Aminodienylesters. I: The Cycloaddition Reactions of *tert*-Aminodienylester with α,β-Unsaturated Carbonyl Compounds, Styrenes, and Quinones

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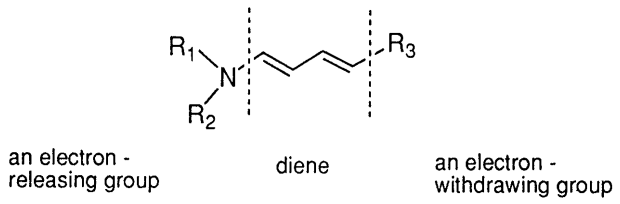
Methyl 5-(*N*,*N*-dimethylamino)-2,4-pentadienoate (*tert*-aminodienylester 1) was synthesized by condensation of methyl crotonate (2) with *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine (3). The reactivity of 1 was investigated with methyl propiolate (4), dimethyl 2-butynedionate (5), dimethyl maleate (6), dimethyl fumarate (7), 2-buten-4-olide (8), 2-cyclohexenone (9), styrene (10), *trans*-β-nitrostyrene (11), 1,4-benzoquinone (19), methyl 1,4-naphtoquinone-5-carboxylate (21), 1,4-naphthoquinone (24), juglone (26), 5-methoxy-1,4-naphthoquinone (28), naphthazarin (31), and naphthazarin dimethyl ether (33). In addition, 5-(*N*,*N*-dimethylamino)-2,4-pentadienenitrile (*tert*-aminodienylnitrile 37) was synthesized by condensation of crotononitrile (36) with 3. The reactivity of 37 was investigated with dimethyl 2-butynedionate (5), and 2-cyclohexenone (9).

Key words aminodienylester; aminodienylnitrile; cycloaddition reaction; 1,4-benzoquinone; 1,4-naphthoquinone

Currently, there is considerable interest in the reaction of nitroenamines and nitrodienamines because of their potential use in synthetic chemistry.[1-3] The center of interest in nitrodienamine chemistry may lie in the enaminic and diene character, and electronic "push–pull" nature. Reactions of aminodienylesters are also of interest from the viewpoint of the analogy with nitrodienamines, as shown in Chart 1. However, the properties of aminodienylesters have been little studied. This report describes the cycloaddition reactions of methyl 5-(*N*,*N*-dimethylamino)-2,4-pentadienoate (*tert*-aminodienylester **1**) with α,β-unsaturated carbonyl compounds, styrenes, 1,4-benzoquinone, and 1,4-naphthoquinones, and in addition, those of 5-(*N*,*N*-dimethylamino)-2,4-pentadienenitrile (*tert*-aminodienylnitrile **37**) with α,β-unsaturated carbonyl compounds.

The *tert*-aminodienylester **1** was prepared by the condensation of methyl crotonate (**2**) with *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine (**3**).[4] That is, reaction of **2** with **3** by heating at 150 °C for 4 h gave **1**, mp 97—98 °C, in 71.2% yield (Chart 1).

First, the reactivity of **1** with α,β-unsaturated carbonyl compounds, methyl propiolate (**4**), dimethyl 2-butynedionate (**5**), dimethyl maleate (**6**), dimethyl fumarate (**7**), 2-buten-4-olide (**8**), and 2-cyclohexenone (**9**), styrene (**10**) and *trans*-β-nitrostyrene (**11**), was investigated. Reactions were generally carried out under reflux in xylene until **1** was no longer detectable. The results are shown in Chart 2 and Table 1. Among the cycloadducts, dimethyl isophthalate (**12**),[5] trimethyl hemimellitate (**13**),[6] methyl 1,3-dihydro-1-oxobenzo[*c*]furan-4-carboxylate (**15**),[7] methyl tetralone-5-carboxylate (**16**),[8] and methyl biphenyl-3-carboxylate (**17**)[9] were identified by direct comparison with authentic samples, and the structures of trimethyl 3,6-cyclohexadiene-1,2,3-tricarboxylate (**14**) and methyl 6-nitrobiphenyl-2-carboxylate (**18**) were identified on the basis of spectroscopic analyses. The ^{1}H-NMR spectrum of **14** showed the presence of two methylene



1 : R_1, R_2 = Me, R_3 = CO_2Me

2 **3** **1**

Chart 1

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proton signals at δ 3.28—3.05 (2H, m), a methine proton signal at δ 4.74 (1H, t, J=4.8 Hz), nine methyl proton signals on three ester groups at δ 3.68 (3H, s) and 3.79 (6H, s), and two olefinic proton signals at δ 7.11 (2H, dd, J=4.8, 3.0 Hz). The structure of **14** was confirmed by its transformation into the aromatic compound **13** (96.8% yield) on treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene. The structure of **18** was similarly assigned from a comparison of the ^{1}H-NMR signals with those of biphenyls. These results also suggest the presence of site selectivity in this annelation reaction, as shown in Chart 2.

Table 1. The Cycloaddition Reactions of the *tert*-Aminodienylester **1** with α,β-Unsaturated Carbonyl Compounds and Styrenes

Initial compound	Reaction product	Reaction time	Yield (%)	mp (°C)
4	**12**	12 h	87.3	67—68
5	**13**	2 h	85.9	101—102
6	**14**	14 h	46.5	50—51
7	**14**	14 h	38.6	50—51
8	**15**	28 h	23.2	178—179
9	**16**	12 h	53.5	51—52
10	**17**	36 h	10.5	161—162
11	**18**	20 h	30.1	70—71

Next, we investigated the cycloaddition reaction of **1** with *p*-benzoquinone (**19**). Reaction of **1** with **19** in xylene at room temperature for 10 min provided dimethyl 9,10-anthraquinone-1,5-dicarboxylate (**20**), mp 251—252 °C, methyl 1,4-naphthoquinone-5-carboxylate (**21**), mp 89—91 °C, and hydroquinone (**22**),[5] mp 172—175 °C, in 55.8%, 13.0% and 7.0% yields, respectively (Chart 3). The anthraquinone **20** was synthesized from 9,10-anthraquinone-1,5-dicarboxylic acid (**23**)[10] by methylation with methanol in the presence of concentrated sulfuric acid in 82.1% yield. This compound **20** was identical with the diester **20** prepared from **1** and **19**. On the other hand, reaction of **1** with **21** for 30 min afforded the annelation product **20** in 78.8% yield. Regioselective formation of **20** may be controlled by the presence or absence of a mutual electronic interaction between the methyl carboxylate and the ketone as shown in Chart 3.

Next, the reactions of **1** with 1,4-naphthoquinone (**24**), juglone (**26**), and 5-methoxy-1,4-naphthoquinone (**28**) were examined (Chart 4). These reactions were generally carried out at room temperature in xylene until **1** was no longer detectable.

Reaction of **1** with **24** for 30 min provided methyl 9,10-anthraquinone-1-carboxylate (**25**),[11] mp 189—190 °C, in 66.7% yield. Reaction of **1** with **26** for 30 min provided methyl 5-hydroxy-9,10-anthraquinone-1-carbox-

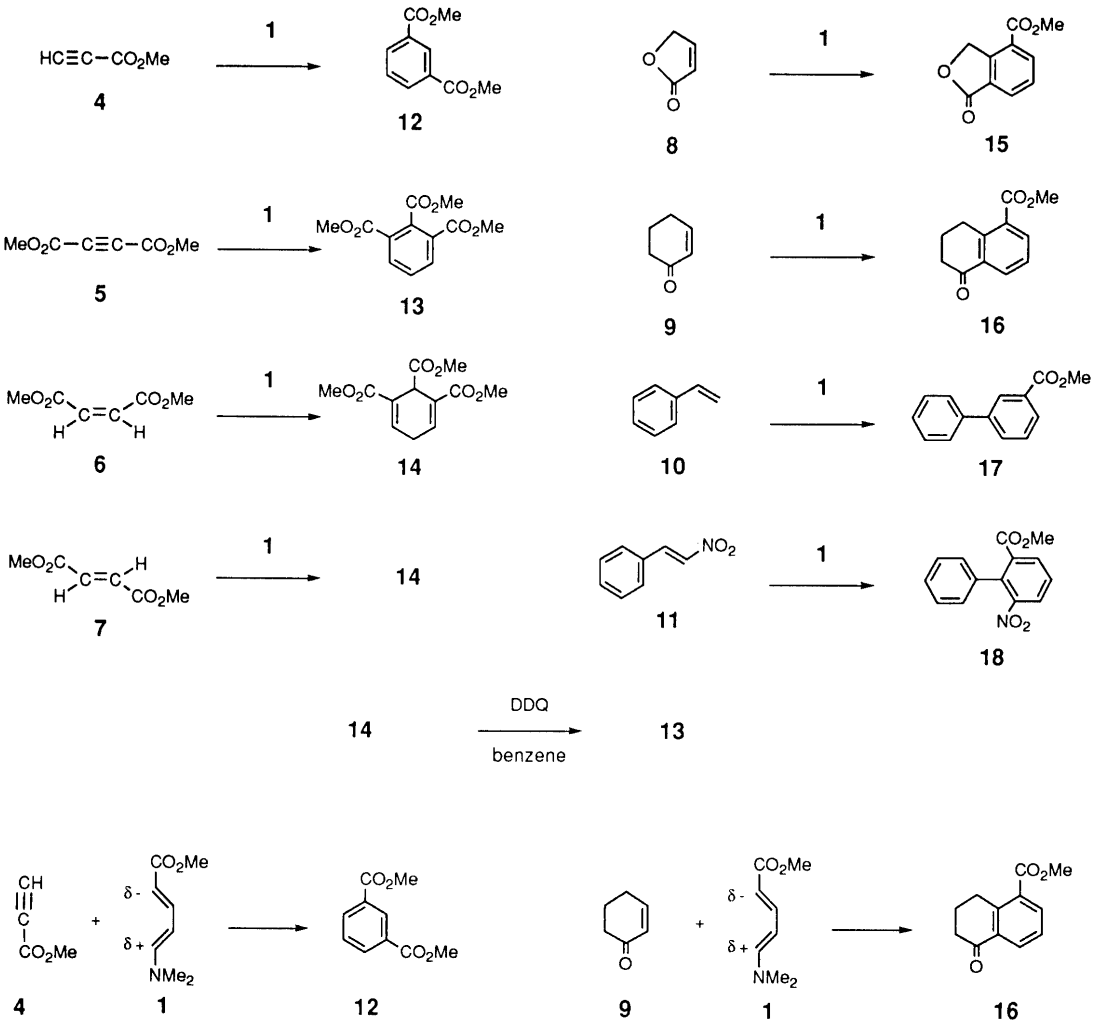

Chart 2

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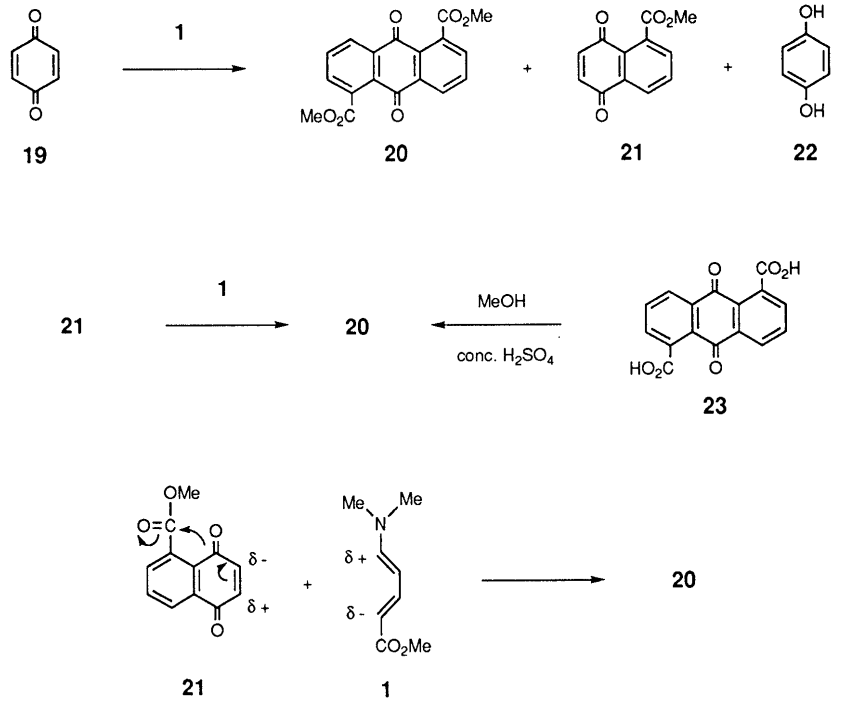

Chart 3

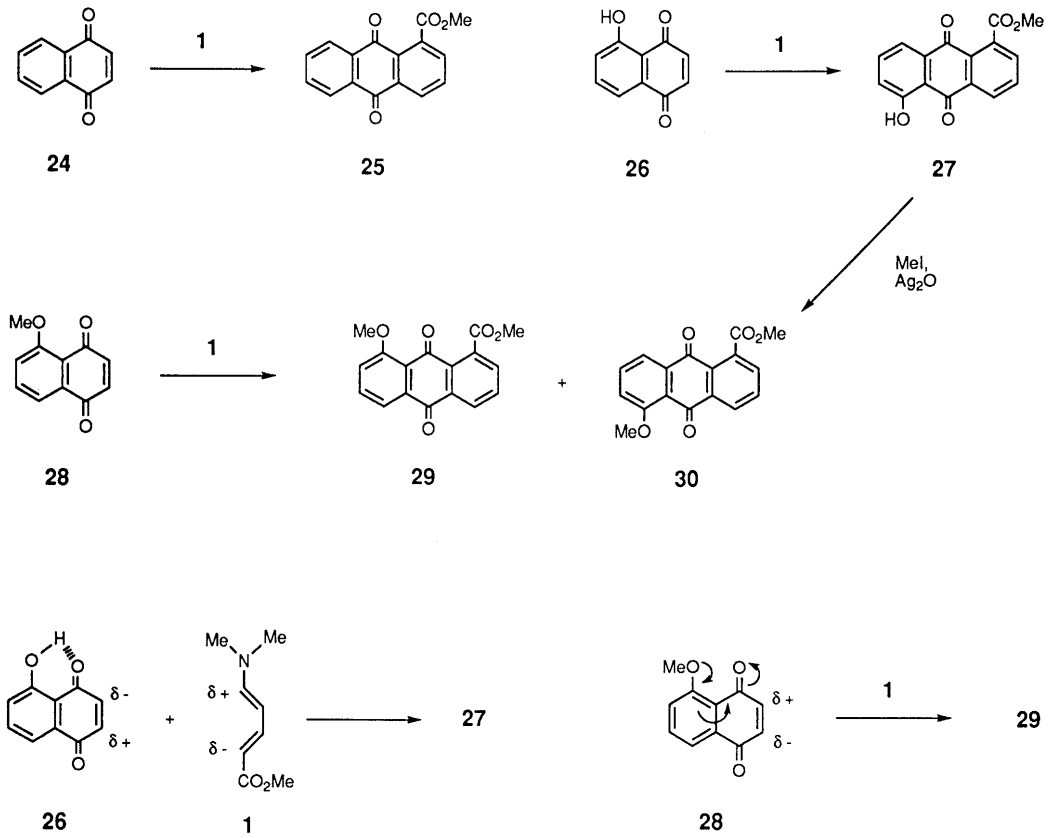

Chart 4

ylate (**27**), mp 187—188 °C, as a sole product in 77.3% yield. Reaction of **1** with the methyl ether of juglone (**28**) for 3 h gave methyl 8-methoxy-9,10-anthraquinone-1-carboxylate (**29**),[12] mp 229—230 °C, and methyl 5-methoxy-9,10-anthraquinone-1-carboxylate (**30**),[12] mp 184—186 °C, in 65.5% and 15.8% yields (ratio of 4 : 1), respectively. On the other hand, reaction of nitrodienamine with **28** was reported to give 1-methoxy-8-nitro-9,10-anthraquinone, yellow needles, mp 253—254 °C, in 46.3% yield as a sole product.[3] Treatment of **27** with methyl iodide in the presence of silver oxide gave the methyl ether **30** in 94.6% yield. This compound **30** was identical with the methyl ester **30** prepared from **1** and **28**. Regioselective formation of methyl methoxy-9,10-anthra-

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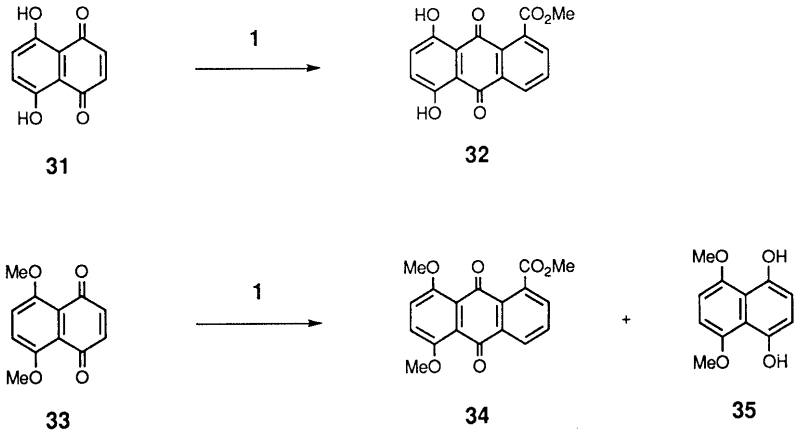
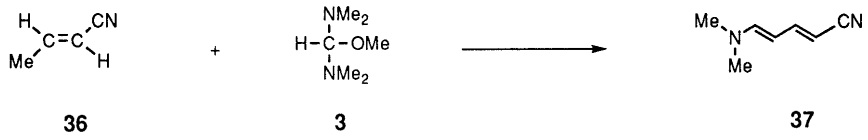
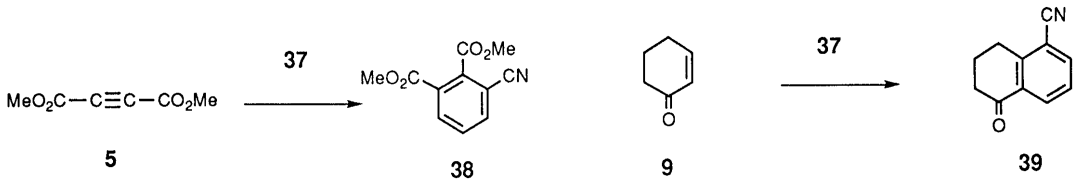


Chart 5





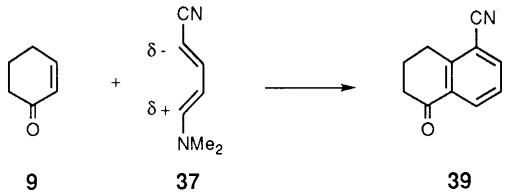


Chart 6

quinone-1-carboxylates **29** and **30** is consistent with the common Diels–Alder reactions of juglones, where the regioselectivity of the annelation reaction may be controlled by hydrogen bonding between the hydroxyl group and the carbonyl group (Chart 4).[3,13]

Reactions of **1** with naphthazarins **31** and **33** were also investigated. Reaction of **1** with naphthazarin (**31**) for 30 min provided methyl 5,8-dihydroxy-9,10-anthraquinone-1-carboxylate (**32**), mp 179—181 °C in 64.5% yield. Treatment of **1** with naphthazarin dimethyl ether (**33**) for 4 h afforded methyl 5,8-dimethoxy-9,10-anthraquinone-1-carboxylate (**34**), mp 188—190 °C, and 5,8-dimethoxynaphthalen-1,4-diol (**35**),[3] mp 168—170 °C, in 79.5% and 15.3% yields, respectively (Chart 5).

In addition, we investigated the reactivities of *tert*-aminodienylnitrile **37** as well as those of **1** and the nitrodienamine. The *tert*-aminodienylnitrile **37** was prepared by the condensation of crotononitrile (**36**) with **3**. That is, reaction of **36** with **3** by heating at 150 °C for 40 min gave **37**, yellow oil, in 62.8% yield, as shown in Chart 6. The reactivity of **37** with α,β-unsaturated carbonyl compounds, **5** and **9**, was investigated. Reactions were generally carried out under reflux in xylene until **37** was no longer detectable. Reaction of **37** with **5** in xylene for 5 h provided the dimethyl 3-cyanobenzene-1,2-dicarboxylate (**38**), yellow oil, in 27.4% yield. Reaction of **37** with **9** in xylene for 280 h provided the 5-cyanotetralone (**39**), mp 146—147 °C, in 37.4% yield. It has become apparent that the *tert*-aminodienylester **1** and *tert*-aminodienylnitrile **37** are potentially useful synthons, like nitrodienamine. The reactivities in cycloaddition were in the order *tert*-aminodienylester > nitrodienamine > *tert*-aminodienylnitrile.

These results provide a new aromatic annelation method with potential utility in the syntheses of aromatic com-

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pounds, naphthoquinones, and anthraquinones.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR-200 or JASCO FT/IR-8000 spectrometer, and ^{1}H-NMR spectra with a JEOL EX-90 or JEOL JNM-α500 spectrometer with tetramethylsilane as an internal standard. MS were recorded with a JEOL JMS-D 300 spectrometer. Elemental analyses were done by Kissei Pharmaceutical Company, Ltd., Matsumoto, Japan. Wakogel C-200 (silica gel) and Merck Kieselgel G nach Stahl (silica gel) were used for column chromatography and thin layer chromatography (TLC), respectively. All runs were carried out under argon.

Methyl 5-(*N*,*N*-Dimethylamino)-2,4-pentadienoate (*tert*-Aminodienyl-ester 1) A mixture of methyl crotonate (3.00 g, 0.03 mol) and *N*,*N*,*N'*,*N'*-tetramethylmethylenediamine (**3**) (5.22 g, 0.03 mol)[4] was heated at 150 °C for 4 h. The reaction mixture was washed with hexane, and then recrystallized to give 3.31 g (71.2%) of **1** as light yellow plates, mp 97—98 °C (from ether). IR (KBr): 1697, 1630, 1595, 1574 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.86 (6H, s, $-NMe_2$), 3.68 (3H, s, $-CO_2Me$), 5.10 (1H, dd, J=12.4, 11.9 Hz, olefinic H), 5.43 (1H, d, J=14.7 Hz, olefinic H), 6.63 (1H, d, J=12.4 Hz, olefinic H), 7.34 (1H, dd, J=14.7, 11.9 Hz, olefinic H). *Anal.* Calcd for $C_8H_{13}N_1O_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.65; H, 8.23; N, 8.99.

General Procedure for Reactions of 1 with α,β-Unsaturated Carbonyl Compounds 4—9 and Styrenes 10 and 11 A solution of **1** (1 mmol) and one of the compounds (1.5 mmol) in xylene (5 ml) was refluxed for an appropriate period until **1** was no longer detectable by TLC. The reaction mixture was concentrated under a vacuum, and the residue was subjected to silica gel column chromatography with appropriate solvents.

Reaction with Methyl Propiolate (4) Reaction period, 12 h. Solvent for chromatography, 30% hexane in ethyl acetate. Product: 169.3 mg (87.3%) of dimethyl isophthalate (**12**), colorless needles (ether), mp 67—68 °C (lit.[5] mp 67—68 °C). IR (KBr): 1724, 1595 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.95 (6H, s, $-CO_2Me$), 7.54 (1H, t, J=7.9 Hz, aromatic H), 8.23 (2H, dd, J=7.9, 1.8 Hz, aromatic H), 8.69 (1H, t, J=1.8 Hz, aromatic H). CI-MS m/z: 195 (M^++1).

Reaction with Dimethyl 2-Butynedionate (5) Reaction period, 2 h. Solvent for chromatography, 50% hexane in ethyl acetate. Product: 216.5 mg (85.9%) of trimethyl hemimellitate (**13**), colorless plates (ether), mp 101—102 °C (lit.[6] mp 102 °C). IR (KBr): 1726, 1585 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.92 (6H, s, $-CO_2Me$), 4.00 (3H, s, $-CO_2Me$), 7.55 (1H, t, J=7.9 Hz, aromatic H), 8.23 (2H, d, J=7.9 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{12}H_{12}O_6$: 252.0634. Found: 252.0671.

Reaction with Dimethyl Maleate (6) Reaction period, 14 h. Solvent for chromatography, 30% hexane in ethyl acetate. Product: 118.4 mg (46.5%) of trimethyl 3,6-cyclohexadiene-1,2,3-tricarboxylate (**14**), colorless plates (ether), mp 50—51 °C. IR (KBr): 1718, 1639 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.28—3.05 (2H, m, methylene H), 3.68 (3H, s, $-CO_2Me$), 3.79 (6H, s, $-CO_2Me$), 4.74 (1H, t, J=4.8 Hz, methine H), 7.11 (2H, dd, J=4.8, 3.0 Hz, olefinic H). *Anal.* Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.57; H, 5.46.

Reaction with Dimethyl Fumarate (7) Reaction period, 14 h. Solvent for chromatography, 30% hexane in ethyl acetate. Product: 98.0 mg (38.6%) of **14**, colorless plates (ether), mp 50—51 °C. This product was identical with **14** previously described.

Reaction with 2-Buten-4-olide (8) Reaction period, 28 h. Solvent for chromatography, 50% benzene in chloroform. Product: 44.5 mg (23.2%) of methyl 1,3-dihydro-1-oxobenzo[*c*]furan-4-carboxylate (**15**), colorless needles (MeOH), mp 178—179 °C (lit.[7] mp 177—179 °C). IR (KBr): 1770, 1707, 1602 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.97 (3H, s, $-CO_2Me$), 5.62 (2H, s, methylene H), 7.79 (1H, t, J=7.6 Hz, aromatic H), 8.10 (1H, dd, J=7.6, 0.8 Hz, aromatic H), 8.33 (1H, dd, J=7.6, 0.8 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{10}H_8O_4$: 192.0423. Found: 192.0446.

Reaction with 2-Cyclohexenone (9) Reaction period, 12 h. Solvent for chromatography, 10% ethyl acetate in hexane. Product: 102.7 mg (53.5%) of methyl tetralone-5-carboxylate (**16**), colorless needles (ether), mp 51—52 °C (lit.[8] mp 53—55 °C). IR (KBr): 1716, 1685, 1587 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.12 (2H, quintet, J=6.4 Hz, methylene H), 2.67 (2H, t, J=6.4 Hz, methylene H), 3.30 (2H, t, J=6.4 Hz, methylene H), 3.91 (3H, s, $-CO_2Me$), 7.36 (1H, t, J=7.8 Hz, aromatic H), 8.05 (1H, dd, J=7.8, 1.4 Hz, aromatic H), 8.23 (1H, dd, J=7.8, 1.4 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{12}H_{12}O_3$: 204.0787. Found: 204.0814.

Reaction with Styrene (10) Reaction period, 36 h. Solvent for chromatography, 40% hexane in chloroform. Product: 22.3 mg (10.5%) of methyl biphenyl-3-carboxylate (**17**), colorless plates (ether), mp 161—162 °C (lit.[5] mp 160—161 °C). IR (KBr): 1722, 1587 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.94 (3H, s, $-CO_2Me$), 7.36 (1H, tt, J=7.3, 1.4 Hz, aromatic H), 7.39 (2H, td, J=7.3, 1.4 Hz, aromatic H), 7.51 (1H, t, J=7.9 Hz, aromatic H), 7.62 (2H, dt, J=7.3, 1.4 Hz, aromatic H), 7.78 (1H, dt, J=7.9, 1.5 Hz, aromatic H), 8.01 (1H, dt, J=7.9, 1.5 Hz, aromatic H), 8.28 (1H, t, J=1.5 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{14}H_{12}O_2$: 212.0835. Found: 212.0825.

Reaction with *trans*-β-Nitrostyrene (11) Reaction period, 20 h. Solvent for chromatography, 30% ethyl acetate in hexane. Product: 51.5 mg (30.1%) of methyl 6-nitrobiphenyl-2-carboxylate (**18**), colorless plates (ether), mp 70—71 °C. IR (KBr): 1730, 1566, 1535 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.56 (3H, s, $-CO_2Me$), 7.20—7.24 (2H, m, aromatic H), 7.37—7.40 (3H, m, aromatic H), 7.55 (1H, t, J=7.9 Hz, aromatic H), 7.87 (1H, dd, J=7.9, 1.5 Hz, aromatic H), 7.98 (1H, dd, J=7.9, 1.5 Hz, aromatic H). *Anal.* Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.54; H, 4.47; N, 5.34.

Preparation of 13 from 14 DDQ (272.4 mg, 1.2 mmol) was added to a solution of **14** (50.0 mg, 0.2 mmol) in benzene (2 ml) and the whole was refluxed for 24 h. The reaction mixture was concentrated under a vacuum, and the residue was subjected to silica gel column chromatography. The eluate with 30% hexane in ethyl acetate gave 48 mg (96.8%) of **13**, colorless plates (ether), mp 101—102 °C (lit.[6] mp 102 °C). This product was identical with **13** previously described.

General Procedure for Reactions of 1 with *p*-Benzoquinone (19) and 1,4-Naphthoquinones 21, 24, 26, 28, 31, and 33 A solution of **1** (1 mmol) and *p*-benzoquinone or a 1,4-naphthoquinone (1.5 mmol) in dry xylene (5 ml) was stirred at room temperature for an appropriate period until **1** was no longer detectable by TLC. The reaction mixture was concentrated under a vacuum, and then the residue was subjected to silica gel column chromatography with appropriate solvents.

Reaction with 19 Reaction period, 10 min. Solvent for chromatography, 25% ethyl acetate in hexane. Product: First eluate, 90.4 mg (55.8%) of dimethyl 9,10-anthraquinone-1,5-dicarboxylate (**20**), light yellow plates (MeOH), mp 251—252 °C. IR (KBr): 1724, 1680, 1575 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.04 (6H, s, $-CO_2Me$), 7.74 (2H, dd, J=7.6, 1.2 Hz, aromatic H), 7.85 (2H, t, J=7.6 Hz, aromatic H), 8.36 (2H, dd, J=7.6, 1.2 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{18}H_{12}O_6$: 324.0633. Found: 324.0613. Second eluate, 28.1 mg (13.0%) of methyl 1,4-naphthoquinone-5-carboxylate (**21**), colorless needles (ether), mp 89—91 °C. IR (KBr): 1732, 1697, 1668, 1577 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.99 (3H, s, $-CO_2Me$), 6.98 (1H, d, J=10.3 Hz, olefinic H), 7.00 (1H, d, J=10.3 Hz, olefinic H), 7.69 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.80 (1H, t, J=7.6 Hz, aromatic H), 8.18 (1H, dd, J=7.6, 1.2 Hz, aromatic H). *Anal.* Calcd for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.70; H, 3.86. Third eluate, 11.6 mg (7.0%) of hydroquinone (**22**), colorless plates (ether), mp 172—175 °C (lit.[5] mp 172—175 °C). IR (KBr): 3167, 1514 cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 6.66 (4H, s, aromatic H), 7.66 (2H, s, –OH). High-resolution EI-MS m/z: Calcd for $C_6H_6O_2$: 110.0369. Found: 110.0370.

Reaction with Methyl 1,4-Naphthoquinone-5-carboxylate (21) Reaction period, 30 min. Solvent for chromatography, 25% ethyl acetate in hexane. Product: 255.3 mg (78.8%) of **20**, light yellow plates (MeOH), mp 251—252 °C. This product was identical with **20** previously described.

Reaction with 1,4-Naphthoquinone (24) Reaction period, 30 min. Solvent for chromatography, 30% ethyl acetate in hexane. Product: 177.4 mg (66.7%) of methyl 9,10-anthraquinone-1-carboxylate (**25**), colorless needles (MeOH), mp 189—190 °C (lit.[11] mp 189 °C). IR (KBr): 1734, 1676, 1593, 1575 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.05 (3H, s, $-CO_2Me$), 7.72 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.79—7.82 (2H, m, aromatic H), 7.84 (1H, t, J=7.6 Hz, aromatic H), 8.24—8.28 (1H, m, aromatic H), 8.29—8.33 (1H, m, aromatic H), 8.41 (1H, dd, J=7.6, 1.2 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{16}H_{10}O_4$: 266.0577. Found: 266.0572.

Reaction with Juglone (26) Reaction period, 30 min. Solvent for chromatography, 30% ethyl acetate in hexane. Product: 218.0 mg (77.3%) of methyl 5-hydroxy-9,10-anthraquinone-1-carboxylate (**27**), yellow needles (MeOH), mp 187—188 °C. IR (KBr): 1732, 1670, 1637,

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1579 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.04 (3H, s, $-CO_2Me$), 7.33 (1H, dd, J=8.2, 1.3 Hz, aromatic H), 7.69 (1H, t, J=2 Hz, aromatic H), 7.73 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.80 (1H, dd, J=8.2, 1.3 Hz, aromatic H), 7.86 (1H, t, J=7.6 Hz, aromatic H), 8.43 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 12.46 (1H, s, –OH). *Anal.* Calcd for $C_{16}H_{10}O_5$: C, 68.08; H, 3.57. Found: C, 68.22; H, 3.73.

Reaction with 5-Methoxy-1,4-naphthoquinone (28) Reaction period, 3 h. Solvent for chromatography, 30% ethyl acetate in hexane. Product: First eluate, 46.8 mg (15.8%) of methyl 5-methoxy-9,10-anthraquinone-1-carboxylate (**30**), yellow needles (MeOH), mp 184—186 °C (lit.[12] mp 184.5—186.0 °C). IR (KBr): 1730, 1676, 1581 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.03 (3H, s, $-CO_2Me$), 4.06 (3H, s, –OMe), 7.36 (1H, dd, J=7.6, 0.9 Hz, aromatic H), 7.66 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.73 (1H, t, J=7.6 Hz, aromatic H), 7.81 (1H, t, J=7.6 Hz, aromatic H), 7.90 (1H, dd, J=7.6, 0.9 Hz, aromatic H), 8.37 (1H, dd, J=7.6, 1.2 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{17}H_{12}O_5$: 296.0685. Found: 296.0706. Second eluate, 193.9 mg (65.5%) of methyl 8-methoxy-9,10-anthraquinone-1-carboxylate (**29**), yellow needles (MeOH), mp 229—230 °C (lit.[12] mp 228.5—229.5 °C). IR (KBr): 1730, 1672, 1581 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.03 (3H, s, $-CO_2Me$), 4.04 (3H, s, –OMe), 7.35 (1H, d, J=8.0 Hz, aromatic H), 7.72 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.73 (1H, t, J=8.0 Hz, aromatic H), 7.76 (1H, t, J=7.6 Hz, aromatic H), 7.94 (1H, d, J=8.0 Hz, aromatic H), 8.33 (1H, dd, J=7.6, 1.2 Hz, aromatic H). High-resolution MS m/z: Calcd for $C_{17}H_{12}O_5$: 296.0682. Found: 296.0664.

Reaction with 5,8-Dihydroxy-1,4-naphthoquinone (31) Reaction period, 30 min. Solvent for chromatography, 30% ethyl acetate in hexane. Product: 260.2 mg (64.5%) of methyl 5,8-dihydroxy-9,10-anthraquinone-1-carboxylate (**32**), yellow needles (MeOH), mp 179—181 °C. IR (KBr): 1730, 1622, 1574 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 4.04 (3H, s, $-CO_2Me$), 7.33 (2H, s, aromatic H), 7.73 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 7.88 (1H, t, J=7.6 Hz, aromatic H), 8.46 (1H, dd, J=7.6, 1.2 Hz, aromatic H), 12.51 (1H, s, –OH), 12.81 (1H, s, –OH). *Anal.* Calcd for $C_{16}H_{10}O_6$: C, 64.43; H, 3.38. Found: C, 64.26; H, 3.49.

Reaction with 5,8-Dimethoxy-1,4-naphthoquinone (33) Reaction period, 4 h. Solvent for chromatography, 30% hexane in ethyl acetate. Product: First eluate, 33.0 mg (15.3%) of 5,8-dimethoxynaphthalen-1,4-diol (**35**), light red needles (MeOH), mp 168—170 °C (lit.[3] mp 168—170 °C). IR (KBr): 1525 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.99 (6H, s, $-CO_2Me$), 6.61 (2H, s, aromatic H), 6.82 (1H, s, aromatic H), 9.09 (2H, s, –OH). High-resolution EI-MS m/z: Calcd for $C_{12}H_{12}O_4$: 220.0766. Found: 220.0751. Second eluate, 259.2 mg (79.5%) of methyl 5,8-dimethoxy-9,10-anthraquinone-1-carboxylate (**34**), orange needles (MeOH), mp 188—190 °C. IR (KBr): 1726, 1670, 1583 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.97 (3H, s, $-CO_2Me$), 4.00 (3H, s, –OMe), 4.01 (3H, s, –OMe), 7.34 (2H, s, aromatic H), 7.71 (1H, dd, J=6.8, 3.2 Hz, aromatic H), 7.72 (1H, t, J=6.8 Hz, aromatic H), 8.26 (1H, dd, J=6.8, 3.2 Hz, aromatic H). *Anal.* Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32. Found: C, 66.18; H, 4.38.

Preparation of 20 from 9,10-Anthraquinone-1,5-dicarboxylic Acid (23) **23**[10] (296 mg, 1 mmol) was added to a solution of concentrated sulfuric acid (1 ml) in methanol and the whole was refluxed for 9 h, then poured into ice water. The precipitate was recrystallized from methanol to give 243.0 mg (82.1%) of **20** as light yellow plates, mp 251—252 °C. This product was identical with **20** previously described.

Preparation of 30 from 27 Methyl iodide (63.9 mg, 0.45 mmol) and silver oxide (347 mg, 15 mmol) were added to a solution of **27** (28.2 mg, 0.1 mmol) in chloroform (3 ml) and the whole was refluxed for 4 h, then filtered. The filtrate was concentrated under a vacuum. The residue was subjected to silica gel column chromatography. The eluate with 50% hexane in ethyl acetate gave 28 mg (94.6%) of **30**, yellow needles (MeOH), mp 184—186 °C (lit.[12] mp 184.5—186.0 °C). This product was identical with **30** previously described.

5-(*N*,*N*-Dimethylamino)-2,4-pentadienenitrile (*tert*-Aminodienylnitrile 37) A mixture of crotononitrile (**36**) (1.34 g, 20 mmol) and **3** (2.64 g, 20 mmol)[4] was heated at 150 °C for 40 min. The reaction mixture was concentrated under a vacuum, and then the residue was subjected to silica gel column chromatography. The eluate with 40% ethyl acetate in hexane gave 1.53 g (62.8%) of **37**, a yellow oil (mixture of *cis* and *trans*). IR (neat): 2200, 1630, 1595, 1580 cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 2.87 (3H, s, –Me), 2.90 (3H, s, –Me), 4.34–5.53 (2H, olefinic H), 6.51–6.94 (2H, olefinic H). High-resolution EI-MS m/z: Calcd for $C_7H_{10}N_2$: 122.0844. Found: 122.0856.

General Procedure for Reactions of 37 with α,β-Unsaturated Carbonyl Compounds 5 and 9 A solution of **37** (1 mmol) and one of the compounds (1.5 mmol) in xylene (5 ml) was refluxed for an appropriate period until **37** was no longer detectable by TLC. The reaction mixture was concentrated under a vacuum, and the residue was subjected to silica gel column chromatography with appropriate solvents.

Reaction with 5 Reaction period, 5 h. Solvent for chromatography, 50% hexane in ethyl acetate. Product: 60 mg (27.4%) of dimethyl 3-cyanobenzene-1,2-dicarboxylate (**38**), a yellow oil. IR (neat): 2240, 1730, 1590 cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.94 (3H, s, $-CO_2Me$), 4.03 (3H, s, $-CO_2Me$), 7.63 (1H, t, J=7.7 Hz, aromatic H), 7.88 (1H, dd, J=7.7, 1.5 Hz, aromatic H), 8.18 (1H, dd, J=7.7, 1.5 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{11}H_9NO_4$: 219.0529. Found: 219.0236.

Reaction with 9 Reaction period, 280 h. Solvent for chromatography, 20% ethyl acetate in hexane. First eluate product: 64 mg (37.4%) of 5-cyanotetralone (**39**) as colorless plates (ether), mp 146—147 °C. IR (KBr): 2220, 1680, 1580 cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 2.16—2.40 (2H, m, methylene H), 2.73 (2H, t, J=6.4 Hz, methylene H), 3.20 (2H, t, J=6.2 Hz, methylene H), 7.44 (1H, dd, J=7.7, 1.5 Hz, aromatic H), 7.82 (1H, dd, J=7.7, 1.5 Hz, aromatic H), 8.26 (1H, dd, J=7.7, 1.5 Hz, aromatic H). High-resolution EI-MS m/z: Calcd for $C_{11}H_9NO$: 171.0681. Found: 171.0659. Second eluate product: 10 mg (8%) of **37**, yellow oil.

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