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Cycloaddition Reactions of 3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one with 6,6-Dialkyl, Cycloalkyl and Diaryl Pentafulvenes

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Abstract: Competing [8+2] and [4+2] modes of additin of 3-ethoxycarbonyl-2H-cyclohepta[b]furan-2-one with dialkyl, cycloalky and diaryl pentafulvenes are described. © 1997 Elsevier Science Ltd.

2H-Cyclohepta[b]furan-2-ones such as **1**, readily obtained from chlorotropone and diethyl malonate can be viewed as an electron deficient heptafulvene.[1] In contrast to the reaction profiles of electron rich heptafulvenes,[2] the cycloaddition reactions of compounds such as **1** have received only limited attention. Potentially this extended 8π array can participate in cycloaddition reactions in a number of different pathways. The [8+2] cycloaddition reactions of **1** with electron rich dienophiles such as enamines and vinyl ethers have been effectively exploited in the synthesis of various alkyl substituted azulenes.[3,4]

Recently we have reported an exclusive [4+2] addition of **1** with aralkenes.[5] Subsequently we have observed that cycloaddition of **1** with acyclic 1,3-dienes proceeds in an [8+2] manner yielding novel hydroazulenoids.[6] As a logical extension of this work it was of interest to examine the cycloadditions of **1** with cross conjugated systems such as pentafulvenes. Except for an isolated report concerned with the reaction of 6,6-dimethylfulvene leading predominantly to an [8+2] adduct,[7] no information has been available in this area. In this paper we report the reactions of other 6,6-dialkyl fulvenes, 6,6-cycloalkyl and 6,6-diarylfulvenes with **1**.

RESULTS AND DISCUSSION

The reaction of **1** with 6,6-dialkyl pentafulvenes in toluene in a Schlenk glass tube at 150-170 °C afforded predominantly [8+2] adducts with only trace amounts of [4+2] adducts (Scheme 1).

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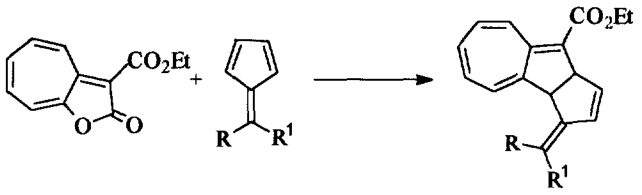


1 **2(a-c)** **3(a-c)**

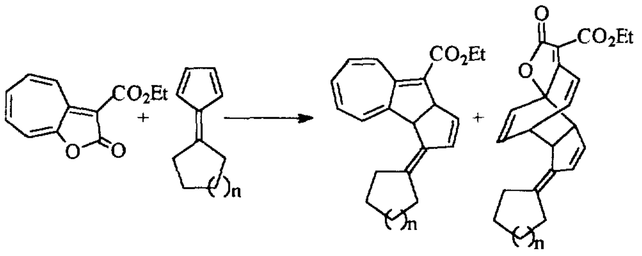
Reactant	Substituents	Product	Yield (%)^a
2a^{i}	R, R^1= -CH$_2$CH$_3$	**3a**	87
2b^{ii}	R= -CH$_3$, R^1= -CH$_2$CH$_3$	**3b**	68
2c^{ii}	R= -CH$_3$, R^1= -CH$_2$CH(CH$_3$)$_2$	**3c**	80

Reaction conditions: (i) Toluene, ST, Ar, 150 °C, 3 h (ii.) Toluene, ST, Ar, 170 °C, 5 h a). Yield based on unreacted 1.

Scheme 1

The products were easily separated by silica gel column chromatography by using ethyl acetate-hexane mixture as the eluent. The IR spectrum of the adducts **3a**, **3b**, and **3c** showed a strong absorption in the range 1695-1697 cm^{-1}, suggesting the presence of only the ester carbonyl group. The ^{1}H NMR of **3a** showed the characteristic doublet at δ 7.45 corresponding to the olefinic proton at the C-8 position. The ^{13}C NMR exhibited the signal corresponding to the carbonyl carbon at δ 165.69.

Interestingly, the reaction of **1** with 6,6-cycloalkyl pentafulvenes showed a different reactivity under similar conditions; both [8+2] and [4+2] adducts were formed in almost equal amounts (Scheme 2).



1 **4(a-c)** **5(a-c)** **6(a-c)**

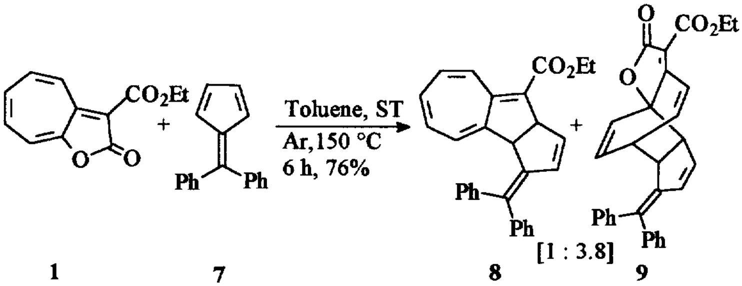
Reactant	n	Yield (%)^a	
		5	**6**
4a	1	46	43
4b	2	39	31
4c	3	37	31

Reaction conditions: Toluene, ST, Ar, 150 °C, 3 h a) Yield based on unreacted 1.

Scheme 2

The products were purified by silica gel column chromatography using ethylacetate-hexane mixture as the eluent. The products were characterized by spectroscopic analysis. The [8+2] adducts showed only one carbonyl absorption around 1690 cm^{-1}, while the [4+2] adducts showed two carbonyl absorptions at around 1770 cm^{-1} and 1700 cm^{-1}.

The reaction of 1 with 6,6-diphenylfulvene also led to a mixture of [8+2] and [4+2] adducts, the latter being the major product (Scheme 3).



Scheme 3

The [8+2] adduct 8, a dark red semisolid showed only one carbonyl absorption at 1682 cm^{-1}. The characteristic olefinic proton at the C-8 position appeared as a doublet at δ 7.49. In the ^{13}C NMR spectrum, the signal corresponding to the carbonyl carbon resonated at δ 166.10. The structure was further supported by the high resolution mass spectrum which showed a molecular ion peak at *m/z* 404.177. The [4+2] adduct 9, a yellow solid gave two carbonyl absorptions in the IR spectrum at 1777 cm^{-1} and 1709 cm^{-1} corresponding to the lactone and ester carbonyl groups respectively. The bridgehead proton resonated at δ 3.84 as a broad doublet in ^{1}H NMR. The ^{13}C NMR showed the characteristic signal of the bridgehead carbon adjacent to oxygen atom at δ 87.32. The other bridgehead carbon signal appeared at δ 54.83. The two carbonyl carbons resonated at δ 167.64 and 167.00. The structure was also supported by satisfactory elemental analysis.

In an effort to rationalize the observed reactivity of 1 with different pentafulvenes, we have carried out some MNDO and AM1 calculations using MOPAC program.[8] The results obtained using the reaction of 1 with 6,6-diphenyl fulvene as an example is illustrated in Figure 1.

It is clear from the correlation diagram that in the case of [8+2] addition, only the interaction of HOMO(1)-LUMO(fulvene) is symmetry allowed. It also validates the proposed regiochemistry of the [8+2] adduct. In the case of [4+2] addition, the interactions of NHOMO(1)-HOMO(fulvene),LUMO(1)-HOMO(fulvene), and HOMO(1)-LUMO (fulvene) are symmetry allowed. The interaction between LUMO(1)-HOMO(fulvene) is unimportant because of the small coefficients at the reacting carbon centers of LUMO(1). The energy gap between NLUMO(1)-HOMO(fulvene) is considerably smaller than that of HOMO(1)-

LUMO(fulvene). Such considerations make it clear that the NLUMO(1)-HOMO(fulvene) interaction controls the [4+2] addition, which is an inverse electron demand Diels-Alder reaction.

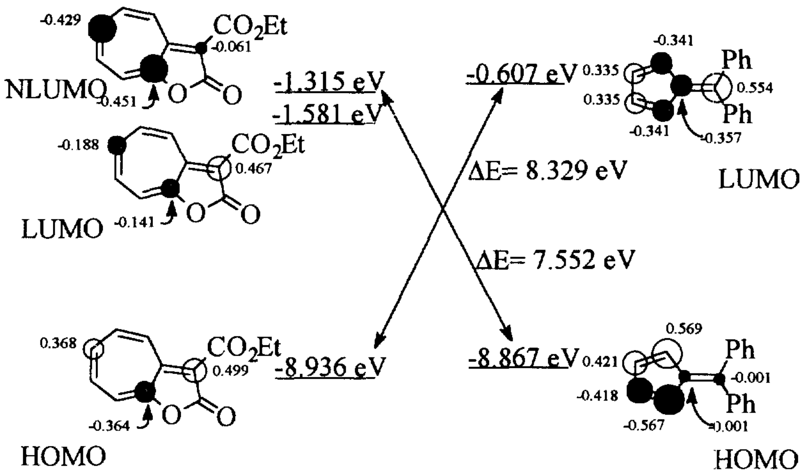


Figure 1. Molecular correlation diagrams of 1 and 6,6-diphenyl fulvene

The HOMO, LUMO and NLUMO energies of some of the reactants are given in Table 1.

Table 5. HOMO-LUMO-NLUMO energies of some of the reactants

Entry	Reactant	HOMO eV	LUMO eV	NLUMO eV
1	3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one	-8.936	-1.581	-1.315
2	6,6- Diphenyl fulvene	-8.867	-0.607	
3	6,6- Tetramethylene fulvene	-8.893	-0.554	
4	6,6- Pentamethylene fulvene	-8.887	-0.565	
5	6,6- Hexamethylene fulvene	-8.893	-0.571	

From the above data it is clear that [4+2] additions in all these cases can be classified as inverse electron demand Diels-Alder reactions. Although it is not possible to draw firm conclusions from the available data, steric factors may also be contributing to [8+2] *vs* [4+2] mode of addition of 1 with various fulvenes.

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EXPERIMENTAL DETAILS

All reactions were carried out in oven dried glassware (120 °C) under an atmosphere of argon. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100-200 mesh). Mixtures of ethyl acetate and hexane were

used as eluents. IR spectra were run on a Perkin-Elmer Model 882 infrared spectrophotometer. ^{1}H and ^{13}C NMR were recorded in the δ scale with TMS as internal reference.

3-(1-Ethyl-propylidene)-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (3a).

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.180 g, 0.82 mmol) and 6,6-diethyl fulvene (0.44 g, 3.28 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk glass tube and heated at 150 °C for 3 h. The reaction mixture was subjected to chromatography on silica gel (1% ethyl acetate-hexane) which afforded the [8+2] adduct **3a** (0.131 g, 87%) as red semisolid. The unreacted furanone (0.073 g) was recovered.

IR, film: 2974, 2942, 2882, 1695, 1640, 1601, 1549, 1463, 1375, 1214, 1132, 1045, 911 cm^{-1}.^{1}H NMR: δ 7.45 (d, J=11.96 Hz, 1H), 6.30 (d, 1H), 5.89 (m, 5H), 4.00 (m, 4H), 2.10 (m, 4H), 1.20 (t, 3H), 0.90 (m, 6H).^{13}C NMR: δ 165.69, 159.46, 153.01, 139.86, 135.47, 134.73, 132.76, 132.37, 130.97, 130.73, 130.07, 126.22, 121.63, 59.15, 53.60, 49.04, 26.13, 23.83, 14.28, 13.60, 12.88. EIMS, *m/z*: 308 (M^{+}, 100), 293 (35), 279 (58), 263 (60), 247 (35), 235 (98), 219 (60), 205 (98), 189 (100), 165 (97), 141 (52), 88 (51), 41 (36).

3-(1-Methyl-propylidene)-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (3b).

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.218 g, 1mmol) and 6-ethyl-6-methyl-fulvene (0.240 g, 2 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk glass tube and heated at 170 °C for 5 h. The reaction mixture when subjected to chromatography on silica gel (1% ethylacetate-hexane) afforded the [8+2] adduct **3b** (0.159 g, 68%) as red semisolid. The unreacted furanone (0.045 g) was recovered. IR, film: 2975, 2938, 2881, 1695, 1600, 1550, 1460, 1374, 1237, 1213, 1132, 1044, 911 cm^{-1}.^{1}H NMR: δ 7.5 (d, J=11.9 Hz, 1H), 6.40 (d, 1H), 5.95 (m, 5H), 4.15 (m, 4H), 2.20 (q, 2H), 1.75 (brs, 3H), 1.25 (t, 3H), 1.00 (t, 3H). ^{13}C NMR: δ 165.81, 159.55, 153.13, 140.66, 135.53, 132.85, 132.43, 131.06, 130.13, 129.65, 128.85, 126.34, 121.78, 59.24, 53.75, 49.49, 27.77, 19.92, 14.31, 13.00. Mass, *m/z*: 295 (M^{+}+1), 294 (M^{+}), 279.

3-(1,3-Dimethyl-butylidine)-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (3c).

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.180 g, 0.82 mmol) and 6-isobutyl-6-methyl fulvene (0.296 g, 2 mmol) in dry toluene(1 mL) were sealed under argon in a Schlenk glass tube and heated at 170 °C for 5 h. The reaction mixture when subjected to chromatography on silica gel (1% ethylacetate-hexane) afforded the [8+2] adduct **3c** (0.202 g, 80%) as red semisolid. The unreacted furanone (0.047 g) was recovered. IR, film: 2964, 2936, 2876, 1697, 1600, 1549, 1464, 1372, 1237, 1214, 1134, 1045, 910 cm^{-1}. ^{1}H NMR: δ 7.44 (d, 1H), 6.35 (d, 1H), 5.90 (m, 5H), 4.05 (m, 4H), 1.90 (m, 3H), 1.65 (brs, 3H), 1.20 (t, 3H), 0.75 (m,6H). ^{13}C NMR: δ 165.75, 160.21, 153.13, 142.36, 141.65, 135.32, 132.79, 132.40, 131.03, 130.10, 126.70, 126.22, 125.57, 59.21, 53.60, 49.67, 43.97, 27.17, 26.46, 22.58, 20.82, 14.31. Mass, *m/z*: 323 (M^{+}+1), 322 (M^{+}), 307.

3-Cyclopentylidene-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (5a) and Diels-Alder adduct 6a.

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.2 g, 0.917 mmol) and 6,6-tetramethylene fulvene (0.476 g, 3.66 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk glass tube and heated at 150 °C for 3 h. The reaction mixture when subjected to chromatography on silica gel as in previous cases, afforded the [8+2] adduct 5a (0.070 g, 46%) as red semisolid and the [4+2] adduct 6a (0.075 g, 43%) as yellow semisolid. The unreacted furanone (0.092 g) was recovered.

Data for compound 5a. IR, film: 2964, 1685, 1452, 1215, 1129, 1047, 912 cm^{-1}. ^1H NMR : δ 7.48 (d, J=12 Hz, 1H), 6.32 (d, 1H), 6.09 (m, 5H), 4.15 (m, 4H), 2.40 (brs, 4H), 1.70 (brs, 4H), 1.29 (t, 3H). ^{13}C NMR : δ 165.96, 159.41, 152.99, 137.95, 135.53, 135.29, 132.85, 132.55, 132.34, 131.09, 130.22, 126.55, 122.31, 59.36, 54.32, 50.62, 32.87, 31.11, 26.93, 26.13, 14.40. EIMS, *m/z*: 307 (M^++1, 9), 306 (M^+, 76), 233 (70), 202 (49), 191 (100), 165 (73), 152 (25), 127 (17), 77 (19), 41 (24).

Data for compound 6a. IR, film: 2963, 2878, 1780, 1716, 1624, 1410, 1293, 1264, 1215, 1073, 1039, 914, 733 cm^{-1}. ^1H NMR: δ 7.15 (d, 1H), 6.95 (d, 1H), 6.28 (d, 1H), 5.95 (m, 3H), 4.28 (q, 2H), 3.65 (m, 1H), 3.13 (brs, 2H), 2.29 (brs, 4H), 1.6 (brs, 4H), 1.28 (t, 3H). ^{13}C NMR: δ 168.26, 168.14, 161.37, 150.21, 136.90, 136.46, 135.20, 131.92, 130.67, 129.48, 120.67, 111.60, 87.92, 61.03, 55.37, 44.24, 39.73, 31.11, 30.51, 26.68, 25.92, 14.01. Analysis calcd. for $C_{22}H_{22}O_4$: C, 75.40%, H, 6.32%; Found: C,75.38%, H, 6.30%.

3-Cyclohexylidene-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ester (5b) and Diels-Alder adduct 6b.

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.2 g, 0.917 mmol) and 6,6-pentamethylene fulvene (0.535 g, 3.66 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk glass tube and heated at 150 °C for 3 h. The reaction mixture when subjected to chromatography on silica gel as in previous case afforded the [8+2] adduct **5b** (0.065 g, 39%) as red semisolid and [4+2] adduct **6b** (0.060 g, 31%) as yellow semisolid. The unreacted furanone (0.085 g) was recovered.

Data for compound 5b. IR, film: 2930, 2860, 1692, 1546, 1457, 1213, 1048 cm^{-1}. ^1H NMR: δ 7.53 (d, J= 11.9 Hz, 1H), 6.34 (dd, 1H), 6.04 (m, 5H), 4.14 (m, 4H), 2.34 (brs, 4H), 1.61 (brs, 6H), 1.30 (t, 3H). ^{13}C NMR: δ 166.06, 160.31, 153.29, 138.29, 135.87, 133.07, 132.62, 131.69, 131.25, 130.53, 130.29, 126.62, 122.06, 59.43, 53.91, 48.96, 33.15, 31.63, 28.35, 27.85, 26.73, 14.50. EIMS, *m/z*: 323 (M^++1, 2), 322 (M^+, 4), 306 (100), 247 (56), 205 (27), 191 (49), 179 (45), 165 (72), 141 (16), 91 (15).

Data for compound 6b. IR, film: 2940, 2861, 1781, 1715, 1622, 1267, 1038 cm^{-1}. ^1H NMR: δ 7.22 (d, 1H), 7.02 (d, 1H), 6.55 (d, 1H), 6.07 (m, 3H), 4.37 (q, 2H), 3.52 (m, 1H), 3.24 (brs, 2H), 2.20 (brs, 4H), 1.55 (brs, 6H), 1.38 (t, 3H). ^{13}C NMR: δ 168.20, 168.12, 161.39, 150.01, 136.02, 135.92, 135.22, 132.45, 131.90, 130.89, 129.54, 120.62, 110.92, 88.01, 61.02, 55.30, 43.62, 40.18, 32.01, 31.24, 28.30, 27.52, 27.10, 26.45. Analysis calcd. for $C_{23}H_{24}O_4$: C, 75.80%; H, 6.63%. Found: C-75.79%, H-6.60%.

3-Cycloheptylidene-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (5c) and Diels-Alder adduct 6c.

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.218g, 1 mmol) and 6,6-hexamethylene fulvene (0.480 g, 3 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk glass tube and heated at 150 °C for 3 h. The reaction mixture when subjected to chromatography on silica gel as usual afforded the [8+2] adduct **5c** (0.080 g, 37%) as red semisolid and [4+2] adduct **6c** (0.075 g, 31%) as yellow semisolid. The unreacted furanone (0.080 g) was recovered.

Data for compound 5c. IR, film: 2929, 2860, 2387, 1700, 1601, 1546, 1452, 1409, 1370, 1215, 1130, 1045, 911 cm^{-1}. ^{1}H NMR: δ 7.47 (d, J= 12.1 Hz, 1H), 4.43 (d, 1H), 5.97 (m, 5H), 4.07 (m, 4H), 2.38 (brs, 4H), 1.50 (brs, 8H), 1.25 (t, 3H).^{13}C NMR: δ 166.10, 159.80, 153.13, 140.75, 135.32, 132.97, 132.82, 132.43, 131.03, 130.94, 130.13, 126.40, 121.78, 59.24, 53.90, 49.40, 33.88, 32.21, 30.07, 28.51, 27.92, 27.68, 14.34. EIMS, *m/z*: 335 (M^++1, 19), 334 (M^+, 70), 261 (48), 205 (32), 202 (40), 191 (66), 179 (70), 165 (100), 152 (29), 141 (32), 91 (21), 67 (21), 55 (27), 41 (36).

Data for compound 6c. IR, film: 2929, 2860, 1780, 1715, 1624, 1452, 1299, 1262, 1072, 1036 cm^{-1}. ^{1}H NMR: δ 7.22 (d, 1H), 7.02 (d, 1H), 6.59 (d, 1H), 6.19 (m, 3H), 4.37 (q, 2H), 3.61 (m, 3H), 2.34 (brs, 4H), 1.54 (brs, 8H), 1.36 (t, 3H). ^{13}C NMR: δ 168.14, 167.00, 161.43, 150.18, 135.35, 133.71, 132.31, 131.32, 130.79, 129.83, 120.64, 110.62, 88.06, 61.06, 55.28, 43.52, 42.27, 32.87, 31.86, 29.92, 28.51, 27.92, 14.04. Analysis calcd. for $C_{24}H_{26}O_4$: C,76.16%; H,6.92%. Found: C, 76.15%; H,6.89%.

3-Benzhydrylidene-3a,9a-dihydro-3H-cyclopenta[a]azulene-9-carboxylic acid ethyl ester (8) and Diels-Alder adduct 9.

3-Ethoxycarbonyl-2H-cyclohepta[b]furan-2-one (0.475 g, 2.17 mmol) and 6,6-diphenyl fulvene (0.752 g, 3.26 mmol) in dry toluene (2 mL) were sealed under argon in a Schlenk glass tube and heated at 150 °C for 6 h. The reaction mixture was subjected to chromatography on silica gel. Elution with 1% ethyl acetate-hexane afforded the [8+2] adduct **8** (0.055 g, 16%) as red semisolid. On subsequent elution with 15% ethylacetate-hexane, the [4+2] adduct **9** (0.225 g, 60%) was obtained as yellow solid (mp. 92-95 °C). The unreacted furanone (0.292 g) was recovered.

Data for compound 8. IR, film: 3052, 3032, 2985, 1682, 1595, 1548, 1447, 1279, 1219, 1132, 1044, 910cm^{-1}. ^{1}H NMR: δ 7.49 (d, J= 11.9 Hz, 1H), 7.22 (m, 10 H), 6.48 (dd, 1H), 5.85 (m, 5H), 4.40 (m, 4H), 1.31 (t, 3H). ^{13}C NMR: δ 166.10, 158.56, 153.13, 146.93, 143.17, 143.11, 140.31, 134.55, 133.59, 133.09, 132.73, 131.18, 130.16, 129.98, 128.64,127.95, 127.30, 126.91, 126.73, 121.21, 59.42, 53.93, 48.68, 14.46.HRMS: $C_{29}H_{24}O_2$: 404.17764; Found: 404.17751.

Data for compound 9. IR, KBr: 3062, 2988, 1777, 1709, 1624, 1447, 1407, 1263, 1072, 1034 cm^{-1}. ^{1}H NMR: δ 7.31 (m, 8H), 7.09 (m, 3H), 6.49 (m, 2H), 6.22 (dd, 1H), 6.12 (d, J= 7.5 Hz, 1H), 5.99 (d, J= 8.67 Hz, 1H),

4.35 (q, 2H), 3.84 (d, 1H), 3.24 (m, 2H), 1.36 (t, 3H).^{13}**C NMR: δ 167.63, 167.00, 161.10, 149.62, 145.26, 142.13, 137.74, 136.46, 135.13, 130.46, 129.56, 129.42, 128.88, 128.37, 127.71, 127.03, 120.56 , 111.48, 87.32, 60.88, 54.83, 43.55, 39.19, 13.89. Analysis calcd. for** $C_{30}H_{24}O_4$: **C, 80.33%; H, 5.39%. Found: C, 80.50%; H,5.35%.**

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