Supporting Information

Recyclable Polyetheretherketone Fiber-Supported N-Heterocyclic Carbene Catalysts for Nucleophilic Acylation of Fluorobenzenes

Xian-Lei Shi,*[ad] Benyu Sun,[a] Qianqian Hu,[a] Kun Liu,[b] Pengyu Li[c] and Juanjuan Wang[a]

[a] *Synerigism Innovative Center of Coal Safety Production in Henan Province, College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R. China. E-mail: shixl@tju.edu.cn; Tel: +86-0391-3986810*

[b] *School of Environment and Materials Engineering, Yantai University, Yantai, Shandong 264005, P. R. China*

[c] *School of Materials and Chemical Engineering, Center for Advanced Materials Research, Zhongyuan University of Technology, Zhengzhou 450007, P. R. China*

[d] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China*

List of Contents:

Experimental details and results

Materials

Commercially available PEEK fiber with a length of 10 cm and a diameter of 30 ± 0.5 μm (from the Changzhou Co-win New Material Technology Co., Ltd.) was used after dried (In order to avoid the possible impacts of water absorption on the subsequent reactions and the consequent possible sources for experimental errors, all the fiber samples before use were dried fully at 60 °C under vacuum in this study). Imidazole, methyl iodide and all other chemicals used were analytical grade and employed without further purification. The solvents of THF, DMF and DMSO were dried and degassed before use, and water was deionized.

Apparatus and instruments

The mechanical properties of different fiber samples were tested with an electronic single fiber strength tester (Quanzhou Meibang Instrument Co., Ltd of China, model YG001E). Elemental analyses were performed on a thermo scientific flash 2000 auto-analyzer. Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr disc. A scanning electron microscope (Hitachi, model S-4800) was used to characterize the surface morphology of the fibers. The solid-state ^{13}C NMR spectra for detecting the fibers were performed on a Varian Infinityplus 300 spectrometer. ^{1}H NMR spectra were recorded on an AVANCE III (Bruker, 400 MHz) instrument using TMS as the internal standard. ^{13}C NMR spectra were recorded on an AVANCE III (Bruker, 101 MHz) instrument with complete proton decoupling.

Preparation of the PEEK fiber-supported NHCs precursor

Step 1. 1,2-Dichloroethane (50 mL) were introduced into a three-necked flask with a condenser (the condenser top attached with a balloon), and the solution was preheated to reflux with stirring. Next, dried PEEK fiber (2.50 g) was immersed into the above refluxing mixture (83 °C) and stirred for 8 h. The above solution was cooled to room temperature, then chloromethyl methyl ether (10.00 g) and stannic chloride (5.05g) were added respectively, and the formed solution was stirred at 60 °C for 40 h. Whereafter, the fiber sample was filtered out and repeatedly washed with etanol (3×20 mL), and then the fiber was dried to constant weight at 60 °C under vacuum to give chloromethyl functionalized PEEK (PEEK-CM, 3.19 g, a weight gain of 27.6%).

Step 2. Imidazole (1.75 g) and acetonitrile (50 mL) were introduced into a three-necked flask with a condenser, and the solution was preheated to reflux with stirring. Next, dried PEEK-CM (2.33 g) was immersed into the above refluxing mixture (83 °C) and stirred for 12 h. The fiber sample was filtered out and repeatedly washed with acetonitrile (3×20 mL), and then the fiber was dried to constant weight at 60 °C under vacuum to give the PEEK-supported imidazole hydrochloride (PEEK-IMHCl, 2.76 g, a weight gain of 18.5%, the content of imidazole hydrochloride was 2.29 mmol g^{-1}).

Step 3. PEEK-IMHCl (2.56 g) was immersed in a 5% (mass percent) sodium carbonate solution (50 mL) at room temperature and stirred for 2 h, then the fiber sample was filtered out and washed with water (3×15 mL), and next dried to constant weight at 60 °C under vacuum to gain imidazole functionalized PEEK (PEEK-IM, 2.32 g, a weight gain of -9.38%, the content of imidazole was 2.83 mmol g^{-1}).

Step 4. A typical procedure for the preparation of PEEK-supported imidazoliums (PEEK-IMRX) is as follows: Methyl iodide (5.0 g, 35 mmol) was dissolved in acetonitrile (40 mL), and dried PEEK-IM (1.04 g) was introduced to the solution. The mixture was stirred under refluxing for 12 h. Then, the fiber sample was filtered out and washed with acetonitrile (3×15 mL), and dried to constant weight at 60 °C under vacuum to gain PEEK-supported methyl imidazolonium iodide salt (PEEK-IMMI, 1.29 g, a weight gain of 24.0%, the content of imidazolonium was 1.37 mmol g^{-1}).

General procedure for nucleophilic acylation of fluorobenzenes

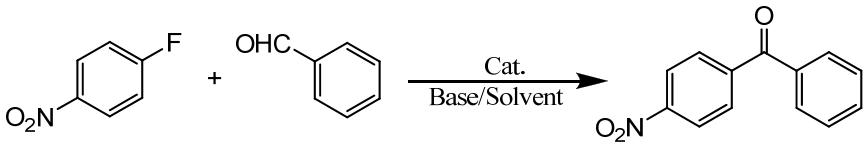
Under an atmosphere of nitrogen, a dried Schlenk flask was charged with 60% sodium hydride in oil (60 mg, 1.5 mmol) and PEEK-IMMI (73 mg, 10 mol%, based on aldehyde). Next, fluorobenzene (1 mmol) and aldehyde (1 mmol) in DMF (10 mL) was added via syringe. The mixture was stirred at 0 °C for 0.5 h and then at room temperature for desired time. Whereafter, a solution of HCl in dioxane (4 M, 0.5 mL) was added slowly via syringe and the mixture was stirred for an additional 1 h at room temperature. Then, the PEEK-IMMI was recovered with a tiny pair of tweezers and rinsed with ethyl acetate (10 mL) and water (10 mL) which was combined to the mixture. Next, the organic layer was washed with saturated brine solution and the aqueous layer was back-extracted with ethyl acetate (3×10 mL), dried over Na_2SO_4, filtered and concentrated. Finally, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to obtain the product. For the recycling process, the recovered PEEK-IMMI after drying was conducted to the next cycle without any further treatment.

Typical gram-scale procedure for nucleophilic acylation of fluorobenzenes

Under an atmosphere of nitrogen, a dried Schlenk flask was charged with 60% sodium hydride in oil (0.60 g, 15 mmol) and PEEK-IMMI (0.73 g, 10 mol%, based on benzaldehyde). Next, 4-fluoronitrobenzene (1.41 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) in DMF (50 mL) was added via syringe. The mixture was stirred at 0 °C for 0.5 h and then at room temperature for 1 h. Whereafter, a solution of HCl in dioxane (4 M, 5 mL) was added slowly via syringe and the mixture was stirred for an additional 1 h at room temperature. Then, the PEEK-IMMI was recovered with a tiny pair of tweezers and rinsed with ethyl acetate (50 mL) and water (50 mL) which was combined to the mixture. Next, the organic layer was washed with saturated brine solution and the aqueous layer was back-extracted with ethyl acetate (3×25 mL), dried over Na_2SO_4, filtered and concentrated. Finally, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to obtain the product (1.95 g, with an isolated yield of 86%).

Optimization results of nucleophilic acylation of fluorobenzenes

Table S1. Optimization of nucleophilic acylation of fluorobenzenes[a]



Entry	Precatalyst	Solven	Base	Cat. amount[b] (mol%)	Temperature (°C) and Time (h)	Yield[c] (%)
1	-	DMF	NaH	-	0 °C 1 h and rt 2 h	Traces
2	PEEK	DMF	NaH	-[d]	0 °C 1 h and rt 2 h	Traces
3	PEEK-IMHCl	DMF	NaH	5[e]	0 °C 1 h and rt 2 h	Traces
4	PEEK-IM	DMF	NaH	5[e]	0 °C 1 h and rt 2 h	Traces
5	PEEK-IMMI	DMF	NaH	5	0 °C 1 h and rt 2 h	80
6	PEEK-IMEB	DMF	NaH	5	0 °C 1 h and rt 2 h	77
7	DMII	DMF	NaH	5	0 °C 1 h and rt 2 h	61
8	PEEK-IMMI	THF	NaH	5	0 °C 1 h and rt 2 h	39
9	PEEK-IMMI	DMSO	NaH	5	0 °C 1 h and rt 2 h	53
10	PEEK-IMMI	MeCN	NaH	5	0 °C 1 h and rt 2 h	46
11	PEEK-IMMI	DMF	Et_3N	5	0 °C 1 h and rt 2 h	NR[f]
12	PEEK-IMMI	DMF	DBU	5	0 °C 1 h and rt 2 h	Traces
13	PEEK-IMMI	DMF	*t*-BuOK	5	0 °C 1 h and rt 2 h	34
14	PEEK-IMMI	DMF	Cs_2CO_3	5	0 °C 1 h and rt 2 h	NR[f]
15	PEEK-IMMI	DMF	NaH	1	0 °C 1 h and rt 2 h	72
16	PEEK-IMMI	DMF	NaH	10	0 °C 1 h and rt 2 h	86
17	PEEK-IMMI	DMF	NaH	15	0 °C 1 h and rt 2 h	87
18	PEEK-IMMI	DMF	NaH	10	0 °C 0.5 h and rt 2 h	89
19	PEEK-IMMI	DMF	NaH	10	0 °C 2.5 h	78
20	PEEK-IMMI	DMF	NaH	10	rt 2 h	53

[a] Reaction conditions: 4-Fluoronitrobenzene (1 mmol), benzaldehyde (1 mmol) with the corresponding catalyst, base (1.5 mmol) and reaction temperature in solvent (10 mL) for desired time under N_2. [b] Catalyst amount based on imidazolium. [c] Isolated yield. [d] PEEK 0.04 g. [e] Based on the content of imidazole. [f] No reaction.

Characterization results

Morphologies

The physical photographs of PEEK, PEEK-CM, PEEK-IMHCl, PEEK-IM, PEEK-IMMI, PEEK-IMMX-1 and PEEK-IMMX-21 were shown in Figure S1. From the apparent morphologies, the original PEEK fiber presented a bright white color (Figure S1a), and with the following functionalizations in preparation process, the colors of PEEK-CM, PEEK-IMHCl, PEEK-IM and PEEK-IMMI turned yellow (Figure S1b-e). Moreover, after catalytic applications and compared with fresh PEEK-IMMI, the colors of PEEK-IMMX-1 and PEEK-IMMX-21 (Figure S1f and g) got more dark. Except for the color change, the fiber samples were gradually shrunk, however, all the samples maintained the fibrous structure no matter whether it was in the preparation or utilization processes.

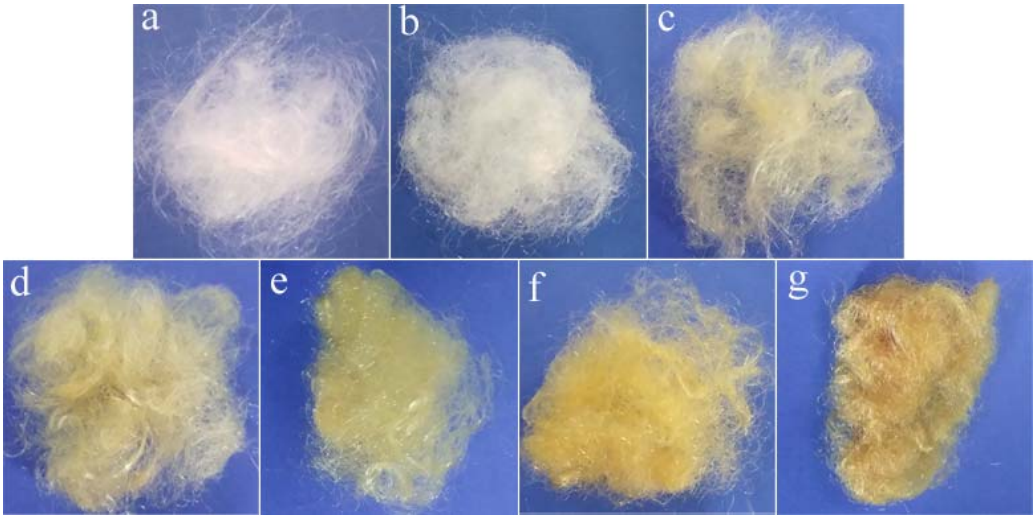


Figure S1. Photographs of (a) PEEK, (b) PEEK-CM, (c) PEEK-IMHCl, (d) PEEK-IM, (e) PEEK-IMMI, (f) PEEK-IMMX-1 and (g) PEEK-IMMX-21.

Elemental analysis

The elemental contents of C, H and N of the resulted fiber samples were determined by organic elemental analysis, the results and the calculated total content of O and halogen are listed in Table S2. The original PEEK fiber got a similar result to its theoretical value (Table S2, entry 1). After chloromethylation, the results show that

there are obvious changes between PEEK-CM and the original PEEK fiber, the contents of C and H were decreased, while the total content of O and X was increased (Table S2, entry 2), due to the chloromethyl groups were rooted to the fiber which contain more Cl. Moreover, after the reaction of PEEK-CM and imidazole to immobilize imidazole groups on the fiber, the N amount of the formed PEEK-IMHCl increased, and other elemental contents were all decreased (Table (Table S2, entry 3). However, after neutralization to remove the hydrogen chloride, the C, H and N contents of PEEK-IM were increased, and a part of Cl was eliminated which shown as the total content of O and X was decreased (Table S2, entry 4), these results also indicated that not all the chloromethyl were reacted with imidazole in step 2. As expected, the content of halogens was increased distinctly after the following reaction with methyl iodide to form PEEK-IMMI, while the C, H and N contents were declined again (Table S2, entry 5), owing to the incoming methyl iodide without N and has less C and H elements. Furthermore, the elemental contents of the recovered PEEK fiber-supported NHCs precursors PEEK-IMMX-1 and PEEK-IMMX-21 also exhibited some changes after the catalytic applications. Compared to the fresh PEEK-IMMI, the C, H and N contents of the recovered PEEK-IMMX-1 and PEEK-IMMX-21 were raised gradually, and the total content of O and X was declined successively (Table S2, entries 6 and 7). On the one hand, PEEK-IMMI was generated to the NHC catalyst in situ during the nucleophilic acylation, and after catalytic reaction the NHC was brought to its precursor by hydrogen chloride, on account of some iodine elements were replaced by Cl, and the atomic weight of Cl was significantly lower than iodine, which could cause the element content changes, and since the fibers contain more C than other elements, and the variations of C contents in the resulted fiber samples would be more significant. On the other hand, It was inevitable that some nucleophilic acylation substrates or products were grafted or adsorbed onto the fiber catalyst during the recycling, and the substrates and products contains more C than other elements, as well as the measurement error was unavoidable too (although tested three times to get the average value), which could also contribute to the test outcome above.

Table S2. Elemental analysis data of PEEK, PEEK-CM, PEEK-IMHCl, PEEK-IM, PEEK-IMMI, PEEK-IMMX-1 and PEEK-IMMX-21.

Entry	Fiber simple	C[a] (%)	H[a] (%)	N[a] (%)	(O and X)[b] (%)
1	PEEK	78.32	4.60	0.14	16.94
2	PEEK-CM	68.00	4.18	0.83	26.99
3	PEEK-IMHCl	63.06	4.14	6.41	26.39
4	PEEK-IM	67.76	4.29	7.97	20.98
5	PEEK-IMMI	55.73	3.73	4.36	36.18
6	PEEK-IMMX-1	59.49	4.21	4.49	31.81
7	PEEK-IMMX-21	61.31	4.27	4.65	29.77

[a] By organic elemental analysis. [b] X= I or Cl, by calculation.

FTIR spectroscopy

The fiber samples were cut into pieces for FTIR detection (KBr disk), and the obtained spectra are shown in Figure S2. As expected, in the spectrum of original PEEK fiber (Figure S2a), the most obvious absorption band around 1645 cm^{-1} was attributed to the C=O vibrational mode, except for overlap, the other two skeletal vibrations of benzene ring were at the peaks of 1487 and 1446 cm^{-1}, moreover, the absorption band at 1010 cm^{-1} was assigned to the ether bond in PEEK polymer chain. After chloromethylation, the absorption band at 1012 cm^{-1} was intensive (Figure S2b), which could be attributed to the new formation of C−Cl bound. After the following reaction with imidazole, the skeletal vibration of imidazole ring was displayed at 1562 cm^{-1} (Figure S2c), and this characteristic absorption still exist in the subsequent fiber samples of PEEK-IM and PEEK-IMMI, respectively (Figure S2d and e). What is more, the recovered PEEK-IMMX-1 and PEEK-IMMX-21 (Figure S2f and g) maintained the nearly identical spectra with that of PEEK-IMMI, indicating the reliability of the fiber-supported NHCs precursor for catalytic cycles.

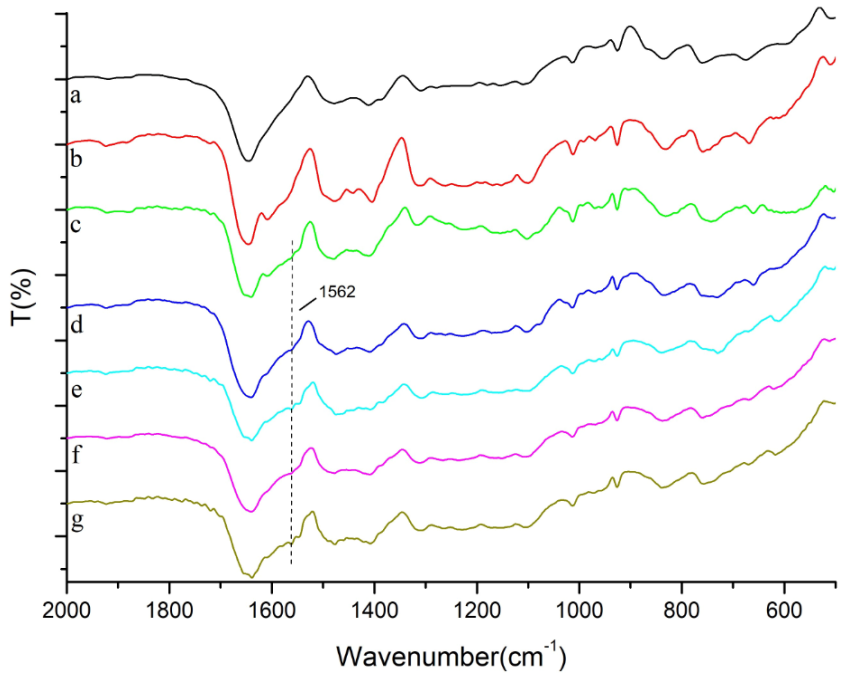


Figure S2. FTIR spectroscopy of (a) PEEK, (b) PEEK-CM, (c) PEEK-IMHCl, (d) PEEK-IM, (e) PEEK-IMMI, (f) PEEK-IMMX-1 and (g) PEEK-IMMX-21.

Mechanical properties

The mechanical properties of fiber sample were mainly affected by the immobilization condition and weight gain. That is, the more vigorous of reaction conditions in the immobilization process, the more breaking strength of the resulted fiber would loss. Correspondingly, a higher weight gain would also reduce the mechanical properties of the fiber sample. Moreover, the cumulative effects would outweigh solitary ones during the multi-step functionalization.

The mechanical properties of PEEK, PEEK-CM, PEEK-IMHCl, PEEK-IM, PEEK-IMMI, PEEK-IMMX-1 and PEEK-IMMX-21were all tested by an electronic single fiber strength tester (For each sample, 30 single fibers were selected randomly to test their breaking strength, tension and elongation, then took averages as the final data of the special fiber sample), and the results are summarized in Table S3. PEEK fiber with the breaking strength and tension of 35.55 cN and 8.82 cN per detx, respectively (Table S3, entry 1). After chloromethylation, a weight gain of 27.6% chloromethyl functionalized PEEK (PEEK-CM) was afforded, and the breaking

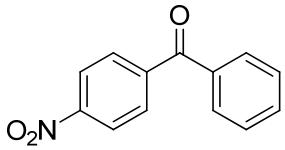
strength of PEEK-CM was cut down to 26.64 cN, and about 75% of the original mechanical properties were maintained, while the elongation was some increased due to the crosslinking in the chloromethylation (Table S3, entry 2). Next, PEEK-CM was reacted with imidazole in refluxed acetonitrile for a long time of 12 h, and the formed PEEK-IMHCl with a weight gain of 18.5%, and the breaking strength reduced dramatically (Table S3, entry 3). We believe that after twice immobilizations adjoined the fiber backbone, and the superimposed weight gain as well as the relatively harsh functionalization conditions which together contributed to the dramatic change in mechanical properties after the incorporation of imidazole. With the following neutralization, the breaking strength and tension of PEEK-IM decreased to 9.53 cN and 2.38 cN per detx, respectively (Table S3, entry 4). However, after the formation of PEEK-IMMI, there was no distinct decline of mechanical properties compared with that of PEEK-IM, *i.e.* 26.7% of the original fiber properties were retained (Table S3, entry 5). Moreover, the recovered PEEK-IMMX-1 and PEEK-IMMX-21 after catalytic applications showed tiny changes from the fresh PEEK fiber-supported NHCs precursor, and there was only a 0.07 cN decrease of the strength after 21 cycles (Table S3, entries 6 and 7), which inferred that the fiber catalyst was hold enough mechanical properties in nucleophilic acylation.

Table S3. Mechanical properties of PEEK, PEEK-CM, PEEK-IMHCl, PEEK-IM, PEEK-IMMI, PEEK-IMMX-1 and PEEK-IMMX-21.

Entry	Fiber simple	Breaking strength (cN)	Tension (cN/detx)	Elongation (%)	Retention rate[a] (%)
1	PEEK	35.55	8.82	20.22	100
2	PEEK-CM	26.64	6.66	26.72	74.94
3	PEEK-IMHCl	10.42	2.60	8.59	29.31
4	PEEK-IM	9.53	2.38	7.41	26.81
5	PEEK-IMMI	9.50	2.37	7.70	26.72
6	PEEK-IMMX-1	9.49	2.37	7.30	26.69
7	PEEK-IMMX-21	9.43	2.35	7.75	26.53

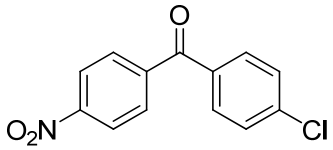
[a] The retention rate was based on the breaking strength of original PEEK fiber.

Physical data, ^{1}H and ^{13}C NMR spectra data of compounds



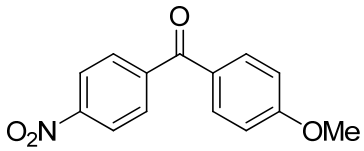
(4-Nitrophenyl)(phenyl)methanone. (3a)[1]

Pale yellow solid, m.p 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.82-7.77 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.76, 149.78, 142.85, 136.29, 133.45, 130.72, 130.11, 128.70, 123.53.



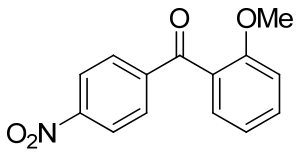
(4-Chlorophenyl)(4-nitrophenyl)methanone. (3b)[1]

Yellow solid, m.p 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.34 (m, 2H), 7.95-7.90 (m, 2H), 7.78-7.73 (m, 2H), 7.55-7.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.62, 149.91, 142.54, 140.10, 134.53, 131.54, 130.65, 129.14, 123.75.



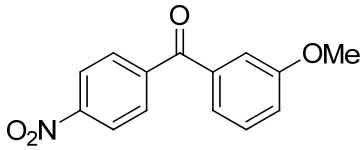
(4-Methoxyphenyl)(4-nitrophenyl)methanone. (3c)[2]

White solid, m.p 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.41, 164.05, 149.39, 143.72, 132.64, 130.30, 128.79, 123.41, 113.94, 55.67.



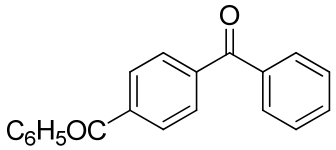
(2-Methoxyphenyl)(4-nitrophenyl)methanone. (3d)[2]

Yellow solid, m.p 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.69-7.43 (m, 2H), 7.21-7.17 (m, 2H), 3.88 (s, 3H); NMR (101 MHz, $CDCl_3$) δ 194.65, 159.94, 149.93, 143.02, 137.66, 130.74, 129.70, 123.58, 122.97, 119.96, 114.39, 55.64.



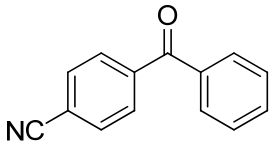
(3-Methoxyphenyl)(4-nitrophenyl)methanone. (3e)[2]

Yellow solid, m.p 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.45-7.12 (m, 4H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.62, 159.93, 149.81, 142.89, 137.64, 130.71, 129.56, 123.54, 122.93, 119.92, 114.33, 55.63.



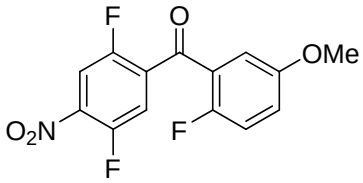
1,4-Dibenzoylbenzen. (3f)[2]

Pale yellow solid, m.p 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 4H), 7.84-7.80 (m, 4H), 7.61-7.56 (m, 2H), 7.53-7.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.05, 140.62, 136.91, 133.04, 130.09, 129.72, 128.53



(4-Cyanophenyl)(phenyl)methanone. (3g)[2]

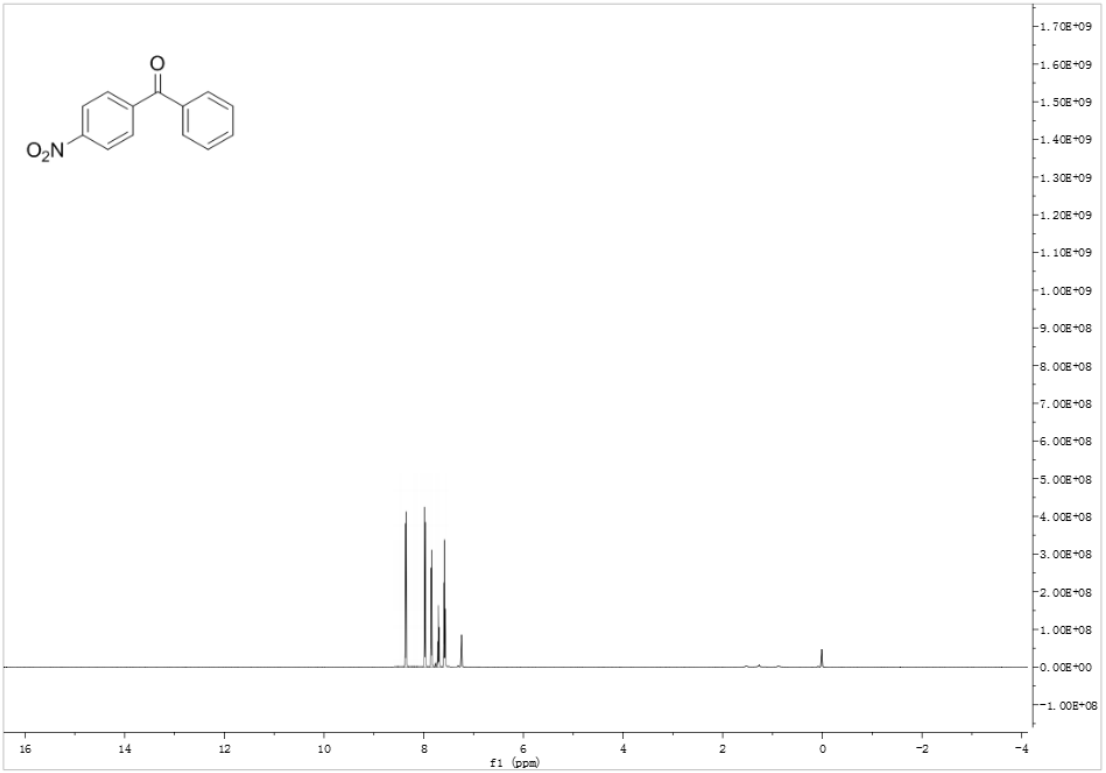
white solid, m.p 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.76-7.74 (m, 4H), 7.65 (t, *J*= 7.6 Hz, 1H), 7.56-7.45 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.03, 141.19, 136.32, 133.30, 132.14, 130.21, 130.03, 128.56, 118.02, 115.59.



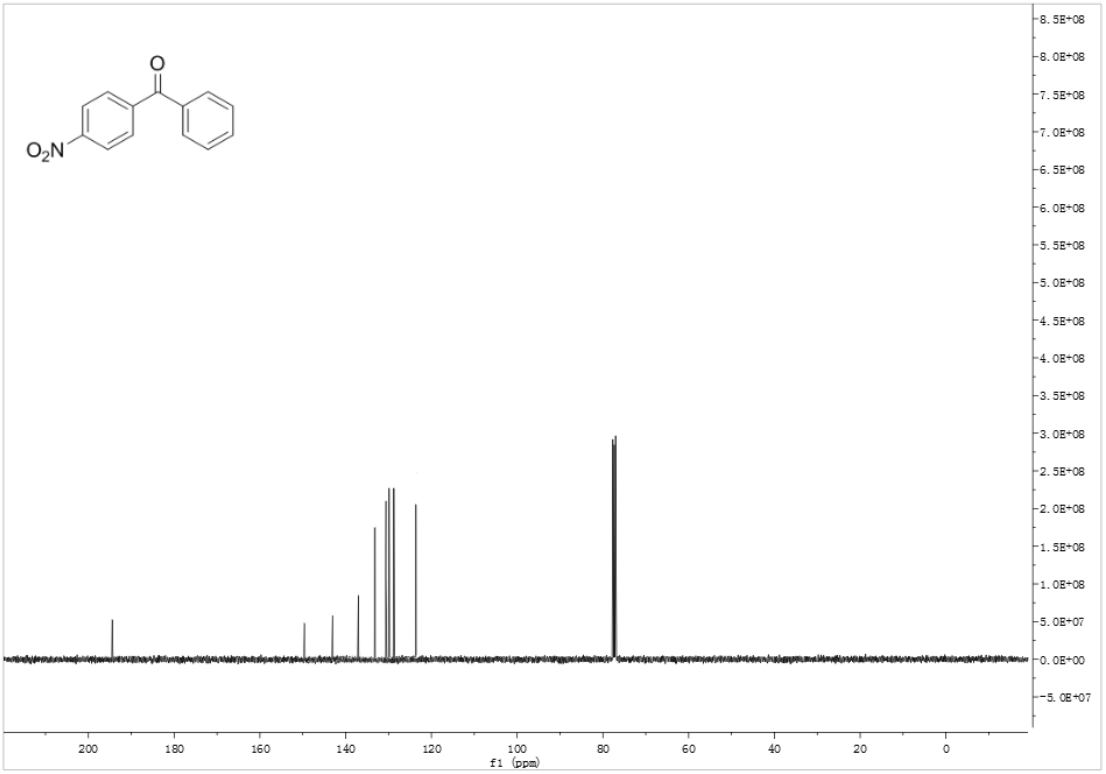
(2,5-Difluoro-4-nitrophenyl)(2-fluoro-5-methoxyphenyl)methanone. (3h)[3]

Yellow solid, m.p 95-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 1H), 7.61-7.53 (m, 1H), 7.30-7.26 (m, 1H), 7.19-7.13 (m, 1H), 7.09-7.03 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.13, 157.15, 156.06, 154.87, 151.51, 138.75, 134.07, 125.24, 122.63, 119.84, 117.46, 114.10, 113.38, 55.86.

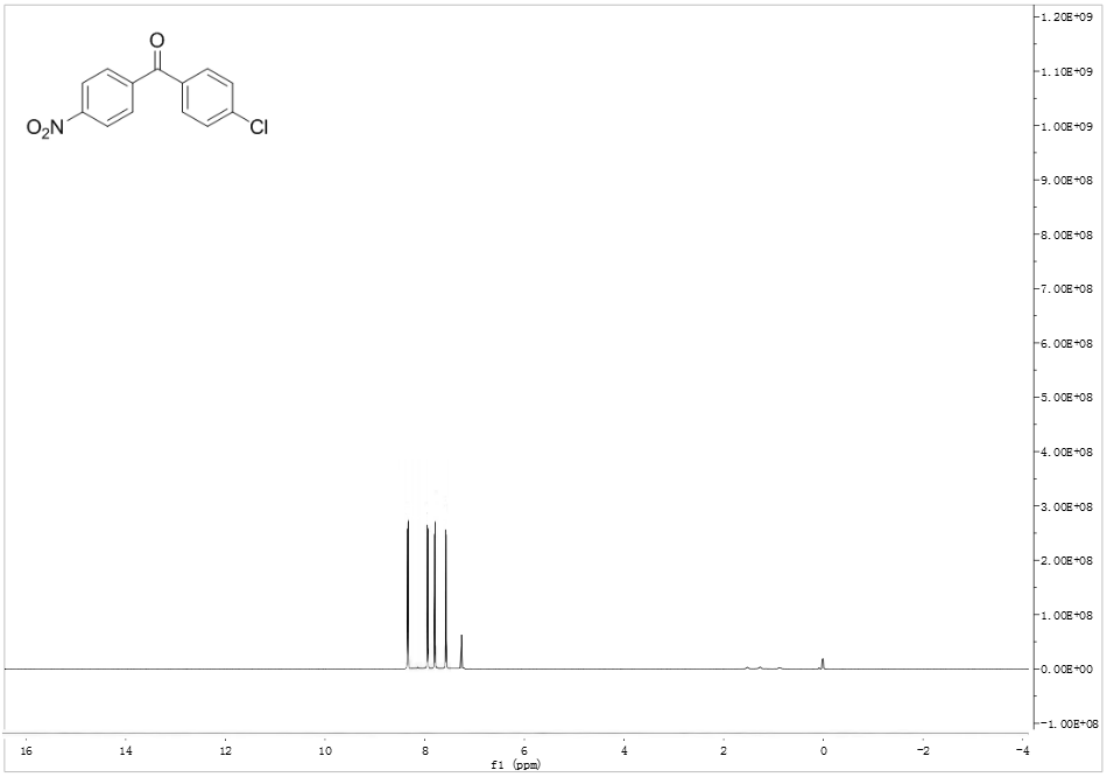
Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds



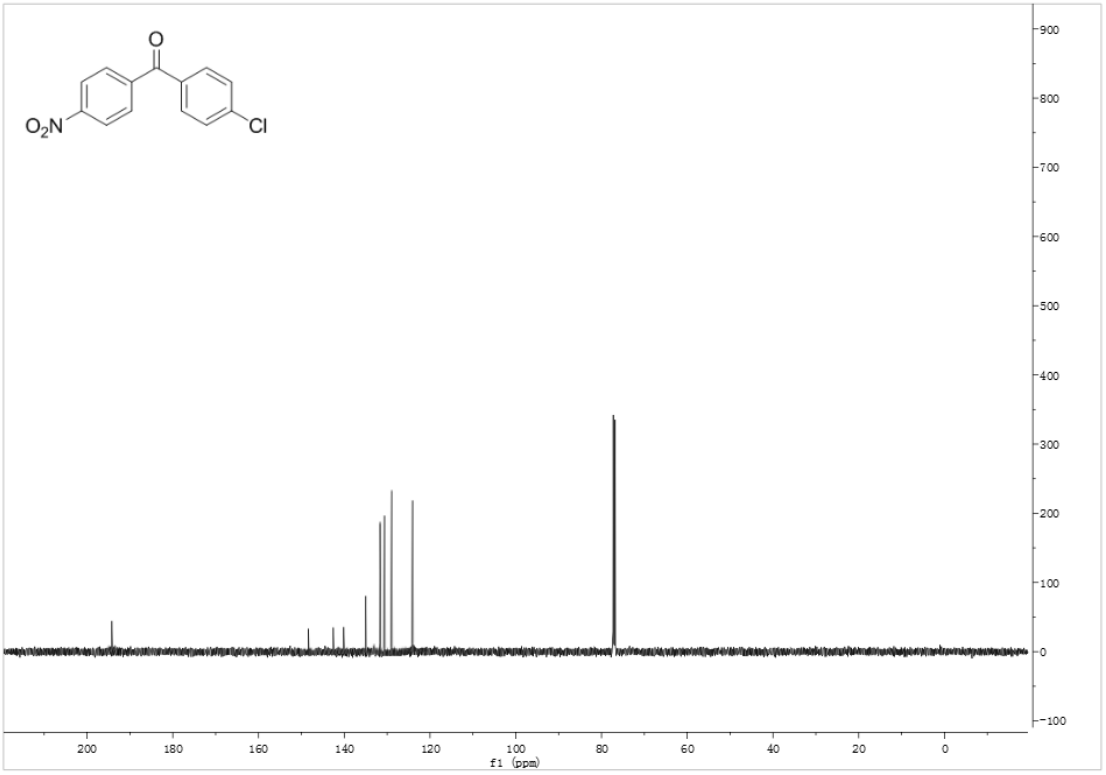
The ^{1}H NMR spectrum of (4-nitrophenyl)(phenyl)methanone (3a).



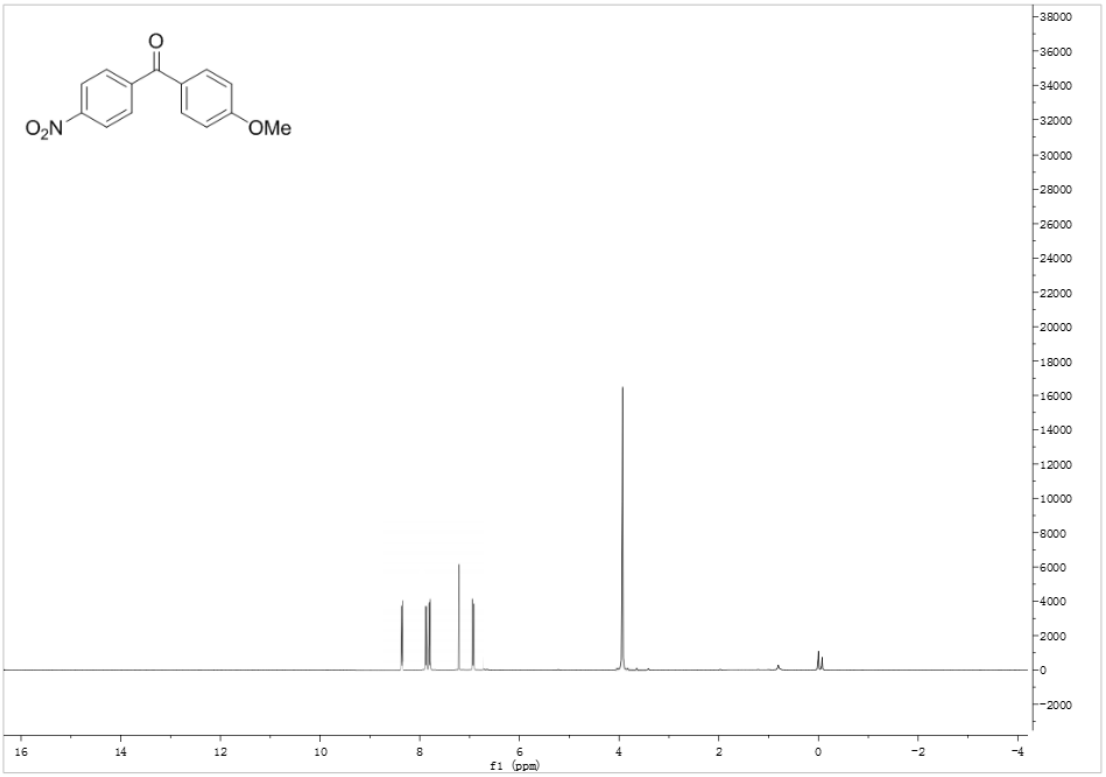
The ^{13}C NMR spectrum of (4-nitrophenyl)(phenyl)methanone (3a).



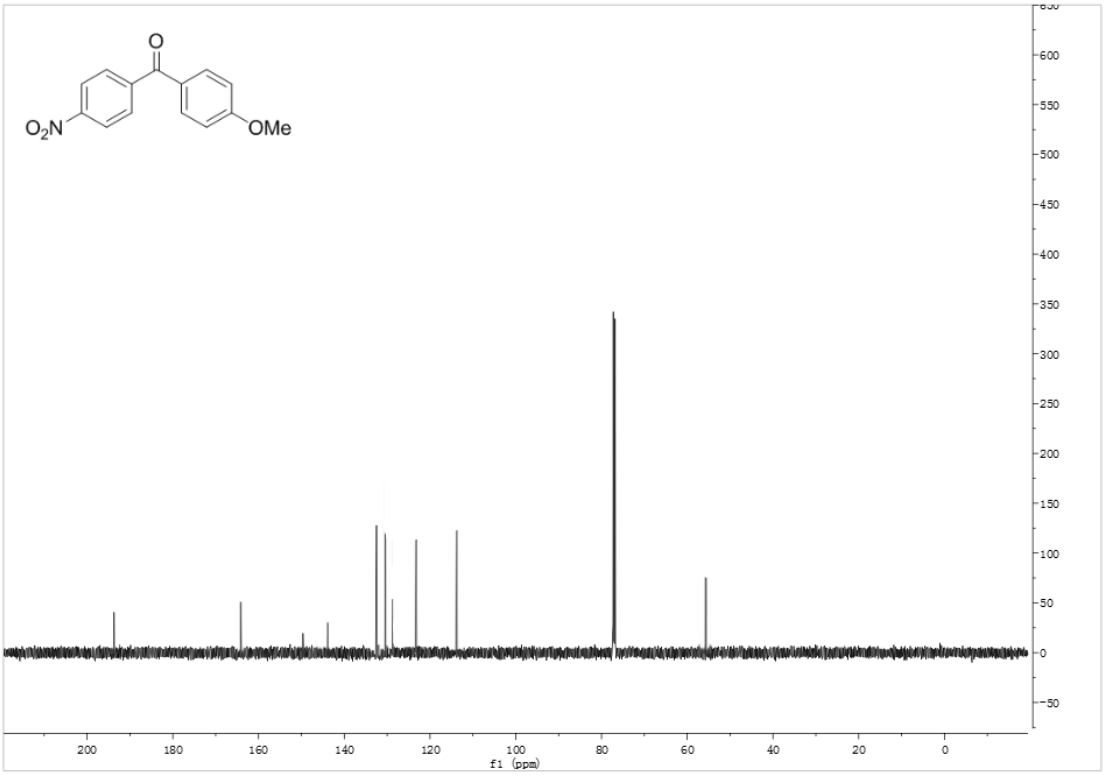
The ^{1}H NMR spectrum of (4-chlorophenyl)(4-nitrophenyl)methanone (3b).



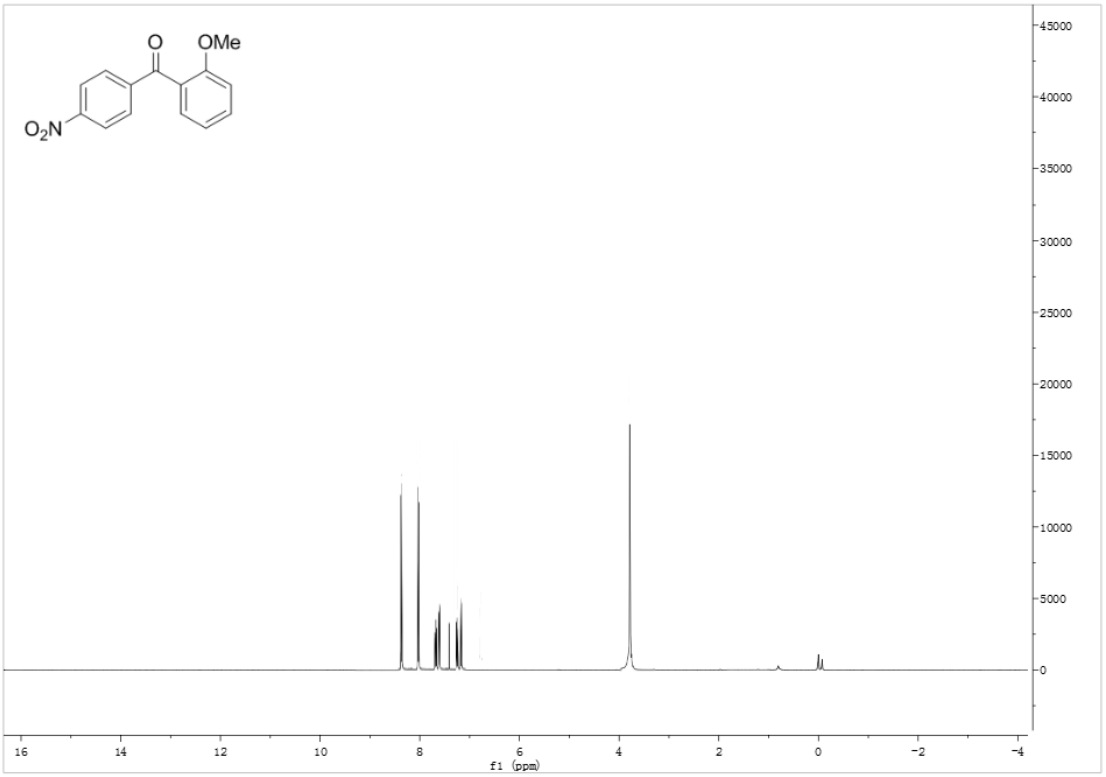
The ^{13}C NMR spectrum of (4-chlorophenyl)(4-nitrophenyl)methanone (3b).



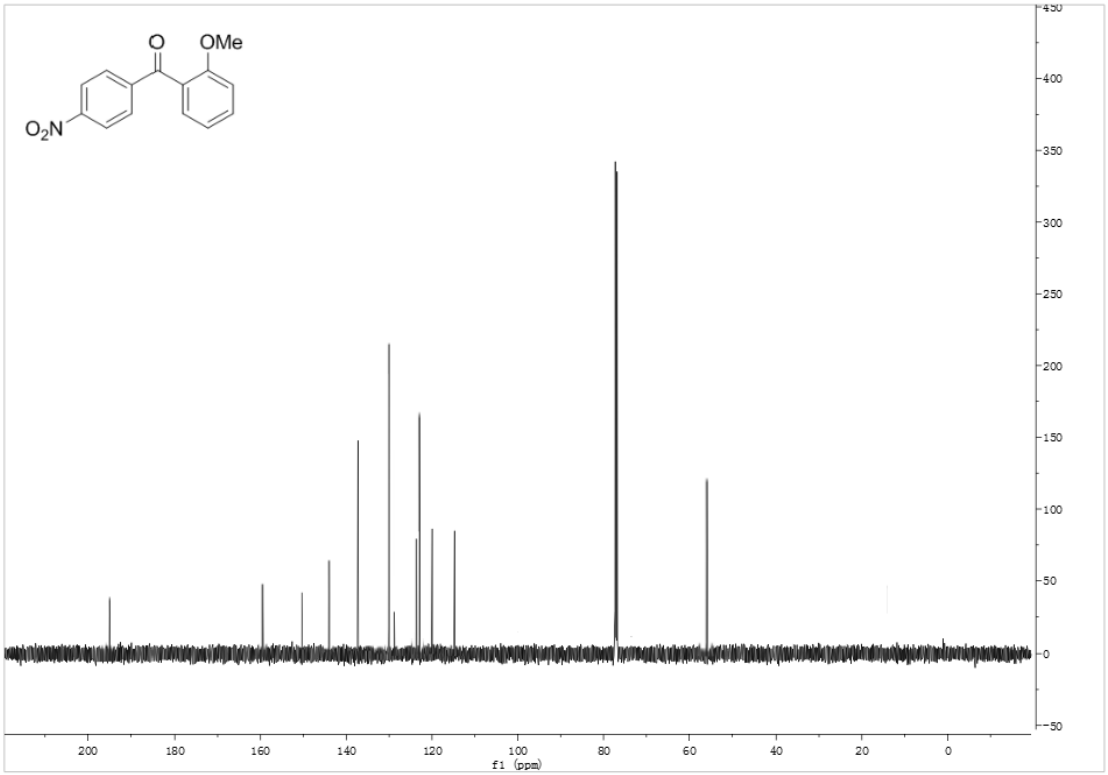
The ^{1}H NMR spectrum of (4-methoxyphenyl)(4-nitrophenyl)methanone (3c).



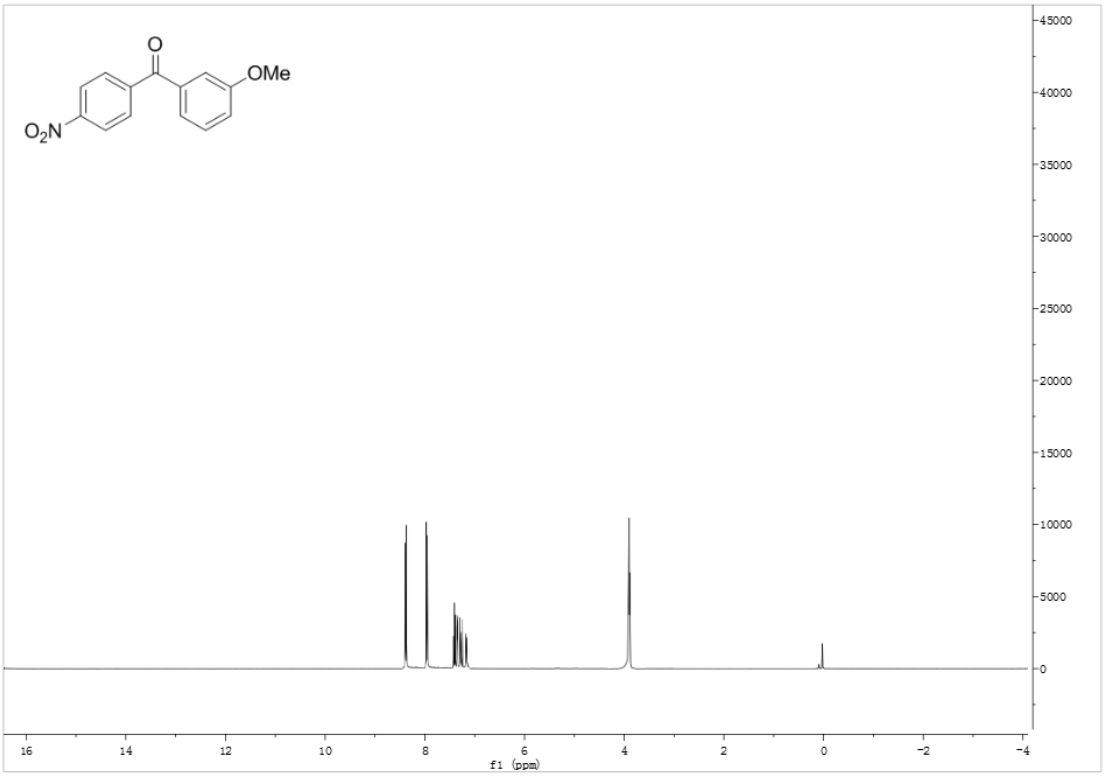
The ^{13}C NMR spectrum of (4-methoxyphenyl)(4-nitrophenyl)methanone (3c).



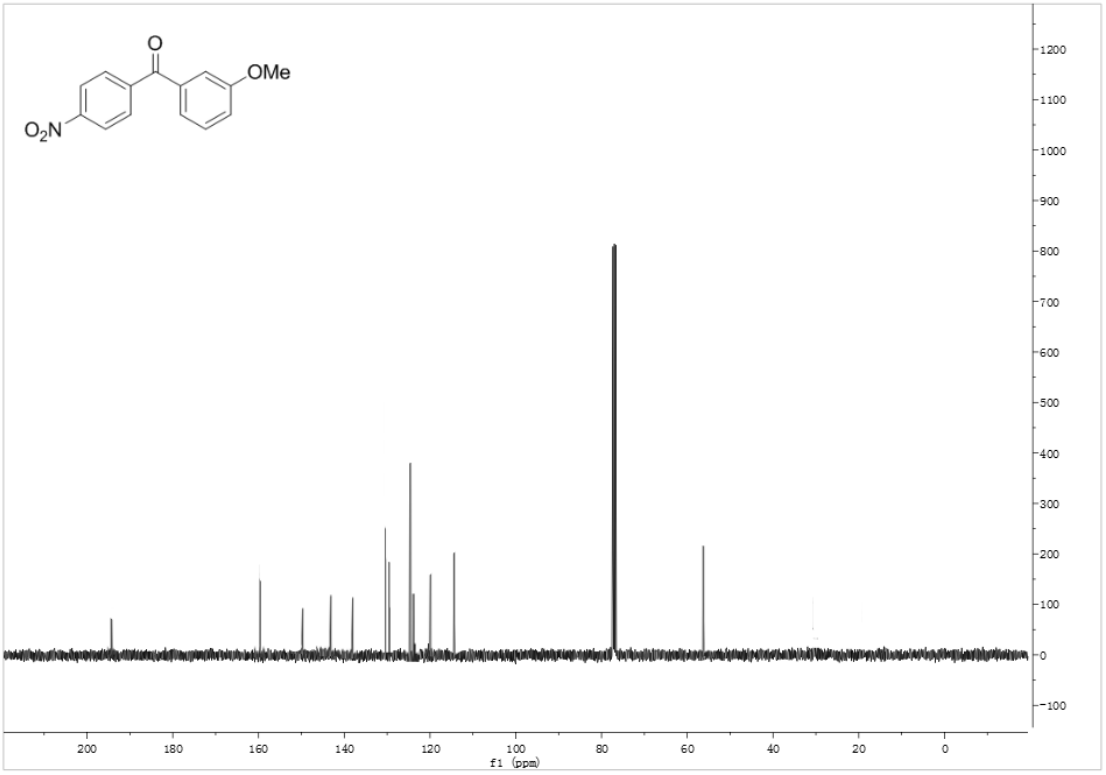
The ^{1}H NMR spectrum of (2-methoxyphenyl)(4-nitrophenyl)methanone (3d).



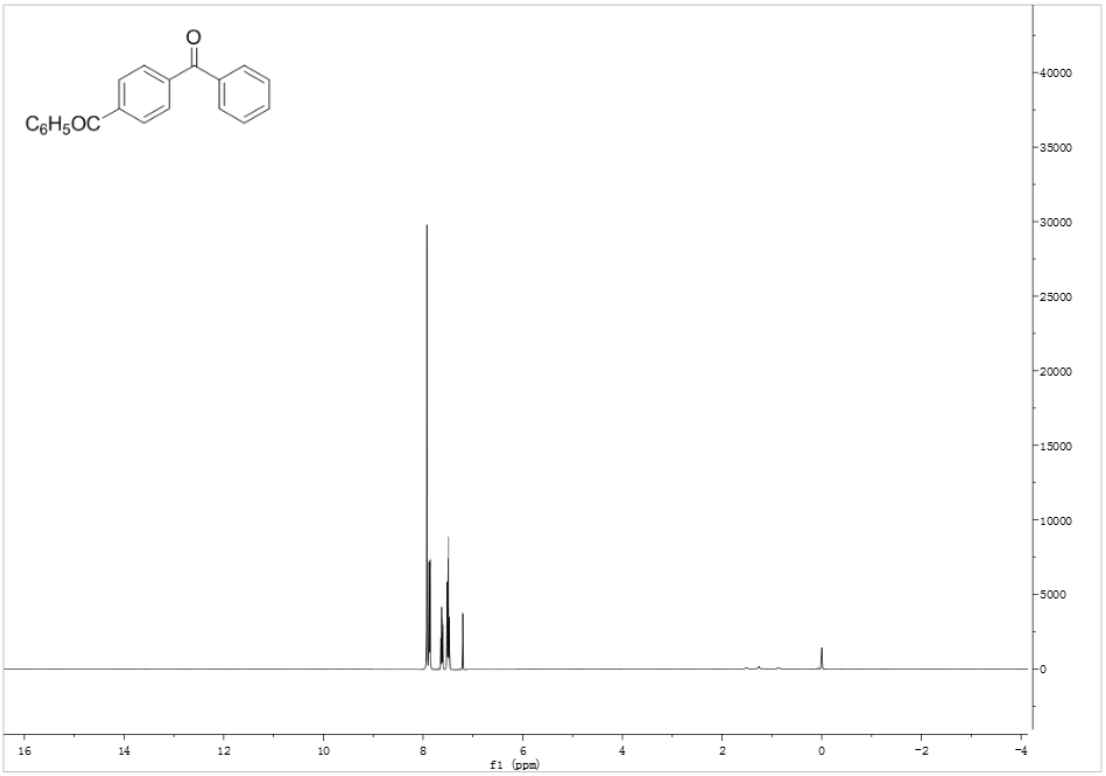
The ^{13}C NMR spectrum of (2-methoxyphenyl)(4-nitrophenyl)methanone (3d).



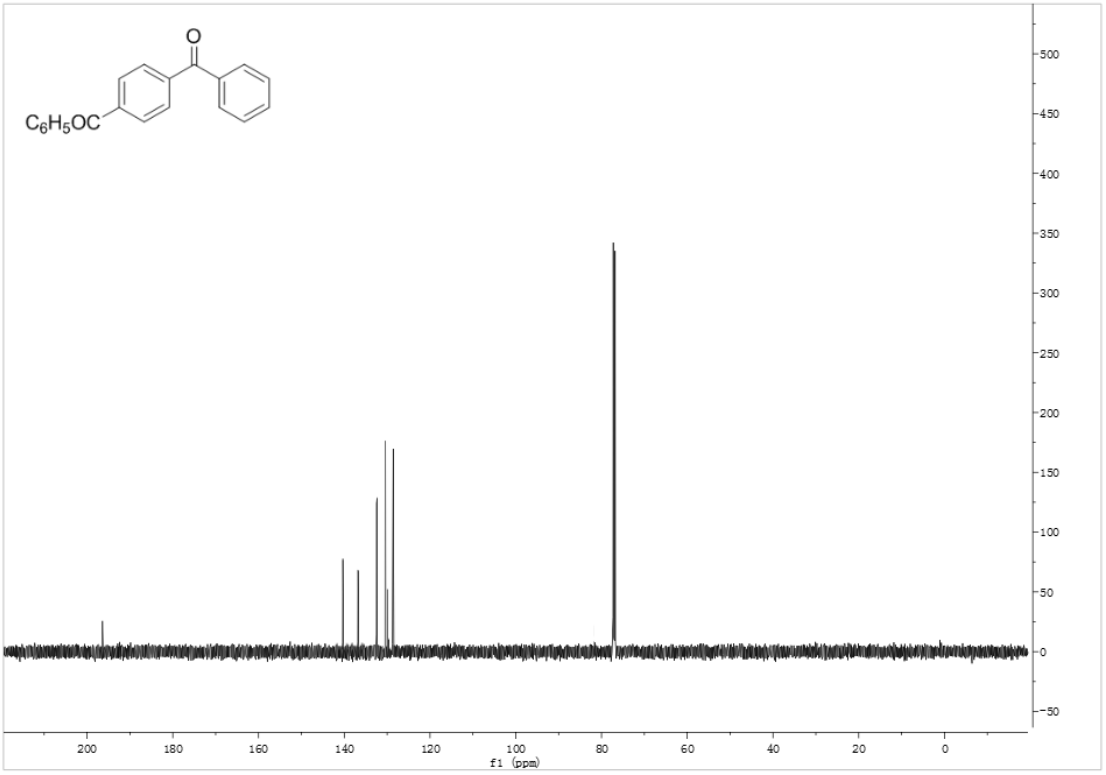
The ^{1}H NMR spectrum of (3-methoxyphenyl)(4-nitrophenyl)methanone (3e).



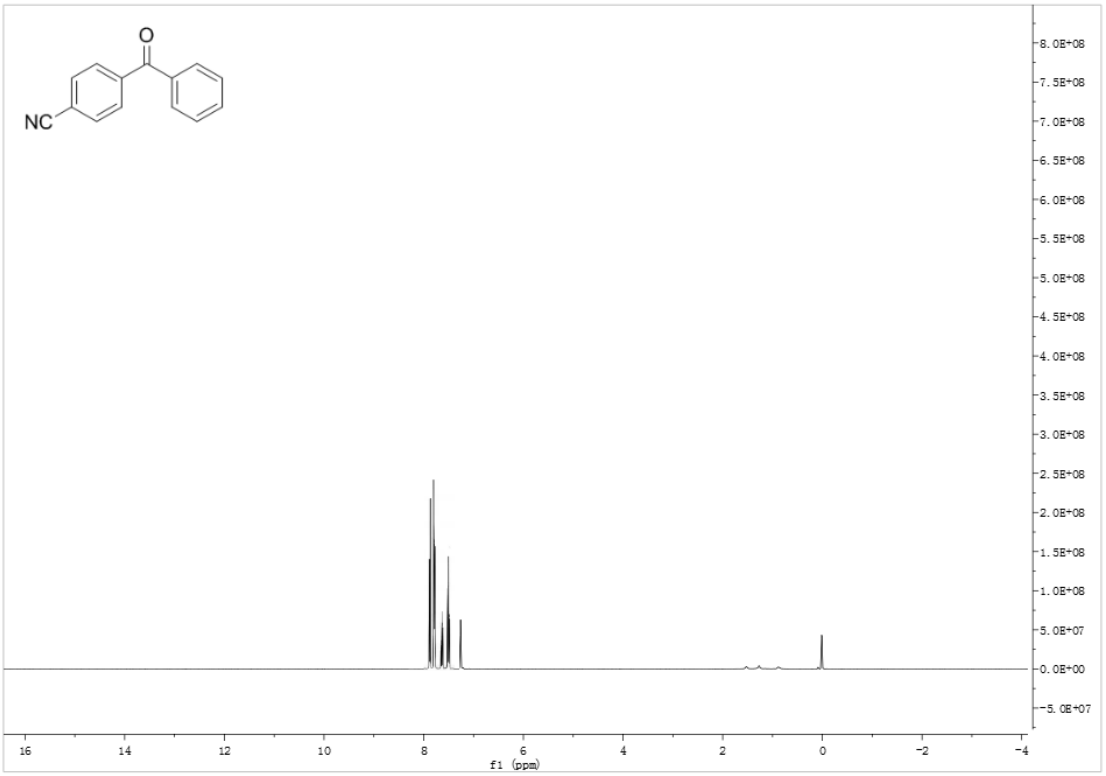
The ^{13}C NMR spectrum of (3-methoxyphenyl)(4-nitrophenyl)methanone (3e).



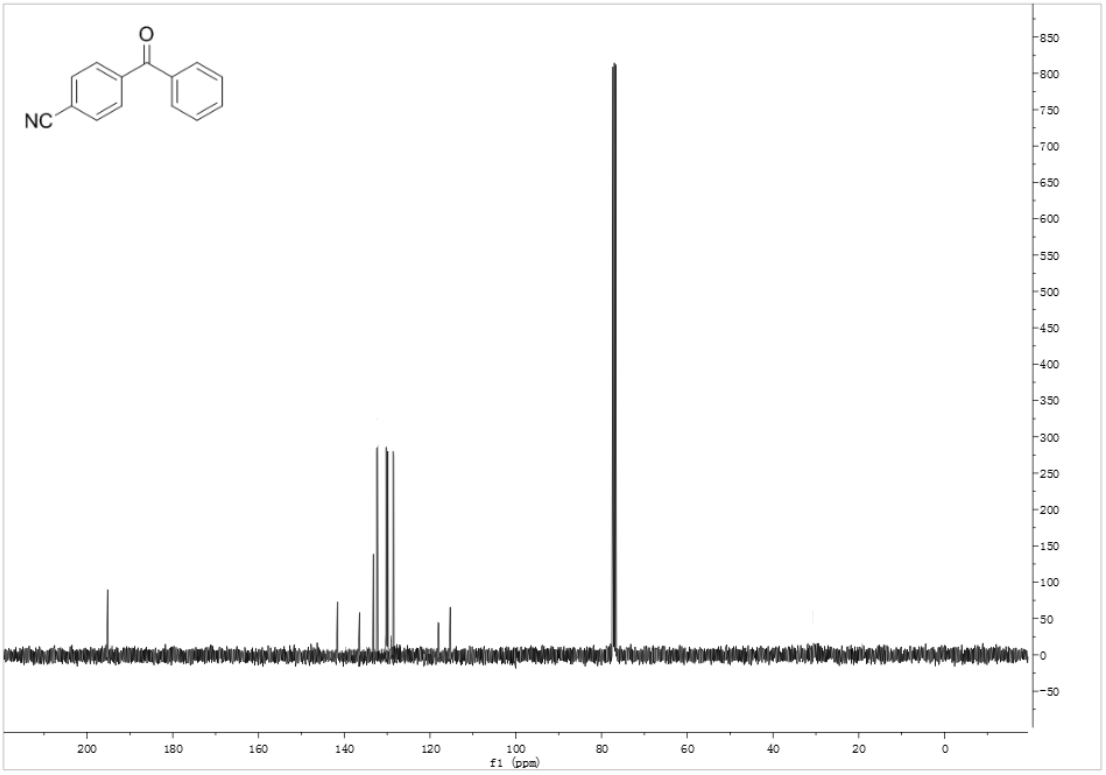
The ^{1}H NMR spectrum of 1,4-dibenzoylbenzen (3f).



The ^{13}C NMR spectrum of 1,4-dibenzoylbenzen (3f).

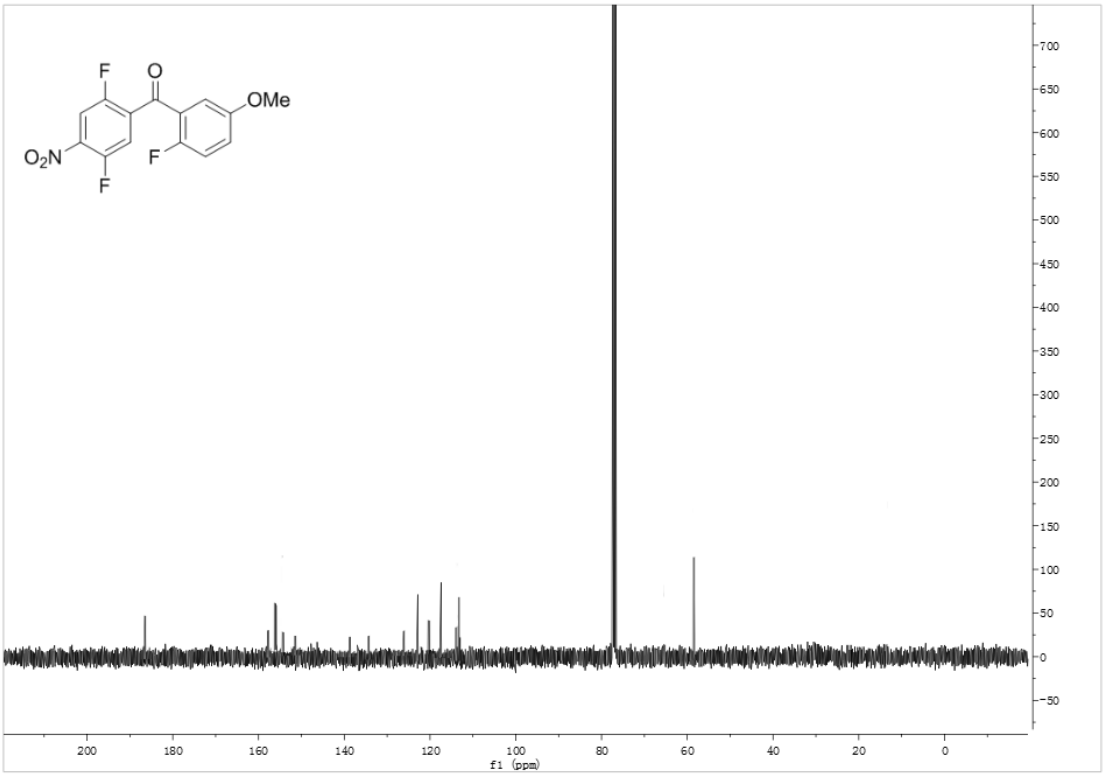


The ^{1}H NMR spectrum of (4-cyanophenyl)(phenyl)methanone (3g).



The ^{13}C NMR spectrum of (4-cyanophenyl)(phenyl)methanone (3g).

The ^{1}H NMR spectrum of (2,5-difluoro-4-nitrophenyl)(2-fluoro-5-methoxyphenyl) methanone (3h).



The ^{13}C NMR spectrum of (2,5-difluoro-4-nitrophenyl)(2-fluoro-5-methoxyphenyl) methanone (3h).

References

[1] J. Brześkiewicz, R. Loska, M. Mąkosza, *J. Org. Chem.* **2018**, *83*, 8499-8508.

[2] Q. Zhou, S. Wei, W. Han, *J. Org. Chem*. **2014**, *79*, 1454-1460.

[3] S. Ito, T. Kitamura, S. Arulmozhiraja, K. Manabe, H. Tokiwa, Y. Suzuki, *Org. Lett.* **2019**, *21*, 2777-2781.