Remarkable Rate Acceleration of Intramolecular Diels-Alder Reaction in Ionic Liquids

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Electronic Supplementary Information

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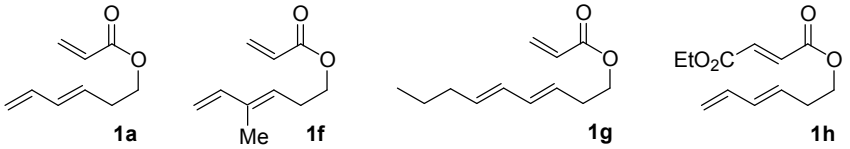
1. General and materials

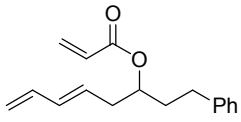
Melting points were uncorrected. ^1H and ^{13}C NMR spectra were taken on a Bruker DPX400 spectrometer, and chemical shifts were reported in parts per million (ppm) using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^1H NMR, and $CDCl_3$ (77.01 ppm) for ^{13}C NMR as an internal standard, respectively. Mass spectra were recorded by a Micromass LCT (ESI-TOF) or a Micromass Auto Spec (EI). Column chromatography was performed on silica gel (Kanto Chemical, neutral, 75-150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 x 4 cm i.d. prepacked column (Kusano pre-packed column Si-10, 40 x 300 mm I. D., silica gel, 50 μm) with UV and RI detectors. Ionic liquids were commercially available.

2. Preparation of triene ester (1)

(*E*)-Hexa-3,5-dienyl acrylate **1a**,[1] (*E*)-4-methylhexa-3,5-dienyl acrylate **1f**,[1] (3*E*,5*E*)-nona-3,5-dienyl acrylate **1g**,[2] and ethyl (*E*)-hexa-3,5-dienyl fumarate **1h**[3] were prepared by the reported procedure.



(*E*)-1-Phenylocta-5,7-dien-3-yl acrylate (1b)

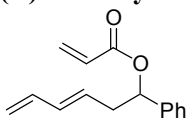


1b

To a solution of 3-phenylpropionaldehyde (1.61 g, 12 mmol) and trimethylpenta-2,4-dienylsilane[4] (1.40 g, 10 mmol) in CH_2Cl_2 (10 mL), $TiCl_4$ (0.55 mL, 5.0 mmol) was slowly added at –60 °C. After being stirred at -40 °C for 15 min, the reaction mixture was quenched with 1M HCl solution (20 mL), extracted with Et_2O (20 mL x 3) and dried over anhydrous $MgSO_4$. After the concentration of combined organic layer under reduced pressure, the resultant residue was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give (*E*)-1-phenylocta-5,7-dien-3-ol **1b-sm** in 41% yield (888 mg, 4.1 mmol). Colorless oil; IR (neat) ν 3388, 3027, 2928, 1005, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.52-2.57 (2H, m), 4.73 (1H, dd, J = 7.1, 5.8 Hz), 5.03 (1H, d, J = 10.5 Hz), 5.15 (1H, d, J = 16.7 Hz), 5.69 (1H, dt, J = 15.1, 7.5 Hz), 6.18 (1H, dd, J = 15.1, 10.5 Hz), 6.32 (1H, dt, J = 16.7, 10.5 Hz), 7.26-7.32 (1H, m), 7.33-7.39 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 73.6, 116.2, 125.8, 127.6, 128.4, 130.0, 134.4, 136.7, 143.8; MS (ESI-TOF) *m*/*z* 225 $[M+Na]^+$; HRMS calcd for $C_{14}H_{18}NaO$ $[M+Na]^+$, 225.1255; found, 225.1235.

To a solution of alcohol **1b-sm** (0.61 g, 3.0 mmol) and Et_3N (0.63 mL, 6.0 mmol) in CH_2Cl_2 (10 mL), acryloyl chloride (0.62 mL, 4.5 mmol) was added at 0 °C. After being stirred at room temperature for 20 h, the reaction mixture was quenched with H_2O (15 mL), extracted with Et_2O (20 mL x 3) and dried over anhydrous $MgSO_4$. The organic layer was evaporated and purified by column chromatography on silica gel to give acrylate **1b** in 88 % yield (678 mg, 2.65 mmol). Colorless oil; IR (neat) ν 3028, 2951, 1722, 1404, 1271, 1195, 1004, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.93-2.09 (2H, m), 2.50 (2H, t, J = 6.6 Hz), 2.65-2.82 (2H, m), 5.08 (1H, d, J = 10.4 Hz), 5.09-5.16 (1H, m), 5.20 (1H, d, J = 17.0 Hz), 5.71 (1H, dt, J = 15.2, 7.4 Hz), 5.90 (1H, dd, J = 10.4, 1.4 Hz), 6.12-6.22 (1H, m), 6.21 (1H, dd, J = 17.3, 10.4 Hz), 6.38 (1H, dd, J = 17.0, 10.4 Hz), 6.49 (1H, dd, J = 17.3, 1.4 Hz), 7.22-7.29 (3H, m), 7.32-7.39 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 35.3, 37.3, 73.2, 116.0, 126.0, 128.3, 128.4, 128.7, 129.0, 130.5, 134.1, 136.8, 141.4, 165.8; MS (ESI-TOF) *m*/*z* 225 $[M+Na]^+$; HRMS calcd for $C_{14}H_{18}NaO$ $[M+Na]^+$, 225.1255; found, 225.1270.

(*E*)-1-Phenylhexa-3,5-dienyl acrylate (1c)

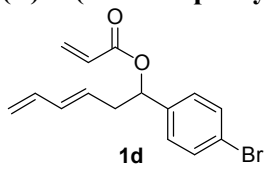


1c

According to the synthetic procedure for **1b-sm**, (*E*)-1-phenylhexa-3,5-dien-1-ol **1c-sm** was prepared in 51% yield (885 mg, 5.1 mmol) by the reaction of benzaldehyde (1.27 g, 12 mmol) with trimethylpenta-2,4-dienylsilane[4] (1.40 g, 10 mmol) in the presence of $TiCl_4$ (0.55 mL, 5.0 mmol). Colorless oil; IR (neat) ν 3388, 3031, 2899, 1005, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.52-2.57 (2H, m), 4.73 (1H, dd, J = 7.1, 5.8 Hz), 5.03 (1H, d, J = 10.5 Hz), 5.15 (1H, d, J = 16.7 Hz), 5.69 (1H, dt, J = 15.1, 7.5 Hz), 6.18 (1H, dd, J = 15.1, 10.5 Hz), 6.32 (1H, dt, J = 16.7, 10.5 Hz), 7.26-7.32 (1H, m), 7.33-7.39 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 73.6, 116.2, 125.8, 127.6, 128.4, 130.0, 134.4, 136.7, 143.8; MS (ESI-TOF) *m*/*z* 197 $[M+Na]^+$; HRMS calcd for $C_{12}H_{14}NaO$ $[M+Na]^+$, 197.0942; found, 197.0947.

According to the synthetic procedure for **1b**, acrylate **1c** was prepared in 76% yield (519 mg, 2.27 mmol) by the reaction of alcohol **1c-sm** (0.52 g, 3.0 mmol) with acryloyl chloride (0.62 mL, 4.5 mmol) in the presence of Et_3N (0.63 mL, 6.0 mmol). Colorless oil; IR (neat) ν 3034, 2946, 1725, 1404, 1267, 1189, 1004, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.59-2.67 (1H, m), 2.68-2.78 (1H, m), 4.99 (1H, d, J = 10.2 Hz), 5.11 (1H, d, J = 16.9 Hz), 5.52-5.61 (1H, m), 5.83 (1H, dd, J = 10.4, 0.9 Hz), 5.84-5.89 (1H, m), 6.04-6.12 (1H, m), 6.15 (1H, dd, J = 17.4, 10.4 Hz), 6.26 (1H, dt, J = 16.9, 10.2 Hz), 6.42 (1H, dd, J = 17.4, 0.9 Hz), 7.26-7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 75.5, 116.1, 126.5, 128.0, 128.5, 128.6, 128.8, 130.8, 134.2, 136.7, 139.9, 165.3; MS (ESI-TOF) m/z 251 $[M+Na]^+$; HRMS calcd for $C_{15}H_{16}NaO_2$ $[M+Na]^+$, 251.1048; found, 251.1057.

(*E*)-1-(4-Bromophenyl)hexa-3,5-dienyl acrylate (1d)

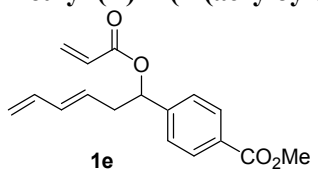


1d

According to the synthetic procedure for **1b-sm**, (*E*)-1-(4-bromophenyl)hexa-3,5-dien-1-ol **1d-sm** was prepared in 49% yield (1.24 g, 4.9 mmol) by the reaction of 4-bromobenzaldehyde (2.22 g, 12 mmol) with trimethylpenta-2,4-dienylsilane[4] (1.40 g, 10 mmol) in the presence of $TiCl_4$ (0.55 mL, 5.0 mmol). Colorless oil; IR (neat) ν 3376, 3011, 2899, 1070, 1009, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.12 (1H, brs, OH), 2.44-2.54 (2H, m), 4.69 (1H, dd, J = 7.4, 5.4 Hz), 5.04 (1H, d, J = 10.2 Hz), 5.16 (1H, d, J = 16.9 Hz), 5.64 (1H, dt, J = 15.1, 7.5 Hz), 6.15 (1H, dd, J = 15.1, 10.2 Hz), 6.31 (1H, dt, J = 16.9, 10.2 Hz), 7.22 (2H, d, J = 8.4 Hz), 7.48 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.5, 72.9, 116.5, 121.3, 127.5, 129.4, 131.5, 134.7, 136.5, 142.8; MS (EI) m/z 252 $[M]^+$; HRMS calcd for $C_{12}H_{12}Br$ $[M-H_2O+H]^+$, 235.0122; found, 235.0111.

According to the synthetic procedure for **1b**, acrylate **1d** was prepared in 80% yield (0.74 g, 2.41 mmol) by the reaction of alcohol **1d-sm** (0.76 g, 3.0 mmol) with acryloyl chloride (0.62 mL, 4.5 mmol) in the presence of Et_3N (0.63 mL, 6.0 mmol). Colorless oil; IR (neat) ν 3011, 2952, 1725, 1406, 1281, 1187, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.58-2.67 (1H, m), 2.68-2.78 (1H, m), 5.04 (1H, d, J = 10.2 Hz), 5.14 (1H, d, J = 16.6 Hz), 5.56 (1H, dt, J = 15.2, 7.2 Hz), 5.82 (1H, t, J = 6.8 Hz), 5.88 (1H, dd, J = 10.4, 1.4 Hz), 6.06-6.15 (1H, m), 6.18 (1H, dd, J = 17.3, 10.4 Hz), 6.29 (1H, dt, J = 16.9, 10.2 Hz), 6.45 (1H, dd, J = 17.3, 1.4 Hz), 7.25 (2H, d, J = 8.5 Hz), 7.30 (2H, d, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.3, 74.8, 116.5, 122.0, 128.18, 128.24, 128.3, 131.2, 131.6, 134.5, 136.6, 139.0, 165.2; MS (ESI-TOF) m/z 329 $[M+Na]^+$; HRMS calcd for $C_{15}H_{15}BrNaO_2$ $[M+Na]^+$, 329.0153; found, 329.0144.

Methyl (*E*)-4-(1-(acryloyloxy)hexa-3,5-dienyl)benzoate (1e)



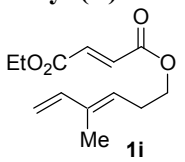
1e

According to the synthetic procedure for **1b-sm**, methyl (*E*)-4-(1-hydroxyhexa-3,5-dienyl)benzoate **1e-sm** was prepared in 68% yield (1.57 g, 6.8 mmol) by the reaction of methyl 4-formylbenzoate (1.97 g, 12 mmol) with trimethylpenta-2,4-dienylsilane[4] (1.40 g, 10 mmol) in the presence of $TiCl_4$ (0.55 mL, 5.0 mmol). Colorless

crystals; Mp. 41.0-42.5 °C; IR (neat) ν 3446, 3011, 2952, 1722, 1281 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (1H, brs, OH), 2.45-2.60 (2H, m), 3.91 (3H, s), 4.80 (1H, dd, J = 7.7, 5.0 Hz), 5.04 (1H, d, J = 10.1 Hz), 5.16 (1H, d, J = 16.6 Hz), 5.65 (1H, dt, J = 15.1, 7.3 Hz), 6.15 (1H, dd, J = 15.1, 10.1 Hz), 6.30 (1H, dt, J = 16.6, 10.1 Hz), 7.42 (2H, d, J = 8.2 Hz), 8.02 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 52.1, 73.1, 116.6, 125.7, 129.2, 129.4, 129.8, 134.9, 136.5, 148.9, 166.9; MS (ESI-TOF) m/z 255 $[M+Na]^+$; HRMS calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$, 255.0997; found, 255.0976. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: 72.35; H, 6.92.

According to the synthetic procedure for **1b**, acrylate **1e** was prepared in 83% yield (714 mg, 2.49 mmol) by the reaction of alcohol **1e-sm** (0.69 g, 3.0 mmol) with acryloyl chloride (0.62 mL, 4.5 mmol) in the presence of Et_3N (0.63 mL, 6.0 mmol). Colorless oil; IR (neat) ν 3011, 2929, 1726, 1404, 1266, 1188 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.52-2.60 (1H, m), 2.60-2.69 (1H, m), 3.83 (3H, s), 4.93 (1H, d, J = 10.3 Hz), 5.03 (1H, d, J = 16.9 Hz), 5.47 (1H, dt, J = 15.4, 7.2 Hz), 5.79 (1H, dd, J = 10.5, 1.4 Hz), 5.81 (1H, t, J = 6.5 Hz), 5.99 (1H, dd, J = 15.4, 10.3 Hz), 6.09 (1H, dd, J = 17.4, 10.5 Hz), 6.18 (1H, dt, J = 16.9, 10.3 Hz), 6.36 (1H, dd, J = 17.4, 1.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 7.95 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.4, 52.1, 78.0, 116.5, 126.3, 128.0, 128.3, 129.8, 131.2, 134.6, 136.5, 144.9, 165.2, 166.7; MS (ESI-TOF) m/z 309 $[M+Na]^+$; HRMS calcd for $C_{17}H_{18}NaO_4$ $[M+Na]^+$, 309.1103; found, 309.1099

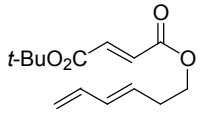
Ethyl (*E*)-4-Methylhexa-3,5-dienyl fumarate (1i)



1i

To a suspension of EDC·HCl (1.92 g, 10 mmol) in CH_2Cl_2 (5.0 mL), (*E*)-4-methylhexa-3,5-dien-1-ol (0.56 g, 5.0 mmol) and fumaric acid mono-ethyl ester (1.44 g, 10 mmol) were added at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was quenched with H_2O (25 mL), extracted with Et_2O (25 mL x 3) and dried over anhydrous $MgSO_4$. After evaporation of the combined organic layer, resultant residue was purified by column chromatography (hexane/Et_2O = 25 : 1) on silica gel to give **1i** in 88% yield (1.04 g, 4.39 mmol). Colorless oil; IR (neat) ν 2980, 1730, 1298, 1258, 1156 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.1 Hz), 1.76 (3H, s), 2.49-2.58 (2H, m), 4.22 (2H, t, J = 7.0 Hz), 4.26 (2H, t, J = 7.1 Hz), 4.98 (1H, d, J = 10.7 Hz), 5.13 (1H, d, J = 17.4 Hz), 5.46 (1H, t, J = 7.3 Hz), 6.36 (1H, dd, J = 17.4, 10.7 Hz), 6.84 (2H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 14.1, 27.6, 61.3, 64.5, 111.8, 126.7, 133.4, 133.8, 136.8, 140.9, 164.9, 165.0; MS (ESI-TOF) m/z 261 $[M+Na]^+$; HRMS calcd for $C_{13}H_{18}NaO_4$ $[M+Na]^+$, 261.1103; found, 261.1108.

***tert*-Butyl (*E*)-hexa-3,5-dienyl fumarate (1j)**



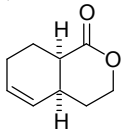
1j

According to the synthetic procedure for **1i**, this compound was obtained in 50% yield (504.5 mg, 2.00 mmol) by the reaction of fumaric acid mono-*tert*-butyl ester[5] (392 mg, 4.0 mmol), EDC·HCl (1.15 g, 6.0 mmol) in CH_2Cl_2 (5.0

mL) at rt for 48 h. Colorless oil; IR (neat) ν 2979, 1718, 1301, 1260, 1147 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (9H, s Hz), 2.42-2.52 (2H, m), 4.23 (2H, t, J = 6.7 Hz), 5.03 (1H, d, J = 10.0 Hz), 5.14 (1H, d, J = 16.7 Hz), 5.66 (1H, dt, J = 15.1, 7.3 Hz), 6.14 (1H, dd, J = 15.1, 10.0 Hz), 6.31 (1H, dt, J = 16.7, 10.0 Hz), 6.74 (1H, d, J = 15.8 Hz), 6.78 (1H, d, J = 15.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 31.8, 64.3, 81.9, 116.3, 129.2, 132.4, 133.6, 135.8, 136.6, 164.1, 165.2; MS (ESI-TOF) m/z 275 $[M+Na]^+$; HRMS calcd for $C_{14}H_{20}NaO_4$ $[M+Na]^+$, 275.1259; found, 275.1276.

2. Intramolecular Diels-Alder reaction of triene ester (1) in [emim]BF_4

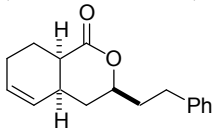
(4a*S,8a*R**)-3,4,4a,7,8,8a-Hexahydro-1*H*-isochromen-1-one (2a)**



2a

A suspension of triene ester **1a** (76.5 mg, 0.50 mmol) in 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4, 7.0 mL) was warmed to 100 °C over 30 min. After being stirred at 100 °C for 6 h, the reaction mixture was cooled to room temperature, then extracted with Et_2O (20 mL x 5). After concentration of the combined organic layer under reduced pressure, resultant mixture was purified by column chromatography (hexane/EtOAc = 3 : 1) on silica gel and by additional MPLC (hexane/EtOAc = 1 : 1) to give **2a** in 80% yield (61.3 mg, 0.402 mmol). The structure was confirmed by comparison of spectrum data with the authentic sample[1] and with the literature.[6]

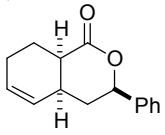
(3*S,4a*S**,8a*R**)-3-Phenethyl-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-1-one (2b)**



2b

According to the synthetic procedure for **2a**, this compound was obtained in 81% yield (103.6 mg, 0.404 mmol) by the reaction of **1b** (128.0 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). Colorless oil; IR (neat) ν 3022, 2941, 2926, 1738, 1203, 1148, 758, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (1H, dt, J = 14.1, 11.6 Hz), 1.81-2.15 (6H, m), 2.16-2.27 (1H, m), 2.60-2.70 (1H, m), 2,71-2,81 (2H, m), 2.86 (1H, ddd, J = 14.0, 9.2, 5.3 Hz), 4.21-4.30 (1H, m), 5.50-5.57 (1H, m), 5.74-5.57 (1H, m), 7.17-7.24 (3H, m), 7.26-7.33 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 23.5, 31.0, 31.4, 33.7, 37.3, 38.3, 77.8, 126.0, 127.5, 128.2, 128.5, 141.1, 174.6; MS (ESI-TOF) m/z 279 $[M+Na]^+$; HRMS calcd for $C_{17}H_{20}NaO_2$ $[M+Na]^+$, 279.1361; found, 279.1351.

(3*R,4a*S**,8a*R**)-3-Phenyl-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-1-one (2c)**

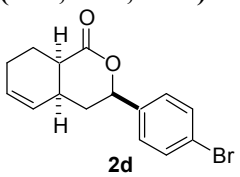


2c

According to the synthetic procedure for **2a**, this compound was obtained in 73% yield (83.3 mg, 0.365 mmol) by the

reaction of **1c** (113.9 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). Colorless oil; IR (neat) ν 3025, 2922, 1732, 1234, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.71 (1H, dt, J = 14.4, 12.0 Hz), 1.91-2.05 (2H, m), 2.07-2.18 (1H, m), 2.20-2.31 (2H, m), 2.80-2.94 (1H, m), 2.92 (1H, td, J = 8.2, 4.6 Hz), 5.31 (1H, dd, J = 12.0, 2.7 Hz), 5.55-5.61 (1H, m), 5.77-5.84 (1H, m), 7.29-7.43 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 23.5, 31.8, 36.4, 38.3, 80.3, 125.8, 127.8, 127.9, 128.3, 128.6, 139.5, 174.3; MS (ESI-TOF) m/z 229 $[M+H]^+$; HRMS calcd for $C_{15}H_{17}O_2$ $[M+H]^+$, 229.1229; found, 229.1216.

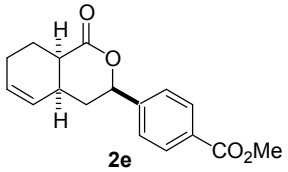
(3*R,4a*S**,8a*R**)-3-(4-Bromophenyl)-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-1-one (2d)**



2d

According to the synthetic procedure for **2a**, this compound was obtained in 72% yield (110.9 mg, 0.361 mmol) by the reaction of **1d** (153.9 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). Colorless oil; IR (neat) ν 3023, 2923, 1731, 1233 1072, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64 (1H, dt, J = 14.4, 12.0 Hz), 1.90-2.03 (2H, m), 2.05-2.17 (1H, m), 2.18-2.30 (2H, m), 2.79-2.91 (1H, m), 2.89 (1H, td, J = 8.2, 4.4 Hz), 5.27 (1H, dd, J = 12.0, 2.6 Hz), 5.52-5.59 (1H, m), 5.77-5.83 (1H, m), 7.23 (2H, d, J = 8.5 Hz), 7.49 (2H, d, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 23.4, 31.7, 36.3, 38.3, 79.5, 122.2, 127.4, 127.7, 127.9, 131.7, 138.5, 174.1; MS (ESI-TOF) m/z 307 $[M+H]^+$; HRMS calcd for $C_{15}H_{16}BrO_2$ $[M+H]^+$, 307.0334; found, 307.0337.

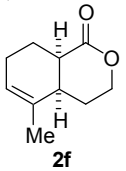
Methyl 4-((3R*,4aS*,8aR*)-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-3-yl)benzoate (2e)



2e

According to the synthetic procedure for **2a**, this compound was obtained in 83% yield (118.9 mg, 0.415 mmol) by the reaction of **1e** (143.4 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). Colorless crystals; Mp. 103-104.5 °C; IR (neat) ν 2950, 2919, 1735, 1709, 1278, 769, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (1H, dt, J = 14.4, 11.9 Hz), 1.89-2.02 (2H, m), 2.04-2.16 (1H, m), 2.19-2.29 (2H, m), 2.81-2.93 (1H, m), 2.91 (1H, td, J = 7.9, 4.5 Hz), 3.90 (3H, s), 5.35 (1H, dd, J = 11.9, 2.5 Hz), 5.52-5.58 (1H, m), 5.76-5.81 (1H, m), 7.42 (2H, d, J = 8.2 Hz), 8.02 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 23.4, 31.7, 36.3, 38.3, 52.1, 79.5, 125.6, 127.7, 127.8, 129.9, 130.0, 144.3, 166.6, 173.9; MS (ESI-TOF) m/z 287 $[M+H]^+$; HRMS calcd for $C_{17}H_{19}O_4$ $[M+H]^+$, 287.1283; found, 287.1297.

(4a*R,8a*R**)-5-Methyl-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-1-one (2f)**

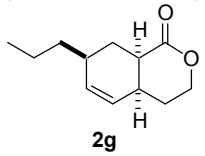


2f

According to the synthetic procedure for **2a**, this compound was obtained in 83% yield (69.4 mg, 0.417 mmol) by the

reaction of **1f** (83.6 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). The structure was confirmed by comparison of spectrum data with the authentic sample.[1]

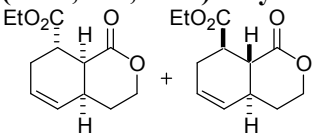
(4a*S,7*S**,8a*R**)-7-Propyl-3,4,4a,7,8,8a-hexahydro-1*H*-isochromen-1-one (2g)**



2g

According to the synthetic procedure for **2a**, this compound was obtained in 48% yield (46.9 mg, 0.241 mmol) by the reaction of **1g** (97.2 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). Colorless oil; IR (neat) ν 2956, 2927, 1728, 1249, 1217, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.0 Hz), 1.19-1.46 (5H, m), 1.69-1.79 (1H, m), 1.82-1.89 (1H, m), 2.09-2.16 (1H, m), 2.16-2.26 (1H, m), 2.49-2.58 (1H, m), 3.01 (1H, ddd, J = 12.3, 6.3, 3.5 Hz) 4.26 (1H, dt, J = 11.5, 3.4 Hz), 4.41 (1H, ddd, J = 11.5, 4.6, 2.7 Hz), 5.58 (1H, ddd, J = 10.0, 4.2, 2.7 Hz), 5.66-5.71 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.7, 27.3, 30.1, 32.8, 35.4, 38.1, 40.1, 69.2, 127.1, 133.7, 174.3; MS (ESI-TOF) m/z 195 $[M+H]^+$; HRMS calcd for $C_{12}H_{19}O_2$ $[M+H]^+$, 195.1385; found, 195.1395.

(4a*S,8*S**,8a*S**)-Ethyl 1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*cis*-2h) and (4a*S**,8R*,8aR*)-ethyl 1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*trans*-2h)**

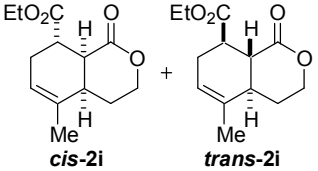


***cis*-2h** ***trans*-2h**

According to the synthetic procedure for **2a**, these compounds were obtained in 86% yield (***cis*-2h**, 82.8 mg, 0.369 mmol; ***trans*-2h**, 13.6 mg, 0.061 mmol; *cis*/*trans* = 6 : 1) by the reaction of **1h** (112.0 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL). The structure of ***trans*-2h** was confirmed by comparison of spectrum data with the literature.[3]

For ***cis*-2h**. Colorless oil; IR (neat) ν 2980, 2906, 1727, 1274, 1197, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.68-1.77 (1H, m), 2.16 (1H, ddd, J = 19.3, 9.6, 5.0 Hz), 2.24-2.35 (1H, m), 2.48-2.58 (1H, m), 2.86-2.95 (1H, m), 3.27 (1H, dd, J = 6.9, 3.1 Hz), 3.45 (1H, dt, J = 6.4, 3.1 Hz), 4.16 (2H, q, J = 7.1 Hz), 4.21-4.34 (2H, m), 5.51 (1H, brd, J = 10.1 Hz), 5.81-5.88 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.9, 28.3, 28.6, 39.0, 40.4, 60.9, 66.4, 127.6, 128.0, 172.2, 173.3; MS (ESI-TOF) m/z 247 $[M+Na]^+$; HRMS calcd for $C_{12}H_{16}NaO_4$ $[M+Na]^+$, 247.0946; found, 247.0951. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: 64.40; H, 7.28.

(4a*R,8*S**,8a*S**)-Ethyl 5-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*cis*-2i) and (4a*R**,8*R**,8a*R**)-ethyl 5-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*trans*-2i)**



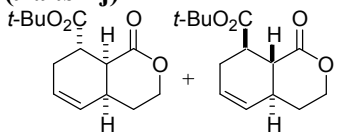
***cis*-2i** ***trans*-2i**

According to the synthetic procedure for **2a**, these compounds were obtained in 84% yield (99.6 mg, 0.418 mmol) as

an inseparatable mixture of *cis*-/*trans*-isomers in a ratio of 3.6 : 1 by the reaction of **1i** (118.8 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL).

For ***cis*-2i**. Colorless oil; IR (neat) ν 2965, 2911, 1728, 1271, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J = 7.1 Hz), 1.65 (3H, s), 1.79-1.89 (1H, m), 2.09-2.20 (1H, m), 2.25-2.37 (1H, m), 2.45-2.54 (1H, m), 2.78-2.87 (1H, m), 3.32 (1H, dd, J = 7.4, 3.2 Hz), 3.37 (1H, dt, J = 5.9, 3.2 Hz), 4.15 (2H, q, J = 7.1 Hz), 4.16-4.32 (2H, m), 5.52-5.57 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.6, 23.8, 26.7, 32.8, 39.1, 41.2, 60.8, 66.2, 123.1, 132.7, 172.5, 173.5; MS (ESI-TOF) m/z 261 $[M+Na]^+$; HRMS calcd for $C_{13}H_{18}NaO_4$ $[M+Na]^+$, 261.1103; found, 261.1105.

(4a*R,8*S**,8a*S**)-*tert*-Butyl 5-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*cis*-2j) and (4a*R**,8*R**,8a*R**)-*tert*-butyl 5-methyl-1-oxo-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylate (*trans*-2j)**

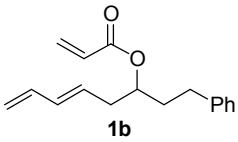


***cis*-2j** ***trans*-2j**

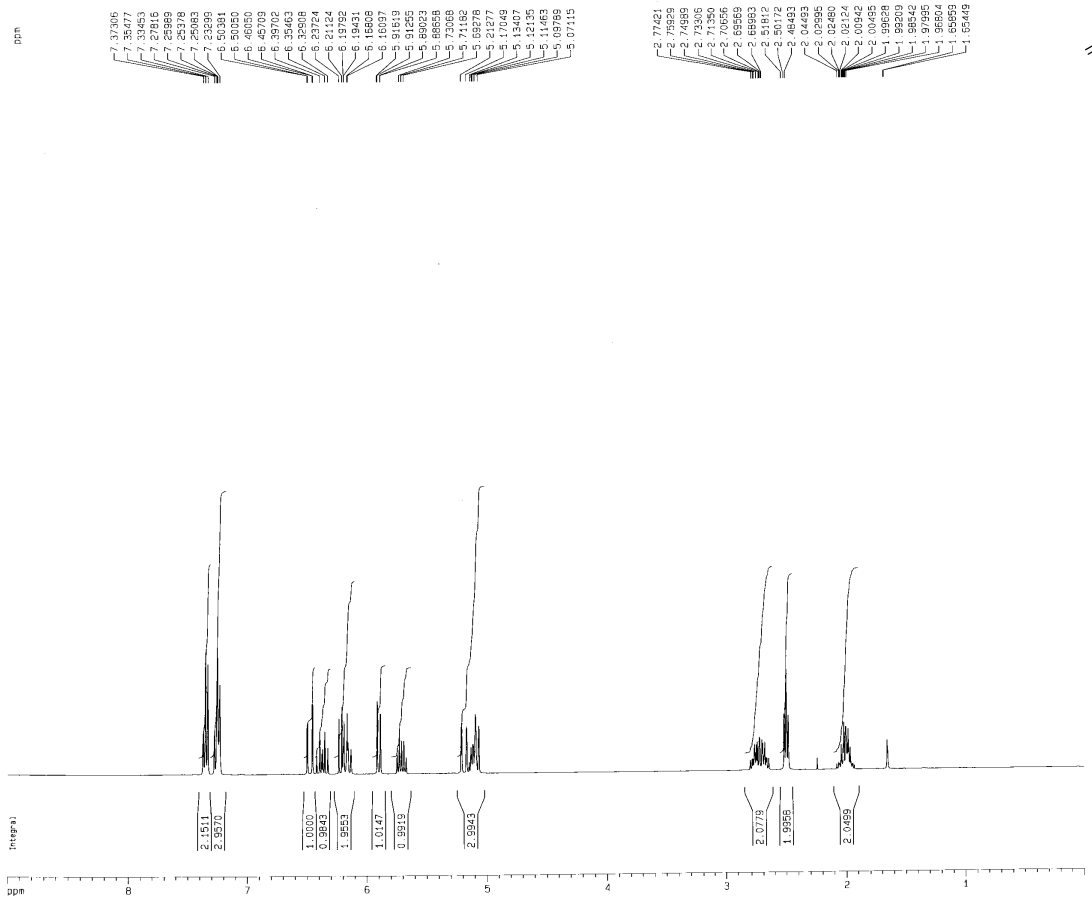
According to the synthetic procedure for **2a**, these compounds were obtained in 70% yield (***cis*-2j**, 78.0 mg, 0.309 mmol; ***trans*-2j**, 10.2 mg, 0.04 mmol; *cis*/*trans* = 7.6 : 1) by the reaction of **1j** (126.3 mg, 0.50 mmol) in [emim]BF_4 (7.0 mL).

For ***cis*-2j**. Colorless oil; IR (neat) ν 2977, 2928, 1725, 1277, 1152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (9H, s), 1.68-1.77 (1H, m), 2.16 (1H, ddd, J = 19.8, 9.8, 4.7 Hz), 2.20-2.29 (1H, m), 2.43-2.53 (1H, m), 2.89-2.94 (1H, m), 3.23 (1H, dd, J = 6.8, 3.0 Hz), 3.36-3.41 (1H, m), 4.21-4.32 (2H, m), 5.51 (1H, brd, J = 10.1 Hz), 5.82-5.89 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 28.0, 28.4, 28.6, 39.9, 40.6, 66.3, 80.9, 127.5, 128.2, 172.4, 172.6; MS (ESI-TOF) m/z 275 $[M+Na]^+$; HRMS calcd for $C_{14}H_{20}NaO_4$ $[M+Na]^+$, 275.1259; found, 275.1247. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: 66.55; H, 7.91.

4. ^{1}H and ^{13}C NMR spectra of triene ester (1)



1b

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RG                       181
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SFO1              400.0324703 MHz

F2 - Processing parameters
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GB                            0
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1D NMR plot parameters
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F2                        0.00 Hz
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HZCM                112.50843 Hz/cm
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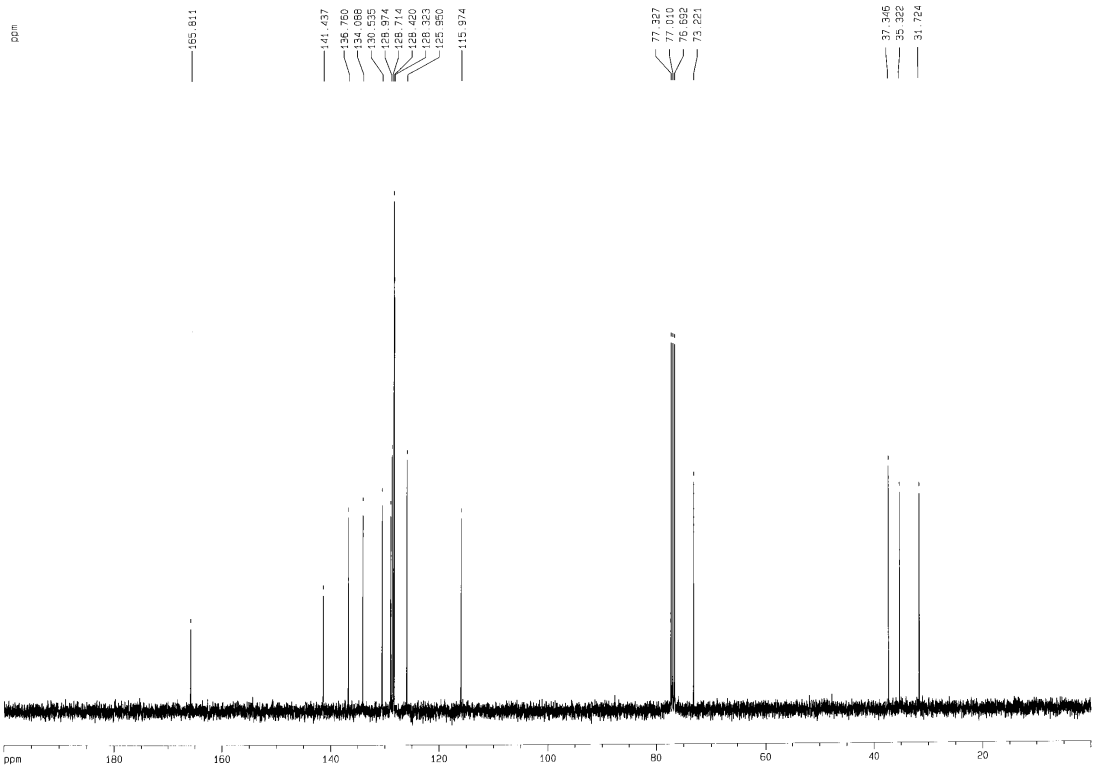


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TD                    65536
SOLVENT               CDCl3
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MCREST            0.00000000 sec
MCWRK             0.01500000 sec

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PL1                    -3.50 dB
SFO1              100.5986886 MHz

======== CHANNEL f2 ========
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NUC2                      1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

F2 - Processing parameters
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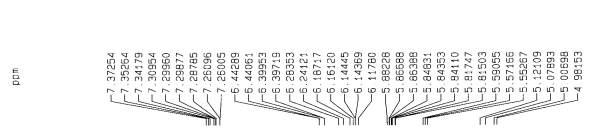
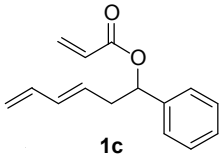
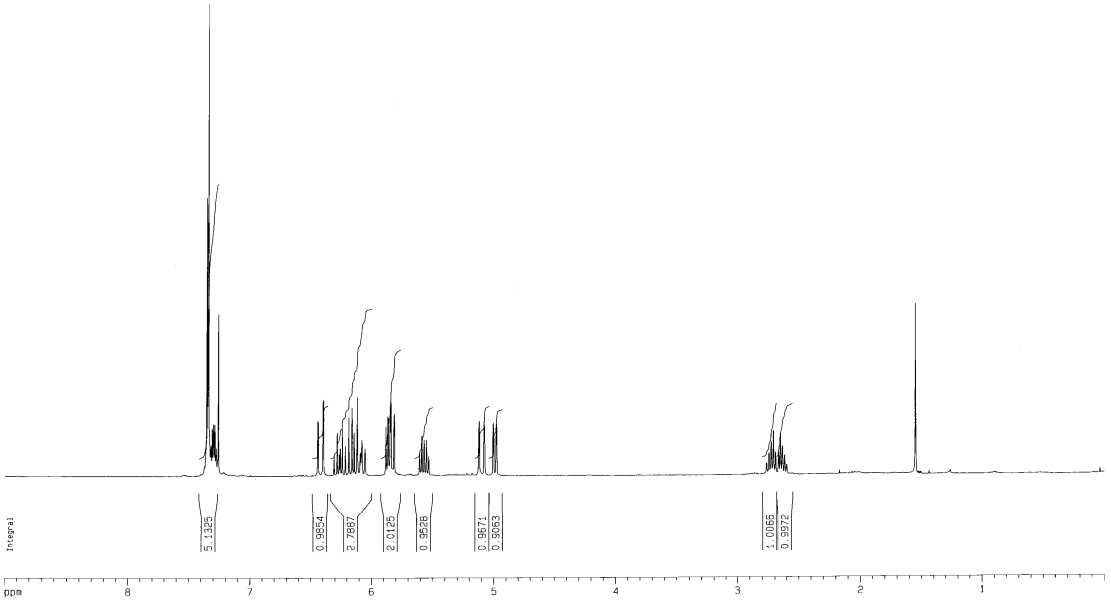




1c

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PROCNO                       1

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F2 - Processing parameters
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1D NMR plot parameters
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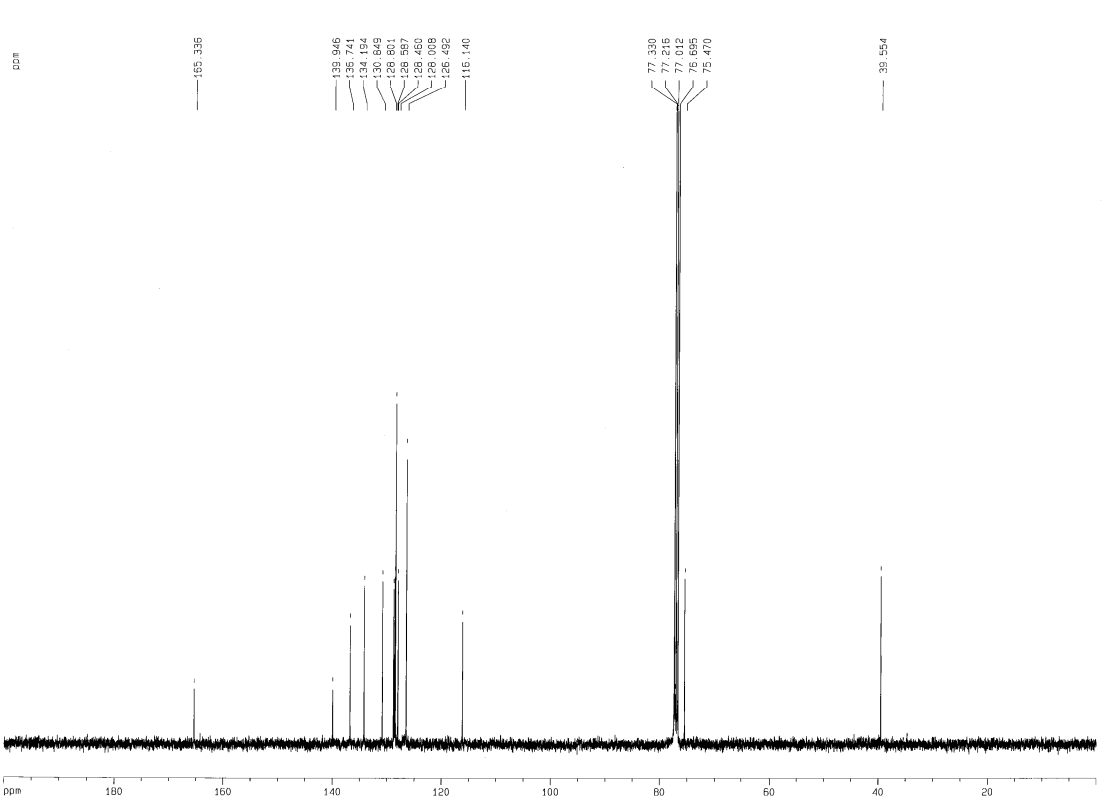


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PROCNO                       1

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PL1                      -3.50 dB
SFO1               100.5986886 MHz

======== CHANNEL f2 ========
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NUC2                        1H
PCPD2                  100.00 usec
PL2                     -4.00 dB
PL12                    17.00 dB
PL13                    17.00 dB
SFO2               400.0316001 MHz

F2 - Processing parameters
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F2                       -0.00 Hz
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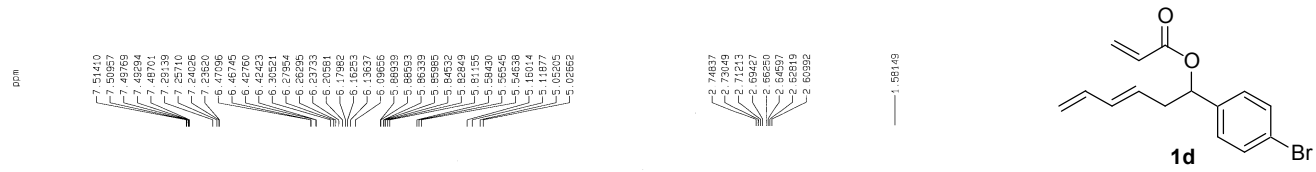

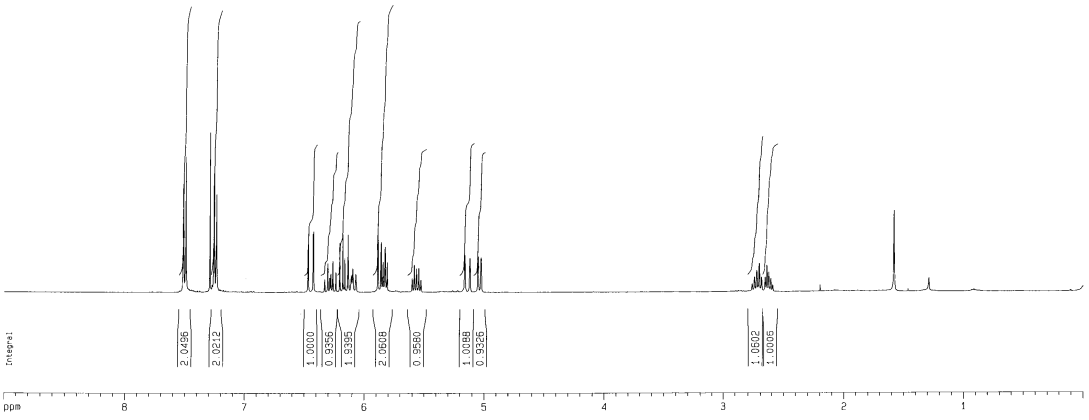


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PROCNO                       1

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MCWRK              0.01500000 sec

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1D NMR plot parameters
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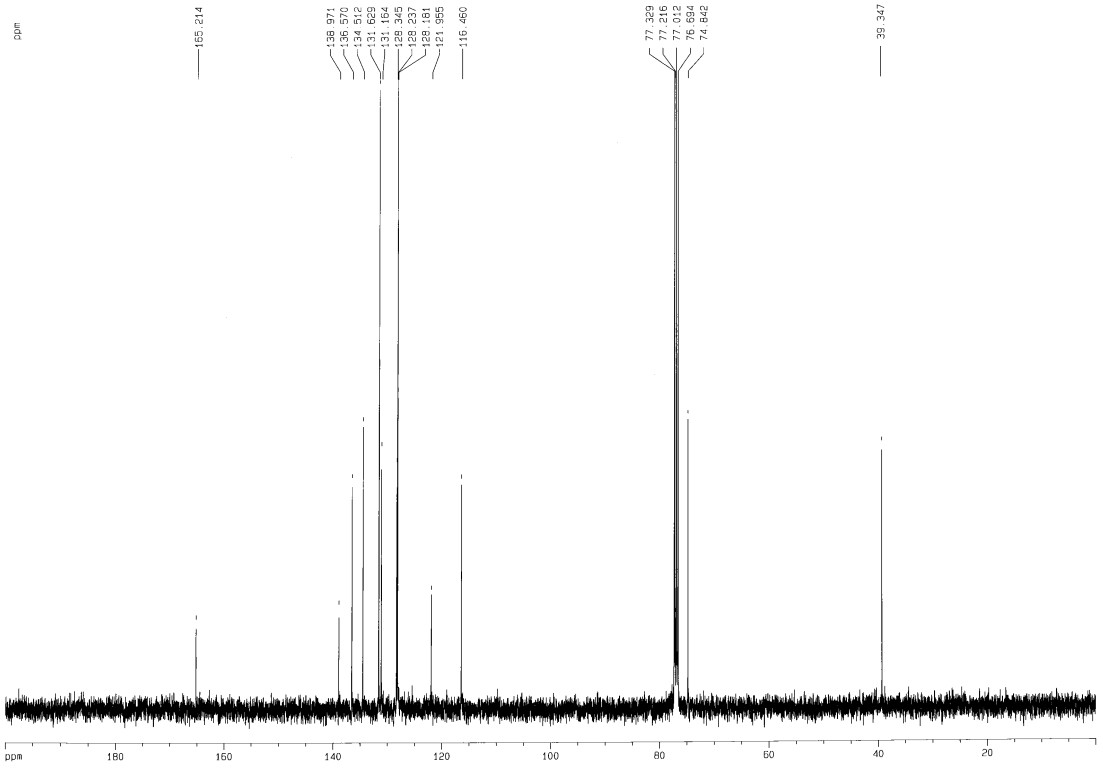
HZCM               112.50844 Hz/cm
```

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Current Data Parameters
NAME                  IMDA4-1d
EXPNO                        2
PROCNO                       1

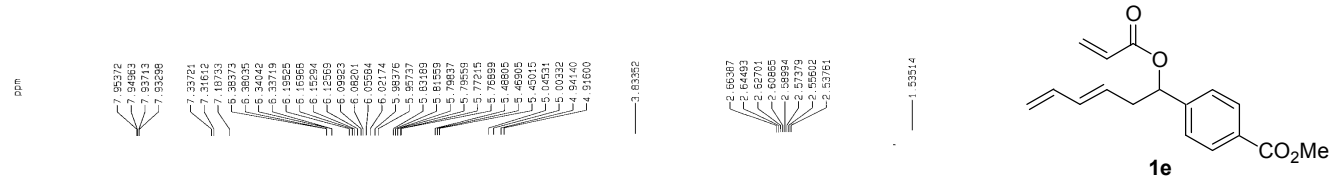
F2 - Acquisition Parameters
Date_              20090423
Time                    21.56
INSTRUM                 spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zgpg30
TD                     65536
SOLVENT                CDCl3
NS                         639
DS                           4
SWH               26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517875 sec
RG                       16384
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1              100.5986886 MHz

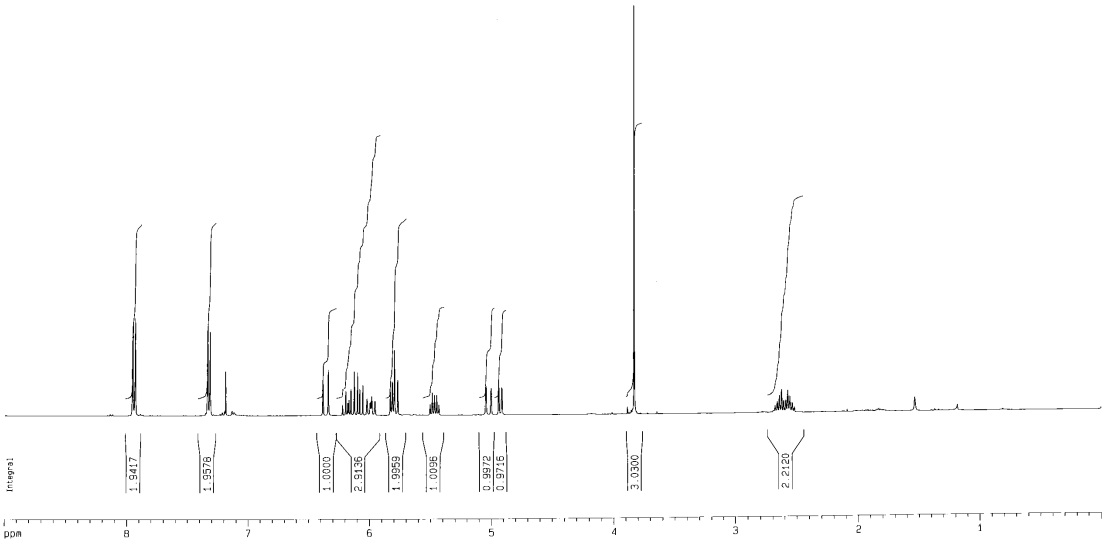
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

F2 - Processing parameters
SI                         32768
SF                100.5876230 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      32.00 cm
CY                      19.00 cm
F1P                   200.000 ppm
F1                   20117.53 Hz
F2P                     -0.000 ppm
F2                      -0.00 Hz
PPMCM                6.25000 ppm/cm
HZCM               628.67267 Hz/cm
```



1e

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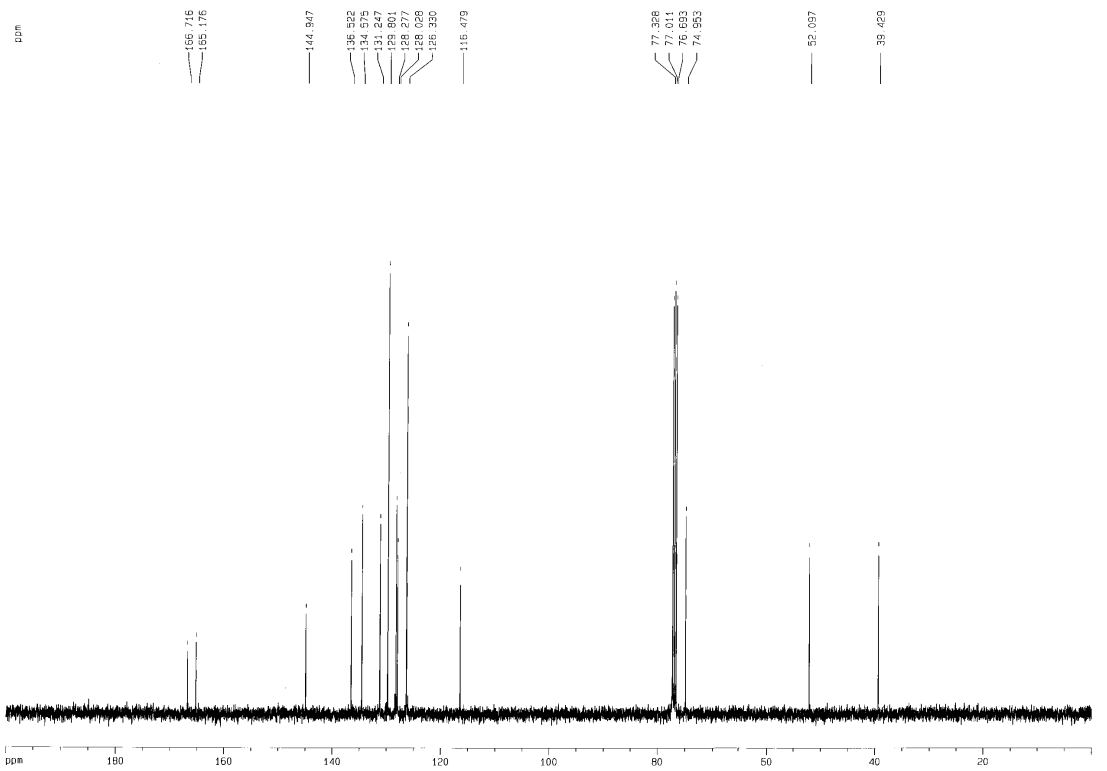
Current Data Parameters
NAME                  IMDA4-1e
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090423
Time                 18.06
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                     203.2
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.50 usec
PL1                   -4.00 dB
SFO1           400.0324703 MHz

F2 - Processing parameters
SI                       32768
SF                 400.0300356 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       32.00 cm
CY                       12.00 cm
F1P                      9.000 ppm
F1                     3600.27 Hz
F2P                      0.000 ppm
F2                       0.00 Hz
PPMCM                 0.28125 ppm/cm
HZCM                112.50845 Hz/cm
```




```
Current Data Parameters
NAME                  IMDA4-1d
EXPNO                        2
PROCNO                       1

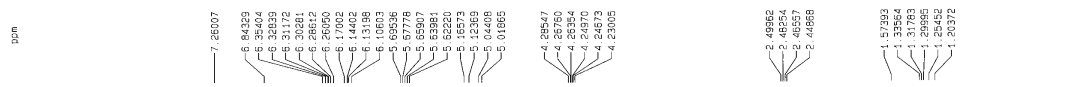
F2 - Acquisition Parameters
Date_              20090423
Time                 18.14
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG              zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     112
DS                       4
SWH               26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517875 sec
RG                    4597.6
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

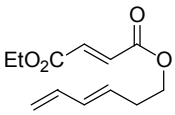
======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -3.50 dB
SFO1           100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -4.00 dB
PL12                  17.00 dB
PL13                  17.00 dB
SFO2           400.0315001 MHz

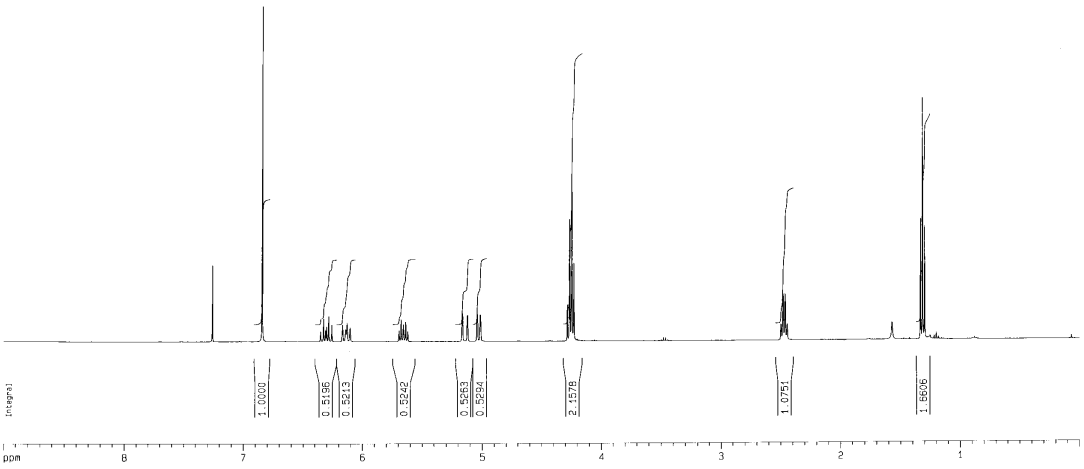
F2 - Processing parameters
SI                       32768
SF                 100.5876246 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       32.00 cm
CY                       13.00 cm
F1P                    200.000 ppm
F1                   20117.53 Hz
F2P                     -0.000 ppm
F2                       -0.00 Hz
PPMCM                 6.25000 ppm/cm
HZCM                628.67267 Hz/cm
```





1h



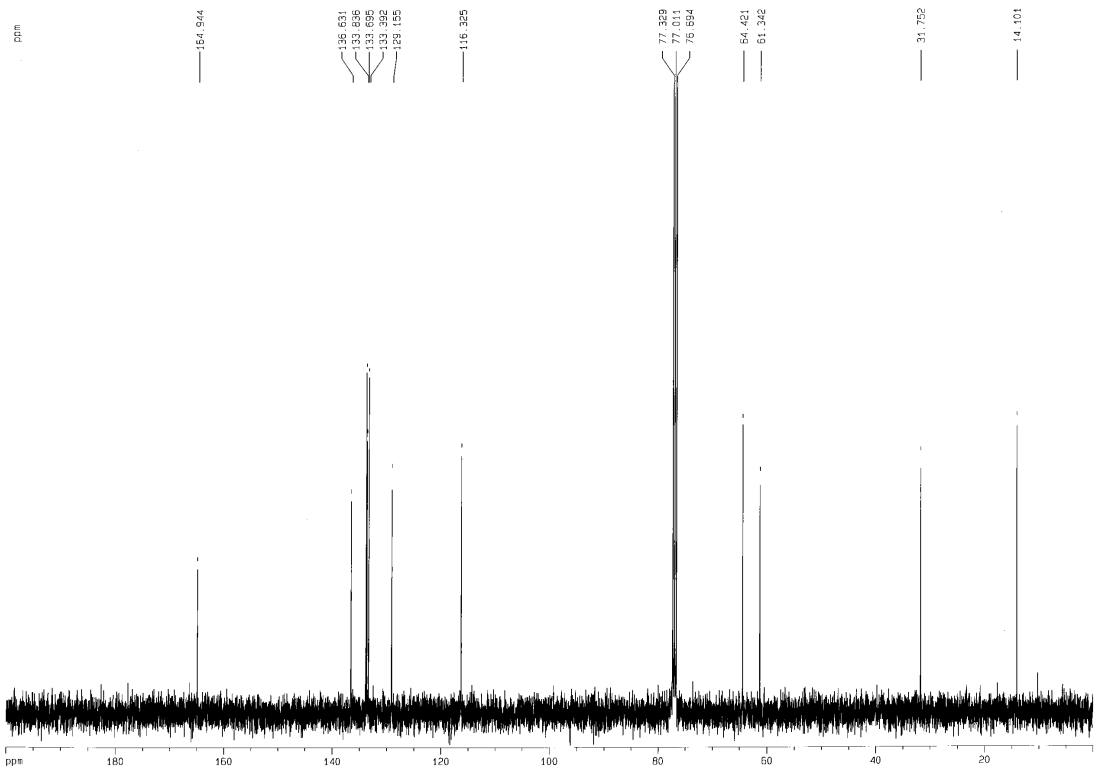

```
Current Data Parameters
NAME                  IMDA4-1h
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20090415
Time                   22.34
INSTRUM                spect
PROBHD    5 mm GNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                           6
DS                           2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                       287.4
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                      11.50 usec
PL1                     -4.00 dB
SF01               400.0324703 MHz

F2 - Processing parameters
SI                         32768
SF                 400.0300065 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         32.00 cm
CY                         10.00 cm
F1P                        9.000 ppm
F1                       3600.27 Hz
F2P                        0.000 ppm
F2                          0.00 Hz
PPMCM                   0.28125 ppm/cm
HZCM                  112.50844 Hz/cm
```




```
Current Data Parameters
NAME                  IMDA4-1h
EXPNO                        2
PROCNO                       1

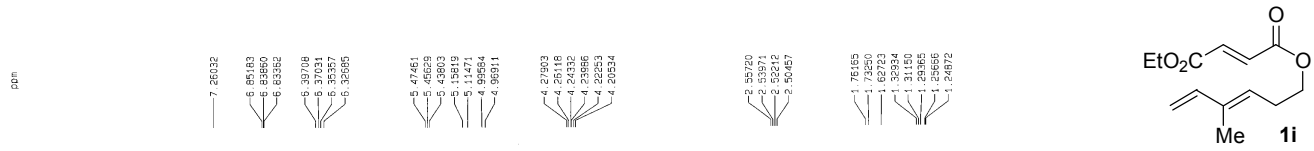
F2 - Acquisition Parameters
Date_               20090415
Time                   22.40
INSTRUM                spect
PROBHD    5 mm GNP 1H/13
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                         111
DS                           4
SWH               26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517675 sec
RG                       13004
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

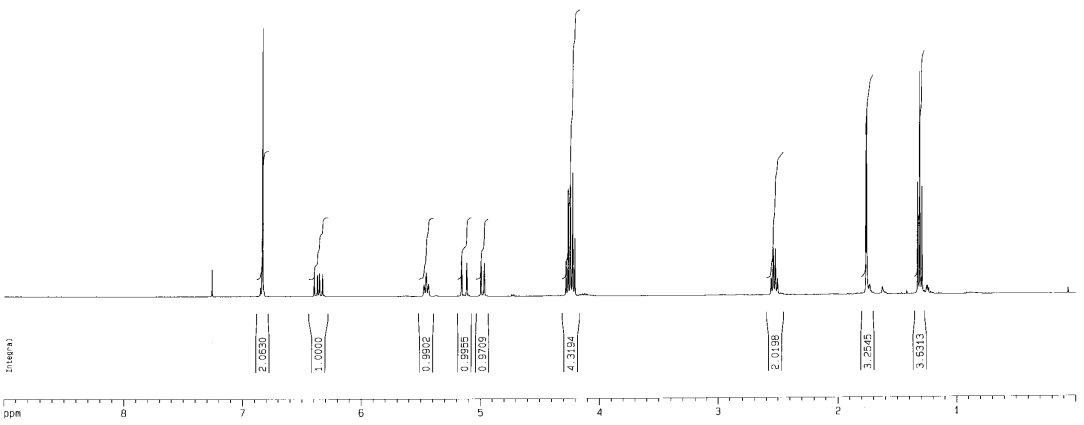
======== CHANNEL f1 ========
NUC1                        13C
P1                      10.00 usec
PL1                     -3.50 dB
SF01               100.5985886 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                  100.00 usec
PL2                     -4.00 dB
PL12                    17.00 dB
PL13                    17.00 dB
SF02               400.0316001 MHz

F2 - Processing parameters
SI                         32768
SF                 100.5876230 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         32.00 cm
CY                         10.00 cm
F1P                      200.000 ppm
F1                     20117.53 Hz
F2P                      -0.000 ppm
F2                         -0.00 Hz
PPMCM                   6.25000 ppm/cm
HZCM                  628.67267 Hz/cm
```





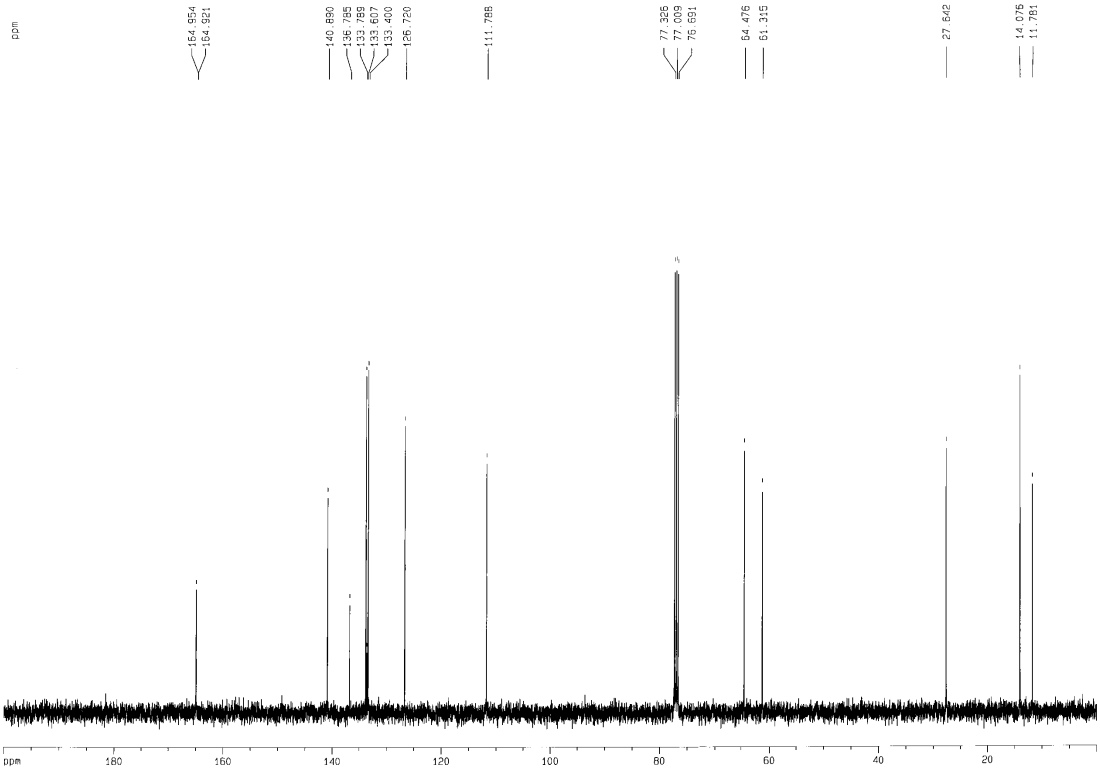

```
Current Data Parameters
NAME                  IMDA4-1i
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090415
Time                   19.18
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                           5
DS                           2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.9584243 sec
RG                         128
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1              400.0324703 MHz

F2 - Processing parameters
SI                         32768
SF                400.0300065 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         32.00 cm
CY                          8.00 cm
F1P                        9.000 ppm
F1                      3600.27 Hz
F2P                        0.000 ppm
F2                         0.00 Hz
PPMCM                  0.28125 ppm/cm
HZCM                 112.50844 Hz/cm
```




```
Current Data Parameters
NAME                  IMDA4-1i
EXPNO                        2
PROCNO                       1

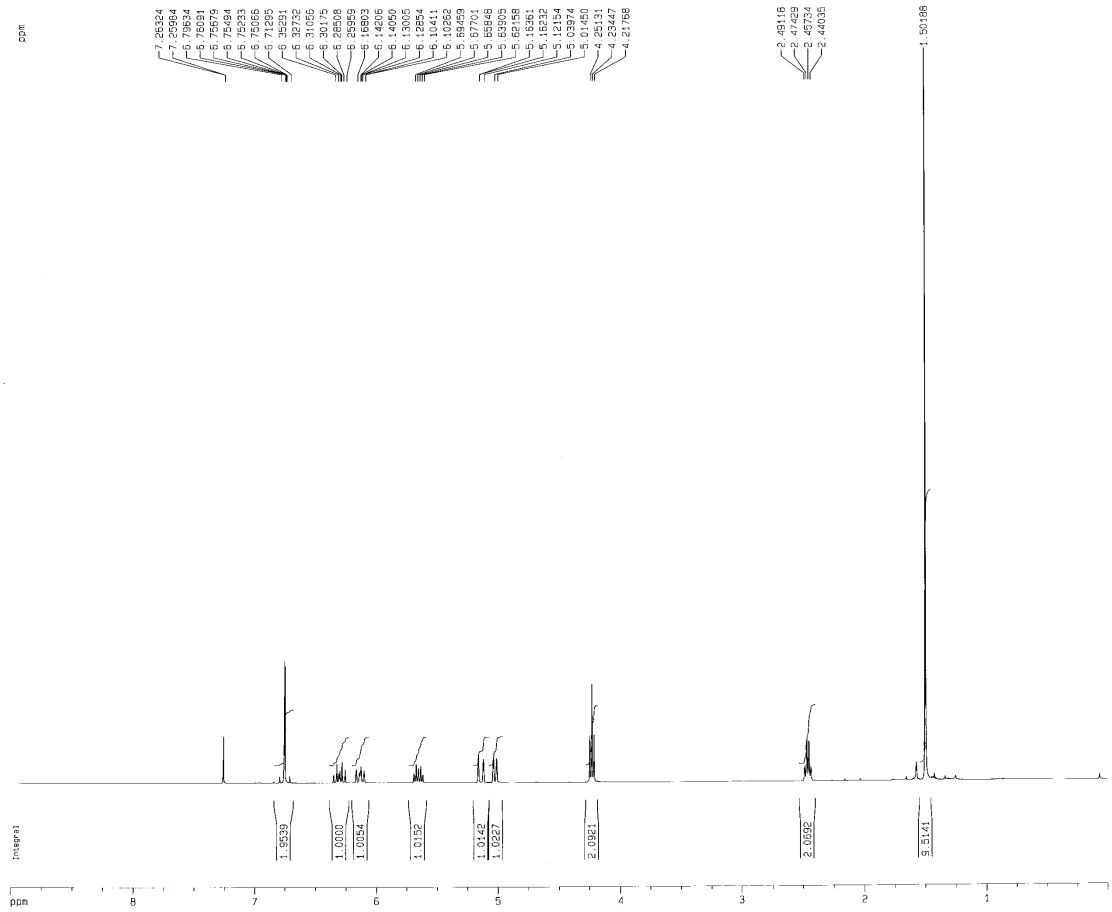
F2 - Acquisition Parameters
Date_              20090415
Time                   19.23
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                          69
DS                           4
SWH                26178.010 Hz
FIDRES              0.399445 Hz
AQ                  1.2517675 sec
RG                     14596.5
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

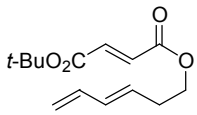
======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1              100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

F2 - Processing parameters
SI                         32768
SF                100.5876248 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         32.00 cm
CY                         10.00 cm
F1P                      200.000 ppm
F1                     20117.53 Hz
F2P                       -0.000 ppm
F2                        -0.00 Hz
PPMCM                  6.25000 ppm/cm
HZCM                 628.67267 Hz/cm
```





1j

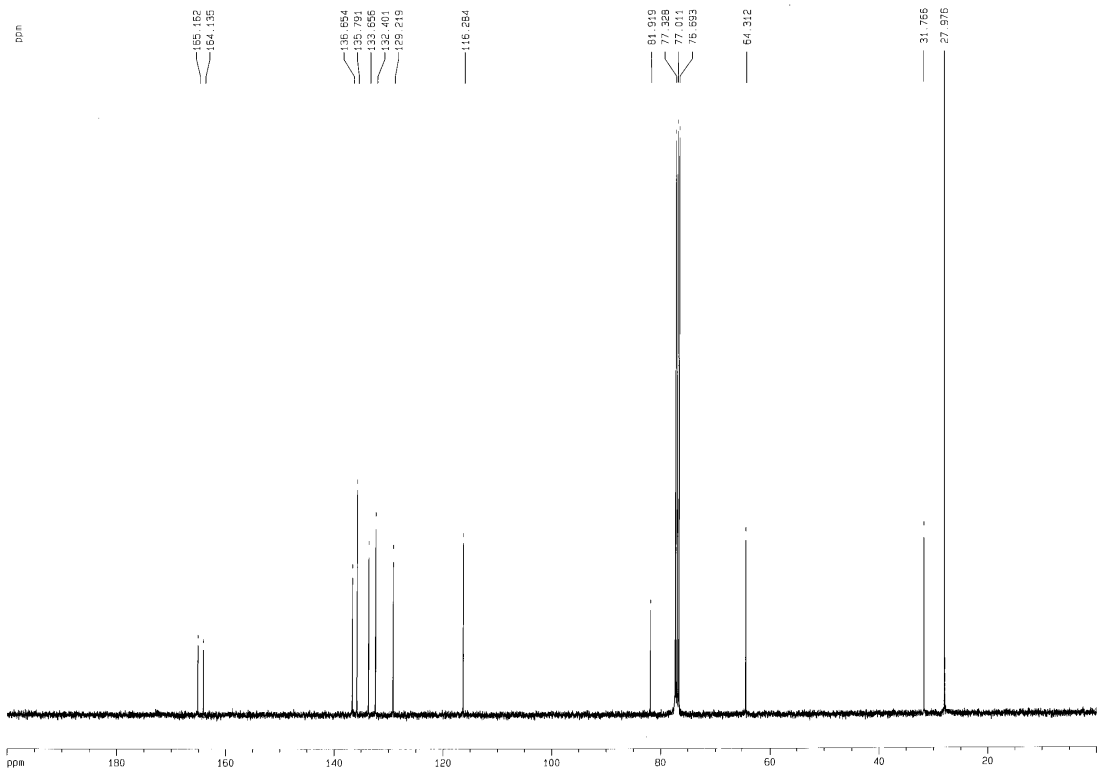
```
Current Data Parameters
NAME                  IMDA4-1j
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_               20090415
Time                   18.04
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                     228.1
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1              400.0324703 MHz

F2 - Processing parameters
SI                        32768
SF                400.0300067 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     32.00 cm
CY                     28.00 cm
F1P                    9.000 ppm
F1                   3600.27 Hz
F2P                    0.000 ppm
F2                     0.00 Hz
PPMCM                0.28125 ppm/cm
HZCM               112.50844 Hz/cm
```




```
Current Data Parameters
NAME                  IMDA4-1j
EXPNO                        5
PROCNO                       1

F2 - Acquisition Parameters
Date_               20090415
Time                   19.01
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                      1000
DS                         4
SWH               26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517875 sec
RG                      8192
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

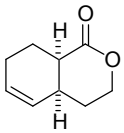
======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1              100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

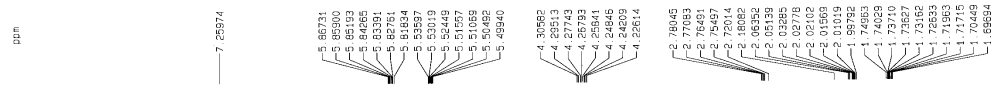
F2 - Processing parameters
SI                        32768
SF                100.5876230 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

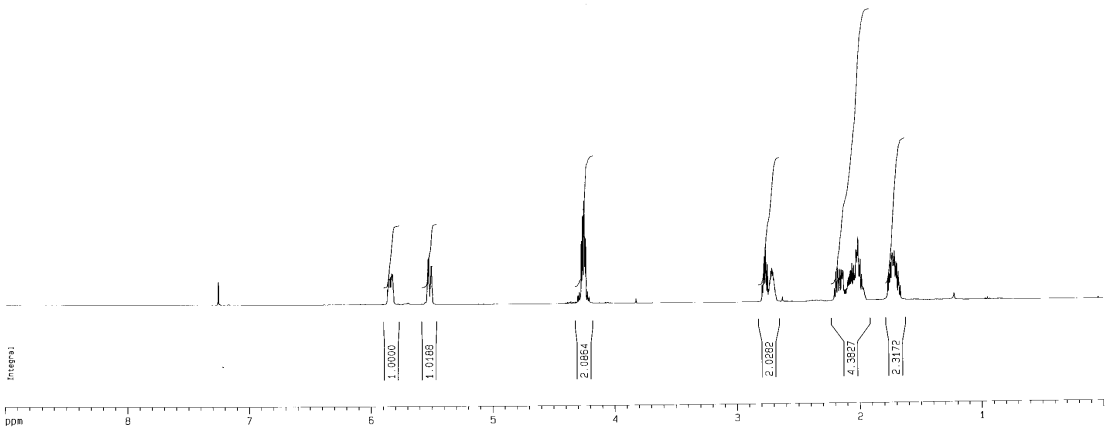
1D NMR plot parameters
CX                     32.00 cm
CY                     19.00 cm
F1P                  200.000 ppm
F1                 20117.53 Hz
F2P                   -0.000 ppm
F2                    -0.00 Hz
PPMCM                6.25000 ppm/cm
HZCM               628.67267 Hz/cm
```

5. ^{1}H and ^{13}C NMR spectra of DA adduct (2)



2a





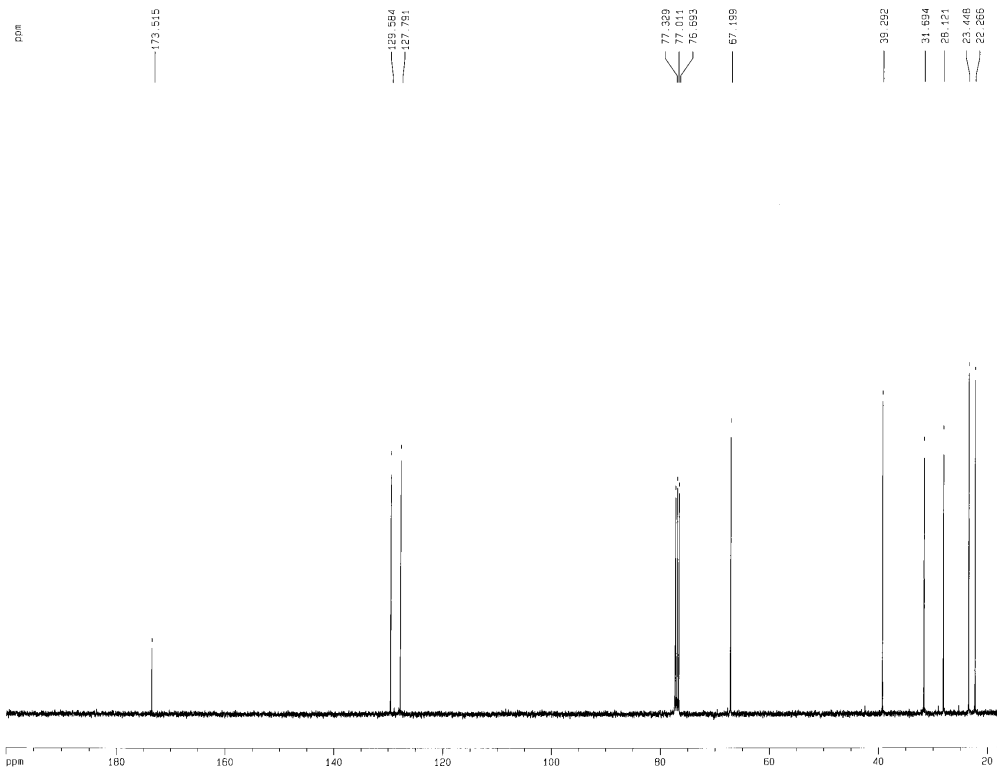
```
Current Data Parameters
NAME                  IMDA4-2a
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090408
Time                   20.34
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH               8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    101.6
DW                 60.400 usec
DE                  6.00 usec
TE                  300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1           400.0324703 MHz

F2 - Processing parameters
SI                        32768
SF                400.0300067 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        32.00 cm
CY                         3.00 cm
F1P                        9.000 ppm
F1                      3600.27 Hz
F2P                        0.000 ppm
F2                         0.00 Hz
PPMCM                  0.28125 ppm/cm
HZCM                 112.50844 Hz/cm
```



```
Current Data Parameters
NAME                  IMDA4-2a
EXPNO                        2
PROCNO                       1

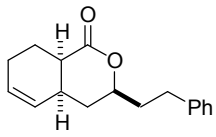
F2 - Acquisition Parameters
Date_              20090408
Time                   20.54
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      212
DS                        4
SWH              26178.010 Hz
FIDRES           0.399445 Hz
AQ               1.2517875 sec
RG                   5160.6
DW                 19.100 usec
DE                  6.00 usec
TE                  300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1           100.5986886 MHz

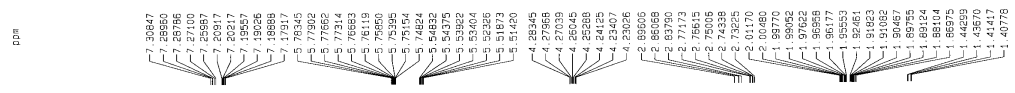
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2           400.0316001 MHz

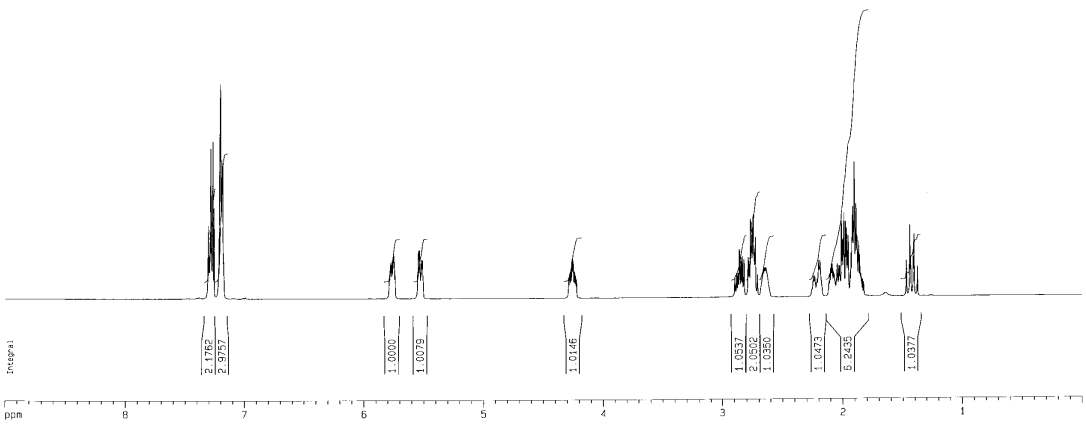
F2 - Processing parameters
SI                        32768
SF               100.5876294 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

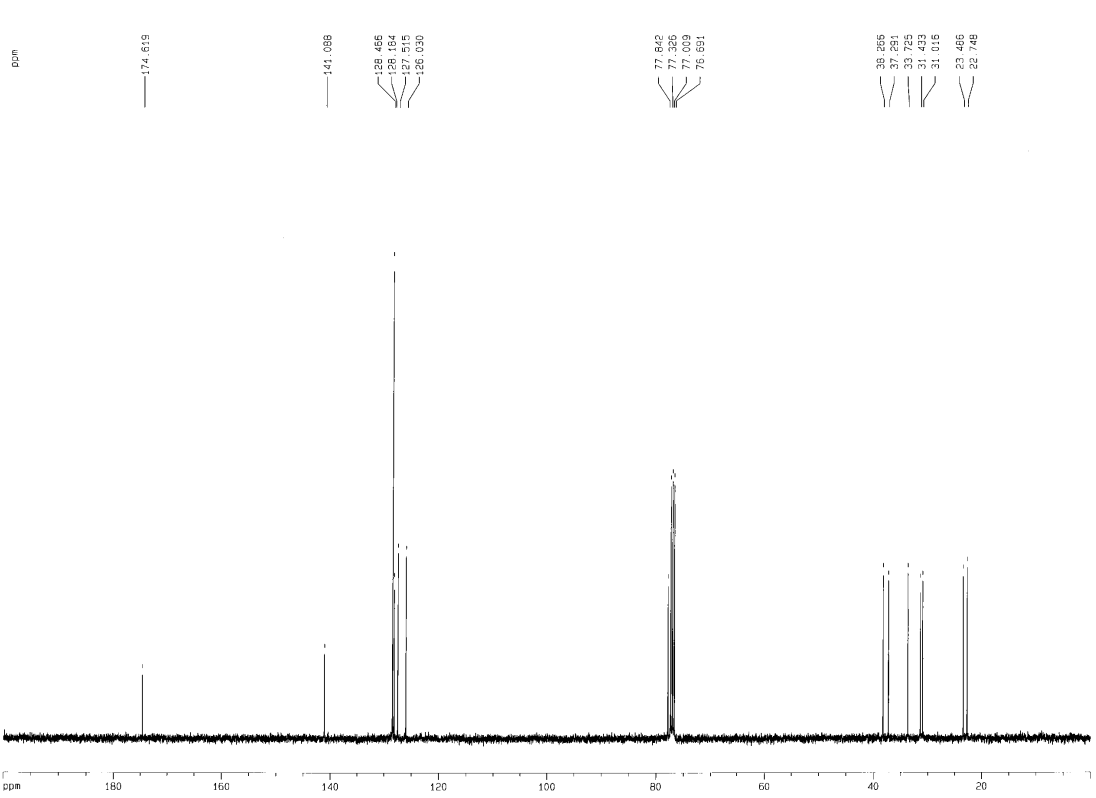
1D NMR plot parameters
CX                        32.00 cm
CY                        10.00 cm
F1P                      200.000 ppm
F1                     20117.53 Hz
F2P                       -0.000 ppm
F2                        -0.00 Hz
PPMCM                  6.25000 ppm/cm
HZCM                 628.67273 Hz/cm
```



2b







```
Current Data Parameters
NAME                  IMDA4-2b
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20090314
Time                   15.32
INSTRUM                spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                          10
DS                           2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                     161.3
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1              400.0324703 MHz

F2 - Processing parameters
SI                         32768
SF                400.0300067 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         32.00 cm
CY                          4.00 cm
F1P                        9.000 ppm
F1                      3600.27 Hz
F2P                        0.000 ppm
F2                         0.00 Hz
PPMCM                  0.28125 ppm/cm
HZCM                 112.50844 Hz/cm
```

```
Current Data Parameters
NAME                  IMDA4-2b
EXPNO                        2
PROCNO                       1

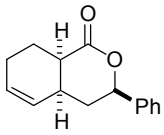
F2 - Acquisition Parameters
Date_               20090314
Time                   15.40
INSTRUM                spect
PROBHD    5 mm QNP 1H/13
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                         137
DS                           4
SWH               26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517875 sec
RG                      8192
DW                    19.100 usec
DE                     6.00 usec
TE                     300.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1              100.5986686 MHz

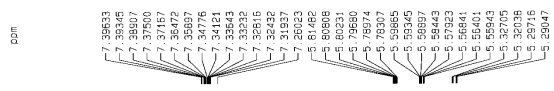
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

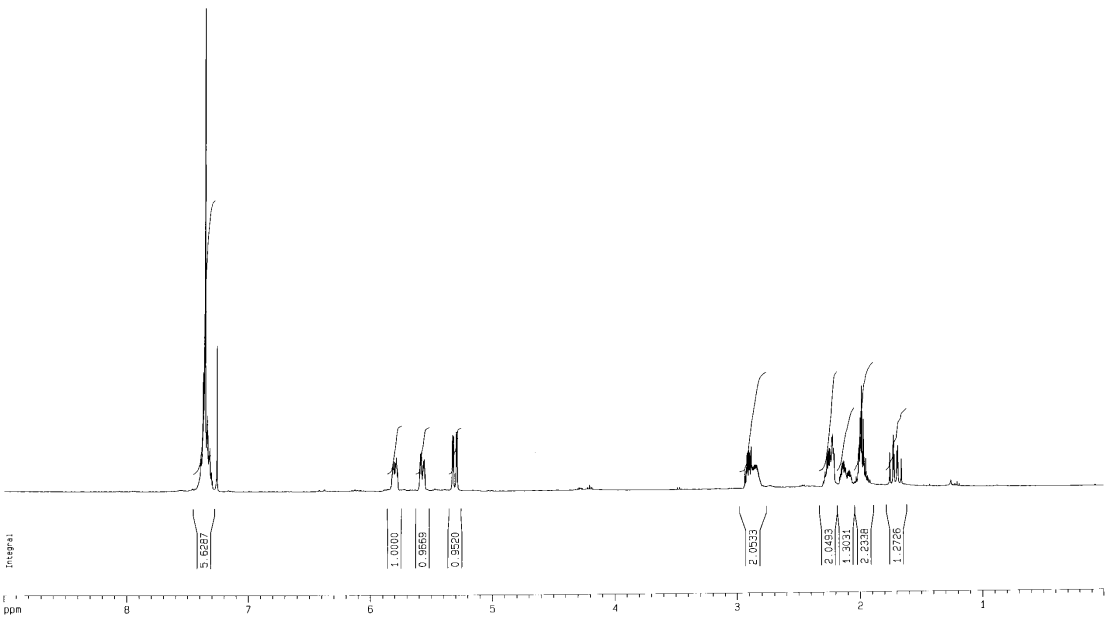
F2 - Processing parameters
SI                         32768
SF                100.5876278 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         32.00 cm
CY                         14.00 cm
F1P                      200.000 ppm
F1                     20117.53 Hz
F2P                       -0.000 ppm
F2                        -0.00 Hz
PPMCM                  6.25000 ppm/cm
HZCM                 628.67273 Hz/cm
```



2c





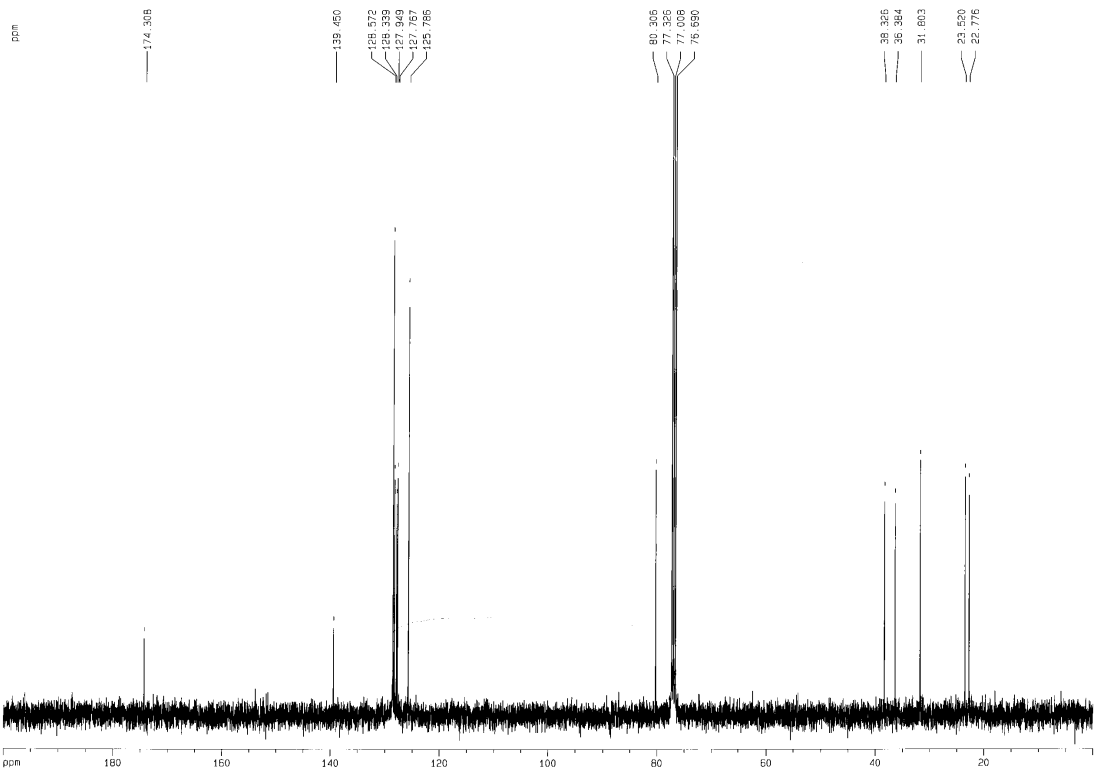
```
Current Data Parameters
NAME                  IMDA4-2c
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090314
Time                   16.03
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      256
DW                 60.400 usec
DE                  6.00 usec
TE                  300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.50 usec
PL1                  -4.00 dB
SFO1           400.0324703 MHz

F2 - Processing parameters
SI                       32768
SF                400.0300065 MHz
WDW                        EM
SSB                         0
LB                   0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                   32.00 cm
CY                    3.00 cm
F1P                9.000 ppm
F1                 3600.27 Hz
F2P                0.000 ppm
F2                    0.00 Hz
PPMCM             0.28125 ppm/cm
HZCM            112.50844 Hz/cm
```



```
Current Data Parameters
NAME                  IMDA4-2c
EXPNO                        2
PROCNO                       1

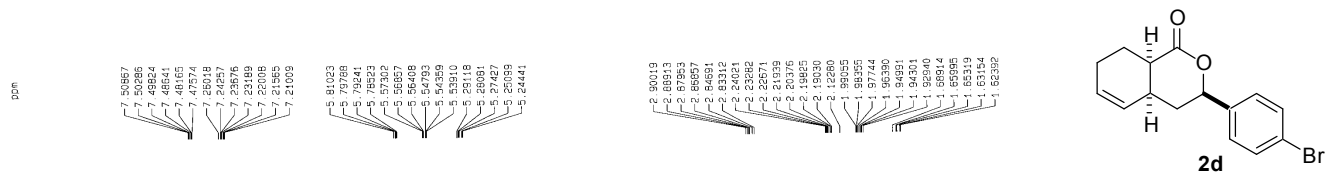
F2 - Acquisition Parameters
Date_              20090314
Time                   16.08
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      161
DS                        4
SWH               26178.010 Hz
FIDRES            0.399445 Hz
AQ                1.2517875 sec
RG                    5160.6
DW                 19.100 usec
DE                  6.00 usec
TE                  300.2 K
D1                2.00000000 sec
D11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                  10.00 usec
PL1                  -3.50 dB
SFO1           100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2               100.00 usec
PL2                  -4.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
SFO2           400.0316001 MHz

F2 - Processing parameters
SI                       32768
SF                100.5676254 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                   32.00 cm
CY                   14.00 cm
F1P                200.000 ppm
F1                 20117.53 Hz
F2P                -0.000 ppm
F2                    -0.00 Hz
PPMCM             6.25000 ppm/cm
HZCM            628.67267 Hz/cm
```



2d

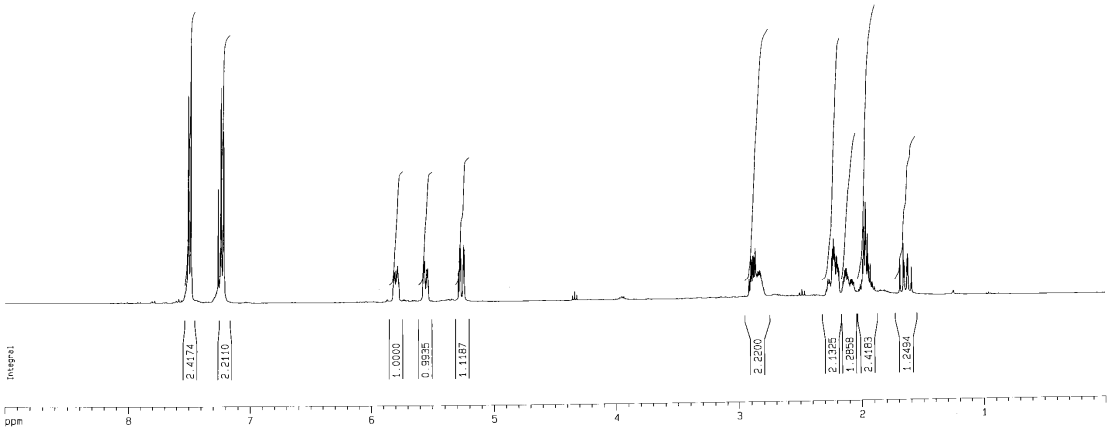
```
Current Data Parameters
NAME                  IMDA4-2d
EXPNO                        1
PROCNO                       1

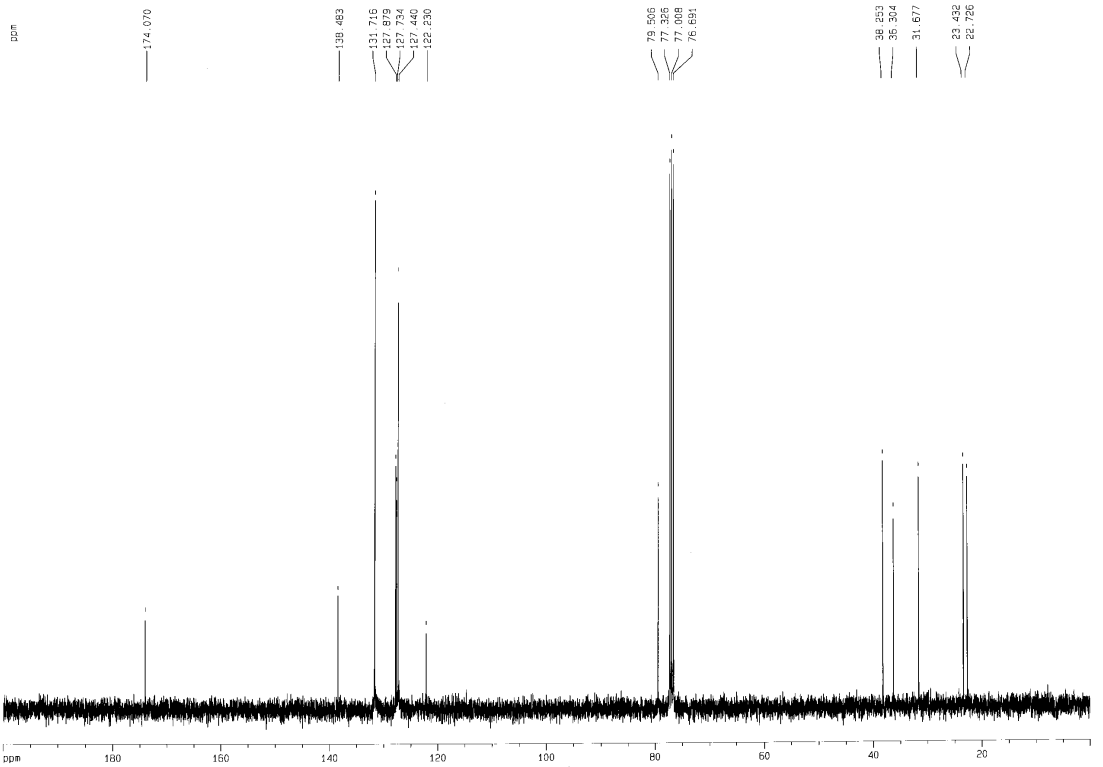
F2 - Acquisition Parameters
Date_              20090314
Time                   16.37
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       28
DS                        2
SWH               8278.146 Hz
FIDRES           0.126314 Hz
AQ                3.9584243 sec
RG                      256
DW                   60.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.50 usec
PL1                   -4.00 dB
SFO1          400.0324703 MHz

F2 - Processing parameters
SI                       32768
SF            400.0300065 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       32.00 cm
CY                        7.00 cm
F1P                       9.000 ppm
F1                     3600.27 Hz
F2P                       0.000 ppm
F2                        0.00 Hz
PPMCM                 0.28125 ppm/cm
HZCM                112.50844 Hz/cm
```






```
Current Data Parameters
NAME                  IMDA4-2d
EXPNO                        2
PROCNO                       1

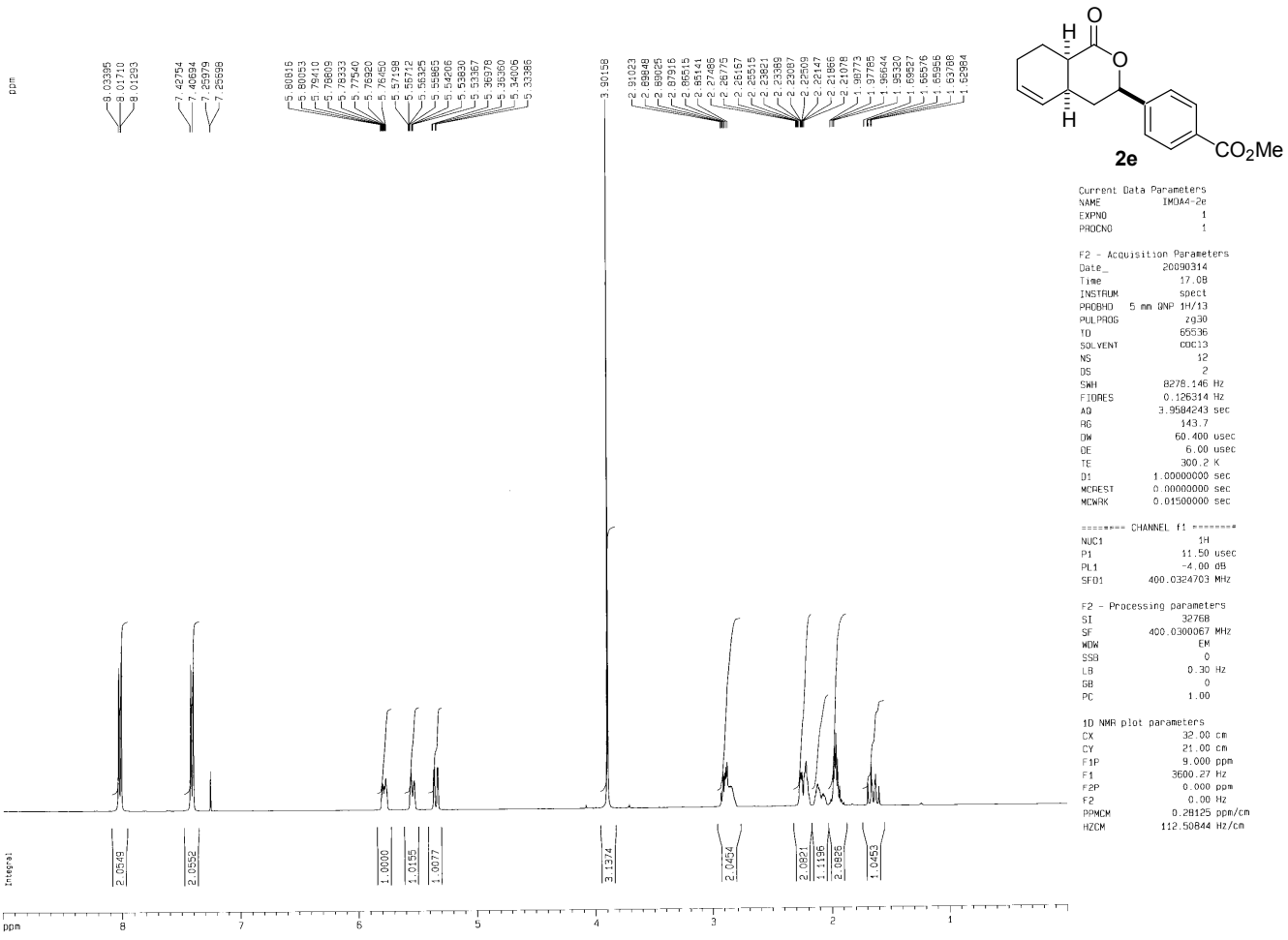
F2 - Acquisition Parameters
Date_              20090314
Time                   16.45
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       90
DS                        4
SWH              26178.010 Hz
FIDRES           0.399445 Hz
AQ                1.2517875 sec
RG                     6502
DW                   19.100 usec
DE                    6.00 usec
TE                   300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -3.50 dB
SFO1          100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -4.00 dB
PL12                  17.00 dB
PL13                  17.00 dB
SFO2          400.0316001 MHz

F2 - Processing parameters
SI                       32768
SF            100.5876270 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       32.00 cm
CY                       15.00 cm
F1P                     200.000 ppm
F1                   20117.53 Hz
F2P                      -0.000 ppm
F2                       -0.00 Hz
PPMCM                 6.25000 ppm/cm
HZCM                628.67267 Hz/cm
```



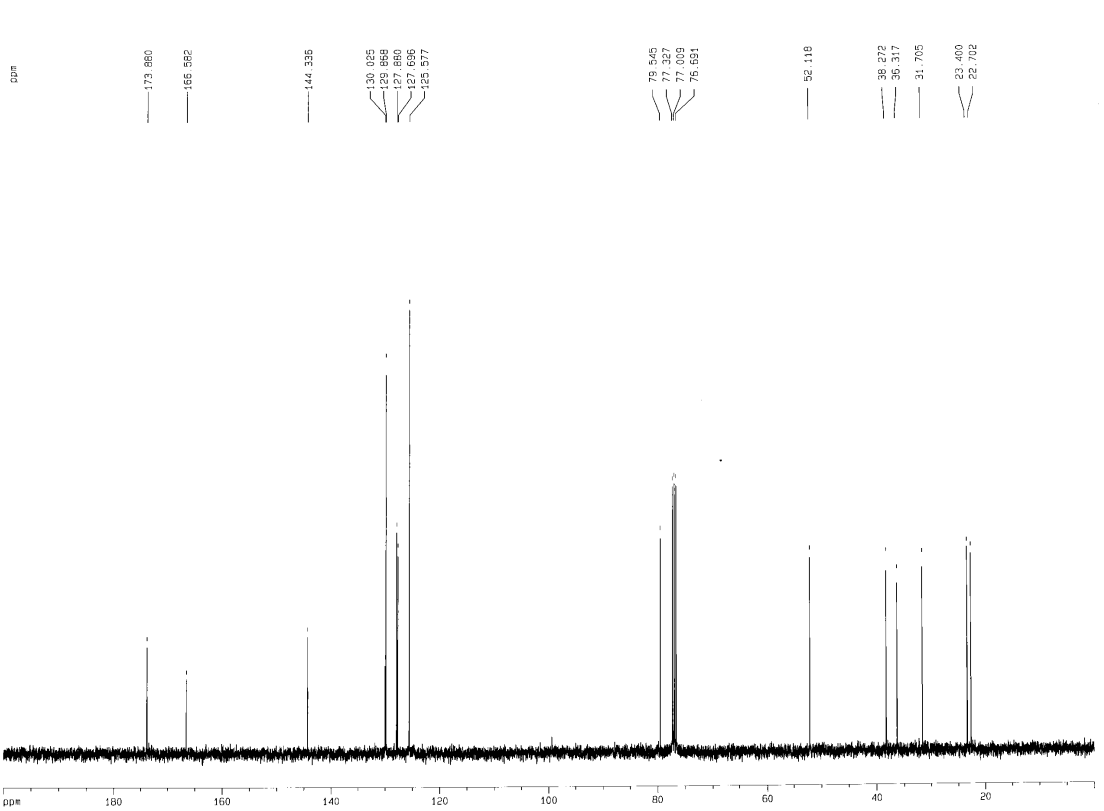
Current Data Parameters
NAME IMOA4-2e
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090314
Time 17.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SF01 400.0324703 MHz

F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 9.000 ppm
F1 3600.27 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.28125 ppm/cm
HZCM 112.50844 Hz/cm



Current Data Parameters
NAME IMOA4-2e
EXPNO 2
PROCNO 1

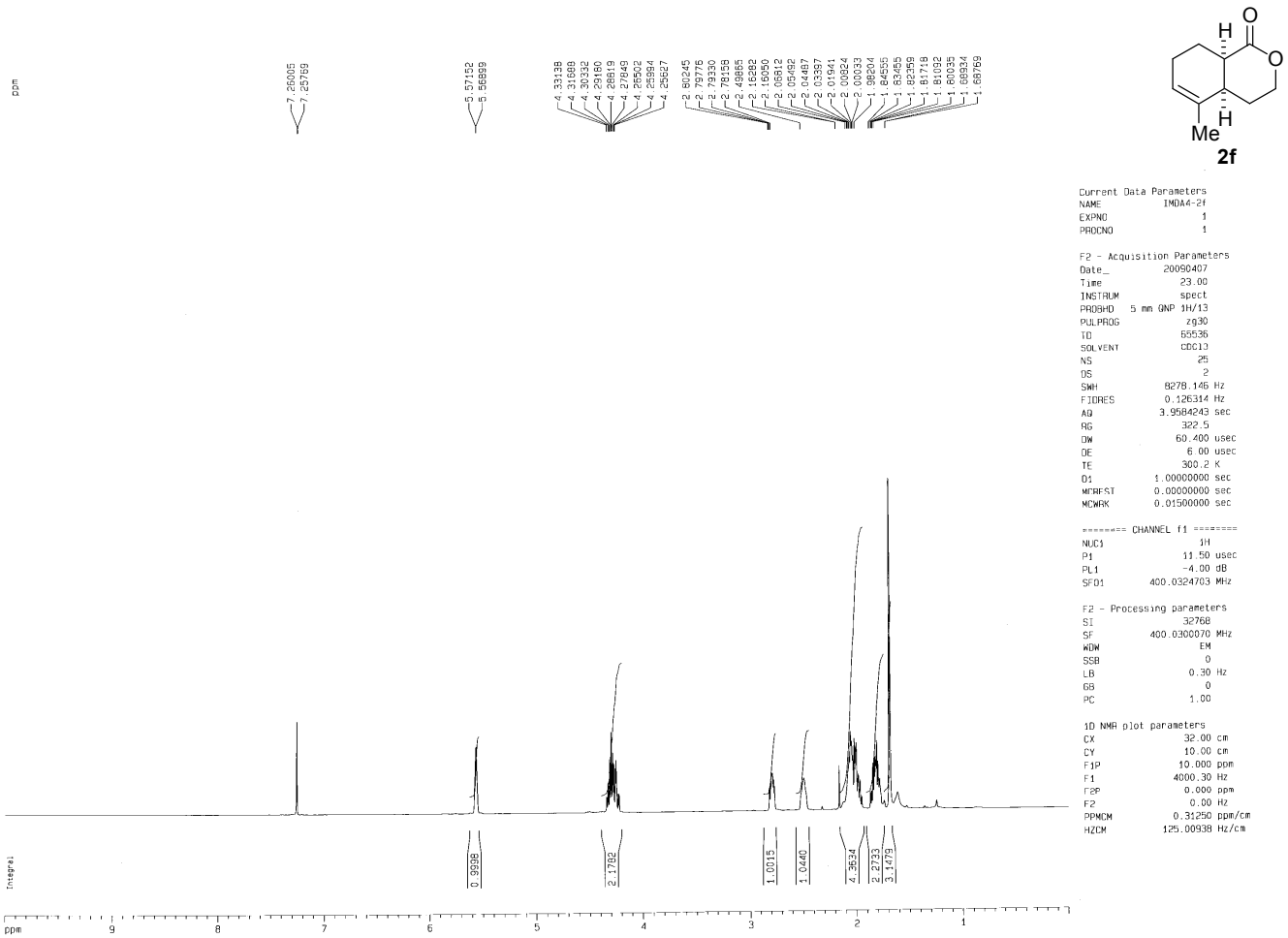
F2 - Acquisition Parameters
Date_ 20090314
Time 17.12
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SF01 100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SF02 400.0316001 MHz

F2 - Processing parameters
SI 32768
SF 100.5876286 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 32.00 cm
CY 13.00 cm
F1P 200.000 ppm
F1 20117.53 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 6.25000 ppm/cm
HZCM 628.67273 Hz/cm



2f

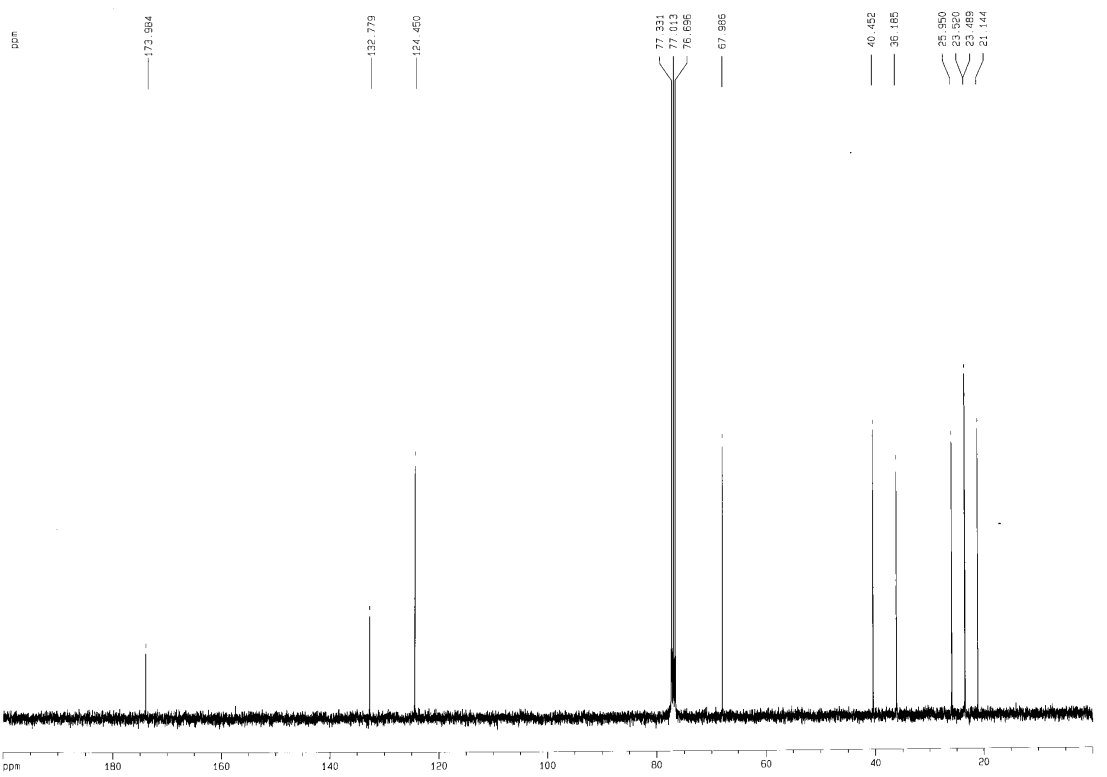
```
Current Data Parameters
NAME                  IMDA4-2f
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090407
Time                   23.00
INSTRUM                spect
PROBHD   5 mm GNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT                CDCl3
NS                        25
DS                         2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     322.5
DW                    60.400 usec
DE                     6.00 usec
TE                    300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1              400.0324703 MHz

F2 - Processing parameters
SI                        32768
SF                400.0300070 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     32.00 cm
CY                     10.00 cm
F1P                   10.000 ppm
F1                  4000.30 Hz
F2P                   0.000 ppm
F2                     0.00 Hz
PPMCM                0.31250 ppm/cm
HZCM               125.00938 Hz/cm
```




```
Current Data Parameters
NAME                  IMDA4-2f
EXPNO                        2
PROCNO                       1

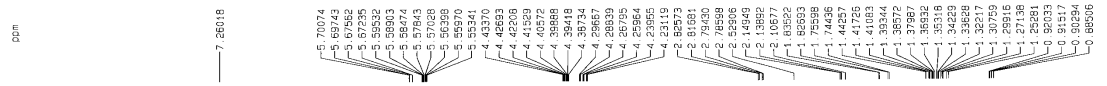
F2 - Acquisition Parameters
Date_              20090407
Time                   22.19
INSTRUM                spect
PROBHD   5 mm GNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                       633
DS                         4
SWH               26178.010 Hz
FIDRES            0.399445 Hz
AQ                1.2517875 sec
RG                    3649.1
DW                    19.100 usec
DE                     6.00 usec
TE                    300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

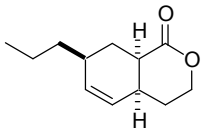
======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1              100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2              400.0316001 MHz

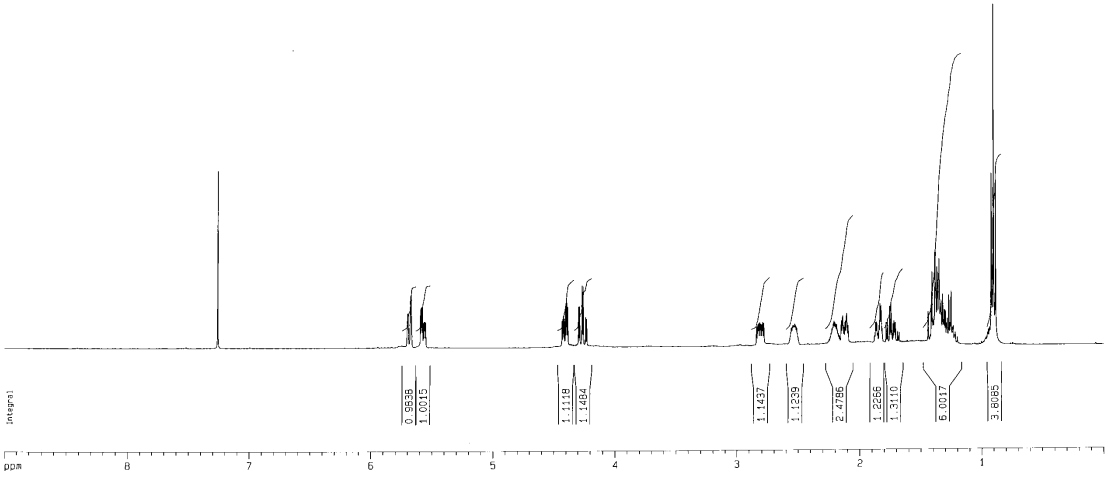
F2 - Processing parameters
SI                        32768
SF                100.5876238 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     32.00 cm
CY                     10.00 cm
F1P                   200.000 ppm
F1                  20117.53 Hz
F2P                   -0.000 ppm
F2                     -0.00 Hz
PPMCM                6.25000 ppm/cm
HZCM               628.67267 Hz/cm
```





2g



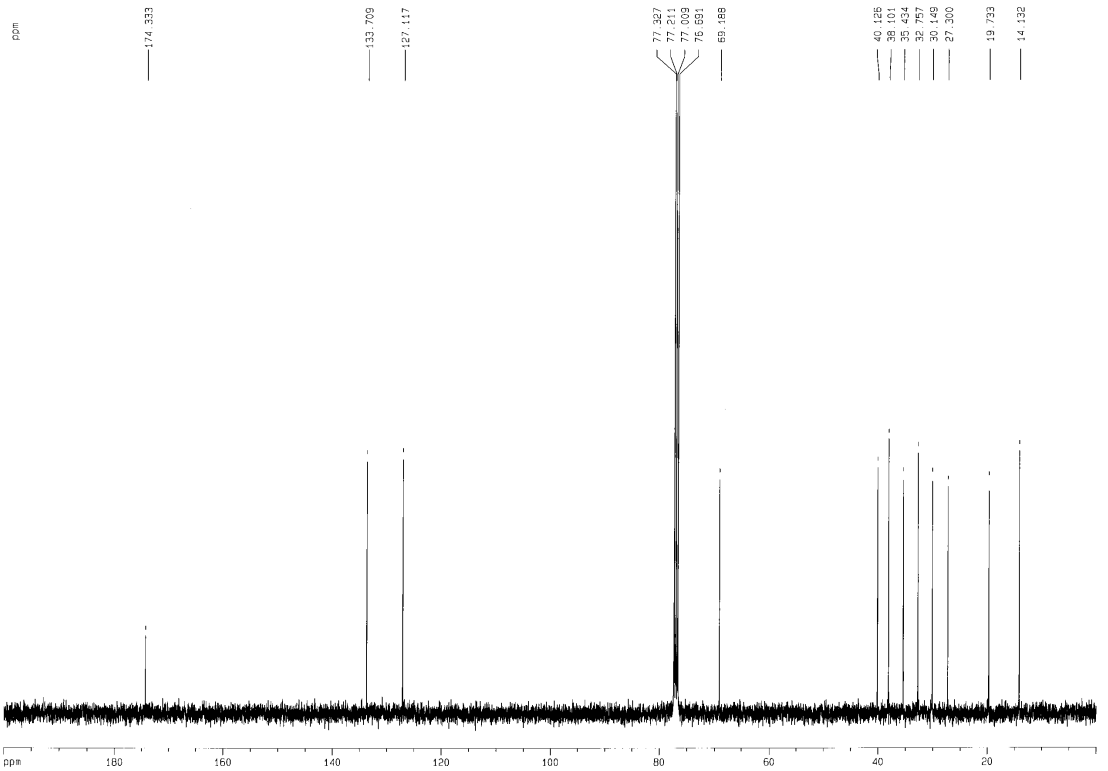
```
Current Data Parameters
NAME                  IMDA4-2g
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20090415
Time                   22.54
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8278.146 Hz
FIDRES           0.126314 Hz
AQ                3.9584243 sec
RG                     287.4
DW                  60.400 usec
DE                   6.00 usec
TE                   300.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.50 usec
PL1                    -4.00 dB
SFO1           400.0324703 MHz

F2 - Processing parameters
SI                       32768
SF                400.0300065 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       32.00 cm
CY                       10.00 cm
F1P                       9.000 ppm
F1                     3600.27 Hz
F2P                       0.000 ppm
F2                        0.00 Hz
PPMCM                 0.28125 ppm/cm
HZCM                112.50844 Hz/cm
```



```
Current Data Parameters
NAME                  IMDA4-2g
EXPNO                        2
PROCNO                       1

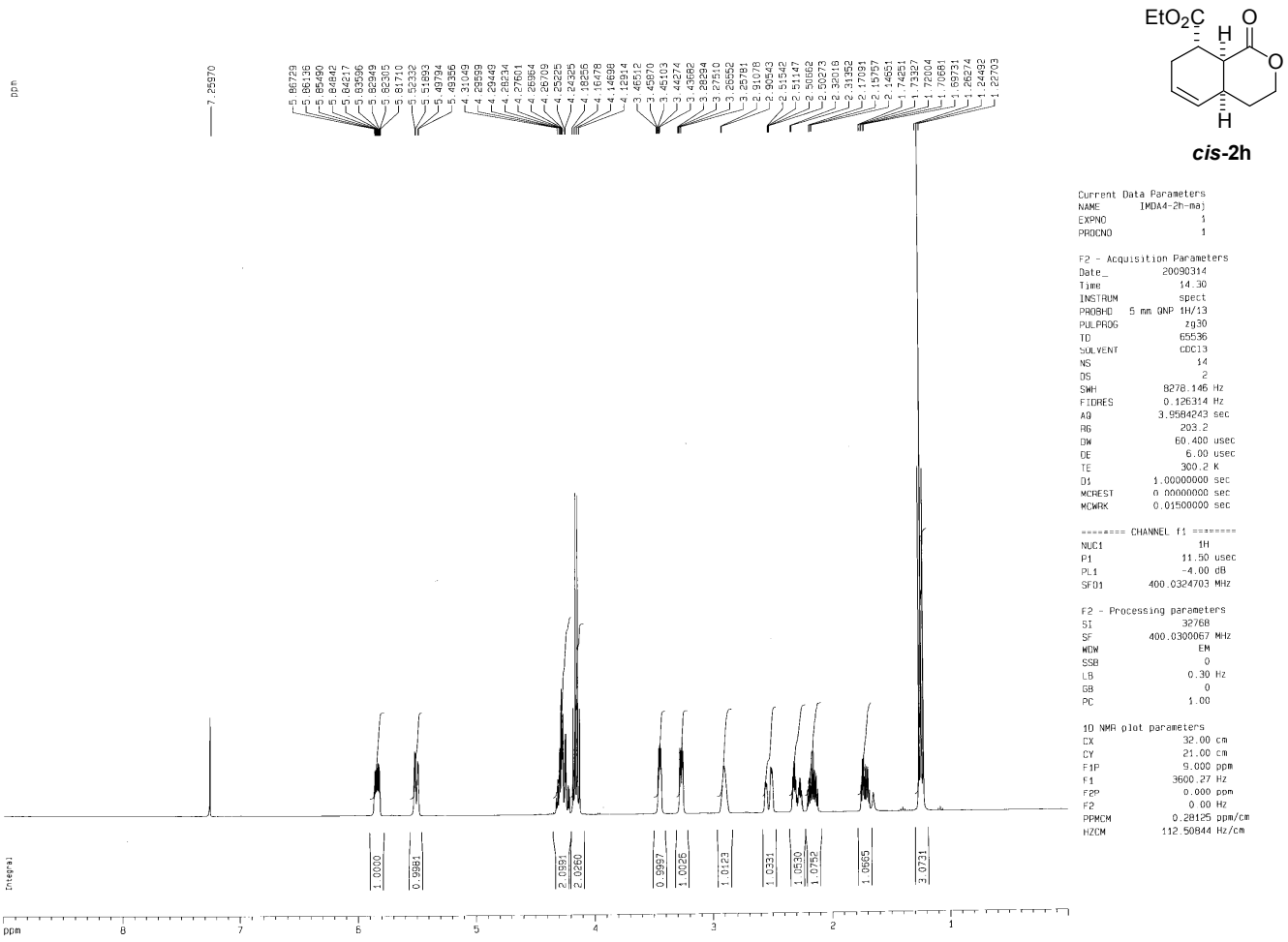
F2 - Acquisition Parameters
Date_              20090415
Time                   22.59
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      430
DS                        4
SWH              26178.010 Hz
FIDRES           0.399445 Hz
AQ                1.2517675 sec
RG                     8192
DW                  19.100 usec
DE                   6.00 usec
TE                   300.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.69999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.00 usec
PL1                    -3.50 dB
SFO1           100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   17.00 dB
PL13                   17.00 dB
SFO2           400.0316001 MHz

F2 - Processing parameters
SI                       32768
SF                100.5876238 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       32.00 cm
CY                        8.00 cm
F1P                     200.000 ppm
F1                    20117.53 Hz
F2P                      -0.000 ppm
F2                       -0.00 Hz
PPMCM                 6.25000 ppm/cm
HZCM                628.67267 Hz/cm
```


EtO2C
O
H
O
H
cis-2h
ppm
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5.86729
5.86195
5.85490
5.84842
5.84217
5.83596
5.82849
5.82305
5.81710
5.52332
5.51893
5.49794
5.49356
4.31049
4.29599
4.29449
4.28234
4.27601
4.26964
4.26709
4.25225
4.24325
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4.14698
4.12914
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3.45870
3.45103
3.44274
3.43682
3.28294
3.27510
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2.50662
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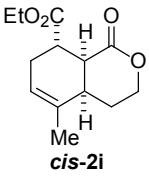
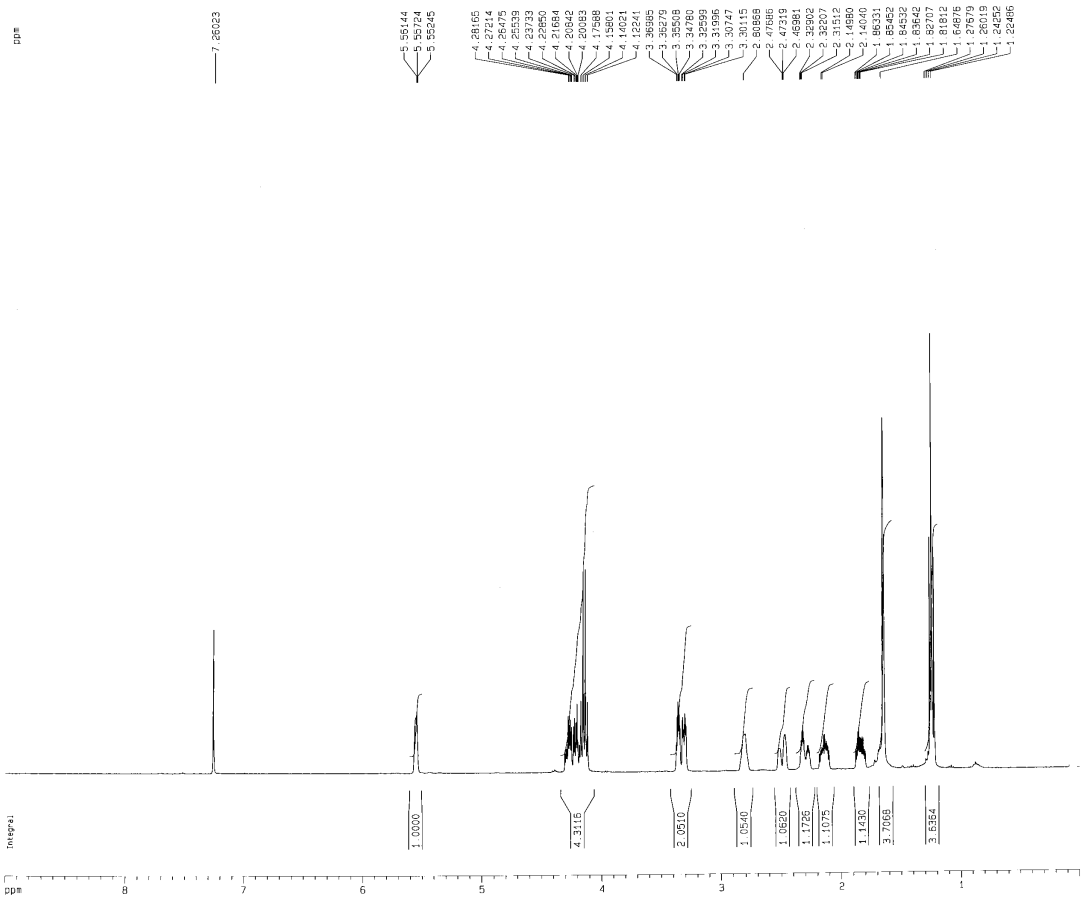
2.35752
2.17241
2.14857
2.14651
1.74251
1.73327
1.72004
1.70681
1.69731
1.26274
1.24492
1.22703
Integral
1.0000
0.9961
2.0991
2.0260
0.9997
1.0026
1.0123
1.0331
1.0530
1.0752
1.0805
3.0731
ppm
8
7
6
5
4
3
2
1
Current Data Parameters
NAME IMDA4-2h-maj
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090314
Time 14.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SF01 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 21.00 cm
F1P 9.000 ppm
F1 3600.27 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.28125 ppm/cm
HZCM 112.50844 Hz/cm
ppm
173.343
172.159
127.958
127.633
77.326
77.008
76.690
66.367
60.935
40.409
39.043
28.600
28.280
22.947
14.137
ppm
180
160
140
120
100
80
60
40
20
Current Data Parameters
NAME IMDA4-2h-maj
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090314
Time 14.36
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 58
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 8192
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999996 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SF01 100.5986886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SF02 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876262 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 10.00 cm
F1P 200.000 ppm
F1 20117.53 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 6.25000 ppm/cm
HZCM 628.67267 Hz/cm



***cis*-2i**

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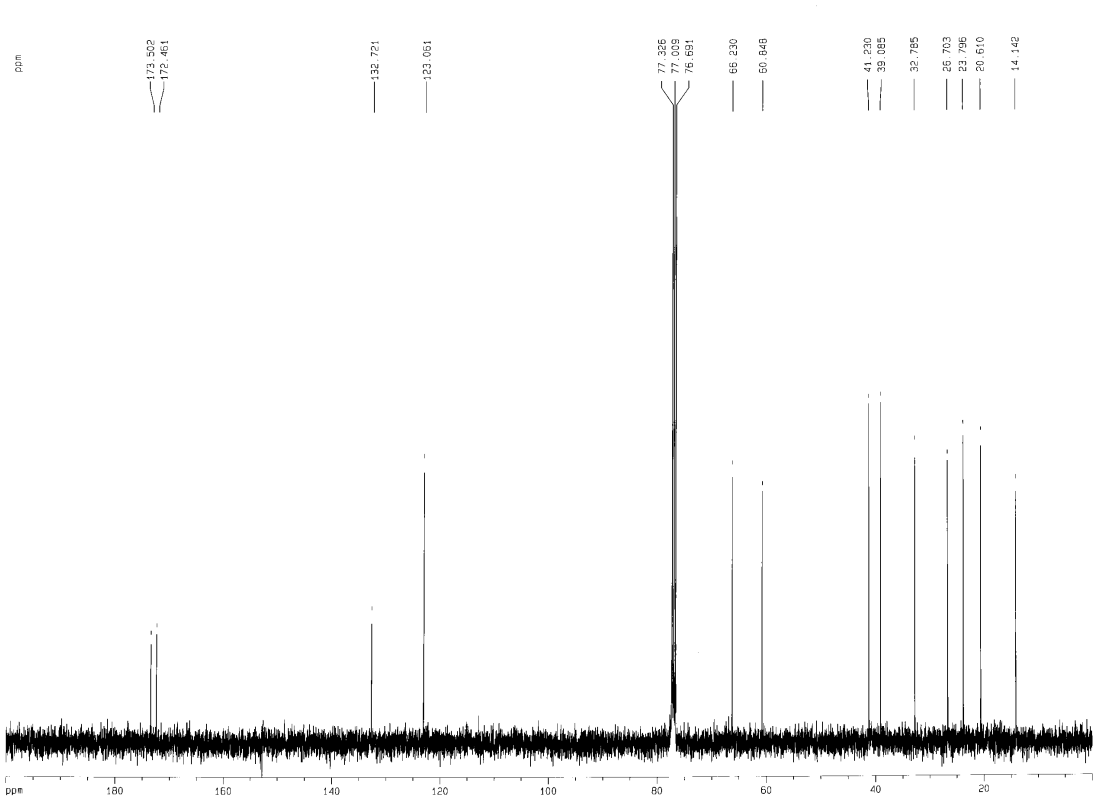
Current Data Parameters
NAME          IMDA4-fum-me
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20090526
Time                  22.29
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       6
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                   322.5
DW                60.400 usec
DE                 6.00 usec
TE                 300.2 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.50 usec
PL1                  -4.00 dB
SFO1           400.0324703 MHz

F2 - Processing parameters
SI                       32768
SF             400.0300065 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                   32.00 cm
CY                   13.00 cm
F1P                  9.000 ppm
F1                 3600.27 Hz
F2P                  0.000 ppm
F2                   0.00 Hz
PPMCM              0.28125 ppm/cm
HZCM             112.50844 Hz/cm
```

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Current Data Parameters
NAME          IMDA4-fum-me
EXPNO                    2
PROCNO                   1

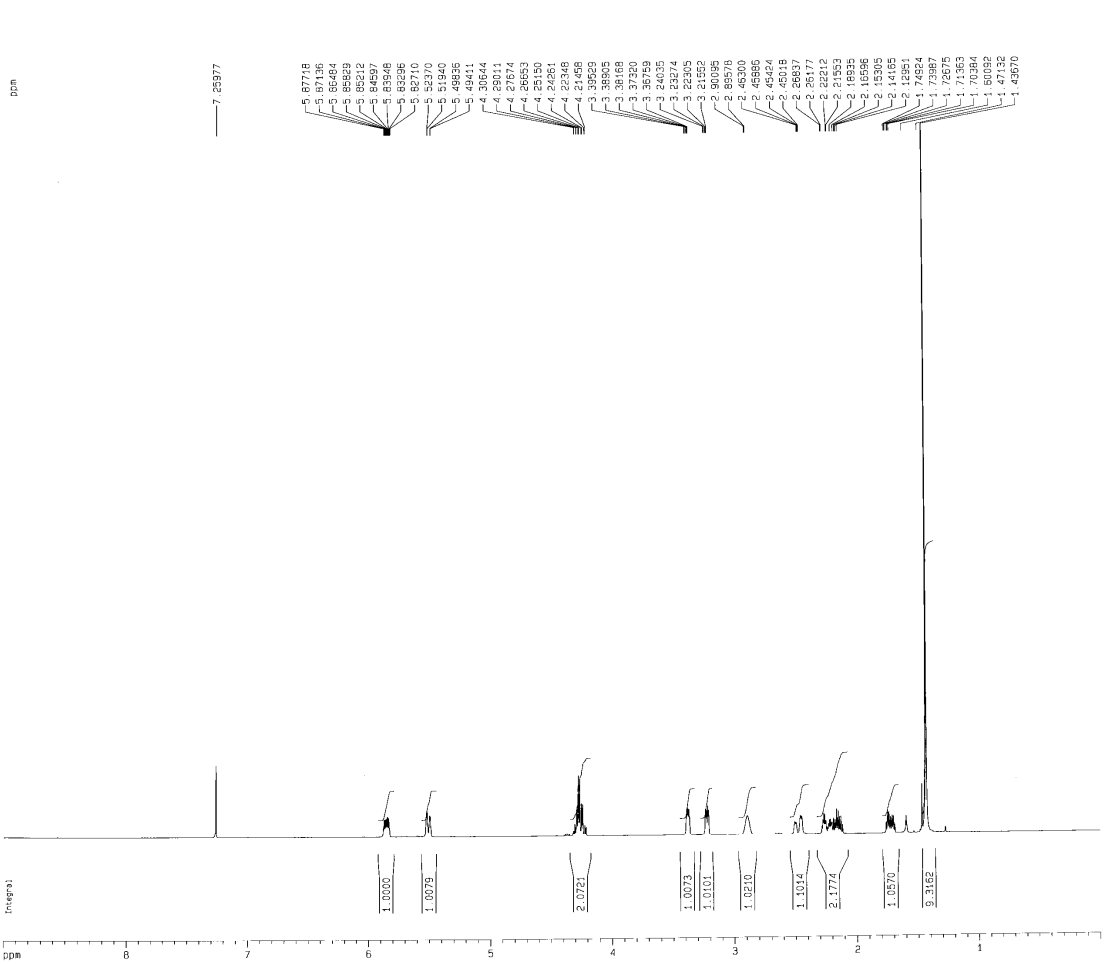
F2 - Acquisition Parameters
Date_              20090526
Time                  22.33
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     312
DS                       4
SWH             26178.010 Hz
FIDRES           0.399445 Hz
AQ               1.2517875 sec
RG                   13004
DW                19.100 usec
DE                 6.00 usec
TE                 300.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.00 usec
PL1                  -3.50 dB
SFO1           100.5986886 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2               100.00 usec
PL2                  -4.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
SFO2           400.0316001 MHz

F2 - Processing parameters
SI                       32768
SF             100.5876238 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   32.00 cm
CY                   10.00 cm
F1P                  200.000 ppm
F1                 20117.53 Hz
F2P                  -0.000 ppm
F2                   -0.00 Hz
PPMCM              6.25000 ppm/cm
HZCM             628.67257 Hz/cm
```


t-BuO2C
O
H
O
H
cis-2j
ppm
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5.67718
5.67136
5.66484
5.65829
5.65212
5.64597
5.63948
5.63296
5.62710
5.62270
5.61840
5.61435
5.49411
4.30644
4.28011
4.27674
4.26653
4.25150
4.24261
4.22348
4.21458
3.39529
3.38905
3.38168
3.37320
3.36759
3.24035
3.23274
3.22305
3.21552
2.90095
2.89578
2.46300
2.45886
2.45424
2.45018
2.26837
2.26177
2.22212
2.21553
2.16935
2.16596
2.15305
2.14165
2.12851
1.74924
1.73987
1.72675
1.71353
1.70084
1.60092
1.47132
1.43670
Integral
1.0000
1.0079
2.0721
1.0073
1.0101
1.0219
1.1014
2.1774
1.0570
5.3162
ppm
8
7
6
5
4
3
2
1
Current Data Parameters
NAME 1MDA4-2j-maj
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090314
Time 14.56
INSTRUM spect
PROBHD 5 mm UNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 23
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 287.4
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 -4.00 dB
SFO1 400.0324703 MHz
F2 - Processing parameters
SI 32768
SF 400.0300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 32.00 cm
CY 45.00 cm
F1P 9.000 ppm
F1 3600.27 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.28125 ppm/cm
HZCM 112.50844 Hz/cm
ppm
172.554
172.371
128.238
127.500
80.945
77.327
77.009
76.691
66.334
40.642
39.881
28.500
28.360
27.957
23.020
ppm
180
160
140
120
100
80
60
40
20
Current Data Parameters
NAME 1MDA4-2j-maj
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090314
Time 15.04
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 103
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 3649.1
DW 19.100 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.50 dB
SFO1 100.5986886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 400.0316001 MHz
F2 - Processing parameters
SI 32768
SF 100.5876246 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 32.00 cm
CY 19.00 cm
F1P 200.000 ppm
F1 20117.53 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 6.25000 ppm/cm
HZCM 628.67267 Hz/cm

6. References

1. (a) Saito, A.; Yanai, H.; Taguchi, T. *Tetrahedron* **2004**, *60*, 12239-12247. (b) Saito, A.; Ito, H.; Taguchi, T. *Org. Lett.* **2002**, *4*, 4619-4621.
2. Yanai, H.; Saito, A.; Taguchi, T. *Tetrahedron* **2005**, *61*, 7087-7093.
3. Zhou, G.; Hu, Q.-Y.; Corey, E. J. *Org. Lett.* **2003**, *5*, 3979-3982.
4. Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1721-1722.
5. Kaur, N.; Zhou, B.; Breitbeil, F.; Hardy, K.; Kraft, K. S.; Trantcheva, I.; Phanstiel, O., IV *Mol. Pharmaceutics* **2008**, *5*, 294-315.
6. Martin, S. F.; Williamson, S. A.; Gist, R. P.; Smith, K. M. *J. Org. Chem.* **1983**, *48*, 5170-5180.