Supporting Information

Facile and Effective Copper-Mediated Cyclization Reaction of Cyclopropylideneacetic Acids (or Esters) and Cyclopropylideneacetonitriles

Xian Huang*[,a,b] , Hongwei Zhou[a] and Wanli Chen[a]

[a]*Department of Chemistry, Zhejiang University(Campus Xixi), Hangzhou 310028, P.R. China*

[b]*State Key Laborary of Oganometallic Chemistry, Shanghai Institue of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P.R. China*

Table of Contents:

Experimental Section

Typical experimental procedure

General. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on spectrometer spectra (400M Hz) with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. All the reactions in this paper were performed directly in air. Solvents except for diethyl ether used in the reaction described here were distilled before use.

Typical Procedure for the synthesis of 3, 4 and 8. Condition A. A solution of **2a** (63 mg, 0.5 mmol) with $CuBr_2$ (450 mg, 2.0 mmol) in CH_3CN/H_2O (4:1, 10 mL) was stirred at 85°C (reflux) for 10 h. The mixture was then diluted with 20mL of saturated NH_4Cl and extracted three times with diethyl ether. The ether phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/diether ether (2:1) as the eluent to afford 70 mg (79%) of **3a**.

Condition B. A solution of **2a** (63 mg, 0.5 mmol) with I_2 (510 mg, 2.0 mmol) and freshly prepared CuI (10 mg, 0.05 mmol) in CH_3CN/H_2O (4:1, 10 mL) was stirred at 85°C (reflux) for 10 h. The mixture was then diluted with 20mL of saturated $Na_2S_2O_3$ and extracted three times with diethyl ether. The ether phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via

chromatography on silica gel with *n*-hexane/diether ether (2:1) as the eluent to afford 55 mg (49%) of **4a**.

4-Bromomethyl-2(5*H*)-furanone (3a): ^{1}H NMR (400M Hz, $CDCl_3$) δ 6.14 (d, 1H, *J* = 1.15 Hz), 4.94 (t, 2H, *J* = 1.10 Hz), 4.23 (s, 2H) ^{13}C NMR (100M Hz, $CDCl_3$) δ 172.5, 163.2, 118.9, 71.9, 22.5. EIMS m/z (relative intensity, %) 178 [M^+ (^{81}Br), 6.53], 176 [M^+ (^{79}Br), 6.27]. IR (neat) 1785, 1751 cm^{-1}; Anal. Calcd. For $C_5H_5BrO_2$: C, 33.93; H, 2.85. Found: C, 33.81; H, 2.81.

4-Iodomethyl-2(5*H*)-furanone (3b): ^{1}H NMR (400M Hz, $CDCl_3$) δ 6.14 (m, 1H), 5.02 (t, 2H, *J* = 0.76 Hz), 4.15 (d, 2H, *J* = 0.80 Hz) EIMS m/z (relative intensity, %) 224 [M^+, 46.75]. IR (neat), 1780, 1740 cm^{-1}; Anal. Calcd. For $C_5H_5IO_2$: C, 26.81; H, 2.25. Found: C, 26.70; H, 2.22.

4-Iodo-5,6-dihydro-2*H*-pyran-2-one (4a): ^{1}H NMR (400M Hz, $CDCl_3$) δ 6.77(s, 1H), 4.37-4.40 (t, 3H, *J* = 6.12 Hz), 2.91-2.95 (m, 2H) EIMS m/z (relative intensity, %) 224 [M^+, 4.69]. IR (neat), 1716 cm^{-1}; Anal. Calcd. For $C_5H_5BrO_2$: C, 26.81; H, 2.25. Found: C, 26.90; H, 2.28.

3-Methyl-4-bromo-5,6-dihydro-2*H*-pyran-2-one (4b): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.36-4.39 (t, 2H, *J* = 6.25 Hz), 2.91-2.95 (m, 2H), 2.06-2.07 (t, 3H, *J* = 1.89 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 162.7, 138.4, 115.8, 65.4, 35.3, 16.9. EIMS m/z (relative intensity, %) 192 [M^+ (^{81}Br), 22.61], 190 [M^+ (^{79}Br), 23.25]. IR (neat) 1716cm^{-1}; Anal. Calcd. For $C_6H_7BrO_2$: C, 37.73; H, 3.69. Found: C, 37.59; H, 3.65.

3-Methyl-4-iodo-5,6-dihydro-2*H*-pyran-2-one (4c): ^{1}H NMR (400M Hz, $CDCl_3$) δ

4.31-4.34 (t, 2H, *J* = 6.14 Hz), 2.99-3.03 (m, 2H), 2.14-2.15 (t, 3H, *J* = 1.87 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 159.9, 133.8, 66.0, 39.3, 21.9. EIMS m/z (relative intensity, %) 238 [M^+, 2.56]. IR (neat) 1714cm^{-1}; Anal. Calcd. For $C_6H_7IO_2$: C, 30.28; H, 2.96. Found: C, 30.15; H, 2.93.

3-Ethyl-4-bromo-5,6-dihydro-2*H*-pyran-2-one (4d): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.34-4.37 (t, 2H, *J* = 6.18 Hz), 2.90-2.94 (t, 2H, *J* = 6.25 Hz), 2.51-2.56 (q, 2H, *J* = 7.48 Hz), 1.07-1.10 (t, 2H, *J* = 7.46 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 161.7, 137.3, 133.5, 64.8, 34.9, 24.1, 11.7. EIMS m/z (relative intensity, %) 206 [M^+ (^{81}Br), 37.15], 204 [M^+ (^{79}Br), 36.36]. IR (neat) 1717cm^{-1}; Anal. Calcd. For $C_7H_9BrO_2$: C, 41.00; H, 4.42. Found: C, 41.15; H, 4.39.

3-Ethyl-4-iodo-5,6-dihydro-2*H*-pyran-2-one (4e): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.27-4.30 (t, 2H, *J* = 6.09 Hz), 2.98-3.01 (t, 2H, *J* = 6.20 Hz), 2.51-2.56 (q, 2H, *J* = 7.48 Hz) 1.07-1.09 (t, 3H, J = 7.46 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 159.4, 138.8, 115.1, 66.0, 39.4, 29.3, 11.8. EIMS m/z (relative intensity, %) 253 [M^++1, 34.93], 252 [M^+, 38.43]. 41 [100] IR (neat) 1714 cm^{-1}; Anal. Calcd. For $C_7H_9IO_2$: C, 33.36; H, 3.60. Found: C, 33.24; H, 3.56.

3-*n*-Propyl-4-bromo-5,6-dihydro-2*H*-pyran-2-one (4f): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.34-4.37 (t, 2H, *J* = 6.25 Hz), 2.91-2.95 (t, 2H, *J* = 6.27 Hz), 2.48-2.52 (t, 2H, *J* = 7.84 Hz), 1.50-1.56 (m, 2H), 0.94-0.98 (t, 3H, *J* = 7.38 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 162.3, 138.2, 132.9, 65.3, 35.5, 32.9, 21.2, 13.8. EIMS m/z (relative intensity, %) 220 [M^+ (^{81}Br), 29.93], 218 [M^+ (^{79}Br), 30.23]. IR (neat) 1714 cm^{-1};

Anal. Calcd. For $C_8H_{11}BrO_2$: C, 43.86; H, 5.06. Found: C, 43.62; H, 5.11.

3-*n*-Propyl-4-iodo-5,6-dihydro-2*H*-pyran-2-one (4g): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.28-4.31 (t, 2H, *J* = 6.19 Hz), 3.00-3.03 (t, 2H, *J* = 6.09 Hz), 2.50-2.54 (t, 2H, *J* = 7.96 Hz), 1.50-1.56 (m, 2H), 0.96-0.99 (t, 3H, *J* = 7.35 Hz) ^{13}C NMR (100M Hz, $CDCl_3$) δ 160.0, 138.4, 116.1, 66.5, 40.2, 38.0, 21.4, 13.9. EIMS m/z (relative intensity, %) 266 [M^+, 25.41]. IR (neat) 1714 cm^{-1}; Anal. Calcd. For $C_8H_{11}IO_2$: C, 36.11; H, 4.17. Found: C, 36.32; H, 4.10

3-Benzyl-4-bromo-5,6-dihydro-2*H*-pyran-2-one (4h): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.19-7.33 (m, 5H), 4.33-4.36 (t, 2H, *J* = 6.28 Hz), 3.90 (s, 2H), 2.96-2.99 (t, 2H, *J* = 6.31 Hz), ^{13}C NMR (100M Hz, $CDCl_3$) δ 161.7, 138.8, 137.3, 131.4, 128.2, 127.9, 126.0, 64.7, 35.8, 25.0. EIMS m/z (relative intensity, %) 268 [M^+ (^{81}Br), 13.02], 266 [M^+ (^{79}Br), 12.99]. IR (neat) 1718cm^{-1}; Anal. Calcd. For $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 53.77; H, 4.22.

3-Benzyl-4-iodo-5,6-dihydro-2H-pyran-2-one (4i): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.19-7.35 (m, 5H), 4.28-4.31(t, 2H, *J* = 6.09 Hz), 3.95(s, 2H), 3.06-3.09(t, 2H, *J* = 6.15 Hz), ^{13}C NMR (100M Hz, $CDCl_3$) δ 159.4, 137.2, 137.1, 128.1, 127.9, 126.1, 116.9, 65.8, 40.7, 39.7. EIMS m/z (relative intensity, %) 314[M^+, 15.09]. IR (neat) 1717cm^{-1}; Anal. Calcd. For $C_{12}H_{11}IO_2$: C, 45.88; H, 3.53. Found: C, 46.02; H, 3.49.

6-Bromo-4,5,6,7-tetrahydro-3*H*-cyclopenta[c]-pyran-1-one (8a): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.77-4.78 (m, 1H), 3.76-3.82(m, 2H), 3.54-3.61(m, 4H), 2.87-3.21(m, 2H) ^{13}C NMR (100M Hz, $CDCl_3$) δ 165.1, 141.4, 128.2, 73.4, 38.4, 37.2, 34.4, 29.4.

EIMS m/z (relative intensity, %) 218 [M^+ (^{81}Br), 6.63], 216 [M^+ (^{79}Br), 6.84]. IR (neat) 1754, 1652 cm^{-1}; Anal. Calcd. For $C_8H_9BrO_2$: C, 44.27; H, 4.18. Found: C, 44.09; H, 4.23.

6-Iodo-4,5,6,7-tetrahydro-3*H*-cyclopenta[c]-pyran-1-one (8b): ^{1}H NMR (400M Hz, $CDCl_3$) δ 4.56-4.58 (m, 1H), 3.84-3.88(m, 2H), 3.30-3.44(m, 4H), 2.68-3.07(m, 2H) ^{13}C NMR (100M Hz, $CDCl_3$) δ 162.8, 133.6, 125.0, 73.4, 44.1, 42.2, 8.29, 2.85. EIMS m/z (relative intensity, %) 264 [M^+, 14.79]. IR (neat) 1749, 1632 cm^{-1}; Anal. Calcd. For $C_8H_9BrO_2$: C, 36.39; H, 3.44. Found: C, 36.18; H, 3.48.

Typical Procedure for the synthesis of 6. Condition A. A solution of **5a** (85 mg, 0.5 mmol) with $CuBr_2$ (450 mg, 2.0 mmol) and LiBr (174 mg, 2.0 mmol) in CH_3CN/H_2O (4:1, 10 mL) was stirred at 85°C (reflux) for 48 h. The mixture was then diluted with 20mL of saturated NH_4Cl and extracted three times with diethyl ether. The ether phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/diether ether (3:2) as the eluent to afford 76 mg (57%) of **6a**.

Condition B. A solution of **5a** (85 mg, 0.5 mmol) with I_2 (510 mg, 2.0 mmol), freshly prepared CuI (10 mg, 0.05 mmol) and LiI (268 mg, 2.0 mmol) in CH_3CN/H_2O (4:1, 10 mL) was stirred at 85°C (reflux) for 56 h. The mixture was then diluted with 20mL of saturated $Na_2S_2O_3$ and extracted three times with diethyl ether. The ether phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified

via chromatography on silica gel with *n*-hexane/diether ether (3:2) as the eluent to afford 85 mg (54%) of **6b**.

3-Benzyl-4-bromo-5, 6- dihydro-2 (1*H*)-pyridinone (6a): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.26-7.34 (m, 5H), 3.93-3.96 (t, 2H, *J* = 6.0 Hz), 3.76 (s, 2H), 3.11-3.14 (t, 2H, *J* = 6.0 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 144.0, 135.0, 129.3, 129.0, 117.1, 116.7, 60.7, 44.6, 40.6. EIMS m/z (relative intensity, %) 267 [M^+ (^{81}Br), 4.23], 265 [M^+ (^{79}Br), 5.33] IR (neat) 3221, 1677 cm^{-1}; Anal. Calcd. For $C_{12}H_{12}BrNO$: C, 54.16; H, 4.54; N, 5.26. Found: C, 54.32; H, 4.41; N, 5.09.

3-Benzyl-4-iodo-5, 6- dihydro-2 (1*H*)-pyridinone (6b): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.25-7.33 (m, 5H), 3.87-3.90 (t, 2H, *J* = 6.1 Hz), 3.79 (s, 2H), 3.14-3.17 (t, 2H, *J* = 6.1 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 143.1, 134.6, 129.0, 128.7, 127.4, 116.7, 111.7, 59.2, 44.2, 39.9. EIMS m/z (relative intensity, %) 313 [M^+, 3.29], IR (neat) 3219, 1676 cm^{-1}; Anal. Calcd. For $C_{12}H_{12}INO$: C, 46.03; H, 3.86; N, 4.47. Found: C, 46.22; H, 3.72; N, 4.39.

3-Methyl-4-bromo-5, 6-dihydro-2 (1*H*)-pyridinone (6c): ^{1}H NMR (400M Hz, $CDCl_3$) δ 3.88-3.91 (t, 2H, *J* = 6.1 Hz), 2.98-3.02 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 146.0, 136.2, 125.7, 60.8, 41.6, 23.5. EIMS m/z (relative intensity, %) 191 [M^+ (^{81}Br), 6.79], 189 [M^+ (^{79}Br), 7.11] IR (neat) 3217, 1672 cm^{-1}; Anal. Calcd. For C_6H_8BrNO: C, 37.92; H, 4.24; N, 7.37. Found: C, 37.79; H, 4.37; N, 7.25.

3-Methyl-4-iodo-5, 6- dihydro-2 (1*H*)-pyridinone (6d): ^{1}H NMR (400M Hz, $CDCl_3$) δ 3.84-3.87 (t, 2H, *J* = 6.1 Hz), 3.00-3.04 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 145.0, 130.6, 116.9, 61.0, 40.2, 22.9. EIMS m/z (relative intensity, %) 237 [M^+, 7.26], IR (neat) 3216, 1672cm^{-1}; Anal. Calcd. For C_6H_8INO: C, 30.40; H, 3.40; N, 5.91. Found: C, 30.28; H, 3.53; N, 5.79.

3-Ethyl-4-bromo-5, 6-dihydro-2 (1*H*)-pyridinone (6e): ^{1}H NMR (400M Hz, $CDCl_3$) δ 3.86-3.89 (t, 2H, *J* = 6.2 Hz), 2.89-2.92 (t, 2H, *J* = 6.2 Hz), 2.52-2.57 (q, 2H, *J* = 7.4 Hz), 1.04-1.08 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 146.7, 136.1, 124.9, 59.2, 39.6, 23.9, 12.1. EIMS m/z (relative intensity, %) 205 [M^+ (^{81}Br), 7.27], 203 [M^+ (^{79}Br), 8.14]. IR (neat) 3220, 1674 cm^{-1}; Anal. Calcd. For $C_7H_{10}BrNO$: C, 41.20; H, 4.94; N, 6.86. Found: C, 41.33; H, 4.81; N, 6.75.

3-Ethyl-4-iodo-5, 6- dihydro-2 (1*H*)-pyridinone (6f): ^{1}H NMR (400M Hz, $CDCl_3$) δ 3.84-3.87 (t, 2H, *J* = 6.2 Hz), 2.87-2.90 (t, 2H, *J* = 6.2 Hz), 2.49-2.54 (q, 2H, *J* = 7.5 Hz), 1.01-1.05 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 146.0, 135.7, 115.8, 60.2, 39.5, 22.4, 12.5. EIMS m/z (relative intensity, %) 251 [M^+, 7.15], IR (neat) 3218, 1673cm^{-1}; Anal. Calcd. For $C_7H_{10}INO$: C, 33.49; H, 4.01; N, 5.58. Found: C, 33.61; H, 4.11; N, 5.45.

Typical Procedure for the synthesis of 7. To a mixture of **4a** (112mg, 0.5mmol), 1-hexyne (50mg, 0.6mmol), and K_2CO_3 (140mg, 1.0mmol) in CH_3CN (10ml) was added $PdCl_2(PPh_3)_2$ (7mg, 0.01mmol) and copper iodide (2mg, 0.01mmol) under N_2

and the reaction was stirred at 50°C for 12h. The mixture was filtered through a short column of silica gel and evaporated. The residue was purified via chromatography on silica gel (eluent: petroleum ether/ethyl acetate =10/1) to afford 81.9 mg of **7a**.

4-Hex-1-ynyl-5,6-dihydro-2*H*-pyran-2-one (7a): ^{1}H NMR (400M Hz, $CDCl_3$) δ 6.10 (s, 1H), 4.39-4.42 (t, 2H, *J* = 6.2 Hz), 2.52-2.55 (m, 2H), 2.42-2.46 (t, 2H, *J* = 7.0 Hz), 1.57-1.59 (m, 2H), 1.43-1.49 (m, 2H), 0.95-0.96 (m, 2H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 164.4, 140.6, 122.9, 103.7, 78.7, 66.4, 30.6, 29.4, 22.3, 19.8, 13.9. EIMS m/z (relative intensity, %) 179 [M^++1, 100], 178 [M^+, 13.9]. IR (neat) 2224, 1702cm^{-1}; Anal. Calcd. For $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.89; H, 7.79.

4-Phenyethynyl-5,6-dihydro-2*H*-pyran-2-one (7b): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.48-7.50 (m, 2H), 7.32-7.41 (m, 3H), 6.18 (s, 1H), 4.37-4.40 (t, 2H, *J* = 6.1 Hz), 2.62-2.64 (m, 2H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 164.1, 139.5, 132.4, 130.3, 129.0, 123.6, 121.6, 100.8, 86.6, 66.4, 29.2. EIMS m/z (relative intensity, %) 198 [M^+, 100]. IR (neat) 2207, 1704cm^{-1}; Anal. Calcd. For $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.51; H, 5.20.

3-Methyl-4-hex-1-ynyl-5,6-dihydro-2*H*-pyran-2-one (7c): δ 4.31-4.34 (t, 2H, *J* = 6.2 Hz), 2.50-2.53 (m, 2H), 2.44-2.47 (t, 2H, *J* = 7.0 Hz), 2.06 (s, 3H), 1.56 -1.60 (m, 2H), 1.44-1.48(m, 2H), 0.93-0.96 (t, 2H *J* = 7.3 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 164.8, 136.5, 133.1, 105.3, 77.9, 65.6, 30.4, 29.6, 23.1, 21.9, 19.6, 13.5, 13.3. EIMS m/z (relative intensity, %) 193 [M^++1, 100], 192 [M^+, 29.6]. IR (neat) 2226, 1703cm^{-1}; Anal. Calcd. For $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.77; H, 8.28.

3-Methyl-4-phenyethynyl-5,6-dihydro-2*H*-pyran-2-one (7d): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.48-7.51 (m, 2H), 7.36-7.40 (m, 3H), 4.38-4.41 (t, 2H, *J* = 6.2 Hz), 2.63-2.65 (m, 2H). 2.17-2.18 (m, 3H).^{13}C NMR (100M Hz, $CDCl_3$) δ 164.4, 138.5, 132.5, 131.7, 129.5, 128.8, 122.6, 101.2, 86.5, 66.1, 29.8, 28.8. EIMS m/z (relative intensity, %) 212 [M^+, 100]. IR (neat) 2205, 1703cm^{-1}; Anal. Calcd. For $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.01; H, 5.58.

3-Methyl-4-hept-1-ynyl-5,6-dihydro-2*H*-pyran-2-one (7e): δ 4.31-4.34 (t, 2H, *J* = 6.2 Hz), 2.50-2.53 (m, 2H), 2.43-2.45 (t, 2H, *J* = 5.1 Hz), 2.06 (s, 3H), 1.58 -1.61 (m, 2H), 1.34-1.41 (m, 4H), 0.90-0.94 (t, 2H *J* = 6.9 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 165.8, 133.9, 130.8, 106.2, 78.5, 66.1, 30.4, 31.4, 29.8, 28.5, 22.5, 20.2, 15.7, 14.3. EIMS m/z (relative intensity, %) 207 [M^++1, 100], 206 [M^+, 19.6]. IR (neat) 2224, 1702cm^{-1}; Anal. Calcd. For $C_{12}H_{16}O_2$: C, 75.69; H, 8.80. Found: C, 75.47; H, 8.67.

3-Methyl-4-(3,3-dimethyl-but-1-ynyl)-5,6-dihydro-2*H*-pyran-2-one (7f): δ 4.31-4.34 (t, 2H, *J* = 6.2 Hz), 2.49-2.53 (m, 2H), 2.05 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 165.7, 133.9, 130.7, 113.9, 77.7, 66.1, 31.1, 29.8, 29.0, 15.7. EIMS m/z (relative intensity, %) 193 [M^++1, 100], 192 [M^+, 31.5]. IR (neat) 2222, 1703cm^{-1}; Anal. Calcd. For $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.71; H, 8.27.

3-Methyl-4-(3-methoxy-prop-1-ynyl-)-5,6-dihydro-2*H*-pyran-2-one (7g): δ 4.34-4.37 (m, 4H), 3.43 (s, 3H), 2.54-2.58 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 165.4, 132.5, 132.3, 99.5, 83.8, 66.1, 60.7, 58.3, 29.4, 15.9. EIMS m/z

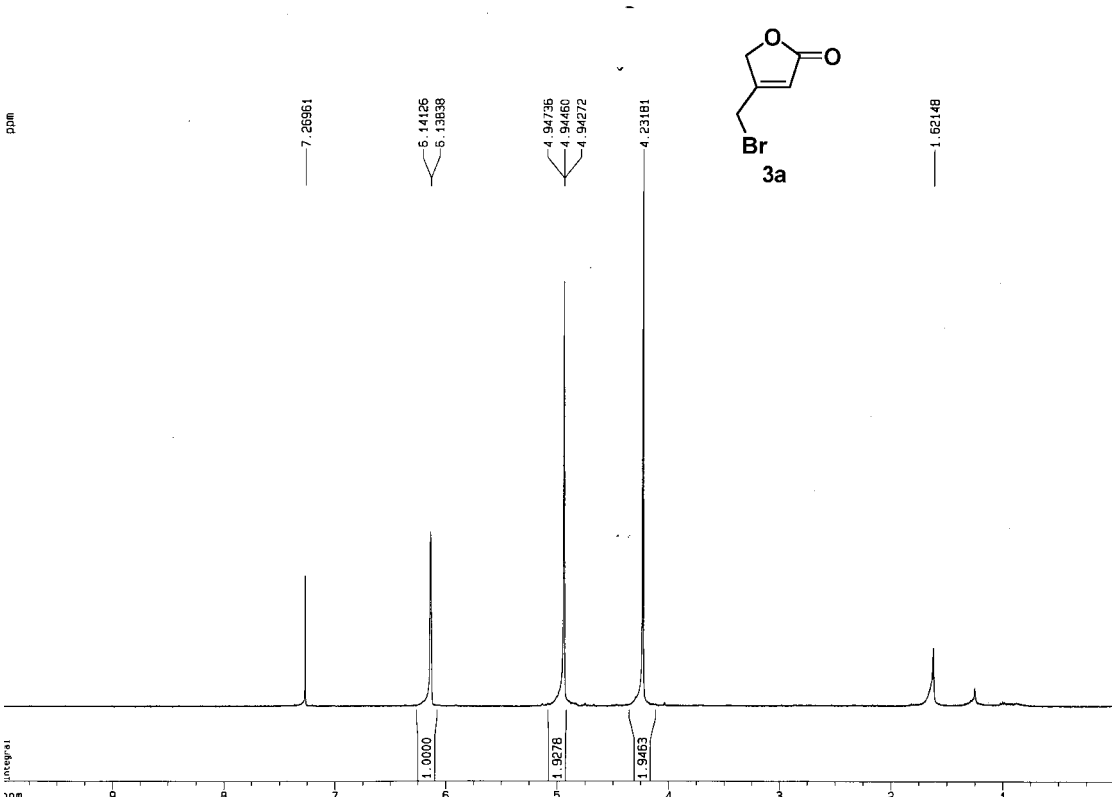
(relative intensity, %) 181 [M^++1, 100], 180 [M^+, 31.5]. IR (neat) 2229, 1705cm^{-1}; Anal. Calcd. For $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.44; H, 6.59.

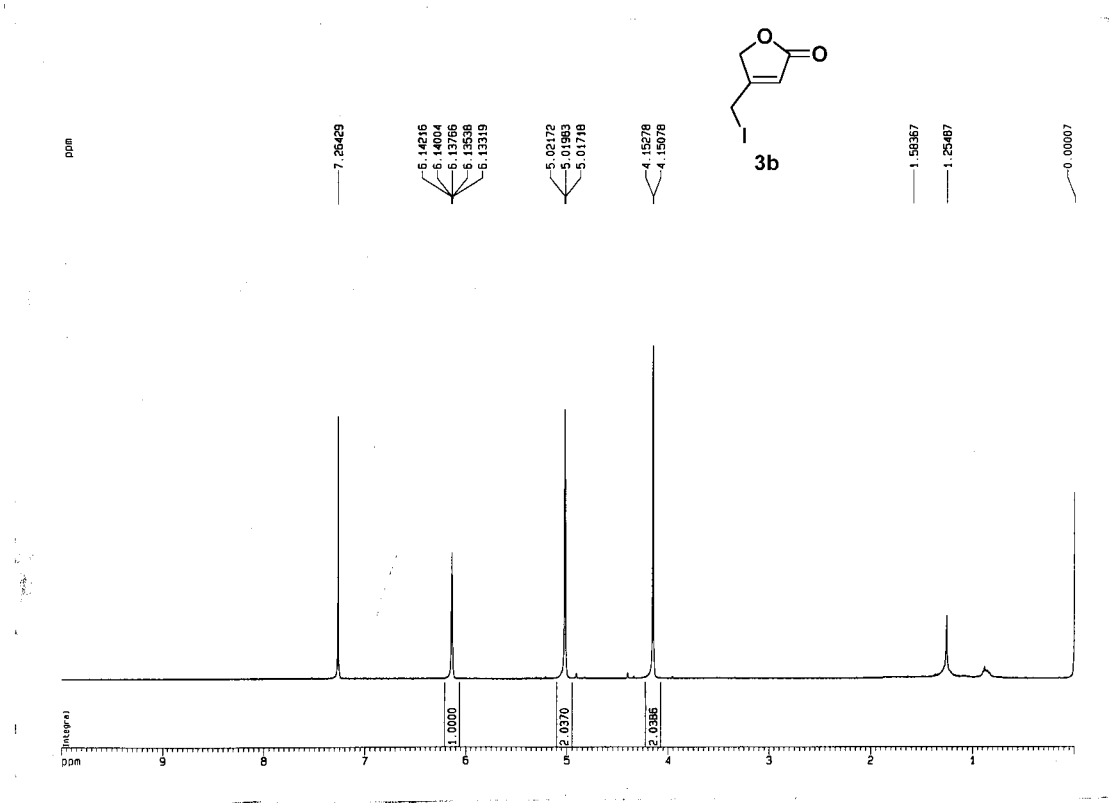
3-Ethyl-4-hex-1-ynyl-5,6-dihydro-2*H*-pyran-2-one (7h): δ 4.29-4.33 (t, 2H, *J* = 6.1Hz), 2.49-2.53 (m, 2H), 2.43-2.47 (t, 2H, *J* = 7.0 Hz), 1.56 -1.59 (m, 2H), 1.43-1.48 (m, 2H), 1.07-1.10 (t, 3H, *J* = 7.4 Hz), 0.93-0.96 (t, 2H *J* = 7.3 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 165.8, 133.9, 130.8, 106.1, 78.5, 66.1, 30.8, 29.8, 22.3, 19.9, 15.7, 13.9. EIMS m/z (relative intensity, %) 226 [M^+, 100]. IR (neat) 2223, 1704cm^{-1}; Anal. Calcd. For $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.45; H, 8.68.

3-Ethyl-4-phenyethynyl-5,6-dihydro-2*H*-pyran-2-one (7i): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.50-7.53 (m, 2H), 7.28-7.42 (m, 3H), 4.40-4.43 (t, 2H, *J* = 6.2 Hz), 2.65-2.69 (m, 2H). 2.42-2.46 (t, 2H, *J* = 7.1 Hz), 1.08-1.11 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100M Hz, $CDCl_3$) δ 164.9, 137.9, 132.4, 132.2, 129.9, 129.0, 122.4, 103.0, 86.2, 66.1, 30.1, 29.6, 23.8, 13.8. EIMS m/z (relative intensity, %) 226 [M^+, 100]. IR (neat) 2203, 1705cm^{-1}; Anal. Calcd. For $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.42; H, 6.12.

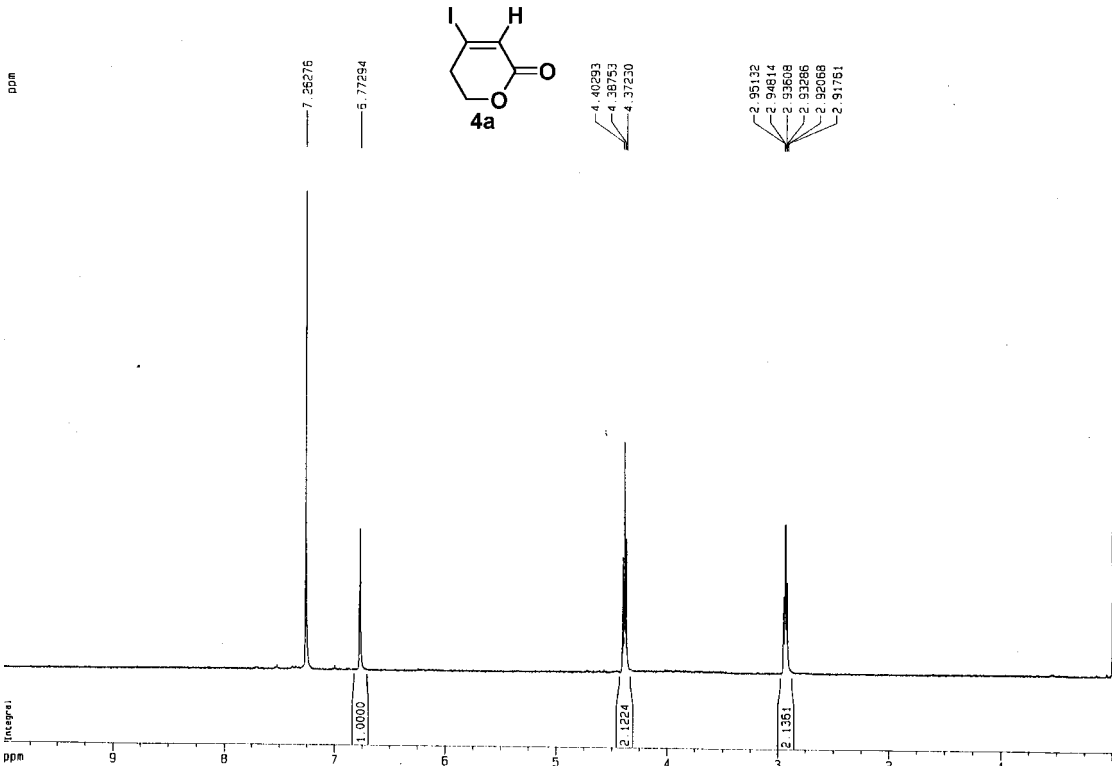
3-Methyl-4-phenyethynyl-5, 6- dihydro-2 (1*H*)-pyridinone (7j): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.44-7.47 (m, 2H), 7.32-7.37 (m, 3H), 3.88-3.91 (t, 2H, *J* = 6.1 Hz), 2.57-2.60 (m, 2H). 2.16-2.17 (m, 3H). ^{13}C NMR (100M Hz, $CDCl_3$) δ 144.7, 136.2, 131.5, 130.2, 128.4, 127.3, 121.5, 101.8, 87.6, 58.2, 28.8, 27.7. EIMS m/z (relative intensity, %) 211 [M^+, 56.4]. IR (neat) 3210, 2205, 1703cm^{-1}; Anal. Calcd. For $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.41; H, 6.08; N, 6.49.

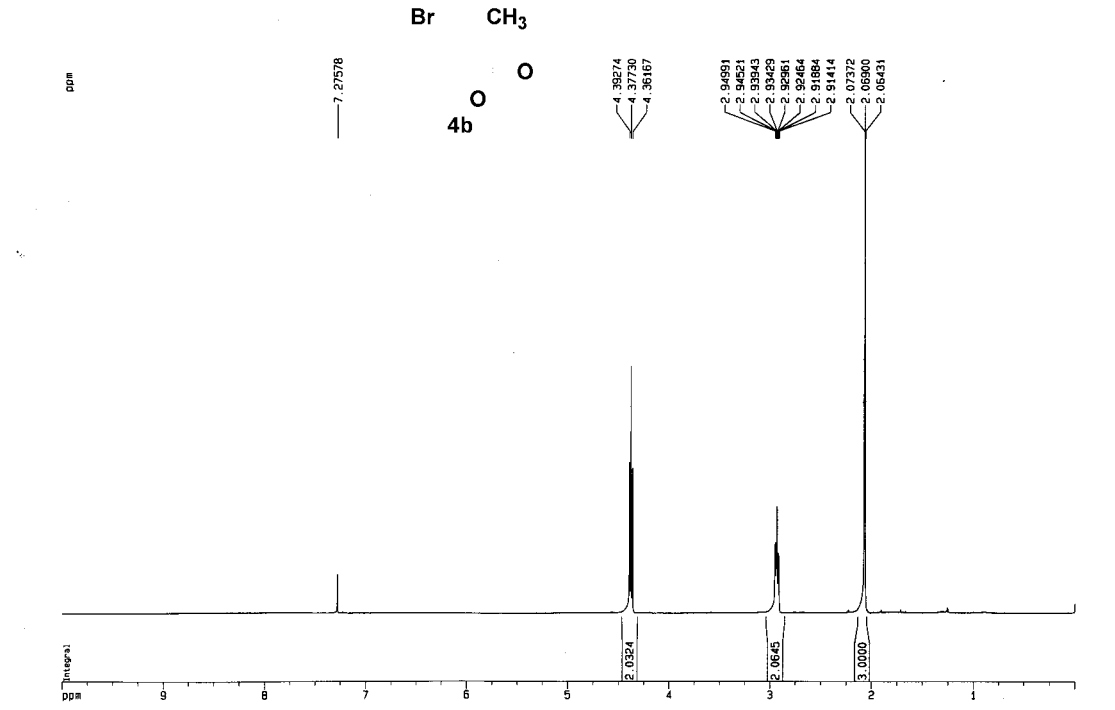
***E*-2-benzyl-3,5-dibromo-pent-2-enoic acid (*E*-14):** ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.6 (b, 1H), 7.24-7.38 (m, 5H), 3.69(s, 2H), 3.57-3.60 (t, 2H, *J* = 6.6 Hz), 3.24-3.28 (t, 2H, *J* = 6.6 Hz). EIMS m/z (relative intensity, %) 350 [M^+(^{81}Br, ^{81}Br), 9.5], 348 [M^+(^{81}Br, ^{79}Br), 18.5], 346 [M^+(^{79}Br, ^{79}Br), 10.5]. IR (neat) 3512cm^{-1}; Anal. Calcd. For $C_{12}H_{12}Br_2O_2$: C, 41.41; H, 3.48. Found: C, 41.23; H, 3.37.

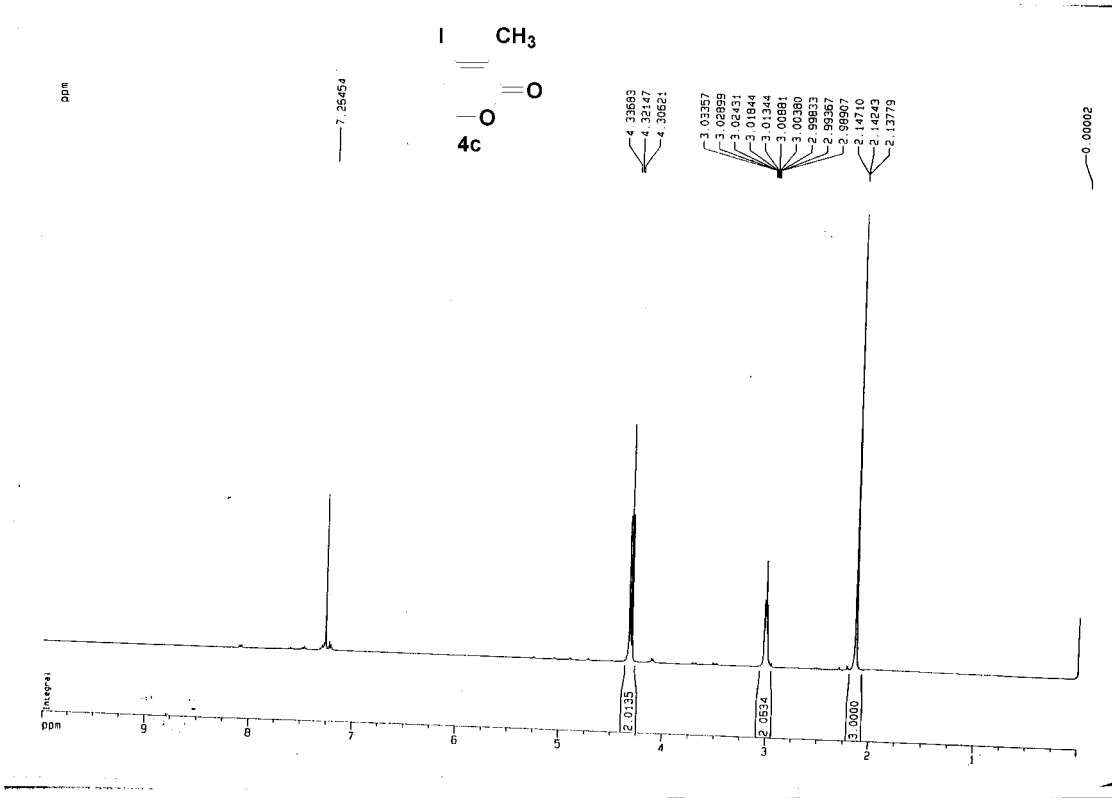

ppm
7.26961
6.14126
6.13838
4.94736
4.94460
4.94272
4.23181
1.62148
Br
3a
Integral
1.0000
1.9278
1.9463


ppm
7.26429
6.14216
6.14004
6.13766
6.13538
6.13319
5.02172
5.01983
5.01718
4.15278
4.15078
1.58367
1.25487
0.00007
I
3b
Integral
1.0000
2.0370
2.0386
ppm

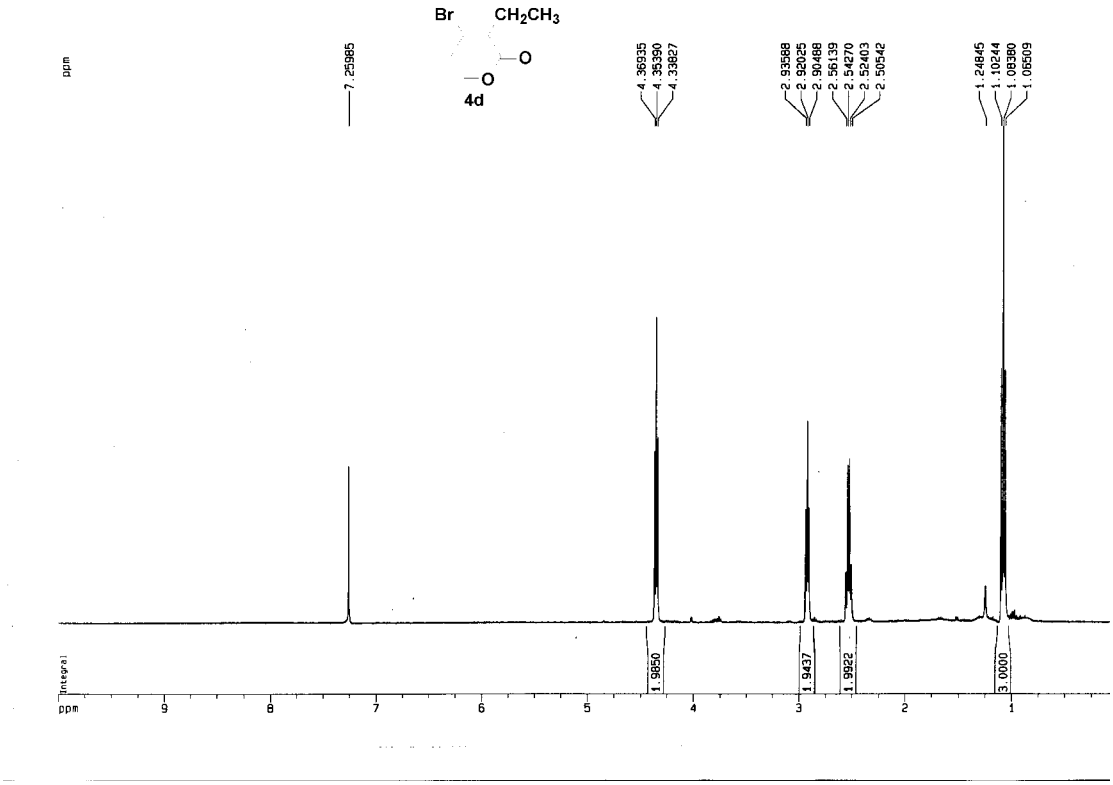
S13

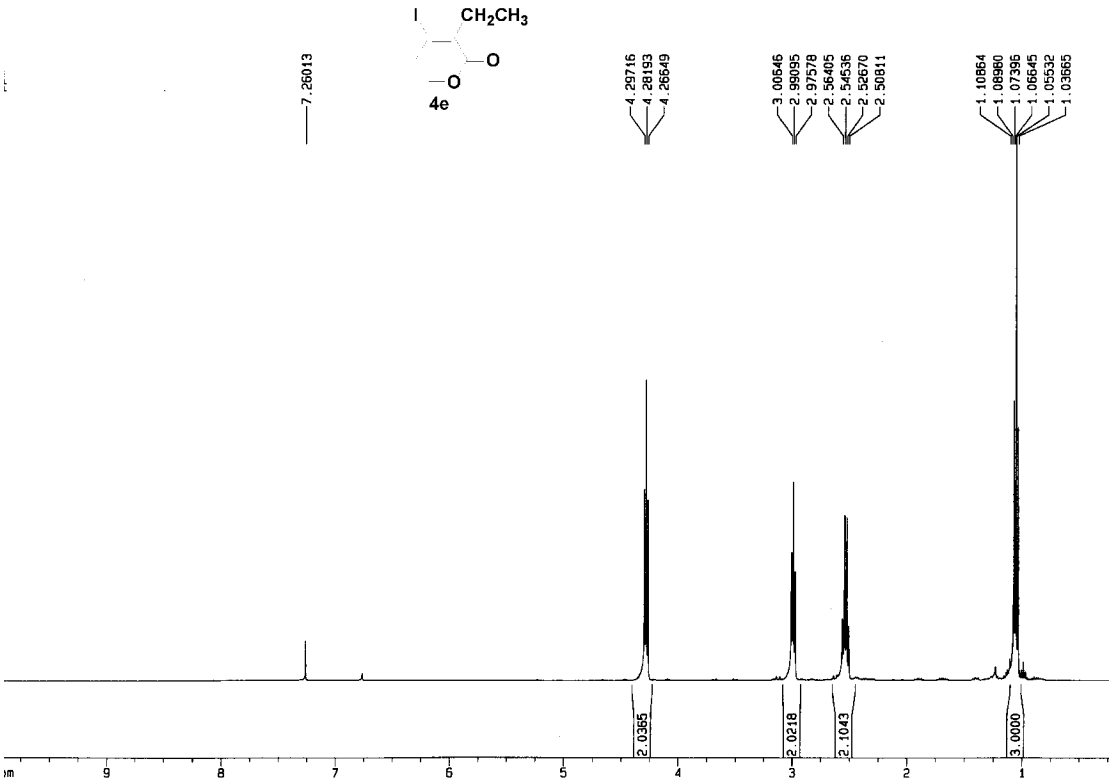

I
H
O
O
4a
ppm
7.26276
5.77294
4.40293
4.38753
4.37230
2.95132
2.94814
2.93608
2.93286
2.92068
2.91761
Integral
1.0000
2.1224
2.1351
ppm
9
8
7
6
5
4
3


Br
CH3
O
O
4b
ppm
7.27578
4.39274
4.37730
4.36167
2.94991
2.94521
2.93943
2.93429
2.92961
2.92464
2.91884
2.91414
2.07372
2.06900
2.06431
Integral
2.0324
2.0645
3.0000
ppm

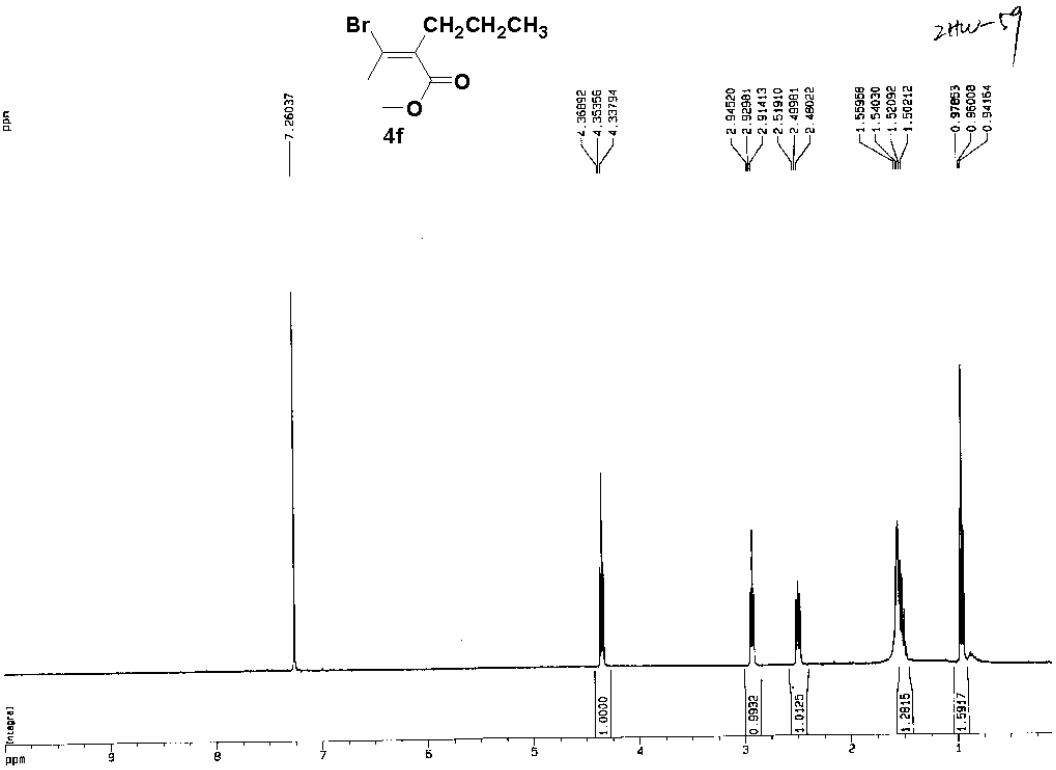

I
CH3
O
O
4c
ppm
7.26454
4.33683
4.32147
4.30621
3.03357
3.02899
3.02431
3.01844
3.01344
3.00881
3.00380
2.99833
2.99367
2.98907
2.14710
2.14243
2.13779
0.00002
Integral
2.0135
2.0534
3.0000
ppm

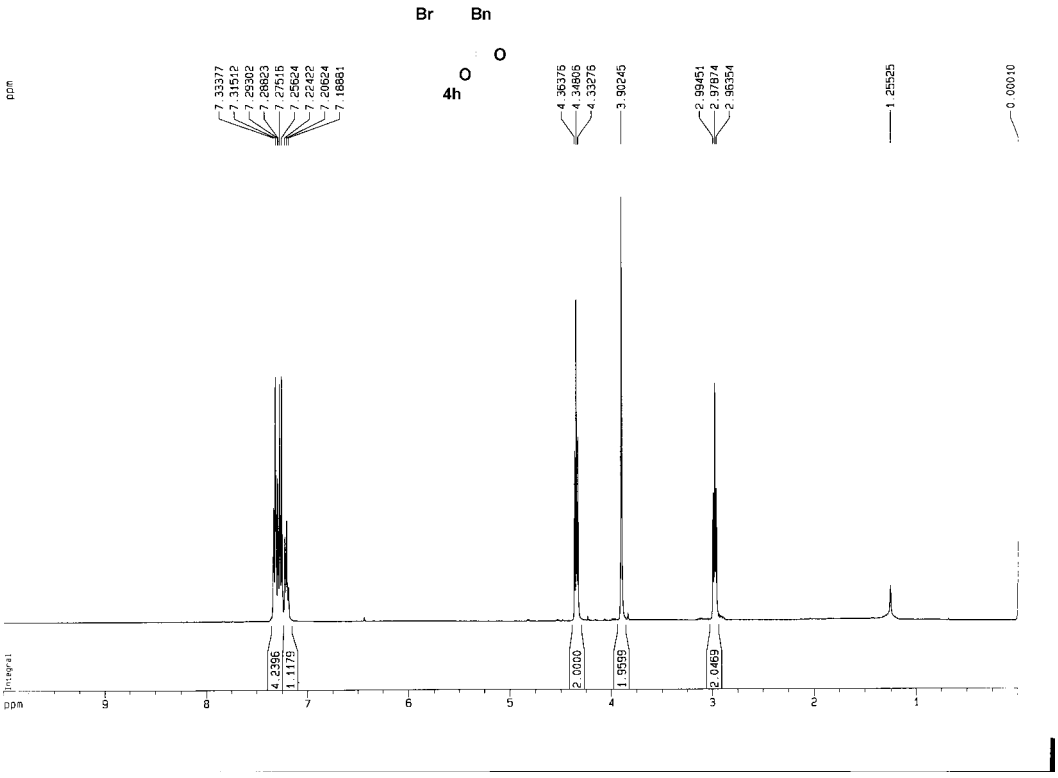
S15

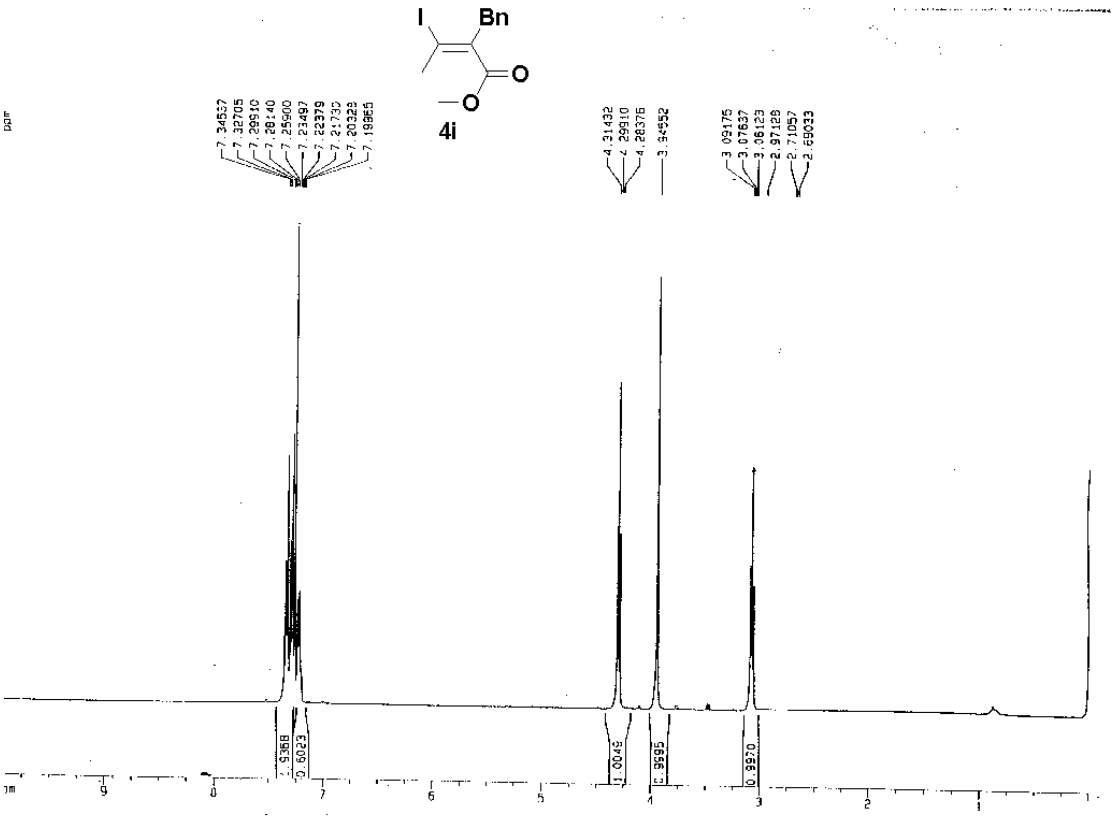

Br
CH2CH3
O
O
4d
7.25985
4.36935
4.35390
4.33827
2.93588
2.92025
2.90488
2.56139
2.54270
2.52403
2.50542
1.24845
1.10244
1.08380
1.06509
1.9850
1.9437
1.9922
3.0000
ppm


I
CH2CH3
O
O
4e
7.26013
4.29716
4.28193
4.26649
3.00646
2.99095
2.97578
2.56405
2.54536
2.52670
2.50811
1.10864
1.08980
1.07396
1.06645
1.05532
1.03665
2.0365
2.0218
2.1043
3.0000

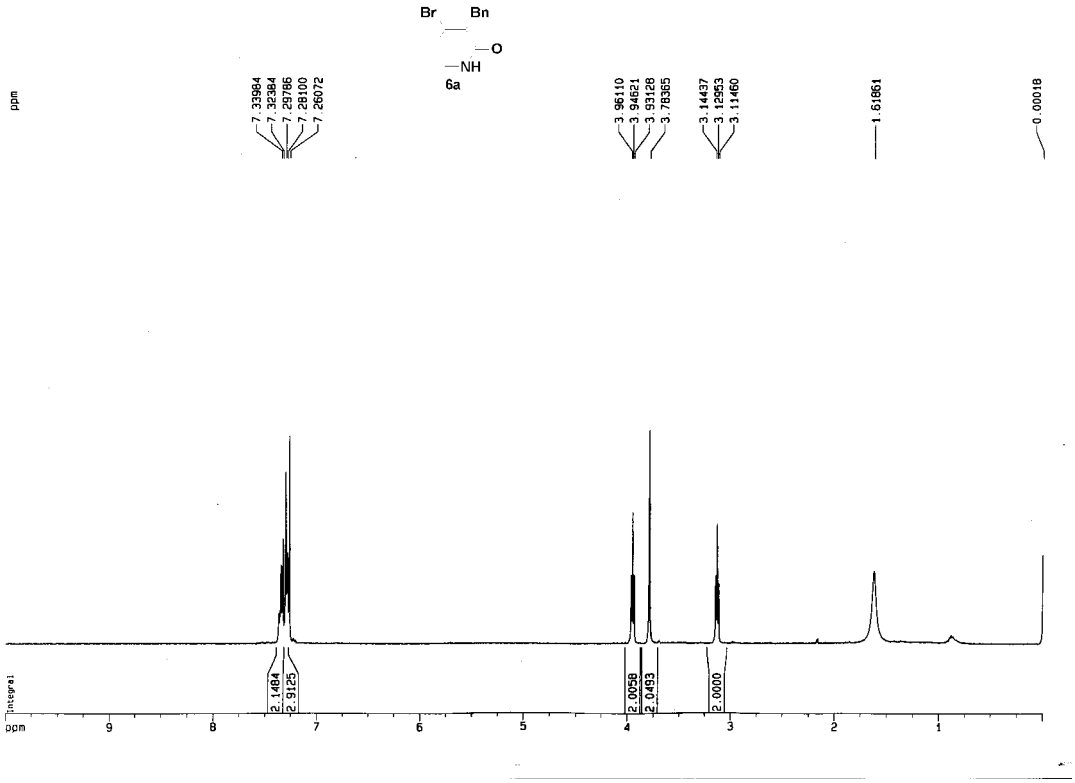
S16

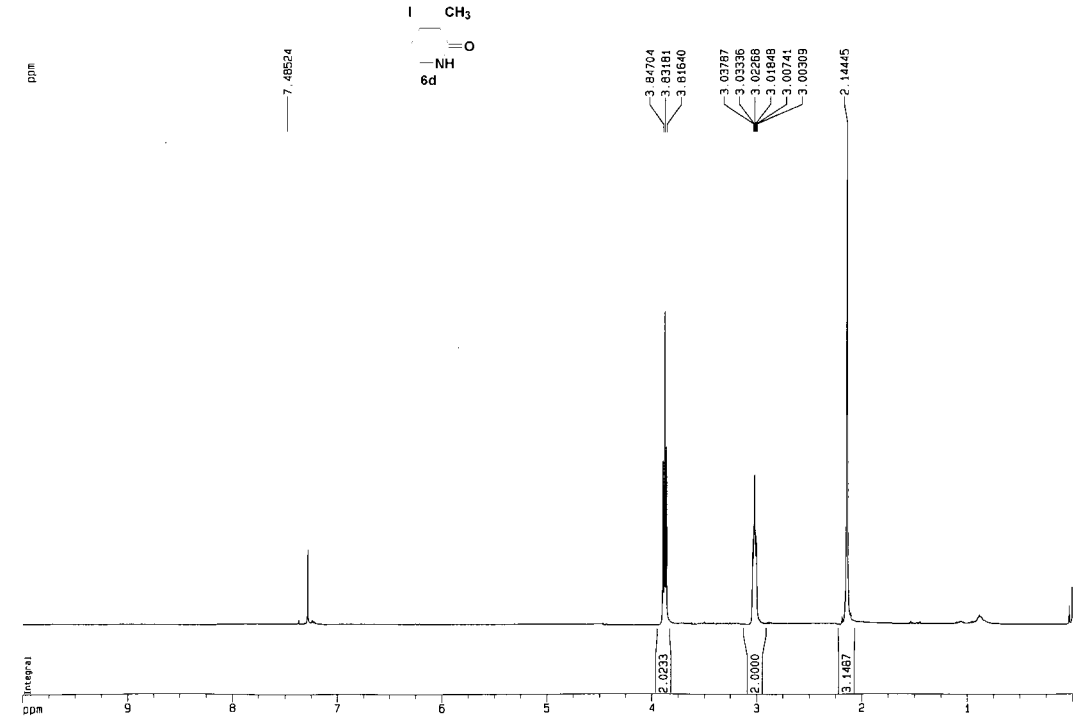

Br
CH2CH2CH3
O
O
4f
2Hw-59
ppm
7.26037
4.36892
4.35356
4.33794
2.94520
2.92981
2.91413
2.51910
2.49981
2.48022
1.55968
1.54030
1.52092
1.50212
0.97853
0.96008
0.94164
Integral
1.0000
0.9932
1.0125
1.2815
1.5917
ppm

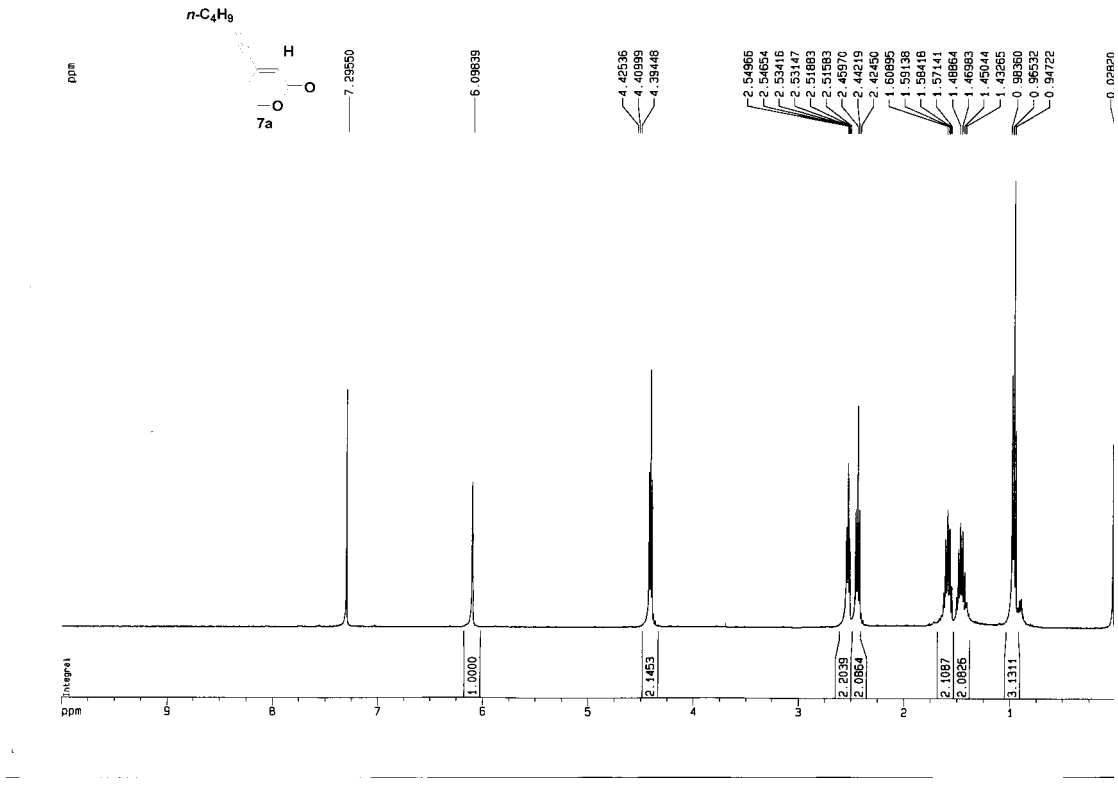

Br
Bn
O
O
4h
ppm
7.33377
7.31512
7.29302
7.28823
7.27515
7.25624
7.22422
7.20624
7.18881
4.36375
4.34805
4.33276
3.90245
2.99451
2.97874
2.96354
1.25525
0.00010
Integral
4.2396
1.1179
2.0000
1.9599
2.0469
ppm

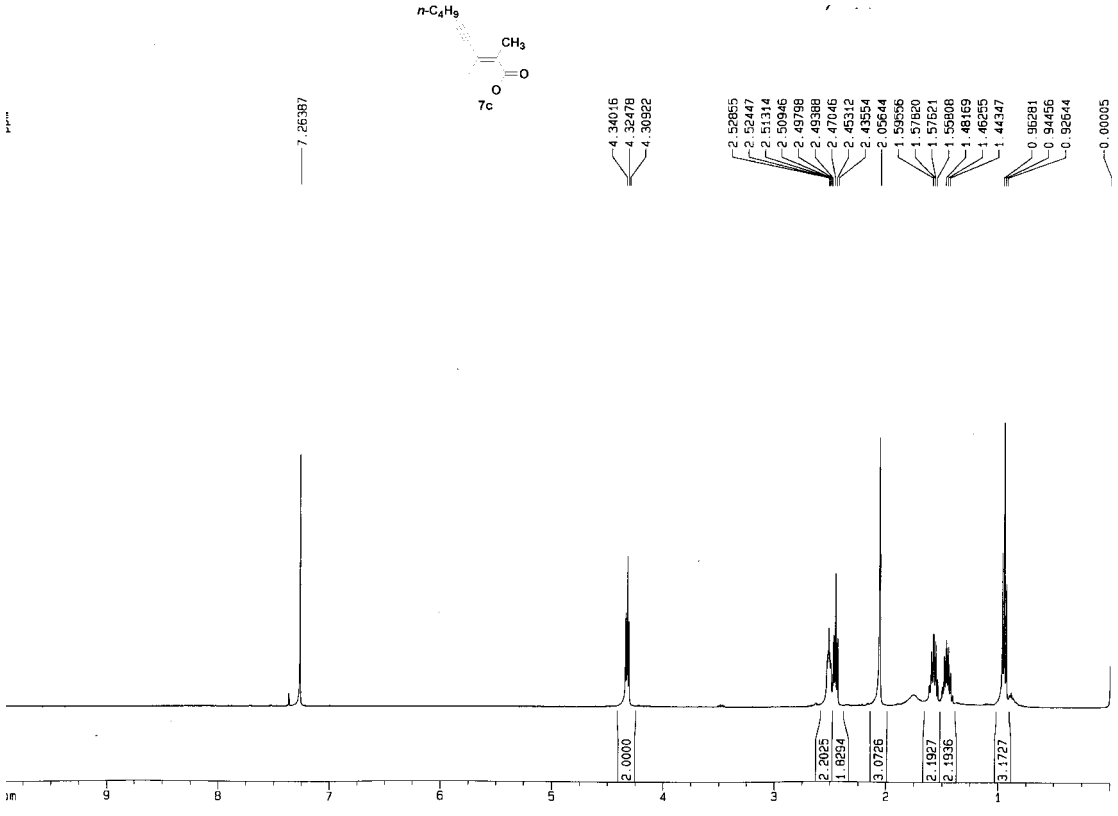

I
Bn
O
O
4i
7.34657
7.32705
7.29910
7.28140
7.25900
7.23497
7.22379
7.21733
7.20323
7.19965
4.31432
4.29910
4.28376
3.94552
3.09175
3.07637
3.06123
2.97128
2.71057
2.69033
5.9368
0.6023
1.0048
1.9695
0.9970

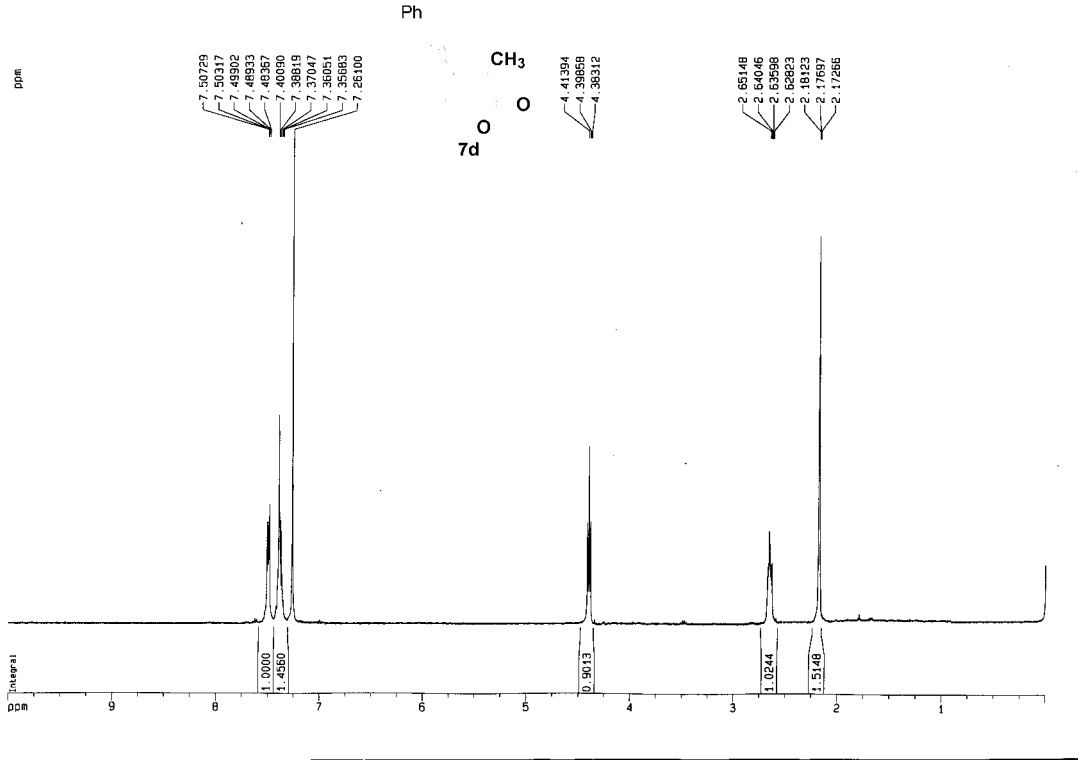
S18

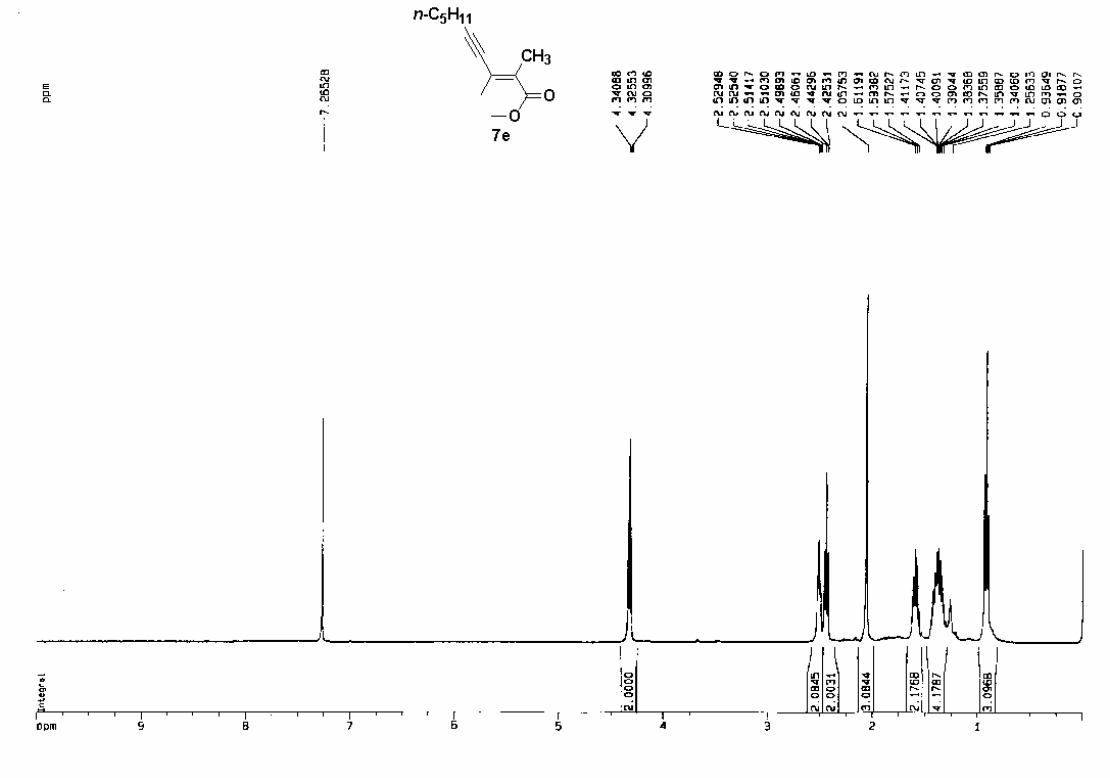

Br
Bn
O
NH
6a
ppm
7.33984
7.32384
7.29786
7.28100
7.26072
3.96110
3.94621
3.93128
3.78365
3.14437
3.12953
3.11460
1.61861
0.00018
Integral
2.1484
2.9125
2.0058
2.0493
2.0000
ppm

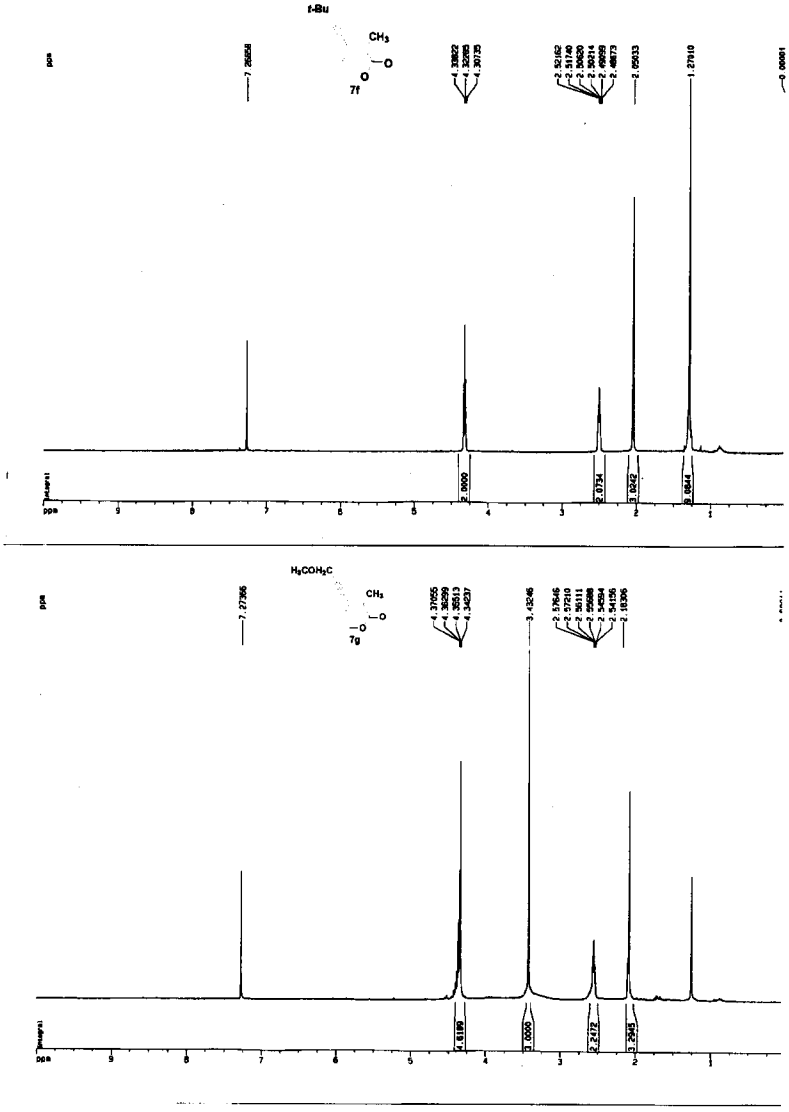

I
CH3
O
NH
6d
ppm
7.48524
3.84704
3.83181
3.81640
3.03787
3.03336
3.02268
3.01848
3.00741
3.00309
2.14445
Integral
2.0233
2.0000
3.1487
ppm


n-C4H9
H
O
O
7a
7.29550
6.09839
4.42536
4.40999
4.39448
2.54966
2.54654
2.53416
2.53147
2.51883
2.51583
2.45670
2.44219
2.42450
1.60895
1.59138
1.56418
1.57141
1.48864
1.46983
1.45044
1.43265
0.98360
0.96532
0.94722
1.0000
2.1453
2.2039
2.0864
2.1087
2.0826
3.1311

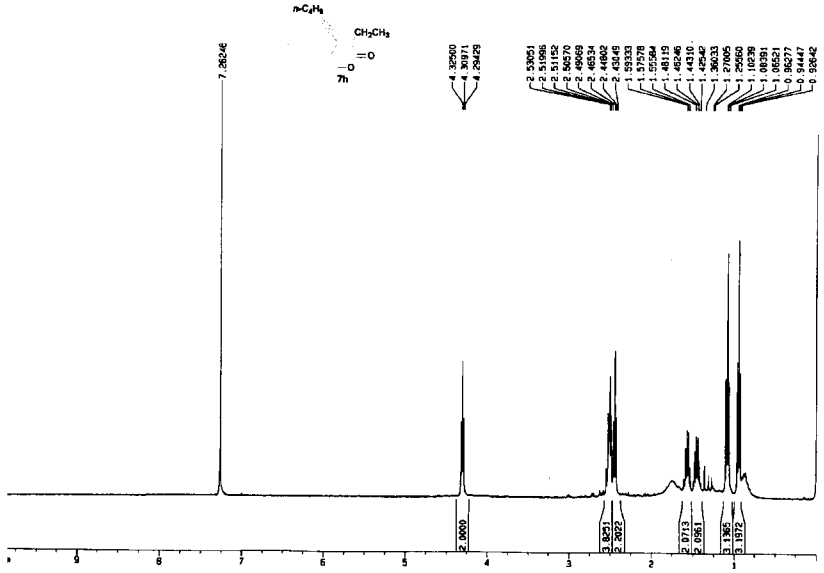

n-C4H9
CH3
O
O
7c
7.26387
4.34016
4.32478
4.30922
2.52855
2.52447
2.51314
2.50946
2.49798
2.49388
2.47046
2.45312
2.43554
2.05644
1.59556
1.57820
1.57621
1.55808
1.48169
1.46255
1.44347
0.96281
0.94456
0.92644
0.00005
2.0000
2.2025
1.8294
3.0726
2.1927
2.1936
3.1727


Ph
CH3
O
O
7d
ppm
Integral
1.0000
1.4560
0.9013
1.0244
1.5148

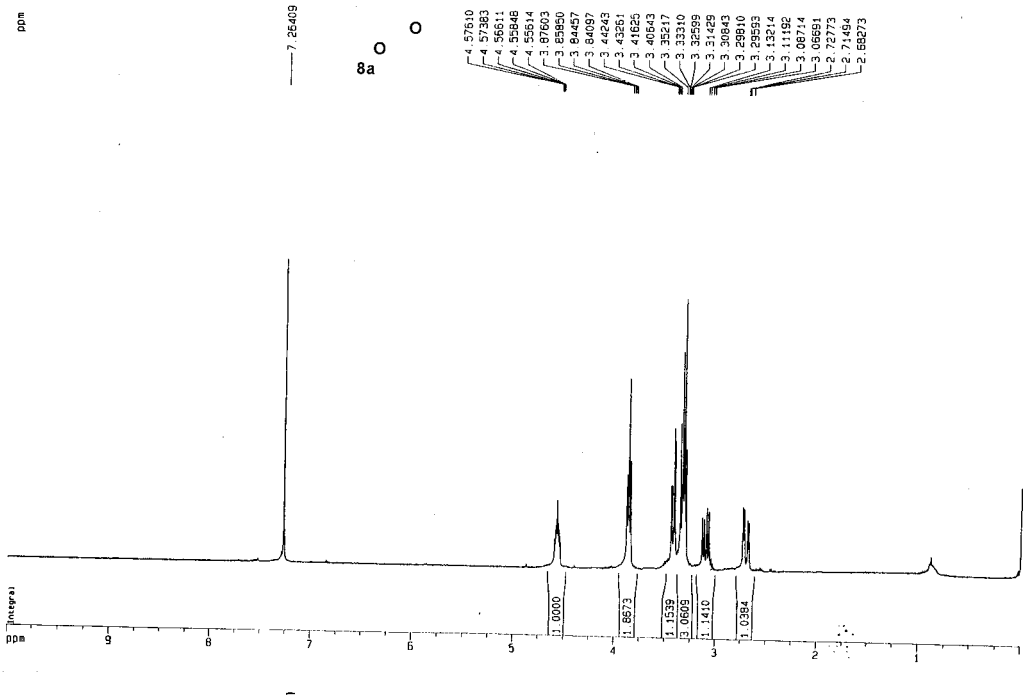

n-C5H11
CH3
O
O
7e
ppm
Integral
2.0000
2.0845
2.0031
3.0844
2.1768
4.1787
3.0968


t-Bu
CH3
O
O
7f
ppm
7.26858
4.38822
4.37055
4.36299
4.35513
4.34237
2.52162
2.51740
2.50920
2.50514
2.49659
2.48873
2.05633
1.27910
0.00001
Integral
2.0000
2.0734
3.0242
9.0844
H3COH2C
CH3
O
O
7g
7.27366
4.37055
4.36299
4.35513
4.34237
3.43246
2.57646
2.57210
2.56311
2.55888
2.54564
2.54156
2.18306
4.6189
3.0000
2.2472
3.2945

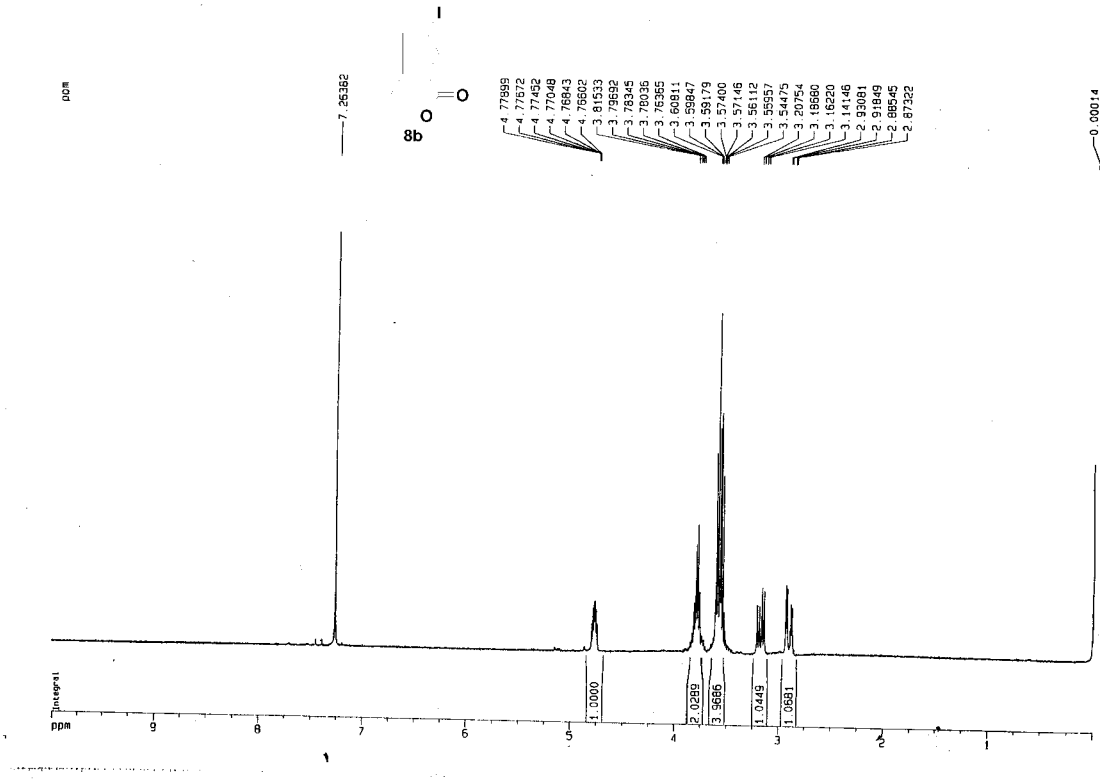
S22

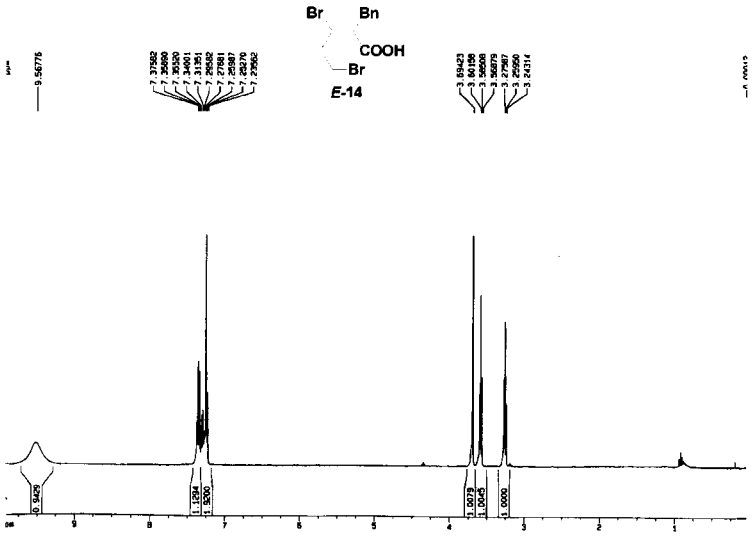


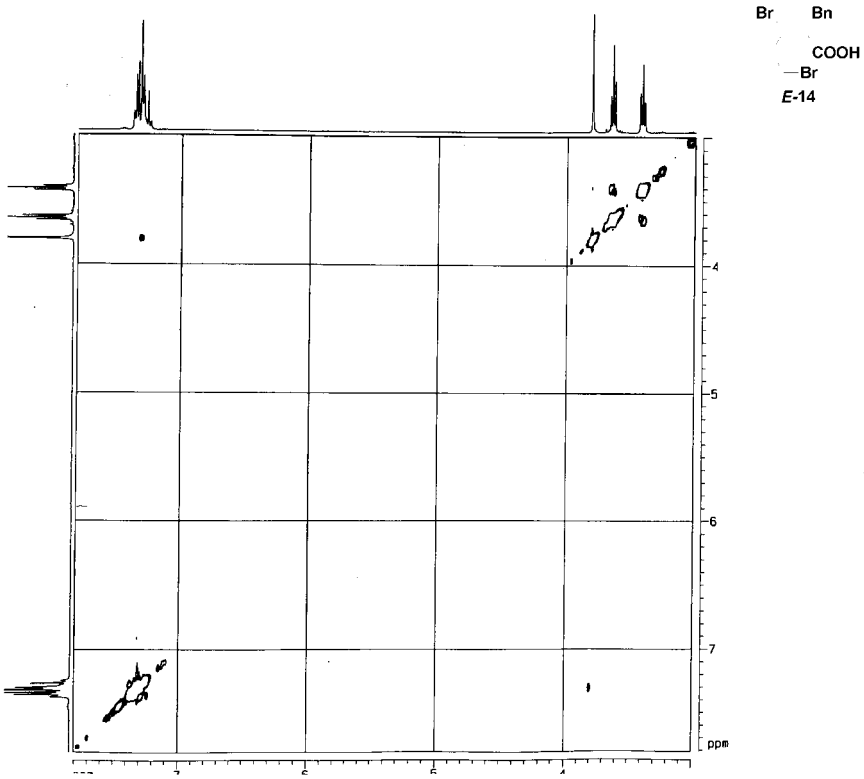
Br

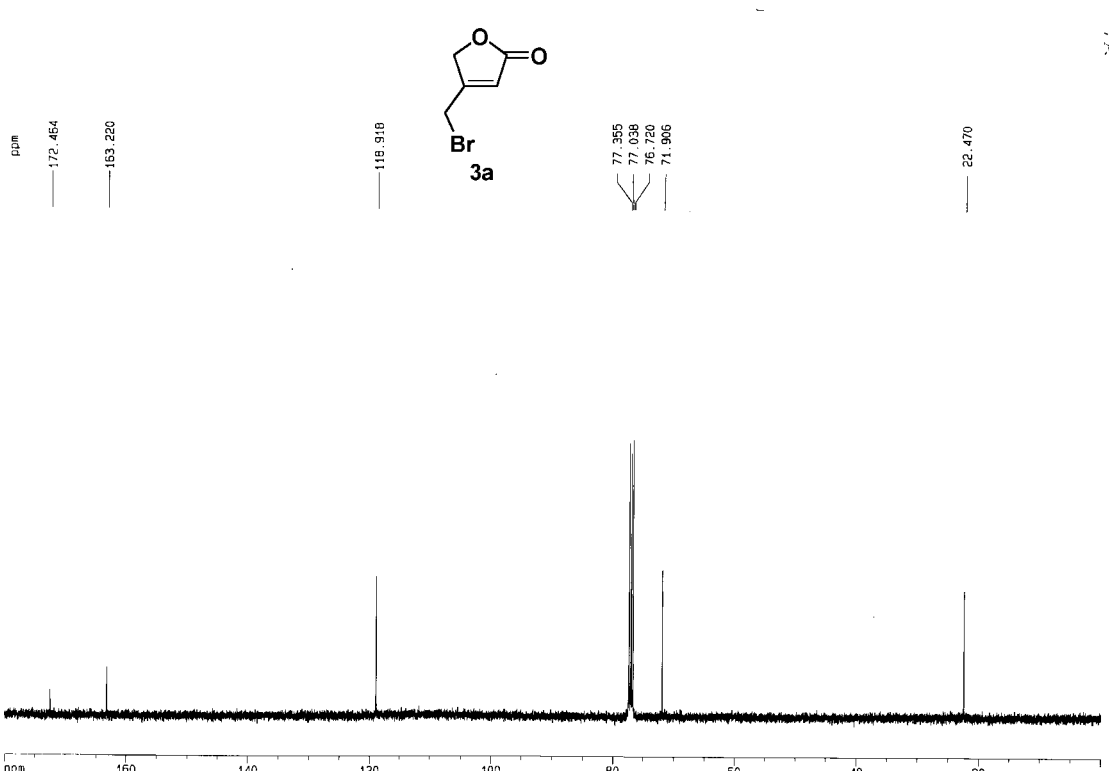


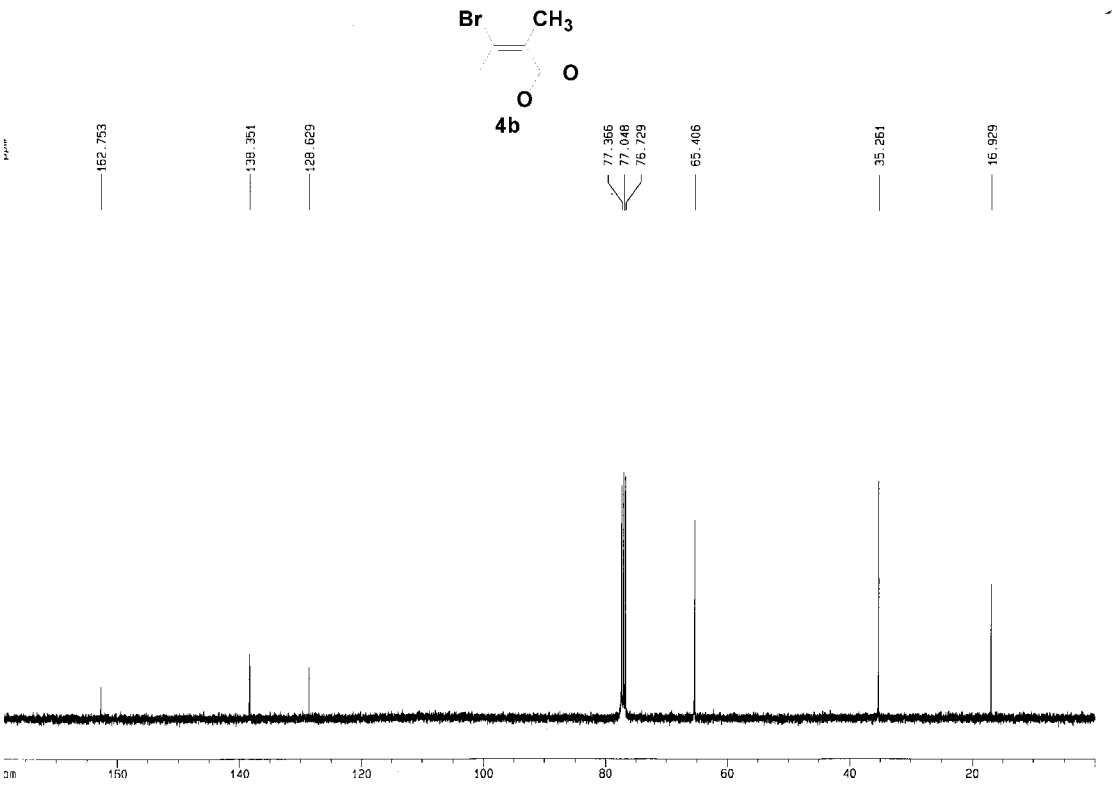
S23

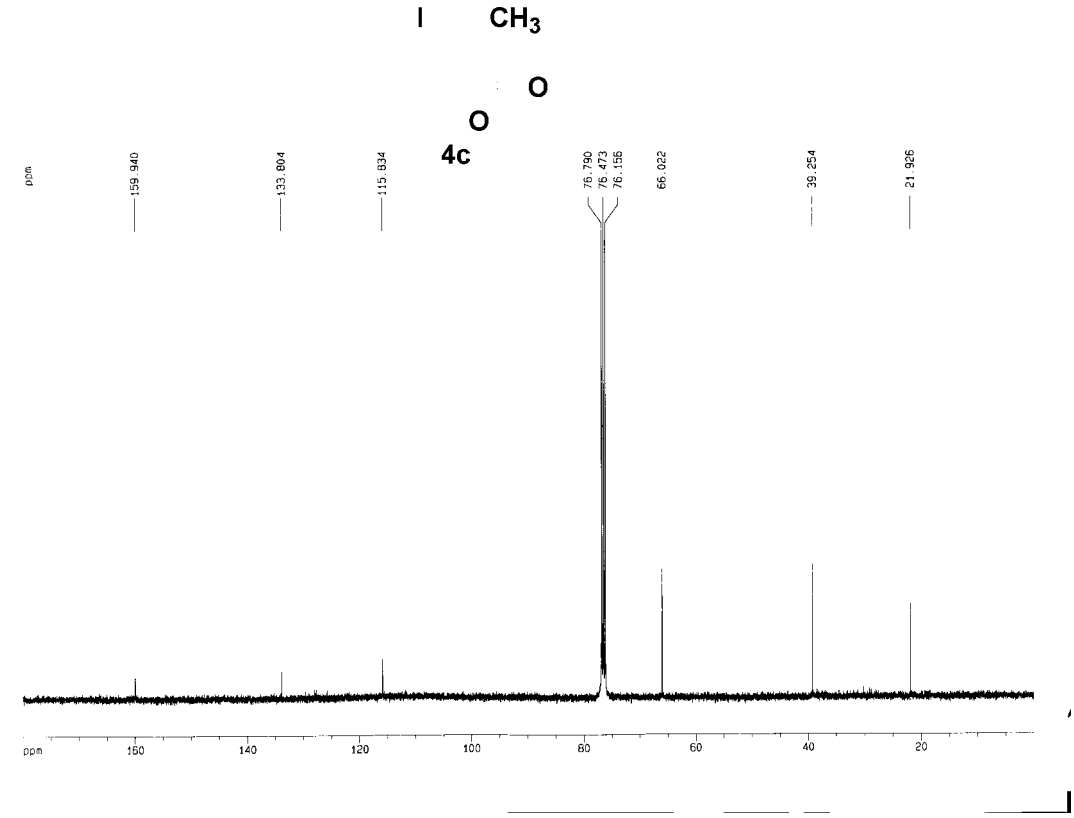

8b
7.26362
0.00014
1.0000
2.0289
3.9686
1.0449
1.0681

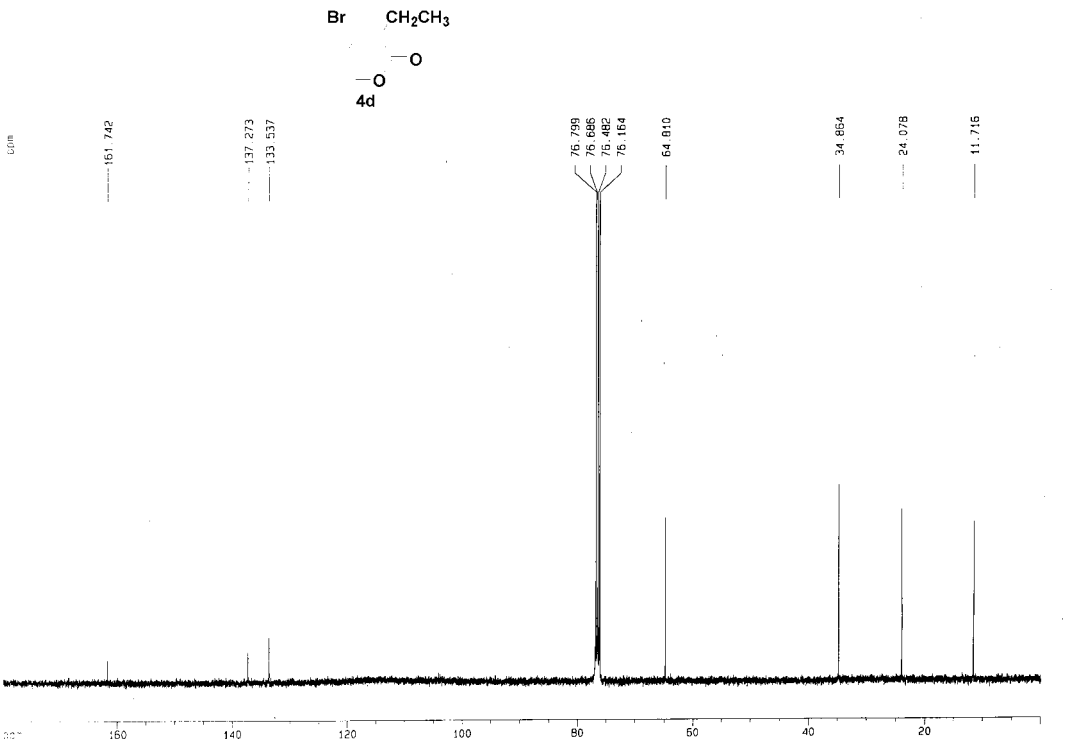

Br
Bn
COOH
Br
E-14
9.56776
0.9409
1.1294
1.1300
1.0079
1.0045
1.0000

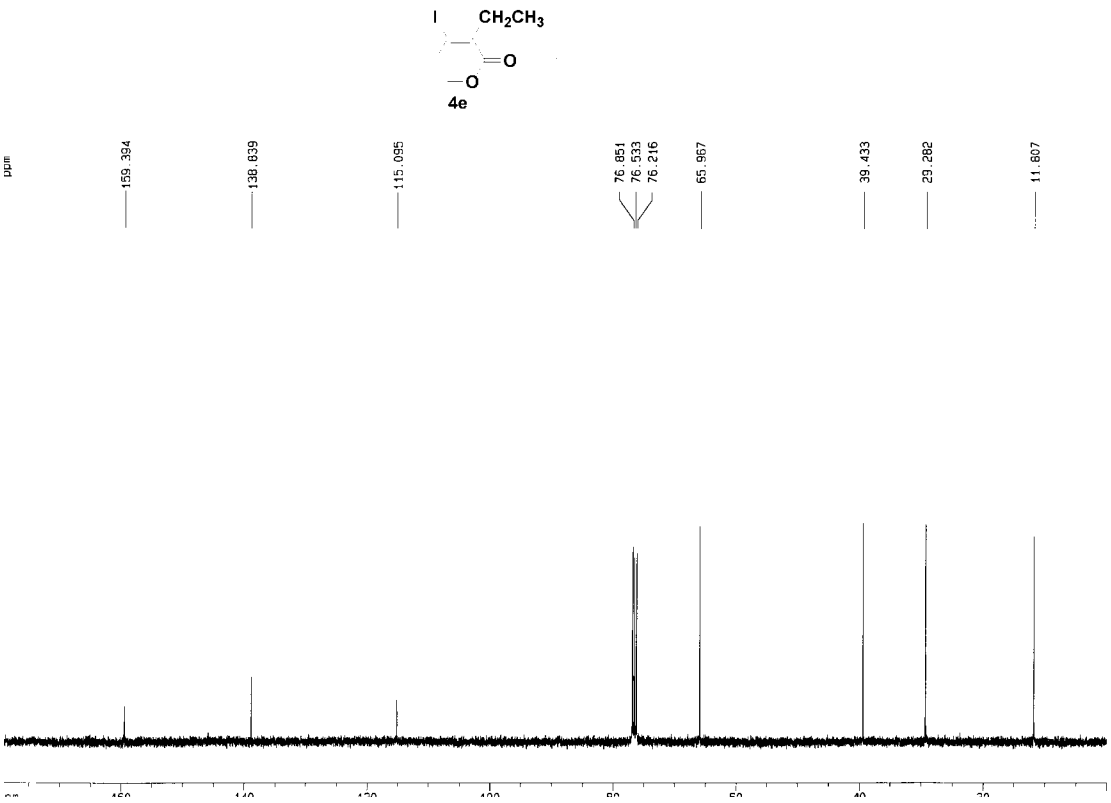

Br
Bn
COOH
Br
E-14
4
5
6
7
ppm

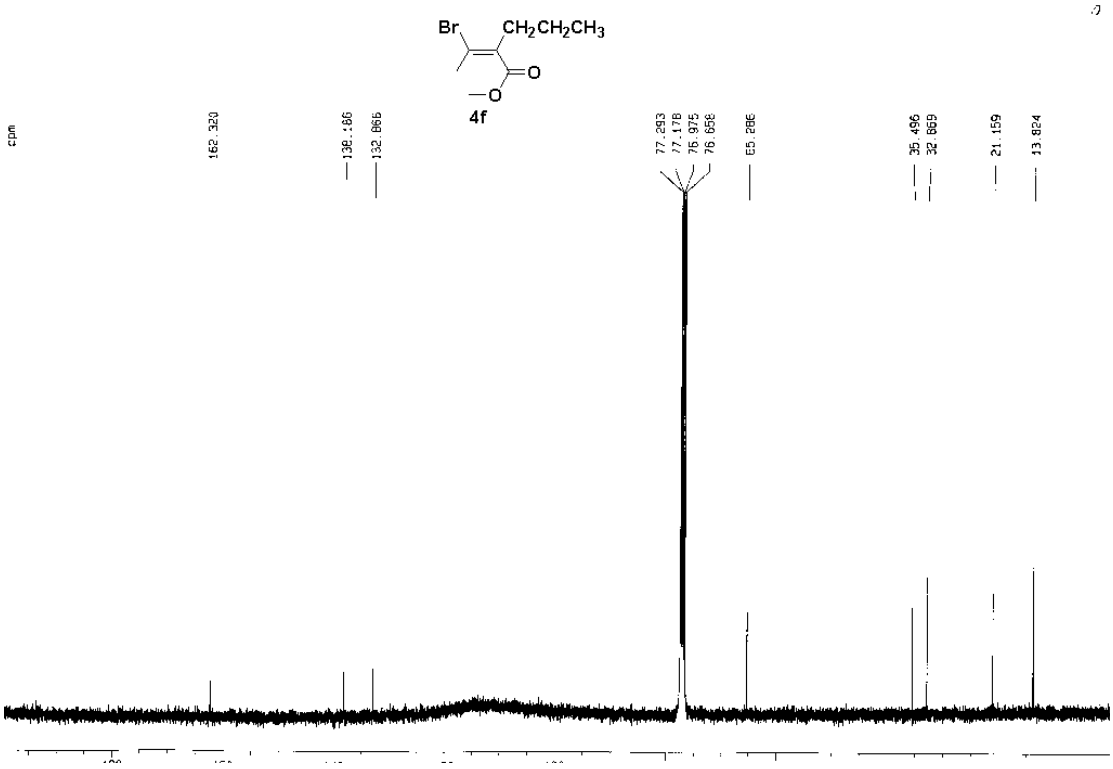

ppm
172.464
163.220
118.918
77.355
77.038
76.720
71.906
22.470
Br
3a

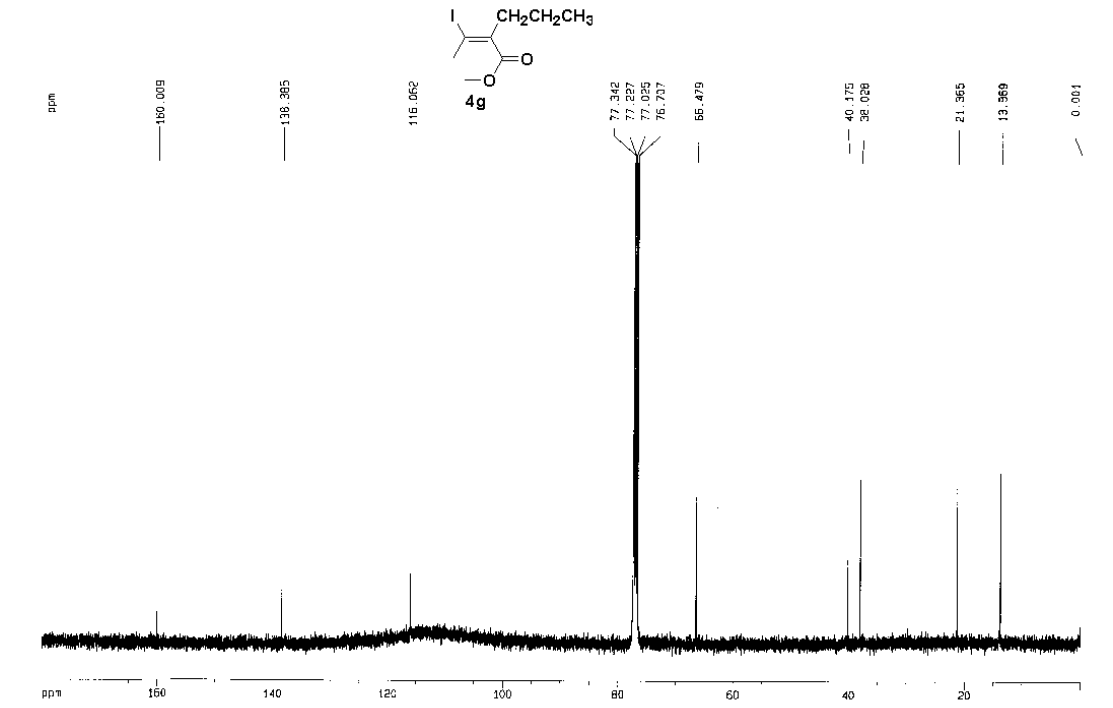

Br
CH3
O
O
4b
162.753
138.351
128.629
77.366
77.048
76.729
65.406
35.261
16.929

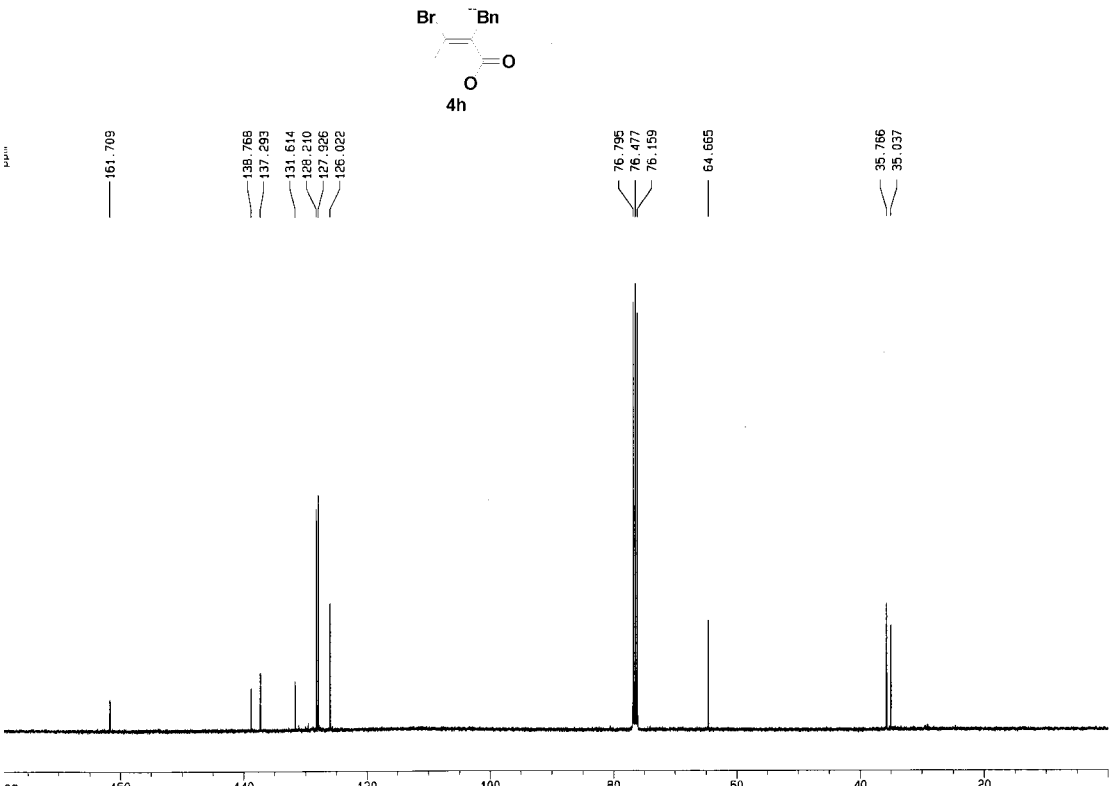

I
CH3
O
O
4c
ppm
159.940
133.804
115.834
76.790
76.473
76.156
66.022
39.254
21.926
ppm
160
140
120
100
80
60
40
20

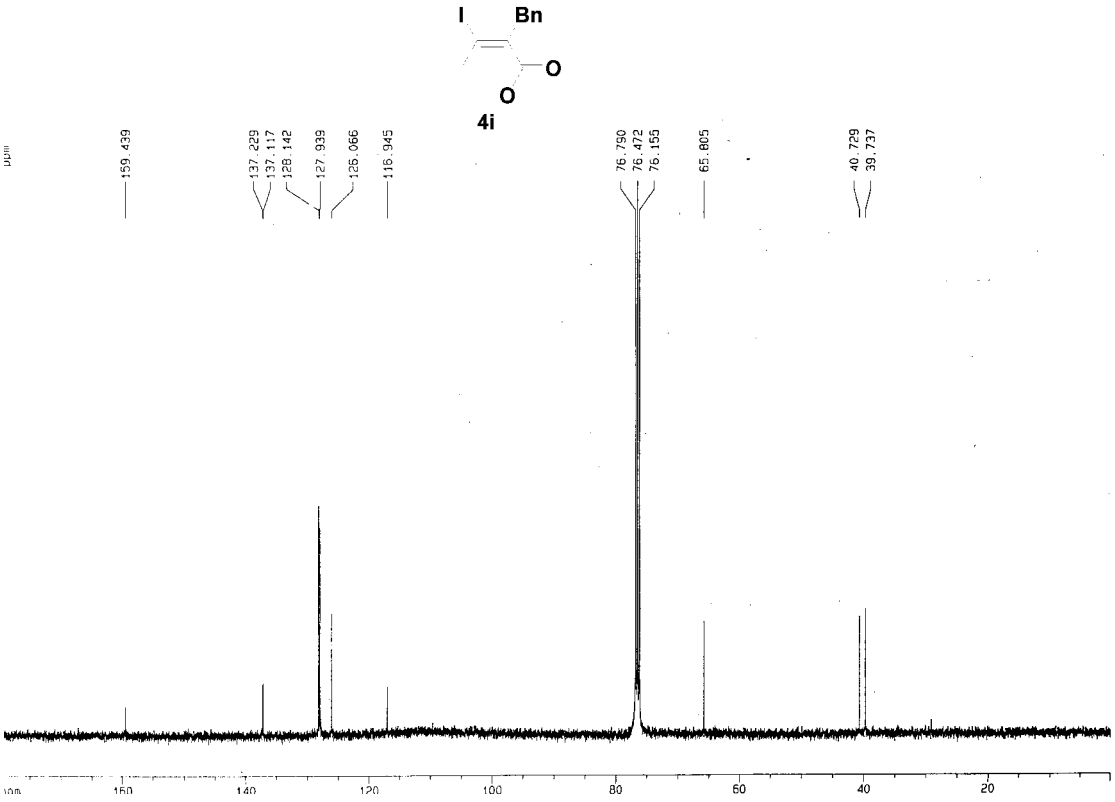

Br
CH2CH3
O
O
4d
ppm
161.742
137.273
133.537
76.799
76.685
76.482
76.164
64.810
34.854
24.078
11.716
160
140
120
100
80
60
40
20

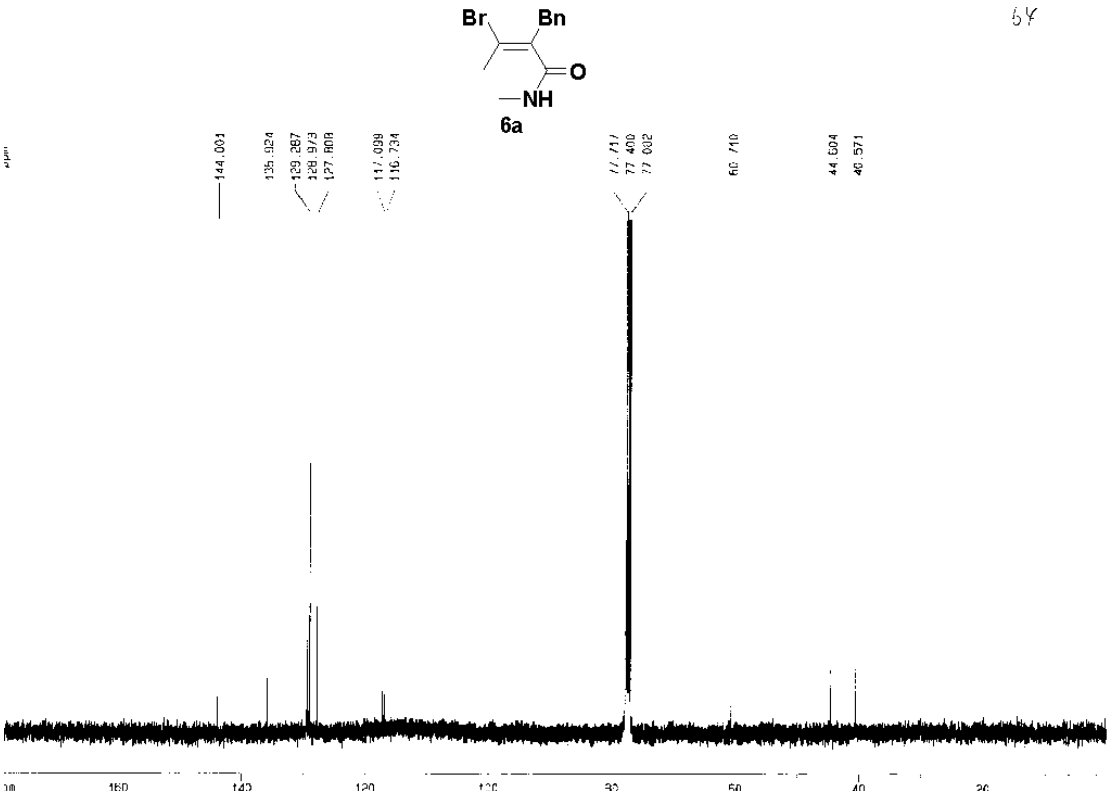

I
CH2CH3
O
O
4e
ppm
159.394
138.639
115.095
76.851
76.533
76.216
65.967
39.433
29.282
11.807

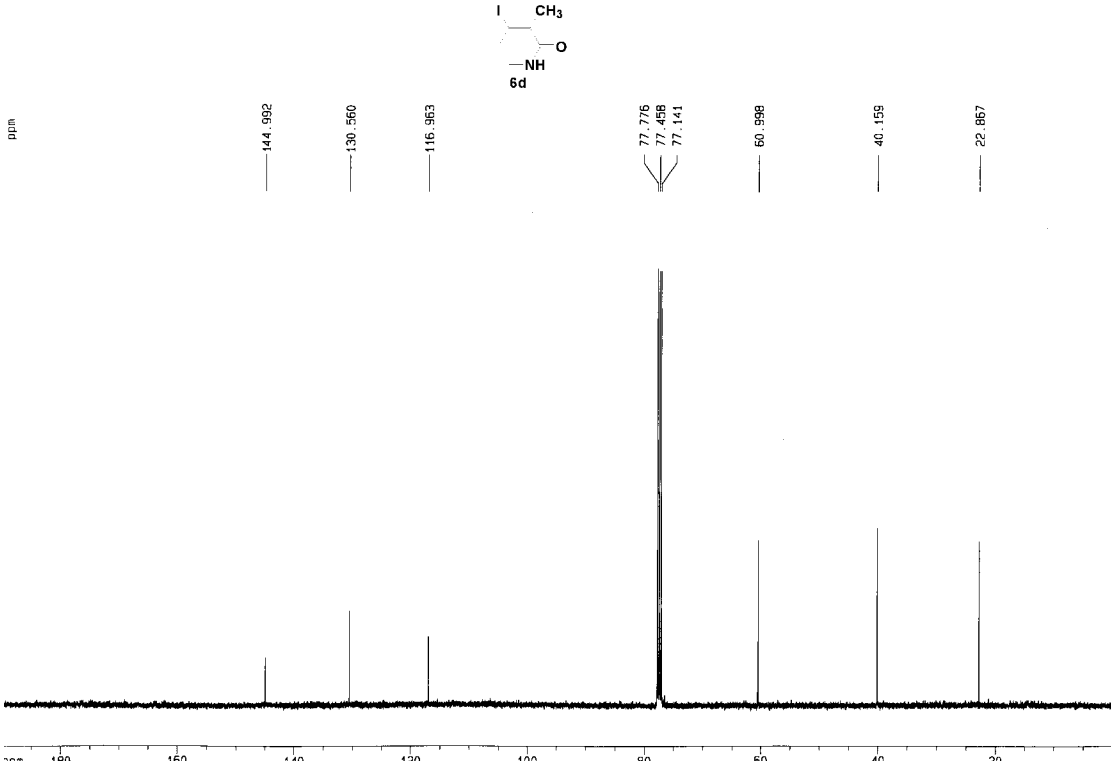

Br
CH2CH2CH3
O
O
4f
ppm
162.320
138.186
132.866
77.293
77.178
76.975
76.658
65.286
35.496
32.869
21.159
13.824

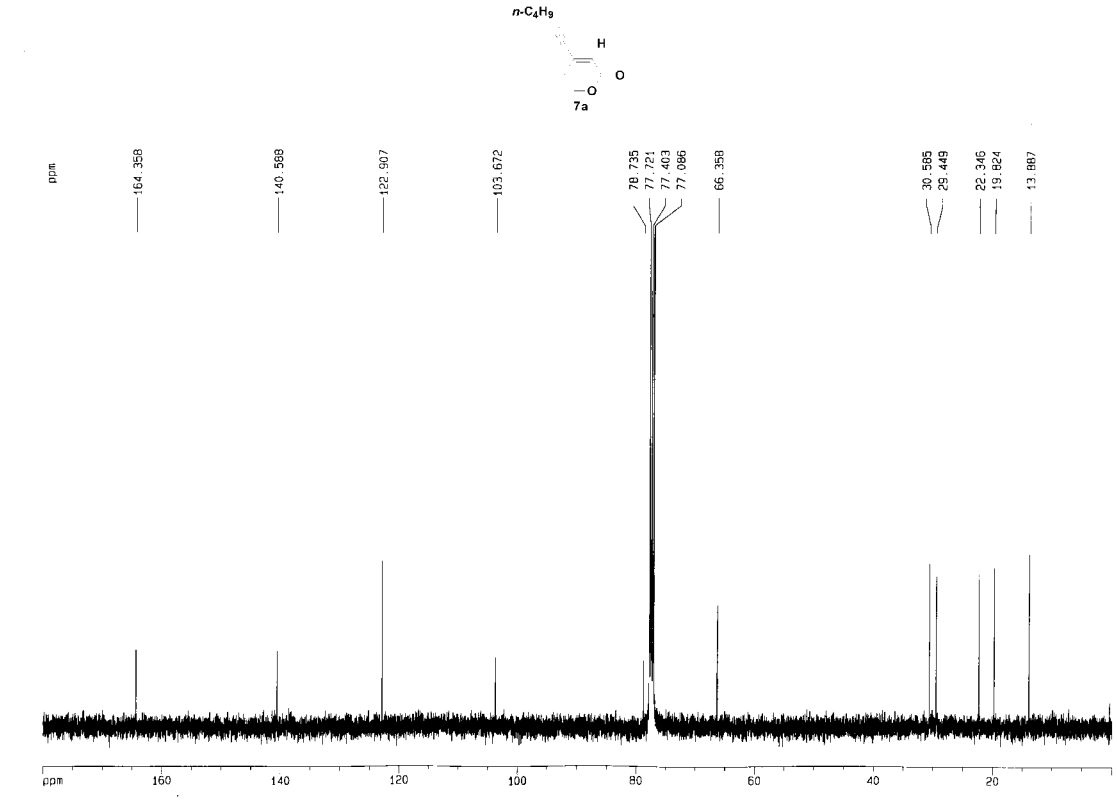

I
CH2CH2CH3
O
O
4g
ppm
160.009
138.385
116.062
77.342
77.237
77.025
76.707
66.479
40.175
38.028
21.365
13.969
0.004
ppm
160
140
120
100
80
60
40
20

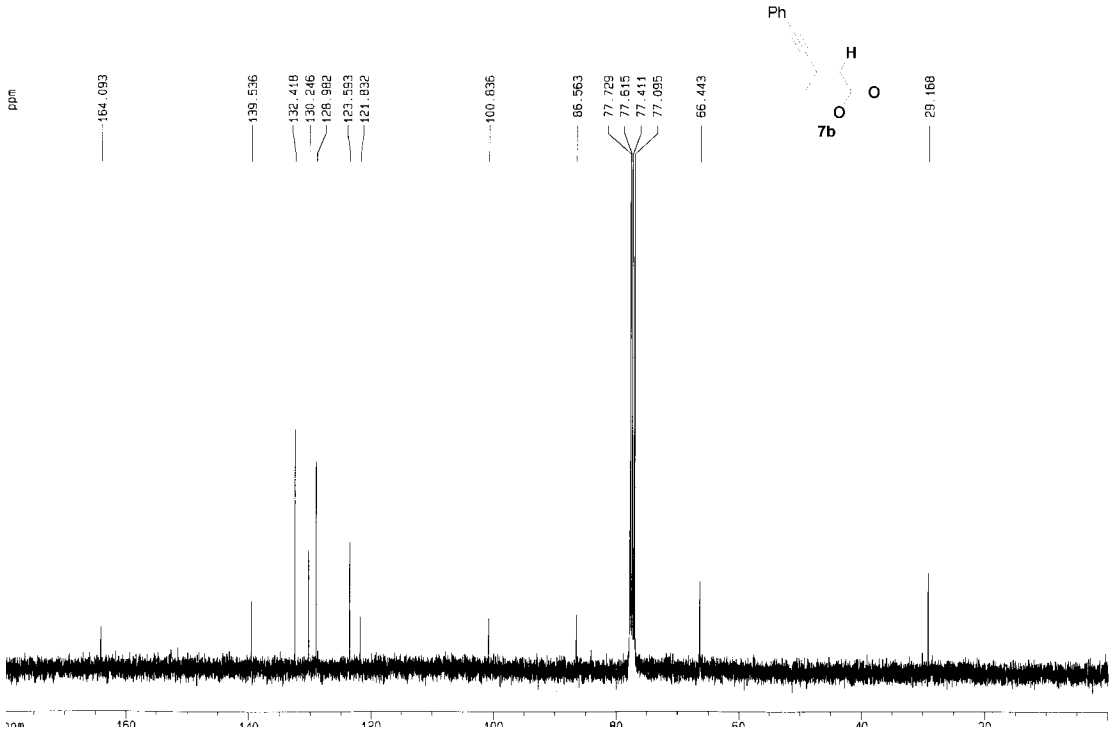

Br
Bn
O
O
4h
161.709
138.766
137.293
131.614
128.210
127.926
126.022
76.795
76.477
76.159
64.665
35.766
35.037

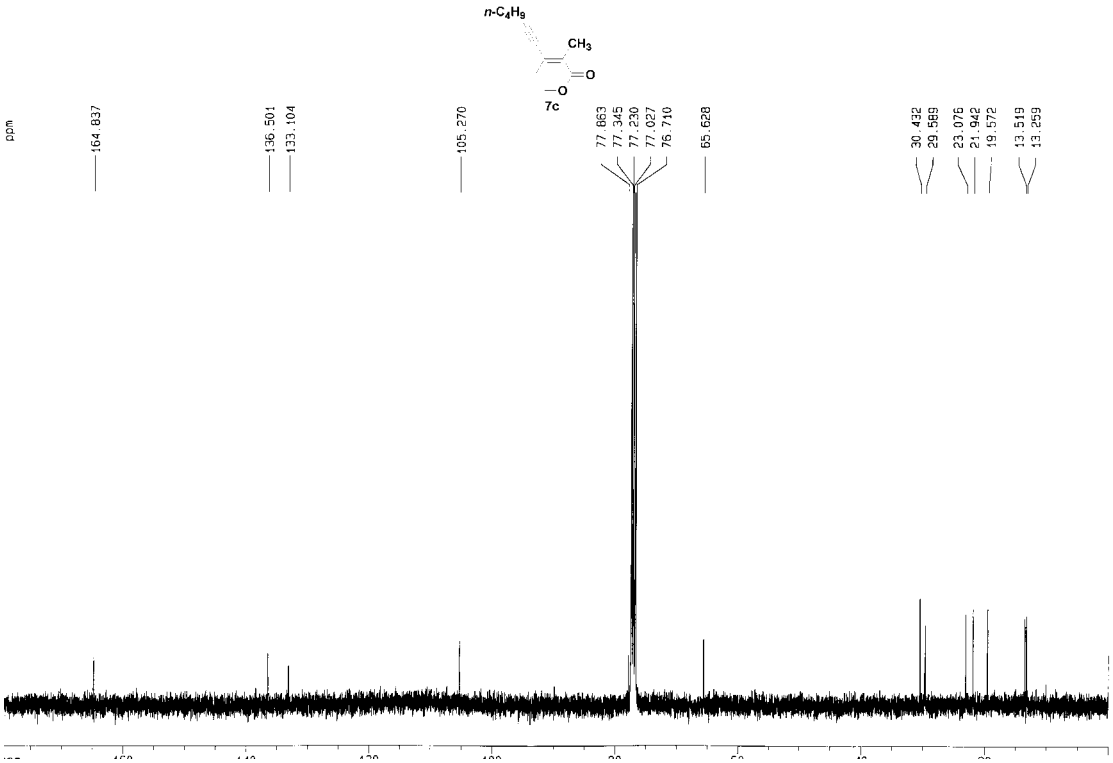

I
Bn
O
O
4i
159.439
137.229
137.117
128.142
127.939
126.066
116.945
76.790
76.472
76.155
65.805
40.729
39.737
ppm
160
140
120
100
80
60
40
20

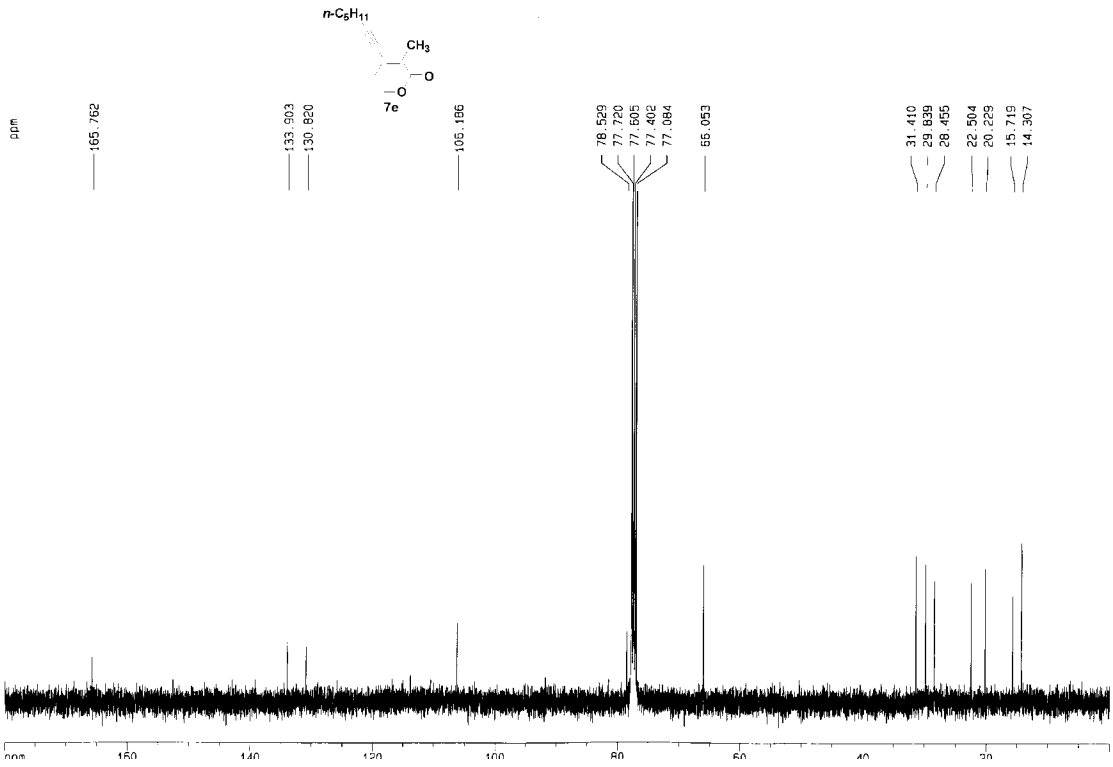

Br
Bn
O
NH
6a
144.003
135.924
129.287
128.973
127.809
117.099
116.734
77.411
77.400
77.002
60.710
44.604
46.571

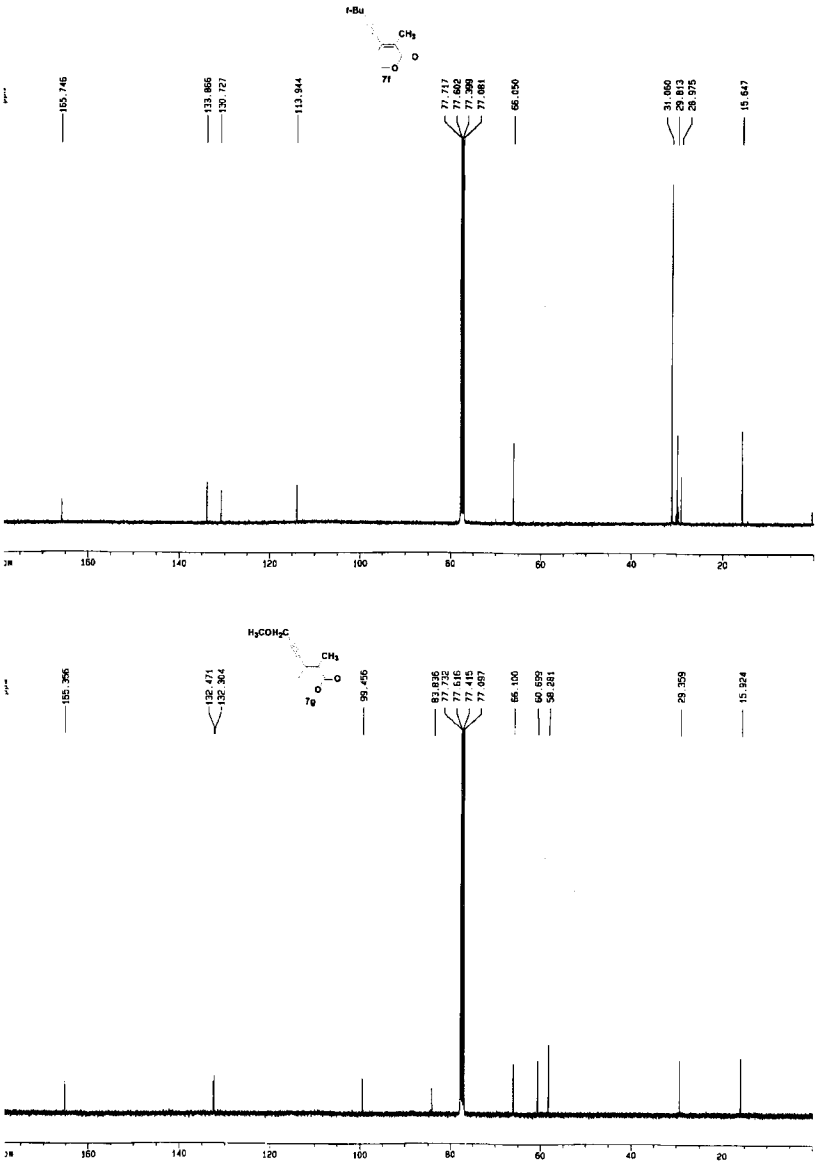

CH3
O
NH
6d
ppm
144.992
130.560
116.963
77.776
77.458
77.141
60.998
40.159
22.867

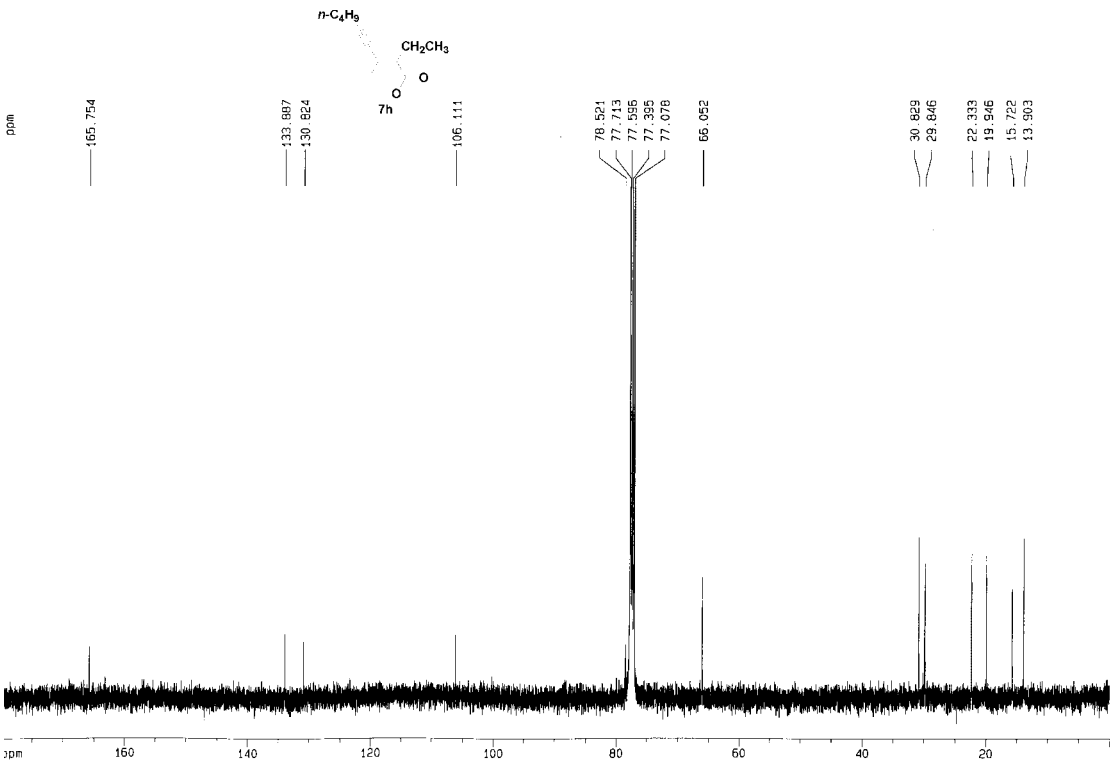

n-C4H9
H
O
O
7a
ppm
164.358
140.588
122.907
103.672
78.735
77.721
77.403
77.086
66.358
30.585
29.449
22.346
19.824
13.887
ppm
160
140
120
100
80
60
40
20

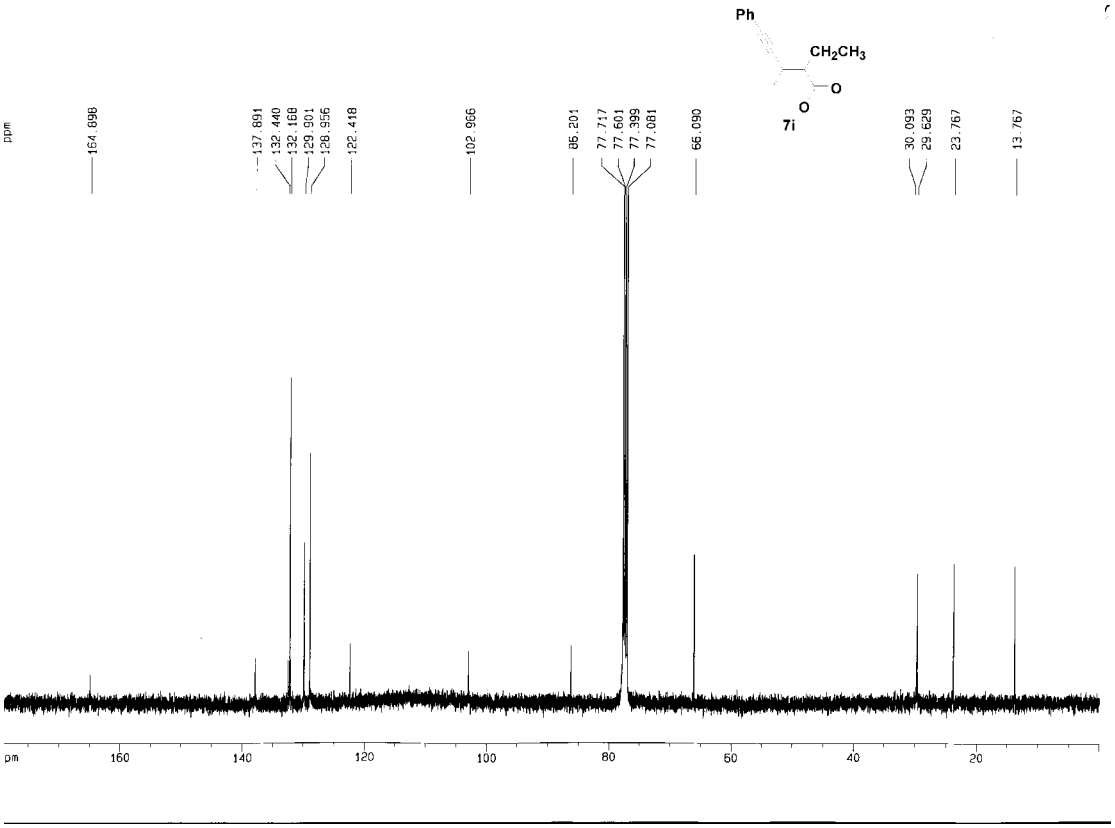

Ph
H
O
O
7b
ppm
164.093
139.536
132.418
130.246
128.982
123.593
121.832
100.836
86.563
77.729
77.615
77.411
77.095
66.443
29.168

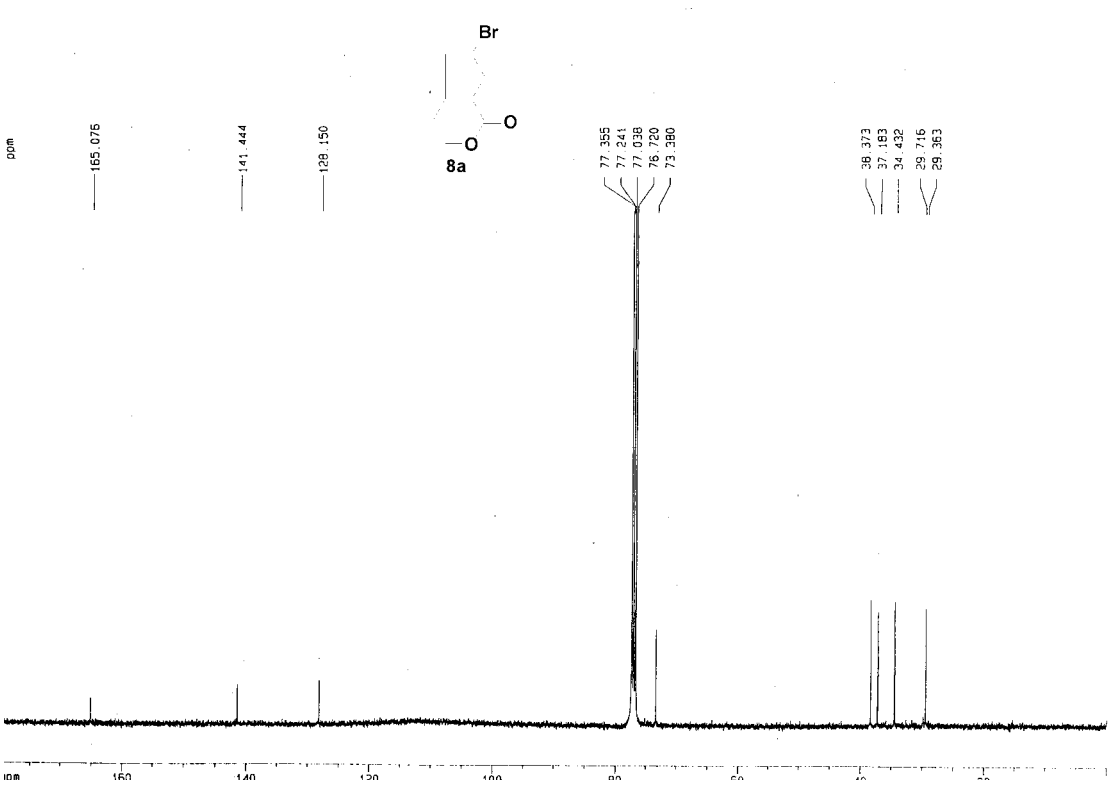

n-C4H9
CH3
O
O
7c
ppm
164.837
136.501
133.104
105.270
77.663
77.345
77.230
77.027
76.710
65.628
30.432
29.589
23.076
21.942
19.572
13.519
13.259


n-C5H11
CH3
O
O
7e
ppm
165.762
133.903
130.820
105.196
78.529
77.720
77.605
77.402
77.084
66.053
31.410
29.839
28.455
22.504
20.229
15.719
14.307


t-Bu
CH3
O
O
7f
165.746
133.866
130.727
113.944
77.717
77.402
77.399
77.081
66.050
31.950
29.813
28.975
15.647
160
140
120
100
80
60
40
20
H3COH2C
CH3
O
O
7g
155.366
132.471
132.364
99.456
83.836
77.733
77.646
77.415
77.097
65.100
60.699
58.281
29.359
15.924
160
140
120
100
80
60
40
20


n-C4H9
CH2CH3
O
O
7h
ppm
165.754
133.887
130.824
106.111
78.521
77.713
77.595
77.395
77.078
66.052
30.829
29.846
22.333
19.946
15.722
13.903
160
140
120
100
80
60
40
20


Ph
CH2CH3
O
O
7i
ppm
164.696
137.891
132.440
132.168
129.901
128.956
122.418
102.966
85.201
77.717
77.601
77.399
77.081
66.090
30.093
29.629
23.767
13.767
160
140
120
100
80
60
40
20


Br
O
O
8a
ppm
165.076
141.444
128.150
77.355
77.241
77.038
76.720
73.380
38.373
37.183
34.432
29.716
29.363

S37