Investigation of Diels–Alder Reaction of 7-Substituted 4-Styrylcoumarins with Symmetrical Dienophiles Leading to 3,4-Annulated Coumarins

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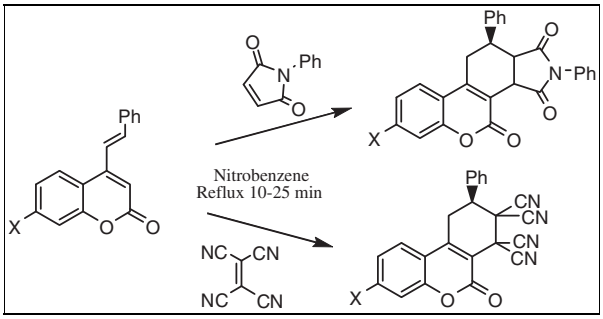

The thermal [4 + 2] cycloaddition reaction of 7-substituted 4-styrylcoumarins with *N*-phenylmaleimide and tetracyanoethylene in nitrobenzene under reflux conditions rapidly gives 3,4-annulated coumarins as the Diels–Alder adducts. The position of the surviving double bond was determined on the basis of NMR and supported by energies of the possible structures. The effects of the 7-substituent and the solvent on the reaction were studied.

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INTRODUCTION

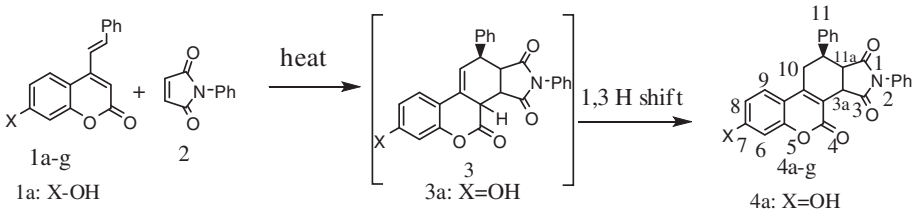
Coumarins (2H-1-benzopyran-2-ones) and polycyclic compounds containing coumarin moiety occur in many plants [1] and have diverse biological activities, namely anticoagulant [2] and antifungal [3]. Because of these properties, coumarins have been of sustained interest in organic synthesis. One of the sites of coumarins that attracts the chemists is the 3–4 double bond. It shows the properties of olefinic double bond and undergoes addition reactions [4,5]. Because of activation by the adjacent carbonyl group, it also functions as a dienophile [6–12]. Coumarins containing a vinyl substituent at the 3 or 4 position behave as dienes, and the corresponding Diels–Alder reaction gives 3,4-annulated coumarins [13,14]. Thus, Diels–Alder reaction of 4-styrylcoumarins with *N*-phenylmaleimide (NPMA) and maleic anhydride has been reported earlier [15–17]. These reactions require long reaction time. Recently, 4-styrylcoumarins have been prepared by the condensation of 4-methylcoumarin with benzaldehydes in the presence of catalytic amount of piperidine [18]. 4-Styrylcoumarin thus prepared is reported to react with different dienophiles in dichloromethane at room temperature to form the corresponding adducts. On the basis of *ab initio* calculations at the Hartree-Fock level using the basis set 6–31 G (d, p), the reaction has been shown to follow normal electron demand pathway and the *endo* adduct is found to be thermodynamically and kinetically more favorable than the *exo* adduct [18].

In our efforts to use the 3,4 double bond in 3,4 annulation of coumarins, we undertook a detailed investigation of the Diels–Alder reaction of 4-styrylcoumarins. In the first report on this reaction, position of the surviving double bond (in ring "C") was not established unambiguously [16], and the subsequent workers maintained the same position [17,18]. We felt that placement of the surviving double bond in the C ring was less favorable than in the B ring. Further, we also thought it interesting to observe the effect of 7-substituent on the Diels–Alder reaction. Thus, we herein report the Diels–Alder reaction of 7-substituted 4-styrylcoumarins with symmetrical dienophiles, NPMA, and tetracyanoethylene (TCE).

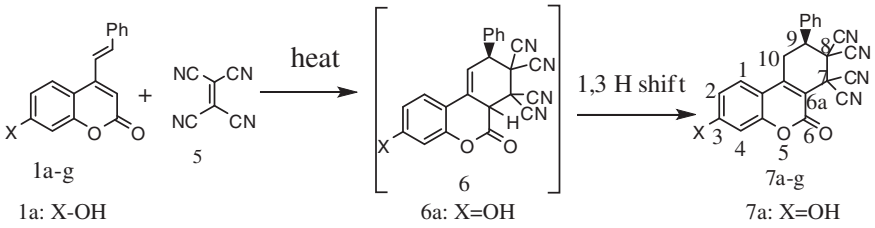
RESULTS AND DISCUSSION

3-Substituted phenols were condensed with acetone dicaroxylic acid to obtain 7-substituted coumarin 4-acetic acids [19]. 4-Styrylcoumarins (**1a–g**) were prepared from the respective coumarin-4-acetic acids by the known procedure [20]. The reaction of **1a** with NPMA and TCE was carried out in boiling nitrobenzene; the latter dienophile was used with a specific aim of locating the surviving double bond (Schemes 1 and 2). TCE is a highly electron-deficient reactive dienophile. The reaction with **1a** : NPMA mole ratio 1:1 gave 72% yield of the product in 60 min. Surprisingly, the reaction with TCE at the same mole ratio gave only 43% of the product in 20 min. In order to enhance

Scheme 1



Scheme 2



the yield of the product, the reaction was carried out with increasing amounts of NPMA and TCE (Table 1).

Diels–Alder reaction is sensitive with respect to solvent and temperature. The reaction of **1a** with NPMA and TCE was carried out in different polar solvents at the reflux temperature as well as in the absence of solvent at 150 °C (Table 2).

In nitrobenzene, the reaction took place very rapidly. In dioxane and *n*-butanol, the reaction was very sluggish, the work-up was tedious, and yields of the products were low. In *n*-butyl cellosolve and *o*-dichlorobenzene, good yields of the products were obtained; however, the isolation was tedious. The reaction took place without solvent at 150 °C, but gave moderate yield of the products. In conclusion, nitrobenzene was the best solvent for reaction. Removal of nitrobenzene and isolation of the product, at the end of reaction, from the reaction mixture were very easy. The product separated on either cooling or addition of hexane or pentane in the ratio of 1:3 (v/v) with stirring. Excellent yields of the products were obtained in short time.

Table 1

Diels–Alder reaction of **1a** with NPMA/TCE using different mole ratios in boiling nitrobenzene.

Entry	Dienophile	Mole ratio **1a** : dienophile	Time[a] (min)	Yield[b] of **4a/7a** (%)
1	NPMA	1:1	60	72
2	NPMA	1:2	20	82
3	NPMA	1:3	20	84
4	TCE	1:1	20	43
5	TCE	1:2	10	83
6	TCE	1:3	10	86

[a]Time for 100% conversion of **1a**.
[b]Isolated yield.

The reaction of 4-styrylcoumarins with styrene, allyl bromide, and ethyl acrylate in dichloromethane at room temperature is reported to furnish the corresponding Diels–Alder adducts [18]. However, the reaction failed in our hands. The products having structure such as **3**, with the surviving double bond exocyclic to the B ring, are reported to be formed in the reaction [18]. This product seems to be less likely when the reaction is carried out in a polar solvent at a high temperature. To decide the location of the double bond, product **7a** was analyzed by ^{1}H NMR. Because of tetracyanosubstitution in the product, location of the double bond could be deciphered easily. NMR spectrum of **7a** was decisive in locating the position of the double bond. It did not show the presence of any olefinic hydrogen; instead, it gave geminally and vicinally coupled methylene and methine protons at 3.7 and 3.89 δ, respectively. ^{13}C NMR also supported the assignment. In the ^{13}C NMR of **7a**, C_{6a} and C_{10a} appeared at 109.73 and 154.10 δ, which correspond to ^{13}C NMR signals of the C_3 and C_4 of 7-hydroxycoumarin [21]. In structure **6a**, the C_{10} is expected to give a peak around 125–130 δ.

To throw more light on the structure, APT and DEPT spectra were recorded to reveal the CH_2, CH, and quaternary carbons. In the APT spectrum (Fig. 1) of **7a**, positive peaks (CH_2, C) were obtained for C_7, C_8, and C_{10} at 47.89, 42.09, and 28.31 δ, respectively, and a negative peak for C_9 (CH) at 42.25 δ. The DEPT spectrum (Fig. 2) of **4b** showed a negative peak for C_{10} at 28.10 δ, indicating that it is CH_2 group. This evidence supports structure **7/4** and not **6/3**.

Table 2

Diels–Alder reaction of **1a** with NPMA/TCE in different solvents.[a]

Entry	Solvent	Dienophile[b]	Time	Yield[c] of **4a/7a** (%)
1	Nitrobenzene	NPMA	20 min	82
2	*o*-Dichlorobenzene	NPMA	1 h 15 min	70
3	*n*-Butyl cellosolve	NPMA	50 min	75
4	*n*-Butanol	NPMA	5 h 30 min	73
5	Dioxane	NPMA	20 h	52
6	Without solvent[d]	NPMA	45 min	55
7	Nitrobenzene	TCE	10 min	83
8	*o*-Dichlorobenzene	TCE	40 min	68
9	*n*-Butyl cellosolve	TCE	60 min	79
10	*n*-Butanol	TCE	10 h	71
11	Dioxane	TCE	14 h	76
12	Without solvent[d]	TCE	1 h	40

[a]Reflux temp.
[b]Diene : dienophile 1:2.
[c]Isolated yield.
[d]Temperature 150 °C.

To have some insight into stabilities of **3a** and **4a**, we optimized the structures using Accelrys Material Studio/ Forcite programme (MS 3.2), and the energy minimized structures are shown in Figure 3. It is seen that **4a** has lower energy than **3a**. This also supports the position of the double bond obtained from ^{1}H NMR and ^{13}C NMR. Such a 1,3-prototropic shift in the primary Diels–Alder adduct leading to more stable product, for example, aromatic ring, is known [22,23].

The 7-substituent in **1** is expected to have some effect on the diene reactivity due to conjugation, as it is suitably placed. To see the effect of 7-substitution, a series of 7-substituted 4-styrylcoumarins was prepared by the known procedure [20].

1b–g were reacted with NPMA and TCE in boiling nitrobenzene (Table 3). All the dienes were reactive and gave the adducts in good yield; however, the time required for complete consumption of the diene varied. Interestingly, when TCE, more reactive dienophile, was used, the effect of 7-substituent was diminished. 7-Unsubstituted diene was the most reactive, and methyl group at the 7-position maintained the reactivity. Electron donating OH/OCH_3

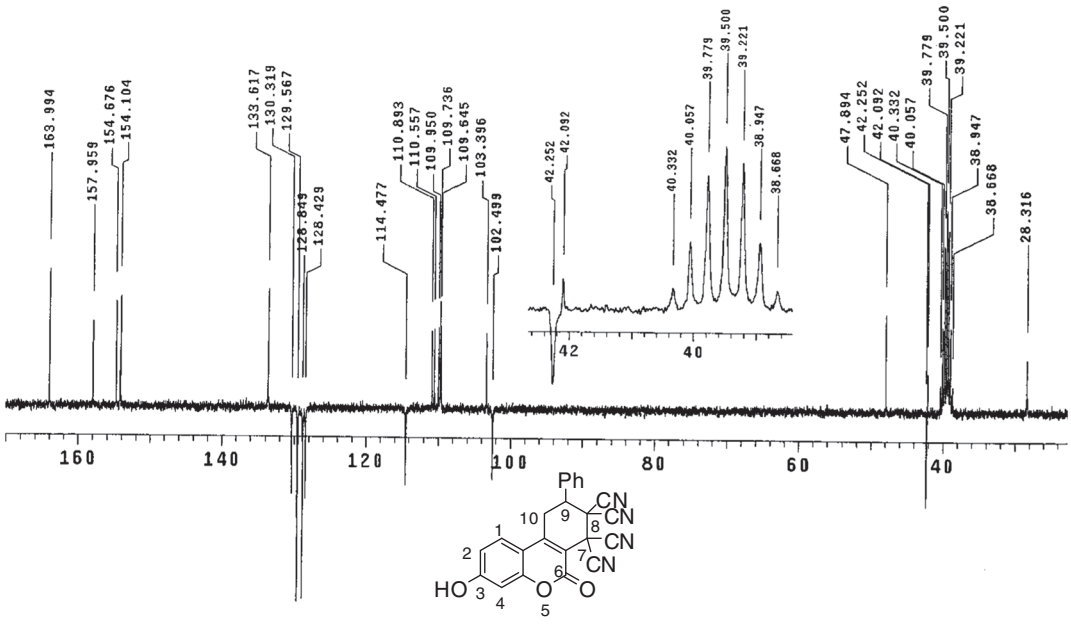


Figure 1. APT spectrum of **7a**.

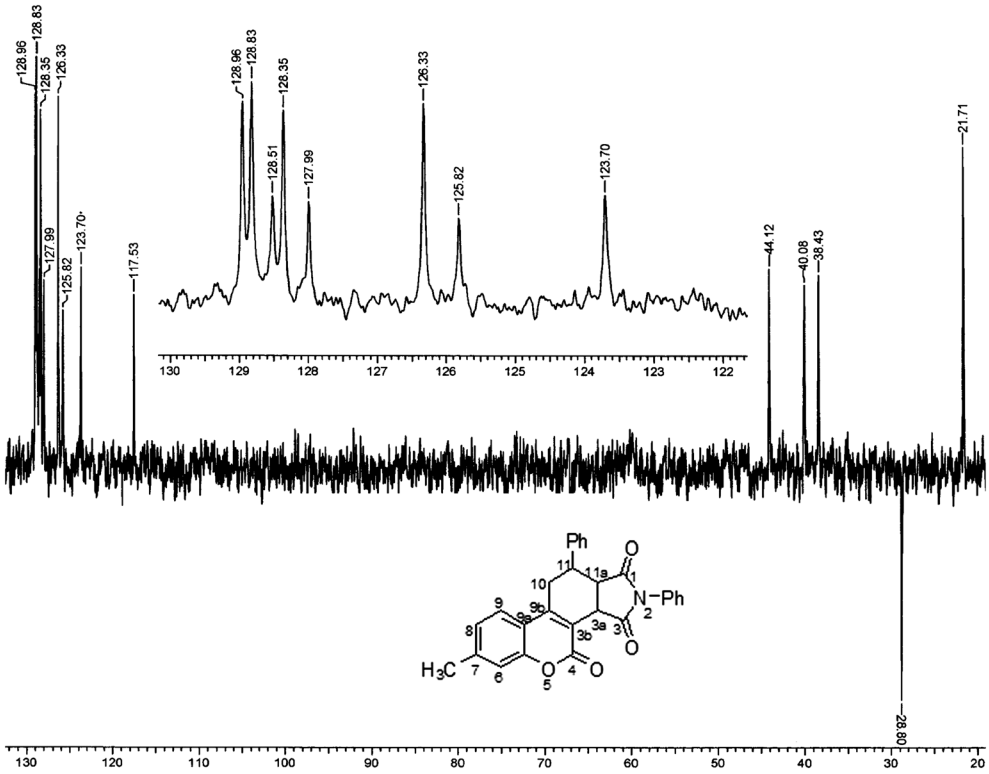


Figure 2. DEPT spectrum of **4b**.

groups decreased the reactivity, whereas converting OH into OTs and OAc decreased the reactivity further. 7-Cl was nearly at par with 7-OH/OCH_3.

EXPERIMENTAL

All the melting points reported are in degree centigrade and are uncorrected. All the IR spectra were recorded on Perkin-Elmer spectrum-100 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury plus 300 (300 MHz) spectrometer in $CDCl_3$/DMSO-d_6 with TMS as an internal standard, and the chemical shifts are expressed in δ unit (ppm). Mass spectra were recorded on Finnigan LCQ Advantage Max spectrometer. Elemental analysis was carried out with a Thermo finnigan, Flash EA 1112. **1a–g** were prepared by the reported procedures [20]. **1a** was tosylated and acylated using p-TsCl and Ac_2O by the standard procedures to obtain **1e** and **1f**, respectively.

General procedure for the synthesis of compound 4a–g.

7-Hydroxy-2,11-diphenyl-3a,10,11,11a-tetrahydro[1]benzopyrano [3,4-e]isoindole-1,3,4(2H)-trione (4a). **1a** (0.264 g, 1 mmol) and NPMA (0.346 g, 2 mmol) were refluxed in nitrobenzene (5 mL) for

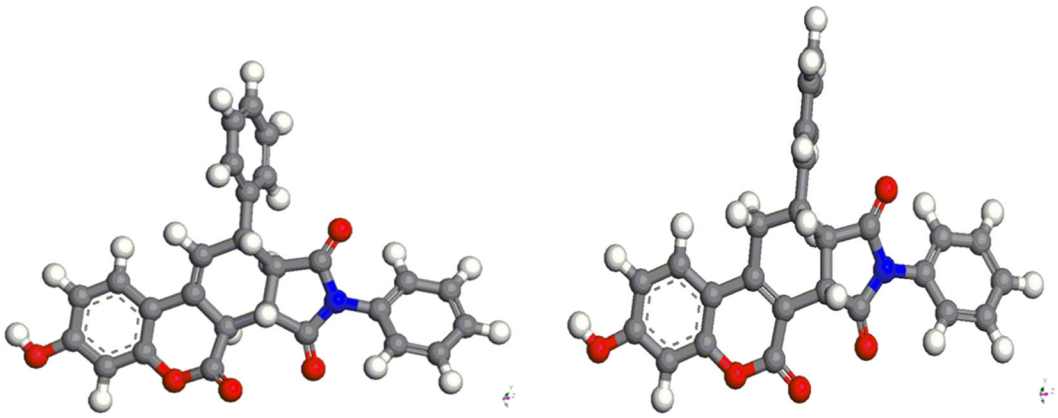


Figure 3. Optimized geometries and energies of **3a** and **4a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3

Diels–Alder reaction of **1a–g** with **2/5** in boiling nitrobenzene.

Entry	Diene **1** (X)	NPMA (**2**)/ TCE (**5**)[a] Dienophile	Time[b] (min)	Yield of **4/7** (%)[c]
1	**1a** (7-OH)	NPMA	20	82
2	**1b** (7-Me)	NPMA	10	84
3	**1c** (7-OMe)	NPMA	20	88
4	**1d** (7-H)	NPMA	10	87
5	**1e** (7-OTs)	NPMA	25	74
6	**1f** (7-OAc)	NPMA	25	78
7	**1g** (7-Cl)	NPMA	20	75
8	**1a** (7-OH)	TCE	10	86
9	**1b** (7-Me)	TCE	10	86
10	**1c** (7-OMe)	TCE	10	81
11	**1d** (7-H)	TCE	10	85
12	**1e** (7-OTs)	TCE	20	80
13	**1f** (7-OAc)	TCE	20	84
14	**1g** (7-Cl)	TCE	15	78

[a]Diene : dienophile = 1:2 (molar).
[b]Time for 100% conversion of 1.
[c]Isolated yield.

20 min. After complete consumption of **1a**, the solution was cooled to room temperature. The precipitated solid was collected by filtration and washed with hexane to remove traces of nitrobenzene. *N*-Hexane was added to the filtrate and stirred for 15 min to obtain second crop of **4a**. **4a** was sufficiently pure and obtained as an off-white solid 0.360 g (82%); mp 299–300 °C; IR (KBr): 3176 (OH), 1782, 1719 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 3.3 (m, 2H, $C_{10}H_2$, merged with water in DMSO), 3.61 (br d, 1H, $C_{11}H$), 3.79 (t, 1H, $C_{11a}H$, $J = 6.6$ and 8.4 Hz), 4.67 (d, 1H, $C_{3a}H$, $J = 8.4$ Hz), 6.79–6.81 (m, 4H, N-Ph), 7.23–7–35 (m, 8H, ArH), 7.76 (d, 1H, C_9H, $J = 8.4$ Hz), 10.61 (br s, 1H, OH, exchangeable with D_2O); ^{13}C NMR (DMSO-d_6): δ 27.77 (C_{10}), 38.58 (C_{11a}), 40.14 (C_{3a}), 44.09 (C_{11}), 102.32 (C_6), 111.03 (C_{9a}), 112.89, 113.19, 126.45, 127.07 (3 CH), 128.29 (4 CH), 128.68 (3 CH), 132.12, 140.48 (N-Cph), 151.35 (C_{9b}), 154.12 (C_7), 159.92 (C_{5a}), 161.29 (C_4), 173.88 (C_1), 175.29 (C_3); MS: *m/z* 438 (M + 1). *Anal*. Calcd for $C_{27}H_{19}NO_5$: C, 74.13; H, 4.38; N, 3.20. Found: C, 73.98; H, 4.35; N, 3.16.

In the cases of **4c–g**, the product did not separate on cooling of the solution. Hence, *n*-hexane (15 mL) was added to the cooled solution, and the solution was stirred for 15 min.

7-Methyl-2,11-diphenyl-3a,10,11,11a-tetrahydro[1] benzopyrano [3,4-e]isoindole-1,3,4(2H)-trione (4b). Off-white solid; Yield: 84%; mp 290–291 °C; IR (KBr): 1780, 1724, 1706 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.48 (s, 3H, Me), 3.31 (t, 2H, $C_{10}H_2$, $J = 5.1$ Hz), 3.70 (dd, 1H, $C_{11a}H$, $J = 8$ and 6 Hz), 3.80 (q, 1H, $C_{11}H$, $J = 6$ and 5.1 Hz), 4.61 (d, 1H, $C_{3a}H$, $J = 8$ Hz), 6.62–6.67 (m, 2H, ArH), 7.13–7.28 (m, 10H, ArH), 7.53 (d, 1H, C_9H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$): δ 21.71 (CH_3), 28.80 (C_{10}), 38.45 (C_{11a}), 40.09 (C_{3a}), 44.13 (C_{11}), 115.97 (C_6), 116.14, 117.53, 123.70, 125.81, 126.33 (2 CH), 127.98, 128.35 (2 CH), 128.51, 128.82 (2 CH), 128.96 (2 CH), 131.21, 139.09 (N-Cph), 143.62 (C_7), 149.69 (C_{9b}), 153.00 (C_{5a}), 160.27 (C_4), 172.56 (C_1), 175.17 (C_3); MS: *m/z* 436 (M + 1). *Anal*. Calcd for $C_{28}H_{21}NO_4$: C, 77.23; H, 4.86; N, 3.22. Found: C, 77.10; H, 4.69; N, 3.02.

7-Methoxy-2,11-diphenyl-3a,10,11,11a-tetrahydro[1]benzopyrano [3,4-e]isoindole-1,3,4(2H)-trione (4c). White solid; Yield: 88%; mp 281–282 °C; IR (KBr): 1777, 1723, 1703 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.29 (t, 2H, $C_{10}H_2$, $J = 5.7$ Hz), 3.70 (d, 1H, $C_{11a}H$, $J = 8.4$ Hz), 3.80 (d, 1H, $C_{11}H$, $J = 5.7$ Hz), 3.90 (s, 3H, OCH_3), 4.57 (d, 1H, $C_{3a}H$, $J = 8.4$ Hz), 6.64 (dd, 2H, ArH), 6.88 (t, 2H, C_6H and C_8H, $J = 2.4$ and 8.7 Hz), 7.21–7.28 (m, 8H, ArH), 7.55 (d, 1H, C_9H, $J = 8.7$ Hz); ^{13}C NMR ($CDCl_3$ + drops of DMSO): δ 28.14 (C_{10}), 38.03 (C_{11a}), 39.98 (C_{3a}), 44.8 (C_{11}), 57.09 (OCH_3) 102.32 (C_6), 111.13, 111.84, 115.13, 126.11, 126.37 (2 CH), 127.13, 127.44 (2 CH), 128.14, 129.11 (2 CH), 129.99 (2 CH), 131.98, 141.12 (N-Cph), 152.32 (C_{9b}), 157.19 (C_{5a}), 159. 87 (C_7), 163.22 (C_4), 173.02 (C_1), 175.31 (C_3); MS: *m/z* 452 (M + 1). *Anal*. Calcd for $C_{28}H_{21}NO_5$: C, 74.49; H, 4.69; N, 3.10. Found: C, 74.23; H, 4.38; N, 3.13.

2,11-Diphenyl-3a,10,11,11a-tetrahydro[1] benzopyrano[3,4-e]isoindole-1,3,4(2H)-trione (4d). Off-white solid; Yield: 87%; mp 278–280 °C; IR (KBr): 1780, 1720, 1702 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 3.3 (m, 2H, $C_{10}H_2$, merged with water in DMSO), 3.65 (br d, 1H, $C_{11a}H$), 3.83 (t, 1H, $C_{11}H$, $J = 7$ Hz), 4.76 (d, 1H, $C_{3a}H$, $J = 8.4$ Hz), 6.82 (d, 2H ArH, $J = 8$ Hz), 7.24–7.49 (m, 10H, ArH), 7.67 (t, 1H, C_8H, $J = 7.8$ Hz), 7.96 (d, 1H, C_9H, $J = 7.8$ Hz), ^{13}C NMR ($CDCl_3$): δ 28.70 (C_{10}), 38.38 (C_{11a}), 40.17 (C_{3a}), 44.03 (C_{11}), 117.25 (C_6), 117.35, 118.54, 123.99, 124.62, 126.34 (2 CH), 127.92, 128.30 (2 CH), 128.48, 128.79 (2 CH), 128.90 (2 CH), 131.21, 132.23, (C_7) 139.06, (N-Cph) 149.74 (C_{9b}), 152.84 (C_{5a}), 160.03 (C_4), 172.56 (C_1), 175.10 (C_3); MS: *m/z* 422 (M + 1). *Anal*. Calcd for $C_{27}H_{19}NO_4$: C, 76.95; H, 4.54; N, 3.32. Found: C, 76.80; H, 4.38; N, 3.21.

2,11-Diphenyl-3a,10,11,11a-tetrahydro[1] benzopyrano[3,4-e]isoindole-1,3,4(2H)-trione-7-yl-tosylate (4e). Off-white solid; Yield: 74%; mp 254–255 °C; IR (KBr): 1780, 1728, 1703 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.48 (s, 3H, CH_3), 3.29 (br t, 2H, $C_{10}H_2$), 3.69 (t, 1H, $C_{11a}H$, $J = 6$ and 8 Hz), 3.80 (q, 1H, $C_{11}H$, $J = 6$ and 8 Hz), 4.58 (d, 1H, $C_{3a}H$, $J = 8$ Hz), 6.65 (dd, 2H, ArH, $J = 7.5$ Hz), 6.92 (d, 1H, C_6H, $J = 2.1$ Hz), 7.15–7.38 (m, 11H, ArH), 7.62 (d, 1H, C_9H, $J = 8.4$ Hz), 7.76 (d, 2H, ArH, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$): δ 21.86 (CH_3), 28.97 (C_{10}), 38.29 (C_{11}a), 40.08 (C_{3a}), 43.94 (C_{11}), 111.22 (C_6), 117.39, 117.50, 119.41, 125.27, 126.27 (2 CH), 128.14, 128.27 (2 CH), 128.5 (2 CH), 128.62, 128.87 (2 CH), 129.03 (2 CH), 130.21 (2 CH), 131.07, 131.80, 138.73 (N-Cph), 146.26 (Me-Cph), 148.98, 151.88 (C_7), 153.22, 159.37 (C_4), 172.23 (C_1), 174.85 (C_3); MS: *m/z* 592 (M + 1). *Anal*. Calcd for $C_{34}H_{25}NO_7S$: C, 69.02; H, 4.26; N, 2.37. Found: C, 68.83; H, 4.23; N, 2.20.

2,11-Diphenyl-3a,10,11,11a-tetrahydro[1] benzopyrano[3,4-e]isoindole-1,3,4(2H)-trione-7-yl-acetate (4f). Off-white solid; Yield: 78%; mp 289–290 °C; IR (KBr): 1766, 1730, 1703 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.31 (s, 3H, CO-CH_3), 3.3 (m, 2H, $C_{10}H_2$, merged with water in DMSO), 3.64 (br d, 1H, $C_{11}H$), 3.84 (t, 1H, $C_{11a}H$, $J = 6$ and 8 Hz), 4.74 (d, 1H, $C_{3a}H$, $J = 8$ Hz), 6.82 (dd, 2H, ArH, $J = 2.4$ and 7.8 Hz), 7.18–7.35 (m, 10H, ArH), 8.01 (d, 1H, C_9H, $J = 9$ Hz); MS: *m/z* 479 (M + 1), *Anal*. Calcd for $C_{29}H_{21}NO_6$: C, 72.64; H, 4.41; N, 2.92. Found: C, 72.50; H, 4.38; N, 2.82.

7-Chloro-2,11-diphenyl-3a,10,11,11a-tetrahydro[1] benzopyrano [3,4-e]isoindole-1,3,4(2H)-trione (4g). Off-white solid; Yield: 75%; mp 269–270 °C; IR (KBr): 1780, 1729 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ 3.3 (m, 2H, $C_{10}H_2$, merged with water in DMSO), 3.64 (q, 1H, $C_{11}H$, $J = 7$ Hz), 3.83 (t, 1H, $C_{11a}H$, $J = 7$ and 8.4 Hz), 4.74 (d, 1H, $C_{3a}H$, $J = 8.4$ Hz), 6.81 (dd, 2H, ArH, $J = 6.8$ and 7.6 Hz), 7.24–7.38 (m, 8H, ArH), 7.45 (dd, 1H, C_8H, $J = 2$

and 8.4 Hz), 7.67 (d, 1H, C_6H, $J = 2$ Hz), 8.4 (d, 1H, C_9H, $J = 8.4$ Hz); ^{13}C NMR (DMSO-d_6): δ 28.1 (C_{10}), 38.7 (C_{11a}), 40.7 (C_{3a}), 44.4 (C_{11}), 117.1 (C_6), 118.0, 118.2, 125.2, 127.2, 127.4, 127.5 (2 CH), 128.7 (4 CH), 128.8, 129.1 (2 CH), 132.5, 136.7 (C_7), 140.7 (N-Cph), 151.0 (C_{9b}), 153.0 (C_{5a}), 159.3 (C-4), 173.8 (C-1), 175.5 (C-3); MS: *m/z* 456 (M + 1), 458 (M + 3). *Anal.* Calcd for $C_{27}H_{18}ClNO_4$: C, 71.13; H, 3.98; N, 3.07. Found: C, 71.03; H, 3.89; N, 3.12.

General procedure for the synthesis of compound 7a–g.

7,7,8,8-Tetracyano-3-hydroxy-9-phenyl-7,8,9,10-tetrahydro[6H] dibenzo[b,d]pyran-6-one (7a). **1a** (0.264 g, 1 mmol) and TCE (0.256 g, 2 mmol) were refluxed in nitrobenzene (5 mL) for 10 min. After complete consumption of **1a**, the solution was cooled to room temperature. Solid was not separated on cooling, then 15 mL *n*-hexane was added, and the solution was stirred for 10 min, when the product separated, which was filtered and washed with hexane to remove traces of nitrobenzene. **7a–g** were purified by column chromatography on silica gel and using chloroform.

Brown solid; Yield: 86%; mp 250–251 °C; IR (KBr): 3453 (OH), 2252 (CN), 1733 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$ + drops of DMSO-d_6): δ 3.70 (d, 2H, $C_{10}H_2$, $J = 8$ Hz), 3.89 (t, 1H, $J = 8$ Hz), 6.91–6.95 (m, 2H, C_2H, and C_4H), 7.52–7.64 (m, 6H, C_1H, and PhH), 10.81 (br s, 1H, C_3OH, exchangeable with D_2O); ^{13}C NMR (DMSO-d_6): δ 28.31 (C_{10}), 42.09 (C_8), 42.25 (C_9), 47.89 (C_7), 102.49 (C_4), 103.39 (C_{10b}), 109.64 (CN) , 109.73 (C_{14}), 109.95 (CN), 110.55 (CN), 110.89 (CN), 114.47 (C_2), 128.42 (C_1), 128.84 (2 CH), 129.56 (2 CH), 130.31, 133.61, 154.10 (C_{10a}), 154.67 (C_{4a}), 157.95 (C_3), 163.99 (C_6); LC-MS: *m/z* 392.9 (M + 1). *Anal.* Calcd for $C_{23}H_{12}N_4O_3$: C, 70.41; H, 3.08; N, 14.28. Found: C, 70.13; H, 3.04; N, 13.99.

7,7,8,8-Tetracyano-3-methyl-9-phenyl-7,8,9,10-tetrahydro [6H]dibenzo[b,d]pyran-6-one (7b). Brown solid, 0.335 mg (86%); mp 232–233 °C; IR (KBr): 2254 (CN), 1714 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.54 (s, 3H, Me), 3.55–3.82 (m, 3H, C_9H, and $C_{10}H_2$), 7.26–7.31(m, 2H, C_2H, and C_4H), 7.55–7.59 (m, 6H, C_1H, and PhH); ^{13}C NMR ($CDCl_3$): δ 22.05 (CH_3), 29.09 (C_{10}), 42.30 (C_8), 43.19 (C_9), 47.84 (C_7), 109.05 (CN), 109.23 (CN), 109.30 (CN), 109.58 (CN), 109.60 (C_{10b}), 114.50 (C_{6a}), 117.91 (C_4), 124.60, 127.26, 128.33 (2 CH), 130.03 (2 CH), 130.90, 132.44, 147.59 (C_3), 151.78 (C_{10a}), 152.99 (C_{4a}), 157.07 (C_6); MS: *m/z* 391 (M + 1). *Anal.* Calcd for $C_{24}H_{14}N_4O_2$: C, 73.84; H, 3.61; N, 14.35. Found: C, 73.13; H, 3.38; N, 14.20.

7,7,8,8-Tetracyano-3-methoxy-9-phenyl-7,8,9,10-tetrahydro [6H]dibenzo[b,d]pyran-6-one (7c). Brown solid; Yield: 81%; mp 231–233 °C; IR (KBr): 2252 (CN), 1714 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.52–3.89 (m, 3H, C_9H, and $C_{10}H_2$), 3.96 (s, 3H, OMe), 6.94–7.0 (m, 2H, C_2H, and C_4H, $J = 2.4$ and 9 Hz), 7.56–7.59 (m, 6H, C_1H, and PhH); ^{13}C NMR ($CDCl_3$): δ 29.11 (C_{10}), 42.25 (C_8), 43.18 (C_9), 47.78 (C_7), 56.27, (OCH_3) 101.25 (C_4), 106.62 (C_{10b}), 109.21 (CN), 109.26 (CN), 109.53 (CN), 109.66 (CN), 110.22 (C_{6a}), 114.50 (C_2), 125.98 (C_1), 128.24 (2 CH), 129.99 (2 CH), 130.86, 132.42, 151.36 (C_{10a}), 155.14 (C_{5a}), 157.19 (C_3), 165.40 (C_6); MS: *m/z* 406 (M + 1). *Anal.* Calcd for $C_{24}H_{14}N_4O_3$: C, 70.93; H, 3.47; N, 13.79. Found: C, 70.63; H, 3.28; N, 13.58.

7,7,8,8-Tetracyano-9-phenyl-7,8,9,10-tetrahydro[6H]dibenzo [b,d]pyran-6-one (7d). White solid; Yield: 85%; mp 224–225 °C; IR (KBr): δ 2257 (CN), 1715 (CO), cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.59–3.84 (m, 3H, C_9H, and $C_{10}H_2$), 7.47–7.79 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$): δ 29.12 (C_{10}), 42.19 (C_8), 43.13 (C_9), 47.73 (C_7), 109.03 (CN), 109.08 (CN), 109.40 (2 CN), 110.49 (C_{10b}) , 116.78 (C_{6a}), 117.91(C_4), 124.80 (C_2), 125.92 (C_1), 128.24 (2 CH), 130.02 (2 CH), 130.93, 132.22, 135.33 (C_3), 151.68 (C_{10a}), 152.84 (C_{5a}), 156.68 (C_6); LC-MS: *m/z* 376.9 (M + 1); *Anal.* Calcd for $C_{23}H_{12}N_4O_2$: C, 73.40; H, 3.21; N, 14.89. Found: C, 72.13; H, 2.98; N, 14.75.

7,7,8,8-Tetracyano-9-phenyl-7,8,9,10-tetrahydro[6H]dibenzo [b,d]pyran-6-one-3-yl-tosylate (7e). Brown solid; Yield: 80%; mp 260–261 °C; IR (KBr): δ 2258 (CN), 1713 (CO), cm^{-1}; ^{1}H NMR ($CDCl_3$ + drops of DMSO-d_6): δ 2.23 (s, 3H, CH_3), 3.60–3.79 (m, 3H, C_9H, and $C_{10}H_2$), 7.02 (d, 1H, C_4H, $J = 2.2$ Hz,), 7.16 (dd, 1H, C_2H, $J = 2.2$ and 8 Hz), 7.32 (d, 2H, ArH, $J = 8.1$ Hz), 7.51 (s, 5H, PhH), 7.67 (t, 3H, C_1H, and 2ArH, $J = 7.5$ and 8.1 Hz); ^{13}C NMR (DMSO-d_6): 21.26 (CH_3) 28.28 (C_{10}), 41.84 (C_8), 42.23 (C_9), 47.79 (C_7), 108.74 (CN), 109.34 (CN), 109.58 (CN), 110.09 (CN), 110.79 (C_4), 116.71 (C_{10b}), 119.17 (C_{6a}), 128.42 (2 CH), 128.59, 128.90 (2 CH), 129.54 (2 CH), 130.36 (2 CH), 130.51(2 CH), 130.86, 133.31, 146.50 (Me-Cph), 152.58, 152.97, 153.06, 157.14 (C_6) ; LC-MS: *m/z* 547 (M + 1); *Anal.* Calcd for $C_{30}H_{18}N_5O_2S$: C, 65.93; H, 3.32; N, 10.25. Found: C, 65.83; H, 3.21; N, 10.01.

7,7,8,8-Tetracyano-9-phenyl-7,8,9,10-tetrahydro[6H]dibenzo [b,d]pyran-6-one-3-yl-acetate (7f). White solid; Yield: 84%; mp 228–229 °C; IR (KBr): δ 2254 (CN), 1762, 1738 (CO), cm^{-1} ; ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 3H, $COCH_3$), 3.55–3.83 (m, 3H, C_9H, and $C_{10}H_2$), 7.25 (dd, 1H, C_2H, $J = 2.4$ and 8.5 Hz), 7.32 (d, 1H, C_4H, $J = 2.4$ Hz), 7.58 (s, 5H, PhH), 7.70 (d, 1H, C_1H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$ + drops of DMSO-d_6): 21.03 (CH_3), 29.05 (C_{10}), 42.10 (C_8), 42.88 (C_9), 47.68 (C_7), 109.08 (CN), 109.17 (CN), 109.22 (CN), 109.31 (CN), 109.59 (C_4), 110.84 (C_{10b}), 114.52 (C_{6a}), 119.76 (C_2), 126.40 (C_1), 128.26 (2 CH), 129.79 (2 CH), 130.66, 132.40, 152.30 (C_{10a}), 153.40 (C_{5a}), 155.48 (C_3), 156.66 (C_6), 168.07 (C-OAc); LC-MS: *m/z* 435 (M + 1). *Anal.* Calcd for $C_{25}H_{14}N_4O_4$: C, 69.12; H, 3.25; N, 12.90. Found: C, 68.83; H, 3.11; N, 12.70.

3-Chloro-7,7,8,8-tetracyano-9-phenyl-7,8,9,10-tetrahydro[6H] dibenzo[b,d]pyran-6-one (7g). White solid; Yield: 78%; mp 282–283 °C; IR (KBr): 2255 (CN), 1732 (CO), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.55–3.83 (m, 3H, C_9H, and $C_{10}H_2$), 7.18–7.22 (br d, 1H, C_4H), 7.46 (dd, 1H, C_2H, $J = 1.8$ and 8.4 Hz), 7.54–7.65 (m, 6H, ArH); MS: *m/z* 411 (M + 1), 413 (M + 2). *Anal.* Calcd for $C_{23}H_{11}ClN_4O_2$: C, 67.24; H, 2.70; N, 13.64. Found: C, 66.93; H, 2.56; N, 13.62.

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REFERENCES AND NOTES

[1] [a] Geissman, T. A. The Chemistry of Flavonoid Compounds; Pergamon Press: Oxford, 1962; [b] Harborne, J. B. The Flavonoids: The Advances in Research Since 1980; Chapman &Hall: London, 1988; [c] Harborne, J. B. The Flavonoids: The Advances in Research Since 1980; Chapman & Hall: London, 1994.

[2] Khan, M. S. Y.; Sharma, P. Indian J Chem 1993, 32B, 374.

[3] MIky, J. A. A.; Farrag, A. A. Indian J Chem 1997, 36B, 357.

[4] Hassana, M. A.; Shibaa, S. A.; Harba, N. S.; Abou-El-Regal, M. K.; El-Metwally, S. A. Syn Commun 2002, 32, 679.

[5] Chada, R. R.; Nayani, K.; Kancharla, J.; Mrunal, P.; Police, N. Synthesis 2009, 399.

[6] Maddela, P.; Narendar Reddy, G. N.; Srinu, G.; Manjulatha, K.; Prasad, J. V.; Kumar, S. P.; Srinivas, O.; Iqbal, J. K.; Anilkumar, K. Synlett 2010, 947.

[7] Rugiada, G.; Assunta, M.; Lucio, M.; Oriana, P.; Ferdinando, P.; Luigi, V. J. Org Chem 2006, 71, 70.

[8] Eleonora, B.; Lucio, M.; Oriana, P. J Org Chem 2010, 75, 4251.
[9] David, A.; Francesco, F.; Oriana, P.; Ferdinando, P.; Luigi, V. J Org Chem 2003, 68, 9263.
[10] Michael, E. J.; Damian, A. A. Org Lett 2009, 11, 757.
[11] Flores-Larios, I. Y.; Lopez-Garrido, L.; Martinez-Martinez, F. J.; Gonzalez, J.; Garcia-Baez, E. V.; Cruz, A.; Padilla-Martinez, I. I. Molecules 2010, 15, 1513.
[12] David, A.; Francesco, F.; Ferdinando, P. J. Org Chem 2002, 67, 7238–7243.
[13] Masahide, Y.; Toyoaki, K.; Chitoshi, G.; Hiroshi, S.; Kenichi, N.; Toru, M.; Kensuke, S. Tetrahedron Lett 1992, 33, 6465.
[14] Toru, M.; Yasuyuki, M.; Seigo, N.; Shinichiro, K.; Masahiko, Y. J Org Chem 1992, 57, 167.
[15] Mustafa, A.; Mohamad, K. J. Am Chem Soc 1955, 77, 1828.
[16] Mustafa, A.; Mohamad, K.; Mohmad, A. A. J Am Chem Soc 1956, 78, 4692.
[17] Soliman, A. Y.; El-Kafrawy, A. F.; Mohamed, F. K.; Baker, H. M.; Abdel-Gawad, A. M. Indian J Chem 1991, 30B, 477.
[18] Shafei, A. E.; Fadda, A. A.; Abdel-Gawad, I. I.; Youssif, E. H. E. Syn Commun 2009, 39, 2954.
[19] Laskowski, S. C.; Clinton, R. O. J Am Chem Soc 1950, 72, 3987.
[20] Shridhar, D. R.; Reddy Sastry, C. V.; Vaidya, N. K.; Moorty, S. R.; Reddi, G. S.; Thapar, G. S. Indian J Chem 1978, 16B, 704.
[21] Duddeck, H.; Kaiser, M. Org Magn Res 1982, 20, 55.
[22] Sabine, L.; Jurgen, L. J Org Chem 1993, 58, 2856–2861.
[23] Gowravaram, S.; Erigala, V. R.; Jhillu, S. Y. Synthesis 2002, 409.

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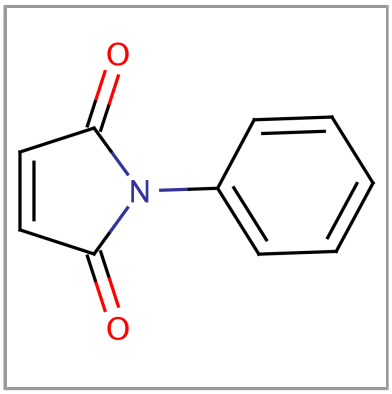

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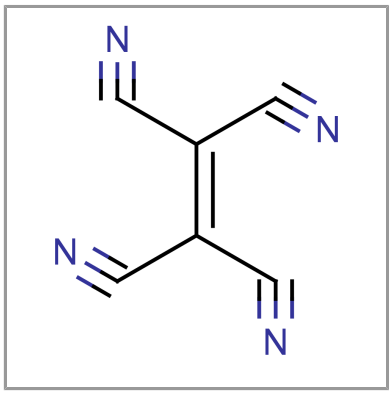

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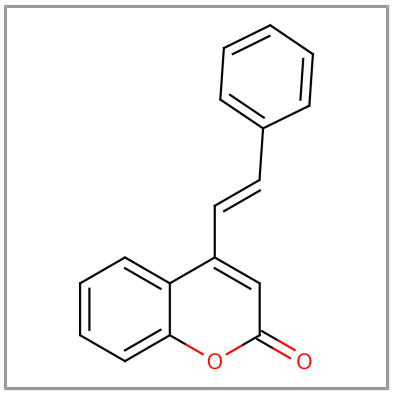

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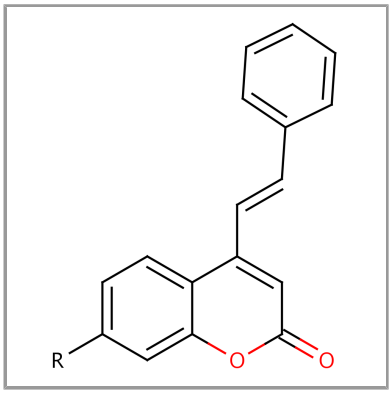

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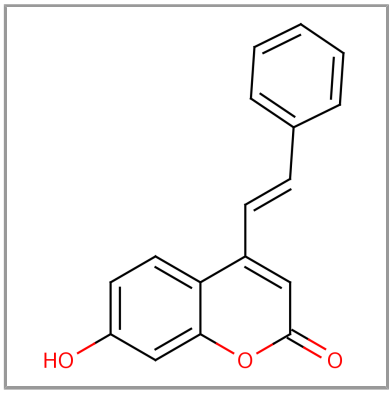

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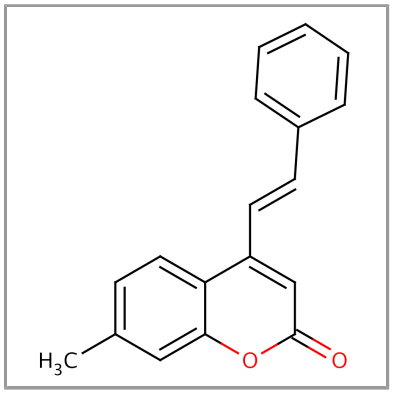

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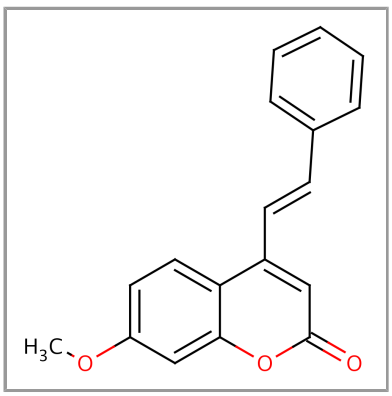

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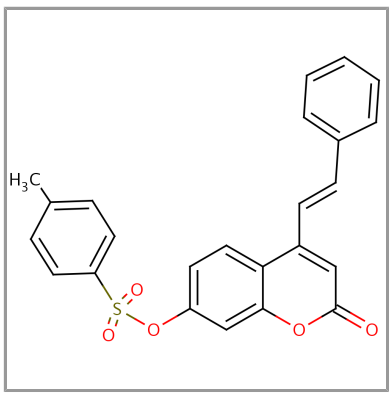

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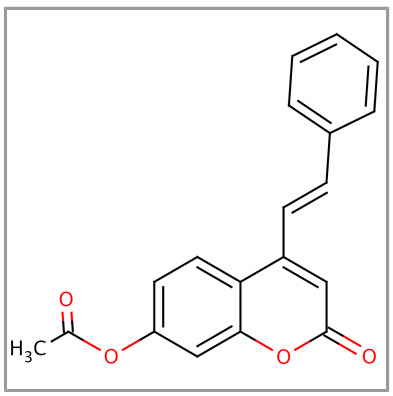

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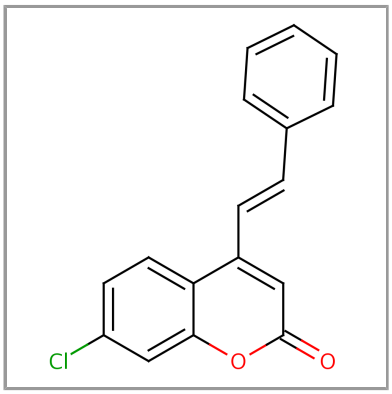

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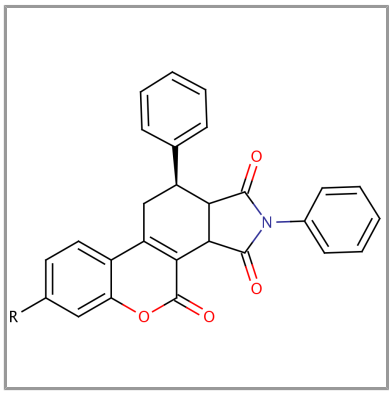

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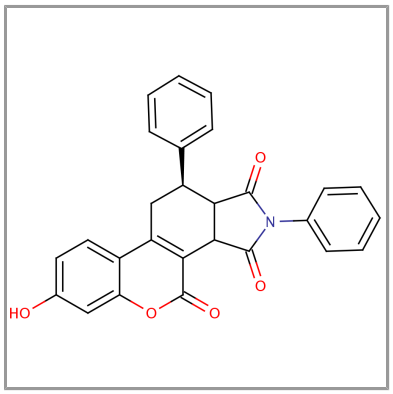

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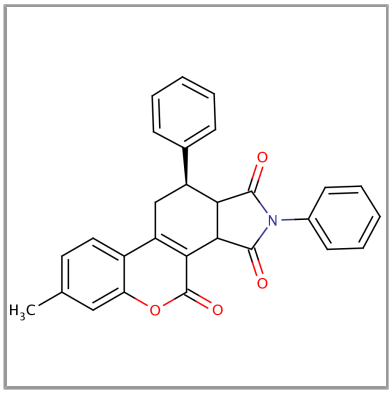

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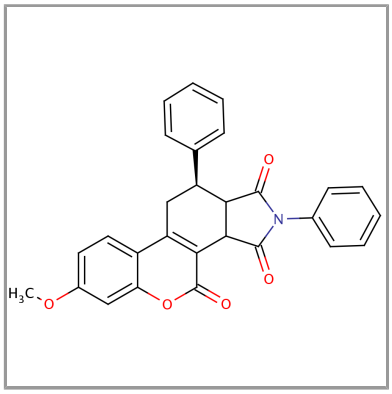

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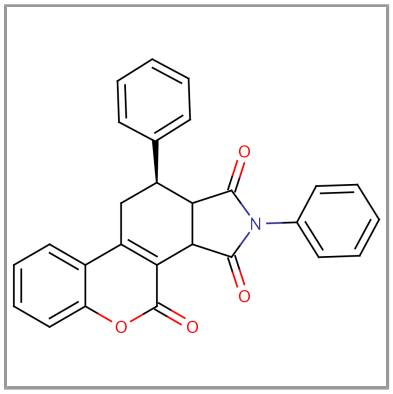

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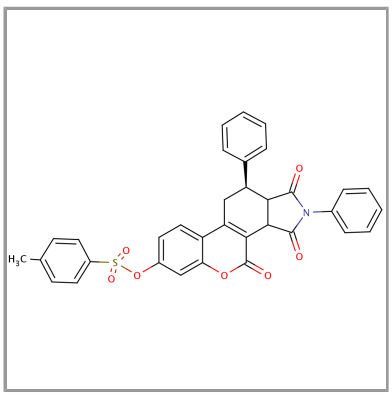

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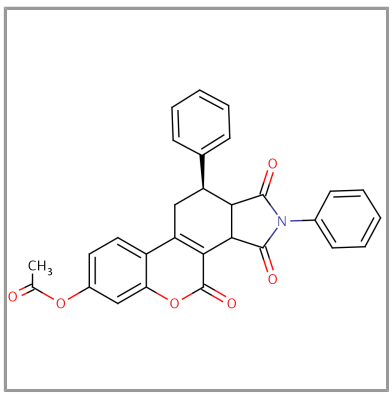

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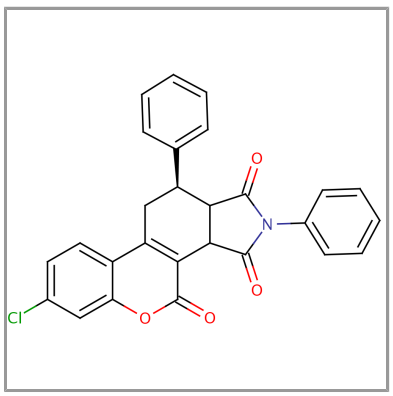

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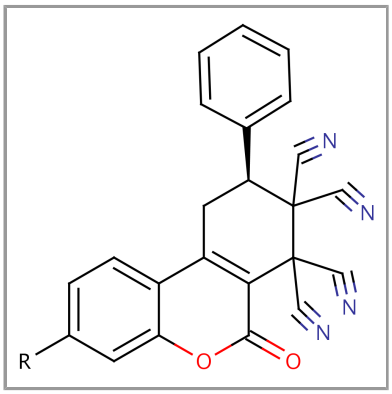

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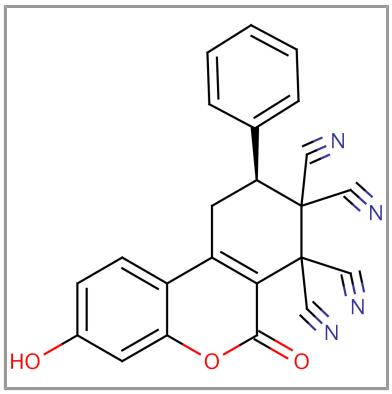

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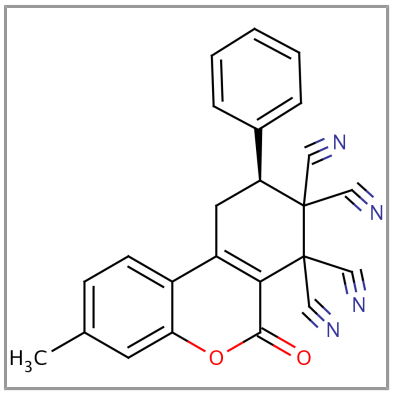

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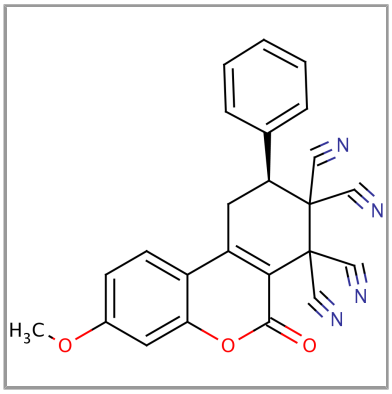

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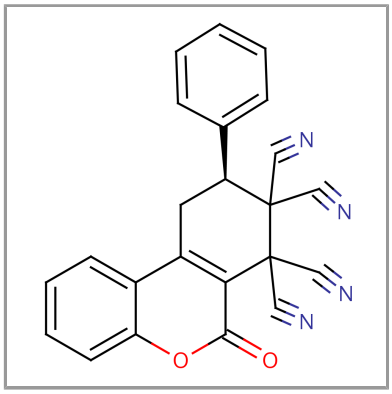

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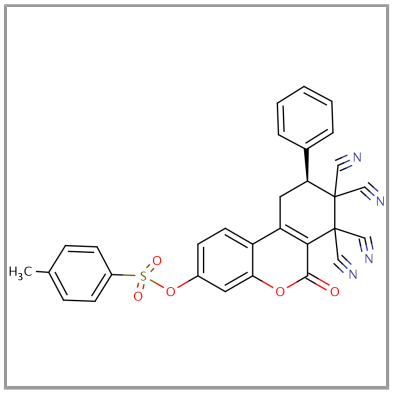

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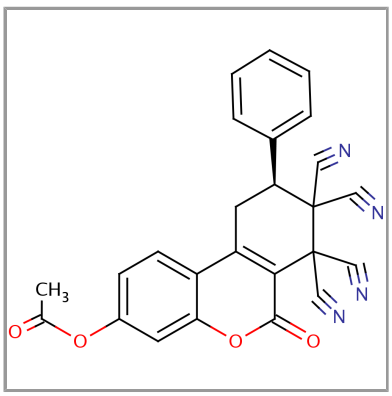

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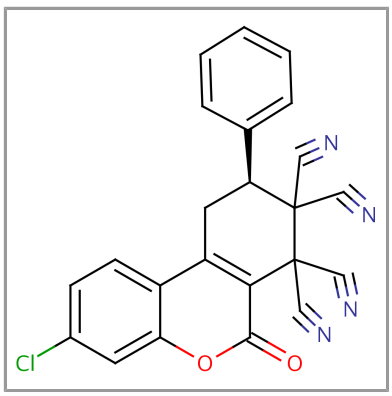

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