# Supplementary information

# Copper-Catalyzed Oxidative Coupling of Acids with Alkanes Involving Dehydrogenation: Facile Access to Allylic Esters and Alkylalkenes

**Cheng-Yong Wang,[a] Ren-Jie Song,[a] Wen-Ting Wei,[a] Jian-Hong Fan,[a] and Jin-Heng Li*[a]**

[a]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China
*E-mail: jhli@hnu.edu.cn.*

## List of Contents

**(A) Typical Experimental Procedure**

**(a) Typical Experimental Procedure for Esterification of Acids with Alkanes**

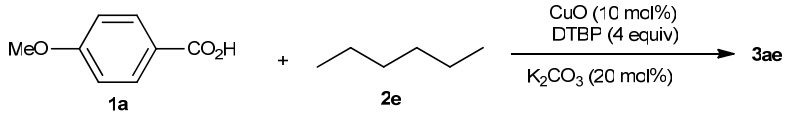
To a Schlenk tube were added acids **1** (0.3 mmol), CuO (10 mol%), $K_2CO_3$ (20 mol%), alkanes **2** (1 mL) and DTBP (4 equiv). Then the tube was charged with argon (1 atm), and was stirred at 120 $^oC$ for 24 h until complete consumption of starting material as monitored by TLC analysis. After the Schlenk tube was cooled to room temperature, diethyl ether was added, then the mixture was washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $Na_2SO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 100:1) to afford the desired products **3**.

**(b) Typical Experimental Procedure for Alkenylation of Cinnamic acid with Alkanes**

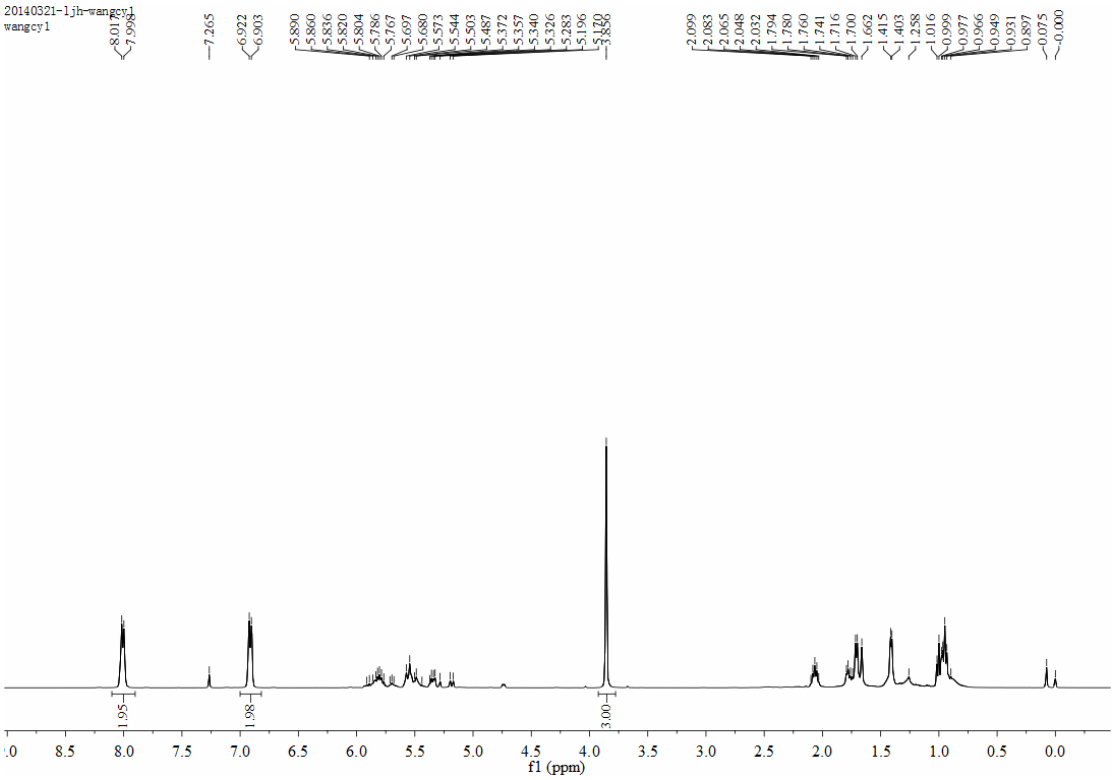
To a Schlenk tube were added cinnamic acid **1t** (0.3 mmol), CuO (10 mol %), $K_2CO_3$ (20 mol%), alkanes **2** (2 mL) and DTBP (4 equiv). Then the tube was charged with argon (1 atm), and was stirred at 120 $^oC$ for 10 h until complete consumption of starting material as monitored by TLC analysis. After the Schlenk tube was cooled to room temperature, diethyl ether was added, then the mixture was washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $Na_2SO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (only hexane) to afford the desired products **4**.

**(B) Reactions with Substrates 2e-g**

**(a)**

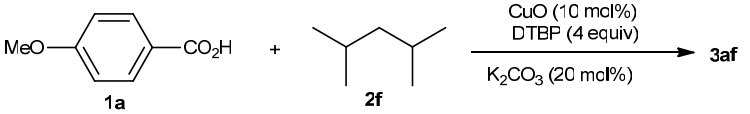



The mixture **3ae** was obtained in 60% yield (46:32:19:3; determined by GC-MS), which could not be isolated by column chromatography.

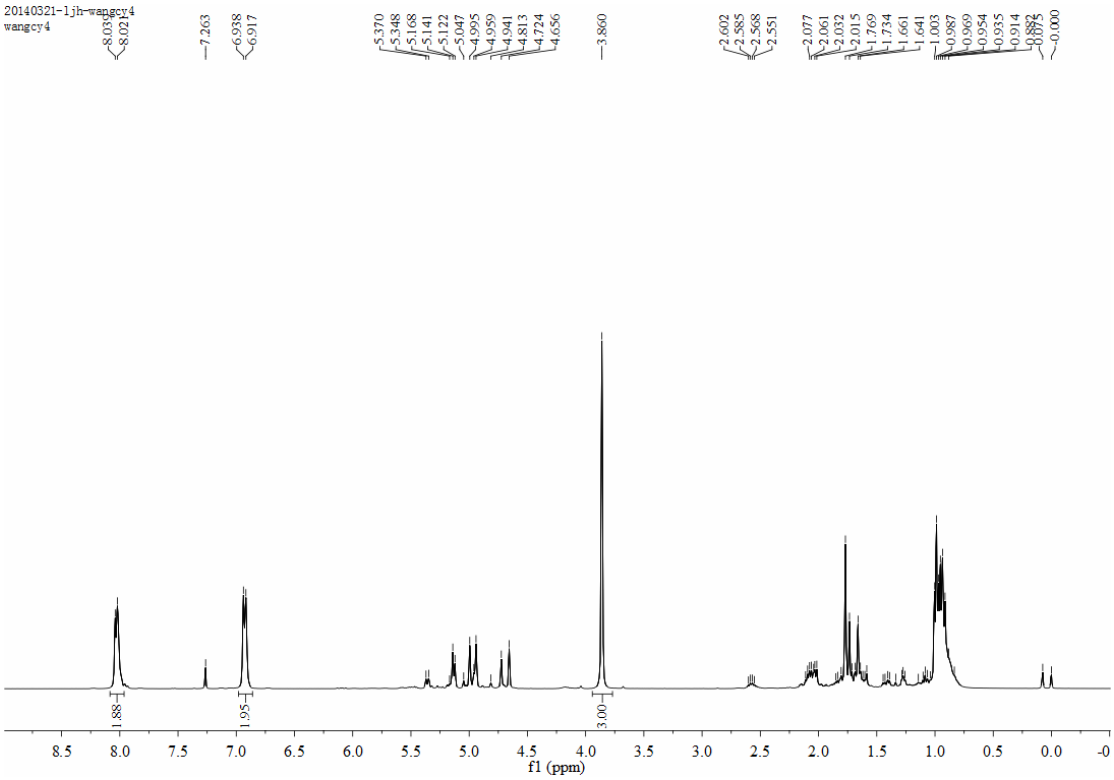



**Scheme S1** $^{1}$H NMR spectra of **3ae**

**(b)**

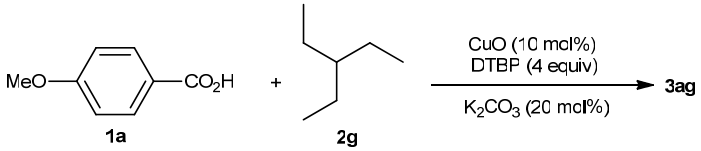



The mixture **3af** was obtained in 62% yield (49:49:2; determined by GC-MS), which could not be isolated by column chromatography.

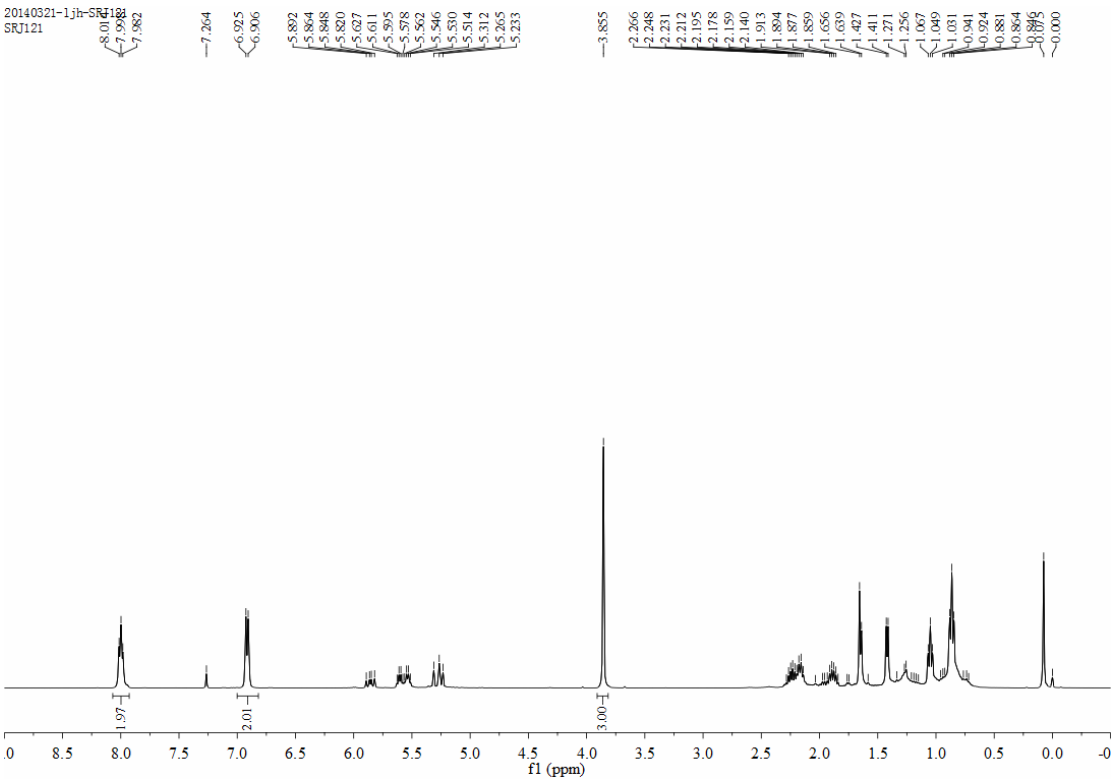



**Scheme S2** $^{1}$H NMR spectra of **3af**

**(c)**

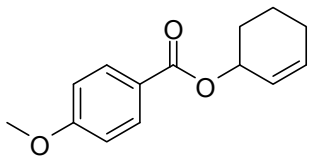



The mixture **3ag** was obtained in 63% yield(56:41:3; determined by GC-MS), which could not be isolated by column chromatography.



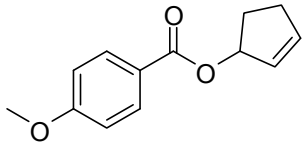

**Scheme S3**. $^{1}$H NMR spectra of **3ag**

## (C) Analytical data



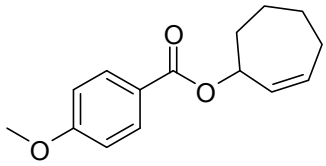
**Cyclohex-2-enyl 4-methoxybenzoate (3aa)**[1]

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.99 (t, *J* = 10.0 Hz, 1H), 5.83 (d, *J* = 10.0 Hz, 1H), 5.48 (s, 1H), 3.38 (s, 3H), 2.16-1.70 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.0, 163.2, 132.6, 131.6, 125.9, 123.1, 113.4, 68.2, 55.4, 28.2, 24.9, 19.0; IR (KBr, $cm^{-1}$): 1717; LRMS (EI 70 ev) *m/z* (%): 232 ($M^+$, 29), 153 (16), 135 (100), 80 (69), 77 (24).



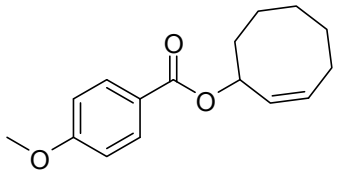
**Cyclopent-2-enyl 4-methoxybenzoate (3ab)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.14 (s, 1H), 5.93 (s, 2H), 3.85 (s, 3H), 2.65-2.50 (m, 1H), 2.44-2.37 (m, 2H), 2.00-1.91(m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.2, 163.1, 137.4, 131.5, 129.5, 123.0, 113.4, 80.7, 55.3, 31.1, 29.8; IR (KBr, $cm^{-1}$): 1715; LRMS (EI 70 ev) *m/z* (%): 218 ($M^+$, 21), 152 (100), 135 (86), 77 (16).



**Cyclohept-2-enyl 4-methoxybenzoate (3ac)**

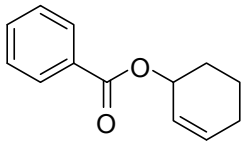
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.78-5.69 (m, 2H), 5.55 (t, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 2.19-2.03 (m, 2H), 1.91-1.89 (m, 2H), 1.76-1.64 (m, 3H), 1.43-1.35 (m, 1H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.6, 163.2, 133.7, 131.7, 131.5, 123.0, 113.5, 74.3, 55.4, 32.8, 28.5, 26.7, 26.6; IR (KBr, $cm^{-1}$): 1716; LRMS (EI 70 ev) *m/z* (%): 246 ($M^+$, 9), 152 (10), 135 (100), 79 (34).



**Cyclohept-2-enyl 4-methoxybenzoate (3ad)**

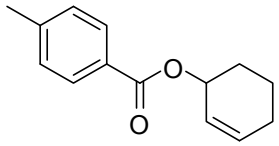
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.06-7.95 (m, 2H), 6.96-6.87 (m, 2H), 5.89-5.84 (m, 1H), 5.74-5.69 (m, 1H), 5.65-5.56 (m, 1H), 3.85 (s, 3H), 2.40-2.27 (m, 1H), 2.15 (m, 1H), 2.04 (m, 1H), 1.71 (m, 2H), 1.64-1.53 (m, 4H), 1.49-1.37 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.7, 163.1, 131.5, 130.8, 129.6, 123.1, 113.4, 72.6,

55.4, 35.1, 28.8, 26.3, 25.8, 23.6; IR (KBr, $cm^{-1}$): 1720; LRMS (EI 70 ev) *m/z* (%): 260 ($M^+$, 3), 152 (13), 135 (100), 77 (11).



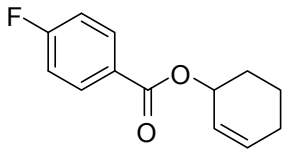
**Cyclohex-2-enyl benzoate (3ba)**[2]

Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 6.01 (d, *J* = 9.2 Hz, 1H), 5.84 (d, *J* = 10.0 Hz, 1H), 5.50 (s, 1H), 2.17-1.73 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ: 166.1, 132.7, 132.6, 130.6, 129.4, 128.1, 125.5, 68.4, 28.2, 24.8, 18.8; IR (KBr, $cm^{-1}$): 1713; LRMS (EI 70 ev) *m/z* (%): 202 ($M^+$, 32), 105 (100), 97 (22), 79 (59).



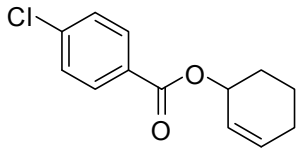
**Cyclohex-2-enyl 4-methylbenzoate (3ca)**[3]

Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.01 (d, *J* = 9.2 Hz, 1H), 5.83 (d, *J* = 9.6 Hz, 1H), 5.50 (s, 1H), 2.40 (s, 3H), 2.16-1.69 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ: 166.3, 143.3, 132.7, 129.6, 128.9, 127.9, 125.8, 68.3, 28.4, 24.9, 21.6, 18.8; IR (KBr, $cm^{-1}$): 1717; LRMS (EI 70 ev) *m/z* (%): 216 ($M^+$, 40), 119 (100), 97 (36), 91 (52).



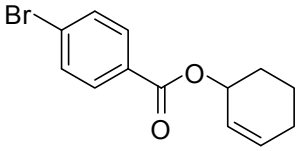
**Cyclohex-2-enyl 4-fluorobenzoate (3da)**[2]

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 8.07 (t, *J* = 6.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 9.6 Hz, 1H), 5.83 (d, *J* = 10.0 Hz, 1H), 5.50 (s, 1H), 2.17-2.06 (m, 2H), 2.00-1.95 (m, 1H), 1.89-1.73 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.9, 165.2, 164.3, 132.9, 132.1, 132.0, 127.0, 126.9, 125.5, 115.4, 115.2, 68.7, 28.3, 24.9, 18.9; IR (KBr, $cm^{-1}$): 1712; LRMS (EI 70 ev) *m/z* (%): 220 ($M^+$, 11), 123 (100), 95 (24), 80 (20).



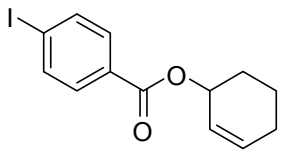

**Cyclohex-2-enyl 4-chlorobenzoate (3ea)**[2]

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 6.01 (d, *J* = 10.0 Hz, 1H), 5.82 (d, *J* = 10.0 Hz, 1H), 5.50 (s, 1H), 2.16-1.76 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.3, 139.1, 133.0, 130.9, 129.1, 128.5, 125.4, 68.7, 28.3, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1713; LRMS (EI 70 ev) *m/z* (%): 238 ($M^+$+2, 3), 236 ($M^+$, 10), 139 (100), 111 (22), 79 (52).



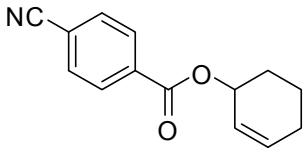

**Cyclohex-2-enyl 4-bromobenzoate (3fa)**[2]

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 6.01 (d, *J* = 9.6 Hz, 1H), 5.82 (d, *J* = 10.0 Hz, 1H), 5.50 (s, 1H), 2.17-1.70 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.4, 133.1, 131.5, 131.1, 129.6, 127.8, 125.4, 68.9, 28.3, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1715; LRMS (EI 70 ev) *m/z* (%): 280 ($M^+$, 11), 201 (32), 183 (100), 97 (26).



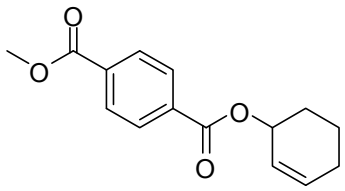
**Cyclohex-2-enyl 4-iodobenzoate (3ga)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.74 (m, 4H), 6.01 (d, *J* = 9.6 Hz, 1H), 5.82 (d, *J* = 10.0 Hz, 1H), 5.49 (s, 1H), 2.17- 1.71 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.7, 137.6, 133.1, 131.1, 130.2, 125.4, 100.5, 68.9, 28.3, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1715; LRMS (EI 70 ev) *m/z* (%): 328 ($M^+$, 22), 231 (100), 203 (15), 201 (25), 81 (61), 76 (29).



**Cyclohex-2-enyl 4-cyanobenzoate (3ha)**[2]

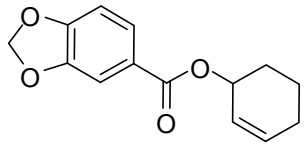
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 6.8 Hz, 2H), 7.74 (d, *J* = 6.8 Hz, 2H), 6.04 (d, *J* = 9.6 Hz, 1H), 5.87 (d, *J* = 9.6 Hz, 1H), 5.53 (s, 1H), 2.18-2.08 (m, 2H), 2.02-1.96 (m, 1H), 1.91-1.84 (m, 2H), 1.74-1.72 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 164.5, 134.6, 133.5, 132.1, 130.1, 125.0, 118.1, 116.2, 69.6, 28.3, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1710; LRMS (EI 70 ev) *m/z* (%): 227 ($M^+$, 10), 130 (100), 102 (29), 79 (61).



**Cyclohex-2-enyl methyl terephthalate (3ia)**[4]

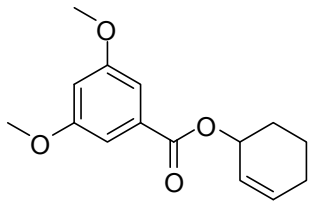
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.10 (s, 4H), 6.03 (d, *J* = 9.6 Hz, 1H), 5.84 (d, *J* = 10.0 Hz, 1H), 5.53 (s, 1H), 3.95 (s, 3H), 2.18-2.02 (m, 2H), 2.00-1.97 (m,

1H), 1.92-1.83 (m, 2H), 1.74-1.71 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.3, 165.4, 134.6, 133.7, 133.2, 129.5, 129.4, 125.3, 69.1, 52.4, 28.3, 24.9, 18.8; LRMS (EI 70 ev) *m/z* (%): 260 ($M^+$, 6), 163 (100), 149 (12), 79 (38).



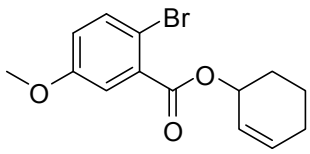
**Cyclohex-2-enyl benzo[*d*][1,3]dioxole-5-carboxylate (3ja)**

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 5.99 (d, *J* = 10.0 Hz, 1H), 5.82 (d, *J* = 10.0Hz, 1H), 5.47 (s, 1H), 2.16-2.00 (m, 2H), 1.96-1.93 (m, 1H), 1.87-1.72 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.4, 151.4, 147.6, 132.8, 125.8, 125.2, 124.8, 109.5, 107.8, 101.7, 68.5, 28.3, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1715; LRMS (EI 70 ev) *m/z* (%): 246 ($M^+$, 6), 166 (100), 149 (64), 121 (20), 80 (82).



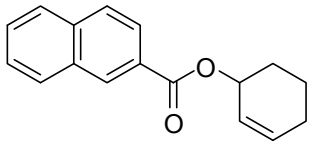
**Cyclohex-2-enyl 3,5-dimethoxybenzoate (3ka)**

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.20 (s, 2H), 6.64 (s, 1H), 6.00 (d, *J* = 9.2 Hz, 1H), 5.83 (d, *J* = 10.0 Hz, 1H), 5.49 (s, 1H), 3.83 (s, 6H), 2.16-1.85 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.9, 160.9, 132.8, 132.6, 125.6, 107.1 (2C), 105.3, 68.8, 55.5, 28.3, 24.9, 18.9; IR (KBr, $cm^{-1}$): 1717; LRMS (EI 70 ev) *m/z* (%): 262 ($M^+$, 28), 182 (100), 166 (38), 138 (20), 81 (34).



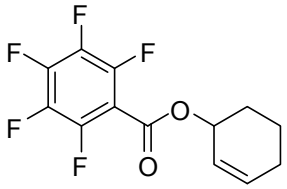

**Cyclohex-2-enyl 2-bromo-5-methoxybenzoate (3la)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.8 Hz, 1H), 7.29 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.02 (d, *J* = 10.0 Hz, 1H), 5.86 (d, *J* = 10.0 Hz, 1H), 5.53 (s, 1H), 3.82 (s, 3H), 2.16-1.96 (m, 2H), 1.97-1.92 (m, 1H), 1.85-1.82 (m, 1H), 1.72-1.68 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 165.8, 158.9, 134.9, 133.5, 133.3, 125.2, 118.5, 116.3, 111.7, 69.7, 55.6, 28.2, 24.9, 18.8; IR (KBr, $cm^{-1}$): 1724; LRMS (EI 70 ev) *m/z* (%): 312 ($M^+$+2, 15), 310 ($M^+$, 14), 215 (34), 213 (59), 80 (100).



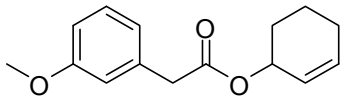

**Cyclohex-2-enyl 2-naphthoate (3ma)**[2]

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 HZ, 2H), 7.57-7.48 (m, 2H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.89 (d, *J* = 10.0Hz, 1H), 5.58 (s, 1H), 2.18-2.06 (m, 2H), 2.02-1.98 (m, 1H), 1.95-1.76 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 166.3, 135.4, 132.8, 132.4, 130.9, 129.2, 128.0, 127.92, 127.94, 127.6, 126.5, 125.7, 125.3, 68.7, 28.4, 24.9, 18.9; IR (KBr, $cm^{-1}$): 1712; LRMS (EI 70 ev) *m/z* (%): 252 ($M^+$, 44), 234 (12), 172 (50), 155 (100), 127 (71), 80 (60).



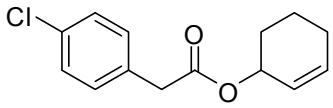

**Cyclohex-2-enyl 2,3,4,5,6-pentafluorobenzoate (3na)**

Yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 6.11-5.96 (m, 1H), 5.83 (d, *J* = 9.9 Hz, 1H), 5.55 (s, 1H), 2.20-1.95 (m, 3H), 1.93-1.65 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 158.62 , 146.43, 144.23 , 143.99 , 141.66, 138.88, 136.34, 134.20, 133.86, 124.18, 108.83, 71.04, 28.08, 24.77, 18.36; IR (KBr, $cm^{-1}$): 1716; LRMS (EI 70 ev) *m/z* (%): 292 ($M^+$, 3), 220 (10), 195 (100), 167 (21), 79 (83).



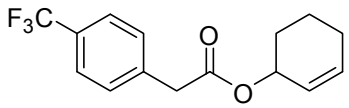
**Cyclohex-2-enyl 2-(3-methoxyphenyl)acetate (3oa)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.23 (t, *J* = 7.6 Hz, 1H), 6.89-6.80 (m, 3H), 5.95 (d, *J* = 10.0 Hz, 1H), 5.70 (d, *J* = 10.0 Hz, 1H), 5.28 (s, 1H), 3.80 (s, 3H), 3.59 (s, 2H), 2.11-1.96 (m, 2H), 1.89-1.83 (m, 1H), 1.77-1.61 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 171.1, 159.6, 135.7, 132.8, 129.5, 125.5, 121.6, 114.7, 112.6, 68.5, 55.2, 41.7, 28.2, 24.8, 18.8; IR (KBr, $cm^{-1}$): 1712; LRMS (EI 70 ev) *m/z* (%): 246 ($M^+$, 9), 121 (34), 81 (100).



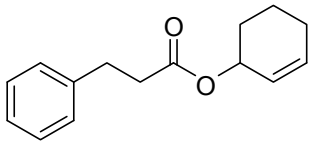
**Cyclohex-2-enyl 2-(4-chlorophenyl)acetate (3pa)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 5.96 (d, *J* = 9.6 Hz, 1H), 5.68 (d, *J* = 9.6 Hz, 1H), 5.27 (s, 1H), 3.58 (s, 2H), 2.11-1.96 (m, 2H), 1.88-1.82 (m, 1H), 1.71-1.62 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 170.8, 133.0, 132.9, 132.7, 130.6, 128.6, 125.3, 68.7, 40.9, 28.3, 24.8, 18.7; IR (KBr, $cm^{-1}$): 1713; LRMS (EI 70 ev) *m/z* (%): 252 ($M^+$+2, 0.5), 250 ($M^+$, 1.8), 81 (100).



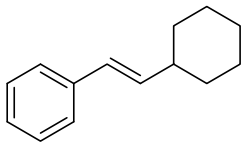
**Cyclohex-2-enyl 2-(4-(trifluoromethyl)phenyl)acetate (3qa)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 5.97 (d, *J* = 9.6 Hz, 1H), 5.69 (d, *J* = 10.0 Hz, 1H), 5.28 (s, 1H), 3.67 (s, 2H), 2.11-1.97 (m, 2H), 1.89-1.83 (m, 1H), 1.73-1.60 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 170.4, 138.2, 133.1, 129.6 (2C), 125.4 (q, *J* = 3.0 Hz, 1C), 125.2, 68.9, 41.4, 28.1, 24.8, 18.7; IR (KBr, $cm^{-1}$): 1712; LRMS (EI 70 ev) *m/z* (%): 284 ($M^+$, 1), 159 (28), 81 (100).



**Cyclohex-2-enyl 3-phenylpropanoate (3ra)**[1]

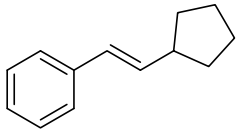
Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 8.0Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 5.94 (d, *J* = 9.6 Hz, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 5.27 (s, 1H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.10-1.95 (m, 2H), 1.87-1.80 (m, 1H), 1.71-1.63 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 172.6, 140.5, 132.7, 128.4, 128.3, 126.2, 125.6, 68.0, 36.2, 31.0, 28.2, 24.8, 18.8; IR (KBr, $cm^{-1}$): 1712; LRMS (EI 70 ev) *m/z* (%): 230 ($M^+$, 0.6), 150 (11), 81 (100), 79 (45).



**(*E*)-(2-cyclohexylvinyl)benzene (3ta)**[5]

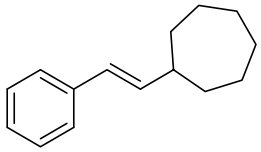
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* =

7.2 Hz, 2H), 7.18 (t, *J* = 6.8 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.20-6.15 (m, 1H), 2.13-2.11 (m, 1H), 1.82-1.75 (m, 4H), 1.70-1.66 (m, 1H), 1.36-1.27 (m, 2H), 1.22-1.14 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 138.0, 136.8, 128.4, 127.2, 126.7, 125.9, 41.1, 32.9, 26.2, 26.0; LRMS (EI 70 ev) *m/z* (%): 186 ($M^+$, 26), 129 (22), 104 (100), 91 (16).



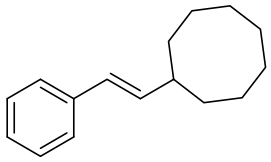
**(*E*)-(2-cyclopentylvinyl)benzene (3tb)**[5]

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 6.8 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.23-6.18 (m, 1H), 2.65-2.56 (m, 1H), 1.87-1.85 (m, 2H), 1.71-1.60 (m, 4H), 1.44-1.35 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 138.0, 135.7, 128.4, 127.8, 126.7, 125.9, 43.8, 33.2, 25.2; LRMS (EI 70 ev) *m/z* (%): 172 ($M^+$, 46), 129 (40), 104 (100), 91 (28).



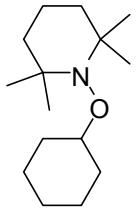
**(*E*)-Styrylcycloheptane (3tc)**[5]

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 6.8 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.24-6.19 (m, 1H), 2.33-2.32 (m, 1H), 1.84-1.80 (m, 2H), 1.72-1.62 (m, 4H), 1.54-1.38 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 138.0, 137.6, 128.3, 126.6, 126.5, 125.8, 43.2, 34.6, 28.3, 26.2; LRMS (EI 70 ev) *m/z* (%): 200 ($M^+$, 55), 143 (24), 129(66), 104 (100), 91 (35).



**(*E*)-Styrylcyclooctane (3td)**[5]

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 6.8 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.24-6.19 (m, 1H), 2.45-2.35 (m, 1H), 1.78-1.72 (m, 2H), 1.61-1.48 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 138.1, 137.8, 128.4, 126.8, 126.6, 125.9, 41.3, 37.4, 31.8, 26.0, 25.1; LRMS (EI 70 ev) *m/z* (%): 214 ($M^+$, 23), 129(57), 104 (100), 91 (29).




**1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (7a)**

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 3.58 (s, 1H), 2.12-1.99(m, 2H), 1.77-1.70 (m, 2H), 1.56-1.41 (m, 7H), 1.25-1.16 (m, 5H), 1.13 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 81.7 , 59.6, 40.3 (2C), 32.9, 26.0, 25.1, 17.3; LRMS (EI 70 ev) *m/z* (%): 239 ($M^+$, 9), 157 (66), 142 (100), 109 (29).

**(D) References**

(1) E. Shi,Y. Shao, S. Chen, H. Hu, Z. Liu, J. Zhang, X. Wan, *Org. Lett.,* 2012*,* **14**, 3384.

(2) W. Wei, C. Zhang, Y. Xu, X. Wan*, Chem. Commun.,* 2011*,* **47**, 10827.

(3) B. Liu, S.-F. Zhu, L.-X. Wang, Q.-L. Zhou, *Tetrahedron: Asymmetry*, 2006, **4**, 634.

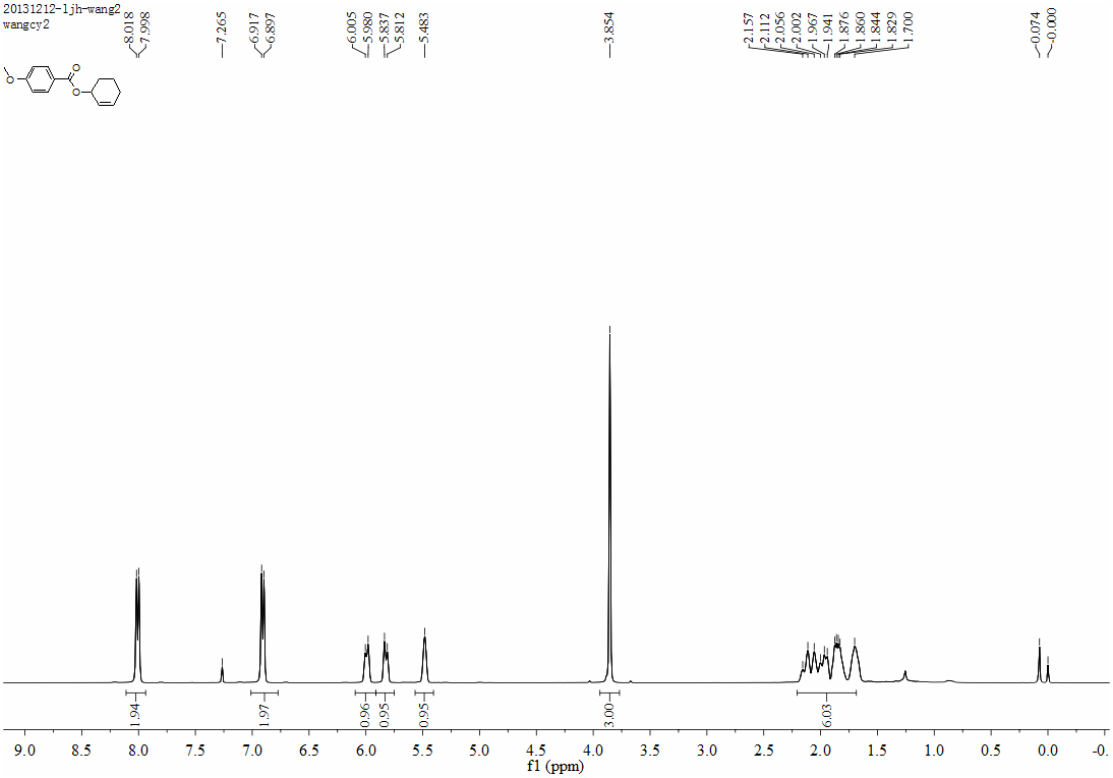
(4) Y. Kengo, F. Keigo, T. Shuji, T. Yoshinao, *J. Org. Chem.,* 1995, **60**, 1365.

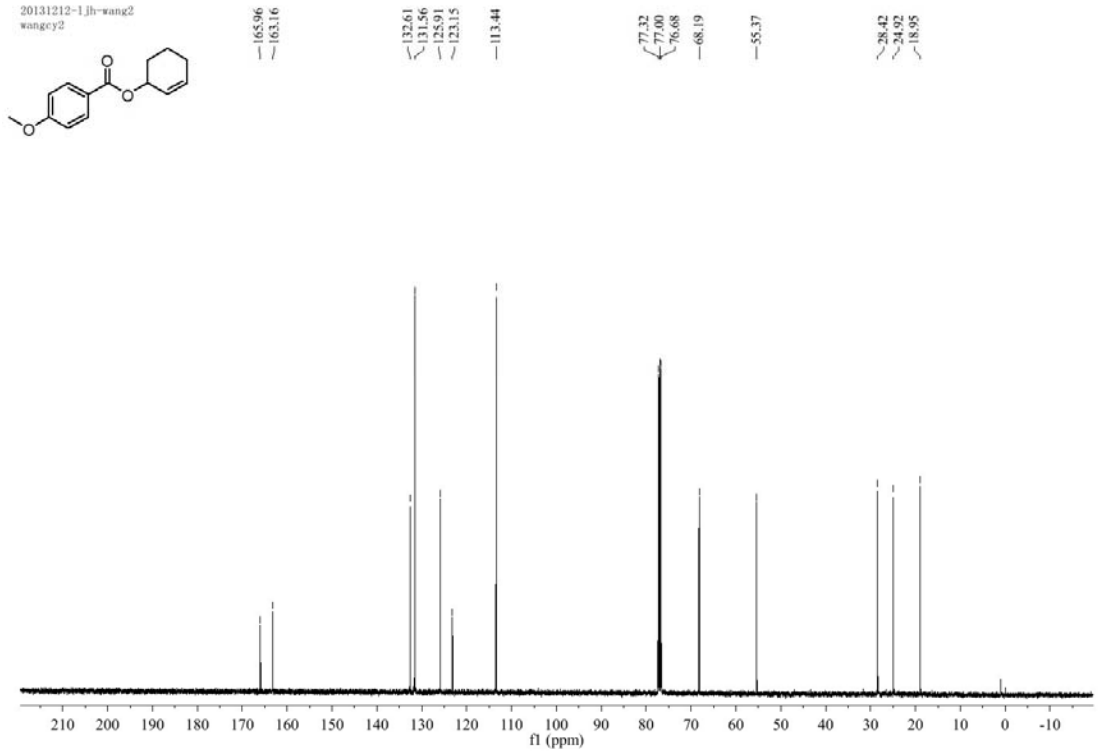
(5) J. Zhao, H. Fang, J. Han, Y. Pan, *Beilstein J. Org. Chem.*, 2013, **9**, 1718.

(6) A. Banaei, B. Rezazadeh, *J. Coord. Chem*., **2013**, 12, 2129.

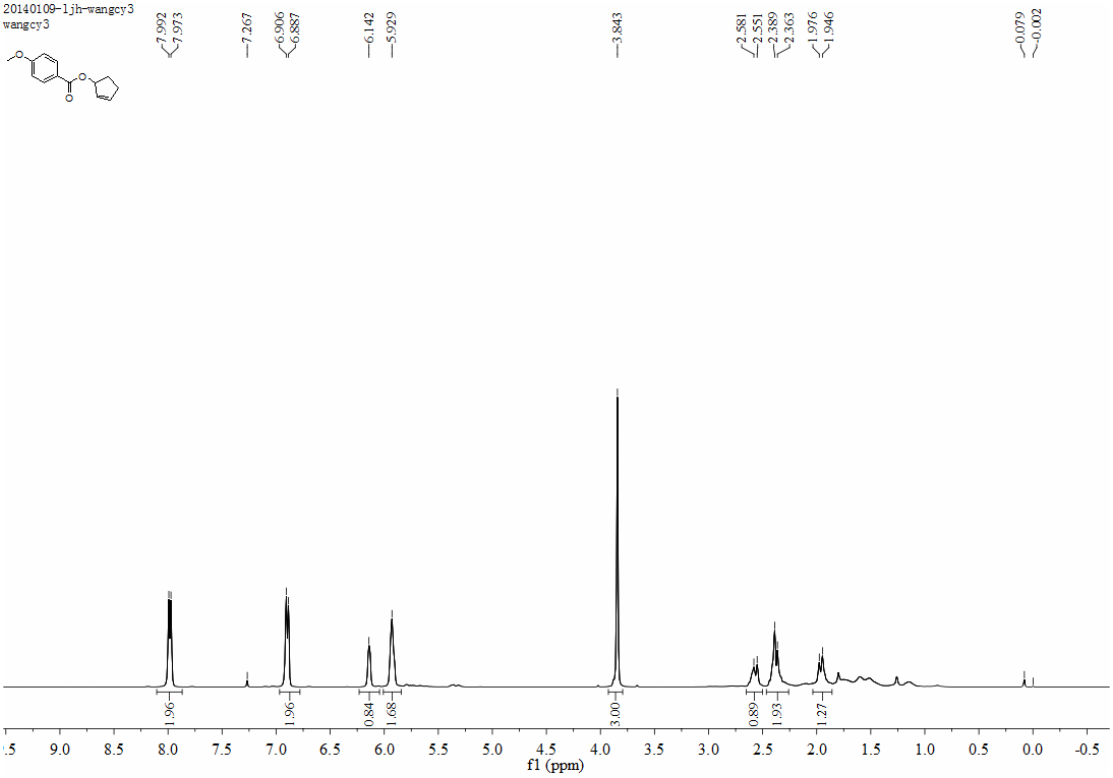
## (E) Spectra

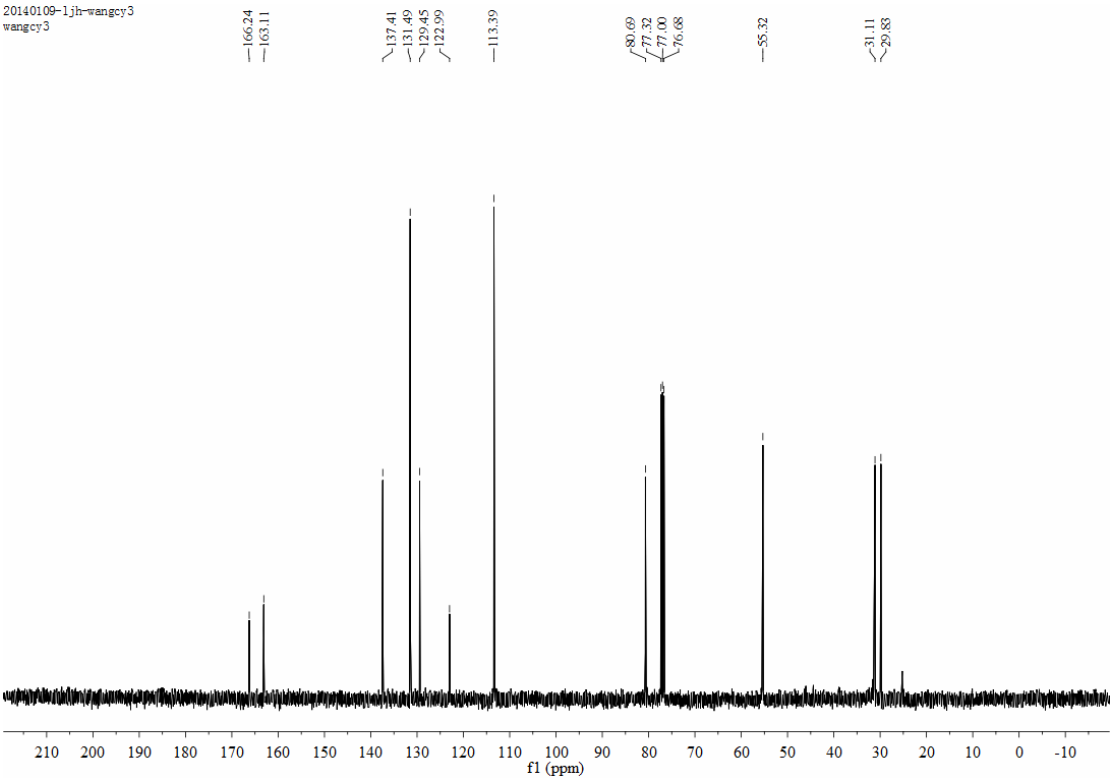
### Cyclohex-2-enyl 4-methoxybenzoate (3aa)



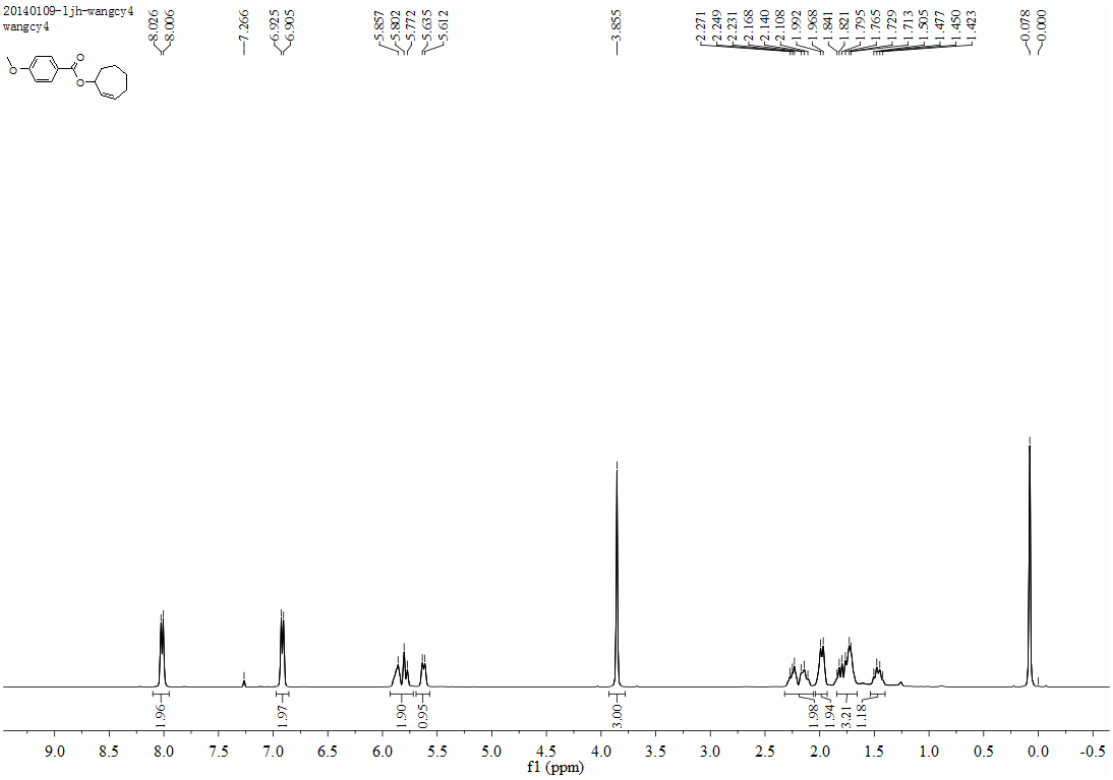



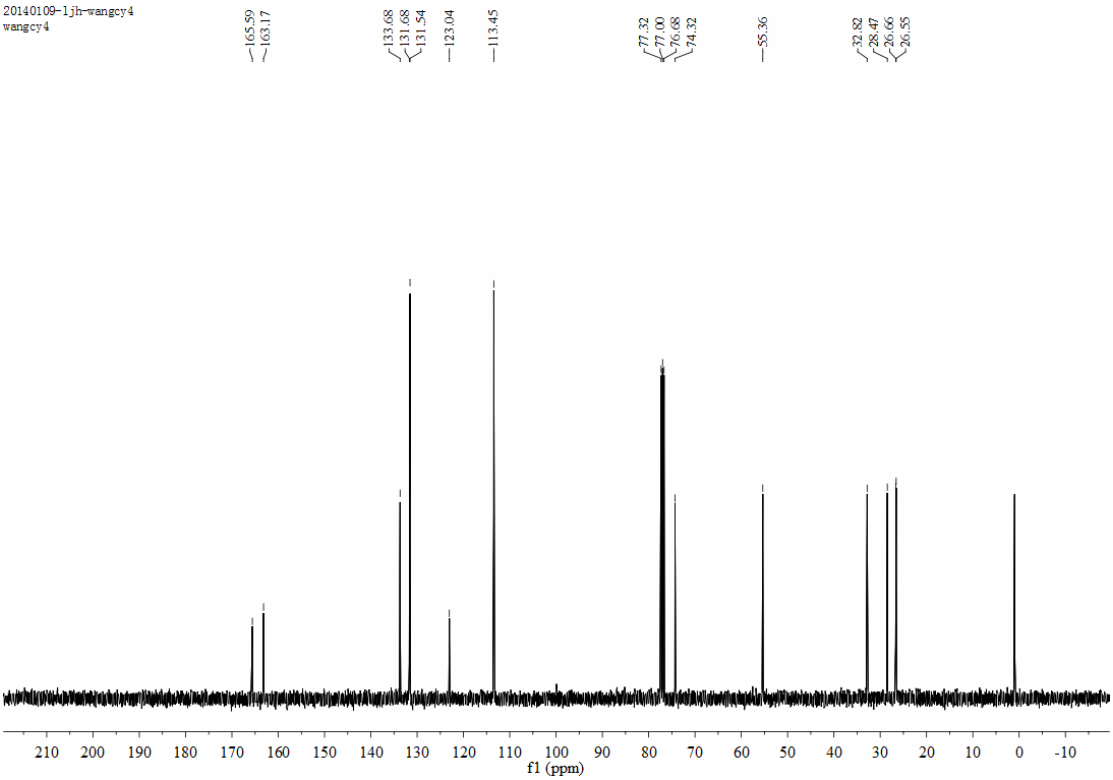
# Cyclopent-2-enyl 4-methoxybenzoate (3ab)



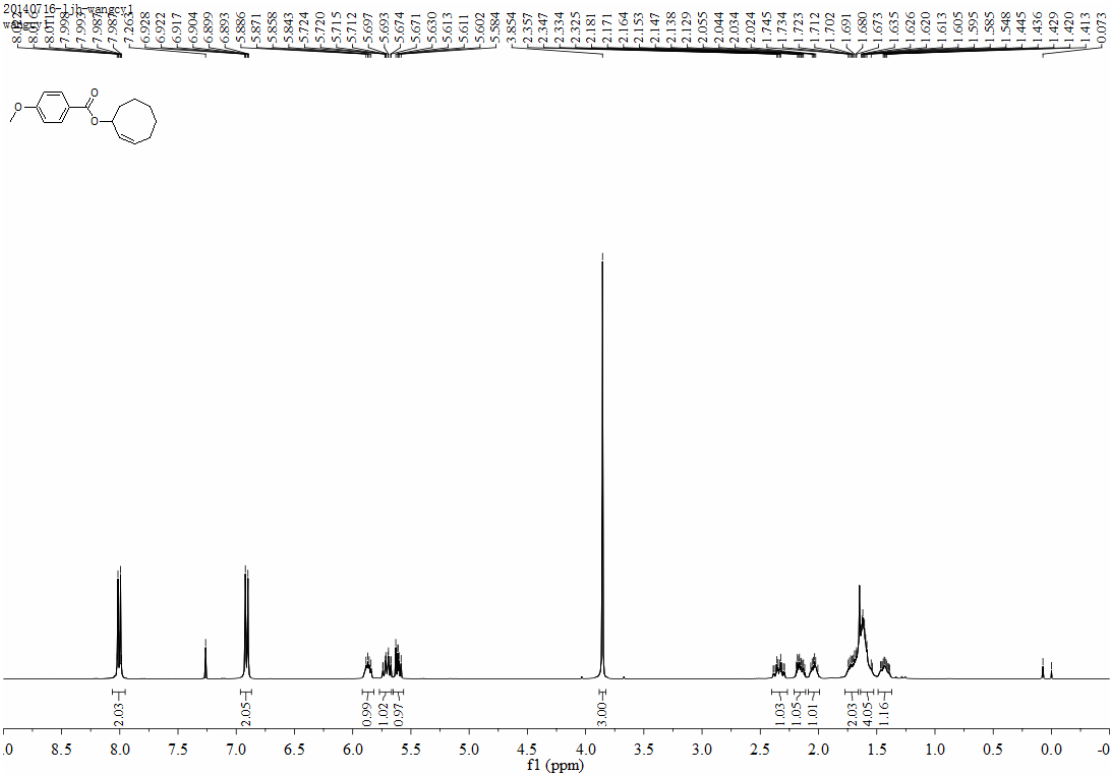



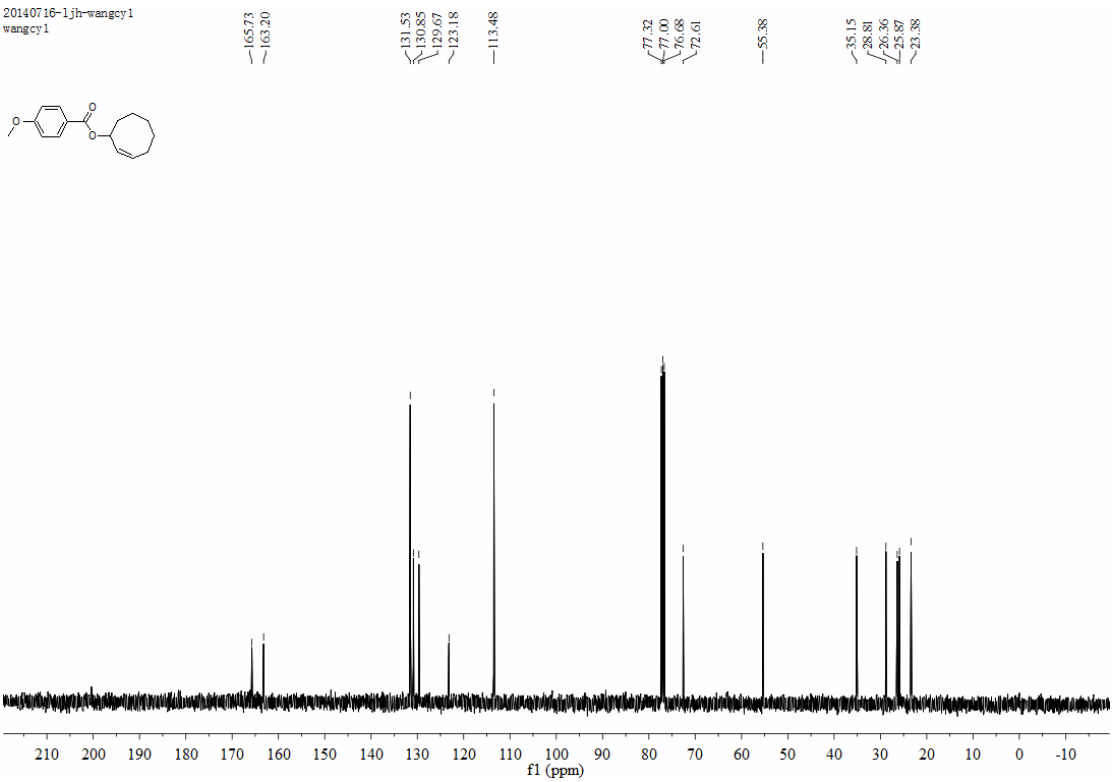
# Cyclohept-2-enyl 4-methoxybenzoate (3ac)



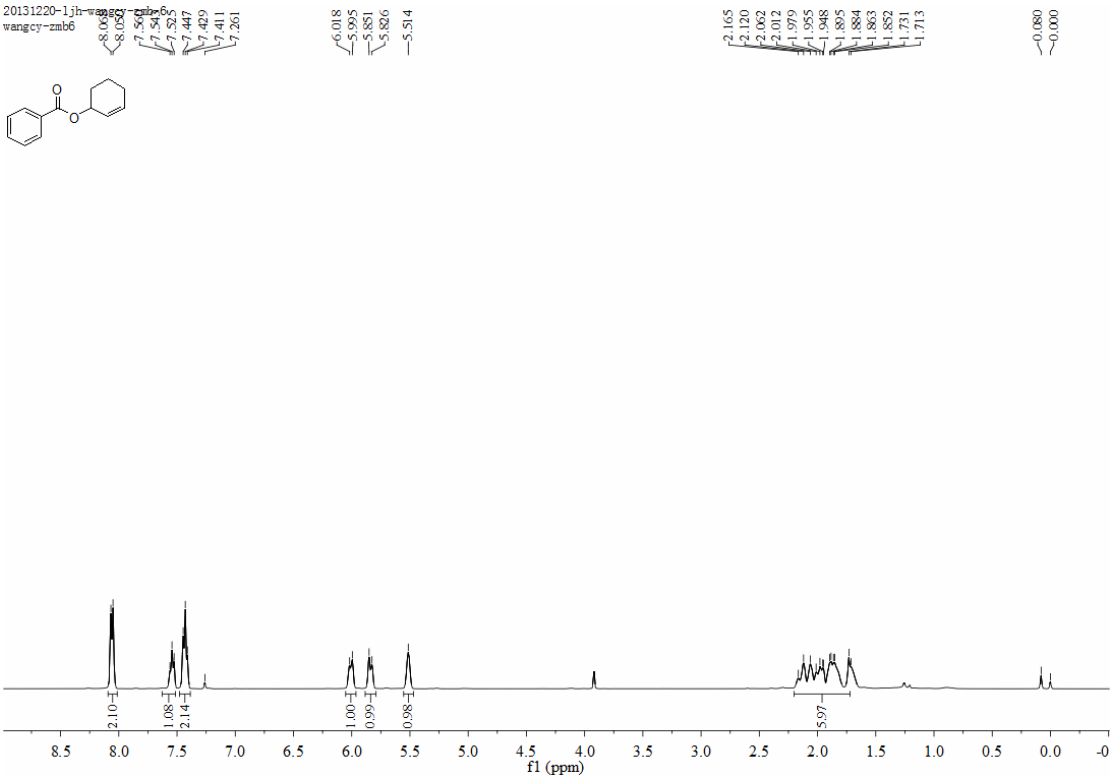



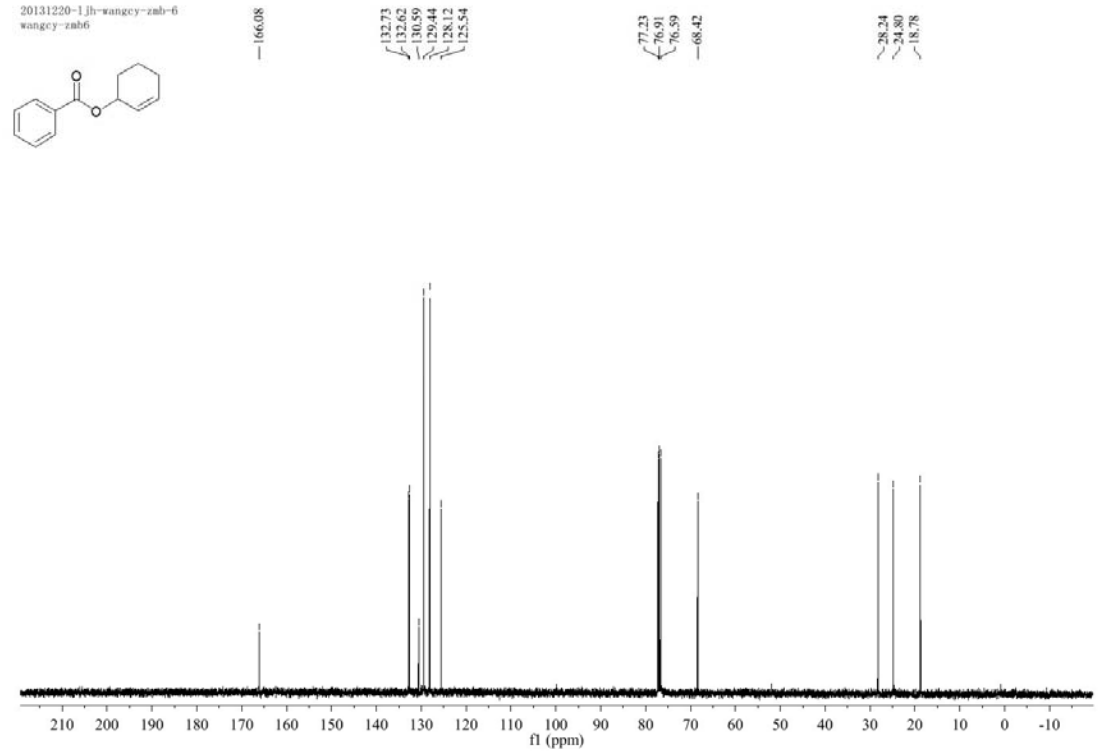
# Cyclooct-2-enyl 4-methoxybenzoate (3ad)



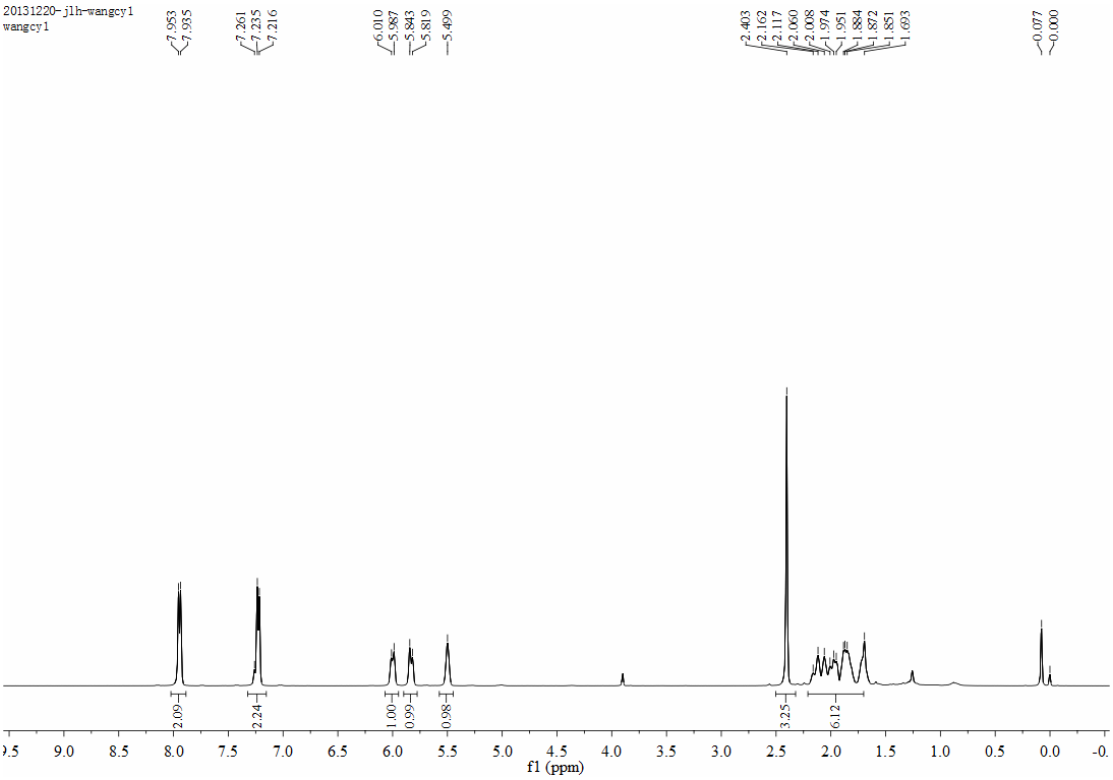



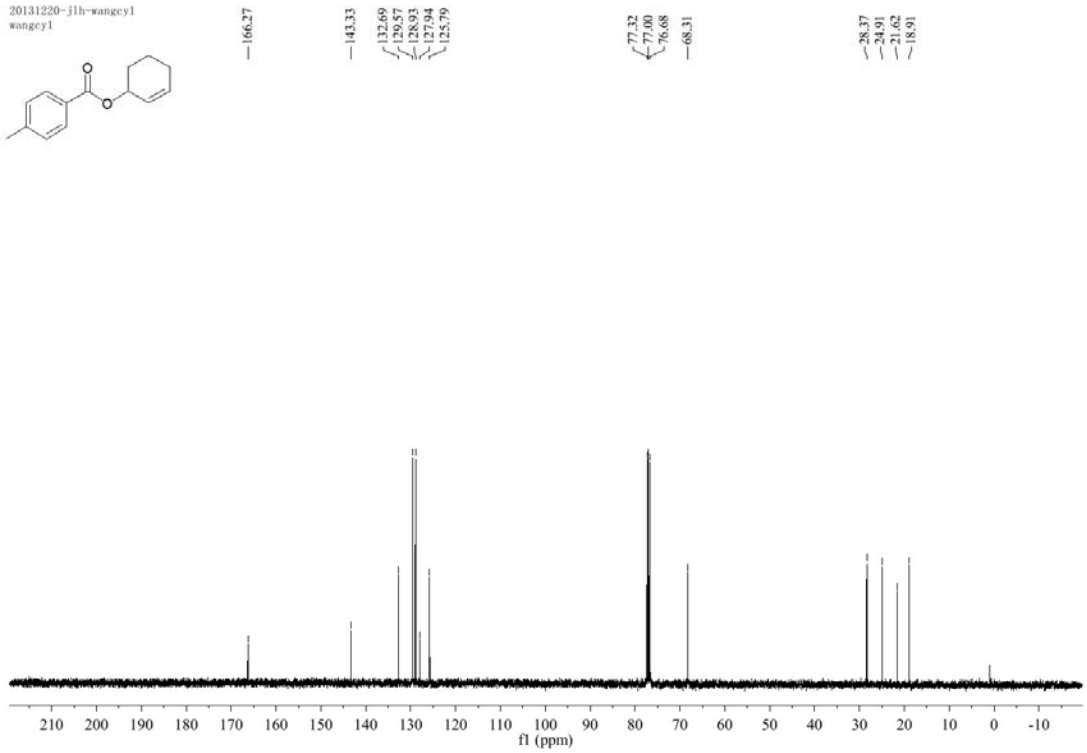
# Cyclohex-2-enyl benzoate (3ba)



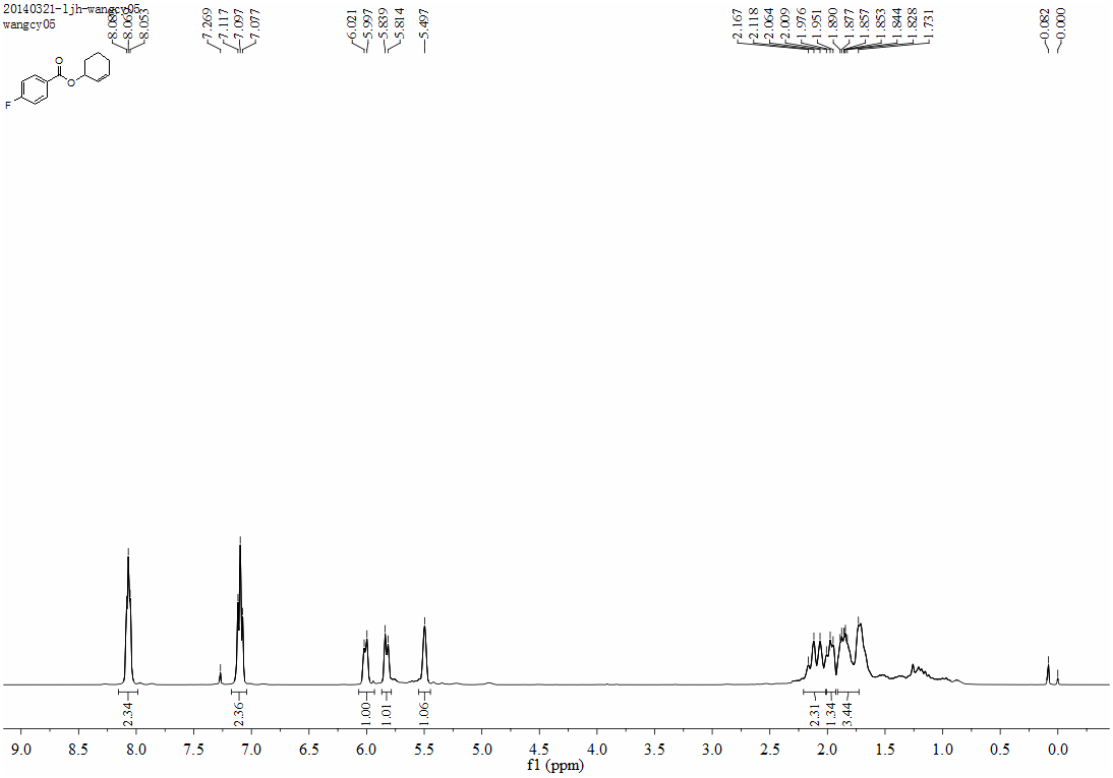



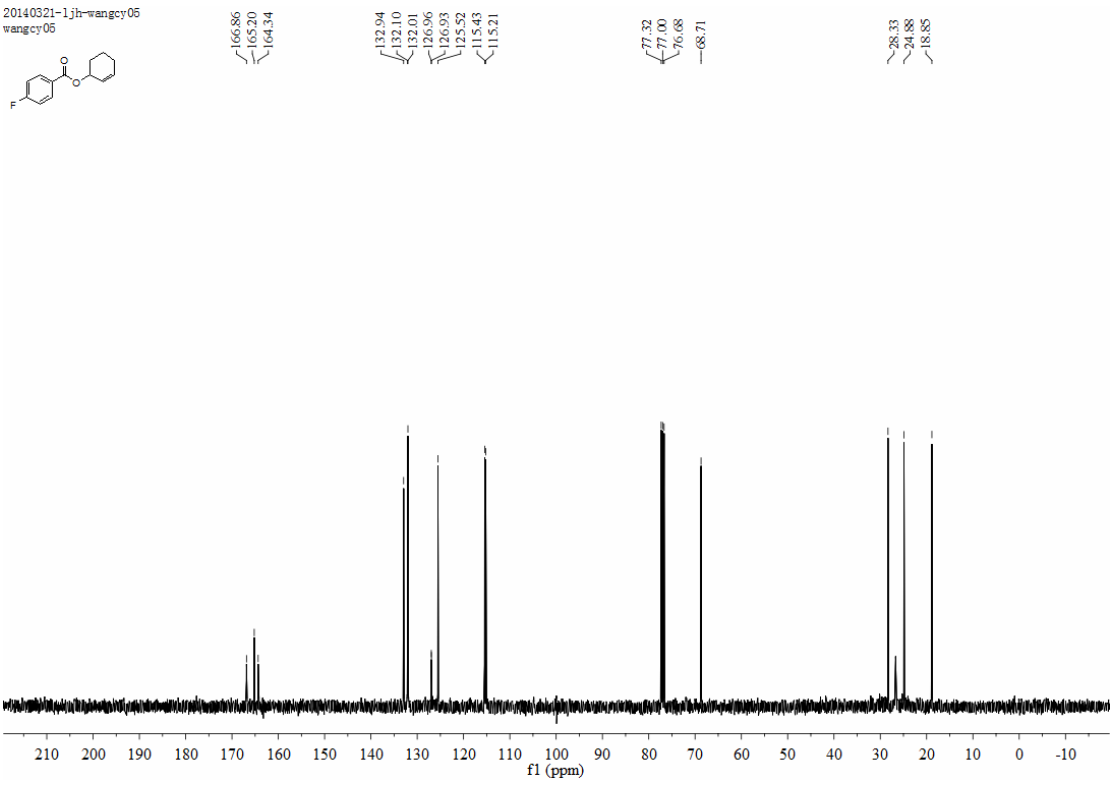
# Cyclohex-2-enyl 4-methylbenzoate (3ca)



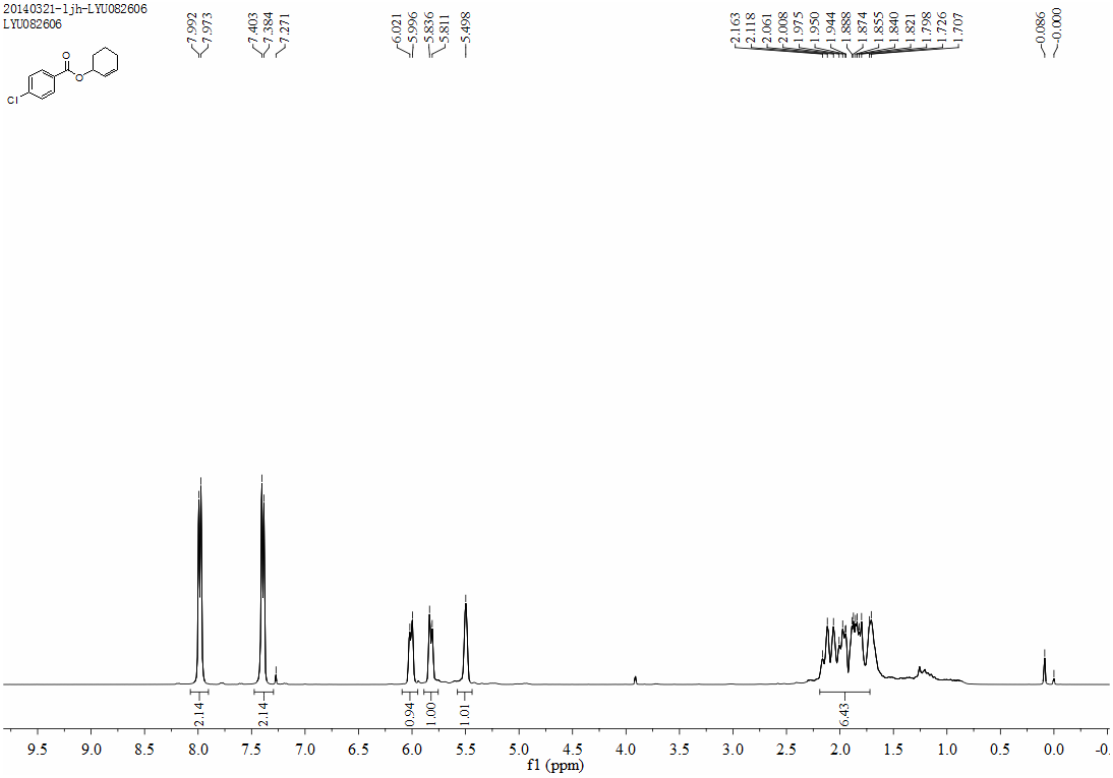



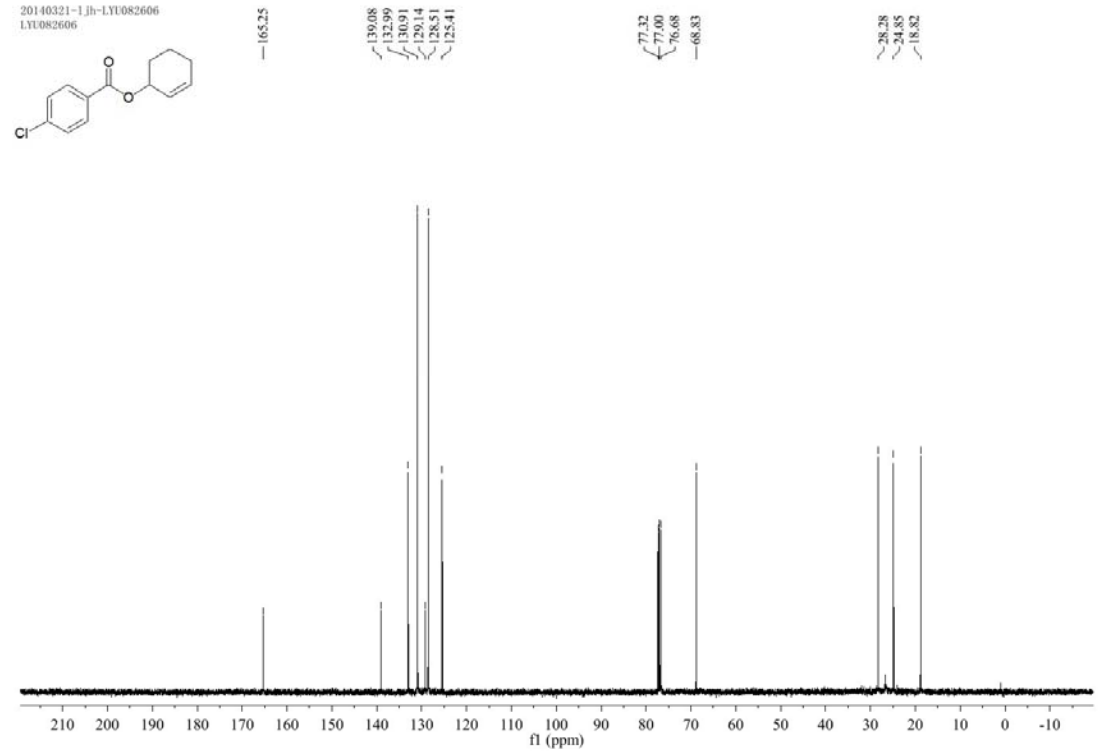
# Cyclohex-2-enyl 4-fluorobenzoate (3da)



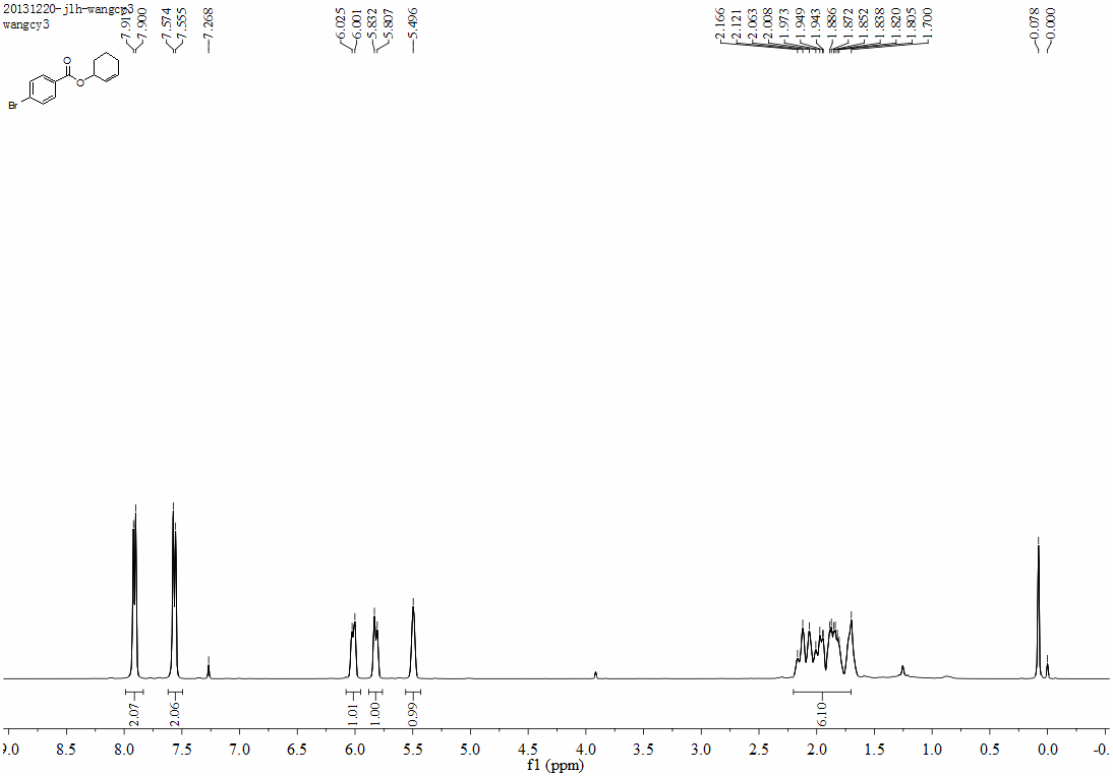



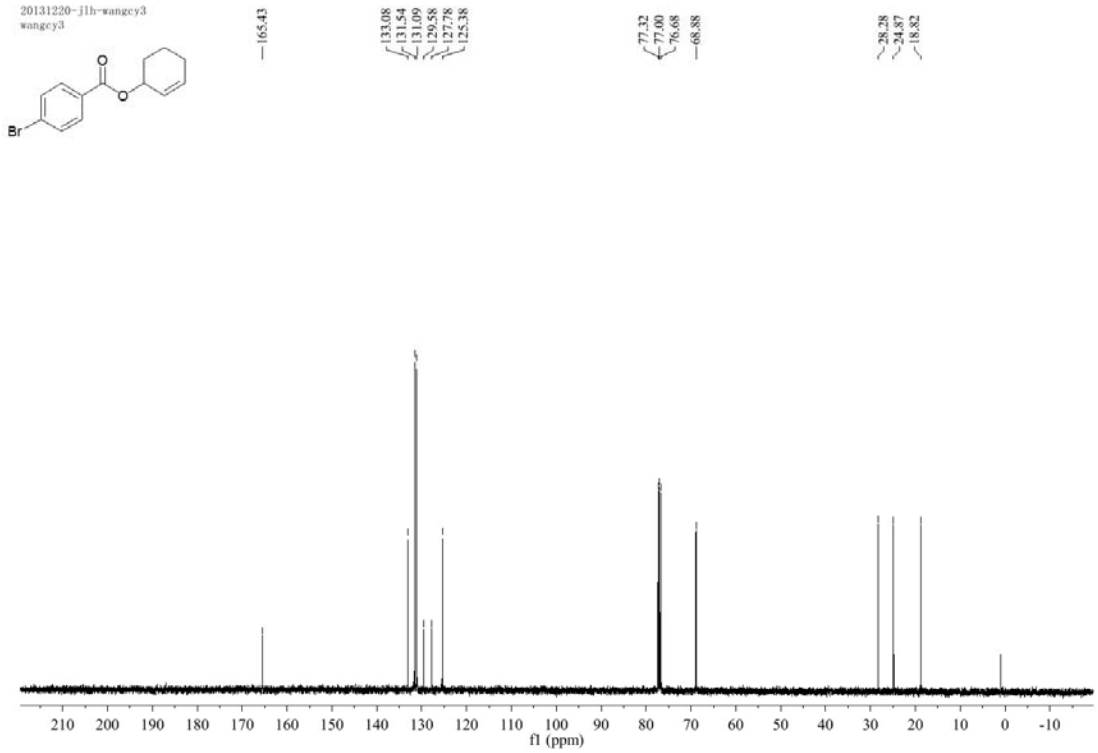
# Cyclohex-2-enyl 4-chlorobenzoate (3ea)



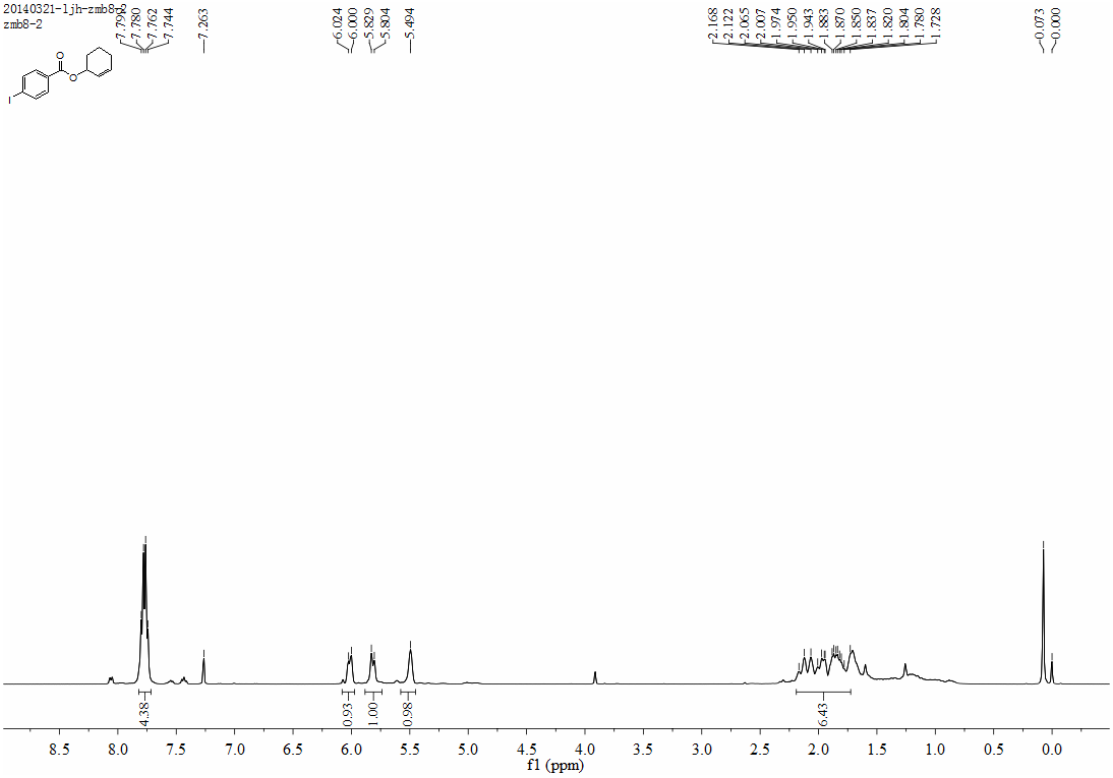



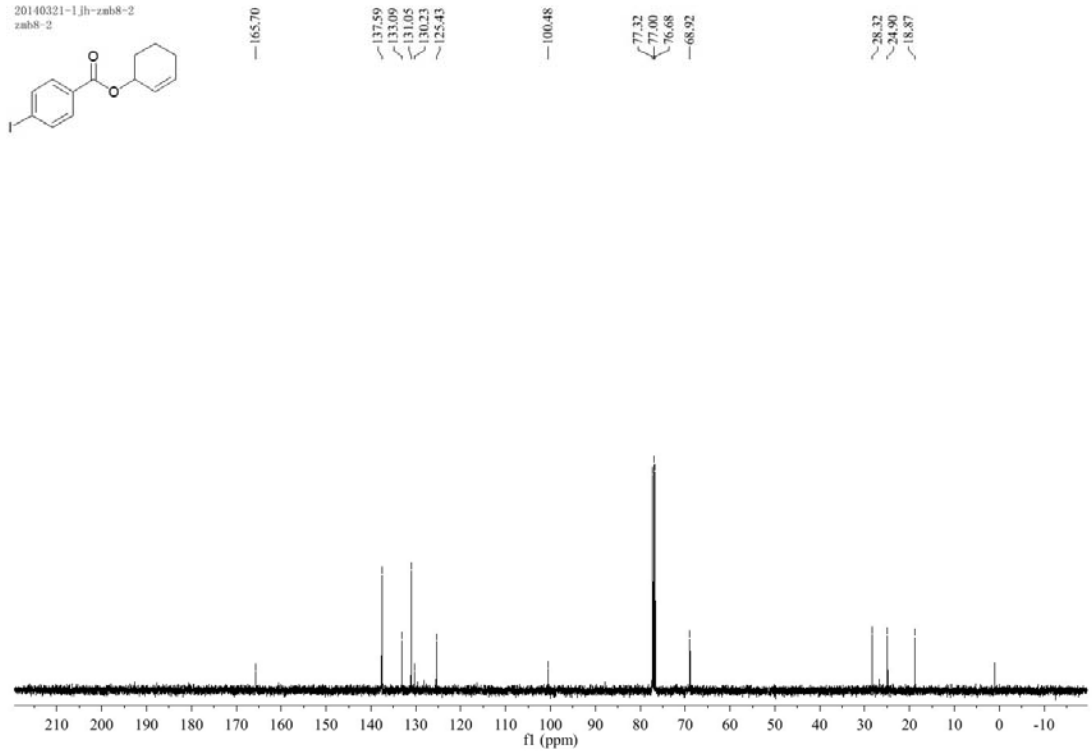
# Cyclohex-2-enyl 4-bromobenzoate (3fa)



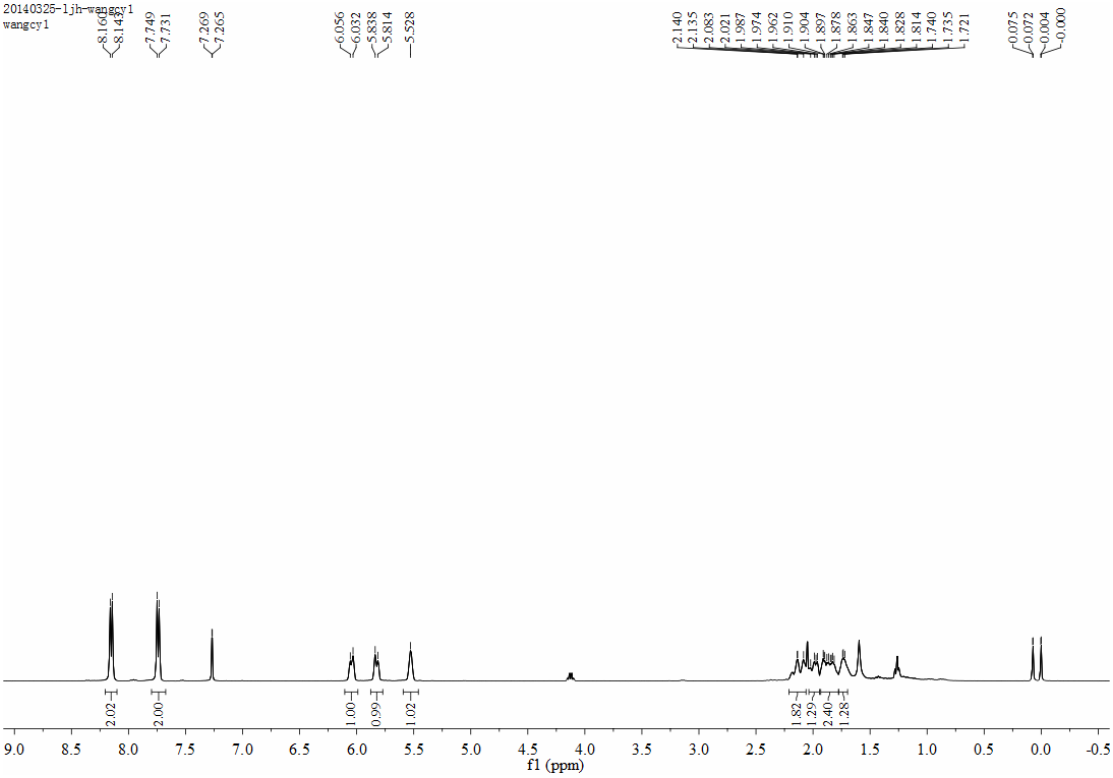



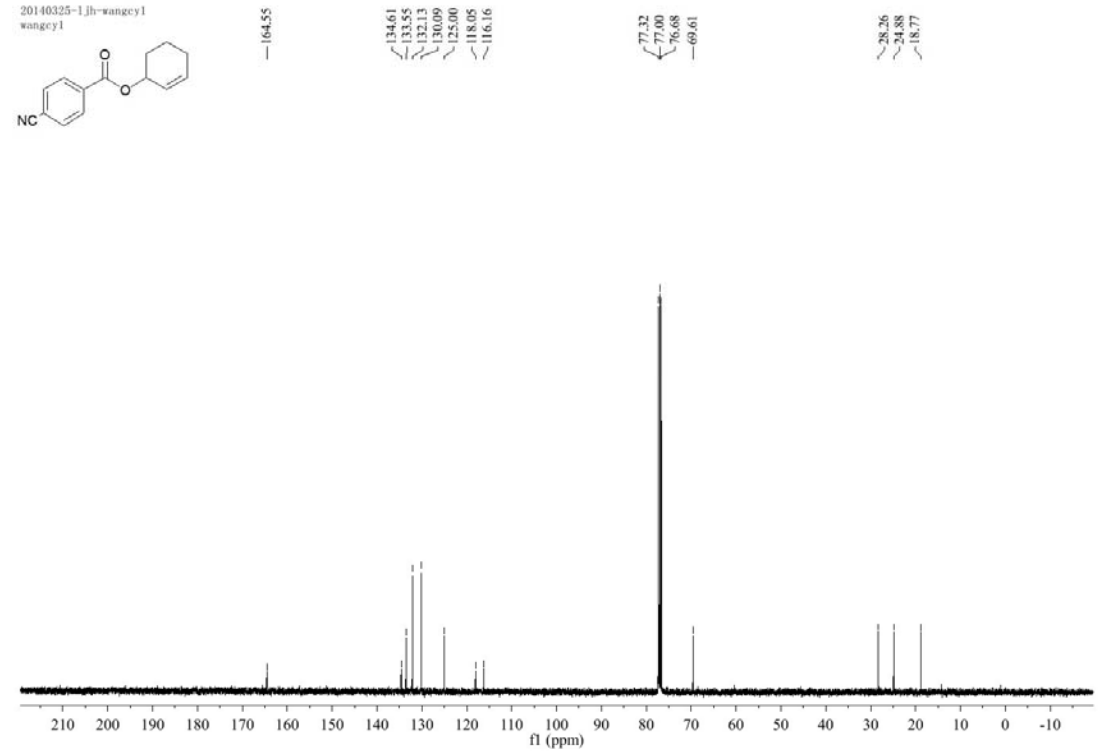
# Cyclohex-2-enyl 4-iodobenzoate (3ga)



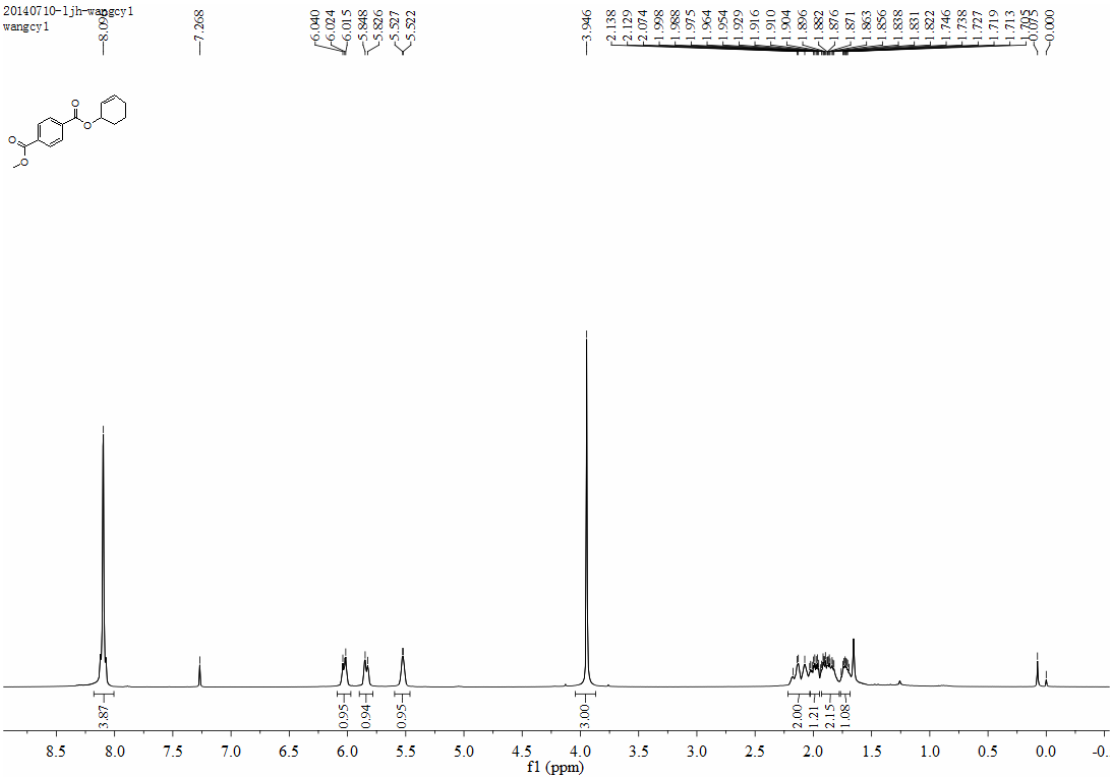



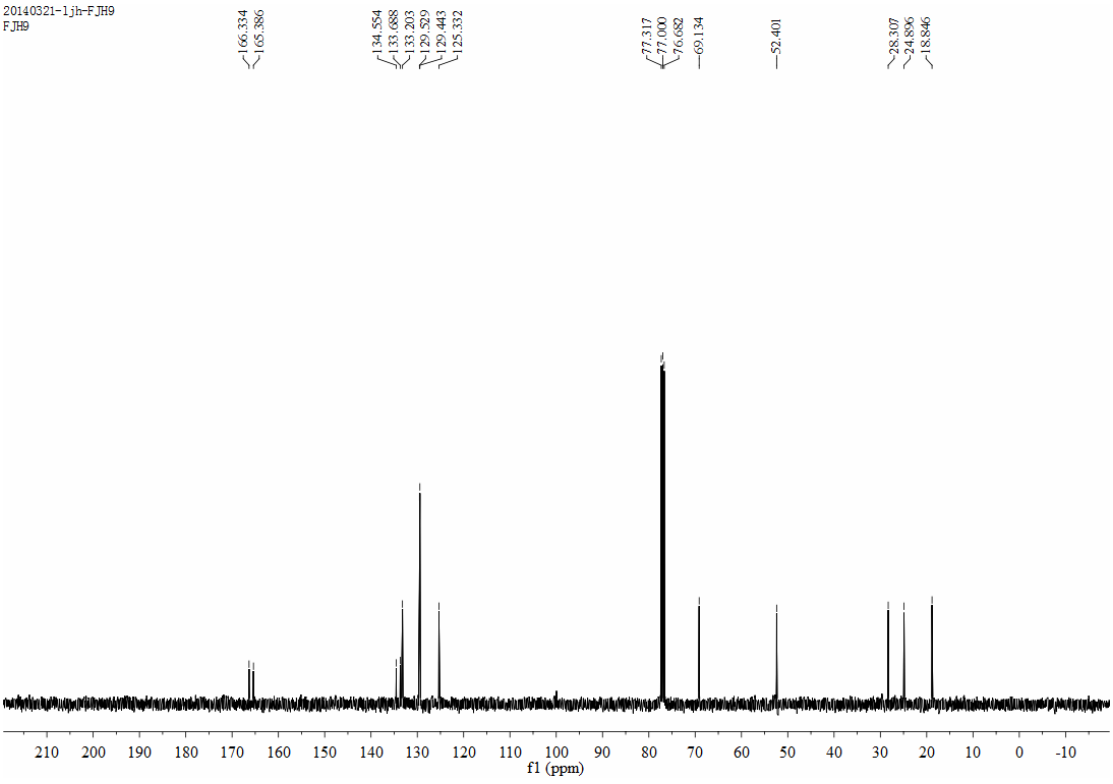
# Cyclohex-2-enyl 4-cyanobenzoate (3ha)



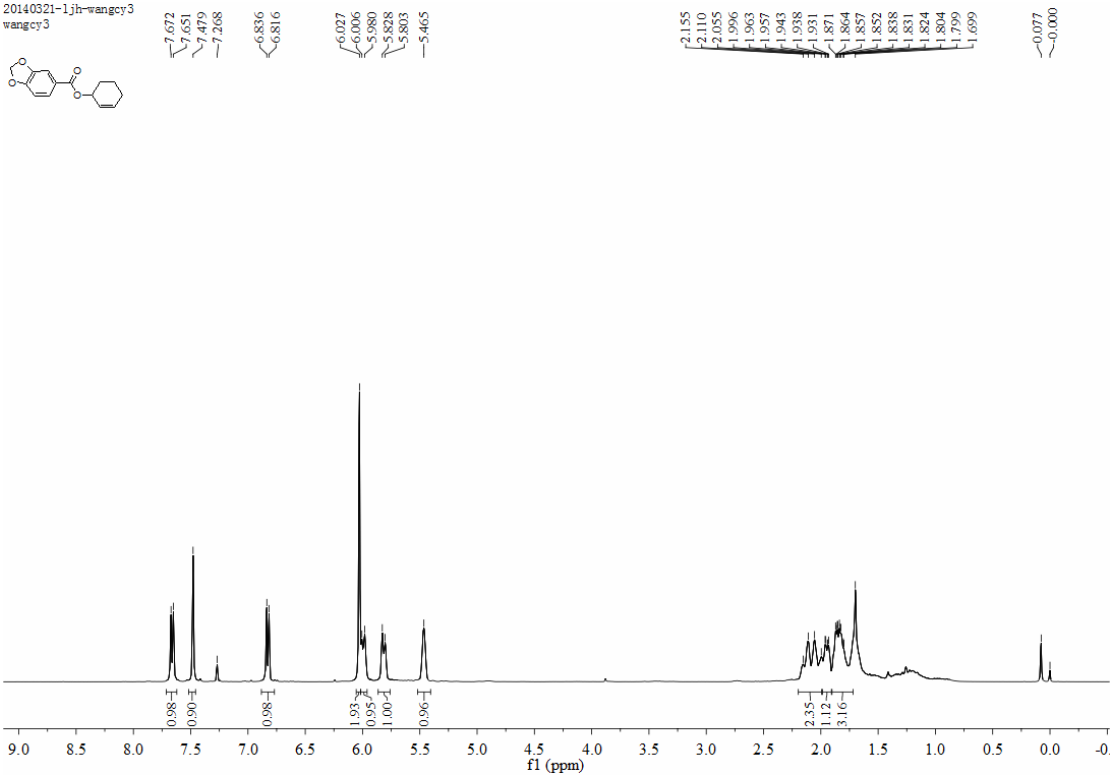



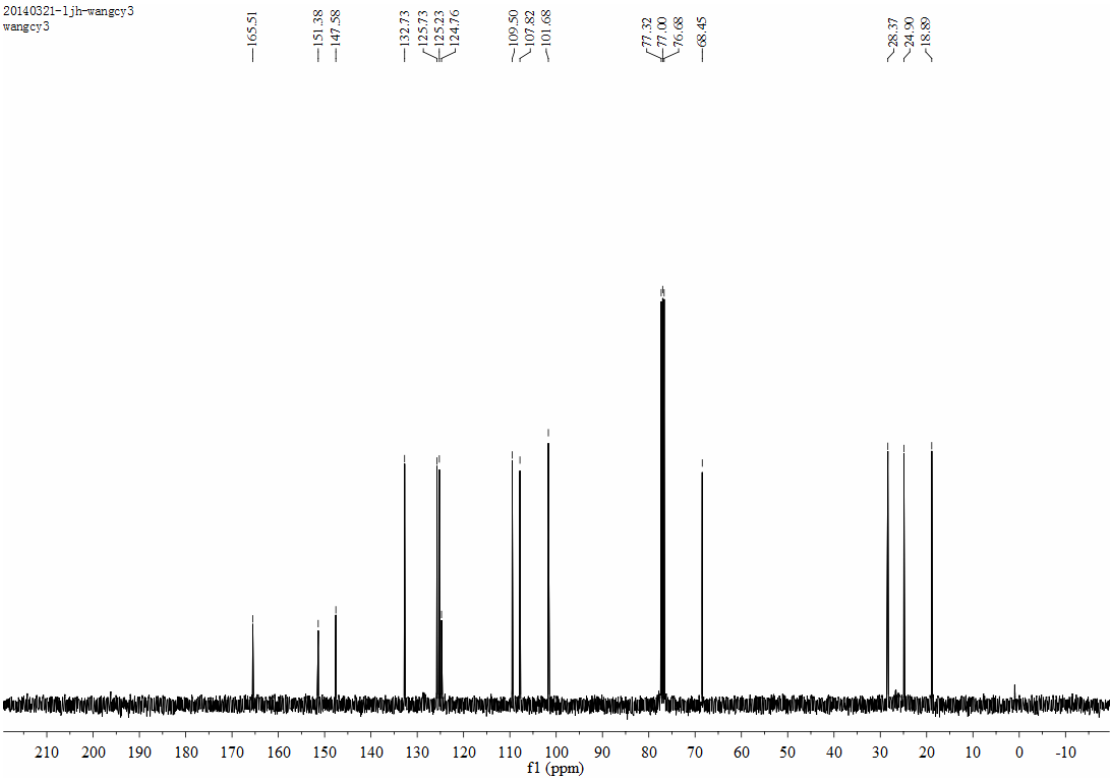
# Cyclohex-2-enyl methyl terephthalate (3ia)



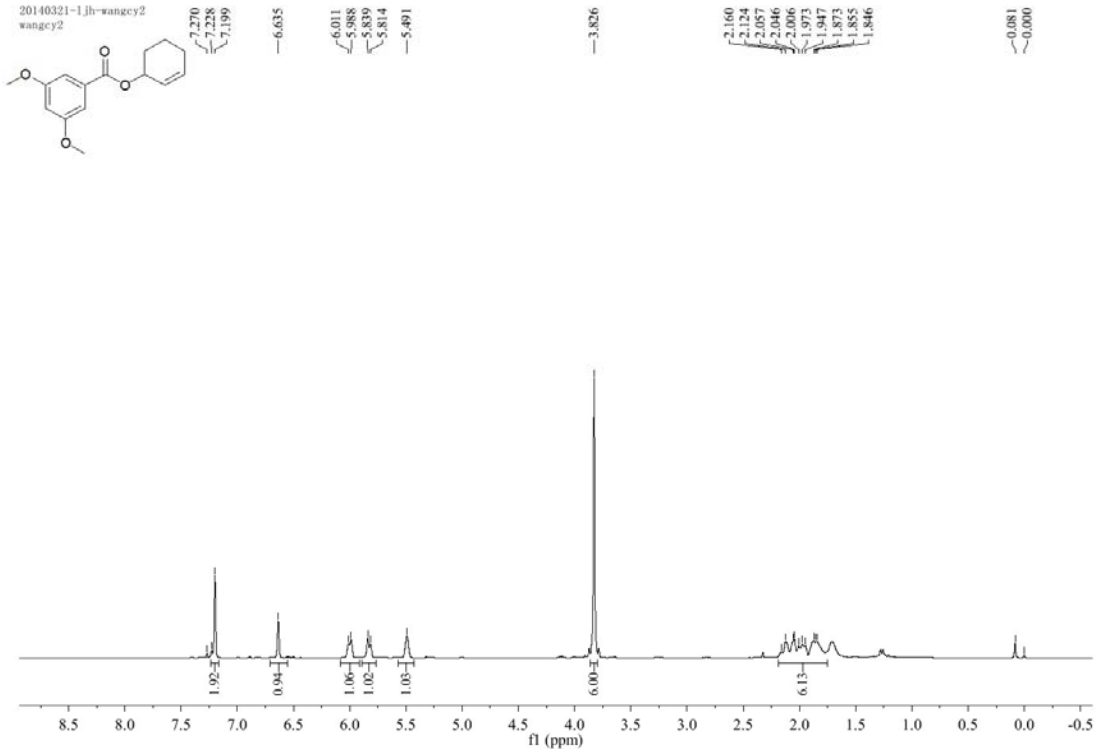



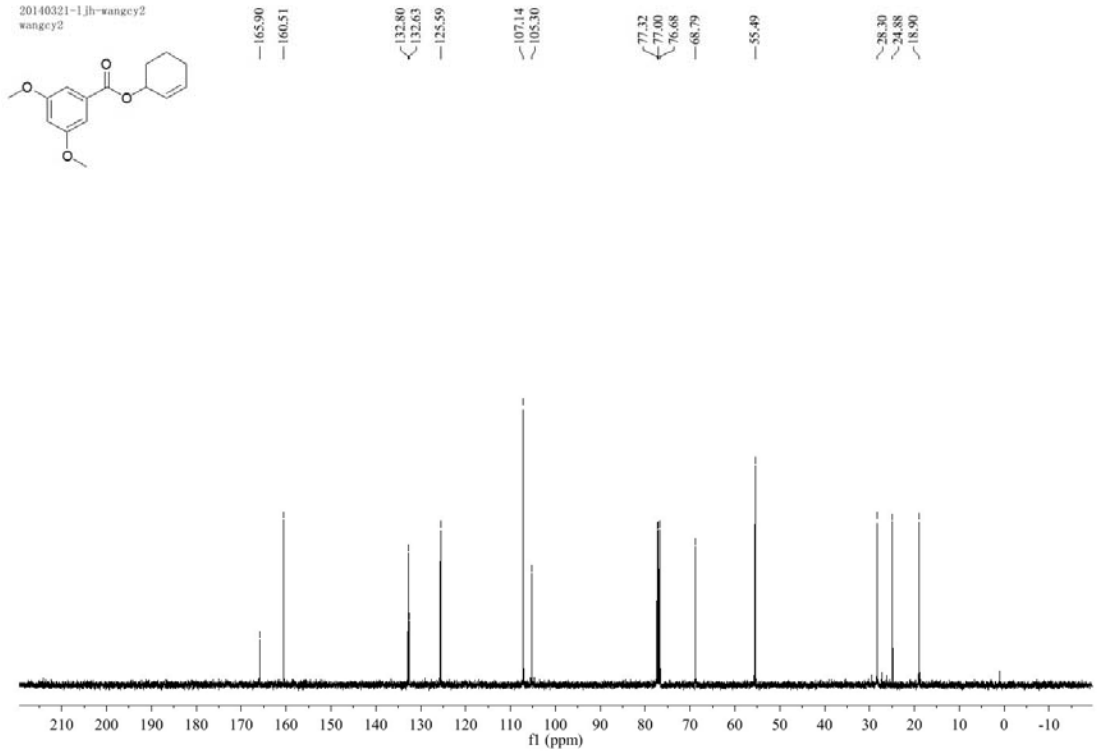
# Cyclohex-2-enyl benzo[*d*][1,3]dioxole-5-carboxylate (3ja)



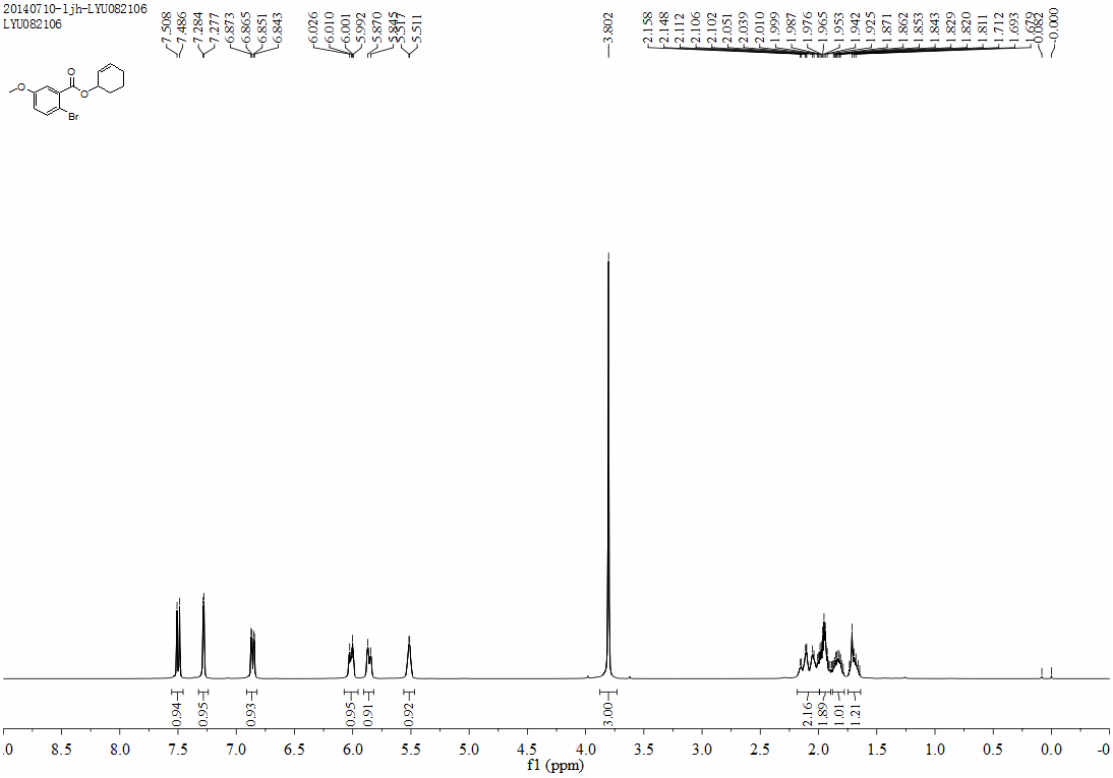



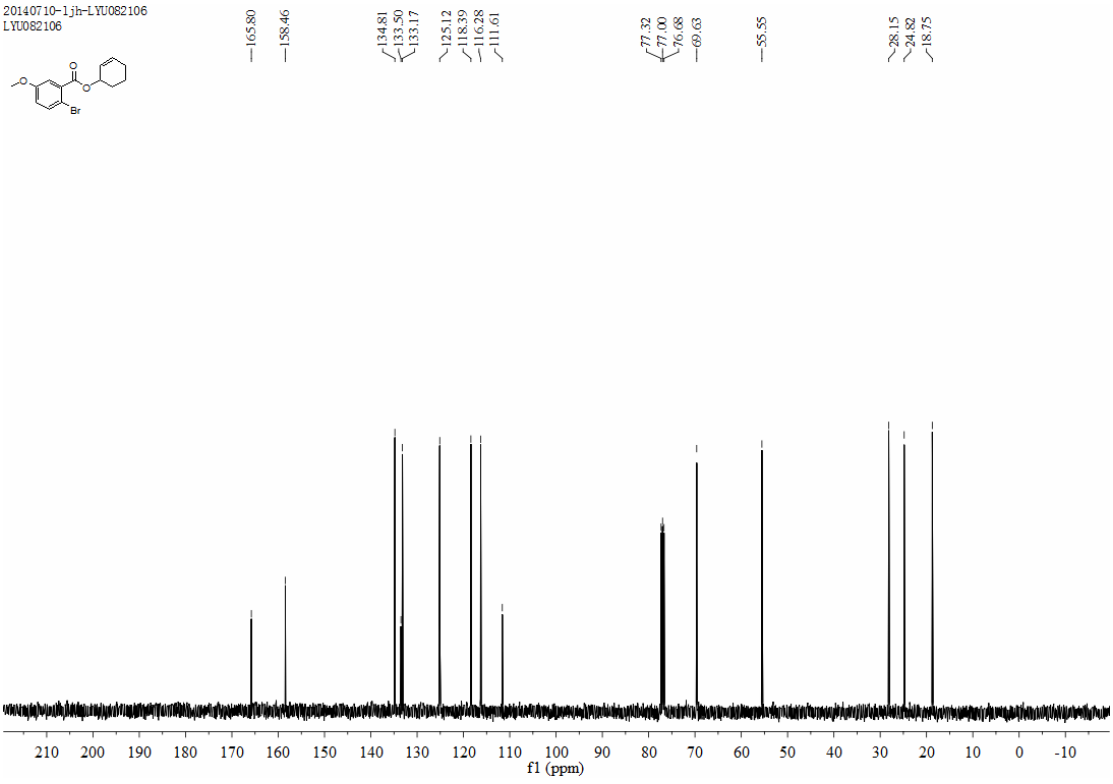
# Cyclohex-2-enyl 3,5-dimethoxybenzoate (3ka)



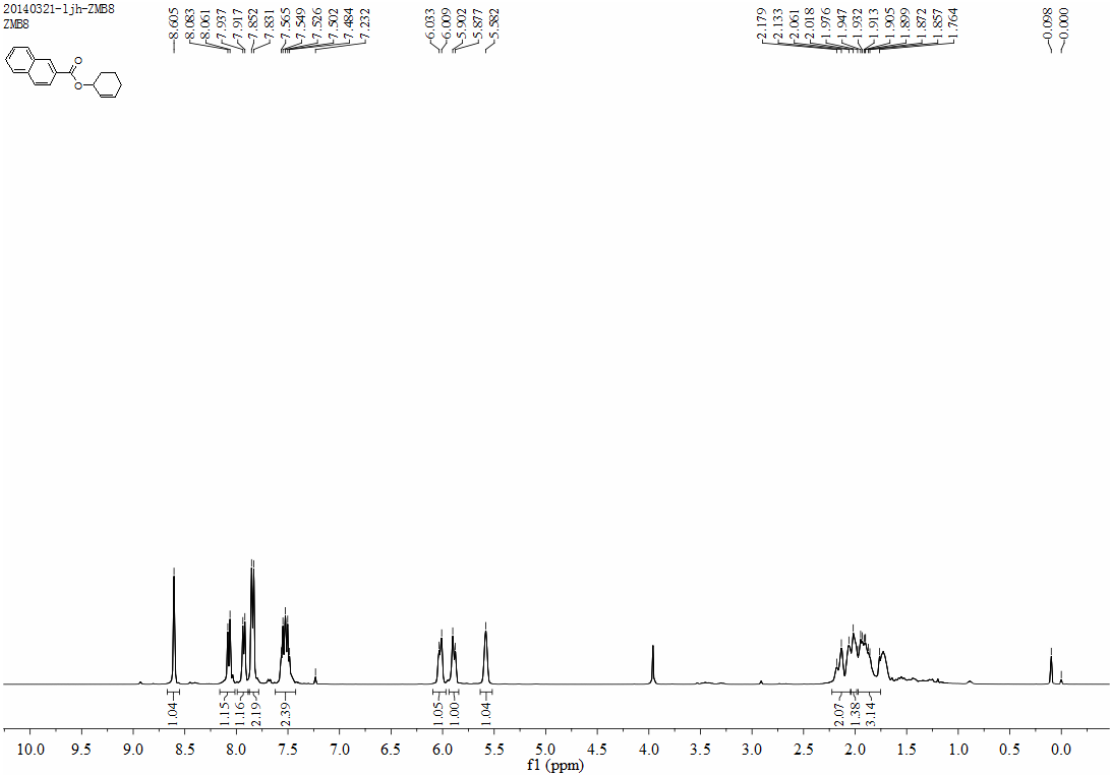



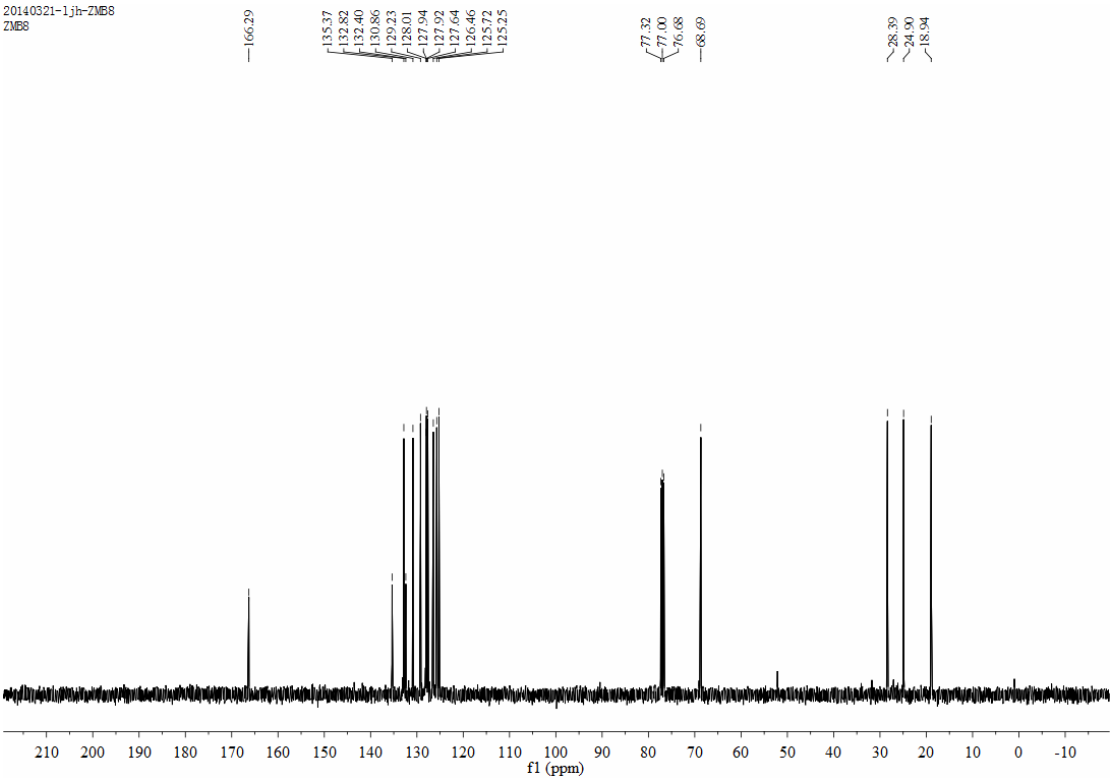
# Cyclohex-2-enyl 2-bromo-5-methoxybenzoate (3la)



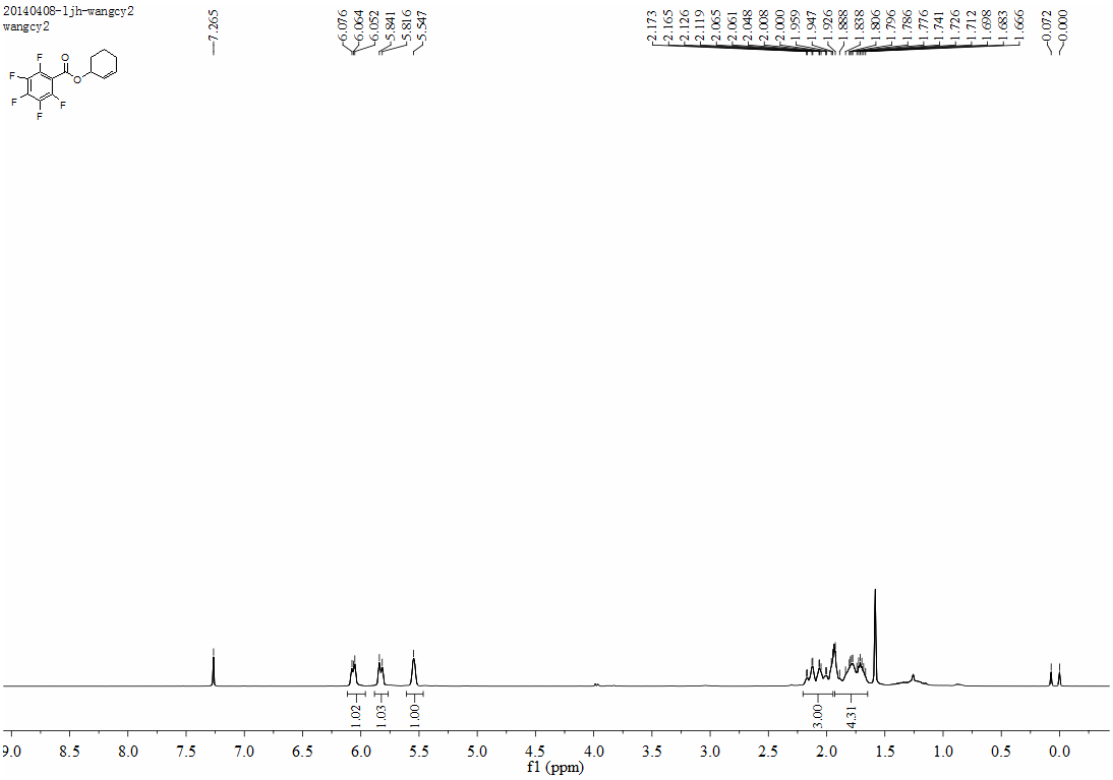



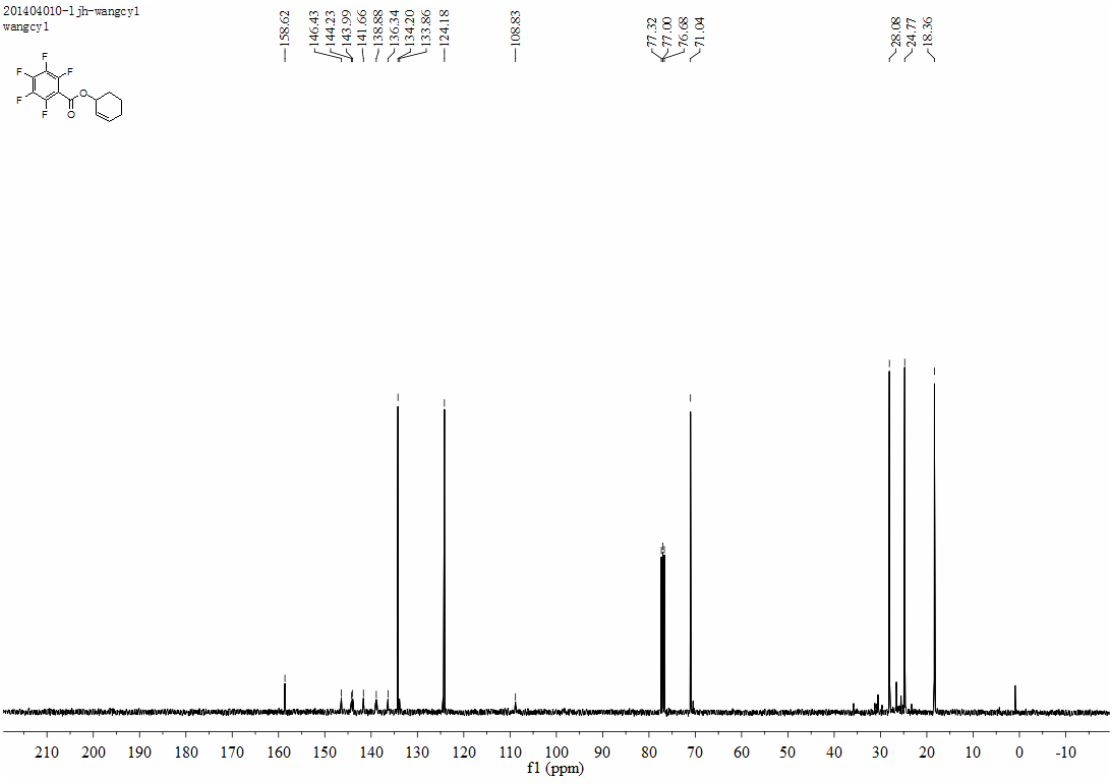
# Cyclohex-2-enyl 2-naphthoate (3ma)



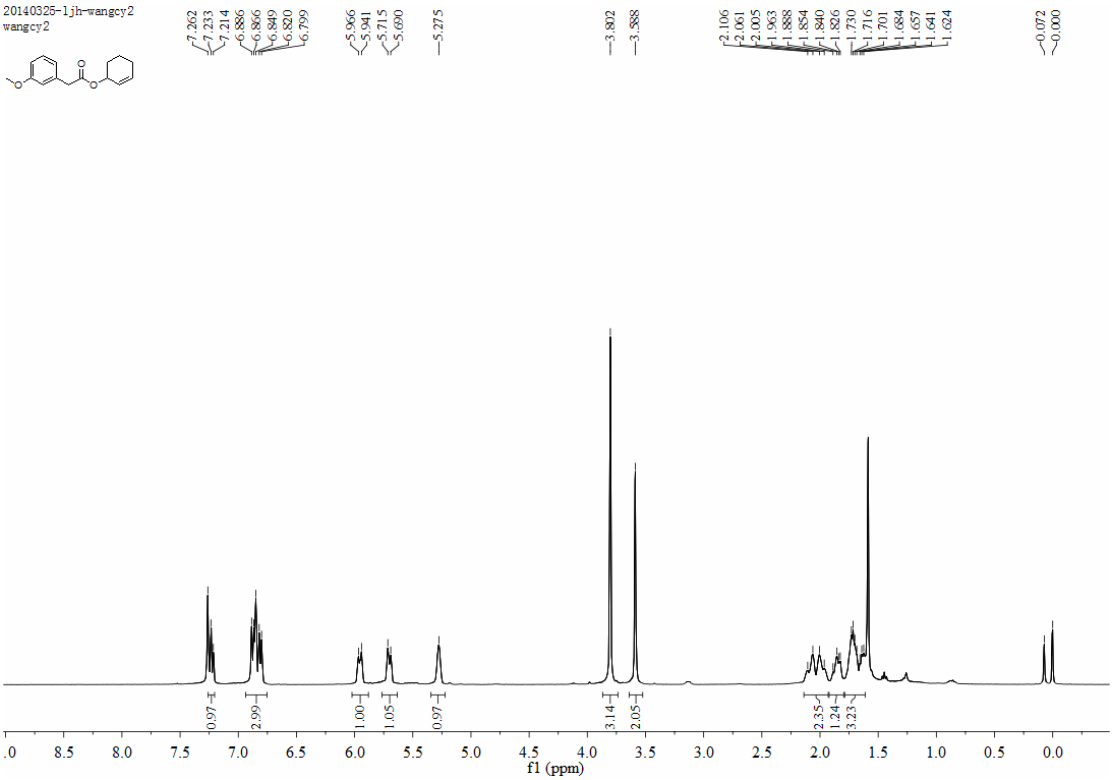



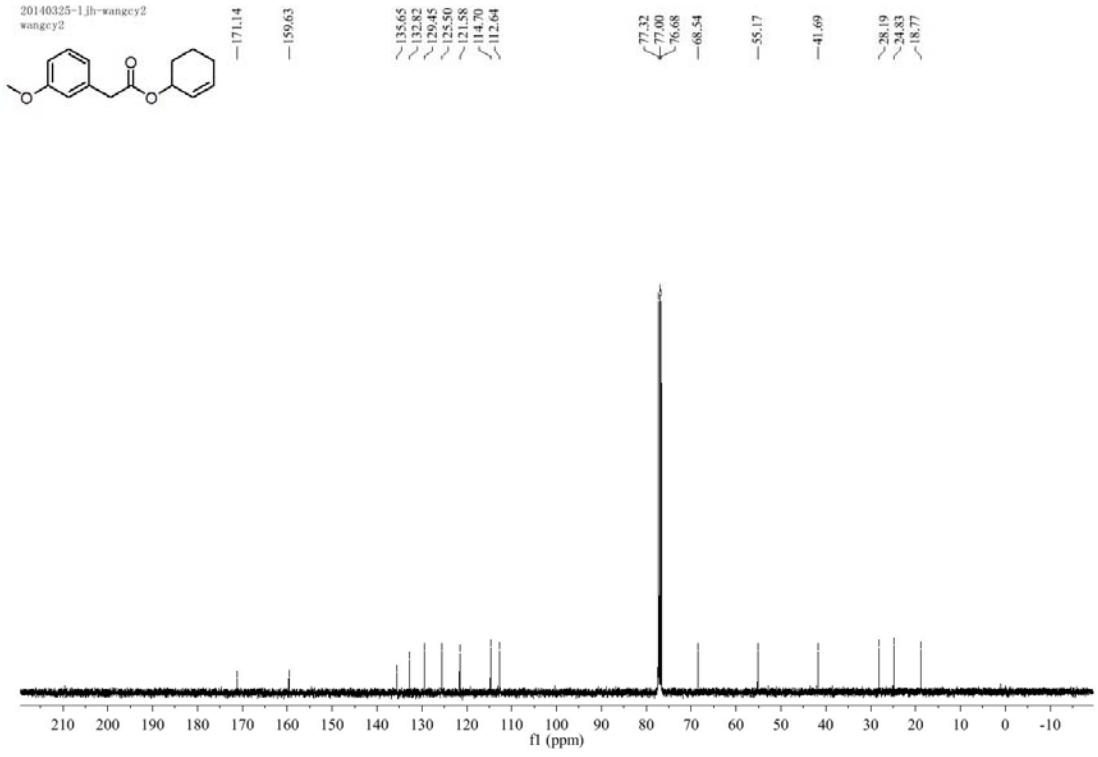
# Cyclohex-2-enyl 2,3,4,5,6-pentafluorobenzoate (3na)



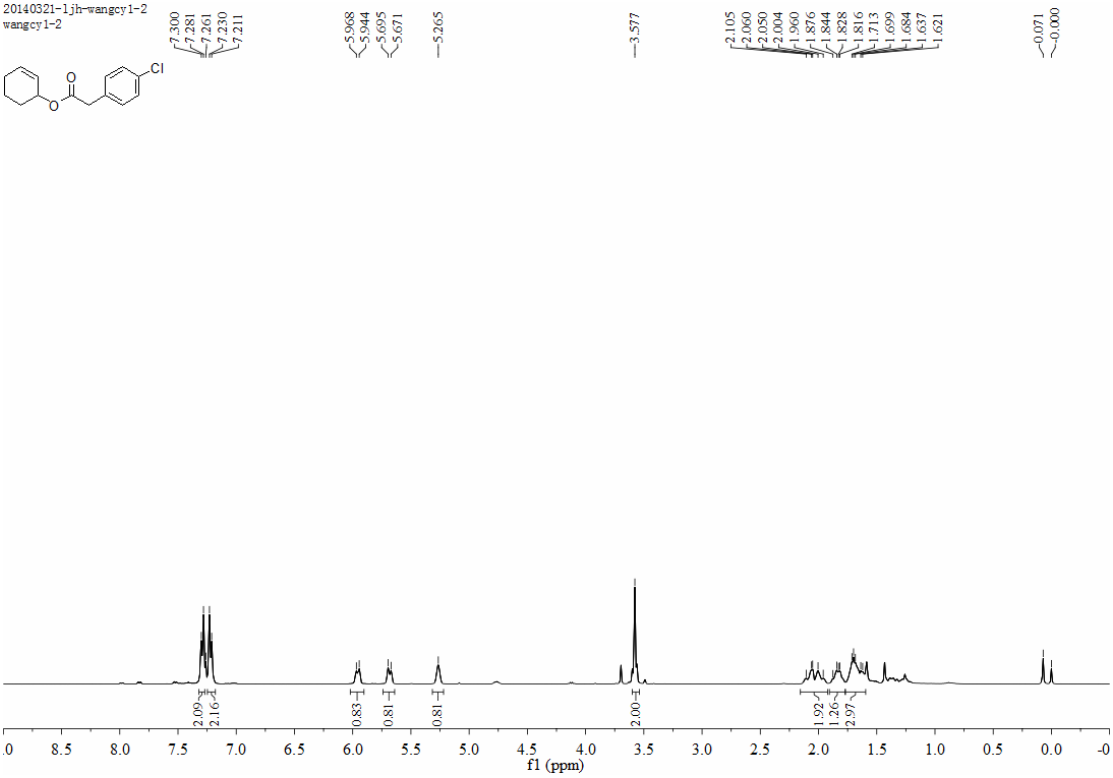



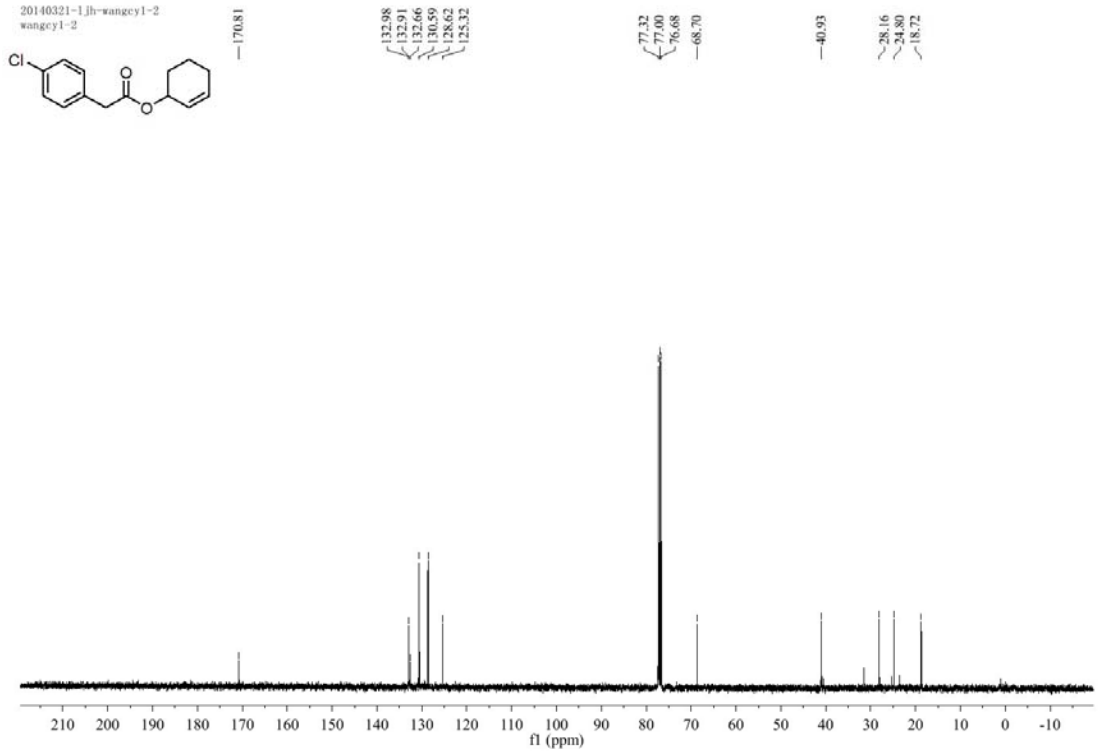
# Cyclohex-2-enyl 2-(3-methoxyphenyl)acetate (3oa)



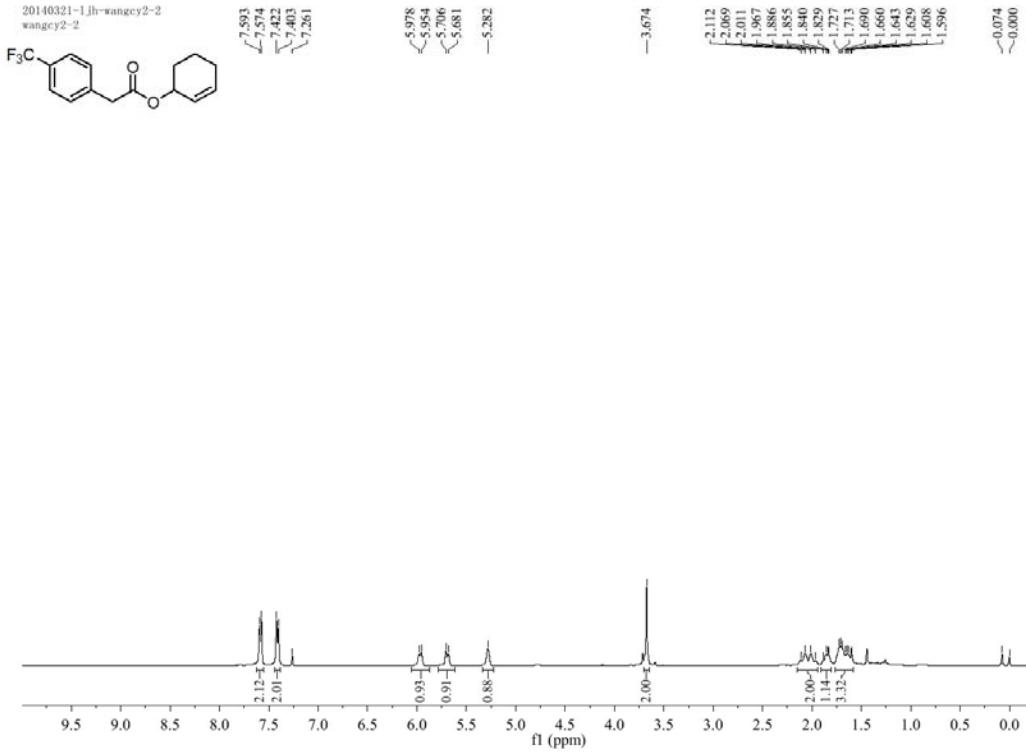



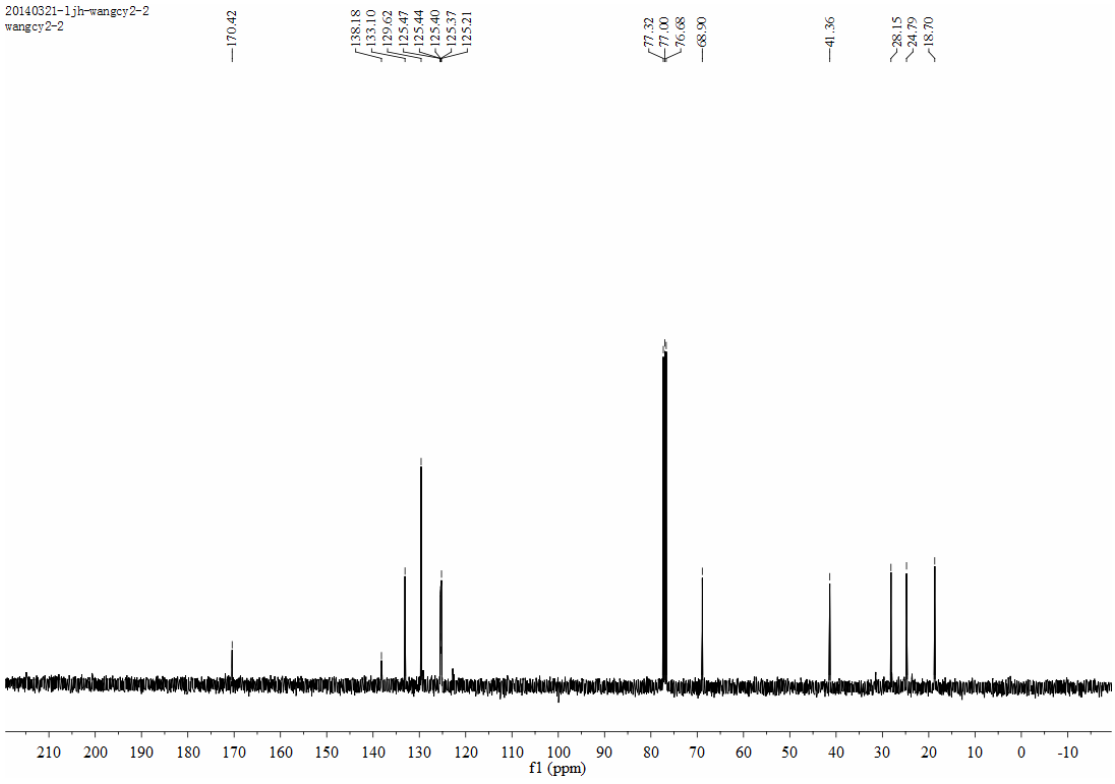
# Cyclohex-2-enyl 2-(4-chlorophenyl)acetate (3pa)



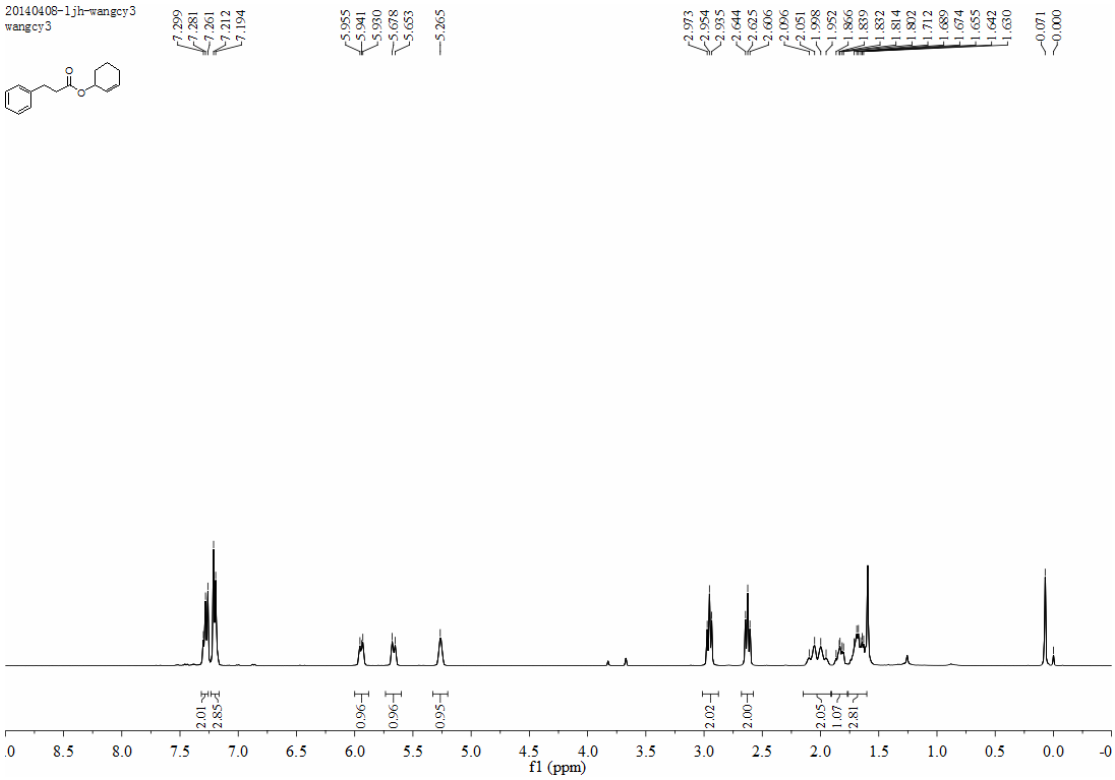



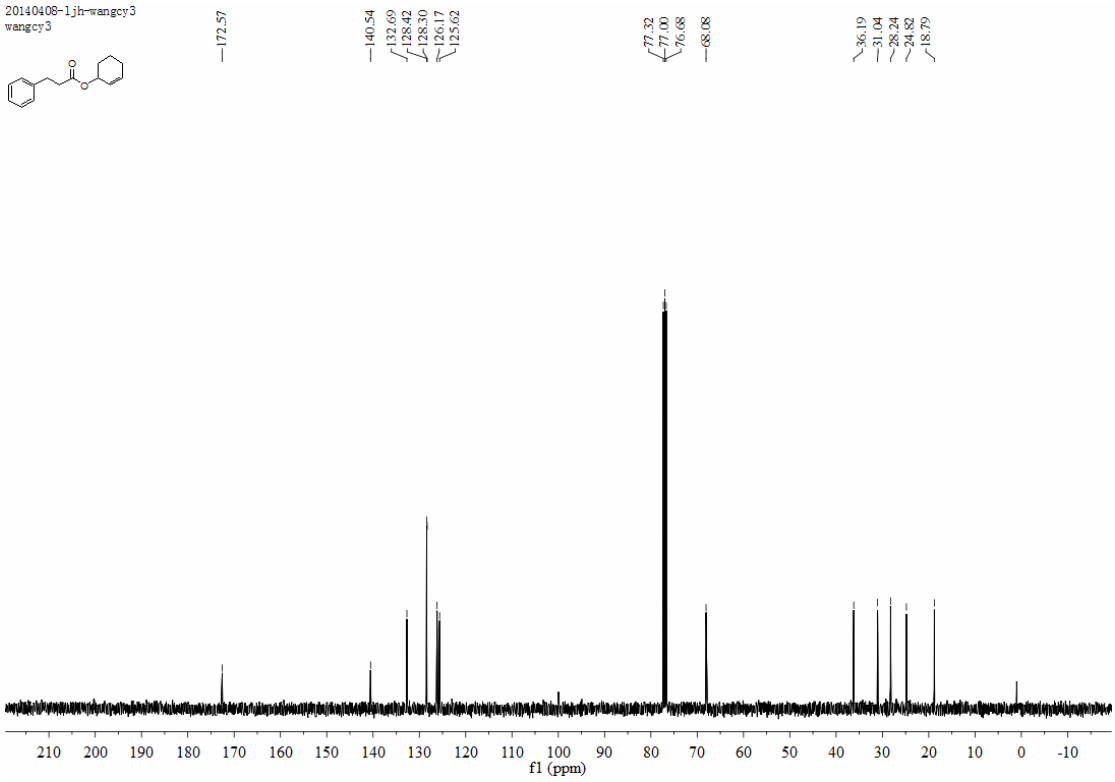
# Cyclohex-2-enyl 2-(4-(trifluoromethyl)phenyl)acetate (3qa)



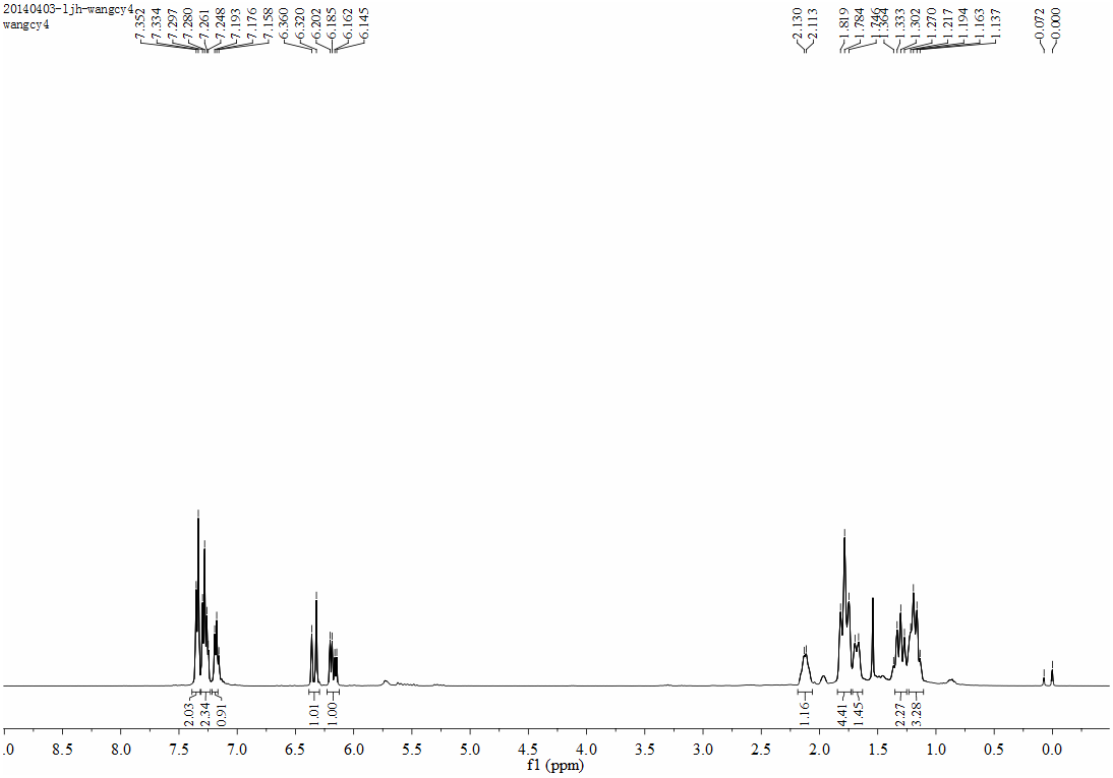



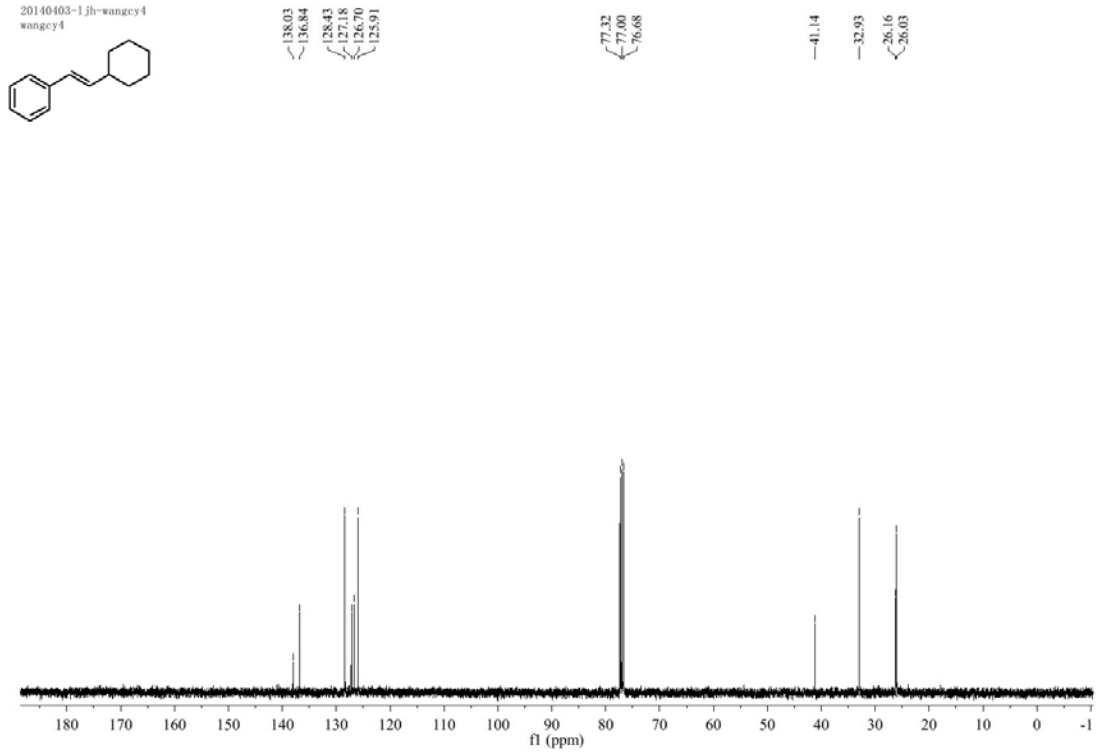
# Cyclohex-2-enyl 3-phenylpropanoate (3ra)



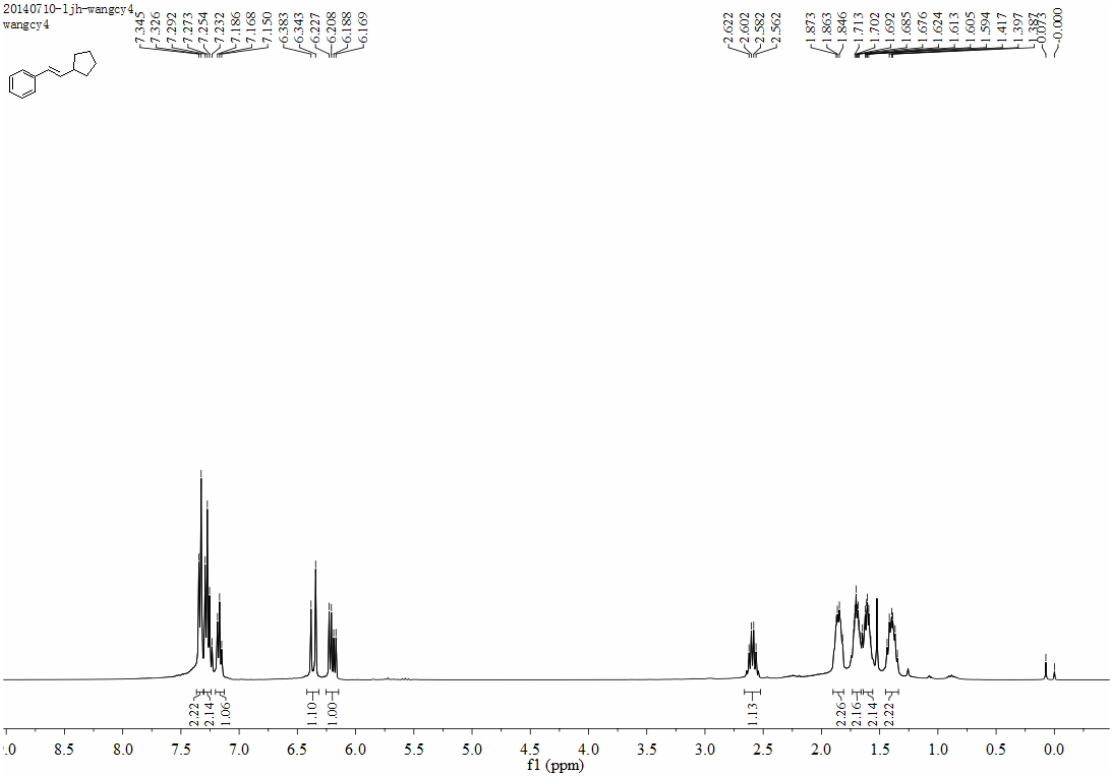



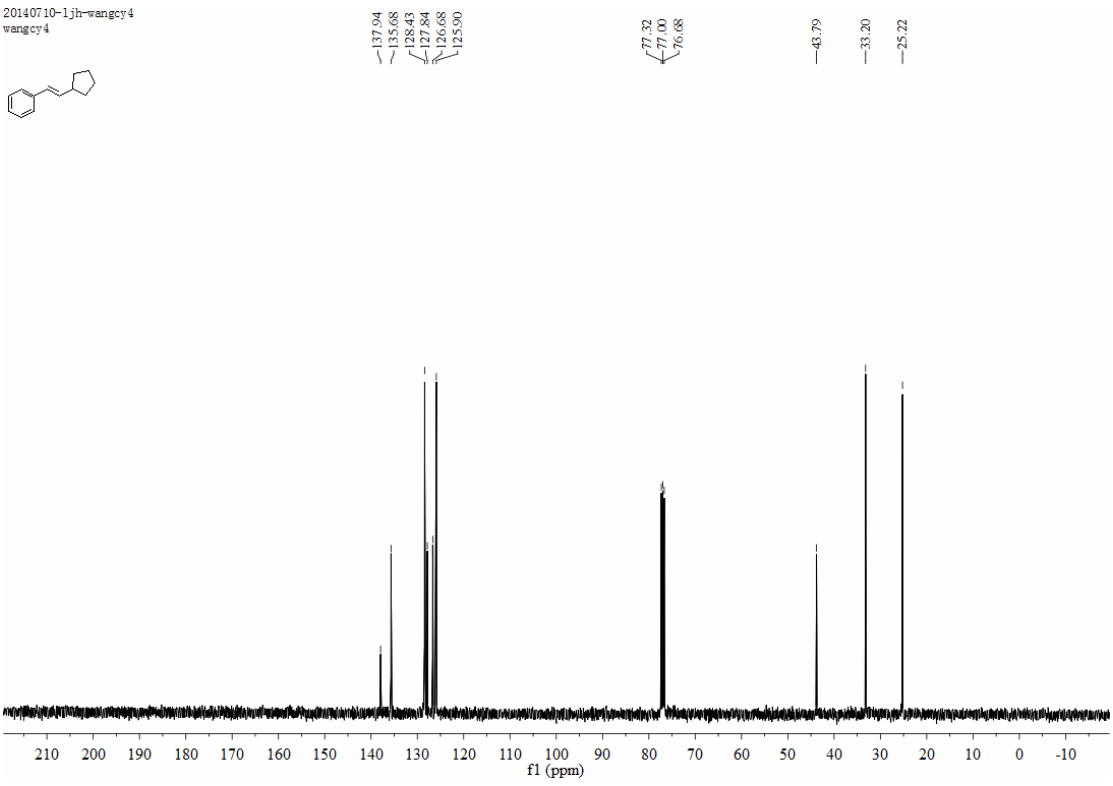
# (*E*)-(2-cyclohexylvinyl)benzene (4ta)



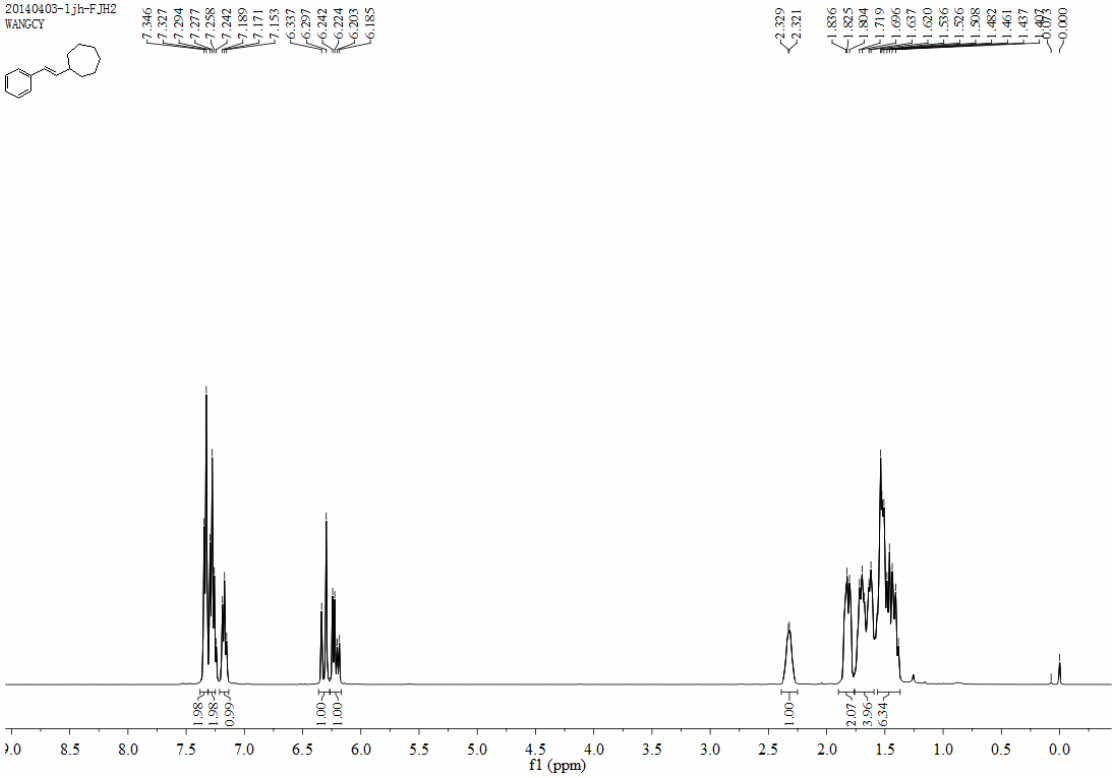



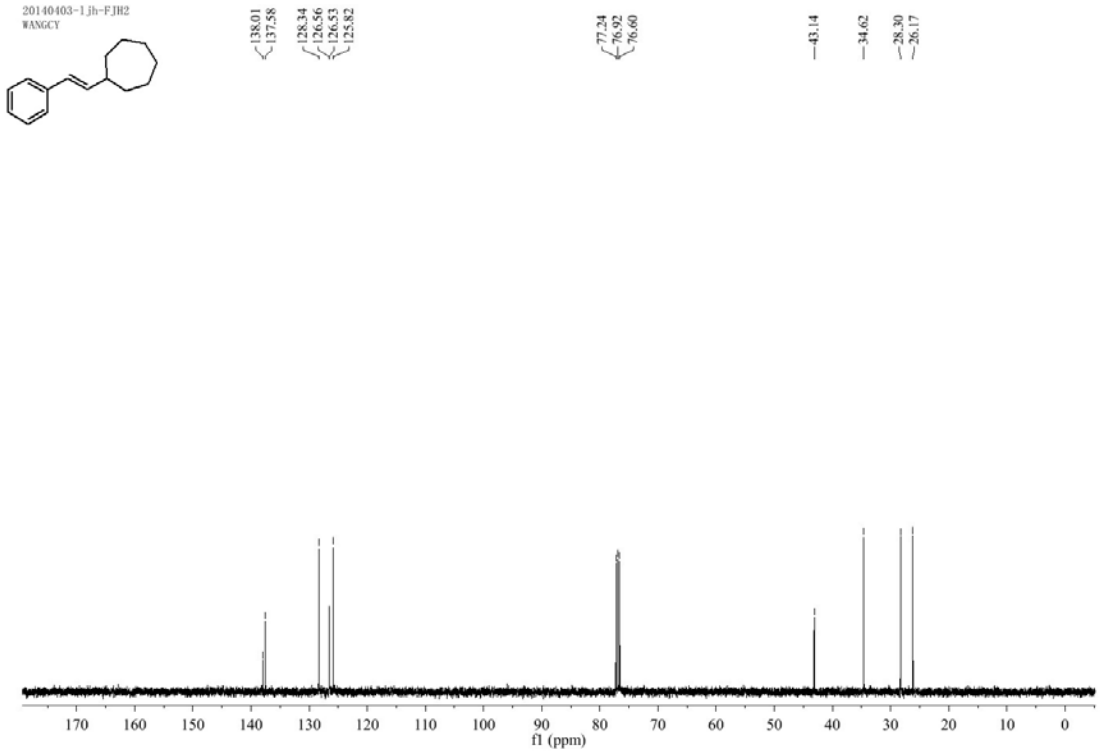
# (*E*)-(2-cyclopentylvinyl)benzene (4tb)



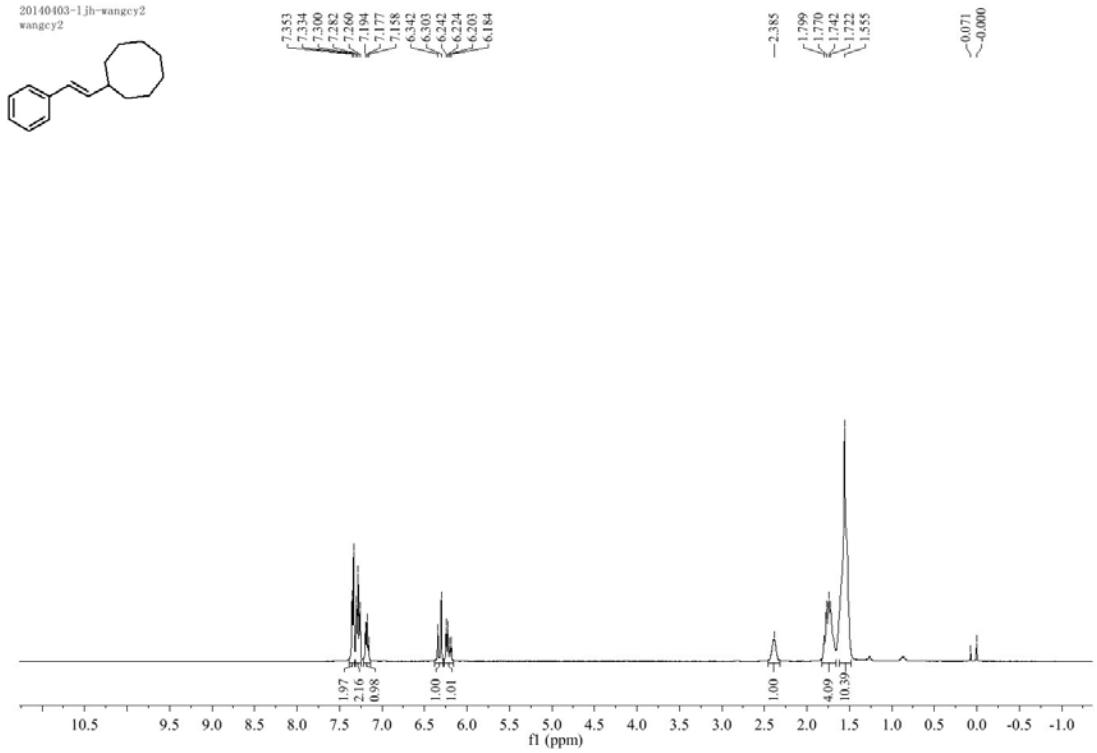



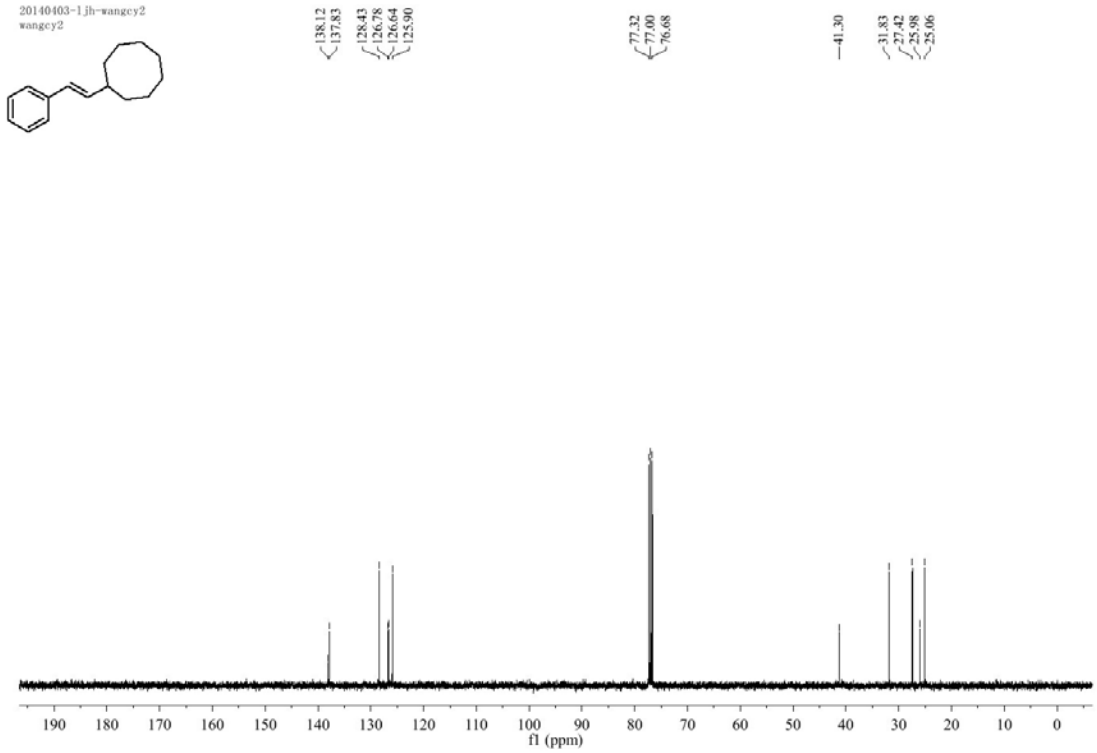
## (*E*)-styrylcycloheptane (4tc)



## (*E*)-styrylcyclooctane (4td)



# 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (7a)