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# Supporting Information

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# Photochemical Rearrangements of Norbornadiene Pauson-Khand Cycloadducts.

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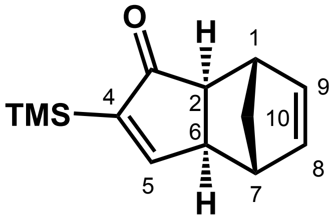
**General methods**: Optical rotations were measured at room temperature (Concentration in g/100 mL). $^1$H and $^{13}$C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. Signal multiplicities in the $^{13}$C spectra have been assigned by HSQC experiments. Photochemical preparative reactions have been performed in a *Rayonet RPR100* reactor equipped with 16 UV lamps (8W, 365 nm). In kinetic studies a *Rayonet*-type reactor equipped with 8 UV lamps (8W, 365 nm) was used. Monitoring of the reaction was done with a *ReactIR 4000* FT-IR apparatus (*Mettler Toledo*) equipped with a *SiComp* ATR probe which was immersed in the solution. The reactions were carried out in a jacketed glass reactor with circulating water at 15ºC. Flash chromatography separations were carried out using $SiO_2$ (70-230 mesh). Silica gel used for filtration or flash chromatography of cobalt complexes was previously washed through with $Et_2O$. Pauson-Khand adducts (+)-**1a**,[1] **1b**,[2] **1d**,[3] **1e**,[4] **1f**,[5] **1h**,[6] are known compounds that have been prepared by reported procedures. The preparation of the remaining PKR adducts is described in the Supporting Information.

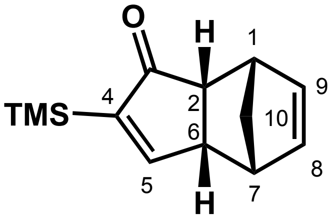


**1a**

**(1*S**,2*S**,6*R**,7*R**)-4-Trimethylsilyl-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, 1a.**

Into a 100 mL pressure reactor purged with nitrogen were placed $Co_2(CO)_8$ (17 mg, 0.044 mmol, 2% mol), trimethylsilylacetylene (0.62 mL, 4.36 mmol), norbornadiene (0.89 mL, 8.71 mmol) and toluene (8 mL). The reactor was quickly flushed with CO and CO overpressure was set to 3.5 bar. The vessel was heated to 90 ºC with vigorous stirring during 20 hours. The reactor was let to cool down, CO removed and the reaction crude heated to 80 ºC in the air with activated charcoal. The crude was then filtered over a pad of celite and the solvent evaporated under reduced pressure to obtain 809 mg (85%) of an off-white solid (*exo*/*endo* 87:13 as determined by $^1$H-NMR). The major (*exo*) isomer was isolated by flash chromatography. Mp: 103 ºC (DSC). IR (film): $\nu_{max}$ 3064, 3029, 2977, 1684, 1570, 1302, 1254, 1246 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.17 (s, 9H, C**H**$_3$-Si), 1.19 (d, *J*=9.6 Hz, 1H, C**H**$_2$ (**10**)), 1.37 (d, *J*=9.6 Hz, 1H, C**H**$_2$ (**10**)), 2.28 (ddd, *J*=5.2, 1.6, 1.2 Hz, 1H, C**H** (**2**)), 2.70 (s, 1H, C**H** (**1**)), 2.84 (m, 1H, C**H** (**6**)), 2.90 (s, 1H, C**H** (**7**)), 6.20 (dd, *J*=5.6, 3.0 Hz, 1H, C**H** (**8**)), 6.27 (dd, *J*=5.6, 3.2 Hz, 1H, C**H** (**9**)), 7.60 (d, *J*=2.4 Hz, 1H, C**H** (**5**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ −1.7

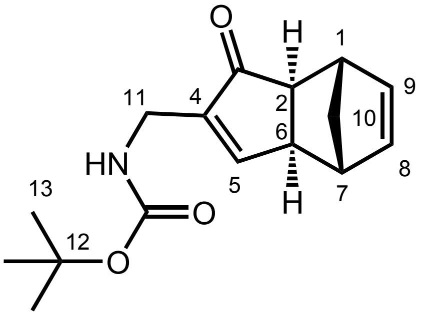
($CH_3$-Si), 41.5 ($CH_2$ (**10**)), 43.2 (CH (**1**)), 44.6 (CH (**7**)), 52.2 (CH (**6**)), 53.6 (CH (**2**)), 137.6 (CH (**8**)), 138.4 (CH (**9**)), 152.3 (Cq (**4**)), 173.2 (CH (**5**)), 213.4 (C=O) ppm.



***endo*-1a**

**(1*S**,2*R**,6*S**,7*R**)-4-Trimethylsilyl-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, *endo*-1a.**

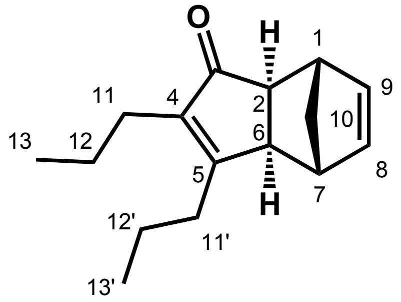
The minor (*endo*) isomer was isolated by flash chromatography of the crude obtained in the preparation of *exo*-**1a**. Mp: 39 ºC (DSC). IR (film): $\nu_{max}$ 3062, 2956, 2898, 2867, 1691, 1571, 1303, 1272, 1246, 848 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.07 (s, 9H, C**H**$_3$-Si), 1.57 (d, *J*=8.4 Hz, 1H, C**H**$_2$ (**10**)), 1.69 (ddd, *J*=8.4, 1.7, 1.7 Hz, 1H, C**H**$_2$ (**10**)), 2.78 (dd, *J*=5.2, 5.2 Hz, 1H, C**H** (**2**)), 2.91 (m, 1H, C**H** (**7**)), 3.16 (s, 1H, C**H** (**1**)), 3.36 (m, 1H, C**H** (**6**)), 5.70 (dd, *J*=5.6, 2.8 Hz, 1H, C**H** (**8**)), 5.85 (dd, *J*=5.6, 2.8 Hz, 1H, C**H** (**9**)), 7.39 (d, *J*=2.4 Hz, 1H, C**H** (**5**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –1.72 ($CH_3$-Si), 44.4 (CH (**7**)), 45.4 (CH (**1**)), 49.6 (CH (**6**)), 51.6 (CH (**2**)), 52.8 ($CH_2$ (**10**)), 132.4 (CH (**8**)), 132.5 (CH (**9**)), 150.4 (Cq (**4**)), 171.7 (CH (**5**)), 213.7 (C=O) ppm. MS (EI): *m/e* 219 ($M^+$+H, 42%), 218 (M+, 73%), 203 ($M^+$–$CH_3$, 57%), 137 ($M^+$-$C_5H_5O$, 82%), 128 (56%), 116 (57%), 83 ($C_5H_7O^+$, 61%), 73 ($C_3H_9Si^+$, 100%), 66 ($C_5H_6^+$, 81%). HRMS (EI) Calc. for $C_{13}H_{18}OSi$ ($M^+$): 218.1127; found: 218.1135.



**1f**

**(1*S**,2*S**,6*S**,7*R**)-*N*-Boc-4-aminomethyl-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, 1f.**

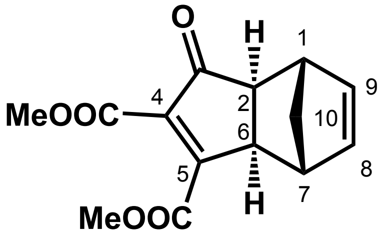
Into a pressure tube fitted with a Teflon screw seal $Co_2(CO)_7PPh_3$ (17.7 mg, 0.0291 mmol, 1% mol) and *N*-Boc-propargylamine (451 mg, 2.91 mmol), norbornadiene (0.59 mL, 5.81 mmol) and dry toluene (3 mL) were added and the tube was purged with CO. The CO overpressure was set to 2.4 bar (36 psi), the tube was closed and heated to 90 ºC with magnetic stirring. After 24 hours heating was stopped and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on $SiO_2$ eluting with hexanes/ethyl acetate (9:1) to afford **1f** as pale yellow oil in 45% yield. IR (film): $\nu_{max}$ 3356, 3061, 2976, 2939, 1694, 1633, 1516, 1366, 1248, 1172 $cm^{-1}$. $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ 1.21 (d, *J*=9.4 Hz, 1H, C**H**$_2$ (**10**)), 1.39 (d, *J*=9.4 Hz, 1H, C**H**$_2$ (1**0**)), 1.43 (s, 9H, C**H**$_3$ (**13**)), 2.32 (d, *J*=4.8 Hz, 1H, C**H** (**2**)), 2.71 (s, 1H, C**H** (**1**)), 2.76 (m, 1H, C**H** (**6**)), 2.92 (s, 1H, C**H** (**7**)), 3.81-3.96 (m, 2H, C**H**$_2$-N (**11**)), 5.02 (bs, 1H, N**H**), 6.21 (dd, *J*=5.4, 3.0 Hz, 1H, C**H** (**8**)), 6.29 (dd, *J*=5.4, 3.0 Hz, 1H, C**H** (**9**)), 7.35 (s, 1H, C**H** (**5**)) ppm. $^{13}C$-NMR (100 MHz, $CDCl_3$): $\delta$ 28.5 ($CH_3$ (**13**)), 36.3 ($CH_2$-NH (**11**)), 41.3 ($CH_2$ (**10**)), 43.0 (CH (**1**)), 43.7 (CH (**7**)), 48.0 (CH (**6**)), 53.0 (CH (**2**)), 79.6 (Cq-O (**12**)), 137.2 (CH (**8**)), 138.6 (CH (**9**)), 147.0 (Cq (**4**)), 155.9 (C=O-O), 160.8 (CH (**5**)), 209.5 (C=O) ppm. MS (CI-$CH_4$): *m/e* 276 ($M^+$+H, 4.3%), 220 ($M^+$+2H–$C_4H_9$, 22%), 176 ($M^+$+2H–$CO_2C_4H_9$, 94%), 57 ($C_4H_9^+$, 100%). HRMS (CI-$CH_4$) Calc. for $C_{16}H_{22}NO_3$ ($M^+$+H): 276.1600; found: 276.1600.



**1h**

**(1*S**,2*S**,6*R**,7*R**)-4,5-Di(*n*-propyl)-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, 1h.**

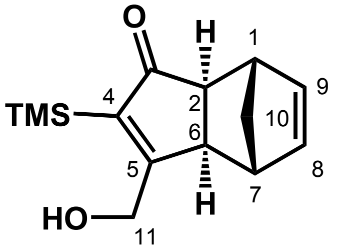
Into 50 mL flask provided with magnetic stirring and a Dimroth condenser, a solution of octacarbonyl dicobalt (358 mg, 1.05 mmol) in hexanes (6 mL), was placed. Then, 4-octyne (0.14 mL, 0.952 mmol) was added dropwise under argon atmosphere, and an outlet was adapted (some bubbling was observed). After 1 hour of stirring, norbornadiene (0.58 mL, 5.71 mmol) was added and the mixture was heated to reflux for 3 hours after which TLC analysis showed that the reaction was complete. The reaction mixture was allowed to cool and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on $SiO_2$ eluting with hexanes/ether (95:5). The title compound was obtained as a colorless oil in 76% yield. IR (film): $\nu_{max}$ 3061, 2961, 2934, 1694, 1631, 1457, 1362, 717 $cm^{-1}$. $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ 0.90 (t, *J*=7.6 Hz, 3H, C**H**$_3$ (**13/13'**)), 0.99 (t, *J*=7.2 Hz, 3H, C**H**$_3$ (**13/13'**)), 1.16 (d, *J*=9.2 Hz, 1H, C**H**$_2$ (**10**)), 1.35 (d, *J*=9.2 Hz, 1H, C**H**$_2$ (**10**)), 1.41 (m, 2H, C**H**$_2$ (**12/12'**)), 1.52 (m, 1H, C**H**$_2$ (**11/11'**)), 1.67 (m, 1H, C**H**$_2$ (**11/11'**)), 2.13 (m, 2H, C**H**$_2$ (**12**/**12'**)), 2.24 (d, *J*=5.2 Hz, 1H, C**H** (**2**)), 2.28 (m, 1H, C**H**$_2$ (**11**/**11'**)), 2.48 (m, 1H, C**H**$_2$ (**11**/**11'**)), 2.68 (d, *J*= 5.2 Hz, 1H, C**H** (**6**)), 2.74 (s, 1H, C**H** (**1**)), 2.90 (s, 1H, C**H** (**7**)), 6.21 (dd, *J*=5.2, 2.8 Hz, 1H, C**H** (**8**)), 6.26 (dd, *J*=5.2, 3.2 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 14.2 ($CH_3$ (**13**/**13'**), 14.3 ($CH_3$ (**13**/**13'**), 21.1 ($CH_2$ (**11**/**11'**)), 21.9 ($CH_2$ (**12**/**12'**)), 25.3 ($CH_2$ (**12**/**12'**)), 31.6 ($CH_2$ (**11**/**11'**)), 41.3 ($CH_2$ (**10**)), 42.2 (CH (**1**)), 43.4 (CH (**1**)), 49.4 (CH (**6**)), 52.1 (CH (**7**)), 137.6 (CH (**8**)), 138.0 (CH (**9**)), 145.1 (Cq (**4**)), 174.6 (Cq (**5**)), 209.9 (C=O) ppm. MS (CI-$CH_4$): *m/e* 247 ($M^+$+H+$CH_4$, 87%), 231 ($M^+$+H, 100%), 201 ($M^+$–$C_2H_5$, 6%), 165 ($M^+$–$C_5H_5$, 8%), 43 ($C_3H_7^+$, 3%) 29 ($C_2H_5^+$, 50%). HRMS (CI-$CH_4$) Calc. for $C_{16}H_{23}O$ ($M^+$+H): 231.1749; found: 231.1753.



**1i**

**(1*S**,2*S**,6*R**,7*R**)-Dimethyl-tricyclo[5.2.1.$0^{2,6}$]-4,8-decadien-3-oxo-4,5-dicarboxylate, 1i.**

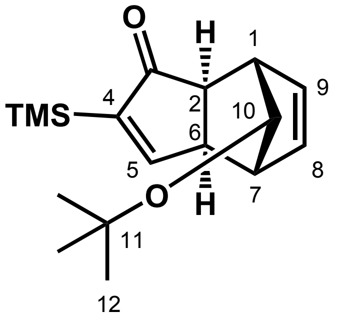
Into a 50 mL flask provided with magnetic stirring, octacarbonyl dicobalt (425 mg, 1.24 mmol) was solved in anhydrous $CH_2Cl_2$ (5 mL) under argon atmosphere. The flask was cooled to 0 ºC and dimethyl acetylenedicarboxylate (145 µL, 1.18 mmol) was added. The flask was let to warm to room temperature and some bubbling was observed (a gas outlet was needed). After 1 hour the mixture was cooled to -20 ºC and norbornadiene (0.72 mL, 7.10 mmol) was added. A solution of *N*-methylmorpholine *N*-oxide (874 mg, 7.46 mmol) in $CH_2Cl_2$ (2.5 mL) was added dropwise, the mixture was stirred for 1 hour at -20 ºC, and then allowed to warm to room temperature for 45 min. TLC analysis showed complete disappearance of the starting red cobalt complex. The solution was filtered on a $SiO_2$ pad and the solvent evaporated under reduced pressure. The crude product was purified by flash chromatography on $SiO_2$ eluting with a hexanes/ethyl acetate (8:2) yielding 166 mg (54%) of **1i**, as white solid. Some *endo* isomer (< 6%) was also isolated in the chromatography. Mp: 80-81 ºC. IR (film): $\nu_{\max}$ 2954, 1729, 1635, 1436, 1278,1028, 710 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 1.37 (d, *J*=10.0 Hz, 1H, C**H**$_2$ (**10**)), 1.52 (d, *J*=10.0 Hz, 1H, C**H**$_2$ (**10**)), 2.54 (d, *J*=5.2 Hz, 1H, C**H** (**2**)), 3.02 (s, 1H, C**H** (**1**)), 3.06 (s, 1H, C**H** (**7**)), 3.09 (d, *J*=5.2 Hz, 1H, C**H** (**6**)), 3.86 (s, 3H, C**H**$_3$-O), 3.90 (s, 3H, C**H**$_3$-O), 6.25 (dd, *J*=5.6, 2.8 Hz, 1H, C**H** (**8**)), 6.36 (dd, *J*=5.6, 3.0 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 41.6 ($CH_2$ (**10**)), 43.4 (CH (**1**)), 44.7 (CH (**7**)), 48.6 (CH (**6**)), 52.6 ($CH_3$-O), 52.9 ($CH_3$-O), 53.9 (CH (**2**)), 137.4 (CH (**8**)), 138.8 (CH (**9**)), 143.1 (Cq (**4**)), 162.3 (C=O-O), 163.1 (Cq (**5**)), 164.1 (C=O-O), 203.0 (C=O) ppm. MS (CI-$NH_3$): *m/e* 263 ($M^+$+H, 84%), 231 ($M^+$–$OCH_3$, 100%), 203 ($M^+$-$COOCH_3$, 87%), 197 ($M^+$+H-$C_5H_6$, 13%). Anal (% calculated, % found): C (64.12, 64.12), H (5.38, 5.46).



**1j**

### (1*S**,2*S**,6*R**,7*R**)-5-Hydroxymethyl-4-trimethylsilyl-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, 1j.

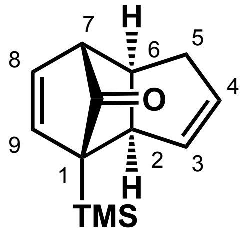
In a pressure tube fitted with a Teflon screw seal, $Co_2(CO)_8$ (57 mg, 0.150 mmol, 5% mol), 3-trimethylsilyl-2-propyn-1-ol (0.44 mL, 3.0 mmol), norbornadiene (1.22 mL, 12.0 mmol) and toluene (3 mL) were placed and the tube was purged with CO. The CO overpressure was set to 2 bar (30 psi), the tube closed and heated to 90 ºC with magnetic stirring. After 48 hours heating was stopped and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on $SiO_2$ (hexanes/ethyl acetate 95:5 to 80:20). The title compound was obtained as yellowish solid in 70% yield (7% of the *endo* isomer was also obtained). Mp: 57-58 ºC. IR (film): $\nu_{max}$ 3423, 3062, 2950, 2898, 1666, 1572, 1324, 1249, 843, 716 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.22 (s, 3H, C**H**$_3$-Si), 1.19 (d, *J*=9.2 Hz, 1H, C**H**$_2$ (**10**)), 1.40 (d, *J*=9.2 Hz, 1H, C**H**$_2$ (**10**)), 2.09 (bs, 1H, O**H**), 2.31 (d, *J*=5.6 Hz, 1H, C**H** (**2**)), 2.92 (m, 2H, C**H** (**1**)+C**H** (**7**)), 3.06 (d, *J*=5.6 Hz, 1H, C**H** (**6**)), 4.55 (dd, *J*=15.0, 5.6 Hz, 1H, C**H**$_2$-O), 4.73 (dd, *J*=15.0, 4.4 Hz, 1H, C**H**$_2$-O), 6.21 (dd, *J*=5.8, 2.8 Hz, 1H, C**H** (**8**)), 6.29 (dd, *J*=5.8, 2.8 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –0.3, ($CH_3$-Si), 41.6 ($CH_2$ (**10**)), 43.2 (CH (**1**)), 44.2 (CH (**7**)), 52.1 (CH (**6**)), 53.7 (CH (**7**)), 61.5 ($CH_2$-O), 137.6 (CH (**8**)), 138.6 (CH (**9**)), 144.6 (Cq (**4**)), 186.8 (Cq (**5**)), 213.5 (C=O) ppm. MS (CI-$NH_3$): *m/e* 266 (M+$NH_4^+$, 15%), 250 ($M^+$+2H, 37%), 249 ($M^+$+H, 100%), 248 ($M^+$, 9%), 233 ([250]–OH, 52%). HRMS (ESI-TOF) Calc. for $C_{14}H_{20}O_2SiNa$ ($M^+$+Na): 271.1130; found 271.1140.



**1l**

### (1*S**,2*S**,6*S**,7*R**,10*S**)-10-*tert*-Butoxy-4-trimethylsilyl-tricyclo[5.2.1.0$^{2,6}$]-4,8-decadien-3-one, *endo*-1l.

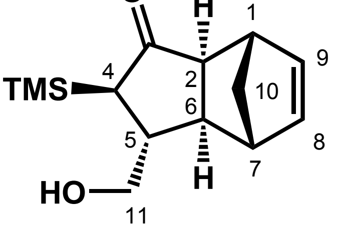
Into a 50 mL flask provided with magnetic stirring, trimethylsilylacetylene hexacarbonyl dicobalt complex (348 mg, 0.906 mmol) and 5 mL of anhydrous $CH_2Cl_2$ were placed under argon atmosphere. 7-*tert*-Butoxy-2,5-norbornadiene (0.18 mL, 0.996 mmol) was added and the flask was cooled to 0 ºC. A solution of *N*-methylmorpholine-*N*-oxide (637 mg, 5.44 mmol) in 2.0 mL of $CH_2Cl_2$ was added dropwise (the flask was washed with 0.5 mL of $CH_2Cl_2$) and the mixture stirred at 0 ºC for 45 min. and let to warm to room temperature. After 20 min. of stirring in the air the suspension was filtered through a pad of $SiO_2$ and the solvent evaporated under reduced pressure. Purification by flash chromatography on $SiO_2$ (hexanes/ether 98:2 to 95:5) afforded 121 mg (46%) of the title compound and 56 mg (21%) of a 1.8:1 mixture of two other diastereomers. Mp: 126-127 ºC. IR (film): $\nu_{max}$ 2972, 1678, 1569, 1241, 834 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.10 (s, 9H, C**H**$_3$-Si), 1.16 (s, 9H, C**H**$_3$ (**12**)), 2.64 (m, 1H, C**H** (**7**)), 2.92 (m, 1H, C**H** (**1**)), 3.04 (dd, *J*=5.2, 5.2 Hz, 1H, C**H** (**2**)), 3.61 (m, 1H, C**H** (**6**)), 3.74 (s, 1H, C**H**-O (**10**)), 5.70 (dd, *J*=5.8, 2.8 Hz, 1H, C**H** (**8**)), 5.80 (dd, *J*=5.8, 2.8 Hz, 1H, C**H** (**9**)), 7.42 (d, *J*=2.0 Hz, 1H, C**H** (**5**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –1.8 ($CH_3$-Si), 28.4 ($CH_3$ (**12**)), 47.9 (CH (**6**)), 48.4 (CH (**7**)), 49.5 (CH (**1**)), 49.8 (CH (**2**)), 73.8 (Cq (**11**)), 84.4 (CH-O (**10**)), 130.9 (CH (**9**)), 131.0 (CH (**8**)), 150.9 (Cq (**4**)), 171.2 (CH (**5**)), 214.2 (C=O) ppm. MS (CI-$NH_3$): *m/e* 308 ($M^+$+$NH_4$, 15%), 291 ($M^+$+H, 100%), 275 ($M^+$–$CH_3$, 1.2%), 234 ($M^+$–$Me_2C$=$CH_2$, 1.9%). Anal. (% calculated, % found): C (70.29, 70.38), H (9.02, 8.71).



**3a**

**Typical experimental procedure. (–)-(1*R*, 2*R*, 6*R*, 7*R*)-1-Trimethylsilyl-tricyclo[5.2.1.$0^{2,6}$]-3,8-decadien-10-one, 3a.** A solution of **1a** (400 mg, 1.83 mmol,) in methanol (100 mL, degassed bubbling nitrogen for 1 hour) was placed into a jacketed (water cooled) reactor fitted with two rubber septa and magnetic stirring. The flask was flushed with nitrogen and irradiated at 365 nm in a *Rayonet* reactor while nitrogen was bubbled through the solution. After four hours, TLC analysis showed total disappearance of the starting product. Solvent was removed *in vacuo* and the crude product purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 98:2) yielding 280 mg (70%) of pure **3a**, a white crystalline solid somewhat volatile under high vacuum. White needles suitable for X-ray analysis were obtained upon evaporation of racemic **3a** from dichloromethane.

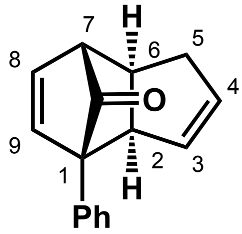
Starting from **(+)-1a** (96% ee), (–)-**3a** (94% ee) was obtained (HPLC, Chiracel OJ, hexane/IPA 98:2, $t_{maj}$ = 7.5 min. $t_{min}$ = 8.2 min). Mp: 52-54 ºC. $[\alpha]_D$ –12.3 (*c* 0.600, $CHCl_3$); IR (KBr): $\nu_{max}$ 3051, 3004, 2952, 2920, 2905, 2850, 1750, 1248, 1103 843, 714 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.15 (s, 9H, C**H**$_3$-Si), 2.12 (d, *J*=17.2 Hz, 1H, C**H**$_2$ (**5**)), 2.44-2.60 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.67 (d, *J*=3.2 Hz, 1H, C**H** (**7**)), 2.90 (m, 1H, C**H** (**6**)), 5.61 (m, 1H, C**H** (**3**)), 5.73 (m, 1H, C**H** (**4**)), 6.39 (dd, *J*=6.8, 0.8 Hz, 1H, C**H** (**8**)), 6.59 (dd, *J*=6.8, 3.6 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –1.9 ($CH_3$-Si), 35.3 ($CH_2$ (**5**)), 40.7 (CH (**2**)), 49.3 (Cq (**1**)), 54.4 (CH (**7**)), 55.6 (CH (**6**)), 128.7 (CH (**3**)), 133.0 (CH (**4**)), 134.7 (CH (**9**)), 137.5 (CH (**8**)), 207.3 (C=O) ppm. MS (EI): *m/e* 218 ($M^+$, 15%), 183 (98%), 167 ($M^+$–$C_4H_3$, 30%), 73 ($C_3H_9Si^+$, 100%). Anal. (% calculated, % found): C (71.50, 71.33), H (8.31, 8.41).



**2a**

**(1*S**,2*S**,4*R**,5*R**,6*R**,7*R**)-5-Hydroxymethyl-4-trimethylsilyl-tricyclo[5.2.1.$0^{2,6}$]-8-decen-3-one, 2a.**

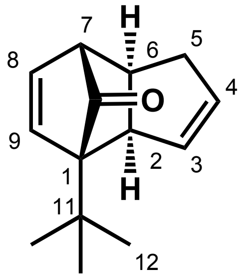
Following the reaction conditions described in the preparation of **3a** but adding benzophenone (60% mol ratio) to the mixture, the title compound was isolated in 80% yield. After 1.5 hours of irradiation the starting material was consumed (4 mmol scale); careful monitoring by TLC was crucial at this moment to avoid formation of inseparable by-products arising from pinacolinic couplings. Pure product (colourless oil) was isolated by flash chromatography ($SiO_2$, hexane/ethyl acetate). IR (film): $\nu_{max}$ 3446, 3061, 2953, 2878, 1705, 1249, 1192, 860, 703 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.12 (s, 9H, C**H**$_3$-Si), 1.21 (d, *J*=9.0 Hz, 1H, C**H**$_2$ (**10**)), 1.43 (d, *J*=9.0 Hz, 1H, C**H**$_2$ (**10**)), 1.89 (bs, 1H, O**H**), 1.97 (m, 1H, C**H** (**5**)), 2.12 (dd, *J*=9.6, 2.0 Hz, 1H, C**H** (**4**)), 2.25 (dd, *J*=8.8, 4.8 Hz, 1H, C**H** (**6**)), 2.36 (dd, *J*=8.8, 0.8 Hz, 1H, C**H** (**2**)), 2.82 (s, 1H, C**H** (**7**)), 3.08 (s, 1H, C**H** (**1**)), 3.54 (dd, *J*=10.4, 7.2 Hz, 1H, C**H**$_2$ (**11**)) , 3.76 (dd, *J*=10.4, 4.0 Hz, 1H, C**H**$_2$ (**11**)), 6.16 (dd, *J*=5.8, 3.2 Hz, 1H, C**H** (**9**)), 6.29 (dd, *J*=5.8, 3.2 Hz, 1H, C**H** (**8**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –1.4 ($CH_3$-Si), 44.6 ($CH_2$ (**10**)), 45.0 (CH (**5**)), 46.7 (CH (**1**)), 47.8 (CH (**6**)), 47.9 (CH (**4**)), 49.2 (CH (**7**)), 57.6 (CH (**2**)), 67.3 ($CH_2$ (**11**)), 138.1 (CH(**9**)), 138.8 (CH (**8**)), 220.5 (C=O) ppm. MS (CI-$CH_4$): *m/e* 251 ($M^+$+H, 28%) 225 (74%), 195 (49%), 185 ($M^+$+H–$C_5H_6$, 49%), 141 (74%), 113 ($M^+$–$C_5H_6$–$SiMe_3$, 100%), 66 ($C_5H_6^+$, 26%). HRMS (CI-$CH_4$) Calc. for $C_{14}H_{23}O_2Si$ ($M^+$+H): 251.1467; found: 251.1458.



**3c**

**(1*S**,2*R**,6*S**,7*R**)-1-Phenyl-tricyclo[5.2.1.0$^{2,6}$]-3,8-decadien-10-one, 3c.**

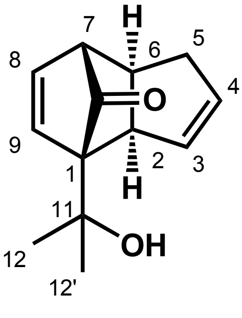
The procedure described for **3a** (irradiation time: 5 hours), starting from **1c**, afforded **3c** in 70% yield as a white solid. Mp: 68-70 ºC. IR (film): $\nu_{max}$ 3065, 2992, 2950, 2912, 2849, 1770, 1604, 1497, 1445, 719 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 2.24-2.32 (m, 1H, C**H**$_2$ (**5**)), 2.60-2.72 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.82 (d, *J*=3.6 Hz, 1H, C**H** (**7**)), 3.26 (m, 1H, C**H** (**6**), 5.34 (m, 1H, C**H** (**3**)), 5.77 (m, 1H, C**H** (**4**)), 6.62 (dd, *J*=6.8, 1.2 Hz, 1H, C**H** (**8**)), 6.69 (dd, *J*=6.8, 3.6 Hz, 1H, C**H** (**9**)), 7.27 (m, 1H, C**H** (**Ar**)), 7.37 (m, 2H, C**H** (**Ar**)), 7.52 (m, 2H, C**H** (**Ar**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 36.4 ($CH_2$ (**5**)), 41.0 (CH (**2**)), 54.6 (CH (**7**)), 56.6 (CH (**6**)), 59.8 (Cq (**1**)), 127.9 (CH (**Ar**)), 128.3 (2xCH (**Ar**)), 128.7 (CH (**3**)), 133.4 (CH (**9**)), 133.9 (CH (**4**)), 136.6 (Cq (**Ar**), 138.5 (CH (**8**)), 203.4 (C=O) ppm. MS (EI): *m/e* = 222 ($M^+$, 71%), 194 ($M^+$–$C_2H_2$, 85 %), 193 ($M^+$–$C_2H_5$, 76%), 156 ($M^+$-$C_5H_6$, 100%), 91 ($C_7H_7^+$, 25%), 77 ($C_6H_5^+$, 25%). Anal. (% calculated, % found): C (86.45, 86.25), H (6.35, 6.37).



**3d**

**(1*S**,2*R**,6*S**,7*R**)-1-*tert*-Butyl-tricyclo[5.2.1.0$^{2,6}$]-3,8-decadien-10-one, 3d.**

The procedure described for **3a** (irradiation time: 5 hours), starting from **1d**, afforded **3d** in 72% yield as a white solid. Mp: 69-70 ºC. IR (KBr): $\nu_{\max}$ 3051, 3000, 2949, 2914, 2868, 1754, 1617, 1364, 808, 727 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 1.11 (s, 9H, C**H**$_3$ (**12**)), 2.14 (d, $J$=17.4 Hz, 1H, C**H**$_2$ (**5**)), 2.50 (dd, $J$=17.4, 10.0 Hz, 1H, C**H**$_2$ (**5**)), 2.62 (m, 2H, C**H** (**7**)+C**H** (**2**)), 2.88 (d, $J$=9.6 Hz, 1H, C**H** (**6**)), 5.72 (ddd, $J$=6.0, 4.0, 2.0 Hz, 1H, C**H** (**4**)), 5.76 (ddd, $J$=5.6, 4.0, 2.0 Hz, 1H, C**H** (**3**)), 6.51 (m, 2H, C**H** (**8**)+C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 27.9 (CH$_3$ (**12**)), 31.0 (Cq (**11**)), 34.8 (CH$_2$ (**5**)), 42.3 (CH (**2**)), 53.0 (CH (**7**)), 54.3 (CH (**6**)), 62.7 (Cq (**1**)), 130.1 (CH (**3**)), 132.5 (CH (**9**)), 132.9 (CH (**4**)), 138.7 (CH (**8**)), 207.3 (C=O) ppm. MS (EI): *m/e* 202 (M$^+$, 6%), 149 (35%), 121 (100%), 91 (37%), 58 (30%), 57 (C$_4$H$_9^+$, 26%). Anal. (% calculated, % found): C (83.12, 83.01), H (8.97, 9.12).

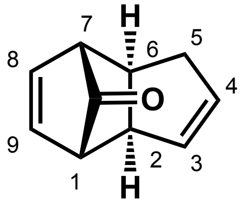


**3e**

**(1*S**,2*R**,6*S**,7*R**)-1-(1-Hydroxy-1-methylethyl)-tricyclo[5.2.1.0$^{2,6}$]-3,8-decadien-10-one, 3e.**

The procedure described for **3a** (irradiation time: 4 hours), starting from **1e**, afforded **3e** in 78% yield as a white solid. Mp: 72-73 ºC. IR (film): $\nu_{\max}$ 3556, 3053, 2976, 2581, 1771, 1619, 1374, 1174, 953, 721 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 1.32 (s, 3H, C**H**$_3$ (**12**/**12'**)), 1.37 (s, 3H, C**H**$_3$ (**12**/**12'**)), 2.15 (m, 1H, C**H**$_2$ (**5**)), 2.51-2.60 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.64 (d, $J$=3.6 Hz, 1H, C**H** (**7**)), 2.79 (bs, 1H, O**H**), 2.99 (m, 1H, C**H** (**6**)), 5.67 (m, 1H, C**H**), 5.94 (m, 1H, C**H**), 6.27 (dd, $J$=7.0, 1.2 Hz, 1H, C**H**), 6.58 (dd, $J$=7.0, 3.6 Hz, 1H, C**H**) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 26.2 (CH$_3$ (**12**/**12'**)), 28.7 (CH$_3$ (**12**/**12'**)), 35.0 (CH$_2$ (**5**)), 42.1 (CH (**2**)), 52.5 (CH (**6**)), 53.1 (CH (**7**)), 63.4 (Cq

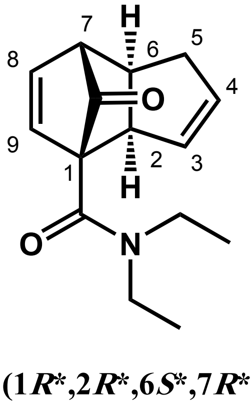
(**1**)), 70.8 (Cq-O (**11**)), 130.2 (CH (**3**)), 130.9 (CH (**4**)), 133.6 (CH (**8**)), 136.2 (CH (**9**)), 208.9 (C=O) ppm. MS (CI-$CH_4$): *m/e* 205 ($M^+$+H, 33%), 204 ($M^+$, 11%), 203 ($M^+$-H, 68%), 189 ($M^+$–$CH_3$), 100%), 188 (16%), 173 (58%), 159 (97%), 145 ($M^+$–$C_3H_7O$, 36%). HRMS (CI-$CH_4$) Calc. for $C_{13}H_{17}O$ ($M^+$+H): 205.1229; found: 205.1225.



**3b**

**(1*S**,2*R**,6*S**,7*R**)-Tricyclo[5.2.1.$0^{2,6}$]-3,8-decadien-10-one, 3b.**

The procedure described for **3a** (irradiation time: 3 hours), starting from **1b**, afforded **3b** in 33% yield as a pale yellow oil. Due to the product volatility *n*-pentane was used instead of methanol, and pentane/ether mixtures were used in chromatographic purification. IR (film): $\nu_{max}$ 3052, 2956, 2850, 1780, 708 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 2.15 (d, *J*=17.2 Hz, 1H, C**H**$_2$ (**5**)), 2.46 (ddd, *J*=14.0, 14.0, 2.8 Hz, 1H, C**H** (**2**)), 2.60 (m, 1H, C**H**$_2$ (**5**)), 2.64 (m, 1H, C**H** (**7**)), 2.77 (m, 1H, C**H** (**1**)), 2.91 (d, *J*=9.2 Hz, 1H, C**H** (**6**)), 5.56 (ddd, *J*=5.6, 4.4, 2.4 Hz, 1H, C**H** (**3**)), 5.77 (ddd, *J*=5.6, 4.4, 2.4 Hz, 1H, C**H** (**4**)), 6.52 (ddd, *J*=7.2, 3.6, 1.2 Hz, 1H, C**H** (**8**), 6.57 (ddd, *J*=7.2, 3.6, 1.2 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 36.0 ($CH_2$ (**5**)), 40.0 (CH (**2**)), 51.3 (CH (**6**)), 51.5 (CH (**1**)), 53.3 (CH (**7**)), 129.8 (CH (**3**)), 133.4 (CH (**4**)), 133.7 (CH (**8**)), 134.5 (CH (**9**)), 205.3 (C=O) ppm. MS (CI-$CH_4$): *m/e* 147 ($M^+$+H, 5.6%), 137 (17%), 113 (11%), 97 (12%), 71 (17%), 41 (20%), 29 (78%), 17 (100%). HRMS (CI-$CH_4$) Calc. for $C_{10}H_{11}O$ ($M^+$+H): 147.0810; found 147.0808.

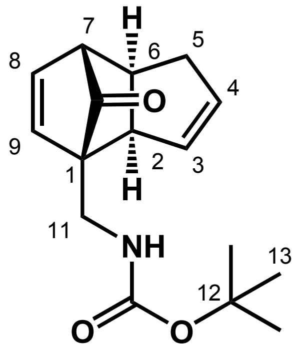


**3g**

**(1*R**,2*R**,6*S**,7*R**)-*N,N*-Diethyl-tricyclo[5.2.1.$0^{2,6}$]-3,8-decadien-10-oxo-1-carboxamide, 3g.**

The procedure described for **3a** (irradiation time: 3.5 hours), starting from **1g**, afforded **3g** in 53% yield as a colorless oil. IR (film): $\nu_{max}$ 3047, 2971, 2850, 1842, 1782, 1631, 1425, 1286, 715 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 1.14 (t, *J*=7.0 Hz, 3H, C**H**$_3$-

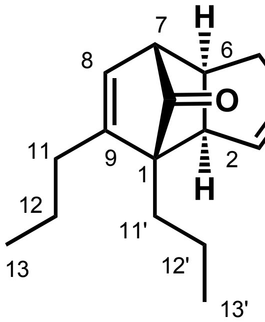
C$H_2$N), 1.16 (t, *J*=7.2 Hz, 3H, C**H**$_3$-C$H_2$N)), 2.20 (d, *J*=18.0 Hz, 1H, C**H**$_2$ (**5**)), 2.47 (ddd, *J*=9.6, 9.6, 2.5 Hz, 1H, C**H** (**2**)), 2.62 (dddd, *J*=18.0, 9.6, 4.4, 4.4 Hz, 1H, C**H**$_2$ (**5**)), 2.77 (d, *J*=3.6 Hz, 1H, C**H** (**7**)), 3.13 (m, 2H, N-C**H**$_2$), 3.33 (dddd, *J*=9.6, 3.6, 1.6, 1.6 Hz, 1H, C**H** (**6**)), 3.41 (m, 2H, N-C**H**$_2$), 5.77 (ddd, *J*=6.0, 2.2, 2.2 Hz, 1H, C**H** (**4**)), 6.04 (ddd, *J*=6.0, 2.2, 2.2 Hz, 1H, C**H** (**3**)), 6.45 (dd, *J*=6.8, 1.2 Hz, 1H, C**H** (**8**)), 6.61 (dd, *J*=6.8, 3.6 Hz, 1H, C**H** (**9**)) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 12.9 (CH$_3$), 14.8 (CH$_3$), 35.7 (CH$_2$ (**5**)), 39.9 (CH$_2$-N), 40.5 (CH (**2**)), 41.7 (CH$_2$-N), 54.6 (CH (**6**)), 54.8 (CH (**7**)), 63.8 (Cq (**1**)), 130.9 (CH (**3**)), 132.4 (CH (**9**)), 133.2 (CH (**4**)), 134.7 (CH (**8**)), 167.2 (C=O-N), 202.3 (C=O) ppm. MS (CI-NH$_3$): *m/e* 246 ($M^+$+H, 100%), 245 ($M^+$, 10%), 218 ($M^+$–$C_2H_3$, 17%), 180 ($M^+$–$C_5H_5$, 45%), 173 ($M^+$–$C_4H_{10}N$, 7.1%). HRMS (CI-CH$_4$) Calc. for $C_{15}H_{20}NO_2$ ($M^+$+H) 246.1494; found: 246.1501.



**3f**

### (1*S**,2*R**,6*S**,7*R**)-*N*-*tert*-Butoxycarbonyl-1-aminomethyl-tricyclo[5.2.1.0$^{2,6}$]-3,8-decadien-10-one, 3f.

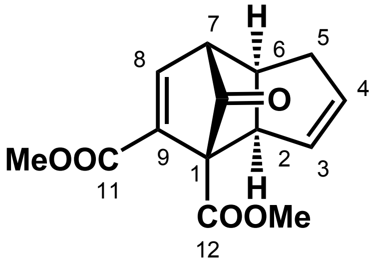
The procedure described for **3a** (irradiation time: 4 hours), starting from **1f**, afforded **3f** (67% yield) as a colorless oil. Some starting material (9%) was recovered in the chromatography. IR (film): $\nu_{\max}$ 3364, 3051, 2977, 1771, 1699, 1505, 1367, 1249, 1171 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 1.43 (s, 9H, C**H**$_3$ (**13**)), 2.14 (d, *J*=14.0 Hz, 1H, C**H**$_2$ (**5**)), 2.56-2.62 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.70 (d, *J*=3.4 Hz, 1H, C**H** (**7**)), 2.87 (d, *J*=6.4 Hz, 1H, C**H** (**6**)), 3.24 (dd, *J*=14.0, 3.0 Hz, 1H, C**H**$_2$–N (**11**)), 3.79 (dd, *J*=14.0, 8.8 Hz, 1H, C**H**$_2$–N (**11**)), 4.87 (bs, 1H, N**H**), 5.55 (m, 1H, C**H** (**3**)), 5.80 (m, 1H, C**H** (**4**), 6.51 (d, *J*=6.8 Hz, 1H, C**H** (**9**)), 6.60 (dd, *J*=6.8, 3.4 Hz, 1H, C**H** (**8**) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 28.4 (CH$_3$ (**13**)), 35.7 (CH$_2$ (**5**)), 36.5 (CH$_2$-NH (**11**)), 41.5 (CH (**2**)), 53.1 (CH (**7**)), 53.3 (CH (**6**)), 58.4 (Cq (**1**)), 79.3 (Cq-O (**12**)), 127.1 (CH (**3**)), 134.4 (CH (**8**)), 134.5 (CH (**4**)), 136.0 (CH (**9**)), 156.4 (O-C=O), 206.0 (C=O) ppm. MS (CI-CH$_4$): *m/e* 276 ($M^+$+H, 100%), 220 ($M^+$+2H–$C_4H_9$, 52%), 176 ($M^+$+2H–$CO_2C_4H_9$, 38%), 130 (16%), 57 ($C_4H_9^+$, 20%). HRMS (CI-CH$_4$) Calc. for $C_{16}H_{22}NO_3$ ($M^+$+H): 276.1600; found: 276.1604.



**3h**

**(1*R**,2*R**,6*S**,7*S**)-1,9-Dipropyl-tricyclo[5.2.1.$0^{2,6}$]-3,8-decadien-10-one, 3h.**

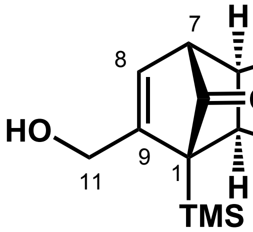
The procedure described for **3a** (irradiation time: 4 hours), starting from **1h**, afforded **3h** (64% yield) as a colorless oil. Some starting material (9%) was recovered in the chromatography. IR (film): $\nu_{max}$ 3052, 2958, 2872, 2849, 1774, 1465, 731 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.96 (t, *J*=7.4 Hz, 3H, C**H**$_3$ (**13/13'**)), 0.98 (t, *J*=6.8 Hz, 3H, C**H**$_3$ (**13/13'**)), 1.32-1.72 (m, 6H, 3xC**H**$_2$), 2.06-2.21 (m, 3H, C**H**$_2$ (**5**)+C**H$_2$** (**11**)), 2.44-2.58 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.60 (d, *J*=4.0 Hz, 1H, C**H** (**7**)), 2.77 (m, 1H, C**H** (**6**)), 5.55 (m, 1H, C**H** (**3**)), 5.77 (m, 1H, C**H** (**4**)), 6.17 (ddd, *J*=4.0, 1.6, 1.6 Hz, 1H, C**H** (**8**) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 14.0 ($CH_3$ (**13/13'**)), 15.3 ($CH_3$ (**13/13'**)), 18.4 ($CH_2$ (**11'**)), 19.8 ($CH_2$), 26.7 ($CH_2$), 31.5 ($CH_2$ (**11**)), 35.9 ($CH_2$ (**5**), 42.4 (CH (**2**)), 53.0 (CH (**7**)), 53.7 (CH (**6**)), 58.7 (Cq (**1**)), 126.0 (CH (**8**)), 128.2 (CH (**3**)), 133.8 (CH (**4**)), 149.7 (Cq (**9**)), 207.4 (C=O) ppm. MS (CI-$CH_4$): *m/e* 231 ($M^+$+H, 100%), 201 ($M^+$–$C_2H_5$, 12%), 165 ($M^+$–$C_5H_6$, 15%). HRMS (CI-$CH_4$) Calc. for $C_{16}H_{23}O$ ($M^+$+H): 231.1749; found: 231.1738.



**3i**

**(1*R**,2*R**,6*S**,7*R**)-Dimethyl-tricyclo[5.2.1.$0^{2,6}$]-3,8-decadien-10-oxo-1,9-dicarboxylate, 3i.**

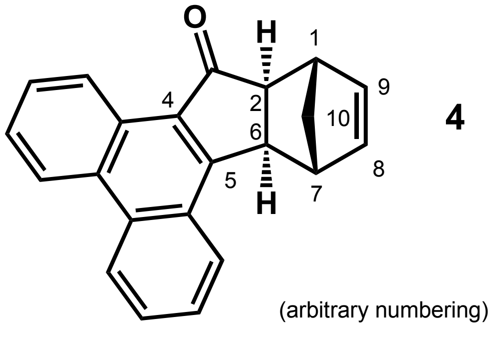
The procedure described for **3a** (irradiation time: 4 hours, *n*-hexane as solvent), starting from **1i**, afforded **3i** (86% yield) as a colorless oil. Some starting material (5%) was recovered in the chromatography. IR (film): $\nu_{max}$ 3001, 2953, 1799, 1743, 1587, 1437, 1310, 1130, 731 $cm^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 2.52 (d, *J*=17.2 Hz, 1H, C**H**$_2$ (**5**)), 2.59 (ddd, *J*=9.2, 9.2, 2.4 Hz, 1H, C**H** (**2**)), 2.67 (m, 1H, C**H**$_2$ (**5**)), 3.01 (d, *J*=3.8 Hz, 1H, C**H** (**7**)), 3.27 (m, 1H, C**H** (**6**)), 3.78 (s, 3H, C**H**$_3$-O), 3.80 (s, 3H, C**H**$_3$-O), 5.82 (m, 1H, C**H** (**3**)), 6.01 (m, 1H, C**H** (**4**)), 7.49 (d, *J*=3.8 Hz, 1H, C**H** (**8**)) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 35.9 (CH$_2$ (**5**)), 41.9 (CH (**2**)), 51.9 (CH (**6**)), 52.2 (CH$_3$-O), 52.3 (CH$_3$-O), 55.5 (CH (**7**)), 63.8 (Cq (**1**)), 128.7 (CH (**4**)), 134.2 (CH (**3**)), 137.3 (Cq (**9**)), 142.6 (CH (**8**)), 162.3 (C=O-O (**11**)), 167.6 (C=O-O (**12**)), 196.2 (C=O) ppm. MS (CI-CH$_4$): *m/e* 263 (M$^+$+H, 8.7%), 231 (M$^+$–CH$_3$O, 33%), 203 (M$^+$–CO$_2$CH$_3$, 100%), 143 (34%), 115 (37%), 66 (C$_5$H$_5^+$, 27%), 59 (CO$_2$H$^+$, 36%). HRMS (CI-CH$_4$) Calc. for C$_{14}$H$_{15}$O$_5$ (M$^+$+H): 263.0919; found: 263.0909.



**3j**

**(1*S**,2*R**,6*R**,7*S**)-1-Trimethylsilyl-9-hydroxymethyl-tricyclo[5.2.1.0$^{2,6}$]-3,8-decadien-10-one, 3j.**

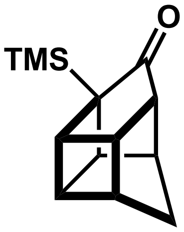
The procedure described for **3a** (irradiation time: 6 hours), starting from **1j**, afforded **3j** (69% yield) as a white solid. Some starting material (10%) was recovered in the chromatography. Mp: 73-74 ºC. IR (film): $\nu_{max}$ 3421, 3055, 2952, 2902, 2850, 1750, 1446, 1251, 836 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 0.19 (s, 9H, C**H**$_3$-Si), 1.45 (bs, 1H, O**H**), 2.12 (m, 1H, C**H**$_2$ (**5**)), 2.48-2.59 (m, 2H, C**H** (**2**)+C**H**$_2$ (**5**)), 2.75 (d, *J*=3.2 Hz, 1H, C**H** (**7**)), 2.96 (m, 1H, C**H** (**6**)), 4.34 (m, 2H, C**H**$_2$-O (**11**)), 5.62 (m, 1H, C**H** (**3**)), 5.72 (m, 1H, C**H** (**4**)), 6.49 (ddd, *J*=3.2, 2.0, 2.0 Hz, 1H, C**H** (**8**)) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ –0.4 (CH$_3$-Si), 35.1 (CH$_2$ (**5**)), 42.2 (CH (**2**)), 50.7 (Cq (**1**)), 54.2 (CH (**7**)), 56.1 (CH (**6**)), 62.0 (CH$_2$-O (**11**)), 127.8 (CH (**8**)), 129.8 (CH (**3**)), 132.9 (CH (**4**)), 150.6 (Cq (**9**)), 206.7 (C=O) ppm. HRMS (ESI-TOF) Calc. for C$_{14}$H$_{20}$O$_2$SiNa (M$^+$+Na): 271.1120; found: 271.1127.



**4**

**(1*S**,4*R**,4a*R**,13a*S**)-13-Oxo-1,4,4a,13a-tetrahydro-1,4-methano-1*H*-indeno[2,1-*l*]phenanthrene, 4.**

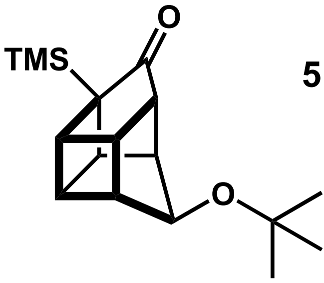
The procedure described for **3a** (irradiation time: 5 hours), starting from **1k**, afforded **4** (52% yield) as a pale yellow solid. Crystallization from dichloromethane gave yellow needles suitable for X-ray analysis. Mp: 238-240 ºC. IR (film): $\nu_{\max}$ 3068, 2985, 2969, 2940, 2872, 1692, 1401, 752, 715 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 1.16 (d, *J*=9.6 Hz, 1H, C**H**$_2$ (**10**)), 1.42 (d, *J*=9.6 Hz, 1H, C**H**$_2$ (**10**), 2.83 (d, *J*=5.6 Hz, 1H, C**H** (**6**)), 3.19 (s, 1H, C**H**), 3.23 (s, 1H, C**H**), 3.69 (d, *J*=5.6 Hz, 1H, C**H** (**2**), 6.40 (dd, *J*=5.6, 2.8 Hz, 1H, C**H**), 6.53 (dd, *J*=5.6, 2.8 Hz, 1H, C**H**), 7.66-7.77 (m, 3H, 3xC**H** (**Ar**)), 7.84 (m, 1H, C**H** (**Ar**)), 8.30 (dd, *J*=8.4, 1.0 Hz, 1H, C**H** (**Ar**)), 8.67 (m, 1H, C**H** (**Ar**)), 8.74 (d, *J*=8.4 Hz, 1H, C**H** (**Ar**)), 9.32 (m, 1H, C**H** (**Ar**)) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 42.5 ($CH_2$ (**10**)), 44.4 (CH), 45.2 (CH), 45.8 (CH (**6**)), 55.0 (CH (**2**)), 122.6 (CH (**Ar**)), 123.7 (CH (**Ar**)), 125.0 (CH (**Ar**)), 125.9 (CH (**Ar**)), 127.1 (CH (**Ar**)), 127.3 (CH (**Ar**)), 127.5 (Cq), 128.2 (CH (**Ar**)), 128.5 (Cq), 129.9 (CH (**Ar**), 130.3 (Cq), 133.5 (Cq), 133.8 (Cq), 137.9 (CH (**8**/**9**)), 138.6 (CH (**8**/**9**)), 159.3 (Cq), 207.8 (C=O) ppm. MS (CI-$CH_4$): *m/e* 297 ($M^+$+H, 100%), 296 ($M^+$, 6.7%), 259 (20%), 231 ($M^+$+H–$C_5H_6$, 42%), 230 ($M^+$–$C_5H_6$, 44%), 67 (60%). HRMS (ESI-TOF) Calc. for $C_{22}H_{17}O$ ($M^+$+H): 297.1279; found: 297.1274.



**5a**

### (1*S**,2*S**,3*R**,4*R**,5*R**,7*R**,8*S**,9*S**)-5-Trimethylsilyl-pentacyclo[$5.3.0.0.^{2,5}0.^{3,9}0^{4,8}$]decan-6-one, 5a.

The procedure described for **3a** (irradiation time: 3.5 hours), starting from ***endo*-1a**, afforded **5a** (83% yield) as a colorless oil after flash chromatograph (hexane/ether 95:5). IR (film): $\nu_{\max}$ 2958, 2855, 1743, 1248, 890, 843 cm$^{-1}$. $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 0.07 (s, 9H, $CH_3$-Si), 1.55 (d, *J*=11.0 Hz, 1H, C**H**$_2$), 1.73 (d, *J*=11.0 Hz, 1H, C**H**$_2$), 2.31 (m, 1H, C**H**), 2.75 (m, 1H, C**H**), 2.79 (m, 1H, C**H**), 2.88-2.94 (m, 2H, 2xC**H**), 3.04-3.12 (m, 2H, 2xC**H**) ppm. $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ –3.2 ($CH_3$-Si), 35.9 (CH), 39.1 (Cq-Si), 40.2 (CH), 41.5 ($CH_2$), 41.7 (CH), 43.3 (CH), 43.4 (CH), 43.8 (CH), 219.5 (C=O) ppm. MS (CI-$CH_4$): *m/e* 219 ($M^+$+H, 22%), 218 ($M^+$, 20%), 203 (100%), 181 (30%), 137 (70%), 73 ($Me_3Si^+$, 31%). HRMS (ESI-TOF) Calc. for $C_{10}H_9O$ ($M^+$–$SiMe_3$): 145.0653; found: 145.0648.



**5l**

**(1*R**,2*R**,3*S**,4*R**,5*S**,7*S**,8*S**,9*S**,10*S**)-10-*tert*-Butoxy-5-trimethylsilyl-pentacyclo[5.3.0.0.$^{2,5}$0.$^{3,9}$0$^{4,8}$]decan-6-one, 5l.**

The procedure described for **3a** (irradiation time: 3.5 hours), starting from ***endo*-1l**, afforded **5l** (87% yield) as a white solid after flash chromatography (hexane/ether 9:1). Mp: 75-77 ºC. IR (film): $\nu_{max}$ 2967, 2901, 1739, 1248, 1089, 843 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 0.05 (s, 9H, C**H**$_3$), 1.18 (s, 9H, C**H**$_3$-Si), 2.65 (m, 1H, C**H**), 2.72 (m, 2H, 2xC**H**), 2.77 (m, 3H, 3xC**H**), 3.19 (m, 1H, C**H**), 3.98 (s, 1H, C**H**-O) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ –3.4 (CH$_3$-Si), 28.5 (CH$_3$-C), 35.9 (CH), 38.5 (CH), 38.9 (CH), 39.3 (Cq-Si), 39.5 (CH), 47.5 (CH), 47.7 (CH), 50.6 (CH), 73.5 (Cq-O), 83.9 (CH-O), 219.2 (C=O) ppm. MS (CI-NH$_3$): *m/e* 308 (M+NH$_4^+$, 100%), 291 (M$^+$+H, 60%), 252 (38%), 235 (12%), 90 (7%). Anal. (% calculated, % found): C (70.29, 70.30), H (9.02, 9.22).

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## **Experimental Data of X-Ray diffraction of 3a and 4.**

*Data Collection*: Measurements for compound **3a** were made on a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co. rotating anode with Mo K$\alpha$ radiation, a graphite monochromator, and a Siemens LT2 low-temperature device ($T$ = -120 ºC). Measurements for compound **4** were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with Mo$_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ($T$ = -173 °C). Full-sphere data collection was used with $\omega$ and $\varphi$ scans.

*Programs used*: Data collection Smart V. 5.060 (Bruker-AXS 2001) and Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-AXS 2001) and absorption correction SADABS V. 2.10 (2003).

*Structure Solution and Refinement*: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[1]

Crystal data for **3a** at 153 K**:** $C_{13}H_{18}O_1Si_1$, 218.36 g mol$^{-1}$, monoclinic, $P2_1$, a = 6.3595(2) Å, b = 7.6380(2) Å, c = 12.7412(4) Å, $\beta$ = 91.4440(10)°, V = 618.69(3) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.172 Mg/m$^3$, $R_1$ = 0.0371 (0.0406), wR2 = 0.0918 (0.0942), for 3632 reflections with I>2$\sigma$(I) (for 3877 reflections [R$_{int}$: 0.0457] with a total measured of 9256 reflections), goodness-of-fit on F$^2$ = 1.070, Flack = 0.04(9), largest diff. peak (hole) = 0.282 (-0.327) e Å$^{-3}$.

Crystal data for **4** at 153 K**:** $C_{22}H_{16}O_2$, 296.35 g mol$^{-1}$, orthorhombic, $P2_12_12_1$, a = 5.4737(3) Å, b = 15.2166(9) Å, c = 16.9657(11) Å, V = 1413.09(15) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.393 Mg/m$^3$, $R_1$ = 0.0404 (0.0481), wR2 = 0.1044 (0.1080), for 7154 reflections with I>2$\sigma$(I) (for 8282 reflections [R$_{int}$: 0.0432] with a total measured of 28270 reflections), goodness-of-fit on F$^2$ = 1.001, largest diff. peak (hole) = 0.498 (-0.295) e Å$^{-3}$.

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[1] G. M. Sheldrick (1998) *SHELXTL Crystallographic System Ver. 5.10*, Bruker AXS, Inc.: Madison, Wisconsin.

***Figure S1.*** Ortep-Plot (50 %) with labeling scheme of **3a.**

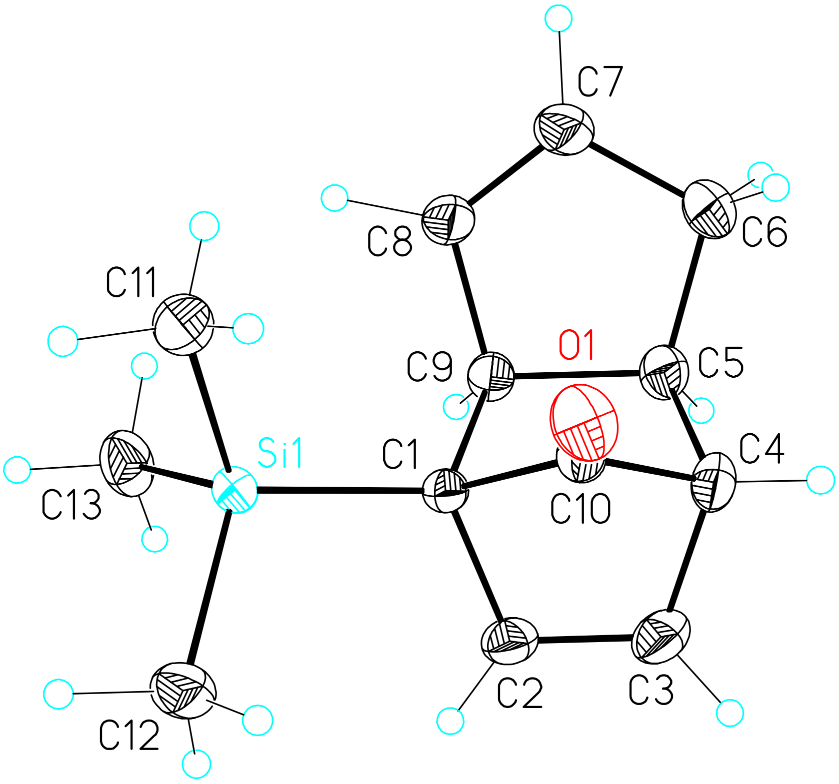

***Figure S2.*** Ortep-Plot (50 %) with labeling scheme of compound **4**.