Tetrahedron 65 (2009) 364–368

Contents lists available at ScienceDirect

Tetrahedron

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

Task-specific ionic liquid as base, ligand and reaction medium for the palladium-catalyzed Heck reaction

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ARTICLE INFO

Article history:
Received 4 August 2008
Received in revised form
30 September 2008
Accepted 13 October 2008
Available online 22 October 2008

Keywords:
Heck reaction
Task-specific ionic liquid (TSIL)
Ethanolamine-functionalized quaternary ammonium salt
4-Di(hydroxyethyl)aminobutyl tributylammonium bromide (DHEABTBAB)

ABSTRACT

A novel ionic liquid, which was based on ethanolamine-functionalized quaternary ammonium salt was designed and synthesized. 4-Di(hydroxyethyl)aminobutyl tributylammonium bromide (DHEABTBAB) **1**, a task-specific ionic liquid, which acts as a base, ligand and reaction medium, exhibits a very high activity and recyclability to palladium-catalyzed Heck reaction. The olefinations of iodoarenes, bromoarenes and chloroarenes with olefins generated the corresponding cross-coupling products in good to excellent yields only in the presence of DHEABTBAB and palladium acetate under phosphine-free reaction conditions. It is noteworthy that palladium and DHEABTBAB could be repeatedly recycled and reused for six consecutive trials without significant loss of their activities.

1. Introduction

The use of ionic liquids (ILs) has received more attention as eco-friendly, reusable and alternative reaction media in organic synthesis because of their unique properties, such as high thermal and chemical stability, negligible vapour pressure, no flammability, high loading capacity and excellent electrical conductivity.[1] A number of organic reactions including hydrogenation, oxidation, C–C bond-forming reactions have already been demonstrated in ILs.[2]

Most recently, much more attention has been focused on the synthesis of functionalized ionic liquids (FILs), through incorporation of additional functional groups as a part of the cation and/or anion, so-called task-specific ionic liquids (TSILs), and their applications in chemical research. The incorporation of functional groups can impart a particular capability to the ionic liquids, enhancing their capacity for catalyst reusability. Moreover, specific functional groups, such as amine, amide, nitrile, ether, alcohol, acid, urea or thiourea, can be incorporated into the ionic liquids for task-specific purposes. They have shown great promise not only as alternative green solvents, but also as reagents or catalysts in organic transformations.[1b,3] However, many of them were focused on the incorporation of functionality into a branch appended to the imidazolium cation. In addition, the synthesis of TSILs is rather complicated and multi-step procedures have to be required.

The Heck reaction is one of the most important, reliable and general reaction for carbon–carbon bond formation in organic synthesis.[4] Palladium compounds, usually complexes with phosphine ligands, are very often used as catalyst precursors in the Heck reaction. Phosphines play a role of stabilizers of in situ formed soluble Pd(0) complexes, which are generally considered as the catalytically active forms.[5] Phosphine-free catalysts have been received great interest recently as less complicated and environment-friendly alternatives to phosphine containing systems.[2b,6] Unfortunately, some of the catalyst systems suffer from drawbacks of ligands sensitivity towards air and moisture, tedious multi-step synthesis, or high cost of ligands. Furthermore, a homogeneous palladium catalyst usually precipitated from the solution, and recycling or recovery of the expensive palladium is difficult. It is desirable to develop a more robust, simple and cost-effective non-phosphine ligand and a recyclable palladium catalyst system for Heck reaction.

In general, the essential requirement for the Heck reaction includes a base, a ligand-stabilized active Pd species, and a reaction medium. This promoted us to design and synthesize a task-specific ionic liquid, which acts as a base, a non-phosphine ligand, as well as an environmentally benign reaction medium in an ion-pair unity. Although phosphine-free palladium-catalyzed Heck reaction in functionalized ionic liquid, which was used as an efficient and

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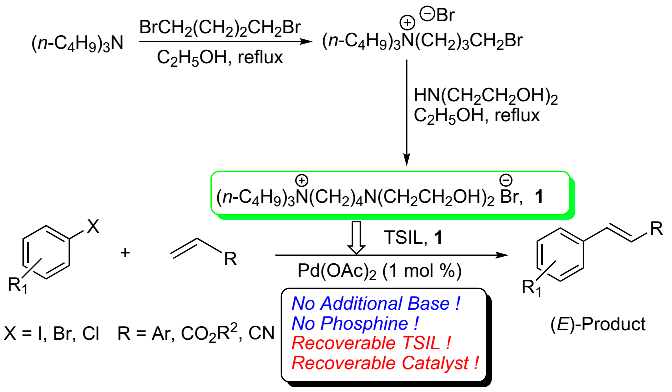
doi:10.1016/j.tet.2008.10.042

recyclable reaction medium in the presence of K_3PO_4 has been reported in our laboratory recently, it is desirable to develop more efficient and multi-functional ionic liquid for palladium-catalyzed Heck reaction.[7] Here, we wish to report our success in the development of a new ionic liquid, which was based on ethanolamine-functionalized quaternary ammonium salt. 4-Di(hydroxyethyl)aminobutyl tributylammonium bromide, **1** exhibits a very high activity and recyclability to palladium-catalyzed Heck reaction (Scheme 1). The olefinations of iodoarenes, bromoarenes and chloroarenes with olefins generated the corresponding cross-coupling products in good to excellent yields only in the presence of **1** and palladium acetate (1 mol %) under phosphine-free reaction conditions. It is noteworthy that palladium and **1** could be repeatedly recycled and reused for six consecutive trials without significant loss of their activities.



Scheme 1. Synthesis of task-specific ionic liquid **1** and its application in the Heck reaction.

2. Results and discussion

The synthesis of task-specific ionic liquid **1** was illustrated in Scheme 1. It was readily prepared through a straightforward two-step procedure from commercially available starting materials and reagents in good yields. Tri(*n*-butyl)amine was reacted with 1,4-dibromobutane with 1:4 molar ratio in ethanol under reflux temperature for 48 h to afford (4-bromobutyl)tri(*n*-butyl)ammonium bromide in 95% yield. This intermediate subsequently reacted with diethanolamine in the presence of K_2CO_3 in ethanol at 80 °C for 24 h to generate the corresponding functionalized ionic liquid **1** in 91% yield. TSIL, **1** was further purified by drying in a vacuum (ca. 2 mmHg) at 100 °C to remove the residual starting materials, reagents or organic solvents.

To examine its activity, **1** was used for the palladium-catalyzed Heck reaction in the absence of any additives. The experimental results revealed that ethanolamine-functionalized ionic liquid **1**, exhibits a very high activity. It is presumably due to the effective *N*,*O*-ligand in organic reactions, such as asymmetric addition of aldehydes or imines,[8] Suzuki and Ullmann reactions,[9] and present reaction.

The effect of palladium source on the Heck reaction of bromobenzene and styrene in the presence of **1** was explored (Table 1). Among the palladium sources tested, simple palladium inorganic salts, such as $Pd(OAc)_2$ and $PdCl_2$, proved to be the best of choice (98% and 96% yields of *trans*-stilbene, respectively). $Pd(CH_3CN)_2Cl_2$, $Pd(PPh_3)_2Cl_2$, $Pd_2(dba)_3$ and Pd/C were inferior and generated *trans*-stilbene in 52%, 47%, 40% and 23% yields, respectively. However, Pd powder (micron) was found to be inactive to the Heck reaction.

During the course of our further optimization of the reaction conditions, when using 1 mol % of $Pd(OAc)_2$ in **1**, the reactions were generally completed in a matter of hours, but the time, as expected, was inversely proportional to the temperature. A reaction temperature of 100 °C was found to be optimal. Thus, the optimized reaction conditions for this Heck reaction are the $Pd(OAc)_2$ (1 mol %) in **1** at 100 °C for 6 h.

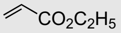
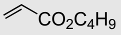
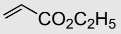
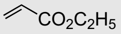
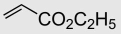
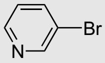
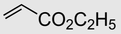
Table 1
Effect of palladium source on the Heck reaction[a]

Entry	Palladium source/amount	Yield[b] (%)
1	Palladium powder (micron, 1 mol %)	0
2	Pd/C (1 mol %)	23
3	$Pd_2(dba)_3$ (1 mol %)	47
4	$Pd(PPh_3)_2Cl_2$ (1 mol %)	40
5	$Pd(CH_3CN)_2Cl_2$ (1 mol %)	52
6	$PdCl_2$ (1 mol %)	96
7	$Pd(OAc)_2$ (1 mol %)	98

[a] Styrene (104 mg, 1.00 mmol), bromobenzene (157 mg, 1.00 mmol), Pd source (0.01 mmol), **1** (2.0 mL) at 100 °C for 6 h.
[b] Isolated yields.

To examine the versatility of this procedure, the Heck reactions of styrene with iodoarenes containing electron-rich, electron-poor or electron-neutral substituents were examined. The results are listed in Table 2. It shows that the stereoselectivities (E/Z >99%, *trans*-products formed), conversions, and yields (>99% yields and conversions) were satisfactory under the present reaction conditions (entries 1–4, Table 2). For bromobenzene, activated and deactivated bromoarenes, excellent yields of cross-coupling products were also isolated under the standard reaction conditions (entries 5–10, Table 2). On the other hand, the relatively hindered substrates, i.e., 2-methyl-bromobenzene and 3-methyl-bromobenzene, also underwent the olefinations and led to the good yields (entries 11–12, Table 2). The scope of this catalytic system with other vinyl substrates, such as ethyl acrylate, butyl acrylate and acrylonitrile, was also examined and good to excellent results were

Table 2
Palladium-catalyzed Heck reaction in TSIL **1**[a]

Entry	Organic halide	Olefin	Yield[b] (%)
1	C_6H_5I	$C_6H_5CH{=}CH_2$	99
2	p-$CH_3C_6H_4I$	$C_6H_5CH{=}CH_2$	99
3	p-$CH_3OC_6H_4I$	$C_6H_5CH{=}CH_2$	99
4	p-$CH_3COC_6H_4I$	$C_6H_5CH{=}CH_2$	99
5	C_6H_5Br	$C_6H_5CH{=}CH_2$	99
6	p-$CH_3COC_6H_4Br$	$C_6H_5CH{=}CH_2$	99
7	p-CNC_6H_4Br	$C_6H_5CH{=}CH_2$	95
8	p-$C_2H_5O_2CC_6H_4Br$	$C_6H_5CH{=}CH_2$	99
9	p-$CH_3C_6H_4Br$	$C_6H_5CH{=}CH_2$	95
10	p-$CH_3OC_6H_4Br$	$C_6H_5CH{=}CH_2$	93
11	m-$CH_3C_6H_4Br$	$C_6H_5CH{=}CH_2$	88
12	o-$CH_3C_6H_4Br$	$C_6H_5CH{=}CH_2$	82
13	p-CNC_6H_4Cl	$C_6H_5CH{=}CH_2$	89
14	p-$CH_3COC_6H_4Cl$	$C_6H_5CH{=}CH_2$	86
15	C_6H_5Cl	$C_6H_5CH{=}CH_2$	66
16	C_6H_5I		99
17	p-$CH_3OC_6H_4I$		99
18	C_6H_5Br		99
19	p-$NO_2C_6H_4Br$		96
20	p-$CH_3OC_6H_4Br$		92
21	p-$CH_3C_6H_4Br$		97
22			90

[a] Olefin (1.00 mmol), organic halide (1.00 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), **1** (2.0 mL) at 100 °C for 6 h.
[b] Isolated yields.

obtained for iodoarenes, bromoarenes including relatively deactivated bromides bearing an methoxy as the substituent, and heteroaryl bromide, such as 3-bromopyridine under identical conditions (entries 16–22, Table 2). It is noteworthy that good yields of desired products were observed for activated chloroarenes (entries 13–14, Table 2). However, a moderate yield of the product was generated for chlorobenzene (entry 15, Table 2) and little or no activity was observed with deactivated aryl chlorides.

In contrast, while no significant colour change was observed in the course of the Heck reaction, carried out in ordinary ionic liquids, such as [Bmim]Br, [Bmim]BF_4 or [Bmim]PF_6, the task-specific ionic liquid **1**–palladium solution rapidly turned black following the addition of bromobenzene, which was indicative of nanoparticle palladium metal formation. It was possible to isolate the palladium nanoparticles from the Heck reactions, which were subsequently analyzed using transmission electron microscopy (TEM), and the TEM image was shown in Figure 1. The nanoparticles obtained from **1** have an average diameter of ca. 4 nm, and such microdissimilarity was in accordance with the macroappearance disparity of the ionic liquid systems. The TEM image also indicated that nanoparticles generated in **1** is evenly distributed and it supports the hypothesis that the ethanolamine-functionalized ionic liquid stabilizes the palladium colloid. The ethanolamine moiety could either co-ordinate to the palladium surface or point away from the surface of the nanoparticle, thereby repelling proximal neighbours. In this case, agglomeration would be prevented and, ultimately, the activity of palladium catalyst was increased.

The recyclability of **1** and palladium was also investigated. When bromobenzene was treated with styrene with 1 mol % $Pd(OAc)_2$ in **1** at 100 °C for 6 h, the desired coupling product was obtained in 99% yield. After extraction of the product from the reaction mixture using ethyl ether, **1** and palladium were recovered and fresh starting materials were charged. Palladium and **1** were recycled six times with no loss of their activities (Fig. 2). Meanwhile, palladium leaching in the catalytic system was also determined. Inductively coupled plasma (ICP) analyses of the extracted organic solvents indicated that Pd content was <0.2 ppm.

The functions of TSIL **1** were shown in Scheme 2. In comparison with the general ionic liquid, our developed **1**, showed particular advantages: (i) it acts as an eco-friendly and recyclable reaction medium; (ii) it acts as a base and an *N*,*O*-ligand, so the Heck reaction can be carried out under no additional ligand and base added reaction conditions; (iii) it is applicable to a broader substrate scope (aromatic iodides, bromides and chlorides); (iv) combination of functional groups including Br, N and OH, enhances Heck reaction and gives high yields of products; (v) Pd catalyst and **1** can be recovered and recycled; (vi) its experimental process is simple.

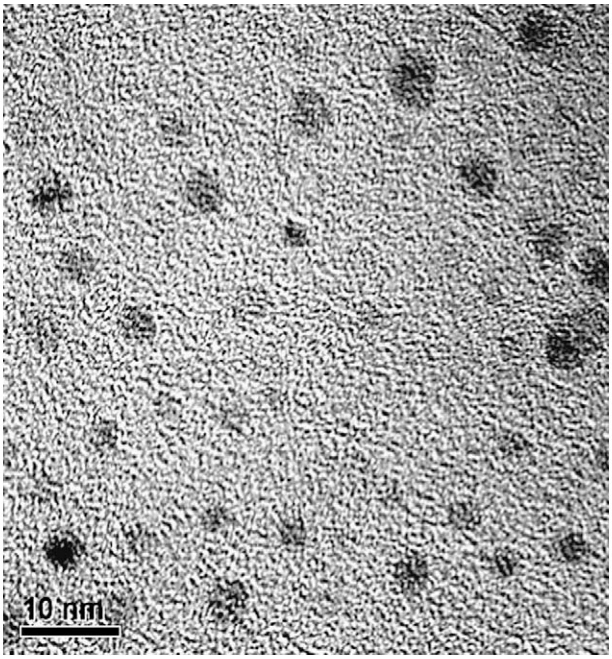


Figure 1. TEM of palladium metal in the Heck reaction carried out in **1**.

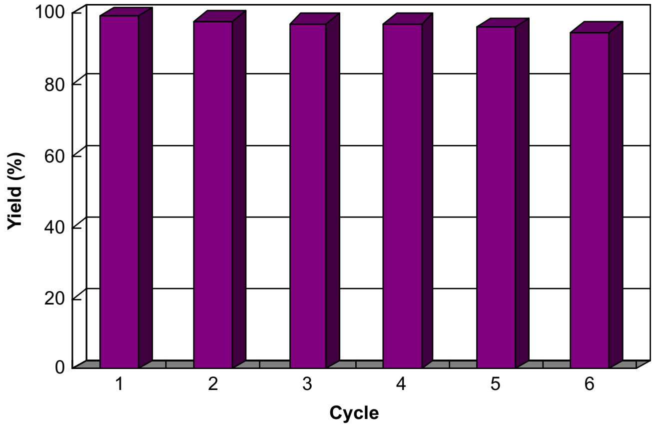
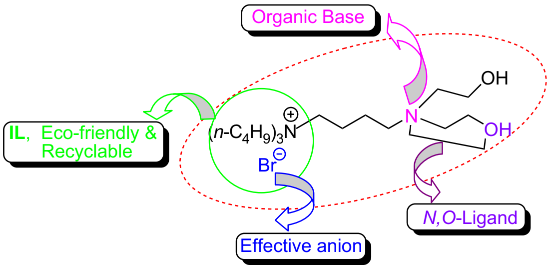


Figure 2. Successive trials by using recoverable **1** and palladium.



Scheme 2. The functions of task-specific ionic liquid **1**.

3. Conclusion

In summary, we have developed an efficient and economic catalyst system for Heck reaction using **1** as solvent, ligand and base in a unity, and palladium acetate as catalyst under phosphine-free reaction conditions. The olefination reactions of olefins with iodoarenes, bromoarenes and chloroarenes generated the corresponding coupling products in good to excellent yields in the presence of **1**, an ideal TSIL for its high activity and easily synthesized. In addition, **1** and palladium can be easily recycled and reused with the same efficacies for six cycles.

4. Experimental

4.1. Physical measurements and materials

Melting points were recorded on a WRS-2B melting point apparatus and are uncorrected. All ^1H NMR spectra were recorded at 300 MHz or 400 MHz by Bruker FT-NMR spectrometers. Chemical shift are given as δ value with reference to tetramethylsilane (TMS) as internal standard. IR spectra were obtained by using a Nicolet NEXUS 470 spectrophotometer. The CHN analysis was performed on a Vario El III elementar. The Pd content was determined by a Jarrell-Ash 1100 ICP analysis. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2. The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and were used without purification prior to use.

4.2. Preparation of 4-di(hydroxyethyl)aminobutyl tributylammonium bromide, 1

In a 100 mL round-bottom flask were introduced successively 30 mL of anhydrous ethanol and 1,4-dibromobutane (8.64 g, 40 mmol). Tri-*n*-butylamine (1.86 g, 10 mmol) in 10 mL of anhydrous ethanol was added drop-wise in 3 h. After the reaction mixture was refluxed for 48 h, ethanol and unreacted starting materials were removed under reduced pressure. The residue was washed with ethyl ether (10 mL×3). The obtained liquid was dried under reduced pressure at 80 °C for 24 h to generate the desired product, (4-bromobutyl)tri(*n*-butyl)ammonium bromide (3.81 g) in 95% yield. ^{1}H NMR (400 MHz, DMSO): δ=3.69 (t, J=6.2 Hz, 2H), 3.56–3.43 (m, 8H), 2.06–1.91 (m, 2×2H), 1.79–1.73 (m, 3×2H), 1.43–1.37 (m, 3×2H), 0.94 (t, J=7.4 Hz, 3×3H). ^{13}C NMR (100 MHz, DMSO): δ=58.1, 57.3, 33.6, 29.0, 23.4, 20.1, 19.1, 12.9. IR (cm^{-1}, film): ν=2961, 2874, 1468, 1382, 740.

To a 50 mL round-bottomed flask, (4-bromobutyl)tri(*n*-butyl)ammonium bromide (2.0 g, 5 mmol), potassium carbonate (0.69 g, 5 mmol) and diethanolamine (0.63 g, 6 mmol) were mixed well in 20 mL of dry ethanol. The mixture was stirred for 24 h at 80 °C. After completion of reaction, ethanol and unreacted starting materials were removed under reduced pressure. The residue was washed with ethyl acetate (5 mL×2), ethyl ether (5 mL×2) and hexane (5 mL×2), respectively. The organic solvent was evaporated under reduced pressure. The residue was dried in a vacuum (ca. 1 mmHg) at 100 °C for 24 h to generate the corresponding product, 4-di(hydroxyethyl)aminobutyl tri(*n*-butyl)ammonium bromide (1.94 g) in 91% yield. Freezing point: −18 °C. ^{1}H NMR (400 MHz, DMSO): δ=3.62 (s, br, 2H), 3.44–3.38 (m, 6H), 3.21–3.15 (m, 8H), 3.00–2.89 (m, 4H), 1.66–1.53 (m, 10H), 1.42–1.35 (m, 3×2H), 0.93 (t, J=6.8 Hz, 3×3H). ^{13}C NMR (100 MHz, DMSO): δ=59.9, 58.2, 57.6, 57.3, 55.8, 26.6, 23.2, 20.3, 19.2, 13.0. IR (cm^{-1}, film): ν=3354, 2956, 2870, 1472, 1385, 749. Anal. Calcd for $C_{20}H_{45}BrN_2O_2$: C, 56.46; H, 10.66; N, 6.58. Found: C, 56.08; H, 10.35; N, 6.99.

4.3. General experimental procedure for the Heck reaction

Under an atmosphere of nitrogen, an oven-dried, two-necked round-bottom flask containing a stir bar was charged with an organic halide (1.00 mmol), olefin (1.00 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), and task-specific ionic liquid, **1** (2.0 mL). The mixture was heated and stirred at 100 °C for 6 h. After completion of the reaction, ethyl ether (3.0 mL×2) was added to the mixture to extract the product. The combined organic layer was washed with water and brine, dried with $MgSO_4$ and evaporated under reduced pressure. The residue was finally purified by flash chromatography on silica gel to give the desired product.

4.4. The recyclability of TSIL, 1 and palladium catalyst

After carrying out the reaction, the mixture was extracted with ethyl ether (3 mL×2). After the neutralization of ammonium salt formed during the reaction with potassium carbonate, **1** and palladium were washed with C_2H_5OH (2 mL) to remove sodium halide through centrifugal separation. The centrifugate containing C_2H_5OH, **1** and palladium was evaporated under reduced pressure. The residue was then washed with Et_2O (3 mL), CH_2Cl_2 (3 mL) and hexane (3 mL), respectively, in order to remove adsorbed organic substrates. After dried under reduced pressure, they can be reused directly without further purification.

4.5. (*E*)-Stilbene

Mp 120–122 °C (lit.[10] mp 120 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.64–7.60 (m, 4H), 7.40–7.27 (m, 4H), 7.24–7.13 (m, 4H). IR (cm^{-1}, KBr): ν=3020, 1631, 1495, 1451, 1364, 962, 764, 692.

4.6. (*E*)-4-Methylstilbene

Mp 121–122 °C (lit.[10] mp 120 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.59 (d, J=7.6 Hz, 2H), 7.50 (d, J=8.0 Hz, 2H), 7.41–7.24 (m, 3H), 7.21–7.16 (m, 4H), 2.31 (s, 3H). IR (cm^{-1}, KBr): ν=3018, 2831, 1632, 1574, 1448, 1365, 969, 809, 749, 690.

4.7. (*E*)-4-Acetylstilbene

Mp 149–151 °C (lit.[9] mp 148–150 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.97 (d, J=8.4 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.43–7.32 (m, 5H), 2.51 (s, 3H). IR (cm^{-1}, KBr): ν=2897, 1708, 1600, 1517, 1368, 1357, 1265, 1178, 1074, 966, 867, 821, 756, 725, 692.

4.8. (*E*)-4-Cyanostilbene

Mp 117–119 °C (lit.[10] mp 117.4–117.7 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.83 (d, J=8.4 Hz, 2H), 7.80 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.56 (t, J=7.4 Hz, 2H), 7.44 (t, J=8.4 Hz, 1H), 7.31 (d, J=16.5 Hz, 1H), 7.19 (d, J=16.5 Hz, 1H). IR (cm^{-1}, KBr): ν=2834, 2362, 1602, 1504, 1364, 973.

4.9. (*E*)-4-Methoxystilbene

Mp 136–138 °C (lit.[11] mp 135–137 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.60 (d, J=6.4 Hz, 2H), 7.50 (d, J=8.4 Hz, 2H), 7.36 (t, J=7.8 Hz, 2H), 7.24 (t, J=6.4 Hz, 1H), 7.16 (d, J=16.4 Hz, 1H), 7.10 (d, J=16.4 Hz, 1H), 6.95 (d, J=8.8 Hz, 2H), 3.80 (s, 3H). IR (cm^{-1}, KBr): ν=2836, 1605, 1512, 1447, 1365, 1297, 1179, 1030, 967, 828, 689.

4.10. (*E*)-Ethyl cinnamate

Oil.[12] ^{1}H NMR (400 MHz, DMSO): δ=7.67 (d, J=16.4 Hz, 1H), 7.62–7.50 (m, 2H), 7.41–7.36 (m, 3H), 6.60 (d, J=16.0 Hz, 1H), 4.18 (q, J=7.2 Hz, 2H), 1.25 (t, J=7.0 Hz, 3H). IR (cm^{-1}, film): ν=3074, 2954, 1709, 1621, 1497, 1312, 772, 687.

4.11. (*E*)-Ethyl 3-(4-nitrophenyl)-2-propenoate

Mp 138–140 °C (lit.[13] mp 139–139.8 °C). ^{1}H NMR (400 MHz, DMSO): δ=8.25 (d, J=8.8 Hz, 2H), 8.20 (d, J=8.8 Hz, 2H), 7.69 (d, J=16.0 Hz, 1H), 6.57 (d, J=16.0 Hz, 1H), 4.22 (q, J=7.0 Hz, 2H), 1.26 (t, J=7.0 Hz, 3H). IR (cm^{-1}, KBr): ν=3075, 2982, 1717, 1644, 1525, 1446, 1354, 1188, 1034, 873, 767, 664.

4.12. (*E*)-Ethyl 4-styrylbenzoate

Mp 106.0–107.5 °C (lit.[14] mp 106.0–106.5 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.96 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.46–7.30 (m, 5H), 7.22 (d, J=16.4 Hz, 1H), 7.13 (d, J=16.4 Hz, 1H), 4.32 (q, J=7.1 Hz, 2H), 1.34 (t, J=7.2 Hz, 3H). IR (cm^{-1}, KBr): ν=3035, 2928, 1711, 1632, 1365, 1277, 1176, 851, 776.

4.13. (*E*)-2-Methylstilbene

Mp 31–32 °C (lit.[12] 30–32 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.58–7.48 (m, 3H), 7.37–7.16 (m, 6H), 7.01 (d, J=16.2 Hz, 2H), 2.36 (s, 3H). IR (cm^{-1}, KBr): ν=2920, 1601, 1495, 1448, 965, 761.

4.14. (*E*)-3-Methylstilbene

Mp 47–48 °C (lit.[15] 48.6–49.2 °C). ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.52–7.50 (m, 2H), 7.35–7.31 (m, 4H), 7.27–7.22 (m, 2H), 7.09–7.07 (m, 3H), 2.38 (s, 3H). IR (cm^{-1}, KBr): ν=3021, 2921, 1600, 1495, 966, 784, 695.

4.15. (*E*)-4-Methylcinnamonitrile

Mp 72–73 °C (lit.[16] mp 71–73 °C). ^{1}H NMR (400 MHz, DMSO): δ=7.58 (d, *J*=16.4 Hz, 1H), 7.53–7.23 (m, 4H), 6.37 (d, *J*=16.4 Hz, 1H), 2.33 (s, 3H). IR (cm^{-1}, KBr): ν=3062, 2956, 2216, 1653, 1624, 1618, 1181, 1110, 978, 801.

4.16. (*E*)-Butyl 3-(4-methoxyphenyl)-2-propenoate

Light yellow liquid.[17] ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.64 (d, *J*=16.8 Hz, 1H), 7.47 (d, *J*=8.7 Hz, 2H), 6.89 (d, *J*=8.7 Hz, 2H), 6.30 (d, *J*=15.9 Hz, 1H), 4.20 (t, *J*=6.6 Hz, 2H), 3.82 (s, 3H), 1.73–1.63 (m, 2H), 1.49–1.37 (m, 2H), 0.97 (t, *J*=7.2 Hz, 3H). IR (cm^{-1}, film): ν=2959, 2934, 1604, 1463, 983, 828.

4.17. (*E*)-Ethyl 3-(3-pyridinyl)-2-propenoate

Light red liquid.[18] ^{1}H NMR (300 MHz, CDCl$_3$): δ=8.73 (s, 1H), 8.56 (d, *J*=4.8 Hz, 1H), 7.87 (d, *J*=8.1 Hz, 1H), 7.64 (d, *J*=16.2 Hz, 1H), 7.38–7.34 (m, 1H), 6.50 (d, *J*=15.9 Hz, 1H), 4.26 (q, *J*=6.8 Hz, 2H), 1.28 (t, *J*=7.2 Hz, 3H). IR (cm^{-1}, film): ν=3054, 2956, 1703, 1604, 1565, 1437, 968, 825.

Acknowledgements

We gratefully acknowledge financial support by the National Natural Science Foundation of China (No. 20772043, 20572031), and the Key Project of Science and Technology of the Department of Education, Anhui Province, China (No. ZD2007005-1).

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