0, 142.1, 139.5, 130.8, 128.8, 128.6, 128.0, 126.5, 124.7, 117.4, 111.1, 105.1, 99.3, 55.4, 48.3, 38.3. IR (neat): ν 1597, 1357, 1261, 1203, 1066 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{23}\text{NO}_2 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 356.1626, found 356.1624.



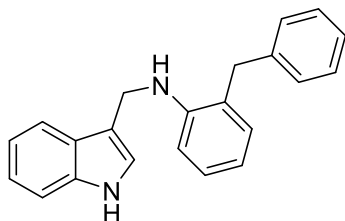
2-Benzyl-N-(3,4,5-trimethoxybenzyl)aniline (4ap)

Pale yellow solid; 78% yield; m. p. 95-96 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.18 (m, 2H), 7.14-7.07 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 1H), 6.70-6.66 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 6.30 (s, 2H), 4.12 (s, 2H), 3.86 (s, 2H), 3.74 (s, 3H), 3.67 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 145.9, 139.5, 137.0, 135.1, 130.8, 128.7, 128.5, 128.0, 126.4, 124.5, 117.5, 111.0, 104.0, 60.9, 56.1, 48.4, 38.3. IR (KBr): ν 1598, 1508, 1352, 1234, 1124 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_3 + \text{H}$ $[\text{M} + \text{H}]^+$ 364.1913, found 364.1916.



2-Benzyl-N-(furan-2-ylmethyl)aniline (4aq)

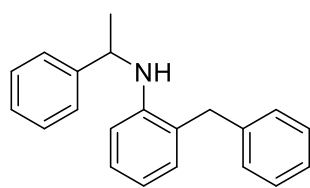
Yellow oil; 62% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.17 (m, 3H), 7.14-7.07 (m, 4H), 6.97 (d, $J = 8.0$ Hz, 1H), 6.68-6.64 (m, 1H), 6.61 (d, $J = 8.0$ Hz, 1H), 6.18-6.16 (m, 1H), 5.92 (d, $J = 4.0$ Hz, 1H), 4.15 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 145.7, 141.8, 139.3, 130.7, 128.8, 128.7, 127.9, 126.5, 125.2, 117.9, 111.2, 110.4, 106.6, 41.4, 38.1. IR (neat): ν 1603, 1513, 1364, 1259, 1146 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{18}\text{H}_{17}\text{NO} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 286.1208, found 286.1206.



N-((1H-Indol-3-yl)methyl)-2-benzylaniline (4ar)

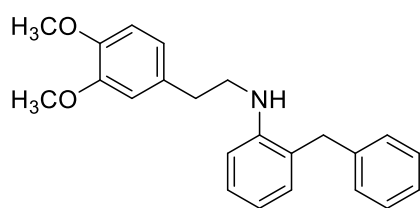
Brownish red oil; 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 7.16-7.10 (m, 6H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.85 (s, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 6.69-6.65 (m, 1H), 4.34 (s, 2H), 3.77 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 139.5, 130.6, 128.8, 128.7, 128.0, 126.7, 126.4, 124.8, 122.6, 122.3, 119.8, 119.0, 117.2, 113.9, 111.2, 110.9, 40.1, 38.1. IR (neat): ν 1598,

1454, 1364, 1264, 1072 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 335.1524, found 335.1526.



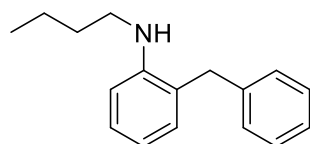
2-Benzyl-N-(1-phenylethyl)aniline (4as)

Yellow solid; 74% yield; m. p. 80-81 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.21 (m, 2H), 7.16-7.10 (m, 5H), 7.08-7.04 (m, 1H), 7.00-6.95 (m, 3H), 6.93-6.89 (m, 1H), 6.58-6.54 (m, 1H), 6.28 (d, $J = 8.0$ Hz, 1H), 4.31-4.30 (m, 1H), 3.87 (s, 2H), 3.81 (s, 1H), 1.20 (d, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 139.7, 130.8, 128.8, 128.7, 128.6, 127.9, 126.8, 126.7, 125.8, 124.5, 117.0, 112.0, 53.2, 38.8, 25.1. IR (KBr): ν 1601, 1513, 1450, 1367, 1068 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{N} + \text{H}$ $[\text{M} + \text{H}]^+$ 288.1752, found 288.1754.



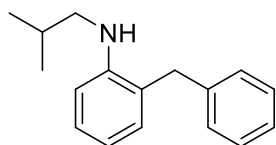
2-Benzyl-N-(3,4-dimethoxyphenethyl)aniline (4at)

Yellow oil; 53% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.08 (m, 4H), 6.97-6.94 (m, 3H), 6.67-6.61 (m, 3H), 6.57-6.55 (m, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 3.67 (s, 2H), 3.44 (br.s, 1H), 3.23 (t, $J = 12.0$ Hz, 2H), 2.67 (t, $J = 12.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 147.7, 146.2, 139.3, 131.7, 130.7, 128.6, 128.5, 127.9, 126.3, 124.9, 120.7, 117.3, 111.9, 111.4, 110.9, 56.0, 55.9, 45.0, 38.0, 35.1. IR (neat): ν 1603, 1514, 1453, 1365, 1262 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_2 + \text{Na}$ $[\text{M} + \text{Na}]^+$ 370.1783, found 370.1780.



2-Benzyl-N-butylaniline (4au)

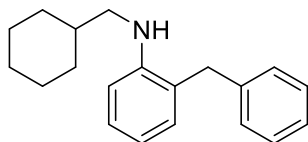
Yellow oil; 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.17 (m, 2H), 7.13-7.09 (m, 4H), 6.97 (d, $J = 8.0$ Hz, 1H), 6.63-6.60 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 3.79 (s, 2H), 3.35 (br.s, 1H), 2.93 (t, $J = 12.0$ Hz, 2H), 1.40-1.32 (m, 2H), 1.16-1.07 (m, 2H), 0.76 (t, $J = 16.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 139.6, 130.7, 128.8, 128.6, 128.0, 126.5, 124.6, 116.8, 43.5, 38.4, 31.4, 20.2, 13.9. IR (neat): ν 1604, 1513, 1453, 1314, 1267 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{17}\text{H}_{21}\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 262.1572, found 262.1573.



2-Benzyl-N-isobutylaniline (4av)

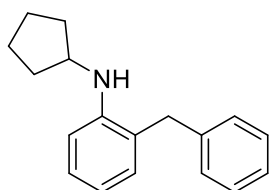
Yellow oil; 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.18 (m, 2H), 7.13-7.08 (m, 4H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.64-6.60 (m, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 3.81 (s, 2H), 3.44 (br.s, 1H), 2.76 (d, $J = 4.0$ Hz, 2H), 1.69-1.62 (m, 1H), 0.71 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 139.6, 130.8, 128.8, 128.6, 128.0, 126.6, 124.5, 116.7, 110.5, 51.7, 38.6, 27.8, 20.4. IR

(neat): ν 1602, 1364, 1259, 1070 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{17}\text{H}_{21}\text{N} + \text{H}$ $[\text{M} + \text{H}]^+$ 240.1752, found 240.1750.



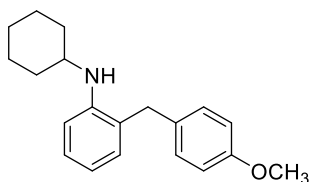
2-Benzyl-N-(cyclohexylmethyl)aniline (4aw)

Yellow oil; 54% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.17 (m, 2H), 7.13-7.08 (m, 4H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.63-6.59 (m, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 3.80 (s, 2H), 3.45 (br.s, 1H), 2.78 (d, $J = 4.0$ Hz, 2H), 1.55-1.54 (m, 3H), 1.43-1.40 (m, 2H), 1.34-1.31 (m, 1H), 1.09-1.03 (m, 3H), 0.74-0.68 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 139.7, 130.8, 128.8, 128.6, 127.9, 126.5, 124.5, 116.6, 110.5, 50.4, 38.6, 37.4, 31.1, 26.6, 26.1. IR (neat): ν 1604, 1513, 1450, 1314, 1263 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{25}\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 302.1885, found 302.1883.



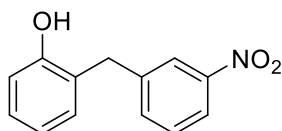
2-Benzyl-N-cyclopentylaniline (4ax)

Yellow solid; 61% yield; m. p. 67-69 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.17 (m, 2H), 7.13-7.07 (m, 4H), 6.97 (d, $J = 8.0$ Hz, 1H), 6.62-6.57 (m, 2H), 3.77 (s, 2H), 3.67-3.64 (m, 1H), 3.38 (br.s, 1H), 1.79-1.74 (m, 2H), 1.41-1.36 (m, 4H), 1.22-1.18 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 139.7, 130.8, 128.8, 128.6, 127.9, 126.5, 124.7, 116.6, 111.6, 54.4, 38.6, 33.5, 23.9. IR (KBr): ν 1604, 1511, 1453, 1354, 1073 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{18}\text{H}_{21}\text{N} + \text{Na}$ $[\text{M} + \text{Na}]^+$ 274.1572, found 274.1575.



N-Cyclohexyl-2-(4-methoxybenzyl)aniline (4py)

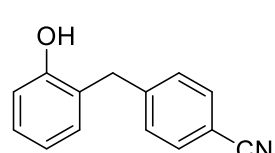
Yellow oil; 44% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.09-7.05 (m, 1H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.96 (d, $J = 4.0$ Hz, 1H), 6.75 (d, $J = 12.0$ Hz, 2H), 6.60-6.56 (m, 2H), 3.72 (s, 2H), 3.70 (s, 3H), 3.37 (br.s, 1H), 3.17-3.13 (m, 1H), 1.79-1.77 (m, 2H), 1.52-1.49 (m, 3H), 1.23-1.18 (m, 2H), 1.11-1.06 (m, 1H), 0.97-0.88 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 145.5, 131.6, 130.8, 129.6, 127.8, 124.9, 116.4, 114.2, 111.2, 55.4, 51.2, 37.7, 33.2, 26.0, 24.7. IR (neat): ν 1602, 1511, 1355, 1246 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{25}\text{NO} + \text{H}$ $[\text{M} + \text{H}]^+$ 296.2014, found 296.2016.



2-(3-Nitrobenzyl)phenol (5f)

Pale yellow oil; 43% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.36-7.32 (m, 1H), 7.08-7.04 (m, 2H), 6.84-6.81 (m, 1H), 6.69 (d, $J = 4.0$ Hz, 1H), 5.06 (s, 1H), 4.00 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 148.4, 143.0, 135.2, 131.0, 129.3, 128.4, 126.1, 123.8, 121.2, 115.7, 35.9. IR (neat): ν 3450, 1595, 1528, 1355, 1096 cm^{-1} .

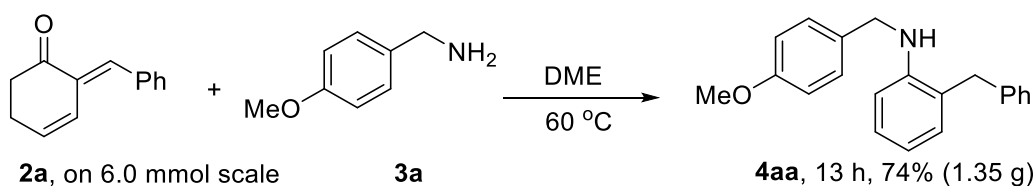
cm⁻¹. ESI HRMS: calcd. for C₁₃H₁₁NO₃+H [M+H]⁺ 230.0817, found 230.0815.



4-(2-Hydroxybenzyl)benzonitrile (**5o**)

White solid; 93% yield; m. p. 124-126 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 12.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14-7.10 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.90-6.86 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 4.02 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 147.0, 132.2, 131.0, 128.2, 125.9, 120.9, 119.2, 115.6, 109.3, 36.3. IR (KBr): ν 3364, 2239, 1591, 1454, 1358, 1225, 756 cm⁻¹. ESI HRMS: calcd. for C₁₄H₁₁NO+H [M+H]⁺ 210.0919, found 210.0917.

IV. Gram-scale synthesis of **4aa**.



In a vial containing a magnetic stirrer was placed (*E*)-2-benzylidenecyclohex-3-en-1-one (**2a**, 1.11 g, 6.0 mmol), (4-methoxyphenyl)methanamine (**3a**, 8.23 g, 60.0 mmol) and DME (60 mL). The reaction mixture was stirred at 60 °C and the reaction process was monitored by TLC analysis. After completion, the solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give product **4aa** in 74% yield.

V. Successive one-pot synthesis of **4aa**.

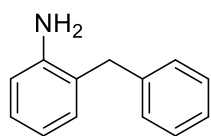
(4-Methoxyphenyl)methanamine (**3a**, 0.27 g, 2.0 mmol) was added to a solution of (*E*)-2-benzylidenecyclohex-3-en-1-one (**2a**, 36.8 mg, 0.2 mmol) in DME (2 mL). The reaction mixture was stirred at 60 °C and monitored by TLC analysis. Upon full conversion of **2a**, **3a** (27.4 mg, 0.2 mmol, 1 equiv) and **2a** (36.8 mg, 0.2 mmol, 1 equiv) were added synchronously. After running five times of the experiments, the solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give product **4aa** in 65% yield.

VI. Derivation of the products

1. Procedure for preparation of 2-benzylaniline (**6**)

In a vial containing a magnetic stirrer was added 2-benzyl-*N*-(4-methoxybenzyl)aniline (**4aa**, 60.6 mg, 0.2

mmol), Pd(OH)₂ (12.2 mg, 20 wt %) and MeOH (10 mL) under H₂ atmosphere (1 atm). The reaction mixture was stirred at 40 °C and monitored by TLC. After 3 h, the reaction mixture was quenched with water and then extracted three times with ethyl acetate. The combined organic layer was washed successively with water and dried over NaSO₄. The solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give product **6**.

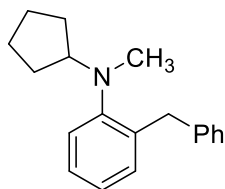


2-Benzylaniline (**6**)

Pale yellow solid; 82% yield, m. p. 53-55 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.23-7.19 (m, 2H), 7.16-7.10 (m, 3H), 7.04-6.98 (m, 2H), 6.71-6.68 (m, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 2H), 3.13 (br.s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 139.5, 131.0, 128.8, 128.6, 127.8, 126.5, 125.2, 118.9, 116.1, 38.2. IR (KBr): ν 1593, 1365, 1265, 1067 cm⁻¹. ESI HRMS: calcd. for C₁₃H₁₃N+Na [M+Na]⁺ 206.0946, found 206.0942.

2. Procedure for the preparation of 2-benzyl-*N*-cyclopentyl-*N*-methylaniline (**7**)

2-Benzyl-*N*-cyclopentylaniline (**4ax**, 50.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol) and CH₃CN (10 mL) were added to a round-bottom flask within a magnetic stirrer. After stirring for 30 min at room temperature, MeI (249.0 μL, 4.0 mmol) was added dropwise and the reaction mixture was continued to stir at room temperature for 72 h. After completion, the solvent was removed under vacuum and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 60:1) to give product **7**.



2-Benzyl-*N*-cyclopentyl-*N*-methylaniline (**7**)

Pale yellow oil; 98% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.12 (m, 7H), 7.08 (d, *J* = 4.0 Hz, 1H), 7.00-6.97 (m, 1H), 4.09 (s, 2H), 3.38-3.34 (m, 1H), 2.48 (s, 3H), 1.71-1.65 (m, 2H), 1.61-1.58 (m, 2H), 1.49-1.45 (m, 2H), 1.41-1.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 142.1, 138.4, 130.6, 129.3, 128.2, 126.9, 125.7, 124.2, 123.1, 65.1, 42.6, 36.9, 31.5, 24.4. IR (neat): ν 1597, 1492, 1451, 1355, 1268 cm⁻¹. ESI HRMS: calcd. for C₁₉H₂₃N+Na [M+Na]⁺ 288.1728, found 288.1726.

VII. References.

- [1] Ren, H.-X.; Song, X.-J.; Wu, L.; Huang, Z.-C.; Zou, Y.; Li, X.; Chen, X.-W.; Tian, F.; Wang, L.-X. *Eur. J. Org. Chem.* **2019**, 715-719.
- [2] Jiang, L.; Li, L.; Li, M.; Yuan, M.-W.; Yuan, M.-L. *Synthetic Commun.* **2023**, 53, 1520-1528.
- [3] Rosamilia, A. E.; Scott, J. L.; Strauss, C. R. *Org. Lett.* **2005**, 7, 1525-1528.

VIII. Copies of ^1H and ^{13}C NMR spectra of new compounds.

