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High, Exoselective Diels–Alder Reaction in 5.0 M Lithium Perchlorate in Diethyl Ether Medium: Efficient Synthesis of Novel Heterocyclic Derivatives Containing a Spirobicyclo[2.2.1]heptane System

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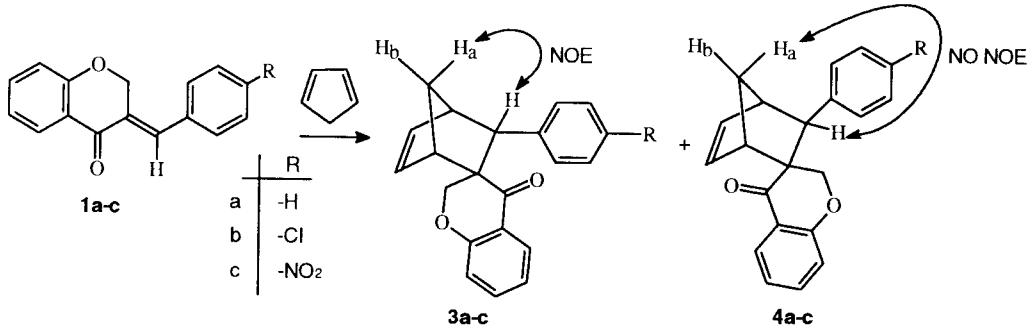
Abstract—Exocyclic arylidene derivatives have been used as dienophiles in Diels–Alder reactions with cyclopentadiene. A series of novel heterocyclic derivatives containing the spiro bicyclo[2.2.1]heptane system is the outcome of such reactions. The reactions proceed with high exoselectivity in the presence of 5.0 M LPDE medium.

Bicyclo[2.2.1]heptane derivatives find widespread use as key intermediates in the synthesis of many complex natural products.[1] Though a plethora of reports are available in the literature involving exocyclic methylene serving as dienophiles[2–4] in the Diels–Alder reaction, there appear to be few reports of the exocyclic benzylidene derivatives acting as dienophiles.[5] While the use of heterogeneous catalyst promoted the Diels–Alder reaction involving exocyclic benzylidene dienophiles, a high degree of stereoselectivity was not attainable.[5] In the present study, it was of interest to promote the Diels–Alder reaction involving such dienophiles with a high degree of stereoselectivity. In recent years, the use of 5.0 M lithium perchlorate in diethyl ether (LPDE) as a medium has attracted considerable attention due to the enhanced rate and selectivity in Diels–Alder reactions.[6] In a continuation of our interest in the area of cycloaddition reactions,[7–10] we report herein the Diels–Alder reaction promoted by 5.0 M LPDE medium.

Results and Discussion

The dienophiles (*E*) 3-arylidene-4-chromanones[7] chosen for our study were prepared according to literature procedure. The Diels–Alder reaction between **1a–c** and cyclopentadiene **2** with various Lewis acid catalysts at different temperatures for 24 h in dichloromethane gave a mixture of *exo* **3a–c** *endo* **4a–c** isomers. (Scheme 1). The stereochemistry of the *exo* **3a–c** and *endo* **4a–c** isomers were established by difference NOE studies. In the case of *exo*



Scheme 1.

Keywords: Diels–Alder reactions; lithium and compounds; spiro compounds.

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Table 1. Reaction of (*E*) 3-arylidene-4-chromanone **1a–c** with cyclopentadiene

Dienophile	Catalyst	*T* (°C)	Dienophile (%)	Products (%)[a]	*exo:endo*[b]
1a	–	rt	100	–	–
	–	−21	100	–	–
	$AlCl_3$[c]	rt	38	32	70:30
		−21	44	23	68:32
		−78	50	19	69:31
	$BF_3{\cdot}OEt_2$[c]	rt	37	34	82:18
		−21	52	22	59:41
		−78	57	20	60:40
	$TiCl_4$[c]	rt	33	38	74:26
		−21	41	30	71:29
	$ZnCl_2$[d]	rt	41	37	71:29
		−21	47	28	73.27
	LPDE[e]	rt	5	78	92:8
1b	$AlCl_3$	rt	42	22	79:21
		−21	47	19	75:25
	$BF_3{\cdot}OEt_2$[c]	rt	51	24	71:29
		−21	55	21	72:28
	$ZnCl_2$[d]	rt	49	21	75:25
		−21	55	17	73:27
	LPDE[e]	rt	2	82	93:7
1c	$ZnCl_2$[d]	rt	51	13	80:20
		−21	55	12	77:23
	$BF_3{\cdot}OEt_2$[c]	rt	45	15	73:27
		−21	50	13	70:30
	LPDE[e]	rt	2	83	93:7

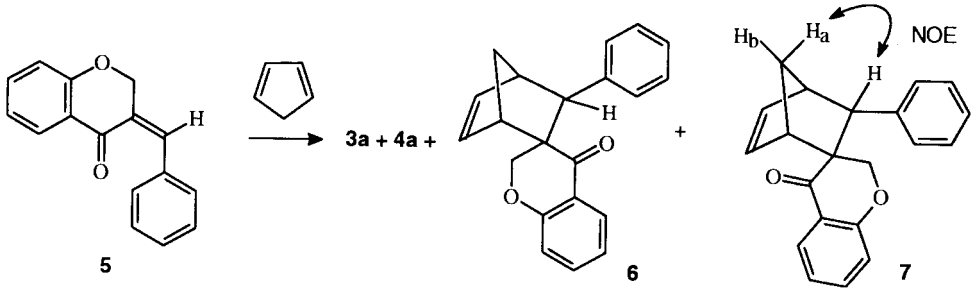
[a] Combined isolated yield of products.
[b] Ratio determined by HPLC.
[c] 1 equiv. of catalyst was used with respect to dienophile.
[d] 1.5 equiv. of catalyst was used with respect to dienophile.
[e] The reaction was performed in a 5.0 M solution of lithium perchlorate in diethyl ether.

isomer **3a**, selective irradiation of the H_a proton at δ 1.84 caused 14.6% enhancement of the signal for the C_3 hydrogen at δ 4.62, so that the C_3 methine hydrogen should be on the *exo* position of the norbornene skeleton, whereas in the case of *endo* isomer **4a**, selective irradiation of the H_a proton at δ 2.20 did not cause any enhancement of the signal for the C_3 hydrogen at δ 3.83. The structure and the stereochemistry of the *exo* isomer **3a** was further corroborated by signal crystal X-ray structure determination of **3a**.[11]

From Table 1, it is evident that in the absence of catalyst, no reaction occurred. While the use of standard Lewis acid catalysts like $AlCl_3$, $BF_3{\cdot}OEt_2$, $TiCl_4$ and $ZnCl_2$ promoted the reaction, the quantity of starting material recovered was great and a low yield of product formation with decreased stereoselectivity was observed. Even at lower temperatures, there was no improvement in selectivity. The best result was obtained when the reaction was carried out in 5.0 M LPDE medium; high exoselectivity was observed with enhanced chemical yields.

It was of further interest to investigate whether the *E* configuration of the exocyclic double bond in the dienophile plays any role in the observed *exo*/*endo* selectivity. The reaction between (*Z*) 3-benzylidene-4-chromanone[12] **5** and cyclopentadiene employing various Lewis acid catalysts for 24 h was studied. (Scheme 2). The *exo* and *endo* stereochemistry was unequivocally determined on the basis of difference NOE experiments. The *exo* adduct **6** in which the C_3 proton had the *endo* orientation the signal due to the C_3 proton at δ 3.06 did not show any NOE enhancement when the H_a proton at δ 2.76 was selectively irradiated. However, in the case of *endo* adduct **7** in which the C_3 proton had the *exo* orientation the signal due to the C_3 proton at δ 3.72 showed a 12% enhancement when the H_a proton at δ 1.85 was selectively irradiated.

It is obvious from Table 2 that in the presence of $AlCl_3$ or $BF_3{\cdot}OEt_2$ at rt complete configurational isomerization of *Z* to *E* occurs. In the presence of $AlCl_3$, 42% of *E* isomer **1a** was isolated, and in the presence of $BF_3{\cdot}OEt_2$, 47% of *E*



Scheme 2.

Table 2. Reaction of (*Z*)-3-benzylidene-4-chromanone **5** with cyclopentadiene

Catalyst	*T* (°C)	**1a** (%)	**5** (%)	Products (%)[a]	**3a:4a:6:7**[b]
$AlCl_3$[c]	rt	42	–	21	76:24:0:0
$BF_3{\cdot}OEt_2$[c]	rt	47	–	19	79:21:0:0
LPDE[d]	rt	3	2	80	12.5:1.5:56:30

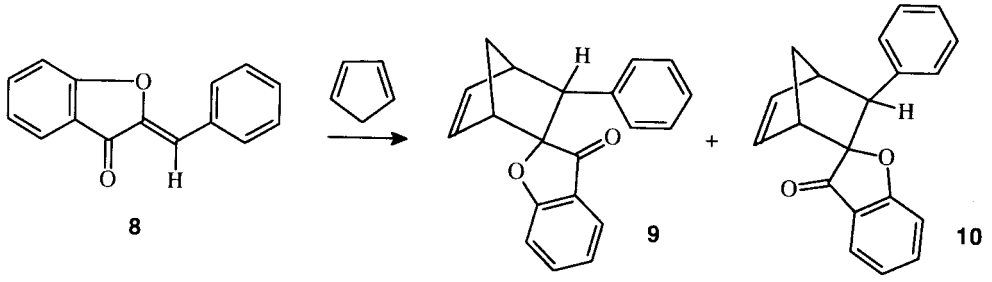
[a] Combined isolated yield of products.
[b] Ratio determined by HPLC.
[c] 1 equiv. of catalyst was used with respect to dienophile.
[d] The reaction was performed in a 5.0 M solution of lithium perchlorate in diethyl ether.

isomer **1a** was obtained. The cycloadducts **6** and **7** arising from the *Z* isomer were not obtained, and only the cycloadducts **3a** and **4a** arising from the *E* isomer are obtained. However, in the presence of 5.0 M LPDE medium, *Z*/*E* isomerization is suppressed to a considerable extent. The cycloadducts arising from both the *Z* (**6**, **7**) and *E* isomers (**3a**, **4a**) are obtained. It should be mentioned that Donnelly and Boyle[13] have reported Simmons Smith reaction of (*Z*) 3-benzylidene-4-chromanone with methylene chloride/zinc–copper couple to form exclusively *trans*-2-phenylcyclopropyl-1-spiro-3-chromanone. In the present study, the cycloadducts **3a**, **4a**, **6** and **7** are obtained from the *Z* isomer in the presence of 5.0 M LPDE medium.

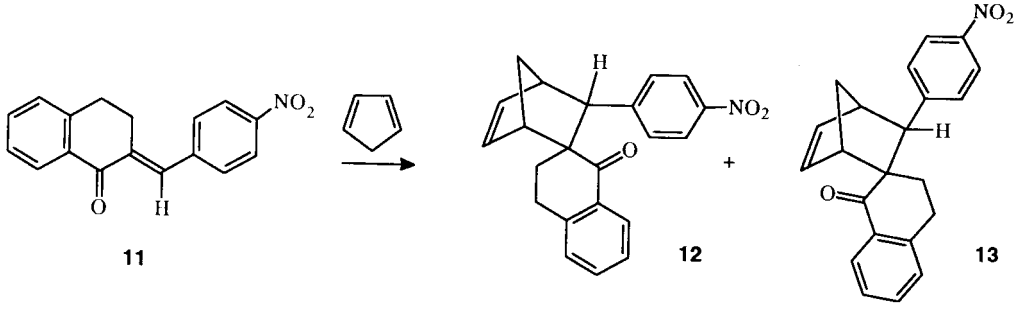
In order to establish the generality of the 5.0 M LPDE promoted Diels–Alder reaction, the reaction of aurone[14] **8** and (*E*) 2-(4-nitrobenzylidene)-1-tetralone[9] **11** with cyclopentadiene was studied (Schemes 3 and 4). The structure and the stereochemistry of the corresponding cycloadducts was confirmed by spectroscopic data and difference NOE studies.

It is clear from Table 3 that once again, the best result was obtained when the reaction was carried out 5.0 M LPDE medium.

Roush and Brown[3] suggested that the *exo* preference with conformationally restricted S-*cis* dienophiles may be due to the difference in dipole moment in the *exo* versus *endo* transition states. Recently Buano et al.[4] suggested that the relative position of substituents, structural factors and



Scheme 3.



Scheme 4.

Table 3. Reaction of aurone **8** and (*E*) 2-(4-nitrobenzylidene)-1-tetralone **11** with cyclopentadiene

Dienophile	Catalyst	*T* (°C)	Dienophile (%)	Products (%)[a]	*exo:endo*[b]
8	$AlCl_3$[c]	rt	33	12	77:23
	$BF_3{\cdot}OEt_2$[c]	rt	37	16	72:28
	LPDE[d]	rt	2	84	96:4
11	$AlCl_3$[c]	rt	50	20	85:15
	$BF_3{\cdot}OEt_2$[c]	rt	47	18	85:15
	LPDE[d]	rt	3	77	89:11

[a] Combined isolated yield of products.
[b] Ratio determined by HPLC.
[c] 1 equiv. of catalyst was used with respect to dienophile.
[d] The reaction was performed in a 5.0 M solution of lithium perchlorate in diethyl ether.

consequently steric effects present in the dienophile should influence the stereoselectivity. Nevertheless, numerous factors such as steric, conformational or electronic effects can interfere with the stereoselectivity of the Diels–Alder reaction.

In conclusion, efficient synthesis of a series of novel heterocyclic derivatives containing spirobicyclo[2.2.1]heptane system has been achieved via Diels–Alder reaction promoted by 5.0 M LPDE medium.

Experimental

General

All the melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL GX 400 spectrometer at 400 and 100.4 MHz, respectively. Mass spectra were recorded on a Finnigan MAT-8230 GC-Mass spectrometer. HPLC was carried out in SHIMADZU LC-9A instrument. The column used was normal phase column with UV detection at 281 nm. (CLC-CN, 4.6ϕX150). Elemental analyses were carried out on a CEST 1106 instrument. Flash column chromatography was performed on silica gel (SISCO, 230–400 mesh).

General procedure for the cycloaddition reaction in the presence of Lewis acid catalyst

Method A. To a stirred mixture of dienophile (1 mmol) in 5 mL of dichloromethane at the specified temperature under nitrogen atmosphere, Lewis acid catalyst (1 mmol) was added. After 15 min excess cyclopentadiene (3 mmol) was added and the mixture was stirred for 24 h. The reaction mixture was washed with water, $NaHCO_3$ solution, brine and dried. Removal of the solvent under reduced pressure gave an oily residue, which was subjected to flash column chromatography (hexane/EtOAc, 9:1). The first fraction afforded *exo* isomer and second fraction afforded *endo* isomer. The ratio of the *exo* and *endo* isomers was determined by HPLC of the crude reaction mixture.

Method B. To a stirred mixture of dienophile (1 mmol) in 2 mL of 5.0 M LPDE under nitrogen atmosphere, cyclopentadiene (3 mmol) was added. After 24 h, methylene chloride (15 mL) and water (25 mL) were added and the aqueous layer was extracted with 2×10 mL of methylene chloride. The combined organic extracts were washed with $NaHCO_3$ solution, brine and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oily residue, which was subjected to flash column chromatography (hexane/EtOAc, 9:1).

***endo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*exo*-4^1-one]}-5-ene (3a).** Colorless crystals, mp: 139–140°C; IR (KBr): 1682 cm^{-1}; ^{1}H NMR: δ 1.53 (d, J=8.8 Hz, 1H), 1.84 (d, J=8.8 Hz, 1H), 2.96 (bs, 1H), 3.27 (bs, 1H), 3.61 (d, J=12.1 Hz, 1H), 3.71 (d, J=12.1 Hz, 1H), 4.62 (d, J=2.4 Hz, 1H), 6.44 (dd, J=5.4, 2.9 Hz, 1H), 6.75 (dd, J=5.4, 2.9 Hz 1H), 6.88–7.46 (m, 8H), 8.01 (dd, J=7.8, 1.5 Hz, 1H); ^{13}C NMR: δ 46.95, 47.37, 47.78, 49.89, 56.49, 73.17, 117.47, 120.29, 121.14, 126.55, 128.11, 128.16, 128.64, 135.44, 135.49, 138.37, 139.10, 161.35, 195.34; MS *m/z*: 302 (M$^+$); Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.41; H, 6.00. Found: C, 83.31; H, 5.90.

***exo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*endo*-4^1-one]}-5-ene (4a).** Colorless oil, IR ($CHCl_3$): 1682 cm^{-1}; ^{1}H NMR: δ 1.75 (d, J=8.8 Hz, 1H), 2.20 (d, J=8.8 Hz, 1H), 3.17 (bs, 1H), 3.29 (bs, 1H), 3.76 (d, J=12.0 Hz, 1H), 3.79 (d, J=12.0 Hz, 1H), 3.83 (bs, 1H), 5.81 (dd, J=5.4, 2.9 Hz, 1H), 6.52 (dd, J=5.4, 2.9 Hz, 1H), 6.85–7.47 (m, 8H), 7.88 (dd, J=7.9, 1.6 Hz, 1H); MS *m/z*: 302 (M$^+$); HRMS (EI): M$^+$, found 302.1308. $C_{21}H_{18}O_2$: requires 302.1307.

***endo*-3-(4-Cholorophenyl)bicyclo[2.2.1]hept-2-spiro-{3^1-[chroman-*exo*-4^1-one]}-5-ene (3b).** Colorless crystals, mp: 100–101°C; IR (KBr): 1684 cm^{-1}; ^{1}H NMR: δ 1.52 (d, J=8.5 Hz, 1H), 1.82 (d, J=8.5 Hz, 1H), 2.96 (bs, 1H), 3.23 (bs, 1H), 3.57 (d, J=11.9 Hz, 1H), 3.67 (d, J=11.9 Hz, 1H), 4.57 (d, J=2.9 Hz, 1H), 6.45 (dd, J=5.4, 3.3 Hz, 1H), 6.71 (dd, J=5.4, 3.3 Hz, 1H), 6.88–7.47 (m, 7H), 7.99 (dd, J=8.3, 2 Hz, 1H); ^{13}C NMR: 46.21, 47.34, 47.70, 49.83, 56.43, 72.91, 117.42, 120.09, 121.17, 128.04, 128.22, 129.89, 132.28, 135.56, 135.78, 137.60, 137.91, 137.97, 161.23, 195.00. MS *m/z*: 336 (M$^+$); Anal. Calcd for $C_{21}H_{17}O_2Cl$: C, 74.98; H, 5.10. Found: C, 75.10; H, 5.07.

***exo*-3-(4-Chlorophenyl)bicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*endo*-4^1-one]}-5-ene (4b).** Colorless oil, IR ($CHCl_3$): 1682 cm^{-1}; ^{1}H NMR: δ 1.75 (d, J=8.7 Hz, 1H), 2.17 (d, J=8.7 Hz, 1H), 3.13 (bs, 1H), 3.30 (bs, 1H), 3.72 (d, J=11.8 Hz, 1H), 3.77 (d, 11.8 Hz, 1H), 3.80 (bs, 1H), 5.81 (dd, J=5.4, 3.3 Hz, 1H), 6.51 (dd, J=5.4, 3.3 Hz, 1H), 6.86–7.50 (m, 7H), 7.89 (dd, J=8.2, 2.0 Hz, 1H); MS *m/z*: 336 (M$^+$); HRMS (EI): M$^+$, 336.0921. $C_{21}H_{17}O_2Cl$ requires 336.0918.

***endo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*exo*-4^1-one]}-5-ene (3c).** Colorless crystals, mp: 139–140°C; IR (KBr): 1684 cm^{-1}; ^{1}H NMR: δ 1.60 (d, J=8.7 Hz, 1H), 1.85 (d, J=8.7 Hz, 1H), 3.04 (bs, 1H) 3.32 (bs, 1H), 3.58 (d, J=11.9 Hz, 1H), 3.69 (d, J=11.9 Hz, 1H) 4.71 (d, J=2.9 Hz, 1H), 6.51 (dd, J=5.4, 3.0 Hz, 1H), 6.75 (dd, J=5.3, 2.9 Hz, 1H), 6.90–7.50 (m, 5H), 7.99 (dd, J=8, 2 Hz, 1H), 8.07 (d, J=8.1 Hz, 2H); ^{13}C NMR: δ 46.85, 47.46, 47.61, 49.92, 57.10, 72.71, 117.55, 119.98, 121.45, 123.36, 128.14, 129.42, 135.87, 136.46, 137.67, 146.64, 147.42, 161.20, 194.63; MS *m/z*: 347 (M$^+$); Anal. Calcd for $C_{21}H_{17}O_4N$: C, 72.60; H, 4.93; N, 4.03. Found: C, 72.46; H, 4.88; N, 3.98.

***exo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*endo*-4^1-one]}-5-ene (4c).** Colorless oil, IR ($CHCl_3$): 1683 cm^{-1}; ^{1}H NMR: δ 1.83 (d, J=8.8 Hz, 1H), 2.23 (d, J=8.8 Hz, 1H), 3.19 (bs, 1H), 3.36 (bs, 1H), 3.70 (d, J=11.9 Hz, 1H), 3.78 (d, J=11.9 Hz, 1H), 3.95 (bs, 1H), 5.95 (dd, J=5.4, 3.0 Hz, 1H), 6.53 (dd, J=5.4, 3.0 Hz, 1H), 6.91–7.52 (m, 5H). 7.88 (dd, J=8.1, 2.0 Hz, 1H), 8.15 (d, J=8.1 Hz, 2H): MS *m/z*: 347 (M$^+$); HRMS (EI): M$^+$, found 347.1152. $C_{21}H_{17}O_4N$ requires 347.1158.

***exo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*exo*-4^1-one]}-5-ene (6).** Colorless oil, IR ($CHCl_3$): 1684 cm^{-1};

^{1}H NMR: δ 1.82 (d, J=8.8 Hz, 1H), 2.76 (d, J=8.8 Hz, 1H), 3.01 (bs, 1H), 3.04 (bs, 1H), 3.06 (d, J=2 Hz, 1H), 4.18 (d, J=11.5 Hz, 1H), 4.33 (d, J=11.5 Hz, 1H), 6.26 (dd, J=5.8, 2.9 Hz, 1H), 6.58 (dd, J=5.8, 2.9 Hz, 1H), 6.71 (m, 1H), 6.85 (d, J=8.3 Hz, 1H), 6.91–7.32 (m, 7H); MS *m/z*: 302 (M^+); HRMS (EI): M^+, 302.1309. $C_{21}H_{18}O_2$ requires 302.1307.

***endo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{3^1[chroman-*endo*-4^1-one]}-5-ene (7).** Colorless oil, IR ($CHCl_3$): 1683 cm^{-1}; ^{1}H NMR: δ 1.53 (d, J=8.7 Hz, 1H), 1.85 (d, J=8.7 Hz, 1H), 2.95 (bs, 1H), 3.11 (bs, 1H), 3.72 (d, J= 3.0 Hz, 1H), 4.48 (d, J=11.7 Hz, 1H), 4.58 (d, J=11.7 Hz, 1H), 6.33 (dd, J=5.3, 3.3 Hz, 1H), 6.65 (m, 1H), 6.75 (d, J=8.3 Hz, 1H), 6.79 (dd, J=5.3, 3.0 Hz, 1H), 6.89–7.35 (m, 7H); MS *m/z*: 302 (M^+); HRMS (EI): M^+, 302.1311. $C_{21}H_{18}O_2$ requires 302.1307.

***endo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{*exo*-2^1-aurone}-5-ene (9).** Colorless crystals, mp: 109–110°C; IR (KBr): 1705 cm^{-1}; ^{1}H NMR: δ 1.63 (d, J=9.3 Hz, 1H), 2.41 (d, J=9.3 Hz, 1H), 3.12 (bs, 1H), 3.34 (bs, 1H), 3.88 (d, J= 3 Hz, 1H), 6.39 (dd, J=5.6, 3.2 Hz, 1H), 6.75 (dd, J=5.6, 3.2 Hz, 1H), 6.84–7.70 (m, 9H); ^{13}C NMR: δ 46.38, 47.64, 52.26, 57.50, 96.51, 113.07, 120.56, 121.58, 124.23, 126.44, 127.76, 128.91, 135.64, 137.64, 138.01, 138.67, 171.55, 204.16; MS *m/z*: 288 (M^+); Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.30; H, 5.60. Found: C, 83.42; H, 5.65.

***exo*-3-Phenylbicyclo[2.2.1]hept-2-spiro-{*endo*-2^1-aurone}-5-ene (10).** Colorless oil, IR ($CHCl_3$): 1702 cm^{-1}; ^{1}H NMR: δ 1.95 (d, J=9.2 Hz, 1H), 2.56 (d, J=9.2 Hz, 1H), 2.91 (bs, 1H), 3.01 (bs, 1H), 3.28 (d, J=1.5 Hz, 1H), 6.32 (dd, J=5.6, 3.3 Hz, 1H), 6.69 (dd, J=5.6, 3.3 Hz, 1H), 6.82–7.95 (m, 9H); MS *m/z*: 288 (M^+); HRMS (EI): M^+, 288.1157. $C_{20}H_{16}O_2$ requires 288.1151.

***endo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hept-2-spiro-{2^1[*exo*-1^1-tetralone]}-5-ene (12).** Colorless crystals, mp: 124–126°C; IR (KBr): 1678 cm^{-1}; ^{1}H NMR: δ 1.3 (m, 2H), 1.55 (d, J=8.8 Hz, 1H), 1.81 (d, J=8.8 Hz, 1H), 2.72 (m, 1H), 2.96 (m, 1H), 3.02 (bs, 1H), 3.28 (bs, 1H), 4.85 (d, J=3.0 Hz, 1H), 6.39 (dd, J=5.4, 3.0 Hz, 1H), 2.96 (m, 1H), 3.02 (bs, 1H), 3.28 (bs, 1H), 4.85 (d, J=3.0 Hz, 1H), 6.39 (dd, J=5.4, 3.0 Hz, 1H), 6.72 (dd, J=5.4, 3.0 Hz, 1H), 7.19–7.49 (m, 5H), 8.05 (d, J=8.1 Hz, 1H), 8.12 (d, J=8.0 Hz, 2H); ^{13}C NMR: δ 27.06, 30.84, 47.31, 47.37, 48.51, 49.33, 58.83, 123.01, 126.64, 128.38, 128.62, 129.64, 131.72, 133.28, 135.88, 137.63, 143.14, 146.25, 149.75, 199.66; MS *m/z*: 345(M^+); Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.49; H, 5.55; N, 4.06. Found: C, 76.37; H, 5.49; N, 4.12.

***exo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hept-2-spiro-{2^1[*endo*-1^1-tetralone]}-5-ene (13).** Colorless oil, IR(CCl_4): 1677 cm^{-1}; ^{1}H NMR: δ 1.56 (m, 2H), 1.8 (d, J=8.8 Hz, 1H), 2.19 (d, J=8.8 Hz, 1H), 2.85 (m, 2H), 3.17 (bs, 1H), 3.21 (bs, 1H), (4.05, d, J=3.1 Hz, 1H) 5.95 (dd, J=5.4, 3.2 Hz, 1H), 6.51 (dd, J=5.4, 3.2 Hz, 1H), 7.15–7.50 (m, 5H), 8.08 (d, J=8.1 Hz, 1H), 8.16 (d, J=8.2 Hz, 2H), MS *m/z*: 345 (M^+); HRMS (EI) M^+, 345.1368. $C_{22}H_{19}NO_3$ requires 345.1366.

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