Supporting information

In-Situ preparation of Graphene Oxide Supported Pd nanoparticles in Ionic Liquid and the Long-term Catalytic Stability for the Heck Reaction

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Fig. S1 shows the FTIR spectra of GO, RGO and Pd/RGO. The FT-IR spectrum of the GO shows a broad absorption band at 3430 cm^{-1}, which is related to O-H group due to the residual moisture in the sample, and absorption bands at 1630 cm^{-1} and 1730 cm^{-1} are related to C=C and C=O groups. The absorption bands at 1050 cm^{-1} and 1390 cm^{-1} can be attributed to the alkoxy C–O and O–H groups. In the FT-IR spectrum of RGO and Pd/RGO, the relative intensity of the C=O stretching at 1730 cm^{-1} significantly decreases, indicating that most carboxyl functionalities have been reduced. These results clearly demonstrate that the GO was reduced after chemical reduction.

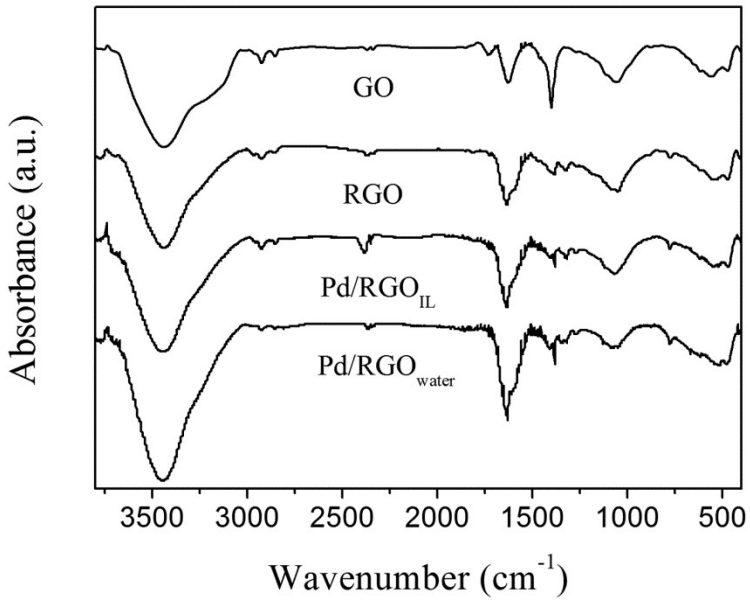


Fig. S1 FT-IR transmittance spectra of GO, RGO and Pd/RGO

Fig. S2 displays the TGA curve of GO, RGO and Pd/RGO. The TGA curve of GO shows a significant weight loss (50%) before 300 °C, presumably due to the removal of adsorbed water and decomposition of the labile oxygen-containing functional groups. For RGO and Pd/RGO, there is only a light weight loss about 19 and 20% from 100 to 800 °C, which indicates that the oxygen-containing groups have been almost reduced by NaBH4 solution. The above results show that Pd/RGO has good thermal stability.

The catalytic activities of Pd/RGO-IL with various Pd loading were evaluated at 130 °C. As shown in Table S1, the product conversion firstly increases, reach a peak value, and then deceases when increasing Pd loading. The highest product conversion of 95% is acquired at the Pd loading of 0.15 mg mL^{-1}. When the Pd mass loading exceeded 0.15 mg mL^{-1}, the product conversion decreases, which may be ascribed to the agglomeration of Pd nanoparticles on the RGO surface resulting in smaller specific surface area.

Fig. S3 shows the stability of Pd/RGO catalyst in IL after the third, sixth and tenth run. It can be clearly seen that there is no precipitation occurring in all cyclic reactions. Our further results show that the Pd/RGO catalyst can be stably suspended in IL for over two months. The Pd/RGO-IL system exhibits good stability.

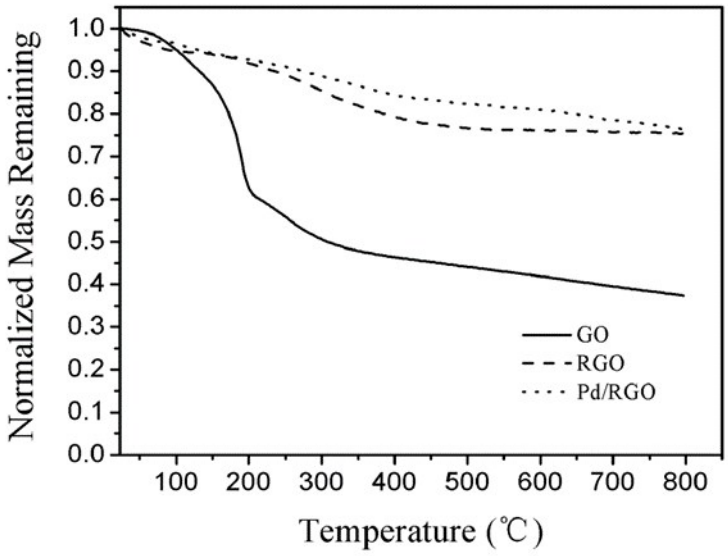


Fig. S2 TGA curves of GO, RGO and Pd/RGO

Table S1. Product conversion for coupling of iodobenzene with butyl acrylate with different Pd loadings

Entry	Pd loading (mg mL^{-1})	conversion(%)
1	0.04	52
2	0.08	69
3	0.15	95
4	0.3	87
5	0.6	71

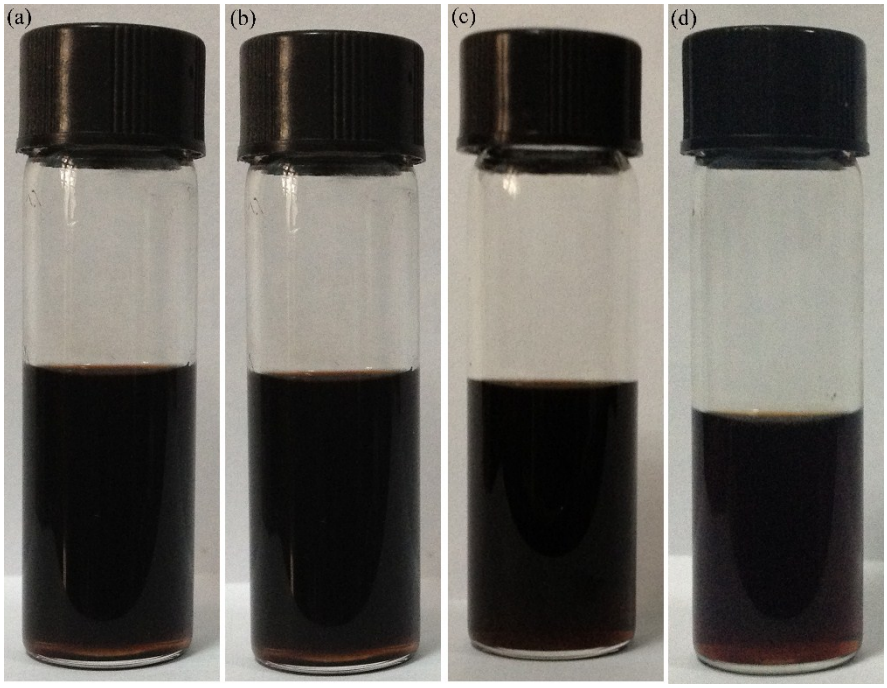


Fig. S3 Photographs (a), (b) and (c) correspond to the stability of Pd/RGO catalyst in IL after the third, sixth and tenth run, respectively.

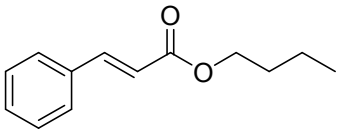
After the reaction completed, the products and Pd/RGO-IL system were extracted with 5% ethyl acetate in petroleum ether (5 mL × 3). Products in the resulting suspension were analyzed by a Gas Chromatograph (GC, Shimadzu GC-2014). The conversion was measured by the normalization method. The formulas are listed below:

$$w_i = \frac{m_i}{m_1 + m_2 + \cdots + m_n} \times 100\% = \frac{f_i A_i}{\sum_{i=1}^{n} (f_i A_i)} \times 100\%$$

m_i, A_i and w_i are respectively the quality, peak area and the quality score of products.

$$f_i = \frac{f_i^{'}}{f_s^{'}} = \frac{m_i / A_i}{m_s / A_s} = \frac{m_i}{m_s} \times \frac{A_s}{A_i}$$

f_i is the relative quantitative calibration factor, subscript i and s are represented product and reference material. N-heptane is chosen for reference material.

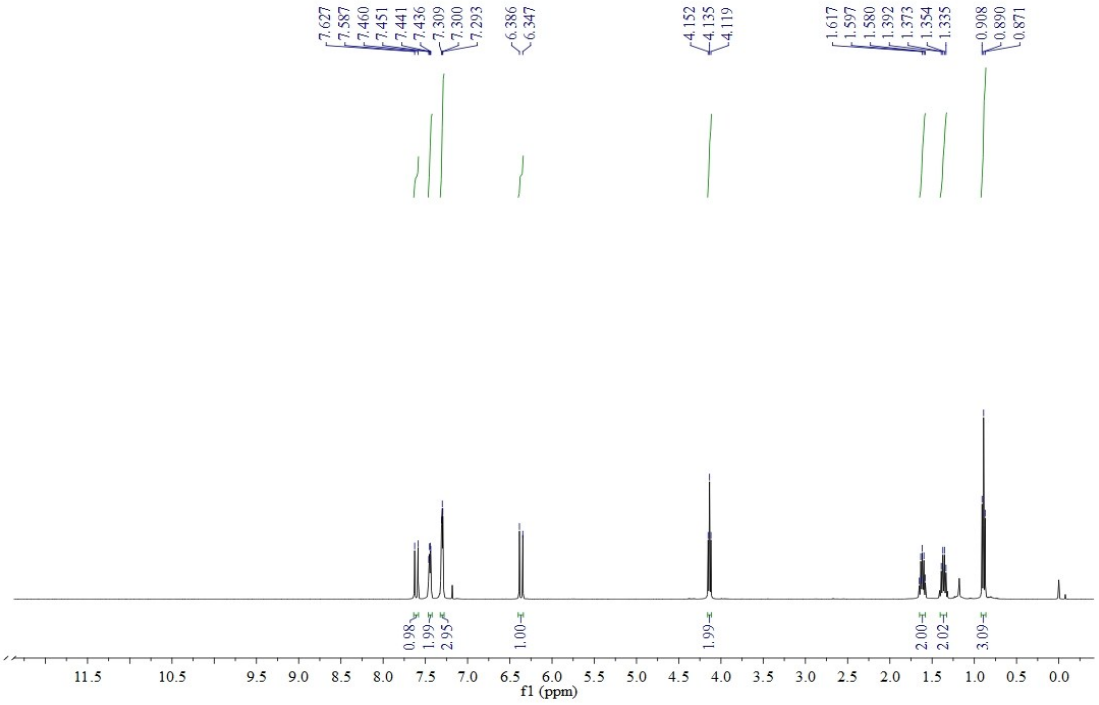


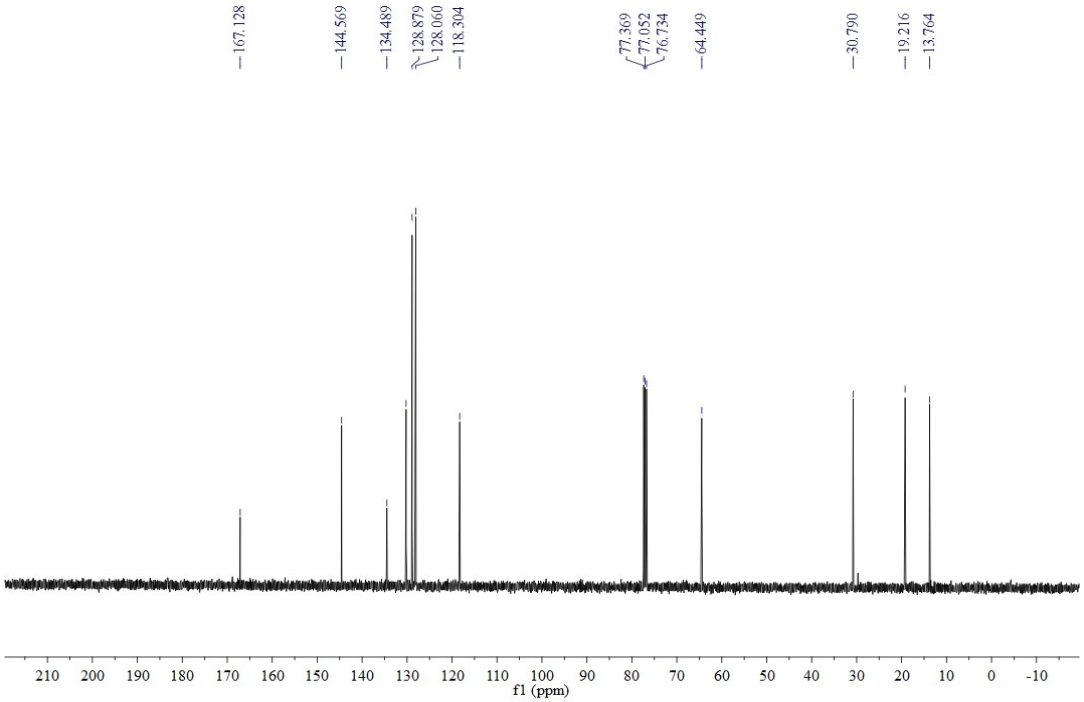
Butyl cinnamate(3a)

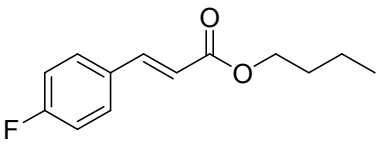
Purified by flush column chromatography (silica gel, Hexane/EtoAc=30/1);

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ 0.90 (t, J=7.2 Hz, 3H), 1.33-1.37 (m, 2H),1.58-1.61 (m, 2H), 4.14 (t, J= 6.8 Hz, 2H), 6.36 (d, J=16.0 Hz, 1H), 7.29-7.30 (m, 3H), 7.43-7.46 (m, 2H) ,7.60 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 13.7, 19.1, 30.7, 64.4, 111.2, 128.0, 128.8, 130.2, 134.4, 144.5, 144.5.





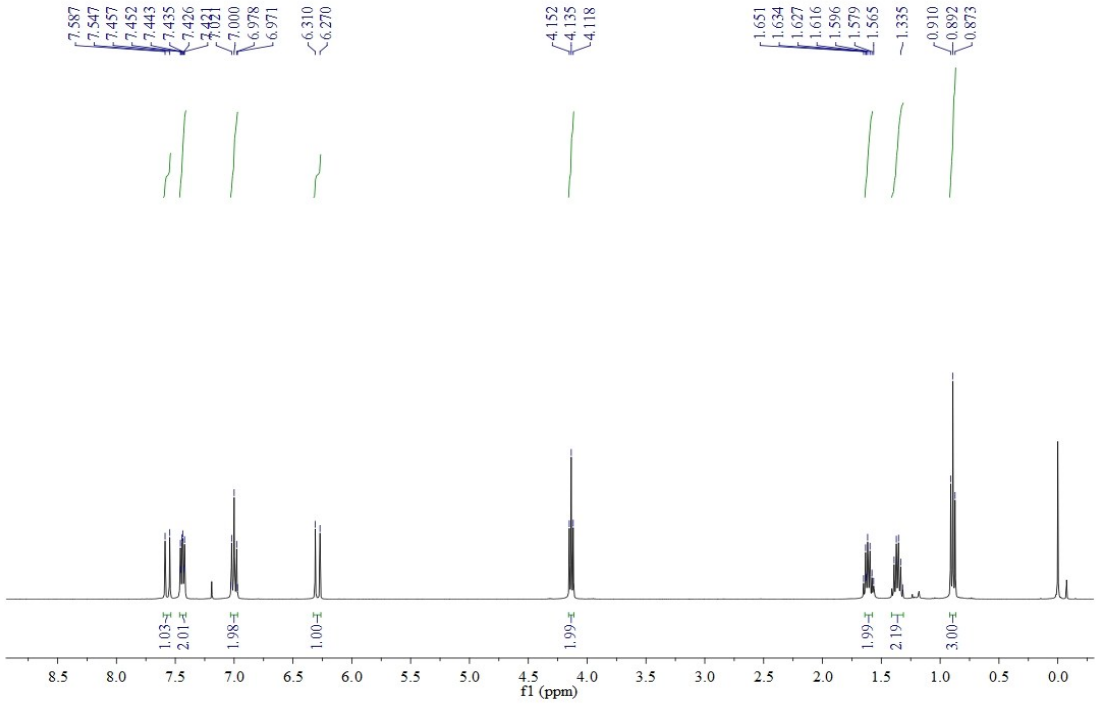


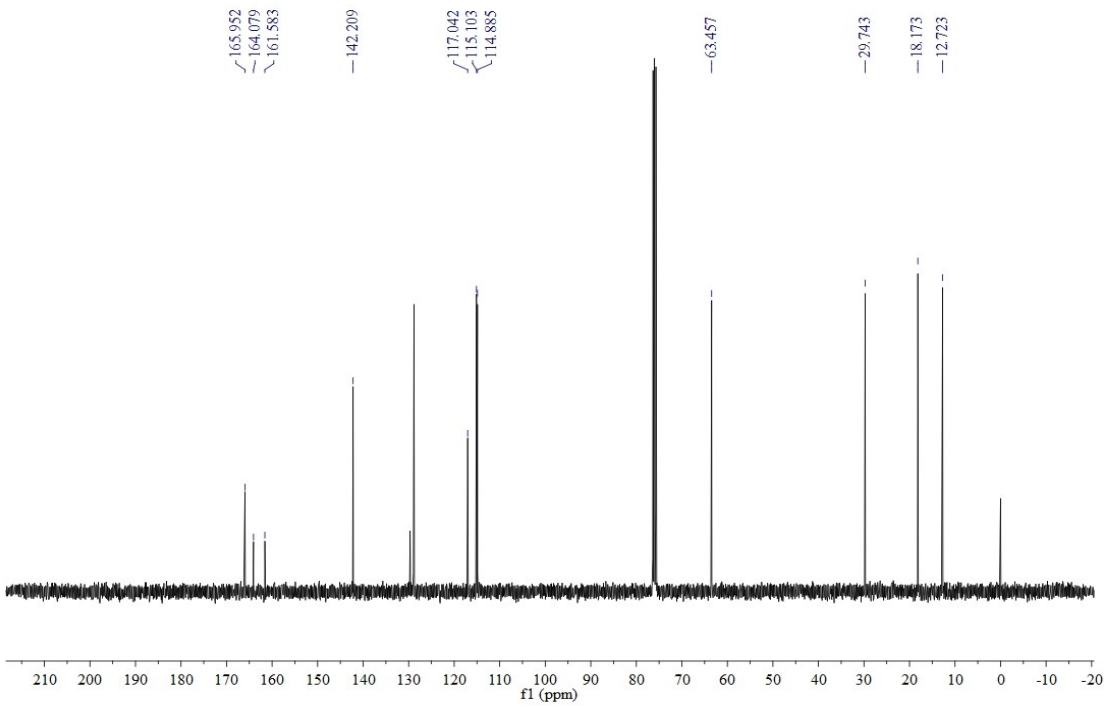
Butyl 3-(4-fluorophenyl)acrylate (3f)

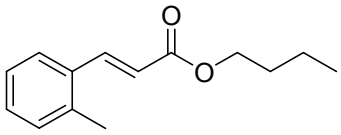
Purified by flush column chromatography (silica gel,Hexane/EtoAc=15/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.89 (t, J=7.2 Hz,3H), 1.35-1.37 (m, 2H), 1.60-1.61 (m, 2H), 4.14 (t, J= 6.8 Hz, 2H), 6.29 (d, J=16.0 Hz, 1H), 6.97-7.02 (m, 2H), 7.42-7.43 (m, 1H), 7.57 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 12.7, 18.1, 29.7, 63.4, 114.8, 115.1, 117.0, 128.8, 128.9, 142.3, 161.5, 164.0, 165.9.





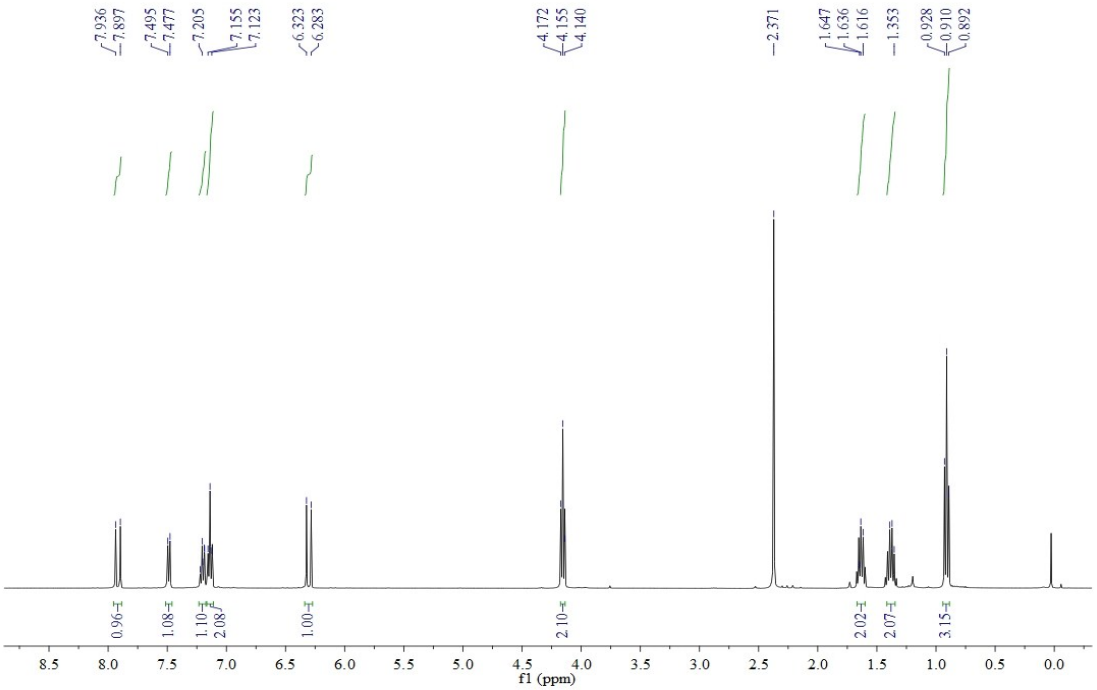


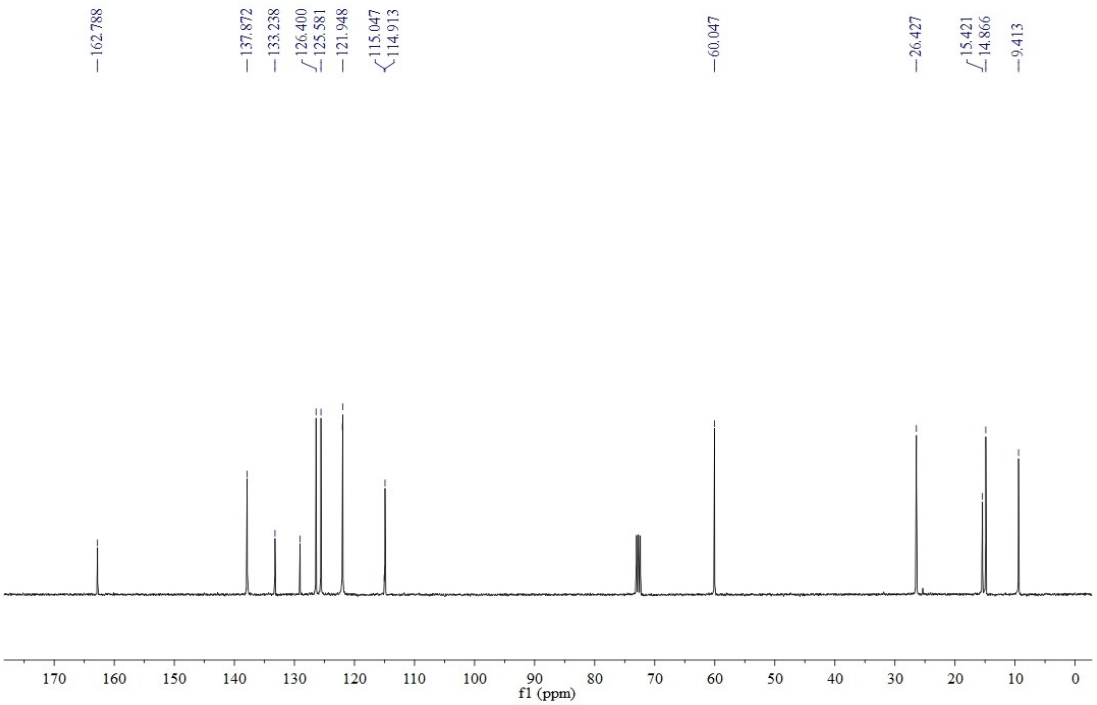
Butyl 3-o-tolylacrylate (3d)

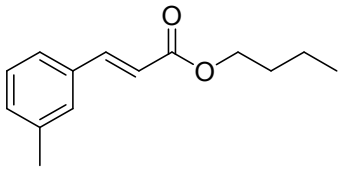
Purified by flush column chromatography (silica gel,Hexane/EtoAc=40/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.91 (t, J=7.2 Hz, 3H), 1.35-1.37 (m, 2H), 1.62-1.63 (m, 2H), 2.37 (s, 3H), 4.16 (t, J= 6.8 Hz, 2H), 6.30 (d, J=16.0 Hz, 1H), 7.12-7.15 (m, 2H), 7.20-7.22 (m, 1H), 7.47-7.49 (m, 1H), 7.80 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 9.4, 14.8, 15.4, 26.4, 60.0, 114.9, 115.0, 121.9, 125.6, 126.0, 133.2, 137.8, 162.7 .





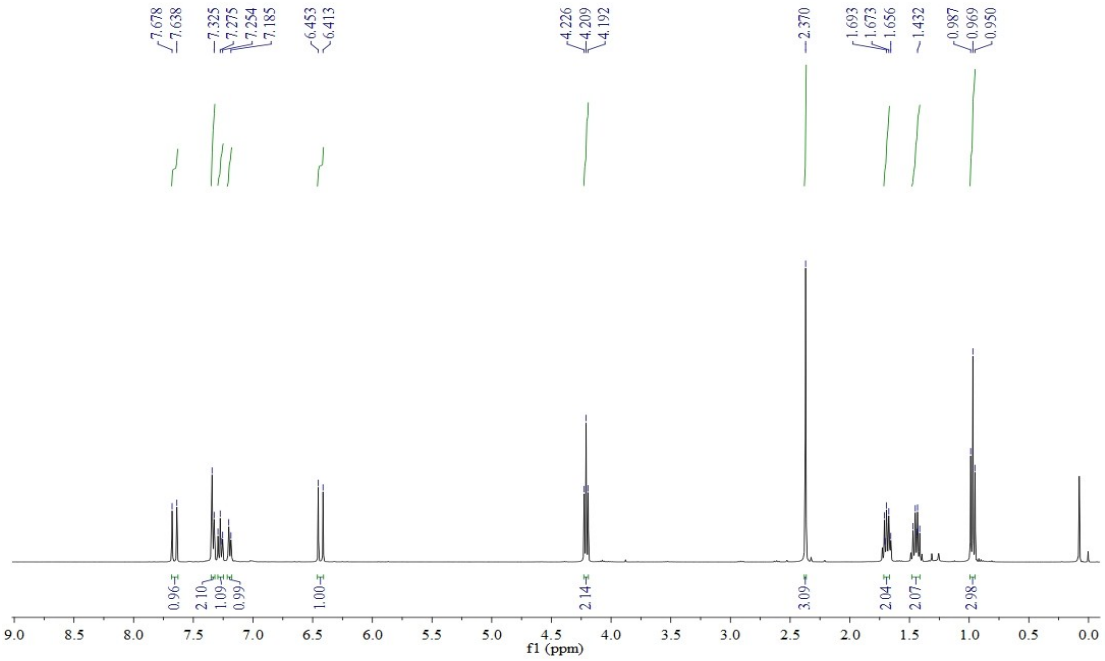


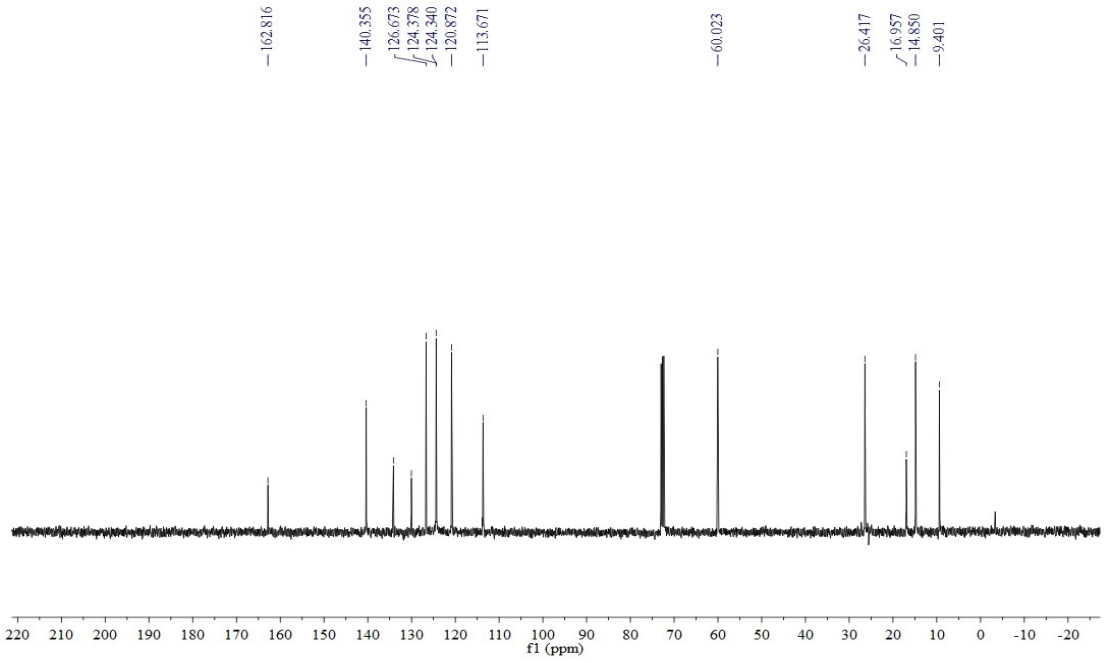
Butyl 3-m-tolylacrylate (3h)

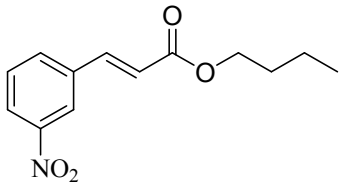
Purified by flush column chromatography(silica gel,Hexane/EtoAc=40/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.97 (t, J=7.2 Hz, 3H), 1.41-1.43 (m, 2H), 1.67-1.69 (m,2H), 2.37 (s, 3H), 4.21 (t, J= 6.8 Hz, 2H), 6.43 (d, J=16.0 Hz, 1H), 7.18-7.20 (m, 1H), 7.25-7.29 (m, 1H), 7.32-7.34 (m, 1H), 7.66 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 9.4, 14.8, 26.5, 51.1, 60.0, 106.7, 114.4, 116.3, 119.1, 124.5, 127.0, 135.6, 153.9, 163.2 .





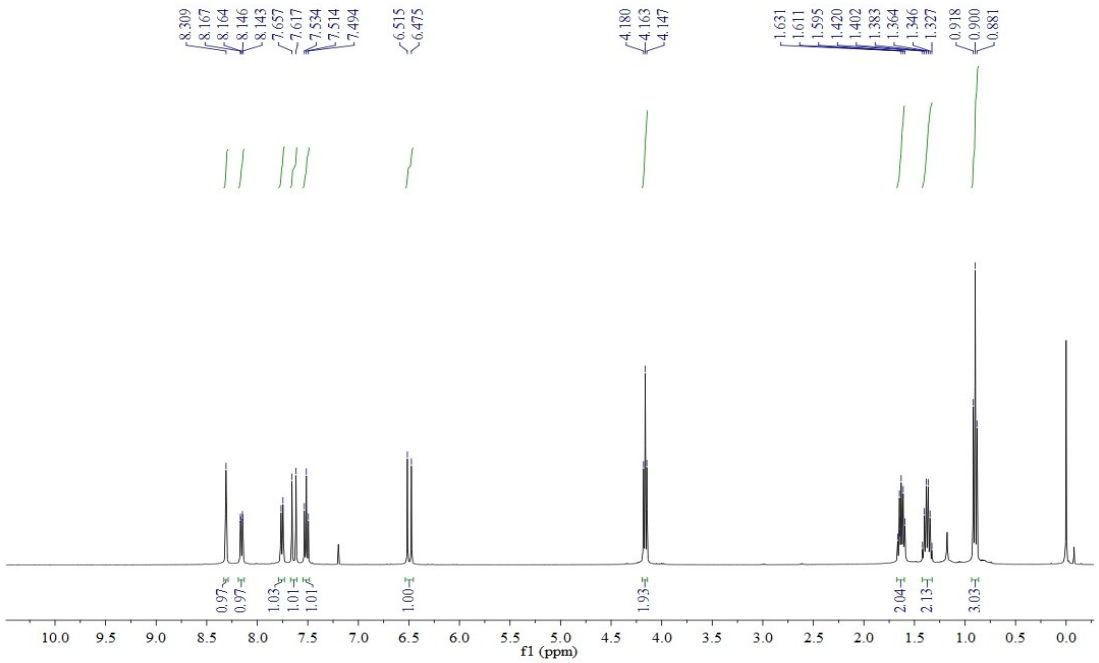


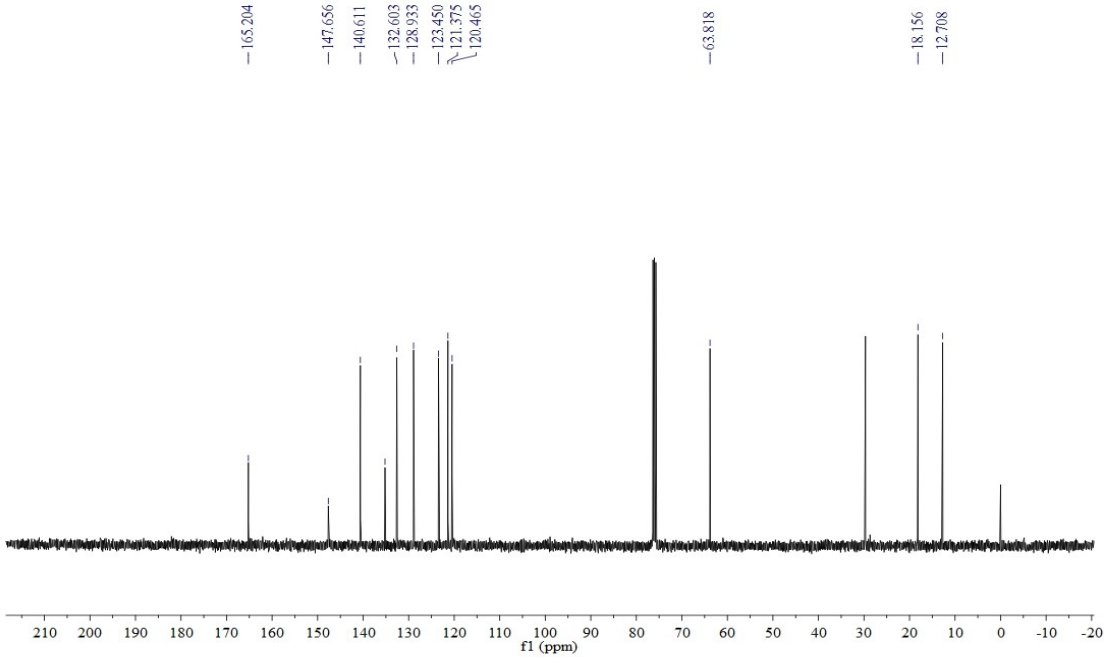
Butyl 3-(3-nitrophenyl)acrylate (3g)

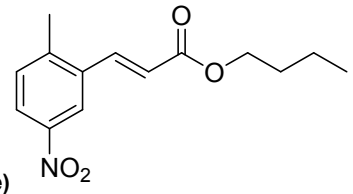
Purified by flush column chromatography(silica gel,Hexane/EtoAc=20/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.90 (t, J=7.2 Hz, 3H), 1.32-1.36 (m, 2H), 1.59-1.63 (m, 2H), 2.46 (s, 3H), 4.16 (t, J=6.8 Hz, 2H), 6.50 (d, J=16.0 Hz, 1H), 7.49-7.53 (m, 1H), 7.64 (d, J=16.0 Hz, 1H), 7.74-7.76 (m, 1H), 8.14-8.15 (m, 1H), 8.31 (s, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 12.7, 18.1, 30.0, 63.8, 120.4, 121.3, 126.4, 128.9, 132.6, 135.2, 140.6, 147.6,165.2 .





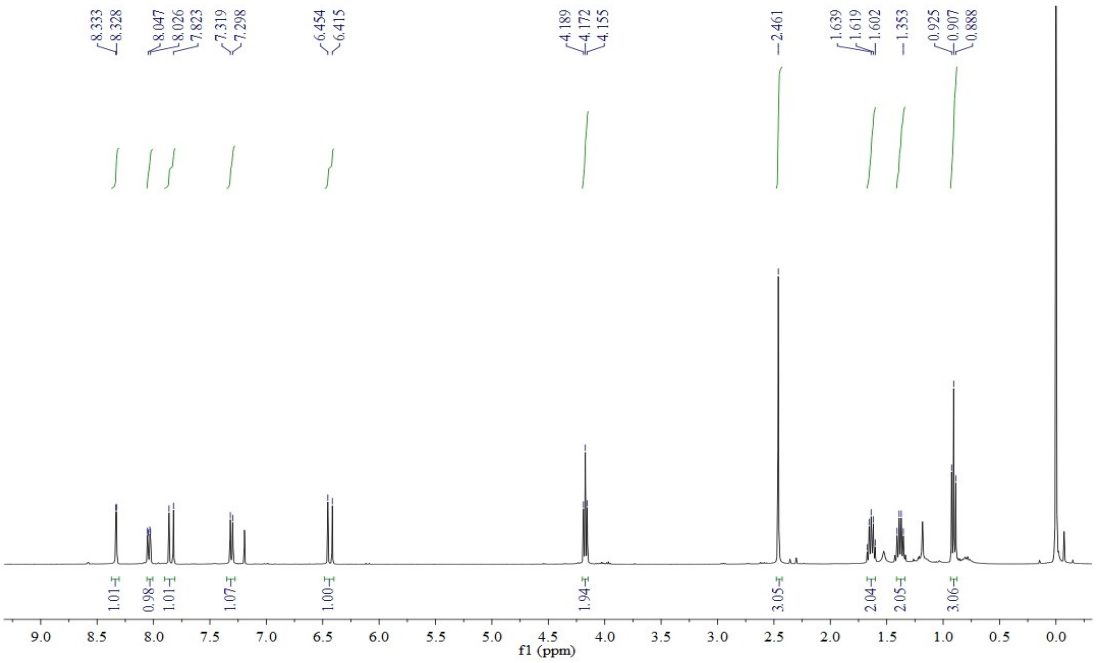


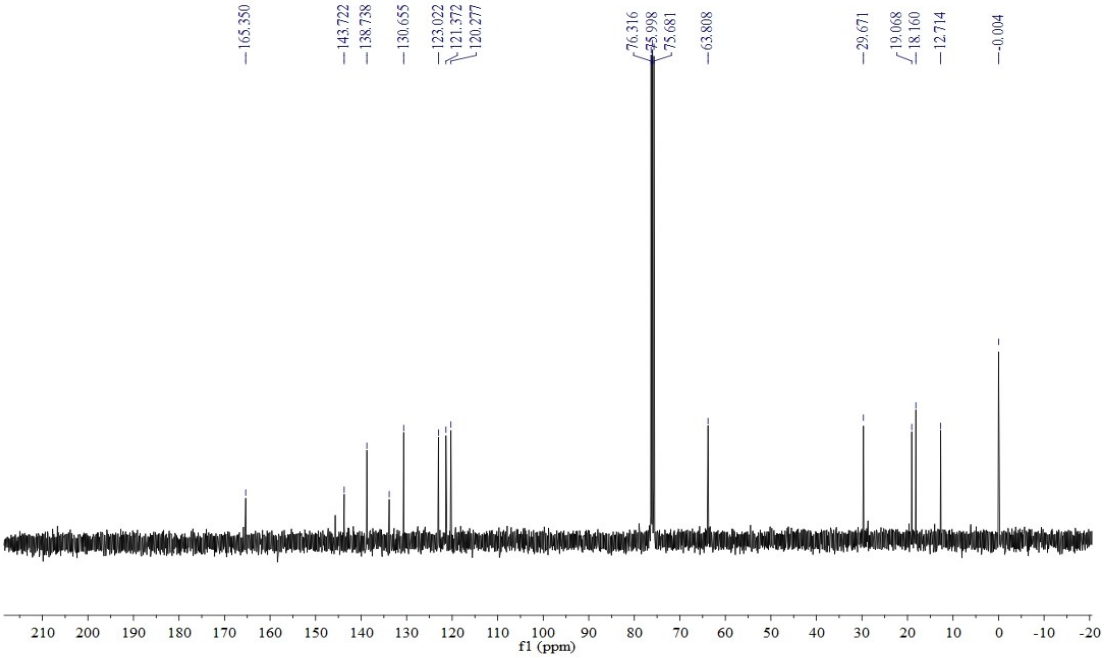
Butyl3-(2-methyl-5-nitrophenyl)acrylate(3e)

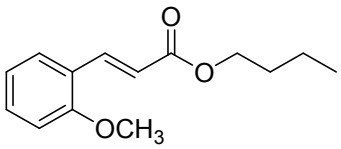
Purified by flush column chromatography (silica gel,Hexane/EtoAc=20/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.91 (t, J=7.2 Hz,3H), 1.36-1.38 (m, 2H), 1.63-1.64 (m, 2H,), 2.46 (s, 3H), 4.17 (t, J=6.8 Hz, 2H), 6.43 (d, J=16.0 Hz, 1H), 7.29-7.31 (m, 1H), 7.82 (d, J=16.0 Hz, 1H,) , 8.02-8.04 (m, 1H), 8.32-8.33 (m, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 18.2, 19.0, 29.7, 63.8, 120.2, 121.3, 123.0, 130.6, 133.8, 138.7, 143.7, 145.8, 165.3 .





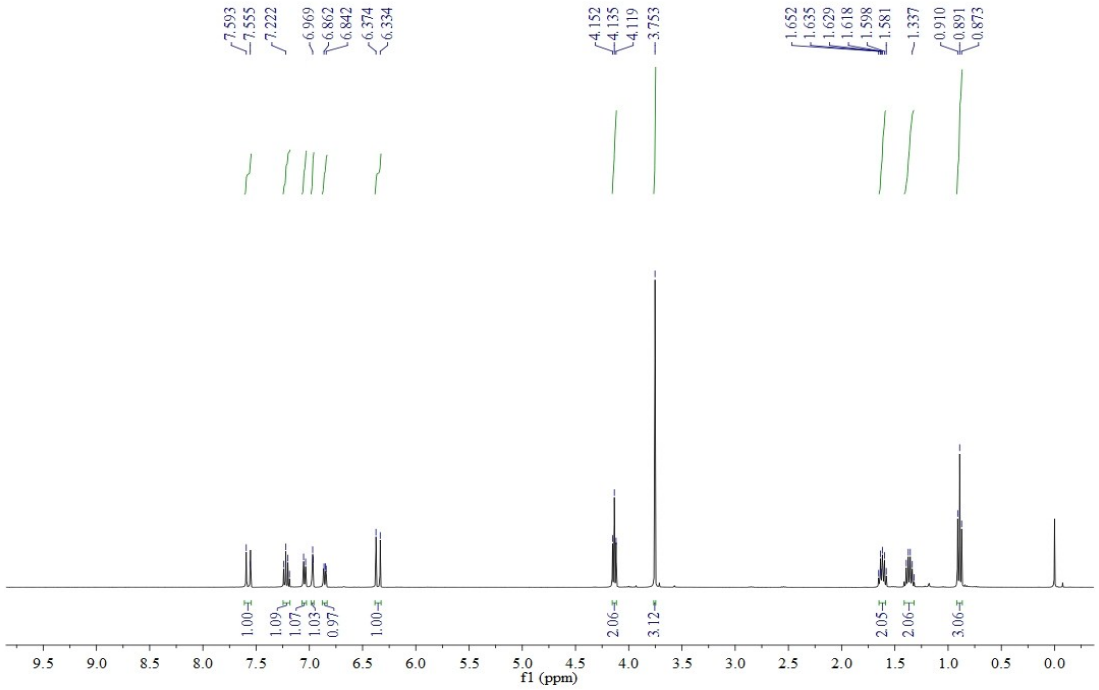


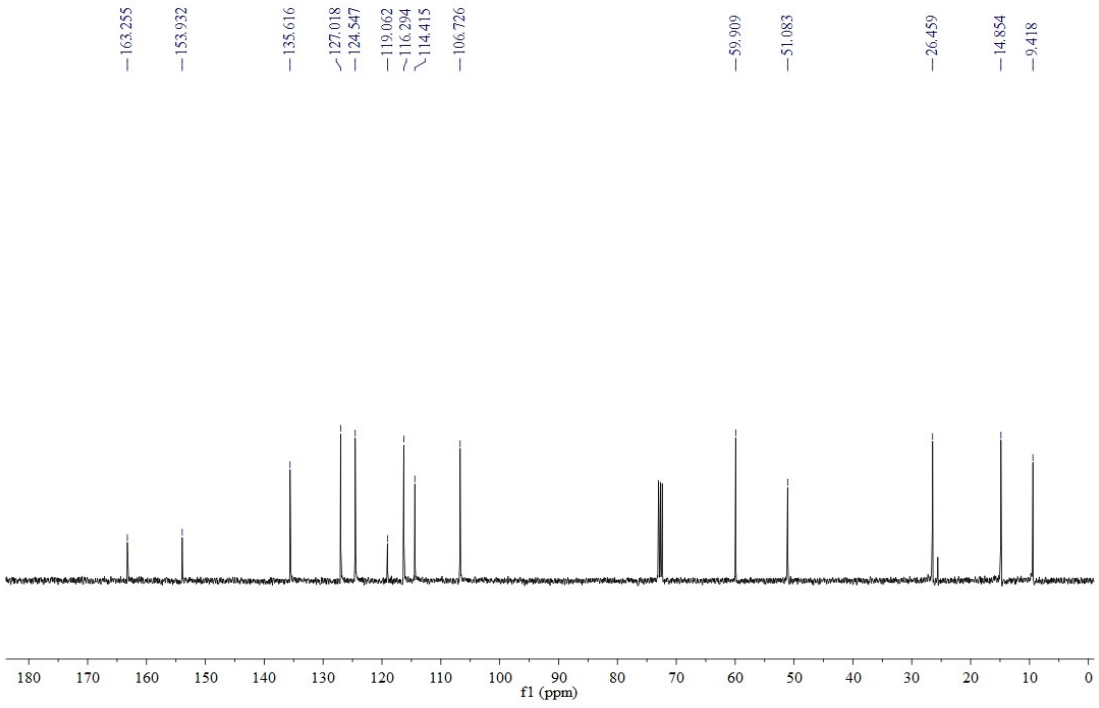
Butyl 3-(2-methoxyphenyl) acrylate (3b)

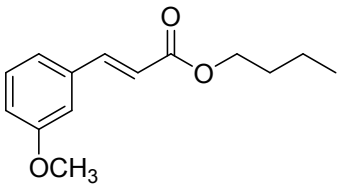
Purified by flush column chromatography(silica gel,Hexane/EtoAc=20/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.89 (t, J=7.6 Hz, 3H), 1.33-1.36 (m, 2H), 1.62-1.65 (m, 2H), 3.75 (s, 3H), 4.14 (t, J= 6.8 Hz, 2H), 6.35 (d, J=16.0 Hz, 1H), 6.84-6.8 6 (m, 1H), 6.96 (s, 1H), 7.03-7.05 (s, 1H), 7.18-7.24 (m, 1H), 7.57 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 9.4, 14.8, 26.4, 50.9, 60.1, 108.5, 111.7, 114.1, 116.4, 125.5, 131.4, 140.1, 155.5, 162.6.





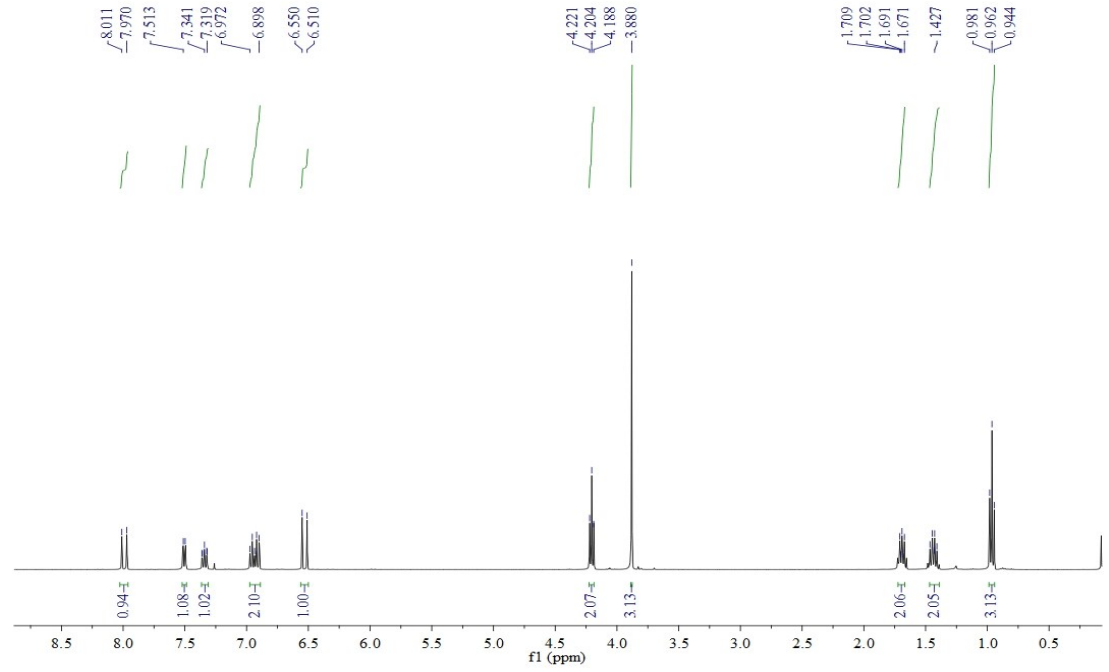


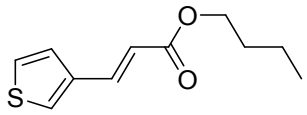
Butyl 3-(3-methoxyphenyl) acrylate (3c)

Purified by flush column chromatography (silica gel,Hexane/EtoAc=20/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.96 (t, J=6.8 Hz, 3H),1.42-1.44 (m, 2H), 1.69-1.70 (m, 2H), 3.88 (s, 3H), 4.21 (t, J= 8.0 Hz, 2H), 6.53 (d, J=16.0 Hz, 1H), 6.89-6.97 (m, 2H), 7.31-7.34 (m, 1H), 7.49-7.51 (m, 1H), 7.80 (d, J=16.0 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 9.4, 14.8, 26.5, 51.1, 60.0, 106.7, 114.4, 116.3, 119.1, 124.5, 127.0, 135.6, 153.9, 163.2 .



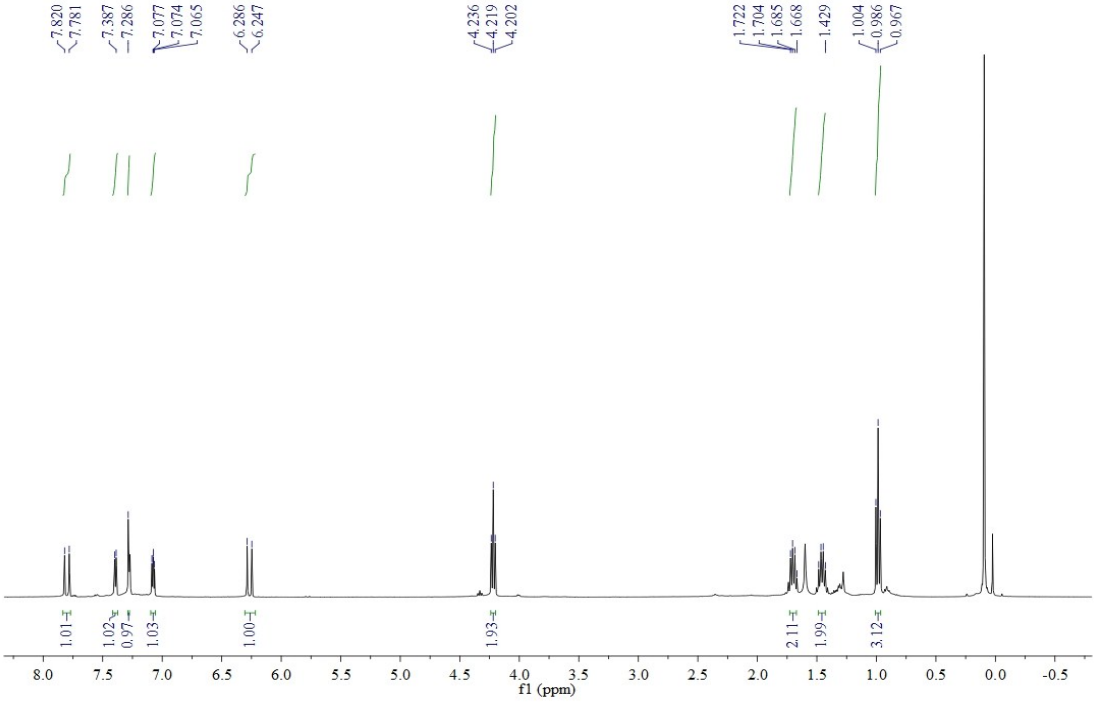


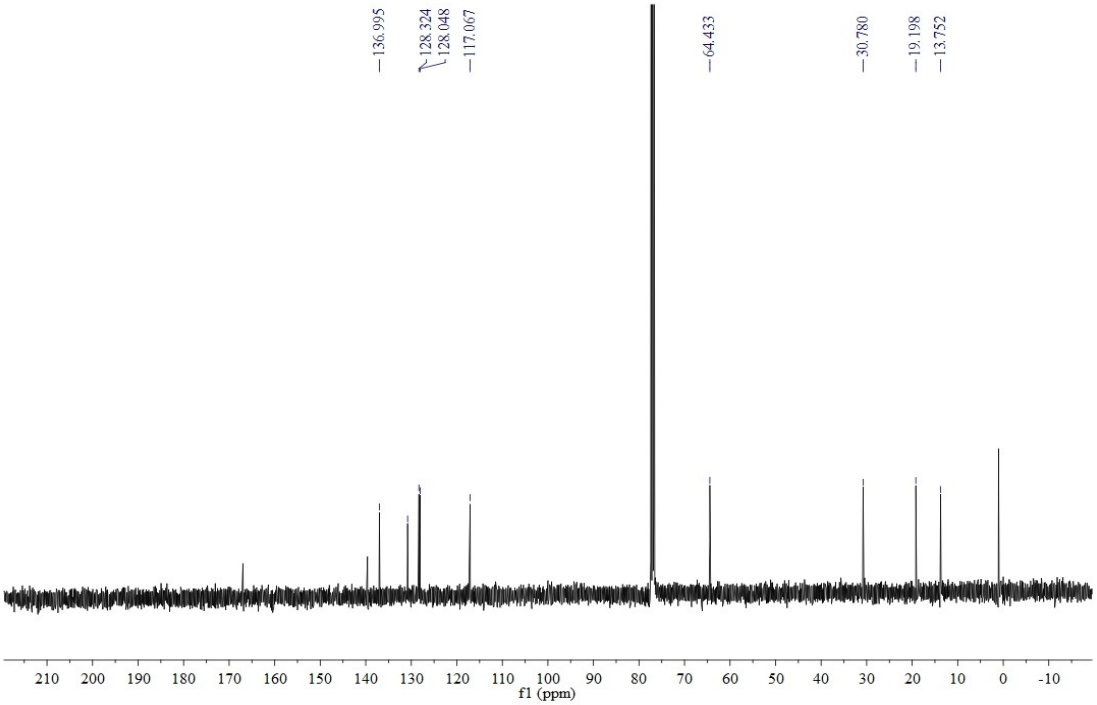
Butyl 3-(thiophen-3-yl)acrylate (3i)

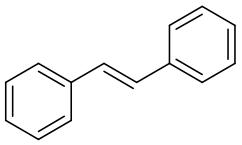
Purified by flush column chromatography (silica gel,Hexane/EtoAc=20/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 0.99 (t, J=7.2 Hz, 3H), 1.44-1.46 (m, 2H), 1.69-1.70 (m, 2H), 4.22 (t, J= 6.8 Hz, 2H), 6.27 (d, J=16.0 Hz, 1H), 7.07-7.08 (m, 1H), 7.28 (s, 1H), 7.39 (d, J=4.8 Hz, 1H) 7.80 (d, J=16 Hz, 1H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 13.7, 19.2, 30.7, 64.4, 117.0, 128.3, 130.8, 136.9, 140.2, 139.7, 167.0 .







1,2-diphenylethene (3k)

Purified by flush column chromatography(silica gel,Hexane/EtoAc=60/1);

^{1}H NMR (400MHz, $CDCl_3$) δ 7.07-7.08 (s, 2H), 7.21-7.23 (m, 2H), 7.32-7.34 (m, 4H,) 7.46-7.48 (m, 21H) ppm.

^{13}C NMR (100MHz,$CDCl_3$) δ 122.1, 123.2, 124.3, 132.9.