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Supporting Information

69451 Weinheim, Germany

Synthesis of Seven-Membered Ring Ketones by Arylative Ring-Expansion of Alkyne-Substituted Cyclobutanones

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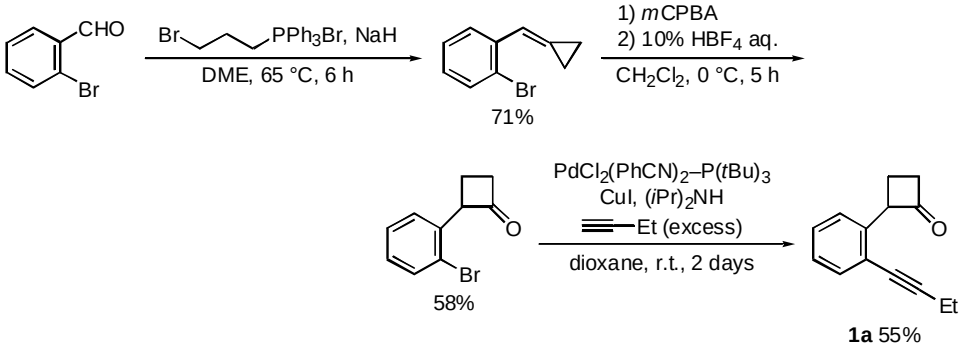
General. All reactions were carried out with standard Schlenk techniques under an argon atmosphere. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300.07 Hz and ^{13}C at 75.46 Hz) spectrometer. All NMR data were obtained in $CDCl_3$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.00 ppm. High resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer.

Materials. Hydroxo(cycloocta-1,5-diene)rhodium(I) dimer[1] and arylboroxins[2] were prepared according to the literature procedures. 1,4-Dioxane was distilled over sodium–benzophenone ketyl. Water was degassed prior to use. All other commercially available resources were used without further purifications.

Preparation of 2-(2-Alk-1-ynylphenyl)cyclobutanones 1

Method A:



[1] R. Usón, L. A. Oro, J. A. Cabeza, *Inorg. Synth.* **1985**, *23*, 126–130.

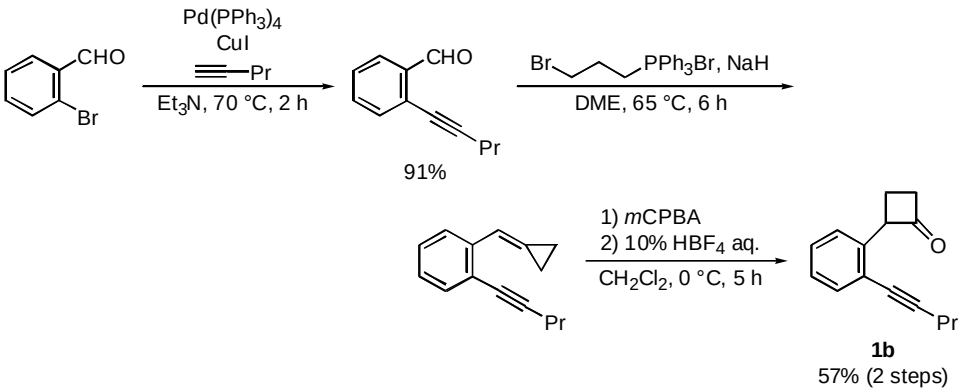
[2] (a) T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **1999**, *121*, 11591–11592. (b) Corey, E. J.; Shibata, T.; Lee, T. W. J. Am. Chem. Soc. 2002, 124, 3808–3809.

2-Bromobenzylidenecyclopropane. To a suspension of 3-bromopropyltriphenylphosphonium bromide (27.9 g, 60 mmol) in DME (100 mL) were added NaH (2.88 g, 120 mmol) and 10 drops of EtOH, and the mixture was heated at 65 °C for 5 h. To the mixture was added 2-bromobenzaldehyde (11.1 g, 60 mmol), and the mixture was heated for 6 h. After cooling to RT, hexane (100 mL) was added to the reaction mixture. The precipitate formed was filtered off, and the volatile materials were removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give 2-bromobenzylidenecyclopropane (8.88 g, 71%).

2-(2-Bromophenyl)cyclobutanone. To a solution of 2-bromobenzylidenecyclopropane (8.88 g, 42.4 mmol) in CH_2Cl_2 (250 mL) was added *m*-chloroperbenzoic acid (ca. 77%, 9.49 g, 42.4 mmol) at 0 °C. After stirring at 0 °C for 3 h, the reaction mixture washed with $NaHCO_3$ saturated aqueous solution and brine, dried over $MgSO_4$, and concentrated. To the crude product in CH_2Cl_2 (150 mL) was added a 10% HBF_4 aqueous solution. After stirring at RT for 2 h, the mixture was extracted with CH_2Cl_2, washed with saturated $NaHCO_3$ aqueous solution and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (deactivated with NEt_3, hexane:AcOEt = 8:1) to give 2-(2-bromophenyl)cyclobutanone (5.53 g, 58%).

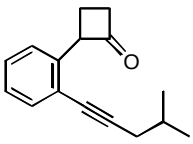
2-(2-But-1-ynylphenyl)cyclobutanone (1a). To a mixture of $PdCl_2(PhCN)_2$ (115 mg, 0.30 mmol, 6 mol%) and CuI (38 mg, 0.20 mmol, 4 mol%) in dioxane (10 mL) was added P(*t*Bu)$_3$ (134 mg, 0.66 mmol, 13 mol%), (*i*Pr)$_2$NH (1.21 g, 12.0 mmol), and 2-(2-bromophenyl)cyclobutanone (1.13 g, 5.0 mmol). After bubbling but-1-yne for 10 min, the mixture was stirred at RT for 2 days. The reaction mixture was filtered and washed with Et_2O. The filtrate was washed with saturated NH_4Cl aqueous solution and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 8:1) to give **1a** (0.55 g, 55%): ^{1}H NMR *d* 1.23 (t, *J* = 7.5 Hz, 3H), 2.24 (ddt, *J* = 11.2, 9.6, 8.4 Hz, 1H), 2.43 (q, *J* = 7.5 Hz, 2H), 2.56 (dq, *J* = 4.8, 10.7 Hz, 1H), 3.03 (dddd, *J* = 17.7, 9.5, 4.8, 2.5 Hz, 1H), 3.21 (dddd, *J* = 18.2, 9.9, 7.8, 2.1 Hz 1H), 4.81 (ddt, *J* = 10.7, 8.5, 2.2 Hz, 1H), 7.14-7.25 (m, 3H), 7.39 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR *d* 13.3, 13.8, 18.8, 45.0, 63.9, 78.4, 96.6, 123.1, 126.9, 127.1, 127.8, 132.5, 138.5, 207.9; IR (neat) 2977, 2234, 1782, 1485, 1447, 1320, 1202, 1071, 758 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{14}O$ (M^+) 198.1045, found 198.1045.

Method B:

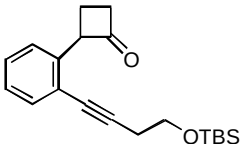


2-Pent-1-ynylbenzaldehyde. To a mixture of 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and pent-1-yne (1.36 g, 20.0 mmol) in Et_3N (15 mL) were added $Pd(PPh_3)_4$ (346 mg, 0.30 mmol, 3 mol%) and CuI (133 mg, 0.70 mmol, 7 mol%). After being heated in a sealed tube at 70 °C for 2 h, the reaction mixture was filtered and washed with Et_2O. The filtrate was washed with saturated NH_4Cl aqueous solution and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 8:1) to give 2-pent-1-ynylbenzaldehyde (1.57 g, 91%).

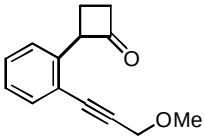
2-(2-Pent-1-ynylphenyl)cyclobutanone (1b). By using the same method as that for the synthesis of **1a**, **1b** (1.10 g, 57%, two steps) was prepared from 2-pent-1-ylbenzaldehyde (1.57 g, 9.12 mmol). ^{1}H NMR *d* 1.04 (t, *J* = 7.2 Hz, 3H), 1.63 (sext, *J* = 7.2 Hz, 2H), 2.23 (ddt, *J* = 11.0, 9.6, 8.5 Hz, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.56 (dq, *J* = 4.8, 10.7 Hz, 1H), 3.03 (dddd, *J* = 17.6, 9.7, 4.9, 2.6 Hz, 1H), 3.21 (dddd, *J* = 18.3, 9.8, 7.9, 2.0 Hz 1H), 4.83 (ddt, *J* = 10.8, 8.4, 2.3 Hz, 1H), 7.15-7.23 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR *d* 13.6, 18.9, 21.6, 22.2, 45.0, 63.9, 79.1, 95.2, 123.2, 126.9, 127.1, 127.8, 132.6, 138.5, 207.9; HRMS (EI) calcd for $C_{15}H_{16}O$ (M^+) 212.1201, found 212.1203.



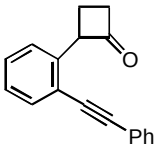
2-[2-(4-Methylpent-1-ynyl)phenyl]cyclobutanone (1c). Prepared according to Method B. ^{1}H NMR *d* 1.03 (d, *J* = 6.3 Hz, 6H), 1.91 (sept, *J* = 6.6 Hz, 1H), 2.21 (ddt, *J* = 11.0, 9.6, 8.4 Hz, 1H), 2.32 (d, *J* = 6.6 Hz, 2H), 2.56 (dq, *J* = 4.8, 10.7 Hz, 1H), 3.03 (dddd, *J* = 17.7, 9.6, 4.8, 2.4 Hz, 1H), 3.21 (dddd, *J* = 18.2, 9.9, 7.8, 2.1 Hz, 1H), 4.85 (ddt, *J* = 10.7, 8.4, 2.3 Hz, 1H), 7.14-7.25 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR *d* 18.9, 22.1, 28.2, 28.8, 45.0, 63.9, 79.8, 94.3, 123.3, 126.9, 127.0, 127.8, 132.6, 138.5, 207.9; HRMS (EI) calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1356.



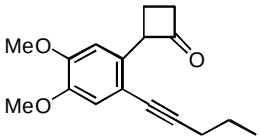
2-{2-[4-(*tert*-Butyldimethylsiloxy)but-1-ynyl]phenyl}cyclobutanone (1d). Prepared according to Method B. ^{1}H NMR *d* 0.08 (s, 6H), 0.90 (s, 9H), 2.21 (ddt, *J* = 11.1, 9.5, 8.4 Hz, 1H), 2.56 (dq, *J* = 4.9, 10.8 Hz, 1H), 2.64 (t, *J* = 7.1 Hz, 2H), 3.03 (dddd, *J* = 17.6, 9.6, 4.8, 2.6 Hz, 1H), 3.20 (dddd, *J* = 18.0, 10.1, 8.1, 2.1 Hz, 1H), 3.81 (t, *J* = 7.1 Hz, 2H), 4.83 (ddt, *J* = 10.8, 8.4, 2.2 Hz, 1H), 7.15-7.25 (m, 3H), 7.39 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR *d* –5.2, 18.3, 18.9, 24.0, 25.9, 45.0, 61.8, 63.8, 79.9, 92.1, 122.9, 126.9, 127.1, 128.0, 132.6, 138.7, 207.9; HRMS (EI) calcd for $C_{20}H_{29}O_2Si$ (M^+ + H) 329.1937, found 329.1935.



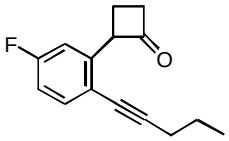
2-[2-(3-Methoxyprop-1-ynyl)phenyl]cyclobutanone (1e). Prepared according to Method B. ^{1}H NMR *d* 2.23 (ddt, *J* = 11.1, 9.5, 8.4 Hz, 1H), 2.58 (dq, *J* = 4.9, 10.8 Hz, 1H), 3.06 (dddd, *J* = 17.7, 9.6, 4.8, 2.5 Hz, 1H), 3.22 (dddd, *J* = 18.3, 9.9, 8.0, 2.0 Hz, 1H), 3.44 (s, 3H), 4.33 (s, 2H), 4.84 (ddt, *J* = 10.8, 8.4, 2.3 Hz, 1H), 7.17-7.31 (m, 3H), 7.45 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR *d* 18.8, 45.1, 57.7, 60.4, 63.7 84.6, 89.7, 121.8, 127.0, 127.2, 128.8, 132.9, 138.9, 207.6; HRMS (EI) calcd for $C_{14}H_{15}O_2$ (M^+ + H) 215.1072, found 215.1071.



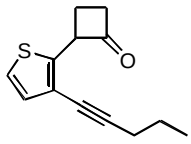
2-(2-Phenylethynylphenyl)cyclobutanone (1f). Prepared according to Method A. ^{1}H NMR *d* 2.31 (ddt, *J* = 11.1, 9.6, 8.5 Hz, 1H), 2.62 (dq, *J* = 4.9, 10.8 Hz, 1H), 3.06 (dddd, *J* = 17.7, 9.6, 4.8, 2.4 Hz, 1H), 3.23 (dddd, *J* = 17.7, 10.3, 8.0, 2.4 Hz, 1H), 4.89 (ddt, *J* = 10.7, 8.5, 2.3 Hz, 1H), 7.23-7.36 (m, 6H), 7.49-7.55 (m, 3H); ^{13}C NMR *d* 19.0, 45.0, 64.0, 87.8, 94.1, 122.3, 123.0, 127.1, 127.4, 128.38, 128.43, 128.6, 131.4, 132.6, 138.9, 207.5; HRMS (EI) calcd for $C_{18}H_{14}O$ (M^+) 246.1045, found 246.1044.



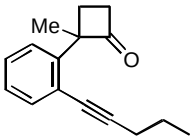
2-(4,5-Dimethoxy-2-pent-1-ynylphenyl)cyclobutanone (1g). Prepared according to Method B. ^{1}H NMR *d* 1.03 (t, *J* = 7.4 Hz, 3H), 1.62 (sext, *J* = 7.2 Hz, 2H), 2.18 (ddt, *J* = 11.0, 9.6, 8.7 Hz, 1H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.55 (dq, *J* = 4.8, 10.7 Hz, 1H), 3.00 (dddd, *J* = 17.5, 9.6, 4.7, 2.4 Hz, 1H), 3.19 (dddd, *J* = 18.4, 9.8, 7.6, 2.0 Hz, 1H), 3.92 (s, 3H), 3.94 (s, 3H), 4.75 (ddt, *J* = 10.7, 8.5, 2.3 Hz, 1H), 6.71 (s, 1H), 6.88 (s, 1H); ^{13}C NMR *d* 13.7, 19.2, 21.6, 22.3, 44.8, 55.90, 55.93, 63.6, 79.0, 93.6, 110.2, 115.0, 115.2, 131.8, 147.6, 148.7, 208.3; HRMS (EI) calcd for $C_{17}H_{20}O_3$ (M^+) 272.1412, found 272.1417.



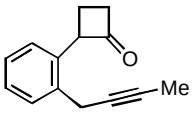
2-(5-Fluoro-2-pent-1-ynylphenyl)cyclobutanone (1h). Prepared according to Method B. ^{1}H NMR *d* 1.03 (t, *J* = 7.4 Hz, 3H), 1.62 (sext, *J* = 7.2 Hz, 2H), 2.19 (ddt, *J* = 10.7, 9.7, 8.6 Hz, 1H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.58 (dq, *J* = 4.9, 10.7 Hz, 1H), 3.03 (dddd, *J* = 17.7, 9.7, 4.9, 2.6 Hz, 1H), 3.22 (dddd, *J* = 18.4, 9.9, 7.9, 2.3 Hz 1H), 4.81 (ddt, *J* = 10.7, 8.4, 2.2 Hz, 1H), 6.86 (dt, $^{4}J_{H-H}$ = 2.4 Hz, $^{3}J_{H-H}$ = $^{3}J_{H-F}$ = 8.4 Hz, 1H), 6.96 (dd, $^{3}J_{H-F}$ = 9.9 Hz, $^{4}J_{H-H}$ = 2.7 Hz, 1H), 7.36 (dd, $^{3}J_{H-H}$ = 8.6 Hz, $^{4}J_{H-F}$ = 5.9 Hz, 1H); ^{13}C NMR *d* 13.6, 18.7, 21.5, 22.1, 45.0, 63.4, 78.1, 94.7, 114.1 (d, $^{2}J_{C-F}$ = 20.9 Hz), 114.2 (d, $^{2}J_{C-F}$ = 23.2 Hz), 119.2 (d, $^{4}J_{C-F}$ = 2.3 Hz), 134.2 (d, $^{3}J_{C-F}$ = 8.1 Hz), 140.7 (d, $^{3}J_{C-F}$ = 8.1 Hz), 161.8 (d, $^{1}J_{C-F}$ = 248.2 Hz), 206.8; HRMS (EI) calcd for $C_{15}H_{15}FO$ (M^+) 230.1107, found 230.1106.



2-(3-Pent-1-ynylthiophen-2-yl)cyclobutanone (1i). Prepared according to Method B. ^{1}H NMR *d* 1.02 (t, *J* = 7.4 Hz, 3H), 1.60 (sext, *J* = 7.2 Hz, 2H), 2.27 (ddt, *J* = 11.1, 9.5, 8.4 Hz, 1H), 2.36 (t, *J* = 6.9 Hz, 2H), 2.60 (dq, *J* = 4.8, 10.8 Hz, 1H), 3.06 (dddd, *J* = 17.6, 9.8, 4.9, 2.5 Hz, 1H), 3.23 (dddd, *J* = 18.5, 9.6, 8.0, 1.7 Hz, 1H), 4.83 (ddt, *J* = 10.6, 8.4, 2.1 Hz, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 7.06 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR *d* 13.6, 20.0, 21.5, 22.2, 45.2, 59.2, 74.8, 93.7, 121.0, 122.9, 130.2, 139.9, 205.6; HRMS (EI) calcd for $C_{13}H_{14}OS$ (M^+) 218.0765, found 218.0770.



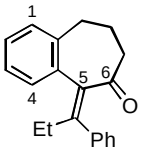
2-Methyl-2-(2-pent-1-ynylphenyl)cyclobutanone (1j). ^{1}H NMR *d* 1.05 (t, *J* = 7.4 Hz, 3H), 1.62 (s, 3H), 1.65 (sext, *J* = 7.4 Hz, 2H), 2.28 (ddd, *J* = 11.8, 9.7, 6.5 Hz, 1H), 2.42 (t, *J* = 6.9 Hz, 2H), 2.68 (ddd, *J* = 11.7, 10.4, 7.5 Hz, 1H), 3.01 (ddd, *J* = 18.0, 10.5, 6.6 Hz, 1H), 3.11 (ddd, *J* = 17.9, 9.7, 7.6 Hz, 1H), 7.11-7.21 (m, 2H), 7.39-7.44 (m, 1H), 7.47-7.51 (m, 1H); ^{13}C NMR *d* ? ? ? ? , 22.1, 23.9, 27.2, 42.6, 67.8, 79.6, 96.3, 121.8, 125.4, 126.5, 127.4, 134.0, 143.9, 212.7; HRMS (CI) calcd for $C_{16}H_{19}O$ (M^+ + H) 227.1436, found 227.1438.



2-(2-But-2-ynylphenyl)cyclobutanone (1k). ^{1}H NMR *d* 1.81 (t, *J* = 2.6 Hz, 3H), 2.18 (ddt, *J* = 11.0, 9.6, 8.4 Hz, 1H), 2.55 (dq, *J* = 5.0, 10.7 Hz, 1H), 3.02 (dddd, *J* = 17.6, 9.7, 5.0, 2.4 Hz, 1H), 3.23 (dddd, *J* = 18.2, 9.9, 7.6, 2.3 Hz, 1H), 3.48 (dq, *J* = 18.3, 2.6 Hz, 1H), 3.56 (dq, *J* = 18.3, 2.6 Hz, 1H), 4.83 (ddt, *J* = 10.6, 8.3, 2.3 Hz, 1H), 7.19-7.28 (m, 3H), 7.40-7.44 (m, 1H); ^{13}C NMR *d* 3.6 18.0, 23.3, 44.6, 61.9, 76.2, 78.3, 126.3, 127.0, 127.3, 129.1, 134.7, 135.4, 207.9; HRMS (EI) calcd for $C_{14}H_{15}O$ (M^+ + H) 199.1123, found 199.1126.

Rhodium-Catalyzed Arylative Ring-Expansion of Alkyne-Substituted Cyclobutanones 1

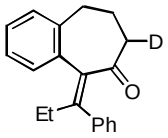
Scheme 1:



5-[(*Z*)-1-Phenylpropylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3aa). To a mixture of $[Rh(OH)(cod)]_2$ (4.6 mg, 0.010 mmol) and triphenylboroxin (62.3 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL) were added P(*t*Bu)$_3$ (8.1 mg, 0.040 mmol), **1a** (39.7 mg, 0.20 mmol), and water (10.8 mg, 0.60 mmol). After heating at 100 °C for 6 h, the reaction mixture was filtered through a pad of Florisil® (ether/AcOEt). The filtrate was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3a** (40.1 mg, 73%) as a white solid: mp 98 °C; ^{1}H NMR *d* 0.87 (t, *J* = 7.2 Hz, 3H), 1.95 (quint, *J* = 6.3 Hz, 2H), 2.30 (t, *J* = 6.6 Hz, 2H), 2.34 (q, *J* = 7.2 Hz, 2H), 2.91-2.99 (m, 2H), 7.17-7.39 (m, 9H); ^{13}C NMR *d* 12.7, 26.2, 28.2, 33.2, 44.2, 126.6, 127.1, 127.9, 128.0, 128.1, 129.1, 129.2, 136.6, 139.7, 140.1, 140.6, 146.2, 205.0; IR (neat) 2936, 1688, 1491, 1450, 1375, 1258, 1208, 911, 735cm^{-1}; HRMS (EI) calcd for

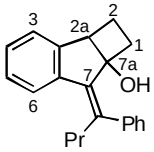
$C_{20}H_{20}O$ (M^+) 276.1514, found 276.1514. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.69; H, 7.32.

Eq. 2:



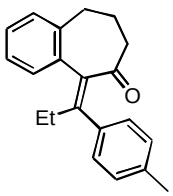
5-[(*Z*)-1-Phenylpropylidene]-5,7,8,9-tetrahydrobenzocyclohepten-7-*d*-6-one (3aa-*d*). The title compound **3aa**-*d* (36.8 mg, 66%, >87% D by ^{1}H NMR) was prepared from **1a** (39.7 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and D_2O (12.0 mg, 0.60 mmol). ^{1}H NMR *d*? 0.87 (t, *J* = 7.4 Hz, 3H), 1.94 (q, *J* = 6.0 Hz, 2H), 2.28 (t, *J* = 6.3 Hz, 1H), 2.34 (q, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 6.2 Hz, 2H), 7.18-7.39 (m, 9H); ^{13}C NMR *d*? 12.7, 26.1, 28.2, 33.1, 43.8 (t, $^1J_{C-D}$ = 19.7 Hz), 126.6, 127.1, 127.97 [overlapping], 128.03, 129.08, 129.14, 136.5, 139.7, 140.0, 140.5, 146.3, 205.1; HRMS (EI) calcd for (M^+) $C_{20}H_{19}DO$ 277.1576, found 277.1579.

Scheme 3:



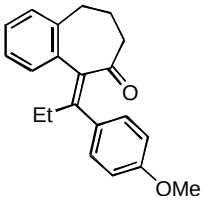
(2a*R,7a*S**)-7-[(*Z*)-1-Phenylbutylidene]-1,2,2a,7-tetrahydrocyclobuta[*a*]inden-7a-ol (5ba).** The title compound **5ba** (46.2 mg, 80%) was prepared from **1b** (42.5 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d*? 1.01 (t, *J* = 7.5 Hz, 3H), 1.47-1.64 (m, 3H), 1.82 (s, 1H), 1.98 (dddd, *J* = 12.2, 10.3, 6.1, 1.8 Hz, 1H), 2.28 (dddd, *J* = 12.3, 9.2, 6.5, 1.2 Hz, 1H), 2.47 (dddd, *J* = 11.4, 10.4, 9.2, 6.6 Hz, 1H), 2.68 (ddd, *J* = 13.3, 10.3, 6.2 Hz, 1H), 2.82 (ddd, *J* = 13.3, 10.3, 6.2 Hz, 1H), 3.48 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.20-7.34 (m, 6H), 7.34-7.42 (m, 2H), 7.60-7.67 (m, 1H); ^{13}C NMR *d*? 14.2, 20.9, 23.2, 35.3, 38.1, 49.8, 82.9, 124.8, 125.0, 126.7, 127.2, 128.1, 128.3, 128.5, 139.1, 141.1, 143.0, 143.1, 147.9; HRMS (EI) calcd for $C_{21}H_{22}O$ (M^+) 290.1671, found 290.1668.

Table 1:

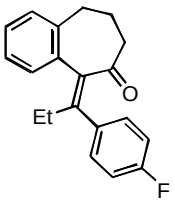


5-[(*Z*)-1-(4-Methylphenyl)propylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ab). The title compound **3ab** (41.1 mg, 71%) was prepared from **1a** (39.7 mg, 0.20 mmol), **2b** (70.8 mg, 0.20

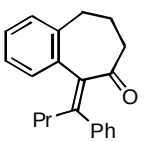
mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.86 (t, *J* = 7.4 Hz, 3H), 1.95 (quint, *J* = 6.2 Hz, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 2.32 (q, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 2.95 (t, *J* = 6.2 Hz, 2H), 7.12-7.32 (m, 8H); ^{13}C NMR *d* 12.8, 21.2, 26.2, 28.1, 33.2, 44.3, 126.6, 127.88, 127.92, 128.8, 129.06, 129.14, 136.6, 136.8, 137.4, 139.7, 139.9, 146.0, 205.3; HRMS (EI) calcd for $C_{21}H_{22}O$ (M^+) 290.1671, found 290.1670.



5-[(*Z*)-1-(4-Methoxyphenyl)propylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ac). The title compound **3ac** (43.2 mg, 70%) was prepared from **1a** (39.7 mg, 0.20 mmol), **2c** (80.4 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.86 (t, *J* = 7.5 Hz, 3H), 1.94 (quint, *J* = 5.4 Hz, 2H), 2.31 (t, *J* = 6.6 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 6.2 Hz, 2H), 3.80 (s, 3H), 6.85-6.90 (m, 2H), 7.16-7.30 (m, 6H); ^{13}C NMR *d* 12.9, 26.4, 28.0, 33.3 44.5, 55.1, 113.5, 126.6, 127.8, 129.06, 129.09, 129.3, 132.4, 136.7, 139.7, 140.0, 145.2, 158.7, 205.8; HRMS (EI) calcd for $C_{21}H_{22}O_2$ (M^+) 306.1620, found 306.1621.

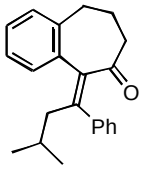


5-[(*Z*)-1-(4-Fluorophenyl)propylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ad). The title compound **3ad** (36.8 mg, 63%) was prepared from **1a** (39.7 mg, 0.20 mmol), **2d** (73.1 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.86 (t, *J* = 7.5 Hz, 3H), 1.95 (quint, *J* = 6.4 Hz, 2H), 2.30 (t, *J* = 6.5 Hz, 2H), 2.31 (q, *J* = 7.8 Hz, 2H), 2.94 (t, *J* = 6.3 Hz, 2H), 6.99-7.07 (m, 2H), 7.17-7.27 (m, 6H); ^{13}C NMR *d* 12.7, 26.1, 28.4, 33.1, 44.1, 115.1 (d, $^2J_{C-F}$ = 20.9 Hz), 126.7, 128.1, 129.1 [overlapping], 129.7 (d, $^3J_{C-F}$ = 8.1 Hz), 136.2, 136.4 (d, $^4J_{C-F}$ = 2.3 Hz), 139.6, 140.4, 145.4, 162.0 (d, $^1J_{C-F}$ = 245.9 Hz), 204.8; HRMS (EI) calcd for $C_{20}H_{19}FO$ (M^+) 294.1420, found 294.1418.

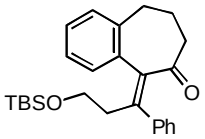


5-[(*Z*)-1-Phenylbutylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ba). The title compound **3ba** (44.6 mg, 74%) was prepared from **1b** (42.5 mg, 0.20 mmol), **2a** (62.3 mg, 0.20

mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.77 (t, *J* = 7.4 Hz, 3H), 1.28 (sext, *J* = 7.5 Hz, 2H), 1.96 (quint, *J* = 5.4 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.96 (t, *J* = 5.4 Hz, 2H), 2.96 (t, *J* = 6.2 Hz, 2H), 7.19-7.38 (m, 9H); ^{13}C NMR *d* 13.9, 21.1, 26.2, 33.2, 36.7, 44.3, 126.6, 127.1, 127.89, 127.92, 128.0, 129.1, 129.3, 136.4, 139.7, 140.68, 140.74, 144.6, 205.3; HRMS (EI) calcd for $C_{21}H_{22}O$ (M^+) 290.1671, found 290.1670.

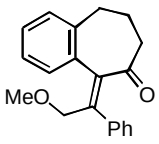


5-[(*Z*)-3-Methyl-1-phenylbutylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ca). The title compound **3ca** (46.2 mg, 76%) was prepared from **1c** (45.3 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.76 (d, *J* = 6.6 Hz, 6H), 1.47 (non, *J* = 6.6 Hz, 1H), 1.97 (br s, 2H), 2.27 (d, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 6.8 Hz, 2H), 2.97 (br s, 2H), 7.17-7.38 (m, 9H); ^{13}C NMR *d* 22.4, 26.2, 26.3, 33.4, 42.8, 44.8, 126.5, 127.2, 127.86, 127.89, 128.1, 129.1, 129.6, 136.1, 139.9, 140.5, 142.0, 143.0, 205.8; HRMS (EI) calcd for $C_{22}H_{24}O$ (M^+) 304.1827, found 304.1829.



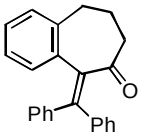
5-[(*Z*)-3-(*tert*-Butyldimethylsiloxy)-1-phenylpropylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3da). The title compound **3da** (40.3 mg, 50%) was prepared from **1d** (65.7 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* –0.11 (s, 6H), 0.81 (s, 9H), 1.88-2.02 (m, 2H), 2.30 (t, *J* = 6.6 Hz, 2H), 2.58 (t, *J* = 6.9 Hz, 2H), 2.89-3.01 (m, 2H), 3.48 (t, *J* = 6.9 Hz, 2H), 7.16-7.43 (m, 9H); ^{13}C NMR *d* –5.5, 18.3, 25.9, 26.2, 33.3, 38.0, 44.3, 60.7, 126.6, 127.2, 128.03 [overlapping], 128.06, 129.0, 129.7, 136.1, 139.7, 140.2, 141.2, 142.4, 205.1; HRMS (CI) calcd for $C_{26}H_{35}O_2Si$ (M^+ + H) 407.2406, found 407.2406.

Scheme 4:

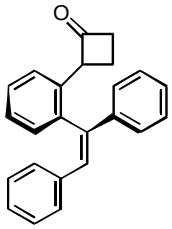


5-[(*E*)-2-Methoxy-1-phenylethylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ea). The title compound **3ea** (22.0 mg, 38%) was prepared from **1e** (42.9 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 1.92-2.14 (m, 2H), 2.38 (t, *J* = 6.8 Hz, 2H),

2.93-3.01 (m, 2H), 3.17 (s, 3H), 4.12 (s, 2H), 7.17-7.23 (m, 1H), 7.23-7.37 (m, 8H); ^{13}C NMR *d* 26.4, 33.8, 45.0, 58.3, 72.5, 126.7, 127.6, 128.2, 128.3, 128.4, 129.37, 129.41, 134.9, 138.2, 138.7, 139.7, 144.9, 205.7; HRMS (EI) calcd for $C_{20}H_{20}O_2$ (M^+) 292.1463, found 292.1459.

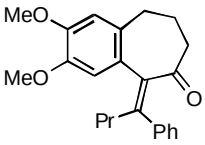


5-Diphenylmethylene-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3fa). The title compound **3fa** (17.6 mg, 27%) was prepared from **1f** (49.3 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 2.06 (quint, *J* = 6.5 Hz, 2H), 2.43 (t, *J* = 6.8 Hz, 2H), 3.00-3.07 (m, 2H), 6.84-6.95 (m, 4H), 7.04-7.17 (m, 5H), 7.24-7.34 (m, 5H); ^{13}C NMR *d* 27.3, 33.8, 44.0, 126.6 127.4, 127.68 [overlapping], 127.74, 128.0, 129.0, 129.7, 130.4, 130.8, 137.0, 140.0, 141.0, 141.1, 141.4, 143.8, 206.1; HRMS (EI) calcd for $C_{24}H_{20}O$ (M^+) 324.1514, found 324.1514.



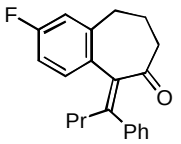
2-{2-[(*Z*)-1,2-Diphenylvinyl]phenyl}cyclobutanone (8fa). This compound was obtained as a byproduct (26%, a mixture of atropisomers) from the reaction of **1f** and **2a**. ^{1}H NMR *d* 1.60-1.94 (m, 2H), 2.76-3.03 (m, 2H), 4.33-4.43 (m, 1H), 6.90-7.00 (m, 2H), 7.08-7.19 (m, 5H), 7.22-7.42 (m, 8H); ^{13}C NMR *d* 20.0, 20.2, 44.9, 45.0, 62.2, 62.7, 126.6, 126.7, 127.2, 127.5, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.9, 129.1, 129.3, 130.7, 130.8, 136.0, 136.7, 136.9, 138.97, 139.02, 140.4, 141.9, 142.6, 208.8, 209.0.

Table 2:

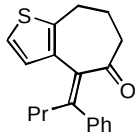


2,3-Dimethoxy-5-[(*Z*)-1-phenylbutylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ga). The title compound **3ga** (47.0 mg, 67%) was prepared from **1g** (54.5 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.78 (t, *J* = 7.4 Hz, 3H), 1.29 (sext, *J* = 6.6 Hz, 2H), 1.95 (quint, *J* = 5.8 Hz, 2H), 2.26-2.36 (m, 4H), 2.88 (t, *J* = 5.9 Hz, 2H), 3.87 (s, 3H), 3.88 (s, 3H), 6.69 (s, 1H), 6.80 (s, 1H), 7.21-7.36 (m, 5H); ^{13}C NMR *d* 14.0, 21.3, 26.4, 33.2, 36.5, 44.5,

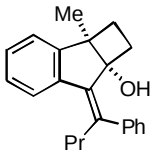
55.9, 56.0, 112.46, 112.54, 127.1, 127.8, 127.9, 128.0, 132.1, 140.5, 140.8, 143.4, 147.2, 148.2, 206.1; HRMS (EI) calcd for $C_{23}H_{26}O_3$ (M^+) 350.1882, found 350.1882.



2-Fluoro-5-[(*Z*)-1-phenylbutylidene]-5,7,8,9-tetrahydrobenzocyclohepten-6-one (3ha). The title compound **3ha** (35.2 mg, 58%) was prepared from **1h** (46.1 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.76 (t, *J* = 7.4 Hz, 3H), 1.26 (sext, *J* = 7.5 Hz, 2H), 1.95 (quint, *J* = 5.7 Hz, 2H), 2.24-2.32 (m, 4H), 2.93 (t, *J* = 6.2 Hz, 2H), 6.89-7.00 (m, 2H), 7.20-7.37 (m, 6H); ^{13}C NMR *d* 14.0, 21.1, 25.9, 33.2, 36.8, 44.1, 113.3 (d, $^2J_{C-F}$ = 20.9 Hz), 116.0 (d, $^2J_{C-F}$ = 22.0 Hz), 127.2, 127.8, 128.1, 130.9 (d, $^3J_{C-F}$ = 8.1 Hz), 132.3 (d, $^4J_{C-F}$ = 3.5 Hz), 139.7, 140.5, 142.2 (d, $^3J_{C-F}$ = 6.9 Hz), 145.4, 162.2 (d, $^1J_{C-F}$ = 247.0 Hz), 204.9; HRMS (EI) calcd for $C_{21}H_{21}FO$ (M^+) 308.1576, found 308.1573.

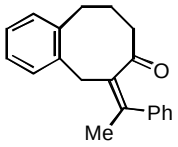


4-[(*Z*)-1-Phenylbutylidene]-4,6,7,8-tetrahydrocyclohepta[*b*]thiophen-5-one (3ia). The title compound **3ia** (42.4 mg, 72%) was prepared from **1i** (43.7 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 0.81 (t, *J* = 7.4 Hz, 3H), 1.30 (sext, *J* = 7.5 Hz, 2H), 2.22 (quint, *J* = 6.0 Hz, 2H), 2.37-2.44 (m, 2H), 2.44-2.52 (m, 2H), 3.07 (t, *J* = 6.0 Hz, 2H), 6.89 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 5.4 Hz, 1H), 7.17-7.34 (m, 5H); ^{13}C NMR *d* 13.9, 21.0, 22.8, 29.1, 36.1, 43.2, 122.8, 127.2, 127.8, 128.0, 129.2, 131.1, 136.1, 139.2, 140.3, 141.8, 206.3; HRMS (EI) calcd for $C_{19}H_{20}OS$ (M^+) 296.1235, found 296.1234.



(2a*R,7a*S**)-2a-Methyl-7-[(*Z*)-1-phenylbutylidene]-1,2,2a,7-tetrahydrocyclobuta[*a*]inden-7a-ol (5ja).** The title compound **5ja** (38.6 mg, 63%) was prepared from **1j** (45.3 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 1.01 (t, *J* = 7.4 Hz, 3H), 1.29 (s, 3H), 1.48-1.65 (m, 2H), 1.62 (s, 1H), 1.72 (ddd, *J* = 10.5, 9.0, 5.3 Hz, 1H), 1.86-2.08 (m, 2H), 2.20 (ddd, *J* = 11.4, 9.0, 6.2 Hz, 1H), 2.66 (ddd, *J* = 13.4, 10.6, 6.0 Hz, 1H), 2.85 (ddd, *J* = 13.4, 10.6, 6.0 Hz, 1H), 7.23-7.34 (m, 6H), 7.34-7.40 (m, 2H), 7.59-7.66 (m, 1H); ^{13}C NMR *d* 14.2, 19.3, 21.0, 31.2,

33.8, 38.2, 51.5, 83.1, 123.5, 124.7, 126.8, 127.1, 128.17, 128.22, 128.7, 139.0, 140.0, 142.8, 143.2, 152.4; IR (neat) 3567, 2961, 1471, 1456, 1159, 911, 706 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{24}O$ (M^+) 304.1827, found 304.1828.



6-[(*Z*)-1-Phenylethylidene]-5,8,9,10-tetrahydrobenzocycloocten-7(6*H*)-one (3ka). The title compound **3ka** (9.5 mg, 17%) was prepared from **1k** (39.7 mg, 0.20 mmol), **2a** (62.3 mg, 0.20 mmol), and H_2O (10.8 mg, 0.60 mmol). ^{1}H NMR *d* 1.74-1.84 (m, 2H), 2.15-2.21 (m, 2H), 2.20 (s, 3H), 2.73-2.79 (m, 2H), 3.78 (s, 2H), 7.06-7.26 (m, 9H); ^{13}C NMR *d* 20.3, 26.6, 32.4, 34.5, 42.1, 126.9, 127.1, 127.2, 127.7, 128.1, 129.9, 130.2, 133.5, 137.5, 139.9, 141.9, 142.7, 212.0; HRMS (EI) calcd for $C_{20}H_{20}O$ (M^+) 276.1514, found 276.1517.