An efficient approach to the cyclotrimerisation of alkynes: solvent-free synthesis of 1,3,5-trisubstituted benzenes using *p*-toluenesulfonic acid monohydrate

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Abstract
An environmentally friendly, efficient method for transforming alkynes into substituted benzenes catalyzed by *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) under solvent-free conditions has been developed, which conforms to the principles of "green" chemistry and overcomes the shortcomings of previous methods for the synthesis of substituted benzenes. The reaction is quite general and provides good to excellent yields.

Keywords: Alkynes, *p*-TsOH·H_2O, cyclotrimerization, solvent-free, 1,3,5-trisubstituted benzenes

Introduction

The development of new transformations that are not only efficient, selective, and high-yielding but that are also environmentally benign is one of the challenge chemists are facing.[1,2] During the last decades, the topic of "green" chemistry has received increasing attention.[1-4] "Green" chemistry aims at the total elimination or at least the minimization of generated waste and the implementation of sustainable processes through the adoption of 12 fundamental principles. An alternative strategy to reduce the *E*-factor of reactions and their impact on the environment is to conduct them under solvent-free conditions. Solvent-free reactions have attracted considerable attention due to environmental safety, the economic viewpoint, easy work-up, high yields of the products and (usually) their short reaction times.[5-10]

The formation of benzene rings from alkynes, named the Reppe cyclotrimerization,[11] has been well known as a useful method and intensively studied in the last fifty years because of the difficulty in obtaining functionalized aromatic compounds.[12-20] However, most of these protocols suffer from the need of using precious metal catalysts, lower yields or harsh operating conditions, and mixtures of 1,3,5- and 1,2,4-trisubstituted benzenes are obtained in general. Recently, we reported that a novel indium(III)-catalyzed cyclotrimerization of alkynes in the presence of 2-iodophenol gave 1,3,5-substituted benzenes with complete regioselectivity. However, the indium(III)-catalyzed cyclotrimerization was less successful with alkynylsilanes (only 15% yield of **2a**) and needed to be carried out in sealed tubes.[21] Meanwhile, considering their expensive nature, inadequate accessibility, toxicity of the additives often used, the generation of toxic waste and the use of organic solvent as well as harsh conditions, there is an urgent need to develop a powerful method with a high regioselectivity to meet the requirement of green chemistry. Here we describe a green approach towards the regioselective synthesis of 1,3,5-trisubstituted benzenes *via* the *p*-TsOH·H_2O-catalyzed[22-28] trimerization of alkynes under solvent-free conditions.

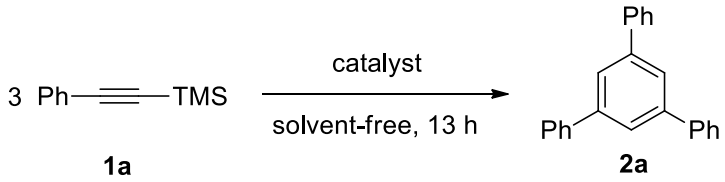
Results and Discussion

In order to identify the optimal reaction conditions, 1-phenyl-2-trimethylsilylacetylene **1a** was chosen as a model substrate. Firstly, the cyclotrimerization was carried out in the presence of 10 mol% TfOH under solvent-free conditions and the desired product **2a** was isolated in 53% yield (Table 1, entry 1). The reaction using TFA, CAN, H_2SO_4, HNO_3 and H_3PO_4 as catalysts produced **2a** only in low yields (Table 1, entries 2, 3 and 10-12). Changing the catalyst to *p*-TsOH·H_2O furnished the product **2a** in 68% yield (Table 1, entry 6). Furthermore, a higher yield was obtained when the amount of *p*-TsOH·H_2O was increased from 0.1 equiv to 0.5 equiv or 1.0 equiv (Table 1, entries 7 and 8). Other catalysts such as oxalic acid, AcOH, HCl, or Lewis acids did not promote the cyclotrimerization reaction (Table 1, entries 4, 5, 9 and 13-16).

Encouraged by the efficiency of the reaction protocol described above, the scope of the substrate was investigated. Typical results are shown in Table 2. The aromatic alkynylsilane **1c** possessing an electron-donating group at the benzene ring (R^1 = 4-$MeOC_6H_4$) reacted smoothly and afforded the desired product **2b** in 95% yield (Table 2, entry 3). Substrates **1i** and **1j** possessing electron-withdrawing groups (R^1 = 4-FC_6H_4, 4-BrC_6H_4) at the benzene ring were also successfully employed in the cyclotrimerization and gave the benzene derivatives **2f** and **2g** in 78% and 82% yields, respectively (Table 2, entries 9 and 10). Significantly, the desired products could be obtained in higher yields from electron rich than from electron poor alkynylsilanes. Moreover, the desilylative cyclotrimerizations of the aromatic alkynylsilanes **1e, 1g, 1h** and **1l** (R^1 = 4-MeC_6H_4, 4-EtC_6H_4, 4-*n*-PrC_6H_4 and 3-MeC_6H_4) also proceeded smoothly to afford benzene derivatives **2c**, **2d**, **2e** and **2h** in high yields with complete regioselectivity (Table 2, entries 5, 7, 8 and 12). However, the comparable treatment of **1m** did not form the desired

benzene derivative **2i** (Table 2, entry 13), presumably due to the steric effect of the substituent in the *ortho*-position of **1m**. Cicero has also reported that 1-ethynyl-2,6-dimethoxybenzene failed to afford 1,3,5-tri(2,6-dimethoxyphenyl)benzene and/or 1,2,4-tri(2,6-dimethoxyphenyl)benzene in the presence of vanadium phthalocyanine.[29] In addition, the aliphatic alkynylsilanes **1n, 1p** and internal alkyl alkyne **1o** in the presence of 1.0 equiv *p*-TsOH·H_2O also underwent a cyclotrimerization smoothly to give the products **2j, 2l** and **2k** in 83%, 86%, and 85% yields, respectively (Table 2, entries 14-16). Furthermore, the terminal alkynes **1b, 1d, 1f** and **1k** also gave the desired results, providing the benzene derivatives in high yields (Table 2, entries 2, 4, 6 and 11).

Table 1. Screening of catalysts for the cyclotrimerization of 1-phenyl-2-trimethylsilylacetylene[a]

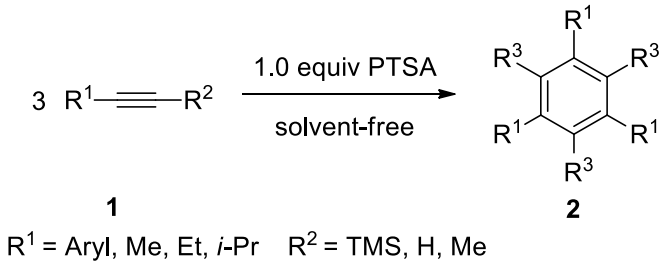


1a **2a**

Entry	Catalyst	Yield (%)[b]
1	TfOH	53
2	TFA	20
3	CAN	15
4	Oxalic acid	0
5	AcOH	0
6	*p*-TsOH·H_2O	68
7	*p*-TsOH·H_2O (0.5 equiv)	79
8	***p*-TsOH·H_2O (1.0 equiv)**	**90**
9	HCl	0
10	H_2SO_4	20
11	HNO_3	28
12	H_3PO_4	30
13	$ZnCl_2$	0
14	$InCl_3$	0
15	$FeCl_3$	0
16	$Cu(OTf)_2$	0

[a]Reaction conditions: the reactions were carried out using **1a** (0.6 mmol) and catalyst (10 mol%) at 60 °C for 3 h and then at 140 °C for 10 h. [b]Isolated yield of pure product based on **1a**.

Table 2. Solvent-free synthesis of substituted benzenes **2** catalyzed by *p*-TsOH·H_2O [a]

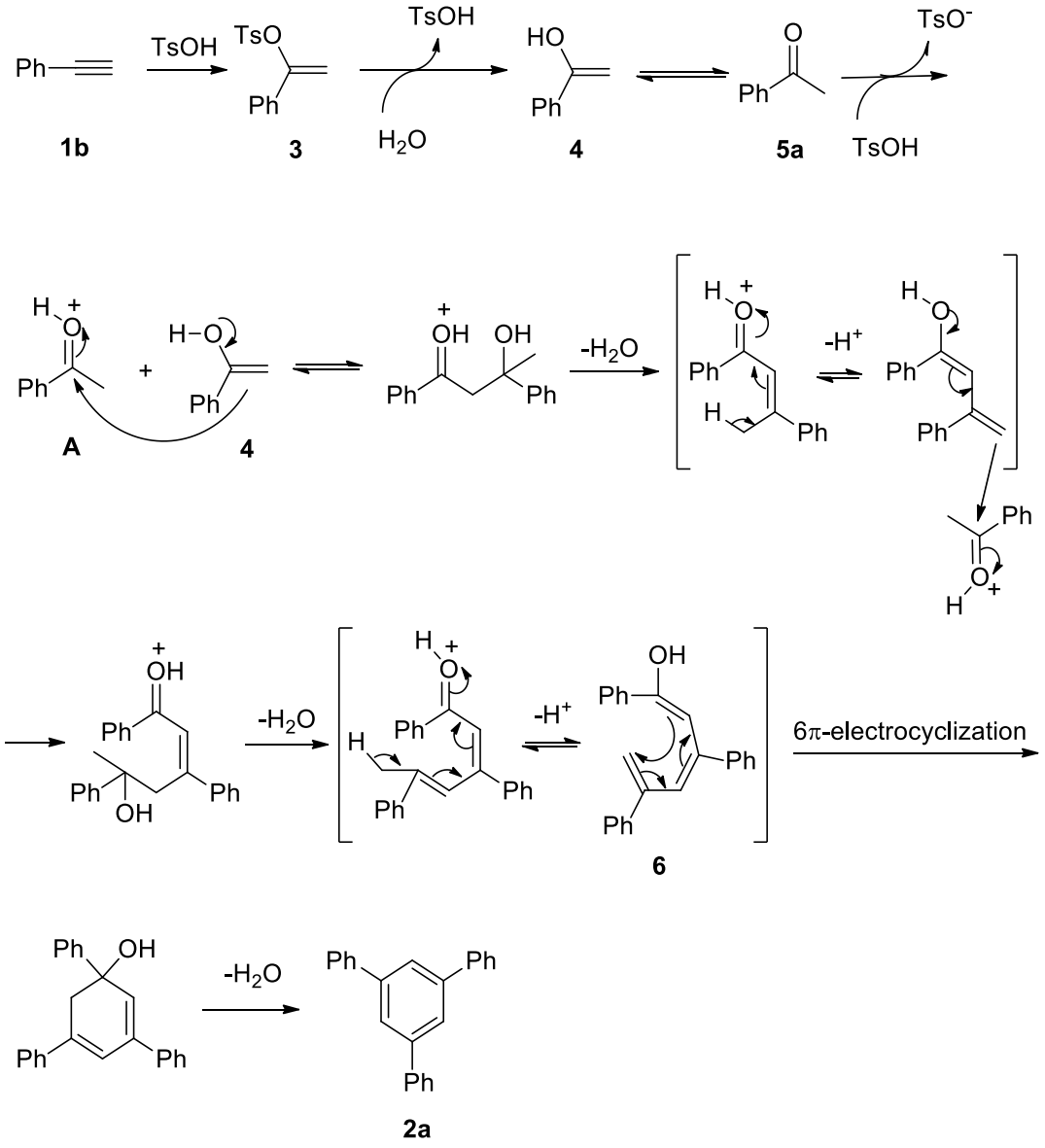


Entry	Alkyne	Product		Time/h[b]	Yield (%)[c]
1	**1a**: R^1 = Ph; R^2 = TMS	**2a**	R^3 = H	13	90
2	**1b**: R^1 = Ph; R^2 = H	**2a**	R^3 = H	14	87
3	**1c**: R^1 = 4-$MeOC_6H_4$; R^2 = TMS	**2b**	R^3 = H	11	95
4	**1d**: R^1 = 4-$MeOC_6H_4$; R^2 = H	**2b**	R^3 = H	13	94
5	**1e**: R^1 = 4-MeC_6H_4; R^2 = TMS	**2c**	R^3 = H	14	91
6	**1f**: R^1 = 4-MeC_6H_4; R^2 = H	**2c**	R^3 = H	15	89
7	**1g**: R^1 = 4-EtC_6H_4; R^2 = TMS	**2d**	R^3 = H	15	88
8	**1h**: R^1 = 4-*n*-PrC_6H_4; R^2 = TMS	**2e**	R^3 = H	19	90
9	**1i**: R^1 = 4-FC_6H_4; R^2 = TMS	**2f**	R^3 = H	24	78
10	**1j**: R^1 = 4-BrC_6H_4; R^2 = TMS	**2g**	R^3 = H	22	82
11	**1k**: R^1 = 4-BrC_6H_4; R^2 = H	**2g**	R^3 = H	24	80
12	**1l**: R^1 = 3-MeC_6H_4; R^2 = TMS	**2h**	R^3 = H	20	83
13	**1m**: R^1 = 2-$MeOC_6H_4$; R^2 = TMS	**2i**	R^3 = H	24	0
14	**1n**: R^1 = Et; R^2 = TMS	**2j**	R^3 = H	23	83
15[d]	**1o**: R^1 = Me; R^2 = Me	**2k**	R^3 = Me	21	85

Table 2. Continued

Entry	Alkyne	Product	Time/h[b]	Yield (%)[c]
16	**1p**: R^1 = *i*-Pr; R^2 = TMS	**2l** R^3 = H	20	86

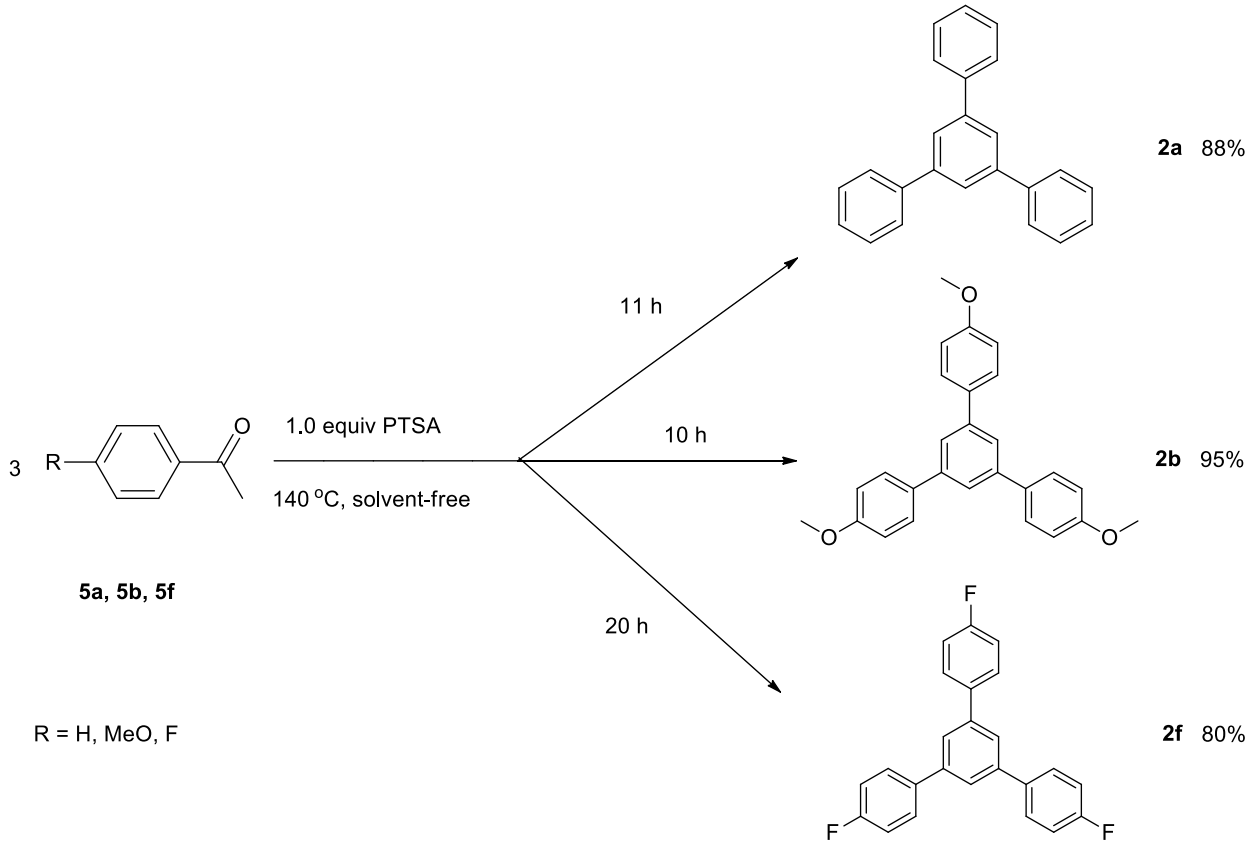
[a]Reaction conditions: 0.6 mmol of **1**, 0.6 mmol of *p*-TsOH·H_2O, 60 °C for 3 h, then 140 °C for the rest of the time. [b]Reaction time used in all. [c]Isolated yield of pure product based on **1**. [d]The reaction was carried out in a sealed tube.



Scheme 1. Proposed rationale for the cyclotrimerisation of phenylacetylene.

A possible rationale for the *p*-TsOH catalyzed cyclotrimerization of arylalkynes (here exemplified for phenylacetylene **1b**) is proposed in Scheme 1. Initially, *p*-TsOH attacks **1b** to form 1-phenylethenyl tosylate, which is subsequently hydrolyzed to form the enol **4** of acetophenone (**5a**).[30-31] The latter undergoes an acid-catalyzed aldol reaction/condensation sequence to form intermediate **6**, which finally, *via* 6π-electrocyclization followed by water elimination, yields 1,3,5-triphenylbenzene (**2a**).[32]

In order to verify our rationale, some intermediate ketones were isolated and tested under the same conditions. A satisfactory result was obtained as we had expected (Scheme 2).[33]



Scheme 2. Synthesis of substituted benzenes **2** from intermediate ketones **5**.

Conclusions

In conclusion, we have developed an environmentally friendly, economical and efficient method for cyclotrimerization of alkynes under solvent-free conditions in the presence of *p*-TsOH·H_2O. The major advantages of the method lie in the cheap catalyst, easy work-up and avoidance of the

use of toxic solvents such as DMF, DMSO, CH_3CN and toluene. Air-tolerant and atom-economical characteristics of the method accord with the concept of modern green chemistry and will be appealing for industries.

Experimental Section

General. All compounds are commercially available and were used without further purification. NMR spectra were recorded on a Bruker AVANCE DPX-400 or Bruker AVANCE DRX-500 instrument with TMS as an internal reference. MS measurements were performed on Bruker Reflex III mass spectrometer (ESI). Elemental analyses were carried out with an Elementar Vario Micro Cube in the School of Chemistry & Chemical Engineering of Guangxi Normal University, China. Flash chromatography was performed with QingDao silica gel (300–400 mesh).

General procedure for the cyclotrimerization of alkynes 1. To a 10 mL flask, alkynes (0.6 mmol) and *p*-TsOH·H_2O (1.0 equiv) were successively added. The mixture was stirred at 60 °C for 3 h and at 140 °C for the rest of the time, which was monitored periodically by TLC. After completion of the reaction, the reaction mixture was neutralized by saturated $NaHCO_3$, and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried by anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography (PE/EA) and gave the corresponding products.

General procedure from alkynes 1 to ketones 5. To a 10 mL flask, alkynes (0.6 mmol) and *p*-TsOH·H_2O (1.0 equiv) were successively added. The mixture was stirred at 60 °C for 3 h, which was monitored periodically by TLC. After completion of the reaction, the reaction mixture was neutralized by saturated $NaHCO_3$, and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried by anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography (PE/EA) and gave the corresponding ketones **5**.

1,3,5-Triphenylbenzene (2a). White solid, mp 172-174 °C (lit.[21, 32] 170-172 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 7.2 Hz, 3H), 7.50 (t, *J* = 7.3 Hz, 6H), 7.72 (d, *J* 7.3 Hz, 6H), 7.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.2, 127.4, 127.5, 128.8, 141.2, 142.4. MS: [M+H$^+$] 307.

1,3,5-Tris(4-methoxyphenyl)benzene (2b). White solid, mp 142-143 °C (lit.[34] 140-142 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 9H), 7.02 (d, *J* 8.6 Hz, 6H), 7.63 (d, *J* 8.6 Hz, 6H), 7.67 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.4, 114.3, 123.8, 128.3, 133.9, 141.8, 159.3. MS: [M+H$^+$] 397.

1,3,5-Tris(4-methylphenyl)benzene (2c). Pale yellow solid, mp 175-176 °C (lit.[35] 177-178 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 9H), 7.29 (d, *J* 7.8 Hz, 6H), 7.60 (d, *J* 8.0 Hz, 6H), 7.73

(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 124.6, 127.2, 129.5, 137.3, 138.4, 142.2. MS: [M+H$^+$] 349.

1,3,5-Tris(4-ethylphenyl)benzene (2d). Pale yellow solid, mp 111-113 ºC (lit.[36] 114 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, *J* 7.6 Hz, 9H), 2.74 (q, *J* 7.6 Hz, 6H), 7.33 (d, *J* 7.8 Hz, 6H), 7.63 (d, *J* 7.9 Hz, 6H), 7.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 15.6, 28.6, 124.6, 127.3, 128.3, 138.7, 142.2, 143.6. MS: [M+H$^+$] 391.

1,3,5-Tris(4-*n*-propylphenyl)benzene (2e). Pale yellow solid, mp 141-143 ºC (lit.[21] 142-143 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, *J* 7.3 Hz, 9H), 1.75-1.67 (m, 6H), 2.69-2.64 (m, 6H), 7.30 (d, *J* 8.0 Hz, 6H), 7.63 (d, *J* 8.1 Hz, 6H), 7.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.9, 24.6, 37.7, 124.6, 127.1, 128.9, 138.6, 142.0, 142.1. MS: [M+H$^+$] 433.

1,3,5-Tris(4-fluorophenyl)benzene (2f). Yellow solid, mp 238-239 ºC (lit.[32] 238-240 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (t, *J* 8.7 Hz, 6H), 7.66-7.62 (m, 6H) 7.67 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 115.69 and 115.86, 124.87, 128.87 and 128.93, 137.03 and 137.05, 141.57, 161.74 and 163.70. MS: [M+H$^+$] 361.

1,3,5-Tris(4-bromophenyl)benzene (2g). Yellow solid, mp 261-263 ºC (lit.[32] 260-261 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* 8.1 Hz, 6H), 7.61 (d, *J* 8.2 Hz, 6H), 7.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 122.1, 125.0, 129.0, 132.1, 139.7, 141.6. MS: [M+H$^+$] 544, 542.

1,3,5-Tris(3-methylphenyl)benzene (2h). White solid, mp 117-118 ºC (lit.[37] 116.8-118.1 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.46 (s, 9H), 7.22 (d, *J* 7.5 Hz, 3H), 7.38 (t, *J* 7.6 Hz, 3H), 7.51 (d, *J* 7.6 Hz, 6H), 7.76 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$): δ 21.5, 124.5, 125.1, 128.2, 128.3, 128.7, 138.4, 141.3, 142.4. MS: [M+H$^+$] 349.

1,3,5-Triethylbenzene (2j).[21] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (t, *J* 7.6 Hz, 9H), 2.71 (q, *J* 7.6 Hz, 6H), 6.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.6, 28.9, 124.8, 144.2. MS: [M+H$^+$] 163.

Hexamethylbenzene (2k). White solid, mp 162-164 ºC (lit.[21] 162-164 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.8, 132.0. MS: [M+H$^+$] 163.

1,3,5-Tri(isopropyl)benzene (**2l**).[21] Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (d, *J* 7.0 Hz, 18H), 3.02-2.94 (m, 3H), 7.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1, 34.3, 122.1, 148.7. MS: [M+H$^+$] 205.

Acetophenone (5a).[38] Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.44-7.42 (m, 2H), 7.54-7.53 (m, 1H), 7.99-7.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.1, 127.8, 128.1, 132.6, 136.6, 197.5. MS: [M+H$^+$] 121.

1-(4-Methoxyphenyl)ethanone (5b).[38] Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (s, 3H), 3.87 (s, 3H), 6.93 (d, *J* 8.8 Hz, 2H), 7.94 (d, *J* 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.3, 55.4, 113.7, 130.4, 130.6, 163.5, 196.8. MS: [M+H$^+$] 151.

1-(4-Fluorophenyl)ethanone (5f).[38] Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.16-7.09 (m, 2H), 8.02-7.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.5, 115.52 and 115.69, 130.86 and 130.94, 133.5, 164.7, 166.7, 196.5. MS: [M+H$^+$] 139.

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