



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

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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.

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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-dienophiles³ as well as heterodienes⁴ and also undergo intramolecular Diels-Alder reactions.⁵ Lewis acids such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$, TFA have been found to catalyze the Diels-Alder reactions of keto-imines⁶ 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 imines⁷ 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 reactions¹⁴ and Diels-Alder reactions¹⁵ 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.

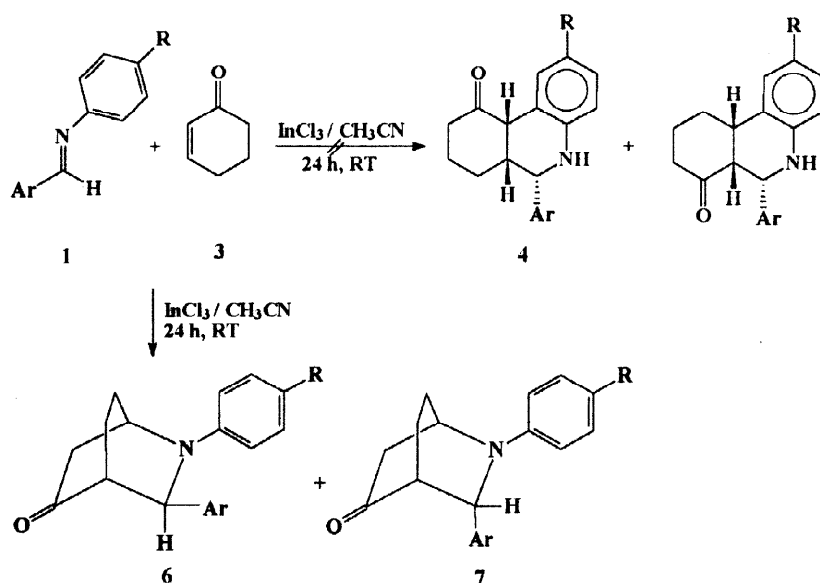
Results and Discussion

The Schiff's bases were prepared according to the published procedure¹⁶ by condensation of substituted anilines with substituted benzaldehydes.

In the presence of 20 mol % indium trichloride (InCl_3), *N*-benzylidene 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.

trichloride (Scheme 2). Since imine acted as a heterodiene in the Diels-Alder reaction of Schiff's base with cyclopentadiene, we envisaged the formation of phenanthridinone derivatives¹ **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



The proposed structure was further ascertained by x-ray analysis²¹ 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 % InCl₃.^a

Entry	Schiff's base	R	Ar	product ratio ^b of 6:7	Overall yield %
1	1a	H	C ₆ H ₅	69 : 31	65
2	1b	NO ₂	C ₆ H ₅	67 : 33	70
3	1c	OCH ₃	C ₆ H ₅	68 : 32	60
4	1d	Cl	C ₆ H ₅	73 : 27	68
5	1j	H	<i>p</i> -Cl-C ₆ H ₄	48 : 52	65
6	1k	Cl	<i>p</i> -Cl-C ₆ H ₃	47 : 53	74
7	1m	CH ₃	C ₆ H ₅	73 : 27	62

^a : All reactions were conducted at room temperature by the addition of 20 mol % InCl₃ 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-one²⁰ 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 cyclohepten-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

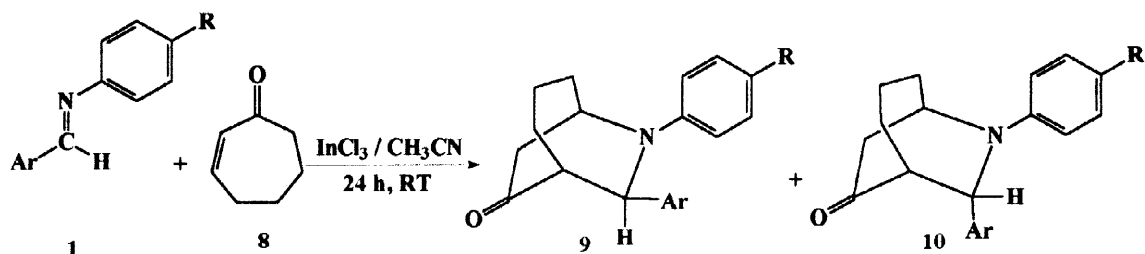


Table 3. Diels-Alder reaction of Schiff's bases with cyclohepten-2-one employing 20 mol % InCl₃.

Entry	Schiff's base	R	Ar	product ratio ^a of 9:10	Time, h	Overall yield %
1	1a	H	C ₆ H ₅	52 : 48	24	56
2	1c	OCH ₃	C ₆ H ₅	65 : 35	26	48
3	1d	Cl	C ₆ H ₅	39 : 61	20	78
4	1k	Cl	<i>p</i> -Cl-C ₆ H ₄	42 : 58	21	68
5	1m	CH ₃	C ₆ H 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 (¹³C NMR) were recorded on a Bruker (75 MHz) spectrometer. Mass spectra were recorded on Varian VG 70-70 H mass spectrometer. Acetonitrile 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) in acetonitrile (10 ml) protected by a guard tube was added indium trichloride (0.110 g, 20 mol %)

and stirred 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 Na₂SO₄, 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₇N: 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₆N₂O₂: 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-3H-cyclopenta[c]quinoline^{7b} (2c)

0.401 g (58%) of brown liquid; IR (Neat) : 3349, 1502 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₉NO: 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-3H-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, CDCl₃) δ 7.36 (m, 5H), 7.03 (d, 1H, *J* = 2.1 Hz), 6.93 (dd, 1H, *J* = 2.2, 8.5 Hz), 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₆ClN: 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-3H-cyclopenta[c]quinoline(2e)

0.663 g (90%) of brown liquid ; IR (Neat) : 3395, 1484 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₈ClN: 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₇NO₂: 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-3H-cyclopenta[c]quinoline(2g)

0.563 g (82%) of brown liquid ; IR (Neat) : 3382, 1487 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₂₀H₂₁N: 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-3H-cyclopenta[c]quinoline(2h)

0.547 g (75%) of yellow liquid ; IR (Neat) : 3362, 1492 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₆N₂O₂: 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₉N: 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₆ClN: 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-3H-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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₈H₁₅Cl₂N: 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₉NO: 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₉NO: 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₈N₂O₃ : 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₉H₁₈N₂O₃ : 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, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 $\times$ 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[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, $J = 3.3$ Hz), 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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