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One-step Synthesis and Highly Regio- and Stereoselective Diels-Alder Cycloadditions of Novel *exo*-2-Oxazolidinone Dienes

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Experimental Section

General. All air and moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. Dioxane and xylene were freshly distilled from sodium. Li_2CO_3 was dried overnight at 100 °C before using. Triethylamine was freshly distilled from NaOH. Further analytical procedures were described elsewhere.[1]

General Procedure for the Preparation of *N*-Aryl-4,5-Dimethylene-2-oxazolidinones 1c-1g. A solution of 2,3-butanedione (**2a**) (3.0 g, 34 mmol) in dry dioxane (10 mL) and triethylamine (5.29 g, 52 mmol) were added dropwise to a magnetically stirred solution of dioxane (10 mL) containing anhydrous Li_2CO_3 (2.5 g, 34 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 30 min. Then, a solution of the corresponding aryl isocyanate (52 mmol) in dioxane (10 mL) was added over a period of 30 min and stirring was continued for 12 h at room temperature. The mixture was filtered and the solvent removed under vacuo. The residue was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 95:5) to give dienes **1c-1g**.

***N*-(*m*-Chlorophenyl)-4,5-dimethylene-2-oxazolidinone (1c).** Using the general procedure with 7.98 g of *m*-chlorophenyl isocyanate (**3c**) gave 3.08 g (40%) of **1c** as pale yellow crystals (CH_2Cl_2/hexane, 1:1): R_f 0.66 (hexane/EtOAc, 8:2); mp 57 °C (dec); IR (KBr) 1770, 1710, 1630, 1590, 1490, 1410, 1310, 1235, 890, 830, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.40 (d, J = 3.2 Hz, 1H, H-7a), 4.80 (d, J = 3.2 Hz, 1H, H-7b), 4.95 (d, J = 3.6 Hz, 1H, H-6a), 5.00 (d, J = 3.6 Hz, 1H, H-6b), 7.21-7.31 (m, 1H, ArH), 7.38-7.49 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.7 (C-7), 87.3 (C-6), 125.0 (C-13), 127.2 (C-9), 128.9 (C-11), 130.6 (C-12), 134.2 (C-8), 135.3 (C-10), 138.3 (C-4), 148.6 (C-5), 152.1 (C-2); MS (70 eV) 223 (M^++2, 16), 221 (M^+, 48), 186 (4), 177 (9), 151 (15), 142 (100), 125 (9), 116 (14), 111 (47), 102 (17), 75 (35), 63 (12), 51 (12). Anal. Calcd for $C_{11}H_8ClNO_2$: C, 59.61; H, 3.64. Found: C, 59.66; H, 3.70.

4,5-Dimethylene-*N*-(*o*-tolyl)-2-oxazolidinone (1d). Using the general procedure with 6.92 g of *o*-tolyl isocyanate (**3d**) gave 3.15 g (45%) of **1d** as a pale yellow oil: R_f 0.61 (hexane/EtOAc, 8:2); IR ($CHCl_3$) 1760, 1740, 1650, 1500, 1400, 1310, 1090, 1020, 810, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 3H, CH_3), 4.01 (d, J = 2.9 Hz, 1H, H-7a), 4.72 (d, J = 2.9 Hz, 1H, H-7b), 4.94 (d, J = 3.5 Hz, 1H, H-6a), 4.98 (d, J = 3.5 Hz 1H, H-6b) 7.21 (dd, J = 6.3, 2.2 Hz, 1H, H-13), 7.25-7.40 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3 (CH_3Ar), 84.6 (C-7), 87.0 (C-6), 127.4 (C-12), 128.4 (C-13), 129.7 (C-11), 131.4 (C-8), 131.6 (C-10), 136.6 (C-9), 138.7 (C-4), 149.0 (C-5), 152.0 (C-2); MS (70 eV): 201 (M^+, 66), 186 (77), 157 (7), 156 (34), 142 (100), 130 (92), 116 (28), 104 (14), 91 (43), 77 (19), 51 (25). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51. Found: C, 71.46; H, 5.63.

4,5-Dimethylene-*N*-(*p*-tolyl)-2-oxazolidinone (1e). Using the general procedure with 6.91 g of *p*-tolyl isocyanate (**3e**) gave 3.15 g (45%) of **1e** as colorless crystals (CH_2Cl_2/hexane, 1:3): R_f 0.63 (hexane/EtOAc, 8:2); mp 79-80 °C; IR (KBr) 1760, 1630, 1510, 1410, 1300, 1225, 1180, 1080, 1020, 890, 865 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 4.30 (d, J = 3.0 Hz, 1H, H-7a), 4.72 (d, J = 3.0 Hz, 1H, H-7b), 4.90 (d, J = 3.5 Hz, 1H, H-6a), 4.95 (d, J = 3.5 Hz, 1H, H-6b), 7.17- 7.35 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3Ar), 84.3 (C-7), 86.7 (C-6), 126.6 (C-9), 130.0 (C-8), 130.2 (C-10), 138.7 (C-11), 138.9 (C-4), 148.8 (C-5), 152.4 (C-2); MS (70 eV): 201 (M^+, 100), 186 (37), 157 (23), 156 (32), 142 (55), 131 (28), 116 (39), 104 (11), 91 (74), 77 (16), 65 (58), 51 (27). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51. Found: C, 71.49; H, 5.65.

4,5-Dimethylene-*N*-(*m*-tolyl)-2-oxazolidinone (1f). Using the general procedure with 6.91 g of *o*-tolyl isocyanate (**3f**) gave 2.8 g (40%) of **1f** as colorless crystals (CH_2Cl_2/hexane, 1:3): R_f 0.65 (hexane/EtOAc, 8:2); mp 54-55 °C; IR (KBr) 1780, 1760, 1640, 1500, 1410, 1310, 1190, 1090, 900, 840, 795 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H, CH_3), 4.34 (d, J = 3.0 Hz, 1H, H-7a), 4.75 (d, J = 3.0 Hz, 1H, H-7b), 4.92 (d, J = 3.5 Hz, 1H, H-6a), 4.97 (d, J = 3.5 Hz, 1H, H-6b), 7.12-7.17 (m, 2H, ArH), 7.23 (dm, J = 7.7 Hz, 1H, H-11), 7.36 (t, J = 7.7 Hz, 1H, H-12); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3 (C-14), 84.6 (C-7), 86.9 (C-6), 123.9 (C-13), 127.5 (C-9), 129.5 (C-11), 129.6 (C-12), 132.9 (C-8), 138.9 (C-4), 139.9 (C-10), 148.9 (C-5), 152.4 (C-2); MS (70 eV) 201 (M^+, 100), 186 (9), 157 (66), 156 (48), 142 (66), 130 (14), 117 (37), 104 (12), 91 (91), 77 (19), 65 (67), 51 (27). Anal. Calcd for $C_{12}H_{11}NO_2$: C 71.63; H 5.51. Found: C 71.65; H 5.78.

***N*-(*o*-Bromophenyl)-4,5-dimethylene-2-oxazolidinone (1g).** Using the general procedure with 10.27 g of *o*-bromophenyl isocyanate (**3g**) gave 5.54 g (60%) of **1g** as pale yellow crystals (CH_2Cl_2/hexane, 1:1): R_f 0.58 (hexane/EtOAc, 8:2); mp 88-89 °C; IR (KBr) 1780, 1635, 1490, 1410, 1310, 1235, 1090, 1020, 890, 810, 790 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.01 (d, J = 3.2 Hz, 1H, H-7a), 4.76 (d, J = 3.2 Hz, 1H, H-7b), 4.96 (d, J = 3.6 Hz 1H, H-6a), 5.00 (d, J = 3.6 Hz, 1H, H-6b), 7.33-7.42 (m, 2H, H-11, H-13), 7.47 (ddd, J = 8.2, 7.0, 1.5 Hz, 1H, H-12), 7.76 (dd, J = 7.8, 1.5 Hz, 1H, H-10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.2 (C-7), 87.5 (C-6), 123.3 (C-9), 129.0 (C-12), 130.6 (C-13), 131.3 (C-11), 132.0 (C-8), 134,1 (C-10), 138.2 (C-4), 148.8 (C-5), 151.5 (C-2); MS (70 eV): 267 (M^++2, 54), 265 (M^+, 55), 186 (71), 157 (35), 155 (35), 142 (100), 115 (50), 102 (32), 75 (35), 51 (16). Anal. Calcd for $C_{11}H_8BrNO_2$: C, 49.65; H, 3.03; N, 5.26. Found: C, 49.62; H, 3.13; N, 5.27.

***N*-(Chloroethyl)-4,5-dimethylene-2-oxazolidinone (1h).** A solution of 2,3-butanedione (**2a**) (3.0 g, 34 mmol) in dry dioxane (10 mL) and triethylamine (5.29 g, 52 mmol) were added dropwise to a magnetically stirred solution of dioxane (10 mL) containing anhydrous Li_2CO_3 (2.5 g, 34 mmol) at 60 °C under N_2 atmosphere and the mixture was stirred for 30 min. Then, a solution of 2-chloroethyl isocyanate (**3h**) (5.49 g, 52 mmol) in dioxane (10 mL) was added over a period of 30 min and stirring was continued for 4 h at 60 °C. The mixture was filtered and the solvent removed under vacuo. The residue was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 95:5) to give 4.16 g (69%) of **1h** (Caution: **1h** decomposes at room

temperature): R_f 0.58 (hexane/EtOAc, 8:2); IR ($CHCl_3$) 1770, 1700, 1650, 1630, 1450, 1410, 1350, 1280, 1150, 1090, 880, 800, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.70 (t, J = 6.1 Hz, 2H, CH_2Cl), 3.86 (t, J = 6.1 Hz, 2H, CH_2N), 4.42 (d, J = 3.5 Hz, 1H, H-7a), 4.79 (d, J = 3.5 Hz, 1H, H-7b), 4.89 (d, J = 3.6 Hz, 1H, H-6a), 4.95 (d, J = 3.6 Hz, 1H, H-6b); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.3 (C-8), 42.9 (C-9), 83.4 (C-7), 87.3 (C-6), 137.3 (C-4), 148.6 (C-5), 153.2 (C-2); MS (70 eV) 175 (M^++2, 11), 173 (M^+, 34), 138 (100), 124 (4), 111 (8), 80 (38), 63 (29).

General Procedure for the Preparation of (5*Z*)-*N*-Substituted-5-ethylidene-4-methylene-2-oxazolidinones 4e-4j. A solution of 2,3-pentanedione (**2b**) (0.35 g, 3.5 mmol) in dry dioxane (1 mL) was added dropwise to a magnetically stirred solution of triethylamine (0.71 g, 7.0 mmol) in dioxane (2 mL) containing anhydrous Li_2CO_3 (0.31 g, 4.2 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 30 min. Then, a solution of the corresponding aryl isocyanate (5.2 mmol) in dioxane (2 mL) was added over a period of 30 min and stirring was continued for 12 h at room temperature. The mixture was filtered and solvent removed under vacuo. The residue was purified by column chromatography over silica gel impregnated with triethylamine (10%) in hexane (hexane/EtOAc, 9:1) to give dienes **4e-4j**.

(5*Z*)-5-Ethylidene-4-methylene-*N*-(*m*-tolyl)-2-oxazolidinone (4e). Using the general procedure with *m*-tolyl isocyanate (**3f**) (0.69 g) gave a mixture of **4e/5b**, which after purification yielded 0.46 g (42%) of **4e** as colorless crystals (CH_2Cl_2/hexane, 1:1) and 0.18 g (15%) of **5b** as colorless crystals (CH_2Cl_2/hexane, 1:1). **4e**: R_f 0.5 (hexane/EtOAc, 9:1); mp 80-81 °C; IR (KBr) 1770, 1700, 1490, 1390, 1270, 1090, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (dt, J = 7.3, 0.7 Hz, 3H, CH_3C=), 2.39 (s, 3H, $ArCH_3$), 4.16 (d, J = 2.9 Hz, 1H, H-7a), 4.56 (d, J = 2.9 Hz, 1H, H-7b), 5.40 (q, J = 7.3 Hz, 1H, H-6b), 7.11-7.17 (m, 2H, ArH), 7.21 (dm, J = 7.6 Hz, 1H, ArH), 7.37 (br t, J = 7.6 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.3 (C-8), 21.2 (CH_3Ar), 81.5 (C-7), 98.9 (C-6), 123.7 (C-14), 126.9 (C-10), 129.5 (C-12), 129.6 (C-13), 133.1 (C-9), 139.2 (C-4), 139.6 (C-11), 143.5 (C-5), 152.9 (C-2); MS (70 eV) 215 (M^+, 86), 200 (7), 170 (30), 156 (17), 132 (100), 91 (41), 65 (24); Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.08; N, 6.50. Found: C, 72.45; H, 6.04; N, 6.41. **5b**: R_f 0.4 (hexane/EtOAc, 4:1); mp 107-108 °C; IR (KBr) 3310, 1770, 1710, 1580, 1490, 1250, 1140, 1060, 950 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 3H, Me-7), 1.66 (d, J = 7.0 Hz, 3H, CH_3C=), 2.33 (s, 3H, CH_3Ar), 4.12 (s, 1 H, OH), 5.06 (q, J = 7.0 Hz, 1H, H-4), 7.11-7.26 (m, 4H, ArH); ^{13}H

NMR (75 MHz, $CDCl_3$) δ 9.9 (Me-7), 21.4 (CH_3Ar), 25.4 (CH_3C=), 87.9 (C-4), 99.6 (C-6), 124.2 (C-14), 127.7 (C-10), 128.7 (C-12), 128.8 (C-13), 133.6 (C-9), 139.0 (C-11), 150.9 (C-5), 153.1 (C-2). Anal. Calcd. for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.15; H, 6.20; N, 5.99.

(5*Z*)-5-Ethylidene-*N*-(*m*-methoxyphenyl)-4-methylene (4f). Using the general procedure with *m*-methoxyphenyl isocyanate (**3i**) (0.77 g) gave 0.31 g (38%) of **4f** as colorless crystals (hexane/CH_2Cl_2, 7:3): R_f 0.4 (hexane/EtOAc, 9:1); mp 83-84 °C, IR (KBr) 1779, 1695, 1636, 1488, 1394, 1279, 1214, 1028, 826, 762, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (d, J = 7.3 Hz, 3H, CH_3C=), 3.82 (s, 3H, OMe), 4.22 (d, J = 2.9 Hz, 1H, H-7a), 4.58 (d, J = 2.9 Hz, 1H, H-7b), 5.43 (q, J = 7.3 Hz, 1H, H-6b), 6.87 (dd, J = 2.2, 2.1 Hz, 1H, ArH), 6.91-6.97 (m, 2H, ArH), 7.39 (dd, J = 8.2, 8.1 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 (C-8), 55.4 (CH_3O), 81.7 (C-7), 99.1 (C-6), 112.6 (C-10), 114.5 (C-12), 119.1 (C-14), 130.4 (C-13), 134.1 (C-9), 139.1 (C-4), 143.1 (C-5), 152.6 (C-2), 160.5 (C-11); MS (70 eV) 231 (M^+, 8), 186 (10), 172 (10), 148 (28), 147 (24), 103 (19), 92 (40), 77 (71), 63 (100), 51 (60). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06; Found: C, 67.57; H, 5.49; N, 6.05

(5*Z*)-*N*-(*o*-Chlorophenyl)-5-ethylidene-4-methylene-2-oxazolidinone (4g). Using the general procedure with *o*-chlorophenyl isocyanate (**3j**) (0.79 g) gave 0.16 g (27%) of **4g** as colorless crystals (hexane/CH_2Cl_2, 7:3): R_f 0.5 (hexane/EtOAc, 9:1); mp 79-80 °C, IR (KBr) 1781, 1696, 1637, 1488, 1395, 1305, 1280, 1215, 1029, 981, 826, 762, 730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.87 (d, J = 7.3 Hz, 3H, CH_3C=), 3.85 (d, J = 3.1 Hz, 1H, H-7a), 4.57 (d, J = 3.1 Hz, 1H, H-7b), 5.43 (q, J = 7.3 Hz, 1H, H-6b), 7.35-7.45 (m, 3H, ArH), 7.52-7.60 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5 (C-8), 82.0 (C-7), 99.6 (C-6), 128.2 (C-13), 130.4 (C-14), 130.5 (C-9), 130.9 (C-11, C-12), 133.4 (C-10), 138.5 (C-4), 143.2 (C-5), 152,1 (C-2); MS (70 eV) 237 (M^++2, 22), 235 (M^+, 63), 200 (12), 190 (6), 154 (39), 152 (100), 151 (41), 138 (17), 129 (12), 111 (33), 90 (10), 75 (33). Anal. Calcd for $C_{12}H_{10}NO_2Cl$: C, 61.15; H, 4.24; N, 5.94. Found: C, 61.16; H, 4.30; N, 6.01.

(5*Z*)-*N*-(*o*-Bromophenyl)-5-ethylidene-4-methylene-2-oxazolidinone (4h). Using the general procedure with *o*-bromophenyl isocyanate (**3g**) (0.56 g) gave 0.08 g (18%) of **4h** as colorless crystals (hexane/CH_2Cl_2, 7:3): R_f 0.70 (hexane/EtOAc, 9:1); mp 78-79 °C, IR (KBr) 1775, 1631, 1620, 1481, 1387, 1298, 1210, 1088, 794 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90 (d, J = 7.3 Hz, 3H, CH_3C=), 3.82 (d, J = 3.0 Hz, 1H, H-7a), 4.59 (d, J = 3.0 Hz, 1H, H-7b), 5.44 (q, J = 7.3 Hz, 1H, H-

6b), 7.30-7.50 (m, 3H, ArH), 7.73 (dd, J = 8.2, 1.5 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.3 (q, J = 128.8 Hz, C-8), 81.8 (t, J = 164.6 Hz, C-7), 99.4 (dq, J = 159.2, 7.2 Hz, C-6), 128.6 (dd, J = 164.9, 8.5 Hz, C-13), 130.4 (dd, J = 165.1, 7.1 Hz, C-14), 130.7 (m, C-10), 130.8 (br d, J = 163.5 Hz, C-11), 130.9 (br d, J = 164.9 Hz, C-12), 133.5 (m, C-9), 138.6 (br s, C-4), 143.3 (m, C-5), 152.0 (C-2); MS (70 eV) 198 (M^+-81, 15), 196 (18), 155 (22), 129 (28), 117 (30), 102 (23), 90 (50), 76 (85), 75 (100), 63 (61), 55 (61). Anal. Calcd for $C_{12}H_{10}NO_2Br$: C, 51.45; H, 3.60; N, 5.00. Found: C, 51.60; H, 3.41; N, 5.10.

(5Z)-5-Ethylidene-4-methylene-*N*-(*o*-tolyl)-2-oxazolidinone (4i). Using the general procedure with *o*-tolyl isocyanate (**3d**) (0.65 g) gave 0.17 g (23%) of **4i** as colorless crystals (hexane/CH_2Cl_2, 7:3): R_f 0.4 (hexane/EtOAc, 9:1); mp 81-82 °C; IR (KBr) 1780, 1697, 1625, 1495, 1395, 1270, 1215, 1030, 980, 817, 770, 725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86 (d, J = 7.3 Hz, 3H, CH_3C=), 2.22 (s, 3H, $ArCH_3$), 3.83 (d, J = 2.8 Hz, 1H, H-7a), 4.53 (d, J = 2.8 Hz, 1H, H-7b), 5.41 (q, J = 7.3 Hz, 1H, H-6b), 7.20 (dm, J = 7.2 Hz, 1H, ArH), 7.25-7.38 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 (C-8), 17.3 (CH_3Ar), 81.7 (C-7), 99.2 (C-6), 127.3 (C-13), 128.4 (C-14), 128.6 (C-12), 131.5 (C-11), 131.55 (C-9), 136.7 (C-10), 139.1 (C-4), 143.3 (C-5), 152.5 (C-2); MS (70 eV) 215 (M^+, 43), 200 (62), 170 (21), 156 (41), 144 (20), 130 (100), 117 (21), 104 (20), 91 (42), 89 (34), 77 (20), 65 (52), 51 (22). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.08; N, 6.50. Found: C, 72.55; H, 6.12; N, 6.49.

(5Z)-*N*-(Chloroethyl)-5-ethylidene-4-methylene-2-oxazolidinone (4j). Using the general procedure with *o*-chloroethyl isocyanate (**3h**) (0.56 g) gave 0.17 g (26%) of **4j** as yellow oil: R_f 0.3 (hexane/EtOAc, 9:1); IR (film) 1781, 1698, 1665, 1445, 1404, 1339, 1246, 1080, 1033, 806, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (d, J = 7.3 Hz, 3H, CH_3C=), 3.71 (t, J = 6.2 Hz, 2H, CH_2Cl), 3.84 (t, J = 6.2 Hz, 2H, CH_2N), 4.23 (d, J = 3.4 Hz, 1H, H-7a), 4.61 (d, J = 3.4 Hz, 1H, H-7b), 5.39 (q, J = 7.3 Hz, 1H, H-6b); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 (C-8), 39.2 (C-9), 42.7 (C-10), 80.4 (C-7), 99.6 (C-6), 137.5 (C-4), 142.9 (C-5), 153.6 (C-2); MS (70 eV) 187 (M^+, 64), 152 (39), 138 (18), 125 (21), 97 (28), 82 (9), 63 (37), 56 (100). Anal. Calcd for $C_8H_{10}NO_2Cl$: C, 51.20; H, 5.37. Found: C, 50.89; H, 5.66.

Crystallography. Crystals were mounted in glass capillaries. Crystallographic measurements were carried out with a CAD4 Enraf-Nonius diffractometer with Mo Kα radiation at room temperature. Two standard reflections were monitored periodically; they showed no change during data collection. ORTEP structures of diene **4c** and adduct **13c** are illustrated in Figures 1 and 2, respectively. Crystal data and data collection parameters are summarized in Table 1. Unit cell parameters were obtained for **4c** from least-squares refinement of 25 reflections in the range $2<2\theta<20°$, and for **13c** in the range $10<2\theta<15°$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. In the case of **4c**, hydrogen atoms were placed in idealized positions and their atomic coordinates refined; for **13c**, hydrogen atoms were found in a Fourier map and their atomic coordinates refined. Unit weights were used in the refinement. Structures were solved using CRYSTALS[2] adapted on a PC computer. Atomic form factors were taken from tables.[3]

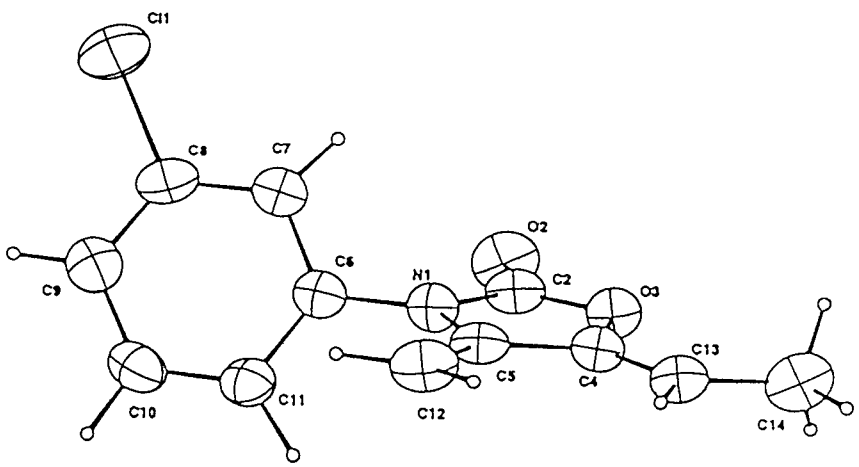


Figure 1. ORTEP structure of diene **4c**.

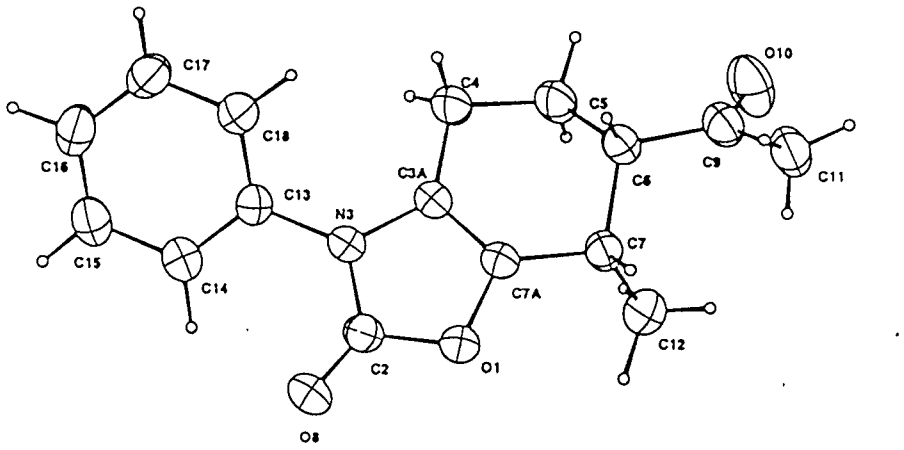


Figure 2. ORTEP structure of adduct **13c.**

References

1. Orduña, A.; Zepeda, L. G.; Tamariz, J. *Synthesis* **1993**, 375.

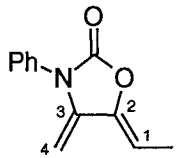
2. Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS, an Advanced Crystallographic Program System*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1994.

3. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

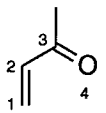
Table 1. Crystal Data for Compounds 4c and 13c

Compound	**4c**	**13c**
Formula	$C_{12}H_{10}ClNO_2$	$C_{16}H_{17}NO_3$
Mw (g mol^{-1})	235.67	271.31
Crystal system	monoclinic	monoclinic
Space group	P $2_1/c$	P $2_1/n$
Crystal size (mm)	0.3 x 0.3 x 0.4	0.4 x 0.4 x 0.5
a (Å)	7.529(1)	10.401(4)
b (Å)	13.299(3)	10.971(2)
c (Å)	11.656(3)	12.801(4)
β (deg)	106.1(2)	107.09(3)
V ($Å^3$)	1121(3)	1396.2(8)
Z	4	4
F(000)	488	576
Radiation	MoKα (λ = .71069 Å)	MoKα (λ = .71069 Å)
μ (cm^{-1})	3.20	0.8337
D_c (g cm^{-3})	1.40	1.29
Scan type	ω/2θ	ω/2θ
2θ scan range (deg)	0.53 + 0.65 tg θ	0.8 + 0.345 tg θ
θ limits (deg)	1 - 25	1 - 25
Temperature	room temperature	room temperature
Octants collected	-8.8; 0. 15; 0, 13	-14, 13; 0, 15; 0, 17
No. of reflections collected	2157	4475
No. of unique reflections collected	1955	4065
No. of unique observed reflections	884 $(Fo)^2 > 3\sigma (Fo)^2$	1944 $(Fo)^2 > 3\sigma (Fo)^2$
Crystal decay (%)	<1	<1
R	0.064	0.041
R_w	0.065 w = 1.0	0.034 w = 1.0
Goodness of fit, s	4.92	2.87
No. of variables	146	234
Lowest residual peak (e $Å^{-3}$)	-.324	-.154
Largest residual peak (e $Å^{-3}$)	.254	.250

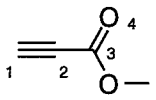
Ab initio RHF/6-31G**, 6-31G* and 3-21G Calculations of Coefficients (C_i) of the Frontier Molecular Orbitals for Diene 1a and Dienophiles 11 and 12



1a, R = H
4a, R = Me



11



12

			HOMO							LUMO						
Method	Compound	Orbital	C_1	C_2	C_3	C_4	C_N	C_O	ΔC_i[a]	C_1	C_2	C_3	C_4	C_N	C_O	ΔC_i[a]
6-31G**	**1a**	$2p_z$	0.246	0.164	-0.209	-0.326	-0.242	0.139	0.080	0.263	-0.245	-0.245	0.258	0.068	0.058	0.005
		$3p_z$	0.209	0.144	-0.192	-0.286	-0.264	0.131	0.077	0.478	-0.351	-0.367	0.477	0.093	0.080	0.001
6-31G**	**4a**	$2p_z$	-0.257	-0.199	0.198	0.320	-0.216	0.150	0.063	0.274	-0.222	-0.245	0.248	0.066	0.050	0.026
		$3p_z$	-0.220	-0.174	0.182	0.283	-0.237	0.146	0.063	0.460	-0.315	-0.371	0.467	0.092	0.067	-0.007
6-31G*	**1a**	$2p_z$	0.259	0.176	-0.217	-0.334	0.235	-0.056	0.075	-0.269	0.250	0.247	-0.262	-0.071	-0.056	0.007
		$3p_z$	0.224	0.150	-0.196	-0.296	0.256	-0.136	0.072	-0.493	0.361	0.373	-0.488	-0.098	-0.079	0.005
6-31G*	**4a**	$2p_z$	-0.268	-0.208	0.204	0.328	-0.211	0.155	0.060	-0.286	0.234	0.253	-0.259	-0.071	-0.048	0.027
		$3p_z$	-0.232	-0.180	0.185	0.294	-0.230	0.150	0.062	-0.483	0.334	0.387	-0.491	-0.100	-0.066	-0.008
3-21G	**1a**	$2p_z$	0.220	0.149	-0.187	-0.285	0.197	-0.118	0.065	-0.238	0.209	0.205	-0.233	-0.051	-0.043	0.005
		$3p_z$	0.268	0.174	-0.228	-0.355	0.304	-0.161	0.087	-0.525	0.385	0.398	-0.520	-0.091	-0.075	0.005
3-21G	**4a**	$2p_z$	-0.228	-0.180	0.175	0.279	-0.174	0.129	0.051	0.250	-0.195	-0.210	0.230	0.051	0.036	0.020
		$3p_z$	-0.283	-0.210	0.215	0.351	-0.269	0.179	0.068	0.523	-0.362	-0.409	0.520	0.093	0.062	0.003
6-31G**	**11**	$2p_z$	0.346	0.366	-0.039	-0.221			-0.020	0.311	-0.208	-0.280	0.254			0.103
		$3p_z$	0.264	0.309	-0.038	-0.179			-0.045	0.563	-0.395	-0.346	0.328			0.168
6-31G**[b]	**12**	$2p_z$	0.374	0.394	-0.034	-0.192			-0.020	0.289	-0.184	-0.338	0.278			0.105
		$3p_z$	0.240	0.269	-0.035	-0.152			-0.029	0.527	-0.375	-0.382	0.348			0.152
6-31G*	**11**	$2p_z$	-0.346	-0.367	0.039	0.221			-0.021	-0.311	0.207	0.281	0.255			0.104
		$3p_z$	0.267	-0.310	0.039	0.179			-0.043	-0.569	0.398	0.346	0.329			0.223
6-31G*[b]	**12**	$2p_z$	-0.376	-0.394	0.034	0.192			-0.018	0.289	-0.183	-0.339	0.279			0.106
		$3p_z$	-0.243	-0.268	0.034	0.153			-0.025	0.529	-0.375	-0.382	0.349			0.154
3-21G	**11**	$2p_z$	0.293	0.303	-0.052	-0.202			-0.010	-0.269	0.174	0.245	-0.228			0.095
		$3p_z$	0.323	0.379	-0.098	-0.245			-0.056	-0.595	0.414	0.353	-0.373			0.181
3-21G	**12**	$2p_z$	-0.310	-0.319	0.056	0.219			-0.009	-0.254	0.153	0.296	-0.243			0.101
		$3p_z$	-0.287	-0.339	0.100	0.263			-0.052	-0.561	0.392	0.387	-0.390			0.169

[a] Carbon 4 - carbon 1 for the dienes and carbon 1 - carbon 2 for the olefins. [b] These values are for the NHOMO, the HOMO does not have any p_z contribution.