Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

for

[bmim]OH promoted hydroalkynylation of nitrile and intramolecular hydroamination of carbon-carbon multiple bond: An efficient and eco-compatible strategy for synthesis of Indolizinones

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Experimental section

The reactions were performed in an open borosil round bottom flask, Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates and visualization on TLC was achieved by UV light (254 and 354 nm. Melting points are uncorrected and were determined on a Buchi Melting point apparatus. The ^{1}H NMR spectra were recorded on a Gemini 400 MHz FT NMR spectrometer; the chemical shifts were reported on δ ppm relative to TMS. The mass spectra were recorded on Shimadzu LCMS-QP8000, LC-MS and AB-4000 Q-trap LC-MS/MS. Elemental analysis for C, H, and N were performed on Perkin Elmer model 2400 CHNS/O analyzer at SAIF Chandigarh. All chemicals were used as received without further purification. NMR spectra were recorded on a Bruker Avance DPX-400 FT spectrometer (400 MHz for ^{1}HNMR, 100 MHz for ^{13}CNMR) using $CDCl_3$ as solvent and TMS as an internal reference. Mass spectra were recorded on a JEOL SX-102 (FAB) mass spectrometer at 70 ev. Elemental analyses were carried out in Coleman automatic carbon, hydrogen and nitrogen analyzer. Silica gel-G was used for TLC. Melting points were determined by open glass capillary method and are uncorrected.

General procedure for preparation of [bmim]OH

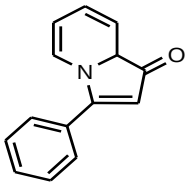
The task specific basic ionic liquid was synthesized according to a reported procedure. Solid KOH (2.3 g, 40 mmol) was added to a solution of [bmim]Br (8.8 g, 40 mmol) in dry CH_2Cl_2 (20 mL), and the mixture was stirred vigorously at room temperature for 10 h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude [bmim]OH as a viscous liquid that was washed with ether (2 × 20 mL) and dried at 90°C for 10 h to prepare the pure ionic liquid for use.

General procedure for synthesis of Indazolin-1-one derivative

A mixture of 2-cyanopyridine (2mmol), phenylacetylene (2mmol), [bmim]OH (10mol%) was irradiated under microwave irradiation for 2-3 min. After completion of the reaction as indicated by TLC, 15 ml of water was added and stirred well. The compound of organic layer were washed with brine and dried over Na_2SO_4 and concentrated by rotatory evaporation. The crude product was purified by chromatography on silica gel (ethyl acetate : petroleum = 1 : 4) to yield the title

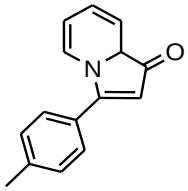
product as yellow oil. After isolation of the product, the remaining aqueous layer containing the ionic liquid was washed with $(C_2H_5)_2O$ (2x10 ml), to remove organic impurity and filtered. The filtrate was extracted with CH_2Cl_2 (2x10 ml), dried over $MgSO_4$ and evaporated under reduced pressure to afford [bmim]OH, which was reused three times without any appreciable decrease in its activity.

5a: 3-Phenyl-8aH-indazolin-1-one



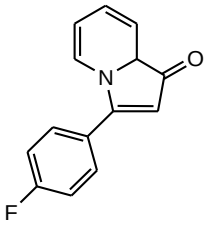
Yellow oil, ^{1}HNMR (400 MHz, $CDCl_3$/TMS): δ_H = 4.17 (d, 1H), 5.26 (m, 1H), 5.60 (m, 1H), 5.7 (s, 1H), 6.17 (m, 1H), 6.19 (d, 1H), 7.14-7.30 (m, 5H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 75.5, 96.6, 107.5, 124.0, 126.4, 126.5, 127.3, 128.0, 128.7, 128.9, 134.3, 136.9, 150.9, 196.5. EIMS: (m/z): 209 (M^+), Anal. calcd. For $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.34; H, 5.31; N, 6.70.

5b: 3-P-tolyl-8aH-indazolin-1-one



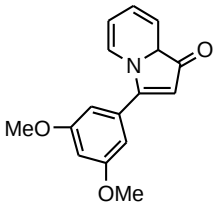
Yellowish solid, mp 71-73°C, ^{1}HNMR (400MHz, $CDCl_3$/TMS) δ_H = 4.17 (d, 1H), 2.35 (s, 3H, CH_3), 5.26 (m, 1H), 5.60 (m, 1H); 5.7 (s, 1H), 6.19 (m, 1H), 6.19 (d, 1H), 7.01-7.18 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 24.3, 75.6, 96.6, 107.5, 124.0, 126.3, 126.4, 127.3, 129.0, 129.1, 131.3, 136.9, 137.6, 150.9, 196.5. EIMS: (m/z): 223 (M^+), Anal. calcd. For $C_{14}H_{13}NO$: C, 80.69; H, 5.87; N, 6.69. Found: C, 80.70; H, 5.88; N, 6.67.

5c: 3-(-4-Flouro-Phenyl)-8aH-indazolin-1-one



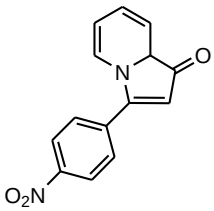
Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 4.17 (d, 1H), 5.26 (m, 1H), 5.60 (m, 1H), 5.7 (s, 1H), 6.17 (m, 1H), 6.19 (d, 1H), 6.92-7.3 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 75.5, 96.6, 107.5, 115.4, 115.6, 124.0, 127.3, 128.0, 128.1, 129.9, 136.9, 150.9, 162.1, 196.5. EIMS: (m/z): 227 (M^+), Anal. calcd. For $C_{14}H_{10}FNO$: C, 74.0; H, 4.44; N, 6.16. Found: C, 74.1; H, 4.45; N, 6.14.

5d: 3-(3,5-Dimethoxy-Phenyl)-8aH-indazolin-1-one



Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 3.73 (s, 6H, OCH_3), 4.17 (d, 1H), 5.26 (m, 1H), 5.60 (m, 1H), 5.7 (s, 1H), 6.17 (m, 1H), 6.19 (d, 1H), 6.16-6.39 (m, 3H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 55.9, 56.0, 75.5, 96.6, 96.7, 102.9, 103.0, 107.5, 124.0, 127.3, 136.3, 136.9, 150.9, 161.6, 161.8, 196.5. EIMS: (m/z): 269 (M^+), Anal. calcd. For $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.19. Found: C, 71.35; H, 5.61; N, 5.22.

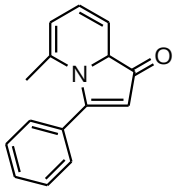
5e: 3-(4-Nitro-Phenyl)-8aH-indazolin-1-one



Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 4.17 (d, 1H), 5.26 (m, 1H), 5.60 (m, 1H), 5.98 (s, 1H), 6.17 (m, 1H), 6.19 (d, 1H), 7.56-8.14 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C =

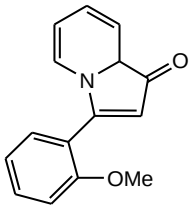
75.5, 96.6, 107.5, 121.0, 121.2, 124.0, 127.3, 127.4, 127.6, 136.9, 140.4, 150.9, 157.6, 196.5. EIMS: (m/z): 223 (M^+), Anal. calcd. For $C_{14}H_{10}N_2O_3$: C, 66.14; H, 3.96; N, 11.02. Found: C, 66.17; H, 3.95; N, 11.00.

5f: 5-methyl-3-Phenyl-8aH-indazolin-1-one



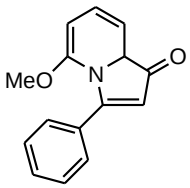
Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 1.71 (s, 3H, CH_3), 4.17 (d, 1H), 5.04 (m, 1H), 5.60 (m, 1H), 5.60 (s, 1H), 6.17 (m, 1H), 7.14-7.30 (m, 5H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 20.7, 73.0, 96.6, 102.2, 124.0, 126.4, 126.6, 127.3, 128.0, 128.7, 128.9, 134.3, 150.9, 152.2, 196.5. EIMS: (m/z): 223 (M^+), Anal. calcd. For $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.70; H, 5.88; N, 6.25.

5g: 3-(2-methoxy-Phenyl) -8aH-indazolin-1-one



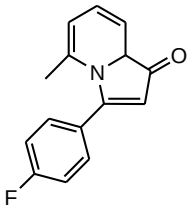
Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 3.73 (s, 3H, OCH_3), 4.17 (d, 1H), 5.26 (m, 1H), 5.51 (s, 1H), 5.60 (m, 1H), 6.17 (m, 1H), 6.19 (s, 1H), 6.72-7.19 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 56.3, 75.5, 96.6, 107.2, 108.5, 114.2, 121.0, 124.0, 127.3, 127.4, 129.0, 136.9, 150.9, 157.7, 196.5. EIMS: (m/z): 239 (M^+), Anal. calcd. For $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.30; H, 5.48; N, 5.85.

5h: 5-(methoxy-3-phenyl-8aH-indazolin-1-one



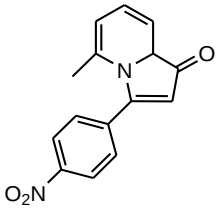
Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 3.50 (s, 3H, OCH_3), 4.17(s, 1H), 4.51 (d, 1H), 5.60 (m, 1H), 5.7 (s, 1H), 6.17 (m, 1H), 6.17 (m, 1H), 7.14-7.30 (m, 5H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 68.0, 69.6, 96.7, 124.0, 126.4, 127.3, 128.0, 128.7, 128.8, 134.3, 150.9, 151.1, 156.1, 196.6. EIMS: (m/z): 239 (M^+), Anal. calcd. For $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 6.69. Found: C, 75.29; H, 5.47; N, 6.71.

5i: 3-(4-Flouro-Phenyl)-5-methyl-8aH-indazolin-1-one



Yellow oil, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 1.71 (s, 3H, CH_3), 4.17 (d, 1H), 5.04 (m, 1H), 5.60 (m, 1H), 5.7 (s, 1H) , 6.17 (m, 1H), 7.92-7.3 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 20.7, 73.0, 96.6, 102.2, 115.4, 115.6, 124.0, 127.3, 128.0, 128.2, 129.9, 150.9, 152.2, 162.1, 196.5. EIMS: (m/z): 241 (M^+), Anal. calcd. For $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 74.64; H, 5.03; N, 5.80.

5j: 5-methyl-3-(4-nitro-Phenyl) -8aH-indazolin-1-one



Yellowish solid, mp 65-67°C, ^{1}HNMR (400MHz, $CDCl_3$/TMS): δ_H = 1.71 (s, 3H, CH_3), 4.17 (d, 1H), 5.04 (m, 1H), 5.60 (m, 1H), 5.98 (s, 1H), 6.17 (m, 1H), 7.56-8.14 (m, 4H). ^{13}CNMR (100MHz, $CDCl_3$/TMS): δ_C = 20.7, 73.0, 96.6, 102.2, 121.0, 121.2, 124.0, 127.3, 127.5, 127.6, 140.4, 147.6, 150.9, 152.2, 196.6. EIMS: (m/z): 268 (M^+), Anal. calcd. For $C_{15}H_{12}N_2O_3$: C, 67.19; H, 4.51; N, 10.44. Found: C, 67.16; H, 4.51; N, 10.44.