IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	**Synthesis of Bioactive Heterocycles Through Multiple C-H Bond Activation**
Project Number	**IMURA0414**
Monash Supervisor(s)	Main Supervisor: **Dr David W. Lupton** Associate Supervisor: NA
Monash Primary Contact:	David.lupton@monash.edu 03 99020327
Monash Head of Department:	Steven Langford Steven.langford@monash.edu
Monash Department:	School of Chemistry
Monash ADRT:	Andrea Robinson, andrea.robinson@monash.edu
IITB Supervisor(s)	Main Supervisor: **Prof. Debabrata Maiti** Associate Supervisor: NA
IITB Primary Contact:	dmaiti@chem.iitb.ac.in
IITB Head of Department:	Prof. R. Murugavel rmv@chem.iitb.ac.in
IITB Department:	Department of Chemistry

Research Academy Themes:
Highlight which of the Academy's Theme(s) this project will address?

Theme Number 3. Clean Energy

The research problem

In current scenario the development of new synthetic strategies, enable of rendering step efficiency and atom-economy along with easily accessible starting materials are highly admirable. In this regard, the C-H activation protocol is one of the most promising approaches. Known protocols have been improved from stoichiometric to catalytic versions. Toxic and hazardous solvents were replaced by more environment benign reaction medium. The preliminary successes are encouraging and hence demands detail investigation in this direction. In this context, synthesis of heterocyclic moieties via C-H activation starting from easy-to-handle, economical materials are extremely important. However in case of polycyclic heterocycles regio-selectivity is of utmost importance.

Project aims

This project propose to further develop transition metal catalyzed protocols for the generation of heterocycles*via* C-H activation involving unactivated organic scaffolds and corresponding coupling partners. Furthermore, attempt will be made towards the regio-selective synthesis of the substituted heterocycles. Our objective is to identify a perfect optimized catalytic condition, which is capable of promoting, multiple C-H bond activation and desired C-C and C-X (X= heteroatom) bond formation, as a simple, economical, efficient and easily scalable, single step process.

Expected outcomes

The proposed project is expected to find application both in academia and in industry. Also we expect that our protocol will be beneficial in further progress regarding C-H activation, which in turn will be reflected by cost reduction in developing drugs, pharmaceuticals and related heterocyclic compounds. The optimized catalytic conditions and the new catalysts proposed to be developed through this scheme would be beneficial to a cross section of organic chemists in expediting their synthetic targets. Organometallic chemists could benefit by the mechanistic insights, which in turn, could be used for further catalysts developments.

How will the project address the Goals of the above Themes?

The discovery of new strategies and protocols that can improve a transformation in terms of steps, atom-economy and versatility in construction of complex scaffolds is a long-lasting target for chemists. In this context, the expanding frontier of C-H bond activation is one of the most attractive research areas of the last decades. The development of catalytic functionalization of unactivated C-H bonds for the synthesis of carbon-carbon and carbon-heteroatom bonds has revolutionized the whole approach towards the synthesis of practically important compounds. The progress in direct regioselective conversion of C-H bonds to C-C bonds has challenged the classical catalytic cross-coupling reactions involving organohalides along with organometallic coupling partners. Despite significant progress in this area, the challenges still persist in terms of selectivity of C-H bond activation, realization of truly efficient catalytic system and generality of reaction conditions.

In current scenario the development of new synthetic strategies, enable of rendering step efficiency and atom-economy along with easily accessible starting materials are highly admirable. In this regard, the C-H activation protocol is one of the most promising approaches. Over the last decade a significant amount of progress has been achieved in this area. Different types of substrates along with various coupling partners have been identified and implemented successfully. Known protocols have been improved from stoichiometric to catalytic versions. Toxic and hazardous solvents were replaced by more environment benign reaction medium. The preliminary successes are encouraging and hence demands detail investigation in this direction. In this context, synthesis of heterocyclic moieties via C-H activation starting from easy-to-handle, economical materials are extremely important. However in case of polycyclic heterocycles regio-selectivity is of utmost importance. Compound like benzofuran, benzothiophene are few of the scaffolds, ubiquitous in natural products, agrochemicals, pharmaceuticals and organic materials.

As an outgrowth of recent experimental studies, this project propose to further develop transition metal catalyzed protocols for the generation of heterocycles*via* C-H activation involving unactivated organic scaffolds and corresponding coupling partners. Furthermore, attempt will be made towards the regio-selective synthesis of the substituted heterocycles. Our objective is to identify a perfect optimized catalytic condition, which is capable of promoting, multiple C-H bond activation and desired C-C and C-X (X= heteroatom) bond formation, as a simple, economical, efficient and easily scalable, single step process. In order to have better understanding of the whole process, an appropriate mixture of experimental and computational mechanistic studies is mandatory. The former part will involve labeling, kinetic isotope and substituent effect studies and detailed quantum-chemical calculations to assess reaction mechanisms and to aid the practical retro-synthetic approach. The computational exploration of the potential energy surfaces is expected to provide vital clues leading to the detection/isolation of key intermediates involved in the catalytic cycle.

wepropose to develop an unprecedented transition metal-catalyzed method for the direct synthesis of region-selective benzofuran,benzothiophene, benzoxapine, phosphindolebenzothiazine and stealthin analogues via C-H activation. Our major focus is to deliver asimple, economical, efficient and easily scalable synthetic method which will bemore acceptable in designing complex target molecules. The methodological developments would be aided by computational insights obtained through the structural and energetic details of the vital intermediates and the transition states.

We intend to concentrate on an appropriate mixture of practical and basic research. We will utilize a combination of mechanistic and fundamental approaches that will correlate synthetic and mechanistic studies. Mechanistic studies will include kinetic isotope effect (KIE), deuterium labeling experiments, DFT calculations, and rate of reaction in terms of Hammett plots, effect of electronic and steric variation on the substrates.

The mechanistic understanding through both experimental and computational approaches toward rational catalyst design forms the premise of this proposal. The call for proposals under 'special initiatives in organic chemistry' with a specific emphasis on C-H bond activation reactions render additional significance to the theme proposed herein.

Scientifically we are focusing to deliver a***simple, economical, efficient and easily scalable synthetic method for the generation of each of the following scaffolds (Figure 1)***

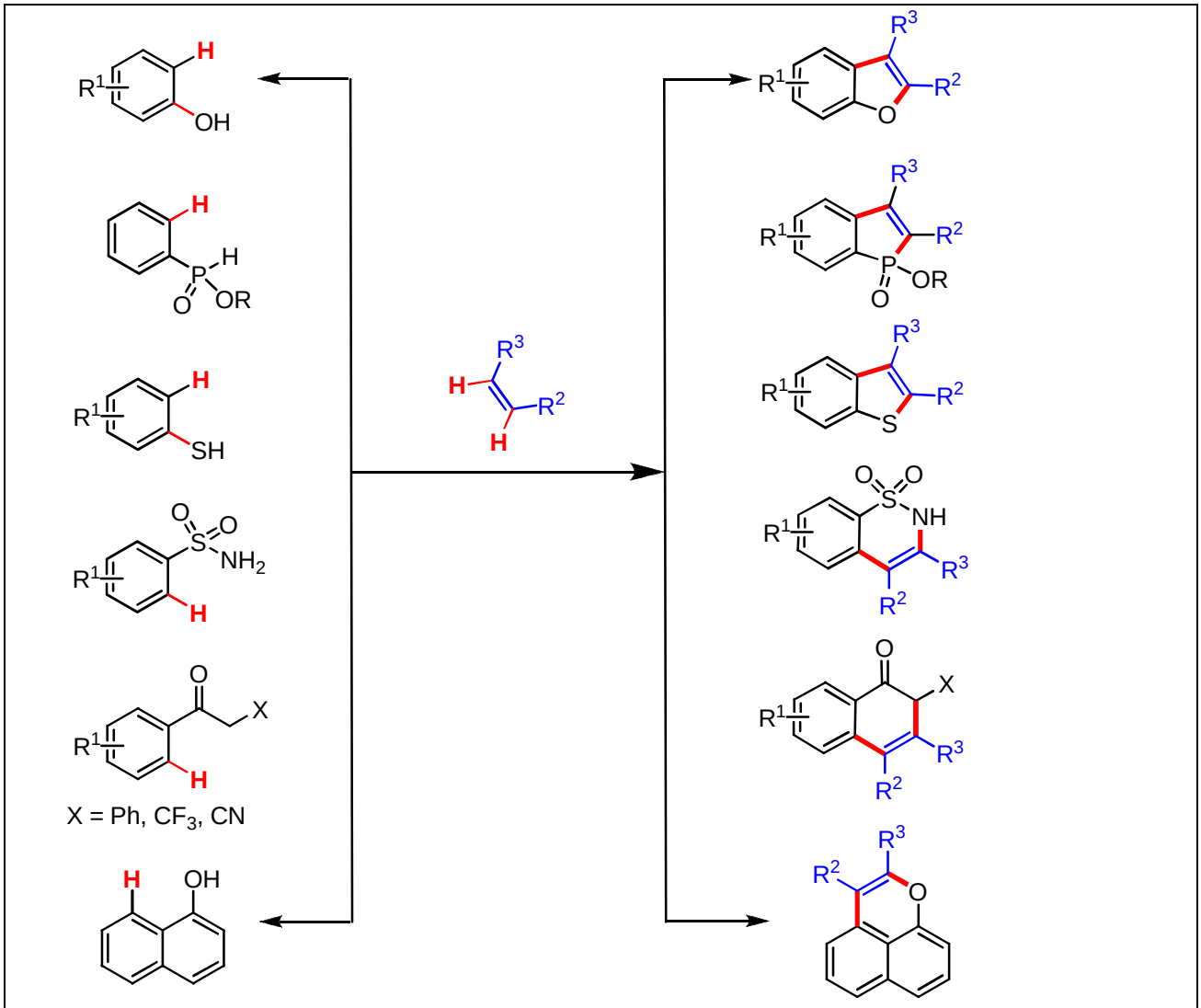
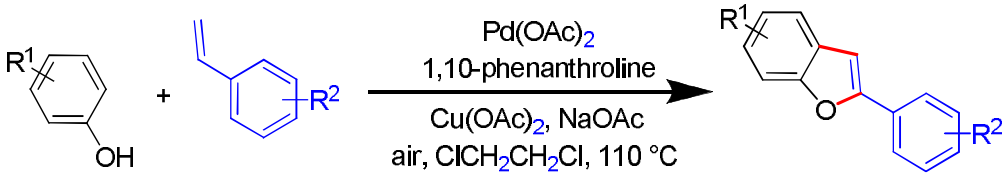


Figure 1. Potential target scaffolds

We will commence by continuing our previous studies with a systematic examination of variations of solvent, base and additives employing styrene as model substrate along with various coupling partners. Then, using optimized conditions, the scope of the protocol will be further explored with various derivatized coupling partners.

We initiated our work hypothesizing that in presence of phenol coupling partner palladium can promote the C-H activation followed by cyclization to furnish the desired product. Obtaining the preliminary results all the parameters were examined and ultimately we successfully obtained the optimized condition to deliver the 2-substituted benzofuran exclusively (Scheme 1).



Scheme 1. Synthesis of 2-substituted benzofuran.

Once done with the styrene derivatives the scope with the internal and terminal olefins were tested with various phenols. Although in most of the cases desired product was obtained but in few instances are there where exocyclic products were obtained as the major product along with the desired benzofuran.
The ligand dependent product composition variation made us curious to delve into the mechanistic intricacies. In case of 2-substituted benzofuran two probable mechanistic pathways have been proposed. One pathway proceeds through O-palladation (Figure 2, pathway 1) and another mechanism involves C-palladation (Figure 3, pathway 2).

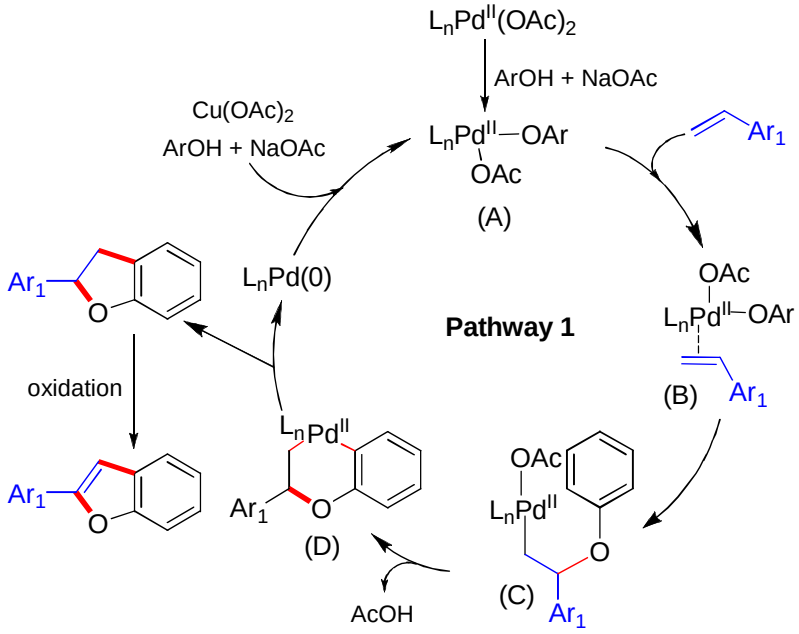


Figure 2. Probable pathway 1

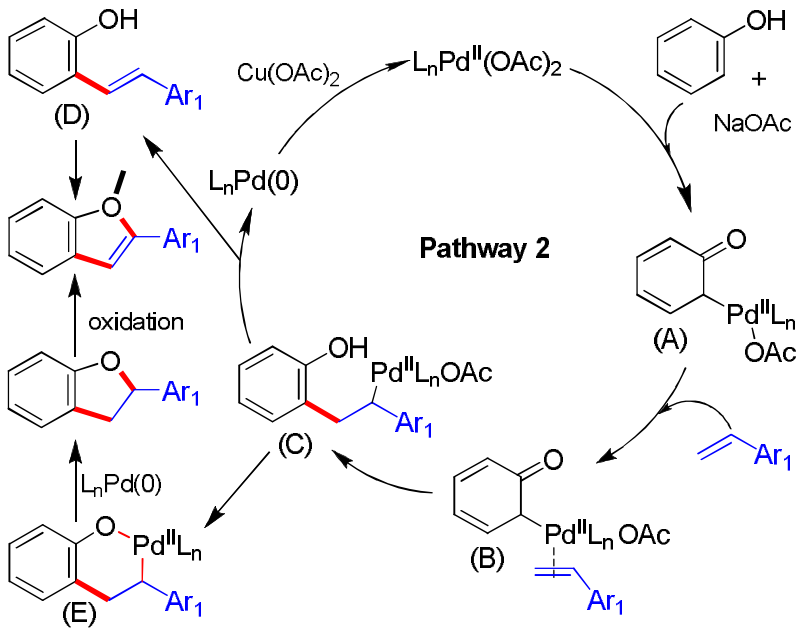


Figure 3. Probable pathway 2

In order to get a better understanding of the mechanistic pathway few preliminary experiments were performed. The first attempt of trapping the intermediate was made using phenol and styrene as substrate and 2-hydroxy stilbene was successfully isolated with 35% yield along with the benzofuran.

This observation is indicative of the fact that 2-hydroxy-stilbene is likely to the intermediate of the transformation. In order to get some more idea of the mechanistic pathway, the kinetics of the reaction was also investigated. It was observed that the reaction follows a first order protocol in terms of 4-nitrophenol where as in case of styrene it follows a negative order (-0.38) dependency. This suggests that probably styrene is also involved in some parallel side reactions. The rate of the reaction was also found to be k = 8.3 x 10^{-6} $M^{0.38}$/sec. The kinetic isotope effect of the reaction was also investigated and found to be 1.84. This low KIE value suggests that reaction does not involve C-H bond activation only in the r.d.s. In other way the r.d.s might involve O-H bond cleavage. These observations would be verified using the computational methods.

References

[1] a) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed* **2012**, *51*, 10236-10254;b) J. Wencel-Delord, T. Droge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740-4761;c) P. Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110*, 824-889;d) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147-1169.

[2] P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879-5918.

[3] a) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315-1345;b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2009**, *110*, 624-655.

[4] G. Zeni, R. C. Larock, *Chem. Rev.* **2006**, *106*, 4644-4680.

[5] G. Zeni, R. C. Larock, *Chem. Rev.* **2004**, *104*, 2285-2309.

[6] a) S.-H. Day, N.-Y. Chiu, L.-T. Tsao, J.-P. Wang, C.-N. Lin, *J. Nat. Prod.* **2000**, *63*, 1560-1562;b) M. r. L. C. Borsato, C. F. F. Grael, G. E. P. Souza, N. P. Lopes, *Phytochemistry* **2000**, *55*, 809-813;c) P. C. Stevenson, N. C. Veitch, *Phytochemistry* **1998**, *48*, 947-951;d) J. H. Tatum, R. A. Baker, R. E. Berry, *Phytochemistry* **1987**, *26*, 2499-2500;e) B. H. Lipshutz, *Chem. Rev.* **1986**, *86*, 795-819;f) R. D. Stipanovic, A. A. Bell, C. R. Howell, *Phytochemistry* **1975**, *14*, 1809-1811;g) S. O. Simonetti, E. L. Larghi, A. B. J. Bracca, T. S. Kaufman, *Nat. Prod. Rep.* **2013**, 10.1039/C1033NP70014C.

[7] a) X. Wang, M. Liu, L. Xu, Q. Wang, J. Chen, J. Ding, H. Wu, *J. Org. Chem.* **2013**;b) M. L. N. Rao, D. N. Jadhav, P. Dasgupta, *Eur. J. Org. Chem.* **2013**, 781-788;c) F. Schevenels, I. n. E. Mark, *Org. Lett.* **2012**, *14*, 1298-1301;d) D.-H. Lee, K.-H. Kwon, C. S. Yi, *J. Am. Chem. Soc.* **2012**, *134*, 7325-7328;e) N. Isono, M. Lautens, *Org. Lett.* **2009**, *11*, 1329-1331;f) L. M. Geary, P. G. Hultin, *Org. Lett.* **2009**, *11*, 5478-5481;g) L. De Luca, G. Nieddu, A. Porcheddu, G. Giacomelli, *Curr. Med. Chem.* **2009**, *16*, 1-20.

[8] U. Sharma, T. Naveen, A. Maji, S. Manna, D. Maiti, *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201305326.

[9] a) A. Lenhart, D. J. Reinert, J. D. Aebi, H. Dehmlow, O. H. Morand, G. E. Schulz, *J. Med. Chem.* **2003**, *46*, 2083-2092;b) H. Dehmlow, J. D. Aebi, S. Jolidon, Y.-H. Ji, E. M. von der Mark, J. Himber, O. H. Morand, *J. Med. Chem.* **2003**, *46*, 3354-3370;c) Y. Okamoto, M. Ojika, Y. Sakagami, *Tetrahedron Lett.* **1999**, *40*, 507-510.

[10] K. C. Nicolaou, H. J. Mitchell, K. C. Fylaktakidou, H. Suzuki, R. M. Rodríguez, *Angew. Chem. Int. Ed.* **2000**, *39*, 1089-1093.

[11] S. K. Chittimalla, T.-C. Chang, T.-C. Liu, H.-P. Hsieh, C.-C. Liao, *Tetrahedron* **2008**, *64*, 2586-2595.

[12] G. Liu, X. Lu, *Tetrahedron* **2008**, *64*, 7324-7330.

[13] T. Pei, C.-y. Chen, L. DiMichele, I. W. Davies, *Org. Lett.* **2010**, *12*, 4972-4975.

[14] M. Ionita, J. Roger, H. Doucet, *ChemSusChem* **2010**, *3*, 367-376.

[15] M. J. Moure, R. SanMartin, E. Dominguez, *Angew. Chem. Int. Ed.* **2012**, *51*, 3220-3224.

[16] K. Shin-ya, K. Furihata, Y. Teshima, Y. Hayakawa, H. Seto, *Tetrahedron Lett.* **1992**, *33*, 7025-7028.

[17] S. J. Gould, C. R. Melville, M. C. Cone, J. Chen, J. R. Carney, *J. Org. Chem.* **1997**, *62*, 320-324.

[18] S.-i. Mohri, M. Stefinovic, V. Snieckus, *J. Org. Chem.* **1997**, *62*, 7072-7073.

[19] G. Qabaja, G. B. Jones, *J. Org. Chem.* **2000**, *65*, 7187-7194.

[20] G. R. Pettit, A. Numata, C. Iwamoto, Y. Usami, T. Yamada, H. Ohishi, G. M. Cragg, *J. Nat. Prod.* **2005**, *69*, 323-327.

[21] D. Acton, G. Hill, B. S. Tait, *J. Med. Chem.* **1983**, *26*, 1131-1137.

[22] J. Fernandez, J. M. Alonso, J. I. Andres, J. M. Cid, A. Diaz, L. Iturrino, P. Gil, A. Megens, V. K. Sipido, A. s. A. Trabanco, *J. Med. Chem.* **2004**, *48*, 1709-1712.

[23] R. Kiyama, T. Honma, K. Hayashi, M. Ogawa, M. Hara, M. Fujimoto, T. Fujishita, *J. Med. Chem.* **1995**, *38*, 2728-2741.

[24] a) S. A. Macgregor, *Chem. Soc. Rev.* **2007**, *36*, 67-76;b) R. Lonsdale, J. N. Harvey, A. J. Mulholland, *Chem. Soc. Rev.* **2012**, *41*, 3025-3038;c) J. E. Eksterowicz, K. N. Houk, *Chem. Rev.* **1993**, *93*, 2439-2461;d) S. Shaik, S. Cohen, Y. Wang, H. Chen, D. Kumar, W. Thiel, *Chem. Soc. Rev.* **2010**, *110*, 949-1017;e) D. Balcells, E. Clot, O. Eisenstein, *Chem Rev* **2010**, *110*, 749-823;f) W. J. Cooper, C. J. Cramer, N. H. Martin, S. P. Mezyk, K. E. O‚ÄôShea, C. v. Sonntag, *Chem. Rev.* **2009**, *109*, 1302-1345;g) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761-1779;h) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 333-348;i) S. Kozuch, S. Shaik, *Acc. Chem. Res.* **2010**, *44*, 101-110;j) M. C. Haibach, S. Kundu, M. Brookhart, A. S. Goldman, *Acc. Chem. Res.* **2012**, *45*, 947-958;k) D. Usharani, D. Janardanan, C. Li, S. Shaik, *Acc. Chem. Res.* **2012**, *46*, 471-482;l) S. Metz, W. Thiel, *Coord. Chem. Rev.* **2011**, *255*, 1085-1103;m) C. E. Webster, M. B. Hall, *Coord. Chem. Rev.* **2003**, *238-239*, 315-331;n) I. P. Georgakaki, L. M. Thomson, E. J. Lyon, M. B. Hall, M. Y. Darensbourg, *Coord. Chem. Rev.* **2003**, *238,Äì239*, 255-266;o) N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704-722;p) B. F. Gherman, C. J. Cramer, *Coord. Chem. Rev.* **2009**, *253*, 723-753;q) J. Goodman, S. A. Macgregor, *Coord. Chem. Rev.* **2010**, *254*, 1295-1306.

[25] M. R. Kuram, M. Bhanuchandra, A. K. Sahoo, *Angew. Chem. Int. Ed.* **2013**, *52*, 4607-4612.

[26] D. Kundu, M. Samim, A. Majee, A. Hajra, *Chem. Asian J.* **2011**, *6*, 406-409.

[27] aR. K. Chinnagolla, S. Pimparkar, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 3032-3035;bM. C. Reddy, R. Manikandan, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 6060-6062.

[28] R. K. Chinnagolla, M. Jeganmohan, *Chem. Commun.* **2014**.

[29] K. Padala, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 9651-9653.

[30] M. C. Reddy, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 481-483.

[31] R. Acharyya, S. Dutta, F. Basuli, S.-M. Peng, G.-H. Lee, L. R. Falvello, S. Bhattacharya, *Inorg. Chem.* **2006**, *45*, 1252-1259.

[32] R. Acharyya, F. Basuli, R.-Z. Wang, T. C. W. Mak, S. Bhattacharya, *Inorg. Chem.* **2003**, *43*, 704-711.

[33] a) A. Banerjee, S. K. Santra, S. K. Rout, B. K. Patel, *Tetrahedron* **2013**, *69*, 9096-9104;b) A. Banerjee, A. Bera, S. Guin, S. K. Rout, B. K. Patel, *Tetrahedron* **2013**, *69*, 2175-2183.

[34] a) A. Sinha, M. Majumdar, M. Sarkar, T. Ghatak, J. K. Bera, *Organometallics* **2013**, *32*, 340-349;b) M. Sarkar, H. Doucet, J. K. Bera, *Chem. Commun.* **2013**, *49*, 9764-9766;cC. B. Bheeter, R. Jin, J. K. Bera, P. H. Dixneuf, H. Doucet, *Adv. Synth. & Catal.* **2014**, *356*, 119-124.

[35] a) S. Mannam, G. Sekar, *Tetrahedron Lett.* **2008**, *49*, 2457-2460;b) S. Mannam, G. Sekar, *Tetrahedron Lett.* **2008**, *49*, 1083-1086.

[36] E. A. Jaseer, D. J. C. Prasad, G. Sekar, *Tetrahedron* **2010**, *66*, 2077-2082.

[37] A. John, M. M. Shaikh, P. Ghosh, *Dalton Trans.* **2009**, 10581-10591.
[38] C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Dalton Trans.* **2010**, *39*, 2515-2524.
[39] a) E. D. Jemmis, A. C. Reddy, *J. Am. Chem. Soc.* **1990**, *112*, 722-727;b) E. D. Jemmis, K. T. Giju, *J. Am. Chem. Soc.* **1998**, *120*, 6952-6964;c) C. M. Nagaraja, P. Parameswaran, E. D. Jemmis, B. R. Jagirdar, *J. Am. Chem. Soc.* **2007**, *129*, 5587-5596;d) W. Tremel, R. Hoffmann, E. D. Jemmis, *Inorg. Chem.* **1989**, *28*, 1213-1224;e) K. Hari Krishna Reddy, E. D. Jemmis, *Dalton Trans.* **2013**, *42*, 10633-10639.
[40] a) M. Jaccob, P. Comba, M. Maurer, P. Vadivelu, P. Venuvanalingam, *Dalton Trans.* **2011**, *40*, 11276-11281;b) M. Jaccob, P. Venuvanalingam, *Eur. J. Org. Chem.* **2011**, *2011*, 3458-3466.
[41] a) P. Ravinder, V. Subramanian, *J. Phy. Chem. A* **2012**, *116*, 6870-6878;b) P. Ravinder, V. Subramanian, *J. Phy. Chem. C* **2013**, *117*, 5095-5100;c) J. Vijaya Sundar, V. Subramanian, *Organometallics* **2012**, *31*, 8525-8536.
[42] a) S. Shaik, D. Danovich, G. N. Sastry, P. Y. Ayala, H. B. Schlegel, *J. Am. Chem. Soc.* **1997**, *119*, 9237-9245;b) A. S. Mahadevi, G. N. Sastry, *Chem. Rev.* **2012**, *113*, 2100-2138.
[43] a) N. Taxak, S. Kalra, P. V. Bharatam, *Inorg Chem* **2013**, *52*, 13496-13508;b) N. Taxak, V. A. Dixit, P. V. Bharatam, *J. Phy. Chem. A* **2012**, *116*, 10441-10450;c) P. V. Bharatam, D. S. Patel, P. Iqbal, *J. Med. Chem.* **2005**, *48*, 7615-7622;d) S. Sundriyal, S. Khanna, R. Saha, P. V. Bharatam, *J. Phys. Org. Chem.* **2008**, *21*, 30-33;e) P. V. Bharatam, S. Khanna, *J. Phy. Chem. A* **2004**, *108*, 3784-3788.
[44] a) P. Bothra, G. Periyasamy, S. K. Pati, *Phys. Chem. Chem. Phys.* **2013**, *15*, 5701-5706;b) S. S. Mallajosyula, S. K. Pati, *J. Phy. Chem. B.* **2007**, *111*, 11614-11618;c) A. K. Manna, S. K. Pati, *Chem. Asian J.* **2009**, *4*, 855-860;d) A. Datta, S. S. Mallajosyula, S. K. Pati, *Acc. Chem. Res.* **2007**, *40*, 213-221.
[45] a) P. Sharma, R. K. Vatsa, D. K. Maity, S. K. Kulshreshtha, *Chem. Phys. Lett.* **2003**, *382*, 637-643;b) P. Dahiya, M. Kumbhakar, D. K. Maity, T. Mukherjee, A. B. R. Tripathi, N. Chattopadhyay, H. Pal, *J. Photochem. Photobiol. A* **2006**, *181*, 338-347.
[46] a) R. Tripathi, N. N. Nair, *J. Am. Chem. Soc.* **2013**, *135*, 14679-14690;b) V. Imandi, S. Kunnikuruvan, N. N. Nair, *Chem. Eur. J.* **2013**, *19*, 4724-4731;cN. N. Nair, *J. Phy. Chem. B* **2011**, *115*, 2312-2321;d) J. N. Moorthy, K. Senapati, K. N. Parida, S. Jhulki, K. Sooraj, N. N. Nair, *J. Org. Chem.* **2011**, *76*, 9593-9601.
[47] a) A. Nijamudheen, A. Datta, *J. Phy. Chem. C* **2013**, *117*, 21433-21440;b) N. T. Patil, A. Nijamudheen, A. Datta, *J. Org. Chem.* **2012**, *77*, 6179-6185;c) A. Nijamudheen, D. Jose, A. Datta, *J. Phy. Chem. C* **2010**, *115*, 2187-2195.
[48] a) R. K. Bera, A. Anoop, C. R. Raj, *Chem. Commun.* **2011**, *47*, 11498-11500;b) S. Roy, A. Anoop, K. Biradha, A. Basak, *Angew. Chem. Int. Ed.* **2011**, *50*, 8316-8319;c) A. GansaÃàuer, A. Fleckhaus, M. A. Lafont, A. Okkel, K. Kotsis, A. Anoop, F. Neese, *J. Am. Chem. Soc.* **2009**, *131*, 16989-16999;d) M. Ikbal, R. Banerjee, S. Atta, D. Dhara, A. Anoop, N. D. P. Singh, *J. Org. Chem.* **2012**, *77*, 10557-10567.
[49] a) R. K. Das, B. Saha, S. M. W. Rahaman, J. K. Bera, *Chem. Eur. J.* **2010**, *16*, 14459-14468;b) M. Majumdar, S. K. Patra, M. Kannan, K. R. Dunbar, J. K. Bera, *Inorg. Chem.* **2008**, *47*, 2212-2222.
[50] A. S. K. Hashmi, W. B. Yang, F. Rominger, I. Crystallographic, *Angew. Chem. Int. Ed.* **2011**, *50*, 5761-5764.
[51] a) M. Anand, R. B. Sunoj, *Org. Lett.* **2011**, *13*, 4802-4805;b) M. Anand, R. B. Sunoj, *Organometallics* **2012**, *31*, 6466-6481.
[52] G. Jindal, R. B. Sunoj, *Chem. Eur. J.* **2012**, *18*, 7045-7049.
[53] A. Thawani, R. Rajeev, R. B. Sunoj, *Chem. Eur. J.* **2013**, *19*, 4069-4077.
[54] M. Anand, R. B. Sunoj, *Org. Lett.* **2012**, *14*, 4584-4587.
[55] a) D. Katayev, Y.-X. Jia, A. K. Sharma, D. Banerjee, C. Besnard, R. B. Sunoj, E. P. Kündig, *Chem. Eur. J.* **2013**, *19*, 11916-11927;b) A. Parija, R. B. Sunoj, *Org. Lett.* **2013**, *15*, 4066-4069;c) D. Roy, R. B. Sunoj, *Org. Bio. Chem.* **2010**, *8*, 1040-1051;d) R. Stephen, R. B. Sunoj, P. Ghosh, *Dalton Trans.* **2011**, *40*, 10156-10161.
[56] a) S. Maity, S. Manna, S. Rana, T. Naveen, A. Mallick, D. Maiti, *J. Am. Chem. Soc.* **2013**, *135*, 3355;b) T. Naveen, S. Maity, U. Sharma, D. Maiti, *J. Org. Chem.* **2013**, *78*, 5949-5954.
[57] S. Maity, T. Naveen, U. Sharma, D. Maiti, *Org. Lett.* **2013**, *15*, 3384-3387.
[58] A. Deb, S. Manna, A. Modak, T. Patra, S. Maity, D. Maiti, *Angew. Chem. Int. Ed.* **2013**, *52*, 9747-9750.

Capabilities and Degrees Required

Degree Requirement: BSc: Chemistry (Hons.) with 70% in Chemistry courses, overall 65%.
MSc: 80% marks (or CPI 9.0) in Chemistry (Hons.)
CSIR/UGC clearance: Students with valid CSIR/UGC rank (research) will get preference.
Research Experience: Minimum 1 year experience (including MSc project)
Students having prior experience in working with C-H activation/funtionalisation will be preferred.