

Supporting Information

Experimental Section

General. All reactions involving air sensitive compounds were carried out under a N₂ atmosphere (99.99%). All glassware was oven-dried (120°C), evacuated and purged with nitrogen. All common reagents and solvents were obtained from commercial suppliers and used without any further purification unless otherwise indicated. Fischer carbene complexes¹ and fulvenes² were prepared following described procedures. Solvents were dried by standard methods and distilled prior to use. Flash column chromatography was carried out on silica gel 60, 230-240 mesh. NMR experiments were carried out on a Bruker AC-300 spectrometer. ¹H NMR spectra were recorded in CDCl₃ at 300.08 MHz at 20°C with tetramethylsilane (δ = 0.0) as the internal standard. ¹³C spectra were recorded in CDCl₃ at 75.46 MHz at 20°C. ¹H NMR splitting pattern abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ¹³C NMR multiplicities were determined by DEPT, abbreviations are: q, CH₃; t, CH₂; d, CH; s, quaternary carbons. NOESY experiments were carried out on a Bruker AMX-400 spectrometer. Standard pulse sequences were employed for the DEPT experiments. In some cases the spectra data is given for the mixture of unseparable tautomers or diastereoisomers (several signals are coincidental). High resolution mass spectra (HRMS) were obtained with a Finnigan Mat95 Mass Spectrometer, electron impact techniques (70 eV) were employed. Elemental analyses were carried out with a Perkin-Elmer 240 B microanalyzer.

Synthesis of indenenes 3a-e. General Procedure. A mixture of the carbene complex **1a-e** (1 mmol) and 6-acetoxyfulvene **2** (1.5 mmol) in MeCN (toluene for **3d-e**) (15 mL) was heated at 80°C (at 100-120°C for **3d-e**) for 8 h. Then the solvent was removed under vacuum, the crude product dissolved in a mixture of hexane/EtOAc (1:1) and air oxidized in an open flask under sunlight or lamp light (6-8 h). The solution was then filtered over Celite and the filtrate concentrated under vacuum. The resulting crude was purified by column chromatography (hexanes/EtOAc, 5:1).

5-(2-Furyl)-7-methoxy-1H-indene / 6-(2-furyl)-4-methoxy-1H-indene (3a): Obtained as a 1:1 mixture of isomers; yield = 75%; ¹H NMR: δ = 3.4 (m, 2H), 3.5 (m, 2H), 3.95 (s, 3H), 4.0 (s, 3H), 6.4-6.5 (m, 3H), 6.6-7.7 (m, 3H), 6.9 (m, 1H), 7.0 (m, 1H), 7.1 (m, 2H), 7.4 (m, 1H), 7.5 (m, 1H), 7.55 (m, 2H); ¹³C NMR: δ = 36.4 (t), 39.5 (t), 52.2 (q), 55.4 (q), 103.0 (d), 104.1 (d), 104.3 (d), 104.5 (d), 109.9 (d), 111.5 (d), 111.6 (d), 112.5 (d), 128.1 (d), 128.9 (s), 129.8 (s), 131.0 (s), 131.6 (d), 132.7 (d), 132.9 (s), 134.9 (d), 141.5 (d), 146.0 (s), 146.9 (s), 153.0 (s), 154.5 (s), 154.6 (s), 155.3 (s); HRMS *m/z* calcd for C₁₄H₁₂O₂ 212.0837; found 212.0833. Anal. Calcd for C₁₄H₁₂O₂: C 79.21, H 5.70. Found: C 79.09, H 5.73.

7-Methoxy-5-phenyl-1H-indene / 4-methoxy-6-phenyl-1H-indene (3b): Obtained as a 2:1 mixture of isomers; yield = 72%; ¹H NMR: δ = 3.4 (t, *J* = 2.0 Hz, 2H), 3.5 (m, 2H), 3.9 (s, 3H), 3.95 (s, 3H), 6.5 (dt, *J* = 5.7, 2.0 Hz, 1H), 6.6 (dt, *J* = 5.4, 2.0 Hz, 1H), 6.9 (dt, *J* = 5.4, 2.0 Hz, 1H), 6.95 (m, 1H), 7.05 (m, 1H), 7.1 (m, 1H), 7.2 (m, 1H), 7.3 (m, 1H), 7.3-7.7 (m, 10H); ¹³C NMR: δ = 36.3 (t), 39.6 (t), 55.3 (q), 55.4 (q), 106.6 (d), 107.7 (d), 113.2 (d), 115.7 (d), 126.9 (d), 127.0 (d), 127.2 (d), 127.3 (d), 128.0 (d), 128.6 (d), 129.5 (s), 131.8 (d), 132.6 (d), 134.9 (d), 139.5 (s), 141.8 (s), 141.9 (s), 142.0

(s), 146.2 (s), 147.1 (s), 153.1 (s), 155.3 (s); HRMS m/z calcd for $C_{16}H_{14}O$ 222.1045; found 222.1044. Anal. Calcd for $C_{16}H_{14}O$: C 86.45, H 6.35. Found: C 86.53, H 6.28.

7-(2-Iodoethoxy)-5-phenyl-1H-indene / 4-(2-iodoethoxy)-6-phenyl-1H-indene (3c): Obtained as a 1:1 mixture of isomers; yield = 69%; 1H NMR: δ = 3.5 (m, 8H), 4.4 (m, 4H), 6.5 (dt, J = 5.4, 2.0 Hz, 1H), 6.6 (dt, J = 5.4, 2.0 Hz, 1H), 6.9 (m, 2H), 7.0 (m, 1H), 7.1 (m, 1H), 7.2-7.6 (m, 12H); ^{13}C NMR: δ = 1.5 (t), 1.7 (t), 36.5 (t), 40.0 (t), 69.1 (t), 68.7 (t), 108.1 (d), 109.6 (d), 113.9 (d), 116.6 (d), 127.0 (d), 127.1 (d), 127.2 (d), 127.3 (d), 128.1 (d), 128.3 (d), 128.6 (d), 130.2 (s), 131.8 (d), 133.0 (d), 133.3 (s), 135.1 (d), 139.6 (s), 141.6 (s), 141.7 (s), 141.9 (s), 146.5 (s), 147.4 (s), 151.38 (s), 153.7 (s); HRMS m/z calcd for $C_{17}H_{15}IO$ 362.0168; found 362.0170. Anal. Calcd for $C_{17}H_{15}IO$: C 56.37, H 4.17. Found: C 56.41, H 4.13.

5-Ethoxycarbonyl-7-(N-pyrrolidinyl)-1H-indene / 6-ethoxycarbonyl-4-(N-pyrrolidinyl)-1H-indene (3d): Obtained as a 1.2:1 mixture of isomers; yield = 69%; 1H NMR: (major isomer) δ = 1.4 (t, J = 7.0 Hz, 3H), 2.0 (m, 4H), 3.5-3.6 (m, 4H), 3.7 (m, 2H), 4.3 (q, J = 7.0 Hz, 2H), 6.5 (m, 1H), 6.8 (dt, J = 5.7, 1.7 Hz, 1H), 7.2 (m, 1H), 7.5 (m, 1H); (minor isomer): δ = 1.4 (t, J = 7.0 Hz, 3H), 2.0 (m, 4H), 3.4 (m, 2H), 3.5 (m, 4H), 4.3 (q, J = 7.0 Hz, 2H), 6.5 (m, 1H), 7.2 (m, 1H), 7.2 (m, 1H), 7.6 (m, 1H); ^{13}C NMR: (mixture of isomers) δ = 14.3 (q), 25.3 (t), 25.7 (t), 39.0 (t), 40.5 (t), 49.5 (t), 50.6 (t), 60.6 (t), 111.2 (d), 112.1 (d), 114.3 (d), 127.5 (s), 129.8 (s), 131.8 (d), 131.9 (d), 132.3 (s), 133.2 (d), 134.0 (d), 145.3 (s), 146.0 (s), 146.7 (s), 167.6 (s); HRMS m/z calcd for $C_{16}H_{19}NO_2$ 257.1416; found 257.1405. Anal. Calcd for $C_{16}H_{19}NO_2$: C 74.67, H 7.45, N 5.45. Found: C 74.74, H 7.39, N 5.40.

7-Dimethylamino-5-phenyl-1H-indene / 4-dimethylamino-6-phenyl-1H-indene (3e): Obtained as a 2:1 mixture of separable isomers; yield = 65%; 1H NMR: (major isomer) δ = 2.95 (s, 6H), 3.5 (m, 2H), 6.5 (dt, J = 5.6, 2.0 Hz, 1H), 7.0 (s, 1H), 7.1 (m, 1H), 7.3-7.5 (m, 4H), 7.6 (m, 2H); (minor isomer) δ = 3.0 (s, 6H), 3.5 (m, 2H), 6.6 (dt, J = 5.4, 2.1 Hz, 1H), 6.9 (dt, J = 5.6, 2.1 Hz, 1H), 7.0 (m, 1H), 7.3-7.5 (m, 4H), 7.6-7.7 (m, 2H); ^{13}C NMR: (major isomer) δ = 39.5 (t), 44.0 (q), 113.5 (d), 116.3 (d), 126.8 (d), 127.2 (d), 128.6 (d), 130.2 (d), 132.7 (d), 135.5 (s), 138.9 (s), 142.0 (s), 146.1 (s), 167.0 (s); (minor isomer) δ = 39.1 (t), 43.0 (q), 112.6 (d), 113.5 (d), 126.9 (d), 127.3 (d), 128.5 (d), 130.2 (s), 132.0 (d), 134.2 (d), 141.1 (s), 142.2 (s), 147.1 (s), 167.1 (s); HRMS m/z calcd for $C_{17}H_{17}N$ 235.1361; found 235.1358. Anal. Calcd for $C_{17}H_{17}N$: C 86.77, H 7.28, N 5.95. Found: C 86.93, H 7.33, N 5.91.

Synthesis of 5-phenyl-1H-inden-7-ol / 6-phenyl-1H-inden-4-ol (4). Indene 3c (180 mg, 0.5 mmol) was dissolved in THF (5 mL) and *t*-BuLi (1 mL, 1.5 mmol, 1.5 N solution in hexanes) was added at $-78^\circ C$. The mixture was stirred at the same temperature for 30 minutes and then it was quenched with water and extracted with ether. The solvent was removed under vacuum and the crude was purified by column chromatography (hexanes/EtOAc, 1:1) to yield indenol 4 as a 2:1 mixture of isomers; yield = 98%; 1H NMR: δ = 3.4 (m, 2H), 3.5 (m, 2H), 4.8-5.2 (brs, 2H), 6.5 (m, 1H), 6.6 (m, 1H), 6.9-7.6 (m, 16H); ^{13}C NMR: δ = 35.6 (t), 39.6 (t), 111.1 (d), 113.3 (d), 113.6 (d), 115.9 (d), 127.0 (d), 127.1 (d), 127.2 (d), 128.6 (d), 132.1 (d), 133.0 (d), 133.3 (d), 134.5 (d), 139.5 (s), 141.2 (s), 141.3 (s), 141.9 (s), 146.7 (s), 147.6 (s), 148.7 (s), 151.2 (s); HRMS m/z calcd for $C_{15}H_{12}O$ 208.0888; found 208.0881. Anal. Calcd for $C_{15}H_{12}O$: C 86.51, H 5.81. Found: C 86.59, H 5.76.

Synthesis of indanones 7. General Procedure. A mixture of the carbene complex **1a,b** (1 mmol) and the corresponding fulvene **5** (1.5 mmol) in MeCN (15 mL) was heated at 80°C for 8 h. Then the solvent was removed under vacuum, the crude product dissolved in a mixture of hexane/EtOAc (1:1) and air oxidized in an open flask under sunlight or lamp light (6-8 h). Then the solution was filtered over Celite and the filtrate concentrated under vacuum. The resulting crude was then dissolved in CH₂Cl₂ (10 mL) and 1N HCl (5mL) was added. The mixture was stirred at 20°C for 2 h and then extracted with CH₂Cl₂. After solvent removal the crude was purified by column chromatography (hexanes/EtOAc, 5:1).

6-(2-Furyl)-3,5,6,7-tetrahydro-7,7-dimethyl-4H-inden-4-one (7a): Yield = 80%; ¹H NMR: δ = 1.0 (s, 3H), 1.3 (s, 3H), 2.5 (dd, J = 17.1, 4.0 Hz, 1H), 2.9 (dd, J = 17.1, 13.1 Hz, 1H), 3.3 (m, 2H), 3.4 (dd, J = 13.1, 4.0 Hz, 1H), 6.0 (d, J = 2.8 Hz, 1H), 6.3 (m, 1H), 6.6 (m, 1H), 6.8 (m, 1H), 7.3 (m, 1H); ¹³C NMR: δ = 22.3 (q), 26.4 (q), 36.8 (s), 38.7 (t), 39.0 (t), 45.5 (d), 107.2 (d), 109.9 (d), 131.7 (d), 136.2 (s), 141.2 (d), 142.3 (d), 154.7 (s), 171.5 (s), 193.1 (s); HRMS m/z calcd for C₁₅H₁₆O₂ 228.1150; found 228.1154. Anal. Calcd for C₁₅H₁₆O₂: C 78.92, H 7.06. Found: C 78.80, H 7.12.

3,5,6,7-Tetrahydro-7,7-dimethyl-6-phenyl-4H-inden-4-one (7b): Yield = 74%; ¹H NMR: δ = 1.1 (s, 3H), 1.2 (s, 3H), 2.5 (dd, J = 16.8, 3.7 Hz, 1H), 3.0 (dd, J = 16.8, 13.7 Hz, 1H), 3.3 (dd, J = 13.7, 3.7 Hz, 1H), 3.35 (m, 2H), 6.7 (m, 1H), 6.8 (m, 1H), 7.1-7.4 (m, 5H); ¹³C NMR: δ = 21.6 (q), 26.1 (q), 36.9 (s), 38.8 (t), 40.8 (t), 52.0 (d), 126.9 (d), 127.9 (d), 129.4 (d), 131.8 (d), 136.4 (s), 139.9 (s), 142.3 (d), 171.9 (s), 194.3 (s); HRMS m/z calcd for C₁₇H₁₈O 238.1358; found 238.1360. Anal. Calcd for C₁₇H₁₈O: C 85.67, H 7.61. Found: C 85.56, H 7.70.

cis/trans 6-(2-Furyl)-3,5,6,7-tetrahydro-7-isopropyl-4H-inden-4-one (7c): Obtained as a 1:1 mixture of diastereoisomers; yield = 70%; ¹H NMR: δ = 0.7 (d, J = 6.9 Hz, 3H), 0.8 (d, J = 6.9 Hz, 3H), 1.0 (d, J = 6.7 Hz, 3H), 1.1 (d, J = 6.7 Hz, 3H), 1.8 (m, 1H), 2.1 (m, 1H), 2.7-3.1 (m, 6H), 3.2 (m, 2H), 3.4 (m, 2H), 3.6-3.8 (m, 2H), 5.9 (d, J = 3.1 Hz, 1H), 6.1 (d, J = 3.1 Hz, 1H), 6.2 (m, 1H), 6.4 (m, 1H), 6.6 (m, 2H), 6.8 (m, 2H), 7.4 (m, 2H); ¹³C NMR: δ = 20.3 (q), 21.1 (q), 21.2 (q), 23.2 (q), 28.6 (d), 31.1 (d), 37.3 (d), 38.1 (t), 38.4 (t), 39.1 (d), 39.2 (t), 44.7 (d), 46.0 (d), 105.2 (d), 105.8 (d), 110.0 (d), 110.1 (d), 135.0 (d), 135.3 (d), 138.4 (s), 139.5 (s), 140.9 (d), 141.1 (d), 141.2 (d), 155.8 (s), 157.2 (s), 164.9 (s), 165.6 (s), 192.7 (s), 193.3 (s); HRMS m/z calcd for C₁₆H₁₈O₂ 242.1307; found 242.1308. Anal. Calcd for C₁₆H₁₈O₂: C 79.31, H 7.49. Found: C 79.18, H 7.44.

cis/trans 6-(2-Furyl)-3,5,6,7-tetrahydro-7-[(E)-2-phenylethenyl]-4H-inden-4-one (7d): Obtained as a 1:1 mixture of diastereoisomers; yield = 71%; ¹H NMR: δ = 2.7 (dd, J = 17.0, 3.9 Hz, 1H), 2.8 (m, 1H), 2.85 (m, 1H), 2.8-2.9 (m, 1H), 3.3-3.45 (m, 4H), 3.5-3.6 (m, 1H), 3.7-3.9 (m, 3H), 5.9 (dd, J = 16.0, 7.2 Hz, 1H), 6.05 (m, 2H), 6.1-6.25 (m, 3H), 6.3 (m, 1H), 6.4 (d, J = 16 Hz, 1H), 6.6 (m, 2H), 6.8 (m, 1H), 6.9 (m, 1H), 7.2-7.4 (m, 12H); ¹³C NMR: δ = 37.3 (t), 38.7 (t), 39.0 (t), 39.5 (d), 41.0 (t), 41.9 (d), 42.4 (d), 44.2 (d), 106.0 (d), 110.0 (d), 110.1 (d), 125.1 (d), 126.2 (d), 126.25 (d), 126.4 (d), 127.5 (d), 127.6 (d), 128.1 (d), 128.4 (d), 128.5 (d), 133.3 (d), 133.4 (d), 133.8 (d), 133.9 (d), 136.6 (s), 136.6 (s), 138.6 (s), 140.0 (s), 141.2 (d), 141.5 (d), 141.9 (d), 142.2 (d), 155.0 (s), 155.3 (s), 163.5 (s), 164.2 (s), 192.6 (s), 192.9 (s); HRMS m/z calcd for C₂₁H₁₈O₂ 302.1307; found 302.1302. Anal. Calcd for C₂₁H₁₈O₂: C 83.42, H 6.00. Found C 83.54, H 6.11.

cis/trans 6-(2-Furyl)-3,5,6,7-tetrahydro-7-(2-methoxycarbonyl-ethyl)-7-methyl-4H-inden-4-one (7e): Obtained as a 1:1 mixture of diastereoisomers; yield = 75%; ^1H NMR: δ = 1.1 (s, 3H), 1.3 (s, 3H), 1.7 (m, 2H), 1.9-2.2 (m, 6H), 2.5-2.7 (m, 2H), 2.9-3.1 (m, 2H), 3.3 (m, 4H), 3.4-3.6 (m, 2H), 3.6 (s, 3H), 3.7 (s, 3H), 6.1 (m, 2H), 6.3 (m, 2H), 6.6 (m, 2H), 6.8-6.9 (m, 2H), 7.3 (m, 2H); ^{13}C NMR: δ = 22.3 (q), 23.8 (q), 29.4 (t), 29.6 (t), 30.8 (t), 32.7 (t), 38.7 (t), 38.9 (t), 39.0 (t), 39.3 (s), 40.0 (s), 40.5 (d), 46.0 (d), 51.6 (q), 51.7 (q), 107.3 (d), 107.8 (d), 110.0 (d), 110.1 (d), 131.2 (d), 132.7 (d), 137.8 (s), 138.4 (s), 141.4 (d), 141.5 (d), 142.0 (d), 143.0 (d), 153.9 (s), 154.0 (s), 168.9 (s), 169.2 (s), 173.5 (s), 173.6 (s), 192.7 (s), 192.8 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$: C 71.98, H 6.71. Found: C 71.87, H 6.75.

Synthesis of 7-acetoxy-5-(2-furyl)-5,6-dihydro-4,4-dimethyl-4H-indene (8). To a suspension of KH (120 mg, 3 mmol) in dimethoxyethane (15 mL) cooled at 0°C , a solution of the indanone 7a (228 mg, 1 mmol) in dimethoxyethane (5 mL) was added. After stirring at the same temperature for 1/2 h acetylchloride (0.9 mL, 1.2 mmol) was added. The mixture was stirred at 20°C for 2 h and then hydrolyzed with aq. sat. NaHCO_3 and extracted with CH_2Cl_2 . After work-up the solvent was removed under vacuum and the crude was purified by column chromatography (hexanes/EtOAc, 5:1) to yield pure compound 8 as a yellow oil; yield = 96%; ^1H NMR: δ = 1.1 (s, 3H), 1.2 (s, 3H), 2.2 (s, 3H), 2.6 (dd, J = 17.6, 3.4 Hz, 1H), 3.1-3.3 (m, 2H), 6.05 (m, 2H), 6.2 (dd, J = 5.4, 1.2 Hz, 1H), 6.3 (m, 1H), 6.4 (dd, J = 5.4, 2.0 Hz, 1H), 7.3 (m, 1H); ^{13}C NMR: δ = 20.9 (q), 24.3 (q), 26.5 (q), 31.8 (t), 35.6 (s), 47.8 (d), 106.8 (d), 109.9 (d), 114.5 (d), 121.6 (d), 130.6 (s), 132.6 (d), 140.8 (d), 145.9 (s), 153.1 (s), 155.3 (s), 168.0 (s); HRMS m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$ 270.1256; found 270.1259. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$: C 75.52, H 6.72. Found: C 75.49, H 6.75.

Synthesis of 4,6-bis(2-furyl)-1,3,4,5-tetrahydro-8-methoxy-3,3-dimethylacenaphthylene (9). A mixture of the carbene complex 1a (164 mg, 0.5 mmol) and fulvene 8 (136 mg, 0.5 mmol) in MeCN (10 mL) was heated at 100°C in a sealed tube for 8 h. The solvent was then removed under vacuum and the crude purified by column chromatography (hexanes/EtOAc, 20:1) to give compound 9 as a yellow oil; yield = 50%; ^1H NMR: δ = 1.1 (s, 3H), 1.3 (s, 3H), 3.0 (dd, J = 10.3, 4.5 Hz, 1H), 3.2 (dd, J = 17.0, 4.5 Hz, 1H), 3.3 (dd, J = 17.0, 10.3 Hz, 1H), 3.4 (m, 2H), 4.0 (s, 3H), 6.0 (m, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 6.5 (m, 1H), 6.55 (m, 1H), 7.1 (s, 1H), 7.3 (m, 1H), 7.5 (m, 1H); ^{13}C NMR: δ = 23.8 (q), 26.6 (q), 29.3 (t), 35.9 (t), 36.0 (s), 45.5 (d), 55.4 (q), 106.1 (d), 106.2 (d), 108.1 (d), 109.9 (d), 111.3 (d), 120.0 (s), 122.8 (d), 128.3 (s), 128.7 (s), 140.5 (d), 141.4 (d), 144.3 (s), 150.5 (s), 153.1 (s), 153.7 (s), 156.9 (s); HRMS m/z calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3$ 346.1569; found 346.1567. Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3$: C 79.73, H 6.40. Found: C 79.64, H 6.45.

(1) (a) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645. (b) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

(2) (a) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. (b) Erden, I.; Xu, F. P.; Sadoun, A.; Smith, W.; Sheff, G.; Ossun, M. *J. Org. Chem.* **1995**, *60*, 813.