**Anomalous Reaction of Rh₂(OAc)₄-Generated Transient Carbonyl Ylides:
Chemoselective Syntheses of Epoxy-bridged Tetrahydropyranone,
Oxepanone, Oxocinone, and Oxoninone Ring Systems**

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Experimental Section

General Procedure. The melting points are uncorrected. The FT-IR spectra were recorded using KBr method. ^1H NMR and ^{13}C NMR spectra (200 MHz and 50.3 MHz, respectively) were referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Mass analyses were performed with an ionizing voltage of 70 eV methods unless otherwise stated. All reactions were carried out under an argon atmosphere and glasswares were dried in an oven before using for catalytic diazo decomposition reaction. Dry solvents have freshly been prepared for every reaction. Analytical thin layer chromatography (TLC) was performed on alumina plates and components were visualized by observation under iodine and UV-Light. Column chromatography was performed on a silica gel (100-200 mesh) column.

General Procedure for the Rhodium(II)-Catalyzed Cycloaddition Reaction of α -Diazo Ketones with α,β -Unsaturated Ketones. To an oven-dried flask containing an anhydrous dichloromethane solution (dried over phosphorous pentoxide) of the appropriate α -diazo ketone (1.1 mmol) and an appropriate α,β -unsaturated ketone (1 mmol) was added 0.5 to 1.0 mol% of rhodium(II) acetate dimer catalyst under an argon atmosphere at room temperature. The progress of the reaction was monitored by TLC until the disappearance of the starting diazo ketones. The solvent was removed under reduced pressure and the resulting residue purified using silica gel/neutral alumina column chromatography (EtOAc-hexane mixture as eluent) to afford the respective epoxy-bridged spirocycles.

Reaction of α -Diazo Ketone **8a with (2*E*)-2-Benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (**16**), Preparation of Compounds **17b** and **18b**.**

A mixture of **16** (190 mg, 0.81 mmol) and α -diazo ketone **8a** (145 mg, 0.81 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (3.6 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (15 mL) for 3.5 h according to the general procedure to afford the diastereomers **17b** and **18b** in 21% (65 mg) and 33% (102 mg) yield, respectively. **17b**: Colorless solid; mp 229-231 °C (CHCl_3 /hexane); IR (KBr) 2939, 2862, 1770, 1630, 1600, 1452, 1376, 1280, 1226, 1030, 1007 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.55 (d, $J=8.0$ Hz, 1H), 7.41-6.97 (m, 8H), 6.87 (s, 1H), 4.54 (s, 1H), 3.02-2.80 (m, 4H), 2.30-1.24 (m, 8H), 1.23 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.2, 141.1, 137.7, 137.5, 134.3, 129.7, 129.4, 128.8, 128.7, 127.6, 126.8, 126.6, 125.6, 114.8, 88.8, 86.2, 54.0, 33.4, 29.6, 27.3, 25.0, 24.0, 20.9, 15.5; MS (FD^+) m/z 386 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_3$: C, 80.80; H, 6.79. Found: C, 80.62; H, 6.73. **18b**: Colorless solid; mp 226-228 °C (CHCl_3 /hexane); IR (KBr) 2936, 2866, 1770, 1630, 1595, 1452, 1377, 1289, 1228, 1049, 1009, 986 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.55-7.32 (m, 1H), 7.30-7.12 (m, 8H), 6.79 (s, 1H), 4.80 (s, 1H), 3.03-2.84 (m, 4H), 2.27-1.39 (m, 8H), 1.34 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 211.7, 137.7, 137.6, 136.9, 129.0, 128.4, 128.1, 127.9, 127.6, 126.5, 126.3, 125.5, 124.0, 113.4, 86.0, 84.1, 53.7, 32.7, 27.6, 26.7, 25.1, 23.0, 19.9, 14.4; MS (EI, 70 eV) m/z 386 (3), 276 (32), 235 (66), 123 (100), 95 (31), 91 (29), 41 (21%). Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_3$: C, 80.80; H, 6.79. Found: C, 80.66; H, 6.77.

Reaction of α -Diazo Ketone **8a with (2*E*)-2-(4-Chlorobenzylidene)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (**16**), Preparation of Compounds **17d** and **18d**.** A

mixture of **16** (240 mg, 0.81 mmol) and α -diazo ketone **8a** (145 mg, 0.81 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (2.9 mg, 0.8 mol%) in anhydrous CH_2Cl_2 (12 mL) for 2.5 h according to the general procedure to afford the diastereomers **17d** and **18d** in 40% (145 mg) and 20% (72 mg) yield, respectively. **17d**: Colorless solid; mp 187-189 °C (CH_2Cl_2 /hexane); IR (KBr) 2940, 1761, 1615, 1577, 1490, 1372, 1268, 1238, 1093 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.44 (d, $J = 8.6$ Hz, 1H), 7.26 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.81-6.76 (m, 2H), 6.60 (d, $J = 2.5$ Hz, 1H), 4.57 (s, 1H), 3.75 (s, 3H), 2.98-2.86 (m, 2H), 2.61-2.36 (m, 2H), 2.08-1.23 (m, 8H), 1.21 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.3, 160.0, 138.3, 137.3, 135.9, 133.0, 122.9, 130.7, 128.9, 127.8, 123.9, 114.5, 113.7, 112.4, 88.8, 85.7, 55.8, 53.7, 33.0, 29.8, 27.0, 24.8, 23.6, 20.6, 15.2; MS (EI, 70 eV) m/z 450 (4, M^+), 341 (6), 311 (8), 301 (8), 300 (14), 298 (37), 297 (100), 272 (6), 263 (9), 191 (10), 189 (8%). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_4\text{Cl}$: C, 71.91; H, 6.04. Found: C, 71.69; H, 6.10. **18d**: Colorless solid; mp 159-161 °C (CH_2Cl_2 /hexane); IR (KBr) 2932, 1767, 1607, 1511, 1465, 1256, 1133, 1106 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.42 (d, $J = 8.6$ Hz, 1H), 7.36-7.25 (m, 5H), 6.73 (d, $J = 2.5$ Hz, 1H), 6.69 (s, 1H), 4.74 (s, 1H), 3.75 (s, 3H), 2.98-2.84 (m, 4H), 2.03-1.23 (m, 8H), 1.32 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.4, 160.0, 139.4, 138.9, 135.2, 132.8, 130.9, 130.8, 128.9,

126.0, 124.6, 114.2, 113.0, 111.9, 86.4, 84.9, 55.8, 54.3, 33.3, 28.4, 27.4, 24.9, 23.7, 20.6, 15.0; MS (EI, 70 eV) m/z 450 (4, M^+), 311 (13), 297 (100), 270 (24), 255 (11), 202 (10), 191 (11), 189 (9), 67 (8%). Anal. Calcd for $C_{27}H_{27}O_4Cl$: C, 71.91; H, 6.04. Found: C, 71.93; H, 6.05.

Reaction of α -Diazo Ketone **8a with (2*E*)-2-(4-Chlorobenzylidene)indan-1-one (**16**),**

Preparation of Compounds **17e and **18e**.** A mixture of **16** (204 mg, 0.81 mmol) and α -diazo ketone **8a** (145 mg, 0.81 mmol) was allowed to react with $Rh_2(OAc)_4$ (3.6 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (10 mL) for 3 h according to the general procedure to afford **17e** and **18e** as a diastereomeric mixture in the ratio of 4:6 (160 mg, 49%). The spectral data for the major diastereomer: Colorless semi-solid; IR (neat) 2937, 2866, 1702, 1561, 1490, 1458, 1090 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.61-7.57 (m, 1H), 7.31-7.20 (m, 7H), 6.79 (s, 1H), 4.41 (s, 1H), 3.75 (s, 2H), 2.33-1.25 (m, 8H), 1.52 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 211.9, 144.8, 141.1, 139.8, 135.8, 133.7, 130.9, 130.0, 131.1, 127.4, 126.3, 125.6, 125.4, 113.8, 91.9, 87.0, 54.3, 34.7, 32.4, 27.3, 23.6, 20.5, 14.8; MS (FD^+) m/z 406 (M^+).

Reaction of α -Diazo Ketone 11a with (2E)-6-Methoxy-2-(4-methoxybenzylidene)-3,4-dihydronaphthalen-1(2H)-one (16), Preparation of Compounds 17f and 18f. A mixture of **16** (238 mg, 0.81 mmol) and α -diazo ketone **11a** (125 mg, 0.81 mmol) was allowed to react with Rh₂(OAc)₄ (3.6 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (20 mL) for 3 h according to the general procedure to afford the diastereomers **17f** and **18f** in 39% (133 mg) and 25% (85 mg) yield, respectively. **17f**: Colorless solid; mp 113-115 °C (CH₂Cl₂/hexane); IR (KBr) 2933, 1764, 1608, 1513, 1495, 1464, 1303, 1255, 1130, 1031 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.45 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.82-6.78 (m, 2H), 6.61 (d, *J* = 2.5 Hz, 1H), 4.54 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.06-2.56 (m, 4H), 1.83 (s, 3H), 1.21 (s, 3H), 1.13 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.9, 160.0, 159.0, 137.6, 131.9, 130.7, 130.0, 127.7, 124.6, 115.4, 114.2, 113.8, 112.2, 88.7, 85.8, 55.9, 54.4, 29.9, 24.9, 23.1, 18.1, 15.4; MS (EI, 70 eV) *m/z* 420 (6, M⁺), 335 (33), 295 (100), 293 (12), 266 (6), 121 (23%). Anal. Calcd for C₂₆H₂₈O₅: C, 74.26; H, 6.71. Found: C, 74.01; H, 6.69. **18f**: Colorless solid, mp 155-157 °C (CH₂Cl₂/hexane); IR (KBr) 2929, 1767, 1607, 1511, 1465, 1393, 1300, 1256, 1133, 1106 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.40 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.71-6.68 (m 3H), 4.70 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.98-2.84 (m 4H), 1.80 (s, 3H), 1.36 (s, 3H), 1.16 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 213.1, 159.9, 158.8, 139.1, 136.6, 132.2, 130.9, 128.6, 125.8, 125.2, 114.7, 114.2, 111.8, 86.4, 85.0, 55.9, 55.8, 54.9, 28.6, 25.8, 23.1, 17.7, 15.5; MS (EI, 70 eV) *m/z* 420 (4, M⁺), 335 (31), 295 (100), 293 (21), 121 (245). Anal. Calcd for C₂₆H₂₈O₅: C, 74.26; H, 6.71. Found: C, 74.20; H, 6.67.

Reaction of α -Diazo Ketone **11a with (2*E*)-2-(4-Chlorobenzylidene)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (**16**), Preparation of Compounds **17g** and **18g**.** A

mixture of **16** (242 mg, 0.81 mmol) and α -diazo ketone **11a** (125 mg, 0.81 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (3.6 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (10 mL) for 2.0 h according to the general procedure to afford the diastereomers **17g** and **18g** in 36% (123 mg) and 27% (93 mg) yield, respectively. **17g**: Colorless solid; mp 162-164 °C (CH_2Cl_2 /hexane); IR (KBr) 2922, 1766, 1606, 1493, 1468, 1397, 1319, 1251, 1110 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.45 (d, $J = 8.6$ Hz, 1H), 7.25 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 8.6$ Hz, 2H), 6.83-6.78 (m, 2H), 6.62 (d, $J = 2.5$ Hz, 1H), 4.54 (s, 1H), 3.76 (s, 3H), 2.95-2.55 (m, 4H), 1.84 (s, 3H), 1.21 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.9, 160.1, 138.3, 137.4, 136.0, 133.1, 133.0, 130.8, 129.0, 127.9, 124.0, 115.6, 113.8, 112.4, 88.7, 85.7, 55.9, 54.4, 29.9, 24.9, 23.0, 18.0, 15.3; MS (EI) m/z 424 (2, M^+), 339 (16), 311 (11), 300 (15), 299 (87), 297 (100), 270 (23), 202 (10%). Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{O}_4\text{Cl}$: C, 70.67; H, 5.93. Found: C, 70.55; H, 5.98. **18g**: Colorless solid; mp 154-156 °C (CH_2Cl_2 /hexane); IR (KBr) 2920, 1767, 1610, 1584, 1493, 1466, 1259, 1133, 1104, 1039 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.39 (d, $J = 8.6$ Hz, 1H), 7.27-7.24 (m, 4H), 6.73-6.68 (m, 3H), 4.70 (s, 1H), 3.76 (s, 3H), 2.93-2.77 (m, 4H), 1.80 (s, 3H), 1.31 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.9, 160.1, 139.5, 139.0, 136.8, 132.9, 131.0, 129.0, 128.2, 126.0, 124.7, 115.0, 114.3, 112.1, 86.4, 84.9, 55.9, 55.0, 28.6,

25.9, 23.2, 17.8, 15.6; MS (EI) m/z 424 (18, M^+), 311 (19), 298 (34), 297 (100), 270 (19), 255 (9), 191 (10%). Anal. Calcd for $C_{25}H_{25}O_4Cl$: C, 70.67; H, 5.93. Found: C, 70.63; H, 5.92.

Reaction of α -Diazo Ketone **11a with (2*E*)-2-(4-Methylbenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (**16**), Preparation of Compounds **17h** and **18h**.** A

mixture of **16** (200 mg, 0.81 mmol) and α -diazo ketone **11a** (125 mg, 0.81 mmol) was allowed to react with $Rh_2(OAc)_4$ (3.6 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (10 mL) for 3.0 h according to the general procedure to afford the diastereomers **17h** and **18h** in 23% (70 mg) and 36% (109 mg) yield, respectively. **17h**: Colorless solid; mp 143-145 °C (CH_2Cl_2 /hexane); IR (KBr) 2928, 1765, 1511, 1470, 1457, 1389, 1299, 1270, 1127, 1107 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 1H), 7.37-7.04 (m, 7H), 6.83 (s, 1H), 4.58 (s, 1H), 3.03-2.91 (m, 3H), 2.69-2.63 (m, 1H), 2.31 (s, 3H), 1.85 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.8, 141.0, 137.1, 136.5, 134.6, 133.8, 129.5, 128.7, 128.5, 126.7, 126.3, 125.4, 115.6, 88.4, 86.0, 54.5, 29.4, 24.7, 23.1, 21.8, 18.1, 15.3; MS (EI) m/z 374 (8, M^+), 289 (48), 249 (100), 248 (33), 247 (64), 234 (16), 233 (77), 215 (19), 105 (50), 97 (84%). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 80.25; H, 6.96. **18h**: Colorless solid; mp 187-189 °C (CH_2Cl_2 /hexane); IR (KBr) 2928, 1765, 1662, 1586, 1510, 1457, 1298, 1132, 1012 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 1H), 7.52-7.04 (m, 7H), 6.75 (s, 1H), 4.75 (s, 1H),

3.17-2.69 (m, 4H), 2.32 (s, 3H), 1.82 (s, 3H), 1.32 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.9, 140.8, 137.6, 136.9, 135.3, 133.8, 129.6, 129.4, 128.6, 128.3, 126.9, 126.0, 124.5, 114.9, 87.4, 84.6, 55.0, 28.3, 25.7, 23.1, 21.8, 17.7, 15.5; MS (EI, 70 eV) m/z 374 (3, M^+), 290 (9), 289 (32), 249 (100), 215 (8), 105 (19). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3$: C, 80.18; H, 7.00. Found: C, 80.31; H, 7.04.

Reaction of α -Diazo Ketone 11a with (2E)-2-Benzylideneoctahydronaphthalen-1(2H)-one (19), Preparation of Compound 20: A mixture of **19** (222 mg, 0.81 mmol) and α -diazo ketone **11a** (125 mg, 0.81 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (2.5 mg, 0.8 mol%) in anhydrous CH_2Cl_2 (15 mL) for 3 h according to the general procedure to afford **20** as a mixture of stereoisomers in the ratio of 1:5 (178 mg, 55%). The spectral data for the major diastereomer: Colorless solid; IR (KBr) 2925, 2853, 1764, 1672, 1588, 1489, 1445, 1149, 1092 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.35-7.16 (m, 4H), 7.03 (d, $J = 8.6$ Hz, 1H), 4.83 (s, 1H), 3.05-2.03 (m 4H), 1.98-0.98 (m, 10H), 1.69 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.4, 142.9, 137.8, 133.1, 131.3, 129.9, 128.4, 113.6, 86.9, 83.6, 54.5, 53.4, 40.2, 34.2, 31.3, 28.3, 26.3, 25.8, 25.6, 22.8, 17.4, 14.2; MS (EI) m/z 400 (11, M^+), 275 (91), 246 (18), 164 (10), 151 (42), 124 (40), 121 (53), 98 (29%).

Reaction of α -Diazo Ketone **8a with (2*E*,6*E*)-2,6-Bis(4-chlorobenzylidene)**

cyclohexanone (21**), Synthesis of Compound **22a**:**

A mixture of **21** (170 mg, 0.5 mmol) and α -diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with Rh₂(OAc)₄ (2.2 mg) in anhydrous CH₂Cl₂ (15 mL) for 4.0 h at room temperature under an argon atmosphere according to the general method to afford product **22a** (173 mg, 70%) as a colorless solid: mp 197-199 °C (CH₂Cl₂/hexane); IR (KBr) 3048, 2935, 2800, 1759, 1488, 1443 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.25-7.04 (m, 8H), 6.73 (s, 2H), 4.90 (s, 1H, OCH), 3.00-2.85 (m, 2H), 2.30-1.30 (m, 12H), 1.21 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.2, 141.7, 140.8, 136.5, 135.8, 132.8, 132.7, 130.8, 130.5, 128.8, 128.7, 123.7, 123.3, 113.8, 88.4, 85.9, 53.6, 32.9, 28.7, 28.1, 27.7, 27.2, 23.5, 20.4, 14.9; MS (EI, 70 eV) m/z 495 (4, M⁺), 494 (7), 386 (11), 385 (43), 384 (24), 383 (58), 343 (32), 279 (28), 123 (100%). Anal. Calcd for C₂₉H₂₈Cl₂O₃: C, 70.30; H, 5.70. Found: C, 70.21; H, 5.62.

Reaction of α -Diazo Ketone **11a with (2*E*,6*E*)-2,6-Bis(4-chlorobenzylidene)**

cyclohexanone (21**), Synthesis of Compound **22b**:**

A mixture of **21** (190 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with Rh₂(OAc)₄ (2.4 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (12 mL) for 3.0 h at room temperature under an

argon atmosphere according to the general method to afford product **22b** (183 mg, 71%) as a colorless solid: mp 182-184 °C (CH₂Cl₂/hexane); IR (KBr) 2974, 2940, 1762, 1488, 1443 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.31-7.24 (m, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.74 (s, 1H), 6.73 (s, 1H), 4.86 (s, 1H), 3.02-2.85 (m, 2H), 2.19-1.80 (m, 4H), 1.72 (s, 3H), 1.18 (s, 3H), 1.11 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.8, 141.8, 140.8, 136.5, 135.9, 133.0, 132.8, 130.8, 130.6, 128.8, 128.7, 123.7, 123.3, 114.8, 88.4, 85.7, 53.3, 28.8, 28.2, 27.8, 22.7, 17.6, 15.4; MS (EI) *m/z* 469 (5, M⁺), 383 (22), 343 (39), 125 (17), 97 (100%), 41 (31). Anal. Calcd for C₂₇H₂₆Cl₂O₃: C 69.09, H 5.58; found C 69.10, H 5.53.

Reaction of α -Diazo Ketone 11a with (2*E*,5*E*)-2,5-Bis(1-naphthylmethylene) cyclopentanone (21), Synthesis of Compound 22d: A mixture of **21** (198 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with Rh₂(OAc)₄ (2.4 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (15 mL) for 3 h at room temperature under an argon atmosphere according to the general method to afford **22d** (201 mg, 75%) as a pale yellow solid: mp 184-186 °C (CH₂Cl₂/hexane); IR (KBr) 2967, 1764, 1439, 1395, 1269 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 8.14 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.99-7.72 (m, 8H), 7.56-7.14 (m, 4H), 4.61 (s, 1H), 2.62-2.42 (m, 4H), 1.89 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.4, 143.6, 140.5, 134.7, 135.6, 134.2, 134.1, 132.4, 132.3, 129.1, 128.9, 128.2, 128.1, 127.2, 126.8, 126.6, 126.4, 125.8, 125.7, 125.2, 122.8, 115.3, 90.8, 87.4, 54.8, 26.1, 25.5, 23.0, 17.9, 15.8. MS (EI) *m/z* (%)

486 (83, M^+), 401 (27), 373 (15), 362 (67), 361 (100), 360 (21), 207 (21), 179 (18), 165 (47), 141 (45), 97 (67). Anal. Calcd for $C_{34}H_{30}O_3$: C 83.91, H 6.21; Found C 84.12, H 6.14.

Reaction of α -Diazo Ketone 11a with (2*E*,5*E*)-2,5-Bis(4-methylbenzylidene)cyclopentanone (21), Synthesis of Compound 22e: A mixture of **21** (160 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (15 mL) for 4.5 h at room temperature under an argon atmosphere according to the general method to afford **22e** (162 mg, 71%) as a pale yellow solid: mp 172-174 °C (CH_2Cl_2 /hexane); IR (KBr) 2965, 2920, 1765, 1511, 1467 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.24-7.16 (m, 2H), 7.13-7.07 (m, 6H), 6.58 (s, 2H), 4.43 (s, 1H), 2.74-2.70 (m, 4H), 2.31 (s, 6H), 1.79 (s, 3H), 1.29 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.0, 139.9, 137.4, 137.2, 137.1, 134.9, 134.4, 129.6, 129.5, 124.9, 124.4, 115.2, 91.2, 87.3, 54.6, 26.1, 23.1, 21.8, 17.7, 15.6; MS (FD $^+$) m/z 414 (M^+). Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.12; H, 7.29. Found: C, 81.34; H, 7.35.

Reaction of α -Diazo Ketone 11b with (2*E*,6*E*)-2,6-Dibenzylidenecyclohexanone (21), Synthesis of Compound 22f: A mixture of **21** (200 mg, 0.70 mmol) and α -diazo ketone

11c (125 mg, 0.70 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (3.5 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (15 mL) for 4.5 h at room temperature under an argon atmosphere according to the general method to afford **22f** (245 mg, 73%) as a pale yellow solid: mp 148-150 °C (CH_2Cl_2 /hexane); IR (KBr) 2963, 2916, 1761, 1509, 1466, 1211 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 7.35-7.09 (m, 10H), 6.87 (s, 2H), 4.93 (s, 1H), 3.12 (d, J = 14.0 Hz, 1H), 2.94 (d, J = 14.0 Hz, 1H), 2.21-1.77 (m, 4H), 1.59 (s, 3H), 1.34-1.00 (m, 4H). ^{13}C NMR (50.3 MHz, CDCl_3): δ 208.3, 140.5, 140.1, 138.3, 137.9, 129.7, 129.4, 128.7, 128.6, 127.1, 125.3, 124.0, 112.2, 86.9, 86.8, 39.0, 28.8, 28.4, 27.7, 15.8, 14.7, 13.1; MS (EI) m/z 398 (22, M^+), 380 (4), 275 (55), 124 (100), 95 (24), 67 (25), 43 (15%). Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_3$: C, 81.38; H, 6.58. Found: C, 81.30; H, 6.60.

Reaction of α -Diazo Ketone 11a with (1E,4E)-1,5-Bis(4-methoxyphenyl)penta-1,4-dien-3-one (21), Synthesis of Compound 22g: A mixture of **21** (162 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (2.4 mg) in anhydrous CH_2Cl_2 (10 mL) for 2 h at room temperature under an argon atmosphere according to the general method to afford **22g** (173 mg, 75%) as a pale yellow solid: mp 170-172 °C (CH_2Cl_2 /hexane); IR (KBr) 2967, 1767, 1606, 1575, 1512 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.36-7.27 (m, 4H), 6.84 (d, J = 8.4 Hz, 4H), 6.68 (d, J = 16.0 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 6.15 (d, J = 16.0 Hz, 1H), 6.05 (d, J = 16.0 Hz, 1H), 4.47 (s, 1H), 3.79 (s, 6H), 1.67 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H); ^{13}C NMR

(50.3 MHz, CDCl₃) δ 213.2, 160.3, 160.1, 133.9, 131.6, 129.8, 129.6, 128.6, 128.5, 128.1, 123.7, 115.0, 114.6, 87.3, 84.2, 55.9, 54.2, 22.2, 18.6, 15.8; MS (FD⁺) m/z 420 (M⁺). Anal. Calcd for C₂₆H₂₈O₅: C, 74.26; H, 6.71. Found: C, 74.01; H, 6.77.

Reaction of α -Diazo Ketone **11a with (1*E*,4*E*)-1,5-Bis(4-methylphenyl)penta-1,4-dien-3-one (**21**), Synthesis of Compound **22h**:** A mixture of **21** (144 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with Rh₂(OAc)₄ (2.4 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (15 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford **22h** (164 mg, 77%) as a pale yellow solid: mp 125-127 °C (CH₂Cl₂/hexane); IR (KBr) 2967, 2924, 1769, 1511 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.28 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 4H), 6.72 (d, J = 16.0 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 4.48 (s, 1H), 2.29 (s, 6H), 1.65 (s, 3H), 1.11 (s, 3H), 1.08 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.8, 138.5, 138.2, 134.2, 134.0, 132.0, 129.8, 129.1, 127.2, 127.1, 124.8, 114.9, 87.1, 84.1, 54.1, 22.1, 21.7, 18.5, 15.7; MS (FD⁺) m/z 388 (M⁺). Anal. Calcd for C₂₆H₂₈O₃: C, 80.38; H, 7.26. Found: C, 80.62; H, 7.22.

Reaction of α -Diazo Ketone 11a with (1*E*,3*E*)-1,3-Bis(4-chlorobenzylidene)-1,3-dihydro-2*H*-inden-2-one (23), Synthesis of Compound 24: A mixture of **23** (207 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with Rh₂(OAc)₄ (2.4 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (15 mL) for 4.5 h at room temperature under an argon atmosphere according to the general method to afford **24** (200 mg, 72%) as a colorless solid: mp 187-189 °C (CH₂Cl₂/hexane); IR (KBr) 2927, 1767, 1488, 1461 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.56-7.24 (m, 5H), 7.22-7.02 (m, 7H), 6.50 (s, 2H), 4.24 (s, 1H), 1.20 (s, 3H), 0.95 (s, 3H), 0.53 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 211.9, 138.5, 132.5, 132.3, 130.7, 130.3, 129.9, 129.3, 129.1, 128.3, 125.3, 123.9, 123.2, 121.2, 116.8, 92.9, 90.2, 54.9, 23.4, 17.6, 12.8; MS (EI) *m/z* 502 (15, M⁺), 377 (83), 376 (62), 341 (31), 311 (35), 278 (42), 276 (65), 97 (100%). Anal. Calcd for C₃₀H₂₄Cl₂O₃: C, 71.58; H, 4.81. Found: C, 71.42; H, 4.83.

Reaction of α -Diazo Ketone 8a with (2*E*,6*E*)-2,6-Bis(2-furylmethylene)cyclohexanone (21), Synthesis of Compound 25: A mixture of **21** (130 mg, 0.5 mmol) and α -diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with Rh₂(OAc)₄ (2.2 mg)

in anhydrous CH_2Cl_2 (15 mL) for 5 h at room temperature under an argon atmosphere according to the general method to afford product **25** (150 mg, 74%) as a colorless solid: mp 201-203 °C (CH_2Cl_2 /hexane); IR (KBr) 2947, 2866, 1760, 1656, 1492, 1443 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.33-7.31 (m, 2H), 6.47 (s, 2H), 6.37-6.19 (m, 4H), 4.88 (s, 1H, 3.56-3.47 (m, 2H), 2.22-1.80 (m, 5H), 1.78-1.40 (m, 7H), 1.18 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.1, 153.3, 152.8, 141.9, 141.8, 140.0, 138.2, 113.7, 113.0, 112.7, 111.5, 111.4, 110.4, 110.2, 88.7, 86.0, 53.4, 32.9, 29.3, 28.3, 27.6, 27.3, 23.5, 20.4, 14.9; MS (EI) m/z 406 (28, M^+), 295 (36), 267 (58), 254 (38), 226 (27), 166 (30), 165 (74), 154 (36), 153 (79), 152 (71), 141 (65), 128 (100%). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_5$: C, 73.87; H, 6.45. Found: C, 73.89; H, 6.50.

Reaction of α -Diazo Ketone 11a with (2E,6E)-2,6-Bis(2-furylmethylene)cyclohexanone (21), Synthesis of Compound 26a: A mixture of **16a** (140 mg, 0.55 mmol) and α -diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $\text{Rh}_2(\text{OAc})_4$ (2.4 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (12 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford product **26a** (150 mg, 72%) as a colorless solid: mp 203-205 °C (CH_2Cl_2 /hexane); IR (KBr) 2945, 2921, 1764, 1595, 1546, 1459 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.35-7.32 (m, 2H), 6.48 (s, 1H), 6.46 (s, 1H), 6.37-6.19 (m, 4H), 4.85 (s, 1H), 3.60-3.48 (m, 2H), 2.31-1.45 (m, 4H), 1.70 (s, 3H), 1.15 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 212.6, 153.3, 152.8, 142.0,

141.8, 140.1, 138.2, 114.7, 112.9, 112.6, 111.5, 111.4, 110.3, 88.7, 85.7, 54.0, 29.4, 28.4, 27.7, 22.6, 17.6, 15.4; MS (EI) m/z 380 (42, M^+), 295 (30), 255 (100), 226 (28), 97 (24), 69 (13%). Anal. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.63; H, 6.35.

Reaction of α -Diazo Ketone 11a with (2*E*,6*E*)-2,6-Bis(2-thienylmethylene)cyclohexanone (21), Synthesis of Compound 26b: A mixture of **21** (157 mg, 0.55 mmol) and α -diazo ketone **8a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg, 1.0 mol%) in anhydrous CH_2Cl_2 (12 mL) for 3 h at room temperature under an argon atmosphere according to the general method to afford product **26b** (161 mg, 71%) as a colorless solid: mp 199-201 °C (CH_2Cl_2 /hexane); IR (KBr) 1763, 1594, 1548, 1456 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 6.47 (s, 1H), 6.45 (s, 1H), 6.37-6.17 (m, 4H), 4.85 (s, 1H), 3.58-3.45 (m, 2H), 2.35-1.49 (m, 4H), 1.68 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.4, 140.1, 138.2, 136.9, 136.7, 130.3, 130.1, 127.8, 127.7, 126.4, 126.2, 114.6, 110.2, 88.9, 85.6, 54.1, 29.3, 28.5, 27.7, 22.6, 17.8, 15.5; MS (FD^+) m/z 412 (M^+). Anal. Calcd for $C_{23}H_{24}O_3S_2$: C, 66.96; H, 5.86; S, 15.54. Found: C, 67.12; H, 5.89; S, 15.49.

Reaction of α -Diazo Ketone **8a with (2*E*,6*E*)-2-Benzylidene-6-(4-methylbenzylidene)cyclohexanone (**27**), Synthesis of Compound **28**:** A mixture of **27** (200 mg, 0.69 mmol) and α -diazo ketone **8a** (130 mg, 0.72 mmol) was allowed to react with Rh₂(OAc)₄ (3.6 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (15 mL) for 3 h according to the general procedure to afford **28** as a mixture of stereoisomers in the ratio of 1:2 (275 mg, 90%). The spectral data for the major diastereomer; Colorless solid: IR (KBr) 2937, 2861, 1764, 1445, 1376, 1032, 925, 703 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 7.29-7.02 (m, 9H), 6.82-6.75 (m, 2H), 4.91 (s, 1H), 3.10-2.94 (m, 2H), 2.32 (s, 3H), 2.24-1.93 (m, 4H), 1.81-1.26 (m, 8H), 1.22 (s, 3H). ¹³C NMR (50.3 MHz, CDCl₃): δ 212.0, 140.0, 139.1, 135.9, 134.7, 134.1, 129.5, 129.0, 128.9, 128.7, 128.0, 126.4, 126.3, 124.1, 123.6, 113.2, 88.0, 85.4, 53.0, 32.4, 28.3, 27.7, 27.3, 26.7, 23.0, 21.0, 19.9, 14.4; MS (FD⁺) *m/z* 440 (M⁺).

Reaction of α -Diazo Ketone **11a with (2*E*,6*E*)-2-Benzylidene-6-(4-methylbenzylidene)cyclohexanone (**27**), Synthesis of Compound **29**:** A mixture of **27** (200 mg, 0.69 mmol) and α -diazo ketone **11a** (110 mg, 0.71 mmol) was allowed to react with Rh₂(OAc)₄ (3.0 mg, 1.0 mol%) in anhydrous CH₂Cl₂ (15 mL) for 3 h according to the general procedure to afford **29** as a mixture of stereoisomers in the ratio of 2:1 (253 mg, 88%). The spectral data for the major diastereomer: Colorless solid: IR (KBr) 2993, 2924, 2862, 1766, 1511, 1465, 1442, 1396, 1132, 1033, 900, 701 cm⁻¹; ¹H NMR (200

MHz, CDCl₃): δ 7.29-7.04 (m, 9H), 6.82-6.79 (m, 2H), 4.84 (s, 1H), 3.09-2.93 (m, 2H), 2.30 (s, 3H), 2.22-1.92 (m, 4H), 1.69 (s, 3H), 1.18 (s, 3H), 1.08 (s, 3H). ¹³C NMR (50.3 MHz, CDCl₃): δ 212.8, 144.2, 140.7, 139.6, 137.6, 135.2, 129.5, 129.4, 129.2, 128.6, 127.0, 126.9, 124.6, 124.5, 124.1, 124.0, 114.6, 88.6, 85.7, 54.2, 28.9, 28.3, 27.8, 22.7, 21.6, 17.6, 15.4; MS (FD⁺) m/z 414 (M⁺).

Reaction of α -Diazo Ketone **8a with (2*E*,6*E*)-2,6-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclohexanone (**42a**), Synthesis of Compound **43a**:** A mixture of **42** (165 mg, 0.5 mmol) and α -diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with 2.2 mg of Rh₂(OAc)₄ in dry DCM (10 mL) for 4 h at room temperature under an argon atmosphere according to the general method to afford product **43a** (177 mg, 74%) as a colorless solid upon purification on silica gel column chromatography (EtOAc/hexane, 2:98); mp 182-184°C: IR (KBr) 2937, 1762, 1595, 1526, 1491, 1445, 1376 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.37–7.15 (m, 10H), 7.05-6.87 (m, 2H), 6.65 (s, 1H), 6.58 (s, 1H), 6.49-6.41 (m, 2H), 4.83 (s, 1H), 3.10-2.98 (m, 2H), 2.27-1.25 (m, 12H), 1.18 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 212.4, 141.6, 139.9, 138.1, 137.9, 133.9, 133.7, 129.0, 127.9, 126.8, 124.7, 124.1, 123.9, 113.6, 88.9, 85.8, 53.5, 32.9, 28.8, 28.6, 27.7, 27.3, 23.5, 20.5, 14.8; MS (FD⁺) m/z 478 (M⁺). Anal. Calcd for C₃₃H₃₄O₃: C, 82.81; H, 7.16. Found: C, 82.89; H, 7.17.

Reaction of α -Diazo Ketone 8b with (2*E*,6*E*)-2,6-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclohexanone (42a), Synthesis of Compound 43b: A mixture of 42 (177 mg, 0.54 mmol) and α -diazo ketone 8c (90 mg, 0.54 mmol) was allowed to react with 2.4 mg of Rh₂(OAc)₄ in dry DCM (10 mL) for 4.5 h at room temperature under an argon atmosphere according to the general method to afford product **43b** (173 mg, 69%) as colorless solid upon purification on silica gel column chromatography (3% EtOAc–hexane); mp 183-185°C: IR (KBr) 1760, 1596, 1528, 1446 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.35–7.15 (m, 10H), 7.06-6.85 (m, 2H), 6.67 (s, 1H), 6.59 (s, 1H), 6.48-6.40 (m, 2H), 4.86 (s, 1H), 3.11-2.96 (m, 2H), 2.39-1.30 (m, 10H), 1.20 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 211.3, 141.5, 139.8, 138.0, 137.8, 133.7, 133.6, 129.1, 127.8, 126.6, 124.8, 124.1, 123.7, 113.7, 88.8, 86.0, 58.9, 33.5, 28.8, 28.3, 27.9, 26.1, 20.5, 16.6; MS (FD⁺) m/z 464 (M⁺). Anal. Calcd for C₃₂H₃₂O₃: C, 82.73; H, 6.94. Found: C, 82.69; H, 7.00.

Single-crystal X-ray Analyses: The single-crystal X-ray analyses were performed on an Enraf-Nonius CAD-4 diffractometer. For all the molecules the crystal orientation, cell refinement and intensity measurements were carried out using the program CAD-4PC.¹ The raw intensity data was corrected for Lorentz Polarization effects. The Lorentz Polarization correction and data reduction were carried out using NRCVAX program.² The structure was solved using direct method. The full matrix least-squares refinement of all non-hydrogen atoms with isotropic temperature factor was carried out using SHELXL-97.³

Single-crystal X-ray Analysis of 17a

The cell parameters, and intensity for compound **17a** were measured using graphite monochromatized MoK α radiation (0.7093) in the range of $\theta = 2\text{--}25^\circ$ at room temperature. Twenty-five reflections with $\theta = 8\text{--}12^\circ$ for compound **17a** were used to get the accurate cell dimensions. Three standard reflections were monitored every 1 h, which showed no significant crystal decay for the entire period of data collection. In the case of **17a**, two molecules were present in the asymmetric unit. The observed angle of oxa-bridge (C1–O10–C7) is 96.9° . The presence of methyl group at the ring juncture (C5) in compound **17a** is at *endo* position with respect to oxido bridge (C1–O10–C7). Additionally, it is notable from both single-crystal X-ray analyses that the existence of *E*-geometric arrangement of olefin as in starting α,β -unsaturated ketones **16**. This observation is in accordance with the literature⁴ reports as it was assigned based on the relative chemical shift value of olefin protons in ^1H NMR of **16**. The final cycles of least squares refinement yielded R-value of $R_1 = 6.9\%$ ($wR_2 = 20.41\%$) for compound **17a** in blocked fashion. The crystal structure analysis of **17a** clearly revealed that the carbonyl

ylide derived from the respective diazo ketone **8b** underwent regio-, chemoselective cycloaddition to C=O group of the arylmethylenecycloalkanones.

Crystal Data for Compound 17a: $C_{25}H_{24}O_3$, $M = 372.44$, $0.23 \times 0.18 \times 0.12$ mm, Orthorhombic, $Fdd2$, $a = 40.222(16)$ Å, $b = 18.798(7)$ Å, $c = 10.308(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 7794(6)$ Å³, $T = 293(2)$ K, $R_1 = 0.0697$, $wR_2 = 0.2041$ on observed data, $z = 16$, $D_{\text{calc.}} = 1.270$ Mg m⁻³, $F(000) = 3168$, Absorption coefficient = 0.082 mm⁻¹, $\lambda = 0.70930$ Å, 1818 reflections were collected on a CAD-4 diffractometer, 991 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.292 and -0.391 e Å⁻³, respectively (Figure S1).

FIGURE S1. ORTEP diagram of the diastereomer **17a**.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for spiro-dioxo compound **17a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	1518(2)	1680(5)	9086(9)	37(2)
C(2)	1464(3)	1841(6)	1.0454(11)	56(3)
C(3)	1701(3)	1321(7)	1.1264(9)	67(3)
C(4)	1896(3)	926(6)	1.0061(9)	50(3)
C(5)	1878(2)	1402(5)	8893(9)	38(2)
C(6)	1829(2)	1002(5)	7690(8)	36(2)
C(7)	1459(2)	1069(5)	7402(8)	38(2)
C(8)	1386(2)	1850(4)	6914(8)	34(2)
O(9)	14409(14)	2225(3)	8131(5)	36(14)
O(10)	13290(14)	1081(3)	8620(6)	414(15)
C(11)	1607(2)	2112(4)	5831(9)	34(2)
C(12)	1553(2)	1679(5)	4661(9)	43(2)
C(13)	1193(3)	1774(6)	4117(10)	55(3)
C(14)	944(2)	1873(5)	5211(9)	42(2)
C(15)	606(2)	1938(5)	4783(11)	51(3)
C(16)	365(3)	2028(5)	5773(13)	59(3)
C(17)	449(3)	2104(6)	6991(13)	61(3)
C(18)	777(2)	2046(5)	7427(10)	43(2)
C(19)	1028(2)	1923(5)	6462(9)	35(2)
C(20)	1798(2)	2687(5)	5924(9)	39(2)
C(21)	1992(2)	3040(5)	4881(9)	41(2)
C(22)	1870(3)	3115(7)	3653(12)	63(3)
C(23)	2062(4)	3452(8)	2688(14)	91(4)
C(24)	2370(4)	3709(7)	3021(16)	88(4)
C(25)	2491(3)	3654(6)	4215(12)	64(3)
C(26)	2305(2)	3314(5)	5197(11)	53(3)
O(27)	20422(17)	727(4)	7000(8)	62(2)
C(28)	2151(3)	1965(6)	8900(15)	74(4)

Table S2. Bond lengths [Å] for spiro-dioxo compound **17a**.

C(1)-C(2)	1.458(14)	C(11)-C(12)	1.471(13)
C(1)-O(10)	1.440(11)	C(12)-C(13)	1.563(14)
C(1)-O(9)	1.454(10)	C(13)-C(14)	1.520(13)
C(1)-C(5)	1.551(12)	C(14)-C(19)	1.335(13)
C(2)-C(3)	1.602(14)	C(14)-C(15)	1.436(13)
C(3)-C(4)	1.643(14)	C(15)-C(16)	1.417(16)
C(4)-C(5)	1.502(13)	C(16)-C(17)	1.307(17)
C(5)-C(6)	1.464(12)	C(17)-C(18)	1.399(14)
C(5)-C(28)	1.525(13)	C(18)-C(19)	1.435(13)
C(6)-O(27)	1.226(11)	C(20)-C(21)	1.486(12)
C(6)-C(7)	1.523(13)	C(21)-C(22)	1.365(15)
C(7)-O(10)	1.361(11)	C(21)-C(26)	1.399(13)
C(7)-C(8)	1.579(12)	C(22)-C(23)	1.410(17)
C(8)-O(9)	1.456(10)	C(23)-C(24)	1.37(2)
C(8)-C(11)	1.508(12)	C(24)-C(25)	1.328(19)
C(8)-C(19)	1.521(13)	C(25)-C(26)	1.411(15)
C(11)-C(20)	1.330(12)		

Table S3. Bond angles [°] for spiro-dioxo compound **17a**.

C(2)-C(1)-O(10)	114.0(7)	C(8)-O(9)-C(1)	106.0(6)
C(2)-C(1)-O(9)	118.5(8)	C(7)-O(10)-C(1)	96.8(6)
O(10)-C(1)-O(9)	102.2(6)	C(20)-C(11)-C(12)	126.4(8)
C(2)-C(1)-C(5)	109.5(7)	C(20)-C(11)-C(8)	123.5(8)
O(10)-C(1)-C(5)	100.7(7)	C(12)-C(11)-C(8)	109.9(7)
O(9)-C(1)-C(5)	110.4(7)	C(11)-C(12)-C(13)	111.5(8)
C(1)-C(2)-C(3)	106.8(8)	C(14)-C(13)-C(12)	111.0(8)
C(2)-C(3)-C(4)	99.6(7)	C(19)-C(14)-C(15)	121.9(9)
C(5)-C(4)-C(3)	108.2(8)	C(19)-C(14)-C(13)	124.1(9)
C(4)-C(5)-C(6)	112.3(7)	C(15)-C(14)-C(13)	114.0(9)
C(4)-C(5)-C(28)	112.0(9)	C(16)-C(15)-C(14)	115.9(10)
C(6)-C(5)-C(28)	117.1(9)	C(17)-C(16)-C(15)	121.9(10)
C(4)-C(5)-C(1)	98.2(7)	C(16)-C(17)-C(18)	122.9(11)
C(6)-C(5)-C(1)	99.1(7)	C(17)-C(18)-C(19)	116.9(10)
C(28)-C(5)-C(1)	116.0(8)	C(14)-C(19)-C(18)	120.3(8)
O(27)-C(6)-C(5)	128.0(8)	C(14)-C(19)-C(8)	121.8(8)
O(27)-C(6)-C(7)	127.2(8)	C(18)-C(19)-C(8)	117.9(8)
C(5)-C(6)-C(7)	104.6(7)	C(11)-C(20)-C(21)	127.9(8)
O(10)-C(7)-C(6)	101.4(7)	C(22)-C(21)-C(26)	120.1(10)
O(10)-C(7)-C(8)	101.9(7)	C(22)-C(21)-C(20)	121.8(8)
C(6)-C(7)-C(8)	108.8(7)	C(26)-C(21)-C(20)	118.1(9)
O(9)-C(8)-C(11)	113.0(6)	C(21)-C(22)-C(23)	120.2(11)
O(9)-C(8)-C(19)	111.3(7)	C(24)-C(23)-C(22)	118.4(13)
C(11)-C(8)-C(19)	107.5(7)	C(25)-C(24)-C(23)	122.5(12)
O(9)-C(8)-C(7)	98.4(6)	C(24)-C(25)-C(26)	120.3(11)
C(11)-C(8)-C(7)	115.5(7)	C(21)-C(26)-C(25)	118.5(11)
C(19)-C(8)-C(7)	111.0(7)		

Single-crystal X-ray Analysis of Compound **18b**

The cell parameters, and intensity for compound **18b** was measured using graphite monochromatized MoK α radiation (0.7107) in the range of $\theta = 2\text{--}22.5^\circ$ at room temperature. Twenty-five reflections with $\theta = 7\text{--}10^\circ$ for compound **18b** were used to get the accurate cell dimension. Three standard reflections were monitored every 1 h, which showed no significant crystal decay for the entire period of data collection. In compound **18b**, the observed angle of oxa-bridge (C1–O12–C9) is 102.0° . The final cycles of least squares refinement yielded R-value of $R_1 = 7.4\%$ ($wR_2 = 18.85\%$) for compound **18b** in blocked fashion.

We further analyzed the crystal packing arrangements in the solid-state architecture of compound **18b** (Figure S3). Packing diagram of molecule **18b** viewed down a -axis, which exhibits the presence of C–H $\cdots$ O hydrogen-bonding in the compound **18b**. The molecules are stabilized and held together in the crystal lattice via strong intermolecular C–H $\cdots$ O interaction between the exo-ketonic oxygen of the acyclic six-membered ring with the H151 hydrogen atom from the neighboring molecule aligned along c -axis (C15–H151 $\cdots$ O29 interaction: C15–H151 = $2.66\text{\AA}$, H151 $\cdots$ O29 = $2.58\text{\AA}$, C15 $\cdots$ O29 = $3.475\text{\AA}$ and $\angle$ C15–H151 $\cdots$ O9 = 155.7° , symmetry code = 1–x, –y, –z). Additionally, C–H $\cdots$ π interaction exists between the hydrogen atoms of the six-membered acyclic ring and the phenyl ring (C23–C28) along b -axis between the neighboring molecules (C–H $\cdots$ π interaction; H22 $\cdots$ Cg = $2.67\text{\AA}$, $\angle$ C2–H22 $\cdots$ Cg = 160.4° and symmetry code = 1+x, y, z, where Cg is the centroid of the phenyl ring C23–C28) forming a two dimensional architecture.

Crystal Data for Compound 18b: $C_{26}H_{26}O_3$, $M = 386.47$, $0.35 \times 0.20 \times 0.10$ mm, Orthorhombic, $PbCa$, $a = 8.027(5)$ Å, $b = 13.870(11)$ Å, $c = 36.175(14)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 4028(4)$ Å³, $T = 293(2)$ K, $R_1 = 0.0741$, $wR_2 = 0.1885$ on observed data, $z = 8$, $D_{\text{calc.}} = 1.275$ Mg m⁻³, $F(000) = 1648$, Absorption coefficient = 0.082 mm⁻¹, $\lambda = 0.7107$ Å, 2602 reflections were collected on a CAD-4 diffractometer, 1460 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.229 and -0.282 e Å⁻³, respectively (Figure S2).

FIGURE S2. ORTEP diagram of diastereomer **18b**.

Figure S3. Solid-state packing diagram compound **18b** viewed down *a*-axis

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for spiro-dioxo compound **18b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O(11)	1487(4)	1189(3)	3667(1)	41(1)
C(21)	35(7)	1380(4)	4253(2)	36(1)
O(29)	3553(6)	336(3)	4662(1)	68(1)
O(12)	2967(5)	-190(3)	3758(1)	51(1)
C(23)	-2292(7)	-606(4)	3270(2)	35(1)
C(13)	-743(6)	50(4)	3829(2)	36(1)
C(28)	-3367(8)	-1288(4)	3421(2)	43(2)
C(1)	3063(7)	702(4)	3587(2)	43(2)
C(20)	305(8)	2368(5)	4244(2)	46(2)
C(2)	3262(9)	592(5)	3172(2)	55(2)
C(7)	4308(9)	1383(6)	4165(2)	51(2)
C(6)	4488(8)	1304(5)	3751(2)	51(2)
C(15)	-1270(10)	-70(5)	4528(2)	48(2)
C(14)	-1703(9)	-434(5)	4139(2)	43(2)
C(10)	702(7)	688(4)	3963(2)	37(2)
C(17)	-1624(9)	1593(5)	4797(2)	51(2)
C(24)	-2356(8)	-495(5)	2888(2)	49(2)
C(8)	3392(8)	563(4)	4340(2)	48(2)
C(4)	4949(13)	2120(8)	3143(2)	78(3)
C(16)	-948(7)	990(4)	4531(2)	40(2)
C(27)	-4406(9)	-1838(5)	3199(2)	51(2)
C(9)	2153(7)	39(5)	4096(2)	42(2)
C(22)	-1066(7)	-35(4)	3474(2)	39(2)
C(25)	-3417(9)	-1033(6)	2669(2)	60(2)
C(26)	-4449(8)	-1711(5)	2825(2)	53(2)
C(18)	-1336(9)	2563(5)	4789(2)	57(2)
C(5)	4690(12)	2246(6)	3559(2)	65(2)
C(19)	-344(9)	2952(5)	4517(2)	59(2)
C(3)	3465(11)	1543(6)	2988(2)	66(2)

Table S5. Bond lengths [Å] for spiro-dioxo compound **18b**.

O(11)-C(10)	1.424(7)	C(20)-C(19)	1.381(9)
O(11)-C(1)	1.463(7)	C(2)-C(3)	1.486(10)
C(21)-C(20)	1.387(8)	C(7)-C(8)	1.496(10)
C(21)-C(16)	1.388(8)	C(7)-C(6)	1.506(9)
C(21)-C(10)	1.521(8)	C(6)-C(5)	1.490(10)
O(29)-C(8)	1.212(7)	C(15)-C(16)	1.494(9)
O(12)-C(1)	1.386(7)	C(15)-C(14)	1.534(9)
O(12)-C(9)	1.421(7)	C(10)-C(9)	1.549(8)
C(23)-C(28)	1.391(8)	C(17)-C(18)	1.366(10)
C(23)-C(24)	1.392(8)	C(17)-C(16)	1.387(8)
C(23)-C(22)	1.463(8)	C(24)-C(25)	1.381(9)
C(13)-C(22)	1.313(8)	C(8)-C(9)	1.515(9)
C(13)-C(14)	1.517(8)	C(4)-C(5)	1.526(11)
C(13)-C(10)	1.537(8)	C(4)-C(3)	1.542(11)
C(28)-C(27)	1.387(9)	C(27)-C(26)	1.365(9)
C(1)-C(2)	1.517(9)	C(25)-C(26)	1.375(10)
C(1)-C(6)	1.535(8)	C(18)-C(19)	1.374(10)

Table S6. Bond angles [°] for spiro-dioxo compound **18b**.

C(10)-O(11)-C(1)	107.8(4)	O(11)-C(10)-C(21)	111.5(4)
C(20)-C(21)-C(16)	119.4(6)	O(11)-C(10)-C(13)	112.2(5)
C(20)-C(21)-C(10)	123.5(6)	C(21)-C(10)-C(13)	108.4(4)
C(16)-C(21)-C(10)	117.0(5)	O(11)-C(10)-C(9)	100.6(4)
C(1)-O(12)-C(9)	102.1(4)	C(21)-C(10)-C(9)	114.6(5)
C(28)-C(23)-C(24)	116.1(6)	C(13)-C(10)-C(9)	109.4(5)
C(28)-C(23)-C(22)	126.0(5)	C(18)-C(17)-C(16)	120.8(7)
C(24)-C(23)-C(22)	117.8(5)	C(25)-C(24)-C(23)	122.2(7)
C(22)-C(13)-C(14)	125.6(5)	O(29)-C(8)-C(7)	123.5(6)
C(22)-C(13)-C(10)	120.6(5)	O(29)-C(8)-C(9)	120.3(6)
C(14)-C(13)-C(10)	113.8(5)	C(7)-C(8)-C(9)	116.1(6)
C(27)-C(28)-C(23)	121.4(6)	C(5)-C(4)-C(3)	108.2(6)
O(12)-C(1)-O(11)	106.0(4)	C(17)-C(16)-C(21)	119.4(6)
O(12)-C(1)-C(2)	110.9(5)	C(17)-C(16)-C(15)	122.1(6)
O(11)-C(1)-C(2)	109.4(5)	C(21)-C(16)-C(15)	118.5(5)
O(12)-C(1)-C(6)	110.7(5)	C(26)-C(27)-C(28)	121.2(7)
O(11)-C(1)-C(6)	108.5(5)	O(12)-C(9)-C(8)	107.9(5)
C(2)-C(1)-C(6)	111.1(5)	O(12)-C(9)-C(10)	102.0(5)
C(19)-C(20)-C(21)	120.2(7)	C(8)-C(9)-C(10)	113.4(5)
C(3)-C(2)-C(1)	111.4(6)	C(13)-C(22)-C(23)	132.4(6)
C(8)-C(7)-C(6)	114.3(6)	C(26)-C(25)-C(24)	120.4(7)
C(5)-C(6)-C(7)	114.3(6)	C(27)-C(26)-C(25)	118.6(7)
C(5)-C(6)-C(1)	112.1(6)	C(17)-C(18)-C(19)	120.0(7)
C(7)-C(6)-C(1)	110.7(5)	C(6)-C(5)-C(4)	112.1(7)
C(16)-C(15)-C(14)	111.7(5)	C(18)-C(19)-C(20)	120.1(7)
C(13)-C(14)-C(15)	114.7(5)	C(2)-C(3)-C(4)	112.5(7)

Single-crystal X-ray Analysis of **22a**

The single-crystal X-ray analysis of **22a** showed that the observed angle of oxido bridge (C4-O7-C1) is 96.0°. The final cycles of least squares refinement yielded R-value of $R_1 = 6.8\%$ ($wR_2 = 11.3\%$) for compound **22a**. The crystal packing arrangements of the compound **22a** in the solid-state architecture and the packing diagram viewed down *b*-axis is shown in Figure S5. The crystal packing pattern revealed close intermolecular links between the molecules, which are associated via only one C-H... π intermolecular interaction between the terminal phenyl rings (C25 to C30) with the acyclic ring hydrogen H51. The C-H... π parameters are as follows C5-H52....Cg; H52....Cg= 3.0695 Å, C5....Cg= 3.858 Å, $\angle$ C5-H52....Cg = 145.70°, symmetry code= $\frac{1}{2}-x, \frac{1}{2}+, -z$, cg is the centroid of the phenyl ring C25 to C30. Additionally, the ketonic O33 oxygen is involved in two intermolecular hydrogen-bonding with the tertiary hydrogen H8 and the phenyl hydrogen H22, respectively forming hydrogen bonded layered architecture along *a*-axis (Figure S5). The H-bonding parameters with symmetry code is depicted in Table S7.

Crystal Data for Compound 22a: $C_{29}H_{28}O_3$, $M = 495.41$, 0.28 x 0.16 x 0.10 mm, Monoclinic, $P2_1/a$, $a = 12.844(5)$ Å, $b = 14.204(5)$ Å, $c = 13.953(3)$ Å, $\beta = 101.11(2)^\circ$, $V = 2497.8(14)$ Å³, $T = 293(2)$ K, $R_1 = 0.0397$, $wR_2 = 0.1059$ on observed data, $z = 4$, $D_{\text{calc.}} = 1.317$ Mg m⁻³, $F(000) = 1040$, Absorption coefficient = 0.289 mm⁻¹, $\lambda = 7093$ Å, 4396 reflections were collected on a CAD-4 diffractometer, 3023 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.203 and -0.256 e Å⁻³, respectively (Figure S4).

FIGURE S4. ORTEP diagram of cycloadduct **22a**.

Table S7. Hydrogen Bonding Parameters for Compound **22a**

D-H.....A(Å)	H.....A(Å)	D.....A(Å)	<D-H.....A(°)
C8-H8.....O33 ¹	H8.....O33=2.449	C8.....O33=3.273	<C8-H8.....O33=153.25
C22-H22.....O33 ²	H22.....O33=2.580	C22.....O33=3.406	<C22-H22...O33=146.23
Symmetry Code 1. -x, 1-y, -z ; 2. 1/2- x, 1/2+y, 1- z

Figure S5. Packing diagram viewed down b-axis showing the hydrogen bonding interaction forming a layered architecture along ac-plane of **22a**.

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for spiro-dioxa compound **22a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl(31)	5324(1)	1345(1)	5228(1)	86(1)
Cl(32)	8630(1)	10777(1)	5227(1)	97(1)
O(10)	13040(1)	3768(1)	11189(1)	42(1)
O(11)	11777(1)	3212(1)	9985(1)	45(1)
C(24)	7831(2)	7526(1)	7715(2)	50(1)
C(28)	8420(2)	9835(2)	5965(2)	62(1)
O(33)	11192(1)	5548(1)	9651(1)	55(1)
C(8)	11316(2)	3991(1)	10403(1)	41(1)
C(16)	7878(2)	5045(1)	8026(1)	41(1)
C(18)	6637(2)	3793(1)	7145(1)	46(1)
C(17)	6938(2)	4636(1)	7751(1)	46(1)
C(12)	8344(2)	6722(1)	7912(1)	44(1)
C(7)	11645(1)	4809(1)	9835(1)	41(1)
C(22)	5467(2)	2457(2)	6805(2)	69(1)
C(19)	7020(2)	3577(2)	6314(2)	59(1)
C(4)	13345(3)	3618(2)	8222(2)	77(1)
C(2)	13641(2)	2908(2)	9911(2)	54(1)
C(25)	8072(2)	8321(1)	7117(1)	49(1)
C(30)	7248(2)	8770(2)	6506(2)	56(1)
C(5)	12465(2)	4238(2)	8460(2)	60(1)
C(3)	13465(3)	2722(2)	8816(2)	72(1)
C(1)	12832(1)	3578(1)	10154(1)	42(1)
C(6)	12676(1)	4500(1)	9558(1)	43(1)
C(15)	8909(2)	4736(2)	7784(2)	48(1)
C(21)	5859(2)	2276(2)	5977(2)	55(1)
C(13)	9336(2)	6438(2)	7546(2)	53(1)
C(14)	9262(2)	5452(2)	7105(2)	58(1)
C(23)	5851(2)	3213(2)	7373(2)	67(1)
C(26)	9087(2)	8671(2)	7143(2)	62(1)
C(20)	6633(2)	2815(2)	5726(2)	67(1)
C(9)	12044(1)	4015(1)	11445(1)	40(1)
C(27)	9258(2)	9426(2)	6565(2)	66(1)
C(34)	13532(2)	5248(2)	9795(2)	58(1)
C(29)	7408(2)	9519(2)	5932(2)	63(1)

Table S9. Bond lengths [Å] for spiro-dioxo compound **22a**.

Cl(31)-C(21)	1.742(2)	C(7)-C(6)	1.514(3)
Cl(32)-C(28)	1.741(2)	C(22)-C(23)	1.370(3)
O(10)-C(9)	1.436(2)	C(22)-C(21)	1.370(3)
O(10)-C(1)	1.443(2)	C(19)-C(20)	1.390(3)
O(11)-C(1)	1.429(2)	C(4)-C(3)	1.510(4)
O(11)-C(8)	1.432(2)	C(4)-C(5)	1.520(3)
C(24)-C(12)	1.320(3)	C(2)-C(1)	1.496(3)
C(24)-C(25)	1.473(3)	C(2)-C(3)	1.524(3)
C(28)-C(27)	1.360(3)	C(25)-C(30)	1.381(3)
C(28)-C(29)	1.368(3)	C(25)-C(26)	1.388(3)
O(33)-C(7)	1.203(2)	C(30)-C(29)	1.370(3)
C(8)-C(7)	1.512(3)	C(5)-C(6)	1.549(3)
C(8)-C(9)	1.570(3)	C(1)-C(6)	1.543(3)
C(16)-C(17)	1.327(3)	C(6)-C(34)	1.519(3)
C(16)-C(15)	1.495(3)	C(15)-C(14)	1.517(3)
C(16)-C(9)#1	1.519(3)	C(21)-C(20)	1.354(3)
C(18)-C(19)	1.380(3)	C(13)-C(14)	1.525(3)
C(18)-C(23)	1.385(3)	C(26)-C(27)	1.384(3)
C(18)-C(17)	1.475(3)	C(9)-C(16)#1	1.519(3)
C(12)-C(13)	1.517(3)	C(9)-C(12)#1	1.524(3)
C(12)-C(9)#1	1.524(3)		

Table S10. Bond angles [°] for spiro-dioxo compound **22a**

C(9)-O(10)-C(1)	106.96(13)	C(4)-C(5)-C(6)	111.1(2)
C(1)-O(11)-C(8)	95.98(13)	C(4)-C(3)-C(2)	112.6(2)
C(12)-C(24)-C(25)	129.1(2)	O(11)-C(1)-O(10)	102.76(13)
C(27)-C(28)-C(29)	121.0(2)	O(11)-C(1)-C(2)	114.14(16)
C(27)-C(28)-Cl(32)	119.9(2)	O(10)-C(1)-C(2)	110.07(15)
C(29)-C(28)-Cl(32)	119.13(19)	O(11)-C(1)-C(6)	101.51(14)
O(11)-C(8)-C(7)	101.59(14)	O(10)-C(1)-C(6)	111.15(15)
O(11)-C(8)-C(9)	100.06(14)	C(2)-C(1)-C(6)	116.18(17)
C(7)-C(8)-C(9)	106.93(15)	C(7)-C(6)-C(34)	111.96(17)
C(17)-C(16)-C(15)	127.00(18)	C(7)-C(6)-C(1)	97.90(14)
C(17)-C(16)-C(9)#1	119.76(17)	C(34)-C(6)-C(1)	117.55(17)
C(15)-C(16)-C(9)#1	112.91(16)	C(7)-C(6)-C(5)	109.10(16)
C(19)-C(18)-C(23)	117.0(2)	C(34)-C(6)-C(5)	111.42(19)
C(19)-C(18)-C(17)	124.44(19)	C(1)-C(6)-C(5)	107.98(17)
C(23)-C(18)-C(17)	118.29(19)	C(16)-C(15)-C(14)	109.21(17)
C(16)-C(17)-C(18)	130.19(19)	C(20)-C(21)-C(22)	121.3(2)
C(24)-C(12)-C(13)	125.28(19)	C(20)-C(21)-Cl(31)	119.88(18)
C(24)-C(12)-C(9)#1	120.72(18)	C(22)-C(21)-Cl(31)	118.82(19)
C(13)-C(12)-C(9)#1	114.00(16)	C(12)-C(13)-C(14)	112.91(18)
O(33)-C(7)-C(8)	127.52(17)	C(15)-C(14)-C(13)	111.52(19)
O(33)-C(7)-C(6)	127.52(18)	C(22)-C(23)-C(18)	122.0(2)
C(8)-C(7)-C(6)	104.96(16)	C(27)-C(26)-C(25)	121.0(2)
C(23)-C(22)-C(21)	119.0(2)	C(21)-C(20)-C(19)	119.0(2)
C(18)-C(19)-C(20)	121.6(2)	O(10)-C(9)-C(16)#1	110.89(14)
C(3)-C(4)-C(5)	111.7(2)	O(10)-C(9)-C(12)#1	112.69(14)
C(1)-C(2)-C(3)	111.25(19)	C(16)#1-C(9)-C(12)#1	108.43(15)
C(30)-C(25)-C(26)	117.1(2)	O(10)-C(9)-C(8)	99.55(14)
C(30)-C(25)-C(24)	119.0(2)	C(16)#1-C(9)-C(8)	116.16(15)
C(26)-C(25)-C(24)	123.9(2)	C(12)#1-C(9)-C(8)	109.02(15)
C(29)-C(30)-C(25)	122.4(2)	C(28)-C(27)-C(26)	119.6(2)
		C(30)-C(29)-C(28)	118.9(2)

Single-crystal X-ray Analysis of **22b**:

Crystal data for the spiro-dioxabicyclo[2.2.1]alkane framework **22b**: $C_{27}H_{26}Cl_2O_3$, $M=469.408$, $0.30\times0.245\times0.14$ mm, Monoclinic, $P2_1/a$, $a=12.512(5)$ Å, $b=14.172(5)$ Å, $c=13.400(7)$ Å, $\beta=96.73(4)^\circ$, $V=2359.7(18)$ Å³, $T=293(2)$ K, $R_1=0.0522$, $wR_2=0.1500$ on observed data, $z=4$, $D_{\text{calc.}}=1.321$ Mg m⁻³, $F(000)=984$, Absorption coefficient= 0.302 mm⁻¹, $\lambda=7093$ Å, 4135 reflections were collected on a CAD-4 diffractometer, 2886 observed reflections ($I\geq 2\sigma(I)$). The largest difference peak and hole=0.286 and -0.256 e Å⁻³, respectively. The single-crystal X-ray analysis of compound **22b** showed that the observed angle of oxido bridge (C4-O7-C1) is 95.96° (Figure S6).

We next examined the packing arrangements of the compound **22b** in the solid-state architecture and the packing diagram viewed down b -axis is shown in Figure S7. The crystal packing pattern revealed close intermolecular links between the molecules, which are associated as dimers via C-H... π hydrogen-bonding interaction between the methyl hydrogen atom and the aromatic rings from either end of the dimeric molecule. The details of the C-H... π interactions is given in Table S11 where Cg1 is the centroid of the phenyl ring C14 to C19 and Cg2 is the centroid of the phenyl ring C21 to C26. Additionally, the dimeric molecules are packed parallel to ac -plane. The dimers are further involved in extensive C-H...O hydrogen bonding interaction, i.e. the bridgehead oxygen atom O2 and ketonic oxygen O30 with tertiary CH and methyl CH from the adjacent dimeric molecules from both sides to form a one dimensional layered architecture along a -axis (Figure S7). The various H-bonding interactions with symmetry codes are shown in Table S12.

Figure S6. ORTEP view of compound **22b**

Figure S7. Solid-state packing diagram of compound **22b** viewed down *b*-axis

Table S11. C-H... π interactions of compound **22b**

C-H... π	H...Cg ($\text{\AA}$)	$\angle$ C-H...Cg ($^\circ$)	Symmetry Code
C29-H29C...Cg1	H29C...Cg1 = 2.859(2)	$\angle$ C29-H29C...Cg1=137.69(4)	1/2-x, 1/2+y, 1-z
C29-H29A...Cg2	H29A...Cg2 = 3.064(3)	$\angle$ C29-H29A...Cg2=142.13(3)	1/2-x, -1/2+y, 1-z

Table S12. Hydrogen bonding parameters for compound **22b**

D-H...A ($\text{\AA}$)	H...A ($\text{\AA}$)	D...A ($\text{\AA}$)	$\angle$ D-H...A ($^\circ$)
C4-H4...O30 ^a	H4...O30 = 2.544	C4...O30 = 3.380	$\angle$ C4-H4...O30 = 154.93
C27-H27A...O30 ^b	H27A...O30 = 2.488	C27...O30 = 3.309	$\angle$ C27-H27A...O30=151.25

^aSymmetry Code; 1-x, 1-y, 1-z; ^bSymmetry Code; 1/2- x, -1/2+y, 1- z.

Table S13. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for spiro-dioxo compound **22b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl(32)	9874(1)	1521(1)	9525(1)	81(1)
Cl(31)	6520(1)	10885(1)	9945(1)	77(1)
O(7)	6626(1)	6969(1)	4825(1)	42(1)
O(6)	8009(1)	6444(1)	5916(1)	37(1)
C(3)	6650(2)	5377(2)	4619(2)	37(1)
O(30)	6245(1)	4614(1)	4429(2)	51(1)
C(5)	7038(2)	6134(2)	6283(2)	35(1)
C(20)	8149(2)	4799(2)	7021(2)	38(1)
C(15)	7836(2)	8787(2)	8553(2)	43(1)
C(9)	6136(2)	4833(2)	7133(2)	42(1)
C(12)	6647(2)	6834(2)	7027(2)	36(1)
C(21)	8484(2)	3951(2)	7618(2)	39(1)
C(4)	6263(2)	6136(2)	5282(2)	37(1)
C(19)	5962(2)	8776(2)	7989(2)	47(1)
C(2)	7646(2)	5781(2)	4235(2)	39(1)
C(11)	5649(2)	6522(2)	7471(2)	45(1)
C(22)	8052(2)	3686(2)	8479(2)	51(1)
C(13)	7194(2)	7621(2)	7256(2)	41(1)
C(24)	9324(2)	2447(2)	8785(2)	48(1)
C(8)	7180(2)	5183(2)	6807(2)	36(1)
C(14)	6976(2)	8387(2)	7948(2)	40(1)
C(16)	7711(2)	9541(2)	9172(2)	47(1)
C(26)	9347(2)	3432(2)	7 354(2)	52(1)
C(17)	6686(2)	9913(2)	9189(2)	47(1)
C(23)	8464(3)	2935(2)	9066(2)	56(1)
C(10)	5753(3)	5518(2)	7893(2)	50(1)
C(18)	5816(3)	9532(2)	8604(2)	53(1)
C(25)	9777(3)	2691(2)	7933(3)	58(1)
C(28)	8613(2)	5113(2)	4407(3)	51(1)
C(27)	8441(3)	7472(2)	4596(3)	60(1)
C(29)	7387(3)	5991(3)	3109(2)	60(1)
C(1)	7728(2)	6687(2)	4871(2)	39(1)

Table S14. Bond lengths [$\text{\AA}$] for spiro-dioxo compound **22b**

Cl(32)-C(24)	1.738(3)
Cl(31)-C(17)	1.736(3)
O(7)-C(4)	1.428(3)
O(7)-C(1)	1.431(3)
O(6)-C(5)	1.434(3)
O(6)-C(1)	1.444(3)
C(3)-O(30)	1.208(3)
C(3)-C(4)	1.510(4)
C(3)-C(2)	1.516(4)
C(5)-C(8)	1.520(3)
C(5)-C(12)	1.526(3)
C(5)-C(4)	1.560(4)
C(20)-C(8)	1.329(3)
C(20)-C(21)	1.477(4)
C(15)-C(16)	1.372(4)
C(15)-C(14)	1.390(4)
C(9)-C(8)	1.510(3)
C(9)-C(10)	1.524(4)
C(12)-C(13)	1.326(4)
C(12)-C(11)	1.511(3)
C(21)-C(22)	1.382(4)
C(21)-C(26)	1.387(4)
C(19)-C(18)	1.376(4)
C(19)-C(14)	1.391(4)
C(2)-C(28)	1.533(4)
C(2)-C(29)	1.534(4)
C(2)-C(1)	1.538(3)
C(11)-C(10)	1.531(4)
C(22)-C(23)	1.387(4)
C(13)-C(14)	1.474(4)
C(24)-C(23)	1.368(4)
C(24)-C(25)	1.376(4)
C(16)-C(17)	1.390(4)
C(26)-C(25)	1.376(4)
C(17)-C(18)	1.376(4)
C(27)-C(1)	1.499(4)

Table S15. Bond angles [°] for spiro-dioxo compound **22b**

C(4)-O(7)-C(1)	95.96(17)	C(28)-C(2)-C(1)	115.6(2)
C(5)-O(6)-C(1)	106.64(17)	C(29)-C(2)-C(1)	112.1(2)
O(30)-C(3)-C(4)	127.3(2)	C(12)-C(11)-C(10)	112.3(2)
O(30)-C(3)-C(2)	127.4(2)	C(21)-C(22)-C(23)	121.7(3)
C(4)-C(3)-C(2)	105.3(2)	C(12)-C(13)-C(14)	129.6(2)
O(6)-C(5)-C(8)	111.83(19)	C(23)-C(24)-C(25)	121.0(3)
O(6)-C(5)-C(12)	112.00(19)	C(23)-C(24)-Cl(32)	119.7(2)
C(8)-C(5)-C(12)	107.68(19)	C(25)-C(24)-Cl(32)	119.3(2)
O(6)-C(5)-C(4)	99.79(18)	C(20)-C(8)-C(9)	127.0(2)
C(8)-C(5)-C(4)	115.2(2)	C(20)-C(8)-C(5)	121.2(2)
C(12)-C(5)-C(4)	110.3(2)	C(9)-C(8)-C(5)	111.5(2)
C(8)-C(20)-C(21)	130.1(2)	C(15)-C(14)-C(19)	117.5(3)
C(16)-C(15)-C(14)	122.4(3)	C(15)-C(14)-C(13)	118.7(2)
C(8)-C(9)-C(10)	109.5(2)	C(19)-C(14)-C(13)	123.6(3)
C(13)-C(12)-C(11)	125.7(2)	C(15)-C(16)-C(17)	118.4(3)
C(13)-C(12)-C(5)	120.1(2)	C(25)-C(26)-C(21)	121.7(3)
C(11)-C(12)-C(5)	114.2(2)	C(18)-C(17)-C(16)	120.8(3)
C(22)-C(21)-C(26)	117.5(3)	C(18)-C(17)-Cl(31)	120.3(2)
C(22)-C(21)-C(20)	124.0(2)	C(16)-C(17)-Cl(31)	119.0(2)
C(26)-C(21)-C(20)	118.3(2)	C(24)-C(23)-C(22)	118.9(3)
O(7)-C(4)-C(3)	101.33(19)	C(9)-C(10)-C(11)	111.4(2)
O(7)-C(4)-C(5)	100.02(19)	C(17)-C(18)-C(19)	119.7(3)
C(3)-C(4)-C(5)	107.2(2)	C(24)-C(25)-C(26)	119.2(3)
C(18)-C(19)-C(14)	121.2(3)	O(7)-C(1)-O(6)	103.40(18)
C(3)-C(2)-C(28)	112.4(2)	O(7)-C(1)-C(27)	112.4(2)
C(3)-C(2)-C(29)	108.6(2)	O(6)-C(1)-C(27)	109.3(2)
C(28)-C(2)-C(29)	109.9(3)	O(7)-C(1)-C(2)	102.0(2)
C(3)-C(2)-C(1)	97.5(2)	O(6)-C(1)-C(2)	109.36(19)
		C(27)-C(1)-C(2)	119.1(2)

Crystal Data for Compound 35a: $C_{31}H_{30}O_3$, $M = 450.55$, $0.30 \times 0.22 \times 0.16$ mm, Triclinic, P-1, $a = 6.794(2)$ Å, $b = 13.029(5)$ Å, $c = 15.484(4)$ Å, $\alpha = 104.35(3)^\circ$, $\beta = 102.48(2)^\circ$, $\gamma = 104.49(4)^\circ$, $V = 1227.8(7)$ Å³, $T = 293(2)$ K, $R_1 = 0.0617$, $wR_2 = 0.1965$ on observed data, $z = 2$, $D_{\text{calc.}} = 1.219$ Mg m⁻³, $F(000) = 480$, Absorption coefficient = 0.077 mm⁻¹, $\lambda = 7.093$ Å, 4301 reflections were collected on a CAD-4 diffractometer, 3015 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.516 and -0.360 e Å⁻³, respectively (Figure S8).

FIGURE S8. ORTEP view of the rearranged product **35a**.

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for spiro-dioxo compound **35a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O(14)	2040(2)	6556(1)	7567(1)	42(1)
O(15)	4616(3)	6188(1)	8591(1)	46(1)
C(12)	-1731(4)	5690(2)	6961(2)	40(1)
C(13)	286(4)	5756(2)	7568(2)	36(1)
C(5)	3462(4)	7652(2)	9267(2)	42(1)
O(33)	2302(4)	6804(2)	10376(1)	76(1)
C(9)	70(4)	5017(2)	8039(2)	42(1)
C(8)	1658(4)	4783(2)	8747(2)	45(1)
C(16)	-1991(4)	6395(2)	6472(2)	45(1)
C(25)	2147(4)	3745(2)	8303(2)	48(1)
C(18)	-4239(4)	7200(2)	5580(2)	52(1)
C(26)	1317(4)	2769(2)	8405(2)	49(1)
C(7)	3640(4)	5804(2)	9237(2)	48(1)
C(27)	1572(4)	1701(2)	7952(2)	45(1)
C(17)	-4005(4)	6417(2)	5964(2)	48(1)
C(11)	-3408(4)	4747(2)	7042(2)	48(1)
C(1)	3836(3)	7026(2)	8363(2)	38(1)
C(28)	69(5)	707(2)	7858(2)	57(1)
C(6)	3034(4)	6770(2)	9737(2)	50(1)
C(19)	-6226(5)	7338(2)	5117(2)	53(1)
C(2)	5554(4)	7852(2)	8162(2)	50(1)
C(4)	5708(5)	8511(2)	9783(2)	58(1)
C(20)	-6183(7)	8240(3)	4796(3)	83(1)
C(10)	-2236(5)	4315(3)	7755(3)	60(1)
C(32)	3264(5)	1637(2)	7606(2)	60(1)
C(34)	1743(5)	8194(3)	9144(3)	61(1)
C(30)	1855(7)	-368(3)	7050(3)	77(1)
C(29)	201(6)	-309(2)	7407(2)	71(1)
C(21)	-8068(10)	8400(5)	4372(3)	107(2)
C(24)	-8201(5)	6588(3)	4978(2)	65(1)
C(3)	6527(5)	8859(3)	9020(2)	72(1)
C(23)	-10048(6)	6741(4)	4534(2)	83(1)
C(22)	-9976(8)	7639(5)	4233(3)	96(1)
C(31)	3386(6)	606(3)	7148(3)	74(1)

Table S17. Bond lengths [Å] for spiro-dioxo compound **35a**.

O(14)-C(13)	1.373(3)	C(26)-C(27)	1.466(4)
O(14)-C(1)	1.409(3)	C(7)-C(6)	1.506(4)
O(15)-C(1)	1.413(3)	C(27)-C(32)	1.382(4)
O(15)-C(7)	1.434(3)	C(27)-C(28)	1.386(4)
C(12)-C(16)	1.348(4)	C(11)-C(10)	1.523(4)
C(12)-C(13)	1.453(3)	C(1)-C(2)	1.521(3)
C(12)-C(11)	1.504(4)	C(28)-C(29)	1.369(5)
C(13)-C(9)	1.343(3)	C(19)-C(20)	1.380(5)
C(5)-C(6)	1.508(3)	C(19)-C(24)	1.384(4)
C(5)-C(34)	1.511(4)	C(2)-C(3)	1.499(4)
C(5)-C(1)	1.543(3)	C(4)-C(3)	1.527(5)
C(5)-C(4)	1.547(4)	C(20)-C(21)	1.398(6)
O(33)-C(6)	1.196(3)	C(32)-C(31)	1.388(5)
C(9)-C(10)	1.507(4)	C(30)-C(29)	1.367(5)
C(9)-C(8)	1.509(4)	C(30)-C(31)	1.375(5)
C(8)-C(25)	1.508(4)	C(21)-C(22)	1.357(7)
C(8)-C(7)	1.523(4)	C(24)-C(23)	1.381(4)
C(16)-C(17)	1.434(4)	C(23)-C(22)	1.357(6)
C(25)-C(26)	1.320(4)		
C(18)-C(17)	1.327(4)		
C(18)-C(19)	1.462(4)		

Table S18. Bond angles [°] for spiro-dioxo compound **35a**.

C(13)-O(14)-C(1)	119.54(17)	C(28)-C(27)-C(26)	119.6(3)
C(1)-O(15)-C(7)	109.71(18)	C(18)-C(17)-C(16)	124.0(3)
C(16)-C(12)-C(13)	125.0(2)	C(12)-C(11)-C(10)	105.4(2)
C(16)-C(12)-C(11)	128.3(2)	O(14)-C(1)-O(15)	110.91(18)
C(13)-C(12)-C(11)	106.7(2)	O(14)-C(1)-C(2)	108.53(19)
C(9)-C(13)-O(14)	131.8(2)	O(15)-C(1)-C(2)	109.66(19)
C(9)-C(13)-C(12)	112.8(2)	O(14)-C(1)-C(5)	115.70(19)
O(14)-C(13)-C(12)	115.36(19)	O(15)-C(1)-C(5)	104.39(18)
C(6)-C(5)-C(34)	113.4(2)	C(2)-C(1)-C(5)	107.5(2)
C(6)-C(5)-C(1)	102.90(19)	C(29)-C(28)-C(27)	121.5(3)
C(34)-C(5)-C(1)	116.1(2)	O(33)-C(6)-C(7)	125.4(3)
C(6)-C(5)-C(4)	109.9(2)	O(33)-C(6)-C(5)	127.1(3)
C(34)-C(5)-C(4)	112.9(2)	C(7)-C(6)-C(5)	107.5(2)
C(1)-C(5)-C(4)	100.5(2)	C(20)-C(19)-C(24)	117.4(3)
C(13)-C(9)-C(10)	109.4(2)	C(20)-C(19)-C(18)	120.2(3)
C(13)-C(9)-C(8)	132.3(2)	C(24)-C(19)-C(18)	122.4(3)
C(10)-C(9)-C(8)	118.3(2)	C(3)-C(2)-C(1)	106.9(2)
C(25)-C(8)-C(9)	110.7(2)	C(3)-C(4)-C(5)	105.1(2)
C(25)-C(8)-C(7)	113.1(2)	C(19)-C(20)-C(21)	121.0(4)
C(9)-C(8)-C(7)	111.0(2)	C(9)-C(10)-C(11)	105.7(2)
C(12)-C(16)-C(17)	125.1(3)	C(27)-C(32)-C(31)	120.3(3)
C(26)-C(25)-C(8)	122.8(3)	C(29)-C(30)-C(31)	119.1(3)
C(17)-C(18)-C(19)	127.7(3)	C(30)-C(29)-C(28)	120.5(3)
C(25)-C(26)-C(27)	126.9(3)	C(22)-C(21)-C(20)	120.1(4)
O(15)-C(7)-C(6)	105.0(2)	C(23)-C(24)-C(19)	121.0(3)
O(15)-C(7)-C(8)	112.3(2)	C(2)-C(3)-C(4)	105.7(2)
C(6)-C(7)-C(8)	109.6(2)	C(22)-C(23)-C(24)	120.8(4)
C(32)-C(27)-C(28)	117.8(3)	C(23)-C(22)-C(21)	119.7(4)
C(32)-C(27)-C(26)	122.5(2)	C(30)-C(31)-C(32)	120.7(3)

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