$Cu(OTf)_2$ Catalyzed Synthesis of Bis(5-methyl-2-furyl)methanes by Condensation of 2-Methylfuran with Carbonyl Compounds under Solvent Free Conditions

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A facile and efficient one-pot three-component synthesis of bis(5-methyl-2-furyl)methanes has been achieved via the reaction of 2-methylfuran with a series of aliphatic and aromatic aldehydes and aliphatic ketones in presence of copper(II) triflate under solvent free conditions. The bis(5-methyl-2-furyl)methanes were obtained in 34%—72% yields and the catalyst was recycled up to four successive cycles without much loss in catalytic activity.

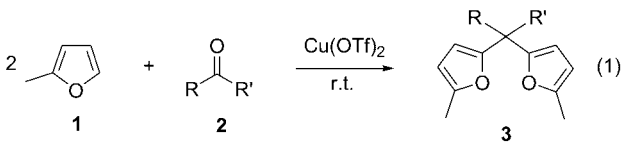
Keywords Lewis acid, copper(II) triflate, 2-methylfuran, bis(5-methyl-2-furyl)methane, multicomponent condensation, solvent free condition

Introduction

Bis(furyl)methanes are industrially important compounds.[1] They have been used as an intermediate for the synthesis of tetraoxaquaterenes[2] and other macromolecules which are used as metal ions carriers.[3,4] Some compounds of this class are of interest in food industry,[5] dye chemistry,[6] copy engineering[7] and agricultural chemistry.[8] Their synthesis is an important and challenging goal. A variety of catalytic systems have been introduced for the synthesis of bis(2-furyl)methanes by condensation of 2-methylfuran with carbonyl compounds[9] such as glacial acetic acid/phosphoric anhydride, sulfonic acid-functionalized mesoporous silicas,[10] MCM-41 supported Mo/Zr mixed oxides,[11] $AuCl_3$, $Hg(ClO_4)_2$, $Tl(ClO_4)_3$ and *p*-TSA,[12] and zeolites.[13] They have also been synthesized by acid catalyzed self-condensation of furfuryl alcohols, but acid-promoted self-condensation of furfuryl alcohol gives low yield along with a mixture of products.[14,15] Recently, Genovese *et al.*[16] has reported $Yb(OTf)_3$ catalyzed solvent free synthesis of triaryl- and triheteroaryl-methanes from substituted aldehydes and 2-methylfuran or methoxybenzene. However, reaction of 2-methylfuran with hexadeuteroacetone in presence of 0.7 mol% $Yb(OTf)_3$ was reported to give only 5% conversion to bis(2-furyl)hexadeuteropropane after 2 d.[11]

Due to high reactivity of furan ring towards electrophilic aromatic substitution large amounts of tarry oligomers and unidentified decomposition materials are generally produced during the reactions of furan heterocycles under conventional Lewis acids. In addition to this, these methodologies are associated with one or more problem from environmental point of view such as relatively long reaction time, costly catalysts, harsh reaction conditions and toxic aqueous waste resulting from the catalyst. The quest for cheap, environmentally friendly catalysts and mild reaction conditions is still a major challenge for the synthesis of bis(furyl)methanes. Thus, development of a simple and more efficient method is still desirable for synthesis of bis(furyl)-methanes. Recently, there has been a growing interest in solvent free reactions in organic synthesis.[17] The advantages associated with solvent free reactions are safety, economy, short reaction time, easy work up procedure, and greener nature.

Recent work in our laboratories has shown that metal triflates are effective reusable catalysts for the development of useful synthetic methods.[18] Herein, we report our efforts towards the development of environmentally benign synthesis of bis(5-methyl-2-furyl)-methanes by the condensation of 2-methylfuran with a series of aliphatic and aromatic aldehydes and aliphatic ketones using $Cu(OTf)_2$ as catalyst under solvent free conditions (Eq. 1).



Results and discussion

In our first attempt, we selected 2-methylfuran (**1**) and benzaldehyde (**2a**)/cyclopentanone (**2k**) as model substrates for the condensation reaction catalyzed by different metal triflates under solvent free conditions.

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Among the metal triflates used $Cu(OTf)_2$, $Yb(OTf)_3$, $Zn(OTf)_2$ and $Sc(OTf)_3$ were found to give the product **3a** or **3k** in good yield and $Cu(OTf)_2$ was found to be most efficient among all catalysts studied to give **3a** in 61% yield (Table 1, Entry 2). After finding $Cu(OTf)_2$ as the best catalyst for this condensation reaction, the effect of catalyst loading, solvent and reaction temperature was investigated. We explored the reaction in the presence of 1, 5, 10, 20 and 30 mol% of $Cu(OTf)_2$ (Table 1, Entries 5—9). It was found that 10 mol% of $Cu(OTf)_2$ was enough to accomplish the reaction at room temperature and increasing the amount of catalyst did not obviously improve the yield. When model reaction was carried out in various solvents such as water, MeOH, PEG-400, DCM, $CHCl_3$, DMF, acetonitrile, and ionic liquid [bmim][BF_4] using $Cu(OTf)_2$ as catalyst, the yield was lower than under solvent free condition. Only $CHCl_3$ and DCM were found to be effective reaction media to give **2a** in 18% and 22% yields, respectively, at room temperature after 6 h. Reaction of **1** with **2a** at higher temperature resulted in sluggish reaction mixture. It should also be pointed out here that the reaction did not proceed in the absence of $Cu(OTf)_2$, confirming the effectiveness of the catalyst.

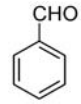
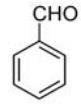
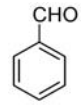
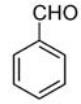
The product **3a** was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral data. It showed a peak at *m/z* 291.0156 for $[M+K]^+$ in MS and a characteristic singlet peak at δ 5.33 in ^{1}H NMR for ethane proton, peak at δ 45.27 in ^{13}C NMR for methane carbon along with other aromatic and aliphatic protons and carbons.

After success of the model reaction, the condensation reaction of **1** was carried out with other aldehydes and aliphatic ketones (**2b**—**2n**) to give corresponding bis(furyl)methanes (**3b**—**3n**) in moderate to good yield (Table 2). The structures of **3a**—**3n** were confirmed by spectral analysis and all the products showed satisfactory spectral data (see supporting information). Aromatic aldehydes with electron withdrawing substituent gave lower yield than aromatic aldehydes with electron donating groups (Table 2, Entry 7). This may be due to stabilization of intermediate **5** by the electron releasing substituents in aryl ring. It is also noteworthy to mention that acetophenone and benzophenone did not result in the formation of expected products. This is in accordance to the literature reports that furan reacts with some methyl ketones in the presence of hydrochloric acid, to give anhydrotetramers, but neither acetophenone nor pinacolone reacts.[19]

It is expected that the reaction mechanism is similar to the previously reported acid catalyzed mechanism.[9] A plausible mechanistic pathway for the reactions that form the bis(5-methyl-2-furyl)methanes is shown in Scheme 1.

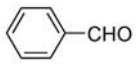
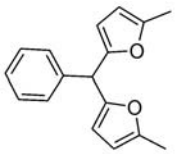
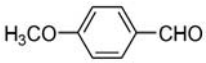
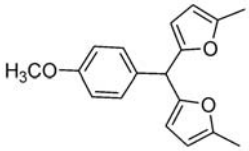
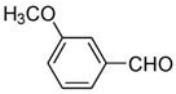
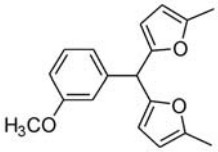
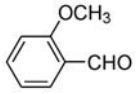
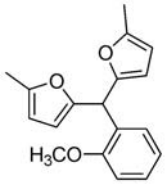
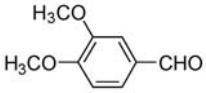
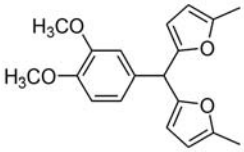
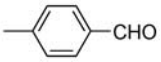
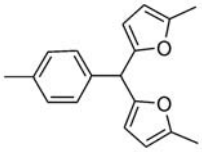
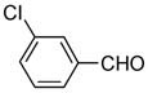
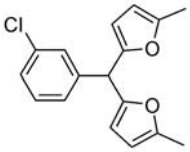
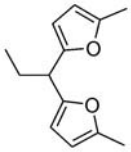
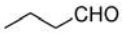
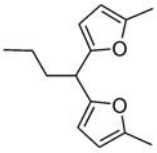
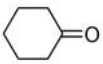
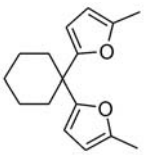
The reaction proceeds through furfuryl alcohol derivative followed by condensation with another molecule of carbonyl compound to give the desired product. However, we did not succeed in isolating (5-methyl-furan-2-yl) (phenyl)methanol (**4a**), instead we observed a peak at *m/z* 171.0717 in mass analysis of reaction mixture for reaction of **1** with **2a** which corresponds to $C_{12}H_{11}O^+$ ion (**5a**) (calculated 171.0810) generated from **4a** and thus confirmed formation of **4a** as intermediate. Similar observations were also made in the reac-

Table 1 Optimization of reaction conditions for the synthesis of bis(furyl)methanes[a]

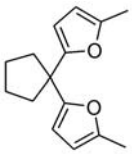
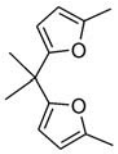
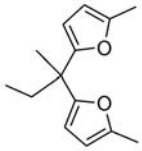
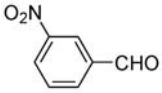
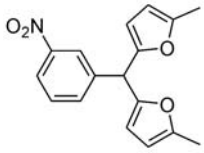
Entry	Substrate	Catalyst (mol%)	Time/h	Yield[b]/%
1		$Zn(OTf)_2$ (10)	6	45
2		$Cu(OTf)_2$ (10)	6	61
3		$Yb(OTf)_3$ (10)	6	40
4		$In(OTf)_3$ (10)	8	34
5		$Cu(OTf)_2$ (1)	6	21
6		$Cu(OTf)_2$ (5)	6	36
7		$Cu(OTf)_2$ (10)	6	51
8		$Cu(OTf)_2$ (20)	6	48
9		$Cu(OTf)_2$ (30)	6	45
10		$Zn(OTf)_2$ (10)	6	36
11		$Sc(OTf)_3$ (10)	6	33
12		$Yb(OTf)_3$ (10)	8	30
13		$In(OTf)_3$ (10)	8	16
14		$La(OTf)_3$ (10)	36	—[c]
15		$Eu(OTf)_3$ (10)	36	12

[a] Reaction conditions: 2-methylfuran (2.0 mmol), carbonyl compound (1.0 mmol), and catalyst. [b] Isolated yield. [c] No product formation was observed, starting material recovered.

Table 2 Cu(OTf)$_2$-promoted reaction of 2-methylfuran (**1**) with carbonyl compounds **2a**—**2n** at room temperature

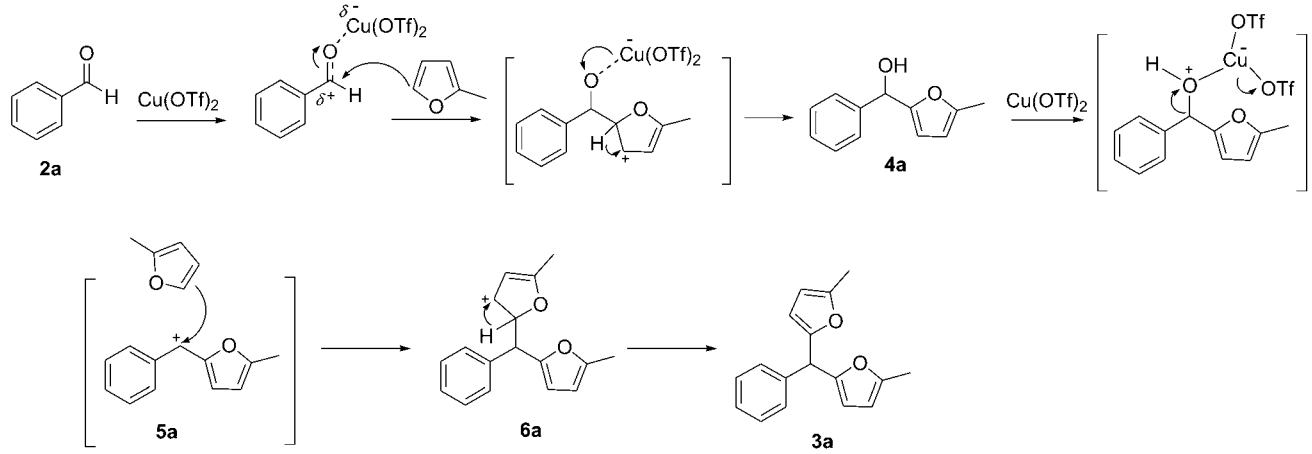
Entry	Carbonyl compound	Substrate **2**	Product[a]	Product **3**	Time/h	Yield[b]/%
1		**2a**		**3a**	6	61
2		**2b**		**3b**	6	63
3		**2c**		**3c**	6	65
4		**2d**		**3d**	6	57
5		**2e**		**3e**	6	66
6		**2f**		**3f**	6	59
7		**2g**		**3g**	8	57
8	CH_3CH_2CHO	**2h**		**3h**	8	60
9		**2i**		**3i**	8	58
10		**2j**		**3j**	6	75

Continued

Entry	Carbonyl compound	Substrate **2**	Product[a]	Product **3**	Time/h	Yield[b]/%
11		**2k**		**3k**	6	51
12		**2l**		**3l**	6	61
13		**2m**		**3m**	6	55
14		**2n**		**3n**	8	34

[a] All products showed satisfactory ^{1}H NMR, ^{13}C NMR and mass spectroscopic data. [b] Isolated yield.

Scheme 1 Proposed mechanism



tion of **1** with **2c**, **2d**, **2e**, **2f**, **2g, 2h**, **2i**, **2k** and **2l** with peaks at *m/z* 201.0871 (calculated 201.0916), 201.0872 (calculated 201.0916), 231.1030 (calculated 231.1021), 205.0409 (calculated 205.0420), 185.0918 (calculated 185.0966), 123.0883 (calculated 123.0804), 137.0752 (calculated 137.0961), 149.0752 (calculated 149.0961), and 123.0883 (calculated 123.0810), respectively, suggesting formation of corresponding furfuryl alcohols as intermediate. Further, evidence for the intermediate **4a** in this pathway was gained by independent synthesis of **4a** from 2-methylfuran and benzaldehyde in the presence of butyl lithium followed by reaction of **4a** with 2-methylfuran catalyzed by $Cu(OTf)_2$ to give **3a**.

Finally, the reusability of the recovered catalyst was investigated by using 2-methylfuran (**1a**) and benzaldehyde (**2a**) as model substrates. After extracting the product **3a** in organic layer, the aqueous layer was concentrated and dried to recover the catalyst. This recovered catalyst was again used for the reaction of **1** and **2a** and this was repeated three times to give **3a** in 56%, 53% and 52% yields, respectively. Thus, the catalyst showed good catalytic activity without noticeable decrease in yield of the product up to four successive cycles.

Conclusions

In summary, we have developed a facile and efficient method for the synthesis of bis(5-methyl-2-furyl)-methanes from the reaction of 2-methylfuran and carbonyl compounds catalyzed by $Cu(OTf)_2$ under solvent

free conditions. The main advantages of this method are mild, clean and solvent-free reaction conditions, moderate to good yields and an environmentally benign catalyst. This reaction system not only provides a novel method for the synthesis of bis(furyl)methanes but also is an environmentally friendly chemical process.

Experimental section

Physical measurements and materials

The ^{1}H NMR and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, and recorded on a Bruker-400 instrument with TMS as an internal standard and $CDCl_3$ as the solvent. Mass spectra (ESI-MS) were recorded using a QSTAR® Elite LX/MS/MS mass spectrometer from applied biosystems. Column chromatography was carried out over silica gel (100—200 mesh, S. D. Fine, India) and TLC was performed using silica gel GF254 (Merck) plates. The chemicals, reagents and solvents were purchased either from Spectrochem, India or Sigma-Aldrich and used as received.

General procedure for the synthesis of bis(5-methyl-2-furyl)methanes

A mixture of 2-methylfuran (2.0 mmol), carbonyl compound (1.0 mmol) and $Cu(OTf)_2$ (10 mol%) was vigorously stirred at room temperatures for 6—36 h (as mentioned in Tables 1 & 2) under solvent free conditions. After completion of the reaction, water (5.0 mL) was added to the reaction mixture and resulting solution was extracted with ethyl acetate (5 mL×3). The combined organic phase was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude residue was purified by passing through a bed of silica gel using ethyl acetate and hexane as eluent.

Spectral data of selected bis(furyl)methanes are given below.

2-Methyl-5-[(5-methylfuran-2-yl)(phenyl)methyl]-furan (3a) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31—7.29 (m, 2H), 7.26—7.24 (m, 3H), 5.88—5.86 (m, 4H), 5.33 (s, 1H), 2.25 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.00, 151.61, 140.17, 128.59, 128.55, 127.12, 108.34, 106.22, 45.27, 13.80; HRMS calcd for $C_{17}H_{16}O_2$ 252.1150, found 291.0156 $[M+K]^+$.

2-[(4-Methoxyphenyl)(5-methylfuran-2-yl)methyl]-5-methylfuran (3b) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13 (d, J=7.46 Hz, 2H), 6.81 (d, J=7.46 Hz, 2H), 5.91—5.86 (m, 4H), 5.32 (s, 1H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.43, 153.06, 151.72, 138.24, 128.41, 128.11, 126.56, 109.84, 108.01, 56.26, 45.27, 13.83; MS (ESI) calcd for $C_{18}H_{18}O_3$ 282.1256, found 289.1176 $[M+Li]^+$, 305.1162 $[M+Na]^+$.

2-[(3-Methoxyphenyl)(5-methylfuran-2-yl)methyl]-5-methylfuran (3c) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.25—7.21 (m, 1H), 6.86—6.79 (m, 3H), 5.88 (s, 4H), 5.31 (s, 1H), 3.77 (s, 3H), 2.55 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.80, 152.84, 151.61, 141.73, 129.54, 121.01, 114.47, 112.40, 108.36, 106.25, 55.34, 45.26, 13.86; HRMS calcd for $C_{18}H_{18}O_3$ 282.1256, found 201.0871 $[M-C_5H_5O]^+$, 305.1178 $[M+Na]^+$, 321.0967 $[M+K]^+$.

2-[(2-Methoxyphenyl)(5-methylfuran-2-yl)methyl]-5-methylfuran (3d) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.27—7.24 (m, 1H), 7.16—7.14 (m, 1H), 6.92—6.90 (m, 2H), 5.88—5.84 (m, 5H), 3.84 (s, 3H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.67, 153.00, 151.22, 129.31, 128.25, 128.11, 120.51, 110.70, 108.03, 106.00, 55.70, 37.48, 13.74; MS (ESI) calcd for $C_{18}H_{18}O_3$ 282.1256, found 201.0872 $[M-C_5H_5O]^+$, 305.1177 $[M+Na]^+$, 321.0968 $[M+K]^+$.

2-[(3,4-Dimethoxyphenyl)(5-methylfuran-2-yl)-methyl]-5-methylfuran (3e) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.83—6.79 (m, 3H), 5.89—5.87 (m, 4H), 5.29 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.06, 151.44, 147.95, 132.51, 120.42, 111.72, 111.02, 108.36, 106.07, 55.85, 44.72, 13.68; MS (ESI) calcd for $C_{19}H_{20}O_4$ 312.1362, found 231.1030 $[M—C_5H_5O]^+$, 335.1145 $[M+Na]^+$, 647.2627 $[2M+Na]^+$.

2-Methyl-5-[(5-methylfuran-2-yl)(*p*-tolyl)methyl]-furan (3f) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.17—7.12 (m, 4H), 5.88—5.87 (s, 4H), 5.31 (s, 1H), 2.34 (s, 3H), 2.25 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.25, 151.54, 137.22, 136.70, 129.32, 128.43, 108.21, 106.21, 44.93, 21.28, 13.82; MS (ESI) calcd for $C_{18}H_{18}O_2$ 266.1307, found 185.0918 $[M-C_5H_5O]^+$, 289.1176 $[M+Na]^+$, 305.0962 $[M+K]^+$.

2-[(3-Chlorophenyl)(5-methylfuran-2-yl)methyl]-5-methylfuran (3g) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.24—7.19 (m, 3H), 7.16—7.10 (m, 1H), 5.88 (s, 4H), 5.30 (s, 1H), 2.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.99, 151.77, 142.06, 129.72, 128.58, 127.26, 126.68, 108.51, 106.20, 99.64, 44.77, 13.68; MS (ESI) calcd for $C_{17}H_{15}ClO_2$ 286.0761, found 105.0409 $[M-C_5H_5O]^+$, 309.0598 $[M+Na]^+$.

2-Methyl-5-[1-(5-methylfuran-2-yl)propyl]furan (3h) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.94—5.84 (m, 4H), 3.85 (t, J=6.71 Hz, 1H), 2.27 (s, 6H), 2.04—1.95 (m, 2H), 0.93 (t, J=6.64 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.39, 153.04, 108.57, 108.28, 43.09, 28.56, 16.00, 14.49; MS (ESI) calcd for $C_{13}H_{16}O_2$ 204.1150, found 123.0883 $[M-C_5H_5O]^+$, 205.0081 $[M+Na]^+$.

2-Methyl-5-[1-(5-methylfuran-2-yl)butyl]furan (3i) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.94 (s, 2H), 5.88 (s, 2H), 3.96 (t, J=6.71 Hz, 1H), 2.27 (s, 6H), 1.94 (t, J=6.71 Hz, 2H), 1.34—1.33 (m, 2H), 0.93 (t, J=6.64 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.19, 150.63, 106.02, 105.90, 38.73, 35.15, 20.63, 13.90, 13.64; MS (ESI) calcd for $C_{14}H_{18}O_2$ 218.1307, found 137.0752 $[M-C_5H_5O]^+$, 241.1987 $[M+Na]^+$.

2-Methyl-5-(1-(5-methylfuran-2-yl)cyclohexyl)furan (3j) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.85 (s, 4H), 2.25 (s, 6H), 2.12 (t, J=6.40 Hz, 4H), 1.53—1.47 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.83, 150.42, 105.94, 105.75, 41.77, 34.14, 26.07, 22.70, 13.82; MS

(ESI) calcd for $C_{16}H_{20}O_2$ 244.1463, found 185.1218 $[M+Na-C_5H_6O]^+$, 283.1164 $[M+K]^+$, 306.0962 $[M+Na+K]^+$.

2-Methyl-5-(1-(5-methylfuran-2-yl)cyclopentyl)-furan (3k) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.87—5.84 (m, 4H), 2.24 (s, 6H), 1.72 (t, J=6.74 Hz, 4H), 1.26 (t, J=6.74 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.36, 150.78, 105.90, 105.65, 47.77, 37.08, 24.16, 13.84; MS (ESI) calcd for $C_{15}H_{18}O_2$ 230.1307, found 149.0752 $[M-C_5H_5O]^+$, 269.0997 $[M+K]^+$.

2-Methyl-5-(2-(5-methylfuran-2-yl)propan-2-yl)-furan (3l) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.86—5.84 (m, 4H), 2.23 (s, 6H), 1.58 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.22, 150.57, 105.87, 104.67, 26.64, 13.79; MS (ESI) calcd for $C_{13}H_{16}O_2$ 204.1150, found 123.0883 $[M-C_5H_5O]^+$, 243.0781 $[M+K]^+$.

2-Methyl-5-(2-(5-methylfuran-2-yl)butan-2-yl)furan (3m) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.90—5.85 (m, 4H), 2.25 (s, 6H), 1.98 (q, J=6.81 Hz, 2H), 1.53 (s, 3H), 0.79 (t, J=6.82 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 157.96, 150.64, 105.79, 105.62, 41.38, 31.86, 22.58, 13.82, 9.04; HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 241.1925 $[M+Na]^+$, 257.0939 $[M+K]^+$.

2-Methyl-5-((5-methylfuran-2-yl)(3-nitrophenyl)-methyl)-furan (3n) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.14 (m, 2H), 7.62—7.60 (m, 2H), 7.52—7.48 (m, 2H), 5.95—5.93 (m, 4H), 5.45 (s, 1H), 2.27 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.12, 151.16, 142.25, 134.64, 129.37, 123.48, 122.21, 108.86, 106.32, 44.70, 13.64.

(5-Methylfuran-2-yl)(phenyl)methanol (4a) ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46—7.40 (m, 2H), 7.39—7.27 (m, 4H), 5.95—5.88 (m, 2H), 5.78 (s, 1H), 2.27 (s, 3H); MS *m/z*: 171.2 $[M-OH]^+$.

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