Tetrahedron Letters 50 (2009) 4335–4339

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Reusable resin Amberlyst 15 catalyzed new convenient protocol for accessing arylated benzene scaffolds ☆

Amit Kumar [a], Manish Dixit [a], Salil P. Singh [a], Resmi Raghunandan [b], Prakas R. Maulik [b], Atul Goel [a,*]

[a] Division of Medicinal and Process Chemistry, Central Drug Research Institute, Lucknow 226 001, India
[b] Division of Molecular and Structural Biology, Central Drug Research Institute, Lucknow 226 001, India

ARTICLE INFO

Article history:
Received 23 February 2009
Revised 3 May 2009
Accepted 12 May 2009
Available online 18 May 2009

Keywords:
Amberlyst 15
Aryl methyl ketone cyclotrimerization
2-Acetylbenzofuran polymerization
X-ray analysis

ABSTRACT

Polyarylated benzene derivatives are useful molecular entities in chemical and material sciences owing to their unique photophysical properties associated with them. In this Letter, we report that 2-acetyl-benzofuran in the presence of Amberlyst 15 at reflux temperature furnished a mixture of dimer, trimer, and tetramer with interesting conformational properties. The protocol was generalized to prepare diverse arylated benzene scaffolds in good yields under similar reaction conditions.

Polyarylated benzene propellers have attracted a great deal of enthusiasm toward leading edge carbon nanotechnology for developing new efficient molecular rotors and new electroluminescent materials for flat-panel displays.[1] Owing to their unique chemical, photophysical, and optical properties, these aromatic scaffolds are not only useful as building blocks for material[1] and biological sciences,[2] but also important for understanding the concept of aromaticity, chemical reactivity, and reaction kinetics.[3] Recently polyaromatic hydrocarbons such as π-conjugated polyaromatics, dendrimers[4] and their derivatives find several applications in liquid crystals,[5] laser dyes,[6] electronic and opto-electronic devices,[7] and molecular wires.[1c,8] 1,2-Terphenyl and 1,3-terphenyls have been used industrially as heat storage and transfer agents and as textile dye carriers whilst the 1,4-terphenyls have found application as a laser dye.[9] In addition, biaryls and teraryls are often present as subunits in numerous biologically active natural products and pharmaceuticals.[2,10] Recently we have demonstrated that 1,2,3-triarylbenzenes are potential compounds for fabricating thermally stable blue organic light emitting diodes.[11]

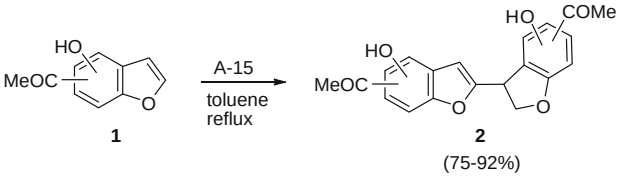
Numerous synthetic methodologies to highly functionalized aromatic π-systems have been reported in the literature. A variety of acid catalysts such as hydrochloric acid,[12] sodium or potassium pyrosulfate in H_2SO_4,[13] aniline hydrochloride,[14] titanium tetrachloride[15] ($TiCl_4$), $SiCl_4$,[16] $SmCl_3$,[17] $CuCl_2$,[18] and Cp_2ZrCl_2[19] and metal oxides[20] of Al, Ti, Cr, and Mn at elevated temperature have been employed to prepare arylated benzenes in moderate to good yields. Recently an interesting article reported[21] the use of cation rhodium complex $[Cp^*Rh(\eta^6\text{-}C_6H_6)](BF_4)_2$ in under neutral conditions as catalyst for the conversion of cyclic ketones to polysubstituted benzenes. Other common approaches for the preparation of polyaromatic compounds include cyclotrimerization of alkynes in the presence of organometallic reagents,[22] palladium- and nickel-catalyzed multifold sequential Suzuki–Miyaura reaction between oligohaloarenes with organometallic partners.[23] However, except few, most of these procedures are often complicated by harsh reaction conditions,[20] the lack of regioselectivity, formation of undesirable 1,2,4-trisubstituted byproducts, and the requirement of expensive or specialized organometal catalysts.[21] Herein, we report highly simple, economical, and environmentally benign reusable Amberlyst 15-catalyzed new protocol for the synthesis of arylated benzenes in good yields.

Amberlyst 15 plays an important role in the synthesis of various aliphatic and aromatic compounds.[24] Recently Shen et al. reported A-15-catalyzed unexpected synthesis of bis benzofuran from 1-(4-methoxyphenoxy)acetone in good yield.[24a] During the studies on the chemistry of naturally occurring benzofuran derivatives, we found that benzofurans functionalized on benzenoid ring with an adjacent hydroxy and acetyl group undergoes pseudodimerization to the corresponding bibenzofurans in the presence of Amberlyst 15 in toluene at reflux temperature (Scheme 1).[25] Some of these

☆ CDRI Communication Number: 7119.

* Corresponding author at present address: Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. Tel.: +49 931 8885393; fax: +49 931 8884755.
E-mail addresses: goela@chemie.uni-wuerzburg.de, agoel13@yahoo.com (A. Goel).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.05.029



Scheme 1.

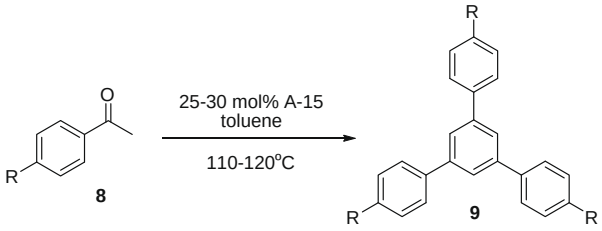
bibenzofurans showed good protein tyrosine phosphatase 1B (PTP-1B) inhibitory activity for the treatment of diabetes.[25b]

In order to prepare diverse bibenzofuran derivatives for biological screening, recently we attempted a similar reaction with 2-acetyl-benzofuran (**3**) in the presence of Amberlyst 15 at reflux temperature. Surprisingly, instead of obtaining bibenzofuran (**4**), we isolated a mixture of dimer (**5**), trimer (**6**), and a tetramer (**7**) of benzofuran as shown in Scheme 2. The structures of these compounds were determined by spectroscopic analysis and unambiguously by a single crystal X-ray analysis (Scheme 2).[26] The conformation of **6** and **7** along with the atom-numbering scheme is shown in Scheme 2. The Trimer **6** and tetramer **7** crystallized in space group *C*2/*c* and *P*4(2)/*nbc*, respectively. The structural analysis showed the presence of intermolecular π···π interaction and weak intra C–H···O interactions in both the compounds. To the best of our knowledge, it is the first report on such a highly hindered, symmetrical, and uniquely formed cyclobutane ring bearing four benzofuran moieties in a juxtaposed manner. In order to optimize the reaction condition, reactions of 2-acetyl-benzofuran (**3**) and A-15 were carried out in the presence of various solvents at refluxing temperature for 10 h (Table 1).

With the demonstration of the utility of this protocol in general, we attempted a reaction with simple acetophenone (**8a**) in the presence of Amberlyst 15 in toluene under reflux temperature for 10 h. To our surprise, after cooling we obtained nice colorless crystals from the reaction mixture. The crystals were filtered, washed with hexane, and dried. The isolated compound was characterized by spectroscopic analysis as 1,3,5-triphenylbenzene (**9a**) (Scheme 3). Fortunately, in this case we only obtained trimerized product and no dimer and tetramer were formed. The cyclotrimerizations of **8a** and **8b** were carried out in grams scale and the yields

Table 1
Reaction of 2-acetyl-benzofuran (**3**) with A-15 in the presence of various solvents

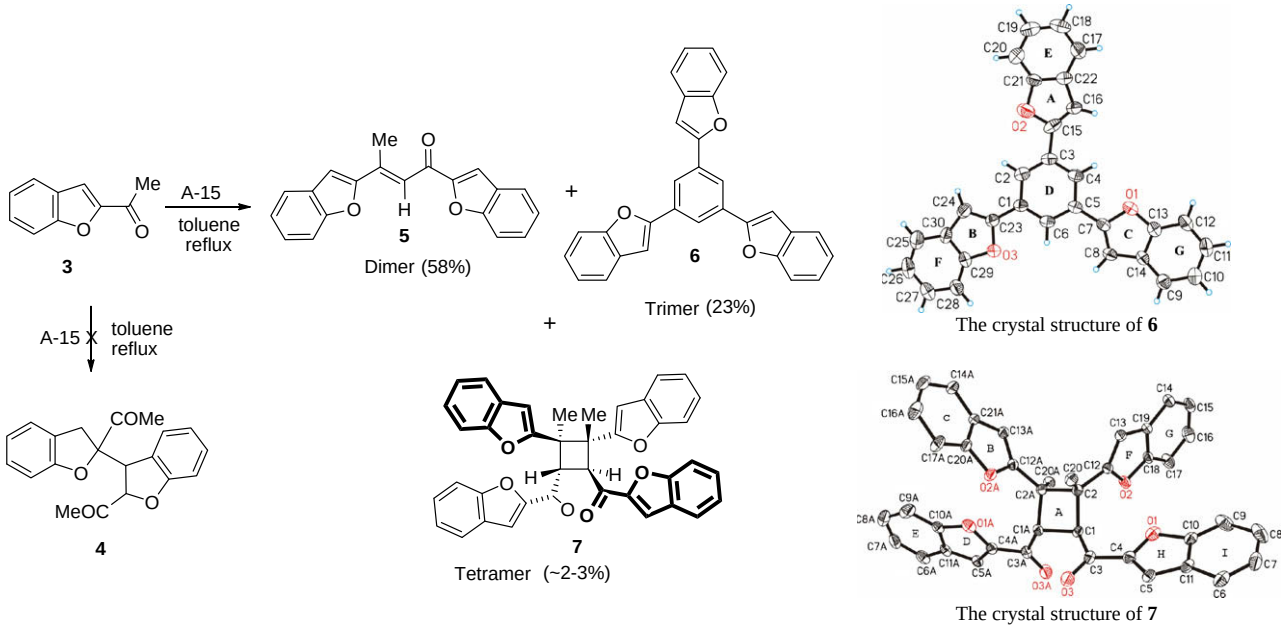
	Solvent	**5**(%)	**6**(%)	**7**(%)
a	Toluene	58	23	3
b	Fluorobenzene	35	10	0
c	Benzene	30	5	0
d	Dichloromethane	20	0	0
e	Tetrahydrofuran	0	0	0
f	Acetonitrile	0	0	0



Scheme 3. Synthesis of 1,3,5-triphenylbenzene.

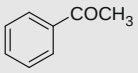
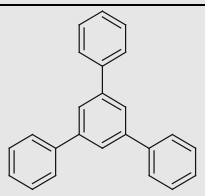
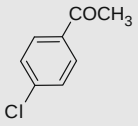
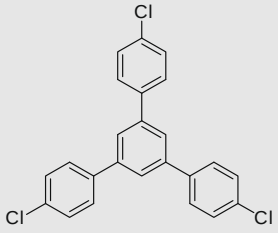
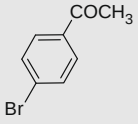
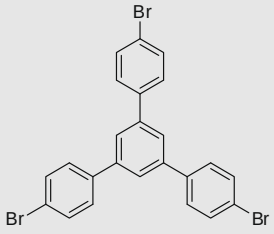
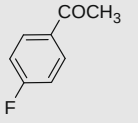
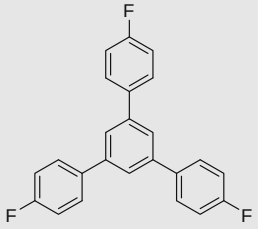
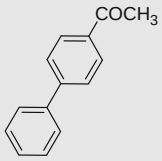
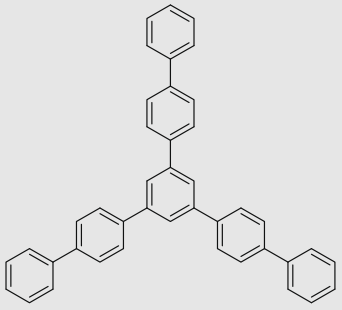
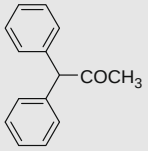
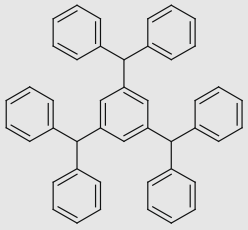
were found satisfactory. The procedure was tested using a variety of aryl/alkyl methyl ketones to furnish useful aromatic scaffolds (**9a–k**) and results are presented in Table 2. It is evident from Table 2 that the reaction with unsubstituted or halogen-substituted acetophenones (**8a–i**) in the presence of A-15 in reflux toluene afforded 1,3,5-triarylbenzenes (**9a–i)** exclusively, whereas the reaction with 4-methyl- and 4-methoxyacetophenone (**8j**,**k**) under similar reaction conditions furnished low yields of aromatic carboxylic acids (**9j**,**k**) together with more than 70% unreacted starting material. The confirmation of isolated 4-methyl- and 4-methoxybenzoic acid (**9j**,**k**) was done by comparing with the data of authentic samples. All the synthesized compounds were characterized by spectroscopic analysis[26] and known compounds were matched with the data of the authentic samples.

A plausible mechanism for the formation of cyclotrimerized products in the presence of Amberlyst 15 is depicted in Scheme 4. The reaction may proceed through the protonation of acetophenone to form intermediates (a) and (b), followed by sequential



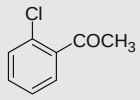
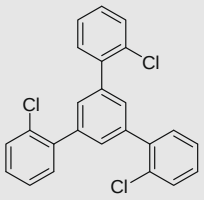
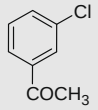
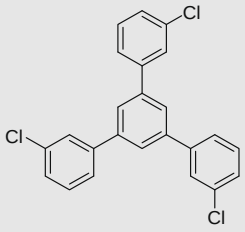
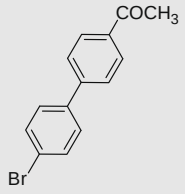
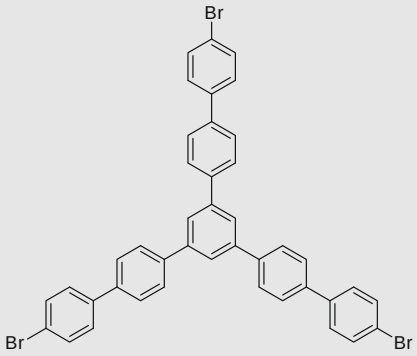
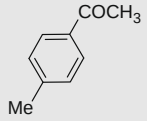
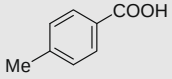
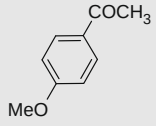
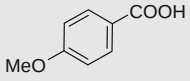
Scheme 2. Synthesis of benzofuran dimer (**5**), trimer (**6**) and tetramer (**7**) and ORTEP structure of **6** and **7** with arbitrary numbering.

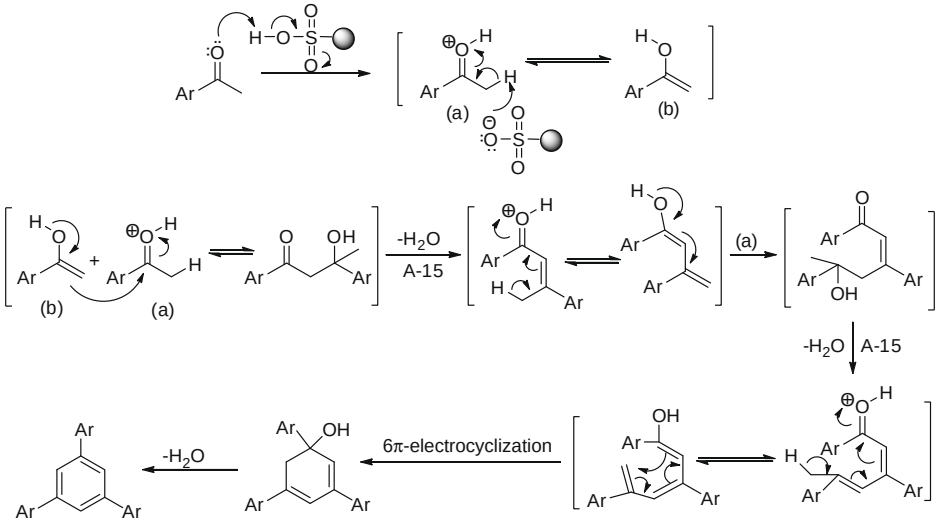
Table 2
Amberlyst 15-catalyzed synthesis of arylated benzenes (**9a-i**) and aromatic carboxylic acids (**9j-k**)

	Reactant (**8**)	Product (**9**)	Time (h)	Yield (%)
a			10	60
b			12	55
c			11	58
d			10	75
e			18	75
f			20	55

(*continued on next page*)

Table 2 (*continued*)

	Reactant (**8**)	Product (**9**)	Time (h)	Yield (%)
g			20	50
h			16	55
i			20	45
j			30	15
k			32	10



Scheme 4. Plausible reaction mechanism for the formation of triarylbenzene.

reactions between the intermediates formed in situ, and further internalization and 6π-electrocyclization in the presence of Amberlyst 15.

In summary, we synthesized and characterized new molecular propeller systems of benzofuran through unique polymerization reaction of 2-acetylbenzofuran in the presence of Amberlyst 15. The structural analysis of a trimer and tetramer of benzofuran revealed the presence of intermolecular π···π interaction and weak intra C–H···O interactions. The Tetramer **7** crystallized in space group *P4*(2)/*nbc*, which rarely occurs in an organic molecule. The new protocol is successfully applied to prepare different aromatic scaffolds in good yields. This is a unique methodology for C–C bond-forming reactions and may be applicable to the synthesis of functionally congested aromatic propeller systems for their potential applications in biological and material sciences. In addition, our simple protocol and reusability of the catalyst are obvious advantages over the known literature reports from both environmental and industrial viewpoints.

Acknowledgments

A.G. thanks the Alexander von Humboldt Foundation, Bonn, and Professor G. Bringmann for his research stay and kind support in Germany. This work is supported by Department of Science and Technology, New Delhi under Ramanna Fellowship Scheme to A.G. (SR/S1/RFPC-10/2006). A.K. and M.D. are grateful to CSIR, New Delhi for research fellowships. The authors thank Sophisticated Analytical Instrument Facility (SAIF), Central Drug Research Institute, Lucknow for providing spectroscopic data for the synthesized compounds.

References and notes

1. (a) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281–1376; (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–553; (c) Tour, J. M. In *Stimulating Concepts in Chemistry*; Vögtle, F., Stoddart, J. F., Shibasaki, M., Eds.; Wiley-VCH: Weinheim, 2000; pp 237–253.
2. (a) Trujillo, J. M.; Jorge, R. E.; Navarro, E.; Boada, J. *Phytochemistry* **1990**, *29*, 2991–2993; (b) Tsuji, K.; Nakamura, K.; Ogino, T.; Konishi, N.; Tojo, T.; Ochi, T.; Seki, N.; Matsuo, M. *Chem. Pharm. Bull.* **1998**, *46*, 279–286; (c) Becker, F. F.; Mukhopadhyay, C.; Hackfeld, L.; Banik, I.; Banik, B. K. *Bioorg. Med. Chem.* **2000**, *8*, 2693–2699.
3. (a) Watson, M. D.; Fechtenkotter, A.; Mullen, K. *Chem. Rev.* **2001**, *101*, 1267–1300. and references cited therein; (b) Krishnamurthy, N.; Reddy, S. C.; Sundaram, E. V. *Indian J. Chem., Sect. A* **1989**, *28*, 288–291.
4. Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, 2001. p 1.
5. Ebert, M.; Jungbauer, D. A.; Kleppinger, R.; Wendorff, J. H.; Kohne, B.; Praefcke, K. *Liq. Cryst.* **1989**, *4*, 53–67.
6. Schneider, D. J.; Landis, D. A.; Fleitz, P. A.; Seliskar, C. J.; Kaufman, J. M.; Steppel, R. N. *Laser Chem.* **1991**, *11*, 49–62.
7. (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738; (b) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875–962.
8. (a) Berresheim, A. J.; Muller, M.; Mullen, K. *Chem. Rev.* **1999**, *99*, 1747–1785; (b) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107–119.
9. (a) Goel, A.; Verma, D.; Singh, F. V. *Tetrahedron Lett.* **2005**, *46*, 8487–8491. and references cited therein; (b) Goel, A.; Verma, D.; Dixit, M.; Raghunandan, R.; Maulik, P. R. *J. Org. Chem.* **2006**, *71*, 804–807; (c) Goel, A.; Singh, F. V.; Dixit, M.; Verma, D.; Raghunandan, R.; Maulik, P. R. *Chem. Asian J.* **2007**, *2*, 239–247.
10. (a) Williams, D. H.; Bardsley, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 1172–1193; (b) Nicolaou, K. C.; Boddy, C. N. C.; Brase, S.; Winssinger, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2096–2152; (c) Singh, F. V.; Kumar, A.; Goel, A. *Tetrahedron Lett.* **2006**, *47*, 7767–7770.
11. Goel, A.; Dixit, M.; Chaurasia, S.; Kumar, A.; Raghunandan, R.; Maulik, P. R.; Anand, R. S. *Org. Lett.* **2008**, *10*, 2553–2556.
12. (a) Dehmlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021–2031; (b) Lyle, R. E.; DeWitt, E. J.; Nichols, N. M.; Cleland, W. *J. Am. Chem. Soc.* **1953**, *75*, 5959–5961; (c) Wirth, H. O.; Kern, W.; Schmitz, E. *Makromol. Chem.* **1963**, *68*, 69–99.
13. (a) Lefeave, R. J. W. *J. Chem. Soc.* **1938**, 1467–1471; (b) Sampey, J. R. *J. Am. Chem. Soc.* **1940**, *62*, 1953; (c) Hopff, H.; Heer, A. *Chimia* **1959**, *13*, 105–108.
14. Clapp, D.; Morton, A. *J. Am. Chem. Soc.* **1936**, *58*, 2172.
15. (a) Li, Z.; Sun, W.-H.; Jin, X.; Shao, C. *Synlett* **2001**, 1947–1949; (b) Iranpoor, N.; Zeynizaded, B. *Synlett* **1998**, 1079–1080; (c) Volz, H.; Lecea, M. J. V. *Tetrahedron Lett.* **1966**, 4683–4689; (d) Ono, F.; Ishikura, Y.; Tada, Y.; Endo, M.; Sato, T. *Synlett* **2008**, 2365–2367; (e) Lu, J.; Tao, Y.; D'iorio, M.; Li, Y.; Ding, J.; Day, M. *Macromolecules* **2004**, *37*, 2442–2449.
16. Elmorsy, S. S.; Pelter, A.; Smith, K.; Hursthouse, M. B.; Ando, D. *Tetrahedron Lett.* **1992**, *33*, 821–824.
17. Cheng, K. J.; Ding, Z. B.; Wu, S. H. *Synth. Commun.* **1997**, *27*, 11–15.
18. Mahmoodi, N. O.; Hajati, N. *J. Chin. Chem. Soc.* **2002**, *49*, 91–94.
19. Shirai, H.; Amano, N.; Hashimoto, Y.; Fukui, E.; Ishii, Y.; Ogawa, M. *J. Org. Chem.* **1991**, *56*, 2253–2256.
20. (a) Hopff, H.; Schweizer, H. R.; Ghertsos, A.; Heer, A.; Solarsky, A. *Chimia* **1958**, *12*, 143–146; (b) Fujii, R. *J. Chem. Soc. Jp., Pure Chem. Sect.* **1948**, *69*, 151–155.
21. Terai, H.; Takaya, H.; Naota, T. *Tetrahedron Lett.* **2006**, *47*, 1705–1708.
22. (a) Yong, L.; Butenschon, H. *Chem. Commun.* **2002**, 2852–2853; (b) Hilt, G.; Vogler, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, 1474–1475; (c) Conte, V.; Elakkari, E.; Floris, B.; Mirruzzo, V.; Tagliatesta, P. *Chem. Commun.* **2005**, 1587–1588.
23. Pena, M. A.; Perez, I.; Sestelo, J. P.; Sarandeses, L. A. *Chem. Commun.* **2002**, 2246–2247.
24. (a) Shen, Y. D.; Wu, H. Q.; An, L. K.; Huang, Z. S.; Bu, X. Z.; Gu, L. Q. *Chin. Chem. Lett.* **2005**, *16*, 1581–1583; (b) Das, B.; Chowdhury, N. *J. Mol. Catal. A: Chem.* **2007**, *263*, 212–215. and references cited therein.
25. (a) Dixit, M.; Sharon, A.; Maulik, P. R.; Goel, A. *Synlett* **2006**, 1497–1502; (b) Dixit, M.; Tripathi, B. K.; Tamrakar, A. K.; Srivastava, A. K.; Kumar, B.; Goel, A. *Bioorg. Med. Chem.* **2007**, *15*, 727–734.
26. In a typical example, a solution of substituted acetophenone (1 mmol) in toluene (7 mL) was added 25–30 mol % of Amberlyst 15 and the reaction mixture was refluxed for 10–32 h. The reaction mixture was allowed to cool, catalyst was filtered off, and washed several times with hot toluene. The filtrate was concentrated under reduced pressure to afford the desired product in good yield.
1,3-Di(benzofuran-2-yl)but-2-en-1-one (***5***): White solid; mp 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (s, 3H, CH_3), 7.15 (s, 1H, CH),7.21–7.52 (m, 4H, ArH), 7.56 (d, J = 7.9 Hz, 1H, ArH), 7.58–7.67 (m, 3H, ArH), 7.73 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.8, 109.47, 111.47, 112.48, 112.56, 117.79, 121.84, 123.22, 123.38, 123.87, 126.61, 127.44, 128.04, 128.60, 143.13, 154.74, 155.37, 155.71, 156.12, 180.76; IR (KBr) 1649 cm^{-1} (CO); MS (ESI) 303 (M^++1).
1,3,5-Tri(benzofuran-2yl)benzene (**6**): White solid; mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.38 (m, 9H, ArH), 7.59–7.67 (m, 6H, ArH), 8.31 (s, 3H, ArH); MS (FAB) 427 (M^++1). X-ray analysis: The structural analysis shows the presence of intermolecular π···π interaction (centroid separation X1A···X1D = 3.6472, X1A···X1E = 3.7985 Å) [symmetry codes: x, 1 + y, z; x, −1 + y, z]. The crystal packing further reveals the formation of intra C–H···O interactions [H2···O2 = 2.53 Å, ∠C2–H2–O2 = 100°, C2–O2 = 2.8366 Å; H4···O1 = 2.44 Å, ∠C4–H4–O1 = 101°, C4–O1 = 2.6967 Å; H6···O3 = 2.44 Å, ∠C6–H6–O3 = 101°, C6–O3 = 2.7939Å].
(3,4-Di(benzofuran-2-yl)-3,4-dimethylcyclobutane-1,2-diyl)bis(benzofuran-2-yl-methanone) (**7**): yellow solid; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.37 (s, 6H, CH_3), 5.58 (s, 2H, CH), 6.67 (s, 2H, CH), 7.14-7.39 (m, 10H, ArH), 7.40-7.71 (m, 8H, ArH); IR (KBr) 1629 cm^{-1}; MS (FAB) 605 (M^++1). X-ray analysis: The structural analysis shows the presence of intermolecular π···π (centroid separation X1B···X1B = 3.5859) (centroid separation X1B···X1C = 3.7095) [symmetry code: 1/2 − x, y, −z], C–H···π interaction [C13–H13···X1C, centroid distance 2.99 Å], (symmetry codes: −x, 1 − y, −z). The crystal packing further reveals the formation of intra- and intermolecular C–H···O interactions [H1–O2 = 2.48 Å, ∠C1–H1–O2 = 108°, C1–O2 = 2.9344 Å).
1,3,5-Triphenylbenzene (**9a**): White solid; mp 170–172 °C (lit.[15b] 170–171 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34–7.53 (m, 9H, ArH), 7.71 (d, J = 8.2 Hz, 6H, ArH), 7.79 (s, 3H, ArH); IR (KBr) 3057, 2928, 1593 cm^{-1}; MS (FAB) 307 (M^++1), (EI^+) 306 (M^+).
1,3,5-Tris(4′-chlorophenyl)benzene (**9b**): White solid; mp 248–249 °C (lit.[15b] 257–259 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 6H, ArH), 7.60 (d, J = 8.4 Hz, 6H, ArH), 7.69 (s, 3H, ArH); IR (KBr) 3020, 2920, 1593 cm^{-1}; MS (FAB) 410 (M^++1).
1,3,5-Tris(4′-bromophenyl)benzene (**9c**): White solid; mp 260–261 °C (lit.[12b] 261–262 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (d, J = 8.6 Hz, 6H, ArH), 7.58 (d, J = 8.6 Hz 6H, ArH), 7.62 (s, 3H, ArH); IR (KBr) 3019, 2926, 1592 cm^{-1}; MS (FAB) 541 (M^++1).
1,3,5-Tris(4′-florophenyl)benzene (**9d**): White solid; mp 238–240 °C (lit.[12b] 244–246 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.03–7.12 (m, 6H, ArH), 7.51–7.58 (m, 9H, ArH); IR (KBr) 3060, 2928, 1603 cm^{-1}; MS (FAB), 360 (M^++1).
1,3,5-Tri(biphenyl)benzene (**9e**): White solid; mp 238–240 °C (lit.[15b] 239–241 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.52 (m, 10H, ArH), 7.57–7.85 (m, 17H, ArH), 7.90 (s, 3H, ArH); IR (KBr) 3050, 2930, 1594 cm^{-1}; MS (FAB) 534 (M^+).
1,3,5-Tris(biphenylmethyl)benzene (**9f**): White solid; mp 112–114 °C (lit.[15c] 113–114 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.27 (s, 3H, CH), 6.61–7.06 (m, 33H, ArH); MS (FAB) 576 (M^+).
1,3,5-Tris(2′-chlorophenyl)benzene (**9g**): White solid; mp 162–164 °C (lit.[15d] 165 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29–7.40 (m, 6H, ArH), 7.44–7.55 (m, 6H, ArH), 7.61 (s, 3H, ArH); IR (KBr) 3021, 2920, 1636 cm^{-1}; MS (FAB) 410 (M^++1).
1,3,5-Tris(3′-chlorophenyl)benzene (**9h**): White solid; mp 168–170 °C (lit.[12b] 171 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33–7.49 (m, 6H, ArH), 7.52–7.61 (m, 3H, ArH), 7.67 (s, 3H, ArH), 7.73 (s, 3H, ArH); IR (KBr) 3022, 2926, 1635 cm^{-1}; MS (FAB) 410 (M^++1).
1,3,5-Tri(4′-bromobiphenyl)benzene (**9i**): White solid; mp >250 °C (lit.[15e] 280 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 6H, ArH), 7.61 (d, J = 8.4 Hz, 6H, ArH), 7.70 (d, J = 8.4 Hz, 6H, ArH), 7.81 (d, J = 8.4 Hz, 6H, ArH), 7.88 (s, 3H, ArH); IR (KBr) 3022, 2926, 1599 cm^{-1}; MS (FAB) 769 (M^++1).