Supporting Information

C–H Carboxylation of heteroarenes with ambient CO$_2$

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General remarks:
Reactions were carried out on a 1.00 mmol scale under a N\textsubscript{2} atmosphere using pre-dried glassware. The following starting materials were synthesized according to previously described methods: 5-methyl-benzo[d]oxazole (1b),\textsuperscript{1} 5-chloro-benzo[d]oxazole (1c),\textsuperscript{1} 2-(4-methylphenyl)-1,3,4-oxadiazole (6a),\textsuperscript{2} and 2-phenyl-1,3,4-oxadiazole (6b).\textsuperscript{2} Other chemicals were obtained from commercial sources, and were used without further purification. DMF was dried over CaH\textsubscript{2} for 8 h, degassed and distilled under reduced pressure. Yields refer to isolated compounds, estimated to be > 95% pure as determined by \textsuperscript{1}H-NMR analysis. Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on Varian-NMR Mercury 300, Unity 300 and Varian-NMR Inova 500 in the solvent indicated; chemical shifts (\textdelta) are given in ppm.

Representative Procedure: Direct Carboxylation of Heteroaromatic C-H bonds Using CO\textsubscript{2}

Methylbenzo[d]oxazole-2-carboxylate (3a): A mixture of benzo[d]oxazole (1a) (118 mg, 0.99 mmol), KOt-Bu (135 mg, 1.20 mmol) and DMF (5.0 mL) was degassed in a Schlenk-tube. The Schlenk-tube was then flushed with CO\textsubscript{2} via a balloon and CO\textsubscript{2} was bubbled through the reaction mixture for 10-20 minutes. After removal of the balloon, the reaction was heated to 100 °C for 18 h. It was then cooled to 65 °C, methyl iodide (2a) (3.00 equiv) was added and the reaction mixture was stirred at 65 °C for 2 h. At ambient temperature, the reaction mixture was diluted with H\textsubscript{2}O (25 mL) and Et\textsubscript{2}O (25 mL). The aqueous layer was extracted with Et\textsubscript{2}O (3 x 25 mL) and the combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}. Purification by column chromatography (n-pentane/Et\textsubscript{2}O = 20/1 \rightarrow 10/1 \rightarrow 7/1 \rightarrow 5/1) yielded 3a (141 mg, 80%) as a colorless solid.
m.p. = 102–104 °C. \( ^1 \text{H-NMR} \ (300 \text{ MHz, CDCl}_3) \): \( \delta = 7.88 \ (\text{ddd, } J = 7.7, 1.5, 0.7 \text{ Hz, } 1\text{H}), \ 7.66 \ (\text{m, } 1\text{H}), \ 7.53 \ (\text{m, } 1\text{H}), \ 7.45 \ (\text{m, } 1\text{H}), \ 4.09 \ (\text{s, } 3\text{H}). \ \ ^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \ \delta = 156.8 \ (\text{C}_q), \ 152.5, \ (\text{C}_q), \ 150.8 \ (\text{C}_q), \ 140.4 \ (\text{C}_q), \ 128.2 \ (\text{CH}), \ 125.8 \ (\text{CH}), \ 122.1 \ (\text{CH}), \ 111.7 \ (\text{CH}), \ 53.6 \ (\text{CH}_3). \ \text{IR (neat): 2956, 1742, 1538, 1440, 1306, 744, 625 cm}^{-1}. \ \text{MS (EI) } m/z \ (\text{relative intensity}) \ 177 ([M^+] 100), \ 119 \ (24), \ 104 \ (45), \ 64 \ (69), \ 43 \ (99). \ \text{HR-MS (EI) } m/z \ \text{calcd for C}_9\text{H}_7\text{NO}_3 177.0426, \ \text{found 177.0427.}

The analytical data are in accordance with those reported in the literature.\(^2,^3\)

Methyl-5-methylbenzo[d]oxazole-2-carboxylate (3b): The representative procedure was followed using 5-methylbenzo[d]oxazole (1b) (134 mg, 1.00 mmol) and KOT-Bu (135 mg, 1.20 mmol). Purification by column chromatography (n-pentane/Et\(_2\)O = 20/1 → 10/1 → 8/1 → 5/1) yielded 3b (129 mg, 66%) as a brown solid.

m.p. = 99–101 °C. \( ^1 \text{H-NMR} \ (300 \text{ MHz, CDCl}_3) \): \( \delta = 7.64 \ (\text{dd, } J = 1.6, 0.8 \text{ Hz, } 1\text{H}), \ 7.52 \ (\text{d, } J = 8.5 \text{ Hz, } 1\text{H}), \ 7.32 \ (\text{m, } 1\text{H}), \ 4.07 \ (\text{s, } 3\text{H}), \ 2.49 \ (\text{s, } 3\text{H}). \ \ ^{13}\text{C-NMR} \ (75 \text{ MHz, CDCl}_3): \ \delta = 156.9 \ (\text{C}_q), \ 152.5 \ (\text{C}_q), \ 149.2 \ (\text{C}_q), \ 140.7 \ (\text{C}_q), \ 135.9 \ (\text{C}_q), \ 129.6 \ (\text{CH}), \ 121.6 \ (\text{CH}), \ 111.1 \ (\text{CH}), \ 53.6 \ (\text{CH}_3), \ 21.5 \ (\text{CH}_3). \ \text{IR (neat):...
3020, 1746, 1554, 1435, 1301, 1110, 807, 631, 433 cm\(^{-1}\). MS (EI) m/z (relative intensity) 191 (100 [M\(^{+}\)]), 146 (65), 118 (62), 104 (41), 77 (74), 51 (48). HR-MS (EI) m/z calcd for C\(_{10}\)H\(_8\)NO\(_3\) 191.0582, found 191.0591.

The analytical data are in accordance with those reported in the literature.\(^2,3\)

\[\text{Methyl-6-chlorobenzo[d]oxazole-2-carboxylate (3c): The representative procedure was followed using 5-chlorobenzo[d]oxazole (1c) (154 mg, 1.00 mmol), and KOt-Bu (135 mg, 1.20 mmol). Purification by column chromatography (n-pentane/Et}_2\text{O} = 20/1 \rightarrow 10/1 \rightarrow 7/1 \rightarrow 6/1) yielded 3c (133 mg, 63%) as a colorless solid. m.p. = 122–124°C. \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.86 (d, J = 2.1 \text{ Hz}, 1H), 7.59 (d, J = 8.9, 1H), 7.49 (dd, J = 8.9, 2.1 \text{ Hz}, 1H), 4.09 (s, 3H). \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 156.5 (\text{C}q), 153.6 (\text{C}q), 149.4 (\text{C}q), 141.4 (\text{C}q), 131.5 (\text{C}q), 128.8 (\text{CH}), 121.9 (\text{CH}), 112.6 (\text{CH}), 53.8 (\text{CH}_3).\) IR (neat): 3098, 2961, 1738, 1544, 1431, 1300, 1155, 812, 701 cm\(^{-1}\). MS (EI) m/z (relative intensity) 211 ([M\(^{+}\)] 100), 167 (32), 124 (67), 104 (50), 98 (41), 63 (64). HR-MS (EI) m/z calcd for C\(_9\)H\(_6\)ClNO\(_3\) 211.0036, found 211.0035.

The analytical data are in accordance with those reported in the literature.\(^2,3\)
**n-Hexyl-5-chlorobenzo[d]oxazole-2-carboxylate (3d):** The representative procedure was followed using 5-chlorobenzo[d]oxazole (1c) (153 mg, 1.00 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-hexyl iodide (2b) (3.00 equiv). Purification by column chromatography (n-pentane/Et₂O = 40/1 → 20/1) yielded 3d (255 mg, 91%) as a pale yellow solid.

m.p. = 48–50 °C. ¹H-NMR (300 MHz, CDCl₃): δ = 7.86 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 8.8, 2.0 Hz, 1H), 4.48 (t, J = 6.8 Hz, 2H), 1.84 (dq, J = 8.4, 6.8 Hz, 2H), 1.53 – 1.22 (m, 6H), 0.93 – 0.86 (m, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ = 156.2 (Cₗ), 153.9 (Cₗ), 149.4 (Cₗ), 141.5 (Cₗ), 131.4 (Cₗ), 128.6 (CH), 121.8 (CH), 112.5 (CH), 67.5 (CH₂), 31.3 (CH₂), 28.4 (CH₂), 25.4 (CH₂), 22.5 (CH₂), 14.0 (CH₃). IR (neat): 3100, 2928, 1738, 1541, 1303, 1154, 919, 813, 637 cm⁻¹. MS (EI) m/z (relative intensity) 281 ([M⁺] 23), 236 (11), 194 (30), 180 (74), 153 (100), 43 (80). HR-MS (EI) m/z calcd for C₁₄H₁₆ClNO₃ 281.0819, found 281.0813.

The analytical data are in accordance with those reported in the literature.⁴

![3e](image)

**n-Butyl-benzo[d]oxazole-2-carboxylate (3e):** The representative procedure was followed using benzo[d]oxazole (1a) (119 mg, 1.00 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-butyl iodide (2c) (3.00 equiv). Purification by column chromatography (n-pentane/Et₂O = 20/1 → 10/1 → 7/1) yielded 3e (139 mg, 64%) as a colorless oil.

¹H-NMR (300 MHz, CDCl₃): δ = 7.89 (m, 1H), 7.66 (ddd, J = 8.3, 8.3, 0.9 Hz, 1H), 7.51 (m, 1H), 7.44 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 4.49 (t, J = 6.8 Hz, 2H), 1.91 – 1.74 (m, 2H), 1.49 – 1.22 (m, 2H), 0.91 – 0.83 (m, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ = 157.2 (Cₗ), 152.6 (Cₗ), 149.0 (Cₗ), 141.5 (Cₗ), 132.9 (Cₗ), 128.7 (CH), 121.8 (CH), 112.7 (CH), 67.5 (CH₂), 31.2 (CH₂), 28.5 (CH₂), 25.5 (CH₂), 22.4 (CH₂), 14.0 (CH₃).
1.59 – 1.37 (m, 2H), 0.98 (t, \( J = 7.4 \) Hz, 3H). \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 156.6 \) (C\(_q\)), 152.8 (C\(_q\)), 150.9 (C\(_q\)), 140.5 (C\(_q\)), 128.1 (CH), 125.7 (CH), 122.1 (CH), 111.7 (CH), 67.0 (CH\(_2\)), 30.5 (CH\(_2\)), 19.0 (CH\(_2\)), 13.6 (CH\(_3\)). IR (neat): 2960, 2874, 1739, 1545, 1292, 842, 744, 429 cm\(^{-1}\). MS (EI) m/z (relative intensity) 219 (32 [M\(^+\)]), 174 (11), 160 (17), 146 (56), 119 (100), 91 (42). HR-MS (EI) m/z calcd for \( \text{C}_{12}\text{H}_{13}\text{NO}_3 \) 219.0895, found 219.0892.

The analytical data are in accordance with those reported in the literature.\(^5\)

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\text{Methyl-benzo[d]thiazole-2-carboxylate (3f):} \quad \text{The representative procedure was followed using benzo[d]thiazole (1d) (138 mg, 1.00 mmol), and KOT-Bu (135 mg, 1.20 mmol). Purification by column chromatography (n-pentane/Et}_2\text{O = 20/1} \rightarrow 10/1 \rightarrow 7/1 \rightarrow 5/1) yielded 3f (131 mg, 66\%) as a yellow solid. m.p. = 92–94 °C. \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 8.24 \) (m, 1H), 7.97 (m, 1H), 7.55 (m, 2H), 4.08 (s, 3H). \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 161.1 \) (C\(_q\)), 158.0 (C\(_q\)), 153.1 (C\(_q\)), 136.8 (C\(_q\)), 127.6 (CH), 127.1 (CH), 125.5 (CH), 122.1 (CH), 53.6 (CH\(_3\)). IR (neat): 2952, 1711, 1494, 1287, 1096, 923, 766, 731, 432 cm\(^{-1}\). MS (EI) m/z (relative intensity) 193 ([M\(^+\)] 59), 162 (19), 135 (100), 108 (26), 90 (22), 69 (23). HR-MS (EI) m/z calcd for \( \text{C}_9\text{H}_7\text{NO}_2\text{S} \) 193.0197, found 193.0199.

The analytical data are in accordance with those reported in the literature.\(^2\)
**n-Hexyl-benzo[d]thiazole-2-carboxylate** (3g): The representative procedure was followed using benzo[d]thiazole (1d) (139 mg, 1.03 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-hexyl iodide (2b) (3.00 equiv). Purification by column chromatography (n-pentane/Et₂O = 20/1) yielded 3g (168 mg, 62%) as a yellow solid.

m.p. = 38–40 °C. ^1H-NMR (300 MHz, CDCl₃): δ = 8.26 (m, 1H), 8.98 (m, 1H), 7.63 – 7.49 (m, 2H), 4.48 (t, J = 6.9 Hz, 2H), 1.94 – 1.75 (m, 2H), 1.55 – 1.25 (m, 6H), 0.94 – 0.87 (m, 3H). ^13C-NMR (75 MHz, CDCl₃): δ = 160.6 (C_q), 158.4 (C_q), 153.2 (C_q), 136.7 (C_q), 127.5 (CH), 127.0 (CH), 125.5 (CH), 122.0 (CH), 67.2 (CH₃), 31.4 (CH₂), 28.5 (CH₂), 25.5 (CH₂), 22.5 (CH₂), 14.0 (CH₃). IR (neat): 3058, 2918, 1728, 1496, 1254, 1099, 865, 765, 583 cm⁻¹. MS (EI) m/z (relative intensity) 263 (10 [M⁺]), 219 (30), 180 (33), 162 (82), 135 (100), 90 (11), 43 (29). HR-MS (EI) m/z calcld for C₁₄H₁₇NO₂S 263.0980, found 263.0988.

**Synthesis of 2-n-Hexyl-4-ethyl-5-phenyloxazole-2,4-dicarboxylate** (5b) and **2-n-Hexyl-4-tert-butyl-5-phenyloxazole-2,4-dicarboxylate** (5b’)

The representative procedure was followed using ethyl 5-phenyloxazole-4-carboxylate (4a) (213 mg, 0.98 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-hexyl iodide (2b) (3.00 equiv). Purification by column chromatography (n-pentane/Et₂O = 10/1 → 7/1 → 5/1) yielded 5b (222 mg, 65%) and 5b’ (11 mg, 3%) as yellow oils.
2-\textit{n}-Hexyl-4-ethyl-5-phenyloxazole-2,4-dicarboxylate (5b): $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 8.19 - 8.06 (m, 2H), 7.56 - 7.44 (m, 3H), 4.53 - 4.34 (m, 4H), 1.81 (dq, $J$ = 8.2, 6.9 Hz, 2H), 1.51 - 1.22 (m, 9H), 0.95 - 0.84 (m, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 161.4 (Cq), 157.4 (Cq), 155.4 (Cq), 150.0 (Cq), 131.3 (CH), 128.9 (CH), 128.6 (Cq), 128.5 (CH), 125.9 (Cq), 67.1 (CH$_2$), 61.8 (CH$_2$), 31.3 (CH$_2$), 28.4 (CH$_2$), 25.4 (CH$_2$), 22.5 (CH$_2$), 14.2 (CH$_3$), 14.0 (CH$_3$). IR (neat): 2931, 2859, 1721, 1549, 1334, 1171, 1093, 763, 690 cm$^{-1}$. MS (EI) m/z (relative intensity) 345 ([M$^+$] 23), 300 (18), 244 (45), 189 (28), 105 (100), 43 (99). HR-MS (EI) m/z calcd for C$_{19}$H$_{23}$NO$_5$ 345.1576, found 345.1577.

2-\textit{n}-Hexyl-4-tert-butyl-5-phenyloxazole-2,4-dicarboxylate (5b$'$): $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 8.06 - 7.98 (m, 2H), 7.53 - 7.44 (m, 3H), 4.42 (t, $J$ = 6.9 Hz, 2H), 1.88 - 1.74 (m, 2H), 1.58 (s, 9H), 1.51 - 1.24 (m, 6H), 0.95 - 0.83 (m, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 160.5 (Cq), 156.6 (Cq), 155.5 (Cq), 150.0 (Cq), 131.0 (CH), 129.9 (Cq), 129.0 (CH), 128.4 (CH), 126.3 (Cq), 83.1 (CH$_2$), 67.0 (Cq), 31.4 (CH$_2$), 28.4 (CH$_2$), 28.1 (CH$_3$), 25.4 (CH$_2$), 22.5 (CH$_2$), 14.0 (CH$_3$). IR (neat): 2931, 1716, 1547, 1367, 1236, 1160, 1094, 844, 690 cm$^{-1}$. MS (EI) m/z (relative intensity) 373 ([M$^+$] 46), 317 (80), 273 (56), 216.
4-Ethyl-2-methyl-5-(2-chlorophenyl) oxazole-2,4-dicarboxylate (5c): The representative procedure was followed using ethyl 5-(2-chlorophenyl) oxazole-4-carboxylate (4b) (259 mg, 1.03 mmol), and KOT-Bu (135 mg, 1.20 mmol). Purification by column chromatography (n-pentane/Et₂O = 10/1 → 5/1 → 3/1 → 2/1) yielded 5c (164 mg, 52%) as an off-white solid. m.p. = 83–85 °C. ¹H-NMR (300 MHz, CDCl₃): δ = 7.56 – 7.52 (m, 2H), 7.47 (ddt, J = 7.6, 7.6, 1.7 Hz, 1H), 7.39 (ddt, J = 7.3, 7.3, 1.7 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.03 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ = 160.3 (C₉), 155.6 (C₉), 155.0 (C₉), 151.1 (C₉), 134.4 (C₉), 132.2 (CH), 132.1 (CH), 131.5 (C₉), 130.0 (CH), 126.5 (CH), 125.7 (C₉), 61.6 (CH₂), 53.5 (CH₃), 14.0 (CH₃). IR (neat): 2991, 1738, 1721, 1551, 1194, 1028, 753, 653 cm⁻¹. MS (EI) m/z (relative intensity) 274 (96), 246 (100), 214 (77), 139 (49), 59 (21). HR-MS (EI) m/z calcd for C₁₄H₁₂ClNO₅ 309.0404, found 309.0410.

Synthesis of 2-n-Butyl-4-ethyl-5-(4-methylbenzyl) oxazole-2,4-dicarboxylate (5d) and 2-Butyl-4-ethyl-5-(1-(4-methylphenyl)pentyl) oxazole-2,4-dicarboxylate (5d’)

The representative procedure was followed using ethyl 5-(4-methylbenzyl) oxazole-4-carboxylate (4c) (242 mg, 0.99 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-butyl iodide (2c)
(3.00 equiv). Purification by column chromatography (n-pentane/Et₂O = 10/1 → 7/1 → 5/1) yielded 5d (174 mg, 51%) and 5d’ (25 mg, 6%) as yellow oils.

\[
\begin{align*}
\text{2-}
&\text{n-Butyl-4-ethyl-5-(4-methylbenzyl)oxazole-2,4-dicarboxylate} \\
&\text{(5d):} \\
&{^1}H-NMR (300 MHz, CDCl}_3): \delta = 7.21 (d, J = 8.0 \text{ Hz}, 2\text{H}), \ \\
&7.11 (d, J = 8.0 \text{ Hz}, 2\text{H}), 4.49 - 4.33 (m, 6\text{H}), 2.31 (s, 3\text{H}), \ \\
&1.82 - 1.68 (m, 2\text{H}), 1.49 - 1.33 (m, 5\text{H}), 0.94 (t, J = 7.4 \text{ Hz}, 3\text{H}). \ \\
&{^{13}}C-NMR (75 MHz, CDCl}_3): \delta = 161.3 (C_q), 160.6 (C_q), 155.4 \\
&(C_q), 150.5 (C_q), 137.0 (C_q), 132.1 (C_q), 129.5 (CH), 129.2 \\
&(C_q), 128.7 (CH), 66.7 (CH_2), 61.5 (CH_2), 31.8 (CH_2), 30.4 \\
&(CH_2), 21.0 (CH_3), 18.9 (CH_2), 14.3 (CH_3), 13.6 (CH_3). \ \\
&\text{IR (neat): 2906, 2874, 1737, 1549, 1249, 1154, 1067, 791,} \\
&655 \text{ cm}^{-1}. \ \\
&MS (EI) m/z (relative intensity) 345 ([M'] 27), 299 \\
&(15), 243 (100), 199 (79), 105 (33), 41 (25). \ \\
&\text{HR-MS (EI) } m/z \text{ calcd for } C_{19}H_{23}NO_5 345.1567, \text{ found 345.1572.}
\end{align*}
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\begin{align*}
\text{5d}
\end{align*}
\]
2-n-Butyl-4-ethyl-5-{1-(4-methylphenyl)pentyl}oxazole-2,4-dicarboxylate (5d'):

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 7.29 (d, $J$ = 8.1 Hz, 2H), 7.12 (d, $J$ = 7.9 Hz, 2H), 4.89 (t, $J$ = 8.0 Hz, 1H), 4.49 - 4.32 (m, 4H), 2.30 (s, 3H), 2.22 - 1.97 (m, 2H), 1.83 - 1.70 (m, 2H), 1.52 - 1.13 (m, 9H), 0.96 (t, $J$ = 7.4 Hz, 3H), 0.85 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 163.7 (C$_q$), 161.4 (C$_q$), 155.4 (C$_q$), 150.3 (C$_q$), 137.0 (C$_q$), 136.8 (C$_q$), 129.4 (CH), 128.6 (C$_q$), 127.9 (CH), 66.6 (CH$_2$), 61.4 (CH$_2$), 42.2 (CH), 33.6 (CH$_2$), 30.4 (CH$_2$), 29.7 (CH$_2$), 22.3 (CH$_2$), 21.0 (CH$_3$), 19.0 (CH$_2$), 14.3 (CH$_3$), 13.8 (CH$_3$), 13.6 (CH$_3$).

IR (neat): 2958, 2872, 1738, 1549, 1375, 1156, 1060, 655 cm$^{-1}$. MS (EI) $m/z$ (relative intensity) 401 ([M$^+$] 53), 355 (100), 312 (82), 256 (98), 212 (49), 105 (38). HR-MS (EI) $m/z$ calcd for C$_{23}$H$_{31}$NO$_5$ 401.2202, found 401.2192.

\[\text{Me} \quad \text{7a} \]

n-Hexyl-5-(4-methylphenyl)-1,3,4-oxadiazole-2-carboxylate (7a):

The representative procedure was followed using 2-(4-methylphenyl)-1,3,4-oxadiazole (6a) (160 mg, 1.00 mmol), KOT-Bu (135 mg, 1.20 mmol) and n-hexyl iodide (2b) (3.00 equiv). Purification by column chromatography (n-pentane/Et$_2$O = 20/1 $\rightarrow$ 15/1 $\rightarrow$ 10/1 $\rightarrow$ 8/1) yielded 7a (146 mg, 51%) as a brown oil.

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ = 8.04 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.2 Hz, 2H), 4.47 (t, $J$ = 6.8 Hz, 2H), 2.44 (s, 3H), 1.91 - 1.75 (m, 2H), 1.54 - 1.23 (m, 6H), 0.97 - 0.81 (m, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta$ = 166.6 (C$_q$), 156.2 (C$_q$), 154.6 (C$_q$), 143.6 (C$_q$), 129.9 (CH), 127.6 (CH), 120.0 (C$_q$), 67.5 (CH$_2$), 31.3 (CH$_2$), 28.4 (CH$_2$), 25.4 (CH$_2$), 22.5 (CH$_2$), 21.70 (CH$_3$), 14.0 (CH$_3$). IR (neat): 2928, 2859, 1743, 1492, 1272, 1170.
1090, 825, 732 cm\(^{-1}\). MS (EI) \(m/z\) (relative intensity) 288 (13 [M\(^+\)]), 244 (16), 187 (69), 159 (100), 117 (73), 91 (57), 43 (59). HR-MS (EI) \(m/z\) calcd for \(C_{16}H_{20}N_2O_3\) 288.1474, found 288.1471.

Methyl-5-(4-methylphenyl)-1,3,4-oxadiazole-2-carboxylate (7b):
The representative procedure was followed using 2-(4-methylphenyl)-1,3,4-oxadiazole (6a) (160 mg, 1.00 mmol), and K\(\text{O}t\)-Bu (135 mg, 1.20 mmol). Purification by column chromatography (n-pentane/E\(\text{t}_2\)O = 10/1 \(\rightarrow\) 5/1 \(\rightarrow\) 4/1 \(\rightarrow\) 3/1) yielded 7b (121 mg, 56%) as a colorless solid.
m.p. = 118–120 °C. \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.04\) (d, \(J = 8.2\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 4.08 (s, 3H), 2.44 (s, 3H). \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 166.7\) (C\(_q\)), 156.1 (C\(_q\)), 154.9 (C\(_q\)), 143.7 (C\(_q\)), 129.9 (CH), 127.6 (CH), 119.9 (C\(_q\)), 53.7 (CH\(_3\)), 21.7 (CH\(_3\)). IR (neat): 2956, 2854, 1741, 1529, 1447, 1202, 1163, 819, 728 cm\(^{-1}\). MS (EI) \(m/z\) (relative intensity) 218 ([M\(^+\)] 81), 159 (100), 131 (21), 117 (54), 91 (56), 65 (18). HR-MS (EI) \(m/z\) calcd for \(C_{11}H_{10}N_2O_3\) 218.0691, found 218.0693.

Methyl-5-phenyl-1,3,4-oxadiazole-2-carboxylate (7c):
The representative procedure was followed using 2-phenyl-1,3,4-oxadiazole (6b) (149 mg, 1.00 mmol), and K\(\text{O}t\)-Bu (135 mg, 1.20 mmol). Purification by column chromatography
(n-pentane/Et₂O = 10/1 → 5/1 → 4/1) yielded 7c (89 mg, 43%) as a colorless solid.

m.p. = 118-119 °C. ¹H-NMR (300 MHz, CDCl₃): δ = 8.20 - 8.13 (m, 2H), 7.65 - 7.50 (m, 3H), 4.09 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ = 166.5 (Cₘ), 156.3 (Cₘ), 154.8 (Cₘ), 132.9 (CH), 129.2 (CH), 127.6 (CH), 122.7 (Cₘ), 53.8 (CH₃). IR (neat): 2963, 1737, 1539, 1378, 1204, 1094, 811, 710, 642 cm⁻¹. MS (EI) m/z (relative intensity) 204 ([M⁺] 44), 145 (100) 103 (20), 77 (64), 43 (17). HR-MS (EI) m/z calcd for C₁₀H₈N₂O₃ 204.0535, found 204.0537.

The analytical data are in accordance with those reported in the literature.⁶
$3b$

(CDCl$_3$, 300 MHz)

$3b$

(CDCl$_3$, 75 MHz)
3e

(CDCl₃, 300 MHz)

3e

(CDCl₃, 75 MHz)
$3f$

(CDCl$_3$, 300 MHz)

$3f$

(CDCl$_3$, 75 MHz)
3g
(CDCl₃, 300 MHz)

3g
(CDCl₃, 75 MHz)
**(5b)**

(CDCl₃, 300 MHz)

**(5b)**

(CDCl₃, 75 MHz)
5b' (CDCl₃, 300 MHz)

5b' (CDCl₃, 75 MHz)
(CDCl₃, 300 MHz)
7a
(CDCl₃, 300 MHz)

7a
(CDCl₃, 75 MHz)
References