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Rhodium(I)-catalysed skeletal reorganisation of benzofused

spiro[3.3]heptanes via consecutive carbon-carbon bond

cleavages

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Electronic Supplementary Information

General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel[®] C-200 (75–150 μ m). Preparative thin-layer chromatography (TLC) was performed on Wakogel[®] B-5F. Proton chemical shifts were referenced to residual CHCl₃ signal at 7.26 ppm. Carbon chemical shifts were referenced to CDCl₃ at 77.0 ppm.

Materials. Benzocyclobutenones¹ were prepared by the literature methods. All other reagents and solvents were obtained from commercial sources and used without further purification.

 ⁽a) K. K. Dhawan, B. D. Gowland and T. Durst, J. Org. Chem., 1980, 45, 922; (b) M. G. Charest, D. R. Siegel and A. G. Myers, J. Am. Chem. Soc., 2005, 127, 8292; (c) X.-F. Fu, Y. Xiang and Z.-X. Yu, Chem. Eur. J., 2015, 21, 4242; (d) P.-H. Chen, N. A. Savage and G. Dong, Tetrahedron, 2014, 70, 4135.

Preparation of Benzofused Spiro[3.3]heptanes 1 and 4



- (a) MePPh₃I (1.2 equiv), *t*-BuOK (1.2 equiv), THF, 0 °C;
- (b) Cp₂TiMe₂ (1.7–2.0 equiv), toluene, 65 °C;
- (c) Cl₃CCOCl (2.0 equiv), POCl₃ (0.5 equiv), Zn(Cu) (3.0 equiv), Et₂O, rt;
- (d) Zn (5.0 equiv), AcOH, 80 °C;
- (e) triphenyl(2-pyridylmethyl)phosphonium chloride (1.5 equiv), BuLi (2.25 equiv), THF,60 °C;
- (f) 2-pyridyl ketone (3.0 equiv), Zn (6.9 equiv), TiCl₄ (2.8 equiv), THF, 80 °C;
- (g) RLi (1.1 equiv), THF, -78 °C.





5 3 3 1 1 N 2

3'-(2-Pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane] (1a). White solid, mp 65–69 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.27–3.38 (m, 4H), 3.48–3.58 (m, 2H), 6.40–6.48 (m, 1H), 7.02–7.11 (m, 2H), 7.12–7.26 (m, 4H), 7.57–7.63 (m, 1H), 8.56 (d, *J* = 5.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.9, 43.3, 44.4, 47.1, 120.2, 120.6, 121.7, 122.8, 122.9, 127.2, 127.7, 135.9, 142.5, 144.5, 149.4, 150.9, 156.7; HRMS (ESI) calcd for C₁₇H₁₆N [M + H]⁺ 234.1277, found 234.1279.



3'-(3-Methyl-2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1b). Yellow solid, mp 79–82 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.35 (s, 3H), 3.26–3.38 (m, 4H), 3.54–3.66 (m, 2H), 6.48–6.52 (m, 1H), 6.97 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.05–7.10 (m, 1H), 7.14–7.24 (m, 3H), 7.38–7.43 (m, 1H), 8.37–8.41 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.0, 42.9, 43.9, 44.4, 47.3, 118.2, 120.2, 120.5, 122.8, 127.1, 127.5, 130.0, 137.4, 142.6, 146.0, 146.7, 151.3, 155.3; HRMS (ESI) calcd for C₁₈H₁₈N [M + H]⁺ 248.1434, found 248.1434.



5-Methoxy-3'-(2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1c). Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 3.22–3.28 (m, 3H), 3.43–3.56 (m, 2H), 3.71 (dt, *J* = 17.0, 3.2 Hz, 1H), 3.85 (s, 3H), 6.40–6.44 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H + 1H), 7.05 (dd, *J* = 7.0, 5.5 Hz, 1H), 7.16–7.21 (m, 2H), 7.60 (dt, *J* = 1.7, 7.6 Hz, 1H), 8.53–8.57 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.8, 43.2, 44.8, 46.2, 55.5, 110.7, 115.5, 120.4, 121.6, 122.9, 129.3, 134.6, 135.8, 144.1, 144.6, 149.3, 153.7, 156.7; HRMS (ESI) calcd for C₁₈H₁₈NO [M + H]⁺ 264.1383, found 264.1383.



5-(Benzyloxy)-3'-(2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1d). Pale yellow solid, mp 84–89 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.24–3.32 (m, 3H), 3.46–3.57 (m, 2H), 3.73 (dt, J = 16.7, 3.2 Hz, 1H), 5.14 (s, 2H), 6.42–6.46 (m, 1H), 6.73 (d, J = 7.0 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 7.03–7.07 (m, 1H), 7.15–7.20 (m, 2H), 7.23–7.32 (m, 3H), 7.34–7.38 (m, 2H), 7.60 (dt, J = 1.7, 7.7 Hz, 1H), 8.54–8.58 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.7, 43.1, 44.4, 46.3, 69.6, 111.8, 115.9, 120.4, 121.6, 122.7, 126.7, 127.5, 128.3, 129.2, 135.2, 135.8, 137.1, 144.2, 144.5, 149.3, 152.6, 156.6; HRMS (ESI) calcd for C₂₄H₂₂NO [M + H]⁺ 340.1696, found 340.1698.



4,5-Dimethoxy-3'-(2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1e). Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 3.25 (s, 2H), 3.36–3.42 (m, 1H), 3.48 (dt, J = 17.3, 2.6 Hz, 1H), 3.59–3.72 (m, 2H), 3.83 (s, 3H), 4.05 (s, 3H), 6.40–6.43 (m, 1H), 6.65 (d, J = 7.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 7.2, 5.7 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.60 (dt, J = 1.8, 7.6 Hz, 1H), 8.55 (d, J = 4.0 Hz, 1H); ¹³C NMR (75.6 MHz, CDCl₃) δ 44.3, 45.0, 45.6, 45.9, 56.3, 58.4, 112.5, 115.7, 120.5, 121.7, 123.3, 133.5, 135.2, 135.8, 143.5, 144.1, 148.6, 149.3, 156.3; HRMS (ESI) calcd for C₁₉H₂₀NO₂ [M + H]⁺ 294.1489, found 294.1489.



2,5-Dimethoxy-3'-(2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1f). Pale yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 3.19–3.26 (m, 1H), 3.39 (s, 2H), 3.41–3.48 (m, 1H), 3.51–3.57 (m, 1H), 3.72 (dt, J = 17.0, 3.3 Hz, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 6.40–6.44 (m, 1H), 6.66 (s, 2H), 7.04 (dd, J = 7.0, 5.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.60 (dt, J = 1.8, 7.6 Hz, 1H), 8.53–8.57 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.5, 43.0, 44.2, 46.2, 56.0, 56.4, 112.2, 114.1, 120.5, 121.7, 122.9, 126.8, 135.9, 136.3, 144.3, 148.3, 149.4, 156.8; HRMS (ESI) calcd for C₁₉H₂₀NO₂ [M + H]⁺ 294.1489, found 294.1488.



3'-[1-(2-Pyridyl)ethylidene]spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane] (**1g).** White solid, mp 111–115 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.04–2.07 (m, 3H), 3.23–3.49 (m, 6H), 7.05–7.09 (m, 2H), 7.13–7.17 (m, 1H), 7.19–7.23 (m, 2H), 7.25–7.28 (m, 1H), 7.61 (dt, *J* = 1.5, 7.8 Hz, 1H), 8.58–8.61 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 15.5, 41.6, 43.2, 44.8, 46.0, 120.2, 120.6, 121.3, 122.8, 127.1, 127.5, 127.6, 135.6, 137.4, 142.5, 148.9, 151.3, 158.7; HRMS (ESI) calcd for C₁₈H₁₈N [M + H]⁺ 248.1434, found 248.1434.



3'-[phenyl(2-pyrydyl)methylene]spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'cyclobutane] (1h). Yellow solid, mp 114–119 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.25–3.39 (m, 4H), 3.48–3.57 (m, 2H), 7.05–7.13 (m, 3H), 7.16–7.30 (m, 6H), 7.32–7.38 (m, 2H), 7.59 (dt, *J* = 2.2, 7.8 Hz, 1H), 8.61 (d, *J* = 4.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 42.4, 43.3, 44.6, 46.4, 120.2, 120.9, 122.8, 123.3, 126.7, 127.1, 127.6, 128.3, 129.1, 133.8, 135.9, 139.3, 140.4, 142.5, 149.2, 151.3, 159.0; HRMS (ESI) calcd for C₂₃H₂₀N [M + H]⁺ 310.1590, found 310.1590.



3'-(2-Pyridylmethylene)-2*H***-spiro[cyclobuta[***a***]naphthalene-1,1'-cyclobutane] (1i). Brown oil; ¹H NMR (500 MHz, CDCl₃) \delta 3.38–3.68 (m, 5H), 3.74–3.80 (m, 1H), 6.54–6.58 (m, 1H), 7.07 (dd,** *J* **= 7.2, 4.3 Hz, 1H), 7.22–7.30 (m, 2H), 7.38–7.48 (m, 2H), 7.62 (dt,** *J* **= 1.5, 7.7 Hz, 1H), 7.75 (d,** *J* **= 8.0 Hz, 1H), 7.82 (d,** *J* **= 8.0 Hz, 1H), 7.88 (d,** *J* **= 8.0 Hz, 1H), 8.56–8.60 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) \delta 41.9, 42.3, 44.2, 47.2, 120.5, 121.5, 121.6, 122.0, 123.0, 124.7, 126.3, 127.8, 128.1, 129.6, 133.1, 135.8, 139.2, 144.5, 145.3, 149.3, 156.6; HRMS (ESI) calcd for C₂₁H₁₈N [M + H]⁺ 284.1434, found 284.1434.**



8-Methyl-3'-(2-pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-

cyclobutane] (1j). Obtained as an unknown mixture of two diastereomerers. Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.35 (d, J = 7.5 Hz, 3H), 3.05–3.52 (m, 5H), 6.40–6.48 (m, 1H),

7.02–7.25 (m, 6H), 7.58–7.65 (m, 1H), 8.56 (br s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 16.37, 16.44, 38.4, 38.9, 42.5, 43.0, 47.6, 47.7, 50.26, 50.29, 120.42, 120.44, 121.5, 121.55, 121.64, 122.47, 122.49, 127.4, 127.51, 127.52, 135.8, 144.91, 144.93, 148.0, 149.3, 149.8, 149.9, 156.7; HRMS (ESI) calcd for C₁₈H₁₈N [M + H]⁺ 248.1434, found 248.1434.

General Procedure for Rhodium(I)-Catalysed Rearrangement of 3'-(2-Pyridylmethylene)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]s 1. A Schlenk tube was charged with 1 (0.100 mmol) and RhCl(PPh₃)₃ (5.0 μ mol, 5 mol% Rh), and the tube was evacuated and backfilled with nitrogen. *p*-Xylene (1.0 mL) was added via a syringe through the septum, and the mixture was heated at 150 °C with stirring for the indicated period of time. The reaction mixture was cooled to room temperature and then filtered through a plug of Florisil[®] washing with hexane–AcOEt (1:1), and the filtrate was concentrated. The residue was purified by preparative TLC on silica gel to afford naphthalene 2.



1-Methyl-3-(2-pyridylmethyl)naphthalene (2a). The general procedure was followed using **1a** (23.3 mg, 0.100 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 3:1, twice) yielded **2a** (20.9 mg, 0.090 mmol, 90%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 2.66 (s, 3H), 4.29 (s, 2H), 7.00–7.14 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.44–7.50 (m, 2H), 7.57 (dt, *J* = 1.5, 7.8 Hz, 1H), 7.59 (s, 1H), 7.77–7.82 (m, 1H), 7.93–7.98 (m, 1H), 8.58 (d, *J* = 4.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.3,

44.8, 121.2, 123.2, 123.9, 125.3, 125.7, 125.8, 128.2, 128.3, 131.4, 133.8, 134.6, 136.5, 136.6, 149.3, 161.0; HRMS (ESI) calcd for C₁₇H₁₆N [M + H]⁺ 234.1277, found 234.1273.



1-Methyl-3-[(3-methyl-2-pyridyl)methyl]naphthalene (2b). The general procedure was followed using **1b** (32.2 mg, 0.130 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) yielded **2b** (27.7 mg, 0.112 mmol, 86%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 2.29 (s, 3H), 2.63 (s, 3H), 4.33 (s, 2H), 7.12–7.16 (m, 1H), 7.23 (s, 1H), 7.41–7.49 (m, 4H), 7.71–7.76 (m, 1H), 7.90–7.95 (m, 1H), 8.468.49 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.0, 19.3, 42.4, 121.7, 123.9, 125.1, 125.2, 125.6, 128.0, 128.1, 131.3, 131.9, 133.6, 134.4, 136.1, 138.0, 146.8, 158.7; HRMS (ESI) calcd for C₁₈H₁₈N [M + H]⁺ 248.1434, found 248.1434.



8-Methoxy-1-methyl-3-(2-pyridylylmethyl)naphthalene (2c). The general procedure was followed using **1c** (39.5 mg, 0.150 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) yielded **2c** (32.3 mg, 0.123 mmol, 82%) as a brown oil. ¹H NMR (500 MHz, CDCl₃) δ 2.84 (s, 3H), 3.90 (s, 3H), 4.23 (s, 2H), 6.74–6.77 (m, 1H), 7.08–7.15 (m, 3H), 7.27–7.36 (m, 2H), 7.49 (s, 1H), 7.56 (dt, *J* = 2.0, 7.8 Hz, 1H), 8.57 (d, *J* = 4.0

Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 25.1, 44.5, 55.2, 104.8, 121.0, 121.2, 123.1, 123.9, 125.69, 125.72, 129.9, 135.7, 136.4, 136.5, 136.8, 149.3, 158.0, 160.9; HRMS (ESI) calcd for C₁₈H₁₈NO [M + H]⁺ 264.1383, found 264.1383. The structure of **2c** was established by NOESY experiments.



8-(Benzyloxy)-1-methyl-3-(2-pyridylmethyl)naphthalene (2d). The general procedure was followed using 1d (50.9 mg, 0.150 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) yielded 2d (41.8 mg, 0.123 mmol, 82%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 2.82 (s, 3H), 4.23 (s, 2H), 5.17 (s, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 7.08–7.16 (m, 3H), 7.24–7.43 (m, 5H), 7.45–7.51 (m, 3H), 7.57 (dt, *J* = 1.5, 7.8 Hz, 1H), 8.57 (d, *J* = 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 25.6, 44.5, 70.6, 106.1, 121.2, 121.3, 123.1, 123.9, 125.6, 125.8, 127.7, 127.8, 128.5, 130.0, 135.6, 136.4, 136.5, 136.8, 136.9, 149.3, 156.9, 160.9; HRMS (ESI) calcd for C₂₄H₂₂NO [M + H]⁺ 340.1696, found 340.1696.



1,2-Dimethoxy-6-(2-pyridylmethyl)-8-methylnaphthalene (2e). The general procedure was followed using **1e** (43.9 mg, 0.150 mmol) for 1.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 3:1, 5 times) yielded **2e** (22.5 mg, 0.077 mmol, 51%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 2.84 (s, 3H), 3.87 (s, 3H), 3.97 (s, 3H), 4.21 (s, 2H), 7.09–7.17 (m, 3H), 7.22–7.27 (m, 1H), 7.47 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.54–7.60 (m, 1H), 8.57 (d, *J* = 4.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 23.5, 44.4, 56.8, 61.1, 114.6,

121.2, 123.2, 124.7, 125.9, 127.1, 130.8, 131.1, 133.8, 134.5, 136.5, 145.3, 149.3, 149.5, 160.9; HRMS (ESI) calcd for $C_{19}H_{20}NO_2 [M + H]^+ 294.1489$, found 294.1489.



5,8-Dimethoxy-3-(2-pyridylmethyl)-1-methylnaphthalene (2f). The general procedure was followed using **1f** (23.8 mg, 0.081 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) yielded **2f** (18.4 mg, 0.063 mmol, 77%) as a pale yellow oil. ¹H NMR (301 MHz, CDCl₃) δ 2.83 (s, 3H), 3.85 (s, 3H), 3.93 (s, 3H), 4.27 (s, 2H), 6.64–6.72 (m, 2H), 7.06–7.17 (m, 3H), 7.54 (dt, *J* = 1.8, 7.5 Hz, 1H), 8.02 (s, 1H), 8.53–8.58 (m, 1H); ¹³C NMR (75.6 MHz, CDCl₃) δ 25.0, 44.9, 55.7, 103.6, 104.4, 119.7, 121.1, 123.2, 124.7, 127.9, 130.7, 135.5, 136.4, 136.5, 149.2, 149.5, 152.2, 161.2; HRMS (ESI) calcd for C₁₉H₂₀NO₂ [M + H]⁺ 294.1489, found 294.1489.



1-Methyl-3-[1-(2-pyridyl)ethyl]naphthalene (2g). The general procedure was followed using **1g** (37.1 mg, 0.150 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 4:1) yielded **2g** (34.6 mg, 0.140 mmol, 93%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 1.79 (d, *J* = 7.5 Hz, 3H), 2.64 (s, 3H), 4.42 (q, *J* = 7.2 Hz, 1H), 7.08–7.12 (m, 1H), 7.13–7.17 (m, 1H), 7.24 (s, 1H), 7.43–7.48 (m, 2H), 7.56 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.63 (s, 1H), 7.78–7.82 (m, 1H), 7.91–7.95 (m, 1H), 8.57–8.60 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.4, 20.5, 47.4, 121.2, 122.2, 123.9, 124.0, 125.3, 125.6, 127.3, 128.3,

131.4, 133.7, 134.4, 136.4, 142.1, 149.1, 165.0; HRMS (ESI) calcd for $C_{18}H_{18}N [M + H]^+$ 248.1434, found 248.1435.



1-Methyl-3-[phenyl(2-pyridyl)methyl]naphthalene (2h). The general procedure was followed using **1h** (30.9 mg, 0.100 mmol) for 0.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 3:1) yielded **3h** (28.5 mg, 0.092 mmol, 92%) as a yellow solid. Mp 106–111 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.63 (s, 3H), 5.82 (s, 1H), 7.11–7.34 (m, 8H), 7.38 (s, 1H), 7.41–7.50 (m, 2H), 7.62 (dt, J = 1.5, 7.5 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.4, 59.4, 121.4, 123.9, 125.5, 125.7, 126.3, 126.5, 128.4, 128.49, 128.54, 129.5, 131.5, 133.6, 134.4, 136.4, 139.8, 142.5, 149.6, 163.1; HRMS (ESI) calcd for C₂₃H₂₀N [M + H]⁺ 310.1590, found 310.1590.



4-Methyl-2-(2-pyridylmethyl)phenanthrene (2i). The general procedure was followed using **1i** (42.6 mg, 0.150 mmol) for 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1, twice) yielded **2i** (27.2 mg, 0.096 mmol, 64%) as a brown solid. Mp 107–111 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.12 (s, 3H), 4.33 (s, 2H), 7.10–7.21 (m, 2H), 7.40–7.43 (m, 1H), 7.53–7.70 (m, 6H), 7.87–7.92 (m, 1H), 8.56–8.61 (m, 1H), 8.85–8.90 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 27.3, 44.3, 121.3, 123.2, 125.5, 125.6, 127.19, 127.23,

127.4, 127.8, 128.6, 128.7, 131.6, 132.5, 133.3, 134.0, 135.9, 136.5, 136.9, 149.4, 160.9; HRMS (ESI) calcd for $C_{21}H_{18}N [M + H]^+ 284.1434$, found 284.1434.



1,4-Dimethyl-2-(2-pyridylmethyl)naphthalene (2j)1,2-dimethyl-4-(2and pyridylmethyl)naphthalene (3j). The general procedure was followed using 1j (37.1 mg, 0.150 mmol) for 8 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 2:1) yielded a mixture of 2j and 3j (57:43, 8.4 mg, 0.034 mmol, 23%) as a yellow oil. The reaction of 1j (24.7 mg, 0.100 mmol) in p-xylene (1.0 mL) in the presence of $[RhCl(cod)]_2$ (1.2 mg, 2.4 μ mol) and (2-MeC₆H₄)₃P (3.0 mg, 9.9 μ mol) for 15 h afforded a mixture of 2j and 3j (57:43, 9.0 mg, 0.036 mmol, 36%). ¹H NMR (301 MHz, CDCl₃) δ 2.49 (s, 3H; minor), 2.58 (s, 3H; major), 2.60 (s, 3H; minor), 2.66 (s, 3H; major), 4.39 (s, 2H; major), 4.59 (s, 2H; minor), 6.89–8.60 (m, 9H; major + minor); ¹³C NMR (126 MHz, CDCl₃) δ 14.5, 14.7, 19.3, 20.8, 42.2, 43.1, 121.0, 121.1, 122.6, 122.8, 124.3, 124.5, 124.59, 124.61, 124.9, 125.0, 125.4, 125.6, 129.9, 130.2, 130.5, 130.8, 131.1, 131.8, 132.2, 132.6, 132.8, 133.2, 133.4, 133.8, 136.4, 136.5, 149.1, 149.2, 161.1, 161.2; HRMS (ESI) calcd for $C_{18}H_{18}N [M + H]^+$ 248.1434, found 248.1434. The structure of the major isomer (2j) was established by NOESY experiments.

compound	R ¹ H NMR					reference
Me He Me	methallyl		2.58		2.66	1
	allyl		2.60		2.66	1
	CH ₂ Br		2.60		2.63	2
	Et		2.60		2.65	3
	2-pyridylmethyl		2.58		2.66	this work
R Me Me	2-pyridylmethyl	2.49		2.60		this work
	Bu	2.48		2.59		4
	Bu	2.47		2.59		5

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3'-Phenylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4a). Obtained as a single diastereomer. White solid, mp 64–69 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.08 (s, 1H), 2.78–2.84 (m, 2H), 3.00–3.06 (m, 2H), 3.14 (s, 2H), 7.01–7.06 (m, 1H), 7.19–7.28 (m, 2H), 7.30–7.35 (m, 2H), 7.39–7.45 (m, 2H), 7.53–7.58 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 42.7, 43.8, 46.3, 73.3, 121.0, 122.6, 125.1, 127.2, 127.4, 127.6, 128.5, 142.6, 146.1, 151.6; HRMS (ESI) calcd for C₁₇H₁₆NaO [M + Na]⁺ 259.1093, found 259.1088; IR (*v*/cm⁻¹): 3302, 1450, 748, 694.



3'-(2-Thienyl)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4b). Obtained as a single diastereomer. Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 2.34 (br s, 1H), 2.87–2.93 (m, 2H), 2.97–3.03 (m, 2H), 3.19 (s, 2H), 7.00–7.05 (m, 2H), 7.12 (dd, J = 3.2, 1.2 Hz, 1H), 7.19–7.31 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 42.1, 44.3, 48.3, 70.8, 120.8, 122.6, 123.3, 124.9, 126.8, 127.2, 127.7, 142.7, 150.8, 151.8; HRMS (ESI) calcd for C₁₅H₁₄NaOS [M + Na]⁺ 265.0658, found 265.0659; IR (ν /cm⁻¹): 3363, 2924, 1142, 748, 702.



3'-Butylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4c). Obtained as a ca. 1:1 mixture of two diastereomers. Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 0.90– 1.12 (m, 3H), 1.35–1.49 (m, 4H), 1.65–1.72 (m, 1H), 1.78–1.85 (m, 1H), 2.42–2.56 (m, 4H), 3.22 (s, 1H), 3.28 (s, 1H), 7.02–7.26 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 14.10, 14.13, 23.0, 25.6, 40.3, 40.6, 41.6, 42.2, 45.0, 45.1, 45.8, 46.0, 71.4, 71.8, 120.2, 120.5, 122.6, 122.8, 127.0, 127.1, 127.4, 127.5, 142.8, 143.1, 151.1, 151.7; HRMS (ESI) calcd for C₁₅H₂₀NaO [M + Na]⁺ 239.1406, found 239.1409; IR (ν /cm⁻¹): 3356, 2954, 2924, 748.



5-Methoxy-3'-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4d). Obtained as a 17:1 mixture of two diastereomers. Pale yellow solid, mp 85–88 °C; ¹H NMR (301 MHz, CDCl₃) δ 1.42 (s, 3H), 2.48–2.61 (m, 4H), 3.15 (s, 2H), 3.45 (s, 1H), 3.87 (s, 3H), 6.71 (d, J = 7.2 Hz, 1H), 6.72 (d, J = 8.7 Hz, 1H), 7.19 (dd, J = 8.4, 7.2 Hz, 1H); ¹³C NMR (75.6 MHz, CDCl₃) δ 28.0, 41.4, 43.6, 47.0, 55.2, 70.3, 109.2, 116.0, 129.0, 136.1, 144.2, 152.7; HRMS (ESI) calcd for C₁₃H₁₆NaO₂ [M + Na]⁺ 227.1043, found 227.1044; IR (ν /cm⁻¹): 3278, 1481, 1265, 1072.



3'-Ethyl-8-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4e). Obtained as a ca. 1:1 mixture of two diastereomers. Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 0.95–1.04 (m, 3H), 1.27–1.32 (m, 3H), 1.55–1.71 (m, 2H), 1.89 (q, *J* = 7.5 Hz, 1H), 2.16– 2.51 (m, 4H), 3.29–3.38 (m, 1H), 7.01–7.25 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 7.5, 7.7, 16.1, 16.9, 33.0, 33.1, 40.2, 41.3, 44.9, 45.1, 45.2, 46.2, 47.97, 48.02, 71.86, 71.90, 120.6, 120.9, 121.3, 121.6, 127.3, 127.4, 127.5, 148.3, 148.7, 150.3, 150.7; HRMS (ESI) calcd for C₁₄H₁₈NaO [M + Na]⁺ 225.1250, found 225.1247; IR (*v*/cm⁻¹): 3363, 2962, 2923, 1458, 748.

8-Methyl-3'-(2-thienyl)spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ol (4f). Obtained as a 1.3:1 mixture of two diastereomers. Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 1.11 (d, J = 7.0 Hz, 3H; major), 1.35 (d, J = 7.5 Hz, 3H; minor), 2.22 (br s, 1H; minor), 2.33 (br s, 1H; major), 2.66–3.05 (m, 4H; major + minor), 3.36 (q, J = 7.2 Hz, 1H; major), 3.44 (q, J = 7.0 Hz, 1H; minor), 6.38–7.37 (m, 7H; major + minor); ¹³C NMR (126 MHz, CDCl₃) δ 16.1, 16.3, 44.1, 44.3, 45.6, 45.9, 47.3, 47.6, 47.71, 47.75, 70.4, 71.0, 121.2, 121.3, 121.4, 123.4, 124.6, 125.0, 125.5, 126.69, 126.73, 127.3, 127.4, 127.55, 127.59, 148.2, 148.4, 149.9, 151.0, 151.50, 151.52; HRMS (ESI) calcd for C₁₆H₁₆NaOS [M + Na]⁺ 279.0814, found 279.0813; IR (*ν*/cm⁻¹): 3371, 2962, 2924, 1450, 748, 702.

8-Ethyl-5-methoxy-3'-methylspiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-

cyclobutane]-3'-ol (4g). Obtained as a single diastereomer. White solid, mp 97–100 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.08 (t, J = 7.0 Hz, 3H), 1.32–1.45 (m, 4H), 1.71–1.81 (m, 1H), 2.29 (dd, J = 12.7, 4.2 Hz, 1H), 2.45 (dd, J = 12.5, 4.5 Hz, 1H), 2.49–2.56 (m, 2H), 3.10 (dd, J = 9.5, 6.0 Hz, 1H), 3.88 (s, 3H), 4.23 (br s, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 12.3, 24.5, 28.0, 42.9, 45.0, 46.7, 53.6, 55.1, 70.9, 109.1, 115.8, 128.7, 135.9, 148.8, 152.5; HRMS (ESI) calcd for C₁₅H₂₀NaO₂ [M + Na]⁺ 255.1356, found 255.1352; IR (ν /cm⁻¹): 3302, 2962, 2924, 1265, 1126.

General Procedure for Rhodium(I)-Catalysed Rearrangement of 3'-Spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,1'-cyclobutane]-3'-ols 4. A Schlenk tube was charged with 4 (0.100 mmol) and [Rh(OH)(cod)]₂ (5.0 μ mol, 10 mol% Rh), and the tube was evacuated and backfilled with nitrogen. *p*-Xylene (1.0 mL) was added via a syringe through the septum, and the mixture was heated at 150 °C with stirring. Silica gel (50–100 mg) was added, and the mixture was further heated at 150 °C. The reaction mixture was cooled to room temperature and then filtered through a plug of Florisil[®] washing with hexane–AcOEt (1:1), and the filtrate was concentrated. The residue was purified by preparative TLC on silica gel to afford naphthalene **5**.

3-Methyl-1-phenylnaphthalene (5a). The general procedure was followed using **4a** (23.5 mg, 0.099 mmol) for 1 h (silica gel: 3 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 50:1) yielded **5a** (11.7 mg, 0.054 mmol, 54%) as a yellow oil and (*E*)-3-(2-methylphenyl)-1-phenylbut-2-en-1-one (**6a**, 6.7 mg, 0.028 mmol, 29%) as a yellow oil. **5a**: ¹H NMR (500 MHz, CDCl₃) δ 2.55 (s, 3H), 7.27–7.29 (m, 1H), 7.33–7.39 (m, 1H), 7.40–7.52 (m, 6H), 7.64 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H). The spectral data matched those reported in the literature.²

(*E*)-3-(2-Methylphenyl)-1-phenylbut-2-en-1-one (6a). ¹H NMR (500 MHz, CDCl₃) δ 2.37 (s, 3H), 2.50 (d, J = 1.0 Hz, 3H), 6.83–6.85 (m, 1H), 7.15–7.28 (m, 4H), 7.46 (t, J = 7.7 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.95–7.99 (m, 2H). The spectral data matched those reported in the literature.³

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3-Methyl-1-(2-thienyl)naphthalene (5b). The general procedure was followed using **4b** (33.0 mg, 0.136 mmol) for 1 h (silica gel: 1 h). Purification by preparative TLC on silica gel (hexane, 5 times) yielded **5b** (8.7 mg, 0.039 mmol, 29%) as a yellow oil and (*E*)-3-(2-methylphenyl)-1-(2-thienyl)but-2-en-1-one (**6b**, 8.4 mg, 0.035 mmol, 25%) as a yellow oil. **5b:** ¹H NMR (500 MHz, CDCl₃) δ 2.54 (s, 3H), 7.17–7.20 (m, 1H), 7.22–7.26 (m, 1H), 7.39–7.49 (m, 4H), 7.63 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 21.5, 125.47, 125.52, 126.0, 127.2, 127.3, 127.4, 127.6, 130.1, 130.4, 132.2, 134.1, 134.8, 141.8 [1C missing]; HRMS (ESI) calcd for C₁₅H₁₂NaS [M + Na]⁺ 247.0552, found 247.0548.

(*E*)-3-(2-Methylphenyl)-1-(2-thienyl)but-2-en-1-one (6b). ¹H NMR (500 MHz, CDCl₃) δ 2.35 (s, 3H), 2.54 (d, *J* = 1.0 Hz, 3H), 6.73–6.76 (m, 1H), 7.10–7.18 (m, 2H), 7.20–7.29 (m, 3H), 7.61–7.65 (m, 1H), 7.68–7.71 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.9, 21.7, 123.2, 125.8, 127.2, 127.8, 128.1, 130.5, 131.1, 133.4, 134.0, 144.3, 146.9, 158.6, 183.4; HRMS (ESI) calcd for C₁₅H₁₄NaOS [M + Na]⁺ 265.0658, found 265.0658; IR (*v*/cm⁻¹): 1643, 1604, 1419, 1265, 1219, 725.

1-Butyl-3-methylnaphthalene (5c). The general procedure was followed using **4c** (32.4 mg, 0.150 mmol) for 2.5 h (silica gel: 2 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 30:1) yielded **5c** (13.8 mg, 0.070 mmol, 46%) as a colorless oil and (*E*)-2-(2-methylphenyl)oct-2-en-4-one (**6c**, 5.1 mg, 0.024 mmol, 16%). **5c:** ¹H NMR (500 MHz, CDCl₃) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.46 (sextet, *J* = 7.5 Hz, 2H), 1.68–1.77 (m, 2H), 2.48 (s, 3H), 3.00–3.06 (m, 2H), 7.17 (s, 1H), 7.40–7.45 (m, 2H), 7.47 (s, 1H), 7.73–7.78 (m, 1H), 7.96–8.01 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 14.0, 21.7, 22.9, 32.7, 33.1, 123.7, 124.7, 125.3, 125.4, 128.0, 128.2, 130.1, 134.2, 135.0, 138.8; HRMS (ESI) calcd for C₁₅H₁₈Na [M + Na]⁺ 221.1301, found 221.1300.

(*E*)-2-(2-Methylphenyl)oct-2-en-4-one (6c). ¹H NMR (500 MHz, CDCl₃) δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.32–1.40 (m, 2H), 1.57–1.66 (m, 2H), 2.29 (s, 3H), 2.42 (s, 3H), 2.49 (t, *J* = 7.5 Hz, 2H), 6.15 (s, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.15–7.25 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 13.9, 19.7, 21.2, 22.4, 26.4, 44.5, 125.7, 126.3, 127.1, 127.6, 130.4, 133.9, 144.2, 174.5, 201.7; HRMS (ESI) calcd for C₁₅H₂₀NaO [M + Na]⁺ 239.1406, found 239.1406; IR (ν /cm⁻¹): 2954, 2931, 1689, 1612, 756.

8-Methoxy-1,3-dimethylnaphthalene (5d). The general procedure was followed using 4d (30.6 mg, 0.150 mmol) for 1 h (silica gel: 2 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) yielded 5d (22.2 mg, 0.119 mmol, 80%) as a green solid and (*E*)-4-(2-methoxy-6-methylphenyl)pent-3-en-2-one (6d, 2.3 mg, 0.011 mmol, 8%) as a yellow oil. 5d: Mp 55–59 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.42 (s, 3H), 2.86 (s, 3H), 3.91 (s, 3H), 6.71–6.76 (m, 1H), 7.03 (s, 1H), 7.26–7.32 (m, 2H), 7.38 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 21.2, 25.0, 55.2, 104.3, 120.6, 123.3, 125.2, 125.5, 130.5, 135.0, 135.3, 136.5, 158.1; HRMS (ESI) calcd for C₁₃H₁₄NaO [M + Na]⁺ 209.0937, found 209.0935.

(*E*)-4-(2-Methoxy-6-methylphenyl)pent-3-en-2-one (6d). ¹H NMR (500 MHz, CDCl₃) δ 2.21 (s, 3H), 2.24 (s, 3H), 2.35 (d, *J* = 1.5 Hz, 3H), 3.77 (s, 3H), 6.09 (d, *J* = 1.5 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 19.4, 20.4, 32.0, 55.6, 108.1, 122.4, 127.2, 127.9, 132.8, 135.2, 153.9, 155.9, 198.9; HRMS (ESI) calcd for C₁₃H₁₆NaO₂ [M + Na]⁺ 227.1043, found 227.1043; IR (ν /cm⁻¹): 2923, 1689, 1612, 1466, 1257, 1173, 1088.

4-Ethyl-1,2-dimethylnaphthalene (5e). The general procedure was followed using **4e** (25.6 mg, 0.127 mmol) for 1 h (silica gel: 5.5 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 30:1) yielded **5e** (15.0 mg, 0.081 mmol, 64%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 1.37 (t, *J* = 7.5 Hz, 3H), 2.48 (s, 3H), 2.58 (s, 3H), 3.07 (q, *J* = 7.5 Hz, 2H), 7.17 (s, 1H), 7.42–7.52 (m, 2H), 8.01–8.08 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 14.4, 15.3, 20.8, 25.8, 124.1, 124.2, 124.4, 125.2, 128.3, 129.1, 130.4, 132.7, 133.2, 137.6; HRMS (ESI) calcd for C₁₄H₁₆Na [M + Na]⁺ 207.1144, found 207.1140.

1,2-Dimethyl-4-(2-thienyl)naphthalene (5f). The general procedure was followed using **4f** (38.8 mg, 0.151 mmol) for 1.5 h (silica gel: 3 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 50:1) yielded **5f** (20.3 mg, 0.085 mmol, 56%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.52 (s, 3H), 2.64 (s, 3H), 7.15–7.22 (m, 2H), 7.39–7.46 (m, 3H), 7.50–7.55 (m, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 14.7, 20.7, 124.0, 125.0, 125.3, 125.8, 126.2, 127.1, 127.2, 129.9, 130.6, 131.3, 131.8, 132.6, 133.1, 142.1; HRMS (ESI) calcd for C₁₆H₁₄NaS [M + Na]⁺ 261.0708, found 261.0711.

1-Ethyl-5-methoxy-2,4-dimethylnaphthalene (5g). The general procedure was followed using 4g (34.9 mg, 0.150 mmol) for 1 h (silica gel: 1.5 h). Purification by preparative TLC on silica gel (hexane:AcOEt = 30:1) yielded 5g (20.0 mg, 0.093 mmol, 62%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 1.23 (t, *J* = 7.8 Hz, 3H), 2.42 (s, 3H), 2.83 (s, 3H), 3.02 (q, *J* = 7.7 Hz, 2H), 3.91 (s, 3H), 6.76 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (75.6 MHz, CDCl₃) δ 14.1, 19.7, 22.1, 25.2, 55.2, 104.0, 116.6, 124.2, 125.4, 131.8, 132.46, 132.55, 134.5, 134.8, 158.7; HRMS (ESI) calcd for C₁₅H₁₈NaO [M + Na]⁺ 237.1250, found 237.1249.

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