Supporting Information

NHC-Catalyzed Oxidative Cyclization Reaction for the Synthesis of 3-Substituted Phthalides

So Won Youn,* Hyoung Sub Song, and Jong Hyub Park

Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea.

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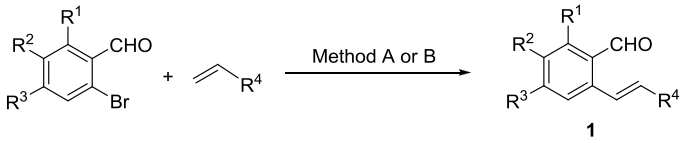
General Information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instrument. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or solvent residual peak. IR spectra were taken as neat for liquids on NaCl plates using FT-IR Spectrophotometer. High Resolution Mass Spectra were measured using EI at 70 eV. GC-MS spectra were recorded on a Perkin Elmer's Clarus 600S GC-system with Turbo mass ver.5.4.2 inert Mass Selective Detector (EI) and Elite-1 column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature T_0 (50 ℃), after holding this temperature for 5 min, the column is heated to the temperature T_1 (ramp, 300 ℃, 10 ℃/min) and hold for additional 10 min. Flash chromatography was performed on silica gel 230-400 mesh. All catalysts were purchased from Sigma-Aldrich or Strem and used as received. Unless otherwise noted, all commercially obtained reagents and solvents were used as received. Anhydrous DMF, DMSO, toluene, $ClCH_2CH_2Cl$, and dioxane were purchased from Sigma-Aldrich in a SureSeal™ bottle and used as received. THF and benzene were distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 and MeCN were distilled from CaH_2 immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV and potassium permanganate.

General Procedure for the Preparation of 2-Alkenylbenzaldehyde Derivatives 1

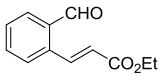


1

Method A: To a solution of 2-bromobenzaldehyde (118 μL, 1.00 mmol, 1 equiv), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 2 mol%) and P(*o*-Tol)$_3$ (6.4 mg, 0.020 mmol, 2 mol%) in NEt_3 (10.0 mL, 0.1 M) was added olefin (1.20 mmol, 1.2 equiv). The resulting mixture was heated under Ar atmosphere at 125 ℃ for 2-12 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with ether (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product.

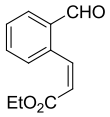
Method B: To a solution of 2-bromobenzaldehyde (118 μL, 1.00 mmol, 1 equiv) in DMF (10.0 mL, 0.1 M) was added *n*Bu_4NOAc (324.2 mg, 1.00 mmol, 1.0 equiv), K_2CO_3 (209.0 mg, 1.50 mmol, 1.5 equiv), KCl (112.0 mg, 1.50 mmol, 1.5 equiv), $Pd(OAc)_2$ (22.5 mg, 0.100 mmol, 10 mol%), olefin (1.20 mmol, 1.2 equiv) . The resulting mixture was heated under Ar atmosphere at 90 ℃ for 4-24 hours. After the reaction was completed, the reaction mixture was diluted with ether and the resulting solution was filtered through a thin pad of Celite. The filtrate was diluted with water and extracted with ether (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product.

(*E*)-Ethyl 3-(2-Formylphenyl)acrylate (1a)



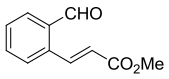
Following the Method B: 86% (175.5 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, J = 7.2 Hz, 3H), 4.29 (q, J = 7.2 Hz, 2H), 6.38 (d, J = 16.0 Hz, 1H), 7.54-7.65 (m, 3H), 7.88 (d, J = 7.6 Hz, 1H), 8.52 (d, J = 15.6 Hz, 1H), 10.31 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 60.8, 123.3, 128.0, 129.8, 132.1, 133.8, 133.9, 136.7, 140.9, 166.2, 191.7. EIMS *m*/*z* 204 (M^+), 175, 159, 147, 131, 103, 77, 51.
Spectral data were consistent with data reported in the literature.[1]

(*Z*)-Ethyl 3-(2-Formylphenyl)acrylate (1a')[2]



A solution of (*Z*)-methyl 3-iodoacrylate (250 μL, 1.913 mmol), 2-formylphenylboronic acid (430.3 mg, 2.870 mmol, 1.5 equiv), $Pd(OAc)_2$ (4.3 mg, 0.019 mmol, 1 mol%), SPhos (16.2 mg, 0.038 mmol, 2 mol%), and K_3PO_4 (812.2 mg, 3.826 mmol, 2 equiv) in THF (3.8 mL, 0.5 M) in a sealed tube was placed under Ar and stirred at 40 ℃ for 17 h. The reaction mixture was diluted with water and extracted with ether (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10) to afford the desired product **1a'** (178.1 mg, 46%) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.11 (t, J = 7.4 Hz, 3H), 4.04 (q, J = 7.1 Hz, 2H), 6.19 (d, J = 12.0 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 12.4 Hz, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.57 (td, J = 1.2, 7.5 Hz, 1H), 7.89 (dd, J = 1.2, 7.6 Hz, 1H), 10.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 60.3, 122.8, 128.5, 129.9, 130.8, 133.2, 133.4, 138.2, 142.1, 165.4, 191.9. EIMS *m*/*z* 204 (M^+), 175, 159, 147, 131, 103, 77, 51.
Spectral data were consistent with data reported in the literature.[3]

(*E*)-Methyl 3-(2-Formylphenyl)acrylate (1b)



Following the Method B: 66% (125.4 mg), a yellow solid (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83 (s, 3H), 6.38 (d, J = 16.0 Hz, 1H), 7.55-7.63 (m, 3H), 7.88 (d, J = 7.2 Hz, 1H), 8.53 (d, J = 16.0 Hz, 1H), 10.29 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.9, 122.7,

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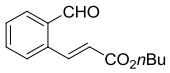
[1] Kundu, K.; McCullagh, J. V.; Morehead, A. T. *J. Am. Chem. Soc.* **2005**, *127*, 16042.

[2] Bryan, C.S.; Lautens, M. *Org. Lett*. **2010**, *12*, 2754.

[3] Xia, W.; Shao, Y.; Gui, W.; Yang, C. *Chem. Commun.* **2011**, *47*, 11098.

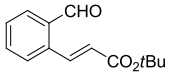
128.0, 129.9, 132.4, 133.8, 133.9, 136.5, 141.3, 166.6, 191.8.
Spectral data were consistent with data reported in the literature.[3]

(*E*)-Butyl 3-(2-Formylphenyl)acrylate (1c)



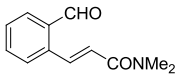
Following the Method B: 73 % (169.4 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.97 (t, J = 7.4 Hz, 3H), 1.44 (sextet, J = 7.4 Hz, 2H), 1.70 (quintet, J = 7.2 Hz, 2H), 4.23 (t, J = 6.8 Hz, 2H), 6.38 (d, J = 15.6 Hz, 1H), 7.54-7.65 (m, 3H), 7.88 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 16.0 Hz, 1H), 10.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 19.2, 30.7, 64.7, 123.3, 128.0, 129.8, 132.1, 133.8, 133.9, 136.7, 140.8, 166.3, 191.7. EIMS *m*/*z* 232 (M^+), 216, 203, 176, 159, 147, 131, 103, 77, 51.
Spectral data were consistent with data reported in the literature.[4]

(*E*)-*tert*-Butyl 3-(2-Formylphenyl)acrylate (1d)



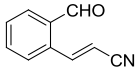
Following the Method B: 77 % (178.7 mg), a yellow oil (EtOAc : *n*-Hexane = 1:10).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.53 (s, 9H), 6.29 (d, J = 16.0 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.56-7.62 (m, 2H), 7.86 (d, J = 7.2 Hz, 1H), 8.40 (d, J = 16.0 Hz, 1H), 10.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1, 80.9, 125.2, 127.9, 129.6, 131.7, 133.7, 133.8, 136.9, 139.6, 165.4, 191.6.
Spectral data were consistent with data reported in the literature.[2]

(*E*)-3-(2-Formylphenyl)-*N*,*N*-dimethylacrylamide (1e)



Following the Method A: 67% (136.1 mg), a brown oil (EtOAc : *n*-Hexane = 3:1).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.07 (s, 3H), 3.17 (s, 3H), 6.76 (d, J = 15.2 Hz, 1H), 7.48-7.52 (m, 1H), 7.59-7.62 (m, 2H), 7.88 (d, J = 7.6 Hz, 1H), 8.33 (d, J = 15.6 Hz, 1H), 10.35 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.9, 37.5, 123.4, 128.0, 129.2, 130.8, 133.8, 133.9, 138.1, 138.2, 166.0, 191.5.
HREIMS *m/z* 203.0947 $(M)^+$, calcd for $C_{12}H_{13}NO_2$ 203.0946.

(*E*)-3-(2-Formylphenyl)acrylonitrile (1f)

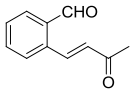


Following the Method A: 55 % (86.4 mg), a pale yellow solid (EtOAc : *n*-Hexane = 1:10).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87 (d, J = 16.4 Hz, 1H), 7.57-7.61 (m, 1H), 7.64-7.68 (m, 2H), 7.85-7.89 (m, 1H), 8.43 (d, J = 16.4 Hz, 1H), 10.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 100.6,

[4] Lin, P.-S.; Jeganmohan, M.; Cheng, C.-H. *Chem.–Asian J.* **2007**, *2*, 1409.

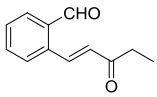
117.6, 127.3, 130.9, 133.3, 134.0, 134.5, 134.7, 148.1, 192.3.
Spectral data were consistent with data reported in the literature.[2]

(*E*)-2-(3-Oxobut-1-enyl)benzaldehyde (1g)



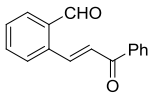
Following the Method A: 38% (66.1 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.46 (s, 3H), 6.60 (d, J = 16.4 Hz, 1H), 7.58-7.69 (m, 3H), 7.87 (d, J = 7.2 Hz, 1H), 8.49 (d, J = 16.4 Hz, 1H), 10.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.0, 127.9, 130.0, 131.7, 133.7, 133.90, 133.92, 136.3, 140.6, 192.6, 198.7.
Spectral data were consistent with data reported in the literature.[3]

(*E*)-2-(3-Oxopent-1-enyl)benzaldehyde (1h)



Following the Method A: 48% (90.3 mg), a brown oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 (td, J = 1.2, 7.0 Hz, 3H), 2.78 (qd, J = 1.2, 7.6 Hz, 2H), 6.61 (d, J = 16.0 Hz, 1H), 7.56-7.67 (m, 3H), 7.87 (d, J = 7.6 Hz, 1H), 8.47 (d, J = 16.8 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.1, 33.3, 127.9, 129.9, 130.9, 133.5, 133.8, 133.9, 136.7, 139.2, 192.4, 201.1. HREIMS *m/z* 188.0835 $(M)^+$, calcd for $C_{12}H_{12}O_2$ 188.0837.

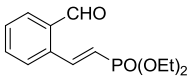
(*E*)-2-(3-Oxo-3-phenylprop-1-enyl)benzaldehyde (1i)[5]



Under argon atmosphere, 2-(1,3-dioxolan-2-yl)benzaldehyde (212.6 mg, 1.193 mmol) was added to the solution of (benzoylmethylene)triphenylphosphorane (453.9 mg, 1.193 mmol, 1 equiv) in CH_2Cl_2 (6 mL, 0.2 M). The mixture was stirred at room temperature for 15 h. The solvent was removed, and the residue was purified by column chromatography on silica gel (Acetone : *n*-Hexane = 1:5). After 2 N HCl was added, the mixture was stirred for 4 h. The resulting solution was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo to afford **1i** (176.9 mg, 63%) as a yellow solid.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, J = 15.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.58-7.63 (m, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.2 Hz, 2H), 8.57 (d, J = 15.6 Hz, 1H), 10.35 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 127.3, 128.1, 128.66, 128.74, 130.0, 132.2, 133.0, 133.9, 134.2, 137.2, 137.6, 141.3, 190.6, 191.8. EIMS *m/z* 236 (M^+), 207, 131, 103, 77, 51.

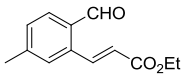
[5] Sánchez-Larios, E.; Holmes, J. M.; Daschner, C. L.; Gravel, M. *Org. Lett.* **2010**, *12*, 5772.

(*E*)-Diethyl 2-Formylstyrylphosphonate (1j)



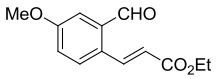
Following the Method A: 69 % (185.0 mg), a pale yellow solid (EtOAc : *n*-Hexane = 3:1).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, J = 6.8 Hz, 6H), 4.20 (quintet, J = 7.0 Hz, 4H), 6.22 (t, J = 18.0 Hz, 1H), 7.53-7.63 (m, 3H), 7.84 (d, J = 7.6 Hz, 1H), 8.27 (dd, J = 17.8, 22.2 Hz, 1H), 10.23 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.4 (d, J = 6.6 Hz), 62.2 (d, J = 5.8 Hz), 119.0, 120.8, 127.8, 129.8, 132.4, 133.5, 133.9, 144.7 (d, J = 7.4 Hz), 191.8. HREIMS *m/z* 268.0861 $(M)^+$, calcd for $C_{13}H_{17}O_4P$ 268.0864.

(*E*)-Ethyl 3-(2-Formyl-5-methylphenyl)acrylate (1k)



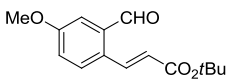
Following the Method B: 88% (191.9 mg), a white solid (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, J = 7.2 Hz, 3H), 2.45 (s, 3H), 4.29 (q, J = 7.1 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.43 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 8.51 (d, J = 16.0 Hz, 1H), 10.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 21.7, 60.7, 122.9, 128.5, 130.6, 131.6, 132.4, 136.6, 141.1, 144.9, 166.2, 191.3. HREIMS *m/z* 218.0945 $(M)^+$, calcd for $C_{13}H_{14}O_3$ 218.0943.

(*E*)-Ethyl 3-(2-Formyl-4-methoxyphenyl)acrylate (1l)



Following the Method B: 74% (173.2 mg), a yellow solid (EtOAc : *n*-Hexane = 1:6).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, J = 7.0 Hz, 3H), 3.89 (s, 3H), 4.28 (q, J = 7.2 Hz, 2H), 6.32 (d, J = 15.6 Hz, 1H), 7.14 (dd, J = 2.6, 8.6 Hz, 1H), 7.38 (d, J = 2.8 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 8.44 (d, J = 16.0 Hz, 1H), 10.35 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 55.7, 60.7, 114.4, 120.8, 121.4, 129.37, 129.42, 135.1, 139.6, 161.0, 166.4, 190.9. EIMS *m*/*z* 234 (M^+), 189, 177, 161, 146, 118, 90.
Spectral data were consistent with data reported in the literature.[6]

(*E*)-*tert*-Butyl 3-(2-Formyl-4-methoxyphenyl)acrylate (1m)

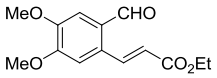


Following the Method B: 70% (183.4 mg), a brown solid (EtOAc : *n*-Hexane = 1:10).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.54 (s, 9H), 3.89 (s, 3H), 6.26 (d, J = 16.4 Hz, 1H), 7.14 (dd, J = 2.8, 8.8 Hz, 1H), 7.38 (d, J = 2.8 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 8.34 (d, J = 15.6 Hz, 1H), 10.37 (s,

[6] Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.

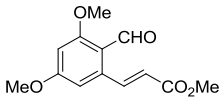
1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.2, 55.6, 80.8, 113.8, 120.9, 123.4, 129.3, 129.8, 135.0, 138.4, 160.8, 165.7, 190.8. EIMS *m*/*z* 262 (M^+), 189, 177, 161, 146, 133, 118, 103, 89, 77, 57.
Spectral data were consistent with data reported in the literature.[7]

(*E*)-Ethyl 3-(2-Formyl-4,5-dimethoxyphenyl)acrylate (1n)



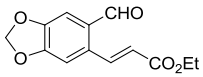
Following the Method B: 63% (166.4 mg), a white solid (EtOAc : *n*-Hexane = 1:5).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.97 (s, 3H), 3.99 (s, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 7.06 (s, 1H), 7.41 (s, 1H), 8.46 (d, *J* = 15.6 Hz, 1H), 10.34 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 56.19, 56.23, 60.8, 109.0, 111.0, 121.9, 127.7, 131.7, 139.3, 150.6, 153.6, 166.3, 189.1. EIMS *m*/*z* 264 (M^+), 219, 207, 191, 175, 163, 147, 130, 119, 105, 89, 77, 51.
Spectral data were consistent with data reported in the literature.[8]

(*E*)-Methyl 3-(2-Formyl-3,5-dimethoxyphenyl)acrylate (1o)



Following the Method B: 59% (147.5 mg), a yellow solid (EtOAc : *n*-Hexane = 1:3).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (s, 3H), 3.89 (s, 3H), 3.91 (s, 3H), 6.25 (d, *J* = 15.6 Hz, 1H), 6.50 (s, 1H), 6.59 (s, 1H), 8.44 (d, *J* = 16.0 Hz, 1H), 10.48 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.8, 55.7, 56.0, 98.9, 105.2, 116.9, 121.5, 139.7, 144.7, 164.71, 164.73, 166.9, 189.8. HREIMS *m/z* 250.0847 $(M)^+$, calcd for $C_{13}H_{14}O_5$ 250.0841.

(*E*)-Ethyl 3-(2-Formyl-4,5-methylenedioxyphenyl)acrylate (1p)



Following the Method A: 36% (89.3 mg), a yellow solid (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, *J* = 7.0 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 6.10 (s, 2H), 6.31 (d, *J* = 15.6 Hz, 1H), 7.06 (s, 1H), 7.35 (s, 1H), 8.42 (d, *J* = 15.6 Hz, 1H), 10.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 60.7, 102.4, 106.5, 108.7, 122.1, 129.4, 133.7, 139.1, 149.4, 152.4, 166.1, 188.6.
Spectral data were consistent with data reported in the literature.[9]

(*E*)-Ethyl 3-(4-Chloro-2-formylphenyl)acrylate (1q)

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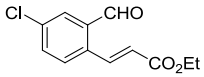
[7] Frey, L. F.; Tillyer, R. D.; Caille, A.-S.; Tschaen, D. M.; Dolling, U.-H.; Grabowski, E. J. J.; Reider, P. J.; Dolling, U.-H. *J. Org. Chem.* **1998**, *63*, 3120.

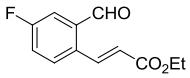
[8] Kishor, P.; Jeganmohan, M. *Org. Lett.* **2012**, *14*, 1134.

[9] Fustero, S.; Moscardó, J.; Sánchez-Roselló, M.; Rodríguez, E.; Barrio, P. *Org. Lett.* **2010**, *12*, 5494.



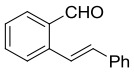
Following the Method B: 92% (219.0 mg), a yellow solid (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, J = 7.0 Hz, 3H), 4.29 (q, J = 6.9 Hz, 2H), 6.37 (d, J = 15.6 Hz, 1H), 7.58 (s, 2H), 7.86 (s, 1H), 8.42 (d, J = 16.0 Hz, 1H), 10.28 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 60.8, 123.7, 129.3, 131.2, 133.8, 134.7, 134.9, 136.2, 139.2, 165.8, 190.0. EIMS *m*/*z* 238 (M^+), 209, 193, 181, 165, 137, 101, 75, 51.
Spectral data were consistent with data reported in the literature.[3]

(*E*)-Ethyl 3-(4-Fluoro-2-formylphenyl)acrylate (1r)



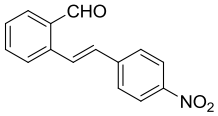
Following the Method B: 71% (157.7 mg), a yellow oil (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, J = 7.2 Hz, 3H), 4.29 (q, J = 7.1 Hz, 2H), 6.35 (d, J = 15.6 Hz, 1H), 7.34 (td, J = 2.7, 8.2 Hz, 1H), 7.59 (dd, J = 2.4, 8.4 Hz, 1H), 7.65 (dd, J = 5.0, 8.6 Hz, 1H), 8.41 (d, J = 15.6 Hz, 1H), 10.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 60.9, 117.4 (d, J = 22.0 Hz), 121.3 (d, J = 22.0 Hz), 123.4, 130.2 (d, J = 7.3 Hz), 133.0, 135.6 (d, J = 7.3 Hz), 139.2, 163.4 (d, J = 252.2 Hz), 166.0, 189.9.
Spectral data were consistent with data reported in the literature.[9]

(*E*)-2-Styrylbenzaldehyde (1s)



Following the Method A: 67 % (172.9 mg), a yellow oil (EtOAc : *n*-Hexane = 1:10).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 16.0 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 16.4 Hz, 1H), 10.33 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 124.8, 127.0, 127.2, 127.6, 128.3, 128.8, 132.3, 132.9, 133.7, 134.0, 136.9, 140.0, 192.7. EIMS *m*/*z* 208 (M^+), 178, 165, 152, 130, 102, 89, 76, 51.
Spectral data were consistent with data reported in the literature.[2, 10]

(*E*)-2-(4-Nitrostyryl)benzaldehyde (1t)



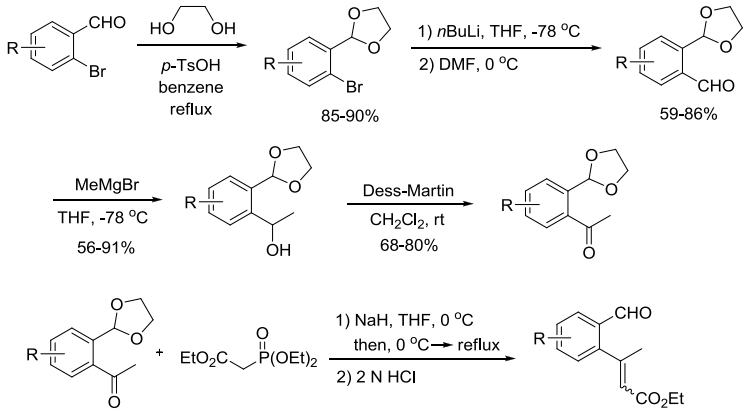
Following the Method A: 67 % (169.6 mg), a brown oil (EtOAc : *n*-Hexane = 1:10).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.11 (d, J = 16.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 8.8 Hz,

[10] Jagdale, A. R.; Youn, S. W. *Eur. J. Org. Chem.* **2011**, 3904.

2H), 8.31 (d, J = 16.4 Hz, 1H), 10.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 124.1, 127.2, 127.4, 128.7, 130.1, 130.8, 133.2, 133.8, 134.0, 138.2, 143.4, 147.1, 193.0. EIMS m/z 253 (M^+), 207, 178, 152, 133, 105, 89, 77, 51.

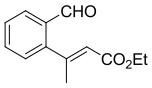
Spectral data were consistent with data reported in the literature.[10]

General Procedure for the Preparation of 2-Alkenylbenzaldehyde Derivatives 3a-c



To a solution of NaH (400.0 mg, 10.0 mmol, 5 equiv) in THF (5.0 mL, 0.4 M) was added ethyl 2-(diethoxyphosphoryl)acetate (2.1 mL, 10.0 mmol, 5 equiv) dropwise at 0 °C. After 20 min, 1-(2-(1,3-dioxolan-2-yl)phenyl)ethanone (384.2 mg, 2.00 mmol, 1 equiv) was added in one portion and the mixture was allowed to warm to reflux over 2.5-12 hour. The reaction was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. After 2 N HCl was added, the mixture was stirred for 4 h. The resulting solution was diluted with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica to afford the desired product.

(*E*)-Ethyl 3-(2-Formylphenyl)but-2-enoate (3a)

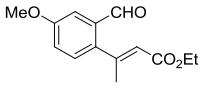


71% (309.7 mg), a yellow oil (EtOAc : *n*-Hexane = 1:8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, J = 7.2 Hz, 3H), 2.56 (d, J = 0.8 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 5.80 (d, J = 1.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.59 (td, J = 1.2, 7.6 Hz, 1H), 7.94 (dd, J = 1.2, 8.0 Hz, 1H), 10.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 21.7, 60.1, 121.8, 128.26, 128.34, 128.9, 132.9, 133.8, 147.0, 154.2, 165.7, 191.1.

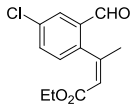
Spectral data were consistent with data reported in the literature.[3]

(*E*)-Ethyl 3-(2-Formyl-4-methoxyphenyl)but-2-enoate (3b)



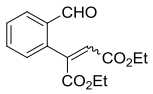
27% (134.0 mg), a colorless oil (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, J = 7.1 Hz, 3H), 2.55 (d, J = 0.9 Hz, 3H), 3.87 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 5.75 (d, J = 1.5 Hz, 1H), 7.14 (dd, J = 2.8, 8.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 2.8 Hz, 1H), 10.08 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 21.8, 55.6, 60.1, 111.1, 121.1, 122.2, 129.6, 134.2, 140.2, 153.4, 159.5, 165.8, 191.0. HREIMS *m/z* 248.1045 $(M)^+$, calcd for $C_{14}H_{16}O_4$ 248.1049.

(*Z*)-Ethyl 3-(4-Chloro-2-formylphenyl)-2-methylacrylate (3c)



43% (purity 92%, 235.6 mg), a yellow oil (EtOAc : *n*-Hexane = 1:8).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (t, J = 7.2 Hz, 3H), 2.21 (d, J = 0.8 Hz, 3H), 3.95 (q, J = 7.2 Hz, 2H), 6.13 (s, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.55 (dd, J = 2.0, 8.4 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 9.98 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 27.9, 60.1, 120.7, 128.6, 128.8, 129.0, 133.7, 134.2, 142.8, 151.9, 164.9, 189.8. HREIMS *m/z* 252.0559 $(M)^+$, calcd for $C_{13}H_{13}ClO_3$ 252.0553.

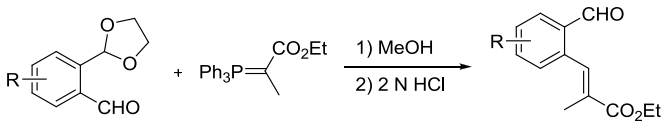
Diethyl 2-(2-Formylphenyl)fumarate & Diethyl 2-(2-Formylphenyl)maleate (3d)



(*E*:*Z* = 6:1)

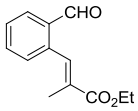
To a solution of 2-bromobenzaldehyde (250 μL, 2.142 mmol), $Pd(OAc)_2$ (24.1 mg, 0.107 mmol, 5 mol%), P(*o*-Tol)$_3$ (65.2 mg, 0.214 mmol, 10 mol%) and NEt_3 (597 μL, 4.283 mmol, 2 equiv) in DMF (21.4 ml, 0.1M) was added diethyl fumarate (1.8 mL, 10.71 mmol, 5 equiv). The resulting mixture was heated under Ar atmosphere at 110 ℃ for 12.5 hours. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with ether (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:8) to afford the desired product (233.3 mg, 39%, *E*:*Z* = 6:1) as a brown oil.
Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H), 3.99 (quintet, J = 6.4 Hz, 2H), 4.22 (quintet, J = 7.2 Hz, 2H), 7.10 (s, 1H), 7.22 (dd, J = 1.6, 7.6 Hz, 1H), 7.53-7.64 (m, 2H), 7.90 (dd, J = 2.2, 7.2 Hz, 1H), 9.98 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 14.0, 60.8, 62.0, 128.5, 128.9, 130.5, 132.2, 133.3, 134.2, 136.1, 144.6, 164.8, 165.3, 191.7. Signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.6 Hz, 3H), 4.08-4.32 (m, 4H), 7.48 (d, J = 7.6 Hz, 1H), 7.53-7.64 (m, 3H), 7.97 (d, J = 8.0 Hz, 1H), 10.21 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 14.1, 61.4, 62.1, 126.8, 129.2, 129.5, 129.6, 133.8, 134.3, 137.9, 143.7, 164.3, 191.1 (1 carbon is missing due to overlapping). HREIMS *m/z* 276.0987 $(M)^+$, calcd for $C_{15}H_{16}O_5$ 276.0998.

General Procedure for the Preparation of 2-Alkenylbenzaldehyde Derivatives 3e-g



To a solution of ethyl 2-(triphenylphosphoranylidene)propionate (543.2 mg, 1.65 mmol, 1.1 equiv) in MeOH (15.0 mL, 0.1 M) was added 2-(1,3-dioxolan-2-yl)benzaldehyde (267.1 mg, 1.50 mmol, 1 equiv). After being stirred at room temperature for 4-12 h, the reaction was quenched with distilled water and extracted with EtOAc (three times). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. After 2 N HCl was added, the mixture was stirred for 4 h. The resulting solution was diluted with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica to afford the desired product.

(*E*)-Ethyl 3-(2-Formylphenyl)-2-methylacrylate (3e)

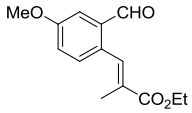


52% (170.1 mg), a colorless oil (EtOAc : *n*-Hexane = 1:8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (t, J = 7.4 Hz, 3H), 1.90 (s, 3H), 4.30 (q, J = 7.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), 10.17 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 14.2, 61.0, 128.4, 129.9, 131.8, 133.6, 135.9, 138.6, 167.6, 191.6 (2 carbons are missing due to overlapping).

Spectral data were consistent with data reported in the literature.[3]

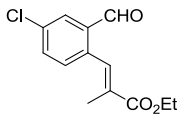
(*E*)-Ethyl 3-(2-Formyl-4-methoxyphenyl)-2-methylacrylate (3f)



64% (238.2 mg), a colorless oil (EtOAc : *n*-Hexane = 1:6).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (t, J = 7.0 Hz, 3H), 1.93 (d, J = 1.2 Hz, 3H), 3.91 (s, 3H), 4.31 (q, J = 7.2 Hz, 2H), 7.18 (dd, J = 2.4, 8.4 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 8.04 (s, 1H), 10.17 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 14.1, 55.4, 60.8, 112.3, 120.6, 131.2, 131.3, 131.4, 134.7, 135.2, 159.5, 167.6, 191.0. HREIMS *m/z* 248.1045 $(M)^+$, calcd for $C_{14}H_{16}O_4$ 248.1049.

(*E*)-Ethyl 3-(4-Chloro-2-formylphenyl)-2-methylacrylate (3g)

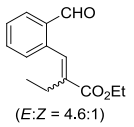


44% (166.4 mg), a colorless oil (EtOAc : *n*-Hexane = 1:20).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (t, J = 7.0 Hz, 3H), 1.89 (d, J = 1.2 Hz, 3H), 4.30 (q, J = 7.2 Hz,

2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.97 (s, 1H), 10.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 14.2, 61.2, 129.3, 131.4, 132.9, 133.6, 134.4, 134.80, 134.84, 137.0, 167.4, 190.1. HREIMS *m/z* 252.0555 $(M)^+$, calcd for $C_{13}H_{13}ClO_3$ 252.0553.

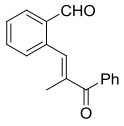
Ethyl 3-(2-Formylphenyl)-2-methylacrylate (3h)



(*E*:*Z* = 4.6:1)

To a solution of NaH (169.4 mg, 4.235 mmol, 3 equiv) in THF (2.8 ml) was added a solution of ethyl 2-(diethoxyphosphoryl)butanoate (1.0 ml, 4.235 mmol, 3 equiv) in THF (5.6 mL) dropwise at 0 ℃. After 20 min, 2-(1,3-dioxolan-2-yl)benzaldehyde (294.0 mg, 1.412 mmol) was added in one portion and the mixture was allowed to slowly warm to room temperature over 2.5 hour. The reaction was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. After 2 N HCl was added, the mixture was stirred for 4 h. The resulting solution was diluted with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Acetone : *n*-Hexane = 1:6) to afford **3h** (274.0 mg, 81%, *E*:*Z* = 4.6:1) as a yellow solid. Signals corresponding to (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 2.31 (q, *J* = 7.5 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 10.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 14.2, 21.0, 60.9, 128.4, 129.5, 129.8, 133.8, 135.6, 137.9, 138.9, 167.3, 191.6 (1 carbon is missing due to overlapping). Signals corresponding to (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.53 (q, *J* = 7.2 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 7.15 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 10.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.0, 13.5, 27.6, 60.4, 127.7, 129.5, 131.4, 133.3, 133.6, 139.2, 140.4, 168.1, 191.9 (1 carbon is missing due to overlapping). HREIMS *m/z* 232.1098 $(M)^+$, calcd for $C_{14}H_{16}O_3$ 232.1099.

(*E*)-2-(2-Methyl-3-oxo-3-phenylprop-1-enyl)benzaldehyde (3i)



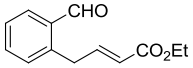
To a solution of NaOH (351.6 mg, 8.791 mmol, 4 equiv) in EtOH (3.0 mL) and water (4.0 mL) was slowly added 2-(diethoxymethyl)benzaldehyde (480.6 mg, 2.308 mmol, 1.1 equiv) at 0 ℃. Subsequently propiophenone (298 μL, 2.198 mmol) was slowly added. The reaction mixture was stirred at ambient temperature for 10 min and then heated to 80 ℃ for 48 h. Then, the mixture was cooled to room temperature and neutralized with 1 N HCl to pH 7. The aqueous layer was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, and dried over

$MgSO_4$, and concentrated in vacuo. After 2 N HCl was added, the mixture was stirred for 4 h. The resulting solution was diluted with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc : *n*-Hexane = 1:10) to afford **3i** (303.4 mg, 55%) as a light yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 3H), 7.39 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.60 (s, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 7.6 Hz, 3H), 10.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 128.3, 128.6, 129.6, 130.1, 131.8, 132.0, 133.7, 137.7, 137.9, 139.0, 139.41, 139.42, 191.8, 198.7.

Spectral data were consistent with data reported in the literature.[11]

(*E*)-Ethyl 4-(2-Formylphenyl)but-2-enoate (6)



A solution of methyl 3-bromoprop-1-ene (378 µL, 4.302 mmol, 1.2 equiv), 2-formylphenylboronic acid (516.0 mg, 3.441 mmol), $PdCl_2(PPh_3)_2$ (60.4 mg, 0.086 mmol, 2 mol%) and Na_2CO_3 (733.0 mg, 6.883 mmol, 2 equiv) in THF (34.4 mL, 0.1 M) and H_2O (9.0 ml) in a sealed tube was placed under Ar and stirred at 80 ℃ for 8 h. The reaction was diluted with CH_2Cl_2 and washed with water. The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:40) to afford 2-allylbenzaldehyde (367.4 mg, 73%) as a colorless oil.

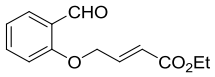
To a solution of 2-allylbenzaldehyde (235.6 mg, 1.612 mmol) in benzene (5.4 ml, 0.3 M) were added ethylene glycol (250 µL, 4.029 mmol, 2.5 equiv) and *p*-TsOH (31.2 mg, 0.161 mmol, 10 mol%). The resulting mixture was refluxed for 7 hours. The reaction was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:40) to afford 2-(2-allylphenyl)-1,3-dioxolane (184.3 mg, 60%) as a colorless oil.

Under Ar atmosphere, to the solution of Grubbs 2nd generation catalyst (13.6 mg, 0.016 mmol, 5 mol%) and 2-(2-allylphenyl)-1,3-dioxolane (61.0 mg, 0.321 mmol) in CH_2Cl_2 (1.6 mL, 0.2 M) was added ethyl acrylate (141 µL, 1.283 mmol, 4 equiv). The mixture was stirred for 11.5 h at room temperature. The resulting solution was quenched with distilled water and extracted CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. After 2 N HCl was added, the mixture was stirred for 15 min. The resulting solution was quenched with distilled water and extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:15) to afford **6** (53.2 mg, 76%) as a colorless oil.

[11] Sánchez-Larios, E.; Holmes, J. M.; Daschner, C. L.; Gravel, M. *Synthesis* **2011**, *12*, 1896.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, J = 7.0 Hz, 3H), 3.98 (dd, J = 1.2, 6.0 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 5.71 (d, J = 15.6 Hz, 1H), 7.14 (dt, J = 6.4, 15.7 Hz, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.56 (td, J = 1.4, 7.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 10.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 35.2, 60.3, 122.6, 127.5, 131.4, 133.6, 133.8, 134.0, 139.7, 146.6, 166.3, 192.4. HREIMS *m/z* 218.0943 $(M)^+$, calcd for $C_{13}H_{14}O_3$ 218.0943.

(*E*)-Ethyl 4-(2-Formylphenoxy)but-2-enoate (8)

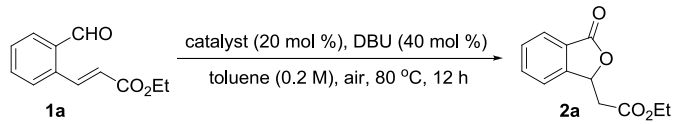


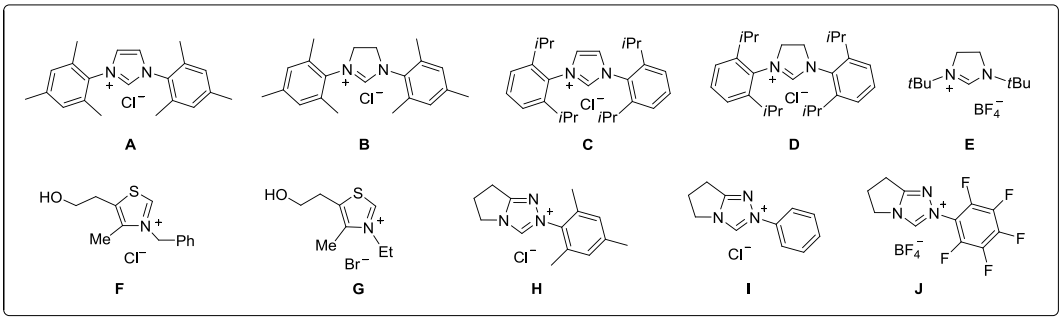
To an ice-cold suspension of NaH (180.2 mg, 7.51 mmol, 1.5 equiv) in DMF (20 mL) was added salicylic aldehyde (610.0 mg, 5.00 mmol). After 20 min, ethyl 4-bromocrotonate (1.41 g, 5.5 mmol, 1.1 equiv) was added and the mixture was stirred at room temperature for 1 h. The reaction was quenched with distilled water and extracted with ether (three times). The combined organic solution was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc : *n*-Hexane = 1:4) to afford **8** (950 mg, 81%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, J = 7.0 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.83 (dd, J = 2.0, 4.0 Hz, 2H), 6.21 (dt, J = 1.8, 15.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 7.10 (dt, J = 4.0, 16.0 Hz, 1H), 7.54 (td, J = 1.6, 7.8 Hz, 1H), 7.86 (dd, J = 1.6, 7.6 Hz, 1H), 10.55 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 60.7, 66.8, 112.5, 121.4, 122.5, 125.1, 128.8, 135.9, 141.1, 160.2, 165.8, 189.3. EIMS *m*/*z* 234 (M^+), 216, 188, 161, 133, 121, 105, 85, 77, 68, 57, 51.
Spectral data were consistent with data reported in the literature.[12]

[12] Knight, R. L.; Leeper, F. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1891.

Screening of Catalysts

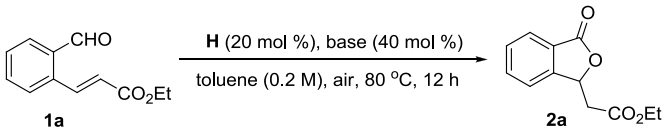




Entry	Catalyst	Yield (%)[a]		Entry	Catalyst	Yield (%)[a]	
		1a	**2a**			**1a**	**2a**
1	**A**	22	36	6	**F**	46	16
2	**B**	11	55	7	**G**	50	17
3	**C**	27	26	8	**H**	0	60 (55)
4	**D**	27	24	9	**I**	16	38
5	**E**	59	-	10	**J**	0	34

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. Value in parentheses indicates an isolated yield.

Screening of Bases

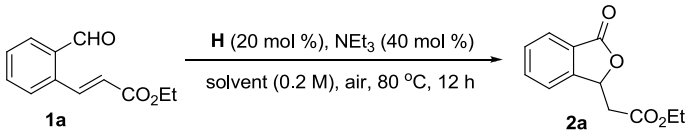


Entry	Base	Yield (%)[a]		Entry	Base	Yield (%)[a]	
		1a	**2a**			**1a**	**2a**
1	DBU	-	60	9	Cs_2CO_3	-	26
2	NEt_3	-	96 (86)	10	K_3PO_4	7	55
3	iPr$_2$NEt	-	84	11	NaH	-	20
4	pyridine	76	-	12	KHMDS	-	73
5	DMAP	-	100	13	NaOAc	20	71 (63)
6	tBuOK	-	34	14	NaOH	56	-
7	Na_2CO_3	19	50	15	KOH	-	51
8	K_2CO_3	5	61	16[b]	NaOMe	-	-

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. Value in parentheses indicates an isolated yield. [b] Ethyl 2-(3-methoxy-1,3-dihydroisobenzofuran-1-yl)acetate resulting from the domino nucleophilic

addition-conjugate addition reaction was observed as a by-product.

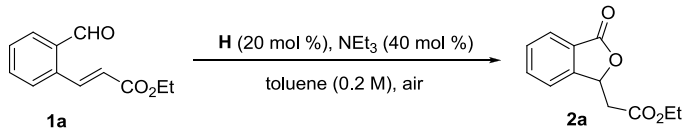
Screening of Solvents



Entry	Solvent	Yield (%)[a]		Entry	Solvent	Yield (%)[a]	
		1a	**2a**			**1a**	**2a**
1	toluene	-	96	7	acetone	21	13
2	benzene	-	71	8	DMF	5	79
3	DCE	17	41	9	DMSO	< 5	53
4	THF	6	22	10	*t*BuOH	11	45
5	dioxane	-	72	11	EtOH	-	28
6	MeCN	-	66				

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard.

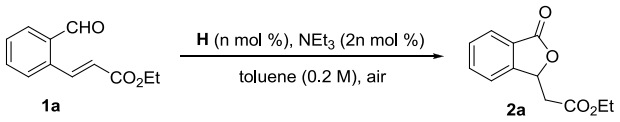
Screening of Temperature



Entry	Temp. (℃)	Time (h)	Yield (%)[a]	
			1a	**2a**
1	80	12	-	96
2	60	11	< 2	80
3[b]	60	11	<5	85
4	40	24	9	64
5	25	24	23	35
6[b]	25	24	-	45

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. [b] Under O_2 (1 atm).

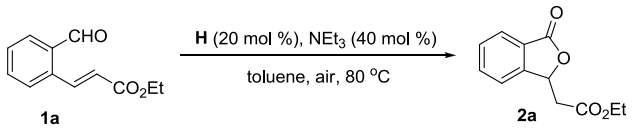
Screening of Catalyst Loading



Entry	**H** (mol%)	NEt_3 (mol%)	Temp. (^oC)	Time (h)	Yield (%)[a]	
					1a	**2a**
1	10	20	80	22	10	72
2	20	40	80	6	-	92
3	10	20	60	24	25	60
4	20	40	60	14	-	90

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard.

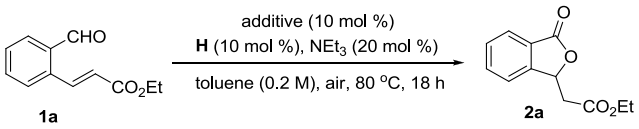
Screening of Solvent Concentration



Entry	toluene (M)	Time (h)	Yield (%)[a]	
			1a	**2a**
1	0.2	6	-	92
2	0.1	12	-	89
3	0.05	12	-	91

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard.

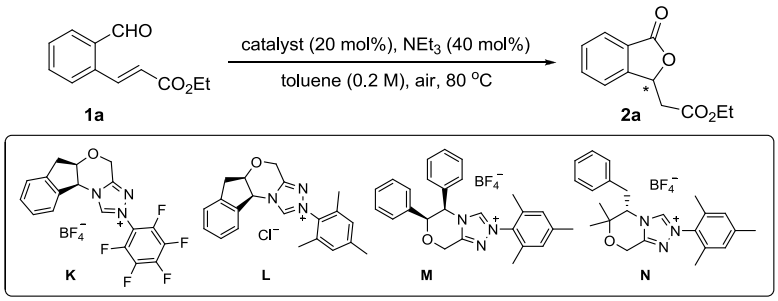
Screening of Lewis Acids



Entry	Lewis Acid	Yield (%)[a]		Entry	Lewis Acid	Yield (%)[a]	
		1a	**2a**			**1a**	**2a**
1	$Zn(OTf)_2$	76	-	8	$Sc(OTf)_3$	57	-
2	$In(OTf)_3$	81	-	9	$Cu(OTf)_2$	66	-
3	$Bi(OTf)_3$	74	-	10	AgOTf	53	-
4	$Mg(OTf)_2$	63	< 5	11	$ZnCl_2$	65	-
5	$Sn(OTf)_2$	74	-	12	$InCl_3$	46	7
6	$FeCl_3$/3AgOTf	60	-	13	$YbCl_3$	40	20
7	$Yb(OTf)_3$	67	-	14	$AlCl_3$	41	17

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard.

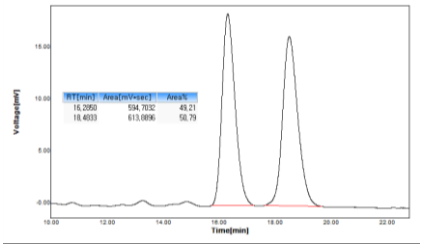
Screening of Chiral NHC Catalysts



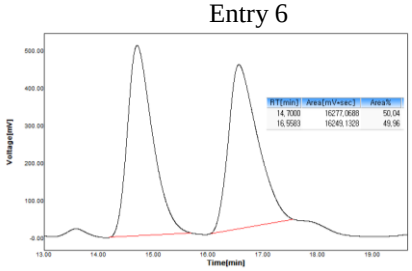
Entry	Catalyst	Time (h)	Yield (%)[a]	Er[b]
1	**K**	6	(83)	55:45
2[c]	**K**	12	79	58:42
3[c-d]	**K**	24	(68)	50:50
4[e]	**K**	12	(15)	ND[f]
5	**L**	24	69	49:51
6	**M**	24	68	50:50
7	**N**	24	45	49:51
8[g]	**K**	15	16	47:53
9[g]	**L**	15	33	44:56
10[g]	**M**	15	29	44:56
11[g]	**N**	15	(8)	ND[f]

[a] Isolated yields. Value in parentheses indicates a yield determined by ^{1}H NMR using trichloroethylene as an internal standard. [b] Enantiomeric ratios (er) were determined by chiral HPLC on a Daicel OD-H column. [c] At 60 °C. [d] Using DMAP instead of NEt_3. [e] Using DBU instead of NEt_3. [f] Not determined. [g] Performed with a carbene preformed from catalyst (20 mol%) and NEt_3 (20 mol%). A solution of catalyst (20 mol%) and NEt_3 (20 mol%) in toluene (0.2 M) was stirred at room temperature for 0.5 h, then **1a** (1 equiv) was added in one portion. The resulting mixture was stirred at 80 °C for 15 h under aerobic conditions.

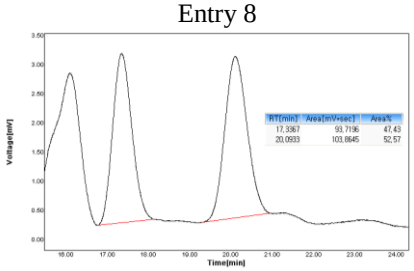
rac-3-(Ethoxycarbonyl)methylphthalide (***rac*-2a**)



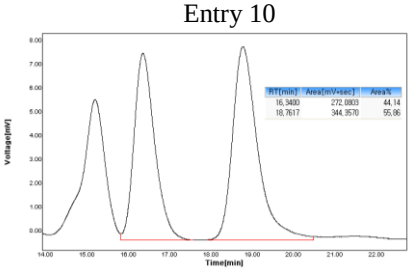
Entry 6



Entry 8



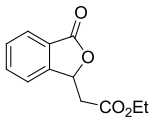
Entry 10



General Procedure for the NHC-Catalyzed Oxidative Cyclization Reactions of 2-Alkenylbenzaldehydes

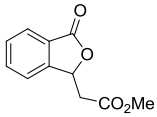
To a solution of the substrate **1**, **3**, **6**, or **8** (0.100 mmol, 1 equiv) in toluene (0.5 mL, 0.2 M) were added 2-mesityl-2,5,6,7-tetrahydropyrrolo[2,1-*c*][1,2,4]triazol-4-ium chloride (**H**) (5.4 mg, 0.020 mmol, 20 mol%) and NEt_3 (6 μL, 0.040 mmol, 40 mol%). The resulting mixture was stirred at the reported temperature for the reported time under aerobic conditions. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with distilled water, extracted with CH_2Cl_2 (three times), dried over $MgSO_4$, and concentrate in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product.

3-(Ethoxycarbonyl)methylphthalide (2a)



86% (18.9 mg), 47% (10.3 mg, from (*Z*)-**1a**), a yellow oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, J = 7.2 Hz, 3H), 2.87 (dd, J = 6.2, 16.6 Hz, 1H), 2.94 (dd, J = 6.8, 16.4 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 5.89 (t, J = 6.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 39.5, 61.2, 76.9, 122.0, 125.8, 126.0, 129.5, 134.2, 148.8, 169.2, 169.8. IR (NaCl) ν_{max} 1768, 1735, 1467, 1379, 1291, 1213, 1179, 1063 cm^{-1}. EIMS *m*/*z* 220 (M^+), 146, 133, 105, 77, 51.
Spectral data were consistent with data reported in the literature.[13]

3-(Methoxycarbonyl)methylphthalide (2b)



90% (18.5 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4)
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.87 (dd, J = 6.4, 16.4 Hz, 1H), 2.93 (dd, J = 7.2, 16.4 Hz, 1H), 3.76 (s, 3H), 5.88 (t, J = 6.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.3, 52.2, 76.9, 122.0, 125.85, 125.88, 129.6, 134.3, 148.7, 169.7, 169.8. IR (NaCl) ν_{max} 2957, 1738, 1612, 1467, 1438, 1350, 1260, 1172, 1067, 1014 cm^{-1}. EIMS *m*/*z* 206 (M^+), 146, 133, 105, 77, 51.
Spectral data were consistent with data reported in the literature.[14]

3-(Butoxycarbonyl)methylphthalide (2c)

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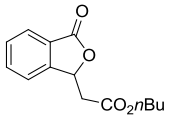
[13] (a) Pedrosa, R.; Sayalero S.; Vicente, M. *Tetrahedron* **2006**, *62*, 10400. (b) Li, G.; Yin, D.; Liang, X-T, *Synth. Commun.* **2004**, *34*, 1183.

[14] Larock, R. C.; Varaprath, S.; Lau, H. H.; Fellows, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 5274.

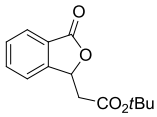


88% (21.8 mg), a yellow oil (EtOAc : *n*-Hexane = 1:5)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J = 7.4 Hz, 3H), 1.36 (sextet, J = 7.4 Hz, 2H), 1.61 (quintet, J = 7.1 Hz, 2H), 2.87 (dd, J = 6.0, 16.4 Hz, 1H), 2.93 (dd, J = 7.2, 16.8 Hz, 1H), 4.16 (t, J = 6.6 Hz, 2H), 5.88 (t, J = 6.6 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6, 19.0, 30.5, 39.5, 65.2, 77.0, 122.0, 125.8, 125.9, 129.5, 134.2, 148.8, 169.3, 169.9. IR (NaCl) ν_{max} 2960, 2932, 2873, 1768, 1736, 1465, 1175, 1062, 1004 cm^{-1}. EIMS m/z 248 (M^+), 146, 133, 105, 77, 51.

Spectral data were consistent with data reported in the literature.[15]

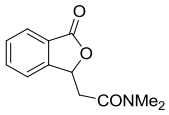
3-(*tert*-Butoxycarbonyl)methylphthalide (2d)



64% (15.9 mg), a colorless oil (EtOAc : *n*-Hexane = 1:5)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 9H), 2.80 (dd, J = 6.6, 16.6 Hz, 1H), 2.87 (dd, J = 6.8, 16.8 Hz, 1H), 5.83 (t, J = 6.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 40.6, 77.3, 82.0, 122.1, 125.8, 126.1, 129.4, 134.2, 149.0, 168.4, 170.0. IR (NaCl) ν_{max} 2980, 2935, 1768, 1467, 1368, 1290, 1215, 1153, 1067, 1003 cm^{-1}. HREIMS m/z 248.1047 $(M)^+$, calcd for $C_{14}H_{16}O_4$ 248.1049.

***N*,*N*-Dimethyl-2-(3-oxo-1,3-dihydroisobenzofuran-1-yl)acetamide (2e)**



80% (17.5 mg), a yellow oil (EtOAc : *n*-Hexane = 3:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.70 (dd, J = 7.2, 16.0 Hz, 1H), 3.00 (s, 3H), 3.01 (s, 3H), 3.10 (dd, J = 6.0, 16.0 Hz, 1H), 6.03 (t, J = 6.6 Hz, 1H), 7.52 (quintet, J = 4.0 Hz, 1H), 7.65 (d, J = 4.0 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.4, 37.3, 38.8, 78.3, 123.1, 125.5, 125.8, 129.3, 134.2, 149.8, 168.5, 170.2. IR (NaCl) ν_{max} 1761, 1646, 1401, 1063, 997 cm^{-1}. EIMS m/z 219 (M^+), 191, 147, 133, 105, 77, 72, 51.

Spectral data were consistent with data reported in the literature.[16]

3-Cyanomethylphthalide (2f)

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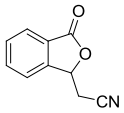
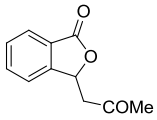
[15] Miura, M.; Tsuda, T.; Satoh, T.; Pivsa-Art, S.; Nomura, M. *J. Org. Chem.* **1998**, *63*, 5211.

[16] Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362.



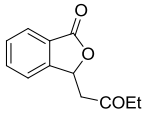
72% (12.5 mg), a brown solid (EtOAc : *n*-Hexane = 1:3), mp 128-130 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.97 (dd, J = 6.8, 16.8 Hz, 1H), 3.09 (dd, J = 5.2, 16.8 Hz, 1H), 5.67 (t, J = 6.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.66 (d, J = 6.8 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.8, 74.6, 114.7, 122.1, 125.7, 126.3, 130.5, 134.8, 146.6, 168.7. IR (NaCl) ν_{max} 1766, 1065 cm^{-1}. EIMS *m*/*z* 173 (M^+), 133, 105, 77, 51.
Spectral data were consistent with data reported in the literature.[16]

3-(2-Oxopropyl)phthalide (2g)



79% (15.0 mg), a white solid (EtOAc : *n*-Hexane = 1:5), mp 38-41 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H), 2.91 (dd, J = 6.4, 17.6 Hz, 1H), 3.14 (dd, J = 6.8, 17.6 Hz, 1H), 5.94 (t, J = 6.4 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.7, 48.1, 76.7, 122.3, 125.8, 129.4, 134.3, 149.4, 170.0, 204.5 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2962, 2930, 2856, 1762, 1723, 1615, 1599, 1468, 1370, 1349, 1287, 1261, 1082, 1038, 950 cm^{-1}. EIMS *m*/*z* 190 (M^+), 175, 147, 133, 129, 105, 77, 51.
Spectral data were consistent with data reported in the literature.[17]

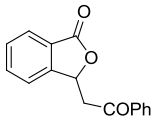
3-(2-Oxobutyl)phthalide (2h)



72% (14.7 mg), a white solid (EtOAc : *n*-Hexane = 1:5), mp 41-45 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.12 (t, J = 7.6 Hz, 3H), 2.53 (ddq, J = 7.4, 14.8, 18.0 Hz, 2H), 2.88 (dd, J = 6.2, 17.0 Hz, 1H), 3.11 (dd, J = 7.2, 17.2 Hz, 1H), 5.96 (t, J = 6.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.5, 36.8, 46.9, 76.9, 122.3, 125.8, 129.4, 134.3, 149.5, 170.0, 207.3 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2924, 1764, 1717, 1610, 1466, 1375, 1288, 1055, 973 cm^{-1}. EIMS *m*/*z* 204 (M^+), 175, 147, 133, 105, 77, 51.
Spectral data were consistent with data reported in the literature.[17b]

3-(2-Oxo-2-phenylethyl)phthalide (2i)

[17] (a) Mal, D.; Pahari, P.; De, S. R. *Tetrahedron* **2007**, *63*, 11781. (b) Zhang, H.; Zhang, S.; Liu, L.; Luo, G.; Duan, W.; Wang, W. *J. Org. Chem.* **2010**, *75*, 368.

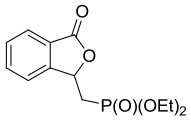


52% (13.1 mg), a brown oil (EtOAc : *n*-Hexane = 1:4)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.40 (dd, J = 7.2, 17.6 Hz, 3H), 3.79 (dd, J = 5.8, 17.8 Hz, 1H), 6.19 (t, J = 6.6 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.7, 77.2, 122.8, 125.8, 125.9, 128.2, 128.8, 129.4, 133.9, 134.3, 136.1, 149.7, 170.2, 196.0. IR (NaCl) ν_{max} 3067, 2960, 2923, 2854, 1762, 1684, 1594, 1477, 1289, 1214, 1073, 998, 974 cm^{-1}. EIMS *m*/*z* 252 (M^+), 147, 133, 105, 77, 51.

Spectral data were consistent with data reported in the literature.[18]

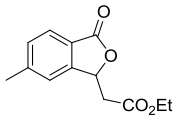
Diethyl (3-Oxo-1,3-dihydroisobenzofuran-1-yl)methylphosphonate (2j)



84% (23.9 mg), a brown oil (EtOAc : *n*-Hexane = 3:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 2.34 (ddd, J = 7.2, 14.0, 15.6 Hz, 1H), 2.42 (ddd, J = 5.2, 13.8, 15.6 Hz, 1H), 4.06-4.18 (m, 2H), 4.19-4.31 (m, 2H), 5.79 (quintet, J = 6.2 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.3 (d, J = 5.8 Hz), 16.4 (d, J = 6.6 Hz), 31.9 (d, J = 140.7 Hz), 62.1 (d, J = 6.6 Hz), 62.6 (d, J = 5.8 Hz), 75.9 (d, J = 3.7 Hz), 122.5, 125.7, 129.5, 134.2, 149.1, 149.2, 169.7. IR (NaCl) ν_{max} 2983, 2927, 2911, 1768, 1611, 1598, 1468, 1344, 1283, 1255, 1216, 1025, 980 cm^{-1}. HREIMS *m/z* 284.0813 $(M)^+$, calcd for $C_{13}H_{17}O_5P$ 284.0814.

3-(Ethoxycarbonyl)methyl-5-methylphthalide (2k)



79% (18.5 mg), a colorless solid (EtOAc : *n*-Hexane = 1:5), mp 87-90 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J = 7.2 Hz, 3H), 2.49 (s, 3H), 2.84 (dd, J = 6.4, 16.4 Hz, 1H), 2.90 (dd, J = 6.8, 16.4 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 5.83 (t, J = 6.6 Hz, 1H), 7.28 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.1, 39.6, 61.2, 76.7, 122.4, 123.4, 125.6, 130.7, 145.5, 149.4, 169.3, 169.9. IR (NaCl) ν_{max} 1767, 1736, 1619, 1380, 1342, 1281, 1181, 1056, 1015 cm^{-1}. HREIMS *m/z* 234.0891 $(M)^+$, calcd for $C_{13}H_{14}O_4$ 234.0892.

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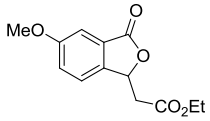
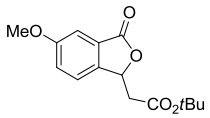
[18] (a) Yaremenko, A. G.; Shelyakin, V. V.; Volochnyuk, D. M.; Rusanov, E. B.; Grygorenko, O. O. *Tetrahedron Lett.* **2013**, *54*, 1195. (b) Paradkar, M. V.; Gadre, S. Y.; Pujari, T. A.; Khandekar, P. P.; Kumbhar, V. B. *Synth. Commun.* **2005**, *35*, 471.

3-(Ethoxycarbonyl)methyl-6-methoxyphthalide (2l)



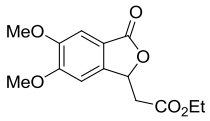
77% (19.3 mg), a white solid (EtOAc : *n*-Hexane = 1:2), mp 58-64 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J = 7.2 Hz, 3H), 2.82 (dd, J = 6.0, 16.4 Hz, 1H), 2.91 (dd, J = 6.8, 16.4 Hz, 1H), 3.87 (s, 3H), 4.21 (q, J = 7.1 Hz, 2H), 5.83 (t, J = 6.4 Hz, 1H), 7.23 (dd, J = 2.0, 8.4 Hz, 1H), 7.33 (d, J = 1.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 39.7, 55.8, 61.2, 76.8, 107.6, 123.0, 123.1, 127.3, 141.1, 160.9, 169.3, 169.9. IR (NaCl) ν_{max} 1767, 1735, 1497, 1324, 1283, 1244, 1179, 1055, 1022, 1005 cm^{-1}. HREIMS *m/z* 250.0841 $(M)^+$, calcd for $C_{13}H_{14}O_5$ 250.0841.

3-(*tert*-Butoxycarbonyl)methyl-6-methoxyphthalide (2m)



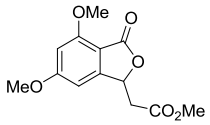
92% (25.6 mg), a white solid (EtOAc : *n*-Hexane = 1:2), mp 65-70 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (s, 9H), 2.75 (dd, J = 6.0, 16.4 Hz, 1H), 2.84 (dd, J = 6.8, 16.0 Hz, 1H), 3.86 (s, 3H), 5.78 (t, J = 6.4 Hz, 1H), 7.22 (dd, J = 2.2, 8.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 40.8, 55.8, 77.2, 81.9, 107.6, 123.0, 127.5, 141.4, 160.9, 168.5, 170.0 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2980, 2934, 1767, 1729, 1497, 1325, 1282, 1153, 1055 cm^{-1}. HREIMS *m/z* 278.1158 $(M)^+$, calcd for $C_{15}H_{18}O_5$ 278.1154.

3-(Ethoxycarbonyl)methyl-5,6-dimethoxyphthalide (2n)



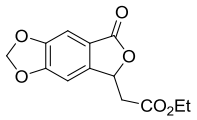
82% (23.0 mg), a yellow solid (EtOAc : *n*-Hexane = 1:2), mp 123-127 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, J = 7.2 Hz, 3H), 2.80 (dd, J = 6.6, 16.6 Hz, 1H), 2.94 (dd, J = 6.4, 16.4 Hz, 1H), 3.94 (s, 3H), 3.96 (s, 3H), 4.22 (q, J = 7.1 Hz, 2H), 5.77 (t, J = 6.6 Hz, 1H), 6.93 (s, 1H), 7.28 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 39.7, 56.3, 56.4, 61.2, 76.3, 103.7, 106.2, 117.9, 143.4, 150.8, 154.9, 169.5, 170.1. IR (NaCl) ν_{max} 2980, 2938, 1757, 1603, 1505, 1502, 1337, 1270, 1227, 1053, 1051, 1008, 1004 cm^{-1}. HREIMS *m/z* 280.0948 $(M)^+$, calcd for $C_{14}H_{16}O_6$ 280.0947.

3-(Ethoxycarbonyl)methyl-5,7-dimethoxyphthalide (2o)



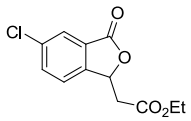
86% (22.9 mg), a white solid (EtOAc : *n*-Hexane = 1:2), mp 138-146 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.81 (dd, J = 5.6, 16.0 Hz, 1H), 2.86 (dd, J = 6.0, 15.2 Hz, 1H), 3.75 (s, 3H), 3.87 (s, 3H), 3.94 (s, 3H), 5.71 (t, J = 6.6 Hz, 1H), 6.43 (s, 1H), 6.47 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.5, 52.2, 55.9, 56.0, 75.5, 97.7, 99.0, 106.4, 153.6, 159.6, 166.9, 167.7, 169.9. IR (NaCl) ν_{max} 2950, 1724, 1723, 1672, 1594, 1268, 1152, 933, 830 cm^{-1}. EIMS *m*/*z* 266 (M^+), 206, 193, 177, 165, 150, 135, 122, 106, 77, 51.
Spectral data were consistent with data reported in the literature.[19]

3-(Ethoxycarbonyl)methyl-5,6-methylenedioxyphthalide (2p)



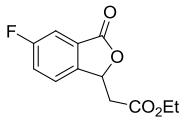
80% (21.1 mg), a white solid (EtOAc : *n*-Hexane = 1:2), mp 124-130 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, J = 7.2 Hz, 3H), 2.78 (dd, J = 6.4, 16.4 Hz, 1H), 2.91 (dd, J = 7.0, 16.6 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 5.74 (t, J = 6.6 Hz, 1H), 6.13 (d, J = 2.8 Hz, 2H), 6.87 (s, 1H), 7.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 39.6, 61.2, 76.3, 102.0, 102.7, 104.4, 119.7, 145.5, 149.5, 153.8, 169.3, 169.4. IR (NaCl) ν_{max} 2964, 2926, 2857, 1740, 1469, 1101, 1027 cm^{-1}. HREIMS *m/z* 264.0633 $(M)^+$, calcd for $C_{13}H_{12}O_6$ 264.0634.

6-Chloro-3-(ethoxycarbonyl)methylphthalide (2q)



69% (17.5 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 86-91 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J = 7.2 Hz, 3H), 2.84 (dd, J = 6.6, 16.6 Hz, 1H), 2.97 (dd, J = 6.8, 16.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 5.86 (t, J = 6.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.64 (dd, J = 1.8, 8.2 Hz, 1H), 7.87 (d, J = 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 39.3, 61.3, 76.8, 123.5, 125.7, 127.8, 134.5, 135.9, 146.9, 168.3, 169.0. IR (NaCl) ν_{max} 2983, 1773, 1735, 1473, 1205, 1182, 1007 cm^{-1}. HREIMS *m/z* 254.0348 $(M)^+$, calcd for $C_{12}H_{11}ClO_4$ 254.0346.

3-(Ethoxycarbonyl)methyl-6-fluorophthalide (2r)

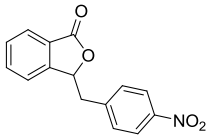


65% (15.5 mg), a brown solid (EtOAc : *n*-Hexane = 1:3), mp 69-75 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J = 7.2 Hz, 3H), 2.85 (dd, J = 6.6, 16.6 Hz, 1H), 2.97 (dd, J = 6.8, 16.8 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 5.86 (t, J = 6.6 Hz, 1H), 7.39 (td, J = 2.4, 8.4 Hz, 1H), 7.51 (dd, J = 4.2, 8.2 Hz, 1H), 7.56 (dd, J = 2.4, 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1,

[19] Choi, P. J.; Sperry, J.; Brimble, M. A. *J. Org. Chem.* **2010**, 75, 7388.

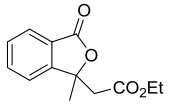
39.4, 61.3, 76.8, 112.2 (d, J = 23.4 Hz), 122.1 (d, J = 23.4 Hz), 124.0 (d, J = 8.0 Hz), 128.2 (d, J = 8.8 Hz), 144.3, 163.3, (d, J = 249.3 Hz), 168.6, 169.1. IR (NaCl) ν_{max} 1773, 1734, 1491, 1268, 1181, 1049, 1008 cm^{-1}. HREIMS *m/z* 238.0639 $(M)^+$, calcd for $C_{12}H_{11}FO_4$ 238.0641.

3-(4-Nitrobenzyl)phthalide (2t)



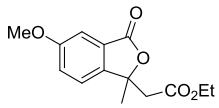
20% (5.4 mg), a yellow solid (EtOAc : *n*-Hexane = 1:4), mp 148-154 ℃.
^1H NMR ($CDCl_3$, 400 MHz) δ 3.26 (dd, J = 7.0, 14.2 Hz, 1H), 3.45 (dd, J = 4.6, 14.6 Hz, 1H), 5.75 (t, J = 6.0 Hz, 1H), 7.377 (d, J = 6.8 Hz, 1H), 7.379 (d, J = 8.8 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.4, 80.1, 121.9, 123.7, 126.1, 126.2. 129.7, 130.6, 134.2, 142.5, 147.2, 148.2, 169.8. HREIMS *m/z* 269.0688 $(M)^+$, calcd for $C_{15}H_{11}NO_4$ 269.0688.

3-(Ethoxycarbonyl)methyl-3-methylphthalide (4a)



58% (13.6 mg), a yellow oil (EtOAc : *n*-Hexane = 1:5)
^1H NMR ($CDCl_3$, 400 MHz) δ 1.10 (t, J = 7.2 Hz, 3H), 1.76 (s, 3H), 2.99 (s, 2H), 4.01 (q, J = 7.2 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 26.3, 44.1, 60.8, 84.2, 121.4, 125.6, 126.0, 129.3, 134.1, 152.5, 168.4, 169.4. IR (NaCl) ν_{max} 2979, 2934, 1769, 1736, 1640, 1467, 1370, 1342, 1287, 1239, 1176, 1115, 1035 cm^{-1}. EIMS *m/z* 234 (M^+), 177, 147, 129, 115, 104, 91, 76, 51.
Spectral data were consistent with data reported in the literature.[20]

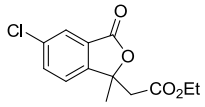
3-(Ethoxycarbonyl)methyl-6-methoxy-3-methylphthalide (4b)



71% (18.6 mg), a colorless oil (EtOAc : *n*-Hexane = 1:3)
^1H NMR ($CDCl_3$, 400 MHz) δ 1.14 (t, J = 7.4 Hz, 3H), 1.74 (s, 3H), 2.95 (s, 2H), 3.86 (s, 3H), 4.03 (q, J = 6.9 Hz, 2H), 7.21 (dd, J = 2.2, 8.6 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 26.4, 44.2, 55.8, 60.8, 84.1, 107.5, 122.4, 122.8, 127.4, 144.9, 160.7, 168.6, 169.4. IR (NaCl) ν_{max} 2982, 2938, 1763, 1734, 1624, 1496, 1466, 1283, 1038 cm^{-1}. HREIMS *m/z* 264.0997 $(M)^+$, calcd for $C_{14}H_{16}O_5$ 264.0998.

[20] Cozzi, P.; Carganico, G.; Orsini, G.; *J. Med. Chem.* **1983**, *26*, 1764.

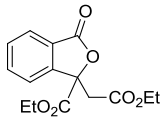
6-Chloro-3-(ethoxycarbonyl)methyl-3-methylphthalide (4c)



70% (18.8 mg), a colorless oil (EtOAc : *n*-Hexane = 1:4)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.13 (t, J = 7.0 Hz, 3H), 1.75 (s, 3H), 2.98 (s, 2H), 4.02 (q, J = 7.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 26.3, 43.8, 60.9, 84.2, 122.9, 125.5, 127.9, 134.3, 135.6, 150.6, 167.9, 168.3. IR (NaCl) ν_{max} 2986, 1768, 1736, 1424, 1257, 1035 cm^{-1}. HREIMS *m/z* 268.0496 $(M)^+$, calcd for $C_{13}H_{13}ClO_4$ 268.0502.

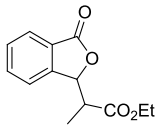
Ethyl 1-(2-Ethoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-1-carboxylate (4d)



59% (17.2 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.0 Hz, 3H), 2.94 (d, J = 16.8 Hz, 1H), 3.58 (d, J = 16.8 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 4.18-4.31 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 14.0, 41.7, 61.3, 62.9, 84.1, 122.1, 125.4, 126.0, 130.5, 134.7, 146.9, 167.9, 168.2, 168.8. IR (NaCl) ν_{max} 2985, 2967, 1783, 1738, 1467, 1375, 1210, 1053 cm^{-1}. HREIMS *m/z* 292.0944 $(M)^+$, calcd for $C_{15}H_{16}O_6$ 292.0947.

Ethyl 2-(3-Oxo-1,3-dihydroisobenzofuran-1-yl)propanoate (4e)



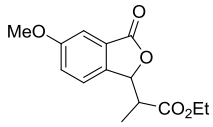
79% (18.5 mg), a colorless oil (EtOAc : *n*-Hexane = 1:4)

The compounds existed as a 51:49 mixture of two diastereomers (*anti*:*syn* = 51:49) in the crude mixture, but after isolation, the ratio became *anti*:*syn* = 81:19.

Signals corresponding to *anti*-**4e**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.07 (d, J = 6.8 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 3.20 (dq, J = 4.6, 7.2 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 5.85 (d, J = 4.4 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.0, 14.1, 42.9, 61.2, 80.8, 122.9, 125.8, 126.9, 129.5, 134.0, 147.0, 170.1, 172.2. Representative signals corresponding to *syn*-**4e**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (d, J = 6.8 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 3.20 (quintet, J = 6.5 Hz, 1H), 4.24 (q, J = 7.4 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.5, 14.1, 44.0, 61.3, 81.1, 122.1, 125.9, 126.4, 129.5, 134.3, 147.9, 172.5 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2985, 2943, 2909, 1769, 1733, 1614, 1596, 1466, 1288, 1186, 1062 cm^{-1}. HREIMS *m/z* 234.0893 $(M)^+$, calcd for $C_{13}H_{14}O_4$ 234.0892.

The relative configuration of two diastereomers was assigned based on spectral correlation with its related congeners.[17b, 21]

Ethyl 2-(5-Methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)propanoate (4f)



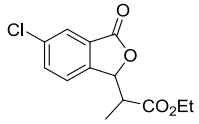
76% (20.1 mg), a colorless oil (EtOAc : *n*-Hexane = 1:4)

The compounds exist as a 48:52 mixture of two diastereomers (*anti*:*syn* = 48:52).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (d, J = 6.8 Hz, 3H, *anti*), 1.15 (d, J = 6.8 Hz, 3H, *syn*), 1.25 (t, J = 7.0 Hz, 3H, *anti*), 1.27 (t, J = 7.0 Hz, 3H, *syn*), 2.84 (quintet, J = 6.7 Hz, 1H, *syn*), 3.14 (quintet, J = 6.5 Hz, 1H, *anti*), 3.86 (s, 3H), 4.20 (dq, J = 7.2, 9.6 Hz, 2H), 5.76 (d, J = 5.2 Hz, 1H, *syn*), 5.78 (d, J = 4.0 Hz, 1H, *anti*), 7.19-7.22 (m, 1H), 7.28-7.36 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.9, 11.6, 14.09, 14.12, 43.0, 44.1, 55.7, 55.8, 61.1, 61.2, 80.7, 81.0, 107.57, 107.64, 122.8, 123.0, 123.1, 123.9, 127.8, 128.3, 139.3, 140.3, 160.9, 170.1, 172.4, 172.5 (2 carbon are missing due to overlapping). IR (NaCl) ν_{max} 2982, 2946, 1769, 1733, 1621, 1497, 1325, 1286, 1059 cm^{-1}. HREIMS *m/z* 264.0998 $(M)^+$, calcd for $C_{14}H_{16}O_5$ 264.0998.

The relative configuration of two diastereomers was assigned based on spectral correlation with its related congeners.[17b, 21]

Ethyl 2-(5-Chloro-3-oxo-1,3-dihydroisobenzofuran-1-yl)propanoate (4g)



64% (17.2 mg), a colorless oil (EtOAc : *n*-Hexane = 1:4),

The compounds exist as a 49:51 mixture of two diastereomers (*anti*:*syn* = 49:51).

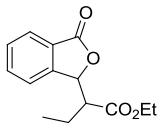
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05 (d, J = 7.6 Hz, 3H, *anti*), 1.19 (d, J = 6.8 Hz, 3H, *syn*), 1.26 (t, J = 7.2 Hz, 3H, *anti*), 1.29 (t, J = 7.0 Hz, 3H, *syn*), 2.87 (quintet, J = 6.7 Hz, 1H, *syn*), 3.20 (dq, J = 4.2, 7.2 Hz, 1H, *anti*), 4.20 (q, J = 7.0 Hz, 2H), 4.23 (q, J = 7.2 Hz, 2H), 5.81 (d, J = 6.0 Hz, 1H, *syn*), 5.83 (d, J = 4.8 Hz, 1H, *anti*), 7.38 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.62 (dd, J = 2.2, 7.6 Hz, 1H), 7.64 (dd, J = 2.0, 8.0 Hz, 1H), 7.87 (s, 1H x 2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.9, 11.9, 14.10, 14.12, 42.7, 44.0, 61.3, 61.4, 80.7, 81.0, 123.5, 124.4, 125.6, 125.8, 128.2, 128.7, 134.3, 134.5, 135.85, 135.90, 145.2, 146.1, 168.58, 168.62, 172.1, 172.3. IR (NaCl) ν_{max} 2986, 1774, 1734, 1469, 1425, 1338, 1293, 1207, 1190, 1054, 1001 cm^{-1}. HREIMS *m/z* 268.0498 $(M)^+$, calcd for $C_{13}H_{13}ClO_4$ 268.0502.

The relative configuration of two diastereomers was assigned based on spectral correlation with its

[21] Guindon, Y.; Slassi, A.; Rancourt, J.; Bantle, G.; Bencheqroun, M.; Murtagh, L.; Ghiro, É.; Jung, G. *J. Org. Chem.* **1995**, *60*, 288.

related congeners.[17b, 21]

Ethyl 2-(3-Oxo-1,3-dihydroisobenzofuran-1-yl)butanoate (4h)



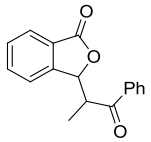
97% (24.1 mg), a colorless oil (EtOAc : *n*-Hexane = 1:4)

The compounds exist as a 53:47 mixture of two diastereomers (*anti*:*syn* = 53:47).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.98 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H, *anti*), 1.28 (t, *J* = 7.2 Hz, 3H, *syn*), 1.65-1.76 (m, 2H), 1.78-1.88 (m, 1H), 1.90-1.99 (m, 1H), 2.61 (td, *J* = 4.0, 8.6 Hz, 1H, *syn*), 2.88 (dt, *J* = 5.2, 9.2 Hz, 1H, *anti*), 4.11 (q, *J* = 7.2 Hz, 2H, *anti*), 4.23 (q, *J* = 6.9 Hz, 2H, *syn*), 5.69 (d, *J* = 7.6 Hz, 1H, *syn*), 5.70 (d, *J* = 4.8 Hz, 1H, *anti*), 7.39 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H x 2), 7.55 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 6.8 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H x 2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.4, 11.9, 14.0, 14.2, 20.7, 22.1, 50.7, 51.9, 60.9, 61.0, 80.3, 80.4, 122.4, 122.9, 125.7, 125.8, 126.1, 126.7, 129.4, 129.5, 133.9, 134.1, 147.3, 148.3, 170.0, 171.6, 172.2 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2974, 2937, 1771, 1732, 1466, 1287, 1184, 1058, 1017 cm^{-1}. HREIMS *m/z* 248.1049 $(M)^+$, calcd for $C_{14}H_{16}O_4$ 248.1049.

The relative configuration of two diastereomers was assigned based on spectral correlation with its related congeners.[17b, 21]

3-(1-Oxo-1-phenylpropan-2-yl)isobenzofuran-1(3*H*)-one (4i)



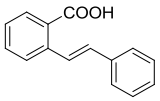
78% (20.8 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4)

The compounds exist as a 45:55 mixture of two diastereomers (*anti*:*syn* = 45:55).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.11 (d, *J* = 7.2 Hz, 3H, *anti*), 1.53 (d, *J* = 7.2 Hz, 3H, *syn*), 3.68 (quintet, *J* = 7.2 Hz, 1H, *syn*), 4.09 (dq, *J* = 5.0, 7.0 Hz, 1H, *anti*), 5.92 (d, *J* = 9.2 Hz, 1H, *syn*), 5.96 (d, *J* = 5.2 Hz, 1H, *anti*), 7.33 (d, *J* = 7.2 Hz, 1H), 7.46-7.69 (m, 11H), 7.88-7.94 (m, 4H), 7.99 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.2, 16.1, 44.8, 46.9, 81.3, 82.1, 123.2, 124.1, 125.72, 125.74, 126.0, 127.0, 128.4, 128.5, 128.9, 129.4, 133.7, 133.8, 133.9, 134.2, 135.5, 135.6, 147.3, 148.8, 170.1, 170.2, 200.6, 201.2 (2 carbons are missing due to overlapping). IR (NaCl) ν_{max} 2969, 2937, 1766, 1681, 1595, 1465, 1447, 1288, 1216, 1061, 972 cm^{-1}. HREIMS *m/z* 266.0943 $(M)^+$, calcd for $C_{17}H_{14}O_3$ 266.0943.

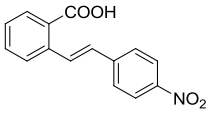
The relative configuration of two diastereomers was assigned based on spectral correlation with its related congeners.[17b, 21]

(*E*)-2-Styrylbenzoic Acid (5s)



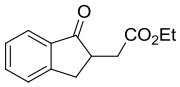
61% (13.7 mg), a white solid (CH_2Cl_2 : MeOH = 20:1), mp 142-148 ℃.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04 (d, J = 16.0 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.4 Hz, 3H), 7.57 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 15.6 Hz, 1H), 8.11 (d, J = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 126.9, 127.26, 127.31, 127.5, 127.9, 128.7, 131.6, 131.8, 133.1, 137.3, 140.2, 172.6 (1 carbon is missing due to overlapping). IR (NaCl) ν_{max} 2925, 1676, 1447, 1309, 967 cm^{-1}. EIMS *m*/*z* 224 (M^+), 185, 178, 129, 115, 105, 97, 83, 73, 69, 60, 57.
Spectral data were consistent with data reported in the literature.[22]

(*E*)-2-(4-Nitrostyryl)benzoic Acid (5t)



38% (10.2 mg), a yellow solid (CH_2Cl_2 : MeOH = 20:1), mp 178-182 ℃.
^{1}H NMR (acetone-d_6, 400 MHz) δ 7.29 (d, J = 16.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 8.27 (d, J = 8.8 Hz, 2H), 8.33 (d, J = 16.0 Hz, 1H). ^{13}C NMR (acetone-d_6, 100 MHz) δ 124.8, 128.0, 128.3, 129.1, 129.4, 130.4, 131.8. 133.1, 133.2, 139.0, 145.2, 147.8, 168.7. EIMS *m*/*z* 269 (M^+), 203, 175, 147, 131.
Spectral data were consistent with data reported in the literature.[23]

Ethyl 2-(1-Oxo-2,3-dihydro-1*H*-inden-2-yl)acetate (7)



71% (15.5 mg), a colorless oil (EtOAc : *n*-Hexane = 1:5)
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, J = 7.0 Hz, 3H), 2.63 (dd, J = 7.8, 16.6 Hz, 1H), 2.89 (dd, J = 4.4, 17.2 Hz, 1H), 2.97 (dd, J = 3.2, 17.2 Hz, 1H), 3.02 (quintet, J = 4.3 Hz, 1H), 3.46 (dd, J = 7.8, 17.0 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 33.0, 35.2, 43.5, 60.7, 124.0, 126.5, 127.5, 134.8, 136.3, 153.3, 172.0, 206.8. IR (NaCl) ν_{max} 2987, 2937, 1734, 1692, 1606, 1480, 1302, 1216, 1178, 1032, 1012 cm^{-1}. EIMS *m*/*z* 218 (M^+), 172, 145, 130, 115, 91, 77, 63.
Spectral data were consistent with data reported in the literature.[24]

Ethyl 2-(4-Oxochroman-3-yl)acetate (9)

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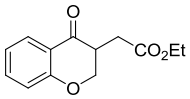
[22] Shahzad, S. A.; Venin, C.; Wirth, T.; *Eur. J. Org. Chem.* **2010**, 3465.

[23] Mitra, P.; Shome, B.; De, S. R.; Sarkar, A.; Mal, D. *Org. Biomol. Chem*. **2012**, *10*, 2742.

[24] Ozaki , S.; Adachi, M.; Sekiya, S.; Kamikawa, R. *J. Org. Chem.* **2003**, *68*, 4586.

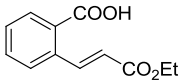


86% (20.1 mg), a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 35-38 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J = 7.0 Hz, 3H), 2.42 (dd, J = 8.0, 17.2 Hz, 1H), 2.94 (dd, J = 5.0, 17.0 Hz, 1H), 3.30-3.38 (m, 1H), 4.19 (qd, J = 1.8, 7.1 Hz, 2H), 4.30 (t, J = 11.6 Hz, 2H), 4.60 (dd, J = 5.4, 11.0 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 7.48 (td, J = 1.6, 7.8 Hz, 1H), 7.89 (dd, J = 1.6, 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 30.3, 42.5, 61.0, 70.2, 117.8, 120.5, 121.5, 127.4, 136.0, 161.7, 171.3, 192.6. IR (NaCl) ν_{max} 2985, 2934, 1734, 1691, 1603, 1480, 1301, 1178, 1037 cm^{-1}. EIMS m/z 234 (M^+), 189, 147, 120, 92, 77, 64, 51.

Spectral data were consistent with data reported in the literature.[25]

(*E*)-2-(3-Ethoxy-3-oxoprop-1-enyl)benzoic Acid (5a)



Under argon atmosphere, phthalaldehydic acid (261.6 mg, 1.708 mmol) was added to the solution of (carbethoxymethylene)triphenylphosphorane (688.0 mg, 1.878 mmol, 1.1 equiv) in DMF (8.5 ml, 0.2 M). The mixture was stirred at room temperature for 25 h. The reaction mixture was diluted with water and extracted with ether (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2 : MeOH = 30:1) to afford the desired product **5a** (177.4 mg, 47%) as a white solid.

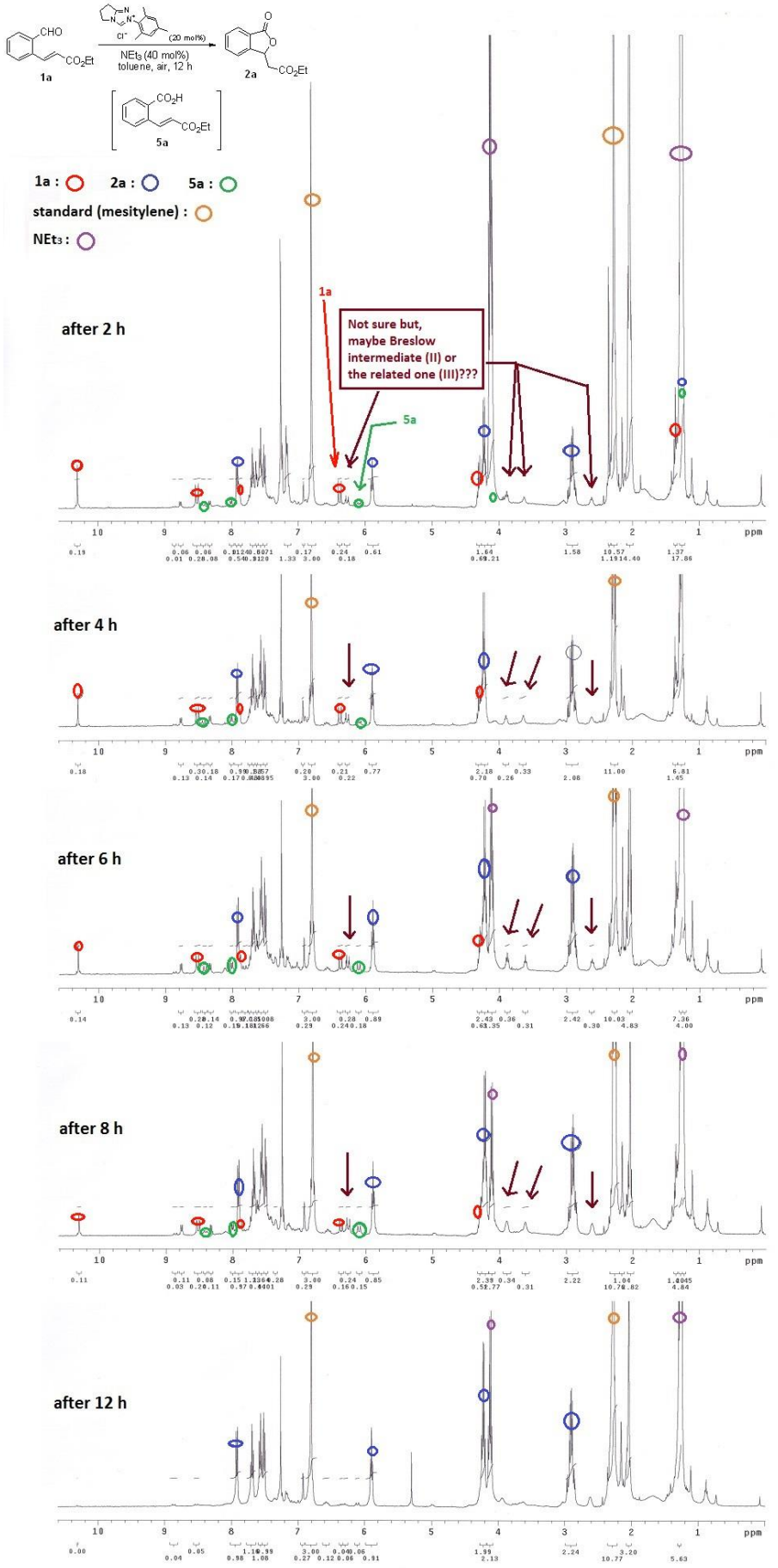
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, J = 6.8 Hz, 3H), 4.16 (q, J = 6.9 Hz, 2H), 6.17 (d, J = 15.6 Hz, 1H), 7.35 (t, J = 7.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 8.54 (d, J = 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 60.5, 118.7, 126.6, 129.1, 130.4, 130.7, 134.7, 135.0, 145.3, 167.5, 173.6. EIMS m/z 220 (M^+), 146, 133, 105.

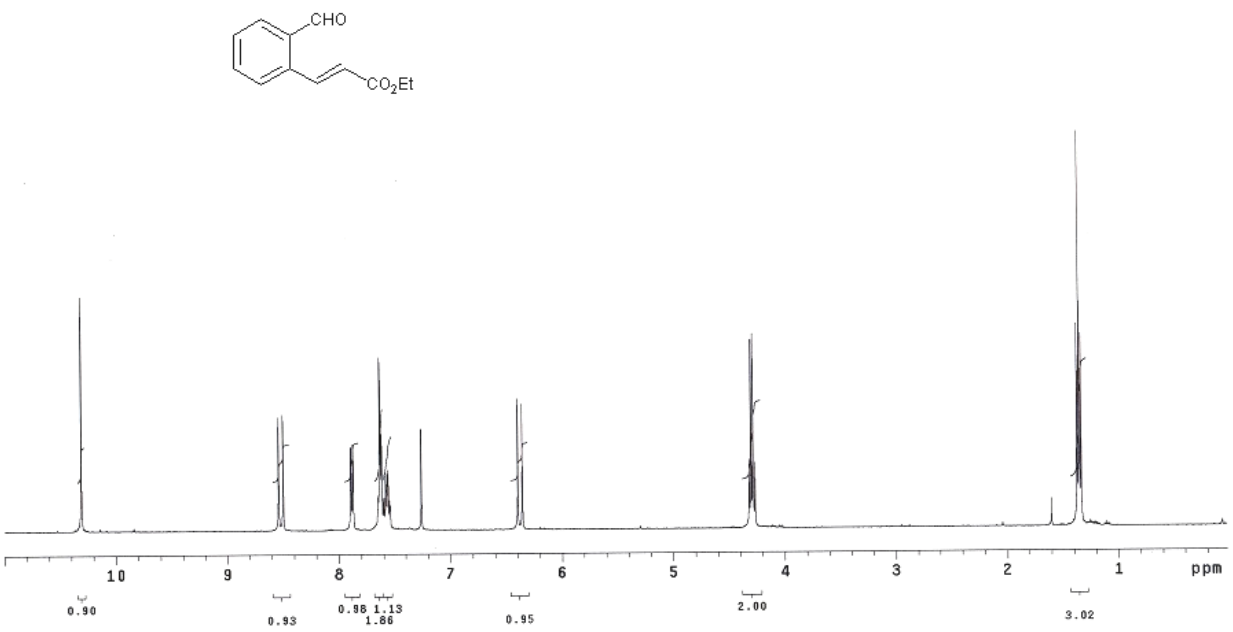
Spectral data were consistent with data reported in the literature.[26]

[25] Kerr, M. S.; de Alaniz, J. R.; Rovis, T. *J. Am. Chem. Soc*. **2002**, *124*, 10298.

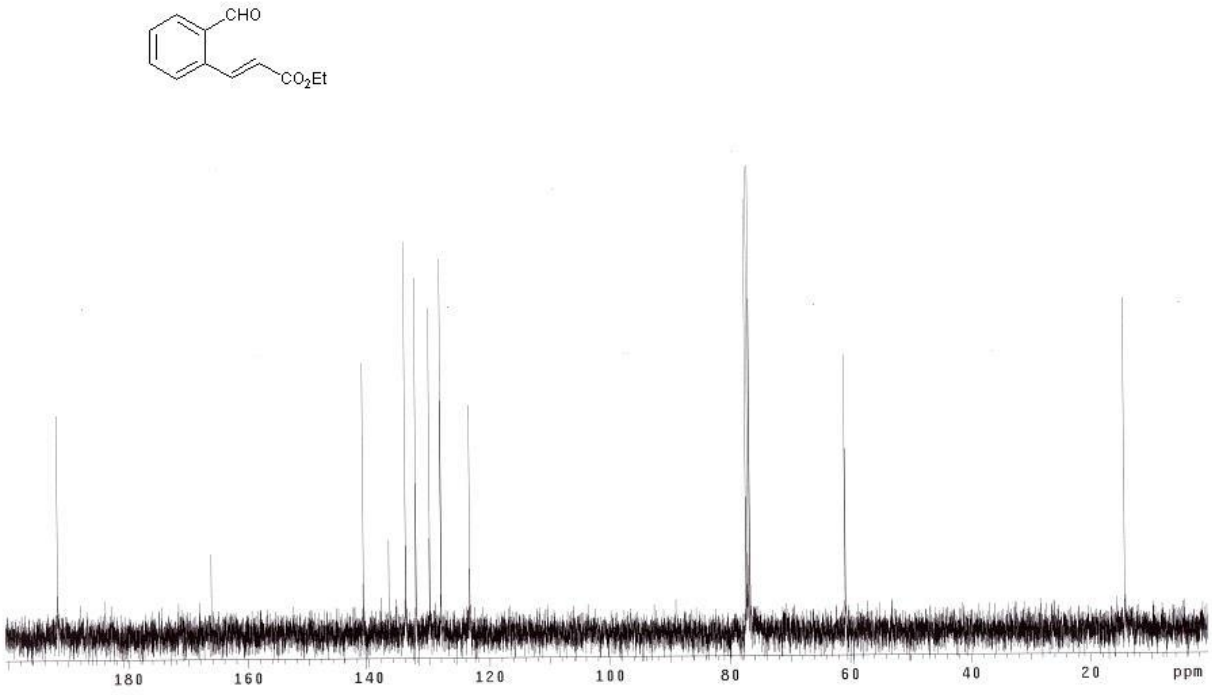
[26] Wu, N.; Messinis, A.; Batsanov, A. S.; Yang, Z.; Whiting, A.; Marder. T. B. *Chem. Commun*. **2012**, *48*, 9986.

^{1}H NMR Analysis Data during the Reaction of 1a (0~12 h)

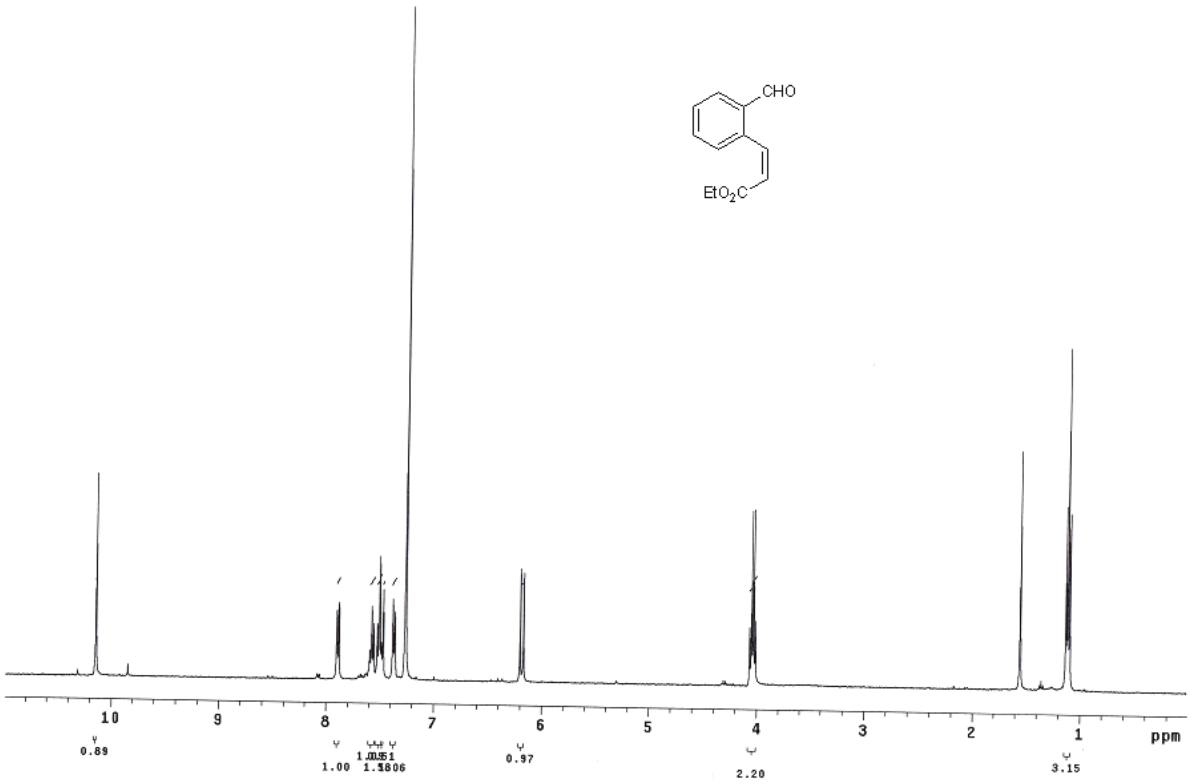




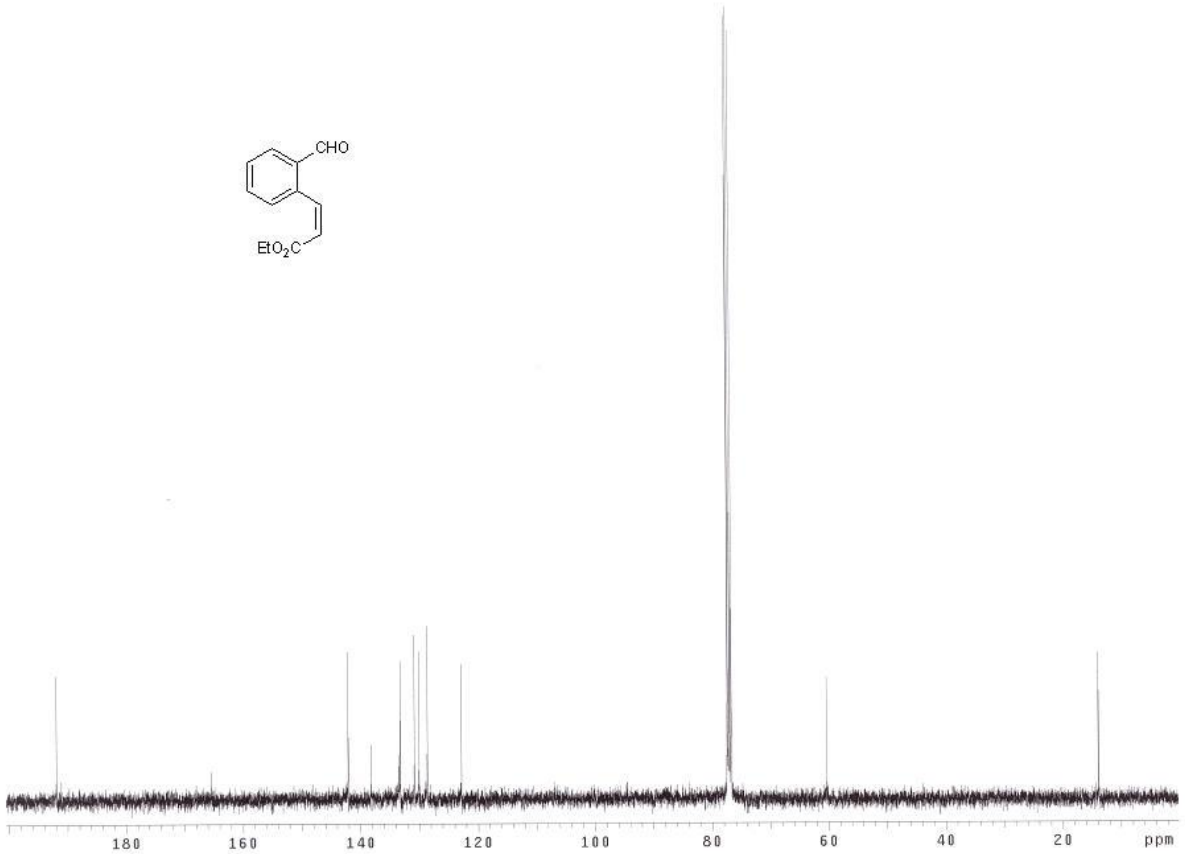
^{1}H NMR Spectrum of Compound **1a** ($CDCl_3$, 400 MHz)



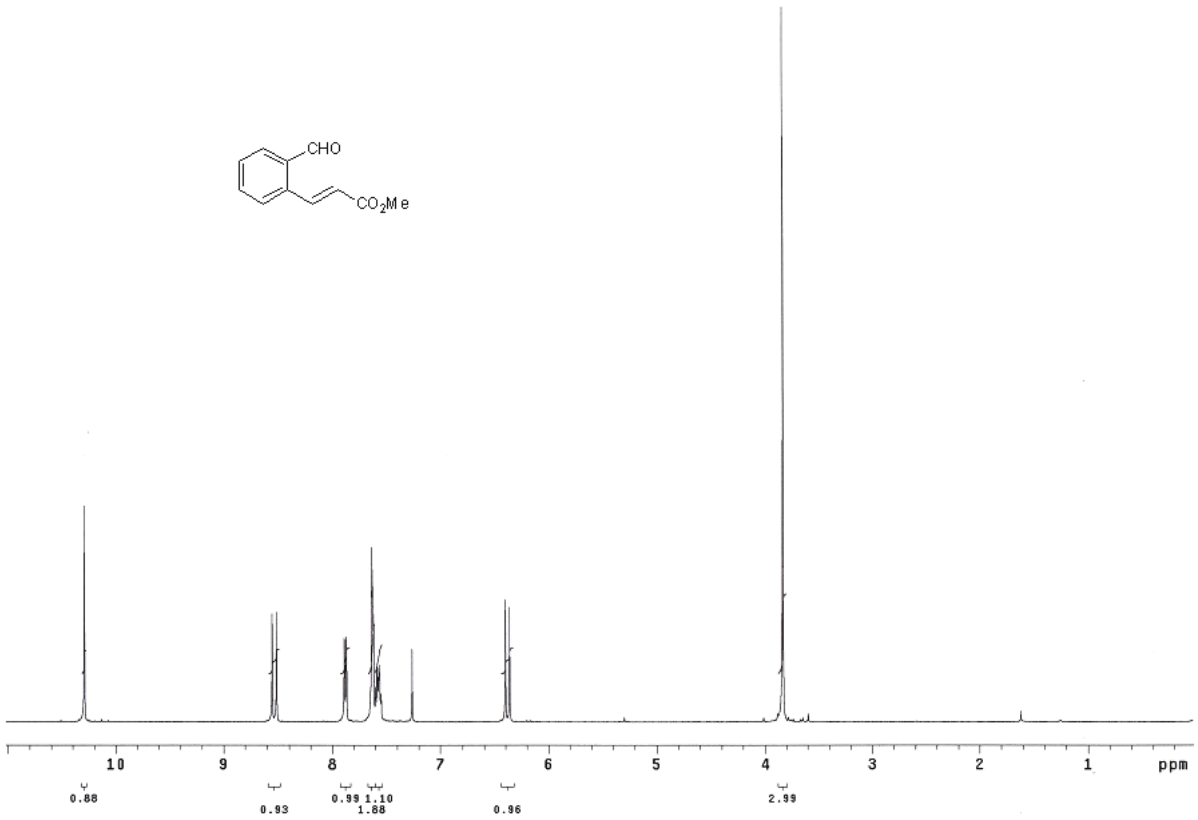
^{13}C NMR Spectrum of Compound **1a** ($CDCl_3$, 100 MHz)



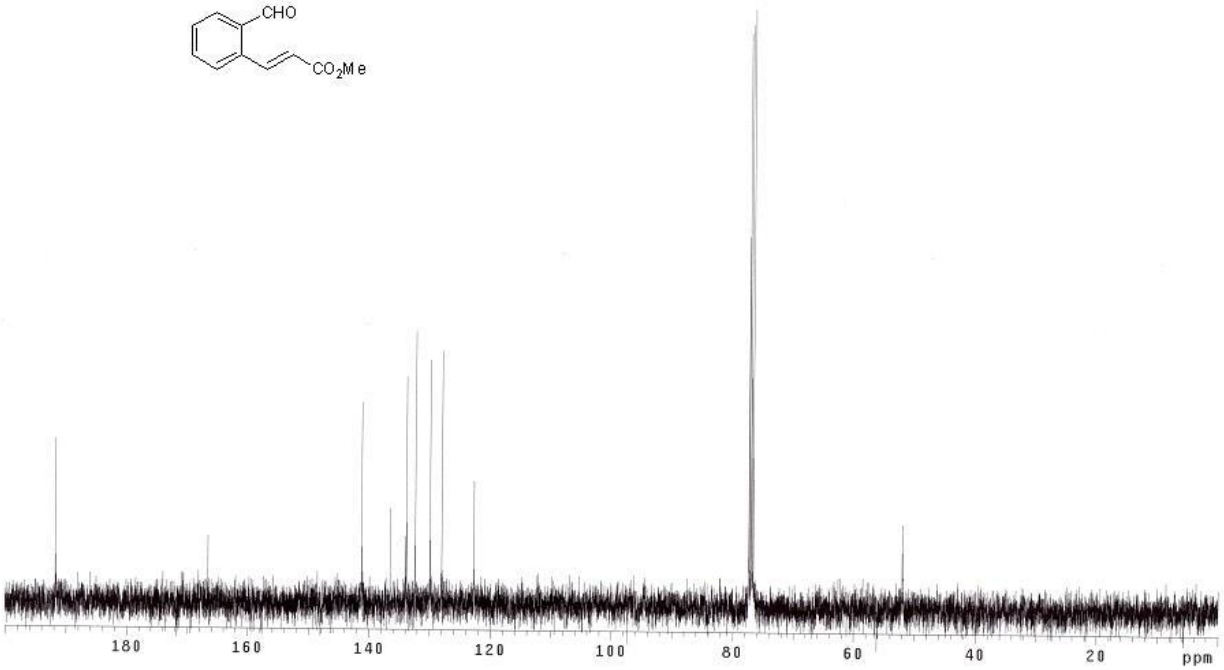
^{1}H NMR Spectrum of Compound **1a'** ($CDCl_3$, 400 MHz)



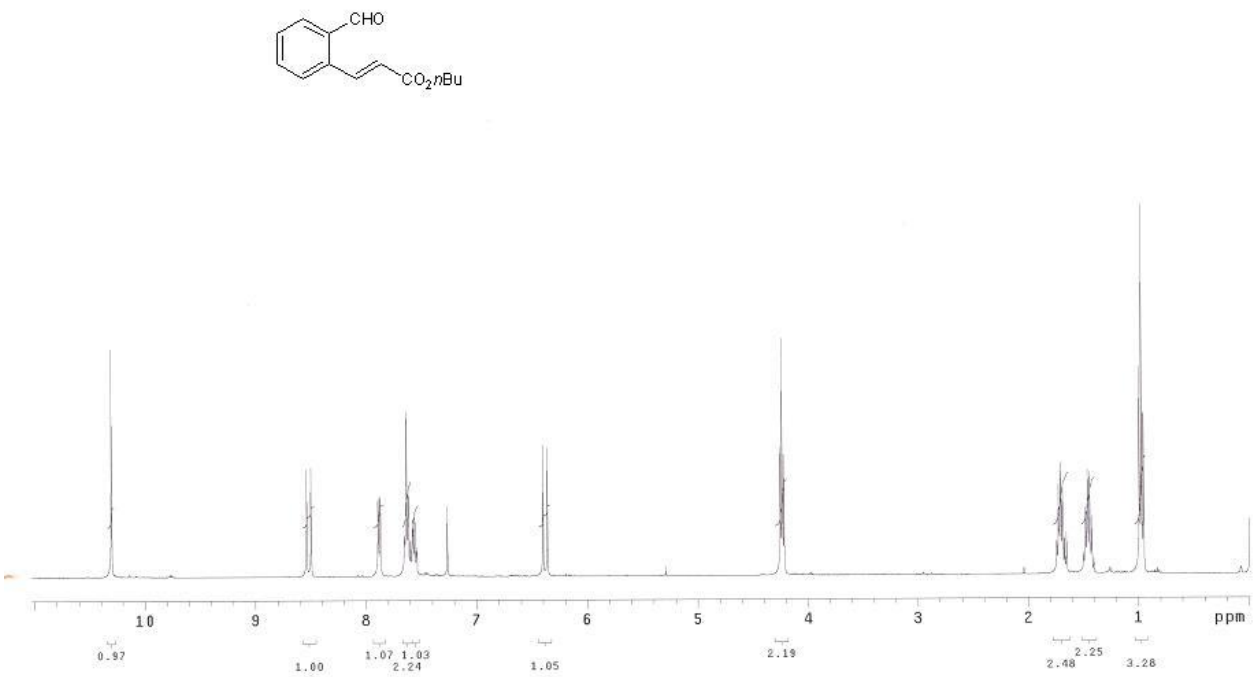
^{13}C NMR Spectrum of Compound **1a'** ($CDCl_3$, 100 MHz)



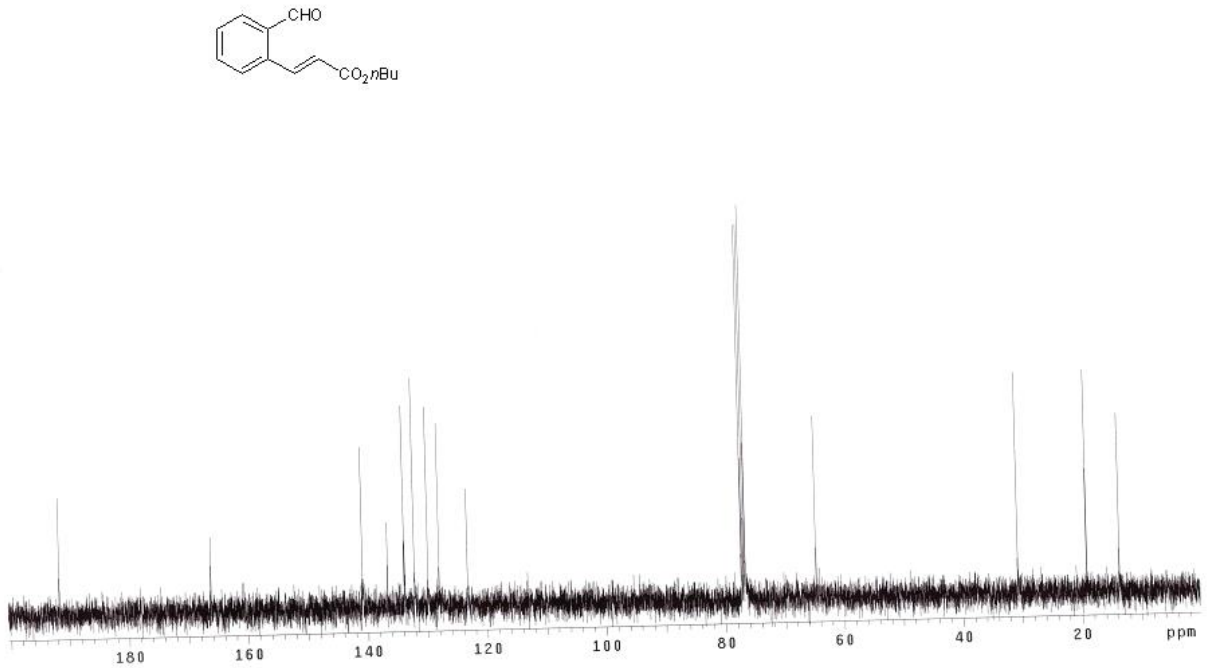
^{1}H NMR Spectrum of Compound **1b** ($CDCl_3$, 400 MHz)



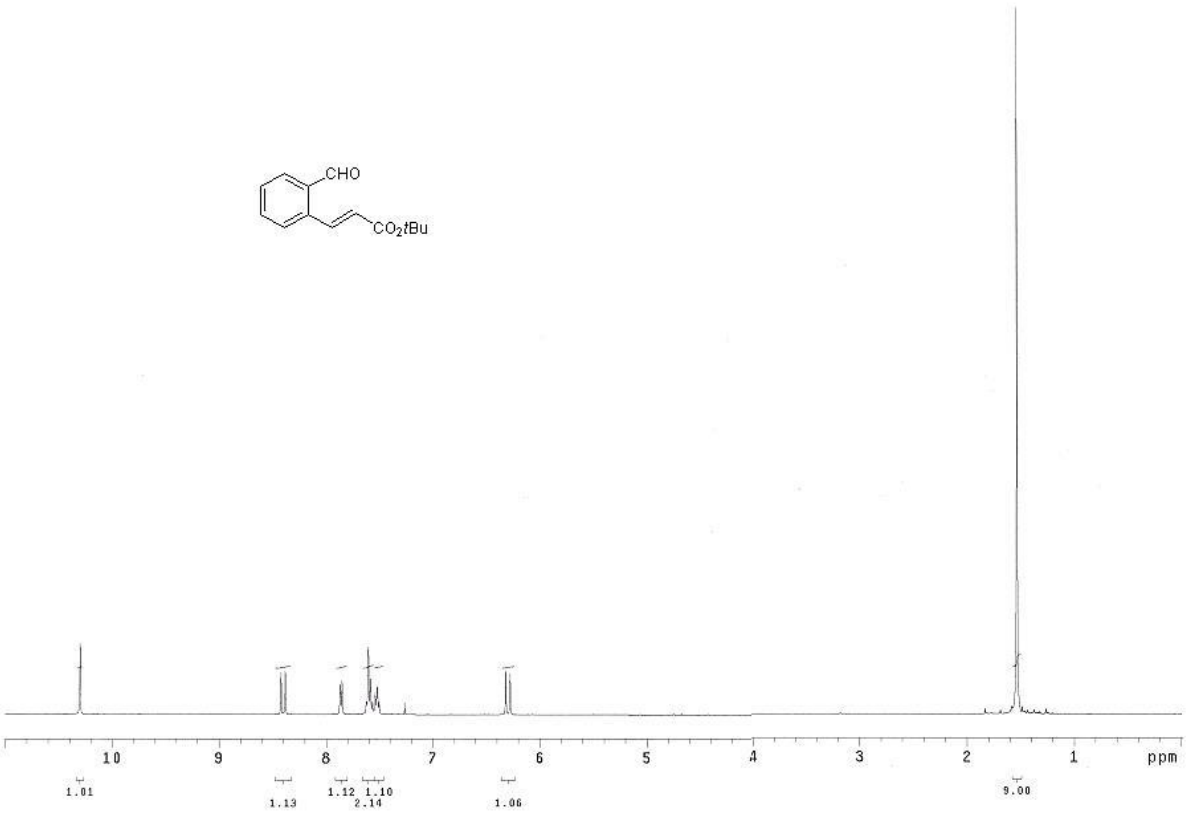
^{13}C NMR Spectrum of Compound **1b** ($CDCl_3$, 100 MHz)



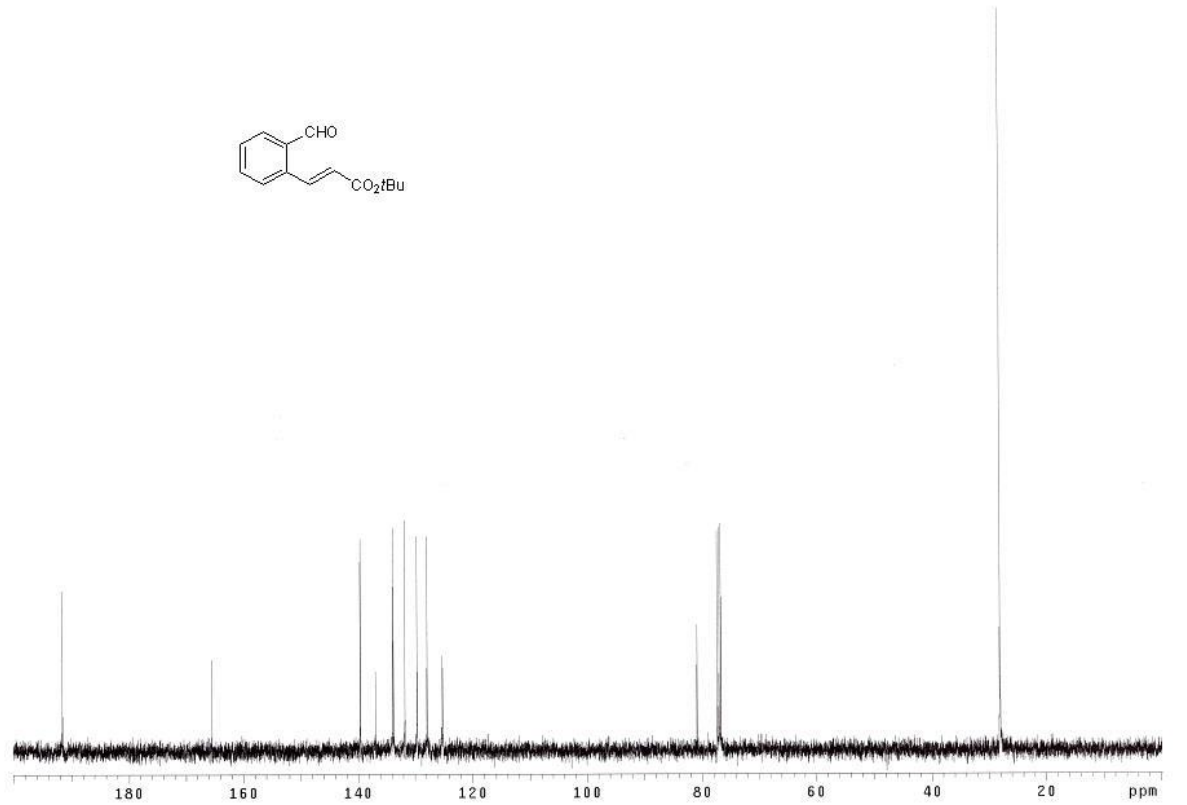
^{1}H NMR Spectrum of Compound **1c** ($CDCl_3$, 400 MHz)



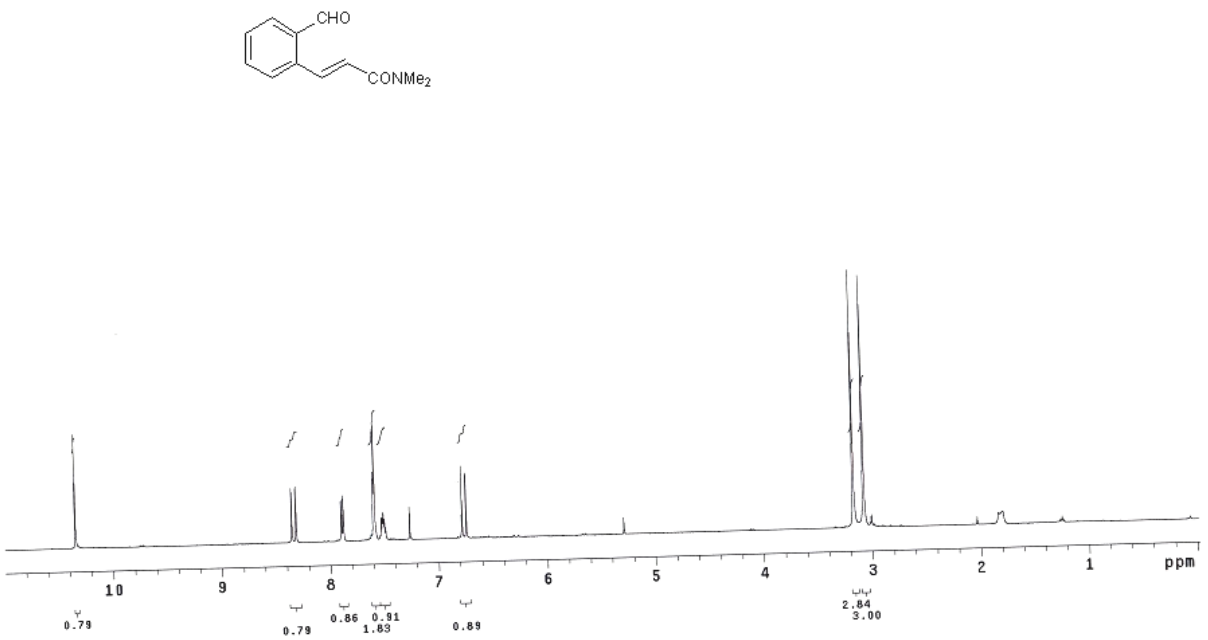
^{13}C NMR Spectrum of Compound **1c** ($CDCl_3$, 100 MHz)



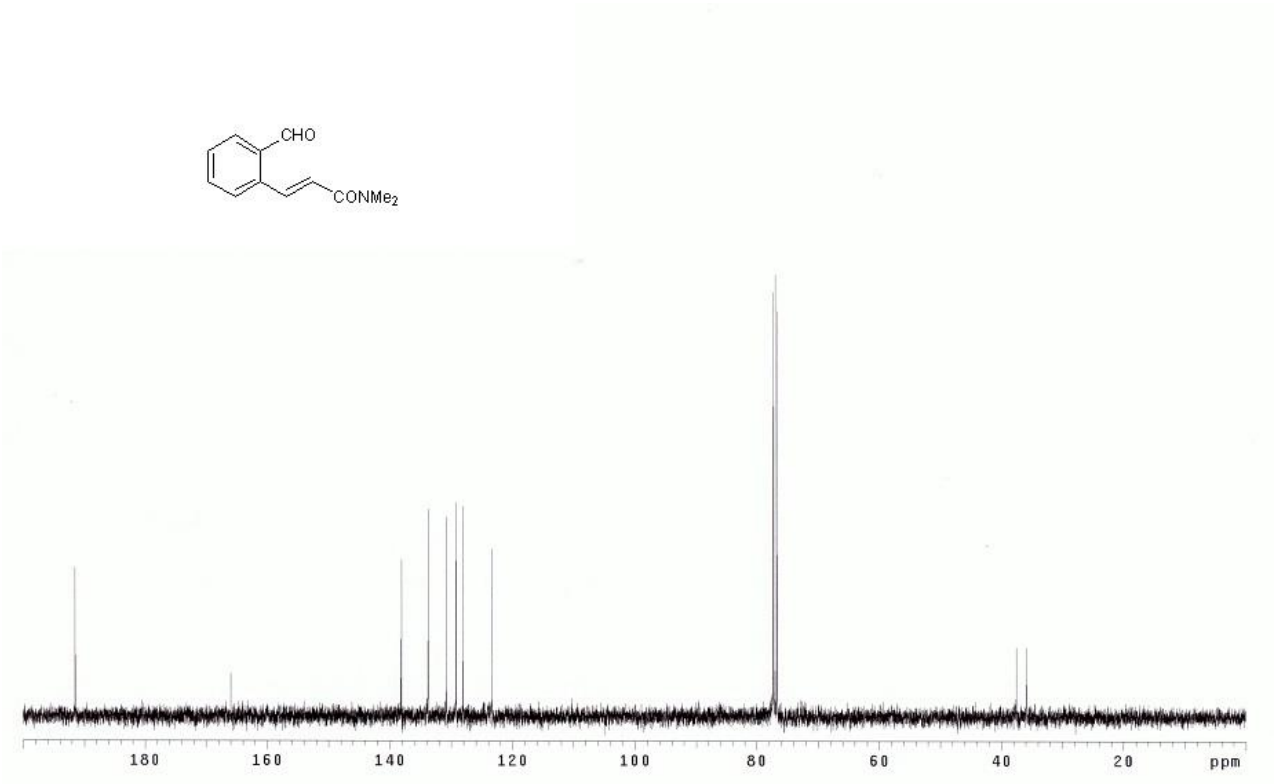
^{1}H NMR Spectrum of Compound **1d** ($CDCl_3$, 400 MHz)



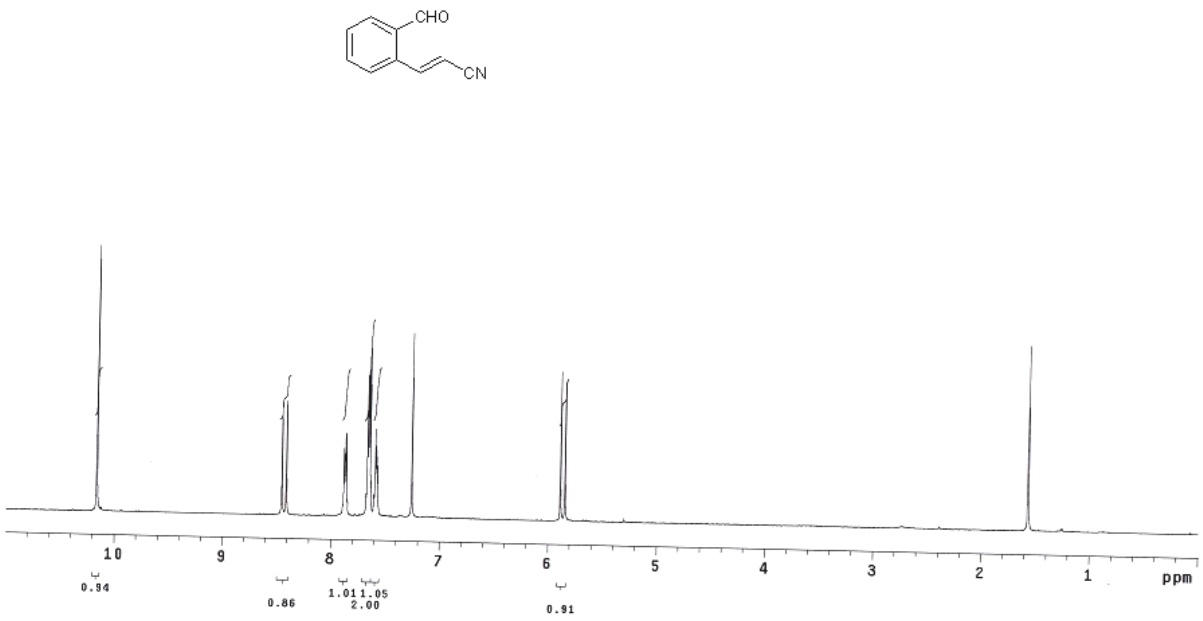
^{13}C NMR Spectrum of Compound **1d** ($CDCl_3$, 100 MHz)



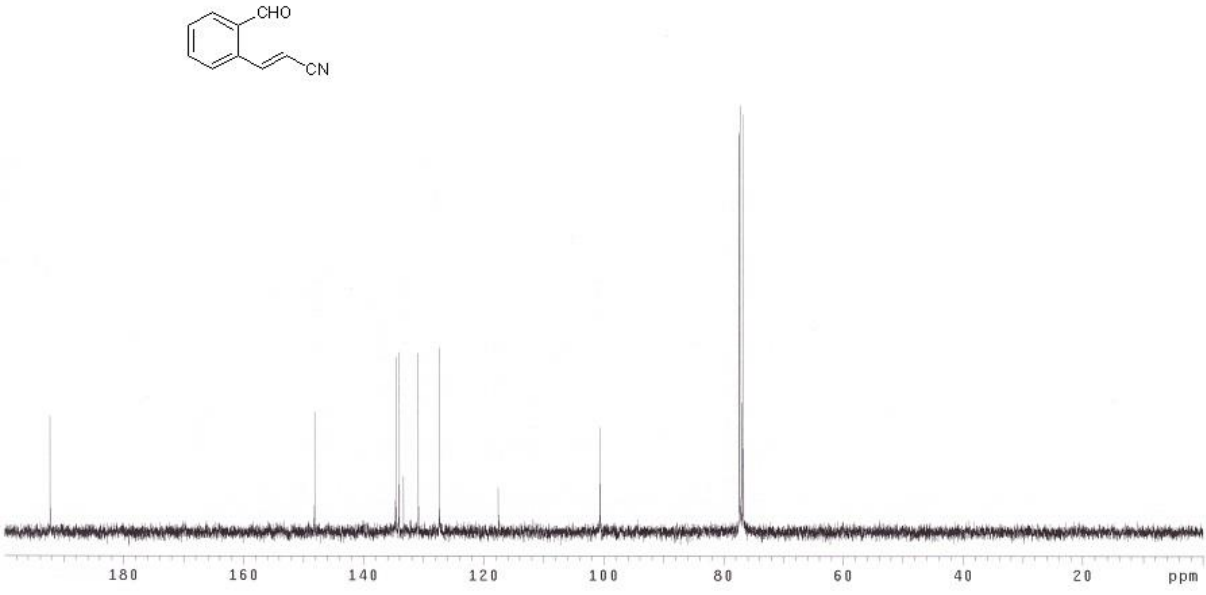
^{1}H NMR Spectrum of Compound **1e** ($CDCl_3$, 400 MHz)



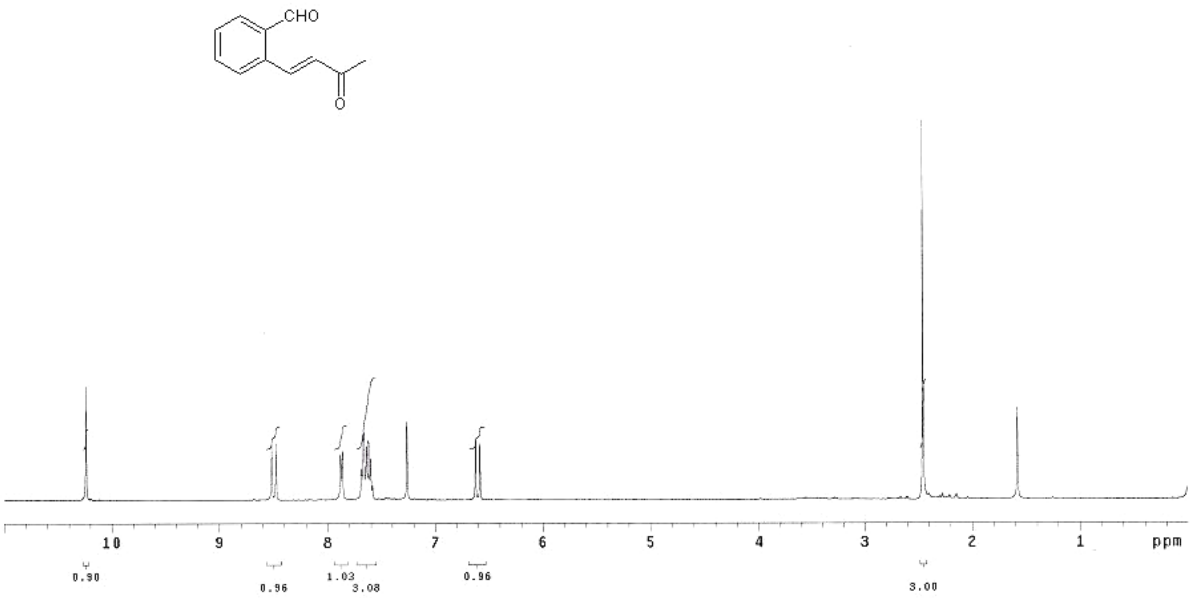
^{13}C NMR Spectrum of Compound **1e** ($CDCl_3$, 100 MHz)



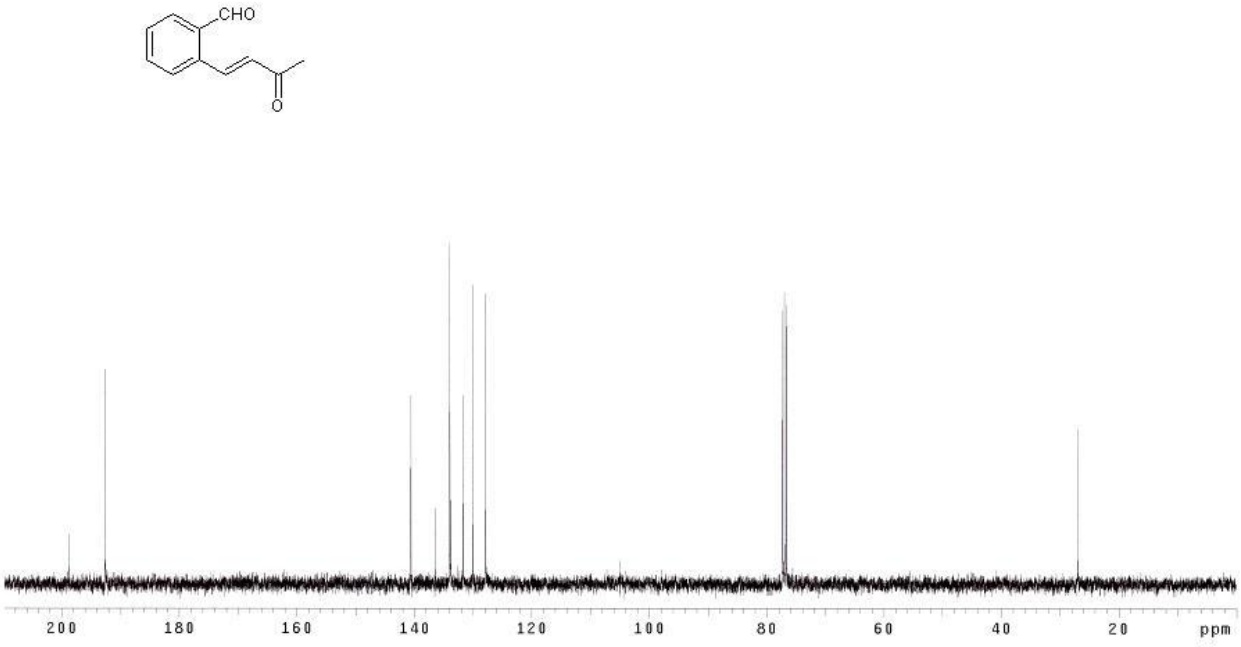
^{1}H NMR Spectrum of Compound **1f** ($CDCl_3$, 400 MHz)



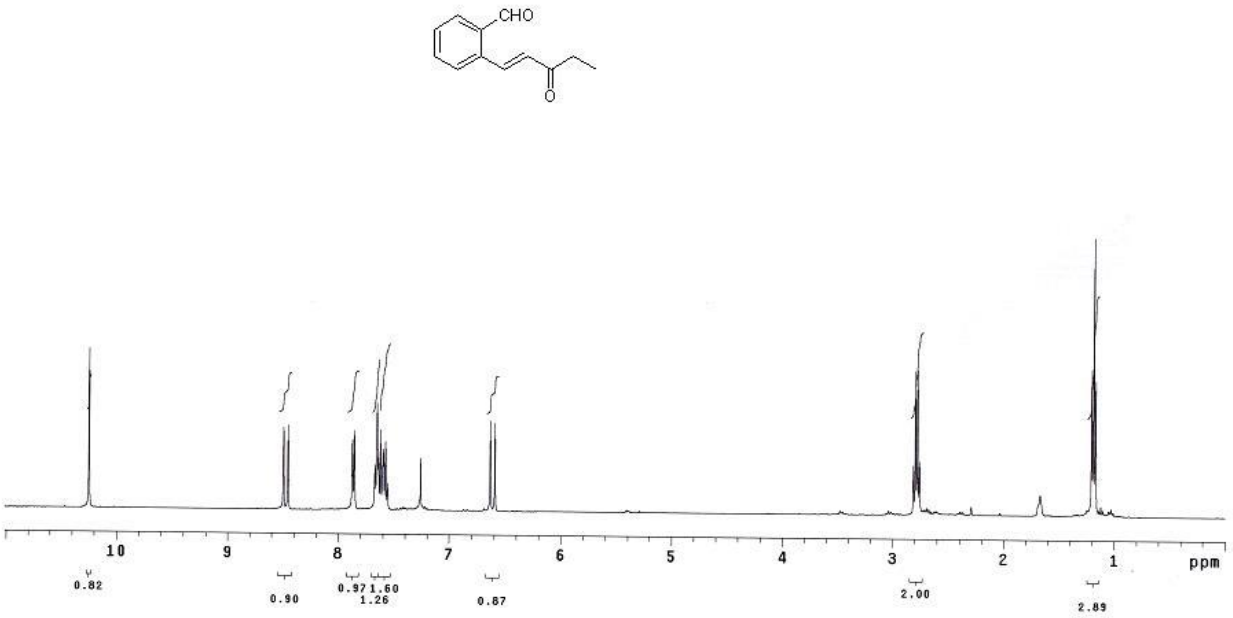
^{13}C NMR Spectrum of Compound **1f** ($CDCl_3$, 100 MHz)



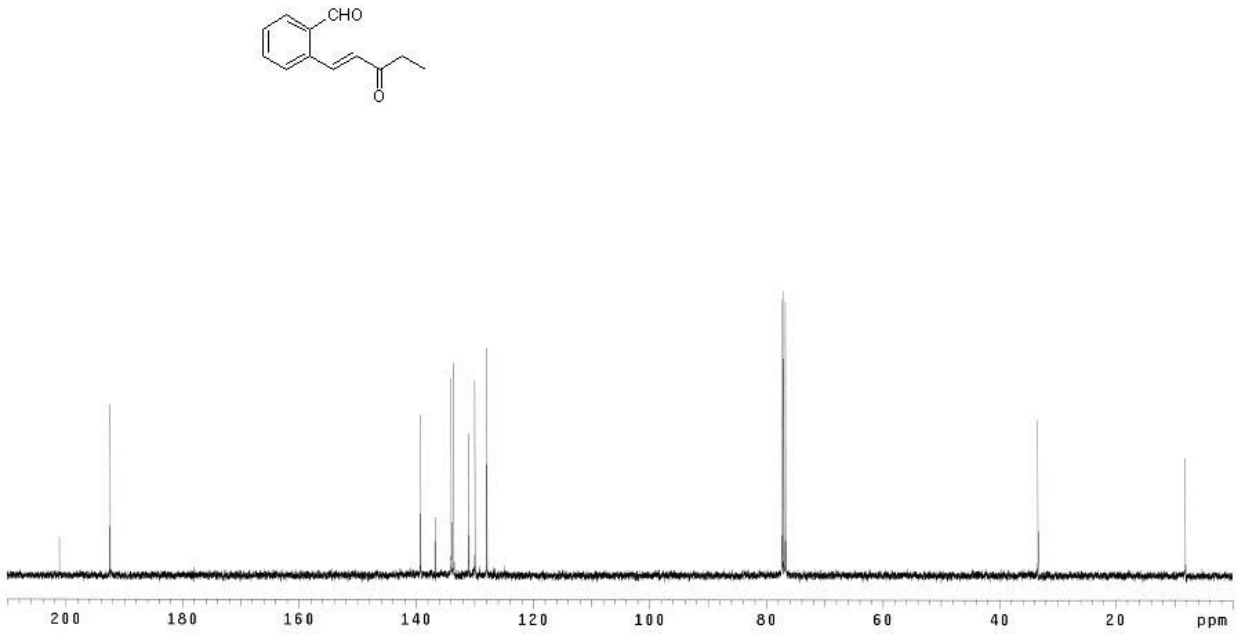
^{1}H NMR Spectrum of Compound **1g** ($CDCl_3$, 400 MHz)



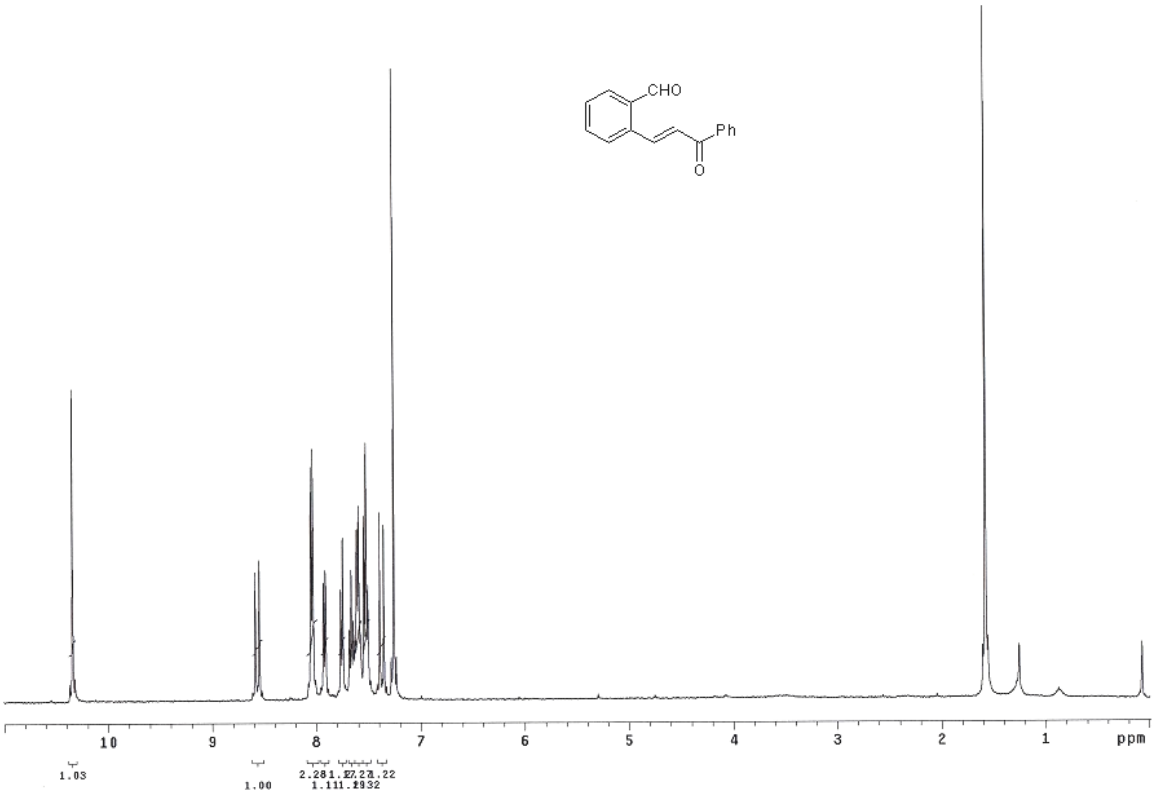
^{13}C NMR Spectrum of Compound **1g** ($CDCl_3$, 100 MHz)



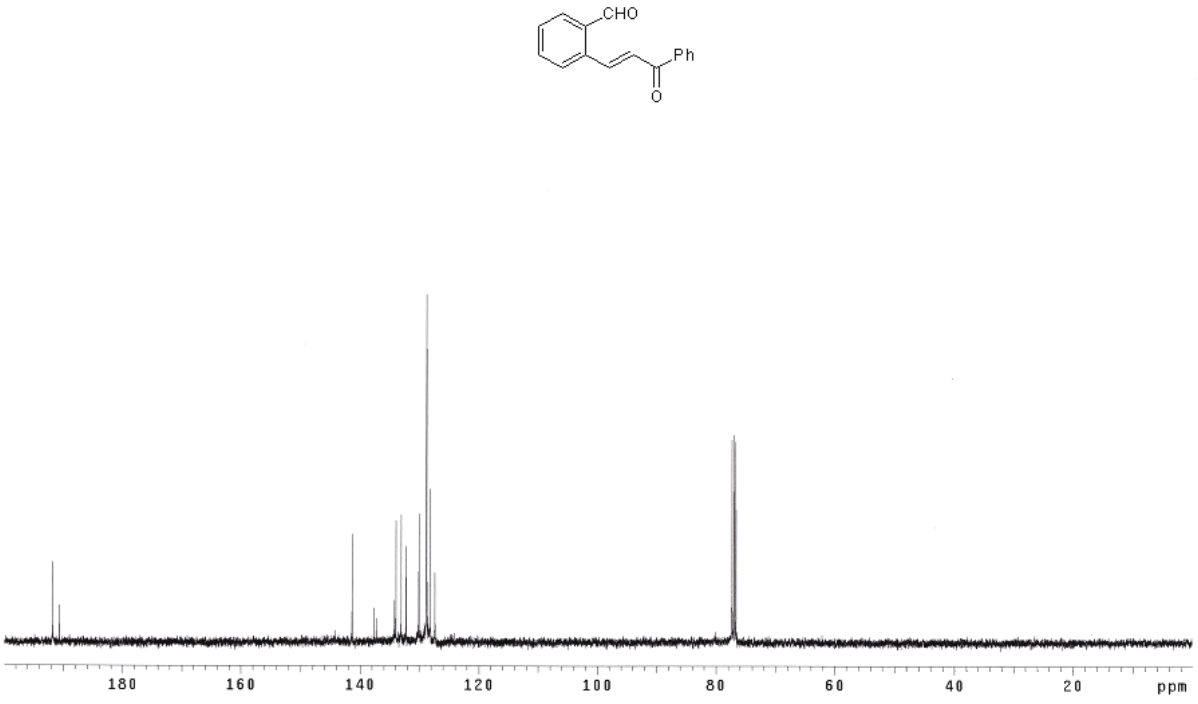
^{1}H NMR Spectrum of Compound **1h** ($CDCl_3$, 400 MHz)



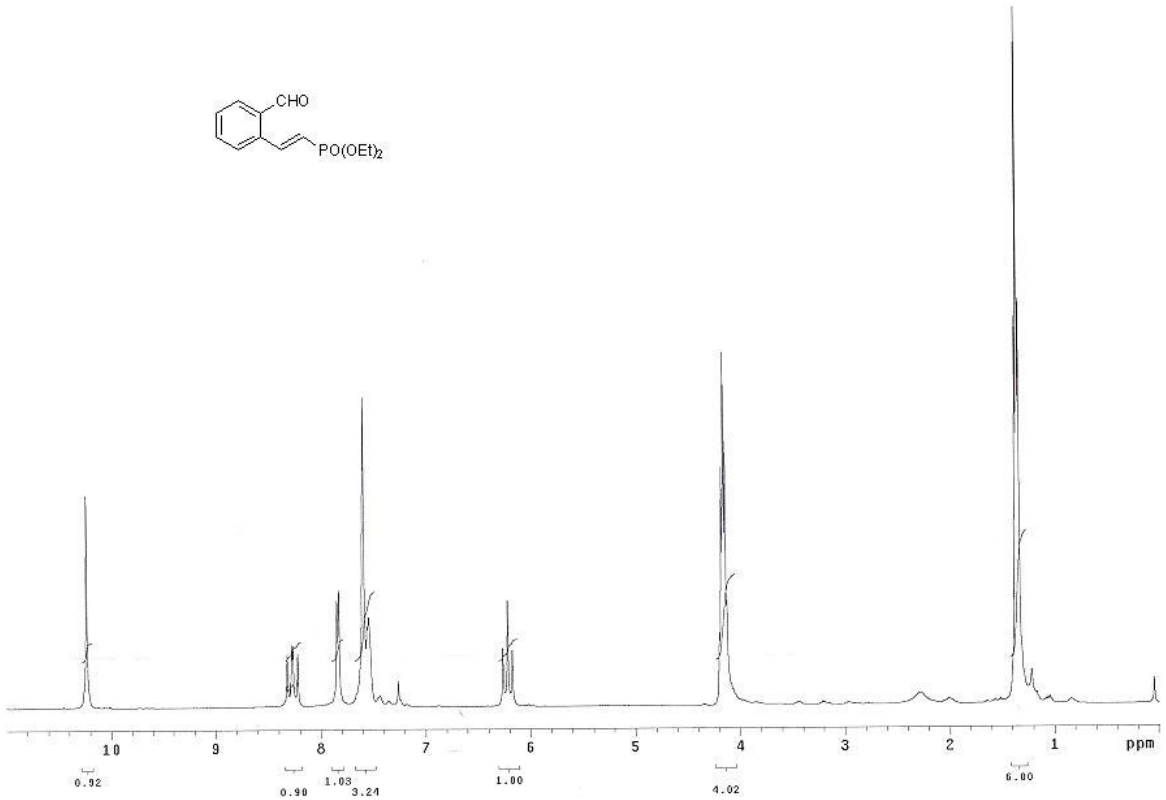
^{13}C NMR Spectrum of Compound **1h** ($CDCl_3$, 100 MHz)



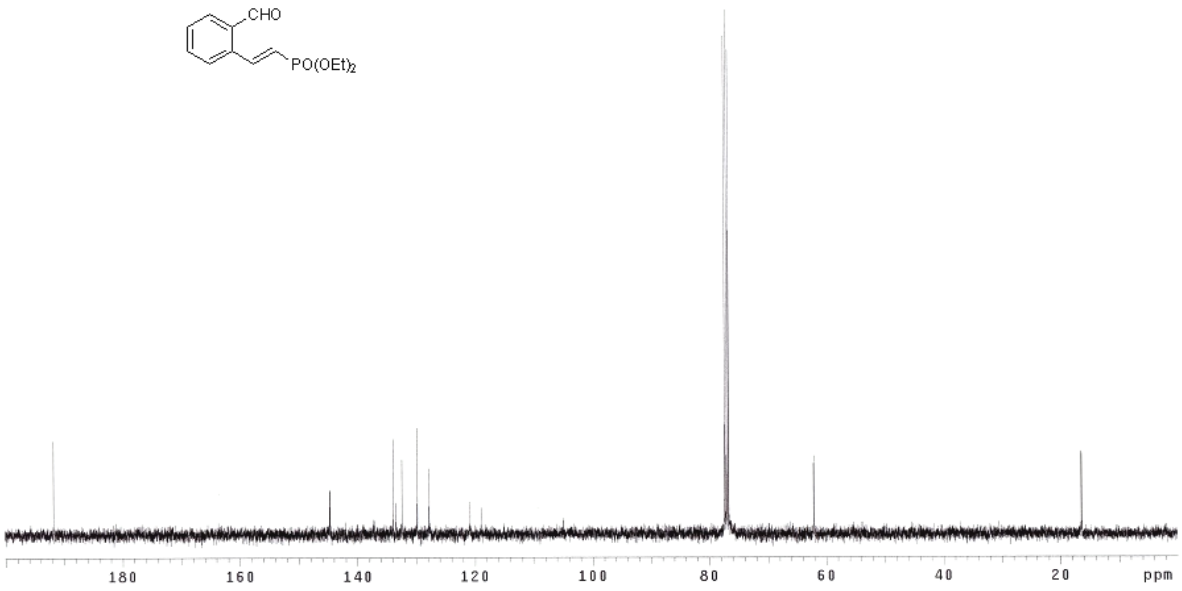
^{1}H NMR Spectrum of Compound **1i** ($CDCl_3$, 400 MHz)



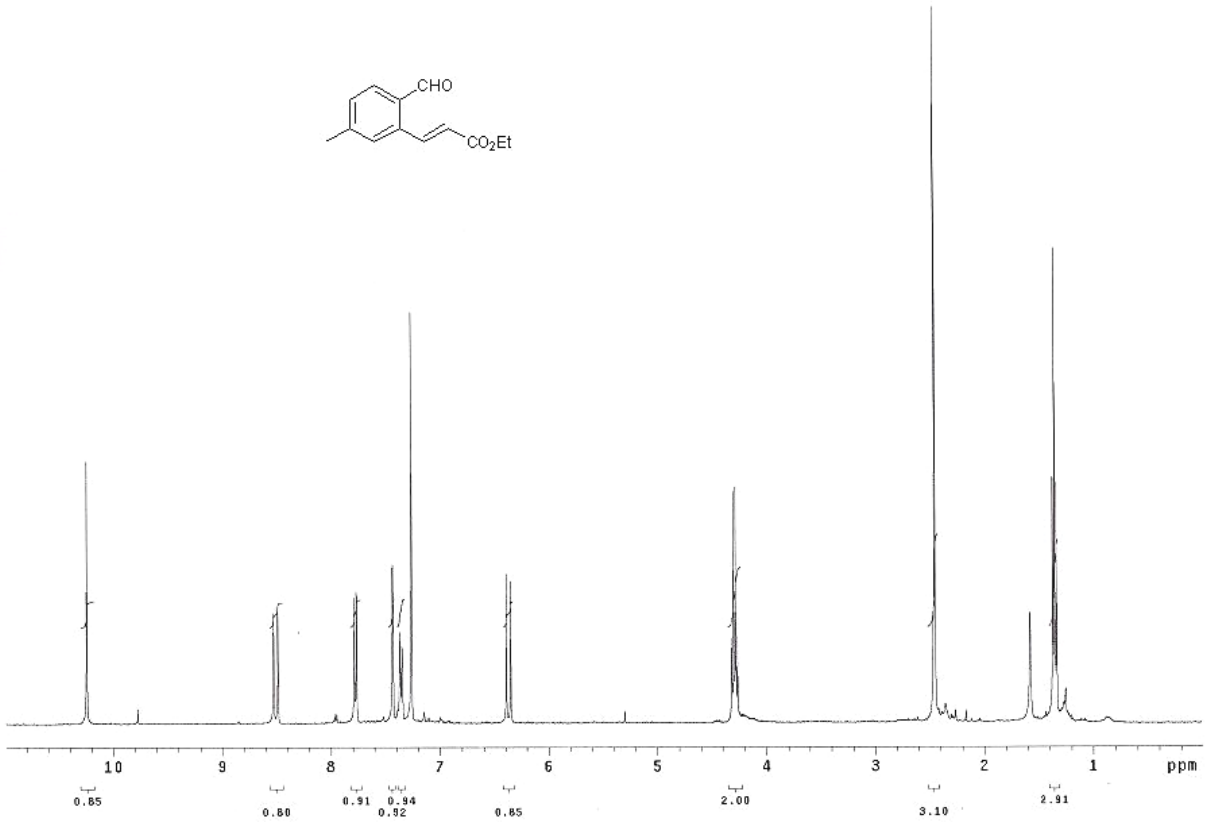
^{13}C NMR Spectrum of Compound **1i** ($CDCl_3$, 100 MHz)



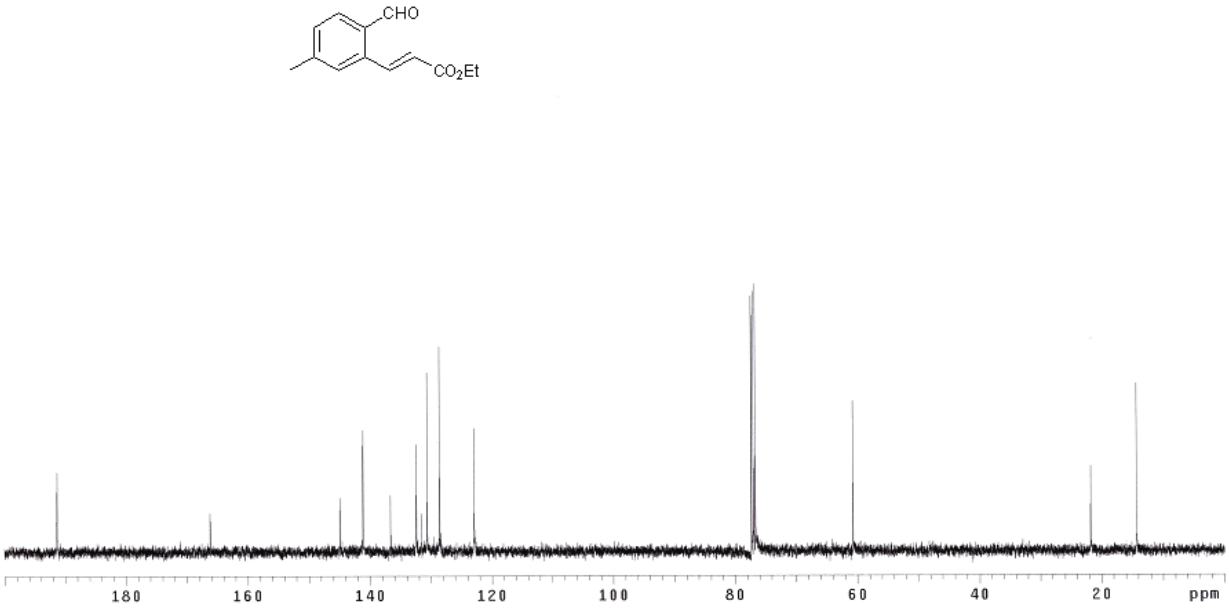
^{1}H NMR Spectrum of Compound **1j** ($CDCl_3$, 400 MHz)



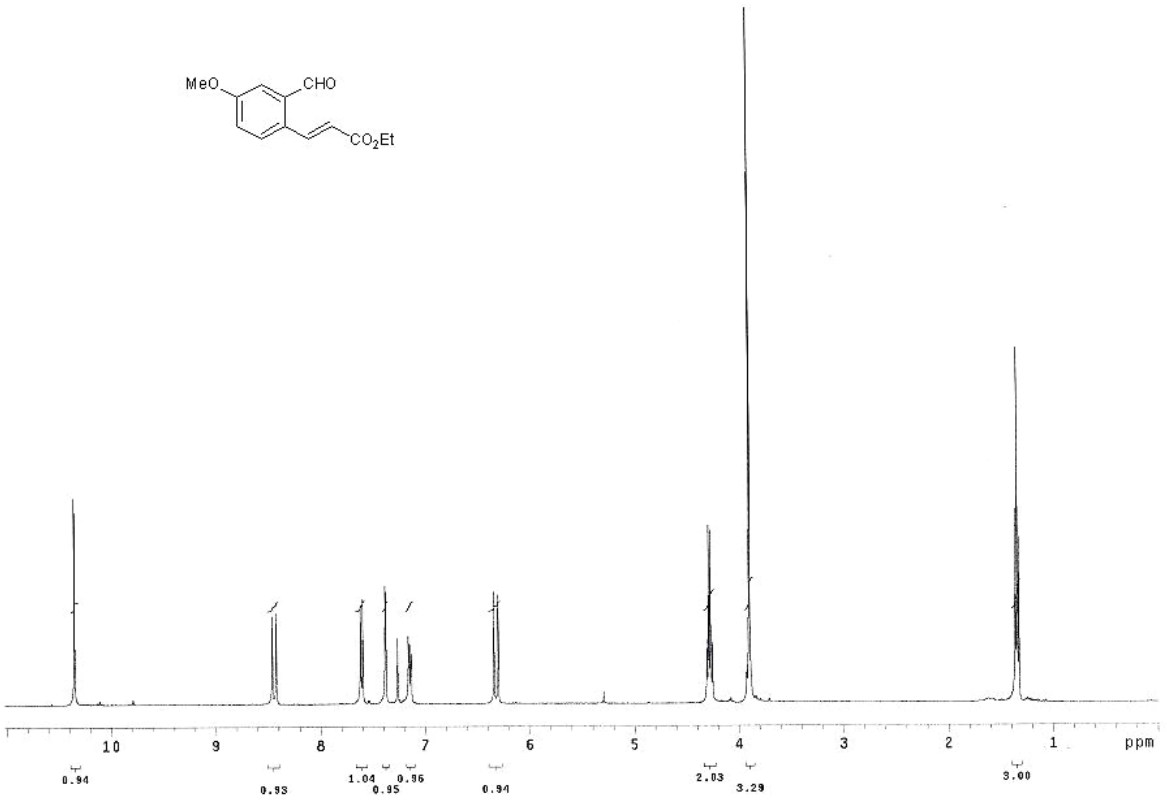
^{13}C NMR Spectrum of Compound **1j** ($CDCl_3$, 100 MHz)



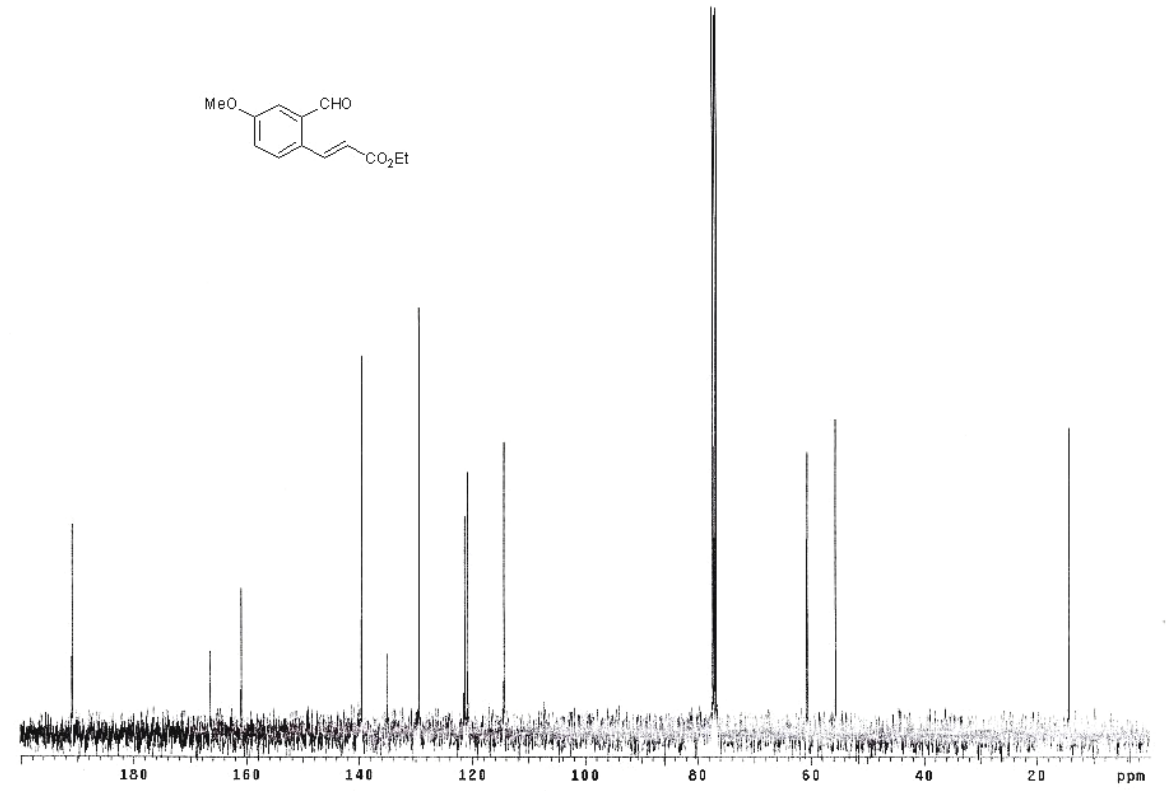
^{1}H NMR Spectrum of Compound **1k** ($CDCl_3$, 400 MHz)



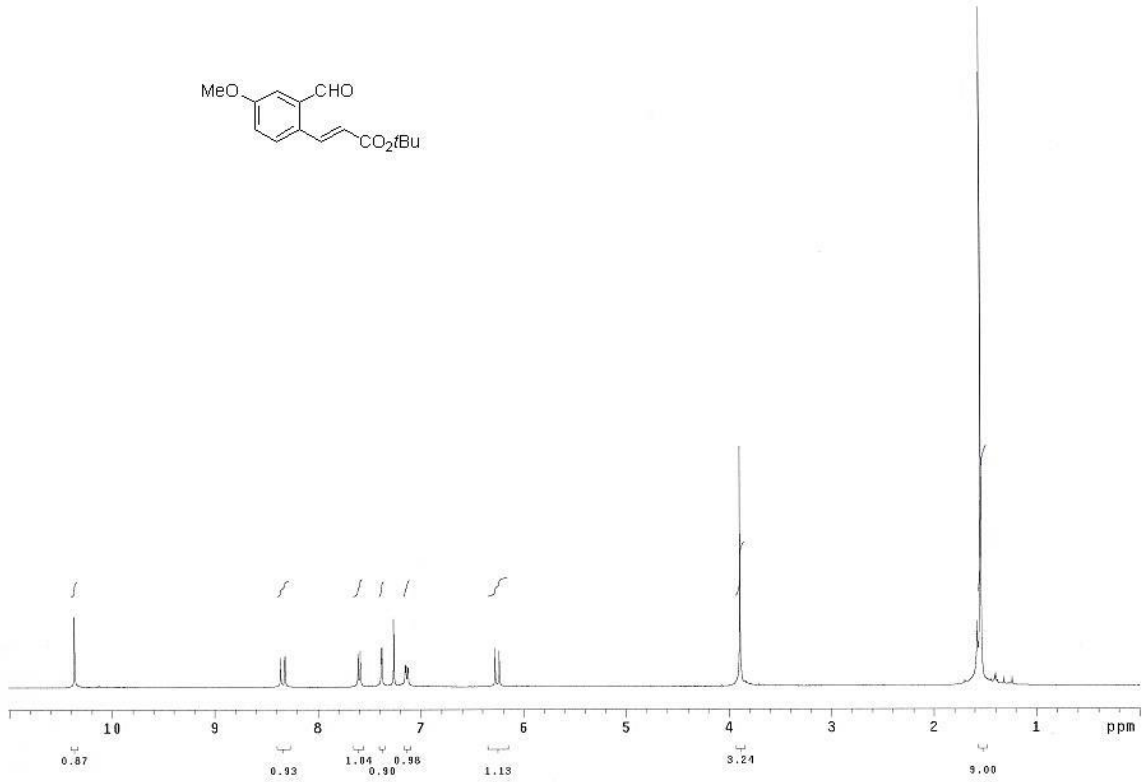
^{13}C NMR Spectrum of Compound **1k** ($CDCl_3$, 100 MHz)



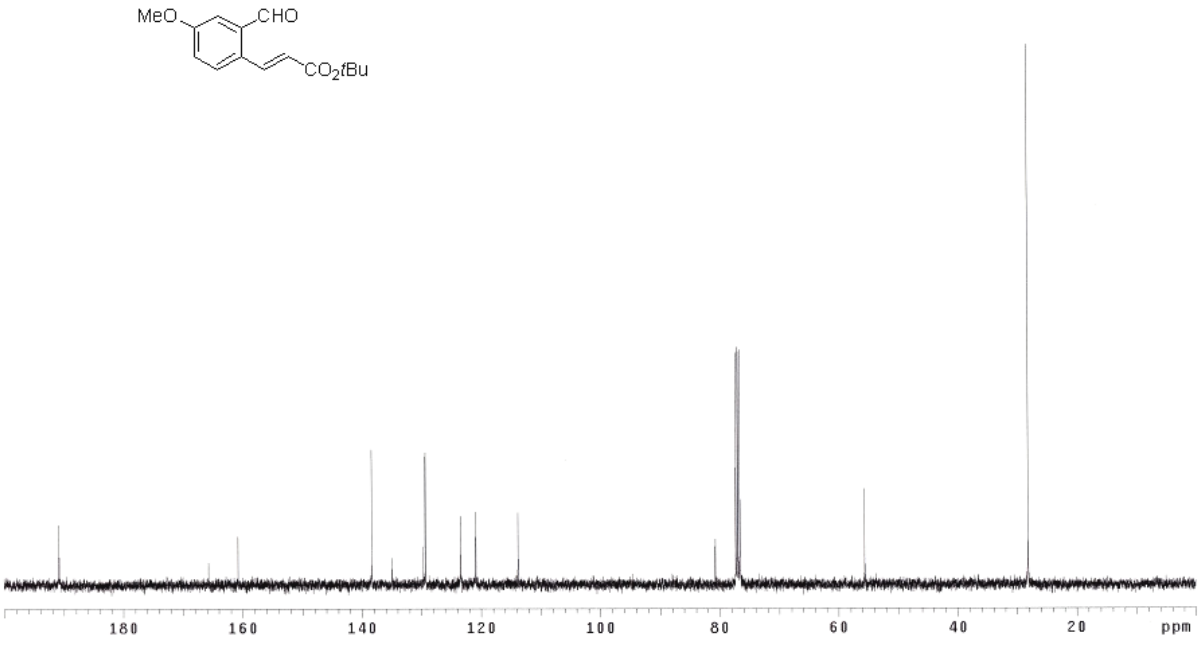
^{1}H NMR Spectrum of Compound **1l** ($CDCl_3$, 400 MHz)



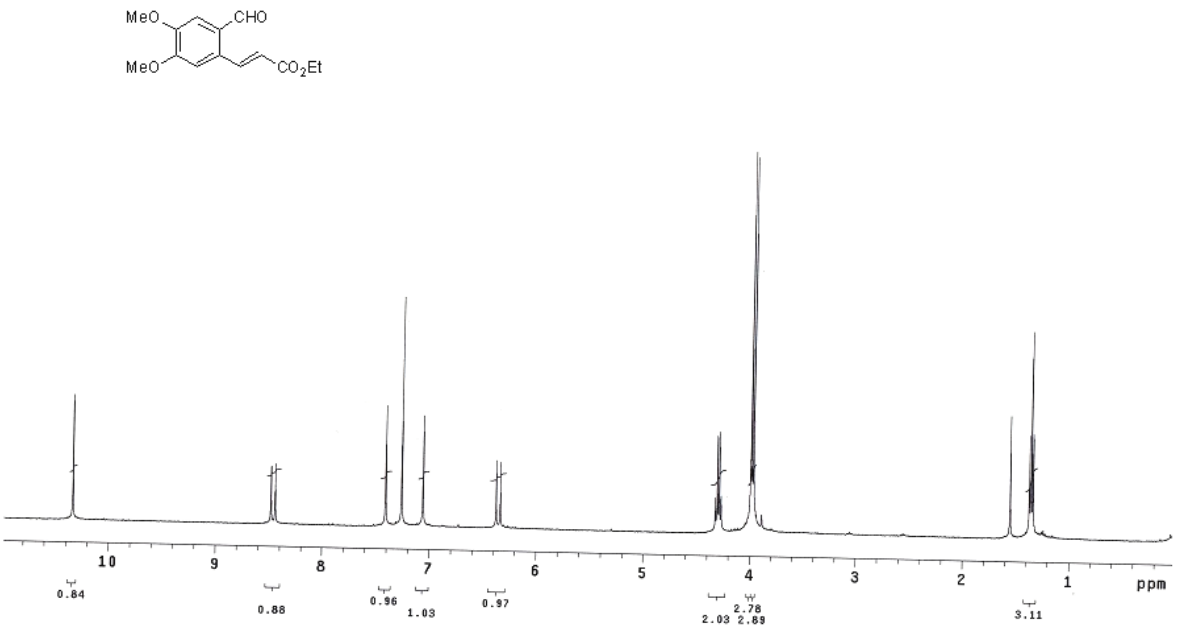
^{13}C NMR Spectrum of Compound **1l** ($CDCl_3$, 100 MHz)



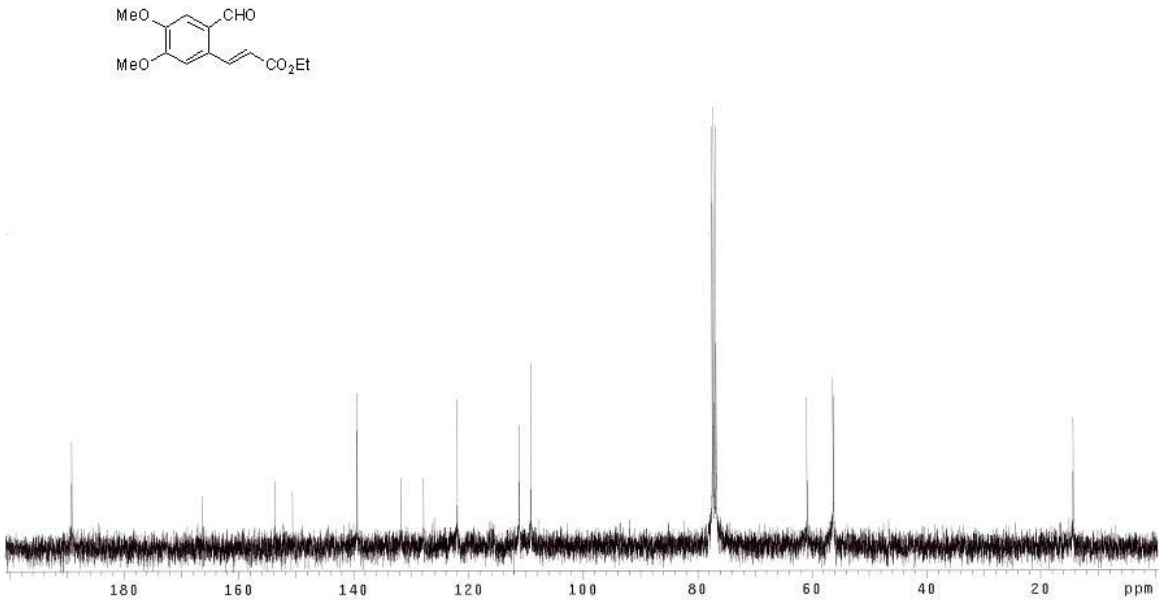
^{1}H NMR Spectrum of Compound **1m** ($CDCl_3$, 400 MHz)



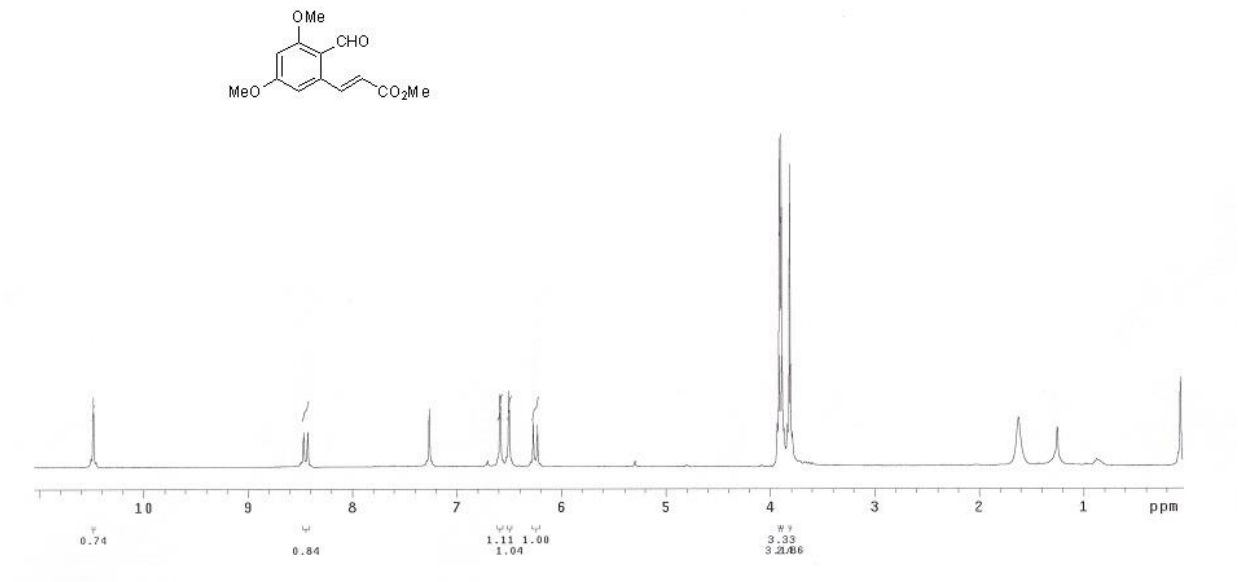
^{13}C NMR Spectrum of Compound **1m** ($CDCl_3$, 100 MHz)



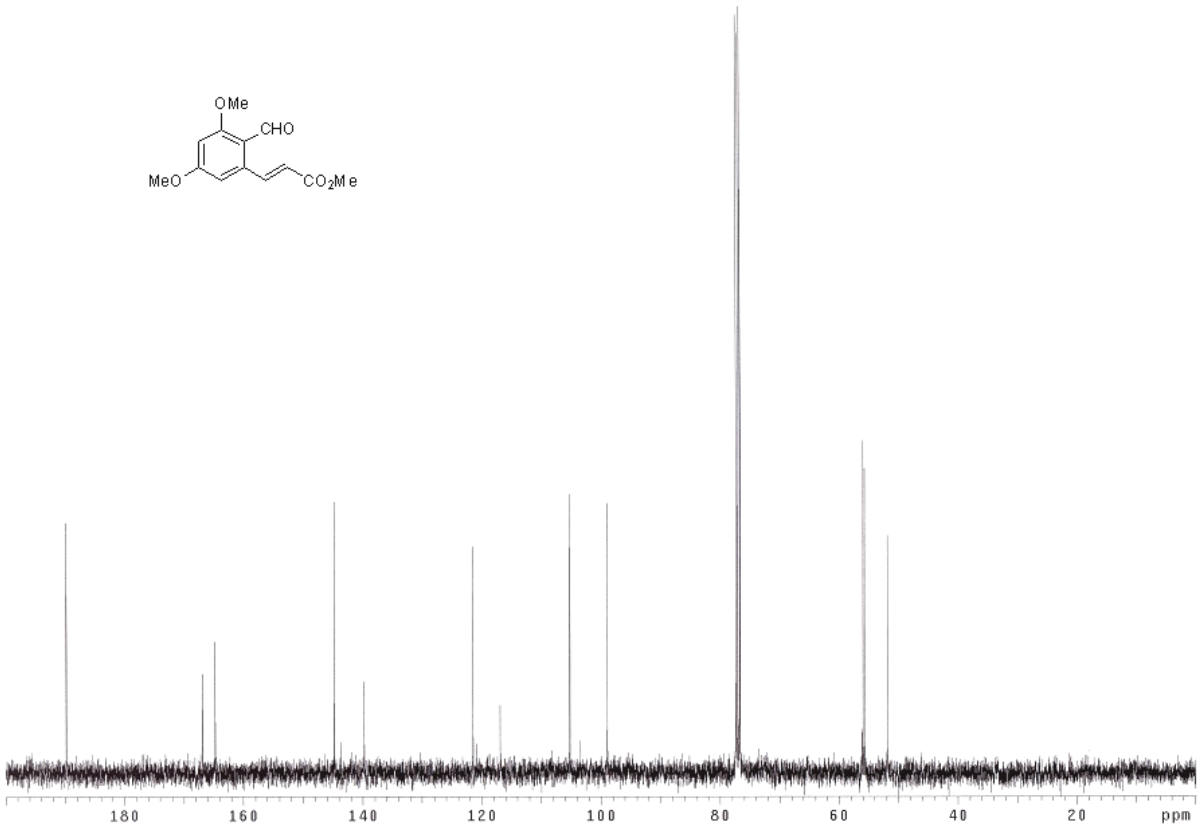
^{1}H NMR Spectrum of Compound **1n** ($CDCl_3$, 400 MHz)



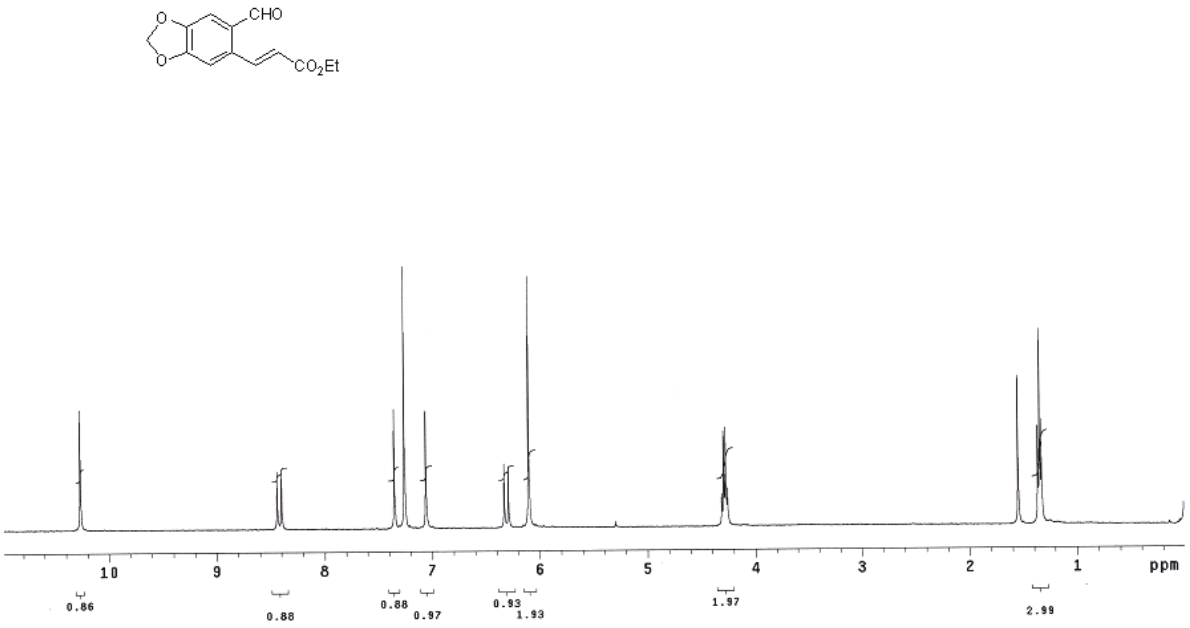
^{13}C NMR Spectrum of Compound **1n** ($CDCl_3$, 100 MHz)



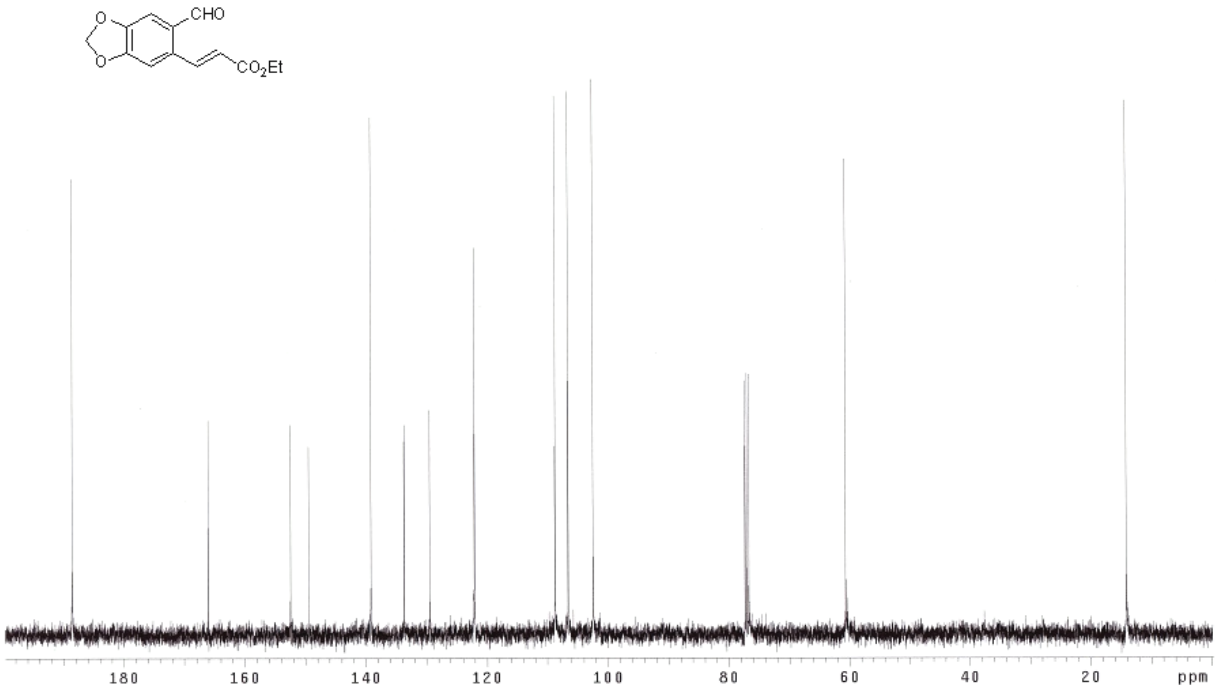
^{1}H NMR Spectrum of Compound **1o** ($CDCl_3$, 400 MHz)



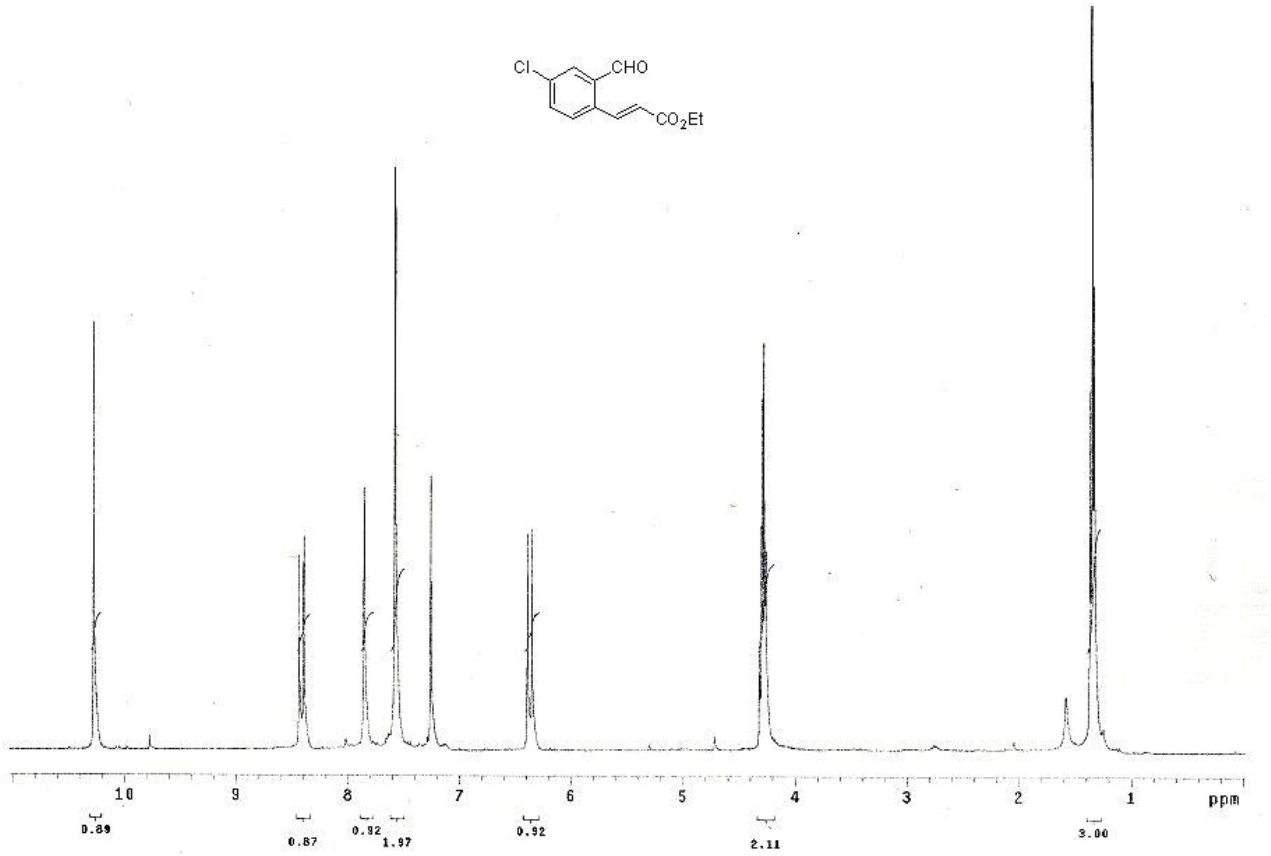
^{13}C NMR Spectrum of Compound **1o** ($CDCl_3$, 100 MHz)



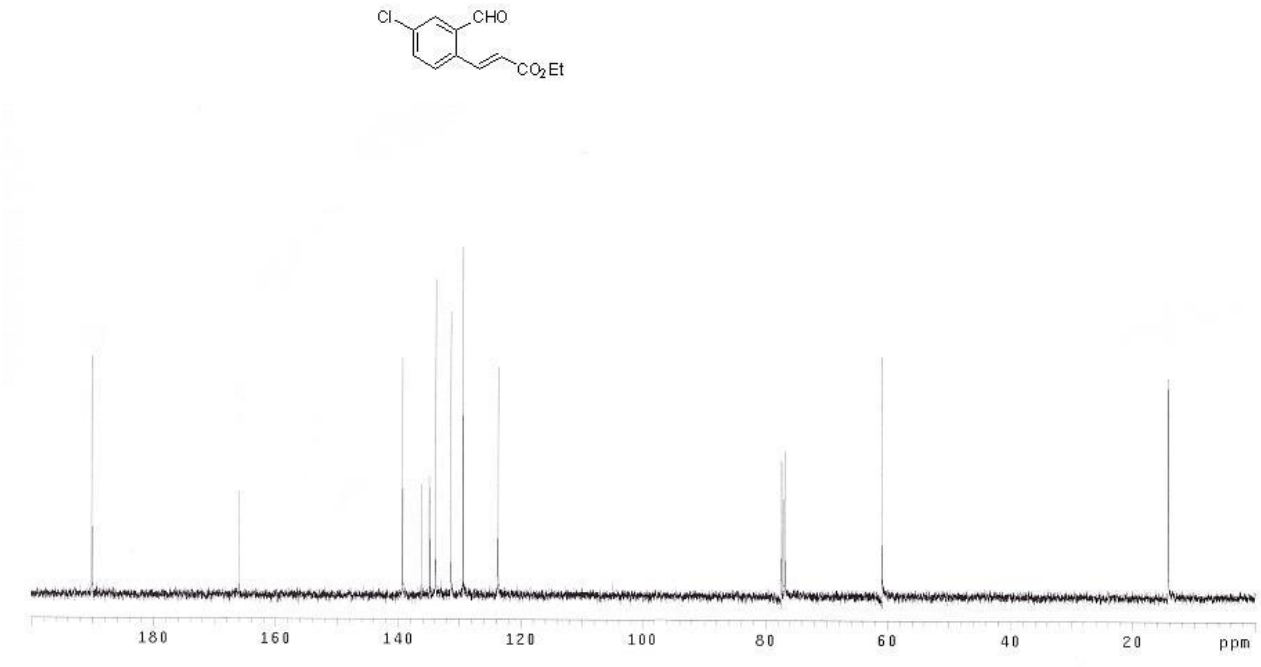
^{1}H NMR Spectrum of Compound **1p** ($CDCl_3$, 400 MHz)



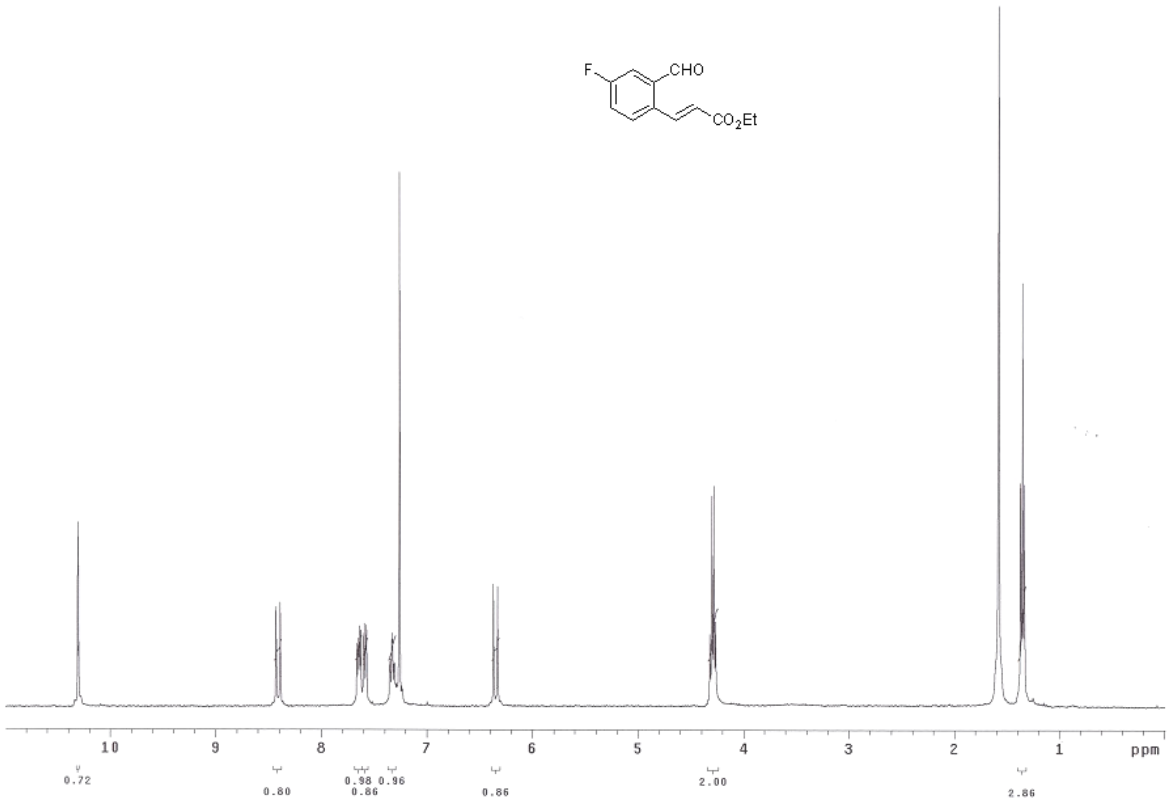
^{13}C NMR Spectrum of Compound **1p** ($CDCl_3$, 100 MHz)



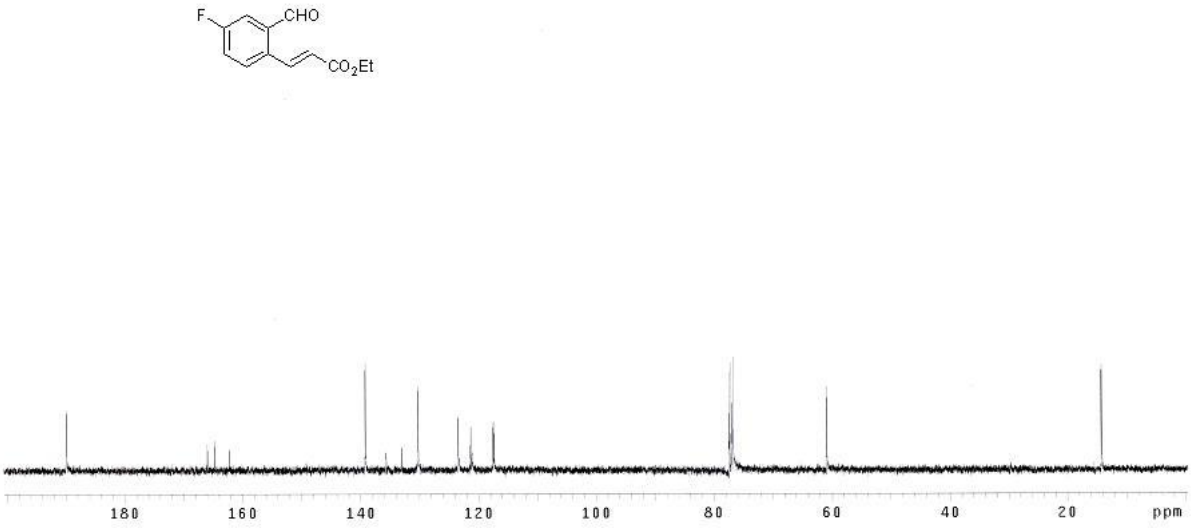
^{1}H NMR Spectrum of Compound **1q** ($CDCl_3$, 400 MHz)



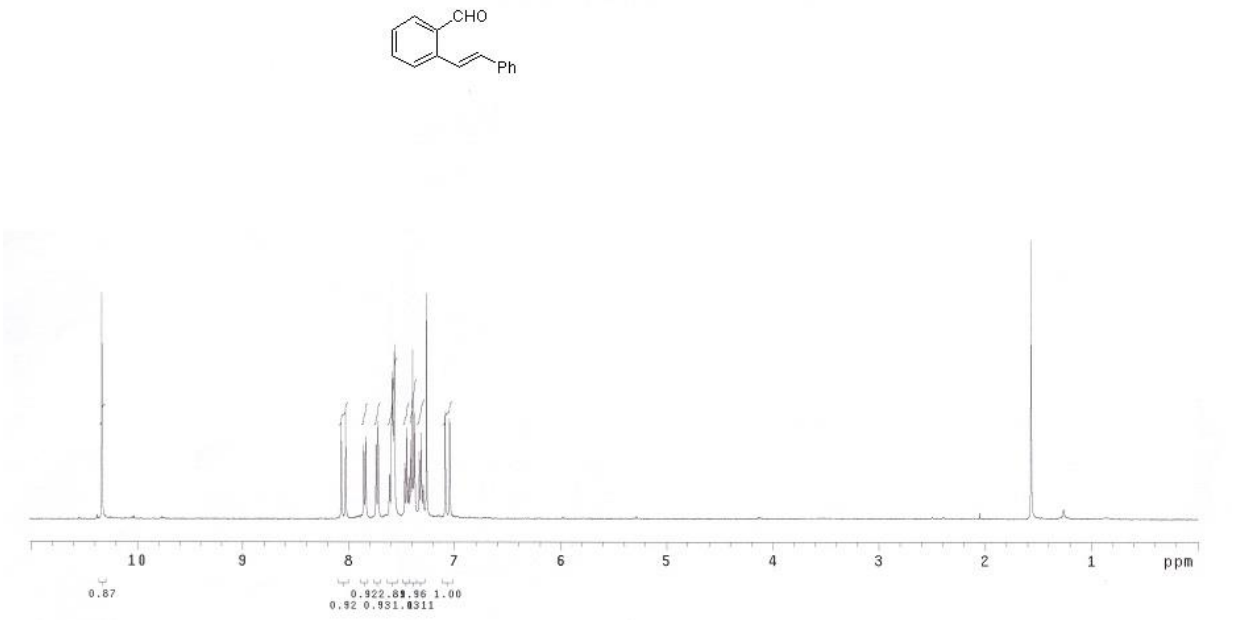
^{13}C NMR Spectrum of Compound **1q** ($CDCl_3$, 100 MHz)



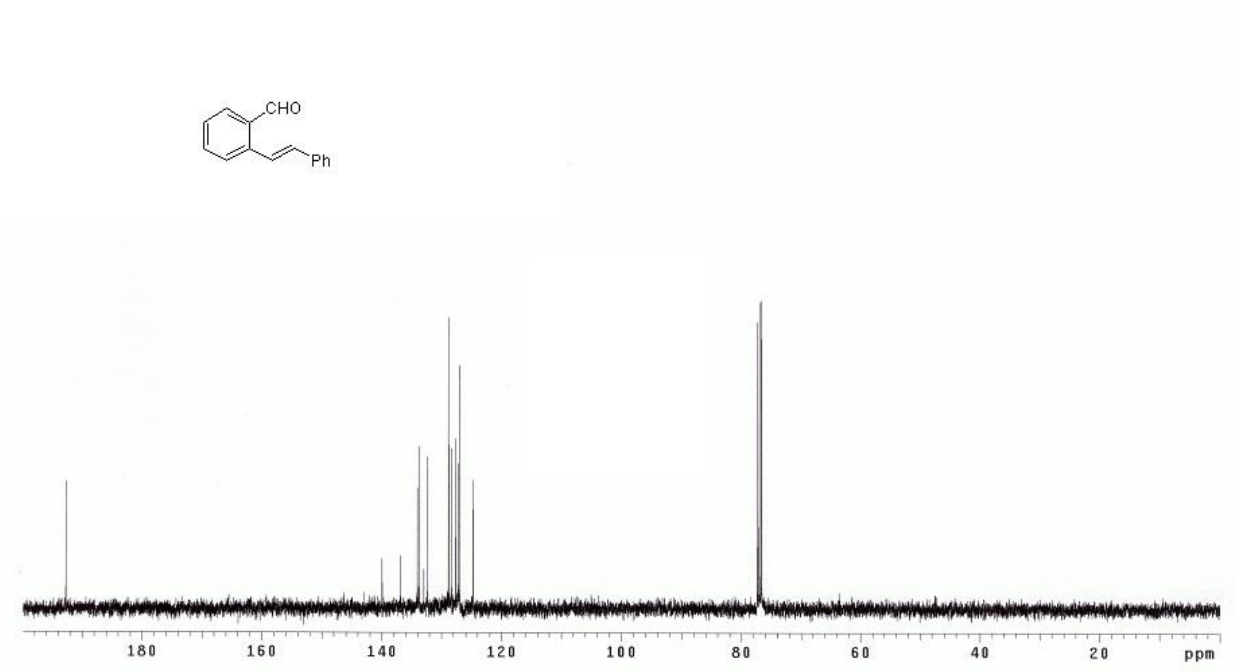
^{1}H NMR Spectrum of Compound **1r** ($CDCl_3$, 400 MHz)



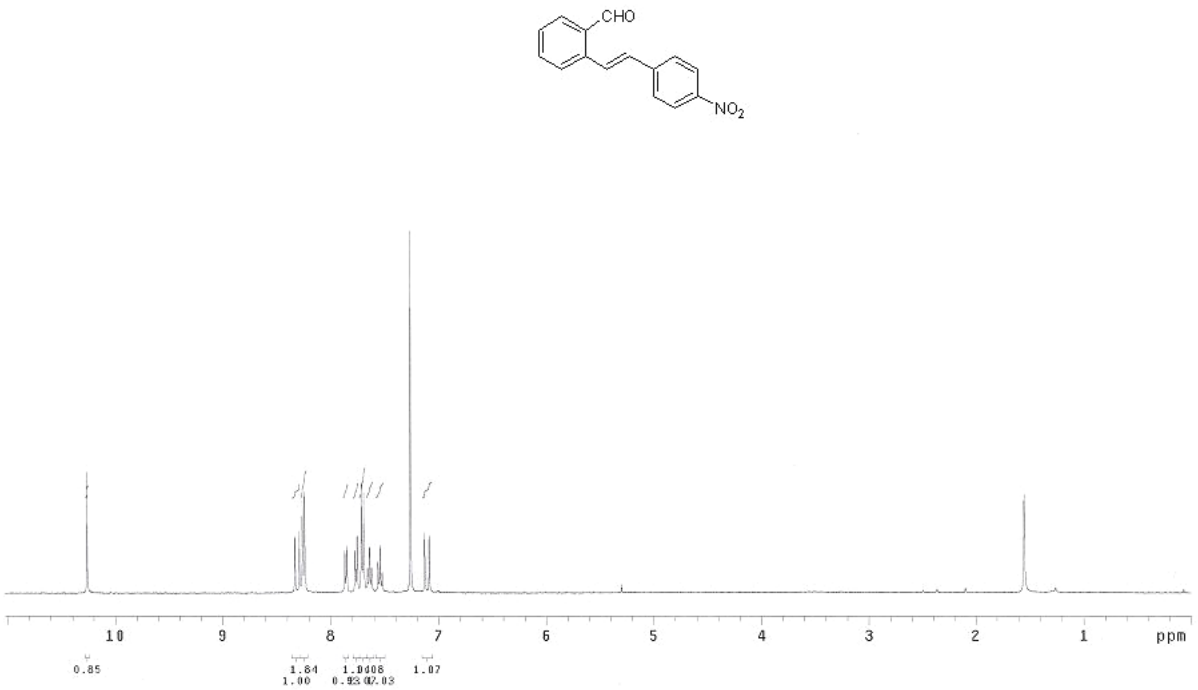
^{13}C NMR Spectrum of Compound **1r** ($CDCl_3$, 100 MHz)



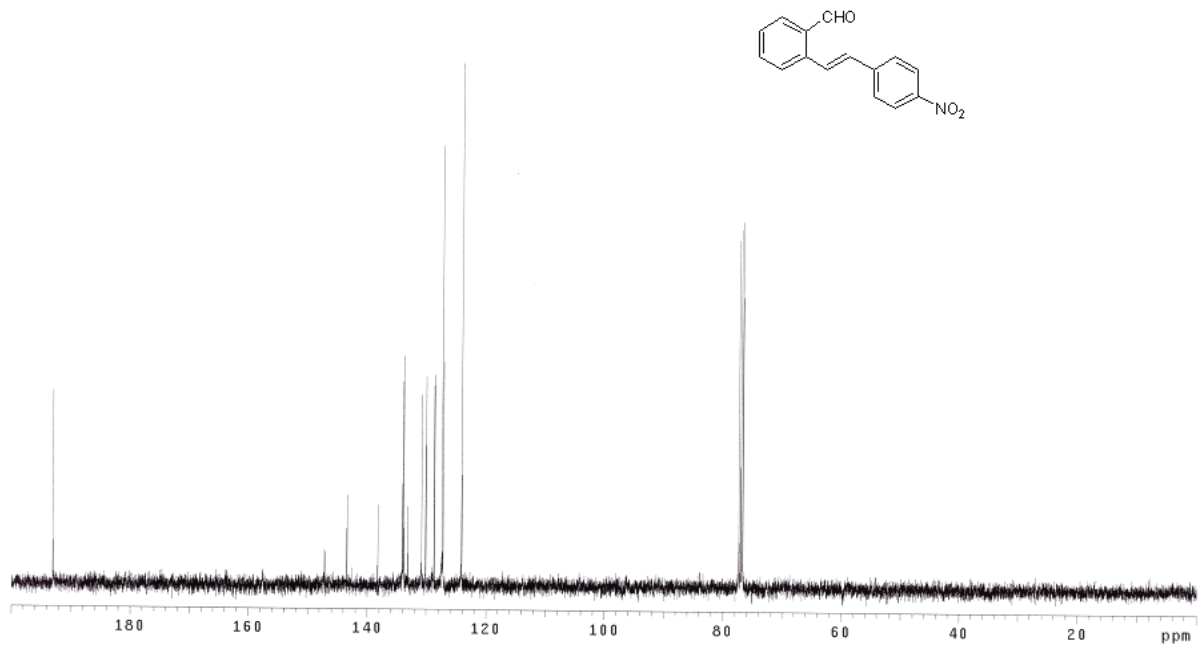
^{1}H NMR Spectrum of Compound **1s** ($CDCl_3$, 400 MHz)



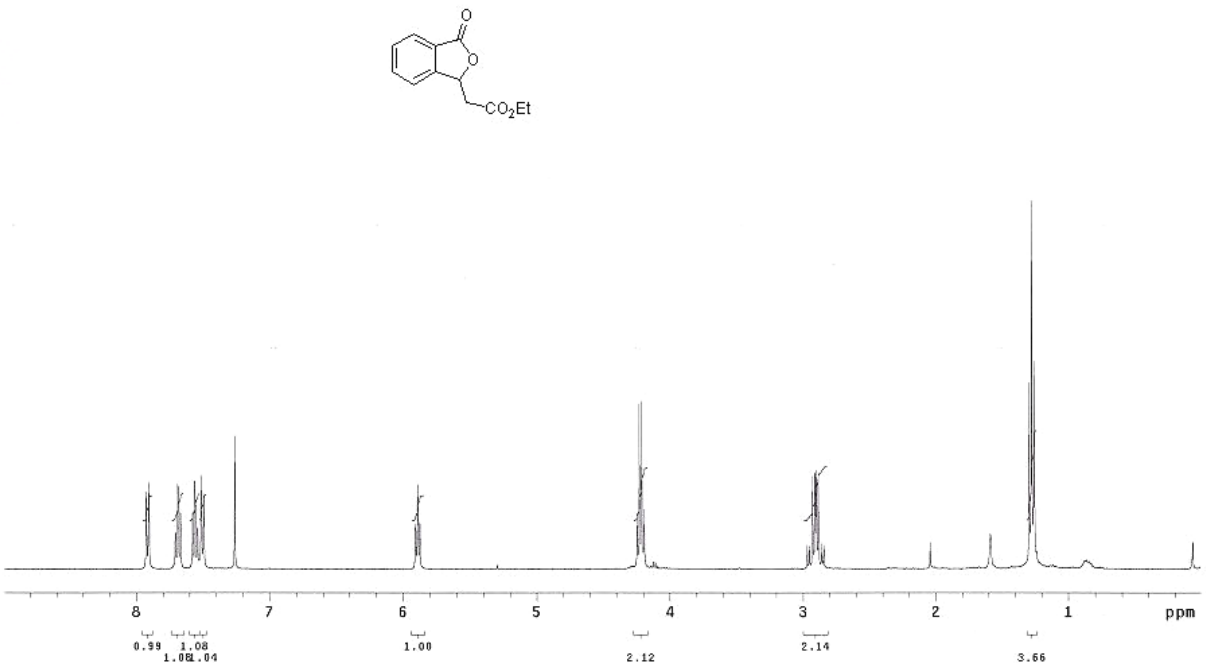
^{13}C NMR Spectrum of Compound **1s** ($CDCl_3$, 100 MHz)



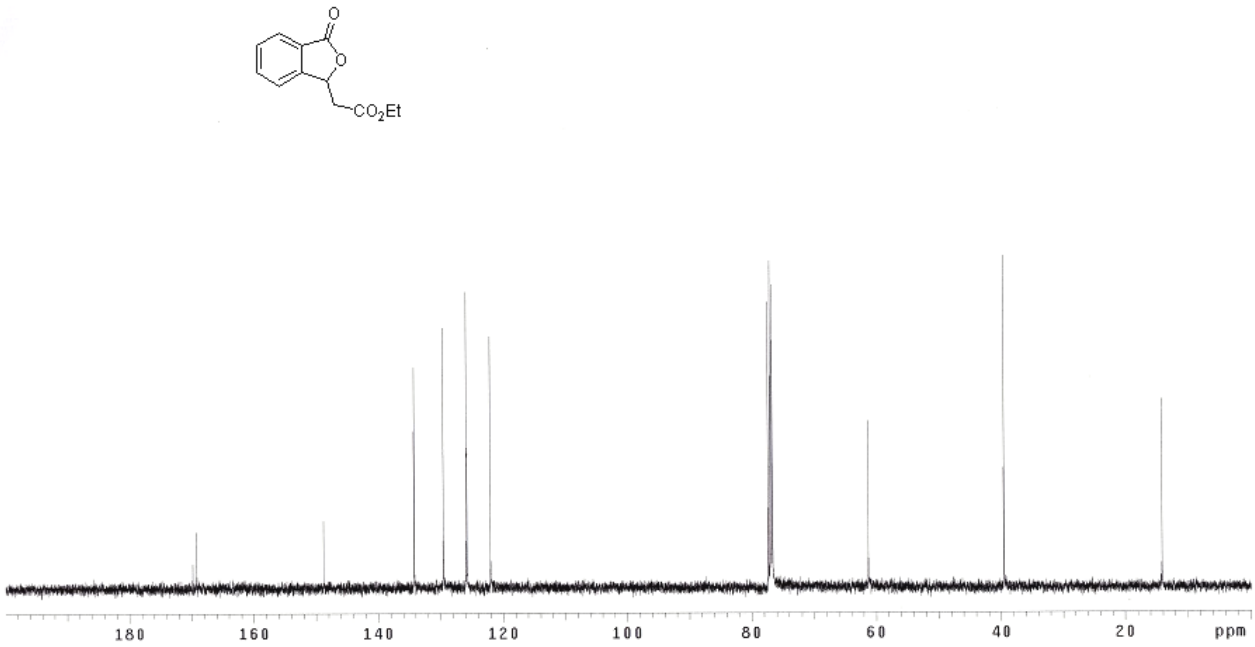
^{1}H NMR Spectrum of Compound **1t** ($CDCl_3$, 400 MHz)



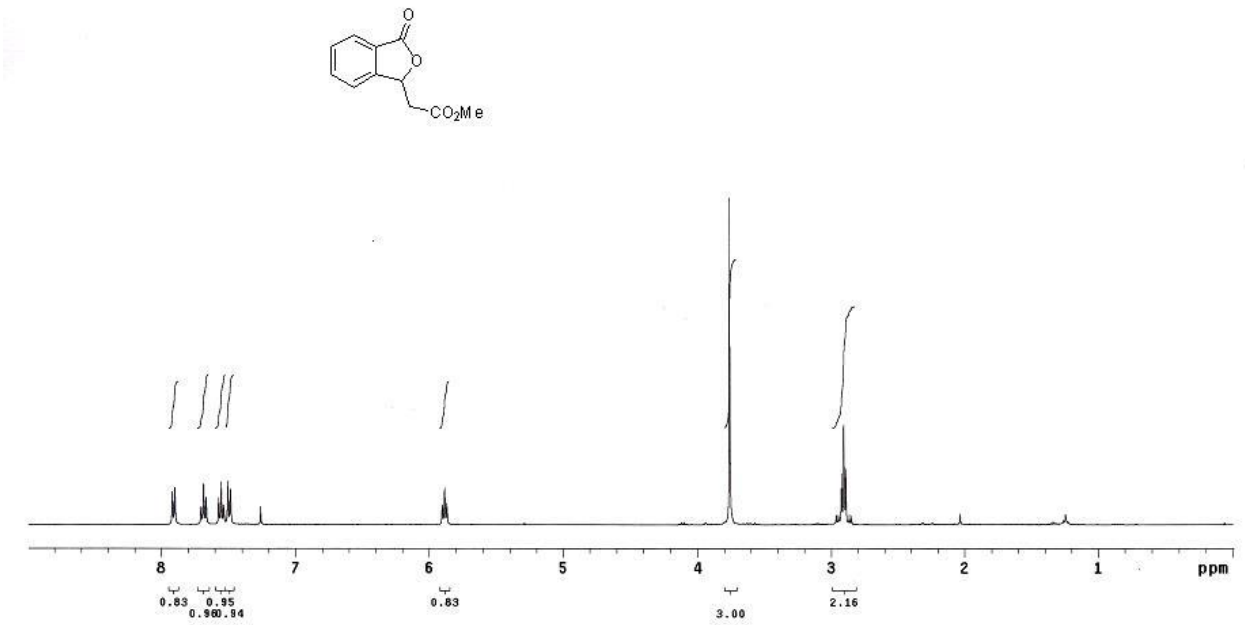
^{13}C NMR Spectrum of Compound **1t** ($CDCl_3$, 100 MHz)



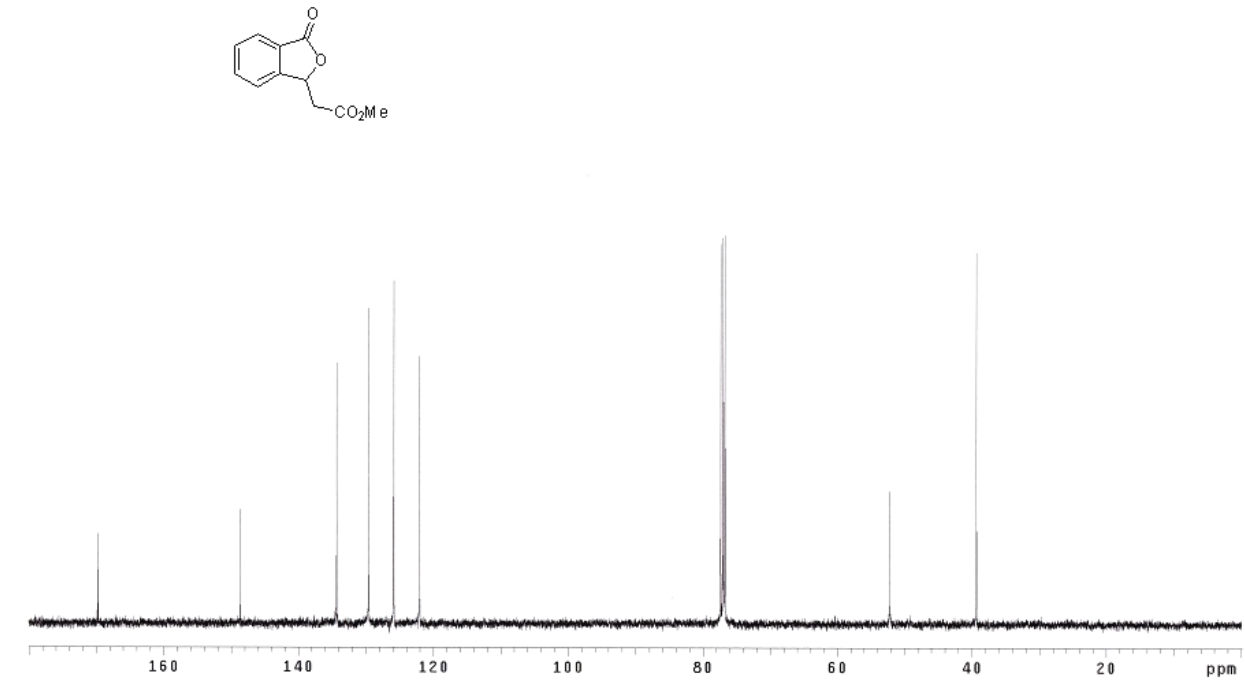
^{1}H NMR Spectrum of Compound **2a** ($CDCl_3$, 400 MHz)



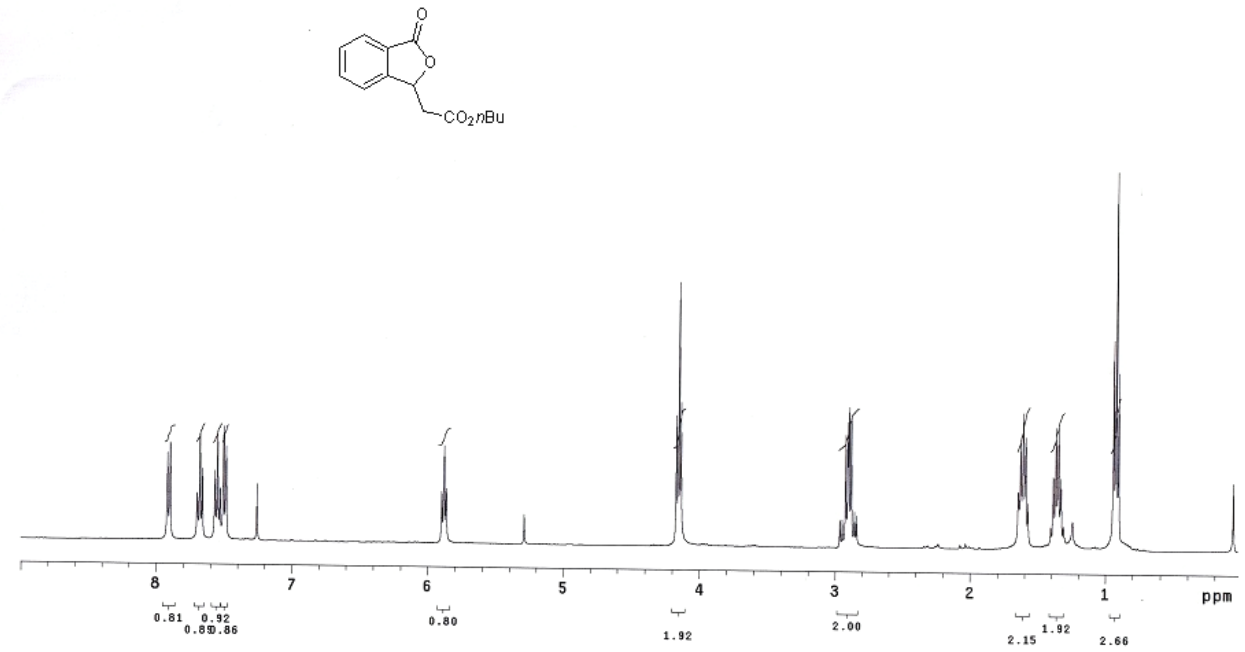
^{13}C NMR Spectrum of Compound **2a** ($CDCl_3$, 100 MHz)



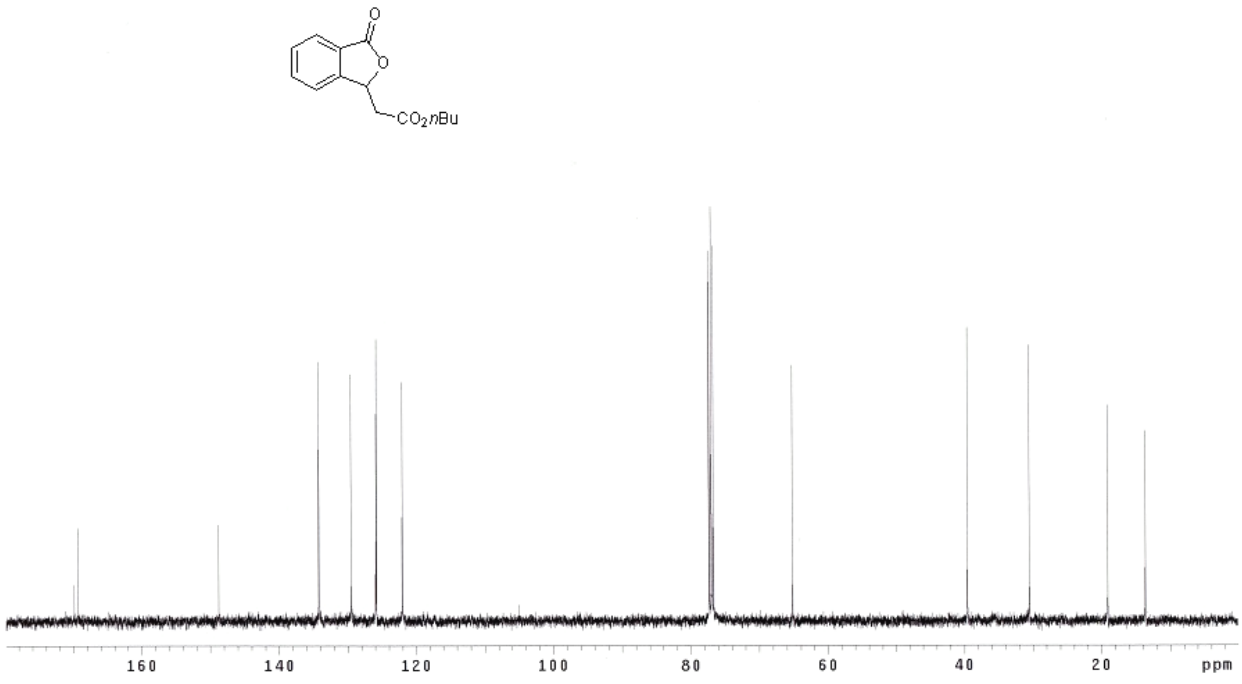
^{1}H NMR Spectrum of Compound **2b** ($CDCl_3$, 400 MHz)



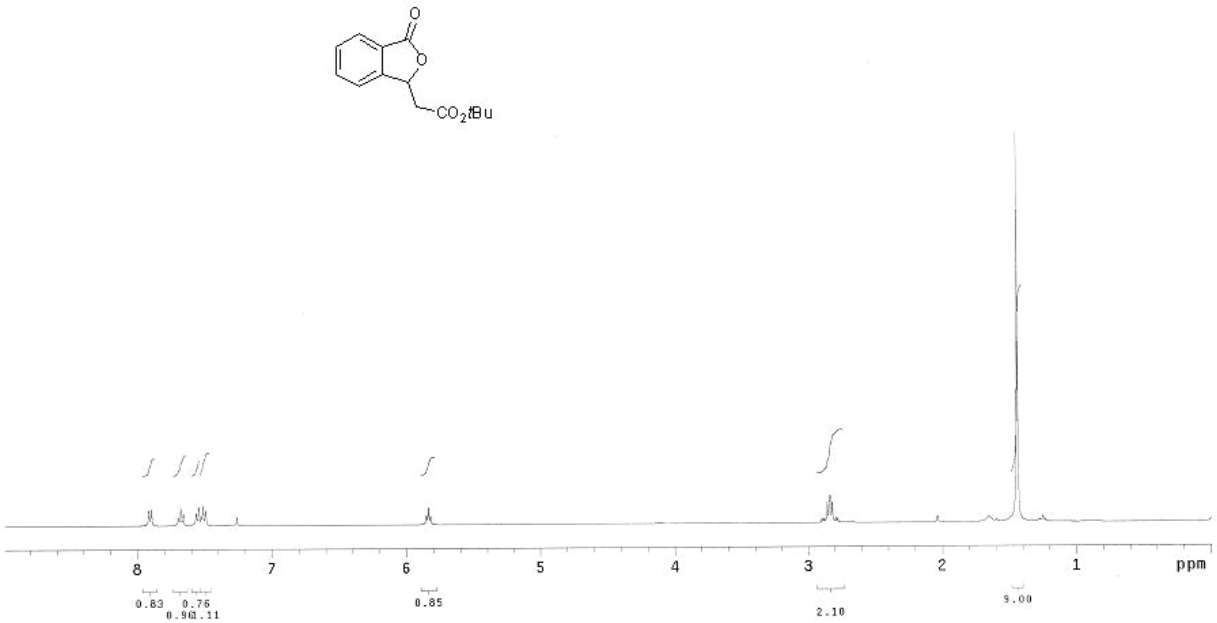
^{13}C NMR Spectrum of Compound **2b** ($CDCl_3$, 100 MHz)



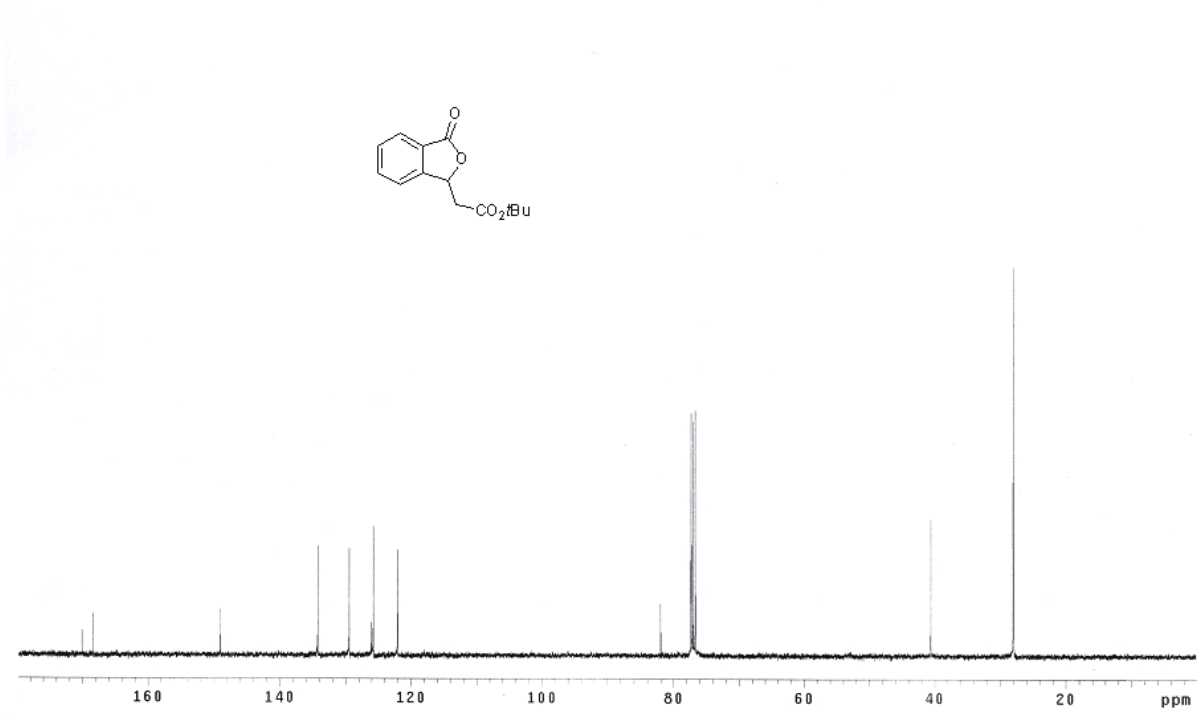
^{1}H NMR Spectrum of Compound **2c** ($CDCl_3$, 400 MHz)



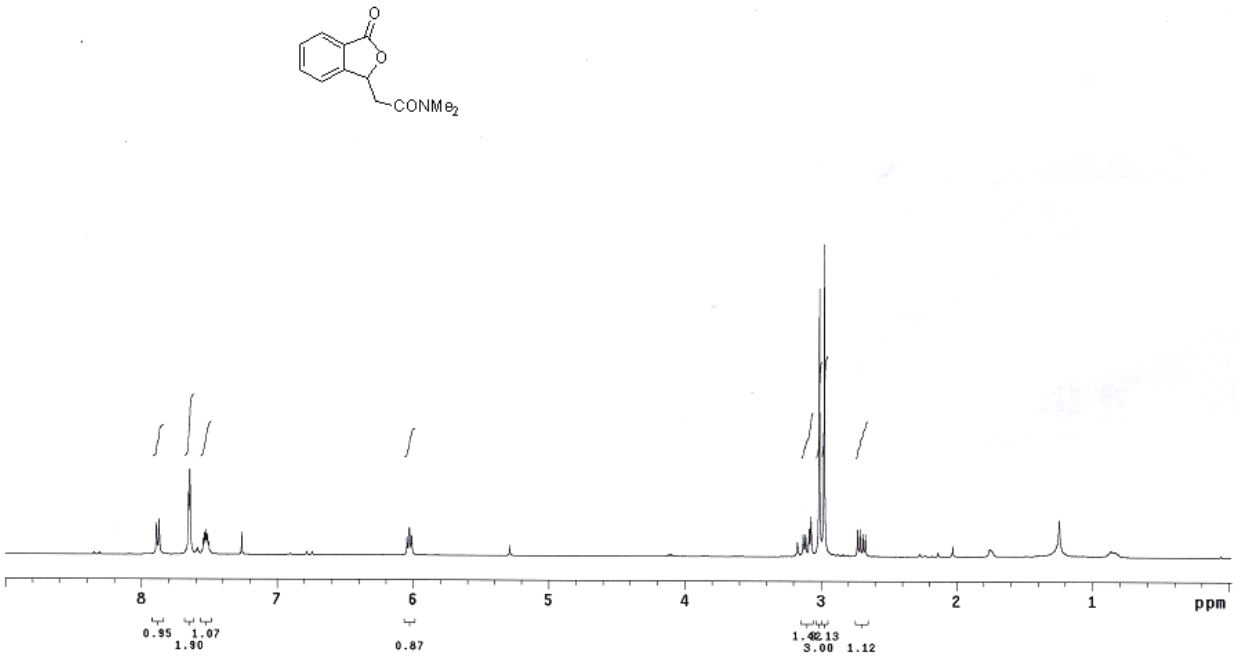
^{13}C NMR Spectrum of Compound **2c** ($CDCl_3$, 100 MHz)



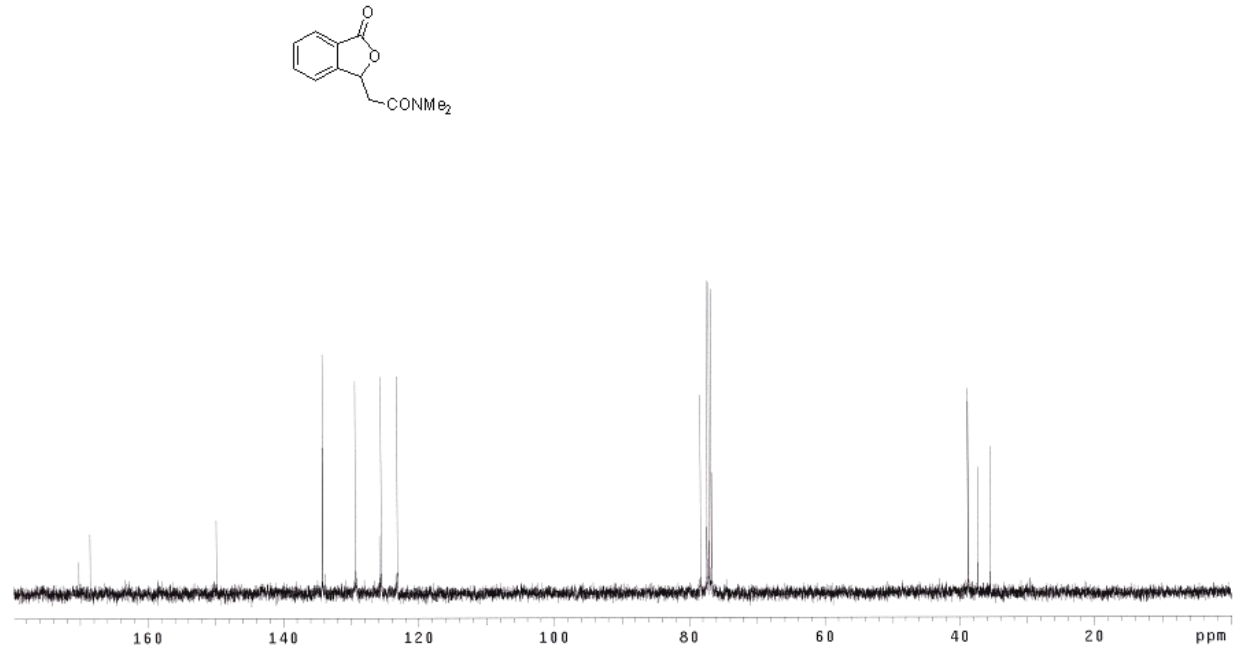
^{1}H NMR Spectrum of Compound **2d** ($CDCl_3$, 400 MHz)



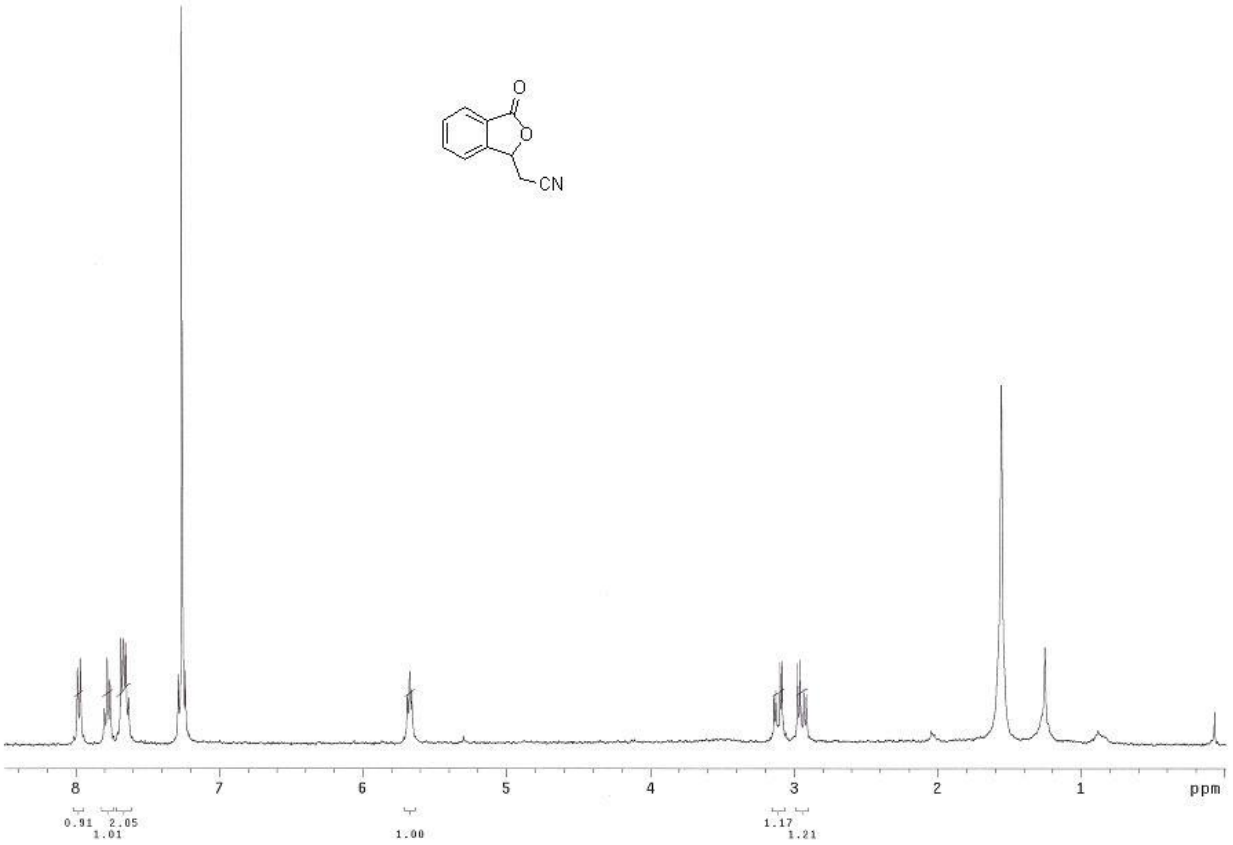
^{13}C NMR Spectrum of Compound **2d** ($CDCl_3$, 100 MHz)



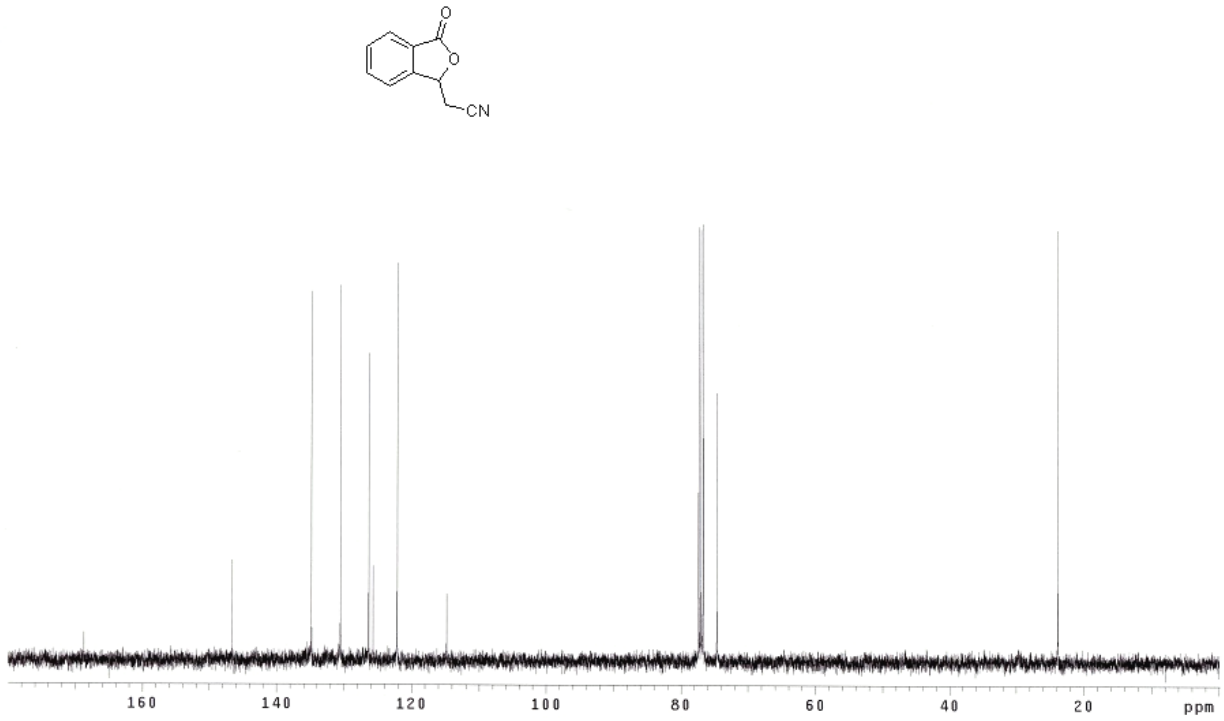
^{1}H NMR Spectrum of Compound **2e** ($CDCl_3$, 400 MHz)



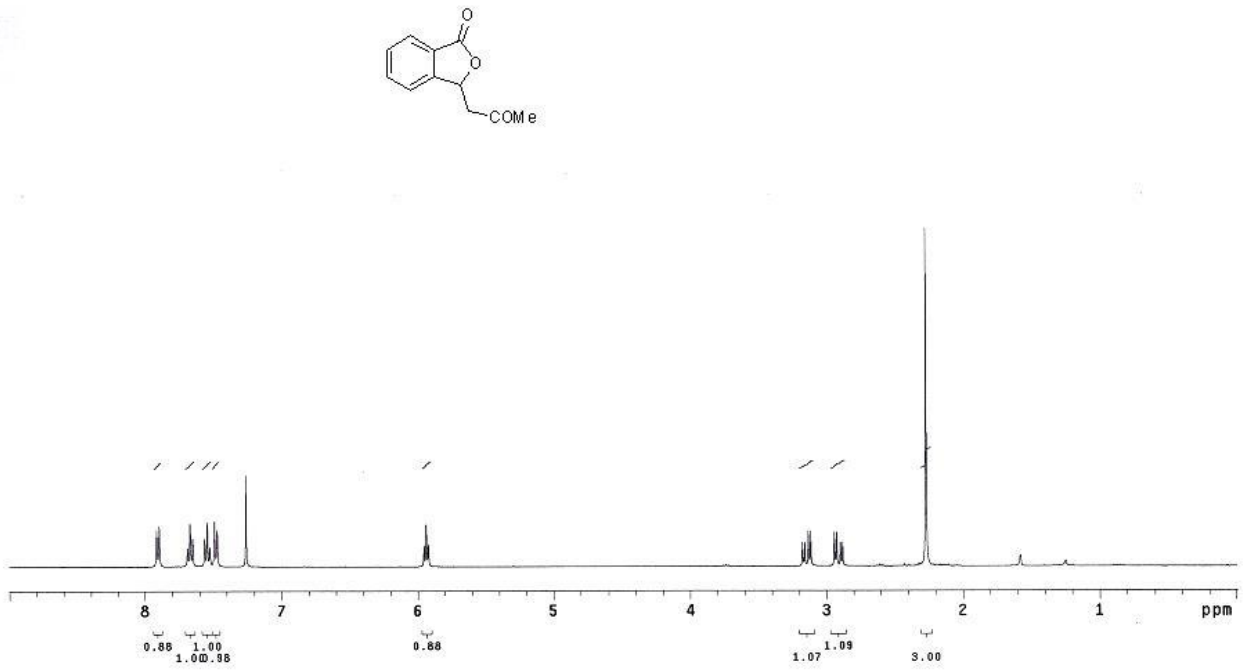
^{13}C NMR Spectrum of Compound **2e** ($CDCl_3$, 100 MHz)



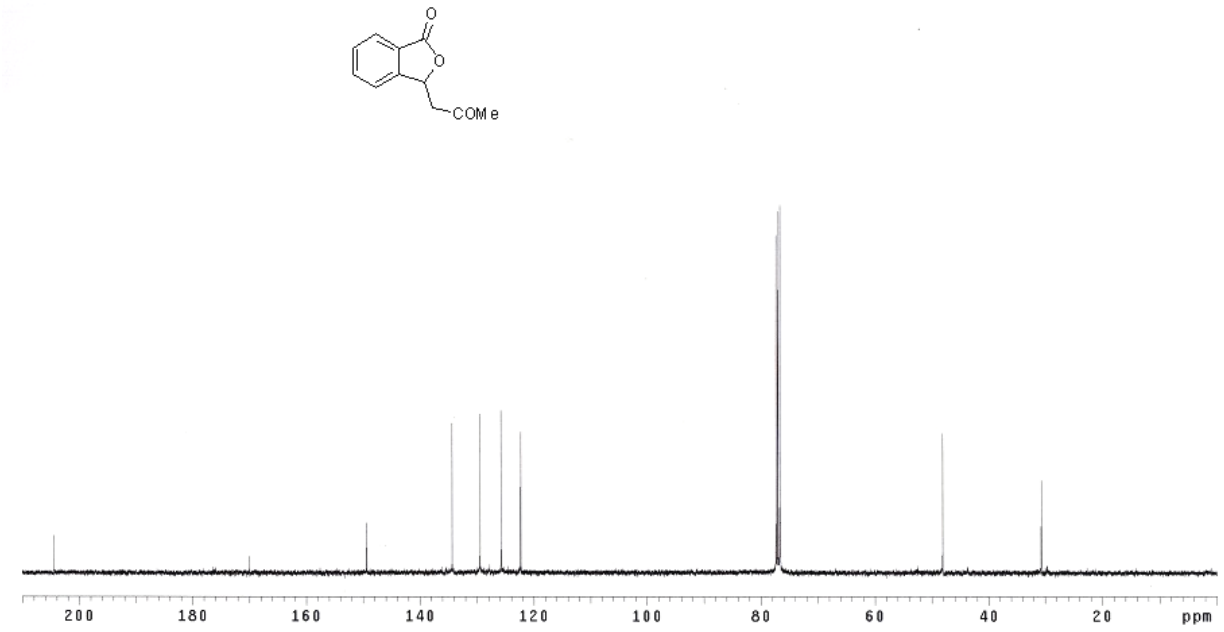
^{1}H NMR Spectrum of Compound **2f** ($CDCl_3$, 400 MHz)



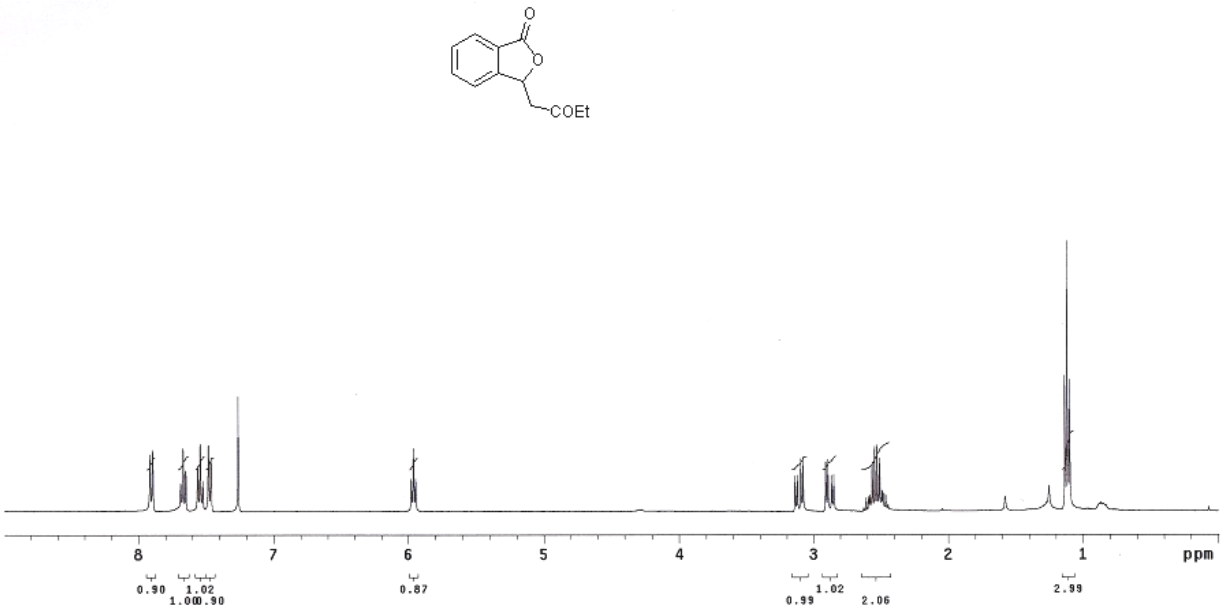
^{13}C NMR Spectrum of Compound **2f** ($CDCl_3$, 100 MHz)



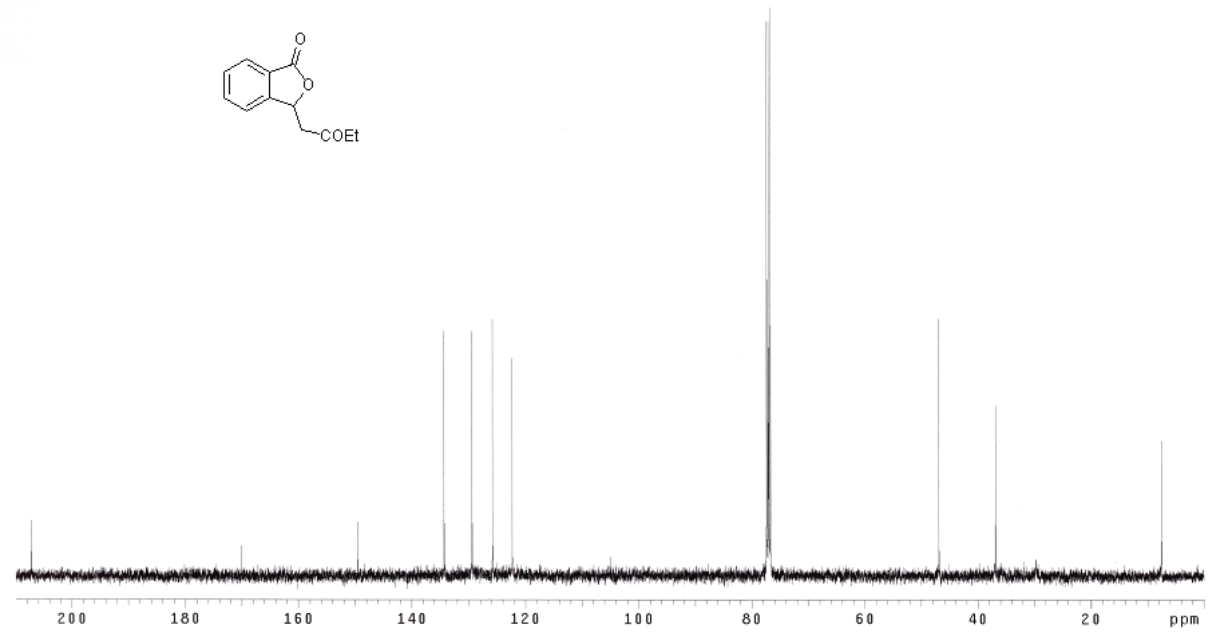
^{1}H NMR Spectrum of Compound **2g** ($CDCl_3$, 400 MHz)



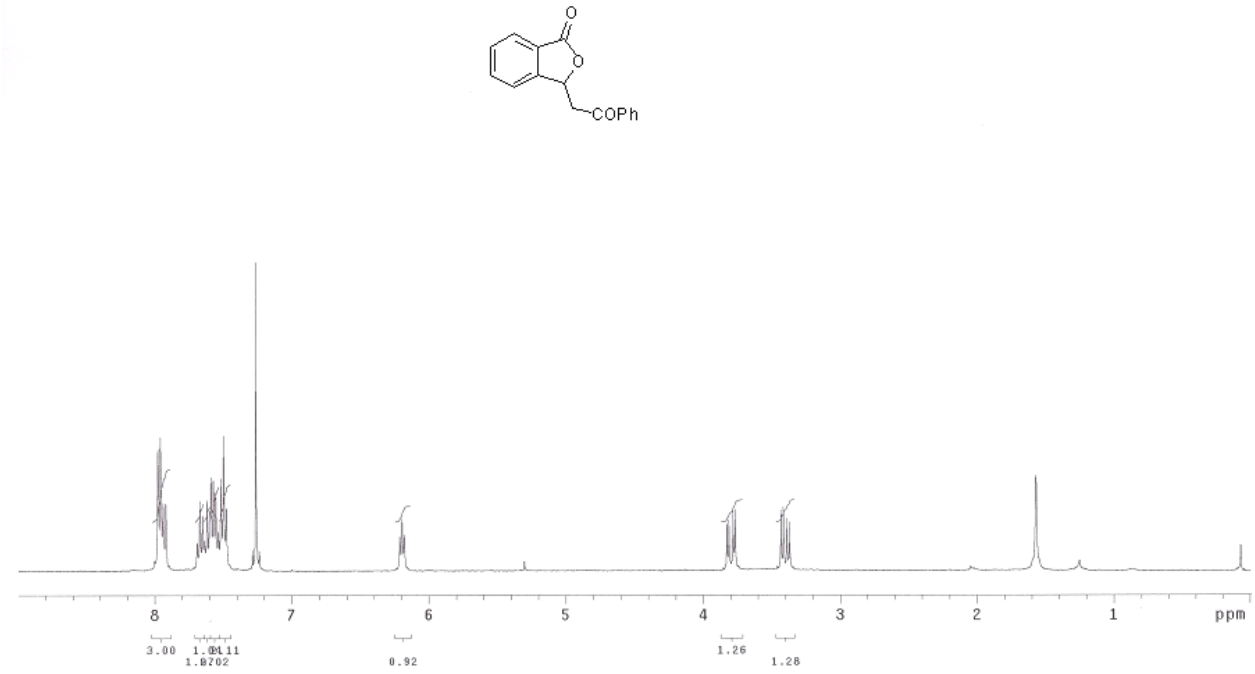
^{13}C NMR Spectrum of Compound **2g** ($CDCl_3$, 100 MHz)



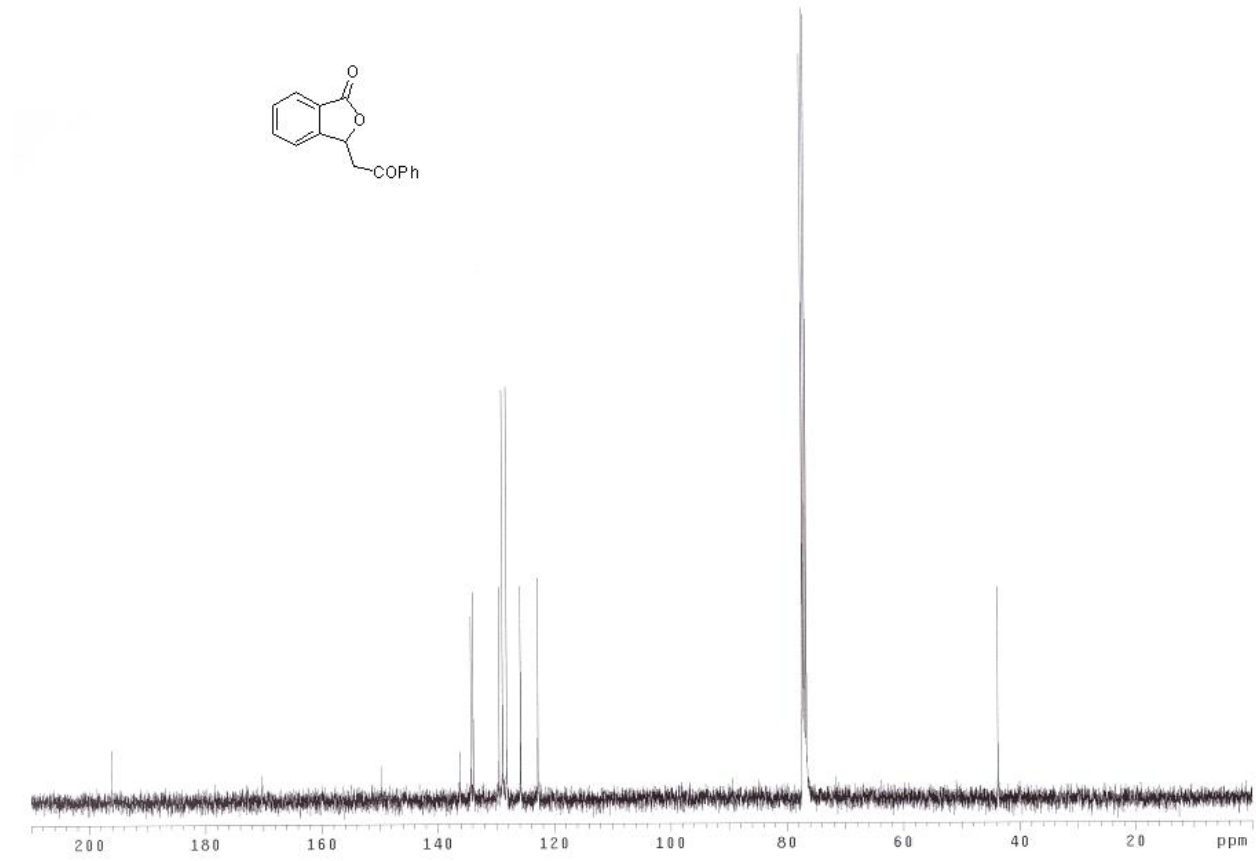
^{1}H NMR Spectrum of Compound **2h** ($CDCl_3$, 400 MHz)



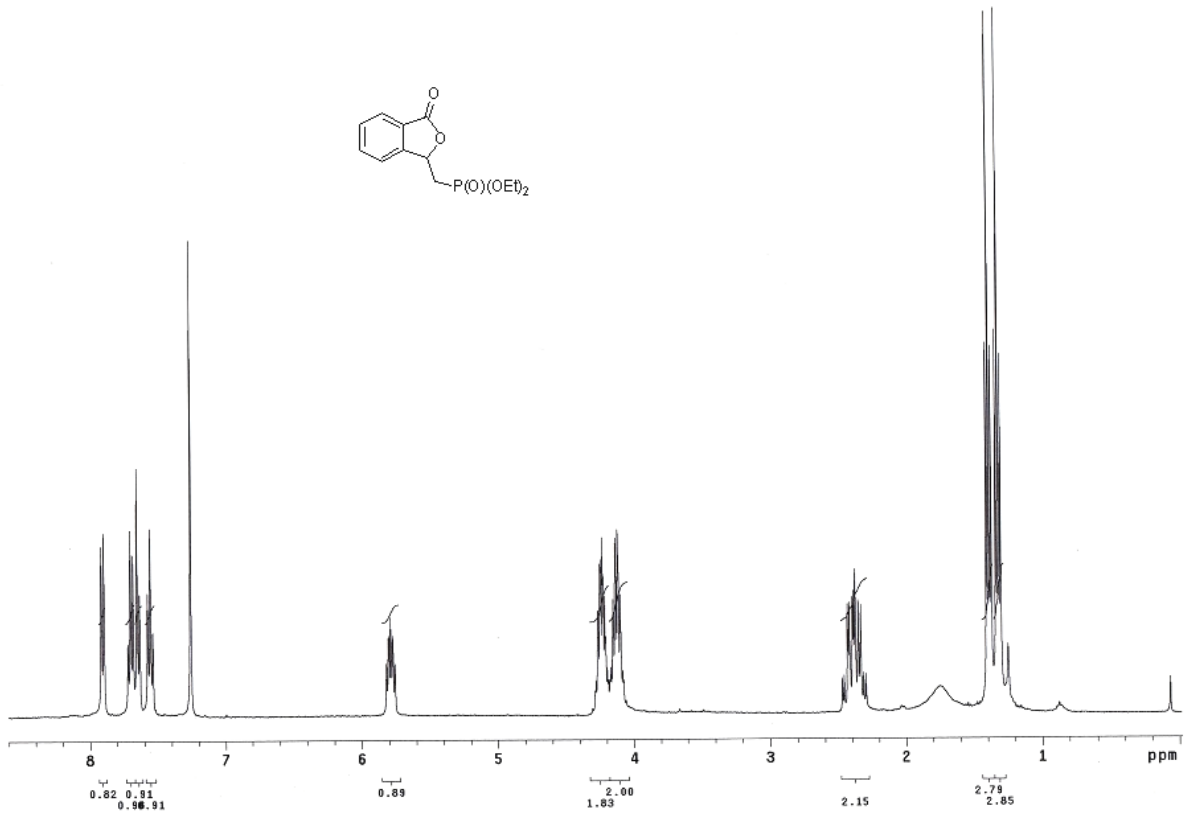
^{13}C NMR Spectrum of Compound **2h** ($CDCl_3$, 100 MHz)



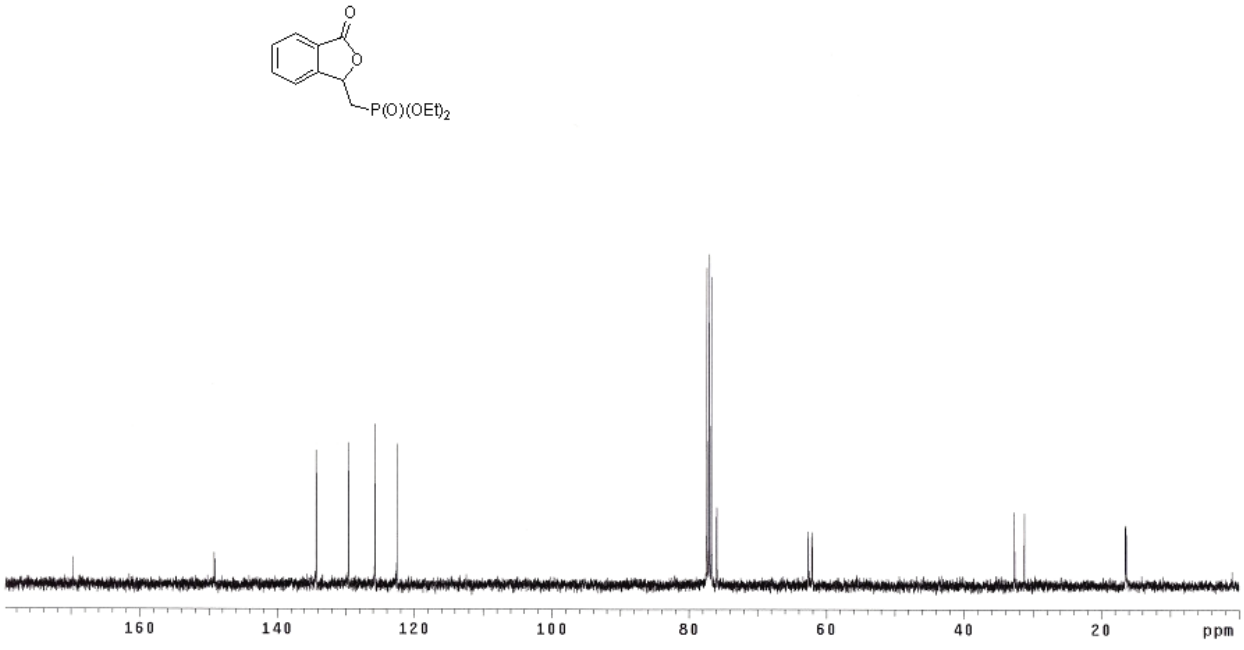
^{1}H NMR Spectrum of Compound **2i** ($CDCl_3$, 400 MHz)



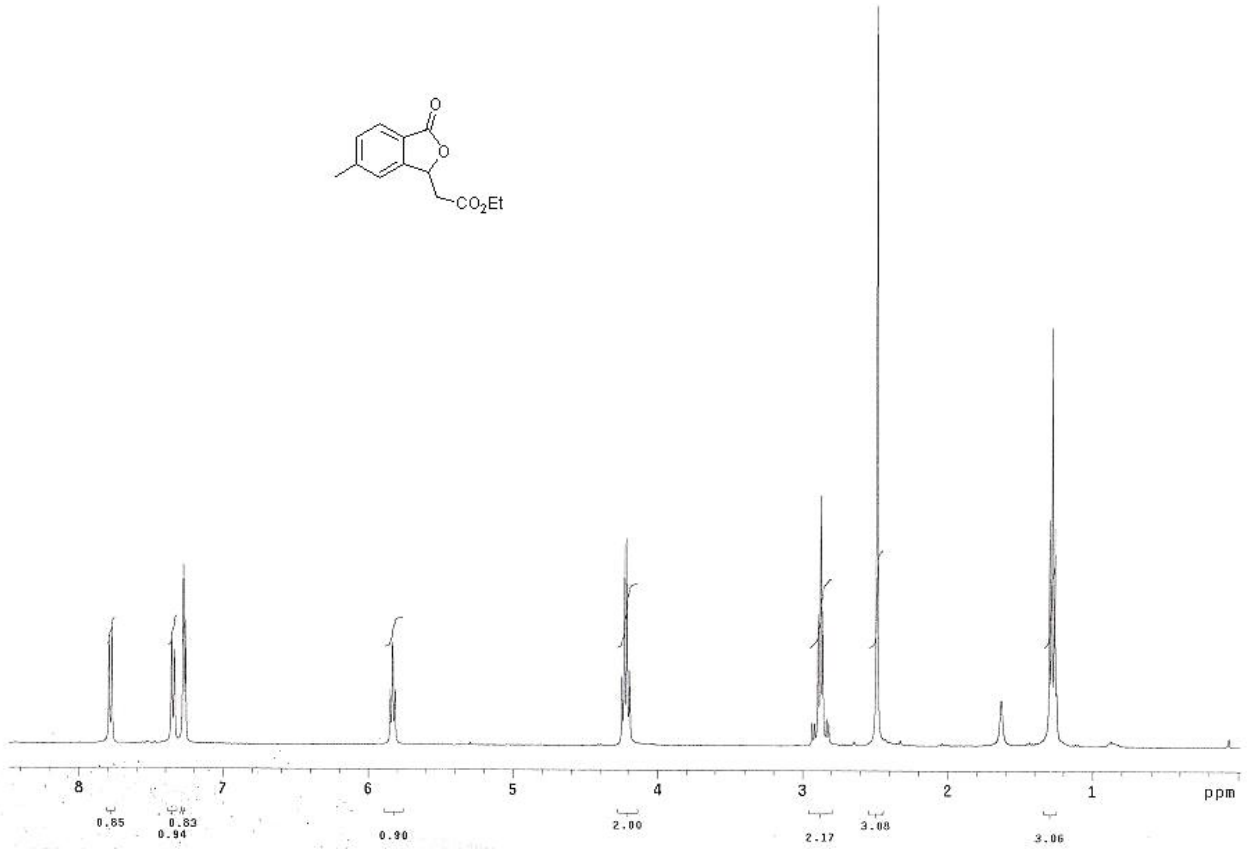
^{13}C NMR Spectrum of Compound **2i** ($CDCl_3$, 100 MHz)



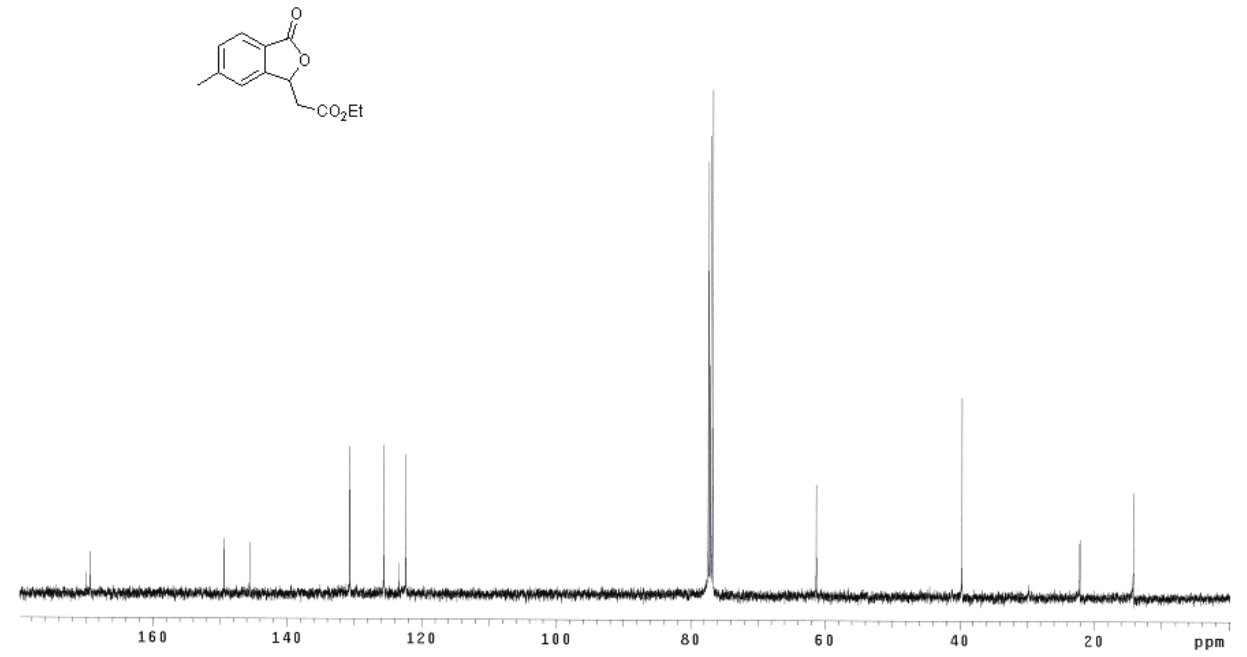
^{1}H NMR Spectrum of Compound **2j** ($CDCl_3$, 400 MHz)



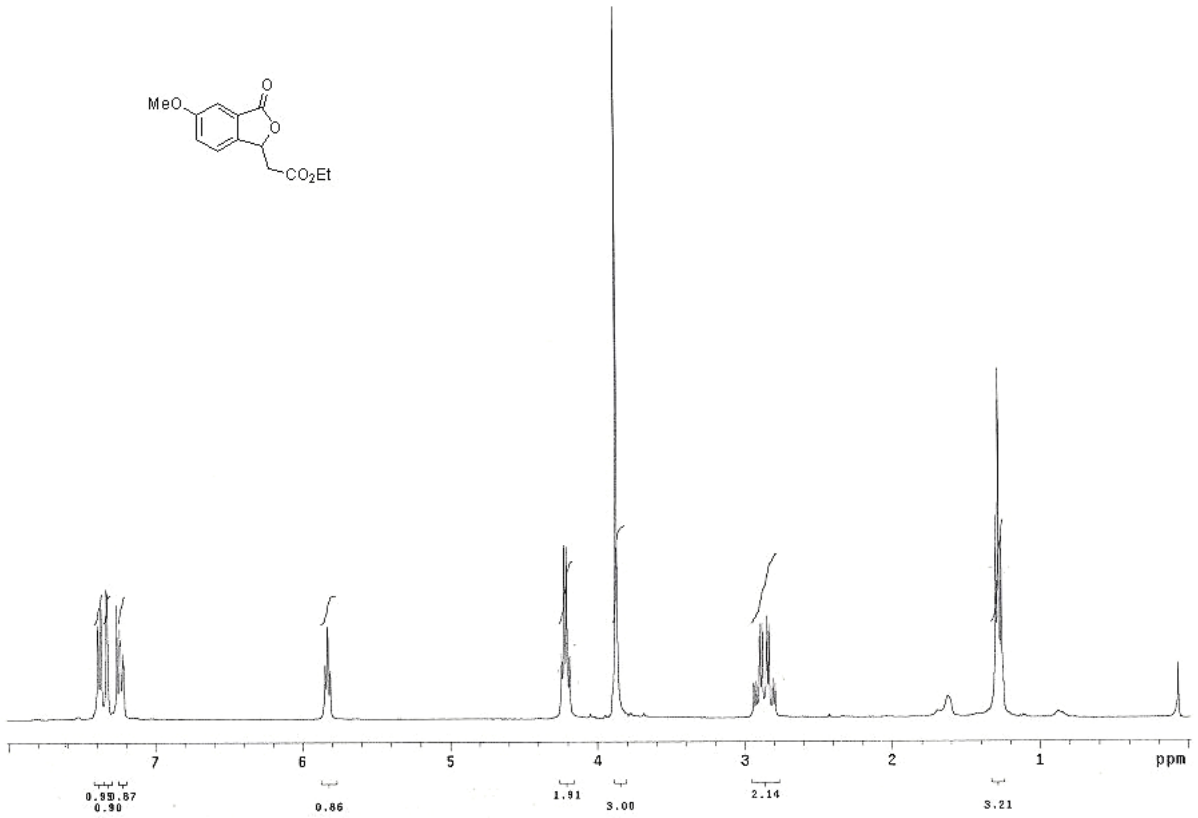
^{13}C NMR Spectrum of Compound **2j** ($CDCl_3$, 100 MHz)



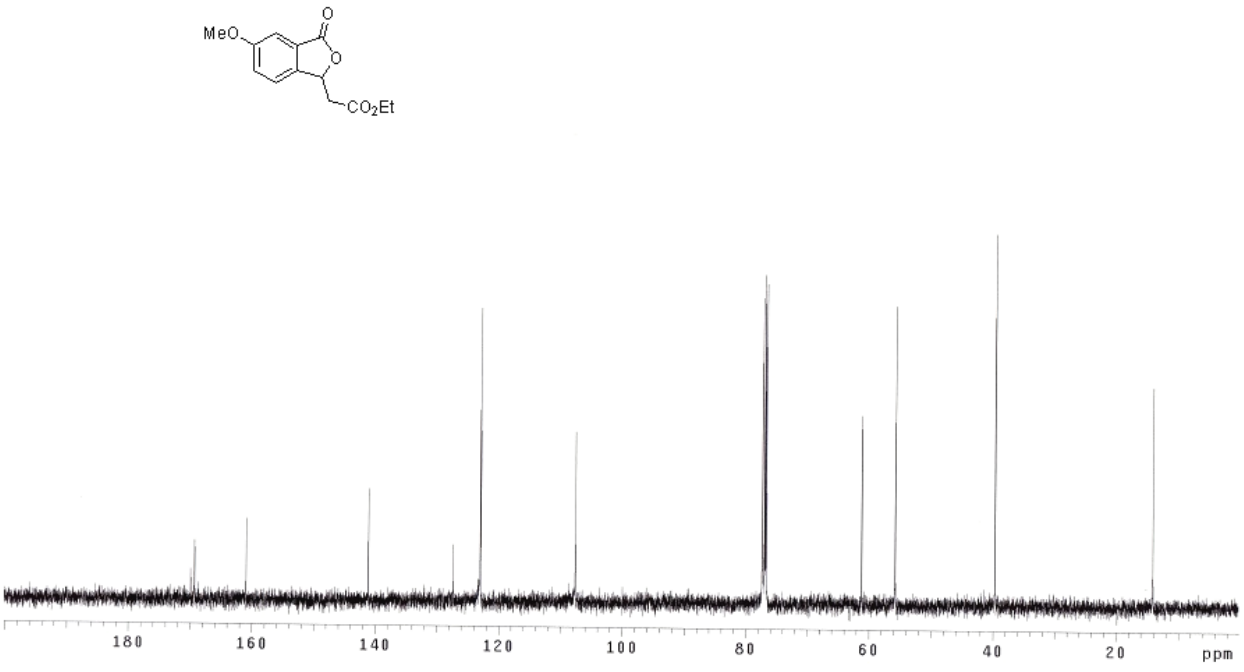
^{1}H NMR Spectrum of Compound **2k** ($CDCl_3$, 400 MHz)



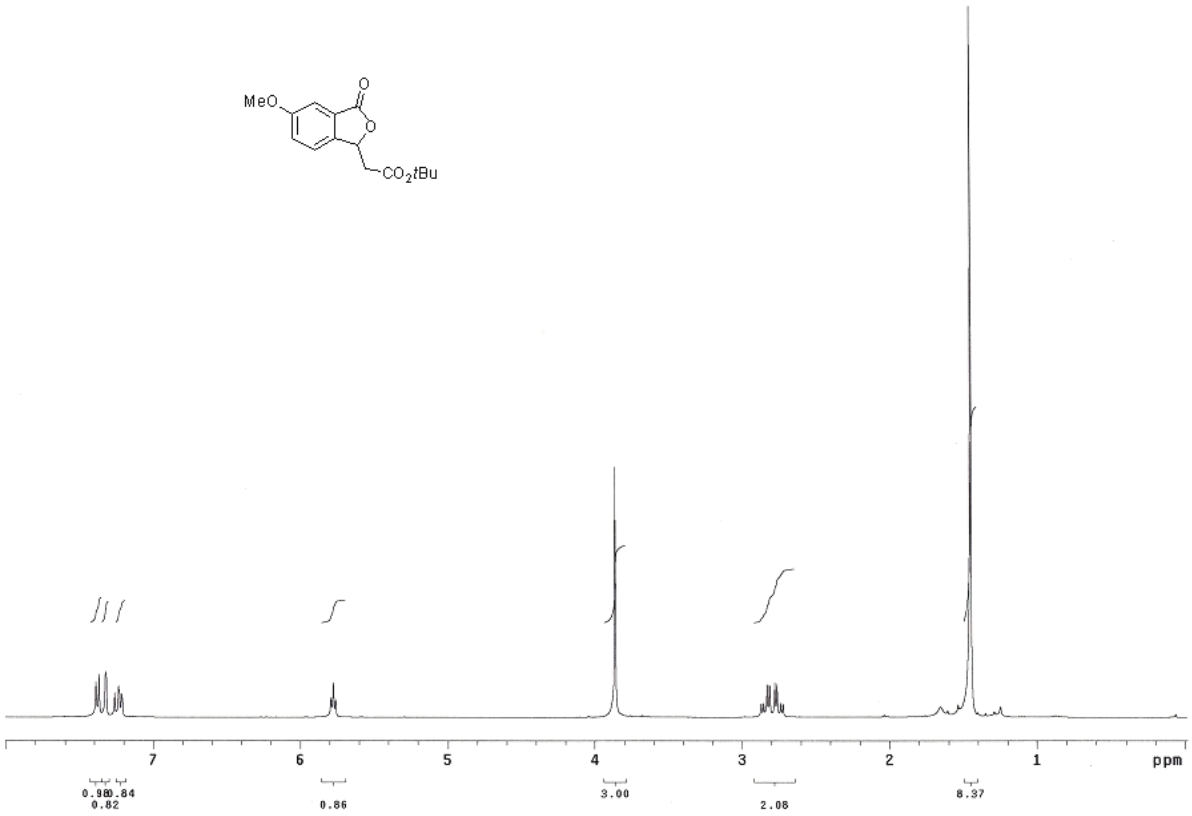
^{13}C NMR Spectrum of Compound **2k** ($CDCl_3$, 100 MHz)



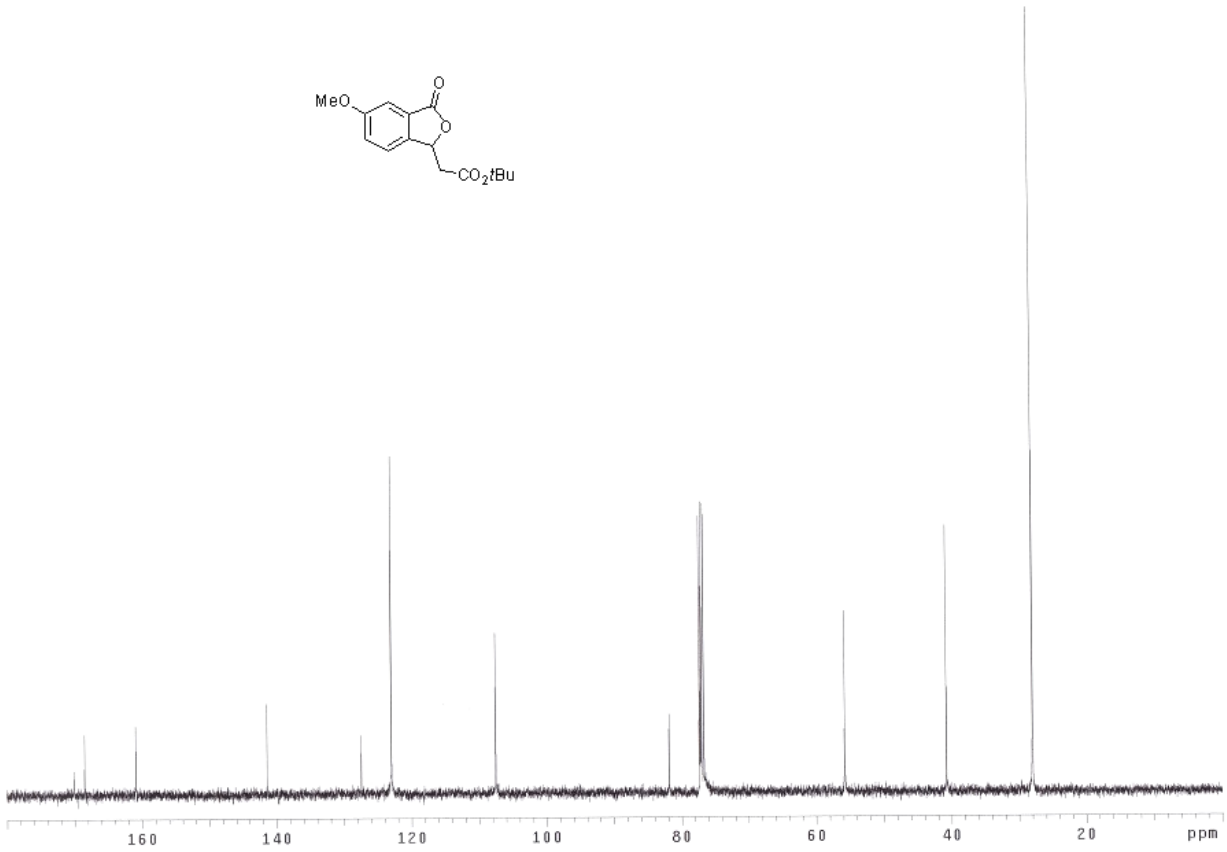
^{1}H NMR Spectrum of Compound **2l** ($CDCl_3$, 400 MHz)



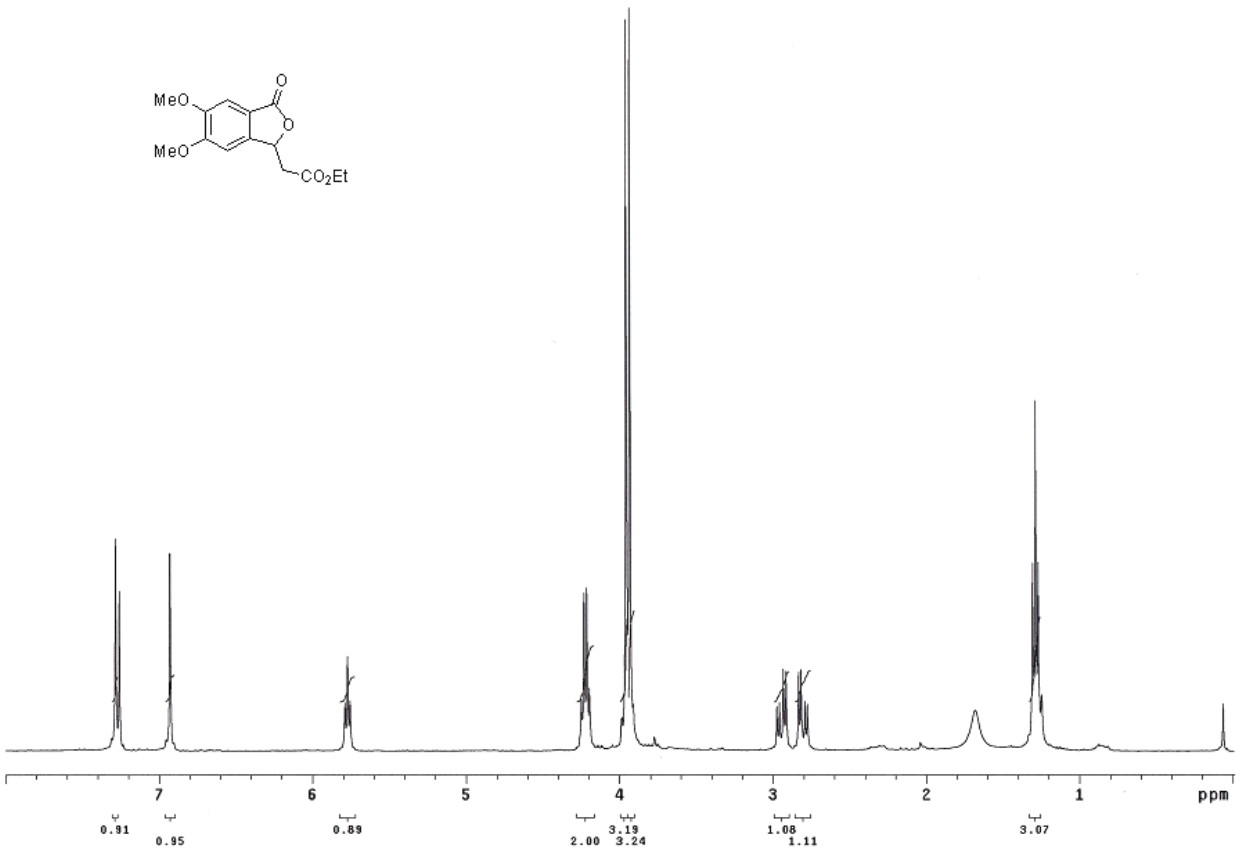
^{13}C NMR Spectrum of Compound **2l** ($CDCl_3$, 100 MHz)



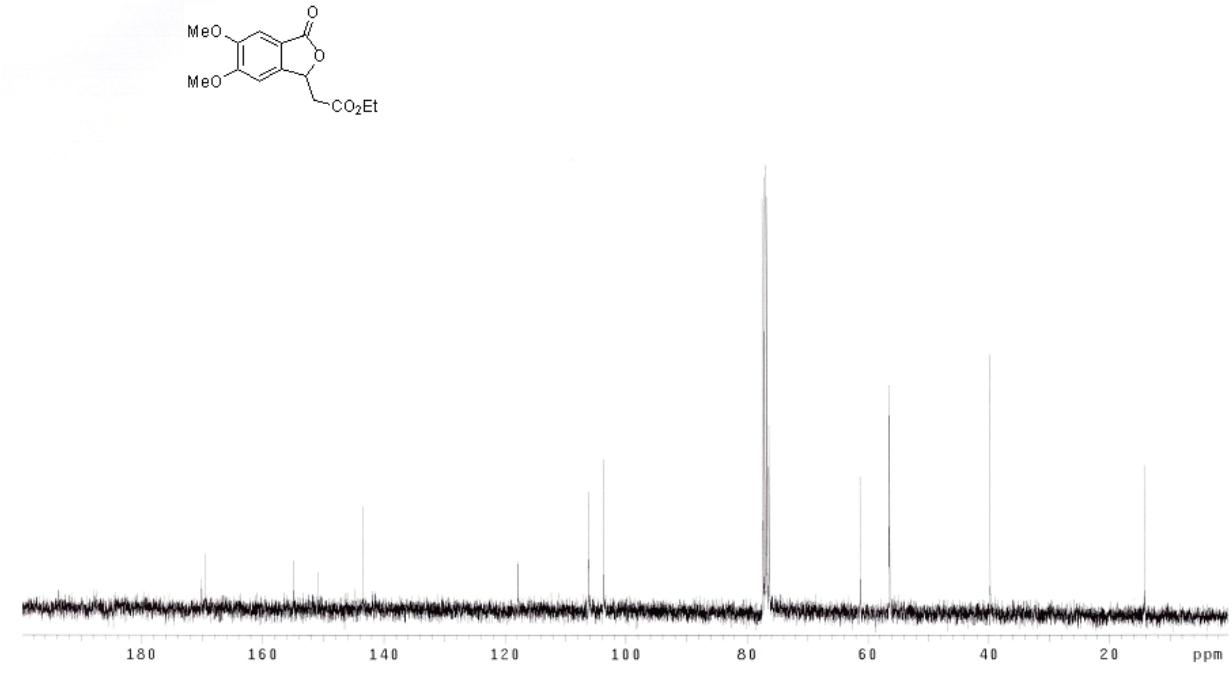
^{1}H NMR Spectrum of Compound **2m** ($CDCl_3$, 400 MHz)



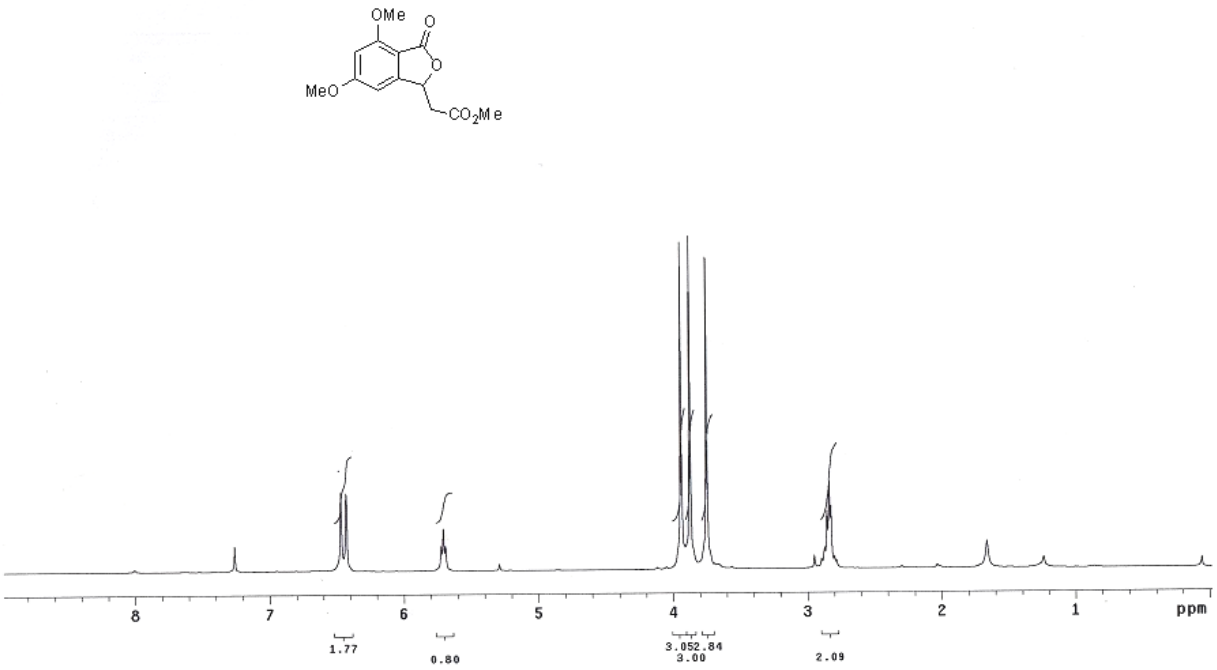
^{13}C NMR Spectrum of Compound **2m** ($CDCl_3$, 100 MHz)



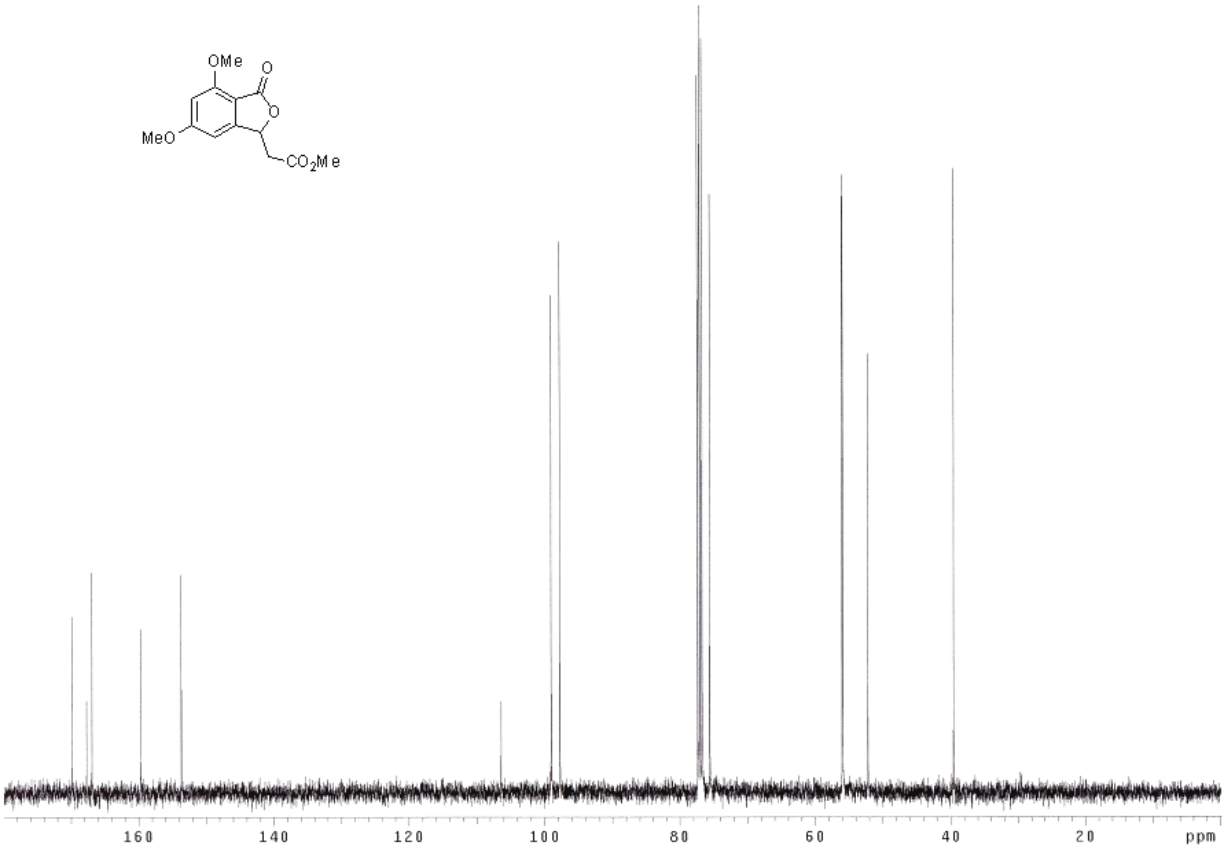
^{1}H NMR Spectrum of Compound **2n** ($CDCl_3$, 400 MHz)



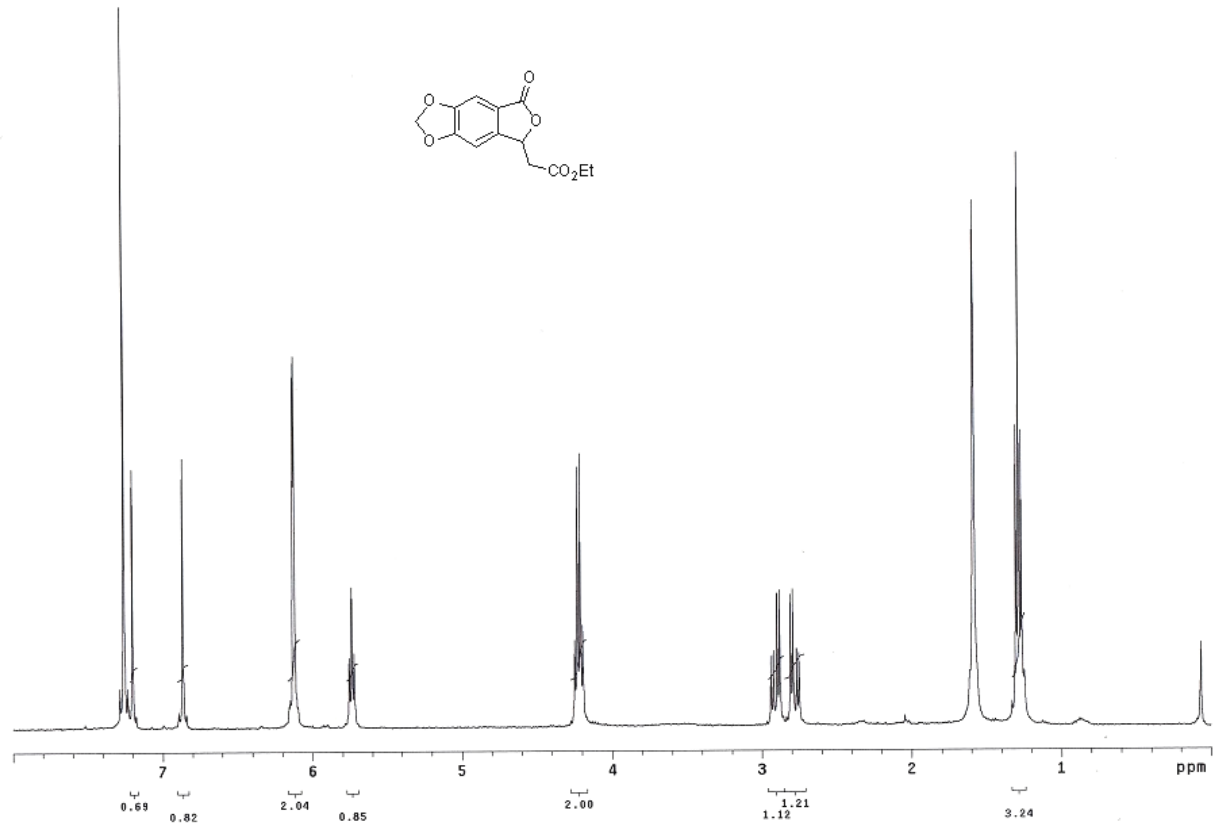
^{13}C NMR Spectrum of Compound **2n** ($CDCl_3$, 100 MHz)



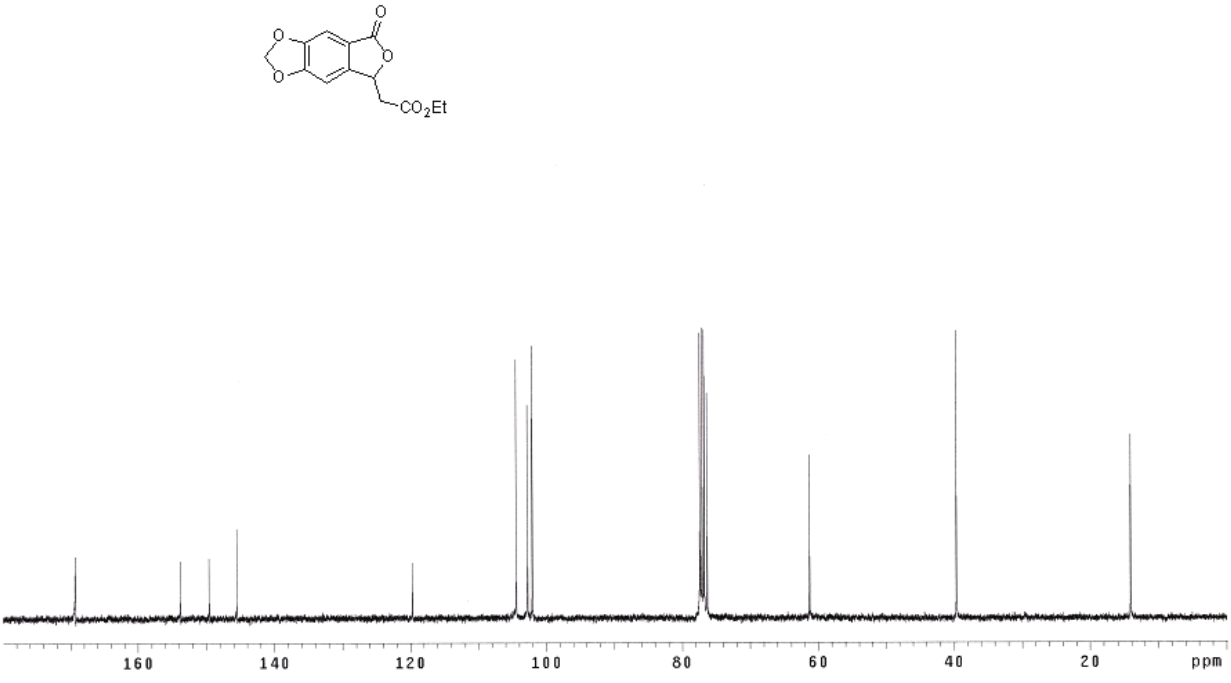
^{1}H NMR Spectrum of Compound **2o** ($CDCl_3$, 400 MHz)



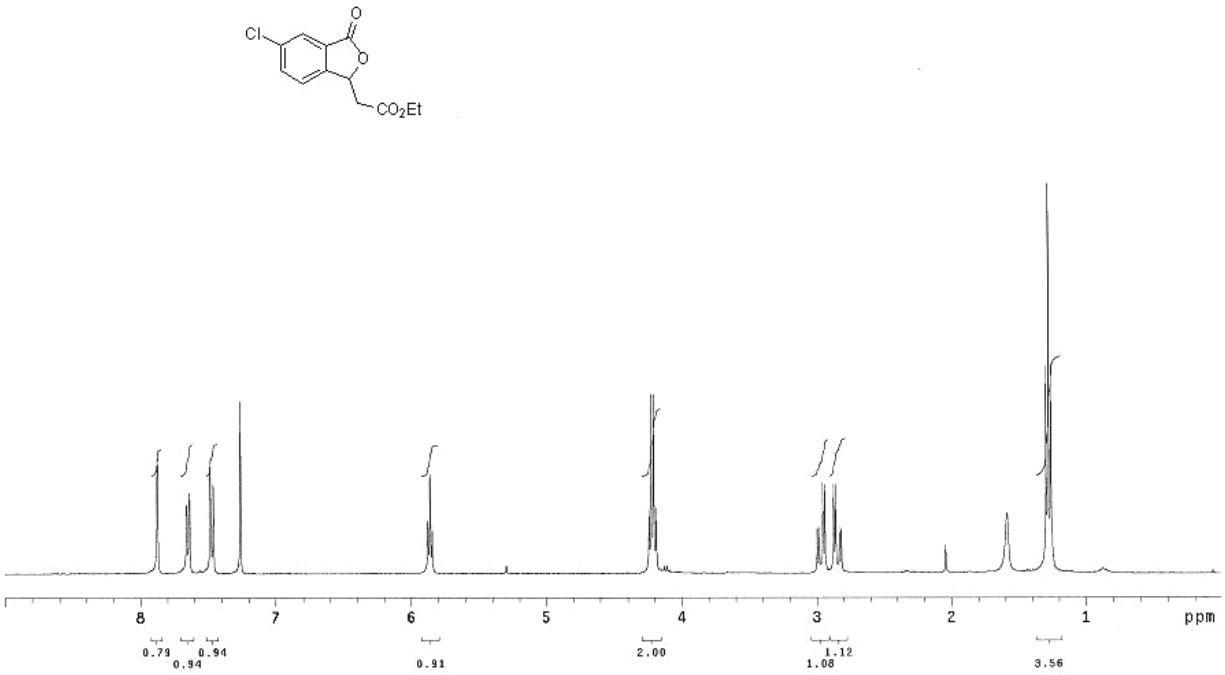
^{13}C NMR Spectrum of Compound **2o** ($CDCl_3$, 100 MHz)



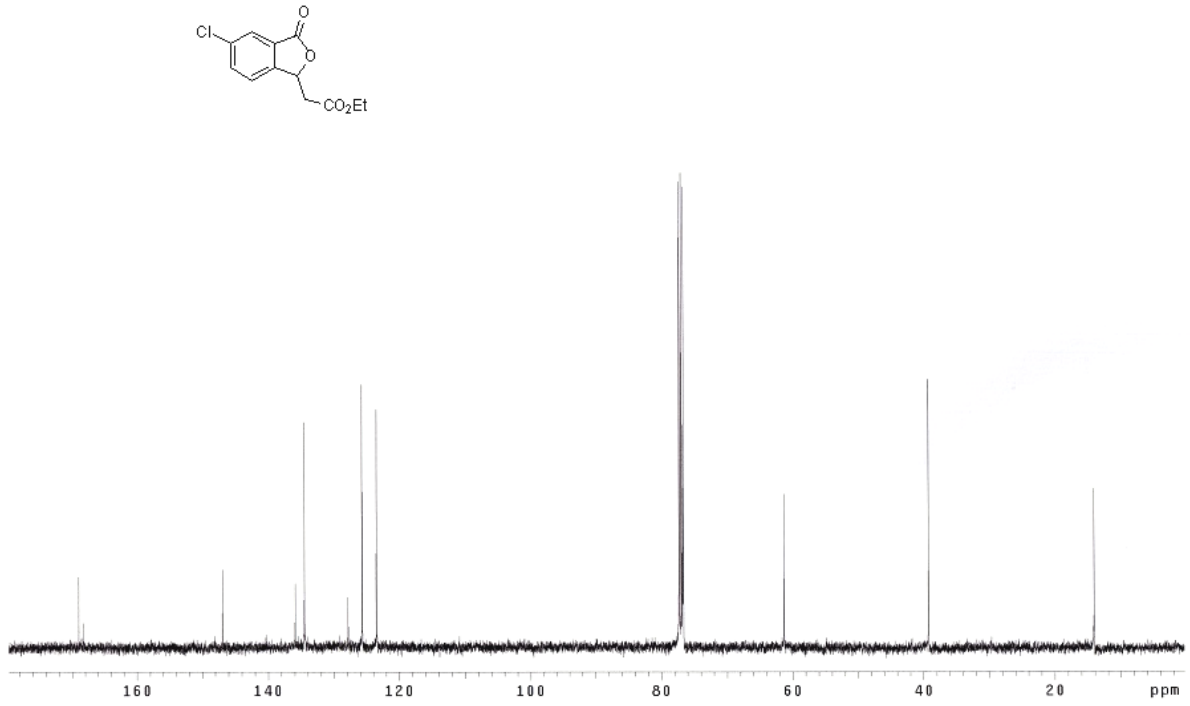
^{1}H NMR Spectrum of Compound **2p** ($CDCl_3$, 400 MHz)



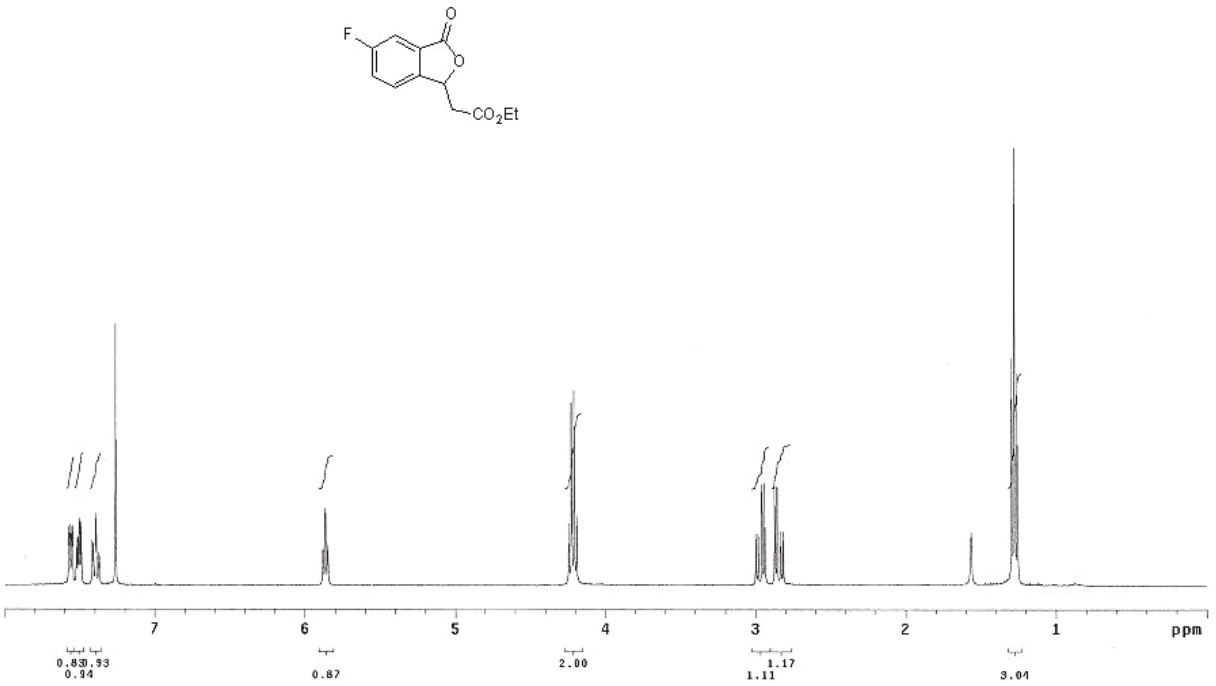
^{13}C NMR Spectrum of Compound **2p** ($CDCl_3$, 100 MHz)



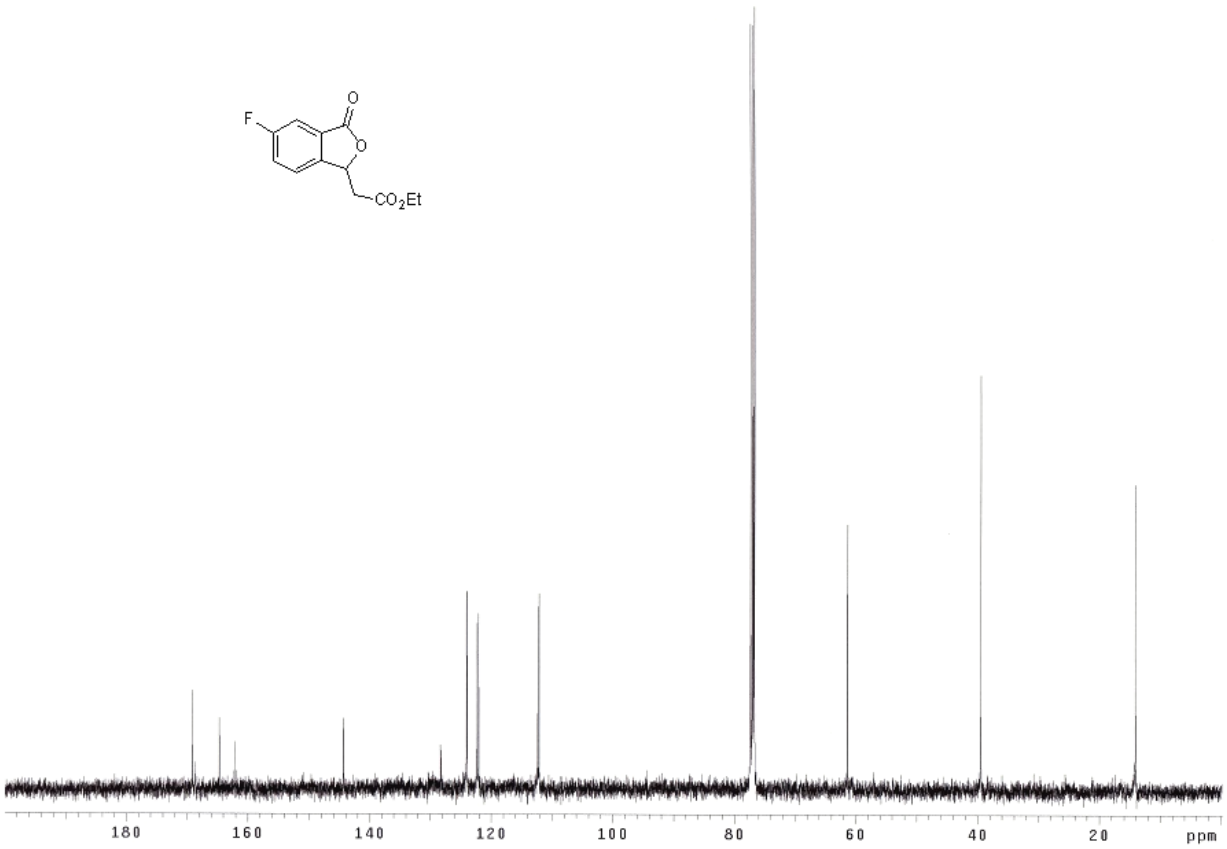
^{1}H NMR Spectrum of Compound **2q** ($CDCl_3$, 400 MHz)



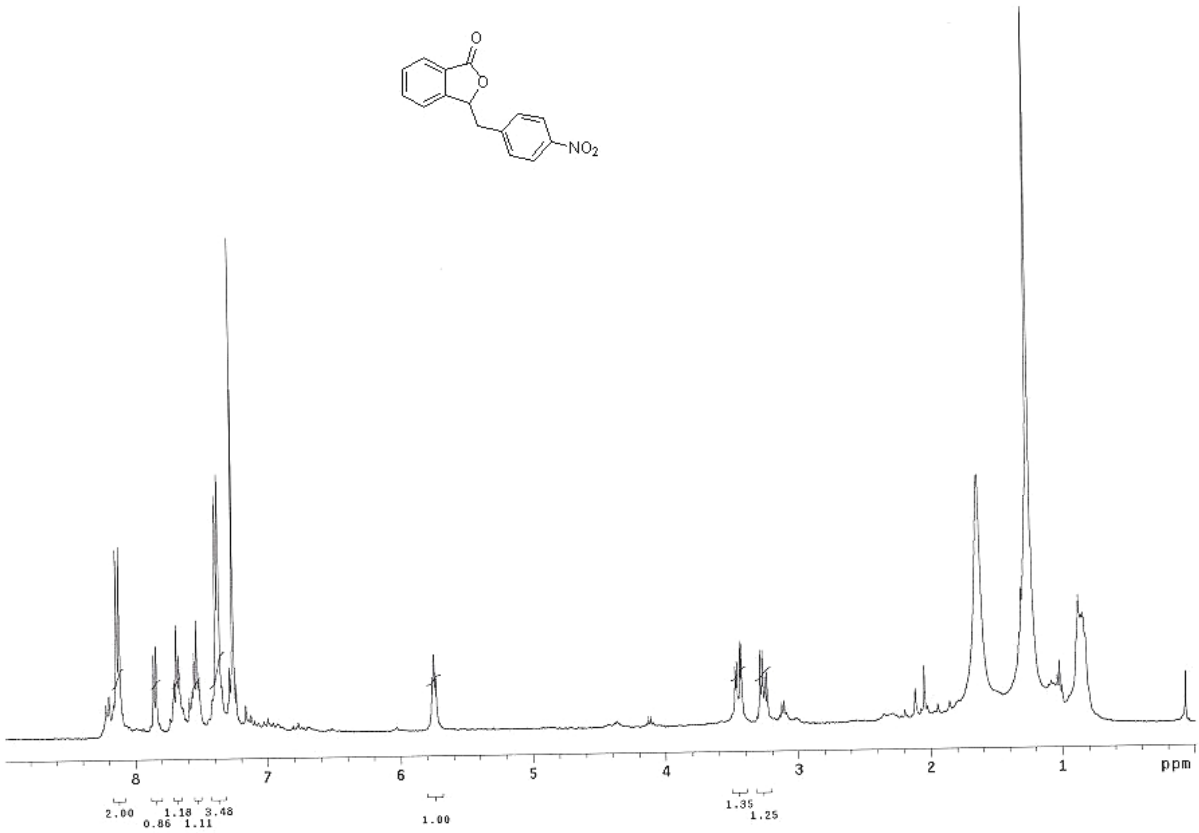
^{13}C NMR Spectrum of Compound **2q** ($CDCl_3$, 100 MHz)



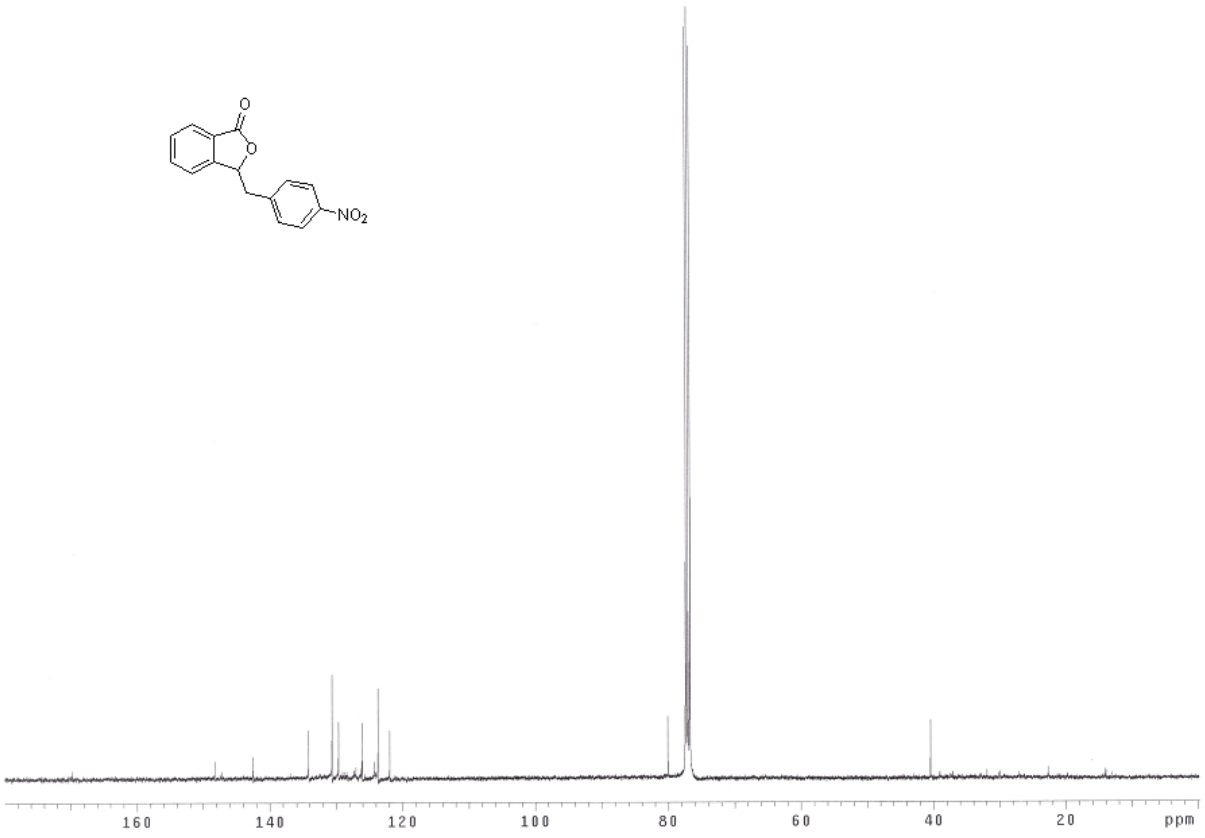
^{1}H NMR Spectrum of Compound **2r** ($CDCl_3$, 400 MHz)



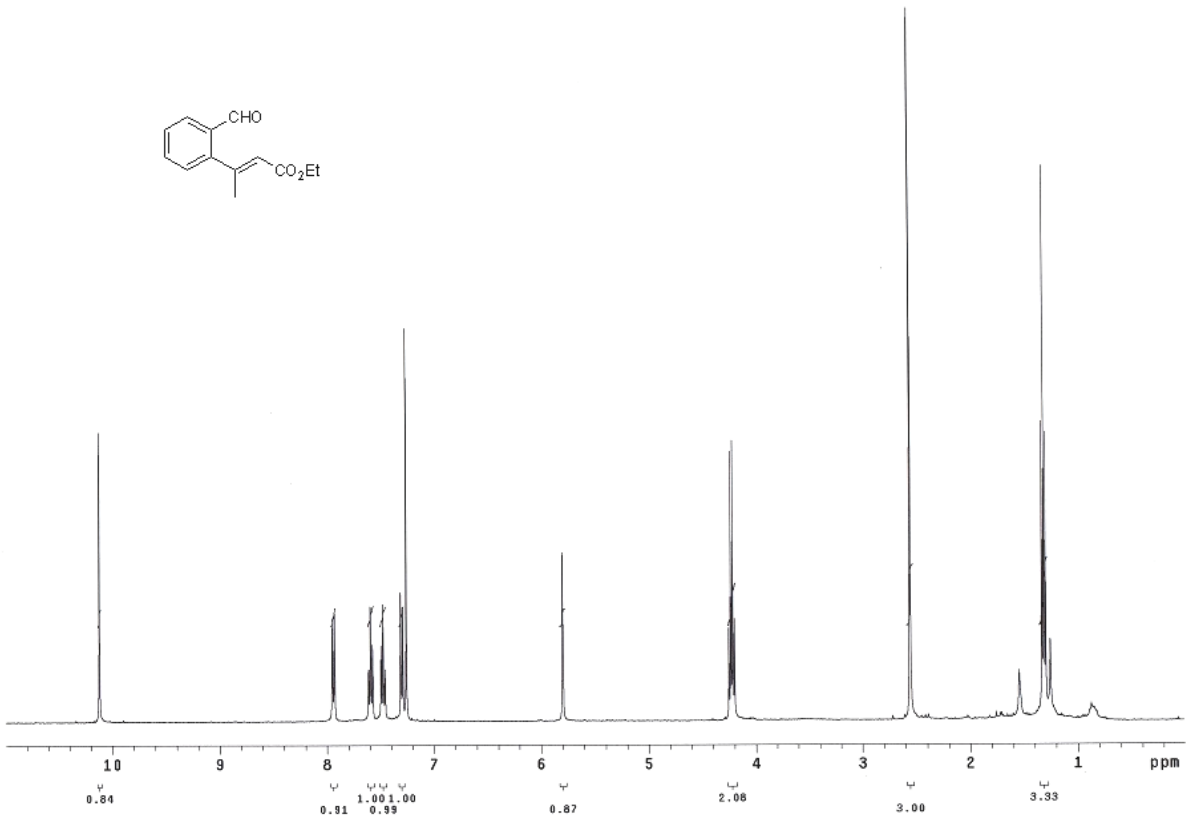
^{13}C NMR Spectrum of Compound **2r** ($CDCl_3$, 100 MHz)



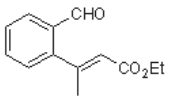
^{1}H NMR Spectrum of Compound **2t** ($CDCl_3$, 400 MHz)

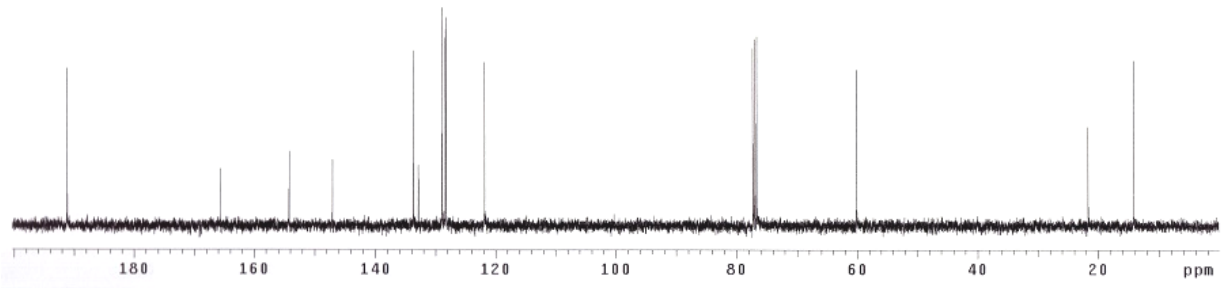


^{13}C NMR Spectrum of Compound **2t** ($CDCl_3$, 100 MHz)

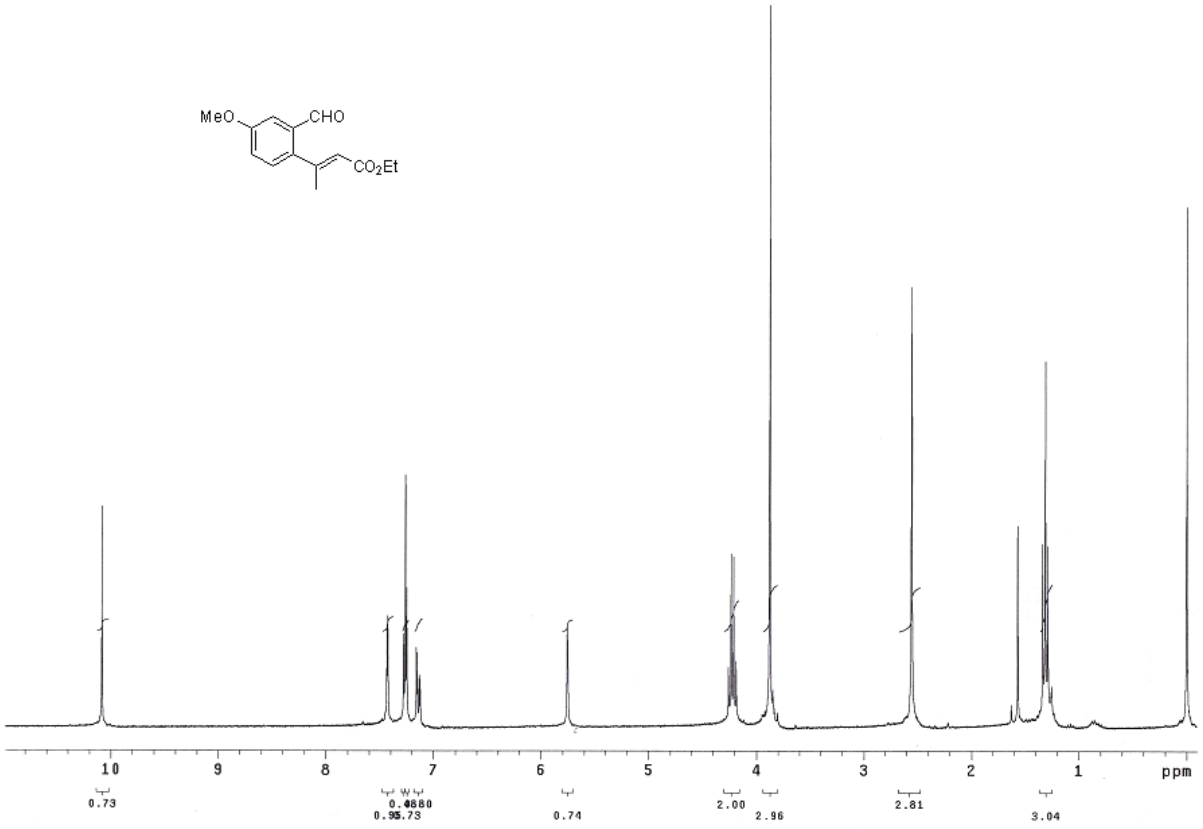


^{1}H NMR Spectrum of Compound **3a** ($CDCl_3$, 400 MHz)

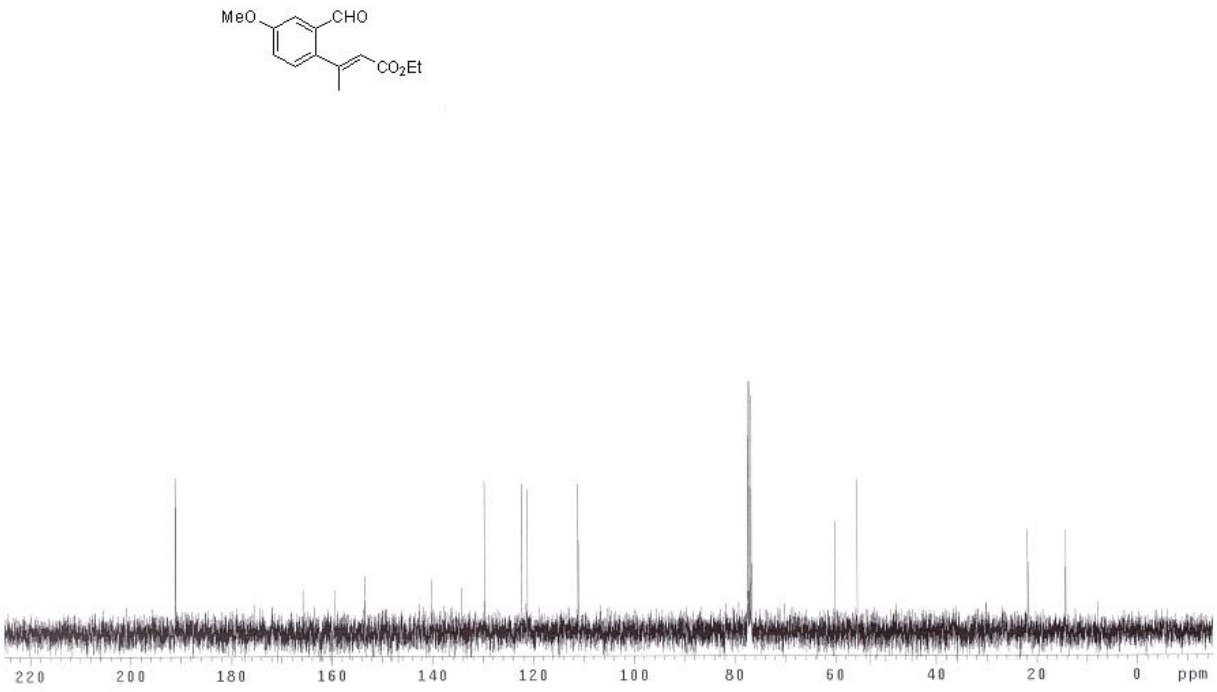




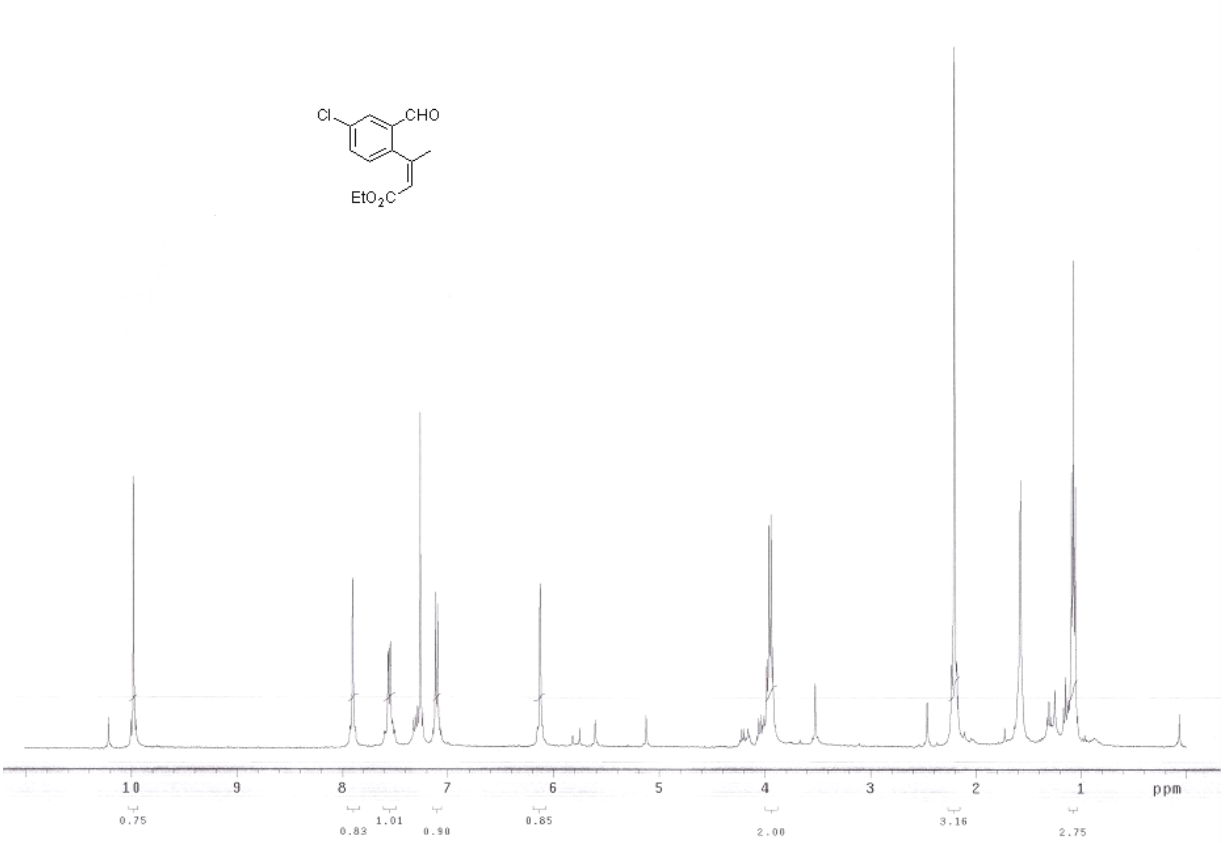
^{13}C NMR Spectrum of Compound **3a** ($CDCl_3$, 100 MHz)



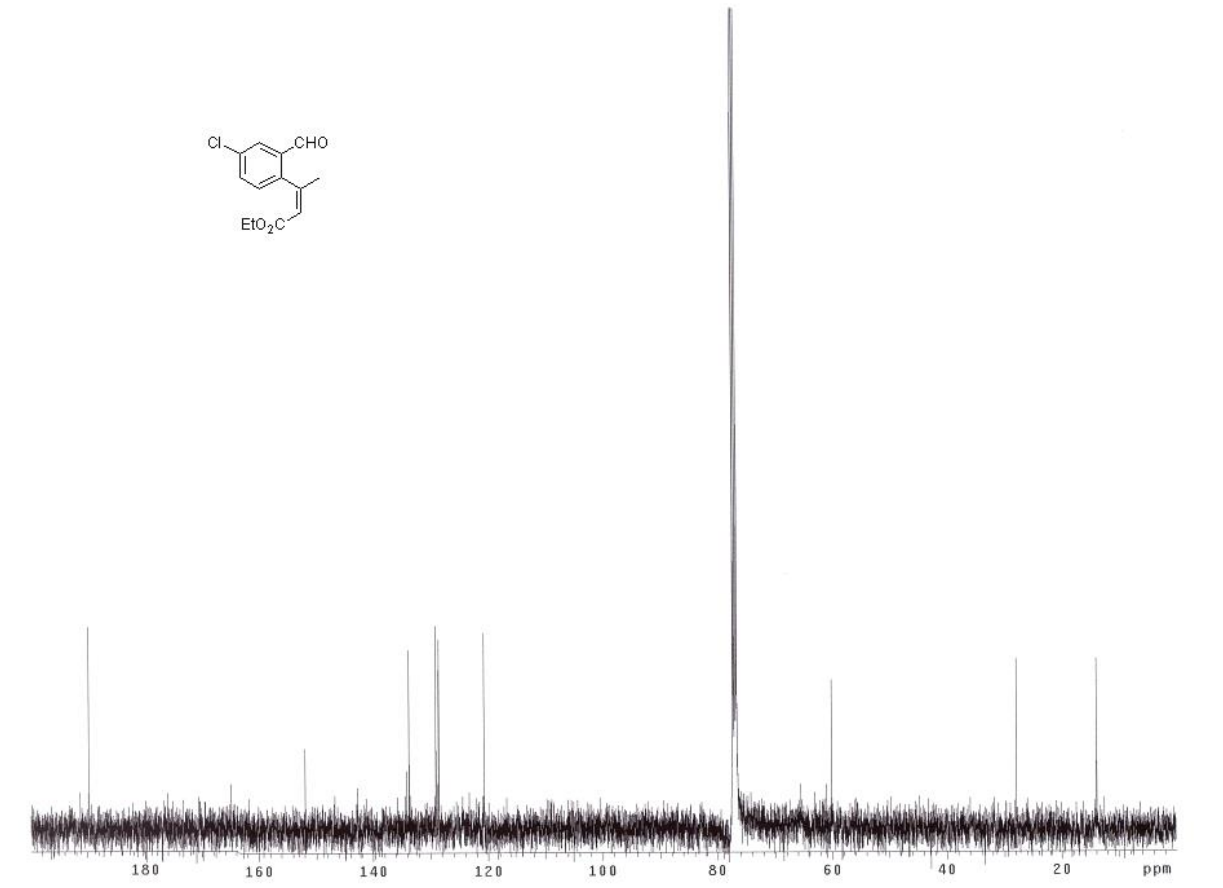
^{1}H NMR Spectrum of Compound **3b** ($CDCl_3$, 400 MHz)



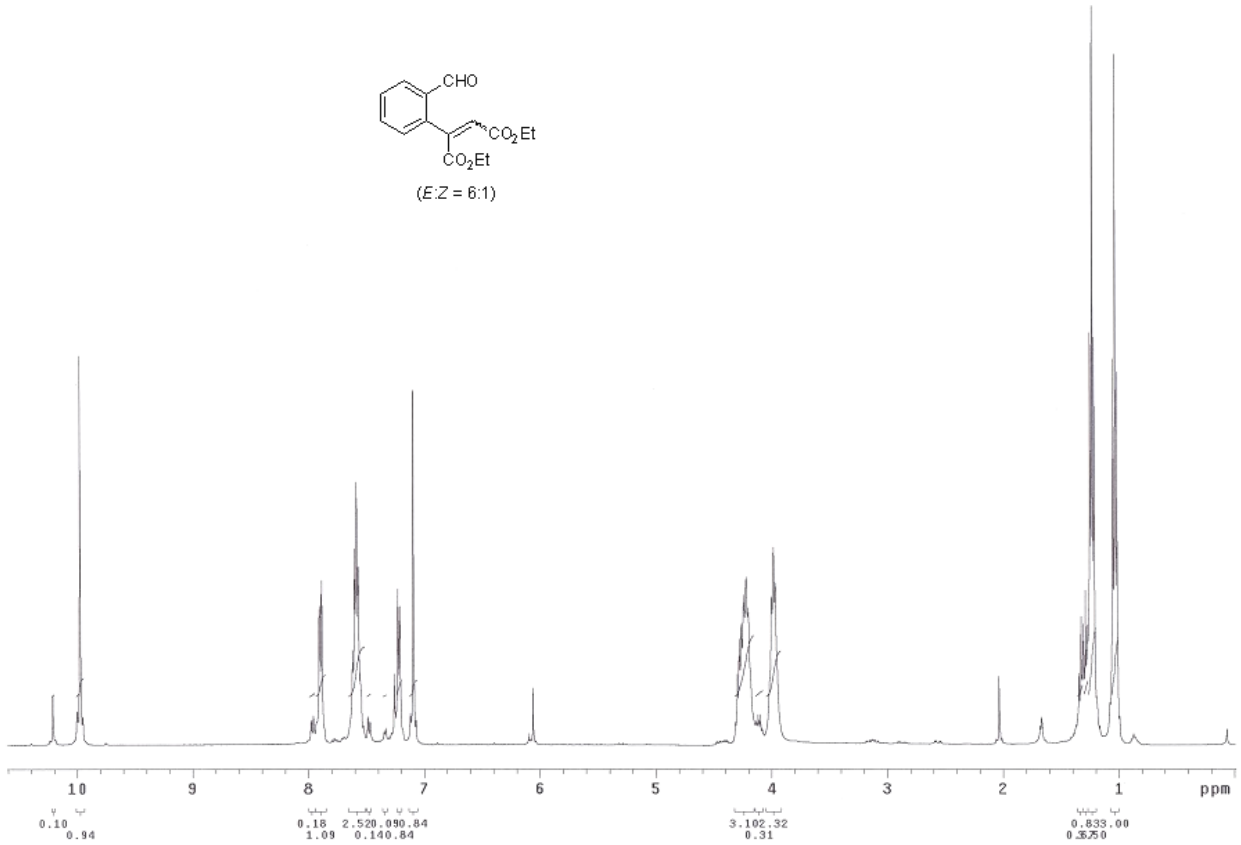
^{13}C NMR Spectrum of Compound **3b** ($CDCl_3$, 100 MHz)



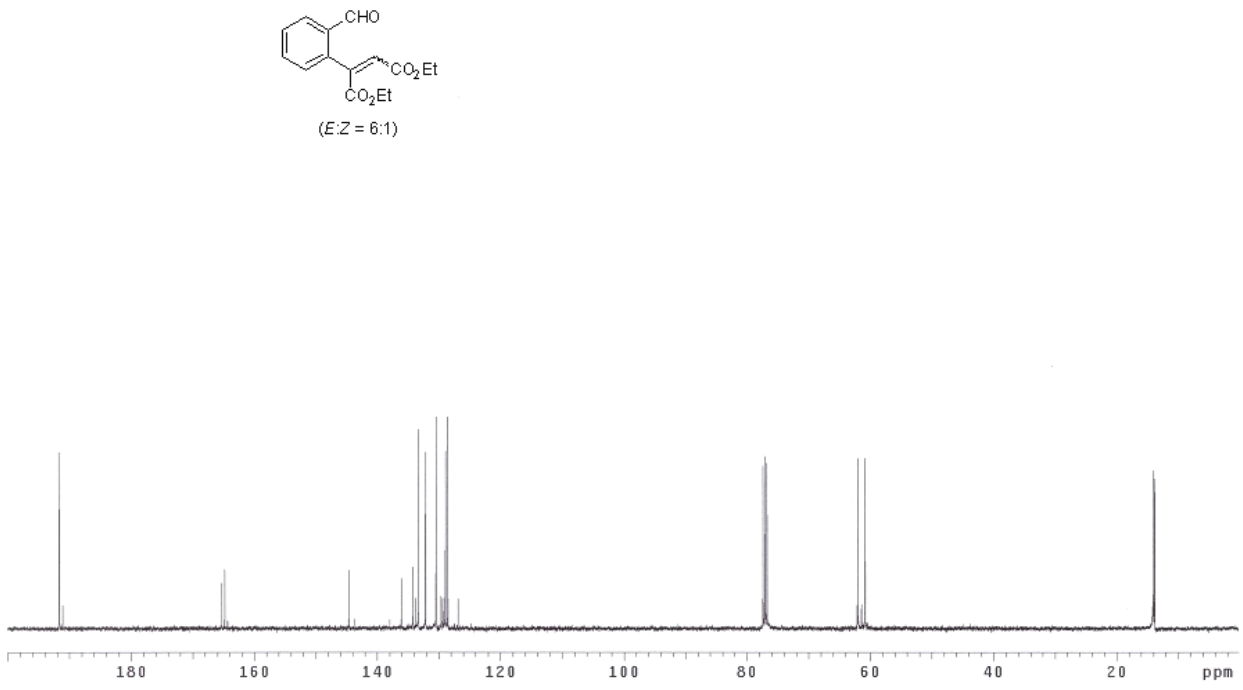
^{1}H NMR Spectrum of Compound **3c** ($CDCl_3$, 400 MHz)



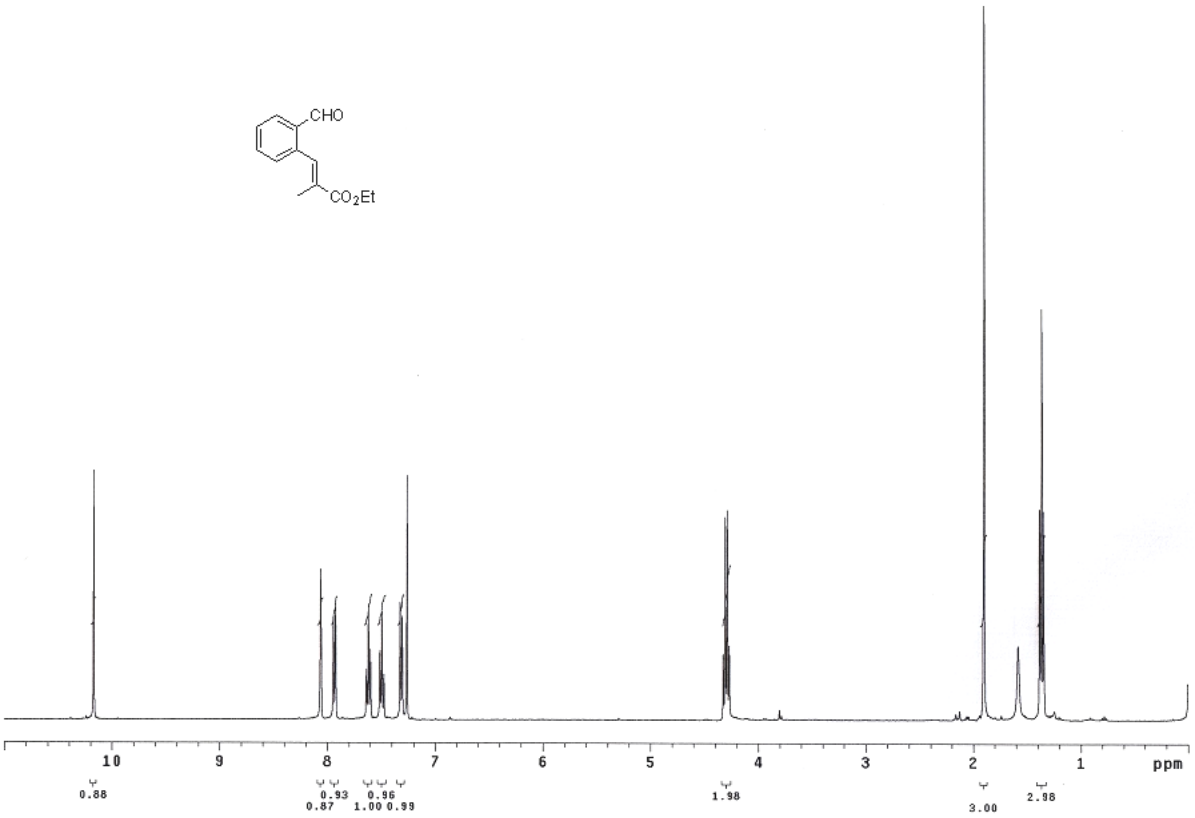
^{13}C NMR Spectrum of Compound **3c** ($CDCl_3$, 100 MHz)



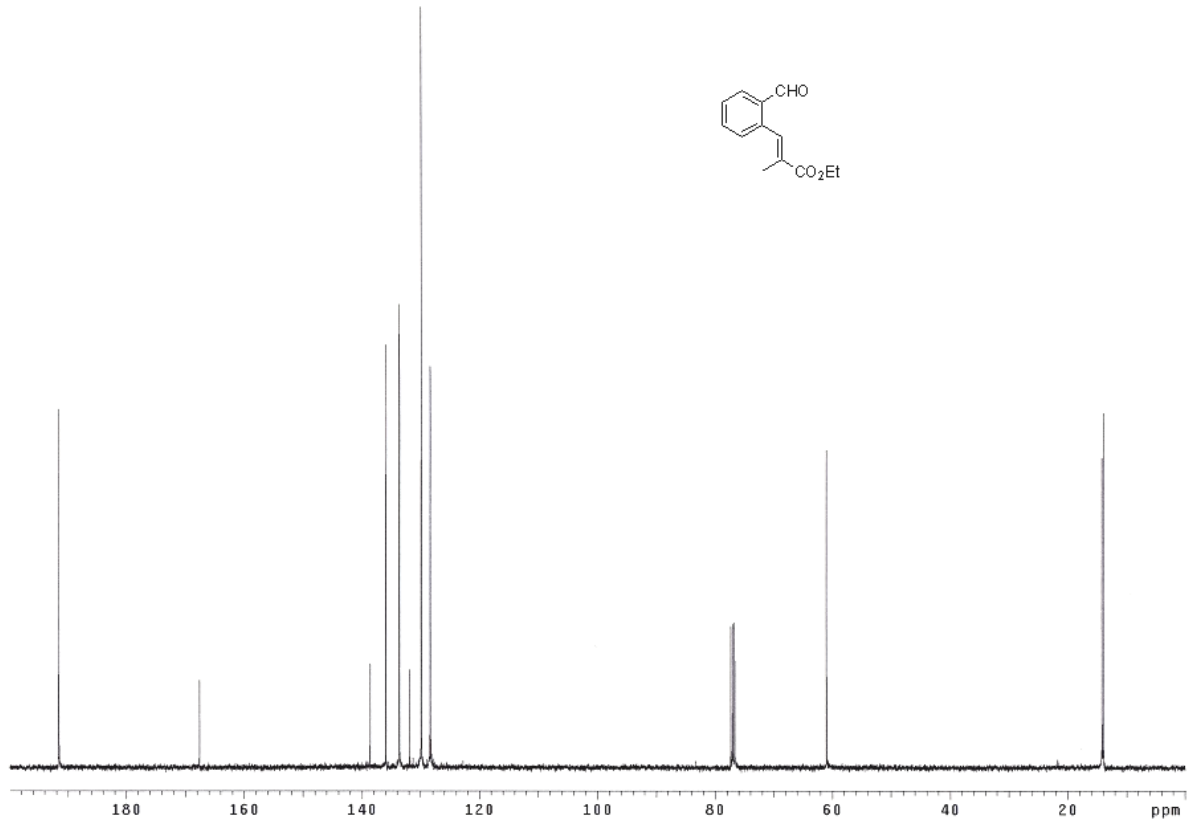
^{1}H NMR Spectrum of Compound **3d** ($CDCl_3$, 400 MHz)



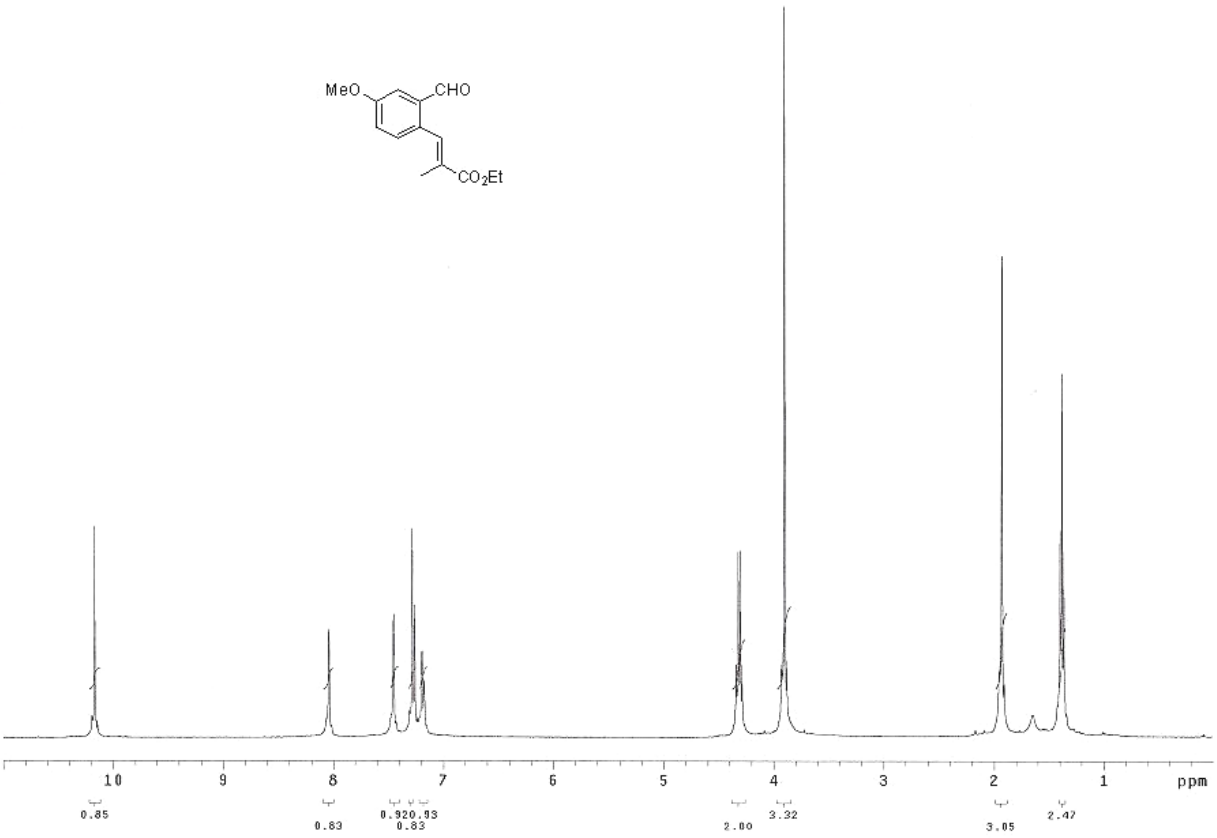
^{13}C NMR Spectrum of Compound **3d** ($CDCl_3$, 100 MHz)



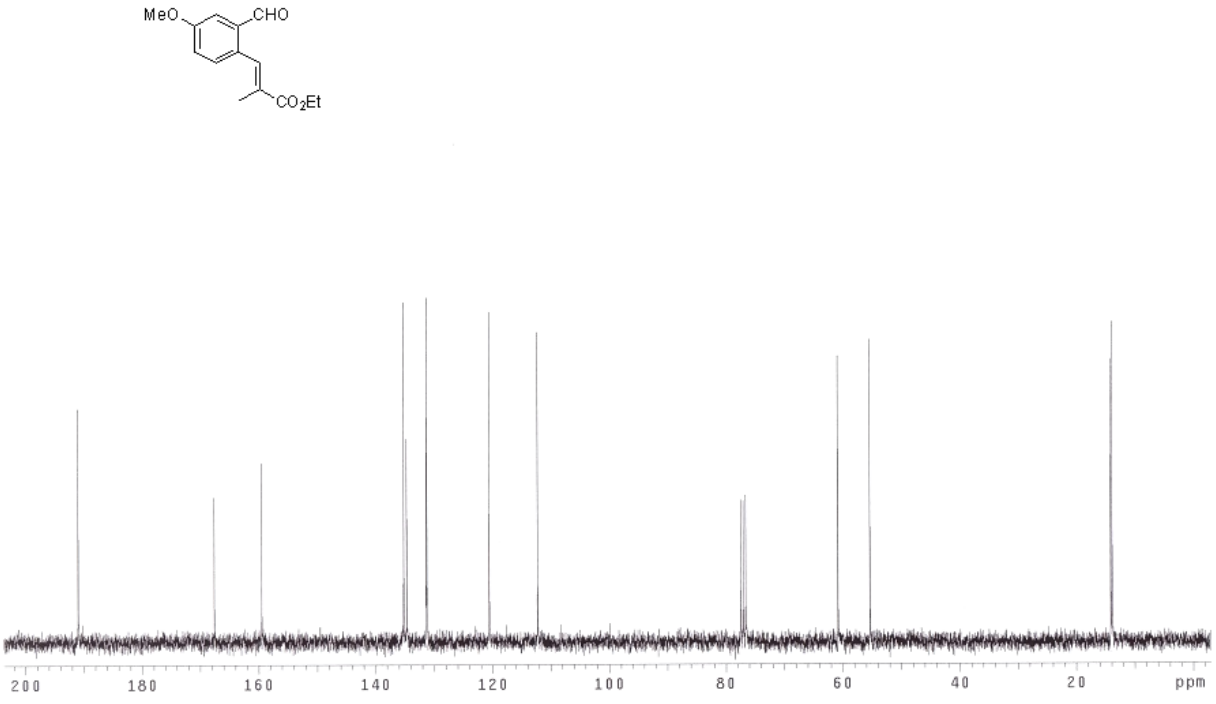
^{1}H NMR Spectrum of Compound **3e** ($CDCl_3$, 400 MHz)



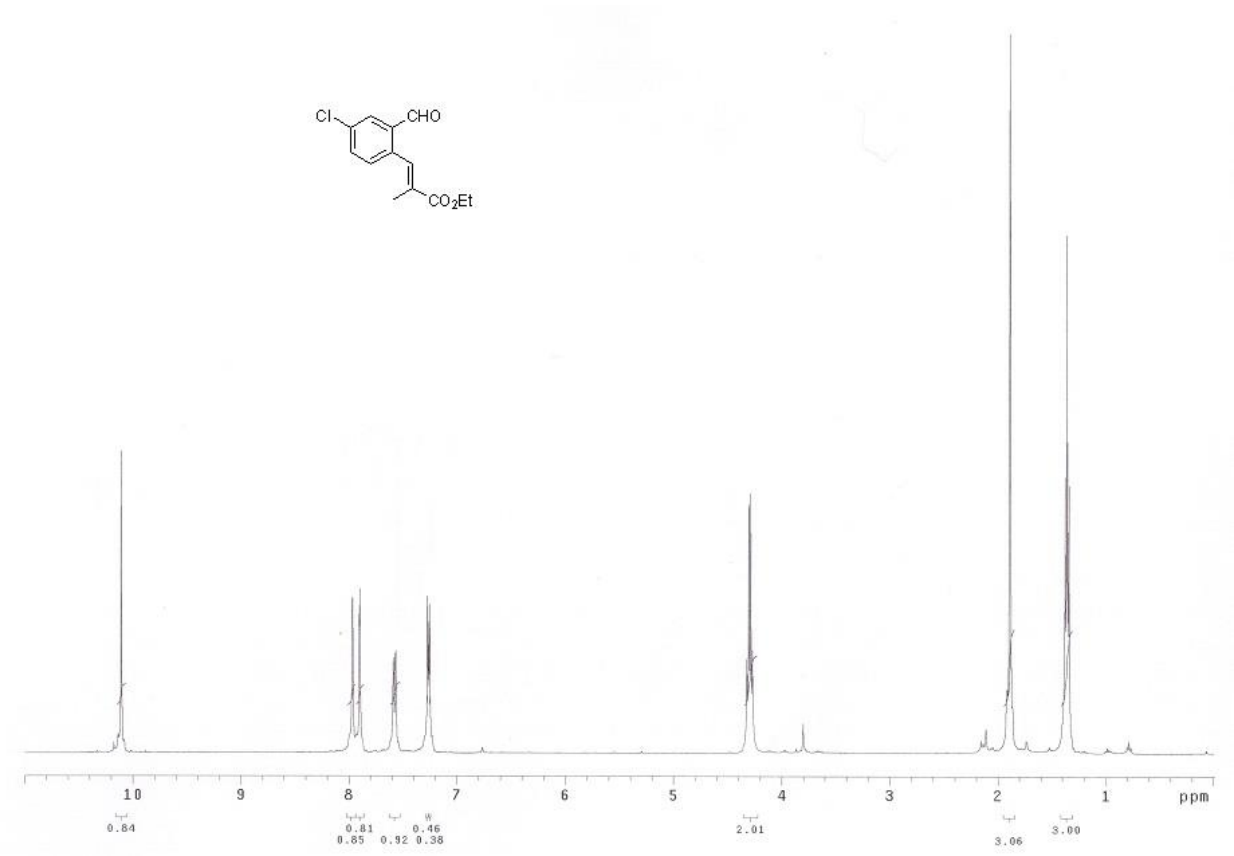
^{13}C NMR Spectrum of Compound **3e** ($CDCl_3$, 100 MHz)



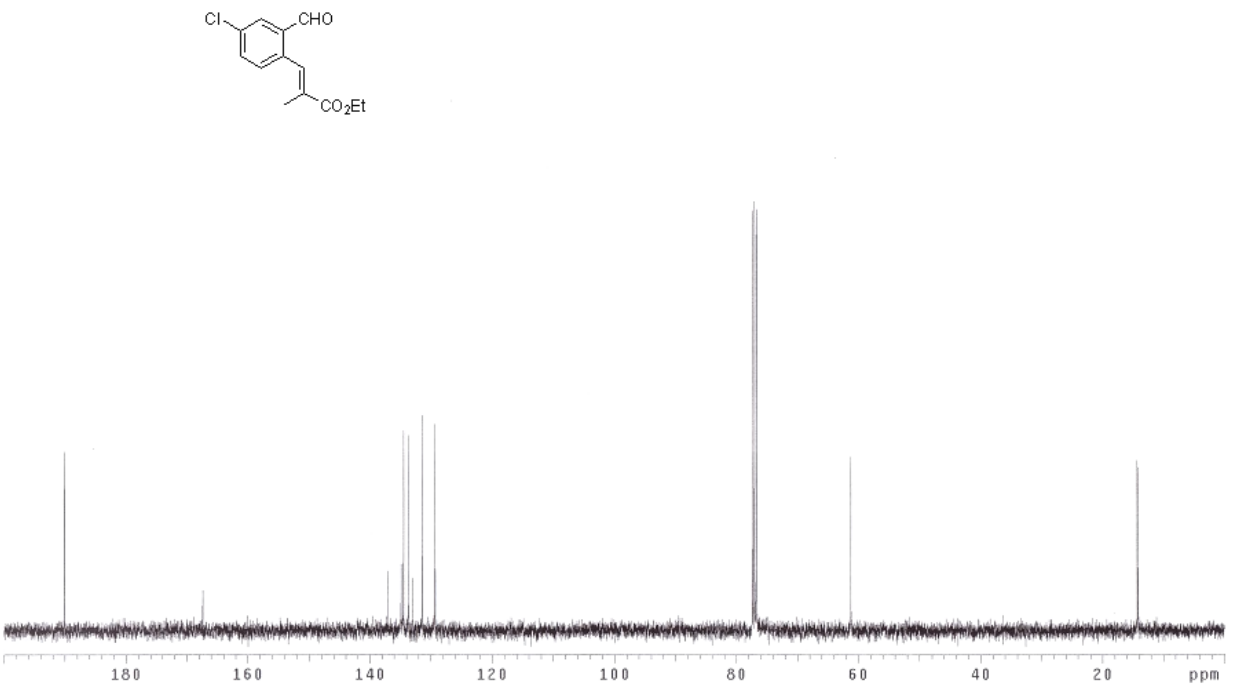
^{1}H NMR Spectrum of Compound **3f** ($CDCl_3$, 400 MHz)



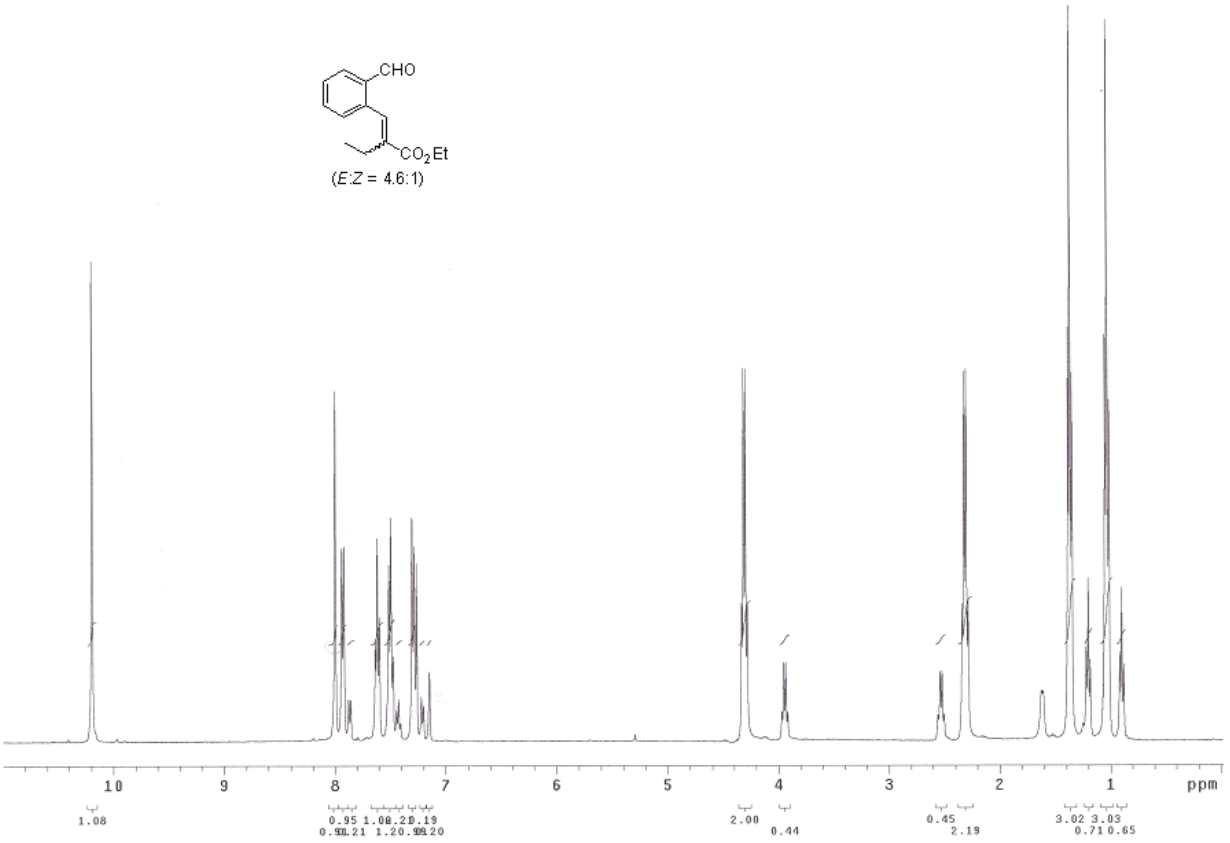
^{13}C NMR Spectrum of Compound **3f** ($CDCl_3$, 100 MHz)



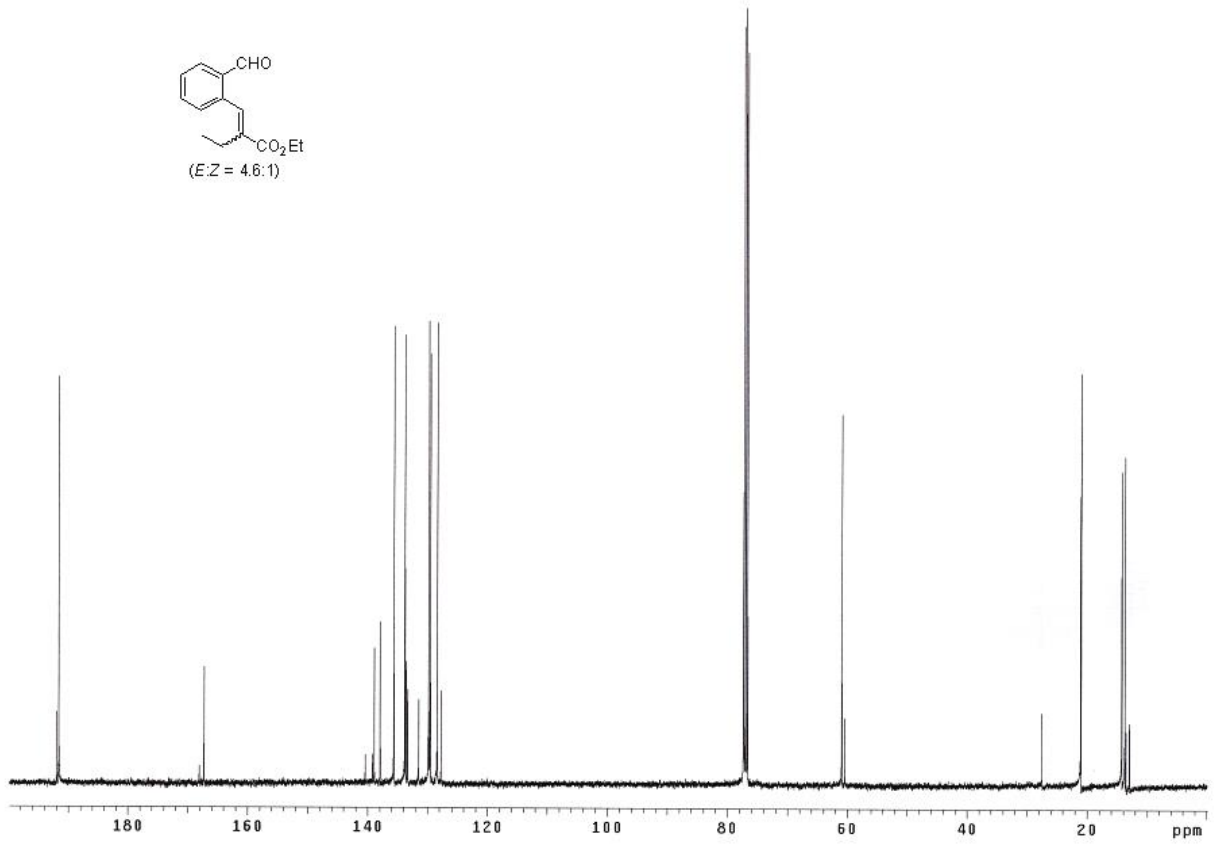
^{1}H NMR Spectrum of Compound **3g** ($CDCl_3$, 400 MHz)



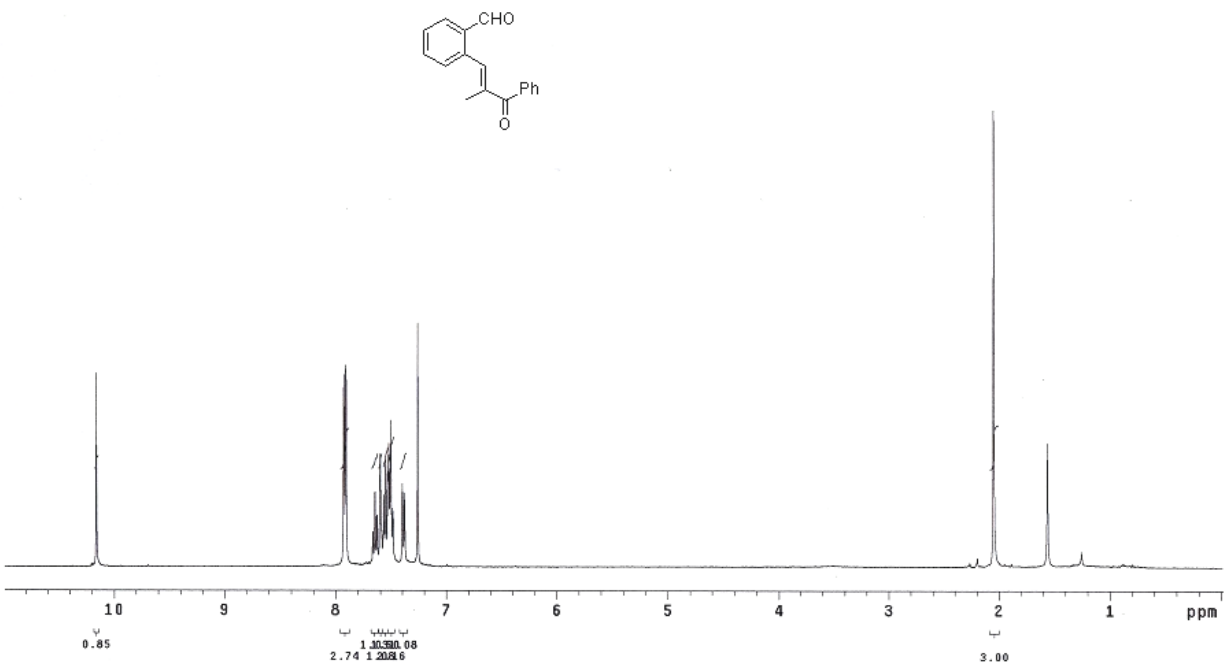
^{13}C NMR Spectrum of Compound **3g** ($CDCl_3$, 100 MHz)



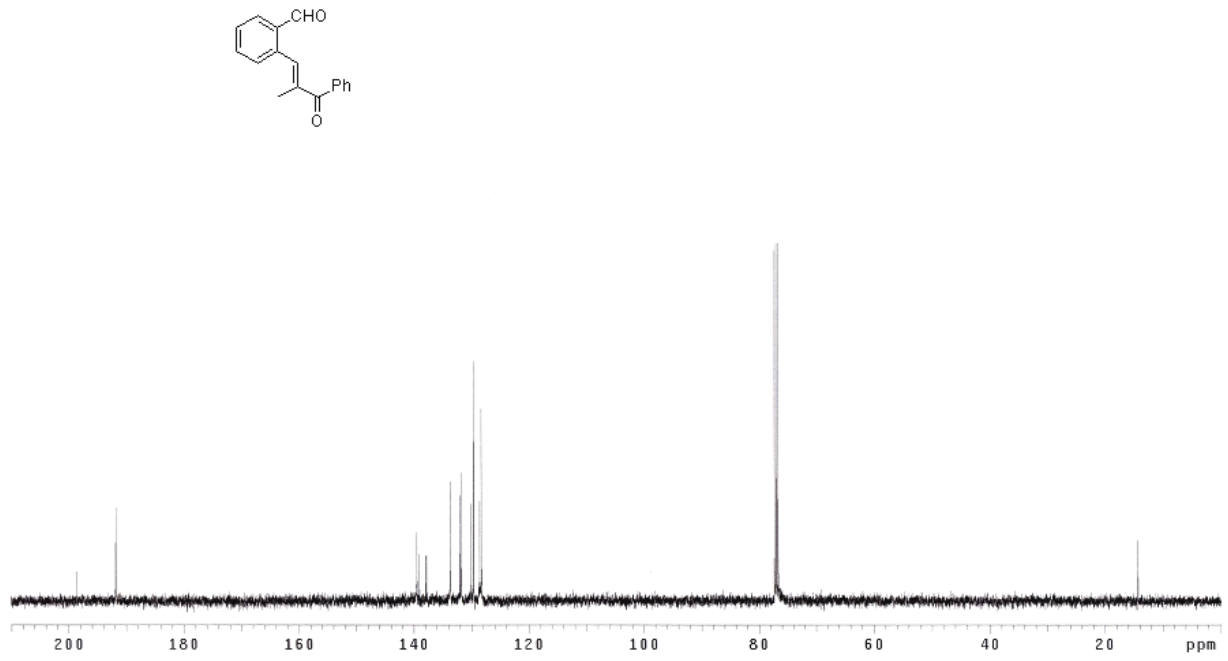
^{1}H NMR Spectrum of Compound **3h** ($CDCl_3$, 400 MHz)



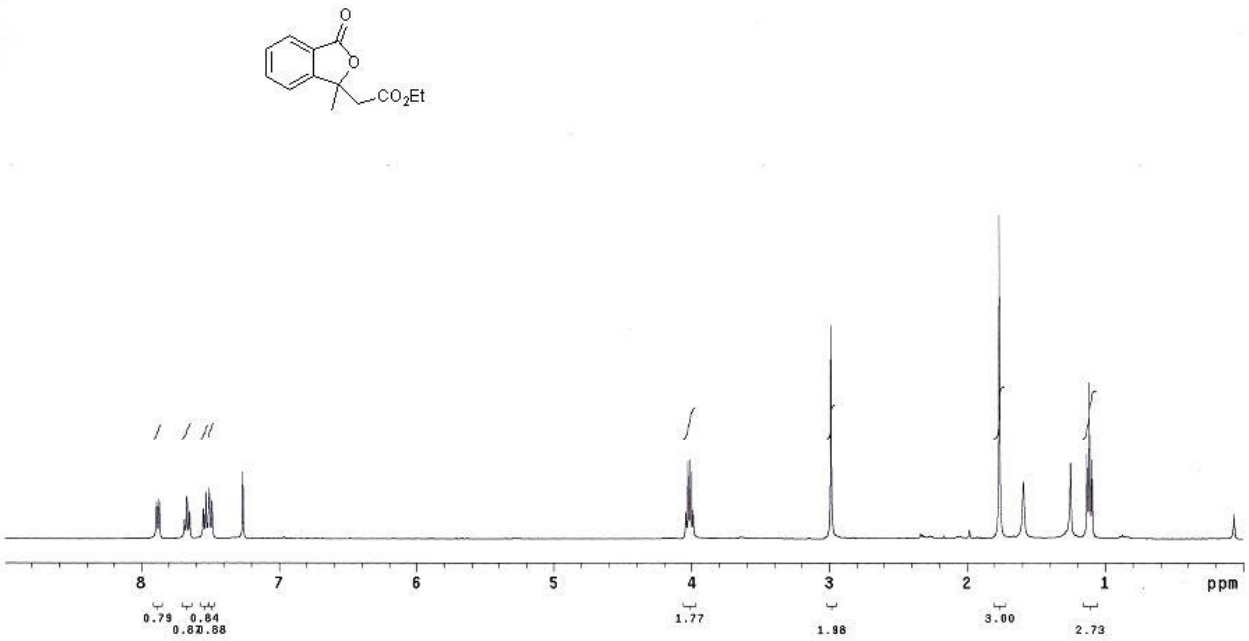
^{13}C NMR Spectrum of Compound **3h** ($CDCl_3$, 100 MHz)



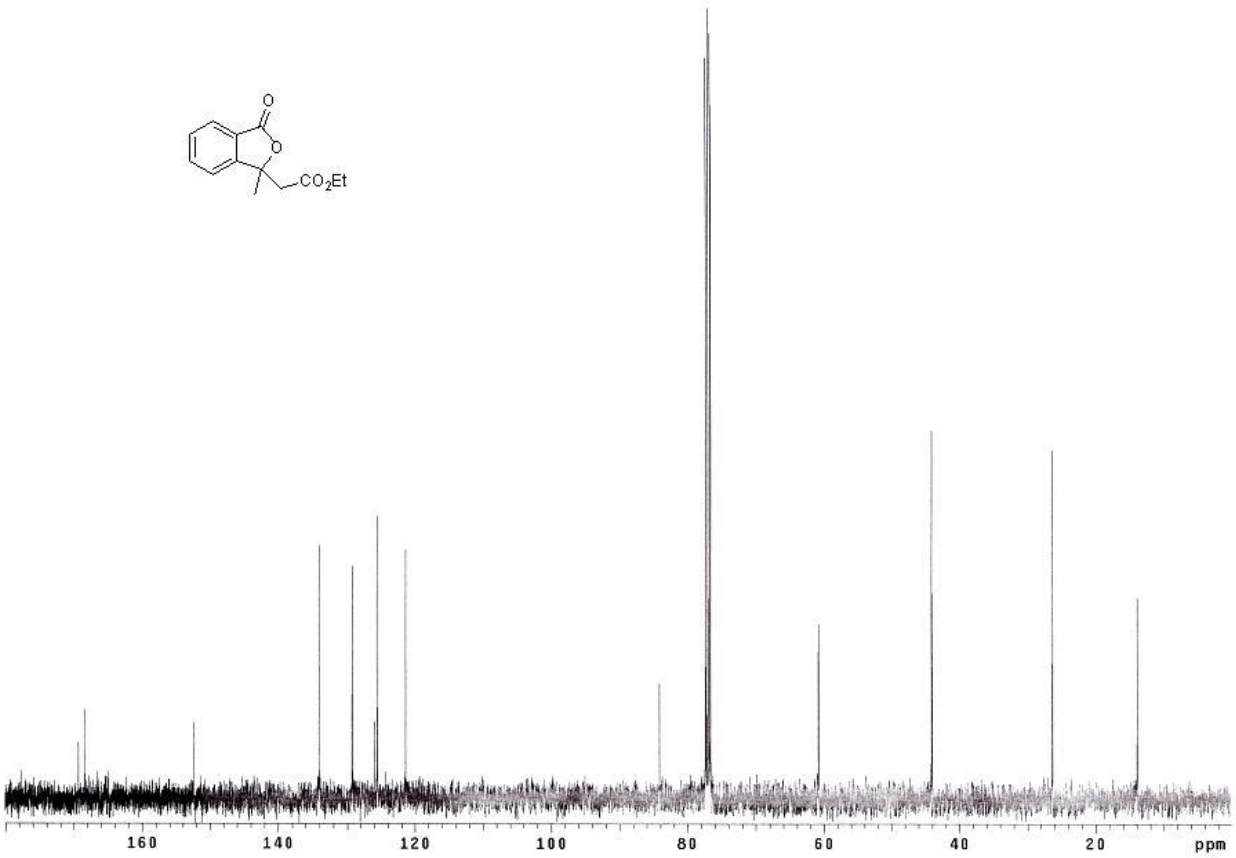
^{1}H NMR Spectrum of Compound **3i** ($CDCl_3$, 400 MHz)



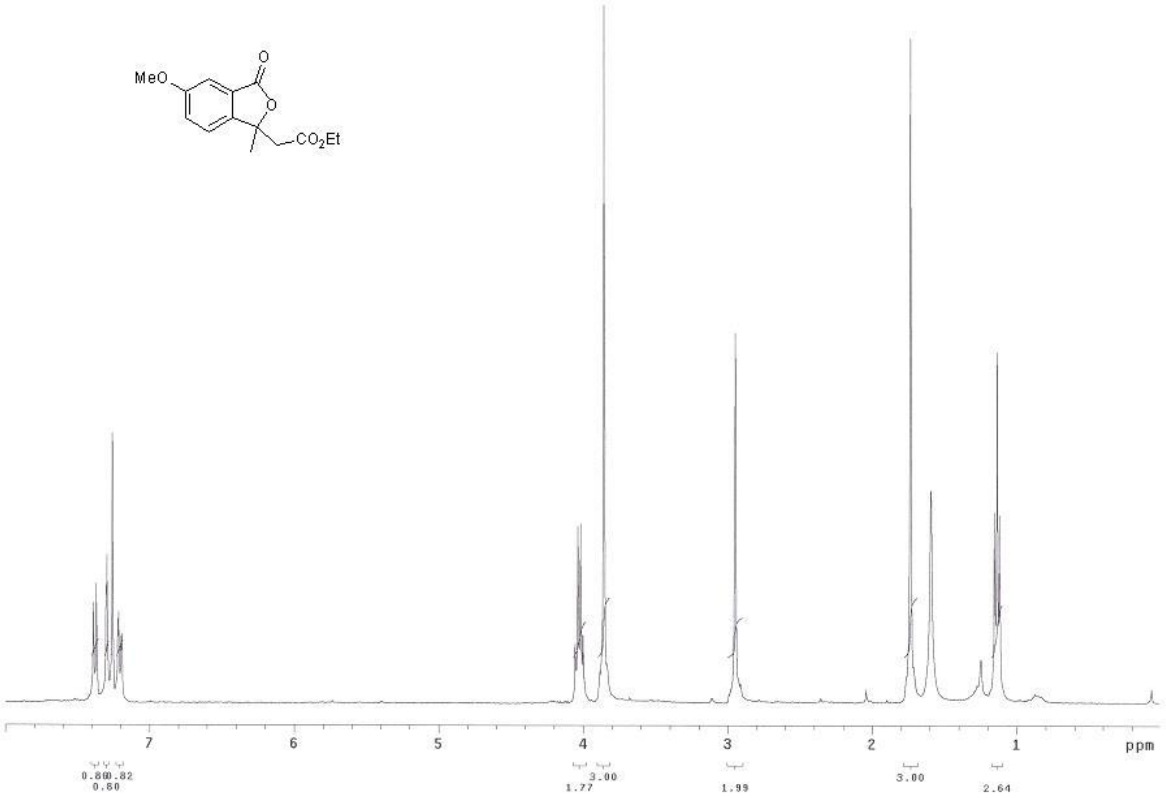
^{13}C NMR Spectrum of Compound **3i** ($CDCl_3$, 100 MHz)



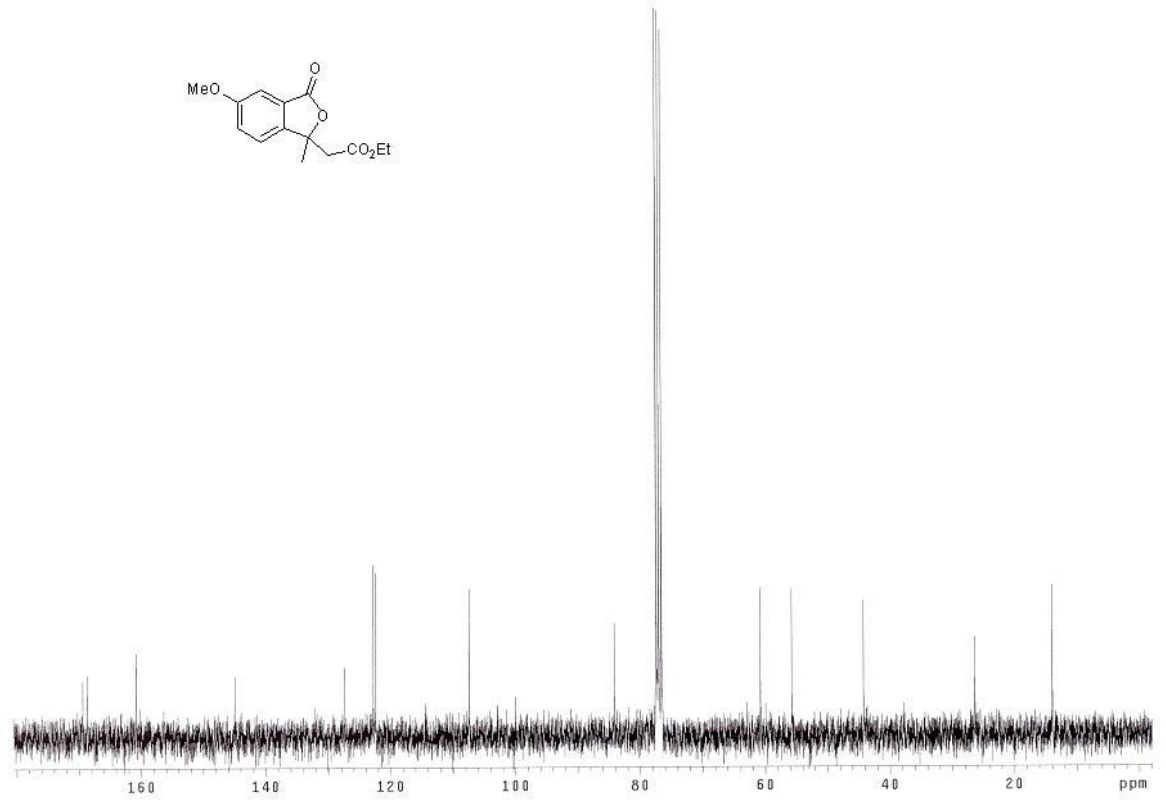
^{1}H NMR Spectrum of Compound **4a** ($CDCl_3$, 400 MHz)



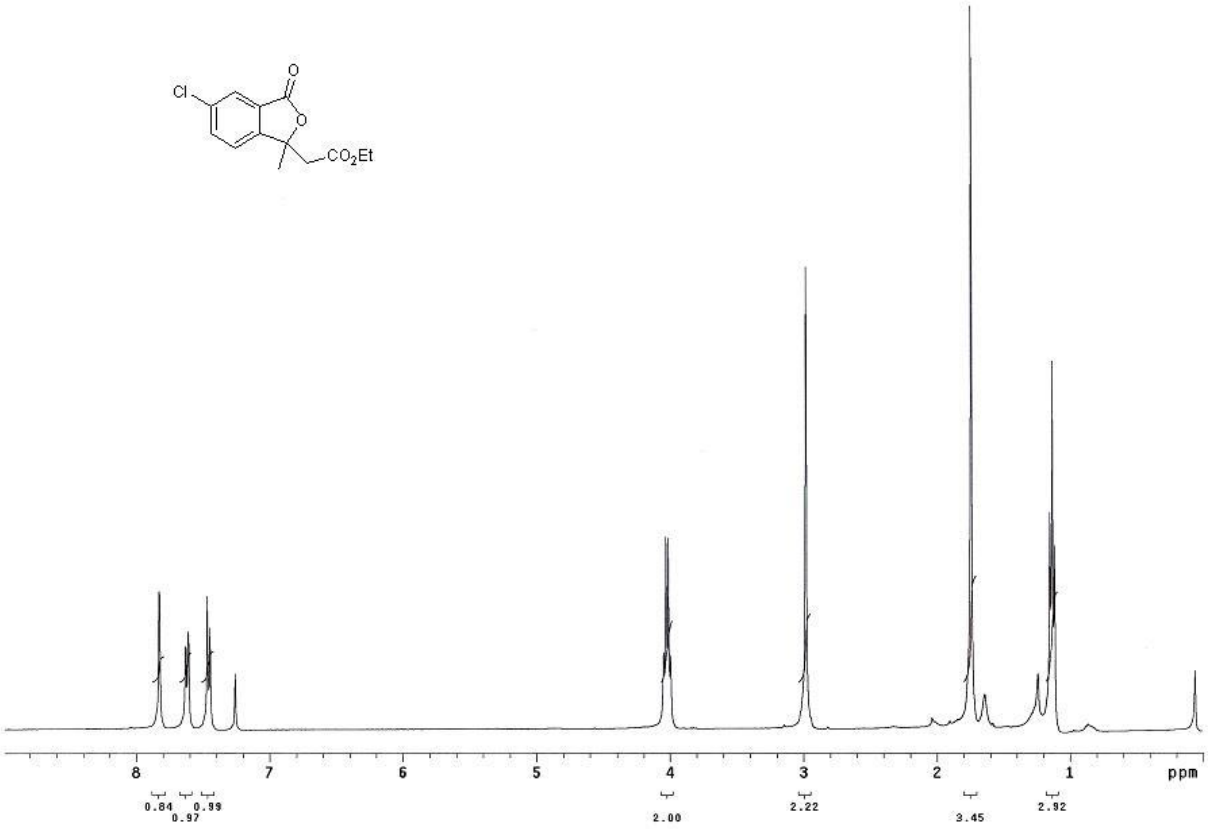
^{13}C NMR Spectrum of Compound **4a** ($CDCl_3$, 100 MHz)



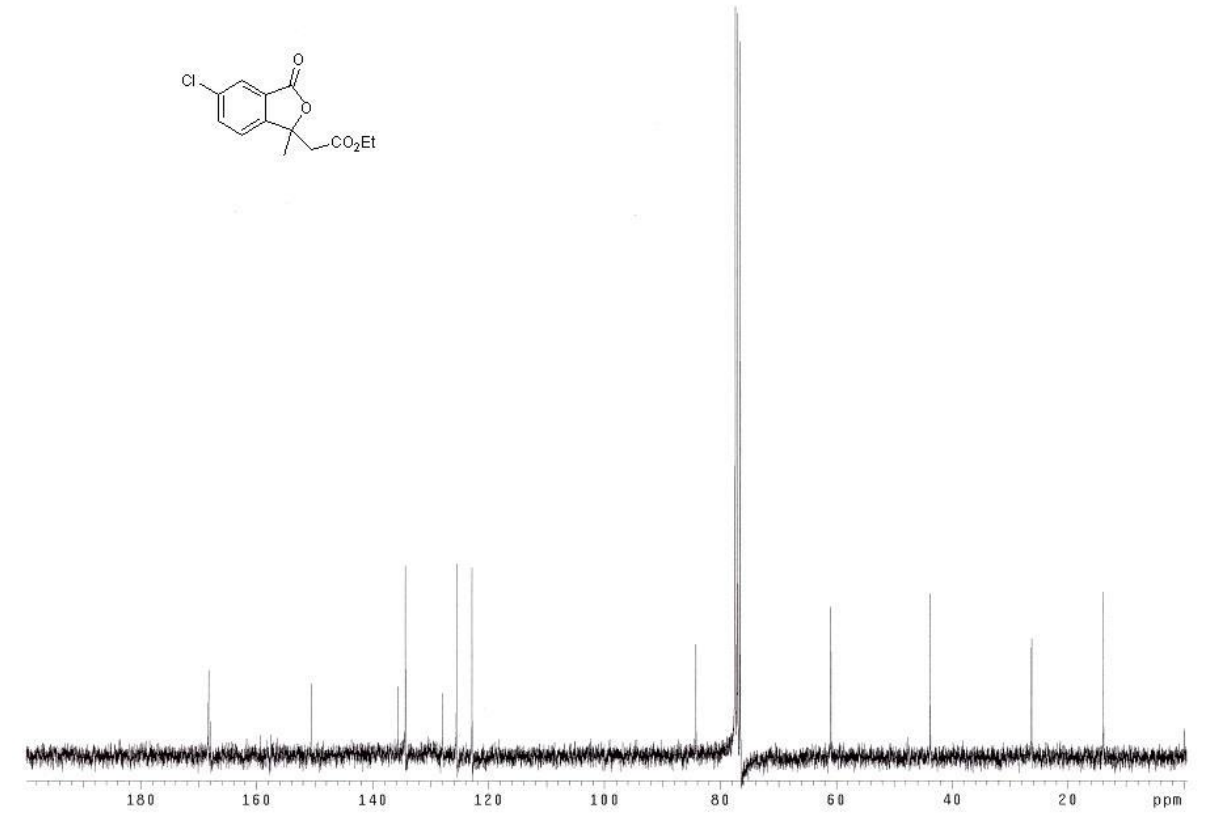
^{1}H NMR Spectrum of Compound **4b** ($CDCl_3$, 400 MHz)



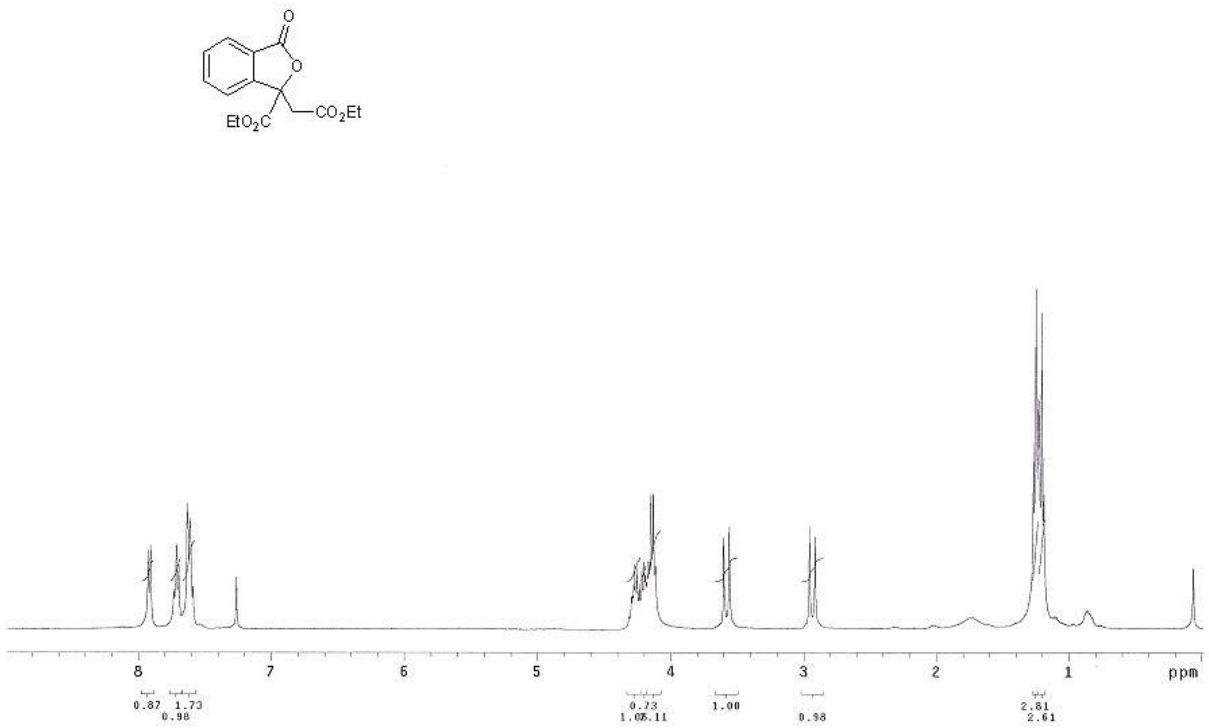
^{13}C NMR Spectrum of Compound **4b** ($CDCl_3$, 100 MHz)



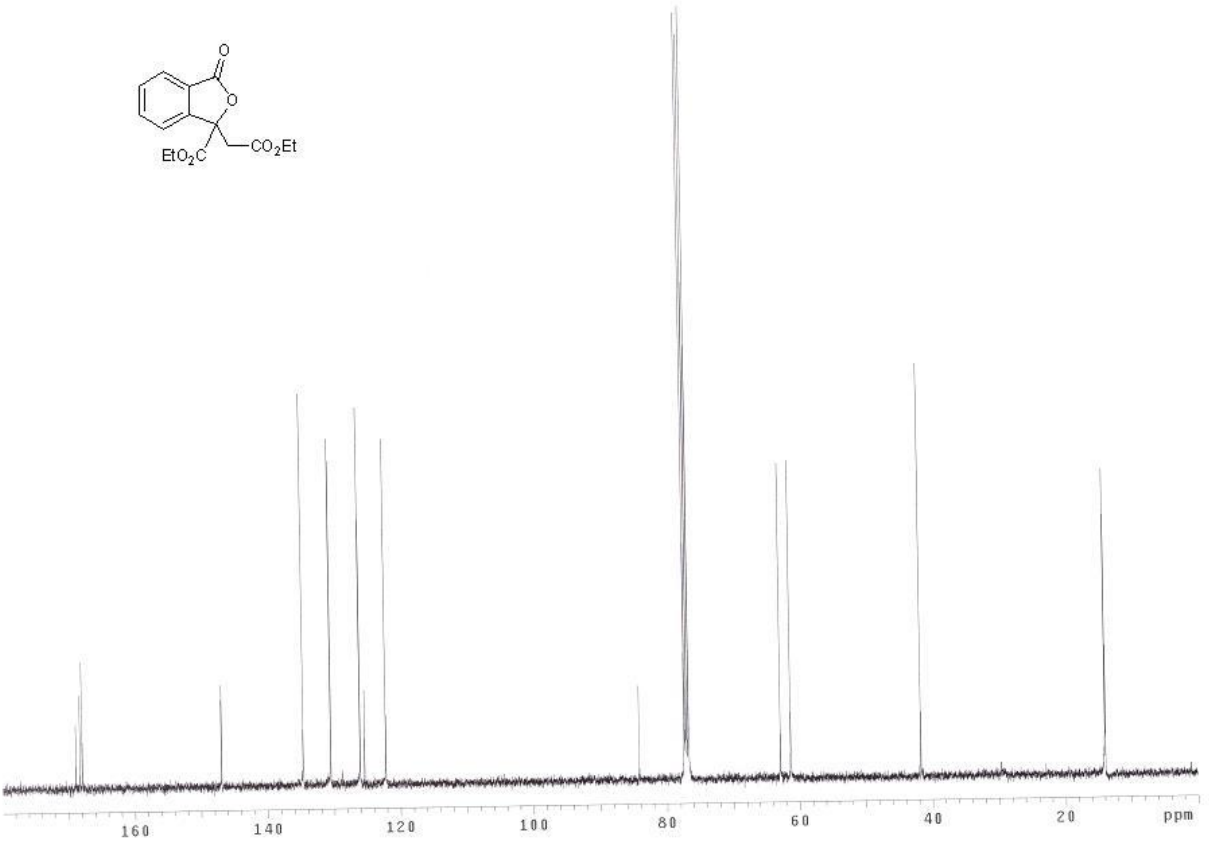
^{1}H NMR Spectrum of Compound **4c** ($CDCl_3$, 400 MHz)



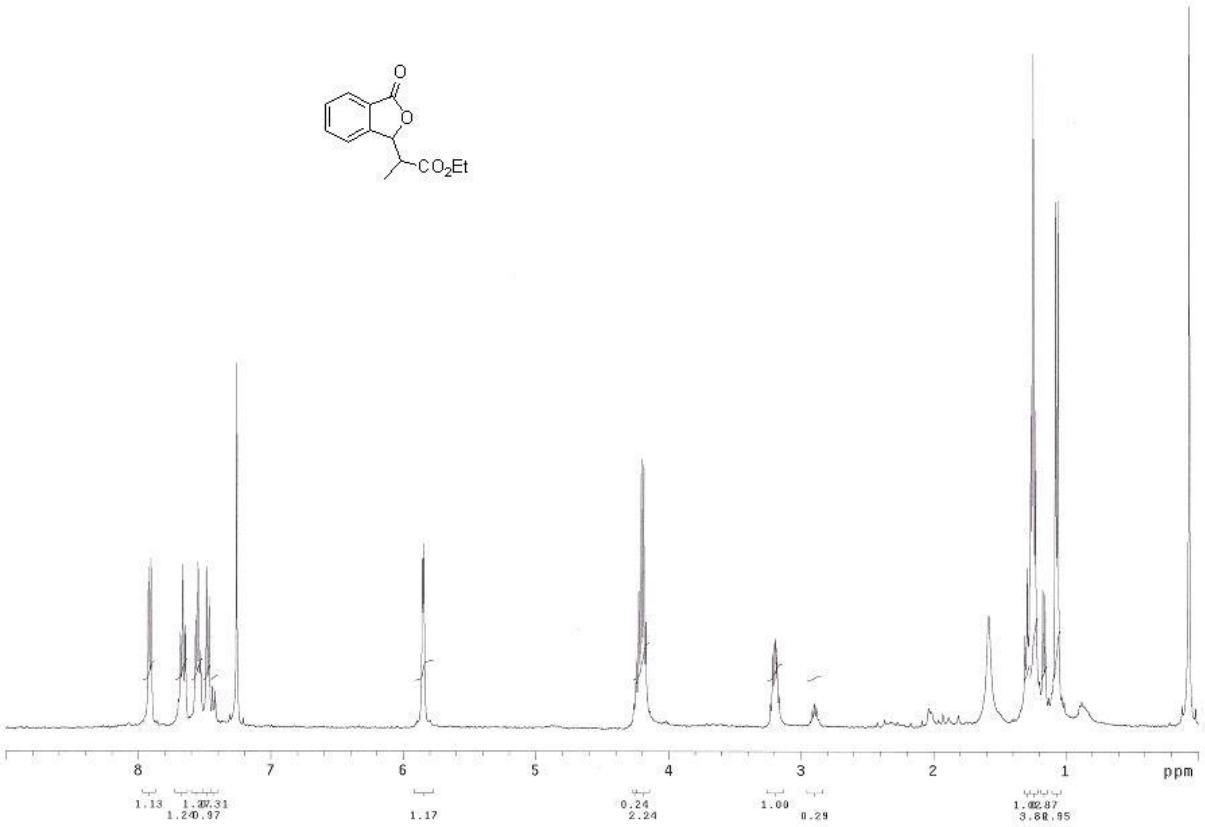
^{13}C NMR Spectrum of Compound **4c** ($CDCl_3$, 100 MHz)



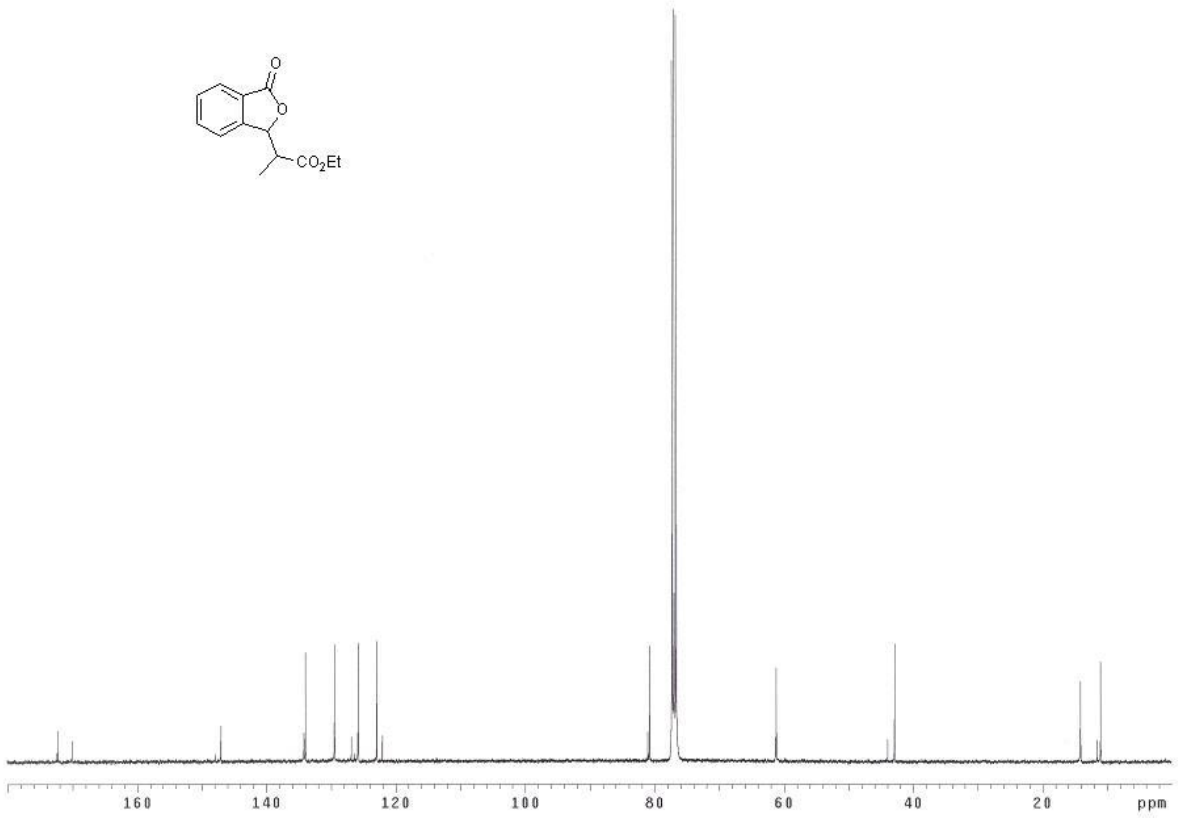
^{1}H NMR Spectrum of Compound **4d** ($CDCl_3$, 400 MHz)



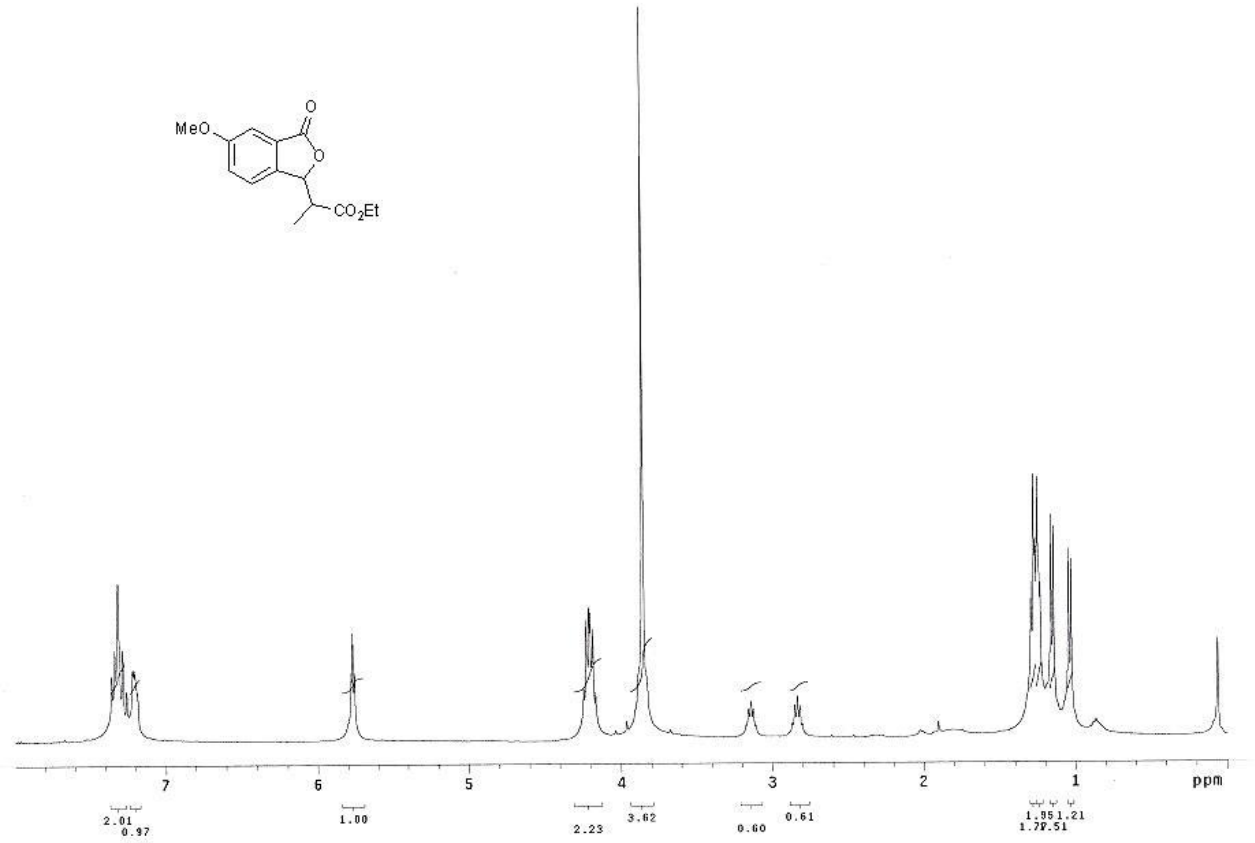
^{13}C NMR Spectrum of Compound **4d** ($CDCl_3$, 100 MHz)



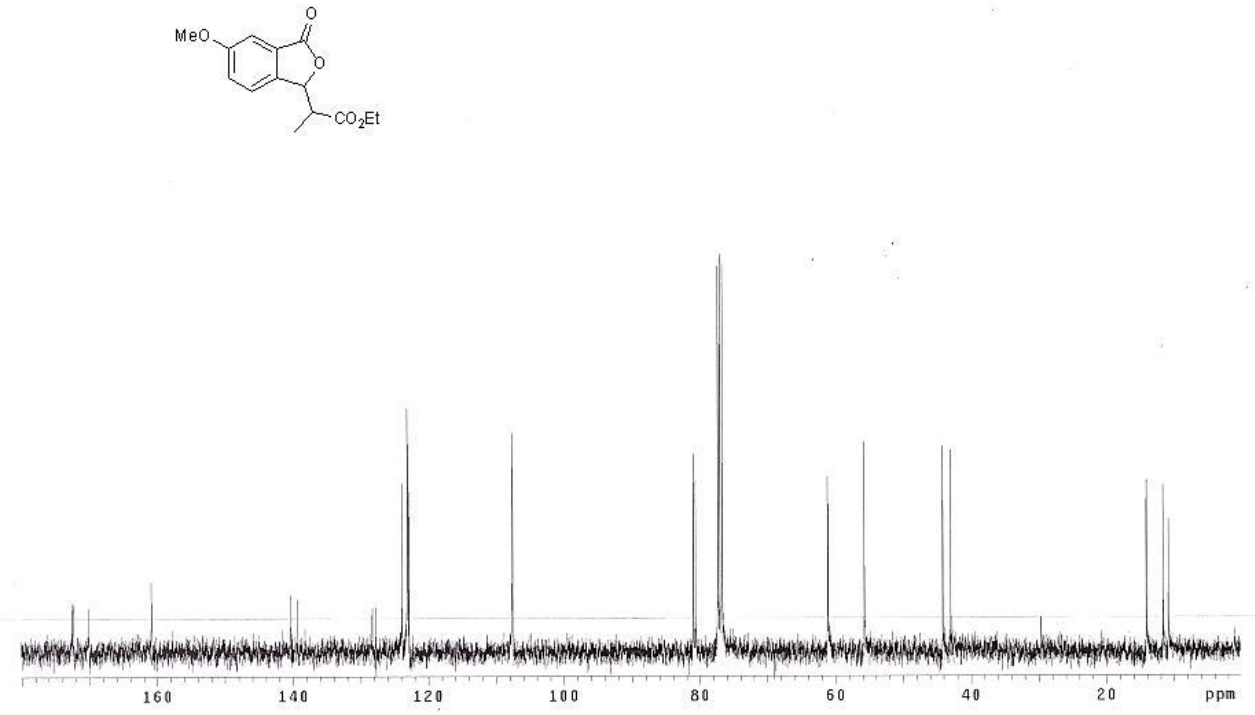
^{1}H NMR Spectrum of Compound **4e** ($CDCl_3$, 400 MHz)



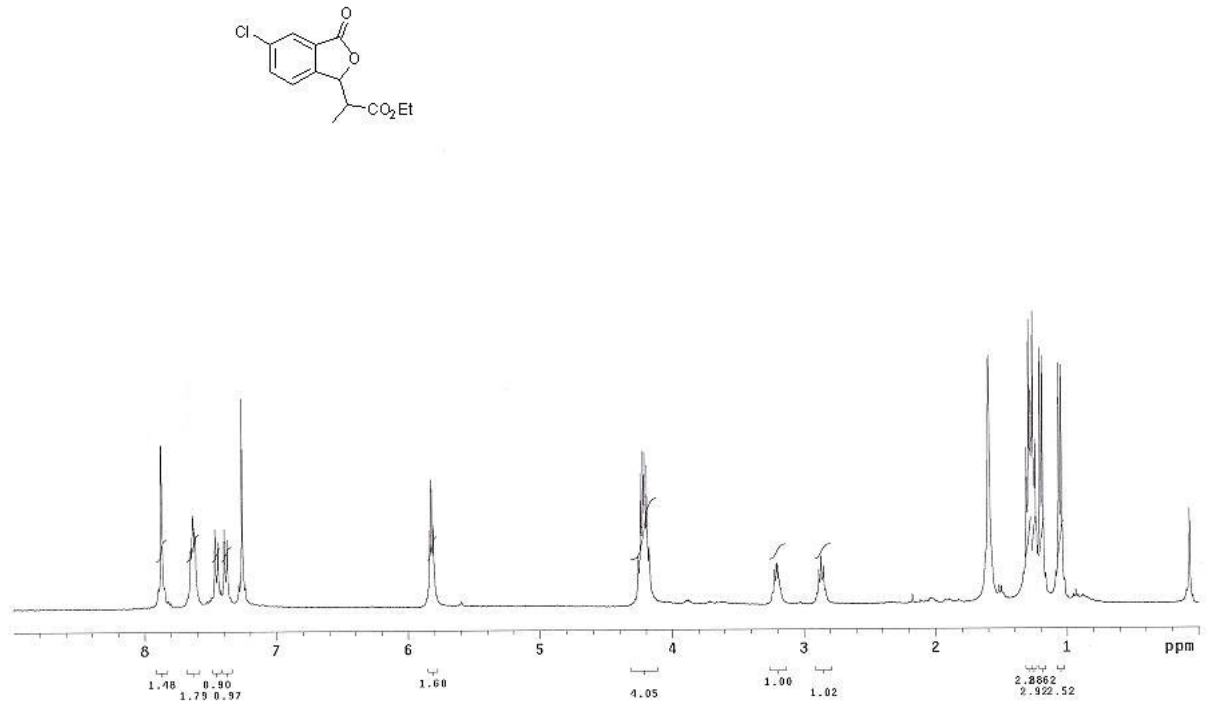
^{13}C NMR Spectrum of Compound **4e** ($CDCl_3$, 100 MHz)



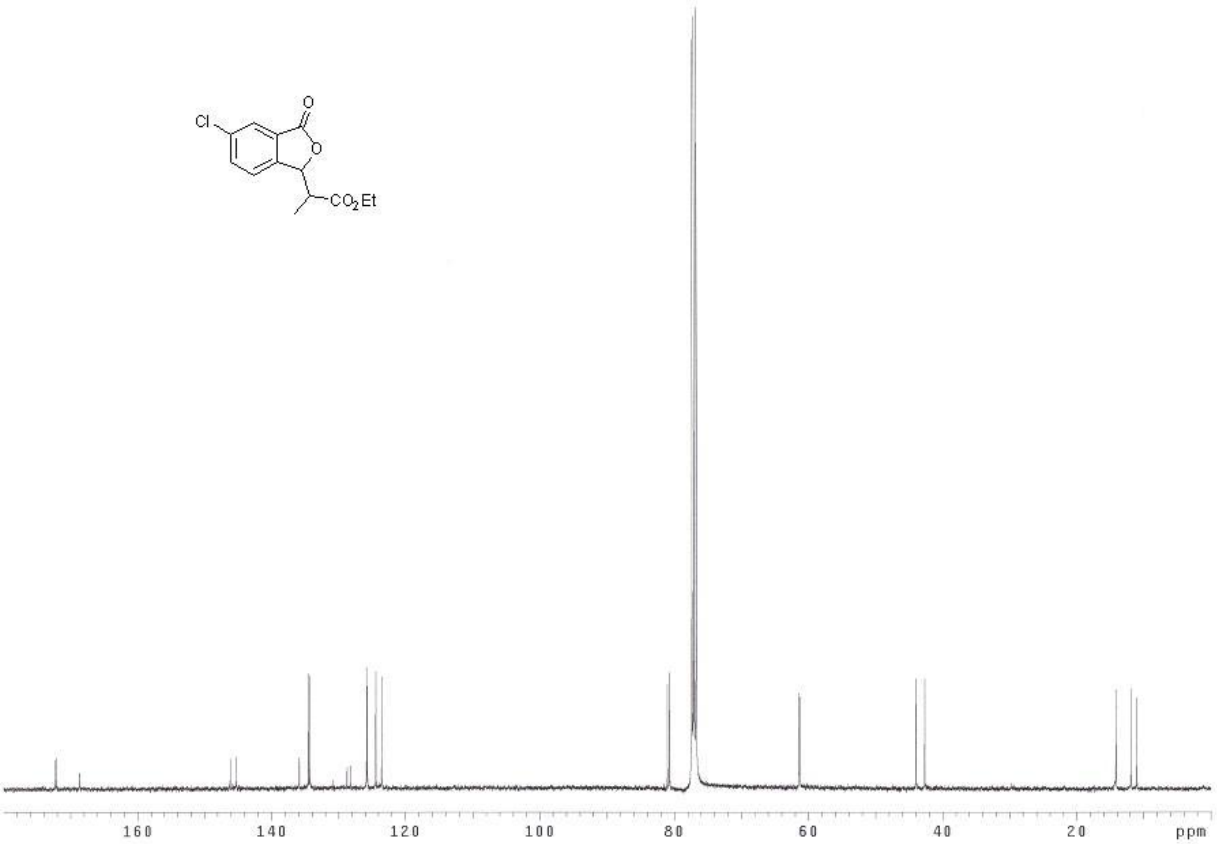
^{1}H NMR Spectrum of Compound **4f** ($CDCl_3$, 400 MHz)



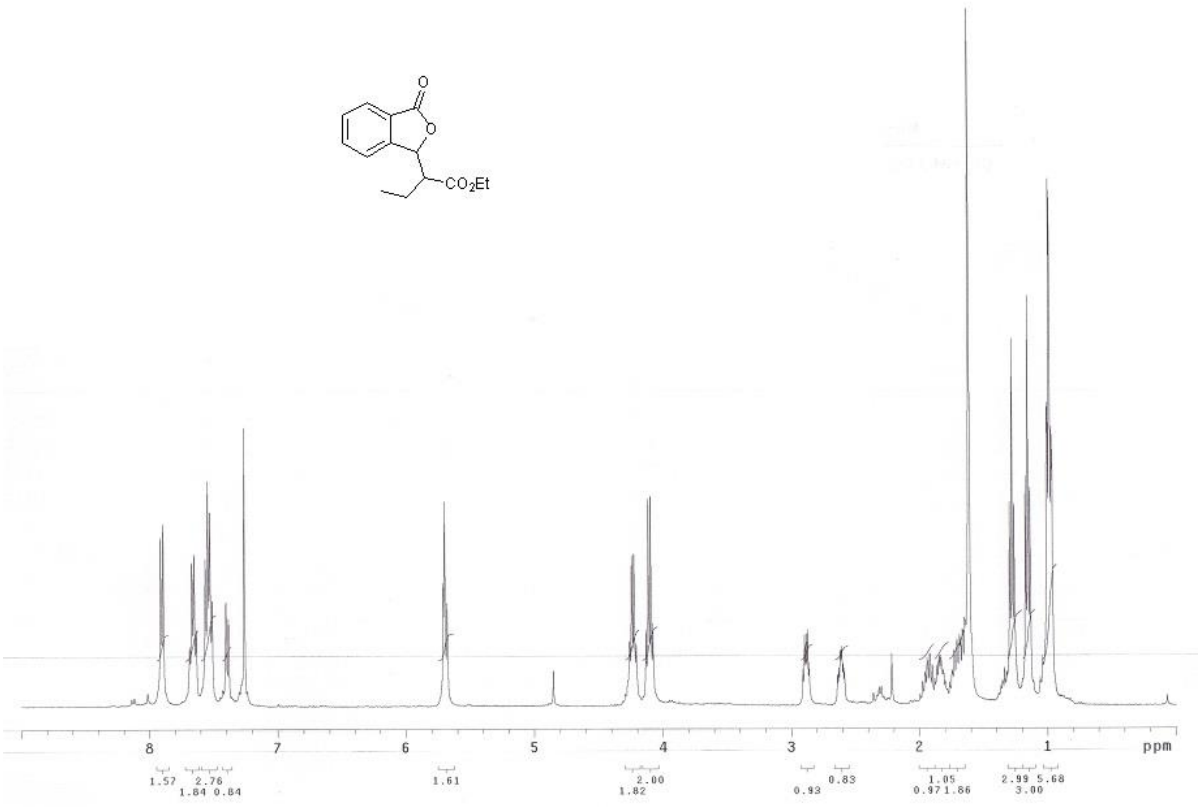
^{13}C NMR Spectrum of Compound **4f** ($CDCl_3$, 100 MHz)



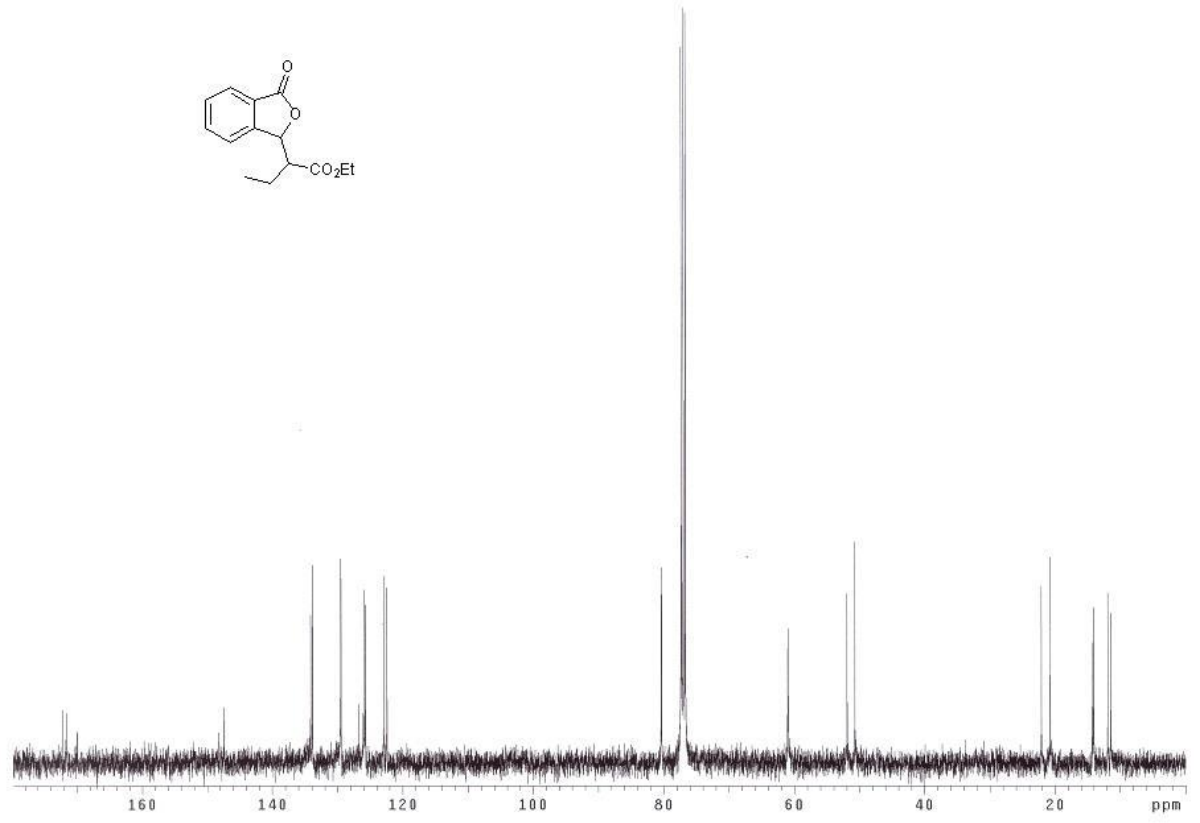
^{1}H NMR Spectrum of Compound **4g** ($CDCl_3$, 400 MHz)



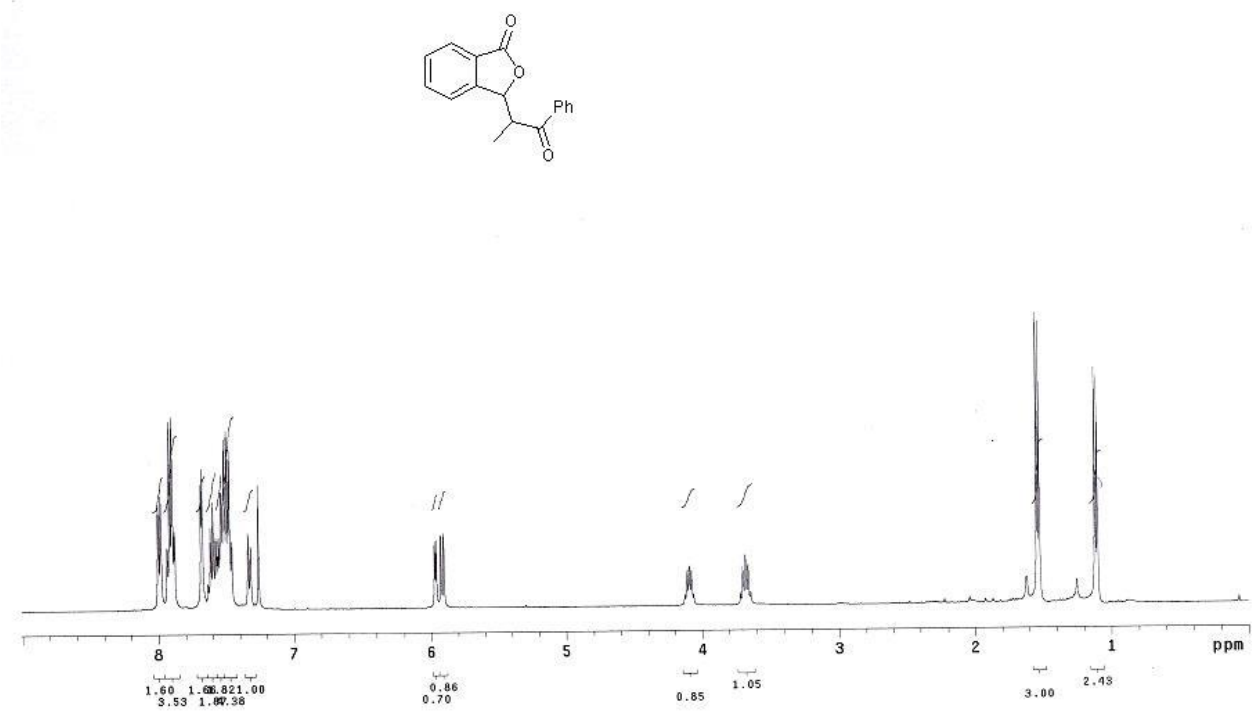
^{13}C NMR Spectrum of Compound **4g** ($CDCl_3$, 100 MHz)



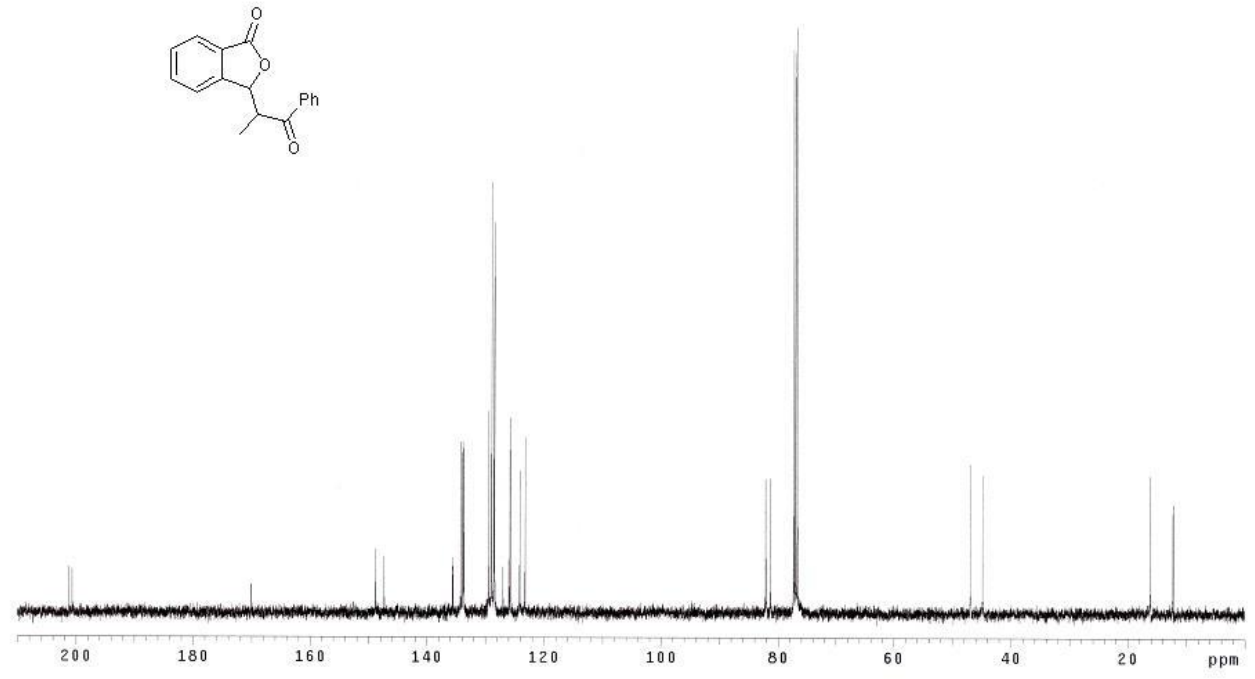
^{1}H NMR Spectrum of Compound **4h** ($CDCl_3$, 400 MHz)



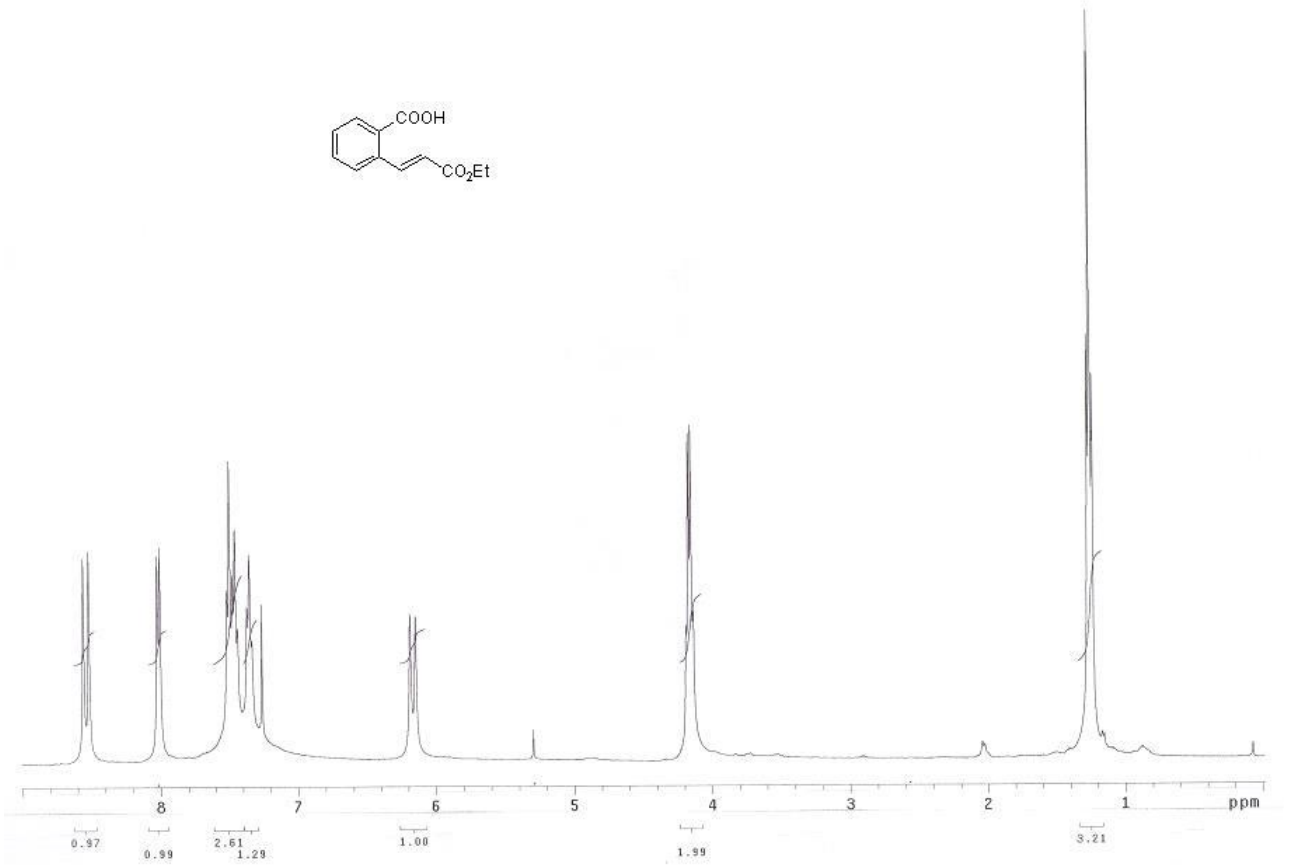
^{13}C NMR Spectrum of Compound **4h** ($CDCl_3$, 100 MHz)



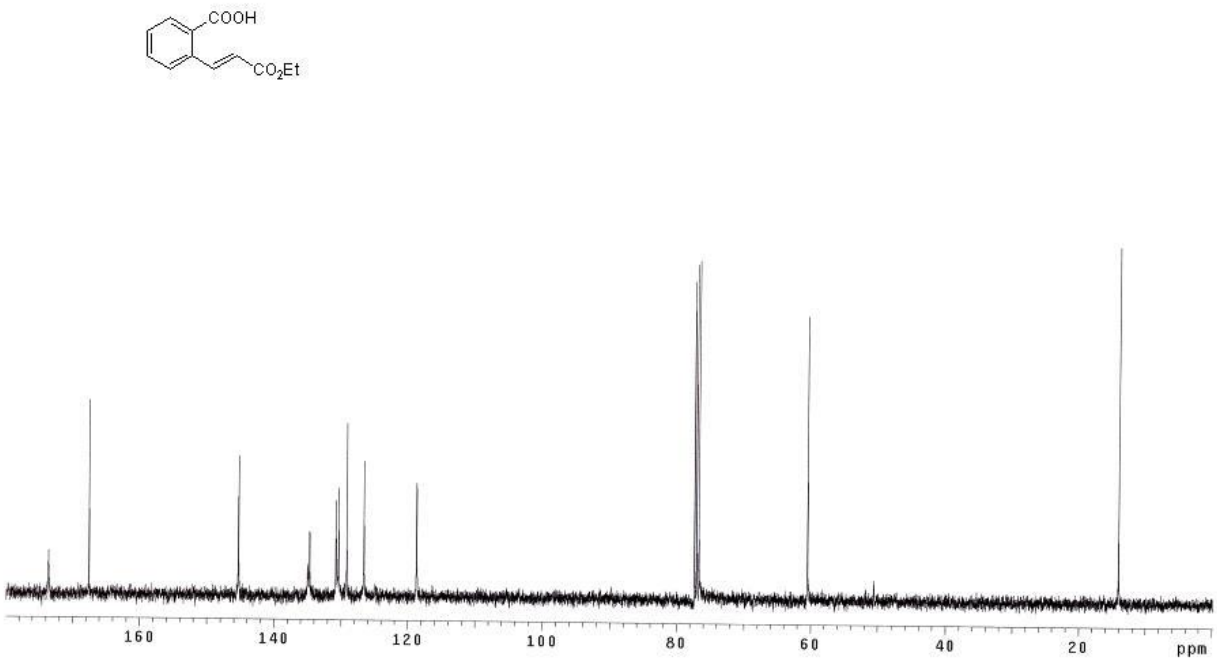
^{1}H NMR Spectrum of Compound **4i** ($CDCl_3$, 400 MHz)



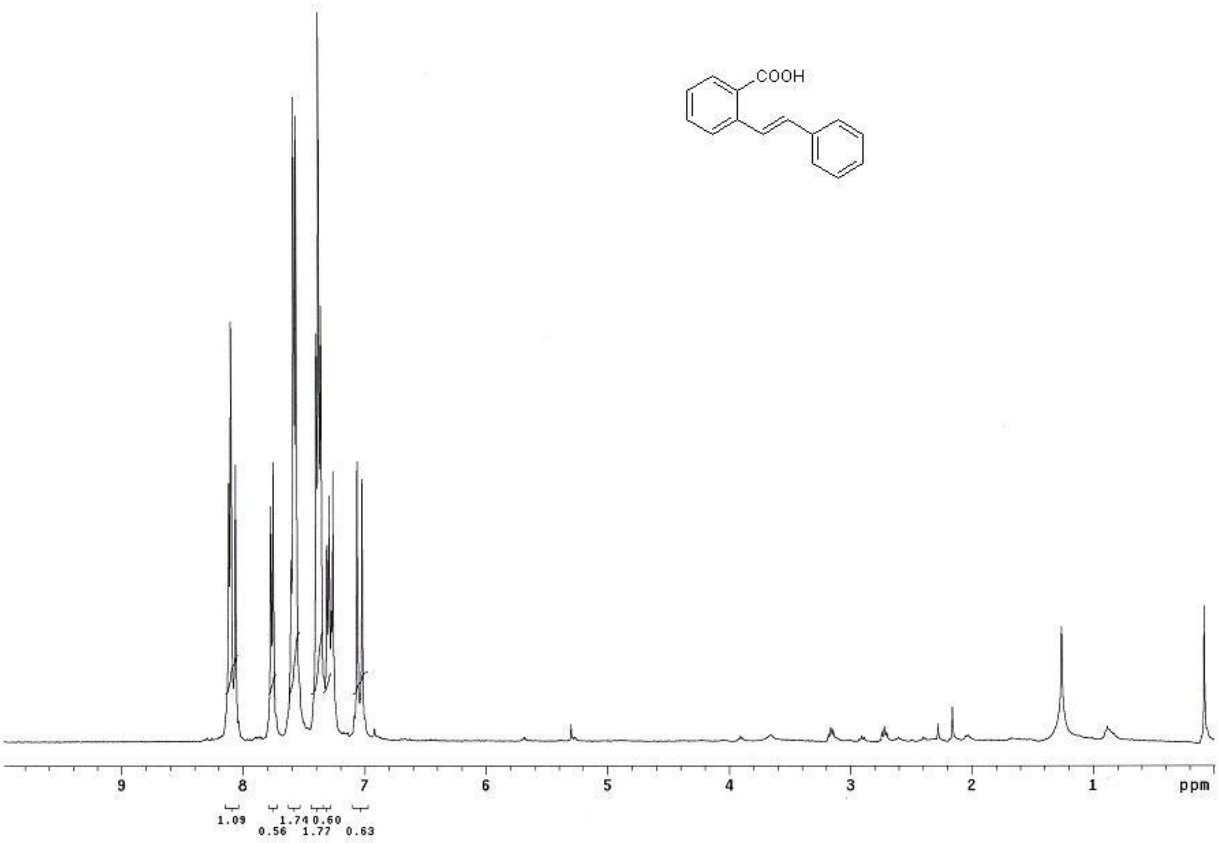
^{13}C NMR Spectrum of Compound **4i** ($CDCl_3$, 100 MHz)



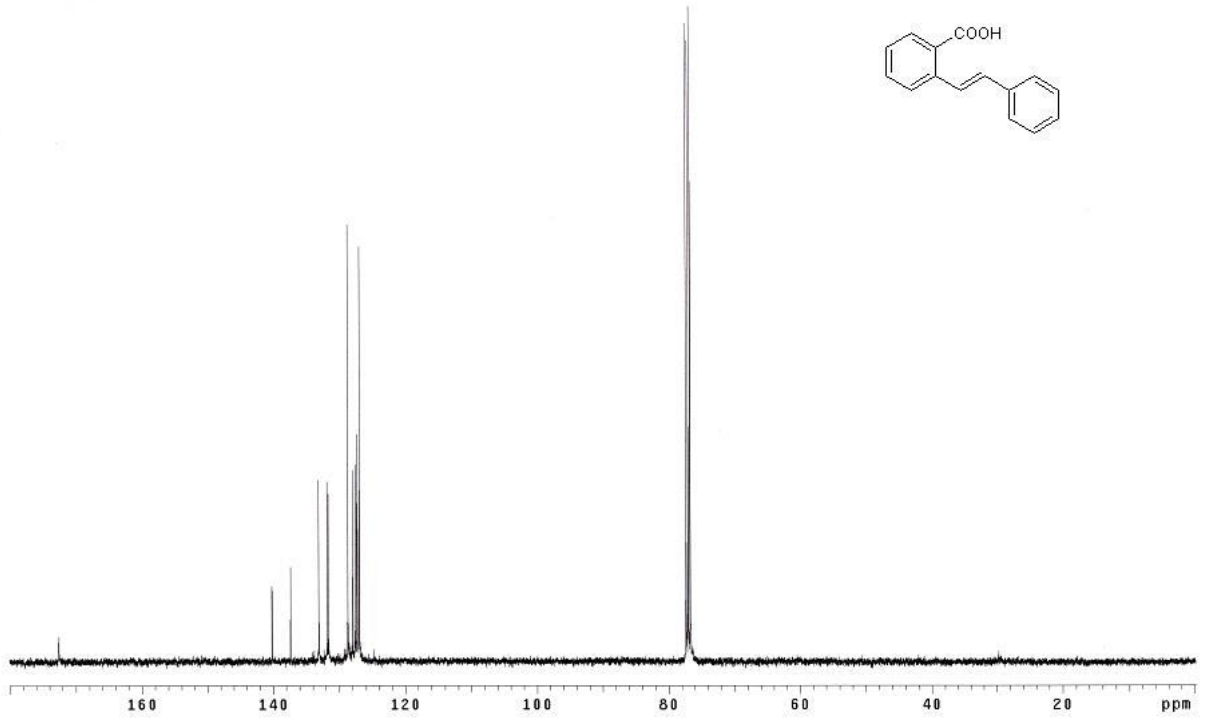
^{1}H NMR Spectrum of Compound **5a** ($CDCl_3$, 400 MHz)



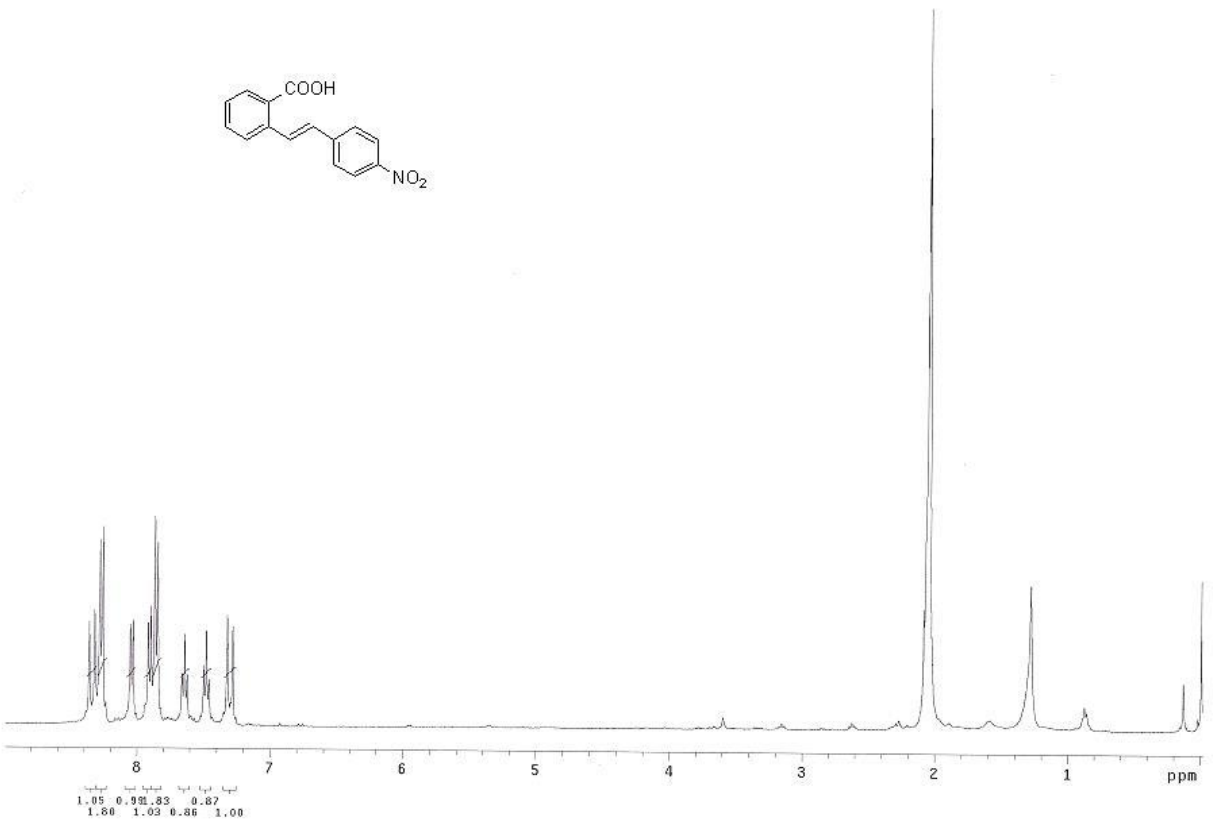
^{13}C NMR Spectrum of Compound **5a** ($CDCl_3$, 100 MHz)



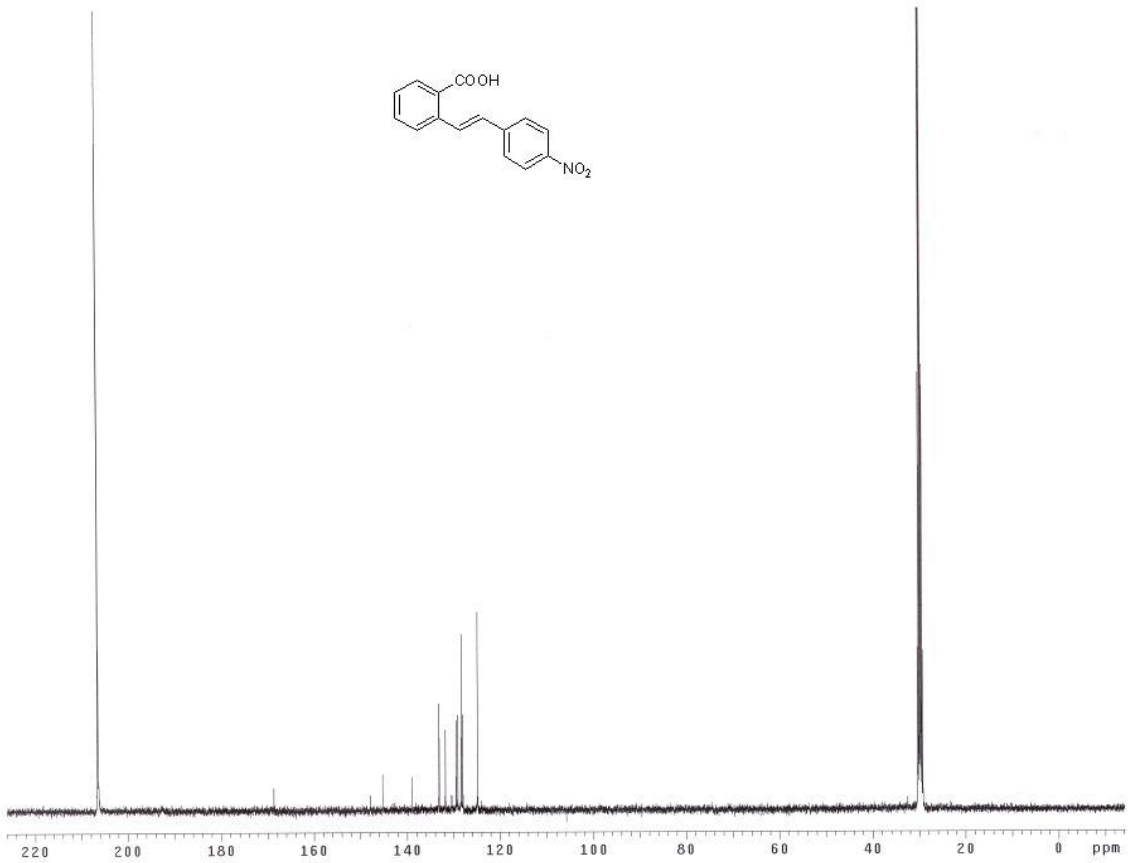
^{1}H NMR Spectrum of Compound **5s** ($CDCl_3$, 400 MHz)



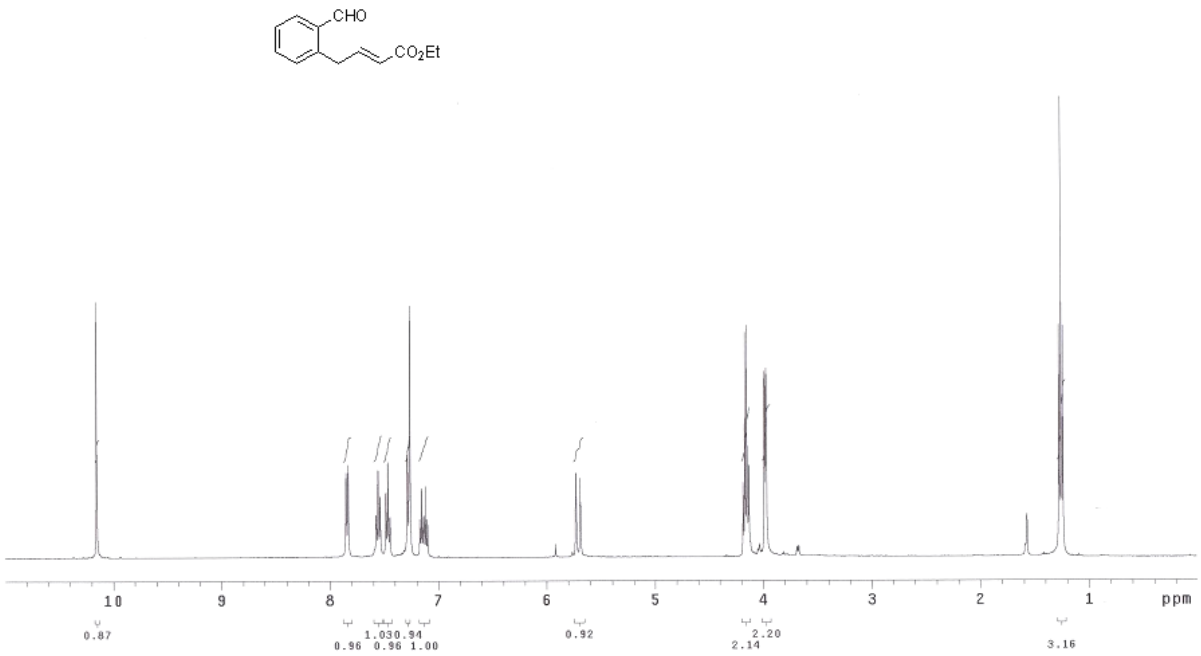
^{13}C NMR Spectrum of Compound **5s** ($CDCl_3$, 100 MHz)



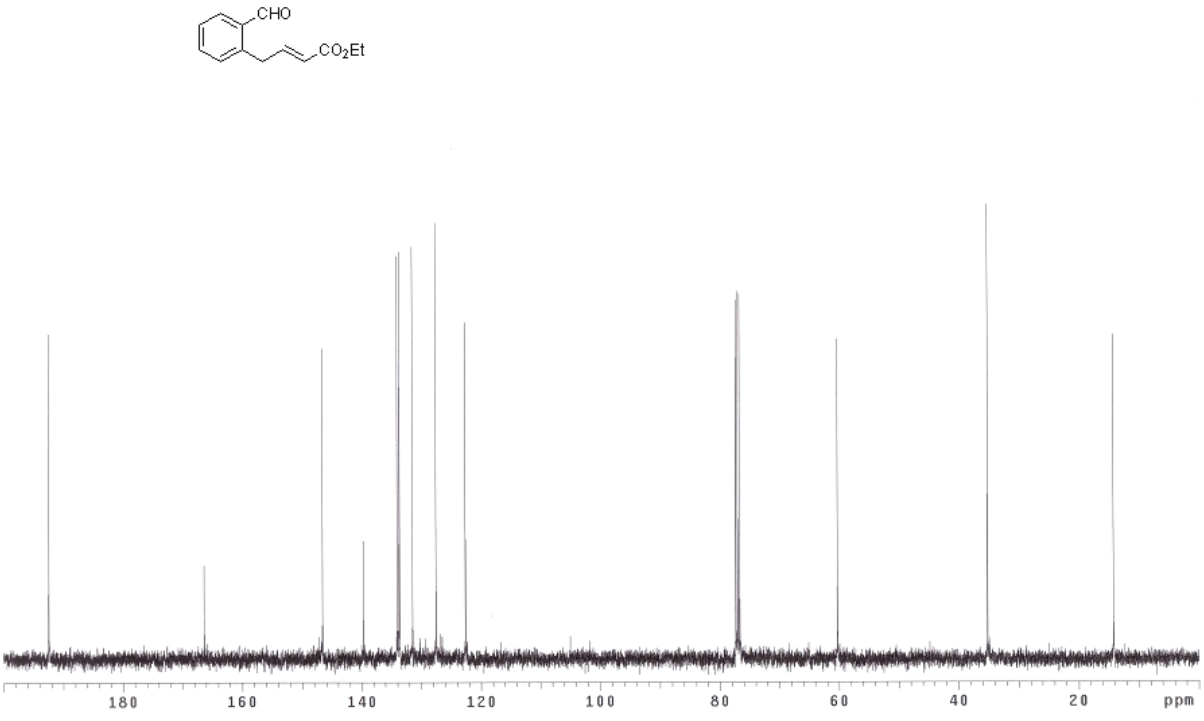
^{1}H NMR Spectrum of Compound **5t** (acetone-d_6, 400 MHz)



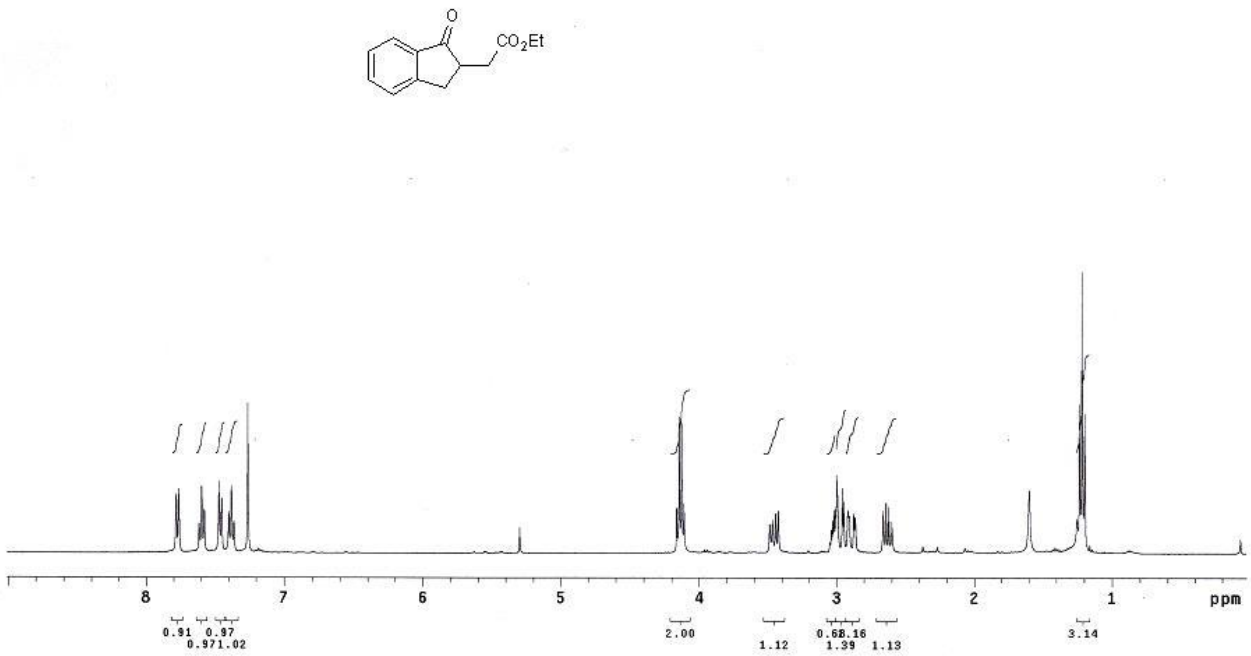
^{13}C NMR Spectrum of Compound **5t** (acetone-d_6, 100 MHz)



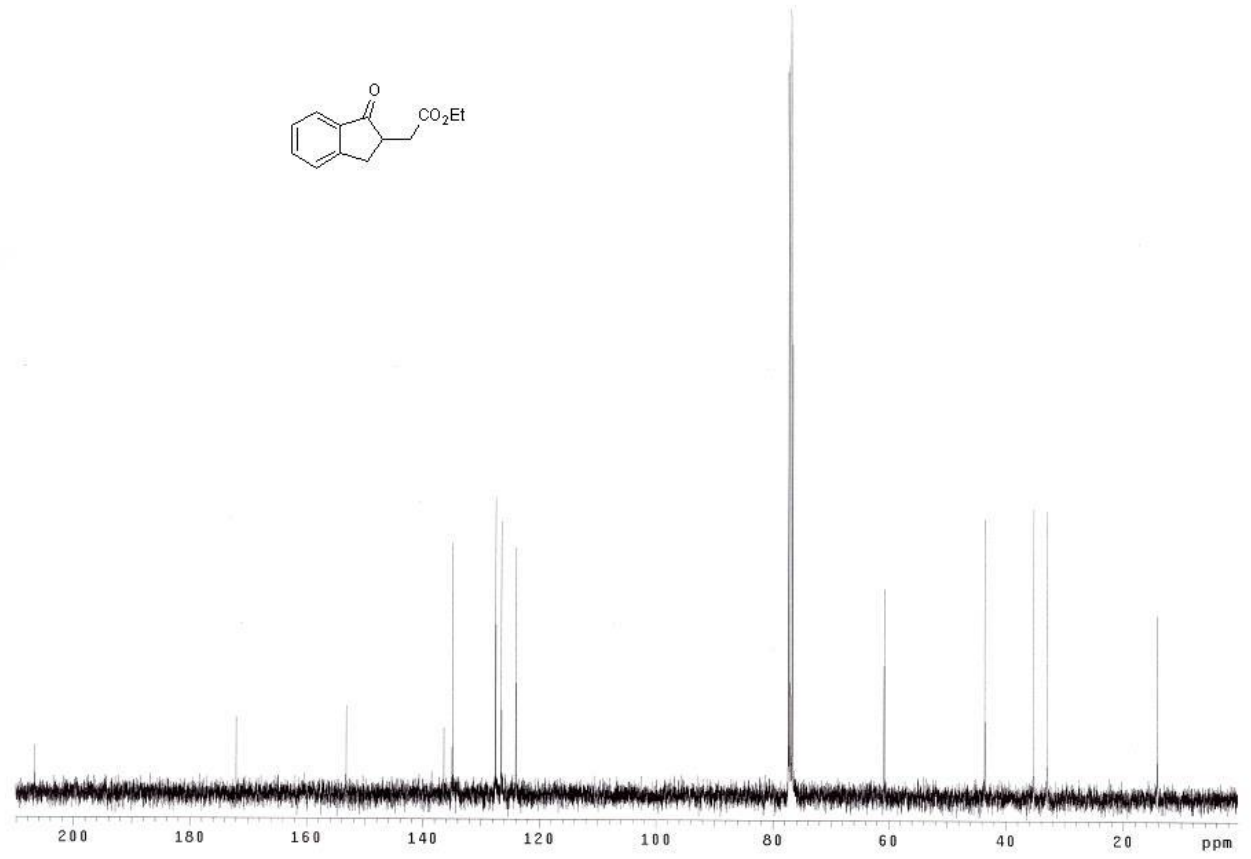
^{1}H NMR Spectrum of Compound **6** ($CDCl_3$, 400 MHz)



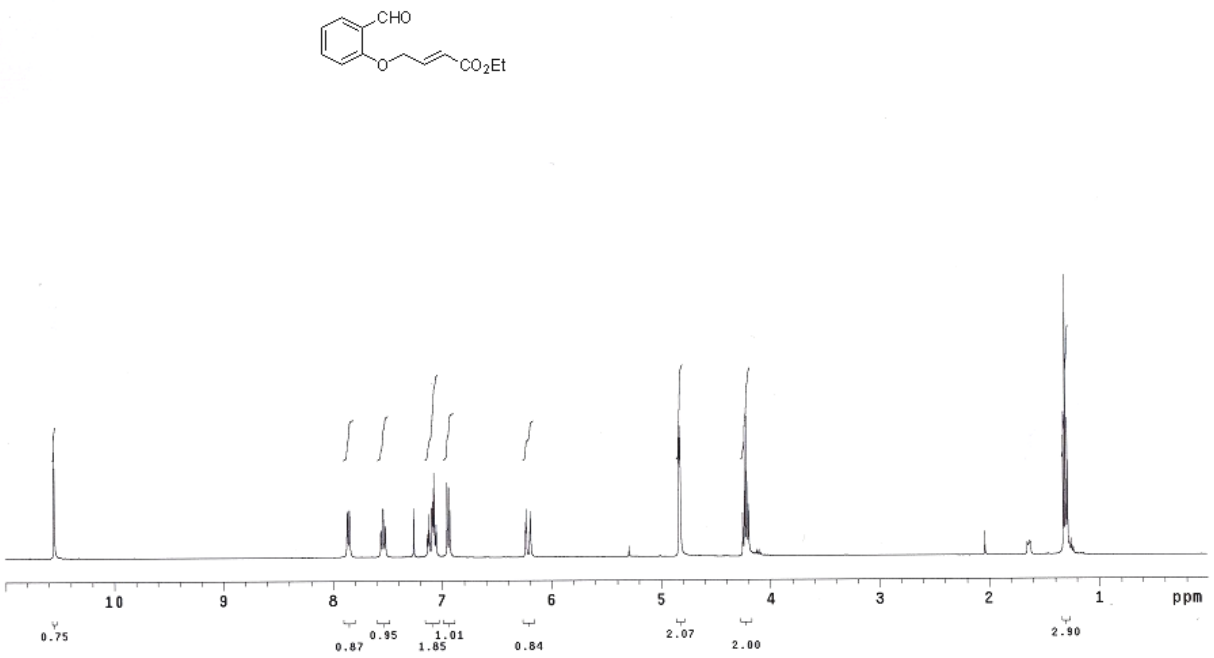
^{13}C NMR Spectrum of Compound **6** ($CDCl_3$, 100 MHz)



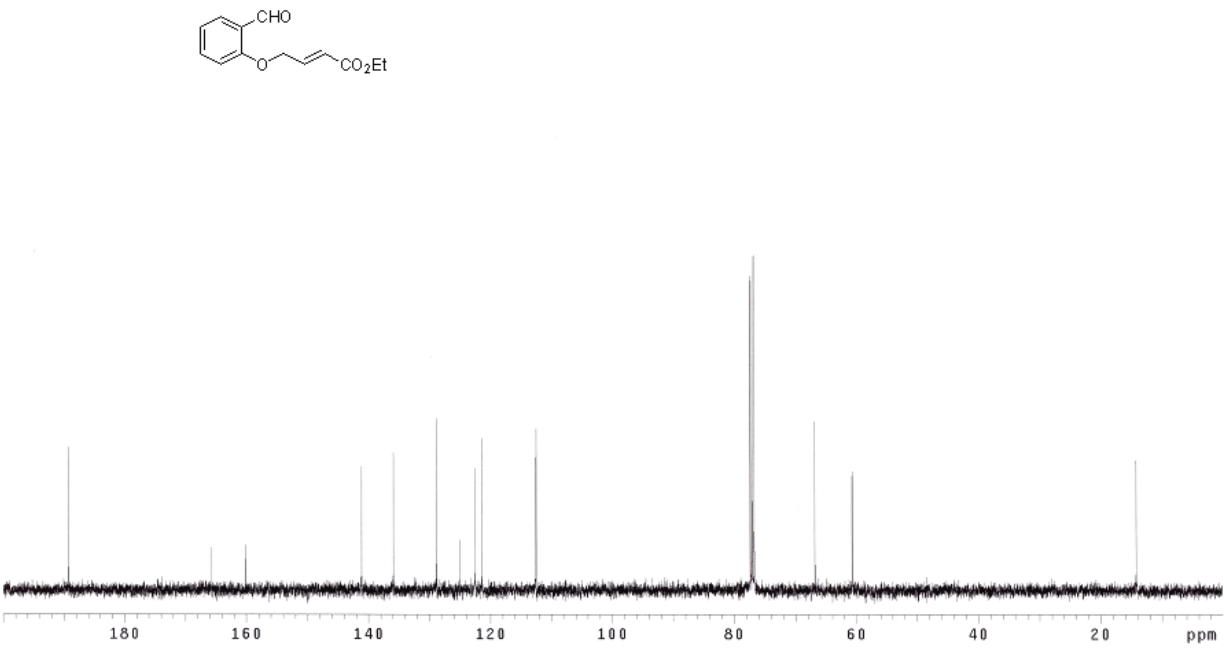
^{1}H NMR Spectrum of Compound **7** ($CDCl_3$, 400 MHz)



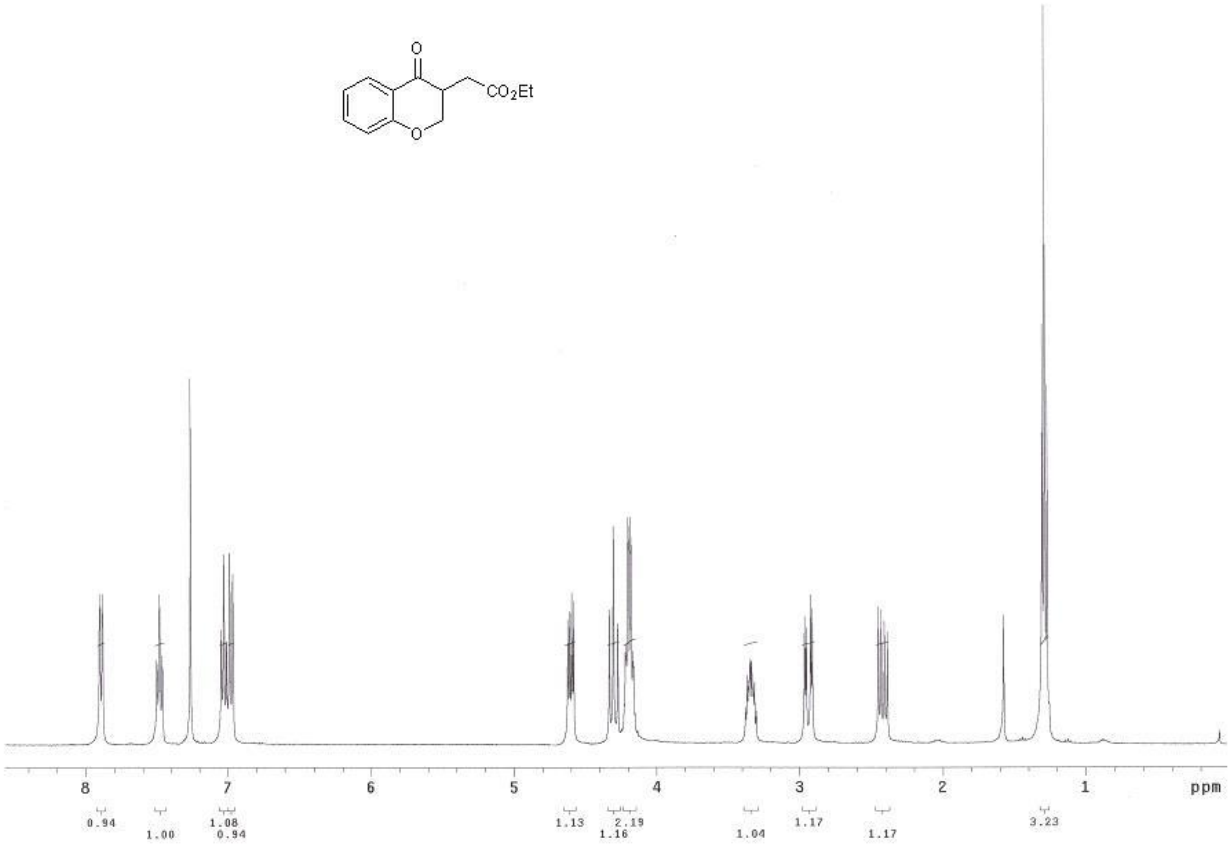
^{13}C NMR Spectrum of Compound **7** ($CDCl_3$, 100 MHz)



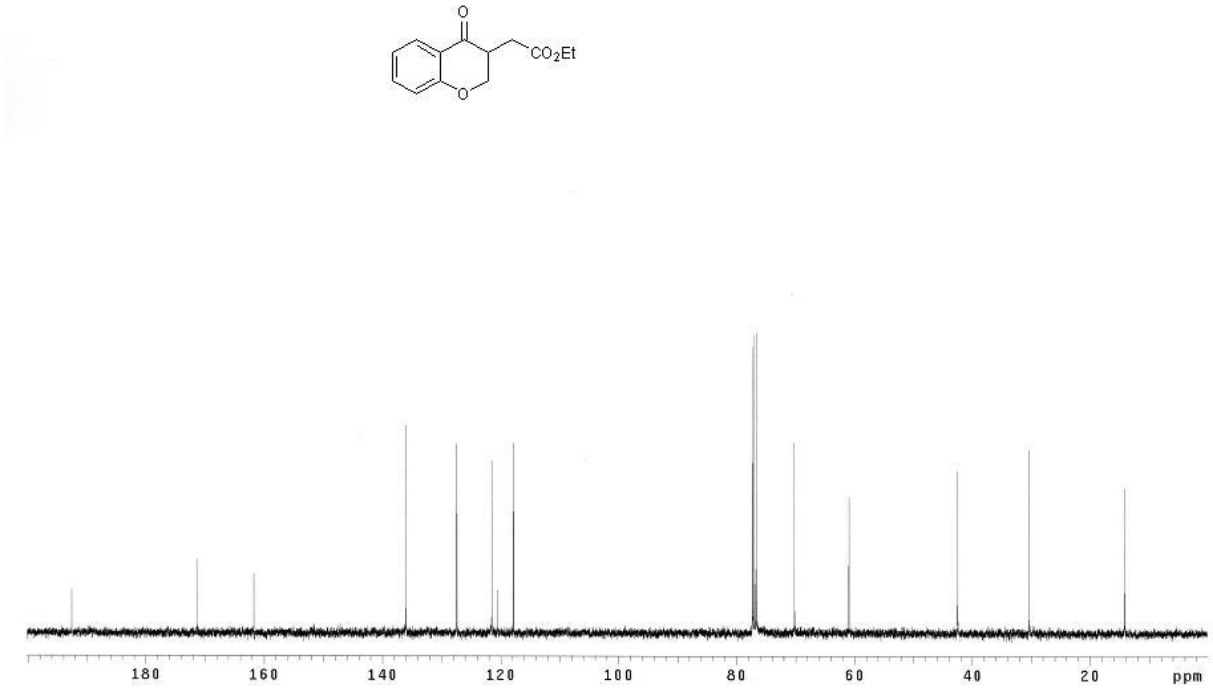
^{1}H NMR Spectrum of Compound **8** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of Compound **8** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of Compound **9** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of Compound **9** ($CDCl_3$, 100 MHz)