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Indium Trichloride ($InCl_3$)Catalyzed Imino Diels-Alder Reactions: An Efficient Synthesis of Cyclopentaquinolines, Azabicyclooctanones and Azabicyclononanones.[1]

Govindarajulu Babu and Paramasivan T. Perumal*

Organic Chemistry Division, Central Leather Research Institute
Adyar, Chennai - 600 020, INDIA.

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Abstract: Anhydrous indium trichloride ($InCl_3$) is found to catalyze the imino Diels-Alder reactions of Schiff's bases with cyclopentadiene, cyclohexen-2-one and cyclohepten-2-one which resulted in facile synthesis of cyclopentaquinolines, azabicyclooctanones and previously unreported series of azabicyclononanones.

Imino Diels-Alder reaction is one of the powerful synthetic methods for the construction of nitrogen heterocycles.[2] Imines derived from aromatic amines act as imino-dienophiles[3] as well as heterodienes[4] and also undergo intramolecular Diels-Alder reactions.[5] Lewis acids such as $BF_3.Et_2O$, TFA have been found to catalyze the Diels-Alder reactions of keto-imines[6] and Schiff's bases.[4] Although Lewis acids promote the reactions, more than stoichiometric amount of the acids are required owing to the strong coordination of the acids to nitrogen atom.[2] Lanthanide triflates have been found to activate imines[7] and promote Diels-Alder reactions.

In literature, indium trichloride is used as catalyst for polymerization reactions,[8] chlorination of chlorophenylsilanes,[9] sulfide synthesis,[10] Friedel Craft's acylation,[11] hydrodechlorination,[12] and aldol condensation of silyl enol ethers.[13] Recently Indium trichloride has been found to catalyze Mukaiyama aldol reactions[14] and Diels-Alder reactions[15] in water owing to its high coordination number and a fast coordination - dissociation equilibrium in aqueous solutions. This behaviour of high coordination and fast coordination dissociation tendency of indium trichloride prompted us to investigate its catalytic activity for imino Diels-Alder reactions of Schiff's bases. In this paper we describe the convergent synthesis of cyclopentaquinolines, azabicyclooctanones and azabicyclononanones by imino Diels-Alder reactions of Schiff's bases with cyclopentadiene, cyclohexen-2-one and cyclohepten-2-one.

Results and Discussion

The Schiff's bases were prepared according to the published procedure[16] by condensation of substituted anilines with substituted benzaldehydes.

In the presence of 20 mol % indium trichloride ($InCl_3$), *N*-benzilidene aniline (**1a**) was treated with cyclopentadiene in acetonitrile at room temperature. The imine acted as a heterodiene and the reaction proceeded smoothly to afford the corresponding tetrahydroquinoline derivative in 75% yield in 30 min.

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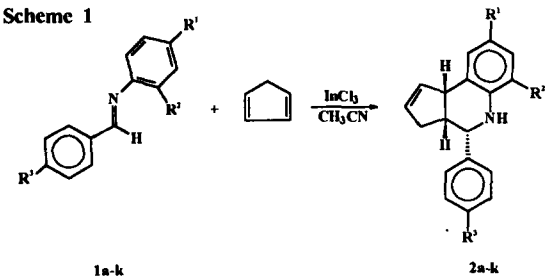
(Scheme 1). Similar results were obtained with a number of other Schiff's bases and the results are summarized in Table 1.

Scheme 1



1a-k 2a-k

Table 1. Reaction of Schiff's bases with cyclopentadiene employing 20 mol %, $InCl_3$[a].

Entry	Schiff's base	Product	Substituents			Time (min.)	Yield (%)[b]	Mp. °C
			R^1	R^2	R^3			
1	**1a**	**2a**	H	H	H	30	75	120 - 121
2	**1b**	**2b**	NO_2	H	H	30	95	172 - 173
3	**1c**	**2c**	OCH_3	H	H	45	58	-
4	**1d**	**2d**	Cl	H	H	30	84	149 - 150
5	**1e**	**2e**	Cl	CH_3	H	30	90	-
6	**1f**	**2f**	H	COOH	H	45	78	205 - 206
7	**1g**	**2g**	H	C_2H_5	H	45	82	-
8	**1h**	**2h**	H	NO_2	H	30	75	-
9	**1i**	**2i**	H	H	CH_3	45	65	64 - 65
10	**1j**	**2j**	H	H	Cl	30	77	141 - 142
11	**1k**	**2k**	Cl	H	Cl	30	80	171 - 172

a : All reactions were conducted at room temperature by addition of 20mol % $InCl_3$ to a mixture of Schiff's base and cyclopentadiene in acetonitrile. b : Isolated yield.

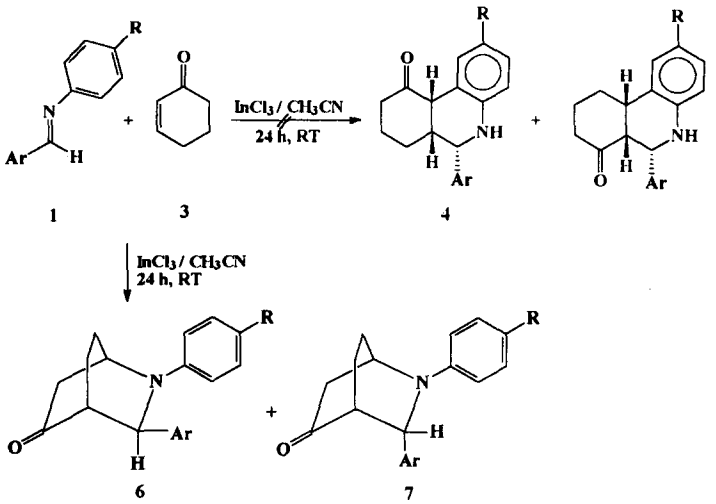
Although, Schiff's bases act as heterodienes in the presence of Lewis acids with cyclopentadiene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene and other dienophiles, the reaction of Schiff's bases as heterodienes with cycloalkenones are unprecedented.

2-cycloalkenones are dienophiles of low reactivity. The coordination of the carbonyl function with Lewis acids increases the reactivity of dienophiles and enhances the yield. The catalysts generally used are $AlCl_3$, $AlBr_3$, BF_3. Et_2O, $ZnCl_2$, $SnCl_4$ and $EtAlCl_2$. Lanthanide shift reagents are also used in the presence of highly reactive or acid sensitive dienes.[17] Diels-Alder reactions of cycloalkenones with 1,3-dienes provide an easy entry into the basic skelata of sesquiterpenes, diterpenes, steroids and alkaloids.[18] We have recently reported the Diels-Alder reaction of cycloalken-2-ones with cyclopentadiene catalyzed by $AlCl_3$.[19]

In continuation of our investigation of activation of imines by indium trichloride, we studied the reaction of cyclohexen-2-one[20] with *N*-benzylidene aniline (**1a**) in acetonitrile using 20 mol % indium

trichloride (Scheme 2). Since imine acted as a heterodiene in the Diels-Alder reaction of Shiff's base with cyclopentadiene, we envisaged the formation of phenanthridinone derivatives[1] **4** and **5**. However, the anticipated products were not obtained. A closer examination of the spectral data revealed the formation of azabicyclo[2.2.2]octanones **6a** and **7a** in a ratio of 69 : 31 amounting to an yield of 65%.

Scheme 2



1 3 4 6 7

The proposed structure was further ascertained by x-ray analysis[21] of the the exo product **6d** formed by the treatment of N-benzylidene p-chloroaniline (**1d**) with cyclohexene-2-one. The reaction seems to proceed through the formation of dienolate ion by strong coordination of indium trichloride with enone. Such activation of enone to behave as diene by coordination with Lewis acid is unprecedented. Thus cyclohexadienolate ion acts as the diene and Schiff's base acts as the dienophile in the hetero Diels-Alder reaction with Schiff's bases. The formation of azabicyclooctanones may also be accounted by Mukiyama aldol reaction of diene, generated *in situ* from cyclohexene-2-one with Schiff's base followed by cyclization under Michael conditions.[22] Similar results were obtained with other Schiff's bases and the results are summarized in Table 2.

Table 2. Diels-Alder reactions of Schiff's bases with cyclohexen-2-one employing 20 mol % $InCl_3$.[a]

Entry	Schiff's base	R	Ar	product ratio[b] of 6:7	Overall yield %
1	**1a**	H	C_6H_5	69 : 31	65
2	**1b**	NO_2	C_6H_5	67 : 33	70
3	**1c**	OCH_3	C_6H_5	68 : 32	60
4	**1d**	Cl	C_6H_5	73 : 27	68
5	**1j**	H	*p*-Cl-C_6H_4	48 : 52	65
6	**1k**	Cl	*p*-Cl-C_6H_3	47 : 53	74
7	**1m**	CH_3	C_6H_5	73 : 27	62

a : All reactions were conducted at room temperature by the addition of 20 mol % $InCl_3$ to a mixture of Schiff's bases and cyclohexen-2-one in acetonitrile and stirred for 24 h.

b : The ratio based on isolation by chromatography.

Further, we examined the reactivity of cyclohepten-2-one with Schiff's bases catalyzed by indium trichloride. Thus, cyclohepten-2-one[20] was treated with *N*-benzylidene aniline (**1a**) in the presence of 20 mol % indium trichloride in acetonitrile and stirred at room temperature (Scheme 3). After 24 h we have obtained azabicyclononanones **9a** and **10a** in a ratio of 52 : 48 in an overall yield of 56%. Therefore cycloheptene-2-one exhibited analogous behaviour to that of cyclohexene-2-one and acted as a diene by coordination with indium trichloride. Similar results were obtained with other Schiff's bases and the results are summarized in Table 3.

Scheme 3

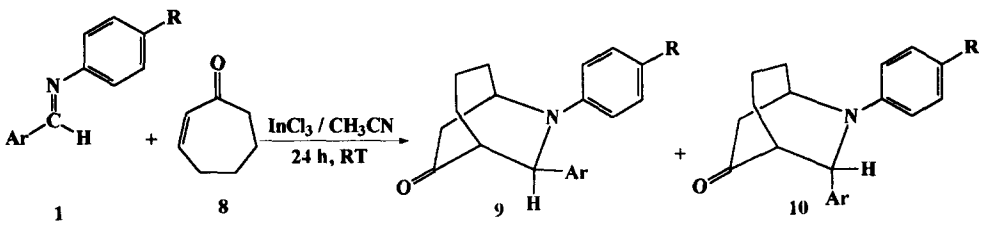


Table 3. Diels-Alder reaction of Schiff's bases with cyclohepten-2-one employing 20 mol % $InCl_3$.

Entry	Schiff's base	R	Ar	product ratio[a] of 9:10	Time, h	Overall yield %
1	**1a**	H	C_6H_5	52 : 48	24	56
2	**1c**	OCH_3	C_6H_5	65 : 35	26	48
3	**1d**	Cl	C_6H_5	39 : 61	20	78
4	**1k**	Cl	*p*-Cl-C_6H_4	42 : 58	21	68
5	**1m**	CH_3	C_6H_5	48 : 52	22	52

a : The ratio based on isolation by chromatography.

In conclusion, the present investigation clearly indicates that indium trichloride exhibits dual behaviour in activating the substrates in hetero Diels-Alder reaction with Schiff's bases. When Schiff's bases are treated with cyclopentadiene, indium trichloride activates the Schiff's base to behave as heterodiene. On the contrary, when Schiff's bases are treated with cycloalkenones, indium trichloride coordinates with cycloalkenones and activates the enone to behave as the diene which provides an unprecedented synthetic route to azabicyclooctanones and azabicyclononanones.

Experimental

General: Melting points were recorded on a Mettler FP 62 instrument and are uncorrected. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrophotometer and are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker (300 MHz) spectrometer and carbon nuclear magnetic resonance (^{13}C NMR) were recorded on a Bruker (75 MHz) spectrometer. Mass spectra were recorded on Varian VG 70-70 H mass spectrometer. Acetronitrile was distilled from calcium hydride and dried over MS 4 Å.

General procedure for the Diels-Alder reaction of Schiff's bases 1a-k with cyclopentadiene.

To a solution of Schiff's base **1a-k** (2.5 mmol) and cyclopentadiene (0.330 g, 5 mmol) inacetonitrile (10 ml) protected by a guard tube was added indium trichloride (0.110 g, 20 mol %)

and tirred at room temperature for 30-45 min. To the reaction mixture aqueous sodium carbonate solution (10 ml) was added and extracted with chloroform (3 × 10 ml). The combined organic layer was washed with water (10 ml) and brine (10 ml), dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography using silica gel (60-120 mesh) and eluted with petroleum ether : ethyl acetate (95:5) to afford the quinolines **2a-k**.

4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline[7a] (2a).

0.339 g (75%) of colourless crystalline solid; Mp. 120–121 °C (lit. Mp. 120 °C); IR (KBr) : 3353, 1478 cm^{-1}; ^1H NMR(300 MHz,$CDCl_3$) δ 7.39 (m,5H), 7.06 (m, 2H), 6.78 (m, 1H), 6.64 (d, 1H, *J* = 7.9 Hz), 5.71 (m, 2H), 4.67 (d, 1H, *J* = 2.9 Hz), 4.15 (d, 1H, *J* = 8.6 Hz), 3.78 (br s, 1H), 3.05 (m, 1H), 2.71 (m, 1H), 1.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 142.8, 134.0, 130.3, 129.0, 128.4, 127.2, 126.4, 126.3, 126.0, 119.1, 115.9, 58.0, 46.4, 46.0, 31.5; MS m/z : 247 (M^+); Anal. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 86.88; H, 6.95; N, 5.68.

8-Nitro-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2b)

0.693 g (95%) of yellow solid; Mp. 172-173 °C; IR (KBr) : 3364, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.37 (m, 5H), 6.55 (d, 1H, *J* = 8.8 Hz), 5.90 (m, 1H), 5.68 (m, 1H), 4.75 (d, 1H, *J* = 3.0 Hz), 4.56 (d, 1H, *J* = 8.6 Hz), 4.09 (m, 1H), 3.05 (m, 1H), 2.63 (m, 1H), 1.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 141.1, 139.8, 133.2, 131.0, 128.7, 127.8, 126.2, 125.6, 123.1, 114.7, 57.2, 45.5, 45.3, 31.4; MS m/z : 292 (M^+); Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.68; H, 5.48; N, 9.54.

8-Methoxy-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline[7b] (2c)

0.401 g (58%) of brown liquid; IR (Neat) : 3349, 1502 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 6.63 (m, 3H), 5.85 (m, 1H), 5.71 (m, 1H), 4.56 (d, 1H, *J* = 2.9 Hz), 4.08 (d, 1H, *J* = 8.8 Hz), 3.76 (s, 3H), 2.91 (m, 1H), 2.71 (m, 1H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 142.9, 139.4, 133.7, 130.6, 128.4, 127.1, 126.6, 116.7, 114.0, 112.3, 58.5, 55.6, 45.8, 45.7, 31.4; MS m/z : 277 (M^+); Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.96; N, 5.05. Found: C, 81.87; H, 6.95; N, 5.07.

8-Chloro-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline[7b] (2d)

0.590 g (84%) of crystalline white solid; Mp. 149-150 °C (lit. Mp. 150 °C); IR (KBr) : 3363, 1470 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 5H), 7.03 (d, 1H, *J* = 2.1 Hz), 6.93 (dd, 1H, *J* = 2.2, 8.5Hz) 6.53 (d, 1H, *J* = 8.5 Hz), 5.81 (m, 1H), 5.68 (m, 1H), 4.59 (d, 1H, *J*= 2.9 Hz), 4.06 (d, 1H, *J* = 8.6 Hz), 3.76 (br s, 1H), 2.99 (m, 1H), 2.62 (m, 1H), 1.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 142.4, 133.4, 130.8, 128.6, 128.5, 127.6, 127.3, 126.3, 126.1, 116.9, 57.9, 46.2, 45.6, 31.0; MS m/z : 281 (M^+), 283 (M^+ + 2); Anal. Calcd. for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.40; H, 5.74; N, 4.98.

8-Chloro-6-methyl-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2e)

0.663 g (90%) of brown liquid ; IR (Neat) : 3395, 1484 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 5H), 6.94 (m, 2H), 5.84 (m, 1H), 5.70 (m, 1H), 4.64 (d, 1H, *J* = 2.5 Hz), 4.11 (d, 1H, *J* = 8.6 Hz), 3.77 (br s, 1H), 2.98 (m, 1H), 2.68 (m, 1H), 2.15 (s, 3H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 142.3, 133.8, 130.8, 128.6, 128.5, 127.4, 127.2, 126.9, 126.5, 126.3, 124.4, 122.7, 57.9, 46.5, 45.7, 31.4, 17.1; MS m/z : 295 (M^+), 297 (M^+ + 2); Anal. Calcd. for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74. Found: C, 76.80; H, 6.11; N, 4.75.

4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline-4-carboxylic acid(2f)

0.567 g (78%) of colourless solid ; Mp. 205-206 °C; IR (KBr) : 3349, 1608, 1491 cm^{-1}; ^1H NMR (300

MHz, $CDCl_3$) δ 7.80 (d, 1H, *J* = 8.0 Hz), 7.38 (m, 5H), 6.64 (m, 2H), 5.81 (m, 1H), 5.65 (m, 1H), 4.75 (d, 1H, *J* = 2.7 Hz), 4.48 (s, 1H), 4.13 (d, 1H, *J* = 8.4 Hz), 3.02 (m, 1H), 2.58 (m, 1H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 150.2, 142.1, 135.5, 134.9, 130.6, 130.0, 128.6, 128.2, 127.1, 127.0, 126.8, 126.1, 116.2, 111.8, 56.4, 45.8, 45.3, 31.7; MS m/z : 291 (M^+); Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.99; H, 5.86; N, 4.82.

6-Ethyl-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2g)

0.563 g (82%) of brown liquid ; IR (Neat) : 3382, 1487 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 6H), 7.02 (m, 1H), 6.82 (m, 1H), 5.93 (m, 1H), 5.73 (m, 1H), 4.72 (d, 1H, *J* = 2.9 Hz), 4.23 (d, 1H, *J* = 8.4 Hz), 3.87 (s, 1H), 3.13 (m, 1H), 2.78 (m, 1H), 2.57 (q, 2H), 1.83 (m, 1H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 134.4, 130.2, 128.5, 128.4, 127.2, 126.8, 126.5, 125.4, 125.3, 118.5, 57.9, 46.6, 45.9, 31.4, 23.8, 12.9; MS m/z : 275 (M^+); Anal. Calcd. for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.48; H, 7.71; N, 5.07.

6-Nitro-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2h)

0.547 g (75%) of yellow liquid ; IR (Neat) : 3362, 1492 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.25 (m, 6H), 6.65 (m, 1H), 5.82 (m, 1H), 5.66 (m, 1H), 4.80 (d, 1H, *J* = 3.3 Hz), 4.18 (d, 1H, *J* = 8.5 Hz), 3.07 (m, 1H), 2.52 (m, 1H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 140.9, 135.4, 133.7, 130.9, 129.6, 128.9, 128.8, 127.6, 126.0, 124.1, 116.3, 56.3, 45.7, 44.8, 31.7; MS m/z : 292 (M^+); Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.62; H, 5.49; N, 9.54.

4-(4-Methylphenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2i)

0.420 g (65%) of colourless solid ; Mp. 64-65 °C; IR (KBr) : 3362, 1476 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, 2H, *J* = 7.7 Hz), 7.24 (d, 2H, *J* = 7.6 Hz), 7.11 (m, 2H), 6.82 (m, 1H), 6.67 (d, 1H, *J* = 7.8 Hz), 5.91 (m, 1H), 5.72 (m, 1H), 4.68 (d, 1H, *J* = 2.7 Hz), 4.16 (d, 1H, *J* = 8.6 Hz), 3.76 (br s, 1H), 3.09 (m, 1H), 2.71 (m, 1H), 2.43 (s, 3H), 1.91 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 139.8, 136.8, 134.0, 130.4, 129.1, 129.0, 126.4, 126.3, 119.1, 115.9, 57.8, 48.4, 48.0, 31.5, 21.1; MS m/z : 261 (M^+); Anal. Calcd. for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 86.90; H, 7.34; N, 5.38.

4-(4-Chlorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2j)

0.540 g (77%) of crystalline white solid ; Mp. 141-142 °C; IR (KBr) : 3364, 1472 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 4H), 7.04 (m, 2H), 6.79 (m, 1H), 6.63 (d, 1H, *J* = 7.9 Hz), 5.88 (m, 1H), 5.67 (m, 1H), 4.62 (d, 1H, *J* = 2.9 Hz), 4.13 (d, 1H, *J* = 8.4 Hz), 3.71 (br s, 1H), 2.98 (m, 1H), 2.60 (m, 1H), 1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 133.9, 130.9, 130.2, 128.9, 128.6, 127.8, 126.3, 125.9, 119.3, 115.9, 57.4, 46.2, 45.8, 31.3; MS m/z : 281 (M^+), 283 (M^+ + 2); Anal. Calcd. for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 77.03; H, 5.74; N, 4.96.

8-Chloro-4-(4-chlorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline(2k)

0.630 g (80%) of colourless solid ; Mp. 171-172 °C; IR (KBr) : 3364, 1472 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 2H), 6.94 (m, 3H), 6.55 (m, 2H), 5.79 (m, 1H), 5.66 (m, 1H), 4.56 (d, 1H, *J* = 2.8 Hz), 4.03 (d, 1H, *J* = 9.1 Hz), 3.72 (s, 1H), 2.94 (m, 1H), 2.56 (m, 1H), 1.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 140.8, 134.3, 133.5, 130.7, 128.6, 128.5, 127.7, 126.2, 123.5, 117.0, 57.3, 46.0, 45.5, 31.2; MS m/z : 315 (M^+), 317 (M^+ +2); Anal. Calcd. for $C_{18}H_{15}Cl_2N$: C, 68.37; H, 4.78; N, 4.43. Found: C, 68.10; H, 4.76; N, 4.45.

General procedure for the Diels-Alder reaction of Schiff's bases 1a-d,j,k,m with cyclohexen-2-one(3)

To a solution of Schiff's base **1a-d,j,k,m** (2.5 mmol) and cyclohexen-2-one (0.360 g, 3.75 mmol) in acetonitrile (10 ml) protected by guard tube was added indium trichloride (0.110 g, 20 mol %) and stirred at room temperature for 24 h. To the reaction mixture aqueous sodium carbonate solution (10 ml) was added and extracted with chloroform (3 × 10 ml). The combined organic layer was washed with water (10 ml) and brine (10 ml), dried over anhydrous sodium sulphate, then concentrated under reduced pressure. The residue was purified by column chromatography using silica gel (230-400 mesh) and eluted with petroleum ether : ethyl acetate (90 : 10) to afford azabicyclo[2.2.2]octanones **6a-d,j,k,m** and **7a-d,j,k,m**.

3-*Exo*-phenyl-2-phenyl-2-azabicyclo[2.2.2]octan-5-one(6a)

0.334 g (45%) of colourless solid; Mp. 123-124 °C; IR (KBr) : 3382, 2936, 1721, 1497 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 6H), 7.14 (m, 2H), 6.64 (m, 2H), 4.80 (d, 1H, J = 1.4 Hz), 4.57 (br s, 1H), 2.81 (m, 1H), 2.73 (m, 1H), 2.45 (m, 1H), 2.39 (m, 1H), 1.91 (m, 1H), 1.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.6, 148.1, 140.0, 130.0, 129.3, 127.8, 125.1, 117.6, 113.0, 62.3, 50.9, 48.1, 42.2, 25.9, 16.3; MS m/z : 277 (M^+); Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.96; N, 5.05. Found: C, 81.98; H, 6.94; N, 5.07.

3-*Endo*-phenyl-2-phenyl-2-azabicyclo[2.2.2]octan-5-one(7a)

0.150 g (20%) of colourless solid; Mp. 113-114 °C; IR (KBr) : 3392, 2928, 1722, 1491 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (m, 6H), 7.18 (m, 2H), 6.65 (m, 2H), 4.66 (d, 1H, J = 2.1 Hz), 4.56 (br s, 1H), 2.82 (m, 1H), 2.71 (m, 1H), 2.46 (m, 1H), 2.22 (m, 2H), 1.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.8, 147.7, 142.1, 129.2, 128.9, 127.5, 125.5, 117.6, 113.2, 65.8, 52.1, 48.4, 45.8, 29.6, 22.6; MS m/z : 277 (M^+); Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.96; N, 5.05. Found: C, 81.88; H, 6.89; N, 5.04.

3-*Exo*-phenyl-2-(4-nitrophenyl)-2-azabicyclo[2.2.2]octan-5-one(6b)

0.377 g (47%) of yellow solid; Mp. 187-188 °C; IR (KBr) : 3368, 2960, 1731, 1599 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99(m, 2H), 7.29 (m, 5H), 6.54 (m, 2H), 4.88 (d, 1H, J = 2.3 Hz), 4.68 (d, 1H, J = 2.0 Hz), 2.76 (m, 1H), 2.65 (m, 1H), 2.52 (m, 1H), 2.32 (m, 1H), 2.06 (m, 1H), 1.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 152.4, 139.2, 138.1, 129.1, 127.9, 126.2, 125.9, 125.7, 113.0, 111.7, 61.9, 50.6, 49.0, 43.0, 25.1, 16.5; MS m/z: 322(M^+); Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C,71.06; H, 5.60; N, 8.66.

3-*Endo*-phenyl-2-(4-nitrophenyl)-2-azabicyclo[2.2.2]octan-5-one(7b)

0.185 g (23%) of yellow solid; Mp. 188-189 °C; IR (KBr) : 3368, 2927, 1729, 1597 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.24 (m, 5H), 6.55 (m,2H), 4.79 (d, 1H, J = 2.3 Hz), 4.66 (m, 1H), 2.86 (m, 1H), 2.71 (m, 1H), 2.49 (m, 1H), 2.16 (m, 2H), 1.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 152.5, 139.3, 138.1, 129.2, 129.1, 128.0, 125.9, 125.7, 125.2, 111.9, 111.7, 65.3, 51.9, 49.2, 45.0, 23.7, 22.1; MS m/z: 322(M^+); Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.56; H, 5.61; N, 8.73.

3-*Exo*-phenyl-2-(4-methoxyphenyl)-2-azabicyclo[2.2.2]octan-5-one(6c)

0.313 g (41%) of yellow solid; Mp. 119-120 °C; IR (KBr) : 3360, 2912, 1718, 1674, 1504 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 5H), 6.73 (d, 2H, J = 7.7 Hz), 6.52 (d, 2H, J = 7.9 Hz), 4.68 (br s, 1H), 4.41 (br s, 1H), 3.67 (s, 3H), 2.71 (m, 2H), 2.39 (m, 2H), 1.78 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

213.8, 151.9, 142.5, 140.3, 129.8, 128.7, 127.2, 126.1, 114.7, 114.1, 62.5, 55.5, 50.9, 48.7,41.8, 26.1, 16.2; MS m/z: 307 (M^+); Anal. Calcd. for $C_{20}H_{21}NO_2$: C,78.15; H, 6.89; N,4.56. Found: C, 78.45; H, 6.92; N,4.57.

3-*Endo*-phenyl-2-(4-methoxyphenyl)-2-azabicyclo[2.2.2]octan-5-one(7c)

0.147 g (19%) of yellow solid ; Mp. 106-107 °C; IR (KBr) : 3376, 2928, 1725, 1507 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 5H), 6.74 (d, 2H, *J* = 8.5 Hz), 6.59 (d, 2H, *J* = 8.5 Hz), 4.57 (br s, 1H), 4.39 (br s, 1H), 3.69 (s, 3H), 2.72 (m, 1H), 2.42 (m, 4H), 1.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 152.0, 142.4, 142.1, 130.0, 128.8, 127.3, 125.6, 114.8, 114.7, 66.1, 55.5, 52.2, 49.3, 46.0, 22.6, 22.2; MS m/z: 307 (M^+); Anal. Calcd. for $C_{20}H_{21}NO_2$: C,78.15; H, 6.89; N,4.56. Found: C, 77.85; H, 6.86; N,4.54.

3-*Exo*-phenyl-2-(4-chlorophenyl)-2-azabicyclo[2.2.2]octan-5-one(6d)

0.385 g (49%) of colourless solid ; Mp. 157-158 °C; IR (KBr) : 3408, 2944, 1725, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.04 (d, 2H, *J* = 8.7 Hz), 6.50 (d, 2H, *J* = 8.7 Hz), 4.70 (br s, 1H), 4.47 (br s, 1H), 2.69 (m, 2H), 2.41 (m, 1H), 2.24 (m, 1H), 1.98 (m, 1H), 1.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 145.5, 139.2, 128.9, 128.7, 127.4, 125.9, 122.2, 114.0, 62.2, 50.7, 48.3, 42.1, 25.7, 16.0; MS m/z: 311 (M^+), 313 (M^+ + 2); Anal. Calcd. for $C_{19}H_{18}ClNO$: C,73.19; H,5.82; N,4.49. Found: C, 72.88; H, 5.79; N,4.47.

3-*Endo*-phenyl-2-(4-chlorophenyl)-2-azabicyclo[2.2.2]octan-5-one(7d)

0.142 g (19%) of colourless solid ; Mp. 144-145 °C; IR (KBr) : 3376, 2928, 1731, 1494 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 5H), 7.07 (d, 2H, *J* = 8.6 Hz), 6.53 (d, 2H, *J* = 8.6 Hz), 4.59 (br s, 1H), 4.46 (br s, 1H), 2.76 (m, 2H), 2.47 (m, 2H), 2.24 (m, 2H), 1.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.0, 145.6, 140.3, 128.9, 128.1, 127.5, 125.3, 122.2, 114.3, 65.7, 51.9, 48.7, 45.6, 22.5, 22.3; MS m/z: 311 (M^+), 313 (M^+ + 2); Anal. Calcd. for $C_{19}H_{18}ClNO$: C,73.19; H,5.82; N,4.49. Found: C, 72.90; H, 5.78; N,4.46.

3-*Exo*-(4-chlorophenyl)-2-phenyl-2-azabicyclo[2.2.2]octan-5-one(6j)

0.242 g (31%) of colourless solid ; Mp. 138-139 °C; IR (KBr) : 3384, 2937, 1722, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 5H), 6.72 (m, 2H), 6.53 (m, 2H), 4.72 (d, 1H, *J* = 1.8 Hz), 4.57 (br s, 1H), 2.66 (m, 2H), 2.41 (m, 1H), 2.19 (m, 2H), 1.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.1, 147.9, 138.6, 134.8, 131.3, 129.5, 129.4, 127.5, 118.3, 113.0, 61.8, 50.7, 48.1, 42.2, 25.9, 16.2; MS m/z: 311 (M^+), 313 (M^+ + 2); Anal. Calcd. for $C_{19}H_{18}ClNO$: C,73.19; H,5.82; N,4.49. Found: C, 72.87; H, 5.75; N,4.45.

3-*Endo*-(4-chlorophenyl)-2-phenyl-2-azabicyclo[2.2.2]octan-5-one(7j)

0.262 g (34%) of colourless solid ; Mp. 126-127 °C; IR (KBr) : 3395, 2927, 1724, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 6.72 (m, 2H), 6.61 (m, 2H), 4.61 (br s, 1H), 4.53 (br s, 1H), 2.74 (m, 2H), 2.48 (m, 1H), 2.24 (m, 2H), 1.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.3, 147.7, 140.2, 133.1, 129.2, 129.1, 127.0, 118.0, 113.3, 65.2, 52.0, 48.5, 45.8, 22.5, 22.3; MS m/z: 311 (M^+), 313 (M^+ + 2); Anal. Calcd. for $C_{19}H_{18}ClNO$: C,73.19; H,5.82; N,4.49. Found: C, 72.86; H, 5.72; N,4.48.

3-*Exo*-(4-chlorophenyl)-2-(4-chlorophenyl)-2-azabicyclo[2.2.2]octan-5-one(6k)

0.299 g (34%) of colourless solid ; Mp. 163-164 °C; IR (KBr) : 3377, 2926, 1730, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 4H), 7.07 (d, 2H, *J* = 8.2 Hz), 6.44 (d, 2H, *J* = 8.3 Hz), 4.66 (br s, 1H), 4.57 (br s, 1H), 2.64 (m, 2H), 2.35 (m, 1H), 2.18 (m, 1H), 1.88 (m, 1H), 1.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.5, 146.3, 137.9, 133.2, 129.2, 129.1, 127.3, 122.7, 114.1, 61.7, 50.5, 48.4, 42.0,

25.7, 16.0; MS m/z: 345 (M^+), 347 ($M^+ + 2$); Anal. Calcd. for $C_{19}H_{17}Cl_2NO$: C,65.91; H,4.95; N,4.05. Found: C, 66.12; H, 4.92; N,4.02.

3-*Endo*-(4-chlorophenyl)-2-(4-chlorophenyl)-2-azabicyclo[2.2.2]octan-5-one(7k)

0.338 g (40%) colourless solid; Mp. 141-142 °C; IR (KBr) : 3374, 2927, 1730, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.06 (d, 2H, J = 8.9 Hz), 6.51 (d, 2H, J = 8.9 Hz), 4.56 (d, 1H, J = 1.4 Hz), 4.44 (br s, 1H), 2.72 (m, 2H), 2.40 (m, 1H), 2.07 (m, 2H), 1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.0, 146.4, 138.8, 133.3, 129.2, 129.1, 127.0, 122.8, 114.6, 65.2, 52.0, 49.0, 45.7, 22.6, 22.3; MS m/z: 345 (M^+), 347 ($M^+ + 2$); Anal. Calcd. for $C_{19}H_{17}Cl_2NO$: C, 65.91; H, 4.95; N, 4.05. Found: C, 65.72; H, 4.97; N, 4.06.

3-*Exo*-phenyl-2-(4-methylphenyl)-2-azabicyclo[2.2.2]octan-5-one(6m)

0.327 g (45%) of colourless solid; Mp. 172-173 °C; IR (KBr) : 3372, 2938, 1726, 1497 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 5H), 6.96 (d, 2H, J = 8.0 Hz), 6.52 (d, 2H, J = 8.1 Hz), 4.75 (br s, 1H), 4.52 (br s, 1H), 2.73 (m, 2H), 2.37 (m, 2H), 2.21 (s, 3H), 1.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.6, 145.8, 140.1, 129.7, 128.6, 127.2, 126.7, 126.0, 112.9, 62.2, 50.8, 48.1, 41.9, 25.9, 20.0, 16.2; MS m/z: 291 (M^+); Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.38; H, 7.23; N, 4.78.

3-*Endo*-phenyl-2-(4-methylphenyl)-2-azabicyclo[2.2.2]octan-5-one(7m)

0.122 g (17%) of colourless solid; Mp. 159-160 °C; IR (KBr) : 3369, 2934, 1730, 1498 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (m, 5H), 6.96 (d, 2H, J = 7.3 Hz), 6.55 (d, 2H, J = 7.9 Hz), 4.60 (br s, 1H), 4.49 (br s, 1H), 2.76 (m, 1H), 2.33 (m, 3H), 2.20 (s, 3H), 1.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.8, 151.2, 145.2, 142.1, 129.7, 128.8, 127.4, 126.9, 125.6, 113.3, 65.9, 52.1, 48.7, 45.9, 25.6, 22.6, 20.1; MS m/z: 291 (M^+); Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.65; H, 7.29; N, 4.82.

General procedure for the Diels-Alder reaction of Schiff's bases 1a,c,d,k,m with cyclohepten-2-one(8)

To a solution of Schiff's base **1a,c,d,k,m** (2.5 mmol) and cyclohepten-2-one (0.413 g, 3.75 mmol) in acetonitrile (10 ml) protected by a guard tube was added indium trichloride (0.110 g, 20 mol %) and stirred at room temperature for 20-26 h. To the reaction mixture aqueous sodium carbonate solution (10 ml) was added and extracted with chloroform (3 × 10 ml). The combined organic layer was washed with water (10 ml) and brine (10 ml), dried over anhydrous sodium sulphate, then concentrated under reduced pressure. The residue was purified by column chromatogaphy using silica gel (230-400 mesh) and eluted with petroleum ether : ethyl acetate (90 : 10) to afford azabicyclo[3.2.2]nonanones **9a,c,d,k,m** and **10a,c,d,k,m**.

7-*Exo*-phenyl-6-phenyl-6-azabicyclo[3.2.2]nonan-8-one(9a)

0.211 g (29%) of colourless solid; Mp. 110-111 °C; IR (KBr) : 3407, 2940, 1729, 1512 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 6H), 7.04 (m, 2H), 6.69 (m, 2H), 5.03 (br s, 1H), 4.50 (br s, 1H), 2.82 (m, 2H), 2.43 (m, 2H), 2.20 (m, 2H), 1.60 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.6, 149.1, 139.9,

128.9, 128.5, 127.4, 127.1, 126.2, 118.3, 116.2, 60.5, 55.9, 54.9, 42.0, 35.2, 24.0, 20.0; MS m/z: 291 (M^+); Anal. Calcd. for $C_{20}H_{21}NO$: C,82.44; H,7.26; N,4.81. Found: C, 82.65; H, 7.23; N,4.76.

7-*Endo*-phenyl-6-phenyl-6-azabicyclo[3.2.2]nonan-8-one(10a)

0.195 g (27%) of colourless solid ; Mp. 153-154 °C; IR (KBr) : 3414, 2936, 1720, 1501 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22 (m, 6H), 6.71 (m, 2H), 6.60 (m, 2H), 4.83 (br s, 1H), 4.65 (br s, 1H), 3.20 (d, 1H, *J* = 5.4 Hz), 2.81 (m, 1H), 2.50 (m, 1H), 2.21 (m, 2H), 1.87 (m, 2H), 1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.5, 147.2, 141.4, 129.3, 128.9, 127.3, 126.9, 126.0, 118.3, 112.1, 64.4, 57.1, 48.8, 44.0, 30.7, 30.6, 20.2; MS m/z: 291 (M^+); Anal. Calcd. for $C_{20}H_{21}NO$: C,82.44; H,7.26; N,4.81. Found: C, 82.75; H, 7.28; N,4.83.

7-*Exo*-phenyl-6-(4-methoxyphenyl)-6-azabicyclo[3.2.2]nonan-8-one(9c)

0.250 g (31%) of yellow solid; Mp. 155-156 °C; IR (KBr) : 3420, 2933, 1722, 1518, 1249 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5H), 6.66 (m, 4H), 4.92 (br s, 1H), 4.35 (br s, 1H), 3.66 (s, 3H), 2.83 (m, 2H), 2.43 (m, 1H), 2.22 (m, 2H), 1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.0, 152.4, 143.5, 140.1, 128.3, 127.4, 126.8, 117.7, 114.0, 59.9, 56.9, 55.4, 55.0, 41.5, 35.7, 23.7, 19.9; MS m/z: 321 (M^+); Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.32; H, 7.18; N, 4.33.

7-*Endo*-phenyl-6-(4-methoxyphenyl)-6-azabicyclo[3.2.2]nonan-8-one(10c)

0.134 g (17%) of yellow solid; Mp. 107-108 °C; IR (KBr) : 3418, 2936, 1728, 1517, 1245 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (m, 5H), 6.77 (d, 2H, *J* = 8.4 Hz), 6.50 (d, 2H, *J* = 8.4 Hz), 4.73 (br s, 1H), 4.56 (br s, 1H), 3.69 (s, 3H), 3.11 (m, 1H), 2.82 (m, 1H), 2.53 (m, 1H), 2.28 (m, 2H), 1.72 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.4, 151.0, 141.9, 141.6, 128.7, 127.1, 125.9, 114.8, 112.6, 64.7, 57.1, 55.8, 48.8, 44.2, 30.8, 30.4, 20.1; MS m/z: 321 (M^+); Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.69; H, 7.24; N, 4.38.

7-*Exo*-phenyl-6-(4-chlorophenyl)-6-azabicyclo[3.2.2]nonan-8-one(9d)

0.247 g (30%) of colourless solid; Mp. 120-121°C; IR (KBr) : 3427, 2927, 1729, 1499 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (m, 5H), 6.99 (d, 2H, *J* = 8.4 Hz), 6.60 (d, 2H, *J* = 8.4 Hz), 4.94 (br s, 1H), 4.38 (br s, 1H), 2.86 (m, 1H), 2.73 (m, 1H), 2.47 (m, 1H), 2.01 (m, 2H), 1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 147.5, 139.2, 128.5, 128.3, 127.1, 127.0, 122.9, 117.2, 59.9, 55.9, 54.6, 41.8, 34.8, 23.7, 19.7; MS m/z: 325 (M^+), 327 (M^+ +2); Anal. Calcd. for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; N, 4.30. Found: C, 73.95; H, 6.21; N, 4.32.

7-*Endo*-phenyl-6-(4-chlorophenyl)-6-azabicyclo[3.2.2]nonan-8-one(10d)

0.386 g (48%) of colourless solid; Mp. 160-161°C; IR (KBr) : 3420, 2938, 1721, 1495 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 7.23 (m, 5H), 7.09 (d, 2H, *J* = 8.9 Hz), 6.50 (m, 2H), 4.74 (br s, 1H), 4.55 (d, 1H, *J* = 2.5 Hz), 3.15 (m, 1H), 2.78 (m, 1H), 2.52 (m, 1H), 2.20 (m, 2H), 1.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 145.1, 141.2, 128.9, 128.8, 127.3, 125.8, 121.2, 116.4, 113.0, 64.4, 56.8, 48.9, 43.7, 30.5, 30.4, 20.0; MS m/z: 325 (M^+), 327 (M^+ +2); Anal. Calcd. for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; N, 4.30. Found: C, 73.32; H, 6.20; N, 4.92.

7-*Exo*-(4-chlorophenyl)-6-(4-chlorophenyl)-6-azabicyclo[3.2.2]nonan-8-one(9k)

0.256 g (29%) of colourless solid ; Mp. 115-116 °C; IR (KBr) : 3428, 2926, 1728, 1498 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.04 (m, 6H), 6.55 (m, 2H), 4.91 (d, 1H, *J* = 2.5 Hz), 4.39 (br s, 1H), 2.95 (m, 2H), 2.46 (m, 1H), 2.14 (m, 2H), 1.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 147.3, 137.8,

131.2, 128.9, 127.0, 117.4, 114.5, 112.8, 59.4, 57.1, 56.2, 41.7, 34.9, 23.7, 19.6; MS m/z: 359 (M^+), 361 (M^+ +2); Anal. Calcd. for $C_{20}H_{19}Cl_2NO$: C, 66.68; H, 5.32; N, 3.89. Found: C, 66.42; H, 5.29; N, 3.88.

7-*Endo*-(4-chlorophenyl)-6-(4-chlorophenyl)-6-azabicyclo[3.2.2]nonan-8-one(10k)

0.353 g (39%) of colourless solid ; Mp. 125-126 °C; IR (KBr) : 3421, 2939, 1722, 1496 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 (m, 5H), 6.57 (m, 3H), 4.68 (br s, 1H), 4.53 (d, 1H, J = 2.1 Hz), 3.09 (m, 1H), 2.70 (m, 1H), 2.52 (m, 1H), 2.19 (m, 2H), 1.84 (m, 2H), 1.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 145.5, 139.4, 133.1, 129.1, 128.8, 127.4, 116.1, 113.1, 112.9, 63.9, 56.7, 48.9, 43.7, 30.5, 29.8, 20.0; MS m/z: 359 (M^+), 361 (M^+ +2); Anal. Calcd. for $C_{20}H_{19}Cl_2NO$: C, 66.68; H, 5.32; N, 3.89. Found: C, 66.97; H, 5.32; N, 3.90.

7-*Exo*-phenyl-6-(4-methylphenyl)-6-azabicyclo[3.2.2]nonan-8-one(9m)

0.190 g (25%) of colourless solid; Mp. 138-139 °C; IR (KBr) : 3417, 2936, 2859, 1718, 1515 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 6.97 (d, 2H, J = 7.8 Hz), 6.62 (d, 2H, J = 8.0 Hz), 4.98 (br s, 1H), 4.42 (br s, 1H), 2.81 (m, 2H), 2.40 (m, 3H), 2.18 (s, 3H), 1.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1, 146.9, 140.0, 129.1, 128.3, 127.5, 127.2, 126.8, 116.3, 59.9, 56.1, 54.9, 41.7, 35.3, 23.8, 20.1, 19.8; MS m/z: 305 (M^+); Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59. Found: C, 82.72; H, 7.61; N, 4.60.

7-*Endo*-phenyl-6-(4-methylphenyl)-6-azabicyclo[3.2.2]nonan-8-one(10m)

0.206 g (27%) of colourless solid; Mp. 148-149 °C; IR (KBr) : 3422, 2936, 1710, 1517 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5H), 6.96 (d, 2H, J = 7.8 Hz), 6.55 (d, 2H, J = 7.9 Hz), 4.81 (br s, 1H), 4.64 (br s, 1H), 3.20 (d, 1H, J = 3.3Hz), 2.80 (m, 1H), 2.56 (m, 1H), 2.26 (m, 5H), 1.95 (m, 2H), 1.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.4, 144.9, 141.6, 130.5, 128.9, 127.7, 126.5, 125.4, 112.6, 111.0, 64.7, 57.6, 48.8, 44.3, 32.0, 29.1, 20.7, 19.3; MS m/z: 305 (M^+); Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59. Found: C, 82.25; H, 7.54; N, 4..56.

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References

1. A part of this work has already been published as a preliminary communication. Babu, G.; Perumal, P. T. *Tetrahedron Lett.*, **1997**, *38*, 5025.
2. a) Weinreb, S. M. in *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I.*Pergamon Press:* Oxford, **1991**, Vol. 5, p.401. b) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*, Academic Press: New York, **1987**, Chaps. 2 and 9.
3. a) Lin, Y. M.; Oh, T. *Tetrahedron Lett.* **1997**, *38*, 727. b) Coz, L. L.; Veyrat-Martin, C.; Wartski, L.; Seyden-Penne, J.; Bois, C.; Philoche-Levisalles, M. *J. Org. Chem.* **1990**, *55*, 4870. c) Maggini, M.; Prato, M.; Scorrano, G. *Tetrahedron Lett.* **1990**, *31*, 6243.
4. a) Grieco, P. A.; Bahsas, A. *Tetrahedron Lett.* **1988**, *29*, 5855. b) Borrione, B.; Prato, M.; Scorrano, G.; Stivanello, M. *J. Chem. Soc., Perkin Trans. 1.* **1989**, 2245. c) Gregoire, P. J.; Mellor, J. M.; Merriman, G. D. *Tetrahedron Lett.* **1991**, *32*, 7099. d) Mellor, J. M.; Merriman, G. D.; Riviere, P. *Tetrahedron Lett.* **1991**, *32*, 7103.

5. a) Linkert, F.; Laschat, S.; Kotila, S.; Fox, T. *Tetrahedron* **1996**, *52*, 955. b) Linkert, F.; Laschat, S.; Knickmeier, M. *Liebigs Ann. Chem.* **1995**, 985. c) Linkert, F.; Laschat, S. *Synlett.* **1994**, 125. d) Lease, T. G.; Shea, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 2248. e) Barleunga, J.; Tomas, M.; Ballesteros, A.; Gotor, V. *J. Chem. Soc., Chem. Commun.* **1989**, 267.
6. a) Lucchini, V.; Prato, M.; Scorrano, G.; Tecilla, P. *J. Org. Chem.* **1988**, *53*, 2251. b) Lucchini, V.; Prato, M.; Scorrano, G.; Tecilla, P. *J. Heterocyclic Chem.* **1986**, *23*, 1153. c) Lucchini, V.; Prato, M.; Quintily, V.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1984**, 48.
7. a) Kobayashi, S.; Araki, M.; Ishitani, H.; Nagayama, S.; Hachiya, I. *Synlett.* **1995**, 233. b) Kobayashi, S.; Ishitani, H.; Nagayama, S. *Synthesis* **1995**, 1195. c) Kobayashi, S.; Ishitani, H.; Nagayama, S. *Chem. Lett.* **1995**, 423.
8. Zulotukhin, M. A.; Sedova, E. A.; Sorokina, Yu, L.; Salazkin, S. N.; Sangalov, Yu. A.; Sultanova, V. S.; Panasenko, A. A.; Khalivov, L. M.; Muslukhov, R. M. *Makromol. Chem.* **1990**, *191*, 1477.
9. Zhun, V. I.; Tsvetkov, A. L.; Sukhikh, A. S.; Sheludyakov, V. D. *Zh. Obshch. Khim.* **1990**, *60*, 1104 *(Russ); Chem. Abst.* **1990**, *113*, 212074d.
10. Mukaiyama, T.; Ohno, T.; Nishimura, T.; Han, J. S.; Kobayashi, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2524.
11. Mukaiyama, T.; Ohno, T.; Nishimura, T.; Suda, S.; Kobayashi, S. *Chem. Lett.* **1991**, 1059.
12. Ohnishi, R.; Suzuki, I.; Ichikawa, M. *Chem. Lett.* **1991**, 841.
13. Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1991**, 949.
14. Loh, T. -P.; Pie, J.; Cao, G. -Q. *Chem. Commun.* **1996**, 1819.
15. Loh, T. -P.; Pie, J.; Lin, M. *Chem. Commun.* **1996**, 2315.
16. Roe, A.; Montgomery, J. A. *J. Am. Chem. Soc.* **1953**, *75*, 910.
17. Fringuelli, F.; Minuti, L.; Radics, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4607.
18. Fringuelli, F.; Taticchi, A. *Org. Prep. Proc. Int.* **1989**, 139.
19. Babu, G.; Sridar, V.; *Ind. J. Chem. Sect. B.* **1996**, *35B*, 711.
20. Garbisch, E. W. Jr. *J. Org. Chem.* **1965**, *30*, 2109.
21. Krishna, R.; Velmurugan, D.; Babu, G.; Perumal, P. T. (Manuscript under preparation).
22. a) Holmes, A. B.; Thompson, J.; Baxter, A. J. G.; Dixon, J. *J. Chem. Soc., Chem. Commun.* **1985**, 37. b) Birkinshaw, T. N.; Tabor, A. B.; Holmes, A. B.; Kaye, P.; Mayne, P. M.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1599. c) Birkinshaw, T. N.; Tabor, A. B.; Holmes, A. B.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1601.