J. Org. Chem. **1996,** *61,* 8329−8331 **8329**

p-Thioquinone Methides: Synthesis and Reaction

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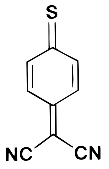
Received May 23, 1996

Unsubstituted *p*-quinone methide (4-methylene-2,5-cyclohexadien-1-one) is very reactive and an unstable compound, which polymerizes spontaneously at room temperature to form dimer, trimer, and polymeric materials, aromatization of the cyclohexadienone moiety supplying the driving force for the reactions.[1,2] However, in substitution of the hydrogen atoms on the exocyclic methylene group of the unsubstituted *p*-quinone methide with electron-withdrawing substituents such as cyano, ester, or trifluoromethyl groups, or with electron-donating substituents such as phenyl and alkylthio groups, the annellation of two benzene rings to the unsubstituted *p*-quinone methide can make the *p*-quinone methide system more stable, and crystalline materials can be isolated at room temperature. This is exemplified by 4-(dicyanomethylene)-,[3] 4-[(alkoxycarbonyl)(cyano)methylene]-,[3,4] 4-[bis(alkoxycarbonyl)methylene]-,[5] 2,6-dialkyl-4-[bis(trifluoromethyl)methylene]-,[6] 2,6-dimethyl-4-(dicyanomethylene)-,[7] 4-(diphenylmethylene)-,[8,9] 4-[(ethylenedithio)methylene]-,[10] and 2,6-dialkyl-4-[(ethylenedithio)-methylene]-2,5-cyclohexadien-1-ones[10] and 10-[bis(methylthio)methylene]-,[10] 10-methylene-,[11−13] and 10-(dicyanomethylene)anthrones.[14] These isolable *p*-quinone methides have been studied with regard to their polymerization behavior[4,5,15] and reactions.[3,6,7,11−13] In contrast to the extensive literature of these *p*-quinone methides,[1,2] very little is known about the corresponding sulfur analogues, the *p*-thioquinone methides, because of the difficulty of isolation, arising from the lower stability of the 2p−3p π bonds of a thiocarbonyl group compared to the 2p−2p π bonds of a carbonyl group.[16] It is expected that the introduction of electron-withdrawing substituents on the exocyclic methylene group and/or the annellation of benzene rings to the *p*-thioquinone methide system as well as the *p*-quinone methide system would make it more stable and isolable as crystals at room temperature. Crystals would allow us to readily study the chemistry of the *p*-thioquinone methides.

In this paper, the synthesis and reactions of novel *p*-thioquinone methides such as 4-(dicyanomethylene)-2,5-cyclohexadiene-1-thione (**1**), 10-methylenethioanthrone (**2a**), and 10-(dicyanomethylene)thioanthrone (**2b**) are described.



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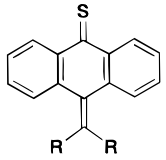

2a: R = H
2b: R = CN

When 4-(dicyanomethylene)-2,5-cyclohexadien-1-one[3] and 10-methyleneanthrone[11] were treated with Lawesson's reagent[17] in toluene under nitrogen, a series of color changes from yellow to green to red was observed within a few minutes, and within 0.5 h orange materials precipitated from the reaction solutions. These materials after filtration were determined on the basis of elemental analyses, spectral data, GPC measurement, and solubility toward solvents to be polymers of 4-(dicyanomethylene)-2,5-cyclohexadiene-1-thione (**1**) and 10-methylenethioanthrone (**2a**), respectively. Observation of the green color characteristic of the thiocarbonyl moiety upon thionation of 4-(dicyanomethylene)-2,5-cyclohexadien-1-one and 10-methyleneanthrone suggests formation of monomeric **1** and **2a** as intermediates. Both **1** and **2a** were too unstable to be isolated as crystals at room temperature, and polymerized. Reaction of 10-(dicyanomethylene)anthrone with Lawesson's reagent under the same conditions gave monomeric **2b** as green needles in 40% yield at rt, the chemical structure being confirmed by spectroscopic and elemental analyses. The observation indicates that stabilization of the *p*-thioquinone methide system requires both the introduction of electron-withdrawing substituents on the exocyclic methylene group and the annellation of the aromatic ring.

The reduction potential of **2b** in CH_2Cl_2 containing tetrabutylammonium perchlorate was measured and found to be −0.44 eV. The reduction appears to be a one-electron process. The reduction potential of **2b** is 0.07 eV lower than that of 4-(dicyanomethylene)-2,5-cyclohexadien-1-one (−0.37 eV) and 0.30 eV lower than that of 7,7,8,8-tetracyanoquinodimethane (−0.02 eV) under the same conditions.

The chemistry of isolated *p*-thioquinone methide **2b** was briefly examined. Reactions of **2b** with phenol and *N*,*N*-dimethylaniline and catalytic hydrogenation of **2b** did not occur, indicating that **2b** is very stable in contrast to the isolable *p*-quinone methides reported previously.[3,4,6,7] Similar with other thioketones,[18−22] **2b** could

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(1) Turner, S. A. *Quart. Rev.* **1964**, *18*, 347.

(2) Patai, S., Ed. *The Chemistry of Quinonoid Compounds II*; Wiley: New York, 1974; pp 1145−1178.

(3) Hyatt, J. A. *J. Org. Chem.* **1983**, *48*, 129.

(4) Iwatsuki, S.; Itoh, T.; Meng, X. *Macromolecules* **1993**, *26*, 1213.

(5) Itoh, T.; Wanibe, T.; Iwatsuki, S. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 963.

(6) Sheppard, W. A. *J. Org. Chem.* **1968**, *33*, 3297.

(7) Takimoto, H. H.; Denault, G. C.; Krbechek, L. O. *J. Org. Chem.* **1964**, *29*, 1899.

(8) Chitwood, J. L.; Gott, P. G.; Krutak, J. J., Sr.; Martin, J. C. *J. Org. Chem.* **1971**, *36*, 2216.

(9) Bistrycki, A.; Herbst, C. *Chem. Ber.* **1903**, *36*, 2335.

(10) Gomper, R.; Schmidt, R. R.; Kutter, E. *Chem. Ber.* **1965**, *684*, 37.

(11) Starnes, W. H., Jr. *J. Org. Chem.* **1970**, *35*, 1974.

(12) Hirakawa, K.; Ogiue, E.; Motoyoshiya, J.; Kakurai, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 319.

(13) Hirakawa, K.; Nakazawa, S. *J. Org. Chem.* **1978**, *43*, 1804.

(14) Takimoto, H.; Krbechek, L. *J. Org. Chem.* **1962**, *27*, 4688.

(15) Iwatsuki, S.; Itoh, T.; Ishiguro, K. *Macromolecules* **1987**, *20*, 939.

(16) Patai, S., Ed. *The Chemistry of the Carbonyl Group*; Interscience Publ.: New York, 1966; pp 917−959. Oae, S., Ed. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977.

(17) Pedersen, B. S.; Scheibye, S.; Nilsson, N.; Lawesson, O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

(18) Strating, J.; Thijs, L.; Zwanenburug, B. *Tetrahedron Lett.* **1966**, 65.

(19) Saito, T.; Koide, A.; Kikuchi, Y.; Motoki, S. *Phosphorus Sulfur* **1983**, *17*, 153.

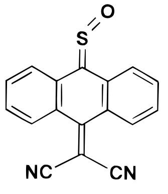
(20) Klingsberg, E. *J. Am. Chem. Soc.* **1964**, *86*, 5290.

(21) Zwanenburug, B.; Thijs, L.; Strating, J. *Tetrahedron Lett.* **1967**, 3453.

(22) Raasch, M. S. *J. Org. Chem.* **1979**, *44*, 632.

S0022-3263(96)00954-1 CCC: $12.00

be readily oxidized to a sulfine **3**, which decomposed gradually to 10-(dicyanomethylene)anthrone when allowed to stand in contact with air, but is stable under nitrogen. The addition reaction of **2b** with AIBN in benzene at 60 °C yielded an adduct **4**.



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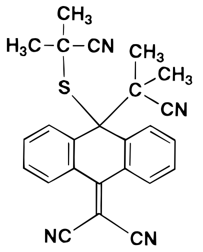

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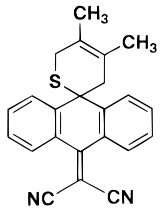
Diels−Alder reaction of **2b** with 2,3-dimethyl-1,3-butadiene gave a spiroadduct **5** by addition to the thiocarbonyl group, as do other thiocarbonyl compounds.[23−25] Reactions of **2b** with vinyl compounds such as butyl vinyl ether, styrene, methyl methacrylate, and methyl acrylate in benzene at 60 °C afforded the adducts **6**, **7**, **8**, and **9**, respectively, assigned on the basis of spectroscopic and elemental analyses.



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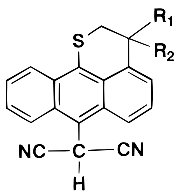
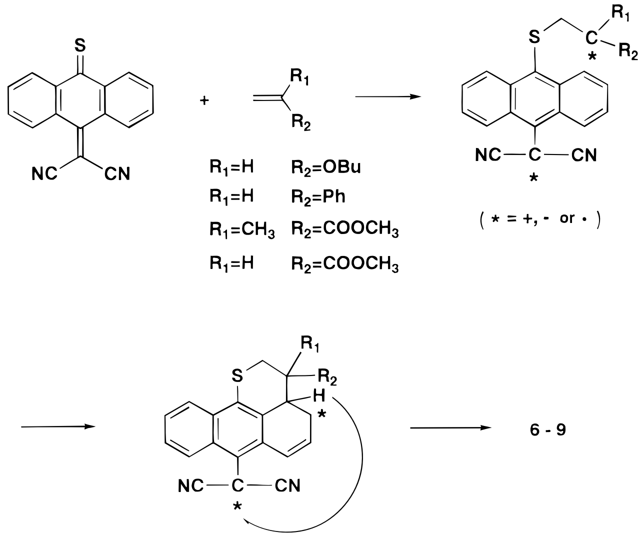


6 R_1=H R_2=OBu
7 R_1=H R_2=Ph
8 R_1=CH_3 R_2=$COOCH_3$
9 R_1=H R_2=$COOCH_3$

Although further work on these systems is necessary before a logical mechanism can be advanced, it appears that these reactions are proceeding via either zwitterionic intermediate formation or diradical intermediate formation as shown in Scheme 1. Sulfine **3** did not undergo an addition reaction with styrene, and unreacted sulfine **3** was recovered quantitatively.

Scheme 1



Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on 270 and 67.8 MHz spectrometers, respectively, in $CDCl_3$ with TMS as an internal standard. Elemental analyses were performed on a C,H,N analyzer. IR spectra were measured in KBr pellets, and the strongest/structurally most important peaks are listed. Column chromatography was performed with Merck 70−230 mesh silica gel. UV−vis spectra were recorded using a diode array spectrometer. Reduction potentials were determined by cyclic voltammetry measurement using CH_2Cl_2 containing tetrabutylammonium perchlorate (0.1 M) as solvent and an Ag/AgCl electrode as reference. The molecular weight of a polymer was determined by gel permeation chromatography (GPC) measurements using standard polystyrenes as reference and THF as an eluent. 2,3-Dimethyl-1,3-butadiene was prepared by the dehydration of pinacol with hydrogen bromide.[26] Styrene, methyl methacrylate, and methyl acrylate were washed with 2% aqueous sodium hydroxide solution and water, dried over anhydrous $MgSO_4$, stirred over CaH_2, and then distilled under reduced pressure. Butyl vinyl ether was purified by distillation from CaH_2 in N_2 atmosphere. All other chemicals were of commercial grade and used without further purification or, if necessary, pufified by distillation or crystallization prior to use.

4-(Dicyanomethylene)-2,5-cyclohexadiene-1-thione (1). The mixture solution of 4-(dicyanomethylene)-2,5-cyclohexadien-1-one[3] (100 mg, 0.64 mmol) and Lawesson's reagent (155 mg, 0.38 mmol) in 20 mL of toluene was refluxed under nitrogen. A green color developed quickly and soon changed to red, and then orange solids deposited. After the mixture was refluxed for 3 h, the resulting orange solids were filtered, washed with hot toluene, CH_2Cl_2, and EtOH, and then dried under reduced pressure. The orange materials were soluble in THF, DMF, DMSO, and concd H_2SO_4 but insoluble in CH_2Cl_2 and $CHCl_3$: yield 85.7 mg (78% yield); mp 130−131 °C; IR (KBr) 3310, 2176, 1565, 1474, 1242, 1162, 1100, 897 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.00−7.64 (broad); M_n (Number-average molecular weight) = 700−3200. Anal. Calcd for $(C_9H_4N_2S)_n$: C, 62.77; H, 2.35; N, 16.27; S, 18.61. Found: C, 62.34; H, 2.28; N, 16.77; S, 18.61.

10-Methylenethioanthrone (2a). The mixture solution of 10-methyleneanthrone[11] (100 mg, 0.49 mmol) and Lawesson's reagent (118 mg, 0.29 mmol) in 20 mL of toluene was refluxed under nitrogen. A green color developed quickly and soon changed to red, and then orange solids deposited. After the mixture was refluxed for 3 h, the resulting orange solids were filtered, washed with hot toluene, CH_2Cl_2, and ethanol, and then dried under reduced pressure. The orange material was insoluble in almost common organic solvents: yield 67.0 mg (62% yield); mp > 270 °C; IR (KBr) 3060, 1564, 1492, 1414, 1314, 742 cm^{-1}. Anal. Calcd for $(C_{15}H_{10}S)_n$: C, 81.04; H, 4.54; S, 14.42. Found: C, 81.52; H, 4.11; S, 14.36.

10-(Dicyanomethylene)thioanthrone (2b). The mixture solution of 10-(dicyanomethylene)anthrone[14] (500 mg, 1.95 mmol) and Lawesson's reagent (510 mg, 1.26 mmol) in 100 mL of toluene was refluxed under nitrogen. A green color developed quickly and remained even after 3 h. The solvent was removed under reduced pressure, and the dark green residue was chromatographed on silica gel with benzene as eluent. The green band was collected, and the product was obtained by evaporation of solvent. The green residue was recrystallized from hexane to give 211 mg (40% yield) of **2b** as green needles: mp 202−203 °C; IR (KBr) 3050, 2198, 1563, 1507, 1259, 1210, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.65 (t, J = 7.92 Hz, 2H), 7.78 (t, J = 7.92 Hz, 2H), 8.20 (d, J = 7.92 Hz, 2H), 8.41 (d, J = 7.92 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 218.7 (C=S), 163.0 (C=C(CN)$_2$), 137.6 (Ar), 132.6 (Ar), 132.3 (Ar), 129.2 (Ar), 127.3 (Ar), 125.9

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[23] Middleton, J. W. *J. Org. Chem.* **1965**, *30*, 1390.

[24] Schonberg, A.; Konig, B. *Chem. Ber.* **1968**, *101*, 725.

[25] Ohnishi, Y.; Akasaki, Y.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3307.

[26] Horning, E. C., Ed. *Organic Synthesis*; Wiley: New York, 1955, Collect. Vol. III, pp 312−316.

(Ar), 114.1 (CN), 82.1 (C=*C*(CN)$_2$); UV (CHCl$_3$) 367 (2.14×10^4), 319 (sh, 8.26×10^3), 288 (2.40×10^4) nm. Anal. Calcd for $C_{17}H_8N_2S$: C, 74.97; H, 2.97; N, 10.29; S, 11.77. Found: C, 75.16; H, 2.84; N, 10.50; S, 11.50.

10-(Dicyanomethylene)thioanthrone *S*-Oxide (3). *m*-CPBA (48 mg, 0.28 mmol) was added to a solution of 50 mg (0.18 mmol) of **2b** in 10 mL of dry CH_2Cl_2 with stirring at rt. The solution turned from green to yellow. After the solution was stirred for 30 min, the solvent was removed under reduced pressure, and the dark yellow residue was chromatographed on silica gel with CH_2Cl_2 as eluent. The yellow band was collected, and the sulfine **3** (46.5 mg, 90% yield) was obtained by evaporation of solvent. The sulfine decomposed to 10-(dicyanomethylene)anthrone when allowed to stand in contact with air for 1 day, but it is stable under nitrogen: mp > 300 °C; IR (KBr) 3015, 2198, 1509, 1087, 760 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.69 (m, 4H), 7.87 (d, $J = 7.92$ Hz, 1H), 8.31 (t, $J = 7.92$ Hz, 2H), 8.98 (d, $J = 7.92$ Hz, 1H); UV (benzene) 388 (1.27×10^4), 340 (1.19×10^4), 288 (1.26×10^4) nm. Anal. Calcd for $C_{17}H_8N_2SO$: C, 70.81; H, 2.80; N, 9.72; S, 11.12; O, 5.55. Found: C, 71.54; H, 2.75; N, 9.53; S, 11.05.

Reaction of 2b with AIBN. **2b** (30 mg, 0.11 mmol), AIBN (23.0 mg, 0.22 mmol), and benzene (2 mL) as solvent were placed in a glass ampule, which was degassed by a freeze–thaw method (repeated three times) and sealed. The ampule was placed at 60 °C for 38 h and then opened. The reaction mixture was evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2 as eluent. The yellow band was collected, and the product **4** (34.5 mg, 77% yield) was obtained by evaporation of solvent: mp 199–200 °C; IR (KBr) 3030, 2946, 2202, 1555, 1505, 1427, 1121, 770 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 6H), 1.33 (s, 6H), 7.64 (t, $J = 7.92$ Hz, 2H), 7.79 (t, $J = 7.92$ Hz, 2H), 8.18 (d, $J = 7.92$ Hz, 2H), 8.62 (d, $J = 7.92$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 164.1 (*C*=C(CN)$_2$), 135.4 (Ar), 132.9 (Ar), 132.5 (Ar), 131.4 (Ar), 129.3 (Ar), 127.3 (Ar), 121.6 (CN), 120.4 (CN), 114.1 (CN), 81.3 (C=*C*(CN)$_2$), 64.2 (C), 46.6 (C), 38.1 (C), 29.6 (CH$_3$), 24.2 (CH$_3$). Anal. Calcd for $C_{25}H_{20}N_4S$: C, 73.49; H, 4.94; N, 13.72; S, 7.85. Found: C, 73.31; H, 5.00; N, 13.85; S, 7.84.

General Procedure for Reactions of 2b with Vinyl Compounds. **2b** (30 mg, 0.11 mmol), vinyl compounds (0.48 mmol) such as 2,3-dimethyl-1,3-butadiene, butyl vinyl ether, styrene, methyl methacrylate, and methyl acrylate, and benzene (2 mL) as solvent were placed in a glass ampule, which was degassed by a freeze–thaw method (repeated three times) and sealed. The ampule was placed at 60 °C for 24 h and then opened. The reaction mixture was evaporated to dryness, and the residue was chromatographed on silica gel with benzene as eluent. The yellow band was collected, and the adducts (**5**–**9**) were obtained by evaporation of solvent.

***2b*-2,3-dimethyl-1,3-butadiene adduct (5)**: yield 37.3 mg (96% yield); mp 154–155 °C; IR (KBr) 3010, 2874, 2820, 2198, 1558, 1529, 1425, 732 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.80 (s, 3H), 1.95 (s, 3H), 2.82 (s, 2H), 3.05 (s, 2H), 7.44 (m, 4H), 7.52 (d, $J = 6.97$ Hz, 2H), 8.01 (d, $J = 6.97$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 166.1 (*C*=C(CN)$_2$), 142.4 (Ar), 132.5 (C=C), 131.0 (Ar), 127.6 (C=C), 127.4 (Ar), 127.3 (Ar), 126.1 (Ar), 124.9 (Ar), 114.2 (CN), 78.7 (C=*C*(CN)$_2$), 77.2 (C), 33.4 (CH$_2$), 20.3 (CH$_3$), 19.4 (CH$_3$); UV (benzene) 319 (1.15×10^4) nm. Anal. Calcd for $C_{23}H_{18}N_2S$: C, 77.92; H, 5.13; N, 7.90; S, 9.05. Found: C, 78.05; H, 5.03; N, 7.88; S, 9.04.

***2b*-butyl vinyl ether adduct (6)**: yield 20.7 mg (53% yield); mp 143–144 °C; IR (KBr) 3040, 2890, 2304, 1524, 1586 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.94 (t, $J = 7.26$ Hz, 3H), 1.44 (m, 2H), 1.67 (m, 2H), 3.35 (m, 1H), 3.56 (m, 2H), 3.71 (m, 1H), 4.95 (d, $J = 7.24$ Hz, 1H), 6.35 (s, 1H), 7.60 (d, $J = 7.59$ Hz, 1H), 7.70 (t, $J = 7.59$ Hz, 3H), 8.18 (d, $J = 7.59$ Hz, 2H), 8.53 (d, $J = 7.59$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 135.7 (Ar), 134.6 (Ar), 133.0 (Ar), 129.4 (Ar), 128.8 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 125.8 (Ar), 125.7 (Ar), 125.2 (Ar), 124.1 (Ar), 123.1 (Ar), 122.2 (Ar), 112.1 (CN), 75.2 (OCH), 67.0 (OCH$_2$), 31.9 (SCH$_2$), 29.7 (CH$_2$), 21.4 (*C*H(CN)$_2$), 19.4 (CH$_2$), 13.9 (CH$_3$); UV (benzene) 433 (8.13×10^3), 413 (8.90×10^3) nm. Anal. Calcd for $C_{23}H_{20}N_2SO$: C, 74.15; H, 5.42; N, 7.52; S, 8.61; O, 4.30. Found: C, 73.48; H, 5.76; N, 7.82; S, 8.58.

***2b*-styrene adduct (7)**: yield 26.4 mg (64% yield); mp 161–162 °C; IR (KBr) 3010, 2982, 2898, 2198, 1637, 1569, 1523, 1465, 1227, 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.44 (dd, $J = 3.30$, 6.94 Hz, 1H), 3.60 (dd, $J = 6.94$, 12.70 Hz, 1H), 4.85 (dd, $J = 3.30$, 12.70 Hz, 1H), 6.38 (s, 1H), 7.05 (d, $J = 9.24$ Hz, 2H), 7.26 (t, $J = 6.27$ Hz, 2H), 7.30 (m, 2H), 7.61 (q, $J = 7.58$ Hz, 2H), 7.76 (t, $J = 7.59$ Hz, 1H), 8.20 (d, $J = 8.91$ Hz, 2H), 8.55 (d, $J = 8.91$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 142.6 (Ar), 137.0 (Ar), 136.9 (Ar), 129.7 (Ar), 129.1 (Ar), 128.8 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 127.4 (Ar), 126.7 (Ar), 126.5 (Ar), 126.2 (Ar), 125.8 (Ar), 122.6 (Ar), 122.4 (Ar), 112.6 (Ar), 112.4 (CN), 47.0 (Ph*C*H), 32.8 (CH$_2$), 21.8 (*C*H(CN)$_2$); UV (benzene) 439 (7.23×10^3), 417 (8.38×10^3) nm. Anal. Calcd for $C_{25}H_{16}N_2S$: C, 79.75; H, 4.29; N, 7.44; S, 8.52. Found: C, 80.49; H, 4.08; N, 6.92; S, 8.51.

***2b*-methyl methacrylate adduct (8)**: yield 21.5 mg (53% yield); mp 94–96 °C; IR (KBr) 3020, 2906, 2232, 1693, 1525, 1587, 1525, 1426, 1251, 1226, 739 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.90 (s, 3H), 3.18 (d, $J = 12.86$ Hz, 1H), 3.71 (s, 3H), 3.73 (d, $J = 12.86$ Hz, 1H), 6.37 (s, 1H), 7.50 (d, $J = 6.93$ Hz, 1H), 7.70 (m, 3H), 8.18 (d, $J = 8.91$ Hz, 1H), 8.23 (d, $J = 8.91$ Hz, 1H), 8.55 (d, $J = 8.91$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 174.6 (C=O), 137.1 (Ar), 135.5 (Ar), 129.7 (Ar), 129.1 (Ar), 128.9 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 125.8 (Ar), 125.3 (Ar), 123.6 (Ar), 122.9 (Ar), 122.1 (Ar), 112.8 (Ar), 112.1 (CN), 52.8 (OCH$_3$), 48.4 (CH$_3$*C*CO), 34.7 (CH$_3$), 25.8 (CH$_2$), 21.7 (*C*H(CN)$_2$); UV (benzene) 435 (4.87×10^3), 413 (5.48×10^3), 278 (3.70×10^4) nm. Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.94; H, 4.34; N, 7.52; S, 8.61; O, 8.59. Found: C, 70.45; H, 4.62; N, 7.73; S, 8.53.

***2b*-methyl acrylate adduct (9)**: yield 23.2 mg (59% yield); mp 222–223 °C; IR (KBr) 3020, 2908, 2230, 1689, 1587, 1526, 1413, 1279, 1237, 998, 733 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.47 (dd, $J = 3.30$, 12.86 Hz, 1H), 3.71 (s, 3H), 3.74 (dd, $J = 4.29$, 12.86 Hz, 1H), 4.55 (dd, $J = 3.30$, 4.29 Hz, 1H), 6.37 (s, 1H), 7.38 (d, $J = 6.92$ Hz, 1H), 7.69 (m, 3H), 8.19 (d, $J = 8.91$ Hz, 1H), 8.24 (d, $J = 8.91$ Hz, 1H), 8.50 (d, $J = 8.58$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.4 (C=O), 135.6 (Ar), 131.5 (Ar), 129.4 (Ar), 128.9 (Ar), 128.1 (Ar), 127.7 (Ar), 127.3 (Ar), 125.8 (Ar), 125.3 (Ar), 123.2 (Ar), 122.2 (Ar), 112.7 (Ar), 112.1 (CN), 52.7 (OCH$_3$), 47.7 (*C*HCO), 27.9 (CH$_2$), 21.4 (*C*H(CN)$_2$); UV (benzene) 434 (7.98×10^3), 413 (8.79×10^3), 278 (3.70×10^4) nm. Anal. Calcd for $C_{21}H_{14}N_2O_2S$: C, 70.37; H, 3.94; N, 7.82; S, 8.94; O, 8.93. Found: C, 71.02; H, 3.80; N, 7.78; S, 8.89.

JO9609541