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An intramolecular Diels–Alder reaction involving fulvenes as 4π components—stereoselective synthesis of novel oxatricyclo[6.4.0.$0^{2,10}$] dodeca-2,11-diene ring system☆

S. Manikandan, M. Shanmugasundaram and R. Raghunathan*

Department of Organic Chemistry, University of Madras, Chennai 600 025, India

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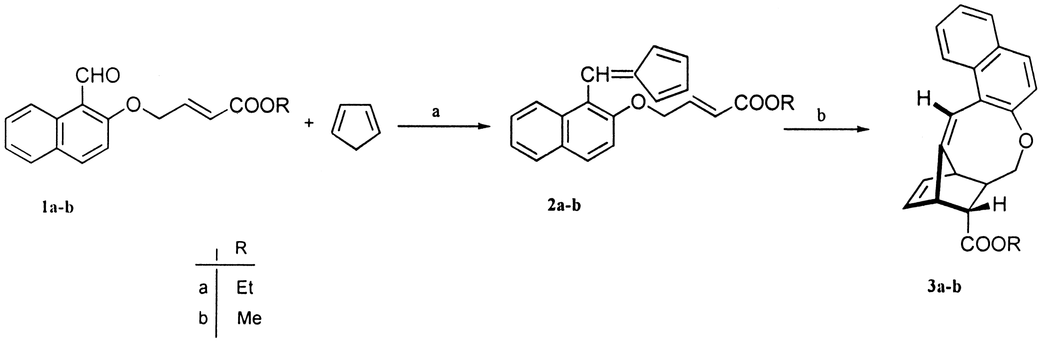
Abstract—Fulvenes acting as 4π components in an intramolecular [4+2] cycloaddition reaction leading to the formation of novel 6-oxatricyclo [6.4.0.$0^{2,10}$] dodeca-2,11-diene ring systems have been described. Importance of steric buttressing effect in promoting the reaction has been discussed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The intramolecular Diels–Alder (IMDA) reaction is one of the powerful strategies for the construction of polycyclic ring systems, and has been successfully applied to the synthesis of natural products.[2] The chemistry of pentafulvenes which display varying periselectivity, has been the subject of great interest both synthetically and theoretically.[3] They have found extensive use as key intermediates in the synthesis of hirustene, capnellene, β-vetivone, viburtinal, hinesol, silphinene and longifolene.[4] Many inter[5] and intramolecular[3] [6+4] cycloaddition reactions involving fulvenes as 6π components have been reported in literature. The use of fulvenes as 4π or 2π components in an intermolecular [4+2] cycloaddition reaction has also been reported.[6,7] Wu and Houk have reported an intramolecular [6+2] cycloaddition reaction involving fulvene as a 6π component.[8] We have recently reported an unprecedented IMDA reaction involving fulvenes as 4π components.[1] In continuation of our work in the area of cycloaddition reactions,[9] herein we disclose an IMDA reaction of fulvenes leading to the stereoselective synthesis of novel 6-oxatricyclo [6.4.0.$0^{2,10}$] dodeca-2,11-diene ring system.

2. Results and discussion

The fulvenes **2a–b** chosen for our study were prepared by the condensation of the corresponding alkyl 4(1-formyl-2-naphthoxy)but-2-enoates **1a**,**b** with cyclopentadiene using diethylamine as base.[10]



	R
a	Et
b	Me

Scheme 1. (a) Et_2NH, MeOH, rt; (b) $LiClO_4$, CH_3NO_2, reflux, 12 h.

☆ See Ref. 1.

Keywords: Diels–Alder reactions; lithium and compounds; fulvenes; steric buttressing effect.

* Corresponding author. Tel.: +91-44-2351269; fax: +91-44-2352494; e-mail: ragharaghunathan@yahoo.com

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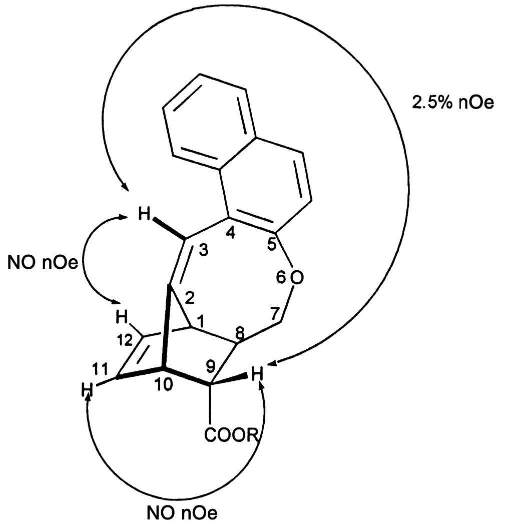


Figure 1. nOe enhancements showing the stereochemistry of cycloadducts **3a**,**b**.

Fulvenes **2a**,**b** were subjected to an IMDA reaction in the presence of lithium perchlorate as a Lewis acid catalyst in nitromethane under reflux for 12 h. [4+2] Cycloaddition reactions occurred in which fulvenes acting as 4π components to afford the novel *endo* tricycloadducts **3a**,**b** in 31 and 33% yields, respectively, (Scheme 1).

The structures assigned for the products were confirmed by ^{1}H, ^{13}C NMR and mass spectra. The structure **3a** was also supported by ^{1}H–^{1}H and ^{1}H–^{13}C COSY data. The stereochemistry of the *endo* cycloadducts **3a**,**b** was established by difference nOe studies (Fig. 1). Specifically, irradiation of the C_{12} olefin proton at δ 6.2 in **3a** caused 5.1% enhancement of the signal for the C_{11} olefin proton at δ 6.3 and 5.9% enhancement of the C_1 bridgehead proton at δ 2.69. Irradiation of the C_{11} olefin proton at δ 6.3 caused 4.1% enhancement of the signal for the C_{12} olefin proton at δ 6.2 and δ 6.7 enhancement of the C_{10} bridgehead proton at δ 3.83. The results of the selective irradiation of C_{11} or C_{12} olefin proton caused no enhancement of the signal for the C_9 methine proton at δ 3.24 proves that the C_9 proton is on the *exo* face. Irradiation of the C_9 methine proton at δ 3.24 resulted 8.4% enhancement of the signal for the C_{10} bridgehead proton at δ 3.83 and 2.5% enhancement of the signal for the C_3 olefin proton at δ 6.16, thus proving that C_3 and C_9 protons are on the same side. Similarly, the selective irradiation of C_9 methine proton at δ 3.25 in **3b** caused 2.5% enhancement of the signal for the C_3 olefin proton and none to the C_{11} olefin proton at δ 6.30.

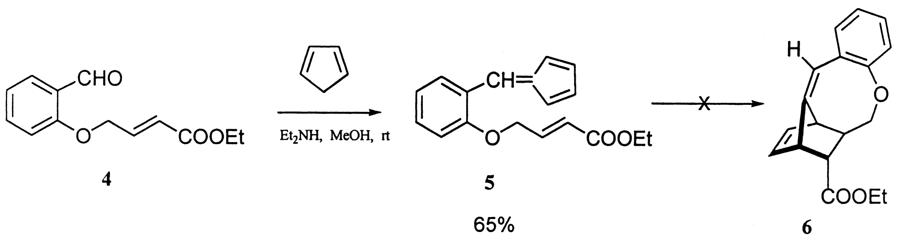
The success of the IMDA reaction involving fulvenes as 4π components encouraged us to examine the fulvene **5** derived from methyl 4-(2-formyl-phenoxy)but-2-enoate **4**. To our surprise, the IMDA reaction of fulvene **5** under a variety of conditions did not afford the anticipated [4+2] product **6** (Scheme 2). The treatment of fulvene **5** in the presence of 5.0 M lithium perchlorate in diethyl ether (LPDE) as a medium at room temperature for 30 min led to unspecific decomposition and no product could be isolated. The same reaction when carried out in the presence of lithium perchlorate in nitromethane under reflux for 12 h, once again proved futile.

Sammes and Weller have reviewed the importance of steric buttressing effect to promote an intramolecular cycloaddition reaction.[11] We envisaged that the introduction of *ortho* substituents adjacent to the *O*-alkenyl tether would lead to successful IMDA reaction.

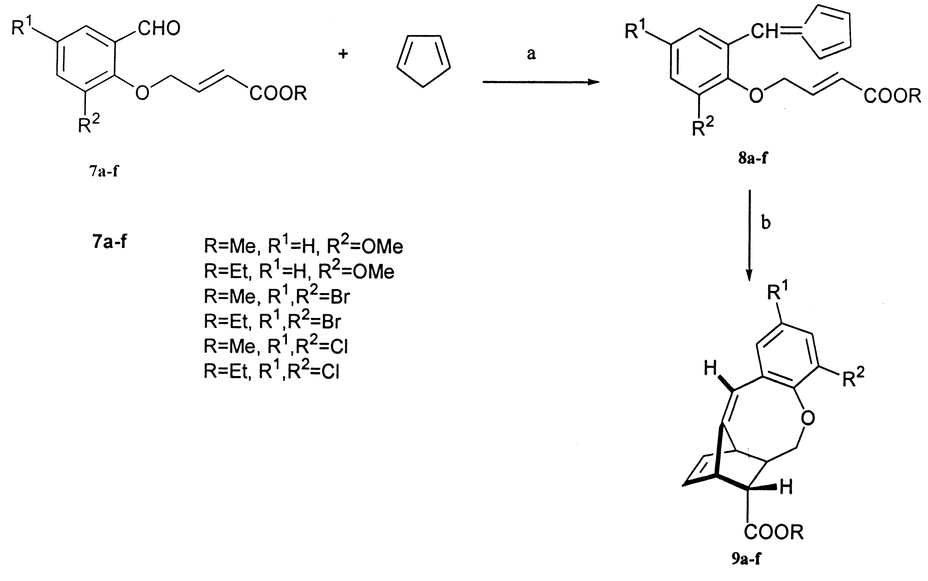
To determine the effect of *ortho* substituents, the IMDA reaction of fulvene **8a** was examined. To our delight, the IMDA reaction of fulvene **8a** in the presence of lithium perchlorate in nitromethane afforded the novel *endo* cycloadduct **9a** in 44% yield. The structure of **9a** was confirmed by spectroscopic data. Assignment of the stereochemistry was performed by correlation to the structurally related cycloadducts **3a**,**b**. The *endo* cycloadduct **9a** was also established on the basis of the coupling constant of C_{10} bridgehead proton and C_9 methine proton. It is well known that for norbornene and its derivatives, the coupling constant between an *endo* and a bridgehead proton is nearly zero, while value between an *exo* and bridgehead proton is ca. 3.0 Hz.[9b,12] The C_9 methine proton resonated as a triplet at δ 3.26 with J=4.0 Hz indicating this proton on the *exo* face and therefore has *endo* stereochemistry.

We next investigated the behavior of a series of fulvenes **8b–f** which bear the *ortho* substituents to explore the scope of the cycloaddition reaction. Under similar conditions, fulvenes **8b–f** underwent [4+2] cycloaddition to afford the corresponding *endo* cycloadduct **9b–f** (Scheme 3). All of the IMDA reactions are completely stereoselective giving only *endo* cycloadducts. No corresponding *exo* cycloadducts were observed in all of these reactions.

The success of the IMDA reactions can be explained on the basis of steric buttressing effect.[11] In the case of fulvenes **3a–b**, the effect arising from steric interaction of the peripheral hydrogen and fulvene moiety assists the attainment of the favorable geometry. The presence of *ortho* substituents in the fulvene **8** might reduce the



Scheme 2.



Scheme 3. (a) Et_2NH, MeOH, rt; (b) $LiClO_4$, CH_3NO_2, reflux, 12 h.

conformationally allowed space occupied by the *O*-alkenyl group, thus forcing it into the proximity of the fulvene group. However, the failure of **5** to cycloadd may thus reflect the absence of such steric buttress for the favorable reaction.

To sum up, we have demonstrated an IMDA reaction involving fulvenes as 4π components which leads to the stereoselective synthesis of the novel tricyclo dodeca ring system. The successful IMDA reaction of fulvenes observed in the present instance clearly brings out the importance of steric buttressing effect for the favorable reaction.

3. Experimental

3.1. General

IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL GX 400 spectrometer or on a Bruker DPX200 at 200 MHz as indicated. Elemental analyses were carried out on a CEST 1106 instrument. MS spectra were recorded on a Finnigan MAT-8230 GC-Mass spectrometer. Flash column chromatography was performed on silica gel (SISCO 230–400 mesh). Compounds **1**, **4** and **7** were prepared according to the literature procedure.[13]

3.2. General procedure for the preparation of fulvenes

To a solution of aldehyde (5 mmol) and cyclopentadiene (15 mmol) in dry methanol (10 mL) was added diethylamine (5 mmol). The mixture was stirred under nitrogen atmosphere at room temperature for 8–12 h until the disappearance of the aldehyde as evidenced by TLC analysis. Acetic acid (5 mmol) was added to the bright yellow solution. The reaction mixture was added with ether and water (10 mL each). The aqueous portion was washed with ether (3×20 mL) and the combined organic layers were washed with water and brine solution (10 mL each), then dried over anhydrous $MgSO_4$. After the removal of the solvent in rotor evaporator, the residue was subjected to column chromatography on silica gel using petroleum ether to afford fulvene.

3.3. General procedure for the synthesis of 6-oxatricyclo $[6.4.0.0^{2,10}]$ dodeca-2,11-diene derivatives

To a refluxing solution of fulvene (1 mmol) in nitromethane (10 mL) under nitrogen atmosphere, lithium perchlorate (1 mmol) was added. The reaction mixture was allowed to reflux for 12 h. Dichloromethane (25 mL) and water (25 mL) were added to the cooled reaction mixture and the aqueous layer was extracted with (2×10 mL) of dichloromethane. The combined extracts were washed with brine solution and dried (anhyd. $MgSO_4$). After the removal of the solvent under vacuum, the residue was subjected to flash column chromatography (petroleum ether/ethylacetate, 9:1) to afford tricyclic adduct.

3.3.1. 6-(2-(Ethyl 4-oxy but-2-enoate)-1-naphthoxy) fulvene (2a). Yellow oil, 65%; IR (CCl_4): 1676 cm^{-1}; ^1H NMR (200 MHz): δ 1.28 (t, J=7.3 Hz, 3H), 4.21 (q, J=7.3 Hz, 2H), 4.79 (dd, J=4.2, 2.2 Hz, 2H), 6.08 (dt, J=16.2, 1.0 Hz, 1H), 6.10–6.52 (m, 4H), 7.49 (s, 1H), 7.02–7.79 (m, 7H).

3.3.2. 6-(2-(Methyl 4-oxy but-2-enoate)-1-naphthoxy) fulvene (2b). Yellow oil, 62%; IR (CCl_4): 1675 cm^{-1}; ^1H NMR (200 MHz): δ 3.73 (s, 3H), 4.81 (dd, J=4.2, 2.0 Hz, 2H), 6.05 (dt, J=16.4, 1.0 Hz, 1H), 6.08–6.49 (m, 4H), 7.41 (s, 1H), 7.05–7.93 (m, 7H).

3.3.3. 6-Oxatricyclo$[6.4.0.0^{2,10}]$ dodeca-2,11-diene[4,5-*a*]naphtho-*endo*-9-carboxylicacid ethyl ester (3a). Colorless oil, 31%; IR (CCl_4): 1735 cm^{-1}; ^1H NMR (400 MHz): δ 1.28 (t, J=7.3 Hz, 3H), 2.02 (m, 1H), 2.69 (bs, 1H), 3.24 (t, J=3.9 Hz, 1H), 3.83 (bs, 1H), 4.14 (q, J=7.3 Hz, 2H), 4.21 (dd, J=12.7, 1.5 Hz, 1H), 4.68 (dd, J=12.7, 1.0 Hz, 1H), 6.16 (s, 1H), 6.20 (dd, J=5.8, 3.4 Hz, 1H), 6.30 (dd, J=5.8, 3.4 Hz, 1H), 7.28–7.87 (m, 6H); ^{13}C NMR (100.4 MHz): δ 14.30, 40.63, 48.15, 49.41, 49.34, 60.55, 75.51, 103.44, 122.40, 124.88, 125.79, 126.17, 127.79, 129.20, 130.42, 132.72, 132.95, 136.62, 155.83, 158.24, 173.00; MS (*m/z*): 332 (M$^+$); Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07; Found: C, 79.37; H, 6.00.

3.3.4. 6-Oxatricyclo[6.4.0.0^{2,10}] dodeca-2,11-diene[4,5-*a*]naphtho-*endo*-9-carboxylicacid methyl ester (3b). Colorless oil, 33%; IR (CCl$_4$): 1735 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.03 (m, 1H), 2.72 (bs, 1H), 3.25 (t, J=3.9 Hz, 1H), 3.7 (s, 3H), 3.82 (bs, 1H), 4.22 (dd, J=12.6, 1.5 Hz, 1H), 4.7 (dd, J=12.6, 1.0 Hz, 1H), 6.16 (s, 1H), 6.21 (dd, J=5.7, 3.4 Hz, 1H), 6.30 (dd, J=5.7, 3.3 Hz, 1H), 7.30–7.88 (m, 6H); ^{13}C NMR (100.4 MHz): δ 29.67, 40.69, 48.13, 49.33, 51.85, 75.47, 2.56, 116.09, 122.39, 124.91, 125.80, 126.20, 127.82, 129.25, 130.45, 132.73, 133.04, 136.67, 155.81, 158.18, 173.55; MS (*m/z*): 318 (M$^+$); Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.21; H, 5.70; Found: C, 79.09; H, 5.61.

3.3.5. 6-(2-(Ethyl 4-oxobut-2-enoate)phenyl) fulvene (5). Yellow oil, 65%; IR (CCl$_4$): 1670 cm^{-1}; ^{1}H NMR (200 MHz): δ 1.32 (t, J=7.3 Hz, 3H), 4.28 (q, J=7.3 Hz, 2H), 4.8 (dd, J=4.1, 2.0 Hz, 2H), 6.2 (dt, J=16.2, 1.0 Hz, 1H), 6.30–6.67 (m, 4H), 7.37 (s, 1H), 6.83–7.6 (m, 5H).

3.3.6. 6-(2-(Methyl 4-oxobut-2-enoate)-3-methoxyphenyl) fulvene (8a). Yellow oil, 53%; IR (CCl$_4$): 1669 cm^{-1}; ^{1}H NMR (200 MHz): δ 3.73 (s, 3H), 3.79 (s, 3H), 4.78 (dd, J=4.1, 2.0 Hz, 2H), 6.10 (dt, J=16.4, 1.2 Hz, 1H), 6.38–6.69 (m, 4H), 7.40 (s, 1H), 6.92–7.71 (m, 4H).

3.3.7. 6-(2-(Ethyl 4-oxobut-2-enoate)-3-methoxyphenyl) fulvene (8b). Red oil, 56%; IR (CCl$_4$): 1672 cm^{-1}; ^{1}H NMR (200 MHz): δ 1.31 (t, J=7.4 Hz, 3H), 3.73 (s, 3H), 4.21 (q, J=7.4 Hz, 2H), 4.82 (dd, J=4.0, 1.1 Hz, 2H), 6.26 (dt, J=17.0, 1.2 Hz, 1H), 6.30–6.68 (m, 4H, fulvene protons), 7.24 (s, 1H), 6.83–7.52 (m, 4H).

3.3.8. 6-(3,5-Dibromo-2-(methyl 4-oxobut-2-enoate) phenyl) fulvene (8c). Yellow oil, 53%; IR (CCl$_4$): 1674 cm^{-1}; ^{1}H NMR (200 MHz): δ 3.78 (s, 3H), 4.64 (dd, J=4.0, 2.0 Hz, 2H), 6.1 (dt, J=16.4, 1.2 Hz, 1H), 6.31–6.59 (m, 4H, fulvene protons), 7.24 (m, 1H), 7.31 (s, 1H), 7.34 (d, J=2.6 Hz, 1H), 7.40 (d, J=2.6 Hz, 1H).

3.3.9. 6-(3,5-Dibromo-2-(ethyl 4-oxobut-2-enoate)phenyl) fulvene (8d). Yellow oil, 53%; IR (CCl$_4$): 1674 cm^{-1}; ^{1}H NMR (200 MHz): δ 1.26 (t, J=7.2 Hz, 3H), 4.21 (q, J=7.2 Hz, 2H), 4.80 (dd, J=4.0, 1.8 Hz, 2H), 6.04 (dt, J=16.8, 1.2 Hz, 1H), 6.20–6.48 (m, 4H, fulvene protons), 7.26 (m, 1H), 7.31 (d, J=2.0 Hz, 1H), 7.41 (s, 1H), 7.46 (d, J=2.0 Hz, 1H).

3.3.10. 6-(3,5-Dichloro-2-(methyl 4-oxobut-2-enoate)-phenyl) fulvene (8e). Yellow oil, 54%; IR (CCl$_4$): 1674 cm^{-1}; ^{1}H NMR (200 MHz): δ 3.76 (s, 3H), 4.62 (dd, J=4.0, 2.1 Hz, 2H), 6.10 (dt, J=16.4, 1.3 Hz, 1H), 6.31–6.62 (m, 4H, fulvene protons), 7.24 (m, 1H), 7.32 (d, J=1.8 Hz, 1H), 7.41 (s, 1H), 7.46 (d, J=1.8 Hz, 1H).

3.3.11. 6-(3,5-Dichloro-2-(ethyl 4-oxobut-2-enoate)phenyl) fulvene (8f). Yellow oil, 63%; IR (CCl$_4$): 1670 cm^{-1}; ^{1}H NMR (200 MHz): δ 1.28 (t, J=7.1 Hz, 3H), 4.24 (q, J=7.1 Hz, 2H), 4.81 (dd, J=4.4, 1.6 Hz, 2H), 6.14 (dt, J=16.7, 1.2 Hz, 1H), 6.31–6.56 (m, 4H, fulvene protons), 7.28 (m, 1H), 7.32 (d, J=1.8 Hz, 1H), 7.44 (s, 1H), 7.52 (d, J=1.8 Hz, 1H).

3.3.12. 6-Oxatricyclo[6.4.0.0^{2,10}] dodeca-2,11-diene[4,5]-2-methoxyphenyl-*endo*-9-carboxylicacid methyl ester (9a). Yellow oil, 44%; IR (CCl$_4$): 1732 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.98 (m, 1H), 2.54 (bs, 1H), 3.26 (t, J=4 Hz, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 3.84 (bs, 1H), 4.32 (dd, J=13.2, 1.8 Hz, 1H), 4.71 (dd, J=13.2, 1.8 Hz, 1H), 6.11 (s, 1H), 6.31 (dd, J=6.2, 3 Hz, 1H), 6.36 (dd, J=6.2, 3 Hz, 1H), 7.26 (d, J=8.0 Hz, 1H), 7.42–7.51 (m, 2H); ^{13}C NMR: δ 28.78, 42.50, 47.58, 49.00, 50.05, 55.32, 75.15, 103.39, 113.93, 121.87, 126.95, 128.05, 128.05, 133.64, 136.65, 154.84, 159.94, 171.84; MS (*m/z*): 298 (M$^+$); Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.45; H, 6.09; Found: C, 72.58; H, 5.99.

3.3.13. 6-Oxatricyclo [6.4.0.0^{2,10}] dodeca-2,11-diene[4,5]-2-methoxyphenyl-*endo*-9-carboxylicacid ethyl ester (9b). Colorless oil, 42%; IR (CCl$_4$): 1732 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.24 (t, J=7.0 Hz, 3H), 2.08 (m, 1H), 2.81 (bs, 1H), 3.25 (t, J=4.0 Hz, 1H), 3.70 (s, 3H), 3.84 (bs, 1H), 4.12 (q, J=7.0 Hz, 2H), 4.24 (dd, J=13.0, 1.0 Hz, 1H), 4.59 (dd, J=13.0, 1.0 Hz, 1H), 6.12 (s, 1H), 6.24 (dd, J=6.0, 3.2 Hz, 1H), 6.38 (dd, J=6.0, 3.2 Hz, 1H), 7.26–7.79 (m, 3H); ^{13}C NMR (100.4 MHz): δ 15.01, 40.63, 47.21, 49.22, 50.12, 55.65, 60.74, 75.21, 103.41, 115.78, 121.80, 124.84, 125.86, 127.84, 132.81, 133.17, 136.64, 154.69, 172.84; MS (*m/z*): 312 (M$^+$); Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.05; H, 6.46; Found: C, 73.12; H, 6.39.

3.3.14. 6-Oxatricyclo [6.4.0.0^{2,10}] dodeca-2,11-diene [4,5] 3,5-dibromophenyl-*endo*-9-carboxylicacid methyl ester (9c). Colorless oil, 31%; IR (CCl$_4$): 1731 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.86 (m, 1H), 2.56 (bs, 1H), 3.14 (t, J=4.1 Hz, 1H), 3.78 (s, 3H), 3.81 (bs, 1H), 4.31 (dd, J=12.8, 1.2 Hz, 1H), 4.76 (dd, J=13.2, 1.8 Hz, 1H), 6.21 (s, 1H), 6.31 (dd, J=6.0, 2.4 Hz, 1H), 6.38 (dd, J=6.0, 2.4 Hz, 1H), 7.31 (d, J=1.8 Hz, 1H), 7.41 (d, J=1.8 Hz, 1H); ^{13}C NMR: δ 28.90, 40.41, 48.64, 49.81, 51.49, 74.43, 103.71, 116.56, 122.31, 125.92, 126.85, 127.04, 130.99, 132.60, 133.74, 136.92, 173.98; MS (*m/z*): 424 (M$^+$); Anal. Calcd for $C_{17}H_{14}O_3Br_2$: C, 48.12; H, 3.33; Found: C, 48.10; H, 3.41.

3.3.15. 6-Oxatricyclo [6.4.0.0^{2,10}] dodeca-2,11-diene[4,5] 3,5-dibromophenyl-*endo*-9-carboxylicacid ethyl ester (9d). Colorless oil, 32%; IR (CCl$_4$): 1732 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.24 (t, J=7.4 Hz, 3H), 2.04 (m, 1H), 2.68 (bs, 1H), 3.14 (t, J=4.0 Hz, 1H), 3.81 (bs, 1H), 4.12 (q, J=7.4 Hz, 2H), 4.31 (dd, J=13.0, 1.0 Hz, 1H), 4.62 (dd, J=13.0, 1.0 Hz, 1H), 6.14 (s, 1H), 6.24 (dd, J=6.1, 3.2 Hz, 1H), 6.34 (dd, J=6.1, 3.2 Hz, 1H), 7.34 (d, J=2.4 Hz, 1H), 7.39 (d, J=2.4 Hz, 1H); ^{13}C NMR (100.4 MHz): δ 14.21, 39.94, 48.64, 49.54, 50.12, 61.04, 76.14, 102.88, 117.92, 121.21, 125.14, 126.71, 128.76, 130.42, 132.14, 133.09, 136.21, 173.04; MS (*m/z*): 438

(M^+); Anal. Calcd for $C_{18}H_{16}O_3Br_2$: C, 49.32; H, 3.68; Found: C, 49.12; H, 3.61.

3.3.16. 6-Oxatricyclo [6.4.0.0^{2,10}] dodeca-2,11-diene [4,5] 3,5-dichlorophenyl-*endo*-9-carboxylicacid methyl ester (9e). Yellow oil, 23%; IR (CCl_4): 1732 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.68 (m, 1H), 2.52 (bs, 1H), 3.14 (t, J=4.2 Hz, 1H), 3.76 (s, 3H), 3.86 (bs, 1H), 4.32 (dd, J=12.2, 1.4 Hz, 1H), 4.76 (dd, J=13.4, 1.8 Hz, 1H), 6.21 (s, 1H), 6.34 (dd, J=6.1, 2.2 Hz, 1H), 6.41 (dd, J=6.0, 2.1 Hz, 1H), 7.36 (d, J=2.2 Hz, 1H), 7.42 (d, J=2.2 Hz, 1H); ^{13}C NMR (100.4 MHz): δ 27.52, 38.64, 47.51, 48.67, 50.34, 75.66, 104.66, 115.71, 120.22, 123.08, 126.71, 130.41, 133.26, 136.44, 154.10, 156.32, 172.91; MS (*m/z*): 336 (M^+); Anal. Calcd for $C_{17}H_{14}O_3Cl_2$: C, 60.71; H, 4.20; Found: C, 60.74; H, 4.21.

3.3.17. 6-Oxatricyclo [6.4.0.0^{2,10}] dodeca-2,11-diene [4,5] 3,5-dichlorophenyl-*endo*-9-carboxylicacid ethyl ester (9f). Yellow oil, 20%; IR (CCl_4): 1732 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.26 (t, J=7.4 Hz, 3H), 2.06 (m, 1H), 2.74 (bs, 1H), 3.14 (t, J=4.2 Hz, 1H), 3.86 (bs, 1H), 4.24 (q, J=7.4 Hz, 2H), 4.31 (dd, J=12.8, 1.2 Hz, 1H), 4.64 (dd, J=12.8, 1.2 Hz, 1H), 6.05 (s, 1H), 6.38 (dd, J=6.1, 3.1 Hz, 1H), 6.42 (dd, J=6.1, 3.1 Hz, 1H), 7.36 (d, J=1.7 Hz, 1H), 7.44 (d, J=1.7 Hz, 1H); ^{13}C NMR (100.4 MHz): δ 14.26, 40.62, 48.61, 48.67, 50.32, 62.21, 75.08, 108.64, 117.33, 122.31, 125.66, 126.72, 128.88, 130.43, 132.32, 133.24, 136.87, 173.81; MS (*m/z*): 350 (M^+); Anal. Calcd for $C_{18}H_{16}O_3Cl_2$: C, 61.71; H, 4.61; Found: C, 61.67; H, 4.56.

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