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Supporting Information

Iron-Catalyzed Benzylation Reaction of Arenes with Benzyl Thiocyanates

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Experimental Section

NMR spectroscopy was performed on a Bruker-300 spectrometer operating at 300 MHz or 500 MHz (\( ^1\)H NMR) and 75 MHz or 125 MHz (\( ^13\)C NMR). IR spectrometric analysis was performed on FTIR (Nicolet IS10). Mass spectrometric analysis was performed on GCMS (SHIMADZU GCMS-QP2010 ultra) and Micromass GCT-MS.

(A) Typical Experimental Procedure

(1) General Experimental Procedure for the Fe-Catalyzed benzylation of aromatic compounds:

A mixture of substrate 2 (20 equiv), benzyl thiocyanate 1 (0.4 mmol) and FeBr\(_3\) (20 mol%) was stirred in a Schlenk tube at 80 °C (oil bath temperature) under air atmosphere until complete consumption of starting material as monitored by TLC and GC-MS analysis. Then the mixture was filtered by a crude column, washed with ethyl acetate, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the corresponding product.

(2) General Experimental Procedure for the synthesis of products 12-17 and 20-21:

A mixture of substrate 2 (10 equiv), benzyl thiocyanate 1 (0.4 mmol), FeBr\(_3\) (20 mol%) and DCE (3 mL) was stirred in a Schlenk tube at 80 °C (oil bath temperature) under air atmosphere until complete consumption of starting material as monitored by TLC and GC-MS analysis. Then the mixture was filtered by a crude column, washed with ethyl acetate, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the corresponding product.

(B) Analytical data for 3-21

2-benzyl-1,4-dimethylbenzene (3)

Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.25 (t, \( J = 7.5 \) Hz, 2H), 7.19-7.15 (m, 1H), 7.11 (d, \( J = 7.5 \) Hz, 2H), 7.04 (d, \( J = 7.6 \) Hz, 1H), 6.95 (d, \( J = 7.7 \) Hz, 1H), 6.92 (s, 1 H), 3.94 (s, 2H), 2.28 (s, 3H), 2.18 (s, 3H); \(^{13}\)C
NMR (125 MHz, CDCl₃) δ 140.5, 138.7, 135.3, 133.4, 130.8, 130.2, 128.7, 128.3, 127.1, 125.8, 39.4, 21.0, 19.2; LRMS (EI, 70 eV) m/z (%): 196 (M⁺, 90), 181(100).

1, 4-dimethyl-2-(4-methylbenzyl)benzene (4)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.05 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 7.7 Hz, 1H), 6.91 (s, 1H), 3.89 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H); ¹³C NMR (125MHz, CDCl₃) δ: 138.9, 137.4, 135.3, 135.2, 133.3, 130.7, 130.1, 129.0, 128.6, 127.0, 39.0, 21.0, 20.9, 19.2; LRMS (EI, 70 eV) m/z (%): 210 (M⁺, 95), 195 (100).

1, 4-dimethyl-2-(2-methylbenzyl)benzene (5)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.13-6.99 (m, 4H), 6.88 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 7.4 Hz, 1H), 6.65 (s, 1H), 3.79 (s, 2H), 2.20 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 138.5, 138.1, 136.5, 135.4, 133.4, 130.0, 129.9(2C), 129.0, 126.9, 126.1, 126.0, 36.6, 21.0, 19.6, 19.1; LRMS (EI, 70 eV) m/z (%): 210 (M⁺, 100).

1, 4-dimethyl-2-(3-methylbenzyl) benzene (6)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.13 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.98-6.89 (m, 5H), 3.89 (s, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.18 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.5, 139.0, 137.8, 135.3, 133.4, 130.7, 130.1, 129.4, 128.2, 127.0, 126.6, 125.7, 39.3, 21.4, 21.0, 19.2; LRMS (EI, 70 eV) m/z (%): 210 (M⁺, 52), 195 (36), 104 (100).

2-(4-methoxybenzyl)-1, 4-dimethyl benzene (7)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 6.96-6.95 (m, 3H), 6.88-6.79 (m, 2H), 6.83 (s, 1H), 6.74 (d, J = 7.5 Hz, 2H), 3.81 (s, 2H), 3.70 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 157.7, 139.1, 135.3, 133.3, 132.5, 130.6, 130.1, 129.6, 127.0, 113.7, 55.2, 38.5, 21.0, 19.2; LRMS (EI, 70 eV) m/z (%): 226 (M⁺, 43), 211 (27), 118 (100).
2-(4-fluorobenzyl)-1, 4-dimethyl benzene (8)¹

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 6.96-6.93 (m, 3H), 6.87-6.80 (m, 4H), 3.79 (s, 2H), 2.18 (s, 3H), 2.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.3 (d, J = 242.2 Hz, 1C), 138.5, 136.2, 136.1, 135.4, 133.3, 130.6, 130.3, 130.0, 129.9 (d, J = 7.8 Hz, 2C), 127.2, 115.0 (d, J = 20.9 Hz, 2C), 38.6, 20.9, 19.1; LRMS (EI, 70 eV) m/z (%): 214 (M⁺, 86), 199 (100).

2-(2-bromobenzyl)-1, 4-dimethylbenzene (9)¹

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.57 (dd, J = 7.9, 1.0 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.08-7.04 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.81 (s, 1H), 4.00 (s, 2H), 2.26 (s, 3H), 2.17 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 139.8, 137.2, 135.5, 133.6, 132.5, 130.5, 130.2, 130.1, 127.6, 127.4, 127.3, 125.0 39.5, 21.0, 19.0; LRMS (EI, 70 eV) m/z (%): 276 (M+2, 45), 274 (M⁺, 46), 195 (100), 180 (74).

3-(2, 5-dimethylbenzyl)thiophene (10)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.24 (dd, J = 5.0, 3.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.96-9.94 (m, 2H), 6.89 (d, J = 5.0, 1.0 Hz, 1H), 6.80 (dd, J = 2.8, 1.1 Hz, 1H), 3.92 (s, 2H), 2.29 (s, 3H), 2.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 141.0, 138.5, 135.4, 133.2, 130.3,130.2, 128.4, 127.1, 125.4, 121.0, 34.3, 21.0, 19.0; LRMS (EI, 70 eV) m/z (%): 202 (M⁺, 100), 187 (80); HRMS (EI) for C₁₃H₁₄S (M⁺): calcd. 202.0816, found 202.0819.

2-benzyl-1, 3, 5-trimethylbenzene (11)²

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.24-7.20 (m, 2H), 7.16-7.13 (m, 1H), 7.01 (d, J = 7.4 Hz, 2H), 6.89 (s, 2H), 4.02 (s, 2H), 2.29 (s, 3H), 2.20 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.1, 137.0, 135.6, 133.8, 128.9, 128.3, 127.8, 125.6, 34.7, 20.9, 20.1; LRMS (EI, 70 eV) m/z (%): 210 (M⁺, 77), 195 (100).
3-benzyl-1,2,4,5-tetramethylbenzene (12)²

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.16-7.05 (m, 3H), 6.93 (d, J = 7.3 Hz, 2H), 6.85 (s, 1H), 4.02 (s, 2H), 2.17 (s, 6H), 2.04 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.3, 136.5, 133.7, 133.1, 123.0, 128.3, 128.0, 125.6, 35.6, 20.6, 15.8; LRMS (EI, 70 eV) m/z (%): 224 (M⁺, 100), 194 (28), 179 (25).

1-benzyl-4-methoxybenzene (13)³

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.23-7.16 (m, 2H), 7.12-7.09 (m, 3H), 7.03 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 3.85 (s, 2H), 3.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 157.9, 141.6, 133.2, 129.8, 128.8, 128.4, 125.9, 113.8, 55.2, 41.0; LRMS (EI, 70 eV) m/z (%): 198 (M⁺, 100), 183 (17).

2-benzyl-4-chloro-1-methoxybenzene (15)⁴

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.21-7.13 (m, 5H), 7.07 (d, J = 8.4 Hz, 1H), 6.95 (s, 1H), 6.69 (d, J = 8.4 Hz, 1H), 3.85 (s, 2H), 3.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 155.9, 140.0, 131.5, 130.0, 128.9, 128.4, 127.0, 126.0, 115.1, 111.5, 55.6, 35.6; LRMS (EI, 70 eV) m/z (%): 232 (M⁺, 75), 91 (100).

2-benzyl-4-chloro-1-methylbenzene (16) and 2-benzyl-1-chloro-4-methylbenzene (17)⁵

(16:17 = 62:38) Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.30-7.19 (m, 2×5H), 7.11-7.08 (m, 2×2H), 6.97 (s, 2×1H), 4.06 (s, 2H), 3.93 (s, 2H), 2.26 (s, 3H), 2.20 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.8, 139.7, 139.4, 138.2, 136.6, 131.7, 131.5, 131.4, 131.1, 129.7, 129.2, 128.9, 128.7, 128.5, 128.4, 126.4, 126.2, 126.1, 39.2, 39.1, 20.9, 19.1; LRMS (EI, 70 eV) m/z (%): 216 (M⁺, 9), 181 (100), 166 (55).

1-benzyl-4-chlorobenzene (18) and 1-benzyl-2-chlorobenzene (19)⁶

(18:19 = 64:36) Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ: 7.29-7.01 (m, 2×9H), 4.02 (s, 2H), 3.86 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 140.5, 139.6, 139.5, 138.7,
134.2, 131.9, 131.0, 130.2, 129.5, 128.9, 128.8, 128.6, 128.5, 128.4, 127.6, 126.8, 126.3, 126.2, 41.2, 39.2; LRMS (EI, 70 eV) m/z (%): 202 (M⁺, 47), 167 (100).

4-benzylphenol (20)

Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.22-7.19 (m, 2H), 7.13-7.09 (m, 3H), 6.98 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 8.3 Hz, 2H), 4.71 (brs, 1H), 3.84 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 153.8, 141.5, 133.4, 130.0, 128.8, 128.4, 126.0, 115.2, 41.0; LRMS (EI, 70 eV) m/z (%): 184 (M⁺, 100), 106 (78).

1, 3, 5-trimethoxy-2-thiocyanatobenzene (21)

Yellow soild; mp 159.3-160.5 °C (lit⁸: mp160-161 °C); ¹H NMR (500 MHz, CDCl₃) δ: 6.15 (s, 2H), 3.92 (s, 6H), 3.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 164.2, 161.3, 111.8, 91.3, 89.7, 56.3, 55.6; LRMS (EI, 70 eV) m/z (%): 225 (M⁺, 100), 179 (34).

(C) References

(D) Spectra

2-benzyl-1,4-dimethylbenzene (3)
2-benzyl-1,4-dimethylbenzene (3)
1, 4-dimethyl-2-(4-methylbenzyl)benzene (4)
1, 4-dimethyl-2-(4-methylbenzyl)benzene (4)
1, 4-dimethyl-2-(2-methylbenzyl)benzene (5)
1, 4-dimethyl-2-(2-methylbenzyl)benzene (5)
1, 4-dimethyl-2-(3-methylbenzyl) benzene (6)
1, 4-dimethyl-2-(3-methylbenzyl) benzene (6)
2-(4-methoxybenzyl)-1, 4-dimethyl benzene (7)
2-(4-methoxybenzyl)-1, 4-dimethyl benzene (7)
2-(4-fluorobenzyl)-1, 4-dimethyl benzene (8)
2-(4-fluorobenzyl)-1, 4-dimethyl benzene (8)
2-(2-bromobenzyl)-1, 4-dimethylbenzene (9)
2-(2-bromobenzyl)-1, 4-dimethylbenzene (9)
3-(2, 5-dimethylbenzyl)thiophen (10)
3-(2, 5-dimethylbenzyl)thiophen (10)
2-benzyl-1, 3, 5-trimethylbenzene (11)
2-benzyl-1, 3, 5-trimethylbenzene (11)
3-benzyl-1,2,4,5-tetramethylbenzene (12)
3-benzyl-1,2,4,5-tetramethylbenzene (12)
1-benzyl-4-methoxybenzene (13) and 1-benzyl-2-methoxybenzene (14)
1-benzyl-4-methoxybenzene (13) and 1-benzyl-2-methoxybenzene (14)
2-benzyl-4-chloro-1-methoxybenzene (15)
2-benzyl-4-chloro-1-methoxybenzene (15)
2-benzyl-4-chloro-1-methylbenzene (16) and 2-benzyl-1-chloro-4-methylbenzene (17)
2-benzyl-4-chloro-1-methylbenzene (16) and 2-benzyl-1-chloro-4-methylbenzene (17)
1-benzyl-4-chlorobenzene (18) and 1-benzyl-2-chlorobenzene (19)
1-benzyl-4-chlorobenzene (18) and 1-benzyl-2-chlorobenzene (19)
4-benzylphenol (20)
4-benzylphenol (20)
1, 3, 5-trimethoxy-2-thiocyanatobenzene (21)
1, 3, 5-trimethoxy-2-thiocyanatobenzene (21)