

Novel synthetic approach in microwave-assisted solid-supported oxidations using ‘in situ’ generated molecular oxygen

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Abstract—Three different types of oxidation reactions were carried out under microwave (MW) conditions in dry media, with nearly quantitative yield, using ‘in situ’, yet separately generated molecular oxygen as the reactive gas. The latter is formed by a controlled decomposition of potassium chlorate (220–306 °C) adsorbed on zeolite support, and is used as a reactive oxidizing agent for the solid-supported oxidations. The MW-assisted oxidations include an oxidative decomplexation of (η^6 -arene)Cr(CO)₃ complexes to the corresponding arenes using silica as solid support (100 °C), an oxidation of fluorene to fluorenone induced by KF-alumina support (150 °C), and oxidation of benzyl alcohol to benzaldehyde using a supported ruthenium catalyst (150 °C). This synthetic approach allows to carry out in synchronized manner two different solid-supported reactions (oxygen generation and oxidation) at different temperatures and on different solid supports together in the same sealed system. It was made possible by tuning the absorption efficiency of MWs through accurate selection of the solid supports employed in the reactions. The high feasibility of this novel synthetic approach resulted from a preliminary study of the interaction between MWs and mineral oxides such as alumina, silica, clay, and zeolite particularly when mixed with additives such as water, ionic liquids or graphite (5% w/w). The use of these MW absorber additives allows the MW transparent or poorly absorbing mineral oxides to be efficiently heated to very high temperatures in few minutes.

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1. Introduction

The use of microwave (MW) irradiation technique as an energy source for organic synthesis,¹ combined with inorganic solids as catalysts or as reaction media,² is rapidly growing. These MW-assisted, solvent-free (dry media) reactions often involve minimal waste, efficient catalyst recycling, faster reaction rates, increased yield, and easier set-up and work-up procedures as compared to the classical synthetic methods. Alumina, silica, clays, and zeolites are most popular as solid supports, exhibiting large and distinctive surface area and catalytic properties.² However, due to technical limitations regarding MW heating in conjunction to gaseous reagents in sealed reaction vessels or under pressure, this approach seems to be impractical for conventional MW ovens currently used for synthetic applications. The development of a new and efficient process, which involves reactive gases such as molecular oxygen (oxidation), hydrogen (reduction), carbon dioxide (carboxylation), carbon monoxide (carbonylation), sulfur dioxide (sulfonylation), and so forth, is therefore imperative for the progress of MW-assisted organic synthesis. To the best of our knowledge, there are only a few examples of reactions assisted by MW, in solution

media, which involved in situ generation of gaseous carbon monoxide from solid molybdenum hexacarbonyl (i.e., directly in the reaction mixture, without the need for external source).³

The aim of this study was to explore the possibility of a highly controlled MW-assisted synthetic process whereby two different solid-supported reactions are carried out in one sealed vessel, so that a reactive gas produced in the first reaction (quantitatively) is used as a reagent by the second reaction (an organic transformation). We hypothesized that the specific interaction between each reaction mixture and MWs may lead to different temperatures even though the two reaction tubes are situated together in the same sealed vessel and exposed to the same irradiation conditions.

2. Results and discussion

In order to prove the feasibility of this approach we chose three different oxidation reactions as models, in which molecular oxygen was used as oxidant (Fig. 1). These were {1} oxidative decomplexation of (η^6 -arene)Cr(CO)₃ complex to the corresponding arene.⁴ {2} Oxidation of fluorene to fluorenone using KF-alumina as solid support.⁵ {3} Oxidation of benzyl alcohol to benzaldehyde using supported ruthenium catalyst.⁶ As a source for molecular oxygen, thermal decomposition of potassium chlorate was chosen,

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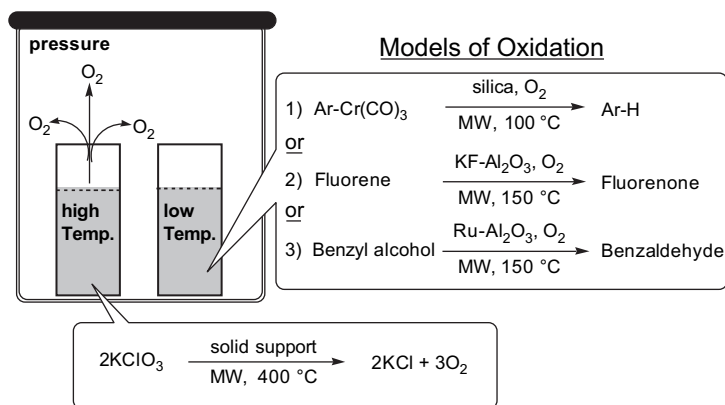


Figure 1. Schematic presentation for three different oxidation reactions performed by ‘in situ’, yet separately generated, molecular oxygen.

which required high temperatures and delivered fixed amounts of reactive gas.

In order to attain the desired temperature and to avoid desorption or decomposition of the adsorbed reactants, the process should be controlled by tuning the coupling efficiency of MWs by the chosen solid support. Hence, we initially investigated the coupling efficiency of various inorganic solids with MWs (Table 1).

As expected, when properly dried, the minerals presented in Table 1 weakly responded to MW irradiation and the maximum temperatures attained (T_{max}) were between 56 and 85 °C. Addition of 5% water (w/w) selectively enhanced the maximum temperature attained and it was found that this effect is highly dependent upon the nature of the mineral. Namely, only minerals such as KF-alumina, clays, and zeolites, which effectively prevent water desorption, interacted efficiently with MWs (Table 1, runs 16, 19, 23–25). Yet, for many organic reactions that involve nonpolar reactants and require high temperature and anhydrous conditions, the idea of using such solid supports as reaction media seems to be impractical. We therefore hypothesized that additives such as ionic liquids⁷ and graphite,⁸ which

possess an appreciable interaction with MWs may profoundly improve MW coupling of the solid supports. These environmentally benign additives are characterized by high boiling points, high affinity to the solid support and low reactivity. Recently, Leadbeter et al. have shown that nonpolar solvents, such as hexane and toluene, which are transparent to MWs, can be heated considerably above their boiling points by MW irradiation using a small quantity of an ionic liquid as additive.^{7c} One should note that for the same purpose Kappe et al. have recently reported on alternative, non-invasive approach that utilized cylinders of the MW absorber silicon carbide (SiC) as passive heating element in nonpolar solvents.⁹

Inspection of the data presented in Table 1 reveals that ionic liquids (5% w/w) such as 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF₄) dramatically improved the interaction between MWs and the mineral oxides such as silica (194 °C, run 3), neutral and basic alumina (183 and 200 °C, runs 7 and 11, respectively), and montmorillonite K-10 (238 °C, run 20). Interestingly, when graphite (5% w/w) and inorganic solids such as alumina or silica were mixed and exposed to MW irradiation, the thermal behavior was utterly dependent upon the nature of the solid.

Table 1. The influence of water, ionic liquids, and graphite as additives, on the interaction between microwaves and mineral solids, when subjected to a rigorous method consisted of 500 W limit and 220 °C preselected maximum temperature for 4 min

Run	Solid used	Additive ^a	T_{max}^b [°C]	Run	Solid used	Additive ^a	T_{max}^b [°C]
1	SiO ₂	None	85	14	Acidic-Al ₂ O ₃	Graphite	230 ^c
2	SiO ₂	H ₂ O	146	15	KF-Al ₂ O ₃	None	56
3	SiO ₂	[emim]BF ₄	194	16	KF-Al ₂ O ₃	H ₂ O	218
4	SiO ₂	Graphite	108	17	KF-Al ₂ O ₃	Graphite	238 ^c
5	Neutral-Al ₂ O ₃	None	59	18	mont. K-10	None	60
6	Neutral-Al ₂ O ₃	H ₂ O	88	19	mont. K-10	H ₂ O	195
7	Neutral-Al ₂ O ₃	[emim]BF ₄	183	20	mont. K-10	[emim]BF ₄	238 ^c
8	Neutral-Al ₂ O ₃	Graphite	232 ^c	21	mont. K-10	Graphite	105
9	Basic-Al ₂ O ₃	None	64	22	mont. KSF	None	60
10	Basic-Al ₂ O ₃	H ₂ O	107	23	mont. KSF	H ₂ O	190
11	Basic-Al ₂ O ₃	[emim]BF ₄	200	24	NH ₄ -Y	‘Dry’ ^c	248 ^{d,e}
12	Acidic-Al ₂ O ₃	None	60	25	Na-Y	‘Dry’ ^c	230 ^{d,e}
13	Acidic-Al ₂ O ₃	H ₂ O	186				

^a Additive (5% w/w) was mixed with the appropriate inorganic solid.

^b Although the temperature in the irradiated solids is not uniform by definition, and its measurement is an average, the reproducibility of the measurements ($n=3$) was acceptable with ca. ± 5 °C.

^c This zeolite was located in internal vessel and periodically irradiated by MW to 300 °C for 2 min until no water drops were observed in the external sealed vessel.

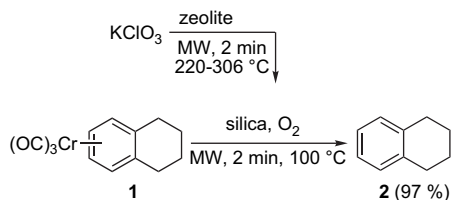
^d Temperature attained within 2.5 min.

^e In these cases, the material showed an excellent response to microwave irradiation and the T_{max} attained was higher than the preselected 220 °C due to microwave instrument’s limitation.

Namely, with the alumina-type solids neutral-, acidic-, and KF-alumina, a considerable increase in T_{\max} was observed (232, 230, and 238 °C, runs 8, 14, and 17, respectively), while mixing graphite with silica or even with montmorillonite K-10 revealed only a modest effect on T_{\max} (108 and 105 °C, runs 4 and 21, respectively).

The obtained thermal data, with data on physical properties (such as acidity/basicity, surface area, and structure) of the above-mentioned mineral oxides, can provide an improved tool for designing highly controlled synthetic processes under solvent-free (dry media) MW conditions.

Based on the significant differences in the ability of mineral oxides to interact with MWs as shown in Table 1, we proceeded to test the above-mentioned oxidation model reactions using generation of molecular oxygen by thermal decomposition of KClO_3 . Thus, an externally sealed vessel was equipped with two separate, open, insert vials (each coated with Teflon shawl), and the vessel was saturated with argon gas. The first vial contained a mixture of potassium chlorate (25% w/w) and ammonium-Y zeolite (dried as mentioned above). The second vial contained tetrahydronaphthalene chromium tricarbonyl complex (**1**) adsorbed on silica (10% w/w) as shown in Figure 1. The system, which related to oxidation model {1}, was exposed to MW irradiation at 500 W for 2 min, producing a pressure of 4 atm, indicating molecular oxygen formation. After cooling to room temperature, the pressure was carefully released and the external vessel was opened. Simple extraction of the arene product from the green silica mixture (indicating the presence of Cr_2O_3) by chloroform led to 97% yield of the product 9,10-tetrahydronaphthalene (**2**) (Scheme 1). The instantaneous liberation of O_2 has occurred at a temperature between 220 and 306 °C, which is far below the known decomposition temperature of potassium chlorate (ca. 400 °C in the absence of MnO_2 catalyst), as shown in Figure 2. This effect is assumed to be due to localized super-heating of the solid. The interaction between neat KClO_3 and MWs was also tested and found to be very weak, so that under the same MW program only a temperature of 31 °C was attained.



Scheme 1. Microwave-assisted oxidative decomplexation of (η^6 -arene)- $\text{Cr}(\text{CO})_3$ complex **1** to the corresponding arene **2**.

Encouraged by these results, we proceeded to test the second and more complicated model {2}. Namely, the oxidation of fluorene (**3**) to fluorenone (**4**) catalyzed by the basic solid $\text{KF-Al}_2\text{O}_3$. Here again, the first vial contained a mixture of potassium chlorate (25% w/w) and ammonium-Y zeolite (dried as mentioned above) and the second vial contained fluorene (**3**) adsorbed on $\text{KF-Al}_2\text{O}_3$ (10% w/w). The system was exposed to MW irradiation at 500 W and the temperature was limited to 150 °C. After 12 min of irradiation, this temperature was reached and a pressure of 4 atm (after ca. 2 min) has evolved. Simple extraction of the product from

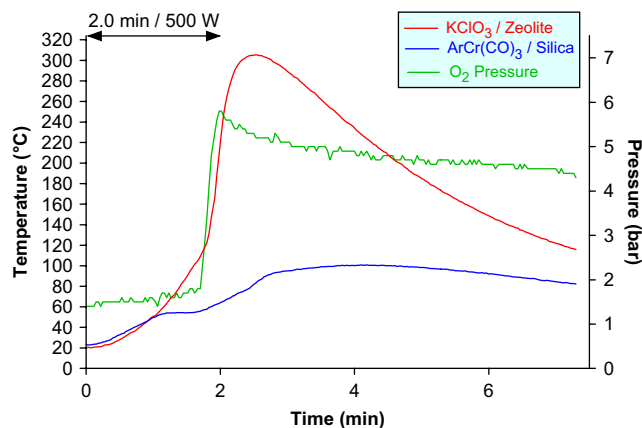


Figure 2. Pressure and temperature profile for oxidative decomplexation of arene chromium tricarbonyl.

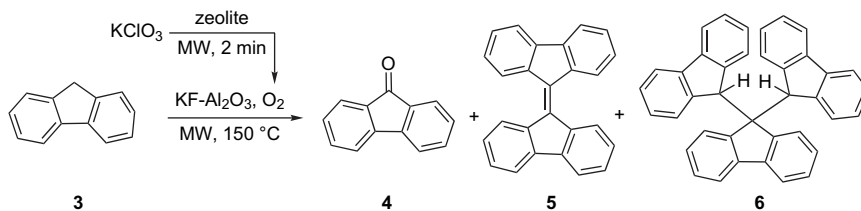
the brown $\text{KF-Al}_2\text{O}_3$ mixture by chloroform led to a mixture containing 98% fluorenone (**4**) and 2% bifluorenylidene (**5**), as determined by ^1H NMR (Table 2, run 1).

In the absence of KClO_3 , i.e., without oxygen release and under air atmosphere (1 atm), the same procedure led to the formation of a mixture of 36% fluorenone (**4**), 2% bifluorenylidene (**5**) and 25% terfluorenyl (**6**) together with unreacted fluorene (**3**) (Table 2, run 2). The selectivity obtained by our system strongly emphasizes the necessity of KClO_3 as an oxygen source in this method.

Addition of $\text{emim}[\text{BF}_4]$ (5 wt %) to the reaction mixture decreased the reaction time to 4 min but yielded a mixture of the products fluorenone (**4**), bifluorenylidene (**5**), and terfluorenyl (**6**) in 89, 4 and 7% yield, respectively (Table 2, run 3). However, the use of graphite as an additive not only decreased the reaction time to 5 min but also exclusively led to 99% fluorenone (**4**) (Table 2, run 4). When the reaction mixture was irradiated for equivalent length of time (4 min) in the absence of additives, the T_{\max} was only 90 °C and the yield of fluorenone product (**4**) was 72% (Table 2, run 7).

Due to a technical limitation regarding stirring of the reaction mixture, this method was found to be restricted to a quantity of less than 2 g in the model reaction {2}. At this quantity, the thermal behavior of the solid supports does not follow exactly the thermal profiles exhibited in Table 1. Thus, increasing the loading quantity of fluorene (**3**) caused a rise of the maximum temperature attained (220 °C), but decreased the yield of the reaction even after long periods of irradiation (Table 2, runs 5 and 6). We assume that despite the relatively high pressure of the oxygen it cannot easily penetrate through the bulk of the $\text{KF-Al}_2\text{O}_3$ support (ca. 2 cm height in 8 mL vial) without stirring, as also visually observed by the color gradient formed by the yellow fluorenone product (**4**) along the column of the reaction mixture. However, we believe that enlarging the external vessel would allow situation of the solid support in such a way that will allow efficient stirring of the reaction mixture and will facilitate the penetration of oxygen. As a consequence, this method may be adaptable to larger quantities.

A plausible mechanism for the formation of bifluorenylidene (**5**) and terfluorenyl (**6**) is shown in Scheme 2. The reaction is

Table 2. Results of the oxidation of fluorene to fluorenone by KF-Al₂O₃ and 'in situ' generated molecular oxygen

Run	Additive	T_{max} (°C)	Time ^c (min)	Product distribution (%)		
				4	5	6
1	None	150	12	98 (93) ^d	2	—
2	None ^a	150	12	36	2	25
3	emim[BF ₄]	150	4	89	4	7
4	Graphite	150	5	99	—	—
5	Graphite ^b	220	4	38	7	7
6	Graphite ^b	220	12	46	14	12
7	None	90	4	72	—	—

^a Under atmospheric pressure (without KClO₃).

^b Fluorene (0.2 g) adsorbed on 1.7 g KF-Al₂O₃ and 0.1 g graphite.

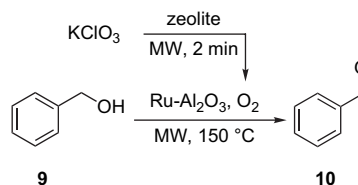
^c Total irradiation time.

^d Isolated yield.

initiated by an oxidation step to yield fluorenone (**4**) via a fluorenyl anion intermediate **7**.⁵ The generated fluorenone (**4**) undergoes a nucleophilic addition by fluorenyl anion **7** at the carbonyl carbon followed by protonation to form fluorenol **8**, which then leads to the observed bifluorenylidene (**5**) by elimination of a water molecule catalyzed by the basic KF-Al₂O₃ support (Scheme 2). The latter undergoes a further nucleophilic addition by **7** followed by protonation that leads to the formation of terfluorenyl (**6**).¹⁰ Thus, it is not surprising that under air atmosphere (i.e., deficiency and low pressure of molecular oxygen), as in the control reaction mentioned above, the terfluorenyl product (**6**) was one of the two major products with 25% yield (Table 2, run 2).

Next, the approach was successfully demonstrated on the oxidation of benzyl alcohol to benzaldehyde, catalyzed by Ru/Al₂O₃ according to model {3}.⁶ The first vial contained the mixture of potassium chlorate and ammonium-Y zeolite as described above and the second vial contained benzyl alcohol (**9**) adsorbed on Ru/Al₂O₃ (10% w/w). The system was exposed to MW irradiation at 500 W for 20 min and the

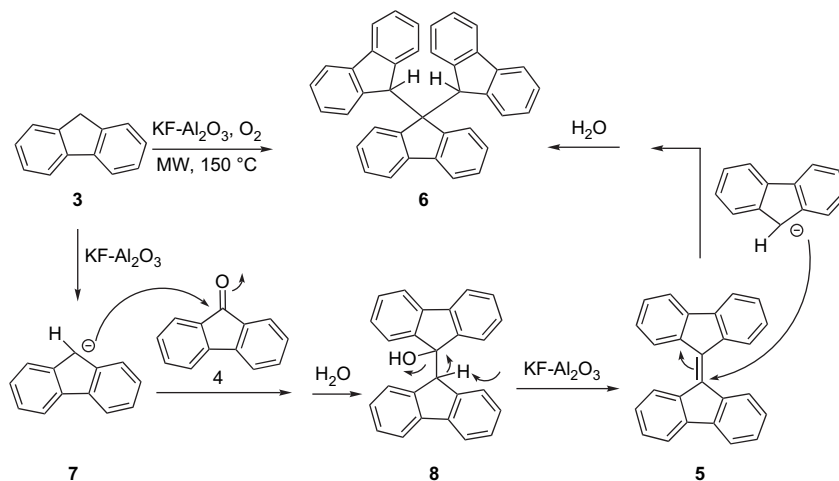
temperature was limited to 150 °C (Table 3). Again, a pressure of 4 atm after ca. 2 min has evolved. Simple extraction of the product from the Ru/Al₂O₃ mixture by chloroform

Table 3. Results of the oxidation of benzyl alcohol to benzaldehyde catalyzed by Ru/Al₂O₃ with 'in situ' generated molecular oxygen

Run	Additive	Time ^a (min)	Benzaldehyde (10) (%)
1	None	10	60
2	None	20	88
3	None ^b	20	8
4	Graphite	20	95

^a Total irradiation time.

^b Under atmosphere pressure (without KClO₃).

**Scheme 2.** A plausible mechanism for the formation of bifluorenylidene (**5**) and terfluorenyl (**6**) in MW-assisted oxidation of fluorene to fluorenone.

gave the benzaldehyde product (**10**) in 88% yield, as determined by ^1H NMR spectroscopy (Table 3, run 2). Irradiation of the reaction mixture for 10 min yielded only 60% of benzaldehyde (**10**) (Table 3, run 1). Under air atmosphere (without KClO_3), the same procedure led to the formation of only 8% benzaldehyde (**10**) together with unreacted benzyl alcohol (**9**) (Table 3, run 3), emphasizing the necessity of KClO_3 as an oxygen source in this system. Addition of graphite (5 wt %) to the reaction mixture improved the yield of benzaldehyde product (**10**) (95%, Table 3, run 4).

3. Conclusion

In summary, the process described herein was made possible by the pronounced differences between the thermal behavior of the mineral oxides such as alumina, silica, clays, and zeolites induced by MW irradiation ($t=4$ min, 500 W, $T_{\text{max}}=56\text{--}248$ °C). We have shown that the temperature of the above-mentioned inorganic solids could be carefully tuned under MW irradiation, a feature that enabled us to design and develop a novel synthetic approach to the MW-assisted solid-supported oxidations with 'in situ', yet separately generated, molecular oxygen. These oxidations included an oxidative decomplexation of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes to the corresponding arenes using silica as solid support (100 °C), an oxidation of fluorene to fluorenone induced by KF-alumina support (150 °C), and oxidation of benzyl alcohol to benzaldehyde using supported ruthenium catalyst (150 °C). This approach consists of a unique process in which two different reactions in different conditions are performed in separated vessels positioned in the same sealed system, using a single cooperative energy source. This process that also benefits from high yield, easy set-up and work-up procedures, and fast reaction rate may be applied to various organic reactions involving gas or volatile reactants, which can be 'in situ' generated in the sealed system under MW conditions.

4. Experimental

4.1. General remarks

^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of CDCl_3 solutions were recorded on Bruker Avance spectrometer. Mass Spectra were recorded on Varian Saturn 2200 instrument at 70 eV. Reactions were performed in a laboratory microwave oven (Ethos SYNTH MW, Milestone Inc., Italy). Mineral oxides were purchased from Aldrich and dried prior to use at 150 °C for 20 h. Zeolites ($\text{NH}_4\text{-Y}$ and Na-Y) were dried under MW heating to 300 °C for 2 min (2–4 times) until no water drops were observed in the external vessel. All other solvents and reagents were obtained from Aldrich or Fluka and used without further purification. Column chromatography was performed with Merck silica gel 60 (230–400 mesh) and TLC was run on precoated Merck silica gel plates 60 F 254 (2.0 mm).

4.2. General procedures

4.2.1. Determination of microwave absorbance of mineral oxides. Mineral oxides were subjected to MW heating

method consisting of 500 W limit and 220 °C preselected maximum temperature for 4 min, in which the temperature, the pressure, and the power source could be efficiently monitored and controlled. All the experiments were performed in sealed systems (PRO-24 Rotor), equipped with Pyrex insert vessel, containing 8.0 g of the tested inorganic solid.

In cases, where an additive was used, we simply mixed and crushed 5% (w/w) of the appropriate additive with the mineral support.

4.2.2. Oxidations. An externally sealed vessel (HPR-1000/10s Rotor) was equipped with two separate, open insert vials (each coated with Teflon shawl). The first vial contained a mixture of potassium chlorate (1.0 g, 25% w/w) and ammonium-Y zeolite (dried as mentioned above). The second vial contained the organic substance to be oxidized (200 mg of **1** or 100 mg of **3** or 100 mg of **9**) adsorbed on the appropriate solid support (silica or $\text{KF-Al}_2\text{O}_3$ or $\text{Ru-Al}_2\text{O}_3$, respectively, 10% w/w). The system was exposed to MW irradiation at 500 W for the required time, producing a pressure of 4–5 atm, due to molecular oxygen generation, as illustrated in Figure 1. After cooling to room temperature, the pressure was carefully released and the external vessel was opened. Oxidation products (**2** or **4** or **10**, respectively) were successfully extracted from the appropriate solid support by CDCl_3 (2 × 1 mL).

Based on ^1H NMR, ^{13}C NMR, and GC–MS data, the products were obtained in a relatively high degree of purity without any additional treatment. Bifluorenylidene (**5**) and terfluorenyl (**6**) were isolated by flash chromatography utilized silica gel 60 (hexane/ethyl acetate gradient elution: 100–80% of hexane in 20 min) and identified by comparing ^1H and ^{13}C NMR and GC–MS spectra with the reported data.¹¹

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