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Preparations and Reactions of 2-Cyanoindole Derivatives

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2-Cyano-1-phenylsulfonylindole (**1a**) and 2-cyano-1-methylindole (**1b**) were prepared by chemical and electrolytic methods in modest yields. Nucleophiles such as sodium benzenethiolate, butyllithium and lithium dimethylcuprate attacked the sulfonyl group of **1a**, whereas they attacked the cyano group of **1b**. 1,3-Dipolar cycloadditions of **1a** and **1b** with 2,4,6-trimethylbenzonitrile oxide occurred at the cyano groups. Electrophilic reactions of **1b** with *N*-bromosuccinimide, Vilsmeir reagent and acetyl chloride afforded the corresponding 3-bromo-, 3-formyl- and 3-acetylindole derivatives in modest or high yields, albeit less rapidly than the reactions of 1-methylindole. Photochemical addition of dimethyl acetylenedicarboxylate to **1b** was followed by cleavage of the cyclobutene intermediate to give dimethyl (2-cyano-1-methylbenzazepine)-3,4-dicarboxylate.

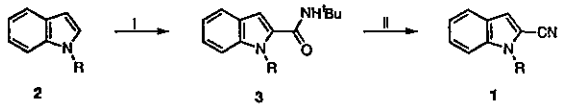
INTRODUCTION

Many natural alkaloids and industrial chemicals are indole derivatives. Electrophilic substitution at C-3 of indole is the normal reaction pathway. However, intramolecular nucleophilic free-radical addition at C-3 of 2-cyano-1-methylindole is accomplished with the assistance of the electron-withdrawing cyano group.[1] The reactivity of 2-cyanoindole derivatives toward electrophile or nucleophile deserves further investigation. Two substrates 2-cyano-1-phenylsulfonylindole **1a** and 2-cyano-1-methylindole **1b** were thus prepared respectively by chemical and electrolytic methods, and their reactions with nucleophiles such as organometallic reagents, or electrophiles such as *N*-bromosuccinimide (NBS) and Vilsmeir reagent, were investigated. Possible reactive sites include the cyano group, the sulfonyl group, C-3 and other phenyl positions.

RESULTS AND DISCUSSION

According to the literature procedure,[2] 1-phenylsulfonylindole **2a** prepared from indole by metallation with BuLi and subsequent sulfonation with phenylsulfonyl chloride, was treated with lithium diisopropylamide (LDA) and *tert*-butylisocyanate to afford amide **3a**. Dehydration of **3a** with phosphoryl chloride gave 2-cyano-1-phenylsulfonylindole in 65% overall yield from indole (Scheme I). Although 2-cyano-1-methylindole can be obtained from 1-methylindole by a similar procedure, a direct preparation according to an electrochemical method[3] is preferable.

Scheme I



2 3 1

series a, R = $PhSO_2$; b, R = Me

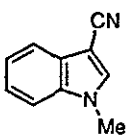
Reagents and conditions. For series a: (i) LDA, THF, $^tBuN{=}C{=}O$, -78 °C (2 h) to r.t. (16 h); 83%. (ii) $POCl_3$, PhH, 80 °C, 24 h; 86%.

Indole was treated with dimethyl oxalate and *t*-BuOK in *N,N*-dimethylformamide (DMF) to give exclusively the *N*-methylation product without complication of C-3 methylation.[4] A cyclic voltammetric (CV) scan of 1-methylindole in NaCN/MeOH showed two-stage oxidation at 1.2 and 1.5 V. Preparative synthesis of 2-cyano-1-methylindole (47% isolated yield) form 1-methylindole was conducted at 1.30 V (referred to a calomel electrode) in a divided cell using a platinum anode and cathode. 3-Cyano-1-methylindole **4** was the side-product (15% isolated yield) under these reaction conditions. Electrolysis in an undivided cell (1.40 V) gave 2-cyano-1-methylindole in an inferior yield (39%). When platinum electrodes were replaced with graphite, the current decreased greatly and less than 5% cyanation products were obtained after 10 h electrolysis. Double cyanation occurred when a higher voltage was applied (Table 1). For example, the electrolytic oxidation at 1.60 V gave 59% 2,3-dicyano-1-methylindole **5** and 9% 2,7-dicyano-1-methylindole **6**. The electrolytic process was monitored by TLC analysis to show that the dicyanoindoles **5** and **6** were derived by further cyanation of the monocyanoindoles **1b** and **4**. The CV scan of **1b** indicating an oxidation at 1.5 V was in agreement with this conclusion.

Dedicated to Professor Fa-Ching Chen (陳發清) on the occasion of his eightieth birthday.

Table 1. Electrochemical Cyanation of 1-Methylindole **2b** (divided cell, platinum anode and cathode, calomel reference electrode, 0.4 M NaCN in MeOH)

Quantity of **2b**/mmol	Oxidative potential/V	Initial current/mA	Reaction time/h	Products (yield/%)
2	1.30	80	10	**1b** (46) + **4** (19)
10	1.30	80	30	**1b** (47) + **4** (15)
2	1.40	100	10	**1b** (50) + **4** (19)
10	1.40	100	24	**1b** (48) + **4** (15)
2	1.50	130	12	**1b** (33) + **4** (12) + **5** (21) + **6** (4)
2	1.60	170	5	**5** (59) + **6** (9)
2	1.70	270	5	**5** (53) + **6** (12)



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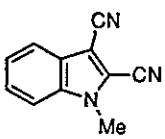

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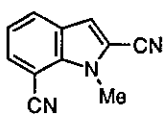

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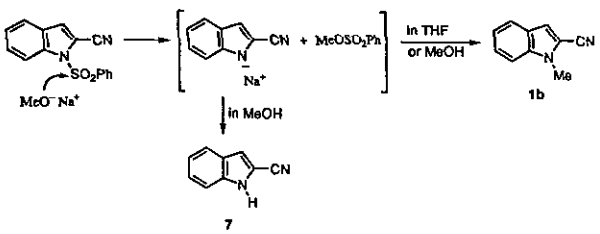
The results of the reactions of 2-cyano-1-phenylsulfonylindole **1a** with nucleophiles are listed in Table 2. When **1a** was treated with sodium methoxide in tetrahydrofuran (THF), 2-cyano-1-methylindole **1b** was obtained as the single product. The reaction of **1a** and sodium methoxide in a protic solvent (MeOH) gave 42% 2-cyanoindole (**7**) in addition to 57% **1b**. The reaction was presumed to occur by primary attack of sodium methoxide on the sulfonyl group to give a 2-cyanoindole anion and methyl phenylsulfonate (Scheme II). A counterattack of the indole anion on methyl phenylsulfonate in aprotic solvent would give 2-cyano-1-methylindole, whereas protonation in a protic solvent would give 2-cyanoindole. Butyllithium reacted with **1a** exclusively at the sulfonyl group rather than at the cyano group or at C-3. A side-product butyl phenyl sulfone was isolated, supporting the proposed mechanism (Scheme II). The nucleophiles *t*-butyllithium and lithium dimethylcuprate followed similar reaction pathways to yield **7**, however, along with the side-products **8** and **9** derived from further attacks at the cyano group.

Scheme II



We have previously demonstrated[5] that α-*N*-methylanilino-α,β-unsaturated nitriles underwent 1,2-additions with hard nucleophiles (e.g., butyllithium and methylmagnesium chloride) but 1,4-additions with soft nucleophiles (e.g., lithium dimethylcuprate and sodium phenylthiolate). The cyclic counterpart, 2-cyano-1-methylindole **1b** reacted with various nucleophiles in simply a 1,2-addition mode to give carbonyl compounds **10-12** (Table 2). The 1,2-addition of sodium phenylthiolate to **1b** gave the amide **13**, presumably derived by hydrolysis of the thioimidate intermediate **A**. The amide **13** was also obtained as a minor product in the reaction with lithium dimethylcuprate. Lithium dimethylcuprate might pick up oxygen to generate methoxide ion,[6] which attacked the cyano group of **1b** to give methyl imidate intermediate, so to yield the observed amide after hydrolysis.

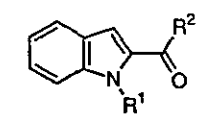
Attempt to enforce the Diels-Alder reaction of 2-cyano-1-phenylsulfonylindole with 1,3-cyclopentadiene at 170 °C or by induction of a Lewis acid $AlCl_3$ failed. The 1,3-dipolar cycloaddition with 2,4,6-trimethylbenzonitrile oxide[7] was achieved by refluxing in THF to give the oxadiazole **14a**. A 1,3-dipolar cycloaddition product **14b** was also obtained from 2-cyano-1-methylindole and 2,4,6-trimethylbenzonitrile oxide. The mass spectra of **14a** and **14b** exhibited respectively intense fragments at m/z 158 (base peak) and 284 (73%), attributed to the moieties of the corresponding indole-2-carbonyl cation radical **B**.[8] Thus 1,3-dipolar cycloadditions occurred in a regiospecific manner to give 1,2,4-oxadiazoles **14a,b** rather than the 1,2,5-oxadiazole isomers.

The photochemical reaction of 2-cyano-1-methylindole with dimethyl acetylenedicarboxylate in the presence of sensitizer acetophenone[9] gave the benzazepin **15** in small yields (6-10%). This reaction probably involved a [2+2] cycloaddition between the 2,3-double bond of the indole **1b** and the triple bond of the acetylenedicarboxylate to give the cyclobutene intermediate **C**, which readily ruptured to give

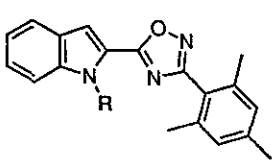
Table 2. Reactions of 2-Cyano-1-phenylsulfonylindole **1a** and 2-Cyano-1-methylindole **1b** with Nucleophiles

Substrate	Nucleophile	Solvent	Reaction temp./°C	Reaction time/h	Products (yield/%)
1a	MeONa	THF	r.t.	16	**1b** (93)
1a	MeONa	MeOH	0	4	**1b** (57) + **7** (42)
1a	PhSNa	THF	68	72	**7** (84)
1a	*n*-BuLi	THF	r.t.	16	**7** (40)[a]
1a	*t*-BuLi	THF	r.t.	72	**7** (52) + **8** (15)[b]
1a	Me_2CuLi	Et_2O	-40 to r.t.	16	**7** (62) + **9** (6)[c]
1b	*i*-Bu_2AlH	$PhCH_3$	-40 to r.t.	16	**10** (47)[d]
1b	*n*-BuLi	THF	0	4	**11** (98)
1b	(*n*-Bu)$_2$CuLi	Et_2O	-40 to r.t.	16	**11** (88)
1b	MeMgCl	THF	0 to r.t.	16	**12** (67)[e]
1b	Me_2CuLi	Et_2O	-40 to r.t.	16	**12** (41) + **13** (17)[f]
1b	PhSNa	THF	68	72	**13** (32)[g]

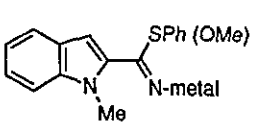
[a] Butyl phenyl sulfone was obtained as a side-product (39%) accompanied by recovery of 57% starting material **1a**.
[b] 27% starting material was recovered. [c] 16% starting material was recovered.
[d] 43% starting material **1b** was recovered. [e] 15% starting material was recovered.
[f] 27% starting material was recovered. [g] 63% starting material was recovered.



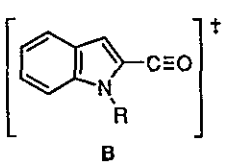
	R^1 =	R^2 =
8	H	*t*-Bu
9	H	Me
10	Me	H
11	Me	*n*-Bu
12	Me	Me
13	Me	NH_2



14a R = $PhSo_2$
14b R = Me



A

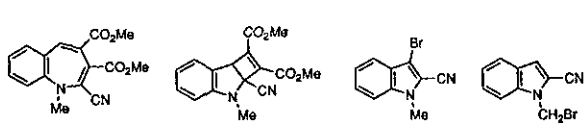


B

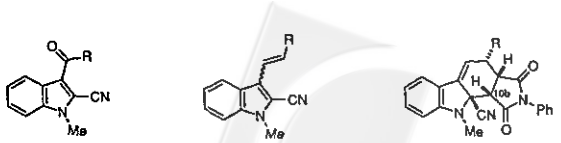
R = $PhSO_2$, *m/z* 284
R = Me, *m/z* 158

the observed product. When 2-cyano-1-phenylsulfonylindole was subjected to photochemical reaction under similar conditions, only cleavage of the sulfonyl group occurred to give 2-cyanoindole **7**.

Finally, electrophilic reactions of 2-cyano-1-methylindole with NBS, Vilsmeir reagent and acyl chloride were investigated. Bromination of **1b** occurred exclusively at C-3, giving **16**, after stirring with NBS for 72 h at room temperature, whereas partial bromination at *N*-methyl group occurred in refluxing CCl_4 solution. The bromoindole **16** was inert in MeONa/MeOH but was reduced by BuLi or Me_2CuLi, giving 2-cyano-1-methylindole. Treatment of **16** with copper(I) cyanide in refluxing DMF afforded 2,3-dicyano-1-methylindole in 74% yield. Vilsmeir formylation (DMF, $POCl_3$)[10] and Friedel-Crafts acylation (MeCOCl, $AlCl_3$) of 2-cyano-1-methylindole were carried out to give **18** and **19** in 87% and 53% yields, respectively. Due to the electron-withdrawing effect of the cyano group, 2-cyano-1-methylindole appeared less reactive than 1-methylindole and generally required several days to complete these electrophilic reactions. 2-Cyano-3-formyl-1-methylindole **18** and 3-acetyl-2-cyano-1-methylindole **19** have been shown to undergo tandem decyanation-hydroxyalkylations on treatments with carbonyl compounds and samarium(II) iodide.[11] Another synthetic application of **18** was demonstrated by its conversion to the indolodienes **20-23** (via Wittig and related reactions) suitable for Diels-Alder reactions. Compound **25** obtained by the Diels-Alder reaction of **22** (*E*-configuration) and *N*-phenylmaleiimide at 160 °C existed as a single isomer. The stereochemistry of **25** was ten-



15 **C** **16** **17**



18 R = H
19 R = Me

20 R = H
21 R = Ph
22 R = CO_2Et
23 R = CN

24 R = H
25 R = CO_2Et

tatively assigned to have H-10b and the cyano group orienting on the same face. If H-10b and the cyano group were on opposite faces, elimination of HCN from the cycloadduct and subsequent oxidative aromatization would be expected to occur at such a high reaction temperature.[12]

From this work, the electron-withdrawing property of the cyano group makes 2-cyano-1-methylindole less electrophilic than 1-methylindole. However, previous work[11] also showed that attachment of a cyano group at C-2 such as in the case of **18** facilitates the subsequent electron-transfer process. Nucleophiles and a 1,3-dipolarophile regardless of their hardness tend to add to the cyano group of **1b**; addition to the 2,3-double bond is realized only in one photochemical reaction with dimethyl acetylenedicarboxylate. In case of 2-cyano-1-phenylsulfonylindole, the sulfonyl group is more susceptible to nucleophilic attack than the cyano group. *o*-Dicyanobenzene is subject to tetramerization to give phthalocyanin, a versatile industrial chemical. It is worthy to investigate the potential use of 2,3-dicyano-1-methylindole on this aspect. 2,3-Dicyanoindole has been synthesized once in a small yield according to a multistep procedure,[13] whereas 2,3-dicyano-1-methylindole is easily accessible either by direct electrochemical conversion of 1-methylindole **2b** or by the substitution of 3-bromo-2-cyano-1-methylindole **16** with CuCN.

EXPERIMENTAL SECTION

Melting points (Yanaco micro melting-point apparatus) are uncorrected. Elemental analyses were carried out on elemental analyzers (Perkin-Elmer 240c or Hereaus CHN-O-RAPID). Infrared spectra were measured on an infrared spectrophotometer (Perkin-Elmer 983G). The ^{1}H NMR spectra were recorded at 200 or 300 MHz spectrometer (Bruker AC-200 or AM-300WB); tetramethylsilane was used as internal standard. ^{13}C NMR spectra were recorded at 50 or 75 MHz. The mass spectra were recorded (using Finnigan TSQ46c spectrometer) at an ionizing voltage 70 eV or 20 eV. The high-resolution mass spectra (HRMS) were recorded (JEOL JMS-HX 110 spectrometer). HPLC was carried out on a chromatograph (Hitachi L-6200) using a μ-Porasil column (7 μm, 25 cm × 0.78 cm) with 5 mL/min flow rate of elution. A potentiostat (Applied Biosystems PWR-3) was used as the power supply in the electrochemical reaction. A calomel reference electrode (double-junction) was purchased (Aldrich). Photochemical reaction was carried out in a Pyrex or quartz test-tube placed 10 cm from a medium-pressure mercury lamp (Conrad-Hanovia 7825) operating at 450W. 2-Cyano-1-phenylsulfonylindole **1a** was prepared via **2a** and **3a** according to the literature method.[2] The physical and spectral data of **1a-3a** were reported.[2]

Electrolytic Oxidation of 1-Methylindole

This reaction was conducted in a well ventilated hood to avoid any possible hazard from the reaction of NaCN. In an H-shaped divided glass cell were placed a platinum gauze (5 × 5 cm, 52 mesh) as the working electrode, a platinum gauze as the cathode and a calomel reference electrode. A solution of NaCN (4.90 g, 0.4 M) in MeOH (250 mL) was added, and followed by addition of 1-methylindole (1.31 g, 1 mmol) in the anode compartment. The potentiometer was applied to start electrochemical reaction at 1.30 V for 30 h. The solution in the anode compartment was taken, concentrated and partitioned between CH_2Cl_2 (50 mL) and water (50 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (50 mL × 4). The combined organic phase was washed with water (50 mL × 2) and brine (50 mL). The organic phase was dried (Na_2SO_4), filtered, concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (20:80) to give 2-cyano-1-methylindole **1b** (0.73 g, 47%) and 3-cyano-1-methylindole **4** (0.23 g, 15%). Electrolytic oxidations of 1-methylindole at various potentials are listed in Table 1 and double cyanation products, 2,3-dicyano-1-methylindole **5** and 2,7-dicyano-1-methylindole **6** were obtained in appropriate conditions.

2-Cyano-1-methylindole 1b[3]

Solid; mp 65-66 °C; TLC (EtOAc/hexane, 20:80) R_f 0.32; IR (KBr) 2222 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (3H, *s*, NMe), 7.00 (1H, *s*), 7.12 (2H, *m*, H-6, 7), 7.33 (1H, *dd*, J = 8.1, 7.6 Hz, H-5), 7.57 (1H, *d*, J = 8.1 Hz, H-4); ^{13}C NMR ($CDCl_3$, DEPT) δ 31.0 (*q*, NMe), 109.8 (2 C, C-2, 7), 112.2 (*d*, C-3), 113.3 (*s*, CN), 121.0 (*d*, C-6), 121.9 (*d*, C-4), 125.4 (*d*, C-5), 125.7 (*s*, C-9), 37.6 (*s*, C-8); MS m/z (rel intensity) 156 (M^+, 100); Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94, Found: C, 76.82; H, 5.18; N, 17.88.

3-Cyano-1-methylindole 4

Oil; bp 115 °C (5 mmHg); TLC (EtOAc/hexane = 20:80) R_f 0.16; IR (neat) 2218 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.76 (3 H, *s*), 7.22-7.35 (3 H, *m*), 7.45 (1 H, *s*, H-2), 7.68 (1 H, *d*, J = 7.4 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 33.3 (NCH_3), 84.9 (C-3), 110.2 (C-7), 115.8 (CN), 119.3 (C-6), 121.8 (C-4), 123.6 (C-5), 127.5 (C-9), 135.4 (C-2), 135.7 (C-8); MS m/z (rel intensity) 156 (M^+, 100); HRMS Calcd for $C_{10}H_8N_2$: 156.0687, Found: 156.0683.

2,3-Dicyano-1-methylindole 5

This compound was also obtained from the following substitution reaction. A mixture of **16** (50 mg, 0.21 mmol)

and CuCN (206 mg, 2.30 mmol) in DMF (12 mL) was heated at reflux for 24 h. The mixture was cooled, quenched by addition of saturated aqueous NH_4Cl solution (20 mL), and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phase was washed with brine, dried (Na_2SO_4), filtered and chromatographed on a silica gel column by elution with EtOAc/hexane (20:80) to give **5** (28 mg, 74%): Solid; mp 188-190 °C; TLC (EtOAc/hexane = 20:80) R_f 0.16; IR (KBr) 2223 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.00 (3 H, *s*), 7.39-7.58 (3 H, *m*), 7.80 (1 H, *d*, J = 7.8 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 32.6 (NCH_3), 95.4 (C-2), 110.3 (CN-2), 111.1 (C-7), 112.5 (CN-3), 115.7 (C-3), 120.9 (C-6), 124.3 (C-4), 126.3 (C-9), 127.7 (C-5), 136.9 (C-8); MS m/z (rel intensity) 181 (M^+, 100); HRMS Calcd for $C_{11}H_7N_3$: 181.0639, Found: 181.0639; Anal. Calcd for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19, Found: C, 72.59; H, 4.09; N, 22.87.

2,7-Dicyano-1-methylindole 6

Solid; mp 138-140 °C; TLC (EtOAc/hexane = 20:80) R_f 0.28; IR (KBr) 2221 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.24 (3 H, *s*), 7.24 (1 H, *s*, H-3), 7.27 (1 H, *dd*, J = 8.2, 7.6 Hz, H-5), 7.74 (1 H, *d*, J = 7.6 Hz, H-6), 7.91 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 33.2 (NCH_3), 95.2 (C-2), 112.3 (CN-2), 113.1 (C-3), 115.2 (CN-7), 117.2 (C-7), 121.0 (C-6), 127.5 (C-9), 127.8 (C-4), 132.5 (C-5), 135.5 (C-8); MS m/z (rel intensiy) 181 (M^+, 100); HRMS Calcd for $C_{11}H_7N_3$: 181.0639, Found: 181.0629.

Exemplary Procedure for Reactions of 2-Cyano-1-phenylsulfonylindole with Nucleophiles

A solution of 2-cyano-1-phenylsulfonylindole (144 mg, 0.51 mmol) in MeOH (5 mL) was added dropwise to a solution of MeONa (33 mg, 0.61 mmol) in MeOH (5 mL) at 0 °C. The mixture was stirred for 4 h, and saturated aqueous NH_4Cl solution was added. After removal of MeOH by rotary evaporator, the residue was extracted with CH_2Cl_2 (10 mL × 3). The organic phase was dried (Na_2SO_4), filtered, concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (10:90) to give 2-cyano-1-methylindole (45 mg, 57%) and 2-cyanoindole **7** (30 mg, 42%). The reactions with other nucleophiles under various conditions are listed in Table 2.

2-Cyanoindole 7

Microneedles; mp 102-103 °C; TLC (EtOAc/hexane = 20:80) R_f 0.29; IR (KBr) 3296 (NH), 2237 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (1 H, *s*, H-3), 7.19 (1 H, *dd*, J = 7.0, 6.0 Hz, H-6), 7.33-7.41 (2 H, *m*), 7.65 (1 H, *d*, J = 8.1 Hz, H-4), 9.04 (1 H, *br s*, NH); ^{13}C NMR ($CDCl_3$) δ 105.9 (C-2), 111.8 (C-3), 114.3 (C-7), 114.4 (CN), 121.6 (C-6), 122.0 (C-4), 126.0 (C-9), 126.1 (C-5), 136.9 (C-8); MS m/z (rel intensity) 142 (M^+, 100); Anal. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71, Found: C, 76.25; H, 4.29; N, 19.36.

2-(1,1-Dimethylpropanoyl)indole 8

Solid; mp 78-80 °C; TLC (EtOAc/hexane = 20:80) R_f 0.48; IR (KBr) 3330 (NH), 1638 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (9 H, *s*), 7.14 (1 H, *dd*, J = 7.5, 7.3 Hz, H-6), 7.25 (1 H, *s*, H-3), 7.30-7.44 (2 H, *m*), 7.71 (1 H, *d*, J = 8.4 Hz, H-4), 9.22 (1 H, *br s*, NH); ^{13}C NMR ($CDCl_3$) δ 28.5 (3 C, Me), 43.4 (C-2'), 109.0 (C-3), 111.8 (C-7), 120.8 (C-6), 123.0 (C-4), 125.9 (C-5), 126.8 (C-2), 132.2 (C-9), 135.9 (C-8). 199.0 (C=O); MS m/z (rel intensity) 201 (M^+, 32), 144 (100). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96, Found: C, 77.21; H, 7.52; N, 7.02.

2-Acetylindole 9

TLC (EtOAc/hexane = 20:80) R_f 0.26; IR (KBr) 3299 (NH), 1643 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (3 H, *s*, CH_3), 7.15-7.22 (2 H, *m*, H-6, 3), 7.31-7.45 (2 H, *m*, H-7, 5), 7.72 (1 H, *d*, J = 8.1 Hz, H-4), 9.04 (1 H, *br s*, NH); MS m/z (rel intensity) 159 (M^+, 55), 144 (100); HRMS Calcd for $C_{10}H_9NO$: 159.0684, Found: 159.0683.

Exemplary Procedure for Reactions of 2-Cyano-1-methylindole with Nucleophiles

Under an atmosphere of nitrogen, a solution of BuLi (1.24 mL, 1.6 M in hexane) was added dropwise to a solution of 2-cyano-1-methylindole (154 mg, 0.99 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 4 h, quenched by addition of saturated aqueous NH_4Cl solution, and extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were washed with brine (30 mL), dried (Na_2SO_4), filtered, concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (5:95) to give 1-methyl-2-pentanoylindole **11** (209 mg, 98%). The reactions with other nucleophiles under various conditions are listed in Table 2.

2-Formyl-1-methylindole 10

TLC (EtOAc/hexane = 20:80) R_f 0.32; ^1H NMR ($CDCl_3$) δ 4.03 (3 H, *s*), 7.18 (1 H, *dd*, J = 8.2, 6.6 Hz, H-6), 7.19 (1 H, *s*, H-3), 7.30 (1 H, *dd*, J = 8.2, 8.2 Hz, H-5), 7.36 (1 H, *d*, J = 6.6 Hz, H-7), 7.70 (1 H, *d*, J = 8.2 Hz, H-4), 9.84 (1 H, *s*, CHO); ^{13}C NMR ($CDCl_3$) δ 31.4 (NCH_3), 110.0 (C-3), 117.3 (C-7), 120.8 (C-6), 123.2 (C-4), 126.0 (C-2), 126.8 (C-5), 135.6 (C-9), 140.7 (C-8), 182.7 (C=O); HRMS Calcd for $C_{10}H_9NO$: 159.0684, Found: 159.0681.

1-Methyl-2-pentanoylindole 11

Solid; mp 82-83 °C; TLC (EtOAc/hexane = 20:80) R_f 0.45; IR (KBr) 1663 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (3 H, *t*, J = 7.4 Hz), 1.41 (2 H, *m*), 1.73 (2 H, *m*), 2.92 (2 H, *t*, J = 7.4 Hz), 4.02 (3 H, *s*), 7.10-7.15 (1 H, *m*), 7.24 (1 H, *s*, H-

3), 7.32-7.34 (2H, *m*), 7.66 (1 H, *d*, J = 8.1 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 22.4 (CH_2), 27.2 (CH_2), 32.0 (NCH_3), 39.6 ($COCH_2$), 110.2 (C-3), 111.0 (C-7), 120.5 (C-6), 122.7 (C-4), 125.6 (C-5), 125.7 (C-2), 134.8 (C-9), 139.9 (C-8), 194.6 (C=O); MS m/z (rel intensity) 215 (M^+, 37), 173 (37), 158 (99), 89 (100); HRMS Calcd for $C_{14}H_{17}NO$: 215.1306, Found: 215.1306.

2-Acetyl-1-methylindole 12

Solid; mp 70-71 °C; TLC (EtOAc/hexane = 20:80) R_f 0.32; IR (KBr) 1652 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.60 (3 H, *s*, $COCH_3$), 4.06 (3 H, *s*, NCH_3), 7.13-7.17 (1 H, *m*), 7.27 (1 H, *s*, H-3), 7.36-7.38 (2 H, *m*), 7.68 (1 H, *d*, J = 8.5 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 27.9 ($COCH_3$), 32.1 (NCH_3), 110.3 (C-3), 111.9 (C-7), 120.6 (C-6), 122.8 (C-4), 125.7 (C-2), 125.9 (C-5), 134.9 (C-9), 140.0 (C-8), 191.6 (C=O); MS m/z (rel intensity) 173 (M^+, 81), 158 (100); HRMS Calcd for $C_{11}H_{11}NO$: 173.0838, Found: 173.0832.

1-Methylindole-2-carboxamide 13

Needles; mp 170-172 °C; TLC (EtOAc/hexane = 20:80) R_f 0.05; IR (KBr) 3365 (NH), 3171 (NH), 1647 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.07 (3 H, *s*, NCH_3) 5.92 (2 H, *br s*, NH_2), 6.93 (1 H, *s*, H-3), 7.16 (1 H, *dd*, J = 7.2, 7.2 Hz, H-6), 7.31-7.41 (2 H, *m*), 7.64 (1 H, *d*, J = 7.9 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 31.6 (NCH_3), 105.1 (C-3), 110.2 (C-7), 120.6 (C-6), 121.9 (C-4), 124.4 (C-5), 125.8 (C-2), 130.4 (C-9), 139.2 (C-8), 164.3 (C=O); MS m/z (rel intensity) 174 (M^+, 100); Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08, Found: C, 69.12; H, 5.82; N, 15.93.

5-(1-Phenylsulfonylindol-2-yl)-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazole 14a

A solution of **1a** (155 mg, 0.55 mmol) and 2,4,6-trimethylbenzonitrile oxide[14] (142 mg, 0.88 mmol) in THF (20 mL) was refluxed for 72 h. The mixture was cooled, concentrated and the residue was chromatographed on a silica gel column by elution with EtOAc/hexane (10:90) to give a 1,3-dipolar cycloaddition product **14a** (66 mg, 27%) accompanied by 70% recovery of **1a**. **14a**: Solid; mp 159-160 °C; TLC (EtOAc/hexane = 20:80) R_f 0.30; IR (KBr) 1610 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (6 H, *s*), 2.34 (3 H, *s*), 6.98 (2 H, *s*), 7.28-7.60 (7 H, *m*), 7.98 (2 H, *d*, J = 7.9 Hz), 8.15 (1 H, *d*, J = 8.1 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.2, 115.3, 118.2, 122.4, 123.5, 124.6, 127.2, 127.3, 128.5, 128.7, 129.1, 129.8, 134.1, 137.4, 137.9, 138.0, 139.9, 168.6 (C=N), 169.4 (C=N); MS m/z (rel intensity) 443 (M^+, 1), 336 (4), 318 (6), 302 (100), 284 (73), 143 (42), 115 (28), 77 (45); HRMS Calcd for $C_{25}H_{21}N_3O_3S$: 443.1299, Found: 443.1301.

5-(1-Methylindol-2-yl)-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazole 14b

The 1,3-dipolar cycloaddition product **14b** (48 mg, 39%), accompanied by 59% recovery of **1b**, was obtained from a solution of **1b** (61 mg, 0.39 mmol) and 2,4,6-trimethylphenylbenzonitrile oxide (101 mg, 0.62 mmol) in THF (20 mL) by a procedure similar to that for **14a**. **14b**: Solid; mp 129-130 °C; TLC (EtOAc/hexane = 20:80) R_f 0.50; IR (KBr) 1600 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (6 H, *s*), 2.35 (3 H, *s*), 4.21 (3 H, *s*, NCH_3), 6.99 (2 H, *s*), 7.20 (1 H, *dd*, J = 7.9, 7.9 Hz, H-6), 7.36-7.45 (2 H, *m*, H-7, 5), 7.52 (1 H, *s*, H-3), 7.74 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 20.3, 21.2, 32.0 (NCH_3), 108.9, 110.3, 121.0, 122.4, 123.3, 123.8, 125.2, 126.8, 128.7, 137.9, 139.7, 139.9, 168.3 (C=N), 169.9 (C=N); MS m/z (rel intensity) 317 (M^+, 12), 158 (100); Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.69; H, 6.03; N, 13.24, Found: C, 75.33; H, 6.01; N, 13.45.

Dimethyl 2-Cyano-1-methylbenzazepine-3,4-dicarboxylate 15

A solution of **1b** (58 mg, 0.37 mmol), dimethyl acetylenedicarboxylate (0.11 mL, 0.89 mmol), acetophenone (0.04 mL, 0.32 mmol) in benzene (5 mL) was placed in a Pyrex tube and irradiated with a medium-pressure mercury lamp for 6 h. The mixture was concentrated and chromatographed on a silica gel colllmn by elution with EtOAc/hexane (10:90) to give **15** (11 mg, 10%) accompanied by 76% recovery of **1b**. **15**: oil; TLC (EtOAc/hexane = 20:80) R_f 0.18; IR (neat) 2216 (CN), 1727 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.19 (3H, *s*, OCH_3), 3.80 (3H, *s*, NCH_3), 3.82 (3 H, *s*, OCH_3), 7.02 (1 H, *d*, J = 8.2 Hz), 7.17 (1 H, *t*, J = 7.5 Hz), 7.24 (1 H, *d*, J = 7.5 Hz), 7.45 (1 H, *dd*, J = 8.2, 7.5 Hz), 8.01 (1 H, *s*); ^{13}C NMR ($CDCl_3$) δ 38.0 (NCH_3), 52.5 (OCH_3), 52.7 (OCH_3), 111.1, 119.3, 125.3, 127.7, 129.2, 129.9, 131.0, 131.4, 132.4, 146.0, 151.9, 164.6 (C=O), 165.4 (C=O); MS m/z (rel intensity) 298 (M^+, 44), 156 (100); HRMS Calcd for $C_{16}H_{14}N_2O_4$: 298.0950, Found: 298.0957.

3-Bromo-2-cyano-1-methylindole 16 and 1-Bromomethyl-2-cyanoindole 17

A solution of **1b** (64 mg, 0.41 mmol) and NBS (80 mg, 0.45 mmol) in CCl_4 (20 mL) was heated at reflux for 24 h. The mixture was cooled and filtered. The filtrate was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (20:80) to give **16** (62 mg, 64%) and 1-bromomethyl-2-cyanoindole **17** (12 mg, 12%), ac-

companied by 13% recovery of **1b**. An improved method by stirring of a solution of **1b** (296 mg, 1.90 mmol) and NBS (372 mg, 2.09 mg) in CCl_4 (30 mL) at room temperature for 72 h gave 91% of **16**. **16**: Solid; mp 88-89 °C; TLC (EtOAc/hexane = 20:80) R_f 0.30; IR (KBr) 2220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (3 H, *s*, NCH_3), 7.28 (1H, *dd*, J = 8.3, 7.2 Hz, H-6), 7.35 (1 H, *d*, J = 8.3 Hz, H-7), 7.46 (1 H, *dd*, J = 8.2, 7.2 Hz, H-5), 7.61 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 32.2 (NCH_3), 101.6 (C-2), 110.3 (C-7), 112.2 (CN), 119.9 (C-3), 120.9 (C-6), 122.1 (C-4), 125.8 (C-9), 126.9 (C-5), 137.4 (C-8); MS m/z (rel intensity) 236 (M^+, 94), 234 (M^+, 100); HRMS Calcd for $C_{10}H_7{}^{79}BrN_2$: 233.9793, Found: 233.9784. **17**: Solid; mp 98-99 °C; TLC (EtOAc/hexane = 20:80) R_f 0.12; IR (KBr) 2222 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (2 H, *s*, NCH_2Br), 7.22 (1 H, *s*, H-3), 7.26 (1 H, *dd*, J = 8.6, 8.2 Hz, H-6), 7.45 (1 H, *dd*, J = 8.2, 8.2 Hz, H-5), 7.54 (1 H, *d*, J = 8.6 Hz, H-7), 7.68 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 68.1 (NCH_2Br), 110.5 (C-3), 112.0 (CN), 113.3 (C-2), 114.9 (C-7), 122.2 (C-6), 122.5 (C-4), 126.5 (C-5), 126.7 (C-9), 137.3 (C-8); MS m/z (rel intensity) 235 (M^+, 48), 233 (M^+, 51), 169 (15), 155 (M^+-Br, 100).

2-Cyano-3-formyl-1-methylindole 18

Vilsmeir reagent was prepared by addition of $POCl_3$ (5 mL, 53.7 mmol) dropwise to DMF (10 mL) at 0 °C and stirring for 1 h. A solution of **1b** (1.12 g, 7.2 mmol) in DMF (7 mL) was added dropwise, the mixture was warmed to room temperature and stirred for six days. The mixture was cooled in an ice bath, quenched by dropwise addition of aqueous $NaHCO_3$ (5%, 50 mL) solution, and extracted with CH_2Cl_2 (50 mL × 4). The extracts were combined and washed with water (50 mL) and brine (50 mL). The organic phase was dried (Na_2SO_4), filtered, concentrated, and chromatographed on a silica gel column by elution with EtOAc/hexane (20:80) to give **18** (1.16 g, 87%) accompanied by 10% recovery of **1b**. **18**: Solid; mp 167-168 °C; TLC (EtOAc/hexane = 20:80) R_f 0.15; IR (KBr) 2223 (CN), 1664 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.97 (3 H, *s*, NCH_3), 7.38-7.43 (2 H, *m*), 7.52 (1 H, *dd*, J = 8.6, 7.8 Hz, H-5), 8.29 (1 H, *d*, J = 8.6 Hz, H-4), 10.16 (1 H, *s*, CHO); ^{13}C NMR ($CDCl_3$) δ 32.2 (NCH_3), 110.4 (C-7), 110.9 (C-3), 117.2 (CN), 122.7 (C-6), 123.4 (C-2), 123.5 (C-9), 124.7 (C-4), 127.4 (C-5), 138.0 (C-8), 183.1 (C=O); MS m/z (rel intensity) 184 (M^+, 75), 183 (100); HRMS Calcd for $C_{11}H_8N_2O$: 184.0635, Found: 184.0620.

3-Acetyl-2-cyano-1-methylindole 19

Acetyl chloride (0.92 mL, 12.9 mmol) was added dropwise to a mixture of **1b** (335 mg, 2.15 mmol) and $AlCl_3$ (573 mg, 4.30 mmol) in toluene (20 mL) at room temperature. The mixture was stirred for 9 days, quenched by addition of water (20 mL), and extracted with EtOAc (10 mL × 4). The organic phase was washed with brine (20 mL), dried (Na_2SO_4), filtered, concentrated, and chromatographed on a silica gel column by elution with EtOAc/hexane (10:90) to give **19** (227 mg, 53%): Solid; mp 138-141 °C; TLC (EtOAc/hexane = 20:80) R_f 0.23; IR (KBr) 2223 (CN), 1645 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (3 H, *s*, $COCH_3$), 3.85 (3 H, *s*, NCH_3), 7.29-7.36 (2 H, *m*), 7.43 (1 H, *dd*, J = 8.2, 8.2 Hz, H-5), 8.27 (1H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 29.4 ($COCH_3$), 31.9 (NCH_3), 110.2 (C-7), 112.6 (C-3), 113.1 (CN), 123.1 (C-2), 123.2 (C-6), 124.1 (C-4), 124.3 (C-9), 126.5 (C-5), 137.4 (C-8), 191.8 (C=O); MS m/z (rel intensity) 198 (M^+, 46), 183 (100); Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13, Found: C, 72.46; H, 5.21; N, 14.02.

Exemplary Procedure for Preparation of Indoledienes 20-23 and Their Diels-Alder Reactions

A BuLi solution (0.80 mL, 1.6 M in hexane) was added dropwise to a solution of methyltriphenylphosphonium bromide (458 mg, 1.28 mmol) in anhydrous THF (20 mL) at -20 °C. The mixture was warmed to 0 °C and stirred for 30 min. A solution of **18** (118 mg, 0.64 mmol) in THF (10 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 24 h. Water (20 mL) was added and the mixture was extracted with EtOAc (10 mL × 3). The combined organic phase was washed with brine (20 mL), dried (Na_2SO_4), filtered, concentrated, and chromatographed on a silica gel column by elution with EtOAc/hexane (10:90) to give **20** (110 mg, 94%). By similar procedures, **21** (97%, containing the *E*- and *Z*-isomers in a ratio of 65:35), **22** (92%, *E*-isomer) and **23** (94%, *E*/*Z* = 86:14) were prepared from benzyltrimethylphosphonium bromide, diethyl ethoxycarbonylmethylphosphonate and diethyl cyanomethylphosphonate, respectively. In a sealed tube was placed **20** (45 mg, 0.25 mmol), *N*-phenylmaleiimide (177 mg, 1.02 mmol) and toluene (2 mL). The mixture was heated (160 °C) for 16 h, cooled, concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (20:80) to give a Diels-Alder adduct **24** (16 mg, 18%). The Diels-Alder reaction of **22** and *N*-phenylmaleiimide was carried out by a similar procedure to give 13% of **25** as a single isomer.

2-Cyano-3-ethenyl-1-methylindole 20

Solid; mp 78-79 °C; TLC (EtOAc/hexane = 20:80) R_f 0.31; IR (KBr) 2216 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (3H, *s*), 5.47 (1H, *d*, J = 11.5 Hz, H-11), 6.00 (1H, *d*, J = 17.9 Hz, H-

11), 6.92 (1H, *dd*, J = 17.9, 11.5 Hz, H-10), 7.22 (1 H, *dd*, J = 8.2, 7.1 Hz, H-6), 7.27 (1 H, *d*, J = 8.2 Hz, H-7), 7.39 (1 H, *dd*, J = 8.2, 7.1 Hz, H-5), 7.84 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 31.3 (NCH_3), 108.6 (C-3), 110.1 (C-7), 113.4 (CN), 116.3 (C-11), 121.2 (C-6), 121.6 (C-4), 124.1 (C-2), 124.3 (C-9), 126.1 (C-10), 126.5 (C-5), 138.2 (C-8); MS m/z (rel intensity) 182 (M^+, 100). HRMS Calcd for $C_{12}H_{10}N_2$: 182.0842, Found: 182.0846.

2-Cyano-3-(2-phenylethenyl)-1-methylindole 21

***E*-isomer:** solid; mp 121-123 °C; TLC (EtOAc/hexane = 20:80) R_f 0.30; HPLC (EtOAc/hexane = 10:90) t_R = 9.8 min; IR (KBr) 2211 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.77 (3 H, *s*), 7.25-7.30 (4 H, *m*), 7.34-7.41 (4 H, *m*), 7.53 (2 H, *d*, J = 7.9 Hz), 7.95 (1 H, *d*, J = 7.8 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 31.4 (NCH_3), 108.7, 110.2, 113.6 (CN), 118.3, 121.4, 121.6, 124.1, 124.3, 126.2, 126.3, 127.8, 128.7, 130.6, 137.2, 138.4; MS m/z (rel intensity) 258 (M^+, 100); HRMS Calcd for $C_{18}H_{14}N_2$: 258.1154; Found: 258.1139. ***Z*-isomer:** Oily solid; TLC (EtOAc/hexane = 20:80) R_f 0.30; HPLC (EtOAc/hexane = 10:90) t_R = 8.5 min; IR (neat) 2214 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (3 H, *s*), 6.72 (1 H, *d*, J = 12.1 Hz, H-11), 6.85 (1H, *d*, J = 12.1 Hz, H-10), 6.97 (1H, *t*, J = 8.0 Hz), 7.07 (1H, *d*, J = 8.2 Hz), 7.14-7.21 (5 H, *m*), 7.27-7.36 (2 H, *m*); ^{13}C NMR ($CDCl_3$) δ 31.5 (NCH_3), 109.4, 109.9, 113.1 (CN), 118.6, 120.9, 122.6, 124.0, 124.1, 125.9, 127.4, 128.2, 128.8, 133.4, 137.2, 138.1; MS m/z (rel intensity) 258 (M^+, 100); HRMS Calcd for $C_{18}N_{14}N_2$: 258.1154, Found: 258.1152.

2-Cyano-3-(2-ethoxycarbonylethenyl)-1-methylindole 22

***E*-isomer:** Pale yellow solid; mp 120-121 °C; TLC (EtOAc/hexane = 20:80) R_f 0.20; IR (KBr) 2217 (CN), 1699 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (3 H, *t*, J = 7.1 Hz), 3.91 (3 H, *s*), 4.30 (2 H, *q*, J = 7.1 Hz), 6.71 (1 H, *d*, J = 16.0 Hz, H-11), 7.30-7.39 (2 H, *m*), 7.48 (1 H, *dd*, J = 8.2, 7.1 Hz, H-5), 7.92 (1H, *d*, J = 8.2 Hz, H-4), 7.93 (1H, *d*, J = 16.0 Hz, H-10); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3), 31.9 (NCH_3), 60.6 (OCH_2), 110.6 (C-7), 111.7 (C-3), 112.5 (CN), 118.9 (C-11), 121.0 (C-2), 121.3 (C-6), 122.8 (C-4), 124.3 (C-9), 126.7 (C-5), 133.5 (C-10), 138.4 (C-8), 167.0 (C=O); MS m/z (rel intensity) 254 (M^+, 72), 239 (1), 226 (15), 209 (100), 182 (42), 166 (7), 152 (8), 140 (11), 127 (6); HRMS Calcd for $C_{15}H_{14}N_2O_2$: 254.1052, Found: 254.1046.

2-Cyano-3-(2*E*-cyanoethenyl)-1-methylindole 23

***E*-isomer:** Solid; mp 192-193 °C; TLC (EtOAc/hexane = 20:80) R_f 0.13; HPLC (EtOAc/hexane = 20:80) t_R = 14.2 min; IR (KBr) 2216 (CN), 2206 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.94 (3 H, *s*), 6.11 (1H, *d*, J = 16.7 Hz), 7.35-7.44 (2 H, *m*), 7.53 (1 H, *dd*, J = 8.2, 7.2 Hz, H-5), 7.59 (1 H, *d*, J = 16.7 Hz), 7.78 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 32.1 (NCH_3), 96.4 (C-11), 111.0 (C-7), 111.6 (CN), 112.0 (CN), 118.3 (C-3), 120.0 (C-2), 120.7 (C-6), 123.5 (C-4), 123.8 (C-9), 127.1 (C-5), 138.3 (C-8), 139.5 (C-10); MS m/z (rel intensity) 207 (M^+, 100); Anal Calcd for $C_{13}H_9N_3$: S, 75.35; H, 4.38; N, 20.28, Found: C, 75.72; H, 4.45; N, 20.06. ***Z*-isomer:** Solid; mp 115-116 °C; TLC (EtOAc/hexane = 20:80) R_f 0.13; HPLC (EtOAc/hexane = 20:80) t_R = 12.0 min; IR (KBr) 2223, 2209 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.96 (3 H, *s*), 5.64 (1 H, *d*, J = 11.9 Hz), 7.34-7.42 (2 H, *m*), 7.43 (1 H, *d*, J = 11.9 Hz), 7.50 (1 H, *dd*, J = 8.2, 8.0 Hz, H-5), 8.06 (1 H, *d*, J = 8.2 Hz, H-4); ^{13}C NMR ($CDCl_3$) δ 32.1 (NCH_3), 98.1 (C-11), 110.5 (C-7), 112.1 (CN), 117.5 (CN), 120.3 (C-3), 120.7 (C-2), 122.6 (C-6), 122.7 (C-4), 123.7 (C-9), 126.9 (C-5), 138.2 (C-8), 138.9 (C-10); MS m/z (rel intensity) 207 (M^+, 100).

Compound 24

Solid; mp > 240 °C; TLC (EtOAc/hexane = 20:80) R_f 0.03; IR (KBr) 2228 (CN), 1715 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (1 H, *m*), 2.85 (1 H, *m*), 3.73 (1 H, *ddd*, J = 8.3, 5.5, 5.4 Hz), 3.97 (3 H, *s*), 4.10 (1 H, *dd*, J = 9.0, 4.8 Hz), 4.50 (1 H, *d*, J = 8.3 Hz), 7.19-7.25 (3 H, *m*), 7.30-7.47 (5 H, *m*), 7.87 (1 H, *d*, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 22.6, 27.3, 31.3, 39.0, 39.4, 104.3, 109.8, 118.7, 119.3, 120.5, 123.1, 124.3, 126.2, 127.8, 129.0, 129.2, 131.2, 137.9, 173.2 (C=O), 175.7 (C=O); MS m/z (rel intensity) 355 (M^+, 100); Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82, Found: C, 74.64; H, 4.83; N, 11.60.

Compound 25

TLC (EtOAc/hexane = 20:80) R_f 0.07; IR (KBr) 2246 (CN), 1712 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (3 H, *t*, J = 7.1 Hz), 3.34 (1 H, *dd*, J = 9.7, 4.7 Hz), 3.92 (3 H, *s*), 4.24-4.32 (3 H, *m*), 4.41 (1 H, *dd*, J = 9.7, 1 Hz), 4.55 (1 H, *dd*, J = 8.4, 1 Hz), 7.11-7.20 (3 H, *m*), 7.27-7.35 (5 H, *m*), 7.87 (1 H, *d*, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 25.3, 31.6, 39.8, 41.8, 42.7, 62.5, 103.0, 109.8, 118.9, 119.2, 120.7, 123.4, 124.4, 126.2, 127.8, 129.2, 131.0, 138.4, 168.9, 172.8, 173.8; MS m/z (rel intensity) 427 (M^+, 58), 353 (100); HRMS Calcd for $C_{25}H_{21}N_3O_4$: 427.1532, Found: 427.1529.

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Cyanoindoles; Electrophilic reactions; Nucleophillic reactions; Diels-Alder reactions; 1,3-Dipolar cycloadditions; Photochemistry.

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