Supporting Information

Co-N-C Catalyst for C-C Coupling Reactions: On the Catalytic Performance and Active Sites

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1. General Remarks

All chemicals (Analytical Grade) were used as received without further purification. The aerobic oxidative coupling reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm).

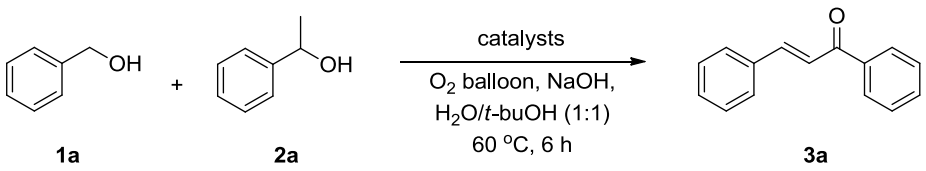
Gas Chromatography (GC) analysis was performed on an Agilent 6890N system equipped with a 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm). The GC yield was obtained from the calibration curve using 1,3,5-trimethylbenzene as an internal standard.

^{1}H NMR spectra were recorded on commercial instruments (500 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, $\delta = 7.26$). ^{13}C NMR spectra were collected on commercial instruments (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta = 77.0$). The structures of the known compounds were confirmed by comparison with commercially available compounds or data published in literature.

The structures of the known compounds were confirmed by comparison with commercially available compounds or data published in literature.

2. Optimization of the catalysts and reaction conditions

Table S1. Screening of the catalysts used in the reaction.[a]

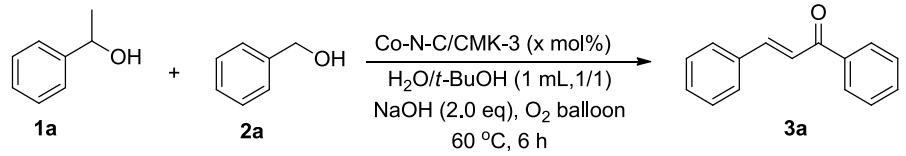


1a **2a** **3a**

Entry	Catalyst	Yield (%)[b]
1	Zn-N-C/CB	trace
2	Cu-N-C/CB	trace
3	Ni-N-C/CB	n.d.
4	Mo-N-C/CB	n.d.
5	Mn-N-C/CB	n.d.
6	Co-N-C/CB	59
7[c]	Co-N-C/rGO	43
8[d]	Co-N-C/PANI	15
9	Co-N-C/CMK-3	71

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), catalyst (30 mg), NaOH (1.0 mmol), H_2O/t-BuOH (1 mL, 1:1, v:v), O_2 balloon, 60 ^oC, 6 h. CB = carbon black, Vulcan XC-72. [b] Yield was determined by GC using 1,3,5-trimethylbenzene as an internal standard. [c] rGO = reduced graphene oxide, 15 mg catalyst was used. [d] PANI = polyaniline, PANI was annealed at 800 ^oC under N_2 before use.

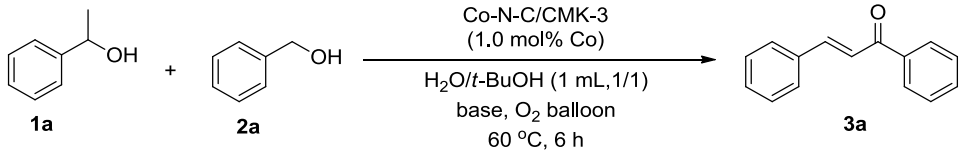
Table S2. Optimization of the amount of Co-N-C/CMK-3 used in the reaction.[a]



Entry	Weight of catalyst (mg)	Co/**1a** (mol%)	Yield (%)[b]
1	5	0.5	54
2	10	1.0	63
3	20	2.0	71
4	30	3.0	68

[a] Reaction conditions: Co-N-C/CMK-3, **1a** 0.5 mmol, **2a** 1.0 mmol, NaOH 1.0 mmol, O_2 balloon, H_2O 0.5 mL, *t*-BuOH 0.5 mL, 60 °C, 6 h. [b] Yield was determined by GC using 1,3,5-trimethylbenzene as an internal standard.

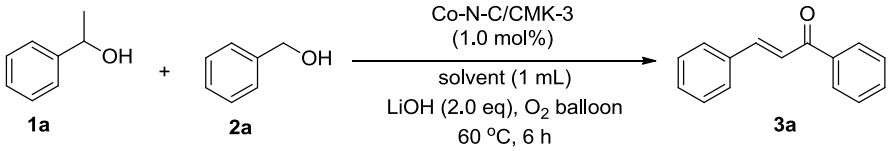
Table S3. Optimization of base.[a]



Entry	Base	Yield (%)[b]
1	NaOH (2 eq)	63
2	K_2CO_3 (2 eq)	1
3	LiOH (2 eq)	69
4	LiOH (3 eq)	72
5	LiOH (1 eq)	57

[a] Reaction conditions: Co-N-C/CMK-3 (1.0 mol% Co), **1a** 0.5 mmol, **2a** 1.0 mmol, base, O_2 balloon, H_2O 0.5 mL, *t*-BuOH 0.5 mL, 60 °C, 6 h. [b] Yield was determined by GC using 1,3,5-trimethylbenzene as an internal standard.

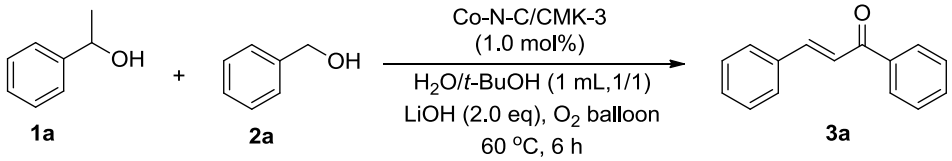
Table S4. Optimization of solvent.[a]



Entry	Solvent	Yield (%)[b]
1	toluene	18
2	*n*-heptane	52
3	EtOH	23
4	*t*-BuOH	39
5	H_2O	54
6	*t*-BuOH/H_2O (4/1, v/v)	62
7	*t*-BuOH/H_2O (1/1, v/v)	69
8	*t*-BuOH/H_2O (1/4, v/v)	62

[a] Reaction conditions: Co-N-C/CMK-3 (1.0 mol% Co), **1a** 0.5 mmol, **2a** 1.0 mmol, LiOH (1.0 mmol), O_2 balloon, solvent 1 mL, 60 °C, 6 h. [b] Yield was determined by GC using 1,3,5-trimethylbenzene as an internal standard.

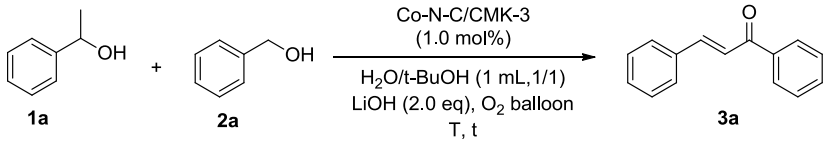
Table S5. Optimization of molar ratios of primary and secondary alcohols.[a]



Entry	**1a**/**2a** (mol/mol)	Yield (%)[b]
1	1/1	66
2	1/1.5	62
3	1/2	69

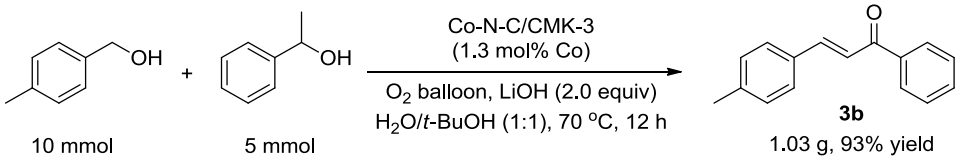
[a] Reaction conditions: Co-N-C/CMK-3 (1.0 mol%), **1a**, **2a**, LiOH (1.0 mmol), O_2 balloon, H_2O 0.5 mL, *t*-BuOH 0.5 mL, 60 °C, 6 h. [b] Yield was determined by GC using 1,3,5-trimethylbenzene as an internal standard.

Table S6. Optimization of reaction temperature and time.[a]



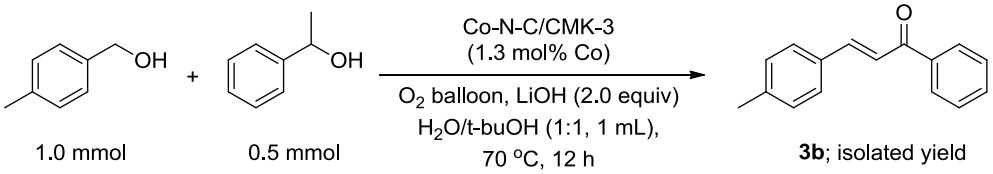
Entry	Temperature(^{o}C)	Time(h)	Conversion of **1a** (%)[b]
1	60	10	81
2	60	12	84
3	70	6	80
4	70	8	88
5	70	10	91
6	70	12	93

[a] Reaction conditions: Co-N-C/CMK-3 (1.0 mol%), **1a** 0.5 mmol, **2a** 1.0 mmol, LiOH (1.0 mmol), O_2 balloon, H_2O 0.5 mL, *t*-BuOH 0.5 mL [b] Conversion was determined by GC using 1,3,5-trimethylbenzene as an internal standard.



Scheme S1. Gram-scale experiment.

Table S7. Recovery and reuse of Co-N-C/CMK-3.



Run	1	2	3	4	5[b]
Yield (%)[a]	94	97	98	79	98

[a] Yield of isolated product. [b] 24 h.

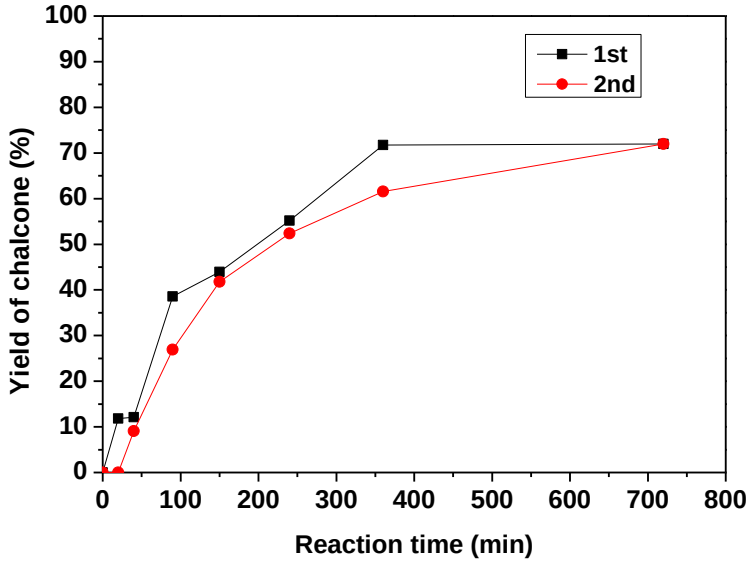


Figure S1. Reaction kinetics of oxidative coupling of benzyl alcohol and 1-phenylethanol in the consecutive runs.

3. Results of different characterizations.

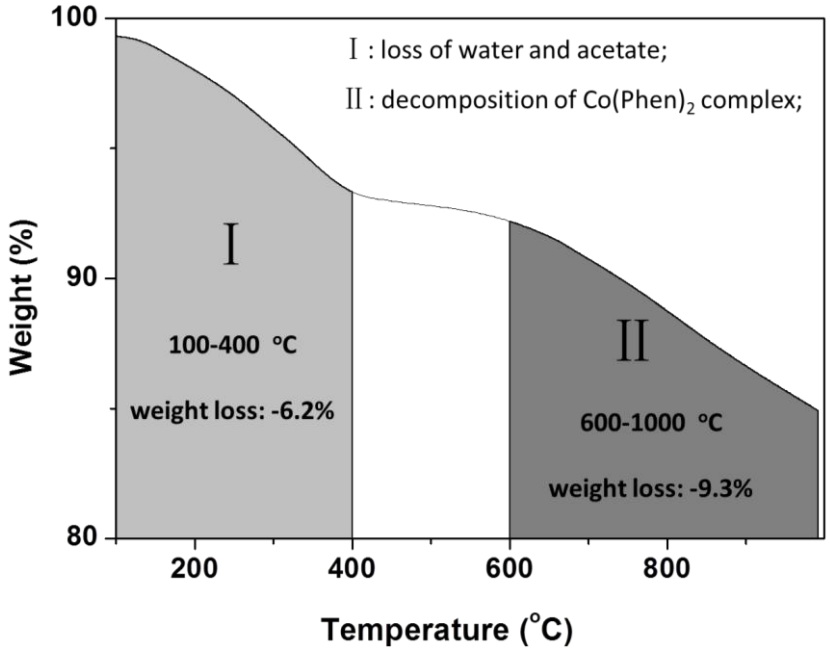


Figure S2. TGA curve of the Co-N-C/CMK-3-nonpyrolysed. Two weight loss stages could be observed from the TG curve. The first one (ca. -6.2%) occurring from 100 ^{o}C to 400 ^{o}C could be ascribed to the evaporation of water and acetate. The second loss (ca. -9.3%) at 600-1000 ^{o}C was due to the decomposition of $Co(Phen)_2$ complex.

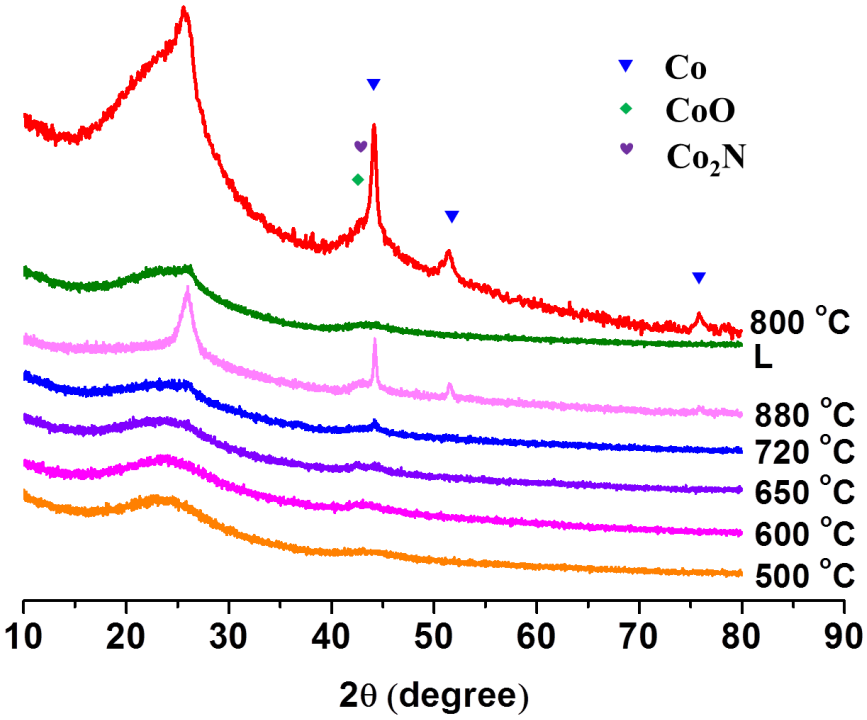


Figure S3. XRD patterns of the Co-N-C/CMK-3 samples pyrolyzed at different temperatures as well as after acid wash (L) treatment. The reflections positioned at 44.2°, 51.5° and 75.9° are due to metallic Co nanoparticles. The broad and barely discernible peaks at about 42.6° are due to CoO and/or Co_2N.

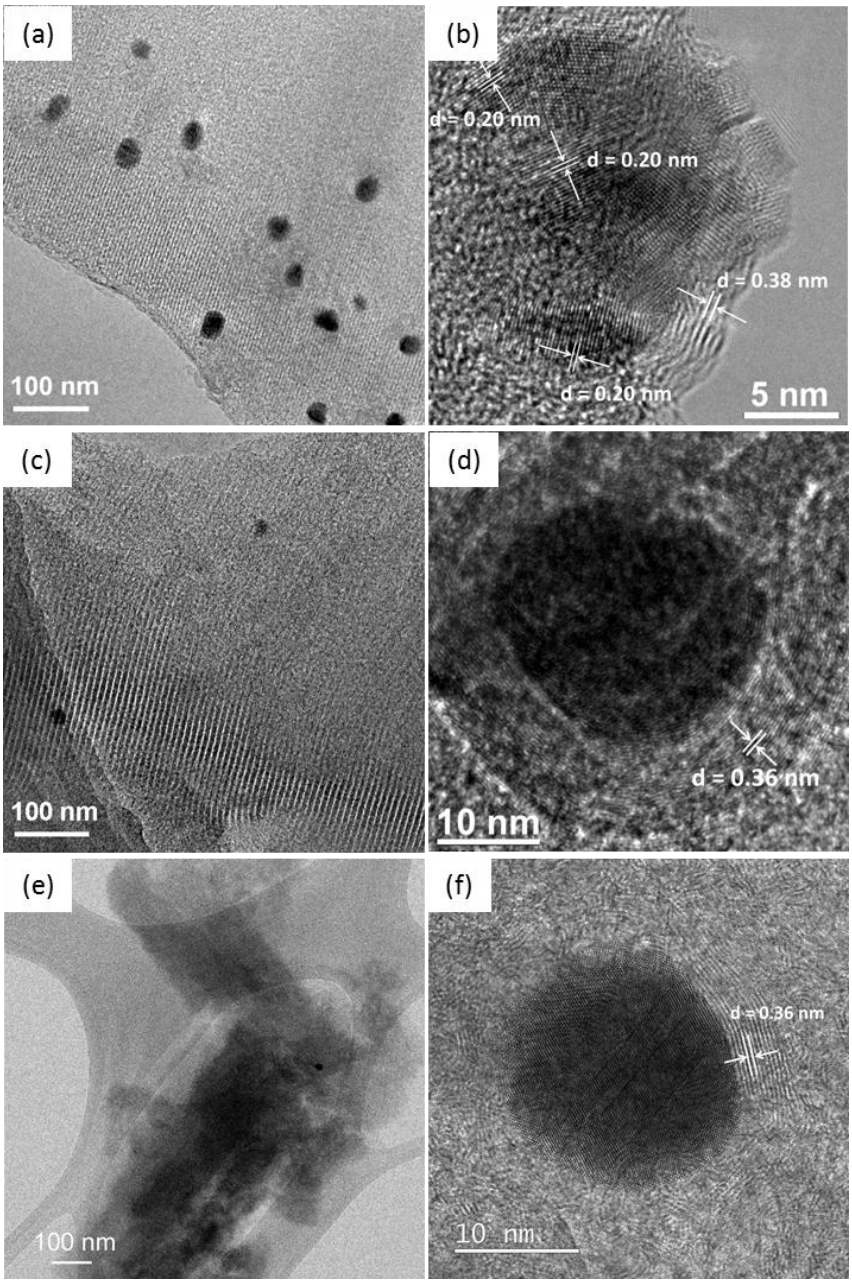


Figure S4. TEM images of (a,b) Co-N-C/CMK-3, (c,d) Co-N-C/CMK-3-L and (e,f) Co-N-C/CMK-3-B-L. The high magnification TEM images reveal the grapitic layers encapsulating the Co nanoparticles. In good agreement with the SEM observation, the TEM images also show that the mojority of the metallic Co nanoparticles were removed by the acid treatment. Furthermore,the high magnification TEM images indicate that the residual Co nanoparticles (after acid treatment) were encapsulated by 2-10 nm thick graphitic nanoshells.

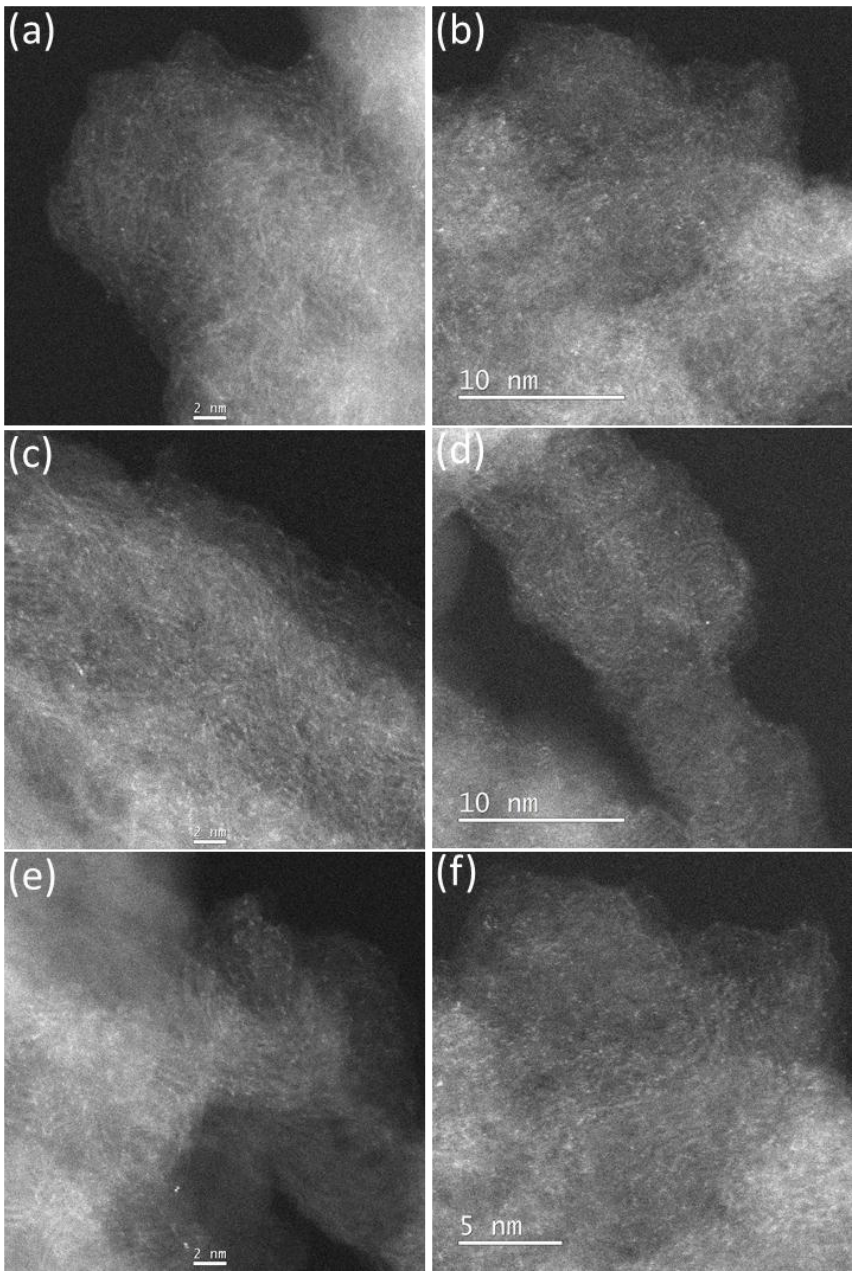


Figure S5. HAADF-STEM images of (a,c,e) Co-N-C/CMK-3 and (b,d,f) Co-N-C/CMK-3-B-L catalysts. The bright dots in the images represent Co single atoms bonded to N within graphtic sheets. A few very bright dots may represent the overlap of two or more Co single atoms projected along the electron beam direction. The estimated number density of the Co single atoms is approximately 0.3 atoms/nm^3.

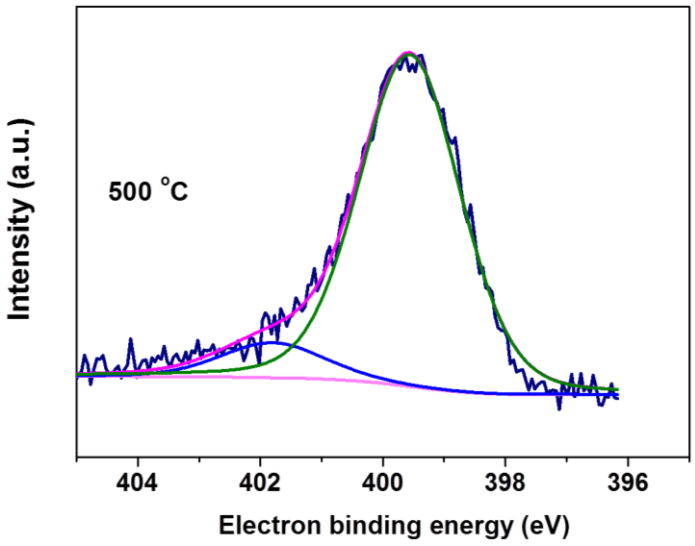


Figure S6. **N 1s XPS spectra of Co-N-C/CMK-3-500 sample**. The predominant N pecies has a binding energy of 399.6 eV, which was higher than that in the active sample (800 ^{o}C, B.E. = 399.2 eV).

Table S8. The detailed deconvolution results of the XPS Spectra. The values in brackets are the compositions of different N-containing species.

Element	Peak Assignment	Electron Binding Energy (eV)			
		Samples			
		Nonpyrolyzed	800 ^{o}C	L	B-L
N 1s	Pyridinic N	398.7 **(13.5%)**	—	—	—
	$[Co(Phen)_2]^{2+}$	400.2 **(86.5%)**	—	—	—
	Co-N-C structures	—	399.0 **(50.8%)**	399.2 **(51.7%)**	399.2 **(45.2%)**
	Graphitic N	—	400.8 **(37.1%)**	401.0 **(34.4%)**	400.6 **(46.6%)**
	Oxidized N	—	402.1 **(12.1%)**	402.4 **(13.9%)**	402.3 **(8.2%)**
Co 2p	—	781.5	780.5	780.7	780.6

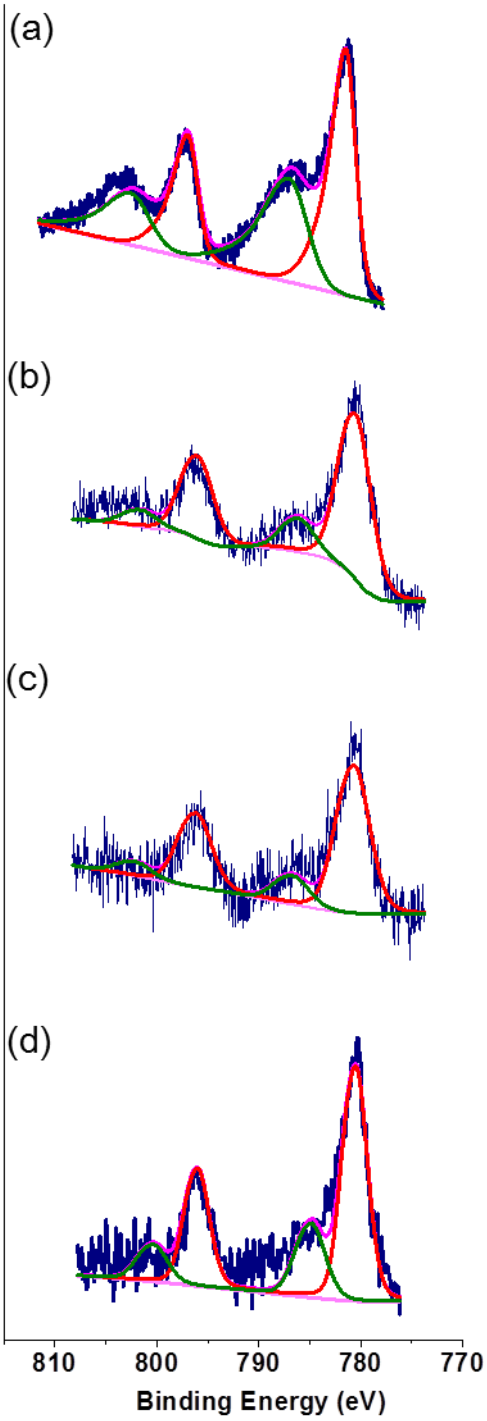


Figure S7. Co 2p XPS spectra of Co-N-C/CMK-3-nonpyrolyzed (a), Co-N-C/CMK-3 (b), Co-N-C/CMK-3 (c) and Co-N-C/CMK-3-B-L (d). The electron binding energy of Co $2p_{3/2}$ in the nonpyrolyzed Co-N-C/CMK-3 is located at 781.5 eV, which can be attributed to Co(Ⅱ) in $Co(Phen)_2(OAc)_2$ complexes. After pyrolysis at 800 ^{o}C, the binding energy shifted to 780.5 eV, indicating that Co centers

in the pyrolysed sample had a higher electron density, and these Co centers can be ascribed Co single atoms bonded with N in the graphitic sheets (structure III in Fig. 3). No Co(0) species (B. E. = 777.9 eV) was detected by XPS, indicating that all the Co(0) nanoparticles were shielded by the thick graphitic layers so that they could not be probed by the surface-sensitive XPS. In the Co-N-C/CMK-3-L and Co-N-C/CMK-3-B-L, almost the same Co $2p_{3/2}$ binding energies were detected as that in the Co-N-C/CMK-3, indicating that the electronic structures of the Co single atoms in the three samples are similiar, if not the same.

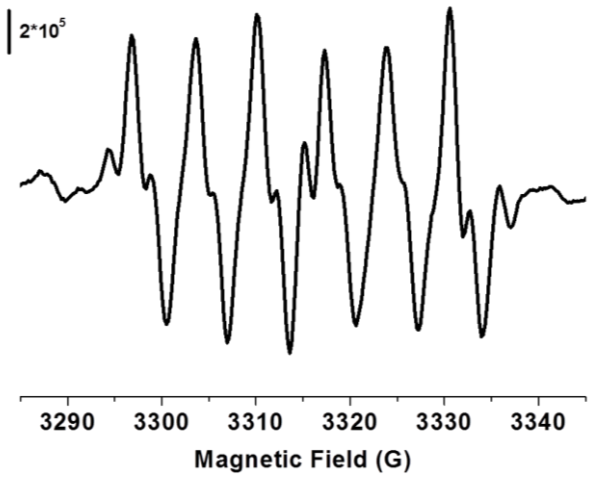
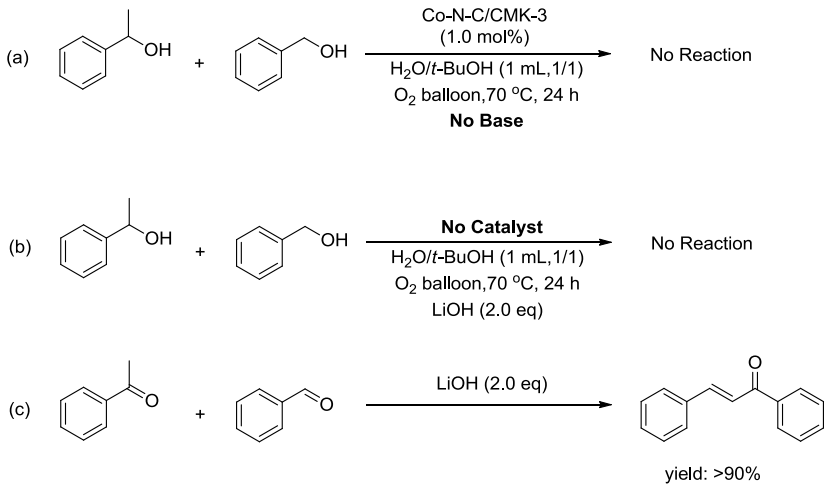


Figure S8. ESR spectra for the superoxide radical ($O_2^{\bullet-}$) adducts with DMPO. Six characteristic peaks were observed at 5 min after the addition of DMPO to the reaction system, suggesting the appearence of the superoxide radical ($O_2^{\bullet-}$) adducts with DMPO [1].



Scheme S2. Control experiments to discriminate the role of the catalyst and the additive fulfilled in the overall reaction.

4. Calculation of TON and TOF values.

A scale-up experiment was performed to determine the TON value of Co-N-C/CMK-3-B-L as follows: 12.2 g (100 mmol) benzyl alcohol, 6.2 g (50 mmol) 1-phenylethanol and 4.2 g (100 mmol) LiOH $\cdot H_2O$ were added to a solvent of 50 mL t-BuOH and 50 mL H_2O. After 10 mg Co-N-C/CMK-3-B-L was added, the mixture was heated to 85 ^oC under O_2 balloon. The sample was analyzed at intervals until the conversion did not change significantly. After 198 h, a conversion of 70% was obtained.

Before calculating the TOF value of the Co-N-C/CMK-3-L catalyst, the mass ratio of Co single atoms accounting for all the cobalt species was estimated as follows: First, after examining many HAADF-STEM and HRTEM images, we estimated that the density of cobalt single atoms (SAs) and nanoparticles (NPs) were 0.2 Co SAs nm^{-2} and 12.5 Co NPs μm^{-2}. Second, the average size of Co NPs was measured to be

32.4 nm, and the number of cobalt atoms in a nanoparticle could be calculated to be: $(32.4\ \text{nm}/0.25\ \text{nm})^3 * 74\% = 1.6*10^6$ (74% is the space utilization in hexagonal closest packing (hcp) structure, 0.25 nm is diameter of cobalt atoms). Based on the above results, the mass ratio of Co single atoms could be estimated to be:

$$\frac{0.20\ \text{nm}^{-2}}{12.5\ \mu\text{m}^{-2} * 1.6 * 10^6 + 0.20\ \text{nm}^{-2}} = \frac{0.20\ \text{nm}^{-2}}{12.5 * 10^{-6}\ \text{nm}^{-2} * 1.6 * 10^6 + 0.20\ \text{nm}^{-2}} = 0.99\%$$

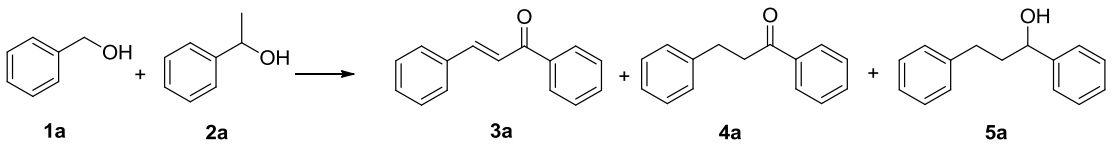
The reaction rate was measured in the initial time of 20 min where the conversion increased linearly with reaction time. A TOF value of 135.1 h^{-1} (0.0375 s^{-1}) was obtained based on a product yield of 10.4% at a reaction time of 20 min.

$$\text{TOF} = \frac{0.5\ \text{mmol} * 10.4\%}{\frac{10\ \text{mg} * 0.68\%}{58.9\ \text{mg/mmol}} * \frac{20}{60}\ \text{h}} = 135\ \text{h}^{-1}$$

(10 mg is the charge of Co-N-C/CMK-3-L catalyst in a batch of reaction; 0.68% is the mass loading of cobalt in the catalyst)

When normalized to the mass ratio of Co single atoms, the TOF value was estimated to be 3.8 s^{-1}.

Table S9. Comparison of TON value between Co-N-C/CMK-3-L and other catalysts in literature. Note that most of the catalysts reported hitherto catalyse the dehydrogenative coupling reaction, while of which only one catalyst, that is, Au-Pd/HT in literature 4, involved in the oxidative reaction pathway.



1a 2a 3a 4a 5a

Entry	Catalysts	Cat. (mol%)	T (^{o}C)	T(h)	Product; Yield	TON	TOF	Ref.
1	$[Cp^*IrCl_2]_2$	2	110	17	**5a**; 75%	37.5	—	[2]
2	$RuCl_2(PPh_3)_3$	5	80	40	**5a**; 82%	16.4	—	[3]
3	Ag/Al_2O_3	4	115	48	**4a**; 80%	20	0.5 h^{-1}	[4]
		4	115	24	**3a**; 38%	9.5		
4	Au-Pd/HT	1/3	120	5	**4a**; 96%	288	20 h^{-1}	[5]
		1	120	7	**3a**; 90%	90		
5	Co-N-C/CMK-3-B-L	0.175	60	6	**3a**; 71%	13257	3.8 s^{-1} *	This work

* TOF value of Co-N-C/CMK-3-L catalyst.

5. **References**

[1] Su, W.; Chen, J.; Wu, L.; Wang, X.; Wang, X.; Fu, X. *Appl. Catal. B* **2008**, *77*, 264-271.

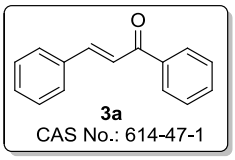
[2] Fujita, K.; Asai, C.; Yamaguchi, T.; Hanasaka, F.; Yamaguchi, R. *Org. Lett.* **2005**, *7*, 4017-4019.

[3] Cho, C. S. *Organometallics* **2003**, *22*, 3608-3610.

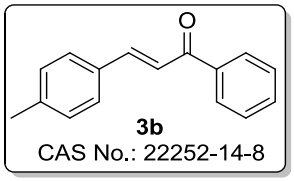
[4] Shimizu, K.; Sato, R.; Satsuma, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 3982-3986.

[5] Liu, X.; Ding, R.-S.; He, L.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *ChemSusChem* **2013**, *6*, 604-608.

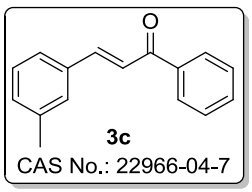
6. Characterization of the obtained products.



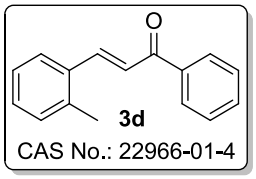
(*E*)-chalcone 3a: The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (75.3 mg, 72% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.44 – 7.43 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.68, 144.95, 138.34, 135.01, 132.87, 130.64, 129.07, 128.73, 128.61, 128.55, 122.24 ppm.



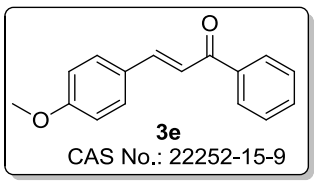
(*E*)-1-phenyl-3-(4-tolyl)prop-2-en-1-one 3b: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (108.6 mg, 98% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.54 – 7.48 (m, 3H), 7.26 – 7.23 (m, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.78, 145.06, 141.20, 138.48, 132.76, 132.27, 129.81, 128.69, 128.59, 128.58, 121.22, 21.64 ppm.



(*E*)-1-phenyl-3-(3-tolyl)prop-2-en-1-one 3c: The reaction was carried out according to the general procedure with *m*-tolylmethanol (122.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (82.6 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.72, 145.17, 138.74, 138.39, 134.95, 132.83, 131.51, 129.14, 128.95, 128.71, 128.60, 125.81, 122.02, 21.44 ppm.

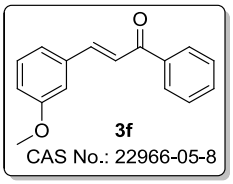


(*E*)-1-phenyl-3-(2-tolyl)prop-2-en-1-one 3d: The reaction was carried out according to the general procedure with *o*-tolylmethanol (122.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (97.4 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 15.5 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.60, 142.59, 138.48, 138.36, 134.04, 132.89, 131.03, 130.37, 128.88, 128.73, 128.63, 126.53, 126.45, 123.27, 19.97 ppm.

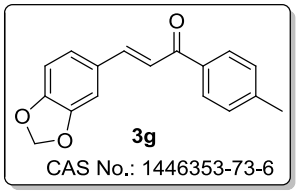


(*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one 3e: The reaction was carried out according to the general procedure with (4-methoxyphenyl)methanol (138.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v)

and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (118.2 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.89, 161.79, 144.81, 138.63, 132.09, 130.32, 128.66, 128.52, 127.74, 119.94, 114.53, 55.52 ppm.

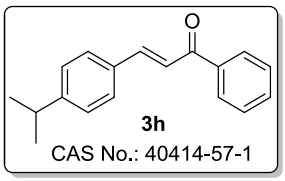


(*E*)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one 3f: The reaction was carried out according to the general procedure with (3-methoxyphenyl)methanol (138.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (59.5 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.27 (s, 1H), 7.17 (s, 1H), 6.98 (dd, *J* = 8.1, 2.2 Hz, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.68, 160.07, 144.86, 138.31, 136.38, 132.89, 130.05, 128.73, 128.61, 122.54, 121.20, 116.42, 113.54, 55.46 ppm.

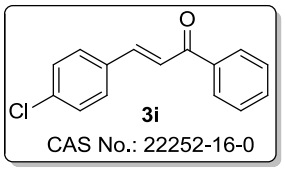


(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(4-tolyl)prop-2-en-1-one 3g: The reaction was carried out according to the general procedure with benzo[*d*][1,3]dioxol-5-ylmethanol (290.3 mg, 1.0 mmol), 1-(*p*-tolyl)ethanol (72.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (127.5 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1

Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.36 (d, *J* = 15.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 1.4 Hz, 1H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 2.42 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.01, 150.00, 148.58, 144.39, 143.66, 136.00, 129.66, 129.48, 128.75, 125.30, 120.29, 108.84, 106.84, 101.81, 21.85 ppm.

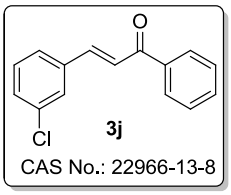


(*E*)-3-(4-*iso*propylphenyl)-1-phenylprop-2-en-1-one 3h: The reaction was carried out according to the general procedure with (4-isopropylphenyl)methanol (150.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (123.8 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 6.2 Hz, 3H), 7.54 – 7.49 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.98 (ddt, *J* = 20.8, 13.8, 6.9 Hz, 1H), 1.29 (dd, *J* = 6.8, 4.8 Hz, 6H) ppm; ^{13}C NMR (126 MHz, CDCl3) δ 190.80, 152.09, 145.07, 138.50, 132.74, 130.10, 128.70, 128.69, 128.58, 127.24, 127.20, 121.33, 34.24, 23.86 ppm.

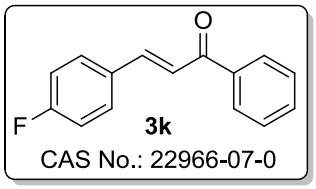


(*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one 3i: The reaction was carried out according to the general procedure with (4-chlorophenyl)methanol (142.6 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (45.9mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.61 – 7.58 (m, 3H), 7.54 – 7.52 (m, 2H), 7.51 – 7.50 (m, 1H), 7.42 – 7.39 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.33, 143.40, 138.15, 136.54, 133.50,

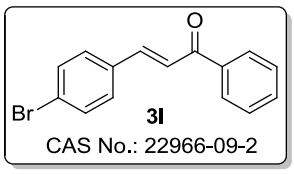
133.02, 129.68, 129.35, 128.77, 128.60, 122.61 ppm.



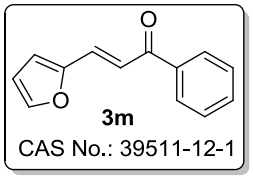
(*E*)-3-(3-chlorophenyl)-1-phenylprop-2-en-1-one 3j: The reaction was carried out according to the general procedure with (3-chlorophenyl)methanol (142.6 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH Ⱨ$_2$O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (41.9 mg, 34% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.65 (s, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.41 – 7.35 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.20, 143.14, 138.02, 136.85, 135.10, 133.11, 130.44, 130.31, 128.80, 128.63, 128.00, 126.89, 123.38 ppm.



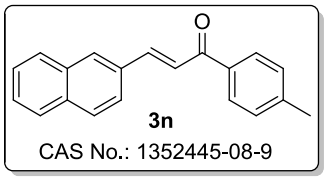
(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one 3k: The reaction was carried out according to the general procedure with (4-fluorophenyl)methanol (126.2 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH Ⱨ$_2$O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (47.2 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 15.7 Hz, 1H), 7.65 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.13 (t, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.42, 164.17 (d, *J* = 251.8 Hz), 143.60, 138.25, 132.94, 131.27, 130.44 (d, *J* = 8.5 Hz), 128.75, 128.58, 121.91, 116.24 (d, *J* = 21.9 Hz) ppm.



(*E*)-3-(4-bromophenyl)-1-phenylprop-2-en-1-one 3l: The reaction was carried out according to the general procedure with (4-bromophenyl)methanol (187.1 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH Ꮒ$_2$O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (53.5 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 15.8 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.50 (m, 7H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.32, 143.45, 138.13, 133.92, 133.03, 132.32, 129.88, 128.78, 128.60, 124.90, 122.69 ppm.

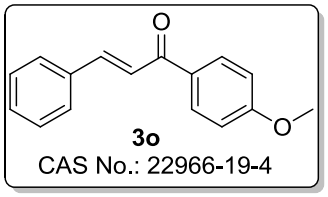


(*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one 3m: The reaction was carried out according to the general procedure with furan-2-ylmethanol (98.1 mg, 1.0 mmol), 1-phenylethanol (61.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH Ꮒ$_2$O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (50.5 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.55 – 7.48 (m, 4H), 6.73 (d, *J* = 3.4 Hz, 1H), 6.54 – 6.52 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.94, 151.79, 145.00, 138.27, 132.84, 130.77, 128.70, 128.52, 119.45, 116.28, 112.76 ppm.

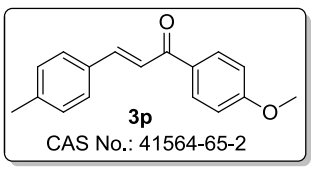


(*E*)-3-(naphthalen-2-yl)-1-(4-tolyl)prop-2-en-1-one 3n: The reaction was carried

out according to the general procedure with naphthalen-2-ylmethanol (158.2 mg, 1.0 mmol), 1-(*p*-tolyl)ethanol (72.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (95.8 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.90 – 7.84 (m, 3H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.06, 144.58, 143.76, 135.81, 134.44, 133.48, 132.60, 130.64, 129.46, 129.34, 128.79, 128.74, 128.55, 127.91, 127.42, 126.85, 123.81, 21.81 ppm.

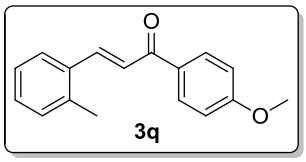


(*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one 3o: The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (101.6 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.55 (d, *J* = 15.7 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 3H), 6.99 (d, *J* = 8.2 Hz, 2H), 3.88 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.79, 163.54, 144.05, 135.19, 131.19, 130.92, 130.43, 129.03, 128.47, 121.98, 113.96, 55.59 ppm.

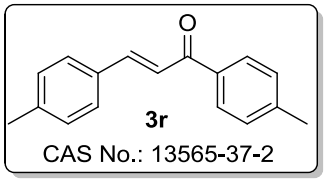


(*E*)-1-(4-methoxyphenyl)-3-(4-tolyl)prop-2-en-1-one 3p: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co)

catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (125.2 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 15.7 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.90, 163.45, 144.14, 140.92, 132.45, 131.33, 130.87, 129.77, 128.49, 120.97, 113.91, 55.58, 21.62 ppm.

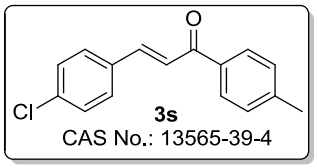


(E)-1-(4-methoxyphenyl)-3-(2-tolyl)prop-2-en-1-one 3q: The reaction was carried out according to the general procedure with *o*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (93.8 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 15.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.22 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.77, 163.54, 141.71, 138.35, 134.24, 131.23, 130.99, 130.94, 130.16, 126.47, 126.41, 123.11, 113.96, 55.59, 19.99 ppm.

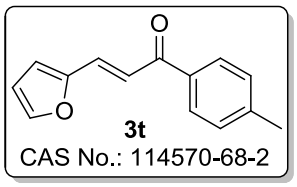


(*E*)-1,3-di-2-tolylprop-2-en-1-one 3r: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(*p*-tolyl)ethanol (72.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (117.9 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 15.7 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H),

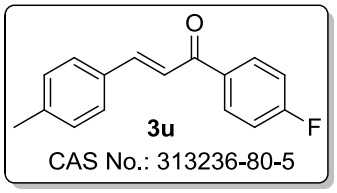
2.45 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.32, 144.68, 143.64, 141.07, 135.86, 132.36, 129.79, 129.42, 128.75, 128.56, 121.19, 21.78, 21.63 ppm.



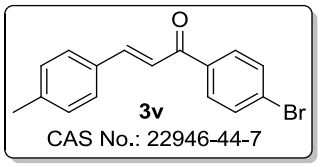
(*E*)-3-(4-chlorophenyl)-1-(4-tolyl)prop-2-en-1-one 3s: The reaction was carried out according to the general procedure with (4-chlorophenyl)methanol (142.6 mg, 1.0 mmol), 1-(*p*-tolyl)ethanol (72.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (114.0 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 15.7 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.74, 143.92, 142.93, 136.37, 135.55, 133.60, 129.65, 129.48, 129.31, 128.75, 122.57, 21.79 ppm.



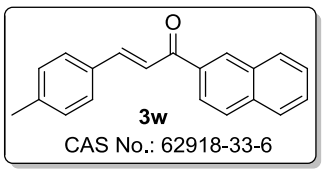
(*E*)-3-(furan-2-yl)-1-(4-tolyl)prop-2-en-1-one 3t: The reaction was carried out according to the general procedure with furan-2-ylmethanol (98.1 mg, 1.0 mmol), 1-(*p*-tolyl)ethanol (72.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (82.9 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 15.3 Hz, 1H), 7.52 (s, 1H), 7.47 (d, *J* = 15.3 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 2.7 Hz, 1H), 6.51 (d, *J* = 1.4 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.40, 151.86, 144.89, 143.70, 135.68, 130.41, 129.42, 128.67, 119.46, 116.07, 112.73, 21.76 ppm.



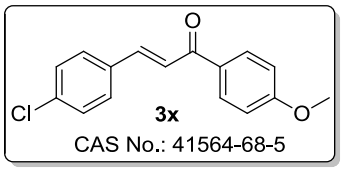
(*E*)-1-(4-fluorophenyl)-3-(4-tolyl)prop-2-en-1-one 3u: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(4-fluorophenyl)ethanol (70.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (89.6 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.00, 165.64 (d, *J* = 254.2 Hz), 145.25, 141.33, 134.78, 132.13, 131.14 (d, *J* = 9.2 Hz), 129.84, 128.62, 120.66, 115.79 (d, *J* = 21.8 Hz), 21.64 ppm.



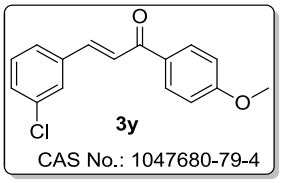
(*E*)-1-(4-bromophenyl)-3-(4-tolyl)prop-2-en-1-one 3v: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(4-bromophenyl)ethanol (100.6 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (144.2 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 15.6 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.56, 145.64, 141.48, 137.16, 131.99, 130.33, 130.11, 129.86, 129.30, 128.68, 120.55, 21.67 ppm.



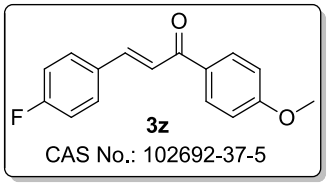
(*E*)-1-(naphthalen-2-yl)-3-(4-tolyl)prop-2-en-1-one 3w: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.2 mg, 1.0 mmol), 1-(naphthalen-2-yl)ethanol (86.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (133.2 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.09 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.83 (m, 3H), 7.66 – 7.52 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.57, 145.09, 141.31, 135.90, 135.66, 132.79, 132.44, 130.07, 129.94, 129.73, 128.76, 128.53, 128.03, 126.96, 124.74, 121.27, 21.77 ppm.



(*E*)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 3x: The reaction was carried out according to the general procedure with (4-chlorophenyl)methanol (142.6 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (126.1 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 15.6 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 15.6 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.44, 163.64, 142.51, 136.26, 133.68, 131.01, 130.93, 129.60, 129.28, 122.38, 113.99, 55.60 ppm.

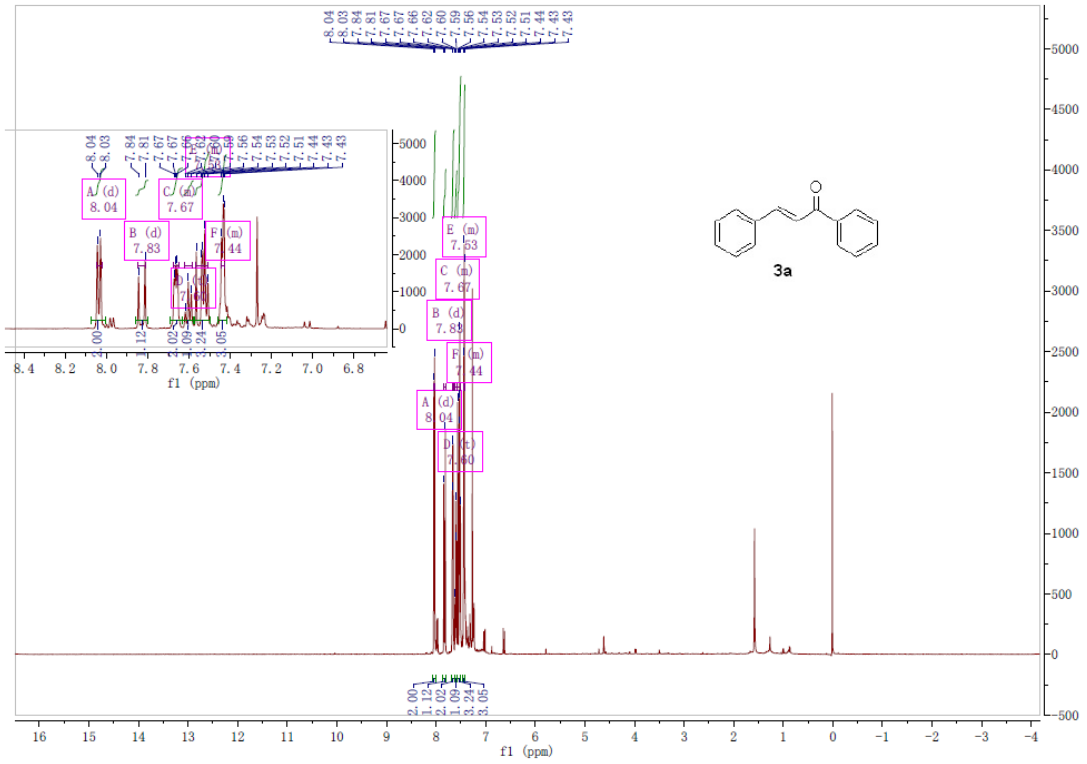


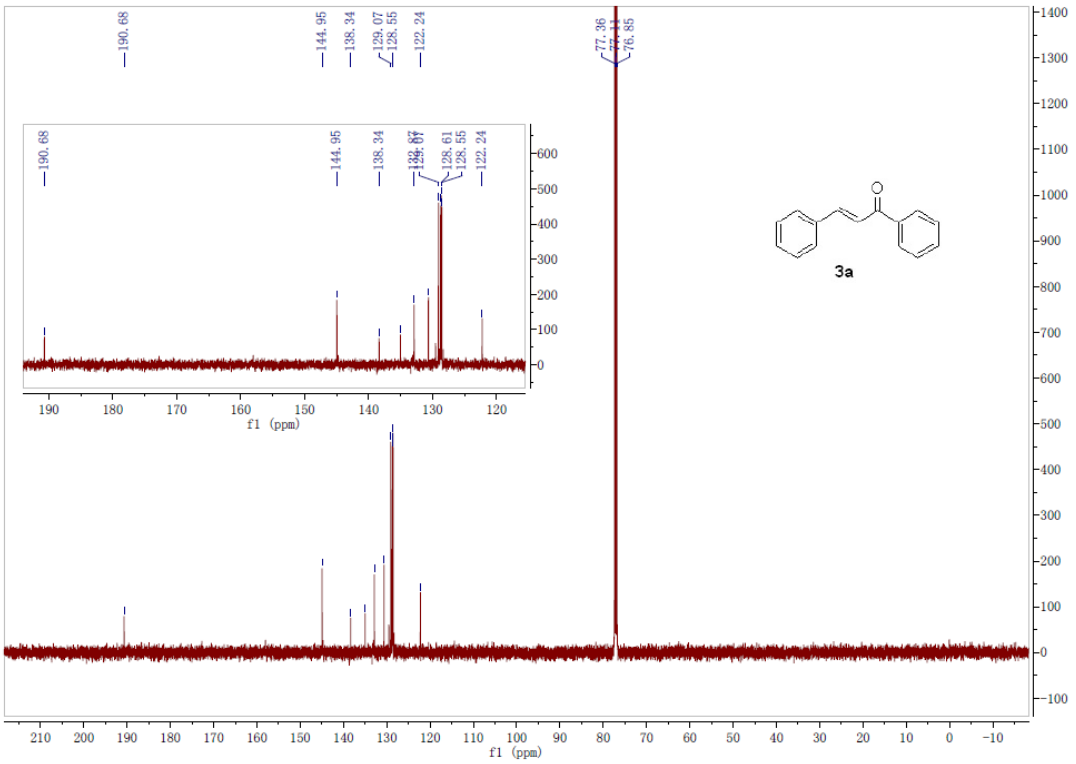
(*E*)-3-(3-chlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 3y: The reaction was carried out according to the general procedure with (3-chlorophenyl)methanol (142.6 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (81.4 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.63 (s, 1H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.38 – 7.32 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.33, 163.71, 142.28, 137.04, 135.01, 130.99, 130.90, 130.69, 130.27, 130.22, 127.89, 126.84, 123.17, 114.02, 113.77, 55.61 ppm.

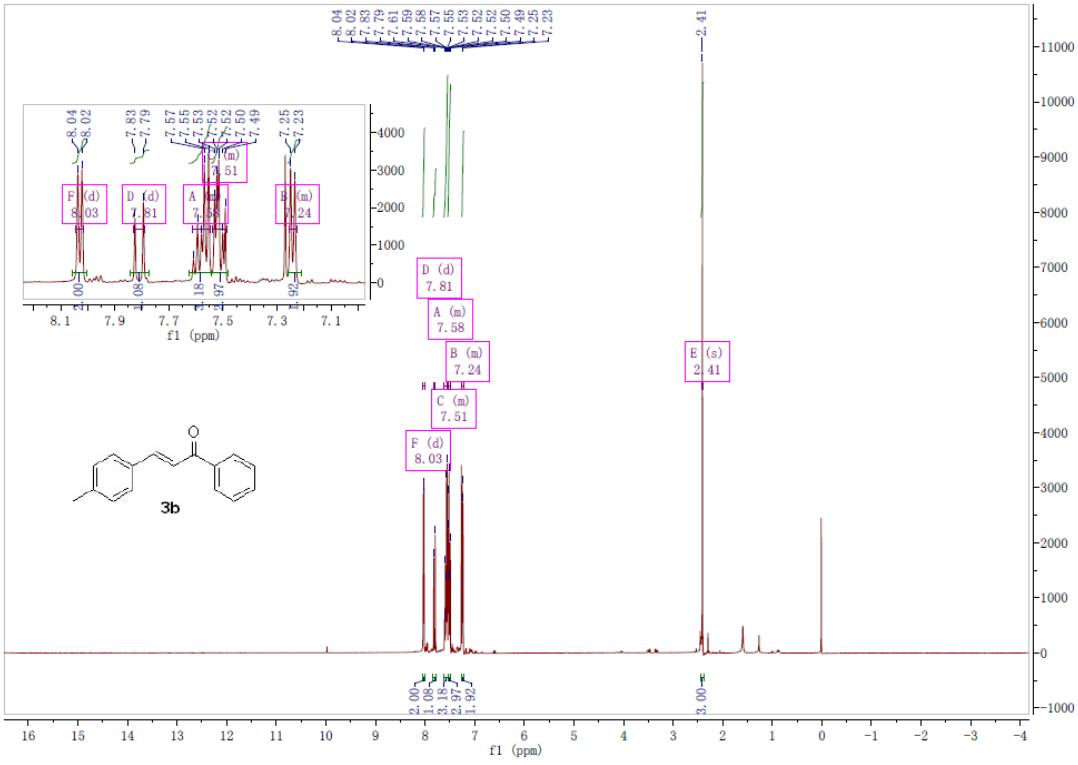


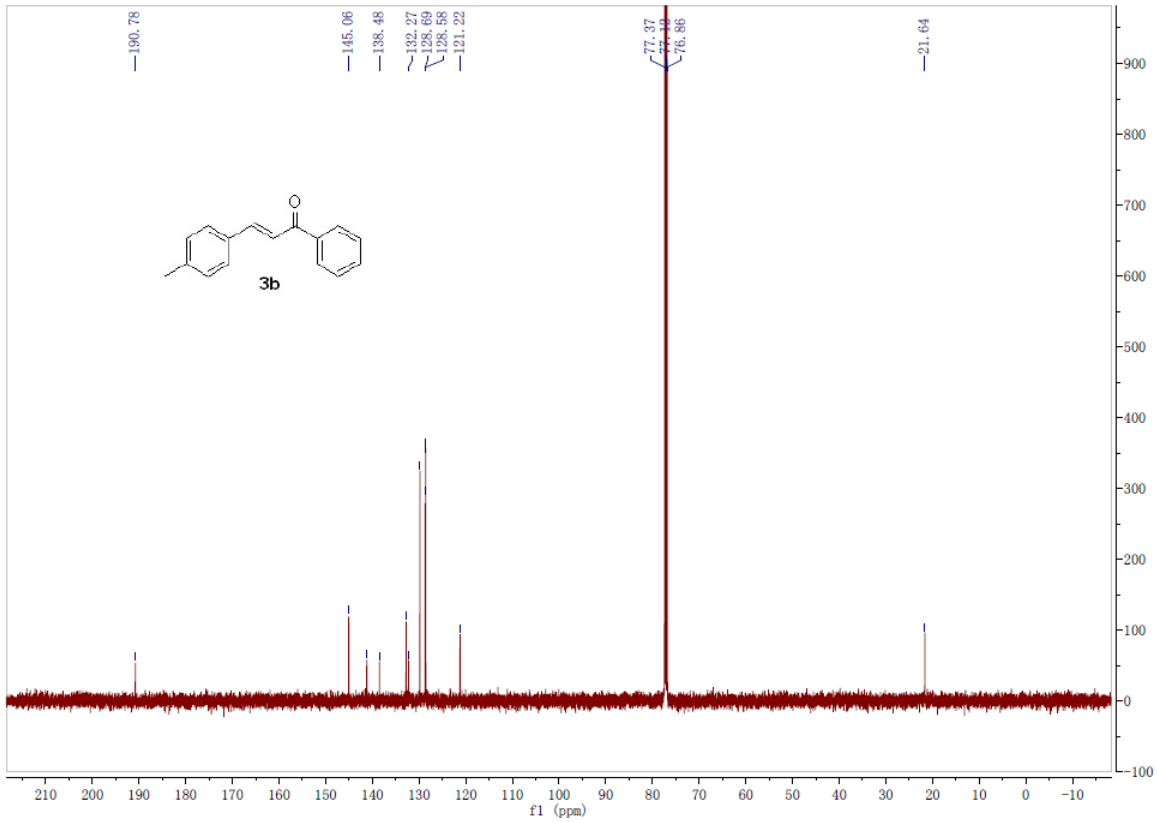
(*E*)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 3z: The reaction was carried out according to the general procedure with (4-fluorophenyl)methanol (126.2 mg, 1.0 mmol), 1-(4-methoxyphenyl)ethanol (76.1 mg, 0.50 mmol), *t*-BuOH/H_2O (1.0 mL, 1/1, v/v) and LiOH·H_2O (42.0 mg, 1.0 mmol) by Co-N-CMK-3-800 (13 mg, 1.3mol% Co) catalyst under O_2 balloon for 12 h. The product was obtained as a yellow solid (98.5 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.55, 164.03 (d, *J* = 251.4 Hz), 163.58, 142.72, 131.10, 130.90, 130.68, 130.32 (d, *J* = 8.5 Hz), 121.67, 116.16 (d, *J* = 21.9 Hz), 113.97, 55.59 ppm.

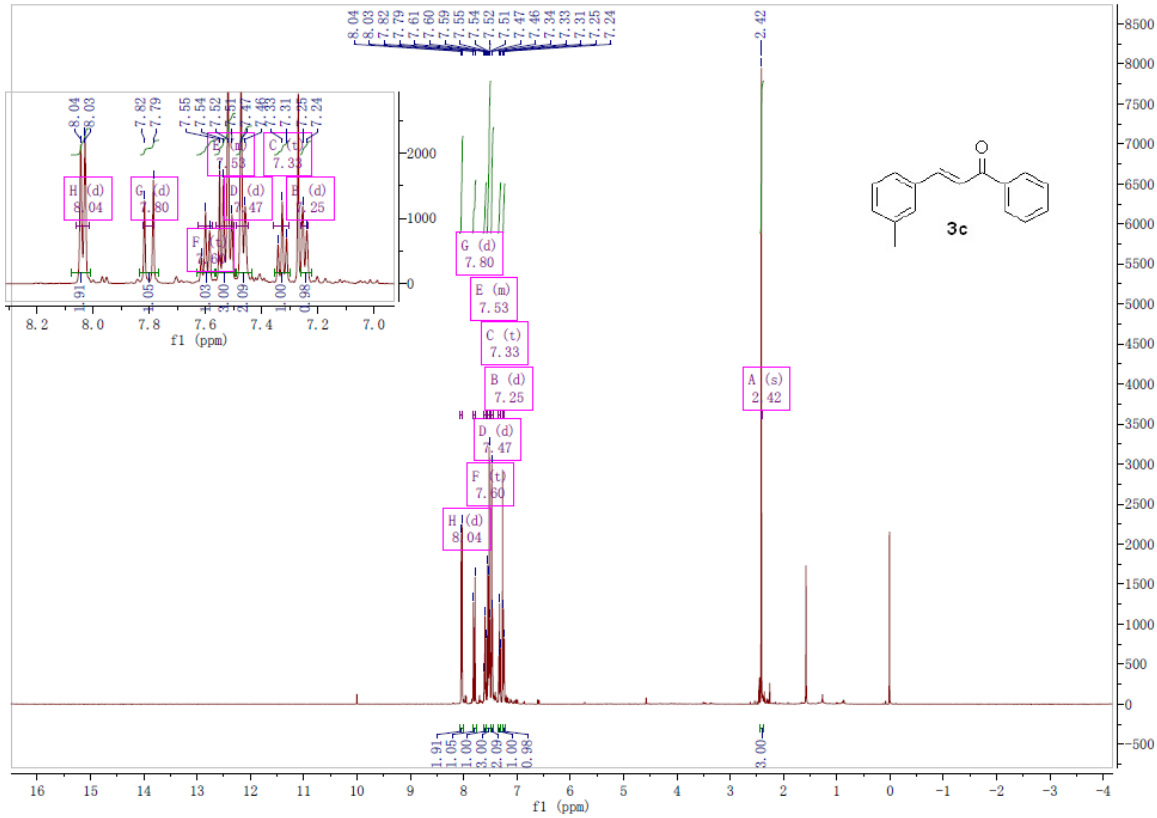
7. Copy of ^{1}H NMR and ^{13}C NMR spectra for products.

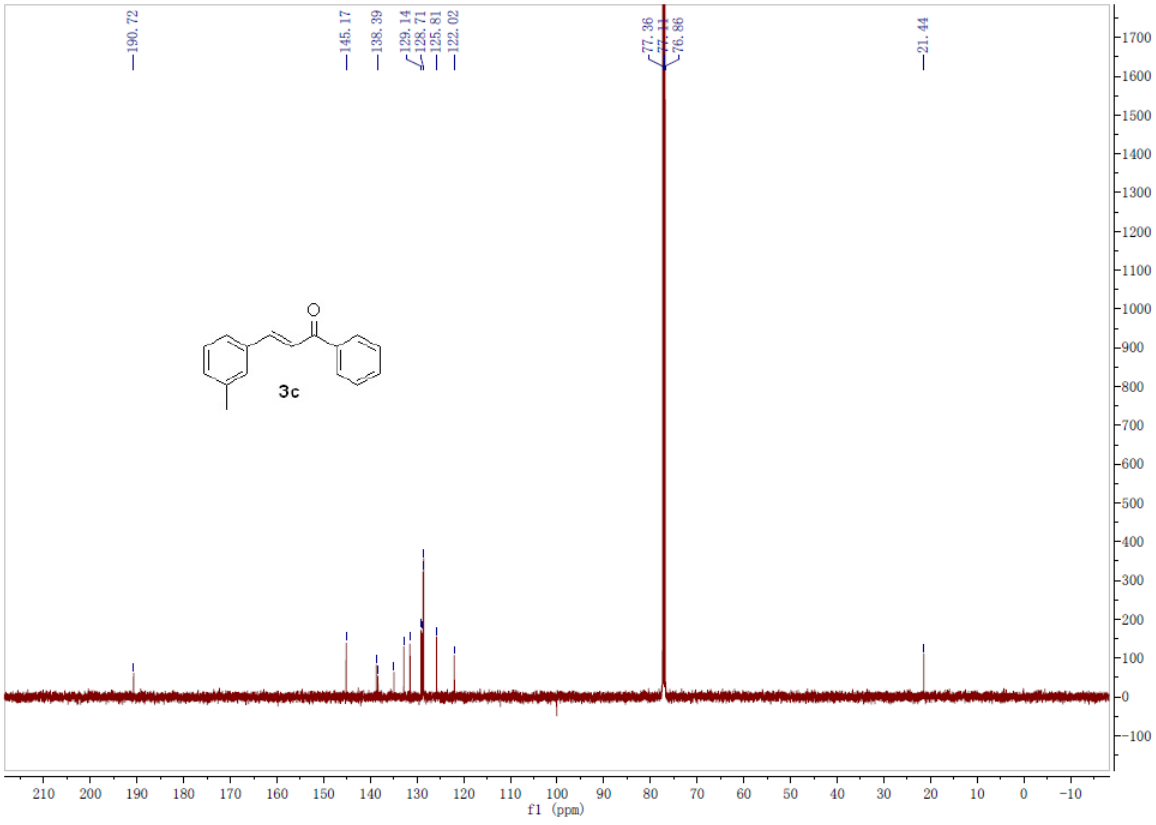


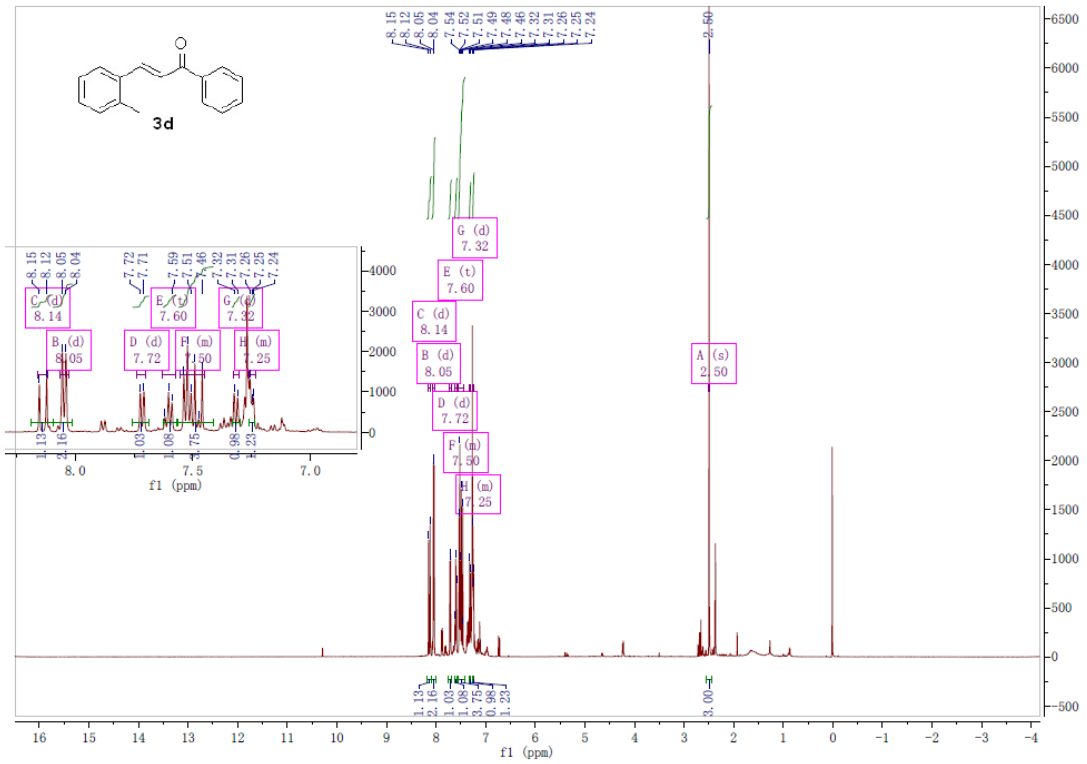

190.68
144.95
138.34
129.07
128.55
122.24
77.36
77.11
76.85
3a
f1 (ppm)

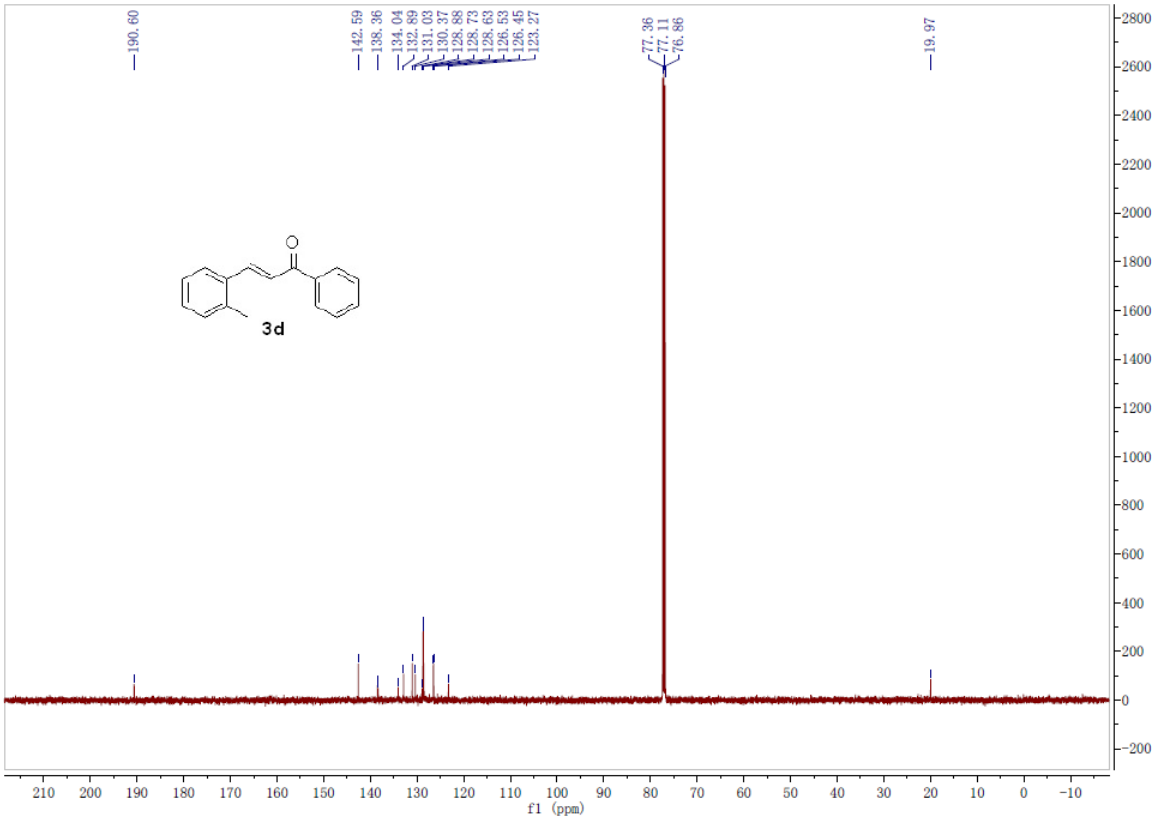

D (d)
7.81
A (m)
7.58
B (m)
7.24
C (m)
7.51
F (d)
8.03
E (s)
2.41
3b
f1 (ppm)

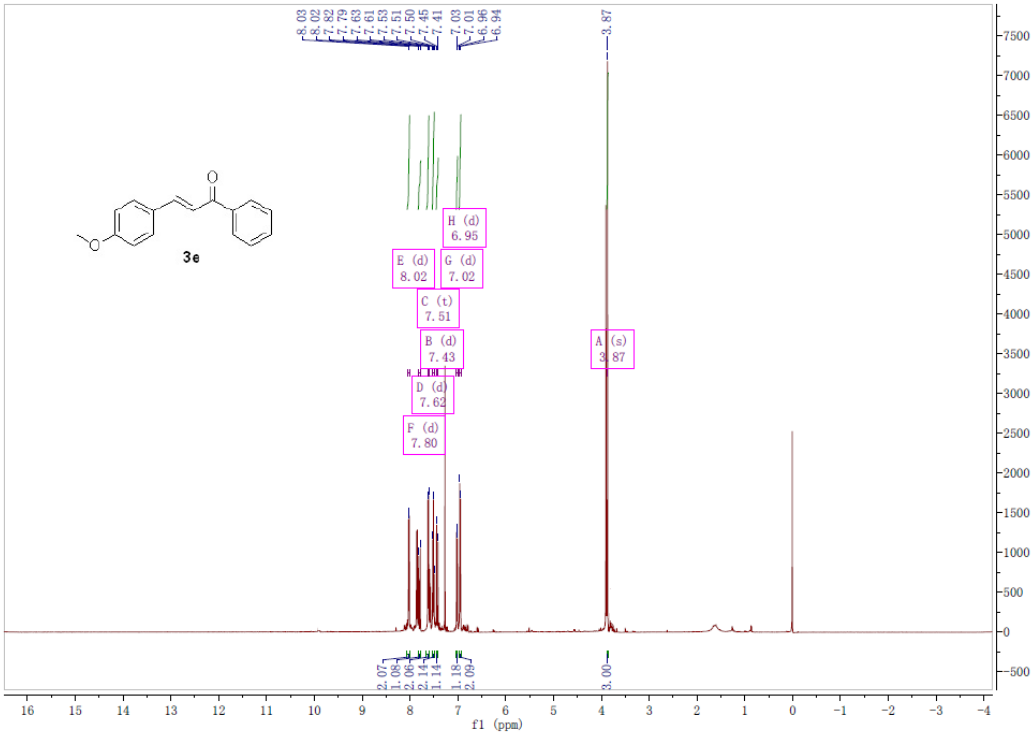

190.78
145.06
138.48
132.27
128.69
128.58
121.22
77.37
77.19
76.86
21.64
3b
f1 (ppm)

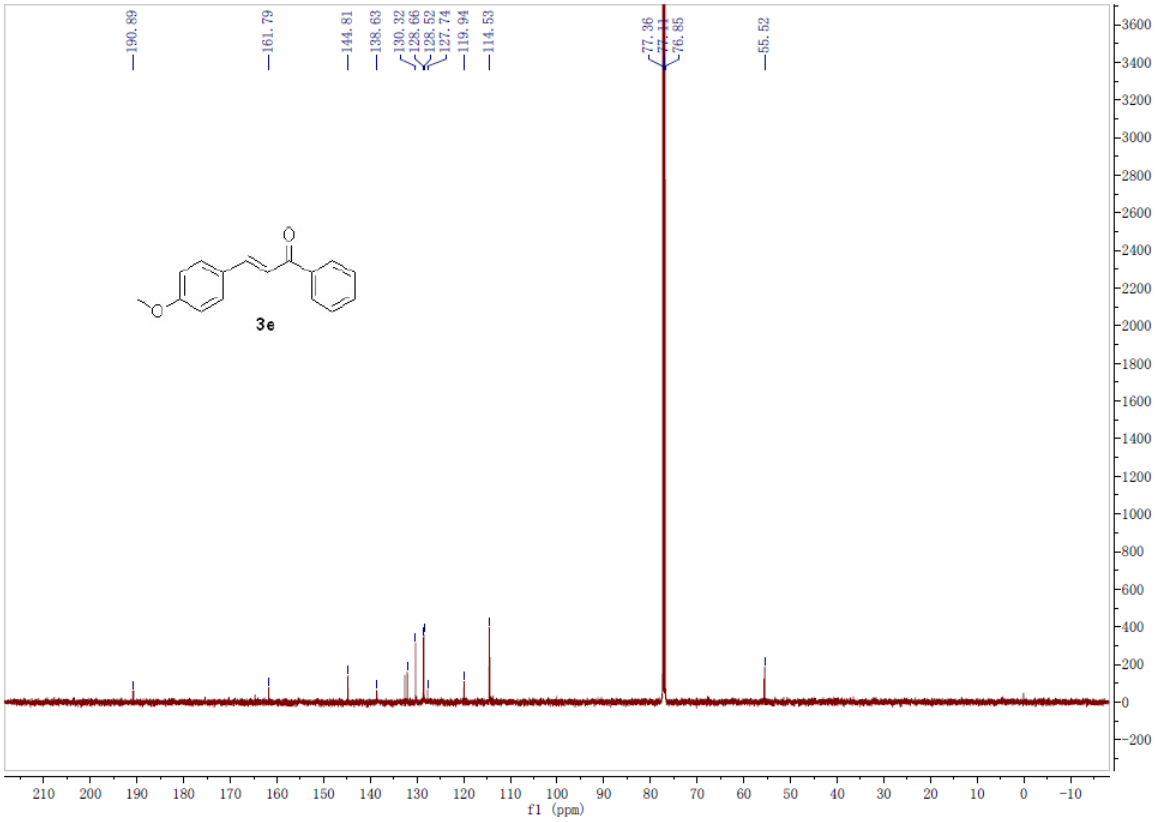

8.04
8.03
7.82
7.79
7.61
7.60
7.59
7.55
7.54
7.52
7.51
7.47
7.46
7.34
7.33
7.31
7.25
7.24
2.42
H (d) 8.04
G (d) 7.80
E (m) 7.53
C (t) 7.33
B (d) 7.25
D (d) 7.47
F (t) 7.50
A (s) 2.42
3c
f1 (ppm)

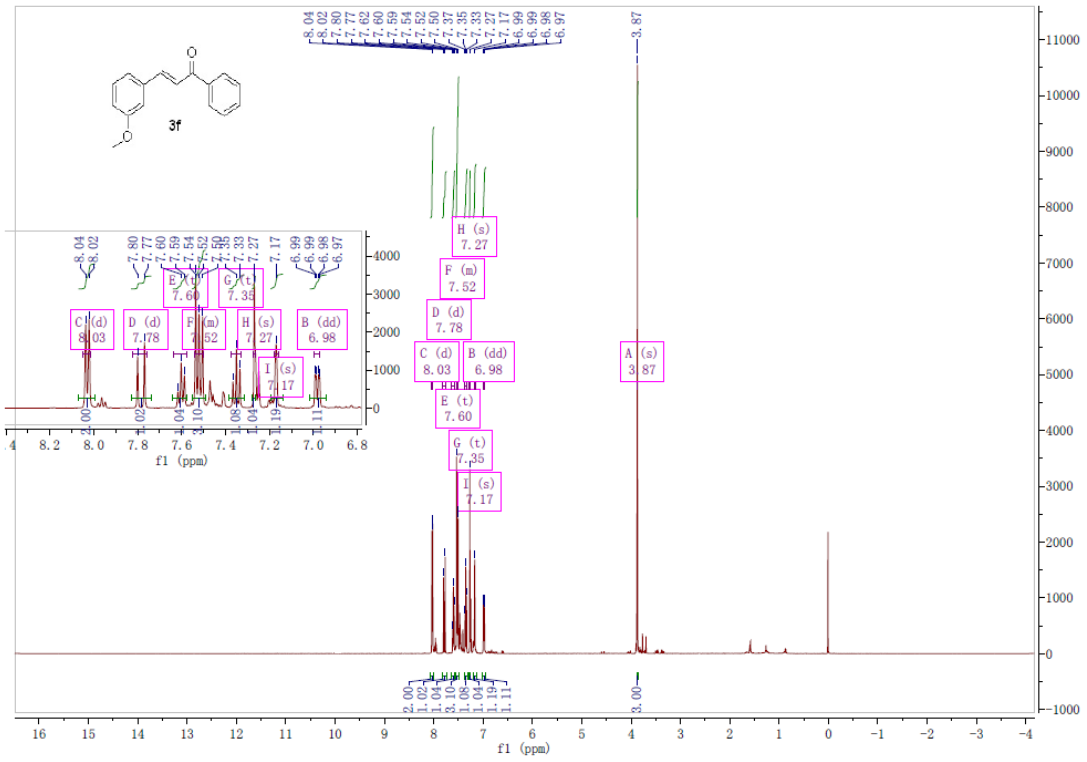

190.72
145.17
138.39
129.14
128.71
125.81
122.02
77.36
77.11
76.86
21.44
3c
f1 (ppm)

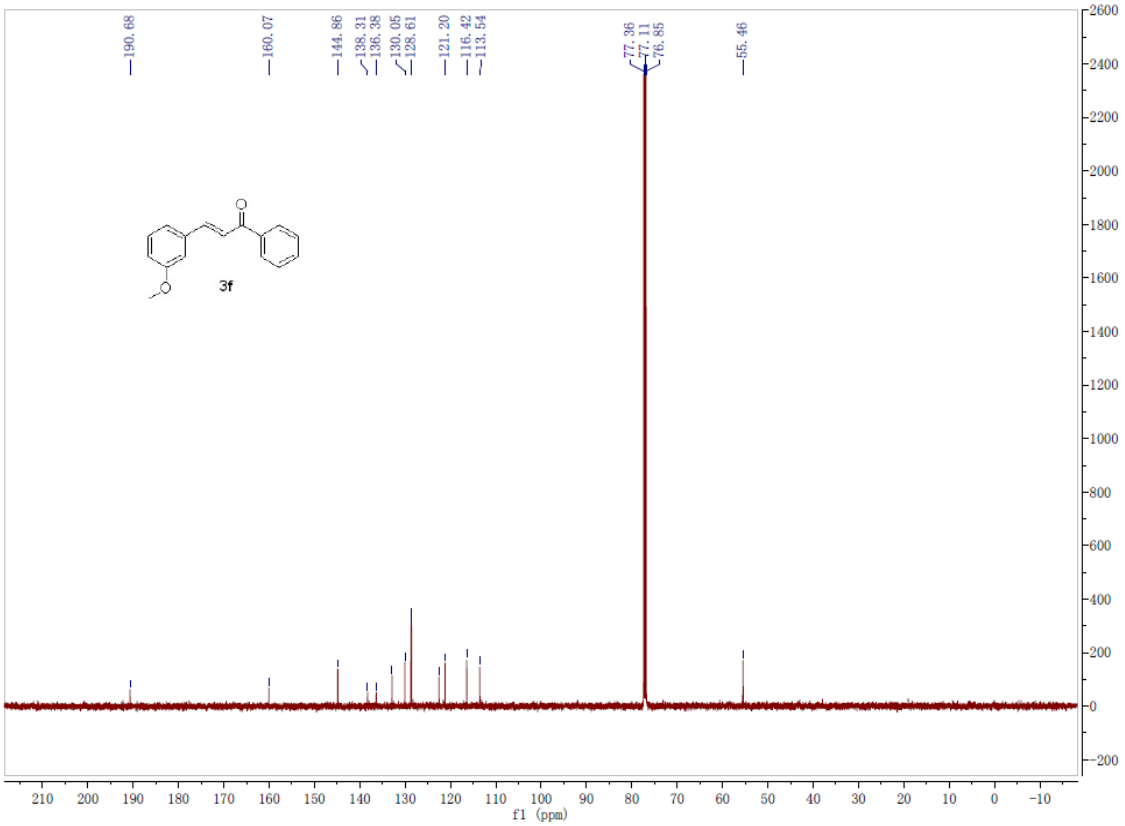

3d
f1 (ppm)

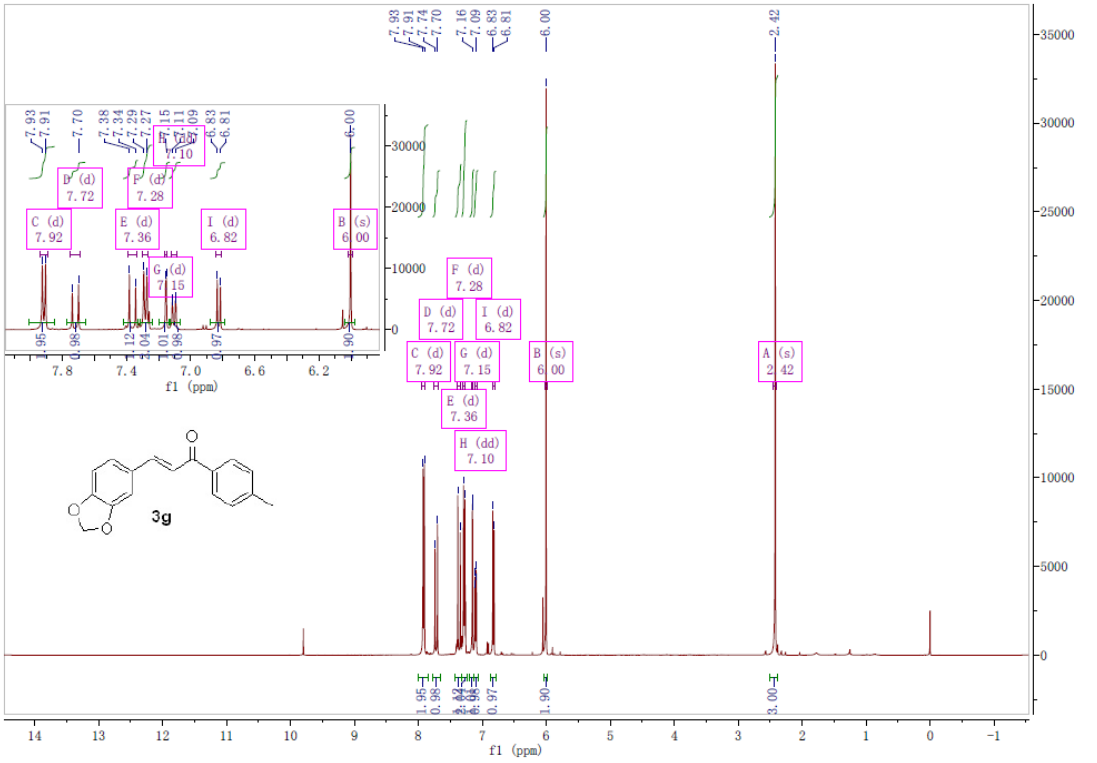

3d
f1 (ppm)

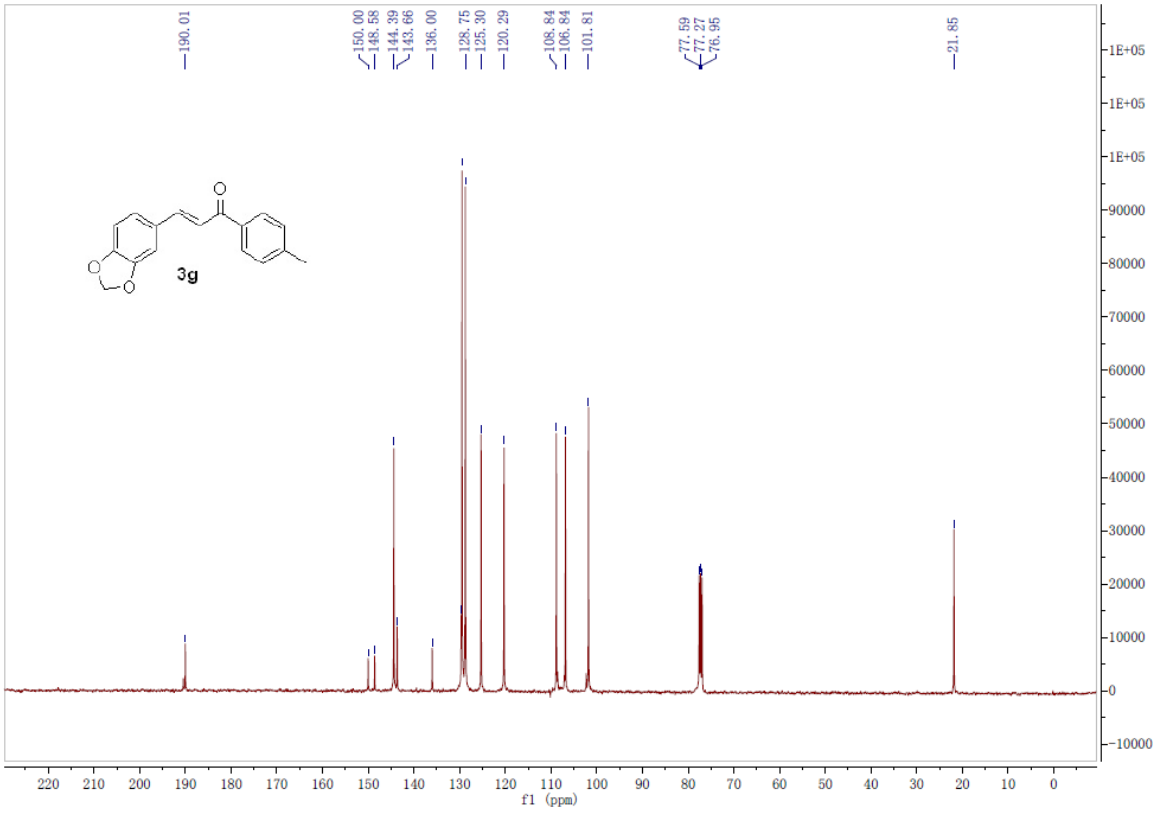

3e
H (d) 6.95
E (d) 8.02
G (d) 7.02
C (t) 7.51
B (d) 7.43
A (s) 3.87
D (d) 7.62
F (d) 7.80
f1 (ppm)


3e
f1 (ppm)


3f
f1 (ppm)


190.68
160.07
144.86
138.31
136.38
130.05
128.61
121.20
116.42
113.54
77.36
77.11
76.85
55.46
3f
f1 (ppm)


7.93
7.91
7.74
7.70
7.16
7.09
6.83
6.81
6.00
2.42
D (d) 7.72
F (d) 7.28
C (d) 7.92
E (d) 7.36
I (d) 6.82
G (d) 7.15
B (s) 6.00
H (dd) 7.10
A (s) 2.42
3g
f1 (ppm)


190.01
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143.66
136.00
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125.30
120.29
108.84
106.84
101.81
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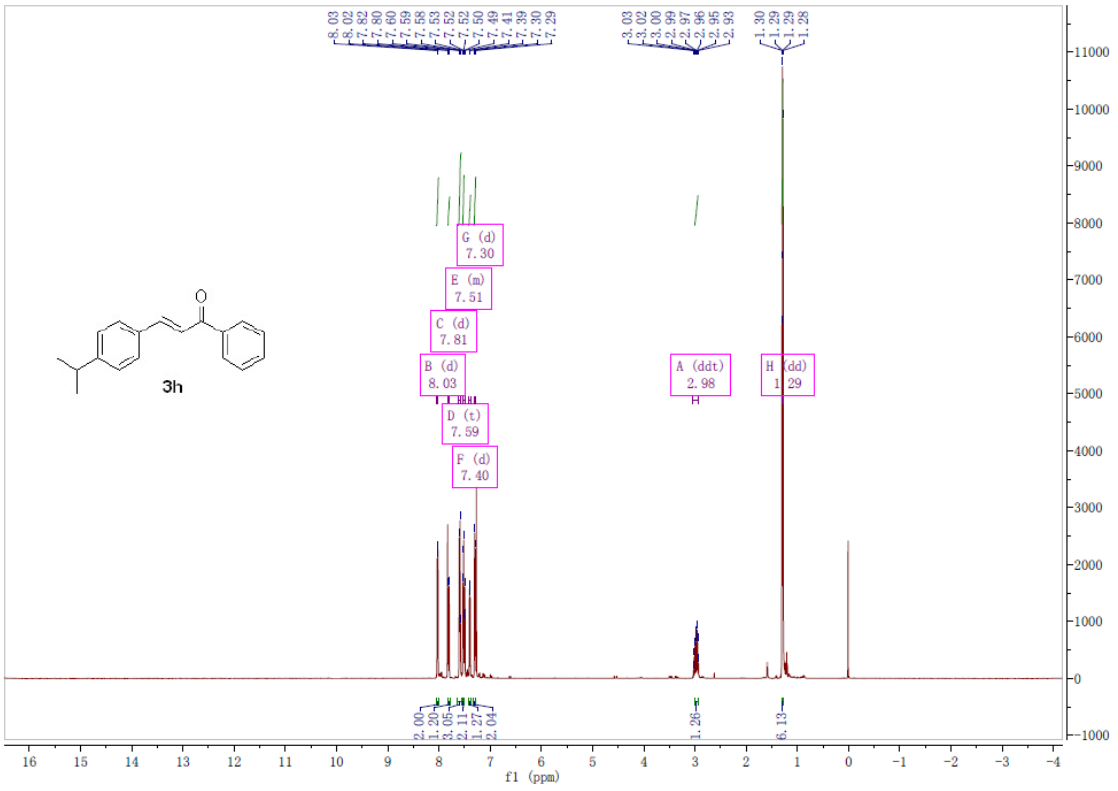
77.27
76.95
21.85
3g
f1 (ppm)


8.03
8.02
7.82
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7.58
7.53
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7.50
7.49
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7.39
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7.29
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3.02
3.00
2.99
2.97
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1.30
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G (d)
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E (m)
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C (d)
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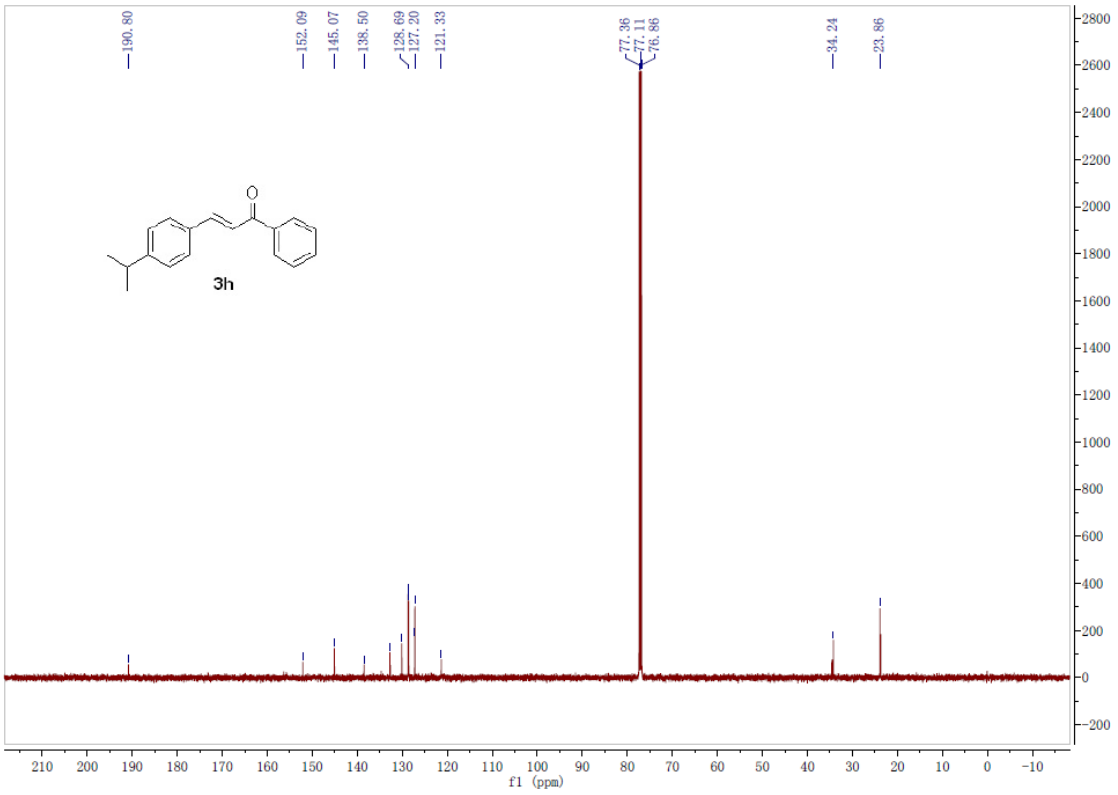
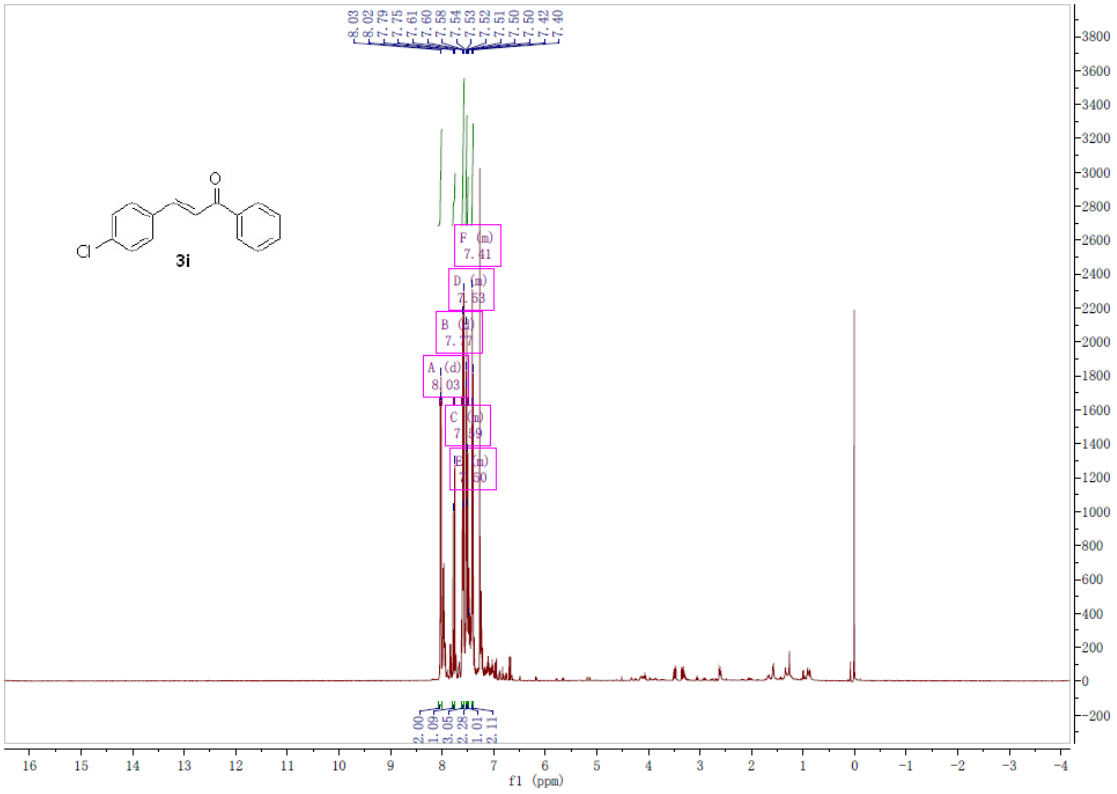
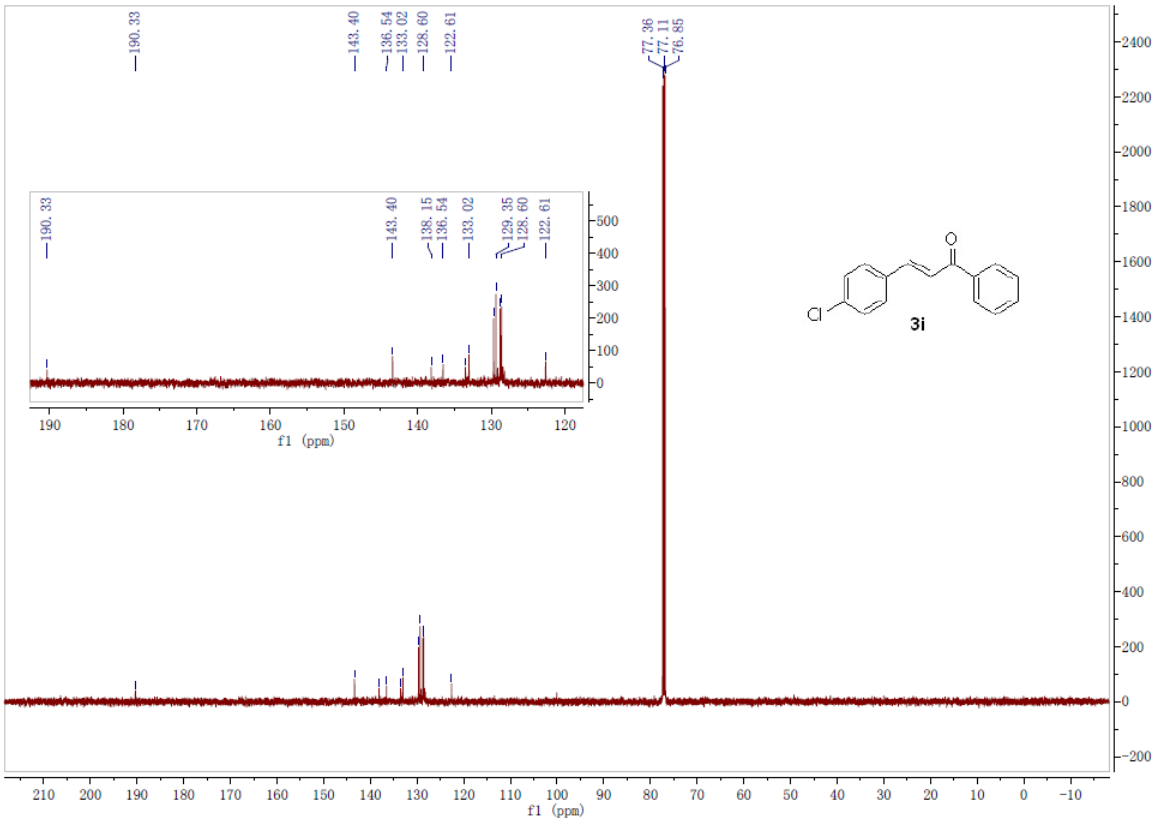
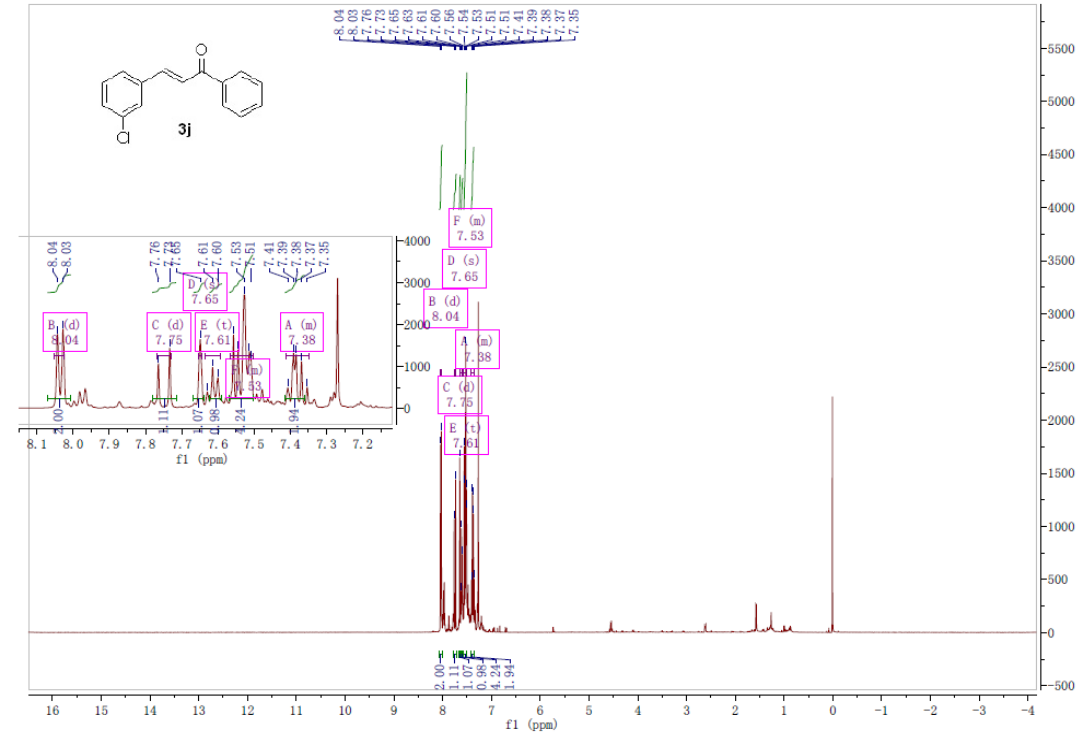
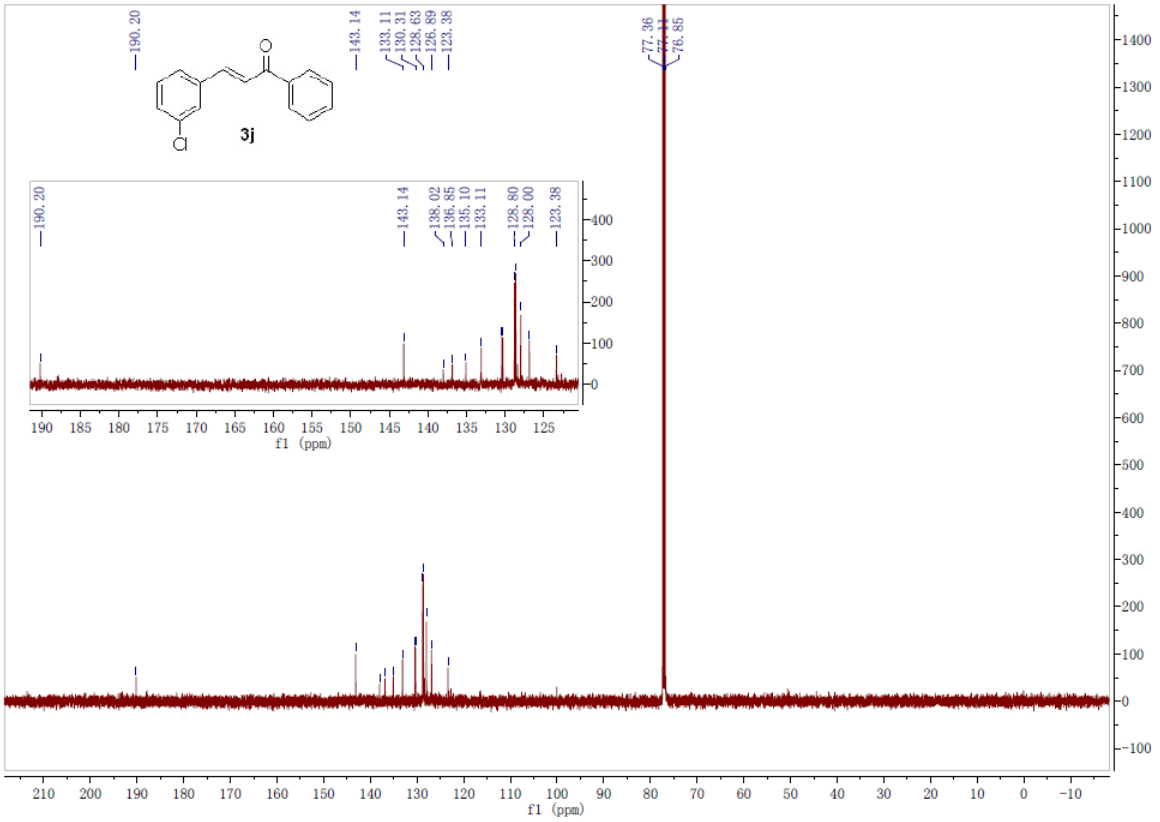
B (d)
8.03
D (t)
7.59
F (d)
7.40
A (ddt)
2.98
H (dd)
1.29
3h
2.00
1.20
3.05
2.11
1.27
2.04
1.26
6.13
f1 (ppm)

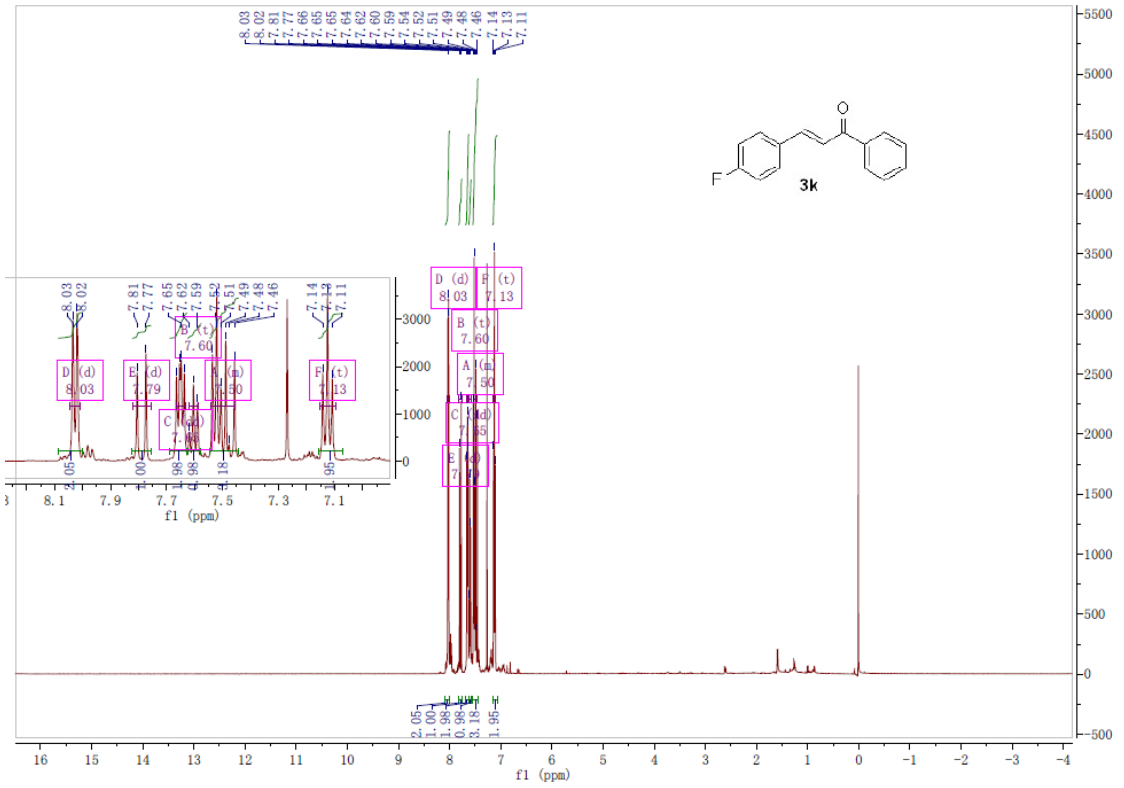

190.80
152.09
145.07
138.50
128.69
127.20
121.33
77.36
77.11
76.86
34.24
23.86
3h
f1 (ppm)

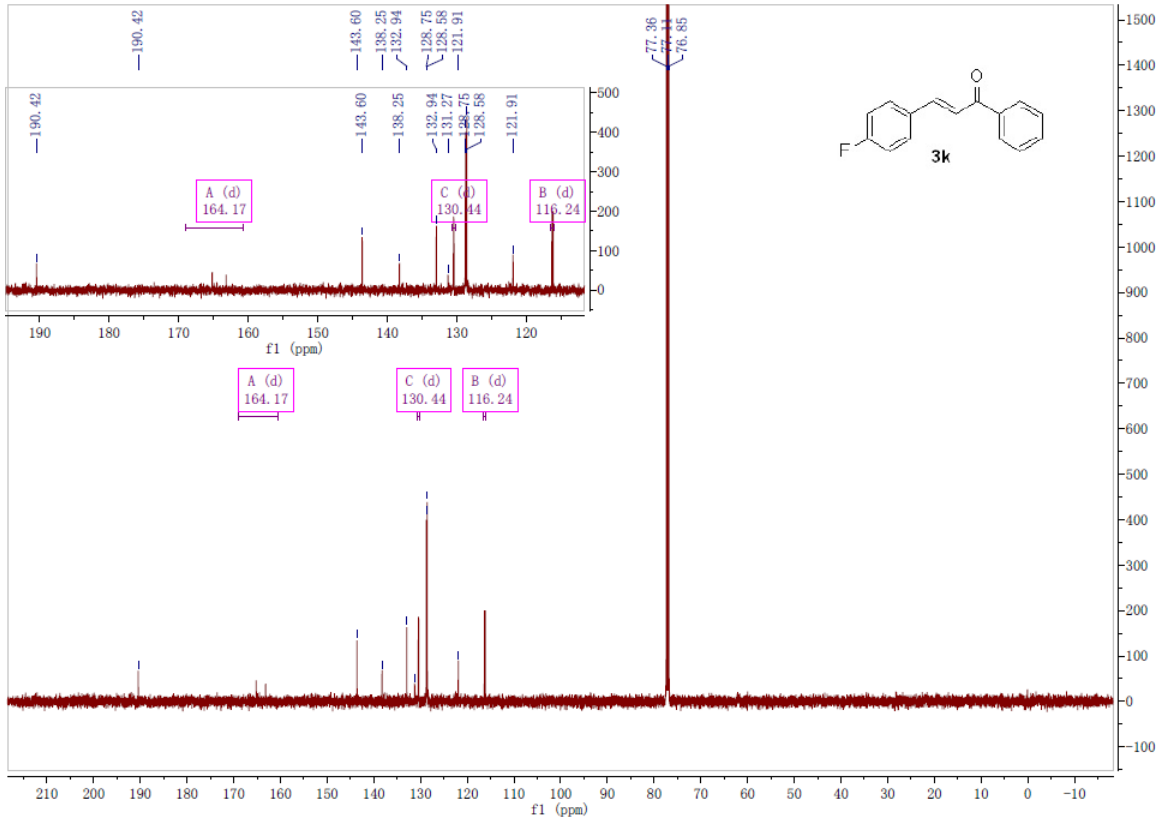

8.03
8.02
7.79
7.75
7.61
7.60
7.58
7.54
7.53
7.52
7.51
7.50
7.42
7.40
O
Cl
3i
F (m)
7.41
D (m)
7.53
B (d)
7.77
A (d)
8.03
C (m)
7.49
E (m)
7.50
2.00
1.09
3.05
2.26
1.01
2.11
f1 (ppm)

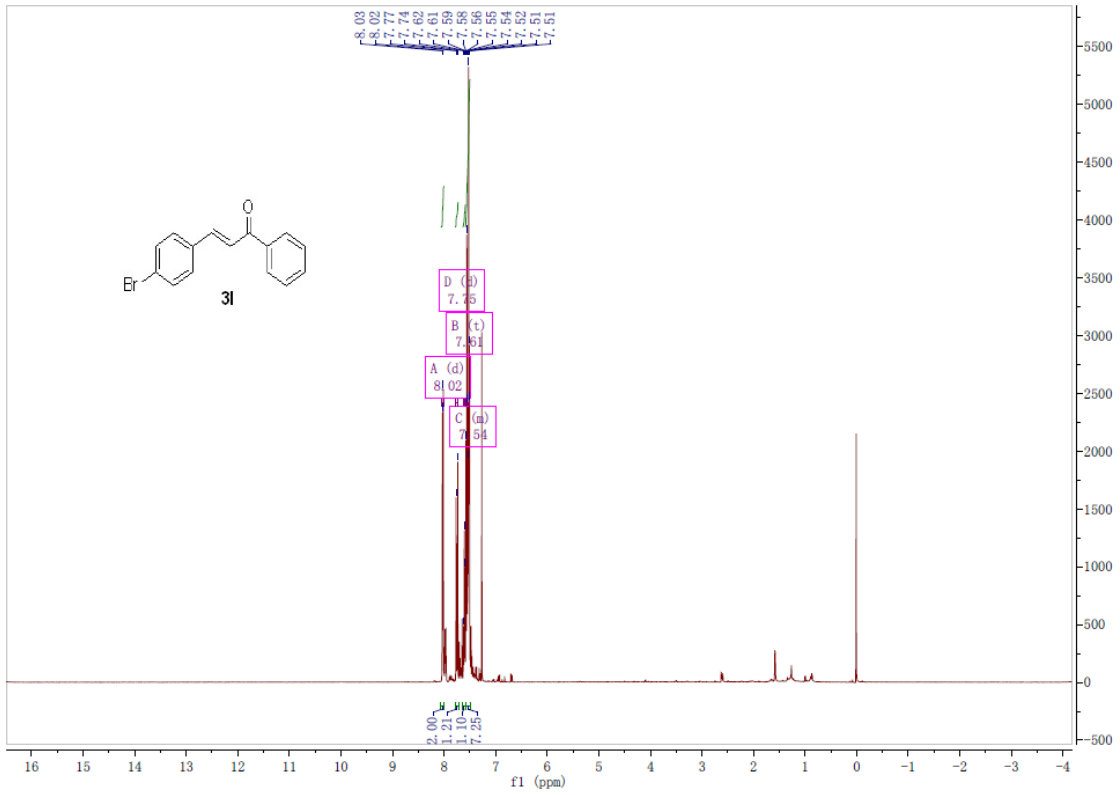

190.33
143.40
136.54
133.02
128.60
122.61
77.36
77.11
76.85
190.33
143.40
138.15
136.54
133.02
129.35
128.60
122.61
f1 (ppm)
Cl
O
3i
f1 (ppm)

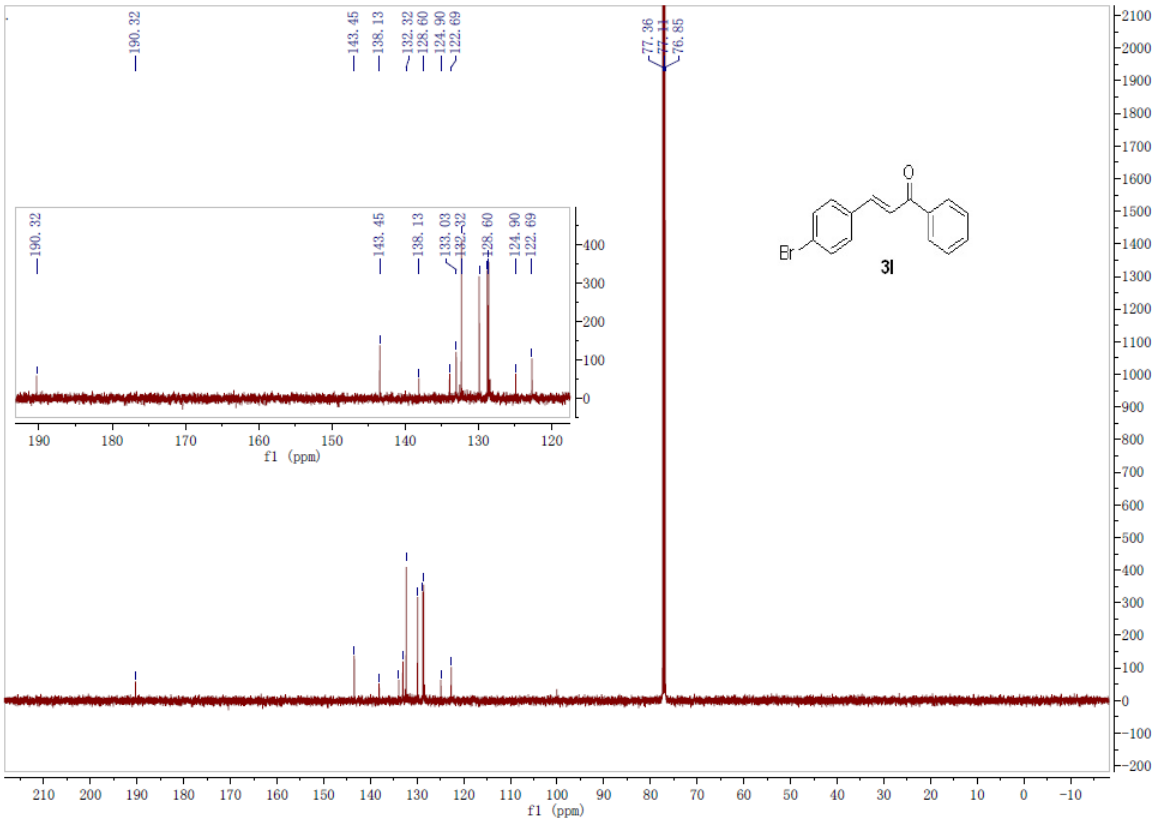

3j
F (m) 7.53
D (s) 7.65
B (d) 8.04
A (m) 7.38
C (d) 7.75
E (t) 7.61
f1 (ppm)

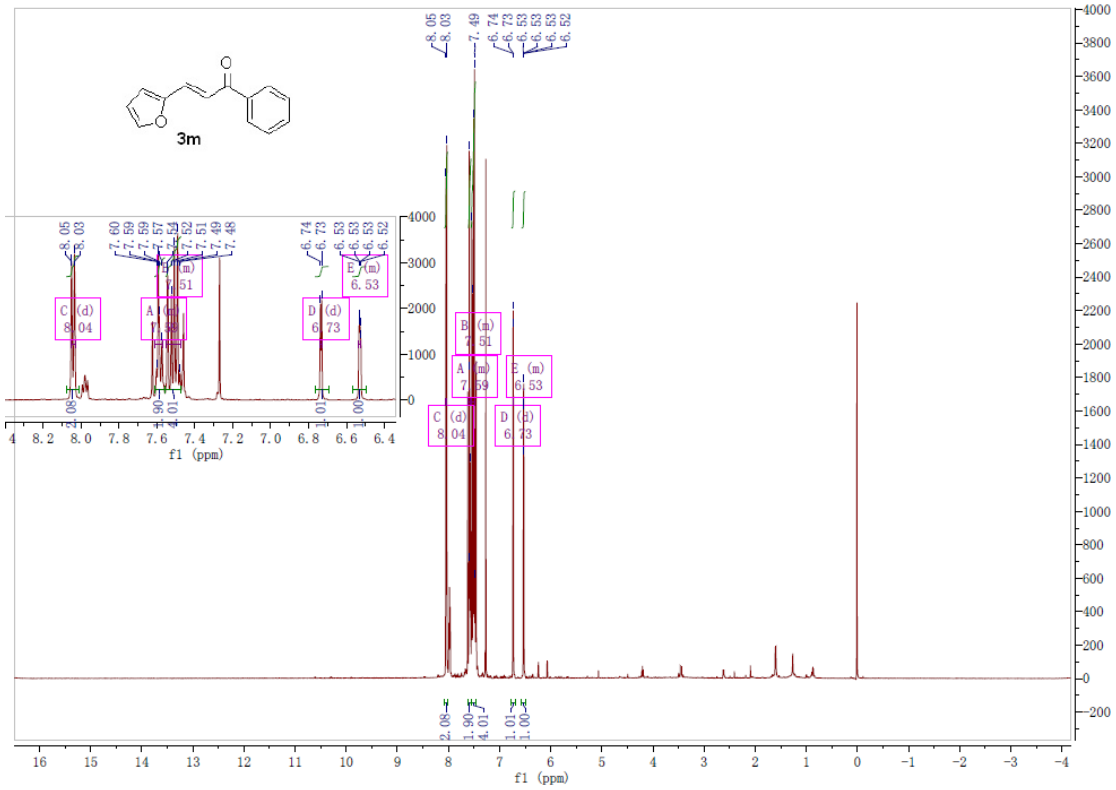

3j
f1 (ppm)

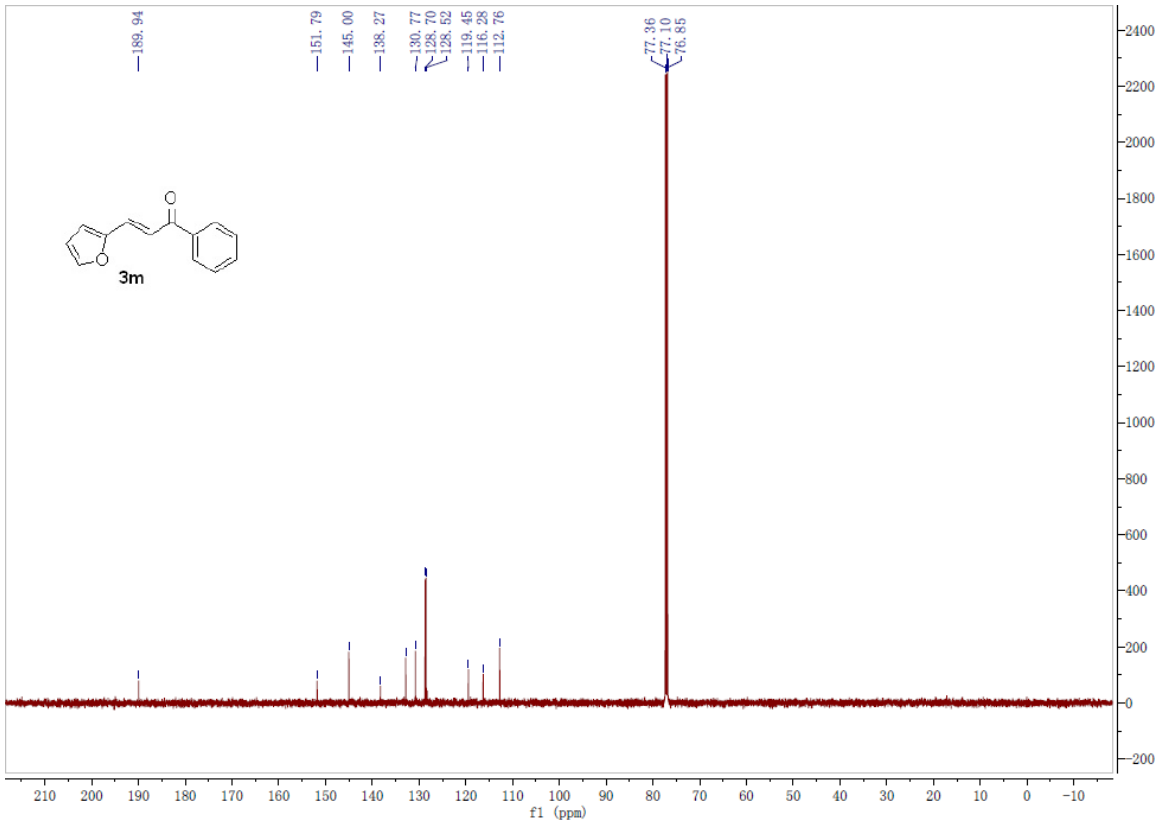

3k
f1 (ppm)

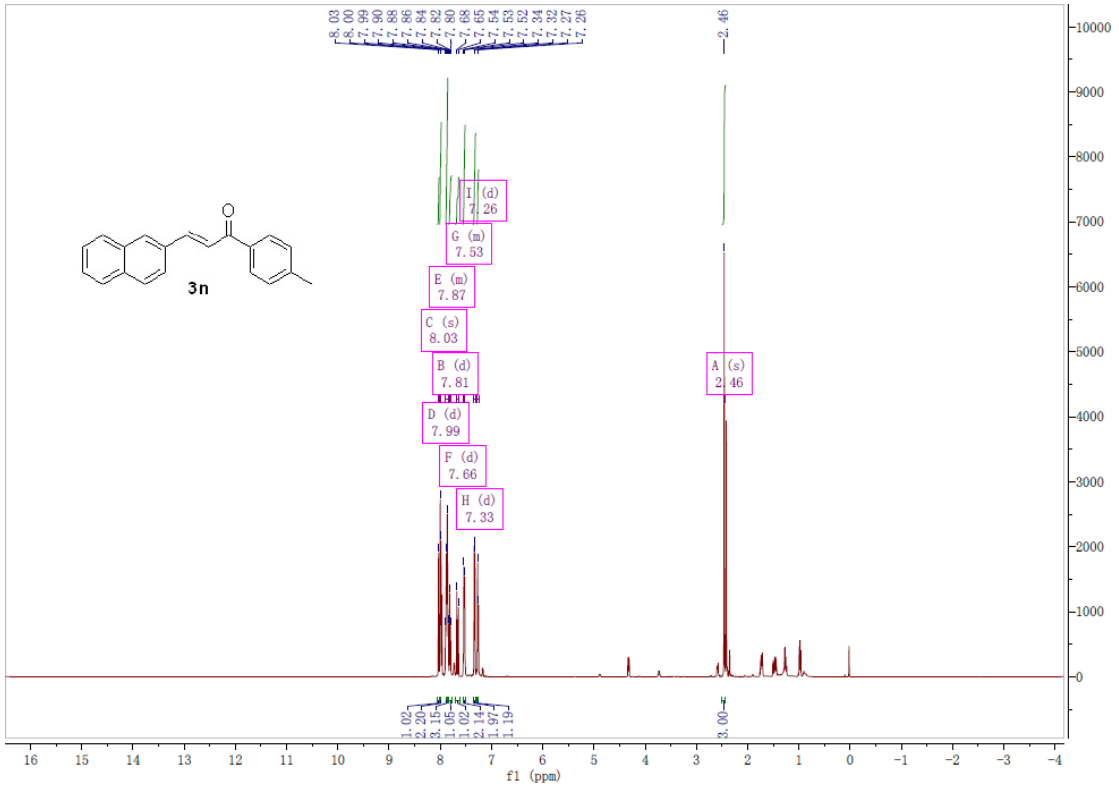

3k
f1 (ppm)

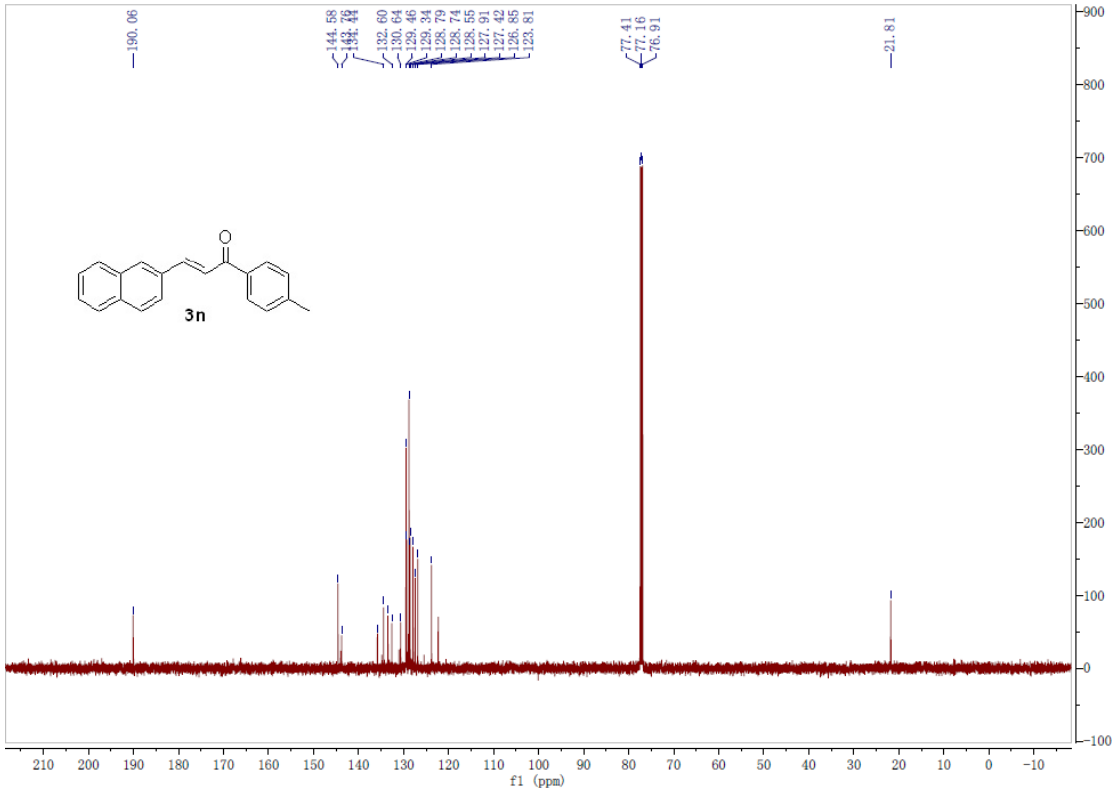

8.03
8.02
7.77
7.74
7.62
7.61
7.59
7.58
7.56
7.55
7.54
7.52
7.51
7.51
O
Br
3l
D (d)
7.75
B (t)
7.61
A (d)
8.02
C (m)
7.54
2.00
1.21
1.19
7.25
f1 (ppm)

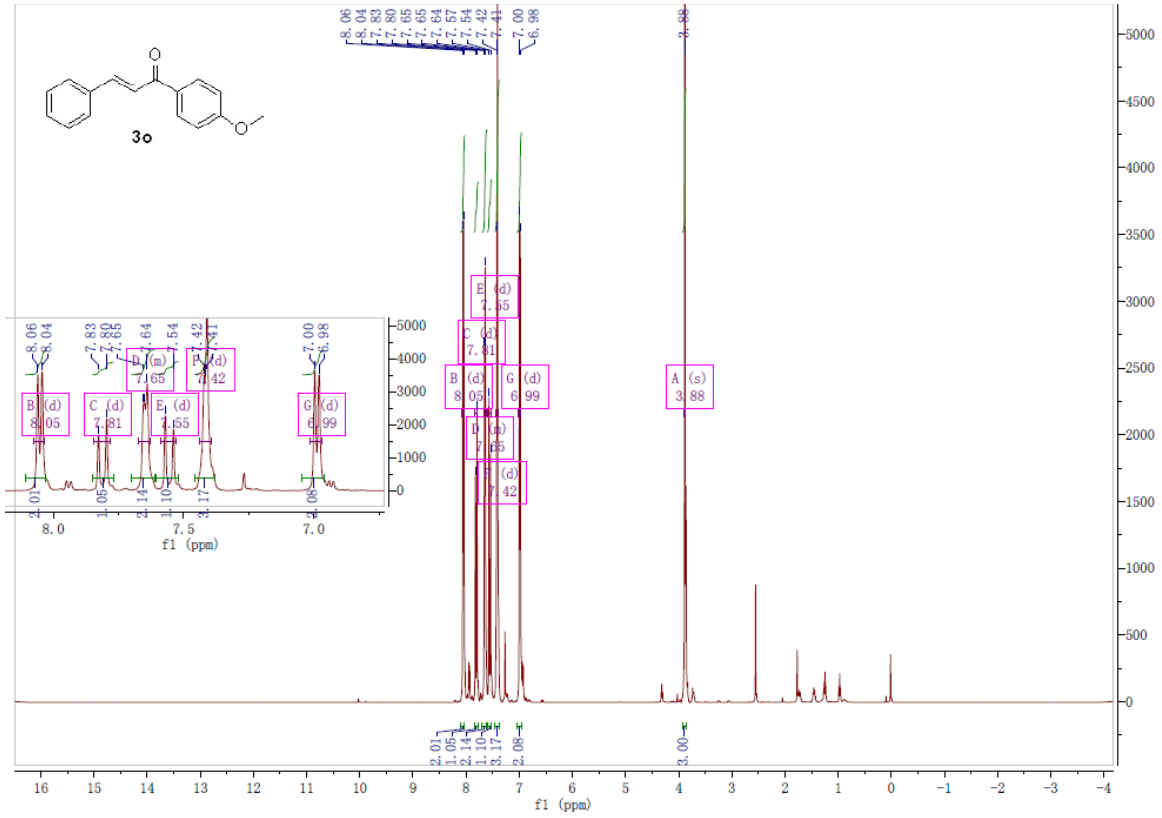

190.32
143.45
138.13
132.32
128.60
124.90
122.69
77.36
77.11
76.85
Br
O
3l
f1 (ppm)

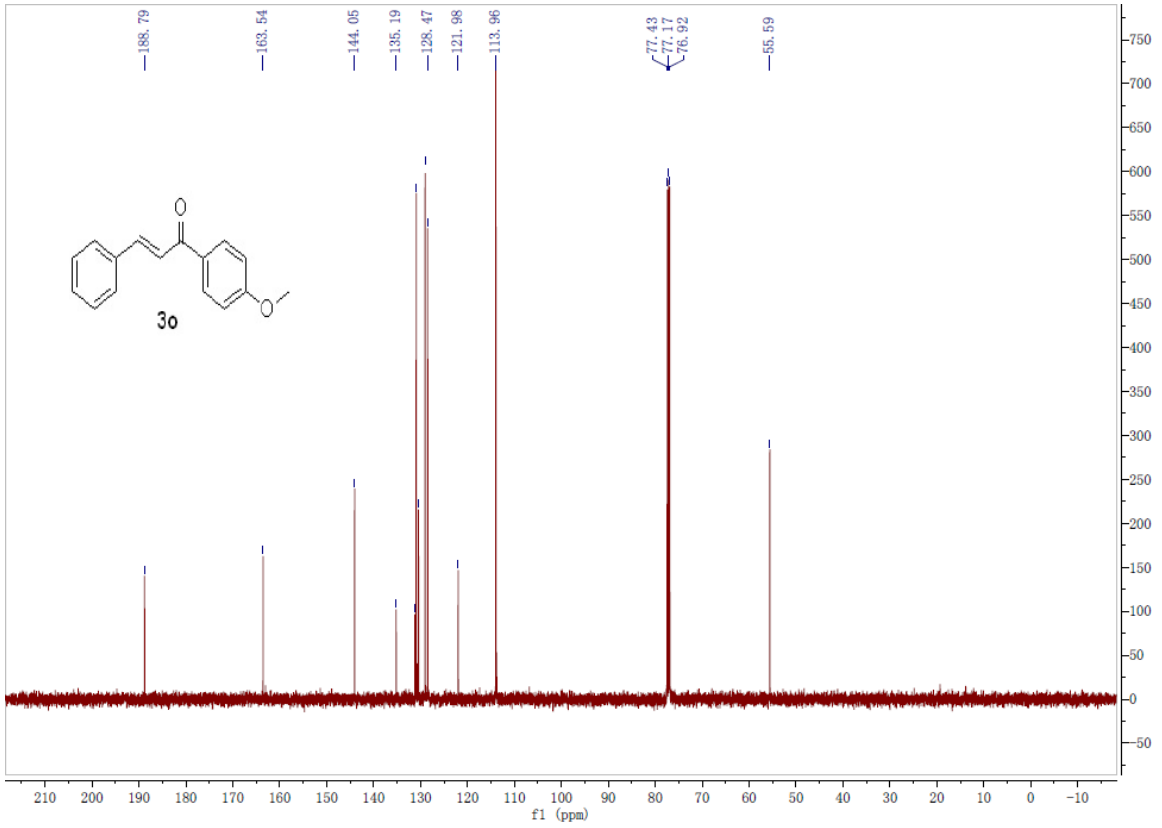

3m
f1 (ppm)

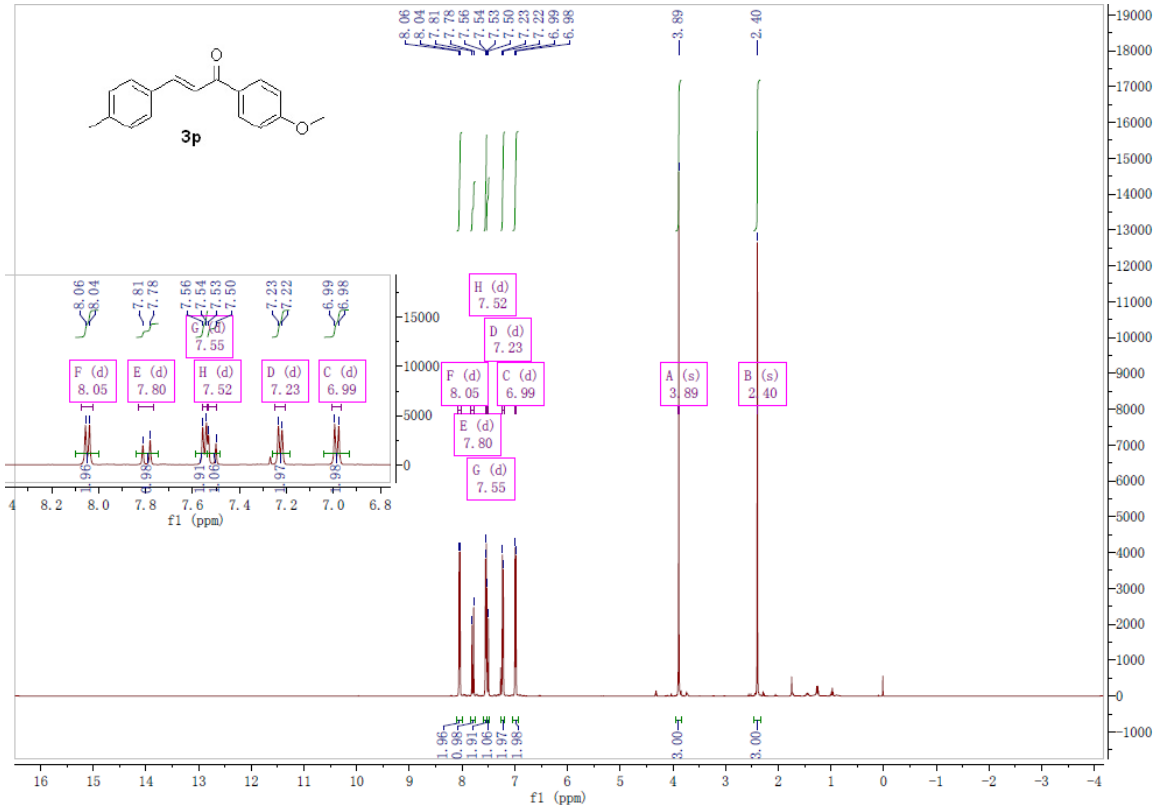

189.94
151.79
145.00
138.27
130.77
128.70
128.52
119.45
116.28
112.76
77.36
77.10
76.85
3m
f1 (ppm)

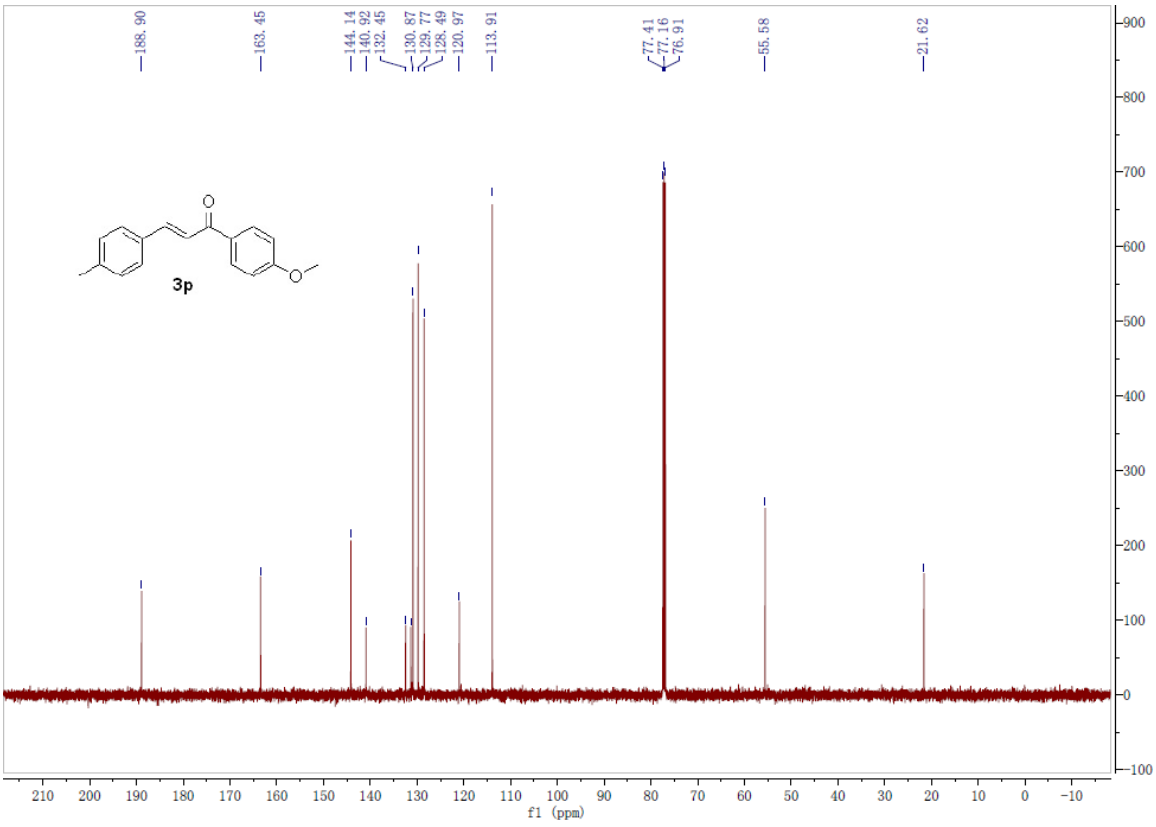

3n
I (d) 7.26
G (m) 7.53
E (m) 7.87
C (s) 8.03
B (d) 7.81
D (d) 7.99
F (d) 7.66
H (d) 7.33
A (s) 2.46
f1 (ppm)

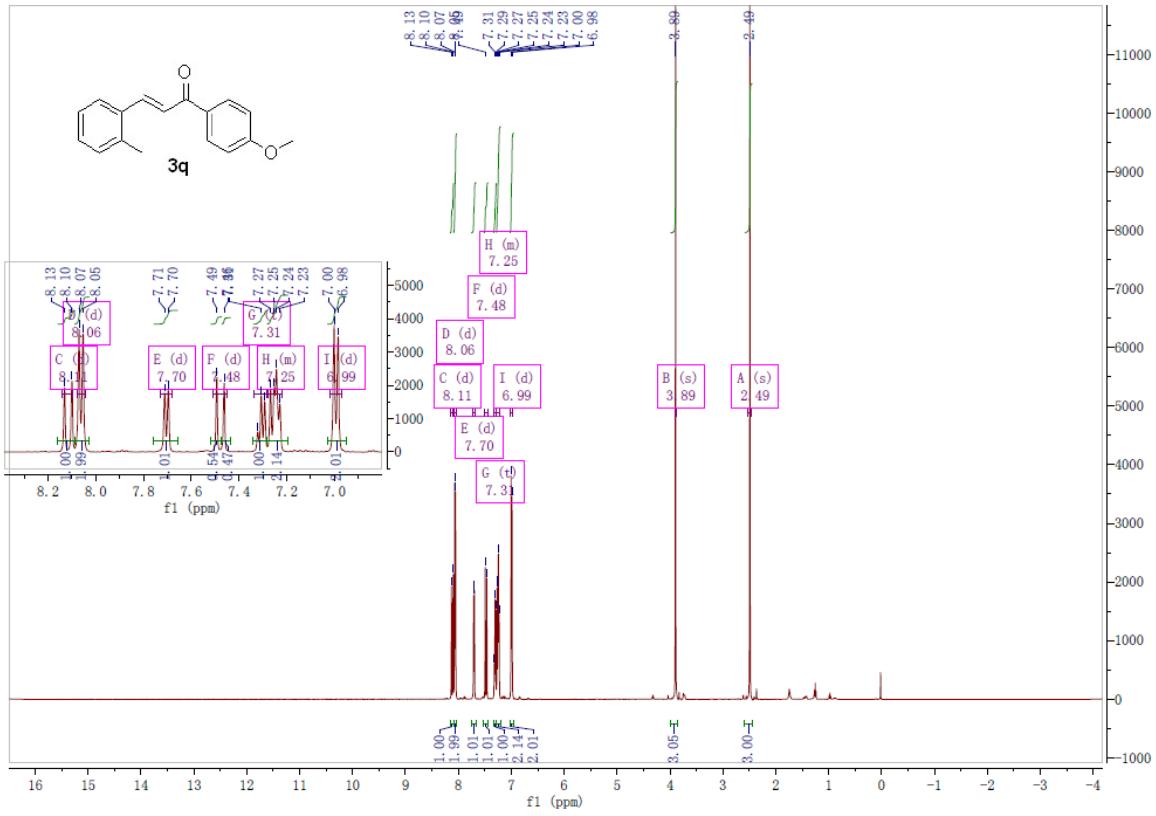

3n
f1 (ppm)

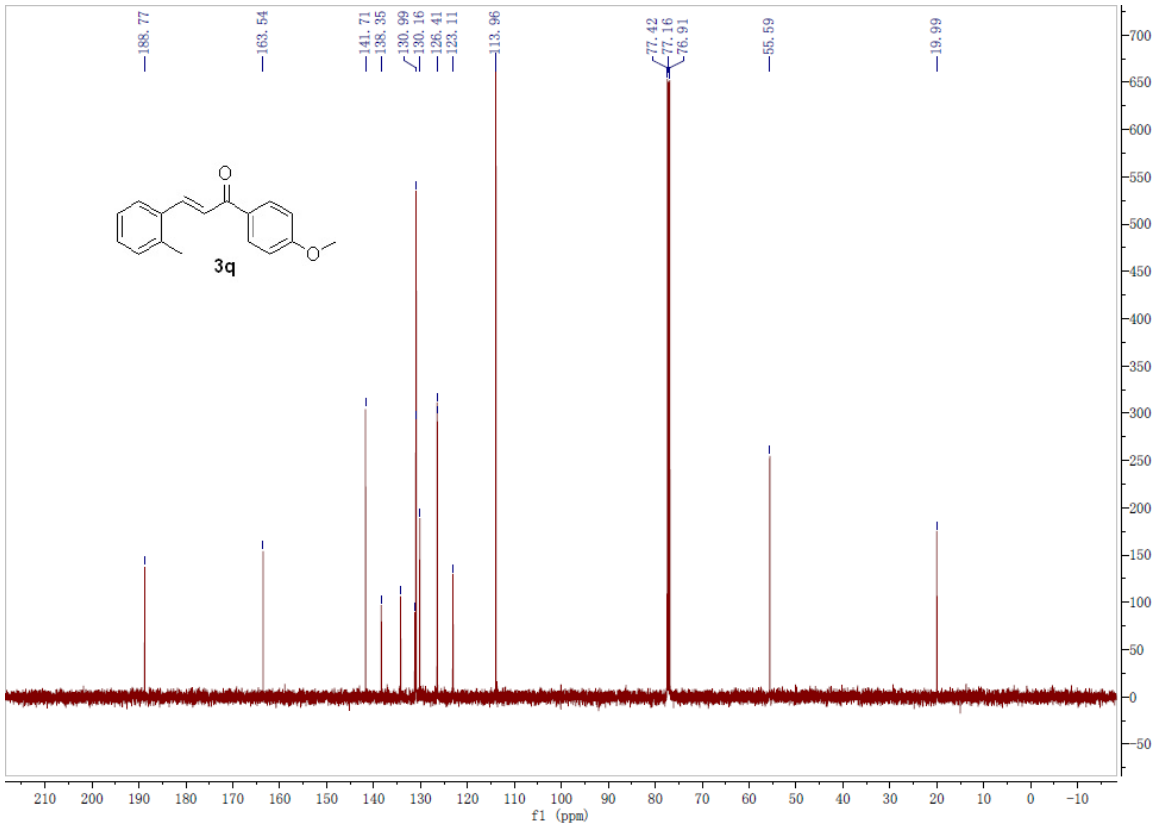

3o
f1 (ppm)

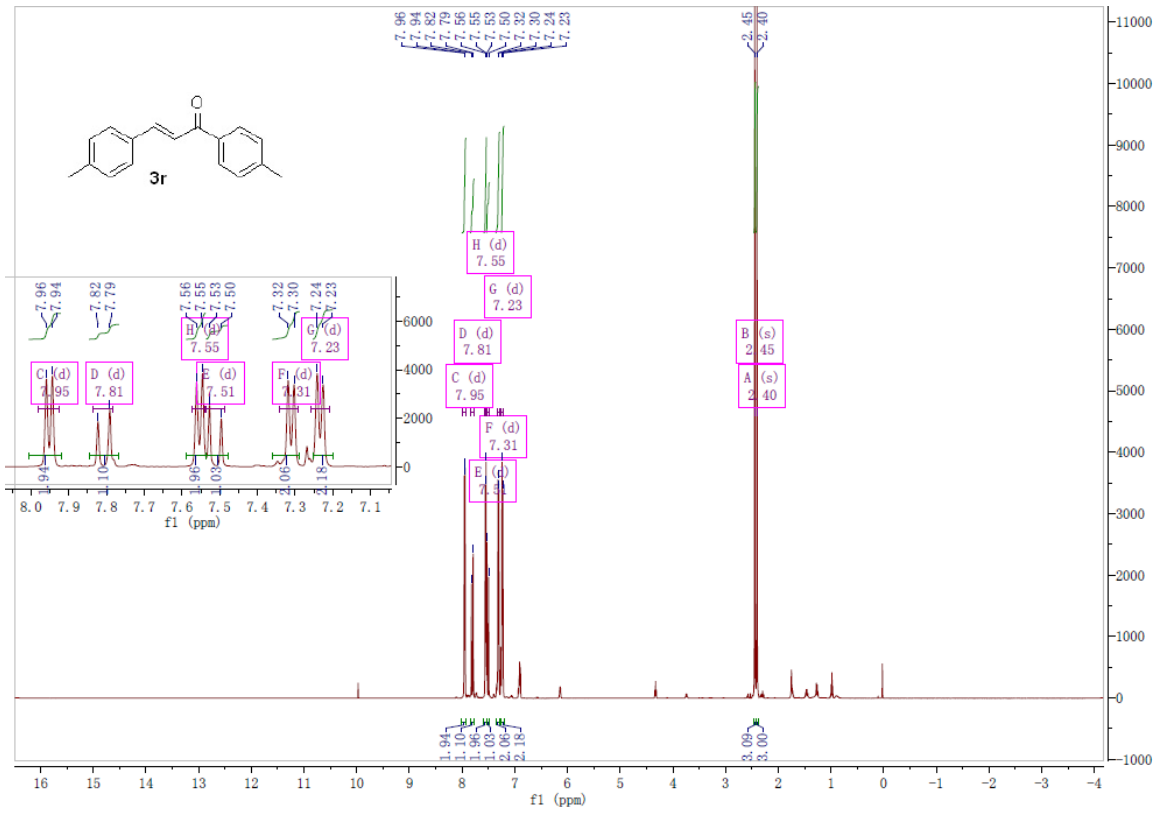

3o
f1 (ppm)

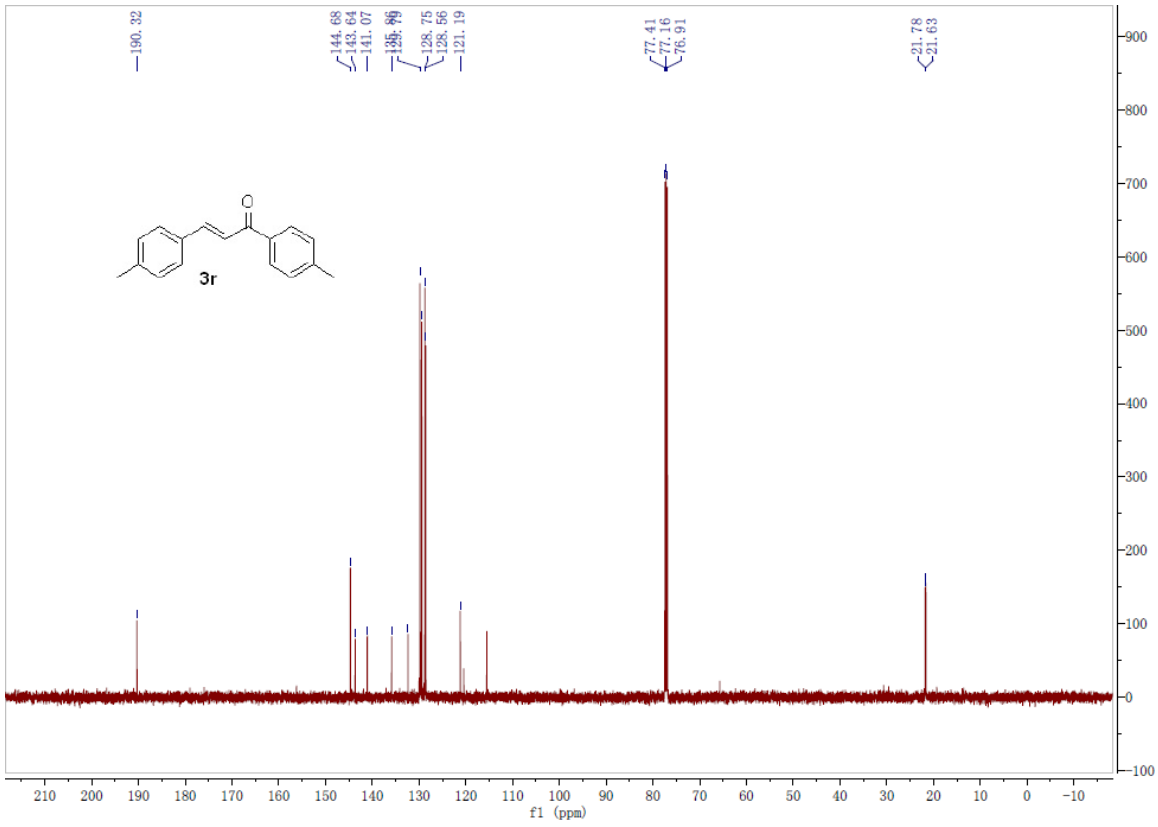

3p
8.06
8.04
7.81
7.78
7.56
7.54
7.53
7.50
7.23
7.22
6.99
6.98
3.89
2.40
F (d) 8.05
E (d) 7.80
H (d) 7.52
D (d) 7.23
C (d) 6.99
G (d) 7.55
A (s) 3.89
B (s) 2.40
f1 (ppm)

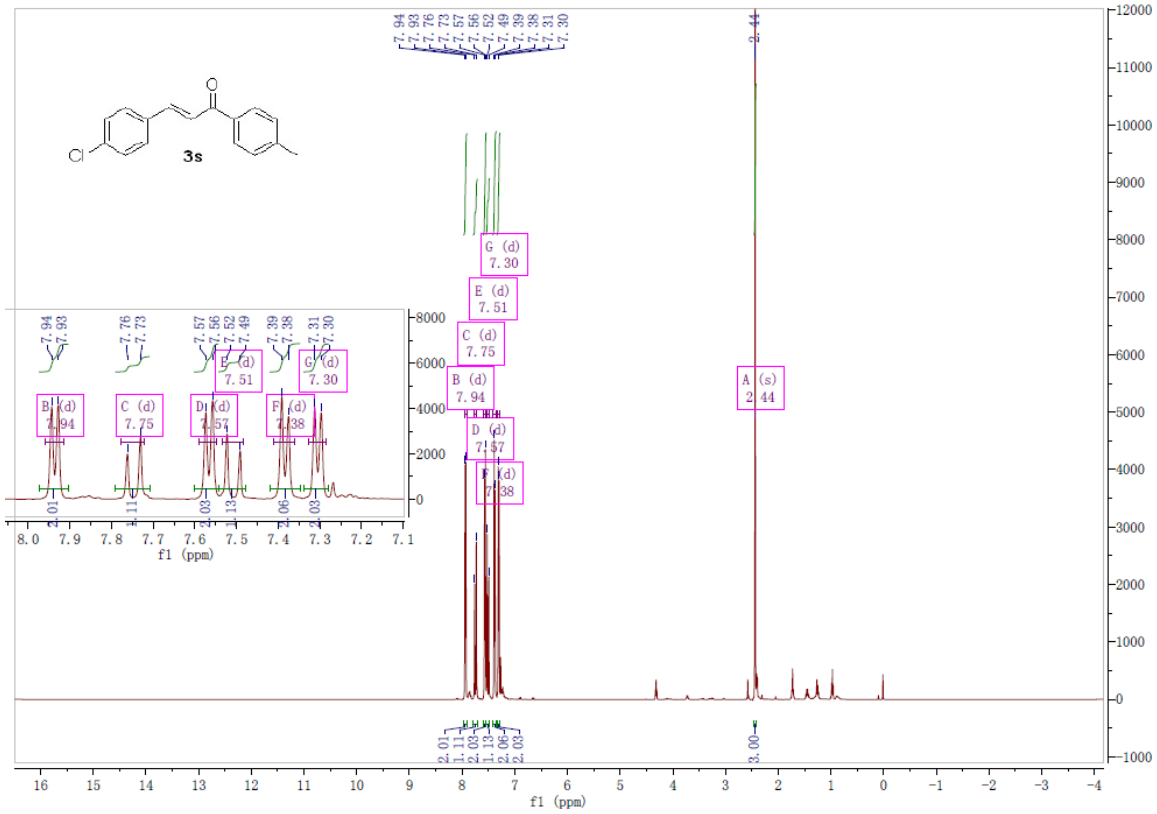

188.90
163.45
144.14
140.92
132.45
130.87
129.77
128.49
120.97
113.91
77.41
77.16
76.91
55.58
21.62
3p
f1 (ppm)

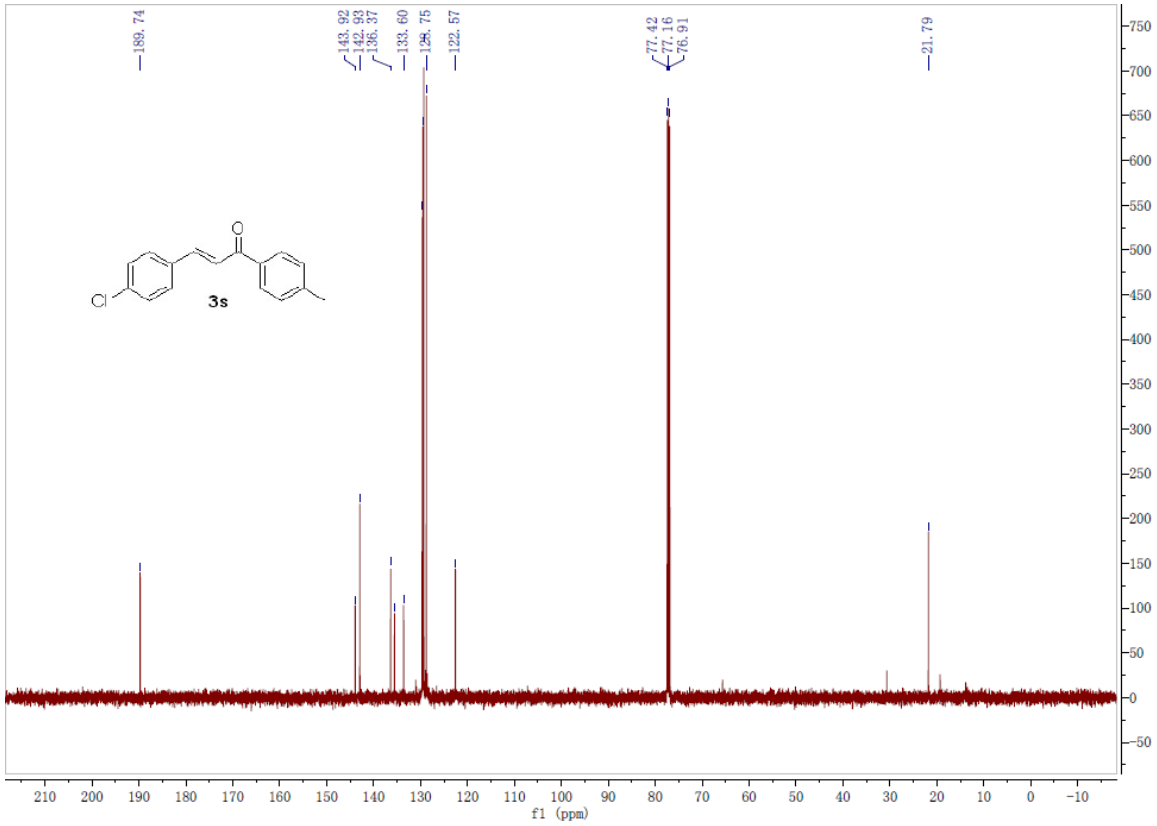

3q
H (m) 7.25
F (d) 7.48
D (d) 8.06
C (d) 8.11
I (d) 6.99
E (d) 7.70
G (t) 7.31
B (s) 3.89
A (s) 2.49
f1 (ppm)

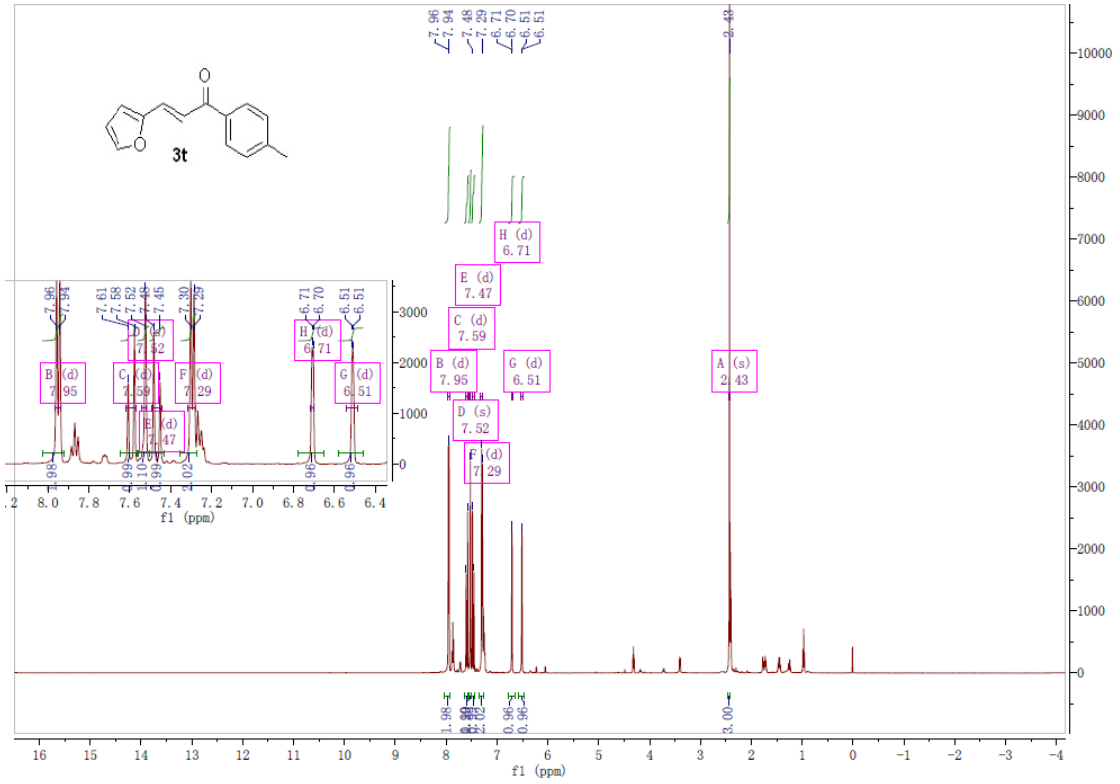

188.77
163.54
141.71
138.35
130.99
130.16
126.41
123.11
113.96
77.42
77.16
76.91
55.59
19.99
3q
f1 (ppm)

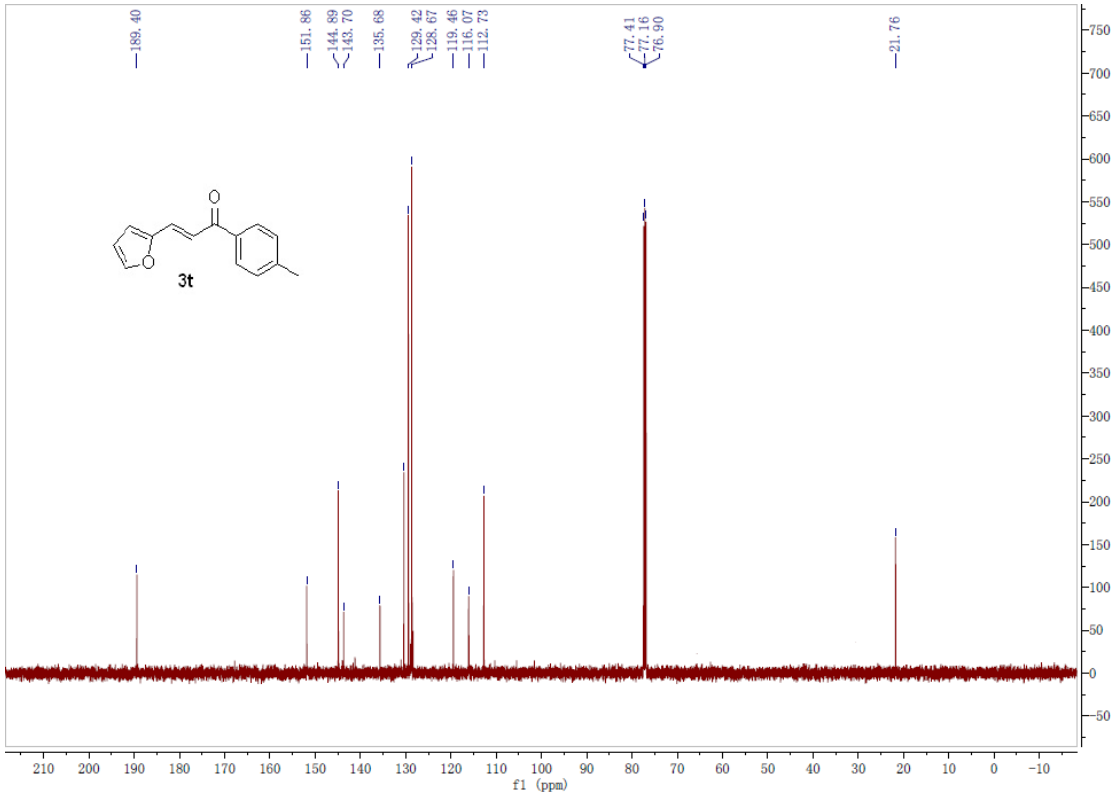

3r
H (d) 7.55
G (d) 7.23
D (d) 7.81
C (d) 7.95
F (d) 7.31
E (d) 7.32
B (s) 2.45
A (s) 2.40
f1 (ppm)

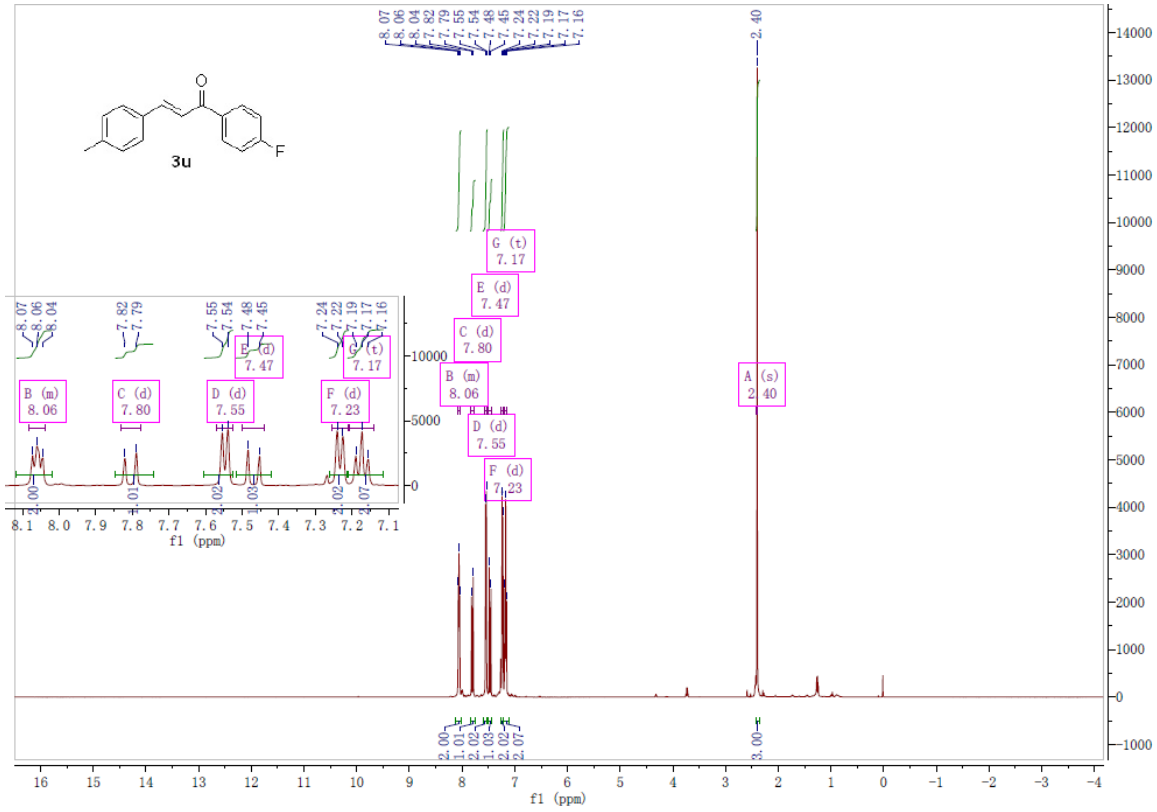

190.32
144.68
143.64
141.07
135.86
135.79
128.75
128.56
121.19
77.41
77.16
76.91
21.78
21.63
3r
f1 (ppm)

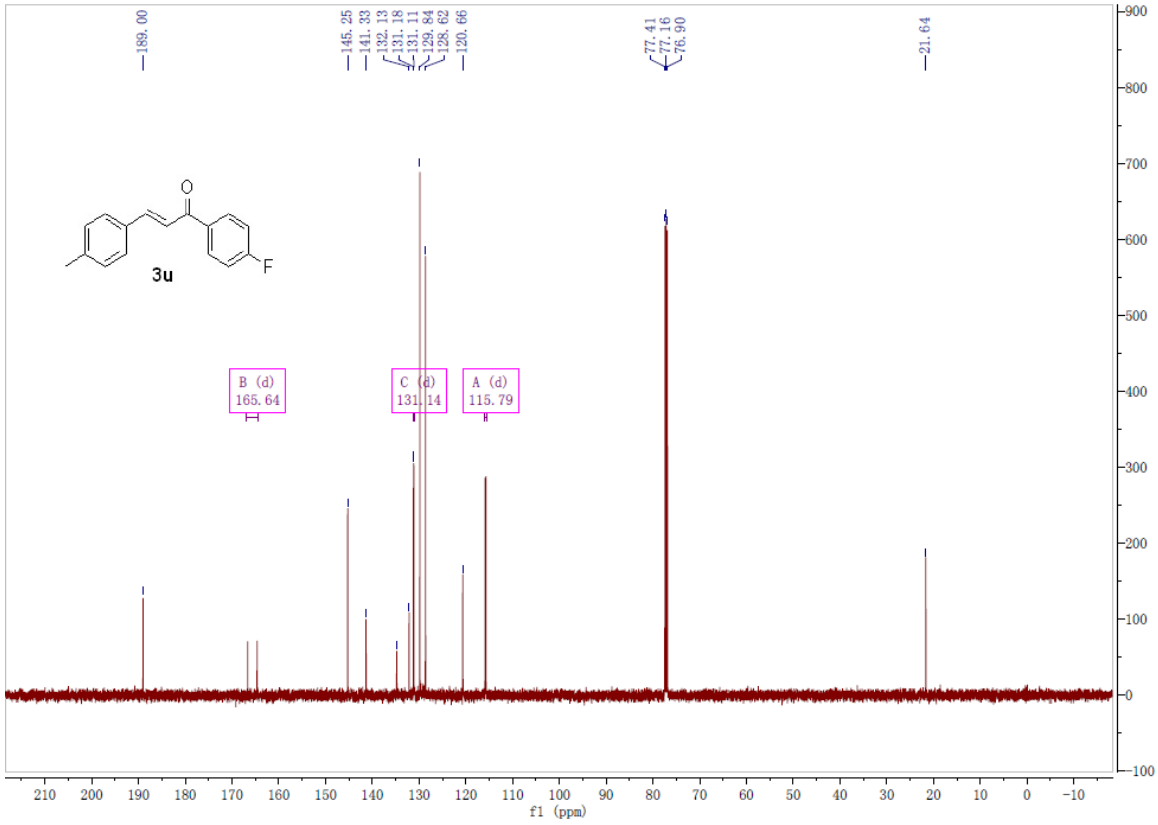

3s
A (s) 2.44
B (d) 7.94
C (d) 7.75
D (d) 7.57
E (d) 7.51
F (d) 7.38
G (d) 7.30
f1 (ppm)

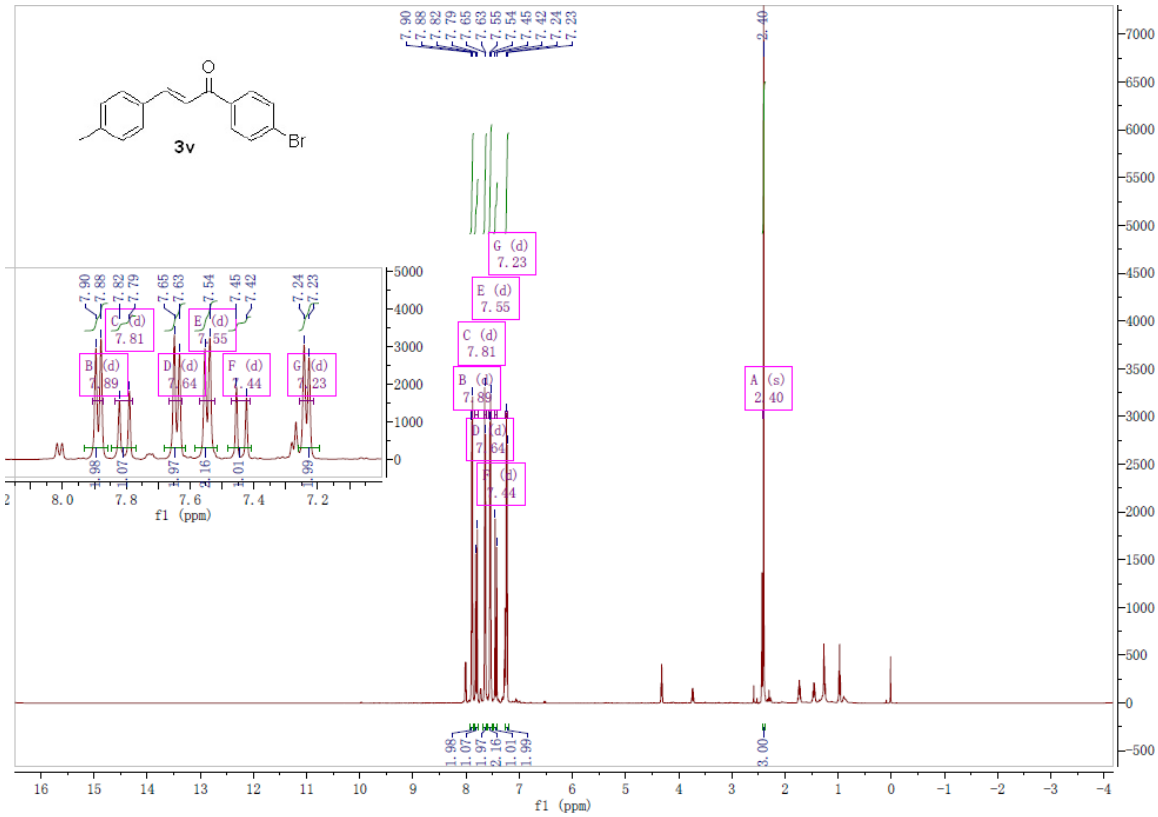

3s
189.74
143.92
142.93
136.37
133.60
129.75
122.57
77.42
77.16
76.91
21.79
f1 (ppm)

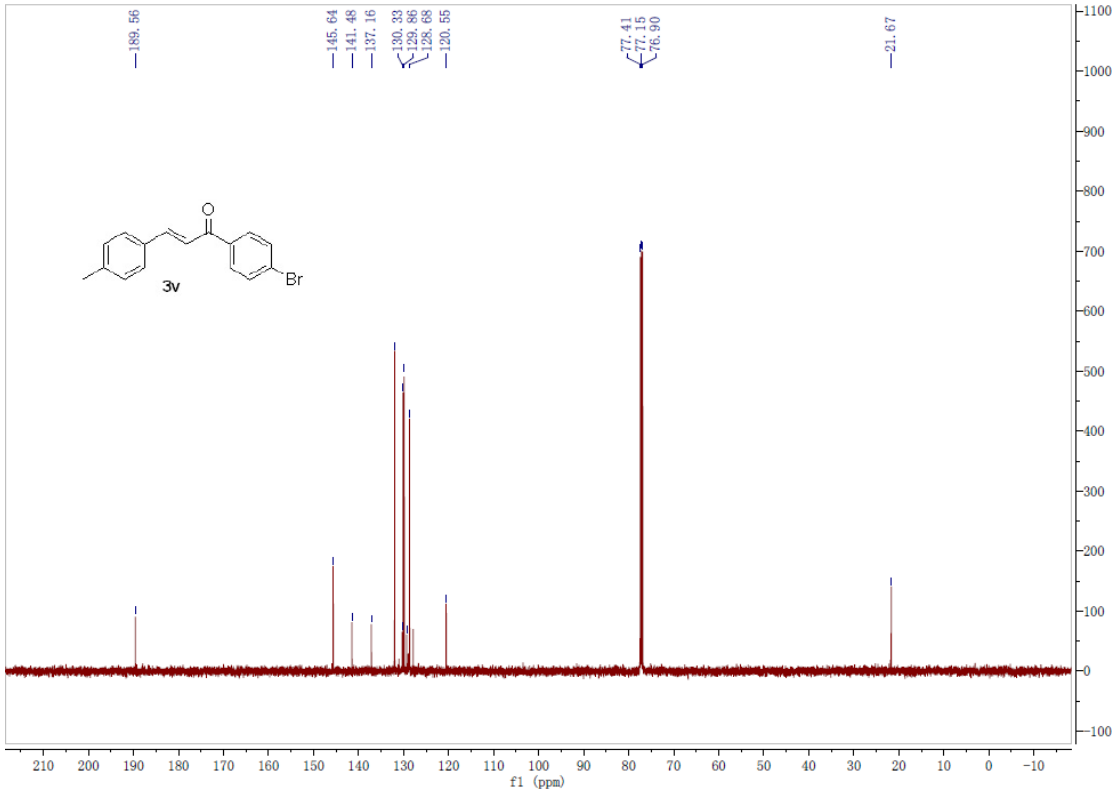

3t
A (s) 2.43
B (d) 7.95
C (d) 7.59
D (s) 7.52
E (d) 7.47
F (d) 7.29
G (d) 6.51
H (d) 6.71
f1 (ppm)

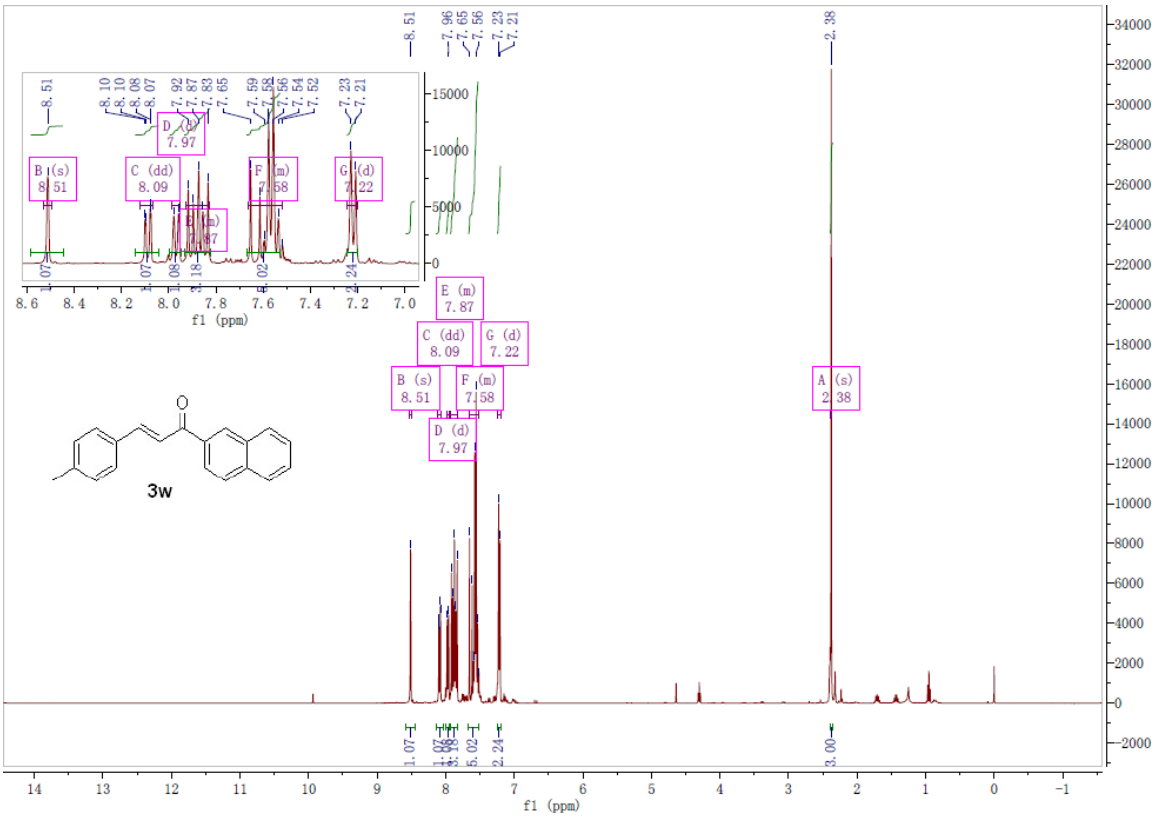

189.40
151.86
144.89
143.70
135.68
129.42
128.67
119.46
116.07
112.73
77.41
77.16
76.90
21.76
3t
f1 (ppm)

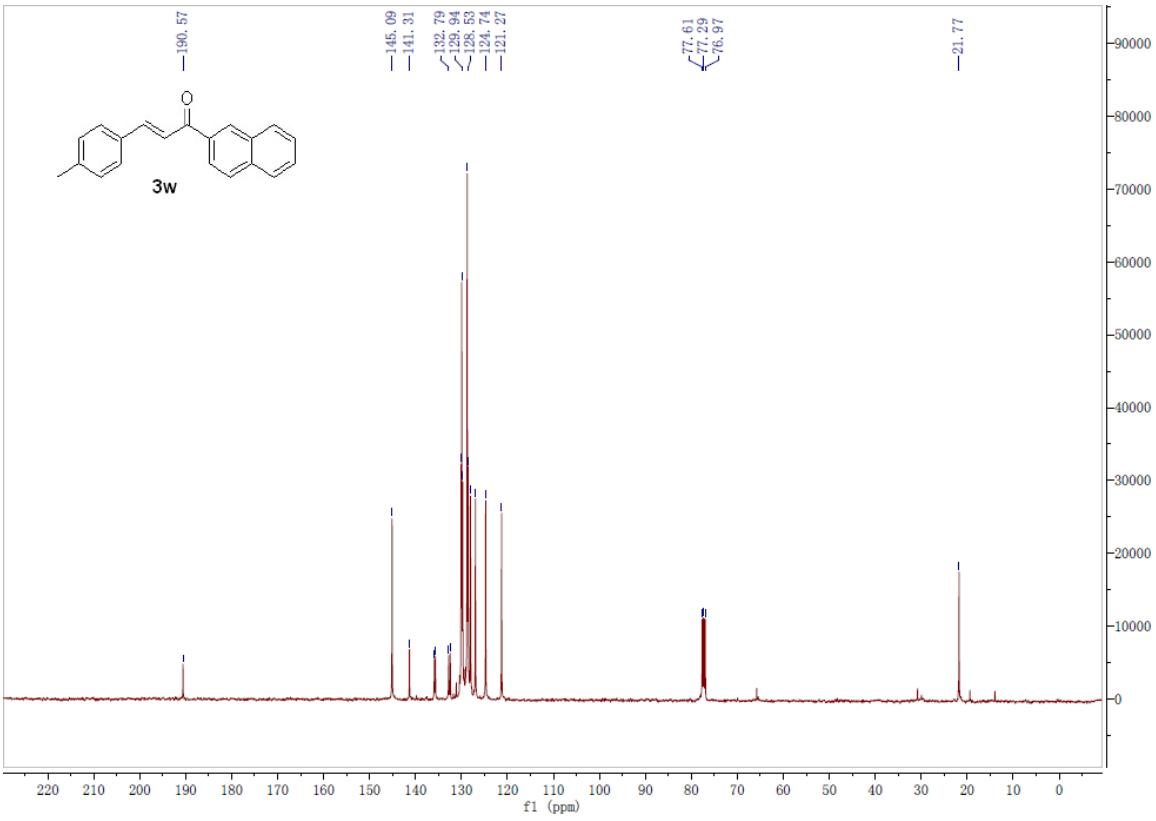

3u
F
8.07
8.06
8.04
7.82
7.79
7.55
7.54
7.48
7.45
7.24
7.22
7.19
7.17
7.16
2.40
G (t)
7.17
E (d)
7.47
C (d)
7.80
B (m)
8.06
D (d)
7.55
F (d)
7.23
A (s)
2.40
f1 (ppm)

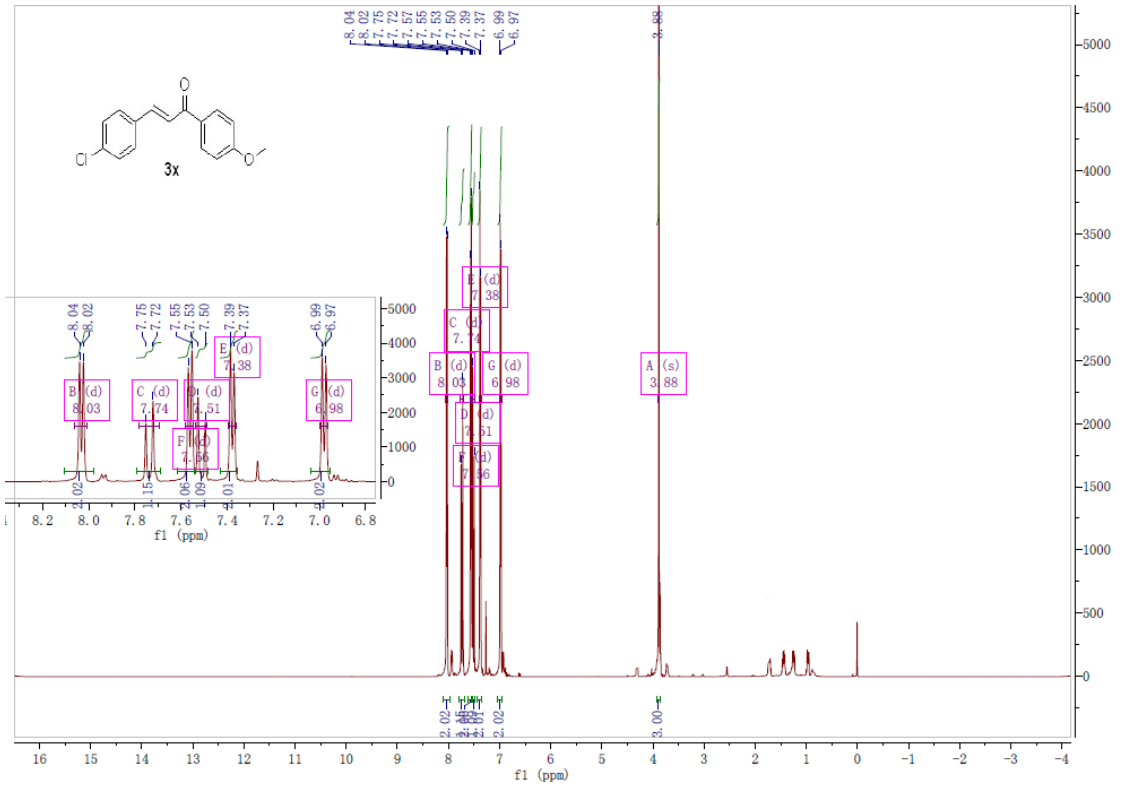

189.00
145.25
141.33
132.13
131.18
131.11
129.84
128.62
120.66
77.41
77.16
76.90
21.64
O
F
3u
B (d)
165.64
C (d)
131.14
A (d)
115.79
f1 (ppm)

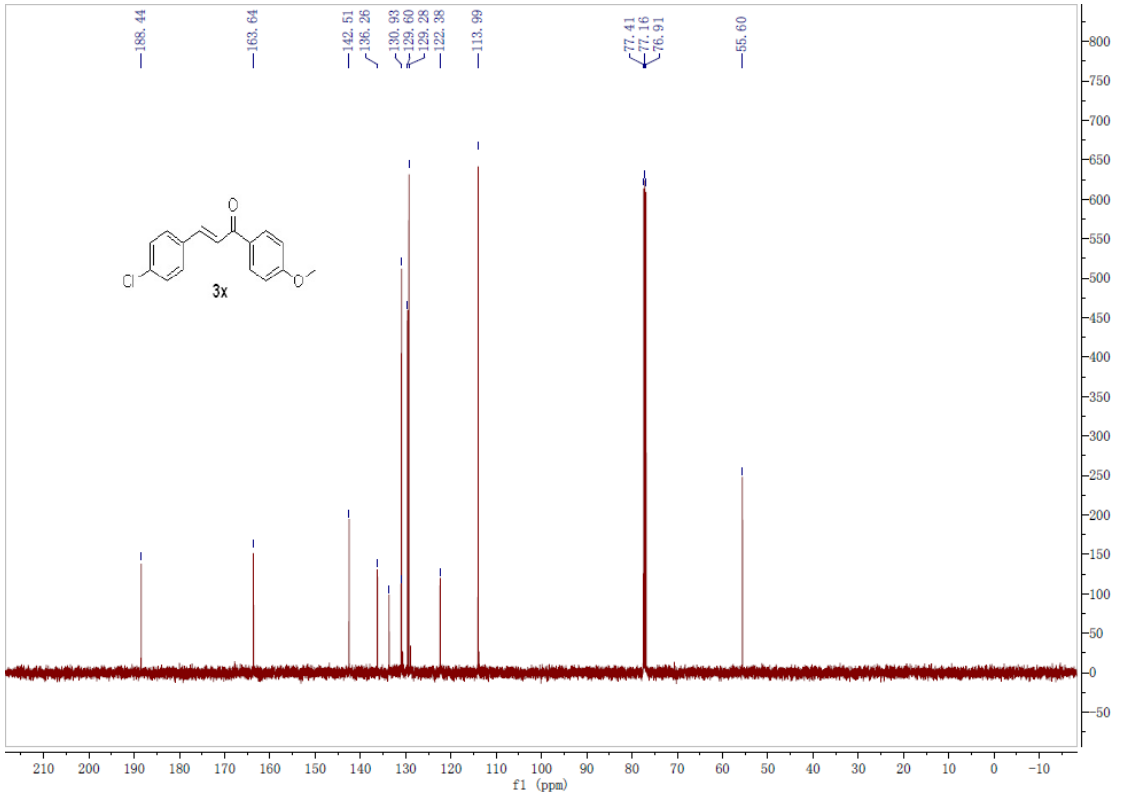

7.90
7.88
7.82
7.79
7.65
7.63
7.55
7.54
7.45
7.42
7.24
7.23
2.40
O
Br
3v
G (d)
7.23
E (d)
7.55
C (d)
7.81
B (d)
7.89
D (d)
7.64
F (d)
7.44
A (s)
2.40
1.98
1.07
1.97
2.16
1.01
1.99
3.00
f1 (ppm)

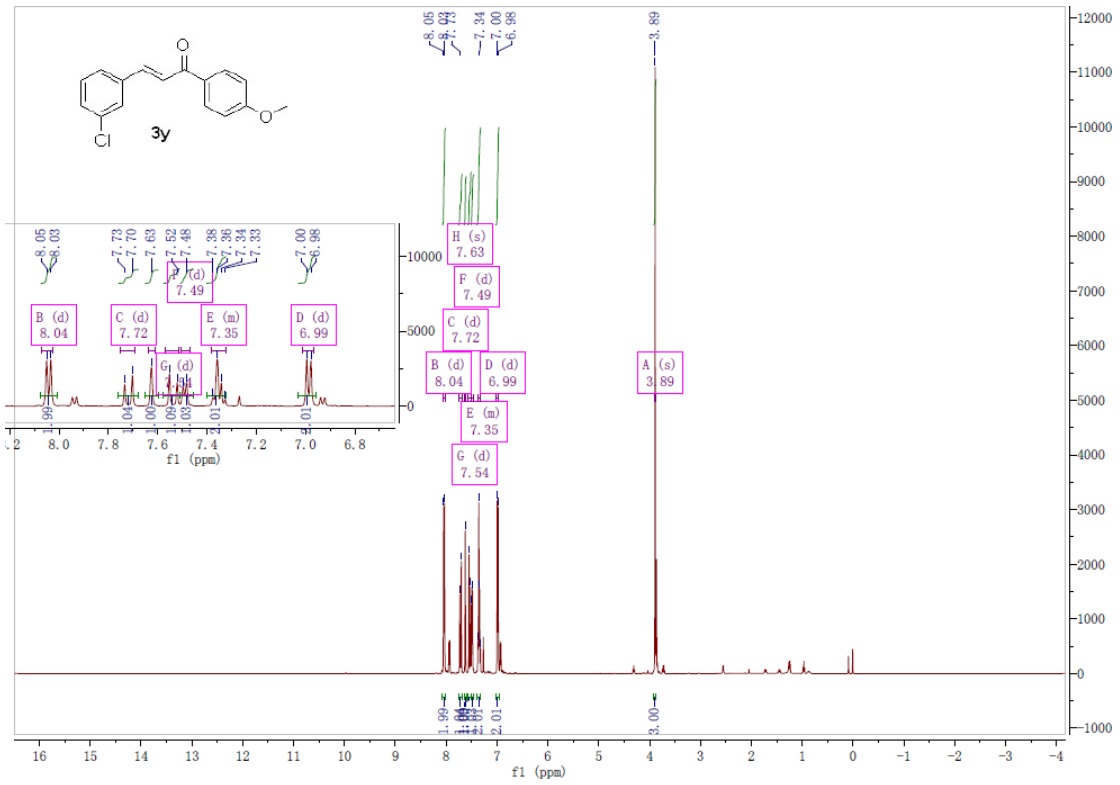

189.56
145.64
141.48
137.16
130.33
129.86
128.68
120.55
77.41
77.15
76.90
21.67
3v
Br
f1 (ppm)

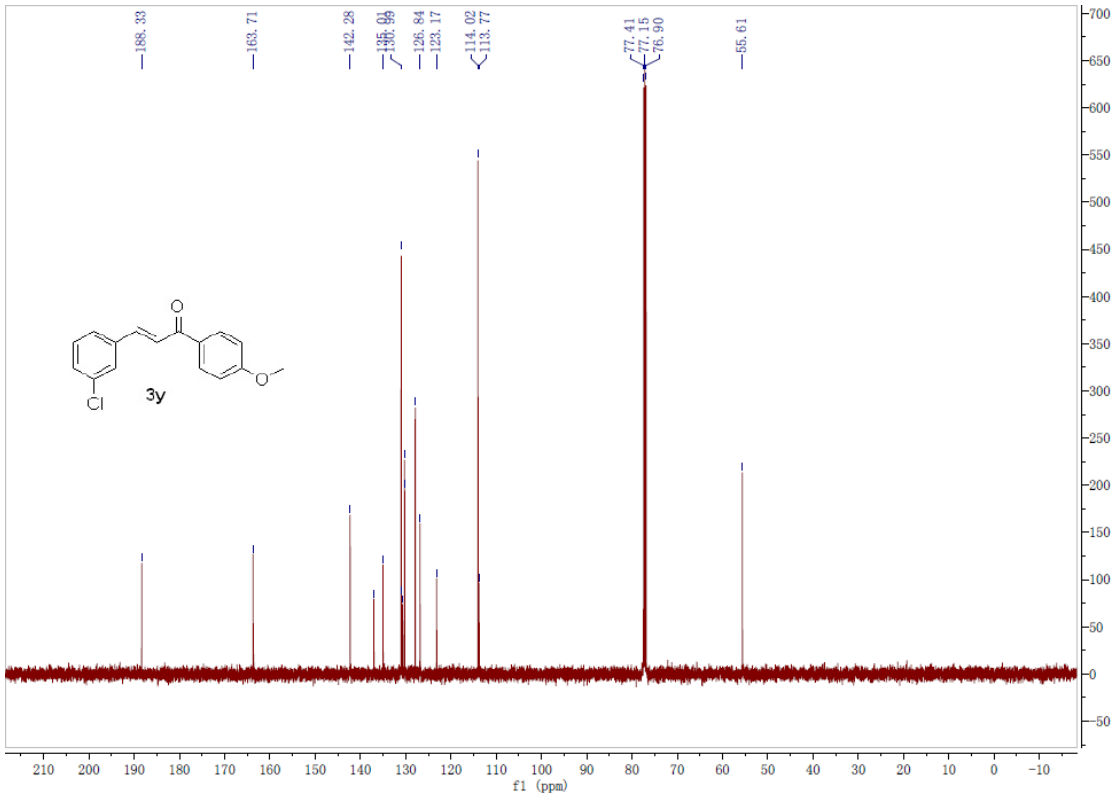

3w
f1 (ppm)

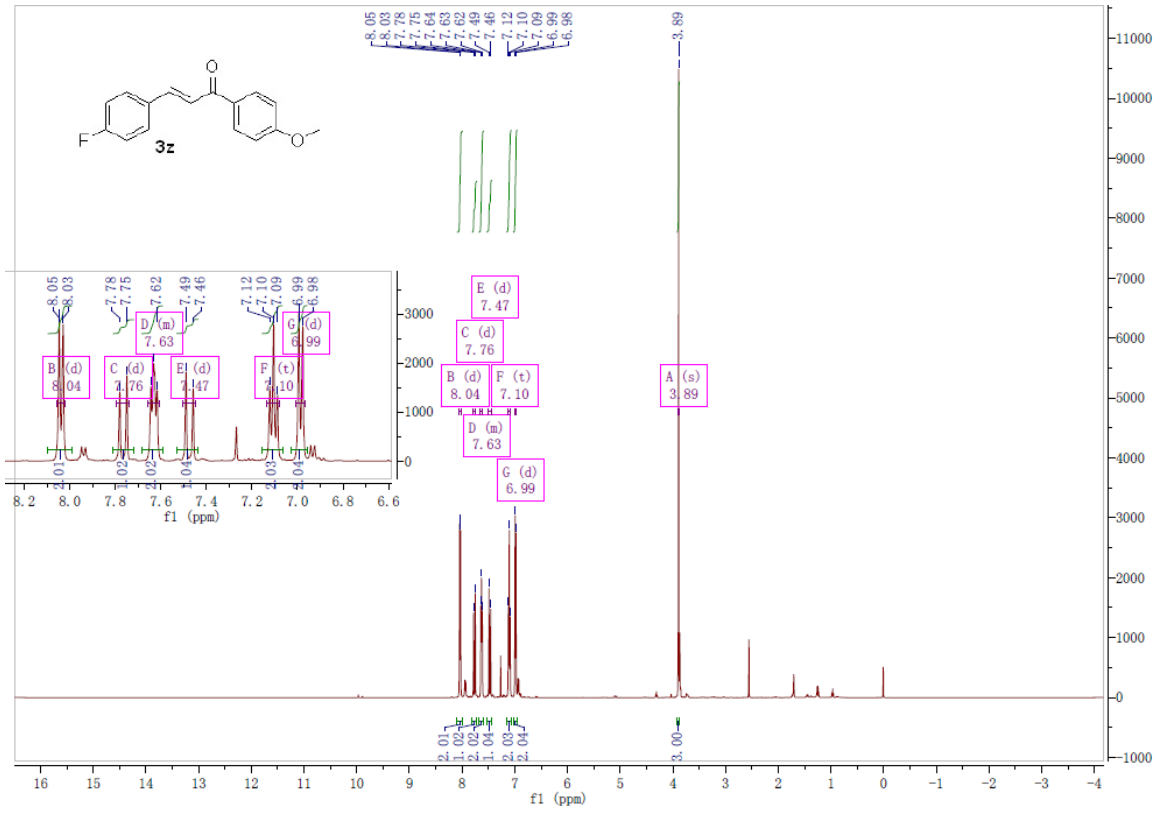

3w
f1 (ppm)

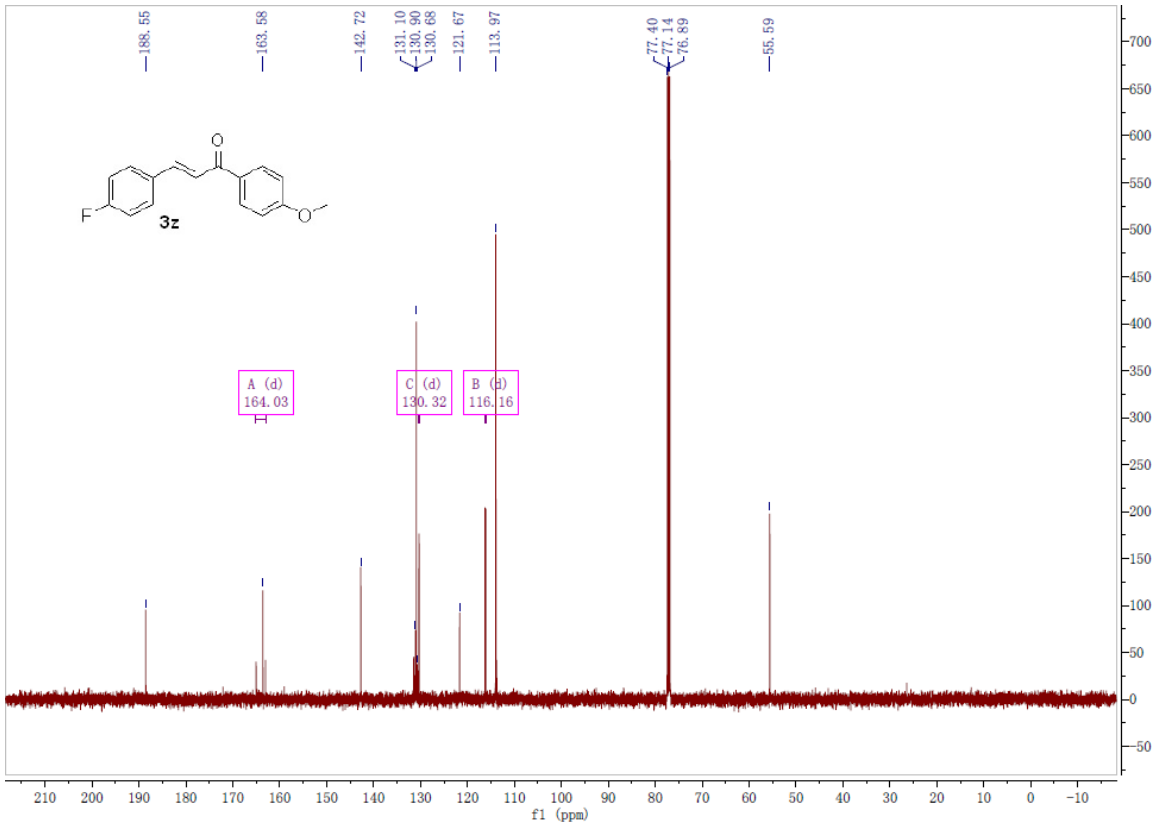

3x
f1 (ppm)


3x
f1 (ppm)


3y
Cl
O
O
8.05
8.03
7.73
7.70
7.63
7.52
7.48
7.38
7.36
7.34
7.33
7.00
6.98
3.89
B (d) 8.04
C (d) 7.72
E (m) 7.35
D (d) 6.99
F (d) 7.49
G (d) 7.54
H (s) 7.63
A (s) 3.89
f1 (ppm)


188. 33
163. 71
142. 28
135. 01
130. 99
126. 84
123. 17
114. 02
113. 77
77. 41
77. 15
76. 90
55. 61
O
O
Cl
3y
f1 (ppm)


3z
F
O
8.05
8.03
7.78
7.75
7.64
7.63
7.62
7.49
7.46
7.12
7.10
7.09
6.99
6.98
3.89
E (d) 7.47
C (d) 7.76
B (d) 8.04
F (t) 7.10
D (m) 7.63
G (d) 6.99
A (s) 3.89
f1 (ppm)


3z
F
O
188.55
163.58
142.72
131.10
130.90
130.68
121.67
113.97
77.40
77.14
76.89
55.59
A (d) 164.03
C (d) 130.32
B (d) 116.16
f1 (ppm)