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Reaction of nitrile ylides with isatins and *o*-benzoquinones: formation of novel spirooxazoline derivatives

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This paper is dedicated to the memory of Professor Josef (Gus) Fried who passed away on 7 August 2001

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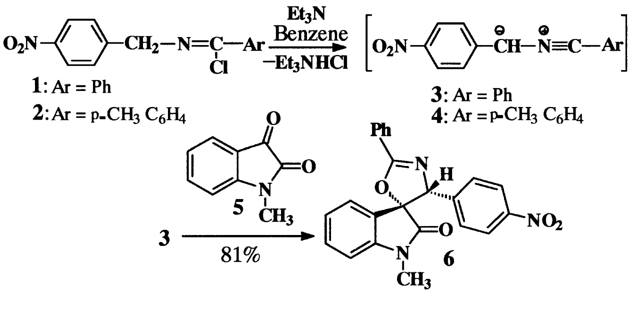
Abstract—Nitrile ylide generated by the base catalysed reaction of imidoyl chlorides underwent dipolar cycloaddition with isatins, phenanthrenequinone and acenaphthenequinone to afford novel spirooxazoline derivatives. © 2002 Published by Elsevier Science Ltd.

The monumental work of Huisgen has established 1,3-dipolar cycloaddition reaction as the most powerful methodology for the construction of five membered heterocycles.[1] In the context of our general interest in the cycloaddition chemistry of 1,2-dicarbonyl compounds[2] we have shown that nitrile oxides and carbonyl ylides undergo facile dipolar cycloaddition to *o*-quinones.[3,4] Very recently we have observed that carbonyl ylides react readily with isatins to afford novel spirooxindole derivatives;[5] isatin and its derivatives have interesting biological activities and have been widely used as precursors of many natural products.[6] In continuation of these studies it was of interest to explore the reaction of nitrile ylides with isatins and other 1,2-dicarbonyl compounds. Although nitrile ylides have been known to react with a variety of dipolarophiles[7–14] including carbonyl compounds such as aldehydes and 1,4-benzoquinones yielding oxazoline derivatives, there has been no report on their reaction with 1,2-dicarbonyl compounds such as isatins or 1,2-quinones. Against this background, we have explored the reactivity of nitrile ylides towards isatins, acenaphthenequinone and phenanthrenequinone. Our results revealing the facile formation of novel spirooxazoline derivatives are presented here.

Our studies were initiated with the reaction of nitrile ylide **3**, generated by the base catalysed reaction of 4-nitro-*N*-benzyl benzimidoyl chloride[15] **1**, and *N*-methyl isatin **5** in benzene at room temperature. The reaction proceeded smoothly to afford an oxazoline fused spirooxindole derivative **6** in 81% yield. As expected, the [2+3] addition occurred across the more electrophilic ketonic carbonyl (Scheme 1).



Scheme 1.

The product was purified by chromatography on a silica gel column, and characterized by spectroscopic analysis. The IR spectrum of **6** showed a band at 1731 cm^{-1}. In the ^{1}H NMR spectrum, the benzylic and methyl protons resonated as singlets at δ 5.79 and 2.91, respectively. In the ^{13}C NMR spectrum of **6**, the amide carbonyl resonated at δ 171.45 whereas the spirocarbon was discernible at δ 87.01. The characteristic imine carbon of the oxazoline ring showed a signal at δ 165.17. These assignments were confirmed by DEPT-135 NMR analysis. In the DEPT-135 NMR spectrum of **6**, a peak at δ 79.29 for the benzylic carbon was positive and the spirocarbon signal at δ 87.01 disappeared. Finally the structure assigned was confirmed unequivocally by single crystal X-ray analysis (Fig. 1).[16]

The reaction was extended to three other isatins and also with nitrile ylide **4** derived from 4-nitro-*N*-benzyl-(4 methyl) benzimidoyl chloride **2**. In all cases, the reaction proceeded smoothly to afford the spirooxindoles. The results are summarized in Table 1.

Keywords: nitrile ylides; dipolar cycloaddition; 1,2-diones; spirooxazolines.

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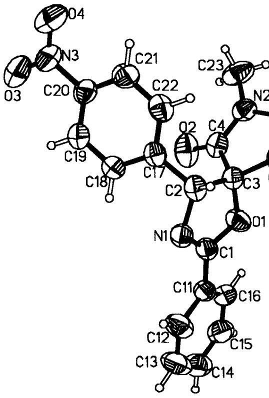
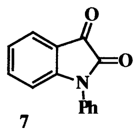
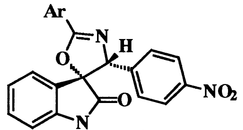
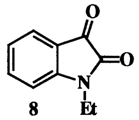
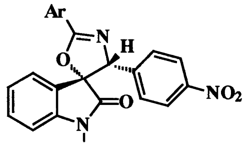
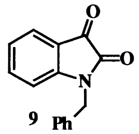
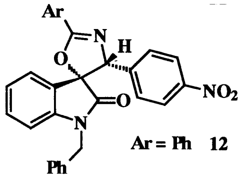
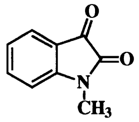
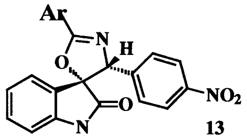
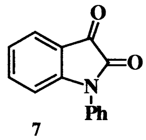
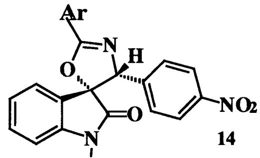
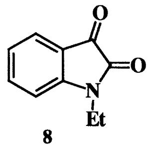
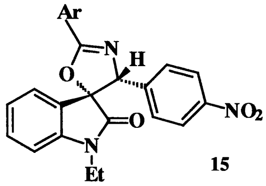
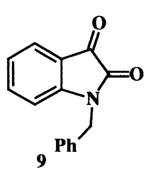
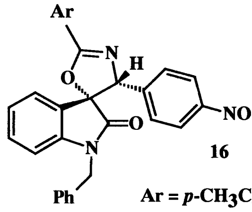


Figure 1.

Table 1. [2+3] Cycloaddition reactions of nitrile ylides **3** and **4** with isatins

Entry	Isatin	Product	Yield (%)
1	 7	 Ar = Ph 10	94
2	 8	 Ar = Ph 11	83
3	 9	 Ar = Ph 12	84
4	 5	 13 Ar = *p*-CH$_3$C$_6$H$_4$	70
5	 7	 14 Ar = *p*-CH$_3$C$_6$H$_4$	90
6	 8	 15 Ar = *p*-CH$_3$C$_6$H$_4$	89
7	 9	 16 Ar = *p*-CH$_3$C$_6$H$_4$	63

1. Reactions of nitrile ylides with 1,2-quinones

In view of the encouraging results obtained with the nitrile ylides and isatins it was of interest to study the reaction of nitrile ylides with acenaphthenequinone and phenanthrenequinone. Thus when acenaphthenequinone **17** was allowed to react with imidoyl chlorides **1** and **2** in presence of triethylamine, products **18** and **19** were obtained (Scheme 2).

The products were purified by chromatography on a silica gel column, and characterized by spectroscopic analysis and single crystal X-ray analysis.[16] Similarly the reaction of **3** and **4** with phenanthrenequinone **20** was also performed as described above to afford the corresponding oxazolines **21** and **22** (Scheme 3).

In conclusion we have found that nitrile ylides undergo facile dipolar cycloaddition with isatins and *o*-benzoquinones to afford novel spirooxazoline derivatives.

2. Experimental

Various substituted isatins were prepared according to the literature procedure.[17]

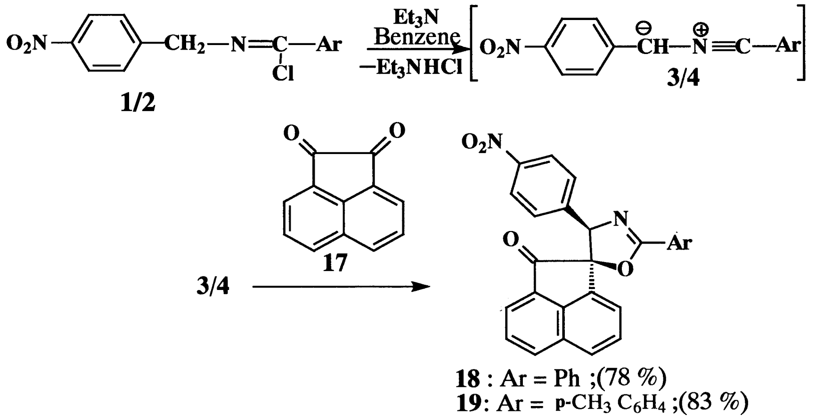
2.1. Synthesis of imidoyl chlorides

2.1.1. 4-Nitro-*N*-benzyl benzimidoyl chloride 1. The preparation of 4-nitro-*N*-benzyl bezimidoyl chloride **1** was carried out according to the known procedure.[15]

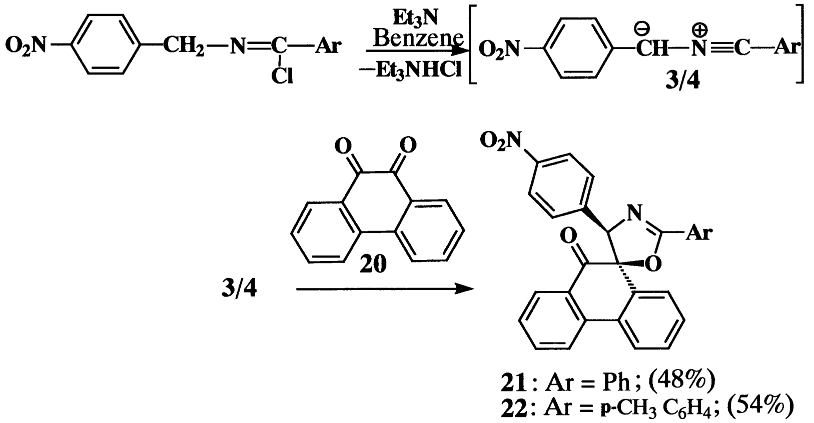
2.1.2. 4-Nitro-*N*-benzyl-(4-methyl) benzimidoyl chloride 2. 4-Nitro benzylamine hydrochloride (1 g, 5.3×10^{-3} mol) was treated with 4-toluoyl chloride (0.819 g, 5.29×10^{-3} mol) in the presence of NaOH (4 mL, 3 M solution) to afford 4-nitro-*N*-benzyl-(4-methyl) benzamide (1 g, 70%). This amide on refluxing with freshly distilled thionyl chloride (2.18 g, 0.0185 mol) afforded the title compound **2** (0.630 g, 60%) as a pale yellow solid; recrystallised from dry cyclohexane. Mp 90–92°C; [Found: C, 62.21; H, 4.47; N, 9.89. $C_{15}H_{13}N_2O_2Cl$ requires C, 62.40; H, 4.54; N, 9.70%]; ν_{max} (KBr) 1676, 1640, 1599, 1517, 1409, 1347, 1105, 1012, 889, 858, 724 cm^{-1}; δ_H (300 MHz, CDCl$_3$) 8.21 (2H, d, J=8.4 Hz, Ar-H), 7.96 (2H, d, J=8.0 Hz, Ar-H), 7.61 (2H, d, J=8.4 Hz, Ar-H), 7.23 (2H, d, J=8.0 Hz, Ar-H), 4.98 (2H, s, NCH_2), 2.41 (3H, s, C$_6$H$_4$CH_3); δ_C (75 MHz, CDCl$_3$) 168.38, 129.30, 129.21, 129.16, 128.35, 128.30, 127.09, 123.88, 123.76, 56.59, 21.50.

2.2. General procedure for the reaction of imidoyl chlorides with isatins and quinones

2.2.1. (3*R*,4*R*′)-1-Methyl-2′-(phenyl)-4′-(4-nitrophenyl)-spiro[3*H*-indole-3, 5′(4′*H*)-oxazol]-2(1*H*)-one 6. The preparation of the cycloadduct **6** from *N*-methyl isatin **5**



Scheme 2.



Scheme 3.

and imidoyl chloride **1** is illustrative of the general procedure for the synthesis of spirooxazolines. *N*-methyl isatin (0.042 g, 2.60×10^{-4} mol) and imidoylchloride **1** (0.10 g, 3.91×10^{-4} mol) were taken up in 2 mL rigorously dried benzene. To this, triethylamine (0.0434 g, 4.30×10^{-4} mol) was added and stirred for 3 h under an atmosphere of argon at room temperature. The orange red reaction mixture turned colourless. It was then filtered through a celite pad using dichloromethane (50 mL) as solvent. Dichloromethane and benzene were removed on a rotary evaporator and the crude product was subjected to chromatography on a silica gel column using hexane–ethyl acetate (85:15) as eluent to afford the title compound **6** (0.084 g, 81%) as colourless crystals; recrystallised from hexane–dichloromethane. Mp 221–223°C; [Found: C, 69.16; H, 4.51; N, 10.40. $C_{23}H_{17}N_3O_4$ requires C, 69.17; H, 4.29; N, 10.52]; ν_{max} (KBr) 1731, 1657, 1607, 1513, 1338, 1088, 1020, 854, 751, 689 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 8.07–8.12 (4H, m, Ar-H), 7.43–7.58 (5H, m, Ar-H), 7.22–7.31 (3H, m, Ar-H), 6.85 (1H, d, *J*=7.8 Hz, Ar-H), 5.79 (1H, s, NC*H*), 2.91 (3H, s, $C_6H_4CH_3$); δ_C (75 MHz, $CDCl_3$) 171.45, 165.17, 147.76, 144.16, 132.29, 131.29, 128.96, 128.54, 127.71, 127.50, 126.63, 124.29, 123.78, 123.33, 108.78, 87.01, 79.29, 26.04.

Crystal data for **6**. $C_{23}H_{17}N_3O_4$. *M* 399.40, orthorhombic, space group *Pbca*, unit cell dimensions $a=16.1255(5)$ Å, $\alpha=90°$; $b=12.2464(4)$ Å, $\beta=90°$; $c=19.9237(6)$ Å, $\gamma=90°$, *R* indices (all data) $R1=0.0938$, $wR2=0.1599$, volume, $Z=3934.5$ (2) $Å^3$, 8, $D_{calc}=1.349$ mg m^{-3}, absorption coefficient=0.094 mm^{-1}, $\lambda=0.71073$ Å, reflections collected 94917. Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995.

2.2.2. (3*R*,4′*R*)-1-Phenyl-2′-(phenyl)-4′-(4-nitrophenyl)-spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 10. *N*-Phenyl isatin (0.025 g, 0.112 mmol) and imidoyl chloride **1** (0.046 g, 0.168 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.0186 g, 0.184 mmol) under the standard procedure to afford the title compound **10** as pale yellow crystals; recrystallised from hexane–dichloromethane. Mp 201–203°C; [Found C, 72.74; H, 4.37; N, 8.84. $C_{28}H_{19}N_3O_4$ requires C, 72.88; H, 4.15; N, 9.11%]; ν_{max} (KBr) 1726, 1651, 1614, 1511, 1346, 1081, 993, 745 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.11–8.16 (4H, m, Ar-H), 7.25–7.65 (11H, m, Ar-H), 6.90 (2H, d, *J*=7.1 Hz, Ar-H), 6.82 (1H, d, *J*=7.8 Hz, Ar-H), 5.86 (1H, s, NC*H*); δ_C (75 MHz, $CDCl_3$) 170.78, 165.36, 147.81, 144.03, 133.15, 132.34, 131.12, 129.70, 129.01, 128.57, 128.43, 127.87, 127.13, 126.60, 125.88, 124.53, 124.22, 123.39, 110.09, 87.22, 80.17.

2.2.3. (3*R*,4′*R*)-1-Ethyl-2′-(phenyl)-4′-(4-nitrophenyl)-spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 11. *N*-Ethyl isatin (0.030 g, 0.171 mmol) and imidoyl chloride **1**

(0.046 g, 0.168 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.0285 g, 0.282 mmol) under the standard procedure to afford the title compound **11** as colourless crystals; recrystallised from hexane–ethyl-acetate. Mp 84–86°C; [Found C, 69.74; H, 4.88; N, 9.89. $C_{24}H_{19}N_3O_4$ requires C, 69.72; H, 4.63; N, 10.16%]; ν_{max} (KBr) 1725, 1650, 1613, 1520, 1467, 1341, 1202, 1023, 844, 751, 691 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 8.08–8.11 (3H, m, Ar-H), 7.41–7.58 (6H, m, Ar-H), 7.18–7.32 (3H, m, Ar-H), 6.85 (1H, d, *J*=7.7 Hz, Ar-*H*), 5.77 (1H, s, NC*H*), 3.55–3.62 (1H, m, NC*H*HCH$_3$), 3.25–3.32 (1H, m, NCH*H*CH$_3$), 0.87–0.95 (3H, m, NCH$_2$C*H*$_3$); δ_C (75 MHz, $CDCl_3$) 171.01, 165.33, 147.75, 144.05, 143.24, 132.28, 131.19, 128.98, 128.54, 127.87, 127.61, 126.66, 124.46, 123.53, 123.24, 108.77, 87.05, 79.57, 34.54, 12.24.

2.2.4. (3*R*,4′*R*)-1-Benzyl-2′-(phenyl)-4′-(4-nitrophenyl)-spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 12. *N*-Benzylisatin (0.046 g, 0.194 mmol) and imidoyl chloride **1** (0.080 g, 0.291 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.032 g, 0.321 mmol) under the standard procedure to afford the title compound **12** as pale yellow crystals; recrystallised from hexane–dichloromethane. Mp 168–170°C; [Found C, 73.12; H, 4.52; N, 8.63. $C_{29}H_{21}N_3O_4$ requires C, 73.25; H, 4.45; N, 8.84%]; ν_{max} (KBr) 1732, 1647, 1604, 1522, 1349, 1172, 1021, 848, 753, 692 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 8.10 (2H, d, *J*=7.2 Hz, Ar-H), 8.02 (2H, d, *J*=8.4 Hz, Ar-H), 7.11–7.59 (11H, m, Ar-H), 6.75–6.80 (3H, m, Ar-H), 5.79 (1H, s, NC*H*), 4.88 (1H, d, *J*=15.3 Hz, C$_6$H$_5$C*H*H), 4.23 (1H, d, *J*=15.3 Hz, C$_6$H$_5$CH*H*); δ_C (75 MHz, $CDCl_3$) 171.58, 165.44, 147.82, 143.63, 143.55, 134.85, 132.34, 131.27, 128.99, 128.63, 128.58, 128.14, 128.02, 127.43, 127.03, 126.66, 124.47, 123.74, 123.42, 109.63, 87.14, 79.53, 43.98.

2.2.5. (3*R*,4′*R*)-1-Methyl-2′-(4-methylphenyl)-4′-(4-nitrophenyl)spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 13. *N*-Methyl isatin (0.024 g, 0.149 mmol) and imidoyl chloride **2** (0.064 g, 0.223 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.024 g, 0.245 mmol) under the standard procedure to afford the title compound **13** as pale yellow crystals; recrystallised from hexane–dichloromethane. Mp 213–215°C; ν_{max} (KBr) 1725, 1646, 1613, 1520, 1467, 1348, 1235, 1076, 996, 830, 764, 744, 685 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.10 (2H, d, *J*=8.4 Hz, Ar-H), 7.96 (2H, d, *J*=7.8 Hz, Ar-H), 7.19–7.57 (m, 7H, Ar-H), 6.84 (1H, d, *J*=7.7 Hz, Ar-H), 5.77 (1H, s, NC*H*), 2.91 (3H, s, NC*H*$_3$) 2.44 (3H, s, C$_6$H$_4$C*H*$_3$). δ_C (75 MHz, $CDCl_3$) 171.53, 165.29, 147.75, 144.31, 144.16, 142.78, 131.23, 129.27, 128.96, 127.74, 127.65, 124.29, 123.85, 123.76, 123.32, 108.74, 86.91, 79.32, 26.04, 21.76. HRMS (EI): M$^+$ found 413.1375. $C_{29}H_{19}N_3O_4$ requires 413.1376.

2.2.6. (3*R*,4′*R*)-1-Phenyl-2′-(4-methylphenyl)-4′-(4-nitrophenyl)spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 14. *N*-Phenyl isatin (0.025 g, 0.112 mmol) and imidoyl chloride **2** (0.048 g, 0.168 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.019 g, 0.184 mmol) under the standard procedure to afford the title compound **14** as pale yellow crystals; recrystallised from hexane–dichloromethane. Mp 105–107°C; [Found C, 73.55; H, 4.40; N, 8.94. $C_{29}H_{21}N_3O_4$ requires C, 73.25; H, 4.45; N, 8.84%]; ν_{max} (KBr) 1740, 1651, 1608, 1514, 1344, 1080, 750, 699 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 8.14 (2H, d, *J*=8.4 Hz, Ar-H), 8.00 (2H, *J*=7.9 Hz, Ar-H), 7.64 (1H, d, *J*=7.1 Hz, Ar-H), 7.25–7.44 (10H, m, Ar-H), 6.90 (1H, d, *J*=7.7 Hz, Ar-H), 6.82 (1H, d, *J*=7.7 Hz, Ar-H), 5.85 (1H, s, NC*H*), 2.45 (3H, s, C$_6$H$_4$C*H*$_3$). δ_C (75 MHz, $CDCl_3$) 170.89, 165.52, 147.82, 144.19, 144.05, 142.87, 133.20, 131.08, 129.72, 129.30, 129.02, 128.43, 127.90, 127.29, 125.91, 124.55, 124.22, 123.83, 123.41, 110.09, 87.14, 80.23, 21.77.

2.2.7. (3*R*,4′*R*)-1-Ethyl-2′-(4-methylphenyl)-4′-(4-nitrophenyl)spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 15. *N*-Ethyl isatin (0.030 g, 0.171 mmol) and imidoyl chloride **2** (0.074 g, 0.257 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.028 g, 0.282 mmol) under the standard procedure to afford the title compound **15** as pale yellow crystals; recrystallised from hexane–ethyl acetate. Mp 186–188°C; [Found C, 70.48; H, 5.13; N, 9.99. $C_{25}H_{21}N_3O_4$ requires C, 70.25; H, 4.95; N, 9.83%]; ν_{max} (KBr) 1725, 1646, 1606, 1513, 1467, 1208, 1175, 1082, 1009, 830, 744, 685 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.09 (2H, d, *J*=8.4 Hz, Ar-H), 7.97 (2H, d, *J*=8.0 Hz, Ar-H), 7.17–7.57 (m, 7H, Ar-H), 6.84 (1H, d, *J*=7.7 Hz, Ar-*H*), 5.75 (1H, s, NC*H*), 3.55–3.62 (1H, m, NC*H*HCH$_3$), 3.24–3.31 (1H, m, NC*H*HCH$_3$), 2.44 (3H, s, C$_6$H$_4$C*H*$_3$), 0.87–0.91 (3H, m, NCH$_2$C*H*$_3$). δ_C (75 MHz, $CDCl_3$): 171.09, 165.45, 147.73, 144.22, 143.22, 142.77, 131.13, 129.25, 128.97, 127.89, 127.74, 124.46, 123.89, 123.51, 123.24, 108.73, 86.95, 79.60, 34.54, 21.75, 12.26.

2.2.8. (3*R*,4′*R*)-1-Benzyl-2′-(4-methylphenyl)-4′-(4-nitrophenyl)spiro[3*H*-indole-3,5′(4′*H*)-oxazol]-2(1*H*)-one 16. *N*-Benzyl isatin (0.044 g, 0.185 mmol) and imidoyl chloride **2** (0.080 g, 0.278 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.030 g, 0.305 mmol) under the standard procedure to afford the title compound **16** as pale yellow crystals; recrystallised from hexane–dichloromethane. Mp 192–194°C; ν_{max} (KBr) 1733, 1650, 1607, 1518, 1349, 1174, 1074, 847, 751, 696 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 7.98–8.05 (4H, m, Ar-H), 7.59 (1H, d, *J*=7.0 Hz, Ar-H), 7.14–7.39 (9H, m, Ar-H), 6.78 (3H, br s, Ar-H), 5.79 (1H, s, NC*H*), 4.89 (1H, d, *J*=15.0 Hz, C$_6$H$_5$C*H*H), 4.23 (1H, d, *J*=15.0 Hz, C$_6$H$_5$CH*H*), 2.44 (3H, s, C$_6$H$_4$C*H*$_3$); δ_C (75 MHz, $CDCl_3$) 171.72, 165.61, 147.75, 143.72, 143.54, 142.94, 134.87, 131.22, 129.29, 128.91, 128.59, 128.15, 127.95, 127.41, 127.08, 124.44, 123.75, 123.42, 109.63, 87.05, 79.49, 43.95, 21.72; HRMS (EI): M$^+$ found 489.1667. $C_{30}H_{23}N_3O_4$ requires 489.1688.

2.2.9. 2′-(4-Phenyl)-4′-(4-nitrophenyl)spiro[acenaphthylene-1(2*H*),5′(4*H*)-oxazol]-2-one 18. Acenaphthenequinone (0.030 g, 0.164 mmol) and imidoyl chloride **1** (0.067 g, 0.247 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.027 g, 0.271 mmol) under the standard procedure to afford the title compound **18** as colourless crystals; recrystallised from hexane–dichloromethane. Mp 204–205°C; ν_{max} (KBr) 1726, 1651, 1521, 1340, 1272, 1017, 830, 780 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 7.97 (2H, d, *J*=8.6 Hz, Ar-H), 7.26–8.28 (11H, m, Ar-H), 7.13 (2H, d, *J*=8.5 Hz, Ar-H), 5.99 (1H, s, NC*H*). δ_C (75 MHz, $CDCl_3$) 197.58, 165.39, 147.57, 144.30, 142.04, 137.22, 132.47, 132.28, 131.98, 130.70, 130.49, 129.23, 129.02, 128.97, 128.59, 128.44, 127.89, 126.69, 123.37, 122.57, 121.99, 120.73, 90.16, 79.68; HRMS (EI): M^+ found 420.1112. $C_{26}H_{16}N_2O_4$ requires 420.1110.

2.2.10. 2′-(4-Methylphenyl)-4′-(4-nitrophenyl)spiro[acenaphthylene-1(2*H*),5′(4*H*)-oxazol]-2-one 19. Acenaphthenequinone (0.033 g, 0.181 mmol) and imidoyl chloride **2** (0.078 g, 0.271 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.030 g, 0.305 mmol) under the standard procedure to afford the title compound **19** as colourless crystals; recrystallised from hexane–dichloromethane. Mp 196–198°C; [Found C, 74.73; H, 4.36; N, 6.48. $C_{27}H_{18}N_2O_4$ requires C, 74.64; H, 4.18; N, 6.45%]; $\nu_{\max}$ (KBr) 1707, 1645, 1599, 1517, 1449, 1334, 1096, 994, 916, 834, 751, 694 cm^{-1}. δ_H (300 MHz, $CDCl_3$): 8.25 (2H, d, *J*=7.0 Hz, Ar-H), 8.14 (1H, d, *J*=7.6 Hz, Ar-H), 7.53–7.81 (9H, m, Ar-H), 7.03–7.25 (3H, m, Ar-H), 6.76 (2H, d, *J*=8.5 Hz, Ar-H), 5.63 (1H, s, NC*H*); δ_C (75 MHz, $CDCl_3$) 195.34, 165.86, 147.17, 144.10, 137.67, 135.53, 133.43, 132.41, 130.15, 129.07, 129.00, 128.94, 128.66, 128.59, 128.23, 127.74, 126.38, 126.24, 123.97, 123.27, 122.44, 92.58, 78.60.

2.2.11. 2′-(4-Phenyl)-4′-(4-nitrophenylspiro[oxazole-5(4*H*),9′(10′*H*)-phenanthren]-10′-one 21. Phenanthrenequinone (0.030 g, 0.144 mmol) and imidoyl chloride **1** (0.059 g, 0.216 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.024 g, 0.237 mmol) under the standard procedure to afford the title compound **21** as colourless crystals crystals; recrystallised from hexane–dichloromethane. Mp 185–187°C; [Found C, 75.51; H, 4.20; N, 5.97. $C_{28}H_{18}N_2O_4$ requires C, 75.33; H, 4.06; N, 6.27%]; $\nu_{\max}$ (KBr) 1726, 1645, 1601, 1520, 1348, 1272, 1073, 1014, 829, 785 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.70–8.17 (10H, m, Ar-H), 7.28 (2H, d, *J*=7.8 Hz, Ar-H), 7.12 (2H, d, *J*=8.4 Hz, Ar-H), 5.97 (1H, s, NC*H*), 2.44 (s, 3H, $C_6H_5CH_3$); δ_C (75 MHz, $CDCl_3$) 197.65, 165.50, 147.59, 144.48, 142.76, 142.02, 137.38, 131.93, 130.79, 130.50, 129.30, 129.22, 128.96, 127.93, 126.62, 123.97, 123.34, 122.50, 120.70, 90.10, 79.73, 21.73.

2.2.12. 2′-(4-Methylphenyl)-4′-(4-nitrophenyl)spiro[oxazole-5(4*H*),9′(10′*H*)-phenanthren]-10′-one 22. Phenanthrenequinone (0.030 g, 0.144 mmol) and imidoyl chloride **2** (0.062 g, 0.216 mmol) taken in 2 mL dry benzene was treated with triethylamine (0.024 g, 0.237 mmol) under the standard procedure to afford the title compound **22** as colourless crystals; recrystallised from hexane–dichloromethane. Mp 204–206°C; $\nu_{\max}$ (KBr) 1706, 1646, 1593, 1513, 1454, 1341, 1268, 1089, 830, 744, 718 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 8.12–8.15 (3H, m, Ar-H), 7.74–7.80 (4H, m, Ar-H), 7.51–7.59 (2H, m, Ar-H), 7.35 (2H, d, *J*=7.9 Hz, Ar-H), 7.03–7.18 (3H, m, Ar-H), 6.76 (2H, d, *J*=8.5 Hz, Ar-H), 5.61 (1H, s, NC*H*), 2.49 (3H, s, $C_6H_5CH_3$); δ_C (75 MHz, $CDCl_3$) 195.53, 166.06, 147.22, 144.34, 143.06, 137.78, 135.55, 133.62, 130.22, 129.48, 129.12, 129.08, 129.01, 128.73, 128.65, 128.34, 127.90,.126.33, 124.04, 123.67, 123.35, 122.20, 92.60, 78.69, 21.82; HRMS (EI): M^+ found 460.1420. $C_{29}H_{20}N_2O_4$ requires 460.1423.

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