Supporting Information

Palladium-Catalyzed C-H Acetoxylation of 2-Methoxyimino-2-Aryl-Acetates and Acetamides

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1. General

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. All the solvents were treated prior to use according to the standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. \(^1\)H NMR spectra were recorded on Varian Mercury 400/600 (400/600 MHz) spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard (CDCl\(_3\): 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. \(^13\)C NMR spectra were recorded on Varian Mercury 400/600 (100/150 MHz) with complete proton decoupling spectrophotometers (CDCl\(_3\): 77.0 ppm). \(^19\)F NMR spectra were recorded on Varian Mercury 400 (400 MHz) spectrophotometers. Chemical shifts are reported in ppm with C\(_6\)F\(_6\) signal at -163 ppm as an external standard. Mass spectra were measured on a Finnigan Trace MS spectrometer (EI) or API 2000 LC/MS/MS (ESI-MS). Melting point was measured with BüCHI Melting Point B-545. IR spectra were measured on a BRUKER TENSOR 27 FT-IR spectrometer. Refractive index were measured on Abbé refractometer (2W).
2. General Procedure and Spectral Data of Substrates

2.1 General Procedure

\[
\begin{align*}
\text{R}^\text{O} \quad + \quad \text{MeO} \cdot \text{NH}_2 \cdot \text{HCl} & \quad \xrightarrow{\text{K}_2\text{CO}_3, \text{EtOH, reflux}} \quad \text{RO} \quad \to \quad \text{R}^\text{O} \quad \to \quad 1
\end{align*}
\]

\(\alpha\)-Ketoesters or ketoamides\(^{1-3}\) (5 mmol, 1.0 equiv), methoxylamine hydrochloride (6-10 mmol, 1.2-2.0 equiv) and \(\text{K}_2\text{CO}_3\) (6-10 mmol, 1.2-2.0 equiv) in EtOH (15 mL) were placed in a dried two-necked flask. The reaction system was stirred and refluxed until the reaction was completed by TLC analysis. After being cooled to room temperature, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, then the residue was purified by flash chromatography on silica gel to give the desired products.

Typical Procedure for Synthesis of compound 1m

\[
\begin{align*}
\text{R}^\text{O} \quad + \quad \text{MeO} \cdot \text{NH}_2 \cdot \text{HCl} & \quad \xrightarrow{\text{K}_2\text{CO}_3, \text{MeOH, reflux}} \quad \text{RO} \quad \to \quad \text{R}^\text{O} \quad \to \quad 1m
\end{align*}
\]

\(\alpha\)-Ketoester (5 mmol, 1.0 equiv), methoxylamine hydrochloride (6 mmol, 1.2 equiv) and \(\text{K}_2\text{CO}_3\) (6 mmol, 1.2 equiv) in MeOH (15 mL) were placed in a dried two-necked flask. The reaction system was stirred and refluxed until the reaction was completed by TLC analysis. After being cooled to room temperature, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, then the residue was purified by flash chromatography on silica gel to give 1m.

2.2 Spectral Data of Substrates

(Z)-ethyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1a)

Yield: 83%, colorless oil, \(n_\text{D}^25 = 1.5276; \text{IR} (\text{KBr}) \nu_{\text{max}} 2981, 2941, 2904, 2837, 1738, 1608, 1575, 1490, 1465, 1432, 1331, 1292, 1251, 1207, 1030, 913, 883, 788, 734, 697, 654 \text{ cm}^{-1}; \text{\(^1H NMR\) (600 MHz, CDCl}_3\) \(\delta 7.28 (t, J = 8.0 \text{ Hz, 1H}), 7.16 (d, J = 1.4 \text{ Hz, 1H}), 7.10 (d, J = 7.7 \text{ Hz, 1H}), 6.95 (dd, J = 8.3, 1.7 \text{ Hz, 1H}), 4.42 (q, J = 7.1 \text{ Hz, 2H}), 4.01 (s, 3H), 3.81 (s, 3H), 1.38 (t, J = 7.2 \text{ Hz, 3H}); \text{\(^13C NMR\) (150 MHz, CDCl}_3\) \(\delta 163.5, 159.7, 150.5, 131.4, 129.7, 118.8, 116.5, 110.8, 62.9, 61.8, 55.2, 14.1; MS: m/z = 237.2 ([M\textsuperscript+]); HRMS m/z: Calcd for C\textsubscript{12}H\textsubscript{13}NO\textsubscript{3}Na\textsuperscript{+} [M+Na\textsuperscript{+}]: 260.0899, Found: 260.0864.

(Z)-ethyl 2-(3-(benzyloxy)phenyl)-2-(methoxyimino)acetate (1b)

Yield: 70%, white solid, m.p. 37-39 °C; IR (KBr) \(\nu_{\text{max}} 2981, 2939, 2902, 1737, 1607, 1574, 1489, 1443, 1330, 1292, 1245, 1203, 1035, 884, 786, 738, 697 \text{ cm}^{-1}; \text{\(^1H NMR\) (600 MHz, CDCl}_3\) \(\delta 7.43-7.31\) (m, 4H), 7.33-7.23 (m, 3H), 7.12 (d, J = 7.3 Hz, 1H), 7.01 (dd, J = 8.3, 0.9 Hz, 1H), 5.06 (s, 2H), 4.40 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); \text{\(^13C NMR\) (150 MHz, CDCl}_3\) \(\delta 163.5, 158.9, 150.5, 136.5, 131.4, 129.8,
128.6, 128.0, 127.5, 119.1, 117.1, 111.9, 70.0, 63.0, 61.8, 14.1; **MS**: m/z = 313.1 ([M⁺]); **HRMS** m/z: Caled for C₁₈H₁₉NO₄Na⁺ [M+Na⁺]: 336.1212, Found: 336.1188.

**(Z)-ethyl 2-(methoxyimino)-2-m-tolylacetate (1c)**

Yield: 63%, colorless oil; **IR** (KBr) ν max 2982, 2940, 2821, 1738, 1611, 1464, 1445, 1369, 1327, 1238, 1177, 1064, 1034, 909, 885, 859, 792, 734, 699, 655 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.40 (s, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 2.35 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.6, 150.8, 138.4, 131.1, 130.0, 128.6, 126.5, 123.3, 62.9, 61.7, 21.3, 14.1; **MS**: m/z = 221.0 [M⁺].

**(Z)-ethyl 2-(methoxyimino)-2-o-tolylacetate (1d)**

Yield: 50%, colorless oil; **IR** (KBr) ν max 2978, 2939, 2902, 2821, 1737, 1603, 1459, 1368, 1322, 1280, 1259, 1220, 1048, 1024, 889, 859, 767, 725, 647 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.36 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.25–7.20 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 2.46 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.4, 151.2, 137.3, 131.2, 129.8, 129.6, 128.8, 125.9, 62.9, 61.7, 20.9, 14.1; **MS**: m/z = 221.0 [M⁺].

**(Z)-ethyl 2-(methoxyimino)-2-(4-methoxyphenyl)acetate (1e)**

Yield: 73%, white solid, m.p. 33–34°C; **IR** (KBr) ν max 2981, 2940, 2905, 2840, 1737, 1611, 1515, 1464, 1331, 1307, 1258, 1223, 1176, 1058, 1032, 891, 859, 795, 610 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.50 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 7.2 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 3.79 (s, 3H), 1.37 (t, J = 6.7 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.8, 161.2, 150.3, 127.6, 122.6, 114.1, 62.6, 61.7, 55.2, 14.1; **MS**: m/z = 237.0 [M⁺]; **HRMS** m/z: Calcd for C₁₂H₁₆NO₄⁺ [M+H⁺]: 238.1079, Found: 238.1042.

**(Z)-ethyl 2-(4-fluorophenyl)-2-(methoxyimino)acetate (1f)**

Yield: 49%, colorless oil; **IR** (KBr) ν max 3078, 2983, 2942, 2904, 2822, 1738, 1600, 1511, 1465, 1370, 1300, 1227, 1160, 1056, 1028, 894, 860, 840, 811, 608, 554, 514 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.56 (dd, J = 8.6, 5.4 Hz, 2H), 7.07 (t, J = 8.4 Hz, 2H), 4.42 (q, J = 7.3 Hz, 2H), 4.01 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 164.8, 163.4, 163.1, 149.6, 128.0, 128.15, 128.10, 126.5, 116.0, 115.98, 115.8, 95.3, 62.9, 61.9, 14.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ –111.1; **MS**: m/z = 225.0 [M⁺].

**(Z)-ethyl 2-(methoxyimino)-2-phenylacetate (1g)**

Yield: 69%, colorless oil; **IR** (KBr) ν max 2981, 2940, 2903, 2821, 1738, 1605, 1464, 1447, 1370, 1331, 1222, 1186, 1058, 1034, 1023, 893, 858, 770, 691, 651 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.57 (d, J = 6.7 Hz, 2H), 7.40–7.36 (m, 3H), 4.42 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.6, 150.6, 142.7, 130.1, 128.7, 126.1, 62.9,
61.8, 14.1; **MS**: m/z = 207.2 [M⁺]; **HRMS** m/z: Calcd for C₁₁H₁₃NO₃Na [M+Na]⁺: 230.0793, Found: 230.0750.

**(Z)-ethyl 2-(4-methoxy-2-methylphenyl)-2-(methoxyimino)acetate (1h)**

Yield: 56%, white solid, **m.p.**: 45-46 °C; **IR** (KBr) νₘₐₓ 2990, 2936, 2843, 2819, 1733, 1609, 1561, 1504, 1454, 1326, 1302, 1252, 1224, 1171, 1132, 1045, 1024, 890, 818, 630 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.27 (t, J = 7.3 Hz, 1H), 6.76 – 6.73 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.8, 160.3, 151.2, 139.3, 130.3, 122.2, 116.9, 111.1, 62.7, 61.6, 55.2, 21.5, 14.1; **MS**: m/z = 251.0 [M⁺].

**(Z)-ethyl 2-(3,4-dimethoxyphenyl)-2-(methoxyimino)acetate (1i)**

Yield: 80%, white solid, **m.p.**: 51-52 °C; **IR** (KBr) νₘₐₓ 2964, 2939, 2912, 2840, 1739, 1646, 1445, 1423, 1329, 1255, 1211, 1170, 1151, 1028, 918, 891, 862, 817, 729, 642 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.25 (d, J = 1.7 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.84 (dd, J = 8.2, 5.3 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 4.00 (d, J = 5.6 Hz, 3H), 3.91 (dd, J = 11.3, 6.7 Hz, 6H), 1.38 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.6, 151.0, 150.4, 149.2, 122.8, 120.0, 110.6, 107.9, 62.7, 62.6, 61.6, 55.8, 55.8, 14.1; **MS**: m/z = 267.0 [M⁺].

**(Z)-ethyl 2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(methoxyimino)acetate (1j)**

Yield: 83%, white solid, **m.p.**: 66-67 °C; **IR** (KBr) νₘₐₓ 2989, 2942, 2908, 2828, 1731, 1591, 1573, 1511, 1469, 1433, 1365, 1333, 1296, 1261, 1247, 1216, 1174, 1129, 1058, 1027, 1009, 912, 887, 859, 831, 806, 732, 656, 624 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.10 (d, J = 1.9 Hz, 1H), 7.05 (dd, J = 8.5, 1.9 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.25 (dd, J = 11.0, 5.1 Hz, 4H), 3.98 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 163.6, 150.1, 145.5, 143.7, 123.4, 119.6, 117.5, 115.1, 64.4, 64.1, 62.8, 61.7, 14.1; **MS**: m/z = 265.0 [M⁺].

**(Z)-ethyl 2-(methoxyimino)-2-(naphthalen-2-yl)acetate (1k)**

Yield: 55%, white solid, **m.p.**: 70-71 °C; **IR** (KBr) νₘₐₓ 2993, 2975, 2943, 2909, 1729, 1601, 1468, 1446, 1367, 1307, 1250, 1219, 1181, 1131, 1054, 1031, 891, 858, 812, 754, 731 cm⁻¹; **¹H NMR** (600 MHz, CDCl₃) δ 7.85–7.80 (m, 5H), 7.50–7.46 (m, 2H), 4.48 (q, J = 7.1 Hz, 2H), 4.06 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); **¹³C NMR** (150 Hz, CDCl₃) δ 163.7, 150.7, 134.0, 132.8, 128.5, 127.7, 127.6, 127.2, 126.8, 126.7, 126.6, 122.5, 63.0, 61.9, 14.2; **MS**: m/z = 257.0 [M⁺].

**(Z)-ethyl 2-(furan-2-yl)-2-(methoxyimino)acetate (1l)**
Yield: 88%, yellowish oil, IR (KBr) νmax 2985, 2943, 2905, 2824, 1741, 1590, 1482, 1446, 1371, 1309, 1228, 1157, 1095, 1069, 1035, 932, 887, 861, 779, 759, 595 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) (ratio of isomers = 4:1, major isomer) δ 7.51 (d, J = 1.0 Hz, 1H), 7.29 (d, J = 3.4 Hz, 1H), 6.53 (dd, J = 3.4, 1.7 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 4.14 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 162.3, 144.7, 143.6, 142.4, 140.0, 119.1, 112.5, 111.7, 63.7, 62.2, 14.0; MS: m/z = 197.0 [M⁺]; HRMS m/z: Calcd for C₇H₁₇NO₆Na⁺ [M+Na⁺]: 220.0586, Found: 220.0543.

(Z)-methyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1m)

Yield: 65%, colorless oil, nD 25 = 1.5375; IR (KBr) νmax 3004, 2942, 2838, 1743, 1608, 1575, 1490, 1464, 1432, 1333, 1290, 1252, 1212, 1173, 1044, 959, 913, 846, 787, 734, 699, 656 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (t, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.02 (s, 3H), 3.93 (s, 2H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 159.7, 150.4, 131.3, 129.7, 118.9, 116.5, 110.9, 62.9, 55.3, 52.3; MS: m/z = 223.0 [M⁺]; HRMS m/z: Calcd for C₁₀H₁₄NO₃Na⁺ [M+Na⁺]: 246.0742, Found: 246.0699.

(Z)-butyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1n)

Yield: 73%, colorless oil, nD 25 = 1.5165; IR (KBr) νmax 2962, 2939, 2875, 2838, 1739, 1608, 1575, 1490, 1465, 1432, 1331, 1290, 1250, 1206, 1046, 912, 866, 784, 736, 697, 655 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.28 (t, J = 8.0 Hz, 1H), 7.16 (s, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 4.36 (t, J = 6.6 Hz, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 1.74-1.70 (m, 2H), 1.46-1.40 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 163.6, 159.7, 150.6, 131.4, 129.7, 118.8, 116.5, 110.7, 65.5, 62.9, 55.2, 30.4, 18.9, 13.5; MS: m/z = 265.0 [M⁺].

(Z)-isopropyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1o)

Yield: 85%, white solid, m.p. 46-47 °C; IR (KBr) νmax 2982, 2940, 2837, 1734, 1608, 1575, 1490, 1465, 1432, 1325, 1288, 1253, 1212, 1105, 1045, 1027, 917, 871, 827, 785, 735, 692, 650 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.28 (dd, J = 14.9, 7.0 Hz, 1H), 7.16 (s, 1H), 7.11 (d, J = 7.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 5.35-5.29 (m, 1H), 4.01 (d, J = 0.5 Hz, 3H), 3.82 (s, 3H), 1.37 (d, J = 6.3 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 163.1, 159.7, 150.7, 131.5, 129.7, 118.8, 116.5, 110.8, 69.9, 62.8, 55.3, 21.8; MS: m/z = 251.0 [M⁺].

(Z)-benzyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1p)

Yield: 66%, colorless oil, nD 25 = 1.5634; IR (KBr) νmax 2939, 2840, 2822, 1744, 1613, 1574, 1488, 1456, 1437, 1322, 1284, 1251, 1207, 1180, 1044, 1025, 954, 902, 787, 743, 731, 696, 656 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.41 (d, J = 7.0 Hz, 2H), 7.37-7.31 (m, 3H), 7.23 (t, J = 8.0 Hz, 1H), 7.06 (dd, J = 9.5, 4.8 Hz, 2H), 6.92 (dd, J = 8.3, 1.9 Hz, 1H), 5.38 (s, 2H), 4.00 (s, 3H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 159.5, 150.1, 134.8, 131.1, 129.6, 128.44, 128.40, 118.7, 116.7, 110.3, 67.1, 62.8, 55.0; MS: m/z = 299.1 [M⁺]; HRMS m/z: Calcd for C₁₉H₁₇NO₆Na⁺ [M+Na⁺]: 322.1055, Found: 322.1024.
(Z)-N-methoxy-2-(methoxyimino)-2-(3-methoxyphenyl)-N-methylacetamide (1q)

Yield: 88%, yellowish oil, n\textsubscript{D}^25 = 1.5455; \textbf{IR} (KBr) \nu\textsubscript{max} 2940, 2821, 1667, 1607, 1574, 1489, 1463, 1427, 1387, 1321, 1302, 1231, 1181, 1043, 982, 900, 809, 790, 689 cm\textsuperscript{-1}; \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) (ratio of isomers = 6:1, major isomer) \delta 7.29 (dd, J = 14.7, 6.8 Hz, 1H), 7.24–7.16 (m, 1H), 7.12 (d, J = 7.7 Hz, 1H), 6.95 (t, J = 9.4 Hz, 1H), 4.02 (d, J = 7.2 Hz, 3H), 3.82 (s, 3H), 3.57 (s, 3H), 3.34 (s, 3H); \textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}) \delta 164.6, 159.7, 152.7, 132.1, 129.6, 118.9, 116.3, 110.7, 62.6, 61.8, 55.3, 31.5; \textbf{MS}: m/z = 252.0 [M\textsuperscript{+}].

(Z)-2-(methoxyimino)-2-(3-methoxyphenyl)-1-morpholinoethanone (1r)

Yield: 78%, white solid, m.p. 88-89 °C; \textbf{IR} (KBr) \nu\textsubscript{max} 2976, 2932, 2856, 2824, 1639, 1606, 1493, 1464, 1443, 1427, 1327, 1275, 1251, 1177, 1112, 1058, 1007, 942, 902, 854, 818, 791, 753, 687, 639 cm\textsuperscript{-1}; \textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}) \delta 7.36–7.25 (m, 1H), 7.22 (s, 1H), 7.14 (d, J = 6.7 Hz, 1H), 6.95 (d, J = 6.0 Hz, 1H), 4.01 (s, 3H), 3.82 (d, J = 7.6 Hz, 4H), 3.73 (s, 3H), 3.61 (d, J = 39.8 Hz, 2H), 3.33 (d, J = 39.4 Hz, 2H); \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) 162.8, 159.6, 151.7, 131.6, 129.7, 118.7, 116.4, 110.5, 66.7, 66.5, 62, 7, 55.2, 46.1, 41.3; \textbf{MS}: m/z = 278.0 [M\textsuperscript{+}].

3. General Procedure and Spectral Data of Products

3.1 Reaction Optimization and Result Summary

Table 1. The Screening of Various Solvents.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)\textsuperscript{b}</th>
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<td>1</td>
<td>HOAc</td>
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<td>2</td>
<td>Ac\textsubscript{2}O</td>
<td>66</td>
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<tr>
<td>3</td>
<td>CF\textsubscript{3}COOH</td>
<td>-</td>
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<tr>
<td>4</td>
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<td>-</td>
</tr>
<tr>
<td>5</td>
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<td>-</td>
</tr>
<tr>
<td>6</td>
<td>CH\textsubscript{3}CN</td>
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<td>7</td>
<td>DMSO</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Toluene</td>
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<tr>
<td>11</td>
<td>HOAc/AC\textsubscript{2}O (2:1)</td>
<td>72</td>
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\textsuperscript{a} The reactions were carried out with 0.30 mmol (1.0 equiv) of 1a, 0.36 mmol (1.2 equiv) of Phl(OAc)\textsubscript{2} and 5 mol% Pd(OAc)\textsubscript{2} in 2.0 mL of solvent at 100 °C.
Table 2. The Screening of Various Catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)_2</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>PdCl\textsubscript{2}</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>Pd(CH\textsubscript{3}CN\textsubscript{2})\textsubscript{2}Cl\textsubscript{2}</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh\textsubscript{3})\textsubscript{4}</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>Pd\textsubscript{2}dba\textsubscript{3}</td>
<td>74</td>
</tr>
<tr>
<td>7</td>
<td>Pd(TFA\textsubscript{2})</td>
<td>73</td>
</tr>
<tr>
<td>8</td>
<td>Pd(PhCN\textsubscript{2})\textsubscript{3}Cl\textsubscript{2}</td>
<td>71</td>
</tr>
<tr>
<td>9\textsuperscript{c}</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The reactions were carried out with 0.30 mmol (1.0 equiv) of 1a, 0.36 mmol (1.2 equiv) of Phl(OAc)\textsubscript{2} and 5 mol% catalyst in 2.0 mL of HOAc/\textsubscript{Ac}_2\textsubscript{O} (1:1) at 100 °C. \textsuperscript{b} Isolated yield. \textsuperscript{c} Without palladium.

Table 3. The Screening of Temperature.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 °C</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>110 °C</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>120 °C</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>80 °C</td>
<td>66</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The reactions were carried out with 0.30 mmol (1.0 equiv) of 1a, 0.36 mmol (1.2 equiv) of Phl(OAc)\textsubscript{2} and 5 mol% Pd(OAc)\textsubscript{2} in 2.0 mL of HOAc/\textsubscript{Ac}_2\textsubscript{O} (1:1). \textsuperscript{b} Isolated yield.

Table 4. The Screening of catalyst loading.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Loading</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 mol%</td>
<td>83</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Isolated yield.
The reactions were carried out with 0.30 mmol (1.0 equiv) of 1a, 0.36 mmol (1.2 equiv) of Phl(OAc)$_2$ and Pd(OAc)$_2$ in 2.0 mL of HOAc/Ac$_2$O (1:1).

Table 5. The Screening of Various Oxidants.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phl(OAc)$_2$</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>K$_2$S$_2$O$_8$</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>Oxone</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Benzoyl peroxide</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>3-ClPhCO$_2$H</td>
<td>-</td>
</tr>
<tr>
<td>6$^c$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The reactions were carried out with 0.30 mmol (1.0 equiv) of 1a, 0.36 mmol (1.2 equiv) of oxidant and 5 mol% Pd(OAc)$_2$ in 2.0 mL of HOAc/Ac$_2$O (1:1).

$^b$ Isolated yield. $^c$ Without oxidant.

3.2 General Procedure

A mixture of substrate 1 (0.3 mmol, 1.0 equiv), iodosobenzene diacetate (0.36 mmol, 1.2 equiv) and Pd(OAc)$_2$ (0.015 mmol, 0.05 equiv) were combined in AcOH (1.0 mL) and Ac$_2$O (1.0 mL) in a dried Schlenk tube under a nitrogen atmosphere. The reaction was stirred at 100 °C and monitored by TLC. Upon completion or no further improvement of reaction, the reaction mixture was cooled to room temperature and was then diluted with ethyl acetate (50 mL). The organic layer was washed sequentially with saturated NaHCO$_3$ (2 x 30 mL), water (2 x 30 mL) and brine (1 x 30 mL) then dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired products.

3.3 Spectral Data of Products

(Z)-ethyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2a)

Yield: 83%, white solid; IR (KBr) v$_{max}$ 2982, 2939, 2842, 1770, 1735, 1610, 1578, 1498, 1414, 1372, 1332, 1300, 1273, 1248, 1191, 1038, 1024, 923, 898, 883, 844, 820, 781, 595 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.14 (d, $J$ = 3.0 Hz, 1H), 7.01 (d, $J$ = 8.9 Hz, 1H), 6.96 (dd, $J$ = 8.9, 3.0 Hz, 1H), 4.34 (q, $J$ = 7.1 Hz, 2H), 4.02 (s, 3H), 3.81 (s, 3H),
2.24 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C\ NMR (150 MHz, CDCl\_3) \delta 169.3, 162.3, 157.2, 147.4, 141.7, 124.4, 124.2, 117.0, 113.1, 63.1, 61.7, 55.7, 20.6, 14.0; MS: m/z = 295.2 [M\^+]; HRMS m/z: C\_14H\_17NO\_6 K [M+K\^+]: 334.0693, Found: 334.0686.

(Z)-ethyl 2-(2-acetoxy-5-(benzyloxy)phenyl)-2-(methoxyimino)acetate (2b)

Yield: 74%, colorless oil; IR (KBr) v\_max 3033, 2983, 2940, 2822, 1767, 1739, 1607, 1572, 1493, 1456, 1241, 1368, 1180, 1036, 896, 742, 698, 650 cm\(^{-1}\); ^{1}H\ NMR (600 MHz, CDCl\_3) \delta 7.43–7.38 (m, 4H), 7.33 (t, J = 6.9 Hz, 1H), 7.24 (s, 1H), 7.03–7.00 (m, 2H), 5.05 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 4.02 (s, 3H), 2.24 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H);

(Z)-ethyl 2-(2-acetoxy-5-(benzyloxy)phenyl)-2-(methoxyimino)acetate (2b)

13C\ NMR (150 MHz, CDCl\_3) \delta 169.3, 162.4, 156.4, 147.4, 141.9, 136.4, 128.6, 128.1, 127.5, 124.5, 124.3, 117.7, 114.2, 70.4, 63.1, 61.7, 20.7, 14.0; MS: m/z = 371.3 [M\^+]; HRMS m/z: Calcd for C\_20H\_21NO\_6 Na [M+Na\^+]: 394.1267, Found: 394.1291.

(Z)-ethyl 2-(2-acetoxy-5-(benzyloxy)phenyl)-2-(methoxyimino)acetate (2b)

Yield: 74%, colorless oil; IR (KBr) v\_max 3033, 2983, 2940, 2822, 1767, 1739, 1607, 1572, 1493, 1456, 1241, 1368, 1180, 1036, 896, 742, 698, 650 cm\(^{-1}\); ^{1}H\ NMR (600 MHz, CDCl\_3) \delta 7.43–7.38 (m, 4H), 7.33 (t, J = 6.9 Hz, 1H), 7.24 (s, 1H), 7.03–7.00 (m, 2H), 5.05 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 4.02 (s, 3H), 2.24 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C\ NMR (150 MHz, CDCl\_3) \delta 169.3, 162.4, 156.4, 147.4, 141.9, 136.4, 128.6, 128.1, 127.5, 124.5, 124.3, 117.7, 114.2, 70.4, 63.1, 61.7, 20.7, 14.0; MS: m/z = 371.3 [M\^+]; HRMS m/z: Calcd for C\_20H\_21NO\_6 Na [M+Na\^+]: 394.1267, Found: 394.1291.
(Z)-ethyl 2-(2-acetoxy-4,5-dimethoxyphenyl)-2-(methoxyimino)acetate (2i)

Yield: 47%, yellow oil; IR (KBr) \( \nu_{\text{max}} \) 3082, 2985, 2942, 2905, 2823, 1777, 1740, 1606, 1503, 1419, 1369, 1328, 1189, 1147, 1102, 1049, 1027, 973, 893, 854, 822, 672, 628, 556, cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.63 (dd, \( J = 8.8, 6.2 \text{ Hz}, 1H \)), 6.99-7.03 (m, 1H), 6.90 (dd, \( J = 8.9, 2.5 \text{ Hz}, 1H \)), 4.35 (q, \( J = 7.1 \text{ Hz}, 2H \)), 4.02 (s, 3H), 2.27 (s, 3H), 1.33 (t, \( J = 7.2 \text{ Hz}, 3H \)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 168.4, 164.4, 162.7, 162.3, 149.1, 146.7, 130.5, 120.4, 113.8, 113.6, 111.4, 111.3, 63.2, 61.8, 20.7, 14.0; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -109.1; MS: m/z = 283.2 [M\(^+\)]; HRMS m/z: Calcd for C\(_{14}\)H\(_{14}\)FNNaO\(_3\) [M+Na\(^+\)]: 306.0754, Found: 306.0753.

(Z)-ethyl 2-(2-acetoxy-4-methoxy-6-methylphenyl)-2-(methoxyimino)acetate (2h)

Yield: 66%, colorless oil; IR (KBr) \( \nu_{\text{max}} \) 2984, 2941, 2904, 2823, 1772, 1738, 1606, 1487, 1446, 1369, 1327, 1263, 1184, 1109, 1038, 1023, 913, 893, 763, 677, 640, 540 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.55 (dd, \( J = 7.8, 1.4 \text{ Hz}, 1H \)), 7.37-7.33 (m, 1H), 7.19 (dd, \( J = 11.1, 4.2 \text{ Hz}, 1H \)), 7.03 (d, \( J = 8.1 \text{ Hz}, 1H \)), 4.26 (q, \( J = 7.1 \text{ Hz}, 2H \)), 3.94 (s, 3H), 2.18 (s, 3H), 1.24 (t, \( J = 7.2 \text{ Hz}, 3H \)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 168.9, 162.4, 148.2, 147.5, 131.1, 129.0, 126.3, 123.9, 123.4, 63.1, 61.7, 20.7, 14.0; MS: m/z = 265.2 [M\(^+\)]; HRMS m/z: Calcd for C\(_{13}\)H\(_{13}\)NO\(_3\)Na [M+Na\(^+\)]: 288.0848, Found: 288.0782.

(Z)-ethyl 2-(2-acetoxy-4-methoxy-6-methylphenyl)-2-(methoxyimino)acetate (2i)

Yield: 85%, colorless oil; IR (KBr) \( \nu_{\text{max}} \) 2979, 2941, 2843, 1774, 1737, 1614, 1574, 1493, 1465, 1368, 1329, 1302, 1202, 1145, 1034, 947, 887, 861, 764, 637, 590 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)) (ratio of isomers = 6:1, major isomer) \( \delta \) 6.68 (d, \( J = 1.9 \text{ Hz}, 1H \)), 6.50 (d, \( J = 2.2 \text{ Hz}, 1H \)), 4.25 (q, \( J = 7.1 \text{ Hz}, 2H \)), 4.00 (s, 3H), 3.77 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H), 1.27 (t, \( J = 7.1 \text{ Hz}, 3H \)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 169.0, 162.0, 160.5, 150.3, 146.3, 140.8, 116.7, 114.1, 106.0, 63.0, 61.6, 55.4, 20.8, 20.2, 13.9; MS: m/z = 309.2 [M\(^+\)]; HRMS m/z: Calcd for C\(_{14}\)H\(_{14}\)NO\(_3\)Na [M+Na\(^+\)]: 332.1110, Found: 332.1132.

(Z)-ethyl 2-(2-acetoxy-4,5-dimethoxyphenyl)-2-(methoxyimino)acetate (2i)

Yield: 82%, colorless oil; IR (KBr) \( \nu_{\text{max}} \) 2797, 2941, 2838, 1771, 1739, 1612, 1516, 1464, 1368, 1303, 1260, 1178, 1140, 1033, 980, 903, 797, 741, 590 cm\(^{-1}\); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.14 (s, 1H), 6.59 (s, 1H), 4.36 (q, \( J = 7.1 \text{ Hz}, 2H \)), 4.01 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 2.25 (s, 3H), 1.35 (t, \( J = 7.1 \text{ Hz}, 3H \)); \(^{13}\)C NMR (100 MHz, DMSO) \( \delta \) 169.16, 162.59, 151.38, 147.4, 146.9, 142.5, 114.5, 109.1, 107.6, 62.8, 61.7, 56.0, 55.8, 20.6, 14.0; MS: m/z = 325.2 [M\(^+\)]; HRMS m/z: Calcd for C\(_{16}\)H\(_{16}\)NO\(_3\)Na [M+Na\(^+\)]: 348.1059, Found: 348.1070.

(Z)-ethyl 2-(7-acetoxy-2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(methoxyimino)acetate (2j)

Yield: 56%, white solid, m.p. 69-70 °C; IR (KBr) \( \nu_{\text{max}} \) 2989, 2941, 2899, 2829, 1773, 1726, 1620, 1577, 1515, 1462, 1415, 1375, 1350, 1307, 1281, 1217, 1174, 1144, 1054, 1033, 984, 931, 904, 882, 800,
742, 597, 553 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.11 (s, 1H), 6.62 (s, 1H), 4.32-4.36 (m, 2H), 4.25 (dd, J = 15.8, 4.4 Hz, 4H), 3.98 (s, 3H), 2.24 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.2, 162.6, 147.2, 145.4, 142.0, 141.5, 116.9, 116.6, 112.2, 64.4, 64.0, 62.9, 61.7, 20.7, 14.0; HRMS m/z: Calcd for C₁₅H₁₇NO₇Na [M+Na]⁺: 346.0903, Found: 346.0905.

(Z)-ethyl 2-(3-acetoxynaphthalen-2-yl)-2-(methoxyimino)acetate (2k)

Yield: 73%, white solid, m.p. 60-62 °C; IR (KBr) νmax 2987, 2942, 2831, 1765, 1724, 1632, 1469, 1441, 1369, 1326, 1273, 1233, 1198, 1156, 1123, 1012, 994, 895, 877, 747 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.07 (s, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.56 (s, 1H), 7.43-7.49 (m, 2H), 4.37 (q, J = 7.2 Hz, 2H), 4.06 (s, 3H), 2.32 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.2, 162.3, 147.9, 145.1, 133.9, 130.9, 129.9, 128.2, 127.7, 127.1, 126.3, 123.0, 120.7, 63.1, 61.7, 20.8, 13.9; HRMS m/z: Calcd for C₁₇H₁₈NO₅ [M+H]⁺: 316.1185, Found: 316.1150.

(Z)-ethyl 2-(3-acetoxynaphthalen-2-yl)-2-(methoxyimino)acetate (2l)

Yield: 17%, yellow oil; IR (KBr) νmax 2985, 2943, 2906, 2825, 1796, 1740, 1606, 1572, 1494, 1464, 1427, 1368, 1248, 1182, 1033, 927, 896, 852, 824, 792, 654 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) (ratio of isomers = 5:1, major isomer) δ 7.28 (d, J = 3.6 Hz, 1H), 6.11 (d, J = 3.7 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.13 (s, 3H), 2.32 (s, 3H), 1.39 (t, J = 6.7 Hz, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 165.6, 161.9, 151.6, 139.1, 135.0, 121.3, 94.8, 63.7, 62.2, 20.6, 14.0; MS: m/z = 255.2 [M⁺]; HRMS m/z: Calcd for C₁₁H₁₃NO₆Na [M+Na]⁺: 278.0641, Found: 278.0618.

(Z)-methyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2m)

Yield: 83%, colorless oil; IR (KBr) νmax 2943, 2906, 2840, 1768, 1743, 1608, 1573, 1494, 1464, 1427, 1368, 1248, 1182, 1033, 927, 896, 852, 824, 745, 654 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 2.8 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H), 6.96 (dd, J = 8.8, 2.8 Hz, 1H), 4.03 (s, 3H), 3.86 (s, 2H), 3.81 (s, 3H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 161.9, 151.6, 139.1, 135.0, 121.3, 94.8, 63.7, 62.2, 20.6, 14.0; MS: m/z = 281.2 [M⁺]; HRMS m/z: Calcd for C₁₃H₁₅NO₆Na [M+Na]⁺: 304.0797, Found: 304.0792.

(Z)-butyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2n)

Yield: 83%, colorless oil; IR (KBr) νmax 2962, 2941, 2875, 2841, 1770, 1741, 1608, 1572, 1494, 1465, 1368, 1247, 1186, 1037, 929, 896, 822, 747, 653 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.14 (s, 1H), 7.01 (d, J = 8.9 Hz, 1H), 6.96 (dd, J = 8.4, 3.5 Hz, 1H), 4.30-4.28 (m, 2H), 4.02 (s, 3H), 3.82 (s, 3H), 2.24 (s, 3H), 1.70–1.67 (m, 2H), 1.40–1.36 (m, 2H), 0.93 (d, J = 2.9 Hz, 1H), 0.92 (dd, J = 7.4, 2.9 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 169.4, 162.5, 157.1, 147.4, 141.7, 124.4, 124.2, 117.1, 112.9, 65.5, 63.1, 55.6, 30.3, 20.7, 18.9, 13.5; MS: m/z = 323.3 [M⁺]; HRMS m/z: Calcd for C₁₆H₂₁NO₆Na [M+Na]⁺: 346.1267, Found: 346.1270.

(Z)-isopropyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2o)
Yield: 75%, white solid, m.p. 55-56 °C; **IR** (KBr) \( \nu_{\text{max}} \) 2983, 2940, 2841, 2824, 1768, 1729, 1614, 1577, 1499, 1459, 1415, 1375, 1272, 1256, 1191, 1174, 1097, 1040, 1015, 917, 895, 872, 825, 778, 745 cm\(^{-1}\); **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 7.12 (s, 1H), 7.01 (d, \( J = 8.9 \) Hz, 1H), 6.97-6.95 (m, 1H), 5.26-5.21 (m, 1H), 4.02 (s, 3H), 3.81 (s, 3H), 2.25 (s, 3H), 1.32 (d, \( J = 6.3 \) Hz, 6H); **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \( \delta \) 169.5, 161.9, 157.1, 147.7, 141.7, 124.4, 124.2, 117.0, 113.0, 69.8, 63.0, 55.6, 21.6, 20.7; **HRMS** m/z: Calcd for C\(_{15}\)H\(_{19}\)NO\(_6\)Na [M+Na]\(^+\): 332.1110, Found: 332.1136.

(Z)-benzyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2p)

Yield: 72%, colorless oil; **IR** (KBr) \( \nu_{\text{max}} \) 2941, 2839, 1766, 1667, 1608, 1572, 1494, 1463, 1368, 1262, 1246, 1187, 1036, 897, 823, 746, 699 cm\(^{-1}\); **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) (ratio of isomers = 5:1, major isomer) \( \delta \) 7.41 – 7.27 (m, 5H), 7.08 (d, \( J = 2.9 \) Hz, 1H), 7.02 – 6.98 (m, 1H), 6.96 – 6.94 (m, 1H), 5.32 (s, 2H), 4.00 (s, 3H), 3.75 (s, 3H), 2.13 (s, 3H).

(Z)-4-methoxy-2-(6-methyl-5-oxo-2,7-dioxa-3,6-diazaoct-3-en-4-yl)phenyl acetate (2q)

Yield: 85%, colorless oil; **IR** (KBr) \( \nu_{\text{max}} \) 2941, 2839, 1766, 1667, 1608, 1571, 1494, 1463, 1368, 1298, 1188, 1045, 983, 900, 818, 788, 758, 627 cm\(^{-1}\); **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) (ratio of isomers = 6:1, major isomer) \( \delta \) 7.13 (d, \( J = 2.9 \) Hz, 1H), 6.98 (d, \( J = 8.9 \) Hz, 1H), 6.96 – 6.94 (m, 1H), 5.32 (s, 2H), 4.00 (s, 3H), 3.75 (s, 3H), 2.26 (s, 3H); **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \( \delta \) 169.6, 163.7, 157.2, 150.1, 141.6, 124.8, 124.6, 116.5, 113.1, 62.7, 61.5, 55.6, 31.4, 20.8; **MS**: m/z = 310.2 [M\(^+\)]; **HRMS** m/z: Calcd for C\(_{14}\)H\(_{18}\)N\(_2\)O\(_6\)Na [M+Na]\(^+\): 333.1063, Found: 333.1072.

(Z)-4-methoxy-2-(1-(methoxyimino)-2-morpholino-2-oxoethyl)phenyl acetate (2r)

Yield: 76%, colorless oil; **IR** (KBr) \( \nu_{\text{max}} \) 2968, 2938, 2858, 1766, 1646, 1608, 1577, 1495, 1463, 1441, 1367, 1274, 1247, 1191, 1113, 1042, 1001, 900, 843, 819, 758, 595 cm\(^{-1}\); **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) (ratio of isomers = 9:1, major isomer) \( \delta \) 7.12 (d, \( J = 2.9 \) Hz, 1H), 7.01 (d, \( J = 8.9 \) Hz, 1H), 6.94 (dd, \( J = 8.9, 2.9 \) Hz, 1H), 6.90 – 6.86 (m, 1H), 6.90 – 6.86 (m, 1H), 5.32 (s, 2H), 4.00 (s, 3H), 3.75 (s, 3H), 3.02 (s, 3H), 2.26 (s, 3H); **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \( \delta \) 169.7, 162.2, 157.2, 149.6, 141.5, 124.8, 123.7, 116.3, 113.6, 66.7, 66.4, 62.8, 55.6, 46.1, 41.4, 21.0; **MS**: m/z = 336.5 [M\(^+\)]; **HRMS** m/z: Calcd for C\(_{16}\)H\(_{20}\)N\(_2\)O\(_6\)Na [M+Na]\(^+\): 359.1219, Found: 359.1191.

(Z)-2-(2-ethoxy-1-(methoxyimino)-2-oxoethyl)-4-methoxyphenyl pivalate (2s)

Yield: 57%, colorless oil; **IR** (KBr) \( \nu_{\text{max}} \) 2977, 2940, 2908, 2839, 1753, 1607, 1577, 1496, 1481, 1464, 1417, 1368, 1246, 1204, 1107, 1032, 924, 887, 859, 827, 798, 758 cm\(^{-1}\); **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 7.03

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(1H, 6.94 (d, J = 1.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 1.34 (s, 9H),
1.30 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 177.0, 161.9, 156.9, 147.4, 142.4, 124.8,
124.0, 116.7, 114.0, 63.0, 61.7, 55.6, 39.1, 27.0, 14.1; MS: m/z = 337.3 [M$^+$]; HRMS m/z: Caled
for C$_{17}$H$_{23}$NO$_3$Na [M+Na]$^+$: 360.1423, Found: 360.1426.

**Procedure for a gram-scale experiment**

\[ \text{O} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{Et} \quad \text{Ac} \quad \text{Ac} \quad \text{Pd(OAc)$_2$ 1 mol\%} \quad \text{HOAc/CH$_3$CO$_2$O, 100 °C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Et} \quad \text{Ac} \]

\[ 1a (5 \text{ mmol} \ 1.186 \text{ g}) \quad (6 \text{ mmol}) \quad 2a \quad 73\% \text{ yield} \]

A mixture of 1a (5.0 mmol, 1.0 equiv), iodobenzene diacetate (6.0 mmol, 1.2 equiv)
Pd(OAc)$_2$ (0.005 mmol, 0.01 equiv) was combined in AcOH (15 mL) and Ac$_2$O (15 mL) in a
dried Schlenk tube under a nitrogen atmosphere. The reaction was stirred at 100 °C and monitored
by TLC. Upon completion or no further improvement of reaction, the reaction mixture was cooled
to room temperature and was then diluted with ethyl acetate. The organic layer was washed
sequentially with saturated NaHCO$_3$, water and brine then dried over anhydrous MgSO$_4$.
Evaporation of the solvent and the resulting oil was purified by flash chromatography on silica gel
to afford product 2a as a white solid with 73% yield.

**4. Typical Procedure for Synthesis of compound 3**

\[ \text{O} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{Et} \quad \text{Ac} \quad \text{Ac} \quad \text{10\% Pd/C, H$_2$} \quad \text{EtOH, 78 \degree C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Et} \quad \text{Ac} \]

\[ 2a \quad 3 \quad 99\% \text{ yield} \]

A suspension solution of 2a (1 mmol) and 10% Pd/C (100 mg) in EtOH (2 mL) at a flask was
transferred to stainless steel autoclave, which was charged with H$_2$ (50 atm). The hydrogenation
was performed at 78 °C for 24 h. After carefully releasing the hydrogen, the reaction mixture was
filtered through Celite. The filtrate was concentrated under reduced pressure to afford the product
3 as a white solid with 99% yield.

**(Z)-ethyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (3)**

\[ \text{O} \quad \text{O} \quad \text{N} \quad \text{Ac} \quad \text{OH} \quad \text{O} \quad \text{Et} \quad \text{Ac} \quad \text{Ac} \quad \text{10\% Pd/C, H$_2$} \quad \text{EtOH, 78 \degree C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Et} \quad \text{Ac} \]

\[ 2a \quad 3 \quad 99\% \text{ yield} \]

Yield: 99%, white solid, m.p. 103-104 °C; IR (KBr) $\nu_{\text{max}}$ 3406, 3101,
2832, 2747, 2595, 1743, 1644, 1605, 1513, 1467, 1435, 1377, 1311,
1213, 1159, 1116, 1035, 958, 858, 816, 754, 720, 646 cm$^{-1}$; $^1$H NMR
(600 MHz, CDCl$_3$) $\delta$ 8.72 (s, 1H), 7.02 (d, $J = 6.5$ Hz, 1H), 6.95 (d, $J = 8.9$ Hz, 1H), 6.81 (dd, $J = 8.9$, 2.9 Hz, 1H), 6.51 (d, $J = 2.9$ Hz, 1H),
5.67 (d, $J = 7.0$ Hz, 1H), 4.34 – 4.20 (m, 2H), 3.72 (s, 3H), 2.05 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.2, 170.8, 153.3, 148.8, 124.4, 119.2, 115.4, 112.8, 62.3, 55.6,
52.2, 22.6, 13.9; HRMS m/z: Caled for C$_{17}$H$_{23}$NO$_3$Na [M+Na]$^+$: 290.1004, Found: 290.0976.
5. X-Ray structure of 2a

Crystal data for 2a: Crystal data for 2a: C_{28}H_{34}N_{12}O_{12}, M = 590.57, orthorhombic, Pbcn, a = 7.6651(6) Å, b = 13.1131(9) Å, c = 29.874(2) Å, α = 90°, β = 90°, γ = 90°, V = 3002.7(4) Å³, Z = 4, T = 298(2), F000 = 1248, final R indices [I>2σ(I)]: R₁ = 0.0418, wR₂ = 0.1173, R indices (all data): R₁ = 0.0485, wR₂ = 0.1216. CCDC 814555. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6. References
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