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To cite this article: Rajendra Surasani , Dipak Kalita & K.B. Chandrasekhar (2013) Indion Ina 225H resin as a novel, selective, recyclable, eco-benign heterogeneous catalyst for the synthesis of bis(indolyl)methanes, Green Chemistry Letters and Reviews, 6:2, 113-122, DOI: [10.1080/17518253.2012.711372](https://doi.org/10.1080/17518253.2012.711372)

To link to this article: <https://doi.org/10.1080/17518253.2012.711372>



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RESEARCH LETTER

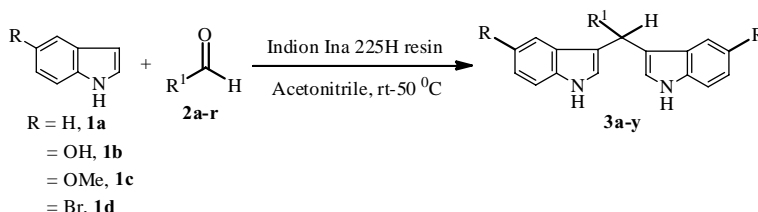
Indion Ina 225H resin as a novel, selective, recyclable, eco-benign heterogeneous catalyst for the synthesis of bis(indolyl)methanes[#]

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(Received 29 August 2011; final version received 11 June 2012)

Indion Ina 225H, is a heterogeneous, selective, recyclable, and eco-benign catalyst for liquid phase electrophilic substitution reactions of indoles with aldehydes to afford the corresponding bis(indolyl)methanes in excellent yields in short reaction time. The versatility of this method has been proved with a wide range of aliphatic and aromatic aldehydes with various stereo-electronic factors. This method shows much better selectivity between aldehydes and ketones. The methodology is well demonstrated toward the synthesis of biologically active bis(indolyl)methanes *viz.* vibrioidole, 4-(di(1H-indol-3-yl)methyl)benzene-1,2-diol and streptindole. The catalyst can be recovered and reused for several runs without loss of activity.



Keywords: Indion Ina 225H resin; indole; bis(indolyl)methane; aldehydes; ketones

Introduction

Indoles and their derivatives possess various biological properties like antibacterial, cytotoxic, antioxidative, and insecticidal activities. Some indole derivatives are used as antibiotics in pharmaceutical industry (1–3). Bis(indolyl)alkanes have received considerable attention because of occurrence in bioactive metabolites of terrestrial and marine origin (4–7). Therefore, the synthesis of these moieties has become interesting target to synthetic organic chemists. Recently Pedro Molina and co-workers (8) have developed new probes, based on bis(indolyl)methane derivatives to sense Cu²⁺ ions among other transition metal ions.

Owing to the ubiquitous nature of indole derivatives in organic compounds and the need to synthesize various bis(indolyl)methane compounds in multi-gram quantities for our ongoing project; we embarked

on developing a new methodology for these compounds. Literature enumerates various methods for synthesis of bis(indolyl)methane using protic acids (9–15), Lewis acids (16–20), and inorganic compounds. However, most of the methods suffer from drawbacks like long reaction times of 4–5 days (21), high catalyst loading and use of expensive catalysts (22–27) or less easily available reagents (28,29), low selectivity (30), use of toxic solvents (31,32), tedious manipulations in the isolation of the pure products (33), unsatisfactory yields, or limited applicability only for aryl aldehydes (34). Furthermore, some of these methods require strictly anhydrous conditions (35–38). Recently, a few methods that circumvent some of these problems have been reported (39–42).

A number of green methods is in vogue for the synthesis of bis(indolyl)methanes using ionic liquids

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[#]DRL-CPS Communication number: IPDO IPM- 00293.

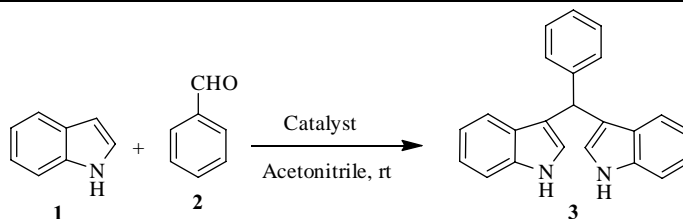
(43–46), various heterogeneous catalyst like Amberlyst resins (47,48), ion-exchange resins (49), silica supported sodium hydrogen sulphate (18), and FeF_3 (50) etc. Few green procedures for the synthesis of bis(indolyl)methanes in aqueous media also reported (39, 51–53). However, for practical utilization, imidazolium-based ionic liquids still suffer from the drawbacks of acute toxicity (54–56) and relatively expensive cost somewhat impractical for larger industrial applications and are not cost-effective for larger industrial preparations. Poor solubility of many organic compounds in aqueous media makes it impractical for large industrial scale and the reactivity of some organic compounds toward water. There are few reports which describe the synthesis of bis(indolylmethanes) from indoles and carbonyl compounds under solvent free conditions (57,58) However, performing the reaction without any solvent is not viable in large scale synthesis from industrial perspective. Recovery and reusability of few catalyst while synthesizing bis(indolylmethanes) also described (50,59,60). Shingare *et al.* reported the recovery and recycling of their catalyst (Cellulose sulphuric acid) twice without loss of activity (59). Pore *et al.* describes the reusability of their catalyst (silica sulphuric acid) for at least three cycles without any change in activity (60). Kamble *et al.* describes the reusability of FeF_3 for four consecutive run (50). The selection of Indion Ina 225H resin as reusable catalyst gives maximum five number of recyclables

compared to other ion-exchange resin *viz.* Amberlyst 15 (no report on recyclability) etc.

The biggest disadvantage in many of the methods is that many Lewis acids are deactivated or sometimes decomposed by nitrogen-containing reactants when the reaction is carried out in large scale. Even when the desired reactions proceed, more than stoichiometric amounts of Lewis acids are required because the acids are trapped by nitrogen (61). Moreover, after completion of the reaction, the excess Lewis acids are destroyed in the aqueous quench, liberating large amounts of harmful mixtures containing metal ions and organic wastes that are detrimental to our delicate eco-system. Further, the use of soluble metal catalysts in these systems often necessitates a tedious catalyst separation step. Consequently, there is a need for a greater catalytically efficient method for these transformations which might work under mild and more economical and environmentally benign conditions. Therefore, the search continues for a better catalyst for the synthesis of bis(indolyl)methane derivatives in terms of operational simplicity, reusability, economic viability, and greater selectivity. For reasons of safety and health hazards especially in large-scale preparation an alternative method was sought and we found that use of cation exchange resin Indion Ina 225H led to better selectivity, highest yield, ease of catalyst recovery and reuse.

The use of resin as a catalyst has significant practical advantages since it is inexpensive and nontoxic. In particular, the chemistry of resin in

Table 1. Screening of catalyst.



Entry	Catalyst ^a	Time (hrs)	Yield (%) ^b
1	Indion Ina 225H	1	98
2	Indion 130	24	NR
3	Amberlyst-15	12	85
4	Dowex 50	24	Traces
5	Amberjet 1200 H	24	NR
6	Amberlite IR 120	24	NR
7	H_2SO_4	2	90
8	<i>p</i> -TsOH	6	80
9	Sulfamic acid	12	78

^a100 mg of the catalyst was used.

^bYields referred to the isolated yield.

Table 2. Effect of solvent on the conversion of indole and benzaldehyde to bis(indolyl)methanes with Indion Ina 225H resin.^a

Entry	Solvent	Temperature (°C)	Yield% ^b
1	Methanol	Reflux	20
2	Ethanol	Reflux	25
3	<i>i</i> -PrOH	Reflux	20
4	H ₂ O	60	NR
5	THF	Reflux	35
6	Toluene	80	40
7	Dichloromethane	Reflux	20
8	2-Methyl THF	Reflux	18
9	Acetonitrile	50	98
10	Acetonitrile	Rt	98

^aAll reactions were carried out using 2:1 mol ratio of indole and benzaldehyde and 100 mg of Indion Ina 225H resin.

^bIsolated yield.

^cNR, no reaction.

organic synthesis has recently received increasing attention over its companion reagents owing to its stability in water and air actively utilized as a catalyst for various types of organic syntheses (62–65). In addition, the growing concern for the influence of the chemical reagents on the environment as well as on human body, recovery and reusability of the chemical reagents have attracted the attention of synthetic organic chemists. Notably pharmaceutical industry has given more importance toward recovery and reuse of chemical reagents to reduce the cost of a product as well as the environmental burden. As part of continuing effort in our laboratory (66–69) toward the development of new methods in organic synthesis, we became interested in the possibility of developing a one-pot synthesis of bis(indolyl)methanes (**3a–y**) catalyzed by Indion Ina 225H resin.

Results and discussion

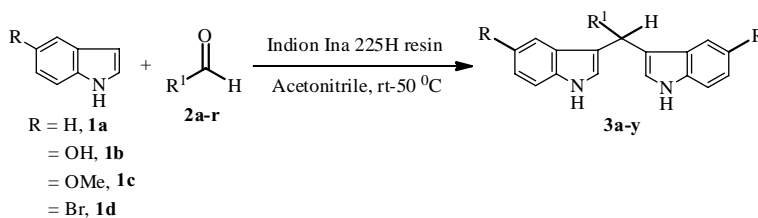
Indion Ina 225H resin is a macro reticular sulfonic acid based cation exchange resin which is inexpensive and commercially available with very low cost. It appears as golden yellow beads. The matrix is styrene divinylbenzene copolymer. To the best of our knowledge there is no report of the use of Indion Ina 225H resin as a catalyst for these types of reactions.

Optimization of reaction conditions and substrate studies

To find out the best catalyst system for the conversion of indole to bis(indolyl)methanes in large scale synthesis we have screened various Lewis acids such as Amberjet 1200H, Amberlite IR 120, Indion 130, Indion Ina 225H, Amberlyst 15, sulphuric acid etc (Table 1). Reaction of indole (2 mmol) and benzaldehyde (1 mmol) was used as a model substrate. As seen from the Table 1, Indion Ina 225H catalyzes the reaction better than other catalyst except sulphuric acid, which is highly corrosive and hazardous and not acceptable for large scale synthesis.

Next, we investigated the catalytic activity of Indion Ina 225H resin with different solvents and the results are summarized in Table 2. While choosing the solvent we have preferably avoided the use of ICH class-1 solvents (benzene, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethane, and 1,1,1-trichloroethane) and ICH class-4 solvents (1,1-diethoxy propane, 1,1-dimethoxy propane, 2,2-dimethoxy propane, isooctane, isopropyl ether, methyl isopropyl ketone, methyltetrahydrofuran, petroleum ether etc) in the synthesis. Among the solvent examined, acetonitrile proved to be the most effective (Table 2, entry 9 and 10).

To explore the generality and scope of this method, a wide variety of substituted indoles and aldehydes were reacted using Indion Ina 225H resin



Scheme 1. General scheme for synthesis of bis(indolyl)methane compounds from aldehydes and indoles.

Table 3. Indion Ina 225H resin catalyzed efficient synthesis of bis(indolyl)methanes.^a




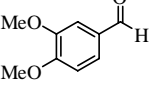

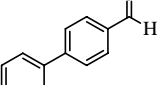

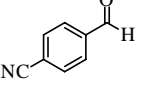

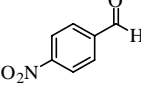

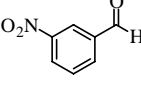

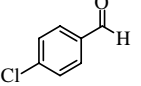

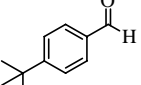
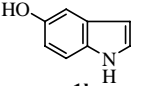
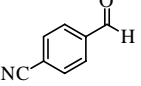
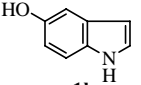
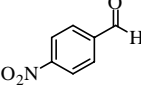
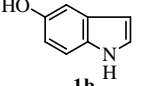
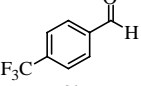
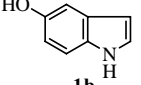
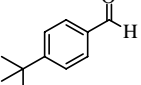
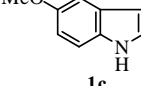
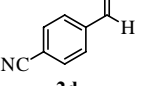
Entry	Indole derivative 1	Carbonyl compound 2	Product ^b 3	Temperature (°C)	Time (hrs)	Yield (%) ^c	M.p (°C) (Ref) ^e
1			3a	50	2.5	90	145–147 (70)
2			3b	50	2.0	92	193–195 (11)
3			3c	50	2.5	95	246–248
4			3d	rt	3.4	95	209–210 (71,72)
5			3e	50	2.1	95	228–230 (73)
6			3f	50	2.3	95	96–98 (34)
7			3g	rt	3.0	93	98–101 (74)
8			3h	rt	2.5	95	70–72
9			3i	rt	2.2	96	212–215
10			3j	rt	2.3	95	225–228
11			3k	rt	2.6	94	146–148
12			3l	rt	2.4	95	144–146
13			3m	rt	2.3	95	110–113

Table 3 (Continued)

Entry	Indole derivative 1	Carbonyl compound 2	Product ^b 3	Temperature (°C)	Time (hrs)	Yield (%) ^c	M.p (°C) (Ref) ^e
14			3n	rt	2.6	95	115–118
15			3o	rt	2.2	89	113–115 (75)
16			3p	50	2.0	92	–
17			3q	50	2.0	93	–
18			3r	50	2.0	93	–
19			3s	50	2.5	90	96–98
20			3t	50	2.0	92	156–158
21			3u	50	2.5	95	105–107
22			3v	50	24h	NR ^d	–
23			3w	50	2.0	95	144–146 (76)
24			3x	50	2.0	93	123–125
25			3y	50	3.0	95	85–87

^aAll reactions were carried out using 2:1 mol ratio of indole and benzaldehyde, 100 mg of Indion Ina 225H resin in acetonitrile at the specified temperature.

^bAll products were characterized by their spectroscopic and physical data and are in agreement with the literature data.

^cIsolated yield.

^dNR, no reaction.

^eMelting points compared with physical data in lit.

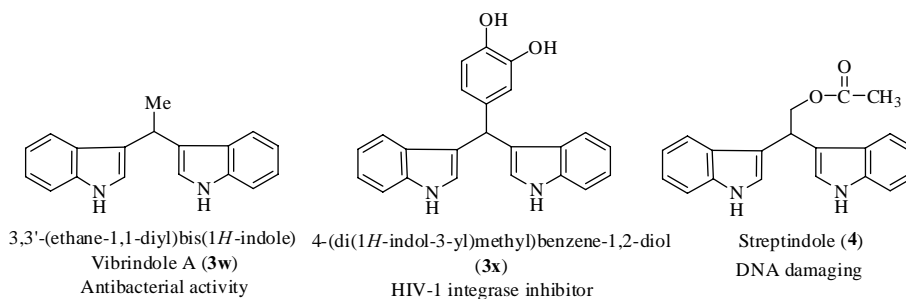


Figure 1. Synthesis of few bioactive bis(indolyl)methanes.

under optimized experimental (Scheme 1) conditions to afford the corresponding bis(indolyl)methane and the results are summarized in Table 3. The isolated products were characterized by spectral analyses.

The effect of electron deficiency and the nature of substituent on the aromatic ring of aldehyde showed some effect on this conversion. The chloro- and nitro-substituted aryl aldehydes required similar times to produce comparable yields than those of their simple electron-rich counterparts. Electron-rich aldehydes like 3,4-dimethoxybenzaldehyde (Table 3, entry 2) and 4-(trifluoromethyl)benzaldehyde (Table 3, entry 11) reacted rapidly with indole and 5-substituted indole to give excellent yields of the products. The reaction works equally good with the aliphatic aldehydes (Table 3, entry 16–18) and indoles in shorter reaction time with high yields. The reaction conditions are mild enough not to induce any isomerization for furfural (Table 3, entry 15) or damage to moieties such as methoxy, which often undergo cleavage in strongly acidic reaction media (Table 3, entry 2 and 13). The selectivity of the aldehydes and ketones was also verified and found that the resin is specific to aldehydes as shown in Table 3 (entry 19–21). As seen from the Table 3 acetophenone (Table 3, entry 22) did not react at all with indole in presence of Indion Ina 225H resin under the reaction condition we studied. On the other hand, no side products were observed in the course of the reactions we studied. The Vibrindole A (**3w**, Table 3, entry 23) and 3,3'-diindolylmethane (**3x**, Table 3, entry 24) synthesized by one-pot has broad range of pharmacological activity (Figure 1). Vibrindole A (**3w**) is a metabolite of the marine

bacterium *Vibrio parahaemolyticus* which exhibit antibacterial activity (**5**). In recent studies on cancer therapeutics, 4-(di(1*H*-indol-3-yl)methyl)benzene-1,2-diol (**3x**) served as a HIV-1 integrase inhibitor (**77**). The products mentioned in Table 3 were isolated without any column purification.

With the aforementioned successful results in hand, we want to enhance the scope of the present methodology toward the synthesis of biologically active bis(indolyl)methane Streptindole (**4**), for its broad range of pharmacological activity (Figure 1). The structure of genotoxic metabolite, streptindole (**4**), isolated from intestinal bacteria *Streptococcus faecium* IB37 has been established as 2,2-di(3-indolyl) ethyl acetate by spectroscopic and synthetic methods by Osawa *et al.* (**78–80**). Chakrabarty *et al.* reported another method for the preparation of Streptindole (**4**) by treatment of indole and glycoaldehyde dimethylacetal in presence of montmorillonite K10 clay under solvent free conditions followed by acylation reaction (**61**). The strategy we followed for the Streptindole (**4**) synthesis is shown in Scheme 2.

Reduction of ethyl di-1*H*-indol-3-ylacetate (**3y**) by $\text{BH}_3\text{-THF}$ complex in THF results the corresponding alcohol **5** in 90% yields. Finally, the alcohol **5** is *O*-acetylated using FeF_3 as a reusable green Lewis acid catalyst (**66**) to afford the corresponding Streptindole (**4**) in 99% yield (Scheme 2). This acylation reaction is facilitated by the action of FeF_3 as a useful reagent which can be recovered and reused for several runs.

Recovery of the resin

After completion of the reaction the resin was filtered and washed with acetonitrile. The recovered resin was

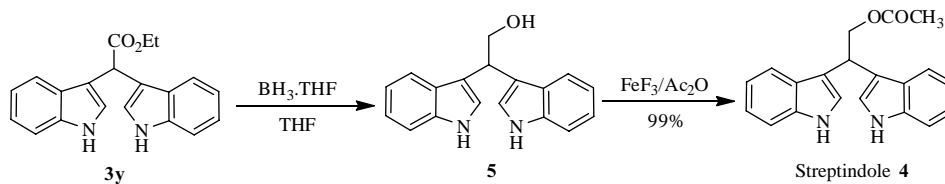
Scheme 2. Synthetic scheme for Streptindole **4**.

Table 4. Indion Ina 225H resin recyclability.^a

Entry	Run	Yield (%) ^b
1	0	95
2	1	93
3	2	92
4	3	90
5	4	90

^aReactions were performed with indole (2 mmol), aldehyde (1 mmol) using 100 mg of Indion INA 225H resin and 1 mL of acetonitrile as a solvent at room temperature for 1 h.

^bIsolated yield.

recycled for consecutive five times for the reaction to furnish the product with little variation in yields (Table 4). Compared to other companion heterogeneous Lewis acid catalyst, resins or supported catalyst, Indion Ina 225H resin has highest number of recovery and reusability which make it more environmentally friendly and economic in terms of reduced cost of the product.

Infrared Spectrum of the recovered Indion Ina 225H and fresh Indioan Ina 225H resin

Infrared spectrum of the recovered (after 5th run) and fresh sample of Indion Ina 225H resin is shown in Figure 2. The FT-IR spectrum shows absorption at 3700–3400 cm^{-1} (-OH stretches). The presence of moisture is evident through the broadness of the peak

around 3600 cm^{-1} due to the bending mode of the adsorbed water in the recovered sample of Indion Ina 225H resin sample (after 5th run). The sulfonic acids on the resin can be readily identified by the appearance of two strong bands at 1400 and 1210–1120 cm^{-1} due to the asymmetric and symmetric stretching vibrations of the S=O group, respectively.

Experimental

General

All compounds proton (^1H) and (^{13}C) NMR spectra were recorded at 25 °C in CDCl_3 on a Varian Mercury operating 400 MHz for proton and carbon nuclei. ^1H NMR data are recorded as follows: Chemical shift (δ) multiplicity is defined as: *s* = singlet; *d* = doublet; *t* = triplet; *q* = quartet; *m* = multiplet, or combinations of the aforementioned. The residual CDCl_3 peak (δ 7.26) residual DMSO peaks (δ 2.50) were used as reference for ^1H NMR spectra. The central peak (δ 77.0) of the CDCl_3 triplet and the central peak (δ 39.5) of the $\text{DMSO}-d^{16}$ heptet were used as references for proton decoupled ^{13}C NMR spectra. Infrared spectra were recorded on a Perkin Elmer Spectrum one FTIR spectrometer. Samples were analyzed as KBr pellets. Agilent 6410 mass spectrometer was used to obtain low and high resolution electron impact mass spectra. HRMS spectra were recorded with Waters LCT Premier XE

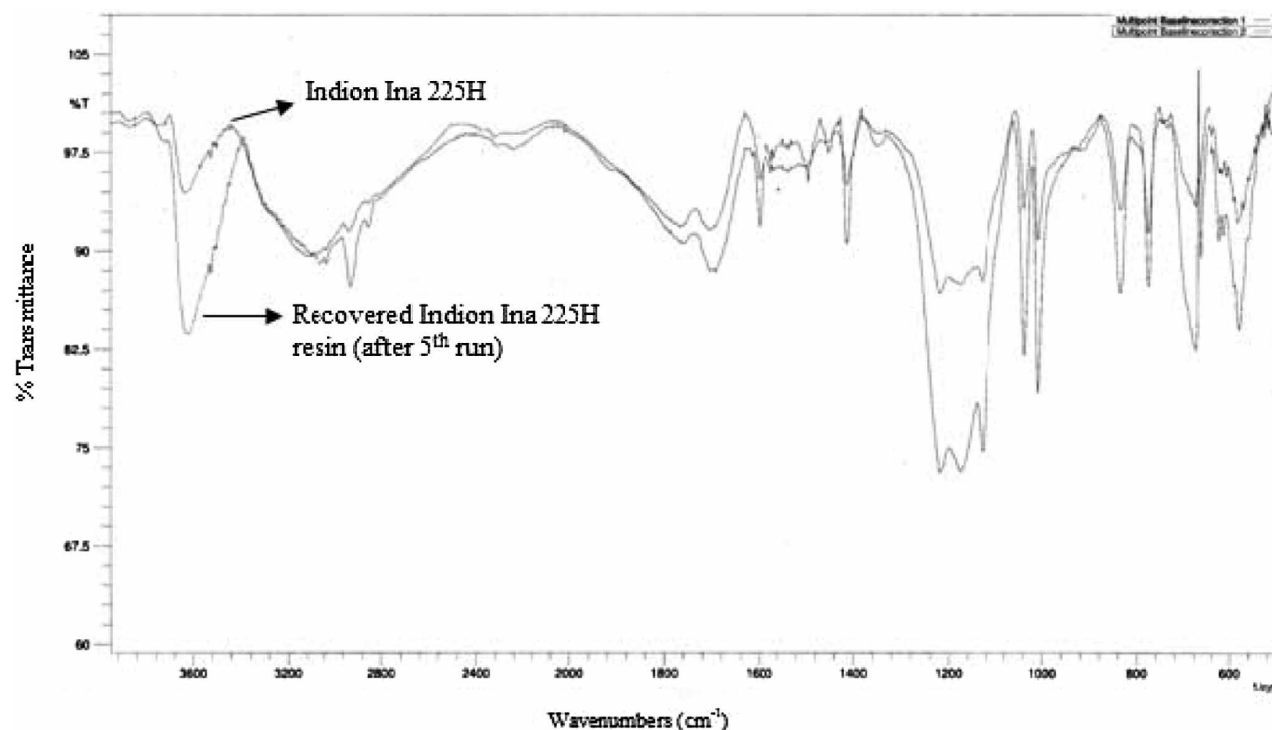


Figure 2. Infrared spectrum of Indion Ina 225H resin.

(Micro mass Qa-TOF) instrument. Melting points were measured on a Buchi B-540 melting point system. All starting materials and reagents were generally available from Sigma-Aldrich, Merck and Lancaster was used as supplied. Remaining all other solvents was commercially available and used without purification. All reactions were performed under nitrogen atmosphere.

A typical experimental procedure

A mixture of indole (**1a**; 200 mmol) and benzaldehyde (**2a**; 100 mmol) and Indion Ina 225H resin (50g with respect to aldehyde) in acetonitrile (500 ml) was stirred at room temperature for an appropriate time (Table 3). The reaction progress was monitored by TLC (EtOAc:Hexane, 10–25% mixture in Hexane) and HPLC, respectively. After complete conversion the heterogeneous mass was filtered and the resin was washed with acetonitrile. The solvent was removed in a rotary evaporator under reduced pressure. To the crude reaction mass heptanes (500 mL) was added and distill off the heptane in a rotary evaporator under reduced pressure to result off-white solid. To this solid again added 200 mL of heptanes and stirred for 15–20 minutes at room temperature. The solid was filtered and dried in an oven in vacuum to afford the pure product (Yield: 90%).

Representative Spectral data

4-[(5-hydroxy-1H-indol-3-yl)(1H-indol-3-yl)methyl]benzonitrile (**3i**): Brick red solid; yield 96%; IR (KBr): 773, 800, 973, 1184, 1456, 1487, 1581, 1604, 2227, 3406; ¹H NMR (400 MHz, DMSO-*d*₆): δ 5.69 (s, 1H, Ar-CH), 6.55–6.70 (m, 4H), 6.69 (d, 2H, *J* = 2.0 Hz), 7.13–7.15 (m, 2H), 7.48 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz), 8.48 (s, 2H, OH), 10.54 (brs, 2H, NH); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 102.97, 108.49, 111.36, 111.79, 115.79, 119.06, 124.18, 127.05, 129.27, 131.10, 131.98, 150.02, 150.83; MS (ES): *m/z* 378.3 (M-H)⁺. HRMS (ESI): calculated for C₂₄H₁₆N₃O₂ (M-H)⁺ 378.1243; found 378.1227.

Conclusions

In conclusion, we have demonstrated that Indion Ina 225H resin is an excellent catalyst for the reaction of indoles and aromatic and aliphatic aldehydes to give the corresponding bis(indolyl)methanes. The catalyst has high activity and can be handle very easily in large scale synthesis. The procedure has the advantages of mild reaction conditions, higher yield of the products, short reaction time, selectivity between aldehydes and ketones, reacts only with aldehydes,

simple experimental procedure, no column chromatography involved, making it a useful, and alternative process for the synthesis of bis(indolyl)methane derivatives in large scale synthesis. The catalyst can be recovered conveniently without losing its catalytic activity and can be reused for several runs. Compared to other heterogeneous catalyst reported in literature, Indion Ina 225H can be recovered and reused for minimum five times which makes the process more economic and environment friendly. The methodology also utilized for the synthesis of naturally occurring bis(indolyl)methane compounds, such as Vibrindole A, 4-(di(1H-indol-3-yl)methyl)benzene-1,2-diol and Streptindole. Further studies on the utilization of this methodology toward the complex natural products are now under progress in the laboratory.

Acknowledgement

The authors thank Dr. Vilas Dahanukar of Dr. Reddy's Laboratories Ltd. for his encouragement and the analytical group for spectral data. Mr. Rajendra Surasani thanks CPS-Dr. Reddy's Laboratories Ltd, Hyderabad, India, for allowing him to pursue this work as a part of his Ph.D. program.

References

- (1) Sundberg, R.J. *The Chemistry of Indoles*; Academic: Newyork, 1970.
- (2) Lounasmaa, M.; Tolvanen, A. *Nat. Prod. Rep.* **2000**, *17*, 175–191.
- (3) Hibino, S.; Chozi, T. *Nat. Prod. Rep.* **2001**, *18*, 66–87.
- (4) Grabe, T.R.; Kobayashi, M.N.; Shimizu, N.; Takesue, M.; Ozawa, H.; Yukawa, J. *J. Nat. Prod.* **2000**, *63*, 596–598.
- (5) Bell, R.; Carmeli, S.; Sar, N. *J. Nat. Prod.* **1994**, *57*, 1584–1586.
- (6) Osawa, T.; Namiki, M. *Tetrahedron Lett.* **1983**, *24*, 4719–4722.
- (7) Guinchard, X.; Vallee, Y.; Denis, J.N. *J. Org. Chem.* **2007**, *72*, 3972–3975.
- (8) Martinez, R.; Espinosa, A.; Tarraga, A.; Molina, P.; *Tetrahedron*, **2008**, *64*, 2184–2191.
- (9) Chatterjee, A.; Manna, S.; Benerji, J.; Pascard, C.; Prange, T.; Shoolery, J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 553–557.
- (10) Earle, M.J.; Fairhurst, R.A.; Heaney, H. *Tetrahedron Lett.* **1991**, *32*, 6171–6174.
- (11) Chen, D.; Yu, L.; Wang, P.G. *Tetrahedron Lett.* **1996**, *37*, 4467–4470.
- (12) Babu, G.; Sridhar, N.; Perumal, P.T. *Synth. Commun.* **2000**, *30*, 1609–1614.
- (13) Yadav, J.S.; Subba Reddy, B.V.; Murthy, V.S.R.; Kumar, G.M.; Madan, C. *Synthesis* **2001**, 783–787.
- (14) Nagarajan, R.; Perumal, P.T. *Tetrahedron* **2002**, *58*, 1229–1232.

- (15) Ji, S.-J.; Zhon, M.-F.; Gu, D.-G.; Wang, S.Y.; Loh, T.-P. *Synlett* **2003**, 2077–2079.
- (16) Roomi, M.; MacDonald, S. *Can. J. Chem.* **1970**, *48*, 139–143.
- (17) Chakrabarty, M.; Ghosh, N.; Basak, R.; Harigaya, Y. *Tetrahedron Lett.* **2002**, *43*, 4075–4078.
- (18) Ramesh, C.; Banerjee, J.; Pal, R.; Das, B. *Adv. Synth. Catal.* **2003**, *345*, 557–559.
- (19) Mahadevan, A.; Sard, H.; Gonzalez, M.; McKew, J.C. *Tetrahedron Lett.* **2003**, *44*, 4589–4591.
- (20) Reddy, A.V.; Ravinder, K.; Reddy, V.L.N.; Goud, T.V.; Ravikanth, V.; Venkateswarlu, Y. *Synth. Commun.* **2003**, *33*, 3687–3694.
- (21) Kamal, A.; Qureshi, A.A. *Tetrahedron* **1963**, *19*, 513–520.
- (22) Harrington, P.E.; Kerr, M.A. *Synlett* **1996**, 1047–1048.
- (23) Reddy, A.V.; Ravinder, K.; Goud, T.V. Krishnaiah, P.; Raju, T.V.; Venkateswarlu, Y. *Tetrahedron Lett.* **2003**, *44*, 6257–6260.
- (24) Kawatsura, M.; Aburatani, S.; Uenishi, J.; *Synlett* **2005**, 2492–2494.
- (25) Arcadi, A.; Bianchi, G.; Chiarini, M.; D'Anniballe, G.; Marinelli, F. *Synlett* **2004**, 944–950.
- (26) Mi, X.; Luo, S.; He, J.; Cheng, J.-P. *Tetrahedron Lett.* **2004**, *45*, 4567–4570.
- (27) Nagrajan, R.; Perumal, P.T. *Tetrahedron* **2002**, *58*, 1229–1232.
- (28) Chalaye-Mauger, H.; Denis, J.-N.; Averbuch-Pouchot, M.-T.; Vallee, Y. *Tetrahedron* **2000**, *56*, 791–804.
- (29) Bandini, M.; Fagioli, M.; Melchiorre, P.; Melloni, A.; Umani-Ronchi, A. *Tetrahedron Lett.* **2003**, *44*, 5843–5846.
- (30) Singh, H.; Singh, K.; *Tetrahedron* **1988**, *44*, 5897–5904.
- (31) Sharma, G.V.M.; Reddy, J.J.; Lakshmi, P.S.; Krishna, P.R. *Tetrahedron Lett.* **2004**, *45*, 7729–7732.
- (32) Farhanullah; Sharon, A.; Maulik, P.R.; Ram, V.J. *Tetrahedron Lett.* **2004**, *45*, 5099–5102.
- (33) Bandgar, V.; Shaikh, K.A.; *Tetrahedron Lett.* **2003**, *44*, 1959–1961.
- (34) Penieres-Carrillo, G.; Gacia-Estrada, J.G.; Gutierrez-Ramirez, J.L.; Alvarez Toledano, C. *Green. Chem.* **2003**, *5*, 337–339.
- (35) Bandini, M.; Cozzi, P.G.; Giacomini, M.; Melchiorre, P.; Selva, S.; Umani-Ronchi, A. *J. Org. Chem.* **2002**, *67*, 3700–3704.
- (36) Noland, W.E.; Christensen, G.M.; Sauer, G.L.; Dutton, G.G.S. *J. Am. Chem. Soc.* **1955**, *77*, 456–457.
- (37) Iqbal, Z.; Jackson, A.H.; Rao, K.R.N. *Tetrahedron Lett.* **1988**, *29*, 2577–2580.
- (38) Ji, S.-J.; Wang, S.-Y. *Ultrason. Sonochem.* **2005**, *12*, 339–343.
- (39) Mohammad, R.; Saidi, N.A.; Torikian, L. *J. Mol. Catal. A.* **2007**, *275*, 109–112.
- (40) Khaksar, S.; Talesh, S.M. *J. Fluorine Chem.* **2012**, *135*, 87–89.
- (41) Sagar, A.D.; Reddy, S.M.; Pulle, J.S.; Yadav, M.V. *Int. J. Chem. Sci.* **2011**, *9*, 1979–1986.
- (42) Liu, C.; Yu, C.J. *Heterocyclic Chem.* **2011**, *48*, 845–848.
- (43) Yadav, J.S.; Reddy, B.V.S.; Sunitha, S. *Adv. Synth. Catal.* **2003**, *345*, 349–352.
- (44) Ji, S.J.; Zhou, M.F.; Gu, D.G.; Jiang, Z.Q.; Loh, T.P. *Eur. J. Org. Chem.* **2004**, *69*, 1584–1587.
- (45) Hagiwara, H.; Sekifuji, M.; Hoshi, T.; Qiao, K.; Yokoyama, C. *Synlett.* **2007**, 1320–1322.
- (46) Gu, D.G.; Ji, S.J.; Jiang, Z.Q.; Zhou, M.F.; Loh, T.P. *Synlett.* **2005**, 959–962.
- (47) Ke, B.; Qin, Y.; Wang, Y.; Wang, F. *Synth. Commun.* **2005**, *35*, 1209–1212.
- (48) Singh, K.; Sharma, S.; Sharma, A. *J. Mol. Cat. A-Chem.* **2011**, *347*, 34–37.
- (49) Feng, X.-L.; Guan, C.J.; Zhao, C.X. *Synth. Commun.* **2004**, *34*, 487–492.
- (50) Kamble, V.T.; Bandgar, B.P.; Suryawanshi, S.B.; Bavikar, S.N. *Aust. J. Chem.* **2006**, *59*, 837–840.
- (51) Sobhani, S.; Safaei, E.; Hasaninejad, A.-R.; Rezazadeh, S. *J. Organomet. Chem.* **2009**, *694*, 3027–3031.
- (52) Ghorbani, V.R.; Veisi, H.; Keypour, H.; Dehghani, F.A.A. *Mol. Divers.* **2010**, *14*, 87–96.
- (53) Ganguly, N.C.; Mondal, P.; Barik, S.K. *Green Chem. Lett. Rev.* **2012**, *5*, 73–81.
- (54) Pretti, C.; Chiappe, C.; Pieraccini, D.; Gregori, M.; Abramo, F.; Monni, G.; Intorre, L. *Green Chem.* **2006**, *8*, 238–240.
- (55) Zhao, D.; Liao, Y.; Zhang, Z. *Clean – Soil, Air, Water.* **2007**, *35*, 42–48.
- (56) Ranke, J.; Stolte, S.; Störmann, R.; Arning, J.Jastorff, B. *Chem. Rev.* **2007**, *107*, 2183–2206.
- (57) Hasaninejad, A.; Zare, A.; Sharghi, H.; Shekohy, M.; Khalifh, R.; Beni, A.S.; Zare, A.R.M. *Can. J. Chem.* **2007**, *85*, 416–420.
- (58) Patil, V.D., Dere, G.B.; Redge, P.A.; Patil, J.J. *Synth. Commun.* **2011**, *41*, 736–747.
- (59) Sadaphal, S.A.; Sonar, S.S.; Ware, M.N.; Shingare, M.S. *Green. Chem. Lett. Rev.* **2008**, *1*, 191–196.
- (60) Pore, D.M.; Desai, U.V.; Thopate, T.S.; Wadgaonakar, P.P. *Arkivoc*, **2006**, *XII*, 75–80.
- (61) Chakrabarty, M.; Ghosh, N.; Basak, R.; Harigaya, Y. *Synth. Commun.* **2004**, *34*, 421–434.
- (62) Alexandratos, S.D. *Ind. Eng. Chem. Res.* **2009**, *48*, 388–398.
- (63) Barbaro, P.; Liguori, F. *Chem. Rev.* **2009**, *109*, 515–529.
- (64) Narsaiah, A.V.; Reddy, A.R.; Reddy, B.V.S.; Yadav, J.S. *The Open Catalysis Journal*, **2011**, *4*, 43–46.
- (65) Qureshi, Z.S.; Deshmukh, K.S.; Tambade, P.J.; Bhanage, B.M. *Tetrahedron Lett.* **2010**, *51*, 724–729.
- (66) Surasani, R.; Kalita, D.; Rao, A.V.D.; Yarbige, Y.; Chandrasekhar, K.B. *J. Fluorine Chem.* **2012**, *135*, 91–96.
- (67) (a) Layek, M.; Gajare, V.; Kalita, D.; Islam, A.; Mukanti, K.; Pal, M. *Tetrahedron*, **2009**, *65*, 4814. (b) Layek, M.; Gajare, V.; Kalita, D.; Islam, A.; Mukanti, K.; Pal, M. *Tetrahedron Lett.* **2009**, *50*, 3867.
- (68) Layek, M.; Rao, A.V., Gajare, V.; Kalita, D.; Barange, D.K.; Islam, A.; Mukanti, K.; Pal, M. *Tetrahedron Lett.* **2009**, *50*, 4878.

- (69) Layek, M.; Rao, L.U.; Kalita, D.; Barange, D.K.; Islam, A.; Mukanti, K.; Pal, M. *Beilstein J. Org. Chem.* **2009**, *46*, 5.
- (70) Deng, J.; Sanchez, T.; Neamati, N.; Briggs, J.M. *J. Med. Chem.* **2006**, *49*, 1684–1692.
- (71) Osawa, T.; Namiki, M.; Suzuki, K.; Mitsuoka, T.; *Mutat. Res.* **1983**, *122*, 299–304.
- (72) Osawa, T.M.; Namiki, M.; *Tetrahedron Lett.* **1983**, *24*, 4719–4722.
- (73) Bartoli, G.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L. *Synthesis.* **2004**, 895–900.
- (74) Khalafi-Nezhad, A.; Parhami, A.; Zare, A.; Moosavi Zare, A.R.; Hasaninejad, F.; Panahi, F. *Synthesis.* **2008**, 617–621.
- (75) An, L.T.; Ding, F.Q.; Zou, J.P.; Lu, X.H.; Zhang, L.L. *Chin. J. Chem.* **2007**, *25*, 822–827.
- (76) Wanga, L.; He, X.; Guo, Y.; Xu, J.; Shao, S. *Lett. Org. Chem.* **2011**, *8*, 60–65.
- (77) Penieres-Carrillo, G.; Garcia-Estrada, J.G.; Gutierrez-Ramirez, J.L.; Alvarez-Toledano, C. *Green. Chem.* **2003**, *5*, 337–339.
- (78) Osawa, T.; Namiki, M.; Suzuki, K.; Mitsuoka, T.; *Mutat. Res.* **1983**, *122*, 299–304.
- (79) Osawa, T.M.; Namiki, M.; *Tetrahedron Lett.* **1983**, *24*, 4719–4722.
- (80) Bartoli, G.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L. *Synthesis.* **2004**, 895–900.