Electronic Supplementary Material (ESI) for Chemical Communications

Ruthenium-catalyzed regioselective oxidative coupling of aromatic and heteroaromatic esters with alkenes under open atmosphere

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Electronic Supplementary Information

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Experimental Section

General procedure for the coupling of aromatic and heteroaromatic esters with alkenes catalyzed by ruthenium complex.

A 25-mL two-neck round bottom flask or a 15-mL pressure tube containing [{$RuCl_2$(*p*-cymene)}$_2$] (0.03 mmol, 3 mol %), $AgSbF_6$ (0.20 mmol, 20 mol %) and $Cu(OAc)_2$ (0.30 mmol, 30 mol %) was evacuated and purged with nitrogen gas three times (Silver salt is moisture sensitive. Thus, the reaction mixture was purged with nitrogen gas). To the flask or tube were then added esters (**1**) (1.00 mmol), alkenes **2** (**2a** and **2b**, 3.0 mmol and **2c-g**, 2.0 mmol) and THF or 1,2-dichloroethane (4.0 mL) via syringes and allowed the reaction mixture to stir at room temperature for 5 min. Then, the reaction mixture was allowed to stir at 100 °C for 12 h under open atmosphere (for a 15-mL pressure tube, a screw cap was used to cover the tube. This reaction is moisture-insensitive). After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **3**. The reaction worked equally in both reaction setups. The pressure tube reaction is advisable in order to avoid the solvent evaporation and get more yields.

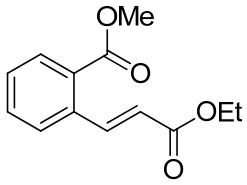
General procedure for de-esterfication reaction.

A two-neck 50 mL round bottom flask fitted with a condenser containing a mixture of **3c** or **3j** (100 mg) and LiOH (1.0 equiv) in 6 mL of THF/MeOH/H_2O (4:1:l). The reaction mixture was refluxed at 80 °C for 12 h. After the reaction, reaction mixture was allowed to cool to room temperature and the reaction mixture was neutralised (pH = 6) using 1N HCl. The product was extracted with ethyl acetate, washed with water and brine. The extract was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4**.

Spectral data and copies of ^1H and ^{13}C NMR spectra of all compounds **3a-y**, **4a** and **4b** are listed below (pages 16 – 65).

Spectral data of compounds 3a-y, 4a and **4b**

(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (**3a**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

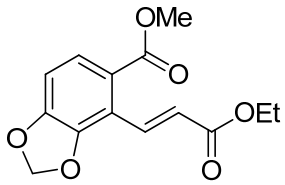
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2975, 1715, 1633, 1266 and 725.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (d, *J* = 16.0 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 6.28 (d, *J* = 16.0 Hz, 1 H), 4.27 (q, *J* = 8.0 Hz, 2 H), 3.92 (s, 3 H), 1.32 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 166.7, 143.7, 136.5, 132.4, 130.9, 129.9, 129.4, 128.0, 121.2, 60.7, 52.5, 14.4.

HRMS (ESI): calc. for [($C_{13}H_{14}O_4$)Na] (M+Na) 257.0790, measured 257.0785.

(*E*)-Methyl 4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3b**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

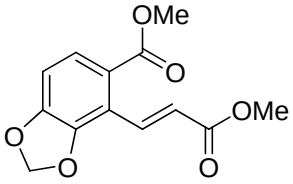
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2956, 1716, 1630, 1266 and 777.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, *J* = 16.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.09 (s, 2 H), 4.24 (q, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 1.31 (d, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 166.9, 150.9, 147.3, 137.4, 126.6, 124.1, 123.9, 118.3, 108.3, 102.2, 60.61, 52.4, 14.4.

HRMS (ESI): calc. for [($C_{14}H_{14}O_6$)Na] (M+Na) 301.0688, measured 301.0684.

(*E*)-Methyl 4-(3-methoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3c**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

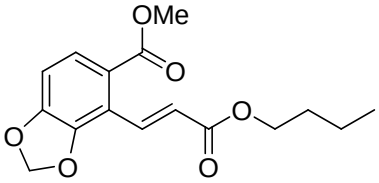
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2923, 1710, 1628, 1590, 1266 and 868.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 16.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.68 (d, *J* = 16.0 Hz, 1 H), 6.08 (s, 2 H), 3.85 (s, 3 H), 3.77 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.6, 166.8, 150.9, 147.4, 137.6, 126.6, 123.8, 123.6, 118.2, 108.3, 102.2, 52.4, 51.8.

HRMS (ESI): calc. for [($C_{13}H_{12}O_6$)Na] (M+Na) 287.0532, measured 287.0541.

(*E*)-Methyl 4-(3-butoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3d**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

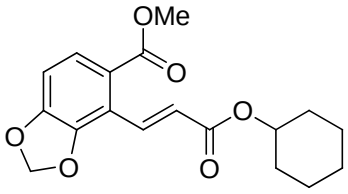
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2912, 1715, 1629, 1266 and 778.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 16.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 6.09 (s, 2 H), 4.18 (t, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 1.68 – 1.66 (m, 2 H), 1.42 – 1.38 (m, 2 H), 0.93 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 166.9, 150.9, 147.3, 137.4, 126.6, 124.1, 124.0, 118.3, 108.3, 102.2, 64.5, 52.3, 30.8, 19.3, 13.8.

HRMS (ESI): calc. for [($C_{16}H_{18}O_6$)Na] (M+Na) 329.1001, measured 329.0995.

(*E*)-Methyl 4-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3e**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

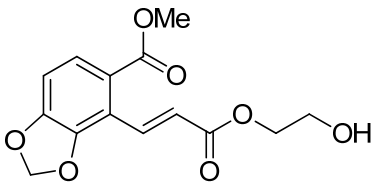
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2933, 1714, 1629, 1584, 1265 and 778.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, *J* = 16.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 6.09 (s, 2 H), 4.89 – 4.83 (m, 1 H), 3.86 (s, 3 H), 1.89 – 1.87 (m, 2 H), 1.75 – 1.72 (m, 2 H), 1.52 – 1.46 (m, 3 H), 1.41 – 1.35 (m, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 166.7, 150.8, 147.3, 137.1, 126.6, 124.6, 123.9, 118.3, 108.2, 102.2, 72.8, 52.3, 31.8, 25.5, 23.9.

HRMS (ESI): calc. for [($C_{18}H_{20}O_6$)Na] (M+Na) 355.1158, measured 355.1159.

(*E*)-Methyl 4-(3-(2-hydroxyethoxy)-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3f**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (30% ethyl acetate in hexanes).

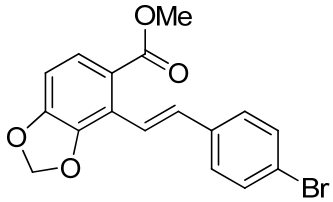
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3477, 2920, 1712, 1630, 1267 and 776.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, *J* = 16.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.07 (s, 2 H), 4.31 (t, *J* = 4.0 Hz, 2 H), 3.86 (d, *J* = 4.0 Hz, 2 H), 3.84 (s, 3 H), 2.71 (bs, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 166.8, 150.9, 147.4, 138.1, 126.7, 123.6, 123.3, 118.0, 108.4, 102.3, 66.4, 61.3, 52.4.

HRMS (ESI): calc. for [($C_{14}H_{14}O_7$)Na] (M+Na) 317.0637, measured 317.0627.

(*E*)-Methyl 4-(4-bromostyryl)benzo[*d*][1,3]dioxole-5-carboxylate (**3g**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

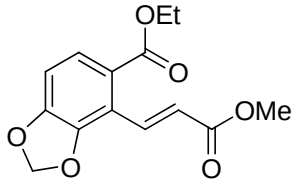
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2972, 1715, 1598, 1480, 1293 and 1016.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, *J* = 16.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.41 (d, *J* = 16.0 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 6.10 (s, 2 H), 3.87 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 150.7, 146.0, 136.8, 133.6, 131.8, 128.3, 126.8, 122.7, 122.6, 121.8, 121.5, 106.7, 101.9, 52.2.

HRMS (ESI): calc. for [($C_{17}H_{13}BrO_4$)Na] (M+Na) 382.9895, measured 382.9899.

(*E*)-Ethyl 4-(3-methoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3h**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (15% ethyl acetate in hexanes).

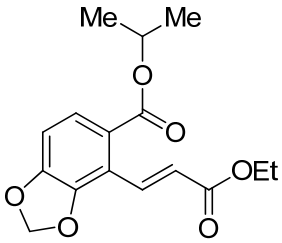
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2990, 1716, 1581, 1279, 819 and 769.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, *J* = 16.0 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.10 (s, 2 H), 4.32 (q, *J* = 8.0 Hz, 2 H), 3.78 (s, 3 H), 1.37 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 166.5, 150.8, 147.3, 137.8, 126.6, 124.3, 123.5, 118.2, 108.4, 102.2, 61.4, 51.9, 14.4.

HRMS (ESI): calc. for [($C_{14}H_{14}O_6$)Na] (M+Na) 301.0688, measured 301.0685.

(*E*)-Isopropyl 4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3i**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (15% ethyl acetate in hexanes).

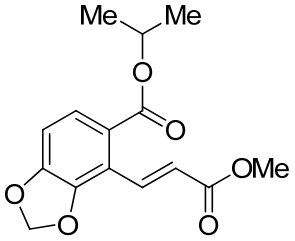
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2983, 1711, 1630, 1260 and 779.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, *J* = 16.0 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 6.07 (s, 2 H), 5.23 – 5.16 (m, 1 H), 4.22 (q, *J* = 8.0 Hz, 2 H), 1.34 (s, 3 H), 1.32 (s, 3 H), 1.29 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 166.1, 150.6, 147.2, 137.7, 126.4, 124.9, 123.7, 117.9, 108.3, 102.1, 69.0, 60.6, 21.9, 14.4.

HRMS (ESI): calc. for [($C_{16}H_{18}O_6$)Na] (M+Na) 329.1001, measured 329.0988.

(*E*)-Isopropyl 4-(3-methoxy-3-oxoprop-1-en-1-yl)benzo[*d*][1,3]dioxole-5-carboxylate (**3j**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (15% ethyl acetate in hexanes).

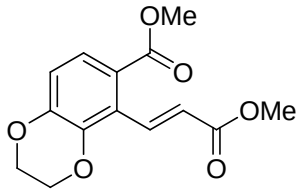
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2995, 1713, 1621, 1289 and 775.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 16.0 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 6.07 (s, 2 H), 5.22 – 5.16 (m, 1 H), 3.76 (s, 3 H), 1.33 (s, 3 H), 1.32 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 166.0, 150.7, 147.3, 137.9, 126.4, 124.8, 123.2, 117.9, 108.3, 102.2, 69.0, 51.8, 21.9.

HRMS (ESI): calc. for [($C_{15}H_{16}O_6$)Na] (M+Na) 315.0845, measured 315.0840.

(*E*)-Methyl 5-(3-methoxy-3-oxoprop-1-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxylate (**3k**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (15% ethyl acetate in hexanes).

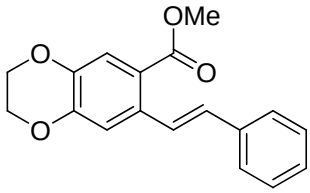
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 1710, 1582, 1272, 1179, 861 and 771.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 16.0 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.48 (d, *J* = 16.0 Hz, 1 H), 4.25 (s, 4 H), 3.80 (s, 3 H), 3.74 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 167.2, 146.9, 142.7, 138.6, 125.2, 124.1, 124.0, 123.9, 117.4, 64.2, 64.1, 52.3, 51.8.

HRMS (ESI): calc. for [($C_{14}H_{14}O_6$)Na] (M+Na) 301.0688, measured 301.0678.

(*E*)-Methyl 7-styryl-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxylate (**3l**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

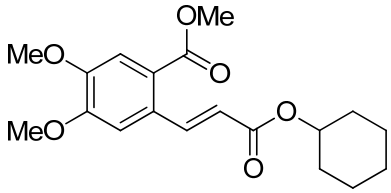
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 1706 and 1270.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 16.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.51 (s, 1 H), 7.33 (t, *J* = 8.0 Hz, 2 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 7.19 (s, 1 H), 6.87 (d, *J* = 16.0 Hz, 1 H), 4.31 – 4.27 (m, 4 H), 3.87 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 147.0, 142.6, 137.7, 134.2, 130.2, 128.7, 127.7, 127.2, 126.8, 121.6, 120.2, 115.4, 64.8, 64.4, 52.1.

HRMS (ESI): calc. for [($C_{18}H_{16}O_4$)Na] (M+Na) 319.0946, measured 319.0948.

(*E*)-Methyl 2-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-4,5-dimethoxybenzoate (**3m**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

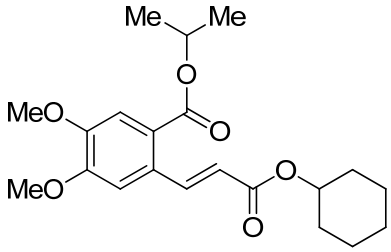
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2938, 2855, 1711, 1597, 1274, 862 and 752.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, *J* = 16.0 Hz, 1 H), 7.44 (s, 1 H), 7.02 (s, 1 H), 6.22 (d, *J* = 16.0 Hz, 1 H), 4.90 – 4.84 (m, 1 H), 3.93 (s, 3 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 1.92 – 1.87 (m, 2 H), 1.76 – 1.73 (m, 2 H), 1.55 – 1.42 (m, 3 H), 1.39 – 1.24 (m, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 166.3, 151.9, 149.6, 143.4, 130.5, 125.6, 120.3, 113.1, 109.7, 72.8, 56.2, 56.1, 52.4, 31.8, 25.5, 23.9.

HRMS (ESI): calc. for [($C_{19}H_{24}O_6$)Na] (M+Na) 371.1471, measured 371.1462.

(*E*)-Isopropyl 2-(3-(cyclohexyloxy)-3-oxoprop-1-en-1-yl)-4,5-dimethoxybenzoate (**3n**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

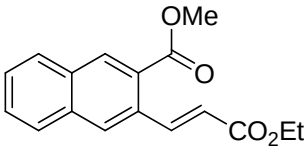
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2948, 1710, 1601, 1279 and 755.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, *J* = 16.0 Hz, 1 H), 7.42 (s, 1 H), 7.01 (s, 1 H), 6.20 (d, *J* = 16.0 Hz, 1 H), 5.27 – 5.21 (m, 1 H), 4.89 – 4.83 (m, 1 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 1.93 – 1.90 (m, 2 H), 1.77 – 1.72 (m, 2 H), 1.54 – 1.41 (m, 3 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.35 – 1.27 (m, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 166.3, 151.7, 149.7, 143.7, 129.9, 123.7, 119.9, 113.1, 109.6, 72.9, 69.3, 56.2, 31.9, 25.5, 24.0, 22.1.

HRMS (ESI): calc. for [($C_{21}H_{28}O_6$)Na] (M+Na) 399.1784, measured 399.1778.

(*E*)-Methyl 3-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-naphthoate (**3o**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

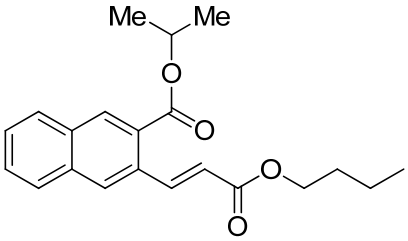
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2983, 1717, 1632, 1276, 863 and 755.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, *J* = 16.0 Hz, 1 H), 8.50 (s, 1 H), 8.00 (s, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.58 (t, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 4.28 (q, *J* = 8.0 Hz, 2 H), 3.96 (s, 3 H), 1.34 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 166.8, 144.5, 134.7, 132.9, 132.7, 132.4, 128.9, 128.8, 128.2, 127.9, 127.7, 120.7, 60.6, 52.6, 14.5.

HRMS (ESI): calc. for [($C_{17}H_{16}O_4$)Na] (M+Na) 307.0946, measured 307.0950.

(*E*)-Isopropyl 3-(3-butoxy-3-oxoprop-1-en-1-yl)-2-naphthoate (**3p**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

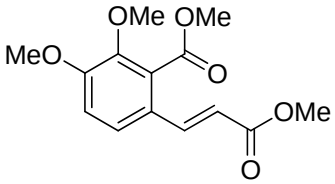
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2963, 1715, 1634, 1270 and 750.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, *J* = 16.0 Hz, 1 H), 8.45 (s, 1 H), 7.99 (s, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 6.37 (d, *J* = 16.0 Hz, 1 H), 5.34 – 5.28 (m, 1 H), 4.22 (t, *J* = 8.0 Hz, 2 H), 1.72 – 1.65 (m, 2 H), 1.46 – 1.43 (m, 2 H), 1.42 (s, 3 H), 1.41 (s, 3 H), 0.95 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 166.6, 144.7, 134.5, 132.7, 132.6, 132.1, 128.9, 128.7, 128.1, 127.8, 127.6, 120.3, 69.3, 64.5, 30.9, 22.1, 19.3, 13.9.

HRMS (ESI): calc. for [($C_{21}H_{24}O_4$)Na] (M+Na) 363.1572, measured 363.1562.

(*E*)-Methyl 2,3-dimethoxy-6-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**3q**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

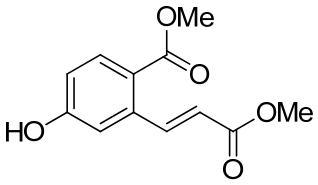
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2958, 1714, 1605, 1269 and 765.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 16.0 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 1 H), 6.94 (d, *J* = 8.0 Hz, 1 H), 6.26 (d, *J* = 16.0 Hz, 1 H), 3.94 (s, 3 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.75 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.3, 167.2, 154.1, 146.2, 140.9, 129.9, 124.7, 123.2, 118.5, 113.6, 61.7, 56.1, 52.8, 51.8.

HRMS (ESI): calc. for [($C_{14}H_{16}O_6$)Na] (M+Na) 303.0845, measured 303.0836.

(*E*)-Methyl 4-hydroxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**3r**).



The catalytic reaction was carried out in DCE solvent.

Colorless semisolid; eluent (20% ethyl acetate in hexanes).

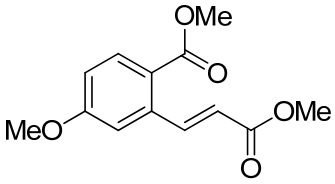
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3356, 2951, 1707, 1601, 1284 and 774.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, *J* = 16.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.01 (s, 1 H), 6.89 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.83 (bs, 1 H), 6.22 (d, *J* = 16.0 Hz, 1 H), 3.87 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 167.0, 159.7, 144.9, 139.1, 133.5, 132.0, 120.6, 116.6, 114.8, 52.3, 52.2.

HRMS (ESI): calc. for [($C_{12}H_{12}O_5$)Na] (M+Na) 259.0582, measured 259.0579.

(*E*)-Methyl 4-methoxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**3s**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (15% ethyl acetate in hexanes).

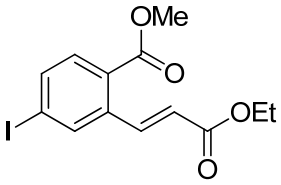
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2949, 1716, 1637, 1272, 861 and 777.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, *J* = 16.0 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.00 (s, 1 H), 6.90 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.24 (d, *J* = 16.0 Hz, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.79 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.1, 166.8, 162.6, 144.6, 139.1, 133.2, 121.8, 120.9, 114.7, 113.2, 55.6, 52.2, 51.9.

HRMS (ESI): calc. for [($C_{13}H_{14}O_5$)Na] (M+Na) 273.0739, measured 273.0734.

(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-iodobenzoate (**3t**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

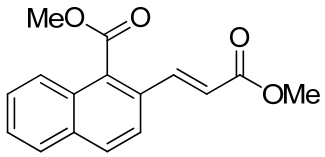
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3420, 2924, 1721, 1684, 1242, 850 and 771.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, *J* = 16.0 Hz, 1 H), 7.91 (s, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 6.25 (d, *J* = 16.0 Hz, 1 H), 4.24 (q, *J* = 8.0 Hz, 2 H), 3.89 (s, 3 H), 1.31 (d, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 166.3, 142.3, 138.4, 138.3, 136.9, 132.3, 128.9, 122.3, 60.8, 52.7, 14.4.

HRMS (ESI): calc. for [($C_{13}H_{13}IO_4$)Na] (M+Na) 382.9756, measured 382.9757.

(*E*)-Methyl 2-(3-methoxy-3-oxoprop-1-en-1-yl)-1-naphthoate (**3u**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

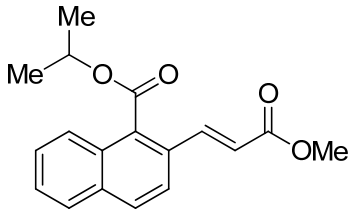
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2950, 1722, 1635, 1223, 821 and 755.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 16.0 Hz, 1 H), 7.86 – 7.83 (m, 3 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.55 - 7.52 (m, 2 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 4.09 (s, 3 H), 3.81 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 167.0, 141.6, 133.9, 132.7, 130.5, 129.9, 129.7, 128.3, 127.9, 127.6, 125.8, 122.7, 120.9, 52.9, 51.9.

HRMS (ESI): calc. for [($C_{16}H_{14}O_4$)Na] (M+Na) 293.0790, measured 293.0793.

(*E*)-Isopropyl 2-(3-methoxy-3-oxoprop-1-en-1-yl)-1-naphthoate (**3v**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

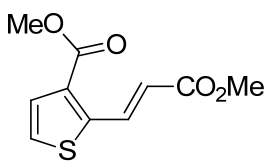
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2954, 1720, 1633, 1220, 815 and 765.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, *J* = 16.0 Hz, 1 H), 7.91 – 7.81 (m, 3 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.55 - 7.51 (m, 2 H), 6.51 (d, *J* = 16.0 Hz, 1 H), 5.55 – 5.49 (m, 1 H), 3.80 (s, 3 H), 1.48 (s, 3 H), 1.46 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 167.0, 141.7, 133.9, 133.2, 130.2, 129.8, 129.3, 128.3, 127.8, 127.6, 125.6, 122.6, 120.5, 70.1, 51.9, 22.1.

HRMS (ESI): calc. for [($C_{18}H_{18}O_4$)Na] (M+Na) 321.1103, measured 321.1099.

(*E*)-Methyl 2-(3-methoxy-3-oxoprop-1-en-1-yl)thiophene-3-carboxylate (**3w**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (12% ethyl acetate in hexanes).

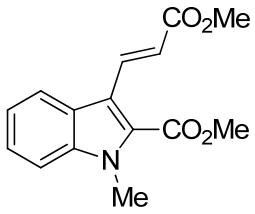
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3107, 2951, 1728, 1624, 1154, 862 and 719.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (d, *J* = 16.0 Hz, 1 H), 7.39 (d, *J* = 4.0 Hz, 1 H), 7.19 (d, *J* = 4.0 Hz, 1 H), 6.28 (d, *J* = 16.0 Hz, 1 H), 3.83 (s, 3 H), 3.73 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 163.2, 145.0, 135.9, 131.9, 130.6, 126.0, 120.0, 52.1, 51.9.

HRMS (ESI): calc. for [($C_{10}H_{10}O_4S$)Na] (M+Na) 249.0197, measured 249.0204.

(*E*)-Methyl 3-(3-methoxy-3-oxoprop-1-en-1-yl)-1-methyl-1H-indole-2-carboxylate (**3x**).



The catalytic reaction was carried out in THF solvent. DCE solvent is not suitable for the reaction.

Colorless oil; eluent (20% ethyl acetate in hexanes).

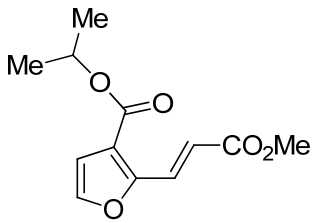
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2922, 1718, 1590, 1275 and 753.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, *J* = 16.0 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.28 – 7.25 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 4.02 (s, 3 H), 4.01 (s, 3 H), 3.82 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3, 162.5, 139.2, 138.4, 128.7, 125.8, 124.6, 122.3, 122.2, 118.2, 117.4, 110.9, 52.4, 51.7, 32.5.

HRMS (ESI): calc. for [($C_{15}H_{15}O_4N$)Na] (M+Na) 296.0899, measured 296.0897.

(*E*)-Isopropyl 2-(3-methoxy-3-oxoprop-1-en-1-yl)furan-3-carboxylate (**3y**).



The catalytic reaction was carried out in DCE solvent.

Colorless oil; eluent (10% ethyl acetate in hexanes).

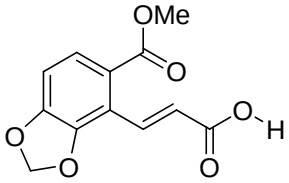
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 1718, 1640, 1263, 830 and 753.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 16.0 Hz, 1 H), 7.37 (d, *J* = 4.0 Hz, 1 H), 7.35 (d, *J* = 4.0 Hz, 1 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 5.19 – 5.13 (m, 1 H), 3.76 (s, 3 H), 1.32 (s, 3 H), 1.31 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 162.2, 153.3, 143.7, 129.9, 120.1, 119.9, 112.8, 68.7, 51.9, 21.9.

HRMS (ESI): calc. for [($C_{12}H_{14}O_5$)Na] (M+Na) 261.0739, measured 261.0737.

(*E*)-3-(5-(Methoxycarbonyl)benzo[*d*][1,3]dioxol-4-yl)acrylic acid (**4a**).



Colorless powder; eluent (75% ethyl acetate in hexanes).

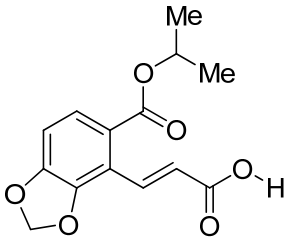
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3013, 2950, 1706, 1685 and 1421.

^{1}H NMR (*d*-MeOH, 400 MHz): δ 8.25 (d, *J* = 16.0 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 6.15 (s, 2 H), 3.85 (s, 3 H).

^{13}C NMR (*d*-MeOH, 100 MHz): δ 167.0, 151.2, 147.5, 137.4, 126.3, 123.6, 117.8, 107.9, 102.5, 58.5.

HRMS (ESI): calc. for [($C_{12}H_{10}O_6$)Na] (M+Na) 273.0375, measured 273.0374.

(*E*)-3-(5-(Isopropoxycarbonyl)benzo[*d*][1,3]dioxol-4-yl)acrylic acid (**4b**).



Colorless semisolid; eluent (75% ethyl acetate in hexanes).

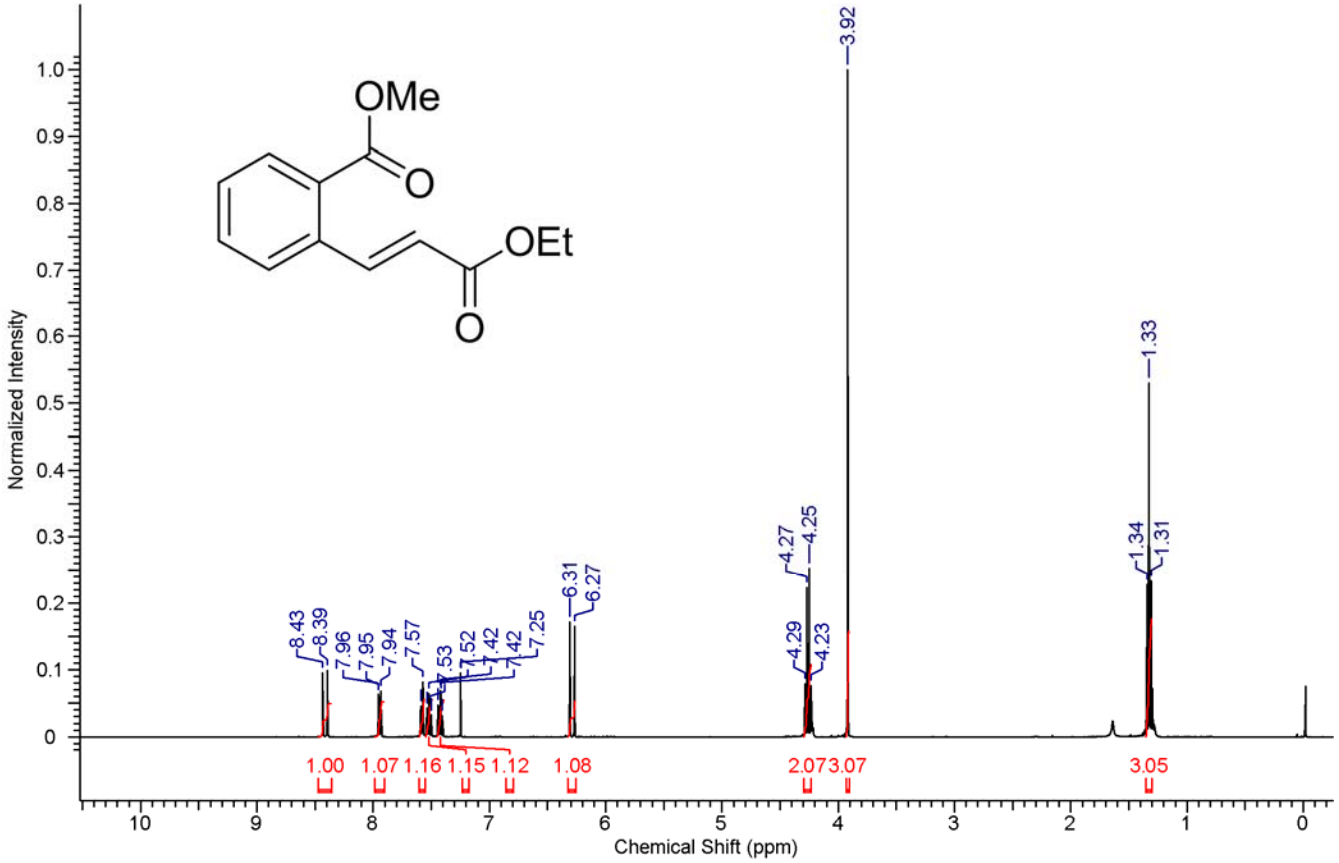
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3017, 1710, 1682, 1421 and 825.

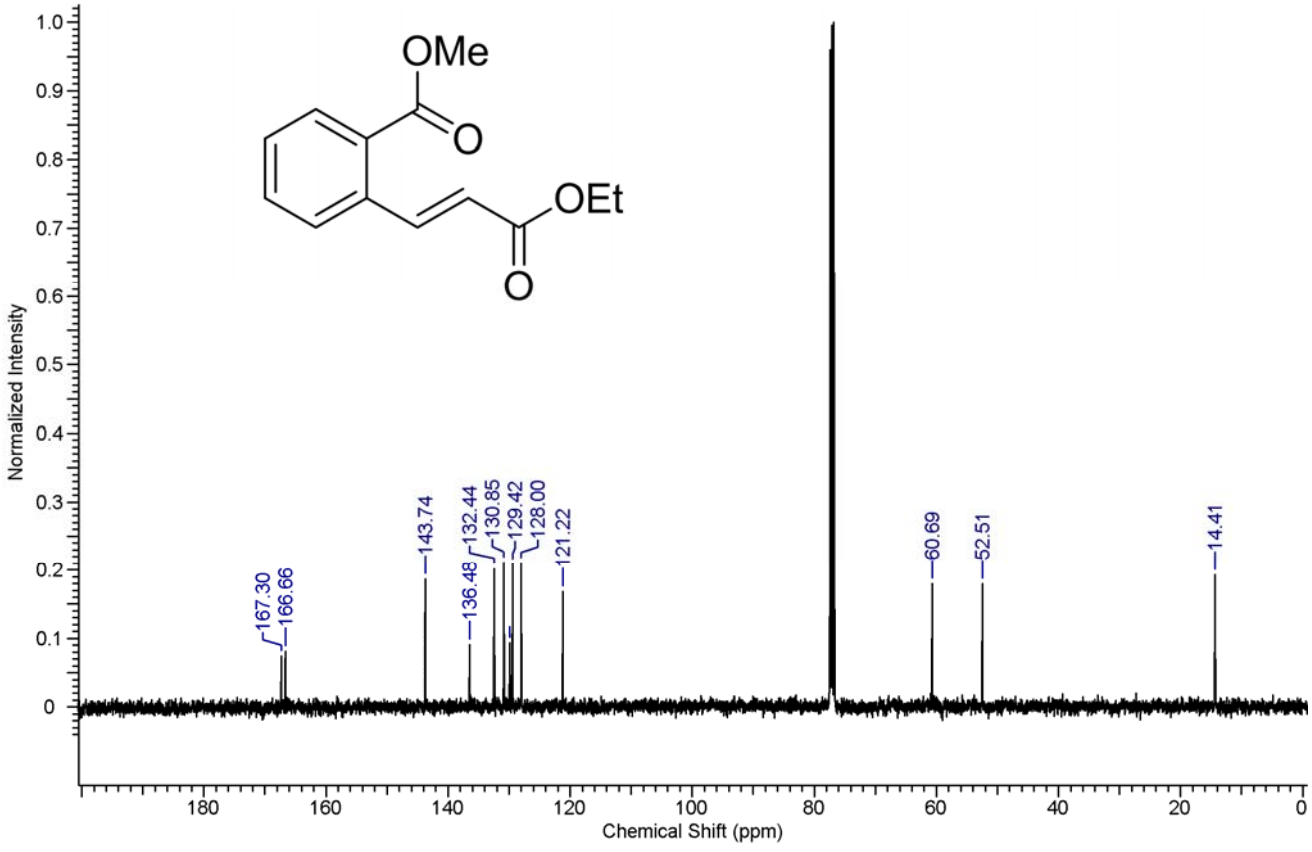
^{1}H NMR (*d*-DMSO, 400 MHz): δ 8.39 (d, *J* = 16.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 6.11 (s, 2 H), 5.25 – 5.19 (m, 1 H), 1.36 (s, 3 H), 1.34 (s, 3 H).

^{13}C NMR (*d*-DMSO, 100 MHz): δ 172.7, 166.0, 150.7, 147.5, 139.8, 126.5, 124.9, 123.1, 117.7, 108.6, 102.3, 69.1, 21.9.

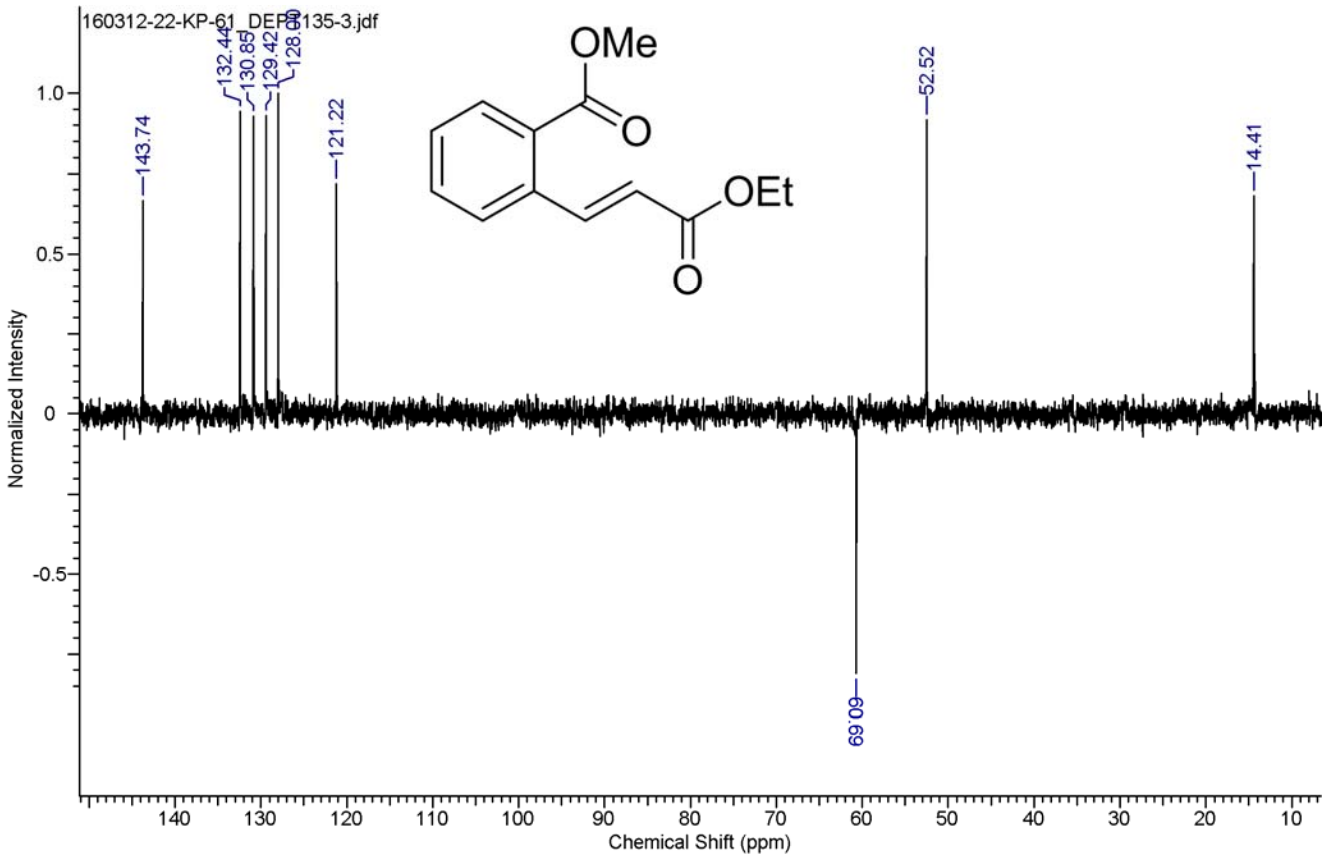
HRMS (ESI): calc. for [($C_{14}H_{14}O_6$)Na] (M+Na) 301.0688, measured 301.0696.

^{1}H and ^{13}C NMR Spectra of Compound **3a**.

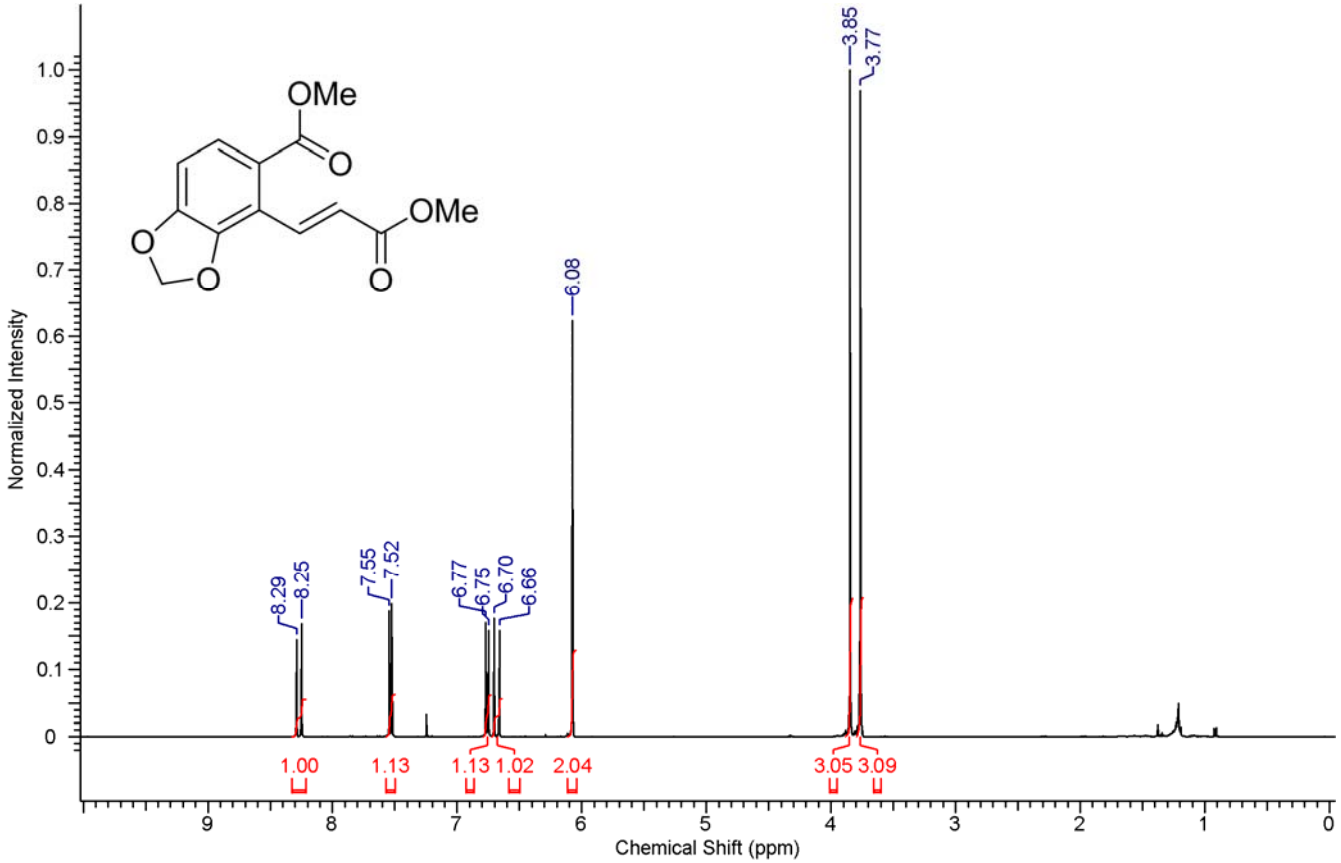


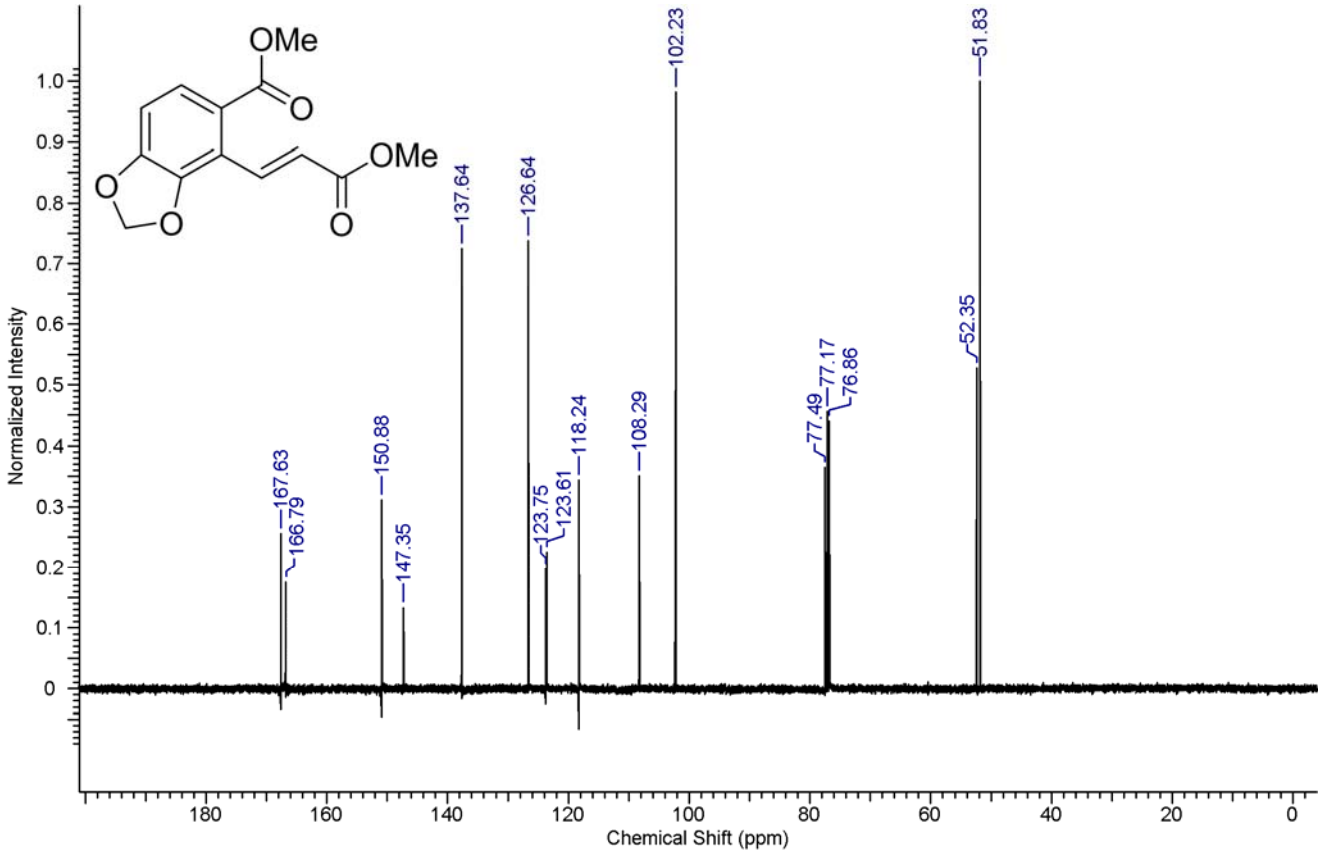


DEPT (135) Spectrum of Compound **3a**.

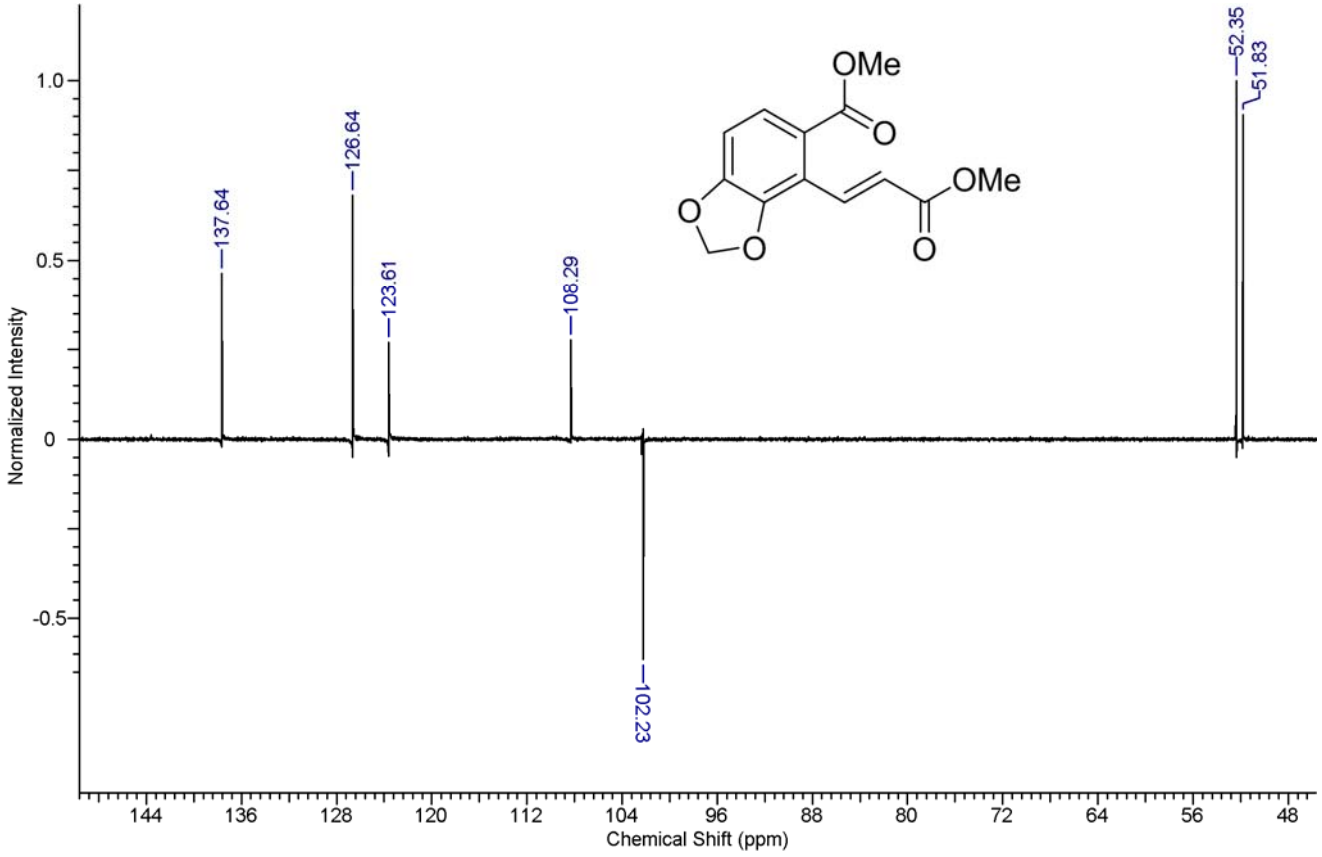


^{1}H and ^{13}C NMR Spectra of Compound **3b**.

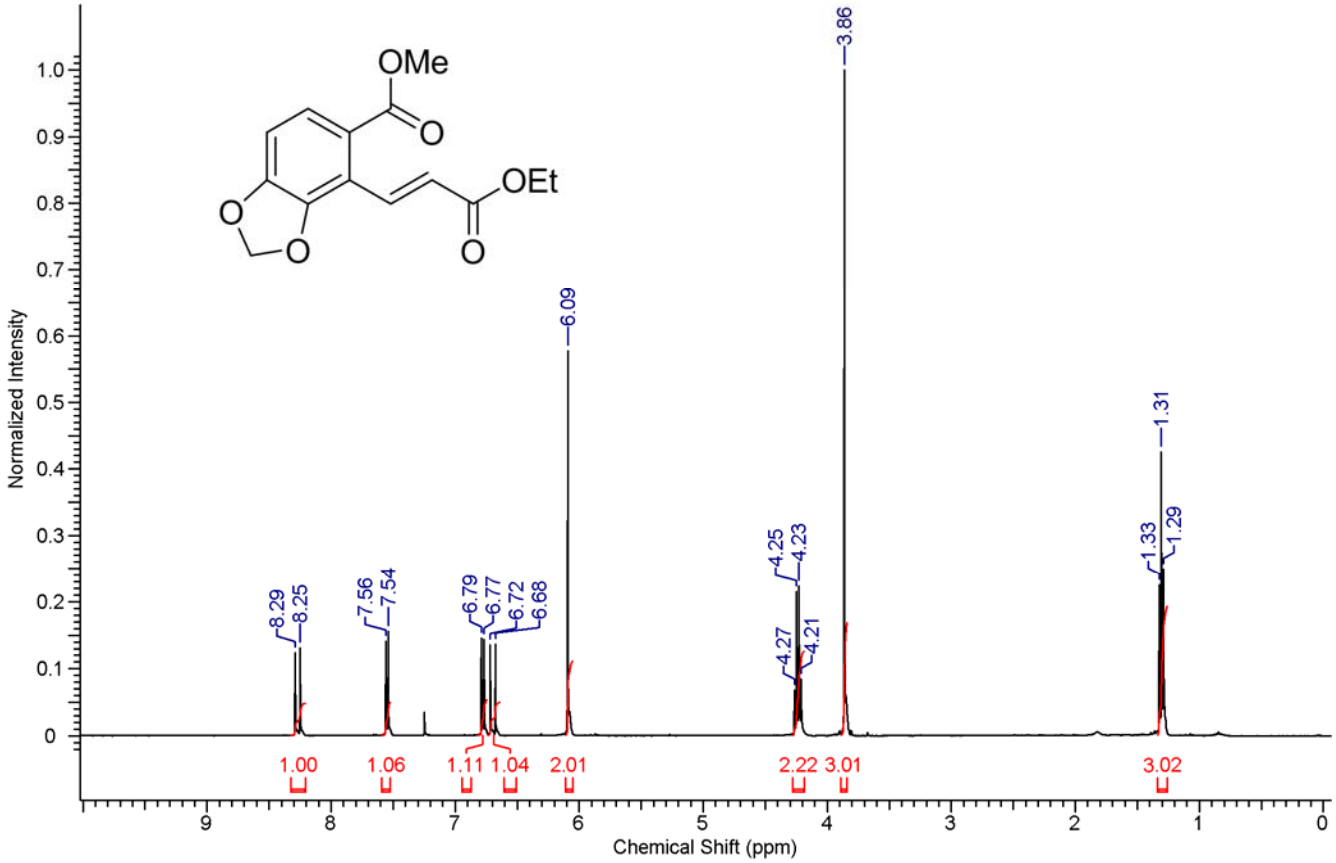


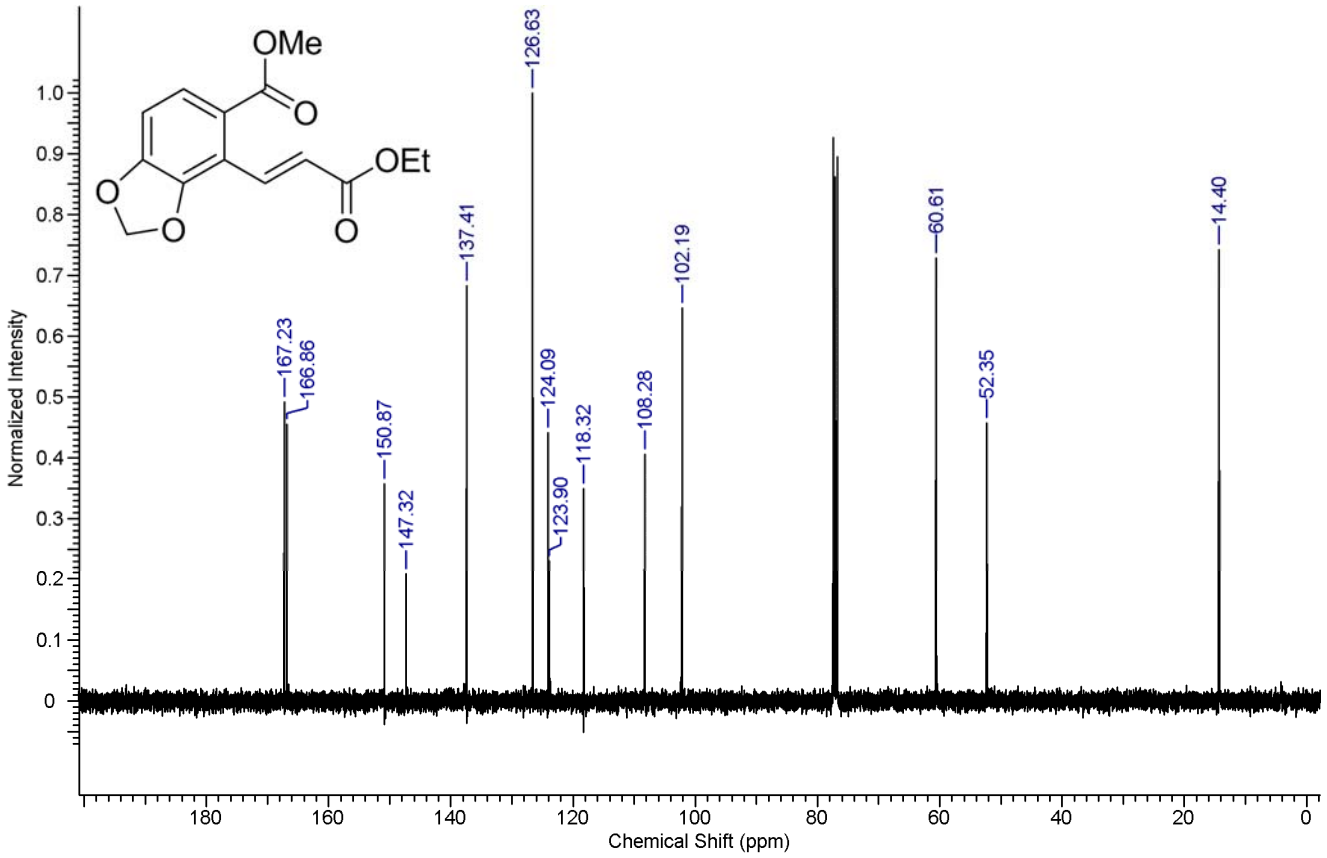


DEPT (135) Spectrum of Compound **3b**.

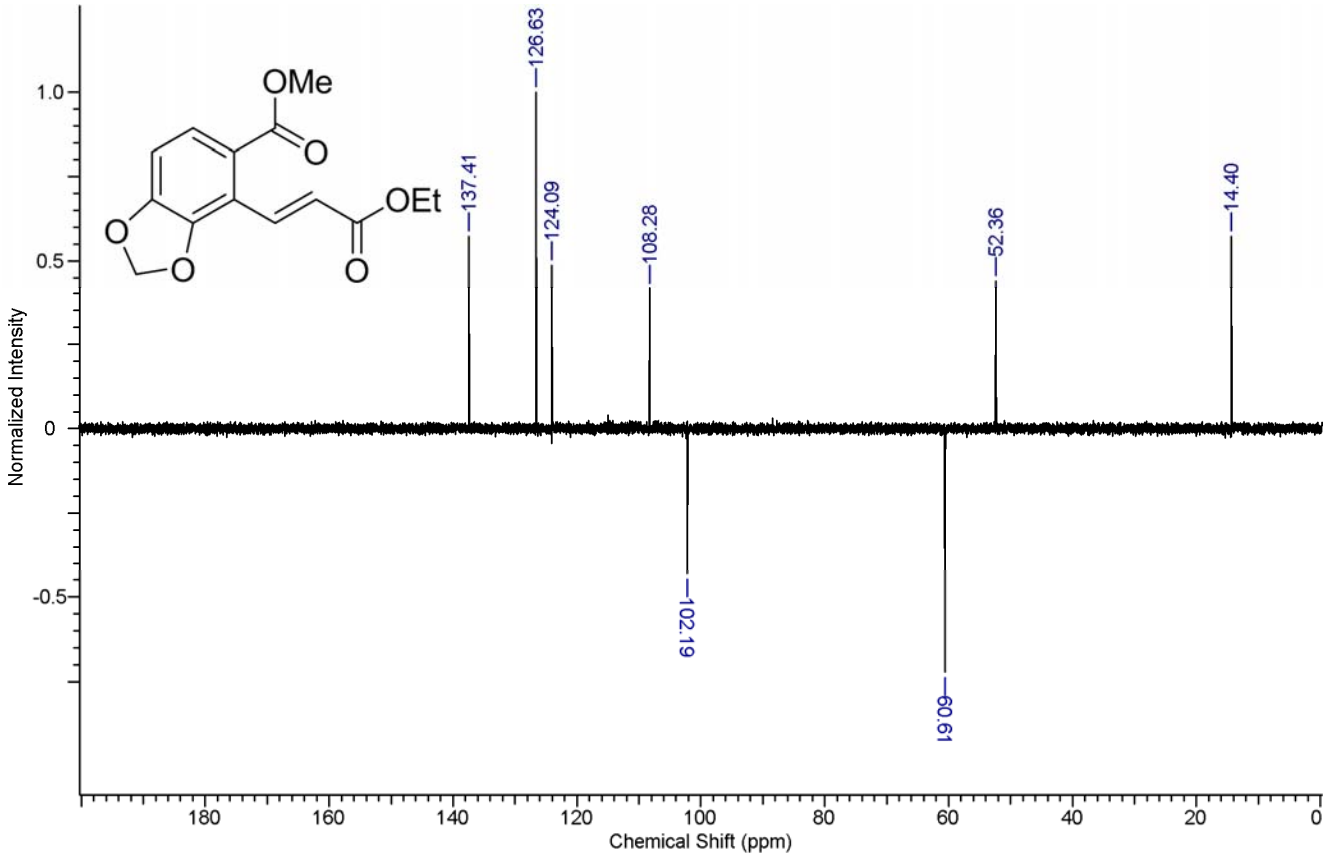


^{1}H and ^{13}C NMR Spectra of Compound **3c**.

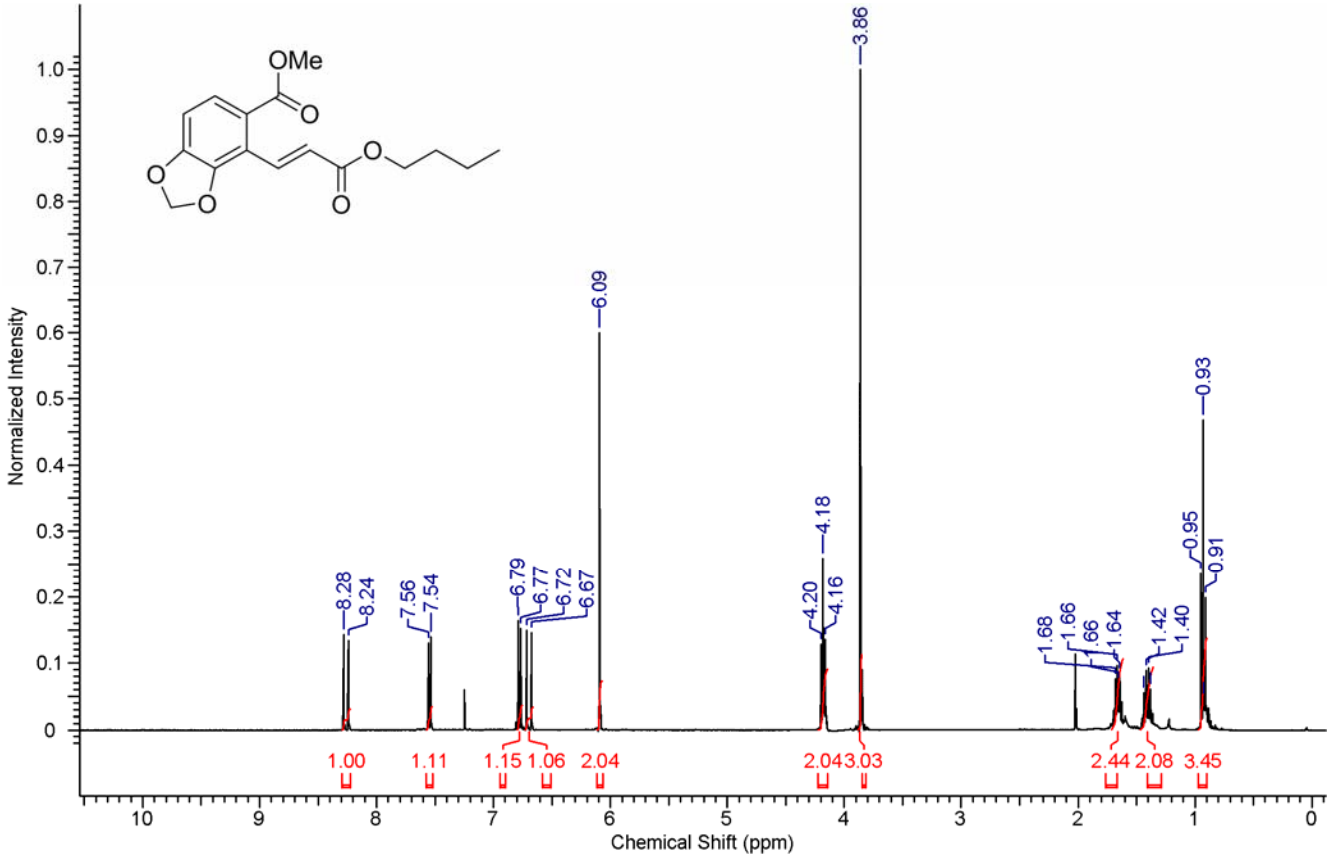


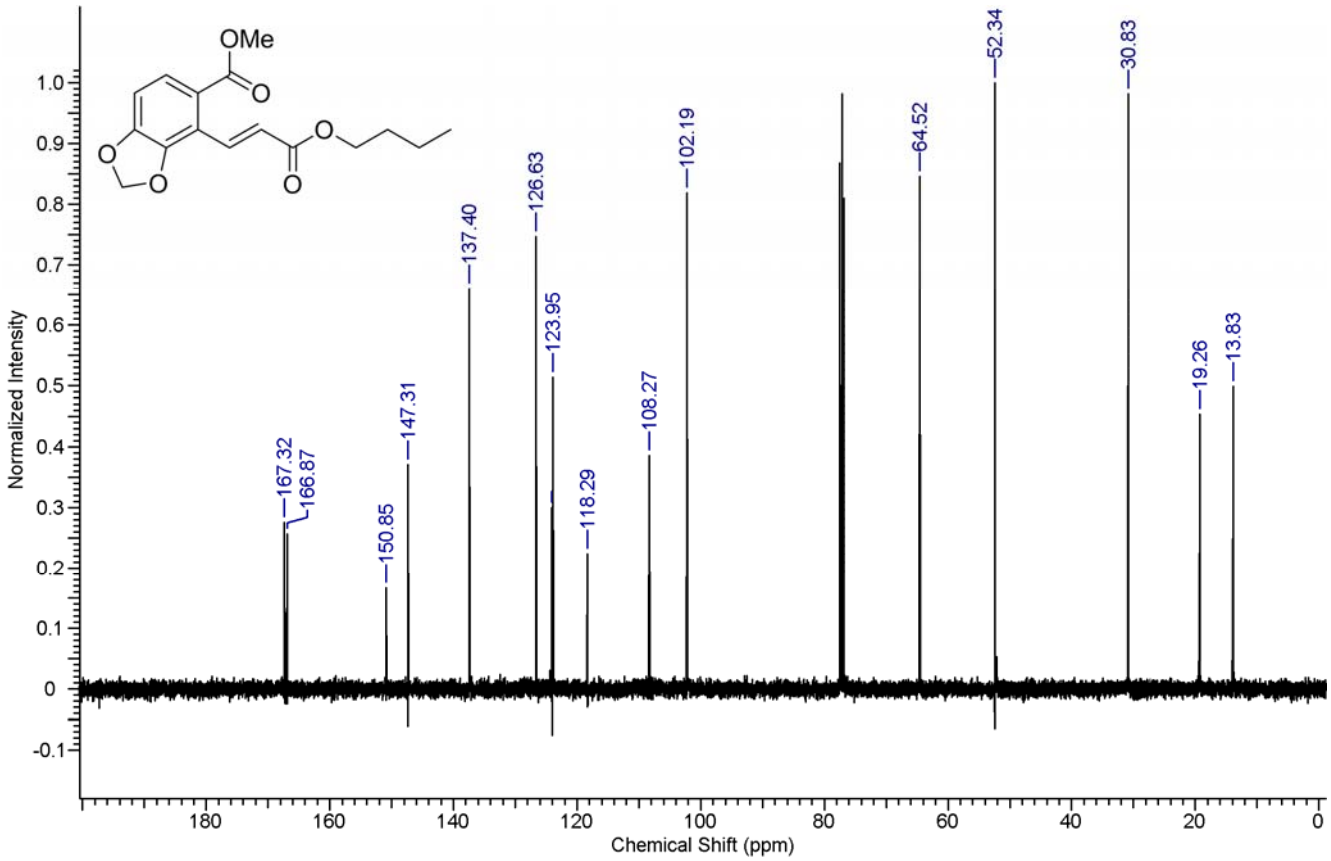


DEPT (135) Spectrum of Compound **3c**.

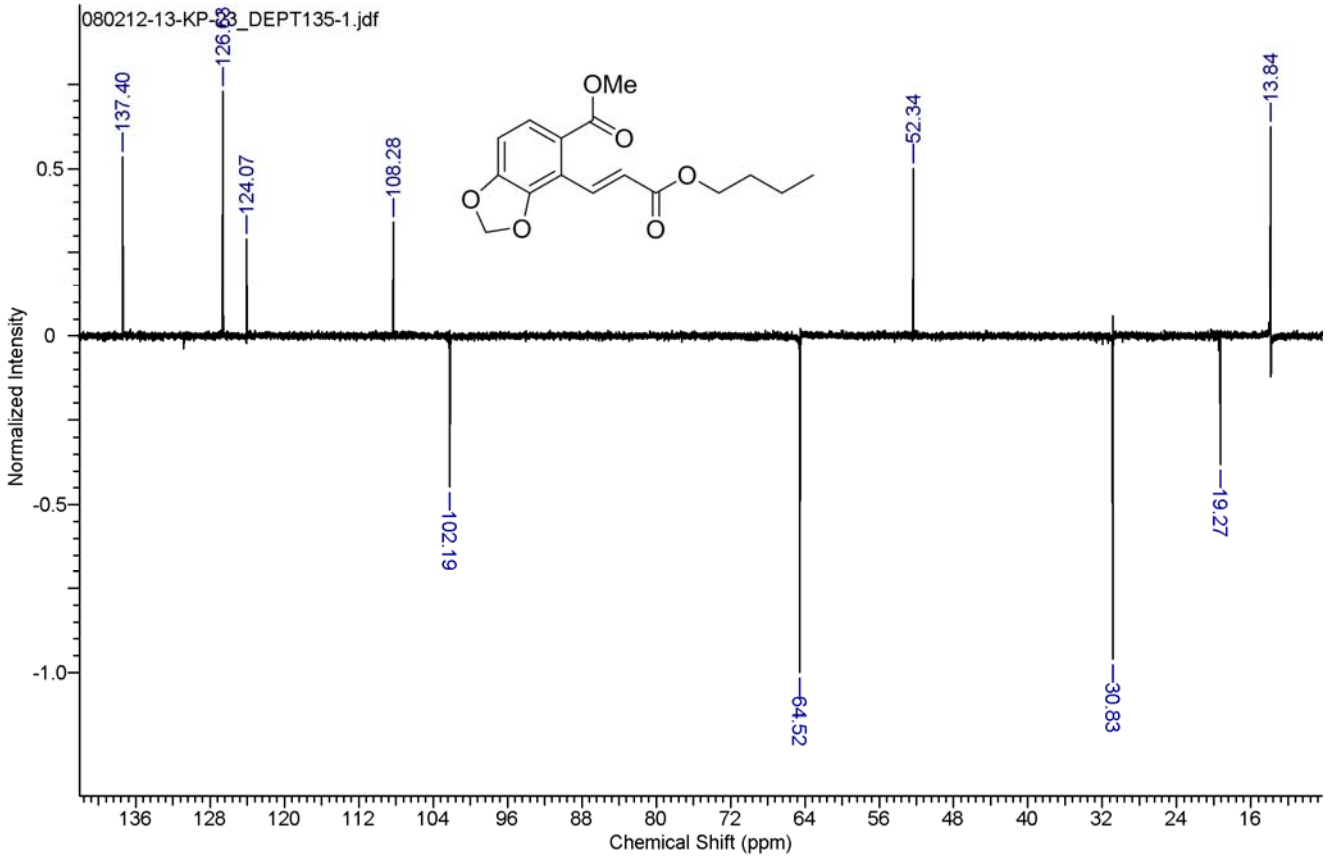


^{1}H and ^{13}C NMR Spectra of Compound **3d**.

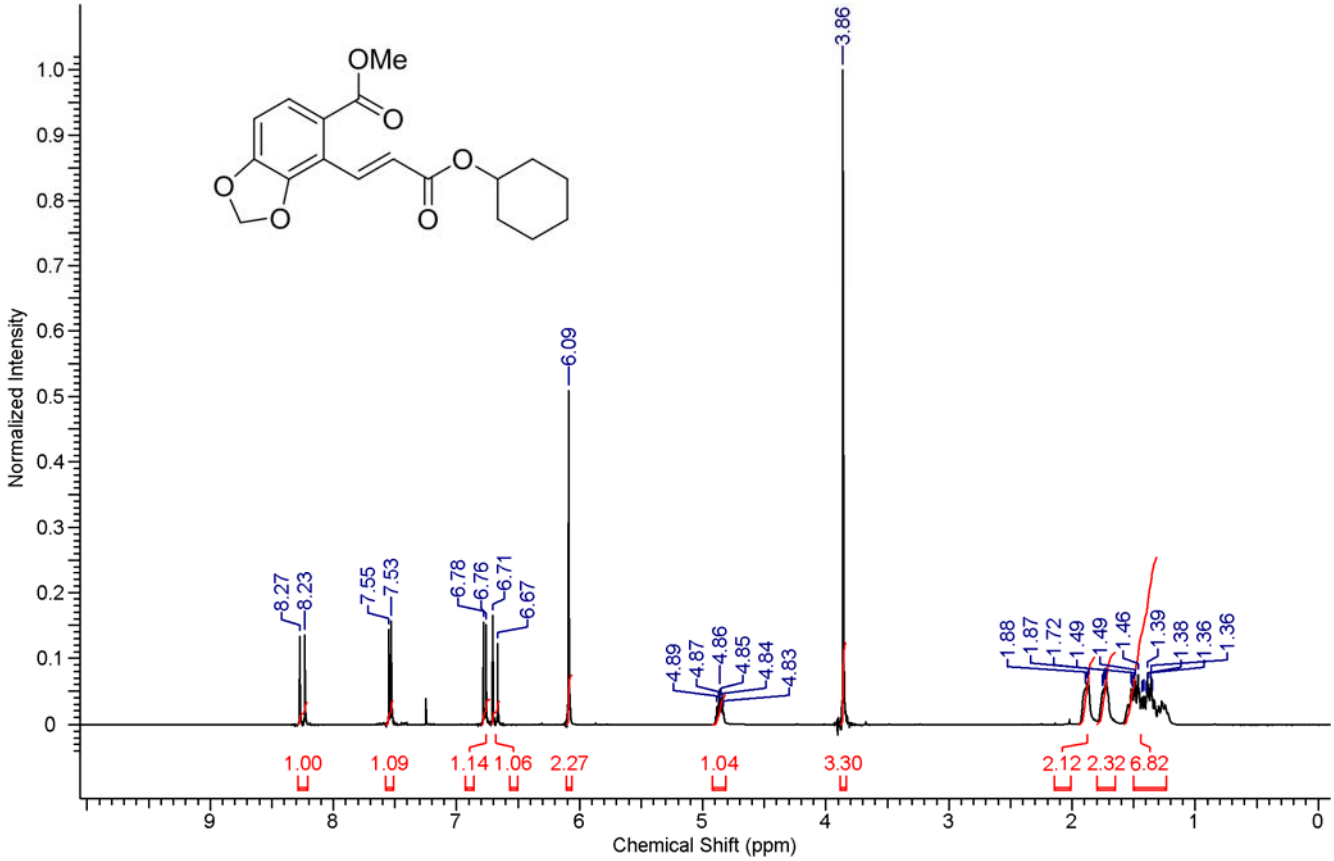


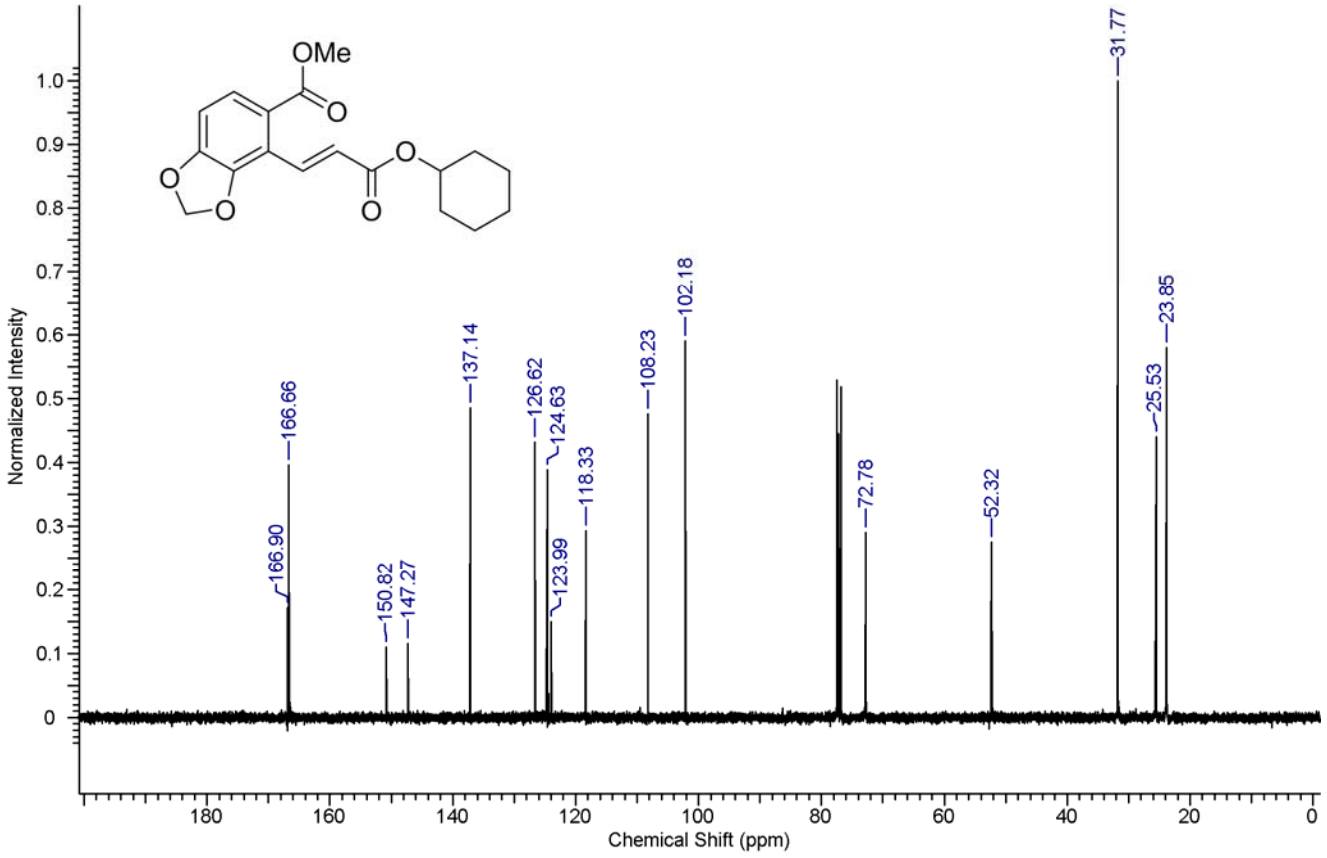


DEPT (135) Spectrum of Compound **3d**.

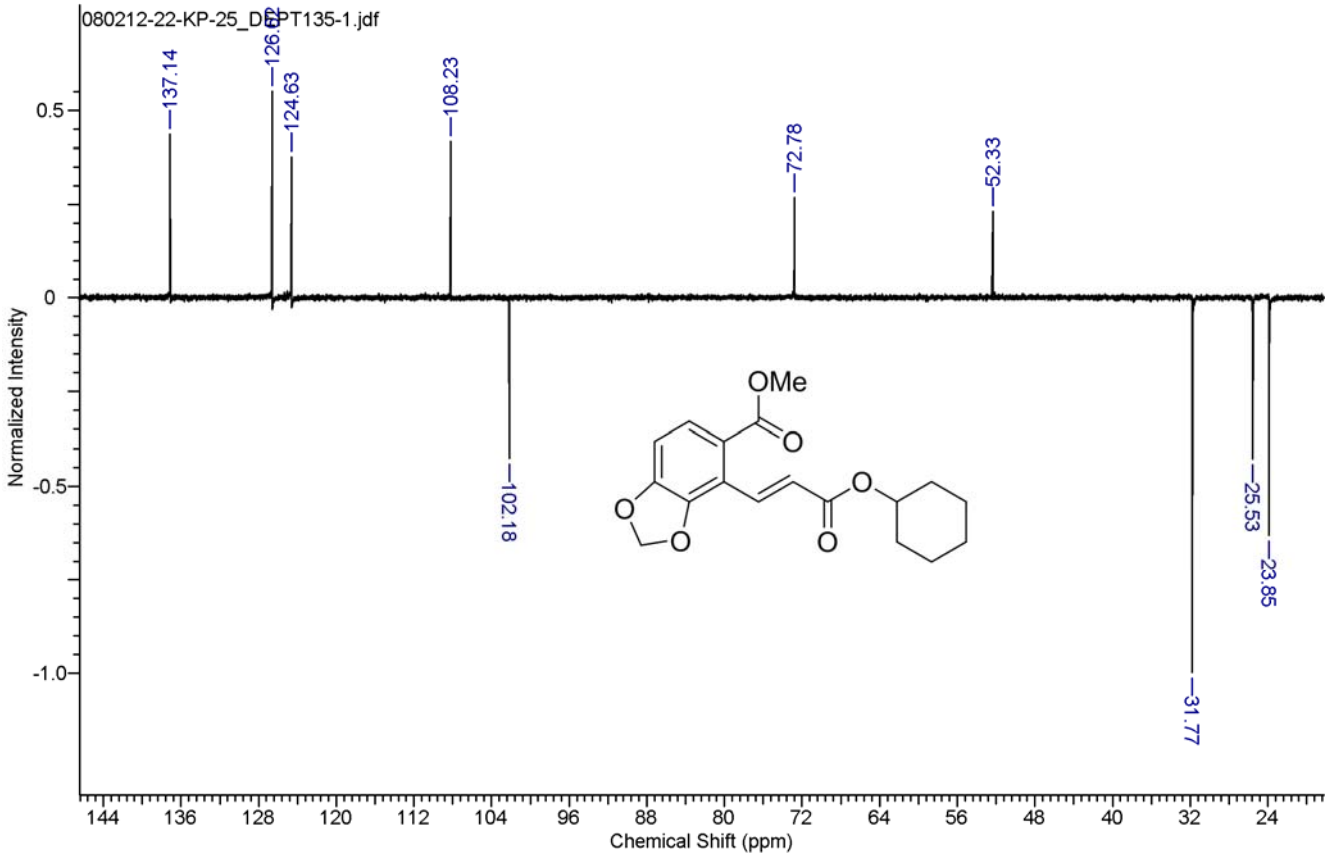


^{1}H and ^{13}C NMR Spectra of Compound **3e**.

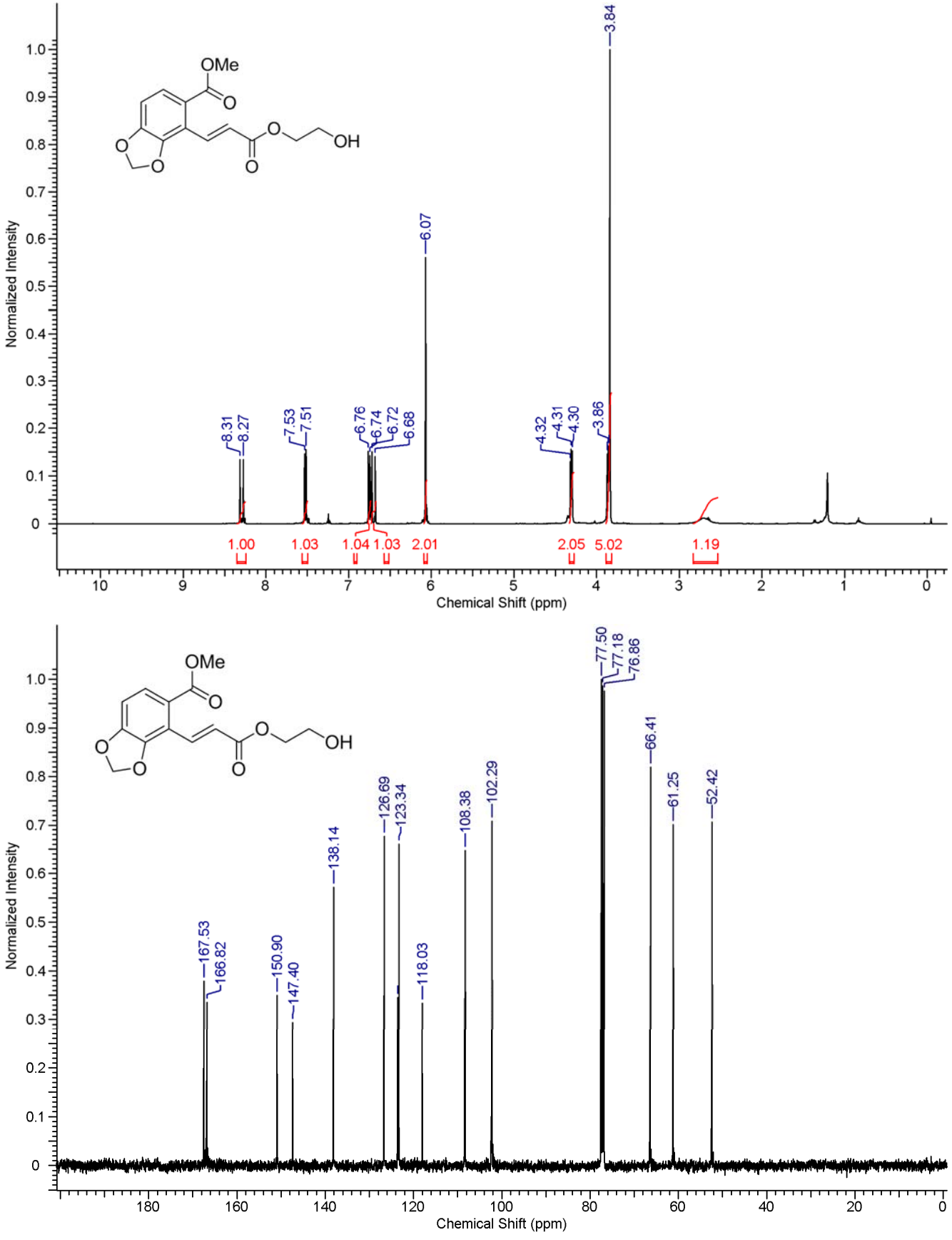




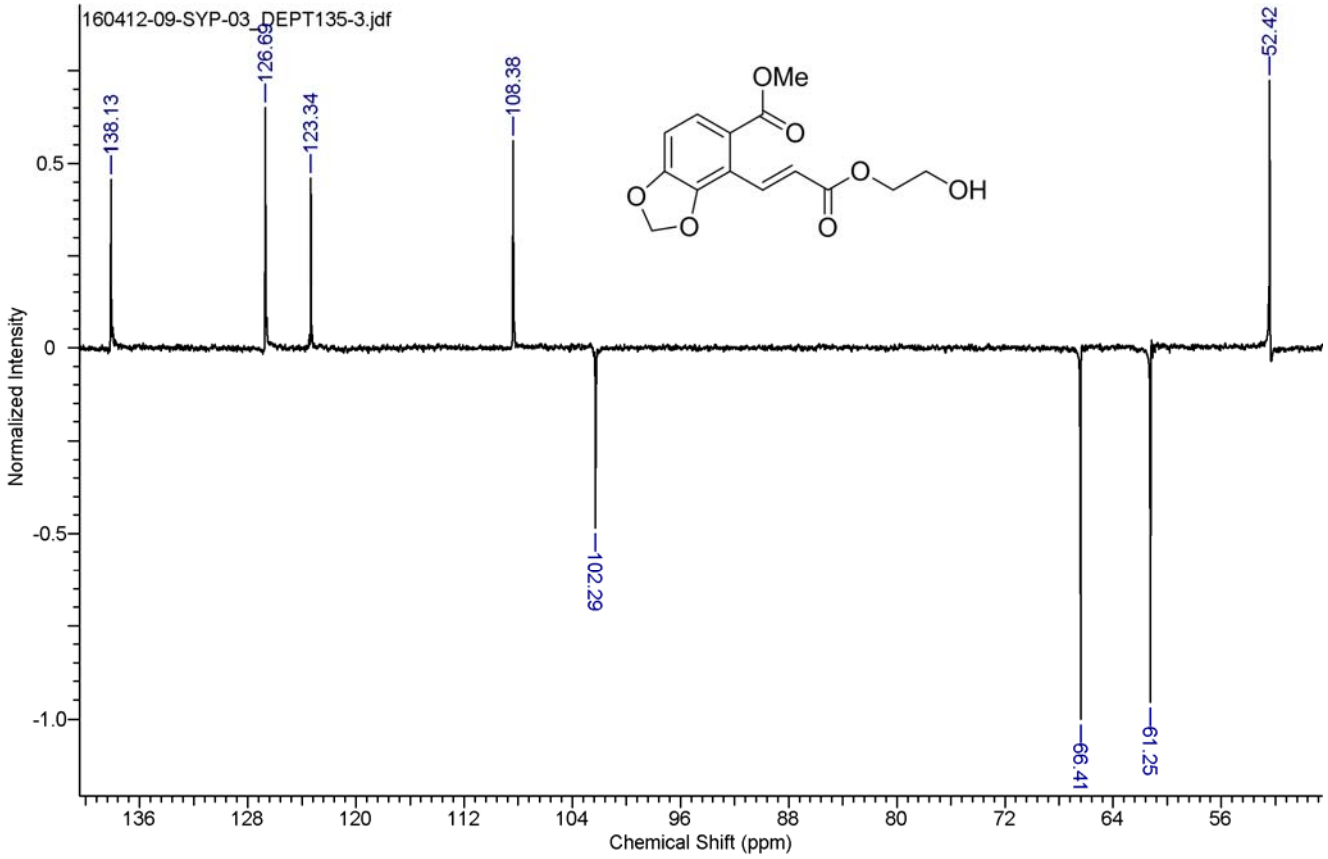
DEPT (135) Spectrum of Compound **3e**.



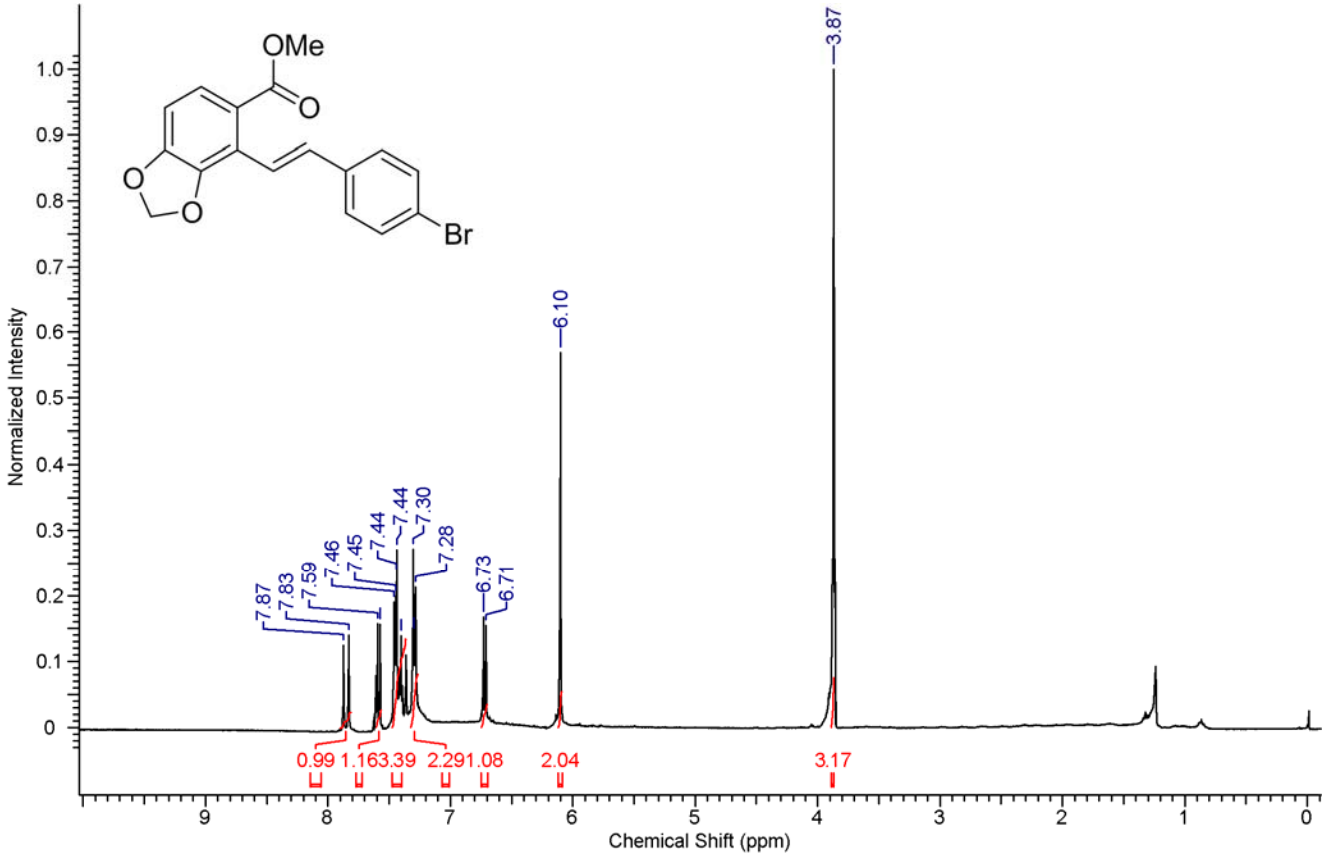
^{1}H and ^{13}C NMR Spectra of Compound **3f**.

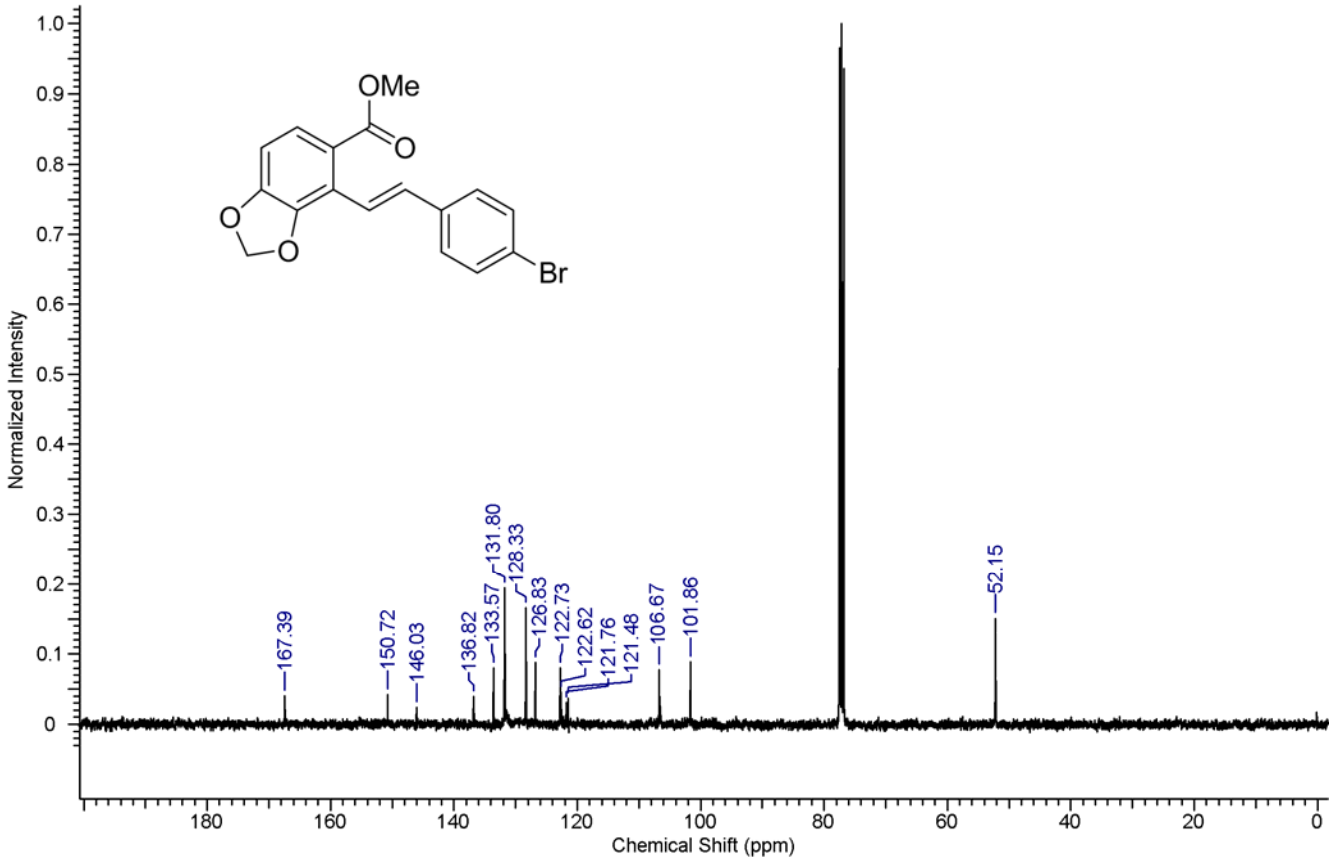


DEPT (135) Spectrum of Compound **3f**.

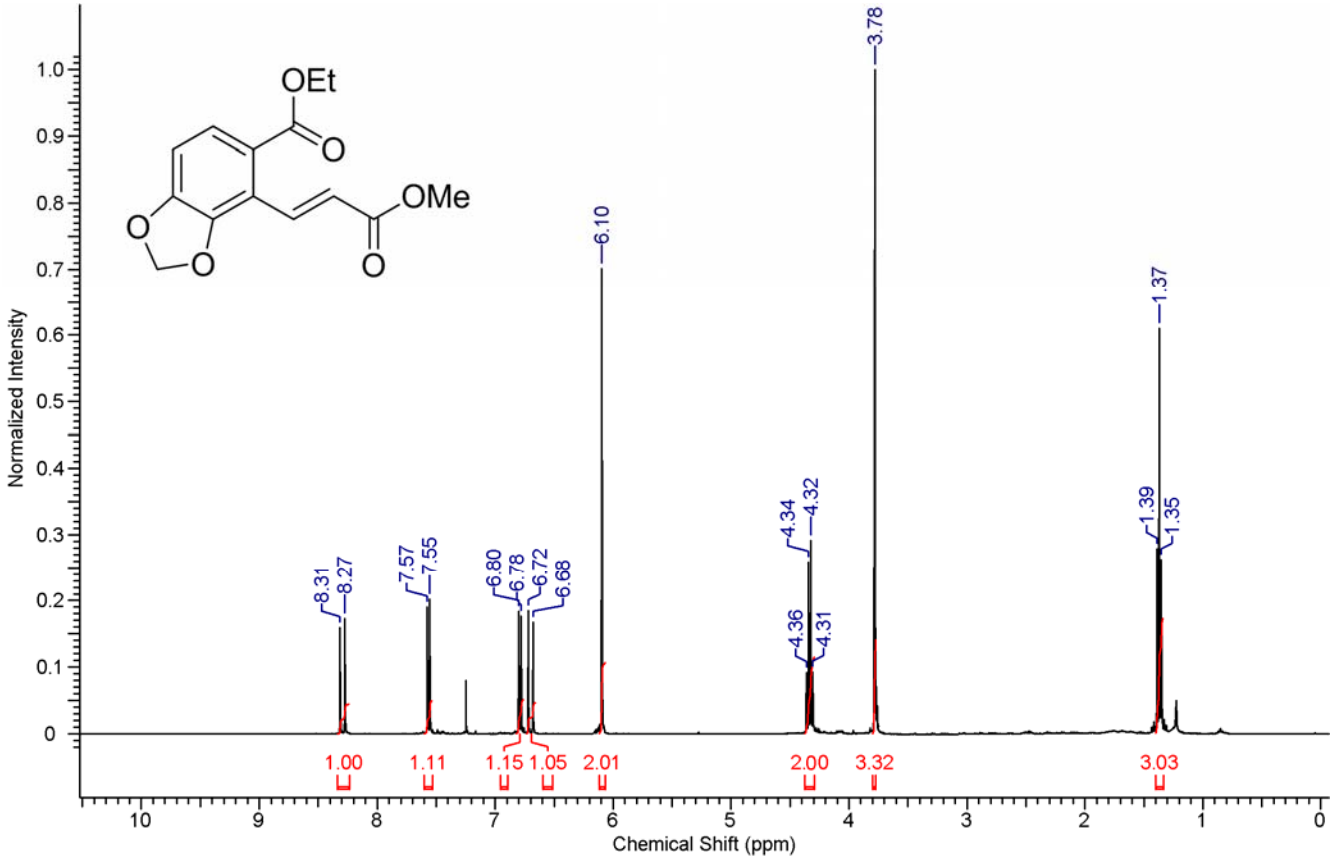


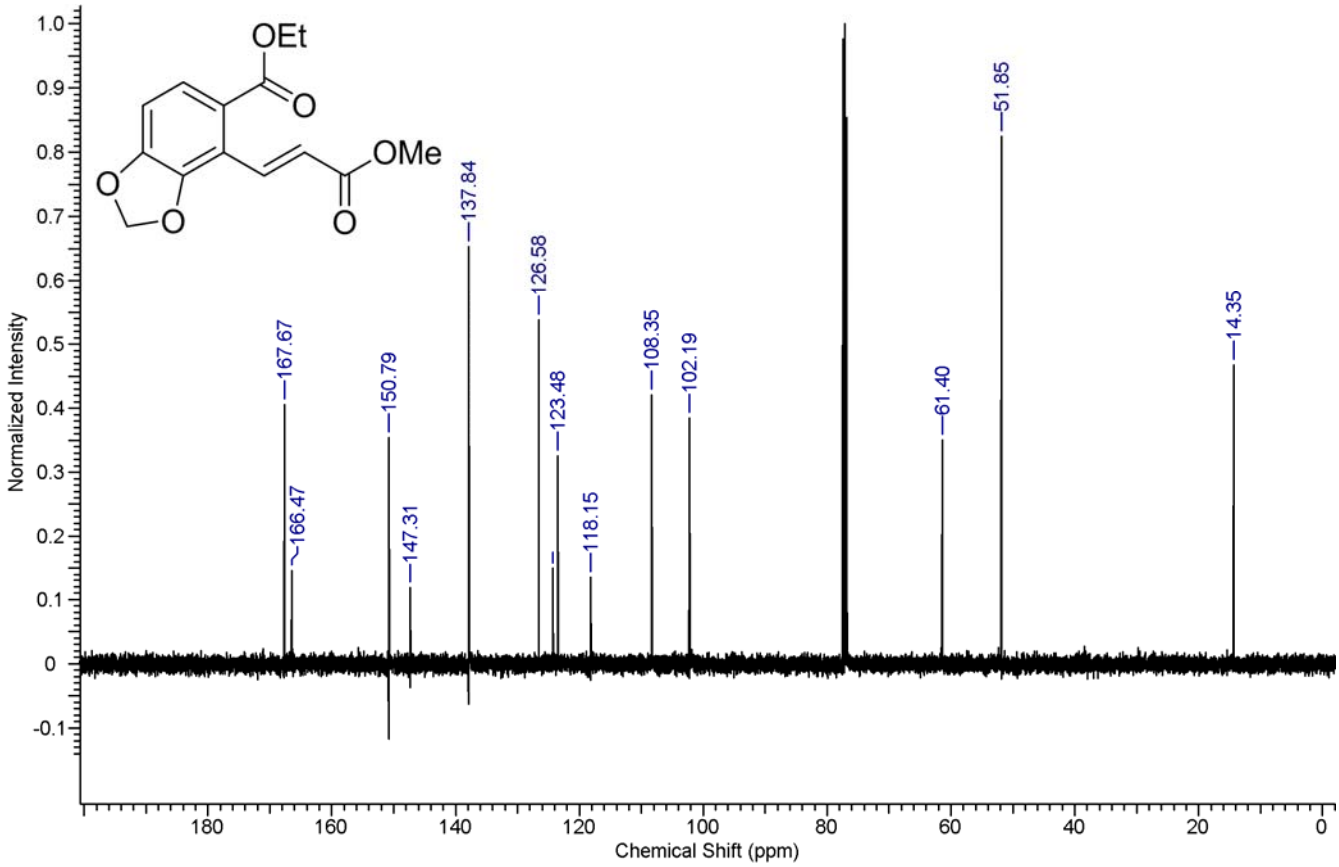
^{1}H and ^{13}C NMR Spectra of Compound **3g**.



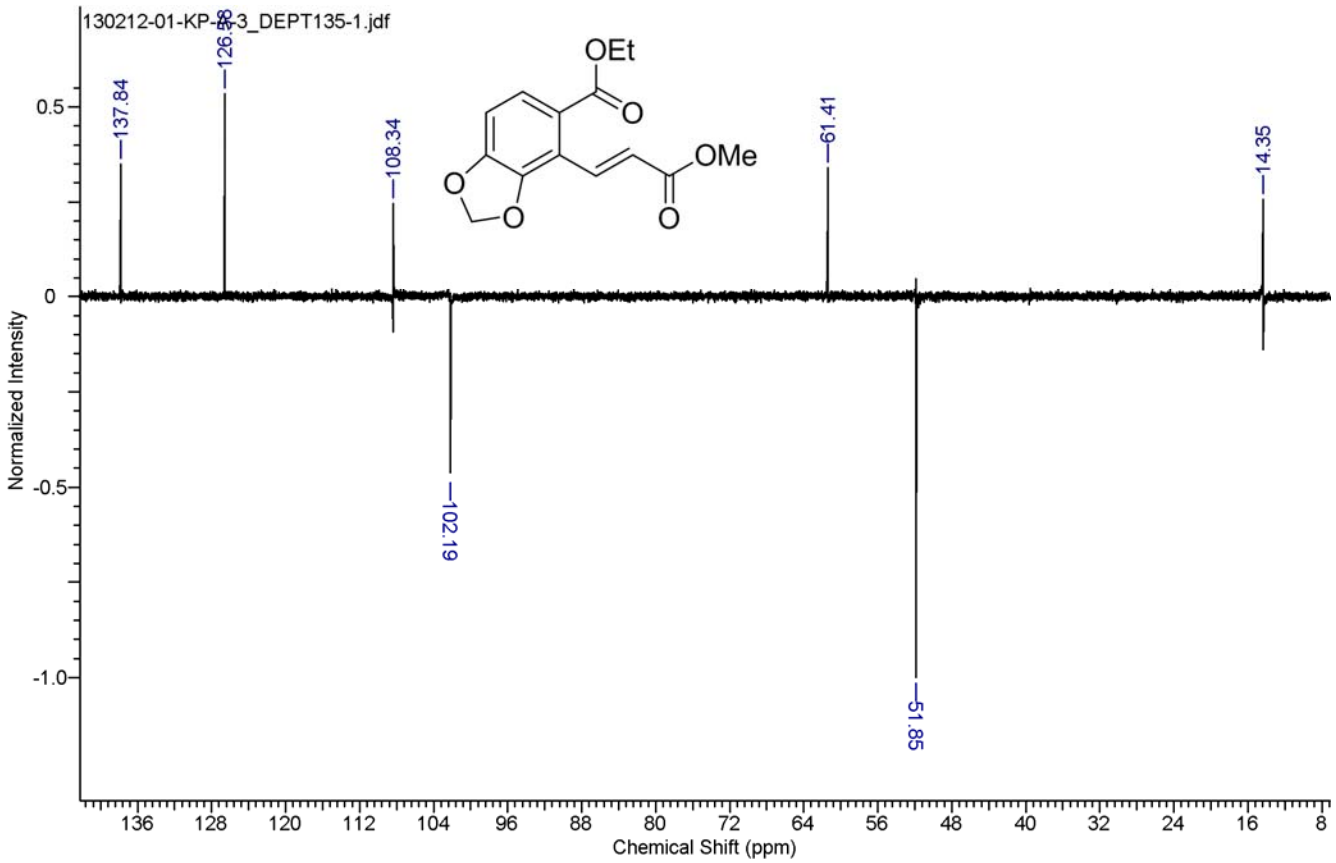


^{1}H and ^{13}C NMR Spectra of Compound **3h**.

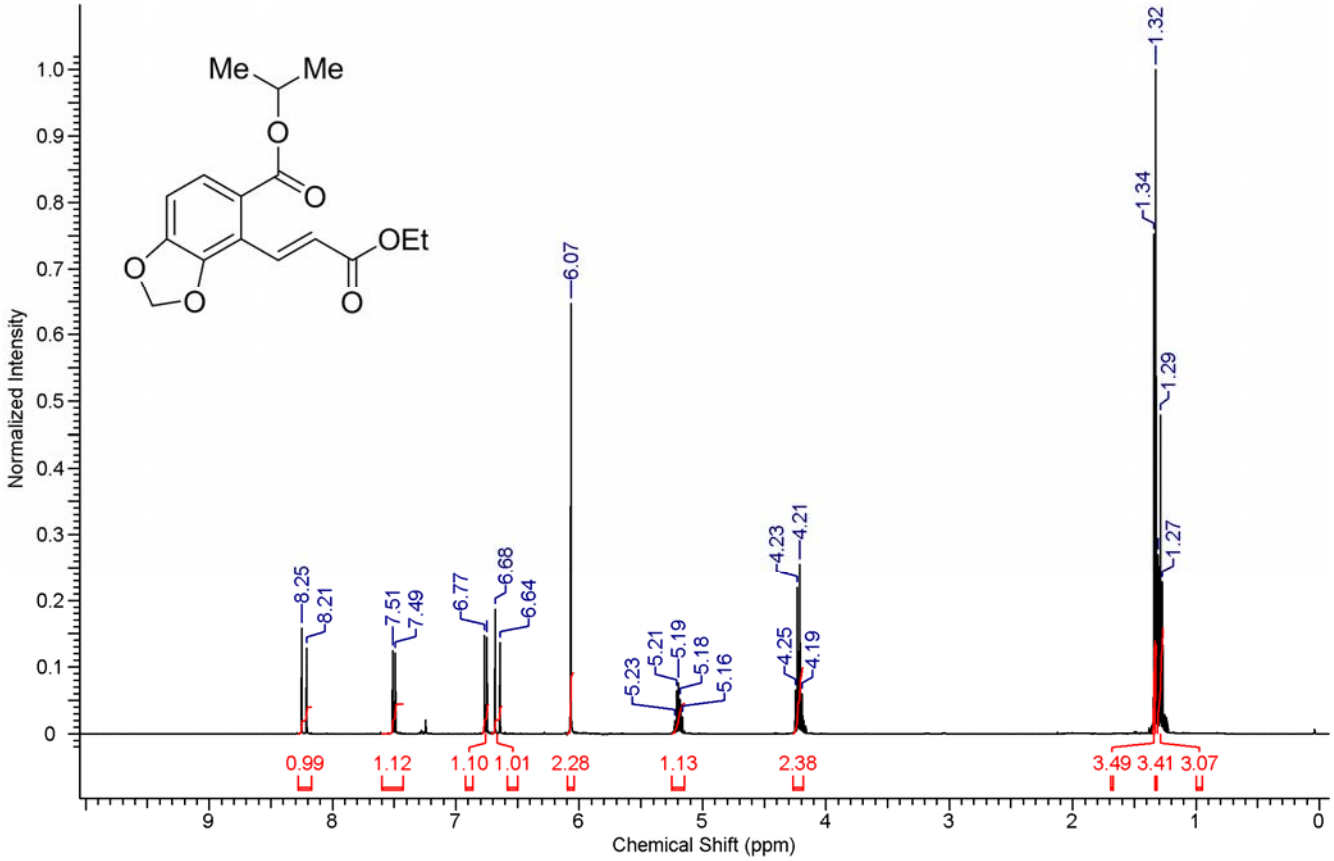


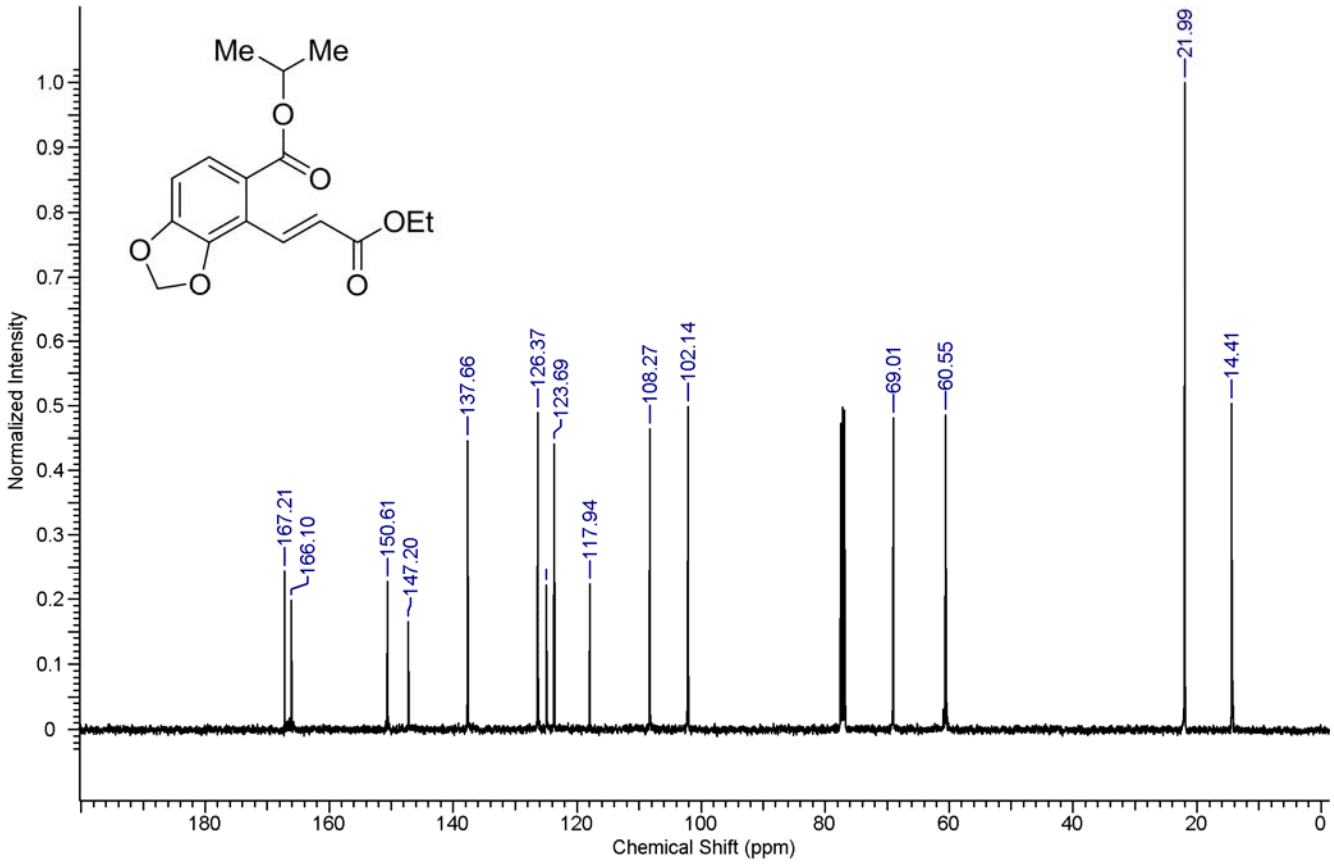


DEPT (135) Spectrum of Compound **3h**.

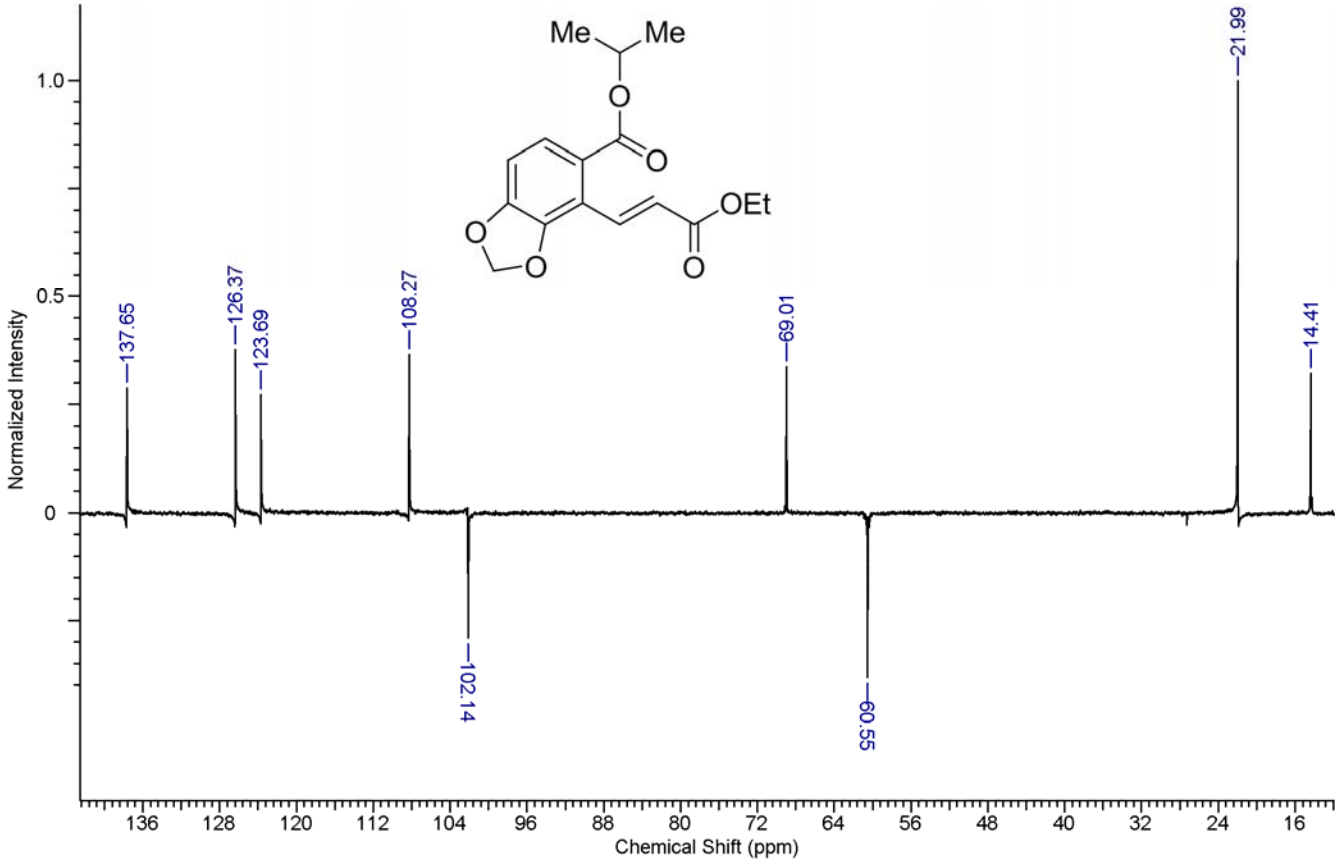


^{1}H and ^{13}C NMR Spectra of Compound **3i**.

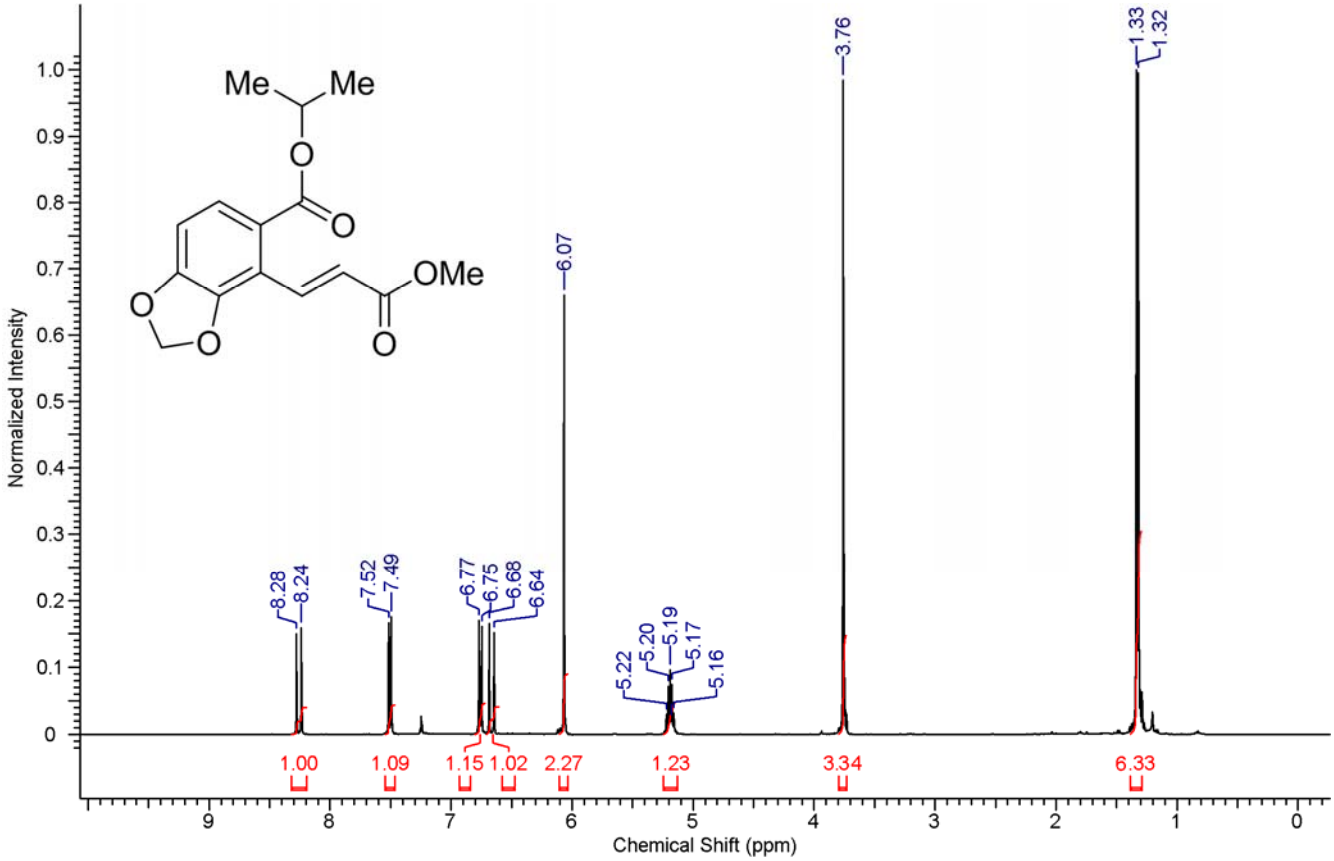


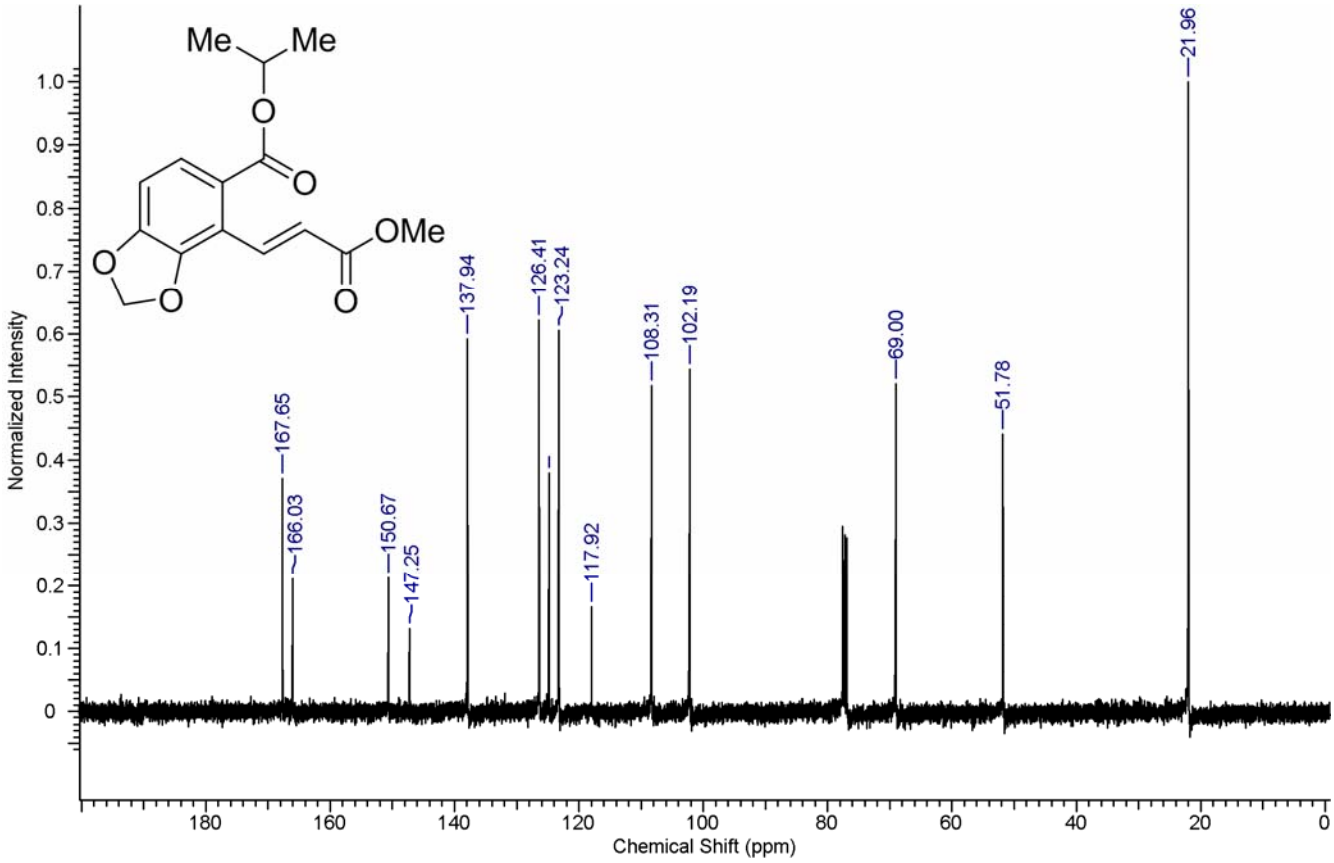


DEPT (135) Spectrum of Compound **3i**.

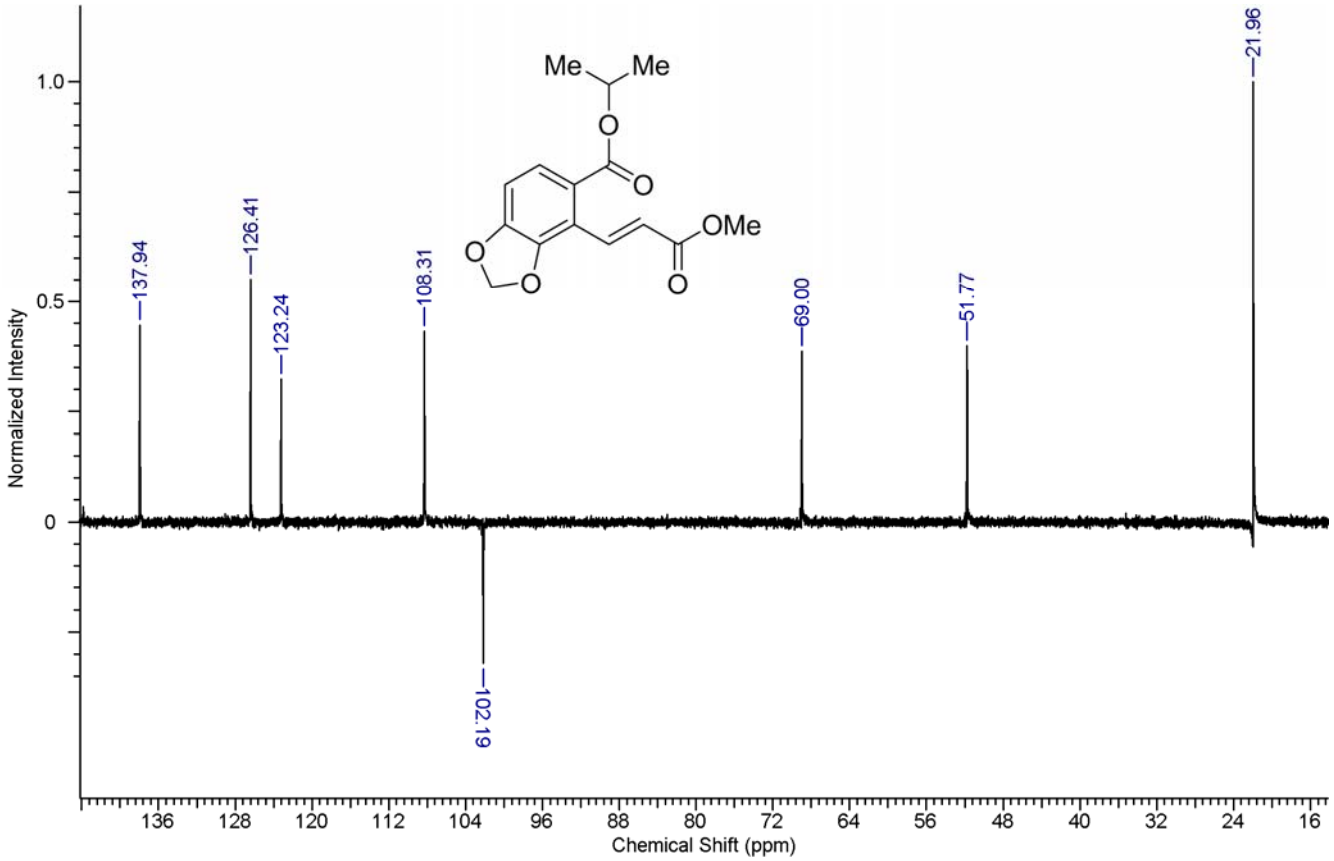


^{1}H and ^{13}C NMR Spectra of Compound **3j**.

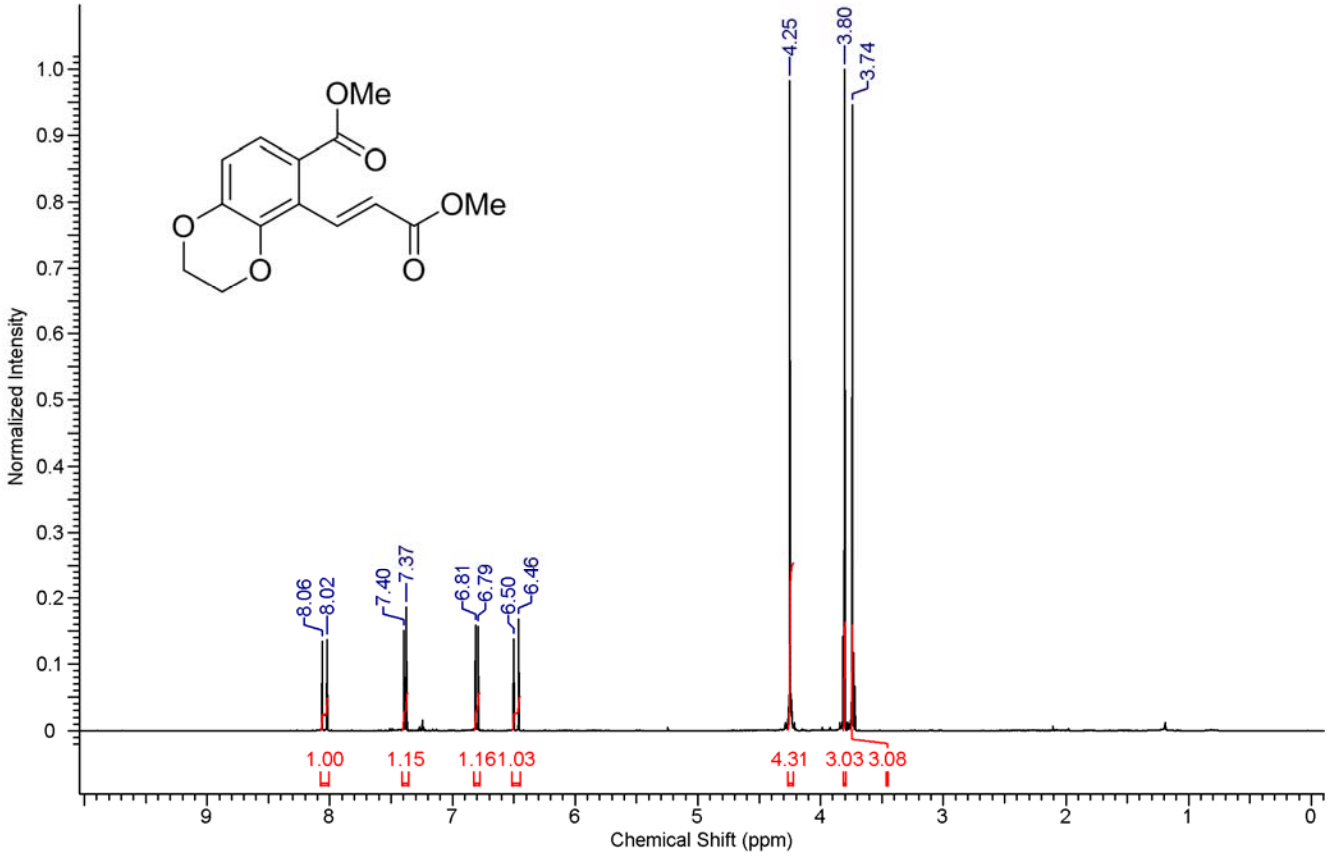


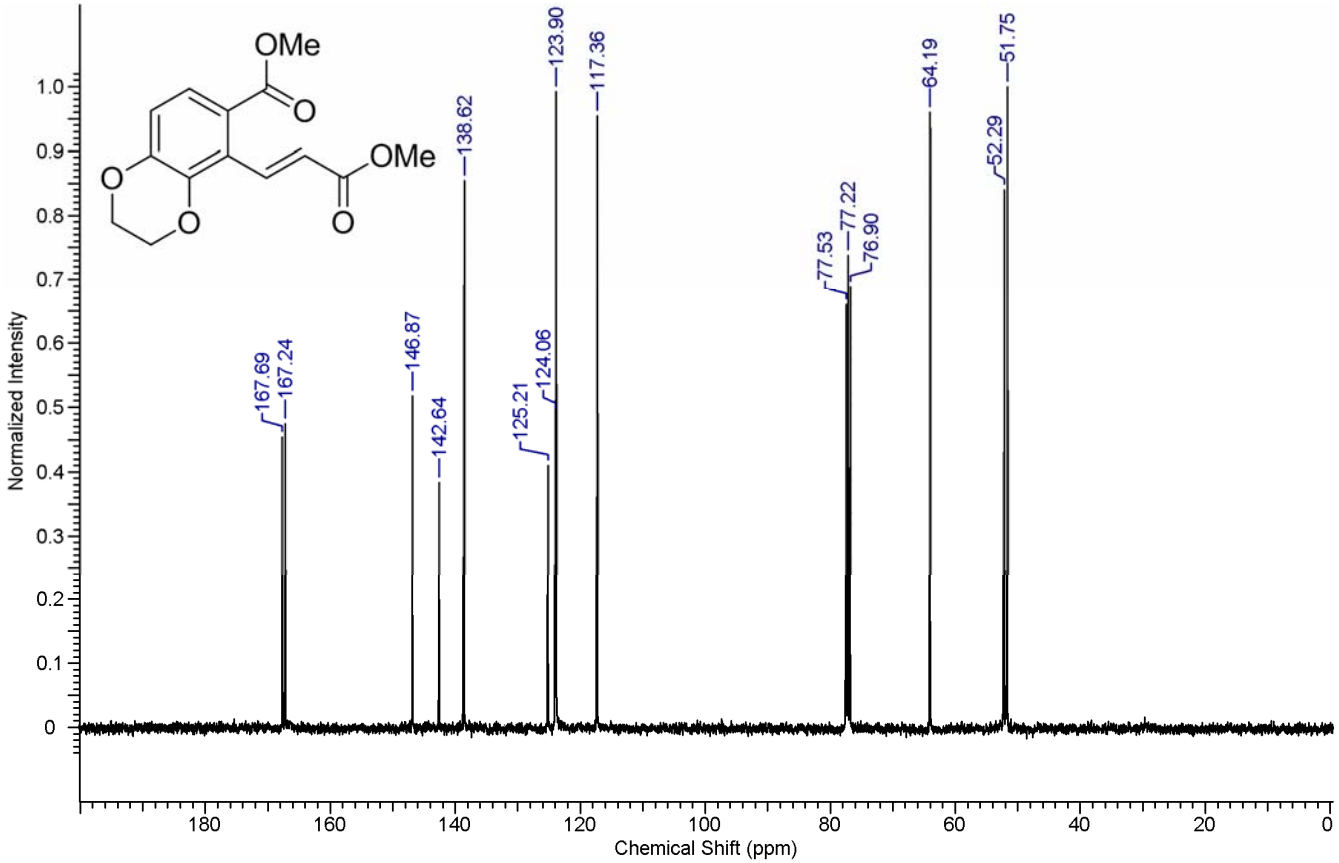


DEPT (135) Spectrum of Compound **3j**.

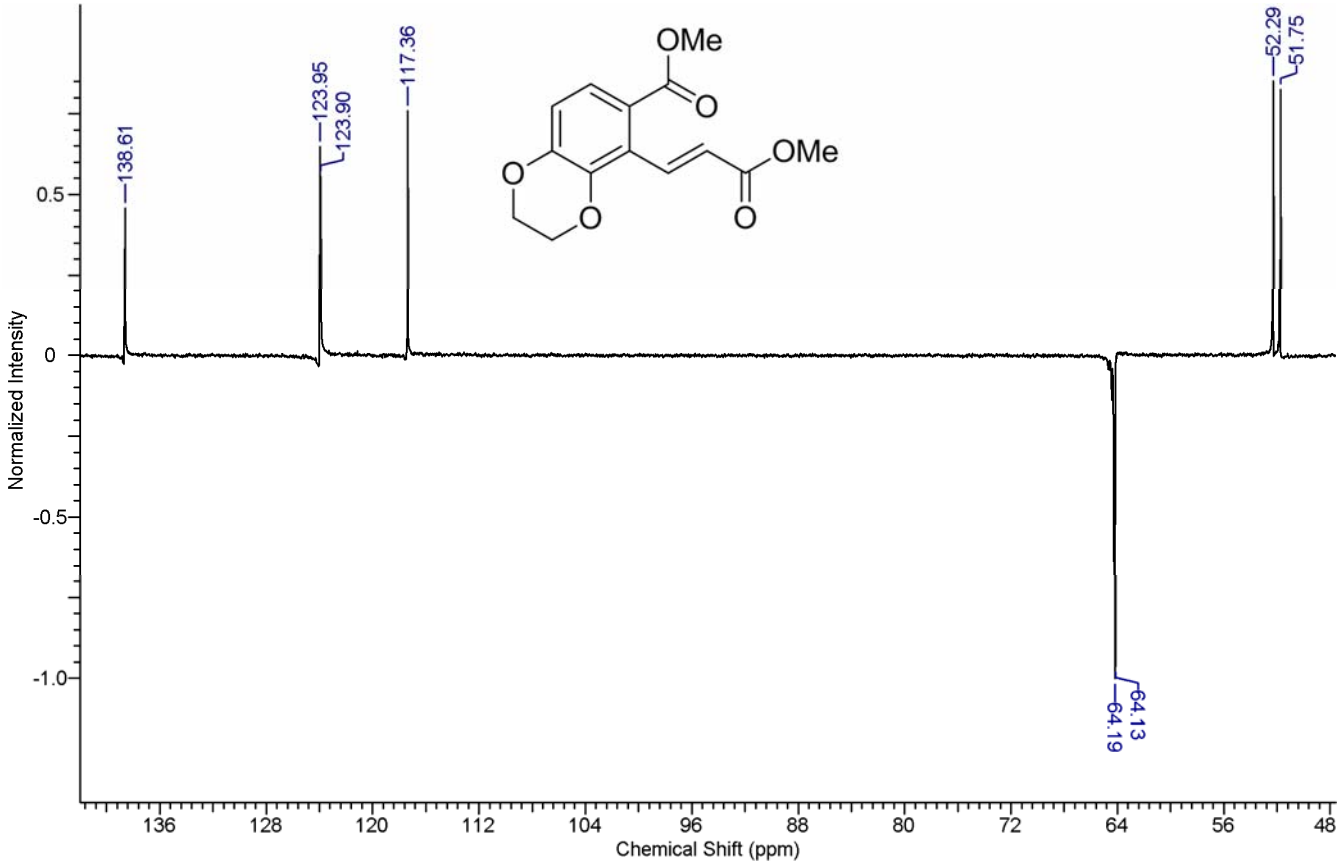


^{1}H and ^{13}C NMR Spectra of Compound **3k**.

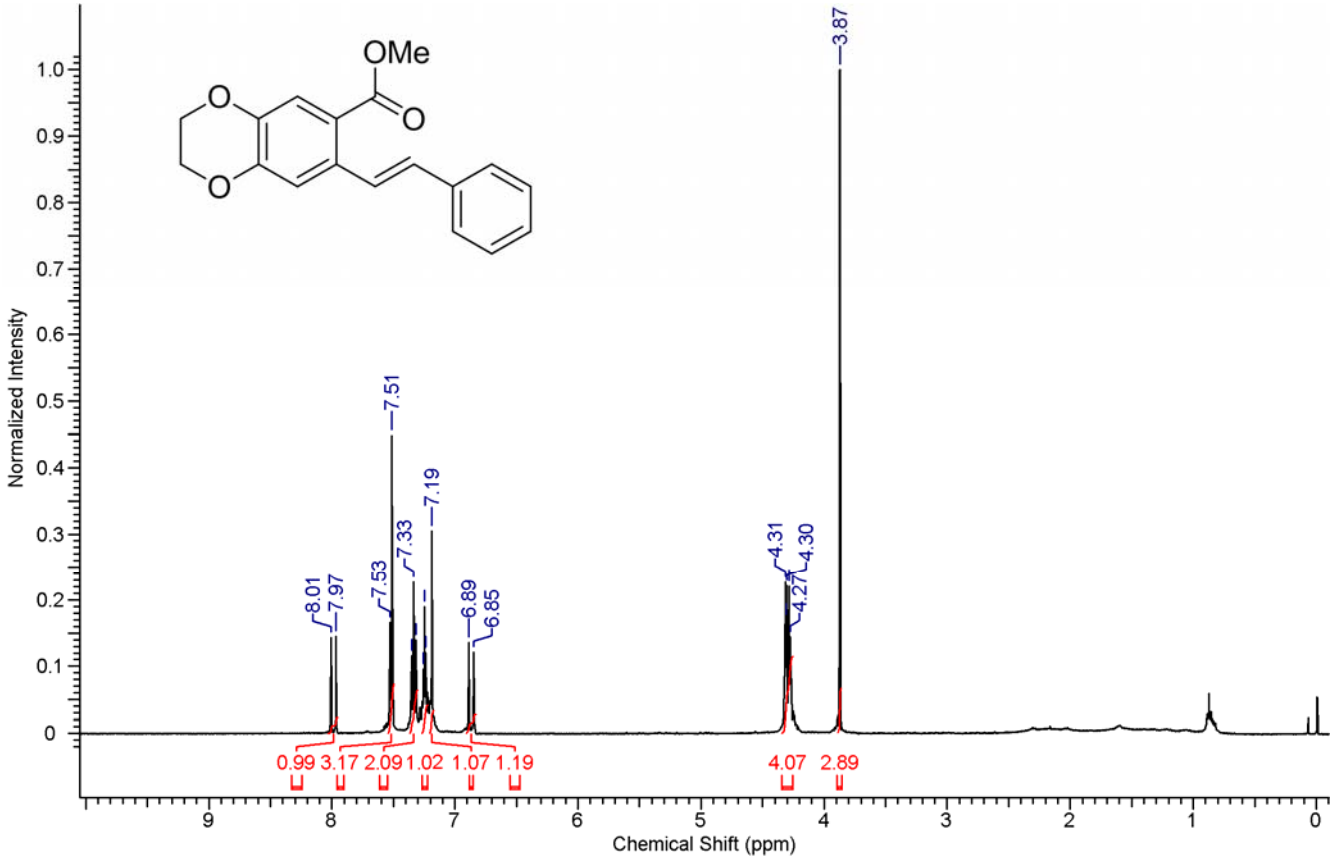


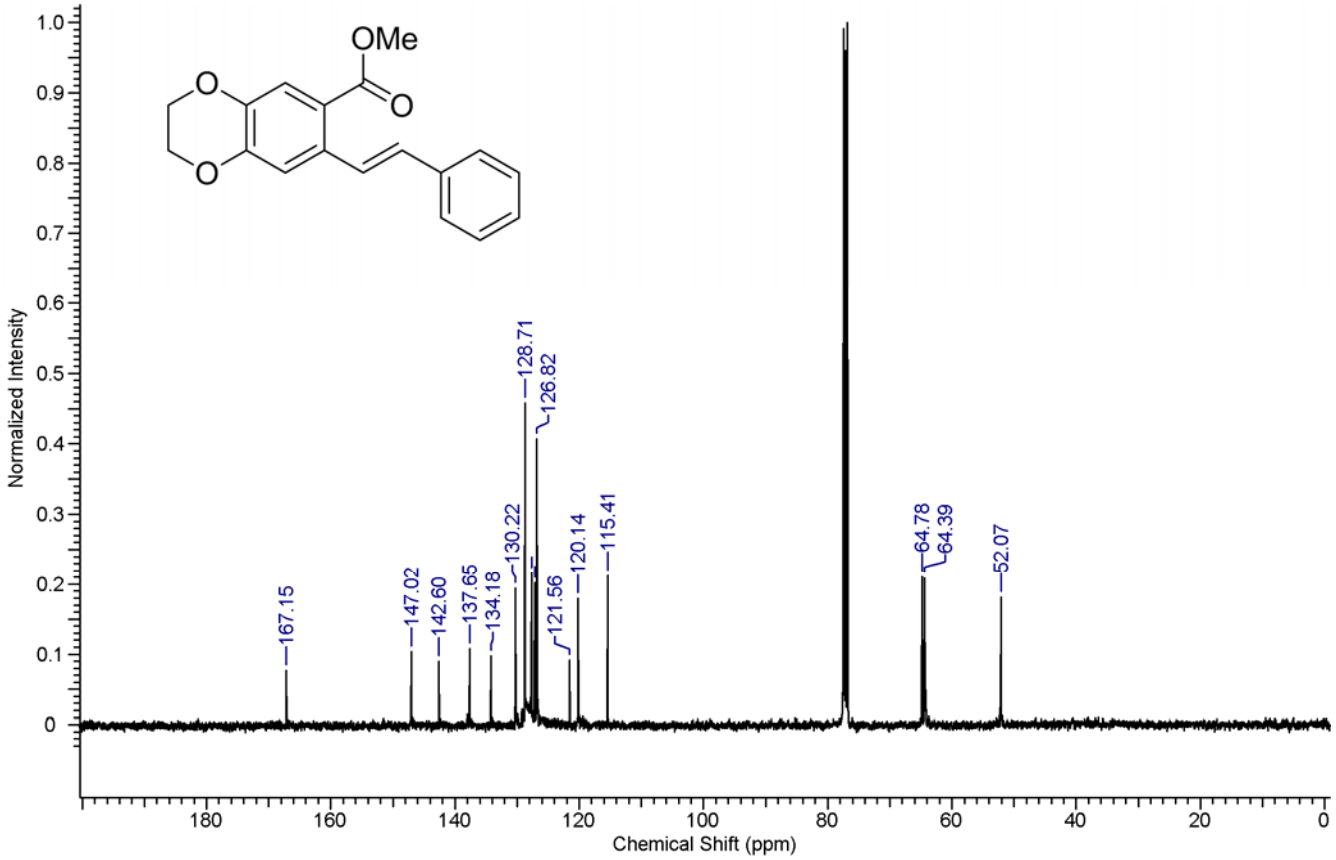


DEPT (135) Spectrum of Compound **3k**.

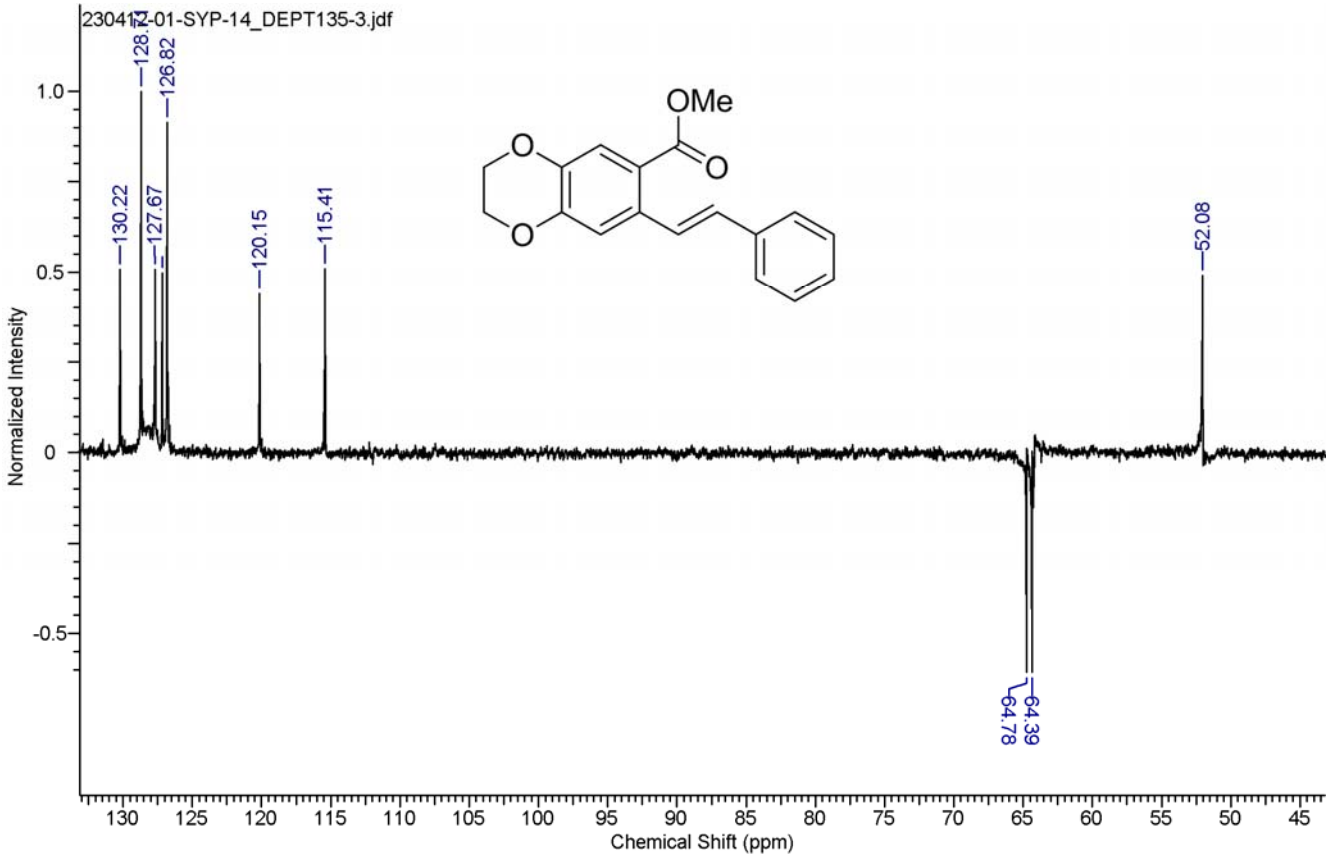


^{1}H and ^{13}C NMR Spectra of Compound **3l**.

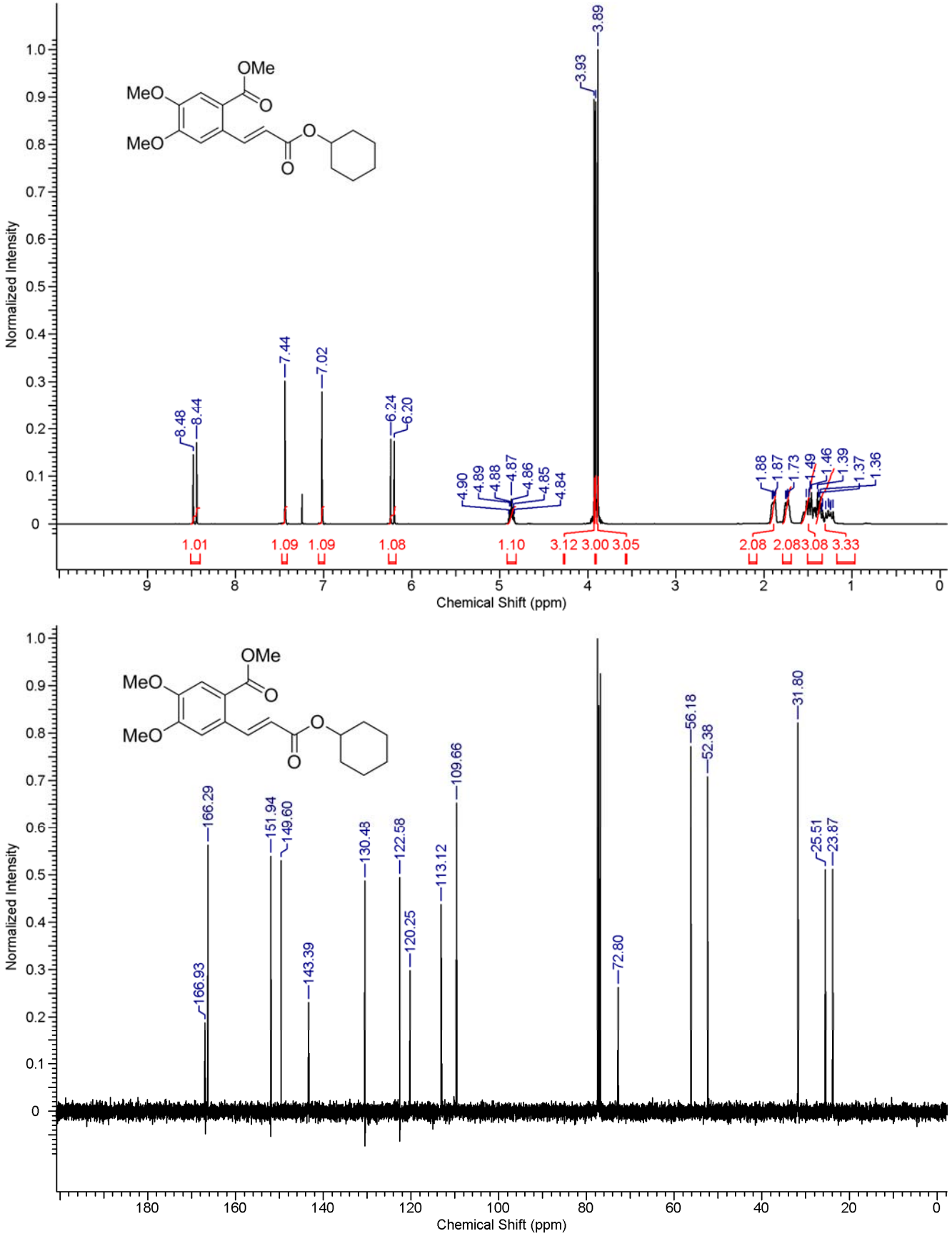




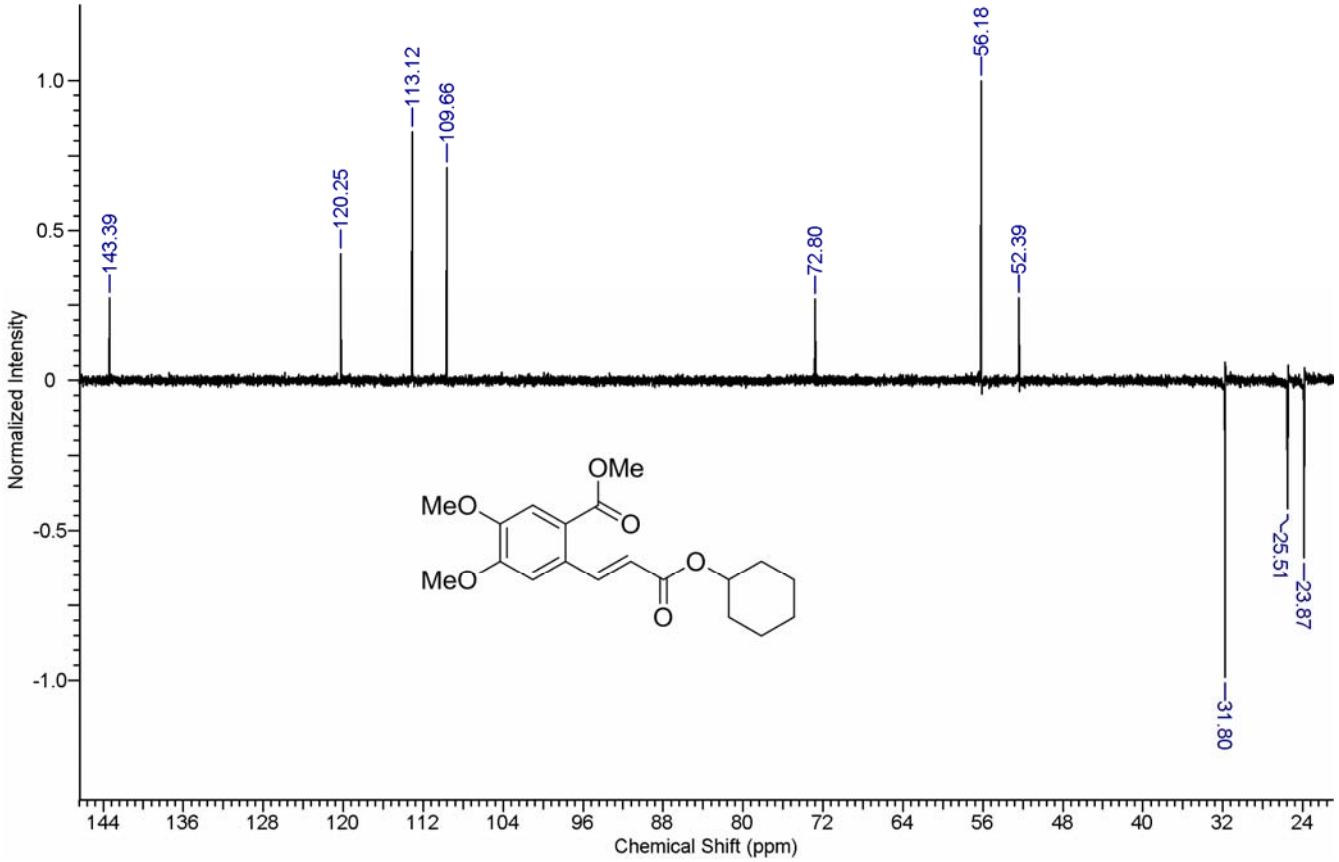
DEPT (135) Spectrum of Compound **3l**.



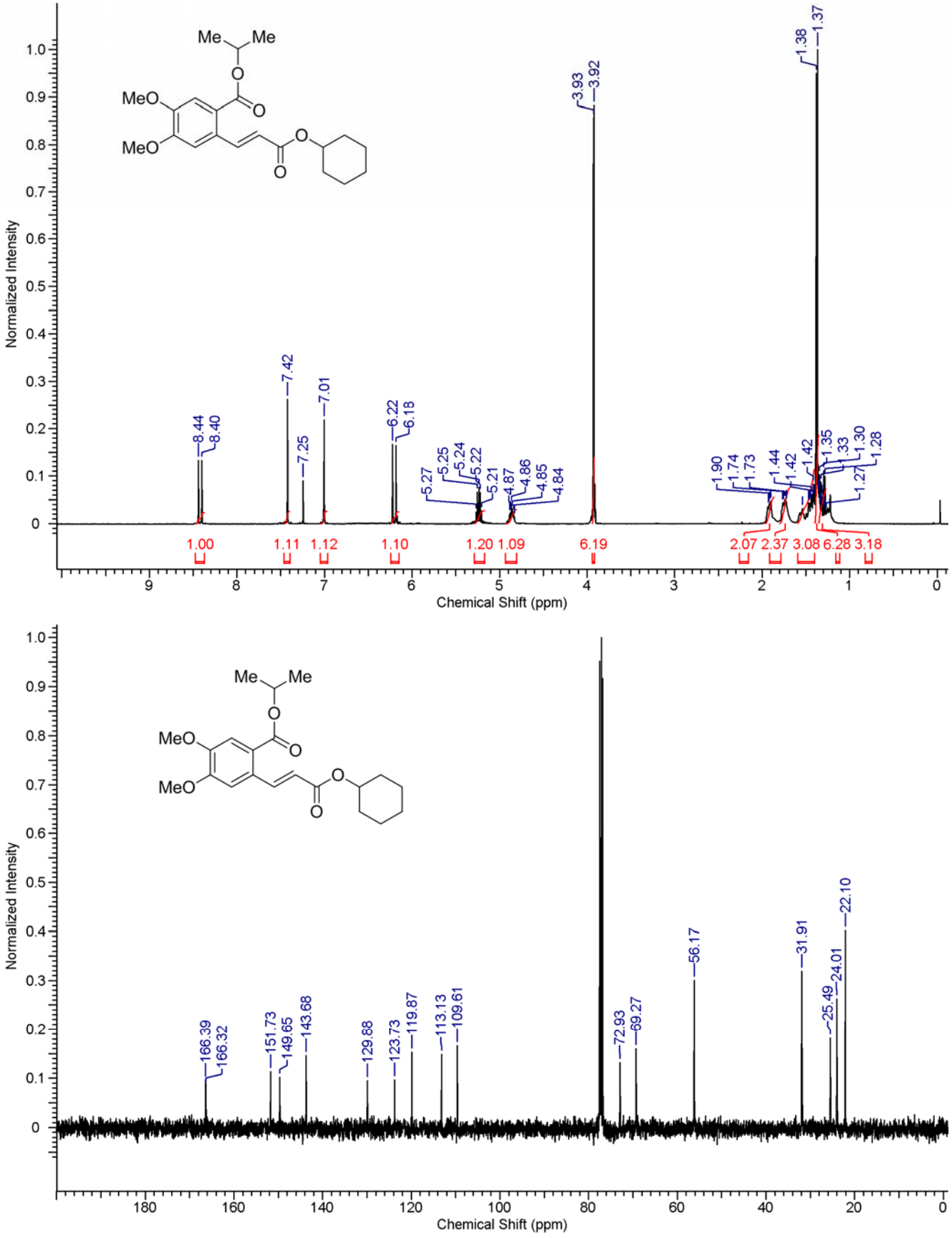
^{1}H and ^{13}C NMR Spectra of Compound **3m**.



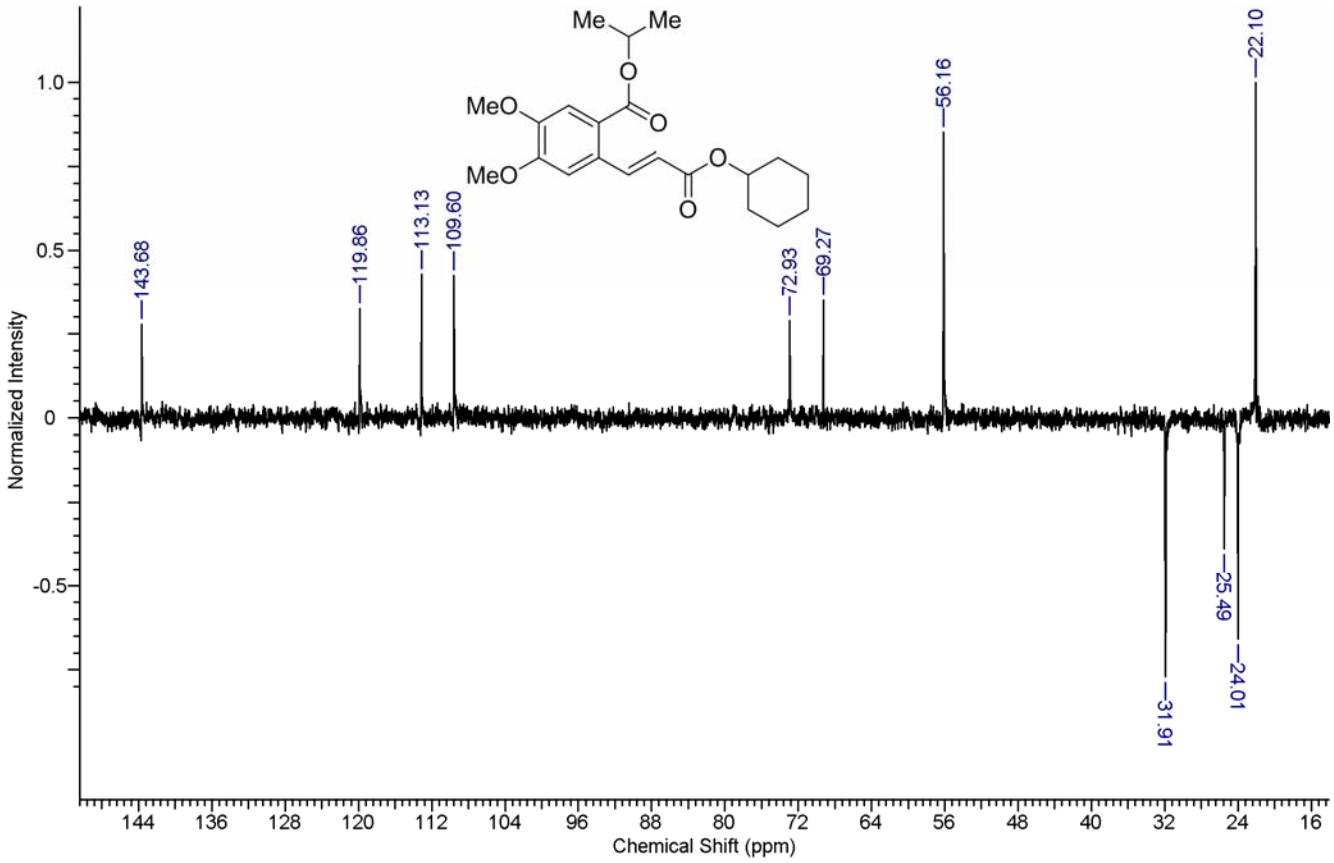
DEPT (135) Spectrum of Compound **3m**.



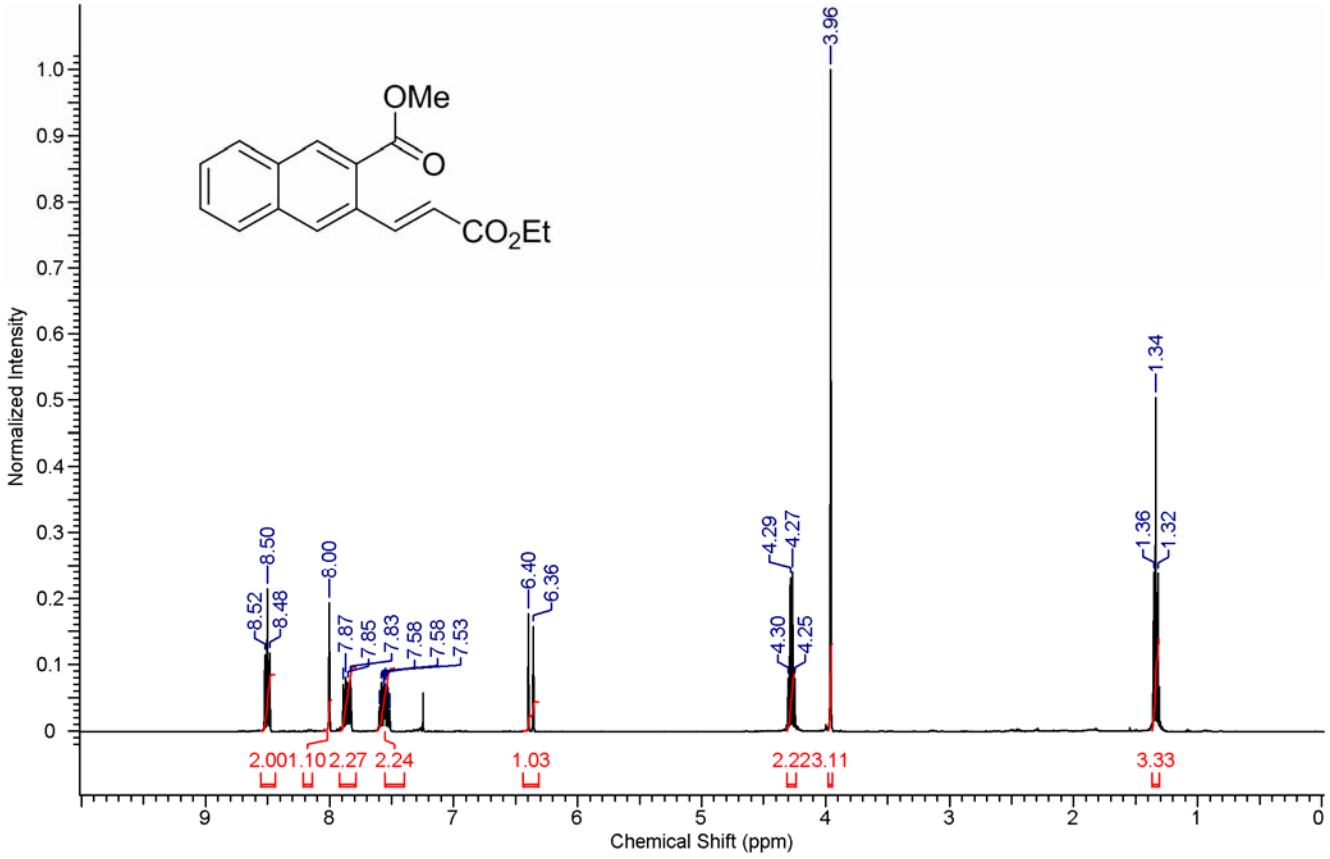
^{1}H and ^{13}C NMR Spectra of Compound **3n**.

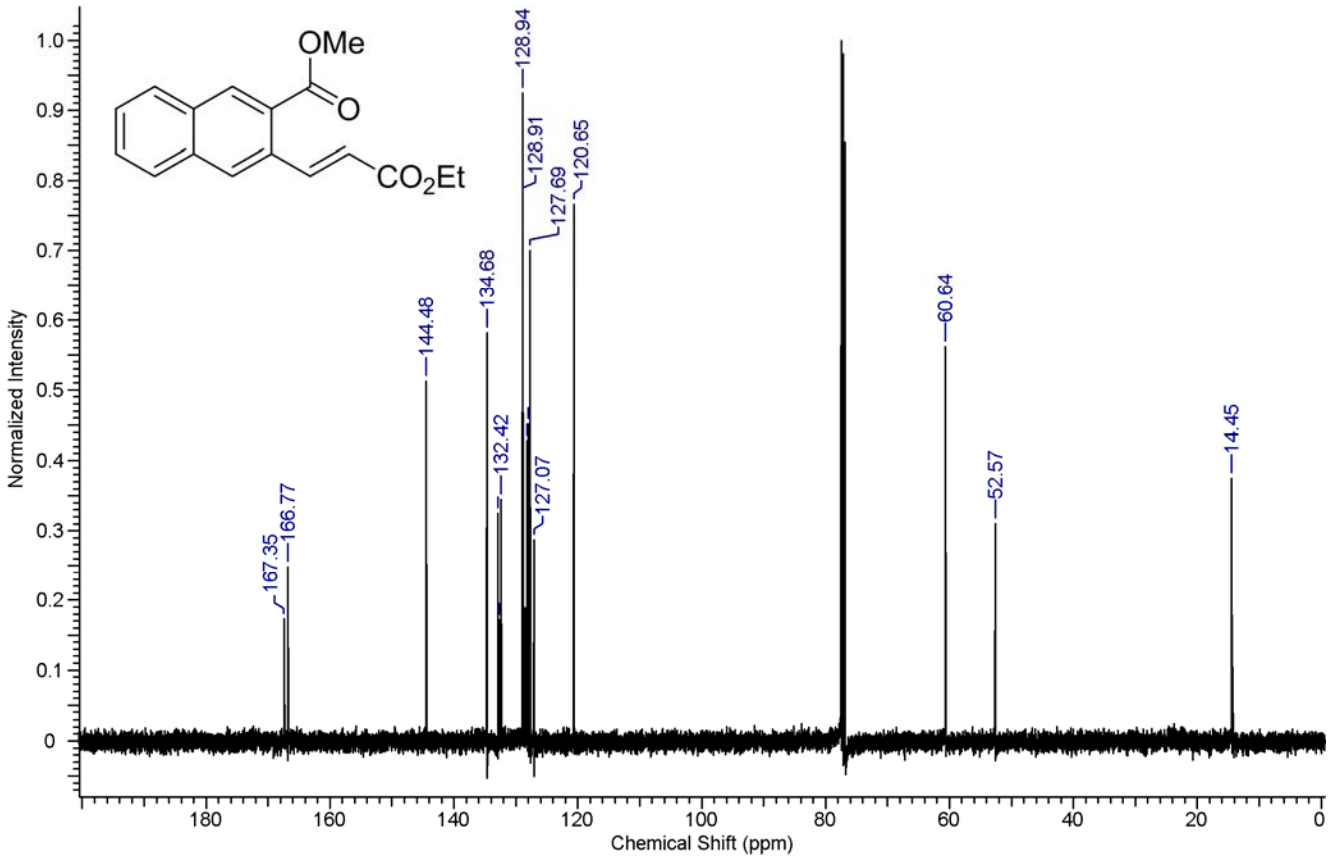


DEPT (135) Spectrum of Compound **3n**.

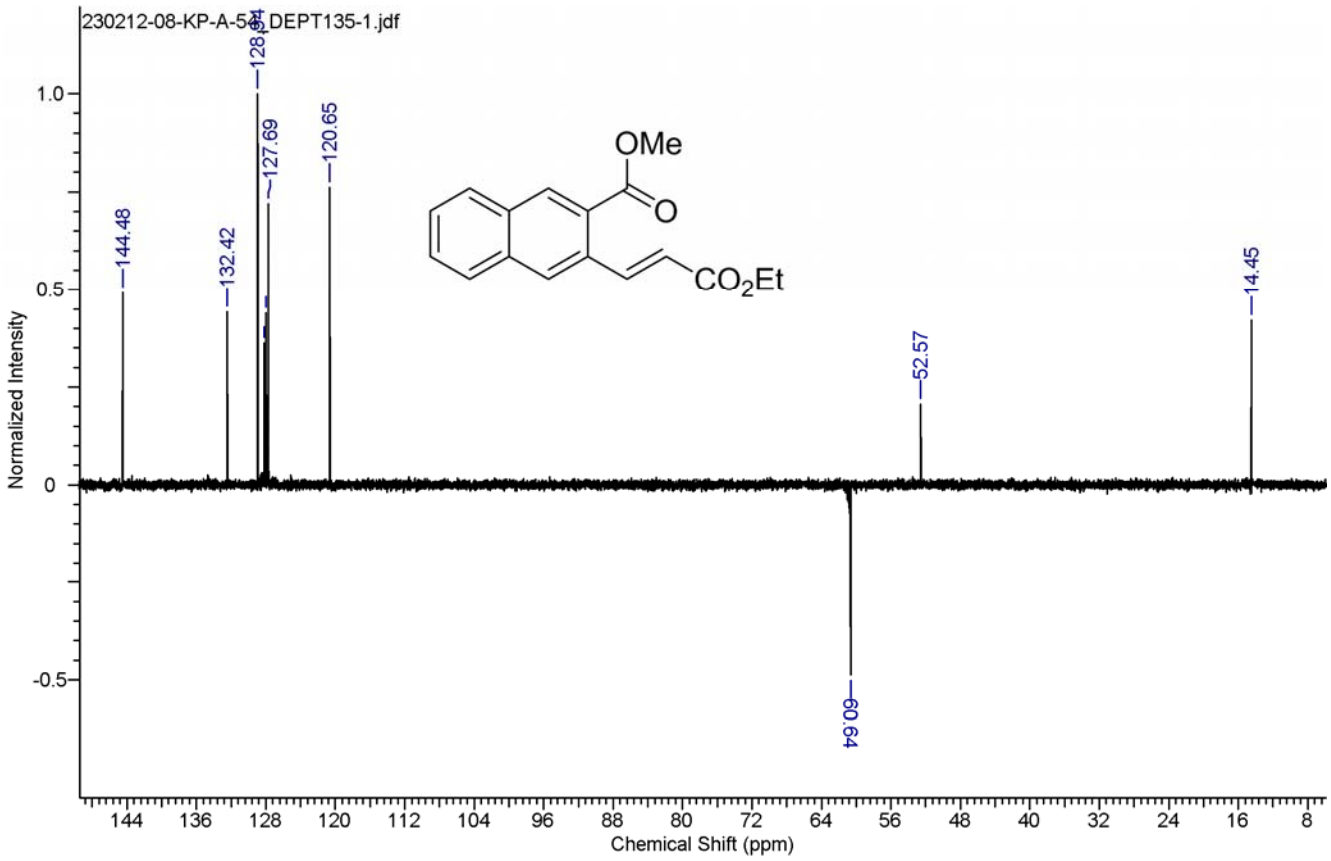


^{1}H and ^{13}C NMR Spectra of Compound **3o**.

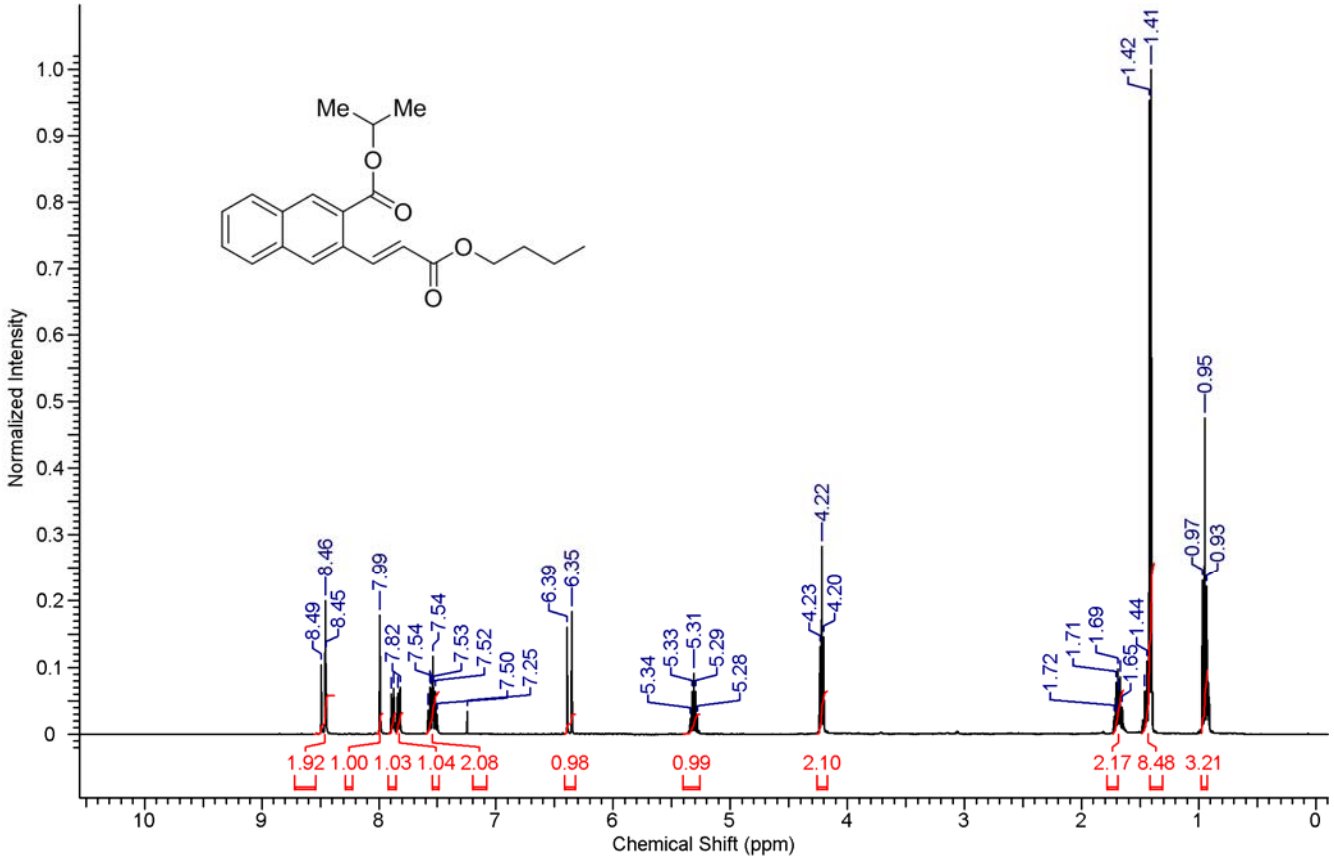


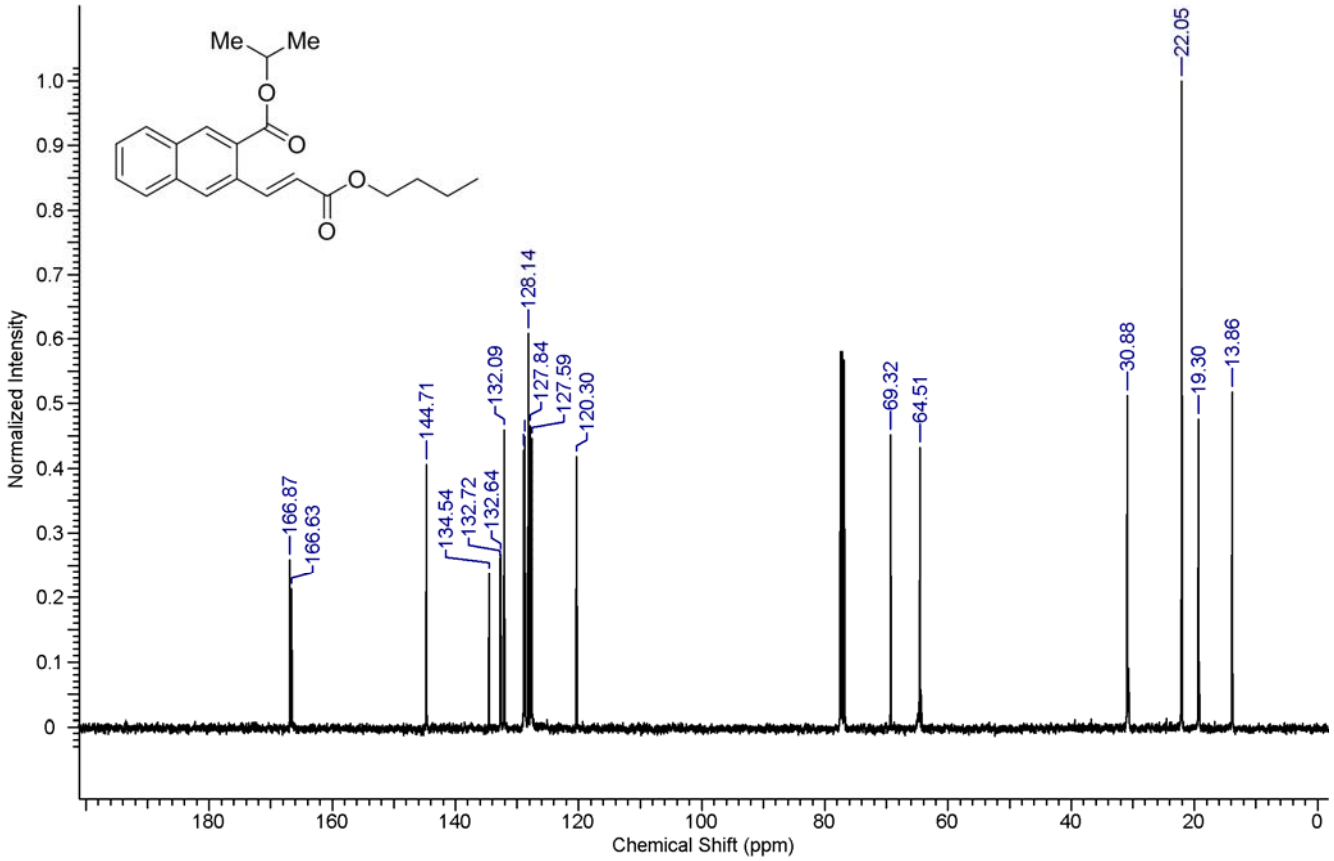


DEPT (135) Spectrum of Compound **3o**.

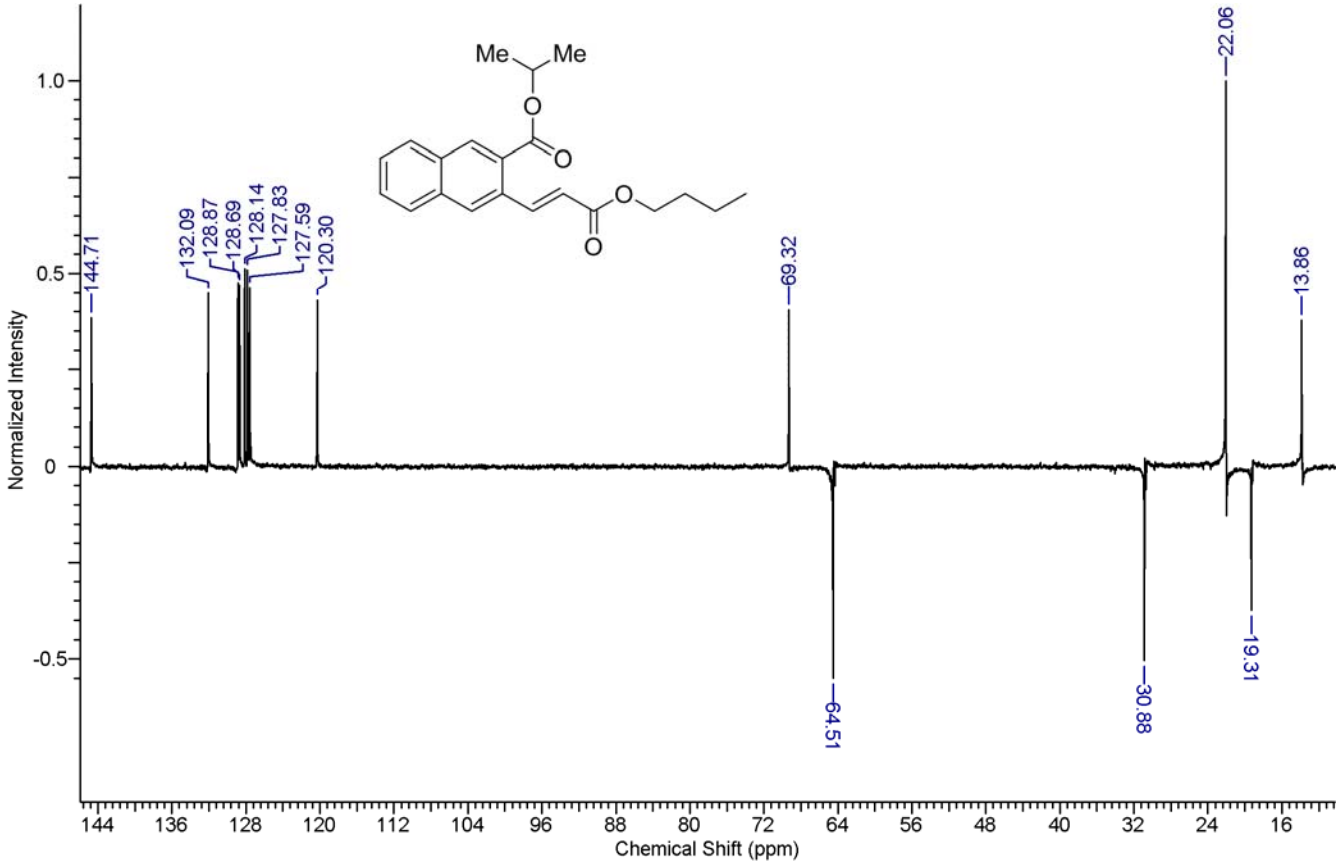


^{1}H and ^{13}C NMR Spectra of Compound **3p**.

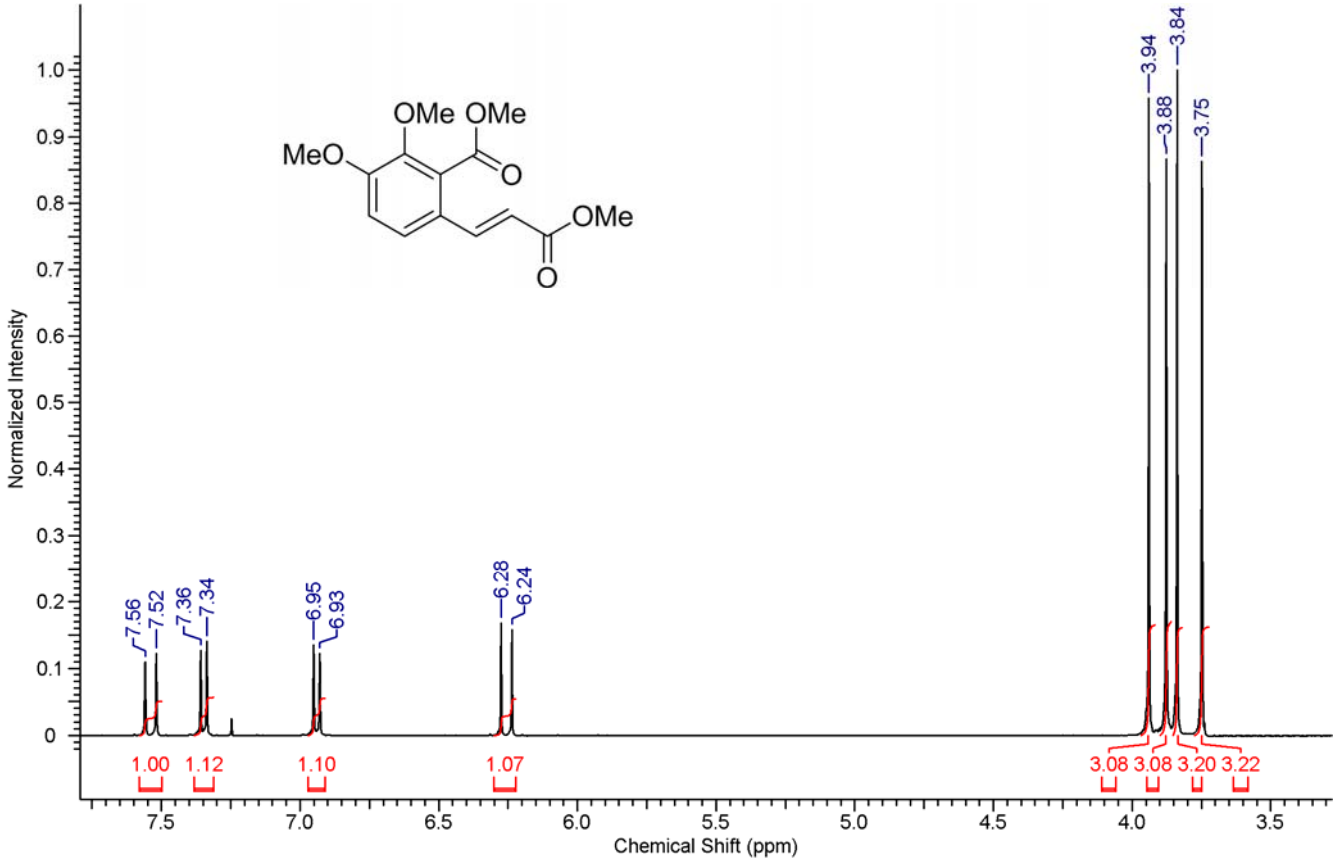


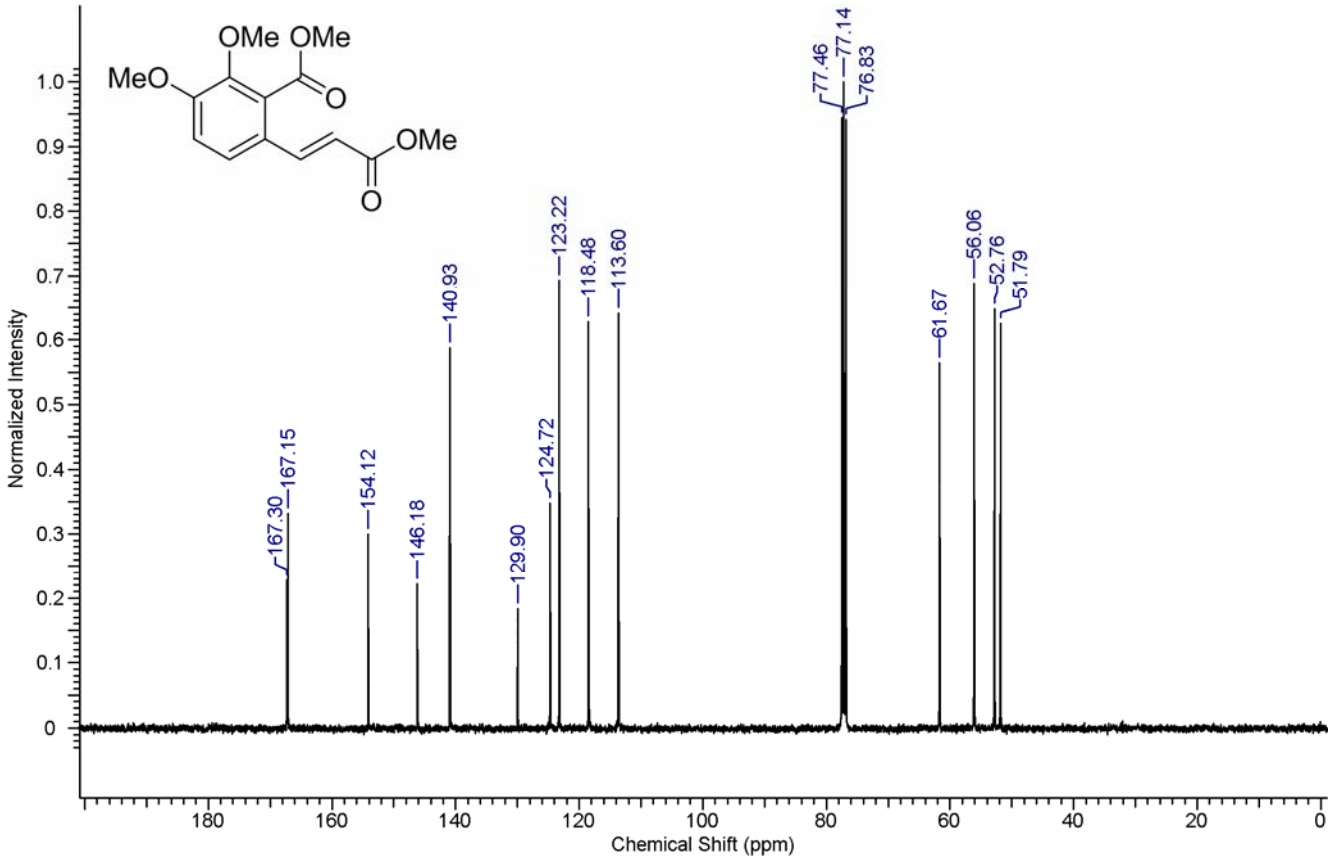


DEPT (135) Spectrum of Compound **3p**.

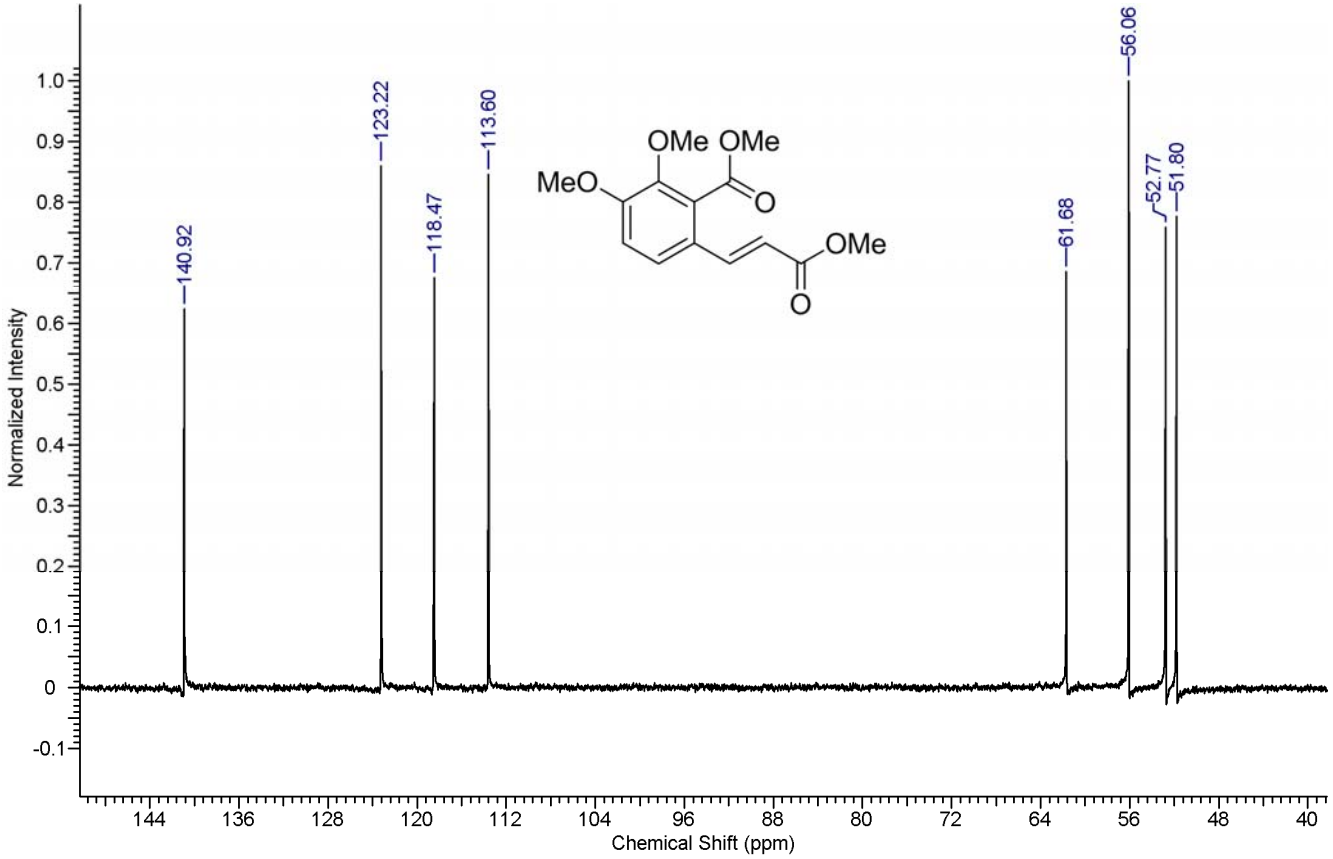


^{1}H and ^{13}C NMR Spectra of Compound **3q**.

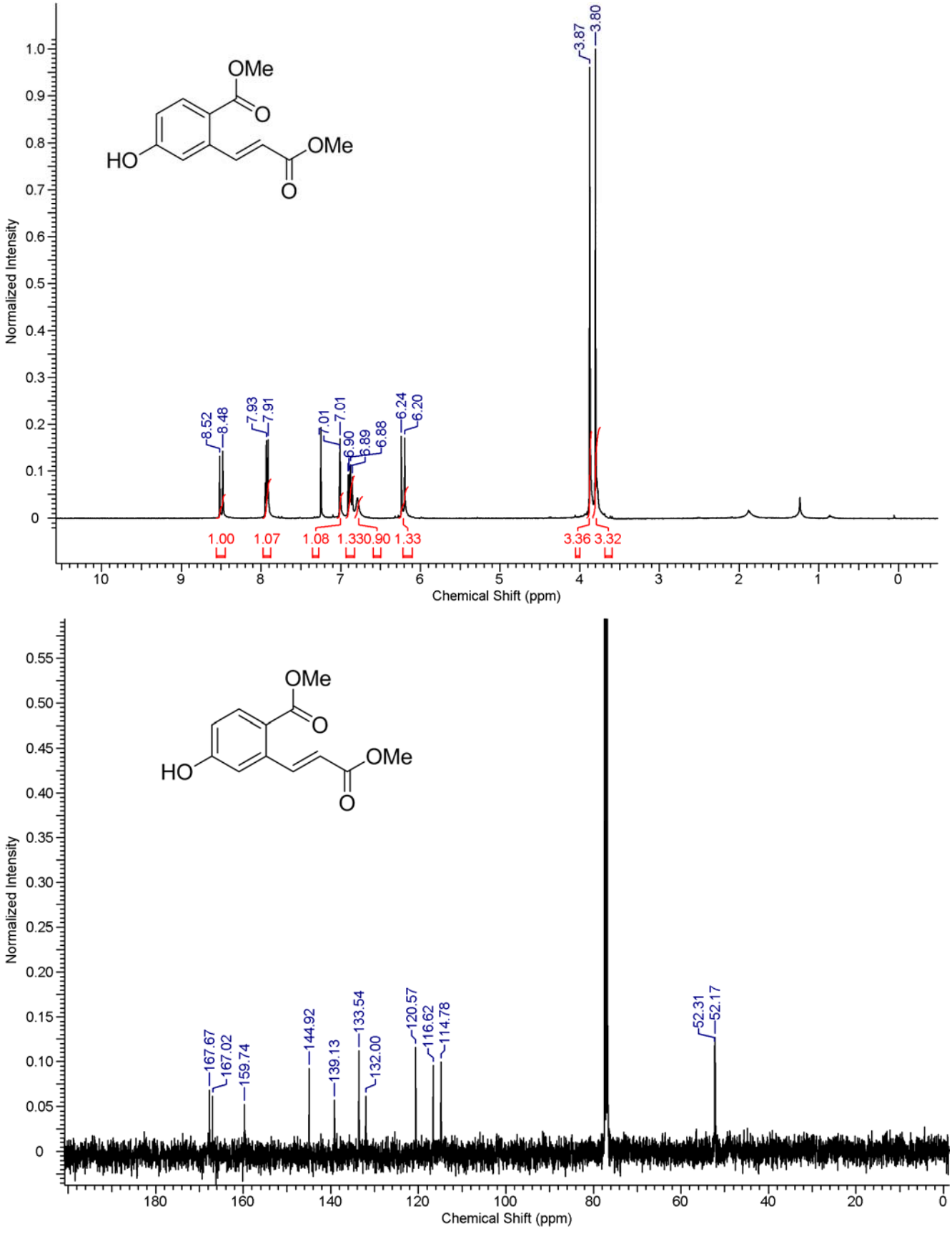




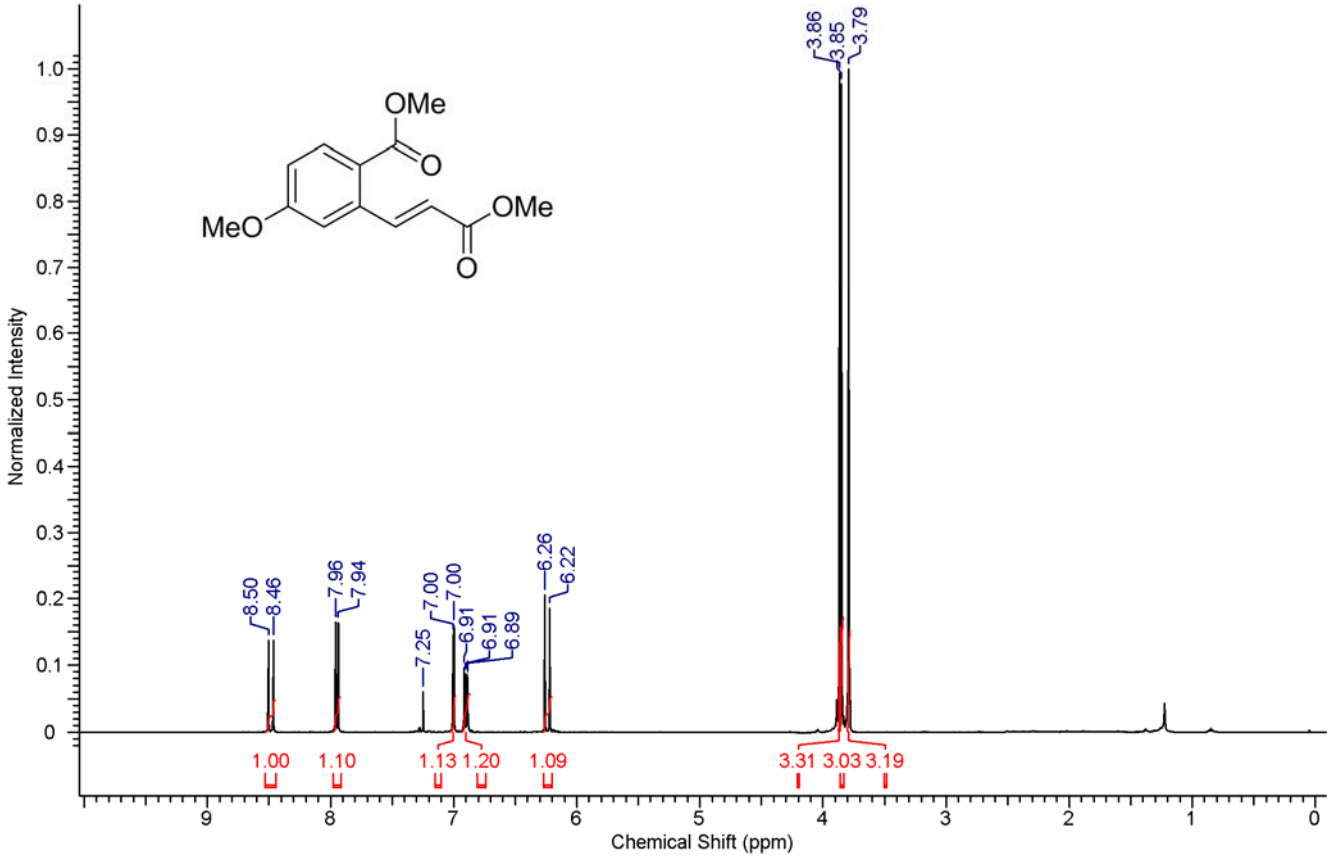
DEPT (135) Spectrum of Compound **3q**.

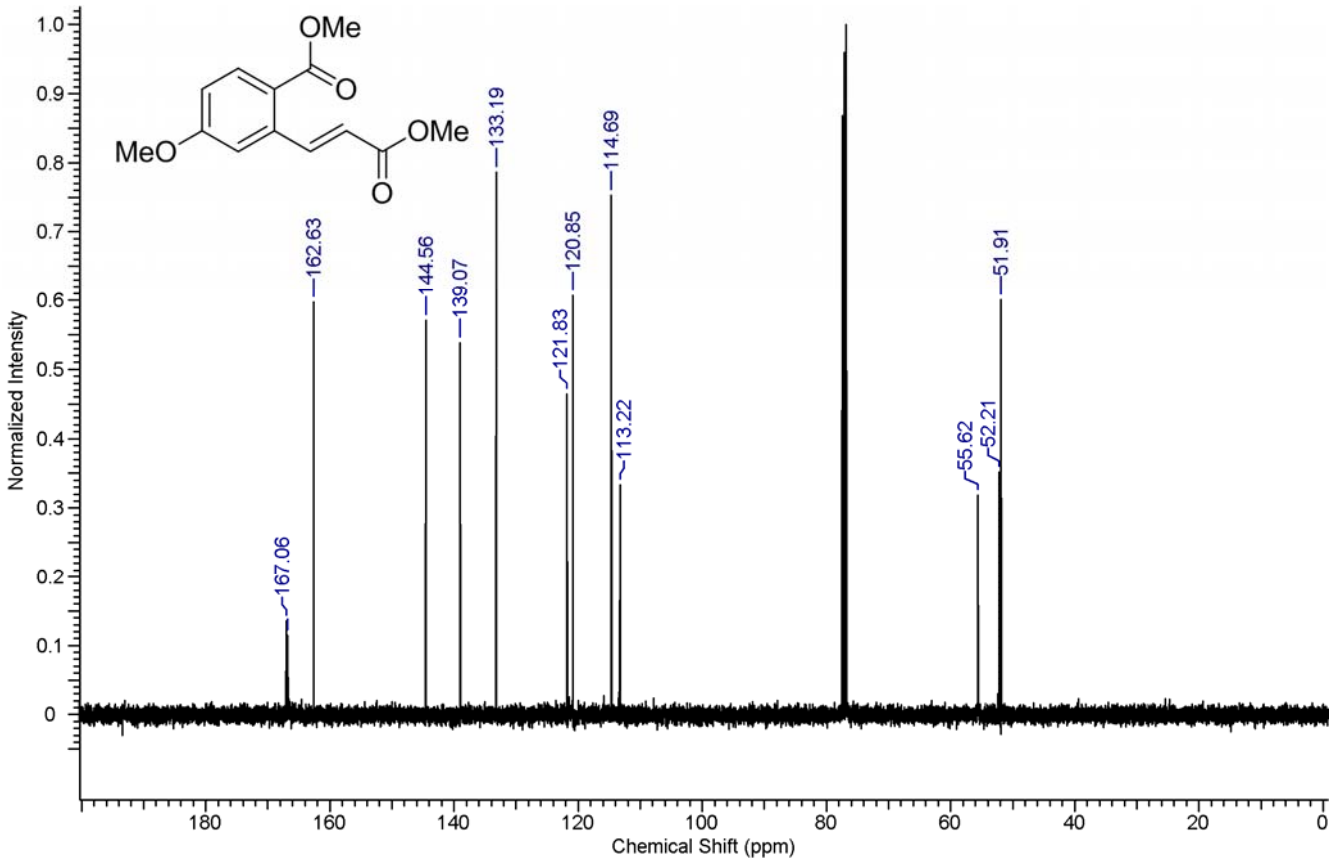


^{1}H and ^{13}C NMR Spectra of Compound **3r**.

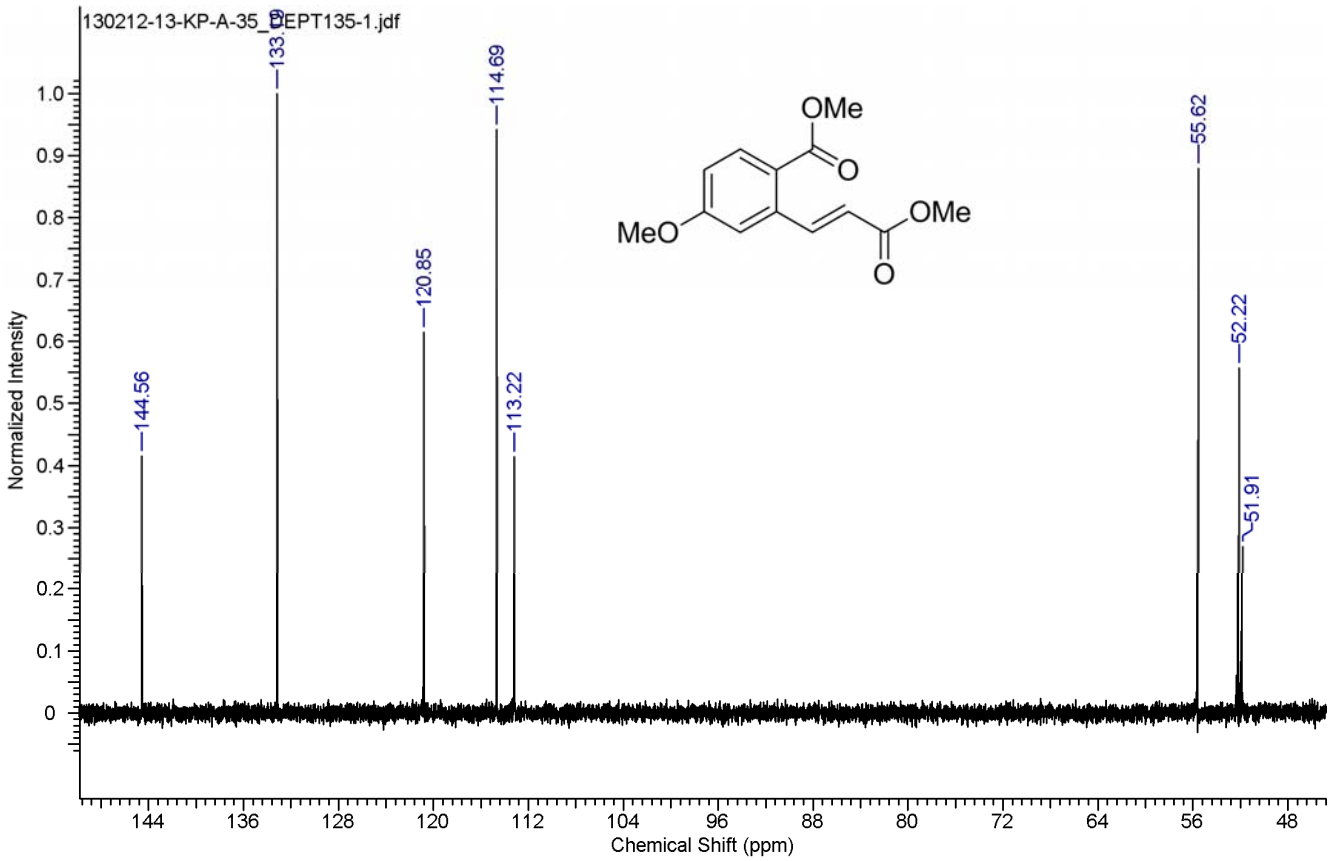


^{1}H and ^{13}C NMR Spectra of Compound **3s**.

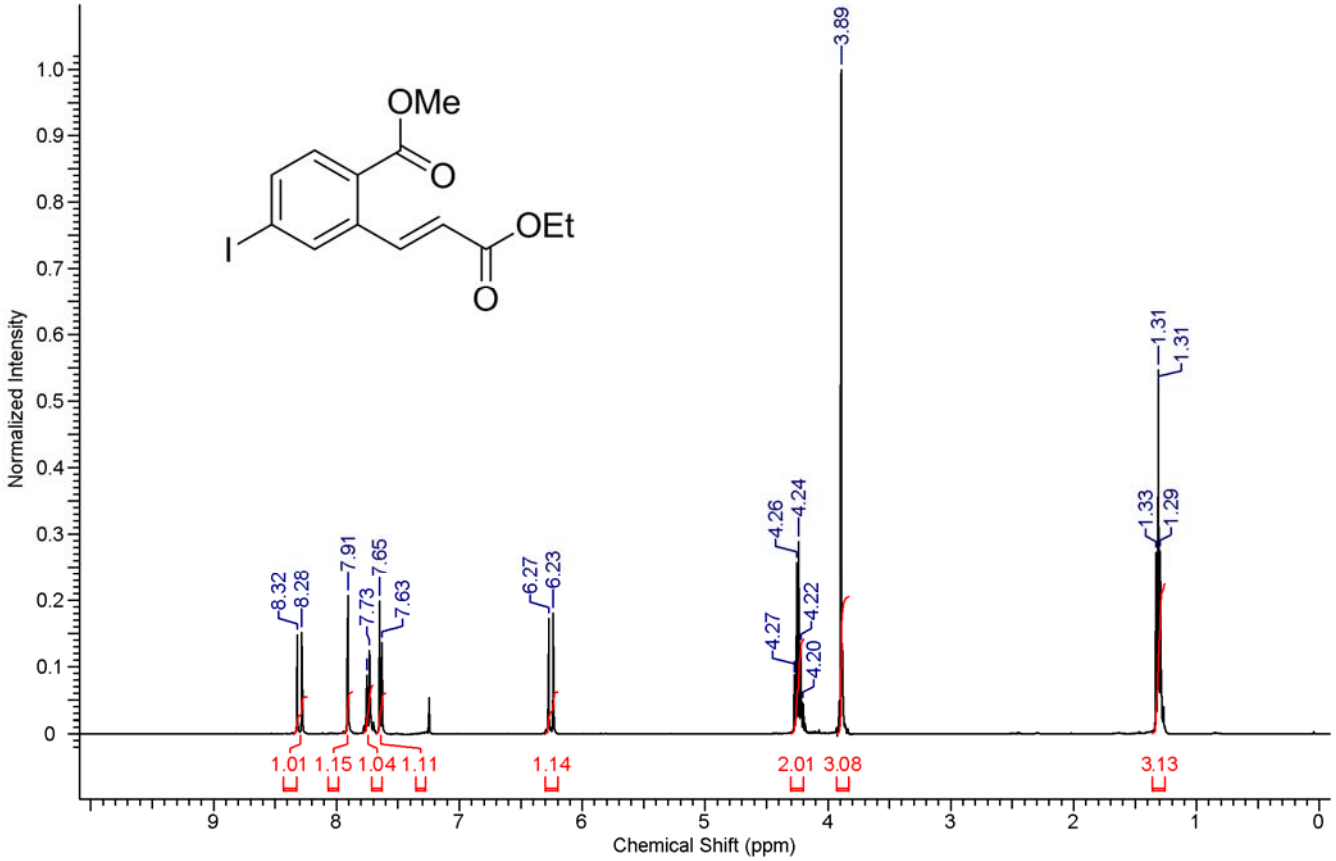


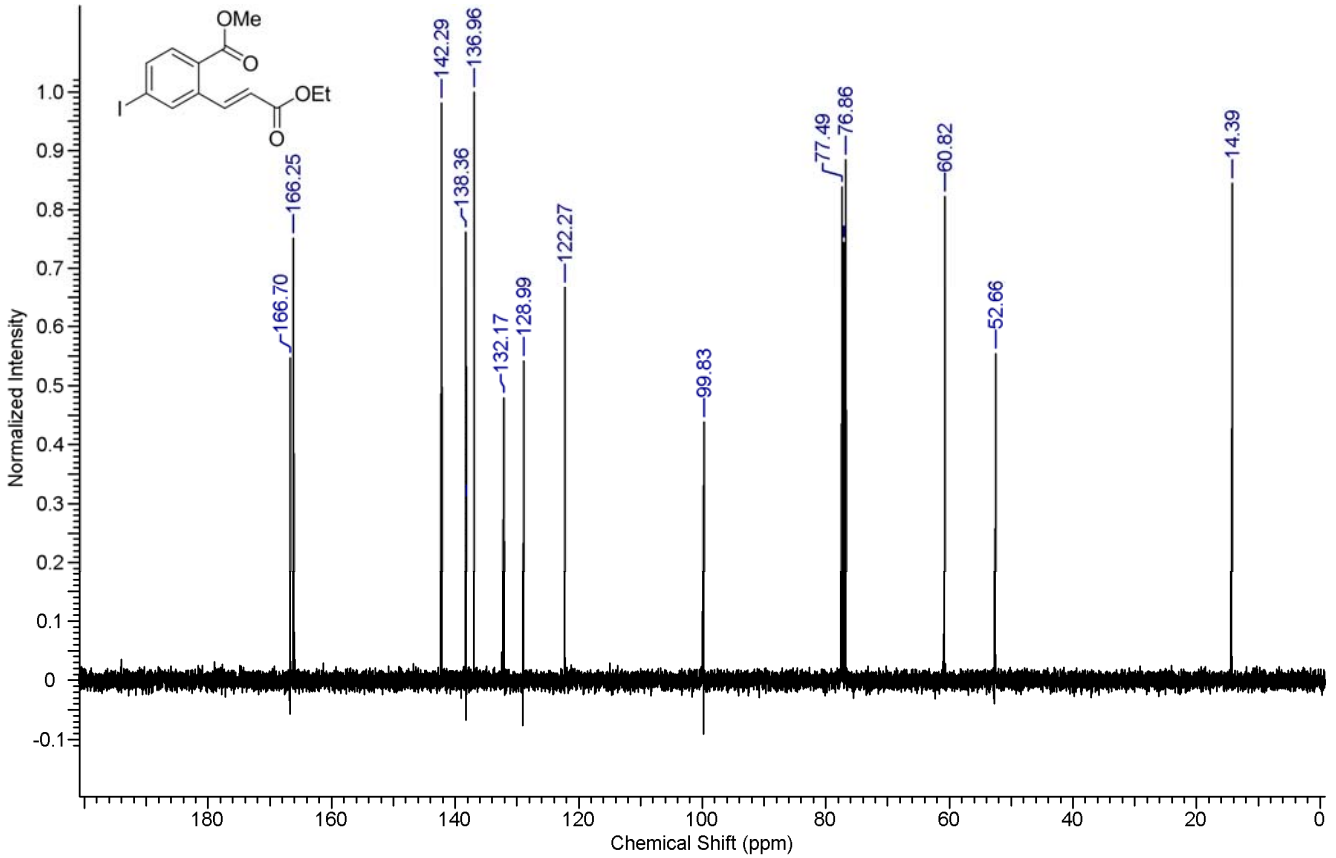


DEPT (135) Spectrum of Compound **3s**.

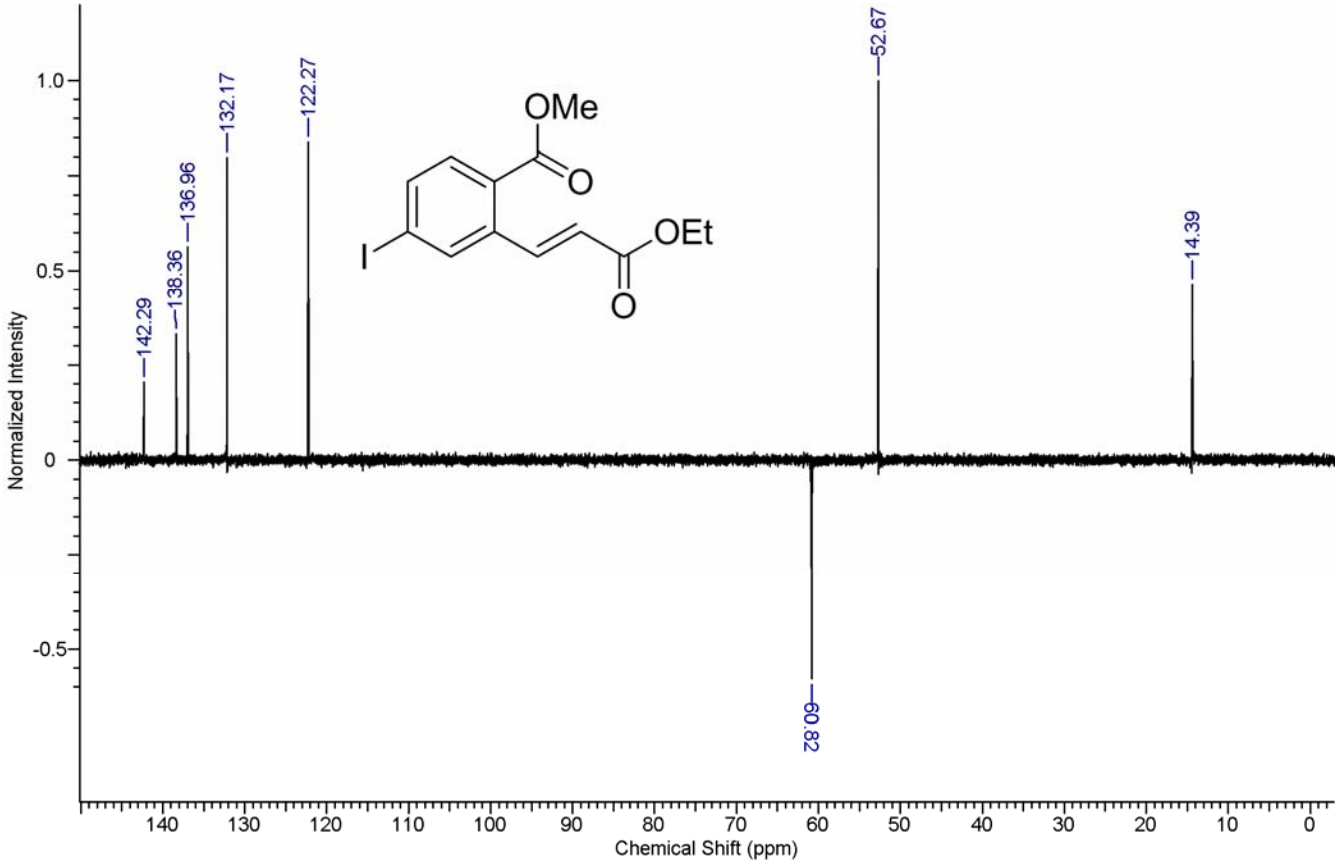


^{1}H and ^{13}C NMR Spectra of Compound **3t**.

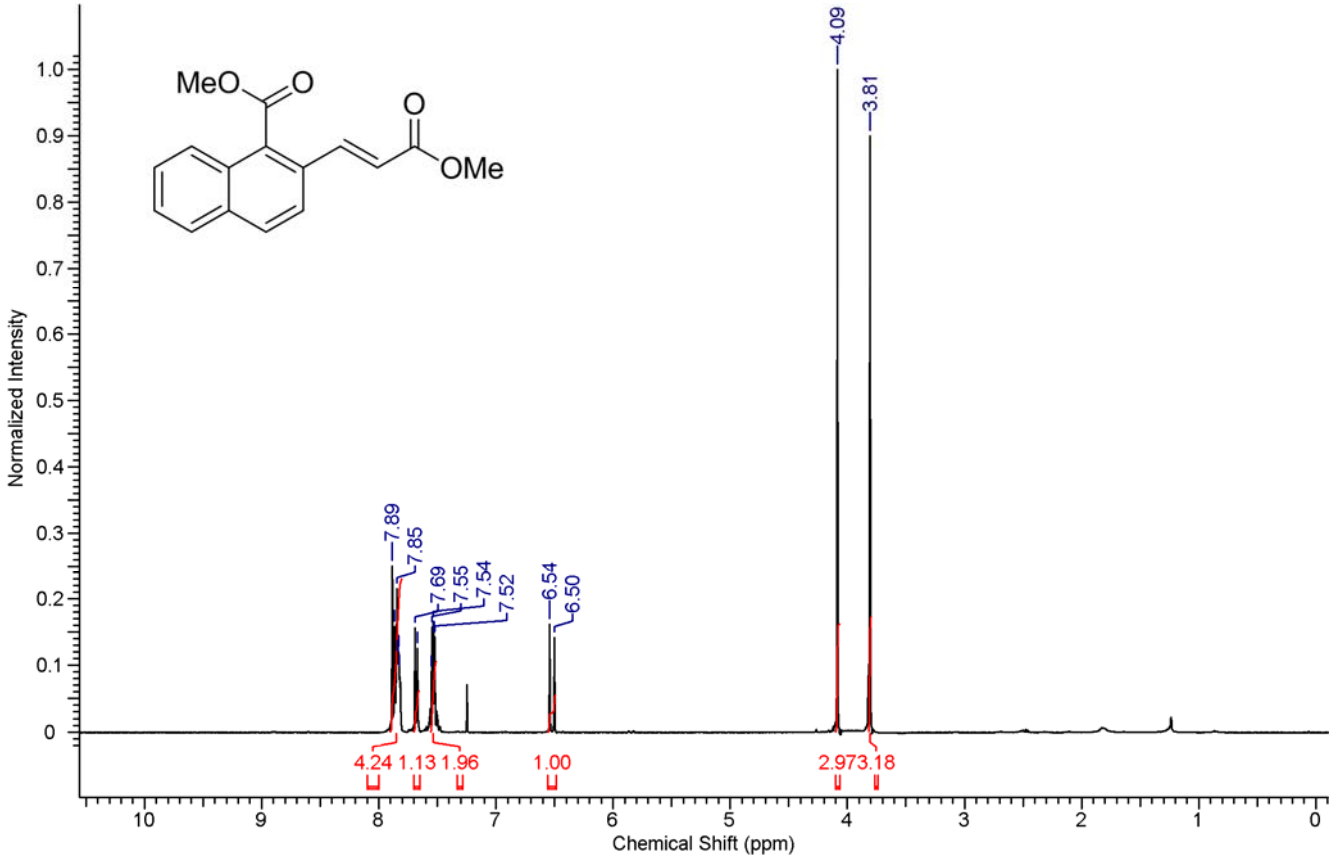


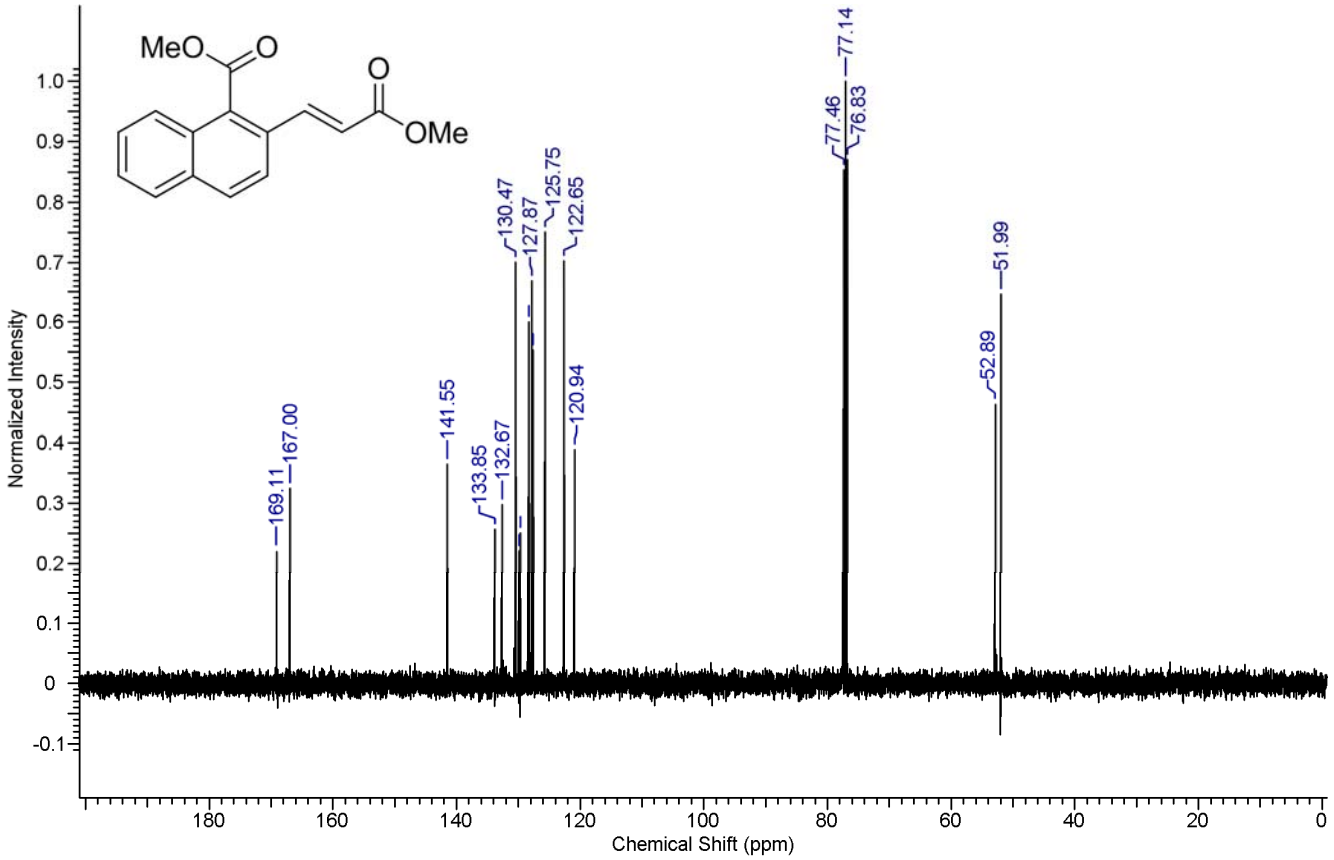


DEPT (135) Spectrum of Compound **3t**.

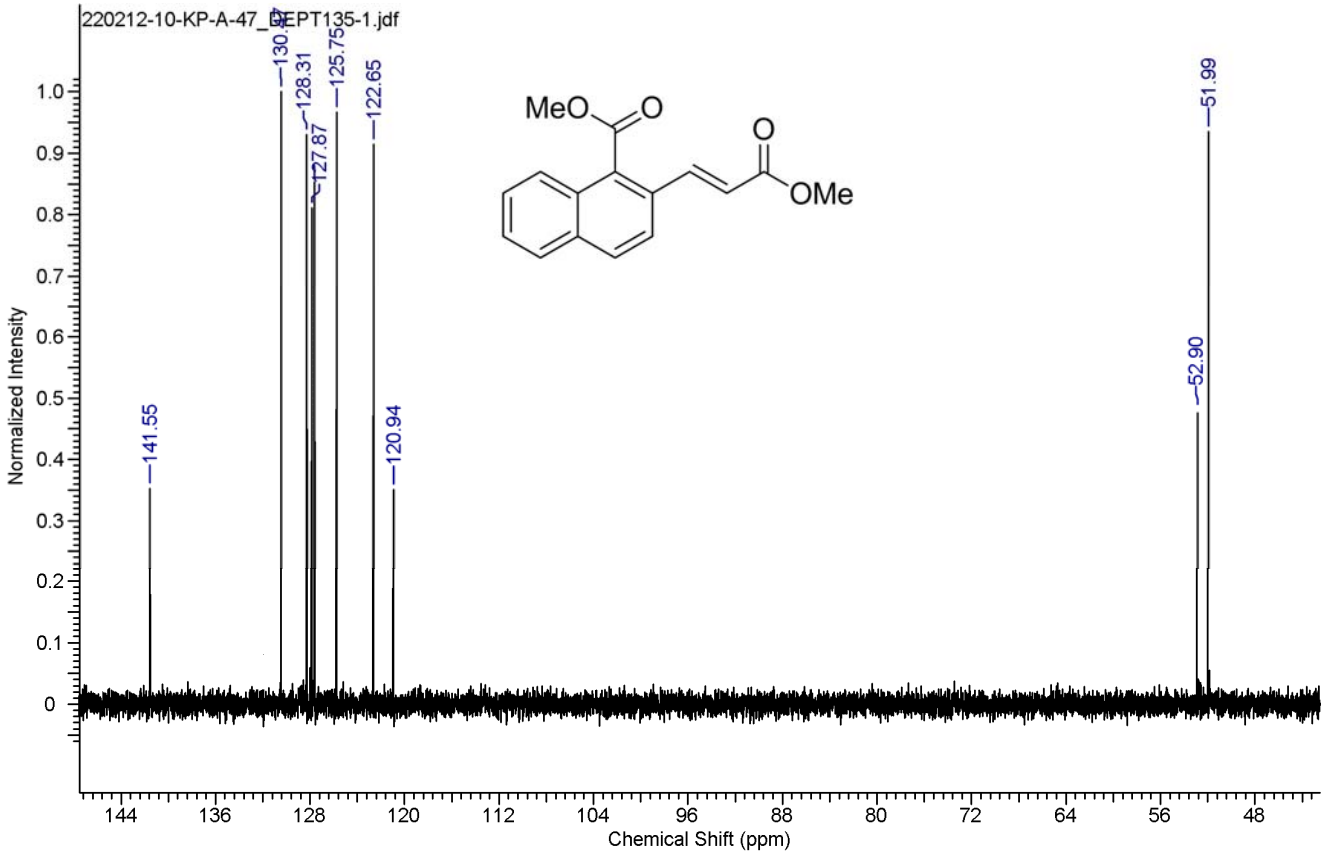


^{1}H and ^{13}C NMR Spectra of Compound **3u**.

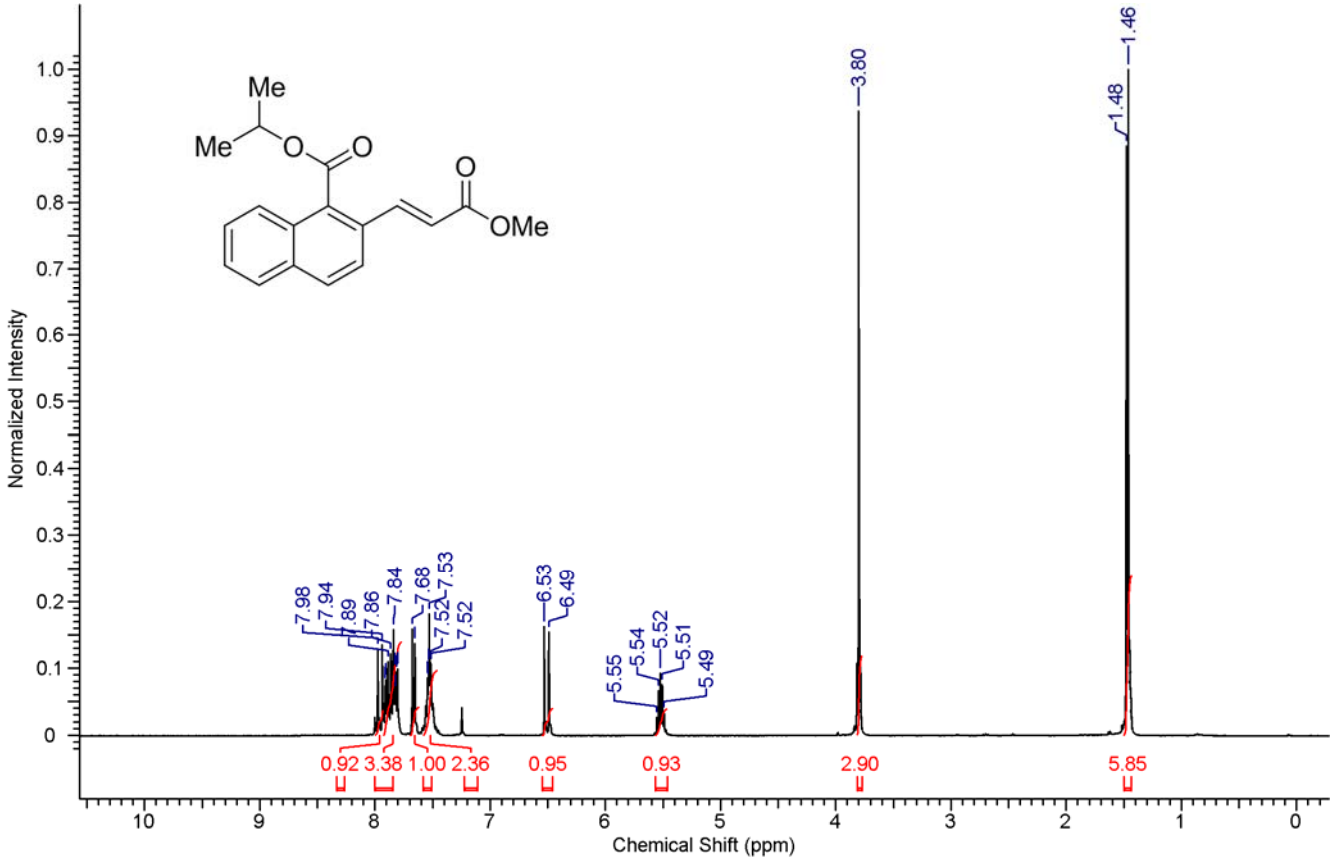


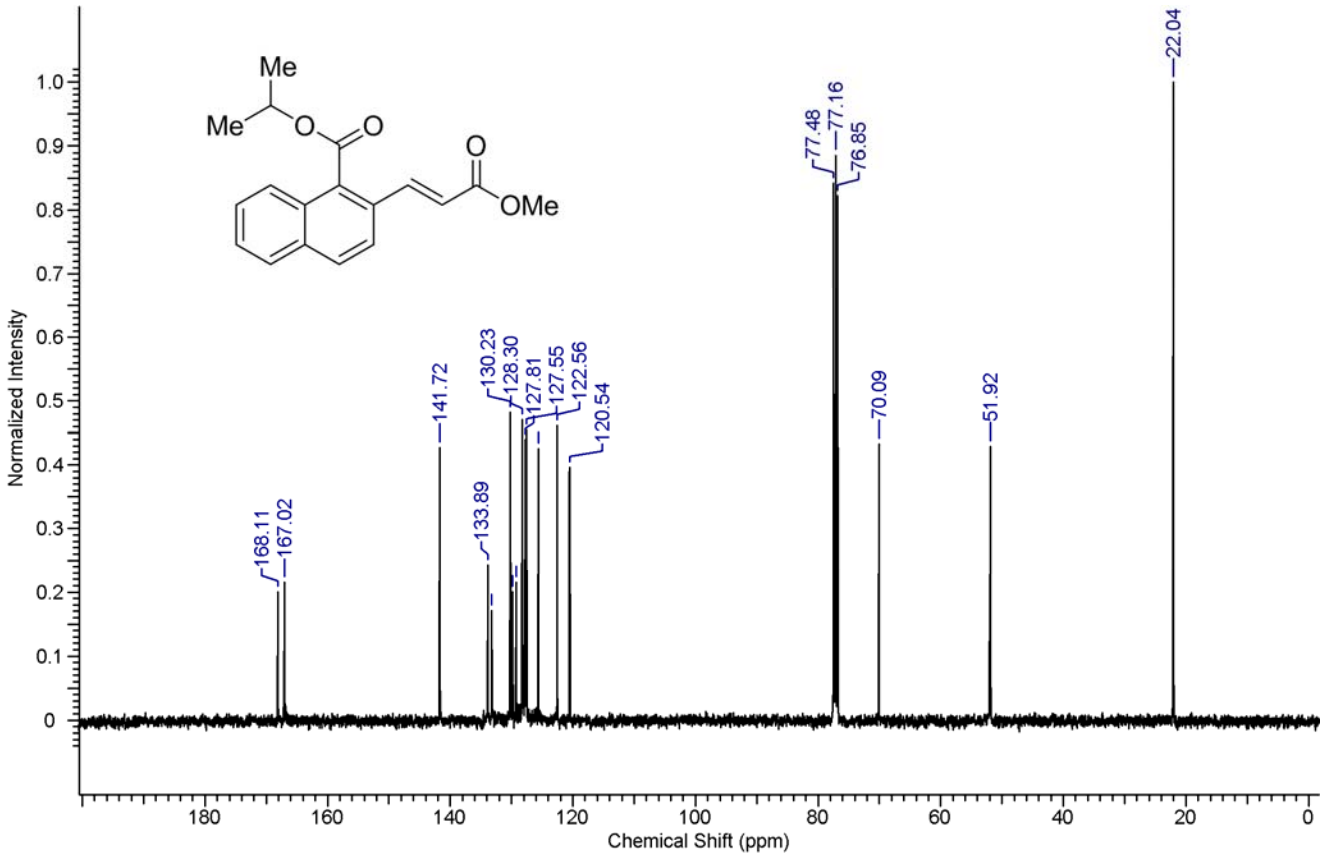


DEPT (135) Spectrum of Compound **3u**.

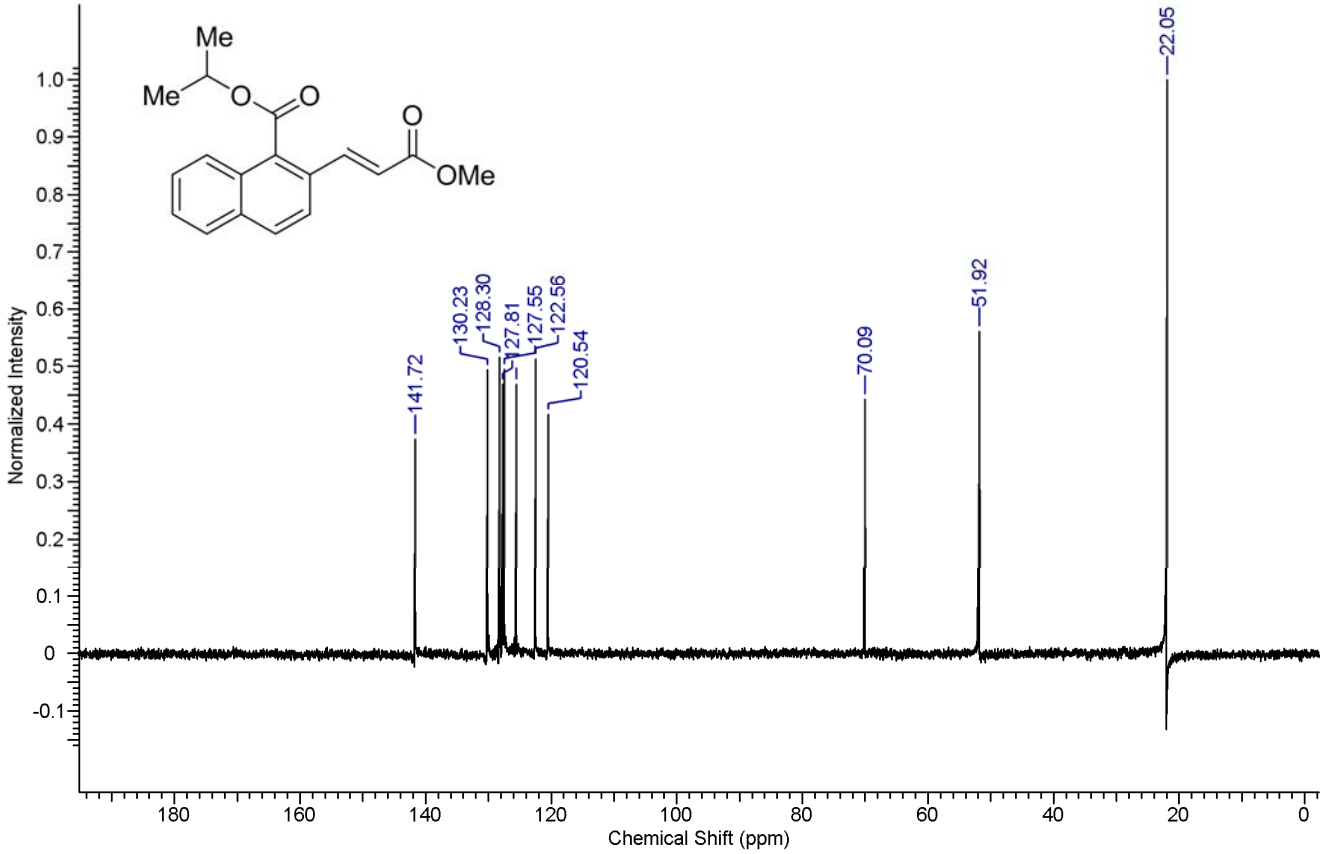


^{1}H and ^{13}C NMR Spectra of Compound **3v**.

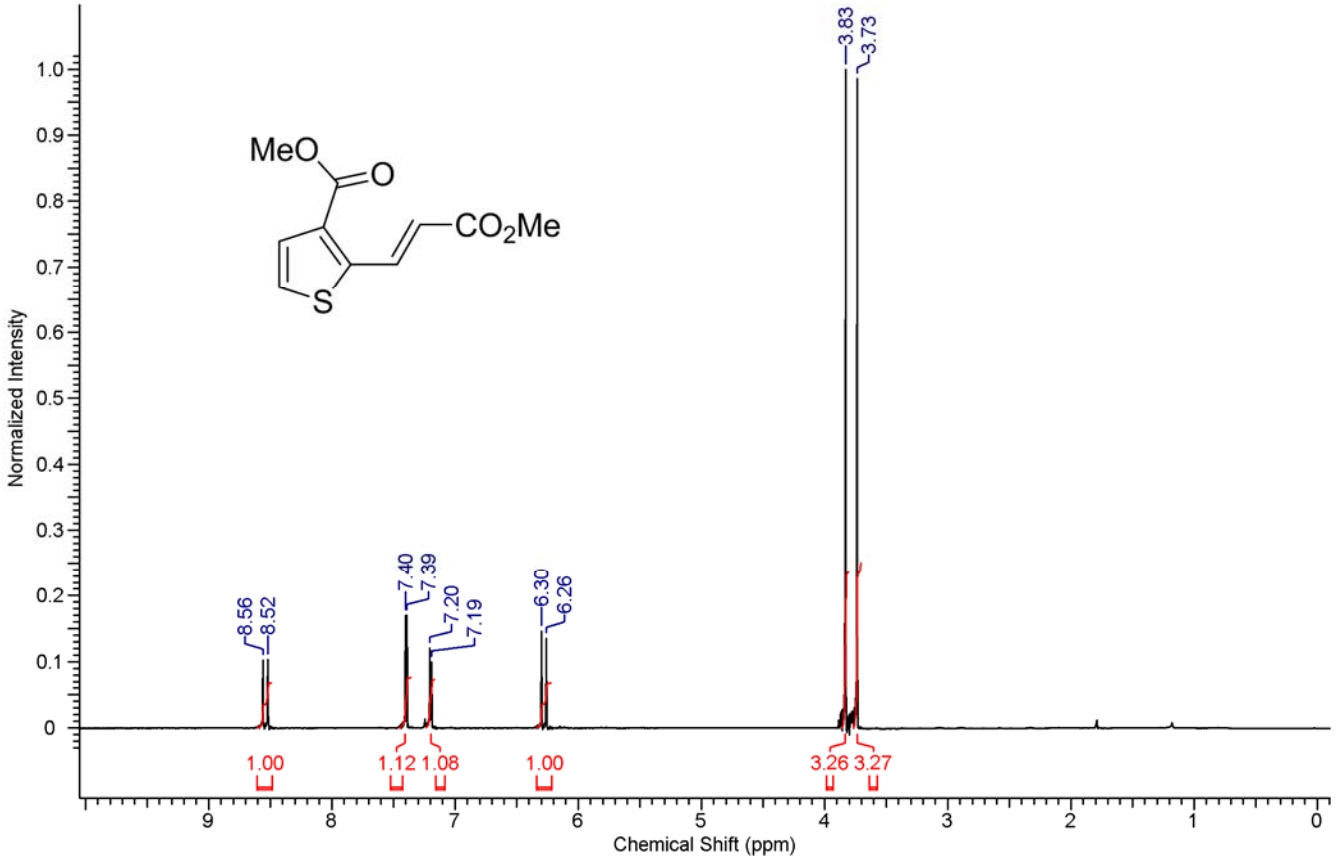


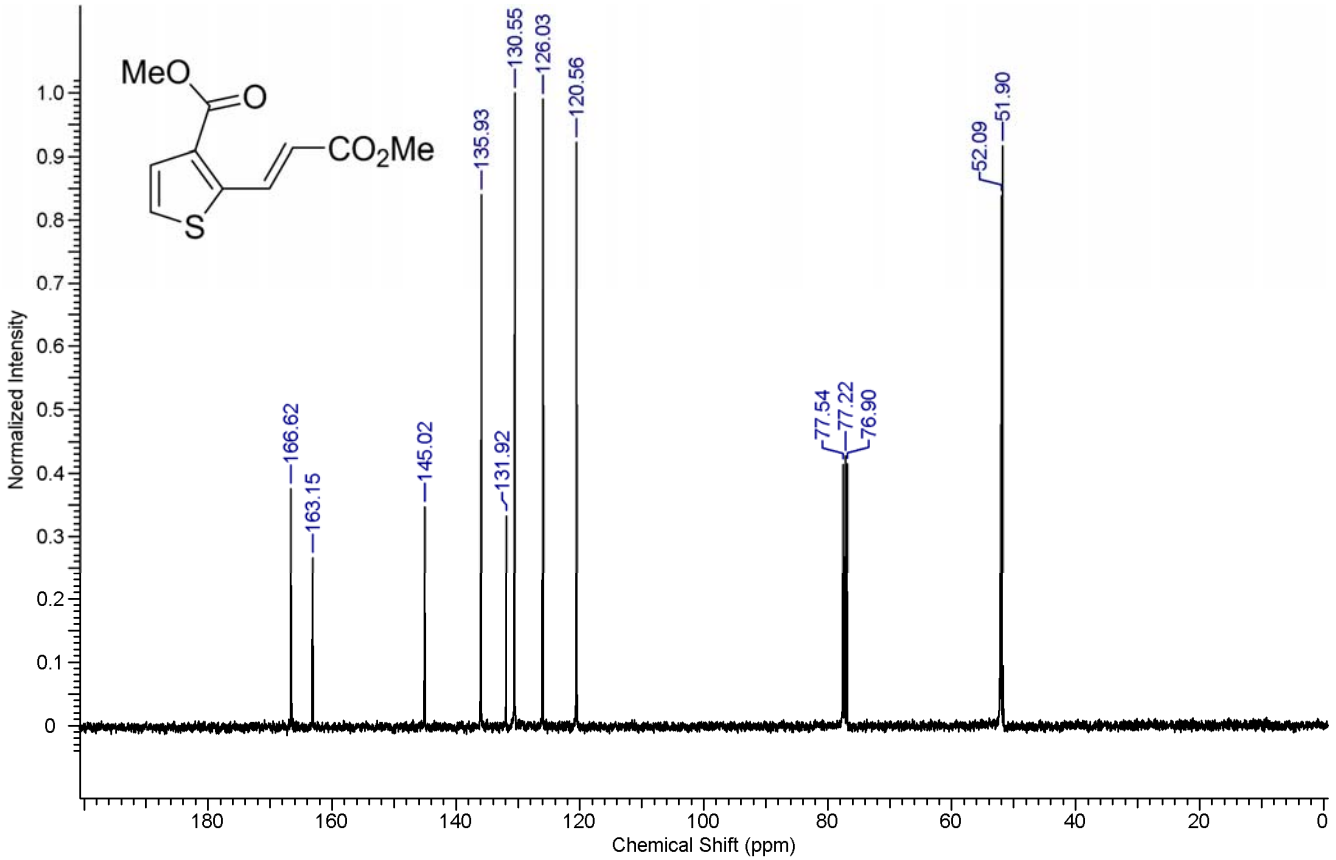


DEPT (135) Spectrum of Compound **3v**.

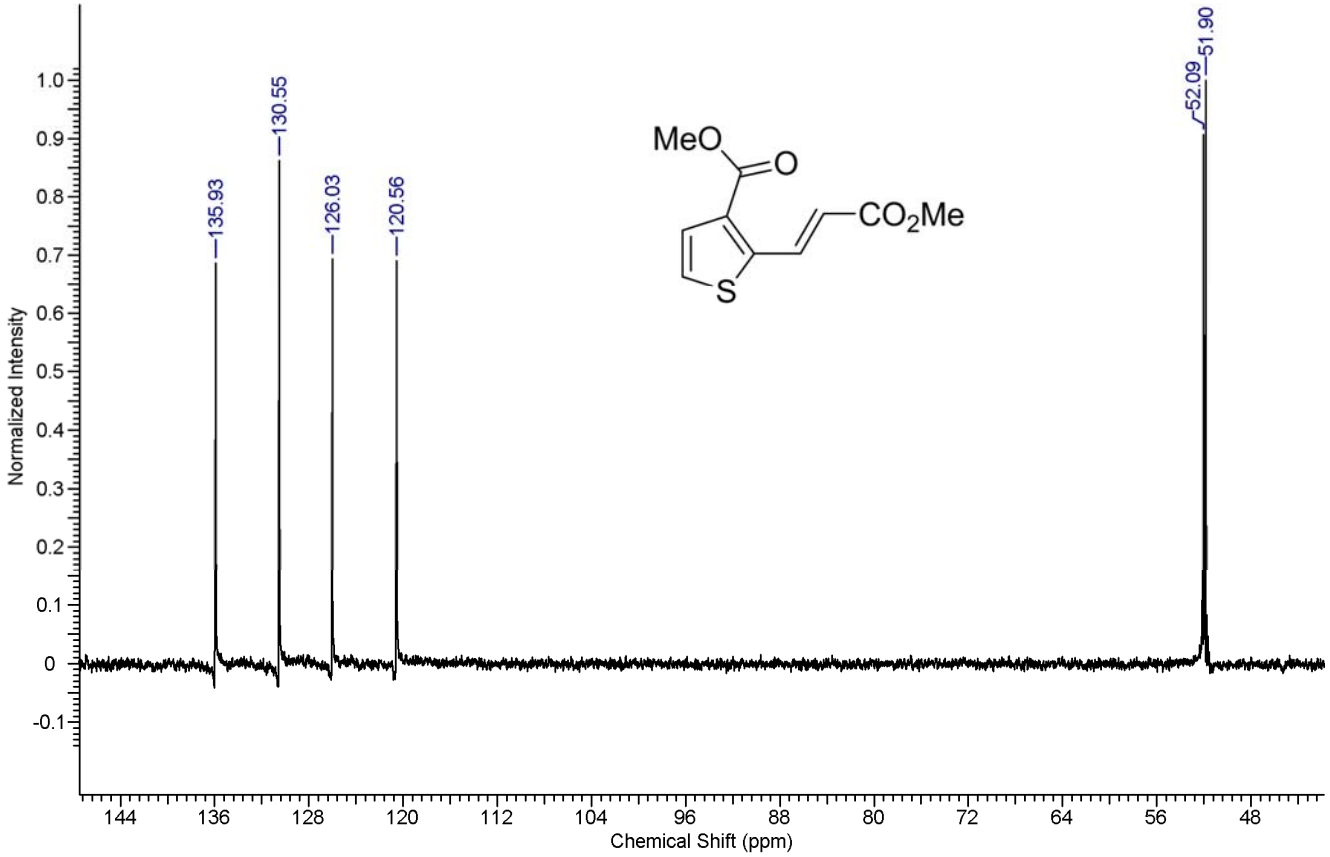


^{1}H and ^{13}C NMR Spectra of Compound **3w**.

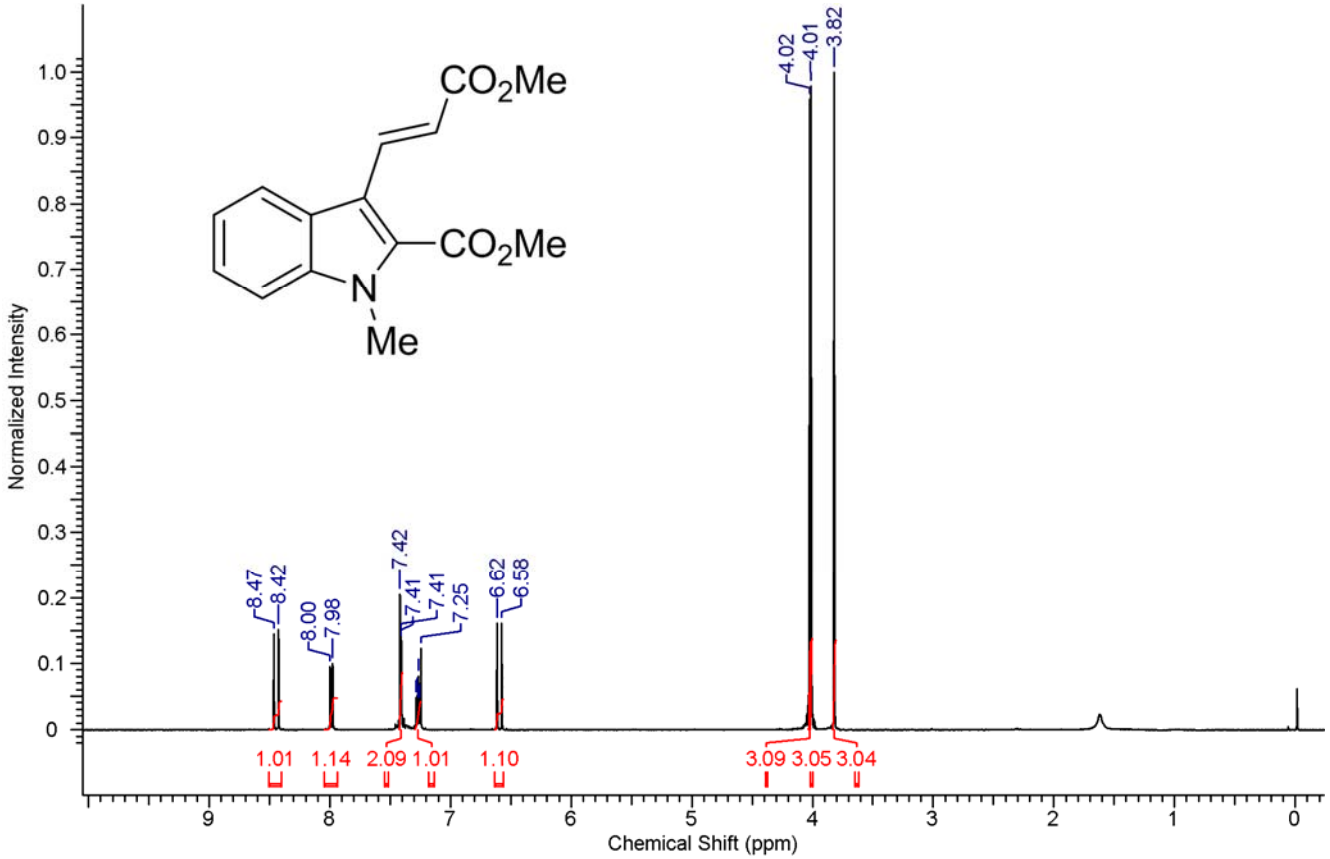


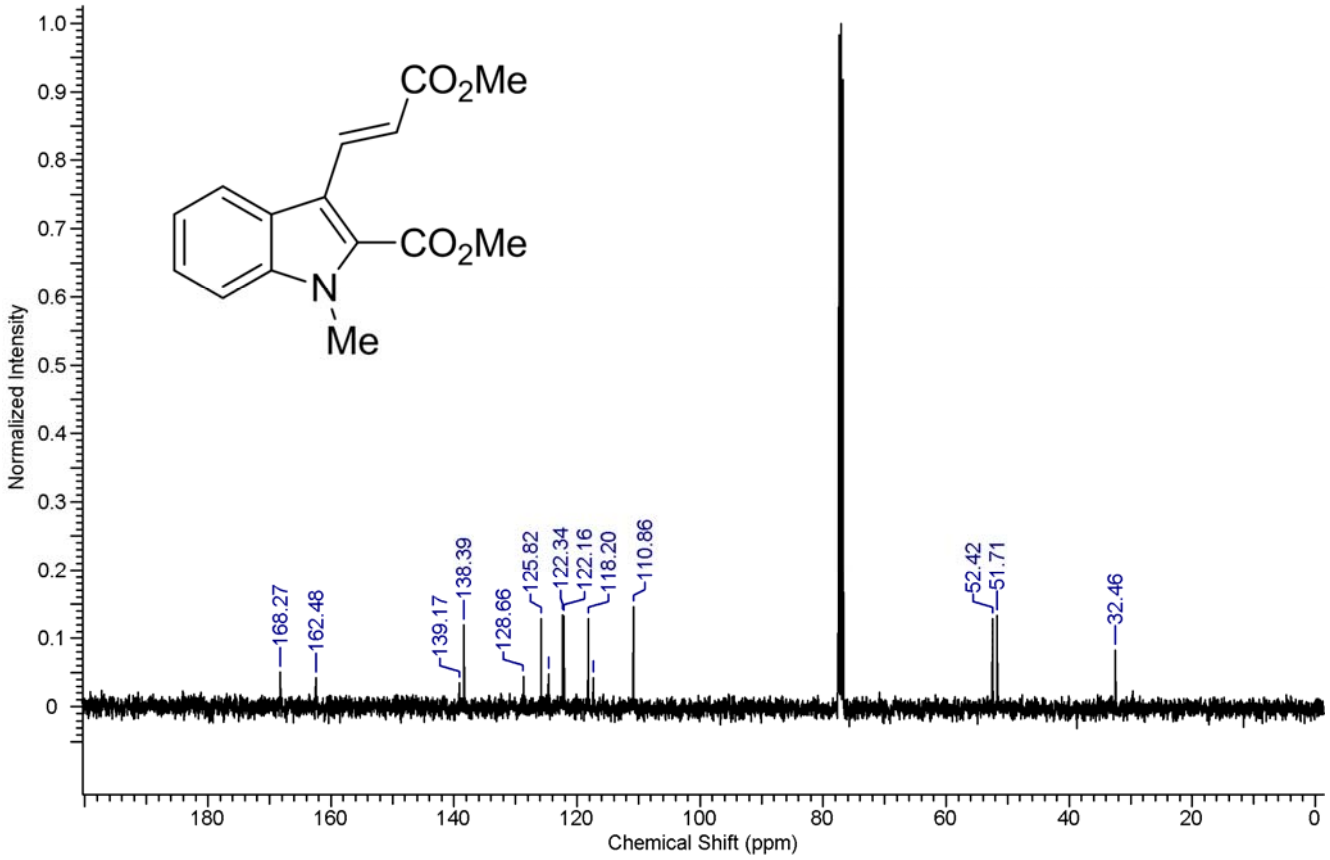


DEPT (135) Spectrum of Compound **3w**.

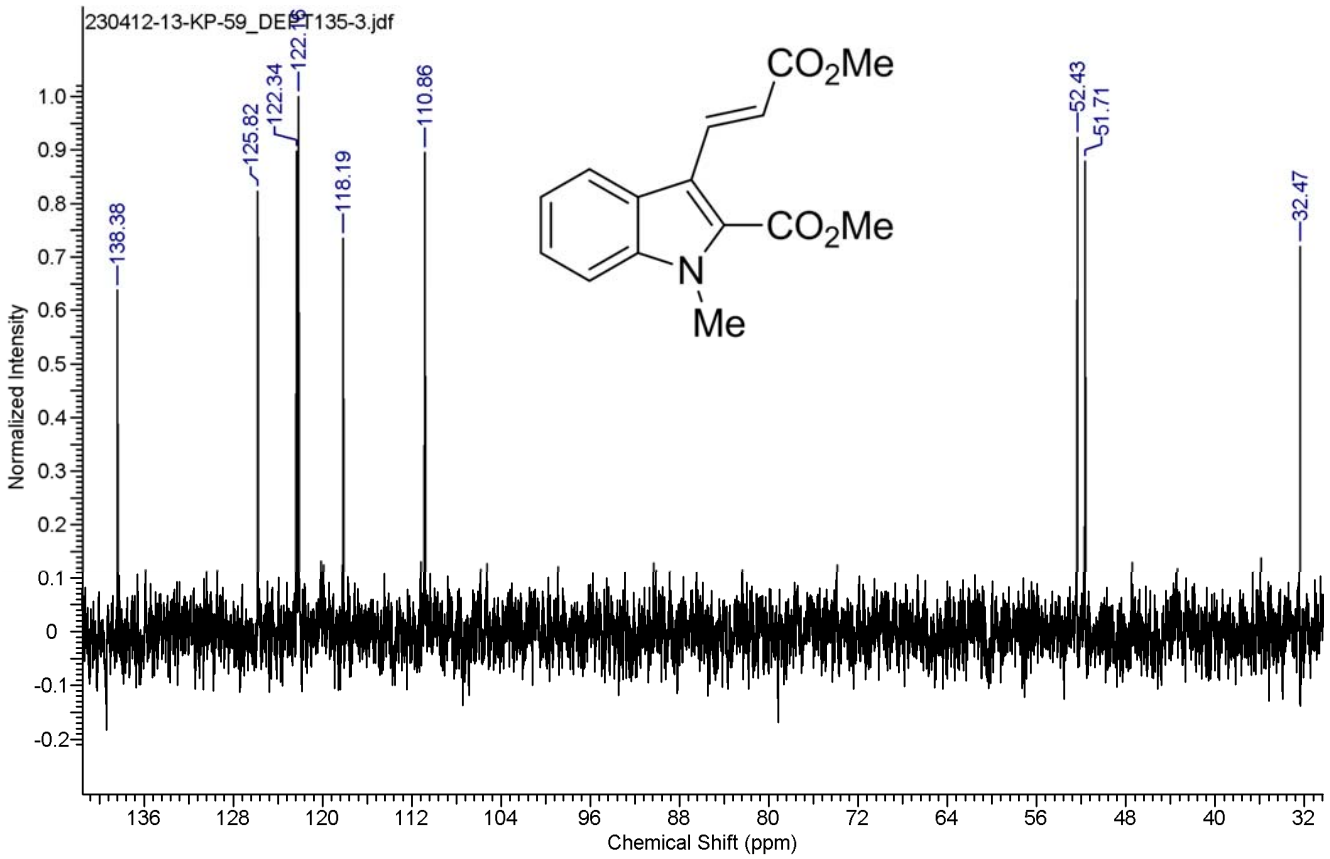


^{1}H and ^{13}C NMR Spectra of Compound **3x**.

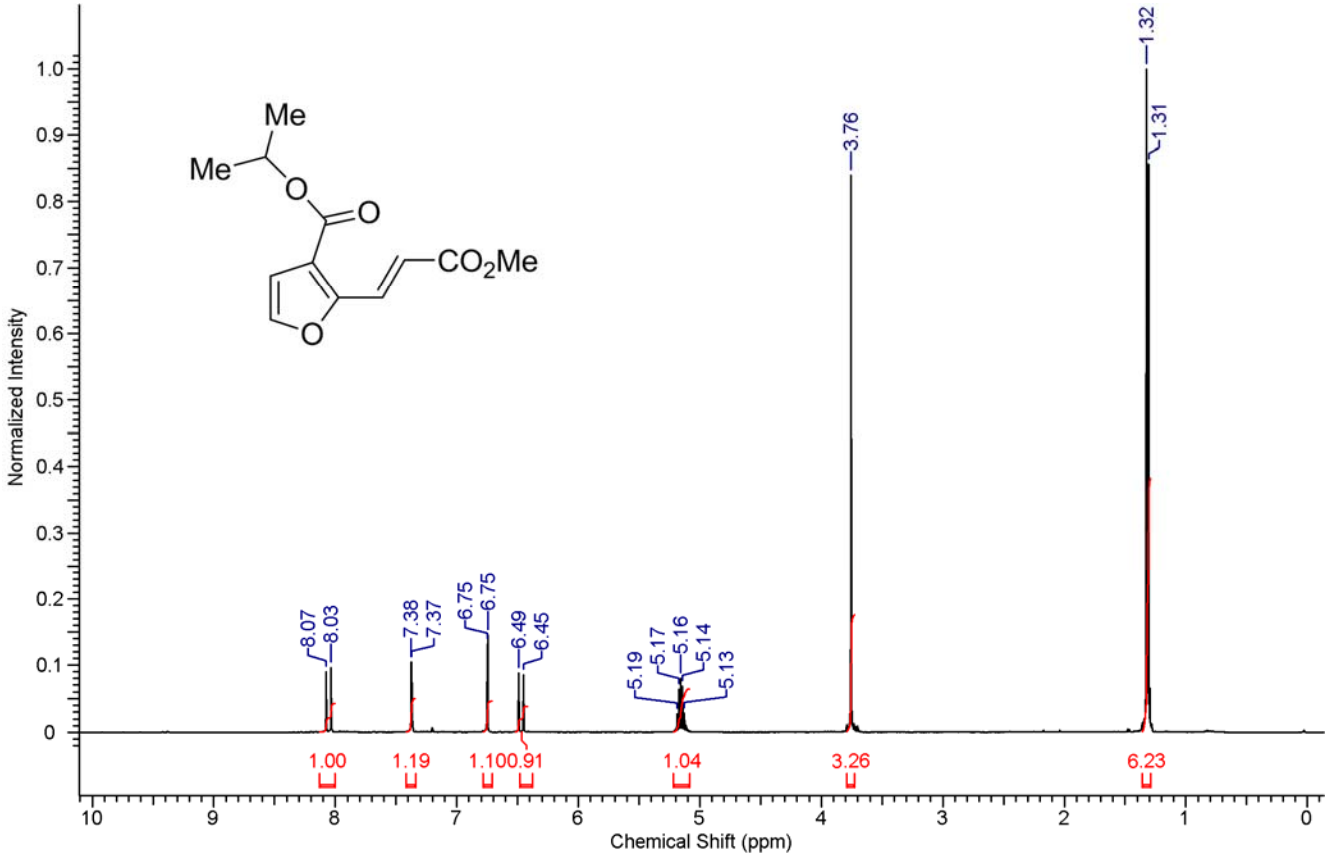


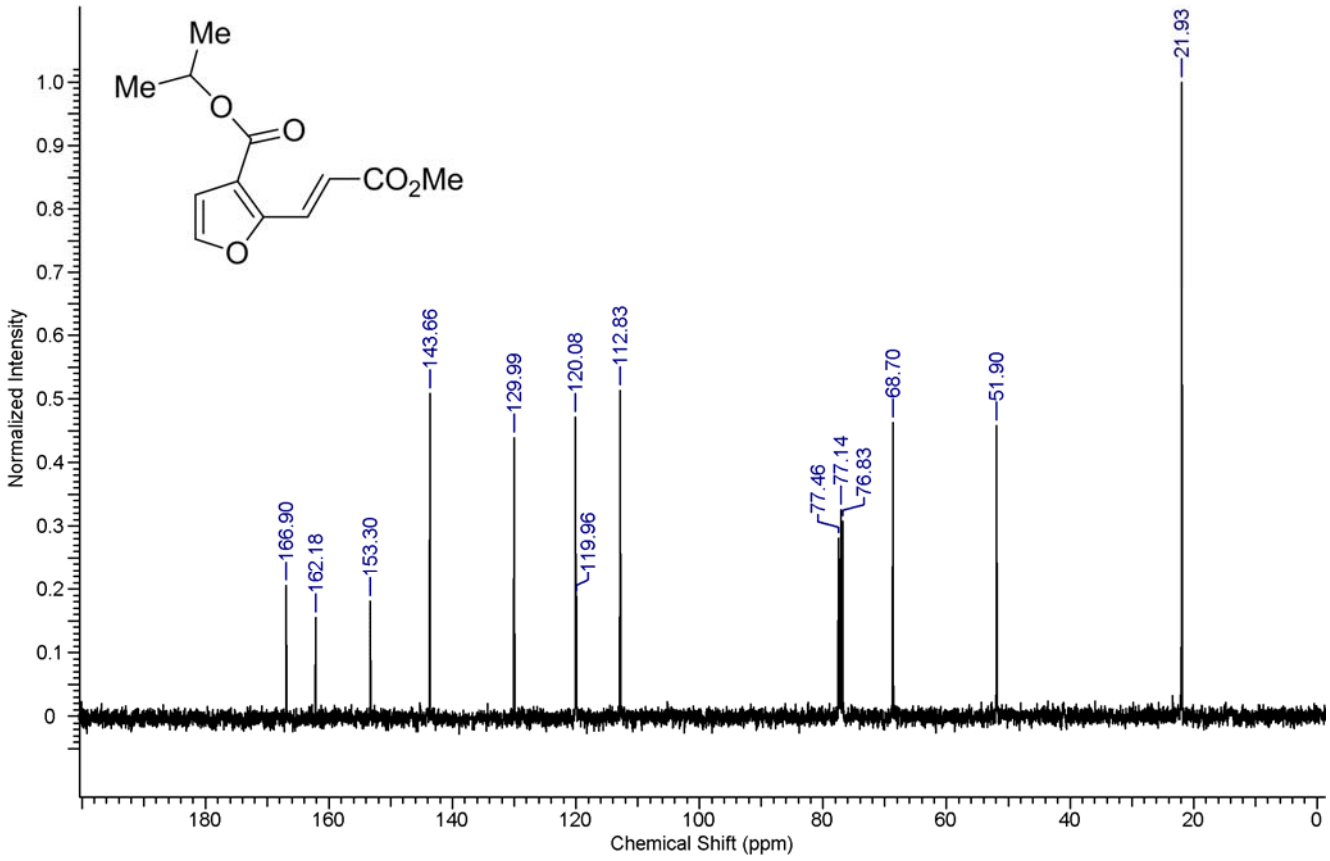


DEPT (135) Spectrum of Compound **3x**.

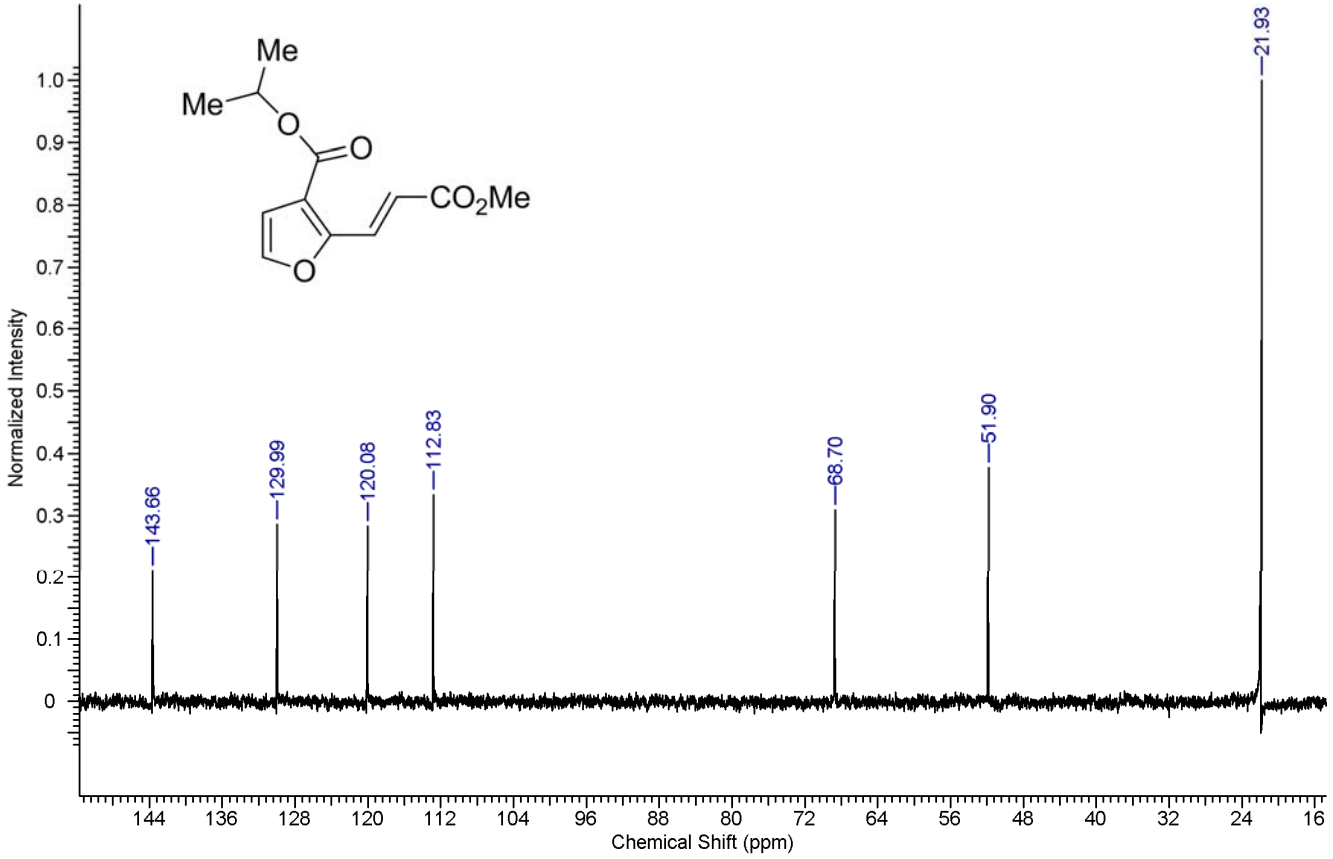


^{1}H and ^{13}C NMR Spectra of Compound **3y**.

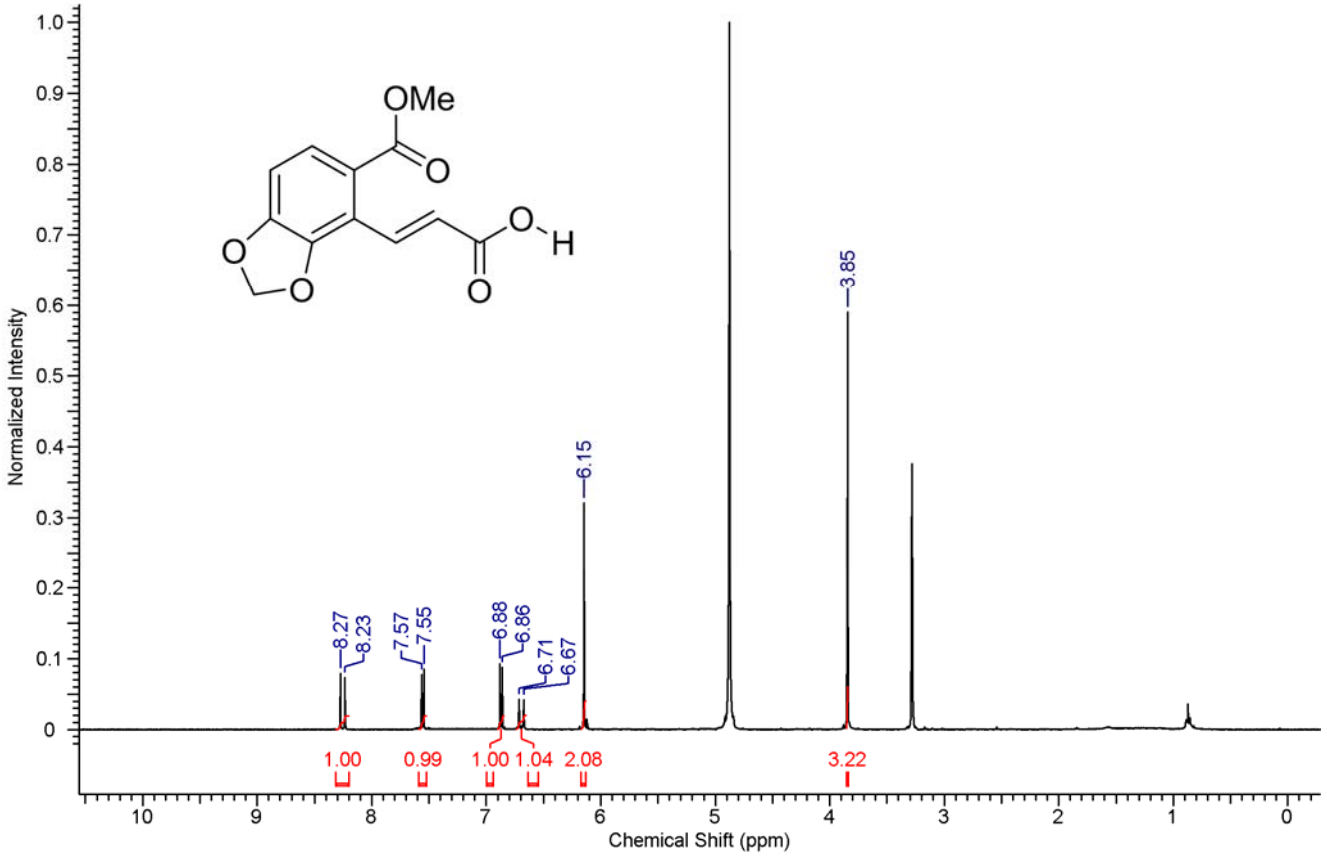


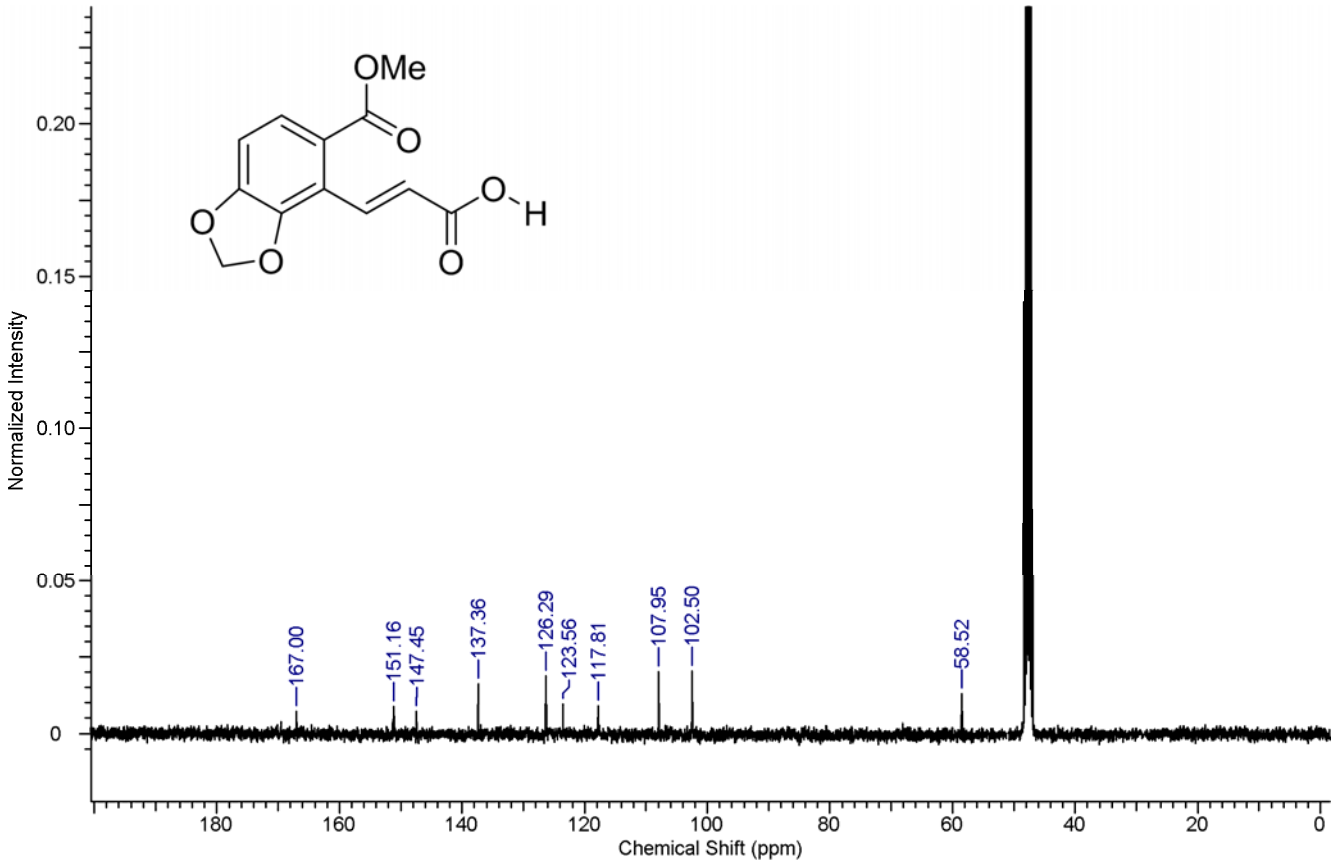


DEPT (135) Spectrum of Compound **3y**.



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





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