Supporting Information for:

Synthesis of Tetrasubstituted Allenes via a 1,4-Palladium Migration/Carbene Insertion/β-H Elimination Sequence

Ge Zhan,†a,b Xiao-Jiao Feng,†a Meng-Yao Li,a,c Xiao-Ming Ji,a Guo-Qiang Lin,†a,b and Chen-Guo Feng,⁎a,b

† These authors contributed equally.

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1. **General Information**

Commercially available reagents were used without further purification unless specified. Tetrahydrofuran was distilled from sodium/benzophenone before use. Unless otherwise stated, reactions were performed with freshly dried solvents utilizing standard Schlenk techniques under pre-dried argon. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and were dipped into a solution of KMnO_{4}. Flash chromatography was performed on silica gel 60 (40-63 µm) under a positive pressure of air. NMR-spectra were recorded on a Bruker Avance II 400 spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for {^1}H NMR and {^{13}}C NMR spectra (CDCl_{3}: δ H = 7.26 ppm, δ C = 77.16 ppm;). {^{19}}F NMR spectra are not calibrated by an internal reference. The multiplicity of all signals was described with standard abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quintet = quint, heptet = hept, m = multiplet, br = broad resonance. Coupling constants (J) are quoted in Hz.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 µm). High-resolution mass spectrometry was measured using an Agilent 6210 TOF LC/MS spectrometer or a Waters Quattro micro GC/MS/MS spectrometer. The synthesis method and data of aryl bromides (1) and diazo compounds (2) were reported following the related references.\textsuperscript{1-4}
2. General Procedure for Synthesis of Allenes

To a 25 mL Schlenk tube charged with a stir bar, aryl bromides (1) (0.2 mmol), diazoesters (2) (0.3 mmol), Pd(OAc)$_2$ (4.48 mg, 0.02 mmol), DPEPhos (16.2 mg, 0.03 mmol) and CsOAc (58 mg, 0.3 mmol) were added. After filled with argon, anhydrous THF (2 mL) were added via a syringe. The mixture was stirred at 80 °C in an oil bath for 2 h. Upon completion, the reaction mixture was washed with brine (15 mL) and extracted with EtOAc (3× 10 mL). The combined organic phase was dried over anhydrous Na$_2$SO$_4$. After that the organic phase was filtered, and concentrated under reduced pressure. The crude products were purified by silica gel chromatography (PE/EA = 20:1 ~ 5:1) to afford pure products (3).

Methyl 2,4,4-triphenylbuta-2,3-dienoate (3a)

White solid, 73-75 °C m.p.; 54.1 mg, 83% yield; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.64-7.58 (m, 2H), 7.47-7.26 (m, 13H), 3.86 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.62, 166.39, 134.75, 132.44, 128.83, 128.78, 128.58, 128.39, 128.33, 128.05, 114.82, 105.30, 52.64; EI-MS (m/z, %): 326 (M$^+$, 5.63), 91 (100), 167 (37.23), 150 (36.03); HRMS (EI): m/z calcd for C$_{23}$H$_{18}$O$_2$ [M$^+$]: 326.1307; found: 326.1315.

Methyl 2,4-diphenyl-4-[(p-tolyl)buta-2,3-dienoate (3b and 3i)

White solid, 73-76 °C m.p.; 49.6 mg, 73% yield for 3b and 44.2 mg, 65% yield for 3i; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.62 (d, $J = 7.1$ Hz, 2H), 7.39-7.23 (m, 10H), 7.20-7.15 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.64, 166.48, 138.36, 134.90, 132.58, 131.71, 129.56, 128.79, 128.67, 128.55, 128.34, 127.97, 114.70, 105.15, 52.61, 21.37; EI-MS (m/z, %): 340 (M$^+$, 80.37), 281 (100), 325 (70.52), 265 (59.67); HRMS (EI): m/z calcd for C$_{24}$H$_{20}$O$_2$ [M$^+$]: 340.1463; found: 340.1457.

Methyl 4-[(4-methoxyphenyl)-2,4-diphenylbuta-2,3-dienoate (3c and 3j)

White solid, 77-80 °C m.p.; 47.7 mg, 67% yield for 3c and 55.5 mg, 78% yield for 3j; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.61 (d, $J = 7.3$ Hz, 2H), 7.46-7.23 (m, 10H), 6.91 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.60, 166.53, 159.84, 135.05, 132.68, 130.01, 128.81, 128.80, 128.57, 128.36, 128.33, 127.96, 126.78, 114.31, 105.08, 55.49, 52.64; EI-MS (m/z, %): 356
(M⁺, 60.00), 297 (100), 252 (57.94), 105 (57.59); HRMS (EI): m/z calcd for C₂₄H₂₀O₃ [M⁺]: 356.1412; found: 356.1408.

Methyl 4-[(1,1'-biphenyl)-4-yl]-2,4-diphenylbuta-2,3-dienoate (3d)

White solid, 93-97 °C m.p.; 60.3 mg, 75% yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.69-7.55 (m, 6H), 7.53-7.24 (m, 13H), 3.85 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 214.84, 166.43, 141.30, 140.64, 134.72, 133.65, 132.42, 129.17, 128.99, 128.90, 128.63, 128.49, 128.38, 128.11, 127.67, 127.58, 127.19, 114.60, 105.41, 52.75; EI-MS (m/z, %): 402 (M⁺, 1.17), 84 (100), 86 (66.50), 47 (19.14); HRMS (EI): m/z calcd for C₂₉H₂₂O₂: 402.1625; found: 402.1620.

Methyl 4-(4-chlorophenyl)-2,4-diphenylbuta-2,3-dienoate (3e)

White solid, 81-87 °C m.p.; 55.4 mg, 77% yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.61-7.57 (m, 2H), 7.44-7.23 (m, 12H), 3.86 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 214.44, 166.22, 134.38, 134.34, 133.33, 132.18, 130.05, 129.08, 128.97, 128.72, 128.66, 128.62, 128.34, 128.23, 114.02, 105.63, 52.76; EI-MS (m/z, %): 360 (M⁺, 58.27), 301 (100), 265 (92.01), 345 (56.13); HRMS (EI): m/z calcd for C₂₃H₁₇O₂Cl [M⁺]: 360.0917; found: 360.0912.

Methyl 4-(4-fluorophenyl)-2,4-diphenylbuta-2,3-dienoate (3f and 3k)

White solid, 78-81 °C m.p.; 57.1 mg, 83% yield for 3f and 51.6 mg, 75% yield for 3k; ¹H NMR (CDCl₃, 400 MHz) δ 7.62-7.56 (m, 2H), 7.38 (m, 10H), 7.04 (t, J = 8.7 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 6214.38, 166.32, 162.85 (d, J = 247.6 Hz), 134.65, 132.32, 130.51 (d, J = 9.1 Hz), 128.93, 128.66 (d, J = 6 Hz), 128.56, 128.33, 128.16, 115.87 (d, J = 21.1 Hz), 114.02, 105.44, 52.71; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.94; EI-MS (m/z, %): 344 (M⁺, 65.95), 285 (100), 105 (96.07), 283 (63.95); HRMS (EI): m/z calcd for C₂₃H₁₇F₂O₂: 344.1213; found: 344.1208.
Methyl 2,4-diphenyl-4-(4-(trifluoromethyl)phenyl)buta-2,3-dienoate (3g and 3l)

White solid, 87-88 °C m.p.; 63.0 mg, 80% yield for 3g and 57.5 mg, 73% yield for 3l; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.67-7.60 (m, 4H), 7.55-7.52 (m, 2H), 7.45-7.22 (m, 8H), 3.87 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.69, 166.08, 138.77, 134.08, 131.91, 130.40 (q, \(J = 33\) Hz), 129.06, 128.77, 128.72, 128.36, 125.87, 125.84, 125.80, 125.77 (q, \(J = 3.3\) Hz), 124.17 (q, \(J = 271\) Hz), 114.03, 105.96, 52.82. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.63; EI-MS (m/z, %): 394 (M\(^+\), 67.16), 335 (100), 105 (66.43), 173 (52.34); HRMS (EI): m/z calcd for C\(_{24}\)H\(_{17}\)O\(_2\)F\(_3\)[M\(^+\)]: 394.1181; found: 394.1175.

Methyl 2,4-diphenyl-4-(m-tolyl)buta-2,3-dienoate (3m)

White solid, 73-75 °C m.p.; 53.0 mg, 78% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.67-7.57 (m, 2H), 7.50-7.19 (m, 11H), 7.15 (d, \(J = 7.2\) Hz, 1H), 3.85 (s, 3H), 2.34 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.63, 166.49, 138.53, 134.89, 134.62, 132.52, 129.32, 129.22, 128.81, 128.73, 128.70, 128.35, 128.01, 125.95, 114.86, 105.17, 52.65, 21.61; EI-MS (m/z, %): 340 (M\(^+\),55.26), 281 (100), 105 (69.33), 165 (41.22); HRMS (EI): m/z calcd for C\(_{24}\)H\(_{20}\)O\(_2\) [M\(^+\)]: 340.1463; found: 340.1467.

Methyl 2,4-diphenyl-4-(o-tolyl)buta-2,3-dienoate (3n)

White solid, 77-79 °C m.p.; 44.2 mg, 65% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.58 (d, \(J = 7.3\) Hz, 2H), 7.39-7.22 (m, 12H), 3.84 (s, 3H), 2.21 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 213.19, 166.44, 137.36, 134.44, 133.96, 132.56, 130.69, 130.38, 128.95, 128.56, 128.52, 128.11, 128.01, 127.18, 126.29, 112.89, 104.88, 52.51, 20.16; EI-MS (m/z, %): 340 (M\(^+\), 6.62), 84 (100), 86 (64.45), 47 (16.97); HRMS (EI): m/z calcd for C\(_{24}\)H\(_{20}\)O\(_2\) [M\(^+\)]: 340.1463; found: 340.1470.

Methyl 4-(naphthalen-2-yl)-2,4-diphenylbuta-2,3-dienoate (3o)

White solid, 102-104 °C m.p.; 53.4 mg, 71% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.85 (d, \(J = 10.2\) Hz, 3H), 7.81-7.76 (m, 1H), 7.64 (d, \(J = 7.3\) Hz, 2H), 7.56 (dd, \(J = 8.5, 1.6\) Hz, 1H), 7.50-7.47 (m, 3H), 7.39 (dd, \(J = 13.6, 7.3\) Hz, 4H), 7.31 (d, \(J = 5.7\) Hz, 1H), 3.88 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 215.04, 166.44, 134.82, 133.54, 133.25, 132.43, 132.12, 128.98, 128.93, 128.74, 128.63, 128.57, 128.51, 128.40, 128.30, 128.11, 127.81, 126.57, 126.54, 126.50, 115.00, 105.46, 52.73; EI-MS (m/z, %): 376
Methyl 4,4-bis(4-fluorophenyl)-2-phenylbuta-2,3-dienoate (3p)

White solid, 83-85 °C m.p.; 54.3 mg, 75% yield; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.61-7.55 (m, 2H), 7.35 (m, 7H), 7.07 (t, $J = 8.7$ Hz, 4H), 3.86 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.11, 166.21, 162.91 ($J = 247.1$ Hz), 132.18, 130.64, 130.61, 130.41 (d, $J = 37.6$ Hz), 128.26, 116.09, 115.87, 113.21, 105.57, 77.48, 77.16, 76.84, 52.79; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -11.30. HRMS (EI): m/z calcd for C$_{27}$H$_{20}$O$_2$: 376.1463; found: 376.1463.

Methyl 2-phenyl-4,4-di-p-tolylbuta-2,3-dienoate (3q)

White solid, 87-89 °C m.p.; 46.0 mg, 65% yield; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.64-7.57 (m, 2H), 7.34-7.26 (m, 7H), 7.18 (d, $J = 8.0$ Hz, 4H), 3.83 (s, 3H), 2.36 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.65, 166.55, 138.29, 132.71, 131.85, 129.52, 128.67, 128.53, 128.33, 127.90, 114.57, 104.98, 52.59, 21.38; EI-MS (m/z, %): 354 (M$,^+$, 0.71), 84 (100), 167 (63.96), 86 (63.93); HRMS (EI): m/z calcd for C$_{25}$H$_{22}$O$_2$: [M]$^+$: 354.1620; found: 354.1619.

Methyl 4,4-bis(4-chlorophenyl)-2-phenylbuta-2,3-dienoate (3r)

White solid, 92-95 °C m.p.; 61.4 mg, 78% yield; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.56 (d, $J = 7.1$ Hz, 2H), 7.41-7.27 (m, 11H), 3.86 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 214.27, 166.01, 134.58, 132.91, 131.88, 129.96, 129.21, 128.73, 128.39, 128.33, 113.20, 105.94, 52.86; EI-MS (m/z, %): 394 (M$,^+$, 60.64), 335 (100), 139 (71.71), 265 (68.23); HRMS (EI): m/z calcd for C$_{23}$H$_{16}$O$_2$Cl$_2$: [M]$^+$: 394.0527; found: 394.0522.
Methyl 2-(4-chlorophenyl)-4,4-diphenylbuta-2,3-dienoate (3s)

![Chemical Structure](image)

White solid, 87-89 °C m.p.; 57.6 mg, 80% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.57 (d, \(J = 8.5\) Hz, 2H), 7.46-7.27 (m, 12H), 3.85 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.77, 166.16, 134.49, 133.96, 130.94, 129.65, 128.92, 128.80, 128.78, 128.58, 115.24, 104.36, 52.76; EI-MS (m/z, %): 360 (M\(^+\), 52.19), 105 (100), 301 (71.32), 265 (68.21); HRMS (EI): m/z calcd for C\(_{23}\)H\(_{17}\)ClO\(_2\)[M]\(^+\): 360.0917; found: 360.0910.

Methyl 4,4-diphenyl-2-(p-tolyl)buta-2,3-dienoate (3t)

![Chemical Structure](image)

White solid, 84-90 °C m.p.; 53.7 mg, 79% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.50 (d, \(J = 8.1\) Hz, 2H), 7.46-7.30 (m, 10H), 7.16 (d, \(J = 8.1\) Hz, 2H), 3.84 (s, 3H), 2.34 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.47, 166.58, 137.96, 134.88, 129.40, 129.32, 128.82, 128.81, 128.34, 128.22, 114.68, 105.21, 52.67, 21.36; EI-MS (m/z, %): 340 (M\(^+\), 2.83), 84 (100), 86 (65.17), 47 (18.68); HRMS (EI): m/z calcd for C\(_{24}\)H\(_{20}\)O\(_2\)[M]\(^+\): 340.1463; found: 340.1467.

Methyl 2-(4-fluorophenyl)-4,4-diphenylbuta-2,3-dienoate (3u)

![Chemical Structure](image)

White solid, 79-81 °C m.p.; 44.7 mg, 65% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.62-7.56 (m, 2H), 7.44-7.32 (m, 10H), 7.04 (t, \(J = 8.7\) Hz, 2H), 3.85 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.58, 166.36, 162.60 (d, \(J = 246.4\) Hz), 134.63, 130.12 (d, \(J = 8.0\) Hz), 128.90, 128.78, 128.51, 115.65 (d, \(J = 21.5\) Hz), 114.99, 104.36, 52.73; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -113.94; EI-MS (m/z, %): 344 (M\(^+\), 65.95), 285 (100), 105 (96.07), 283 (63.95); HRMS (EI): m/z calcd for C\(_{23}\)H\(_{17}\)FO\(_2\)[M]\(^+\): 344.1213; found: 344.1208.

Methyl 4,4-diphenyl-2-(m-tolyl)buta-2,3-dienoate (3v)

![Chemical Structure](image)

White solid, 79-81 °C m.p.; 55.0 mg, 81% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.30-7.45 (m, 2H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.09 (d, \(J = 7.6\) Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 214.49, 166.51, 138.18, 134.85, 132.33, 128.94, 128.88, 128.82, 128.81, 128.48, 128.35, 125.47, 114.67, 105.38, 52.63, 21.67; EI-MS (m/z, %): 340 (M\(^+\), 2.83), 84 (100), 86 (65.17), 47 (18.68); HRMS (EI): m/z calcd for C\(_{24}\)H\(_{20}\)O\(_2\)[M]\(^+\): 340.1463; found: 340.1459.

Methyl 2-(3-fluorophenyl)-4,4-diphenylbuta-2,3-dienoate (3w)
White solid, 69-74 °C m.p.; 48.1 mg, 71% yield; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.68-7.21 (m, 13H), 6.98 (s, 1H), 3.85 (d, $J = 3.1$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 214.86, 166.03, 163.0 (d, $J = 236$ Hz), 134.58, 134.42, 129.99, 128.87 (d, $J = 8$ Hz), 128.61, 123.97, 115.37, 114.93 (d, $J = 21.1$ Hz), 104.41, 52.82; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.85; EI-MS (m/z, %): 344 (M$^+$, 65.95), 285 (100), 105 (96.07), 283 (63.95); HRMS (EI): m/z calcd for C$_{23}$H$_{17}$FO$_2$: 344.1213; found: 344.1208.

**Methyl 2-(naphthalen-2-yl)-4,4-diphenylbuta-2,3-dienoate (3y)**

White solid, 101-105 °C m.p.; 54.1 mg, 72% yield; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.23 (s, 1H), 7.86-7.77 (m, 3H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.48-7.44 (m, 6H), 7.42-7.34 (m, 6H), 3.90 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 215.18, 166.52, 134.75, 133.54, 132.98, 129.57, 128.89, 128.86, 128.57, 128.48, 128.17, 127.67, 127.46, 126.40, 126.33, 126.05, 115.15, 105.39, 52.76; EI-MS (m/z, %): 376 (M$^+$, 10.01), 84 (100), 86 (63.29), 57 (49.28); HRMS (EI): m/z calcd for C$_{27}$H$_{20}$O$_2$: 376.1463; found: 376.1466.

**Methyl 4,4-diphenyl-2-(thiophen-3-yl)buta-2,3-dienoate (3z)**

White solid, 71-75 °C m.p.; 55.1 mg, 83% yield; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.89 (dd, $J = 2.7$, 1.3 Hz, 1H), 7.44-7.32 (m, 9H), 7.28-7.22 (m, 3H), 3.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 215.05, 166.28, 134.76, 131.77, 128.87, 128.46, 127.36, 125.32, 123.81, 115.08, 101.11, 52.66; EI-MS (m/z, %): 332 (M$^+$, 9.88), 84 (100), 86 (62.13), 47 (32.21); HRMS (EI): m/z calcd for C$_{21}$H$_{26}$SO$_2$: 332.0871; found: 332.0876.

### 2. Gram-Scale Synthesis

To a 250 mL Schlenk tube charged with a stir bar, aryl bromides (1a) (4.5 mmol), diazoesters (2a) (6.75 mmol), Pd(OAc)$_2$ (101.1 mg, 0.45 mmol), DPEPhos (363.5 mg, 0.675 mmol) and CsOAc (1.3 g, 6.75 mmol) were added. After filled with argon, anhydrous THF (45 mL) were added via a syringe. The mixture was stirred at 80 °C in an oil bath for 2 h. Upon completion, the reaction mixture was washed with brine (30 mL) and extracted with EA (3×25 mL). The combined organic phase was dried over anhydrous Na$_2$SO$_4$. After that the organic phase was filtered, and concentrated under reduced pressure. The crude products were purified by silica gel chromatography (PE/EA = 20:1) to afford pure products (3a), as a white solid (79%,1.16 g).
3. Parallel Experiments and KIE Studies

(1) Synthesis of \( d_2-1a \):

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{CD}_3\text{I} \quad \text{THF} \quad \text{reflux, 2h} \\
\Rightarrow & \quad [\text{Ph}_3\text{P(}\text{CD}_3\text{)}] \quad \text{1} \text{n-BuLi, THF, 0°C} \\
\Rightarrow & \quad 2)\text{2-Bromobenzophenone, 0°C-rt} \\
\rightarrow & \quad \text{1a-D}_2
\end{align*}
\]

In a J-Young Schlenk tube, PPh\(_3\) (2.5 mmol, 656 mg, 1.0 equiv) in 3.5 mL THF was added, and CD\(_3\)I (2.5 mmol, 0.16 ml, 1.0 equiv) was then added dropwise into the solution, which resulted in the immediate appearance of a white suspension. After the addition was complete, the reaction mixture was refluxed for 2 h. During the cooling of the reaction mixture to room temperature, a large amount of a white precipitate was formed, and the resulting white solid was isolated on a filter, washed with EA (3 x 10 ml) and dried under vacuum to give 998 mg of \([\text{Ph}_3\text{P(}\text{CD}_3\text{)}]I\) (98% yield). 96% D atom incorporation (\(^1\)H NMR analysis).

An oven dried flask charged with \([\text{Ph}_3\text{P(}\text{CD}_3\text{)}]I\) (2.4 mmol, 998 mg, 1.1 equiv.) and THF (7.0 mL) was cooled to 0 °C. Then 2.5 M n-BuLi (2.43 mmol, 0.97 mL, 1.2 equiv) was added dropwise and the resulting yellow suspension was stirred for 30 minutes. To this suspension, a solution of aryl bromides (1a) (2.25 mmol, 587.5 mg, 1.0 equiv) was added in one portion and the resulting mixture was warmed to room temperature and further stirred at room temperature for 5 h. Water and EA were added to the reaction mixture, separated and the aqueous phase was extracted with EA (3 x 10 mL). The combined organic phases were washed with brine, dried over Na\(_2\)SO\(_4\) and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography using hexanes as eluent to obtain the product \(1a-\text{D}_2\) as a colorless oil, 431 mg, 74% (two steps), 94% D atom incorporation (\(^1\)H NMR analysis).

(2) Parallel Experiments:

The parallel reactions of aryl bromides (1a) were carried out under the reaction conditions which were described in Figures S1 and S2, stopped at arbitrary reaction times, and analyzed by \(^1\)H NMR spectroscopy (Figures S1 and S2). As a result, the slope values of two graphs were 0.0094 mM/min and 0.002 mM/min, respectively, and thus the KIE value was 4.7.
Figure S1. Determination of a reaction rate when 1a was used as a substrate.

Figure S2. Determination of a reaction rate when 1a-D₂ was used as a substrate.
5. References


$^{1}H$ NMR, $^{13}C$ NMR and $^{19}F$ NMR Spectras of Products