Supporting Information

for

Iron-catalyzed decarboxylative alkenylation of cycloalkanes with arylvinylcarboxylic acids via a radical process

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1. Experimental Section

**General Information:** All reactions were carried out under a nitrogen atmosphere. Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography (TLC) was performed on glass plates of Silica Gel GF-254 with detection by UV light. Standard techniques for synthesis under inert gas atmosphere by using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stop-cock (Synthware) were employed. All starting materials and reagents were commercially available. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE400M spectrometer. The chemical shift references were as follows: (¹H) CDCl₃, 7.26 ppm (CHCl₃); (¹³C) CDCl₃, 77.00 ppm (CDCl₃). HRMS spectra were carried out at Micromass GCT (TOF MS El⁺). Melting points were determined on a Melt-Temp apparatus (X-4) from Beijing Fukai Electro-optic Instrument Plant and are uncorrected.

**General Procedure:** To a Schlenk tube equipped with a magnetic stir bar were added Fe(acac)₃ (21.2 mg, 0.06 mmol) and cinnamic acid (0.3 mmol) under a nitrogen atmosphere. Cycloalkane (2.0 mL, 15–25 mmol) and DTBP (di-tert-butyl peroxide, 0.6 mmol, 113 μL) were added under nitrogen and the resulting reaction mixture was kept stirring at 120 °C for 24 h. After cooling to room temperature and removal of volatiles the products were isolated by flash column chromatography (PE).

Products 3a, 3e, 3j, 3k, 3p, 4a, 4c, 4e, 4f, 3b, 3l, 3d, 3n and 4b, are known compounds. ¹H and ¹³C NMR spectra of these compounds have been confirmed to be identical to those of known samples (3a, 3e, 3h, 3j, 3k, 3p, 4a, 4c, 4e and 4f) [1], (3b and 3l) [2], 3d [3], 3n [4], 4b [5]).
2. Characterization data for 3a–p and 4a–f.

\[(E)-(2\text{-Cyclohexylvinyl})\text{benzene (3a, known compound)}\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33–7.22 (m, 4H), 7.16–7.12 (m, 1H), 6.32 (d, \(J = 16.1\) Hz, 1H), 6.15 (dd, \(J = 16.0, 6.9\) Hz, 1H), 2.18–2.00 (m, 1H), 1.86–1.59 (m, 5H), 1.40–1.07 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.02, 136.70, 128.38, 127.26, 126.66, 125.91, 41.12, 32.93, 26.16, 26.03.

\[(E)\text{-}1\text{-}(2\text{-Cyclohexylvinyl})\text{-4-methylbenzene (3b, known compound)}\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.22 (d, \(J = 8.1\) Hz, 2H), 7.06 (d, \(J = 8.0\) Hz, 2H), 6.29 (d, \(J = 16.0\) Hz, 1H), 6.10 (dd, \(J = 16.0, 6.9\) Hz, 1H), 2.29 (s, 3H), 2.13–2.05 (m, 1H), 1.84–1.63 (m, 5H), 1.35–1.12 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 136.29, 135.73, 135.26, 129.09, 127.06, 125.81, 41.11, 33.01, 26.19, 26.06, 21.06.

\[(E)\text{-}1\text{-}(2\text{-Cyclohexylvinyl})\text{-3-methylbenzene (3c)}\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20–7.06 (m, 3H), 6.97–6.95 (m, 1H), 6.29 (d, \(J = 16.0\) Hz, 1H), 6.13 (dd, \(J = 16.0, 6.9\) Hz, 1H), 2.29 (s, 3H), 2.18–2.03 (m, 1H), 1.86–1.60 (m, 5H), 1.40–1.08 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.96, 137.79, 136.47, 128.29, 127.46, 127.33, 126.61, 123.11, 41.14, 32.97, 26.17, 26.04, 21.33. HRMS (TOF MS El\(^+\)) \(m/z\) calcld for [C\(_{15}\)H\(_{20}\)] 200.1565, found 200.1553.

\[(E)\text{-}1\text{-}(2\text{-Cyclohexylvinyl})\text{-2-methylbenzene (3d, known compound)}\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 7.0\) Hz, 1H), 7.39–7.29 (m, 3H), 6.77 (d, \(J = 15.8\) Hz, 1H), 6.26 (dd, \(J = 15.8, 7.0\) Hz, 1H), 2.54 (s, 3H), 2.44–2.30 (m, 1H), 2.11–1.85 (m, 5H), 1.65–1.34 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.10, 137.10, 134.81, 130.05, 126.63, 125.92, 125.34, 125.09,
(E)-1-(2-Cyclohexylvinyl)-4-methoxybenzene(3e, known compound): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (d, $J = 8.7$ Hz, 1H), 6.72 (d, $J = 8.7$ Hz, 1H), 6.19 (d, $J = 16.0$ Hz, 1H), 5.94 (dd, $J = 16.0$, 6.9 Hz, 1H), 3.67 (s, 3H), 2.04-1.96 (m, 1H), 1.76–1.53 (m, 5H), 1.25–1.04 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.57, 134.65, 130.84, 126.94, 126.55, 113.83, 55.15, 41.07, 33.06, 26.17, 26.06.

(2C)-1-(2-Cyclohexylvinyl)-3-methoxybenzene(3f): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 (t, $J = 7.9$ Hz, 1H), 6.96–6.86 (m, 2H), 6.72 (dd, $J = 8.1$, 2.1 Hz, 1H), 6.30 (d, $J = 16.0$ Hz, 1H), 6.16 (dd, $J = 16.0$, 6.8 Hz, 1H), 3.78 (s, 3H), 2.12–2.06 (m, 1H), 1.85–1.63 (m, 5H), 1.34–1.14 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.76, 139.51, 137.07, 129.33, 127.13, 118.60, 112.35, 111.22, 55.07, 41.08, 32.89, 26.14, 26.00. HRMS (TOF MS EI$^+$) m/z calcd for [C$_{15}$H$_{20}$O] 216.1514, found 216.1510.

(2C)-1-(2-Cyclohexylvinyl)-2-methoxybenzene(3g): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (dd, $J = 7.6$, 1.1 Hz, 1H), 7.14 (ddd, $J = 8.8$, 7.7, 1.1 Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 1H), 6.69 (d, $J = 16.1$ Hz, 1H), 6.14 (dd, $J = 16.1$, 7.0 Hz, 1H), 3.78 (s, 3H), 2.23–2.05 (m, 1H), 1.88–1.61 (m, 5H), 1.38–1.11 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.27, 137.27, 127.66, 127.04, 126.12, 121.72, 120.54, 110.70, 55.31, 41.53, 33.04, 26.17, 26.05. HRMS (TOF MS EI$^+$) m/z calcd for [C$_{15}$H$_{20}$O] 216.1514, found 216.1505.

(2C)-1-(2-Cyclohexylvinyl)-4-fluorobenzene(3h, known compound): White solid, mp 34–35 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 6.34 (d, $J = 16.1$ Hz, 1H), 6.25 (dd, $J = 16.0$, 6.6 Hz, 1H), 2.17-2.09 (m, 1H), 1.87–1.64 (m, 5H), 1.33-1.16 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.27, 137.27, 127.66, 127.04, 126.12, 121.72, 120.54, 110.70, 55.31, 41.53, 33.04, 26.17, 26.05. HRMS (TOF MS EI$^+$) m/z calcd for [C$_{15}$H$_{20}$O] 216.1514, found 216.1505.
(E)-1-(2-Cyclohexylvinyl)-3-fluorobenzene(3i): Colorless oil, \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (td, \(J = 7.9, 6.1\) Hz, 1H), 7.04 (dd, \(J = 10.4, 8.1, 4.8\) Hz, 2H), 6.88–6.82 (m, 1H), 6.29 (d, \(J = 16.0\) Hz, 1H), 6.16 (dd, \(J = 15.9, 6.8\) Hz, 1H), 2.14–2.06 (m, 1H), 1.87–1.62 (m, 5H), 1.35–1.11 (m, 5H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.15 (d, \(J = 244.7\) Hz), 140.50 (d, \(J = 7.7\) Hz), 138.17, 129.77 (d, \(J = 8.5\) Hz), 126.31 (d, \(J = 2.5\) Hz), 121.82 (d, \(J = 2.6\) Hz), 113.42 (d, \(J = 21.4\) Hz), 112.31 (d, \(J = 21.7\) Hz), 41.08, 32.81, 26.12, 25.99. HRMS (TOF MS Ei) \(m/z\) calcd for [C\(_{14}\)H\(_{17}\)F] 204.1314, found 204.1320.

(E)-1-(2-Cyclohexylvinyl)-2-fluorobenzene(3j, known compound): Colorless oil, \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42–7.38 (m, 1H), 7.16–6.93 (m, 3H), 6.50 (d, \(J = 16.2\) Hz, 1H), 6.22 (dd, \(J = 16.1, 7.0\) Hz, 1H), 2.16–2.09 (m, 1H), 1.87–1.61 (m, 5H), 1.39–1.10 (m, 5H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.00 (d, \(J = 248.0\) Hz), 139.26 (d, \(J = 4.1\) Hz), 127.83 (d, \(J = 8.3\) Hz), 126.85 (d, \(J = 4.0\) Hz), 125.76 (d, \(J = 12.3\) Hz), 123.88 (d, \(J = 3.5\) Hz), 119.61 (d, \(J = 3.9\) Hz), 115.50 (d, \(J = 22.3\) Hz), 41.52, 32.84, 26.14, 26.00.

(E)-1-Chloro-4-(2-cyclohexylvinyl)benzene(3k, known compound): Colorless oil, \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25–7.17 (m, 4H), 6.27 (d, \(J = 16.0, 1\) Hz), 6.13 (dd, \(J = 16.0, 6.8\) Hz, 1H), 2.14–2.06 (m, 1H), 1.80–1.65 (m, 5H), 1.32–1.14 (m, 5H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.46, 136.54, 132.20, 128.50, 127.11, 126.09, 41.10, 32.84, 26.12, 25.99.

(E)-1-Chloro-2-(2-cyclohexylvinyl)benzene(3l, known compound): Colorless oil, \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (dd, \(J = 7.7, 1.4\) Hz, 1H), 7.29 (dd, \(J = 7.9, 1.1\) Hz, 1H), 7.17–7.04 (m, 2H), 6.72 (d, \(J = 15.9\) Hz, 1H), 6.13 (dd, \(J = 15.9, 7.0\) Hz, 1H), 2.18–2.13 (m, 1H), 1.87–1.61 (m, 5H), 1.38–1.10 (m, 5H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.56, 136.05, 132.66, 129.51, 127.68, 126.62, 126.46, 123.62, 41.31, 32.83, 26.13, 25.97.
(E)-1,3-Dichloro-2-(2-cyclohexylvinyl)benzene (3m): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.28 (d, $J = 16.4$ Hz, 1H), 6.14 (dd, $J = 16.3$, 6.7 Hz, 1H), 2.24-2.16 (m, 1H), 1.89–1.64 (m, 5H), 1.40–1.17 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.16, 135.49, 134.34, 128.23, 127.38, 120.98, 41.52, 32.51, 26.17, 25.89. HRMS (TOF MS El$^+$) m/z calcd for [C$_{14}$H$_{16}$Cl$_2$] 254.0629, found 254.0625.

(E)-1-Bromo-4-(2-cyclohexylvinyl)benzene (3n, known compound): White solid, mp 39–40 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.25 (d, $J = 16.1$ Hz, 1H), 6.13 (dd, $J = 16.0$, 6.7 Hz, 1H), 2.13-2.05 (m, 1H), 1.87–1.54 (m, 5H), 1.38–1.04 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.54, 136.95, 131.41, 127.44, 126.14, 120.28, 41.08, 32.79, 26.11, 25.98.

(E)-1-(2-Cyclohexylvinyl)-3-(trifluoromethyl)benzene (3o): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (s, 1H), 7.46–7.30 (m, 3H), 6.34 (d, $J = 16.1$ Hz, 1H), 6.22 (dd, $J = 16.0$, 6.7 Hz, 1H), 2.18–2.06 (m, 1H), 1.83–1.63 (m, 5H), 1.35–1.11 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.85 (d, $J = 13.6$ Hz), 130.90 (q, $J = 32.0$ Hz), 129.13 (d, $J = 1.1$ Hz), 128.81, 126.12, 125.67, 123.22 (q, $J = 3.8$ Hz), 122.96, 122.57 (q, $J = 3.8$ Hz), 41.19, 32.81, 26.13, 26.00. HRMS (TOF MS El$^+$) m/z calcd for [C$_{15}$H$_{17}$F$_3$] 254.1282, found 254.1291.

(E)-2-(2-Cyclohexylvinyl)thiophene (3p, known compound): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.04 (d, $J = 5.1$ Hz, 1H), 6.90 (dd, $J = 5.1$, 3.5 Hz, 1H), 6.84 (d, $J = 3.6$ Hz, 1H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.01 (dd, $J = 15.8$, 6.9 Hz, 1H), 2.12–1.99 (m, 1H), 1.82–1.72 (m, 5H), 1.33–1.11 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.38, 136.69, 127.10, 124.13, 122.89, 120.61, 40.89, 32.77, 26.11, 25.97.
(E)-(2-Cyclopentylvinyl)benzene (4a, known compound): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34–7.29 (m, 2H), 7.25 (dd, $J = 10.4$, 4.9 Hz, 2H), 7.14 (ddd, $J = 8.5$, 2.5, 1.2 Hz, 1H), 6.35 (d, $J = 15.9$ Hz, 1H), 6.18 (dd, $J = 15.8$, 7.7 Hz, 1H), 2.62–2.51 (m, 1H), 1.90–1.78 (m, 2H), 1.74–1.52 (m, 4H), 1.44–1.32 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.90, 135.56, 128.39, 127.88, 126.65, 125.88, 43.78, 33.18, 25.21.

(E)-1-(2-Cyclopentylvinyl)-4-methylbenzene (4b, known compound): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, $J = 6.5$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.39 (ddd, $J = 15.8$, 7.7, 1.7 Hz, 1H), 2.93–2.73 (m, 1H), 2.55 (s, 3H), 2.21–1.58 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.15, 135.12, 134.37, 129.05, 127.76, 125.78, 43.78, 33.20, 25.19, 21.01.

(E)-1-(2-Cyclopentylvinyl)-4-fluorobenzene (4c): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31–7.23 (m, 2H), 6.98–6.93 (m, 2H), 6.31 (d, $J = 15.8$ Hz, 1H), 6.09 (dd, $J = 15.8$, 7.8 Hz, 1H), 2.71–2.42 (m, 1H), 1.95–1.22 (m, 48H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.82 (d, $J = 245.5$ Hz), 135.35 (d, $J = 15.8$, 7.8 Hz, 1H), 134.07 (d, $J = 3.2$ Hz), 127.27 (d, $J = 7.8$ Hz), 126.71, 115.23 (d, $J = 21.4$ Hz), 43.75, 33.19, 25.20. HRMS (TOF MS EI$^+$) m/z calcd for [C$_{13}$H$_{15}$F] 190.1158, found 190.1151.

(E)-1-Chloro-2-(2-cyclopentylvinyl)benzene (4d): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (s, 1H), 7.24–7.06 (m, 3H), 6.27 (d, $J = 15.8$ Hz, 1H), 6.18 (dd, $J = 15.8$, 7.4 Hz, 1H), 2.68–2.41 (m, 1H), 1.92–1.30 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.82, 137.17, 134.35, 129.56, 126.63, 126.55, 125.77, 124.14, 43.71, 33.09, 25.20. HRMS (TOF MS EI$^+$) m/z calcd for [C$_{13}$H$_{15}$Cl] 206.0862, found 206.0861.
\[(E)-\text{Styrylcycloheptane}(4e, \text{known compound})\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 (dd, \(J = 8.3, 1.1\) Hz, 2H), 7.25 (dd, \(J = 10.4, 4.9\) Hz, 2H), 7.17–7.10 (m, 1H), 6.30 (d, \(J = 16.0\) Hz, 1H), 6.19 (dd, \(J = 15.9, 7.4\) Hz, 1H), 2.37–2.24 (m, 1H), 1.83–1.78 (m, 2H), 1.68-1.37 (m, 10H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.09, 137.53, 128.38, 126.70, 126.61, 125.90, 43.20, 34.71, 28.38, 26.25.

\[(E)-\text{Styrylcyclooctane}(4f, \text{known compound})\]: Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33–7.28 (m, 2H), 7.24 (dd, \(J = 10.4, 4.9\) Hz, 2H), 7.13 (dd, \(J = 10.2, 4.3\) Hz, 1H), 6.30 (d, \(J = 16.0\) Hz, 1H), 6.18 (dd, \(J = 15.9, 7.4\) Hz, 1H), 2.43–2.30 (m, 1H), 1.79–1.44 (m, 14H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.08, 137.61, 128.35, 126.88, 126.58, 125.89, 41.29, 31.83, 27.43, 25.98, 25.06.
3. $^1$H and $^{13}$C NMR spectra

$^1$H- and $^{13}$C NMR of 3a
$^1$H- and $^{13}$C NMR of 3b
$^1$H- and $^{13}$C NMR of 3c
$^1$H- and $^{13}$C NMR of 3d
$^1$H- and $^{13}$C NMR of 3e
$^{1}$H- and $^{13}$C NMR of 3f
$^1$H- and $^{13}$C NMR of 3g
$^1$H- and $^{13}$C NMR of 3h
$^1$H- and $^{13}$C NMR of 3i
$^1$H- and $^{13}$C NMR of 3j
$^1$H- and $^{13}$C NMR of 3k
$^{1}$H- and $^{13}$C NMR of 3l
$^1$H- and $^{13}$C NMR of 3m

![NMR Spectra](image)
$^1$H- and $^{13}$C NMR of 3n
$^1$H- and $^{13}$C NMR of 3o
$^1$H- and $^{13}$C NMR of 3p
$^1$H- and $^{13}$C NMR of 4a
$^1$H- and $^{13}$C NMR of 4b
$^1$H- and $^{13}$C NMR of 4c
$^1$H- and $^{13}$C NMR of 4d
$^1$H- and $^{13}$C NMR of 4e
$^1$H- and $^{13}$C NMR of 4f
4. References


