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Fe(III)-catalyzed trityl benzyl ether formation and disproportionation cascade reactions to yield benzaldehydes

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ABSTRACT

During investigating water-compatible Lewis acids catalyzed etherifications using alcohols as alkylating reagents directly, we developed Fe(III)-catalyzed trityl benzyl ether formations irradiated by microwave. Then an in situ trityl benzyl ether formation and disproportionation cascade reaction was achieved to yield the benzaldehyde products with good functional group tolerances under neat conditions at relative higher temperatures. The substituent effects of the substrates on the etherification and disproportionation were explored by changing the substitutions on benzyl alcohols and triarylmethanols using chemical kinetic plots methods and the mechanism of the transformation was studied by crossover experiments. The etherification and disproportionation cascade process could be conveniently scaled up in laboratory without losing much efficiency.

1. Introduction

Selective oxidation of primary alcohols, especially benzyl alcohols into benzaldehydes is a fundamental and indispensable transformation in organic synthesis. Generally, the oxidation of benzyl alcohols to benzaldehydes in laboratory is completed by several methods, involving the use of stoichiometric amounts of inorganic oxidants such as manganese[1] and chromium salts,[2] activated DMSO-mediated Swern oxidation,[3] hypervalent iodine based reagents,[4] TPAP/NMO oxidative system,[5] TEMPO oxidation,[6] molecular oxygen with transition-metal catalysts[7] and so on. Nowadays, it has become a routine procedure to achieve the selective oxidation of benzyl alcohols in laboratory.

As many environmental issues are recognized and the supply of most useful metal ores is being exhausted,[8] less toxic and costly earth-abundant metals, such as sodium, potassium, calcium, aluminium, titanium and iron based green catalysts have attracted much attention[9] and should be preferably chosen as reagents in laboratory and industry in view of sustainable chemistry. Despite the numerous transformations based on the sustainable metal derived catalysts that have been developed so far,[10] many limitations are still present in this area of research and these remaining challenges will provide many opportunities for researchers.

2. Results and discussion

As part of our research on the investigation of water-compatible Lewis acids catalyzed methods of etherification using alcohols as alkylating reagents, we compared the sustainable metal iron[11] with precious metal gold in the formation of trityl benzyl ether **3** from benzyl alcohol **1** and triphenylmethanol **2**, developed in our group previously.[12] Interestingly, we found that when 0.05 mol % $Ph_3PAuNTf_2$ was used as catalyst, the ether **3** could be generated in 92% yield, however, no product could be detected at the same catalysis loading of $FeCl_3 \cdot 6H_2O$. Increasing the catalyst loading of $FeCl_3 \cdot 6H_2O$ to 10 mol % results in complete consumption of the starting materials and furnished the product **3** in a yield of 87% despite lower temperature compared to $Ph_3PAuNTf_2$ conditions (Scheme 1).

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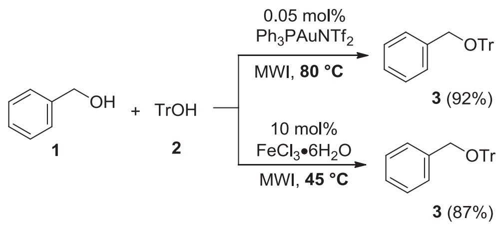


Scheme 1. Au(I) and Fe(III)-catalyzed formation of trityl benzyl ether **3**.

This promising result promoted us to examine the scope of the Fe(III)-catalyzed etherification. To our delight, all the selected substrates gave moderate to excellent yields under the standard conditions (**3a**–**3p**, Fig. 1). The etherification had good tolerance of functional groups and those substrates with electron-donating, electron-withdrawing or halogen groups could give good yields.

Unexpected results were obtained as we raised the temperature of reaction between benzyl alcohol **1** and triphenylmethanol **2** from 45 °C to 55 °C under microwave irradiation. We observed that the benzaldehyde **4** and triphenylmethane were isolated exclusively instead of the corresponding ether **3** as shown in Scheme 2, indicating that a disproportionation of the ether[13] occurred under the catalysis of $FeCl_3\cdot 6H_2O$. To test this hypothesis, we performed some controlled experiments. We heated the intermediate **3** in the absence of $FeCl_3\cdot 6H_2O$ and found no benzaldehyde. We also treated benzyl alcohol with $FeCl_3\cdot 6H_2O$ under oxygen atmosphere and trace amount of benzaldehyde could be detected, which excluded the possibility of formation of the benzaldehyde from cleavage of trityl ether and sequent oxidation of the benzyl alcohol.[14] To further exclude the influence of oxygen, the reaction was also carried out at nitrogen atmosphere and the benzaldehyde product still could be yielded (Scheme 2). The reaction was also examined in classical heating oil baths to afford the product efficiently only consuming much longer reaction time (more than 24 h). It was noteworthy that the reaction could proceed smoothly under neat conditions and the triphenylmethanol could be readily renewed from the by-product triphenylmethane in one step.[15] This one-pot sequence provides us a robust and alternative Fe(III)-catalyzed strategy to prepare benzaldehydes via trityl benzyl ether formation and disproportionation.

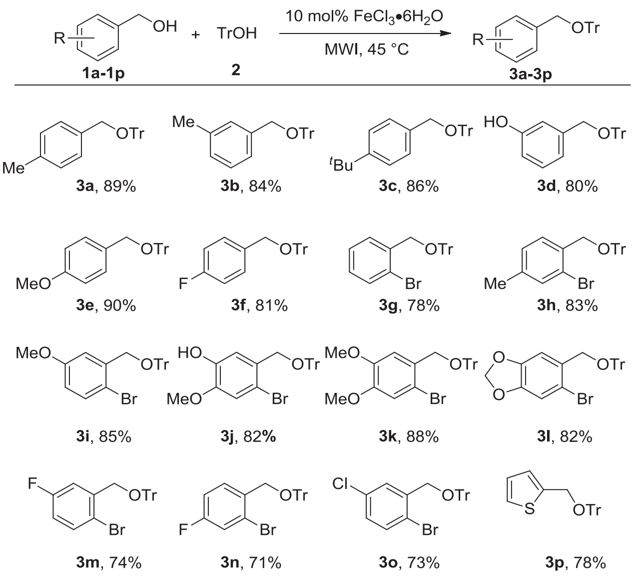
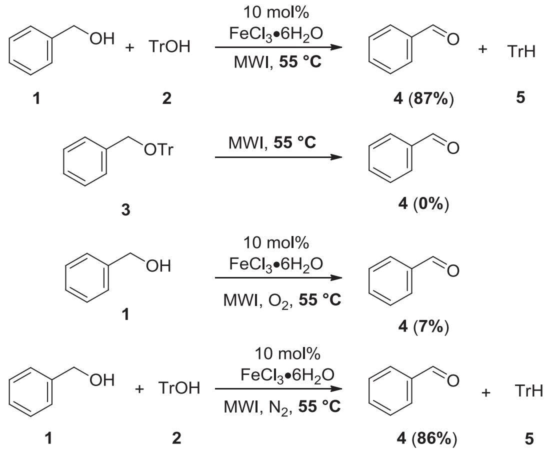


Fig. 1. Scope of Fe(III)-catalyzed formation of trityl benzyl ethers.



Scheme 2. Fe(III)-catalyzed formation of benzaldehyde and controlled experiments.

With these results in hand, we further optimized and investigated the etherification and disproportionation cascade reaction by employing substituted benzyl alcohols. In all cases, no additional solvents were required in the oxidation and the reaction profiles were so clean that the crude product could be subjected to the silica gel column chromatography directly. The benzyl alcohols with electron donating substituents on the phenyl ring could be transformed to the corresponding benzaldehydes in excellent yields (**4a**–**4e**, Fig. 2). The substrates with electron-withdrawing groups resulted in a slight decrease in efficiency (**4f** and **4g**, Fig. 2). The 2-bromosubstituted substrates were chosen considering that the benzaldehydes with halogens could be utilized as important synthetic intermediates.[16] Satisfactory results were obtained in all the selected bromosubstituted substrates (**4h**–**4o**, Fig. 2). More sensitive aromatic aldehydes such as thiophene-2-carbaldehyde could also be synthesized but with a relatively lower yield due to the generation of some unidentifiable impurities (**4p**, Fig. 2).

The substituent effects of the substrates on the etherification and disproportionation were explored by changing the

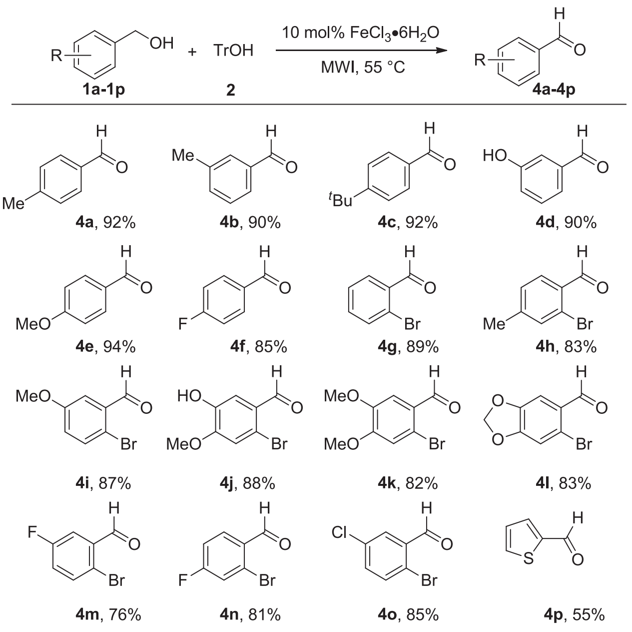
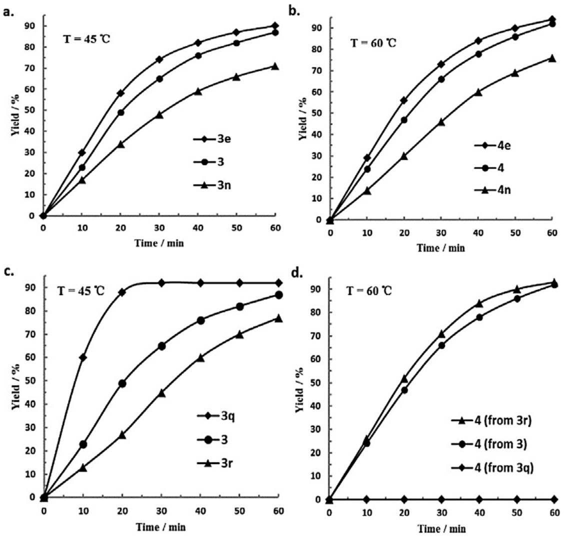


Fig. 2. Scope of Fe(III)-catalyzed disproportionation of trityl benzyl ethers.

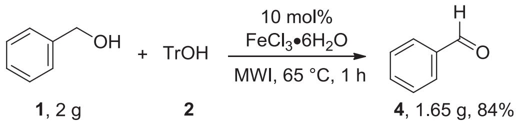
substitutions on benzyl alcohols or triarylmethanols. First, we chose **1**, **1e** and **1n** as the substrates to perform the reaction at 45 °C for 1 h at a 5 mol % loading of catalyst by using triphenylmethanol as the alkylating reagent. The etherification reactions were monitored every ten minutes and the isolated yields of **3**, **3e** and **3n** were plotted versus the time; thus providing the corresponding kinetic plots **a** and **b** in Scheme 3. The plots of disproportionation were described using the same procedure but with temperature increased to 55 °C. Comparing the two plots, we observed that the substituent effects of benzyl alcohols have consistent influence on the etherification and disproportionation. The richer the electron density of the aromatic system is, the faster the reactions proceed.



Scheme 3. Influences of electron effects on the etherification and disproportionation. [a] Plot of etherification of benzyl alcohols **1**, **1e** and **1n** with triphenylmethanol. [b] Plot of disproportionation of benzyl alcohols **1**, **1e** and **1n** (for **1e**, the temperature was 50 °C). [c] Plot of etherification of triphenylmethanol **2**, tri(4-methoxyphenyl)methanol **2q** and tri(4-chlorophenyl)methanol **2r** with benzyl alcohol. [d] Plot of disproportionation of triarylmethanols **2**, **2q** and **2r**.

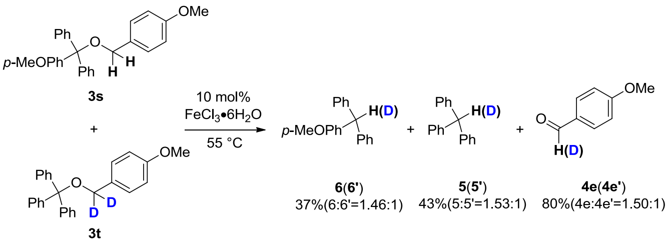
To complement the study of benzyl alcohol substitution we set out to examine the substituent effects of triarylmethanols by utilizing triphenyl-methanol **2**, tri(4-methoxyphenyl)methanol **2q** and tri(4-chlorophenyl)methanol **2r**, which were reacted with benzyl alcohol **1** under the standard conditions. As shown in Scheme 3, the substituent effects of **2**, **2q** and **2r** on the etherification and disproportionation reactions were totally opposite. The tri(4-methoxyphenyl)methanol **2q** underwent fastest in the formation of ether (**c** in Scheme 3). On the contrary, the disproportionation of **2q** became very difficult and the benzaldehyde **4** could not be detected after 1 h at 55 °C (**d** in Scheme 3). We also attempted to increase the temperature to 80 °C, but the etherification and disproportionation of **2q** remained unsuccessful.

We wished to explore the feasibility of performing the reaction on larger scale. We found that the etherification and disproportionation cascade reaction could be conveniently scaled up to 2 g without losing much efficiency by elevating the temperature from 55 °C to 65 °C. This allows the gram-scale synthesis of benzaldehyde derivatives in laboratory (Scheme 4).



Scheme 4. Gram-scale synthesis of benzaldehyde.

To probe the mechanism of this disproportionation, we prepared the ether **3s** with the methoxyl substitution on one phenyl ring of trityl group[17] and **3t** deuterated on the benzyl position.[18] Under standard conditions, this substrate underwent a deuterium crossover. The corresponding benzaldehydes **4e** and deuterated benzaldehyde **4e′** were detected together with non-crossover products triarylmethanes **5′**, **6** and crossover products **5**, **6′** assisted by NMR technique (Scheme 5). These results indicated that the hydride transfer might occur in an intermolecular manner in the disproportionation when the oxygen of substrates was coordinated with iron.



Scheme 5. Mechanism determination by crossover experiments.

3. Conclusions

In summary, we described a sustainable Fe(III)-catalyzed trityl benzyl etherification formation and disproportionation cascade reaction to produce benzaldehydes in gram scales under neat conditions. The influence of the substitutions of the triphenylmethanols and benzyl alcohols was examined by using designed substrates. The reaction mechanistically involves in situ formation and the following disproportionation of trityl benzyl ethers. This procedure provides a robust and environmentally compatible route to synthesize gram quantities of substituted benzaldehydes in a laboratory setting.

4. Experimental section

4.1. General information

Reagents were obtained commercially and used without further purification. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 (200–300 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to $CDCl_3$ and DMSO-d_6. HR-ESI-MS were recorded on a Bruker SolariX 7.0T instrument. IR spectra were recorded on a Bruker IFS 55 spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus. Microwave reactions were performed on CEM discover microwave reactor.

4.2. General procedures for the synthesis of trityl benzyl ethers

The benzyl alcohols substrates (**1a**–**1p**) (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (0.002 mmol, 5.4 mg) and triphenylmethanol **2** (0.2 mmol, 52 mg) were mixed in a dried vessel. Then the reaction was irradiated under the microwave at 45 °C for 1 h. The crude mixture was purified by a flash column chromatography to give the trityl benzyl ethers (**3a**–**3p**).

*4.2.1. (((3-Methylbenzyl)oxy)methanetriyl)tribenzene (**3b**).* White solid in 84% yield (EtOAc/petroleum ether=1:200): Mp 76.4–77.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62–7.55 (m, 6H), 7.36

(t, J=7.7 Hz, 6H), 7.31–7.26 (m, 5H), 7.23 (s, 1H), 7.14 (d, J=7.0 Hz, 1H), 4.20 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.37, 139.24, 138.02, 128.95, 128.39, 128.04, 127.91, 127.20, 124.26, 87.15, 65.96, 21.70; IR (thin film, cm^{-1}) 3085, 3057, 3031, 2865, 2345, 1818, 1609, 1595, 1490, 1448, 1371, 1220, 1001; HRMS (ESI): Calcd for $C_{27}H_{24}NaO$ 387.171936, Found 387.172068.

*4.2.2. (((4-(tert-Butyl)benzyl)oxy)methanetriyl)tribenzene (**3c**).* White solid in 86% yield (EtOAc/petroleum ether=1:200): Mp 116.7–117.3 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.58–7.55 (m, 6H), 7.44–7.40 (m, 2H), 7.37 (d, J=8.4 Hz, 2H), 7.34 (t, J=7.6 Hz, 6H), 7.29–7.26 (m, 3H), 4.19 (s, 2H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 150.19, 144.41, 136.37, 128.97, 128.03, 127.18, 126.91, 125.37, 87.06, 65.64, 34.71, 31.62. IR (thin film, cm^{-1}) 3421, 2958, 2920, 1958, 1596, 1489, 1448, 1218, 1031; HRMS (ESI): Calcd for $C_{30}H_{30}KO$ 445.192800, Found 445.192824.

*4.2.3. (((2-Bromo-4-methylbenzyl)oxy)methanetriyl)tribenzene (**3h**).* White solid in 83% yield (EtOAc/petroleum ether=1:150): Mp 109.2–110.4 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 (d, J=7.8 Hz, 1H), 7.55–7.50 (m, 6H), 7.33 (t, J=7.6 Hz, 7H), 7.25–7.27 (m, 3H), 7.19 (d, J=7.6 Hz, 1H), 4.20 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.19, 138.66, 135.58, 132.92, 128.93, 128.54, 128.35, 128.08, 127.31, 122.18, 87.40, 65.58, 20.95; IR (thin film, cm^{-1}) 3420, 3059, 3020, 2922, 2851, 2254, 1489, 1447, 1081, 1036; HRMS (ESI): Calcd For $C_{27}H_{23}BrNaO$ 465.082167, Found 465.082448.

*4.2.4. 4-Bromo-2-methoxy-5-((trityloxy)methyl)phenol (**3j**).* White solid in 82% yield (EtOAc/petroleum ether=1:50): Mp 160.1–161.9 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (d, J=7.4 Hz, 6H), 7.35 (s, 1H), 7.31–7.34 (m, 6H), 7.24 (d, J=7.3 Hz, 3H), 6.96 (s, 1H), 5.57 (s, 1H), 4.11 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 146.21, 145.17, 144.16, 131.60, 128.94, 128.08, 127.29, 114.99, 114.85, 111.28, 87.40, 65.37, 56.48; IR (thin film, cm^{-1}) 3508, 3058, 3029, 2928, 2851, 1958, 1640, 1579, 1500, 1448, 1280, 1202, 1153, 1031; HRMS (ESI): Calcd for $C_{27}H_{23}BrNaO_3$ 497.071364, Found 497.072277.

*4.2.5. (((2-Bromo-4,5-dimethoxybenzyl)oxy)methanetriyl)tribenzene (**3k**).* White solid in 88% yield (EtOAc/petroleum ether=1:80): Mp 115.7–117.5 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (d, J=7.4 Hz, 6H), 7.32 (t, J=7.6 Hz, 7H), 7.27 (s, 2H), 7.25 (d, J=7.5 Hz, 2H), 7.22 (s, 1H), 6.96 (s, 1H), 4.19 (s, 2H), 3.92 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 148.70, 148.57, 144.18, 130.79, 129.90, 128.91, 128.11, 127.36, 115.42, 112.32, 111.96, 87.49, 65.48, 56.41, 56.29; IR (thin film, cm^{-1}) 3421, 3072, 3024, 2921, 2851, 1958, 1659, 1632, 1050, 1448, 1266, 1211, 1159, 1031; HRMS (ESI): Calcd for $C_{28}H_{25}BrNaO_3$ 511.086708, Found 511.087927.

*4.2.6. 5-Bromo-6-((trityloxy)methyl)benzo[d][1,3]dioxole (**3l**).* White solid in 82% yield (EtOAc/petroleum ether=1:100): Mp 110.9–112.0 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.52–7.48 (m, 6H), 7.31–7.33 (m, 6H), 7.27 (s, 2H), 7.26–7.24 (m, 2H), 6.94 (s, 1H), 5.99 (s, 2H), 4.13 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 144.08, 128.90, 128.12, 127.35, 112.61, 108.98, 101.84, 87.49, 65.64; IR (thin film, cm^{-1}) 3420, 3071, 3023, 2923, 2851, 2253, 1632, 1503, 1487, 1448, 1421, 1263, 1238, 1119, 1051; HRMS (ESI): Calcd for $C_{27}H_{21}BrNaO_3$ 495.056524, Found 495.056627.

*4.2.7. (((2-Bromo-5-fluorobenzyl)oxy)methanetriyl)tribenzene (**3m**).* White solid in 74% yield (EtOAc/petroleum ether=1:200): Mp 124.3–125.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.59 (dd, J=8.8, 5.3 Hz, 1H), 7.49 (dd, J=9.6, 3.1 Hz, 1H), 7.45 (dd, J=8.4, 1.1 Hz, 6H), 7.38 (t, J=7.8 Hz, 6H), 7.29 (t, J=7.3 Hz, 3H), 7.13 (td, J=8.5, 3.1 Hz, 1H), 4.12 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.37, 160.75, 143.26, 139.96, 139.91, 133.88, 133.82, 128.13, 128.09, 127.32, 116.15, 116.00, 115.45, 115.43, 115.23, 115.07, 87.04, 64.69; IR (thin film, cm^{-1}) 3060, 3019, 2923, 2853, 1957, 1605, 1599, 1580, 1466, 1445, 1227, 1148, 1111, 1086, 1029, 900; HRMS (ESI): Calcd for $C_{26}H_{20}BrFKO$ 485.029010, Found 485.031314.

*4.2.8. (((2-Bromo-4-fluorobenzyl)oxy)methanetriyl)tribenzene (**3n**).* White solid in 71% yield (EtOAc/petroleum ether=1:200): Mp 167.5–168.2 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.73 (dd, J=8.5, 6.2 Hz, 1H), 7.52–7.48 (m, 6H), 7.32 (t, J=7.6 Hz, 6H), 7.25–7.27 (m, 5H), 7.09 (td, J=8.4, 2.6 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 162.46, 160.81, 144.01, 134.60, 134.57, 129.69, 129.64, 128.88, 128.14, 127.41, 122.20, 122.14, 119.77, 119.61, 114.68, 114.54, 87.60, 65.20; IR (thin film, cm^{-1}) 3452, 2921, 2851, 1958, 1641, 1596, 1493, 1447, 1225, 1078, 809; HRMS (ESI): Calcd for $C_{26}H_{20}BrFKO$ 485.029810, Found 485.031314.

*4.2.9. (((2-Bromo-5-chlorobenzyl)oxy)methanetriyl)tribenzene (**3o**).* White solid in 73% yield (EtOAc/petroleum ether=1:200): Mp 128.8–130.2 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.76 (d, J=2.6 Hz, 1H), 7.49–7.51 (m, 6H), 7.38 (d, J=8.4 Hz, 1H), 7.32–7.35 (m, 6H), 7.26–7.27 (m, 3H), 7.11 (dd, J=8.4, 2.6 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 143.84, 140.48, 133.77, 133.38, 128.85, 128.53, 128.20, 127.47, 119.75, 87.75, 65.41; IR (thin film, cm^{-1}) 3452, 3059, 2921, 2851, 1958, 1641, 1596, 1493, 1447, 1225, 1078; HRMS (ESI): Calcd For $C_{26}H_{20}BrClNaO$ 485.027790, Found 485.027826.

*4.2.10. 2-((Trityloxy)methyl)thiophene (**3p**).* White solid in 78% yield (EtOAc/petroleum ether=1:150): Mp 89.4–90.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.50 (d, J=5.0 Hz, 1H), 7.43 (d, J=7.9 Hz, 6H), 7.37 (t, J=7.7 Hz, 6H), 7.29 (t, J=7.2 Hz, 3H), 7.01–6.97 (m, 1H), 6.96 (s, 1H), 4.22 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.44, 141.01, 128.11, 128.05, 127.20, 126.78, 125.54, 125.13, 86.68, 61.01; IR (thin film, cm^{-1}) 3058, 3032, 2864, 1961, 1596, 1490, 1448, 1376, 1338, 1218, 1180, 1150, 1066, 1032; HRMS (ESI): Calcd for $C_{24}H_{20}NaOS$ 379.112707, Found 379.113021.

*4.2.11. 4,4′,4″-((Benzyloxy)methanetriyl)tris(methoxybenzene) (**3q**).* White solid in 92% yield (EtOAc/petroleum ether=1:80): Mp 142.5–144.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.35 (d, J=4.3 Hz, 4H), 7.33–7.29 (m, 6H), 7.27 (dt, J=8.7, 4.3 Hz, 1H), 6.90 (d, J=8.8 Hz, 6H), 4.07 (s, 2H), 3.73 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 157.98, 138.77, 136.26, 129.31, 128.30, 127.09, 126.65, 113.23, 85.57, 64.78, 55.00; IR (thin film, cm^{-1}) 3031, 2996, 2952, 2928, 2901, 2832, 2046, 1916, 1607, 1580, 1505, 1465, 1454, 1442, 1415, 1379, 1302, 1246, 1175, 1153, 1086, 1063, 1027; HRMS (ESI): Calcd for $C_{29}H_{28}NaO_4$ 463.187980, Found 463.188392.

*4.2.12. 4,4′,4″-((Benzyloxy)methanetriyl)tris(chlorobenzene) (**3r**).* White solid in 77% yield (EtOAc/petroleum ether=1:200): Mp 146.0–147.8 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.46–7.41 (m, 12H), 7.38–7.33 (m, 4H), 7.31–7.27 (m, 1H), 4.09 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 141.90, 137.89, 132.25, 129.95, 128.36, 128.25, 127.38, 126.88, 85.35, 65.35; IR (thin film, cm^{-1}) 3067, 3029, 2899, 2866, 1607, 1588, 1487, 1453, 1402, 1378, 1306, 1245, 1219, 1175, 1156, 1093, 1066, 1013; HRMS (ESI): Calcd for $C_{26}H_{19}Cl_3NaO$ 475.039369, Found 475.039101.

*4.2.13. (((4-Methoxybenzyl)oxy)(4methoxyphenyl)methylene)dibenzene (**3s**).* White solid in 93% yield (EtOAc/petroleum ether=1:100): Mp 77.4–78.1 °C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.58–7.54 (m, 4H), 7.46–7.42 (m, 2H), 7.34 (t, J=7.8 Hz, 6H), 7.25–7.27 (m, 2H), 6.95–6.91 (m, 2H), 6.90–6.87 (m, 2H), 4.14 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 158.97, 158.72, 144.89, 136.13, 131.50, 130.58, 128.68, 128.00, 127.03, 113.87, 113.28, 86.78, 65.54, 55.45, 55.39; IR (thin film, cm^{-1}) 3434, 3057, 3032, 2999, 2953, 2931, 2865, 2835, 2549, 2490, 2051, 1961, 1737, 1611, 1585, 1512, 1463, 1446, 1300, 1249, 1176, 1153; HRMS (ESI): Calcd for $C_{28}H_{26}NaO_3$ 433.174722, Found 433.177415.

*4.2.14. 2d-(((4-Methoxybenzyl)oxy)methanetriyl)tribenzene (**3t**).* White solid in 90% yield (EtOAc/petroleum ether=1:100): Mp 129.2–131.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51–7,52 (m, 6H), 7.29–7.32 (m, 8H), 7.23–7.25 (m, 3H), 6.91–6.87 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.03, 144.44, 131.31, 128.95, 128.75, 128.02, 127.18, 113.90, 87.07, 55.48; IR (thin film, cm^{-1}) 3421, 3072, 3024, 2958, 2934, 2836, 2187, 2083, 1892, 1611, 1581, 1511, 1490, 1461, 1445, 1298, 1239, 1071, 1031; HRMS (ESI): Calcd for $C_{27}H_{22}D_2NaO_2$ 405.178204, Found 405.179404.

4.3. General procedures for the synthesis of benzaldehydes

The benzyl alcohols substrates (**1a**–**1p**) (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (0.002 mmol, 5.4 mg) and triphenylmethanol **2** (0.2 mmol, 52 mg) were mixed in a dried vessel. Then the reaction was irradiated under the microwave at 55 °C for 1 h. The crude mixture was purified by a flash column chromatography to afford the benzaldehydes (**4a**–**4p**).

4.4. General procedures for the plotting of kinetic curves in Scheme 3

To a dried vessel the substituted benzyl alcohols (**1**, **1e** and **1n**) (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (0.002 mmol, 5.4 mg) and triarylmethanol (**2**, **2q** and **2r**) (0.2 mmol) were added. Then the reaction was irradiated under the microwave at 45 °C or 60 °C for 10 min, 20 min, 30 min, 40 min, 50 min and 60 min respectively. And then the products were isolated by a flash column chromatography to get the yields. Each yield experiment was performed for three times and the average values of the yields were used. The yield curves were obtained by plotting the average yields versus time.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.07.040

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