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One-pot Synthesis of Tetrahydrobenzo[*b*]pyrans Catalyzed by PEG-1000 Bridged Primary Amine Functionalized Dicationic Ionic Liquid in Water

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A novel poly (ethylene glycol) bridged primary amine functionalized dicationic ionic liquid ([PA-PEG_{1000}-DIL][BF_4]) was synthesized and characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR and ESI-MS. The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis indicated the high thermal stability of [PA-PEG_{1000}-DIL][BF_4]. It was used as an efficient and recyclable catalyst for the synthesis of substituted tetrahydrobenzo[*b*]pyrans through a one-pot three-component condensation of aromatic aldehydes, malononitrile and dimedone in 86% ~ 96% yields within 10 ~ 30 min in water. This method offers several advantages such as mild reaction conditions, simple operation and environmental friendliness. Furthermore, the catalyst could be easily recovered and reused for at least five runs without obvious loss of catalytic activity.

Keywords: Primary amine; Poly(ethylene glycol); Ionic liquid; Tetrahydrobenzo[*b*]pyran; Water.

INTRODUCTION

Tetrahydrobenzo[*b*]pyrans and their derivatives have attracted strong interest due to their useful biological and pharmacological properties, such as anti-coagulant, diuretic, spasmolytic, anticancer and anti-anaphylactic activity.[1] Some 2-amino-4*H*-pyrans can be employed as photoactive materials, pigments and potential biodegradable agrochemicals.[2] Furthermore, substituted 4*H*-pyrans also constitute a structural unit of some natural products.[3] Generally, the conventional methods for the synthesis of these heterocyclic compounds involve acid- or base-catalyzed condensation of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with aromatic aldehydes and malononitrile. A number of procedures have been reported using a variety of catalysts such as hexadecyltrimethyl ammonium bromide (HTMAB),[4a] rare earth perfluorooctanoate ($RE(PFO)_3$),[4b] (*S*)-proline,[4c] tetramethyl ammonium hydroxide (TMAH),[4d] tetrabutylammonium fluoride (TBAF),[4e] MgO,[4f] *N*-methylimidazole,[4g] Na_2SeO_4,[4h] $CeCl_3 \cdot 7H_2O$,[4i] K_3PO_4,[4j] $Ce(SO_4)_2 \cdot 4H_2O$,[4k] LiBr,[4l] tetrabutylammonium bromide (TBAB),[4m] 1,4-diazabicyclo[2.2.2]octane (DABCO)[4n] and phenylboronic acid.[4o] Occasionally, these reactions were performed under microwave[5] and ultrasound[6] irradiations or in an electrocatalytic system.[7] However, each of them suffers from at least one of the following limitations: low yields, long reaction times, harsh reaction conditions, poor catalyst recyclability, application of special apparatus and tedious work-up procedures. Consequently, the investigation for the efficient and environmentally benign method to construct these valuable heterocyclic compounds is still attractive.

Ionic liquids (ILs) have attracted considerable attention for the application in organic transformation due to their favorable properties in relation to green chemistry including high thermal and chemical stability, excellent electrical conductivity and negligible vapor pressure.[8] In recent years, functionalized ionic liquids (FILs), which incorporate functional groups as a part of the cation and/or anion, have been developed and applied in various fields.[9] FILs have been used not only as alternative solvents, but also as reagents and/or catalysts in synthetic organic chemistry. Base functionalized ionic liquids are one of the important FILs and have aroused unprecedented interest.[10] A number of basic ionic liquids including 1,1,3,3-*N,N,N',N'*-tetramethylguanidinium trifluoroacetate (TMGT),[11a] 1-butyl-3-methyl imidazolium hydroxide ([bmim][OH]),[11b,11c] *N,N*-dimethylaminoethylbenzyldimethylammonium chloride ([$PhCH_2Me_2N^+CH_2CH_2NMe_2$][$Cl^-$]),[11d] triethylenetetraammonium trifluoroacetate ([TETA][TFA]),[11e] 4-amino-1-(2,3-dihydroxy propyl) pyridinium hydroxide ([ADPPY][OH]),[11f] triethylammonium acetate ([TEAA])[11g] and 2-hydroxyethylammonium formate[11h] have been successfully used as catalysts for the synthesis of tetrahydrobenzo[*b*]pyrans derivatives.

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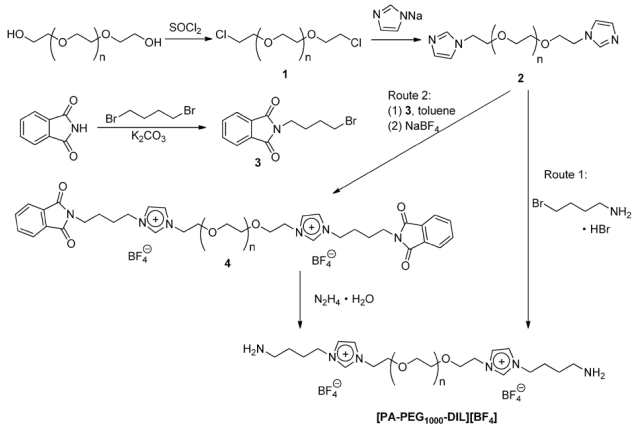
In a continuation of our research on poly(ethylene glycol) functionalized bridged dicationic ionic liquids,[12] we herein reported a novel primary amine functionalized poly(ethylene glycol) bridged dicationic ionic liquid ([PA-PEG_{1000}-DIL][BF_4]) (Scheme I) and used it as efficient and recyclable catalyst for the preparation of tetrahydrobenzo-[*b*]pyrans derivatives in water.

Scheme I The synthetic route of [PA-PEG_{1000}-DIL][BF_4]



RESULTS AND DISCUSSION

The preparation route of primary amine functionalized poly(ethylene glycol) bridged dicationic ionic liquid is shown in Scheme I. It was readily prepared through a six-step procedure from commercially available starting materials and reagents with good yields. Firstly, the PEG-1000 dichloride (**1**) and PEG-1000 bridged di-imidazolium compound (**2**) were prepared according to our previous reported method.[12] Two methods for preparing [PA-PEG_{1000}-DIL][BF_4] were investigated. The first method was the classical approach with the quaternization of PEG-1000 bridged di-imidazolium compound and 4-bromobutan-1-amine hydrobromide. However, this method suffered from tedious workup and it was almost impossible to purify the ILs. In the other method, the quaternization of PEG-1000 bridged di-imidazolium compound and *N*-(4-bromobutyl)-phthalimide (**3**) was conducted, and then the Br^- was exchanged with BF_4^-. Finally, the target ionic liquid [PA-PEG_{1000}-DIL][BF_4] could be obtained in high purity by hydrazinolysis. The thermal property of this ionic liquid was determined by thermal gravimetric analysis (TGA, Fig. 1) and differential scanning calorimetry (DSC, Fig. 2). From Fig. 1, we found that the [PA-PEG_{1000}-DIL][BF_4] has good thermal stability. As depicted in Fig. 2, this ionic liquid has a low glass transition temperature of -37 °C. In addition, the solubility of [PA-PEG_{1000}-DIL][BF_4] was determined at room temperature. In general, it is soluble in water, dichloromethane, acetone, acetonitrile, dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF), and insoluble in petroleum ether, hexane, cyclohexane, ethyl ether and ethyl acetate.

[PA-PEG_{1000}-DIL][BF_4] was then used to catalyze the one-pot three-component condensation to prepare tetrahydrobenzo[*b*]pyrans in water. To optimize the reaction conditions, benzaldehyde, malononitrile and dimedone were chosen as the model reactants. Selected results from our screening experiments are summarized in Table 1. Only 71% yield was obtained when [PA-PEG_{1000}-DIL][BF_4] was used as both catalyst and solvent, which might result from the inefficient mass transfer due to high viscosity of ionic liquid (Table 1, Entry 1). The yield was lower when the reaction was carried out in water under reflux without any catalyst (Table 1, Entry 2). Subsequently, the influence of catalyst loading on the reaction was examined. It is clear that the yield was promoted along with the increase of catalyst loading, and the optimal catalyst loading was 5 mol% (Table 1, Entries 3-7). In addition, low temperature decelerated the reaction rate and lead to lower yields (Table 1,

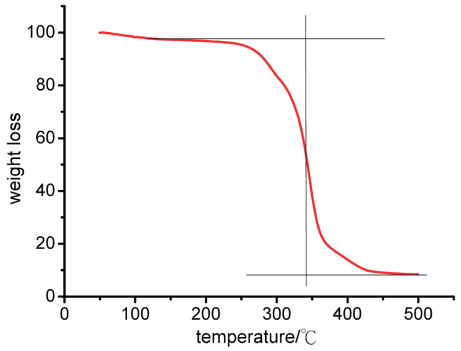


Fig. 1. The TGA spectra of [PA-PEG_{1000}-DIL][BF_4].

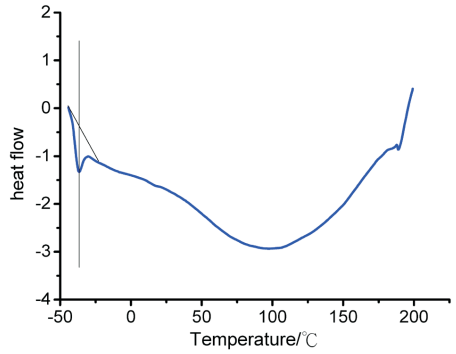
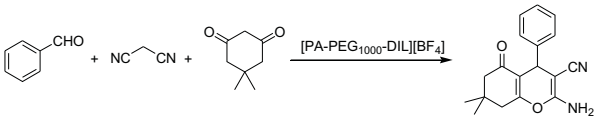


Fig. 2. The DSC spectra of [PA-PEG_{1000}-DIL][BF_4].

Table 1. Screening reaction conditions for the model condensation[a]



Entry	Catalyst loading (%)	T (°C)	Solvent	t (min)	Yield (%)[b]
1	10	100	-	20	71
2	-	100	H_2O	20	38
3	1	100	H_2O	20	53
4	3	100	H_2O	20	85
5	5	100	H_2O	20	92
6	7	100	H_2O	20	91
7	10	100	H_2O	20	92
8	5	90	H_2O	20	86
9	5	80	H_2O	30	79

[a] Reaction conditions: benzaldehyde (2 mmol), malononitrile (2 mmol), dimedone (2 mmol), water (2 mL).
[b] Isolated yield.

Entries 8-9).

The simple recovery and reuse of catalyst is highly preferable in terms of green synthetic process. The reusability of [PA-PEG_{1000}-DIL][BF_4] was exemplified on the above model reaction. After the separation of product by filtration, the liquor containing the catalyst was reused for the next run without any treatment. As shown in Fig. 3, the [PA-PEG_{1000}-DIL][BF_4]/H_2O system could be reused at least five runs without obvious loss of the catalytic activity.

Subsequently, we investigated the scope and generality of the present method by the reaction of various aromatic aldehydes with malononitrile and dimedone under the optimized conditions. The results are listed in Table 2. Aromatic aldehydes with electron-withdrawing groups

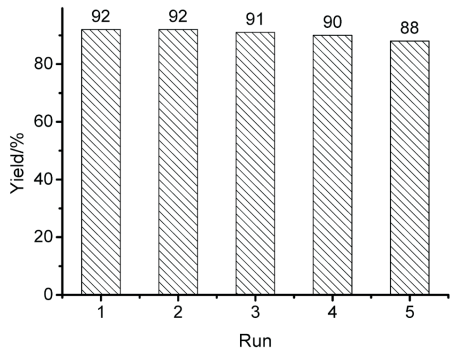
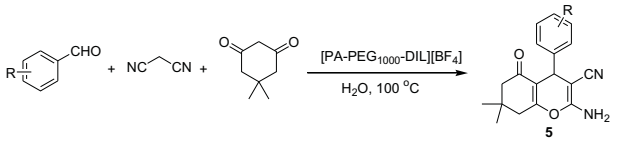


Fig. 3. The recycling of [PA-PEG_{1000}-DIL][BF_4]/H_2O system.

Table 2. Synthesis of tetrahydrobenzo[*b*]pyrans catalyzed by [PA-PEG_{1000}-DIL][BF_4] in water[a]



Entry	R	t (min)	Product	Yield(%)[b]
1	H	20	**5a**	92
2	4-Cl	12	**5b**	95
3	3-Cl	12	**5c**	94
4	2-Cl	15	**5d**	94
5	4-Br	12	**5e**	95
6	4-F	12	**5f**	94
7	4-NO_2	10	**5g**	96
8	3-NO_2	10	**5h**	96
9	2-NO_2	15	**5i**	94
10	2,4-Cl_2	15	**5j**	93
11	4-CH_3	30	**5k**	90
12	4-OH	25	**5l**	89
13	4-CH_3O	25	**5m**	91
14	3-OH-4-CH_3O	30	**5n**	88
15	4-Me_2N	30	**5o**	86
16	2-Furyl	20	**5p**	90

[a] Reaction conditions: aromatic aldehyde (2 mmol), malononitrile (2 mmol), dimedone (2 mmol), [PA-PEG_{1000}-DIL][BF_4] (0.1 mmol), water (2 mL), 100 °C.
[b] Isolated yield.

(such as nitro and halides) (Table 2, Entries 2-10) required a shorter reaction time but provided higher yields than those with electron-donating groups (such as methyl, hydroxyl, methoxyl and *N,N*-dimethylamino) (Table 2, Entries 11-15). Notably, the sterically demanding *ortho* and *meta* substituents did not hamper the reaction (Table 2, Entries 2-4 and Entries 7-9). Moreover, heteroaromatic aldehyde could also successfully convert to the corresponding tetrahydrobenzo[*b*]pyran product with excellent yield (Table 2, Entry 16).

CONCLUSION

In summary, we have prepared a novel primary amine functionalized poly(ethylene glycol) bridged dicationic ionic liquid and used it as catalyst for the synthesis of tetrahydrobenzo[*b*]pyran derivatives by the one-pot three-component reaction of aromatic aldehydes, malononitrile and dimedone in water. The attractive features of this protocol are environmental benign, mild reaction conditions, short reaction times, excellent yields, broad substrate scope, simple work-up procedure and good reusability.

EXPERIMENTAL

General. All reagents were commercially available and used without further purification. Melting points were determined on digital melting-point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance III (500 MHz) and tetramethylsilane (TMS) was used as internal standard. Mass spectra were taken on Agilent Liquid chromatography-mass spectrometry (LC-MS) 1100 series instrument in the electrospray ionization [positive electrospray ionization (ESI)] mode. IR spectra were recorded in KBr disks with a Shimadzu Prestige-21 FT-IR spectrometer. The thermo gravimetric analysis (TGA) was performed on Mettler Toledo TGA/SDTA851e thermal analyzer. Samples were loaded into an aluminium oxide crucible and heated at a rate of 20 ^{o}C·min^{-1} from 50 ^{o}C to 500 ^{o}C under N_2. The differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC823e, and heated at a rate of 10 ^{o}C·min^{-1} from -50 ^{o}C to 200 ^{o}C under N_2. *N*-(4-bromobutyl)phthalimide (**3**) was synthesized by a modified synthetic procedure described in the literature.[13]

Synthesis of primary amine functionalized poly(ethylene glycol) bridged dicationic ionic liquid

Synthesis of *N*-(4-bromobutyl)phthalimide (3).[13] A mixture of phthalimide (7.4 g, 0.05 mol), K_2CO_3 (20.7 g, 0.15 mol) and 1,4-dibromobutane (18.1 mL, 0.15 mol) was stirred in acetone (100 mL) at 50 ^{o}C for 12 h. The solvent was then evaporated under vacuum and the residue was dissolved in water (100 mL) and CH_2Cl_2 (50 mL). The organic layer was separated out and the aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic solution was dried over Na_2SO_4, filtered and concentrated to give the crude product, pure *N*-(4-bromobutyl)-phthalimide was obtained as a colorless solid by column chromatography (silicagel, ethyl acetate/petroleum = 1:4), 12.2 g, yield 86%. M. P.: 73-74 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 2H), 1.95-1.81 (m, 4H).

Synthesis of compound 4. A mixture of **2** (20.5 g) and **3** in toluene (80 mL) was stirred at 70 ^{o}C for 48 h. An oily liquid gradually precipitated from the toluene solution along with the reaction. After completion, the solvent was removed in vacuum and the residue was washed repeatedly with ethyl acetate, followed by evaporation under reduced pressure to yield yellow oil. Subsequently, $NaBF_4$ (8.4 g) and CH_2Cl_2 (50 mL) were added and the mixture was stirred at ambient temperature for 48 h. After filtration and removal of solvent, **4** was obtained and used directly for the next reaction. ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 9.18 (s, 2H), 7.86-7.81 (m, 8H), 7.80 (d, *J* = 1.5 Hz, 2H), 7.78 (d, *J* = 1.4 Hz, 2H), 4.36-4.31 (m, 4H), 4.21 (t, *J* = 7.1 Hz, 4H), 3.78-3.73 (m, 4H), 3.59 (t, *J* = 6.9 Hz, 4H), 3.54-3.40 (m, 88H), 1.85-1.75 (m, 4H), 1.59-1.50 (m, 4H).

Synthesis of [PA-PEG$_{1000}$-DIL][BF$_4$]. A mixture of hydrazine hydrate (80%, 30 mL) and **4** in methanol (60 mL) was heated under reflux for 12 h. Then the solvent and excess hydrazine hydrate was removed by evaporation in vacuum, the residue obtained was dissolved in CH_2Cl_2 and the phthalhydrazide precipitated was filtered off. After the solvent was removed, ionic liquid [PA-PEG$_{1000}$-DIL][BF$_4$] was finally obtained (21.5 g, yield 80%). ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 9.25 (s, 2H), 7.83 (s, 2H), 7.78 (s, 2H), 4.37-4.33 (m, 4H), 4.21 (t, *J* = 7.2 Hz, 4H), 3.79-3.75 (m, 4H), 3.67-3.28 (m, 107H), 2.70 (t, *J* = 7.2 Hz, 4H), 1.84 (dt, *J* = 14.8, 7.3 Hz, 4H), 1.45 (dt, *J* = 14.6, 7.3 Hz, 4H); ^{13}C NMR (126 MHz, *d*-DMSO, ppm) δ 136.88, 123.32, 122.65, 70.23, 70.06, 69.99, 68.56, 49.30, 48.72, 27.07, 26.04; IR (cm^{-1}) 3421, 2865, 1563, 1453, 1348, 1297, 1250, 1088, 946, 844, 757, 643, 546; ESI-MS: 396.45 (M^{2+}/2, n = 16), 410.63 (M^{2+}/2, n = 17), 424.51 (M^{2+}/2, n = 18), 440.00 (M^{2+}/2, n = 19).

General procedure for the synthesis of tetrahydrobenzo[*b*]pyran derivatives. Aromatic aldehyde (2 mmol), malononitrile (2 mmol), dimedone (2 mmol) and [PA-PEG$_{1000}$-DIL][BF$_4$] (0.1 mmol) were added into H_2O (2 mL), the mixture was stirred under reflux for certain time. The end of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, the precipitate was filtered out and washed with water. The resulting solid was purified by recrystallization from ethanol (95%) to afford the pure product. All the products are reported compounds and their melting points and ^{1}H NMR data were found to be identical with those reported in literature.

Characterization data of products. 5a: White solid; M. P.: 229-230 ^{o}C (Lit.[4d] M. P.: 228-230 ^{o}C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.32-7.16 (m, 5H), 6.10 (s, 2H), 4.32 (s, 1H), 2.56-2.46 (m, 2H), 2.24 (d, 1H), 2.15 (d, 1H), 1.05 (s, 3H), 0.98 (s, 3H). **5b**: White solid; M. P.: 210-212 ^{o}C (Lit.[4g] M. P.: 209-210 ^{o}C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 2H), 4.18 (s, 1H), 2.54-2.48 (m, 2H), 2.25 (d, *J* = 16.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 1.04 (s, 3H), 0.96 (s, 3H). **5c**: White solid; M. P.: 224-226 ^{o}C (Lit.[4a] M. P.: 224-225 ^{o}C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.28-7.18 (m, 4H), 4.56 (s, 2H), 4.40 (s, 1H), 2.50-2.46 (m, 2H), 2.25 (s, 2H), 1.12 (s, 3H), 1.06 (s, 3H). **5d**: White solid; M. P.: 215-217 ^{o}C (Lit.[4g] M. P.: 215-216 ^{o}C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.36-7.14 (m, 4H), 7.04 (s, 2H), 4.58 (s, 1H), 2.58-2.46 (m, 2H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.08 (d, *J* = 16.0 Hz, 1H), 1.04 (s, 3H), 0.98 (s, 3H). **5e**: White solid; M. P.: 208-210 ^{o}C (Lit.[4d] M. P.: 207-209 ^{o}C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.50 (d, *J* =

8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 2H), 4.22 (s, 1H), 2.56-2.44 (m, 2H), 2.25 (d, *J* = 16.0 Hz, 1H), 2.13 (d, *J* = 16.0 Hz, 1H), 1.07 (s, 3H), 0.99 (s, 3H). **5f**: White solid; M. P.: 190-192 °C (Lit.[11c] M. P.: 190-191 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.23-7.15 (m, 2H), 7.10-7.04 (m, 2H), 7.01 (s, 2H), 4.20 (s, 1H), 2.54 (s, 2H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 1.03 (s, 3H), 0.97 (s, 3H). **5g**: Yellow solid; M. P.: 178-180 °C (Lit.[4k] M. P.: 179-181 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 8.05-7.46 (m, 4H), 5.06 (s, 2H), 4.54 (s, 1H), 2.54-2.48(m, 2H), 2.25 (s, 2H), 1.05 (s, 3H), 1.01 (s, 3H). **5h**: Yellow solid; M. P.: 208-209 °C (Lit.[4a] M. P.: 208-211 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.98-7.42 (m, 4H), 4.98 (s, 2H), 4.54 (s, 1H), 2.50-2.44 (m, 2H), 2.26 (s, 2H), 1.06 (s, 3H), 1.02 (s, 3H). **5i**: Yellow solid; M. P.: 228-229 °C (Lit.[4m] M. P.: 227-230 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.96-7.48 (m, 4H), 5.97 (s, 2H), 5.06 (s, 1H), 2.46 (s, 2H), 2.15 (m, 2H), 1.08 (s, 3H), 0.97 (s, 3H). **5j**: White solid; M. P.: 193-194 °C (Lit.[4c] M. P.: 192-194 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.56 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 2H), 4.71 (s, 1H), 2.63-2.47 (m, 2H), 2.27 (d, *J* = 16.0 Hz, 1H), 2.13 (d, *J* = 16.0 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H). **5k**: White solid; M. P.: 214-216 °C (Lit.[4g] M. P.: 214-215 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 4.12 (s, 1H), 2.58-2.46 (m, 2H), 2.28 (s, 3H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 1.06 (s, 3H), 0.98 (s, 3H). **5l**: Yellow solid; M. P.: 203-205 °C (Lit.[4d] M. P.: 204-205 °C); ^{1}H NMR (500 MHz, *d*-$DMSO_3$, ppm) δ 7.12-6.76 (m, 4H), 5.36 (s, 2H), 4.24 (s, 1H), 2.44 (s, 2H), 2.24-2.16 (m, 2H), 1.10 (s, 3H), 1.05 (s, 3H). **5m**: Yellow solid; M. P.: 201-202 °C (Lit.[4m] M. P.: 201-203 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.16 (s, 1H), 3.72 (s, 3H), 2.54-2.44 (m, 2H), 2.25 (d, *J* = 16.0 Hz, 1H), 2.09 (d, *J* = 16.0 Hz, 1H), 1.05 (s, 3H), 0.97 (s, 3H). **5n**: White solid; M. P.: 238-240 °C (Lit.[4a] M. P.: 237-239 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 6.85 (s, 1H), 6.78-6.56 (m, 3H), 5.25 (s, 2H), 4.30 (s, 1H), 3.88 (s, 3H), 2.40 (s, 2H), 2.26-2.22 (m, 2H), 1.10 (s, 3H), 1.06 (s, 3H). **5o**: Yellow solid; M. P.: 223-225 °C (Lit.[4m] M. P.: 223-225 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.25-7.13 (m, 4H), 4.68 (s, 2H), 4.42 (s, 1H), 2.96 (s, 6H), 2.52-2.48 (m, 2H), 2.25 (s, 2H), 1.04 (s, 3H), 0.98 (s, 3H). **5p**: White solid; M. P.: 225-227 °C (Lit.[4l] M. P.: 225-226 °C); ^{1}H NMR (500 MHz, *d*-DMSO, ppm) δ 7.36-6.18 (m, 3H), 5.26 (s, 2H), 4.44 (s, 1H), 2.53 (s, 2H), 2.29 (s, 2H), 1.09 (s, 3H), 1.02 (s, 3H).

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