Electronic supplementary information for

Copper-catalyzed three-component reactions of phenols, acyl chlorides and Wittig reagents for the synthesis of β-aryloxyl acrylates

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General experimental information

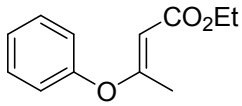
All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H and ^{13}C NMR were recorded in 400 MHz apparatus. The frequency for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm using TMS as internal standard. HRMS data were obtained under ESI model in the spectrometer equipped with ion trap analyzer. Melting points were tested in X-4A instrument without correcting temperature.

General procedure for the synthesis of alkyl acrylates 4 and 6.

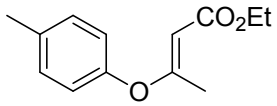
In a 25 mL round bottom flask, yilde **2** (0.45 mmol) was resolved in CH_2Cl_2 (2 mL), and acyl chloride **3** (0.45 mmol), Et_3N (0.45 mmol) as well as phenol **1** (0.3 mmol), CuBr (0.03 mmol), **L3** (0.06 mmol), Cs_2CO_3 (0.6 mmol), DMF (2 mL) were then employed. For the synthesis of **6**, all reagents except phenol and DMF were doubled. The resulting mixture was stirred at 90 ^{o}C for 8 h (TLC). The reaction was allowed to stand to cool down to room temperature, and 10 mL water was added. The heterogeneous mixture was the extracted with ethyl acetate (3 ×10 mL). The combined organic layer was dried overnight with anhydrous Na_2SO_4. The solution was then collected by filtration, and the solvent was removed at reduced pressure. The residue was subjected to silica gel column chromatography to give pure products

using mixed petroleum ether and ethyl acetate (V_{PET}: V_{EA} = 60:1).

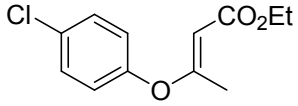
Characterization data



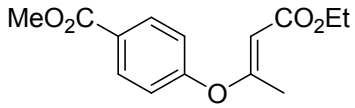
(*E*)-Ethyl 3-phenoxybut-2-enoate (4a).[1] Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, 2 H, *J* = 6.0 Hz), 7.14 (t, 1 H, *J* = 8.0 Hz), 6.94 (d, 2 H, *J* = 8.0 Hz), 4.78 (s, 1 H), 4.01 (q, 2 H, *J* = 6.7 Hz), 2.42 (s, 3 H), 1.13 (t, 3 H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 167.7, 153.3, 130.1, 125.6, 121.5, 96.1, 59.5, 18.5, 14.3.



(*E*)-Ethyl 3-(*p*-tolyloxy)but-2-enoate (4b).[1] Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, 2 H, *J* = 8.0 Hz), 6.82 (d, 2 H, *J* = 8.0 Hz), 4.78 (s, 1 H), 4.01 (q, 2 H, *J* = 8.0 Hz), 2.40 (s, 3 H), 2.28 (s, 3 H), 1.13 (t, 3 H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 166.7, 150.1, 134.2, 129.4, 120.2, 94.9, 58.4, 19.8, 17.4, 13.3.

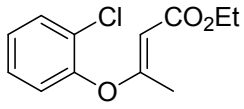


(*E*)-Ethyl 3-(4-chlorophenoxy)but-2-enoate (4c). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, 2 H, *J* = 8.0 Hz), 6.89 (d, 2 H, *J* = 8.0 Hz), 4.78 (s, 1 H), 4.02 (q, 2 H, *J* = 8.0 Hz), 2.40 (s, 3 H), 1.14 (t, 3 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3, 167.3, 151.9, 131.1, 130.1, 122.9, 96.7, 59.6, 18.3, 14.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{12}H_{13}ClNaO_3$: 263.0451; found: 263.0470.

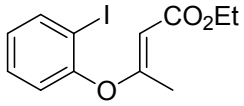


(*E*)-Methyl 4-(4-ethoxy-4-oxobut-2-en-2-yloxy)benzoate (4d). White solid, m.p. 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, 2 H, *J* = 8.0 Hz), 7.09 (d, 2 H, *J* = 8.0 Hz), 4.92 (s, 1 H), 4.10 (q, 2 H, *J* = 8.0 Hz), 3.92 (s, 3 H), 2.49 (s, 3 H), 1.21 (t, 3 H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 167.2, 166.2, 157.3, 131.8,

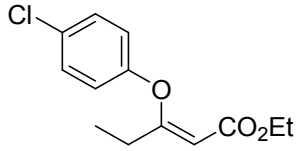
127.4, 121.2, 97.9, 59.7, 52.2, 18.2, 14.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{17}O_5$: 265.1076; found: 265.1070.



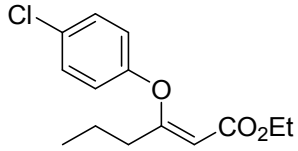
(*E*)-Ethyl 3-(2-chlorophenoxy)but-2-enoate (4e).[1] Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, 1 H, *J* = 8.0 Hz), 7.22 (t, 1 H, *J* = 8.0 Hz), 7.12 (t, 1 H, *J* = 8.0 Hz), 7.02 (d, 1 H, *J* = 8.0 Hz), 4.68 (s, 1 H), 4.02 (q, 2 H, *J* = 8.0 Hz), 2.45 (s, 3 H), 1.14 (t, 3 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 167.3, 149.2, 130.9, 128.2, 127.1, 126.8, 123.6, 96.1, 59.6, 17.9, 14.3.



(*E*)-Ethyl 3-(2-iodophenoxy)but-2-enoate (4f).[1] Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, 1 H, *J* = 8.0 Hz), 7.34 (t, 1 H, *J* = 8.0 Hz), 7.04 (d, 1 H, *J* = 8.0 Hz), 6.94 (t, 1 H, *J* = 8.0 Hz), 4.74 (s, 1 H), 4.09 (q, 2 H, *J* = 6.7 Hz), 2.54 (s, 3 H), 1.19 (t, 3 H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 167.2, 153.2, 140.0, 129.9, 127.4, 122.7, 96.4, 90.4, 59.6, 18.3, 14.3.

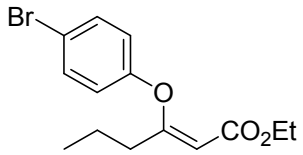


(*Z*)-Ethyl 3-(4-chlorophenoxy)pent-2-enoate (4g). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, 2 H, *J* = 8.0 Hz), 6.92 (d, 2 H, *J* = 8.0 Hz), 5.48 (s, 1 H), 4.09 (q, 2 H, *J* = 6.7 Hz), 2.24 (q, 2 H, *J* = 8.0 Hz), 1.18 (t, 3 H, *J* = 8.0 Hz), 1.09 (t, 3 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 164.5, 154.3, 129.5, 128.2, 118.9, 104.3, 59.9, 26.8, 14.1, 11.0. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{16}ClO_3$: 255.0788; found: 255.0790.

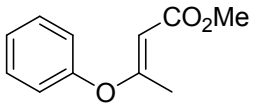


(*Z*)-Ethyl 3-(4-chlorophenoxy)hex-2-enoate (4h). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, 2 H, *J* = 8.0 Hz), 6.85 (d, 2 H, *J* = 8.0 Hz), 5.41 (s, 1 H),

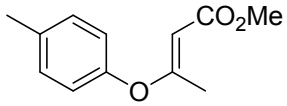
4.01 (q, 2 H, J = 8.0 Hz), 2.12 (t, 2 H, J = 8.0 Hz), 1.50-1.41 (m, 2 H), 1.11 (t, 3 H, J = 8.0 Hz), 0.85 (t, 3 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 164.3, 154.4, 129.5, 128.1, 118.8, 105.5, 59.8, 35.5, 19.9, 14.1, 13.4. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{18}ClO_3$: 269.0944; found: 269.0944.



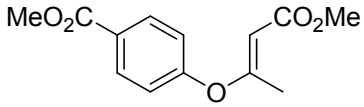
(*Z*)-Ethyl 3-(4-bromophenoxy)hex-2-enoate (4i). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, 2 H, J = 8.0 Hz), 6.87 (d, 2 H, J = 8.0 Hz), 5.49 (s, 1 H), 4.08 (q, 2 H, J = 8.0 Hz), 2.19 (t, 2 H, J = 8.0 Hz), 1.58-1.48 (m, 2 H), 1.17 (t, 3 H, J = 6.0 Hz), 0.92 (t, 3 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 164.4, 155.0, 132.5, 119.2, 115.6, 105.7, 59.9, 35.5, 19.8, 14.1, 13.4. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{18}BrO_3$: 313.0439; found: 313.0443.



(*E*)-Methyl 3-phenoxybut-2-enoate (4j). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, 2 H, J = 8.0 Hz), 7.15 (t, 1 H, J = 8.0 Hz), 6.94 (d, 2 H, J = 8.0 Hz), 4.80 (s, 1 H), 3.55 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 167.0, 152.4, 128.9, 124.6, 120.5, 94.9, 49.8, 17.4. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{11}H_{12}NaO_3$: 215.0684; found: 215.0672.

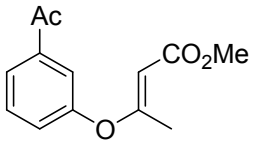


(*E*)-Methyl 3-(*p*-tolyloxy)but-2-enoate (4k). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, 2 H, J = 8.0 Hz), 6.82 (d, 2 H, J = 8.0 Hz), 4.79 (s, 1 H), 3.54 (s, 3 H), 2.41 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 167.1, 150.1, 134.3, 129.4, 120.2, 94.5, 49.7, 19.8, 17.4. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_{14}NaO_3$: 229.0841; found: 229.0850.

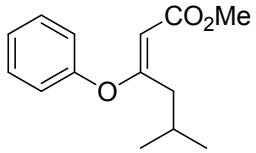


(*E*)-Methyl 4-(4-methoxy-4-oxobut-2-en-2-yloxy)benzoate (4l). Pale yellow liquid;

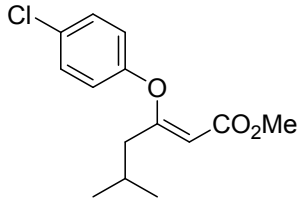
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, 2 H, *J* = 8.0 Hz), 7.01 (d, 2 H, *J* = 8.0 Hz), 4.87 (s, 1 H), 3.85 (s, 3 H), 3.56 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 167.7, 166.1, 157.3, 131.7, 127.5, 121.1, 97.7, 52.1, 50.9, 18.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{15}O_5$: 251.0919; found: 251.0903.



(*E*)-Methyl 3-(3-acetylphenoxy)but-2-enoate (4m). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, 1 H, *J* = 8.0 Hz), 7.53 (s, 1 H), 7.42 (t, 1 H, *J* = 8.0 Hz), 7.16 (d, 1 H, *J* = 8.0 Hz), 4.77 (s, 1 H), 3.55 (s, 3 H), 2.53 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 172.3, 167.6, 153.7, 139.2, 130.2, 126.1, 125.5, 121.2, 96.7, 50.8, 26.5, 18.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{14}NaO_4$: 257.0790; found: 257.0790.

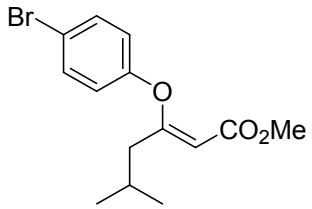


(*E*)-Methyl 5-methyl-3-phenoxyhex-2-enoate (4n). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, 2 H, *J* = 7.0 Hz), 7.22 (t, 1 H, *J* = 7.0 Hz), 7.00 (d, 2 H, *J* = 8.0 Hz), 4.85 (s, 1 H), 3.60 (s, 3 H), 2.85 (d, 2 H, *J* = 8.0 Hz), 2.22-2.14 (m, 1 H), 1.06 (d, 6 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9, 167.7, 153.6, 129.9, 125.6, 121.5, 96.1, 50.7, 39.7, 27.3, 22.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{19}O_3$: 235.1334; found: 235.1333.

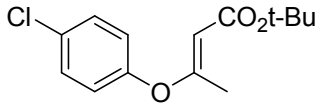


(*Z*)-Methyl 3-(4-chlorophenoxy)-5-methylhex-2-enoate (4o). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, 2 H, *J* = 8.0 Hz), 6.91 (d, 2 H, *J* = 8.0 Hz), 5.47 (s, 1 H), 3.63 (s, 3 H), 2.09 (d, 2 H, *J* = 8.0 Hz), 1.90-1.82 (m, 1 H), 0.91 (d, 6 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 164.7, 154.2, 129.5, 128.3, 118.9, 106.1, 50.8, 42.6, 26.2, 22.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}ClO_3$:

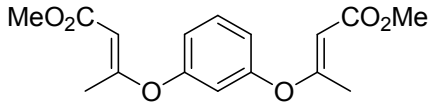
269.0944; found: 269.0942.



(*Z*)-Methyl 3-(4-bromophenoxy)-5-methylhex-2-enoate (4p). Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, 2 H, *J* = 8.0 Hz), 6.86 (d, 2 H, *J* = 8.0 Hz), 5.48 (s, 1 H), 3.62 (s, 3 H), 2.08 (d, 2 H, *J* = 8.0 Hz), 1.88-1.82 (m, 1 H), 0.91 (d, 6 H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 164.6, 154.7, 132.5, 119.3, 115.6, 106.2, 51.1, 42.6, 26.2, 22.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}BrO_3$: 313.0439; found: 313.0436.



(E)-*tert*-Butyl 3-(4-chlorophenoxy)but-2-enoate (4q). Pale yellow solid, m.p. 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, 2 H, *J* = 8.0 Hz), 6.89 (d, 2 H, *J* = 8.0 Hz), 4.71 (s, 1 H), 2.36 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 152.1, 130.7, 130.0, 129.5, 122.9, 98.8, 79.7, 28.3, 17.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}ClO_3$: 269.0944; found: 269.0938.

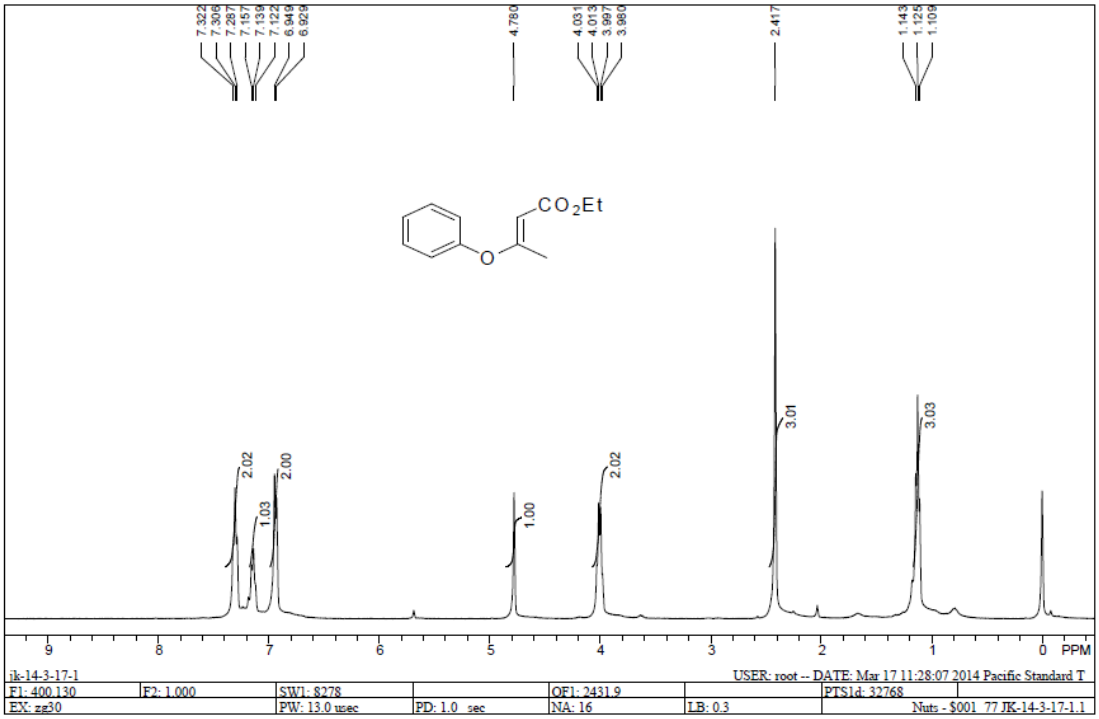


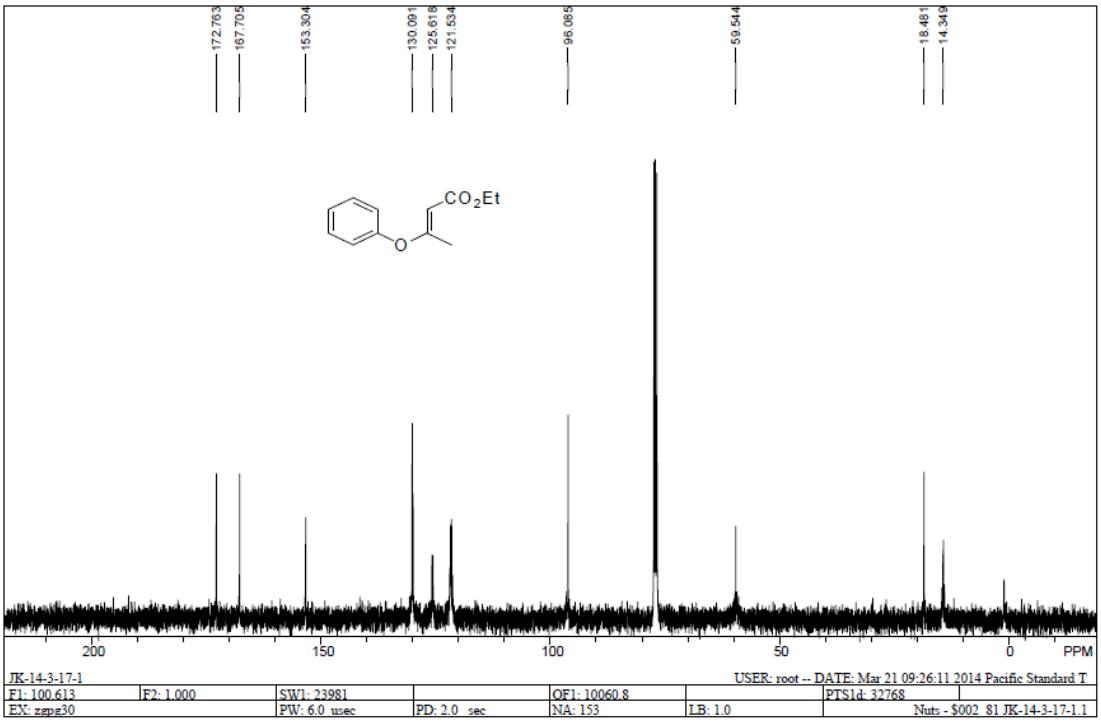
(*E*, *E*)-Dimethyl 3,3'-(1,3-phenylenebis(oxy))bis(but-2-enoate) (6). White solid, m.p. 112-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, 1 H, *J* = 8.0 Hz), 6.90 (d, 2 H, *J* = 8.0 Hz), 6.73 (s, 1 H), 4.94 (s, 2 H), 3.64 (s, 6 H), 2.47 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 167.7, 154.6, 130.9, 118.6, 115.0, 96.9, 50.8, 18.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{18}NaO_6$: 329.1001; found: 329.0995.

References

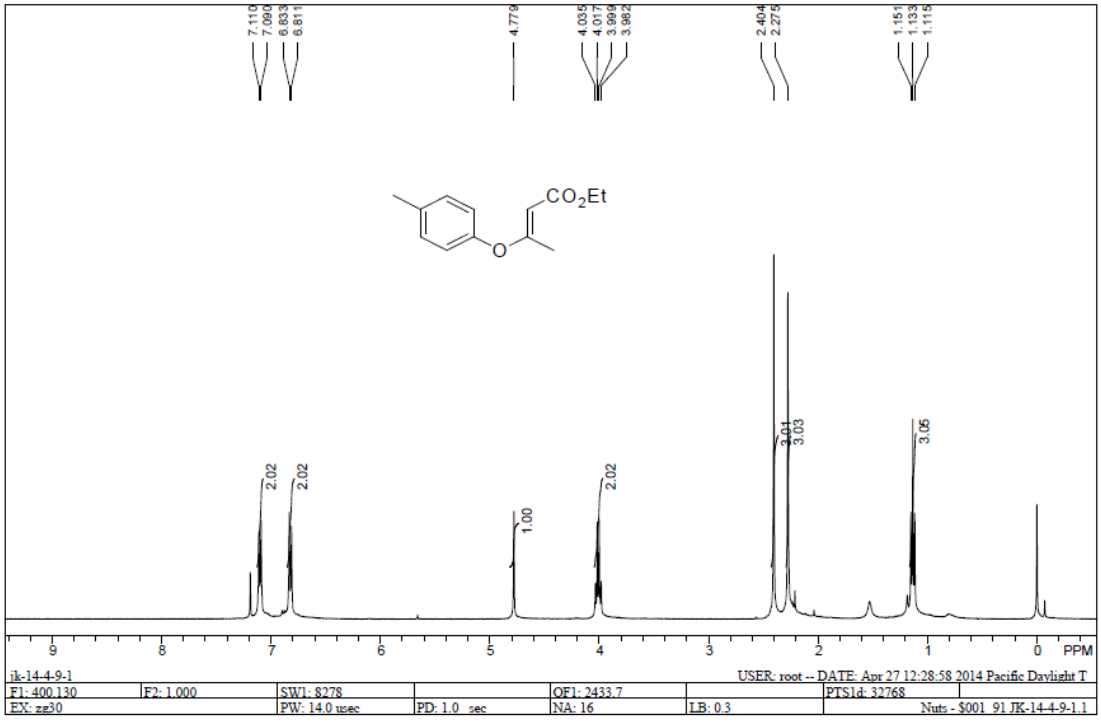
(1) G. W. Stewart, M. Shevlin, A. D. G. Yamagata, A. W. Gibson, S. P. Keen, J. P. Scott, *Org. Lett.* 2012, **14**, 5440.

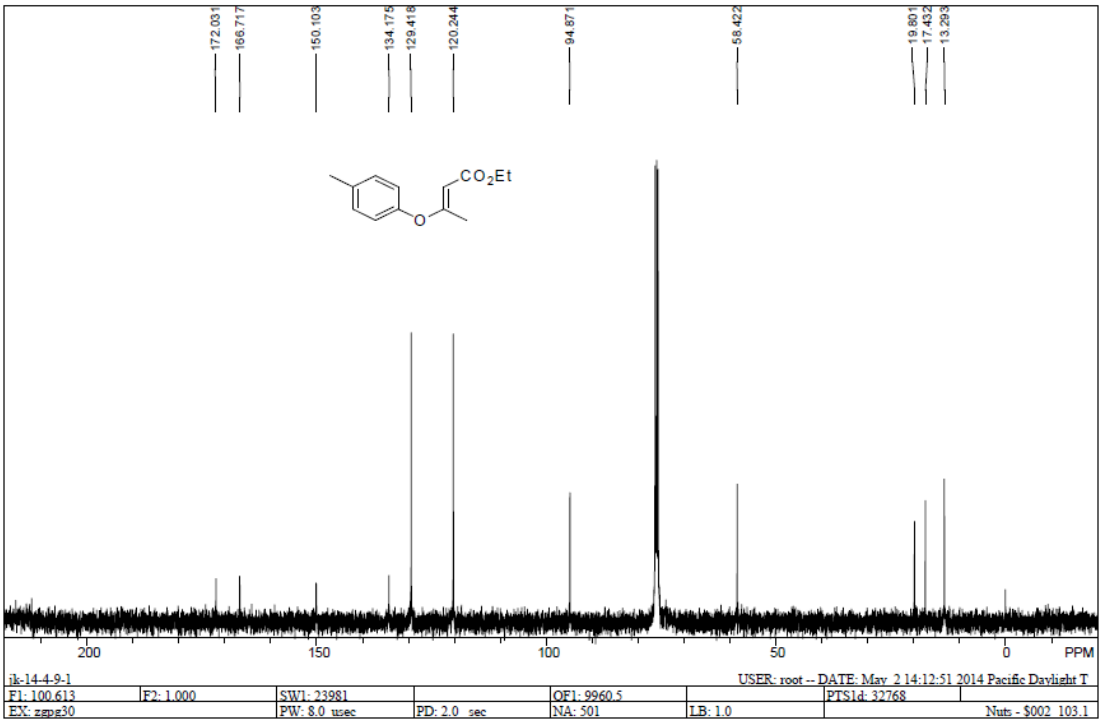
^{1}H and ^{13}C NMR of **4a**



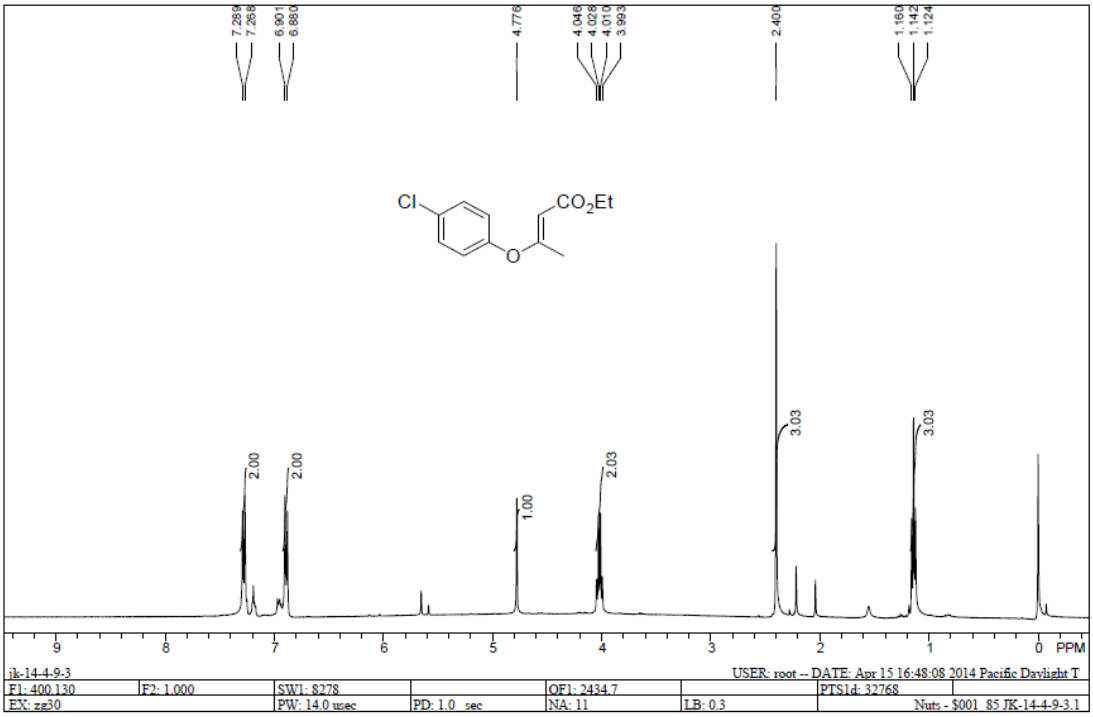


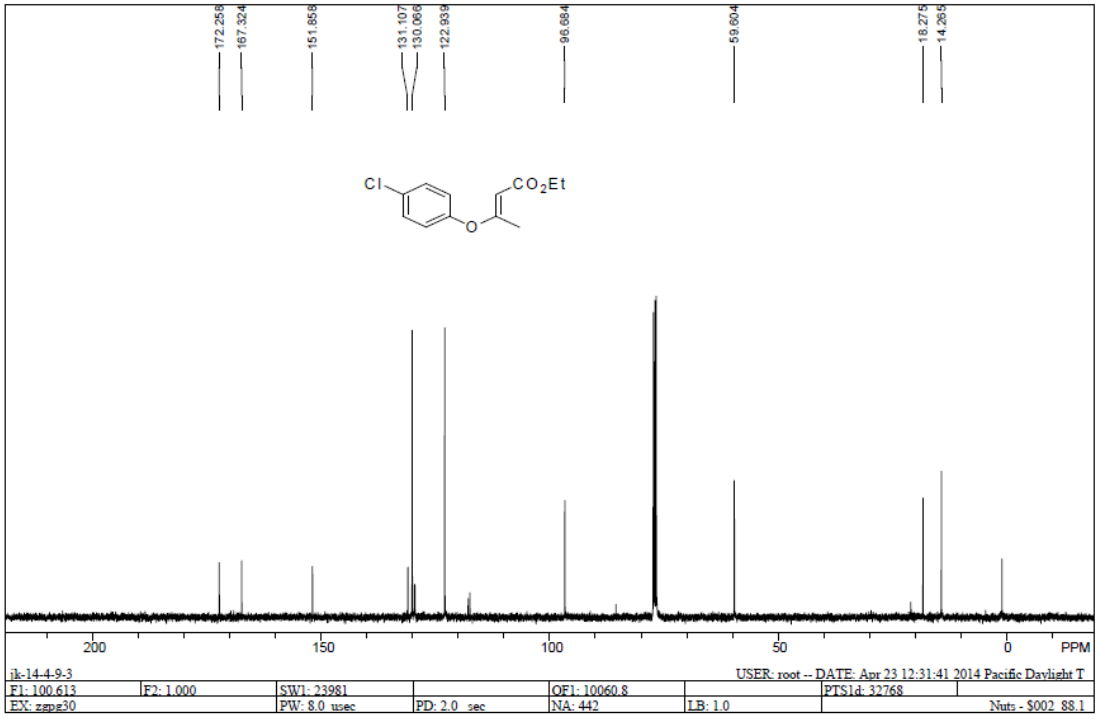
^{1}H and ^{13}C NMR of **4b**



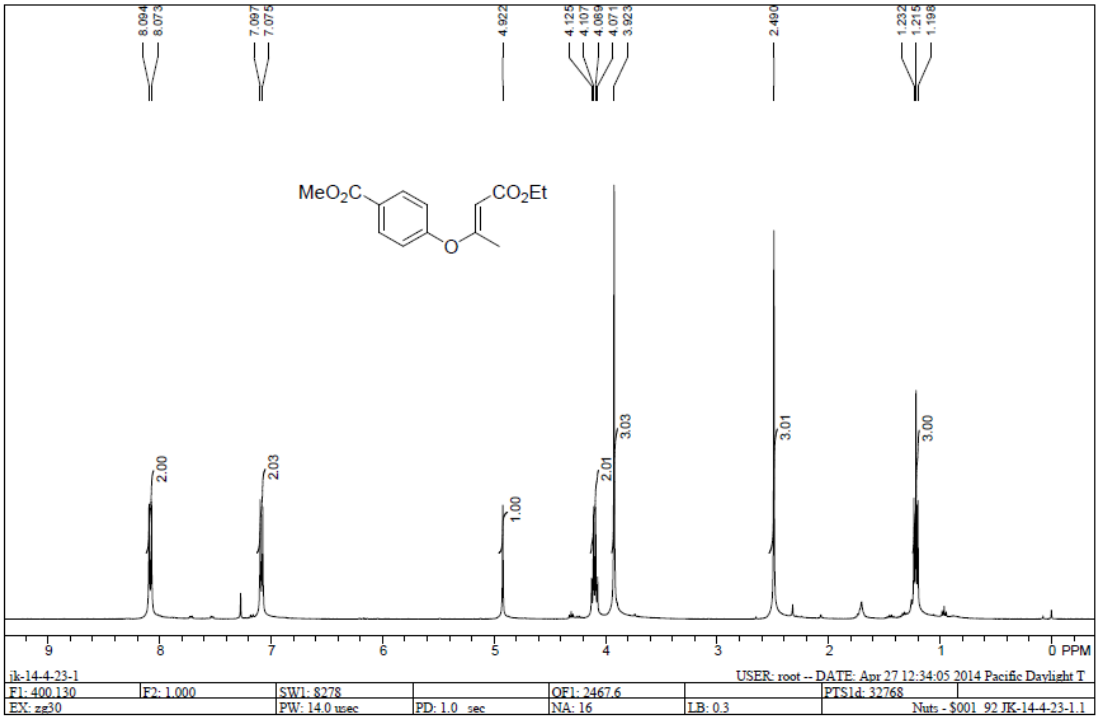


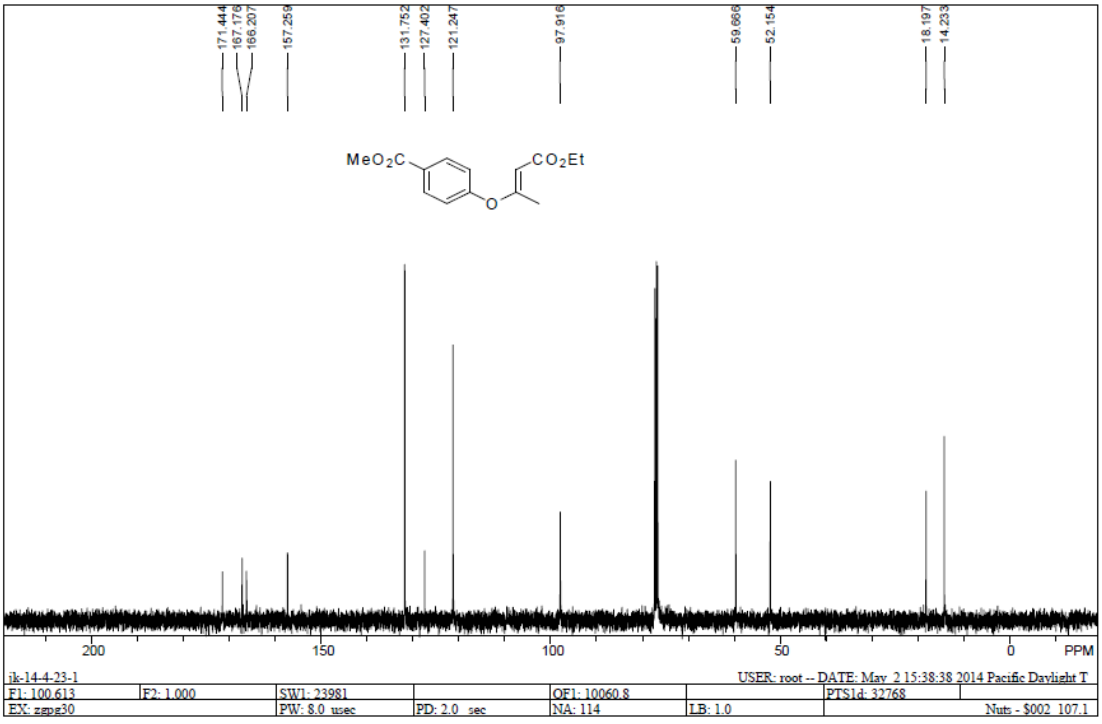
^{1}H and ^{13}C NMR of **4c**



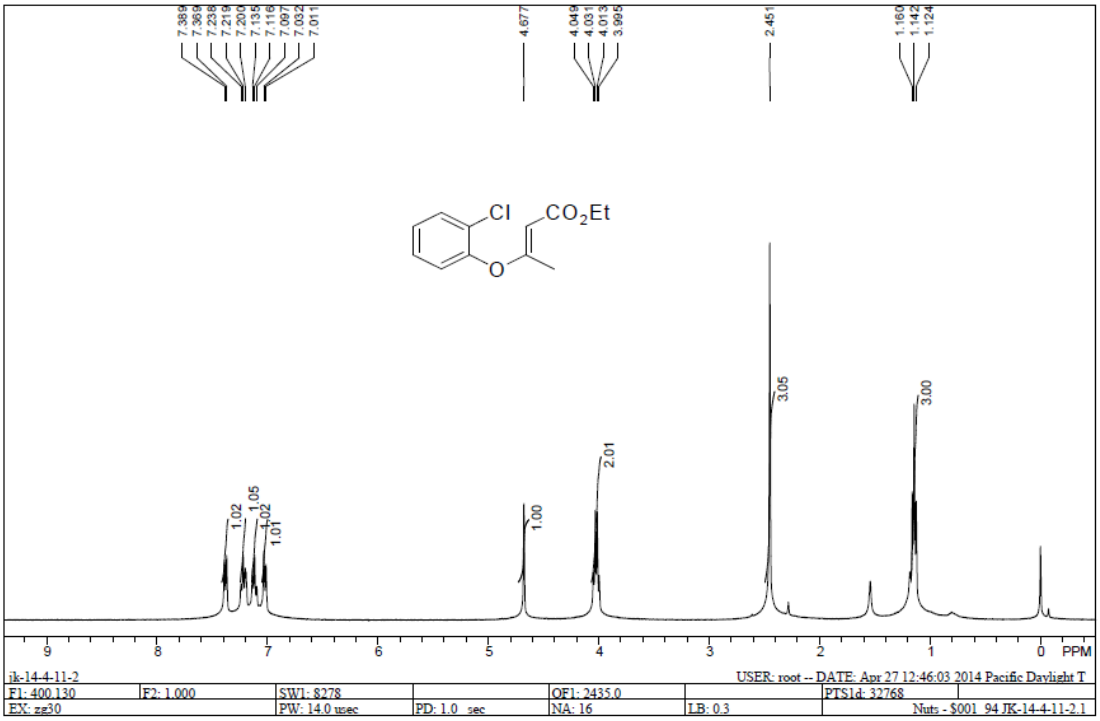


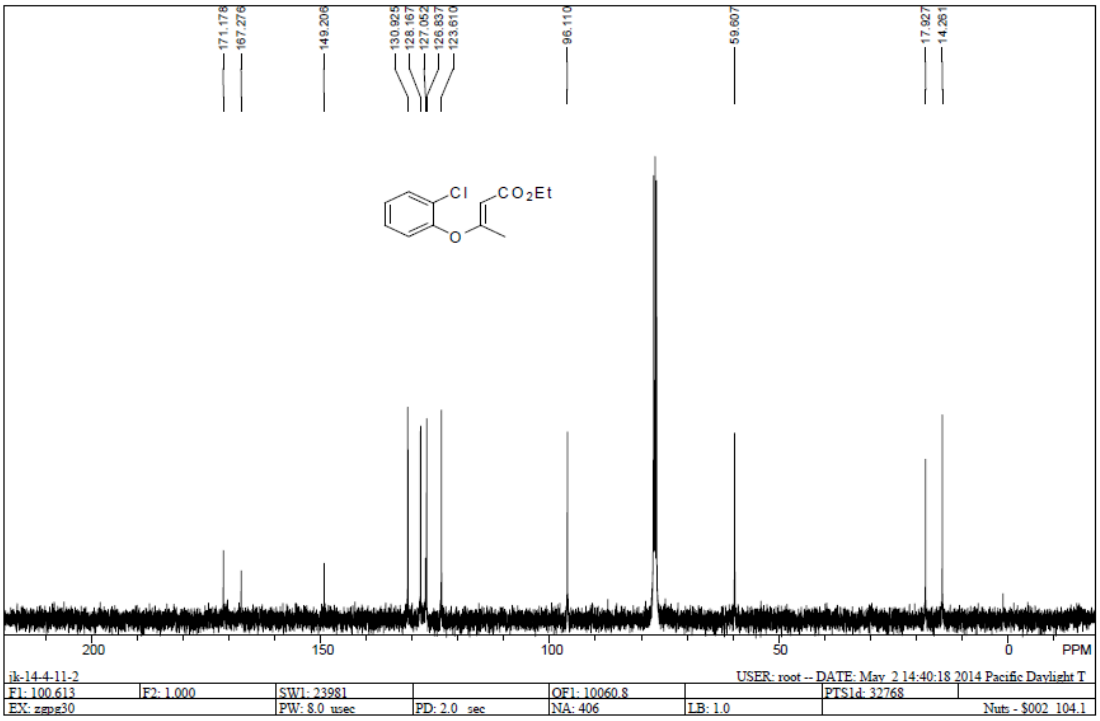
^{1}H and ^{13}C NMR of **4d**



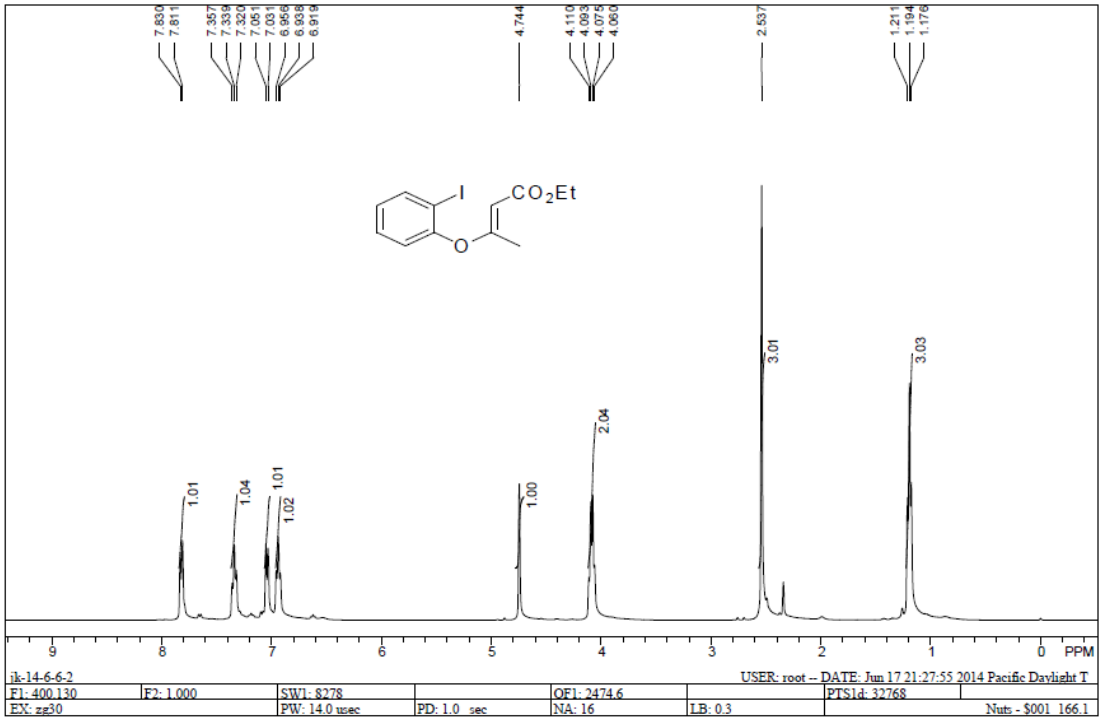


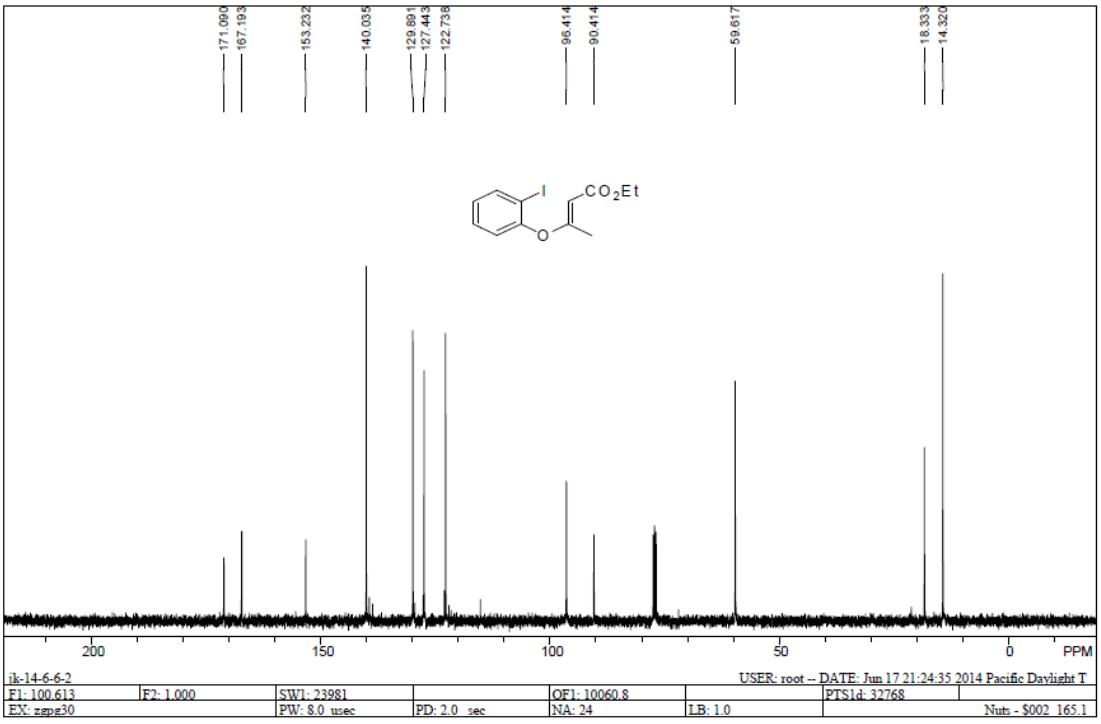
^{1}H and ^{13}C NMR of **4e**



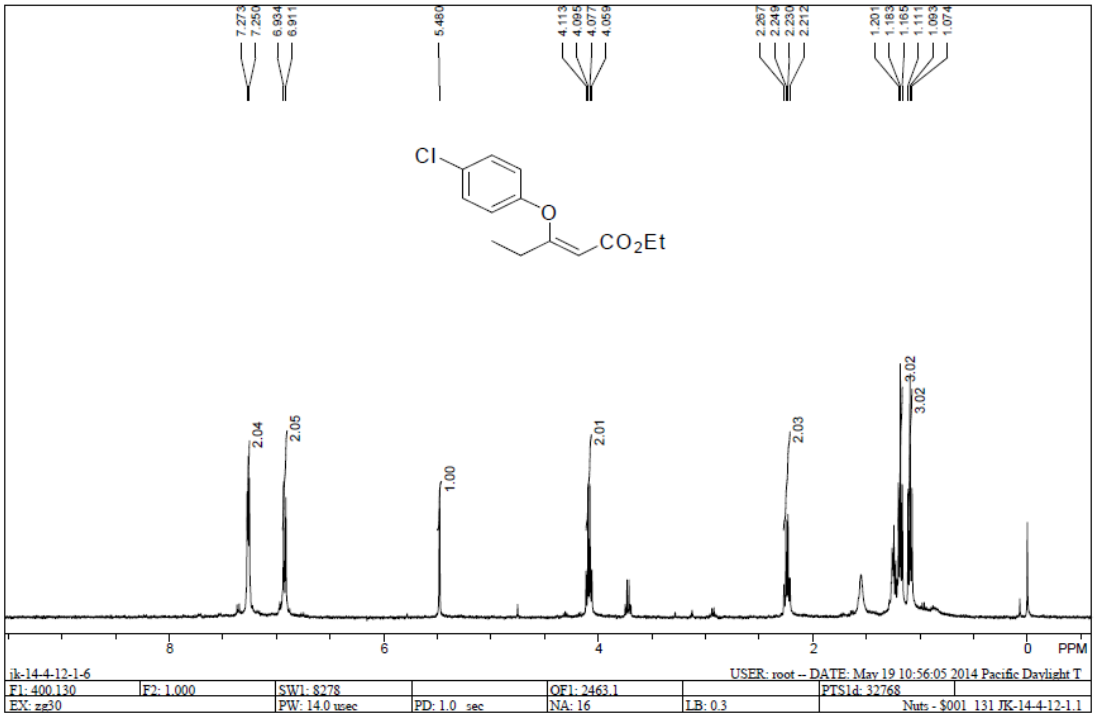


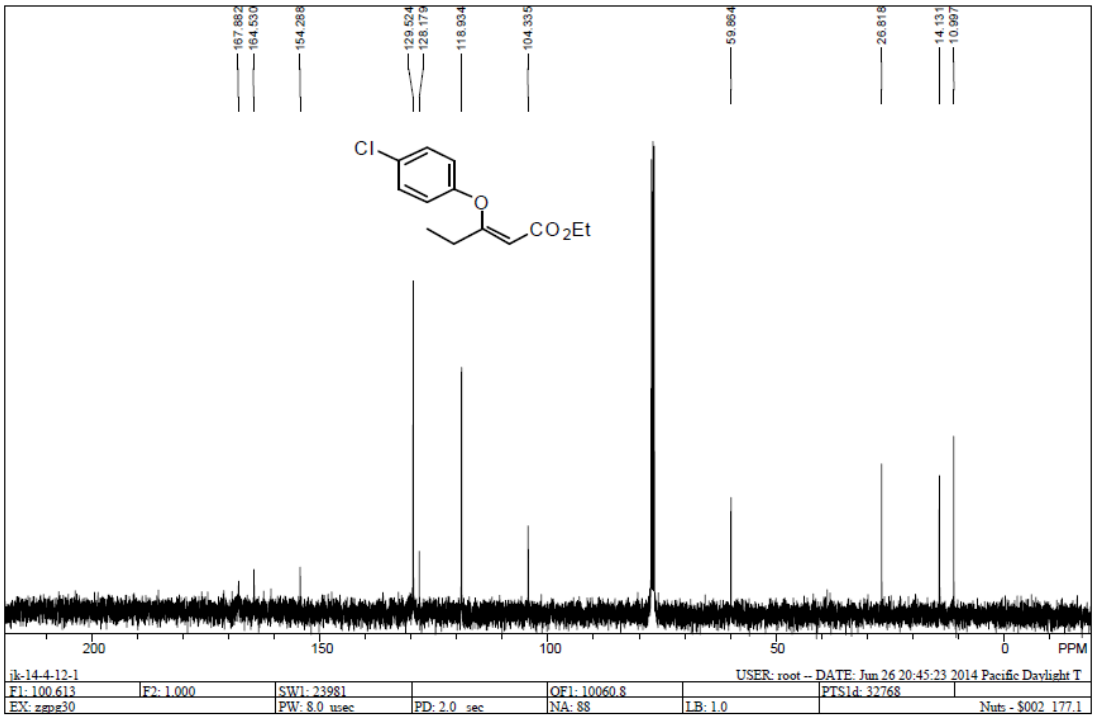
^{1}H and ^{13}C NMR of **4f**



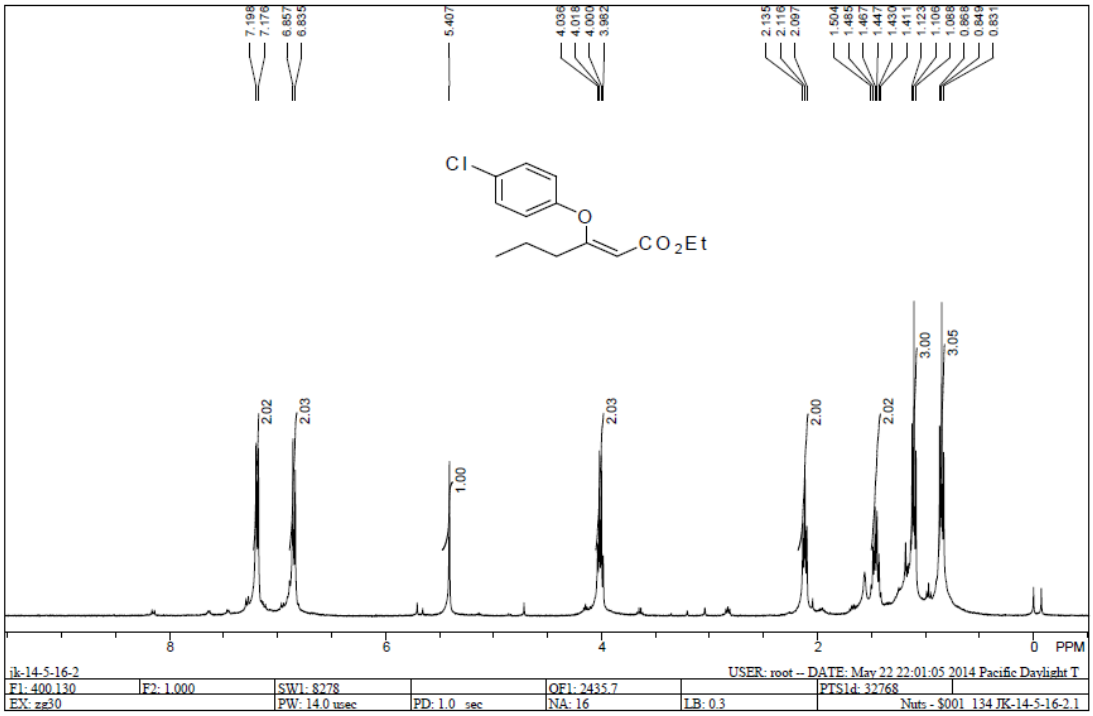


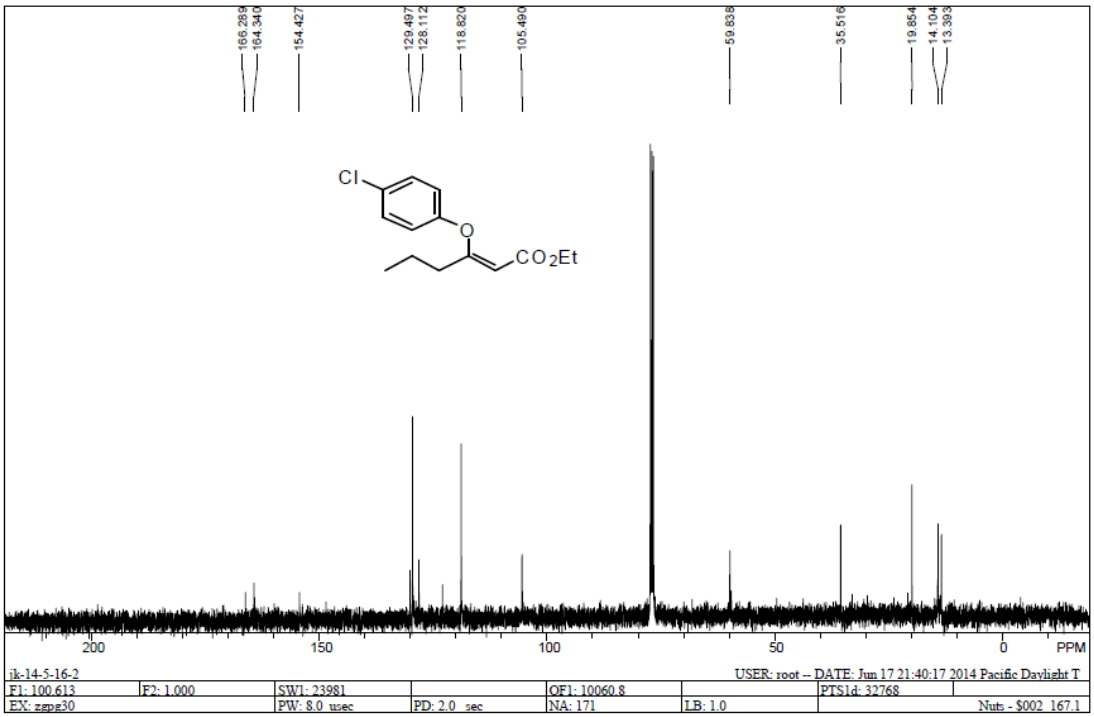
^{1}H and ^{13}C NMR of **4g**



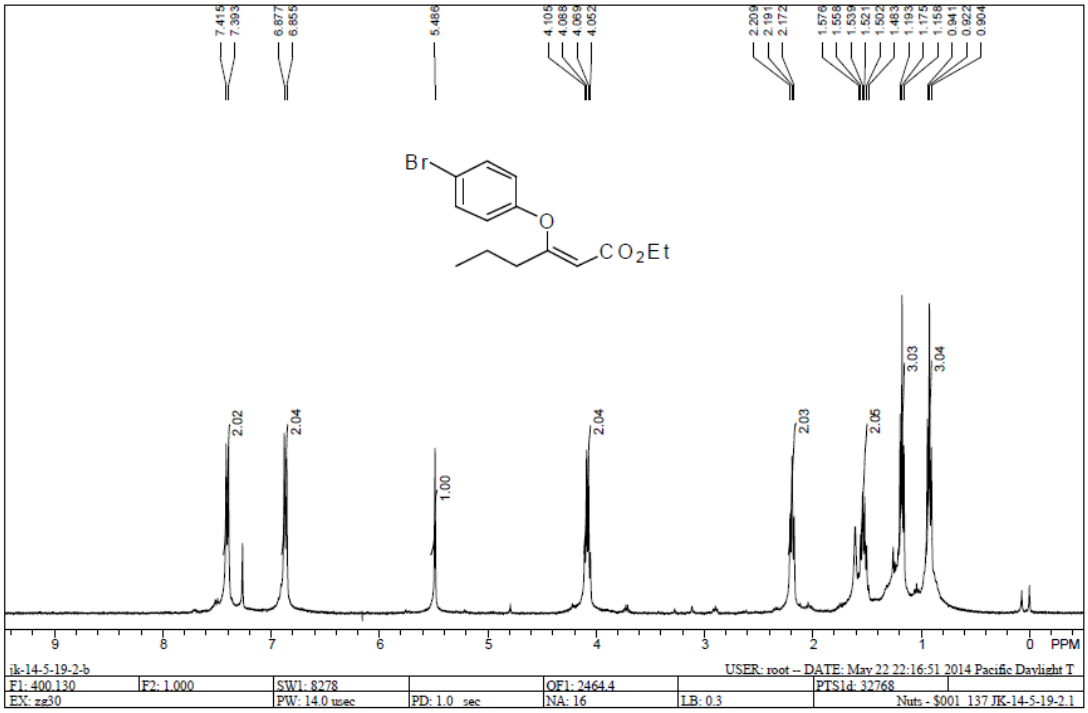


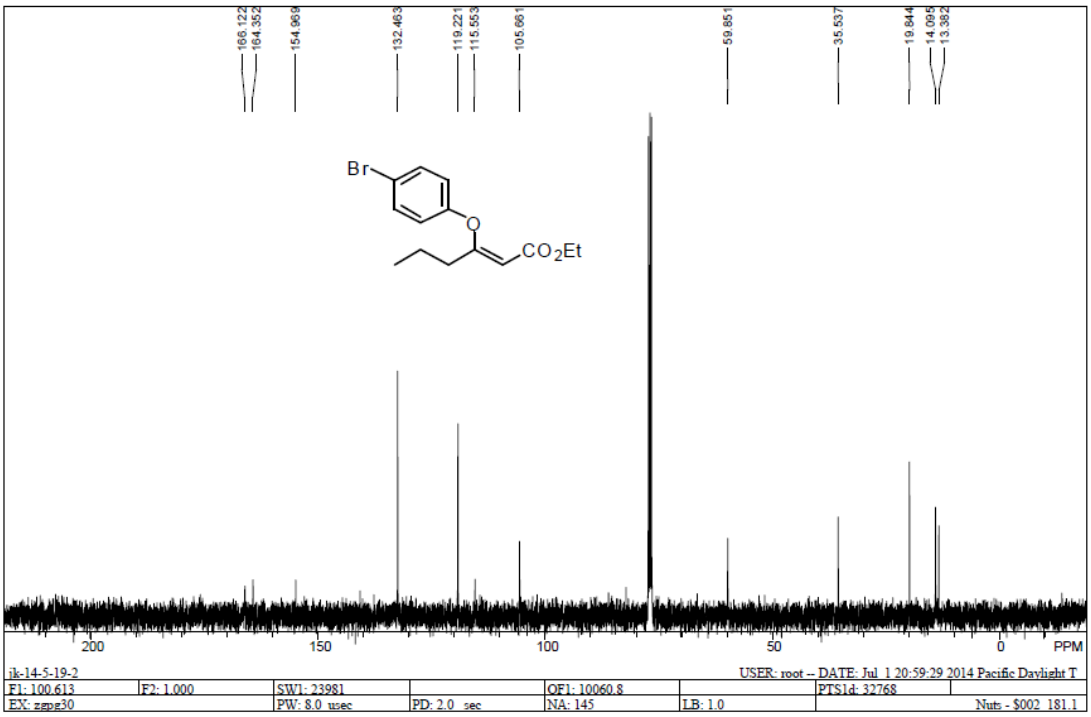
^{1}H and ^{13}C NMR of **4h**



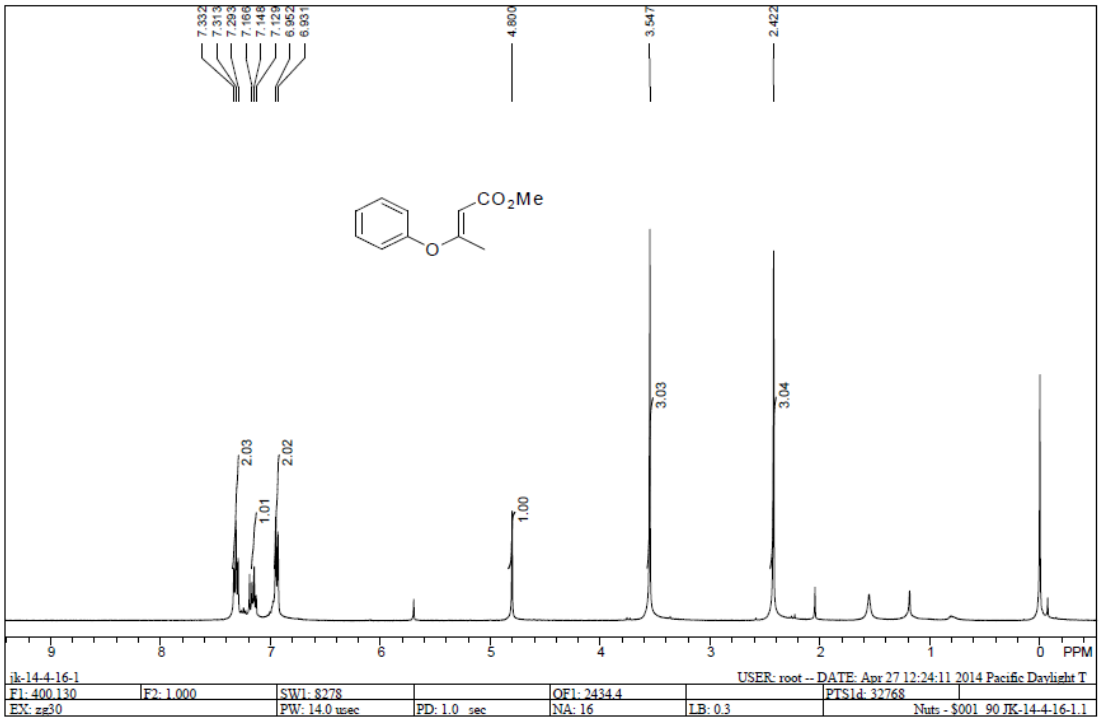


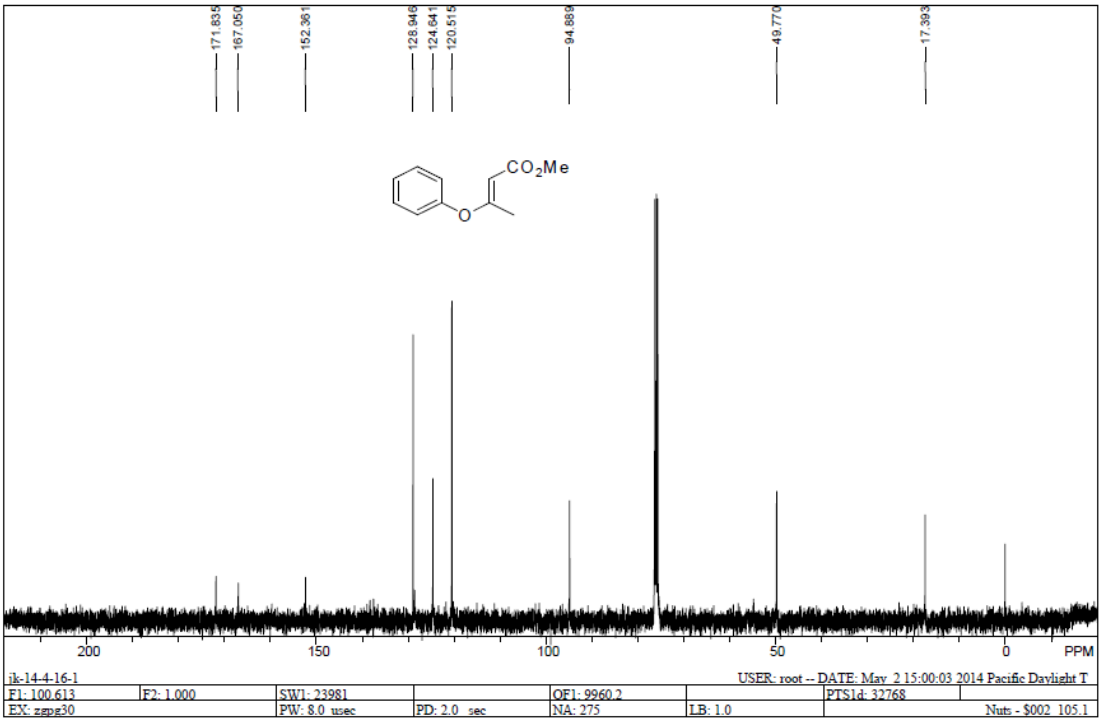
^{1}H and ^{13}C NMR of **4i**



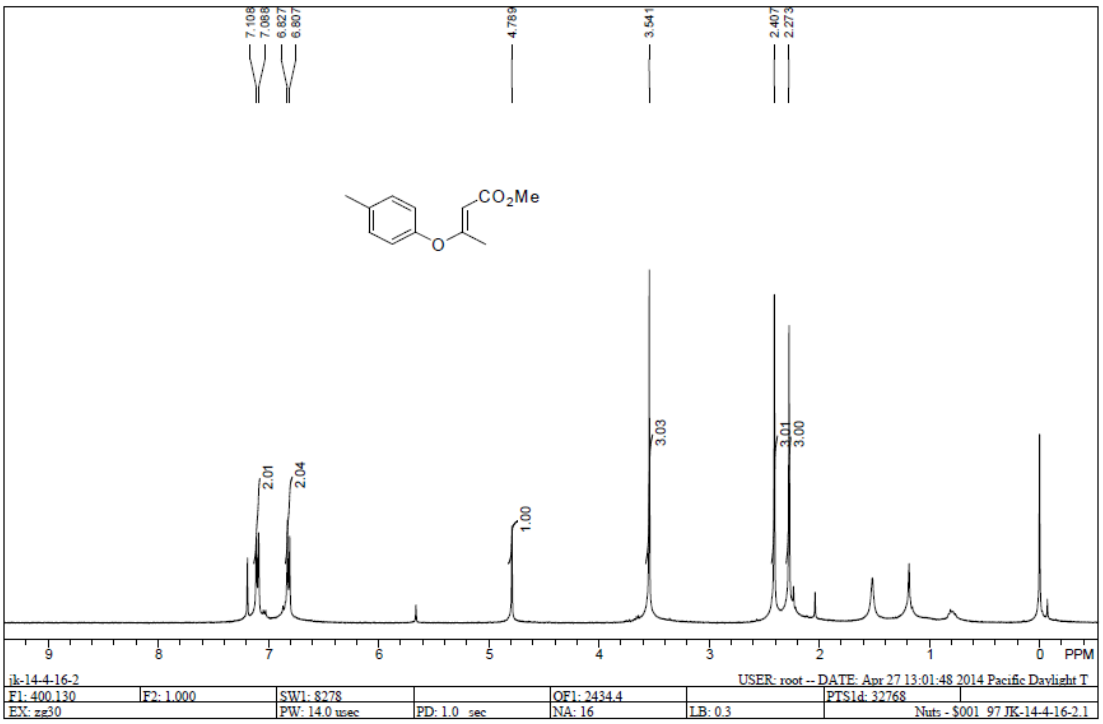


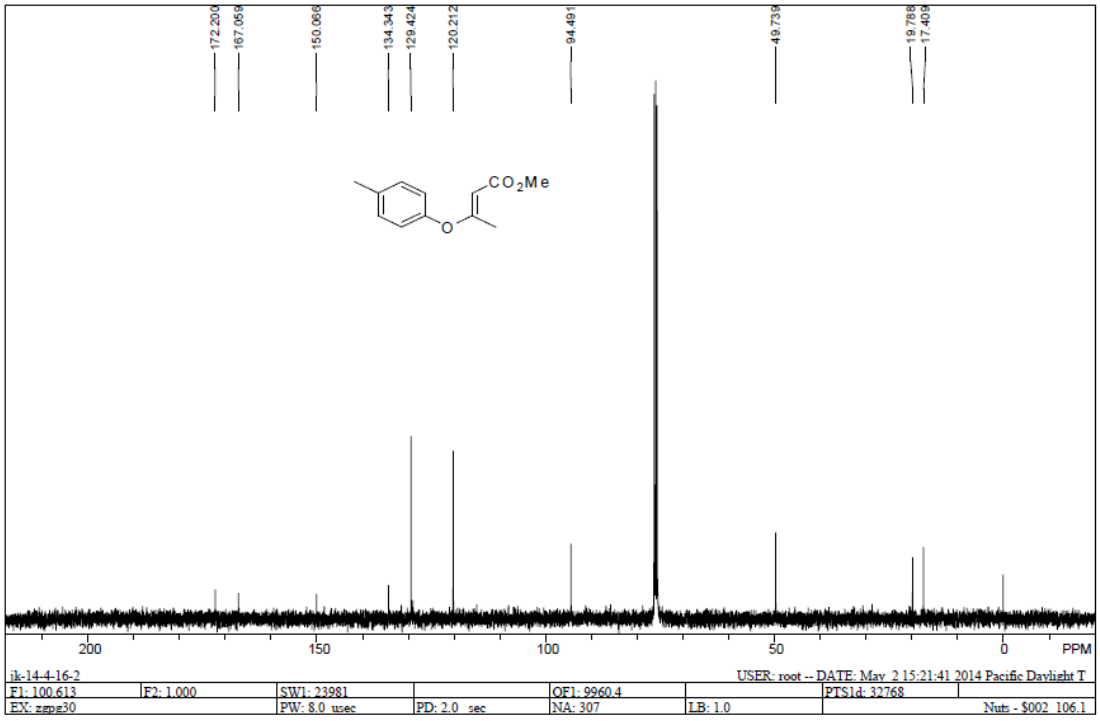
^{1}H and ^{13}C NMR of **4j**



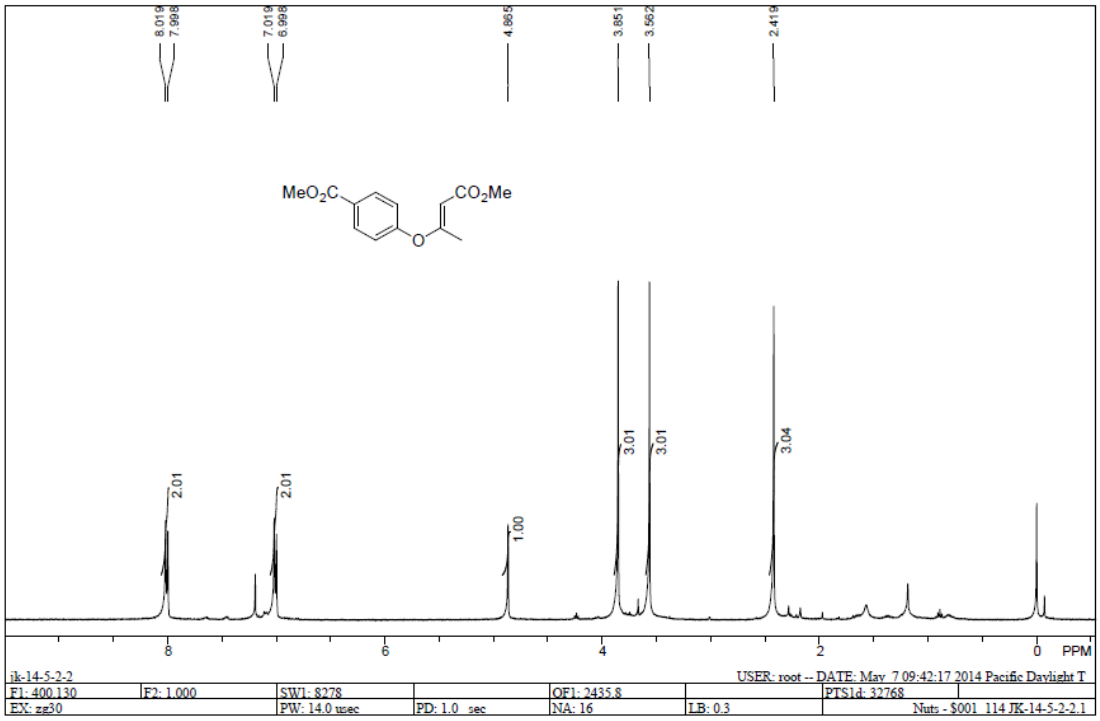


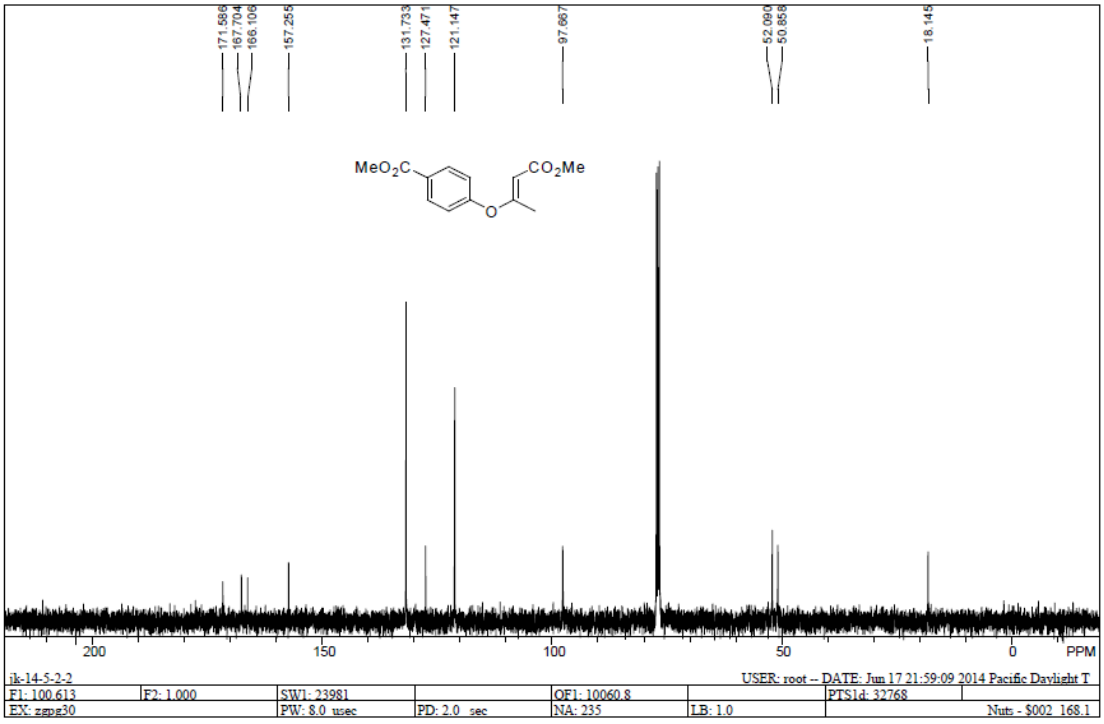
^{1}H and ^{13}C NMR of **4k**



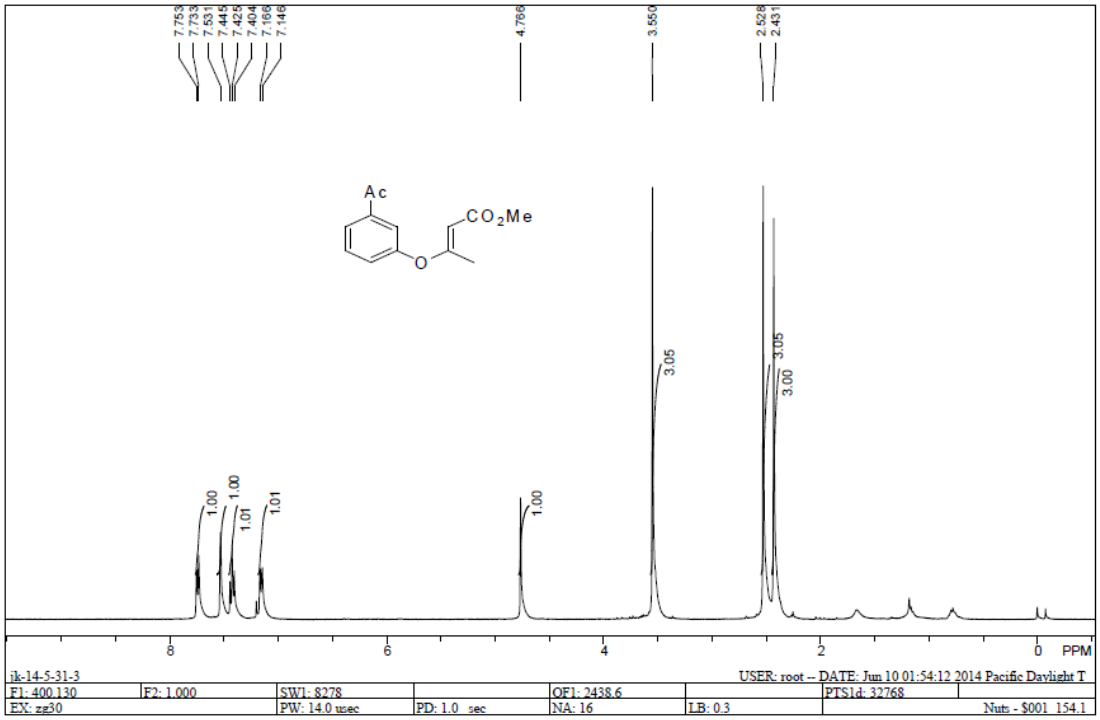


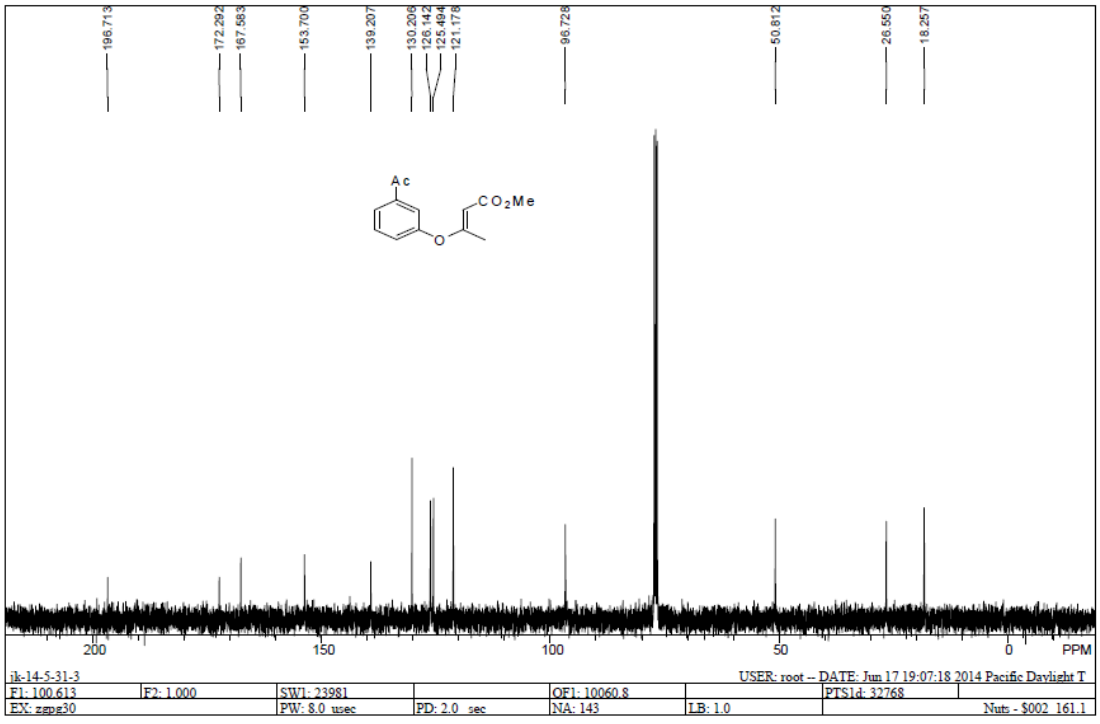
^{1}H and ^{13}C NMR of **4l**



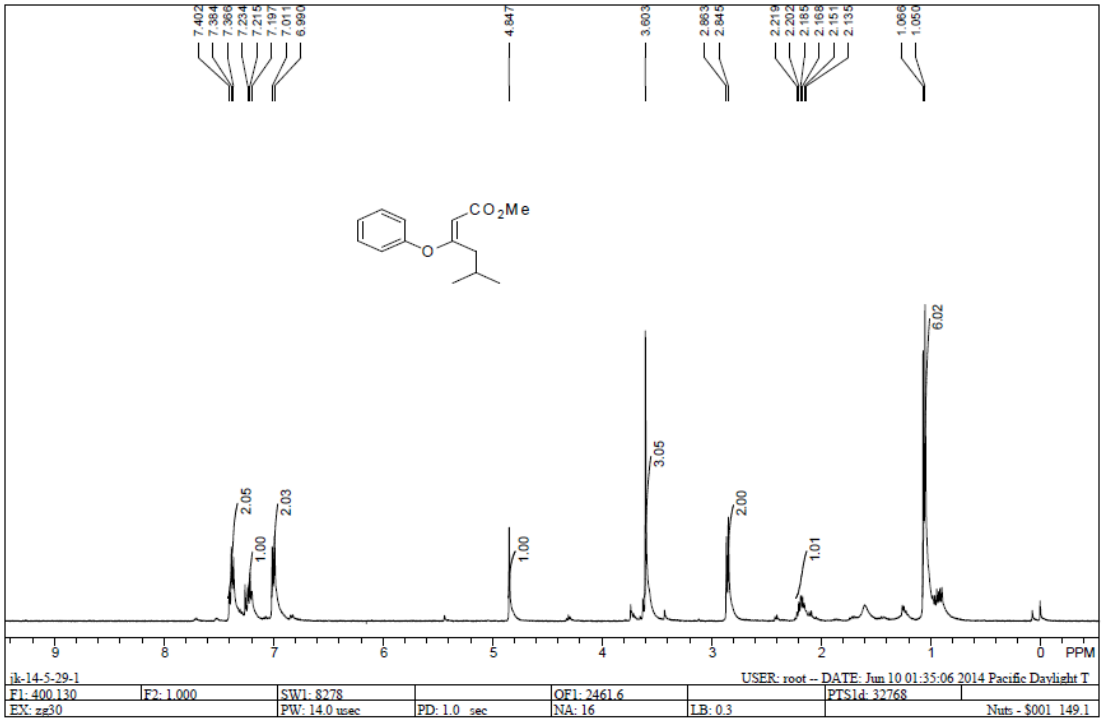


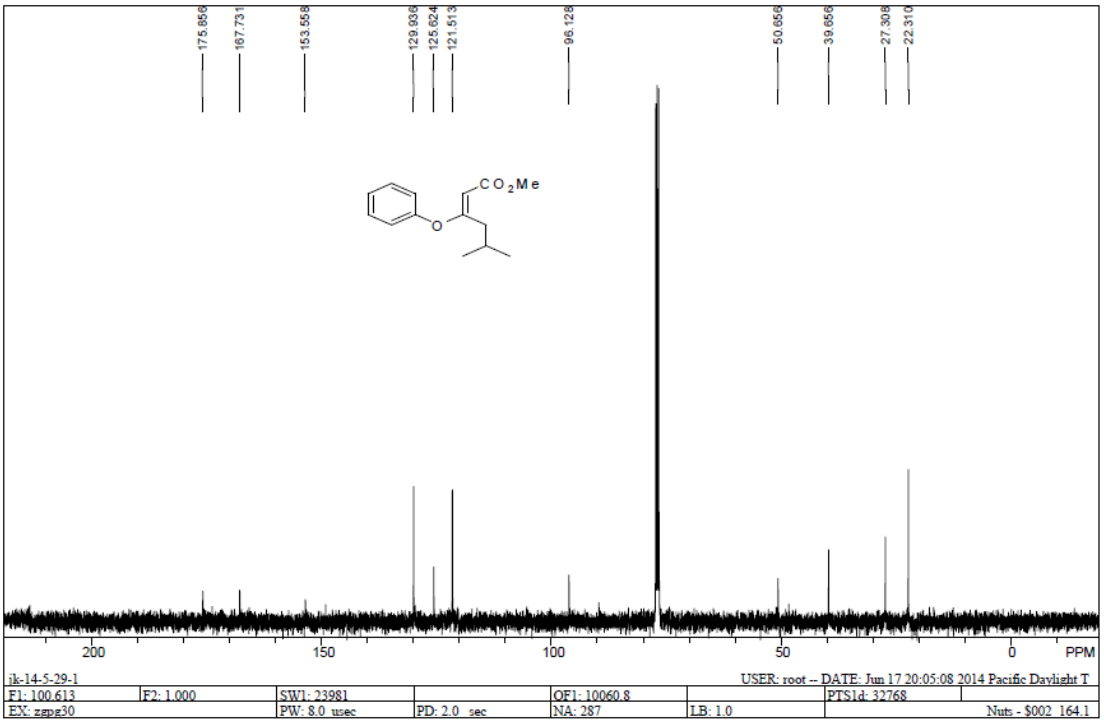
^{1}H and ^{13}C NMR of **4m**



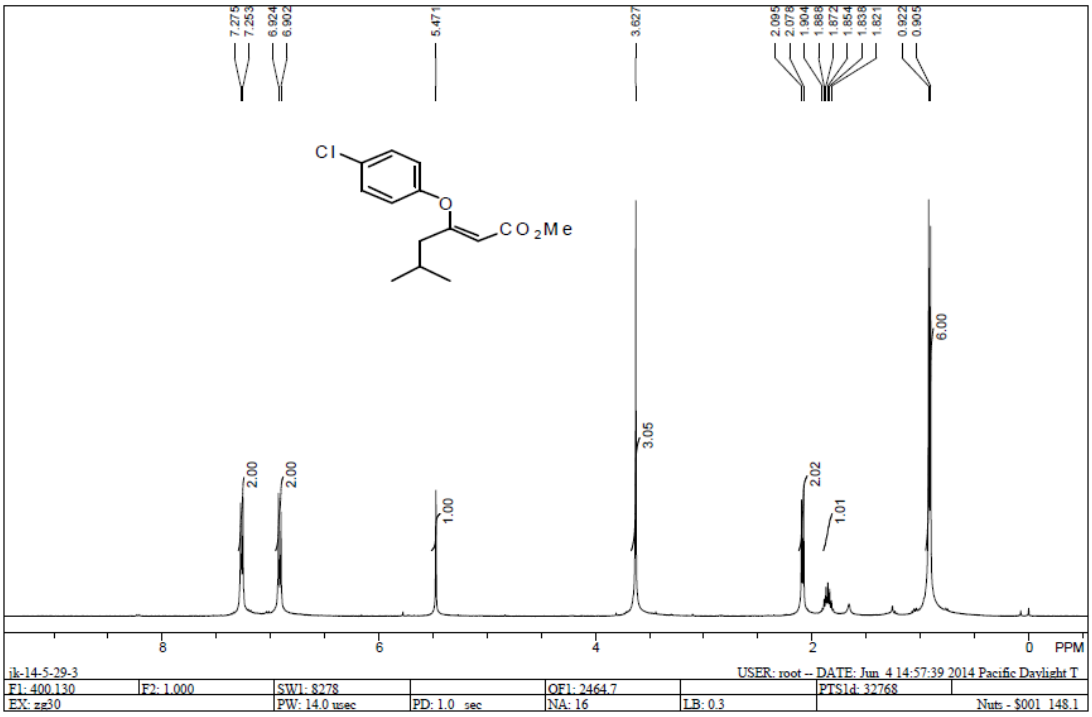


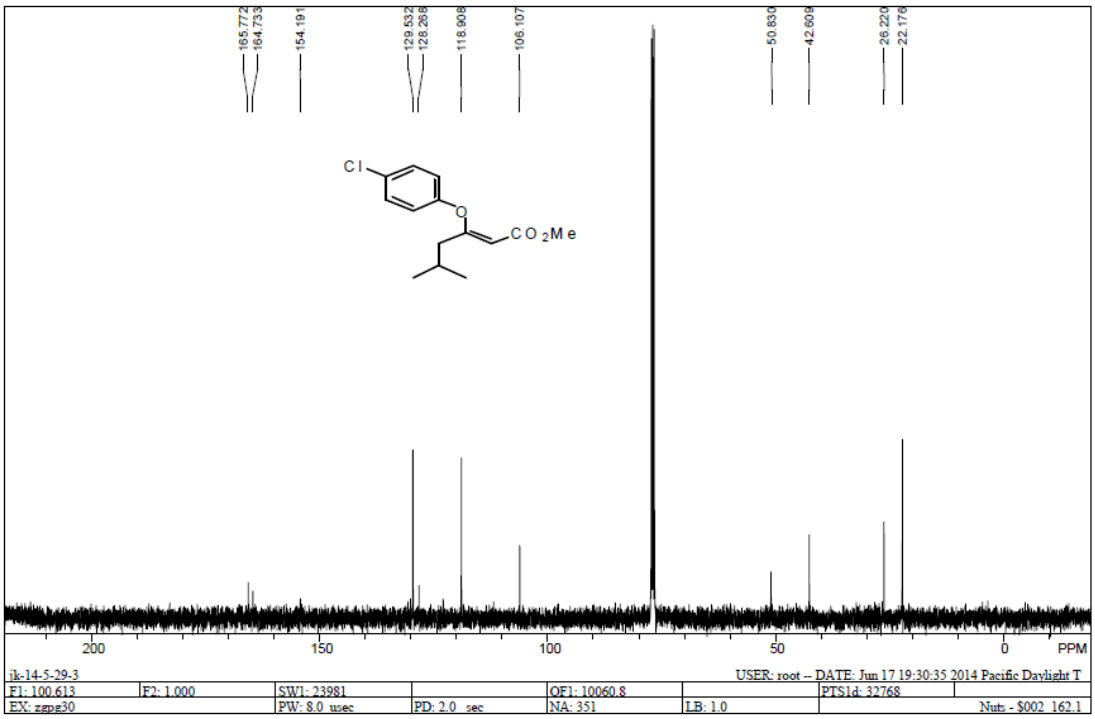
^{1}H and ^{13}C NMR of **4n**



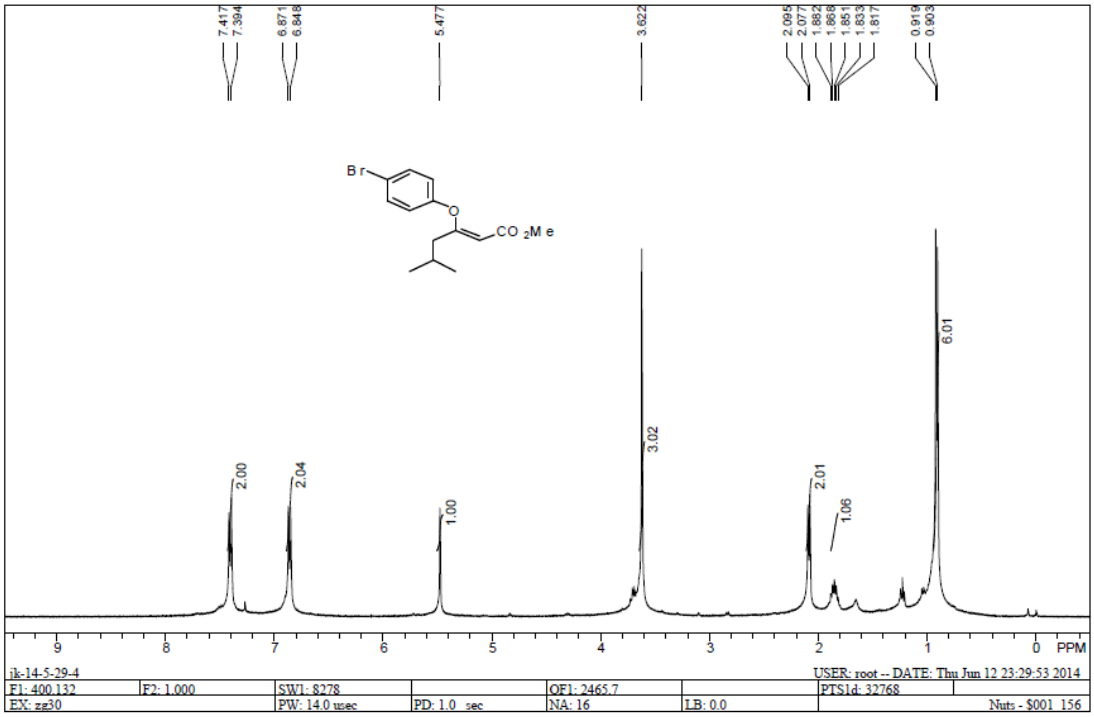


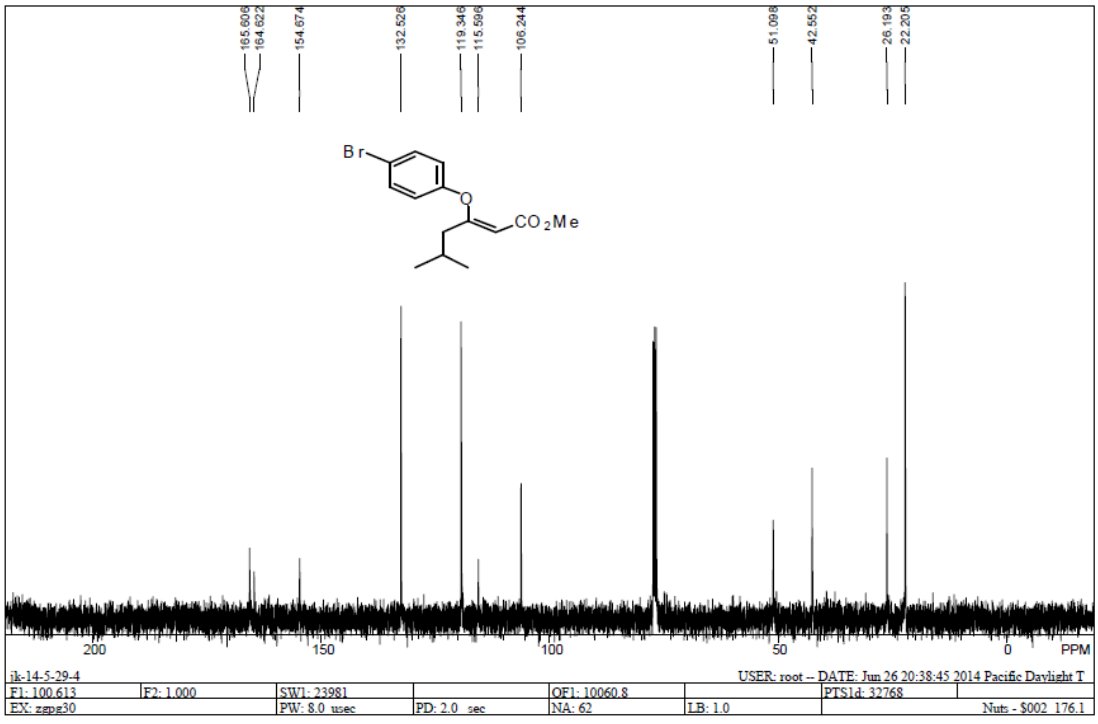
^{1}H and ^{13}C NMR of **4o**



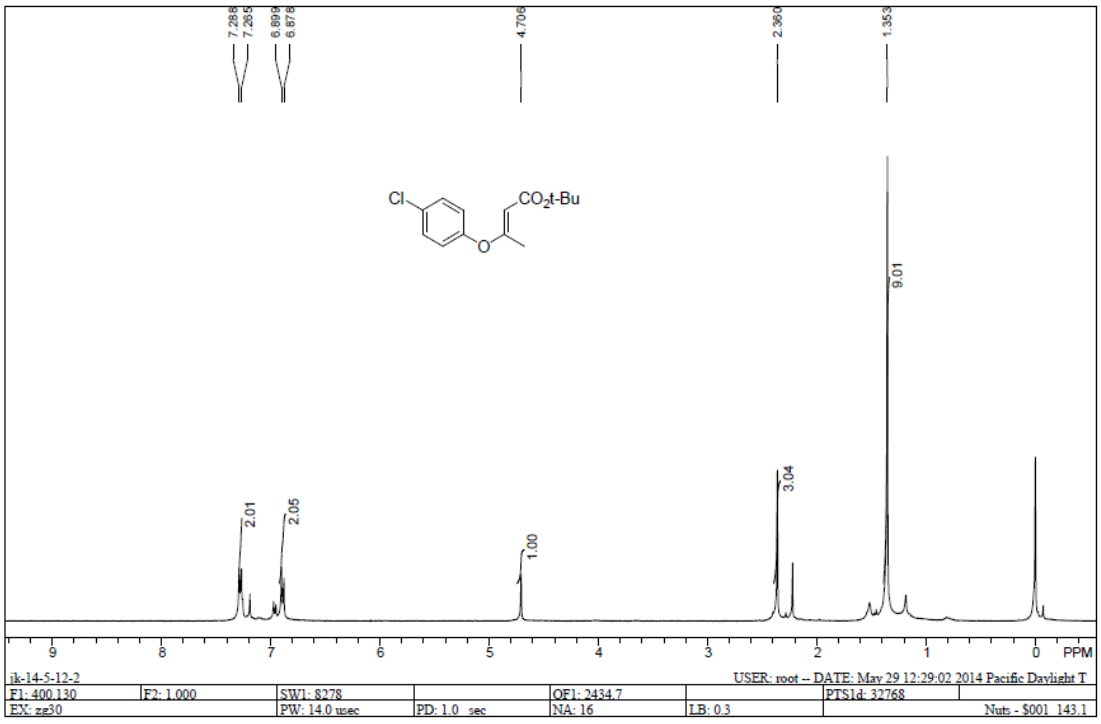


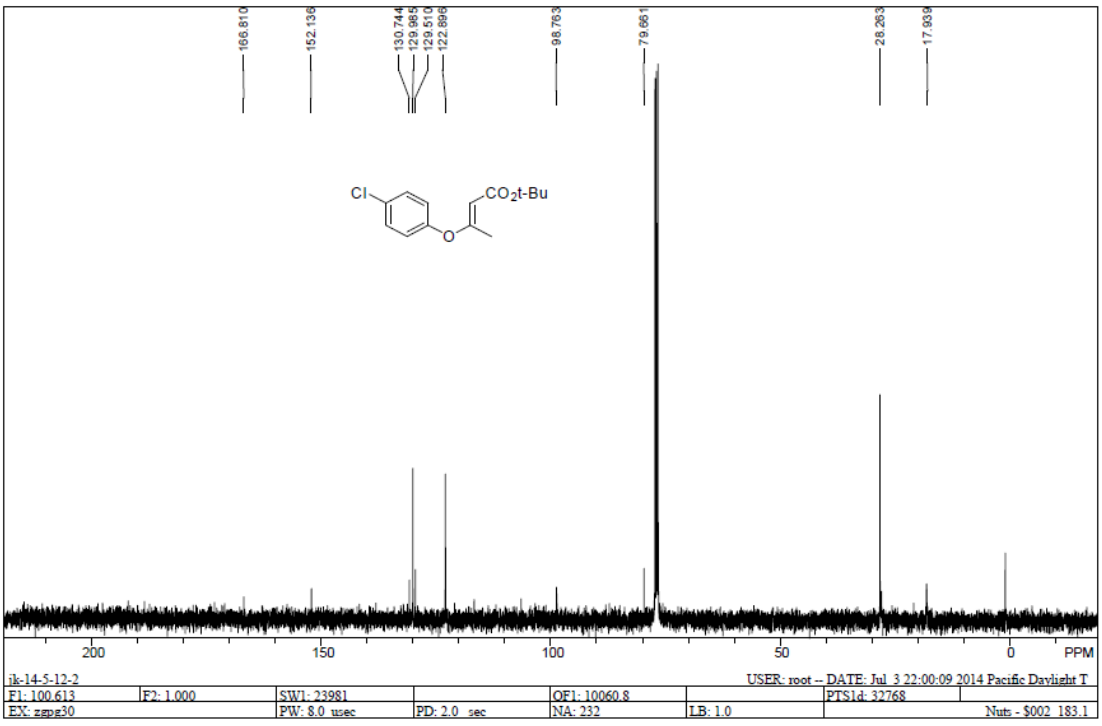
^{1}H and ^{13}C NMR of **4p**





^{1}H and ^{13}C NMR of **4q**





^{1}H and ^{13}C NMR of **6**