Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information for:

Synthesis of α,β-Unsaturated γ-Amino Esters with a Quaternary Center by Ruthenium-Catalyzed Codimerization of *N*-Acetyl α-Arylenamines and Acrylates

Qiu-Shi Wang, Jian-Hua Xie, Lu-Chuan Guo and Qi-Lin Zhou*

State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China.

CONTENTS:

General: All the air or moisture sensitive reactions and manipulations were performed under nitrogen atmosphere by using standard Schlenk techniques and Vacuum Atmospheres Drybox (VAC DRI-LAB HE 493). Melting points were measured on a RY-I apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AV 400 spectrometers or a Varian Mercury Plus 400 spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm down field from internal Me_4Si. Mass spectra were recorded on IonSpec FT-ICR mass spectrometer with ESI resource. GC analyses were performed using Hewlett Packard Model HP 6890 Series. *N*,*N*-Dimethylformamide and 1,2-dichloroethane were distilled from calcium hydride before use. Toluene and

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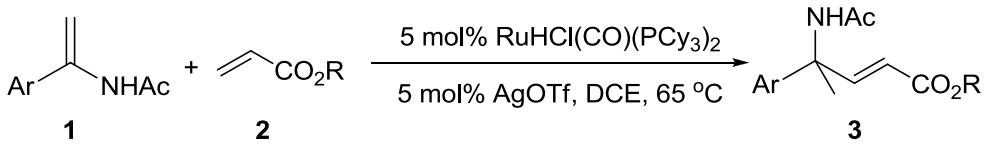
dioxane were distilled from sodium/benzophenone ketyl. Acrylates were purified by vacuum distillation. The *N*-acetyl enamines were prepared from the corresponding aromatic ketones according to the literature methods, unless otherwise stated.[1] AgX (X = BF_4^-, OTf^-, ClO_4^-, PF_6^- and SbF_6^-) were purchased from Aldrich Co. and used without further purification. $RuHCl(CO)(PCy_3)_2$ [2] and $NaBAr_F$ [3] was prepared according to the literature methods.

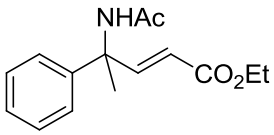
(A) General Procedure for Codimerizaiton of *N*-Acetyl Enamines with Acrylates



1 **2** **3**

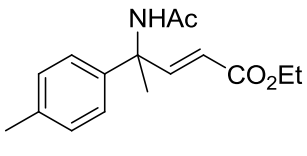
General procedure: To a dry Schlenk tube equipped with a stirring bar was added $RuHCl(CO)(PCy_3)_2$ (7.3 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), enamine (0.2 mmol), 4Å molecular sieves (100 mg), and degassed anhydrous 1,2-dichloroethane (3 mL) under an nitrogen atmosphere. The mixture was stirred at room temperature for 5 min and a yellow solution was obtained. The acrylate (1.0 mmol) was added into the Schlenk tube and the slightly yellow solution was stirred at 65 °C under nitrogen for 3~72 h. After removal of molecular sieves by filtration, the product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate. The substrate conversion was determined by measuring the weight of the recovery of *N*-acetyl enamine, and the yield was determined by measuring the weight of the product.

(*E*)-ethyl 4-acetamido-4-phenylpent-2-enoate (3a)



96 % yield, white solid, m.p.: 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.11 (m, 6H), 6.56 (brs, 1H), 5.75 (d, *J* = 15.9 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.80 (s, 3H), 1.64 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.4, 150.7, 143.3, 128.5, 127.3, 125.4, 119.9, 60.41, 59.16, 26.29, 23.67, 14.10. HRMS (ESI) calcd for $C_{15}H_{19}NO_3Na$ ($[M+Na]^+$): 284.1257; Found: 284.1258.

(*E*)-ethyl 4-acetamido-4-p-tolylpent-2-enoate (3b)



91 % yield, white solid, m.p.: 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 15.9 Hz, 1H), 7.16 (dd, *J* = 33.7, 8.2 Hz, 4H), 6.63 (brs, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.88 (s, 3H), 1.72 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.4, 151.0, 140.4, 136.8, 129.1, 125.3, 119.6, 60.3, 58.8, 26.1, 23.6, 20.7, 14.0. HRMS (ESI) calcd for

[1] M. J. Burk, G. Casy, N. B. Johnson, *J. Org. Chem.* **1998,** *63*, 6084.
[2] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* **1999**, *18*, 2043.
[3] M. Brookhart, B. Grant Jr., A. F. Volpe, *Organometallics*, **1992**, *11*, 3920.

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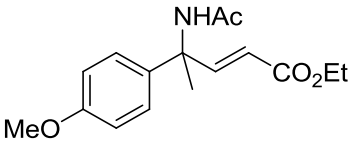
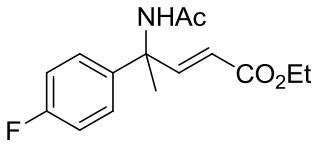
$C_{16}H_{21}NO_3Na$ ([M+Na]$^+$): 298.1414; Found: 298.1418.

(*E*)-ethyl 4-acetamido-4-(4-methoxyphenyl)pent-2-enoate (3c)



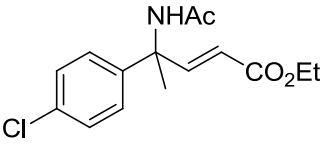
90 % yield, colorless oil, solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 16.3, 12.3 Hz, 3H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.43 (brs, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 4.17 (dd, *J* = 14.1, 7.0 Hz, 2H), 3.78 (s, 3H), 1.93 (s, 3H), 1.77 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.21, 166.44, 158.65, 151.02, 135.25, 126.73, 119.54, 113.77, 60.34, 58.75, 55.10, 25.92, 23.70, 14.06. HRMS (ESI) calcd for $C_{16}H_{21}NO_4Na$ ([M+Na]$^+$): 314.1363; Found: 314.1367.

(*E*)-ethyl 4-acetamido-4-(4-fluorophenyl)pent-2-enoate (3d)



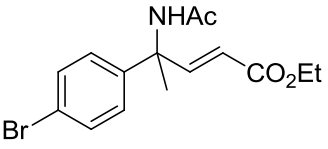
85 % yield, colorless oil, solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 15.9 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.03 – 6.92 (m, 2H), 6.70 (brs, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.89 (s, 3H), 1.69 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.3, 161.7 (d, *J* = 245.0 Hz), 150.4, 139.1 (d, *J* = 3.0 Hz), 127.2 (d, *J* = 8.1 Hz), 120.0, 115.1(d, *J* = 21.0 Hz), 60.5, 58.6, 26.7, 23.5, 14.1. HRMS (ESI) calcd for $C_{15}H_{18}FNO_3Na$ ([M+Na]$^+$): 302.1163; Found: 302.1157.

(*E*)-ethyl 4-acetamido-4-(4-chlorophenyl)pent-2-enoate (3e)



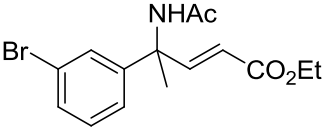
90 % yield, white solid, m.p.: 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 6.67 (brs, 1H), 5.84 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.90 (s, 3H), 1.67 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.3, 150.0, 141.9, 133.0, 128.5, 126.9, 120.3, 60.5, 58.7, 26.8, 23.5, 14.1. HRMS (ESI) calcd for $C_{15}H_{18}ClNO_3Na$ ([M+Na]$^+$): 318.0867; Found: 318.0868.

(*E*)-ethyl 4-acetamido-4-(4-bromophenyl)pent-2-enoate (3f)



93 % yield, white solid, m.p.: 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 12.1 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.87 (brs, 1H), 5.80 (d, *J* = 15.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.83 (s, 3H), 1.59 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.2, 149.9, 142.5, 131.4, 127.2, 121.0, 120.2, 60.5, 58.6, 26.8, 23.4, 14.1. HRMS (ESI) calcd for $C_{15}H_{18}BrNO_3Na$ ([M+Na]$^+$): 362.0362; Found: 362.0361

(*E*)-ethyl 4-acetamido-4-(3-bromophenyl)pent-2-enoate (3g)



87 % yield, white solid, m.p.: 124–126 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.35 – 7.35 (m, 1H), 7.30 (d, *J* = 15.9 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.70 (brs, 1H), 5.82 (d, *J* = 15.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.88 (s,

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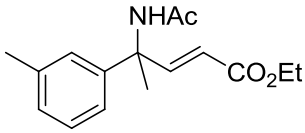
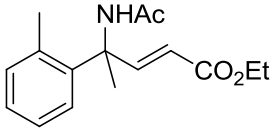
3H), 1.64 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 166.2, 149.7, 145.8, 130.3, 130.0, 128.5, 124.1, 122.6, 120.5, 60.6, 58.7, 26.8, 23.5, 14.1 HRMS (ESI) calcd for $C_{15}H_{18}BrNO_3Na$ ([M+Na]$^+$): 362.0362; Found: 362.0368.

(*E*)-ethyl 4-acetamido-4-m-tolylpent-2-enoate (3h)



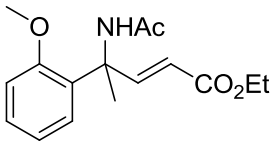
88 % yield, colorless oil, solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 15.9 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.12 (m, 2H), 7.06 – 7.05 (m, 1H), 6.37 (brs, 1H), 5.84 (d, *J* = 15.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.91 (s, 3H), 1.75 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.08, 166.44, 150.86, 143.28, 138.11, 128.42, 128.14, 126.08, 122.45, 119.76, 60.36, 59.12, 26.04, 23.74, 21.47, 14.09. HRMS (ESI) calcd for $C_{16}H_{21}NO_3Na$ ([M+Na]$^+$): 298.1414; Found: 298.1411.

(*E*)-ethyl 4-acetamido-4-o-tolylpent-2-enoate (3i)



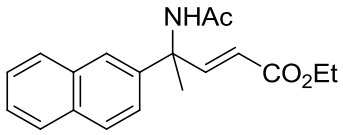
22 % yield, white solid, m.p.: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.20 – 7.14 (m, 3H), 5.98 (s, 1H), 5.63 (d, *J* = 16.0 Hz, 1H), 4.16 (qd, *J* = 7.1, 2.8 Hz, 2H), 2.35 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 166.4, 151.7, 140.8, 135.5, 132.8, 127.9, 126.5, 126.0, 119.8, 60.5, 60.1, 25.8, 23.9, 22.2, 14.2. HRMS (ESI) calcd for $C_{16}H_{21}NO_3Na$ ([M+Na]$^+$): 298.1414; Found: 298.1406.

(*E*)-ethyl 4-acetamido-4-(2-methoxyphenyl)pent-2-enoate (3j)



83 % yield, slight yellow oil, solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 15.9 Hz, 1H), 7.33 – 7.26 (m, 2H), 6.96 – 6.91 (m, 2H), 6.45 (brs, 1H), 5.78 (d, *J* = 15.9 Hz, 1H), 4.17 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.81 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 166.7, 156.6, 152.4, 130.6, 129.0, 127.3, 120.6, 118.7, 112.0, 60.2, 58.5, 55.3, 24.3, 24.0, 14.1. HRMS (ESI) calcd for $C_{16}H_{21}NO_4Na$ ([M+Na]$^+$): 314.1363; Found: 314.1360.

(*E*)-ethyl 4-acetamido-4-(naphthalen-2-yl)pent-2-enoate (3k)



95 % yield, white solid, m.p.: 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.49 – 7.38 (m, 4H), 6.90 (brs, 1H), 5.88 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.83 (s, 3H), 1.73 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 166.4, 150.6, 140.6, 132.9, 132.3, 128.3, 127.9, 127.3, 126.1, 126.0, 124.1, 123.5, 112.0, 60.4, 59.1, 26.3, 23.4, 14.0. HRMS (ESI) calcd for $C_{19}H_{21}NO_3Na$ ([M+Na]$^+$): 334.1414; Found: 334.1408.

(*E*)-methyl 4-acetamido-4-phenylpent-2-enoate (3l)

92 % yield, white solid, m.p.: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* =

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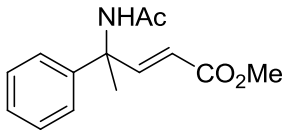
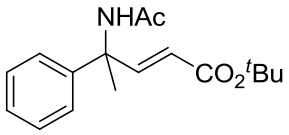


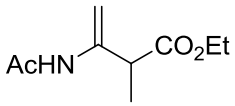
16.0 Hz, 1H), 7.35 – 7.22 (m, 5H), 6.63 (brs, 1H), 5.86 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 1.89 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.8, 151.1, 143.2, 128.5, 127.3, 125.3, 119.4, 59.1, 51.5, 26.3, 23.6. HRMS (ESI) calcd for $C_{14}H_{17}NO_3Na$ ($[M+Na]^+$): 270.1101; Found: 270.1102.

(E)-tert-butyl 4-acetamido-4-phenylpent-2-enoate (3m)



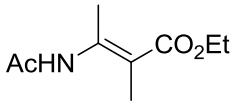
88 % yield, slight yellow oil, solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 7.22 (d, *J* = 15.9 Hz, 1H), 6.33 (brs, 1H), 5.78 (d, *J* = 15.9 Hz, 1H), 1.93 (s, 3H), 1.78 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 165.7, 149.5, 143.4, 128.5, 127.3, 125.5, 121.6, 80.5, 59.2, 28.0, 26.3, 23.8. HRMS (ESI) calcd for $C_{17}H_{23}NO_3Na$ ($[M+Na]^+$): 312.1570; Found: 312.1575.

Ethyl 3-acetamido-2-methylbut-3-enoate (5)



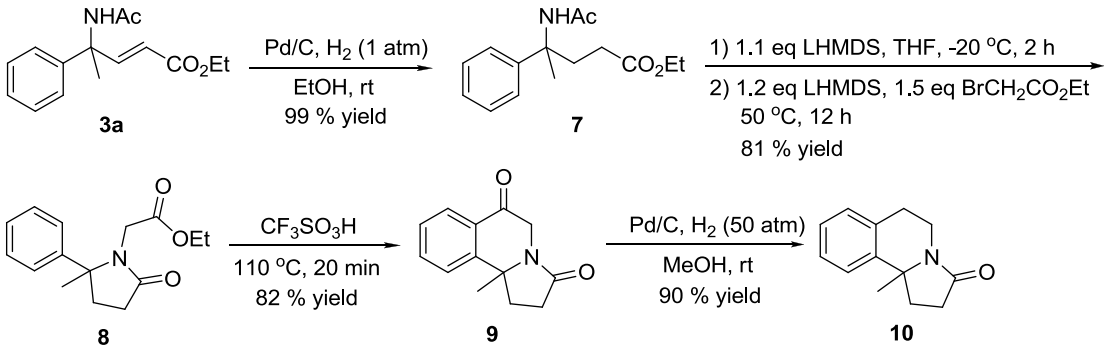
46 % yield, slight yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (brs, 1H), 5.71 (s, 1H), 4.70 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.20 (q, *J* = 7.2 Hz, 1H), 2.07 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 168.9, 138.6, 101.3, 61.3, 45.4, 24.7, 16.9, 14.0. HRMS (ESI) calcd for $C_9H_{15}NO_3Na$ ($[M+Na]^+$): 208.0944; Found: 08.0943.

(*E*)-ethyl 3-acetamido-2-methylbut-2-enoate (6)



38 % yield, slight yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (brs, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.10 (s, 3H), 1.84 (s), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.0, 142.8, 115.2, 60.4, 24.3, 19.1, 14.4, 14.2. HRMS (ESI) calcd for $C_9H_{15}NO_3Na$ ($[M+Na]^+$): 208.0944; Found: 208.0949.

(B) Synthesis of Tricyclic Compound 10



Ethyl 4-acetamido-4-phenylpentanoate (7)

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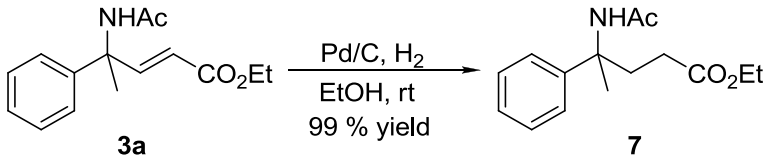
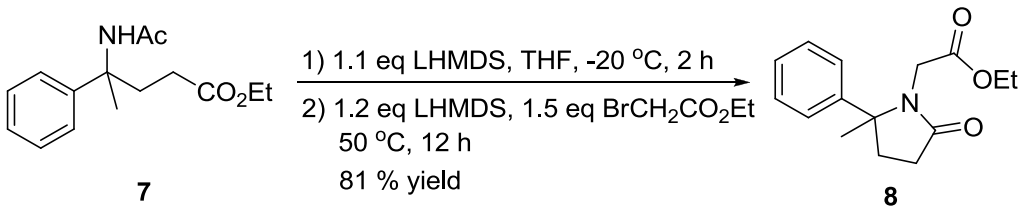


3a **7**

(*E*)-Ethyl 4-acetamido-4-phenylpent-2-enoate (**3a**) (0.26 g, 1 mmol) was dissolved in absolute ethanol (10 ml) in a Schlenk tube. The reaction mixture was purged with nitrogen. A catalytic amount (21mg, 2 mol%) of 10% palladium–charcoal was added to the mixture, and the mixture was purged with hydrogen and stirred under hydrogen (1 atm) for 20 h. The mixture was filtered through Celite, the vessel was washed with dichloromethane (3 × 10 ml). The organic phases were collected and dried over anhydrous magnesium sulfate. After removal of solvent under vacuum the product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate to give a colorless oil **7** (0.26g, 99% yield), which solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.23 – 7.16 (m, 1H), 6.89 (brs, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.34 – 2.20 (m, 2H), 2.20 – 2.09 (m, 2H), 1.89 (s, 3H), 1.68 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 169.4, 144.8, 128.1, 126.4, 125.0, 60.4, 57.9, 36.5, 29.2, 25.4, 23.7, 14.0. HRMS (ESI) calcd for $C_{15}H_{21}NO_3Na$ ($[M+Na]^+$): 286.1414; Found: 286.1415.

Ethyl 2-(2-methyl-5-oxo-2-phenylpyrrolidin-1-yl)acetate (8)

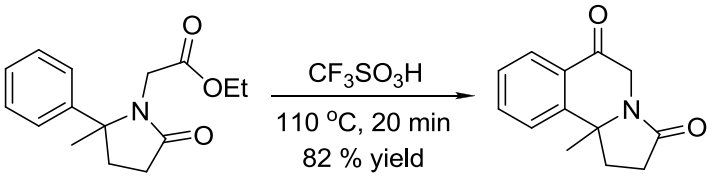


7 **8**

Ethyl 4-acetamido-4-phenylpentanoate (**7**) (0.26g, 1 mmol) was dissolved in anhydrous tetrahydrofuran (10 ml) in a Schlenk tube. The reaction mixture was cooled to –20 °C. 1.1 eq LHMDS (1.1 mL, 1.06 M in THF) was slowly added to the mixture over 30 minutes. The mixture was stirred for 2 h under –20 °C. The reaction mixture was slowly added another 1.2 eq LHMDS (1.2 mL, 1.06 M in THF) under –20 °C over 30 minutes and followed with 1.5eq ethyl 2-bromoacetate. The mixture turned to a bright yellow solution, and was stirred at 50 °C under nitrogen for another 12 h. The reaction was quenched with 1N HCl (1 mL), and was added a saturated $NaHCO_3$ until the pH = 7. The mixture was extracted with dichloromethane (3 × 10 ml) and the organic extracts were collected and dried over anhydrous magnesium sulfate. After removal of solvent the product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate to give a colorless oil **8** (0.21g, 81% yield), which solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 6.3 Hz, 2H), 4.17 (d, *J* = 17.4 Hz, 1H), 4.08 (qd, *J* = 7.1, 2.1 Hz, 2H), 3.31 (d, *J* =

17.4 Hz, 1H), 2.52 – 2.34 (m, 2H), 2.21 – 2.07 (m, 2H), 1.64 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 168.6, 144.0, 128.6, 127.3, 125.1, 65.8, 60.9, 42.0, 36.8, 29.0, 24.6, 13.8. HRMS (ESI) calcd for $C_{15}H_{19}NO_3Na$ ($[M+Na]^+$): 284.1257; Found: 284.1262.

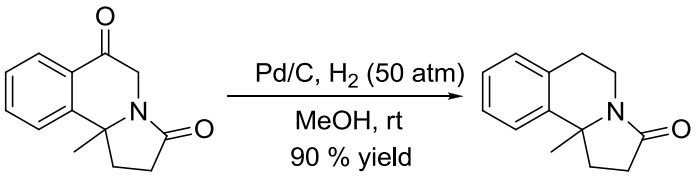
10b-methyl-1,2-dihydropyrrolo[2,1-a]isoquinoline-3,6(5H,10bH)-dione (9)[4]



8 **9**

The mixture of ethyl 2-(2-methyl-5-oxo-2-phenylpyrrolidin-1-yl)acetate (**8**) (0.13g, 0.5 mol) and 0.8mL of trifluoromethanesulfonic acid was stirred for 20 min at 110 °C. After cooling in an ice bath the solution was diluted with 1 mL of H_2O, and then adjusted to pH=7 with saturated $NaHCO_3$ solution. After addition of Et_2O and brine (each 10 mL) the ether phase was separated and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined ether extracts were dried with anhydrous magnesium sulfate and the solvent was removed in vacuum. The crude product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate to give a colorless oil **9** (88mg, 82% yield), which solidified to a white solid after standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.63 (td, *J* = 7.7, 1.3 Hz, 1H), 7.40 (dd, *J* = 11.1, 4.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 4.86 (d, *J* = 19.2 Hz, 1H), 3.84 (d, *J* = 19.2 Hz, 1H), 2.72 – 2.34 (m, 5H), 1.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 172.7, 149.0, 134.8, 128.7, 127.7, 127.5, 124.3, 60.9, 46.0, 33.6, 29.6, 27.0. HRMS (ESI) calcd for $C_{13}H_{13}NO_2Na$ ($[M+Na]^+$): 238.0838; Found: 238.0839.

10b-methyl-1,2,5,6-tetrahydropyrrolo[2,1-a]isoquinolin-3(10bH)-one (10)[5]



9 **10**

10b-Methyl-1,2-dihydropyrrolo[2,1-a]isoquinoline-3,6(5H,10bH)-dione (**9**) (0.11g, 0.5 mmol) was dissolved in absolute methanol (5 ml), a catalytic amount (26mg, 5 mol%) of 10% palladium–charcoal was added to the mixture. The mixture was purged

[4] E. Reimann, C. Ettmayr, *Monatshefte für Chemie* **2004**, *135*, 959.

[5] (a) H. Geng, K. Huang, T. Sun, W. Li, X. Zhang, L. Zhou, W. Wu, X. Zhang, *J. Org. Chem.*, **2011**, *76*, 332. (b) S. M. Allin, S. L. James, W. P. Martin, T. A. D. Smith, M. R. J. Elsegood, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 3029.

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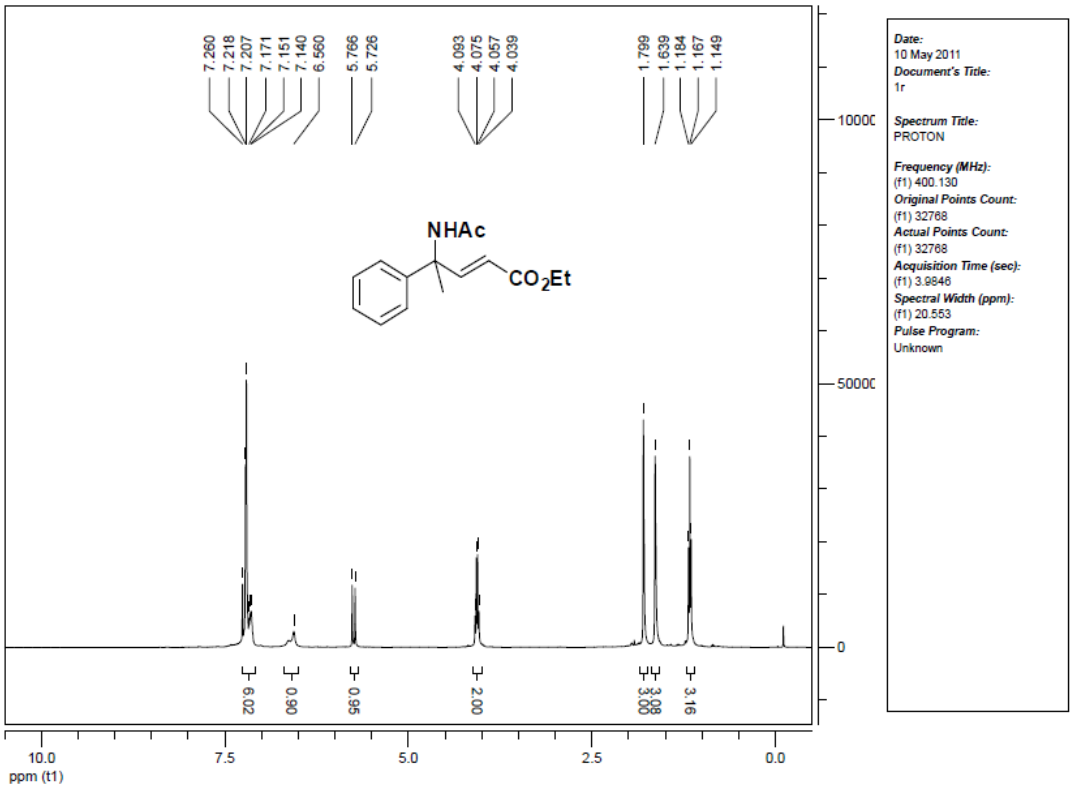
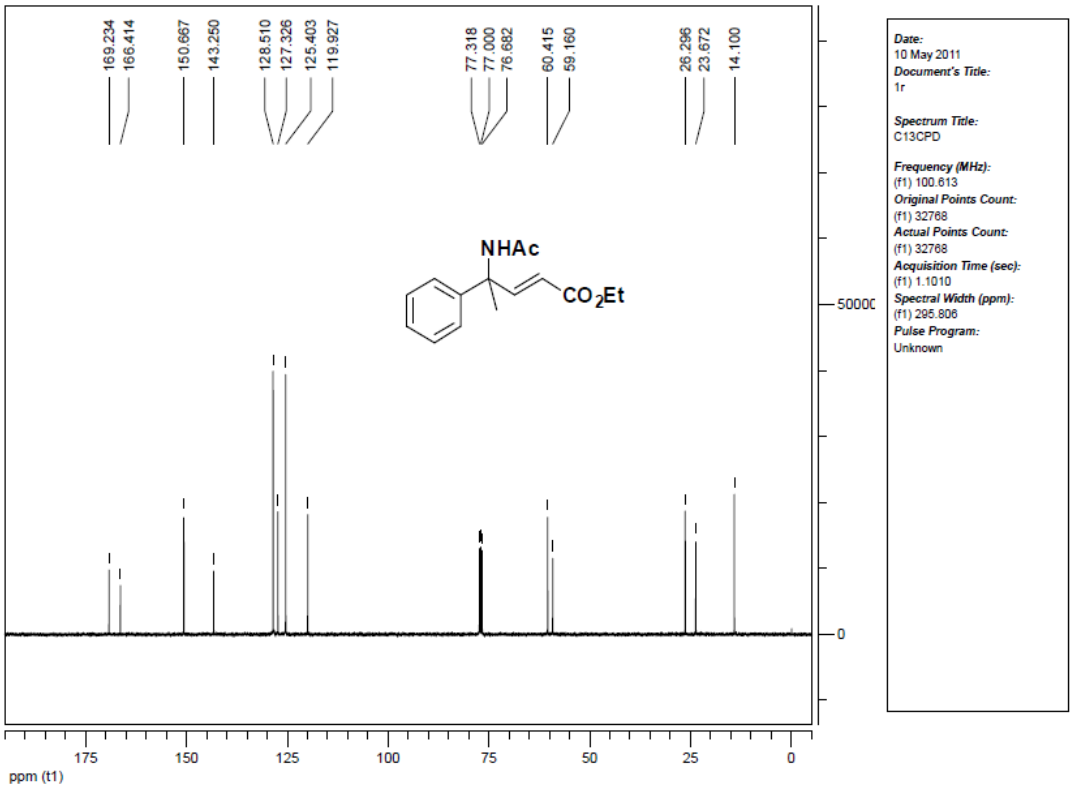
with hydrogen three times and was stirred for 20 h under 50 atm of H_2 at room temperature. After releasing the hydrogen slowly, the mixture was filtered through Celite, the reaction vessel was washed with dichloromethane (3 × 10 ml). The organic phases were collected, dried over anhydrous magnesium sulfate. After removal of solvent the crude product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate to give a colorless oil **10** (91mg, 90 % yield), which solidified to a white solid after standing at room temperature.[5b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.03 (m, 4H), 4.32 (dd, *J* = 13.0, 6.4 Hz, 1H), 3.12 (td, *J* = 12.5, 4.4 Hz, 1H), 3.05 – 2.90 (m, 1H), 2.86 – 2.74 (m, 1H), 2.71 – 2.59 (m, 1H), 2.53 – 2.37 (m, 2H), 2.13 (dd, *J* = 22.1, 11.0 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 142.7, 132.3, 129.2, 126.7, 126.6, 125.0, 61.1, 34.6, 34.0, 30.7, 28.5, 27.4. HRMS (ESI) calcd for $C_{13}H_{15}NONa$ ($[M+Na]^+$): 224.1046; Found: 224.1050.

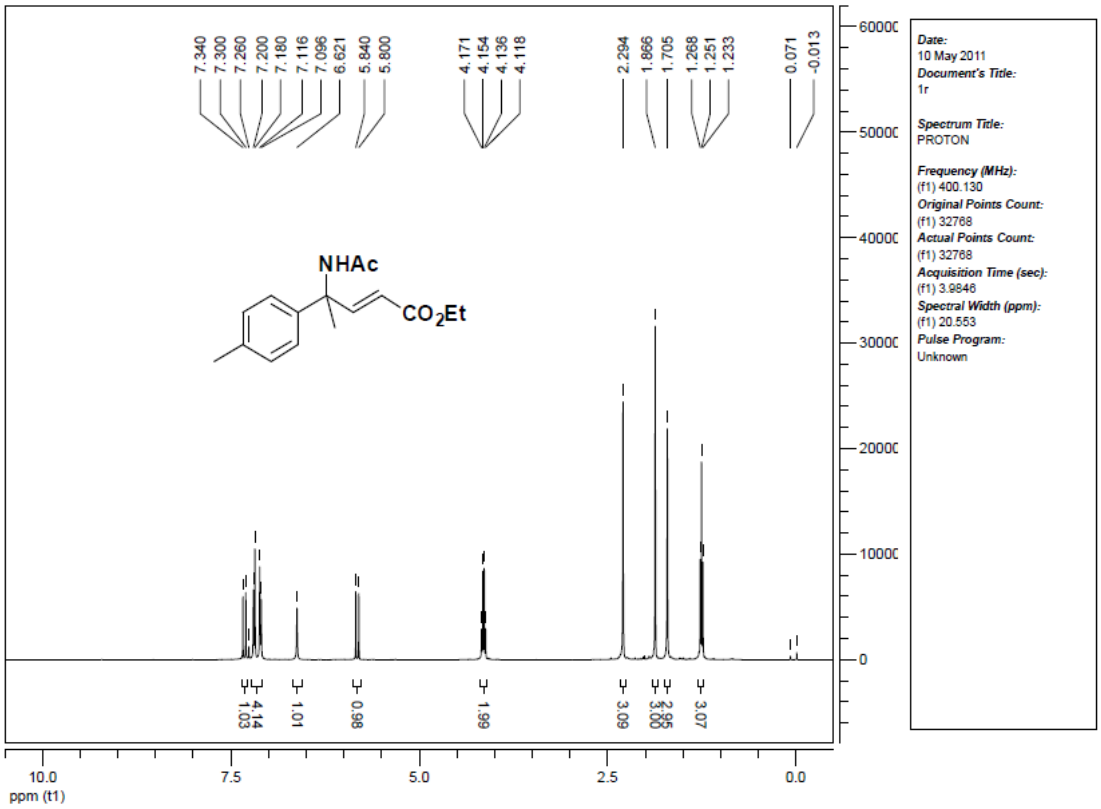
(C) NMR Spectrum of New Substrates and Products

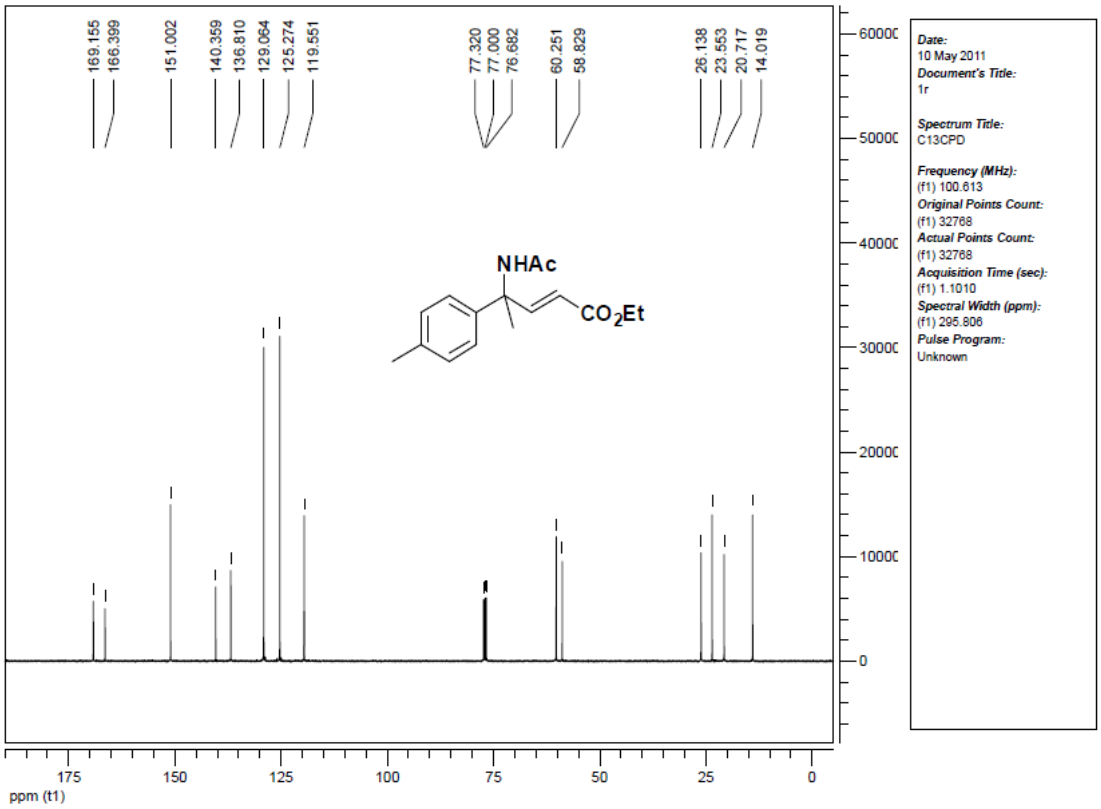
(*E*)-ethyl 4-acetamido-4-phenylpent-2-enoate (3a)





(*E*)-ethyl 4-acetamido-4-p-tolylpent-2-enoate (3b)





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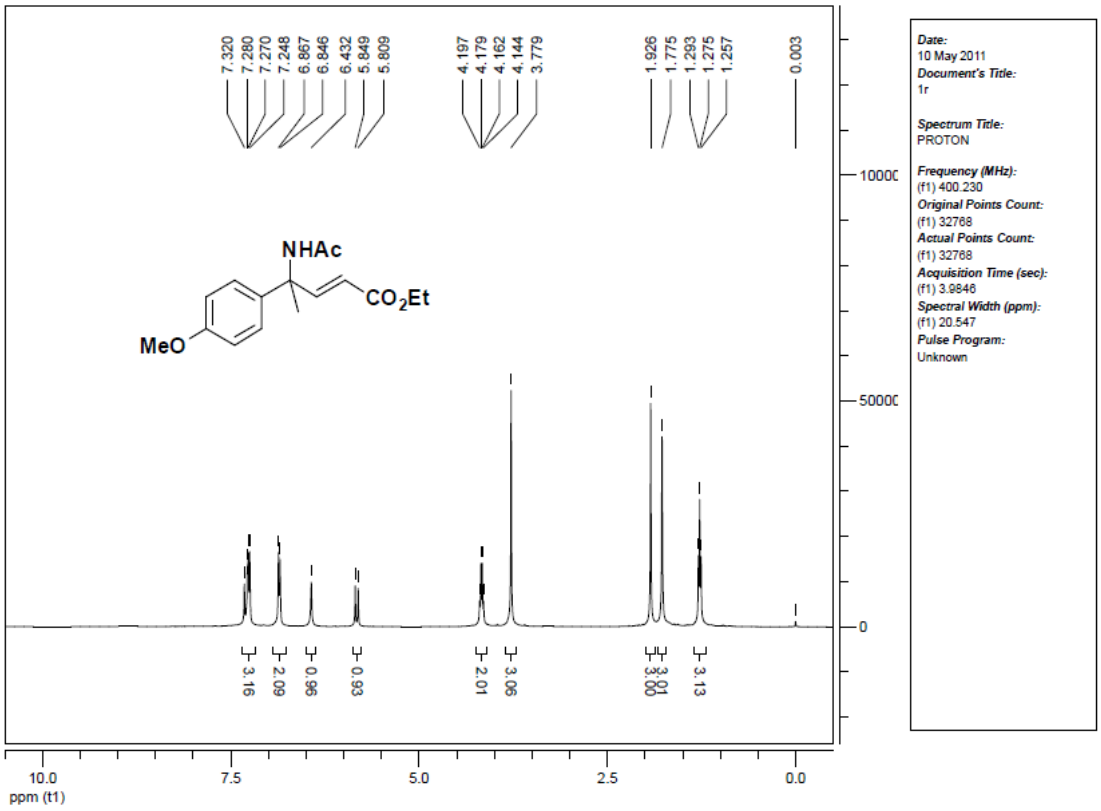
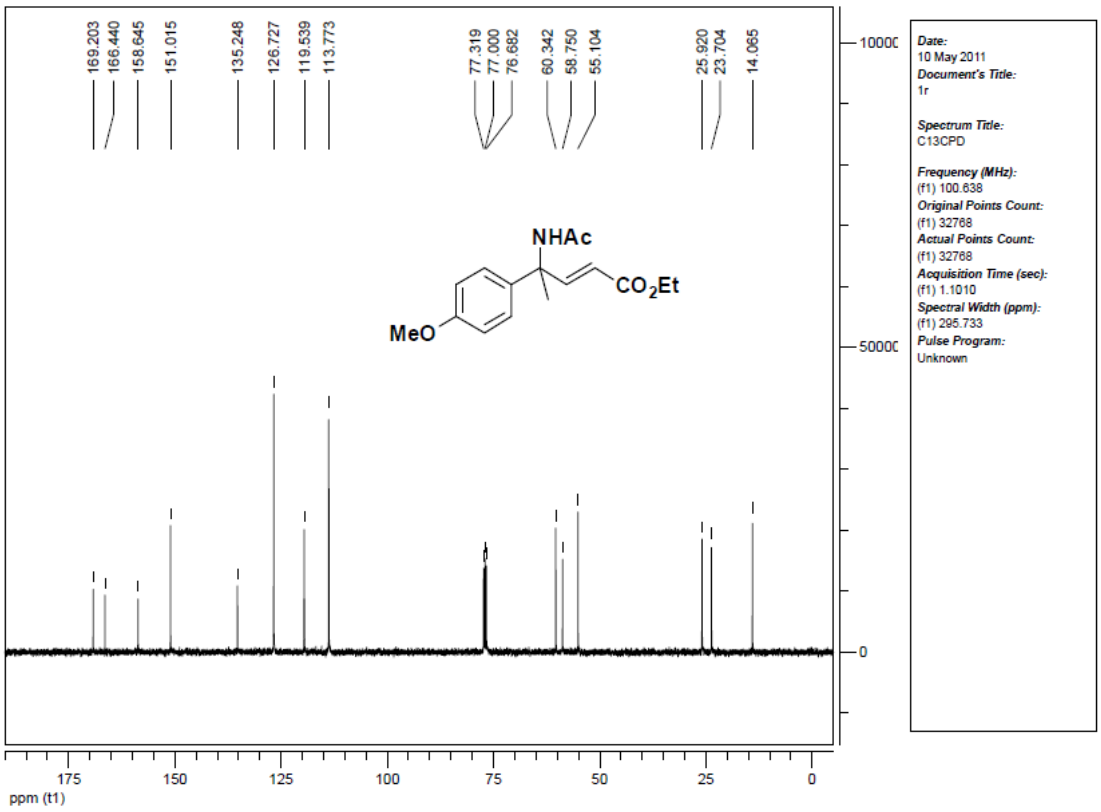
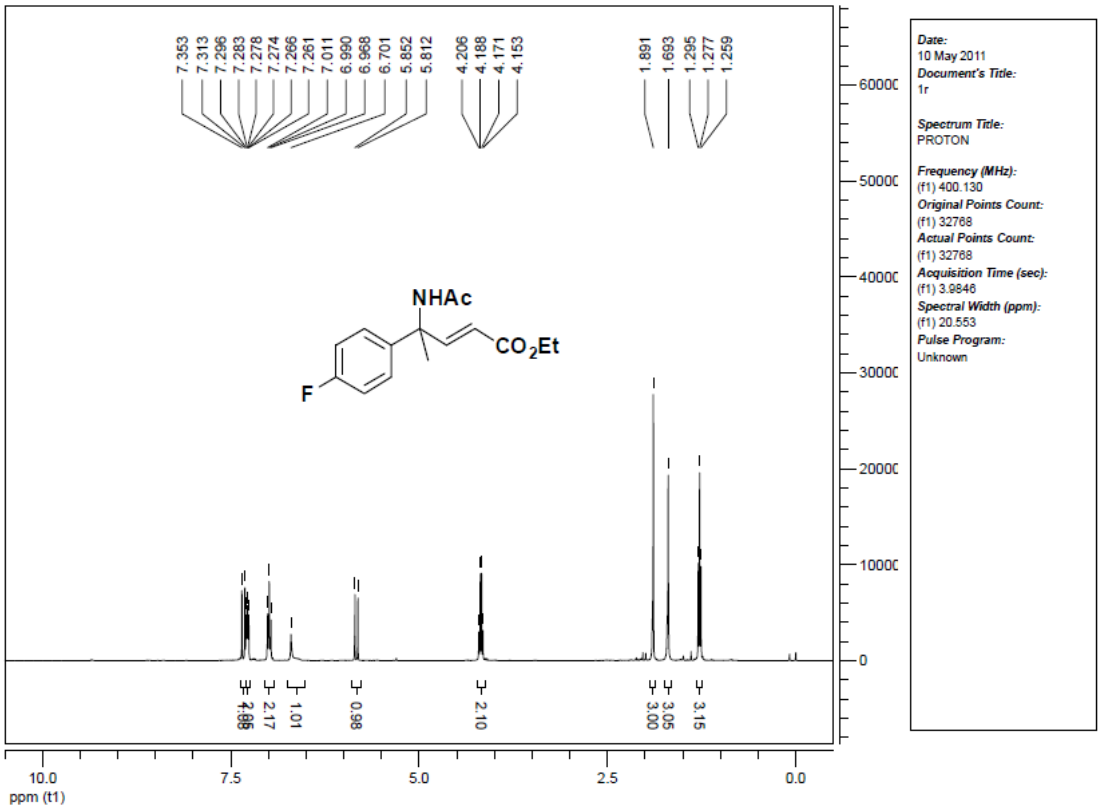
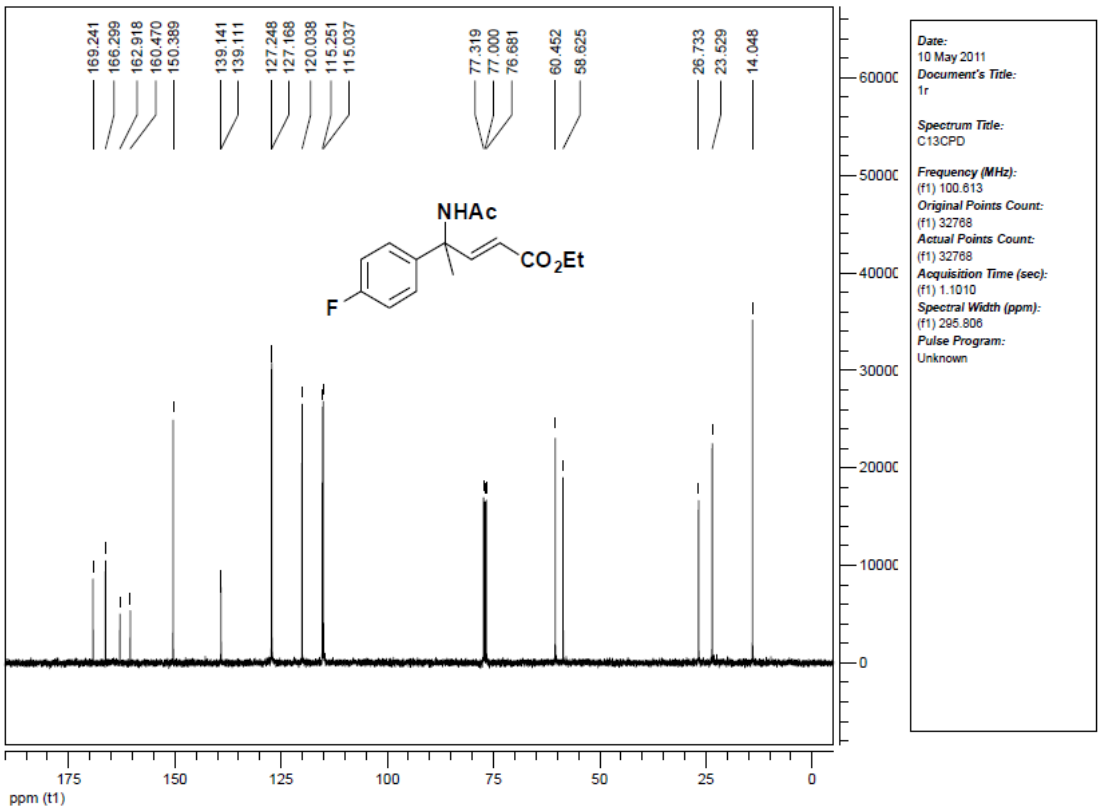
(*E*)-ethyl 4-acetamido-4-(4-methoxyphenyl)pent-2-enoate (3c)



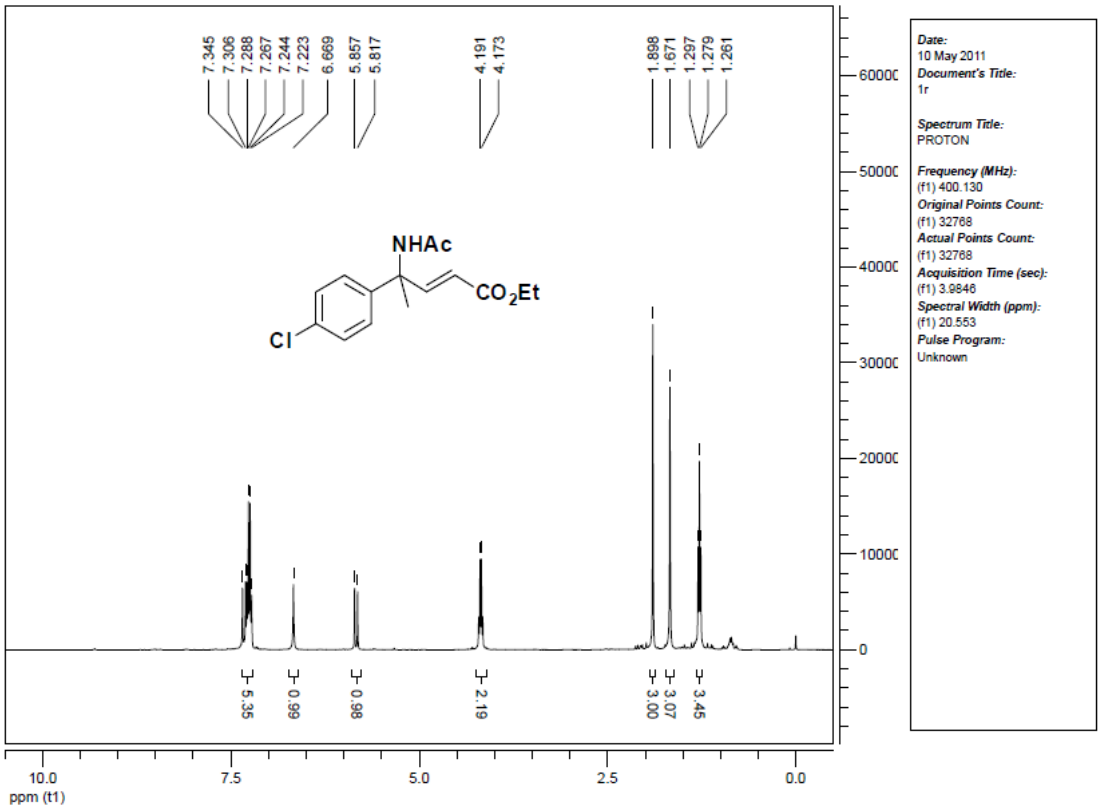


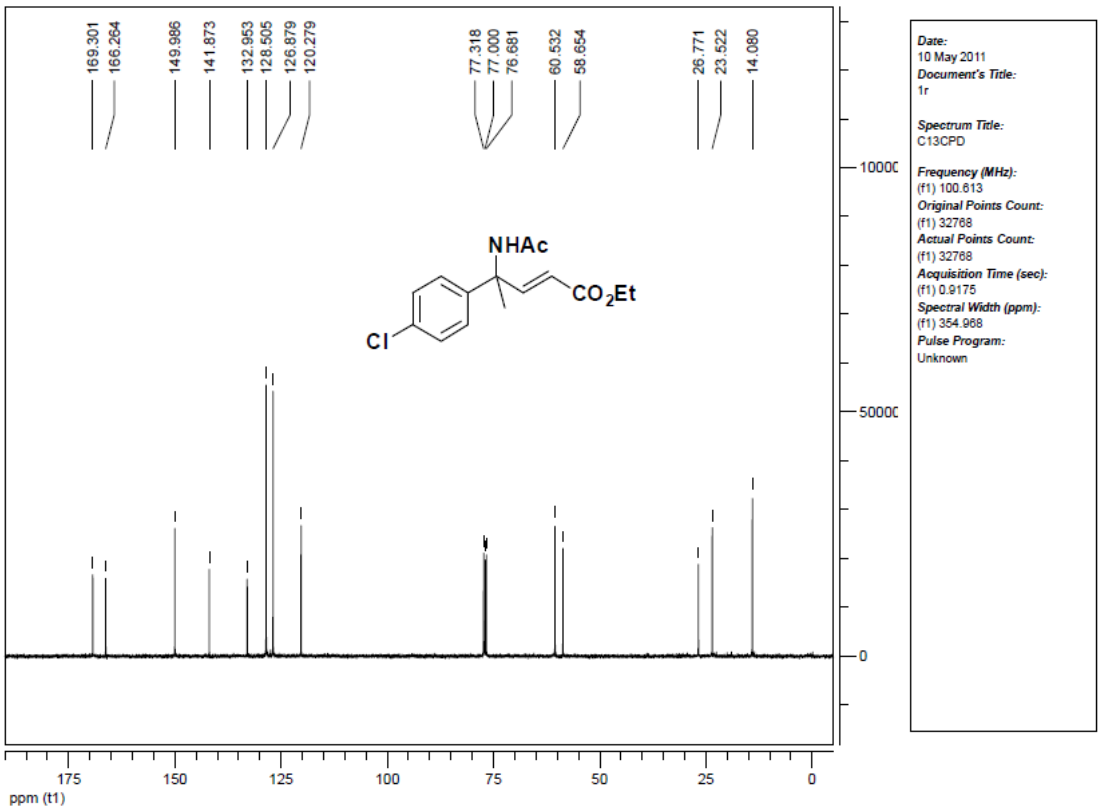
(E)-ethyl 4-acetamido-4-(4-fluorophenyl)pent-2-enoate (3d)



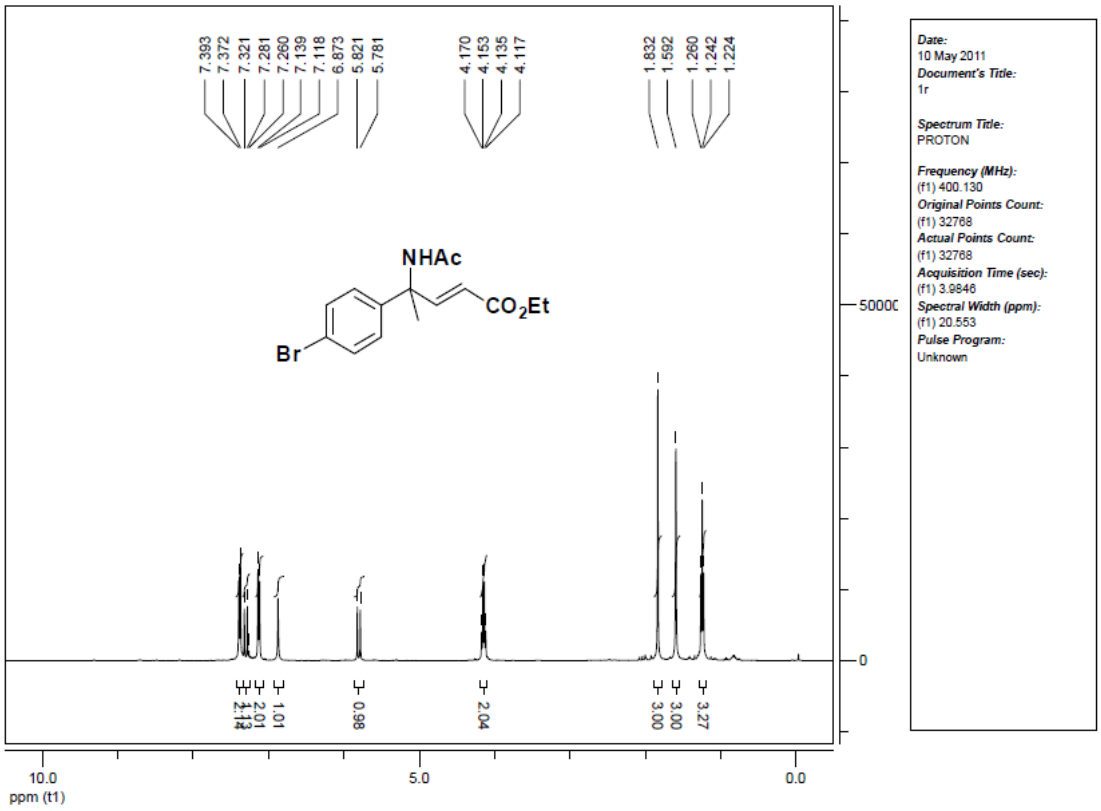


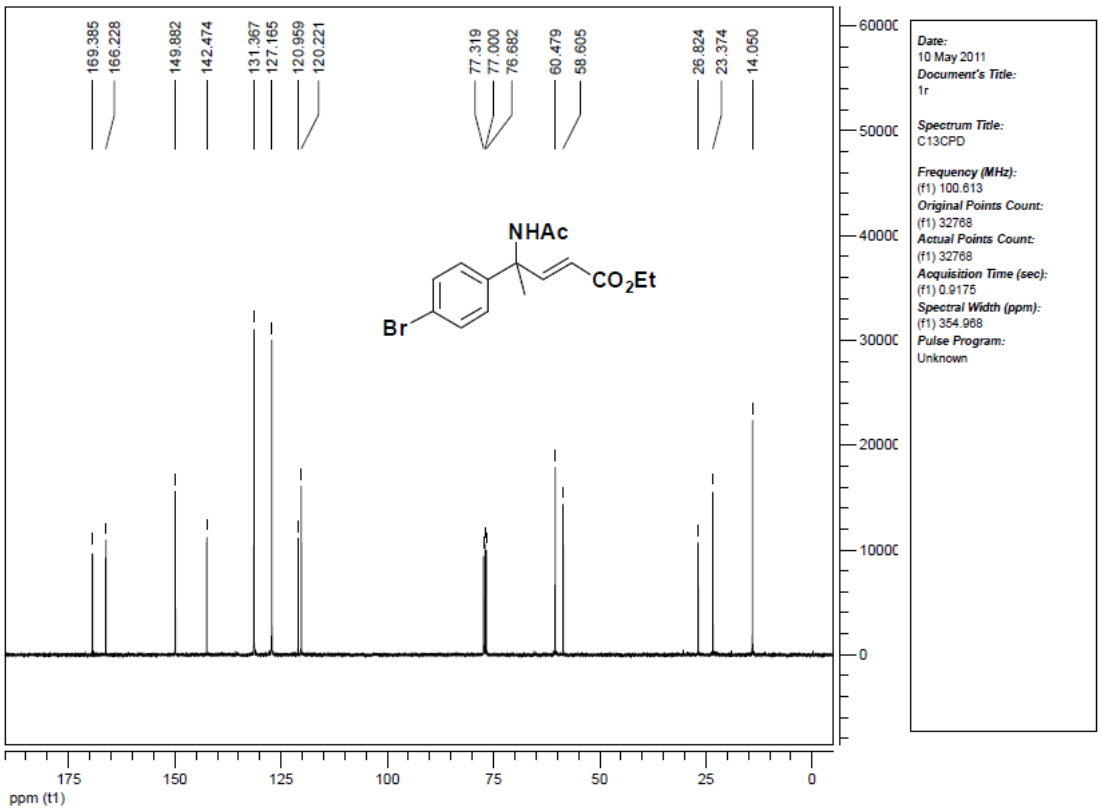
(*E*)-ethyl 4-acetamido-4-(4-chlorophenyl)pent-2-enoate (3e)



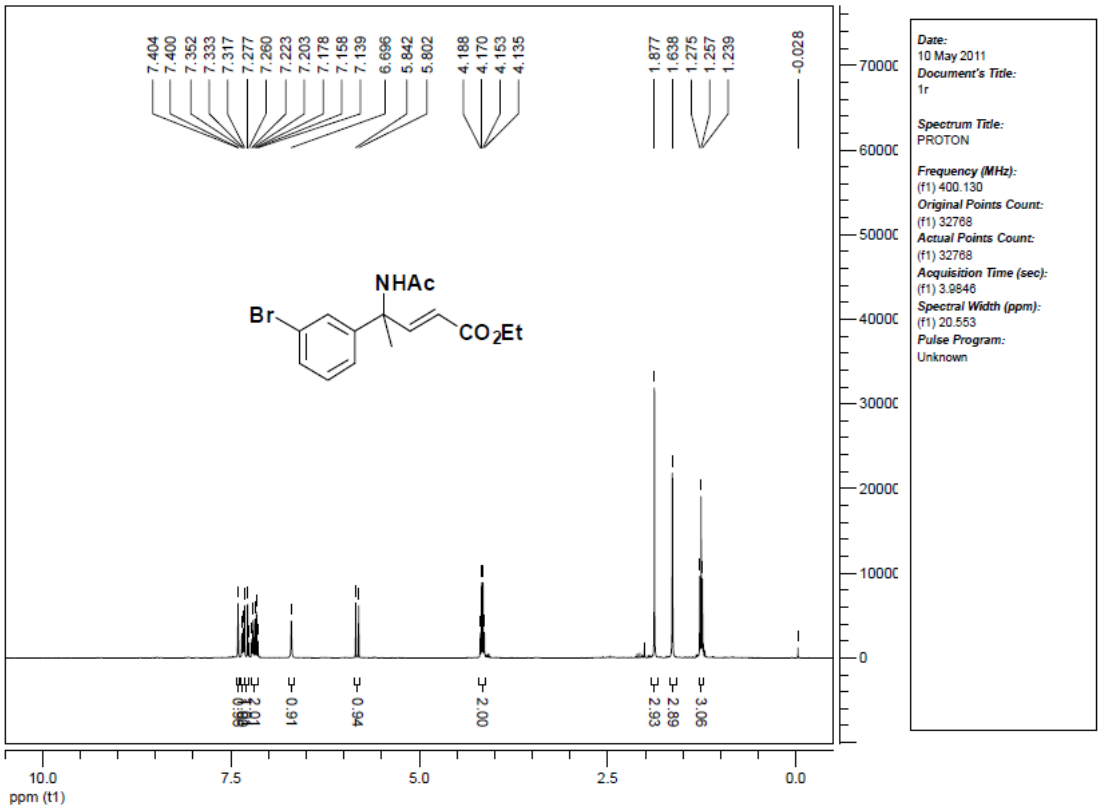


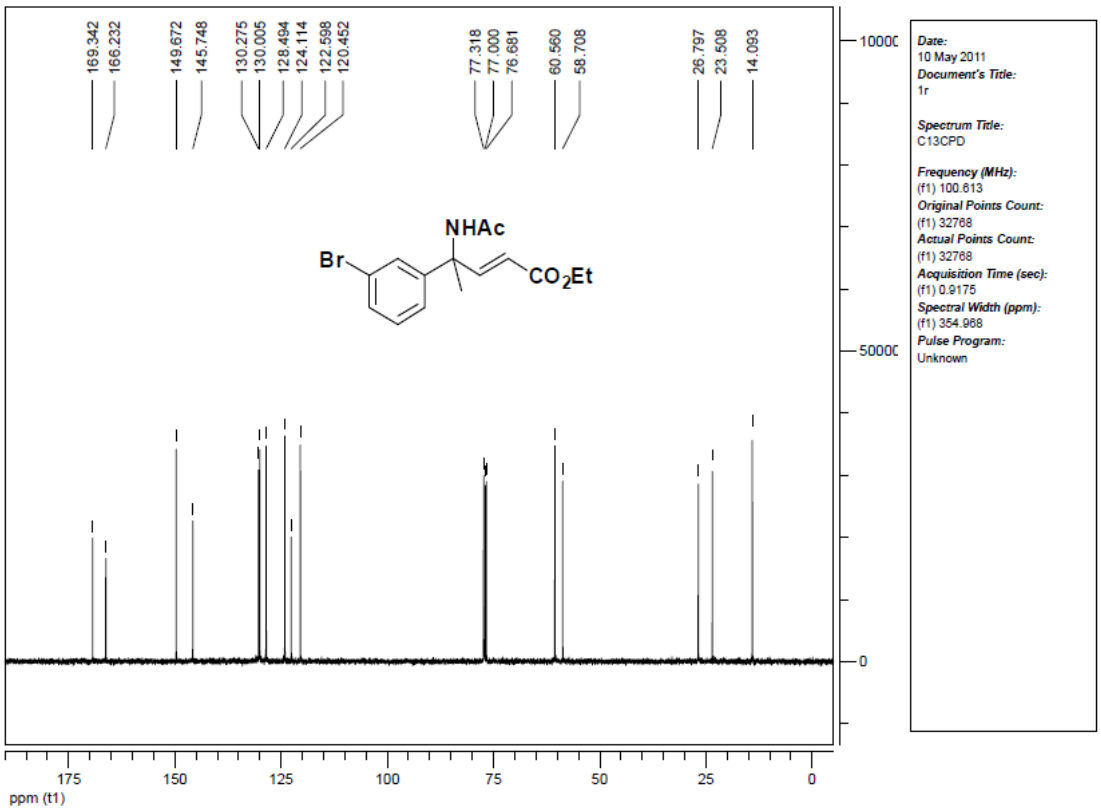
(*E*)-ethyl 4-acetamido-4-(4-bromophenyl)pent-2-enoate (3f)



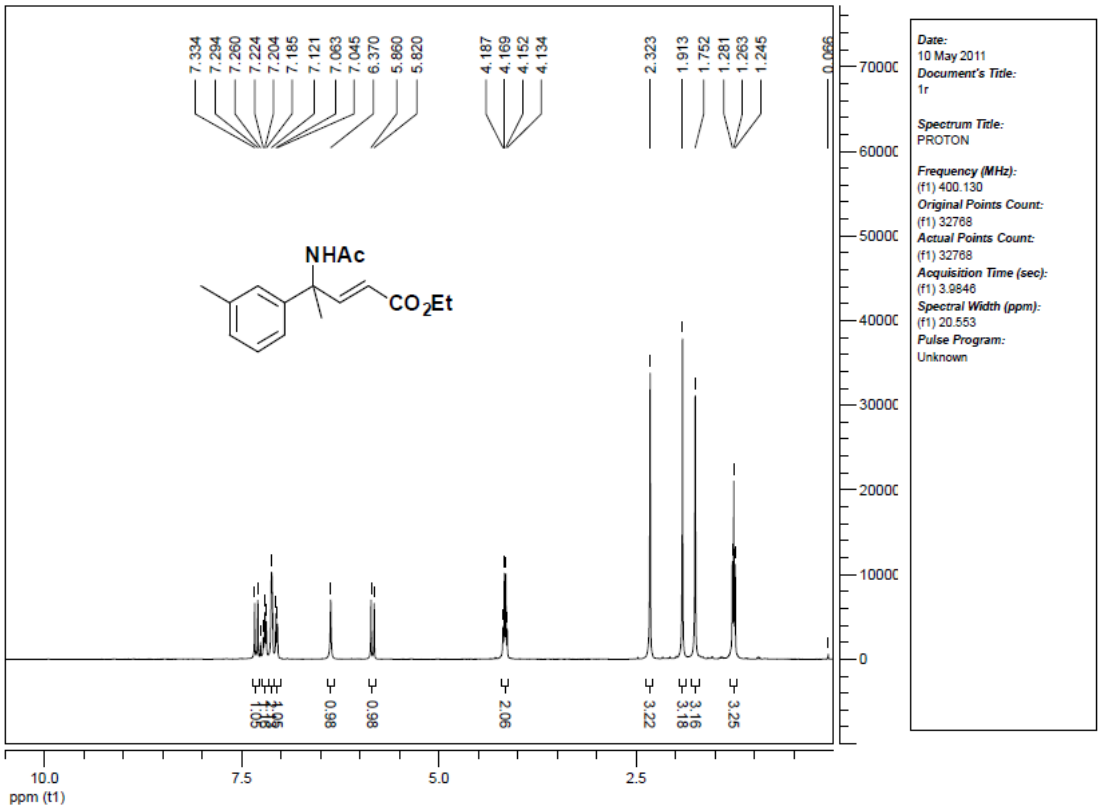


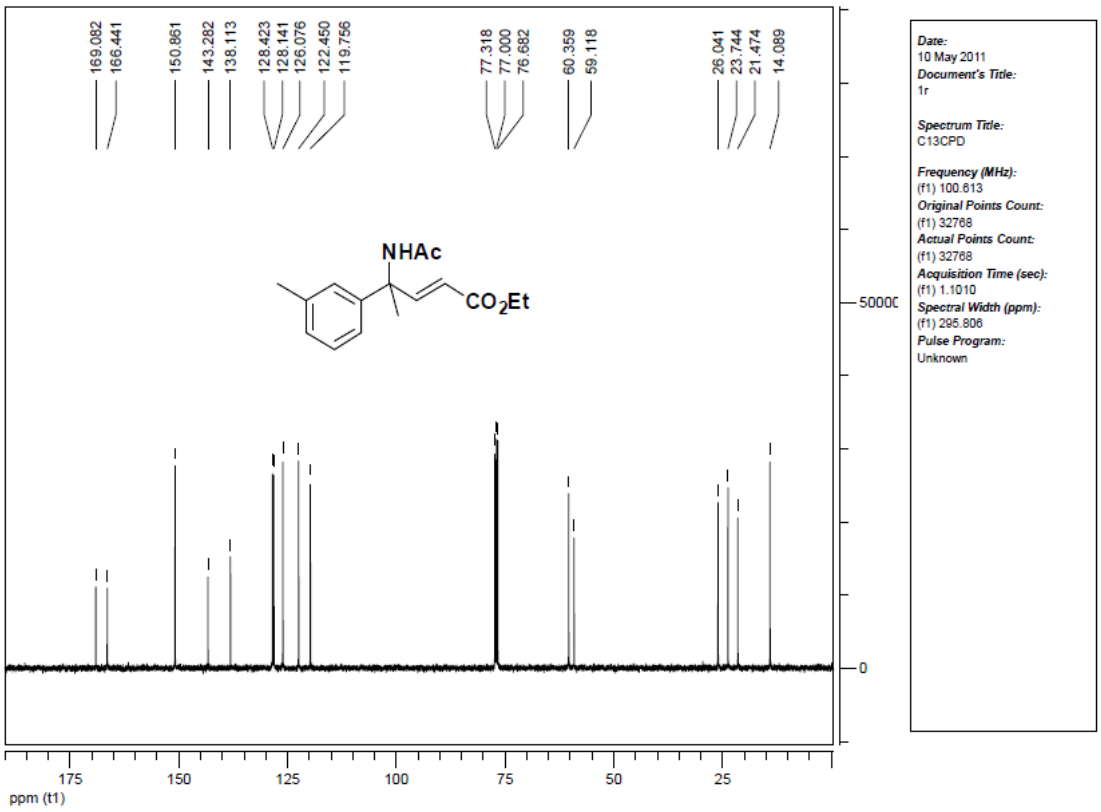
(*E*)-ethyl 4-acetamido-4-(3-bromophenyl)pent-2-enoate (3g)



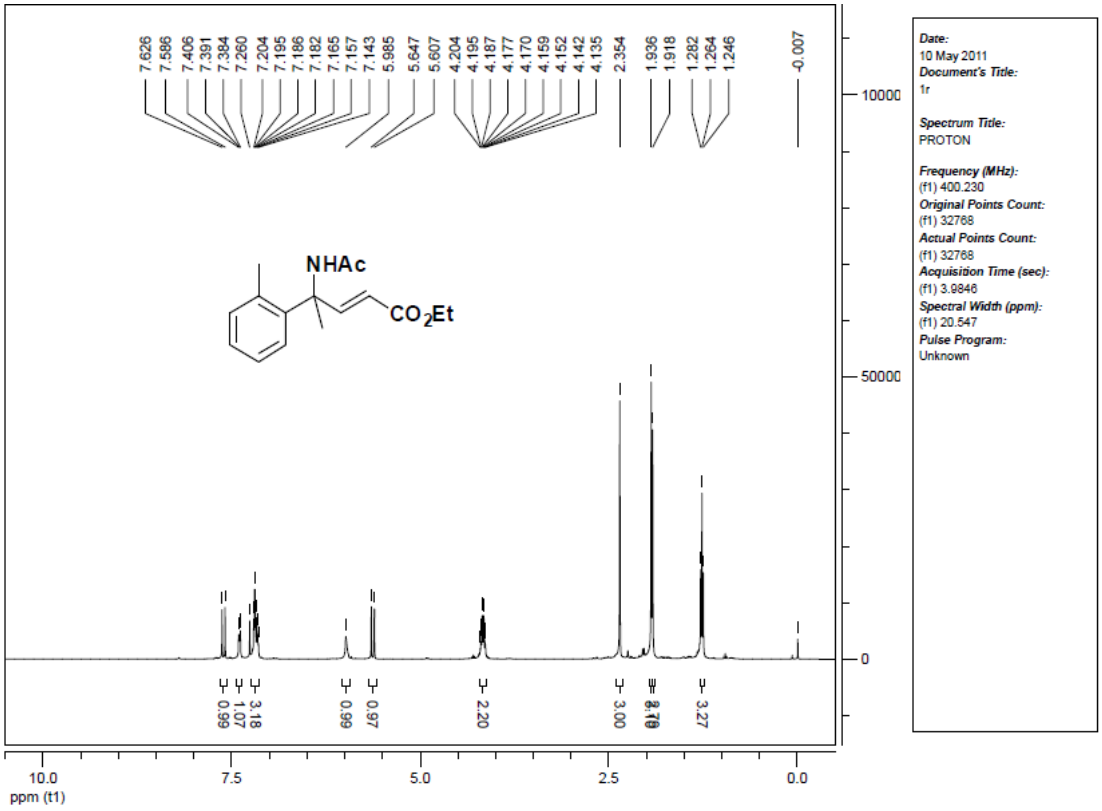


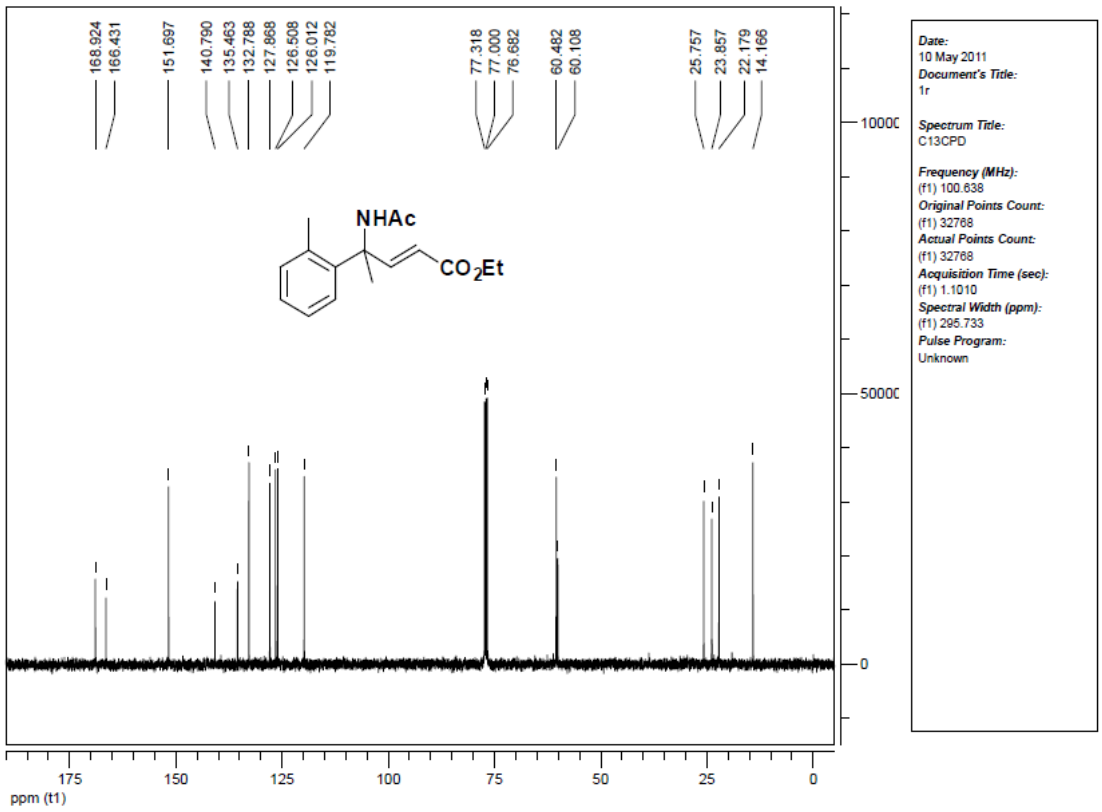
(*E*)-ethyl 4-acetamido-4-m-tolylpent-2-enoate (3h)





(*E*)-ethyl 4-acetamido-4-o-tolylpent-2-enoate (3i)





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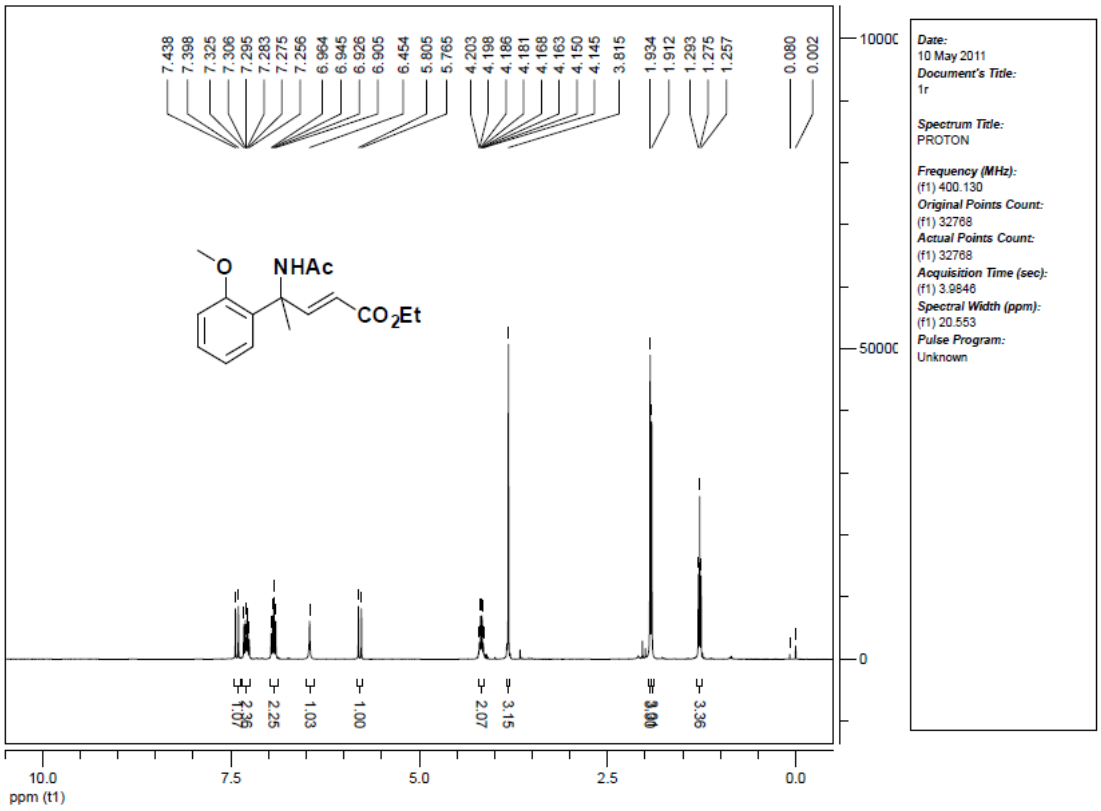
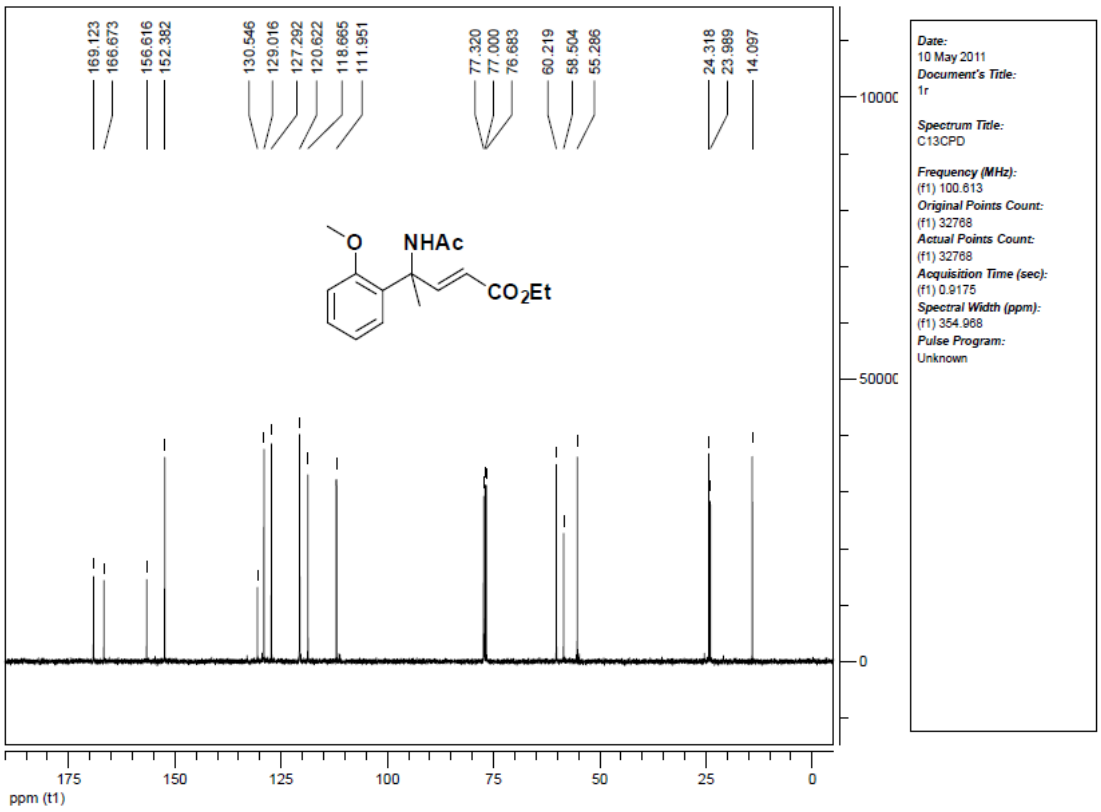
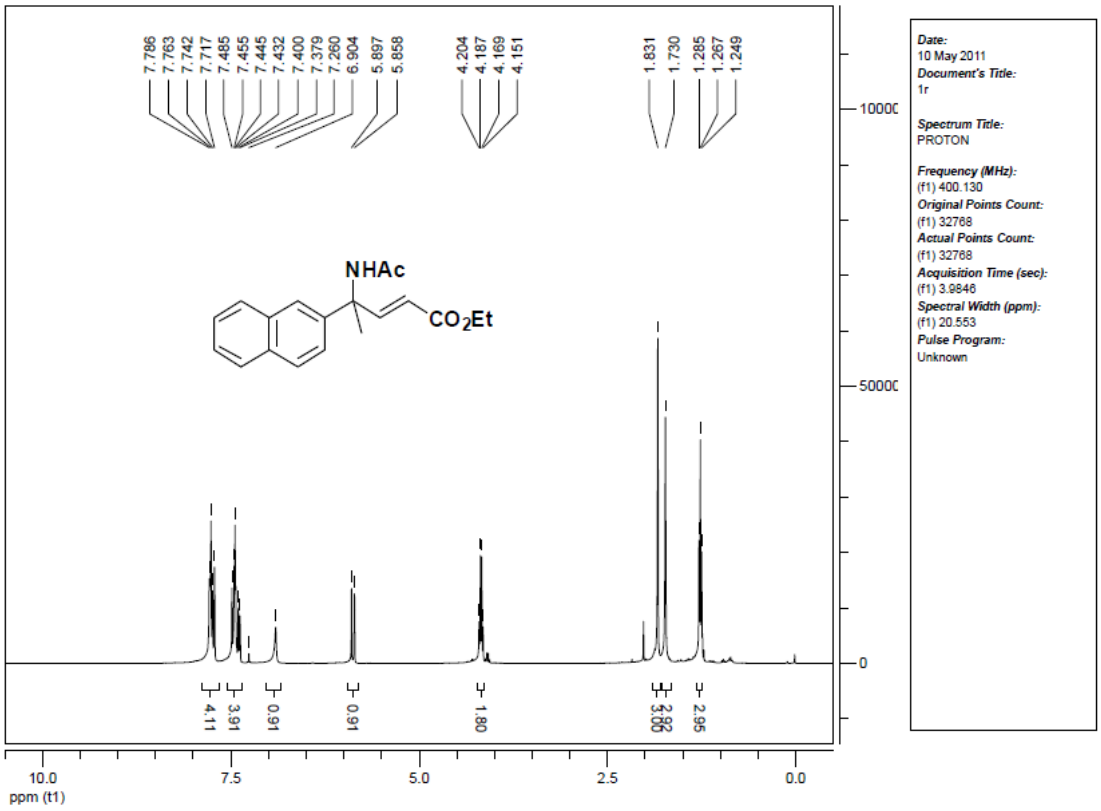
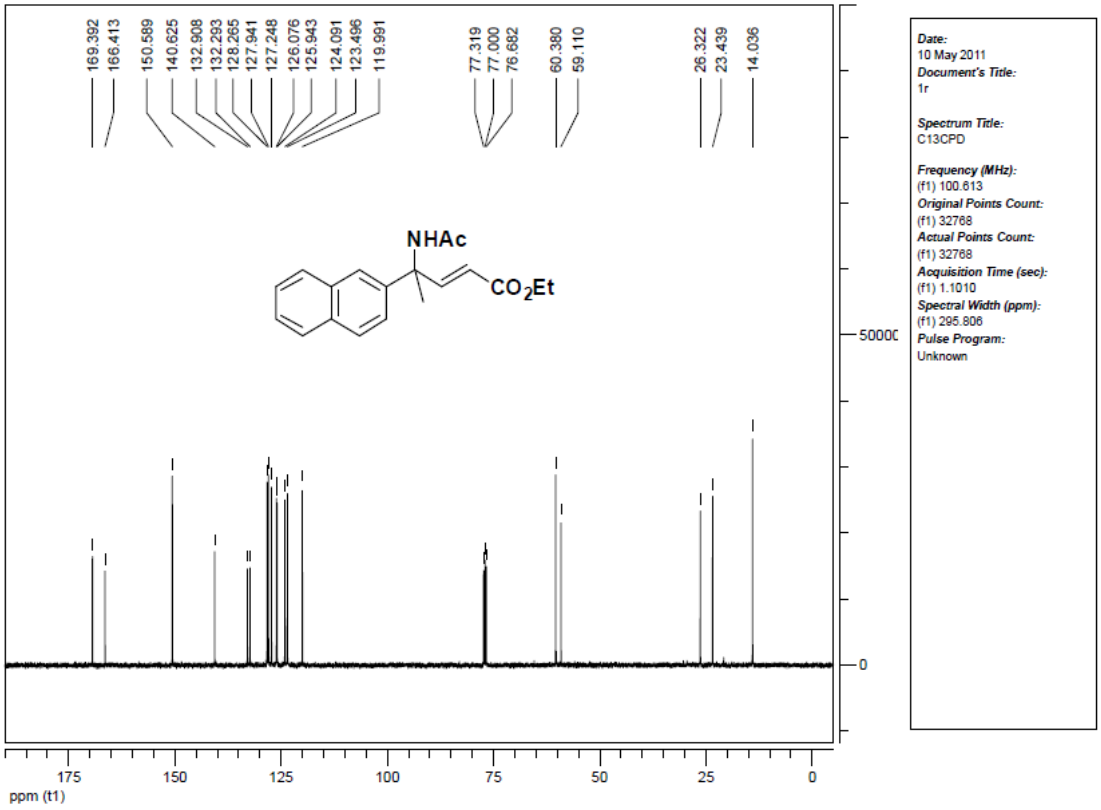
(*E*)-ethyl 4-acetamido-4-(2-methoxyphenyl)pent-2-enoate (3j)



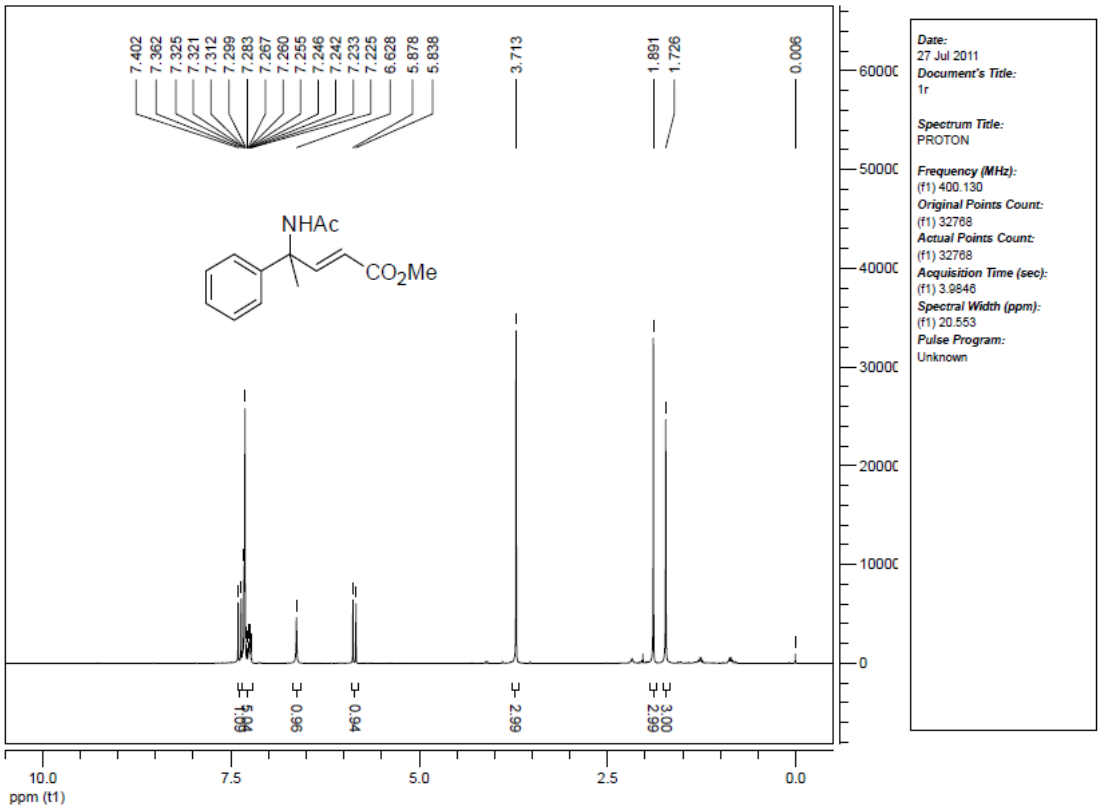


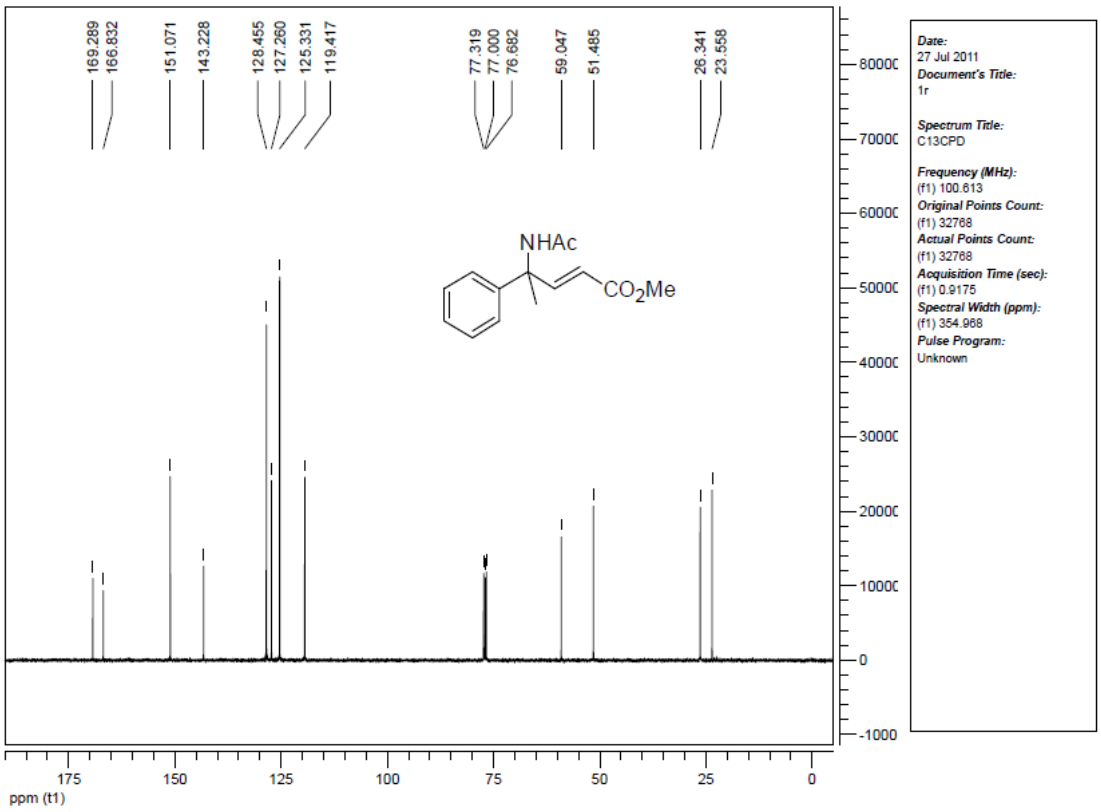
(*E*)-ethyl 4-acetamido-4-(naphthalen-2-yl)pent-2-enoate (3k)



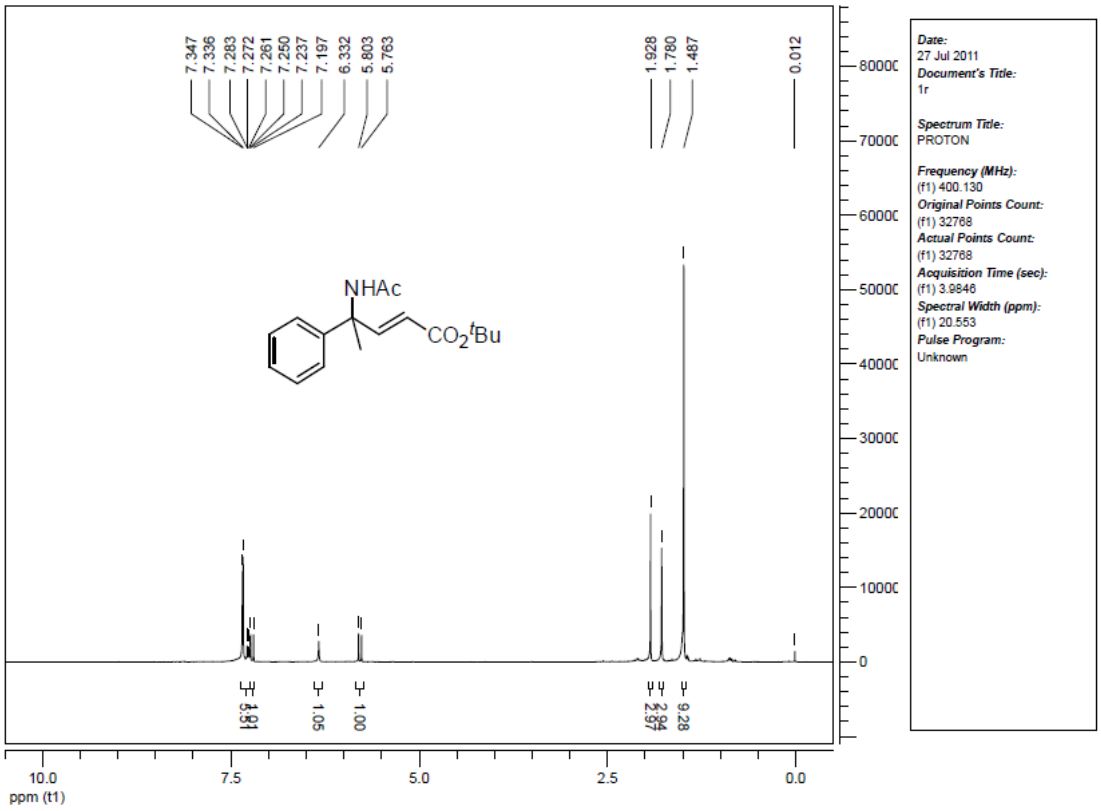


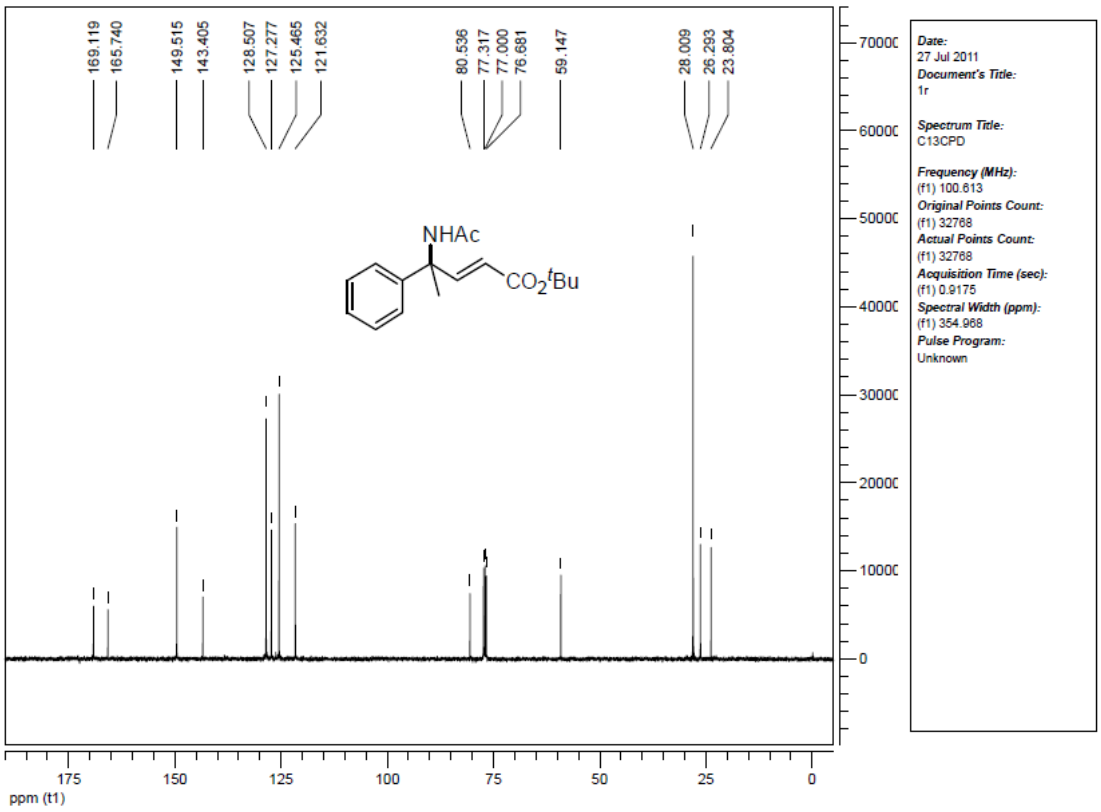
(*E*)-methyl 4-acetamido-4-phenylpent-2-enoate (3l)



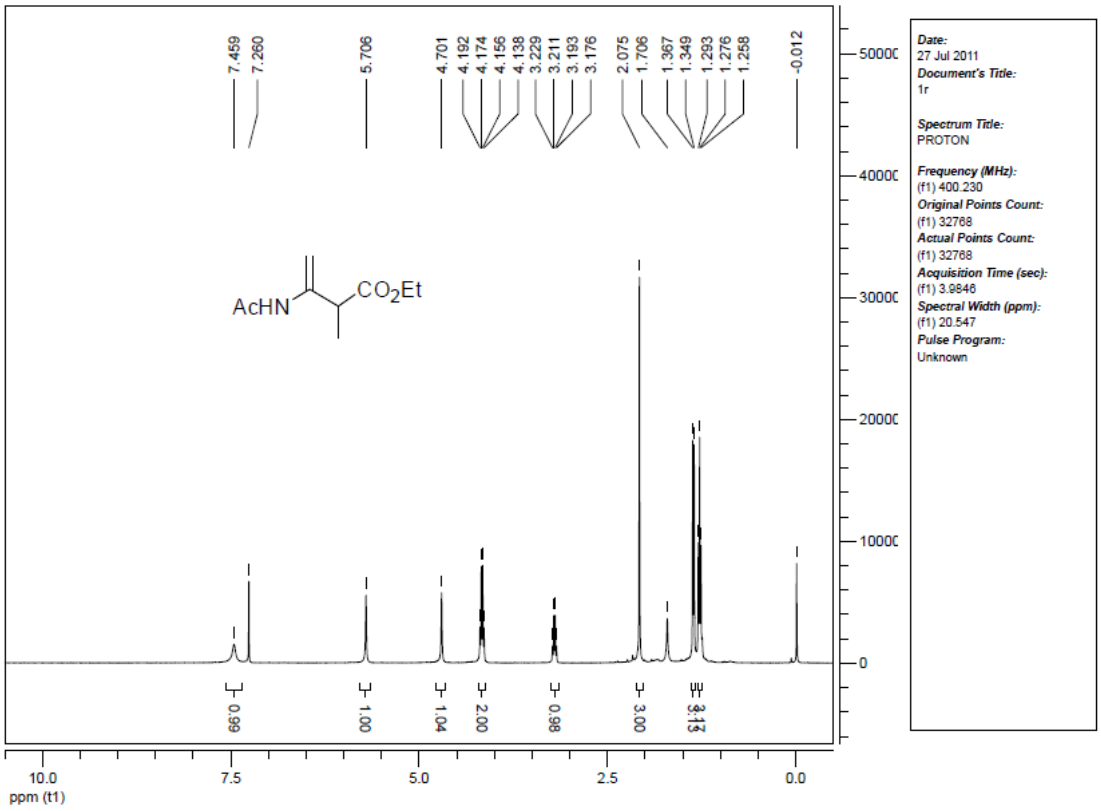


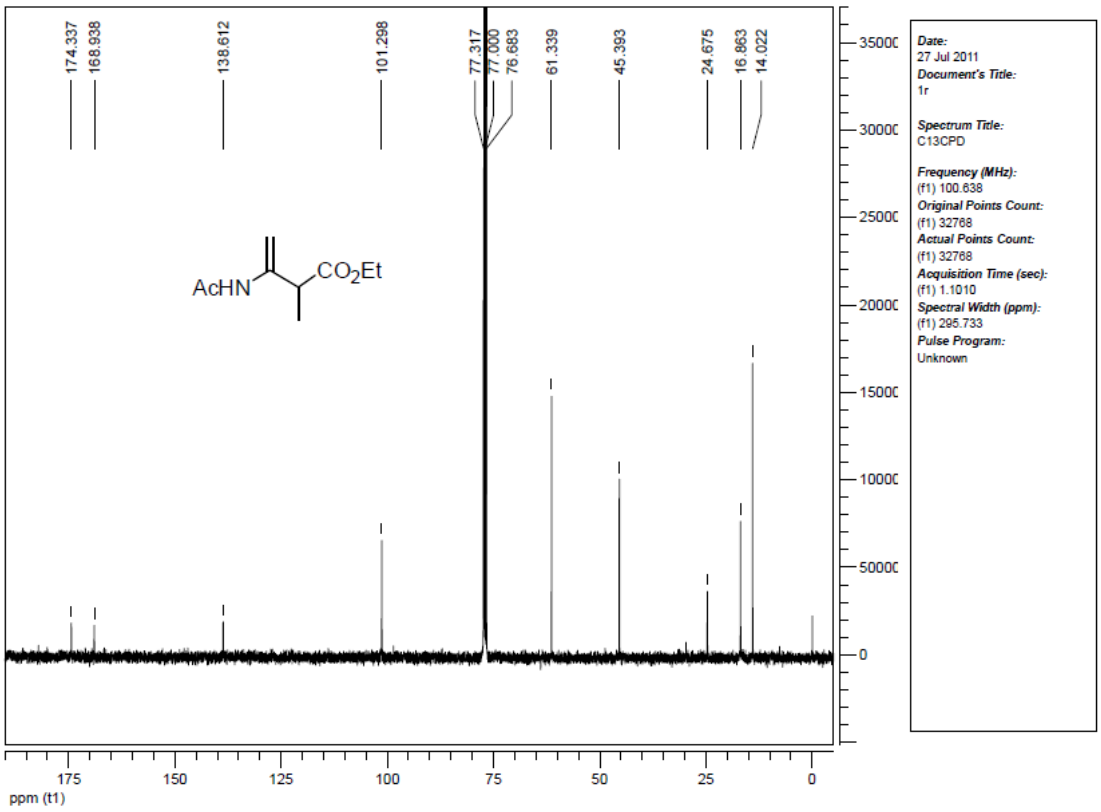
(*E*)-tert-butyl 4-acetamido-4-phenylpent-2-enoate (3m)



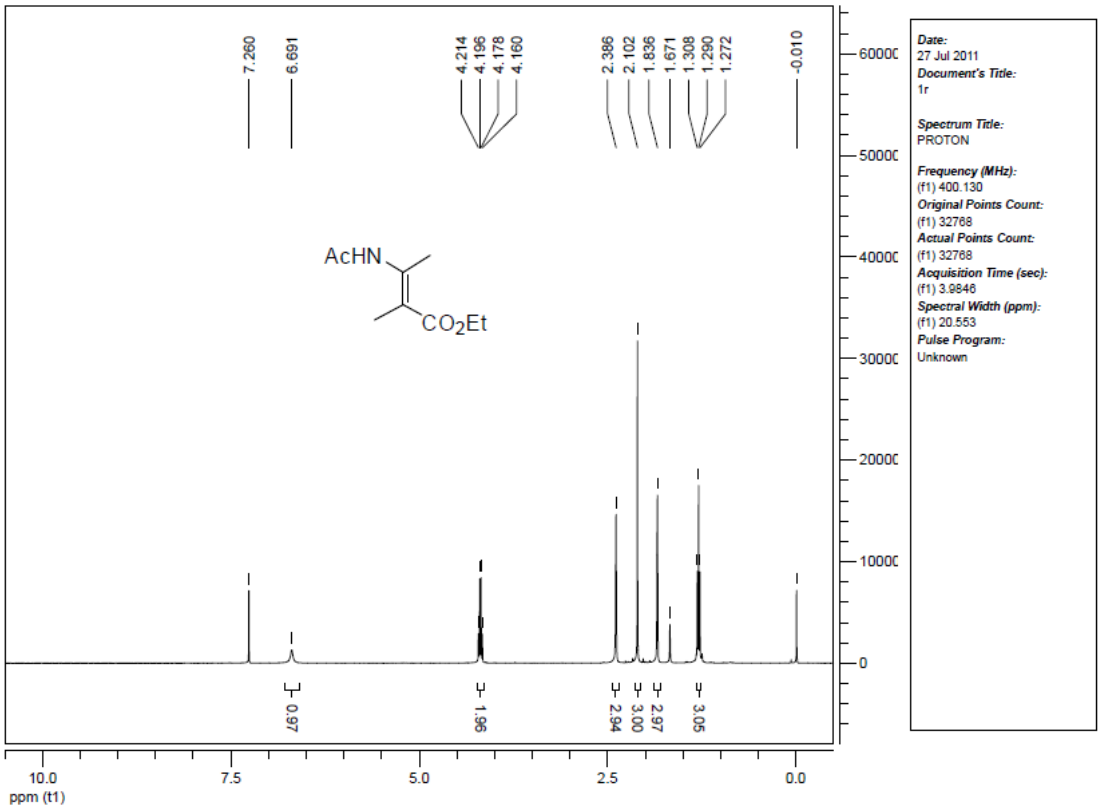


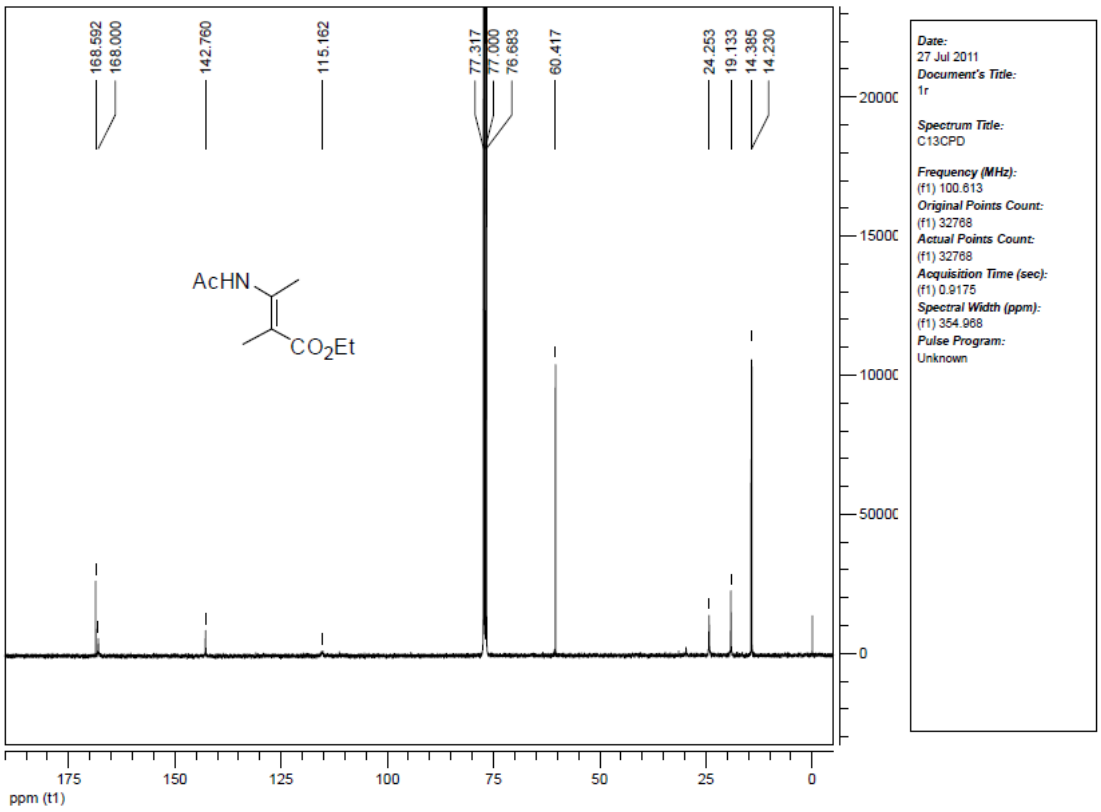
Ethyl 3-acetamido-2-methylbut-3-enoate (5)



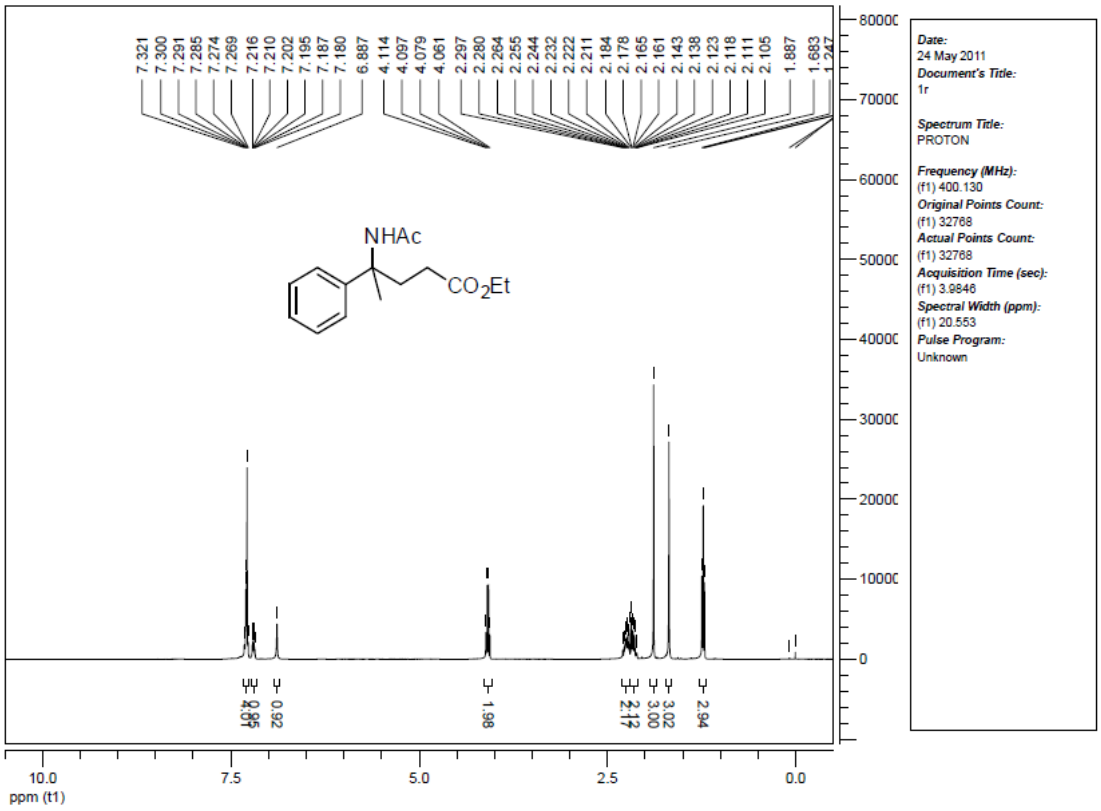


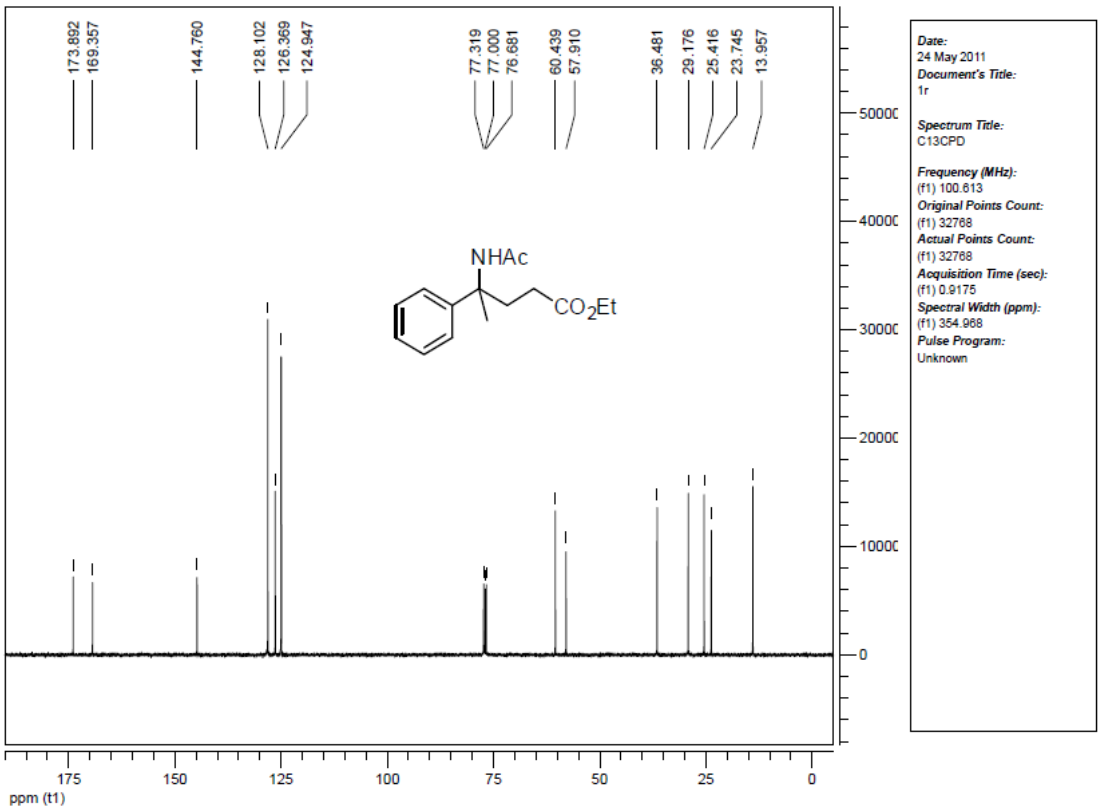
(*E*)-ethyl 3-acetamido-2-methylbut-2-enoate (6)





Ethyl 4-acetamido-4-phenylpentanoate (7)





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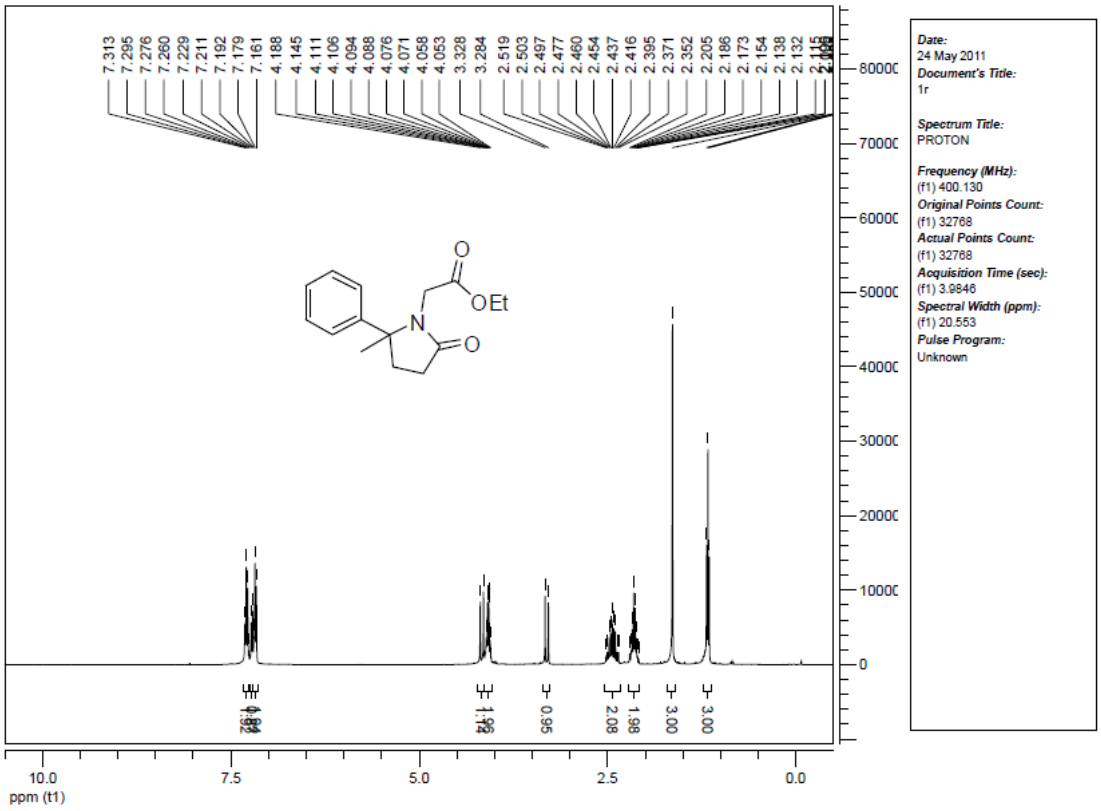
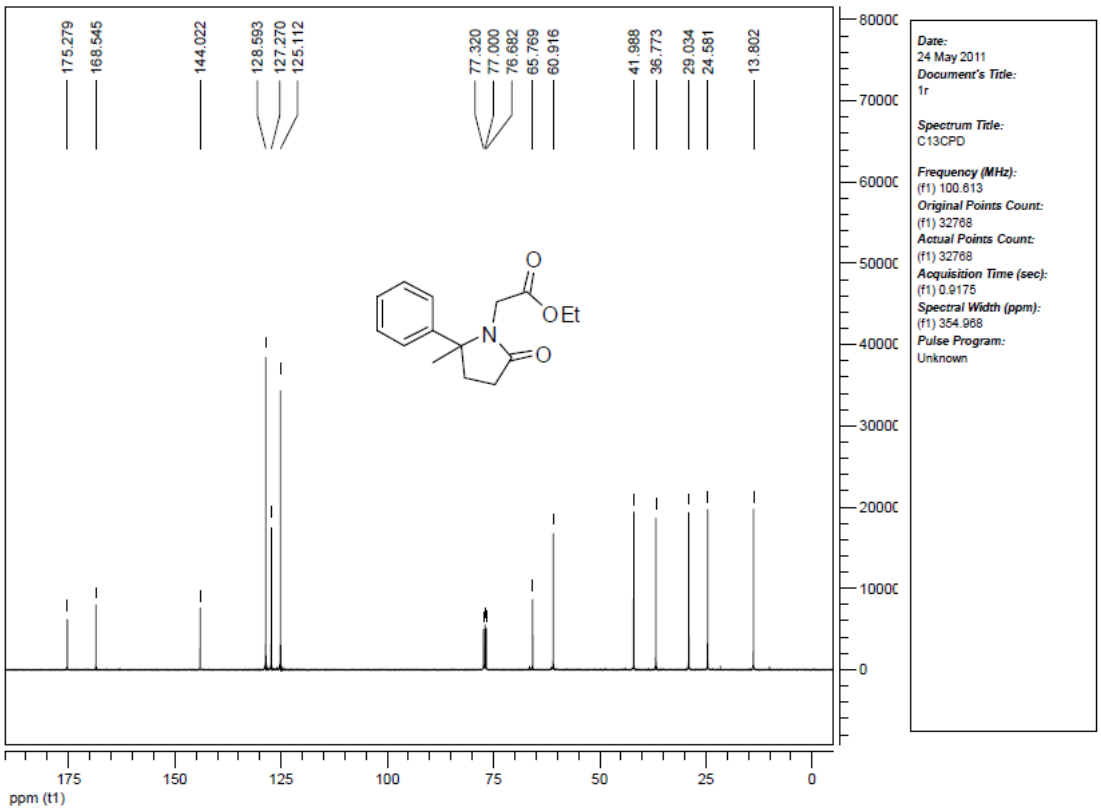
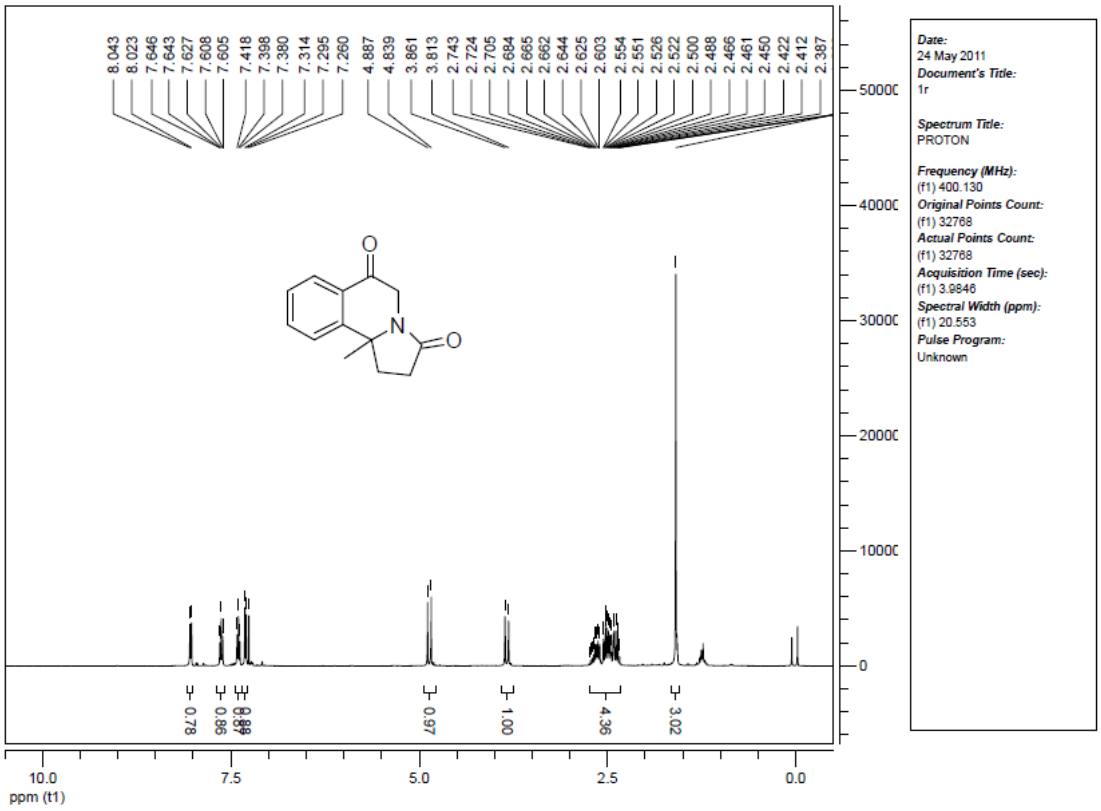
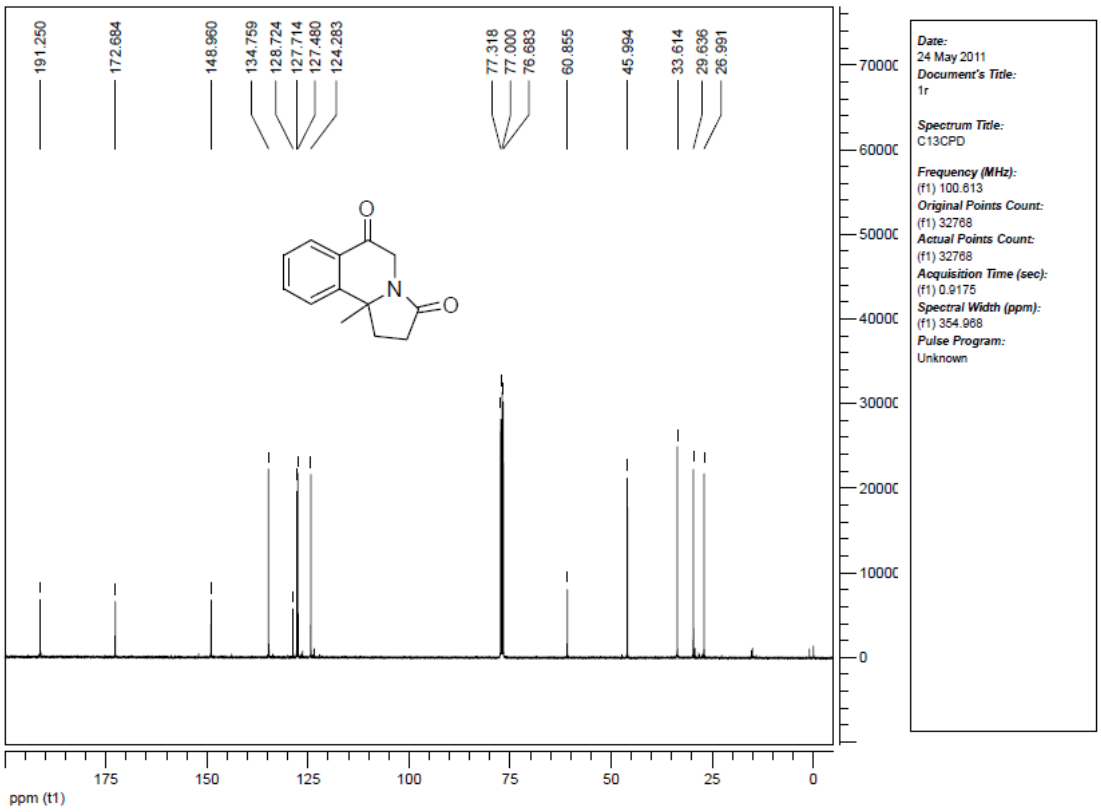
Ethyl 2-(2-methyl-5-oxo-2-phenylpyrrolidin-1-yl)acetate (8)





10b-methyl-1,2-dihydropyrrolo[2,1-a]isoquinoline-3,6(5H,10bH)-dione (9)





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10b-methyl-1,2,5,6-tetrahydropyrrolo[2,1-a]isoquinolin-3(10bH)-one (10)