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A simple access to triarylmethane derivatives from aromatic aldehydes and electron-rich arenes catalyzed by $FeCl_3$

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Abstract

Under 'open-flask' and mild conditions, arenes condense smoothly with aromatic aldehydes in the presence of catalytic amount of $FeCl_3$. The reaction tolerated a variety of substitutions and functional groups. This method provides a facile and direct access to symmetrical and unsymmetrical triarylmethane derivatives.

Keywords: Triarylmethane; Diarylmethane; $FeCl_3$; Catalyzed

1. Introduction

Triarylmethanes (TRAMs) constitute an important class of compounds[1] that are ubiquitous in material,[2] medicals,[3] and dyes.[4] Numerous methods have been developed for the synthesis of TRAMs. However, most of them require complex procedures or harsh reaction conditions.[5] The Friedel–Crafts[6] type catalytic alkylation of aromatic rings with aromatic aldehydes and their imines are emerging as effective methods for TRAMs formation.[7] Very recently, several mild and efficient triaryl- and triheteroarylmethanes formations were reported, which used $[Ir(COD)Cl]_2$–$SnCl_4$,[7a] $AuCl_3$,[7b] $Cu(OTf)_2$, and $Sc(OTf)_3$[7j] as catalysts. The quest for cheap, environmentally friendly catalysts, and mild reaction conditions is still a major challenge.

$FeCl_3$ is a 'green' and efficient catalyst in modern organic synthesis.[8] It has become the focus of attention in several environmentally friendly and atom-economical organic transformations. Recent reports on $FeCl_3$ catalyzed arylation of benzyl alcohols and benzyl carboxylates,[9] hydroarylation of styrenes,[10] benzylation of 1,3-dicarbonyl compounds,[11] and intramolecular hydroamination and hydroalkoxylation of alkenes[12] have highlighted the applications of $FeCl_3$ in organic synthesis. In this contribution, we disclose a simple and practical synthesis of TRAMs derivatives from aromatic aldehydes and arenes catalyzed by $FeCl_3$. Mild reaction conditions and environmentally friendly catalyst make this transformation an attractive option for the straightforward preparation of triarylmethanes.

2. Results and discussion

The initial $FeCl_3$ catalyzed TRAMs formation[13,14] was carried out with benzaldehyde **1a** and *p*-xylene **2a**. After extensive studies on the reaction conditions, we found that the addition of acetic anhydride can improve the yield of **3a** dramatically (Scheme 1).[15] It was shown that, in the presence of acetic anhydride, the reactions proceeded smoothly with both electron-rich and electron-poor aromatic aldehydes and acetylation of arenes was not observed in these reactions. Longer reaction times were required (50 h) when highly electron deficient *p*-nitrobenzaldehyde was used (Scheme 1, **3e**).

Further researches revealed that various arenes could be condensed with aromatic aldehydes effectively (Table 1).

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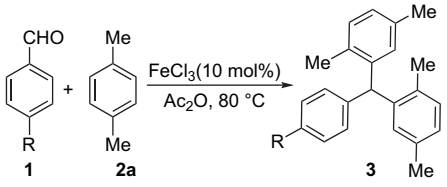
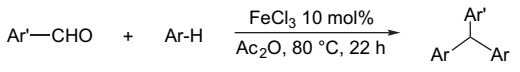


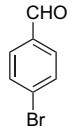
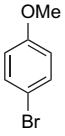
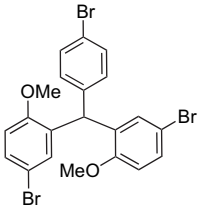
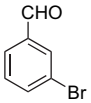
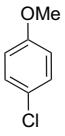
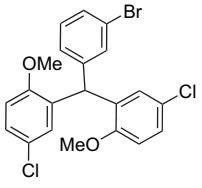
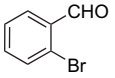
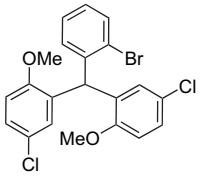
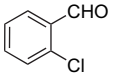
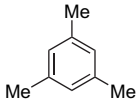
3a(79%), R=H(**1a**), 22 h **3b**(78%), R=Br(**1b**), 22 h
3c(75%), R=Cl(**1c**), 22 h **3d**(85%), R=Me(**1d**), 10 h
3e(70%), R=NO_2(**1e**), 50 h

Scheme 1. $FeCl_3$ catalyzed TRAMs formations.

Table 1
$FeCl_3$ catalyzed reaction of arenes with aromatic aldehydes[a]



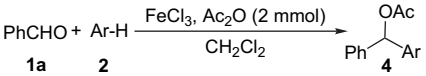
1 **2** **3**

Entry	Ar′CHO	Ar–H	Product	Yield[b] (%)
1	 **1b**	 **2c**	 **3f**	80
2	 **1g**	 **2b**	 **3g**	77
3	 **1f**	**2b**	 **3h**	59
4	**1b**	**2b**	**3i**	89
5	**1a**	**2b**	**3j**	83
6[c,d]	**1g**	**2a**	**3k**	90
7[c]	 **1h**	**2a**	**3l**	80
8[e]	**1a**	 **2d**	**3m**	70

[a] Reaction conditions: aldehyde (1 mmol), arene (4 mmol), Ac_2O (3 mmol).
[b] Isolated yield.
[c] The reaction was carried out with 2 mL **2a**.
[d] The reaction time was 16 h.
[e] The reaction was carried out with 1 mL **2d**.

Even the bulky 1,3,5-trimethylbenzene could be used and the desired product was isolated in 70% yield (entry 8). When high electron donating group (MeO−) substituted **2b** and **2c** were used, the desired products were obtained with high regioselectivity (entries 1–5). Importantly, this method provides a mild and controlled entry into halogen substituted TRAMs. These halides are synthetically useful because they afford a direct and regioselective introduction of a wide variety of functional groups via simple cross-coupling reactions. Obviously, electron-rich aromatic rings are necessary for this Friedel–Crafts type reaction.

Interestingly, when the reaction between benzaldehydes **1a** and *p*-xylene was carried out at 0 °C, the mono-aromatic substitution product **4a** was isolated in 43% yield. The reaction with bulky arenes **2d** and **2e** provided **4b** and **4c**, respectively, in good to high yield at room temperature (Scheme 2).



4a (43%) Ar-H = *p*-xylene (**2a**), 0 °C, 12 h
4b (92%) Ar-H = mesitylene (**2d**), r.t., 2 h
4c (70%) Ar-H=1,2,4,5-tetramethylbenzene (**2e**), r.t., 6 h

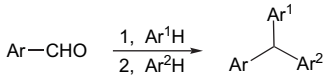
Scheme 2.

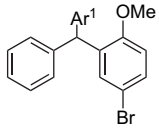
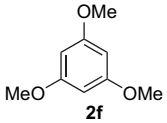
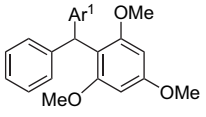
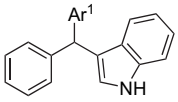
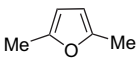
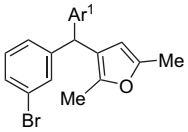
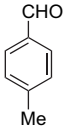
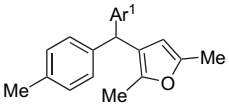
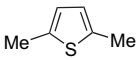
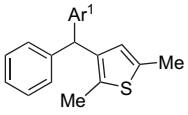
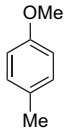
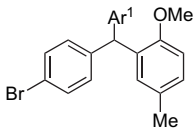
We considered whether our described mono-aromatic substitution procedure could be adapted toward a convenient one-pot synthesis of unsymmetrical TRAMs starting from aromatic aldehydes and arenes, thus avoiding the isolation of the diarylmethane intermediates. To our delight, this sequential one-pot procedure proceeded very well with bulky arenes **2d** and **2e** (Table 2). A variety of unsymmetrical TRAMs and thiophene, furan and indole substituted hetroaryldiarylmethanes were isolated in good yields.[16]

To extend this method further to synthesis of unsymmetrical TRAMs that do not contain bulky arene, we also performed aromatic substitution with **4d**. As shown in Scheme 3, the bromine substituted **3u** was obtained in high yield.

From these results, we proposed that aldehydes react with acetic anhydride to form more reactive geminal diacetates in situ,[17] and the following arylation of diacetates provide TRAMs or diarylmethane derivatives. The different reactivity of aldehydes and benzyl acetate in the iron catalyzed arylation reaction was also observed by Beller and co-workers.[9d] Further research was carried out to clarify the role of Ac_2O and $FeCl_3$. First, the reaction between benzaldehyde and Ac_2O was carried out and the diacetate **5a** was obtained in 60% isolated yield (Eq. 1). The purified **5a** was reacted with **2a**. To our surprise, benzaldehyde was isolated in 46% yield and the desired **3a** was only isolated in 51% yield in this case (Eq. 2). We thought benzaldehyde came from the deprotected diacetate[18] and there is an equilibrium between aldehyde **1a** and diacetate **5a**. Next, we investigated the reaction between **2a** and purified **5a** in the presence of Ac_2O. The desired **3a** was isolated in 78% yield and a small amount of benzaldehyde **1a** (Eq. 3). Following conclusions were drawn from these results: (a) in the presence of Ac_2O and catalytic amount of

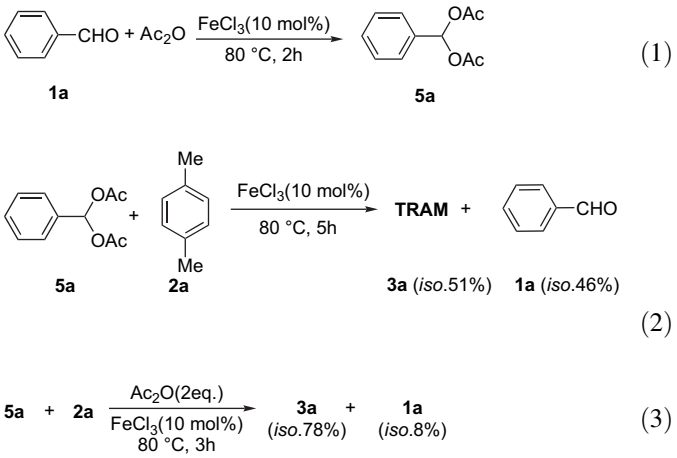
Table 2
One-pot $FeCl_3$ catalyzed unsymmetrical triarylmethanes formation[a]



Entry	ArCHO	Ar^1H	Ar^2H	Product	Yield[b] (%)
1[c]	**1a**	**2d**	**2c**	 **3n**	89
2	**1a**	**2d**	 **2f**	 **3o**	47
3	**1a**	**2d**	 **2g**	 **3p**	65
4	**1g**	**2d**	 **2h**	 **3q**	63
5	 **1d**	**2d**	**2h**	 **3r**	91
6	**1a**	**2d**	 **2i**	 **3s**	61
7	**1b**	**2e**	 **2j**	 **3t**	65

[a] Reaction conditions: aldehyde (1 mmol), arene (4 mmol), $FeCl_3$ (10 mol %), Ac_2O (2 mmol), CH_2Cl_2 (2 mL), rt.
[b] Isolated yield.
[c] The reaction with second arene was carried out at 80 °C.

$FeCl_3$, aldehyde was converted into more reactive geminal diacetate in situ, (b) there is an equilibrium between aldehyde and diacetate. Due to $FeCl_3$ catalyzed TRAM formation and the presence of the Ac_2O, we postulated that this equilibrium would be mainly shifted to diacetate.



3. Conclusion

In summary, we have developed an efficient $FeCl_3$ catalyzed alkylation of arenes with aromatic aldehydes. This method provides a facile and direct access to symmetrical and unsymmetrical triarylmethane and diarylmethane derivatives. The presence of acetic anhydride is crucial to this $FeCl_3$ catalyzed TRAMs formations. In addition, the reaction tolerated a variety of substitutions and functional groups. The readily available, cheap, low toxic, and easy-handling iron catalyst, plus the 'open-flask' and mild reaction conditions, is noteworthy.

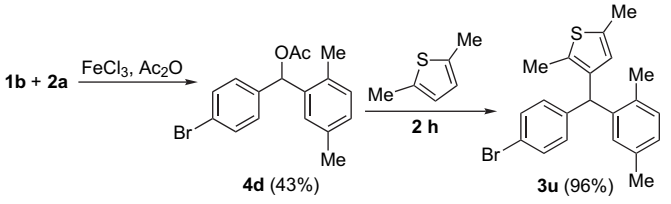
4. Experimental section

4.1. General procedures

All the reactions were carried out under air atmosphere. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (J values) were reported in hertz (Hz). Elemental analyses are performed on an Elementar Analysensysteme GmbH, VarioEL III or Flash EA 1112 series of the Thermo Electron Corporation. High resolution mass spectra were recorded on a Waters Q-Tof micro™ spectrometer by electrospray ionization (ESI) mass spectrometer; GC using an Agilent gas chromatograph 4890D. Preparative TLC was performed using silica gel as the stationary phase. Unless otherwise noted, all starting materials were commercially available and were used without further purification.

4.2. General procedure for synthesis of triarylmethanes *3a*, *3b*, *3c*, *3d*, *3e*, *3k*, and *3l*

To a 10-mL flask, benzaldehyde (1 mmol), acetic anhydride (3 mmol), anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol), and *p*-xylene



Scheme 3.

(2 mL) were successively added, and then the mixture was magnetically stirred at 80 °C for 22 h. The solvent was concentrated under reduced pressure by an aspirator, and the residue was purified by preparative TLC using petroleum as an eluent to afford **3a**, **3b**, **3c**, **3d**, **3k**, and **3l**; for **3e**: 10:1 petroleum/ethyl acetate was used as an eluent.

*4.3. General procedure for synthesis of triarylmethanes **3g**, **3f**, **3h**, **3i**, **3j**, and **3m***

Benzaldehyde (1 mmol), acetic anhydride (3 mmol), anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol), and electronic-rich arene (4 mmol) were successively added to a 10-mL flask. The reaction mixture was stirred at 80 °C for 22 h. The mixture was purified by preparative TLC using 10:1 petroleum/ethyl acetate as eluent to afford **3g**, **3f**, **3h**, **3i**, and **3j**; for **3m**: 1 mL mesitylene was used, and petroleum was used as an eluent for purification.

*4.4. General procedure for synthesis of diphenylmethyl acetate **4a**, **4b**, **4c**, and **4d***

Aldehyde (1 mmol), acetic anhydride (2 mmol), electronic-rich arene (1 mmol), dichloromethane (DCM), (2 mL) and anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) were sequentially added to a 10-mL flask. Then the mixture was stirred at room temperature for 2 h; for synthesis of **4a**: 0 °C, 12 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **4a**, **4b**, **4c**, and **4d**.

*4.5. General procedure for one-pot synthesis of unsymmetrical triarylmethanes **3n**, **3o**, **3p**, **3q**, **3r**, **3s**, and **3t***

Aldehyde (1 mmol), acetic anhydride (2 mmol), electronic-rich arene (1 mmol), DCM (2 mL), and anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) were sequentially added to a 10-mL flask, and the mixture was magnetically stirred at room temperature for 2 h. Then another arene (2 mmol) was added to the system, and the reaction mixture was stirred at room temperature; for synthesis of **3n**: 80 °C. The reaction was monitored by GC until completion. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **3n**, **3o**, **3p**, **3q**, **3r**, **3s**, and **3t**.

*4.6. Synthesis of unsymmetrical triarylmethanes **3u***

Diphenylmethyl acetate **4d** (0.5 mmol), 2,5-dimethylthiophene (0.5 mmol), DMC (2 mL), and anhydrous $FeCl_3$ (0.05 mmol) were sequentially added to a 10-mL flask, and the mixture was magnetically stirred at room temperature for 2 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **3u**.

*4.7. General procedure for synthesis of diacetate **5a***

Aldehyde (1 mmol), acetic anhydride (2 mmol), and anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) were sequentially added to a 10-mL flask, and the mixture was magnetically stirred at 80 °C for 2 h and then the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **5a**.

*4.8. The reaction of diacetate (**5a**) with p-xylene*

To a 10-mL flask, diacetate (**5a**) (1 mmol), *p*-xylene (2 mL), and anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) were successively added, and then the mixture was magnetically stirred at 80 °C for 5 h. The solvent was concentrated under reduced pressure by an aspirator, and the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **3a** and **1a**.

*4.9. The reaction of diacetate (**5a**) with p-xylene in the presence of acetic anhydride*

To a 10-mL flask, diacetate (**5a**) (1 mmol), acetic anhydride (2 mmol), *p*-xylene (2 mL), and anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) were successively added, and then the mixture was magnetically stirred at 80 °C for 3 h. The solvent was concentrated under reduced pressure by an aspirator, and the residue was purified by preparative TLC using 10:1 petroleum/ethyl acetate as an eluent to afford **3a** and **1a**.

4.10. Characterization data of compounds

*4.10.1. 2,2′-(Phenylmethylene)bis(1,4-dimethylbenzene) (**3a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.20–7.16 (m, 1H), 7.03–7.02 (m, 4H), 6.94–6.92 (d, J=7.5 Hz, 2H), 6.54 (s, 2H), 5.63 (s, 1H), 2.18 (s, 6H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.8, 135.0, 133.5, 130.2, 129.9, 129.9, 128.3, 127.0, 126.1, 50.5, 21.3, 19.2. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.77; H, 7.83.

*4.10.2. 2,2′-((4-Bromophenyl)methylene)bis(1,4-dimethylbenzene) (**3b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.36 (d, J=8.4 Hz, 2H), 7.04–7.03 (d, J=7.6 Hz, 2H), 6.95–6.94 (d, J=8.6 Hz, 2H), 6.90–6.88 (d, J=8.3 Hz, 2H), 6.50 (s, 2H), 5.57 (s, 1H), 2.20 (s, 6H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.1, 135.2, 133.3, 131.5, 131.3, 130.3, 129.7, 127.2, 120.0, 49.9, 21.2, 19.2. Calcd for $C_{23}H_{23}Br$: C, 72.82; H, 6.11. Found: C, 72.88; H, 6.25.

*4.10.3. 2,2′-((4-Chlorophenyl)methylene)bis(1,4-dimethylbenzene) (**3c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (d, J=8.3 Hz, 2H), 7.05–7.03 (d, J=7.6 Hz, 2H), 6.96–6.93 (d, J=8.3 Hz, 4H), 6.50 (s, 2H), 5.59 (s, 1H), 2.20 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 41.2, 135.1, 133.3, 131.9,

131.1, 130.3, 129.7, 128.4, 127.1, 49.8, 21.2, 19.1. Calcd for $C_{23}H_{23}Cl$: C, 82.49; H, 6.92. Found: C, 82.68; H, 7.22.

*4.10.4. 2,2′-(p-Tolylmethylene)bis(1,4-dimethylbenzene) (**3d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–7.01 (m, 4H), 6.93–6.89 (m, 4H), 6.55 (s, 2H), 5.58 (s, 1H), 2.31 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.2, 135.9, 135.4, 133.9, 130.6, 130.3, 130.2, 129.4, 127.3, 50.5, 21.7, 21.5, 19.7; MS calcd for $C_{24}H_{26}$ (M+Na): 337.2, found: 337.1. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.43; H, 8.12.

*4.10.5. 2,2′-((4-Nitrophenyl)methylene)bis(1,4-dimethylbenzene) (**3e**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (d, J=8.6 Hz, 2H), 7.20–7.18 (d, J=8.6 Hz, 2H), 7.08–7.06 (d, J=7.6 Hz, 2H), 6.99–6.98 (d, J=7.3 Hz, 2H), 6.47 (s, 2H), 5.72 (s, 1H), 2.21 (s, 6H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 146.6, 140.4, 135.6, 133.5, 130.7, 129.8, 129.0, 127.7, 123.6, 50.4, 21.3, 19.3; HRMS calcd for $C_{23}H_{23}NO_2$ (M+Na): 368.1627, found: 368.1631.

*4.10.6. 2,2′-((4-Bromophenyl)methylene)bis(4-bromo-1-methoxybenzene) (**3f**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.37 (d, J=8.4 Hz, 2H), 7.34–7.31 (m, 2H), 6.90–6.88 (d, J=8.4 Hz, 2H), 6.82–6.81 (d, J=2.4 Hz, 2H), 6.75–6.72 (d, J=8.7 Hz, 2H), 5.98 (s, 1H), 3.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 141.2, 133.5, 132.2, 131.4, 130.9, 130.6, 120.3, 112.7, 112.4, 55.9, 42.9. Calcd for $C_{21}H_{17}Br_3O_2$: C, 46.62; H, 3.17. Found: C, 46.47; H, 3.57.

*4.10.7. 2,2′-((3-Bromophenyl)methylene)bis(4-chloro-1-methoxybenzene) (**3g**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.34 (m, 1H), 7.20–7.17 (m, 3H), 7.15–7.12 (m, 1H), 6.95–6.93 (d, J=7.6 Hz, 1H), 6.80–6.78 (d, J=8.7 Hz, 2H), 6.70–6.69 (d, J=2.6 Hz, 2H), 6.02 (s, 1H), 3.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 144.7, 132.8, 132.1, 129.8(2C), 129.6, 127.8, 127.7, 125.4, 122.6, 112.0, 55.9, 43.1; HRMS calcd for $C_{21}H_{17}BrCl_2O_2$ (M+Na): 472.9687, found: 472.9692.

*4.10.8. 2,2′-((2-Bromophenyl)methylene)bis(4-chloro-1-methoxybenzene) (**3h**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 1H), 7.21–7.16 (m, 3H), 7.11–7.07 (m, 1H), 6.83–6.79 (m, 3H), 6.63–6.62 (d, J=2.6 Hz, 2H), 6.31 (s, 1H), 3.69 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 141.8, 133.2, 132.5, 130.2, 129.4, 128.2, 127.7, 127.2, 125.5, 125.3, 112.0, 56.1, 43.6. HRMS calcd for $C_{21}H_{17}BrCl_2O_2$ (M+Na): 472.9687, found: 472.9704.

*4.10.9. 2,2′-((4-Bromophenyl)methylene)bis(4-chloro-1-methoxybenzene) (**3i**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.37 (d, J=8.4 Hz, 2H), 7.19–7.16 (m, 2H), 6.91–6.89 (d, J=8.4 Hz, 2H), 6.79–6.77 (d, J=8.7 Hz, 2H), 6.69–6.68 (d, J=2.5 Hz, 2H), 5.99 (s, 1H), 3.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 141.3, 133.1, 131.4, 130.9, 129.5, 127.6, 125.3, 120.3, 112.0, 55.9, 43.0. Calcd for $C_{21}H_{17}BrCl_2O_2$: C, 55.78; H, 3.79. Found: C, 56.06; H, 4.04.

*4.10.10. 2,2′-(Phenylmethylene)bis(4-chloro-1-methoxybenzene) (**3j**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.20 (m, 3H), 7.18–7.15 (m, 2H), 7.04–7.02 (d, J=7.1 Hz, 2H), 6.79–6.76 (d, J=8.6 Hz, 2H), 6.73–6.72 (d, J=2.6 Hz, 2H), 6.06 (s, 1H), 3.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 142.0, 133.8, 129.6, 129.2, 128.3, 127.3, 126.4, 125.2, 111.9, 55.9, 43.3. Calcd for $C_{21}H_{18}Cl_2O_2$: C, 67.57; H, 4.86. Found: C, 67.72; H, 5.12.

*4.10.11. 2,2′-((3-Bromophenyl)methylene)bis(1,4-dimethylbenzene) (**3k**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (d, J=7.8 Hz, 1H), 7.18 (s, 1H), 7.14–7.10 (m, 1H), 7.05–7.03 (d, J=7.6 Hz, 2H), 6.96–6.92 (m, 3H), 6.50 (s, 2H), 5.59 (s, 1H), 2.20 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 141.0, 135.3, 133.4, 132.8, 130.4, 129.9, 129.8, 129.5, 128.5, 127.3, 122.6, 50.2, 21.3, 19.2. Calcd for $C_{23}H_{23}Br$: C, 72.82; H, 6.11. Found: C, 72.80; H, 6.26.

*4.10.12. 2,2′-((2-Chlorophenyl)methylene)bis(1,4-dimethylbenzene) (**3l**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 1H), 7.18–7.10 (m, 2H), 7.05–7.04 (d, J=7.6 Hz, 2H), 6.96–6.94 (d, J=7.6 Hz, 2H), 6.85–6.83 (m, 1H), 6.49 (s, 2H), 5.94 (s, 1H), 2.19 (s, 6H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.3, 135.0, 134.7, 133.6, 131.0, 130.2, 129.6, 129.5, 127.6, 127.2, 126.5, 47.4, 21.3, 19.0. Calcd for $C_{23}H_{23}Cl$: C, 82.49; H, 6.92. Found: C, 82.42; H, 7.19.

*4.10.13. 2,2′-(Phenylmethylene)bis(1,3,5-trimethylbenzene) (**3m**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.24 (m, 2H), 7.17 (m, 2H), 6.77 (s, 5H), 5.88 (s, 1H), 2.25 (s, 6H), 1.86 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.7, 137.0, 135.4, 130.4, 128.9, 128.2, 125.9, 50.9, 21.5, 20.6. Calcd for $C_{25}H_{28}$: C, 91.41; H, 8.59. Found: C, 91.25; H, 8.94.

*4.10.14. 2-((5-Bromo-2-methoxyphenyl)(phenyl)methyl)-1,3,5-trimethylbenzene (**3n**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (m, 1H), 7.22–7.13 (m, 3H), 6.95–6.91 (m, 3H), 6.79 (s, 2H), 6.75–6.73 (d, J=8.8 Hz, 1H), 6.07 (s, 1H), 3.64 (s, 3H), 2.24 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 142.4, 137.4, 136.2, 135.8, 133.1, 132.9, 130.2, 130.0, 128.5, 128.0, 125.6, 112.7, 112.0, 55.8, 45.3, 21.8. 20.8. Calcd for $C_{23}H_{23}BrO$: C, 69.88; H, 5.86. Found: C, 69.67; H, 5.69.

*4.10.15. 2-(Mesityl(phenyl)methyl)-1,3,5-trimethoxybenzene (**3o**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.15 (m, 2H), 7.11–7.09 (m, 1H), 7.02–7.00 (d, J=7.6 Hz, 2H), 6.74 (s, 2H), 6.13 (s, 3H), 3.79 (s, 3H), 3.49 (s, 6H), 2.22 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.5, 144.7, 138.2, 137.6, 134.5, 129.6, 128.4, 127.6, 124.9, 112.1, 91.5, 55.7, 55.2, 43.0, 21.3, 20.7. Calcd for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.47; H, 7.24.

*4.10.16. 3-(Mesityl(phenyl)methyl)-1H-indole (**3p**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.36–7.34 (d, J=8.2 Hz, 1H), 7.29–7.27 (d, J=7.9 Hz, 1H), 7.23–7.19 (m, 3H), 7.17–7.13 (m, 3H), 7.04–7.00 (m, 1H), 6.84 (s, 2H), 6.60–6.59 (m, 1H), 6.10 (s, 1H), 2.28 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.7, 137.2, 136.5, 135.6, 130.0, 128.8, 127.9, 127.8, 125.5, 123.8, 122.0, 119.9, 119.3, 116.8, 111.0, 42.8, 21.6, 20.8; HRMS calcd for $C_{24}H_{23}N$ [M+Na]: 348.1728, found: 348.1731.

*4.10.17. 3-((3-Bromophenyl)(mesityl)methyl)-2,5-dimethylfuran (**3q**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.28 (m, 1H), 7.24–7.23 (d, J=7.9 Hz, 1H), 7.11–7.07 (m, 1H), 7.01–6.99 (m, 1H), 6.83 (s, 2H), 5.57 (s, 1H), 5.54 (s, 1H), 2.26 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 146.6, 146.3, 136.8, 136.4, 135.9, 130.9, 130.1, 129.7, 128.7, 126.6, 122.5, 118.5, 107.9, 41.6, 21.7, 20.8, 13.5, 11.9. Calcd for: C, 68.93; H, 6.05. Found: C, 68.60; H, 6.18.

*4.10.18. 3-(Mesityl(p-tolyl)methyl)-2,5-dimethylfuran (**3r**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–7.03 (d, J=7.2 Hz, 2H), 6.97–6.96 (d, J=6.7 Hz, 2H), 6.82 (s, 2H), 5.60 (s, 1H), 5.56 (s, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 2.17 (s, 3H), 2.05 (s, 6H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 146.4, 140.3, 137.3, 137.0, 135.5, 134.9, 130.0, 128.8, 127.9, 119.6, 108.2, 41.5, 21.7, 21.0, 20.8, 13.6, 11.9. Calcd for $C_{23}H_{26}O$: C, 86.75; H, 8.23. Found: C, 86.81; H, 7.98.

*4.10.19. 3-(Mesityl(phenyl)methyl)-2,5-dimethylthiophene (**3s**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.17–7.16 (m, 1H), 7.04–7.02 (d, J=7.6 Hz, 2H), 6.83 (s, 2H), 6.13–6.13 (d, J=0.6 Hz, 1H), 5.68 (s, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 2.10 (s, 3H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.3, 137.1, 137.1, 135.6, 134.2, 131.7, 130.0, 128.3, 128.2, 127.7, 125.6, 45.5, 21.7, 20.8, 15.3, 13.2. Calcd for $C_{22}H_{24}S$: C, 82.45; H, 7.55. Found: C, 82.06; H, 7.32.

*4.10.20. 3-((4-Bromophenyl)(2-methoxy-5-methylphenyl)-methyl)-1,2,4,5-tetramethylbenzene (**3t**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.25 (m, 2H), 7.04–7.04 (m, 1H), 6.93 (s, 1H), 6.84–6.82 (d, J=8.3 Hz, 1H), 6.77–6.75 (d, J=8.3 Hz, 2H), 6.74–6.73 (m, 1H), 6.14 (s, 1H), 3.69 (s, 3H), 2.20 (s, 6H), 2.18 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 143.9, 140.3, 134.1, 133.9, 130.9, 130.7, 130.4, 129.9, 129.6, 128.5, 128.1, 118.6, 110.3, 55.7, 45.2, 20.8 (2C), 17.6. Calcd for $C_{25}H_{27}BrO$: C, 70.92; H, 6.43. Found: C, 71.08; H, 6.52.

*4.10.21. 3-((4-Bromophenyl)(2,5-dimethylphenyl)methyl)-2,5-dimethylthiophene (**3u**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.04–7.02 (d, J=7.6 Hz, 1H), 6.95–6.91 (m, 3H), 6.62 (s, 1H), 6.06 (s, 1H), 5.38 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.6, 137.9, 135.4, 134.8, 133.2, 131.4 (2C), 130.9, 130.3, 129.2, 127.3, 127.2, 120.0, 46.5, 21.3, 19.2, 15.3, 13.0. Calcd for $C_{21}H_{21}BrS$: C, 65.45; H, 5.49. Found: C, 65.50; H, 5.46.

*4.10.22. (2,5-Dimethylphenyl)(phenyl)methyl acetate (**4a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 5H), 7.20 (s, 1H), 7.03 (s, 3H), 2.32 (s, 3H), 2.24 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 139.6, 137.8, 135.5, 132.6, 130.6, 128.7, 128.4, 127.8, 127.6, 127.5, 74.3, 21.3, 21.2, 19.0; HRMS calcd for $C_{17}H_{18}O_2$ (M+Na): 277.1205 found, 277.1212.

*4.10.23. Mesityl(phenyl)methyl acetate (**4b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.29–7.23 (m, 3H), 7.13–7.11 (d, J=7.5 Hz, 2H), 6.86 (s, 2H), 2.28 (s, 9H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 139.7, 137.9, 137.8, 133.0, 129.9, 128.3, 127.1, 125.6, 72.7, 21.2, 21.0, 20.6; HRMS calcd for $C_{18}H_{20}O_2$ (M+Na): 281.1361, found: 291.1364.

*4.10.24. Phenyl(2,3,5,6-tetramethylphenyl)methyl acetate (**4c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.31–7.22 (m, 3H), 7.12–7.10 (m, 2H), 6.98 (s, 1H), 2.23 (s, 6H), 2.18 (s, 3H), 2.17 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 140.1, 135.7, 134.3, 133.8, 132.0, 128.2, 126.9, 125.6, 73.2, 21.1, 20.5, 16.2. Calcd for: C, 80.82; H, 7.85. Found: C, 80.66; H, 8.09.

*4.10.25. (4-Bromophenyl)(2,5-dimethylphenyl)methyl acetate (**4d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.16–7.14 (m, 3H), 7.03 (s, 2H), 6.96 (s, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 138.7, 137.3, 135.7, 132.6, 131.6, 130.7, 129.2, 128.9, 127.5, 121.9, 73.7, 21.3, 21.2, 19.0; HRMS calcd for $C_{17}H_{17}BrO_2$ (M+Na): 355.0310, found: 355.0312.

*4.10.26. Diacetate (**5a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.52–7.51 (m, 2H), 7.42–7.40 (m, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 135.4, 129.8, 128.6, 126.7, 89.7, 20.9.

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