Supplementary Information

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

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1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used as received. Ni(cod)2 and K3PO4 were obtained from Wako Chemicals. 1,2-Bis(dicyclohexylphosphino)ethane (dcype) was obtained from Kanto Chemical. Dry t-AmilOH was purchased from Sigma-Aldrich and used as received. 1-Benzyl-1H-benzo[d]imidazole (1B), 1-phenyl-1H-benzo[d]imidazole (1C), 4-(2-(1H-benzo[d]imidazol-1-yl)ethyl)morpholine (1D), 1-(methoxymethyl)-1H-benzo[d]imidazole (1E), 1,5,6-trimethyl-1H-benzo[d]imidazole (1F), 1-benzyl-1H-imidazole (1H), 1-methyl-4,5-diphenyl-1H-imidazole (1N), 4-(1-methyl-1H-imidazol-4-yl)benzonitrile (1O), phenyl dimethylcarbamate (2a), naphthalen-2-yl dimethylcarbamate (2b), naphthalen-1-yl dimethylcarbamate (2j), 4-methoxyphenyl dimethylcarbamate (2e), methyl 3-((dimethylcarbamoyl)oxy)benzoate (2f), [1,1′-biphenyl]-4-yl dimethylcarbamate (2l), 3,4-dihyronaphthalen-2-yl dimethylcarbamate (2k), 3,4-dihyronaphthalen-1-yl dimethylcarbamate (2m), 5-(benzo[d][1,3]dioxol-5-yl)-2-phenyloxazole (5D), and 3,4-bis(dicyclohexylphosphino)thiophene (dcypt) were synthesized according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of argon in flame-dried glassware using standard vacuum-line techniques. All C–H coupling reactions were performed in 20-mL glass vessel tubes equipped with J. Young® O-ring tap and heated in an 8-well reaction block (heater + magnetic stirrer) unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) or Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns using hexane/EtOAc as an eluent.

Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART) and Thermo Fisher Scientific Exactive (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (1H 600 MHz, 13C 150 MHz) spectrometer and a JEOL JNM-ECA-400 (1H 400 MHz, 13C 100 MHz) spectrometer. Chemical shifts for 1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm). Chemical shifts for 13C NMR are expressed in ppm relative to CDCl3 (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.
2. Substrate Structure of Imidazoles, Carbamates, Chloroarenes, Thiazoles, and Oxazoles

Imidazoles 1

![Imidazole Structures](image-url)
Carbamates 2

![Diagram of carbamates 2]

Chloroarenes 4

![Diagram of chloroarenes 4]

Thiazoles and Oxazoles 5

![Diagram of thiazoles and oxazoles 5]
3. Preparation of Starting Materials

Ethyl 1-methyl-1H-imidazole-4-carboxylate (1P)

To a solution of ethyl 1H-imidazole-4-carboxylate (700 mg, 5.0 mmol, 1.0 equiv) in THF (15 mL) was added NaH (60% dispersion in paraffin liquid: 300 mg, 7.5 mmol, 1.5 equiv) at 0 °C. After stirring the mixture for 30 min, methyl iodide (781 mg, 5.5 mmol, 1.1 equiv) was added at 0 °C and the solution was stirred overnight at room temperature. The mixture was quenched by the addition of water, then extracted several times with EtOAc, dried over Na$_2$SO$_4$, and filtrated. The solution was concentrated in vacuo. The crude mixture was purified by Isolera® (hexane/EtOAc = 1:1 to EtOAc) to afford 1P as a yellow solid (615 mg, 80% yield).

1H NMR (400 MHz, CDCl$_3$): δ 7.58 (s, 1H), 7.45 (s, 1H), 4.36 (q, $J$ = 7.2 Hz, 2H), 3.74 (s, 3H), 1.39 (t, $J$ = 7.2 Hz, 3H);

13C NMR (100 MHz, CDCl$_3$): δ 162.5, 138.3, 133.8, 125.9, 60.1, 33.5, 14.1;

HRMS (ESI) m/z calcd for C$_7$H$_{10}$N$_2$O$_2$Na $[M+Na]^+$: 177.0634, found 177.0633.

3,4-Dimethylphenyl dimethylcarbamate (2c)

To a solution of 3,4-dimethylphenol (611 mg, 5.0 mmol, 1.0 equiv) and N,N-dimethyl-4-aminopyridine (DMAP: 6.1 mg, 0.050 mmol, 1 mol%) in dichloroethane (4 mL) were added Et$_3$N (843 µL, 6.0 mmol, 1.2 equiv) and N,N-dimethylcarbamoyl chloride (505 µL, 5.5 mmol, 1.1 equiv). This mixture was stirred overnight at 70 °C. The reaction mixture was quenched by the addition of saturated NaHCO$_3$ aq, and then the mixture was extracted four times with CH$_2$Cl$_2$. The combined organic layer was dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 10:1) to afford 2c as a white solid (980 mg, quant).

1H NMR (400 MHz, CDCl$_3$): δ 7.09 (d, $J$ = 8.0 Hz, 1H), 6.89 (s, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 3.08 (s, 3H), 2.99 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H); 13C NMR (100 MHz, CDCl$_3$): δ 155.3, 149.4, 137.5, 133.4, 130.1, 122.7, 118.8, 36.6, 36.4, 19.8, 19.1; HRMS (ESI) m/z calcd for C$_{11}$H$_{15}$NO$_2$Na [M+Na]$^+$: 216.0995, found 216.0991.
3-(tert-Butyl)phenyl dimethylcarbamate (2d): Purification by flash silica-gel column chromatography (hexane/EtOAc = 10:1) afforded 2d as a white solid (751 mg, 97% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29 (dd, $J = 8.4$, 7.6 Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.10 (s, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 3.10 (s, 3H), 3.01 (s, 3H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.0, 152.7, 151.3, 128.6, 122.2, 118.74, 118.71, 36.6, 36.4, 34.7, 31.2; HRMS (DART) $m/z$ calcd for C$_{13}$H$_{20}$NO$_2$ [M+H]$^+$: 222.1494, found 222.1490.

3-(Dimethylamino)phenyl dimethylcarbamate (2g): Purification by flash silica-gel column chromatography (hexane/EtOAc = 4:1) afforded 2g as a brown liquid (900 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18 (t, $J = 8.0$ Hz, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 6.45 (d, $J = 8.0$ Hz, 1H), 6.44 (s, 1H), 3.09 (s, 3H), 3.00 (s, 3H), 2.93 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.1, 152.5, 151.6, 129.4, 109.6, 109.5, 105.9, 40.5, 36.6, 36.4; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{16}$N$_2$O$_2$Na $[M+Na]^+$: 231.1104, found 231.1100.

Pyridin-3-yl dimethylcarbamate (2h): Purification by flash silica-gel column chromatography (hexane/EtOAc = 1:1 to EtOAc) afforded 2h as a yellow liquid (721 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.46–8.42 (m, 2H), 7.52 (dd, $J = 8.4$, 4.0 Hz, 1H), 7.30 (dd, $J = 8.4$, 4.0 Hz, 1H), 3.12 (s, 3H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.0, 148.1, 146.2, 143.5, 129.3, 123.6, 36.7, 36.4; HRMS (ESI) $m/z$ calcd for C$_{8}$H$_{16}$N$_2$O$_2$Na $[M+Na]^+$: 189.0634, found 189.0630.

7-Methoxy-3,4-dihyronaphthalen-2-yl dimethylcarbamate (2l):...
NaH (55% dispersion in paraffin liquid: 1.15 g, 27 mmol, 1.8 equiv) was placed in a 300-mL flask under a stream of argon, and THF (24 mL) was added to the flask. To this suspension, 7-methoxy-3,4-dihydronaphthalen-2(1H)-one (2.82 g, 16 mmol, 1.0 equiv) in THF (8 mL) was added dropwise. The resulting mixture was stirred at room temperature for 5 min. A solution of 1,2-n,N,N-dimethylcarbamoyl chloride (2.21 mL, 24 mmol, 1.5 equiv) in THF (4 mL) was added, and then the mixture was stirred for an additional 30 min. The reaction was quenched by the addition of water. The mixture was extracted three times with tert-butyl methyl ether, and the combined organic layer was washed with water and brine, dried over Na$_2$SO$_4$, and then filtered. The filtrate was concentrated in vacuo. The crude residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 3:1) to afford 2l as a pale yellow oil (3.26 g, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.01 (d, $J$ = 7.6 Hz, 1H), 6.63 (dd, $J$ = 7.6, 2.4 Hz, 1H), 6.57 (d, $J$ = 2.4 Hz, 1H), 6.17 (s, 1H), 3.77 (s, 3H), 3.01 (s, 3H), 2.97 (s, 3H), 2.92 (t, $J$ = 8.0 Hz, 2H), 2.51 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.3, 154.2, 152.1, 134.7, 127.7, 125.3, 113.9, 111.9, 111.2, 55.2, 36.44, 36.35, 27.7, 27.0; HRMS (DART) m/z calcld for C$_{14}$H$_{18}$NO$_3$ [M+H]$^+$: 248.1287, found 248.1287.

![Image](image.png)

7-Methoxy-3,4-dihydronaphthalen-1-yl dimethylcarbamate (2n): Purification by flash silica-gel column chromatography (hexane/EtOAc = 3:1) afforded 2n as a pale yellow oil (1.45 g, 39% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.05 (d, $J$ = 8.0 Hz, 1H), 6.72–6.68 (m, 2H), 5.73 (t, $J$ = 4.4 Hz, 1H), 3.78 (s, 3H), 3.13 (s, 3H) 2.99 (s, 3H), 2.79 (t, $J$ = 8.0 Hz, 2H), 2.41 (dt, $J$ = 8.0, 4.4 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 158.1, 154.5, 145.6, 132.2, 128.5, 128.0, 115.6, 111.6, 107.6, 55.1, 36.6, 36.2, 26.5, 22.3; HRMS (DART) m/z calcld for C$_{14}$H$_{18}$NO$_3$ [M+H]$^+$: 248.1287, found 248.1282.

![Image](image.png)

7-Fluoro-3,4-dihydronaphthalen-1-yl dimethylcarbamate (2o): Purification by flash silica-gel column chromatography (hexane/Et$_2$O = 1:1) afforded 2o as a yellow oil (1.02 g, 71% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.10–7.04 (m, 1H), 6.88–6.80 (m, 2H), 5.77 (t, $J$ = 4.4 Hz, 1H), 3.12 (s, 3H),
2.99 (s, 3H), 2.81 (t, J = 7.6 Hz, 2H), 2.43 (dt, J = 7.6, 4.4 Hz, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 161.7 (d, J\(_{C,F}\) = 241.2 Hz), 154.4, 145.1 (d, J\(_{C,F}\) = 1.9 Hz), 133.0 (d, J\(_{C-F}\) = 8.6 Hz), 131.7 (d, J\(_{C-F}\) = 2.9 Hz), 128.5 (d, J\(_{C-F}\) = 7.6 Hz), 116.3, 113.8 (d, J\(_{C-F}\) = 20.9 Hz), 107.9 (d, J\(_{C-F}\) = 23.9 Hz), 36.6, 36.3, 26.6, 22.1; HRMS (DART) m/z calcld for C\(_{13}\)H\(_{15}\)FNO\(_2\) [M+H\(^+\)]: 236.1087, found 236.1087.

4-Methyl-3,4-dihydronaphthalen-1-yl dimethylcarbamate (2p): Purification by flash silica-gel column chromatography (hexane/EtOAc = 4:1) afforded 2p as a white solid (2.34 g, 65% yield). \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.26–7.10 (m, 4H), 5.64 (t, J = 4.4 Hz, 1H), 3.13 (s, 3H), 3.07–2.93 (m, 4H), 2.60 (ddd, J = 16.8, 6.4, 4.4 Hz, 1H), 2.23 (ddd, J = 16.8, 6.4, 4.4 Hz, 1H), 1.31 (d, J = 6.4 Hz, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 154.9, 145.4, 141.4, 130.4, 127.9, 126.2, 126.1, 120.7, 113.6, 36.7, 36.4, 31.9, 29.9, 20.1; HRMS (DART) m/z calcld for C\(_{14}\)H\(_{18}\)NO\(_2\) [M+H\(^+\)]: 232.1338, found 232.1339.

4-(tert-Butyl)cyclohex-1-en-1-yl dimethylcarbamate (2q)

To a solution of 4-(tert-butyl)cyclohexanone (462.8 mg, 3.0 mmol, 1.0 equiv) in THF (4.5 mL) was slowly added lithium diisopropylamide [LDA: prepared from diisopropylamine (333.9 mg, 3.3 mmol, 1.1 equiv) and 1.6 M of n-BuLi in hexane (2.06 mL, 3.3 mmol, 1.1 equiv) in 4.5 mL of THF] at 0 °C. After stirring the solution for 1 h, N,N-dimethylcarbamoyl chloride (413.6 mL, 4.5 mmol, 1.5 equiv) was added at 0 °C and the mixture was allowed to warm up to room temperature. The solution was stirred overnight, and then NaHCO\(_3\) aq was added to quench the reaction. The mixture was extracted three times with EtOAc, washed with brine, dried over Na\(_2\)SO\(_4\), and then filtered. The mixture was concentrated in vacuo. The crude mixture was purified by flash silica-gel column chromatography (hexane/EtOAc = 50:1 to 10:1) to afford 2q as a colorless liquid (193 mg, 29% yield). \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 5.35 (t, J = 2.8 Hz, 1H), 2.95 (s, 3H), 2.93 (s, 3H), 2.38–2.21 (m, 1H), 2.17–2.05 (m, 2H), 1.96–1.80 (m, 2H), 1.42–1.30 (m, 2H), 0.89 (s, 9H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 155.0, 148.7,
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

113.5, 43.4, 36.4, 36.2, 32.1, 28.2, 27.3, 25.0, 24.0; HRMS (DART) m/z calcd for C_{13}H_{24}NO_{2} [M+H]^+: 226.1807, found 226.1810.

(E)-2-Phenylprop-1-en-1-yl dimethylcarbamate (2r)

To a solution of 2-phenylpropanaldehyde (2.7 mL, 20.2 mmol, 1.0 equiv) in dichloroethane (40 mL) were added Et_3N (4.8 mL, 34.4 mmol, 1.7 equiv), N,N-dimethyl-4-aminopyridine (DMAP: 610.8 mg, 5 mmol, 25 mol%) and N,N-dimethylcarbamoyl chloride (2.5 mL, 27.2 mmol, 1.3 equiv). This mixture was stirred overnight at 80 °C. The reaction mixture was quenched by the addition of saturated NH_4Cl aq, and then the mixture was extracted three times with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over Na_2SO_4, concentrated in vacuo. The residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 5:1) to afford 2r as a colorless oil (3.48 g, 85% yield, E/Z = 5:3).

1H NMR (400 MHz, CDCl_3): δ 7.49–7.21 (m, 15H, (E and Z)), 7.16 (d, J = 1.4 Hz, 1H, (Z)), 3.01 (s, 5H, (E)), 2.96 (s, 5H, (E)), 2.91 (s, 3H, (Z)), 2.84 (s, 3H, (Z)), 2.07 (d, J = 1.4 Hz, 5H, (E)), 1.99 (d, J = 1.4 Hz, 3H, (Z)); 13C NMR (100 MHz, CDCl_3): δ 153.5, 139.2, 137.8, 133.8, 131.8, 128.2, 127.7, 127.6, 126.6, 125.4, 118.7, 116.8, 36.35, 36.27, 35.74, 35.70, 18.5, 13.3; HRMS (DART) m/z calcd for C_{13}H_{24}NO_{2} [M+H]^+: 206.1181, found 206.1184.

tert-Pentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (4t)

To a solution of indomethacin (3.58 g, 10 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) were added oxalyl chloride (1.29 mL, 15 mmol, 1.5 equiv) and a few drops of DMF at room temperature, and then this solution was stirred for 1 h. To the mixture were added t-AmylOH (3.24 mL, 30 mmol, 3.0 equiv),
Et₃N (3.06 mL, 22 mmol, 2.2 equiv), and N,N-dimethyl-4-aminopyridine (DMAP: 12.2 mg, 0.10 mmol, 1.0 equiv) at 0 °C. This solution was allowed to warm up to room temperature and stirred for 3 h. The reaction was quenched by the addition of NaHCO₃ aq and extracted three times with CH₂Cl₂, dried over Na₂SO₄, and then filtered. The resulting solution was concentrated in vacuo. The crude mixture was purified by flash silica-gel column chromatography (hexane/EtOAc = 10:1 to 4:1) to afford 4t as a yellow solid (1.41 g, 33% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 9.2 Hz, 1H), 6.66 (dd, J = 9.2, 2.0 Hz, 1H), 3.83 (s, 3H), 3.58 (s, 2H), 2.37 (s, 3H), 1.75 (q, J = 8.0 Hz, 2H), 1.41 (s, 6H), 0.81 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 170.0, 168.2, 155.9, 139.1, 135.6, 134.0, 131.1, 130.8, 129.0, 114.9, 113.3, 111.6, 101.2, 83.5, 55.6, 33.3, 31.6, 25.5, 13.3, 8.1; HRMS (DART) m/z calcd for C₂₄H₂₇ClNO₄[M+H]⁺: 428.1629, found 428.1627.

Benzo[b]thiophene-2,3-diylbis(dicyclohexylphosphine) (L1)

To a 50-mL round-bottom glass flask containing a magnetic stirring bar were added 2,3-dibromobenzo[b]thiophene (1.46 g, 5.0 mmol, 1.0 equiv) and dry Et₂O (5 mL). After cooling at −78 °C, a solution of n-BuLi in hexane (1.6 M, 3.2 mL, 1.0 equiv) was added at −78 °C over 10 min. After stirring the mixture at −78 °C for 1 h, a solution of chlorodicyclohexylphosphine (1.22 g, 5.25 mmol, 1.05 equiv) in Et₂O (1.5 mL) was added at −78 °C over 15 min. The resulting mixture was further stirred at −78 °C for 30 min. Then a solution of n-BuLi in hexane (1.6 M, 3.2 mL, 1.0 equiv) was added at −78 °C over 10 min. After stirring the mixture at −78 °C for 1 h, a solution of chlorodicyclohexylphosphine (1.22 g, 5.25 mmol, 1.05 equiv) in Et₂O (1.5 mL) was added at −78 °C over 10 min. The resulting mixture was further stirred at −78 °C for 30 min. After warming to room temperature, the reaction was quenched with water, extracted with hexane, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The reaction mixture was purified by reprecipitation with toluene (0.50 mL) and methanol (25 mL) to afford benzo[b]thiophene-2,3-diylbis(dicyclohexylphosphine) (L1) as a white solid (1.13 g, 43% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (brs, 1H), 7.86 (dd, J = 8.4, 4.0 Hz, 1H), 7.42–7.31 (m, 2H), 2.49 (brs, 2H), 2.00 (brs, 6H), 1.90–1.50 (m, 14H), 1.49–0.95 (m, 22H); ³¹P NMR (162 MHz, CDCl₃) δ −13.2 (d, J = 160 Hz, 1P), −16.2 (d, J = 160 Hz, 1P); HRMS (DART) m/z calcd for C₃₂H₃₀P₂S [M+H]⁺: 527.3030 found 527.3034.

2,3-Bis(dicyclohexylphosphino)thiophene (L2)
To a 50-mL round-bottom glass flask containing a magnetic stirring bar were added 2,3-dibromothiophene (967 mg, 4.0 mmol, 1.0 equiv) and dry Et₂O (4 mL). After cooling at −78 °C, a solution of n-BuLi in hexane (1.6 M, 2.5 mL, 1.0 equiv) was added at −78 °C over 10 min. After stirring the mixture at −78 °C for 1 h, a solution of chlorodicyclohexylphosphine (977 mg, 4.2 mmol, 1.05 equiv) in Et₂O (1.25 mL) was added at −78 °C over 15 min. The resulting mixture was further stirred at −78 °C for 30 min. Then a solution of n-BuLi in hexane (1.6 M, 2.5 mL, 1.0 equiv) was added at −78 °C over 10 min. After stirring the mixture at −78 °C for 1 h, a solution of chlorodicyclohexylphosphine (977 mg, 4.2 mmol, 1.05 equiv) in Et₂O (1.25 mL) was added at −78 °C over 10 min. The resulting mixture was further stirred at −78 °C for 30 min. After warming up to room temperature, the reaction was quenched with water, extracted with hexane, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The reaction mixture was purified by reprecipitation with toluene (0.40 mL) and methanol (20 mL) to afford 2,3-bis(dicyclohexylphosphino)thiophene (L₂) as a white solid (1.05 g, 55% yield). \( ^1H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.56 (d, \( J = 5.2 \) Hz, 1H), 7.17 (d, \( J = 5.2 \) Hz, 1H) 1.93–1.80 (m, 8H), 1.78–1.47 (m, 16H), 1.32–1.00 (m, 20H); \( ^{31}P \) NMR (162 MHz, CDCl₃) \( \delta \) −19.0 (d, \( J = 129 \) Hz, 1P), −20.8 (d, \( J = 129 \) Hz, 1P); HRMS (DART) \( m/z \) calcd for \( C_{28}H_{47}P_2S \) [M+H]⁺: 477.2874 found 477.2867.
3. Ni-Catalyzed C–H Arylation of Imidazoles with Phenol Derivatives (C–H/C–O Coupling) and Chloroarenes (C–H/C–Cl Coupling)

General Procedure: A 20-mL glass vessel equipped with a J. Young® O-ring tap containing a magnetic stirring bar and K₃PO₄ (255.0 mg, 1.20 mmol, 3.0 equiv) was dried with a heatgun for 3 min in vacuo and filled with N₂ after cooling to room temperature. To this vessel were added Ni(OTf)₂ (14.2 mg, 0.040 mmol, 10 mol%), imidazole 1 (0.40 mmol, 1.0 equiv) and aryl carbamate 2 (0.60 mmol, 1.5 equiv). Then the vessel was introduced into an argon-atmosphere glovebox. To the reaction vessel was added 1,2-bis(dicyclohexylphosphino)ethane (dcype: 20.6 mg, 0.050 mmol, 12 mol%). The vessel was taken out of the glovebox, then dry t-AmylOH (1.6 mL) was added under a stream of N₂. The vessel was sealed with an O-ring tap and then heated at 110 °C for 18–36 h in an 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a silica gel pad with EtOAc as the eluent. The filtrate was concentrated and the residue was subjected to PTLC or flash silica-gel column chromatography to afford 2-arylimidazole 3.

3Aa: 82% (C–H/C–O coupling)  
81% (C–H/C–Cl coupling)

1-Methyl-2-phenyl-1H-benzo[d]imidazole (3Aa)¹⁶: Purification by PTLC (hexane/EtOAc = 4:1) afforded 3Aa as a white solid (68.2 mg, 82% yield by C–H/C–O coupling; 67.3 mg, 81% yield by C–H/C–Cl coupling). ¹H NMR (400 MHz, CDCl₃): δ 7.85–7.81 (m, 1H), 7.79–7.75 (m, 2H), 7.55–7.49 (m, 3H), 7.41–7.37 (m, 1H), 7.35–7.28 (m, 2H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 142.9, 136.5, 130.1, 129.6, 129.3, 128.5, 122.6, 122.3, 119.7, 109.5, 31.5; HRMS (DART) m/z calcd for C₁₄H₁₃N₂ [M+H]⁺: 209.1079, found 209.1076.

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

3Ba: 53% (C–H/C–O coupling)
69% (C–H/C–Cl coupling)

1-Benzyl-2-phenyl-1H-benzo[d]imidazole (3Ba)\(^\text{17}\): Purification by Isolera\(^\text{®}\) (hexane/EtOAc = 10:1 to EtOAc) afforded 3Ba as a white solid (60.5 mg, 53% yield by C–H/C–O coupling: 78.1 mg, 69% yield by C–H/C–Cl coupling). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.87 (d, \(J = 8.0 \text{ Hz}, 1\)H), 7.68 (d, \(J = 8.0 \text{ Hz}, 2\)H), 7.48–7.38 (m, 3H), 7.35–7.24 (m, 4H), 7.22 (dd, \(J = 7.2, 5.4 \text{ Hz}, 2\)H), 7.09 (d, \(J = 5.4 \text{ Hz}, 2\)H), 5.44 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 154.1, 143.2, 136.3, 136.0, 130.1, 129.8, 129.2, 129.0, 128.7, 127.7, 125.9, 123.0, 122.6, 119.9, 110.5, 48.3; HRMS (DART) \(m/z\) calcd for C\(_{20}\)H\(_{17}\)N\(_2\) [M+H\(^+\)]: 285.1392, found 285.1390.

3Ca: 88% (C–H/C–O coupling)
86% (C–H/C–Cl coupling)

1,2-Diphenyl-1H-benzo[d]imidazole (3Ca)\(^\text{18}\): Purification by Isolera\(^\text{®}\) (hexane/EtOAc = 10:1 to EtOAc) afforded 3Ca as a white solid (95.0 mg, 88% yield by C–H/C–O coupling: 93.2 mg, 86% yield by C–H/C–Cl coupling). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.89 (d, \(J = 7.2 \text{ Hz}, 1\)H), 7.56 (d, \(J = 8.4 \text{ Hz}, 2\)H), 7.53–7.41 (m, 3H), 7.38–7.22 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 152.3, 143.0, 137.2, 136.9, 129.9, 129.8, 129.39, 129.36, 128.5, 128.2, 127.3, 123.3, 122.9, 119.8, 110.4; HRMS (DART) \(m/z\) calcd for C\(_{19}\)H\(_{15}\)N\(_2\) [M+H\(^+\)]: 271.1235, found 271.1230.

3Da: 84%

4-(2-(2-phenyl-1H-benzo[d]imidazol-1-yl)ethyl)morpholine (3Da): Purification by PTLC (EtOAc) afforded 3Da as a yellow oil (103.3 mg, 84% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (dd, $J = 7.6$, 2.4 Hz, 1H), 7.79–7.74 (m, 2H), 7.55–7.45 (m, 3H), 7.43–7.38 (m, 1H), 7.34–7.26 (m, 2H), 4.35 (t, $J = 6.8$ Hz, 2H), 3.54 (t, $J = 4.4$ Hz, 4H), 2.70 (t, $J = 6.8$ Hz, 2H), 2.30 (t, $J = 4.4$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.0, 143.0, 135.4, 130.5, 129.7, 129.4, 128.6, 122.7, 122.4, 119.9, 109.9, 66.6, 57.4, 53.7, 42.2; HRMS (DART) $m/z$ calcd for C$_{19}$H$_{22}$N$_3$O$[M+H]^+$: 308.1763, found 308.1767.

1-(Methoxymethyl)-2-phenyl-1H-benzo[d]imidazole (3Ea): Purification by PTLC (hexane/EtOAc = 4:1) afforded 3Ea as a yellow solid (50.1 mg, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95–7.88 (m, 2H), 7.86–7.81 (m, 1H), 7.55–7.47 (m, 4H), 7.35–7.29 (m, 2H), 5.45 (s, 2H), 3.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.4, 142.8, 136.0, 130.0, 129.7, 129.5, 128.6, 123.2, 122.9, 119.9, 110.0, 75.0, 56.5; HRMS (DART) $m/z$ calcd for C$_{15}$H$_{15}$N$_2$O$[M+H]^+$: 239.1184, found 239.1183.

1,5,6-Trimethyl-2-phenyl-1H-benzo[d]imidazole (3Fa): Purification by Isolera® (hexane/EtOAc = 10:1 to 1:1) afforded 3Fa as a white solid (69.1 mg, 65% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J = 7.6$ Hz, 2H), 7.57 (s, 1H), 7.51–7.41 (m, 3H), 7.12 (s, 1H), 3.76 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.8, 141.5, 135.1, 131.8, 131.1, 130.4, 129.3, 129.2, 128.5, 119.7, 109.8, 31.5, 20.5, 20.2; HRMS (DART) $m/z$ calcd for C$_{16}$H$_{17}$N$_2$O$[M+H]^+$: 237.1392, found 237.1396.

1-Methyl-2-phenyl-1H-imidazole (3Ga)$^{19}$: The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by PTLC (EtOAc) afforded 3Ga as a colorless oil (40.5 mg, 64% yield by C–H/C–O coupling: 51.8 mg, 81% yield by C–H/C–Cl coupling).

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Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)  
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

^1H NMR (400 MHz, CDCl$_3$): δ 7.63 (d, $J = 8.0$ Hz, 2H), 7.49–7.38 (m, 3H), 7.13 (d, $J = 1.6$ Hz, 1H), 6.97 (d, $J = 1.6$ Hz, 1H), 3.76 (s, 3H); ^13C NMR (100 MHz, CDCl$_3$): δ 147.7, 130.5, 128.51, 128.47, 128.4, 128.3, 122.2, 34.4; HRMS (DART) m/z calcd for C$_{10}$H$_{11}$N$_2$[M+H]$^+$: 159.0922, found 159.0920.

3Ha: 64% (C–H/C–O coupling)  
64% (C–H/C–Cl coupling)

1-Benzyl-2-phenyl-1H-imidazole (3Ha): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by PTLC (EtOAc) afforded 3Ha as a yellow solid (59.8 mg, 64% yield by C–H/C–O coupling: 60.4 mg, 64% yield by C–H/C–Cl coupling).

^1H NMR (400 MHz, CDCl$_3$): δ 7.59–7.51 (m, 2H), 7.42–7.25 (m, 6H), 7.18 (s, 1H), 7.07 (d, $J = 7.2$ Hz, 2H), 6.95 (s, 1H), 5.20 (s, 2H); ^13C NMR (100 MHz, CDCl$_3$): δ 148.1, 136.9, 130.4, 128.9, 128.8, 128.68, 128.66, 128.4, 127.8, 126.4, 121.2, 50.2; HRMS (DART) m/z calcd for C$_{16}$H$_{15}$N$_2$[M+H]$^+$: 235.1235, found 235.1230.

N$_2$Bu$_3$Ib: 49%

1-Butyl-2-(naphthalen-2-yl)-1H-imidazole (3Ib): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Ib as a yellow solid (48.7 mg, 49% yield). ^1H NMR (400 MHz, CDCl$_3$): δ 8.04 (s, 1H), 7.95–7.81 (m, 3H), 7.71 (d, $J = 7.6$ Hz, 1H), 7.55–7.46 (m, 2H), 7.19 (s, 1H), 7.05 (s, 1H), 4.06 (t, $J = 7.6$ Hz, 2H), 1.79–1.70 (m, 2H), 1.33–1.21 (m, 2H), 0.86 (t, $J = 7.6$ Hz, 3H); ^13C NMR (100 MHz, CDCl$_3$): δ 147.6, 133.0, 128.6, 128.4, 128.2, 128.17, 128.1, 127.7, 126.5, 126.4, 126.3, 120.5, 46.6, 33.1, 19.2, 13.5 (one peak is overlapping); HRMS (DART) m/z calcd for C$_{17}$H$_{19}$N$_2$[M+H]$^+$: 251.1548, found 251.1542.

NMe$_2$N$_2$Ja: 82%
1-Methyl-5-(naphthalen-2-yl)-2-phenyl-1H-imidazole (3Ja): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by flash silica-gel column chromatography (hexane/EtOAc = 4:1 to EtOAc) afforded 3Ja as a white solid (93.3 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.95–7.84 (m, 4H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.56–7.46 (m, 4H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.32 (s, 1H), 3.73 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.6, 135.4, 133.3, 132.6, 130.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.7, 127.6, 127.4, 126.6, 126.44, 126.36, 33.9 (one peak is overlapping); HRMS (DART) m/z calcd for C$_{20}$H$_{17}$N$_2$ [M+H]$: 285.1392, found 285.1397.

3Ka: 65%

1-Methyl-2-phenyl-5-(p-tolyl)-1H-imidazole (3Ka): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by flash silica-gel column chromatography (hexane/EtOAc = 4:1 to 1:1) afforded 3Ka as a white solid (65.0 mg, 65% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.46 (dd, $J = 8.4$, 7.6 Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.17 (s, 1H), 3.66 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 149.1, 137.7, 135.4, 131.0, 129.4, 128.7, 128.5, 128.4, 128.0, 127.7, 127.6, 127.3, 126.6, 126.44, 126.36, 33.6, 21.2; HRMS (DART) m/z calcd for C$_{17}$H$_{17}$N$_2$ [M+H]$: 249.1392, found 249.1395.

3La: >95%

1-Methyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)-1H-imidazole (3La) $^{20}$: The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by PTLC (hexane/EtOAc = 1:1) afforded 3La as a white solid (122.4 mg, >95% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.74–7.67 (m, 4H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.52–7.41 (m, 3H), 7.28 (s, 1H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.4, 137.7, 135.4, 131.0, 129.4, 128.7, 128.5, 128.52, 128.4, 127.3, 127.2, 33.6, 21.2; HRMS (DART) m/z calcd for C$_{17}$H$_{14}$F$_3$N$_2$ [M+H]$: 303.1109, found 303.1108.

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

3Ma: 82%
1-Methyl-5-phenyl-1H-1,2,4-triazole (3Ma): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h. Purification by PTLC (EtOAc) afforded 3Ma as a white solid (52.2 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.94 (s, 1H), 7.70–7.66 (m, 2H), 7.54–7.48 (m, 3H), 3.99 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.5, 150.6, 130.0, 128.8, 128.5, 127.8, 36.9; HRMS (DART) m/z calcd for C$_9$H$_{10}$N$_3$[M+H]$^+$: 160.0875, found 160.0875.

3Nb: 87%
1-Methyl-2-(naphthalen-2-yl)-4,5-diphenyl-1H-imidazole (3Nb): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) and dcypt (22.9 mg, 0.050 mmol, 12 mol%) instead of Ni(OTf)$_2$/dcype for 36 h. Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Nb as a white solid (125.1 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.21 (s, 1H), 7.98–7.85 (m, 4H), 7.58 (d, $J$ = 8.4 Hz, 2H), 7.56–7.41 (m, 7H), 7.23 (t, $J$ = 8.0 Hz, 2H), 7.15 (t, $J$ = 7.6 Hz, 1H), 3.58 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.9, 138.0, 134.7, 133.2, 133.1, 131.2, 130.9, 130.7, 129.0, 128.6, 128.4, 128.33, 128.26, 128.1, 127.8, 127.0, 126.6, 126.52, 126.49, 126.3, 33.3 (one peak is overlapping); HRMS (DART) m/z calcd for C$_{26}$H$_{21}$N$_2$[M+H]$^+$: 361.1705, found 361.1708.

3Ob: 72%
4-(1-Methyl-2-(naphthalen-2-yl)-1H-imidazol-4-yl)benzonitrile (3Ob): The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) and dcypt (22.9 mg, 0.050 mmol, 12 mol%) instead of Ni(OTf)$_2$/dcype for 36 h. Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Ob as a yellow solid (89.2 mg, 72% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.12 (s, 1H), 7.98–7.86 (m, 5H), 7.80 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 2H), 7.58–7.50 (m, 2H), 7.39 (s,
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

1H), 3.83 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 148.9, 139.4, 138.6, 133.3, 133.0, 132.4, 128.4, 128.3, 128.2, 127.8, 127.3, 126.9, 126.7, 126.0, 125.1, 120.1, 119.3, 109.6, 34.9; HRMS (DART) m/z calcd for C21H16N3 [M+H]+: 310.1344, found 310.1349.

NMe
O
93% (combined yield)

Ethyl 1-methyl-2-(naphthalen-2-yl)-1H-imidazole-4-carboxylate (3Pb), tert-Pentyl 1-methyl-2-(naphthalen-2-yl)-1H-imidazole-4-carboxylate (3Pb'): The reaction was performed by using Ni(cod)2 (11.0 mg, 0.040 mmol, 10 mol%) and dcypt (22.9 mg, 0.050 mmol, 12 mol%) instead of Ni(OTf)2/dcyype and 1P as a starting material for 36 h. Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Pb (37.5 mg, 33% yield, white solid) and 3Pb' (77.6 mg, 60% yield, white solid).

3Pb: 1H NMR (400 MHz, CDCl3): δ 8.11 (s, 1H), 7.93–7.83 (m, 3H), 7.76 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.55–7.48 (m, 2H), 4.41 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 163.0, 148.8, 133.2, 132.9, 132.7, 128.6, 128.3, 128.2, 127.7, 126.9, 126.8, 126.6, 126.0, 60.4, 35.0, 14.4 (one peak is overlapping); HRMS (DART) m/z calcd for C17H17N2O2 [M+H]+: 281.1290, found 281.1289.

3Pb': 1H NMR (400 MHz, CDCl3): δ 8.13 (s, 1H), 7.93–7.85 (m, 3H), 7.79 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.54–7.50 (m, 2H), 3.82 (s, 3H), 1.94 (q, J = 7.2 Hz, 2H), 1.57 (s, 6H), 0.97 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 162.1, 148.6, 134.2, 132.9, 132.7, 128.5, 128.3, 128.2, 127.7, 127.6, 127.2, 126.9, 126.6, 126.2, 83.2, 35.0, 33.6, 25.8, 8.4; HRMS (DART) m/z calcd for C20H23N2O2 [M+H]+: 323.1760, found 323.1757.

NMe
O
3Ac: 74%

2-(3,4-Dimethylphenyl)-1-methyl-1H-benzo[d]imidazole (3Ac): Purification by PTLC (hexane/EtOAc = 4:1) afforded 3Ac as a white solid (69.6 mg, 74% yield). 1H NMR (400 MHz, CDCl3): δ 7.84–7.79 (m, 1H), 7.57 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.35–7.22 (m, 4H), 3.79 (s, 3H), 2.324 (s, 3H), 2.317 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 153.9, 142.8, 134.2, 133.3, 132.9, 128.5, 128.3, 128.2, 127.7, 127.6, 127.2, 126.9, 126.6, 126.2, 83.2, 35.0, 33.6, 25.8, 8.4; HRMS (DART) m/z calcd for C16H17N2 [M+H]+: 237.1392, found 237.1387.

S19
2-(3-(tert-Butyl)phenyl)-1-methyl-1H-benzo[d]imidazole (3Ad): Purification by PTLC (hexane/EtOAc = 4:1) afforded 3Ad as a white solid (78.0 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.87–7.83 (m, 1H), 7.82–7.77 (m, 1H), 7.57–7.48 (m, 2H), 7.46 (dd, J = 8.0, 7.6 Hz, 1H), 7.42–7.36 (m, 1H), 7.35–7.27 (m, 2H), 3.86 (s, 3H), 1.39 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 154.4, 151.7, 143.0, 136.6, 129.9, 128.3, 126.8, 126.6, 126.5, 122.6, 122.3, 119.8, 109.5, 34.9, 31.6, 31.3; HRMS (DART) m/z calcd for C₁₈H₂₁N₂⁺: 265.1705, found 265.1700.

2-(4-Methoxyphenyl)-1-methyl-1H-benzo[d]imidazole (3Ae): Purification by PTLC (hexane/EtOAc = 1:1) afforded 3Ae as a white solid (57.2 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.80 (dd, J = 8.0, 3.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.35–7.25 (m, 3H), 7.00 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.6, 153.6, 142.8, 136.4, 130.7, 122.4, 122.3, 122.1, 119.4, 114.0, 109.4, 55.2, 31.5; HRMS (DART) m/z calcd for C₁₅H₁₅N₂O⁺: 239.1184, found 239.1181.

tert-Pentyl 3-(1-methyl-1H-benzo[d]imidazol-2-yl)benzoate (3Af): Purification by PTLC (hexane/EtOAc = 10:1) and GPC afforded 3Af as a colorless liquid (69.1 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.37 (s, 1H), 8.13 (d, J = 6.8 Hz, 1H), 7.95 (d, J = 6.8 Hz, 1H), 7.84 (d, J = 4.0 Hz, 1H), 7.59 (t, J = 6.8 Hz, 1H), 7.42–7.30 (m, 3H), 3.85 (s, 3H), 1.94 (q, J = 7.2 Hz, 2H), 1.58 (s, 6H), 0.98 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.8, 152.7, 142.8, 136.4, 133.3, 132.4, 130.4, 130.3, 129.9, 128.6, 122.8, 122.4, 119.7, 109.6, 83.9, 33.5, 31.5, 25.5, 8.2; HRMS (DART) m/z calcd for C₂₀H₂₃N₂O₂⁺ [M+H]⁺: 323.1760, found 323.1756.
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

3Ag: 67%

N,N-Dimethyl-3-(1-methyl-1H-benzo[d]imidazol-2-yl)aniline (3Ag): Purification by Isolera® (hexane/EtOAc = 10:1 to 1:2) afforded 3Ag as a yellow oil (67.0 mg, 67% yield). 1H NMR (400 MHz, CDCl3): δ 7.86–7.80 (m, 1H), 7.41–7.27 (m, 4H), 7.11 (s, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.01 (s, 6H); 13C NMR (100 MHz, CDCl3): δ 154.7, 150.7, 142.9, 136.5, 130.8, 129.0, 122.5, 122.2, 119.7, 117.2, 113.6, 113.4, 109.5, 40.5, 31.6; HRMS (DART) m/z calcd for C16H18N3 [M+H]+: 252.1501, found 252.1501.

3Ah: 95%

1-Methyl-2-(pyridin-3-yl)-1H-benzo[d]imidazole (3Ah): Purification by Isolera® (hexane/EtOAc = 1:1 to EtOAc) afforded 3Ah as a white solid (79.6 mg, 95% yield). 1H NMR (400 MHz, CDCl3): δ 9.02 (s, 1H), 8.75 (dd, J = 4.0, 1.6 Hz, 1H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 7.85–7.80 (m, 1H), 7.52–7.30 (m, 4H), 3.89 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 150.6, 149.8, 143.0, 136.8, 136.5, 126.5, 123.5, 122.7, 120.0, 109.7, 31.6; HRMS (DART) m/z calcd for C13H12N3 [M+H]+: 210.1031, found 210.1025.

3Ai: 92%

2-[(1,1'-Biphenyl)-4-yl]-1-methyl-1H-benzo[d]imidazole (3Ai) 21: Purification by Isolera® (hexane/EtOAc = 5:1 to EtOAc) afforded 3Ai as a white solid (105.2 mg, 92% yield). 1H NMR (400 MHz, CDCl3): δ 7.98–7.80 (m, 3H), 7.72 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.40–7.27 (m, 4H), 3.85 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 153.4, 142.9, 142.3, 140.0, 136.6, 129.7, 128.9, 128.8, 127.8, 127.2, 127.1, 122.7, 122.4, 119.7, 109.6, 31.7; HRMS (DART) m/z calcd for C20H17N2 [M+H]+: 285.1392, found 285.1393.

**Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)**

**C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation**

1-Methyl-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (3Ab): Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Ab as a white solid (103.0 mg, >95% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.15 (s, 1H), 7.91–7.78 (m, 5H), 7.51–7.45 (m, 2H), 7.32–7.24 (m, 3H), 3.75 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.5, 142.9, 136.5, 133.4, 132.7, 129.1, 128.3, 128.2, 127.6, 127.3, 127.0, 126.5, 126.1, 122.6, 119.6, 109.5, 31.5; HRMS (DART) m/z calcd for C$_{18}$H$_{15}$N$_2$ [M+H]$^+$: 259.1235, found 259.1235.

1-Methyl-2-(naphthalen-1-yl)-1H-benzo[d]imidazole (3Aj): Purification by PTLC (hexane/EtOAc = 20:1 to EtOAc) afforded 3Aj as a white solid (98.6 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.92–7.87 (m, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 8.4$ Hz, 1H), 7.56–7.41 (m, 3H), 7.40–7.32 (m, 2H), 3.60 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.9, 143.2, 135.9, 133.5, 132.1, 130.2, 128.8, 128.4, 127.8, 127.2, 126.3, 125.4, 125.0, 122.7, 122.3, 120.0, 109.5, 31.0; HRMS (DART) m/z calcd for C$_{18}$H$_{15}$N$_2$ [M+H]$^+$: 259.1235, found 259.1230.

(3S,4R)-3-Ethyl-4-((1-methyl-2-(naphthalen-2-yl)-1H-imidazol-5-yl)methyl)dihydrofuran-2(3H)-one (3Qb): Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3Qb as a colorless oil (92.2 mg, 69% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.03 (s, 1H), 7.93–7.83 (m, 3H), 7.71 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.54–7.48 (m, 2H), 6.94 (s, 1H), 4.47 (dd, $J = 9.2$, 7.2 Hz, 1H), 3.98 (dd, $J = 9.2$, 7.2 Hz, 1H), 3.66 (s, 3H), 2.92 (dd, $J = 15.6$, 5.2 Hz, 1H), 2.81–2.63 (m, 2H), 2.33 (q, $J = 6.4$ Hz, 1H), 1.85–1.73 (m, 2H), 1.08 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 178.1, 148.8, 133.3, 133.2, 129.8, 128.34, 128.28, 128.1, 127.8, 126.81, 126.76, 126.7, 126.6, 126.3, 71.1, 46.7, 39.2, 32.0, 28.5, 22.6, 11.1; HRMS (DART) m/z calcd for C$_{21}$H$_{33}$N$_2$O$_2$ [M+H]$^+$: 335.1760, found 335.1762.

NMeO

pilocarpine derivative

3Qb: 69%
**Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)**

**C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:**

Solvent-accelerated Imidazole C–H Activation

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**3As: 66%**

*4-(1-Methyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3As):* The reaction was performed by using Ni(cod)$_2$ (11.0 mg, 0.040 mmol, 10 mol%) instead of Ni(OTf)$_2$ for 36 h with 4-chlorobenzonitrile. Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) afforded 3As as a white solid (62.0 mg, 66% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.86–7.78 (m, 3H), 7.45–7.31 (m, 3H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 151.4, 142.9, 136.7, 134.6, 132.4, 129.9, 123.6, 123.0, 120.2, 118.2, 113.3, 109.8, 31.8; HRMS (DART) $m/z$ calcd for C$_{15}$H$_{12}$N$_3$[M+H]$^+$: 234.1031, found 234.1038.

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**indomethacin derivative 3At: 26%**

*tert-Pentyl 2-(5-methoxy-2-methyl-1-(4-(1-methyl-1H-benzo[d]imidazol-2-yl)benzoyl)-1H-indol-3-yl)acetate (3At):* Purification by Isolera® (hexane/EtOAc = 100:1 to EtOAc) afforded 3At as a white solid (55.0 mg, 26% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.87–7.82 (m, 3H), 7.45–7.30 (m, 3H), 7.00–6.96 (m, 2H), 6.67 (dd, $J = 8.8$, 2.0 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 3.59 (s, 2H), 2.40 (s, 3H), 1.76 (q, $J = 8.0$ Hz, 2H), 1.42 (s, 6H), 0.82 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.0, 168.6, 156.0, 152.2, 142.9, 136.7, 135.6, 134.2, 130.8, 129.9, 129.7, 123.4, 122.8, 120.1, 115.1, 113.6, 111.7, 109.7, 101.4, 83.5, 55.6, 33.3, 31.8, 31.6, 25.5, 13.4, 8.1 (two peaks are overlapping); HRMS (ESI) $m/z$ calcd for C$_{32}$H$_{33}$N$_3$O$_4$Na [M+Na]$^+$: 546.2363, found 546.2360.
5. Ni-Catalyzed C–H Alkenylation of Imidazoles with Enol Derivatives

A 50-mL glass Schlenk tube containing a magnetic stirring bar and K$_3$PO$_4$ (670.3 mg, 3.0 mmol, 3.0 equiv) was dried with a heatgun for 3 min in vacuo and filled with argon after cooling to room temperature. Ni(OTf)$_2$ (35.7 mg, 0.10 mmol, 10 mol%), imidazole 1 (1.0 mmol, 1.0 equiv), alkenyl carbamate 2 (1.5 mmol, 1.5 equiv), and 3,4-bis(dicyclohexylphosphino)thiophene (dcypt: 57.2 mg, 0.12 mmol, 12 mol%) were placed in a 20-mL glass Schlenk tube under an argon atmosphere. Then, to it was added dry degassed t-AmylOH (4.0 mL) under a stream of argon. The resultant t-AmylOH solution was transferred into the 50-mL Schlenk tube under a stream of argon via cannula. The reaction mixture was stirred at 120 °C for 36 h. After cooling the reaction mixture to room temperature, the mixture was diluted with EtOAc, and the organic layer was washed with water and brine, dried over Na$_2$SO$_4$, and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash silica-gel column chromatography to afford 2-alkenylimidazole 3.

3Ak: 87%

2-(3,4-Dihyronaphthalen-2-yl)-1-methyl-1H-benzo[d]imidazole (3Ak): Purification by flash silica-gel column chromatography (hexane/EtOAc = 3:1) afforded 3Ak as a white solid (225.7 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J$ = 7.2 Hz, 1H), 7.40–7.20 (m, 7H), 6.99 (s, 1H), 3.96 (s, 3H), 3.08–2.97 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.8, 142.7, 136.6, 135.6, 133.1, 131.1, 129.1, 128.3, 127.6, 127.3, 126.7, 122.8, 122.3, 119.6, 109.4, 32.1, 27.8, 26.3; HRMS (DART) m/z calcd for C$_{18}$H$_{17}$N$_2$[M+H]$^+$: 261.1392, found 261.1392.

3Al: 86%

2-(7-Methoxy-3,4-dihyronaphthalen-2-yl)-1-methyl-1H-benzo[d]imidazole (3Al): Purification by flash silica-gel column chromatography (hexane/EtOAc = 2:1) afforded 3Al as a white solid (249.2...
mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (dd, $J$ = 6.8, 2.4 Hz, 1H), 7.40–7.27 (m, 3H), 7.13 (d, $J$ = 8.0 Hz, 1H), 6.93 (s, 1H), 6.81–6.75 (m, 2H), 3.94 (s, 3H), 3.83 (s, 3H), 3.00–2.90 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.4, 153.8, 142.6, 136.6, 134.0, 131.1, 129.7, 128.4, 127.7, 122.9, 122.3, 119.6, 113.4, 112.9, 109.4, 55.3, 32.1, 26.9, 26.8; HRMS (DART) m/z calcd for C$_{19}$H$_{19}$N$_2$O [M+H]$^+$: 291.1497, found 291.1496.

2-(3,4-Dihyronaphthalen-1-yl)-1-methyl-1H-benzo[d]imidazole (3Am): Purification by flash silica-gel column chromatography (hexane/EtOAc = 2:1) afforded 3Am as a pale brown solid (134.7 mg, 52% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J$ = 6.4 Hz, 1H), 7.40–7.27 (m, 3H), 7.24–7.16 (m, 2H), 7.10 (t, $J$ = 7.2 Hz, 1H), 6.78 (d, $J$ = 7.2 Hz, 1H), 6.53 (t, $J$ = 4.8 Hz, 1H), 3.60 (s, 3H), 2.94 (t, $J$ = 8.4 Hz, 2H), 2.60–2.50 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.0, 143.0, 135.8, 135.4, 134.6, 132.8, 129.7, 127.8, 127.7, 126.8, 124.7, 122.6, 122.1, 119.9, 109.4, 31.0, 27.5, 23.4; HRMS (DART) m/z calcd for C$_{18}$H$_{17}$N$_2$ [M+H]$^+$: 261.1392, found 261.1391.

2-(7-Methoxy-3,4-dihyronaphthalen-1-yl)-1-methyl-1H-benzo[d]imidazole (3An): Purification by flash silica-gel column chromatography (hexane/EtOAc = 2:1) afforded 3An as a yellow oil (193.4 mg, 67% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J$ = 6.4 Hz, 1H), 7.40–7.27 (m, 3H), 7.13 (d, $J$ = 8.4 Hz, 1H), 6.74 (dd, $J$ = 8.0, 2.8 Hz, 1H), 6.55 (t, $J$ = 4.4 Hz, 1H), 6.38 (d, $J$ = 2.8 Hz, 1H), 3.56 (s, 3H), 2.61 (s, 3H), 2.86 (t, $J$ = 7.6 Hz, 2H), 2.56–2.48 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.4, 152.7, 142.8, 135.7, 135.2, 133.7, 129.5, 128.4, 127.4, 122.5, 122.0, 119.7, 112.2, 111.0, 109.3, 55.2, 30.9, 26.5, 23.7; HRMS (DART) m/z calcd for C$_{19}$H$_{19}$N$_2$O [M+H]$^+$: 291.1497, found 291.1493.
**Supplementary Information** (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

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3Ao: 66%

2-(7-Fluoro-3,4-dihydronaphthalen-1-yl)-1-methyl-1H-benzo[d]imidazole (3Ao): Purification by flash silica-gel column chromatography (hexane/EtOAc = 2:1) afforded 3Ao as a white solid (184.9 mg, 66% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 6.8$ Hz, 1H), 7.42–7.29 (m, 3H), 6.60–6.53 (m, 2H), 3.63 (s, 3H), 2.90 (t, $J = 8.0$ Hz, 2H), 2.59–2.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.8 (d, $J_{C-F}$ = 241.8 Hz), 152.2, 142.8, 135.7, 134.5 (d, $J_{C-F}$ = 7.6 Hz), 130.80, 130.78, 129.1, 128.9 (d, $J_{C-F}$ = 7.6 Hz), 122.8, 122.2, 119.9, 114.1 (d, $J_{C-F}$ = 21.0 Hz), 111.8 (d, $J_{C-F}$ = 22.9 Hz), 109.5, 31.0, 26.7, 23.5; HRMS (DART) m/z calcd for C$_{18}$H$_{16}$FN$_2$ [M+H]$^+$: 279.1298, found 279.1293.

3Ap: 69%

1-Methyl-2-(4-methyl-3,4-dihydronaphthalen-1-yl)-1H-benzo[d]imidazole (3Ap): Purification by flash silica-gel column chromatography (hexane/EtOAc = 2:1) afforded 3Ap as a yellow oil (187.9 mg, 69% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85–7.79 (m, 1H), 7.40–7.20 (m, 5H), 7.11 (dt, $J = 7.8$, 1.6 Hz, 1H), 6.79 (d, $J = 7.8$ Hz, 1H), 6.46 (t, $J = 7.8$ Hz, 1H), 3.60 (s, 3H), 3.08 (q, $J = 6.8$ Hz, 1H), 2.71 (ddd, $J = 16.8$, 6.8, 4.0 Hz, 1H), 2.37 (ddd, $J = 16.8$, 6.8, 4.0 Hz, 1H), 1.36 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.0, 142.9, 140.2, 135.8, 133.1, 131.9, 129.2, 128.0, 126.6, 126.4, 124.8, 122.5, 122.0, 119.8, 109.3, 31.6, 31.2, 30.9, 20.0; HRMS (DART) m/z calcd for C$_{19}$H$_{19}$N$_2$ [M+H]$^+$: 275.1548, found 275.1545.

3Bk: 87%

1-Benzyl-2-(3,4-dihydronaphthalen-2-yl)-1H-benzo[d]imidazole (3Bk): Purification by flash silica-gel column chromatography (hexane/EtOAc = 3:1) afforded 3Bk as a white solid (293.1 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 6.8$ Hz, 1H), 7.42–7.29 (m, 3H), 6.60–6.53 (m, 2H), 3.63 (s, 3H), 2.90 (t, $J = 8.0$ Hz, 2H), 2.59–2.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.8 (d, $J_{C-F}$ = 241.8 Hz), 152.2, 142.8, 135.7, 134.5 (d, $J_{C-F}$ = 7.6 Hz), 130.80, 130.78, 129.1, 128.9 (d, $J_{C-F}$ = 7.6 Hz), 122.8, 122.2, 119.9, 114.1 (d, $J_{C-F}$ = 21.0 Hz), 111.8 (d, $J_{C-F}$ = 22.9 Hz), 109.5, 31.0, 26.7, 23.5; HRMS (DART) m/z calcd for C$_{18}$H$_{16}$FN$_2$ [M+H]$^+$: 279.1298, found 279.1293.
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
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87% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.40–7.22 (m, 7H), 7.20–7.10 (m, 4H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.76 (s, 1H), 5.54 (s, 2H), 3.00–2.93 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.3, 143.0, 136.7, 136.5, 135.6, 133.1, 130.8, 129.1, 128.8, 128.4, 127.8, 127.6, 127.3, 126.6, 125.9, 123.2, 122.6, 119.8, 110.1, 48.7, 27.8, 26.4; HRMS (DART) m/z calcd for C$_{24}$H$_{21}$N$_2$ [M+H]$^+$: 337.1705, found 337.1705.

3Dk: 80%

4-(2-(2-(3,4-Dihyronaphthalen-2-yl)-1H-benzo[d]imidazol-1-yl)ethyl)morpholine (3Dk): Purification by flash silica-gel column chromatography (CH$_2$Cl$_2$/MeOH = 24:1) afforded 3Dk as a pale yellow oil (288.6 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.82–7.76 (m, 1H), 7.42–7.40 (m, 1H), 7.33–7.28 (m, 2H), 7.27–7.21 (m, 3H), 7.19–7.16 (m, 1H), 7.07 (s, 1H), 4.46 (t, $J = 7.6$ Hz, 2H), 3.68 (t, $J = 4.8$ Hz, 4H), 3.08–2.94 (m, 4H), 2.85 (t, $J = 7.6$ Hz, 2H), 2.51 (t, $J = 4.8$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.9, 142.9, 135.8, 135.5, 133.1, 130.7, 129.2, 128.4, 127.7, 127.1, 126.7, 122.8, 122.4, 119.8, 109.7, 66.8, 57.5, 54.0, 42.9, 27.8, 26.7; HRMS (DART) m/z calcd for C$_{23}$H$_{26}$N$_2$O [M+H]$^+$: 360.2076, found 360.2077.

3Rk: 86%

1-((Benzyloxy)methyl)-2-(3,4-dihyronaphthalen-2-yl)-1H-benzo[d]imidazole (3Rk): Purification by flash silica-gel column chromatography (hexane/EtOAc = 4:1) afforded 3Rk as a yellow oil (314.4 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87–7.83 (m, 1H), 7.45–7.30 (m, 9H), 7.25–7.18 (m, 3H), 7.15 (d, $J = 7.6$ Hz, 1H), 5.68 (s, 2H), 4.70 (s, 2H), 3.03–2.99 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.4, 142.4, 136.5, 136.1, 135.6, 133.1, 131.9, 131.8, 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 126.5, 123.3, 122.8, 119.6, 109.6, 72.9, 70.3, 27.6, 26.1; HRMS (DART) m/z calcd for C$_{25}$H$_{23}$N$_2$O [M+H]$^+$: 367.1810, found 367.1817.
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

3Aq: 75%

2-(4-(tert-Butyl)cyclohex-1-en-1-yl)-1-methyl-1H-benzo[d]imidazole (3Aq): Purification by Isolera® (hexane/EtOAc = 10:1 to EtOAc) and GPC afforded 3Aq as a white solid (80.4 mg, 75% yield). 1H NMR (400 MHz, CDCl3): δ 7.73 (d, J = 8.8 Hz, 1H), 7.30–7.19 (m, 3H), 6.18 (dd, J = 2.8, 2.4 Hz, 1H), 3.76 (s, 3H), 2.77 (d, J = 15.2 Hz, 1H), 2.56–2.28 (m, 2H), 2.10–1.97 (m, 2H), 1.50–1.28 (m, 2H), 0.93 (s, 9H); 13C NMR (100 MHz, CDCl3): δ 155.0, 142.5, 136.1, 133.4, 128.6, 122.2, 121.9, 119.4, 109.2, 43.5, 32.2, 31.4, 29.3, 27.4, 27.1, 23.9; HRMS (DART) m/z calcd for C18H25N2 [M+H]+: 269.2018, found 269.2018.

3Ar: 29%

(E)-1-Methyl-2-(2-phenylprop-1-en-1-yl)-1H-benzo[d]imidazole (3Ar): Purification by flash silica-gel column chromatography (hexane/EtO = 3:1) afforded 3Ar as a pale yellow solid (72.8 mg, 29% yield). 1H NMR (400 MHz, CDCl3): δ 7.83–7.78 (m, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.45–7.27 (m, 6H), 6.71 (s, 1H), 3.81 (s, 3H), 2.73 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 151.0, 147.4, 143.1, 143.0, 135.0, 128.4, 128.2, 126.1, 122.4, 122.0, 119.5, 112.7, 108.9, 29.8, 18.5; HRMS (DART) m/z calcd for C17H17N2 [M+H]+: 249.1392, found 249.1392.

6. Ni-Catalyzed C–H Coupling of Thiazoles and Oxazoles

General Procedure: A 20-mL glass vessel equipped with a J. Young® O-ring tap containing a magnetic stirring bar and K3PO4 (255.0 mg, 1.20 mmol, 3.0 equiv) was dried with a heatgun for 3 min in vacuo and filled with N2 after cooling to room temperature. To this vessel were added 1,3-azole 5 (0.40 mmol, 1.0 equiv) and aryl carbamate 2 (0.60 mmol, 1.5 equiv). Then the vessel was introduced into an argon-atmosphere glovebox. To the reaction vessel were added Ni(cod)2 (11.0 mg, 0.040 mmol, 10 mol%) and 1,2-bis(dicyclohexylphosphino)ethane (dcype: 20.6 mg, 0.050 mmol, 12 mol%). The
vessel was taken out of the glovebox, then dry t-AmyLOH (1.6 mL) was added under a stream of N2. The vessel was sealed with an O-ring tap and then heated at 110 °C for 18–36 h in an 8-well reaction block with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a silica gel pad with EtOAc as an eluent. The filtrate was concentrated and the residue was subjected to PTLC or flash silica-gel column chromatography to afford 2-arylazoles 6.

6Ab: 90%

4,5-Dimethyl-2-(naphthalen-2-yl)thiazole (6Ab): Purification by PTLC (hexane/EtOAc = 20:1) afforded 6Ab as a pale yellow solid (86.0 mg, 90% yield). 1H NMR (400 MHz, CDCl3): δ 8.33 (s, 1H), 7.97 (dd, J = 8.8, 2.0 Hz, 1H), 7.91–7.78 (m, 3H), 7.51–7.43 (m, 2H), 2.41 (s, 3H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 163.3, 149.4, 133.7, 133.3, 131.2, 128.50, 128.46, 127.7, 126.7, 126.5, 125.1, 123.8, 14.8, 11.5 (one peak is overlapping); HRMS (DART) m/z calcd for C15H14NS [M+H]+: 240.0847, found 240.0846.

6Aa: 91%

4,5-Dimethyl-2-phenylthiazole (6Aa): Purification by PTLC (hexane/EtOAc = 10:1) afforded 6Aa as a colorless liquid (69.1 mg, 91% yield). 1H NMR (400 MHz, CDCl3): δ 7.86 (dd, J = 8.0, 2.4 Hz, 2H), 7.42–7.33 (m, 3H), 2.38 (s, 6H); 13C NMR (100 MHz, CDCl3): δ 163.3, 149.3, 133.9, 129.3, 128.8, 126.5, 126.1, 14.8, 11.4; HRMS (DART) m/z calcd for C11H12NS [M+H]+: 190.0690, found 190.0686.

6Ba: 54%

4-Methyl-2-phenylthiazole (6Ba): Purification by Isolera® (hexane/EtOAc = 100:1 to 10:1) afforded 6Ba as a yellow liquid (37.8 mg, 54% yield). 1H NMR (400 MHz, CDCl3): δ 7.92 (d, J = 7.6 Hz, 2H), 7.45–7.35 (m, 3H), 6.85 (s, 1H), 2.50 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 167.5, 153.8,

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
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133.8, 129.7, 128.8, 126.4, 113.4, 17.2; HRMS (DART) m/z calcd for C_{10}H_{10}NS [M+H]^+: 176.0534, found 176.0535.

6Ak: 59%

2-(3,4-Dihyronaphthalen-2-yl)-4,5-dimethylthiazole (6Ak): Reaction was performed by using Ni(OTf)$_2$ (35.7 mg, 0.10 mmol, 10 mol%) and 3,4-bis(dicyclohexylphosphino)thiophene (dcyp: 57.2 mg, 0.12 mmol, 12 mol%) instead of Ni(cod)/dcype. Purification by flash silica-gel column chromatography (hexane/Et$_2$O = 6:1) afforded 6Ak as a yellow solid (141.8 mg, 59% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.19–7.14 (m, 5H), 2.97–2.83 (m, 4H), 2.38 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 164.3, 148.9, 135.7, 133.7, 132.7, 127.7, 127.4, 127.1, 126.6, 126.2, 125.9, 27.8, 25.0, 14.8, 11.5; HRMS (DART) m/z calcd for C$_{15}$H$_{16}$NS [M+H]^+: 242.1003, found 242.1002.

6Ca: 56%

2-Phenyloxazole (6Ca): Purification by PTLC (hexane/EtOAc = 20:1) afforded 6Ca as a colorless liquid (32.6 mg, 56% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05 (d, $J$ = 7.6 Hz, 2H), 7.69 (d, $J$ = 2.0 Hz, 1H), 7.50–7.40 (m, 3H), 7.23 (d, $J$ = 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 161.9, 138.5, 130.3, 128.7, 128.3, 127.4, 126.3; HRMS (DART) m/z calcd for C$_9$H$_8$NO [M+H]^+: 146.0606, found 146.0603.

6Ci: 63%

2-[(1,1'-Biphenyl)-4-yl]oxazole (6Ci): Purification by PTLC (hexane/EtOAc = 10:1) afforded 6Ci as a white solid (55.8 mg, 63% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, $J$ = 8.4 Hz, 2H), 7.69 (s, 1H), 7.66 (d, $J$ = 8.4 Hz, 2H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.44 (t, $J$ = 8.4 Hz, 2H), 7.36 (t, $J$ = 8.4 Hz, 1H), 7.24 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 161.8, 142.9, 140.1, 138.5, 128.8, 128.4, 127.8, 127.4, 127.0, 126.7, 126.3; HRMS (DART) m/z calcd for C$_{15}$H$_{12}$NO [M+H]^+: 222.0919, found 222.0920.
4,5-Dimethyl-2-phenylthiazole (6Da)

Reaction was performed by using Ni(OTf)₂ (14.2 mg, 0.040 mmol, 10 mol%) instead of Ni(cod). Purification by flash silica-gel column chromatography (hexane/EtOAc = 10:1 to 4:1) afforded 6Da as a white solid (78.9 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, J = 8.4 Hz, 2H), 7.49–7.39 (m, 3H), 7.28 (s, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.14 (s, 1H), 6.85 (d, J = 8.4 Hz, 1H), 5.97 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.5, 151.0, 148.1, 147.8, 130.1, 128.7, 127.4, 126.1, 122.3, 122.1, 118.2, 108.7, 104.7, 101.3; HRMS (DART) m/z calcd for C₁₆H₁₂NO₃[M+H]⁺: 266.0817, found 266.0813.

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

7. $^1$H NMR and $^{13}$C NMR Spectra
$^1$H NMR of 1P (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 1P (100 MHz, CDCl$_3$)
$^1$H NMR of 2c (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 2c (100 MHz, CDCl$_3$)

![NMR spectrum of 2c](image)

2c
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 2d (400 MHz, CDCl₃)

2d

00'6
$^{13}$C NMR of 2d (100 MHz, CDCl$_3$)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 2g (400 MHz, CDCl₃)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 2g (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 2h (400 MHz, CDCl$_3$)

2h

Me$_2$N

O

O

$^1$H NMR of 2h (400 MHz, CDCl$_3$)
**Supplementary Information** (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 2h (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{1}H$ NMR of 2l (400 MHz, CDCl₃)
$^{13}$C NMR of 2l (100 MHz, CDCl$_3$)

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

![Chemical Structure](image)
$^1$H NMR of 2n (400 MHz, CDCl$_3$)
$^{13}$C NMR of 2n (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 2o (400 MHz, CDCl$_3$)

![NMR spectrum of 2o](image)
$^{13}$C NMR of 2o (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

^1H NMR of 2p (400 MHz, CDCl₃)
$^{13}$C NMR of 2p (100 MHz, CDCl$_3$)
$^1$H NMR of 2q (400 MHz, CDCl₃)

![NMR spectrum of 2q](image)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 2q (100 MHz, CDCl₃)
$^{1}$H NMR of 2r (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 2r (100 MHz, CDCl$_3$)

2r (E/Z = 5/3)
$^1$H NMR of 4t (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C-H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C-H Activation

$^{13}$C NMR of 4t (100 MHz, CDCl$_3$)
$^1$H NMR of L1 (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{31}$P NMR of L1 (160 MHz, CDCl₃)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

\[ \text{H NMR of } L_2 (400 MHz, CDCl}_3 \]
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

$^{31}$P NMR of L2 (160 MHz, CDCl₃)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Aa (400 MHz, CDCl$_3$)

3Aa
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

{\textsuperscript{13}C} NMR of 3Aa (100 MHz, CDCl\textsubscript{3})
$^1$H NMR of 3Ba (400 MHz, CDCl$_3$)

3Ba
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ba (100 MHz, CDCl$_3$)

![Chemical Structure of 3Ba](image)
$^1$H NMR of 3Ca (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ca (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Da (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Da (100 MHz, CDCl$_3$)
$^1$H NMR of 3Ea (400 MHz, CDCl$_3$)

Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C−H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C−H Activation

3Ea
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ea (100 MHz, CDCl$_3$)
$^{1}H$ NMR of 3Fa (400 MHz, CDCl$_3$)

3Fa
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Fa (100 MHz, CDCl$_3$)
$^1$H NMR of 3Ga (400 MHz, CDCl$_3$)

3Ga
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ga (100 MHz, CDCl$_3$)

3Ga
$^{1}H$ NMR of $3Ha$ (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ha (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ib (400 MHz, CDCl$_3$)

3Ib
$^{13}$C NMR of 3Ib (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ja (400 MHz, CDCl$_3$)

3Ja
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ja (100 MHz CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^3$H NMR of 3Ka (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3La (400 MHz, CDCl$_3$)

3La
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^13$C NMR of 3La (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ma (400 MHz, CDCl$_3$)

3Ma
$^{13}$C NMR of 3Ma (100 MHz, CDCl$_3$)

3Ma
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Nb (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Nb (100 MHz, CDCl$_3$)
$^1$H NMR of 3Ob (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ob (100 MHz, CDCl$_3$)

3Ob
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Pb (400 MHz, CDCl₃)

![NMR谱图](image)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Pb (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Pb' (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of $3Pb'$ (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ac (400 MHz, CDCl$_3$)

3Ac
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ac (100 MHz, CDCl$_3$)

3Ac
$^1$H NMR of 3Ad (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ad (100 MHz, CDCl$_3$)

3Ad
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ae (400 MHz, CDCl$_3$)
$^{13}$C NMR of 3Ae (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{1}H$ NMR of 3Af (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Af (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ag (400 MHz, CDCl$_3$)

$^1$H NMR of 3Ag (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ag (100 MHz, CDCl$_3$)

![NMR spectrum of 3Ag](image)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$\text{H NMR of 3Ah (400 MHz CDCl$_3$)}$

3Ah
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

\[ ^{13}C\text{ NMR of 3Ah (100 MHz, CDCl}_3\text{)} \]
$^1$H NMR of 3Ai (400 MHz, CDCl$_3$)
$^{13}$C NMR of 3Ai (100 MHz, CDCl$_3$)

![Chemical Structure](image)
$^1$H NMR of 3Ab (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ab (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

\[ \text{\(^1H\) NMR of 3Aj (400 MHz, CDCl\textsubscript{3})} \]

\[ \text{3Aj} \]
$^{13}$C NMR of 3Aj (100 MHz, CDCl$_3$)
$^1$H NMR of 3Qb (400 MHz, CDCl$_3$)

pilocarpine derivative 3Qb
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of $3Qb$ (100 MHz, CDCl$_3$)

pilocarpine derivative $3Qb$
1H NMR of 3As (400 MHz, CDCl₃)

3As
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3As (100 MHz, CDCl$_3$)

3As
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3At (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3At (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ak (400 MHz, CDCl$_3$)

3Ak

X: parts per million: 1H

Y: intensity

Abundance
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ak (100 MHz, CDCl$_3$)

3Ak
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

\(^{1}H\) NMR of 3A1 (400 MHz, CDCl\(_3\))
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3AI (100 MHz, CDCl$_3$)

3AI
$^1$H NMR of 3Am (400 MHz, CDCl$_3$)
$^{13}$C NMR of 3Am (100 MHz, CDCl$_3$)

3Am
$^1$H NMR of 3An (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3An (100 MHz, CDCl$_3$)
3H NMR of 3Ao (400 MHz, CDCl₃)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Ao (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ap (400 MHz, CDCl$_3$)

![NMR spectrum of 3Ap](image_url)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^\text{13}$C NMR of 3Ap (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

\[^{1}H\text{NMR of }3\text{Bk (400 MHz, CDCl}_3\text{)}\]
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Bk (100 MHz, CDCl$_3$)

3Bk
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Dk (400 MHz, CDCl$_3$)
\textsuperscript{13}C NMR of \textit{3Dk} (100 MHz, CDCl\textsubscript{3})
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

\[
\text{C NMR of 3Rk (100 MHz, CDCl)}_3
\]
$^1$H NMR of 3Aq (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 3Aq (100 MHz, CDCl$_3$)

3Aq
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^1$H NMR of 3Ar (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)

C-H Arylation and Alkenylation of Imidazoles by Nickel Catalysis: Solvent-accelerated Imidazole C-H Activation

$^{13}$C NMR of 3Ar (100 MHz, CDCl$_3$)

X: parts per Million: TSP
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 6Ab (100 MHz, CDCl$_3$)

![NMR Spectrogram of 6Ab](image)
$^1$H NMR of 6Aa (400 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 6Aa (100 MHz, CDCl$_3$)

![NMR Spectrum of 6Aa](image)
$^1$H NMR of 6Ba (400 MHz, CDCl₃)
$^{13}$C NMR of 6Ba (100 MHz, CDCl$_3$)
$^1$H NMR of 6Ak (400 MHz, CDCl₃)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 6Ak (100 MHz, CDCl$_3$)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{1}$H NMR of 6Ca (400 MHz CDCl$_3$)

6Ca
$^{13}$C NMR of 6Ca (100 MHz, CDCl$_3$)
$^1$H NMR of 6Ci (400 MHz, CDCl₃)
Supplementary Information (Muto, Hatakeyama, Yamaguchi, Itami)
C–H Arylation and Alkenylation of Imidazoles by Nickel Catalysis:
Solvent-accelerated Imidazole C–H Activation

$^{13}$C NMR of 6Da (100 MHz, CDCl$_3$)