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Supporting Information for:

Iron-Catalyzed Arylation of α-Aryl-α-diazoesters

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CONTENTS:

1.	General Information	S2
2.	Typical Procedure of Iron-Catalyzed Arylation	S2
3.	Analytical Data of Arylation Products	S3
4.	Transformations of Arylation Products	
5.	NMR Spectra of Arylation Products	
6.	References	S43

1. General Information:

All reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified and dried using standard procedures.¹ FeCl₃ (Aldrich, \geq 99.998% (metals basis)), FeCl₃.6H₂O (Aldrich, \geq 98%), CoCl₂, and NiCl₂ were purchased form Aldrich, Acros, and Alfa-Aesar Co, Ltd and used as received. All of the diazo compounds were prepared according to the literature procedures.² NaBAr_F was prepared at hundreds gram scale starting from easily accessible 1-bromo-3,5-bis(trifluoromethyl)benzene in one port with 60–70% yield following the slightly modified literature procedures.³ Melting points were measured on a RY–I apparatus and uncorrected. NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (¹H NMR), 100 MHz (¹³C NMR). Chemical shifts (δ values) were reported in ppm down field from internal Me₄Si (¹H and ¹³C NMR). High Resolution Mass Spectra (HRMS) were recorded on an IonSpec FT-ICR mass spectrometer with Electron Spray Ionization (ESI) resource.

2. Typical Procedure of Iron-Catalyzed Arylation



The FeCl₃ (2.4 mg, 0.015 mmol, 5 mol%), 1,10-phenanthroline (phen, 3.2 mg, 0.018 mmol, 6 mol%), NaBAr_F.3H₂O (42.3 mg, 0.045 mmol, 15 mol%) were introduced into a Schlenk tube in argon-filled glovebox. After 3 mL 1,2-dichloroethane (DCE) was added, the resulting suspension was stirred at room temperature under an argon atmosphere for 4 h. Then 1 mL DCE solution of methyl α -diazophenylacetate **1a** (52.8 mg, 0.3 mmol) and *N*,*N*-dimethylaniline **2a** (54.5 mg, 0.45 mmol) was injected into the reaction mixture in one portion. The resulting mixture was stirred at 70 °C for specified time. The product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 15:1, v/v) as eluent. The analytical data for methyl 2-(4-

(dimethylamino)phenyl)-2-phenylacetate 3aa are listed below.

3. Analytical Data of Arylation Products

Methyl 2-(4-(dimethylamino)phenyl)-2-phenylacetate (3aa)⁴

White solid; mp = 49–50 °C; 93% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.30–7.27 (m, 4H, Ar-H), 7.24–7.20 (m, 1H, Ar-NMe₂ H), 7.17 (d, J = 8.7 Hz, 2H, Ar-H), 6.67 (d, J = 8.7 Hz, 2H, Ar-H), 4.94 (s, 1H, CH), 3.71 (s, 3H, CH₃), 2.90 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.5, 149.7, 139.3, 129.2, 128.4, 126.9, 126.3, 112.5, 56.1, 52.1, 40.4; HRMS (ESI) Calcd for [C₁₇H₂₀NO₂, M + H]⁺: 270.1489; Found: 270.1487.

Methyl 2-(2-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ba)



Colorless oil; 83% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.34 (m, 1H, Ar-H), 7.24–7.17 (m, 1H, Ar-H), 7.16– 7.14 (m, 4H, Ar-H), 6.69 (d, J = 8.8 Hz, 2H, Ar-H), 5.35 (s,

1H, CH), 3.71 (s, 3H, CH₃), 2.92 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 149.7, 137.3, 134.0, 129.9, 129.5, 129.3, 128.2, 126.7, 124.2, 112.5, 52.9, 52.3, 40.4; HRMS (ESI) Calcd for [C₁₇H₁₉ClNO₂, M + H]⁺: 304.1099; Found: 304.1107; Anal. Calcd for C₁₇H₁₈ClNO₂: C, 67.21; H, 5.97; N, 4.61. Found: C, 67.13; H, 6.18; N, 4.67.

Methyl 2-(3-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ca)



2.92 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.9, 149.8, 141.3, 134.2, 129.6, 129.2, 128.6, 127.2, 126.7, 125.5, 112.6, 55.7, 52.3, 40.5; HRMS (ESI) Calcd for [C₁₇H₁₉ClNO₂, M + H]⁺: 304.1099; Found: 304.1106; Anal. Calcd for C₁₇H₁₈ClNO₂: C, 67.21; H, 5.97; N, 4.61. Found: C, 66.95; H, 5.87; N, 4.51.

Methyl 2-(4-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3da)



3H, CH₃), 2.90 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 149.7, 137.9, 132.8, 129.8, 129.0, 128.5, 125.7, 112.5, 55.3, 52.2, 40.4; HRMS (ESI) Calcd for [C₁₇H₁₉ClNO₂, M + H]⁺: 304.1099; Found: 304.1106; Anal. Calcd for C₁₇H₁₈ClNO₂: C, 67.21; H, 5.97; N, 4.61. Found: C, 67.60; H, 6.39; N, 4.51.

Methyl 2-(3-bromophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ea)



Colorless oil; 87% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.45 (s, 1H, Ar-H), 7.35 (d, J = 7.6 Hz, 1H, Ar-H), 7.23 (d, J = 8.2 Hz, 1H, Ar-H), 7.16–7.13 (m, 3H, Ar-H), 6.69 (d, J = 8.3 Hz, 2H, Ar-H), 4.88 (s, 1H, CH), 3.72 (s, 3H,

CH₃), 2.91 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 149.7, 141.6, 131.4, 130.1, 129.9, 129.1, 127.1, 125.5, 112.6, 55.6, 52.2, 40.5; HRMS (ESI) Calcd for [C₁₇H₁₉BrNO₂, M + H]⁺: 348.0594; Found: 348.0590; Anal. Calcd for C₁₇H₁₈BrNO₂: C, 58.63; H, 5.21; N, 4.02. Found: C, 58.33; H, 5.13; N, 3.95.

Methyl 2-(4-(dimethylamino)phenyl)-2-o-tolylacetate (3fa)



Colorless oil; 85% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.24 (d, J = 4.1 Hz, 1H, Ar-H), 7.18–7.14 (m, 3H, Ar-H), 7.09 (d, NMe₂ J = 8.4 Hz, 2H, Ar-H), 6.67 (d, J = 8.4 Hz, 2H, Ar-H), 5.11 (s,

1H, CH), 3.70 (s, 3H, CH₃), 2.89 (s, 6H, 2CH₃), 2.27 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 149.5, 137.5, 136.2, 130.4, 129.5, 127.8, 127.0, 126.0, 125.3, 112.4, 52.8, 52.1, 40.4, 19.7; HRMS (ESI) Calcd for [C₁₈H₂₁NO₂Na, M + Na]⁺: 306.1465; Found: 306.1471; Anal. Calcd for C₁₈H₂₁NO₂: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.02; H, 7.61; N, 4.81.

Methyl 2-(4-(dimethylamino)phenyl)-2-p-tolylacetate (3ga)

Colorless oil; 88% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.19–7.15 (m, 4H, Ar-H), 7.10 (d, J = 8.7 Hz, 2H, Ar-H), Me NMe₂ 6.67 (d, J = 8.7 Hz, 2H, Ar-H), 4.91 (s, 1H, CH), 3.70 (s, 3H, CH₃), 2.89 (s, 6H, 2CH₃), 2.30 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 149.6, 136.5, 136.3, 129.11, 129.10, 128.2, 126.5, 112.5, 55.7, 52.0, 40.5, 20.9; HRMS (ESI) Calcd for [C₁₈H₂₁NO₂Na, M + Na]⁺: 306.1465; Found: 306.1473; Anal. Calcd for C₁₈H₂₁NO₂: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.01; H, 7.77; N, 4.72.

Methyl 2-(4-(dimethylamino)phenyl)-2-(2-methoxyphenyl)acetate (3ha)

OMe CO_2Me White solid; mp = 110–111 °C; 79% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.23–7.17 (m, 3H, Ar-H), 7.02 (d, J = 7.6 Hz, 1H, Ar-H), 6.86 (t, J = 7.6 Hz, 2H, Ar-H), 6.71 (d, J = 8.4 Hz, 1H, Ar-H), 5.18 (s, 1H, CH), 3.81 (s, 3H, CH₃), 3.69 (s, 3H, CH₃), 2.92 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.9, 156.7, 149.6, 129.7, 129.0, 128.4, 128.1, 125.0, 120.4, 112.6, 110.2, 55.4, 52.0, 50.0, 40.5; HRMS (ESI) Calcd for [C₁₈H₂₂NO₃, M + H]⁺: 300.1594; Found: 300.1600; Anal. Calcd for C₁₈H₂₁NO₃: C, 72.22; H, 7.07; N, 4.68. Found: C, 71.94; H, 7.36; N, 4.50.

Methyl 2-(4-(dimethylamino)phenyl)-2-(3-methoxyphenyl)acetate (3ia)

MeO NMe₂ CO_2Me Colorless oil; 80% yield; ¹H NMR (400 MHz, CDCl₃): $<math>\delta$ 7.23–7.17 (m, 3H, Ar-H), 6.90–6.86 (m, 2H, Ar-H), δ 6.77 (d, J = 8.2 Hz, 1H, Ar-H), 6.68 (d, J = 8.4 Hz, 2H,

Ar-H), 4.91 (s, 1H, CH), 3.74 (s, 3H, CH₃), 3.71 (s, 3H, CH₃), 2.90 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.3, 159.6, 149.6, 140.8, 129.3, 129.2, 126.1, 120.8, 114.3, 112.5, 112.2, 56.0, 55.1, 52.1, 40.5; HRMS (ESI) Calcd for [C₁₈H₂₂NO₃, M + H]⁺: 300.1594; Found: 300.1587; Anal. Calcd for C₁₈H₂₁NO₃: C, 72.22; H, 7.07; N, 4.68. Found: C, 71.91; H, 7.30; N, 4.56.

Methyl 2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)acetate (3ja)



(s, 3H, CH₃), 3.70 (s, 3H, CH₃), 2.90 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 158.5, 149.6, 131.4, 129.4, 129.0, 126.7, 113.8, 112.5, 55.2, 55.1, 52.0, 40.5; HRMS (ESI) Calcd for [C₁₈H₂₂NO₃, M + H]⁺: 300.1594; Found: 300.1595; Anal. Calcd for C₁₈H₂₁NO₃: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.02; H, 7.03; N, 4.64.

Methyl 2-(4-(dimethylamino)phenyl)-2-(naphthalen-2-yl)acetate (3ka)

CO₂Me Colorless oil; 86% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.78–7.75 (m, 4H, Ar-H), 7.43–7.39 (m, 3H, Ar-H), NMe₂ 7.21 (d, J = 8.8 Hz, 2H, Ar-H), 6.68 (d, J = 8.8 Hz, 2H,

Ar-H), 5.11 (s, 1H, CH), 3.74 (s, 3H, CH₃), 2.89 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 149.7, 136.8, 133.3, 132.4, 129.3, 128.1, 127.9, 127.5, 126.9, 126.8, 126.2, 126.0, 125.8, 112.6, 56.2, 52.1, 40.5; HRMS (ESI) Calcd for [C₂₁H₂₂NO₂, M + H]⁺: 320.1646; Found: 320.1643.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-(dimethylamino)phenyl)acetate (3la)

Colorless oil; 80% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.16 (d, J = 8.4 Hz, 2H, Ar-H), 6.82 (s, 1H, Ar-H), δ 6.75–6.71 (m, 2H, Ar-H), 6.68 (d, J = 8.4 Hz, 2H, Ar-H),

5.89 (s, 2H, CH₂), 4.85 (s, 1H, CH), 3.71 (s, 3H, CH₃), 2.91 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 149.6, 147.7, 146.5, 133.2, 129.0, 126.4, 121.6, 112.6, 109.0, 108.0, 100.9, 55.6, 52.1, 40.5; HRMS (ESI) Calcd for [C₁₈H₂₀NO₄, M + H]⁺: 314.1387; Found: 314.1378; Anal. Calcd for C₁₈H₁₉NO₄: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.67; H, 6.64; N, 4.38.

Methyl 2-(4-(dimethylamino)phenyl)-2-(thiophen-3-yl)acetate (3ma)

White solid; mp = 64–65 °C; 92% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.24–7.23 (m, 1H, Ar-H), 7.18 (d, *J* = 8.8 Hz, 2H, NMe₂ Ar-H), 7.14 (s, 1H, Ar-H), 7.01 (d, *J* = 4.4 Hz, 1H, Ar-H), 6.67 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.95 (s, 1H, CH), 3.70 (s, 3H, CH₃), 2.91 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.1, 149.7, 139.5, 128.9, 127.9, 126.0, 125.5, 122.3, 112.5, 52.1, 51.6, 40.5; HRMS (ESI) Calcd for [C₁₅H₁₇NO₂SNa, M + Na]⁺: 298.0872; Found: 298.0865; Anal. Calcd for C₁₅H₁₇NO₂S: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.34; H, 6.12; N, 4.98.

tert-Butyl 3-(1-(4-(dimethylamino)phenyl)-2-methoxy-2-oxoethyl)-1H-indole -1carboxylate (3na)



Colorless oil; 88% yield; ¹H NMR (400 MHz, CDCl₃): δ
8.11 (d, J = 2.4 Hz, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.36
² (d, J = 7.8 Hz, 1H, Ar-H), 7.28–7.25 (m, 3H, Ar-H), 7.15 (t, J = 7.6 Hz, 1H, Ar-H), 6.68 (d, J = 8.8 Hz, 2H, Ar-H),

5.06 (s, 1H, CH), 3.73 (s, 3H, CH₃), 2.89 (s, 6H, 2CH₃), 1.65 (s, 9H, 3CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.9, 149.8, 149.7, 135.4, 129.5, 129.0, 124.9, 124.3, 124.2, 122.4, 119.2, 118.6, 115.2, 112.6, 83.5, 52.2, 47.6, 40.4, 28.1; HRMS (ESI) Calcd for [C₂₄H₂₉N₂O₄, M + H]⁺: 409.2122; Found: 409.2127.

Methyl 2-(4-(diethylamino)phenyl)-2-phenylacetate (3ab)⁵

Colorless oil; 88% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.32–7.27 (m, 4H, Ar-H), 7.24–7.20 (m, 1H, Ar-H), 7.13 (d, NEt₂ J = 8.8 Hz, 2H, Ar-H), 6.61 (d, J = 8.8 Hz, 2H, Ar-H), 4.92 (s, 1H, CH), 3.71 (s, 3H, CH₃), 3.30 (q, J = 7.6 Hz, 4H, 2CH₂), 1.12 (t, J = 7.6 Hz, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.5, 146.8, 139.4, 129.3, 128.4, 126.8, 124.9, 111.5, 56.0, 52.0, 44.2, 12.5; HRMS (ESI) Calcd for [C₁₉H₂₄NO₂, M + H]⁺: 298.1802; Found: 298.1802.

Methyl 2-phenyl-2-(4-(pyrrolidin-1-yl)phenyl)acetate (3ac)



White solid; mp = 69–70 °C; 90% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.30–7.29 (m, 4H, Ar-H), 7.22–7.21 (m, 1H, Ar-H), 7.16 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.51 (d, *J* = 7.8 Hz, 2H, Ar-H), 4.94 (s, 1H, CH), 3.71 (s, 3H, CH₃), 3.29–3.19 (m, 4H,

2NCH2), 2.02–1.90 (m, 4H, 2CH2); ¹³C NMR (100 MHz, CDCl₃): δ 173.6, 147.0, 139.5, 129.3, 128.4, 126.8, 111.6, 56.1, 52.1, 47.5, 25.4; HRMS (ESI) Calcd for [C₁₉H₂₂NO₂, M + H]⁺: 296.1645; Found: 296.1653. This compound is known and the spectroscopic data match those reported.⁴

Methyl 2-(4-(benzyl(methyl)amino)phenyl)-2-phenylacetate (3ad) ⁵



Colorless oil; 82% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.29–7.26 (m, 6H, Ar-H), 7.22–7.18 (m, 4H, Ar-H), 7.15–7.13 (m, 2H, Ar-H), 6.67 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.92 (s, 1H, CH), 4.46 (s, 2H, CH₂), 3.68 (s, 3H, CH₃), 2.96 (s, 3H, CH₃);

¹³C NMR (100 MHz, CDCl₃): δ 173.4, 148.8, 139.3, 138.8, 129.3, 128.5, 128.4, 126.9, 126.8, 126.6, 126.2, 112.2, 56.5, 56.0, 52.1, 38.5; HRMS (ESI) Calcd for [C₂₃H₂₃NO₂Na, M + Na]⁺: 368.1621; Found: 368.1614.

Methyl 2-(4-(dimethylamino)-2-methylphenyl)-2-phenylacetate (3ae)

Colorless oil; 88% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.30–7.27 (m, 2H, Ar-H), 7.24–7.22 (m, 3H, Ar-H), 7.10 (d, J Me NMe₂ = 9.4 Hz, 1H, Ar-H), 6.56–6.55 (m, 2H, Ar-H), 5.13 (s, 1H, CH), 3.71 (s, 3H, CH₃), 2.90 (s, 6H, 2CH₃), 2.24 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.7, 149.6, 138.7, 136.9, 128.8, 128.7, 128.3, 126.8, 124.9, 114.6, 110.3, 52.8, 52.1, 40.4, 20.2; HRMS (ESI) Calcd for [C₁₈H₂₁NO₂Na, M + Na]⁺: 306.1465; Found: 306.1471.

Methyl 2-(4-(dimethylamino)-2-methoxyphenyl)-2-phenylacetate (3af)



Methyl 2-(3-chloro-4-(dimethylamino)phenyl)-2-phenylacetate (3ag)



Colorless oil; 17% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.36– 7.28 (m, 6H, Ar-H), 7.15 (d, *J* = 8.3 Hz, 1H, Ar-H), 7.01 (d, *J* ² = 8.3 Hz, 1H, Ar-H), 4.94 (s, 1H, CH), 3.75 (s, 3H, CH₃), 2.79 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.8, 149.5,

138.3, 133.5, 130.8, 128.7, 128.4, 128.2, 127.6, 127.5, 120.0, 56.0, 52.5, 43.7; HRMS (ESI) Calcd for [C₁₇H₁₉ClNO₂, M + H]⁺: 304.1099; Found: 304.1102.

Methyl 2-(2,4-dimethoxyphenyl)-2-phenylacetate (3ai)⁶



(ESI) Calcd for $[C_{18}H_{18}O_4Na, M + Na]^+$: 309.1097; Found: 309.1101.

Methyl 2-phenyl-2-(2,4,6-trimethoxyphenyl)acetate (3aj)⁶



Ar-H), 5.31 (s, 1H, CH), 3.80 (s, 3H, CH₃), 3.78 (s, 6H, 2CH₃), 3.68 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 174.1, 160.4, 158.1, 138.9, 129.2, 127.9, 126.5, 109.5, 90.9, 55.7, 55.2, 51.9, 45.7; HRMS (ESI) Calcd for [C₁₈H₂₀O₅Na, M + Na]⁺: 339.1203; Found: 339.1203.

4. Transformations of Arylation Products



4.1 Synthesis of methyl 2-(4-aminophenyl)-2-phenylacetate (4)⁷



A dry Schlenk tube under an N₂ atmosphere was charged with **3aa** (51 mg, 0.19 mmol, 1 equiv) and CH₂Cl₂ (2 mL) and cooled to -78 °C. PhIO (167 mg, 0.76 mmol, 4 equiv) was added in one portion under an N₂ flush and azidotrimethylsilane (TMSN₃, 87 mg, 0.76 mmol, 4 equiv) was added slowly. A small sample was taken after 4 h and quenched with H₂O (1 mL). ¹H NMR showed clean conversion to a bisazide. The -78 °C reaction was hydrolyzed by throwing directly into 20 °C solution of aqueous saturated NaHCO₃/THF (1:1, 10 mL) and stirred vigorously for 48 h. 1M HCl was added until neutral. THF was removed in vacuo, and residue partitioned between H₂O (10 mL). The organic phase separated and the aqueous phase back-extracted with CH₂Cl₂ 3 times. The combined organic extracts were dried over Na₂SO₄, and solvents

removed in vacuo and the residue was purified by silica gel chromatography (PE/EA = 4:1) gave compound **4** as a yellow oil in 89% yield (41 mg, 0.17 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.30–7.25 (m, 5H, Ar-H), 7.09 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.64 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.93 (s, 1H, CH), 3.73 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 173.4, 145.5, 139.2, 129.5, 128.5, 128.4, 127.0, 115.2, 56.2, 52.2.

4.2 Synthesis of methyl 2,2-diphenylacetate (5)⁸



In a 25 mL pear-shaped flask equipped with a magnetic stir bar, **3aa** (390 mg, 1.45 mmol, 1 equiv) was dissolved in iodomethane (0.9 mL, 14.5 mmol, 10 equiv). The neat reaction mixture was stirred at ambient temperature for 8 h at which time TLC analysis showed the starting material to be completely consumed. The iodomethane was removed in vacuo to furnish the quaternary ammonium iodide quantitatively without need for further purification. The quaternary ammonium salt was dissolved/suspended in THF (8.0 mL) and added to a rapidly stirring solution of sodium (334 mg, 14.5 mmol, 10 equiv) in liquid ammonia (approx. 50 mL) at -78 °C. After 3.5 min, the cold reaction mixture was treated with benzylmethyl ether (4 mL) and the deep blue color was supplanted almost immediately by a bright orange. The mixture was then treated with isopropanol (20 mL) and stirred at -78 °C for another 5 min by which time all color had dissipated from the reaction. Diethyl ether (20 mL) and saturated aqueous ammonium chloride (20 mL) were added carefully and the reaction vessel was allowed to warm to room temperature. The organic phase was then dried over Na₂SO₄, concentrated, and the residue purified by a column chromatography on silica gel (PE/EA = 20:1) to give **5** as a white solid in 93% yield (305 mg, 1.35 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.34–7.31 (m, 7H, Ar-H), 7.28–7.24 (m, 3H, Ar-H), 5.04 (s, 1H, CH), 3.74 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.9, 138.6, 128.6, 128.6, 127.3, 57.0, 52.3.





A dry Schlenk tube equipped with a magnetic stir bar was charged with **3aa** (538 mg, 2 mmol, 1 equiv) and CH₂Cl₂ (5 mL). To the resultant stirring solution was added methyl trifluoromethanesulfonate (MeOTf, 394 mg, 2.4 mmol, 1.2 equiv) in one portion at rt. The solution was stirred at rt for 2 h, at which time TLC analysis indicated complete consumption of 3aa. The MeOTf and CH₂Cl₂ was removed in vacuo to furnish ammonium triflate. The the *N*,*N*,*N*-trimethylanilinium trifluoromethanesulfonate (68 mg, 0.157 mmol, 1 equiv), bis(cyclooctadiene)nickel (Ni(COD)₂, 8.6 0.0314 mmol. 0.2 equiv), 1,3-bis(2,4,6mg, trimethylphenyl)imidazoliumchloride (IMes.HCl, 10.8 mg, 0.0314 mmol, 0.2 equiv), phenylboronic acid (38 mg, 0.314 mmol, 2 equiv) and K₃PO₄ (100 mg, 0.471 mmol, 3 equiv) were combined in a Schlenk tube in argon-filled glovebox, 1.0 mL degassed dioxane was added. The heterogeneous mixture was heated to 80 $\,^\circ$ C and stirred for 12 h. Upon cooling to rt the mixture was filtered through a plug of silica, washing with EA. The solvent was removed in vacuo and the residue was purified by a column chromatography on silica gel (PE/EA = 20:1) to afford 6 in 73% yield (35 mg, 0.116) mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.57–7.54 (m, 4H, Ar-H), 7.45–7.28 (m, 10H, Ar-H), 5.08 (s, 1H, CH), 3.77 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 172.9, 140.6, 140.2, 138.5, 137.6, 129.0, 128.73, 128.66, 128.6, 127.34, 127.29, 127.1, 56.7, 52.4.

4.4 Synthesis of 4-(amino(phenyl)methyl)-N,N-dimethylaniline (7)



A Schlenk tube under an N₂ atmosphere was charged with **3aa** (100 mg, 0.37 mmol, 1

equiv), NaOH (44 mg, 1.1 mmol, 3 equiv), MeOH (2 mL), H₂O (1 mL). This reaction mixture was stirred overnight at 60 °C. The residue was subsequently acidified with 1M HCl to pH = 2. The reaction mixture was extracted with CH_2Cl_2 3 times. The combined organic extracts were dried over Na₂SO₄, and solvents removed in vacuo to give corresponding carboxylic acid in 97% yield (91 mg, 0.36 mmol) as a colorless solid. The carboxylic acid (51 mg, 0.2 mmol, 1 equiv), CHCl₃ (4 mL), conc. H₂SO₄ (0.15 mL) were added to a Schlenk tube under N₂ atmosphere. The heterogeneous mixture was heated to 40 °C and NaN₃ (59 mg, 0.9 mmol, 4.5 equiv) was added in 5 portions in 90 min, then reaction mixture was stirred 4 h at 80 °C. Upon cooling to 0 °C the mixture was subsequently alkalized with 1M NaOH to pH > 11. The organic phase separated and the aqueous phase back-extracted with CHCl₃ 3 times. The combined organic extracts were dried over Na₂SO₄, and solvents removed in vacuo and the residue was purified by silica gel chromatography (PE/EA = 2:1) to gave the title compound 7 in 70% yield (31 mg, 0.14 mmol) as a yellow solid. Mp = 80-82 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, J = 7.4 Hz, 2H, Ar-H), 7.30 (t, J = 7.3 Hz, 2H, Ar-H), 7.23–7.18 (m, 3H, Ar-H), 6.69 (d, J = 8.6 Hz, 2H, Ar-H), 5.14 (s, 1H, CH), 2.91 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 149.6, 146.2, 133.7, 128.3, 127.6, 126.8, 126.6, 112.6, 59.1, 40.7; HRMS (ESI) Calcd for $[C_{15}H_{18}N_2Na, M + Na]^+$: 249.1362; Found: 249.1577; Anal. Calcd for C₁₅H₁₈N₂: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.35; H, 7.86; N, 12.41.

4.5 Synthesis of 4-(2-azido-1-phenylethyl)-*N*,*N*-dimethylaniline (8)



A 100 mL three-neck flask was charged with **3aa** (538 mg, 2 mmol, 1 equiv), LiAlH₄ (76 mg, 2 mmol, 1 equiv), 20 mL THF under N₂ atmosphere. The mixture was stirred for 2 h at 60 °C and quenched by H₂O, 10% aqueous NaOH (3.0 mL) carefully at 0 °C. The solution was then filtered and washed with EtOAc. The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography (PE/EA = 2:1) to afford the corresponding alcohol in 98% yield as a white solid. Mp = 88–90 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.32–7.18 (m, 5H, Ar-H), 7.13 (d, J = 8.7 Hz, 2H, Ar-H), 6.70 (d, J = 8.7 Hz, 2H, Ar-H), 4.11 (s, 3H, CH, CH₂), 2.91 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 149.5, 142.1, 128.9, 128.6, 128.2, 126.5, 112.9, 66.3, 52.7, 40.6; HRMS (ESI) Calcd for [C₁₆H₁₉NONa, M + Na]⁺: 264.1359; Found: 264.1355. The alcohol (121 mg, 0.5 mmol, 1 equiv), Ph₃P (262 mg, 1.0 mmol, 2 equiv), diethyl azodicarboxylate (DEAD, 174 mg, 1.0 mmol, 2 equiv) were added to a Schlenk tube under N₂ atmosphere at 0 °C, then diphenylphosphoryl azide (DPPA, 165 mg, 0.6 mmol, 1.2 equiv) was added slowly. The solution was stirred for 2 h at 0 °C. The solvent was removed under reduced pressure to give the crude product, which was purified by silica gel column chromatography (PE/EA = 10:1) to afford the product in 90% yield as a colorless oil (120 mg, 0.45 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.15 (m, 5H, Ar-H), 7.06 (d, J = 8.3 Hz, 2H, Ar-H), 6.65 (d, J = 8.4 Hz, 2H, Ar-H), 4.11 (t, J = 7.7 Hz, 1H, CH), 3.77 (d, J = 7.7 Hz, 2H, CH₂), 2.85 (s, 6H, 2CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 149.3, 141.9, 128.8, 128.4, 127.8, 126.6, 112.5, 55.5, 49.6, 40.3; HRMS (ESI) Calcd for $[C_{16}H_{19}N_4, M + H]^+$: 267.1604; Found: 267.1605.

5. NMR Spectra of Arylation Products



Methyl 2-(4-(dimethylamino)phenyl)-2-phenylacetate (3aa)

Value

Value



Methyl 2-(2-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ba)



Methyl 2-(3-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ca)



Methyl 2-(4-chlorophenyl)-2-(4-(dimethylamino)phenyl)acetate (3da)



Methyl 2-(3-bromophenyl)-2-(4-(dimethylamino)phenyl)acetate (3ea)











Methyl 2-(4-(dimethylamino)phenyl)-2-(2-methoxyphenyl)acetate (3ha)



Methyl 2-(4-(dimethylamino)phenyl)-2-(3-methoxyphenyl)acetate (3ia)







Methyl 2-(4-(dimethylamino)phenyl)-2-(naphthalen-2-yl)acetate (3ka)



Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-(dimethylamino)phenyl)acetate (3la)



Methyl 2-(4-(dimethylamino)phenyl)-2-(thiophen-3-yl)acetate (3ma)







Methyl 2-(4-(diethylamino)phenyl)-2-phenylacetate (3ab)







Methyl 2-(4-(benzyl(methyl)amino)phenyl)-2-phenylacetate (3ad)



Methyl 2-(4-(dimethylamino)-2-methylphenyl)-2-phenylacetate (3ae)



Methyl 2-(4-(dimethylamino)-2-methoxyphenyl)-2-phenylacetate (3af)



Methyl 2-(3-chloro-4-(dimethylamino)phenyl)-2-phenylacetate (3ag)







Methyl 2-phenyl-2-(2,4,6-trimethoxyphenyl)acetate (3aj)



Methyl 2-(4-aminophenyl)-2-phenylacetate (4)





Methyl 2-([1,1'-biphenyl]-4-yl)-2-phenylacetate (6)

4-(Amino(phenyl)methyl)-N,N-dimethylaniline (7)



2-(4-(Dimethylamino)phenyl)-2-phenylethan-1-ol







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