

## Double 1,4-Rhodium Migration Cascade in Rhodium-Catalysed Arylative Ring-Opening/Spirocyclisation of (3-Arylcyclobutylidene)acetates

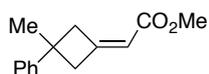
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### Supporting Information

**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  $\mu\text{m}$ ). Preparative thin-layer chromatography was performed on silica gel 60 PF<sub>254</sub> (Merck). Proton chemical shifts were referenced to the residual CHCl<sub>3</sub> signal at 7.26 ppm. Carbon chemical shifts were referenced to the central peak of CDCl<sub>3</sub> at 77.0 ppm.

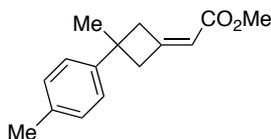
**Materials.** Cyclobutane derivatives<sup>1</sup> and sodium tetraarylborates<sup>2</sup> were prepared by the literature methods. All other commercially available chemical resources were used as received without further purification.



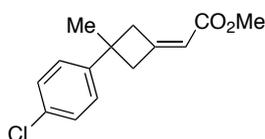
**Methyl 2-(3-methyl-3-phenylcyclobutylidene)acetate (1a):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.50 (s, 3H), 2.83–2.94 (m, 1H), 3.16–3.33 (m, 2H), 3.38–3.48 (m, 1H), 3.71 (s, 3H), 5.73–5.78 (m, 1H), 7.17–7.27 (m, 3H), 7.30–7.38 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  30.7, 40.0, 45.2, 46.4, 50.9, 113.8, 125.1, 125.8, 128.4, 149.7, 162.0, 166.9; HRMS (EI) calcd for

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- (1) (a) H. Paulse, S. Antons, A. Brandes, M. Lögers, S. N. Müller, P. Naab, C. Schmeck, S. Schneider and J. Stoltefuß, *Angew. Chem., Int. Ed.*, 1999, **38**, 3373; (b) S. Danappe, A. Pal, C. Alexandre, A.-M. Aubertin, N. Bourguignon and F. Huet, *Tetrahedron*, 2005, **61**, 5782; (c) D. Crépin, J. Dawick and C. Aïssa, *Angew. Chem., Int. Ed.*, 2010, **49**, 620; (d) J. Chen, G. T. Collins, B. Levant, J. Woods, J. R. Deschamps and S. Wang, *ACS Med. Chem. Lett.*, 2011, **2**, 620.
- (2) (a) T. Alaviuhkola, J. Bobacka, M. Nissinen, K. Rissanen, A. Ivaska and J. Pursiainen, *Chem. Eur. J.*, 2005, **11**, 2071; (b) R. Shintani, Y. Tsutsumi, M. Nagaosa, T. Nishimura and T. Hayashi, *J. Am. Chem. Soc.*, 2009, **131**, 13588.

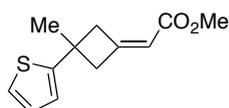
$C_{14}H_{16}O_2$  [M]<sup>+</sup> 216.1150, found 216.1150.



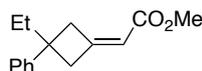
**Methyl 2-[3-methyl-3-(4-methylphenyl)cyclobutylidene]acetate (1b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 1.48 (s, 3H), 2.34 (s, 3H), 2.84–2.90 (m, 1H), 3.15–3.21 (m, 1H), 3.23–3.30 (m, 1H), 3.38–3.43 (m, 1H), 3.71 (s, 3H), 5.75 (br s, 1H), 7.12–7.17 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ 20.9, 30.7, 39.6, 45.3, 46.5, 50.9, 113.7, 125.0, 129.0, 135.3, 146.7, 162.2, 166.9; HRMS (EI) calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub> [M]<sup>+</sup> 230.1307, found 230.1305.



**Methyl 2-[3-(4-chlorophenyl)-3-methylcyclobutylidene]acetate (1c):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 1.47 (s, 3H), 2.85–2.91 (m, 1H), 3.13–3.19 (m, 1H), 3.24–3.31 (m, 1H), 3.35–3.41 (m, 1H), 3.71 (s, 3H), 5.74–5.78 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ 30.6, 39.7, 45.2, 46.4, 51.0, 114.1, 126.6, 128.5, 131.6, 148.1, 161.1, 166.8; HRMS (EI) calcd for C<sub>14</sub>H<sub>15</sub>ClO<sub>2</sub> [M]<sup>+</sup> 250.0761, found 250.0762.

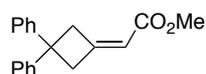


**Methyl 2-[3-methyl-3-(2-thienyl)cyclobutylidene]acetate (1d):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 1.63 (s, 3H), 2.90–2.96 (m, 1H), 3.17–3.23 (m, 1H), 3.25–3.32 (m, 1H), 3.43–3.50 (m, 1H), 3.71 (s, 3H), 5.75–5.78 (m, 1H), 6.87 (d, *J* = 3.5 Hz, 1H), 6.94 (dd, *J* = 3.5, 5.0 Hz, 1H), 7.16 (d, *J* = 5.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ 29.3, 37.5, 47.7, 48.9, 51.0, 114.4, 122.1, 123.2, 126.7, 154.2, 160.9, 166.7; HRMS (EI) calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>S [M]<sup>+</sup> 222.0715, found 222.0718.

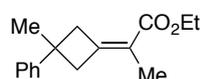


**Methyl 2-(3-ethyl-3-phenylcyclobutylidene)acetate (1e):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.69 (t, *J* = 7.3 Hz, 3H), 1.78 (q, *J* = 7.3 Hz, 2H), 2.88–2.97 (m, 1H), 3.11–3.19 (m, 1H),

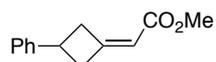
3.26–3.43 (m, 2H), 3.71 (s, 3H), 5.70–5.75 (m, 1H), 7.12–7.24 (m, 3H), 7.28–7.36 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  9.2, 35.6, 43.4, 44.2, 44.4, 50.9, 113.5, 125.7, 126.1, 128.0, 147.4, 162.5, 166.9; HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2$   $[\text{M}]^+$  230.1307, found 230.1308.



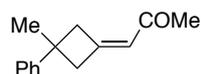
**Methyl 2-(3,3-diphenylcyclobutylidene)acetate (1f):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.58–3.61 (m, 2H), 3.71 (s, 3H), 3.89–3.92 (m, 2H), 5.74–5.77 (m, 1H), 7.12–7.34 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  46.3, 47.6, 47.8, 51.0, 113.1, 126.0, 126.4, 128.4, 148.2, 161.0, 166.7; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_2$   $[\text{M}]^+$  278.1307, found 278.1302.



**Ethyl 2-(3-methyl-3-phenylcyclobutylidene)propanoate (1g):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H), 1.48 (s, 3H), 1.75 (s, 3H), 2.81–2.92 (m, 1H), 3.08–3.24 (m, 2H), 3.34–3.47 (m, 1H), 4.18 (q,  $J = 7.2$  Hz, 2H), 7.16–7.23 (m, 1H), 7.24–7.37 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  13.4, 14.4, 31.2, 38.6, 44.3, 46.9, 59.9, 121.1, 125.2, 125.6, 128.3, 150.0, 153.0, 167.7; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_2$   $[\text{M}]^+$  244.1463, found 244.1466.



**Methyl 2-(3-phenylcyclobutylidene)acetate<sup>3</sup> (1h):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.91–3.02 (m, 1H), 3.14–3.31 (m, 2H), 3.55–3.72 (m, 2H), 3.70 (s, 3H), 5.69–5.73 (m, 1H), 7.16–7.35 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  35.6, 40.1, 41.1, 51.0, 112.7, 126.31, 126.33, 128.5, 144.5, 163.1, 166.9.

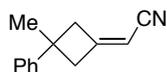


**1-(3-Methyl-3-phenylcyclobutylidene)propan-2-one (5):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.50 (s, 3H), 2.19 (s, 3H), 2.86–2.93 (m, 1H), 3.21–3.30 (m, 2H), 3.43–3.49 (m, 1H), 6.08–6.11 (m, 1H), 7.18–7.27 (m, 3H), 7.31–7.36 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  30.2,

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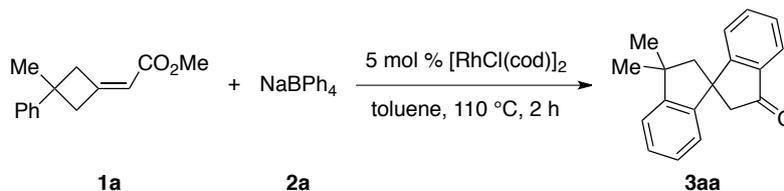
(3) [167823-68-9]

30.8, 40.2, 45.5, 47.0, 123.6, 125.0, 125.8, 128.4, 149.5, 160.2, 197.8; HRMS (EI) calcd for  $C_{14}H_{16}O$   $[M]^+$  200.1201, found 200.1200.

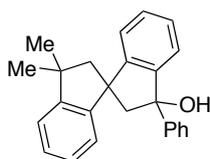


**2-(3-Methyl-3-phenylcyclobutylidene)acetonitrile (8):**  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  1.54 (s, 3H), 2.91–3.00 (m, 1H), 3.05–3.15 (m, 1H), 3.23–3.39 (m, 2H), 5.29–5.34 (m, 1H), 7.21–7.30 (m, 3H), 7.35–7.42 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  30.4, 39.1, 44.9, 45.3, 93.4, 116.1, 124.9, 126.1, 128.5, 148.6, 166.6; HRMS (EI) calcd for  $C_{13}H_{13}N$   $[M]^+$  183.1048, found 183.1052.

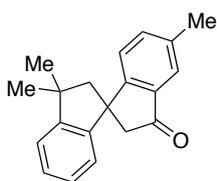
### General Procedures for the Rhodium-Catalysed Arylative Ring-Opening/Spirocyclisation of Cyclobutylideneacetates



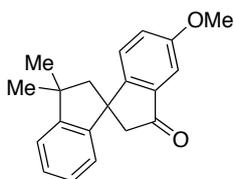
**3',3'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3aa).** To a Schlenk tube under nitrogen were added  $[RhCl(cod)]_2$  (2.6 mg, 5.3  $\mu$ mol, 10 mol % Rh), sodium tetraphenylborate (**2a**, 34.0 mg, 0.100 mmol), and toluene (1.0 mL). The solution was stirred for ca. 3 min at r.t., after which **1a** (22.0 mg, 0.102 mmol) were added, and the mixture was heated for 2 h at 110 °C. After cooling, the reaction mixture was filtered through a plug of Florisil® washing with hexane–AcOEt (2:1), and the filtrate was concentrated. The residue was purified by preparative TLC on silica gel (hexane:AcOEt = 7:1) to afford **3aa** (21.0 mg, 79%) as a pale yellow solid: mp 87–88 °C;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  1.36 (s, 3H), 1.50 (s, 3H), 2.28 (d,  $J$  = 13.2 Hz, 1H), 2.51 (d,  $J$  = 13.2 Hz, 1H), 2.89 (d,  $J$  = 18.9 Hz, 1H), 3.08 (d,  $J$  = 18.9 Hz, 1H), 6.61–6.66 (m, 1H), 7.09–7.17 (m, 1H), 7.20–7.30 (m, 3H), 7.39–7.46 (m, 1H), 7.57–7.64 (m, 1H), 7.77–7.81 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  29.4, 31.1, 43.6, 52.8, 55.1, 58.3, 122.1, 122.8, 123.2, 125.5, 127.6, 127.7, 127.8, 135.5, 136.3, 147.9, 151.8, 162.3, 206.0; HRMS (EI) calcd for  $C_{19}H_{18}O$   $[M]^+$  262.1358, found 262.1359.



**3',3'-Dimethyl-3-phenyl-2,2',3,3'-tetrahydro-1,1'-spirobi[inden]-3-ol (4).** A mixture of **1a** (21.6 mg, 0.100 mmol), **2a** (102.1 mg, 0.298 mmol), and  $[\text{RhCl}(\text{cod})]_2$  (2.5 mg, 5.1  $\mu\text{mol}$ ) in toluene (1.0 mL) was heated for 3 h at 115 °C. Preparative TLC of the concentrated reaction mixture on silica gel afforded **4** (19.6 mg, 58%) as a pale yellow solid: mp 152–153 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.24 (s, 3H), 1.40 (s, 3H), 2.00 (d,  $J = 13.2$  Hz, 1H), 2.30 (d,  $J = 13.2$  Hz, 1H), 2.37 (br s, 1H), 2.81 (d,  $J = 13.5$  Hz, 1H), 2.92 (d,  $J = 13.8$  Hz, 1H), 6.94–7.06 (m, 2H), 7.13–7.41 (m, 11H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  29.8, 31.2, 43.2, 57.0, 57.7, 62.3, 84.9, 121.9, 123.9, 124.37, 124.43, 126.2, 127.1, 127.20, 127.23, 127.7, 128.1, 129.3, 147.0, 147.4, 149.4, 151.5, 151.8; HRMS (EI) calcd for  $\text{C}_{25}\text{H}_{24}\text{O}$   $[\text{M}]^+$  340.1827, found 340.1829.

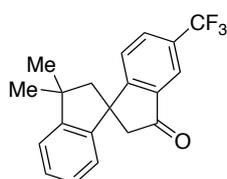


**3',3',5-Trimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3ab).** According to the general procedure, **3ab** (19.2 mg, 70%) was obtained as a white solid from **1a** (21.4 mg, 0.099 mmol) and sodium tetrakis(4-methylphenyl)borate (**2b**, 39.6 mg, 0.099 mmol): mp 139–140 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.35 (s, 3H), 1.49 (s, 3H), 2.25 (d,  $J = 13.2$  Hz, 1H), 2.44 (s, 3H), 2.48 (d,  $J = 13.2$  Hz, 1H), 2.87 (d,  $J = 18.6$  Hz, 1H), 3.06 (d,  $J = 18.9$  Hz, 1H), 6.61–6.65 (m, 1H), 7.08–7.17 (m, 2H), 7.19–7.28 (m, 2H), 7.40–7.45 (m, 1H), 7.57–7.59 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  21.1, 29.4, 31.1, 43.5, 52.5, 55.5, 58.2, 122.1, 122.7, 123.2, 125.1, 127.5, 127.6, 136.5, 136.8, 137.8, 148.1, 151.7, 159.7, 206.1; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{20}\text{O}$   $[\text{M}]^+$  276.1514, found 276.1515.



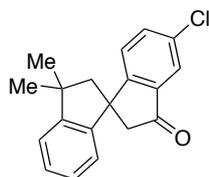
**5-Methoxy-3',3'-dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3ac).**

According to the general procedure, **3ac** (23.0 mg, 79%) was obtained as a pale yellow solid from **1a** (21.6 mg, 0.100 mmol) and sodium tetrakis(4-methoxyphenyl)borate (**2c**, 46.3 mg, 0.100 mmol): mp 132–133 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.34 (s, 3H), 1.48 (s, 3H), 2.24 (d, *J* = 13.2 Hz, 1H), 2.47 (d, *J* = 12.9 Hz, 1H), 2.89 (d, *J* = 18.9 Hz, 1H), 3.09 (d, *J* = 18.9 Hz, 1H), 3.87 (s, 3H), 6.62–6.66 (m, 1H), 7.09–7.29 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 29.4, 31.0, 43.5, 52.2, 55.66, 55.70, 58.1, 103.7, 122.1, 123.1, 125.0, 126.3, 127.5, 127.6, 137.6, 148.0, 151.7, 155.0, 159.7, 205.9; HRMS (EI) calcd for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> [M]<sup>+</sup> 292.1463, found 292.1462.



**3,3'-Dimethyl-5-(trifluoromethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one**

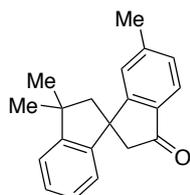
**(3ad)**. According to the general procedure, **3ad** (13.5 mg, 41%) was obtained as a white solid from **1a** (21.6 mg, 0.100 mmol) and sodium tetrakis[4-(trifluoromethyl)phenyl]borate (**2d**, 60.9 mg, 0.099 mmol): mp 101–102 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.37 (s, 3H), 1.51 (s, 3H), 2.30 (d, *J* = 13.2 Hz, 1H), 2.49 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 18.9 Hz, 1H), 3.14 (d, *J* = 19.2 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 7.10–7.33 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.80–7.87 (m, 1H), 8.03–8.07 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ 29.4, 31.1, 43.8, 53.1, 55.1, 58.2, 120.3 (q, <sup>3</sup>*J*<sub>C-F</sub> = 4.1 Hz), 122.4, 123.1, 123.7 (q, <sup>1</sup>*J*<sub>C-F</sub> = 271.9 Hz), 126.4, 127.8, 128.1, 130.6 (q, <sup>2</sup>*J*<sub>C-F</sub> = 33.0 Hz), 131.9 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.4 Hz), 136.6, 147.0, 151.9, 165.3, 204.4; HRMS (EI) calcd for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>O [M]<sup>+</sup> 330.1231, found 330.1230.



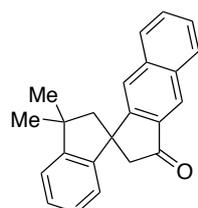
**5-Chloro-3,3'-dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one** (**3ae**).

According to the general procedure but using [RhCl(cod)]<sub>2</sub> (2.5 mg, 5.1 μmol) and 1,3-bis(diphenylphosphino)propane (DPPP, 4.1 mg, 9.9 μmol), **3ae** (19.6 mg, 66%) was obtained as a white solid from **1a** (21.6 mg, 0.100 mmol) and sodium tetrakis(4-chlorophenyl)borate (**2d**, 48.0 mg, 0.100 mmol): mp 130–131 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>,

300 MHz)  $\delta$  1.35 (s, 3H), 1.49 (s, 3H), 2.27 (d,  $J = 13.2$  Hz, 1H), 2.46 (d,  $J = 13.2$  Hz, 1H), 2.90 (d,  $J = 19.2$  Hz, 1H), 3.10 (d,  $J = 19.2$  Hz, 1H), 6.63 (d,  $J = 7.8$  Hz, 1H), 7.10–7.30 (m, 4H), 7.55 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.74 (d,  $J = 1.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  29.4, 31.0, 43.6, 52.6, 55.3, 58.2, 122.2, 122.6, 123.1, 126.9, 127.7, 127.9, 134.3, 135.5, 137.8, 147.3, 151.7, 160.3, 204.5; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{17}^{35}\text{ClO}$   $[\text{M}]^+$  296.0968, found 296.0968.

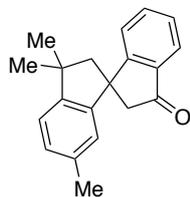


**3',3',6-Trimethyl-2,2',3,3'-tetrahydro-1,1'-spiro[indene]-3-one (3af).** According to the general procedure, **3af** (15.8 mg, 57%) was obtained as a white solid from **1a** (21.7 mg, 0.100 mmol) and sodium tetrakis(3-methylphenyl)borate (**2f**, 39.8 mg, 0.100 mmol): mp 124–125 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.35 (s, 3H), 1.50 (s, 3H), 2.25 (d,  $J = 12.9$  Hz, 1H), 2.39 (s, 3H), 2.50 (d,  $J = 13.2$  Hz, 1H), 2.86 (d,  $J = 18.9$  Hz, 1H), 3.06 (d,  $J = 18.9$  Hz, 1H), 6.62–6.67 (m, 1H), 7.04 (br s, 1H), 7.10–7.17 (m, 1H), 7.20–7.30 (m, 3H), 7.68 (d,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  22.2, 29.4, 31.1, 43.6, 52.7, 55.3, 58.2, 122.1, 122.7, 123.3, 125.6, 127.5, 127.6, 129.2, 134.2, 146.8, 148.1, 151.8, 162.7, 205.5; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{20}\text{O}$   $[\text{M}]^+$  276.1514, found 276.1518.

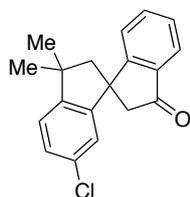


**3',3'-Dimethyl-2,2',3,3'-tetrahydrospiro[cyclopenta[*b*]naphthalene-1,1'-indene]-3-one (3ag).** According to the general procedure, **3ag** (15.8 mg, 51%) was obtained as a pale yellow solid from **1a** (21.6 mg, 0.100 mmol) and sodium tetrakis(2-naphthyl)borate (**2f**, 51.9 mg, 0.096 mmol): mp 126–127 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.38 (s, 3H), 1.54 (s, 3H), 2.37 (d,  $J = 13.5$  Hz, 1H), 2.61 (d,  $J = 13.5$  Hz, 1H), 3.00 (d,  $J = 18.5$  Hz, 1H), 3.17 (d,  $J = 18.5$  Hz, 1H), 6.66 (d,  $J = 7.5$  Hz, 1H), 7.09–7.16 (m, 1H), 7.23–7.30 (m, 2H), 7.47–7.58 (m, 2H), 7.67 (s, 1H), 7.78 (d,  $J = 8.5$  Hz, 1H), 8.02 (d,  $J = 7.5$  Hz, 1H), 8.35 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  29.6, 31.1, 43.7, 52.8, 55.9, 59.3, 122.1, 123.5, 123.6, 124.0, 126.4, 127.6, 127.7,

128.1, 128.5, 130.4, 132.6, 134.2, 137.8, 148.7, 151.8, 156.1, 206.1; HRMS (EI) calcd for  $C_{23}H_{20}O$   $[M]^+$  312.1514, found 312.1509.

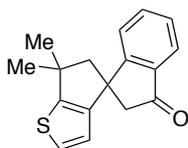


**3',3',6'-Trimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3ba).** According to the general procedure, **3ba** (18.0 mg, 65%) was obtained as a pale yellow solid from **1b** (23.1 mg, 0.100 mmol) and **2a** (34.1 mg, 0.100 mmol): mp 86–87 °C;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  1.34 (s, 3H), 1.48 (s, 3H), 2.22 (s, 3H), 2.26 (d,  $J = 13.2$  Hz, 1H), 2.50 (d,  $J = 13.2$  Hz, 1H), 2.88 (d,  $J = 18.6$  Hz, 1H), 3.06 (d,  $J = 18.9$  Hz, 1H), 6.40–6.44 (m, 1H), 7.02–7.15 (m, 2H), 7.23–7.30 (m, 1H), 7.39–7.47 (m, 1H), 7.58–7.65 (m, 1H), 7.77–7.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  21.2, 29.5, 31.1, 43.2, 52.8, 55.2, 58.5, 121.9, 122.8, 123.7, 125.5, 127.8, 128.6, 135.5, 136.3, 137.3, 148.1, 148.9, 162.3, 206.1; HRMS (EI) calcd for  $C_{20}H_{20}O$   $[M]^+$  276.1514, found 276.1515.



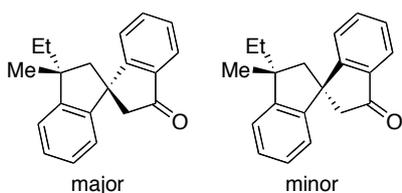
**6'-Chloro-3',3'-dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3ca).**

According to the general procedure, **3ca** (13.0 mg, 48%) was obtained as a white solid from **1c** (22.9 mg, 0.091 mmol) and **2a** (34.4 mg, 0.101 mmol): mp 87–88 °C;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  1.34 (s, 3H), 1.47 (s, 3H), 2.28 (d,  $J = 13.2$  Hz, 1H), 2.52 (d,  $J = 13.2$  Hz, 1H), 2.87 (d,  $J = 18.9$  Hz, 1H), 3.07 (d,  $J = 18.9$  Hz, 1H), 6.59 (d,  $J = 2.1$  Hz, 1H), 7.09–7.28 (m, 3H), 7.42–7.48 (m, 1H), 7.60–7.67 (m, 1H), 7.77–7.82 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  29.3, 30.9, 43.3, 52.7, 54.9, 58.3, 123.0, 123.4, 123.5, 125.4, 128.0, 128.1, 133.1, 135.7, 136.3, 149.9, 150.3, 161.3, 205.3; HRMS (EI) calcd for  $C_{19}H_{17}^{35}ClO$   $[M]^+$  296.0968, found 296.0966.



**3,3-dimethyl-2,2',3,3'-tetrahydrospiro[cyclopenta[*b*]thiophene-1,1'-indene]-3'-one**

**(3da)**. According to the general procedure, **3da** (13.0 mg, 57%) was obtained as a pale yellow solid from **1d** (18.9 mg, 0.085 mmol) and **2a** (34.0 mg, 0.099 mmol): mp 84–85 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.44 (s, 3H), 1.52 (s, 3H), 2.54 (d, *J* = 13.2 Hz, 1H), 2.81 (d, *J* = 13.2 Hz, 1H), 2.91 (d, *J* = 18.9 Hz, 1H), 3.04 (d, *J* = 19.2 Hz, 1H), 6.33 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 5.1 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.37–7.45 (m, 1H), 7.57–7.65 (m, 1H), 7.76 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 30.8, 31.5, 42.8, 50.4, 53.5, 63.4, 120.1, 122.9, 125.1, 127.9, 128.9, 135.5, 135.7, 148.0, 153.2, 161.6, 205.6; HRMS (EI) calcd for C<sub>17</sub>H<sub>16</sub>OS [M]<sup>+</sup> 268.0922, found 268.0920.



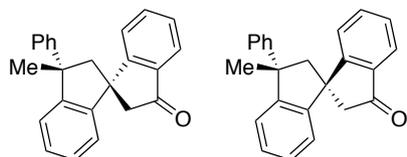
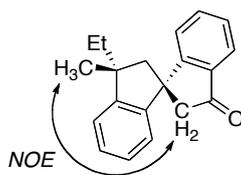
**(1RS,3'RS)-**

**and**

**(1SR,3'RS)-3'-Ethyl-3'-methyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3ea).**

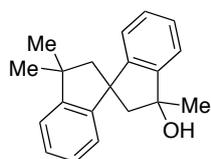
According to the general procedure, **3ea** (17.5 mg, 63%, dr 68:32 estimated by <sup>1</sup>H NMR) was obtained as a colourless oil from **1e** (23.1 mg, 0.100 mmol) and **2a** (34.2 mg, 0.100 mmol): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) **major**: δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.33 (s, 3H), 1.72–1.96 (m, 2H), 2.11 (d, *J* = 13.2 Hz, 1H), 2.58 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 18.6 Hz, 1H), 3.07 (d, *J* = 18.6 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 7.09–7.28 (m, 4H), 7.38–7.46 (m, 1H), 7.56–7.64 (m, 1H), 7.75–7.81 (m, 1H); **minor**: δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.44 (s, 3H), 1.64 (q, *J* = 7.5 Hz, 2H), 2.36 (d, *J* = 13.5 Hz, 1H), 2.43 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 18.9 Hz, 1H) 3.04 (d, *J* = 18.9 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 7.09–7.28 (m, 4H), 7.38–7.46 (m, 1H), 7.56–7.64 (m, 1H), 7.75–7.81 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 9.2, 9.5, 26.4, 29.1, 33.9, 35.3, 47.26, 47.31, 52.7, 52.8, 54.4, 55.26, 55.28, 55.5, 122.4, 122.77, 122.80, 122.9, 123.3, 123.4, 125.4, 125.5, 127.4, 127.57, 127.60, 127.7, 127.8, 135.5, 136.2, 136.4, 148.4, 151.0, 151.1, 162.5, 162.7, 206.0; HRMS (EI) calcd for C<sub>20</sub>H<sub>20</sub>O [M]<sup>+</sup> 276.1514; found: 276.1513.

The stereochemistry of **3ea** (major) was established by <sup>1</sup>H NOE experiment.



**(1*RS*,3'*SR*)-3'-methyl-3'-phenyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-3-one (3fa).**

According to the general procedure, **3fa** (28.7 mg, 88%, dr 51:49 estimated by  $^1\text{H}$  NMR) was obtained as a yellow oil from **1f** (27.8 mg, 0.100 mmol) and **2a** (34.1 mg, 0.100 mmol):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  **diastereomer 1** 1.79 (s, 3H), 2.56 (d,  $J = 13.5$  Hz, 1H), 2.95 (d,  $J = 13.5$  Hz, 1H), 2.99 (d,  $J = 18.9$  Hz, 1H), 3.15 (d,  $J = 18.9$  Hz, 1H), 6.71–6.77 (m, 1H), 6.99–7.04 (m, 1H), 7.11–7.40 (m, 9H), 7.53–7.59 (m, 1H), 7.79 (d,  $J = 7.5$  Hz, 1H); **diastereomer 2** 1.86 (s, 3H), 2.31 (d,  $J = 19.2$  Hz, 1H), 2.41 (d,  $J = 19.2$  Hz, 1H), 2.57 (d,  $J = 13.5$  Hz, 1H), 2.95 (d,  $J = 13.5$  Hz, 1H), 3.00 (d,  $J = 18.9$  Hz, 1H), 3.16 (d,  $J = 18.9$  Hz, 1H), 6.71–6.77 (m, 1H), 7.04–7.10 (m, 1H), 7.13–7.48 (m, 9H), 7.60–7.67 (m, 1H), 7.77–7.82 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  **diastereomer 1** 28.9, 51.9, 53.2, 55.4, 61.2, 122.9, 123.4, 124.6, 125.6, 126.2, 126.9, 127.87, 127.90, 127.9, 128.3, 135.6, 136.2, 148.7, 149.2, 151.0, 161.9, 205.7; **diastereomer 2** 29.7, 51.6, 52.8, 52.9, 60.8, 122.9, 123.2, 124.7, 125.3, 126.5, 126.9, 127.6, 127.9, 128.1, 128.3, 135.4, 136.9, 148.5, 148.9, 149.5, 161.2, 205.8; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{20}\text{O}$   $[\text{M}]^+$  324.1514, found 324.1516.

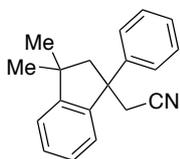


**3,3',3'-Trimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[inden]-3-ol (6).** The reaction of **5** (30.0 mg, 0.150 mmol) and **2a** (51.0 mg, 0.149 mmol) was carried out at 130 °C in toluene for 2.5 h. Preparative TLC of the concentrated crude reaction mixture on silica gel afforded a mixture of **6** and one diastereomer of **7** (16.0 mg, 75:25 estimated by  $^1\text{H}$  NMR, **6**: 29%, **7**: 10%). **6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.99 (s, 3H), 1.39 (s, 3H), 1.96 (s, 3H), 2.56 (d,  $J = 13.2$  Hz, 1H), 2.64 (d,  $J = 13.2$  Hz, 1H), 3.17 (d,  $J = 15.6$  Hz, 1H), 3.31 (d,  $J = 15.6$  Hz, 1H), 7.15–7.40 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  30.0, 30.4, 32.0, 42.7, 52.9, 55.1, 55.7, 65.0,

122.8, 125.4, 125.7, 125.9, 126.4, 126.8, 127.7, 128.1, 128.3, 145.8, 148.1, 152.4; HRMS (EI) calcd for C<sub>20</sub>H<sub>22</sub>O [M]<sup>+</sup> 278.1671, found 278.1671.



**(3-Methyl-1,3-diphenylcyclobutyl)propan-2-one (7).** The reaction of **5** (19.8 mg, 0.099 mmol) and **2a** (34.1 mg, 0.100 mmol) was carried out at 110 °C in toluene for 1.5 h. Preparative TLC of the concentrated crude reaction mixture on silica gel gave two fractions. The more polar fraction consisted of a mixture of **6** and one diastereomer of **7** (11.7 mg, 7:93 estimated by <sup>1</sup>H NMR, **6**: 3%, **7**: 40%). The less polar fraction contained another diastereomer of **7** (11.9 mg, 43%). **7**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ **diastereomer 1 (more polar)** 1.26 (s, 3H), 1.65 (s, 3H), 2.78 (s, 2H), 2.83 (d, *J* = 12.3 Hz, 2H), 2.97 (d, *J* = 12.3 Hz, 2H), 7.19–7.42 (m, 10H); **diastereomer 2 (less polar)** 1.59 (s, 3H), 1.68 (s, 3H), 2.72–2.80 (m, 2H), 2.98–3.05 (m, 2H), 3.10 (s, 2H), 7.04–7.34 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ **diastereomer 1 (more polar)** 31.5, 33.4, 38.0, 39.0, 46.3, 57.4, 125.2, 125.3, 125.7, 126.5, 128.1, 128.3, 148.4, 151.9, 207.7; **diastereomer 2 (less polar)** 31.7, 33.7, 36.7, 38.2, 46.1, 57.3, 124.9, 125.1, 125.6, 126.0, 128.0, 128.1, 149.1, 152.5, 208.0.



**2-(3,3-Dimethyl-1-phenyl-2,3-dihydro-1H-inden-1-yl)acetonitrile (9).** The reaction of **8** (27.5 mg, 0.150 mmol) and **2a** (51.0 mg, 0.149 mmol) was carried out at 110 °C in toluene for 1 h. Preparative TLC of the concentrated crude reaction mixture on silica gel gave two fractions. The more polar fraction consisted of a mixture of **9** and one diastereomer of **10** (9.3 mg, 43:57 estimated by <sup>1</sup>H NMR, **9**: 10%, **10**: 14%). The less polar fraction contained another diastereomer of **10** (8.8 mg, 22%). **9**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.99 (s, 3H), 1.40 (s, 3H), 2.41 (d, *J* = 13.5 Hz, 1H), 2.57 (d, *J* = 13.0 Hz, 1H), 3.03 (s, 2H), 7.20–7.44 (m, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ (as a mixture with **diastereomer 2**) 28.9, 29.9, 30.2, 31.6, 33.4, 33.7, 37.5, 38.4, 42.8, 45.2, 52.3, 56.2, 117.7, 118.2, 123.0, 125.0, 125.2, 125.8, 125.9, 126.6, 126.77, 126.8, 127.1, 128.55, 128.59, 128.62, 146.5, 150.5, 152.4; HRMS (EI) calcd for C<sub>19</sub>H<sub>19</sub>N [M]<sup>+</sup> 261.1517, found 261.1513.



**(3-Methyl-1,3-diphenylcyclobutyl)acetonitrile (10).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  **diastereomer 1 (less polar)** 1.61 (s, 3H), 2.69 (d,  $J = 12.0$  Hz, 2H), 2.91 (s, 2H), 3.09 (d,  $J = 13.5$  Hz, 2H), 7.08–7.32 (m, 10H); **diastereomer 2 (more polar)** 1.28 (s, 3H), 2.50 (s, 2H), 2.80 (d,  $J = 12.0$  Hz, 1H), 2.91 (d,  $J = 12.5$  Hz), 7.20–7.44 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  **diastereomer 1 (less polar)** 33.4, 34.0, 36.2, 37.4, 45.2, 117.9, 124.8, 125.5, 125.6, 126.6, 128.3, 128.5, 147.0, 151.4.

