Electronic Supporting Information for

Aromatization Modulates the Activity of Small Organic Molecules as Promoters for Carbon-Halogen Bond Activation

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Contents

1. General Information

Experimental. Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon or oven-driven sealed tube (with a Teflon screw cap). Air- and moisture-sensitive liquids and solutions were transferred by syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC was performed on silica gel GF_{254} plates. The TLC plates were visualized by either ultraviolet light (λ = 254 nm). Purification of products was accomplished by flash column chromatography on silica gel (InnochemSilicaFlashP60, 230-400 mesh).

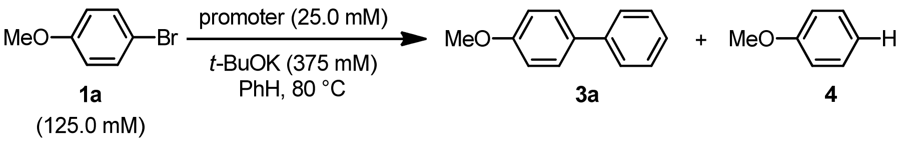
Chemicals. Reagent grade benzene was purchased from Aladdin and was distilled over sodium-potassium alloy under an argon atmosphere. The distilled benzene was further deoxygenated by three freeze-pump-thaw cycles before use. Indoline and *t*-BuOK was purchased from J&K Scientific and TCI respectively and used without further purification. 4-iodoanisole, 4-bromoanisole, chlorobenzene, which stored in glove box before use. Other chemicals were purchased from various commercial sources and were used as received. Other chemicals were synthesized following the published procedures.

Analytical. NMR spectra were recorded on a Bruker AVANCE III HD 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometer. The ^{1}H NMR spectra were calibrated against the peak of tetramethylsilane (TMS, 0 ppm) and the ^{13}C NMR spectra were calibrated against the peak of $CDCl_3$ (77.16 ppm). GC analysis was performed on a Shimadzu GC-2010 instrument equipped with a FID detector using nitrogen as the carrier gas. GC-MS analysis was performed on a Shimadzu GCMS-QO2010SE instrument equipped with an EIS detector using helium as the carrier gas.

2. The Model Coupling Reaction Employing Different Promoters

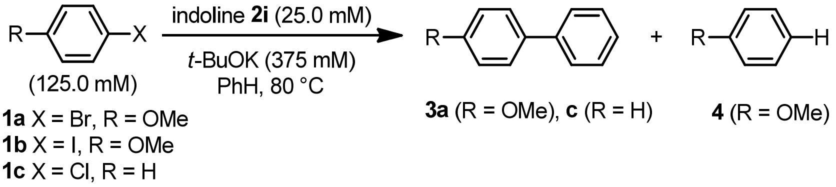
A variety of additives were employed in the coupling reaction to find an effective molecule to achieve the activation of carbon-bromide bond in bromoarene **1a**. For those promoters employed in this test, $PhNHCH_3$ (**2a**) and *p*-$MeOPhNHCH_3$ (**2b**) were purchased from J&K Scientific; *p*-$HOPhNHCH_3$ (**2c**),[1] *p*-$Me_2NPhNHCH_3$ (**2d**),[2] *p*-$PhPhNHCH_3$ (**2e**),[1] *N*-methyl-1-naphthylamine (**2f**),[3] *N*-methyl-2-naphthylamine (**2g**),[4] and 5-methoxy-*N*-methyl-[1,1'-biphenyl]-2-amine (**2h**)[5] were synthesized following the published procedure.

2.1 Procedure for the model reaction employing *N*-methylaniline derivatives (2a-h) as the promoter



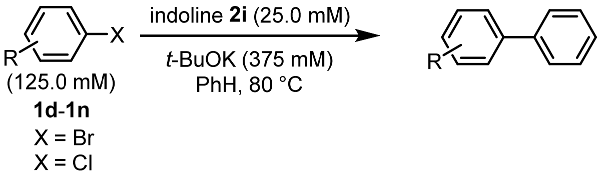
To a 10 mL Schlenk tube charged with **1a** (93.5 mg, 0.50 mmol) and *t*-BuOK (168 mg, 1.50 mmol) and additives (0.10 mmol) was added dry benzene (4 mL) under argon. The reaction mixture was stirred in an oil bath at 85 °C for 19 h. After cooled to room temperature, a solution of *n*-dodecane (4 mL, specific concentration) in toluene was added as the standard, followed by water. After stirred for 2 min, the organic layer was separated and analyzed by GC to obtain both conversion and yield of the reaction.

2.2 General procedure for the model reactions employing indoline (2i) as the promoter



To a 10 mL Schlenk tube charged with aryl halides (0.50 mmol) and *t*-BuOK (168 mg, 1.50 mmol) and indoline (0.10 mmol) was added dry benzene (4 mL) under argon. The reaction mixture was stirred in an oil bath at 85 °C for 12 h. After cooled to room temperature, a solution of *n*-dodecane (4 mL, specific concentration) in toluene was added as the standard, followed by water. After stirred for 2 min, the organic layer was separated and analyzed by GC to obtain both conversion and yield of the reaction.

2.3 Procedure for the BHAS reactions of various haloarenes employing indoline (2i) as the promoter



To a 10 mL Schlenk tube charged with aryl halides (0.50 mmol) and *t*-BuOK (168 mg, 1.50 mmol) and indoline (0.10 mmol) was added dry benzene (4 mL) under argon. The reaction mixture was stirred in an oil bath at 85 °C for 12 h. After cooled to room temperature, a solution of *n*-dodecane (4 mL, specific concentration) in ether was added as the standard, followed by water. After stirred for 2 min, an aliquot of the organic layer was taken and analyzed by GC to obtain the conversion of the substrate. Then the rest organic phase was separated, dried over Na_2SO_4 and concentrated. After purification by flash column chromatography, the product was obtained. The spectroscopic data were consistent with those reported in literature.[6]

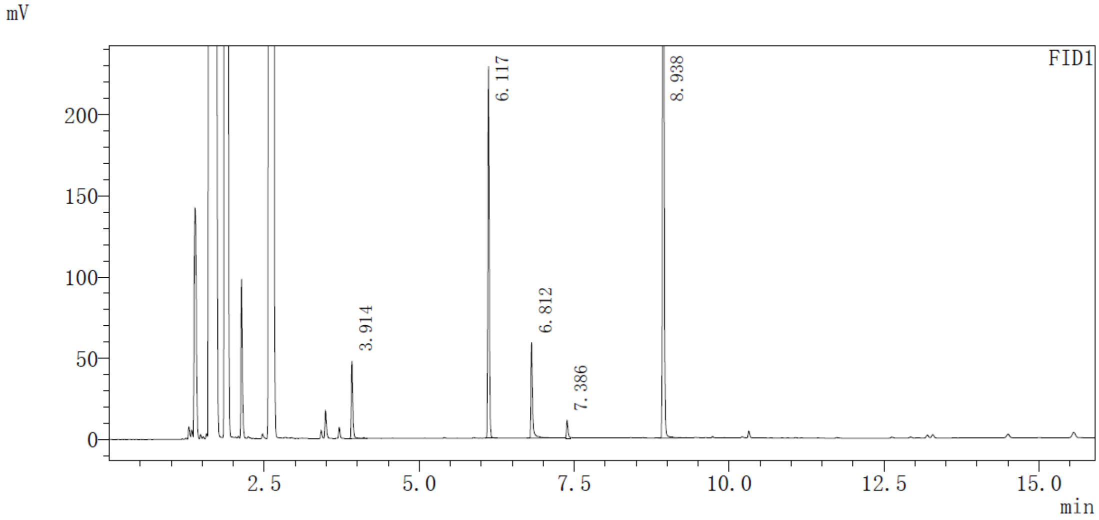


Figure S1. Representative GC trace of the model reaction mixture of **1b** as substrate. GC conditions: capillary column (0.25 mm × 30 m), constant pressure mode (160 kPa), inlet temperature 250 °C, split ratio 30:1, FID temperature 300 °C, initial temperature 50 °C, keep for 1.5 min, temperature elevation rate 25 °C/min, final temperature 260 °C, keep for 2 min.

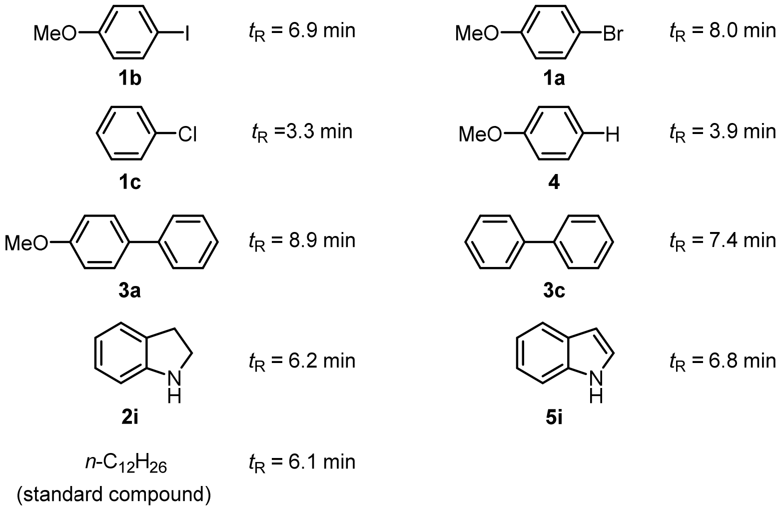
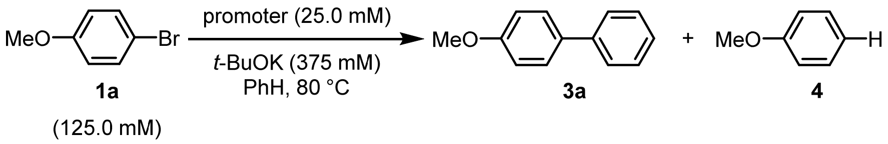


Figure S2. Retention times for identified components in the model reaction under the specified GC conditions. The retention times were determined by GC analysis of authentic samples.

2.4 Results

Table S1. Conversion and yield data for the model reaction employing *N*-methylaniline derivatives (**2a-h)** as the promoter



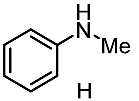
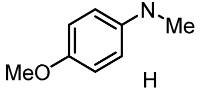
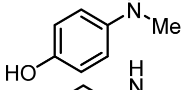
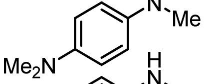
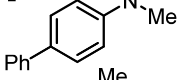
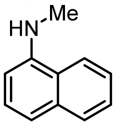
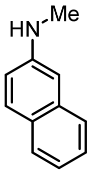
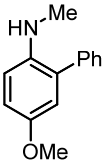
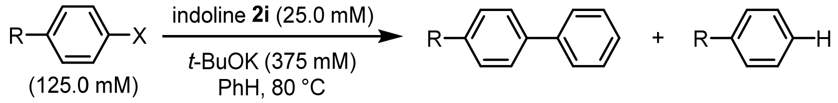
Entry	Promoters	Conversion (%)	Yield (%)	
		1a	**3a**	**4**
1	 (**2a**)	6	3	<1
2	 (**2b**)	17	9	3
3	 (**2c**)	20	10	3
4	 (**2d**)	30	15	6
5	 (**2e**)	13	8	2
6	 (**2f**)	5	0.7	0.2
7	 (**2g**)	10	3	0.6
8	 (**2h**)	10	1	1.7

Table S2. Conversion and yield data for the model reactions employing indoline (**2i**) as the promoter.



(125.0 mM)
1a X = Br, R = OMe
1b X = I, R = OMe
1c X = Cl, R = H

3a (R = OMe), **c** (R = H)

4 (R = OMe)

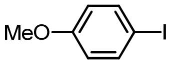
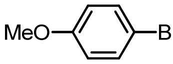
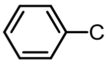
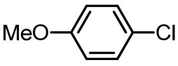
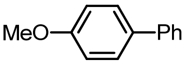
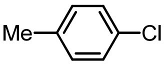
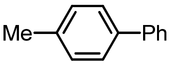
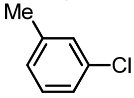
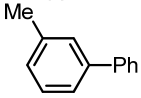
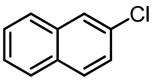
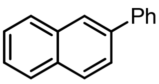
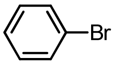
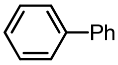
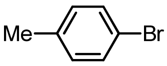
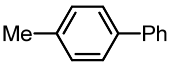
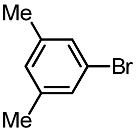
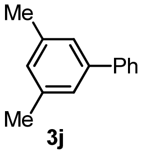
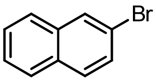
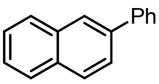
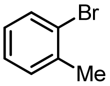
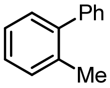
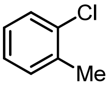
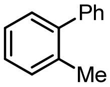
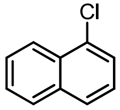
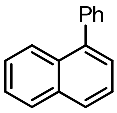
Entry	Substrate	Conversion (%)	Yield (%)	
			3a/3c	**4**
1	 (**1b**)	>99	79	15
2	 (**1a**)	>99	74	13
3	 (**1c**)	70	56	N/A

Table S3. Conversion and yield data for the BHAS reactions of various haloarenes employing indoline (**2i**) as the promoter.

Entry	Substrate	Product	Conversion	Isolated yield (GC yield)
1	 **1d**	 **3a**	66%	36% (40%)
2	 **1e**	 **3e**	64%	45% (52%)
3	 **1f**	 **3f**	65%	53% (59%)
4	 **1g**	 **3g**	89%	53% (61%)
5	 **1h**	 **3c**	98%	74% (79%)
6	 **1i**	 **3e**	89%	78% (83%)
7	 **1j**	 **3j**	75%	53% (57%)
8	 **1k**	 **3g**	99%	65% (70%)
9	 **1l**	 **3l**	50%	26% (30%)
10	 **1m**	 **3l**	35%	11% (20%)
11	 **1n**	 **3n**	35%	19% (23%)

Note: For the reactions employing the substrates with an *ortho*-substitution, the yields were generally low (entries 9-11).

4-methoxybiphenyl (3a):

^{1}H NMR (400MHz, CDCl$_3$): δ 7.54 (m, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 114.4, 55.5.

4-methylbiphenyl (3e):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.61 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 21.2.

3-methylbiphenyl (3f):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.62 (m, 2H), 7.31-7.35 (m, 6H), 7.20 (d, J = 7.4 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 141.4, 138.5, 128.8, 127.3, 126.6, 124.4, 21.7.

2-phenylnaphthalene (3g):

^{1}H NMR (400MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.986-7.83 (m, 3H), 7.71-7.76 (m, 3H), 7.46-7.53 (m, 4H), 7.36-7.40 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 129.0, 128.6, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 126.0, 125.7.

Biphenyl (3h):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.64-7.67 (m, 4H), 7.48-7.53 (m, 4H), 7.37-7.42 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 128.9, 127.4, 127.3.

3,5-Dimethyl-1,1'-biphenyl (3j):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.39-7.44 (m, 2H), 7.33-7.36 (m, 1H), 7.24 (br s, 2H), 7.03 (s, 1H), 2.38 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 141.4, 138.4, 129.0, 128.8, 127.3, 127.2, 125.2, 21.6.

2-methylbiphenyl (3l):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.40-7.34 (m, 3H), 7.31-7.26 (m, 4H), 2.30 (s, 3H).

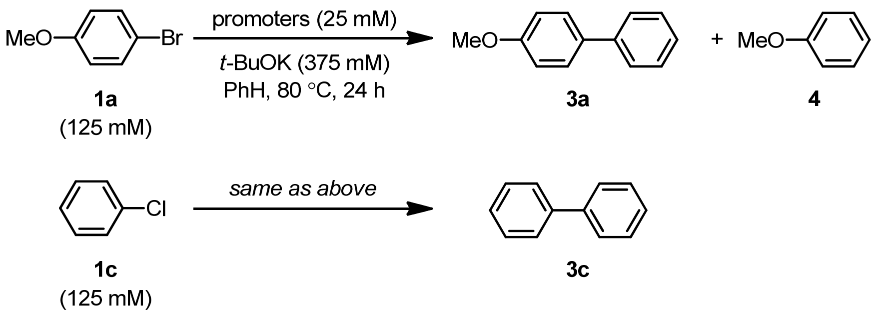
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 135.5, 130.4, 130.0, 129.3, 128.2, 127.4, 126.9, 125.9, 20.6.

1-phenylnaphthalene (3n):

^{1}H NMR (400MHz, $CDCl_3$): δ 7.92-7.85 (m, 3H), 7.55-7.40 (m, 9H).

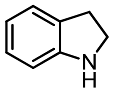
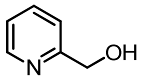
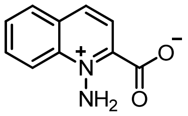
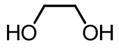
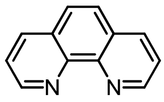
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.4, 133.9, 131.7, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 126.1, 126.0, 125.9, 125.5.

3. Comparison of Different Promoters



Following the experimental procedure described in section 2.2, a variety of promoters which have been reported to furnish the activation of carbon-bromide bonds were employed in the model coupling reactions (shown above) to compare with the reactivity of the indoline/*t*-BuOK system. For those promoters employed in this test, 2-pyrididyl carbinol, ethylene glycol, and 1,10-phenanthroline were purchased from J&K Scientific; quinolone-1-amino-2-carboxylic acid[7] was synthesized following the published procedure. The results were summarized in Table S4.

Table S4. Conversion and yield data for the model reaction employing different promoters.

promoters					
conversion of **1a** (%)	99	89	33	11	8
yield of **3a** (%)	74	37	22	0.6	1
yield of **4** (%)	18	19	4	0.5	0.5
conversion of **1c** (%)	70	18	4	4	4
yield of **3c** (%)	56	0.6	<1	<1	<1

Note: For the reaction employing 2-pyrididyl carbinol as the promoter, the original publication reported 81% yield of **3a** when **1a** was used as the substrate. However, under identical conditions we only obtained 37% yield of **3a** after repeating for several times.

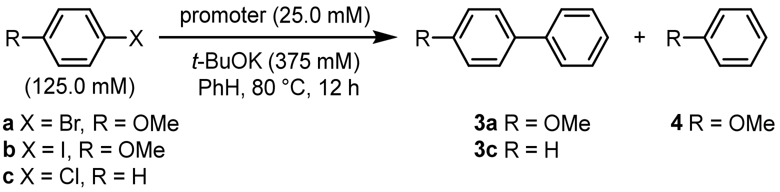
4. Effect of Promoter Structure on Activity

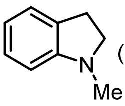
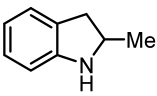
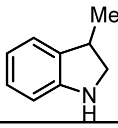
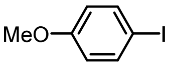
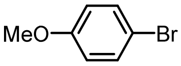
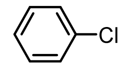
Following the experimental procedure described in Section 2.2, a variety of indoline derivatives were employed in the BHAS reaction as promoters to gain insight into the relationship between structure on reactivity. For those promoters employed in this study, 1,2,3,4-tertrahydroquinoline (**2k**) and 2-methylindoline (**2p**) were purchased from J&K Scientific; 3,3-dimethylindoline (**2j**),[8] *N*-isobutylaniline (**2l**),[9] 1-methylindoline (**2o**),[10] 3-methylindoline (**2q**),[11] cis-(2,3)-dimethylindoline (**2r**),[12] trans-(2,3)-dimethylindoline (**2s**),[13] 5-methylindoline (**2t**),[13] 5-methoxylindoline (**2w**), [14] and *N*,*N*-dimethylindolin-5-amine (**2x**)[15] were synthesized following the published procedure.

4.1 Effect of alkyl substitution

First, indoline derivatives bearing methyl substitution at different positions were employed as promoters (Table S5). The results indicated that the first step might be the deprotonation process between indoline and *t*-BuOK to afford *N*-centered anion, which was similar to the *N*-methylaniline/*t*-BuOK system in the initiation mechanism.

Table S5. Conversion and yield data for the model reaction employing various promoters.

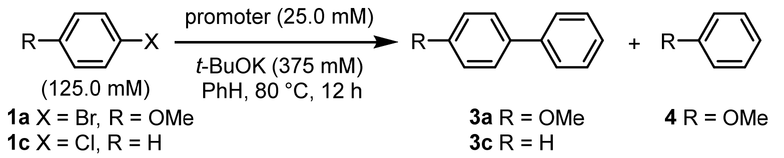


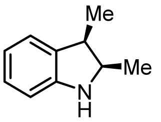
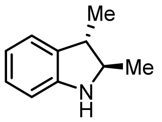
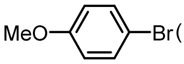
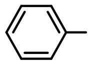
Entry	ArX	 (**2o**)			 (**2p**)			 (**2q**)		
		conv.(%)	yield(%)		conv.(%)	yield(%)		conv.(%)	yield(%)	
			3	4		3	4		3	4
1	 (**1b**)	18	10	2	99	72	18	98	70	17
2	 (**1a**)	21	4	<1	97	64	17	95	70	14
3	 (**1c**)	<1	0	N/A	56	54	N/A	60	54	N/A

4.2 Effect of stereochemistry

Second, 2,3-dimethyl substituted indoline with either cis or trans stereochemistry were employed as promoters (Table S6). The results indicated that the generated *N*-centered radical (Int-2) is then deprotonated by *t*-BuOK to form a radical anion (Int-3), which was agreement with proposed mechanism.

Table S6. Conversion and yield data for the model reaction employing various promoters considering stereochemistry effect.

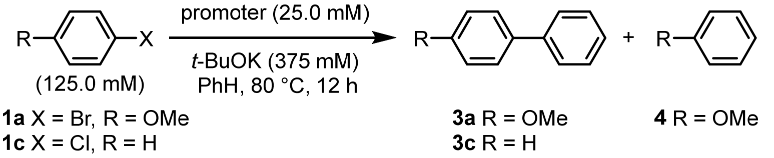


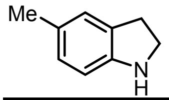
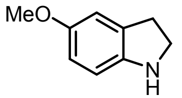
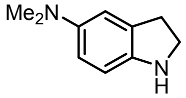
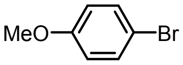
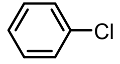
Entry	ArX	 (**2r**)			 (**2s**)		
		conv.(%)	yield(%)		conv.(%)	yield(%)	
			3	**4**		**3**	**4**
1	 (**1a**)	57	47	7	30	21	7
2	 (**1c**)	23	15	N/A	10	1	N/A

4.3 Effect of electronic substituent

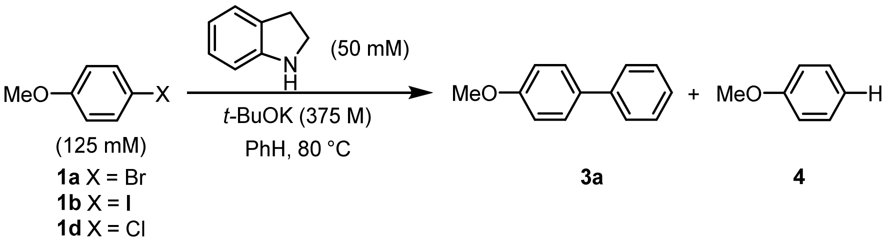
Third, indoline derivatives with different electronic substituents were employed as promoters (Table S7). The results indicated that the activity of the model reaction had no obvious improvements by employing indoline derivatives baring electron-donating substituents on its benzene cycle. The reason might that the rate of the side reaction where the indoline was directly oxidized to indole without the participation of substrate might be improved compared to the main initiation cycle, which was known as side reaction.

Table S7. Conversion and yield data for the model reaction employing various promoters considering electronic effect.



Entry	ArX	 (**2t**)			 (**2w**)			 (**2x**)		
		conv.(%)	yield(%)		conv.(%)	yield(%)		conv.(%)	yield(%)	
			3	**4**		**3**	**4**		**3**	**4**
1	 (**1a**)	-	-	-	63	45	13	38	19	7
2	 (**1c**)	50	30	N/A	10	1	N/A	10	2	N/A

5. The Kinetic Profiles for the Indoline-Promoted Reactions



Kinetic profiles of the BHAS reactions of ArI (**1b**), ArBr (**1a**), and ArCl (**1d**) were acquired by GC. A 25 mL Schlenk tube equipped with magnetic stirrer was charged with *t*-BuOK (336 mg, 3.00 mmol), and diphenyl (77.0 mg, 0.50 mmol, as internal standard) in a glove box. Dry benzene (6.0 mL) taken by a Hamilton syringe was added under a balloon pressure of argon. The reaction mixture was stirred in an oil bath at 85 °C for 5 minutes. To another 25 mL Schlenk flask charged with the indoline as additive (0.60 mmol) was added dry benzene (3.0 mL) under argon, and then 2.0 mL of the resulting solution was transferred by another Hamilton syringe to the former flask to start the reaction. Aliquots (ca. 0.1 mL) were taken from the reaction mixture at an interval of some mixture. Each aliquot was placed into a sample bottle containing an aqueous solution of water (ca. 0.8 mL) and ether (ca. 0.5 mL). After shaking, the organic phases were separated and analyzed by GC to measure the concentrations of indoline and its related end-product. The kinetic data are summarized at Table S8 and were used to construct Figure S3, S4, S5.

Table S8. Kinetic data for the model reaction employing indoline (**2i**) as promoter

entry	(A)				(B)				(C)			
	time (min)	[**1b**] (mM)	[**3a**] (mM)	[**4**] (mM)	time (min)	[**1a**] (mM)	[**3a**] (mM)	[**4**] (mM)	time (min)	[**1d**] (mM)	[**3a**] (mM)	[**4**] (mM)
1	10	112.4	6.3	3.9	10	118.0	6.8	2.8	10	124.6	0	0
2	20	106.4	9.5	5.5	20	104.5	13.7	6.1	20	123.9	1.2	0
3	30	100.7	13.0	7.2	30	95.0	19.5	7.1	30	123.9	1.3	0.4
4	40	88.1	20.2	10.7	40	85.9	25.1	10.2	40	122.5	0.9	0.6
5	50	75.9	29.0	14.2	50	77.8	30.7	11.8	50	121.4	1.5	0.9
6	60	64.5	35.4	16.6	60	70	35.3	13.4	60	117.2	4.5	1.8
7	70	56	40.9	18.5	70	61.6	41	14.8	70	111	7.7	3.4
8	80	47.7	51.5	22.1	80	54.2	45.4	15.9	80	105	10.5	5.3
9	90	40.7	51.5	22.1	90	47.9	50.1	17.0	90	99.8	13.4	5.8
10	100	34.8	56	23.2	100	41.1	55.9	18.2	100	95.7	15.7	6.8
11	110	29.3	60.2	24.4	110	35.7	59.5	18.9	110	91.3	18.7	7.9
12	120	23.8	65.1	25.4	120	32	63.2	19.9	120	86.9	19.5	8.6
13	135	18.5	68.6	26.5	130	27.3	65.9	20.4	130	83	23	9.5
14	150	14.8	72	27.1	140	23.4	69.8	20.8	140	77.7	28	10.6
15	165	11.8	74.5	27.5	150	22.5	71.9	21.1	150	67.7	33.7	12.4
16	180	8.9	76.5	28	165	17.9	73.4	19	180	67.7	33.7	12.4
17	195	6.4	77.6	28.2	180	15.6	74.7	21.5	195	62.6	37.2	13.1
18	225	1.56	81.1	29.1	195	14	76.3	22	210	58.3	40.6	14
19	255	0.4	81.4	29.4	225	12.5	78.3	22.2	225	53.8	43	14.5
20	285	0	82.6	29.4	255	11.1	79.6	22.4	240	49.9	46.5	14.5
21					290	10	80.8	22.3	255	47.3	49	15.5
22					310	9.4	80.6	22.4	270	45.2	51.2	16.1
23					330	8.8	81.3	22.4	285	41.7	52.9	16.2
24					405	7.7	81.6	22.6	315	38.8	55.2	16.2
25					495	6.2	82.7	22.5	345	37.4	56.7	16.6
26									375	36.4	56.7	16.6
27									405	36	57.4	17
28									450	36.1	57.5	16.8

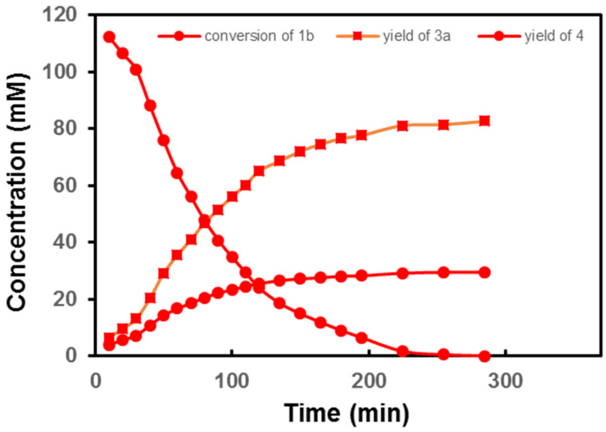


Figure S3. The kinetic profile of the conversion and yield for the model reaction between 4-iodoanisole (**1b)** and benzene.

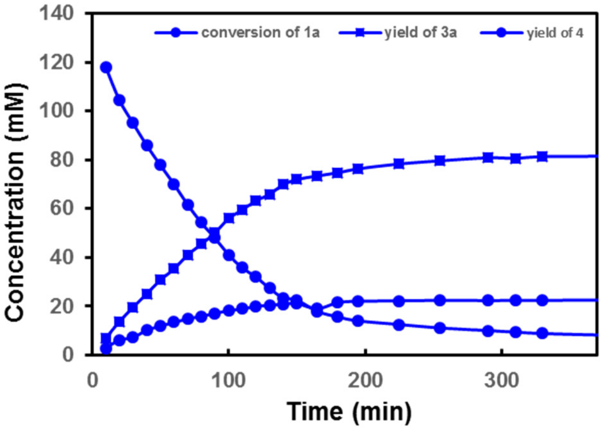


Figure S4. The kinetic profile of the conversion and yield for the model reaction between 4-bromoanisole (**1a)** and benzene.

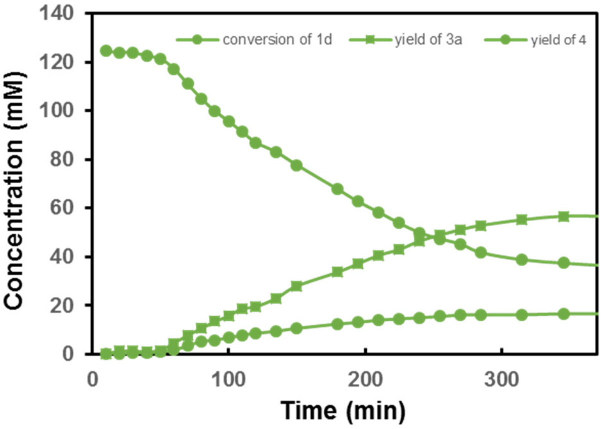


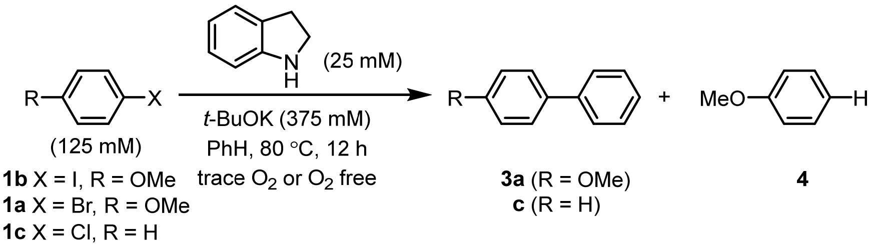
Figure S5. The kinetic profile of the conversion and yield for the model reaction between 4-chloroanisole (**1d)** and benzene.

6. Effect of Oxygen on the Initiation

Indoline was employed as promoter in the model reaction between aryl halides and benzene to gain insight into the differences of the reactivity under trace oxygen and oxygen free conditions. And kinetic detection also was conducted to judge whether the induction period would be affected by the amount of oxygen for the activation of carbon-chloride bonds.

6.1 Comparison of the reactions conducted under trace O_2 and O_2-free conditions

(1) The reactions of ArI **1b**, ArBr **1a**, and ArCl **1c** employing indoline as promoter were tested under normal argon-protected atmosphere (referred to as “trace O_2” condition) and rigorous oxygen-free atmosphere (referred to as “O_2-free” condition).



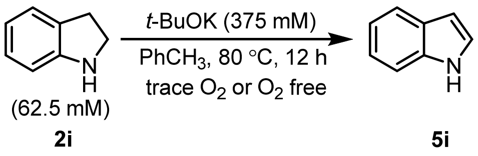
The experiments were conducted following the experimental procedure described in Section 2.2, except that:

For “O_2-free” condition, the freshly distilled anhydrous benzene (from sodium/benzophenone under Ar) was deoxygenated by three freeze-pump-thaw cycles before use, and the reactions were set up in a reaction tube sealed with a Teflon screw valve under argon;

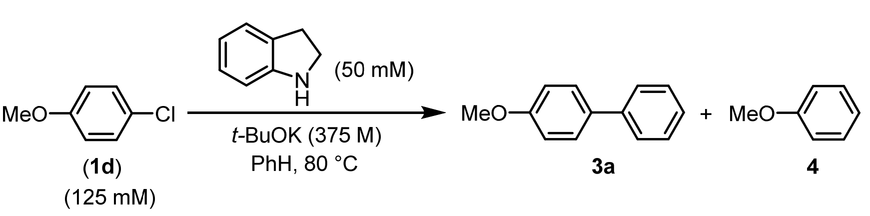
For “Trace O_2” condition, the distilled benzene was used without further degas procedure and the reactions were set up using a Schlenk tube with a rubber septum under argon.

The results were summarized in Scheme 2 in the main text.

(2) The background reaction, i.e. the conversion of indoline under the reaction conditions without haloarene substrate, was tested under both “Trace O_2” and “O_2-free” conditions following the experimental procedure was described in Section 2.2 (except that no haloarene substrate was added). The results were shown in Scheme 2 in the main text.



6.2 Kinetic profiles for the reaction of ArCl 1d: the effect of O_2



(1) Acquisition of the kinetic profile in the presence of O_2: A 25 mL Schlenk tube equipped with magnetic stirrer was charged with 4-chloroanisole (143 mg, 1.0 mmol), *t*-BuOK (336 mg, 3.00

mmol), and diphenyl (77.0 mg, 0.50 mmol, as internal standard) in a glove box. Dry benzene (6.0 mL) taken by a Hamilton syringe was added under a balloon pressure of argon. The reaction mixture was stirred in an oil bath at 85 °C for 5 minutes. To another 25 mL Schlenk flask charged with the indoline as additive (0.60 mmol) was added dry benzene (3.0 mL) under argon, and then 2.0 mL of the resulting solution was transferred by another Hamilton syringe to the former flask to start the reaction. After that, a balloon of oxygen was attached to the reaction flask. During the reaction progress, aliquots (ca. 0.1 mL) were taken from the reaction mixture at an interval of ca. 5 min. Each aliquot was placed into a sample bottle containing a mixture of water (ca. 0.8 mL) and ether (ca. 0.5 mL). After shaking, the organic phases were separated and analyzed by GC. The acquired kinetic data were shown in Table S9, which were used to construct Figure 2A in the main text.

(2) Acquisition of the kinetic profile with injection of O_2 during the induction period: A 25 mL Schlenk tube equipped with magnetic stirrer was charged with 4-chloroanisole (143 mg, 1.0 mmol), *t*-BuOK (336 mg, 3.00 mmol), and diphenyl (77.0 mg, 0.50 mmol, as internal standard) in a glove box. Dry benzene (6.0 mL) taken by a Hamilton syringe was added under a balloon pressure of argon. The reaction mixture was stirred in an oil bath at 85 °C for 5 minutes. To another 25 mL Schlenk flask charged with the indoline as additive (0.60 mmol) was added dry benzene (3.0 mL) under argon, and then 2.0 mL of the resulting solution was transferred by another Hamilton syringe to the former flask to start the reaction. Aliquots (ca. 0.1 mL) were taken from the reaction mixture at an interval of ca. 5 min. Each aliquot was placed into a sample bottle containing a mixture of water (ca. 0.8 mL) and ether (ca. 0.5 mL). After shaking, the organic phases were separated and analyzed by GC. After reacting for 30 minutes (still during the induction period), pure oxygen (10 mL) was injected to the reaction by a syringe. Sampling and GC analysis were continued for ca. 5 h. The acquired kinetic data were shown in Table S9, which were used to construct Figure 2B in the main text.

Table S9. Kinetic data for the 4-chloroanisole (**1d**). (A) In the presence of O_2; (B) With injection of oxygen at 30 minutes.

Entry	(A)				(B)					
	time (min)	[**1d**] (mM)	[**3a**] (mM)	[**4**] (mM)	time (min)	[**1d**] (mM)	[**3a**] (mM)	[**4**] (mM)	[indoline] (mM)	[indole] (mM)
1	10	122.2	7.6	2.0	5	125	0	0	43	1.8
2	20	108.3	18	4.5	13	125.4	0.18	0	43.5	1.8
3	30	97.4	27.6	6.6	20	125	0.15	0	43.5	1.8
4	40	86.3	37.5	8.3	28	123.9	0.4	0	43.4	1.8
5	50	78.7	44.8	9.3	35	117	2.9	1.1	26.5	16.6
6	60	73.4	49.8	9.9	45	113.3	6.4	1.9	14.7	24.7
7	70	71.8	54.3	10.2	55	108.9	8.4	2.3	9.3	29.3
8	80	69.7	55.4	10.2	65	108.5	9.1	2.4	6.3	35.7
9	90	69.5	56.1	10.4	75	107.6	8.9	2.3	4.4	36.4
10	100	66.7	55.7	10.4	85	108.8	9.3	2.3	3.4	38.9
11	110	69.4	56.1	10.3	100	108	8.9	2.3	2.3	38.4
12	120	67.2	56.1	10.3	115	107.8	9.1	2.3	1.6	38.2
13	135	66.9	56.6	10.5	130	108.8	9	2.4	1.6	37.1
14	160	69.4	56	10.3	145	108.7	9.2	2.3	1.4	36.7
15	210	69.2	56	10.4	165	108.8	9.3	2.4	1.1	37.4
16	300	68.5	55.5	10.2	210	108.6	9.1	2.2	0.7	36.8
					285	108.8	9.3	2.4	0	38.6

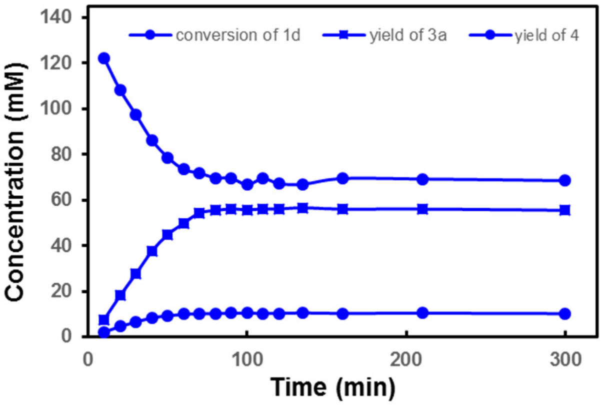


Figure S6. Kinetic profile for the model reaction between **1d** and benzene under Ar in the presence of O_2.

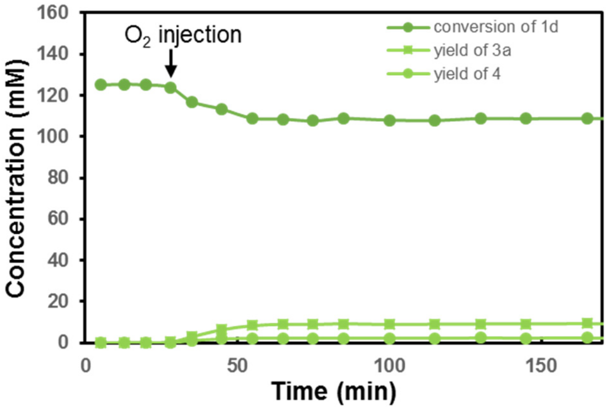
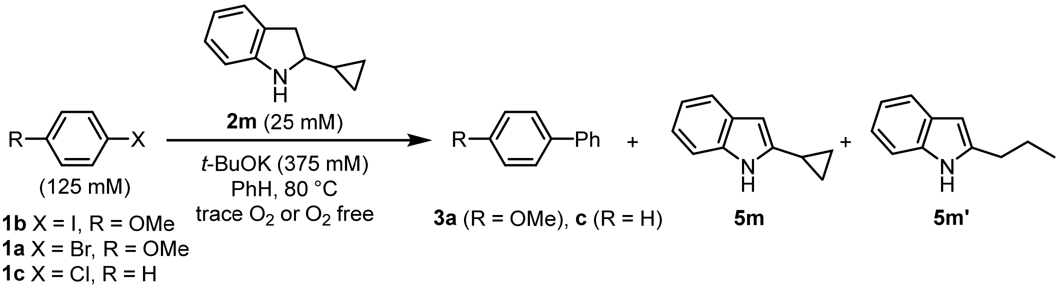


Figure S7. Kinetic profile for the model reaction between **1d** and benzene under Ar with injection of O_2.

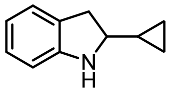
7. Mechanistic Study Employing Cyclopropyl-Substituted Indoline as a Probe

Aiming to gain insight into possible radical intermediate(s) involved in the reaction, 2-cyclopropylindoline (**2m**) and 3-cyclopropylindoline (**2n**) were employed in the BHAS reaction as mechanistic probes. Generation of radical intermediate with the radical centered on C2 or C3 position of indoline could induce radical ring-opening of the cyclopropane ring, producing the corresponding end-product. whether the related *N*-centered radical anion was existed in the initiation mechanism and further competition experiments were conducted to verify whether it could be a direct electron donor for substrate. 2-cyclopropylindoline and 3-cyclopropylindoline were synthesized following published procedure. [16]

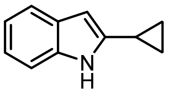
7.1 The model reaction employing 2-cyclopropylindoline (2m) as the probe molecule



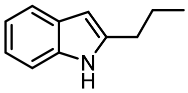
Following the experimental procedure described in Section 2.2, the reaction employing indoline **2m** as the promoter were conducted. GC-MS and NMR analysis disclosed the formation of both **5m** and **5m'** as the end-product of indoline **2m**. The results were given in Table S10.



t_R = 7.8 min



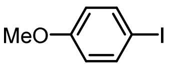
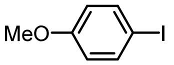
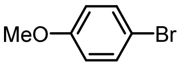
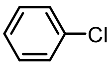
t_R = 8.8 min



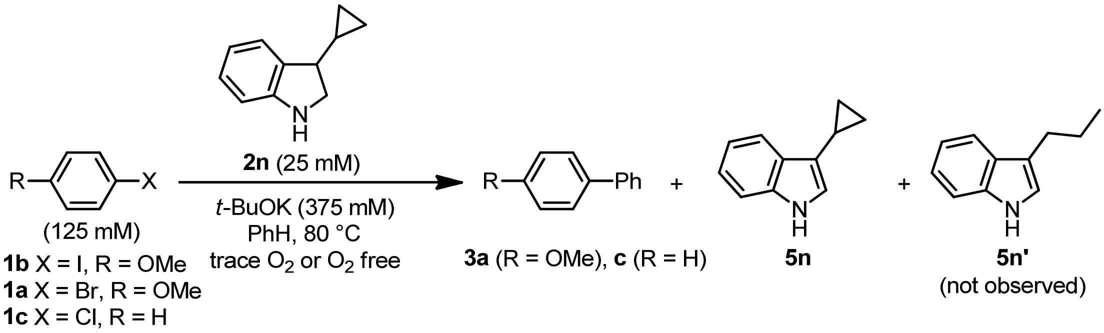
t_R =8.4 min

n-dedocane t_R = 6.1 min

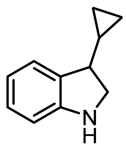
Table S10. Conversion and yield data for the model reaction employing 2-cyclopropylindoline (**2m**) as promoter under trace O$_2$ and O$_2$ free condition.

Entry	ArX	trace O$_2$						O$_2$ free					
		conv.(%)		yield(%)				conv.(%)		yield(%)			
		1a-1c	**2m**	**3a/3c**	**4**	**5m**	**5m'**	**1a-1c**	**2m**	**3a/3c**	**4**	**5m**	**5m'**
1	 **1a** (5 mM)	90	95	65	26	65	7	91	21	67	17	6	2
2	 **1a** (125 mM)	98	95	76	18	86	2	45	20	29	10	8	<1
3	 **1b** (125 mM)	41	99	20	5	82	4	10	23	1	<1	1	<1
4	 **1c** (125 mM)	21	97	11	N/A	74	6	1	13	1	N/A	1	<1

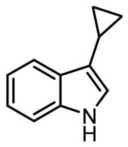
7.2 The model reaction employing 3-cyclopropylindoline (2n) as the probe molecule



Following the experimental procedure described in Section 2.2, the reaction employing indoline **2n** as the promoter were conducted. GC-MS and NMR analysis disclosed the formation of **5n** as the end-product of indoline **2n**. The results were given in Table S11. The ring opening end-product **5n'** was never observed, indicating that no indoline-derived radical species with the radical locating at C3-position was generated in the reaction.

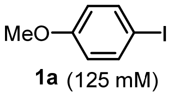
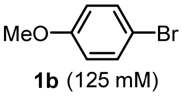
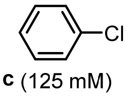


t_R = 7.9 min

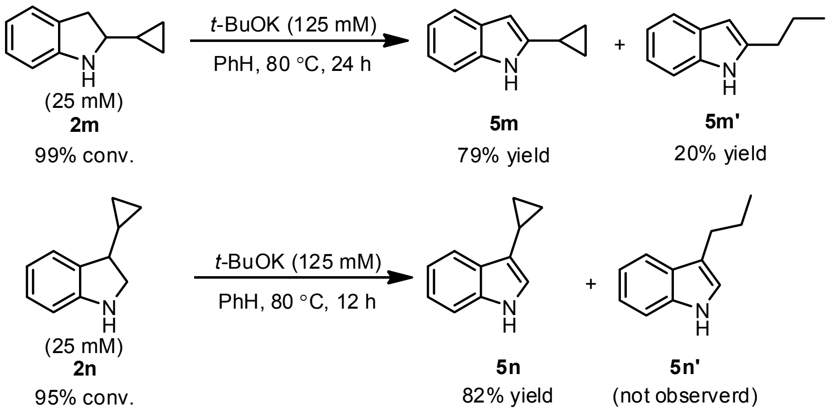


t_R = 8.9 min

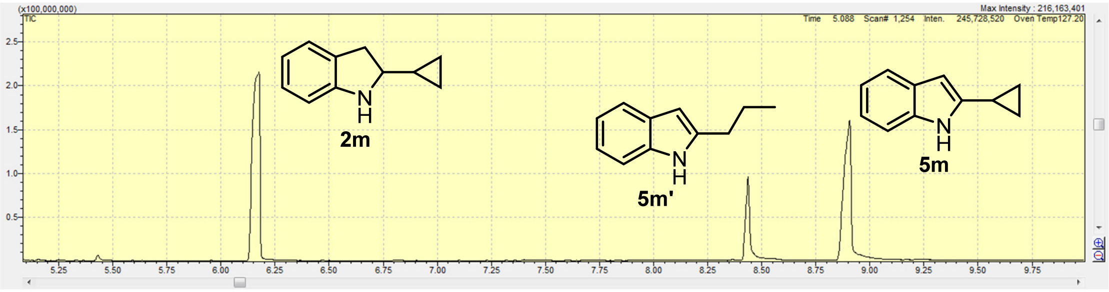
Table S11. Conversion and yield data for the model reaction employing 3-cyclopropylindoline (**2n**) as promoter under trace O_2 and O_2 free condition.

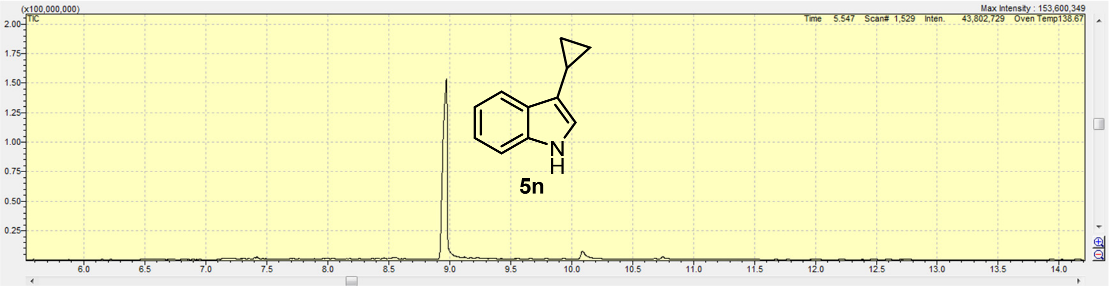
Entry	ArX	trace O_2						O_2 free					
		conv.(%)		yield(%)				conv.(%)		yield(%)			
		1a-1c	**2n**	**3a/3c**	**4**	**5n**	**5n'**	**1a-1c**	**2n**	**3a/3c**	**4**	**5n**	**5n'**
1	 **1a** (125 mM)	98	99	75	18	70	<1	36	40	15	5	24	<1
2	 **1b** (125 mM)	87	95	63	15	70	<1	19	30	4	2	15	<1
3	 **1c** (125 mM)	20	99	7	N/A	71	<1	10	6	<1	N/A	4	<1

7.3 The background reaction of 2-cyclopropylindoline (2m) and 3-cyclopropylindoline (2n)



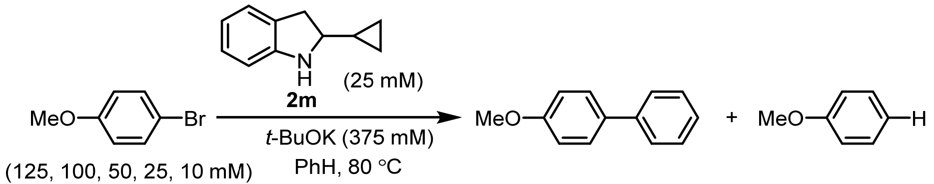
The background reaction, i.e. the conversion of indoline probe molecules **2m** and **2n** under the standard reaction conditions without haloarene substrate, was tested under both “Trace O_2” and “O_2-free” conditions following the experimental procedure was described in Section 2.2 (except that no haloarene substrate was added).





The results indicated that, the same as their behaviors in the model reactions, 2-cyclopropylindoline **2m** could produce a mixture of indole end-product **5m** and **5m’**, while 3-cyclopropylindiline **2n** could only produce indole **5n** as the end-product. This indicated that trace oxygen played an important role in the conversion of indole to indoline, and the involved radical intermediate has the radical locating at the C2 position of indoline.

7.4 Competition experiment



1a **3a** **4**

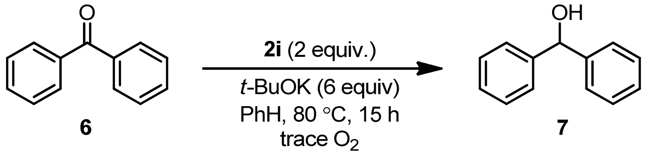
To probe whether the C2-centered radical species involves in the electron transfer process, a series of reactions were conducted employing bromoarene **1a** with different concentrations. The results of this competition experiment (Table S12) showed that, the ratio of **5m**/**5m’** increased as the concentration of haloarene **1a** increased (Scheme 4b in the main text). This clearly indicated that the radical species arising from the oxidation of indoline acted as an electron donor to participate in the SET-initiated activation of haloarenes.

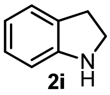
Table S12. Conversion and yield data for the model reaction of different concentration of substrate employing 2-cyclopropylindoline (**2m**) as promoter.

Entry	[MeOPhBr] **1a**	conversion of **1a** (%)	yield of **3a** (%)	yield of **4** (%)	yield of **5m** (%)	yield of **5m'** (%)	**5m/5m'**
1	10 mM	88	51	9	70	29	2.41
2	25 mM	60	21	9	81	15	5.41
3	50 mM	47	24	6	85	10	8.50
4	100 mM	36	17	5	65	6	10.8
5	125 mM	30	19	4	88	6	14.7

8. The Reduction Reaction by Using the Indoline/*t*-BuOK/O_2 System

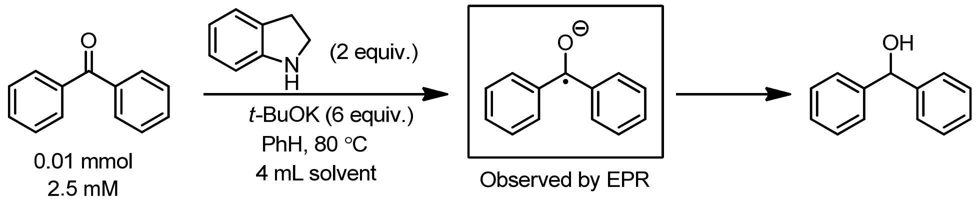
8.1 The reduction of benzophenone



Condition	Conversion	Yield
 **2i**	>99%	61% GC 57% isolated
without **2i**	10%	<1.0%

To a 10 mL Schlenk tube charged with benzophenone (0.5 mmol), *t*-BuOK (336 mg, 3.0 mmol), and indoline (1.0 mmol) was added dry benzene (4 mL) under argon. The reaction mixture was stirred in an oil bath at 85 °C for 15 h. After cooled to room temperature, a solution of *n*-dodecane (4 mL, with a specific concentration) in ether was added as the standard, followed by water. After stirred for 2 min, the organic layer was separated and analyzed by GC, GC-MS, and NMR to obtain the conversion and yield of diphenylmethanol.

It was observed that, during the reduction reaction of benzophenone a deep blue color gradually developed, which was the iconic color of the benzophenone radical anion. EPR experiment was conducted for the diluted reaction mixture, and the results showed that benzophenone radical anion indeed formed in the reduction. The measured EPR spectrum and the simulated one were shown in Figure S8. The experimental EPR parameters obtained from simulation, as well as those reported in literature,[17] were summarized in the Table S13. The result confirmed that the indoline/*t*-BuOK/O_2 system had a potent reductive power.



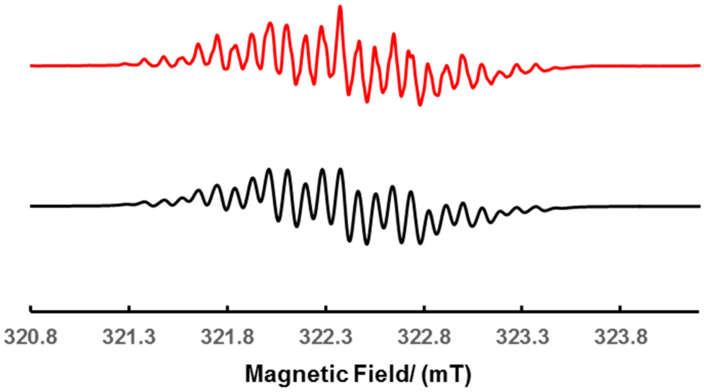


Figure S8. Experimental (red) and simulated (black) EPR spectra of the benzophenone anion radical measured at room temperature.

Table S13. EPR spectroscopic parameters of the benzophenone anion radical observed in the reduction of benzophenone.

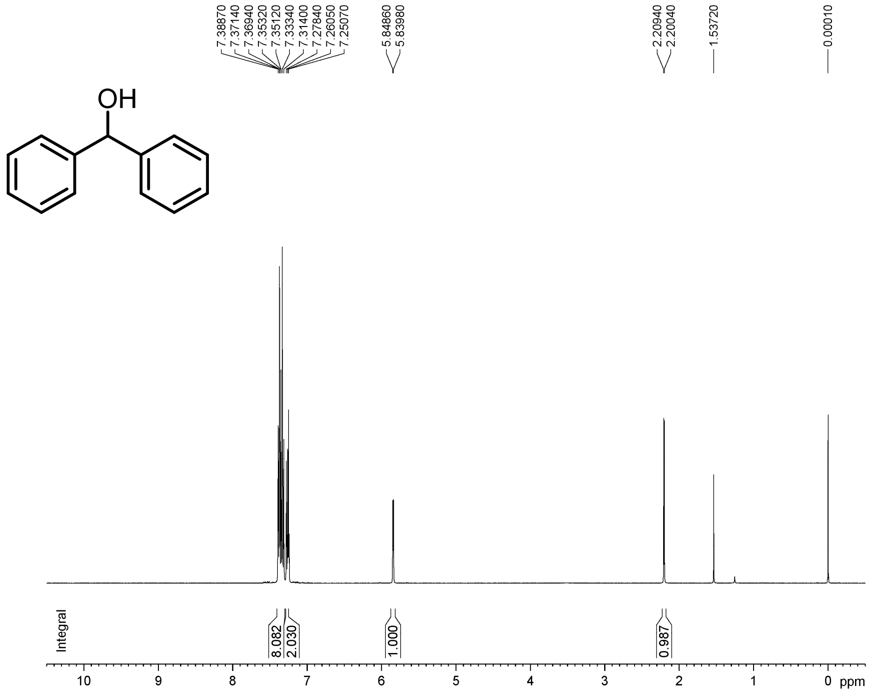
		Hyperfine coupling constants (MHz)			
	g factor	*a*(2H,p)	*a*(4H,o)	*a*(4H,m)	Line width (mT)
Experimental	2.0037	9.72	7.68	2.72	0.0057
Reported	2.0033	9.83	8.01	2.93	-

The isolated product, benzhydrol (**7**), exhibited identical spectroscopic data to those the reported in literature.[18]

^{1}H NMR (400MHz, $CDCl_3$): δ 7.43-7.35 (m, 8H), 7.32-7.27 (m, 2H), 5.88 (d, J = 3.5 Hz, 1H), 2.24 (d, J = 3.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 128.6, 127.7, 126.6, 76.4.

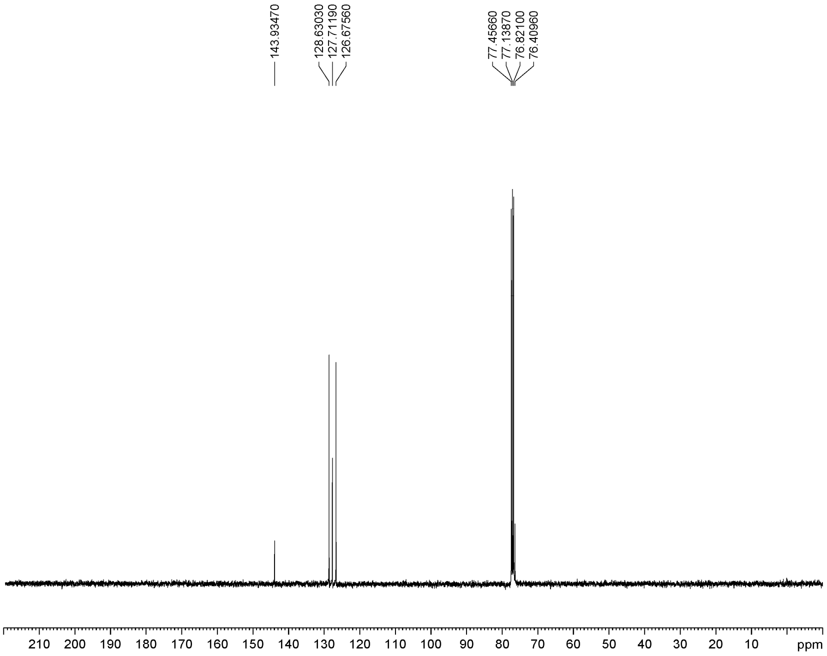
^{1}H NMR:



```
NAME              YH722-2
EXPNO                  10
PROCNO                  1
Date_            20170910
Time                21.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    130
DW                 62.400 usec
DE                   6.50 usec
TE                  299.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300134 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR:



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PROCNO                  1
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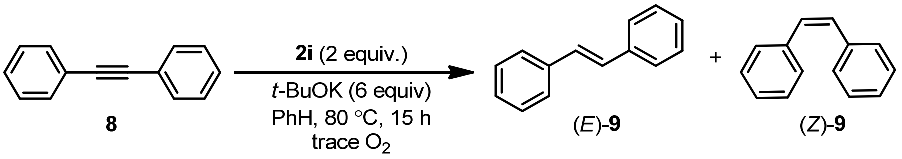
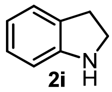
TD                  65536
SOLVENT             CDCl3
NS                    300
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127567 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

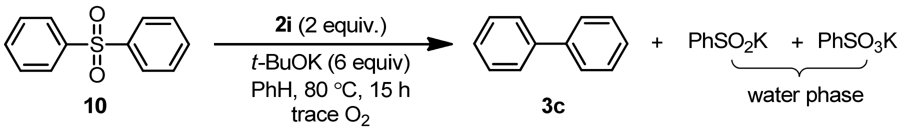
8.2 The reduction of diphenylaceylene

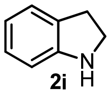


Condition	Conversion	Yield (GC)
 **2i**	70%	36% Z 32% E
without **2i**	1.0%	N.D.

The experiment was conducted following the experimental procedure described above (except that diphenylacetylene as substrate was added).

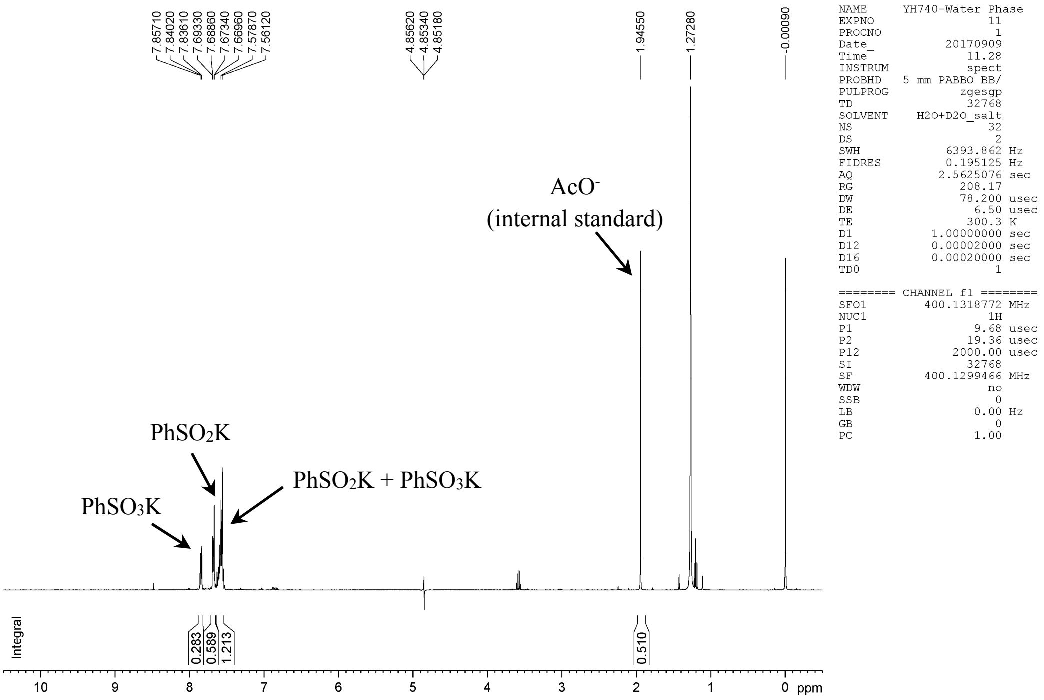
8.3 The reductive cleavage of diphenyl sulfone



Condition	Conversion	Yields
 **2i**	94%	26% PhPh 58% $PhSO_2K$ 28% $PhSO_3K$
without **2i**	11%	2.0% PhPh 7.0% $PhSO_2K$ 6.0% $PhSO_3K$

The experiment was conducted following the experimental procedure described above (except that diphenyl sulfone as substrate was added). And after cooled to room temperature, a solution of *n*-dodecane (4 mL, with a specific concentration) in ether was added as the standard, followed by sodium acetate aqueous solution (4 mL, with a specific concentration). After stirred for 2 min, the organic layer was separated and analyzed by GC and GC-MS to obtain the conversion and the yield of biphenyl, and the water phase was analyzed by NMR to obtain the yield of the benzenesulfinite and benzenesulfonate salts.

Water-peak-suppressed ^{1}H NMR of the water phase for the reductive cleavage of diphenyl sulfone, showing the production of both potassium benzenesulfinite and potassium benzenesulfonate:



```
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PROCNO                    1
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Time                  11.28
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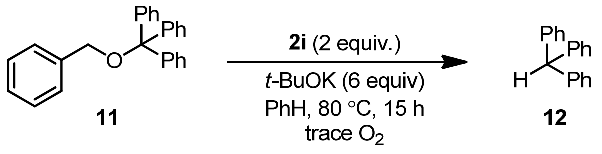
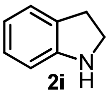
PULPROG              zgesgp
TD                    32768
SOLVENT        H2O+D2O_salt
NS                       32
DS                        2
SWH                6393.862 Hz
FIDRES             0.195125 Hz
AQ                2.5625076 sec
RG                   208.17
DW                   78.200 usec
DE                     6.50 usec
TE                    300.3 K
D1               1.00000000 sec
D12              0.00002000 sec
D16              0.00020000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1318772 MHz
NUC1                     1H
P1                     9.68 usec
P2                    19.36 usec
P12                 2000.00 usec
SI                    32768
SF              400.1299466 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

8.4 The reductive cleavage of benzyl trityl ether



Promoter	Conversion	Yield
 **2i**	50%	38% GC 30% isolated
without **2i**	5.0%	<1.0%

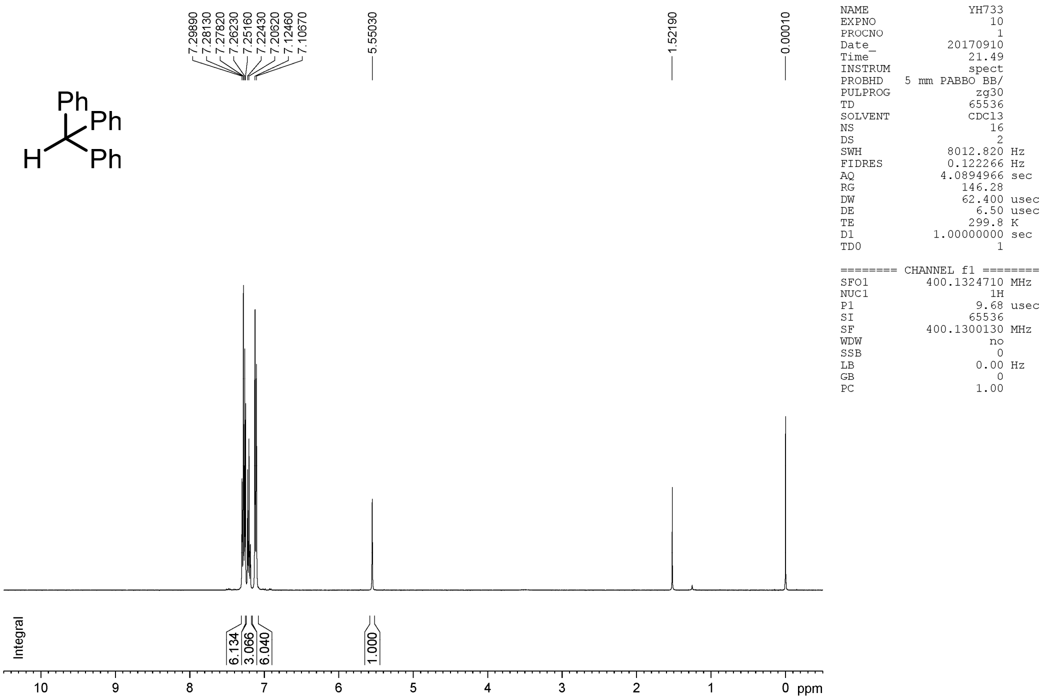
The experiment was conducted following the experimental procedure described above (except that trityl ether **11** was used as substrate). After cooled to room temperature, a solution of *n*-dodecane and 1,3,5-trimethoxybenzene (4 mL, with specific concentrations) in ether was added as the standards, followed by water. After stirred for 2 min, the organic layer was separated and analyzed by GC, GC-MS, NMR to obtain the conversion and yield.

The product triphenylmethane (**12**) was obtained by flash column chromatography. The spectroscopic data were consistent with those reported in literature.[19]

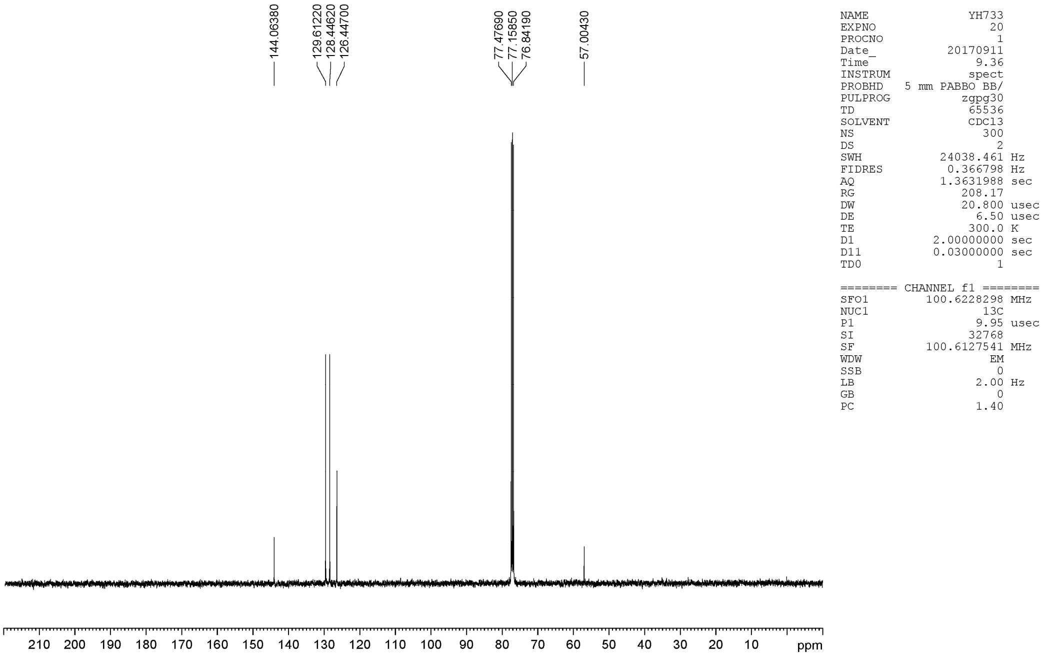
^{1}H NMR (400MHz, $CDCl_3$): δ 7.33-7.13 (m, 15H), 5.58 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 129.6, 128.4, 126.4, 57.0.

^{1}H NMR:



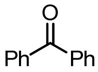
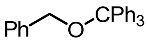
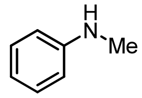
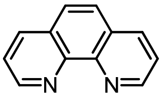
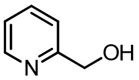
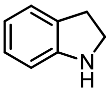
^{13}C NMR:



8.5 The reduction reaction employing different promoters

Following the experimental procedure described above, the reduction reactions employing different small molecules as reductants were conducted. The yields of products from reduction or reductive cleavage were listed in Table S14 for comparison. The results indicated that the indoline/*t*-BuOK/O_2 system exhibited best performance in single electron reduction.

Table S14. Yields for the reduction reactions employing various small organic molecules as reductants.

Substrate Promoter		$PhSO_2Ph$	$Ph-C\equiv C-Ph$	
	48%	6.5% PhPh $<1.0\%$ $PhSO_2K$ 13% $PhSO_3K$	1.1% Z 2.0% E	4.4%
	N.D.	51% PhPh 48% $PhSO_2K$ $<1.0\%$ $PhSO_3K$	N.D.	N.D.
	80%	15% PhPh 85% $PhSO_2K$ $<1.0\%$ $PhSO_3K$	9.2% Z 3.6% E	3.0%
	61% GC 57% isolated	26% PhPh 58% $PhSO_2K$ 28% $PhSO_3K$	36% Z 32% E	38% GC 30% isolated

9. DFT Computational Study

9.1 General Procedure

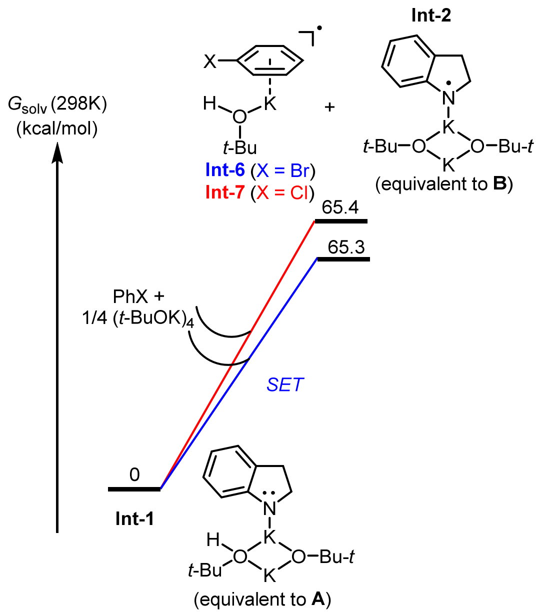
All calculations were performed using the Gaussian 09 program.[20] Geometry optimization and vibrational analysis were performed with the B3LYP method using 6-31G(d) basis set for all atoms except iodine, which used the LANL2DZ basis set (referred to as BS1). Single point energies were calculated at the M06-2X[21]/6-311+G(d,p) level (LANL2DZ for iodine) with the solvent effects modeled using the CPCM solvation model (solvent = benzene, referred to as BS2). Gibbs free energies in benzene at 298.15 K were calculated by adding the zero-point vibrational energy obtained from the B3LYP frequency calculation to the M06-2X solution-phase electronic potential energies. Exception: **Int-6** and **Int-7** were optimized at M062X/6-31G(d) level of the theory due to failure to optimize these structures under the B3LYP/6-31G(d) level of the theory.

In this DFT computational study, *t*-BuOK was considered as a tetramer,[16] and the byproduct *t*-BuOH and KX were considered as a dimer complex in the form of $(t\text{-BuOH}\cdot\text{KX})_2$.

The calculated zero-point correction, thermal correction to energy, thermal correction to enthalpy, thermal correction to Gibbs free energy (under BS1), and electric energy *E* (under BS2) were summarized in the table below.

Structure	Zero-point correction (BS1)	Thermo correction to (BS1)			*E* (BS2)
		energy	enthalpy	Gibbs free energy	
PhI	0.090079	0.095984	0.096928	0.058305	-242.934879
PhBr	0.090906	0.096593	0.097538	0.060037	-2805.773029
PhCl	0.091255	0.096749	0.097693	0.061475	-691.801292
Ph•	0.087653	0.092022	0.092966	0.059610	-231.514350
O_2	0.003775	0.006138	0.007082	-0.016204	-150.307681
$(t\text{-BuOK})_4$	0.500961	0.538007	0.538951	0.432418	-3332.130561
$(t\text{-BuOK})_3\text{•KO}_2$	0.379669	0.412825	0.413769	0.311622	-3249.430231
t-BuOH	0.13616	0.142898	0.143842	0.107144	-233.634106
$(t\text{-BuOH•KI})_2$	0.275951	0.299956	0.300900	0.214434	-1690.083536
$(t\text{-BuOH•KBr})_2$	0.276811	0.300586	0.301530	0.216733	-6815.756461
$(t\text{-BuOH•KCl})_2$	0.277145	0.300720	0.301664	0.215154	-2587.800403
Int-1	0.401899	0.428611	0.429555	0.341257	-2031.004736
Int-2	0.389548	0.416662	0.417607	0.324314	-2030.359841
Int-3	0.389446	0.416213	0.417157	0.328193	-2030.364026
Int-4	0.378971	0.405622	0.406566	0.314500	-2029.791237
Int-5	0.380633	0.406904	0.407848	0.319322	-2029.825702
Int-6	0.227961	0.244023	0.244967	0.182419	-3639.343873
Int-7	0.228563	0.244363	0.245307	0.183990	-1525.371512
TS-1	0.385303	0.411451	0.412395	0.324794	-2030.357349

9.2 The Results of SET process between Int-1 and PhBr, PhCl



9.3 Coordinates and Energies of Stationary Points

PhI, G_{sol} = -242.8765744 Hatree

C	-2.66014800	-1.20814900	0.00000000
C	-1.26084000	-1.21577500	0.00000100
C	-0.57430900	-0.00002500	-0.00000400
C	-1.26082500	1.21576300	-0.00000300
C	-2.66010600	1.20817400	0.00000400
C	-3.36238300	0.00000900	-0.00000100
H	-3.19687100	-2.15354700	0.00000400
H	-0.72049300	-2.15684300	-0.00000100
H	-0.72042200	2.15680000	-0.00000500
H	-3.19684500	2.15356300	0.00000900
H	-4.44898200	0.00004300	-0.00000400
I	1.56519400	0.00000000	0.00000000

PhBr, G_{sol} = -2805.7129918 Hatree

C	-2.18131200	-1.20787800	0.00000100
C	-0.78483200	-1.21598400	0.00000600
C	-0.10278100	-0.00002000	-0.00001900
C	-0.78482300	1.21597600	-0.00000400
C	-2.18127700	1.20789900	0.00001100
C	-2.88180300	0.00000600	-0.00000500
H	-2.71877600	-2.15225600	0.00000400
H	-0.23389500	-2.15019700	0.00000600
H	-0.23383200	2.15015900	-0.00000500

H	-2.71876000	2.15226700	0.00001600
H	-3.96799700	0.00003500	-0.00001000
Br	1.81069200	0.00000000	0.00000100

PhCl, G_{sol} = -691.7398165Hatree

C	-1.57446700	-1.20778900	0.00000200
C	-0.17825400	-1.21642300	0.00000600
C	0.50423500	-0.00001400	-0.00001300
C	-0.17824900	1.21641800	-0.00000500
C	-1.57444200	1.20780600	0.00001200
C	-2.27509500	0.00000300	-0.00000700
H	-2.11248200	-2.15180400	0.00000300
H	0.37483200	-2.14971700	0.00000400
H	0.37487900	2.14968800	-0.00000800
H	-2.11247600	2.15181000	0.00001500
H	-3.36124600	0.00002500	-0.00001400
Cl	2.26436100	0.00000000	0.00000200

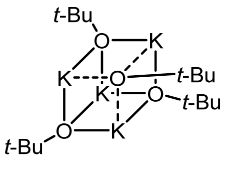
Ph·, G_{sol} = -231.4547402 Hatree

C	-1.21448400	0.63274300	-0.00000600
C	-1.22666100	-0.77198600	0.00002200
C	-0.00001200	-1.40033000	-0.00001000
C	1.22666400	-0.77197700	-0.00000800
C	1.21449700	0.63271600	0.00001800
C	-0.00000300	1.32501700	-0.00000500
H	-2.15494700	1.17922700	-0.00002800
H	-2.16313400	-1.32355400	-0.00000900
H	2.16310700	-1.32359900	-0.00002600
H	2.15493900	1.17923900	0.00001100
H	0.00002700	2.41158300	-0.00002200

O_2, G_{sol} = -150.3238852 Hatree

O	0.00000000	0.00000000	0.60710800
O	0.00000000	0.00000000	-0.60710800

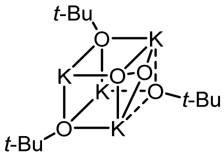
(t-BuOK)$_4$, G_{sol} = -3331.698143 Hatree



O	1.31832400	1.31832400	-1.31832400
O	1.31832400	-1.31832400	1.31832400
O	-1.31832400	1.31832400	1.31832400
O	-1.31832400	-1.31832400	-1.31832400
K	-1.31549400	-1.31549400	1.31549400
K	1.31549400	1.31549400	1.31549400
K	1.31549400	-1.31549400	-1.31549400
K	-1.31549400	1.31549400	-1.31549400
C	-2.11660100	-2.11660100	-2.11660100
C	-3.02897800	-1.25127700	-3.02897800
C	-1.25127700	-3.02897800	-3.02897800
C	-3.02897800	-3.02897800	-1.25127700
H	-3.67168400	-0.60827200	-2.41070900
H	-2.41070900	-0.60827200	-3.67168400
H	-3.68195500	-1.84584300	-3.68195500
H	-0.60827200	-3.67168400	-2.41070900
H	-1.84584300	-3.68195500	-3.68195500
H	-0.60827200	-2.41070900	-3.67168400
H	-3.68195500	-3.68195500	-1.84584300
H	-2.41070900	-3.67168400	-0.60827200
H	-3.67168400	-2.41070900	-0.60827200
C	-2.11660100	2.11660100	2.11660100
C	-3.02897800	3.02897800	1.25127700
C	-3.02897800	1.25127700	3.02897800
C	-1.25127700	3.02897800	3.02897800
H	-2.41070900	3.67168400	0.60827200
H	-3.67168400	2.41070900	0.60827200
H	-3.68195500	3.68195500	1.84584300
H	-2.41070900	0.60827200	3.67168400
H	-3.68195500	1.84584300	3.68195500
H	-3.67168400	0.60827200	2.41070900
H	-1.84584300	3.68195500	3.68195500
H	-0.60827200	2.41070900	3.67168400
H	-0.60827200	3.67168400	2.41070900
C	2.11660100	-2.11660100	2.11660100
C	3.02897800	-1.25127700	3.02897800
C	1.25127700	-3.02897800	3.02897800
C	3.02897800	-3.02897800	1.25127700
H	3.67168400	-0.60827200	2.41070900
H	2.41070900	-0.60827200	3.67168400
H	3.68195500	-1.84584300	3.68195500
H	0.60827200	-3.67168400	2.41070900
H	1.84584300	-3.68195500	3.68195500
H	0.60827200	-2.41070900	3.67168400

H	3.68195500	-3.68195500	1.84584300
H	2.41070900	-3.67168400	0.60827200
H	3.67168400	-2.41070900	0.60827200
C	2.11660100	2.11660100	-2.11660100
C	3.02897800	1.25127700	-3.02897800
C	1.25127700	3.02897800	-3.02897800
C	3.02897800	3.02897800	-1.25127700
H	3.67168400	0.60827200	-2.41070900
H	2.41070900	0.60827200	-3.67168400
H	3.68195500	1.84584300	-3.68195500
H	0.60827200	3.67168400	-2.41070900
H	1.84584300	3.68195500	-3.68195500
H	0.60827200	2.41070900	-3.67168400
H	3.68195500	3.68195500	-1.84584300
H	2.41070900	3.67168400	-0.60827200
H	3.67168400	2.41070900	-0.60827200

$(t\text{-BuOK})_3\cdot KO_2$, G_{sol} = -3249.118609 Hatree



O	-2.02357300	-0.80550900	-0.17062500
O	0.34458600	2.04223900	-0.32974400
O	1.65026300	-1.42128700	-0.15592900
K	2.05784900	0.79598000	1.27124700
K	-1.69654100	1.42571900	1.25550900
K	-0.01611900	-0.11854000	-1.73942800
K	-0.36865700	-2.17340400	1.31841100
C	2.68065900	-2.23797200	-0.58457200
C	2.49464400	-3.68787600	-0.05789400
C	2.73611000	-2.29378700	-2.13618000
C	4.05168600	-1.71410400	-0.07452400
H	2.47420900	-3.68589300	1.04145800
H	1.54122900	-4.09708800	-0.42238600
H	3.29278600	-4.37259600	-0.37455200
H	2.88898700	-1.28264700	-2.53969300
H	3.54342500	-2.93152000	-2.52067400
H	1.78667400	-2.68446600	-2.52963700
H	4.90039200	-2.33602900	-0.38915800
H	4.22663200	-0.69730900	-0.45481800
H	4.05220300	-1.68047300	1.02437200
C	0.56053000	3.31259600	-0.83168900

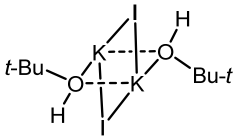
C	-0.55393800	4.29049700	-0.36654000
C	1.92533800	3.87715100	-0.34840400
C	0.57034100	3.30003400	-2.38543100
H	-1.53319100	3.93225000	-0.71601300
H	-0.57226500	4.34071100	0.73132600
H	-0.42051100	5.31311200	-0.74427600
H	2.74035500	3.21962700	-0.68431900
H	2.13601000	4.88640600	-0.72686900
H	1.94341400	3.92229200	0.74962700
H	0.74308300	4.29022300	-2.82838300
H	1.36350400	2.63000400	-2.74726100
H	-0.39447300	2.93007800	-2.76135100
C	-3.26179900	-1.25450700	-0.59217300
C	-3.32948100	-1.31907500	-2.14274000
C	-3.55383200	-2.67693900	-0.03864800
C	-4.39135500	-0.30772700	-0.10042100
H	-3.14764200	-0.32056100	-2.56510100
H	-2.55470500	-2.00127100	-2.52097200
H	-4.29803900	-1.67079400	-2.52280700
H	-3.53316000	-2.66095200	1.06058600
H	-4.53061000	-3.07322300	-0.34700200
H	-2.78444100	-3.37923800	-0.39111000
H	-5.39459400	-0.62729600	-0.41245600
H	-4.38435000	-0.25816500	0.99792100
H	-4.22713100	0.70498500	-0.49587800
O	-0.02726800	-0.08952900	2.75237200
O	0.18282700	1.17343000	3.15838600

t-BuOH, G_{sol} = -233.5269675 Hatree

O	-0.01453700	0.00008800	1.45195500
H	-0.94488600	-0.00084000	1.72916400
C	0.00543900	0.00001700	0.01451000
C	-0.68897200	-1.26637400	-0.51026400
C	-0.69176600	1.26478900	-0.51042200
C	1.49078100	0.00159300	-0.35653800
H	-0.20860400	-2.15997300	-0.09817300
H	-1.74671700	-1.28063400	-0.21483200
H	-0.65072500	-1.32319800	-1.60449300
H	-0.21305500	2.15957000	-0.09896700
H	-0.65421700	1.32123800	-1.60469400
H	-1.74939200	1.27700500	-0.21446400
H	1.62247300	0.00175700	-1.44388200
H	1.98332100	0.88855800	0.05550800

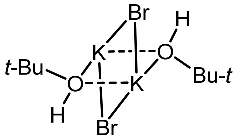
H	1.98519800	-0.88434300	0.05547700

(*t*-BuOH·KI)$_2$, G_{sol} = -1689.869102 Hatree



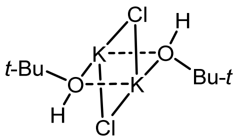
H	-2.46240100	0.37454400	-0.07908300
C	-3.34419300	-1.44469100	0.00071400
C	-4.55232200	-0.83957700	-0.72523300
H	-5.42470900	-1.49767700	-0.63816200
H	-4.82206600	0.13601300	-0.30178800
H	-4.33380200	-0.70143000	-1.79025600
C	-2.94081600	-2.78905100	-0.60715100
H	-2.79863900	-2.69700000	-1.69066400
H	-2.00256600	-3.14780900	-0.17096000
H	-3.72071100	-3.53887000	-0.43155400
C	-3.62367400	-1.58344500	1.50492100
H	-2.76307600	-2.03331000	2.01529600
H	-3.83392300	-0.60481000	1.95449700
H	-4.49119500	-2.22898500	1.68625400
O	-2.19306000	-0.56816200	-0.17850200
K	0.00412200	0.03460900	1.79214700
I	-1.37726100	2.74104600	-0.00442800
H	2.46017300	-0.37484900	0.07330700
C	3.34474700	1.44314700	-0.00697300
C	3.62899300	1.58052800	-1.51042000
H	4.49813500	2.22450800	-1.68949600
H	3.83892900	0.60127900	-1.95877900
H	2.77070100	2.03145400	-2.02373800
C	2.94183400	2.78856000	0.59890000
H	2.00518200	3.14846500	0.16025500
H	2.79680700	2.69765400	1.68212900
H	3.72329700	3.53706600	0.42466000
C	4.54964400	0.83642900	0.72293800
H	4.32775800	0.69917900	1.78738800
H	4.81911400	-0.13980500	0.30083100
H	5.42331600	1.49311500	0.63818200
O	2.19157400	0.56852000	0.16909500
K	-0.00233300	-0.03207800	-1.79179800
I	1.37617300	-2.74068900	0.00922300

(t-BuOH·KBr)$_2$, G$_{sol}$ = -6815.539728 Hatree



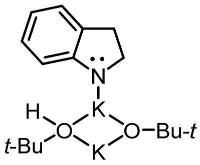
C	4.60485700	-0.67320800	-0.76879800
C	3.63032200	0.25383800	-0.03053800
H	4.51443700	-1.70569200	-0.40944900
H	4.39648400	-0.66620200	-1.84442600
H	5.64226200	-0.35345100	-0.61842700
C	3.72638800	1.69283500	-0.54297100
C	3.86884200	0.19587200	1.48733300
H	2.92284100	2.30330600	-0.11722400
H	4.69205400	2.13662600	-0.27720100
H	3.62854200	1.71887300	-1.63463600
H	4.89453800	0.48707800	1.74076100
H	3.19056300	0.88381800	2.00776500
H	3.70500800	-0.82036500	1.86723000
O	2.27285200	-0.16314900	-0.30799200
K	0.00178600	-0.00052700	1.68650700
K	-0.00054800	0.00149200	-1.80816800
O	-2.27311400	0.16256500	-0.30734400
C	-3.63065600	-0.25411100	-0.03012700
C	-4.60491800	0.67380100	-0.76768100
C	-3.72720800	-1.69270900	-0.54361700
C	-3.86908800	-0.19721200	1.48779700
H	-4.51412000	1.70599500	-0.40759400
H	-4.39656800	0.66750900	-1.84331800
H	-5.64243100	0.35429400	-0.61751000
H	-2.92404400	-2.30380200	-0.11805000
H	-4.69314800	-2.13625100	-0.27843500
H	-3.62906700	-1.71801900	-1.63527300
H	-4.89484300	-0.48836800	1.74105100
H	-3.19087900	-0.88565000	2.00764000
H	-3.70502000	0.81871100	1.86844700
H	2.16138100	-1.13112500	-0.15173900
H	-2.16105000	1.13017000	-0.14920600
Br	-0.38829700	2.68462500	0.06259900
Br	0.38802300	-2.68478900	0.06184300

(t-BuOH·KCl)$_2$, G$_{sol}$ = -2587.585249 Hatree



C	-4.55417500	0.80020200	-0.91753600
C	-3.71462500	-0.13823700	-0.03911100
H	-4.37419000	1.84934900	-0.65383400
H	-4.29772300	0.66426900	-1.97425600
H	-5.62509100	0.60021600	-0.79679600
C	-3.91665300	-1.60099100	-0.44001700
C	-4.04374400	0.07274100	1.44780600
H	-3.23972800	-2.25160400	0.12306300
H	-4.94859600	-1.91610400	-0.25020500
H	-3.70714300	-1.73923300	-1.50680500
H	-5.10293400	-0.12036600	1.65296400
H	-3.45253200	-0.61033400	2.07056000
H	-3.82502500	1.10391400	1.75133800
O	-2.31216200	0.13574300	-0.25331600
K	0.00011000	0.00239500	1.73335700
K	-0.00022500	0.00246700	-1.75036400
O	2.31181600	-0.13334300	-0.25112100
C	3.71586300	0.13447900	-0.03914000
C	4.54967300	-0.80427800	-0.92269300
C	3.92282800	1.59773600	-0.43558900
C	4.04754400	-0.08291000	1.44625900
H	4.36572100	-1.85359800	-0.66245600
H	4.29170700	-0.66337100	-1.97839900
H	5.62167000	-0.60928300	-0.80339400
H	3.25082800	2.24938200	0.13217100
H	4.95678800	1.90772500	-0.24828600
H	3.71010500	1.74068000	-1.50110600
H	5.10784400	0.10589700	1.64968800
H	3.46001200	0.59989800	2.07277600
H	3.82599000	-1.11438000	1.74665600
Cl	0.45563500	-2.48859900	0.09323000
Cl	-0.45854700	2.49272500	0.09290900
H	-2.12140000	1.09640300	-0.11507600
H	2.11789600	-1.09363900	-0.11421400

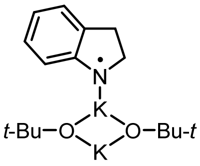
Int-1, G_{sol} = -2030.663479 Hatree



C	2.89996800	-1.92976300	-0.19991600
C	1.60692900	-1.39375600	-0.46929000
C	0.47543300	-2.10670900	-0.00506300
C	0.66023100	-3.29274700	0.72545900
C	1.93372900	-3.79363200	0.99945300
C	3.06249100	-3.09706000	0.52353200
C	3.91351600	-0.95606800	-0.76193600
C	3.00881500	-0.06553100	-1.66075300
H	-0.53647100	-1.77641500	-0.24634800
H	-0.21715800	-3.84829400	1.05509300
H	2.05443600	-4.72261900	1.54968000
H	4.06066300	-3.48309600	0.72571000
H	4.37638100	-0.36708000	0.04655300
H	3.33228000	0.98463800	-1.66928300
H	4.72923900	-1.42940500	-1.32035400
H	3.07733700	-0.42185500	-2.70456700
N	1.62345100	-0.19970200	-1.16245500
K	-0.89405400	0.68958200	-1.86378500
O	0.63730300	1.64791400	0.40296600
C	1.28972100	2.91045900	0.55562200
C	2.68811600	2.71255200	1.16577000
H	3.31903400	2.10673600	0.50669100
H	3.19201200	3.67246300	1.33160600
H	2.61183600	2.19523300	2.12941400
C	1.39803500	3.60897400	-0.81328200
H	0.39818700	3.76838600	-1.23844000
H	1.88582700	4.58756600	-0.73137600
H	1.98154900	2.99911300	-1.51280100
C	0.41144100	3.74302200	1.49954300
H	0.82195300	4.74874500	1.64512500
H	-0.60260100	3.83875400	1.09427800
H	0.34389400	3.26346400	2.48472800
O	-2.46078100	-0.06114700	-0.04513900
K	-0.83211600	-0.02362400	1.83946000
C	-3.78477500	-0.44231500	-0.15751000
C	-4.10680500	-1.60014300	0.82560500
H	-3.44161500	-2.45022300	0.62867600
H	-3.93901500	-1.26823500	1.86128200
H	-5.14486200	-1.95312500	0.75745300
C	-4.72508600	0.74853300	0.15832200

H	-4.51773100	1.57921100	-0.52926100
H	-5.79057700	0.49294900	0.07612600
H	-4.53841400	1.11025300	1.17829800
C	-4.09047900	-0.93975500	-1.59772500
H	-5.12348000	-1.28903700	-1.72889100
H	-3.92919600	-0.12330300	-2.31878600
H	-3.41522900	-1.76604600	-1.85520600
H	1.18494600	0.96540600	-0.20565300

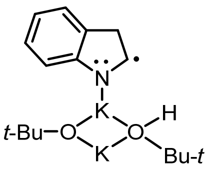
Int-2, G_{sol} = -2030.035527 Hatree



C	-3.82705800	1.42264100	-0.11394500
C	-2.63653400	0.68624000	0.18769400
C	-2.35206800	-0.54017300	-0.47794600
C	-3.26950400	-0.98910700	-1.41840900
C	-4.43913000	-0.26129100	-1.71182700
C	-4.72091800	0.95132700	-1.05864500
C	-3.84141200	2.65832000	0.74668700
C	-2.51127200	2.50995500	1.54111300
H	-1.43978000	-1.10565400	-0.25393400
H	-3.08434700	-1.92732300	-1.93536800
H	-5.13640700	-0.64329400	-2.45270100
H	-5.62856900	1.50075900	-1.29639900
H	-3.86468500	3.57852500	0.14973500
H	-1.82165900	3.34535900	1.35707100
H	-4.71590700	2.68908600	1.40891200
H	-2.67441600	2.48098200	2.62738100
N	-1.85827800	1.26359200	1.12710300
K	0.76631400	0.21380400	1.49135700
O	2.28291400	1.11401600	-0.33427500
C	3.18011400	2.15883800	-0.30373300
C	2.62243800	3.38568900	-1.07121700
H	1.66937700	3.69831200	-0.62550300
H	3.30504300	4.24720200	-1.06801500
H	2.42425300	3.11045600	-2.11573000
C	3.47195000	2.59231800	1.16140000
H	3.86445600	1.73685500	1.72848400
H	4.19879000	3.41265100	1.23898200
H	2.54155700	2.92846000	1.64296100
C	4.52893300	1.74196900	-0.95305900

H	5.29151000	2.53281400	-0.92671500
H	4.92915000	0.86069600	-0.43489700
H	4.36560400	1.47232200	-2.00688200
O	0.47901800	-1.94307200	0.08402300
K	1.79587600	-0.84087700	-1.76052500
C	0.58634600	-3.24479000	0.53671300
C	-0.68242000	-4.06233500	0.18507700
H	-1.56395800	-3.60201400	0.64777400
H	-0.83502100	-4.05735000	-0.90224000
H	-0.62625300	-5.10800100	0.51820600
C	1.81459000	-3.94954900	-0.10540700
H	2.72892800	-3.38127800	0.11747400
H	1.96343800	-4.97875400	0.24852300
H	1.69114800	-3.99251200	-1.19821000
C	0.77381900	-3.27509500	2.07982900
H	0.85658700	-4.29078400	2.49009500
H	1.68771500	-2.72929300	2.35724700
H	-0.08292300	-2.78626600	2.56428000

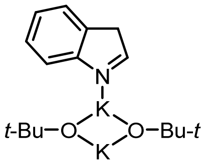
Int-3, G_{sol} = -2030.035833 Hatree



C	-2.87499800	-2.01530800	0.24427600
C	-1.58087200	-1.45245000	0.45360500
C	-0.44572700	-2.12738500	-0.05517700
C	-0.63053500	-3.30938100	-0.78596800
C	-1.90665200	-3.83572200	-1.01798800
C	-3.03385200	-3.18186600	-0.48350000
C	-3.87171600	-1.13635800	0.97185800
C	-2.96566100	-0.00494500	1.41721700
H	0.56478300	-1.77198900	0.15606700
H	0.24419400	-3.84125300	-1.15832500
H	-2.02546200	-4.75631800	-1.58262600
H	-4.02568400	-3.60507800	-0.63630700
H	-4.71234300	-0.81174400	0.33516100
H	-4.34306200	-1.67496100	1.81947300
N	-1.61874800	-0.26893500	1.16795900
K	0.88211700	0.63678200	1.91191400
O	-0.61008700	1.76504400	-0.37389800
C	-1.35042200	2.99420900	-0.51756600
C	-2.71155000	2.69809700	-1.16411800

H	-3.27681000	1.99331600	-0.54219500
H	-3.30261800	3.61407500	-1.28263500
H	-2.57454500	2.24955100	-2.15574600
C	-1.54107200	3.63325400	0.86830200
H	-0.56713400	3.83052400	1.33496400
H	-2.07961700	4.58552600	0.79916000
H	-2.11732000	2.96542500	1.51849300
C	-0.49529700	3.89577900	-1.41275500
H	-0.96820300	4.87392600	-1.55228900
H	0.49577700	4.05061500	-0.97068100
H	-0.36319600	3.44269500	-2.40358900
O	2.41768800	-0.05309100	0.04358000
K	0.79878800	0.03770500	-1.84646300
C	3.74525400	-0.42794000	0.14601400
C	4.07367300	-1.56118400	-0.86273700
H	3.41584100	-2.42079900	-0.68366600
H	3.90159900	-1.20806700	-1.89066900
H	5.11456300	-1.90720800	-0.80408100
C	4.67631700	0.77639100	-0.14396500
H	4.46416400	1.58998500	0.56231600
H	5.74358400	0.52642400	-0.06878400
H	4.48587700	1.15955100	-1.15534800
C	4.05615700	-0.95511400	1.57444600
H	5.09098100	-1.30221500	1.69556900
H	3.89397500	-0.15543200	2.31412300
H	3.38578400	-1.79027600	1.81561700
H	-1.13853000	1.09319400	0.16859800
H	-3.23164400	0.70173900	2.19898600

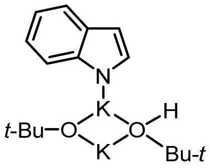
Int-4, G$_{sol}$ = -2029.476737 Hatree



C	-3.76360700	1.44769200	-0.03964200
C	-2.62462400	0.66859200	0.23472700
C	-2.34022000	-0.50721800	-0.45805200
C	-3.24919200	-0.88798900	-1.45398300
C	-4.38566000	-0.12156400	-1.73888100
C	-4.65443200	1.05862500	-1.03147000
C	-3.72612600	2.62095700	0.90498500
C	-2.44895400	2.32068600	1.65703700
H	-1.44997500	-1.10800800	-0.23950900

H	-3.07009700	-1.80474900	-2.01027000
H	-5.07249900	-0.44647500	-2.51599600
H	-5.54049300	1.64646500	-1.25814600
H	-3.66921400	3.59589200	0.40016400
H	-4.58874200	2.67140200	1.58471300
N	-1.84467100	1.24431900	1.28443900
K	0.80153900	0.14891900	1.53863100
O	2.19442100	1.14830500	-0.32746800
C	3.07499400	2.20731600	-0.30368200
C	2.46895800	3.44305800	-1.01836300
H	1.52693200	3.72560900	-0.53116200
H	3.13581100	4.31681500	-1.01631000
H	2.23892900	3.19129500	-2.06229900
C	3.41382900	2.60979100	1.16037000
H	3.84175100	1.74789500	1.69108900
H	4.12932500	3.44056300	1.23205600
H	2.49621800	2.91764400	1.68364900
C	4.40521100	1.82974400	-1.01235200
H	5.15497700	2.63300200	-0.99417300
H	4.83888900	0.94284900	-0.53225000
H	4.20726000	1.58298300	-2.06579700
O	0.48247200	-1.95634900	0.07607900
K	1.63217700	-0.74733800	-1.80851800
C	0.61717700	-3.26898200	0.48783100
C	-0.66529500	-4.08223600	0.17954400
H	-1.52405900	-3.63611200	0.69595300
H	-0.87173100	-4.05144600	-0.89832200
H	-0.59017500	-5.13548200	0.48385500
C	1.81389900	-3.94900200	-0.23439500
H	2.73513000	-3.38065500	-0.04335200
H	1.98500200	-4.98669400	0.08310500
H	1.63499400	-3.96196500	-1.32008500
C	0.88255000	-3.33895400	2.01829900
H	0.99244400	-4.36445300	2.39649600
H	1.80580100	-2.79360700	2.26407300
H	0.04784800	-2.87061300	2.55871200
H	-2.04843900	2.94883500	2.44984900

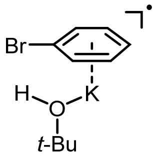
Int-5, G_{sol} = -2029.476737 Hatree



C	-2.81225600	-2.04711000	0.28944600
C	-1.50187300	-1.50675200	0.53270900
C	-0.35841200	-2.16464600	0.03215200
C	-0.52807300	-3.31280800	-0.74344200
C	-1.81671100	-3.82724200	-1.00915100
C	-2.95020500	-3.21070600	-0.49110000
C	-3.71396600	-1.17668600	0.97419000
C	-2.92119000	-0.20241900	1.55608100
H	0.64693500	-1.80342700	0.25937400
H	0.34717900	-3.84179700	-1.11655000
H	-1.91790900	-4.73122200	-1.60519000
H	-3.93574200	-3.63170200	-0.68151800
N	-1.57273000	-0.35452800	1.29985900
K	0.90571200	0.66489200	1.94926800
O	-0.71777500	1.72164300	-0.32945800
C	-1.55594200	2.87715800	-0.53884000
C	-2.87211800	2.44287100	-1.20221000
H	-3.39874300	1.71015500	-0.58048600
H	-3.53522200	3.30096100	-1.36299300
H	-2.67430800	1.97985000	-2.17653800
C	-1.82675500	3.55836400	0.81296600
H	-0.88209200	3.85441300	1.28603700
H	-2.44025800	4.45817100	0.68927100
H	-2.35851600	2.87891800	1.48853800
C	-0.75866100	3.80847400	-1.45676000
H	-1.30867900	4.73606900	-1.64861500
H	0.20541500	4.06423400	-1.00292900
H	-0.56589600	3.32635600	-2.42344200
O	2.40427900	0.03851000	0.03650300
K	0.72234700	-0.01190100	-1.80500900
C	3.75388700	-0.26087500	0.08429700
C	4.10647400	-1.36543300	-0.94814000
H	3.50421600	-2.26179200	-0.75387300
H	3.87737100	-1.01349000	-1.96541100
H	5.16624100	-1.65380300	-0.93190000
C	4.60384700	0.99644500	-0.22862700
H	4.37430700	1.79090700	0.49391000
H	5.68548700	0.80623600	-0.19709100
H	4.35253800	1.37675900	-1.22765100
C	4.14853500	-0.78163900	1.49412900
H	5.20509100	-1.07072700	1.57246600
H	3.96996300	0.00123400	2.24790900
H	3.53571400	-1.65511500	1.75186900
H	-3.25923100	0.63210700	2.16554800

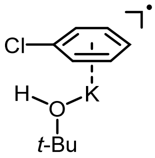
H	-1.19780200	1.04322400	0.23801100
H	-4.79159300	-1.26481900	1.03876900

Int-6 (PhBr·K·*t*-BuOH), G_{sol} = -3639.161454 Hatree



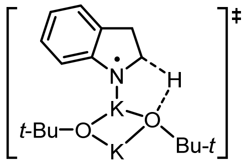
C	-3.18507700	-1.37516400	0.46319800
C	-2.21275500	-1.11728400	1.49217000
C	-1.40908900	0.05841200	1.33387400
C	-1.37860900	0.69428700	0.12094100
C	-2.11559800	0.25832000	-1.02583300
C	-3.14354900	-0.70625400	-0.73762100
H	-2.33016800	-1.55053600	2.47829100
H	-0.81581300	0.43332000	2.16233400
H	1.16776700	0.34153000	-0.84224700
H	-2.15579800	0.87216500	-1.91580200
H	-3.88977400	-0.91681200	-1.50050800
H	-3.96364600	-2.11337200	0.64024100
C	2.66694900	-0.53249800	0.07884100
C	3.62252000	0.59217400	-0.31241500
H	4.49578400	0.61250300	0.34692500
H	3.96188700	0.45638500	-1.34355500
H	3.11629900	1.56128400	-0.23665800
C	2.13997700	-0.33130900	1.49866200
H	1.60993300	0.62362100	1.57553000
H	1.43973600	-1.13163000	1.76791600
H	2.95991000	-0.33393000	2.22418600
C	3.33873000	-1.89198300	-0.06635000
H	2.64298000	-2.69537600	0.20599500
H	3.66413900	-2.04700700	-1.09929200
H	4.20876100	-1.96447400	0.59266800
O	1.56624400	-0.54954900	-0.84176500
K	-0.51785400	-2.10338800	-0.63646100
Br	-0.24982000	2.23773900	-0.09434100

Int-7 (PhCl·K·*t*-BuOH), G_{sol} = -1525.187522 Hatree



C	3.24683300	-0.87810300	0.47495200
C	3.16917900	-0.26215600	-0.75216000
C	2.09998200	0.64624000	-1.07242300
C	1.35135900	1.09827100	0.06091900
C	1.41217500	0.50923700	1.29595300
C	2.27156500	-0.62015500	1.49968500
H	3.91790300	-0.47465000	-1.51191900
H	2.12629000	1.24348700	-1.97496300
H	-1.12948900	0.60959300	-0.87691400
H	0.79918000	0.88768500	2.10860200
H	2.41779600	-1.00221500	2.50293300
H	4.05634400	-1.57599600	0.67550800
C	-2.61939400	-0.25130500	0.07300500
C	-2.11074900	0.04076900	1.48324700
H	-2.93736000	0.05612200	2.20096400
H	-1.39250600	-0.72484500	1.80096600
H	-1.60603200	1.01193100	1.51375600
C	-3.60323200	0.82203800	-0.38616600
H	-3.12772700	1.80917900	-0.35721200
H	-3.92705400	0.62210000	-1.41182400
H	-4.48371600	0.85058300	0.26310300
C	-3.25033700	-1.63568100	-0.00314700
H	-3.55655100	-1.85775500	-1.02969300
H	-2.53571100	-2.40149300	0.32299000
H	-4.12725200	-1.69621800	0.64783300
O	-1.51042700	-0.28728200	-0.83723800
K	0.61795100	-1.76892600	-0.57552700
Cl	0.23787800	2.45502400	-0.19320000

TS-1, G_{sol} = -2030.032555 Hatree

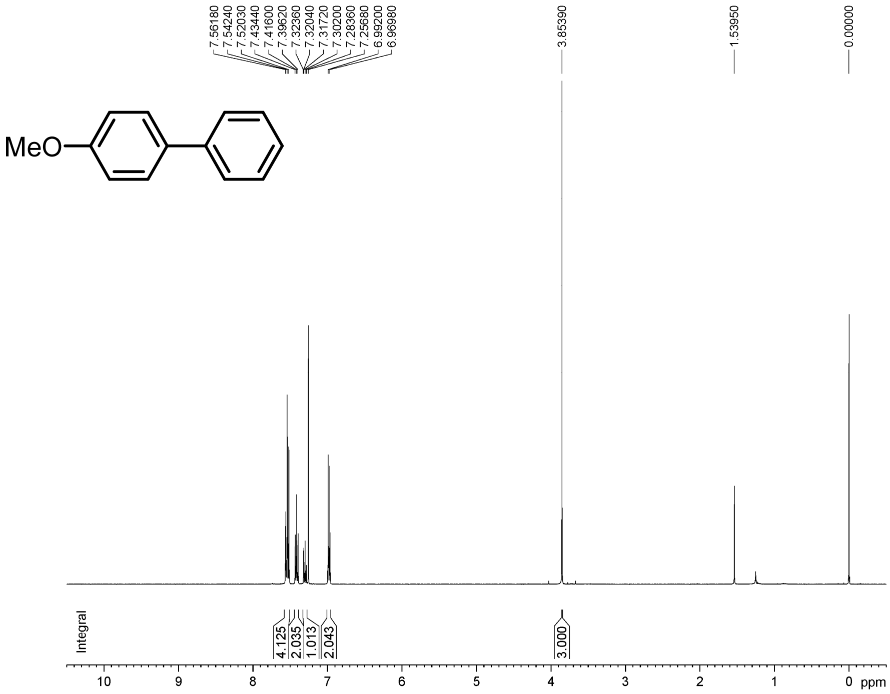


C	-2.49049900	-1.80210500	-0.00690500
C	-1.43041900	-1.80304200	0.95195500
C	-0.41012000	-2.77662000	0.86011600
C	-0.43703000	-3.68367500	-0.20187500
C	-1.45730100	-3.64940600	-1.16760300
C	-2.49815000	-2.70536900	-1.05974700
C	-3.43093500	-0.69118300	0.38766800
C	-2.54571000	0.07173000	1.39384900
H	0.39472600	-2.79648200	1.58954900

H	0.35048700	-4.42923100	-0.28401300
H	-1.45741500	-4.36756900	-1.98292800
H	-3.30089600	-2.69604500	-1.79499700
H	-3.77829000	-0.08079900	-0.45518700
H	-4.33223200	-1.10183900	0.87534200
N	-1.50792700	-0.76515000	1.84565600
K	0.75336500	0.89439800	1.90811500
O	-1.00038300	1.51675900	-0.14503300
C	-1.35669700	2.81846100	-0.58009400
C	-2.79696300	2.83038000	-1.12852100
H	-3.51534000	2.56689600	-0.34376900
H	-3.07249600	3.81674700	-1.52143100
H	-2.89735600	2.09902900	-1.93958100
C	-1.23932200	3.81460200	0.59385800
H	-0.20504500	3.84866700	0.96293900
H	-1.51933800	4.83411200	0.30134500
H	-1.89288600	3.50890000	1.42010800
C	-0.37321500	3.21796500	-1.69546800
H	-0.55451900	4.23940900	-2.05270200
H	0.65974900	3.15606200	-1.33374400
H	-0.47616700	2.54074700	-2.55397800
O	2.23796700	-0.01674000	0.13600700
K	0.29063100	-0.53662100	-1.35577400
C	3.59037400	-0.09719300	-0.12119600
C	4.31172600	1.19926000	0.33789800
H	3.86473300	2.06698300	-0.16411900
H	4.18357400	1.33157700	1.42215200
H	5.39043300	1.19715100	0.12849000
C	4.22118000	-1.30319200	0.62169700
H	3.72851600	-2.23200300	0.30717700
H	5.30027100	-1.40698700	0.44120600
H	4.06527500	-1.19545900	1.70345900
C	3.85217500	-0.27433800	-1.64418400
H	4.91876300	-0.33040600	-1.90143700
H	3.37889700	-1.20243400	-1.99865500
H	3.41621100	0.57028600	-2.19612200
H	-1.84263400	0.97279000	0.60161200
H	-3.04271400	0.65038100	2.17873000

10. NMR Spectra of the Products of BHAS Reactions

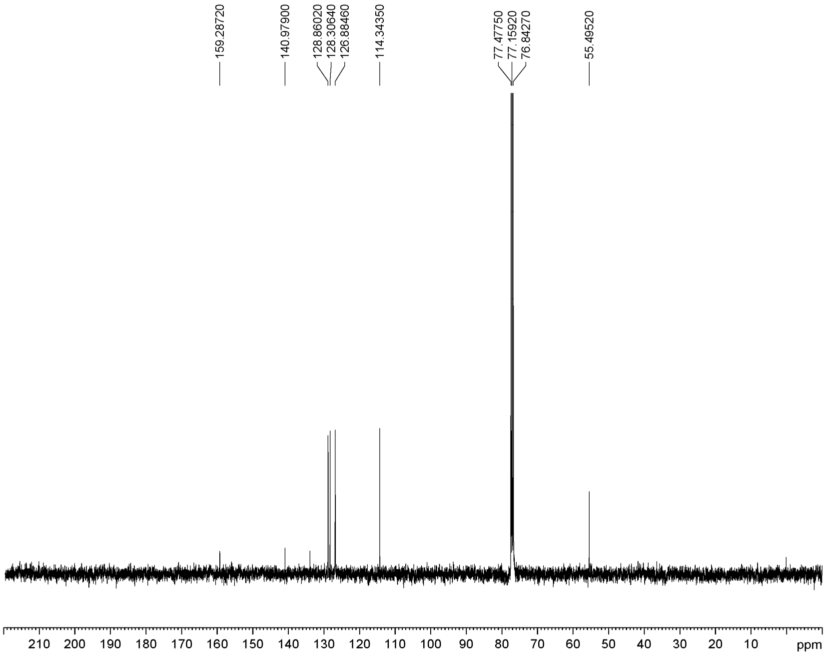
^{1}H NMR of **3a**



```
NAME             YH786-1-2
EXPNO                   10
PROCNO                   1
Date_             20171110
Time                 16.23
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                  146.28
DW                  62.400 usec
DE                    6.50 usec
TE                   296.3 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                    9.68 usec
SI                   65536
SF             400.1300110 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

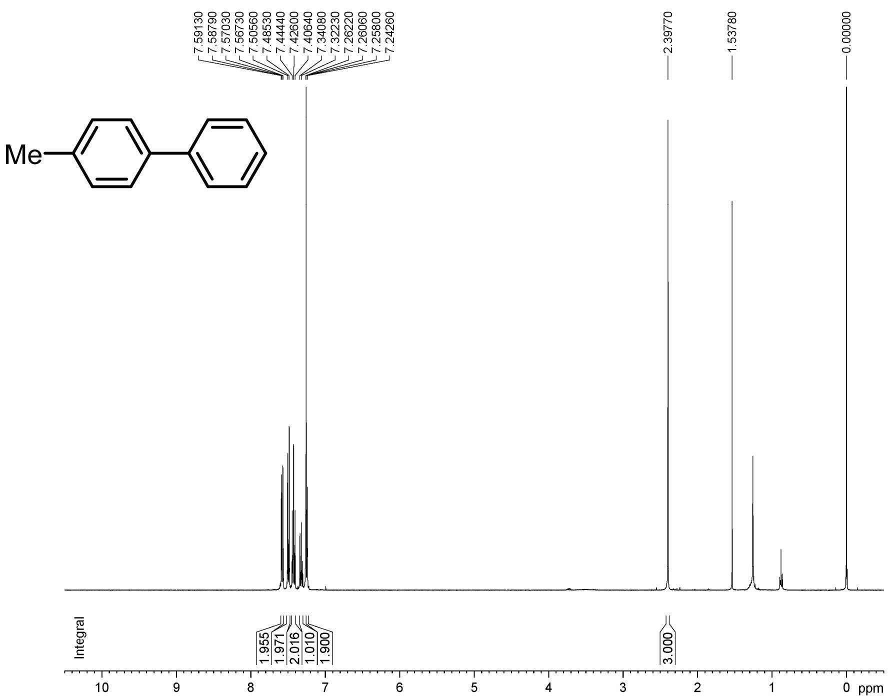
^{13}C NMR of **3a**



```
NAME             YH786-1-2
EXPNO                   11
PROCNO                   1
Date_             20171110
Time                 16.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     300
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  208.17
DW                  20.800 usec
DE                    6.50 usec
TE                   296.8 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                    9.95 usec
SI                   32768
SF             100.6127548 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

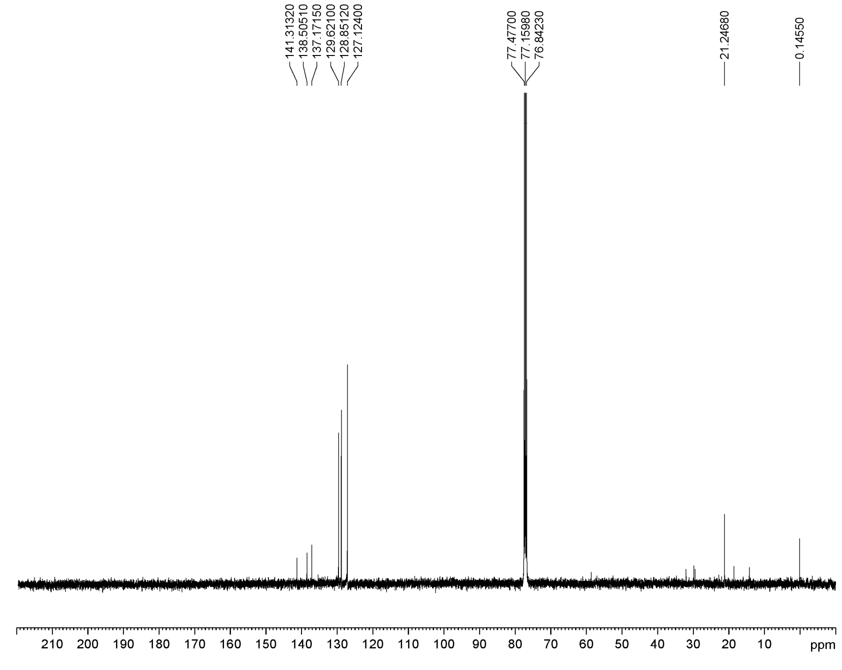
^{1}H NMR of **3e**



```
NAME       YH780-2-again
EXPNO                 11
PROCNO                 1
Date_           20171108
Time               12.55
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                160.46
DW                62.400 usec
DE                  6.50 usec
TE                 296.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300106 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

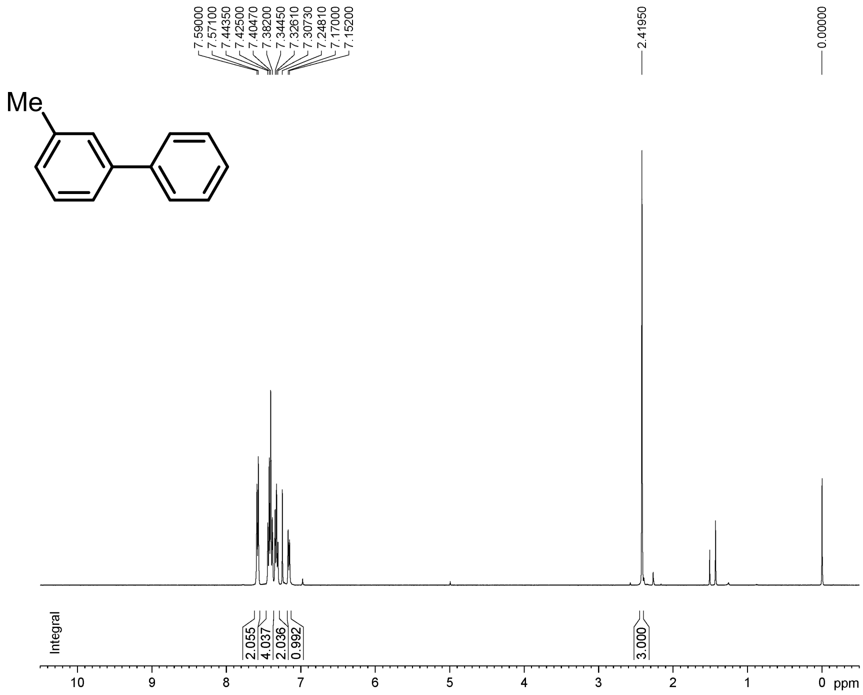
^{13}C NMR of **3e**



```
NAME       YH780-2-again
EXPNO                 12
PROCNO                 1
Date_           20171109
Time                3.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  3072
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 296.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127545 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

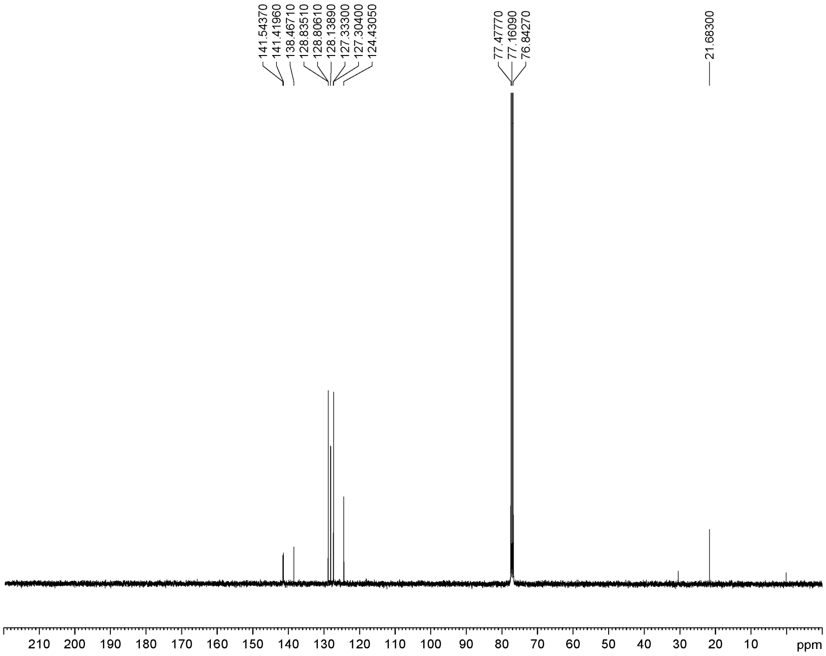
^{1}H NMR of **3f**



```
NAME              YH479-2
EXPNO                  10
PROCNO                  1
Date_            20161203
Time                21.30
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 115.32
DW                 62.400 usec
DE                   6.50 usec
TE                  302.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.95 usec
SI                  65536
SF            400.1300154 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

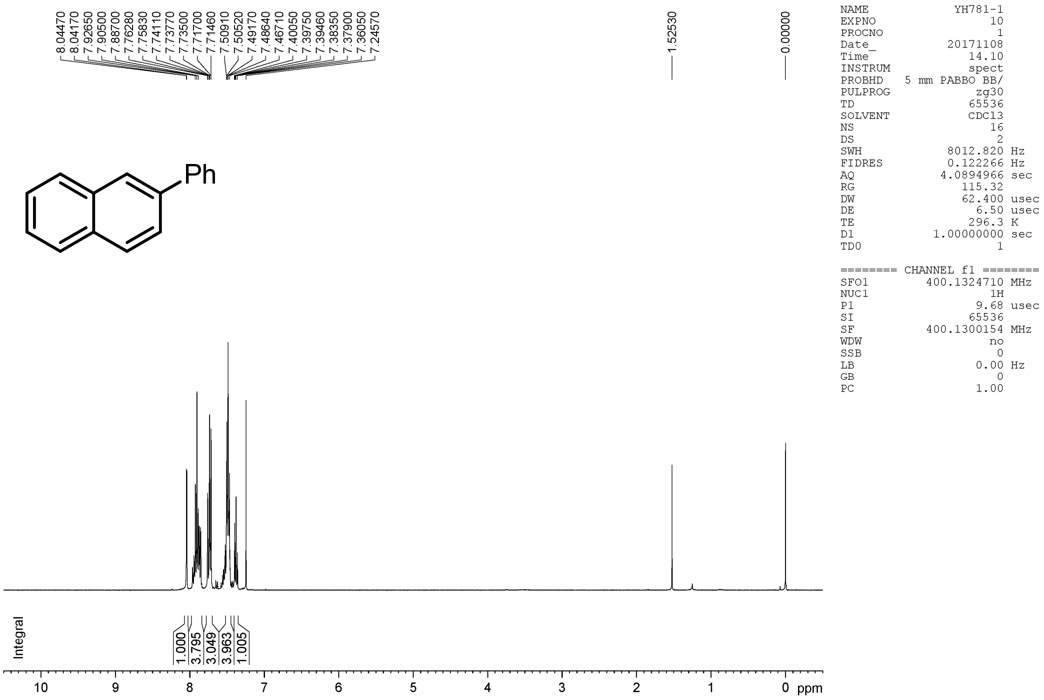
^{13}C NMR of **3f**



```
NAME              YH479-2
EXPNO                  11
PROCNO                  1
Date_            20161204
Time                 1.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  303.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127532 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

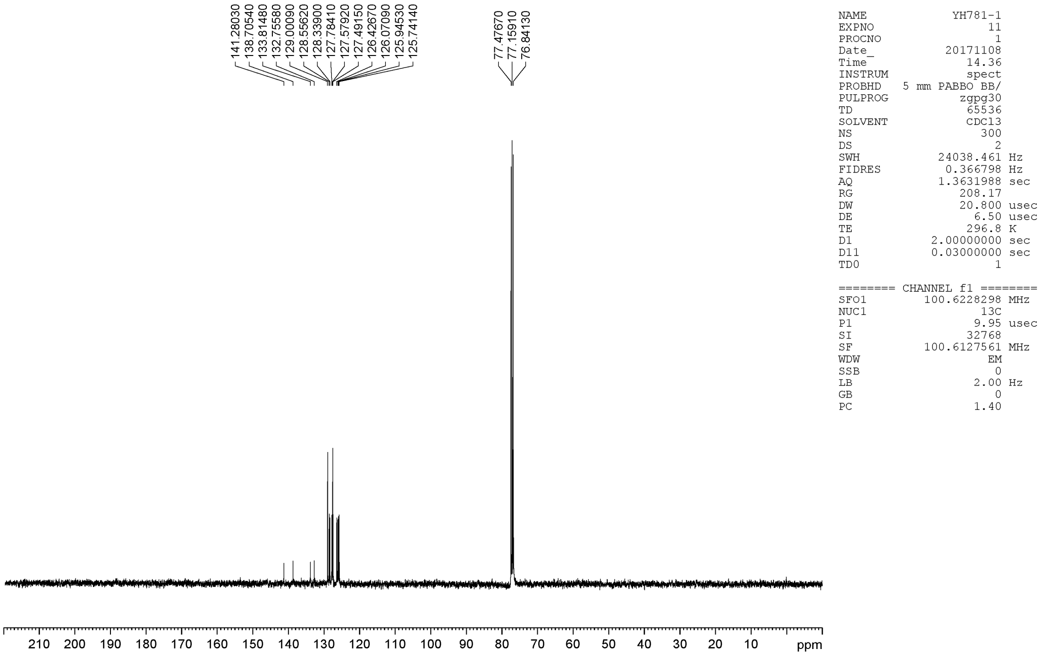
^{1}H NMR of **3g**



```
NAME              YH781-1
EXPNO                  10
PROCNO                  1
Date_            20171108
Time                14.10
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                 115.32
DW                 62.400 usec
DE                   6.50 usec
TE                  296.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.68 usec
SI                  65536
SF            400.1300154 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

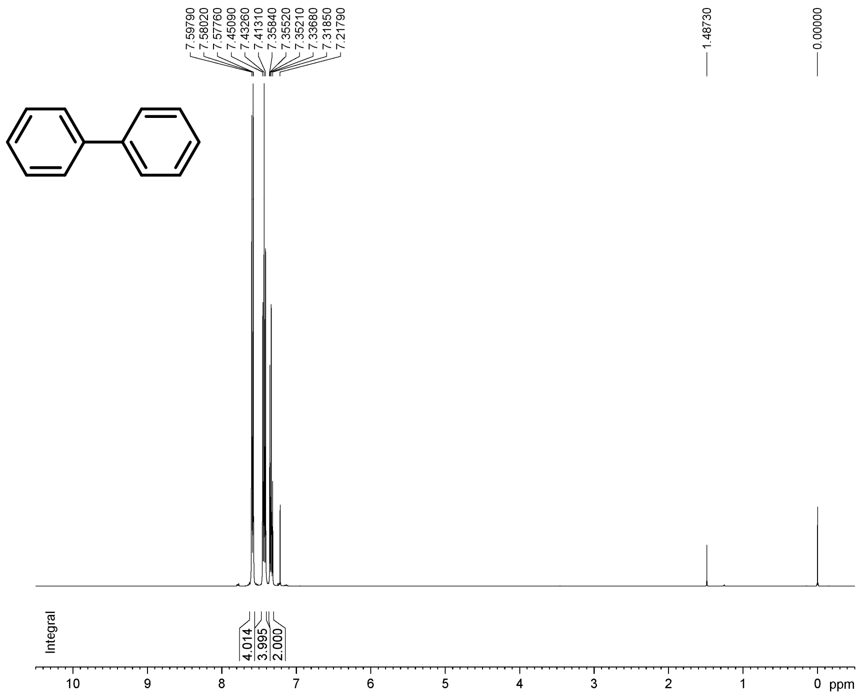
^{13}C NMR of **3g**



```
NAME              YH781-1
EXPNO                  11
PROCNO                  1
Date_            20171108
Time                14.36
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    300
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 208.17
DW                 20.800 usec
DE                   6.50 usec
TE                  296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.95 usec
SI                  32768
SF            100.6127561 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

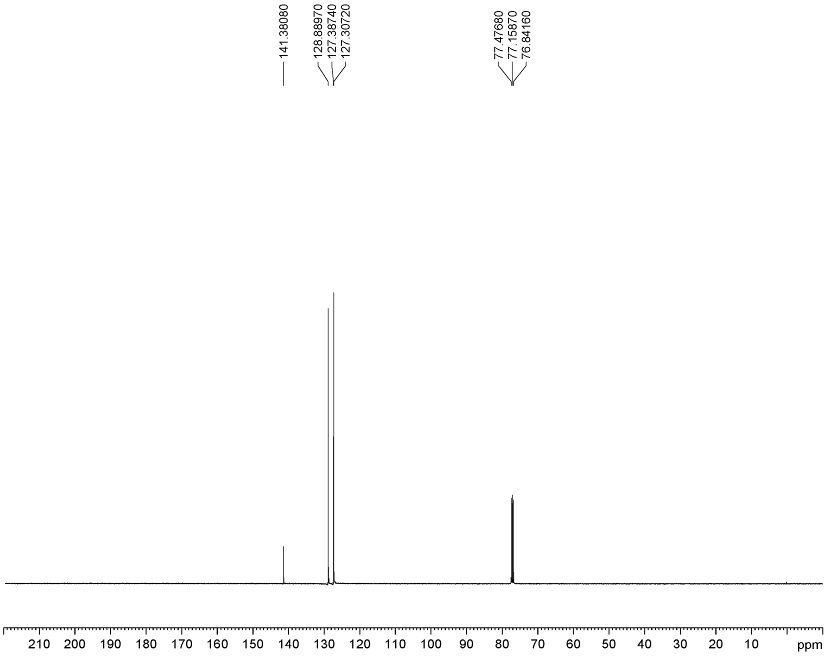
^{1}H NMR of **3c**



```
NAME            YH796-5
EXPNO                10
PROCNO                1
Date_          20171118
Time              15.36
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                57.49
DW               62.400 usec
DE                 6.50 usec
TE                297.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                 9.68 usec
SI                65536
SF          400.1300265 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

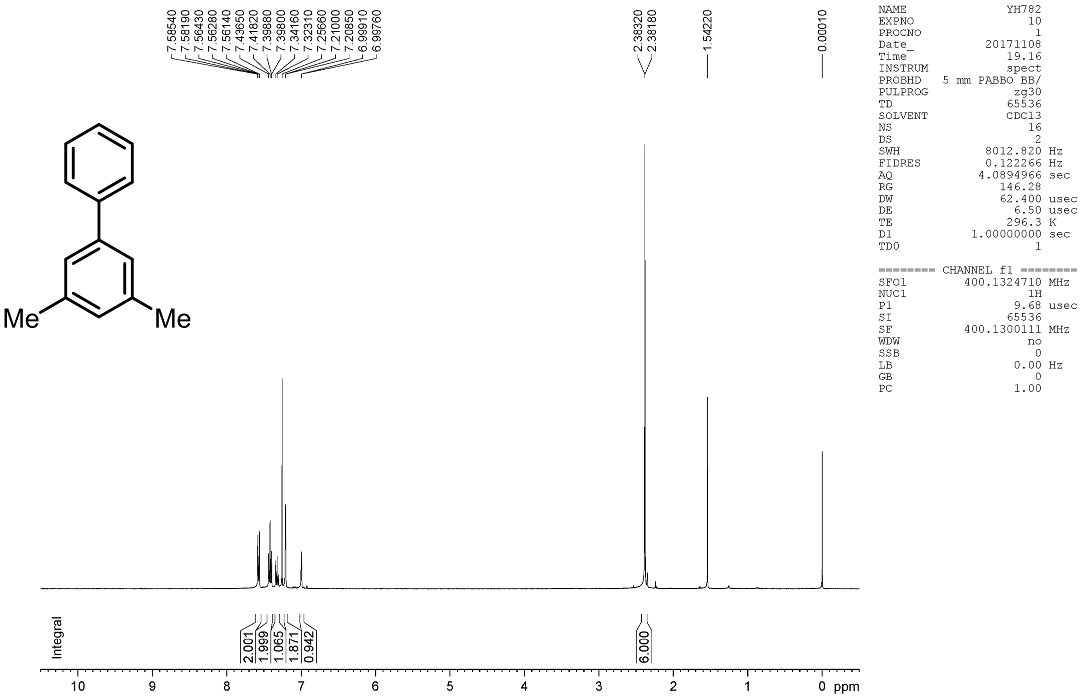
^{13}C NMR of **3c**



```
NAME            YH796-5
EXPNO                11
PROCNO                1
Date_          20171119
Time               3.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               208.17
DW               20.800 usec
DE                 6.50 usec
TE                297.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.95 usec
SI                32768
SF          100.6127587 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

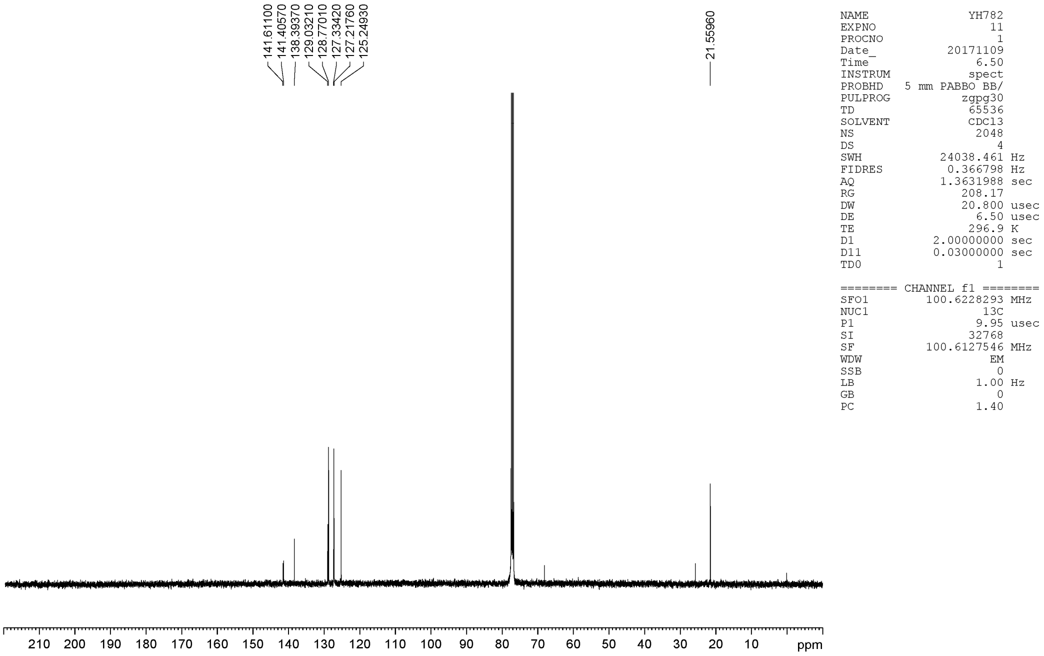
^{1}H NMR of **3j**



```
NAME               YH782
EXPNO                 10
PROCNO                 1
Date_           20171108
Time               19.16
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                146.28
DW                62.400 usec
DE                  6.50 usec
TE                 296.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300111 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

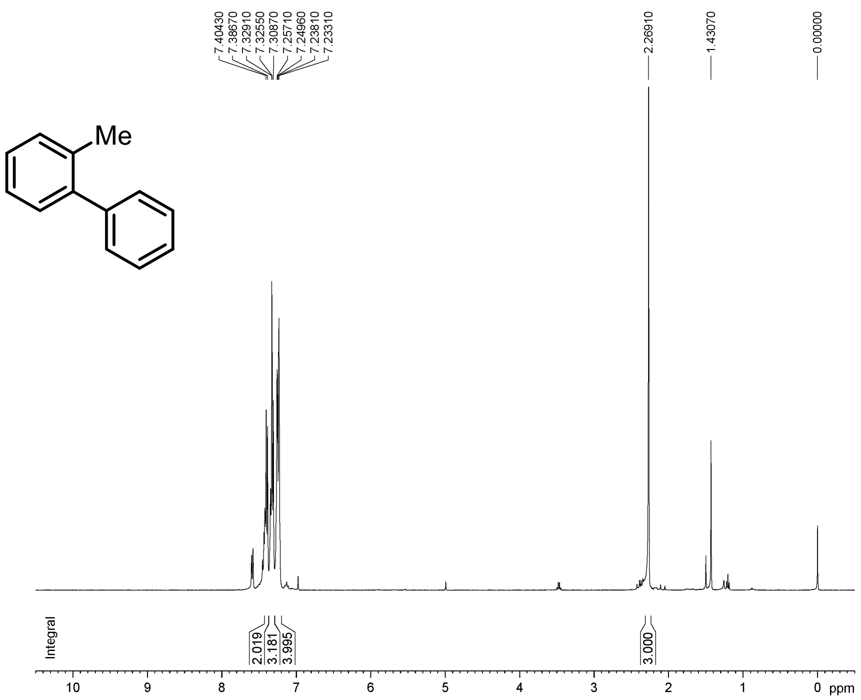
^{13}C NMR of **3j**



```
NAME               YH782
EXPNO                 11
PROCNO                 1
Date_           20171109
Time                6.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 296.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127546 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

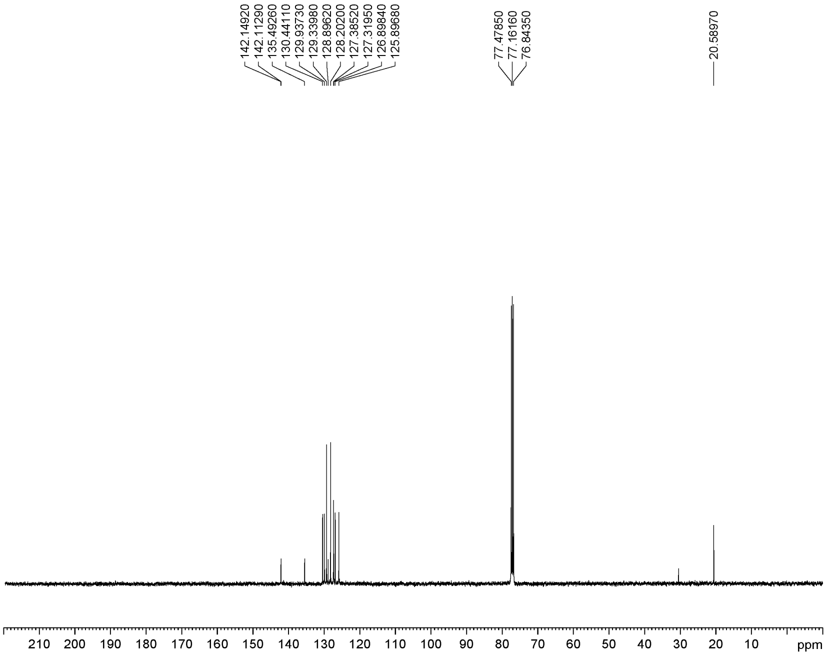
^{1}H NMR of **3l**



```
NAME            YH479-3
EXPNO                10
PROCNO                1
Date_          20161205
Time              12.47
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                82.47
DW               62.400 usec
DE                 6.50 usec
TE                302.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                 9.95 usec
SI                65536
SF          400.1300191 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

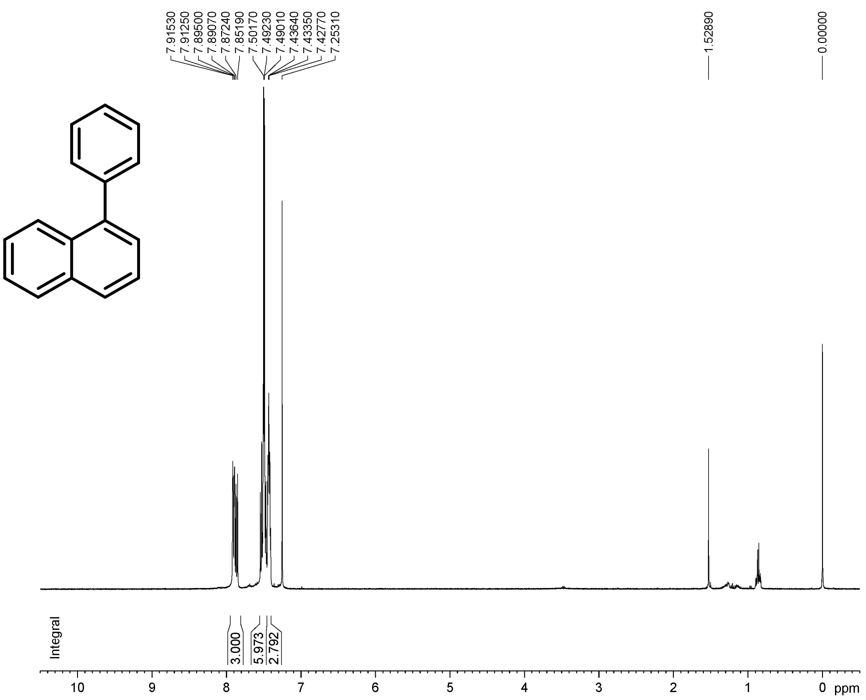
^{13}C NMR of **3l**



```
NAME            YH479-3
EXPNO                11
PROCNO                1
Date_          20161205
Time              13.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  500
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               208.17
DW               20.800 usec
DE                 6.50 usec
TE                302.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                 9.95 usec
SI                32768
SF          100.6127543 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.40
```

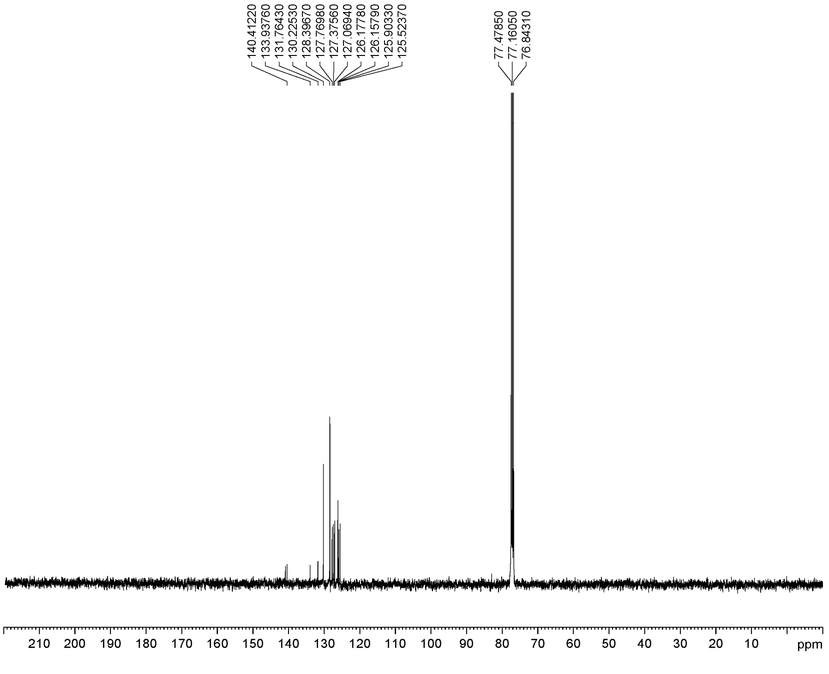
^{1}H NMR of **3n**



```
NAME             YH796-1
EXPNO                 10
PROCNO                 1
Date_           20171118
Time               16.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 82.47
DW                62.400 usec
DE                  6.50 usec
TE                 297.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                  9.68 usec
SI                 65536
SF           400.1300124 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

^{13}C NMR of **3n**



```
NAME             YH796-1
EXPNO                 11
PROCNO                 1
Date_           20171118
Time               16.46
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                208.17
DW                20.800 usec
DE                  6.50 usec
TE                 297.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.95 usec
SI                 32768
SF           100.6127546 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```

References

[1] V. Blanco, D. A. Leigh, V. Marcos, J. A. Morales-Serna, A. L. Nussbaume, *J. Am. Chem*. Soc. **2014**, *136*, 4905-4908.

[2] P. Garcia, Y. Y. Lau, M. R. Perry, L. Schafer, *Angew. Chem. Int. Ed*. **2013**, *52*, 9144-9148; *Angew. Chem.* **2013***, 125,* 9314-931.

[3] R. A. Green, J. F. Hartwigs, *Angew. Chem. Int. Ed*. **2015**, *54*, 3768-3772; *Angew. Chem.* **2015***, 127,* 3839-3843.

[4] P. Ji, C. Jang, K. Manna, Z. Lin, X. Feng, A. Urban, Y. Song, W. Bin, *Asian. J. Am. Chem*. Soc. **2017**, *139*, 7004-7011.

[5] a) T. Kiguchi, N. Kuninobu, Y. Takahashi, Y. Yoshida, T. Naito, I. Ninomiya, *Synthesis* **1989**, *10*, 778-781; b) C. Suzuki, K. Hirano, T. Satoh, M. Miura, *Org. Lett*. **2013**, *15*, 3990-3993.

[6] a) H. Yang, L. Zhang, L. Jiao, *Chem. Eur. J*. **2017**, 23, 65-59; b) W. Hao, Z. Xi, M. Cai, *Synthetic. Communication*, **2012**, *42*, 2396-2406.

[7] Y. Qiu, Y. Liu, K. Yang, W. Hong, Z. Li, Z. Wang, Z. Yang, S. Jiang, *Org. Lett*. **2011**, *13*, 3556-3559.

[8] K. Takamatsu, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem*. **2015**, *80*, 3242-3249.

[9] G. Zhang, Z. Yin, S. Zheng, *Org. Lett*. **2016**, *18*, 300-303.

[10] X. Jiang, C. Wang, Y. Wei, D. Xue, Z. Liu, J. Xiao, *Chem. –Eur. J.* **2014**, 20, 58-63.

[11] S. R. Kandukuri, J. A. Schiffner, M. Oestreich, *Angew. Chem. Int. Ed*. **2012**, *51*, 1265-1269; *Angew. Chem.* **2012***, 124,* 1291-1295.

[12] D. Robinson, T. Bertrand, J. –C. Carry, F. Halley, A. Karlsson, M. Mathieu, H. Minoux, M. A. Perrin, B. Robert, L. Schio, W. Sherman, *J. Chem. Inf. Model*. **2016**, *56*, 886-894.

[13] F. Chen, A. -E. Surkus, L. Hi, M. M. Pohl, J. Radnik, C. Topf, K. Junge, M. Beller, *J. Am. Chem*. Soc. **2015**, *137*, 11718-11724.

[14] D. Yang, S. Mao, Y. -R. Gao, D. -D. Gao, S. -H. Guo, B. Li, Y.-Q. Yang, *RSC*. Adv. **2015**, *5*, 23727-23736.

[15] a) C. Helgen, C. G. Bochet, *J. Org. Chem*. **2003**, *68*, 2483-2486; b) S. M. Bromidge, S. Dabbs, D. T. Davies, D. M. Duckworth, L. T. Forbes, P. Ham, G. E. Jones, F. D. King, D. V. Saunders, S. Starr, K. M. Thewlis, P. A. Wyman, F. E. Blaney, C. B. Naylor, F. Bailey, T. P. Blakbum, V. Holland, G. A. Kennett, G. J. Riley, M. D. Wood, *J. Med. Chem*. **1998**, *41*, 1598-1612; c) S. Miltsov, V. Karavan, A. Misharev, J. Alonsochamarro, M. Puyol, *Tetrahedron Lett*. **2016**, *57*, 641-644.

[16] W.-B. Liu, D. P. Schuman, Y.-F. Yang, A. A. Toutov, Y. Liang, H. F. T. Klare, N. Nesnas, M. Oestreich, D. G. Blackmond, S. C. Virgil, S. Banerjee, R. N. Zare, R. H. Grubbs, K. N. Houk, B. M. Stoltz, *J. Am. Chem. Soc*. **2017**, *139*, 6867-6879.

[17] J. Säuberlich, O. Brede, D. Beckert, *J. Phys. Chem*. **1996**, *100*, 18101-18107.

[18] M. Kuriyama, R. Shimazawa, R. Shirai, *J. Org. Chem*. **2008**, *73*, 1597-1600.

[19] J. J. Eisch, S. Dutta, *Organometallics* **2005**, *24*, 3355-3358.

[20] Full citation of Gaussian 09: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam,

J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; *Gaussian 09, revision B.01*; Gaussian Inc.: Wallingford, CT, 2010.

[21] a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241; b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157-167.