

Supporting Information

Pd-catalyzed chemoselective threefold cross-coupling of triarylbismuths with benzylic bromides

Maddali L.N. Rao^{*}, Ritesh J. Dhanorkar

*Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016,
India*

maddali@iitk.ac.in

Contents

1.	General Experimental.....	S2
2.	Experimental procedure of cross-coupling reactions.....	S2
3.	Characterization data of cross-coupling products.....	S3-S18
4.	References.....	S19

1. General Information

All reactions were performed in an oven-dried schlenk tubes under N₂ atmosphere. Triarylbiomuths were prepared according to the standard literature procedures.¹ Benzylic bromides were prepared according to literature methods.² Potassium phosphate was purchased from Himedia chemicals and was used as such for coupling reactions. *N,N*-dimethyl acetamide (DMA) was dried over calcium sulphate and distilled under high vacuum at 50-60 °C before using for the reaction. All other solvents were purified according to the standard methods. Column chromatography was performed on 100-200 mesh silica gel using hexane:ethyl acetate as eluent. Crude reaction mixtures and pure products were analyzed by Gas Chromatography (Perkin Elmer). ¹H NMR and ¹³C NMR spectra were recorded on a JEOL-Lambda (500 MHz) spectrometer using CDCl₃ as solvent. HRMS spectra were measured on Waters CAB155 GCT Premier analyzer.

2. Experimental:

Representative cross-coupling procedure:

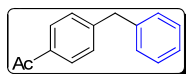
A hot-oven dried schlenk tube was charged with 4-acetylbenzyl bromide (0.875 mmol, 0.186 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), K₃PO₄ (1.5 mmol, 0.318 g), Pd(PPh₃)₄ (0.0225 mmol, 0.026 g) and DMA (3 mL) solvent under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 1 hour, cooled to rt, quenched with water (10 mL) and extracted with ethyl acetate (3x20 mL). The combined organic extract was washed with water (2x10 mL), brine (10 mL), dried over anhydrous MgSO₄ and concentrated. The crude product mixture was purified using silica gel by column chromatography (1% EtOAc/Hexane) to afford 1-(4-Benzylphenyl)ethanone (**2.1**) as colourless oil (0.111 g, 71%).

Note: In the case of products **3.34-3.37**, the corresponding benzyl bromides were added after addition of the solvent in the above procedure.

All the products were identified by spectroscopic analysis.

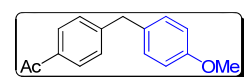
3. Characterization data

4-Acetyldiphenylmethane³ (2.1)



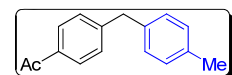
Colorless liquid (111 mg, 71%), R_f (5% EtOAc/Hexane) 0.27; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 7.8 Hz, 2H), 7.32-7.17 (m, 7H), 4.03 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.84, 146.79, 139.99, 135.16, 129.21, 129.07, 128.89, 128.62, 126.38, 41.85, 26.61. IR (neat, cm^{-1}): 2924, 1682, 1606, 1357, 1267, 1181, 953, 815, 591, 567. HRMS (ES^+): calcd. for $\text{C}_{15}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}]^+$ 211.1123; found 211.1124.

1-(4-(4-Methoxybenzyl)phenyl)ethanone⁴ (2.2)



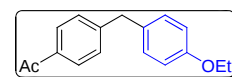
White solid (134 mg, 75%), mp 42-44 °C, R_f (5% EtOAc/Hexane) 0.20; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.97 (s, 2H), 3.78 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.77, 158.16, 147.27, 135.15, 132.09, 129.86, 128.94, 128.59, 114.0, 55.23, 40.98, 26.52. IR (KBr, cm^{-1}): 1675, 1603, 1511, 1411, 1359, 1269, 1250, 1208, 1109, 1074, 1017, 915, 809, 599. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240.1150; found 240.1154.

1-(4-(4-Methylbenzyl)phenyl)ethanone (2.3)



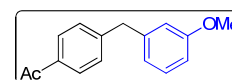
White solid (109 mg, 65%), mp 67-69 °C, R_f (5% EtOAc/Hexane) 0.30; ^1H NMR (500 MHz, CDCl_3): δ 7.87 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.05 Hz, 2H), 7.06 (d, J = 8.05 Hz, 2H), 3.98 (s, 2H), 2.56 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.78, 147.11, 136.95, 135.92, 135.16, 129.28, 129.01, 128.78, 128.59, 41.46, 26.53, 20.98. IR (KBr, cm^{-1}): 2921, 1680, 1603, 1511, 1411, 1356, 1269, 957, 866, 815, 799, 597. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 224.1201; found 224.1203.

1-(4-(4-Ethoxybenzyl)phenyl)ethanone (2.4)



Pale yellow liquid (132 mg, 70%), R_f (5% EtOAc/Hexane) 0.25; ^1H NMR (500 MHz, CDCl_3): δ 7.86 (d, J = 8.25 Hz, 2H), 7.25 (d, J = 7.95 Hz, 2H), 7.06 (d, J = 8.55 Hz, 2H), 6.81 (d, J = 8.55 Hz, 2H), 3.99 (q, J = 6.9 Hz, 2H), 3.95 (s, 2H), 2.55 (s, 3H), 1.38 (t, J = 7.02 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.81, 157.51, 147.33, 135.12, 131.94, 129.88, 129.01, 128.58, 114.61, 63.39, 40.99, 26.56, 14.80. IR (neat, cm^{-1}): 2980, 2926, 1511, 1681, 1607, 1510, 1412, 1358, 1267, 1245, 1077, 1115, 1047, 810, 680, 602. HRMS (ES^+): calcd. for $\text{C}_{17}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 255.1385; found 255.1384.

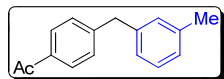
1-(4-(3-Methoxybenzyl)phenyl)ethanone (2.5)



Brown liquid (113 mg, 63%), R_f (5% EtOAc/Hexane) 0.20; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.23-7.20 (m, 1H), 6.77 (d, J = 8.05 Hz, 2H), 6.71 (s, 1H), 4.00 (s, 2H), 3.77 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.73, 159.76, 146.55,

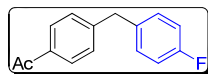
141.52, 135.22, 129.54, 129.04, 128.58, 121.28, 114.80, 111.50, 55.09, 41.84, 26.50. IR (neat, cm^{-1}): 2917, 1680, 1601, 1488, 1357, 1267, 1149, 1048, 752, 722, 698. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240.1150; found 240.1159.

1-(4-(3-Methylbenzyl)phenyl)ethanone^{3(a)} (2.6)



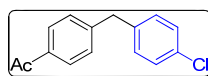
Colorless liquid (116 mg, 69%), R_f (5% EtOAc/Hexane) 0.30; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.20-7.17 (m, 1H), 7.03 (d, J = 7.45 Hz, 1H), 6.99-6.97 (m, 2H), 3.99 (s, 2H), 2.57 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.83, 146.94, 139.92, 138.23, 135.17, 129.67, 129.06, 128.60, 128.48, 127.13, 125.93, 41.82, 26.55, 21.36. IR (neat, cm^{-1}): 2919, 1681, 1604, 1412, 1267, 1181, 1017, 957, 749, 700. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 224.1201; found 224.1203.

1-(4-(4-Fluorobenzyl)phenyl)ethanone (2.7)



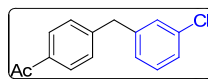
Colorless liquid (107 mg, 63%), R_f (5% EtOAc/Hexane) 0.27; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 8.4 Hz, 2H), 7.26-7.24 (m, 2H), 7.13-7.11 (m, 2H), 6.99-6.96 (m, 2H), 3.99 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.73, 161.55 (d, $J_{\text{C-F}}$ = 243.23 Hz), 146.54, 135.67, 135.35, 130.31 (d, $J_{\text{C-F}}$ = 8.35 Hz), 128.99, 128.68, 115.41 (d, $J_{\text{C-F}}$ = 21.46 Hz), 41.01, 26.55. IR (neat, cm^{-1}): 2920, 1681, 1606, 1508, 1412, 1358, 1268, 1222, 815, 583, 538. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{13}\text{FO}$ $[\text{M}]^+$ 228.0950; found 228.0950.

1-(4-(4-Chlorobenzyl)phenyl)ethanone (2.8)



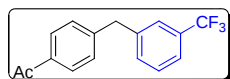
Light yellow liquid (109 mg, 60%), R_f (5% EtOAc/Hexane) 0.27; ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 8.3 Hz, 2H), 7.27-7.24 (m, 4H), 7.10 (d, J = 8.6 Hz, 2H), 3.99 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.75, 146.15, 138.46, 135.38, 132.26, 130.23, 129.13, 128.73, 128.70, 41.15, 26.57. IR (neat, cm^{-1}): 2919, 1681, 1606, 1490, 1409, 1357, 1268, 1090, 1015, 811, 791. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{13}\text{ClO}$ $[\text{M}]^+$ 244.0655; found 244.0650.

1-(4-(3-Chlorobenzyl)phenyl)ethanone (2.9)



Colorless liquid (111 mg, 61%), R_f (5% EtOAc/Hexane) 0.29; ^1H NMR (500 MHz, CDCl_3): δ 7.89 (d, J = 8.3 Hz, 2H), 7.27-7.26 (m, 2H), 7.22-7.20 (m, 2H), 7.15 (s, 1H), 7.05-7.06 (m, 1H), 4.00 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.71, 145.75, 142.00, 135.45, 134.39, 129.84, 129.08, 128.98, 128.72, 127.07, 126.62, 41.44, 26.56. IR (neat, cm^{-1}): 2920, 1681, 1606, 1595, 1412, 1357, 1267, 1181, 780. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{13}\text{ClO}$ $[\text{M}]^+$ 244.0655; found 244.0650.

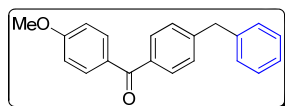
1-(4-(3-(Trifluoromethyl)benzyl)phenyl)ethanone (2.10)



Colorless liquid (110 mg, 53%), R_f (5% EtOAc/Hexane) 0.30; ^1H NMR (500 MHz, CDCl_3): δ 7.90 (d, J = 8.55 Hz, 2H), 7.48 (d, J = 7.65 Hz, 1H), 7.43 (s, 1H), 7.42-7.39 (m, 1H), 7.34 (d, J = 7.65 Hz, 1H), 7.26 (d, J = 8.55 Hz, 2H), 4.08 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.70, 145.52, 140.91, 135.54, 132.27, 131.06, 130.80, 129.07, 128.79, 125.54, 123.36, 123.33, 41.55, 26.56. IR (neat, cm^{-1}): 2919, 1681, 1606, 1595, 1412, 1357, 1267, 1181, 780.

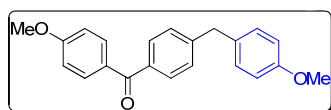
¹): 2922, 1682, 1605, 1358, 1330, 1266, 1162, 1122, 1073, 794. HRMS (ES⁺): calcd. for C₁₆H₁₃F₃O [M+H]⁺ 279.0997; found 279.0994.

(4-Benzylphenyl)(4-methoxyphenyl)methanone (3.1)



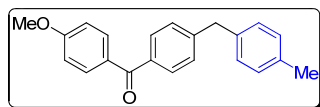
White solid (173 mg, 76%), mp 55-56 °C, *R_f* (5% EtOAc/Hexane) 0.26; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 5H), 7.25-7.21 (m, 2H), 6.95 (d, *J* = 8.75 Hz, 2H), 4.06 (s, 2H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.23, 163.06, 145.52, 140.18, 136.11, 132.44, 130.28, 130.11, 128.95, 128.67, 128.58, 126.34, 113.44, 55.48, 41.88. IR (KBr, cm⁻¹): 2920, 1649, 1601, 1414, 1313, 1282, 1256, 1170, 1029, 929, 846, 760, 700. EI (m/z) calcd. for C₂₁H₁₈O₂ [M]⁺ 302.1307; found 302.1305.

(4-(4-Methoxybenzyl)phenyl)(4-methoxyphenyl)methanone (3.2)



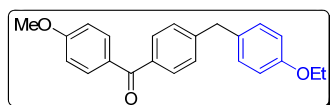
White solid (179 mg, 72%), mp 70-72 °C, *R_f* (5% EtOAc/Hexane) 0.22; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.05 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8.05 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.26, 163.05, 158.13, 146.02, 136.03, 132.44, 132.27, 130.30, 130.11, 129.90, 128.59, 113.98, 113.46, 55.48, 55.26, 40.99. IR (KBr, cm⁻¹): 2839, 1645, 1604, 1510, 1413, 1252, 1172, 1028, 929, 839, 752. EI (m/z) calcd. for C₂₂H₂₀O₃ [M]⁺ 332.1412; found 332.1413.

(4-Methoxyphenyl)(4-(4-methylbenzyl)phenyl)methanone (3.3)



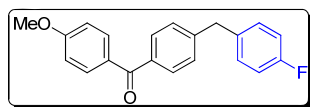
White solid (189 mg, 79%), mp 67-69 °C, *R_f* (5% EtOAc/Hexane) 0.34; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.05 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.13-7.09 (m, 4H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.01 (s, 2H), 3.88 (s, 3H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.25, 163.04, 145.86, 137.13, 136.02, 135.88, 132.44, 130.30, 130.10, 129.27, 128.83, 128.65, 113.46, 55.48, 41.47, 21.01. IR (KBr, cm⁻¹): 2919, 1649, 1602, 1510, 1415, 1313, 1282, 1256, 1170, 1029, 929, 846. EI (m/z) calcd. for C₂₂H₂₀O₂ [M]⁺ 316.1463; found 316.1461.

(4-(4-Ethoxybenzyl)phenyl)(4-methoxyphenyl)methanone (3.4)



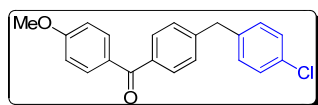
White solid (187 mg, 72%), mp 52-54 °C, *R_f* (5% EtOAc/Hexane) 0.20; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 8.75 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.05 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.01 (q, *J* = 6.9 Hz, 2H), 3.99 (s, 2H), 3.88 (s, 3H), 1.40 (t, *J* = 7.05 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.25, 163.04, 157.49, 146.06, 136.0, 132.43, 132.11, 130.30, 130.09, 129.88, 128.56, 114.53, 113.43, 63.37, 55.47, 41.0, 14.83. IR (KBr, cm⁻¹): 2971, 2923, 1645, 1605, 1509, 1318, 1265, 1242, 1170, 1116, 1021, 932, 841, 754, 685, 582. EI (m/z) calcd. for C₂₃H₂₂O₃ [M]⁺ 346.1569; found 346.1562.

(4-(4-Fluorobenzyl)phenyl)(4-methoxyphenyl)methanone (3.5)



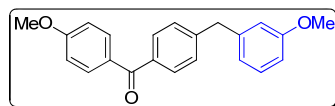
White solid (135 mg, 56%), mp 82-84 °C, R_f (5% EtOAc/Hexane) 0.35; ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 8.9 Hz, 2H), 7.70 (d, J = 8.05 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 7.17-7.15 (m, 2H), 7.01-6.98 (m, 2H), 6.95 (d, J = 8.6 Hz, 2H), 4.02 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.15, 163.11, 161.52 (d, $J_{\text{C-F}}$ = 243.22 Hz), 145.27, 136.27, 135.85, 132.44, 130.50, 130.16 (d, $J_{\text{C-F}}$ = 8.3 Hz), 128.71, 128.48, 115.41, 113.49 (d, $J_{\text{C-F}}$ = 29.8 Hz), 55.53, 41.01. IR (KBr, cm^{-1}): 2927, 1645, 1603, 1504, 1316, 1282, 1264, 1217, 1022, 931, 843, 831, 750, 663. HRMS (ES^+): calcd. for $\text{C}_{21}\text{H}_{18}\text{FO}_2$ [$\text{M}+\text{H}$] $^+$ 321.1291; found 321.1290.

(4-(4-Chlorobenzyl)phenyl)(4-methoxyphenyl)methanone (3.6)



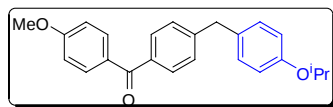
White solid (142 mg, 56%), mp 91-92 °C, R_f (5% EtOAc/Hexane) 0.35; ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 8.85 Hz, 2H), 7.69 (d, J = 8 Hz, 2H), 7.28-7.25 (m, 4H), 7.13 (d, J = 8.05 Hz, 2H), 6.95 (d, J = 9.2 Hz, 2H), 4.02 (s, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 195.24, 163.24, 144.98, 138.77, 136.48, 132.57, 130.54, 130.34, 130.27, 128.88, 128.63, 113.74, 113.48, 55.67, 41.30. IR (KBr, cm^{-1}): 2916, 1643, 1597, 1570, 1489, 1292, 1282, 1259, 1146, 1111, 1017, 929, 859, 768, 603. HRMS (ES^+): calcd. for $\text{C}_{21}\text{H}_{18}\text{ClO}_2$ [$\text{M}+\text{H}$] $^+$ 337.0995; found 337.0990.

(4-(3-Methoxybenzyl)phenyl)(4-methoxyphenyl)methanone (3.7)



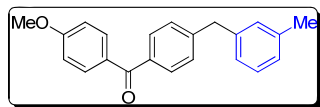
Brown liquid (158 mg, 64%), R_f (5% EtOAc/Hexane) 0.25; ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.05 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.65 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 7.65 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.75 (s, 1H), 4.02 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.24, 163.05, 159.73, 145.32, 141.72, 136.11, 132.44, 130.25, 130.11, 129.54, 128.67, 121.36, 114.85, 113.44, 111.46, 55.45, 55.14, 41.87. IR (neat, cm^{-1}): 2934, 2836, 1649, 1601, 1488, 1457, 1313, 1282, 1257, 1170, 1148, 1030, 928, 849, 769, 744, 699, 585. EI (m/z) calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_3$ [M] $^+$ 332.1412; found 332.1412.

(4-(4-Isopropoxybenzyl)phenyl)(4-methoxyphenyl)methanone (3.8)



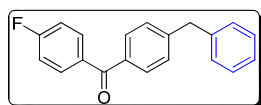
Brown liquid (192 mg, 71%), R_f (5% EtOAc/Hexane) 0.27; ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.45 Hz, 2H), 7.27 (d, J = 8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.53-4.49 (m, 1H), 3.98 (s, 2H), 3.88 (s, 3H), 1.33 (d, J = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.28, 163.03, 156.39, 146.06, 135.98, 132.44, 132.06, 130.30, 130.09, 129.90, 128.60, 115.92, 113.44, 69.82, 55.46, 41.0, 22.04. IR (neat, cm^{-1}): 2975, 1649, 1602, 1508, 1415, 1314, 1282, 1256, 1171, 1147, 1118, 1029, 954, 930, 845, 754, 687. EI (m/z) calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_3$ [M] $^+$ 360.1725; found 360.1723.

(4-(3-Methylbenzyl)phenyl)(4-methoxyphenyl)methanone (3.9)



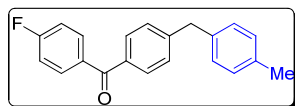
White solid (138 mg, 58%), mp 48-50 °C, R_f (5% EtOAc/Hexane) 0.35; ^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 8.85 Hz, 2H), 7.69 (d, J = 7.95 Hz, 2H), 7.28 (d, J = 8.25 Hz, 2H), 7.22-7.19 (m, 1H), 7.05-7.00 (m, 3H), 6.95 (d, J = 8.55 Hz, 2H), 4.01 (s, 2H), 3.88 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.29, 163.06, 145.69, 140.10, 138.21, 136.06, 132.45, 130.11, 129.98, 129.73, 128.69, 128.46, 127.09, 125.98, 113.46, 55.45, 41.84, 21.38. IR (KBr, cm^{-1}): 2920, 1645, 1602, 1505, 1458, 1410, 1316, 1282, 1262, 1170, 1022, 930, 810, 742, 702, 683. HRMS (ES^+): calcd. for $\text{C}_{22}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 317.1542; found 317.1546.

(4-Benzylphenyl)(4-fluorophenyl)methanone (3.10)



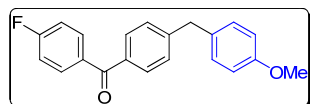
Light yellow liquid (164 mg, 75%), R_f (5% EtOAc/Hexane) 0.89; ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.81 (m, 2H), 7.70 (d, J = 8.25 Hz, 2H), 7.32-7.28 (m, 4H), 7.25-7.20 (m, 3H), 7.17-7.13 (m, 2H), 4.06 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 194.94, 165.27 (d, $J_{\text{C-F}}$ = 251.57 Hz), 146.24, 140.01, 135.37, 133.96, 132.6 (d, $J_{\text{C-F}}$ = 8.35 Hz), 130.28, 128.96, 128.86, 128.63, 126.42, 115.5 (d, $J_{\text{C-F}}$ = 21.46 Hz), 41.91. IR (neat, cm^{-1}): 3028, 1657, 1600, 1501, 1410, 1278, 1229, 929, 853, 758, 682, 578. EI (m/z) calcd. for $\text{C}_{20}\text{H}_{15}\text{FO}$ $[\text{M}]^+$ 290.1107; found 290.1105.

(4-Fluorophenyl)(4-(4-methylbenzyl)phenyl)methanone (3.11)



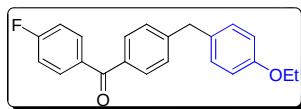
White solid (183 mg, 80%), mp 44-45 °C, R_f (5% EtOAc/Hexane) 0.89; ^1H NMR (500 MHz, CDCl_3): δ 7.82 (dd, J = 8.92, 6 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.25 Hz, 2H), 7.15-7.09 (m, 6H), 4.02 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 194.95, 165.25 (d, $J_{\text{C-F}}$ = 251.5 Hz), 146.58, 136.97, 135.97, 135.27, 133.98, 132.53 (d, $J_{\text{C-F}}$ = 9.53 Hz), 130.26, 129.30, 128.83, 128.80, 115.34 (d, $J_{\text{C-F}}$ = 22.65 Hz), 41.49, 21.0. IR (KBr, cm^{-1}): 2920, 1657, 1601, 1506, 1379, 1229, 1183, 1112, 930, 852, 746, 682, 598, 483. EI (m/z) calcd. for $\text{C}_{21}\text{H}_{17}\text{FO}$ $[\text{M}]^+$ 304.1263; found 304.1263.

(4-Fluorophenyl)(4-(4-methoxybenzyl)phenyl)methanone (3.12)



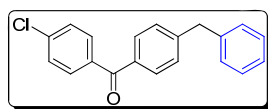
Yellow solid (163 mg, 68%) mp 46-47 °C, R_f (5% EtOAc/Hexane) 0.75; ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.81 (m, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 8.25 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.25 Hz, 2H), 6.85 (d, J = 8.75 Hz, 2H), 4.00 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 194.95, 165.2 (d, $J_{\text{C-F}}$ = 252.7 Hz), 158.18, 146.74, 135.26, 133.97, 132.52 (d, $J_{\text{C-F}}$ = 8.35 Hz), 132.09, 130.26, 129.91, 128.73, 115.35 (d, $J_{\text{C-F}}$ = 21.45 Hz), 114.0, 55.23, 41.02. IR (KBr, cm^{-1}): 2835, 1657, 1600, 1510, 1410, 1302, 1279, 1246, 1178, 1155, 1035, 930, 851, 824, 747. EI (m/z) calcd. for $\text{C}_{21}\text{H}_{17}\text{FO}_2$ $[\text{M}]^+$ 320.1213; found 320.1212.

(4-Fluorophenyl)(4-(4-ethoxybenzyl)phenyl)methanone (3.13)



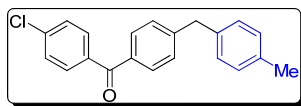
White solid (178 mg, 71%), mp 45-47 °C, R_f (5% EtOAc/Hexane) 0.77; ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.81 (m, 2H), 7.70 (d, J = 8.25 Hz, 2H), 7.29 (d, J = 8.25 Hz, 2H), 7.16-7.10 (m, 4H), 6.84 (d, J = 8.25 Hz, 2H), 4.01 (q, J = 6.9 Hz, 2H), 3.99 (s, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 194.93, 165.23 (d, $J_{\text{C-F}}$ = 252.76 Hz), 157.54, 146.78, 135.24, 133.95, 132.52 (d, $J_{\text{C-F}}$ = 9.53 Hz), 131.93, 130.24, 129.89, 128.73, 115.34 (d, $J_{\text{C-F}}$ = 21.46 Hz), 114.56, 63.37, 41.02, 14.82. IR (KBr, cm^{-1}): 2980, 2925, 1657, 1600, 1510, 1477, 1393, 1302, 1278, 1244, 1177, 1155, 1048, 929, 851, 821, 752, 629, 577, 517. EI (m/z) calcd. for $\text{C}_{22}\text{H}_{19}\text{FO}_2$ $[\text{M}]^+$ 334.1369; found 334.1369.

(4-Benzylphenyl)(4-chlorophenyl)methanone (3.14)



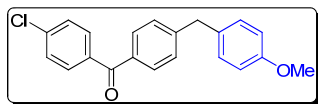
White solid (161 mg, 70%), mp 86-87 °C, R_f (5% EtOAc/Hexane) 0.90; ^1H NMR (500 MHz, CDCl_3): δ 7.74-7.68 (m, 5H), 7.44 (d, J = 7.75 Hz, 2H), 7.31-7.30 (m, 4H), 7.2 (d, J = 7.30 Hz, 2H), 4.06 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.11, 146.43, 143.51, 139.97, 138.68, 136.04, 135.12, 131.34, 130.30, 130.14, 128.87, 128.74, 126.42, 41.93. IR (KBr, cm^{-1}): 3281, 3082, 3024, 2910, 1647, 1587, 1483, 1453, 1399, 1186, 1112, 1087, 1013, 928, 897, 839, 745, 697. EI (m/z) calcd. for $\text{C}_{20}\text{H}_{15}\text{ClO}$ $[\text{M}]^+$ 306.0811; found 306.0818.

(4-Chlorophenyl)(4-(4-methylbenzyl)phenyl)methanone (3.15)



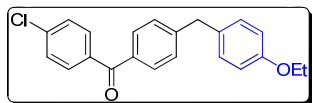
White solid (181 mg, 75%), mp 90-91 °C, R_f (5% EtOAc/Hexane) 0.90; ^1H NMR (500 MHz, CDCl_3): δ 7.73 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.25 Hz, 2H), 7.44 (d, J = 8.70 Hz, 2H), 7.29 (d, J = 8.25 Hz, 2H), 7.13-7.08 (m, 4H), 4.02 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 195.16, 146.79, 138.67, 136.93, 136.07, 136.01, 135.05, 131.35, 130.30, 130.15, 129.32, 128.82, 128.52, 41.52, 21.02. IR (KBr, cm^{-1}): 2909, 1647, 1604, 1310, 1280, 1112, 1088, 1012, 929, 792, 766, 737, 500, 471. EI (m/z) calcd. for $\text{C}_{21}\text{H}_{17}\text{ClO}$ $[\text{M}]^+$ 320.0968; found 320.0968.

(4-Chlorophenyl)(4-(4-methoxybenzyl)phenyl)methanone (3.16)



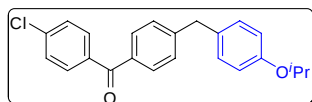
White solid (170 mg, 68%), mp 77-78 °C, R_f (5% EtOAc/Hexane) 0.80; ^1H NMR (500 MHz, CDCl_3): δ 7.73 (d, J = 8.75 Hz, 2H), 7.70 (d, J = 8.25 Hz, 2H), 7.44 (d, J = 8.70 Hz, 2H), 7.29 (d, J = 8.25 Hz, 2H), 7.12 (d, J = 8.25 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.00 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.17, 158.19, 146.95, 138.67, 136.05, 135.02, 132.05, 131.35, 130.30, 129.91, 128.76, 128.55, 114.01, 55.28, 41.04. IR (KBr, cm^{-1}): 3000, 2931, 2834, 1657, 1606, 1511, 1411, 1398, 1303, 1283, 1246, 1175, 1089, 1035, 1015, 928, 848, 744, 627, 514. EI (m/z) calcd. for $\text{C}_{21}\text{H}_{17}\text{ClO}_2$ $[\text{M}]^+$ 336.0917; found 336.0919.

(4-Chlorophenyl)(4-(4-ethoxybenzyl)phenyl)methanone (3.17)



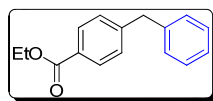
White solid (191 mg, 73%), mp 69-70 °C, R_f (5% EtOAc/Hexane) 0.86; ^1H NMR (500 MHz, CDCl_3): δ 7.72 (d, J = 8.55 Hz, 2H), 7.69 (d, J = 7.95 Hz, 2H), 7.44 (d, J = 8.55 Hz, 2H), 7.28 (d, J = 7.95 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.85 Hz, 2H), 4.01 (q, J = 7 Hz, 2H), 3.99 (s, 2H), 1.40 (t, J = 7 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.17, 157.56, 147.01, 138.66, 136.06, 135.0, 131.90, 131.35, 130.30, 129.90, 128.79, 128.54, 114.59, 63.40, 41.05, 14.84. IR (KBr, cm^{-1}): 2979, 2931, 2899, 2826, 1923, 1646, 1603, 1514, 1471, 1410, 1394, 1315, 1298, 1289, 1252, 1177, 1146, 1116, 1086, 1052, 1012, 960, 932, 848, 816. HRMS (ES^+): calcd. for $\text{C}_{22}\text{H}_{20}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 351.1152; found 351.1158.

(4-Chlorophenyl)(4-(4-isopropoxybenzyl)phenyl)methanone (3.18)



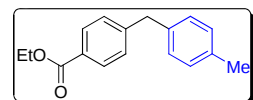
White solid (193 mg, 71%), mp 68-70 °C, R_f (5% EtOAc/Hexane) 0.86; ^1H NMR (500 MHz, CDCl_3): δ 7.73 (d, J = 8.55 Hz, 2H), 7.70 (d, J = 8.25 Hz, 2H), 7.44 (d, J = 8.55 Hz, 2H), 7.29 (d, J = 7.95 Hz, 2H), 7.09 (d, J = 8.55 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 4.53-4.49 (m, 1H), 3.99 (s, 2H), 1.32 (d, J = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.17, 156.47, 146.99, 138.64, 136.05, 134.98, 131.84, 131.34, 130.30, 129.90, 128.81, 128.53, 115.97, 69.85, 41.05, 22.04. IR (KBr, cm^{-1}): 2980, 1651, 1606, 1583, 1508, 1244, 1118, 1086, 1012, 1012, 952, 928, 838, 739, 674. HRMS (ES^+): calcd. for $\text{C}_{23}\text{H}_{22}\text{ClO}_2$ $[\text{M}+\text{H}]^+$ 365.1308; found 365.1306.

Ethyl 4-benzylbenzoate^{3(b)} (3.19)



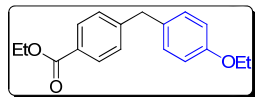
Colorless liquid (139 mg, 77%), R_f (5% EtOAc/Hexane) 0.59; ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 8.25 Hz, 2H), 7.31-7.22 (m, 5H), 7.17 (d, J = 7.35 Hz, 2H), 4.36 (q, J = 6.87 Hz, 2H), 4.03 (s, 2H), 1.38 (t, J = 7.10 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.55, 146.35, 140.15, 129.75, 128.90, 128.85, 128.56, 128.41, 126.33, 60.79, 41.94, 14.33. IR (neat, cm^{-1}): 2981, 1610, 1366, 1277, 1177, 1104, 1021, 754, 741, 705. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240.1150; found 240.1154.

Ethyl 4-(4-methylbenzyl)benzoate⁵ (3.20)



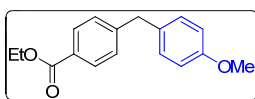
Colorless liquid (153 mg, 80%), R_f (5% EtOAc/Hexane) 0.61; ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 7.75 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 7.8 Hz, 2H), 4.36 (q, J = 6.85 Hz, 2H), 3.99 (s, 2H), 2.32 (s, 3H), 1.38 (t, J = 7.10 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.59, 146.67, 137.11, 135.86, 129.73, 129.25, 128.85, 128.78, 128.32, 60.77, 41.46, 21.0, 14.33. IR (neat, cm^{-1}): 2981, 1610, 1513, 1276, 1176, 1106, 1021, 739. EI (m/z) calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 254.1307; found 254.1306.

Ethyl 4-(4-ethoxybenzyl)benzoate (3.21)



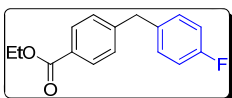
Colorless liquid (154 mg, 72%), R_f (5% EtOAc/Hexane) 0.55; ^1H NMR (500 MHz, CDCl_3): δ 7.95 (d, J = 8.25 Hz, 2H), 7.23 (d, J = 8.25 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.35 (q, J = 7.35 Hz, 2H), 4.00 (q, J = 7.7 Hz, 2H), 3.96 (s, 2H), 1.39 (t, J = 6.87 Hz, 3H), 1.37 (t, J = 7.10 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.59, 157.47, 146.89, 132.10, 129.82, 129.71, 128.79, 128.29, 114.53, 63.38, 60.77, 41.0, 14.84, 14.34. IR (neat, cm^{-1}): 2980, 1716, 1611, 1511, 1477, 1366, 1277, 1245, 1177, 1107, 1048, 1021, 747. EI (m/z) calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_3$ $[\text{M}]^+$ 284.1412; found 284.1411.

Ethyl 4-(4-methoxybenzyl)benzoate⁶ (3.22)



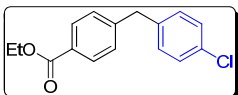
White solid (149 mg, 74%), mp 40-41 °C, R_f (5% EtOAc/Hexane) 0.50; ^1H NMR (500 MHz, CDCl_3): δ 7.95 (d, J = 8.25 Hz, 2H), 7.23 (d, J = 8.25 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.71 Hz, 2H), 4.36 (q, J = 7.32 Hz, 2H), 3.97 (s, 2H), 3.78 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.57, 158.10, 146.84, 132.24, 129.83, 129.72, 128.71, 128.30, 113.96, 60.77, 55.26, 40.98, 14.33. IR (KBr, cm^{-1}): 2835, 1715, 1611, 1511, 1441, 1366, 1277, 1247, 1177, 1107, 1035, 1022, 832, 747. EI (m/z) calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3$ $[\text{M}]^+$ 270.1256; found 270.1255.

Ethyl 4-(4-fluorobenzyl)benzoate⁷ (3.23)



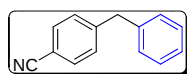
Colorless liquid (135 mg, 70%), R_f (5% EtOAc/Hexane) 0.55; ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 8.25 Hz, 2H), 7.22 (d, J = 8.25 Hz, 2H), 7.13-7.10 (m, 2H), 6.99-6.96 (m, 2H), 4.36 (q, J = 7.35 Hz, 2H), 3.99 (s, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.50, 161.53 (d, $J_{\text{C-F}}$ = 242.02 Hz), 146.13, 135.82, 130.31, 129.84, 128.73 (d, $J_{\text{C-F}}$ = 10.73 Hz), 128.59, 115.3 (d, $J_{\text{C-F}}$ = 21.46 Hz), 60.85, 41.03, 14.35. IR (neat, cm^{-1}): 2981, 1716, 1610, 1509, 1277, 1223, 1105, 1021, 781. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{15}\text{FO}_2$ $[\text{M}]^+$ 258.1056; found 258.1059.

Ethyl 4-(4-chlorobenzyl)benzoate⁸ (3.24)



Colorless liquid (122 mg, 59%), R_f (5% EtOAc/Hexane) 0.55; ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.25 Hz, 2H), 7.22 (d, J = 8.25 Hz, 2H), 7.09 (d, J = 8.75 Hz, 2H), 4.36 (q, J = 7.35 Hz, 2H), 3.99 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166.45, 145.71, 138.60, 132.19, 130.25, 129.85, 128.84, 128.77, 128.65, 60.85, 41.16, 14.33. IR (neat, cm^{-1}): 3033, 1716, 1610, 1491, 1277, 1177, 1105, 1016. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{15}\text{ClO}_2$ $[\text{M}]^+$ 274.0761; found 274.0760.

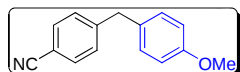
4-Benzylbenzonitrile^{3(b)} (3.25)



Colorless liquid (101 mg, 70%), R_f (5% EtOAc/Hexane) 0.75; ^1H NMR (500 MHz, CDCl_3): δ 7.57 (d, J = 8.25 Hz, 2H), 7.33-7.22 (m, 5H), 7.16 (d, J = 6.89 Hz, 2H), 4.03 (s, 2H). ^{13}C NMR

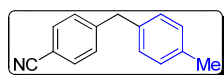
(125 MHz, CDCl₃): δ 146.68, 139.28, 132.25, 129.59, 128.90, 128.71, 126.62, 118.94, 109.98, 41.91. IR (neat, cm⁻¹): 3063, 2227, 1604, 1497, 1453, 1413, 1177, 1112, 1073, 915, 855, 797, 761, 726, 699, 593, 544. EI (m/z) calcd. for C₁₄H₁₁N [M]⁺ 193.0891; found 193.0891.

4-(4-Methoxybenzyl)benzonitrile⁵ (3.26)



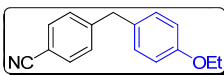
White solid (119 mg, 71%), mp 45-47 °C, *R_f* (5% EtOAc/Hexane) 0.67; ¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 8.25 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.70 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 2H), 3.79 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 158.29, 147.20, 132.22, 131.33, 129.89, 129.46, 119.0, 114.09, 109.85, 55.22, 41.04. IR (KBr, cm⁻¹): 2836, 2226, 1610, 1511, 1301, 1247, 1117, 1110, 1034, 810, 761, 572. EI (m/z) calcd. for C₁₅H₁₃NO [M]⁺ 223.0997; found 223.0999.

4-(4-Methylbenzyl)benzonitrile⁹ (3.27)



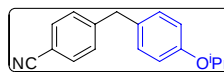
White solid (113 mg, 73%), mp 53-55 °C, *R_f* (5% EtOAc/Hexane) 0.75; ¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 8.25 Hz, 2H), 7.27 (d, *J* = 8.25 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 3.99 (s, 2H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 147.02, 136.23, 136.20, 132.21, 129.51, 129.38, 128.78, 118.98, 109.86, 41.50, 20.97. IR (neat, cm⁻¹): 2921, 2226, 1606, 1513, 1438, 1413, 1021, 809, 758, 568, 481. EI (m/z) calcd. for C₁₅H₁₃N [M]⁺ 207.1048; found 207.1047.

4-(4-Ethoxybenzyl)benzonitrile (3.28)



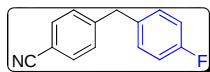
white solid (137 mg, 78%), mp 55-57 °C, *R_f* (5% EtOAc/Hexane) 0.69; ¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 8.25 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.70 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.00 (q, *J* = 7.07 Hz, 2H), 3.96 (s, 2H), 1.40 (t, *J* = 6.87 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 157.71, 147.25, 132.23, 131.21, 129.89, 129.49, 119.01, 114.70, 109.88, 63.42, 41.08, 14.81. IR (KBr, cm⁻¹): 3406, 3037, 2977, 2924, 2880, 2229, 1609, 1509, 1476, 1389, 1300, 1245, 1172, 1114, 1045, 922, 862, 809, 592, 547, 512. HRMS (ES⁺): calcd. for C₁₆H₁₆NO [M+H]⁺ 228.1232; found 228.1232.

4-(4-OⁱPrbenzyl)benzonitrile (3.29)



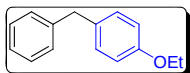
Colorless liquid (145 mg, 77%), *R_f* (5% EtOAc/Hexane) 0.69; ¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 8.25 Hz, 2H), 7.26 (d, *J* = 8.25 Hz, 2H), 7.04 (d, *J* = 8.70 Hz, 2H), 6.82 (d, *J* = 8.25 Hz, 2H), 4.53-4.48 (m, 1H), 3.95 (s, 2H), 1.31 (d, *J* = 5.95 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 156.62, 147.24, 132.21, 131.14, 129.89, 129.50, 119.0, 116.05, 109.85, 69.88, 41.06, 22.02. IR (neat, cm⁻¹): 3400, 3032, 2977, 2931, 2227, 1653, 1508, 1466, 1413, 1383, 1373, 1297, 1243, 1181, 1119, 954, 858, 809, 591, 547. HRMS (ES⁺): calcd. for C₁₇H₁₈NO [M+H]⁺ 252.1388; found 252.1388.

4-(4-Fluorobenzyl)benzonitrile¹⁰ (3.30)



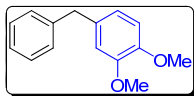
White solid (105 mg, 68%), mp 52-54 °C, R_f (5% EtOAc/Hexane) 0.73; ^1H NMR (500 MHz, CDCl_3): δ 7.57 (d, J = 8.25 Hz, 2H), 7.26 (d, J = 8.25 Hz, 2H), 7.12-7.09 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 4.00 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 161.67 (d, $J_{\text{C-F}}$ = 243.22 Hz), 146.46, 134.96, 132.35, 130.38 (d, $J_{\text{C-F}}$ = 8.33 Hz), 129.51, 118.87, 115.58 (d, $J_{\text{C-F}}$ = 21.46), 110.21, 41.07. IR (KBr, cm^{-1}): 3050, 2935, 2227, 1604, 1508, 1430, 1414, 1223, 1172, 1159, 1092, 1018, 859, 814, 766, 562, 537. EI (m/z) calcd. for $\text{C}_{14}\text{H}_9\text{FN}$ $[\text{M}]^+$ 212.0876; found 212.0875.

1-Benzyl-4-ethoxybenzene (3.31)



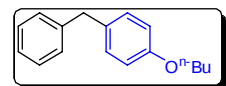
Colorless liquid (142 mg, 89%), R_f (Hexane) 0.59; ^1H NMR (500 MHz, CDCl_3): δ 7.29-7.27 (m, 2H), 7.20-7.17 (m, 3H), 7.09 (d, J = 8.85 Hz, 2H), 6.82 (d, J = 8.85 Hz, 2H), 4.01 (q, J = 7.02 Hz, 2H), 3.92 (s, 2H), 1.40 (t, J = 6.85 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 157.29, 141.59, 133.07, 129.82, 128.79, 128.39, 125.92, 114.43, 63.37, 41.01, 14.86. IR (neat, cm^{-1}): 3061, 3027, 2979, 2905, 1612, 1510, 1494, 1453, 1392, 1244, 1175. HRMS (ES^+): calcd. for $\text{C}_{15}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 213.1279; found 213.1272.

4-Benzyl-1,2-dimethoxybenzene¹¹ (3.32)



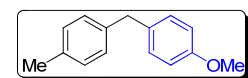
Colorless liquid (159 mg, 93%), R_f (5% EtOAc/Hexane) 0.30; ^1H NMR (500 MHz, CDCl_3): δ 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 6.80 (d, J = 8.05 Hz, 1H), 6.74-6.70 (m, 2H), 3.93 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 148.85, 147.32, 141.34, 133.60, 128.73, 128.42, 126.01, 120.84, 112.15, 111.10, 55.86, 55.75, 41.44. IR (neat, cm^{-1}): 3025, 2999, 2933, 2833, 1590, 1515, 1494, 1463, 1452, 1259, 1236, 1138, 1029. HRMS (ES^+): calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 229.1229; found 229.1225.

1-Benzyl-4-n-butoxybenzene (3.33)



Colorless liquid (172 mg, 95%), R_f (Hexane) 0.55; ^1H NMR (500 MHz, CDCl_3): δ 7.29-7.26 (m, 2H), 7.20-7.17 (m, 3H), 7.09 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.95 (s, 2H), 3.93-3.91 (m, 2H), 1.78-1.72 (m, 2H), 1.51-1.46 (m, 2H), 0.97 (t, J = 7.45 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 157.50, 141.61, 132.98, 129.80, 128.79, 128.39, 125.92, 114.42, 67.64, 41.01, 31.35, 19.24, 13.85. IR (neat, cm^{-1}): 3027, 2957, 2929, 2871, 1612, 1510, 1494, 1453, 1244, 1174, 1071. HRMS (ES^+): calcd. for $\text{C}_{17}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$ 241.1592; found 241.1599.

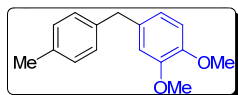
1-Methoxy-4-(4-methylbenzyl)benzene¹² (3.34)



Colorless liquid (145 mg, 92%), R_f (Hexane) 0.45; ^1H NMR (500 MHz, CDCl_3): δ 7.10-7.05 (m, 6H), 6.82 (d, J = 8.6 Hz, 2H), 3.88 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H). ^{13}C NMR

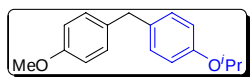
(125 MHz, CDCl₃): δ 157.85, 138.50, 135.41, 133.52, 129.76, 129.09, 128.66, 113.80, 55.23, 40.56, 20.98. IR (neat, cm⁻¹): 3002, 2923, 2835, 1610, 1511, 1440, 1301, 1246, 1175. EI (m/z) calcd. for C₁₅H₁₆O [M]⁺ 212.1201; found 212.1203.

1,2-Dimethoxy-4-(4-methylbenzyl)benzene (3.35)



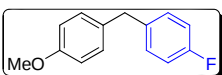
Colorless liquid (171 mg, 94%), *R_f* (5% EtOAc/Hexane) 0.29; ¹H NMR (500 MHz, CDCl₃): δ 7.10-7.06 (m, 4H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.72-6.70 (m, 2H), 3.89 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 2.31 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 148.84, 147.28, 138.29, 135.48, 133.92, 129.10, 128.60, 120.77, 112.11, 111.11, 55.87, 55.75, 41.03, 20.99. IR (neat, cm⁻¹): 3000, 2933, 2833, 1590, 1513, 1463, 1259, 1236, 1152, 1138, 1029. EI (m/z) calcd. for C₁₆H₁₈O₂ [M]⁺ 242.1307; found 242.1302.

1-Isopropoxy-4-(4-methoxybenzyl)benzene (3.36)



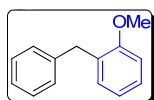
Colorless liquid (159 mg, 83%), *R_f* (Hexane) 0.35; ¹H NMR (500 MHz, CDCl₃): δ 7.10-7.05 (m, 4H), 6.83-6.79 (m, 4H), 4.52-4.47 (m, 1H), 3.85 (s, 2H), 3.78 (s, 3H), 1.31 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 157.84, 156.13, 133.71, 129.74, 127.68, 116.04, 115.84, 113.79, 69.91, 55.23, 40.10, 22.08. IR (neat, cm⁻¹): 2976, 2930, 1610, 1508, 1465, 1242, 1178, 1120. EI (m/z) calcd. for C₁₇H₂₀O₂ [M]⁺ 256.1463; found 256.1465.

1-Fluoro-4-(4-methoxybenzyl)benzene ¹³(3.37)



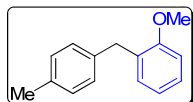
Colorless liquid (105 mg, 64%), *R_f* (Hexane) 0.39; ¹H NMR (500 MHz, CDCl₃): δ 7.13-7.07 (m, 4H), 6.97-6.94 (m, 2H), 6.83 (d, *J* = 8.55 Hz, 2H), 3.89 (s, 2H), 3.78 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 161.32 (d, ¹*J*_{C-F} = 243.56 Hz), 158.01, 137.22, 133.03, 130.11 (d, ³*J*_{C-F} = 7.20 Hz), 129.75, 115.14 (d, ²*J*_{C-F} = 21.60 Hz), 113.90, 55.24, 40.15. IR (neat, cm⁻¹): 3002, 2908, 2835, 1609, 1584, 1509, 1439, 1301, 1246, 1222, 1177, 1156. EI (m/z) calcd. for C₁₄H₁₃FO [M]⁺ 216.0950; found 216.0957.

1-Benzyl-2-methoxybenzene ^{3b} (3.38)



Colorless liquid (85 mg, 57%), *R_f* (Hexane) 0.49; ¹H NMR (500 MHz, CDCl₃): δ 7.27-7.17 (m, 6H), 7.06 (d, *J* = 6.1 Hz, 1H), 6.88-6.85 (m, 2H), 3.97 (s, 2H), 3.81 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 157.41, 141.11, 130.39, 129.73, 129.05, 128.34, 127.50, 125.85, 120.55, 110.47, 55.44, 35.93. IR (neat, cm⁻¹): 3061, 3026, 2936, 2835, 1600, 1587, 1492, 1244, 1111. EI (m/z) calcd. for C₁₄H₁₄O [M]⁺ 198.1045; found 198.1042.

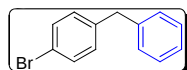
1-Methoxy-2-(4-methylbenzyl)benzene (3.39)



Colorless liquid (78 mg, 49%), *R_f* (Hexane) 0.37; ¹H NMR (500 MHz, CDCl₃): δ 7.19-7.17 (m, 1H), 7.11-7.04 (m, 5H), 6.87-6.84 (m, 2H), 3.93 (s, 2H), 3.81 (s, 3H), 2.30 (s, 3H). ¹³C NMR

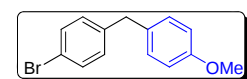
(125 MHz, CDCl_3): δ 157.38, 137.98, 135.28, 130.32, 129.99, 129.04, 128.93, 127.38, 120.53, 110.43, 55.43, 35.44, 21.11. IR (neat, cm^{-1}): 3002, 2921, 2834, 1599, 1492, 1463, 1513, 1438, 1243, 1111, 1030. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{16}\text{O}[\text{M}]^+$ 212.1201; found 212.1202.

1-Benzyl-4-bromobenzene¹² (4.1)



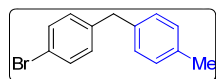
Colorless liquid (143 mg, 77%), R_f (Hexane) 0.95; ^1H NMR (500 MHz, CDCl_3): δ 7.41 (d, J = 8.7 Hz, 2H), 7.31-7.28 (m, 2H), 7.23-7.21 (m, 1H), 7.17 (d, J = 6.85 Hz, 2H), 7.07 (d, J = 8.25 Hz, 2H), 3.94 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 140.41, 140.06, 131.50, 130.65, 128.83, 128.54, 126.27, 119.90, 41.26. IR (neat, cm^{-1}): 3026, 1601, 1487, 1452, 1403, 1071, 1029, 821, 787, 742, 697, 578, 477. EI (m/z) calcd. for $\text{C}_{13}\text{H}_{11}\text{Br}[\text{M}]^+$ 246.0044; found 246.0047.

1-Bromo-4-(4-methoxybenzyl)benzene¹³ (4.2)



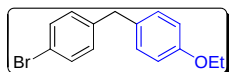
Colorless liquid (168 mg, 81%), R_f (Hexane) 0.65; ^1H NMR (500 MHz, CDCl_3): δ 7.40 (d, J = 8.25 Hz, 2H), 7.08 (d, J = 8.70 Hz, 2H), 7.05 (d, J = 8.70 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.87 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.08, 140.55, 132.52, 131.44, 130.51, 129.78, 119.78, 113.94, 55.23, 40.37. IR (neat, cm^{-1}): 2633, 1611, 1511, 1486, 1246, 1176, 1036, 1011, 794, 553. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{BrO}[\text{M}]^+$ 276.0150; found 276.0154.

1-Bromo-4-(4-methylbenzyl)benzene¹⁴ (4.3)



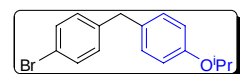
Colorless liquid (160 mg, 82%), R_f (Hexane) 0.90; ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 8.25 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.06-7.04 (m, 4H), 3.89 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 140.39, 137.38, 135.81, 131.45, 130.58, 129.23, 128.71, 119.80, 40.85, 21.06. IR (neat, cm^{-1}): 2919, 1513, 1486, 1403, 1070, 1011, 801, 791, 751, 537, 484. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{Br}[\text{M}]^+$ 260.0201; found 260.0207.

1-Bromo-4-(4-ethoxybenzyl)benzene (4.4)



White solid (187 mg, 86%), mp 47-49 °C, R_f (Hexane) 0.50; ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 8.25 Hz, 2H), 7.05-7.03 (m, 4H), 6.82 (d, J = 8.70 Hz, 2H), 4.00 (q, J = 6.85 Hz, 2H), 3.86 (s, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 157.43, 140.59, 132.37, 131.42, 130.52, 129.76, 119.76, 114.51, 63.38, 40.38, 14.84. IR (KBr, cm^{-1}): 3031, 2979, 2906, 1612, 1583, 1510, 1486, 1439, 1394, 1300, 1245, 1175, 1115, 1071, 1048, 1011, 923, 797, 575, 515. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{15}\text{BrO}[\text{M}]^+$ 290.0306; found 290.0308.

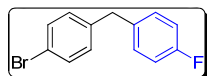
1-Bromo-4-(4-*i*Prbenzyl)benzene (4.5)



Colorless liquid (199 mg, 83%), R_f (Hexane) 0.50; ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 8.55 Hz, 2H), 7.05-7.04 (m, 4H), 6.81 (d, J = 8.55 Hz, 2H), 4.53-4.48 (m, 1H), 3.86 (s,

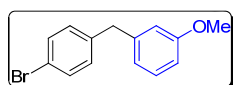
2H), 1.32 (d, $J = 6.15$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 156.34, 140.57, 132.33, 131.42, 130.54, 129.77, 119.76, 115.92, 69.85, 40.38, 22.04. IR (neat, cm^{-1}): 3026, 2973, 2918, 1609, 1506, 1485, 1382, 1371, 1240, 1179, 1117, 1070, 1010, 953, 791, 623, 559, 515. HRMS (ES^+): calcd. for $\text{C}_{16}\text{H}_{18}\text{BrO} [\text{M}+\text{H}]^+$ 305.0541; found 305.0541.

1-Bromo-4-(4-fluorobenzyl)benzene (4.6)



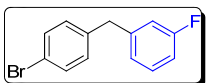
Colorless liquid (159 mg, 80%), R_f (Hexane) 0.91; ^1H NMR (500 MHz, CDCl_3): δ 7.40 (d, $J = 8.25$ Hz, 2H), 7.12-7.09 (m, 2H), 7.03 (d, $J = 8.25$ Hz, 2H), 7.0-6.95 (m, 2H), 3.89 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 161.45 (d, $^1J_{\text{C-F}} = 243.22$ Hz), 139.87, 136.08, 131.55, 130.52, 130.24 (d, $^3J_{\text{C-F}} = 7.15$ Hz), 120.03, 115.3 (d, $^2J_{\text{C-F}} = 21.46$ Hz), 40.39. IR (neat, cm^{-1}): 2918, 1603, 1508, 1487, 1223, 1156, 1094, 1070, 1012, 843, 536, 471. EI (m/z) calcd. for $\text{C}_{13}\text{H}_{10}\text{BrF} [\text{M}]^+$ 263.9950; found 263.9950.

1-(4-Bromobenzyl)-3-methoxybenzene (4.7)



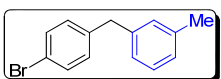
Colorless liquid (169 mg, 81%), R_f (Hexane) 0.55; ^1H NMR (500 MHz, CDCl_3): δ 7.40 (d, $J = 8.3$ Hz, 2H), 7.22-7.19 (m, 1H), 7.06 (d, $J = 8.3$ Hz, 2H), 6.75 (d, $J = 8.3$ Hz, 2H), 6.69 (s, 1H), 3.90 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.76, 141.99, 139.88, 131.53, 130.66, 129.55, 121.25, 119.95, 114.75, 111.44, 55.18, 41.37. IR (neat, cm^{-1}): 2917, 1739, 1599, 1485, 1258, 1223, 1168, 1070, 1031, 801, 695. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{BrO} [\text{M}]^+$ 276.0150; found 276.0157.

1-(4-Bromobenzyl)-3-fluorobenzene (4.8)



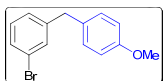
Colorless liquid (139 mg, 70%), R_f (Hexane) 0.92; ^1H NMR (500 MHz, CDCl_3): δ 7.42 (d, $J = 8.25$ Hz, 2H), 7.27-7.22 (m, 1H), 7.05 (d, $J = 8.25$ Hz, 2H), 6.93 (d, $J = 7.35$ Hz, 1H), 6.92-6.88 (m, 1H), 6.85-6.83 (m, 1H), 3.91 (s, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 162.90 (d, $^1J_{\text{C-F}} = 244.4$ Hz), 142.9 (d, $^3J_{\text{C-F}} = 7.1$ Hz), 139.21, 131.60, 130.62, 124.44, 120.18, 115.7 (d, $^2J_{\text{C-F}} = 21.46$ Hz), 113.29, 113.13, 40.92. IR (neat, cm^{-1}): 2921, 1615, 1589, 1486, 1448, 1248, 1136, 1071, 1011, 798, 780, 686, 477. EI (m/z) calcd. for $\text{C}_{13}\text{H}_{10}\text{BrF} [\text{M}]^+$ 263.9950; found 263.9950.

1-(4-Bromobenzyl)-3-methylbenzene (4.9)



Colorless liquid (131 mg, 67%), R_f (Hexane) 0.89; ^1H NMR (500 MHz, CDCl_3): δ 7.41-7.39 (m, 3H), 7.18 (d, $J = 7.60$ Hz, 1H), 7.07-6.96 (m, 4H), 3.89 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 141.32, 140.34, 140.22, 138.17, 131.50, 130.68, 129.66, 128.48, 125.91, 119.85, 41.22, 21.35. IR (neat, cm^{-1}): 3024, 2918, 1606, 1486, 1402, 1093, 1011, 797, 775, 741, 695, 471. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{Br} [\text{M}]^+$ 260.0201; found 260.0207.

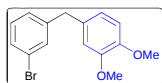
1-Bromo-3-(4-methoxybenzyl)benzene (4.10)



Colorless liquid (139 mg, 67%), R_f (Hexane) 0.56. ^1H NMR (500 MHz, CDCl_3): δ 7.32-7.31 (m, 2H), 7.15-7.12 (m, 1H), 7.10-7.08 (m, 3H), 6.84 (d, $J = 8.30$ Hz, 2H), 3.88 (s, 2H), 3.79 (s, 3H)

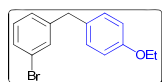
ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 158.12, 143.92, 132.24, 131.77, 129.94, 129.86, 129.10, 127.42, 122.50, 113.98, 55.23, 40.62 ppm. IR (neat, cm^{-1}): 3001, 2930, 2834, 1611, 1592, 1567, 1510, 1438, 1301, 1247, 1177, 1036. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{BrO}$ $[\text{M}]^+$ 276.0150; found 276.0166.

4-(3-Bromobenzyl)-1,2-dimethoxybenzene (4.11)



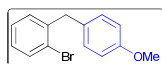
Colorless liquid (168 mg, 73%), R_f (5% EtOAc/Hexane) 0.27. ^1H NMR (500 MHz, CDCl_3): δ 7.32 (s, 2H), 7.16-7.09 (m, 2H), 6.81 (d, J = 8.25 Hz, 1H), 6.71-6.70 (m, 1H), 6.67 (d, J = 1.85 Hz, 1H), 3.89 (s, 2H), 3.86 (s, 3H), 3.83 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 149.01, 147.62, 143.73, 132.64, 131.75, 129.95, 129.17, 127.38, 122.53, 120.95, 112.16, 111.27, 55.90, 55.84, 41.06 ppm. IR (neat, cm^{-1}): 2999, 2933, 2906, 2833, 1591, 1567, 1515, 1464, 1439, 1417, 1260, 1236, 1154, 1029. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{15}\text{BrO}_2$ $[\text{M}]^+$ 306.0255; found 306.0250.

1-Bromo-3-(4-ethoxybenzyl)benzene (4.12)



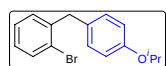
Colorless liquid (151 mg, 69%), R_f (Hexane) 0.50. ^1H NMR (500 MHz, CDCl_3): δ 7.31 (s, 2H), 7.15-7.10 (m, 1H), 7.08-7.06 (m, 3H), 6.83 (d, J = 8.55 Hz, 2H), 4.01 (q, J = 7.02 Hz, 2H), 3.88 (s, 2H), 1.40 (t, J = 6.87 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 157.51, 143.97, 132.09, 131.77, 129.93, 129.84, 129.09, 127.43, 122.50, 114.56, 63.40, 40.64, 14.85 ppm. IR (neat, cm^{-1}): 3031, 2979, 2925, 1612, 1592, 1567, 1510, 1425, 1392, 1245, 1176, 1070. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{15}\text{BrO}$ $[\text{M}]^+$ 290.0306; found 290.0309.

1-Bromo-2-(4-methoxybenzyl)benzene (4.13)



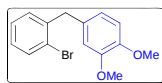
Colorless liquid (123 mg, 59%), R_f (Hexane) 0.47. ^1H NMR (500 MHz, CDCl_3): δ 7.57-7.55 (m, 1H), 7.24-7.20 (m, 1H), 7.13-7.09 (m, 3H), 7.08-7.05 (m, 1H), 6.84 (d, J = 8.55 Hz, 2H), 4.05 (s, 2H), 3.79 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 158.04, 140.76, 132.80, 131.50, 130.92, 129.95, 127.76, 127.43, 124.77, 113.85, 55.22, 40.85 ppm. IR (neat, cm^{-1}): 3059, 2999, 2953, 2931, 1611, 1584, 1566, 1511, 1465, 1439, 1301, 1105, 1036, 1026. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{BrO}$ $[\text{M}]^+$ 276.0150; found 276.0159

1-Bromo-2-(4-isopropoxybenzyl)benzene (4.14)



Colorless liquid (145 mg, 62%), R_f (Hexane) 0.50. ^1H NMR (500 MHz, CDCl_3): δ 7.55 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 7.13-7.05 (m, 4H), 6.81 (d, J = 8.6 Hz, 2H), 4.53-4.48 (m, 1H) 4.04 (s, 2H), 1.32 (d, J = 6.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 156.33, 140.81, 132.76, 131.29, 130.93, 129.95, 127.72, 127.40, 124.78, 115.82, 69.82, 40.85, 22.07 ppm. IR (neat, cm^{-1}): 3059, 2976, 2927, 1611, 1508, 1466, 1439, 1383, 1372, 1297, 1242, 1119. EI (m/z) calcd. for $\text{C}_{16}\text{H}_{17}\text{BrO}$ $[\text{M}]^+$ 304.0463; found 304.0466.

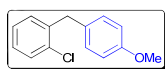
4-(2-Bromobenzyl)-1,2-dimethoxybenzene (4.15)



Colorless liquid (173 mg, 75%), R_f (5% EtOAc/Hexane) 0.27. ^1H NMR (500 MHz, CDCl_3): δ 7.56 (d, J = 7.95 Hz, 1H), 7.21 (t, J = 7.35 Hz, 1H), 7.11-7.06 (m, 2H), 6.80 (d, J = 8.25 Hz, 1H), 6.74-

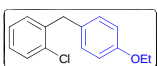
6.70 (m, 2H), 4.05 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 148.92, 147.50, 140.63, 132.78, 131.98, 130.83, 127.80, 127.44, 124.74, 120.98, 112.32, 111.18, 55.85, 55.79, 41.29 ppm. IR (neat, cm^{-1}): 3058, 2998, 2933, 2833, 1590, 1515, 1464, 1439, 1417, 1259, 1237, 1153, 1140, 1027. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{15}\text{BrO}_2$ $[\text{M}]^+$ 306.0255; found 306.0259

1-Chloro-2-(4-methoxybenzyl)benzene¹⁵ (4.16)



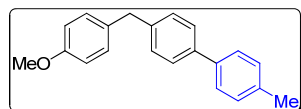
Colorless liquid (129 mg, 74%), R_f (Hexane) 0.59. ^1H NMR (500 MHz, CDCl_3): δ 7.37-7.35 (m, 1H), 7.17-7.10 (m, 5H), 6.84 (d, J = 8.35 Hz, 2H), 4.04 (s, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 158.04, 139.09, 134.11, 131.53, 130.85, 129.89, 129.48, 127.52, 126.78, 113.86, 55.22, 38.29 ppm. IR (neat, cm^{-1}): 3062, 2999, 2953, 2932, 2908, 2834, 1612, 1511, 1470, 1441, 1301, 1037. EI (m/z) calcd. for $\text{C}_{14}\text{H}_{13}\text{ClO}$ $[\text{M}]^+$ 232.0655; found 232.0650.

1-Chloro-2-(4-ethoxybenzyl)benzene (4.17)



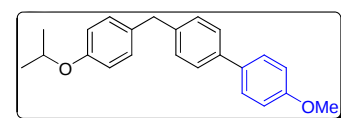
Colorless liquid (131 mg, 71%), R_f (Hexane) 0.65. ^1H NMR (500 MHz, CDCl_3): δ 7.37-7.35 (m, 1H), 7.17-7.12 (m, 3H), 7.09 (d, J = 8.30 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.03 (s, 2H), 4.00 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 6.72 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 157.40, 139.13, 134.11, 131.37, 130.85, 129.88, 129.46, 127.49, 126.76, 114.44, 63.36, 38.30, 14.86 ppm. IR (neat, cm^{-1}): 3062, 2979, 2926, 1612, 1583, 1511, 1476, 1444, 1393, 1300, 1244, 1115, 1050, 1038. EI (m/z) calcd. for $\text{C}_{15}\text{H}_{15}\text{ClO}$ $[\text{M}]^+$ 246.0811; found 246.0815.

4-(4-Methoxybenzyl)-4'-methylbiphenyl (5.1)



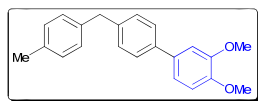
Colorless liquid (73%), R_f (Hexane) 0.45. ^1H NMR (500 MHz, CDCl_3): δ 7.50-7.46 (m, 4H), 7.24-7.22 (m, 4H), 7.14 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.96 (s, 2H), 3.79 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 157.98, 140.38, 138.86, 138.13, 136.78, 133.17, 129.87, 129.41, 129.13, 126.98, 126.82, 113.90, 55.24, 40.65, 21.07 ppm. IR (neat, cm^{-1}): 3026, 2837, 2917, 1610, 1511, 1499, 1302, 1247, 1175, 1034, 802, 787. HRMS (ES^+): calcd. for $\text{C}_{42}\text{H}_{40}\text{NaO}_2$ $[\text{2M}+\text{Na}]^+$ 599.2926; found 599.2923.

4-(4-Isopropoxybenzyl)-4'-methoxybiphenyl (5.2)



Colorless liquid (63%), R_f (5% EtOAc/Hexane) 0.35. ^1H NMR (500 MHz, CDCl_3): δ 7.51-7.45 (m, 4H), 7.22 (d, J = 7.95 Hz, 2H), 7.11 (d, J = 8.55 Hz, 2H), 6.96 (d, J = 8.85 Hz, 2H), 6.82 (d, J = 8.55 Hz, 2H), 4.53-4.48 (m, 1H), 3.94 (s, 2H), 3.84 (s, 3H), 1.32 (d, J = 6.1 Hz, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 158.97, 156.26, 140.08, 138.52, 133.61, 133.03, 129.86, 129.17, 127.97, 126.73, 115.93, 114.14, 69.87, 55.32, 40.65, 22.09 ppm. IR (neat, cm^{-1}): 2916, 2974, 1607, 1511, 1499, 1292, 1240, 1271, 1182, 1037, 807. HRMS (ES^+): calcd. for $\text{C}_{23}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 333.1855; found 333.1853.

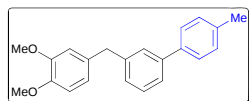
3,4-Dimethoxy-4'-(4-methylbenzyl)biphenyl (5.3)



Colorless liquid (69%), R_f (5% EtOAc/Hexane) 0.25. ^1H NMR (500 MHz, CDCl_3): δ 7.46 (d, $J = 8.25$ Hz, 2H), 7.23 (d, $J = 8.25$ Hz, 2H), 7.13-7.11 (m, 5H), 7.08 (d, $J = 2.15$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 3.98 (s, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 2.32 (s, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3): δ 149.06, 148.41, 140.11, 138.77, 137.99, 135.59, 134.09, 129.19, 129.16, 128.77, 126.88, 119.19, 111.42, 110.33, 55.95, 55.88, 41.10, 21.00 ppm. IR (neat, cm^{-1}): 3058, 2967, 1591, 1570, 1475, 1426, 1223, 1202, 1071, 782. EI (m/z) calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$ 318.1620; found 318.1625.

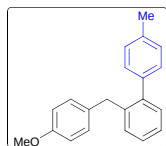
3-(3,4-Dimethoxybenzyl)-4'-methylbiphenyl (5.4)



Colorless liquid (90%), R_f (5% EtOAc/Hexane) 0.27. ^1H NMR (500 MHz, CDCl_3): δ 7.45 (d, $J = 7.9$ Hz, 2H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 1H), 7.22 (d, $J = 7.9$ Hz, 2H), 7.13 (d, $J = 7.65$ Hz, 1H), 6.80 (d, $J = 8.25$ Hz, 1H), 6.76 (d, $J = 1.80$ Hz, 1H), 6.73 (d, $J = 1.8$

Hz, 1H), 3.98 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 148.93, 141.78, 141.26, 137.00, 133.53, 133.11, 130.57, 129.41, 128.79, 127.46, 126.99, 124.75, 120.94, 112.24, 111.23, 92.80, 55.90, 55.82, 41.56, 21.07 ppm. IR (neat, cm^{-1}): 2998, 2933, 2833, 1590, 1514, 1463, 1416, 1260, 1235, 1153, 1139, 1029. EI (m/z) calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$ 318.1620; found 318.1625.

2-(4-Methoxybenzyl)-4'-methylbiphenyl (5.5)



Colorless liquid (111 mg, 59%), R_f (Hexane) 0.48. ^1H NMR (500 MHz, CDCl_3): δ 7.25-7.23 (m, 2H), 7.18-7.16 (m, 4H), 7.12-7.10 (m, 1H), 6.90 (d, $J = 8.25$ Hz, 2H), 6.83 (d, $J = 8.55$ Hz, 1H), 6.75 (d, $J = 8.55$ Hz, 2H), 3.89 (s, 2H), 3.76 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 138.90, 138.71, 130.12, 131.10, 130.03, 129.95, 129.76, 129.16, 128.71, 127.74, 127.24,

125.99, 113.86, 113.63, 55.21, 38.08, 21.15 ppm. IR (neat, cm^{-1}): 3022, 2930, 2833, 1611, 1583, 1511, 1481, 1464, 1246, 1176, 1037. EI (m/z) calcd. for $\text{C}_{21}\text{H}_{20}\text{O}$ $[\text{M}]^+$ 288.1514; found 288.1519.

4. References:

1. H. Suzuki and Y. Matano, (ed.), *Organobismuth Chemistry*, Elsevier, Amsterdam, 2001.
2. J. Carsten Pieck, D. Kuch, F. Grolle, U. Linne, C. Haas and T. Carell, *J. Am. Chem. Soc.*, 2006, **128**, 1404-1405.
3. (a) M. Amatore and C. Gosmini, *Chem.-Eur. J.*, 2010, **16**, 5848-5852; (b) M. Amatore and C. Gosmini, *Chem. Commun.*, 2008, **40**, 5019-21.
4. K. Itami, M. Mineno, T. Kamei and J. Yoshida, *Org. Lett.*, 2002, **4**, 3635-3638.
5. C. Kofink and P. Knochel, *Org. Lett.*, 2006, **8**, 4121-4124.
6. Y-H. Chen, M. Sun and P. Knochel, *Angew. Chem. Int. Ed.*, 2009, **48**, 2236-2239.
7. C. Duplais, A. Krasovskiy, A. Wattenberg and B. H. Lipshutz, *Chem. Commun.*, 2010, **46**, 562-564.
8. Y-S. Suh, J-S. Lee, S-H. Kim and R. D. Rieke, *J. Organomet. Chem.*, 2003, **684(1-2)**, 20-36.
9. F. D. Lewis and J. R. Petisce, *Tetrahedron*, 1986, **42**, 6207-6217.
10. A. Metzger, F. M. Piller and P. Knochel, *Chem. Commun.*, 2008, **40**, 5824-5826.
11. J. R. Schmink and N. E. Leadbeater, *Org. Lett.*, 2009, **11**, 2575-78.
12. R. B. Bedford, M. Huwe and M. C. Wilkinson, *Chem. Commun.*, 2009, **5**, 600-602.
13. G. Sun and Z. Wang, *Tetrahedron Lett.*, 2008, **49**, 4929-4932.
14. R. B. Bedford, M. A. Hall, G. R. Hodges, M. Huwe and M. C. Wilkinson, *Chem. Commun.*, 2009, **50**, 6430-6432.
15. G. Sun and Z. Wang, *Tetrahedron Lett.*, 2008, **49**, 4929-4932.