SUPPLEMENTARY MATERIAL FOR:
Synthesis of furan-bridged 10-membered rings through [8+2]-cycloaddition of dienylfurans and acetylenic esters

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General Experimental. Nuclear Magnetic Resonance (^1H and ^{13}C NMR) spectra were recorded on a Bruker AF200 (200 MHz), Bruker AF400 (400 MHz), or Varian AF (200 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) relative to an internal chloroform reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet 5DXC FT-IR or Perkin-Elmer model 281 spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak); only diagnostic bands (excluding C-H stretches) above 1500 cm^{-1} are reported. Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (EI) or chemical ionization (CI) or on a Hewlett-Packard GC-MS 5970B with Mass Selection Detector: m/e value is reported, followed by the relative intensity in parentheses. Melting points were taken on a Fisher-Johns melting point apparatus (Model 12-144) equipped with a calibrated thermometer. Flash column chromatography was performed using thick-walled glass columns and “flash grade” silica gel (Bodman 230-400 mesh). Preparative thin layer chromatography was performed using precoated 1000 micron 20 x 20 silica gel plates purchased from Whatman. Routine thin layer chromatography (TLC) was performed using precoated 0.25mm silica gel plates purchased from Whatman. Combustion analysis results were obtained from Desert Analytics Laboratory or Galbraith Laboratories.

Tetrahydrofuran (THF), diethyl ether, and 1,4-dioxane were distilled from sodium / benzophenone ketyl. Dichloromethane, N,N-dimethylformamide (DMF) and toluene were distilled from calcium hydride before use. All reaction solvents were distilled for purity. All other reagents were obtained from commercial suppliers and used without further purification.

Starting Materials. Compound **10a**,¹ **10c**,¹ **10d**,² **10e**,³ **10f**,³ **10g**,⁴ **2**,⁵ **5a**,⁶ **6**,⁷ ethyl 4-oxo-2-pentynoate,⁸ and 1-(2-furylethynyl)cyclohexene⁹ were prepared according literature procedures.

¹ Herndon, J. W.; Wang, H. *J. Org. Chem.* **1998**, *63*, 4564-4565.

² Zhang, Y.; Herndon, J. W. *Org. Lett.* **2003**, *5*, 2043-2045.

³ Eberbach, W.; Roser, J. *Heterocycles* **1985**, *23*, 2797-2802.

⁴ Kobayashi, A.; Kouya, S.; Yamashita, K. *Agri. Biol. Chem.* **1976**, *40*, 2257-2260.

⁵ Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517-2526.

⁶ Van Reijendam, J. W.; Heeres, G. J.; Janssen, M. J. *Tetrahedron* **1970**, *26*, 1291-1301.

General Procedure I. Coupling of Dienylfuran Derivatives and Tetraenophiles. A solution of dienylfuran derivative (1.0 mmol, 1 equiv) and tetraenophile (2.0 mmol, 2 equiv) in dioxane (2 mL) was stirred at 85°C for 10 h. The reaction mixture was then concentrated on a rotary evaporator. The residue was submitted to flash chromatography on triethylamine-prewashed silica gel using 5:1 hexane/ethyl acetate as the eluent.

General Procedure II. Three-component Coupling of Enyne-aldehydes(ketones), α,β -unsaturated carbene complexes, and DMAD. A solution of enyne-aldehyde and ketone (0.5 mmol, 1 equiv) and carbene complex (0.7 mmol, 1.4 equiv) in dioxane (30 mL) was heated under nitrogen and kept at gentle reflux (80°C) for 1 h. DMAD (1.0 mmol, 2 equiv) was added in one portion and the reaction mixture was stirred at 80°C for an additional 2h period. The resulting reaction mixture was allowed to cool to room temperature and then concentrated on a rotary evaporator. The residue was purified by flash chromatography on triethylamine-prewashed silica gel (slurry-pack using 99:1 hexane:triethylamine) using 5:1 hexane/ethyl acetate as the eluent.

REACTION IN SCHEME 2

General Procedure I was followed using dienylfuran **6**⁷ (240 mg, 2.0 mmol, 1:1 mixture of Z & E isomers) and DMAD (568 mg, 4.0 mmol). Two compounds were isolated and identified as [8+2]-adduct **7** (170 mg, 32% yield, 65% yield based on Z isomer) and [4+2]-adduct **8** (202 mg, 38% yield, 77% yield based on E isomer). The [8+2]-cycloadduct **8** is a minor contaminant (about 10%) in the purified Diels-Alder adduct **7**.

Compound **8**: ¹H NMR (C₆D₆): δ 6.13 (d, 1 H, J = 5.6 Hz), 5.98 (ddd, 1 H, J = 11.8, 6.0, 3.2 Hz), 5.91 (d, 1 H, J = 5.6 Hz), 5.64 (ddd, 1 H, J = 11.8, 9.9, 3.9 Hz), 5.57 (br s, 1 H), 4.93 (d, 1 H, J = 6.0 Hz), 3.64 (ddd, 1 H, J = 13.8, 3.9, 3.2 Hz), 3.38 (s, 3 H), 3.24 (s, 3 H), 3.19 (dd, 1 H, J = 13.8, 9.9 Hz); ¹³C NMR (C₆D₆): δ

⁷ Ben Attra, T.; Le Bigot, Y.; El Gharbi, R.; Delmas, M.; Gaset, A. *Synth. Commun.* **1992**, 22, 1421-1425.

⁸ Lautens, M.; Fillion, E. *J. Org. Chem.* **1997**, 62, 4418-4427.

⁹ Siebeneicher, H.; Doye, S. *Eur. J. Org. Chem.* **2002**, 1213-1220.

170.4, 166.5, 158.5, 141.9, 134.5, 133.9, 127.2, 125.0, 101.4, 83.7, 52.2, 51.9, 35.2; IR (neat): 1724 cm^{-1} ; LRMS (EI): m/z 262, 260, 229, 203, 171, 134, 115, 91, 77, 59; HRMS: calcd for $\text{C}_{14}\text{H}_{14}\text{O}_5$ 262.08412, found 262.08404.

Compound **7**: ^1H NMR (C_6D_6): δ 7.00 (br s, 1 H), 6.54 (d, 1 H, $J = 3.3$ Hz), 6.25 (dd, 1 H, $J = 10.0, 3.0$ Hz), 6.06 (dd, 1 H, $J = 3.3, 2.0$ Hz), 5.70 (ddd, 1 H, $J = 10.0, 5.2, 3.0$ Hz), 3.82 (dd, 1 H, $J = 8.9, 5.2$ Hz), 3.48 (s, 3 H), 3.27 (s, 3 H), 2.68 (dt, 1H, $J = 17.8, 5.2$ Hz), 2.10 (ddt, 1 H, $J = 17.8, 8.9, 3.0$ Hz); ^{13}C NMR (C_6D_6): δ 173.1, 169.0, 152.1, 143.2, 131.0, 130.1, 126.1, 121.6, 111.9, 111.7, 52.1, 51.7, 41.2, 26.1; IR (neat): 1729 cm^{-1} ; LRMS (EI): m/z 262, 230, 203, 171, 144, 131, 115, 91, 77, 59; HRMS: calcd for $\text{C}_{14}\text{H}_{14}\text{O}_5$ 262.08412, found 262.08441.

REACTIONS IN TABLE 1

Coupling of Enyne-aldehyde 10a, Carbene complex 3, and DMAD (Entry A of Table 1). General Procedure II was followed using enyne-aldehyde **10a**¹ (88 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol), and DMAD (142 mg, 1.0 mmol). Compound **12a** was obtained as a colorless oil (137 mg, 64 %yield).

Compound **12a**: ^1H NMR (C_6D_6): δ 5.57 (s, 1 H), 4.20 (m, 1H), 3.36 (s, 3 H), 3.31 (s, 3 H), 3.23 (s, 3 H), 2.81 (dd, 1 H, $J = 16.9, 8.0$ Hz), 2.69 (m, 1 H), 2.37 (m, 3 H), 2.24 (m, 1 H), 2.14 (dt, 1 H, $J = 13.5, 8.0$ Hz), 2.02 (m, 1 H), 1.91 (m, 3 H), 1.62 (m, 2 H), 1.51 (m, 2 H), 1.39 (m, 1 H), 1.33-1.12(m, 2 H), 0.90 (t, 3 H, $J = 7.4$ Hz); ^{13}C NMR (C_6D_6): δ 168.8, 167.5, 154.3, 150.0, 148.3, 148.0, 142.8, 132.1, 130.1, 113.1, 80.5, 57.5, 51.6, 51.5, 47.0, 35.1, 33.0, 32.8, 29.8, 29.6, 29.3, 28.3, 25.5, 23.0, 14.9; IR (neat): 2952, 1729 cm^{-1} ; LRMS (EI): m/z 428, 381, 270, 255, 212, 115; HRMS: calcd for $\text{C}_{25}\text{H}_{32}\text{O}_6$ 428.21989, found 428.22078.

Coupling of Enyne-aldehyde 10a, Carbene complex 3, and DMAD in Two Pots (Entry B of Table 1). A solution of enyne-aldehyde **10a**¹ (88 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol) in dioxane (30 mL) was heated to 80°C; the heating was continued for a 12h period. The resulting reaction mixture was allowed to cool to room temperature and then concentrated on a rotary evaporator. The

residue was submitted to flash chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent. Crude compound **11a** was obtained in 78% yield (112 mg, 0.39 mmol). A solution of compound **11a** (112g, 0.39 mmol) and DMAD (142 mg, 1.0 mmol) in dioxane (2 mL) was stirred at 80°C for 2 h. The reaction mixture was then concentrated under reduced pressure. Flash chromatography on triethylamine-prewashed silica gel using 5:1 hexane/ethyl acetate as the eluent afforded compound **12a** in 79% yield (131 mg, 61% yield in two steps).

Compound **11a**: ^1H NMR (C_6D_6): δ 6.95 (s, 1H), 5.85 (m, 1H), 3.32 (s, 3H), 2.80 (t, 2H, $J = 7.4$ Hz), 2.50-2.20 (m, 6H), 2.03 (m, 2H), 1.85-1.20 (m, 8H), 0.91 (t, 3H, $J = 7.4$ Hz).

Coupling of Enyne-ketone 10c, Carbene complex 3, and DMAD (Entry C of Table 1). General Procedure II was followed using enyne-ketone **10c**¹ (95 mg, 0.50 mmol), carbene complex **3** (212 mg, 0.70 mmol), and DMAD (142 mg, 1.00 mmol). Compound **12c** was obtained as a colorless oil (128 mg, 58 % yield).

Compound **12c**: ^1H NMR (C_6D_6): δ 4.43 (m, 1 H), 3.37 (s, 6 H), 3.28 (s, 3 H), 2.84 (dd, 1 H, $J = 16.9$, 8.0 Hz), 2.74 (m, 1 H), 2.42 (m, 3 H), 2.27 (m, 1 H), 2.16 (dt, 1 H, $J = 13.5$, 8.0 Hz), 2.08 (m, 1 H), 1.98 (m, 3 H), 1.92 (s, 3 H), 1.68 (m, 2 H), 1.56 (m, 2 H), 1.46 (m, 1 H), 1.40-1.18 (m, 2 H), 0.94 (t, 3 H, $J = 7.4$ Hz); ^{13}C NMR (C_6D_6): δ 168.9, 168.2, 156.1, 150.0, 148.1, 147.8, 141.5, 137.0, 129.2, 112.9, 88.0, 57.4, 51.7, 51.5, 46.3, 34.9, 32.8, 32.3, 29.7, 28.6, 28.2, 25.6, 23.4, 23.0, 20.8, 15.0; IR (neat): 2953, 1727 cm^{-1} ; LRMS (EI): m/z 442, 395, 351, 323, 207, 111, 79, 59; HRMS: calcd for $\text{C}_{26}\text{H}_{34}\text{O}_6$ 442.23554, found 442.23517.

Coupling of Enyne-aldehyde 10d, Carbene complex 3, and DMAD (Entry D of Table 1). General Procedure II was followed using enyne-aldehyde **10d**² (106 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol), and DMAD (142 mg, 1.0 mmol). No adduct incorporating DMAD was observed. Crude compound **11d** was obtained as a colorless oil (119 mg, 72% yield).

Compound **11d**: ^1H NMR (CDCl_3): δ 7.40-7.12 (m, 6 H), 6.52 (d, 1 H, $J = 1.9$ Hz), 5.60 (m, 1 H), 3.50 (s, 3 H), 2.37 (m, 2 H), 2.11 (m, 2 H), 1.75 (m, 2 H), 1.55 (quintet, 2 H, $J = 7.0$ Hz), 1.35-1.18 (m, 4 H), 0.79 (t, 3 H, $J = 7.0$ Hz).

Coupling of Enyne-aldehyde 10e, Carbene complex 3, and DMAD (Entry E of Table 1). General Procedure II was followed using enyne-aldehyde **10e**³ (96 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol), and DMAD (142 mg, 1.0 mmol). No adduct incorporating DMAD was observed. Crude compound **11e** was obtained as a colorless oil (112 mg, 74% yield).

Compound **11e**: ¹H NMR (CDCl₃): δ 7.22 (d, 1 H, J = 1.9 Hz), 6.27 (d, 1 H, J = 1.9 Hz), 5.60 (m, 1 H), 3.58 (s, 3 H), 2.37 (m, 2 H), 2.10 (m, 2 H), 1.65 (m, 4 H), 1.37-1.16 (m, 4 H), 1.18 (s, 9 H), 0.89 (t, 3 H, J = 7.0 Hz).

Coupling of Enyne-aldehyde 10f, Carbene complex 3, and DMAD (Entry F of Table 1). General Procedure II was followed using enyne-aldehyde **10f**³ (96 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol), and DMAD (142 mg, 1.0 mmol). Compound **12f** was obtained as a colorless oil (120 mg, 62% yield).

Compound **12f**: ¹H NMR (C₆D₆): δ 6.03 (d, 1 H, J = 2.3 Hz), 5.61 (d, 1 H, J = 2.3 Hz), 5.52 (s, 1 H), 4.42 (m, 1 H), 3.43 (s, 3 H), 3.34 (s, 3 H), 3.30 (s, 3 H), 2.97 (dd, 1 H, J = 16.6, 6.7 Hz), 2.66 (m, 1 H), 1.98 (m, 1 H), 1.68 (m, 1 H), 1.60 (m, 1 H), 1.33 (m, 1 H), 1.22 (s, 9 H); ¹³C NMR (C₆D₆): δ 168.9, 167.9, 155.4, 153.8, 147.0, 143.7, 133.6, 128.8, 126.9, 102.8, 81.2, 57.5, 51.6, 46.1, 34.9, 33.2, 32.0, 20.0, 25.8; IR (neat): 2951, 1729 cm⁻¹; LRMS (EI): m/z 388, 329, 297, 269, 241, 194, 111, 57; HRMS: calcd for C₂₂H₂₈O₆ 388.18859, found 388.18886.

Coupling of Enyne-aldehyde 10g, Carbene complex 3, and DMAD (Entry G of Table 1). General Procedure II was followed using enyne-aldehyde **10g**⁴ (76 mg, 0.5 mmol), carbene complex **3** (212 mg, 0.7 mmol), and DMAD (142 mg, 1.0 mmol). Compound **12g** was obtained as a colorless oil (122 mg, 60% yield).

Compound **12g**: ¹H NMR (C₆D₆) δ 6.50 (d, 1 H, J = 6.2 Hz), 6.42 (dd, 1 H, J = 6.2, 2.2 Hz), 5.55 (br s, 1 H), 4.03 (m, 1 H), 3.40 (s, 3 H), 3.31 (s, 3 H), 3.23 (s, 3 H), 2.78 (dd, 1 H, J = 17.5, 8.2 Hz), 2.66 (m, 1 H), 1.94 (m, 1 H), 1.66 (m, 1 H), 1.54 (m, 1 H), 1.30 (m, 1 H), 0.34 (s, 9 H); ¹³C NMR (C₆D₆): δ 168.6,

167.1, 160.7, 150.8, 145.0, 138.9, 130.8, 130.6, 112.9, 81.1, 57.4, 51.6, 47.7, 35.1, 32.1, 25.3, 1.6; IR (neat): 2945, 1728 cm^{-1} ; LRMS (EI): m/z 404, 389, 329, 271, 241, 213, 89, 73, 59; HRMS: calcd for $\text{C}_{21}\text{H}_{28}\text{O}_6\text{Si}$ 404.16552, found 404.16576.

REACTIONS IN TABLE 2

Coupling of Dienylfuran 13a with DMAD (Entry A of Table 2). General Procedure I was followed using dienylfuran **13a** (see ahead) (174 mg, 1.0 mmol) and DMAD (284 mg, 2.0 mmol). Compound **14a** was isolated as a colorless oil (266 mg, 84 % yield).

Compound **14a**: ^1H NMR (C_6D_6) δ 6.04 (dd, 1 H, J = 6.0, 2.5 Hz), 5.97 (ddd, 1 H, J = 6.0, 2.2, 0.8 Hz), 5.88 (m, 1 H), 5.38 (dd, 1 H, J = 10.0, 5.5 Hz), 3.47 (s, 3 H), 3.32 (ddd, 1 H, J = 13.5, 10.0, 1.1 Hz), 3.26 (s, 3 H), 2.96 (dd, 1 H, J = 13.5, 5.5 Hz), 2.19 (m, 2 H), 2.14 (m, 1 H), 1.74 (td, 1 H, J = 13.4, 3.9 Hz), 1.64 (tm, 2 H, J = 14.3 Hz), 1.31 (qt, 1 H, J = 13.4, 3.5 Hz), 1.22 (m, 1 H); ^{13}C NMR (C_6D_6 , 400MHz): δ 170.5, 166.2, 155.2, 143.5, 142.5, 138.8, 133.5, 124.6, 118.3, 113.3, 83.3, 52.3, 52.1, 35.3, 35.2, 29.0, 28.3, 27.3; IR (neat): 2929, 1729 cm^{-1} ; LRMS (EI): m/z 316, 330, 272, 193, 115, 91, 77, 59; HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{O}_5$ 316.13108, found 316.13098.

Coupling of Dienylfuran 13b with DMAD (Entry B of Table 2). General Procedure I was followed using dienylfuran **13b** (see ahead) (188 mg, 1.0 mmol) and DMAD (284 mg, 2.0 mmol). Compound **14b** was isolated as a colorless oil (255 mg, 77 %yield).

Compound **14b**: ^1H NMR (C_6D_6): δ 6.30 (d, 1 H, J = 5.7 Hz), 6.26 (d, 1 H, J = 5.7 Hz), 5.37 (dm, 1 H, J = 9.0 Hz), 3.71(dm, 1 H, J = 14.5 Hz), 3.33 (s, 3 H), 3.29 (s, 3 H), 3.11 (dd, 1 H, J = 14.5, 9.0 Hz), 2.22 (m, 3 H), 1.89 (m, 1 H), 1.72 (s, 3 H), 1.57 (m, 2 H), 1.30 (m, 2 H); ^{13}C NMR (C_6D_6): δ 170.4 (C), 167.4 (C), 151.0 (C), 139.8 (C), 137.9 (C), 137.8 (C), 137.7 (CH), 127.2 (CH), 119.2 (CH), 113.0 (C), 90.2 (C), 52.1 (CH₃), 51.9 (CH₃), 38.0 (CH₂), 34.7 (CH₂), 28.4 (CH₂), 27.3 (CH₂), 26.5 (CH₂), 21.3 (CH₃); IR (neat): 2929, 1730 cm^{-1} ; LRMS (EI): m/z 330, 283, 228, 169, 91, 44; HRMS: calcd for $\text{C}_{19}\text{H}_{22}\text{O}_5$ 330.14672, found 330.14696.

Coupling of Dienylfuran 13c with DMAD (Entry C of Table 2). General Procedure I was followed using dienylfuran **13c** (see ahead) (204 mg, 1.0 mmol) and DMAD (284 mg, 2.0 mmol). Compound **14c** was isolated as a colorless oil (274 mg, 79% yield).

Compound **14c**: ^1H NMR (CDCl_3): δ 6.74 (d, 1 H, $J = 5.8$ Hz), 6.26 (d, 1 H, $J = 5.8$ Hz), 5.48 (ddd, 1 H, $J = 9.7, 5.1, 1.9$ Hz), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.27 (s, 3 H), 3.09 (dd, 1 H, $J = 14.0, 9.7$ Hz), 2.91 (ddd, 1 H, $J = 14.0, 5.1, 2.5$ Hz), 2.42 (dm, 1 H, $J = 13.8$ Hz), 2.30 (dm, 1 H, $J = 13.8$ Hz), 2.23 (dm, 1 H, $J = 13.8$ Hz), 1.88 (m, 3 H), 1.46 (qt, 1 H, $J = 12.7, 3.6$ Hz), 1.36 (qt, 1 H, $J = 12.7, 3.6$ Hz); ^{13}C NMR (CDCl_3): δ 169.5 (C), 166.4 (C), 149.3 (C), 140.3 (C), 137.5 (C), 131.7 (CH), 128.3 (CH), 120.4 (CH), 114.5 (C), 110.6 (C), 52.6 (CH_3), 52.4 (CH_3), 50.8 (CH_3), 35.2 (CH_2), 33.9 (CH_2), 28.2 (CH_2), 27.5 (CH_2), 26.4 (CH_2); IR (neat): 2930, 1730 cm^{-1} ; LRMS (EI): m/z 346, 315, 255, 193, 135, 59; HRMS: calcd for $\text{C}_{19}\text{H}_{22}\text{O}_6$ 346.14164, found 346.14219.

Coupling of Dienylfuran 13a with Ethyl 4-oxo-2-pentynoate (Entry D of Table 2). General Procedure I was followed using dienylfuran **13a** (174 mg, 1.0 mmol) and ethyl 4-oxo-2-pentynoate⁸ (280 mg, 2.0 mmol). The silica gel used for flash chromatography was not prewashed with triethylamine. Two compounds were isolated and identified as [8+2]-adducts **14d-minor** (19 mg, 6% yield) and **14d-major** (255 mg, 81% yield).

Compound **14d-minor**: ^1H NMR (CDCl_3): δ 6.53 (dd, 1 H, $J = 5.9, 2.7$ Hz), 6.26 (dd, 1 H, $J = 5.9, 2.2$ Hz), 5.56 (br s, 1 H), 5.36 (ddd, 1 H, $J = 9.6, 6.0, 2.1$ Hz), 4.18 (q, 2 H, $J = 7.1$ Hz), 3.04 (dd, 1 H, $J = 13.2, 9.6$ Hz), 2.92 (dd, 1 H, $J = 13.2, 6.0$), 2.47 (m, 1 H), 2.39 (m, 1 H), 2.30 (s, 3 H), 2.21 (m, 1 H), 1.89 (m, 3 H), 1.53 (qt, 1 H, $J = 12.6, 3.5$ Hz), 1.40 (qt, 1 H, $J = 12.6, 3.5$ Hz), 1.28 (t, 3 H, $J = 7.1$ Hz).

Compound **14d-major**: ^1H NMR (CDCl_3): δ 6.49 (dd, 1 H, $J = 6.0, 2.3$ Hz), 6.39 (dd, 1 H, $J = 6.0, 1.9$ Hz), 5.88 (br s, 1 H), 5.28 (ddd, 1 H, $J = 10.4, 6.2, 1.7$ Hz), 4.19 (q, 2 H, $J = 7.0$ Hz), 3.26 (dd, 1 H, $J =$

13.7, 10.4 Hz), 2.57 (dd, 1 H, $J = 13.7, 6.2$), 2.44 (m, 1 H), 2.34 (m, 1 H), 2.32 (s, 3 H), 2.23 (m, 1 H), 1.90 (m, 3 H), 1.48 (qt, 1 H, $J = 12.6, 3.5$ Hz), 1.35 (qt, 1 H, $J = 12.6, 3.5$ Hz), 1.26 (t, 3 H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3): δ 206.3, 165.3, 155.9, 154.5, 143.1, 134.1, 131.9, 124.0, 117.1, 112.7, 82.4, 61.6, 34.9, 34.8, 29.7, 28.6, 27.8, 26.7, 14.1; IR (neat): 2933, 1730 cm^{-1} ; LRMS (EI): m/z 314, 268, 225, 197, 91, 43; HRMS: calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4$ 314.15181, found 314.15194.

If the silica gel was pretreated with triethylamine, alkylidenefuranones (see below) derived from the [8+2]-cycloadducts were obtained in addition to the initially-formed cycloadducts. Although moderately unstable, the conformationally less mobile alkylidenefuranones were deemed ideal substrates for NOE studies. The [8+2]-cycloadducts could be partly transformed to the alkylidenefuranones shown below through treatment with silica gel in 90:10:1 hexanes/ethyl acetate/triethylamine at room temperature for 1 h. Prominent off-diagonal correlations in the NOESY spectrum are depicted in the drawing. The regiochemistry of the [8+2]-cycloadducts was assigned based on NOESY correlations in the alkylidenefuranones.

Alkylidenefuranone derived from 14d-minor: ^1H NMR (CDCl_3): δ 6.64 (dd, 1 H, $J = 6.0, 2.2$ Hz, H_A), 6.32 (dd, 1 H, $J = 6.0, 1.8$ Hz, H_B), 5.77 (br s, 1 H, H_C), 5.36 (dd, 1 H, $J = 8.2, 7.6$ Hz, H_D), 5.13 (d, 1 H, $J = 3.2$ Hz, H_E), 4.79 (d, 1 H, $J = 3.2$ Hz, H_F), 3.09 (dd, 1 H, $J = 14.2, 7.6$ Hz, $\text{H}_\text{G or H}$), 3.03 (dd, 1 H, $J = 14.2, 8.2$ Hz $\text{H}_\text{G or H}$), 2.47 (m, 1 H), 2.38 (m, 1 H, H_I), 2.24 (m, 1 H, H_J), 1.94 (m, 3 H), 1.51 (qt, 1 H, $J = 12.6, 3.6$ Hz), 1.41 (12.6, 3.6 Hz); ^{13}C NMR (CDCl_3): δ 170.1, 153.8, 153.2, 152.6, 144.1, 131.8, 129.7, 125.4, 117.4, 114.0, 93.5, 78.5, 34.9, 29.1, 28.1, 27.1, 26.2; IR (neat): 2930, 1768 cm^{-1} . Prominent NOESY correlations are depicted in the drawing.

Alkylidenefuranone derived from 14d-major: ^1H NMR (C_6D_6): δ 5.94 (dd, 1 H, $J = 6.0, 2.0$ Hz, H_A), 5.76 (dd, 1 H, $J = 6.0, 1.4$ Hz, H_B), 5.69 (br s, 1 H, H_C), 4.91 (dd, 1 H, $J = 9.8, 6.5$ Hz, H_D), 4.70 (d, 1 H, $J = 2.8$ Hz, H_E), 4.35 (d, 1 H, $J = 2.8$ Hz, H_F), 2.96 (dd, 1 H, $J = 13.7,$

9.8 Hz, H_G or H), 2.37 (dd, 1 H, J = 13.7, 6.5, H_G or H), 2.14 (m, 3 H), 1.66 (m, 3 H), 1.28 (m, 2 H); ¹³C NMR (C₆D₆): δ 167.8, 156.9, 154.8, 150.7, 144.4, 134.0, 133.5, 124.8, 116.6, 112.5, 94.2, 79.2, 35.4, 29.4, 28.7, 27.7, 27.6; IR (neat): 2930, 1768 cm⁻¹. Prominent NOESY correlations are depicted in the drawing.

Coupling of Dienylfuran 13f with DMAD (Entry F of Table 2). General Procedure I was followed using dienylfuran **13f** of 85% purity (see ahead) (200 mg, 0.98 mmol) and DMAD (278 mg, 1.96 mmol) in the presence of phenanthrene (87 mg, 0.49 mmol). After purification on triethylamine-treated silica gel, cycloadduct **14f** (71 mg, 23% yield) was obtained. Analysis of the crude NMR (prior to chromatography) revealed that cycloadduct **14f** was produced in 56% yield based on integration of the peak at δ 8.4 in phenanthrene relative to the peak at δ 4.98 in cycloadduct **14f**. Cycloadduct **14f** appears to partially decompose on a triethylamine-treated silica gel column.

Compound **14f**: ¹H NMR (C₆D₆): δ 6.07 (dd, 1 H, J = 5.9, 0.9 Hz), 5.97 (dd, 1 H, J = 5.9, 1.8 Hz), 5.90 (ddd, 1 H, J = 7.3, 2.6, 2.6 Hz), 5.76 (dd, 1 H, J = 1.8, 0.9 Hz), 4.98 (br d, 1 H, J = 7.3 Hz), 4.68 (m, 1 H), 3.38 (s, 3 H), 3.24 (s, 3 H), 2.71 (m, 1 H), 2.07 (dd, 1 H, J = 13.9, 5.5 Hz), 1.7-1.1 (m, 6 H); ¹³C NMR (CDCl₃): δ 168.8, 167.6, 155.2, 144.4, 140.3, 131.7, 131.6, 130.9, 121.0, 103.8, 83.6, 51.71, 51.65, 44.6, 34.9, 27.2, 21.9, 21.0; IR (neat): 1728 cm⁻¹; Mass Spec (Electrospray): 317 (M+1).

PREPARATION OF DIENYLFURANS THAT ARE NEW COMPOUNDS

Preparation of Dienylfuran 13a. To a solution of methyltriphenylphosphonium bromide (2.19 g, 6.0 mmol) in dry ethyl ether (40 mL) was added *n*-butyllithium (3.75 mL of a 1.6 M hexane solution, 6.0 mmol) dropwise at 0°C. The colorless solution turned pink immediately upon addition. The solution was stirred for 40 min at 0°C, and 1-formyl-2-(furyl)cyclohexene¹⁰ (0.71 g, 4.0 mmol) in ethyl ether (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. To the thick dark mixture 30 mL of 1% aqueous hydrochloric acid solution was added, and the mixture was extracted three times with ethyl ether. The organic layers were combined, washed with

¹⁰ Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319-11320.

saturated aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated on a rotary evaporator. The crude product was purified by flash chromatography on silica gel using 50:1 hexanes/ethyl acetate as the eluent. Compound **13a** was obtained as a pale yellow oil after removal of solvent (0.53 g, 75% yield).

Compound **13a**. ^1H NMR (CDCl_3): δ 7.26 (br s, 1 H), 7.00 (dd, 1 H, $J = 17.8, 11.1$ Hz), 6.26 (m, 1 H), 6.14 (d, 1 H, $J = 6.7$ Hz), 5.15 (d, 1 H, $J = 17.8$ Hz), 4.92 (d, 1 H, $J = 11.1$ Hz), 2.35 (br s, 2 H), 2.20 (br s, 2 H), 1.58 (br s, 4 H); ^{13}C NMR (CDCl_3): δ 154.9, 141.6, 137.0, 132.6, 127.0, 112.6, 110.9, 109.4, 28.9, 25.8, 22.8, 22.5; LRMS (EI): m/z 174, 145, 131, 115, 105, 91, 77, 65, 51; HRMS: calcd for $\text{C}_{12}\text{H}_{14}\text{O}$ 174.10447, found 174.10507.

Preparation of Dienylfuran 13b. *Synthesis of 1-formyl-2-(5-methylfuryl)cyclohexene:* To a solution of 2-methylfuran (5.73 g, 69 mmol) in dry tetrahydrofuran (300 mL) was added *n*-butyllithium (43.2 mL of a 1.6 M hexane solution, 69 mmol) dropwise at -15°C . The solution was stirred for 30 min at -15°C and 1.5 h at 0°C , and then cooled to -78°C . Anhydrous cerium(III) chloride (15.9 g, 64.4 mmol, cooled down to 0°C before adding) was added in one portion and the reaction mixture was stirred for 1.5 h at -78°C . At the same temperature, 2-(*i*-propoxymethylene)cyclohexanone (5.8 g, 34 mmol)¹¹ in tetrahydrofuran (30 mL) was added dropwise and the resulting mixture was stirred for an additional 1 h period. The reaction was quenched by adding 100 mL of 4% aqueous acetic acid solution. The mixture was extracted three times with ethyl ether. The organic layers were combined, washed with saturated aqueous ammonium chloride solution and brine, dried over sodium sulfate, and concentrated on a rotary evaporator. The crude product was dissolved in tetrahydrofuran (60 mL). At 0°C , 150 mL of dilute sulfate acid (0.5 M) was added. After being stirred for 30 min at 0°C , the reaction mixture was diluted with cold water. The mixture was extracted three times with dichloromethane. The organic layers were combined, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, and

¹¹ Harding, K.E.; Ligon, R.C. *Synth. Commun.* **1974**, *4*, 297-301.

concentrated on a rotary evaporator. The residue was submitted to flash chromatography on silica gel using 5:1 hexanes/ethyl acetate as the eluent. Pure product was obtained as a pale solid (5.1 g, 79% yield). *Synthesis of dienylfuran 13e*: To a solution of methyltriphenylphosphonium bromide (2.19 g, 6.0 mmol) in dry ethyl ether (40 mL) was added *n*-butyllithium (3.75 mL of a 1.6 M hexane solution, 6.0 mmol) dropwise at 0°C. The colorless solution turned pink immediately upon addition. The solution was stirred for 40 min at 0°C, and 1-formyl-2-(5-methylfuryl)cyclohexene (0.76 g, 4.0 mmol) in ethyl ether (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. To the thick dark mixture 30 mL of 1% aqueous hydrochloric acid solution was added, and the mixture was extracted three times with ethyl ether. The organic layers were combined, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated on a rotary evaporator. The crude product was purified by flash chromatography on silica gel using 50:1 hexanes/ethyl acetate as the eluent. Compound **13b** was obtained as a pale yellow oil after removal of solvent (0.55 g, 73% yield).

Compound **13b**: ^1H NMR (CDCl_3): δ 7.19 (dd, 1 H, $J = 17.8, 11.1$ Hz), 6.18 (d, 1 H, $J = 3.0$), 6.00 (d, 1 H, $J = 3.0$), 5.26 (d, 1 H, $J = 17.8$ Hz), 5.03 (d, 1 H, $J = 11.1$ Hz), 2.44 (m, 2 H), 2.36 (m, 2 H), 2.34 (s, 3 H), 1.70 (m, 4 H); ^{13}C NMR (CDCl_3): δ 153.2, 151.4, 137.2, 131.5, 127.2, 112.1, 110.4, 106.9, 28.9, 25.8, 22.8, 22.6, 13.9; LRMS (EI): m/z 188, 145, 117, 91, 43; HRMS: calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ 188.12012, found 188.11958.

Preparation of Dienylfuran 13c. *Synthesis of 1-formyl-2-(5-methoxyfuryl)cyclohexene*: To a solution of 2-methoxyfuran (3.08 g, 30 mmol) in dry tetrahydrofuran (150 mL) was added *n*-butyllithium (18.8 mL of a 1.6 M hexane solution, 30 mmol) dropwise at -15°C. The solution was stirred for 30 min at -15°C and 1.5 h at 0°C, and then cooled to -78°C. Anhydrous cerium(III) chloride (6.9 g, 28.0 mmol, cooled down to 0°C before adding) was added in one portion and the reaction mixture was stirred for 1.5 h at -78°C. At the same temperature, 2-(*i*-propoxymethylene)cyclohexanone¹¹ (2.52 g, 15 mmol) in tetrahydrofuran (15 mL) was added dropwise and the resulting mixture was stirred for an additional 1 h period. The reaction was quenched by adding 50 mL of 4% aqueous acetic acid solution. The mixture was extracted three times with ethyl ether. The organic layers were combined, washed with saturated aqueous ammonium chloride and brine, dried over sodium sulfate, and concentrated on a rotary evaporator. The crude product was dissolved in tetrahydrofuran (30 mL). At 0°C, 70 mL of dilute

sulfate acid (0.5 M) was added. After being stirred for 30 min at 0°C, the reaction mixture was diluted with cold water. The mixture was extracted three times with dichloromethane. The organic layers were combined, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated on a rotary evaporator. The residue was submitted to flash chromatography on silica gel using 5:1 hexanes/ethyl acetate as the eluent. Pure product was obtained as a pale solid (2.2 g, 71% yield). **Synthesis of dienylfuran 13c:** To a solution of methyltriphenylphosphonium bromide (2.19 g, 6.0 mmol) in dry ethyl ether (40 mL) was added *n*-butyllithium (3.75 mL of a 1.6 M hexane solution, 6.0 mmol) dropwise at 0°C. The colorless solution turned pink immediately upon addition. The solution was stirred for 40 min at 0°C, and 1-formyl-2-(5-methoxyfuryl)cyclohexene (0.83 g, 4.0 mmol) in ethyl ether (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. To the thick dark mixture 30 mL of 1% aqueous hydrochloric acid solution was added, and the mixture was extracted three times with ethyl ether. The organic layers were combined, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated on a rotary evaporator. The crude product was purified by flash chromatography on silica gel using 50:1 hexanes/ethyl acetate as the eluent. Compound **13c** was obtained as a pale yellow oil after removal of solvent (0.53 g, 65% yield).

¹H NMR (CDCl₃) δ 7.18 (dd, 1 H, J = 17.4, 11.4 Hz), 6.15 (d, 1 H, J = 3.2), 5.23 (d, 1 H, J = 17.4), 5.18 (d, 1 H, J = 3.2 Hz), 5.02 (d, 1 H, J = 11.4 Hz), 3.80 (s, 3 H), 2.41 (m, 2 H), 2.30 (m, 2 H), 1.68 (m, 4 H); ¹³C NMR (CDCl₃): δ 161.0, 144.9, 137.0, 130.5, 126.4, 111.7, 110.9, 80.9, 57.6, 28.2, 25.7, 22.6, 22.4; LRMS (EI): m/z 204, 172, 144, 91; HRMS: calcd for C₁₃H₁₆O₂ 204.11503, found 204.11456.

Preparation of Dienylfuran 13f. The following is an adaptation of a literature procedure.¹² A mixture of 1-(2-furylethynyl)cyclohexene¹³ (2.00 g, 11.7 mmol), Lindlar's catalyst (0.50 g, 0.23 mmol, 2 mol%) in quinoline (0.25 mL), methanol (4.75 mL) and dichloromethane (45 mL) was placed in a thick-walled glass tube, which was then placed on a Paar Hydrogenation apparatus and pressurized to 26 psi with hydrogen. The mixture was shaken on the apparatus for a total of 40 h. At hours #13 and #27, the system was depressurized, additional Lindlar's catalyst (0.50 g, 0.23 mmol, each time) was added, and

¹² Nicolaou, K.C.; Petasis, N.A.; Uenishi, J.; Zipkin, R.E. *J. Am. Chem. Soc.* **1982**, *104*, 5555-5557.

¹³ Siebeneicher, H.; Doye, S. *Eur. J. Org. Chem.* **2002**, 1213-1220

the system was repressurized. The mixture was filtered and partitioned between water and pentane in a separatory funnel. The organic layer was filtered through a pad of silica gel to afford cis alkene **13f** (0.36 g, 18 % yield). The alkene is of about 85% purity based on a comparison with an internal standard (phenanthrene). Chromatographic separation does not improve the quality of the product. This compound is stable for no more than two weeks if stored in the freezer. In our hands, this procedure was not completely reliable and would often fail for no apparent reason.

Compound **13f**: 7.32 (d, 1 H, $J = 2.0$ Hz), 6.37 (m, 2 H), 6.17 (d, 1 H, $J = 12.8$ Hz), 5.92 (d, 1 H, $J = 12.8$ Hz), 5.89 (m, 1 H), 2.15 (m, 4 H), 1.68 (m, 4 H).

TRANSFORMATIONS OF [8+2]-CYCLOADDUCTS – SCHEME 3

Methanolysis of [8+2]-cycloadduct – Compound 15 of Scheme 3. Cycloadduct **14a** (159 mg, 0.5 mmol) was dissolved in ether (20 mL). To the solution was added methanol (3 mL) and concentrated HCl (1 mL). The reaction mixture was stirred vigorously for 9 h at room temperature. The aqueous layer was extracted with ether (3x10 mL). The ethereal layers were combined, washed with saturated aqueous NaHCO₃ solution (10 mL), and dried over sodium sulfate. Purification using silica gel column chromatography with 1: 5 (v/v) ethyl acetate/hexanes as the eluent afforded the product **15** (138 mg, 0.40 mmol) in 79% yield.

Compound **15**: ¹H NMR (C₆D₆, 400MHz): δ 5.89 (dd, 1 H, $J = 6.0, 1.7$ Hz), 5.73 (dd, 1 H, $J = 2.8, 1.7$ Hz), 5.54 (dd, 1 H, $J = 12.1, 5.0$ Hz), 5.28 (dd, 1 H, $J = 6.0, 2.8$ Hz), 4.66 (t, 1 H, $J = 12.1$ Hz), 3.46 (s, 3 H), 3.34 (m, 1 H), 3.33 (s, 3 H), 3.02 (s, 3 H), 2.65 (dd, 1 H, $J = 12.1, 5.0$ Hz), 1.89 (m, 3 H), 1.70 (m, 1 H), 1.50 (m, 1 H), 1.30 (m, 3 H); Irradiated at δ 5.54 ppm: δ 4.66 (d, $J = 12.1$ Hz), 2.65 (d, $J = 12.1$ Hz); ¹H NMR (CDCl₃): δ 6.11 (dd, 1 H, $J = 6.0, 1.7$ Hz), 5.75 (dd, 1 H, $J = 2.8, 1.7, 1.7$ Hz), 5.64 (dd, 1 H, $J = 6.0, 2.8$ Hz), 5.35 (dd, 1 H, $J = 12.1, 5.0$ Hz), 4.36 (t, 1 H, $J = 12.1$ Hz), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.20 (m, 1 H), 3.16 (s, 3 H), 2.46 (dd, 1 H, $J = 12.1, 5.0$ Hz), 2.00 (m, 2 H), 1.76 (m, 1 H), 1.65 (m, 2 H), 1.36 (m, 3 H); ¹³C NMR (C₆D₆, 400MHz): δ 170.2, 166.8, 141.2, 137.0, 132.9, 132.1, 125.3, 124.5, 118.5, 84.9, 51.8, 51.7, 49.5, 45.7, 32.7, 29.4, 24.7, 24.1, 21.5; IR (neat, cm⁻¹): 1729 (s) cm⁻¹; MS(CI): 317 (100, M⁺-OMe), 256 (35), 225 (22), 195 (31), 169 (24), 91 (26), 59 (42); No parent ion was observed using electrospray or EI ionization either, however the presence of three methoxy groups is undeniable based on the ¹H and ¹³C NMR spectra. Shipment to an external facility for HRMS afforded results suggestive of decomposition. External

shipment for combustion analysis (Galbraith Laboratories) was also unsuccessful: Calcd for C₁₉H₂₄O₆ C – 65.50%, H – 6.94%, found C – 60.55%, H – 6.75%.

The diastereotopic protons in the doubly allylic CH₂ group are occurring at δ 4.66 and δ 2.65, and this assignment is supported by the decoupling experiment. Based on this PI's experience, this chemical shift difference for two protons on the same carbon is somewhat extreme. An *ab initio* calculation of the NMR (B3LYP at the 6-31G** level) for a simplified derivative of **15** (COOMe's replaced by H) predicts that these two protons are differ by 1.39 ppm in their chemical shift.

Reaction of [8+2]-cycloadduct 14a with dichlorocarbene – Compound 16 of Scheme 3. A 30 mL two-necked round bottomed flask was charged with 3 mL (40% w/w) NaOH, 1 mol% of tetrabutylammonium bromide (TBAB) and chloroform (3 mL) under nitrogen. These ingredients were stirred for 10 min at 45 °C. Cycloadduct **14a** (253 mg, 0.8 mmol) was added to the reaction mixture and stirred vigorously for 20 min. The reaction mixture was cooled to room temperature and extracted with ether (3x10 mL). The ethereal layers were combined, washed with water, and dried over magnesium sulfate. Purification using silica gel column chromatography with 1: 3 (v/v) ethyl acetate/hexanes as the eluent afforded the 11-membered ring compound **16** (163 mg, 0.45 mmol) in 56% yield.¹⁴

Compound **16**: ¹H NMR (CDCl₃, 400MHz): δ 6.71 (d, 1 H, J = 3.4 Hz), 6.57 (d, 1 H, J = 3.4 Hz), 5.07 (ddd, 1 H, J = 11.6, 4.4, 1.6 Hz), 3.89 (s, 3 H), 3.84 (s, 3 H), 3.28 (ddd, 1 H, J = 13.4, 4.4, 1.6 Hz), 3.21 (dq, 1 H, J = 13.1, 1.6 Hz), 2.74 (dd, 1 H, J = 13.4, 11.6 Hz), 2.16 (m, 2 H), 1.92 (m, 3 H), 1.65 (m, 2 H). Irradiated at δ 5.07: δ 3.28 (d, J = 13.4 Hz), 2.74 (d, J = 13.4 Hz). ¹³C NMR (CDCl₃, 400MHz): δ 169.7 (C), 166.4 (C), 151.1 (C), 147.0 (C), 142.1 (C), 139.3 (C), 136.1 (C), 128.4 (C), 119.8 (CH), 114.2 (CH), 109.5 (CH), 53.0 (CH₃), 52.9 (CH₃), 42.4 (CH₂), 35.3 (CH₂), 34.9 (CH₂), 29.3 (CH₂), 28.7 (CH₂); IR (neat, cm⁻¹): 2929 (m), 1732 (s); LRMS (EI): 362, 330, 295, 267, 165, 59; HRMS: Calcd. 362.09210; found 362.09189.

¹⁴ The yield has not been optimized, and only tetrabutylammonium bromide has been examined as the phase transfer catalyst. It has been noted that different phase transfer catalysts can have a profound effect on the yields of dichlorocarbene additions. It is reported that in the case of styrene the yield increased from 38% to 76% when benzyltriethylammonium bromide was used as phase transfer catalysts instead of tetrabutylammonium bromide. Jayachandran, J.P.; Wang, M.L. *Synth. Comm.* **1999**, *29*, 4101-4112.

THEORETICAL CHEMISTRY

All energy minimizations were performed using Gaussian 03W.¹⁵ Structures were drawn using the program CHEM-3D, minimized using MM2, and a Gaussian Input File was created. The structure was then minimized in Gaussian 03 using the B3LYP method and the 6-31G* basis set. NMR calculations were conducted using the B3LYP method and the 6-31G** basis set. Relevant energy-minimized structures and their SCF energies are in the picture below. All values are in Hartrees (1 Hartree = 627 kcal/mol). The ΔE values in the manuscript involve transformations between energy minima.

¹⁵ Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Stefanov, B.B.; Liu, A.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, M.; Callacombe, M.; Gill, P.M.W.; Johnson, B.G.; Chen, W.; Wong, M.W.; Andres, J.L.; Head-Gordon, M.; Replogle, E.S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1998.

Proton NMR Spectrum of Compound **7** (about 10% **8** as an impurity)

Carbon-13 NMR Spectrum of Compound **7** (about 10% **8** as an impurity)

Proton NMR Spectrum of Compound **8**.

Carbon-13 NMR Spectrum of Compound 8.

Proton NMR Spectrum of Compound **12a**.

Carbon-13 NMR Spectrum of Compound **12a**.

Proton NMR Spectrum of Compound **12c**.

Carbon-13 NMR Spectrum of Compound **12c**.

Proton NMR Spectrum of Compound **12f**.

Carbon-13 NMR Spectrum of Compound **12f**.

Proton NMR Spectrum of Compound **12g**.

Carbon-13 NMR Spectrum of Compound **12g**.

Proton NMR Spectrum of Compound **14a**.

Carbon-13 NMR Spectrum of Compound **14a**.

Proton NMR Spectrum of Compound **14b**.

Carbon-13 NMR Spectrum of Compound **14b**.

Proton NMR Spectrum for Compound **14c**.

Carbon-13 NMR of Compound **14c**.

Proton NMR Spectrum of Compound **14d** (major).

Carbon-13 NMR of Compound **13d** (major).

exp307-3
Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
UNITY-400 "fatman"
Relax. delay 2.000 sec
Pulse: 38.2 degrees
Acq. time 1.19 sec
Width 2500.0 Hz
5480 repetitions
OBSERVE C13, 100.562393 MHz
DECOUPLE H1, 339.9304768 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
Single precision data
DATA PROCESSING
AQ 1.0000000000000000
FT size 65536
Total time 16 hr, 3 min, 3 sec

Proton NMR Spectrum of Compound **14f**.

VAN3

8 Sep 2004
9/3 8+2#5 mix of fraction post 7 days in open air
EXP-1

Carbon-13 NMR Spectrum of Compound **14f**.

Proton NMR Spectrum of Compound **15**.

Carbon-13 NMR Spectrum of Compound **15**.

Proton NMR Spectrum of Compound **16**.

Carbon-13 NMR Spectrum of Compound 16.