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Graphical Abstract

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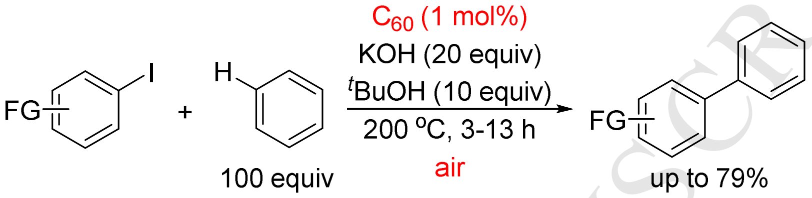

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ABSTRACT

C_{60} at 1 mol% loading catalyzed the direct C-H arylation of benzene with aryl iodides in air to yield biaryls. The in situ generation of electron rich $C_{60}(OH)^{2\bullet-}$, from C_{60} and OH^-, reduced the aryl iodides to aryl radicals for arylation of benzene. The large surface area and spherical shape of C_{60} facilitated this process.

Keywords:
C_{60}
Direct C-H arylation
Reduction
Biaryl

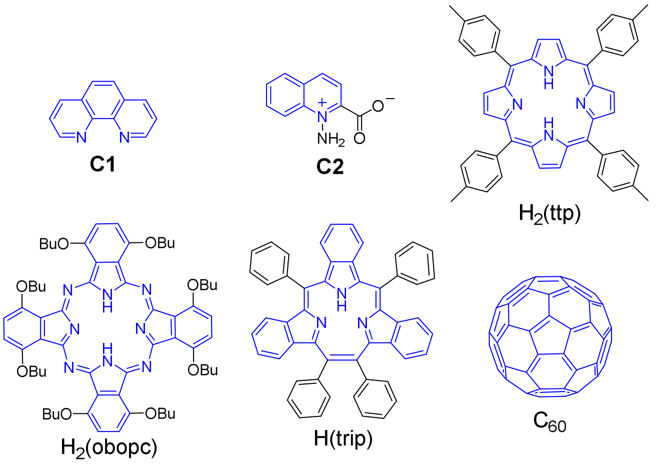
1. Introduction

Cross-coupling reactions are widely used to construct biaryl motifs, which are commonly found in functional materials such as organic semiconductors and organic light emitting diodes[1] as well as in pharmaceuticals.[2] The strategy of forming aryl-aryl bond has evolved from using second row[3] to first row[4] transition metal catalysts, and from activated arenes[3,5] to parent arenes via direct C-H arylation.[6-8]

The organocatalytic direct C-H arylation is first reported by Itami in 2008,[9] which has emerged as a new approach for the biaryl synthesis. It is mechanistic interesting, that transition metals are not required in the bond breaking and making processes.[10] The often expensive metal catalysts themselves and the pharmaceutical requirement to remove metallic impurities afterwards could be avoided. Thus the cross-coupling of unreactive aromatic C-H bonds with aryl halides leads to a cheaper and more environmentally friendly reaction.

Later, various organocatalysts were found to catalyze the direct C-H arylation in the presence of strong base, such as DMEDA (*N*,*N'*-dimethylethylenediamine),[6a] 1,10-Phenanthroline,[6b] quinoline-amino-carboxylic acid,[6c] zwitterionic radical[6d] and amino-linked N-heterocyclic carbine.[6e] However, the catalyst loadings usually required 20 mol% and N_2 atmosphere for satisfactory results. Alternatively, metal and base

Table 1. Selected surface area of organocatalysts for catalytic direct C-H arylation (highlighted in blue)[a]



Entry	Catalyst	Surface area / Å^2	loading / mol%	ref
1	**C1**	30.6	20	6b
2	**C2**	20.6	20	6c
3	H_2(ttp)	81.8	5	11a
4	H_2(obopc)	120.6	3	11c
5	H(trip)	90.0	1	11b
6	C_{60}	149.6	1	this work

[a] estimated by Spartan '10 at Semi-Empirical/AM1 level

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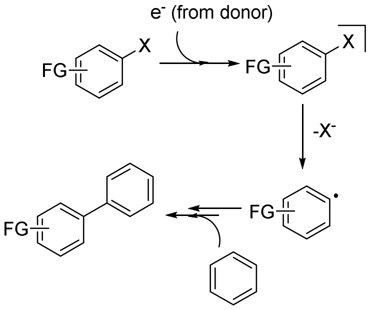
free, photocatalytic protocol using Eosin Y as photocatalyst has been discovered by König.[7] Our group has reported the air-compatible organocatalysts such as H_2(ttp) (5 mol%),[11a] H(trip) (1 mol%)[11b] and H_2(obopc) (3 mol%).[11c] The larger surface area of these catalysts tends to allow lower catalyst loading (Table 1, entries 1-5).

A general accepted mechanism of these strong base-promoted organocatalytic direct C-H arylation was initiated by one electron reduction of aryl halide by an electron donor to generate an aryl halide radical anion. This radical anion eliminates a halide anion to give an aryl radical. The aryl radical then adds to an arene to yield the biaryl product (Scheme 1).[10,12] A recent report suggested that in situ deprotonation of the organocatalyst gives anionic electron-rich alkene species as the electron donor.[13] The one electron reduction of aryl halides by organic electron donors has been well documented.[14] Alternatively, reduction of aryl halides via photo-induced electron transfer using PDI (perylenediimide) photocatalyst has been reported.[15]



Scheme 1. General mechanism of organocatalytic direct C-H arylation

Donor-acceptor π-π interaction was found to be important in the one-electron reduction via electron transfer from organic superelectron donor.[16] Hence, the electron-rich organocatalyst with larger surface area may enhance the π-π interaction with the aryl halides and facilitates the electron transfer process.

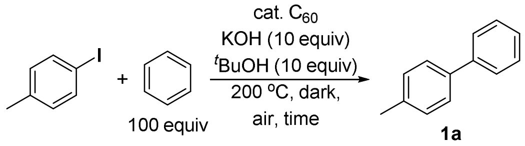
Inspired by the report from Fukuzumi and Kadish, C_{60} can be readily reduced by MeO^- to generate a mixture of electron-rich $C_{60}(OMe)_2^{\bullet-}$ and $C_{60}^{\bullet-}$ radical anion.[17] Taking the advantage of large surface area of C_{60} and its spherical shape to maximize π-π interaction (Table 1, entry 6), the combination of C_{60} and a strong base serves as the potential reducing agent for aryl halides in catalytic direct C-H arylation. Herein we report the C_{60}-catalyzed direct C-H arylation of benzene with aryl iodides in air with only 1 mol% loading of C_{60}.

2. Results and discussion

Initially, treatment of 4-iodotoluene (1 equiv) with KOH (10 equiv), ^{t}BuOH (10 equiv) and C_{60} (5 mol%) in benzene (100 equiv) at 200 °C under N_2 for 2.5 h gave direct C-H arylation product 4-methylbiphenyl **1a** in 59% yield (Table 2, entry 1). To our delight, the reaction was compatible with air and yielded 68% of **1a** in 3 h (Table 2, entry 2).

With 2.5 mol% C_{60} loading, the reaction took 6.5 h for completion to yield 65% of **1a** (Table 2, entry 3). Further lowering the catalyst loading to 1 mol% produced **1a** in 71% yield in 9 h (Table 2, entry 4). Surprisingly, the reaction also proceeded smoothly with only 0.1 mol% of C_{60} to yield 58% of **1a** in 36 h (Table 2, entry 5). The high catalytic activity of C_{60} is consistent with its large surface area (Table 1).

Table 2. C_{60} loading effects on C_{60}-catalyzed direct C-H arylation of benzene

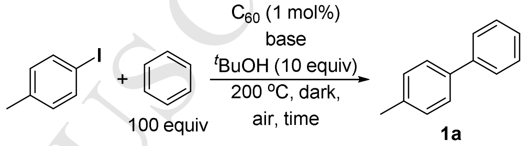


Entry	C_{60} loading/ mol%	Time / h	Yield **1a** / %[a]
1[b]	5	2.5	59
2	5	3	68
3	2.5	6.5	65
4	1	9	71
5	0.1	36	58
6	0	72	32

[a] GC yield.

[b] Under N_2

Table 3. Base effects on C_{60}-catalyzed direct C-H arylation of benzene



Entry	Bases	Equiv	Time / h	Yield **1a** / %[a]
1	NaOH	10	36	12
2	KOH	10	9	71
3	CsOH	10	3	47
4[b]	KOH	10	30	14
5[b]	^{t}BuOK	10	3	40
6	KOH	20	3.5	71
7	KOH	30	3	57
8[c]	KOH	20	15	60

[a] GC yield.

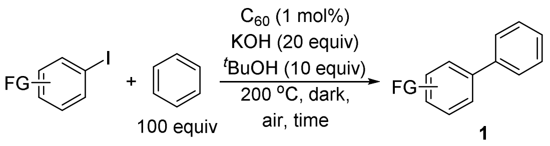
[b] Without ^{t}BuOH.

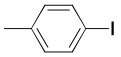
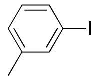
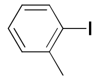
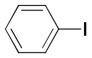
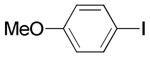
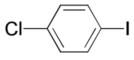
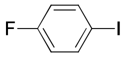
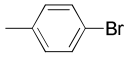
[c] 180 °C

Control experiment without C_{60} yielded 32% of **1a** in 72 h (Table 2, entry 6). The formation of **1a** is accounted by the direct reduction of 4-iodotoluene by KOH via single electron transfer to give the corresponding aryl iodide radical anion, which further reacts according to the mechanism depicted in Scheme 1.[14a] Alternatively, 4-iodotoluene reacts with KOH to generate an aryne intermediate, which is then trapped by benzene.[18] Therefore, the formation of **1a** in the absence of C_{60} is minor due to its longer reaction time and much lower product yield. The conditions shown in Table 1, entry 4 was chosen for investigations on base effects at reasonably low C_{60} loading (1 mol%) and short reaction time.

The cations of group 1 metal hydroxides affect the coupling reaction significantly. Among the three Group 1 metal hydroxides examined, KOH was the best base (Table 3, entries 1-3). Although CsOH took a shorter reaction time, lower yield of **1a** was resulted due to the co-formation of significant amounts of 4-*t*-butoxytoluene and 3-*t*-butoxytoluene (Table 3, entry 3). The nucleophilic aromatic substitution of 4-iodotoluene with *t*-butoxide, formed in situ from KOH and ^{t}BuOH, through benzyne mechanism became significant.[19] Without any ^{t}BuOH, the yield of **1a** decreased significantly even after 30 h (Table 3, entry 4). We reasoned that ^{t}BuOH help to solubilize KOH better in benzene.

Table 4. C_{60}-catalyzed direct C-H arylation of benzene with aryl iodides



Entry	Aryl Halides	Time / h	Product	Yield / %[a]
1		3.5	**1a**	71
2		5	**1b**	79
3		13	**1c**	43
4		3	**1d**	78
5		3.5	**1e**	71
6		3.5	**1f** **1g**[b]	Trace 74
7		4.5	**1h** **1g**[b]	38 47
8		72	**1a**	11

[a] GC yield.

[b] **1g** = *p*-terphenyl

The direct use of ^tBuOK instead of KOH/^tBuOH combination was not satisfactory (Table 3, entry 5). **1a** was yielded in 40% after 3 h with the co-formation of 4-*t*-butoxytoluene and 3-*t*-butoxytoluene in about 1:1 ratio from GCMS analysis.[20] Increasing the KOH loading to 20 equiv shortened the reaction time to 3.5 h (Table 3, entry 6). 30 Equiv of KOH led to significant substitution products and hence decreased **1a** yield (Table 3, entry 7).

Finally, we attempted to carry out the coupling reaction at milder temperature. The reaction at 180 °C was slowed down to 15 h with only 60% yield of **1a** (Table 3, entry 8). Therefore we selected the conditions in Table 2, entry 6 as the optimal conditions to examine the substrate scopes.

The optimized conditions proved to be general to various aryl iodides (Table 4). 3-Iodotoluene as well as iodobenzene underwent smooth direct C-H arylation with benzene to give **1b** and **1d** in good yields (Table 4, entries 2 and 4). Electron rich 4-iodoanisole reacted well to produce **1e** in 71% yield (Table 4, entry 5). The sterically demanding 2-iodotoluene gave the coupling product **1c** in 43% yield (Table 4, entry 3). Cross-coupling involving aryl bromide was unsatisfactory (Table 4, entry 8).

4-Chloroiodobenzene underwent double-arylation with benzene to yield 74% of *p*-terphenyl **1g** as the major product in 3.5 h, with only trace amount of mono-arylated product 4-chlorobiphenyl **1f** formed (Table 4, entry 6). The double-arylation was less extensive for 4-fluoroiodobenzene, yielding 38% of mono-arylated product 4-fluorobiphenyl **1h** and 47% of di-arylated product **1g** after 4.5 h (Table 4, entry 7). The mono-arylation occurs selectively at the more easily reduced Ar-I bond.[21]

To gain more insight on the C-H cleavage step, a competition experiment was performed by reacting 4-iodotoluene with an equimolar mixture of benzene and benzene-d_6 (eq 1). The KIE was measured to be 1.11±0.01 from GCMS analysis. Therefore the C-H bond cleavage is not rate-determining.

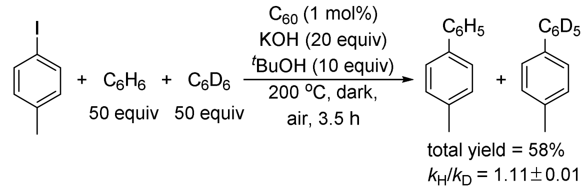
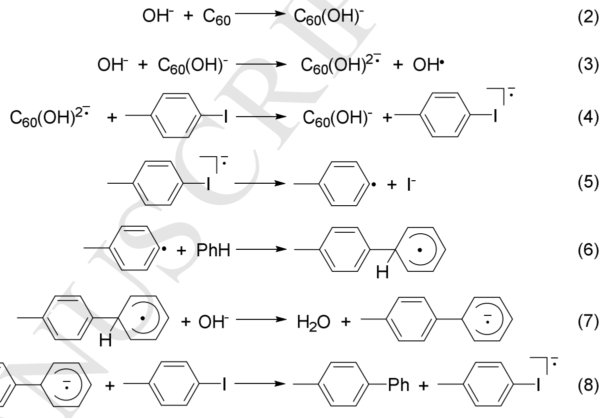


Table 5. Reaction enthalpies and Gibbs free energies at 298K and 473K using B3LYP/SVP. All energies are given in kcal/mol.



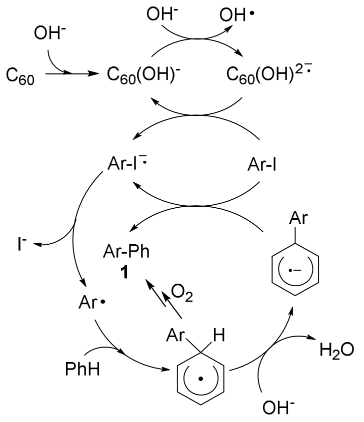
Reaction	ΔE	ΔG (298 K)	ΔG (473 K)
2	-115.6	-103.7	-84.4
3	10.2	6.8	-7.7
4	-19.3	-21.0	-8.9
5	10.2	4.0	0.4
6	-21.5	-7.2	0.3
7	-90.6	-91.9	-92.8
8	-14.8	-14.8	-15.7

To gain mechanistic understandings on the C_{60}-catalyzed direct C-H arylation and the nature of electron donor, we carried out DFT calculations and evaluated the thermodynamics of each reaction steps at both 298 K and 473 K using 4-iodotoluene as substrate (Table 5). The calculations were performed using hybrid functional B3LYP[22] with split-valence-ζ plus polarization basis sets (SVP)[23] implemented in Gaussian 03.[24]

As C_{60} is an ideal electron receptor, it easily reacts with OH^- to form $C_{60}(OH)^-$ anion (eq 2).[25] The reaction is highly favorable with ΔG of -84.4 kcal/mol at 473 K. This agrees with the spontaneous addition of MeO^- to C_{60} giving $C_{60}(OMe)^-$ with equilibrium constant estimated to be 4.3×10^5 M^{-1}.[17] Further reaction of $C_{60}(OH)^-$ with OH^- produces hydroxyl radical and $C_{60}(OH)^{2\bullet-}$ (eq 3). Although it is endergonic at 298 K, it becomes exergonic at 473 K, indicating that temperature plays an essential role for this step. $C_{60}(OH)^{2\bullet-}$ then transfers an electron to 4-iodotoluene to generate an aryl iodide radical anion with the recovery of $C_{60}(OH)^-$ (eq 4). It is shown that $C_{60}(OH)^{2\bullet-}$ is the reducing agent for 4-iodotoluene. Direct electron transfer from $C_{60}(OH)^-$ to 4-iodotoluene is endergonic by more than 50 kcal/mol and therefore $C_{60}(OH)^-$ is not the electron donor.

The cleavage of C-I bond in aryl iodide radical anion to form aryl radical and iodide is more favorable at 473 K (eq 5). The addition of aryl radical to benzene generate cyclohexadienyl radical (eq 6), which can easily be deprotonated by excess OH^- to generate biaryl radical anion with ΔG of -92.8 kcal/mol (eq 7).[10] Biaryl radical anion then transfer electron to 4-iodotoluene to yield another aryl iodide radical anion and furnish the biaryl product (eq 8).

Based on the experimental findings, DFT calculations and previous accepted mechanism, a catalytic cycle for the C_{60}-catalyzed direct C-H arylation is proposed in Scheme 2. Instead of deprotonation of electron donor precursor by base,[13] the reaction is initiated by addition of OH^- to C_{60} to form $C_{60}(OH)^-$, which is faster in the presence of O_2.[25] Then, a single electron transfer from another OH^- to $C_{60}(OH)^-$ generates the $C_{60}(OH)^{2\bullet-}$. $C_{60}(OH)^{2\bullet-}$ with a large surface area interacts with Ar-I via π-π interaction and reduces it to form an aryl iodide radical anion, which undergoes Ar-I cleavage to eliminate I^- and produces an aryl radical . The aryl radical adds to benzene to generate a cyclohexadienyl radical intermediate, which is deprotonated by OH^- to give biaryl radical anion.[10] This radical anion undergoes one electron transfer to Ar-I to yield the coupling product **1** and the new aryl iodide radical anion to complete the catalytic cycle. Alternatively, direct aromatization of the cyclohexadienyl radical with O_2 also leads to **1**.[26] The reaction is thus compatible with air.

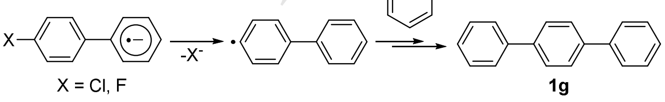


Scheme 2. Proposed catalytic cycle of C_{60}-catalyzed direct C-H arylation

The formation of *p*-terphenyl **1g** from 4-haloiodobenzene is due to a competitive intramolecular reduction process (Scheme 3). Instead of electron transfer to another aryl iodide substrate, the 4-halobiaryl radical anion eliminates the halide anion to give biaryl radical, which couples with benzene to yield **1g**.

3. Conclusions

In summary, C_{60} reacts with KOH to give electron rich $C_{60}(OH)^{2\bullet-}$ for the reduction of aryl iodides, which initiates the catalytic direct C-H arylation of benzene in air. The large surface area of C_{60} greatly enhances the catalytic activity and allows loading down to 0.1 mol%.



Scheme 3. Proposed mechanism for *p*-terphenyl formation

4. Experimental section

4.1 General.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography in air. ^1H NMR spectra were recorded on a Bruker AvanceIII 400 (400 MHz) spectrometer. Spectra were referenced internally to the solvent residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (*J*) are reported in hertz (Hz). GC-MS analysis was conducted on a GCMS-QP2010 Plus system using a Rtx-5MS column (30 m x 0.25 mm). The details of GC program are as follow: The column oven temperature and injection temperature were 100.0 and 290.0 ^oC. Helium was used as carrier gas. Flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with pressure 68.8 kPa. The total flow, column flow and purge flow were 13.5, 0.95 and 3.0 mL min^{-1}, respectively. Split mode injection with split ratio 10.0 was applied. Samples were injected as solutions in hexane. The GC oven was held at 100.0 ^oC for 2 min, ramped to 250.0 ^oC at 30.0 ^oC min^{-1}, and held at 250.0 ^oC for 1 min. The detector was a quadrupole MS with 70 eV electron impact ionization. Naphthalene was used as internal standard. Unless specified, all the reactions were carried out in a closed system under air and dark in a thick-wall glass tube equipped with a Teflon-stoppered Rotaflo stopcock. The reaction vessel was covered with aluminum foil to protect from light and was heated on an aluminum block. Cardboard was used as protective shield around the heater. The reactions were duplicated and the yields are the average yields. The coupling products are known compounds and with identical properties to those reported in the literature.

4.2 Procedures for the C_{60} loading effects on catalytic direct C-H arylation of benzene.

4.2.1. With 5 mol% C_{60} under N_2. C_{60} (8.1 mg, 0.0112 mmol), 4-iodotoluene (48.8 mg, 0.224 mmol), KOH (125 mg, 2.24 mmol) and ^tBuOH (215 μL, 2.24 mmol) were dissolved in benzene (2.0 mL, 22.4 mmol). The mixture was degassed for three freeze-pump-thaw cycles and heated at 200 °C. After confirming the complete consumption of the aryl halide by GCMS analysis the solvent was removed by rotary evaporator. The crude residue was purified by column chromatography (silica gel, 230-400 mesh) eluting with hexane to afford the 4-methylbiphenyl **1a**.

4.2.2. With 5 mol% C_{60} under air. C_{60} (8.1 mg, 0.0112 mmol), 4-iodotoluene (48.8 mg, 0.224 mmol), KOH (125 mg, 2.24 mmol), ^tBuOH (215 μL, 2.24 mmol) were dissolved in benzene (2.0 mL, 22.4 mmol). The mixture was heated at 200 °C. After confirming the complete consumption of the aryl halide by GCMS analysis the solvent was removed by rotary evaporator. The crude residue was purified by column chromatography (silica gel, 230-400 mesh) eluting with hexane to afford the 4-methylbiphenyl **1a**.

4.2.3. With 2.5 mol% C_{60} under air. The procedures follow the same as 5 mol% C_{60} under air except C_{60} (4.0 mg, 0.0056 mmol) was used.

4.2.4. With 1 mol% C_{60} under air. The procedures follow the same as 5 mol% C_{60} under air except C_{60} (1.6 mg, 0.00224 mmol) was used.

4.2.5. With 0.1 mol% C_{60} under air. The procedures follow the same as 5 mol% C_{60} under air except C_{60} (0.16 mg, 0.224 μmol) was used.

4.2.6. Without C_{60} under air. The procedures follow the same as 5 mol% C_{60} under air except no C_{60} was added.

4.3 Procedures for the base effects on catalytic direct C-H arylation of benzene.

4.3.1. With 10 equiv NaOH. C_{60} (1.6 mg, 0.00224 mmol), 4-iodotoluene (48.8 mg, 0.224 mmol), NaOH (89.6 mg, 2.24 mmol), ^{t}BuOH (215 μL, 2.24 mmol) were dissolved in benzene (2.0 mL, 22.4 mmol). The mixture was heated at 200 °C. After confirming the complete consumption of the aryl halide by GCMS analysis the solvent was removed by rotary evaporator. The crude residue was purified by column chromatography (silica gel, 230-400 mesh) eluting with hexane to afford the 4-methylbiphenyl **1a**.

4.3.2. With 10 equiv CsOH. The procedures follow the same as 10 equiv NaOH except CsOH (336 mg, 2.24 mmol) was used.

4.3.3. With 10 equiv KOH and without ^{t}BuOH. The procedures follow the same as 10 equiv NaOH except KOH (125 mg, 2.24 mmol) and no ^{t}BuOH were used.

4.3.4. With 10 equiv ^{t}BuOK and without ^{t}BuOH. The procedures follow the same as 10 equiv NaOH except ^{t}BuOK (251 mg, 2.24 mmol) and no ^{t}BuOH were used.

4.3.5. With 20 equiv KOH. The procedures follow the same as 10 equiv NaOH except KOH (251 mg, 4.48 mmol) was used.

4.3.6. With 30 equiv KOH. The procedures follow the same as 10 equiv NaOH except KOH (377 mg, 6.72 mmol) was used.

4.3.7. With 20 equiv KOH at 180 ^{o}C. The procedures follow the same as 10 equiv NaOH except KOH (251 mg, 4.48 mmol) was used and the reaction was heated at 180 °C.

4.4 General Procedures for the C_{60}-catalytic direct C-H arylation of benzene with aryl halides.

C_{60} (0.00224 mmol), aryl halides (0.224 mmol), KOH (4.48 mmol) and ^{t}BuOH (2.24 mmol) were dissolved in benzene (2.0 mL, 22.4 mmol). The mixture was heated at 200 °C. After confirming the complete consumption of the aryl halide by GCMS analysis the solvent was removed by rotary evaporator. The crude residue was purified by column chromatography (silica gel, 230-400 mesh) eluting with hexane to afford the corresponding biaryls **1**.

*4.4.1. 4-Methylbiphenyl (**1a**).*[4b] 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 7.24 (d, *J* = 7.9 Hz, 2 H), 7.32 (t, *J* = 7.3 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 7.4 Hz, 2 H).

*4.4.2. 3-Methylbiphenl (**1b**).*[4b] 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 7.17 (d, *J* = 7.3 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 2 H), 7.39-7.45 (m, 4 H), 7.59 (d, *J* = 7.3 Hz, 2 H).

*4.4.3. 2-Methylbiphenyl (**1c**).*[4b] 43% yield. Inseparable with biphenyl by column chromatography. ^{1}H NMR(400 MHz, $CDCl_3$) δ 2.27 (s, 3 H), 7.24-7.26 (m, 4 H), 7.31-7.35 (m, 3 H), 7.40 (d, *J* =7.3 Hz, 2 H).

*4.4.4. Biphenyl (**1d**).*[4b] 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 7.60 (d, *J* = 7.4 Hz, 4 H).

*4.4.5. 4-Methoxybiphenyl (**1e**).*[4b] 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3 H), 6.98 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 2 H), 7.54 (t, *J* = 8.3 Hz, 4 H).

*4.4.6. 4-Chlorobiphenyl (**1f**).* Attempted purification by column chromatography was failed due to trace amount formation.

*4.4.7. p-Terphenyl (**1g**).*[4b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.3 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 4 H), δ 7.65 (d, *J* = 7.6 Hz, 4 H), δ 7.68 (s, 4 H).

*4.4.8. 4-Fluorobiphenyl (**1h**).*[4b] 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.6 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.53-7.56 (m, 4 H).

Acknowledgments

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Supplementary Material

Details of competition experiment, ^{1}H NMR spectra of the isolated products and a typical GCMS spectrum. Supplementary data associated with this article can be found in the online version, at

Supplementary Materials

C_{60}-Catalyzed direct C-H arylation of benzene with aryl iodides in air

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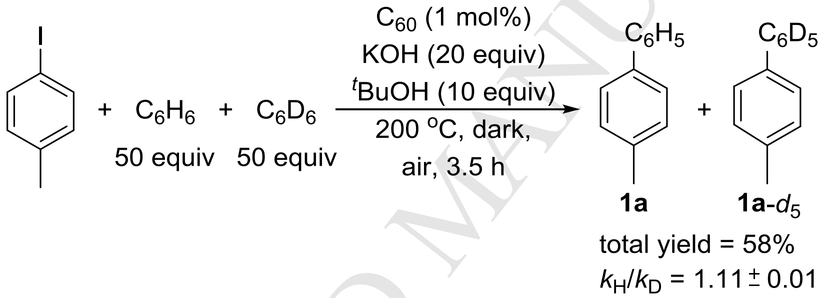
3. GCMS Spectrum 7

Competition Experiment. C_{60} (1.6 mg, 0.00224 mmol), 4-iodotoluene (48.8 mg, 0.224 mmol), KOH (251 mg, 4.48 mmol), ^{t}BuOH (215 μL, 2.24 mmol) were added in benzene (1.0 mL, 11.2 mmol) and benzene-d_6 (0.991 mL, 11.2 mmol). The mixture was heated at 200 °C. The isotopic ratio was determined from the relative ratio of the total absolute intensities of m/z at 168 (**1a**) and at 173 (**1a**-d_5) from retention time 6.292 min to 6.483 min in GCMS analysis. The intensity ratio of **1a**/**1a**-d_5 gave the KIE value, e.g. 7388282/6660115 = 1.11.



Product	m/z	Total absolute intensities
1a	168	7388282
1a-d_5	173	6660115

^{1}H NMR Spectra of Products

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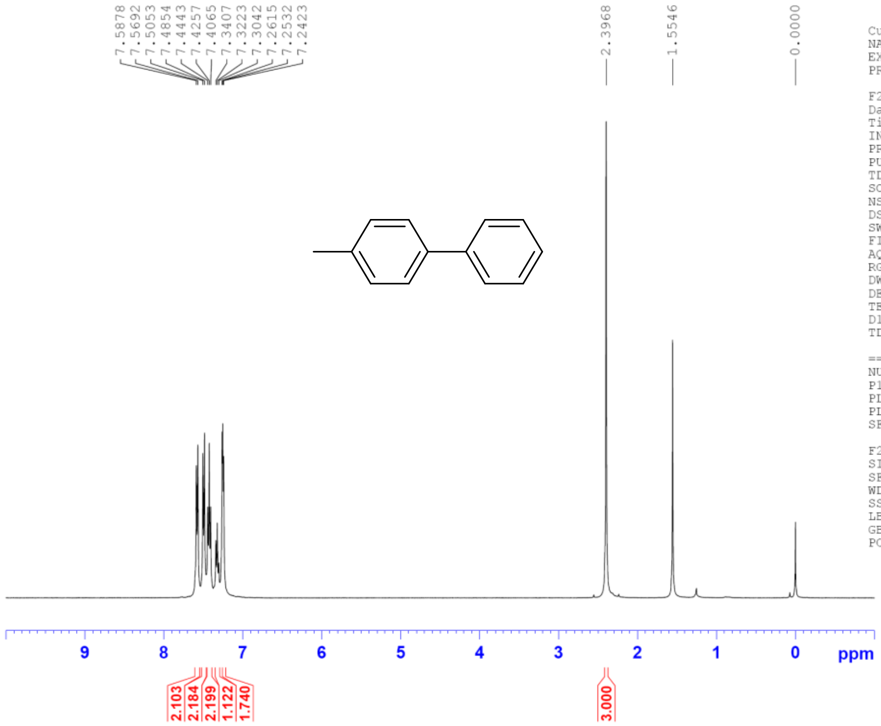

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DS                       2
SWH              12019.230 Hz
FIDRES            0.183399 Hz
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RG                     203
DW                  41.600 usec
DE                    6.50 usec
TE                   294.7 K
D1              1.00000000 sec
TD0                      1

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GB        0
PC                    1.00
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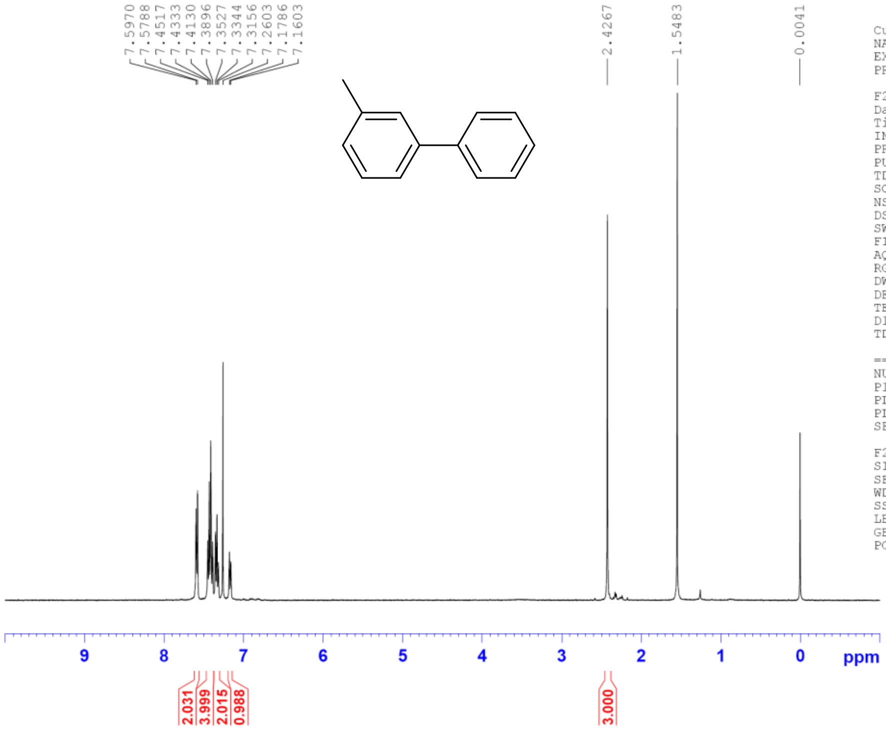

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TD                   65536
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DS                       2
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     128
DW                  41.600 usec
DE                    6.50 usec
TE                   298.7 K
D1              1.00000000 sec
TD0                      1

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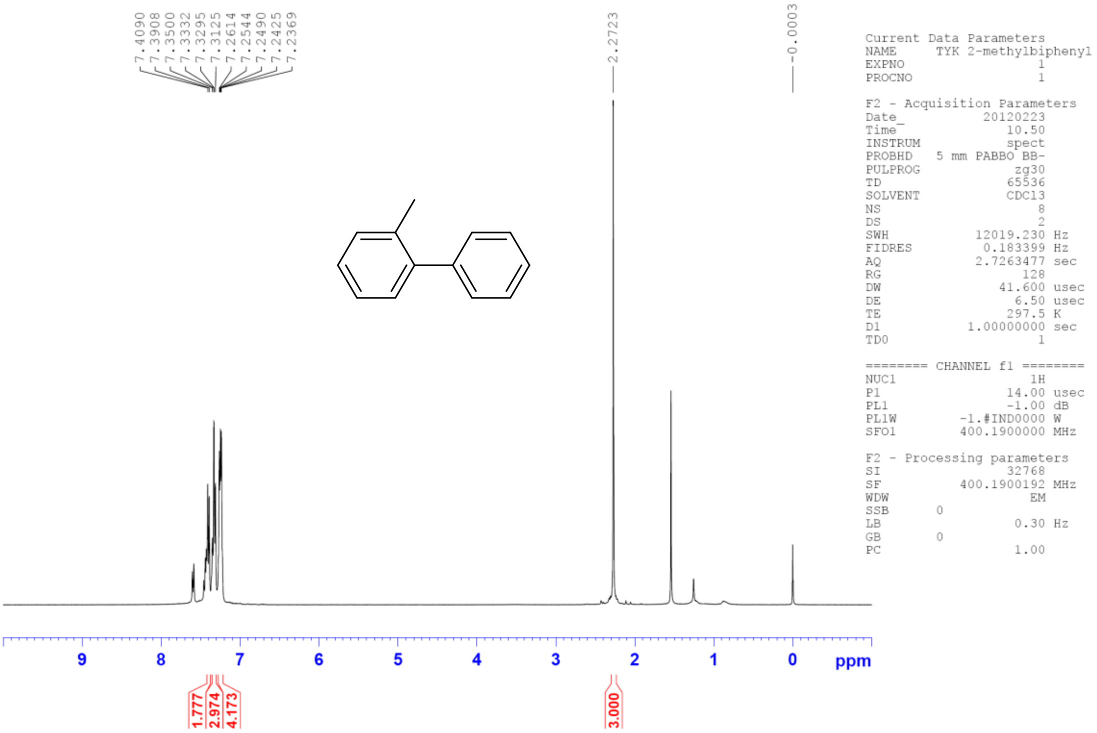

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DS                       2
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FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     128
DW                  41.600 usec
DE                    6.50 usec
TE                   297.5 K
D1              1.00000000 sec
TD0                      1

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PL1                  -1.00 dB
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SFO1           400.1900000 MHz

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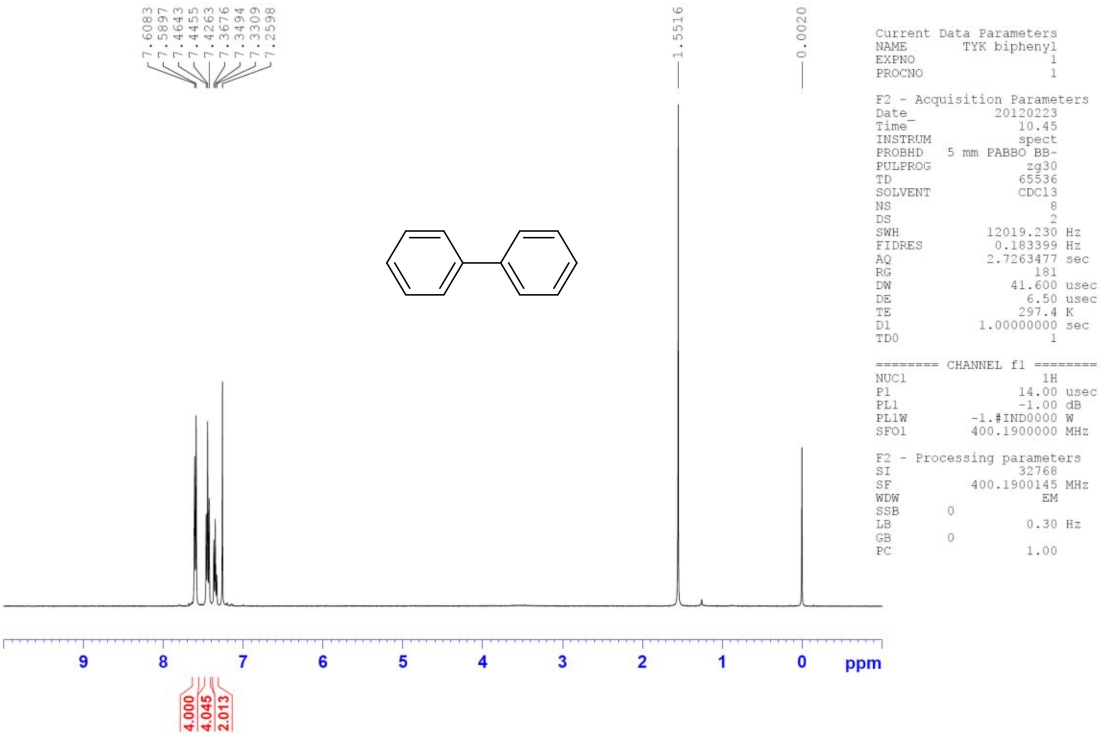
```

Biphenyl **1d**



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TD0                      1

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F2 - Processing parameters
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PC                    1.00
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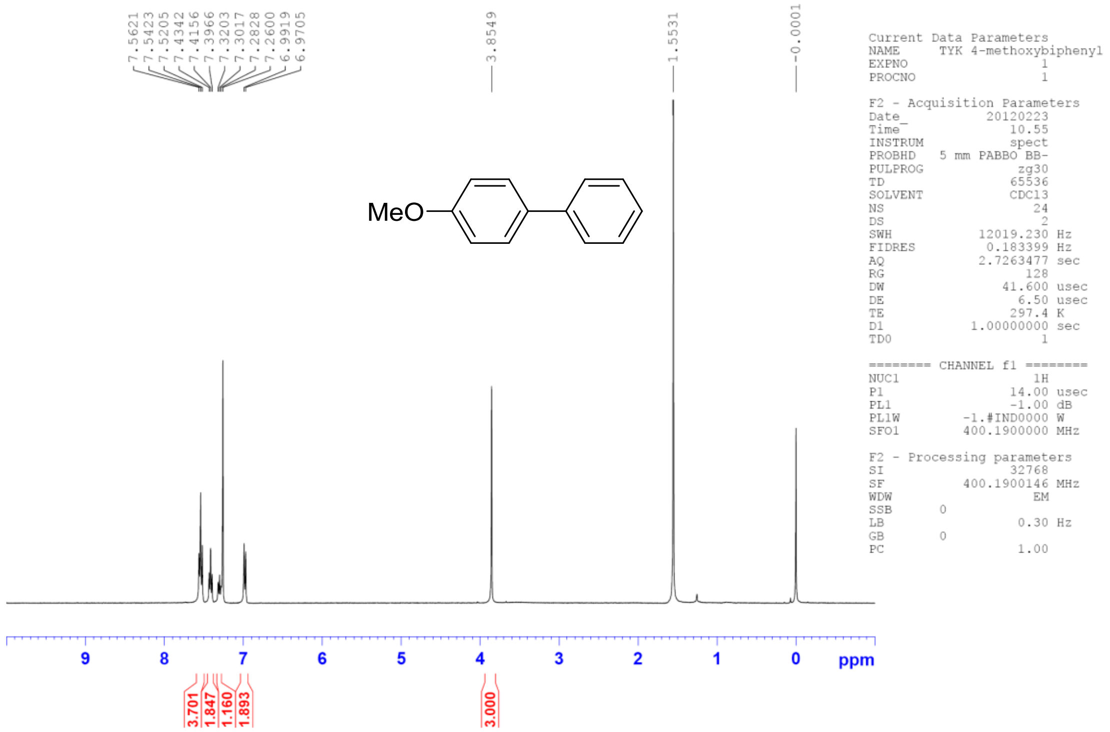
4-Methoxybiphenyl **1e**



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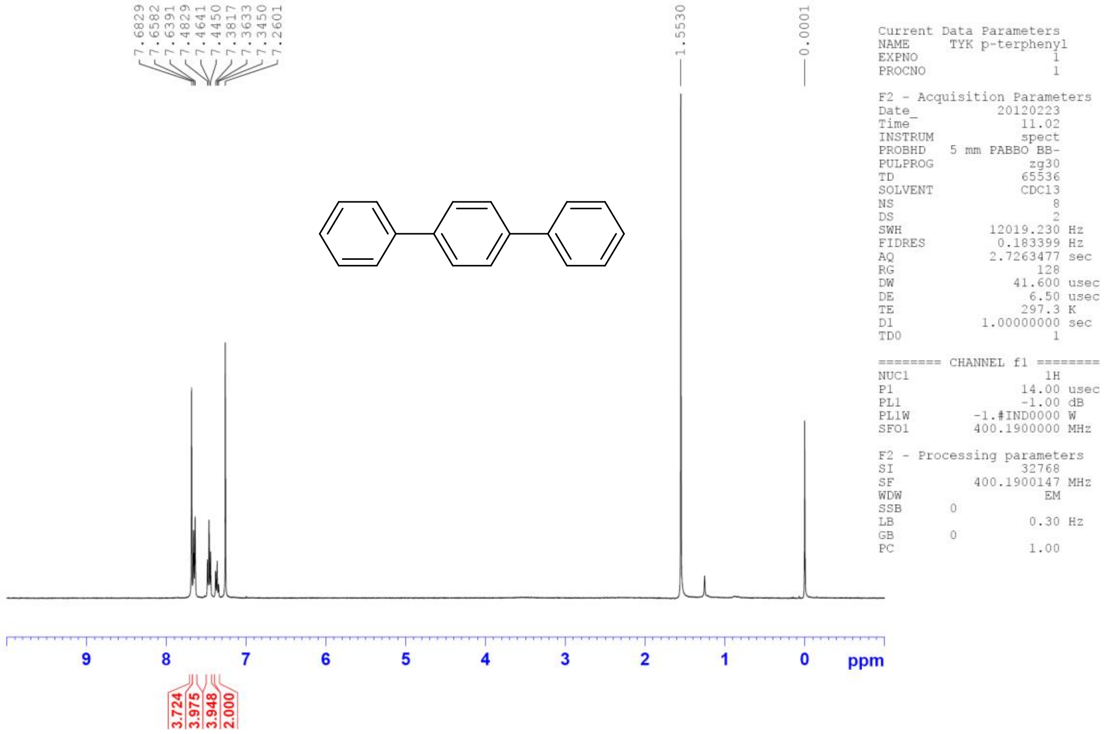

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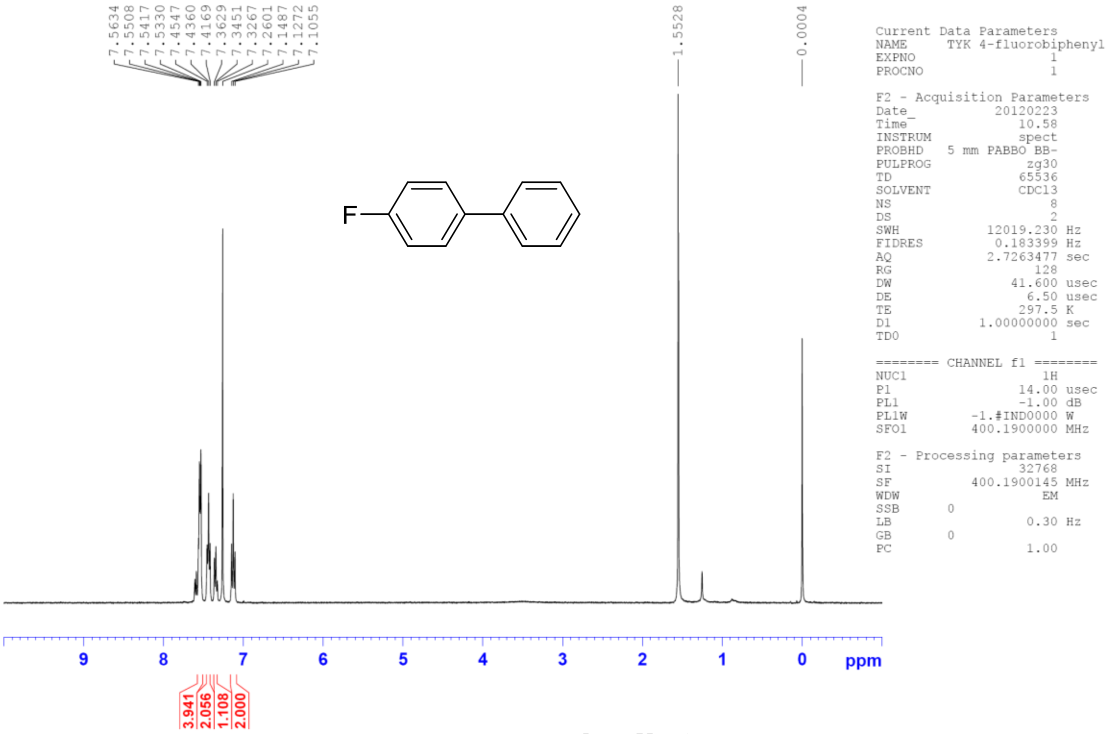

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PROCNO                       1

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FIDRES                0.183399 Hz
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RG                         128
DW                      41.600 usec
DE                        6.50 usec
TE                       297.5 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
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P1                       14.00 usec
PL1                      -1.00 dB
PL1W               -1.#IND0000 W
SFO1               400.1900000 MHz

F2 - Processing parameters
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GCMS Spectrum

Typical spectrum showing the product analysis of C_{60}-catalyzed direct C-H arylation of benzene with 4-iodotoluene

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Sample Amount	: 1
Dilution Facto	: 1
Vial #	: 10
Injection Volume	: 1
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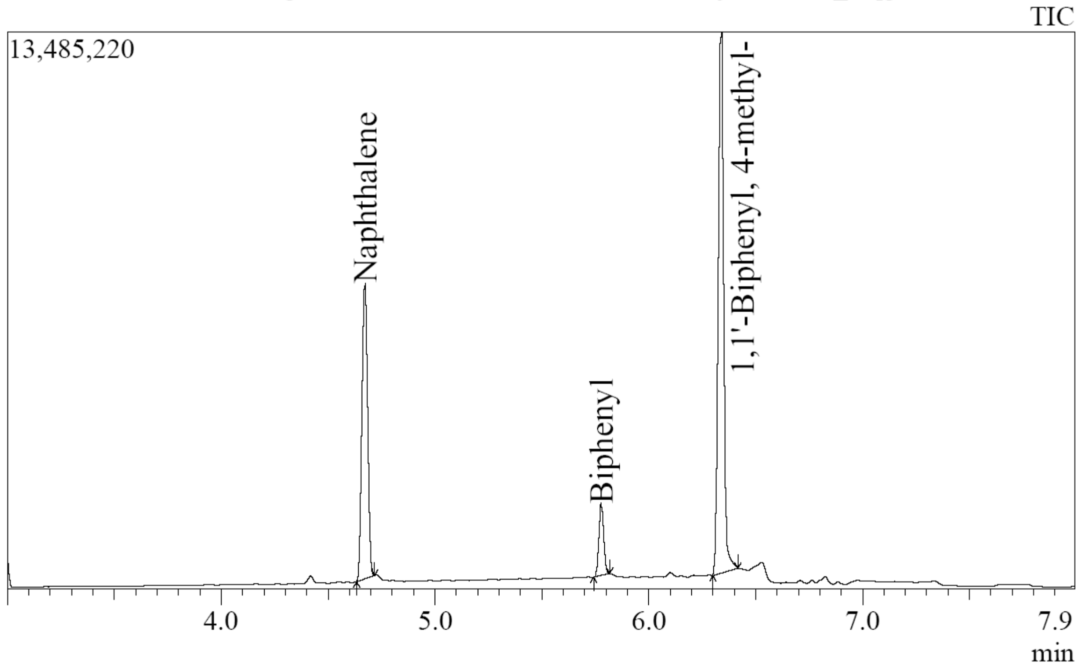

Quantitative Result Table

Name	ID#	I.Time	R.Time	F.Time	m/z	Area
Naphthalene	1	4.625	4.671	4.975	128.00	7828051
Biphenyl	2	5.733	5.777	5.892	154.00	1121653
1,1'-Bipheny	3	6.300	6.337	6.533	168.00	6325634