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Atom-economy click synthesis of tetrahydrobenzo[*b*]-pyrans using carbon-based solid acid as a novel, highly efficient and reusable heterogeneous catalyst

Maryam Moghaddas · Abolghasem Davoodnia

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Abstract Carbon-based solid acid has been used as a mild and efficient heterogeneous catalyst for the synthesis of tetrahydrobenzo[*b*]pyran derivatives via a one-vessel, three-component cyclocondensation of dimedone, aryl aldehydes, and malononitrile with high atom economy ranging from 94.2 to 95.4 %. The remarkable features of this new method are short reaction times, high yields, clean reaction profiles, and simple work-up procedure. The reactions were performed in ethanol and the catalyst could be recycled after a simple work-up, and used for many runs without significant loss of its activity. However, using aliphatic aldehydes, moderate yields of the products were obtained. The structure of the catalyst was confirmed by FT-IR spectroscopy, energy dispersive X-ray, X-ray diffraction, and the N_2 adsorption/desorption analysis techniques.

Keywords Carbon-based solid acid · Heterogeneous catalysis · Reusable catalyst · One-vessel reaction · Tetrahydrobenzo[*b*]pyrans

Introduction

Pyrans, benzo[*b*]pyrans, and tetrahydrobenzo[*b*]pyrans are of considerable interest because of their wide range of biological properties, such as anticoagulant, spasmolytic, diuretic, antiproliferative, anticancer, and antianaphylactin activities [1–5]. A number of these compounds are useful as photoactive materials [6] or constitute the structural unit of a series of natural products [7]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative disease,

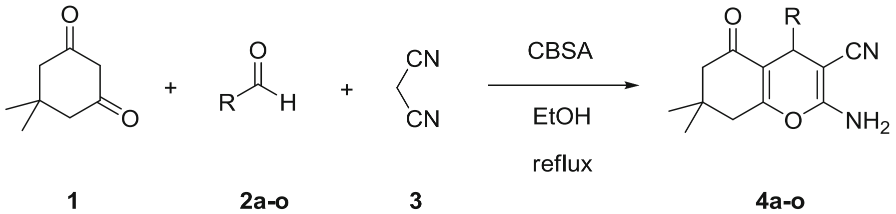
M. Moghaddas · A. Davoodnia (✉)
Department of Chemistry, Faculty of Sciences, Mashhad Branch, Islamic Azad University,
Mashhad, Iran
e-mail: adavoodnia@yahoo.com; adavoodnia@mshdiau.ac.ir

including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS-associated dementia, and Down's syndrome as well as for the treatment of schizophrenia and myoclonus [8]. Hence, an easy access to pyran derivatives is highly desirable as they possess unique pharmacological properties.

The most straightforward synthesis of tetrahydrobenzo[*b*]pyrans involves a one-vessel, three-component cyclocondensation of dimedone, aryl aldehydes, and malononitrile in the presence of several catalysts such as SO_3H-bearing solid catalyst (PEG-SAC) [9], piperazine under solvent-free ball-milling conditions [10], I_2 [11], KF/Al_2O_3 under ultrasound irradiation [12], basic ionic liquid [13], nano-mixed metal oxides [14], nano-ZnO [15, 16], $PhB(OH)_2$ [17], tetrabutylammonium bromide (TBAB) [18], Na_2SeO_4 [19], 1,4-diazabicyclo[2.2.2]octane (DABCO) [20], ionic liquid [bmim][BF_4] [21], and 2,2,2-trifluoroethanol (TFE) [22]. However, many of these procedures are not entirely satisfactory and suffer from long reaction times, expensive reagents, unsatisfactory yields of products, harsh reaction conditions, or tedious work-up using homogeneous liquid catalysts. These problems prompted us towards further investigation in search of a new reusable heterogeneous catalyst, which will carry out the synthesis of tetrahydrobenzo[*b*]pyrans under simpler experimental set-up, and green and eco-friendly conditions.

The development of heterogeneous catalysts and how they affect specific transformations in chemical synthesis has become a major area of research. The potential advantages of these materials over homogeneous systems, in terms of their simplified recovery and reusability, could potentially allow for the development of environmentally benign chemical procedures in both academic and industrial settings. Catalysts of this type have the potential to make the processes in which they are applied cleaner, safer, higher-yielding, and relatively inexpensive [23–26].

During the course of our recent studies directed towards the development of practical and environmentally friendly procedures for the synthesis of organic compounds using reusable catalysts [27–32], we investigated the application of a carbon-based solid acid (CBSA), which can be easily prepared by heating naphthalene and concentrated sulfuric acid [33], as a catalyst for a series of organic transformations. This reusable heterogeneous catalyst performed well and showed a high level of catalytic activity in the Mannich [34] and Biginelli [35] reactions, as well as in the synthesis of tetrasubstituted imidazoles [36]. This fact prompted us to investigate the catalytic activity of this material in the synthesis of tetrahydrobenzo[*b*]pyrans (Scheme 1).



Scheme 1 CBSA catalyzed synthesis of tetrahydrobenzo[*b*]pyrans

Experimental

All the chemicals were purchased from Merck and Aldrich and used without purification. Melting points of the compounds were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ^{1}H NMR (500 MHz) spectra were recorded with Bruker 500 spectrometer.

Preparation of CBSA catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (>96 %, 200 ml) at 250 °C under a flow of N_2. After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 250 °C for 5 h, which resulted in a black solid. The solid was then ground to a powder and was washed repeatedly in boiling water until impurities such as sulfate ions were no longer detected in the wash water. The density of the SO_3H groups was measured using NaOH (0.01 mol L^{-1}) as titrant by acid–base potentiometric titration. The amount of SO_3H attached to the polycyclic aromatic carbon was 2.81 mmol/g. The resulting black powder was insoluble in solvents such as water, methanol, ethanol, benzene, and hexane even at their boiling temperatures [33].

General procedure for the synthesis of tetrahydrobenzo[b]pyrans **4a-o** catalyzed by CBSA

A mixture of dimedone **1** (2 mmol), an aromatic or aliphatic aldehyde **2a-o** (2 mmol), malononitrile **3** (2 mmol), and CBSA (0.07 g) in ethanol (5 ml) was heated under reflux for 10–30 min. During the procedure, the reaction was monitored by TLC. Upon completion, the catalyst was filtered under hot condition. After cooling the fiterate, the precipitated solid was filtered and recrystallized from ethanol to give products **4a-o** in high yields.

Selected ^{1}H NMR and FT-IR data

2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran 4e (Ar = 4-ClC_6H_4)

^{1}H NMR (500 MHz, DMSO-d_6): δ 0.95 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.10 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH_2), 2.24 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH_2), 2.45–2.55 (m, 2H, diastereotopic protons in CH_2 overlapped with solvent), 4.19 (s, 1H, CH), 7.05 (s br., 2H, NH_2), 7.17 (d, $J = 8.4$ Hz, 2H, arom-H), 7.34 (d, $J = 8.4$ Hz, 2H, arom-H); IR (KBr disc): υ 3,380, 3,182, 2,958, 2,188, 1,675, 1,636, 1,491, 1,365, 1,216 cm^{-1}.

2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran 4i (Ar = 4-MeOC$_6$H$_4$)

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 0.94 (s, 3H, CH$_3$), 1.04 (s, 3H, CH$_3$), 2.08 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.24 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.43–2.57 (m, 2H, diastereotopic protons in CH$_2$ overlapped with solvent), 3.71 (s, 3H, OCH$_3$), 4.12 (s, 1H, CH), 6.83 (d, $J = 8.7$ Hz, 2H, arom-H), 6.93 (s br., 2H, NH$_2$), 7.04 (d, $J = 8.7$ Hz, 2H, arom-H); IR (KBr disc): υ 3,378, 3,185, 2,953, 2,198, 1,685, 1,655, 1,509, 1,370, 1,249, 1,213, 1,034 cm^{-1}.

2-Amino-3-cyano-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran 4j (Ar = 4-MeC$_6$H$_4$)

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 0.95 (s, 3H, CH$_3$), 1.05 (s, 3H, CH$_3$), 2.09 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.24 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.25 (s, 3H, CH$_3$), 2.43–2.57 (m, 2H, diastereotopic protons in CH$_2$ overlapped with solvent), 4.13 (s, 1H, CH), 6.95 (s br., 2H, NH$_2$), 7.02 (d, $J = 8.0$ Hz, 2H, arom-H), 7.08 (d, $J = 8.0$ Hz, 2H, arom-H); IR (KBr disc): υ 3,427, 3,331, 2,958, 2,192, 1,675, 1,602, 1,510, 1,368, 1,249, 1,206, 1,140, 1,033 cm^{-1}.

2-Amino-3-cyano-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrobenzo[b]pyran 4 k (Ar = 3-O$_2$NC$_6$H$_4$)

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 0.96 (s, 3H, CH$_3$), 1.04 (s, 3H, CH$_3$), 2.11 (d, $J = 16.1$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.27 (d, $J = 16.1$ Hz, 1H, one proton of diastereotopic protons in CH$_2$), 2.55 (s, 2H, diastereotopic protons in CH$_2$), 4.42 (s, 1H, CH), 7.17 (s br., 2H, NH$_2$), 7.55–7.70 (m, 2H, arom-H), 7.97 (t, $J = 1.7$ Hz, 1H, arom-H), 8.05-8.10 (m, 1H, arom-H); IR (KBr disc): υ 3,432, 3,321, 2,957, 2,186, 1,664, 1,599, 1,530, 1,375, 1,350, 1,251, 1,211, 1,138, 1,038 cm^{-1}.

Results and discussion

Characterization of the catalyst

The catalyst was characterized by FT-IR spectroscopy, energy dispersive X-ray (EDX), X-ray diffraction (XRD), and the N$_2$ adsorption/desorption analysis (BET) techniques.

The FT-IR spectrum of the catalyst exhibits the SO$_2$ symmetric and asymmetric stretching modes in 1,100–1,250 cm^{-1}. The spectrum also shows a broad OH stretching absorption around 2,500–3,600 cm^{-1} (Fig. 1).

The EDX spectrum of CBSA is shown in Fig. 2. The EDX pattern shows the clear presence of C, O, and S in the sample which indicates the SO$_3$H groups are

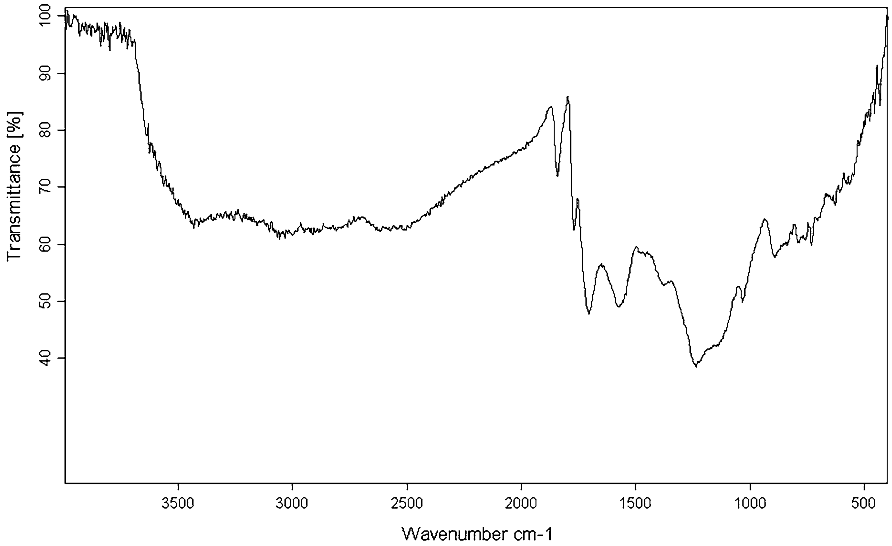


Fig. 1 FT-IR spectrum of CBSA catalyst

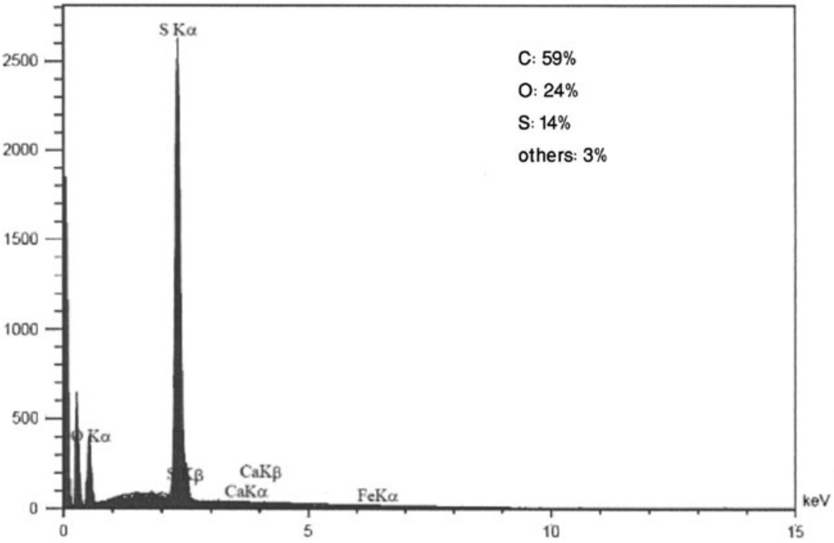


Fig. 2 EDX spectrum of CBSA catalyst

successfully attached to the aromatic carbon atoms. The mass percentages of C, O and S atoms are 59, 24, and 14 %, respectively.

The XRD pattern exhibits two broad, weak diffraction peaks ($2\theta = 10$–30°, 35–50°) attributable to amorphous carbon (Fig. 3).

The N_2 adsorption–desorption isotherm of the catalyst is shown in Fig. 4. The majority of isotherms have been grouped into six types by IUPAC classification (I,

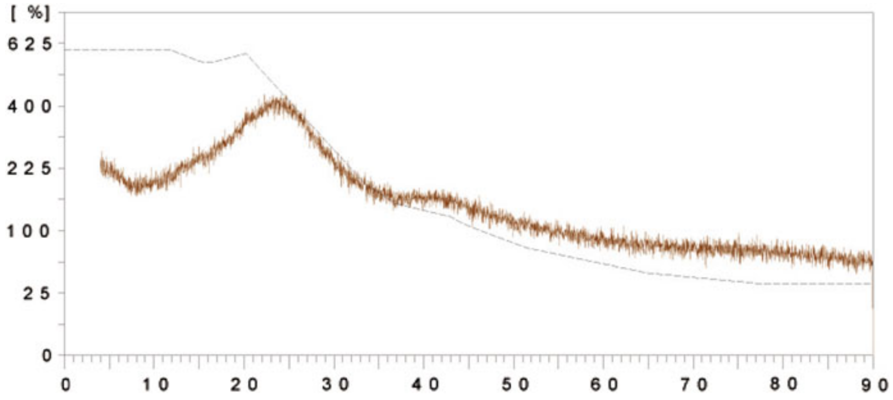


Fig. 3 XRD pattern of CBSA catalyst

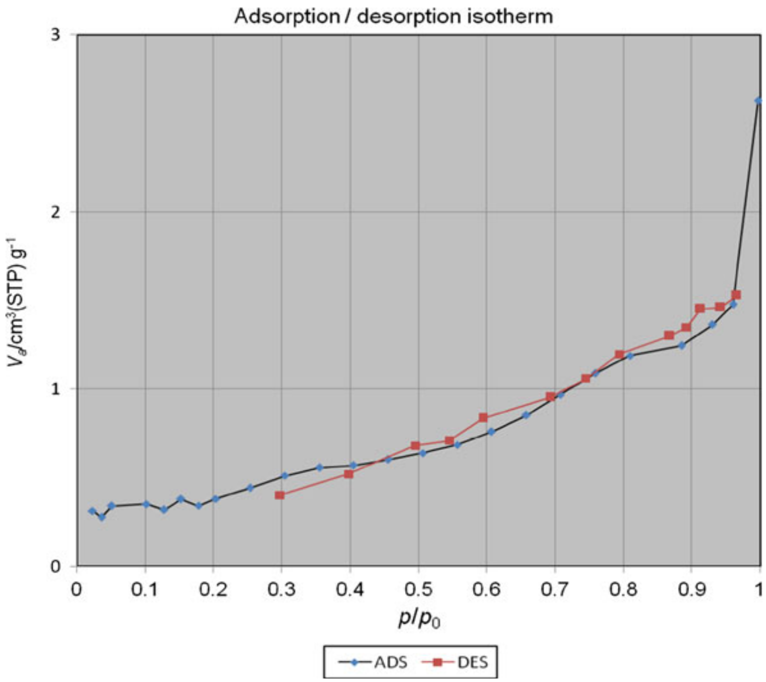


Fig. 4 N_2 adsorption–desorption isotherm of CBSA catalyst

II, III, IV, V, and VI) [37]. The shape of the isotherm of the CBSA catalyst in this paper is type II. A Type II isotherm is the form of isotherm that is normally obtained with non-porous or macroporous adsorbents. Average pore diameter measured by the BET method is 10.172 nm.

Table 1 Effect of CBSA catalyst amount, solvent, and temparature on the model reaction

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Yield[a] (%)
1	–	H_2O	Reflux	120	–
2	–	$CHCl_3$	Reflux	120	–
3	–	CH_3CN	Reflux	120	–
4	–	EtOH	Reflux	120	Trace
5	–	–	120	120	–
6	0.05	H_2O	Reflux	60	30
7	0.05	$CHCl_3$	Reflux	120	Trace
8	0.05	CH_3CN	Reflux	70	20
9	0.05	EtOH	Reflux	30	65
10	0.05	–	120	60	20
11	0.07	H_2O	Reflux	30	55
12	0.07	$CHCl_3$	Reflux	90	20
13	0.07	CH_3CN	Reflux	30	45
14	0.07	EtOH	Reflux	15	95
15	0.07	–	120	30	30
16	0.10	H_2O	Reflux	30	57
17	0.10	$CHCl_3$	Reflux	100	25
18	0.10	CH_3CN	Reflux	20	46
19	0.10	EtOH	Reflux	15	95
20	0.10	–	120	30	36
21	0.15	EtOH	Reflux	20	96
22	0.10	EtOH	r.t.	120	20

Reaction conditions: dimedone **1** (2 mmol), 4-chlorobenzaldehyde **2e** (2 mmol), and malononitrile (2 mmol)

[a] Isolated yields

Synthesis of tetrahydrobenzo[b]pyrans using CBSA catalyst

The CBSA catalyst is amorphous carbon consisting of polycyclic aromatic carbon sheets with attached SO_3H groups that functions as a strong solid acid with a high density of acid sites and therefore can promote the reactions. To search for the optimal conditions for the synthesis of tetrahydrobenzo[*b*]pyrans, the synthesis of compound **4e** was selected as a model reaction. The reaction was carried out by heating a mixture of dimedone (2 mmol), 4-cholorobenzaldehyde (2 mmol), and malononitrile (2 mmol) in the absence or presence of CBSA as catalyst in different solvents, including H_2O, $CHCl_3$, CH_3CN, EtOH, and also under solvent-free conditions. The results are summarized in Table 1. No or a trace product was obtained in the absence of the catalyst at reflux temperature in solvent or 120 °C under solvent-free conditions even after reaction for 120 min (entries 1–5), whereas good results were obtained in the presence of a catalytic amount of CBSA. Also, as shown, the reaction in EtOH gave better results in terms of yield as well as reaction time than others. The reaction temperature also strongly influenced the reaction.

Table 2 CBSA catalyzed synthesis of tetrahydrobenzo[*b*]pyran derivatives 4a-o

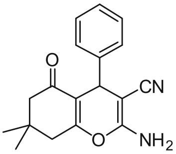
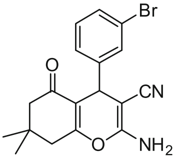
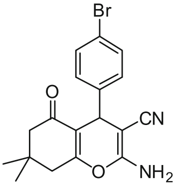
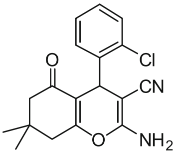
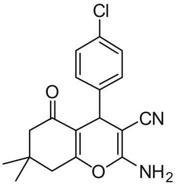
Entry	R	Product[a]	Time (min)	Yield[b] (%)	m.p. (°C)	
					Found	Reported
1	C_6H_5	 **4a**	18	90	229–231	230–232 [14]
2	$3\text{-}BrC_6H_4$	 **4b**	15	93	230–232	227–229 [18]
3	$4\text{-}BrC_6H_4$	 **4c**	15	98	217–218	215 [19]
4	$2\text{-}ClC_6H_4$	 **4d**	15	93	217–219	218–220 [18]
5	$4\text{-}ClC_6H_4$	 **4e**	15	95	218–219	215–216 [22]

Table 2 continued

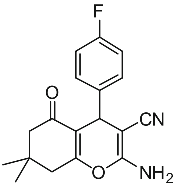
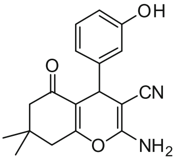
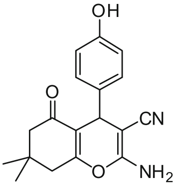
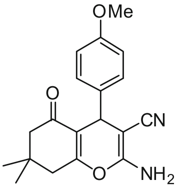
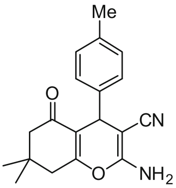
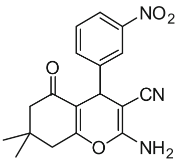
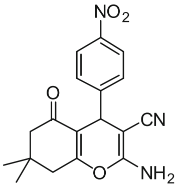
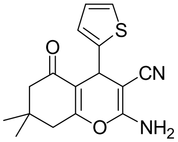
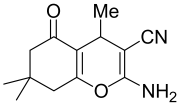
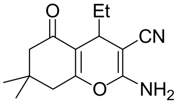
Entry	R	Product[a]	Time (min)	Yield[b] (%)	m.p. (°C)	
					Found	Reported
6	4-FC_6H_4	 **4f**	15	90	180–182	176–178 [18]
7	3-HOC_6H_4	 **4g**	20	85	227–229	225 [19]
8	4-HOC_6H_4	 **4h**	17	90	210–212	209–211 [14]
9	4-$MeOC_6H_4$	 **4i**	18	85	198–199	193–195 [15]
10	4-MeC_6H_4	 **4j**	17	90	216–218	215–218 [17]

Table 2 continued

Entry	R	Product[a]	Time (min)	Yield[b] (%)	m.p. (°C)	
					Found	Reported
11	3-$O_2NC_6H_4$	 **4k**	10	90	212–214	210–212 [17]
12	4-$O_2NC_6H_4$	 **4l**	10	93	180–182	183–185 [13]
13	2-thienyl	 **4m**	15	86	220–222	224–226 [21]
14	Me	 **4n**	30	58	176–177	177–179 [17]
15	Et	 **4o**	30	53	195–197	193–194 [17]

Reaction conditions: dimedone **1** (2 mmol), aromatic or aliphatic aldehyde **2a-o** (2 mmol), malononitrile **3** (2 mmol), CBSA (0.07 g), EtOH (5 ml), reflux

[a] All the products were characterized by their IR spectral data and a comparision of their melting points with those of authentic samples. The structures of some products were also confirmed by ^{1}H NMR analysis

[b] Isolated yields

Only a low yield of the product **4e** was obtained in EtOH at room temperature in the presence of 0.10 g catalyst in the model reaction (entry 22). The best result was obtained when the reaction was conducted in refluxing EtOH in the presence of

Table 3 Comparison of the efficiencies of different catalysts for the synthesis of tetrahydrobenzo[*b*]pyrans

Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T (°C)	Other			
Piperazine	–	r.t.	Ball-milling	20–120	88–96	[10]
I_2	DMSO	120	–	180–240	80–92	[11]
KF/Al_2O_3	EtOH	27-34	Ultrasound irradiation	20–240	81–98	[12]
Basic ionic liquid	EtOH/H_2O	Reflux	–	5–240	50–94	[13]
Nano mixed metal oxides	EtOH	Reflux	–	35–45	90–94	[14]
Nano ZnO	H_2O	80	–	20–180	50–98	[15]
Nano ZnO	EtOH/H_2O	r.t.	–	180–240	79–91	[16]
$PhB(OH)_2$	EtOH/H_2O	Reflux	–	30	61–88	[17]
TBAB	EtOH	Reflux	–	20–140	87–95	[18]
Na_2SeO_4	EtOH/H_2O	Reflux	–	40–210	80–98	[19]
DABCO	H_2O	Reflux	–	120	75–97	[20]
[bmim][BF_4]	[bmim][BF_4]	80	–	30–120	85–95	[21]
TFE	TFE	Reflux	–	300	80–95	[22]
CBSA	EtOH	Reflux	–	10–20	85–98	This work

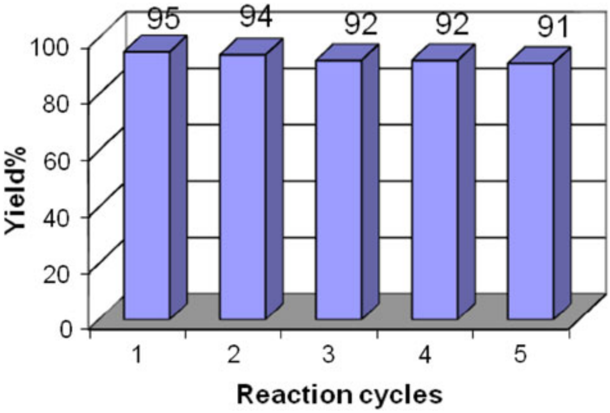
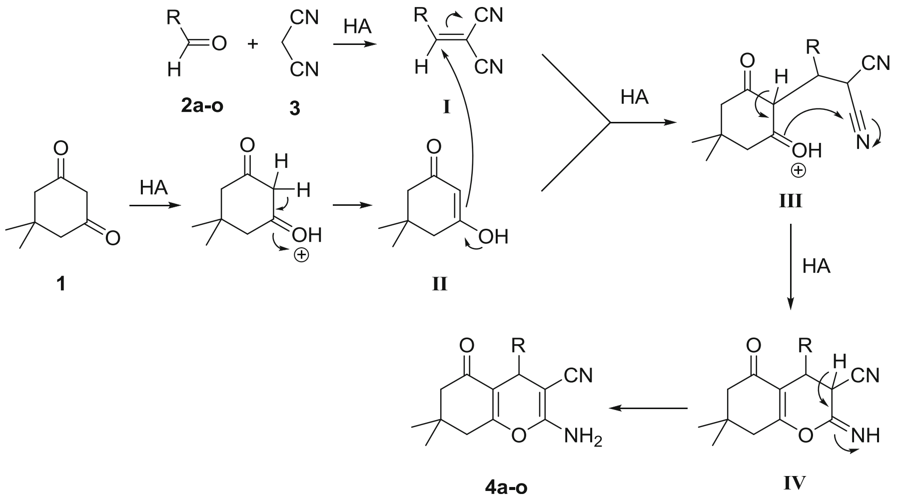


Fig. 5 Reusability of CBSA for the synthesis of compound **4e**

0.07 g of the CBSA catalyst (entry 14). No significant improvement in yield was observed using a higher amount of the catalyst (entries 19 and 21).

Encouraged by this success, we extended the reaction of dimedone, and malononitrile with a range of aromatic aldehydes under the optimized reaction conditions. In all cases, the expected products were obtained in high yields in short reaction times. The results are summarized in Table 2. As shown, aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents reacted successfully with dimedone and malononitrile to give the corresponding



Scheme 2 Plausible mechanism for the formation of tetrahydrobenzo[*b*]pyrans in the presence of CBSA ≡ HA as catalyst

tetrahydrobenzo[*b*]pyran products in high yields over short reaction times. The results also show that the aromatic aldehydes with electron-withdrawing groups react faster and the yields are more than the aromatic aldehyde with electron-donating groups. These reactions have high atom economy ranging from 94.2 to 95.4 %. The reaction of dimedone and malononitrile with aliphatic aldehydes under the optimized reaction conditions was also tested. As shown in Table 2 (entries 14 and 15), in these cases, the moderate yields of the products were obtained.

To show the merit of the present methodology, we compared the obtained results using CBSA as a heterogeneous catalyst with other reported results for the synthesis of tetrahydrobenzo[*b*]pyrans in the presence of various homogeneous, heterogeneous, and supported catalysts. This comparison is shown in Table 3. As can be seen, our reaction conditions showed a shorter reaction time with high yields of the desired products.

Reusability of the catalyst was also investigated. After the completion of the reaction, the catalyst was readily recovered from the reaction mixture by a simple filtration. In this catalyst, SO_3H groups have been covalently bound to the polycyclic aromatic carbon sheets. Thus, the catalyst has high stability and could behave as a recyclable solid catalyst without the danger of leaching that is observed in most supported catalysts. The separated catalyst was washed with cold ethanol and subsequently dried at 60 °C under vacuum for 1 h before being reused in a similar reaction. We found that the catalyst could be used at least five times with only a slight reduction in activity (Fig. 5).

A plausible mechanism may proceed as depicted in Scheme 2. The reaction occurs via initial formation of the dicyano olefin [**I**], prepared by Knoevenagel condensation of aryl aldehydes **2a-o** and malononitrile **3**, which reacts with intermediate [**II**] obtained from dimedone **1** to give the intermediate [**III**] which subsequently cyclizes to afford the desired compounds **4a-o** via the intermediate [**IV**]. The catalyst CBSA ≡ HA facilitates the formation of the intermediates [**I**], [**II**], [**III**], and [**IV**].

Conclusions

In conclusion, we describe a mild and efficient procedure for the preparation of tetrahydrobenzo[*b*]pyrans through the one-vessel, three-component reaction of dimedone, aryl aldehydes, and malononitrile using a catalytic amount of CBSA as a heterogeneous catalyst in refluxing EtOH. The reactions have high atom economy ranging from 94.2 to 95.4 %. This procedure offers several advantages including clean reactions, high yields, short reaction times, low cost of the catalyst, and environmentally non-harmful media, as well as a simple experimental and isolated procedure, which makes it a useful and attractive protocol for the synthesis of these compounds. However, using aliphatic aldehydes, the moderate yields of the products were obtained. The catalyst can be recycled after simple handling, and used at least five times without any substantial reduction in its catalytic activity.

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References

1. L. Bonsignore, G. Loy, D. Secci, A. Calignano, Eur. J. Med. Chem. **28**, 517 (1993)
2. G.R. Green, J.M. Evans, A.K. Vong, in *Comprehensive Heterocyclic Chemistry II*, ed. by A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Pergamon, Oxford, 1995), pp. 469–500
3. K. Rehse, W. Schinkel, Arch. Pharm. **316**, 988 (1983)
4. I. Fatima, R. Saxena, G. Kharkwal, M.K. Hussain, N. Yadav, K. Hajela, P.L. Sankhwar, A. Dwivedi, J. Steroid Biochem. Mol. Biol. **138**, 123 (2013)
5. A.E.F.G. Hammam, O.I. Abd El-Salam, A.M. Mohamed, N.A. Hafez, Indian J. Chem. Sect. B Org. Chem. Incl. Med. Chem. **44**, 1887 (2005)
6. D. Armetso, W.M. Horspool, N. Martin, A. Ramos, C. Seoane, J. Org. Chem. **54**, 5190 (1989)
7. S. Hatakeyama, N. Ochi, H. Numata, S. Takano, J. Chem. Soc. Chem. Commun. 1202 (1988)
8. C.S. Konkoy, D.B. Fick, S.X. Cai, N.C. Lan, J.F.W. Keana, PCT Int. Appl. WO Patent 200075123. Chem. Abstr. **134**, 29313a (2001)
9. S. Paul, S. Ghosh, P. Bhattacharyya, A.R. Das, RSC Adv. **3**, 14254 (2013)
10. M. Amirnejad, M.R. Naimi-Jamal, H. Tourani, H. Ghafuri, Monatsh. Chem. **144**, 1219 (2013)
11. R.S. Bhosale, C.V. Magar, K.S. Solanke, S.B. Mane, S.S. Choudhary, R.P. Pawar, Synth. Commun. **37**, 4353 (2007)
12. J.T. Li, W.Z. Xu, L.C. Yang, T.S. Li, Synth. Commun. **34**, 4565 (2004)
13. J. Zheng, Y. Li, Mendeleev Commun. **21**, 280 (2011)
14. S. Rathod, B. Arbad, M. Lande, Chin. J. Catal. **31**, 631 (2010)
15. M. Hosseini-Sarvari, S. Shafiee-Haghighi, Chem. Heterocycl. Compd. **48**, 1307 (2012)
16. P. Bhattacharyya, K. Pradhan, S. Paul, A.R. Das, Tetrahedron Lett. **53**, 4687 (2012)
17. S. Nemouchi, R. Boulcina, B. Carboni, A. Debache, C. R. Chim. **15**, 394 (2012)
18. S. Gurumurthi, V. Sundari, R. Valliappan, E. J. Chem. **6**, S466 (2009)
19. R. Hekmatshoar, S. Majedi, Kh Bakhtiari, Catal. Commun. **9**, 307 (2008)
20. D. Tahmassebi, J.A. Bryson, S.I. Binz, Synth. Commun. **41**, 2701 (2011)
21. Y. Li, B. Du, X. Wang, D. Shi, S. Tu, J. Heterocycl. Chem. **43**, 685 (2006)
22. S. Khaksar, A. Rouhollahpour, S. Mohammadzadeh Talesh, J. Fluorine Chem. **141**, 11 (2012)

23. V.S. Gerard, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry* (Elsevier, San Diego, 2000)
24. K. Wilson, J.H. Clark, Pure Appl. Chem. **72**, 1313 (2000)
25. N. Seifi, M.H. Zahedi-Niaki, M.R. Barzegari, A. Davoodnia, R. Zhiani, A.A. Kaju, J. Mol. Catal. A Chem. **260**, 77 (2006)
26. M. Zeinali-Dastmalbaf, A. Davoodnia, M.M. Heravi, N. Tavakoli-Hoseini, A. Khojastehnezhad, H.A. Zamani, Bull. Korean Chem. Soc. **32**, 656 (2011)
27. A. Davoodnia, M. Bakavoli, R. Moloudi, M. Khashi, N. Tavakoli-Hoseini, Chin. Chem. Lett. **21**, 1 (2010)
28. N. Tavakoli-Hoseini, A. Davoodnia, Asian J. Chem. **22**, 7197 (2010)
29. A. Davoodnia, A. Khojastehnezhad, N. Tavakoli-Hoseini, Bull. Korean Chem. Soc. **32**, 2243 (2011)
30. A. Davoodnia, Synth. React. Inorg. Met-Org. Nano-Met. Chem. **42**, 1022 (2012)
31. N. Mohammadzadeh-Dehsorkh, A. Davoodnia, N. Tavakoli-Hoseini, M. Moghaddas, Synth. React. Inorg. Met-Org. Nano-Met. Chem. **41**, 1135 (2011)
32. A. Davoodnia, A. Zare-Bidaki, H. Behmadi, Chin. J. Catal. **33**, 1797 (2012)
33. M. Hara, T. Yoshida, A. Takagaki, T. Takata, J.N. Kondo, S. Hayashi, K. Domen, Angew. Chem. Int. Ed. **43**, 2955 (2004)
34. A. Davoodnia, A. Tavakoli-Nishaburi, N. Tavakoli-Hoseini, Bull. Korean Chem. Soc. **32**, 635 (2011)
35. M. Moghaddas, A. Davoodnia, M.M. Heravi, N. Tavakoli-Hoseini, Chin. J. Catal. **33**, 706 (2012)
36. N. Tavakoli-Hoseini, A. Davoodnia, Chin. J. Chem. **29**, 203 (2011)
37. K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. **57**, 603 (1985)