Three-component Aza-Diels-Alder reactions using $Yb(OTf)_3$ catalyst under conventional/ultrasonic techniques

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The $Yb(OTf)_3$ catalyzed formal aza-Diels-Alder (or Povarov) reaction of cyclopentadiene and 1,3-cyclohexadiene with in situ-generated N-arylimines under conventional/ultrasonic techniques is herein described. This kind of three-component Povarov reaction results in quinoline and phenanthridine derivatives, which are important biological compounds.

Keywords: multi-component reaction, aza-Diels-Alder reaction, Povarov reaction, ultrasonic irradiation, lanthanide triflates, quinoline, phenanthridine

1. Introduction

Multi-component reactions allow the construction of several new bonds in a one-pot reaction. Therefore, multi-component reactions (MCRs) have increasing importance in synthetic organic chemistry and their methods provide significant benefits over conventional synthesis [1]. Among these benefits, a high degree of atomic economy, easier progress of reactions, decreased reaction times, low power consumption, and less handling of toxic substances are also the most important [2].

Quinoline and phenanthridine derivatives are one of the most important classes of natural products and exhibit a wide spectrum of biological activities such as psychotropic, cytotoxic, anti-allergic, anti-inflammatory, antipyretic, estrogenic, antimicrobial, antibacterial, antimalarial, antiplatelet, antitumoral and, anticancer, as insecticides, for the inhibition of HIV-1RT and as, dopamine D_1 receptor agonists [3]. The aza-Diels-Alder (or Povarov) reaction is a powerful and efficient means for the preparation of quinolines and phenanthridines [4]. The imines derived from aromatic amines and aldehydes act as heterodienes and react with various dienophiles in the presence of different acid catalysts. Lewis acids like $AlCl_3$ [5], $ZnCl_2$ [6], $BF_3.OEt_2$ [7], $TiCl_4$ [8], $InCl_3$ [9], $ZrCl_4$ [10], trifluoro acetic acid [11], p-TsOH [12], and HBF_4 [13] have been found to catalyze these reactions. However, Lewis acids often promote these reactions more than the stoichiometric amounts of the acids required because the acids can be trapped by the nitrogen of both the reactant and product. In recent years, lanthanide triflates [14], CAN [15], L-proline [16], protic acids [17], montmorrillonite clay [18] and polymer-supported benzotriazole [19] have been reported to promote these reactions. Furthermore, lanthanide triflates are stable in water and only a

catalytic amount of the triflate is enough to complete these reactions. Moreover the aza-Diels-Alder reactions have been reported to proceed under photochemical conditions and microwave heating, as well as in aqueous media and ionic liquids [20].

Sonochemistry is the application of ultrasound to chemical reactions and processes. Luche and co-workers have written a number of studies that provided the fundamentals of sonochemistry [21]. In recent years, ultrasound irradiation has increasingly been used in organic synthesis [22]. This technique is able to activate many organic reactions due to cavitational collapse. Cavitation induces high temperatures and pressures inside the bubbles, leading to turbulent flow of the liquid and increased mass transfer [23]. Compared with traditional methods, this technique provides higher yields and selectivities, shorter reaction times and milder reaction conditions [24].

In this study, we have reported on the one-pot three-component, catalytic aza-Diels-Alder reaction using ytterbium (III) triflate (ytterbium (III) trifluoromethane sulfonate) under conventional/ultrasonic conditions.

2. Material and Methods

2.1 General Methods

NMR spectra and 2D experimental studies were determined on a Bruker Avance III-500 MHz NMR. Chemical shifts are given in ppm downfield from Me_4Si in $CDCl_3$ solution. Coupling constants are given in Hz. The FTIR spectra were recorded on a Perkin-Elmer FT-IR spectrometer (ATR) and absorption frequencies are reported in cm^{-1}. MS spectra were recorded on a Thermo Elemental X Series ICP-MS. Ultrasonication was performed in a Bandelin-Sonorex Ultrasonic Bath (Super RK) with a frequency of 35 kHz and a power of 230 W. The internal dimensions of the ultrasonic cleaner tank were 240x140x100 mm with liquid holding capacity of 3L. The reactor was a 100 mL pyrex round-bottom flask. The reaction flasks were suspended at the center of the bath, and the addition or removal of water controlled the temperature of the water bath. Melting points were measured on a Gallenkamp melting-point apparatus. Silica gel 60 (Merck) was used for column separation. TLC was conducted on standard conversion aluminum sheets pre-coated with a 0.2-mm layer of silica gel. All reagents were commercially available. Toluene was distilled and stored on sodium wire before use.

*2.2 General Procedure for the Synthesis of Tetrahydroquinolines and Hexahydrophenanthridines under Conventional Conditions (**4a-p** and **6a-d**)*

Aryl amine (1.00 mmol), aromatic aldehyde (1.00 mmol), freshly distilled cyclopentadiene or 1,3-cyclohexadiene (3.00 mmol) were added successively to a solution of $Yb(OTf)_3$ (62.2 mg, 0.1 mmol) in dry PhMe (5.00 mL) at room temperature. The reaction was refluxed at 110 ^{o}C for 6h under a nitrogen atmosphere. After completion of the reaction, as indicated by TLC monitoring, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3x10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in a vacuum, and the resulting product was purified by column

chromatography over silica gel to afford the corresponding tetrahydroquinolines and hexahydrophenanthridines.

*2.3 General Procedure for the Synthesis of Tetrahydroquinolines and Hexahydrophenanthridines under Ultrasonic Irradiation (**4a-p** and **6a-d**)*

For the ultrasound-assisted method, a mixture of $Yb(OTf)_3$ (12.4 mg, 0.02 mmol), aryl amine (1.00 mmol), aromatic aldehyde (1.00 mmol) and freshly distilled cyclopentadiene or 1,3-cyclohexadiene (3.00 mmol) in dry PhMe (3.00 mL) was irradiated with ultrasound of low power (with a frequency of 35 kHz and a nominal power of 230W) at 50 ^{o}C under a nitrogen atmosphere for 40 minutes. The reaction flask was located at the maximum energy area in the cleaner and the surface of the reactants was placed slightly lower than the level of the water. The addition or removal of water controlled the temperature of the water bath. After completion of the reaction, as indicated by TLC monitoring, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3x10 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in a vacuum. The resulting product was purified by column chromatography over silica gel to afford the corresponding tetrahydroquinolines and hexahydrophenanthridines.

*2.3.1 cis-6-phenyl-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4a**)*

Pale white crystals, m.p. 105-107 ^{o}C. FTIR (ATR, cm^{-1}): 3377, 3053, 3024, 2914, 2848, 1602, 1573, 1516, 1494, 1460, 1401, 1375, 1355, 1291, 1273, 1240, 1141, 1095, 1088, 1029, 813, 788, 751, 729. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.86-1.91 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.72-2.77 (dt, J_1= 8.50 Hz, J_2= 2.00 Hz, 1H), 3.10-3.15 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.00 Hz, 1H), 4.28-4.29 (d, J= 8.50 Hz, 1H), 4.50 (br s, 1H), 4.75-4.76 (d, J= 2.00 Hz, 1H), 5. 66 (br s, 1H), 5.94 (br s, 1H), 7.21-7.23 (d, J= 8.00 Hz, 1H), 7.28-7.30 (d, J= 8.50 Hz, 1H), 7.33-7.47 (m, 5H), 7.56-7.58 (d, J= 8.00 Hz, 2H), 7.75-7.77 (d, J= 8.00 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.35, 46.17, 47.05, 58.25, 118.77, 119.52, 120.21, 123.66, 125.08, 125.11, 126.71, 127.35, 127.38, 128.63, 130.67, 132.59, 134.02, 139.83, 143.07. MS *m/z* (ESI): 298 (M^+),245, 232, 211, 195, 172.

*2.3.2 cis-6-(4-bromophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4b**)*

Brown cyrstals, m.p. 170-172 ^{o}C. FTIR (ATR, cm^{-1}): 3372, 3050, 2912, 2847, 1580, 1575, 1516, 1486, 1461, 1394, 1355, 1292, 1240, 1195, 1141, 1070, 1008, 812, 789, 752, 728. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.84-1.88 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.65-2.70 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.04-3.10 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz 1H), 4.25-4.27 (d, J= 8.50 Hz, 1H), 4.41 (br s, 1H), 4.70-4.71 (d, J=2.50 Hz, 1H), 5.65 (br s, 1H), 5.94 (br s, 1H), 7.20-7.22 (d, J= 8.50 Hz, 1H), 7.29-7.31 (d, J= 8.00 Hz, 1H), 7.39-7.45 (m, 4H), 7.54-7.57 (d, J= 8.00 Hz, 2H), 7.74-7.77 (t, J= 8.50 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.23, 45.96, 46.89, 57.72, 119.06, 119.43, 120.17, 121.10, 123.65, 125.18, 127.26, 128.40, 128.66, 130.54, 131.71, 132.56, 133.98, 139.42, 142.08. MS *m/z* (ESI): 376 (M^+), 311, 221, 205, 168.

*2.3.3 cis-6-(4-chlorophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4c**)*

Pale white crystals, m.p. 166-168 °C. FTIR (ATR, cm^{-1}): 3395, 3062, 3024, 2926, 2908, 2845, 1570, 1517, 1487, 1458, 1395, 1372, 1353, 1292, 1270, 1238, 1136, 1085, 1009, 815, 789, 772, 753, 737. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.84-1.89 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.66-2.71 (dt, J_1= 8.50 Hz, J_2= 3.00 Hz, 1H), 3.04-3.10 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 3.00 Hz, 1H), 4.26-4.28 (d, J= 8.50 Hz, 1H), 4.42 (br s, 1H), 4.73 (d, J= 3.00 Hz, 1H), 5.65 (br s, 1H), 5.95 (br s, 1H), 7.19-7.23 (d, J= 8.00 Hz, 1H), 7.28-7.33 (d, J= 8.00 Hz, 1H), 7.39-7.45 (m, 4H), 7.50-7.52 (d, J= 8.00 Hz, 2H), 7.74-7.77 (t, J= 7.00 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.26, 46.05, 46.93, 57.70, 119.06, 119.46, 120.20, 123.69, 125.20, 127.29, 128.06, 128.68, 128.79, 130.57, 132.60, 133.06, 134.02, 139.48, 141.58. MS *m/z* (ESI): 332 (M+), 293, 266, 245, 216, 194, 172.

*2.3.4 trans-6-(4-chlorophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4c'**)*

pale yellow oil, ^{1}H NMR ($CDCl_3$, 500 MHz): 2.09-2.13 (d, J= 16.50 Hz, 1H), 2.50-2.54 (m, 1H), 2.73-2.78 (dd, J_1= 10.50 Hz, J_2= 7.00 Hz, 1H), 3.80-3.82 (d, J= 10.50 Hz, 1H), 4.11 (br s, 1H), 4.55 (br s, 1H), 5.72 (br s, 1H), 6.05 (br s, 1H), 7.31-7.34 (m, 2H), 7.37-7.50 (m, 6H), 7.62-7.64 (d, J= 8.00 Hz, 1H), 7.77-7.83 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz):35.78, 42.81, 47.57, 57.80, 118.20, 119.43, 119.81, 122.96, 125.24, 127.75, 128.25, 128.63, 128.80, 130.01, 132.71, 133.72, 136.21, 139.83, 141.45

*2.3.5 cis- 6-(p-tolyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4d**)*

Pale white cyrstals, m.p. 122-124 °C. FTIR (ATR, cm^{-1}): 3376, 3051, 3020, 2918, 2870, 2849, 1611, 1600, 1573, 1514, 1495, 1459, 1398, 1375, 1356, 1291, 1240, 1195, 1141, 1107, 1032, 1020, 999, 811, 787, 753, 728. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.80-1.85 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.32 (s, 3H), 2.63-2.69 (dt, J_1= 8.50 Hz, J_2= 3.00 Hz, 1H), 2.99-3.05 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 3.00 Hz, 1H), 4.18-4.20 (d, J= 8.50 Hz, 1H), 4.39 (br s, 1H), 4.63-4.64 (d, J= 3.00 Hz, 1H), 5.58 (br s, 1H), 5.86 (br s, 1H), 7.12-7.14 (d, J= 8.50 Hz, 1H), 7.15-7.17 (m, 2H), 7.19-7.21 (d, J= 8.50 Hz, 1H), 7.31-7.35 (m, 2H), 7.36-7.38 (d, J= 8.50 Hz, 2H), 7.66-7.68 (t, J= 7.00 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 20.10, 30.34, 45.16, 46.04, 57.00, 117.63, 118.49, 119.18, 122.60, 124.00, 125.58, 126.33, 127.58, 128.24, 129.66, 131.54, 133.01, 135.97, 138.92, 139.01. MS *m/z* (ESI): 311 (M^+), 246, 220, 206, 169.

*2.3.6 cis-6-(4-methoxyphenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4e**)*

White cyrstals, m.p. 129-131 °C. FTIR (ATR, cm^{-1}): 3377, 3051, 2997, 2948, 2928, 2834, 1610, 1573, 1510, 1459, 1399, 1375, 1355, 1293, 1241, 1172, 1141, 1107, 1032, 839, 813, 788, 753, 732. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.88-1.93 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.70-2.76 (dt, J_1= 8.50 Hz, J_2= 3.00 Hz, 1H), 3.04-3.10 (ddd, J_1= 8.50 Hz, J_2= 6.50 Hz, J_3= 3.00 Hz, 1H), 3.85 (s, 3H), 4.24-4.26 (d, J= 8.50 Hz, 1H), 4.43 (s, 1H), 4.69-4.70 (d, J= 3.00 Hz, 1H), 5.66 (br s, 1H), 5.94 (br s, 1H), 6.95-6.97 (d, J= 8.50 Hz, 2H), 7.20-7.22 (d, J= 8.00 Hz, 1H), 7.27-7.29 (d, J= 8.50 Hz, 1H), 7.37-7.42 (m, 2H), 7.47-7.49 (d, J= 8.50 Hz, 2H), 7.73-7.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.40, 46.32, 47.07, 55.38, 57.73, 113.99, 118.71, 119.57, 120.22, 123.66, 125.06, 125.11, 127.40, 127.80, 128.64, 130.72, 132.61, 134.10, 135.21, 139.99, 158.94. MS *m/z* (ESI): 327 (M^+), 263, 221, 205, 169.

*2.3.7 cis-4-(6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinolin-6yl)phenol (**4f**)*

Pale yellow cyrstals, m.p. 80-82 ^{o}C. FTIR (ATR, cm^{-1}): 3367, 3048, 3011, 2926, 2868, 1600, 1580, 1569, 1513, 1444, 1403, 1375, 1355, 1285, 1235, 1216, 1160, 1100, 1082, 1040,1014, 833, 789,769. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.88-1.93 (dd, J_1= 8.50 Hz, J_2= 7.50 Hz, 1H), 2.70-2.75 (dt, J_1= 8.50 Hz, J_2= 3.00 Hz, 1H), 3.04-3.10 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 3.00 Hz, 1H), 4.25-4.27 (d, J= 8.50 Hz, 1H), 4.43 (br s, 1H), 4.69-4.70 (d, J= 3.00 Hz, 1H), 4.91 (br s, 1H), 5.67 (br s, 1H), 5.94 (br s, 1H), 6.88-6.90 (d, J= 8.50 Hz, 2H), 7.20-7.22 (d, J= 8.50 Hz, 1H), 7.27-7.29 (d, J= 8.50 Hz, 1H), 7.39-7.44 (m, 4H), 7.74-7.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.36, 46.30, 47.04, 57.72, 115.41, 118.73, 119.55, 120.20, 123.65, 125.05, 125.10, 127.37, 128.00, 128.63, 130.69, 132.60, 134.08, 135.38, 139.93, 154.85. MS *m/z* (ESI): 313 (M^+), 248, 220, 205, 169.

*2.3.8 cis-4-(6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinolin-6-yl)benzonitrile (**4g**)*

Pale white cyrstals, m.p. 208-210 ^{o}C. FTIR (ATR, cm^{-1}): 3361, 3044, 2961, 2931, 2905, 2844, 2226, 1606, 1573, 1521, 1477, 1439, 1400, 1373, 1357, 1338, 1292, 1242, 1194, 1152, 1094, 1031, 813, 790, 752, 735. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.71-1.76 (dd, J_1= 8.50 Hz, J_2= 7.00 Hz, 1H), 2.55-2.60 (dt, J_1= 8.50 Hz, J_2= 3.00 Hz, 1H), 2.99-3.05 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 3.00 Hz, 1H), 4.20-4.22 (d, J= 8.50 Hz, 1H), 4.35 (br s, 1H), 4.72 (br s, 1H), 5.57 (br s, 1H), 5.88 (br s, 1H), 7.13-7.15 (d, J= 8.50 Hz, 1H), 7.24-7.26 (d, J= 8.50 Hz, 1H), 7.33-7.39 (m, 2H), 7.60-7.62 (d, J= 8.00 Hz, 2H), 7.64-7.65 (d, J= 8.00 Hz, 2H), 7.67-7.71 (t, J= 8.00 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.16, 45.77, 46.82, 58.03, 111.29, 118.82, 119.35, 119.46, 120.15, 123.71, 125.32, 127.17, 127.46, 128.73, 130.37, 132.50, 132.58, 133.96, 138.90, 148.55. MS *m/z* (ESI): 323 (M^+), 258, 221, 206,170.

*2.3.9 cis-6-(4-nitrophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4h**)*

Pale red cyrstals, m.p. 212-214 ^{o}C. FTIR: 3376, 3100, 3077, 3055, 2929, 2907, 2873, 2846, 1596, 1573, 1509, 1476, 1402, 1342, 1293, 1241, 1150, 1108, 1034, 1013, 860, 817, 791, 771, 751, 723. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.71-1.76 (dd, J_1= 8.50 Hz, J_2= 6.50 1H), 2.57-2.62 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.01-3.07 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.22-4.23 (d, J= 8.50 Hz, 1H), 4,38 (br s, 1H), 4.77-4.78 (d, J= 2.50 Hz, 1H), 5.58 (br s, 1H), 5.89 (br s, 1H), 7.14-7.16 (d, J= 8.50 Hz, 1H), 7.18 (br s, 1H), 7.25-7.27 (d, J= 8.00 Hz, 1H), 7.34-7.40 (m, 2H), 7.66-7.68 (d, J= 8.50 Hz, 2H), 7.69-7.71 (d, J= 8.00 Hz, 2H), 8.20-8.22 (d, J= 8.50 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.19, 45.77, 46.84, 57.90, 119.38, 119.60, 120.18, 123.74, 123.95, 125.36, 125.41, 127.18, 127.51, 128.77, 130.37, 132.61, 133.99, 138.84, 147.33, 150.60. MS *m/z* (ESI): 343 (M^+), 297, 277, 231, 173.

*2.3.10 cis-6-(2-nitrophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4i**)*

Pale yellow cyrstals, m.p. 106-108 ^{o}C. FTIR: 3372, 3060, 3051, 2921, 2850, 1620, 1608, 1571, 1515, 1470, 1440, 1392, 1337, 1310, 1285, 1262, 1148, 1082, 1039, 1015, 802, 773, 753, 724. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.83-1.87 (dd, J_1= 8.50 Hz, J_2= 6.00 Hz, 1H), 2.73-2.78 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.35-3.40 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.27 (br s, 1H) 4.29-4.31 (d, J= 8.50 Hz, 1H), 5.24-5.25 (d, J= 2.50 Hz, 1H), 5.66 (br

s, 1H), 5.98 (br s, 1H), 7.15-7.16 (d, *J*= 7.50 Hz, 1H), 7.47-7.50 (t, *J*= 7.50 Hz, 1H), 7.52-7.54 (m, 2H), 7.61-7.64 (t, *J*= 7.00 Hz, 1H), 7.75-7.78 (m, 2H), 7.85-7.87 (m, 1H), 8.06-8.08 (d, *J*= 8.00 Hz, 1H), 8.34-8.36 (m, 1H), 8.46-8.47 (d, *J*= 8.00 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.14, 43.79, 46.78, 53.18, 113.25, 123.67, 124.55, 126.01, 126.04, 126.53, 126.85, 127.75, 128.77, 130.01, 131.12, 131.26, 133.54, 133.90, 148.20, 155.80. MS *m/z* (ESI): 343 (M^+), 297, 277, 231, 173.

*2.3.11 cis-6-(4-pyridin-2-yl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4j**)*

Pale orange oil. FTIR: 3377, 3050, 3006, 2919, 2847, 1619, 1591, 1574, 1514, 1453, 1434, 1401, 1374, 1354, 1287, 1240, 1196, 1144, 1098, 1047, 1031, 813, 788, 770, 752, 733. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.90-1.94 (dd, J_1= 8.50 Hz, J_2= 7.00 Hz, 1H), 2.46-2.50 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.41-3.46 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.30 4.32(d, *J*= 8.50 Hz, 1H), 4.81-4.82 (d, *J*= 2.50 Hz, 1H), 5.47 (br s, 1H), 5.61 (br s, 1H), 5.91 (br s, 1H), 7.18-7.20 (d, *J*= 7.50 Hz, 1H), 7.26-7.30 (m, 2H), 7.37-7.44 (m, 3H), 7.48-7.50 (d, *J*= 7.50 Hz, 1H), 7.68-7.78 (m, 3H), 7.90-7.92 (d, *J*= 8.50 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.56, 44.12, 47.10, 57.99, 109.64, 118.53, 118.91, 120.09, 120.46, 122.11, 124.92, 125.10, 127.22, 128.45, 130.16, 132.64, 134.25, 136.59, 139.25, 148.93, 160.59. MS *m/z* (ESI): 299 (M^+), 233, 220, 206, 156.

*2.3.12 cis-6-(thiophen-2-yl)-6,6a,7,9a-tetrahydro-5H-bezo[h]cyclopenta[c]quinoline (**4k**)*

Pale orange oil. FTIR (ATR, cm^{-1}): 3287, 3080, 3010, 2970, 2882, 1610, 1589, 1574, 1518, 1458, 1424, 1401, 1378, 1348, 1290, 1240, 1191, 1134, 1092, 1041, 1019, 823, 768, 751. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.11-2.16 (dd, J_1= 8.00 Hz, J_2= 7.50 Hz, 1H), 2.78-2.84 (dt, J_1= 8.00 Hz, J_2= 3.00 Hz, 1H), 3.10-3.16 (ddd, J_1= 8.00 Hz, J_2= 6.00 Hz, J_3= 3.00 Hz, 1H), 4.22-4.24 (d, *J*= 8.00 Hz, 1H), 4.53 (br s, 1H), 4.99-5.00 (d, *J*= 3.00 Hz, 1H), 5.67 (br s, 1H), 5.92 (br s, 1H), 7.03-7.05 (t, *J*= 3.50 Hz, 1H), 7.17-7.19 (d, *J*= 9.00 Hz, 2H), 7.26-7.29 (m, 2H), 7.36-7.41 (m, 2H), 7.70-7.74 (t, *J*= 9.00 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 32.04, 46.20, 46.86, 54.67, 119.18, 119.58, 120.47, 123.62, 123.83, 124.13, 125.14, 126.67, 127.21, 128.20, 128.53, 129.01, 130.63, 132.48, 133.92, 139.20, 146.34 . MS *m/z* (ESI): 304 (M^+), 239, 221, 206, 170.

*2.3.13 cis-6-(furan-3-yl)-6,6a,7,9a-tetrahydro-5H-bezo[h]cyclopenta[c]quinoline (**4l**)*

Pale yellow oil. FTIR (ATR, cm^{-1}): 3385, 3090, 3054, 2948, 2926, 2869, 2855, 1574, 1517, 1463, 1403, 1387, 1356, 1293, 1270, 1240, 1161, 1140, 1096, 1067, 1026, 873, 788, 752, 730. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.12-2.17 (dd, J_1= 8.50 Hz, J_2= 6.00 Hz, 1H), 2.71-2.76 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.06-3.12 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.21-4.23 (d, *J*= 8.50 Hz, 1H), 4.37 (br s, 1H), 4.65-4.66 (d, *J*= 2.50 Hz, 1H), 5.68 (br s, 1H), 5.91 (br s, 1H), 6.53 (br s, 1H), 7.18-7.20 (d, *J*= 8.50 Hz, 1H), 7.27-7.29 (d, *J*= 8.50 Hz, 1H), 7.37-7.43 (m, 3H), 7.46-7.47 (d, *J*= 3 Hz, 1H), 7.56-7.57 (d, *J*= 3Hz, 1H), 7.70-7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 32.11, 44.85, 46.81, 50.95, 109.53, 114.97, 118.96, 119.53, 120.55, 123.64, 125.12, 127.37, 128.62, 130.63, 132.55, 134.19, 139.19, 143.25. MS *m/z* (ESI): 288 (M^+), 223, 192, 156.

4.3.14 cis-6-(5-methylfuran-2-yl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline ***(4m)***

Pale yellow oil. FTIR (ATR, cm^{-1}): 3350, 3060, 3012, 2967, 2864, 1621, 1600,1584, 1519, 1468, 1444, 1403, 1362, 1343, 1270, 1238, 1181, 1142, 1083, 1042, 1012, 943, 834, 768, 736. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.14-2.18 (dd, J_1= 8.50 Hz, J_2= 6.50 Hz, 1H), 2.22 (s, 3H), 2.64-2.67 (dt, J_1=8.50 Hz, J_2= 2.50 Hz, 1H), 3.12-3.17 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.09-4.11 (d, *J*= 8.50 Hz, 1H), 4.45 (br s,1H), 4.56 (br s), 5.86 (br s, 1H), 6.11 (br s), 7.06-7.08 (d, *J*= 8.50 Hz, 1H), 7.15-7.17 (d, *J*= 8.50 Hz, 1H), 7.26-7.30 (t, *J*= 6.50 Hz, 4H), 7.62-7.64 (t, *J*= 6.50 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 13.74, 32.53, 42.77, 47.00, 52.86, 106.24, 106.46, 119.08, 119.77, 120.73, 123.78, 125.16, 125.23, 127.43, 128.67, 130.77, 132.63, 134.13, 139.49, 151.38, 154.05. MS *m/z* (ESI): 302 (M^+), 237, 221, 206, 170.

2.3.15 trans-6-(5-methylfuran-2-yl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline ***(4m')***

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.25-2.28 (m, 1H), 2.45 (s, 3H), 2.71-2.80 (m, 1H), 3.20-3.26 (m, 1H), 3.46 (br s), 4.25-4.27 (d, *J*= 16.00 Hz, 1H), 4.65 (br s, 1H), 5.96 (br s, 1H), 6.20 (br s, 1H), 7.05 (br s, 1H), 7.11-7.12 (d, *J*= 3.00 Hz, 1H), 7.37-7.42 (m, 2H), 7.67-7.72 (m, 2H), 7.82-7.85 (t, *J*= 7.50 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 14.14, 32.41, 42.64, 46.85, 50.92, 106.36, 106.97, 120.20, 122.03, 124.90, 125.21, 126.68, 127.72, 128.50, 130.71, 133.67, 135.71, 138.68, 144.50, 151.32, 153.66

2.3.16 cis-6-(2,4-dimethylphenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline ***(4n)***

Pale white cyrstals, m.p. 132-134 ^{o}C. FTIR (ATR, cm^{-1}): 3379, 3051, 3006, 2919, 2850, 1614, 1573, 1517,1456, 1400, 1375, 1356, 1290, 1240, 1141, 1106, 1032, 812, 787, 752, 729. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.83-1.84 (dd, J_1= 8.50 Hz, J_2=7.00 Hz, 1H), 2.36 (s, 3H), 2.38 (s, 3H), 2.76-2.82 (dt, J_1= 8.50 Hz, J_2= 2.00 Hz, 1H), 3.11-3.17 (ddd, J_1= 8.50 Hz, J_2= 6.50 Hz, J_3= 2.00 Hz, 1H), 4.27-4.28 (d, *J*= 8.50 Hz, 1H), 4.36 (br s, 1H), 4.91-4.92 (d, *J*= 2.00 Hz, 1H), 5.67 (br s, 1H), 5.93 (br s, 1H), 7.05 (br s, 1H), 7.12-7.14 (d, *J*= 8.00 Hz, 1H), 7.21-7.23 (d, *J*= 8.50 Hz, 1H), 7.27-7.29 (d, *J*= 8.50 Hz, 1H), 7.37-7.42 (m, 2H), 7.69-7.76 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.11, 21.01, 31.47, 43.27, 47.24, 54.27, 118.64, 119.55, 120.27, 123.66, 125.07, 125.12, 126.16, 126.96, 127.38, 128.64, 130.83, 131.38, 132.59, 134.05, 134.96, 136.57, 137.86, 140.53. MS *m/z* (ESI): 326 (M^+), 261, 222, 207, 171.

2.3.17 cis-6-(2,4-dichlorophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline ***(4o)***

Pale yellow cyrstals, m.p. 80-82 ^{o}C. FTIR (ATR, cm^{-1}): 3367, 3052, 3030, 2949, 2928, 2868, 2841, 1589, 1575, 1560, 1517, 1468, 1401, 1383, 1354, 1290, 1267, 1240, 1196, 1145, 1100, 1048, 1034, 864, 814, 790, 752, 731. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.74-1.79 (dd, J_1= 8.50 Hz, J_2= 6.50 Hz, 1H), 2.58-2.64 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.25-3.30 (ddd, J_1= 8.50 Hz, J_2= 6.50 Hz, J_3= 2.50 Hz, 1H), 4.22 (br s, 1H), 4.24-4.26 (d, *J*= 8.50 Hz, 1H), 5.06-5.07 (d, *J*= 2.50 Hz, 1H), 5.23 (br s, 1H), 5.62 (br s, 1H), 5.93 (br s, 1H), 7.17-7.19 (d, *J*= 8.00 Hz,

1H), 7.27-7.29 (d, *J*= 8.50 Hz, 1H), 7.32-7.34 (dd, J_1= 8.50 Hz, J_2= 2.00 Hz, 1H), 7.36-7.42 (m, 3H), 7.69-7.71 (d, *J*= 8.00 Hz, 1H), 7.72-7.74 (dd, J_1= 8.50 Hz, J_2= 2.00 Hz, 1H), 7.77-7.79 (d, *J*= 8.50 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz):31.35, 42.09, 46.70, 54.33, 119.37, 119.45, 120.44, 123.83, 125.27, 127.31, 127.46, 128.78, 128.94, 129.57, 130.46, 132.63, 133.50, 134.15, 138.87, 139.40. MS *m/z* (ESI): 366 (M^+), 300, 245, 171.

*2.3.18 trans-6-(2,4-dichlorophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4o'**)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.99-2.01 (d, *J*= 10.00 Hz, 1H), 2.38-2.42 (m, 1H), 2.72-2.76 (m, 1H), 2.95-2.97 (d, *J*= 8.50 Hz, 1H), 3.25 (br s, 1H), 4.47-4.49 (d, *J*= 8.00 Hz, 1H), 4.59 (br s, 1H), 5.50 (br s, 1H), 5.70 (br s, 1H), 7.15-7.17 (d, *J*= 8.50 Hz, 1H), 7.30-7.32 (d, *J*= 8.50 Hz, 1H), 7.37-7.42 (m, 4H), 7.53-7.55 (d, *J*= 8.50 Hz, 1H), 7.61-7.63 (m, 1H), 7.75-7.78 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 37.20, 43.40, 48.05, 55.15, 118.70, 119.03, 121.90, 122.93, 125.08, 126.76, 127.15, 127.62, 128.65, 129.20, 130.03, 132.45, 133.50, 134.40, 140.53, 141.02

*2.3.19 cis-6-(2,4-difluorophenyl)-6,6a,7,9a-tetrahydro-5H-benzo[h]cyclopenta[c]quinoline (**4p**)*

White cyrstals, m.p. 128-130 ^{o}C. FTIR (ATR, cm^{-1}): 3359, 3064, 3030, 2924, 2904, 2848, 1614, 1595, 1573, 1517, 1498, 1463, 1425, 1398, 1375, 1356, 1293, 1271, 1246, 1143, 1129, 1091, 1034, 956, 856, 849, 818, 791, 757, 739. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.85-1.90 (dd, J_1= 8.50 Hz, J_2= 7.00 Hz, 1H), 2.64-2.69 (dt, J_1= 8.50 Hz, J_2= 2.50 Hz, 1H), 3.17-3.23 (ddd, J_1= 8.50 Hz, J_2= 6.00 Hz, J_3= 2.50 Hz, 1H), 4.27-4.29 (d, *J*= 8.50 Hz, 1H), 5.03-5.04 (d, *J*= 2.50 Hz, 1H), 5.66 (br s, 1H), 5.95 (br s, 1H), 6.84-6.88 (t, *J*= 8.50 Hz, 1H), 6.97-7.00 (t, *J*= 8.50 Hz, 1H), 7.20-7.22 (d, *J*= 8.50 Hz, 1H), 7.30-7.32 (d, *J*= 8.50 Hz, 1H), 7.39-7.45 (m, 2H), 7.74-7.81 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 31.45, 43.53, 46.62, 50.71, 119.24, 119.37, 120.34, 123.73, 125.20, 127.27, 128.70, 130.39, 132.53, 134.12, 139.43, 158.79, 161.90, 163.63. MS *m/z* (ESI): 334 (M^+), 269, 222, 207, 171.

*2.3.20 cis-6-phenyl-5,6,6a,7,10,10a-hexahydrobenzo[c]phenanthridine (**6a**)*

Pale yellow oil. FTIR (ATR, cm^{-1}): 3374, 3050, 3027, 2915, 2862, 1600, 1582, 1512, 1490, 1462, 1400, 1370, 1345, 1282, 1271, 1230, 1137, 1092, 1080, 1019, 815, 776, 752, 731. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.45-1.47 (m, 1H), 1.87-1.95 (m, 1H), 1.97-1.99 (m, 1H), 2.21-2.25 (m, 1H), 3.98 (br s, 1H), 4.55 (br s, 1H), 4.82 (br s, 1H), 5.83 (br s, 1H), 6.32 (br s, 1H), 7.28-7.32 (m, 1H), 7.34-7.39 (m, 1H), 7.41-7.47 (m, 5H), 7.57-7.59 (d, *J*= 7.50 Hz, 2H), 7.75-7.80 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 17.22, 25.45, 37.57, 39.05, 59.88, 117.99, 118.64, 119.74, 125.00, 125.15, 126.35, 126.77, 127.13, 127.39, 128.45, 128.52, 128.62, 129.55, 132.54, 132.62, 133.17, 133.82, 134.90, 137.36, 137.82, 140.97, 142.32. MS *m/z* (ESI): 312 (M^+), 233, 184, 156.

*2.3.21 cis-4-(-5,6,6a,7,10,10a-hexahydrobenzo[c]phenanthridin-6-yl)benzonitrile (**6b**)*

Pale yellow oil. FTIR (ATR, cm^{-1}): 3368, 3055, 3007, 2951, 2910, 2860, 2837, 1604, 1570, 1530, 1505, 1480, 1440, 1360, 1290, 1250, 1155, 1092, 1020, 856, 815, 792, 752. ^{1}H NMR

($CDCl_3$, 500 MHz): 1.40-1.45 (m, 1H), 2.27-2.32 (m, 1H), 2.70-2.77 (m, 1H), 3.06-3.13 (m, 1H), 3.40 (br s, 1H), 4.70 (br s, 1H), 5.30 (br s, 1H), 5.70 (br s, 1H), 6.54 (br s, 1H), 7.17-7.22 (m, 1H), 7.37-7.40 (m, 1H), 7.43-7.49 (m, 2H), 7.52-7.56 (m, 2H), 7.69-7.76 (m, 2H), 7.80-7.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 23.94, 29.71, 39.30, 40.68, 56.17, 109.26, 115.43, 118.40, 121.76, 123.25, 123.98, 125.94, 130.97, 137.72, 141.89, 142.54. MS *m/z* (ESI): 337 (M^+), 285, 260, 184.

*2.3.22 cis-6-(4-chlorophenyl)-5,6,6a,7,10,10a-hexahydrobenzo[c]phenanthridine (**6c**)*

Pale yellow oil. FTIR (ATR, cm^{-1}): 3385, 3060, 3004, 2947, 2928, 2840, 1575, 1524, 1485, 1468, 1385, 1375, 1351, 1284, 1270, 1240, 1126, 1082, 1012, 823, 787, 770, 753, 736. ^{1}H NMR ($CDCl_3$, 500 MHz):1.80-1.82 (m, 1H), 1.84-1.87 (m, 1H), 1.90-1.93 (m, 1H), 2.10-2.13 (m, 1H), 3.89 (br s, 1H), 4.39 (br s, 1H), 4.72 (br s, 1H), 5.75 (br s, 1H), 6.24 (br s, 1H), 7.09-7.12 (d, *J*= 7.50 Hz, 1H), 7.21-7.23 (d, *J*= 8.50 Hz, 1H), 7.33-7.37 (m, 4H), 7.44-7.46 (d, *J*= 8.50 Hz, 2H), 7.69-7.72 (t, *J*= 7.50 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): 16.11, 25.43, 28.68, 36.44, 52.20, 117.30, 118.63, 119.14, 123.81, 124.08, 124.19, 125.66, 125.88, 126.48, 127.24, 127.45, 127.56, 128.02, 129.68, 130.02, 132.08, 133.26, 134.04, 134.95, 136.48, 137.68, 138.11, 139.79. MS *m/z* (ESI): 346 (M^+), 267, 185, 157.

*2.3.23 cis-6-(2,4-dichlorophenyl)-5,6,6a,7,10,10a-hexahydrobenzo[c]phenanthridine (**6d**)*

Pale yellow oil. FTIR (ATR, cm^{-1}): 3385, 3073, 3058, 2949, 2917, 2875, 1584, 1573, 1562, 1516, 1471, 1456, 1397, 1339, 1281, 1221, 1116, 1098, 1043, 856, 801, 790, 753, 731. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.90-1.92 (m, 1H), 1.94-1.96 (m, 1H), 2.27-2.29 (m, 1H), 2.39-2.41 (m, 1H), 3.98 (br s, 1H), 4.31 (br s, 1H), 5.12 (br s, 1H), 5.84 (br s, 1H), 6.33 (br s, 1H), 7.30-7.32 (d, *J*= 8.50 Hz, 1H), 7.37-7.39 (d, *J*= 8.50 Hz, 1H), 7.41-7.44 (m, 2H), 7.48-7.54 (m, 2H), 7.76-7.78 (d, *J*= 8.50 Hz, 2H), 7.84-7.86 (d, *J*= 8.50 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): 17.53, 25.37, 29.71, 37.19, 56.19, 115.09, 118.65, 119.60, 120.90, 121.13, 122.41, 123.37, 123.90, 124.78, 125.18, 126.72, 126.93, 128.44, 128.59, 129.15, 129.72, 130.95, 132.59, 133.28, 135.22,137.86, 140.05, 141.50. MS *m/z* (ESI): 381 (M^+), 302, 220, 184, 156.

3. Results and Discussions

Although 2,3-dihydrofuran and 3,4-dihydro-2H-pyran have been extensively used in three-component aza-Diels-Alder reactions, there are very limited examples of tetrahydroquinolines and hexahydrophenanthridines synthesized by means of the aza-Diels-Alder reactions of cyclopentadiene and 1,3-cyclohexadiene.

In this work, we described a mild and efficient approach for the synthesis of tetrahydroquinoline and hexahydrophenanthridine derivatives via an aza-Diels-Alder reaction using ytterbium (III) triflate as the catalyst with moderate to good yields (Scheme 1, Scheme 2, Table 1 and Table 2). The reaction was first explored by stirring a mixture of 1-naphtylamine, benzaldehyde and cyclopentadiene with 10 mol% of ytterbium (III) triflate at room temperature in CH_3CN for 24 h (Table 3). The N-arylimine was generated in situ by the interaction of 1-naphtylamine with benzaldehyde but the tetrahydroquinoline product was not observed. Then, the same reaction was performed in refluxing CH_3CN for 24 h but again the

tetrahydroquinoline product was not observed. Then, we changed the solvent to PhMe. The tetrahydroquinoline product was not observed at room temperature. When the reaction was performed in refluxing PhMe, the tetrahydroquinoline product was observed with a 55% yield after 6 h (Table 3). The results showed that the reaction temperature had a significant effect on the reaction and further experiments were carried out at 110 ^{o}C in PhMe.

Finally, we also performed the same experiments under ultrasonic irradiation in order to observe the effect of the ultrasonic irradiation. 1-naphtylamine, benzaldehyde and cyclopentadiene, with 10 mol% of ytterbium (III) triflate at room temperature in PhMe for 4h did not give the corresponding tetrahydroquinoline. As shown in Table 3, changing the reaction temperature from room temperature to 50 ^{o}C gave the tetrahydroquinoline product a 73% yield and the reaction was completed in 40 min.

In order to observe the effect of the amount of ytterbium (III) triflate on the reaction, we also performed the experiments using different amounts of catalyst. As shown in Table 3, when the amount of ytterbium (III) triflate decreased to 10%, 5% and 2%, the yield of the corresponding tetrahydroquinoline increased to 73%, 75% and 79%, respectively.

From the results above, it has been shown that 1-naphtylamine, benzaldehyde and cyclopentadiene, with 2 mol% of ytterbium (III) triflate at 50 ^{o}C in PhMe under ultrasonic irradiation presented an efficient procedure in terms of high yield and shorter reaction time.

With these optimal reaction conditions, we then examined a variety of aromatic and hetero-aromatic aldehydes in conventional and ultrasound-promoted catalytic aza-Diels-Alder reactions. Several N-arylimines (formed in situ from aromatic aldehydes and 1-naphtylamine in PhMe) reacted smoothly with cyclopentadiene under conventional and ultrasonic techniques to afford the corresponding tetrahydroquinolines. In every case ultrasonic irradiation improved the yields and the reactions were completed in 40 minutes (Table 1). The ultrasonic method was equally effective for both electron-rich and electron-deficient aromatic aldehydes. Furthermore, thienyl, furanyl and pyridinyl rings worked well without any decomposition under these reaction conditions.

We also performed the catalytic aza-Diels-Alder reaction of 1-naphtylamine, aromatic aldehydes and 1,3-cyclohexadiene under conventional and ultrasonic techniques. The reactions proceeded smoothly to give the hexahydrophenathridine derivatives with moderate yields (Table 2).

The products were isolated from the reaction mixture by chromatographic purification and identified by FTIR, ^{1}H NMR, ^{13}C NMR and mass spectroscopic data. Each of the products proved to be a pure, single diastereoisomer, by their NMR spectra.

COSY and NOE studies were carried out to determine the absolute configuration of the newly generated stereogenic centre of the products. In most cases, the product was obtained as a single *cis*-isomer. The aza-Diels-Alder reaction of cyclopentadiene, 1-naphtylamine and aromatic aldehydes (4-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde and 5-methyl-2-furan carboxaldeyde) gave the corresponding tetrahydroquinolines as a mixture of *cis*- and *trans*-

isomers (**4c**-**4c′**, **4m**-**4m′**, **4o**-**4o′**), while favoring the *cis*-isomer. The isomers could be easily separated by column chromatography on silica gel. The ratio of the isomers was determined from ^{1}H NMR spectra of the crude products. Using conventional methods the obtained ratios of *cis*- and *trans*- isomers were 98:2, 98:2 and 93:7, respectively. Under ultrasonic irradiation, the ratios of *cis*- and *trans*- isomers were 92:8, 80:20 and 90:10, respectively. The stereoconfigurations of **4c** and **4c′** were determined by COSY and NOE experiments (Fig 1). The ^{1}H-^{1}H-COSY spectra of compound **4c** showed cross peaks between H_2 and H_3, and among H_4, H_{7a}, H_3 and H_5, respectively. The NOE experiment of compound **4c** showed correlations among H_4, H_2, H_3 and H_5. The ^{1}H-^{1}H-COSY spectra of compound **4c′** showed cross peaks among H_2, H_3, H_6 and H_{7a}; and between H_4 and H_3, respectively. The NOE experiment of compound **4c′** showed correlation between H_3 and H_4.

4. Conclusion

In conclusion, we have described a simple and efficient method for the synthesis of tetrahydroquinolines and hexahydrophenathridines via a three-component one-pot aza-Diels-Alder reaction of 1-naphtylamine, aromatic aldehydes and cyclic dienes using commercially available ytterbium (III) trifluoromethanesulfonate ($Yb(OTf)_3$) as the catalyst.

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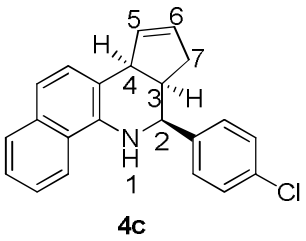
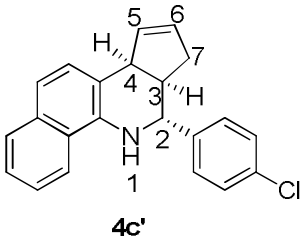
Figure 1. Compounds **4c** and **4c′**

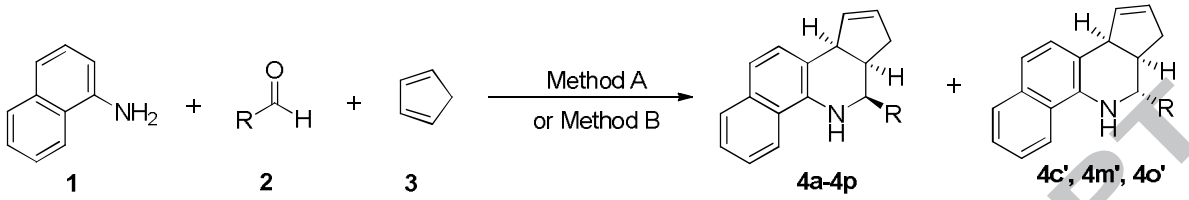


4c



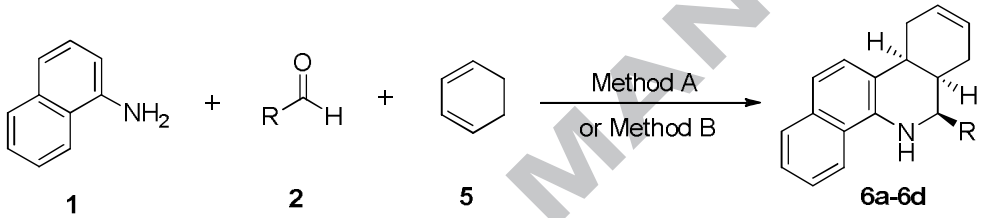
4c'

Scheme 1. One-pot aza-Diels-Alder reaction of amine, aldehydes and cyclopentadiene catalyst by $Yb(OTf)_3$



Method A: 10 mol% $Yb(OTf)_3$, reflux in PhMe at 110 ^oC for 6h.
Method B: 2 mol% $Yb(OTf)_3$, ultrasound in PhMe at 50 ^oC for 40 min.

Scheme 2. One-pot aza-Diels-Alder reaction of amine, aldehydes and 1,3-cyclohexadiene catalyst by $Yb(OTf)_3$



Method A: 10 mol% $Yb(OTf)_3$, reflux in PhMe at 110 ^oC for 6h.
Method B: 2 mol% $Yb(OTf)_3$, ultrasound in PhMe at 50 ^oC for 40 min.

Table 1. Direct aza-Diels-Alder reaction with cyclopentadiene

Entry	R	Compound	% Yield (Method A)[a,c]	% Yield (Method B)[b,c]
1	Phenyl	4a	55	79
2	4-Bromophenyl	4b	54	76
3	4-Chlorophenyl	4c+4c′	56[d]	82[d]
4	4-Methylphenyl	4d	55	78
5	4-Methoxyphenyl	4e	49	72
6	4-Hydroxyphenyl	4f	52	83
7	4-Cyanophenyl	4g	58	79
8	4-Nitrophenyl	4h	47	74
9	2-Nitrophenyl	4i	50	78
10	2-Pyridinyl	4j	46	68
11	2-Thiophenyl	4k	43	57
12	3-Furanyl	4l	52	77
13	5-Methyl-2-furanyl	4m+4m′	45[d]	67[d]
14	2,4-Dimethylphenyl	4n	65	81
15	2,4-Dichlorophenyl	4o+4o′	53[d]	65[d]
16	2,4-Difluorophenyl	4p	67	86

[a]Method A: 1-naphthylamine (1 mmol), aromatic aldehyde (1 mmol), cyclopentadiene (3 mmol), 10 mol% $Yb(OTf)_3$, dry toluene (3 mL), at 110 ^oC, 6 h.

[b]Method B: 1-naphthylamine (1 mmol), aromatic aldehyde (1 mmol), cyclopentadiene (3 mmol), 2 mol% $Yb(OTf)_3$, dry toluene (3 mL), ultrasonic irradiation, at 50 ^oC, 40 min.

[c]Isolated yield.

[d]Combined yields of two isomer.

Table 2. Direct aza-Diels-Alder reaction with 1,3-cyclohexadiene

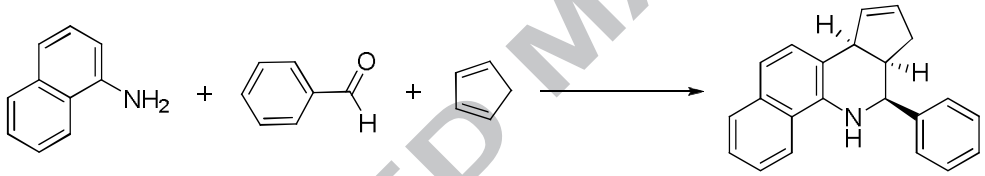
Entry	R	Compound	Yield % (Method A)[a,c]	Yield % (Method B)[b,c]
1	Phenyl	6a	15	27
2	4-Cyanophenyl	6b	12	21
3	4-Chlorophenyl	6c	14	24
4	2,4-Dichlorophenyl	6d	10	16

[a]Method A: 1-naphthylamine (1 mmol), aromatic aldehyde (1 mmol), 1,3-cyclohexadiene (3 mmol), 10 mol% $Yb(OTf)_3$, dry toluene (3 mL), at 110 ^oC, 6 h.

[b]Method B: 1-naphthylamine (1 mmol), aromatic aldehyde (1 mmol), 1,3-cyclohexadiene (3 mmol), 2 mol% $Yb(OTf)_3$, dry toluene (3 mL), ultrasonic irradiation, at 50 ^oC, 40 min.

[c]Isolated yield.

Table 3. The direct aza-Diels-Alder reaction[a]



Entry	Method	Solvent	Catalyst	Temperature (^oC)	Time	Yield (%)[b]
1	Stirring	CH_3CN	10% $Yb(OTf)_3$	r.t	24 h	-
2	Refluxing	CH_3CN	10% $Yb(OTf)_3$	80	24 h	-
3	Stirring	PhMe	10% $Yb(OTf)_3$	r.t	24 h	-
4	Refluxing	PhMe	10% $Yb(OTf)_3$	110	6 h	55
5	Ultrasound	PhMe	10% $Yb(OTf)_3$	r.t	4 h	-
6	Ultrasound	PhMe	10% $Yb(OTf)_3$	50	40 min	73
7	Ultrasound	PhMe	5% $Yb(OTf)_3$	50	40 min	75
8	Ultrasound	PhMe	2% $Yb(OTf)_3$	50	40 min	79

[a]Reaction conditions: 1-naphthylamine (1 mmol), benzaldehyde (1 mmol), cyclopentadiene (3 mmol), dry toluene (3 mL)

[b]Isolated yield

•Aza-Diels-Alder reaction performed under conventional/ultrasonic techniques •Ultrasonic irradiation provided higher yields and shorter reaction times •Ultrasound-assisted reactions occurred in milder conditions