

Supporting Information

Nickel-catalysed intramolecular alkene insertion into cyclobutanones

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General. All reactions were carried out with standard Schlenk and glove box techniques under a nitrogen atmosphere. Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 2000 (¹H at 300.07 Hz and ¹³C at 75.46 Hz) spectrometer. Proton chemical shifts were referenced to residual solvent signals in CDCl₃ (δ 7.26). Carbon chemical shifts were referenced to the deuterated solvent signals in CDCl₃ (δ 77.00). High resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer.

Materials. Toluene was dried and deoxygenized using an alumina/catalyst column system (GlassContour Co). Ni(cod)₂ was recrystallized from toluene. All other commercially available chemical resources were used without further purifications. 3-Styrylclobutanones **1a**, **1b** and **1c** were prepared by Pd(P(*t*-Bu)₃)₂ catalyzed coupling reaction of 3-(2-bromophenyl)cyclobutanone with the corresponding tri-*n*-butylvinyltins. Naphthalene derived substrate **1h** was prepared from 3-(1-bromonaphthalen-2-yl)cyclobutanone in an analogous manner. 3-Styrylclobutanones **1d**, **1f** and **1g** were prepared by 1,4-addition of the corresponding (2-vinyl-phenyl)cuprates generated from (2-vinyl-phenyl)magnesiumbromides and CuI to 3-hexylcyclobutenone. 3-Styrylclobutanone **1e** was prepared by an analogous 1,4-addition reaction to 3-phenylcyclobutenone.

3-(2-Isopropenylphenyl)cyclobutanone (**1b**)

¹H NMR δ 2.08 (d, J = 0.6 Hz, 3H), 3.17-3.28 (m, 2H), 3.37-3.49 (m, 2H), 3.91 (quint, J = 8.3 Hz, 1H), 4.86 (t, J = 0.9 Hz, 1H), 5.25 (d, J = 1.5 Hz, 1H), 7.14-7.40 (m, 4H); ¹³C NMR

δ 25.0, 25.7, 55.0, 115.5, 124.8, 126.3, 127.4, 128.0, 139.9, 143.7, 145.1, 207.1; HRMS (CI) calcd for C₁₃H₁₅O (M⁺ + H) 187.1123, found 187.1124.

3-(2-Propenylphenyl)cyclobutanone (1c)

¹H NMR δ 1.92 (dd, J = 6.5, 1.7 Hz, 3H), 3.18-3.30 (m, 2H), 3.39-3.50 (m, 2H), 3.87 (quint, J = 8.4 Hz, 1H), 6.10 (dq, J = 15.5, 6.7 Hz, 1H), 6.58 (dd, J = 15.6, 1.5 Hz, 1H), 7.19-7.31 (m, 3H), 7.40-7.45 (m, 1H); ¹³C NMR δ 18.9, 26.0, 53.4, 124.7, 126.6, 126.8, 127.0, 128.4, 128.6, 137.3, 139.1, 206.6; HRMS (EI) calcd for C₁₃H₁₄O (M⁺) 186.1045, found 186.1047.

3-Hexyl-3-(2-vinylphenyl)cyclobutanone (1d)

¹H NMR δ 0.81-0.85 (m, 3H), 1.00-1.30 (m, 8H), 1.82- 1.89 (m, 2H), 3.10-3.20 (m, 2H), 3.41-3.50 (m, 2H), 5.30 (dd, J = 10.8, 1.2 Hz, 1H), 5.62 (dd, J = 17.3, 1.4 Hz, 1H), 6.88 (dd, J = 17.3, 10.7 Hz, 1H), 7.10-7.14 (m, 1H), 7.22-7.27 (m, 2H), 7.49-7.54 (m, 1H); ¹³C NMR δ 14.0, 22.5, 25.5, 29.3, 31.6, 38.0, 41.0, 58.2, 115.8, 126.9, 127.1, 127.3, 128.1, 135.5, 136.3, 142.6, 206.9; HRMS (CI) calcd for C₁₈H₂₅O (M⁺ + H) 257.1905, found 257.1909.

3-Phenyl-3-(2-vinylphenyl)cyclobutanone (1e)

¹H NMR δ 3.57-3.67 (m, 2H), 3.80-3.89 (m, 2H), 5.15 (dd, J = 11.1, 1.2 Hz, 1H), 5.58 (dd, J = 17.3, 1.4 Hz, 1H), 6.47 (dd, J = 17.4, 11.1 Hz, 1H), 7.14-7.58 (m, 9H); ¹³C NMR δ 41.3, 61.6, 115.8, 125.7, 126.4, 127.5, 127.6, 127.7, 127.9, 128.6, 135.7, 137.2, 142.7, 146.6, 206.3; HRMS (EI) calcd for C₁₈H₁₆O (M⁺) 248.1201, found 248.1203.

3-Hexyl-3-(2-isopropenylphenyl)cyclobutanone (1f)

¹H NMR δ 0.82-0.87 (m, 3H), 1.10-1.30 (m, 8H), 1.83-1.89 (m, 2H), 2.09 (s, 3H), 3.03-3.13 (m, 2H), 3.33-3.42 (m, 2H), 4.86 (d, J = 0.9 Hz, 1H), 5.21 (t, J = 1.7 Hz, 1H), 7.07-7.15 (m, 2H), 7.19-7.25 (m, 2H); ¹³C NMR δ 14.0, 22.6, 25.5, 26.4, 29.5, 31.6, 38.3, 42.6, 58.3, 116.4, 126.1, 126.3, 129.0, 129.5, 142.5, 142.8, 145.5, 207.6; HRMS (CI) calcd for C₁₉H₂₇O (M⁺ + H) 271.2062, found 271.2059.

3-(4-Fluoro-2-vinylphenyl)-3-hexylcyclobutanone (1g)

¹H NMR δ 0.79-0.90 (m, 3H), 1.00-1.40 (m, 8H), 1.78-1.85 (m, 2H), 3.08-3.18 (m, 2H), 3.36-3.45 (m, 2H), 5.34 (dd, J = 11.4, 0.6 Hz, 1H), 5.62 (d, J = 17.1 Hz, 1H), 6.81 (ddd, J =

17.2, 10.7, 1.4 Hz, 1H), 6.93 (dt, $J = 8.3, 2.8$ Hz, 1H), 7.06 (dd, $J = 8.6, 5.9$ Hz, 1H), 7.19 (dd, $J = 9.9, 2.7$ Hz, 1H); ^{13}C NMR δ 14.0, 22.5, 25.5, 29.3, 31.6, 37.7, 41.0, 58.4, 113.4 (d, $^2J_{\text{C-F}} = 21.9$ Hz), 114.0 (d, $^2J_{\text{C-F}} = 20.8$ Hz), 116.9, 129.8 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 134.5, 138.3 (d, $^3J_{\text{C-F}} = 6.9$ Hz), 138.4 (d, $^4J_{\text{C-F}} = 3.5$ Hz), 161.6 (d, $^1J_{\text{C-F}} = 243.2$ Hz), 206.5; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{OF}$ (M^+) 274.1733, found 274.1734.

3-(1-Vinylnaphthalen-2-yl)cyclobutanone (1h)

^1H NMR δ 3.26-3.37 (m, 2H), 3.43-3.56 (m, 2H), 4.18 (quint, $J = 8.4$ Hz, 1H), 5.42 (dd, $J = 17.9, 2.0$ Hz, 1H), 5.84 (dd, $J = 11.4, 2.1$ Hz, 1H), 7.12 (dd, $J = 17.9, 11.3$ Hz, 1H), 7.45-7.55 (m, 3H), 7.81-7.87 (m, 2H), 8.10-8.15 (m, 1H); ^{13}C NMR δ 26.1, 54.8, 121.9, 122.6, 125.5, 126.2, 128.0, 131.6, 132.1, 133.9, 135.1, 137.2, 207.0 (two carbons are missing); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ (M^+) 222.1045, found 222.1045.

General procedure for nickel-catalysed reaction of 1

A toluene solution (1.0 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.020 mmol), $\text{P}(c\text{-Hex})_3$ (11.2 mg, 0.040 mmol) and 3-styrylcyclobutanone **1** (0.20 mmol) was stirred in a Schlenk-type flask under a nitrogen atmosphere at 100 °C for 2-12 h. The reaction mixture was cooled, concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane : ethyl acetate) to afford the product **2**.

The structure of the products **2** were assigned based on the high resolution mass spectral data and ^1H and ^{13}C NMR data.

8-Methyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2b)

^1H NMR δ 1.50 (d, $J = 0.9$ Hz, 3H), 1.57 (dt, $J = 8.6, 3.7$ Hz, 1H), 1.68-1.79 (m, 1H), 1.84-2.04 (m, 2H), 2.22 (dt, $J = 18.6, 2.9$ Hz, 1H), 2.40 (dd, $J = 18.6, 1.5$ Hz, 1H), 3.42 (t, $J = 2.9$ Hz, 1H), 7.20-7.30 (m, 4H); ^{13}C NMR δ 15.2, 26.3, 31.1, 36.4, 41.8, 50.3, 122.7, 123.6, 126.7, 126.9, 139.0, 143.1, 212.5; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}$ (M^+) 186.1045, found 186.1048.

12-Methyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2c)

^1H NMR δ 1.14 (d, $J = 6.3$ Hz, 3H), 1.35-1.50 (m, 1H), 1.96-2.10 (m, 2H), 2.13-2.31 (m,

2H), 3.34-3.43 (m, 2H), 7.16-7.26 (m, 4H); ^{13}C NMR δ 21.9, 32.0, 34.5, 36.6, 42.4, 59.7, 123.9, 125.3, 126.8, 127.2, 137.3, 142.4, 211.4; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}$ (M^+) 186.1045, found 186.1045.

1-Hexyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2d)

^1H NMR δ 0.90-0.96 (m, 3H), 1.35-1.54 (m, 9H), 1.69-2.01 (m, 5H), 2.06-2.16 (m, 1H), 2.27 (d, $J = 18.3$ Hz, 1H), 3.60 (t, $J = 2.9$ Hz, 1H), 7.18-7.34 (m, 4H); ^{13}C NMR δ 14.1, 22.7, 24.2, 24.3, 29.9, 30.2, 31.8, 35.1, 41.3, 45.6, 53.0, 121.6, 125.3, 126.6, 127.0, 137.0, 144.8, 211.8; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}$ (M^+) 256.1827, found 256.1825.

1-Phenyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2e)

^1H NMR δ 1.87-1.98 (m, 1H), 2.07-2.30 (m, 3H), 2.55 (d, $J = 18.0$ Hz, 1H), 2.71 (dd, $J = 18.3, 3.0$ Hz, 1H), 3.74 (t, $J = 2.6$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 7.11-7.26 (m, 3H), 7.35-7.50 (m, 5H); ^{13}C NMR δ 24.3, 30.9, 46.5, 53.1, 123.8, 125.4, 127.0, 127.1, 127.3, 128.6, 136.2, 141.4, 145.2, 210.6 (one carbon is missing); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{16}\text{O}$ (M^+) 248.1201, found 248.1204.

1-Hexyl-8-methyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2f)

^1H NMR δ 0.89-0.95 (m, 3H), 1.30-1.61 (m, 13H), 1.80-2.03 (m, 5H), 2.30 (d, $J = 18.3$ Hz, 1H), 7.20-7.30 (m, 4H); ^{13}C NMR δ 14.1, 15.4, 22.7, 24.1, 30.2, 31.0, 31.8, 32.1, 35.3, 40.6, 45.5, 50.3, 121.4, 122.7, 126.5, 126.7, 139.6, 145.0, 212.5; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{26}\text{O}$ (M^+) 270.1984, found 270.1981.

5-Fluoro-1-hexyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-trien-9-one (2g)

^1H NMR δ 0.88-0.96 (m, 3H), 1.30-1.54 (m, 9H), 1.66-1.99 (m, 5H), 2.05-2.16 (m, 1H), 2.26 (d, $J = 18.6$ Hz, 1H), 3.56 (t, $J = 2.7$ Hz, 1H), 6.90-7.01 (m, 2H), 7.20 (dd, $J = 8.3, 5.3$ Hz, 1H); ^{13}C NMR δ 14.1, 22.7, 24.2, 24.3, 29.9, 30.2, 31.8, 35.3, 41.0, 45.6, 53.0, 112.5 (d, $^2J_{\text{C-F}} = 21.9$ Hz), 113.5 (d, $^2J_{\text{C-F}} = 20.8$ Hz), 123.2 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 139.0 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 140.4 (d, $^4J_{\text{C-F}} = 3.5$ Hz), 161.5 (d, $^1J_{\text{C-F}} = 243.2$ Hz), 211.0; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{OF}$ (M^+) 274.1733, found 274.1736.

Tetracyclo[10.2.2.0^{2,11}.0^{5,9}]hexadeca-2,4,6,8,10-pentaen-13-one (2h)

¹H NMR δ 1.65-1.82 (m, 2H), 1.97-2.10 (m, 1H), 2.16-2.31 (m, 2H), 2.41 (dd, $J = 18.5, 2.3$ Hz, 1H), 3.60 (t, $J = 2.6$ Hz, 1H), 4.47 (d, $J = 2.4$ Hz, 1H), 7.40-7.57 (m, 3H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 8.07 (d, $J = 8.7$ Hz, 1H); ¹³C NMR δ 23.3, 25.4, 37.1, 41.5, 47.6, 122.0, 123.0, 125.1, 126.4, 127.2, 128.8, 129.5, 131.6, 132.7, 140.7, 211.6; HRMS (EI) calcd for C₁₆H₁₄O (M⁺) 222.1045, found 222.1044.