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Efficient and selective alkylation of arenes and heteroarenes with benzyl and allyl ethers using a Ir/Sn bimetallic catalyst

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Abstract—A high-valent heterobimetallic catalyst namely $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ (5 mol %), or dual catalyst system of $[Ir(COD)Cl]_2$ (1 mol %) and $SnCl_4$ (4 mol %), promotes the benzylation or allylation of arenes and heteroarenes using ethers as the alkylating agents. An electrophilic mechanism is proposed from a Hammett correlation.

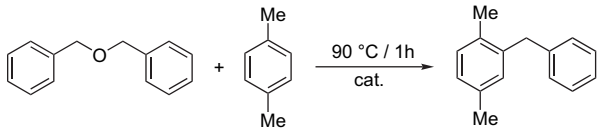
1. Introduction

Motifs bearing diarylmethane and their heteroarene analogues constitute an integral part of a number of bioactive compounds and pharmaceuticals. They are also used as precursors for electroactive and photoactive oligomers and polymers.[1,2] Friedel–Crafts alkylation (FCA) is a fundamental tool for the synthesis of diarylmethanes. Early work on FCA for diarylmethanes used alkyl halides as the alkylating agents, employing traditional Lewis acid (LA) catalysts.[3,4] More recent literature shows the emergence of late d-block and f-block metal catalysts and a switch from alkyl halide to alcohol, ester, ether or olefin as the alkylating agents.[5,6] A survey of the literature shows that there are fewer studies in Lewis acid catalyzed alkylation of arenes using benzyl and allyl ethers as the alkylating agent. Among the later studies, use of stoichiometric $TMSNTf_2$ and $AgClO_4$/$SnCl_4$ as catalysts are noteworthy.[7] To our knowledge, the truly catalytic versions include reactions mediated by $Sc(OTf)_3$, $Hf(OTf)_4$ or $SiCl_2(OTf)_2$, the catalyst loading being 10 mol % in each case.[8]

Our continuing success in developing efficient bimetallic pathways for carbon–carbon bond formation,[9] led us to recently propose a dual-reagent Ir/Sn catalyst system for the alkylation of arenes and heteroarenes using π-activated alcohols as the alkylating agents.[10] For secondary benzyl alcohols, a control experiment suggested the possible intermediacy of an ether during alkylation.[10b] This prompted us to study utilization of an ether as the alkylating agent in aromatic alkylation. Herein we present Ir/Sn mediated benzylation or allylation of arenes and heteroarenes using ether as the alkylating agent leading to the formation of diarylmethanes. The catalyst could be either a heterobimetallic catalyst, namely $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ **A**, having a Ir^{III}/Sn^{IV} motif, or a dual catalyst system of $[Ir(COD)Cl]_2$ (1%) and $SnCl_4$ (4%). An electrophilic mechanism is suggested from a Hammett correlation study.

2. Results and discussion

Taking dibenzyl ether **1** and *p*-xylene **2** as the model substrates, optimization studies were carried out varying reaction temperature and catalysts. In the presence of catalytic **A** (5 mol %), the reaction at 90 °C afforded the desired alkylated product **3** in 41% yield after 1 h (Scheme 1). Gratifyingly, under similar conditions the dual catalyst system of $[Ir(COD)Cl]_2$ (1%) and $SnCl_4$ (4%) resulted in 100% conversion of ether **1** to alkylated product **3** after 1 h, and the product was isolated in 82% yield. Similar reaction at 65 °C gave 34% of **3** after 48 h, while at room temperature there was no reaction. Importantly (i) the reaction could be conducted in an air atmosphere in the presence of trace amounts of moisture without any loss of product yield, and (ii) individually either $[Ir(COD)Cl]_2$ or $SnCl_4$ was poorly reactive.



1 2 3

$[Ir_2(COD)_2(SnCl_3)_2Cl_2(\mu\text{-}Cl)_2]$ (5%) 41%
$[Ir(COD)Cl]_2$ (1%) /$SnCl_4$ (4%) 82%

Scheme 1. Model reaction of dibenzyl ether **1** with *p*-xylene **2**.

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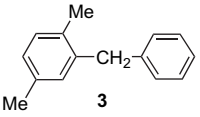
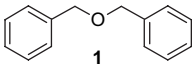
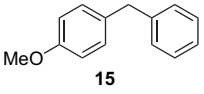
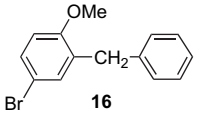
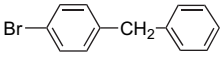
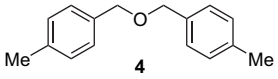
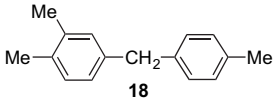
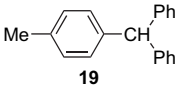
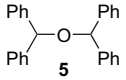
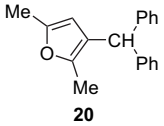
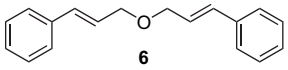
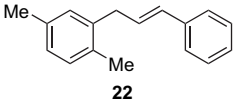
The clear superiority of the Ir/Sn dual catalyst system became evident from further screening of the model reaction using a catalyst combination of low-valent late transition metal d^8/d^{10} complex (1 mol %) with $SnCl_4$ (4 mol %). In each case the reaction was conducted at 90 °C for 1 h. Among these, $IrCl(CO)(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$ gave <10% of product, while $[Rh(COD)Cl]_2$, $CoCl(PPh_3)_3$, $RhCl(PPh_3)_3$, $NiCl_2(PPh_3)_2$, $PdCl_2(PPh_3)_2$, and $PtCl_2(PPh_3)_2$ were ineffective. Next we explored the effect of Lewis acid partner to $[Ir(COD)Cl]_2$, the best transition metal complex in our case. Interestingly $InCl_3$ and $SnCl_2$ led to less than 30% of product, while $AlCl_3$, $BF_3{\cdot}Et_2O$, $Sc(OTf)_3$, and $ZnCl_2$ showed very poor catalytic activity.

Utilizing the optimized parameters, we tested the general applicability of the Ir/Sn dual catalyst system for the alkylation of ethers, by varying both the ether and the arene/heteroarene. The results show that in our case the catalyst promotes both benzylation and allylation, and the corresponding alkylated products were obtained in modest to excellent yields depending on substrates (Tables 1–3).

In the case of symmetrical benzyl and allyl ethers, both alkyl groups migrated. Moreover, for heteroarenes, or electron-rich arenes, the reactions took shorter time and the product yield is generally high. Thus the reactions of dibenzyl ether **1**, bis(*p*-methylbenzyl)ether **4**, *sec*-benzyl ether **5**, and dicinnamyl ether **6**, with activated arenes such as tolune, *p*-xylene, *o*-xylene, and anisole were complete within 1 h and gave the corresponding alkylated products **3**, **15**, **18**, **19**, and **22** in 56–99% yields (Table 1, entries 1, 2, 5, 6, and 9). Similarly, ether **5** reacted with 2,5-dimethylfuran affording 91% of **20** after 0.5 h (entry 7). On the other hand, reaction of ethers **1** and **5** with non-activated arenes such as benzene, bromobenzene, and 4-bromoanisole took 1–48 h for completion, and the desired alkylated products **16**, **17**, and **21** were isolated in 46–67% yields (entries 3, 4, and 8).

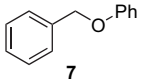
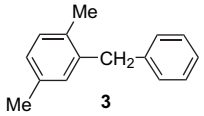
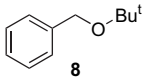
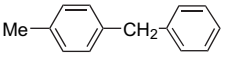
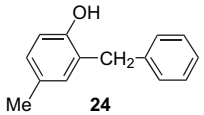
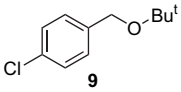
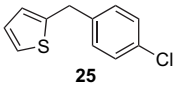
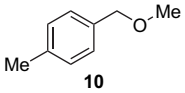
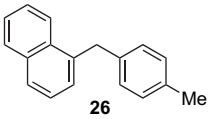
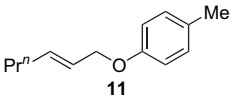
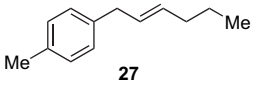
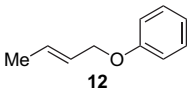
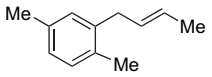
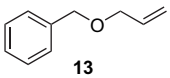
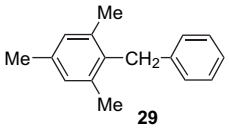
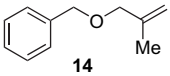
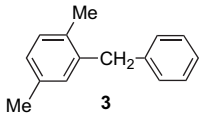
We have further established that for unsymmetrical ethers, the catalyst system is completely selective with respect to benzyl and allyl transfer. Thus benzyl phenyl ether **7** or alkyl benzyl ethers **8**–**10** reacted well with arenes and heteroarenes leading to selective benzyl transfer, and the products **3**, **23**–**26** were isolated in good yields (Table 2, entries 1–5).

Table 1. Selective benzylation and allylation of aromatics with symmetrical ethers catalyzed by Ir/Sn dual catalyst system[a]

Entry	Ether	Arene	Time (h)	Yield (%)	Product	Regioisomer
1		*p*-Xylene	1	82	 **3**	—
2	 **1**	Anisole	0.5	99	 **15**	35:65 (*o*/*p*)
3		4-Bromoanisole	1	67	 **16**	—
4		Bromobenzene	24	57	 **17**	35:65 (*o*/*p*)
5	 **4**	*o*-Xylene	0.5	84	 **18**	35:65 (*o*/*p*)
6		Toluene	1	76	 **19**	20:80 (*o*/*p*)
7	 **5**	2,5-Dimethylfuran	0.5	91	 **20**	—
8		Benzene	48	46	 **21**	—
9	 **6**	*p*-Xylene	1	56	 **22**	—

[a] Reaction conditions: ether (0.25 mmol), arene (8 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol, 1%), $SnCl_4$ (0.01 mmol, 4%), temp 90 °C.

Table 2. Selective benzylation and allylation of aromatics with unsymmetrical ethers catalyzed by Ir/Sn dual catalyst system[a]

Entry	Ether	Arene	Time (h)	Yield (%)	Product	Regioisomer
1	 **7**	*p*-Xylene	6	88	 **3**	—
2	 **8**	Toluene	1	87	 **23**	40:60 (*o*/*p*)
3		*p*-Cresol	6	65	 **24**	—
4	 **9**	Thiophene	1	84	 **25**	80:20 (2/3)
5	 **10**	Naphthalene	0.25	80	 **26**	85:15 (α/β)
6	 **11**	Toluene	3	64	 **27**	10:90 (*o*/*p*)[b]
7	 **12**	*p*-Xylene	1	69	 **28**	65:35 (*E*/*Z*)
8	 **13**	Mesitylene	24	92	 **29**	—
9	 **14**	*p*-Xylene	1	86	 **3**	—

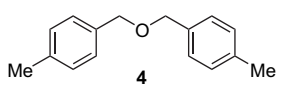
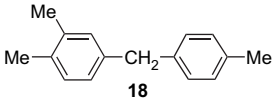
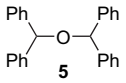
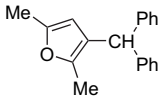
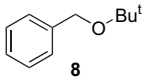
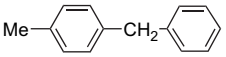
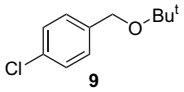
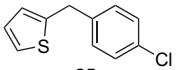
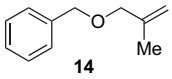
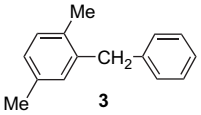
[a] Reaction conditions: ether (0.25 mmol), arene (8 mmol), $[Ir(COD)Cl]_2$ (0.0025 mmol, 1%), $SnCl_4$ (0.01 mmol, 4%), temp 90 °C.
[b] (*E*/*Z*) undetermined.

For the reaction of **7** we also isolated phenol as a side product. Similarly reactions of allyl aryl ethers **11** and **12** with arenes led to selective allyl transfer, affording **27** and **28** in modest yields (entries 6 and 7). Since both benzyl and allyl groups are π-activated, we were prompted to check whether unsymmetrical ethers having both allyl and benzyl groups would lead to the formation of mixed alkylated products. Interestingly, the reaction of allyl benzyl ethers **13** and **14** with arenes led to exclusive benzyl transfer with the formation of benzylated products **29** and **3**, respectively, in excellent yields (entries 8 and 9).

As pointed out earlier, the isolated heterobimetallic complex $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ **A** also shows catalytic activity in the present alkylation reaction at a loading of 5 mol %. Catalyst **A** is well suited to electron-rich arenes and heteroarenes (Table 3). Thus in the presence of catalytic **A**, the reaction of bis(*p*-methylbenzyl)ether **4** and *sec*-benzyl ether **5** with *o*-xylene and 2,5-dimethylfuran afforded corresponding alkylated products **18** and **20** in 79% and 85% yields, respectively (Table 3, entries 1 and 2). For unsymmetrical ethers such as benzyl *tert*-butyl ether **8** and *tert*-butyl 4-chlorobenzyl ether **9** with toluene and thiophene gave products **23** and **25** in 78% and 72% yields, respectively, after 1 h (entries 3 and 4). Similarly ether **14** reacted with *p*-xylene to afford the desired benzylated product **3** in 71% yield (entry 5).

Preliminary Hammett studies have been undertaken for the present Ir/Sn catalysis in order to assess the nature of the transition state from the reaction constants, i.e., the *ρ*-values with respect to arene as well as ether. This was attempted by monitoring the product (vide ^{1}H NMR with *N*,*N*-dimethylaniline as the internal reference) for the initial part of the reaction. The data for the reactions of benzyl *tert*-butyl ether with four different arenes (anisole, toluene, ethyl benzene, benzene) fitted well into pseudo-first-order rate plots, from which rate constants (k_Y) were evaluated. The relative rate constant $\log(k_Y/k_H)$ values linearly correlated with Hammett substituent constants (σ_p) (Fig. 1a) and from the plot,

Table 3. Selective benzylation of different arenes, heteroarenes with ethers catalyzed by Ir/Sn bimetallic complex **A**[a]

Entry	Ether	Arene	Time (h)	Yield (%)	Product	Regioisomer
1	 **4**	*o*-Xylene	0.5	79	 **18**	35:65 (*o*/*p*)
2	 **5**	2,5-Dimethylfuran	0.5	85	 **20**	—
3	 **8**	Toluene	1	78	 **23**	40:60 (*o*/*p*)
4	 **9**	Thiophene	1	72	 **25**	80:20 (2/3)
5	 **14**	*p*-Xylene	1	71	 **3**	—

[a] Reaction conditions: ether (0.25 mmol), arene (8 mmol), $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ (0.0025 mmol, 1%), temp 90 °C.

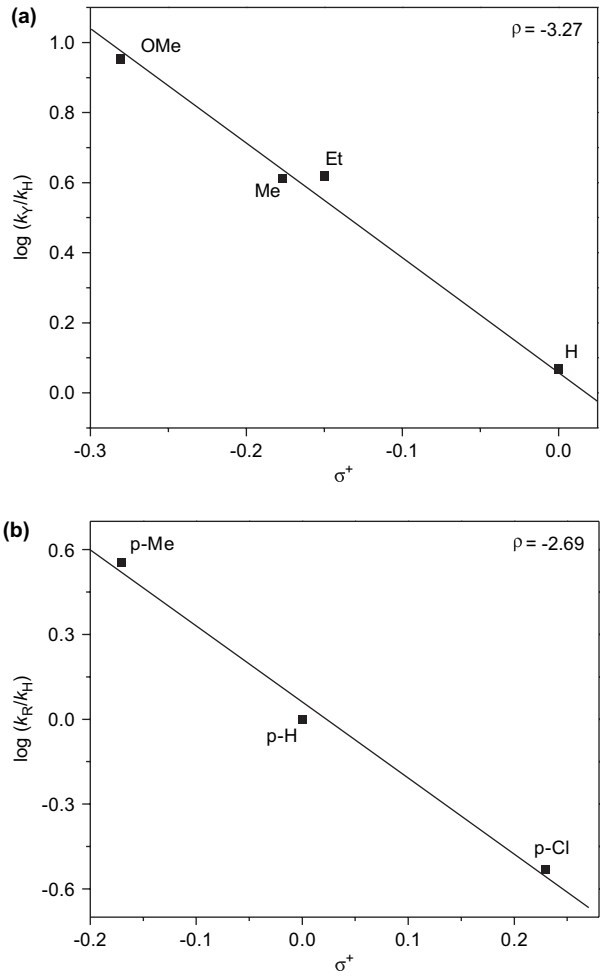


Figure 1. Hammett plot of $\log(k_Y/k_H)$ versus σ_p^+ and $\log(k_R/k_H)$ versus σ_p^+: (a) with respect to arene; (b) with respect to ether.

Hammett reaction constant ρ was found to be moderate negative (−3.27). This moderate negative ρ value (between −2 to −4) indicates that no distinct cation is formed in the arene ring but electrons flow out of the ring and some loss of conjugation may be suspected.[11] Similar study with *p*-xylene and three different *para*-substituted benzyl *tert*-butyl ether 4-R–$C_6H_4CH_2$–O′Bu (R=H, Cl, Me) (Fig. 1b), resulted a moderate negative Hammett reaction constant ρ value (−2.69). This moderate ρ value supports an electrophilic pathway of the present alkylation reaction and indicates the possibility of generation of weak positive charge (δ+) at the benzylic center of the ether.[11]

Based on (i) the bimetallic nature of the Ir/Sn catalyst system, (ii) the observed selectivity in case of unsymmetrical ethers, and (iii) Hammett correlation studies on both arenes and ethers, an electrophilic transition state is speculated as the initial activation step (Fig. 2). Further studies are required to validate the above proposal.

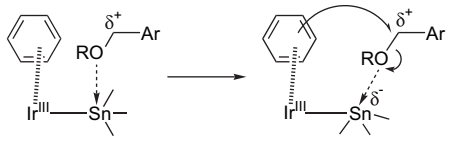


Figure 2. Proposed initial activation pathway.

3. Conclusion

In summary we have demonstrated here a Ir/Sn mediated benzylation and allylation of aromatics using respective ethers as the alkylating agents to afford valuable diarylmethanes selectively. The reactions could be performed using a distinct heterobimetallic catalyst, namely

$[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ **A** or a dual catalyst system of $[Ir(COD)Cl]_2$ (1%) and $SnCl_4$ (4%). The results clearly establish the interplay of bimetallic reactivity. Attempts to isolate the active catalyst, which equals in turn over frequency to that of the combination of $[Ir(COD)Cl]_2/4SnCl_4$ is being persued in our laboratory. While the detailed catalytic pathway remains to be established, preliminary studies indicate that the reaction is electrophilic in nature.

4. Experimental

4.1. General comments

All the reactions were carried out under a dry, oxygen-free argon atmosphere using standard vacuum lines and Schlenk techniques. Solvents were dried by the usual methods and distilled before use. Pre-coated silica gel $60F_{254}$ (Merck) was used for thin layer chromatography and silica gel 60–120 mesh (SRL) was used for column chromatography. $IrCl_3 \cdot xH_2O$ (Arora Mathey Ltd.), 1,5-cyclooctadiene (Aldrich) and tin tetrachloride (Fluka) were commercially available and were used directly. $[Ir(COD)(\mu\text{-}Cl)]_2$ was prepared according to the literature procedure.[12] $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ **A** was prepared according to the previously reported procedure.[10]

^1H (200 MHz) NMR spectra were recorded on a BRUKER-AC 200 spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), coupling constant (Hz). ^{13}C (54.6 MHz) NMR spectra were recorded on a BRUKER-AC 200 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 77.0 ppm). Elemental analyses were carried out using a CHNS/O Analyzer Perkin Elmer 2400 Series II instrument. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

4.2. Procedure for the preparation of ethers

All the ethers in Table 1 and 2 were prepared following the literature procedures.[13]

4.3. Preparation of diarylmethane 3 using heterobimetallic catalyst $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ A

A 10-mL Schlenk flask equipped with a magnetic bar, was charged with high-valent heterobimetallic complex, $[Ir_2(COD)_2(SnCl_3)_2(Cl)_2(\mu\text{-}Cl)_2]$ **A** (3 mg, 0.0025 mmol), and *p*-xylene (1 mL, 8 mmol). The flask was degassed with argon and placed into a constant temperature bath at 90 °C. After the mixture was stirred vigorously for 5 min, dibenzyl ether **1** (50 mg, 0.25 mmol) was added, and the reaction was allowed to continue at 90 °C for 1 h. Then the reaction mixture was quenched with aqueous NH_4F solution and extracted with diethyl ether (4×25 mL). The combined extracts were washed with water (2×10 mL), brine (2×10 mL), dried over anhydrous magnesium sulfate, the solvent removed under reduced pressure and the resultant oil subjected to column chromatography over silica gel (60–120 mesh, eluent: 60–80 °C pet. ether) to give the corresponding benzylated product **3** as a colorless oil in 40 mg, 41% isolated yield.

4.4. Preparation of diarylmethane 3 using dual catalyst system of $[Ir(COD)Cl]_2$ (1%) and $SnCl_4$ (4%)

$[Ir(COD)(\mu\text{-}Cl)]_2$ (1.7 mg, 0.0025 mmol), $SnCl_4$ (1.2 μL, 0.01 mmol), and *p*-xylene (1 mL, 8 mmol) were taken in a 10-mL Schlenk flask and the mixture was stirred vigorously for 5 min at 90 °C. Dibenzyl ether **1** (50 mg, 0.25 mmol) was added to it, and the reaction was allowed to continue at 90 °C for 1 h (TLC monitoring). The reaction mixture was quenched with aqueous NH_4F solution and extracted with diethyl ether (4×25 mL). The combined extracts were washed with water (2×10 mL), brine (2×10 mL), dried over anhydrous magnesium sulfate, and the solvent removed under reduced pressure. The crude reaction mixture was subjected to column chromatography (silica gel 60–120 mesh, eluent: 60–80 °C pet. ether) and the corresponding benzylated product **3** was isolated as a colorless oil in 80 mg, 82% isolated yield.

The procedures given above were followed in all cases.

4.5. Spectral data of products

Compounds **3**, **15**–**19**, and **21**–**29** are reported in the literature for which CAS registry no. and literature references are given. All products gave satisfactory spectral data and were compared with authentic samples wherever possible.

4.5.1. 2-Benzyl-1,4-dimethylbenzene (3) [13540-50-6].[14] Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.22 (s, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 3.97 (s, 2H, C*H*$_2$), 6.96–7.30 (m, 8H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 19.1, 20.9, 39.4, 125.8, 127.0, 128.3, 128.6, 130.2, 130.7, 133.4, 135.3, 138.6, 140.5.

4.5.2. 4-Benzyl-anisole (15) [834-14-0].[15] Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 3.78 (s, 3H, *OCH*$_3$), 3.93 (s, 2H, C*H*$_2$), 6.81–7.19 (m, 9H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 41.6, 55.3, 113.9, 126.0, 128.4, 128.6, 129.7, 133.3, 141.6, 158.0.

4.5.3. 2-Benzyl-anisole (15A) [883-90-9].[16] Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 3.82 (s, 3H, *OCH*$_3$), 3.98 (s, 2H, C*H*$_2$), 6.85–6.91 (m, 2H, Ar*H*), 7.05–7.08 (m, 1H, Ar*H*), 7.13–7.26 (m, 6H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 35.9, 55.4, 110.4, 120.5, 125.8, 127.4, 128.3, 129.0, 129.7, 130.3, 141.1, 157.4.

4.5.4. 2-Benzyl-4-bromoanisole (16) [41876-52-2].[17] Colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 3.77 (s, 3H, *OCH*$_3$), 3.90 (s, 2H, C*H*$_2$), 6.71 (d, ^3J(H,H)=8.6 Hz, 1H, Ar*H*), 7.14–7.24 (m, 7H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 35.7, 55.6, 112.1, 112.8, 126.1, 128.4, 128.9, 130.0, 132.1, 132.9, 140.1, 156.5.

4.5.5. Benzylbromobenzene (17) [*o*-isomer 23450-18-2 and *p*-isomer 2116-36-1].[18] Colorless oil; ^1H NMR

(200 MHz, $CDCl_3$) δ (ppm) (*ortho* isomer) 4.12 (s, 2H, CH_2), 7.03–7.59 (m, 9H, Ar*H*); (*para* isomer) 3.93 (s, 2H, CH_2), 7.03–7.59 (m, 9H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*ortho*+*para*) 41.3, 41.7, 119.9, 124.9, 126.0, 126.2, 126.3, 127.4, 127.8, 128.4, 128.5, 128.8, 129.0, 130.6, 131.1, 131.5, 132.8, 139.4, 140.1, 140.4.

4.5.6. (4-Methylbenzyl)dimethylbenzene (18) [3-isomer 28952-43-4 and 4-isomer 28952-42-3].[19] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (3-isomer) 2.13 (s, CH_3), 2.22 (s, CH_3), 2.28 (s, CH_3), 2.31 (s, CH_3), 3.97 (s, 2H, CH_2), 6.94–7.08 (m, 7H, Ar*H*); (4-isomer) 2.22 (s, CH_3), 2.31 (s, CH_3), 3.87 (s, 2H, CH_2), 6.94–7.08 (m, 7H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (3-+4-isomer) 15.4, 19.3, 19.8, 20.7, 21.0, 39.6, 41.1, 125.4, 126.3, 128.0, 128.2, 128.5, 128.7, 129.1, 129.7, 130.2, 134.1, 135.3, 135.4, 136.5, 136.9, 138.5, 138.9.

4.5.7. (Diphenylmethyl)toluene (19) [*o*-isomer 17016-20-5 and *p*-isomer 603-37-2].[20] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (*ortho* isomer) 2.22 (s, 3H, CH_3), 5.71 (s, 1H, C*H*), 6.99–7.32 (m, 14H, Ph); (*para* isomer) 2.34 (s, 3H, CH_3), 5.54 (s, 1H, C*H*), 6.99–7.32 (m, 14H, Ph). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*ortho*+*para*) 19.9, 21.0, 53.6, 56.5, 126.2, 126.4, 128.3, 129.0, 129.4, 129.5, 129.6, 135.8, 141.0, 144.2.

4.5.8. 3-(Diphenylmethyl)-2,5-dimethylfuran (20). Light yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.08 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 5.19 (s, 1H, C*H*), 5.64 (s, 1H, C*H* furan ring), 7.12–7.31 (m, 10H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 11.7, 13.6, 47.5, 107.7, 121.8, 126.2, 128.3, 128.8, 144.1, 145.8, 149.2. Anal. ($C_{19}H_{18}O$) calcd, C: 86.98, H: 6.92; found, C: 86.71, H: 7.01.

4.5.9. Triphenylmethane (21) [519-73-3].[21] White solid; mp 92–95 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 5.57 (s, 1H, C*H*), 7.00–7.35 (m, 15H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 56.9, 126.3, 128.3, 129.5, 143.9.

4.5.10. (*E*)-1,4-Dimethyl-2-(3-phenyl-2-propenyl)benzene (22) [189562-31-0].[16a] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.31 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.51 (d, ^3J(H,H)=4.8 Hz, 2H, CH_2), 6.34–6.38 (m, 2H, C*H*:C*H*), 7.00–7.10 (m, 3H, Ar*H*), 7.20–7.39 (m, 5H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*E*+*Z*) 18.9, 20.9, 29.7, 36.9, 126.1, 127.0, 128.5, 128.7, 130.0, 130.1, 130.8, 133.2, 135.5, 137.6, 138.0.

4.5.11. Benzyltoluene (23) [*o*-isomer 713-36-0 and *p*-isomer 620-83-7].[22] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (*ortho* isomer) 2.26 (s, 3H, CH_3), 4.00 (s, 2H, CH_2), 7.10–7.29 (m, 9H, Ar*H*); (*para* isomer) 2.33 (s, 3H, CH_3), 3.96 (s, 2H, CH_2), 7.10–7.29 (m, 9H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*ortho*+*para*) 19.6, 21.0, 38.8, 40.8, 41.1, 125.9, 126.1, 127.0, 128.4, 128.7, 129.2, 129.6, 129.8, 130.1, 130.4, 131.7, 135.7, 136.5, 137.4, 138.3, 138.8, 139.8.

4.5.12. 2-Benzyl-4-methylphenol (24) [716-96-1].[23] Light yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.26 (s, 3H, CH_3), 3.96 (s, 2H, CH_2), 6.67–6.71 (m, 1H, Ar*H*), 6.91–6.94 (m, 2H, Ar*H*), 7.20–7.30 (m, 5H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 20.5, 36.3, 115.6, 126.3, 126.7, 128.2, 128.6, 130.1, 131.5, 140.0, 151.4.

4.5.13. (4-Chlorobenzyl)thiophene (25) [2-isomer 63877-95-2].[24] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (2-isomer) 4.14 (s, 2H, CH_2), 6.80–6.82 (m, 1H, C*H* thiophene ring), 6.86–7.02 (m, 2H, C*H* thiophene ring), 7.12–7.36 (m, 4H, Ar*H*); (3-isomer) 3.97 (s, 2H, CH_2), 6.80–6.82 (m, 1H, C*H* thiophene ring), 6.86–7.02 (m, 2H, C*H* thiophene ring), 7.12–7.36 (m, 4H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (2-+3-isomers) 35.3, 35.8, 121.4, 124.1, 125.3, 125.8, 126.8, 128.2, 128.5, 128.6, 129.9, 130.0, 131.9, 132.3, 138.8, 139.0, 140.8, 143.3.

4.5.14. (4-Methylbenzyl)naphthalene (26) [α-isomer 20204-71-1 and β-isomer 20204-73-3].[25] White solid; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (α-isomer) 2.31 (s, 3H, CH_3), 4.42 (s, 2H, CH_2), 7.09–8.03 (11H, Ar*H*); (β-isomer) 2.32 (s, 3H, CH_3), 4.11 (s, 2H, CH_2), 7.09–8.03 (11H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (α+β) 21.0, 38.7, 41.8, 124.3, 125.3, 125.6, 126.0, 127.1, 127.3, 127.6, 127.7, 128.1, 128.7, 129.0, 129.2, 132.2, 134.0, 135.5, 137.0, 137.6.

4.5.15. 2-Hex-2-enyl-toluene (27) [*o*-isomer 496783-63-2 and *p*-isomer 496783-65-4].[8b] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) (*ortho*+*para*) 0.87/0.88 (two triplets, CH_3), 1.31–1.44 (m, CH_2), 1.99 (q, ^3J(H,H)=6.7 Hz, CH_2), 2.28/2.31 (two singlet, CH_3), 3.27–3.31 (m, CH_2), 5.47–5.52 (m, C*H*=C*H*), 6.90–7.12 (m, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*ortho*+*para*) 13.6, 19.3, 20.9, 22.6, 34.6, 36.6, 38.6, 125.9, 126.0, 128.0, 128.3, 128.9, 129.2, 130.0, 131.6, 131.7, 135.3, 136.2, 138.0, 139.1.

4.5.16. 2-But-2-enyl-1,4-dimethylbenzene (28) [37849-09-5].[26] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.68 (d, ^3J(H,H)=5.9 Hz, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.27 (d, ^3J(H,H)=5.5 Hz, 2H, CH_2), 5.47–5.54 (m, 2H, C*H*:C*H*), 6.96–7.06 (m, 3H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) (*E*+*Z*) 12.8, 17.8, 18.8, 20.9, 29.7, 31.0, 36.5, 124.5, 126.0, 126.7, 128.6, 129.3, 129.7, 130.0, 133.0, 135.3, 138.9.

4.5.17. 2-Benzyl-1,3,5-trimethylbenzene (29) [4453-79-6].[27] Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 2.20 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 4.01 (s, 2H, CH_2), 6.89 (s, 2H, Ar*H*), 6.99–7.03 (m, 2H, Ar*H*), 7.14–7.23 (m, 3H, Ar*H*). ^{13}C NMR (54.6 MHz, $CDCl_3$) δ (ppm) 20.1, 20.9, 34.7, 125.7, 127.8, 128.3, 128.9, 133.8, 135.6, 137.0, 140.1.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.068.

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