An Indium-Mediated Allylative/Transesterification DFT-Directed Approach to Chiral $C_{(3)}$-Funtionalized Phthalides

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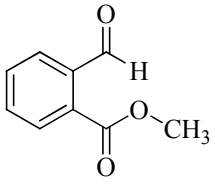
Table of Contents

1. General information:

Materials were obtained from commercial suppliers (Sigma-Aldrich) and were used without further purification. Dry (DCM) dichloromethane, THF (tetrahydrofuran), DMF (dimethylformamide) and toluene were obtained by Puresolv MD 5 purification system. All reactions were performed under an inert atmosphere. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F_{254}, EMD Merck. Flash column chromatography was performed over Silicycle ultrapure silica gel (230-400 mesh). NMR spectra were obtained with a Bruker DPX-300 (^{1}H 300 MHz, ^{13}C 75.5 MHz) in $CDCl_3$. The chemical shifts are reported as δ values (ppm) relative to tetramethylsilane. Enantiomeric excess was measured on an Agilent 1100 series high pressure liquid chromatography (HPLC) with (OD-H or AS-H) column, wavelength = 245 nm. Mass spectra were obtained on an MSI/Kratos concept IS Mass spectrometer. Optical rotations were recorded on a Perkin elmer 341 with sodium lamp polarimeter. FT-IR spectra were obtained on an ATI Mattson Research Series spectrometer using KBr discs and solids were mixed with Nujol.

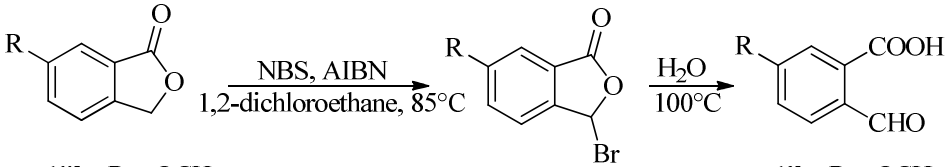
2. Representative procedure A: Synthesis of alkyl 2-formylbenzoate:

Iodomethane (0.6 mL, 9.5mmol) was added to a stirred solution of 2-formylbenzoic acid (0.765 g, 5.1 mmol) and potassium carbonate (0.387 g, 2.8 mmol) in DMF (4 mL). The reaction mixture was refluxed for 4 h, diluted with water (8 mL) and extracted with DCM. The combined organic phases were washed with 1N HCl (4 mL), saturated aqueous $NaHCO_3$ (4 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) to yield **1a** as a colorless oil (0.673 g, 80.4%).



Methyl 2-formylbenzoate (1a): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.59 (s, 1H), 7.97-7.90 (m, 2H), 7.65-7.62 (m, 2H), 3.96 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.3, 166.9, 137.1, 134.5, 133.1, 132.5, 130.5, 128.5, 52.9. HRMS (EI): m/z calcd for $C_9H_8O_3$ (M^+): 164.0473; found: 164.0468.

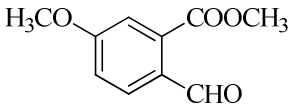
3. Representative procedure B: Synthesis of 5-substituted 2-formylbenzoic acid:



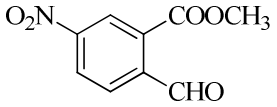
1''b R = OCH_3
1''c R = NO_2
1''d R = Br
1''e R = $HNCOOCH_2CH(CH_3)_2$
1''f R = ph

1'b R = OCH_3
1'c R = NO_2
1'd R = Br
1'e R = $HNCOOCH_2CH(CH_3)_2$
1'f R = ph

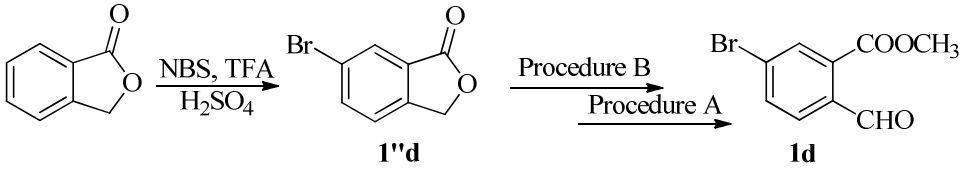
1,2-Dichloroethane (25 mL) was added to a mixture of 6-methoxyphthalide (670 mg, 4.5 mmol), N-bromosuccinimide (890 mg, 5 mmol), azobisisobutyronitrile (41 mg, 0.2 mmol) and refluxed for 1 h. The reaction mixture was kept in an ice bath for 2 hours then filtered. The solvent was removed under reduced pressure. Water (10 mL) was then added and the resulting mixture refluxed for 1 h. The reaction mixture was then cooled to room temperature and extracted with EtOAc. The combined organic phases were dried and concentrated under reduced pressure.



Methyl 2-formyl-5-methoxybenzoate (1b): Starting 6-methoxyphthalide was prepared by the reported procedure of Napoletano *et al.*[1] The representative procedures B and A outlined above were then followed, respectively. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.39 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.1 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 190.5, 166.6, 163.2, 134.4, 130.8, 129.4, 117.4, 115.3, 55.7, 52.7. HRMS (EI): m/z calcd for $C_{10}H_{10}O_4$ (M^+): 194.0579; found: 194.0573.



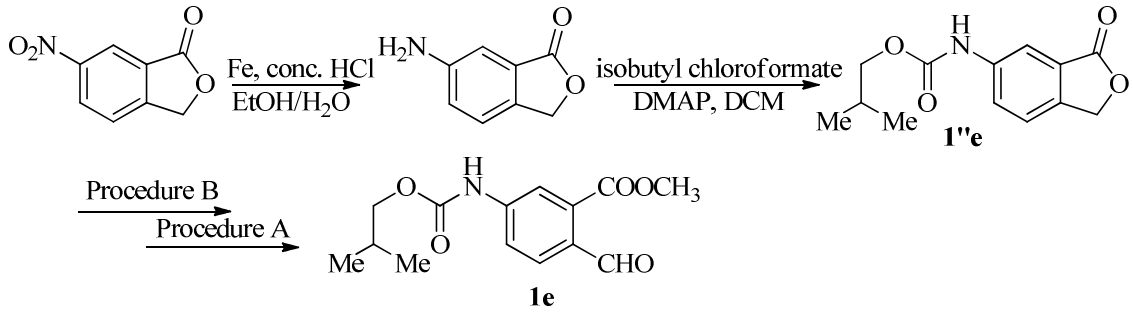
Methyl 2-formyl-5-nitrobenzoate (1c): The starting 6-nitrophthalide was prepared by the reported procedure of Wang, J. *et al.*[2] Thereafter, the representative procedures B and A outlined above were followed, respectively. m.p. = 62-64 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.67 (s, 1H), 8.80 (d, *J* = 2.1 Hz, 1H), 8.47-8.43 (m, 1H), 8.08 (d, *J* = 8.4, 1H), 4.03 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 190.5, 164.7, 150.0, 141.5, 133.0, 130.1, 127.2, 125.8, 53.6. HRMS (EI): m/z calcd for $C_9H_7NO_5$ (M^+): 209.0324; found: 209.0326.



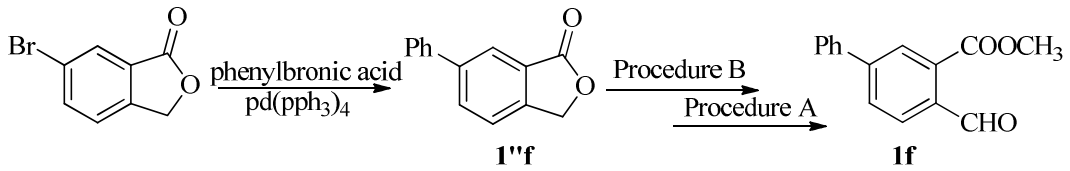
1"d **1d**

Methyl 5-bromo-2-formylbenzoate (1d): 6-Bromophthalide **1"d** was prepared by portion wise addition of phthalide (1g, 7.45 mmol) to a mixture of triflouroacetic acid (TFA) (3.7 mL) and sulphuric acid (1.7 mL) at room temperature for 9h. The reaction mixture was stirred at r.t. for 60 h, then poured onto ice and extracted with ethyl acetate. The combined organic phases were subsequently washed with a saturated solution of sodium bicarbonate and brine. After evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 9/1) to yield the desired product. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 1.8 Hz, 1H), 7.80 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 169.5, 145.2, 137.2, 128.7, 127.9, 123.9, 123.1, 69.6. The representative procedures B and A outlined above were followed to prepare **1d** which was isolate as a light yellow solid. m.p. = 114-116 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.57 (s, 1H), 8.11 (d, *J* = 1.8

Hz, 1H), 7.80 (s, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 3.99 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 191.0, 165.4, 135.7, 133.5, 133.4, 130.0, 128.1, 53.2. HRMS (EI): m/z calcd for $C_9H_7BrO_3$ (M^+): 241.9579; found: 241.9577.

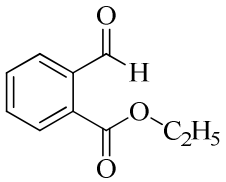


Methyl 2-formyl-5-((isobutoxycarbonyl)amino)benzoate (1e): 6-Aminophthalide was prepared by the reported procedure of Pokhodylo, N. T. and coworkers.[4] 4-Dimethylamino pyridine (DMAP) (0.12 g, 1 mmol) and isobutyl chloroformate (1.5 g, 11 mmol) were added to a mixture of 6-aminophthalide (1.49 g, 10 mmol) in acetonitrile (30 mL). The reaction mixture was stirred at room temperature overnight. After evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield carbamate **1"e.** ^{1}H-NMR (300MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 5.26 (s, 2H), 3.94 (d, *J* = 6.6 Hz, 2H), 1.98-1.89 (m, 1H), 0.92 (d, 6.9 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.2, 153.9, 140.9, 139.6, 126.4, 125.1, 122.7, 114.9, 71.6, 69.7, 27.94, 19.02. HRMS (EI): m/z calcd for $C_{13}H_{15}NO_4$ (M^+): 249.1001; found: 249.1006. The representative procedure B and A was followed recpectively to yield **1e** as a light yellow solid. m.p. = 104-106 °C. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 10.50 (s, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.45 (s, 1H), 4.00 (d, *J* = 6.6 Hz, 2H), 3.95 (s, 3H), 2.04-1.89 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 190.9, 166.6, 153.2, 142.9, 133.7, 131.1, 130.2, 120.8, 119.2, 71.9, 52.8, 27.9, 19.0. HRMS (EI): m/z calcd for $C_{14}H_{17}NO_5$ (M^+): 279.1107; found: 279.1110.

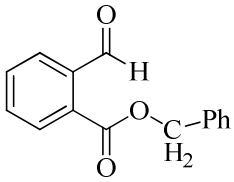


Methyl 4-formyl-[1,1'-biphenyl]-3-carboxylate (1f): For preparation of the intermediate **1"f** toluene (2.3 mL) was added to a mixture of 6-bromophthalide (280 mg, 1.3 mmol), phenylbronic acid (319.4 mg, 2.6 mmol), tetrakis(triphenylphosphine)palladium ($pd(pph_3)_4$) (75.7 mg, 0.065 mmol) and sodium carbonate solution (1.9 mL, 2M). The reaction mixture was refluxed for 5h followed by adding water (2 mL) and extraction with ethylacetate (10 mL, 3 times). The combined organic phase was dried and concentrated under the reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield the desired product. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.93 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.65-7.60 (m, 3H), 7.50-7.43 (m, 3H), 5.38(s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ =

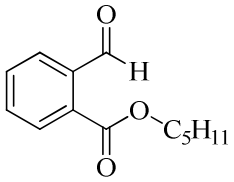
171.2, 145.4, 142.8, 139.5, 133.3, 129.2, 128.3, 127.3, 124.1, 122.6, 69.7. HRMS (EI): m/z calcd for $C_{14}H_{10}O_2$ (M^+): 210.0681; found: 210.0684. The representative procedures B and A outlined above were then followed, respectively, to yield **1f** as a white solid. m.p. = 77-79 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.62 (s, 1H), 8.15 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.48-7.40 (m, 3H), 3.40 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 191.6, 166.7, 145.7, 138.6, 130.5, 129.1, 128.9, 128.8, 127.2, 52.8. HRMS (EI): m/z calcd for $C_{15}H_{12}O_3$ (M^+): 240.0786; found: 240.0783.



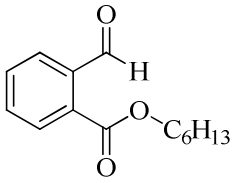
Ethyl 2-formylbenzoate (1g): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.90 (s, 1H), 7.96-7.88 (m, 2H), 7.63-7.60 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.1, 166.3, 137.0, 132.9, 132.5, 132.3, 130.3, 128.3, 61.9, 14.3. HRMS (EI): m/z calcd for $C_{10}H_{10}O_3$ (M^+): 178.0630; found: 178.0627.



Benzyl 2-formylbenzoate (1h): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.62 (s, 1H), 7.97-7.87 (m, 2H), 7.58-7.55 (m, 2H), 7.46-7.33 (m, 5), 5.39 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 191.7, 165.8, 136.9, 135.2, 132.7, 132.2, 131.7.3, 130.2, 128.5, 128.3, 128.2, 128.2, 67.3, HRMS (EI): m/z calcd for $C_{15}H_{12}O_3$ (M^+): 240.0786; found: 240.0783.

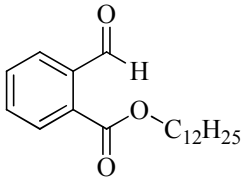


Pentyl 2-formylbenzoate (1i): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.59 (s, 1H), 7.93-7.86 (m, 2H), 7.61-7.58 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 1.75-1.73 (m, 2H), 1.37-1.36 (m, 6H), 0.89 (t, *J* = 6.6, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.0, 166.3, 137.0, 132.9, 132.4, 132.2, 130.3, 128.3, 66.0, 28.3, 28.1, 22.3, 13.9. HRMS (EI): m/z calcd for $C_{13}H_{16}O_3$ (M^+): 220.1099; found: 220.1096.

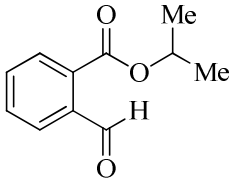


Hexyl 2-formylbenzoate (1j): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.59 (s, 1H), 7.95-7.87 (m, 2H), 7.63-7.57 (m, 2H), 4.34 (t, *J* = 3.6 Hz, 2H), 1.80-1.70 (m, 2H), 1.43-1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C-

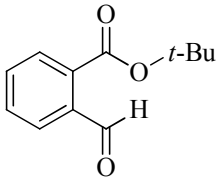
NMR (75 MHz, $CDCl_3$): δ = 192.0, 166.2, 137.0, 132.8, 132.2, 130.3, 128.3, 66.0, 31.3, 28.5, 25.6, 22.5, 13.9. HRMS (EI): m/z calcd for $C_{14}H_{18}O_3$ (M^+): 234.1256; found: 234.1250.



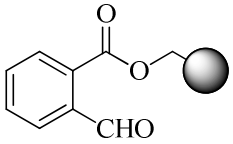
Dodecyl 2-formylbenzoate (1k): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.62 (s, 1H), 7.98-7.91 (m, 2H), 7.65-7.62 (m, 2H), 4.37 (t, *J* = 6.6 Hz, 2H), 1.81-1.76 (m, 2H), 1.43-1.26 (m, 18H), 0.87 (t, J = 6.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.0, 166.3, 137.1, 132.9, 132.4, 132.2, 130.3, 128.3, 66.0, 31.9, 29.6, 29.5, 29.5, 29.3, 29.2, 28.6, 26.0, 24.7, 22.7, 14.1. HRMS (EI): m/z calcd for $C_{20}H_{30}O_3$ (M^+): 318.2195; found: 318.22047.



Isopropyl 2-formylbenzoate (1l): m.p. = 77-79 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.45 (s, 1H), 7.81-7.67 (m, 2H), 7.51-7.41 (m, 2H), 5.20-5.05 (m, 1H), 1.24 (d, *J* = 6, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 192.0, 165.7, 136.9, 132.8, 132.0, 130.2, 128.2, 69.7, 21.8. HRMS (EI): m/z calcd for $C_{11}H_{12}O_3$ (M^+): 192.0786; found: 192.0781.



***tert*-Butyl 2-formylbenzoate (1m):** To a vigorously stirred suspension of anhydrous magnesium sulphate (3.2 g, 27 mmol) in DCM (27 mL), sulphuric acid (0.4 mL, 6.7 mmol) was added. The reaction mixture was stirred for 15 minutes; 2-carboxy benzaldehyde (1 g, 6.7 mmol) and *tert*-butanol (3.2 mL) were added and stirred for 18 h at room temperature followed by quenching with saturated sodium bicarbonate (75 mL). The organic phase was separated, washed with brine and dried. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1) to yield **1m** as a white solid (1.1 g, 80.0%). m.p. = 80-81 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.58 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.70-7.65 (m, 1H), 7.57-7.47 (m, 2H), 6.54 (s, 1H), 1.44 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 196.2, 146.5, 134.3, 130.5, 127.2, 125.2, 123.3, 98.0, 77.8, 28.7. HRMS (EI): m/z calcd for $C_{12}H_{14}O_3$ (M^+): 206.0943; found: 206.0937.

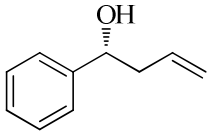


2-Formylphenylcarboxymethyl polystyrene (1n): 1n was synthesized by following the procedure reported by Knepper K. and coworkers.[4] Spectroscopic data was in full agreement with spectral data of an authentic sample.

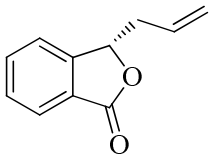
4. Representative procedure C: Synthesis of substituted (*R*)-3-allylisobenzofuran-1(3H)-one:

THF (6 mL) was added to a mixture of (1*R*, 2*S*)-2-amino-1,2-diphenylethanol (213.2 mg, 1 mmol) and indium powder (114.8 mg, 1 mmol) followed by addition of anhydrous pyridine (0.16 mL, 2 mmol), allyl bromide (0.17 mL, 2 mmol) and *n*-hexane (1 mL). The reaction mixture was stirred for 30 min. at room temperature then cooled to -78°C and substrate **1a** (82.05 mg, 0.5 mmol) in THF (1 mL) added dropwise. The reaction mixture was stirred for 1 h then saturated ammonium chloride was added (1mL) and extracted with ethyl acetate. After drying with anhydrous sodium sulfate and evaporation of the solvents in vacuum, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2a** as a colorless oil (67.4 mg, 77%).

5. Determination of the absolute stereochemistry:

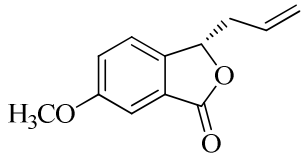


(*R*)-1-phenylbut-3-en-1-ol (6): Representative Procedure C was followed. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.30-7.39 (m, 5H), 5.77-5.91 (m, 1H), 5.15-5.22 (m, 1H), 4.75 (t, J = 7 Hz, 1H), 2.50-2.59 (m, 2H), 2.22 (s, 1H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.0, 134.5, 128.5, 127.7, 125.9, 118.5, 73.4, 43.96. The absolute stereochemistry was determined by comparison of the sign of optical rotation with reported literature values ($[\alpha]^{20}_D$= +37 (c = 1, $CHCl_3$)).[5]

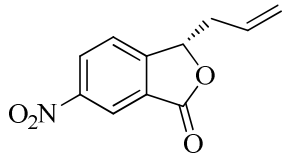


(*R*)-3-allylisobenzofuran-1(3H)-one (2a): Representative Procedure C was followed to prepare **2a** from substrates **1a**, **1g-l**, and **1n**. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2a** from substrate (**1g** (54.1 mg, 62%), **1h** (50.6 mg, 58%), **1i** (52.3 mg, 60%), **1j** (48.1 mg, 55%), **1k** (49.8 mg, 57%), **1l** (68.1 mg, 78%), **1n** (45.3 mg, 52%)). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.57-7.47 (m, 2H), 5.85-5.71 (m, 1H), 5.53 (t, *J* = 6 Hz, 1H), 5.23-5.15 (m, 2H), 2.81-2.62 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.5, 149.4, 134.0, 131.3, 129.3, 126.3, 125.7, 122.1, 119.8, 80.3, 38.7. IR: 1760. HRMS (EI): m/z calcd for $C_{11}H_{10}O_2$ (M^+): 174.0681; found: 174.0677. For **2a** prepared from **1a** $[\alpha]^{20}_D$= +62.60 (c = 1.98, $CHCl_3$). For **2a** prepared from **1g** $[\alpha]^{20}_D$= +61.50 (c = 1.90, $CHCl_3$). For **2a** prepared from **1h** $[\alpha]^{20}_D$= +61.4 (c = 1.95, $CHCl_3$). For **2a** prepared from **1i** $[\alpha]^{20}_D$= +60.4 (c = 1.5, $CHCl_3$). For **2a** prepared from **1j** $[\alpha]^{20}_D$= +59.2 (c = 1.5, $CHCl_3$). For **2a** prepared from **1k** $[\alpha]^{20}_D$= +57.0 (c = 1.50, $CHCl_3$). For **2a** prepared from **1l** $[\alpha]^{20}_D$= +58.0 (c = 1.6,

$CHCl_3$). For **2a** prepared from **1n** $[\alpha]^{20}_D$= +4.2 (c = 0.6, $CHCl_3$). The enantioselectivity was determined by HPLC analysis on a chiral column (OD-H, hexane/*i*prOH 95:5, flow rate 0.5 $mLmin^{-1}$, wavelength = 245 nm). For **2a** prepared from **1a** enantiomeric excess = 80%, (t_{minor} = 20.07 min (*S*), area% = 9.9476; t_{major} = 18.82 min (*R*), area% = 90.0524). For **2a** prepared from **1g** enantiomeric excess = 79%, (t_{minor} = 19.52 min (*S*), area% = 10.5755; t_{major} = 18.56 min (*R*), area% = 89.4245). For **2a** prepared from **1h** enantiomeric excess = 76%, (t_{minor} = 20.06 min (*S*), area% = 12.0013; t_{major} = 18.75 min (*R*), area% = 87.9987. For **2a** prepared from **1i** enantiomeric excess = 71%, (t_{minor} = 19.39 min (*S*), area% = 14.4569; t_{major} = 18.37 min (*R*), area% = 85.5431). For **2a** prepared from **1j** enantiomeric excess = 65%, (t_{minor} = 19.40 min (*S*), area% = 17.5536; t_{major} = 18.39 min (*R*), area% = 82.4464). For **2a** prepared from **1k** enantiomeric excess = 50%, (t_{minor} = 19.79 min (*S*), area% = 25.1805; t_{major} = 18.54 min (*R*), area% = 74.8195). For **2a** prepared from **1l** enantiomeric excess = 64%, (t_{minor} = 18.87 min (*S*), area% = 18.1187; t_{major} = 17.96 min (*R*), area% = 81.8813). For **2a** prepared from **1n** enantiomeric excess = 0.12% (racemic), (t_{minor} = 20.07 min (*S*), area% = 49.9405; t_{major} = 18.645 min (*R*), area% = 50.0595). Absolute configuration assigned as (*R*) by comparison of optical rotation with a literature value. [6]

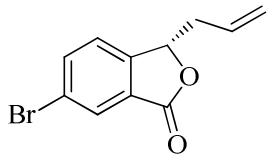


(*R*)-3-allyl-6-methoxyisobenzofuran-1(3H)-one (2b): Representative Procedure C was followed. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2b** (68.4 mg, 67%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.20-7.24 (m, 1H), 5.80-5.69 (m, 1H), 5.47 (t, *J* = 5.9 Hz, 1H), 5.21-5.14 (m, 2H), 3.87 (s, 3H), 2.71-2.60 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.5, 160.7, 141.8, 131.3, 127.6, 122.9, 122.8, 119.7, 107.5, 80.12, 55.8, 38.8. IR: 1760. HRMS (EI): m/z calcd for $C_{12}H_{12}O_3$ (M^+): 204.0786; found: 204.0782. $[\alpha]^{20}_D$= +15.3 (c = 0.32, $CHCl_3$). The enantioselectivity was determined by HPLC analysis on a chiral column (OD-H, hexane/*i*prOH 99:1, flow rate 0.5 $mLmin^{-1}$, wavelength = 245 nm) to be 77%: t_{minor} = 31.92 min (*S*), area% = 11.5177, t_{major} = 33.11 min (*R*), area% = 88.4823.

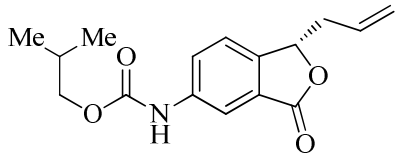


(*R*)-3-allyl-6-nitroisobenzofuran-1(3H)-one (2c): Representative Procedure C was followed. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2c** (74.5 mg, 68%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 8.56 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 5.81-5.65 (m, 2H), 5.25-5.19 (m, 2H), 2.88-2.71 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.8, 154.5, 149.1, 130.1, 128.8, 128.1, 123.5, 121.4, 120.8, 80.2, 38.2. IR: 1766. HRMS (EI): m/z calcd for $C_{11}H_9NO_4$ (M^+): 219.0532; found: 219.0536. $[\alpha]^{20}_D$= +11.05 (c = 0.57, $CHCl_3$). The enantioselectivity was determined

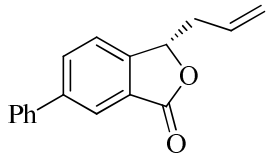
by HPLC analysis on a chiral column (AS-H, hexane/*i*prOH 80:20, flow rate 1 mLmin^{-1}, wavelength = 245 nm) to be 45%: t_{minor} = 12.64 min (*S*), area% = 27.2280, t_{major} = 16.23 min (*R*), area% = 72.7719.



(*R*)-3-allyl-6-bromoisobenzofuran-1(3H)-one (2d): Representative Procedure C was followed. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2d** (87.3 mg, 69%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 1.6 Hz, 1H), 7.77 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.35 (d, *J* = 6 Hz, 1H), 5.80-5.66 (m, 1H), 5.48 (t, *J* = 6 Hz, 1H), 5.21-5.15 (m, 2H), 2.72-2.65 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.8, 148.0, 137.1, 130.9, 128.9, 123.7, 120.3, 80.2, 38.6. IR: 1769. HRMS (EI): m/z calcd for $C_{11}H_9O_2$ (M^+): 215.9786; found: 215.9789. $[\alpha]^{20}_D$= +0.28 (c = 11.8, $CHCl_3$), The enantioselectivity was determined by HPLC analysis on a chiral column (AS-H, hexane/*i*prOH 90:10, flow rate 1 mLmin^{-1}, wavelength = 245 nm) to be 69%: t_{minor} = 14.78 min (*S*), area% = 15.5908, t_{major} = 16.50 min (*R*), 84.4092.



(*R*)-isobutyl (3-allyl-1-oxo-1,3-dihydroisobenzofuran-5-yl)carbamate (2e): Representative Procedure C was followed. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2e** (94.2 mg, 65%). m.p. = 130-133 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.82 (s, 1H), 7.39 (d, *J* = 8.4, Hz, 1H), 6.70 (s, 1H), 5.81-5.67 (m, 1H), 5.47 (t, *J* = 6 Hz, 1H), 5.20-5.13 (m, 2H), 3.97 (d, *J* = 6.6 Hz, 2H), 2.76-2.58 (m, 2H), 2.05-1.91 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.2, 153.7, 144.0, 139.6, 131.3, 127.3, 124.9, 122.8, 119.9, 114.9, 80.3, 71.9, 38.9, 28.1, 19.1. IR: 1754, 1713. HRMS (EI): m/z calcd for $C_{16}H_{19}NO_4$ (M^+): 289.1314; found: 289.1319. $[\alpha]^{20}_D$= +40.8 (c = 0.13, $CHCl_3$). The enantioselectivity was determined by HPLC analysis on a chiral column (AS-H, hexane/*i*prOH 90:10, flow rate 1 mLmin^{-1}, wavelength = 245 nm) to be 69%: t_{major} = 27.32 min (*S*), area% = 86.1189, t_{minor} = 32.38 min (*R*), area% = 13.8811.



(*R*)-3-allyl-6-phenylisobenzofuran-1(3H)-one (2f): Representative Procedure C was followed. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) to yield **2f** (84.1 mg, 67%). m.p. = 80-82 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 7.91 (dd, *J* = 6.6, 1.6 Hz, 1H), 7.65-7.62 (m, 2H), 7.67-7.43 (m, 4H), 5.87-5.76 (m, 1H), 5.59 (t, *J* = 6 Hz, 1H), 5.27-5.19 (m, 2H), 2.80-2.96 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.5, 148.2, 142.9, 139.5, 133.2, 131.3, 129.2, 128.3, 127.4, 127.2,

124.1, 122.5, 119.9, 80.3, 38.9. IR: 1755. HRMS (EI): m/z calcd for $C_{17}H_{14}O_2$ (M^+): 250.0994; found: 250.0992. $[\alpha]^{20}_D$= +35.1 (c = 0.71, $CHCl_3$). The enantioselectivity was determined by HPLC analysis on a chiral column (AS-H, hexane/*i*prOH 90:10, flow rate 1 mLmin^{-1}, wavelength = 245 nm) to be 68%: t_{minor} = 14.89 min (*S*), area% = 15.9145, t_{major} = 20.20 min (*R*), area% = 84.0855.

6. Transesterification under different reaction conditions:

7

Isopropyl 2-phenylacetate: Isopropyl 2-phenylacetate **7** was prepared by using the protocol previously reported by Ranu[7] and applying the following conditions:

Condition A: In a 25 mL round bottom flask**,** 2-propanol (6 mL) was mixed with methyl phenylacetate (150 mg, 1 mmol) and it was refluxed for 6 hours.

Condition B: Indium (173 mg, 1.5 mmol) and bromine (360 mg, 2.25 mmol) were added to the mixture described in condition A.

Condition C: Pyridinium salt was prepared by the addition of toluene (3 mL) to a mixture of pyridine (1 mL) and HBr 48% (2 mL) and then the solvent was removed under reduced pressure. Pyridinium salt (240 mg, 1.5 mmol) was used instead of indium and bromine in condition B.

Condition D: Indium (173 mg, 1.5 mmol), bromine (360 mg, 2.25 mmol) and pyridinium salt (240 mg, 1.5 mmol) were used as a catalyst.

The product's spectra obtained from conditions B and C were in full agreement with spectral data of an authentic sample.

7. DFT calculations:

Transition states (*R*)-**TS1** and (*S*)-**TS2** correspond to the enantiodetermining first-order saddle points for (*R*)- vs (S)-allylation, while (*R*)-**TS3** and (*S*)-**TS4** correspond to the subsequent transesterification transitions generated from (*R*)-**TS1** and (*S*)-**TS2** in the presence of pyridinium salt (pyr-H^+). Moreover, (*R*)-**TS5** and (S)-**TS6** refer to the transesterification transition states formed in the absence of pyr-H^+ and a ligand **3** bound indium complex. Lastly, (*R*)-**TS7** and (*S*)-**TS8** correspond to the lowest energy (*R*)- and (*S*)-enantiodeterming allylation transition states for benzaldehyde addition. The respective local minima referred to below corresponding to the direct products and precomplexes of the transition states discussed herein which were located using the **I**ntrinsic **R**eaction **C**oordinate (IRC) method. All of the reported calculations were carried using the Gaussian 09revB.01 and Gaussview 5.0.8 suite of programs.[8]

(*R*)-TS1

(*R*)-TS1 had one and only one imaginary frequency (imaginary frequency = -137.55).

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.469160 (Hartree/Particle)
Thermal correction to Energy= 0.507381
Thermal correction to Enthalpy= 0.508326
Thermal correction to Gibbs Free Energy= 0.391689
Sum of electronic and zero-point Energies= -1404.994358
Sum of electronic and thermal Energies= -1404.956137
Sum of electronic and thermal Enthalpies= -1404.955193
Sum of electronic and thermal Free Energies= -1405.071830

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C	-2.20858200	-0.25216500	0.29993800	C	-4.28590800	-1.85046900	3.92976200
N	-1.12767600	0.30371400	-0.64065800	C	-3.33985300	-3.97980100	3.22224700
In	-0.27007400	2.22490000	-0.29240200	H	-1.72240200	-3.84186400	1.77110700
C	1.28483900	2.94948700	-1.70923100	H	-3.41158300	-0.08504300	3.04058300
H	0.83492900	3.90018100	-2.01451300	H	-4.99061300	-1.28412400	4.53471900
H	1.25667400	2.21597100	-2.52286000	H	-3.31166600	-5.06606100	3.27811700
C	2.59504500	3.11370000	-1.08660300	H	-4.95198400	-3.78298100	4.66450000
C	3.61961600	2.18758300	-1.08403900	C	3.91455100	0.14123200	1.08792800
H	3.57912000	1.29758800	-1.70926400	C	4.77655800	0.91615500	1.91047000
H	4.57689200	2.42979100	-0.63108900	C	4.35822000	-1.17660800	0.72034800
O	-0.52515400	-2.04427200	0.78078200	C	6.02230100	0.44932300	2.35069600
In	0.49828700	-1.13049800	-0.62534400	H	4.45916400	1.91380500	2.20135400
O	1.55352200	0.48456800	0.23321400	C	5.62611600	-1.62636700	1.16278700
C	2.66734600	0.88497400	0.77530600	C	6.45646400	-0.83054100	1.96554900
H	-1.54585400	0.37730600	-1.57685300	H	6.64307400	1.07823600	2.98168900
H	-2.67480300	0.58368800	0.83387900	H	5.95273600	-2.62093600	0.88457300
C	-3.30472200	-0.94326000	-0.51179500	H	7.42020700	-1.21049700	2.29060800
C	-5.36602300	-2.10714500	-2.08463900	H	2.58311500	1.80800700	1.34788500
C	-4.50279200	-0.23965600	-0.77221200	Br	-0.01688800	2.84579000	2.25460700
C	-3.15569800	-2.24429600	-1.04876600	Br	-2.34882800	3.76133200	-0.99800400
C	-4.17724300	-2.81999700	-1.82688700	Br	0.70039100	-1.65942400	-3.17475300
C	-5.52644300	-0.81297900	-1.55159300	C	3.56040300	-2.15810500	-0.05211300
H	-4.63526800	0.76050100	-0.36462000	O	2.32317000	-2.07789800	-0.29691100
H	-2.25239300	-2.81131500	-0.84528800	O	4.25477600	-3.22920800	-0.47436100
H	-4.04773000	-3.82279800	-2.22786900	C	3.54339400	-4.31971000	-1.20148900
H	-6.44053500	-0.25442800	-1.73960400	H	3.07576100	-3.91651300	-2.10288200
H	-6.15361500	-2.55373700	-2.68716700	H	4.32720700	-5.03483700	-1.44967900
H	-0.94534400	-0.42612600	2.03115100	H	2.79469700	-4.76809200	-0.54263500
C	-2.46998400	-1.89255000	2.28435100	H	2.75072600	4.03576500	-0.52139100
C	-4.26423700	-3.25910700	4.00443600				
C	-2.44730500	-3.29930200	2.36910300				

Minima: Precomplex of (*R*)-TS1

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.468738 (Hartree/Particle)
Thermal correction to Energy= 0.508336

Thermal correction to Enthalpy=	0.509280
Thermal correction to Gibbs Free Energy=	0.387495
Sum of electronic and zero-point Energies=	-1404.997165
Sum of electronic and thermal Energies=	-1404.957567
Sum of electronic and thermal Enthalpies=	-1404.956622
Sum of electronic and thermal Free Energies=	-1405.078408

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C	-2.21055400	-0.32656200	0.07352300	C	-4.62866000	-2.03572800	3.43336600
N	-1.05444900	0.33025600	-0.70211600	C	-3.36845300	-4.06838600	2.97703300
In	-0.56815200	2.37725800	-0.25031400	H	-1.57804500	-3.80059000	1.76824600
C	0.66831600	3.36384400	-1.73373400	H	-3.82466900	-0.21496800	2.59206300
H	-0.05248200	3.99131700	-2.27789900	H	-5.47084600	-1.53125300	3.90187500
H	1.03528300	2.58200000	-2.41256200	H	-3.23362900	-5.14208500	3.09120800
C	1.78240500	4.19272600	-1.17548000	H	-5.18923900	-4.00480200	4.15966400
C	3.11036000	3.92911300	-1.28072200	C	4.23771900	0.22585900	0.72280800
H	3.48192500	3.06091500	-1.82560700	C	5.28538800	1.12948500	1.04592700
H	3.85516300	4.58613600	-0.83379200	C	4.54748600	-1.18138200	0.65683300
O	-0.45229600	-1.91582100	0.85441900	C	6.60486200	0.69848800	1.25967000
In	0.61621500	-1.05472100	-0.54859000	H	5.05920400	2.18966800	1.11766800
O	1.87340400	0.52952200	0.02026900	C	5.87537900	-1.59269900	0.88421800
C	2.97643600	0.94062900	0.49451500	C	6.90026300	-0.66881100	1.17088100
H	-1.34141300	0.39088300	-1.69005600	H	7.38096000	1.42031600	1.49314400
H	-2.83564900	0.46792800	0.49625400	H	6.11355400	-2.64828400	0.84139200
C	-3.09126200	-1.13713800	-0.87941600	H	7.91298200	-1.02587500	1.33175700
C	-4.75239000	-2.51062100	-2.73200700	H	3.01099100	2.00238500	0.75333300
C	-4.22016600	-0.50385800	-1.44980400	Br	0.14714600	2.53966200	2.29119600
C	-2.80892100	-2.47346400	-1.24881100	Br	-2.97703700	3.51256400	-0.22509600
C	-3.63293100	-3.15312500	-2.16560700	Br	1.09069300	-1.67743100	-3.02445000
C	-5.04496600	-1.18093800	-2.36865000	C	3.55311800	-2.26218800	0.40484100
H	-4.45517400	0.52192500	-1.17174500	O	2.34508500	-2.10137100	0.08429600
H	-1.95685600	-2.98574800	-0.81318200	O	4.04781700	-3.50357300	0.55520200
H	-3.40287800	-4.18137800	-2.43551000	C	3.15443900	-4.67347000	0.31379900
H	-5.90917200	-0.67640000	-2.79453400	H	2.77694500	-4.64106700	-0.71138000
H	-5.38691400	-3.03765400	-3.44083500	H	3.79589900	-5.53994900	0.47185500
H	-1.19955000	-0.32083200	1.96463100	H	2.33125800	-4.65476600	1.03285500
C	-2.59530600	-1.93012300	2.06830200	H	1.47915500	5.09115600	-0.63069800
C	-4.47007300	-3.42982700	3.58060800				
C	-2.43644500	-3.32165000	2.22795400				

Minima: Direct product of (*R*)-TS1

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.471966 (Hartree/Particle)
Thermal correction to Energy=	0.510246
Thermal correction to Enthalpy=	0.511191
Thermal correction to Gibbs Free Energy=	0.393785
Sum of electronic and zero-point Energies=	-1405.051103
Sum of electronic and thermal Energies=	-1405.012822
Sum of electronic and thermal Enthalpies=	-1405.011878
Sum of electronic and thermal Free Energies=	-1405.129284

C	1.96490900	0.47265900	1.11722400	C	3.78249000	2.22132900	1.53745500
C	2.19575900	-0.87154400	0.32252500	C	3.82764000	0.15988400	2.82849300
N	0.92628500	-1.14029600	-0.49115200	C	4.97941000	0.60492200	3.50480000
In	-0.78524500	-1.93504300	0.39903800	C	4.93422900	2.67006600	2.21521100
C	-3.63603700	-0.39425300	-3.48167300	H	3.29978800	2.83812700	0.78633800
H	-3.87144000	-1.25237700	-4.10925200	H	3.39874600	-0.80793300	3.08230600
H	-3.14165700	0.44718000	-3.96448400	H	5.43391800	-0.02217600	4.26867000
C	-3.93587700	-0.38431400	-2.16622500	H	5.35489300	3.64510000	1.97815500
C	-3.68955200	0.77620500	-1.22512100	H	6.42777800	2.20902800	3.72324500
H	-3.13857400	1.57048200	-1.73747500	C	-3.03920900	1.38054400	1.21389700
H	-4.66109800	1.19912400	-0.92512000	C	-3.70443300	0.97839800	2.39127400
O	1.39906700	1.49759000	0.27106100	C	-2.56530000	2.72867800	1.15470400
In	0.04132400	0.84706800	-1.00182300	C	-3.89950300	1.85002400	3.47840600
O	-1.60825100	-0.14771000	-0.15820700	H	-4.08391000	-0.03751800	2.45816500
C	-2.98844500	0.34001600	0.08630000	C	-2.77775200	3.60761700	2.24712000
H	1.18560700	-1.69642300	-1.31493400	C	-3.43555700	3.17543400	3.40637000
H	2.31428600	-1.66660500	1.06813600	H	-4.41123600	1.49467200	4.36872600
C	3.41817800	-0.92713400	-0.59327000	H	-2.40949000	4.62573900	2.18385000
C	5.65750700	-1.17492000	-2.32328000	H	-3.57952700	3.85913300	4.23768800
C	4.14481000	-2.13784500	-0.66950600	H	-3.54603200	-0.52870600	0.45436000
C	3.83290100	0.16209400	-1.39514700	Br	-0.81060700	-2.24297800	2.95357200
C	4.94352300	0.03849600	-2.25065600	Br	-1.87141300	-3.97772000	-0.70977700
C	5.25475800	-2.26519100	-1.52688100	Br	0.27501500	1.09607200	-3.56591800
H	3.84242400	-2.98268900	-0.05285400	C	-1.81387800	3.27832900	0.00607200
H	3.29799900	1.10495700	-1.34390100	O	-1.10921200	2.60509500	-0.80861500
H	5.25133900	0.88649700	-2.85809100	O	-1.90204400	4.61182600	-0.13517100
H	5.80110400	-3.20448200	-1.57071500	C	-1.10201000	5.28526500	-1.19799300
H	6.51433200	-1.26788500	-2.98653200	H	-1.42528100	4.93033700	-2.17972000
H	1.23078700	0.21789500	1.90539800	H	-1.32103900	6.34520100	-1.07016900
C	3.22499000	0.96047600	1.83082100	H	-0.03967300	5.07871900	-1.04285000
C	5.53971200	1.86304900	3.19913300	H	-4.42682000	-1.25478900	-1.7229650

(*S*)-TS2

(*S*)-TS2 had one and only one imaginary frequency (imaginary frequency = -129.17).

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.468830 (Hartree/Particle)
Thermal correction to Energy=	0.507102
Thermal correction to Enthalpy=	0.508046
Thermal correction to Gibbs Free Energy=	0.390969
Sum of electronic and zero-point Energies=	-1404.989652
Sum of electronic and thermal Energies=	-1404.951380
Sum of electronic and thermal Enthalpies=	-1404.950436
Sum of electronic and thermal Free Energies=	-1405.067513

C	-2.16066600	-0.63498800	1.11275000	C	2.82156100	2.86496600	-1.93587100
C	-2.32726300	0.16269600	-0.24318300	H	2.74540300	2.72310000	-3.01653600
N	-0.92735200	0.37234200	-0.82292600	C	3.94537800	2.37040100	-1.30834600
In	0.18217700	2.14224500	-0.37834800	H	4.78939200	2.01565500	-1.89119000
C	1.68456200	3.49715700	-1.27930700	H	4.10098300	2.50573100	-0.23954300
H	1.95002300	4.06942700	-0.38211300	O	-1.22741000	-1.73317400	0.96784800
H	1.06971000	4.09441000	-1.95881500	In	0.29878300	-1.28821100	-0.19802100

O	1.77905700	0.19647600	-0.82619600	H	-6.42155400	0.18959300	2.93844000
C	2.99088700	0.06933100	-1.29797700	H	-5.22704400	-3.94502400	2.51404600
H	3.12318100	0.18126600	-2.37415900	H	-6.92926300	-2.24718000	3.20381600
H	-1.00404000	0.37823200	-1.84991800	C	4.12267800	-0.57447500	-0.59599600
H	-2.74639300	1.14072100	0.01581700	C	6.52659400	-1.65078900	0.48457400
C	-3.24292900	-0.46498600	-1.29402400	C	4.15073100	-1.07916100	0.74621200
C	-4.92839600	-1.51884200	-3.32654900	C	5.30581300	-0.67541500	-1.37147900
C	-4.15274500	0.36729600	-1.98612700	C	6.49166800	-1.21203600	-0.85113700
C	-3.19417700	-1.83838200	-1.63319300	C	5.36252200	-1.58620300	1.26868700
C	-4.02867400	-2.35931700	-2.63944900	H	5.29164300	-0.30961700	-2.39464700
C	-4.98952200	-0.15122000	-2.99385400	H	7.37754700	-1.27738600	-1.47562800
H	-4.20901100	1.42444400	-1.73409700	H	5.38252200	-1.96152700	2.28550400
H	-2.52008000	-2.50267500	-1.10133500	H	7.44053700	-2.05472100	0.90970000
H	-3.98051800	-3.41817600	-2.88337300	Br	0.92382900	-3.15358500	-1.87613300
H	-5.68367500	0.50616400	-3.51243100	Br	-1.83430600	3.91686500	-0.33842900
H	-5.57252100	-1.92381300	-4.10368200	Br	0.80023400	1.90724000	2.20371100
H	-1.73779100	0.09564400	1.82401400	C	2.96161000	-1.24100600	1.62615400
C	-3.49694900	-1.10140800	1.68462700	O	1.78920800	-1.53046500	1.24151300
C	-5.97769100	-1.92918200	2.78359400	O	3.23871700	-1.16589000	2.93393500
C	-3.78389200	-2.47159700	1.84986900	C	2.15403800	-1.42570000	3.92657100
C	-4.45804800	-0.14653400	2.09007100	H	1.32669300	-0.73584700	3.74776900
C	-5.69140000	-0.55608200	2.63142200	H	1.82295700	-2.46373900	3.83505900
C	-5.01754000	-2.88411300	2.39334100	H	2.62386300	-1.24370600	4.89282300
H	-3.03124100	-3.19739100	1.55914200				
H	-4.24386400	0.91608300	1.98861500				

Minima: Precomplex of (*S*)-TS2

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.468697 (Hartree/Particle)
Thermal correction to Energy=	0.508292
Thermal correction to Enthalpy=	0.509236
Thermal correction to Gibbs Free Energy=	0.388624
Sum of electronic and zero-point Energies=	-1404.997449
Sum of electronic and thermal Energies=	-1404.957854
Sum of electronic and thermal Enthalpies=	-1404.956910
Sum of electronic and thermal Free Energies=	-1405.077521

C	-2.08597400	-0.61980500	1.08916900	O	2.01157800	-0.10573100	-1.11734600
C	-2.29824200	0.13603900	-0.27510800	C	3.26585500	0.00662500	-1.24276900
N	-0.89725100	0.48360300	-0.81859900	H	3.61292100	0.60960600	-2.08837600
In	-0.12959300	2.42749700	-0.29755200	H	-0.96797700	0.54563400	-1.84577600
C	0.73710600	3.73311900	-1.78591200	H	-2.81634200	1.07253000	-0.04297700
H	1.04890400	4.63313400	-1.23959900	C	-3.12077700	-0.57711700	-1.34935200
H	-0.12593800	3.98919700	-2.41828800	C	-4.64834400	-1.76594700	-3.43069200
C	1.85121300	3.15692500	-2.60239700	C	-3.90351500	0.21686900	-2.22138100
H	1.55817500	2.41195200	-3.34753600	C	-3.11734300	-1.97911000	-1.53544100
C	3.16678800	3.47718700	-2.50238400	C	-3.87617300	-2.56665800	-2.56565400
H	3.91413900	3.01198900	-3.14343200	C	-4.65989600	-0.36758500	-3.25470600
H	3.52514100	4.21731000	-1.78696300	H	-3.92640300	1.29696000	-2.08543100
O	-1.08309600	-1.65094200	0.96038600	H	-2.53040400	-2.61089800	-0.87766600
In	0.35852500	-1.21985600	-0.31340500	H	-3.86449400	-3.64686500	-2.69176900

H	-5.25714300	0.26063800	-3.91160400	H	5.69066800	0.22474200	-1.93210500
H	-5.23332000	-2.22341300	-4.22527500	H	7.76874000	-0.57453500	-0.84873200
H	-1.71231000	0.15019800	1.78853100	H	5.43203500	-2.18745000	2.39808700
C	-3.38405600	-1.16894200	1.68434700	H	7.63367900	-1.78753600	1.34227500
C	-5.76993300	-2.16665100	2.85399400	Br	0.69184100	-3.12641200	-2.04443800
C	-3.50974700	-2.53730800	1.99960400	Br	-2.14893100	3.76130100	0.77596000
C	-4.46099600	-0.29949800	1.97475600	Br	1.46050900	1.87358300	1.76085500
C	-5.64666300	-0.79459200	2.55027100	C	3.02107800	-1.58247800	1.55621900
C	-4.69472800	-3.03487900	2.57864700	O	1.87687500	-1.70673300	1.03895000
H	-2.67154900	-3.19417300	1.79092600	O	3.19146800	-1.79915200	2.86850700
H	-4.37906900	0.76379500	1.75835200	C	2.01356000	-2.19627800	3.69536200
H	-6.46714900	-0.11362600	2.76578500	H	1.25049500	-1.41665100	3.63930700
H	-4.77666200	-4.09356200	2.81623000	H	1.62080000	-3.14983200	3.33291400
H	-6.68460700	-2.54910800	3.30145800	H	2.41337600	-2.28899700	4.70472000
C	4.34795300	-0.55905300	-0.42557300				
C	6.73188600	-1.44093000	0.84667000				
C	4.28069800	-1.25238300	0.83364300				
C	5.62618200	-0.31823500	-0.99322600				
C	6.80856800	-0.76344400	-0.37894600				
C	5.47768800	-1.67032300	1.44700000				

Minima: Direct product of (*S*)-TS2

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.472157 (Hartree/Particle)
Thermal correction to Energy= 0.510414
Thermal correction to Enthalpy= 0.511358
Thermal correction to Gibbs Free Energy= 0.394624
Sum of electronic and zero-point Energies= -1405.050707
Sum of electronic and thermal Energies= -1405.012450
Sum of electronic and thermal Enthalpies= -1405.011505
Sum of electronic and thermal Free Energies= -1405.128240

C	-2.31178800	-0.43877000	0.97558000	C	-4.17097900	0.83320900	-2.10704500
C	-2.41058800	0.44352000	-0.33285300	C	-3.34100300	-1.43700200	-1.84148200
N	-0.99212300	0.62150800	-0.88549100	C	-4.17521500	-1.86147900	-2.89214700
In	0.32922600	2.06258000	-0.15485700	C	-5.00600700	0.41133600	-3.16011200
C	0.09823600	0.33875700	4.15260100	H	-4.17488500	1.87869900	-1.80350800
H	-0.18264500	-0.71418000	4.15364000	H	-2.71219200	-2.15951700	-1.33077700
H	-0.56802000	1.02629000	4.67046900	H	-4.17606300	-2.90775800	-3.18908100
C	1.22006100	0.77467900	3.54169400	H	-5.64830200	1.13011600	-3.66367200
H	1.46425500	1.83922500	3.56854900	H	-5.65258800	-1.27065800	-4.37015900
C	2.21933200	-0.11453700	2.83477200	H	-1.86035100	0.22456300	1.73705600
H	3.16861300	-0.10347800	3.39283300	C	-3.68229400	-0.85600200	1.50377200
H	1.85662000	-1.14607300	2.83426600	C	-6.21960800	-1.60236400	2.52725300
O	-1.44417600	-1.58196000	0.78624700	C	-4.03683000	-2.21577100	1.61252900
In	0.18774300	-1.14811700	-0.21505100	C	-4.60440400	0.12919200	1.92629300
O	1.35502800	0.42813800	0.53766900	C	-5.86594100	-0.24011800	2.43029600
C	2.55822600	0.38208200	1.40492400	C	-5.29872100	-2.58781500	2.11892400
H	2.88615200	1.42232000	1.50531600	H	-3.31400700	-2.96535500	1.30724000
H	-1.05935200	0.69460000	-1.90733600	H	-4.33944100	1.18342500	1.86757000
H	-2.79820700	1.42103700	-0.02434200	H	-6.56605400	0.52822300	2.75097300
C	-3.32802500	-0.08147200	-1.43562300				
C	-5.00959500	-0.94017600	-3.55771100				

H	-5.56033000	-3.64105600	2.19674400
H	-7.19305800	-1.88901200	2.91877900
C	3.71718700	-0.36767500	0.73654700
C	6.08589200	-1.55187500	-0.34110400
C	3.83089300	-1.78580800	0.59245100
C	4.81101600	0.41735200	0.31757600
C	5.97777100	-0.15471700	-0.22314200
C	5.01703600	-2.35949900	0.07139800
H	4.75490200	1.49721000	0.42517300
H	6.79479600	0.48714000	-0.54141300
H	5.08411700	-3.43774100	-0.02721500
H	6.98317600	-2.00492500	-0.75214100
Br	0.89399500	-2.15868900	-2.51171600
Br	1.76813000	3.20538400	-1.95958800
Br	-0.45617600	3.85120700	1.51460800
C	2.73150400	-2.72264600	0.90891000
O	1.49063500	-2.46179700	0.79272000
O	3.12218100	-3.94015000	1.31188400
C	2.09374100	-4.99628600	1.54515100
H	1.44571200	-4.69680900	2.37266800
H	1.51143200	-5.14833000	0.63274100
H	2.67214000	-5.88435000	1.79901300

(*R*)-TS3

(*R*)-TS3 had one and only one imaginary frequency (imaginary frequency = -46.12).

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.575962 (Hartree/Particle)
Thermal correction to Energy= 0.619265
Thermal correction to Enthalpy= 0.620210
Thermal correction to Gibbs Free Energy= 0.491881
Sum of electronic and zero-point Energies= -1653.616735
Sum of electronic and thermal Energies= -1653.573432
Sum of electronic and thermal Enthalpies= -1653.572488
Sum of electronic and thermal Free Energies= -1653.700816

C	-2.43280400	-0.08027600	-0.57430500	H	-4.70302700	1.06414200	0.48425400
C	-1.88074100	-1.43058100	0.03020200	H	-3.36256500	-1.49347100	-2.72214700
N	-0.47514600	-1.16584400	0.63785900	H	-5.70277800	-1.73923600	-3.51825500
In	1.25709400	-1.70295100	-0.49154700	H	-7.06235400	0.82720900	-0.31454200
C	4.29412500	-2.39859600	-2.35124300	H	-7.56786700	-0.57970100	-2.31888400
H	3.95723500	-1.52827900	-2.90941200	C	4.17933300	1.36947200	0.14042200
H	4.33156300	-3.33425800	-2.90469100	C	4.15532600	3.82756500	1.50116500
C	4.66444300	-2.35584600	-1.05226200	C	3.03284300	2.17957000	0.14089400
H	4.99749200	-3.27780800	-0.57601100	C	5.33393600	1.78777900	0.81726100
C	4.69817700	-1.14130400	-0.14257600	C	5.31394800	3.02379500	1.49859600
H	4.32678600	-1.40498400	0.85661900	C	2.99838500	3.40785600	0.81331700
H	5.75156700	-0.85947300	0.00523900	H	6.23220700	1.17749300	0.82626100
O	-2.26938600	1.02754000	0.36062100	H	6.20041700	3.35622300	2.03240100
In	-0.52354200	0.87192200	1.24889000	H	2.10594200	4.02741800	0.80822700
O	2.46524700	-0.04216500	-0.65637000	H	4.15348900	4.77370700	2.03523300
C	3.97663000	0.09750500	-0.66453500	Br	-0.16041700	2.11488700	3.44002500
H	4.24305400	0.27557600	-1.71306400	Br	2.08292700	-3.59694800	1.06126800
H	-0.39923000	-1.76735900	1.47074500	Br	0.51489600	-2.50638500	-2.82012700
H	-1.75865200	-2.11647400	-0.81383300	C	1.90791100	1.61474700	-0.68738600
C	-2.75386500	-2.12775600	1.07059900	O	0.64664300	1.60701000	-0.23058500
C	-4.27490300	-3.54566100	3.00339200	O	2.05188700	2.00896100	-2.01022400
C	-2.93398300	-3.52591000	0.96572000	H	-0.32131600	3.11296800	-0.96553800
C	-3.35156300	-1.44615000	2.15793700	C	-0.33915500	4.99076700	-1.83645700
C	-4.10482300	-2.15062300	3.11529800	C	-2.25873200	3.81410700	-1.01166800
C	-3.68862100	-4.23205300	1.92202500	C	-1.13576200	6.07155000	-2.21773100
H	-2.48503600	-4.06309200	0.13240900	H	0.73386900	4.96357800	-1.97930800
H	-3.24954500	-0.36889400	2.24896200	C	-3.08981600	4.87560800	-1.37893500
H	-4.56104400	-1.61289600	3.94296500	H	-2.59870100	2.89667500	-0.53309900
H	-3.81763900	-5.30709600	1.82317300	C	-2.52623300	6.01518600	-1.98678800
H	-4.85697300	-4.08746600	3.74493500	H	-0.67453200	6.93486000	-2.68256200
H	-1.80911200	0.11930900	-1.46351400	H	-4.15434700	4.80620700	-1.18848700
C	-3.87755000	-0.20975200	-1.04647500	H	-3.15941500	6.84821700	-2.27612200
C	-6.54418200	-0.47718500	-1.96653600	N	-0.91913300	3.90546700	-1.25175600
C	-4.93102900	0.44816200	-0.37977300	C	1.12201100	1.49547400	-3.04590400
C	-4.16762000	-0.99442800	-2.18579200	H	0.12669700	1.30569200	-2.63481600
C	-5.49260200	-1.13183100	-2.64094100	H	1.07525000	2.27707100	-3.80668800
C	-6.25733500	0.31528700	-0.83711000	H	1.54560200	0.58317300	-3.47379000

Minima: Precomplex of (*R*)-TS3

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.576293 (Hartree/Particle)
Thermal correction to Energy=	0.620986
Thermal correction to Enthalpy=	0.621930
Thermal correction to Gibbs Free Energy=	0.487477
Sum of electronic and zero-point Energies=	-1653.621254
Sum of electronic and thermal Energies=	-1653.576561
Sum of electronic and thermal Enthalpies=	-1653.575617
Sum of electronic and thermal Free Energies=	-1653.710070

C	-2.06855600	-1.02780100	-0.60303100	H	-4.58584900	-0.64223400	0.47266900
C	-1.07992900	-1.95755600	0.20248400	H	-2.46461500	-2.97245200	-2.47805400
N	0.14389000	-1.10615400	0.63892300	H	-4.56232000	-4.17459300	-3.04829200
In	1.95346400	-1.24896400	-0.54117700	H	-6.69976600	-1.83870400	-0.10318200
C	4.76711800	-0.75329800	-2.48783100	H	-6.69410700	-3.61645300	-1.86245200
H	4.09022900	-0.06594200	-2.98971500	C	3.42619100	2.66656100	0.15807300
H	5.08006300	-1.62275900	-3.06190000	C	2.76955200	4.93202600	1.74950900
C	5.22396700	-0.55642300	-1.23004800	C	2.13426300	3.24820000	0.11581700
H	5.90942500	-1.29242400	-0.80803300	C	4.38253300	3.24784900	1.01000300
C	4.90922000	0.60975100	-0.30991000	C	4.06089500	4.37650400	1.79219500
H	4.81038300	0.24358300	0.72194900	C	1.79536200	4.35940000	0.91161100
H	5.78275800	1.27835600	-0.31406100	H	5.37946700	2.82714600	1.08399000
O	-2.30181600	0.22909500	0.10176100	H	4.81615900	4.81010900	2.44246900
In	-0.64875400	0.83266100	0.97703500	H	0.79614600	4.78410600	0.86804400
O	2.42479000	0.63744200	-0.60465200	H	2.52054600	5.79489200	2.36038000
C	3.66009900	1.41665400	-0.69659800	Br	-0.92278000	2.14194600	3.15540800
H	3.76735600	1.73831100	-1.74366500	Br	3.29016400	-2.89732200	0.95748500
H	0.45168700	-1.47762900	1.55076400	Br	1.31636300	-2.36565900	-2.79248400
H	-0.72304400	-2.70813100	-0.50965000	C	1.10719800	2.69490800	-0.80741300
C	-1.65061500	-2.70611100	1.40581900	O	-0.02716200	2.21194200	-0.42171300
C	-2.56721400	-4.18381100	3.65227700	O	1.34344900	2.90010500	-2.09746200
C	-1.28384900	-4.06035000	1.58146100	H	-2.06553900	2.88757100	-1.34001300
C	-2.49044500	-2.10291800	2.37264000	C	-3.20975000	4.44999200	-2.03819200
C	-2.94285500	-2.83546000	3.48560600	C	-4.04450800	2.45483800	-0.99418500
C	-1.73686300	-4.79606900	2.69314200	C	-4.50727200	4.93828800	-2.19648900
H	-0.64434800	-4.54174900	0.84415700	H	-2.32509800	4.98556300	-2.35932300
H	-2.80800600	-1.07131100	2.25394700	C	-5.35755600	2.91140100	-1.13508900
H	-3.58911500	-2.35703400	4.21764900	H	-3.75084800	1.50717800	-0.54476200
H	-1.44480400	-5.83700400	2.80833300	C	-5.59355300	4.16169500	-1.74054000
H	-2.91823400	-4.74775900	4.51310600	H	-4.65957900	5.90291000	-2.66611400
H	-1.54955200	-0.80415500	-1.55006200	H	-6.17409900	2.29546000	-0.77722100
C	-3.37741600	-1.73264800	-0.94618100	H	-6.60908500	4.52744900	-1.85655000
C	-5.77479000	-3.09322900	-1.61003700	N	-3.02289400	3.23576600	-1.44820600
C	-4.58474100	-1.41476700	-0.29009500	C	0.42394800	2.36733700	-3.14574500
C	-3.38396900	-2.72880400	-1.94886300	H	0.17150200	1.32792500	-2.92638200
C	-4.57264400	-3.40880400	-2.27608700	H	-0.47126000	2.99317900	-3.18706200
C	-5.77603500	-2.09096500	-0.61925400	H	0.99381000	2.44733900	-4.07109000

Minima: Direct product of (*R*)-TS3

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.576293 (Hartree/Particle)
Thermal correction to Energy=	0.620253
Thermal correction to Enthalpy=	0.621197
Thermal correction to Gibbs Free Energy=	0.491121
Sum of electronic and zero-point Energies=	-1653.616516
Sum of electronic and thermal Energies=	-1653.572556
Sum of electronic and thermal Enthalpies=	-1653.571611
Sum of electronic and thermal Free Energies=	-1653.701688

C	-2.46049400	0.00363400	-0.55651300	H	-4.68339900	1.20818800	0.53555100
C	-1.93667200	-1.37383000	0.01366600	H	-3.45526400	-1.35727100	-2.70943300
N	-0.52496600	-1.15745700	0.62829300	H	-5.80804500	-1.51299200	-3.49045800
In	1.19493800	-1.71239000	-0.50415100	H	-7.05501100	1.06156700	-0.24759100
C	4.23613100	-2.45904200	-2.40121100	H	-7.62337100	-0.30363400	-2.26402100
H	3.92550200	-1.56995600	-2.94477500	C	4.20249300	1.26244300	0.17166100
H	4.25102700	-3.38534600	-2.97124600	C	4.20206100	3.69044000	1.58071000
C	4.60024900	-2.44997600	-1.10005000	C	3.06856300	2.08956700	0.17645900
H	4.90544900	-3.38898800	-0.63872300	C	5.35616100	1.64529800	0.86991400
C	4.66196300	-1.25432300	-0.16732900	C	5.34708200	2.86720400	1.57675700
H	4.27964600	-1.52721800	0.82482800	C	3.04618700	3.30504100	0.87072100
H	5.72162000	-1.00266300	-0.00884000	H	6.24426100	1.02020400	0.87561400
O	-2.25902900	1.08825600	0.39804400	H	6.23170600	3.17366100	2.12884100
In	-0.50711500	0.87363400	1.25891400	H	2.16460300	3.93993800	0.86811800
O	2.45993400	-0.07893100	-0.68115100	H	4.20984900	4.62560300	2.13375100
C	3.98333300	0.01609400	-0.66711500	Br	-0.07133300	2.05145400	3.46924800
H	4.26136000	0.21112900	-1.70925300	Br	2.01327900	-3.60851900	1.04864700
H	-0.46875100	-1.77294200	1.45235400	Br	0.44939600	-2.49253400	-2.83618100
H	-1.83051800	-2.04073800	-0.84758900	C	1.95133000	1.54138100	-0.67646400
C	-2.82500300	-2.07731300	1.03638100	O	0.67553800	1.55697000	-0.23784400
C	-4.38314200	-3.50600000	2.93057100	O	2.11241000	1.98806900	-1.98992200
C	-3.04152000	-3.46689700	0.89372900	H	-0.21988400	3.06200900	-0.98091300
C	-3.40335400	-1.40980100	2.14258500	C	-0.15402800	4.92356100	-1.88646300
C	-4.17537000	-2.11964700	3.08080800	C	-2.11636500	3.87206000	-0.99765400
C	-3.81499800	-4.17832800	1.83082300	C	-0.89626000	6.04292200	-2.26631900
H	-2.60626100	-3.99286800	0.04610100	H	0.91200500	4.83190300	-2.05330600
H	-3.27069100	-0.33864600	2.26292800	C	-2.89458000	4.97362500	-1.36301300
H	-4.61698900	-1.59288300	3.92330000	H	-2.49815100	2.98308500	-0.49755500
H	-3.97280000	-5.24644900	1.70292000	C	-2.28165200	6.07003600	-2.00174400
H	-4.98016200	-4.05195600	3.65702900	H	-0.39808600	6.87140100	-2.75573200
H	-1.84224300	0.20584100	-1.44863700	H	-3.95653500	4.96789800	-1.14734000
C	-3.91325500	-0.07590400	-1.01563300	H	-2.87300400	6.93402500	-2.28896300
C	-6.59429900	-0.24069500	-1.91818300	N	-0.78001500	3.88278900	-1.26961000
C	-4.93860900	0.60992000	-0.33329600	C	1.22264000	1.46857900	-3.05616600
C	-4.23865900	-0.83686900	-2.16140200	H	0.21033700	1.28879400	-2.68366300
C	-5.57083300	-0.92326900	-2.60797700	H	1.20930200	2.24371500	-3.82481600
C	-6.27202200	0.52813400	-0.78202200	H	1.65375300	0.55015500	-3.46303900

(S)-TS4

(S)-TS4 had one and only one imaginary frequency (imaginary frequency = -62.53).

# opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solv
ent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.575134 (Hartree/Particle)
Thermal correction to Energy= 0.619095
Thermal correction to Enthalpy= 0.620040
Thermal correction to Gibbs Free Energy= 0.488622
Sum of electronic and zero-point Energies= -1653.625801
Sum of electronic and thermal Energies= -1653.581840
Sum of electronic and thermal Enthalpies= -1653.580896
Sum of electronic and thermal Free Energies= -1653.712314

C	-2.49077000	-0.42561000	-0.63975100	H	-4.77353600	0.92514800	0.10082200
C	-1.87944000	-1.65476500	0.13260600	H	-3.40149200	-2.30685000	-2.40927500
N	-0.46738700	-1.24720900	0.64505400	H	-5.72899300	-2.71860700	-3.16684700
In	1.22419400	-1.71182200	-0.55347000	H	-7.11924300	0.52460500	-0.66761700
C	7.01665100	-1.27878800	-1.06684900	H	-7.60401100	-1.30537600	-2.30195400
H	6.64661400	-2.20578600	-1.50448300	C	3.89664600	1.30866900	0.74646300
H	8.07473500	-1.24440800	-0.81258700	C	3.81605100	3.84555500	1.96963300
C	6.20630200	-0.22033500	-0.85113200	C	2.86376000	2.21533200	0.45183200
H	6.62528800	0.68934800	-0.41800700	C	4.89023000	1.66509900	1.67331800
C	4.73310000	-0.18735900	-1.20339300	C	4.84926500	2.93677900	2.27928900
H	4.52799800	0.64251700	-1.89325200	C	2.81096400	3.48516100	1.05249300
H	4.46316200	-1.12107400	-1.71270600	H	5.67686800	0.96210900	1.93161200
O	-2.36714900	0.80121400	0.14137700	H	5.61481300	3.21504600	2.99878900
In	-0.66124600	0.82554500	1.11608100	H	2.00881300	4.17936000	0.81612000
O	2.38655200	-0.06902700	-0.42952500	H	3.78916000	4.82169500	2.44582800
C	3.79755000	-0.02550500	0.02684500	Br	-0.58600900	2.06305600	3.33744100
H	3.96906200	-0.85084000	0.72770400	Br	2.49224700	-3.68607600	0.50641500
H	-0.30744200	-1.77042000	1.51943800	Br	0.69615200	-2.24570000	-3.01454200
H	-1.75062800	-2.45623200	-0.60179900	C	1.84268400	1.76567700	-0.55374800
C	-2.68890300	-2.21947100	1.29892700	O	0.54479300	1.70981100	-0.26383600
C	-4.05768600	-3.37935100	3.49808500	O	2.18424500	2.11335800	-1.82027100
C	-2.63647900	-3.61380700	1.52973300	H	-0.59706700	3.13980100	-1.06470700
C	-3.44134300	-1.41202800	2.18460800	C	-0.81799000	5.01000200	-1.90658300
C	-4.11989600	-1.98941000	3.27419800	C	-2.60831200	3.54581800	-1.26811000
C	-3.31448200	-4.19222100	2.61921100	C	-1.72848100	5.96999100	-2.35043700
H	-2.06790600	-4.24886400	0.85252800	H	0.25633700	5.13869800	-1.95187600
H	-3.51136300	-0.34151000	2.02031200	C	-3.55068600	4.48115000	-1.70342400
H	-4.69690200	-1.35660500	3.94427100	H	-2.84947400	2.57852800	-0.82903100
H	-3.26565700	-5.26647000	2.77927300	C	-3.11016200	5.70356700	-2.24903600
H	-4.58262900	-3.82230000	4.34095500	H	-1.36093600	6.90114400	-2.76511200
H	-1.87661400	-0.31782900	-1.55086900	H	-4.60591300	4.25121700	-1.61418900
C	-3.93158200	-0.66788500	-1.08328500	H	-3.83158500	6.43905700	-2.59121300
C	-6.58540400	-1.12786700	-1.96510400	N	-1.28177200	3.83963900	-1.38522300
C	-4.99030500	0.13154400	-0.60706000	C	1.34043600	1.74121600	-2.98618300
C	-4.20965300	-1.69258200	-2.01681500	H	0.32266700	1.48895300	-2.68218800
C	-5.52813000	-1.92518200	-2.45075900	H	1.34152800	2.61150400	-3.64475300
C	-6.31044300	-0.09768000	-1.04425500	H	1.82186000	0.89307200	-3.47780100

Minima: precomplex of (S)-TS4

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.575506 (Hartree/Particle)
Thermal correction to Energy= 0.620574
Thermal correction to Enthalpy= 0.621518
Thermal correction to Gibbs Free Energy= 0.485144
Sum of electronic and zero-point Energies= -1653.629049
Sum of electronic and thermal Energies= -1653.583981
Sum of electronic and thermal Enthalpies= -1653.583037
Sum of electronic and thermal Free Energies= -1653.719411

C	-2.17939600	-0.93629700	-0.60901900	H	-4.70256000	-0.27072700	0.30530600
C	-1.30022900	-1.92389000	0.25205400	H	-2.65456600	-2.94717700	-2.39212000
N	-0.02252100	-1.16476700	0.70320900	H	-4.82203500	-3.97974900	-3.02634800
In	1.76863500	-1.49709800	-0.41972900	H	-6.88693500	-1.29578100	-0.33759300
C	7.28969000	0.33376400	-1.56558200	H	-6.95374900	-3.15910600	-2.00445300
H	7.17300200	-0.70637900	-1.86953700	C	3.78191500	2.11591500	0.40577200
H	8.30871300	0.69589500	-1.43829100	C	3.37937400	4.66110600	1.58596000
C	6.22511900	1.13930600	-1.35871200	C	2.61437000	2.86316600	0.13323900
H	6.39707700	2.17578600	-1.06203500	C	4.73744100	2.65381200	1.28864100
C	4.78170800	0.71790600	-1.53318100	C	4.54363500	3.92074500	1.87077200
H	4.28167400	1.37629200	-2.25693500	C	2.40811200	4.12922600	0.71923600
H	4.74381500	-0.30544500	-1.92880600	H	5.62560800	2.07647100	1.53144900
O	-2.32774400	0.35324700	0.05957400	H	5.28949000	4.32222000	2.55180300
In	-0.63910500	0.86732900	0.92444400	H	1.50618700	4.69582700	0.50212000
O	2.59534900	0.26666500	-0.51094600	H	3.22359700	5.63565200	2.04021100
C	3.94058100	0.73460300	-0.21999300	Br	-0.83898400	2.34664700	2.99398400
H	4.42906100	0.07343100	0.50950400	Br	3.27275600	-3.20446900	0.79681100
H	0.21499100	-1.51284500	1.64493100	Br	1.16206800	-2.36378900	-2.78119300
H	-0.99152100	-2.72701800	-0.42460300	C	1.57428200	2.32668300	-0.79742600
C	-1.96316900	-2.57501200	1.46341500	O	0.39890600	1.94771700	-0.43367100
C	-3.05007100	-3.86966200	3.74428400	O	1.82927100	2.53655200	-2.08944800
C	-1.69779200	-3.94064200	1.71522800	H	-2.50884600	3.86692400	-0.98935900
C	-2.78574900	-1.86545000	2.37039800	C	-4.10503900	4.95889000	-1.68136900
C	-3.32351400	-2.50838800	3.50082100	C	-4.16394200	2.65104900	-1.01301800
C	-2.23612200	-4.58603600	2.84487000	C	-5.46655200	4.93206400	-1.98503900
H	-1.07145500	-4.50087000	1.02344900	H	-3.48183300	5.83677400	-1.79772100
H	-3.02282000	-0.82153200	2.19014500	C	-5.52969900	2.58851100	-1.30657300
H	-3.95617800	-1.95038600	4.18699100	H	-3.58021400	1.80775100	-0.63798700
H	-2.02246700	-5.63751900	3.02037000	C	-6.18766300	3.73454200	-1.79477900
H	-3.46711400	-4.36387600	4.61836500	H	-5.94635200	5.82798300	-2.36085800
H	-1.61433900	-0.77890300	-1.54312600	H	-6.06091000	1.65663300	-1.15575000
C	-3.52854300	-1.54195900	-0.98443600	H	-7.24766300	3.69685400	-2.02624600
C	-6.00413700	-2.71049800	-1.72249400	N	-3.50566600	3.82916100	-1.21021100
C	-4.73385900	-1.07865600	-0.41880100	C	0.87230000	2.07052800	-3.13293700
C	-3.57412100	-2.58966300	-1.93267500	H	0.81426400	0.97928100	-3.10381000
C	-4.80215300	-3.17380700	-2.29640300	H	-0.10889600	2.52142700	-2.96593400
C	-5.96434200	-1.65980300	-0.78446800	H	1.30805600	2.41058600	-4.07203500

Minima: Direct product of (S)-TS4

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.575677 (Hartree/Particle)
Thermal correction to Energy= 0.619929
Thermal correction to Enthalpy= 0.620873
Thermal correction to Gibbs Free Energy= 0.488649
Sum of electronic and zero-point Energies= -1653.625855
Sum of electronic and thermal Energies= -1653.581603
Sum of electronic and thermal Enthalpies= -1653.580659
Sum of electronic and thermal Free Energies= -1653.712883

C	-2.57890300	-0.20765800	-0.63795200				
C	-2.06394800	-1.50951400	0.08723300	H	-3.63851500	-1.91721300	-2.49652400
N	-0.62824200	-1.23024700	0.62120600	H	-5.99728800	-2.11448500	-3.24895100
In	1.01553200	-1.71342800	-0.60810900	H	-7.12467800	1.07696200	-0.55817300
C	6.80333800	-1.92807300	-0.99274600	H	-7.75579600	-0.61866000	-2.28457100
H	6.31679800	-2.74790200	-1.52049500	C	3.97087900	0.96719100	0.88480500
H	7.83743200	-2.08422600	-0.69037500	C	3.97717600	3.44210500	2.20707300
C	6.16126300	-0.77061800	-0.72786500	C	2.98521000	1.92713300	0.61116000
H	6.69099600	0.02651700	-0.20450200	C	4.96588400	1.22762800	1.83900300
C	4.73231300	-0.47624500	-1.14254200	C	4.96389900	2.47532100	2.49636700
H	4.69546200	0.43850900	-1.74861400	C	2.97298300	3.17136500	1.25644900
H	4.35594400	-1.30365000	-1.75596500	H	5.71839200	0.48231700	2.07849500
O	-2.35654400	0.97651700	0.18231400	H	5.72596600	2.69080100	3.24066000
In	-0.65229500	0.84398000	1.15135700	H	2.20553200	3.90917100	1.03923000
O	2.36295500	-0.13283300	-0.44039000	H	3.98667700	4.39639100	2.72635400
C	3.78591300	-0.29631700	0.06949000	Br	-0.50792200	1.97973400	3.42022800
H	3.79524000	-1.19176000	0.69783600	Br	2.25391400	-3.72614200	0.40191700
H	-0.50736900	-1.80484300	1.46830400	Br	0.51644300	-2.13435400	-3.08506600
H	-1.99302100	-2.28956900	-0.67776800	C	2.00358800	1.47624600	-0.44390300
C	-2.91780600	-2.05942700	1.22760000	O	0.66111800	1.56294700	-0.20228000
C	-4.39279800	-3.20663200	3.36370200	O	2.38423000	1.99564200	-1.68317500
C	-3.01665000	-3.46317600	1.36641000	H	-0.10604500	3.06495900	-1.00169700
C	-3.57367700	-1.23542000	2.17280200	C	-0.03182900	4.91230400	-1.94068700
C	-4.30456900	-1.80628800	3.23127700	C	-2.03002300	3.73020300	-1.34722300
C	-3.74763500	-4.03548700	2.42456100	C	-0.78126400	5.95962400	-2.47906000
H	-2.52566400	-4.10993300	0.64135000	H	1.05094900	4.90169300	-1.92778200
H	-3.53185300	-0.15477700	2.07692700	C	-2.81646500	4.75823900	-1.87407100
H	-4.80613800	-1.16024700	3.94775700	H	-2.42882400	2.82758200	-0.88609100
H	-3.81519400	-5.11695500	2.51325300	C	-2.18923100	5.88326900	-2.44578200
H	-4.95840900	-3.64450000	4.18255800	H	-0.27153500	6.81225100	-2.91187900
H	-1.96636300	-0.11838300	-1.55277700	H	-3.89608900	4.67363100	-1.83502200
C	-4.03723200	-0.32025200	-1.07707600	H	-2.78728900	6.68939800	-2.85939000
C	-6.72434500	-0.53586700	-1.95014400	N	-0.67160700	3.83989100	-1.39643900
C	-5.03024000	0.52614100	-0.54401100	C	1.67767000	1.56386800	-2.91150500
C	-4.39705100	-1.26883800	-2.06161200	H	0.59671500	1.50234400	-2.75722800
C	-5.73258200	-1.37993000	-2.49196700	H	1.90766800	2.32884400	-3.65514700
C	-6.36704500	0.41856800	-0.97736700	H	2.07467600	0.59867300	-3.23633500
H	-4.74828400	1.26419000	0.19999500				

Pyridinium salt

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opt=calcfc freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.103690 (Hartree/Particle)
Thermal correction to Energy=	0.108015
Thermal correction to Enthalpy=	0.108959
Thermal correction to Gibbs Free Energy=	0.076192
Sum of electronic and zero-point Energies=	-248.602384
Sum of electronic and thermal Energies=	-248.598060
Sum of electronic and thermal Enthalpies=	-248.597116
Sum of electronic and thermal Free Energies=	-248.629883

C	0.67324900	1.19869600	-0.00002500	N	1.32092700	-0.00003300	0.00001600
C	-0.72270900	1.22038700	-0.00001200	H	2.34267700	-0.00002800	0.00017100
C	-1.42923500	0.00003200	0.00002600				
C	-0.72276400	-1.22035400	-0.00000800				
C	0.67319500	-1.19872700	-0.00003100				
H	1.28722300	2.09065700	-0.00001200				
H	-1.23954000	2.17258300	-0.00001900				
H	-2.51474400	0.00005700	0.00007500				
H	-1.23963800	-2.17252700	-0.00000600				
H	1.28712700	-2.09071800	-0.00001900				

(*R*)-TS5

(*R*)-TS5 had one and only one imaginary frequency (imaginary frequency = -1369.52).

# opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solv
ent=thf,smd)

- Thermochemistry-

Zero-point correction=	0.232783 (Hartree/Particle)
Thermal correction to Energy=	0.246971
Thermal correction to Enthalpy=	0.247915
Thermal correction to Gibbs Free Energy=	0.190784
Sum of electronic and zero-point Energies=	-690.987298
Sum of electronic and thermal Energies=	-690.973111
Sum of electronic and thermal Enthalpies=	-690.972166
Sum of electronic and thermal Free Energies=	-691.029297

C	1.24651300	-1.06082700	0.23313100	C	2.27129400	2.57308400	-0.31753600
O	1.30863600	-1.65625400	1.45339300	H	0.98312200	4.30712300	-0.13505600
O	1.75195600	-1.71531700	-0.82797500	H	3.29774500	0.66578500	-0.41760100
C	2.01543800	-3.17589800	-0.72076700	H	3.15924900	3.15500300	-0.55022800
H	2.81282100	-3.35642700	0.00379300	H	-1.68732700	0.38607900	1.50677700
H	2.32229400	-3.47053800	-1.72528700	C	-2.32180800	0.26378900	-0.56797900
H	1.10047900	-3.69502300	-0.42343800	H	-2.64178100	1.31015500	-0.65728100
C	-1.23474300	0.14660800	0.53184900	H	-1.85545100	-0.02515700	-1.52223500
O	-0.70552900	-1.20589800	0.57199200	C	-3.51437600	-0.62385800	-0.28980200
H	0.15888600	-1.55269500	1.53882100	H	-3.28221500	-1.67442300	-0.10513300
C	-0.04280300	1.06965400	0.27944000	C	-4.80014800	-0.20960600	-0.26064000
C	-0.11469400	2.47343500	0.21140600	H	-5.07262100	0.83107500	-0.43730900
C	1.04061600	3.22265900	-0.08234400	H	-5.61617500	-0.90242300	-0.05976900
H	-1.06300300	2.97888900	0.37710200	C	1.19460900	0.42751300	0.06775800
C	2.35067900	1.17050400	-0.24658900				

Minima: Precomplex of (*R*)-TS5

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opt=(calcfc,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent
=thf,smd)

- Thermochemistry-

Zero-point correction= 0.237988 (Hartree/Particle)
Thermal correction to Energy= 0.252661
Thermal correction to Enthalpy= 0.253606
Thermal correction to Gibbs Free Energy= 0.195142
Sum of electronic and zero-point Energies= -691.036525
Sum of electronic and thermal Energies= -691.021852
Sum of electronic and thermal Enthalpies= -691.020908
Sum of electronic and thermal Free Energies= -691.079371

C	1.77949700	-0.79675700	0.21670700	C	1.49225800	2.93783200	-0.22043600
O	1.56537500	-1.63862600	1.12539600	H	-0.23206000	4.20604900	0.14307200
O	2.76275300	-0.98464900	-0.71399900	H	2.99894900	1.41406800	-0.45165900
C	3.58538000	-2.21379800	-0.61310500	H	2.17018400	3.75672600	-0.44445300
H	4.10425400	-2.24180400	0.34965900	H	-1.91817600	-0.01860500	1.48583100
H	4.29758400	-2.14108700	-1.43607100	C	-2.44412000	-0.19329600	-0.61365200
H	2.95145500	-3.09832600	-0.72396300	H	-2.79625500	0.83677600	-0.73002400
C	-1.40671300	-0.27534700	0.54374700	H	-1.91650100	-0.47510100	-1.53756700
O	-1.00030100	-1.66993500	0.57814700	C	-3.62197500	-1.11725700	-0.39414500
H	-0.20028600	-1.79779000	1.14343400	H	-3.37187100	-2.15800000	-0.18704500
C	-0.28351500	0.76494100	0.34387900	C	-4.91714100	-0.73610400	-0.44780200
C	-0.71750100	2.11385700	0.37183300	H	-5.20485700	0.29619200	-0.64827000
C	0.14471300	3.18717700	0.10503400	H	-5.72605900	-1.44888500	-0.29301400
H	-1.75830100	2.32410700	0.60546600	C	1.09638100	0.52703600	0.07440000
C	1.95595600	1.61694400	-0.23175100				

Minima: Direct product of (*R*)-TS5

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opt=(calcfc,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent
=thf,smd)

- Thermochemistry-

Zero-point correction= 0.237425 (Hartree/Particle)
Thermal correction to Energy= 0.251743
Thermal correction to Enthalpy= 0.252687
Thermal correction to Gibbs Free Energy= 0.196014
Sum of electronic and zero-point Energies= -691.029413
Sum of electronic and thermal Energies= -691.015096
Sum of electronic and thermal Enthalpies= -691.014152
Sum of electronic and thermal Free Energies= -691.070825

C	-0.46793600	1.30827900	0.29521600
O	-0.95390600	2.23048100	1.29309800
O	-0.35349100	2.02516300	-0.92387200

C	0.50549900	3.22171300	-0.89350400
H	0.11155500	3.96450900	-0.19321300
H	0.48559600	3.61439800	-1.91328400
H	1.53114500	2.95062200	-0.61770500
C	0.89039100	-0.70018500	0.61124800
O	0.82283900	0.78587700	0.77588200
H	-0.78409500	1.86013600	2.18761600
C	-0.53470200	-1.08178500	0.26313500
C	-1.10027400	-2.35727300	0.11254000
C	-2.46615600	-2.44996700	-0.22852500
H	-0.50612400	-3.25590500	0.25722800
C	-2.66896400	-0.00737300	-0.26724100
C	-3.24533900	-1.28558500	-0.41729900
H	-2.92721100	-3.42777200	-0.34574700
H	-3.26250900	0.89104000	-0.41175300
H	-4.29615600	-1.37830900	-0.67999100
H	1.20632800	-1.10086400	1.58147600
C	1.92587300	-1.07347700	-0.47299200
H	1.89703000	-2.16183700	-0.61772500
H	1.61035900	-0.60542500	-1.41698700
C	3.32963500	-0.63285000	-0.11848500
H	3.44258400	0.42267900	0.13691900
C	4.41457400	-1.43721500	-0.11278100
H	4.34709600	-2.49644100	-0.36132400
H	5.40234200	-1.05543900	0.14107200
C	-1.31284600	0.07012400	0.07744900

(*S*)-TS6

(*S*)-TS6 had one and only one imaginary frequency (imaginary frequency = -1391.29).

# opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solv
ent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.232763 (Hartree/Particle)
Thermal correction to Energy= 0.246896
Thermal correction to Enthalpy= 0.247840
Thermal correction to Gibbs Free Energy= 0.190903
Sum of electronic and zero-point Energies= -690.986331
Sum of electronic and thermal Energies= -690.972198
Sum of electronic and thermal Enthalpies= -690.971254
Sum of electronic and thermal Free Energies= -691.028191

C	-0.93901100	1.21383600	0.18083700	H	0.41837800	-3.16022700	-0.65129900
O	-0.29545200	1.77708500	1.23787400	C	-2.49832500	-0.77481100	0.40325400
O	-1.78497600	1.97725200	-0.53547700	C	-2.70782300	-2.16479800	0.34814300
C	-1.70844200	3.45714300	-0.40624000	H	-1.81840800	-4.09596700	-0.07345300
H	-1.97280400	3.75534600	0.61069900	H	-3.30873100	-0.10921200	0.68813400
H	-2.43598500	3.83068400	-1.12817200	H	-3.68497800	-2.57548800	0.58830100
H	-0.70023900	3.79690600	-0.65804200	H	1.35623500	-0.59933700	-1.73093700
C	1.13961700	-0.40987000	-0.66902900	C	2.34890300	-0.89971400	0.17343100
O	0.91124300	1.01468400	-0.49465600	H	2.17035500	-0.68009900	1.23454600
H	0.71374900	1.48343500	0.74829200	H	2.40066600	-1.99437000	0.06773900
C	-0.16822200	-1.10622200	-0.28732200	C	3.66004400	-0.29825600	-0.28088900
C	-0.38559400	-2.49533300	-0.34496000	H	3.88835100	-0.40823500	-1.34475500
C	-1.65121200	-3.02281400	-0.02420200	C	4.54816600	0.32634100	0.52189800

H	4.35987200	0.46359900	1.58662500
H	5.48689300	0.71945500	0.13450800
C	-1.22474500	-0.25527900	0.09606000

Minima: Precomplex of (*S*)-TS6

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opt=(calcfc,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent
=thf,smd)

- Thermochemistry-

Zero-point correction= 0.238346 (Hartree/Particle)
Thermal correction to Energy= 0.252995
Thermal correction to Enthalpy= 0.253939
Thermal correction to Gibbs Free Energy= 0.195595
Sum of electronic and zero-point Energies= -691.045186
Sum of electronic and thermal Energies= -691.030537
Sum of electronic and thermal Enthalpies= -691.029592
Sum of electronic and thermal Free Energies= -691.087937

C	0.75915800	1.35239700	0.22210400	C	3.06561400	-1.58972300	-0.40024300
O	-0.23783800	1.75092300	0.87727200	H	2.57898700	-3.70335500	-0.34657000
O	1.59321500	2.24234000	-0.39686900	H	3.21350500	0.56240100	-0.37610400
C	1.30439900	3.68716800	-0.24271800	H	4.11764000	-1.74002100	-0.62621100
H	0.32931100	3.92323500	-0.67876100	H	-1.56682300	-2.11582600	0.61854700
H	2.10476000	4.18905800	-0.78819600	C	-1.98297000	-0.50342600	-0.74966900
H	1.31936600	3.96498600	0.81532500	H	-1.69594300	0.53981400	-0.92677000
C	-1.20949800	-1.09262800	0.46583400	H	-1.67762100	-1.08191000	-1.63587500
O	-1.53666000	-0.41873000	1.72075700	C	-3.48304100	-0.61306600	-0.58695200
H	-1.22568300	0.51975400	1.64046600	H	-3.85928000	-1.60752600	-0.33071300
C	0.30257100	-1.17801500	0.20406700	C	-4.36299700	0.39698000	-0.75641700
C	0.84372900	-2.47358800	0.05226000	H	-4.03753800	1.40663800	-1.00646100
C	2.20198100	-2.68910700	-0.24219100	H	-5.43517900	0.24004600	-0.64751100
H	0.18393300	-3.33029000	0.16544300	C	1.18915800	-0.06618700	0.04539100
C	2.55536700	-0.29134800	-0.25911600				

Minima: Direct product of (*S*)-TS6

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opt=(calcfc,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent
=thf,smd)

- Thermochemistry-

Zero-point correction= 0.237159 (Hartree/Particle)
Thermal correction to Energy= 0.251598
Thermal correction to Enthalpy= 0.252542
Thermal correction to Gibbs Free Energy= 0.195278
Sum of electronic and zero-point Energies= -691.029327
Sum of electronic and thermal Energies= -691.014888
Sum of electronic and thermal Enthalpies= -691.013944
Sum of electronic and thermal Free Energies= -691.071209

C	-0.39790100	1.27761300	0.22837500	C	-3.22312300	-1.36038000	0.31444600
O	-0.34950700	1.94186400	1.50724200	H	-2.95372800	-3.41936100	-0.30403000
O	-0.85506900	2.22306800	-0.72727400	H	-3.19211400	0.74699400	0.85869700
C	-0.06038500	3.45868800	-0.84363000	H	-4.27275700	-1.49705200	0.56218400
H	-0.12175000	4.04586700	0.07780400	H	1.10877500	-0.54493800	-1.68273500
H	-0.50857500	4.01012200	-1.67408600	C	1.99975300	-1.46034300	0.07461800
H	0.98555500	3.22346000	-1.07166000	H	1.85269700	-1.44746100	1.16167100
C	0.91369000	-0.60569100	-0.60315800	H	1.84298400	-2.49592300	-0.26766000
O	0.95900800	0.78694200	-0.06143400	C	3.40665000	-1.03309000	-0.28250200
H	0.21444900	1.42115200	2.12124500	H	3.61878200	-0.94594300	-1.35179200
C	-0.51356600	-1.04357400	-0.32916100	C	4.39167300	-0.78618300	0.60705800
C	-1.10851100	-2.30239900	-0.50574700	H	4.22436100	-0.85576200	1.68172200
C	-2.47258500	-2.45242300	-0.17767500	H	5.39212900	-0.50356800	0.28315100
H	-0.53763900	-3.14566200	-0.88572000	C	-1.26393600	0.03685900	0.15758100
C	-2.61986300	-0.09689700	0.48361800				

(*R*)-TS7

(*R*)-TS7 had one and only one imaginary frequency (imaginary frequency = -170.49).

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.426154 (Hartree/Particle)
Thermal correction to Energy= 0.460191
Thermal correction to Enthalpy= 0.461135
Thermal correction to Gibbs Free Energy= 0.351655
Sum of electronic and zero-point Energies= -1177.181904
Sum of electronic and thermal Energies= -1177.147868
Sum of electronic and thermal Enthalpies= -1177.146923
Sum of electronic and thermal Free Energies= -1177.256403

C	-2.11282300	-0.50160400	1.22520200	C	-4.70184100	0.66727100	-2.94907100
C	-2.16178700	0.35941700	-0.09263100	H	-3.55714000	2.01513400	-1.70558300
N	-0.74076500	0.35749800	-0.69414600	H	-3.06597700	-2.19859800	-0.86814300
In	0.65582100	1.78788300	0.12219900	H	-4.66349200	-2.74318200	-2.68352600
C	1.30397000	2.01928200	2.22183500	H	-5.16287400	1.46922900	-3.52073800
H	0.37047100	1.79888100	2.75339600	H	-5.72135300	-0.91800100	-4.02608400
H	1.50417100	3.09673700	2.21300700	H	-1.49373400	0.08504700	1.92761500
C	2.44864400	1.24751500	2.68975100	C	-3.48556200	-0.68684800	1.86790400
H	3.43568200	1.67127100	2.49371000	C	-6.01440700	-1.00293500	3.11169700
C	2.39175400	0.01509900	3.30822500	C	-4.01055700	-1.97373200	2.10186700
H	3.28381400	-0.42985300	3.73901500	C	-4.23244100	0.44333200	2.27379000
H	1.43584300	-0.42145000	3.59394900	C	-5.48945700	0.28714400	2.88776700
O	-1.45685800	-1.78418300	0.99770800	C	-5.26819900	-2.13172100	2.71899200
In	-0.00222500	-1.57915300	-0.29823700	H	-3.42404400	-2.83681300	1.80449700
O	1.72261100	-0.76918700	0.47633700	H	-3.83656700	1.44500100	2.11652200
C	2.63551300	-1.24123800	1.31099100	H	-6.05403000	1.16538600	3.19284400
H	-0.82287500	0.57634000	-1.69525700	H	-5.66179300	-3.13091300	2.89314600
H	-2.39427200	1.38724500	0.20534000	H	-6.98430700	-1.12435100	3.58862200
C	-3.17848500	-0.04912400	-1.15968400	C	4.06962700	-1.15708600	1.02075200
C	-5.01813600	-0.67624700	-3.23265300	C	4.96115300	-1.92243100	1.81696000
C	-3.79070500	0.97412100	-1.92066200	C	4.57093700	-0.39618800	-0.06419600
C	-3.50749900	-1.39475800	-1.44940300	C	6.33516500	-1.92212600	1.53339200
C	-4.41918600	-1.70385700	-2.47655900	H	4.57439900	-2.51353700	2.64448500

C	5.94643300	-0.39852700	-0.34170300	H	2.32079800	-2.01457600	2.01495700
H	3.88854700	0.18145700	-0.68035500	Br	-0.89991300	3.95720400	0.01289800
C	6.83084600	-1.15780200	0.45496300	Br	2.30989800	2.20443100	-1.87889500
H	7.01608700	-2.51190400	2.14091700	Br	0.79576600	-3.63477300	-1.58128500
H	6.33124100	0.18334400	-1.17499700				
H	7.89551300	-1.15704800	0.23487300				

(*S*)-TS8

(*S*)-TS8 had one and only one imaginary frequency (imaginary frequency = -125.27).

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/lanl2dz scrf=(iefpcm,solvent=thf,smd)

- Thermochemistry-

Zero-point correction= 0.427158 (Hartree/Particle)
Thermal correction to Energy= 0.460864
Thermal correction to Enthalpy= 0.461809
Thermal correction to Gibbs Free Energy= 0.354137
Sum of electronic and zero-point Energies= -1177.182032
Sum of electronic and thermal Energies= -1177.148326
Sum of electronic and thermal Enthalpies= -1177.147381
Sum of electronic and thermal Free Energies= -1177.255053

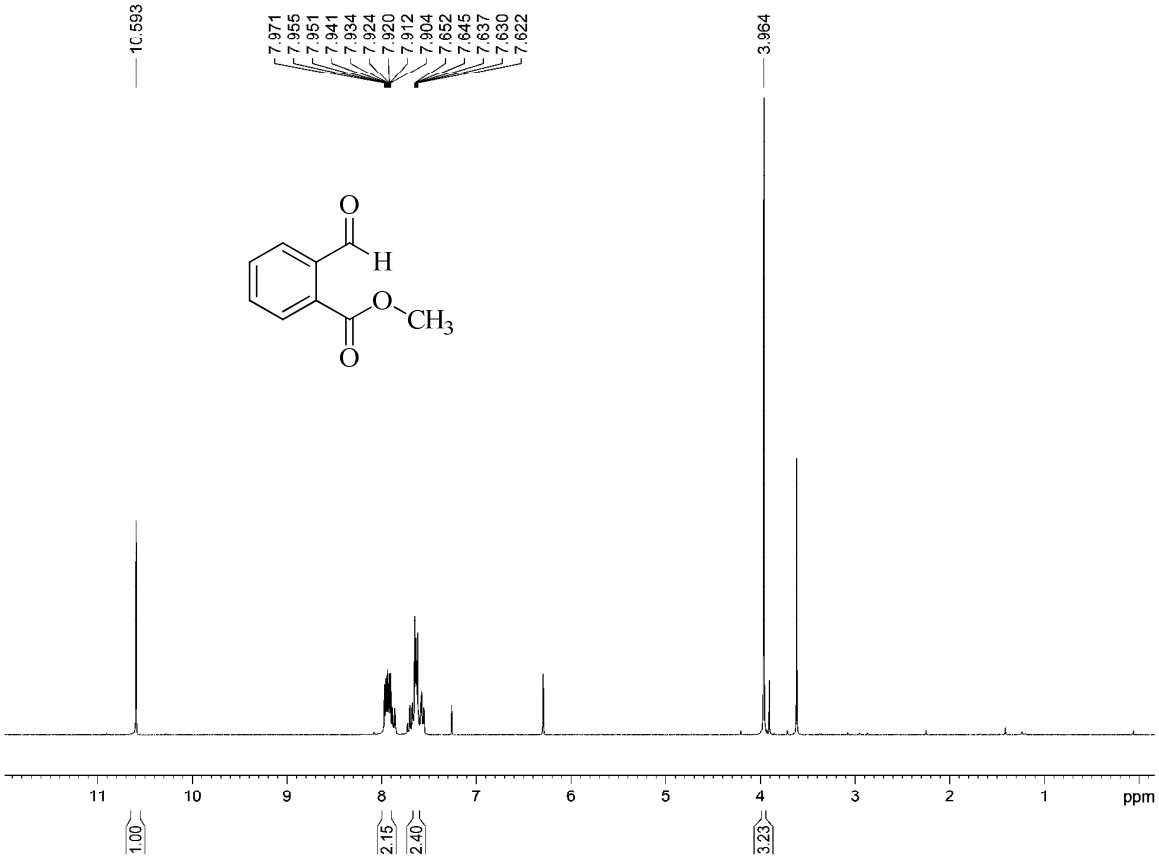
C	-1.64501400	-1.18142600	1.04635900	H	-6.35686500	-1.09268600	-3.15055300
C	-2.07918700	0.00063800	0.06648000	H	-1.09123200	-0.68163900	1.85992700
N	-0.82004800	0.49025500	-0.65778800	C	-2.83585900	-1.89815500	1.66564400
In	0.23936700	2.07859100	0.35611300	C	-5.07197300	-3.19179900	2.83043600
C	0.86205700	2.08082700	2.46719500	C	-3.28518300	-3.13695900	1.16260500
H	0.32775400	1.24470100	2.93196200	C	-3.50712600	-1.31850200	2.76442300
H	0.44636800	3.04160300	2.79110000	C	-4.62161200	-1.95763400	3.34214200
C	2.31827700	2.01707500	2.61236000	C	-4.39695100	-3.78015700	1.74113800
H	2.86716800	2.94356400	2.42794400	H	-2.75093400	-3.59294700	0.33486200
C	3.04807400	0.88253200	2.88610600	H	-3.15899700	-0.37155600	3.17378600
H	4.12618900	0.93321600	3.01378600	H	-5.12909200	-1.50078300	4.18879300
H	2.55725000	-0.04255000	3.17968700	H	-4.73380900	-4.73652900	1.34694300
O	-0.75927600	-2.12668100	0.38391600	H	-5.92929300	-3.68959300	3.27785500
In	0.48619100	-1.16548500	-0.77531900	C	3.94177300	-1.11952300	0.91565600
O	1.88197500	0.00541100	0.20835300	C	5.58610800	-3.34226200	1.46509400
C	3.14651900	0.05699300	0.56583300	C	3.36351000	-2.34307500	1.34391600
H	3.68454200	0.96864200	0.30576900	C	5.35152700	-1.01463700	0.78813400
H	-1.09573400	0.86427300	-1.57416800	C	6.16765900	-2.12527400	1.05256000
H	-2.43047900	0.80249800	0.72576100	C	4.18497100	-3.44576900	1.61536200
C	-3.23268500	-0.31734200	-0.88608700	H	2.29135100	-2.42652600	1.50145200
C	-5.49464300	-0.87763400	-2.52390700	H	5.79337800	-0.07278700	0.47100000
C	-4.52628800	0.12832800	-0.52329400	H	7.24545600	-2.04633500	0.94166400
C	-3.09181800	-1.03719500	-2.09530900	H	3.74354200	-4.38084900	1.94844500
C	-4.21145300	-1.31471100	-2.90482500	H	6.21747400	-4.20179600	1.67531800
C	-5.64716200	-0.15067300	-1.32654200	Br	1.77948600	-2.41897600	-2.58463500
H	-4.65669500	0.69967400	0.39309600	Br	1.88860200	3.14611500	-1.39169900
H	-2.12349900	-1.38821500	-2.43683600	Br	-1.77867800	3.83023100	0.41932800
H	-4.07814700	-1.87038400	-3.83010300				
H	-6.62978300	0.20323600	-1.02367800				

8. References:

1) Napoletano, M.; Norcini, G.; Pellacini, F.; Marchini, F.; Morazzoni, G.; Ferlenga, P.; Pradella, L. *Bioorg. Med. Chem. Lett*. **2001**, *11*, 33.
2) Wang, J.; Johnson, D. M. *Polym. Int.* **2009**, *58*, 1234.
3) Pokhodylo, N. T.; Matiychuk, V. S.; Obushak, M. D. *Chem. Heterocycl. Compd*. **2010**, *46*, 140.
4) Knepper, K.; Ziegert, R. E.; Brase, S. *Tetrahedron*, **2004**, *60*, 8591.
5) Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481-8490.
6) Pedrosa, R.; Sayalero, S.; Vicente, M. *Tetrahedron*, **2006**, *62*, 10400-10407.
7) Ranu, B.; Dutta, P.; Sarkar, A. *J. Org. Chem.* **1998**, *63*, 6027-6028.
8) Frisch, M. J.; et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

9. Spectra:

1a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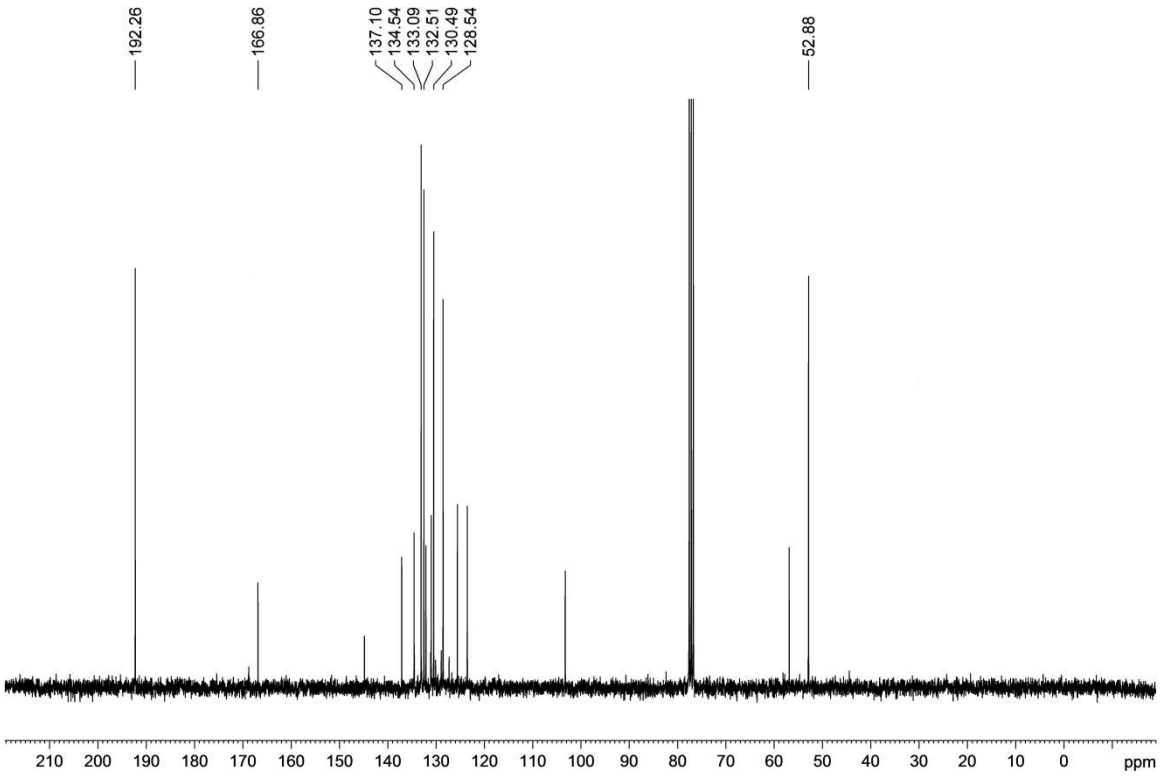
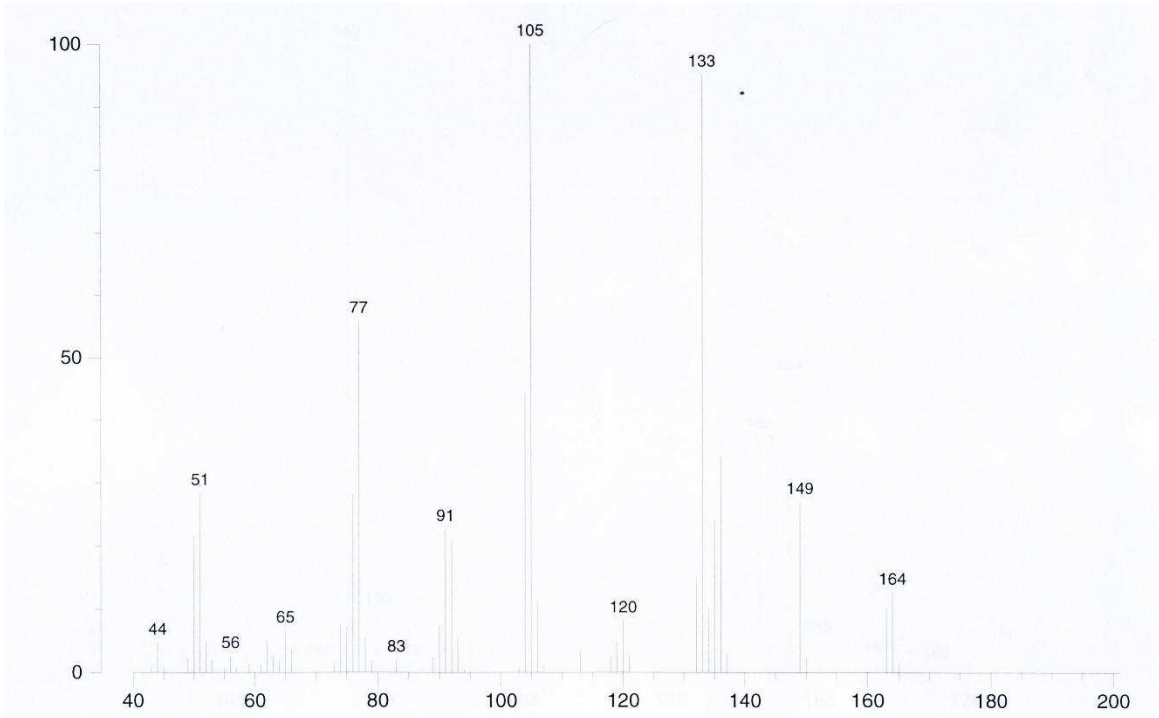
7.955
7.951
7.941
7.934
7.924
7.920
7.912
7.904
7.652
7.645
7.637
7.630
7.622
3.964
O
H
O
CH3
O
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.15
2.40
3.23

1a


192.26
166.86
137.10
134.54
133.09
132.51
130.49
128.54
52.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1a


100
50
0
105
133
77
51
91
149
164
120
65
44
56
83
40 60 80 100 120 140 160 180 200

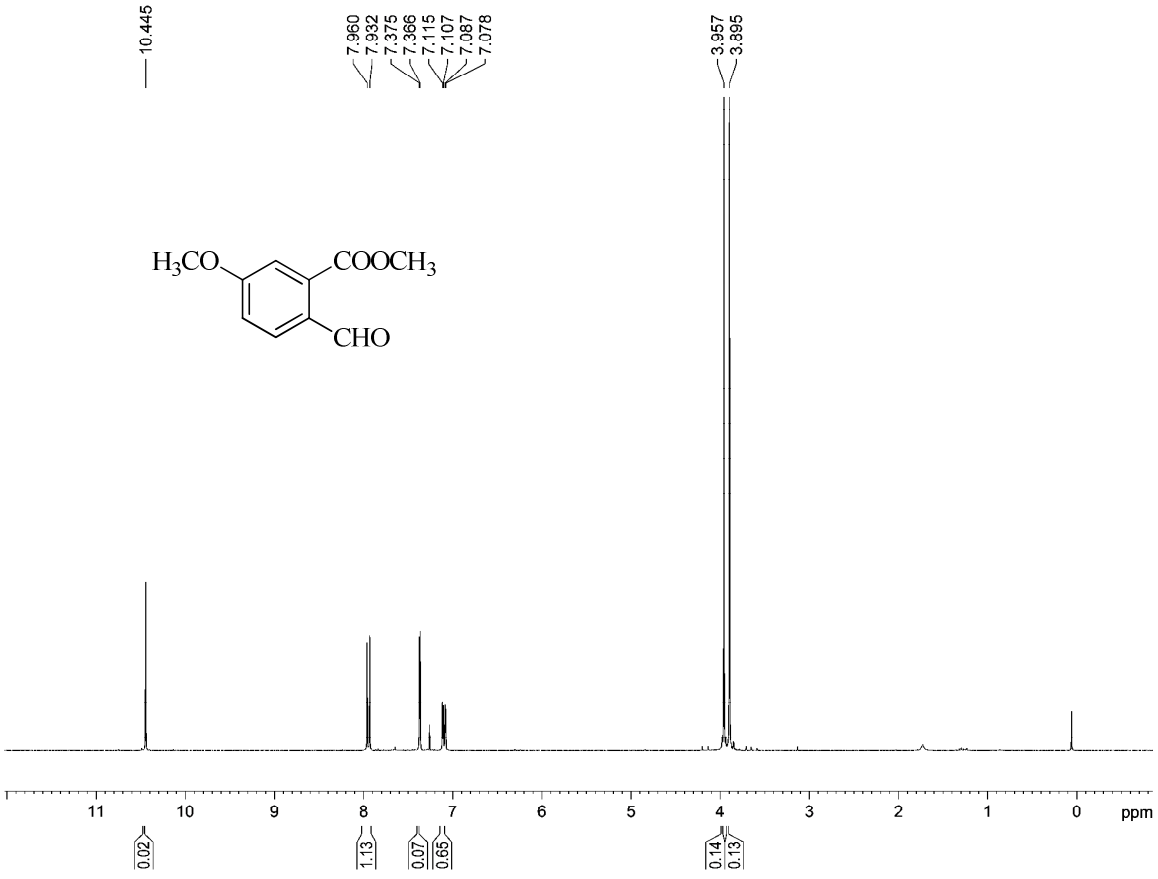
Formula search on scan 1 of 0726pk0002

Mass	Int	Dev ppm	12 C	1 H	16 O
164.04682	790477	-96.22	13	8	0
		-3.22	9	8	3

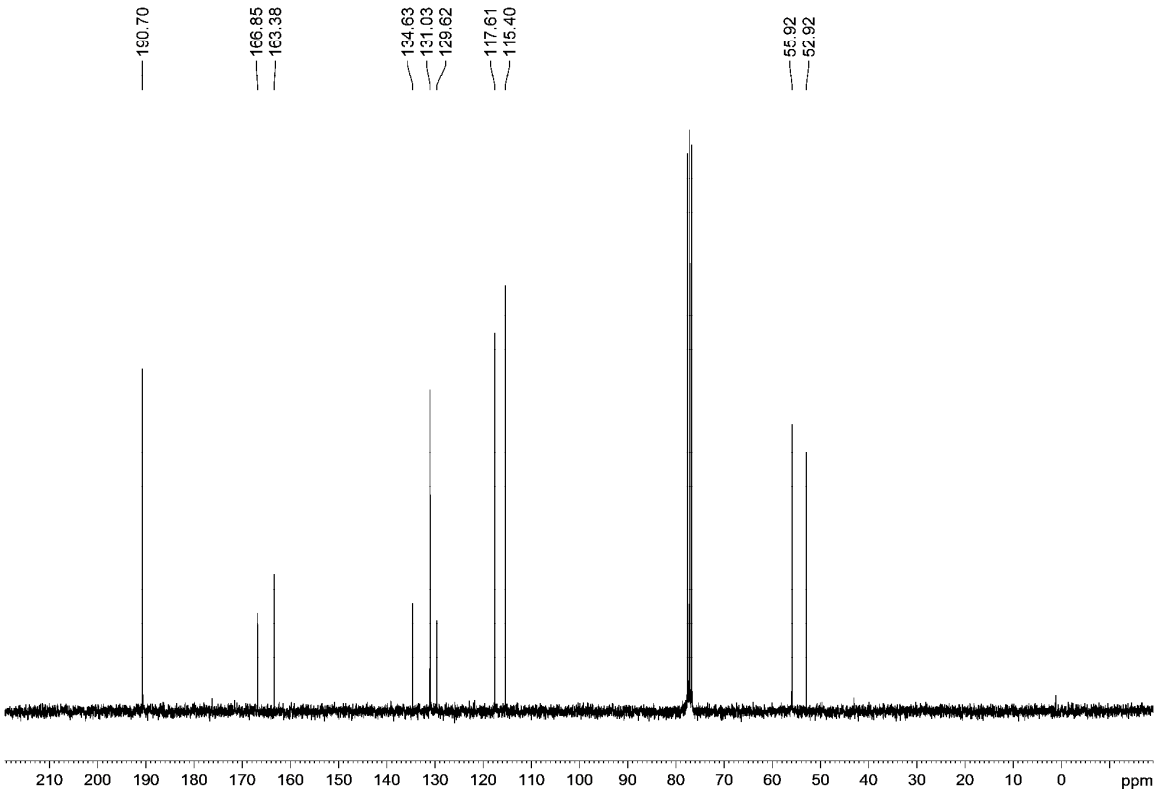
Calculated isotope distribution :

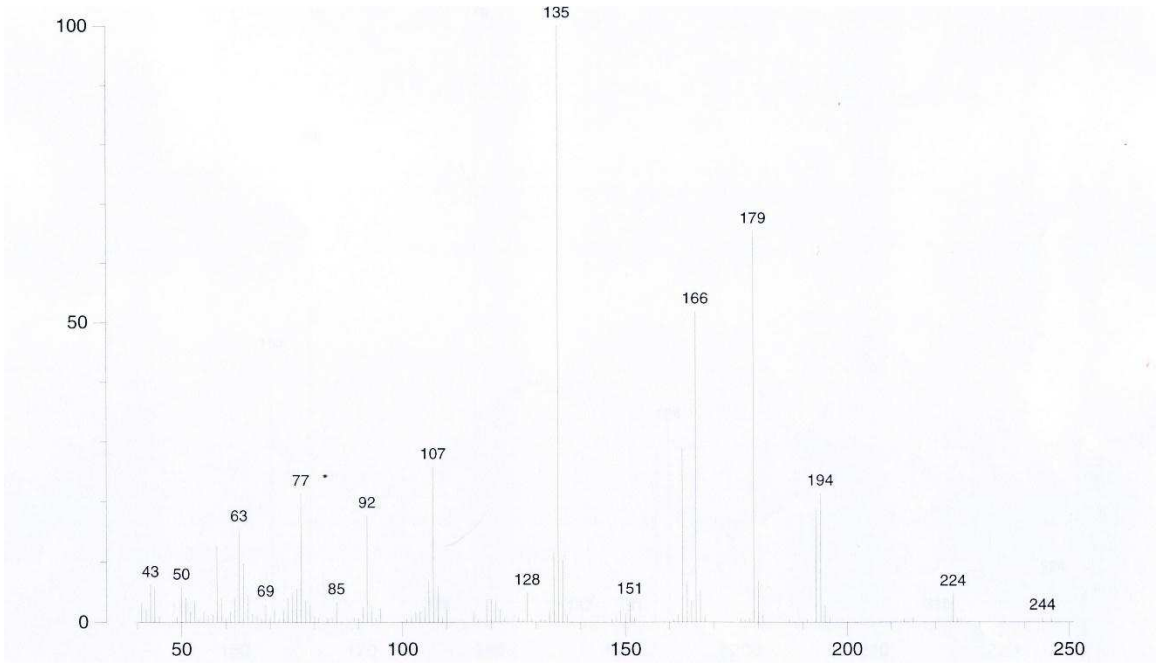
	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	164.04734	90.8248	9	0	8	3
2	165.05070	9.1752	8	1	8	3

1b



1b


190.70
166.85
163.38
134.63
131.03
129.62
117.61
115.40
55.92
52.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


100
50
0
135
179
166
107
77
92
63
194
43
50
69
85
128
151
224
244
50 100 150 200 250

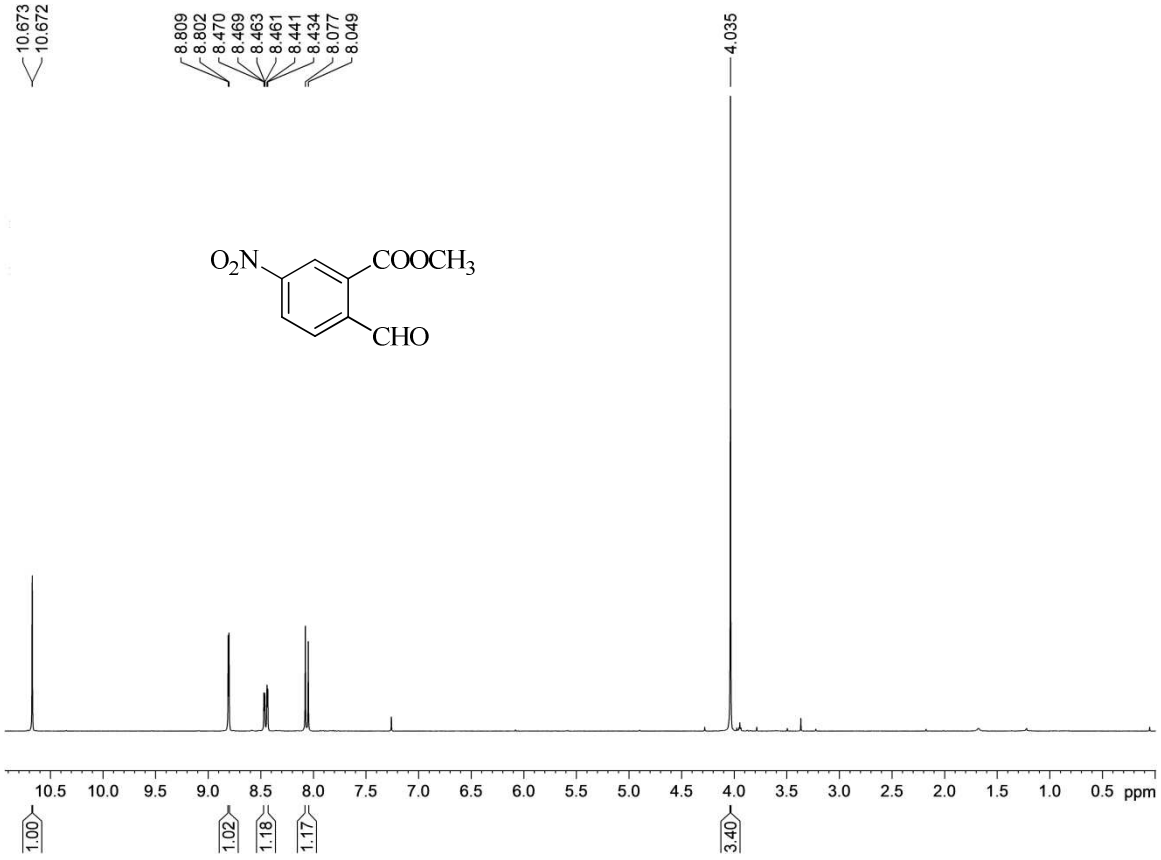
Formula search on scan 1 of 0912pk0002

Mass	Int	Dev ppm	12 C	1 H	16 O
194.05728	225647	-3.26	10	10	4

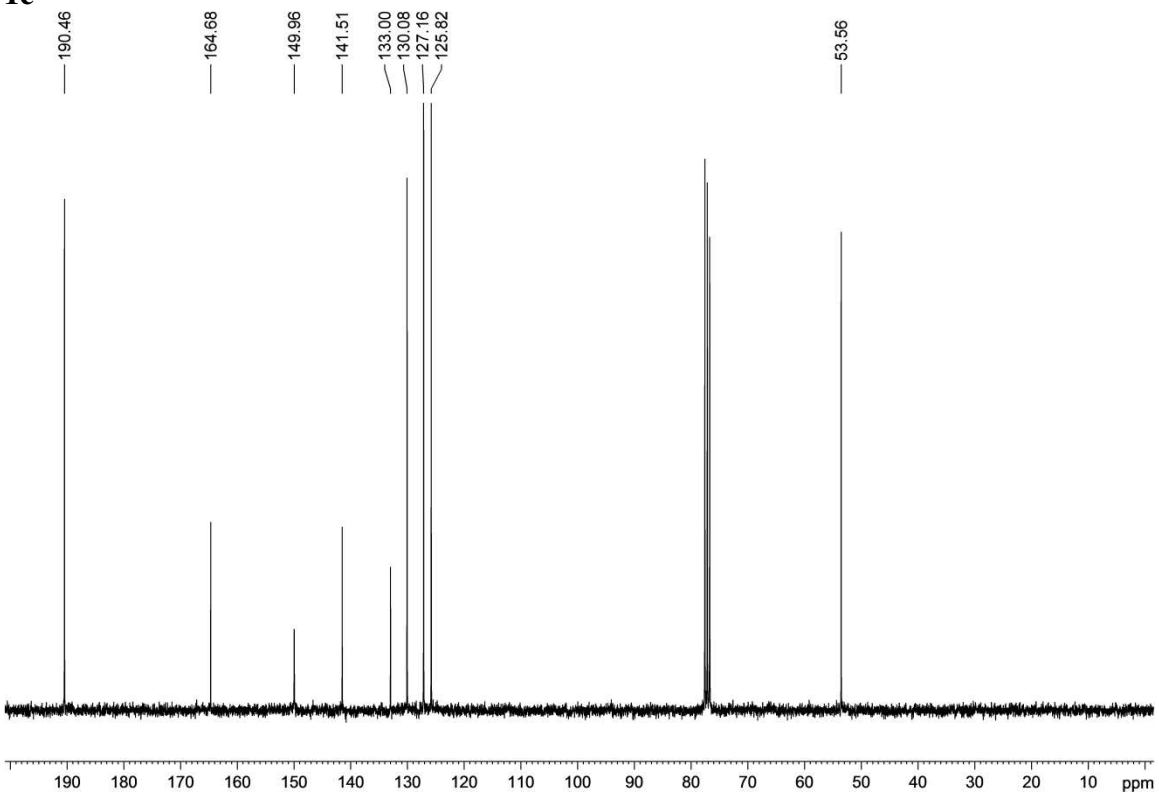
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	194.05791	89.9082	10	0	10	4
2	195.06126	10.0918	9	1	10	4

1c



1c


190.46
164.68
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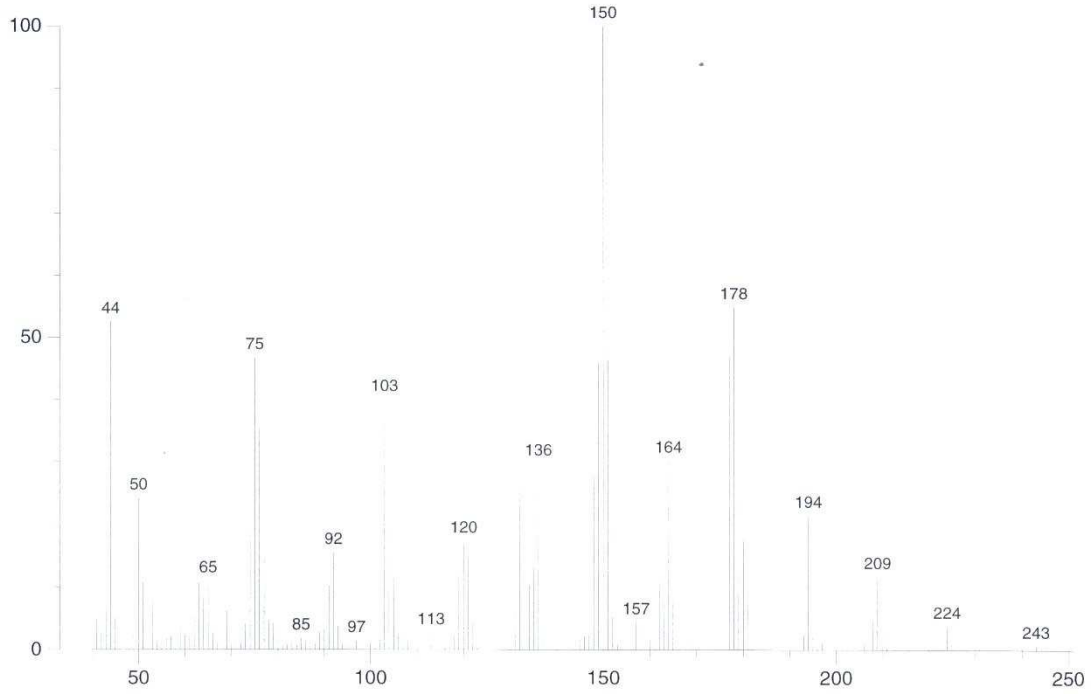
141.51
133.00
130.08
127.16
125.82
53.56
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1c


100
50
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150
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75
103
136
164
50
194
92
120
209
65
157
224
85
97
113
243
50
100
150
200
250

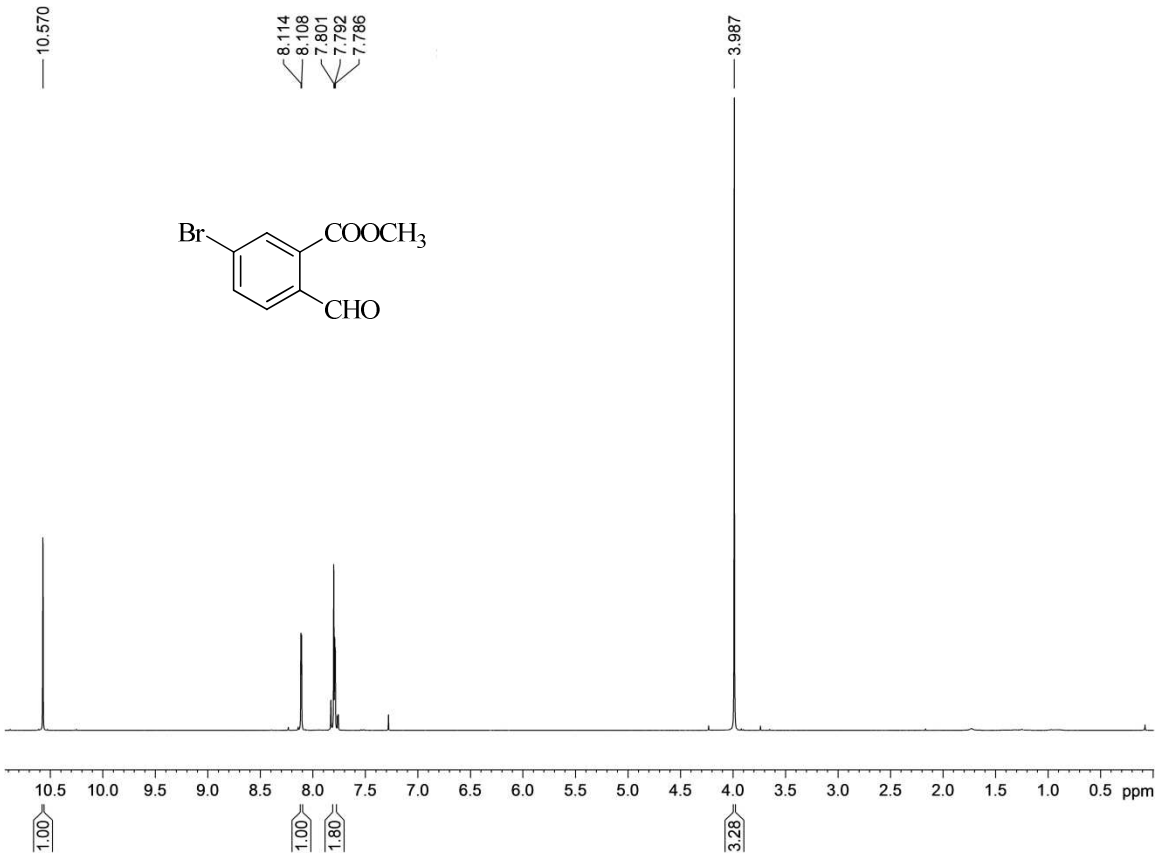
Formula search on scan 1 of 0123pk0002

Mass	Int	Dev ppm	12 C	1 H	14 N	16 O
209.03256	1254689	-59.50	10	9	0	5
		0.66	9	7	1	5

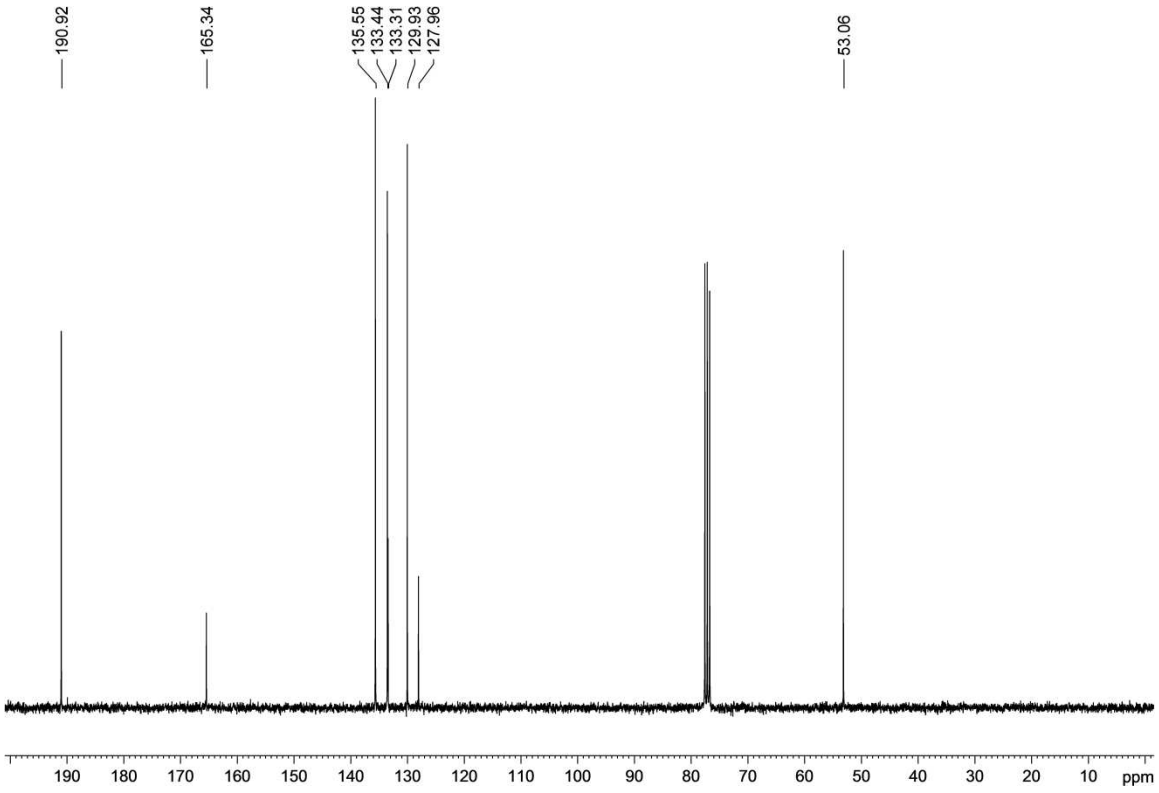
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	14 N	16 O
1	209.03242	90.8248	9	0	7	1	5
2	210.03578	9.1752	8	1	7	1	5

1d



1d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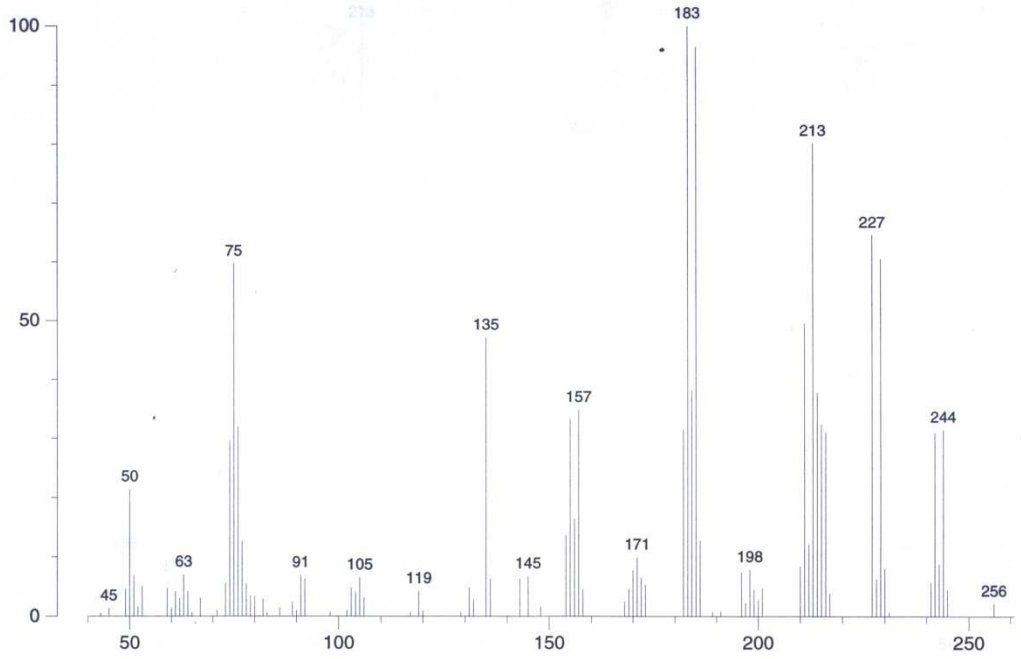
135.55
133.44
133.31
129.93
127.96
53.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

1d



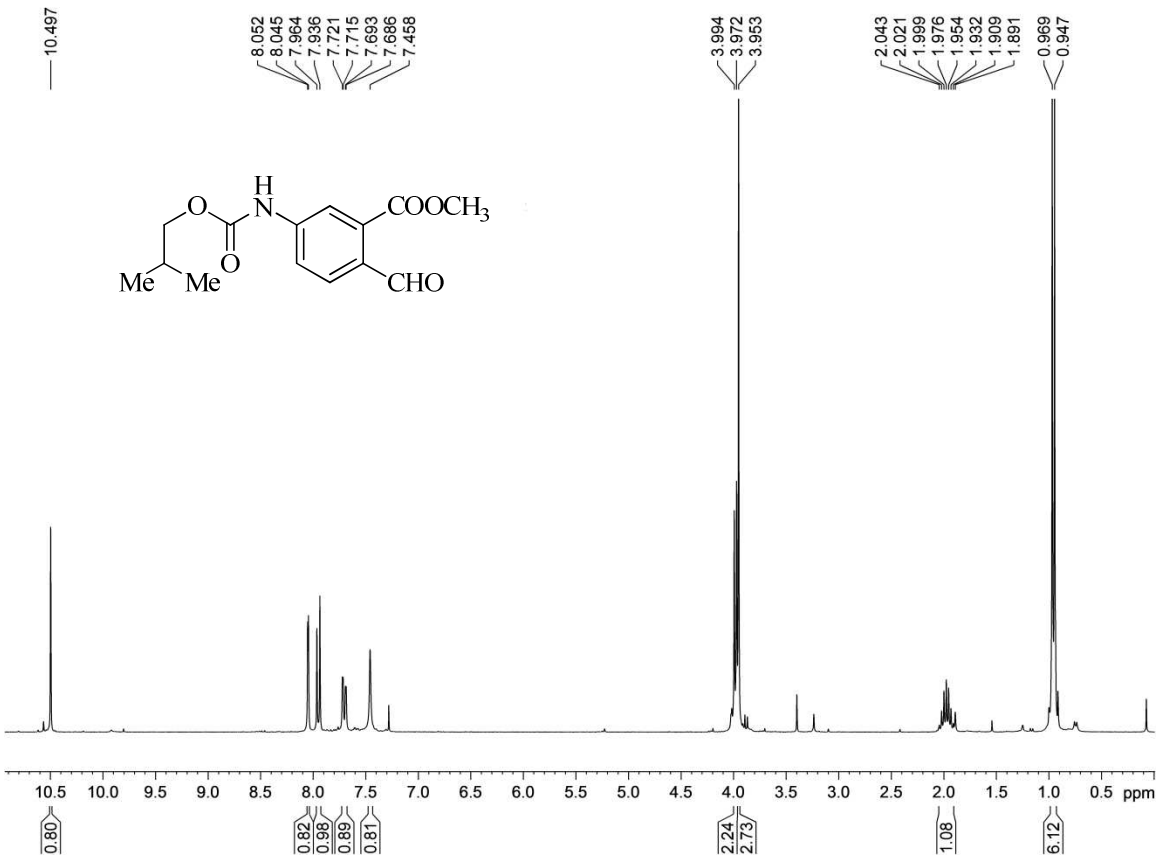
Formula search on scan 1 of 1107pk0002

Mass	Int	Dev ppm	12 C	1 H	16 O	79 Br
241.95774	74384	-63.52	13	7	0	1
		-0.46	9	7	3	1

Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O	79 Br	81 Br
1	241.95786	45.9028	9	0	7	3	1	0
2	243.95594	44.9219	9	0	7	3	0	1
3	242.96121	4.6372	8	1	7	3	1	0
4	244.95929	4.5381	8	1	7	3	0	1

1e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7.686
7.458
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3.972
3.953
2.043
2.021
1.999
1.976
1.954
1.932
1.909
1.891
0.969
0.947
H
N
O
O
O
Me
Me
COOCH3
CHO
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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0.82
0.98
0.89
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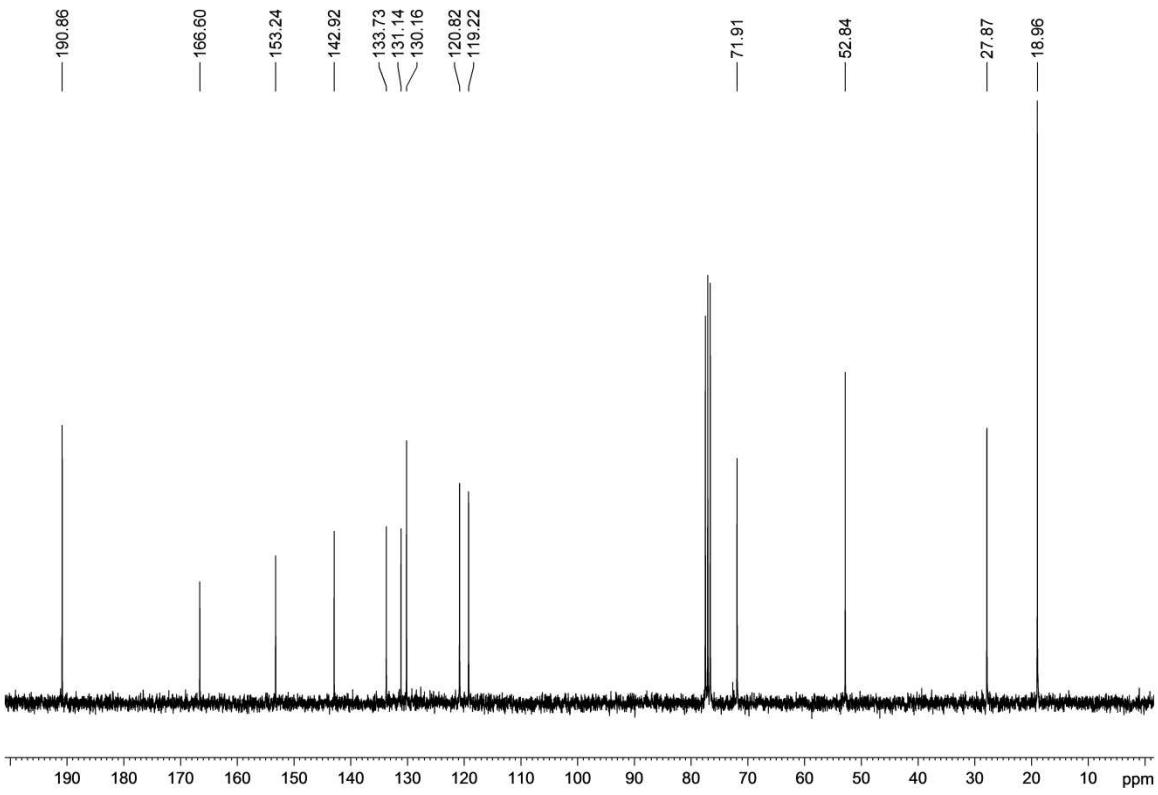
2.24
2.73
1.08
6.12

1e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142.92
133.73
131.14
130.16
120.82
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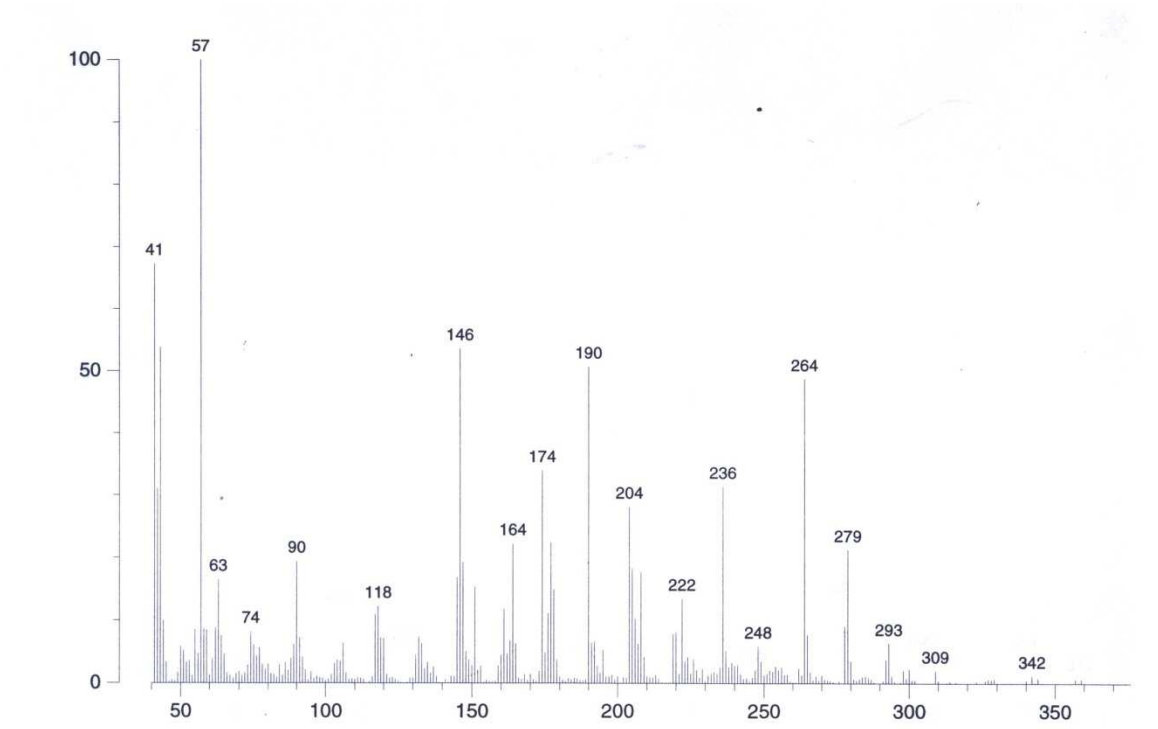
71.91
52.84
27.87
18.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1e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63
118
222
74
248
293
309
342
50 100 150 200 250 300 350

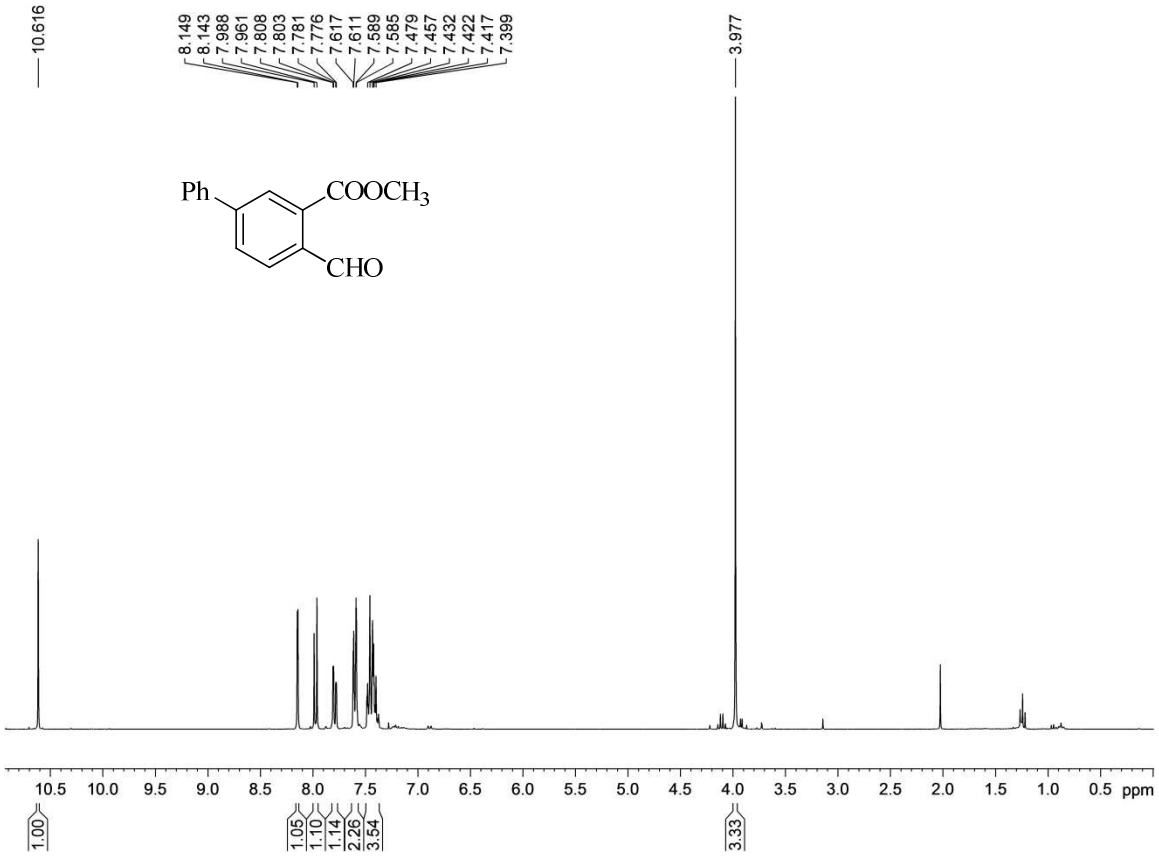
Formula search on scan 1 of 1020pk0007

Mass	Int	Dev ppm	12 C	1 H	14 N	16 O
279.11096	1048949	31.69	18	15	0	3
		76.74	17	13	1	3
		-44.02	15	19	0	5
		1.04	14	17	1	5

Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	14 N	16 O
1	279.11067	86.4196	14	0	17	1	5
2	280.11403	13.5804	13	1	17	1	5

1f



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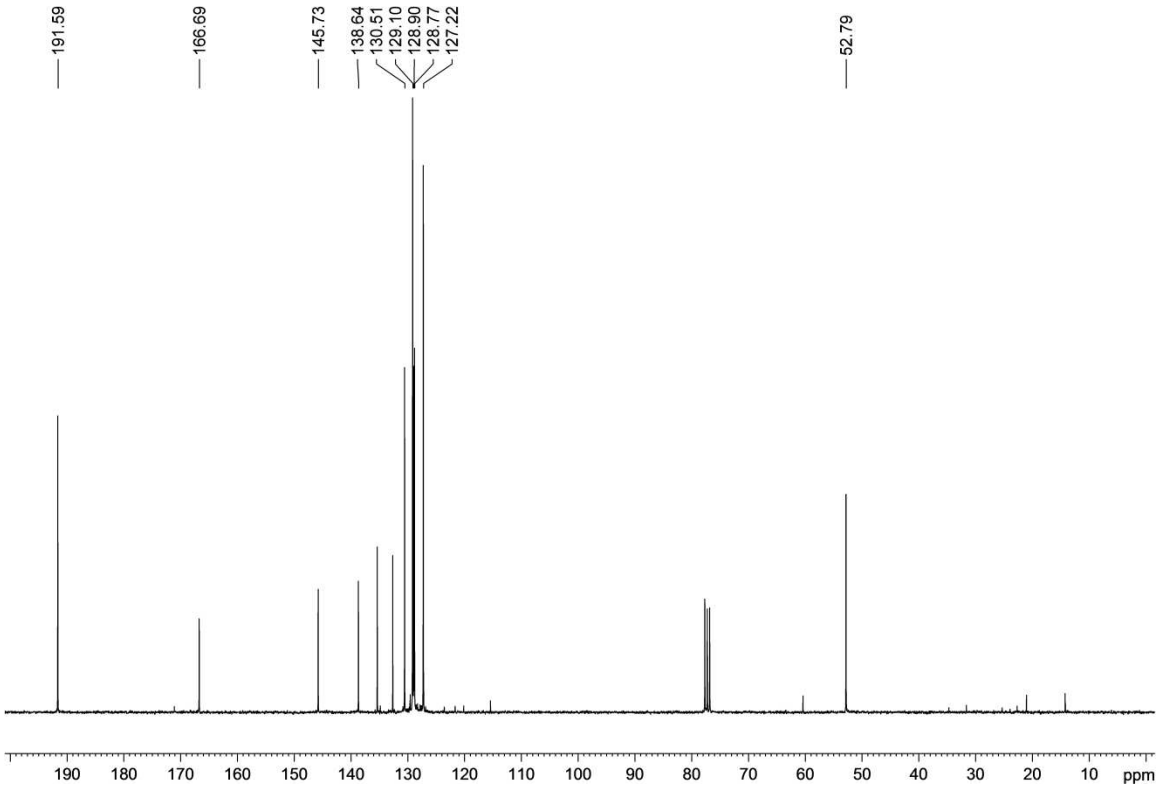
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145.73
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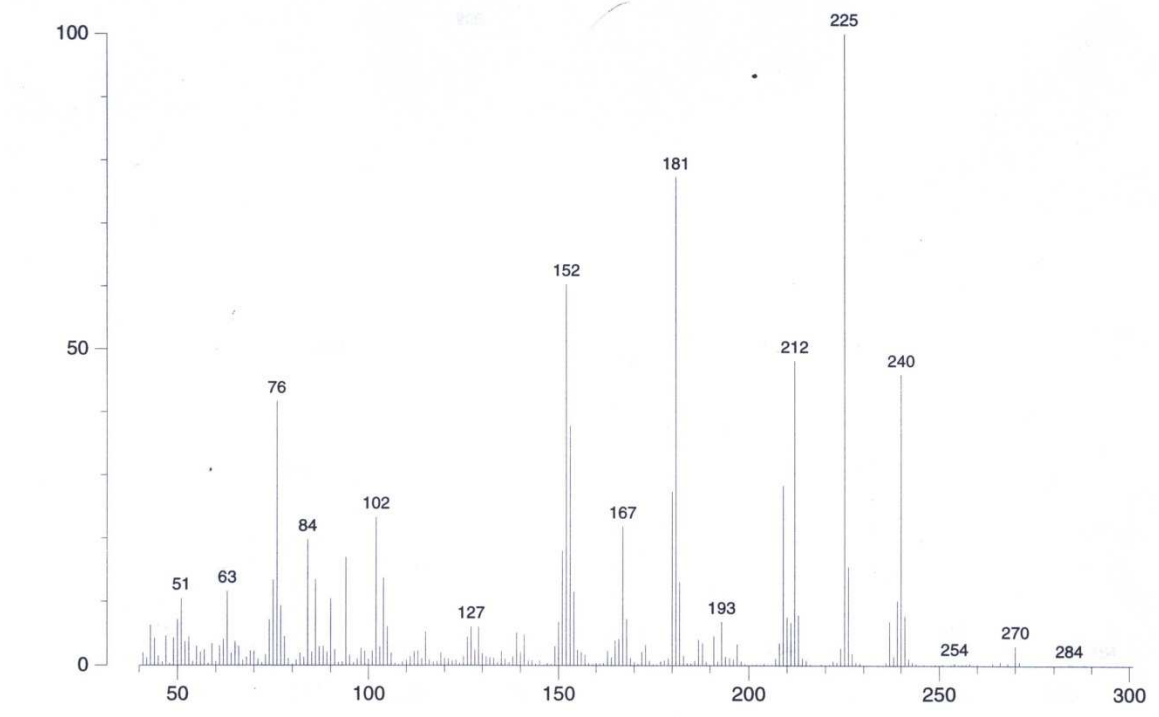
130.51
129.10
128.90
128.77
127.22
52.79
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1f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76
102
84
167
51
63
127
193
254
270
284
50 100 150 200 250 300

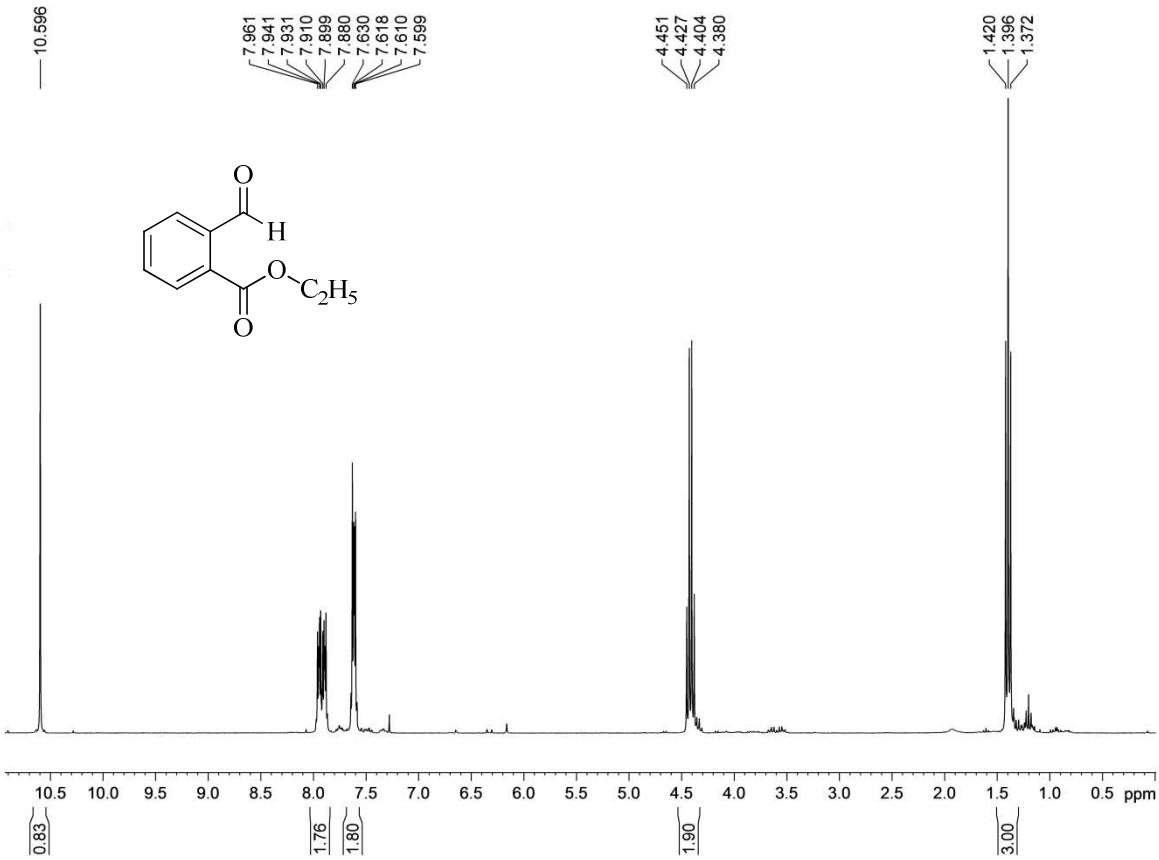
Formula search on scan 1 of 0105pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
240.07825	1510988	-65.18	19	12	0
		86.37	18	8	1
		-1.64	15	12	3

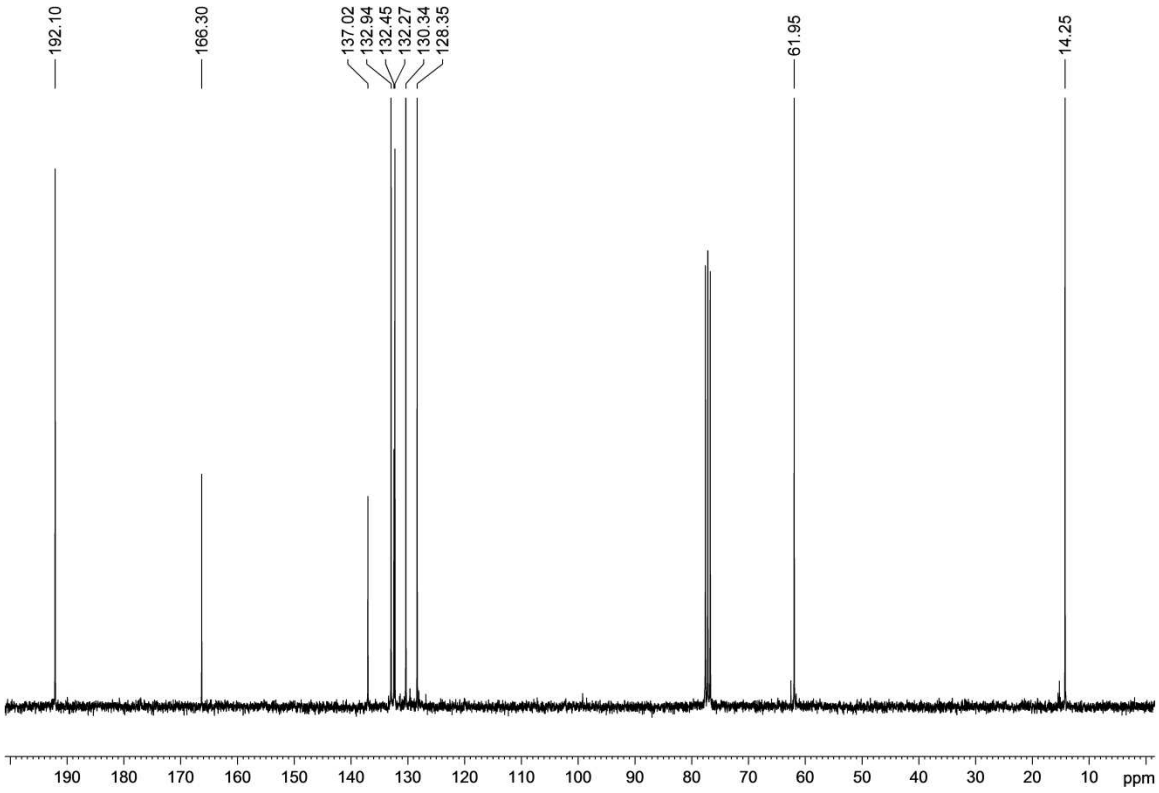
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	240.07864	84.6312	15	0	12	3
2	241.08200	14.2493	14	1	12	3
3	242.08535	1.1196	13	2	12	3

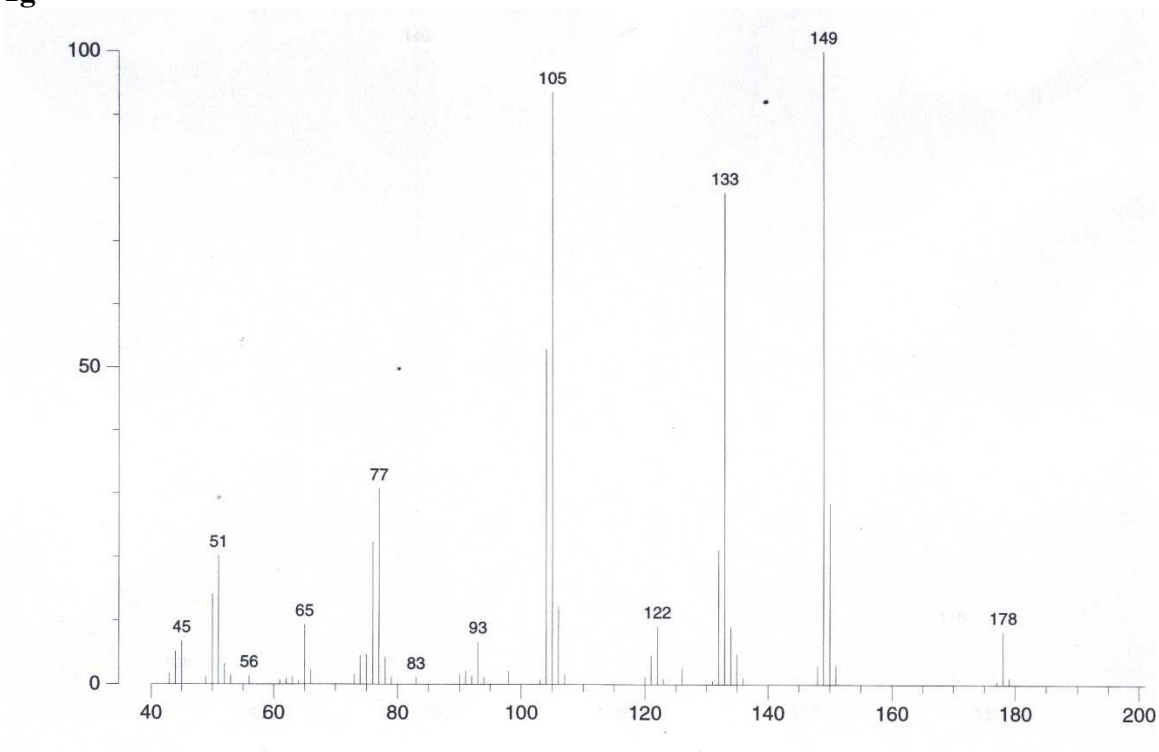
1g



1g


192.10
166.30
137.02
132.94
132.45
132.27
130.34
128.35
61.95
14.25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1g


100
50
0
149
105
133
77
51
65
45
56
83
93
122
178
40 60 80 100 120 140 160 180 200

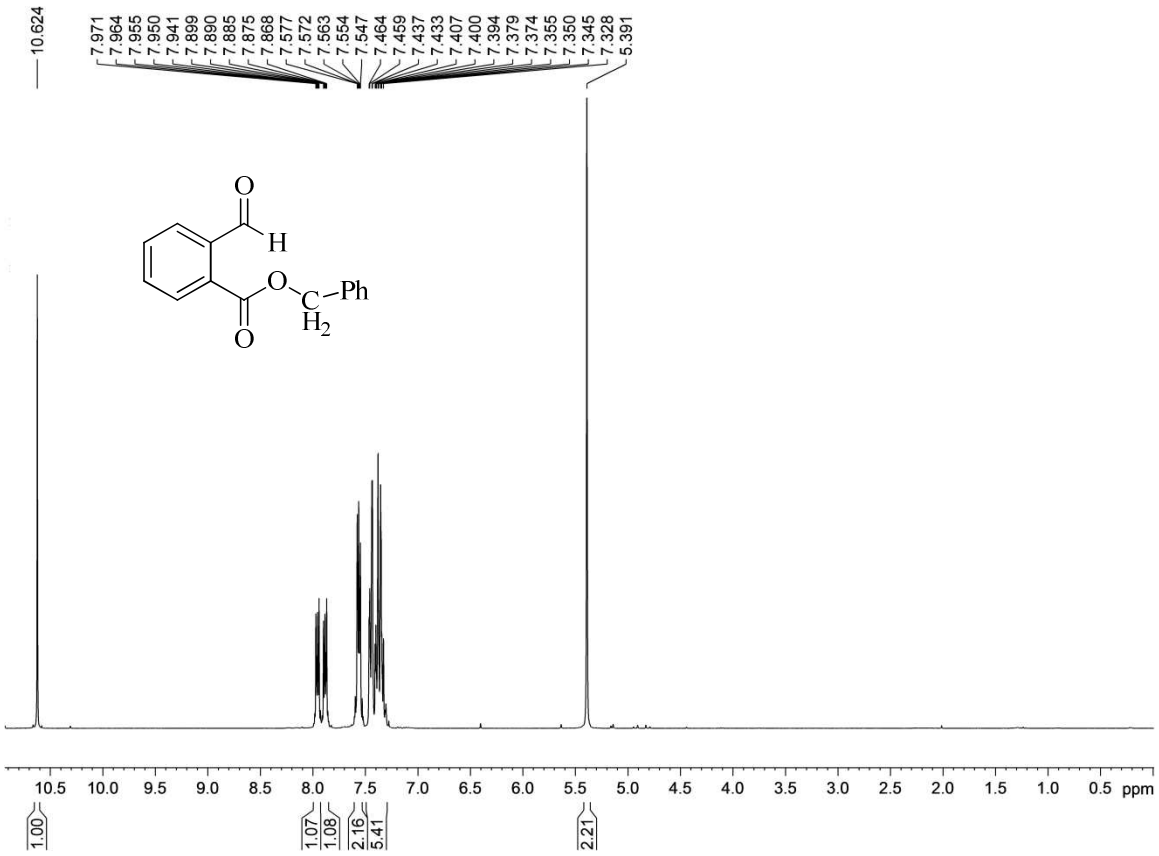
Formula search on scan 1 of 0726pk0003

Mass	Int	Dev ppm	12 C	1 H	16 O
178.06273	872399	-87.15	14	10	0
		-1.47	10	10	3

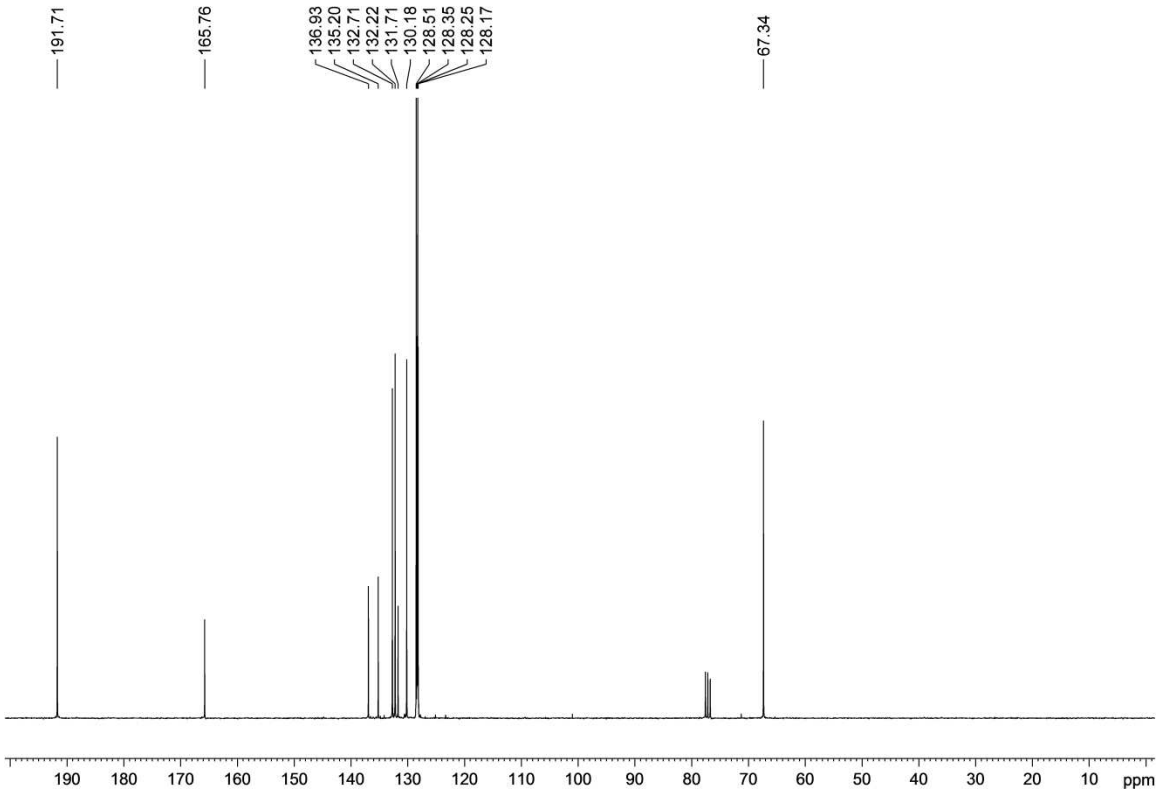
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	178.06299	89.9082	10	0	10	3
2	179.06635	10.0918	9	1	10	3

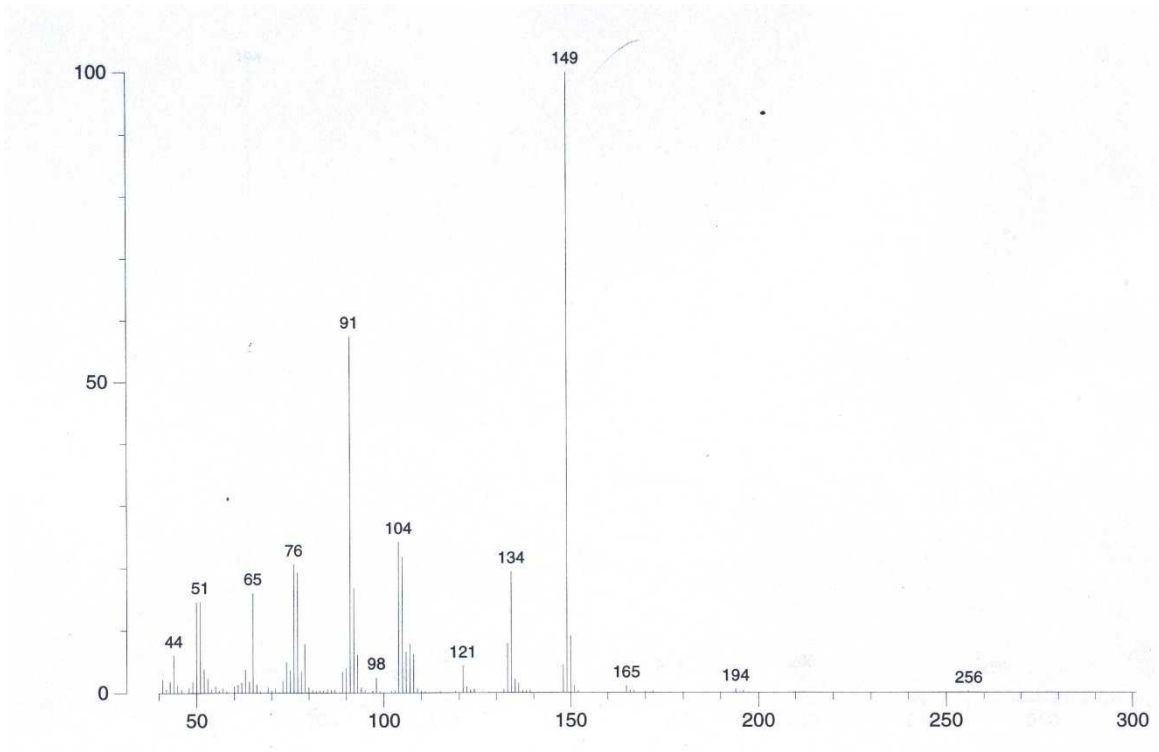
1h



1h


191.71
165.76
136.93
135.20
132.71
132.22
131.71
130.18
128.51
128.35
128.25
128.17
67.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1h


100
50
0
149
91
104
76
134
65
51
44
98
121
165
194
256
50 100 150 200 250 300

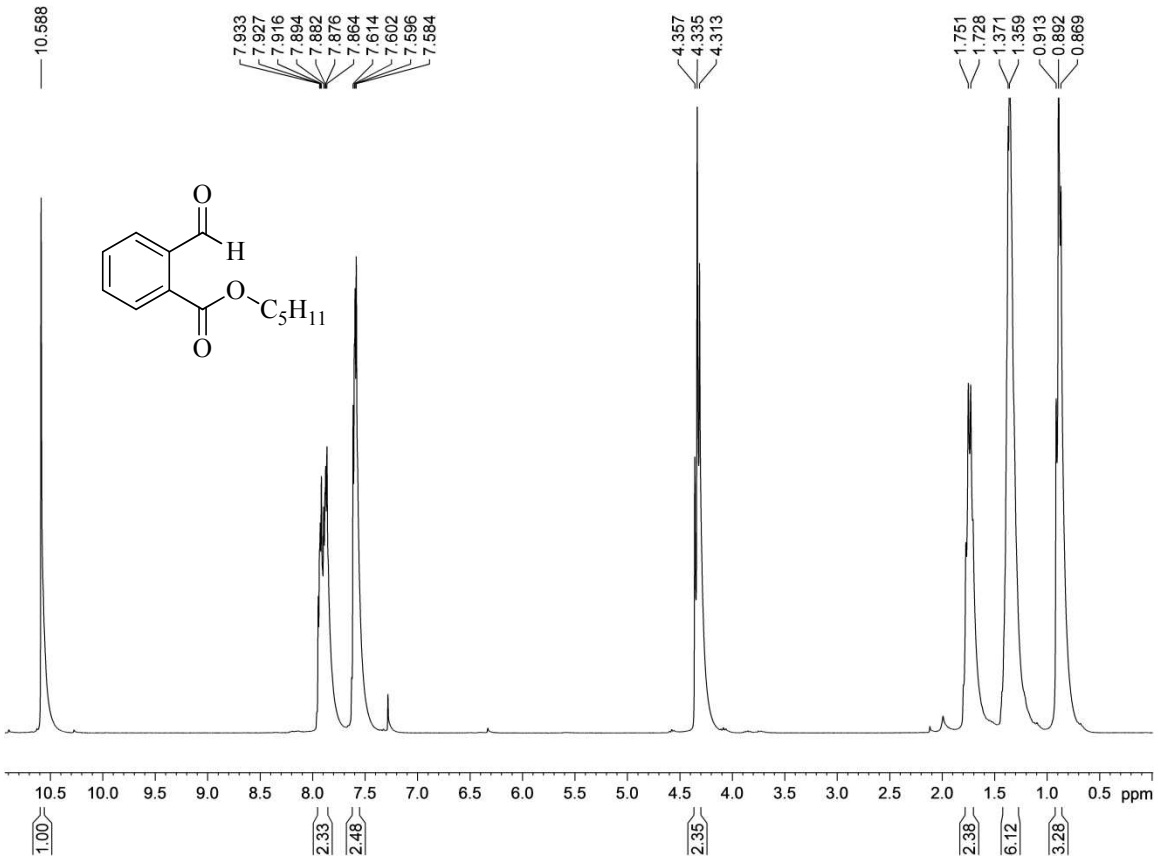
Formula search on scan 1 of 0213pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
240.07825	322386	-1.64	15	12	3

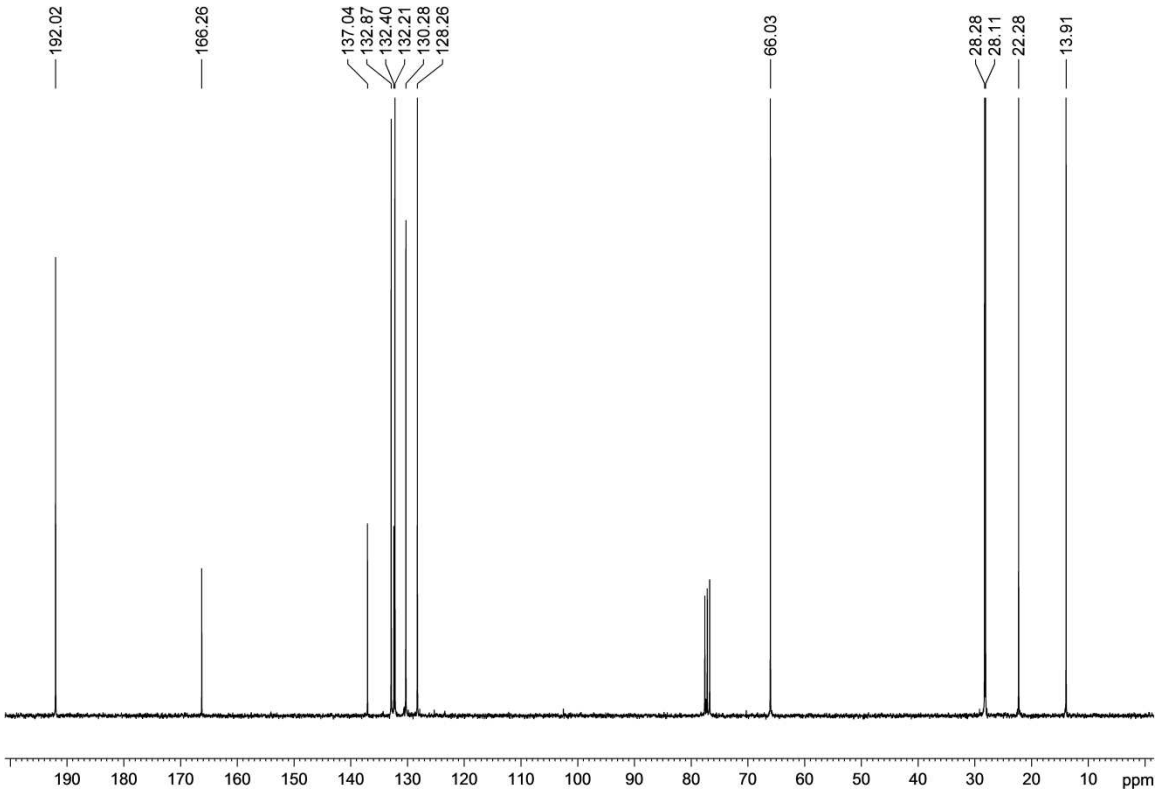
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	240.07864	84.6312	15	0	12	3
2	241.08200	14.2493	14	1	12	3
3	242.08535	1.1196	13	2	12	3

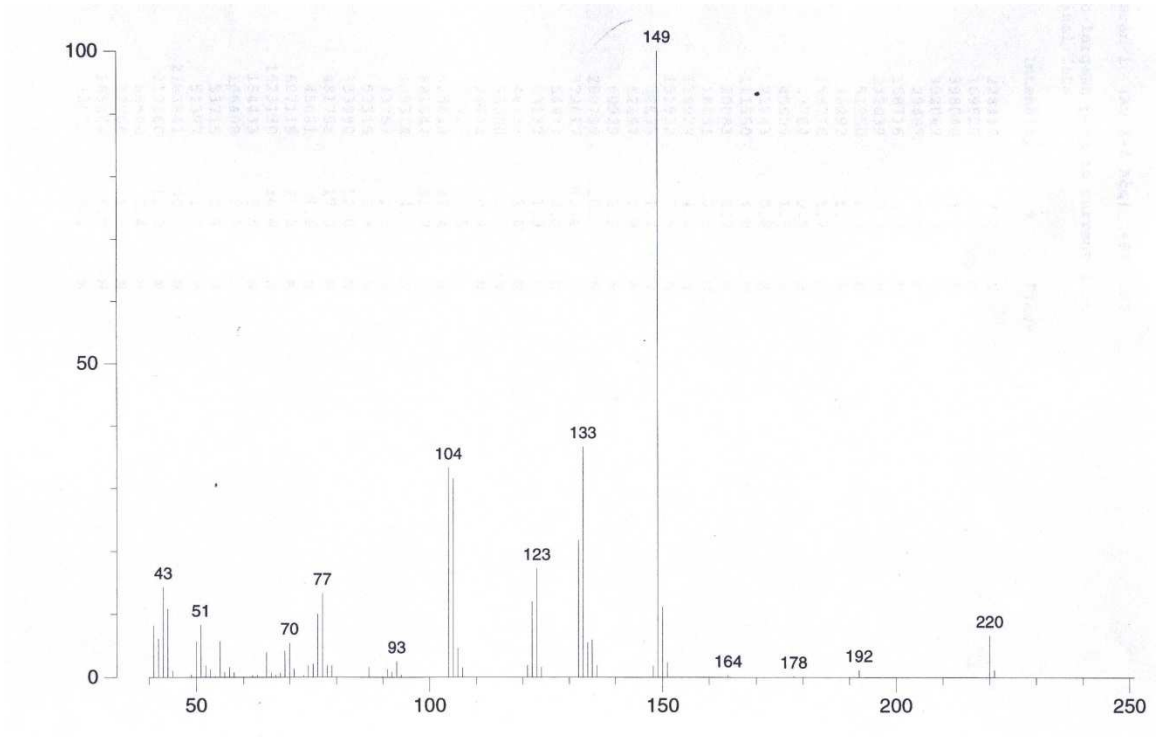
1i



1i


192.02
166.26
137.04
132.87
132.40
132.21
130.28
128.26
66.03
28.28
28.11
22.28
13.91
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1i


100
50
0
149
133
104
123
43
77
51
70
93
164
178
192
220
50 100 150 200 250

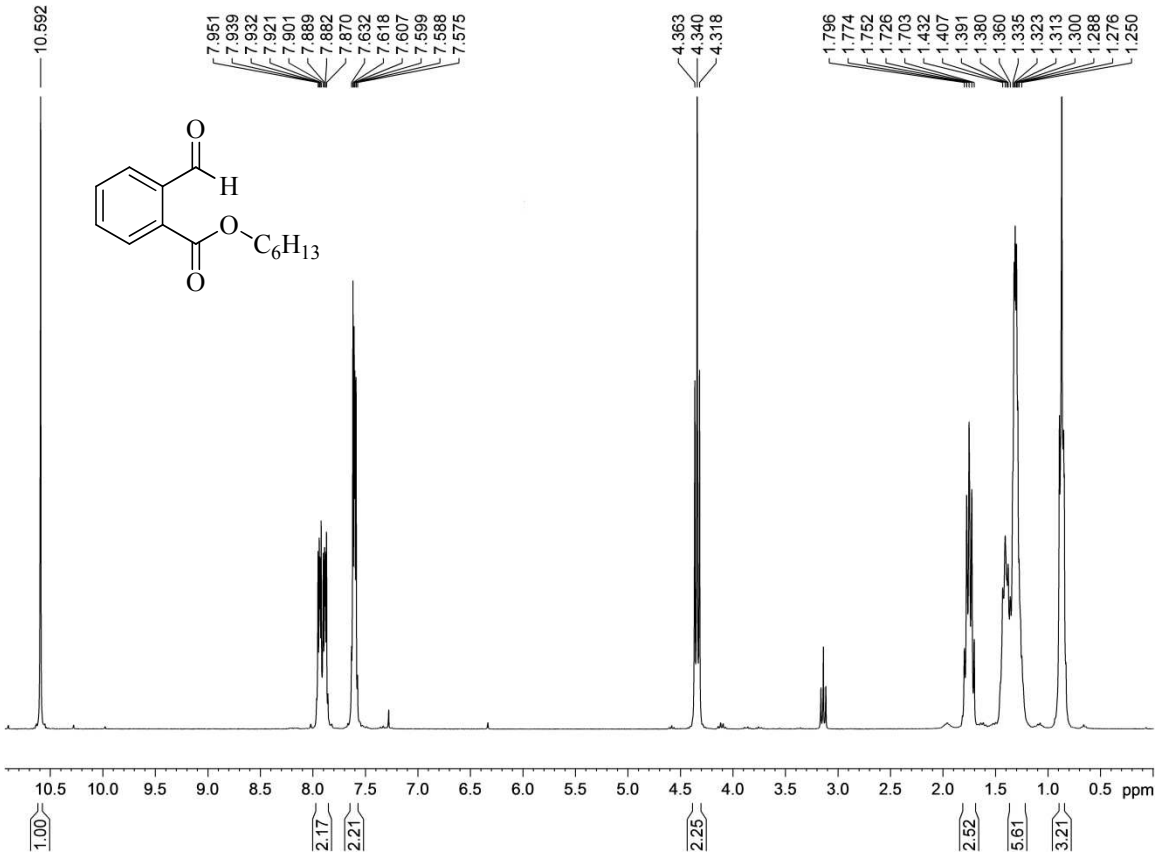
Formula search on scan 1 of 0726pk0004

Mass	Int	Dev ppm	12 C	1 H	16 O
220.10961	64358	-1.53	13	16	3

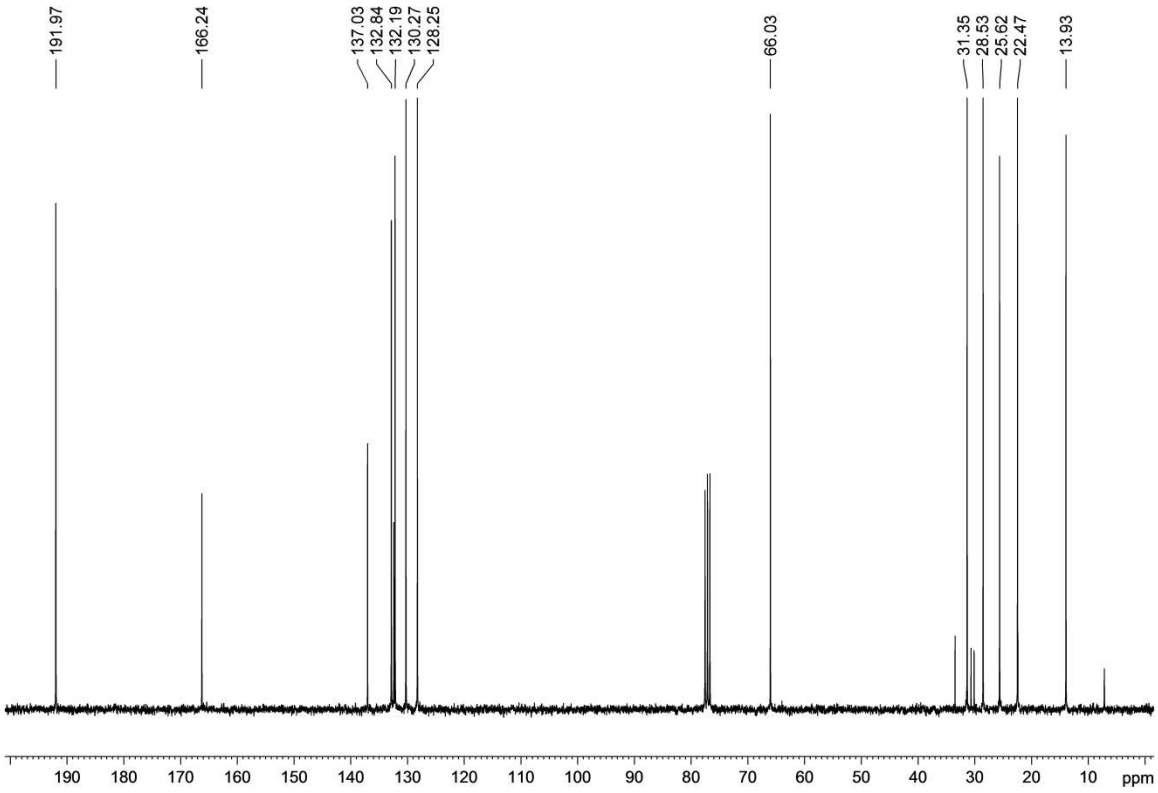
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	220.10994	87.2661	13	0	16	3
2	221.11330	12.7339	12	1	16	3

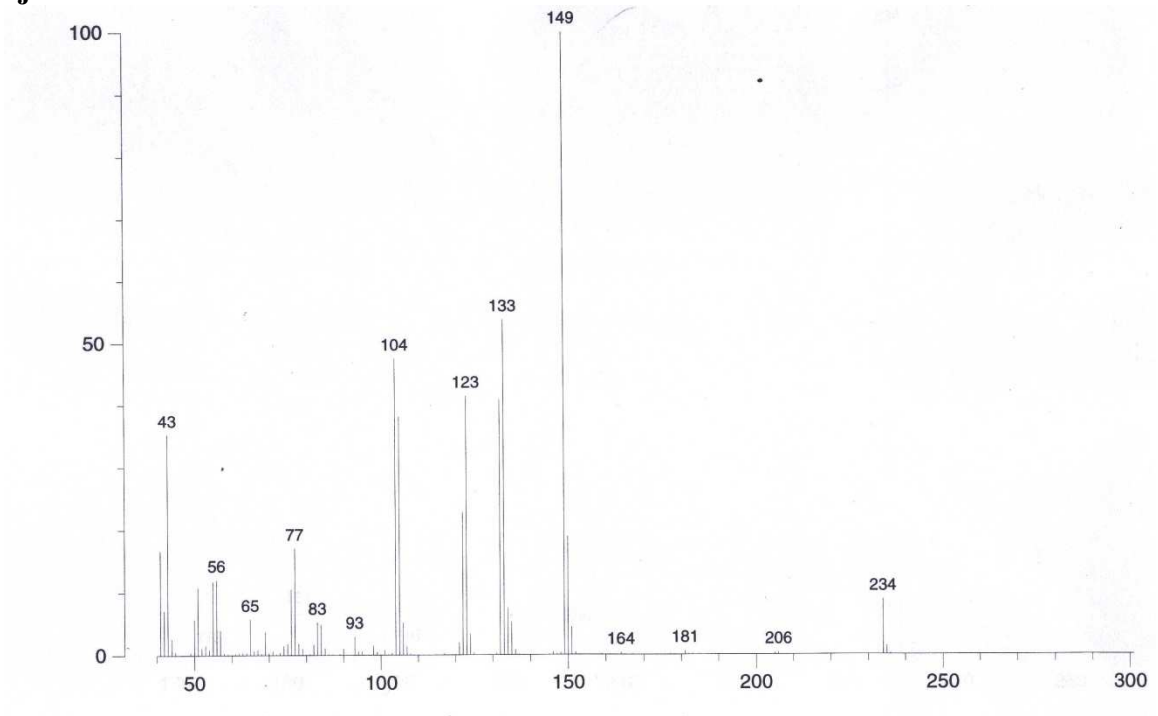
1j



1j


191.97
166.24
137.03
132.84
132.19
130.27
128.25
66.03
31.35
28.53
25.62
22.47
13.93
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1j


100
50
0
149
133
104
123
43
77
56
65
83
93
164
181
206
234
50 100 150 200 250 300

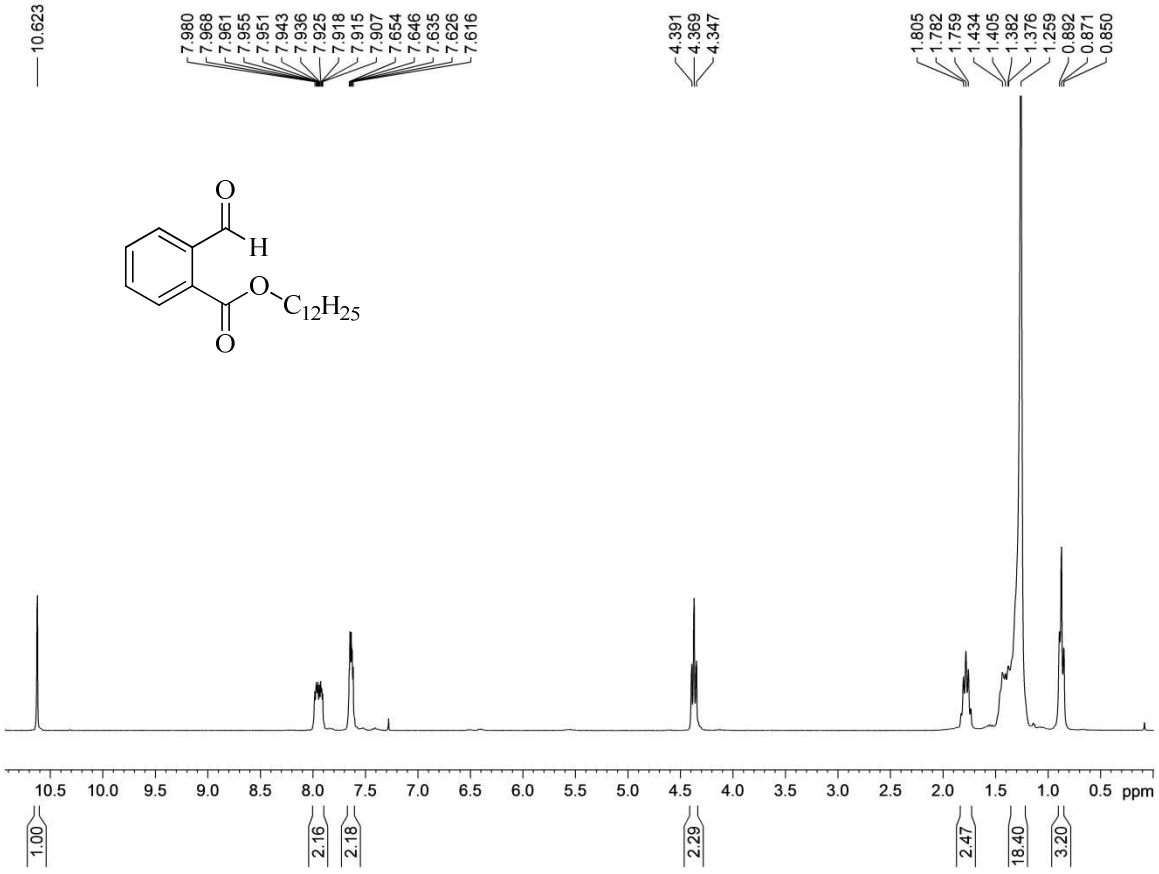
Formula search on scan 1 of 0726pk0005

Mass	Int	Dev ppm	12 C	1 H	16 O
234.12501	543599	-2.50	14	18	3

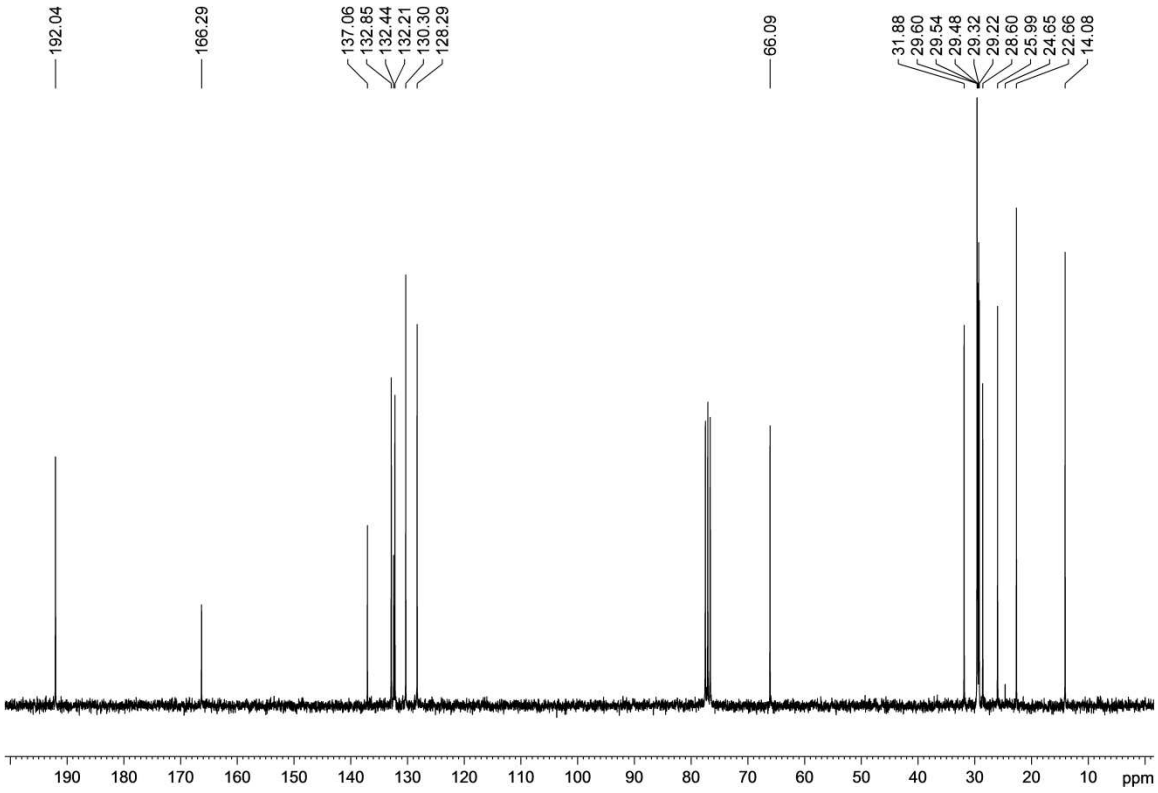
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	234.12559	86.4196	14	0	18	3
2	235.12895	13.5804	13	1	18	3

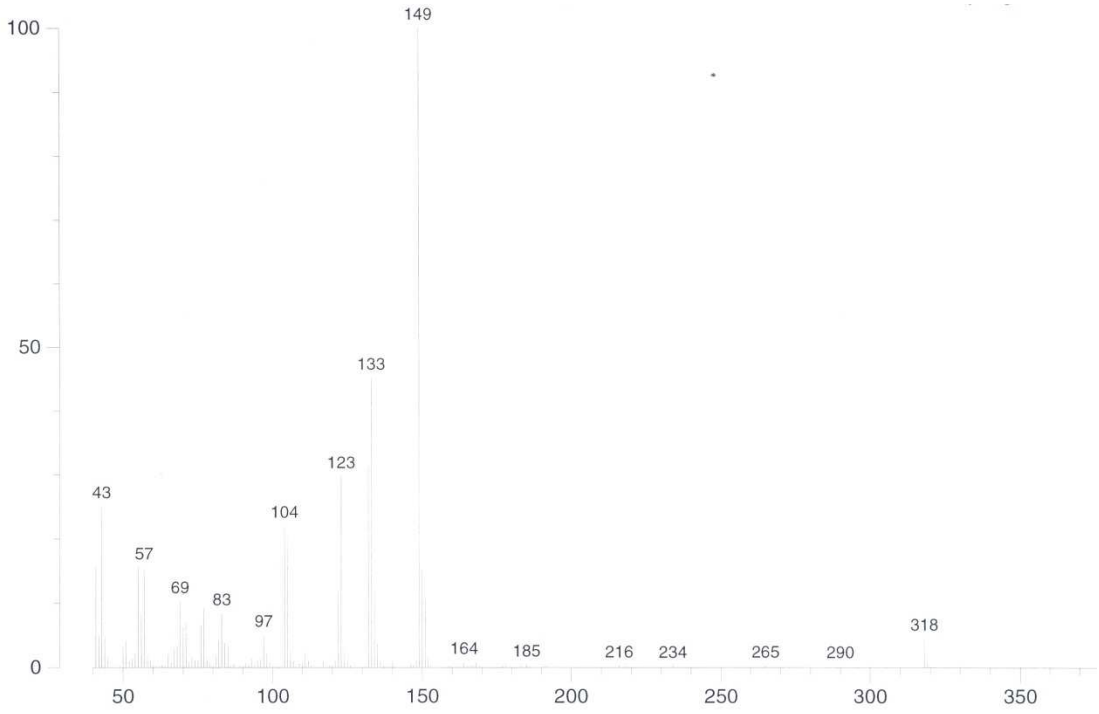
1k



1k


192.04
166.29
137.06
132.85
132.44
132.21
130.30
128.29
66.09
31.88
29.60
29.54
29.48
29.32
29.22
28.60
25.99
24.65
22.66
14.08
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1k


100
50
0
149
133
123
104
43
57
69
83
97
164
185
216
234
265
290
318
50 100 150 200 250 300 350

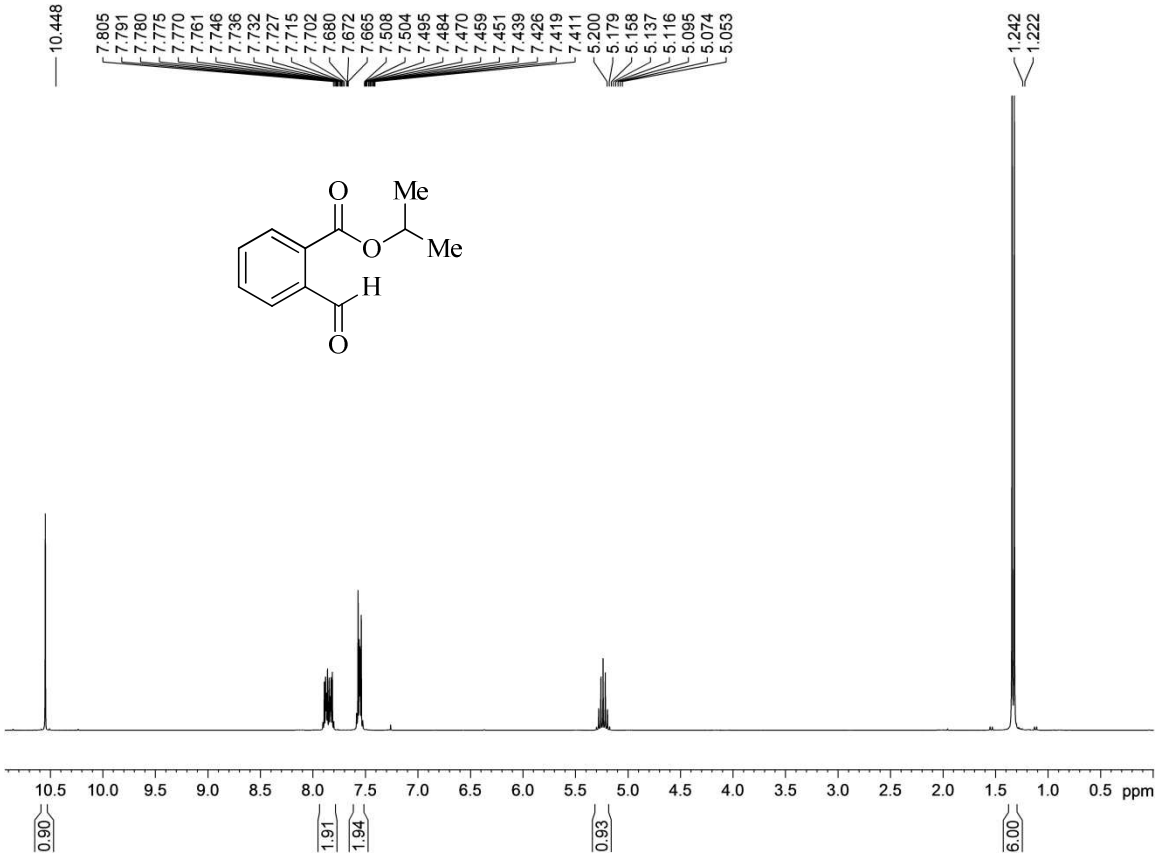
Formula search on scan 1 of 0726pk0006

Mass	Int	Dev ppm	12 C	1 H	16 O
318.22047	2128593	-44.87	24	30	0
		69.47	23	26	1
		3.07	20	30	3

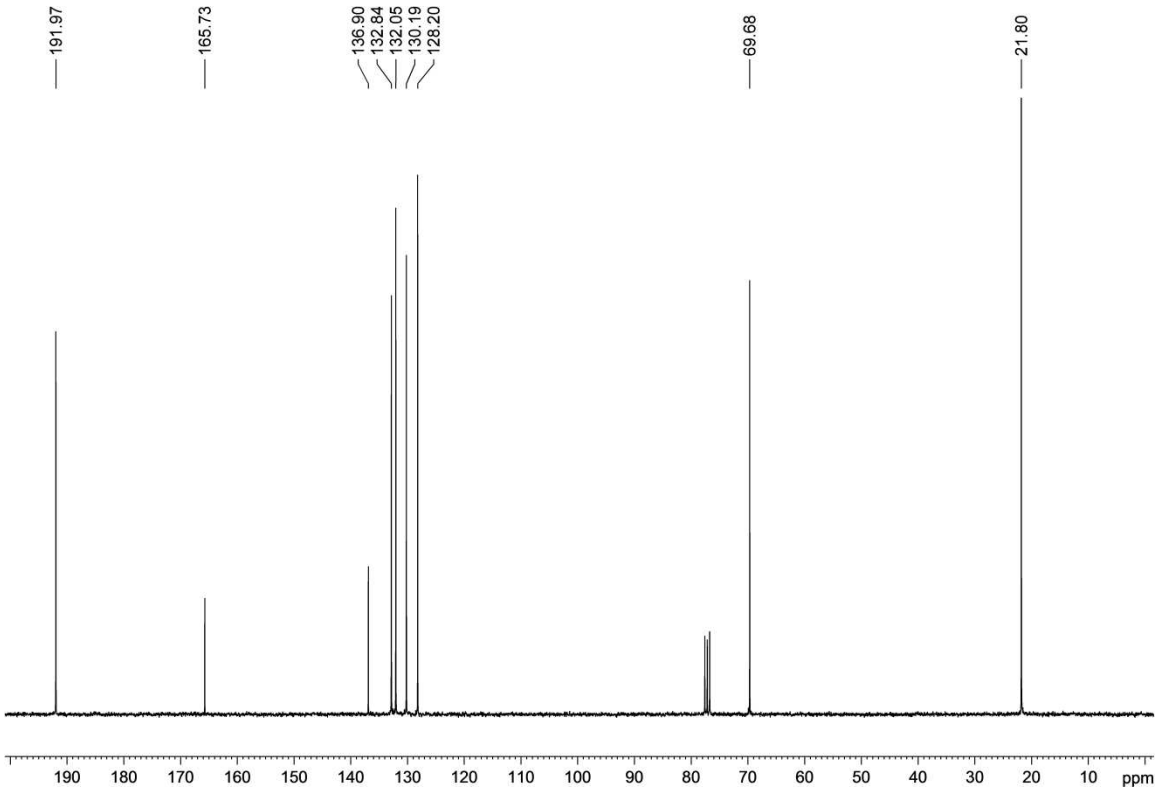
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	318.21950	80.1006	20	0	30	3
2	319.22285	17.9819	19	1	30	3
3	320.22621	1.9175	18	2	30	3

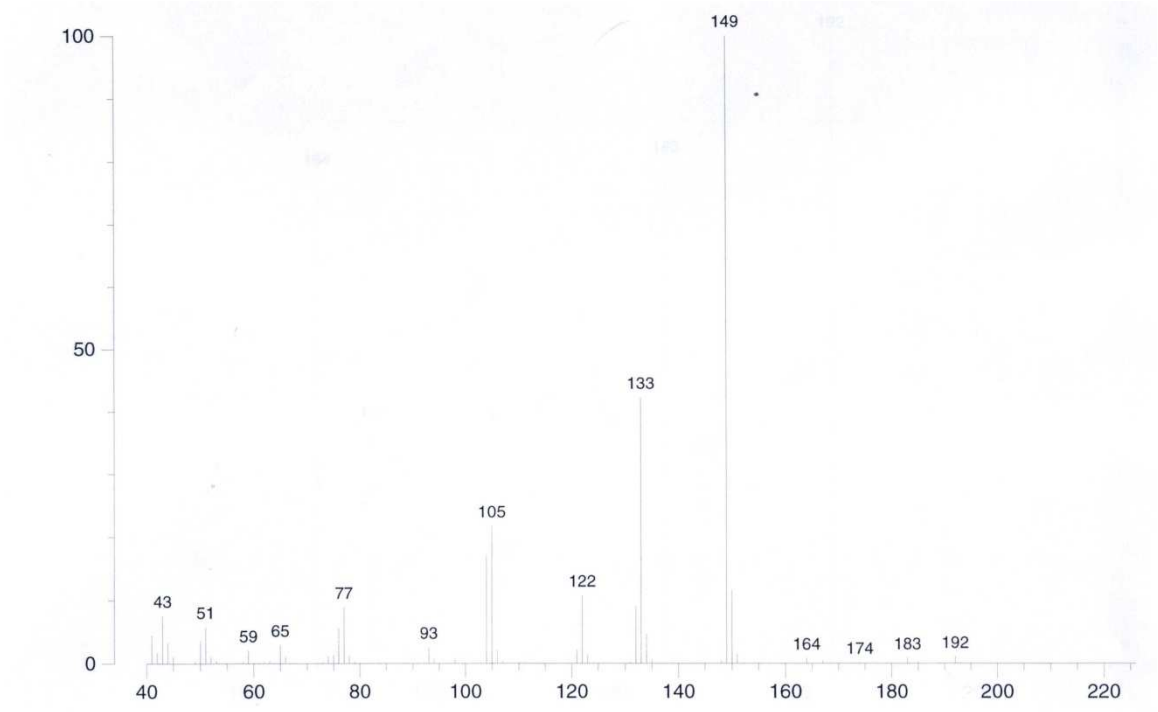
1l



1l


191.97
165.73
136.90
132.84
132.05
130.19
128.20
69.68
21.80
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1l


100
50
0
149
133
105
122
77
43
51
59
65
93
164
174
183
192
40 60 80 100 120 140 160 180 200 220

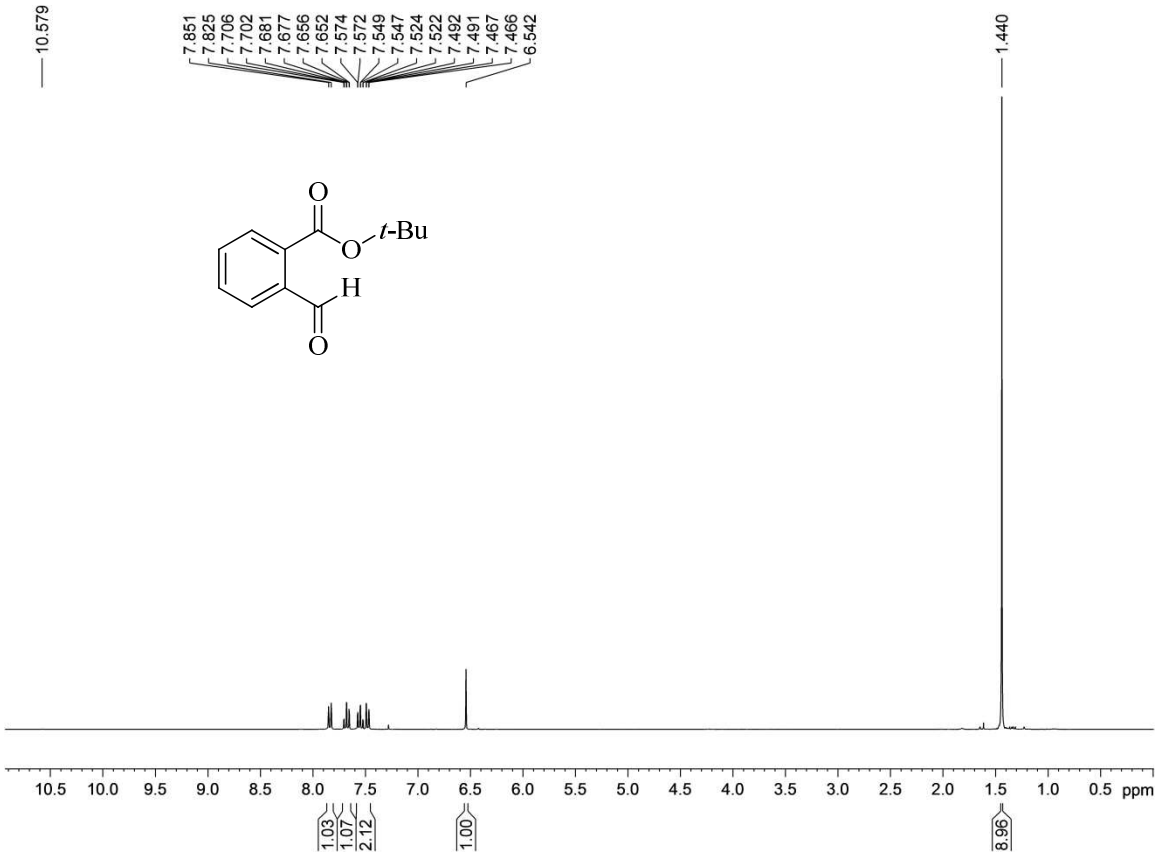
Formula search on scan 1 of 0906pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
192.07809	958766	-82.31	15	12	0
		-2.88	11	12	3

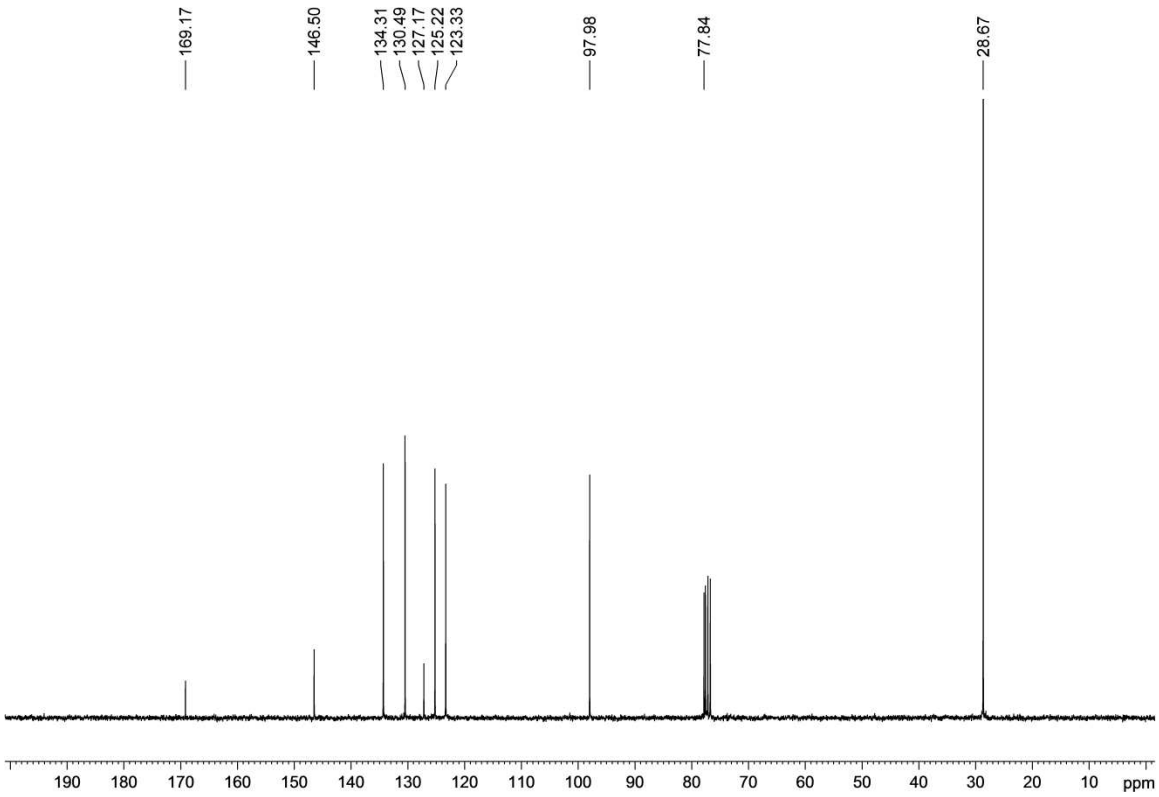
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	192.07864	89.0099	11	0	12	3
2	193.08200	10.9901	10	1	12	3

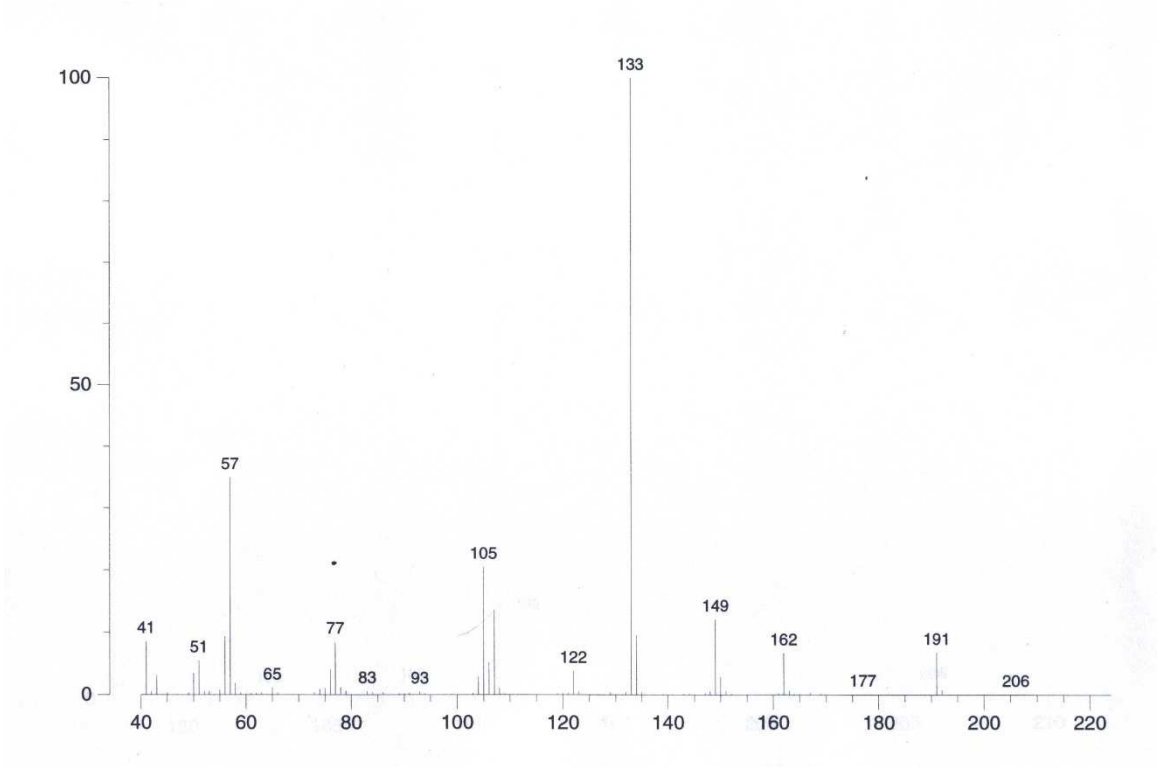
1m



1m


169.17
146.50
134.31
130.49
127.17
125.22
123.33
97.98
77.84
28.67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1m


100
50
0
133
57
105
149
41
51
77
162
191
65
83
93
122
177
206
40 60 80 100 120 140 160 180 200 220

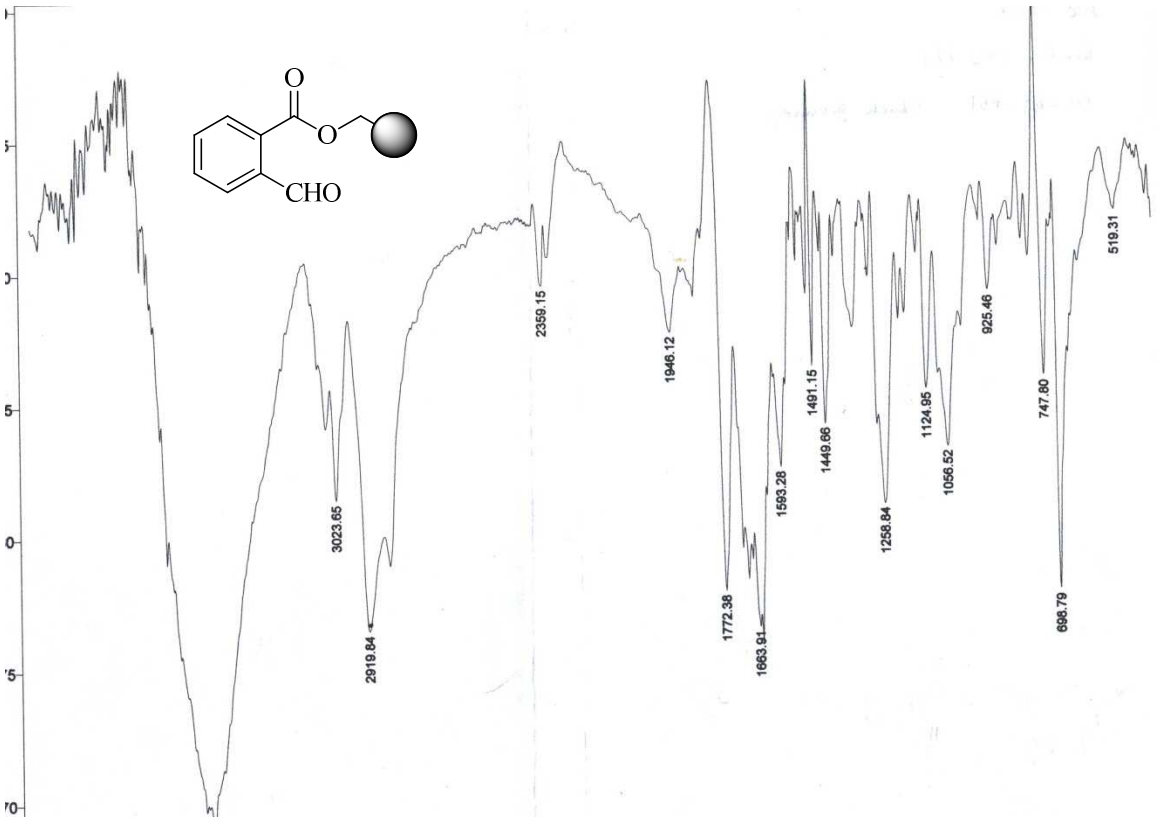
Formula search on scan 1 of 0912pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
206.09373	18265	99.79	15	10	1
		-2.74	12	14	3

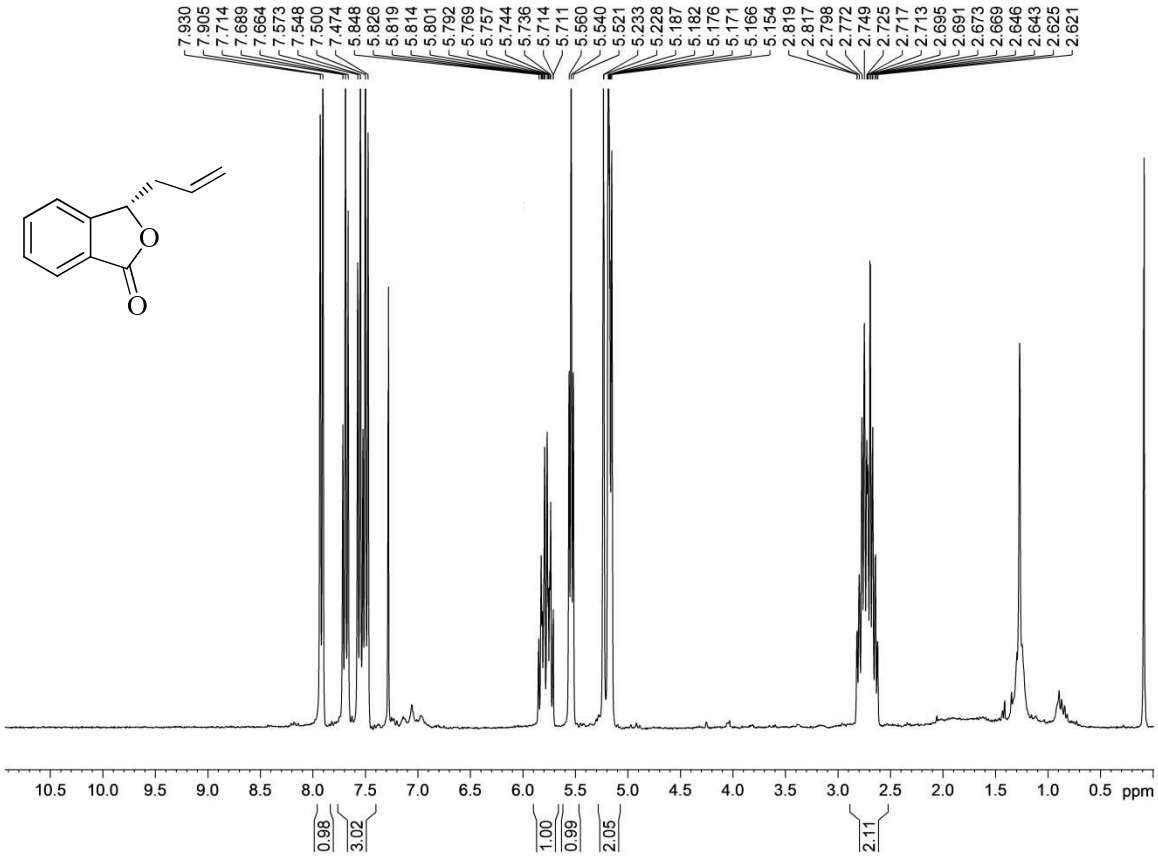
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	206.09429	88.1294	12	0	14	3
2	207.09765	11.8706	11	1	14	3

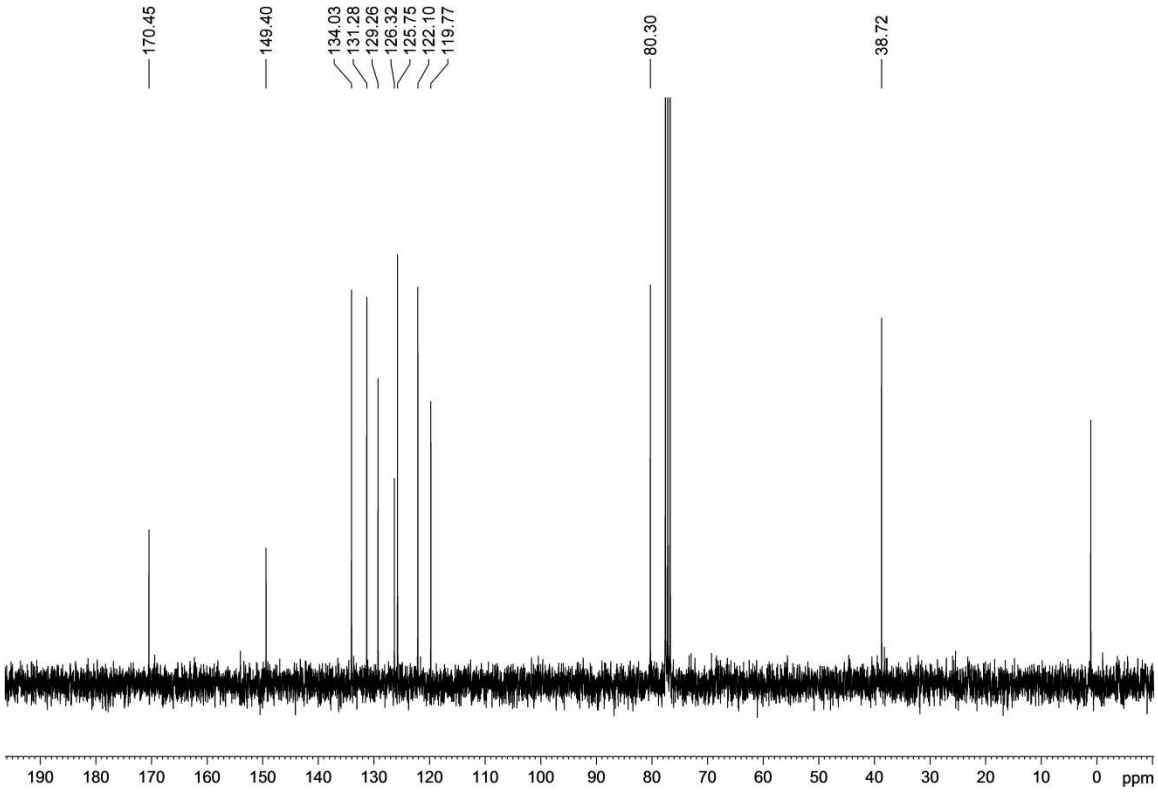
1n



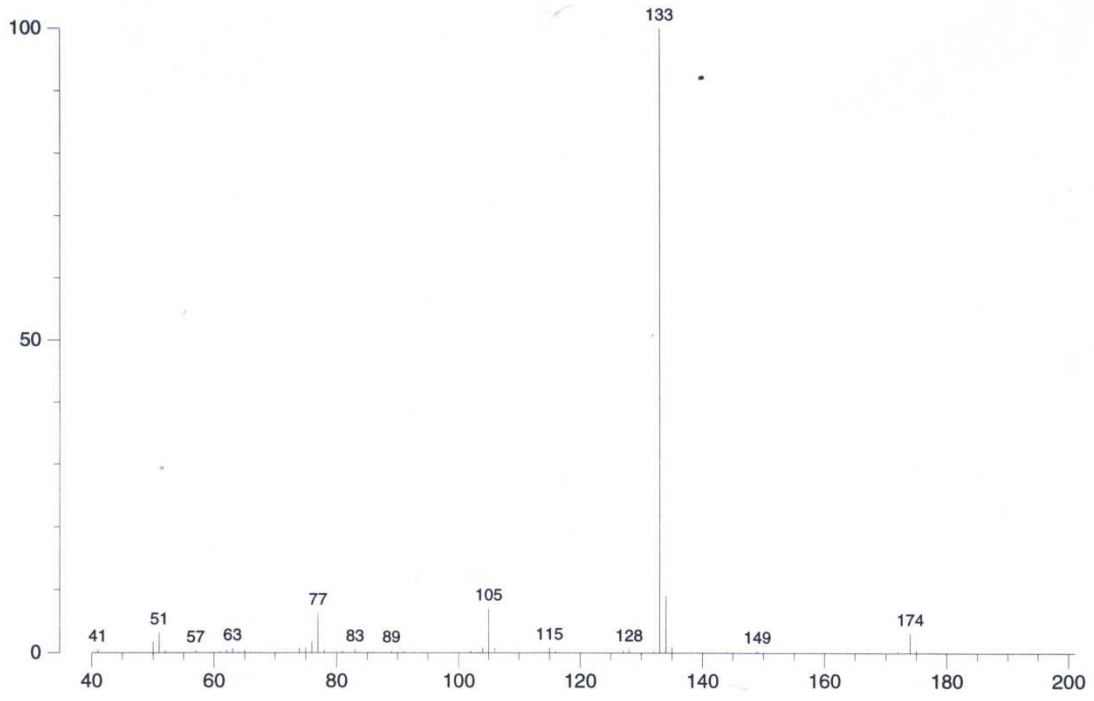
2a


7.930
7.905
7.714
7.689
7.664
7.573
7.548
7.500
7.474
5.848
5.826
5.819
5.814
5.801
5.792
5.769
5.757
5.744
5.736
5.714
5.711
5.560
5.540
5.521
5.233
5.228
5.187
5.182
5.176
5.171
5.166
5.154
2.819
2.817
2.798
2.772
2.749
2.725
2.717
2.713
2.695
2.691
2.673
2.669
2.646
2.643
2.625
2.621
O
O
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
3.02
1.00
0.99
2.05
2.11

2a


170.45
149.40
134.03
131.28
129.26
126.32
125.75
122.10
119.77
80.30
38.72
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2a


100
50
0
133
105
77
51
41
57
63
83
89
115
128
149
174
40 60 80 100 120 140 160 180 200

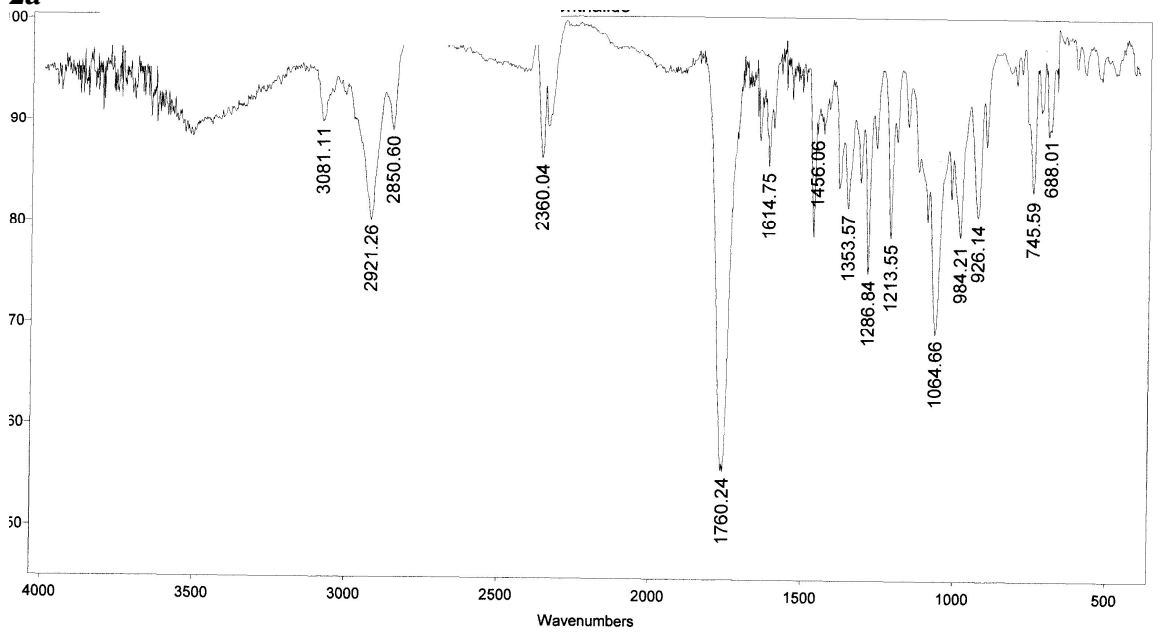
Formula search on scan 1 of 0906pk0002

Mass	Int	Dev ppm	12 C	1 H	16 O
174.06770	1612956	-2.16	11	10	2

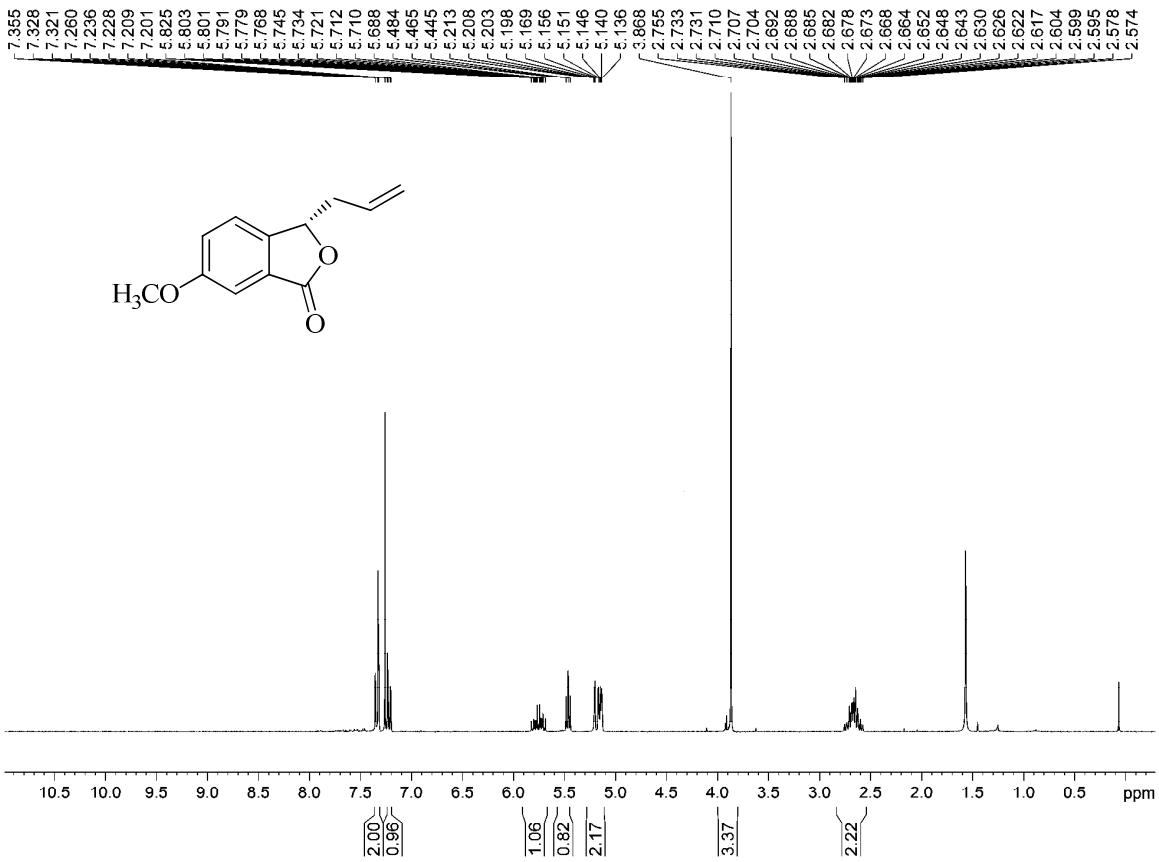
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	174.06808	89.0099	11	0	10	2
2	175.07143	10.9901	10	1	10	2

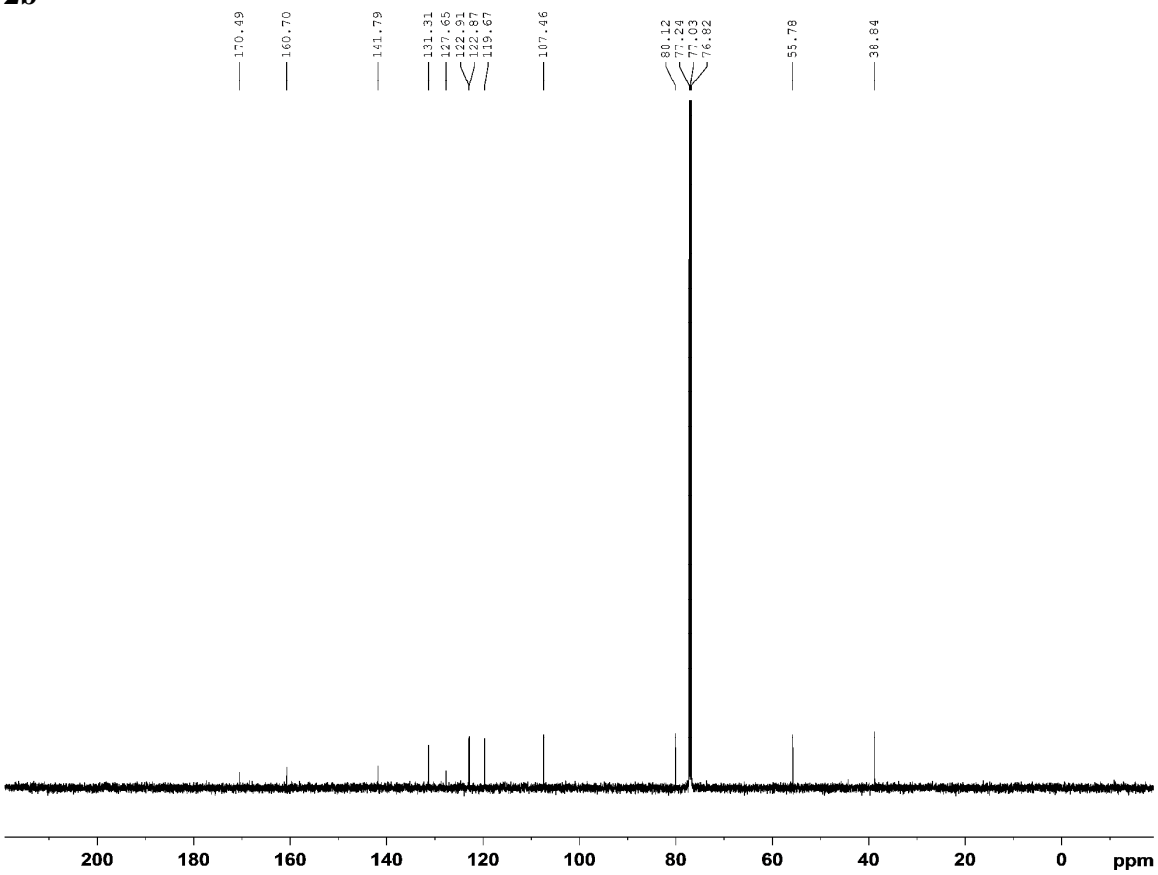
2a



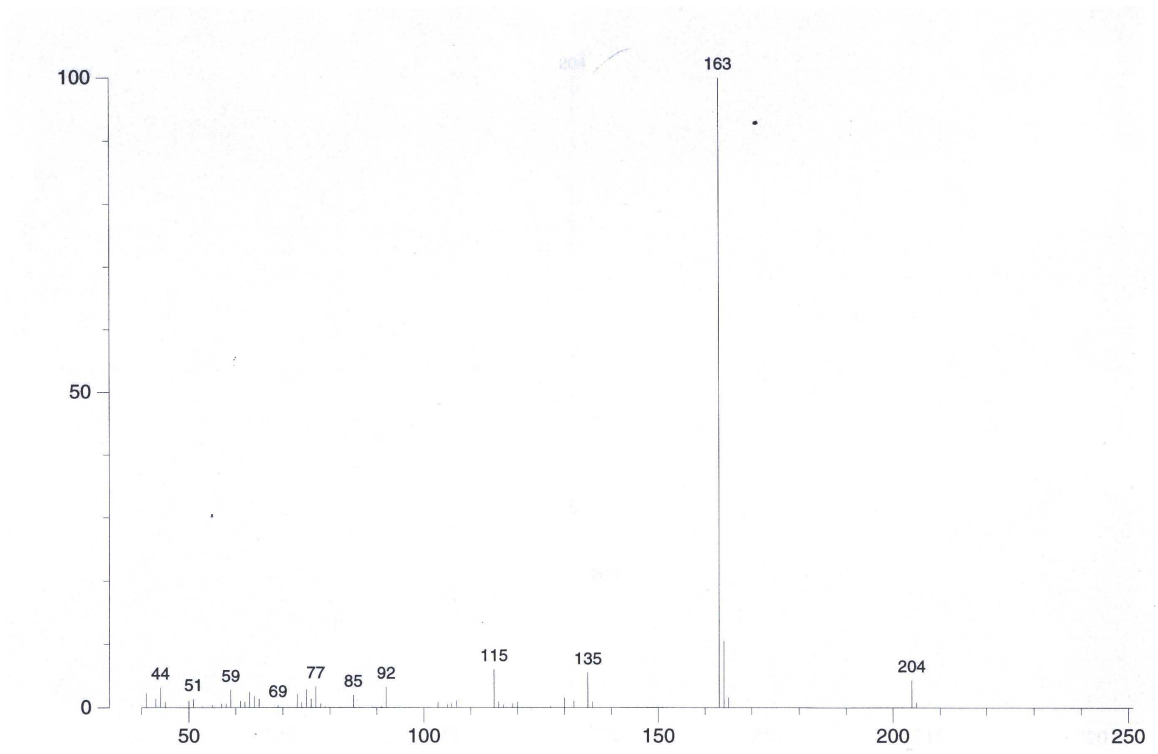
2b


7.355
7.328
7.321
7.260
7.236
7.228
7.209
7.201
5.825
5.803
5.801
5.791
5.779
5.768
5.745
5.734
5.721
5.712
5.710
5.688
5.484
5.465
5.445
5.213
5.208
5.203
5.198
5.169
5.156
5.151
5.146
5.140
5.136
3.868
2.755
2.733
2.731
2.710
2.707
2.704
2.692
2.688
2.685
2.682
2.678
2.673
2.668
2.664
2.652
2.648
2.643
2.630
2.626
2.622
2.617
2.604
2.599
2.595
2.578
2.574
H3CO
O
O
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
0.96
1.06
0.82
2.17
3.37
2.22

2b


170.49
160.70
141.79
131.31
127.65
122.91
122.87
119.67
107.46
80.12
77.24
77.03
76.82
55.78
38.84
200
180
160
140
120
100
80
60
40
20
0
ppm

2b


100
50
0
163
44
51
59
69
77
85
92
115
135
204
50
100
150
200
250

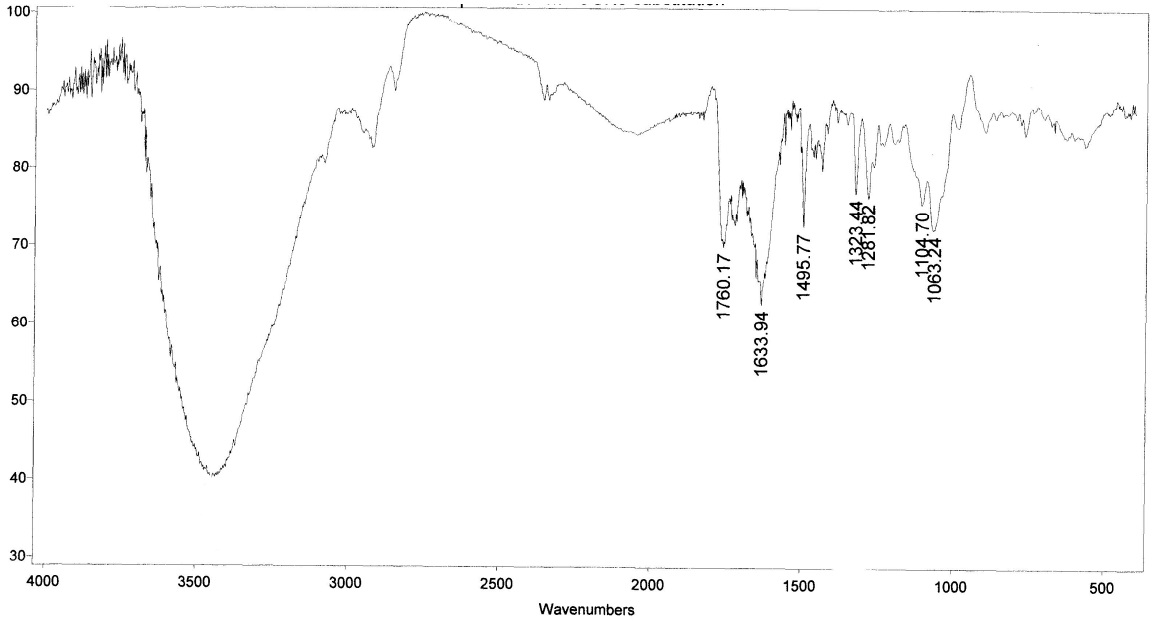
Formula search on scan 1 of 0920pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
204.07817	2265503	-2.34	12	12	3

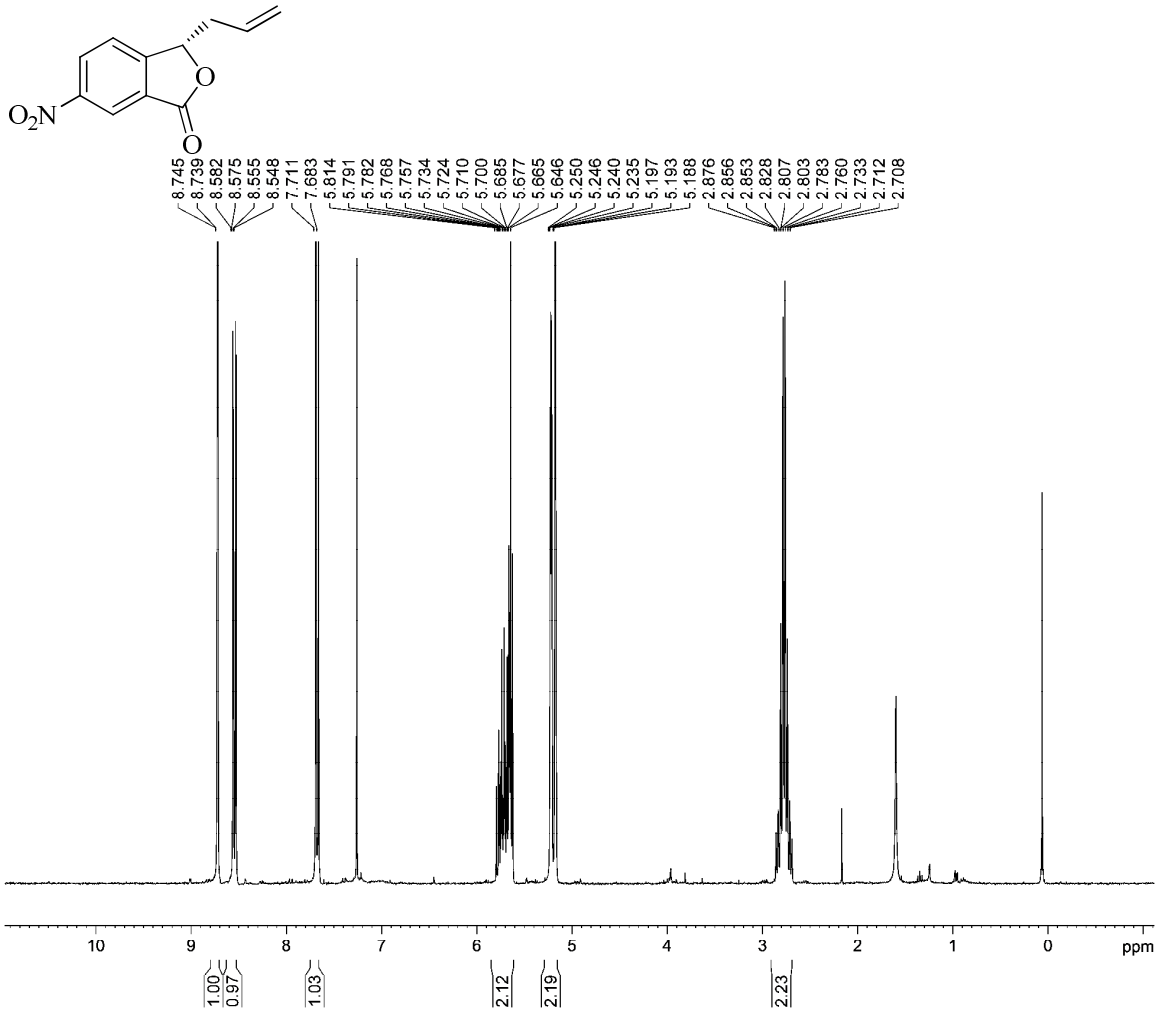
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	204.07864	88.1294	12	0	12	3
2	205.08200	11.8706	11	1	12	3

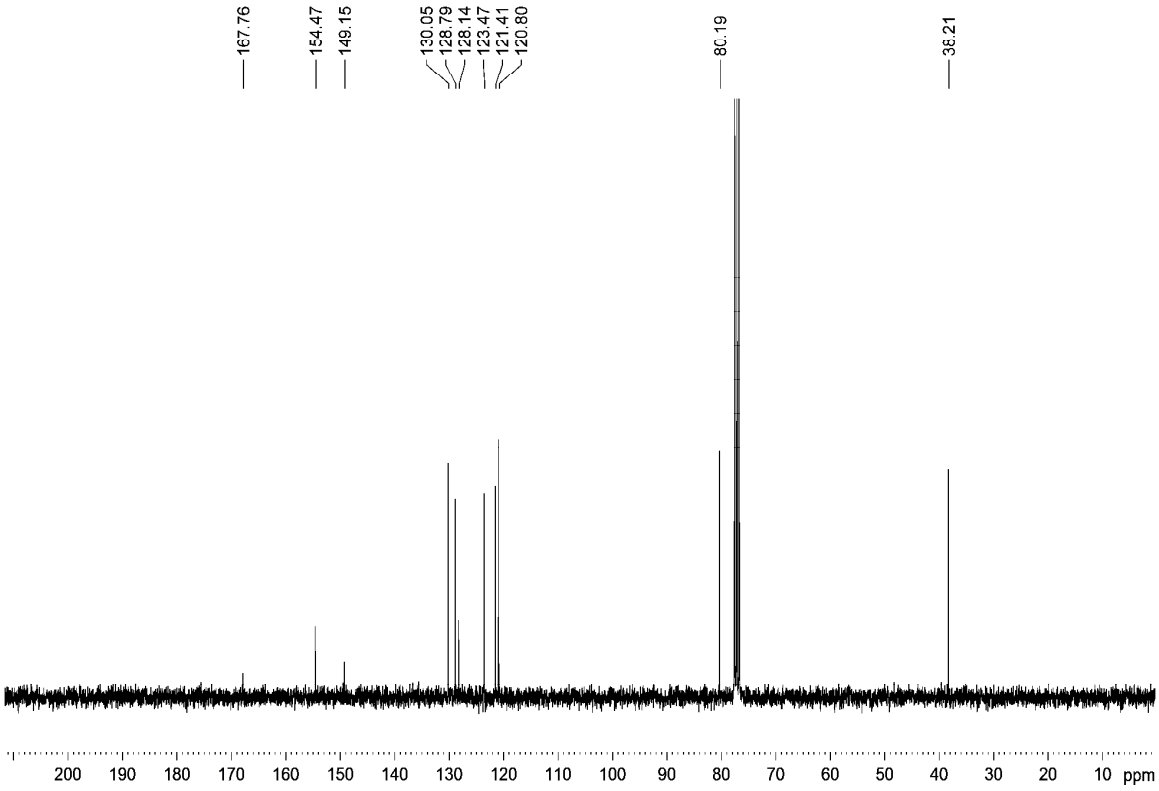
2b



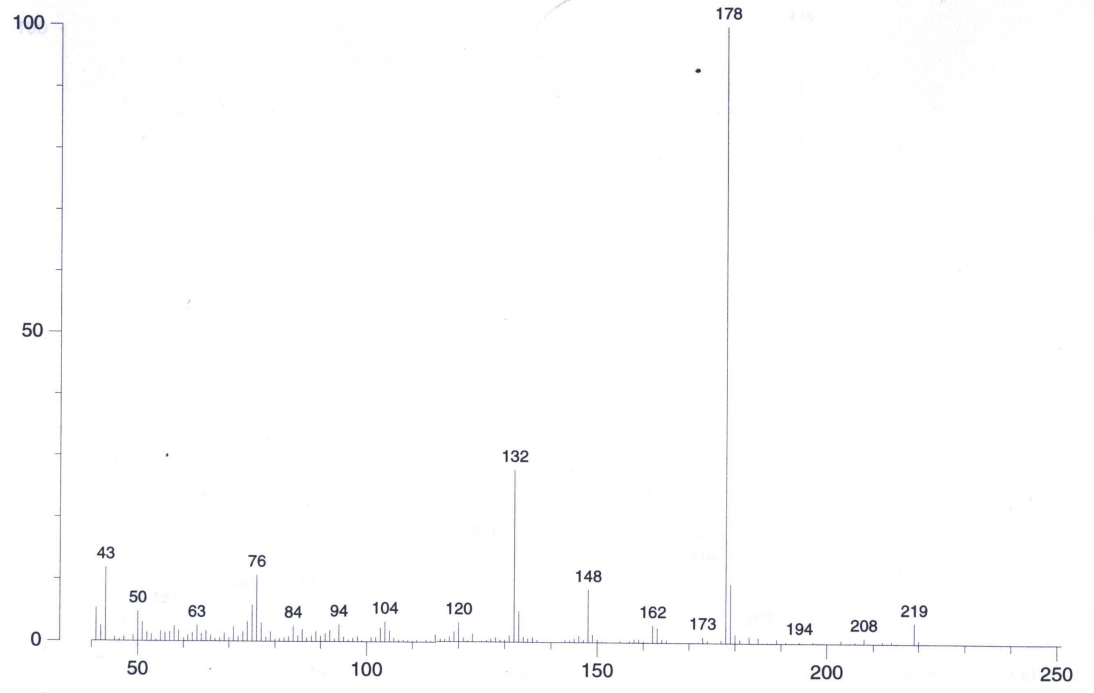
2c


O2N
O
O
8.745
8.739
8.582
8.575
8.555
8.548
7.711
7.683
5.814
5.791
5.782
5.768
5.757
5.734
5.724
5.710
5.700
5.685
5.677
5.665
5.646
5.250
5.246
5.240
5.235
5.197
5.193
5.188
2.876
2.856
2.853
2.828
2.807
2.803
2.783
2.760
2.733
2.712
2.708
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.97
1.03
2.12
2.19
2.23

2c


167.76
154.47
149.15
130.05
128.79
128.14
123.47
121.41
120.80
80.19
38.21
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2c


100
50
0
178
132
43
76
50
63
84
94
104
120
148
162
173
194
208
219
50
100
150
200
250

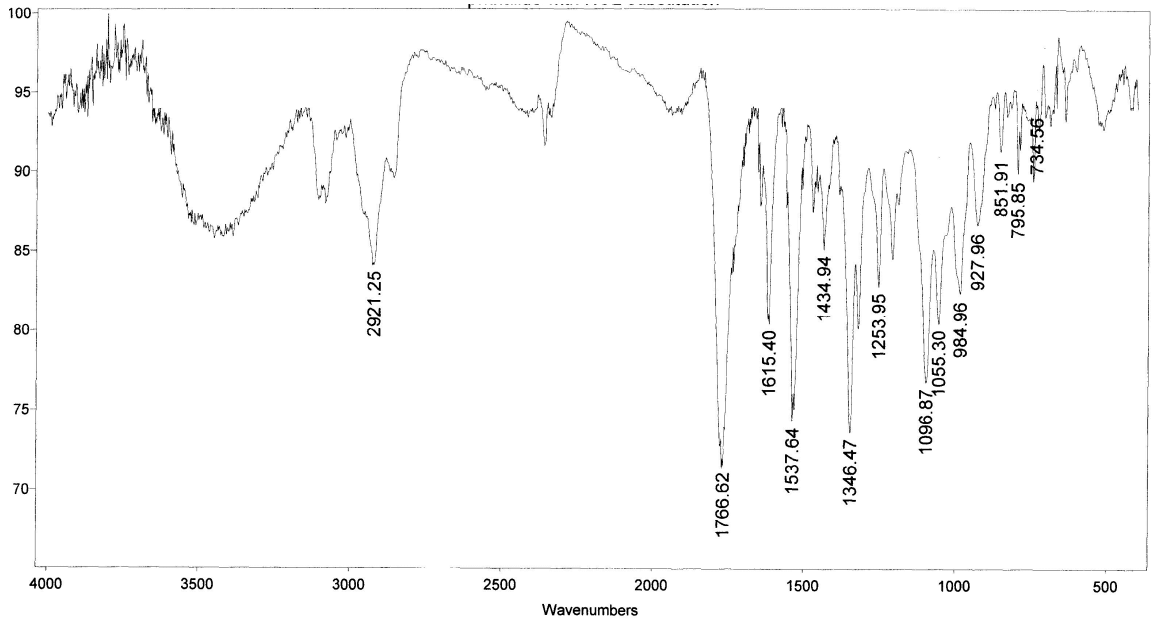
Formula search on scan 1 of 1031pk0010

Mass	Int	Dev ppm	12 C	1 H	14 N	16 O
219.05360	721030	-67.64	15	9	1	1
		41.06	15	7	0	2
		98.47	14	5	1	2
		-55.40	12	11	0	4
		2.01	11	9	1	4

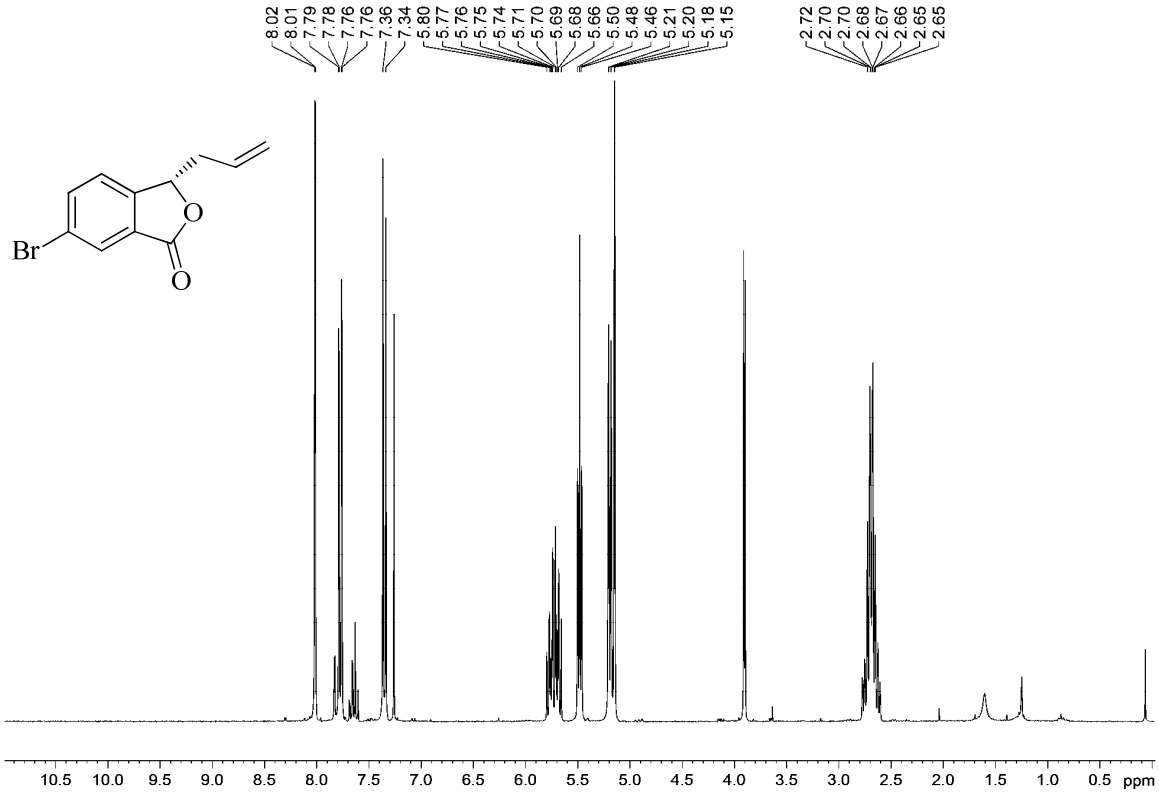
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	14 N	16 O
1	219.05316	89.0099	11	0	9	1	4
2	220.05651	10.9901	10	1	9	1	4

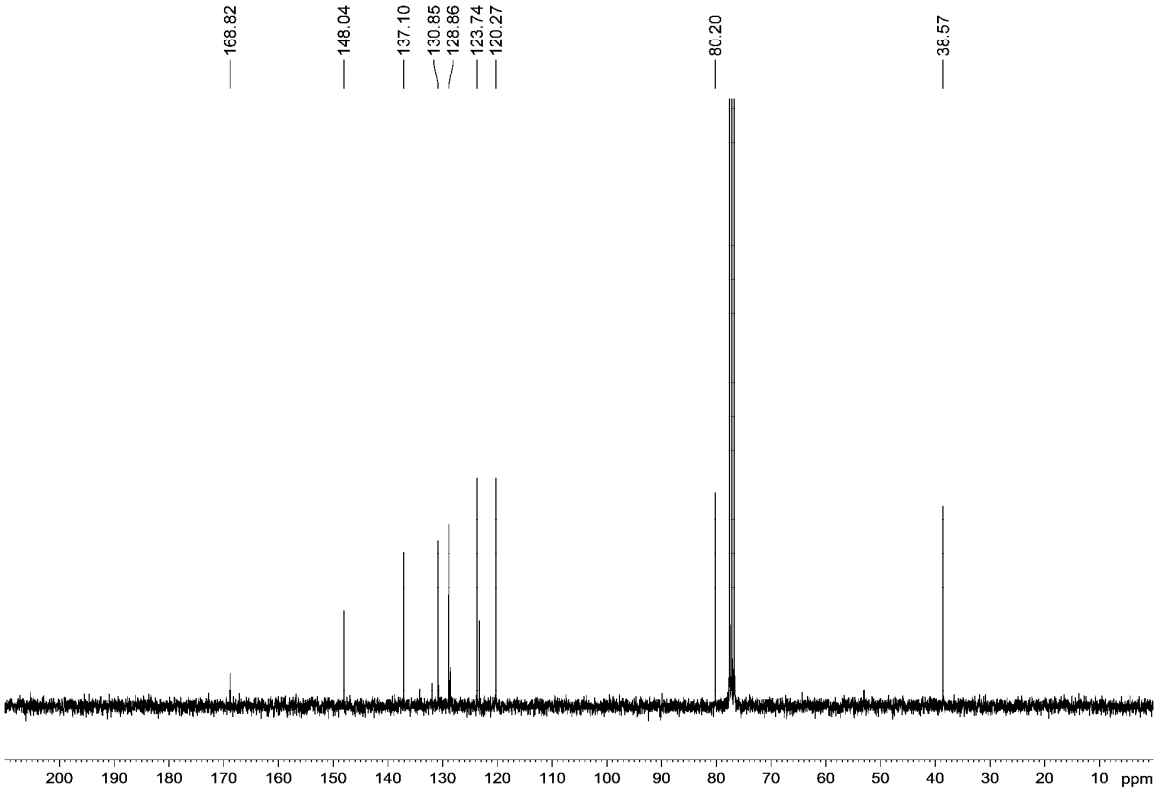
2c



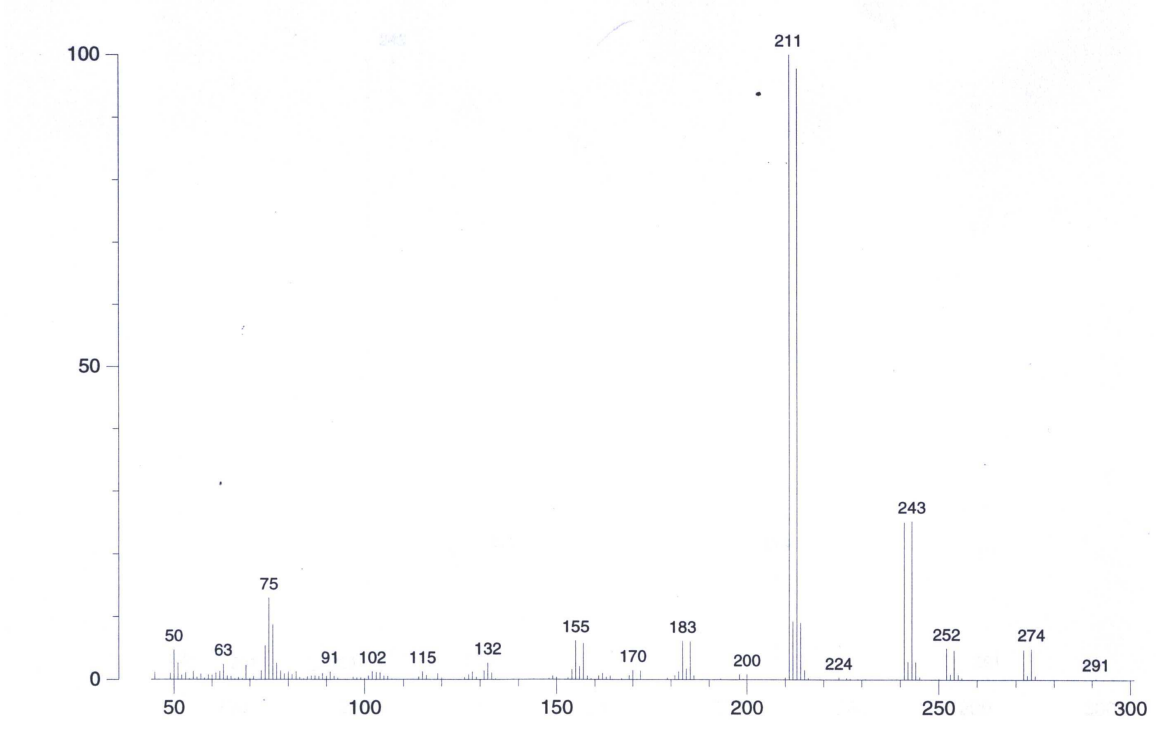
2d


8.02
8.01
7.79
7.78
7.76
7.76
7.36
7.34
5.80
5.77
5.76
5.75
5.74
5.71
5.70
5.69
5.68
5.66
5.50
5.48
5.46
5.21
5.20
5.18
5.15
2.72
2.70
2.70
2.68
2.67
2.66
2.65
2.65
Br
O
O
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

2d


168.82
148.04
137.10
130.85
128.86
123.74
120.27
80.20
38.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2d


100
50
0
211
243
75
50
63
91
102
115
132
155
170
183
200
224
252
274
291
50 100 150 200 250 300

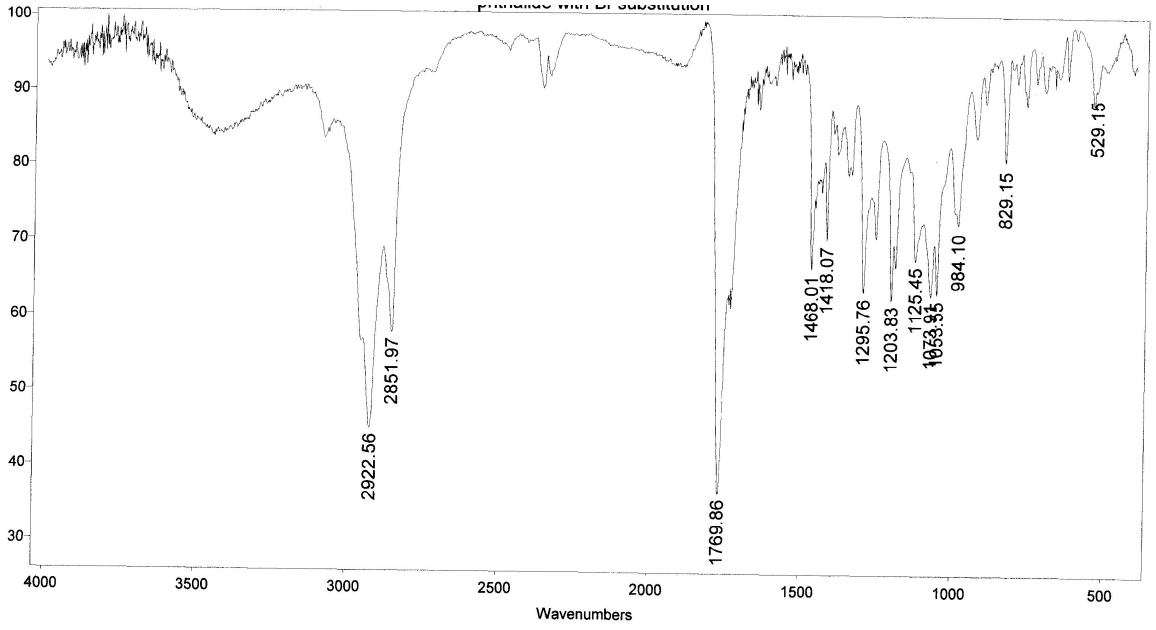
Formula search on scan 1 of 0123pk0003

Mass	Int	Dev ppm	12 C	1 H	16 O	79 Br
251.97894	645799	85.23	14	5	0	1
		1.38	11	9	2	1

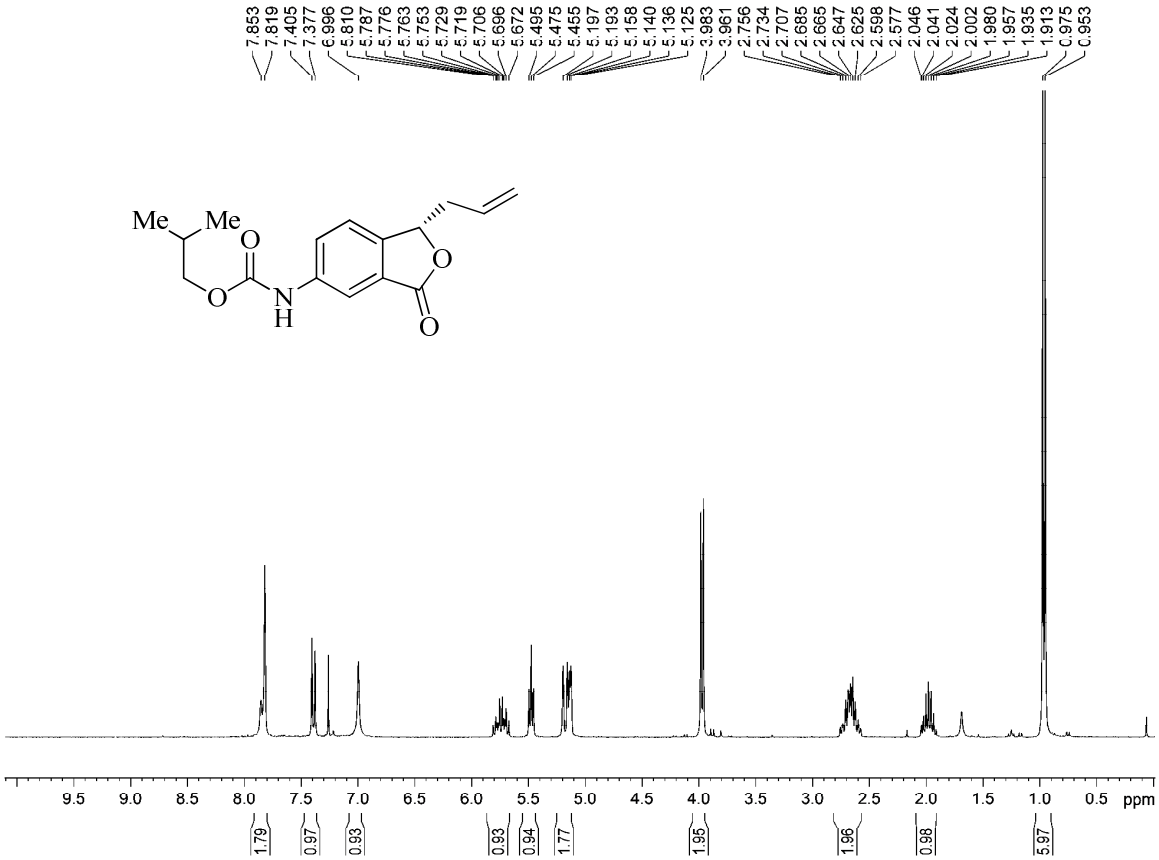
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O	79 Br	81 Br
1	251.97859	44.9856	11	0	9	2	1	0
2	253.97667	44.0243	11	0	9	2	0	1
3	252.98195	5.5544	10	1	9	2	1	0
4	254.98003	5.4357	10	1	9	2	0	1

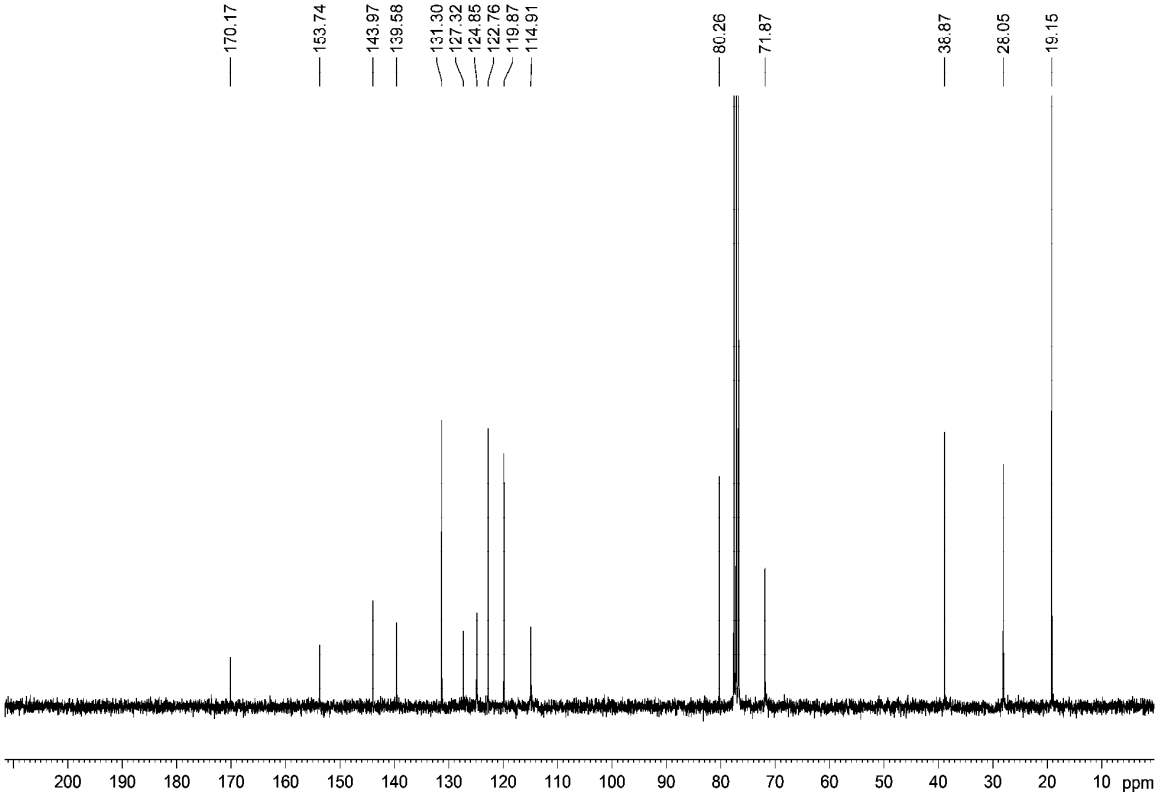
2d



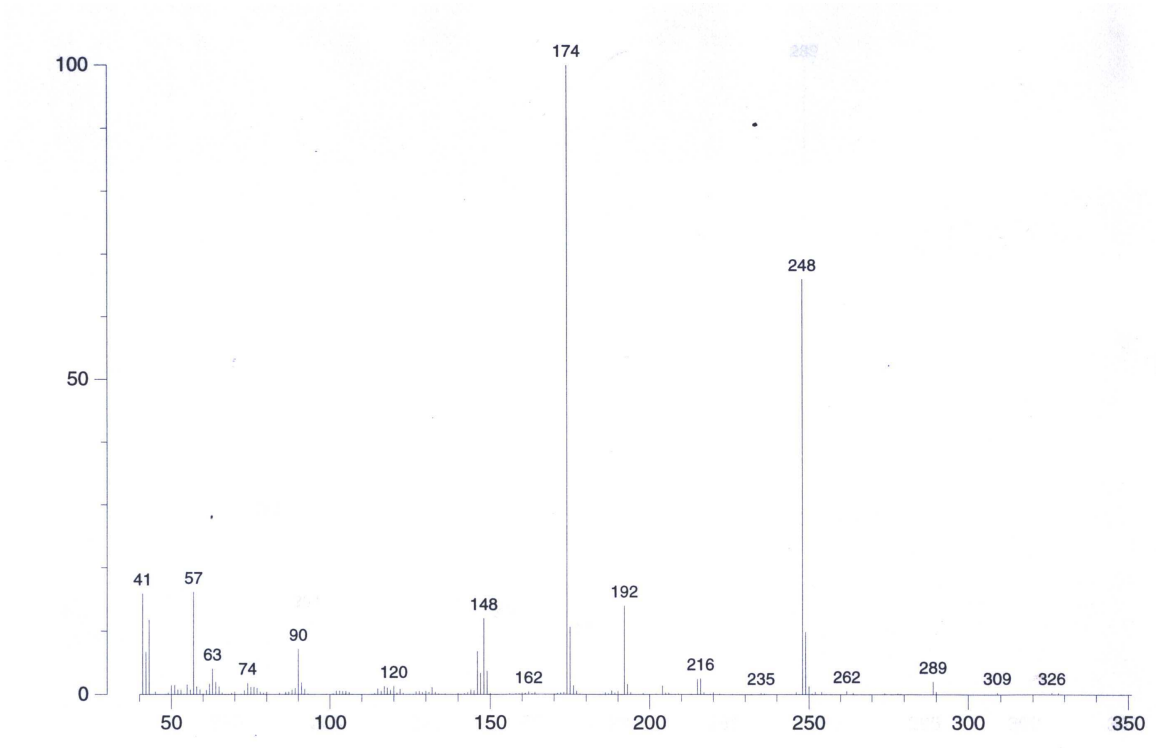
2e


7.853
7.819
7.405
7.377
6.996
5.810
5.787
5.776
5.763
5.753
5.729
5.719
5.706
5.696
5.672
5.495
5.475
5.455
5.197
5.193
5.158
5.140
5.136
5.125
3.983
3.961
2.756
2.734
2.707
2.685
2.665
2.647
2.625
2.598
2.577
2.046
2.041
2.024
2.002
1.980
1.957
1.935
1.913
0.975
0.953
Me
Me
O
O
N
H
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.79
0.97
0.93
0.93
0.94
1.77
1.95
1.96
0.98
5.97

2e


170.17
153.74
143.97
139.58
131.30
127.32
124.85
122.76
119.87
114.91
80.26
71.87
36.87
26.05
19.15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2e


100
50
0
174
248
41
57
63
74
90
120
148
162
192
216
235
262
289
309
326
50 100 150 200 250 300 350

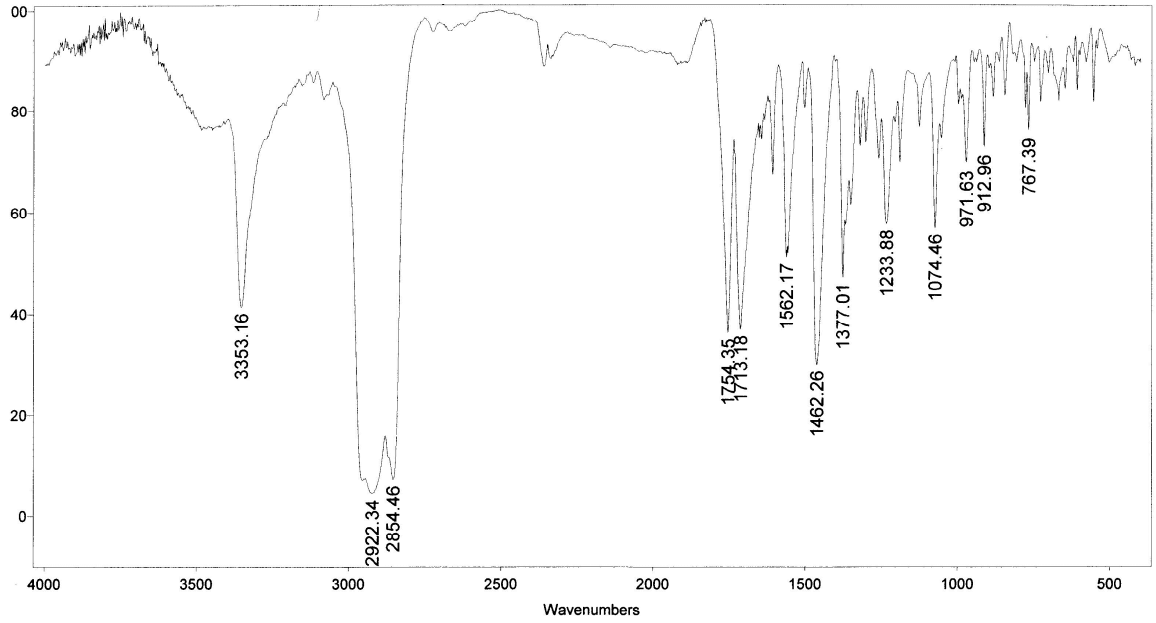
Formula search on scan 1 of 1031pk0009

Mass	Int	Dev ppm	12 C	1 H	14 N	16 O
289.13185	31273	-51.22	20	19	1	1
		31.12	20	17	0	2
		74.62	19	15	1	2
		-41.95	17	21	0	4
		1.54	16	19	1	4

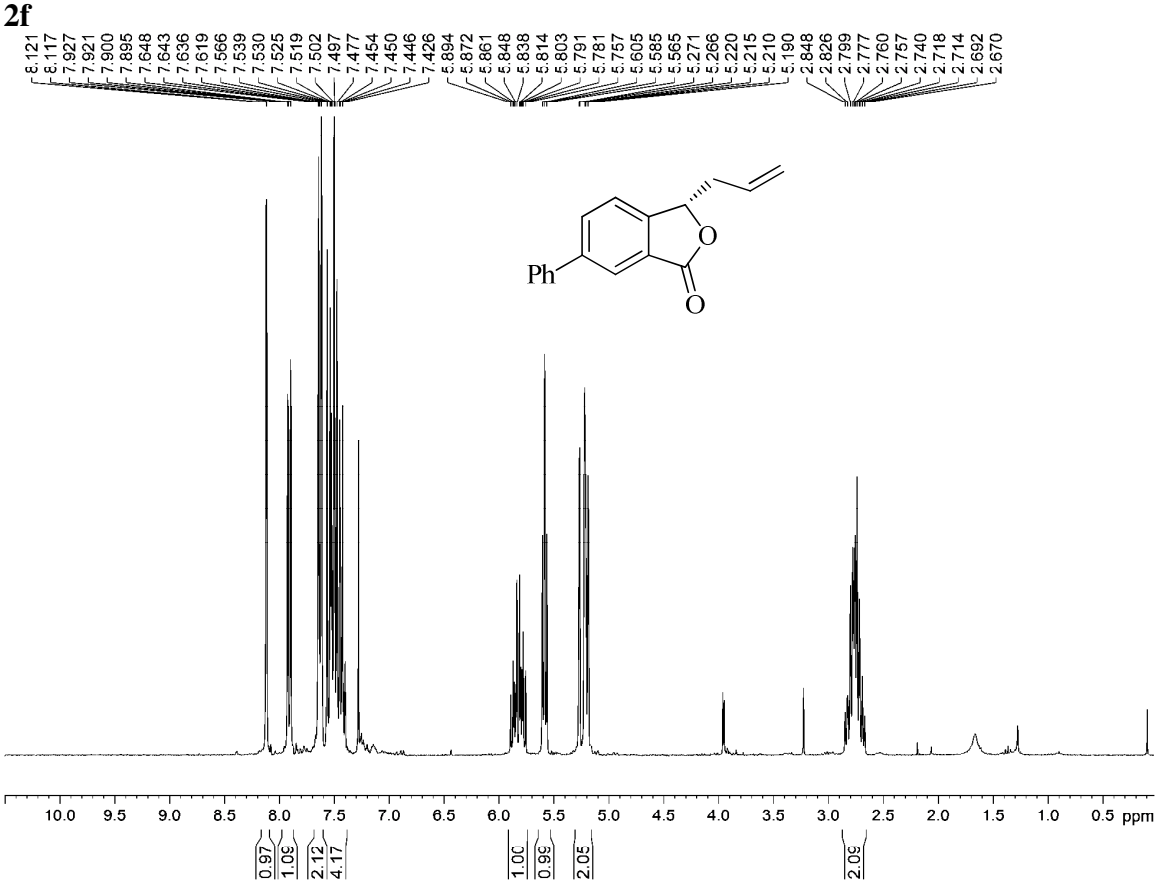
Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	14 N	16 O
1	289.13141	83.7021	16	0	19	1	4
2	290.13476	15.0324	15	1	19	1	4
3	291.13812	1.2655	14	2	19	1	4

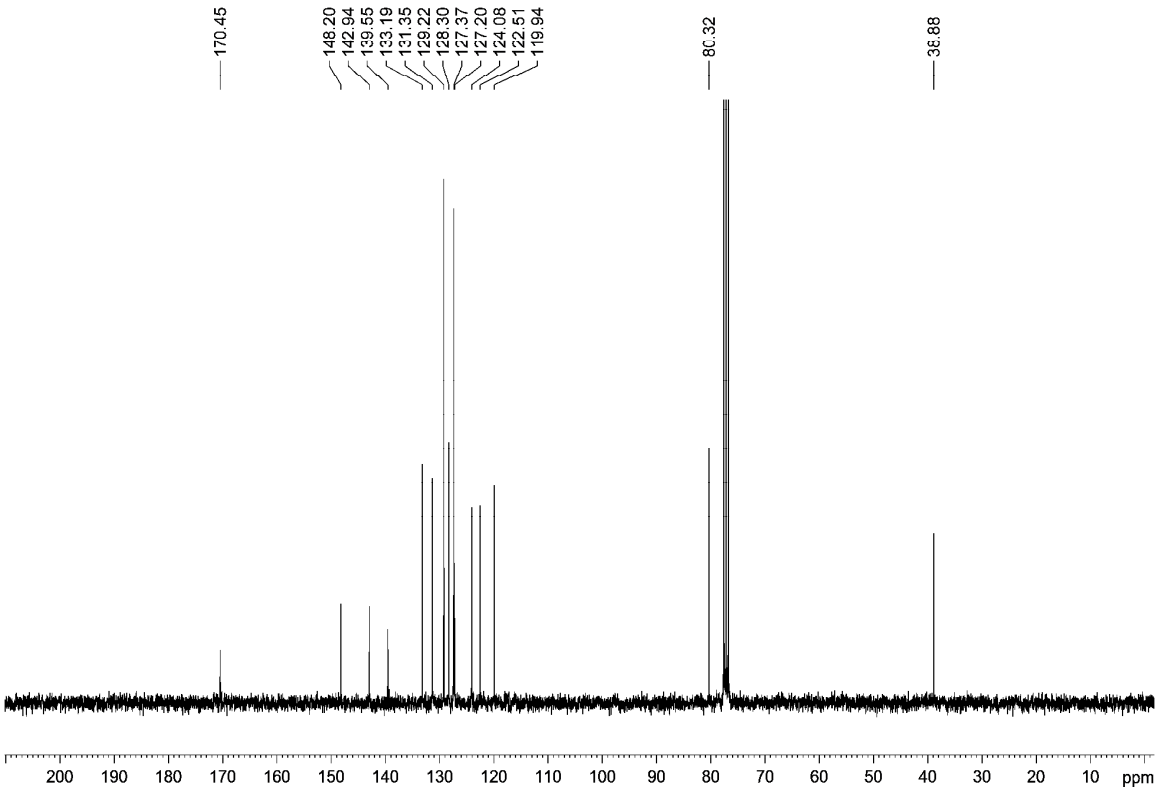
2e



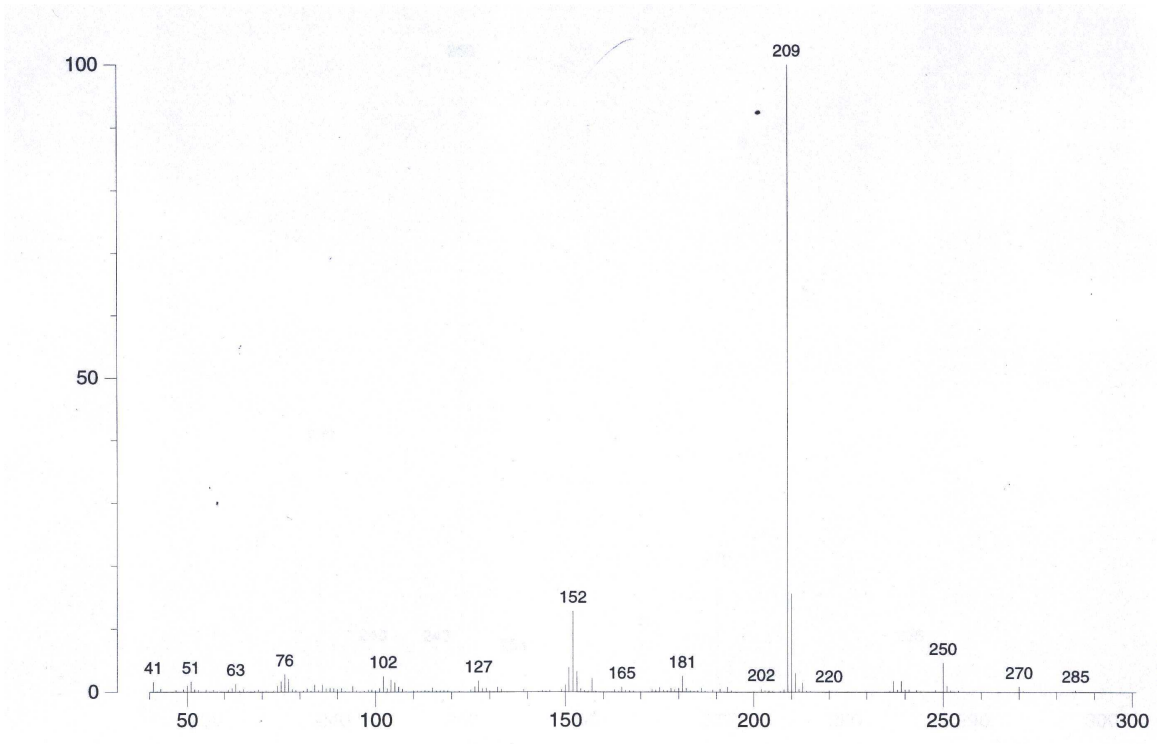
2f


8.121
8.117
7.927
7.921
7.900
7.895
7.648
7.643
7.636
7.619
7.566
7.539
7.530
7.525
7.519
7.502
7.497
7.477
7.454
7.450
7.446
7.426
6.894
6.872
6.861
6.848
6.838
6.814
6.803
6.791
6.781
6.757
6.605
6.585
6.565
6.271
6.266
6.220
6.215
6.210
6.190
2.848
2.826
2.799
2.777
2.760
2.757
2.740
2.718
2.714
2.692
2.670
Ph
O
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
1.00
2.12
4.17
1.00
0.99
2.05
2.05

2f


170.45
148.20
142.94
139.55
133.19
131.35
129.22
128.30
127.37
127.20
124.08
122.51
119.94
80.32
36.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

2f


100
50
0
209
152
41 51 63 76 102 127 165 181 202 220 250 270 285
50 100 150 200 250 300

Formula search on scan 1 of 0113pk0001

Mass	Int	Dev ppm	12 C	1 H	16 O
250.06841	507	-39.34	20	10	0
		21.66	16	10	3
250.09924	3169199	83.94	20	10	0
		-0.54	17	14	2
		-85.03	14	18	4

Calculated isotope distribution :

	Accurate Mass	% Rel. Abundance	12 C	13 C	1 H	16 O
1	250.09938	82.7847	17	0	14	2
2	251.10273	15.7968	16	1	14	2
3	252.10609	1.4185	15	2	14	2

2f