

Supporting Information

Efficient Medium Ring Size Bromolactonization Using a Sulfur-based Zwitterionic Organocatalyst

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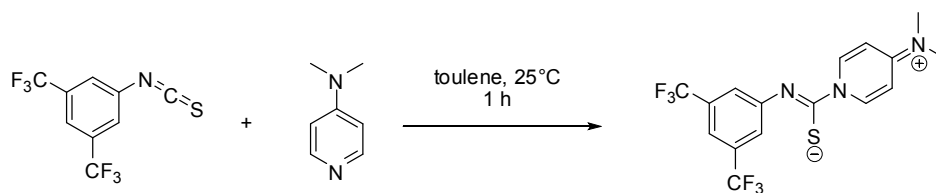
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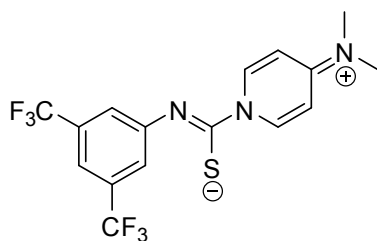
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(A) General. All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a Varian 3100 FTIR spectrophotometer and reported in wave numbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), Bruker DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^1H NMR and to chloroform (δ 77.0) for the ^{13}C NMR measurements. Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode. High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

(B) Catalyst preparation



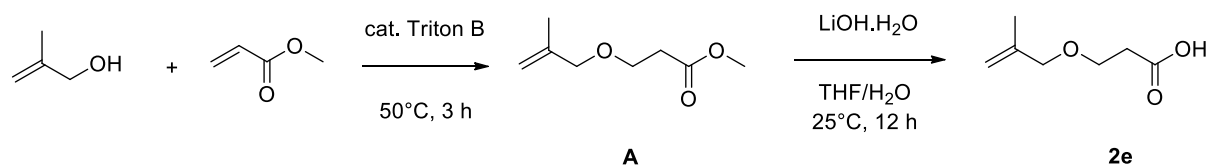
Preparation of (Z)-N-3,5-bis(trifluoromethyl)phenyl-4-(dimethyliminio)pyridine-1(4H)-carbimidothioate as the Zwitterionic Catalyst. The catalyst was prepared according to the method in literature.¹ 4-dimethylaminopyridine (335 mg, 2.7 mmol, 1.0 eq) was added to a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.5 mL, 2.7 mmol, 1.0 eq) in toluene (5 mL). The mixture was stirred at 25°C for 1 h. The solid product was recrystallized from hot toluene, filtered and dried under vacuum.



(Z)-N-3,5-bis(trifluoromethyl)phenyl-4-(dimethyliminio)pyridine-1(4H)-carbimidothioate (1a)

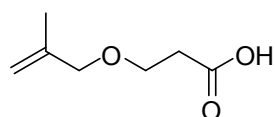
89%, Yellow solid. mp 102.0-104.0 °C . IR (KBr): 1640, 1553, 1373, 1275, 1106, 884, 689 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂): δ 9.58 (d, *J* = 7.6 Hz, 2H), 7.54 (s, 2H), 7.51 (s, 1H), 6.65 (d, *J* = 8.2 Hz, 2H), 3.23 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 149.7, 129.0, 128.2, 125.7, 125.2, 120.4, 106.5, 38.9, 21.4.

(C) Substrate preparation



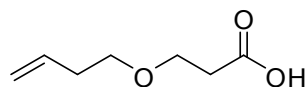
Representative Procedure for the Preparation of Alkenoic Acid 2e, and 2l. Both steps are based on methods in literature.^{2,3} A catalytic amount of Triton B (benzyltrimethylammonium hydroxide) (40% in methanol, 0.6 mL) was placed in a dried flask and the solvent was removed under reduced pressure. Allyl alcohol (2.3 mL, 33 mmol, 1.1 eq) was then added, followed by methyl acrylate (2.7 mL, 30 mmol, 1.0 eq) after 15 min. The mixture was stirred at 50°C for 3 h. The mixture was filtered over a mixture Celite-silica gel and concentrated under vacuum. The intermediate product **A** was used without purification for the next step.

Product **A** was dissolved in a THF/H₂O mixture (1:1 v/v, 150 mL total). LiOH.H₂O (10.1 g, 240 mmol, 8 eq) was then added at 25°C and the mixture stirred for 12 h. The aqueous fraction was washed with ether (2 x 80 mL) and acidified with 2 M HCl to pH 1. The aqueous phase was extracted with ether (3 x 80 mL). The combined organic extracts were washed with brine (100 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (hexane: EtOAc 10:1) gave alkenoic acid **2e**.



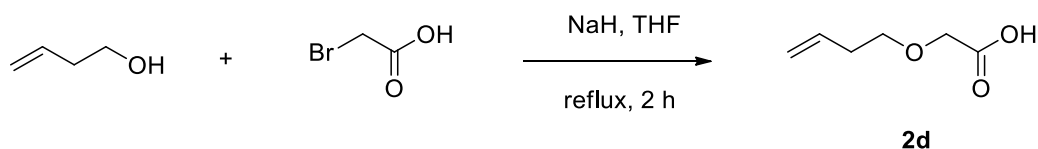
3-(2-methylallyloxy)propanoic acid (**2e**)

21%; Pale yellow oil. IR (Neat): 3080, 1717, 1431, 1192, 1106 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 4.96 (d, *J* = 0.7 Hz, 1H), 4.90 (s, 1H), 3.92 (s, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.65 (t, *J* = 6.3 Hz, 2H), 1.73 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 177.0, 141.8, 112.6, 75.1, 64.9, 34.9, 19.3; HRMS (ESI) calcd for C₇H₁₂O₃Na *m/z* [M + Na]⁺: 167.0679; found: 167.0672.

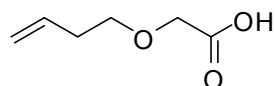


3-(but-3-enyloxy)propanoic acid (**2l**)

30%; Colourless oil. IR (Neat): 3079, 1717, 1427, 1112 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 5.83-5.77 (m, 1H), 5.09 (dd, $J=17.2$, 1.8 Hz, 1H), 5.03 (dd, $J=10.1$, 1.9 Hz, 1H), 3.72 (t, $J=6.2$ Hz, 2H), 3.52 (t, $J=6.9$ Hz, 2H), 2.64 (t, $J=6.2$ Hz, 2H), 2.36-2.31 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 177.4, 134.9, 116.5, 70.5, 65.7, 34.8, 33.9; HRMS (ESI) calcd for $\text{C}_7\text{H}_{11}\text{O}_3$ m/z $[\text{M} - \text{H}]^-$: 143.0714; found: 143.0712.

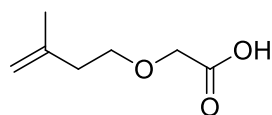


Representative Procedure for the Preparation of Alkenoic Acid 2d, 2f, 2k, and 2o. The preparation is based on the method in literature.⁴ 3-Buten-1-ol (1.7 mL, 20 mmol, 1.1 eq) was added dropwise to an ice-cold, stirred suspension of NaH (60% dispersed in mineral oil, 2.2 g, 55 mmol, 3.0 eq) in THF (30 mL). After 15 min, a solution of bromoacetic acid (2.5 g, 18.2 mmol, 1.0 eq) in THF (5 mL) was added dropwise. The mixture was stirred under reflux for 2 h. The reaction was quenched with water (30 mL). The aqueous phase was washed with ether (2 x 30 mL) and acidified with 2 M HCl to pH 1. The aqueous phase was then extracted with ether (3 x 30 mL). The combined organic extracts were washed with brine (100 mL), dried with Na_2SO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (hexane: EtOAc 10:1) gave alkenoic acid **2d**.



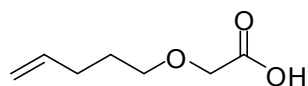
2-(but-3-enyloxy)acetic acid (**2d**)⁵

53%; Brown oil. ^1H NMR (500 MHz, CDCl_3): δ 5.85-5.78 (m, 1H), 5.12 (dd, $J = 17.1$, 1.5 Hz, 1H), 5.08 (dd, $J = 10.4$, 1.5 Hz, 1H), 4.14 (s, 2H), 3.63 (t, $J = 6.7$ Hz, 2H), 2.40 (q, $J = 6.7$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 175.1, 134.4, 117.0, 71.1, 67.7, 33.9; MS (ESI) $[\text{M} - \text{H}]^-$: 129.0.



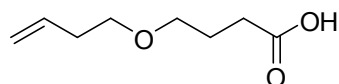
2-(3-methylbut-3-enyloxy)acetic acid (**2f**)⁴

71%; Yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 4.81 (s, 1H), 4.76 (s, 1H), 4.14 (s, 2H), 3.69 (t, $J = 7.0$ Hz, 2H), 2.36 (q, $J = 7.0$ Hz, 2H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 175.0, 142.1, 112.0, 70.2, 67.7, 37.5, 22.5; MS (ESI) $[\text{M} - \text{H}]^-$: 143.1.



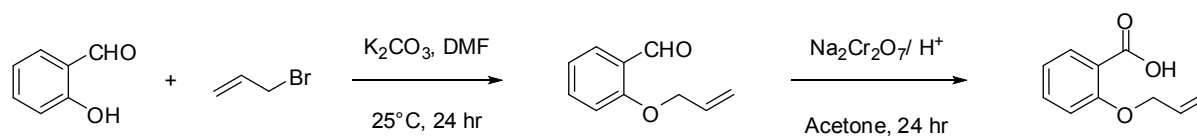
2-(pent-4-enyloxy)acetic acid (2k)⁶

49%; Pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 5.85-5.77 (m, 1H), 5.04 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.98 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.11 (s, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.15 (q, *J* = 7.0 Hz, 2H), 1.74 (q, *J* = 6.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 175.5, 137.8, 115.0, 71.3, 67.7, 29.9, 28.5; MS (ESI) [*M* - H]⁻: 143.1.



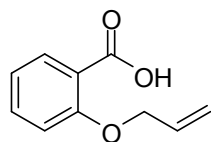
4-(but-3-enyloxy)butanoic acid (2o)

45%; Pale yellow oil. IR (Neat): 3079, 1707, 1422, 1111 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 5.86-5.77 (m, 1H), 5.08 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.49-3.46 (m, 4H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.34-2.30 (m, 2H), 1.93-1.87 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 179.6, 135.3, 116.4, 70.2, 69.5, 34.1, 31.0, 24.7; HRMS (ESI) calcd for C₈H₁₃O₃ *m/z* [*M* - H]⁻: 157.0870; found: 157.0867.



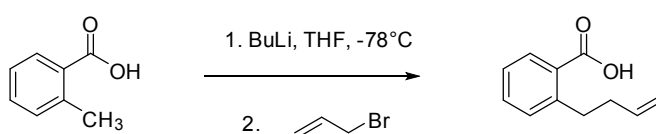
Procedure for the Preparation of Alkenoic Acid 2g. The preparation is based on a modified method in literature.⁷ Allyl bromide (2.9 mL, 33 mmol, 1.1 eq) was added dropwise to a stirred suspension of salicylaldehyde (3.7 g, 30 mmol, 1 eq) and K₂CO₃ (6.2 g, 45 mmol, 1.5 eq) in DMF (20 mL). The mixture was stirred at 25°C for 24 h. The reaction was diluted with EtOAc (30 mL) and successively washed with 20% NaOH (2 x 30 mL), water (3 x 50 mL) and brine (1 x 50 mL). The organic layer was concentrated under vacuum and the residue was used without purification for the next step.

The residue was dissolved in acetone (50 mL) and cooled in an ice bath. Jones reagent (prepared from 10.0 g of Na₂Cr₂O₇·2H₂O, 6.6 mL of H₂SO₄ and 20 mL of water) was added dropwise. The ice bath was removed and the mixture stirred at 25°C for 24 h. Upon completion of the reaction, volatile solvents were removed under reduced pressure. The residue was diluted with water (40 mL) and extracted with EtOAc (3 x 60 mL). The combined organic extracts were washed with water (3 x 150 mL), followed by brine (150 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (hexane: EtOAc 5:1) gave alkenoic acid **2g**.

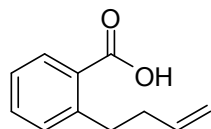


2-(allyloxy)benzoic acid (2g)⁸

64%; White solid. ¹H NMR (500 MHz, CDCl₃): δ 8.17 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.12-6.05 (m, 1H), 5.49 (d, *J* = 17.4 Hz, 1H), 5.42 (d, *J* = 10.6 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 165.5, 157.2, 134.9, 133.7, 130.9, 122.3, 120.4, 118.0, 113.0, 70.7; MS (ESI) [*M* - H]⁻: 177.0

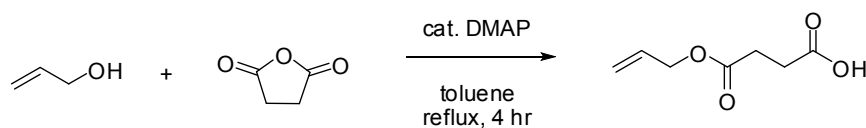


Preparation of Alkenoic Acid 2h. The preparation is based on the method in literature.^[7] *n*-Butyllithium (13.8 mL, 1.6M in hexane, 22 mmol, 2.2 eq) was added dropwise to a solution of 2-methylbenzoic acid (1.36 g, 10 mmol, 1.0 eq) in anhydrous THF (25 mL) at -78°C. The resulting mixture was stirred for 15 minutes and then warmed to -20°C over 1 h. This solution was quickly cannulated into a solution of allyl bromide (3.0 g, 25 mmol, 2.5 eq) in anhydrous THF (15 mL) at -78°C. The resulting mixture was stirred at -78°C for 1 h and then at room temperature for 10 minutes. The reaction was quenched with 10% HCl (30 mL) and the reaction mixture was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were concentrated under vacuum. The crude product was redissolved in diethyl ether (20 mL) and extracted with aqueous 20% KOH (3 x 20 mL). The combined aqueous phase was washed with ether (2 x 40 mL) and acidified with 2 M HCl to pH 1. The aqueous phase was then extracted with ether (3 x 50 mL). The combined organic extracts were washed with water (100 mL), brine (100 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (hexane: EtOAc 10:1) gave alkenoic acid **2h**.

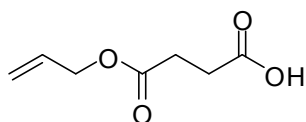


2-(but-3-enyl)benzoic acid (2h)⁷

50%; Colourless liquid. ¹H NMR (500 MHz, CDCl₃): δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.49 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32-7.29 (m, 2H), 5.95-5.87 (m, 1H), 5.06 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.99 (dd, *J* = 10.1, 0.9 Hz, 1H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.42 (dt, *J* = 7.8, 6.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 173.4, 144.9, 138.1, 132.9, 131.7, 131.3, 128.1, 126.1, 114.9, 35.6, 34.2; MS (ESI) [*M* - H]⁻: 175.1.

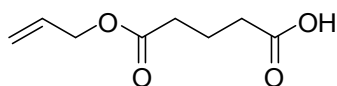


Representative Procedure for the Preparation of Alkenoic Acid 2i and 2m. The preparation is based on the method in literature.⁹ Succinic anhydride (3.00 g, 30 mmol, 1.0 eq) and 4-dimethylaminopyridine (122 mg, 3 mmol, 0.1 eq) were first dissolved in toluene (40 mL). Allyl alcohol (2.1 mL, 30 mmol, 1.0 eq) was then added dropwise and the mixture stirred under reflux for 4 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (hexane: EtOAc 4:1) to give alkenoic acid **2i**.



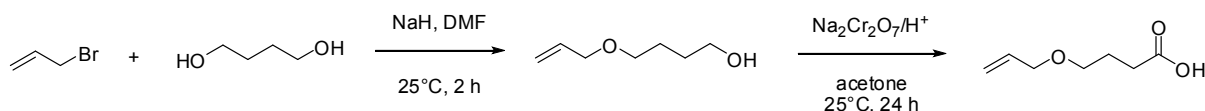
4-(allyloxy)-4-oxobutanoic acid (**2i**)⁹

89%; Colourless oil. ¹H NMR (300 MHz, CDCl₃): δ 5.92-5.82 (m, 1H), 5.31 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.20 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.58 (d, *J* = 5.3 Hz, 2H), 2.70-2.59 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 178.2, 171.8, 131.9, 118.4, 65.5, 28.9, 28.8; MS (ESI) [*M* - H]⁻: 157.1.



5-(allyloxy)-5-oxopentanoic acid (**2m**)

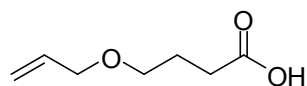
78%; Colourless oil. IR (Neat): 3459, 1713, 1196 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.93-5.82 (m, 1H), 5.29 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.20 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 2.43-2.38 (m, 4H), 1.96 (q, *J* = 7.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 179.0, 172.5, 132.0, 118.3, 65.2, 33.0, 32.9, 19.7; HRMS (ESI) calcd for C₈H₁₁O₄ *m/z* [*M* - H]⁻: 171.0657; found: 171.0657.



Representative Procedure for the Preparation of Alkenoic Acid 2j and 2n. The preparation is based on the method in literature.¹⁰ 1,4-butanediol (4.4 mL, 50 mmol, 1.7 eq) was added dropwise to an ice-cold, stirred suspension of NaH (60% dispersed in mineral oil, 1.7 g, 40 mmol, 1.3 eq) in DMF (40 mL). After 30 min, allyl bromide (2.6 mL, 30 mmol, 1.0 eq) was added dropwise. The mixture

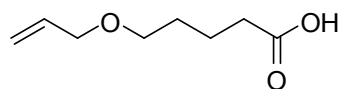
was stirred at 25°C for 2 h. The reaction was quenched with water (40 mL) and extracted with EtOAc (3 x 60 mL). The combined organic extracts were concentrated under vacuum and the residue was used without purification for the next step.

The residue was dissolved in acetone (50 mL) and cooled in an ice bath. Jones reagent (prepared from 10.0 g of Na₂Cr₂O₇·2H₂O, 6.6 mL of H₂SO₄ and 20 mL of water) was added dropwise. The ice bath was removed and the mixture stirred at 25°C for 24 h. Upon completion of the reaction, volatile solvents were removed under reduced pressure. The residue was diluted with water (40 mL) and extracted with EtOAc (3 x 60 mL). The combined organic extracts were washed with water (3 x 150 mL), followed by brine (150 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (hexane: EtOAc 10:1) gave alkenoic acid **2j**.



4-(allyloxy)butanoic acid (2j)

55%; Colourless oil. IR (Neat): 3083, 1713, 1417, 1251, 1098 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 5.93-5.85 (m, 1H), 5.26 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.16 (dd, *J* = 10.4 Hz, 1.3 Hz, 1H), 3.97 (d, *J* = 5.8 Hz, 2 H), 3.48 (t, *J* = 6.1 Hz, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 1.91 (q, *J* = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): 179.5, 134.6, 116.9, 71.8, 68.9, 30.9, 24.7; HRMS (ESI) calcd for C₇H₁₁O₃ *m/z* [M - H]⁻: 143.0714; found: 143.0714.

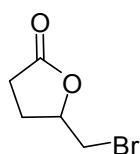


5-(allyloxy)pentanoic acid (2n)

39%; Colourless oil. IR (Neat): 3082, 1710, 1416, 1172, 1102 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 5.94-5.87 (m, 1H), 5.27 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.97-3.95 (m, 2H), 3.45 (t, *J* = 6.1 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 1.75-1.63 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 179.6, 134.8, 116.9, 71.8, 69.7, 33.7, 29.0, 21.5; HRMS (ESI) calcd for C₈H₁₃O₃ *m/z* [M - H]⁻: 157.0870; found: 157.0867.

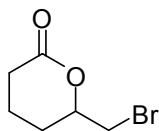
(D) Medium ring size bromolactonization

General Procedure for the Bromolactonization of 4-Pentenoic Acid and 5-Hexenoic Acid. To a solution of acid (0.25 mmol, 1.0 eq), catalyst (0.05 mmol, 0.1 eq) in CH₂Cl₂ (5 mL) in the dark at 25°C was added N-bromosuccinimide (89 mg, 0.5 mmol, 2 eq). The mixture was stirred and quenched by saturated Na₂SO₃ (2 mL) upon completion of reaction. The solution was diluted with water (2 mL) and extracted with CH₂Cl₂ (3 x 5 mL). The combined organic extracts were washed with brine (5.0 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (CH₂Cl₂ as eluent) to yield the corresponding lactones.



5-(bromomethyl)dihydrofuran-2(3H)-one (3a)¹¹

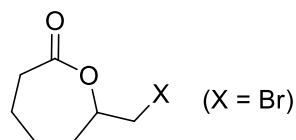
Pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 4.74-4.69 (m, 1H), 3.52 (d, *J* = 5.1 Hz, 2H), 2.65-2.47 (m, 2H), 2.44-2.35 (m, 1H), 2.10-2.05 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 176.1, 77.7, 34.1, 28.2, 26.0. MS (ESI) [*M* + *H*]⁺: 181.1.



6-(bromomethyl)tetrahydro-2H-pyran-2-one (3b)¹²

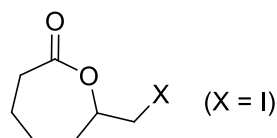
Pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 4.49-4.44 (m, 1H), 3.49-3.43 (m, 2H), 2.58-2.54 (m, 1H), 2.44-2.37 (m, 1H), 2.07-2.03 (m, 1H), 1.94-1.90 (m, 1H), 1.90-1.83 (m, 1H), 1.70-1.63 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 170.3, 78.4, 33.8, 29.2, 26.1, 17.9; MS (ESI) [*M* + *H*]⁺: 192.9, 194.9.

General Procedure for the Bromolactonization of 6-Heptenoic Acid. To a solution of 6-heptenoic acid (0.035 mL, 0.25 mmol, 1.0 eq) in CH₂Cl₂ (5 mL) in the dark at 0°C was added zwitterionic catalyst (4.9 mg, 0.025 mmol, 0.05 eq) and *N*-bromosuccinimide (89 mg, 0.5 mmol, 2.0 eq). The mixture was stirred for 6 h at 0°C and quenched by saturated Na₂SO₃ (3 mL). The solution was diluted with water (5 mL) and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were washed with brine (20 mL), dried with Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (CH₂Cl₂ as eluent) to yield the corresponding lactone **3c**.



7-(bromomethyl)oxepan-2-one (3c)

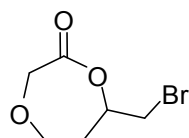
Colourless oil. IR (Neat): 1732, 1174, 754 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.48-4.42 (m, 1H), 3.54-3.51 (m, 1H), 3.43-3.39 (m, 1H), 2.74-2.69 (m, 1H), 2.61-2.58 (m, 1H), 2.20-2.18 (m, 1H), 2.02-1.96 (m, 2H), 1.65-1.55 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 174.0, 79.2, 34.7, 34.2, 33.0, 27.9, 22.8; HRMS (EI) calcd for $\text{C}_7\text{H}_{11}^{79}\text{BrO}_2$ m/z $[\text{M}]^+$: 205.9942; found 205.9940.



7-(iodomethyl)oxepan-2-one (3c)⁴

Yellow oil. ^1H NMR: (CDCl_3 , 500 MHz): δ 4.35-4.30 (m, 1H), 3.37-3.34 (m, 1H), 3.29-3.25 (m, 1H), 2.74-2.69 (m, 1H), 2.61-2.55 (m, 1H), 2.21-2.18 (m, 1H), 2.01-1.94 (m, 2H), 1.72-1.59 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 173.9, 79.4, 34.8, 34.4, 27.8, 22.7, 7.6; MS (ESI) $[\text{M} + \text{Na}]^+$: 276.9.

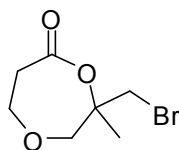
General Procedure for the Bromolactonization of Alkenoic Acids. To a solution of alkenoic acid **2** (0.25 mmol, 1.0 eq) in CH_2Cl_2 (5 mL) in the dark at 0°C was added zwitterionic catalyst (4.9 mg, 0.0125 mmol, 0.05 eq) and *N*-bromosuccinimide (89 mg, 0.5 mmol, 2.0 eq). The mixture was stirred for at 0°C and monitored by TLC. Upon completion, the solution was quenched by saturated Na_2SO_3 (3 mL). The solution was diluted with water (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were washed with brine (20 mL), dried with Na_2SO_4 , filtered and concentrated under vacuum. The residue was purified by flash column chromatography (column was first flushed with some hexane and then eluted with CH_2Cl_2 : hexane : EtOAc 6:2:1) to yield the corresponding lactone **3**.



7-(bromomethyl)-1,4-dioxepan-2-one (3d)

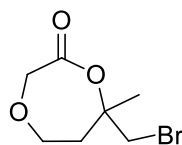
Pale yellow oil. IR (Neat): 1720, 1301, 1128, 738 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.79-4.75 (m, 1H), 4.40 (d, J = 15.8 Hz, 1 H), 4.30 (d, J = 15.8 Hz, 1 H), 4.08-4.04 (m, 1H), 3.79-3.76 (m, 1H), 3.60-3.52 (m, 1H), 3.50-3.48 (m, 1H), 2.25-2.16 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.4, 77.4,

70.9, 70.1, 34.3, 33.5; HRMS (ESI) calcd for $C_6H_9^{79}BrO_3Na$ m/z $[M + Na]^+$: 230.9627; found: 230.9632; HRMS (ESI) calcd for $C_6H_9^{81}BrO_3Na$ m/z $[M + Na]^+$: 232.9607; found: 232.9616.



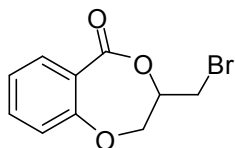
3-(bromomethyl)-3-methyl-1,4-dioxepan-5-one (3e)

Yellow oil. IR (Neat): 1723, 1264, 909, 737 cm^{-1} ; 1H NMR: ($CDCl_3$, 500 MHz): δ 3.97 (d, $J = 14.0$ Hz, 1H), 3.86 (d, $J = 13.8$ Hz, 1H), 3.84-3.82 (m, 2H), 3.58 (d, $J = 10.8$ Hz, 1H), 3.54 (d, $J = 10.8$ Hz, 1H), 3.00-2.87 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 81.6, 76.3, 65.9, 40.4, 35.7, 21.8; HRMS (ESI) calcd for $C_7H_{11}^{79}BrO_3Na$ m/z $[M + Na]^+$: 244.9784; found: 244.9782.



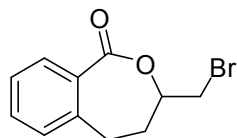
7-(bromomethyl)-7-methyl-1,4-dioxepan-2-one (3f)

Yellow oil. IR (Neat): 1729, 1433, 1283, 1136, 987, 736 cm^{-1} ; 1H NMR: ($CDCl_3$, 500 MHz): δ 4.37-4.30 (m, 2H), 3.99-3.91 (m, 1H), 3.90-3.86 (m, 1H), 3.73 (d, $J = 10.1$ Hz, 1H), 3.49 (d, $J = 10.1$ Hz, 1H), 2.47-2.38 (m, 1H), 2.26-2.21 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6, 82.4, 66.7, 65.5, 39.2, 35.2, 24.9; HRMS (ESI) calcd for $C_7H_{11}^{79}BrO_3Na$ m/z $[M + Na]^+$: 244.9784; found: 244.9780.



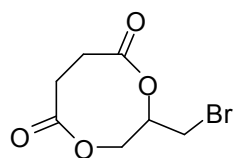
3-(bromomethyl)-2H-benzo[e][1,4]dioxepin-5(3H)-one (3g)

Yellow oil. 1H NMR: ($CDCl_3$, 500 MHz): δ 7.99-7.97 (m, 1H), 7.58-7.54 (m, 1H), 7.09-6.98 (m, 2H), 4.49-4.34 (m, 3H), 3.97-3.93 (m, 1H), 3.88-3.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 158.6, 135.2, 133.0, 121.2, 117.9, 113.3, 69.5, 46.9, 33.4; HRMS (ESI) calcd for $C_{10}H_{10}^{79}BrO_3$ m/z $[M + H]^+$: 256.9808; found: 256.9806; HRMS (ESI) calcd for $C_{10}H_{10}^{81}BrO_3$ m/z $[M + H]^+$: 258.9787; found: 258.9788.



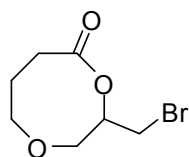
3-(bromomethyl)-4,5-dihydrobenzo[c]oxepin-1(3H)-one (3h)

Yellow oil. IR (Neat): 3083, 1727, 1300, 738 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 7.70 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.47 (dt, $J = 7.6$, 1.4 Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 4.27-4.21 (m, 1H), 3.55 (dd, $J = 10.8$, 6.2 Hz), 3.48 (dd, $J = 10.8$, 5.3 Hz), 3.02-2.95 (m, 1H), 2.81-2.78 (m, 1H), 2.21-2.11 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.2, 137.5, 132.8, 131.0, 130.2, 128.9, 127.5, 76.9, 32.7, 32.4, 29.3; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}^{79}\text{BrO}_2\text{Na}$ m/z $[\text{M} + \text{Na}]^+$: 276.9835; found: 276.9847.



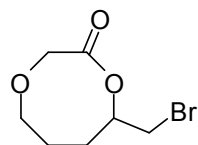
2-(bromomethyl)-1,4-dioxocane-5,8-dione (3i)

Pale yellow oil. IR (Neat): 1738, 1161, 758 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.58-4.54 (m, 1H), 4.52-4.48 (m, 1H), 4.34-4.30 (m, 1H), 3.81-3.78 (m, 1H), 3.75-3.71 (m, 1H), 2.73-2.69 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 176.7, 171.4, 65.4, 46.7, 32.1, 29.5, 28.7; HRMS (EI) calcd for $\text{C}_7\text{H}_{10}^{79}\text{BrO}_4$ m/z $[\text{M} + \text{H}]^+$: 236.9762; found 236.9762.



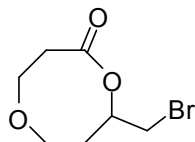
3-(bromomethyl)-1,4-dioxocane-5-one (3j)

Pale yellow oil. IR (Neat): 1715, 1172, 738 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.25-4.21 (m, 1H), 3.87-3.77 (m, 4H), 3.58-3.54 (m, 2H), 2.50-2.47 (m, 2H), 1.95-1.90 (m, 2H); ^{13}C NMR: (CDCl_3 , 125 MHz): δ 179.0, 71.5, 70.0, 49.0, 32.9, 30.6, 24.5; HRMS (ESI) calcd for $\text{C}_7\text{H}_{11}^{79}\text{BrO}_3\text{Na}$ m/z $[\text{M} + \text{Na}]^+$: 244.9784; found: 244.9785.



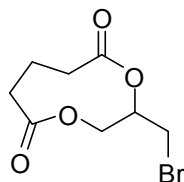
8-(bromomethyl)-1,4-dioxocane-2-one (3k)

Pale yellow oil. IR (Neat): 1752, 1126, 737 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.25-4.13 (m, 4H), 3.63-3.58 (m, 1H), 3.45-3.39 (m, 2H), 1.82-1.71 (m, 4H); ^{13}C NMR: (CDCl_3 , 125 MHz): δ 170.1, 79.0, 67.0, 64.6, 33.7, 29.6, 24.2; HRMS (ESI) calcd for $\text{C}_7\text{H}_{12}^{79}\text{BrO}_3$ m/z $[\text{M} + \text{H}]^+$: 222.9964; found: 222.9966.



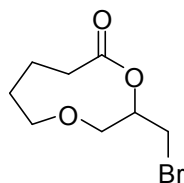
8-(bromomethyl)-1,5-dioxocan-2-one (3l)

Pale yellow oil. IR (Neat): 1719, 1116, 911 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.36-4.31 (m, 1H), 3.86-3.83 (m, 1H), 3.75-3.62 (m, 5H), 2.62 (t, $J = 6.2$ Hz, 2H), 2.44-2.41 (m, 1H), 1.96-1.91 (m, 1H); ^{13}C NMR: (CDCl_3 , 125 MHz): δ 176.3, 68.1, 66.0, 50.0, 36.9, 36.2, 34.7; HRMS (ESI) calcd for $\text{C}_7\text{H}_{11}^{79}\text{BrO}_3\text{Na}$ m/z $[\text{M} + \text{Na}]^+$: 244.9784; found: 244.9794.



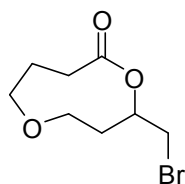
2-(bromomethyl)-1,4-dioxonane-5,9-dione (3m)

Pale yellow oil. IR (Neat): 1737, 1038, 912 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.57-4.54 (m, 1H), 4.49-4.45 (m, 1H), 4.35-4.30 (m, 1H), 3.81-3.78 (m, 1H), 3.75-3.70 (m, 1H), 2.50-2.45 (m, 4H), 2.02-1.96 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 177.5, 172.1, 65.0, 46.8, 32.8, 32.7, 32.0, 19.6; HRMS (EI) calcd for $\text{C}_8\text{H}_{12}^{79}\text{BrO}_4$ m/z $[\text{M} + \text{H}]^+$: 250.9919, found 250.9920.



3-(bromomethyl)-1,4-dioxonan-5-one (3n)

Pale yellow oil. IR (Neat): 1712, 1364, 1170, 738 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.24-4.20 (m, 1H), 3.85-3.77 (m, 4H), 3.54-3.51 (m, 2H), 2.39 (t, $J = 7.0$ Hz, 2H), 1.75-1.70 (m, 2H), 1.69-1.62 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 179.3, 71.6, 70.9, 49.1, 33.5, 33.1, 29.5, 21.3; HRMS (ESI) calcd for $\text{C}_8\text{H}_{14}^{79}\text{BrO}_3$ m/z $[\text{M} + \text{H}]^+$: 237.0121; found: 237.0070.



4-(bromomethyl)-1,5-dioxonan-6-one (3o)

Pale yellow oil. IR (Neat): 1714, 1266, 1174, 736 cm^{-1} ; ^1H NMR: (CDCl_3 , 500 MHz): δ 4.36-4.31 (m, 1H), 3.87-3.84 (m, 1H), 3.69-3.65 (m, 1H), 3.61-3.58 (m, 2H), 3.51-3.45 (m, 2H), 2.44 (t, $J = 7.3$ Hz, 2H), 1.94-1.87 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 178.8, 69.7, 67.8, 49.7, 36.9, 36.2, 30.8, 24.7; HRMS (ESI) calcd for $\text{C}_8\text{H}_{13}^{79}\text{BrO}_3\text{Na}$ m/z $[\text{M} + \text{Na}]^+$: 258.9940; found: 258.9934; HRMS (ESI) calcd for $\text{C}_8\text{H}_{13}^{81}\text{BrO}_3\text{Na}$ m/z $[\text{M} + \text{Na}]^+$: 260.9920; found: 260.9930.

Table S1. Solvent screening

CH2=CHCH2CH2CH2CH2C(=O)OH (2c)
 $\xrightarrow[0^\circ\text{C, 6 h}]{2.0 \text{ eq NBS, } \mathbf{1a} \text{ (5 mol\%)}}$
BrC1C(=O)OCC1 (3c)

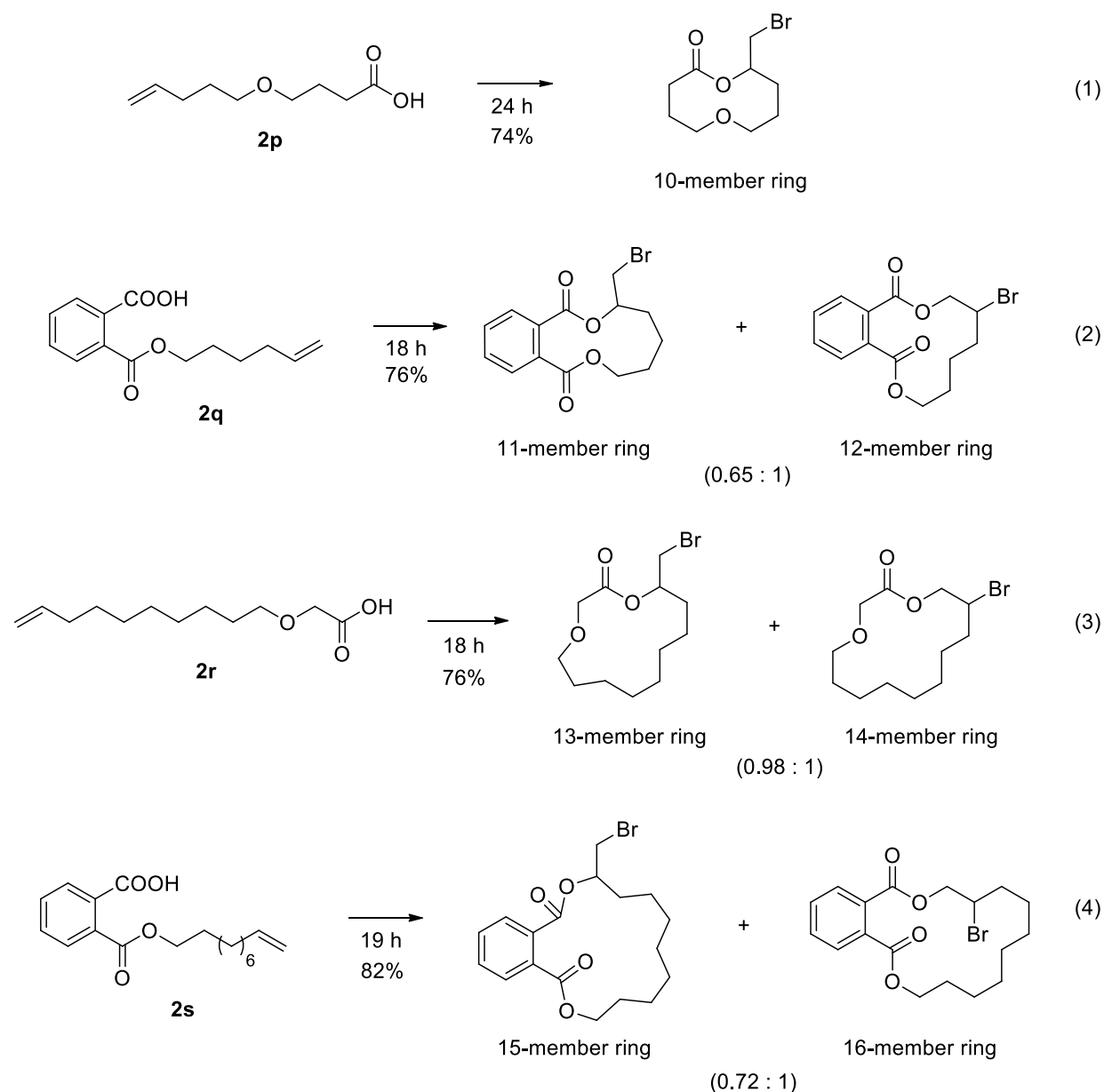
Entry	Solvent	Isolated yield (%)	Entry	Solvent	Isolated yield (%)
1	THF	0	6	EtOH	5
2	CS ₂	0	7	EtOAc	6
3	Chlorobenzene	0	8	1,2-dichloroethane	28
4	Toluene	0	9	CHCl ₃	52
5	MeCN	0	10	CH ₂ Cl ₂	54

Table S2. Catalyst loading optimization

CH2=CHCH2CH2CH2CH2C(=O)OH (2c)
 $\xrightarrow[CH_2Cl_2, 0^\circ\text{C, 6 h}]{2.0 \text{ eq NBS, catalyst } \mathbf{1a}}$
BrC1C(=O)OCC1 (3c)

Entry	Catalyst loading (mol%)	Isolated product yield (%)
1	0	0
2	2	37
3	5	54
4	10	31
5	20	9

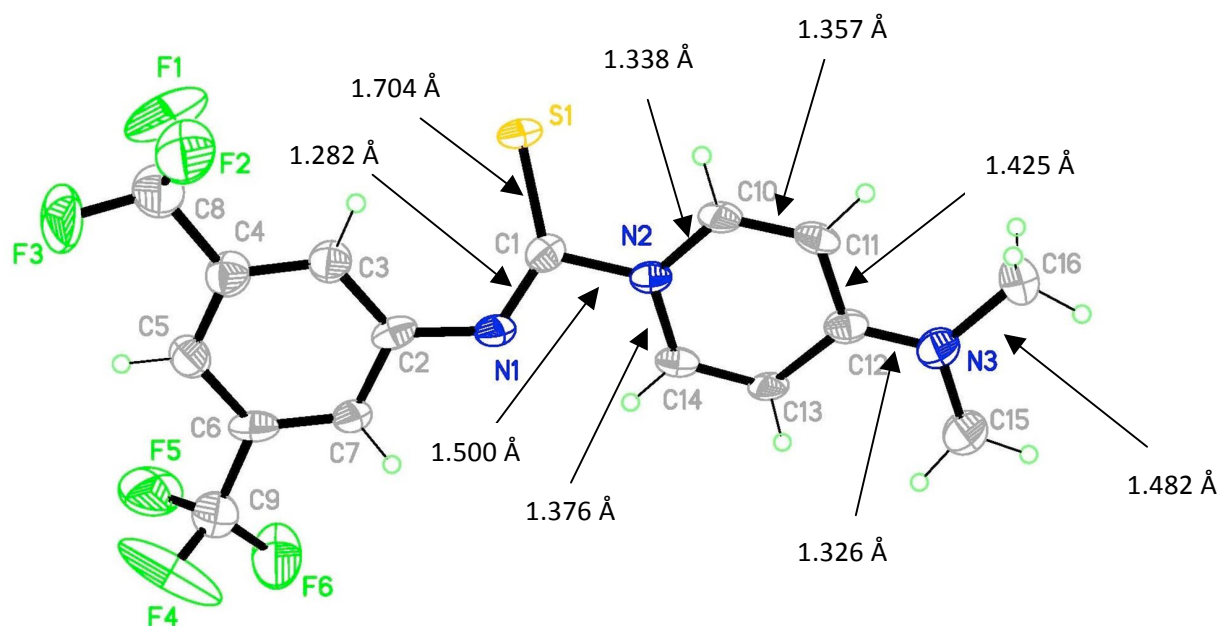
Scheme S1. Examination of larger ring size lactonization



Note:

1. Reactions were carried out with olefinic acid **2** (0.25 mmol), catalyst **1a** (0.0125 mmol), NBS (0.5 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C.
2. The reaction yields were determined by ^1H NMR on the crude product with hexamethylbenzene as the internal standard.
3. The exo/endo product ratios were determined by ^1H NMR.

Figure S1. X-ray structure of **1a**



Structure analysis:

Based on the X-ray crystallographic data, the N(3)-C(12) bond length is 1.326 Å which exhibits a strong C-N double bond character. The double bond character of C(10)-C(11) and C(13)-C(14), and the single bond character of C(11)-C(12) and C(12)-C(13), indicate that there is a distortion of the aromatic character and a strong cationic character of N(3). A strong single bond character of S(1)-C(1) and a strong double bond character of N(1) and C(1) are observed as indicated by the bond lengths. For catalyst **1a**, the negative charge can delocalize in the N(1)-C(1)-S(1) system and the positive charge can delocalize in the DMAP systems. Based on the data from the X-ray crystallographic study, it appears that species **1a-I** is dominated.

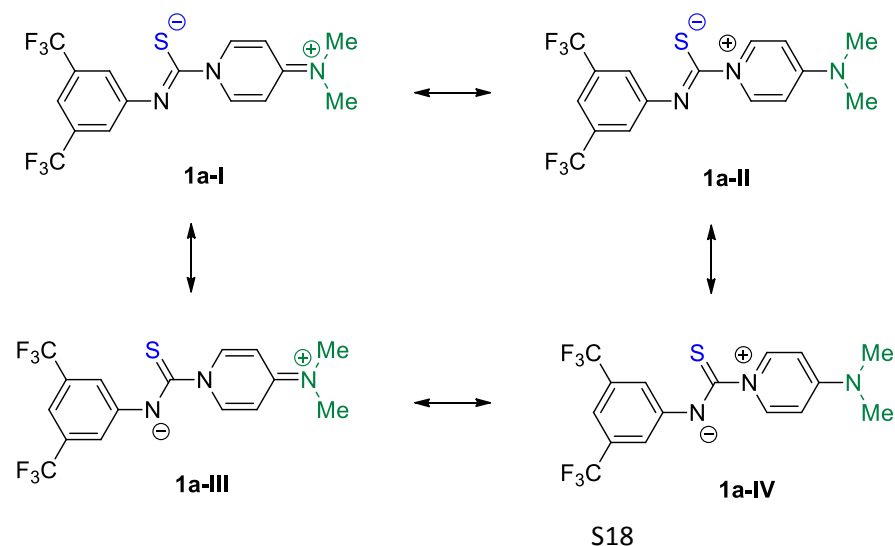


Figure S2. ^1H NMR of **1a** at various temperatures

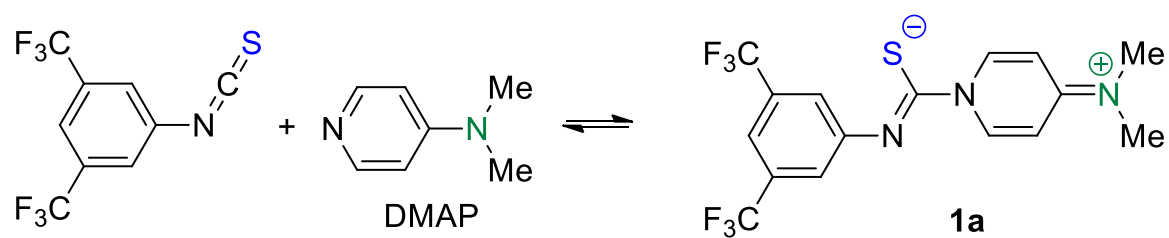
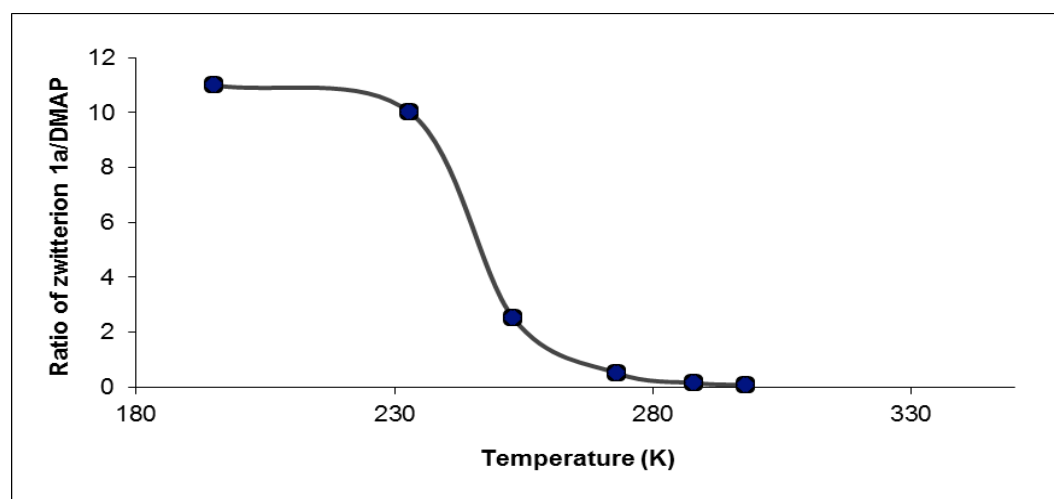
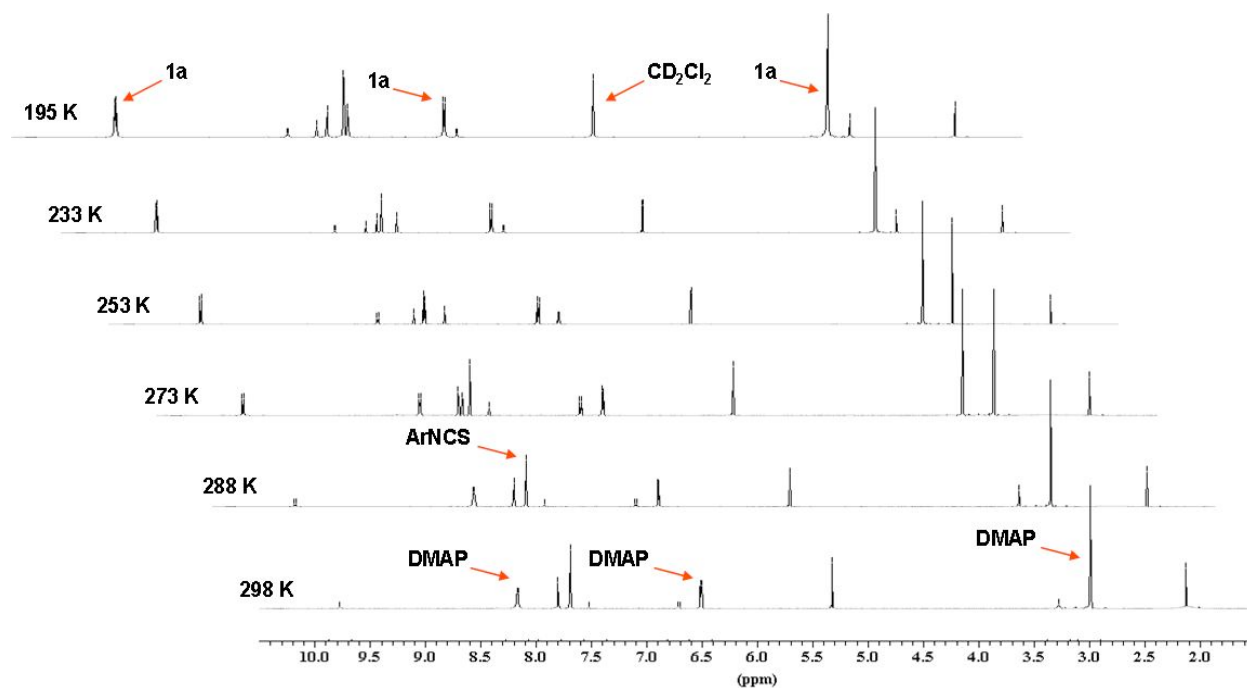
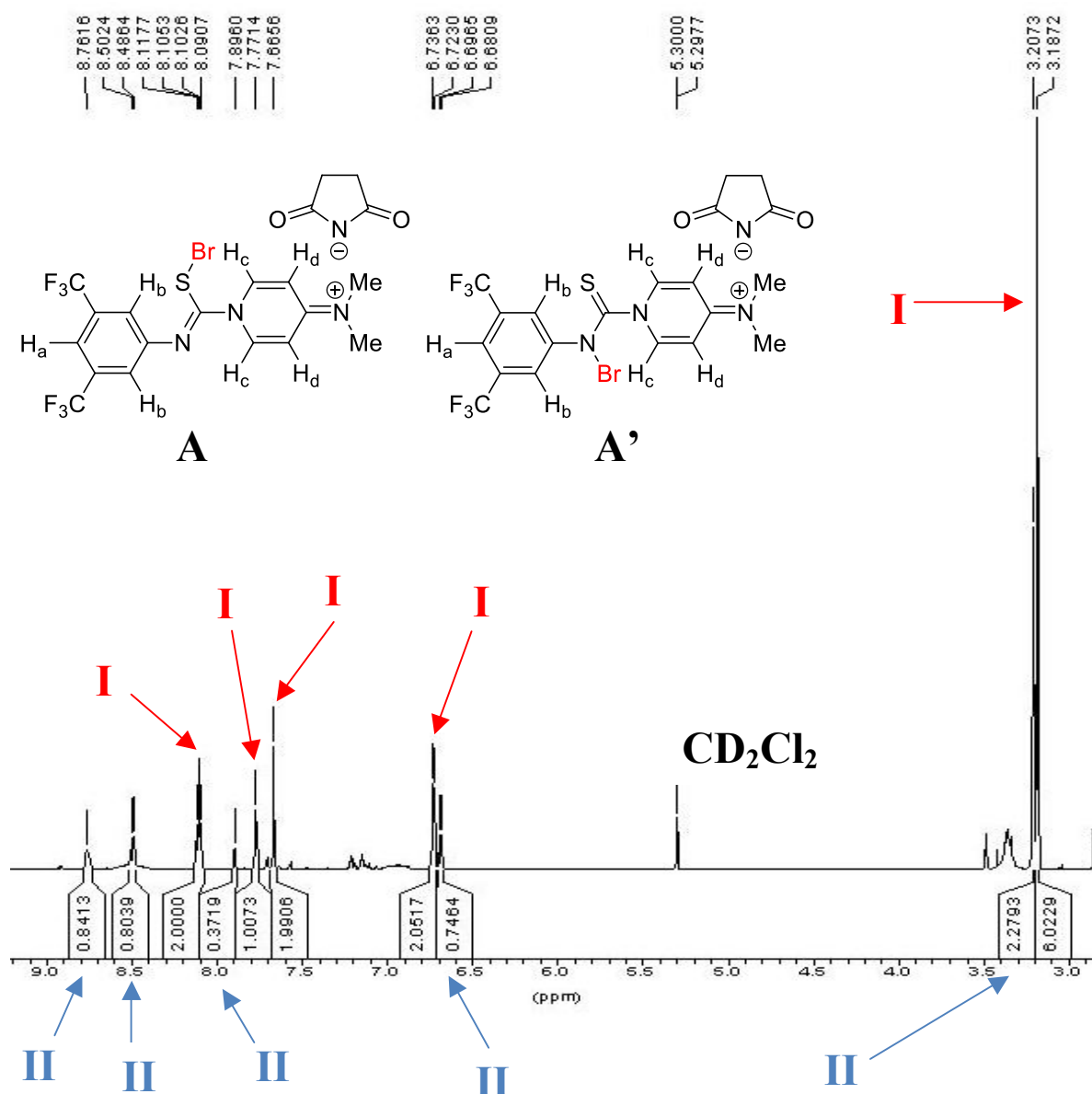


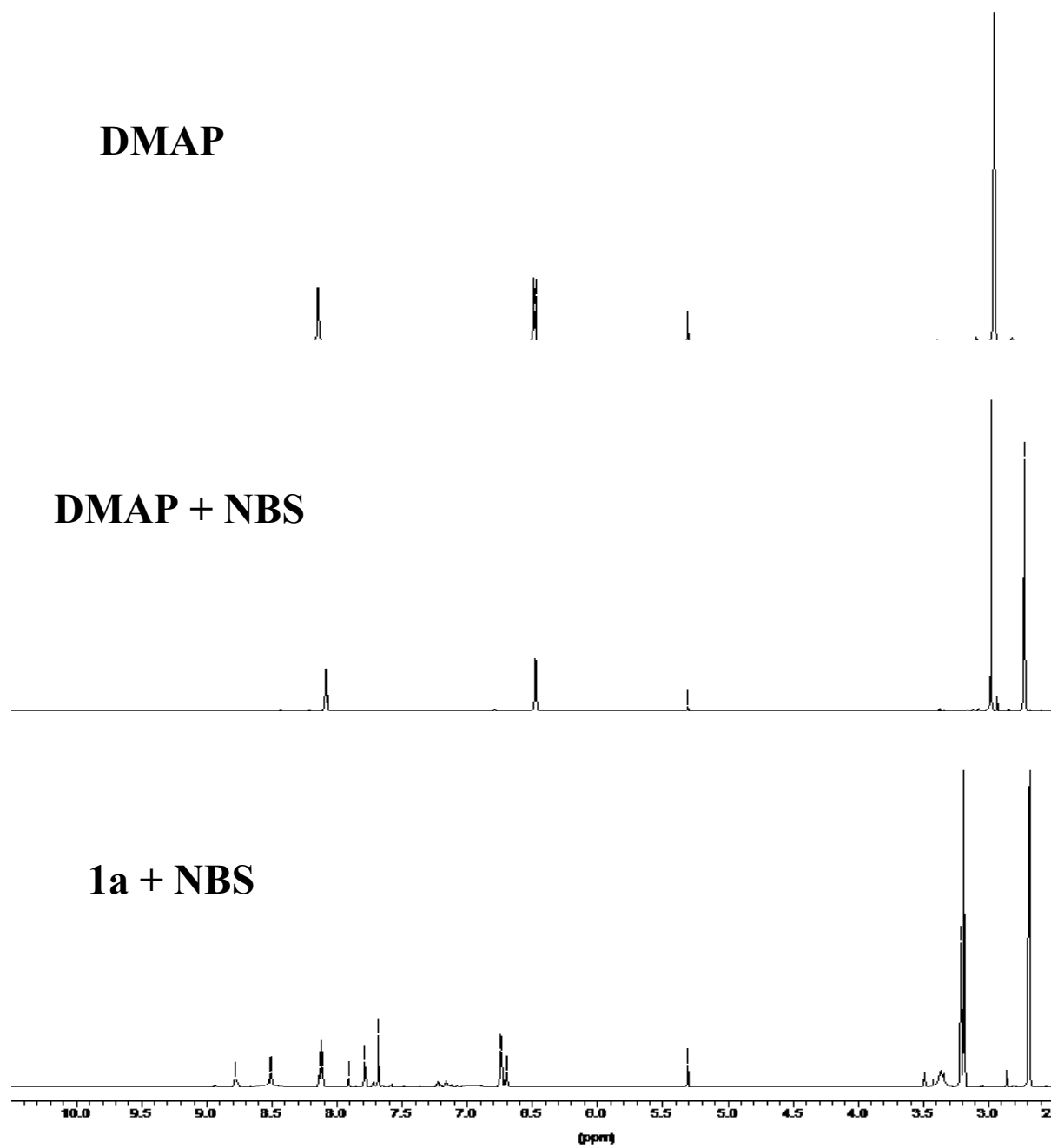
Figure S3. ^1H NMR spectra of the **1a**-NBS complex



Notes:

The NMR experiment was conducted using **1a** (0.1 mmol) and NBS (0.1 mmol) in CD_2Cl_2 (0.4 mL) at 25 °C. ^1H NMR of the mixture gave two set of proton signals (**I** and **II**) which might correspond to two species. The ratio of the two species is *c.a.* 2.5:1. Since the negative charge in **1a** can delocalize between the S and the N atoms, we suspected that the two species might be the S-Br complex **A** and the N-Br complex **A'**. Both proposed species **A** and **A'** contain the proton signals ratio $\text{H}_a:\text{H}_b:\text{H}_c:\text{H}_d:\text{Me} = 1(\text{singlet}):2(\text{singlet}):2(\text{doublet}):2(\text{doublet}):3(\text{singlet})$.

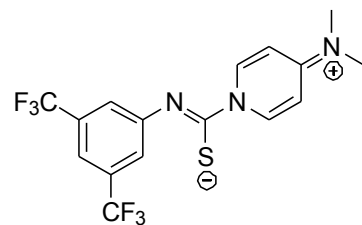
Figure S4. ^1H NMR spectra of the DMAP-NBS and **1a**-NBS complexes



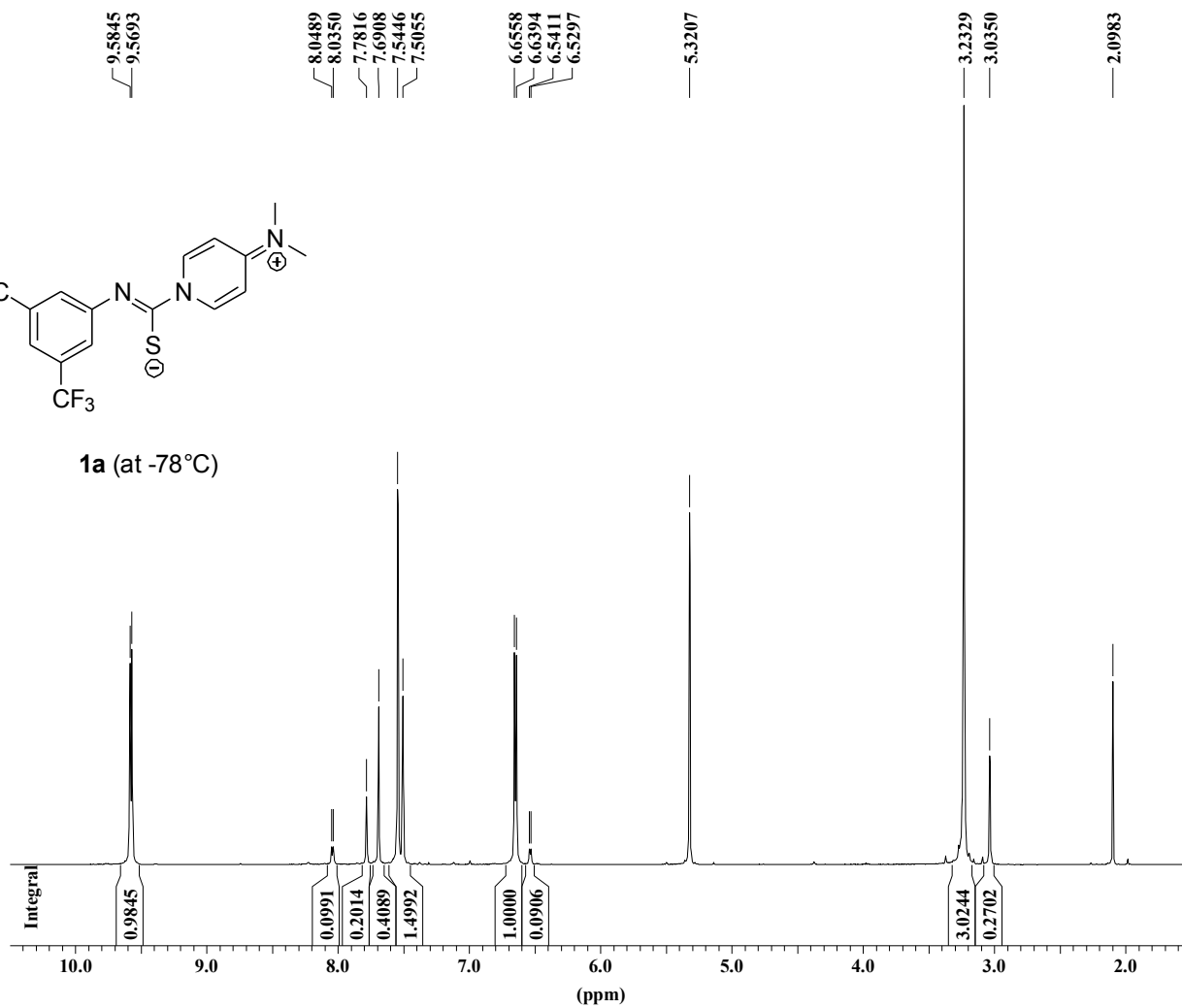
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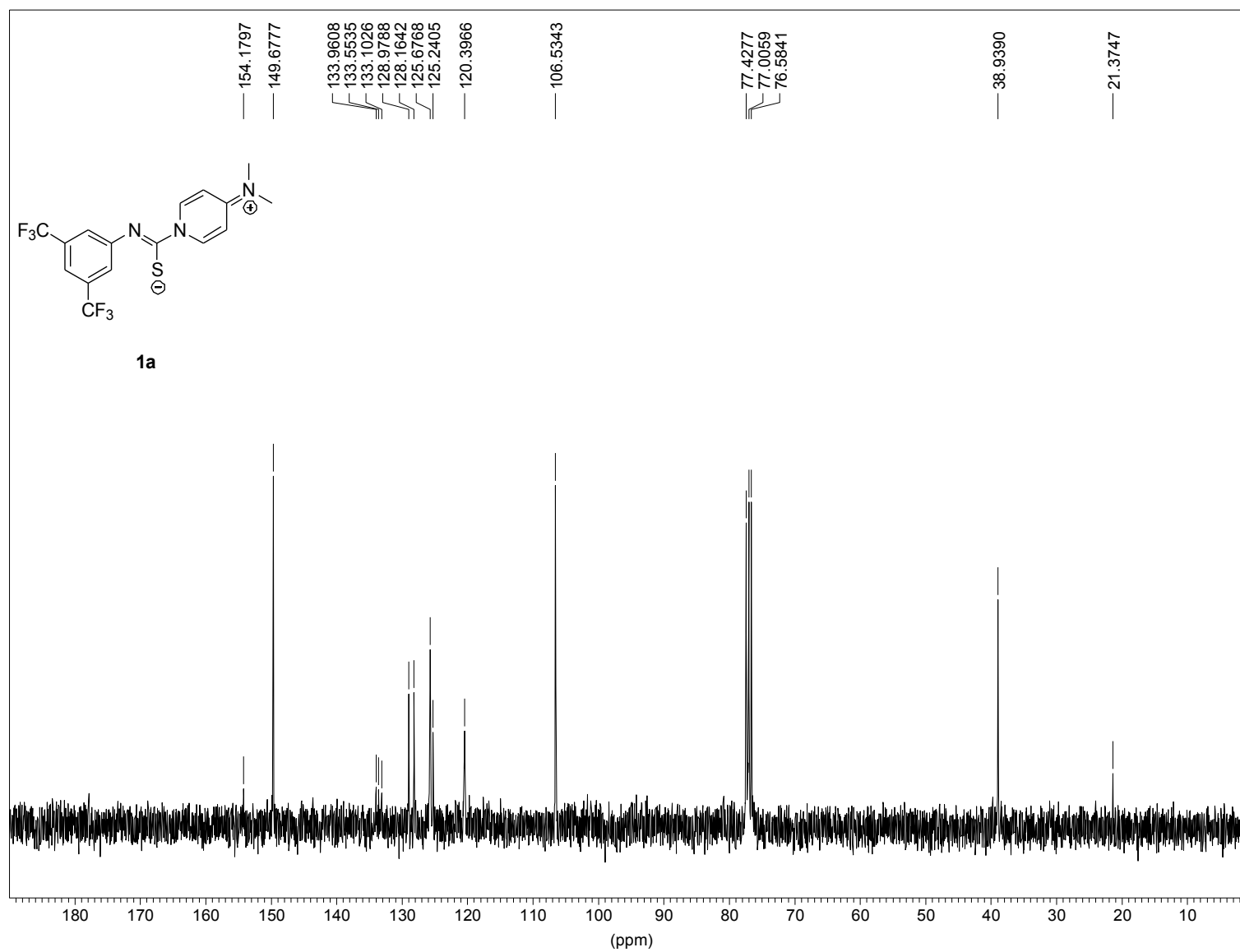
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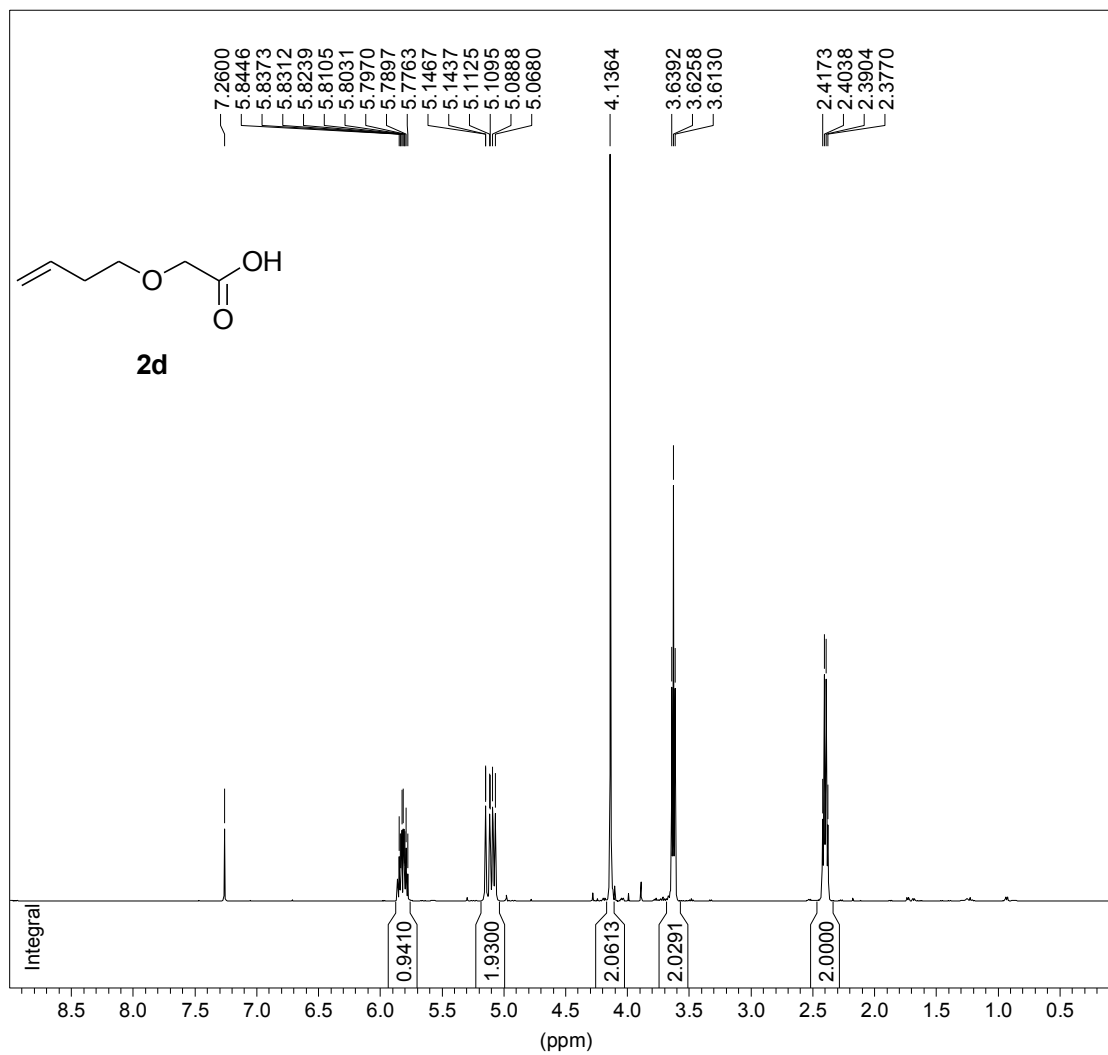


1a (at -78 °C)



*** Current Data Parameters ***
NAME : zy0330
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 12
OI : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
*** Processing Parameters ***
LB : 0.30 Hz
SF : 500.1300189 MHz





*** Current Data Parameters ***

NAME : ya0505
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 4251.96 Hz
PULPROG : zg
SFO1 : 500.2342520 MHz
SOLVENT : CDCl3
SW : 19.9906 ppm
TD : 32768

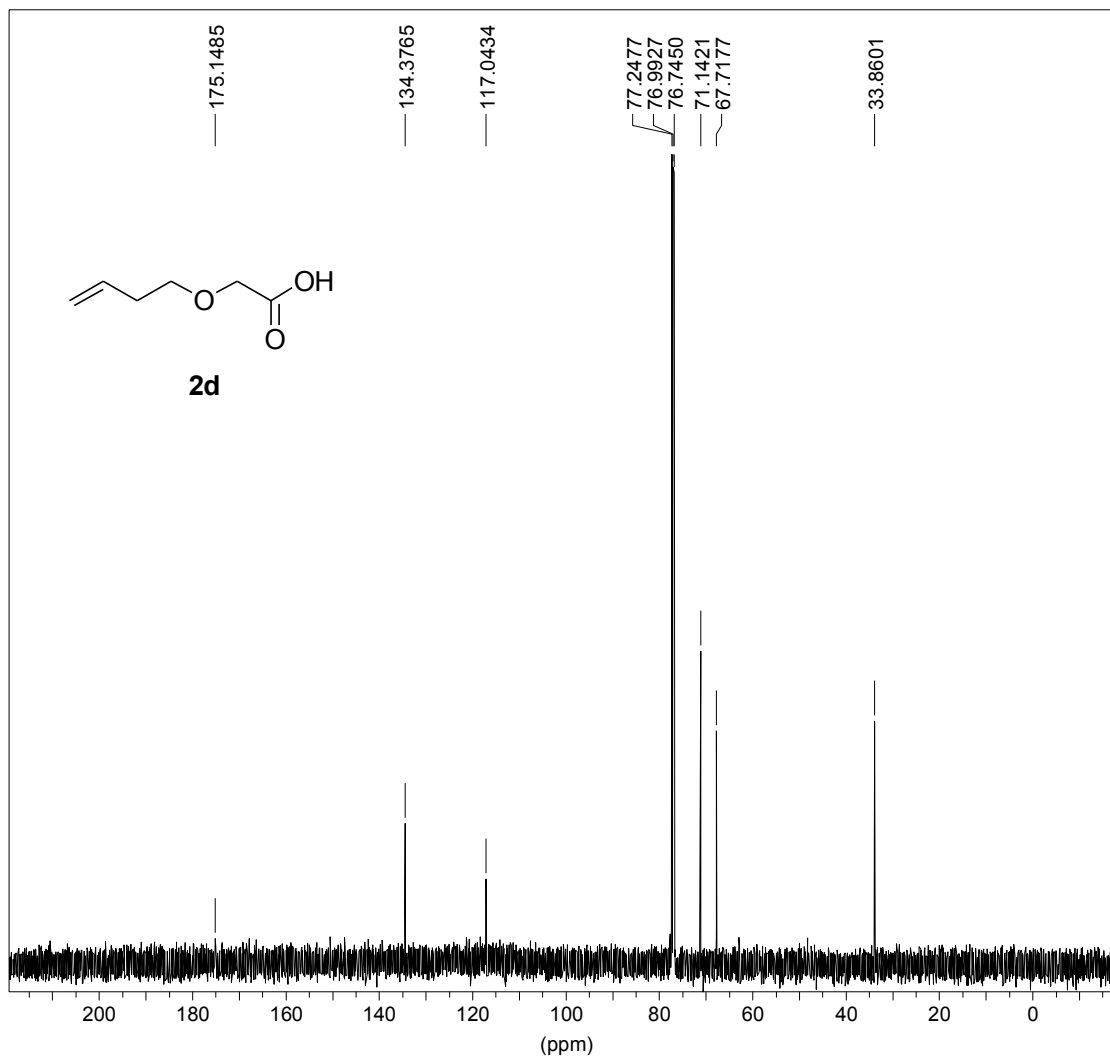
*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

7-Ob ether acid



*** Current Data Parameters ***

NAME : ya0505
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

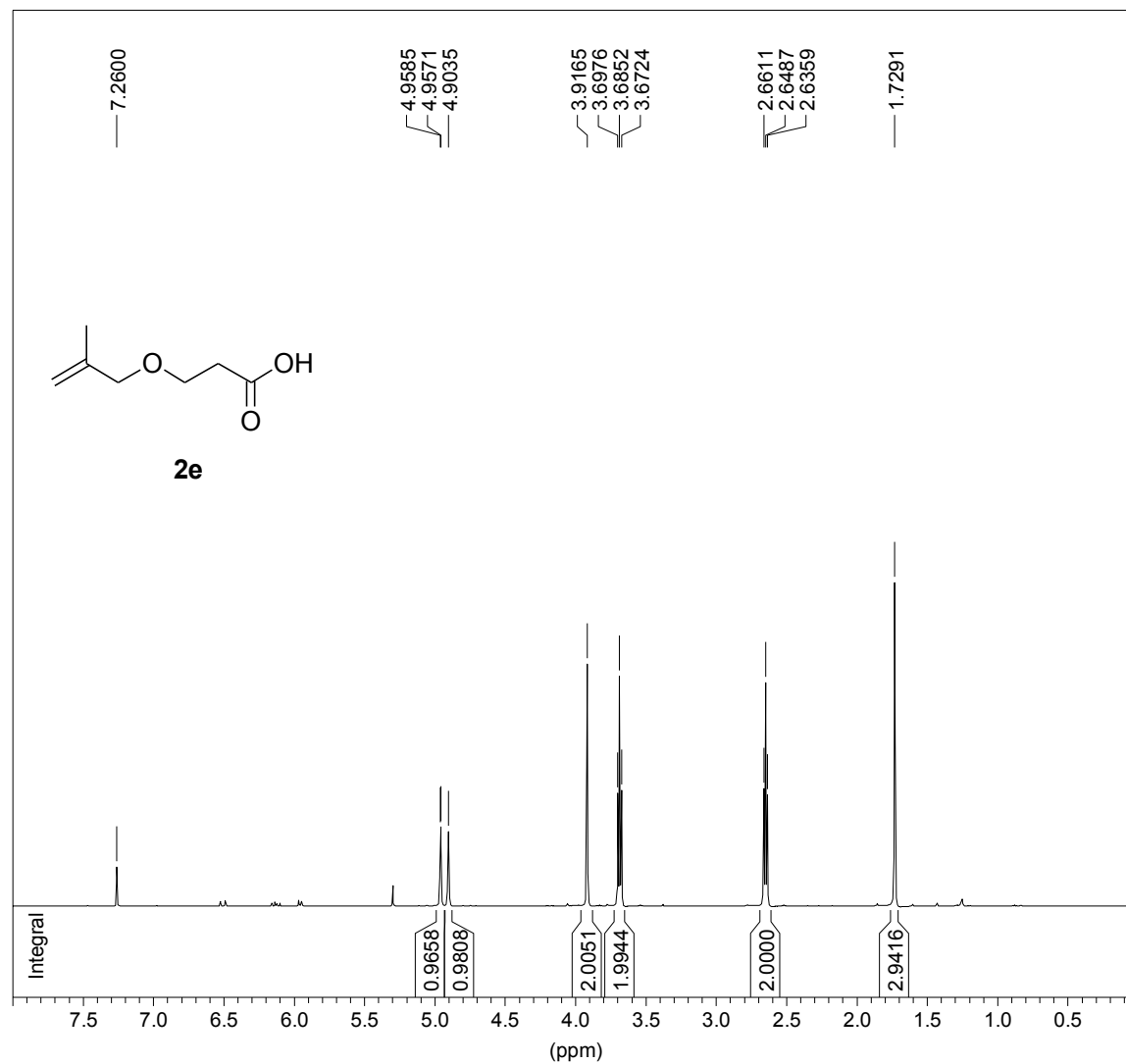
INSTRUM : spect
LOCNUC : 2H
NS : 202
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0531

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 24

NUCLEUS : off

O1 : 2751.27 Hz

PULPROG : zg

SFO1 : 500.2327513 MHz

SOLVENT : CDCl3

SW : 15.0080 ppm

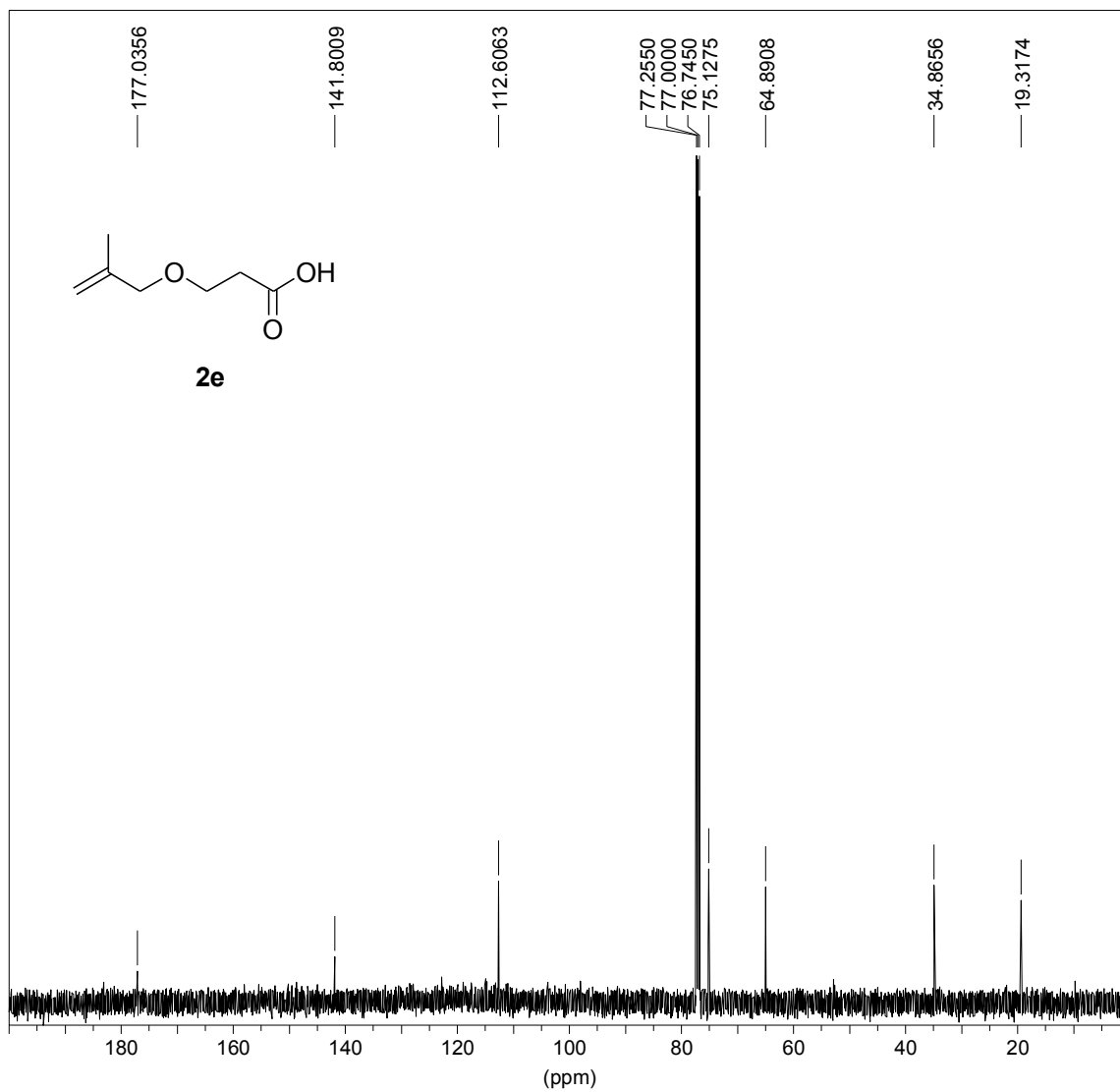
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0531
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
INSTRUM : spect
LOCNUC : 2H
NS : 231
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

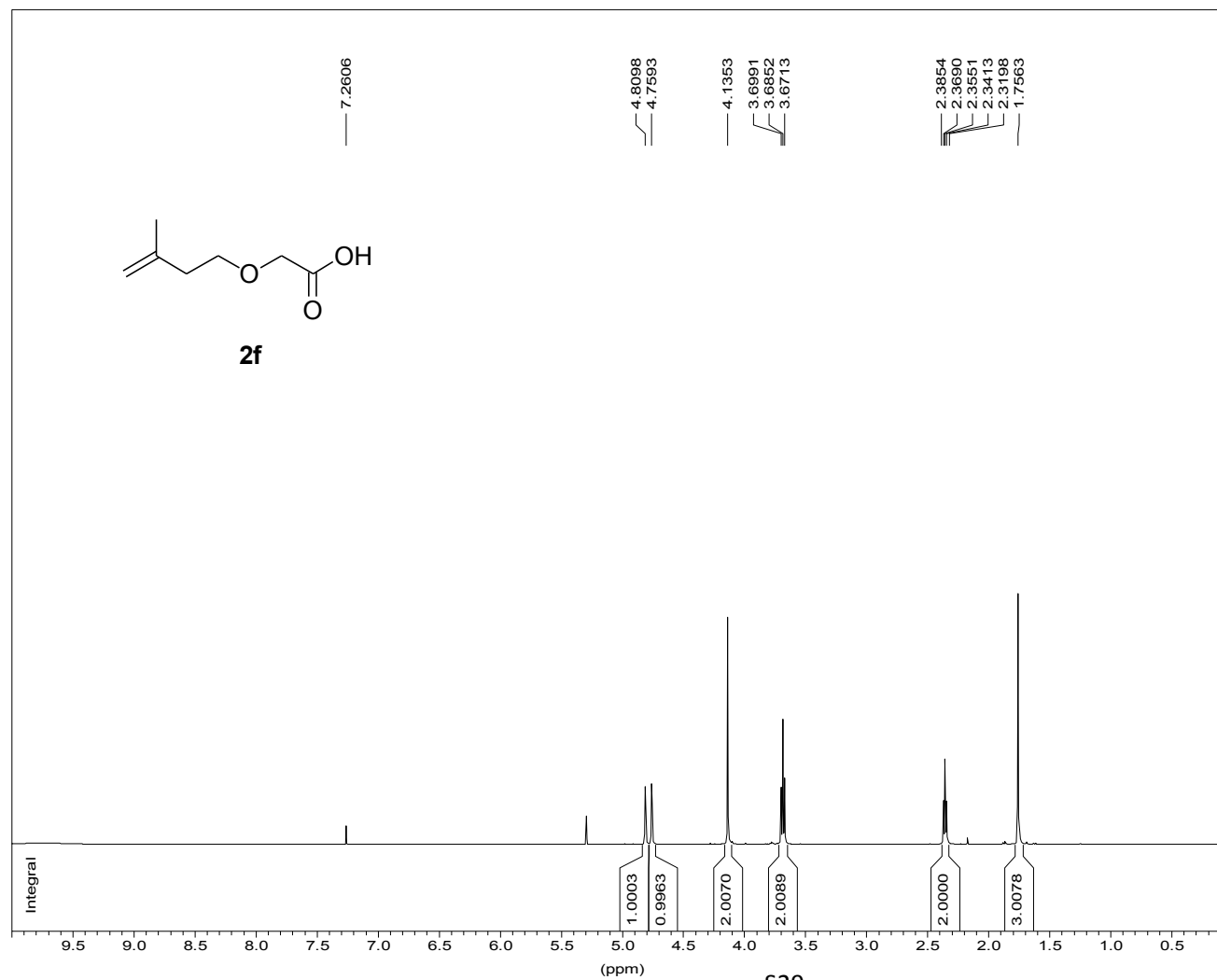
LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500

CH₂=C(Me)(CH₂)₂O acid (7)



*** Current Data Parameters ***

NAME : cya0630
EXPNO : 1
PROCNO : 1

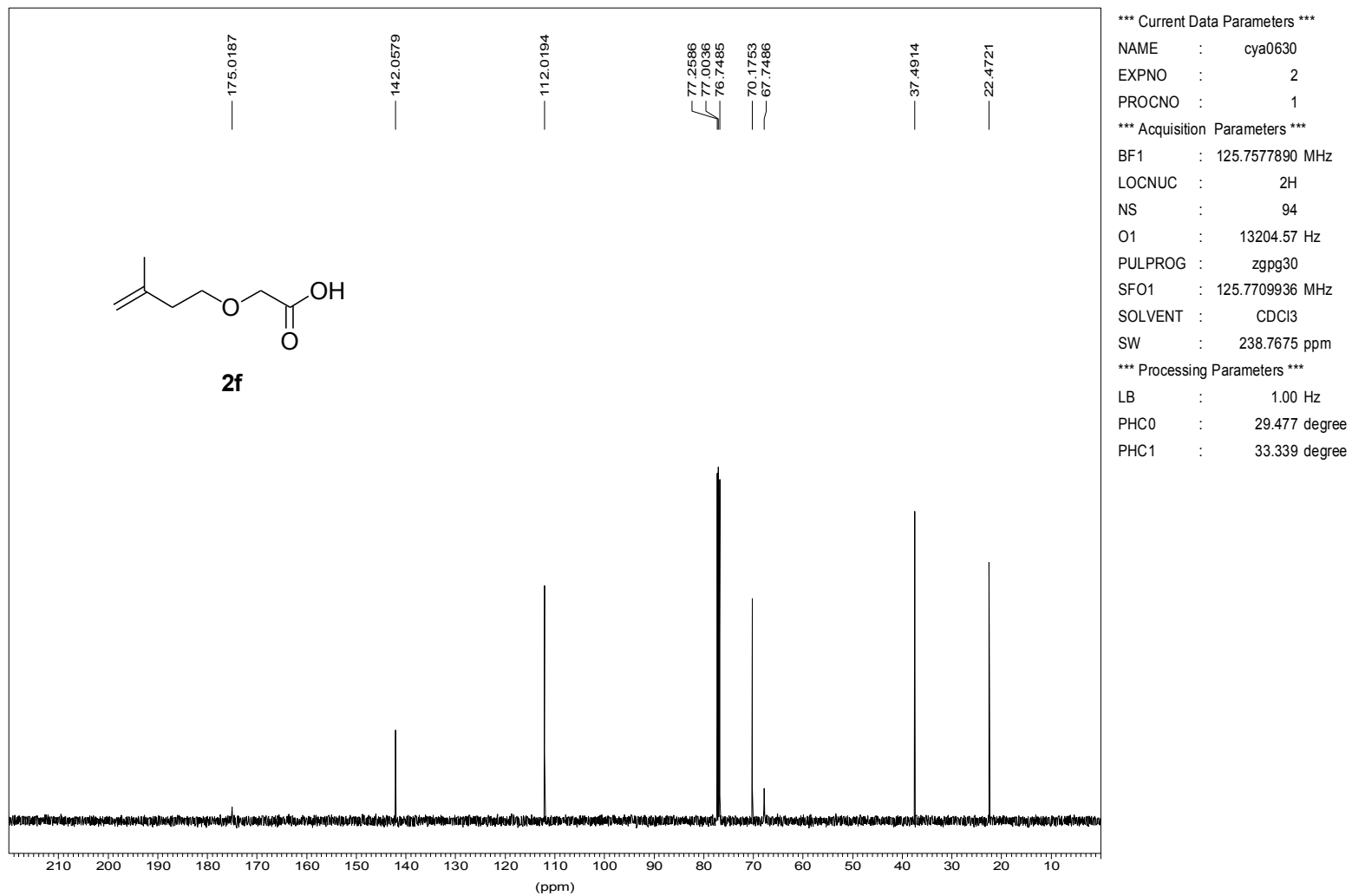
*** Acquisition Parameters ***

BF1 : 500.1300000 MHz
LOCNUC : 2H
NS : 12
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm

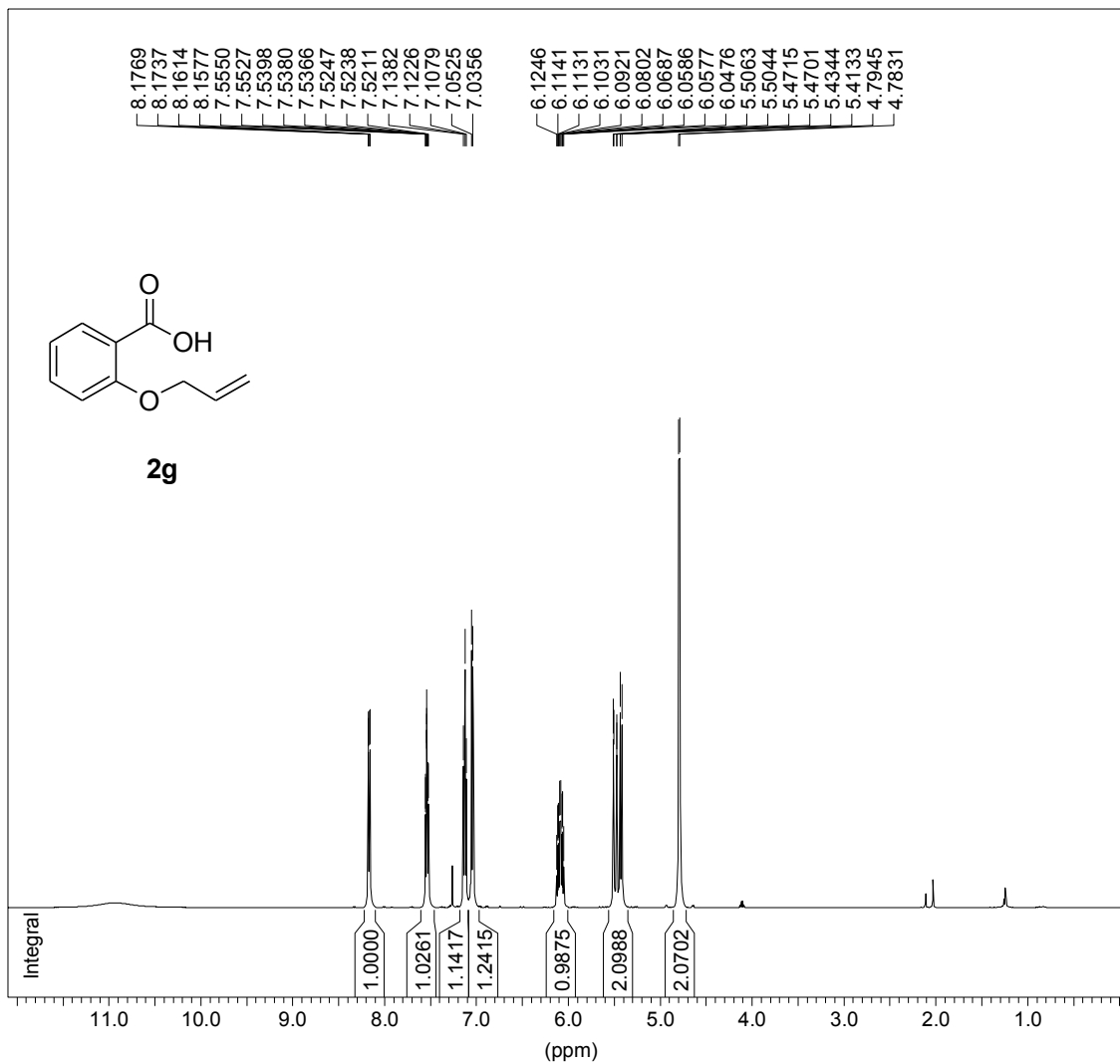
*** Processing Parameters ***

LB : 0.30 Hz
PHC0 : 270.067 degree
PHC1 : -2.582 degree

¹³C AMX500



2-allyloxybenzoic acid



*** Current Data Parameters ***

NAME : ya0510
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl₃
SW : 15.0080 ppm
TD : 32768

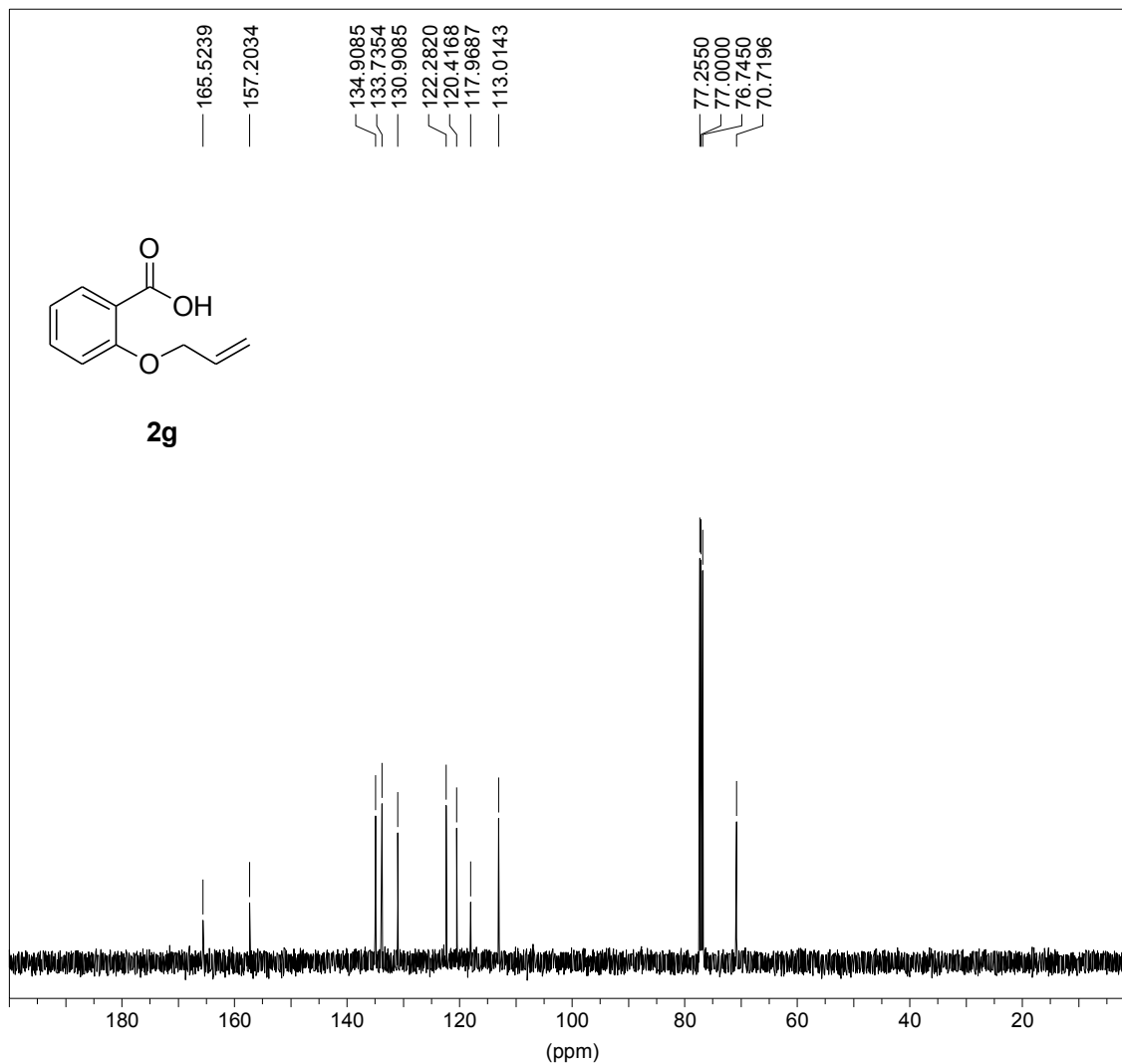
*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

2-allyloxybenzoic acid



*** Current Data Parameters ***

NAME : ya0510

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 83

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

*** Processing Parameters ***

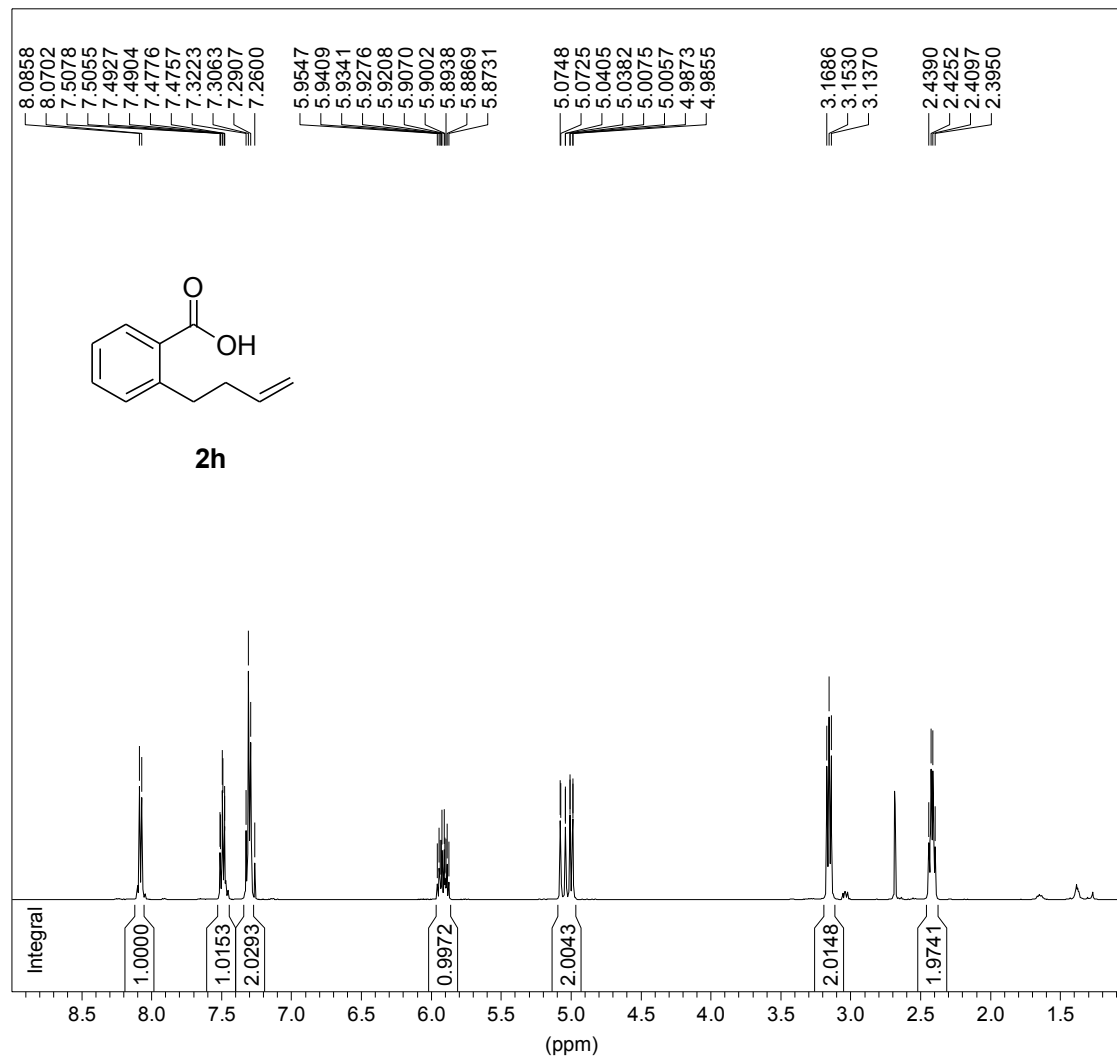
LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

S32

Ph 7-0 substrate



*** Current Data Parameters ***

NAME : ya1018
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768
TE : 298.0 K

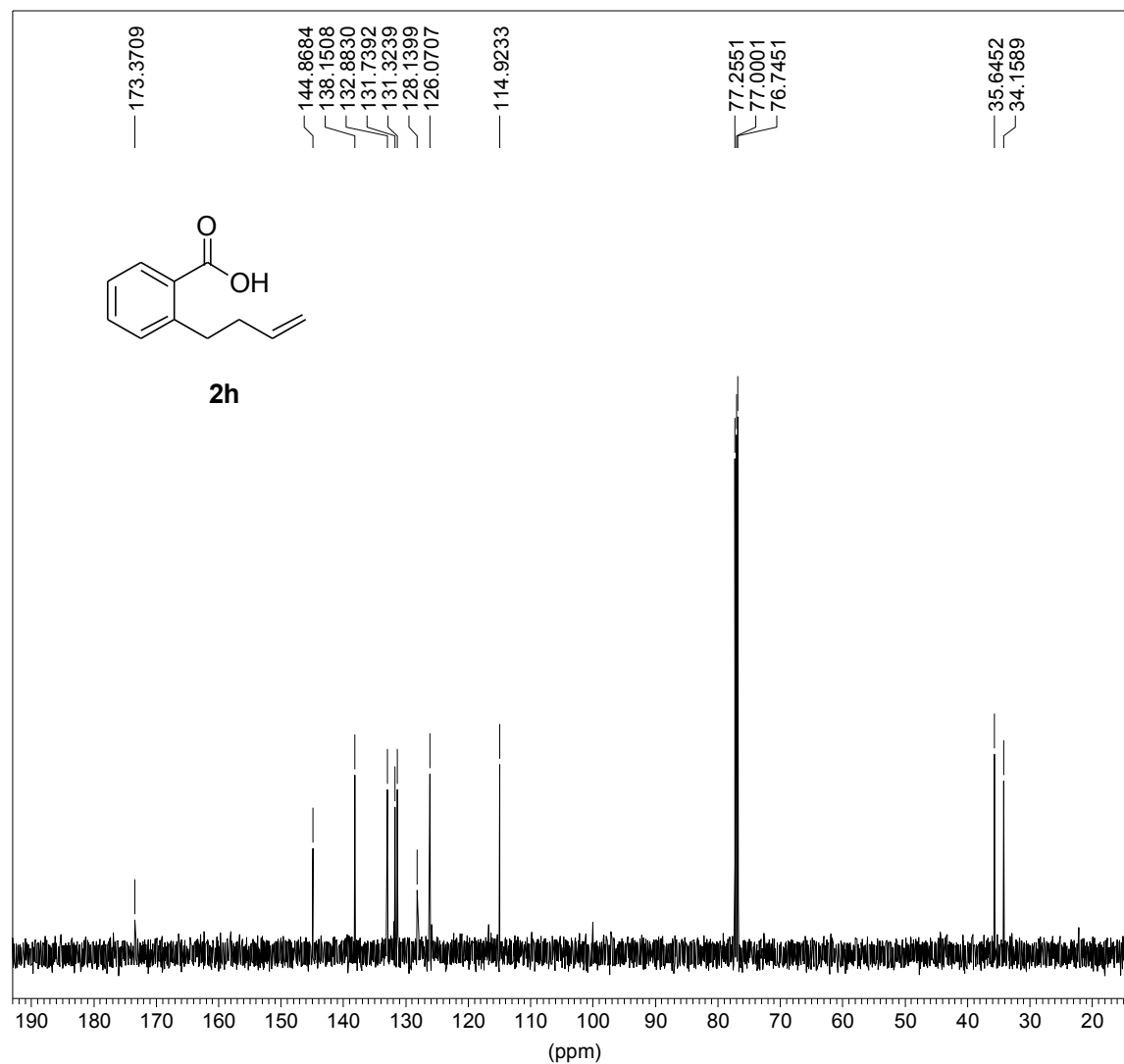
*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

Ph 7-0 substrate



*** Current Data Parameters ***

NAME : ya1018

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 64

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

TE : 298.1 K

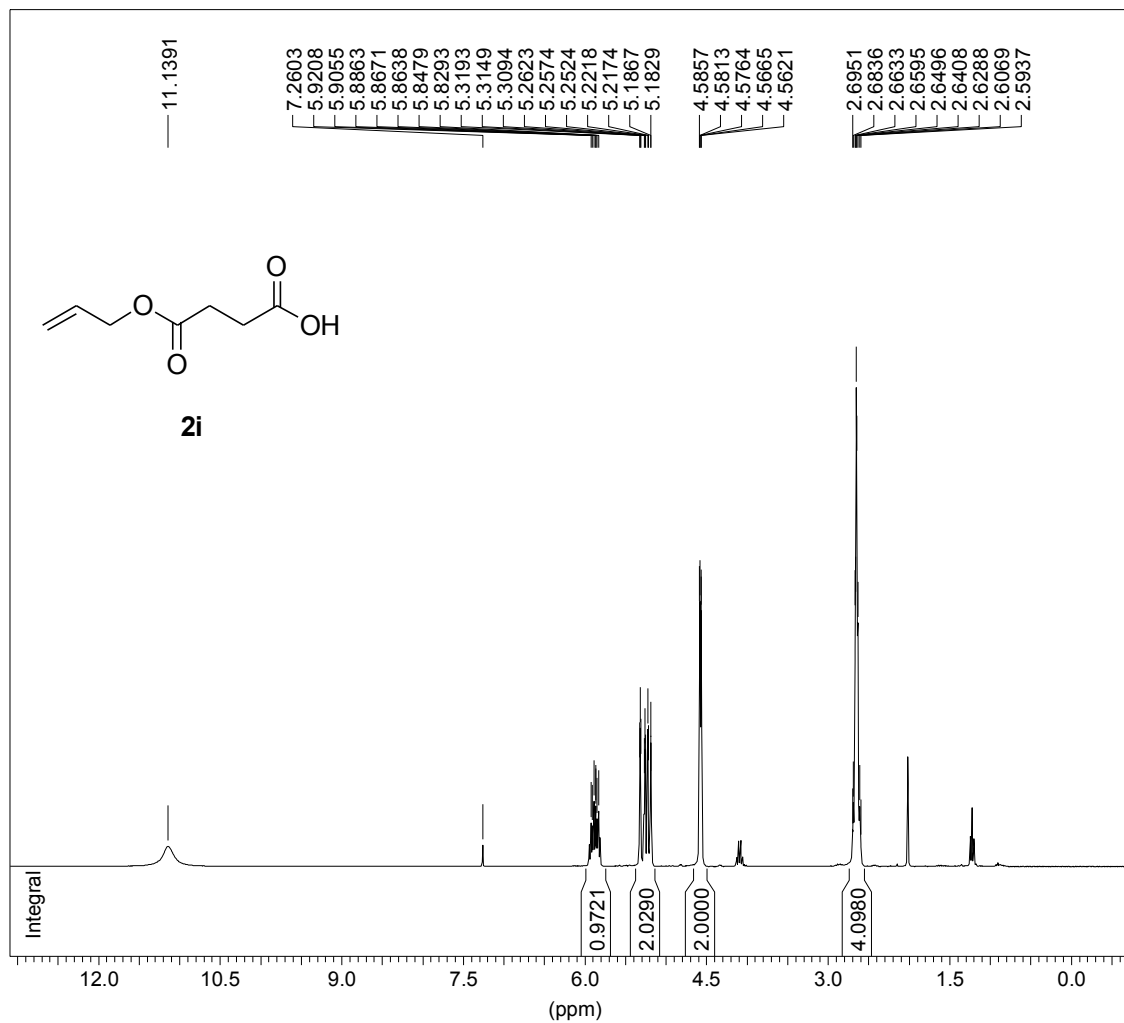
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

S34



*** Current Data Parameters ***

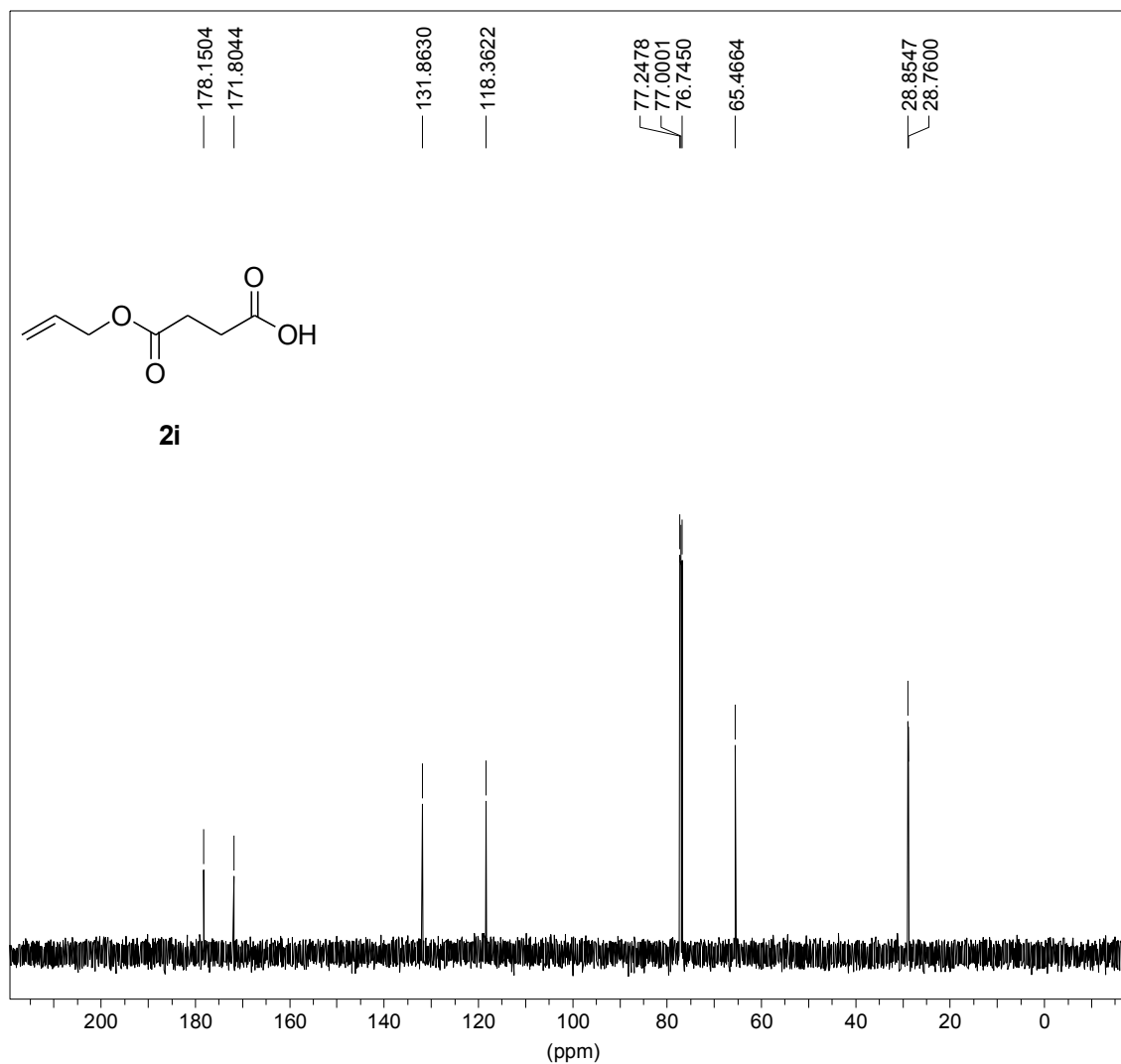
NAME : ag05cya
 EXPNO : 4
 PROCNO : 1
 *** Acquisition Parameters ***
 INSTRUM : spect
 LOCNUC : 2H
 NS : 8
 NUCLEUS : off
 O1 : 1853.43 Hz
 PULPROG : zg30
 SFO1 : 300.1318534 MHz
 SOLVENT : CDCl3
 SW : 17.9519 ppm
 TD : 32768

*** Processing Parameters ***

LB : 0.30 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya1026
EXPNO : 7
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 42
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

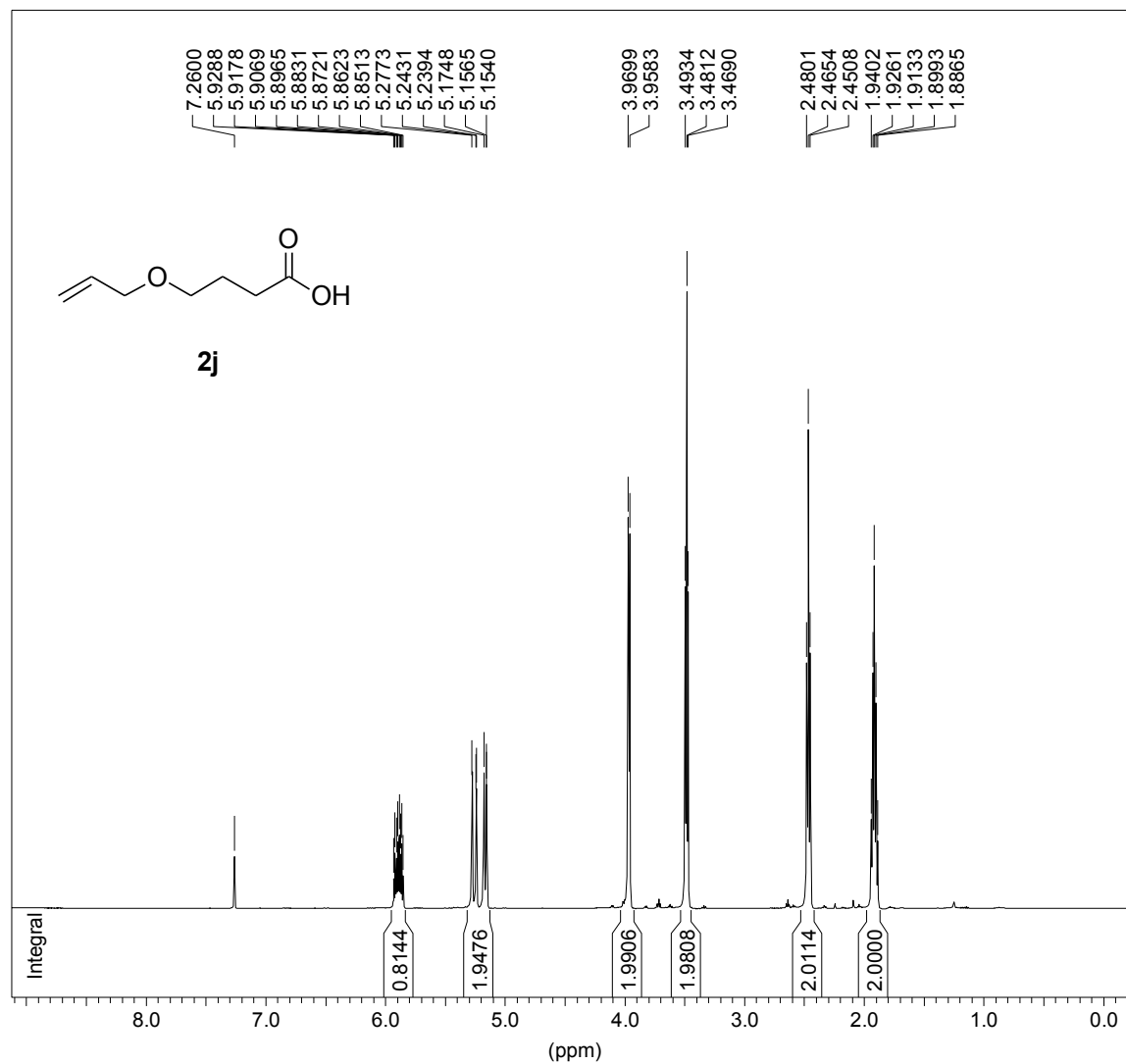
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

8-0b ether-acid substrate pure



*** Current Data Parameters ***

NAME : ya0104

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 12

NUCLEUS : off

O1 : 4251.96 Hz

PULPROG : zg

SFO1 : 500.2342520 MHz

SOLVENT : CDCl3

SW : 19.9906 ppm

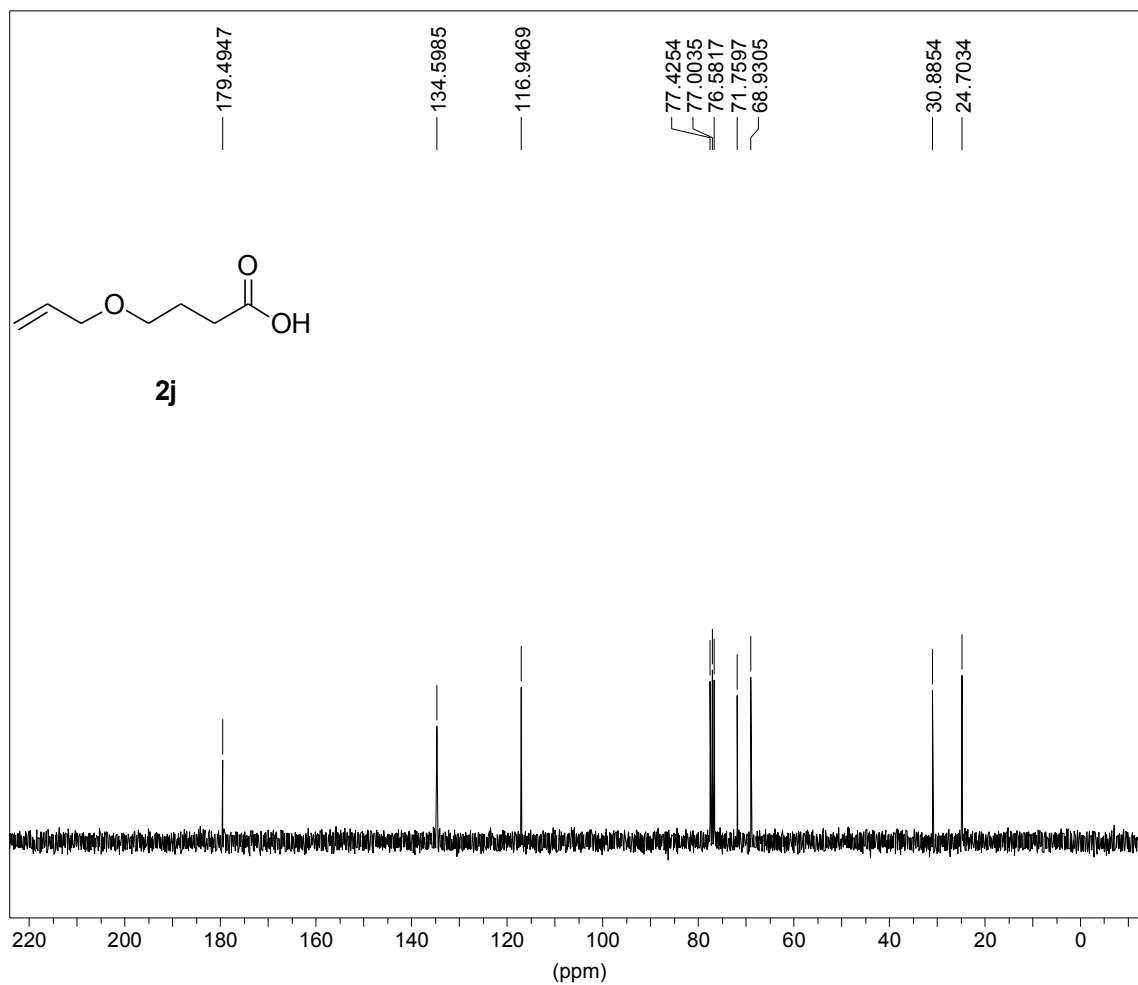
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ja07cya
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

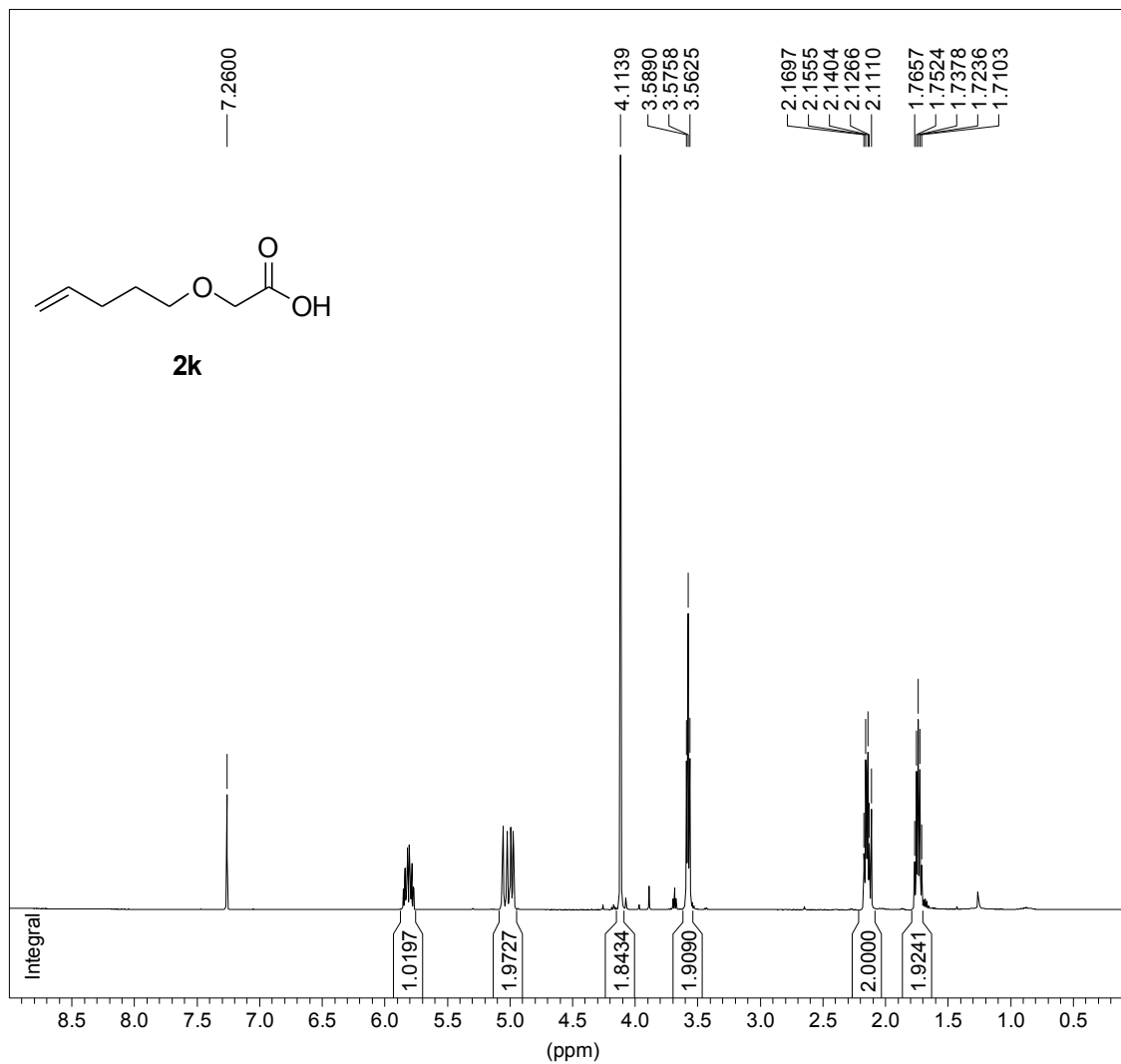
INSTRUM : spect
LOCNUC : 2H
NS : 49
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
SW : 238.2968 ppm
TD : 32768

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

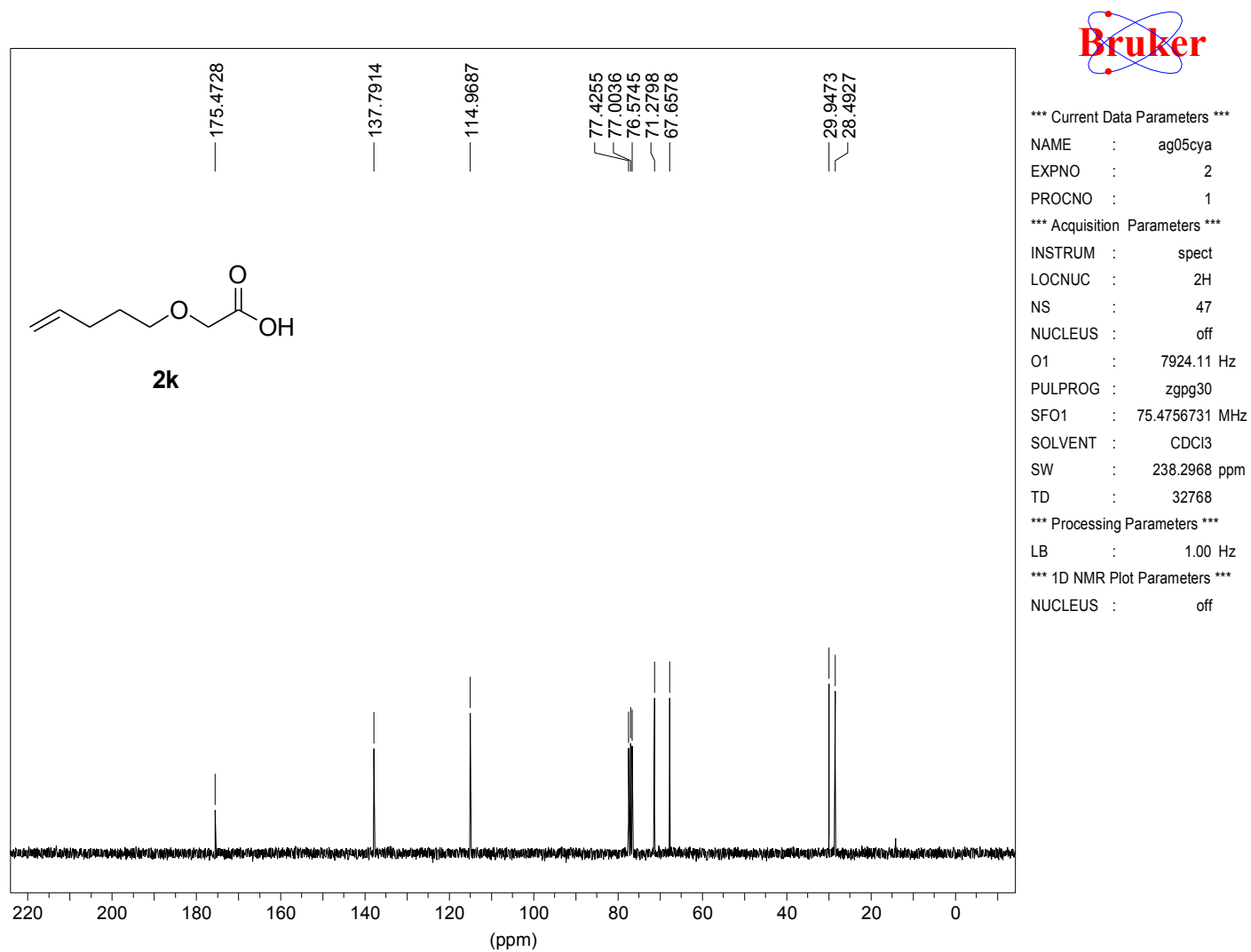
NAME : ya1207
 EXPNO : 1
 PROCNO : 1
 *** Acquisition Parameters ***
 INSTRUM : spect
 LOCNUC : 2H
 NS : 12
 NUCLEUS : off
 O1 : 2751.27 Hz
 PULPROG : zg
 SFO1 : 500.2327513 MHz
 SOLVENT : CDCl3
 SW : 15.0080 ppm
 TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



S40



*** Current Data Parameters ***

NAME : ag05cya
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

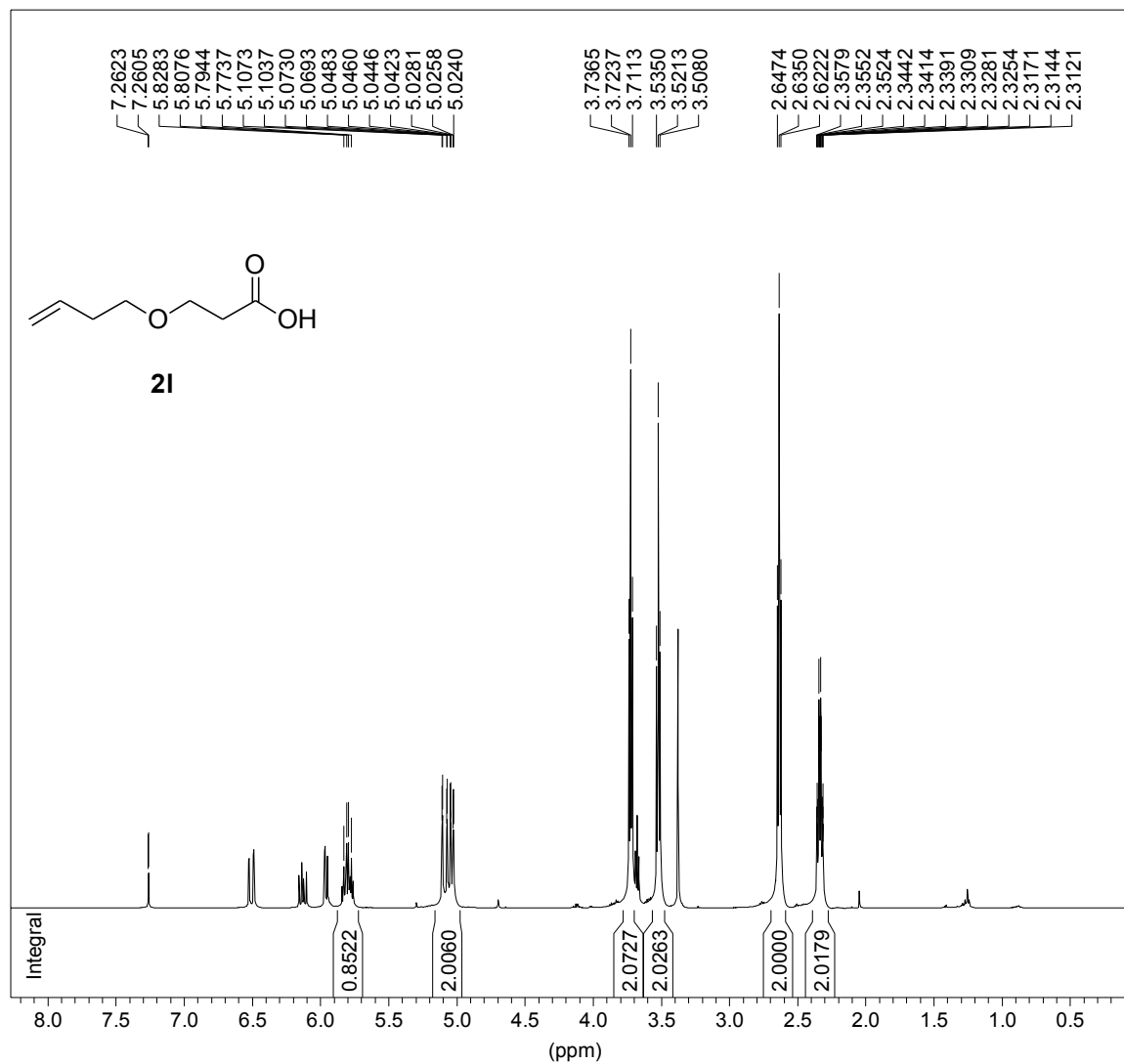
INSTRUM : spect
LOCNUC : 2H
NS : 47
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
SW : 238.2968 ppm
TD : 32768

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0510b

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 24

NUCLEUS : off

O1 : 2751.27 Hz

PULPROG : zg

SFO1 : 500.2327513 MHz

SOLVENT : CDCl₃

SW : 15.0080 ppm

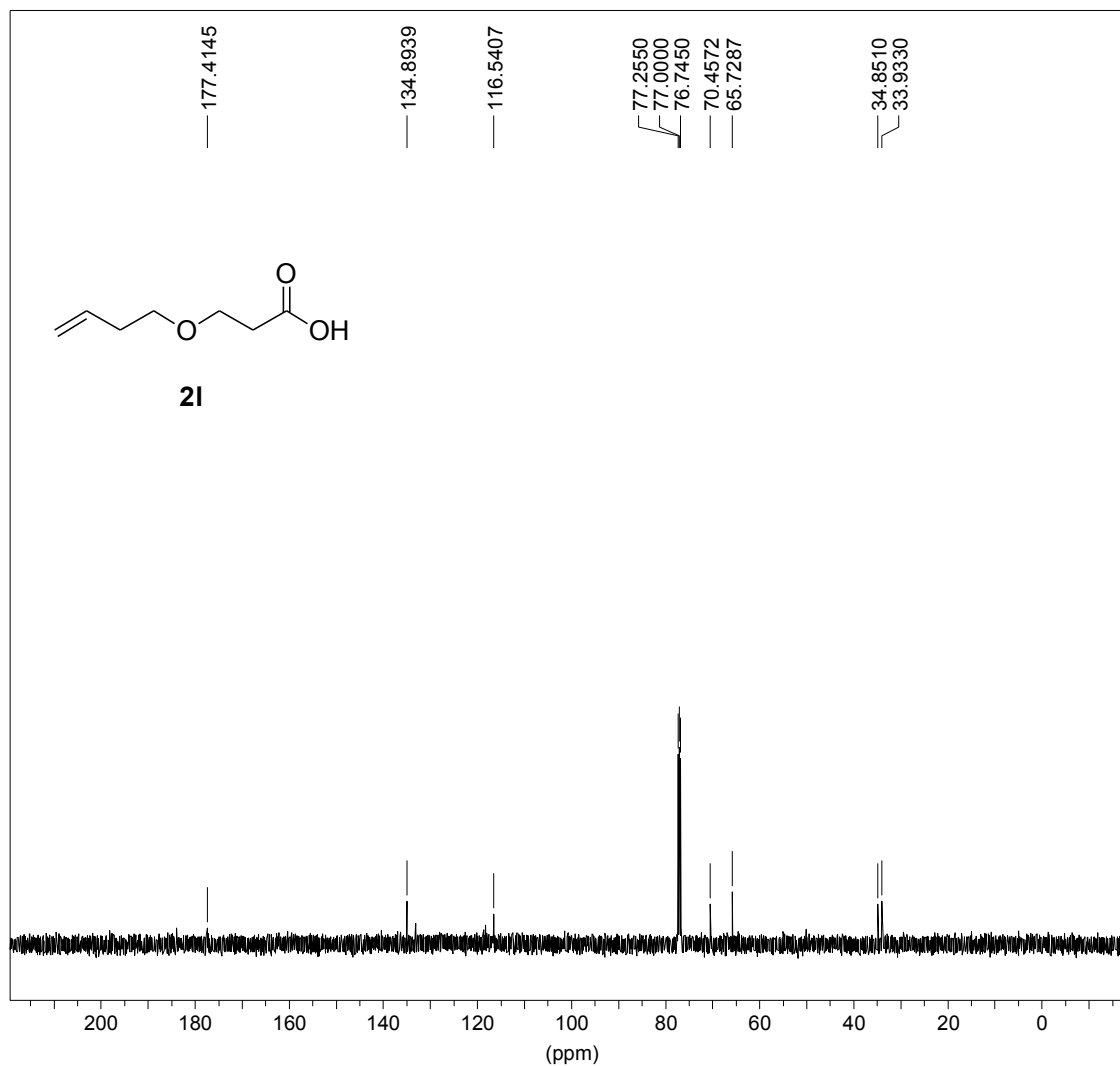
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0510b
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

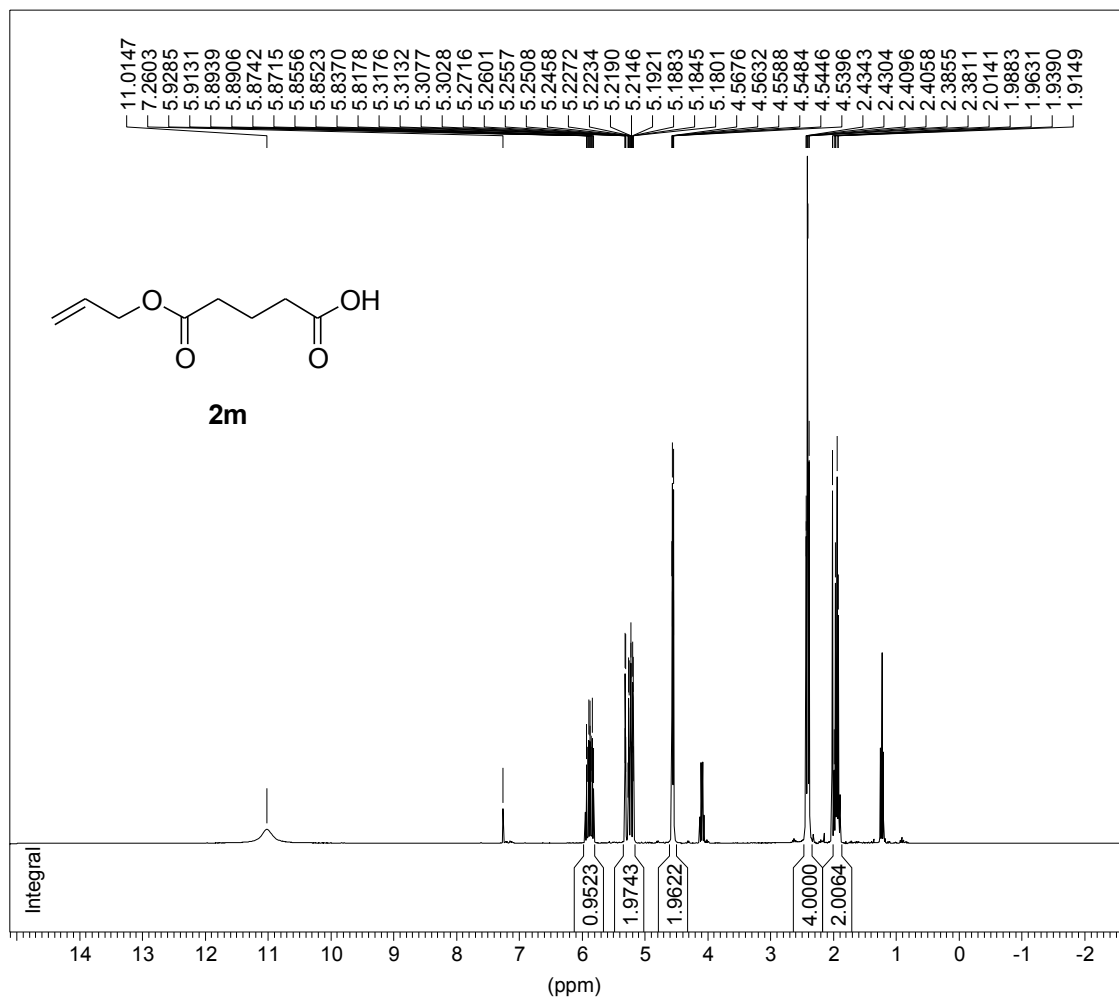
INSTRUM : spect
LOCNUC : 2H
NS : 67
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ag05cya

EXPNO : 5

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 8

NUCLEUS : off

O1 : 1853.43 Hz

PULPROG : zg30

SFO1 : 300.1318534 MHz

SOLVENT : CDCl3

SW : 17.9519 ppm

TD : 32768

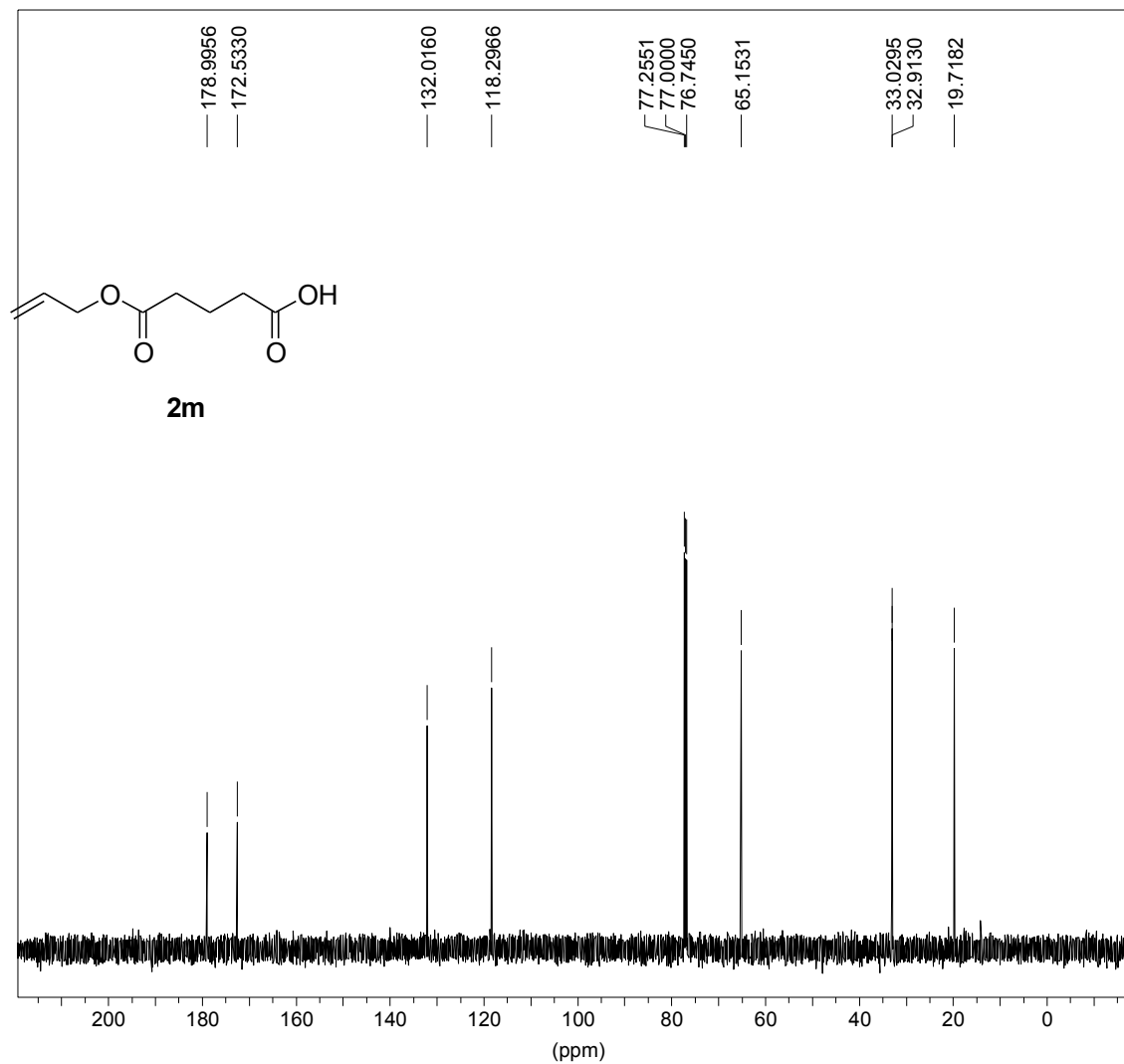
*** Processing Parameters ***

LB : 0.30 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

9 C cmpd



*** Current Data Parameters ***

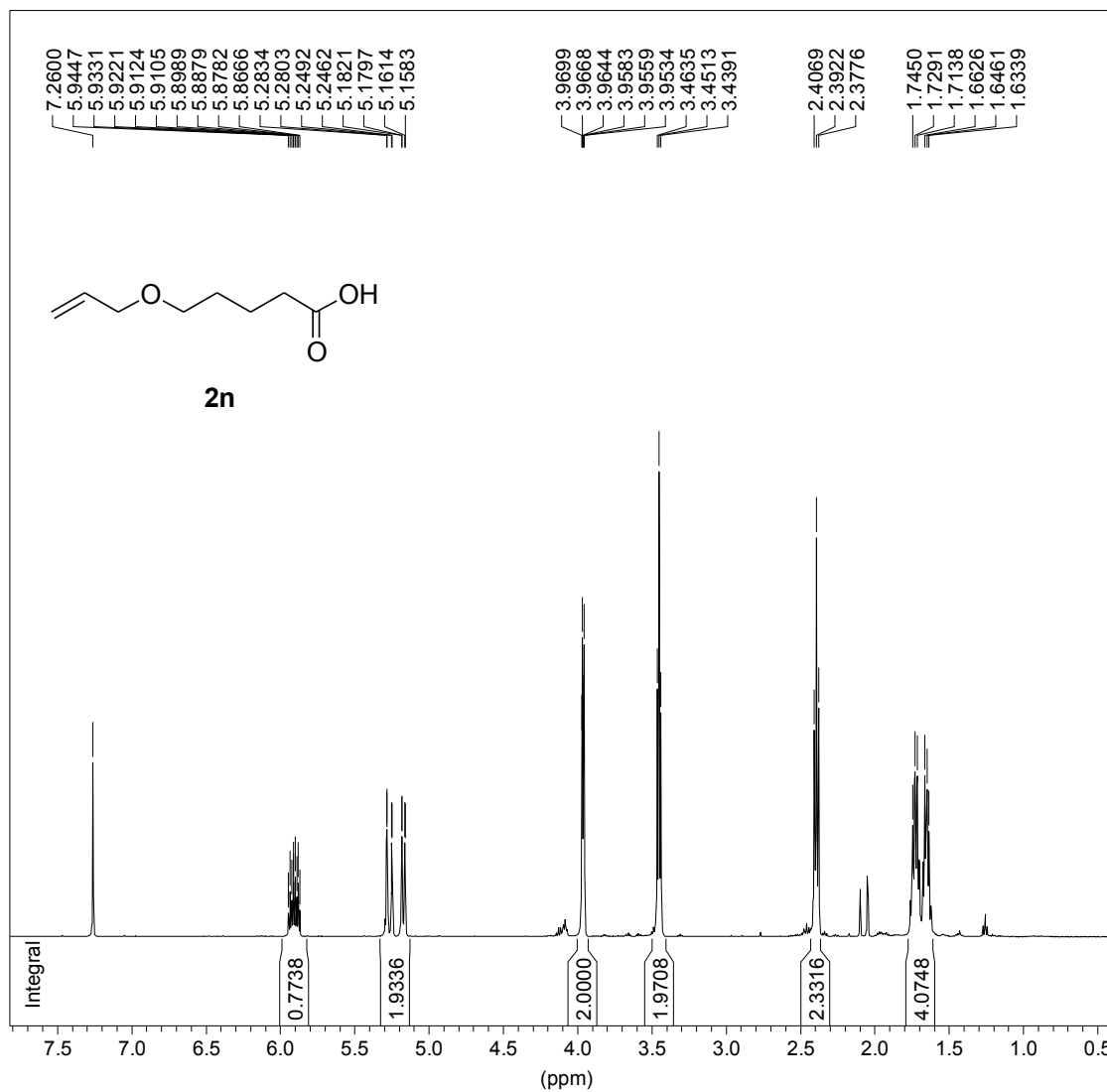
NAME : ya1026
EXPNO : 9
PROCNO : 1
*** Acquisition Parameters ***
INSTRUM : spect
LOCNUC : 2H
NS : 46
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0324
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

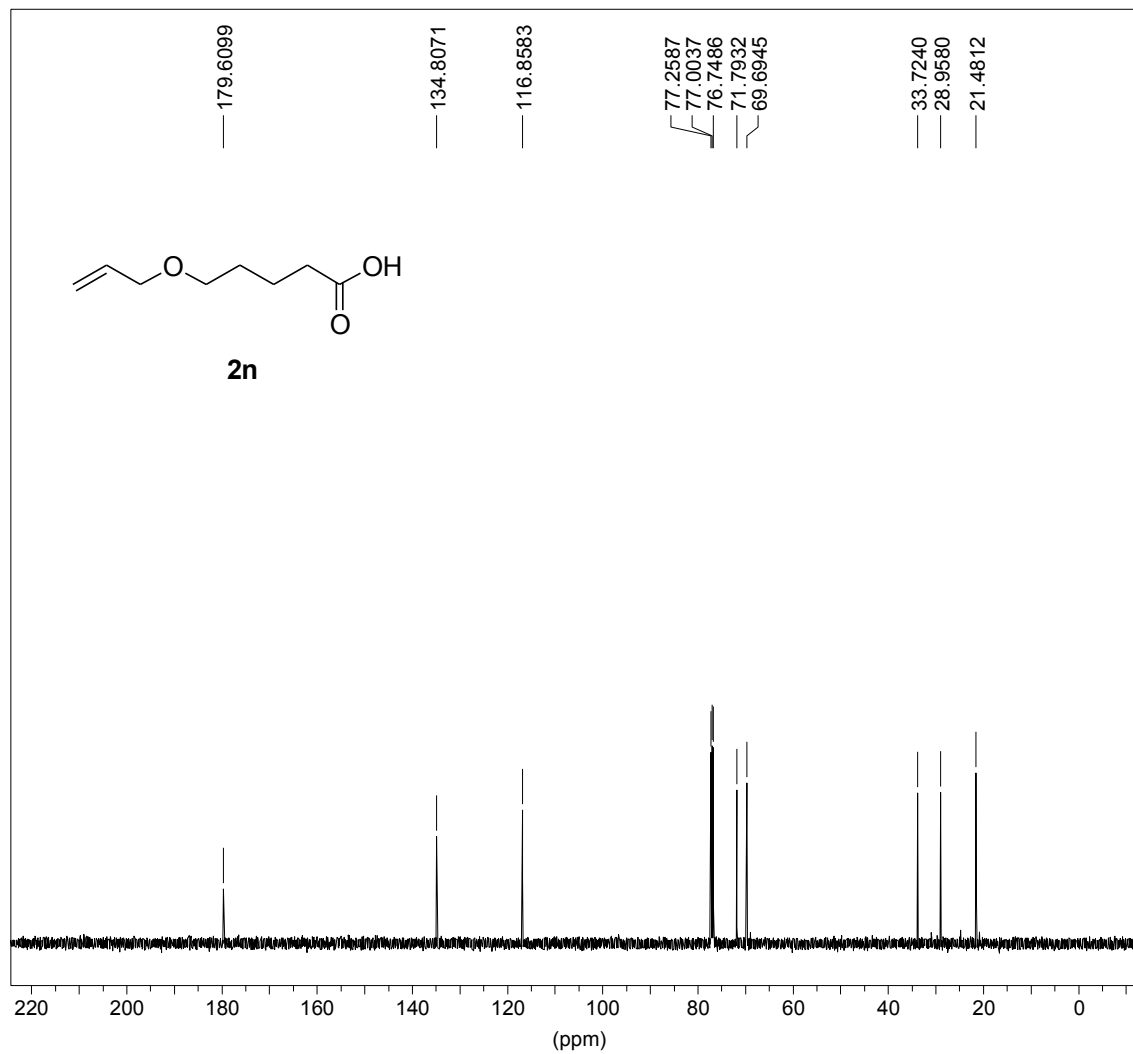
INSTRUM : spect
LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 4251.96 Hz
PULPROG : zg
SFO1 : 500.2342520 MHz
SOLVENT : CDCl3
SW : 19.9906 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : cya0215
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

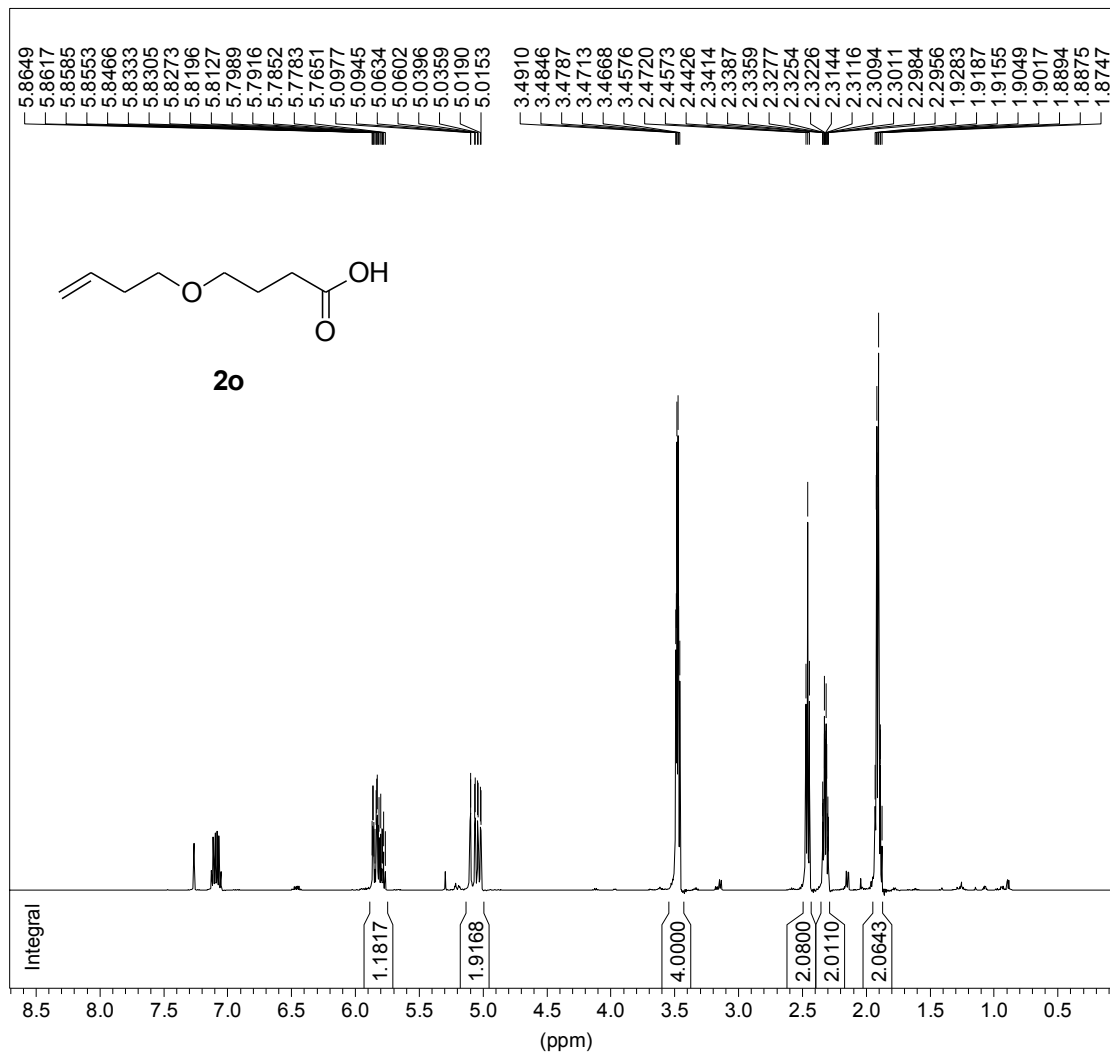
INSTRUM : av500
LOCNUC : 2H
NS : 56
NUCLEUS : off
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0524
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

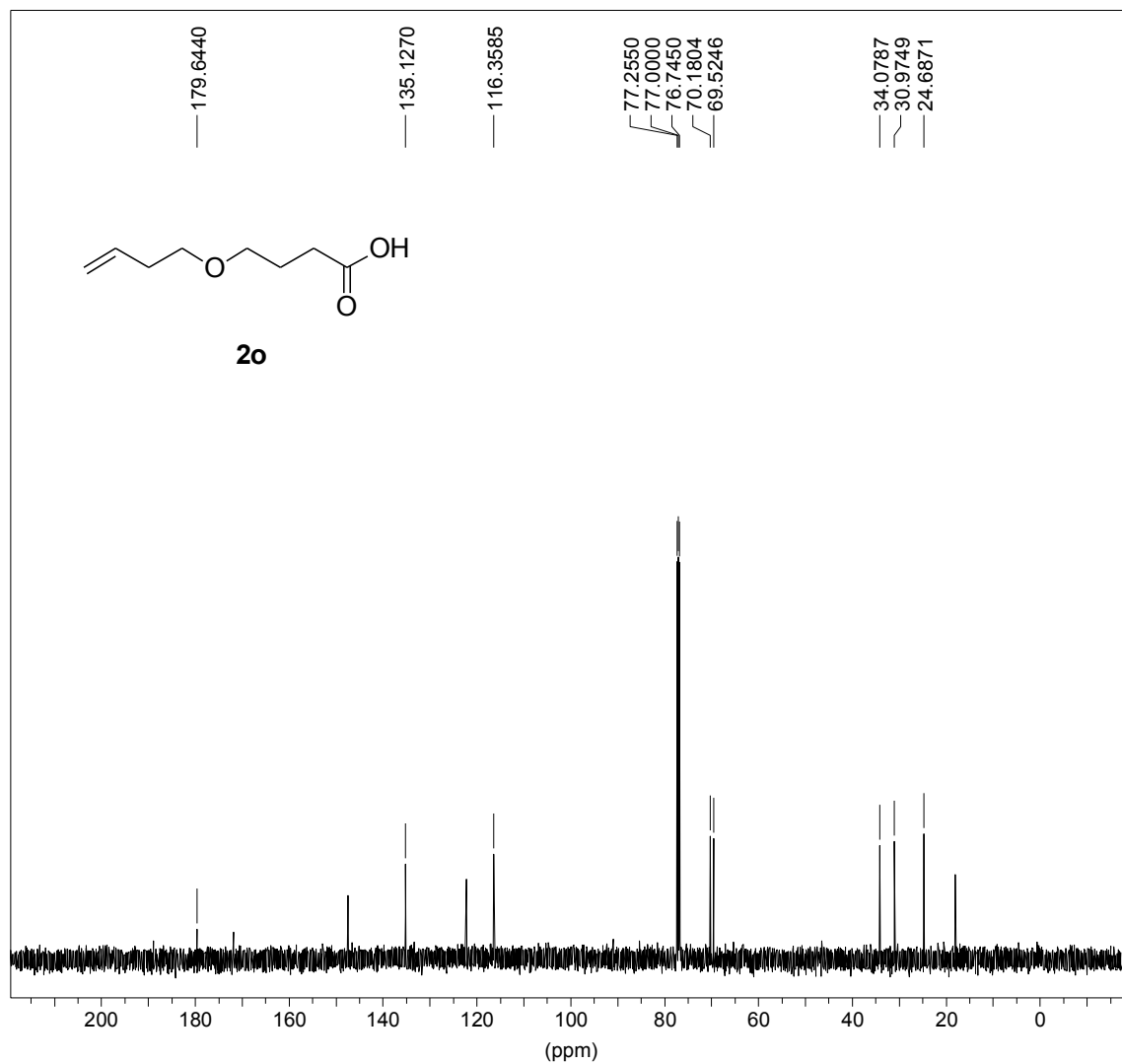
INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0524

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 95

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

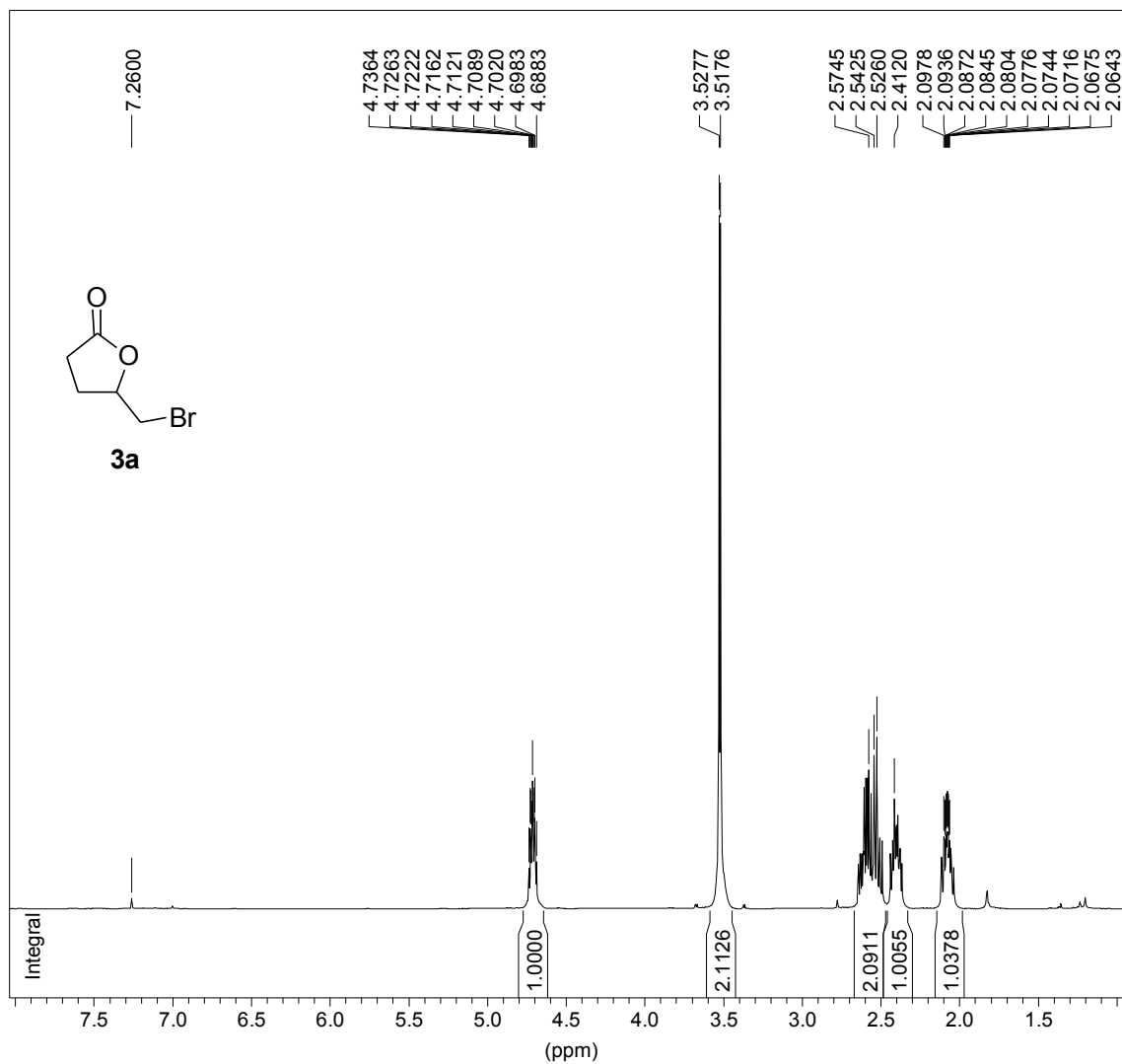
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

5-membered lactone



*** Current Data Parameters ***

NAME : ya0510b

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 24

NUCLEUS : off

O1 : 2751.27 Hz

PULPROG : zg

SFO1 : 500.2327513 MHz

SOLVENT : CDCl3

SW : 15.0080 ppm

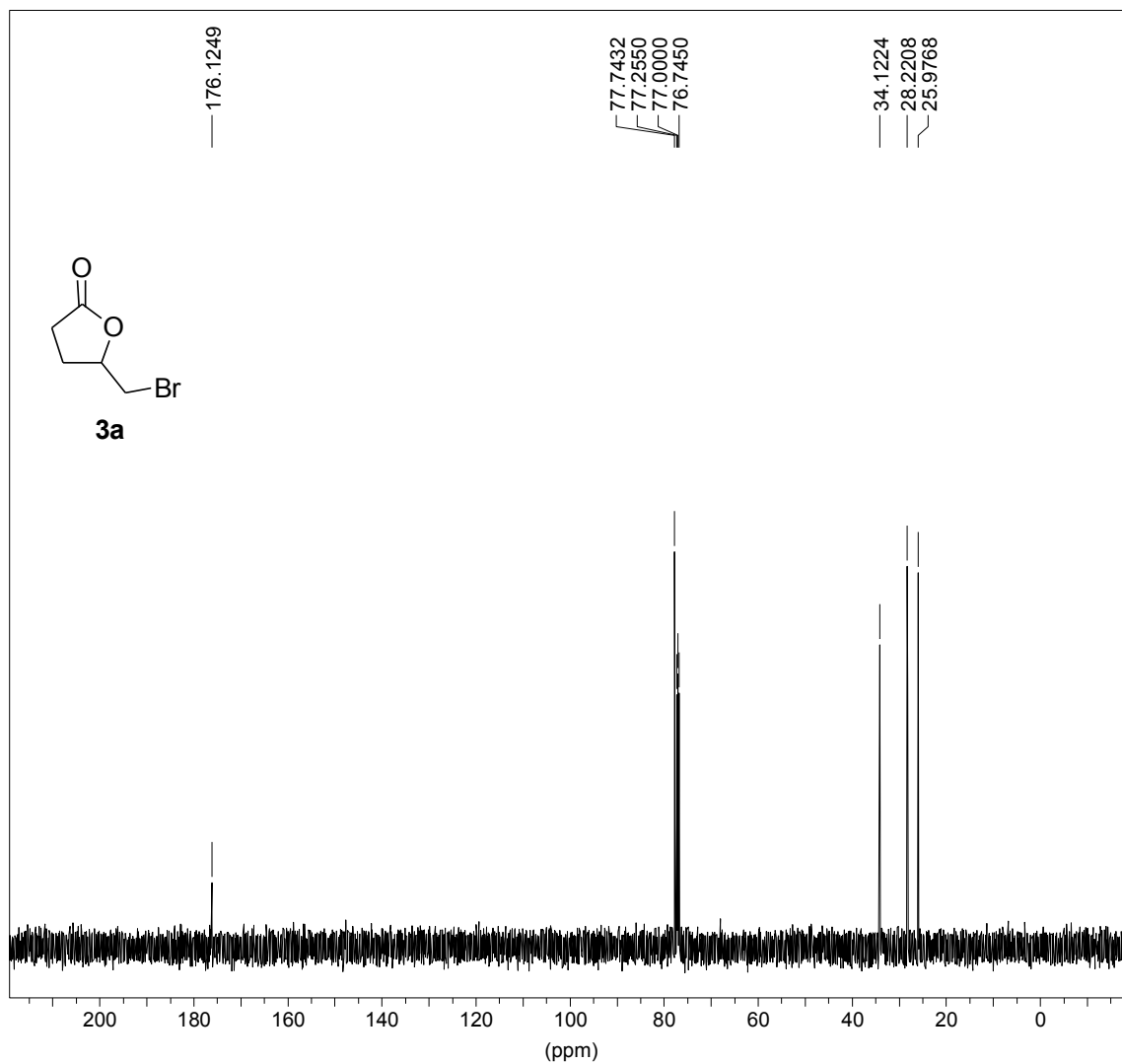
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0510b
EXPNO : 4
PROCNO : 1

*** Acquisition Parameters ***

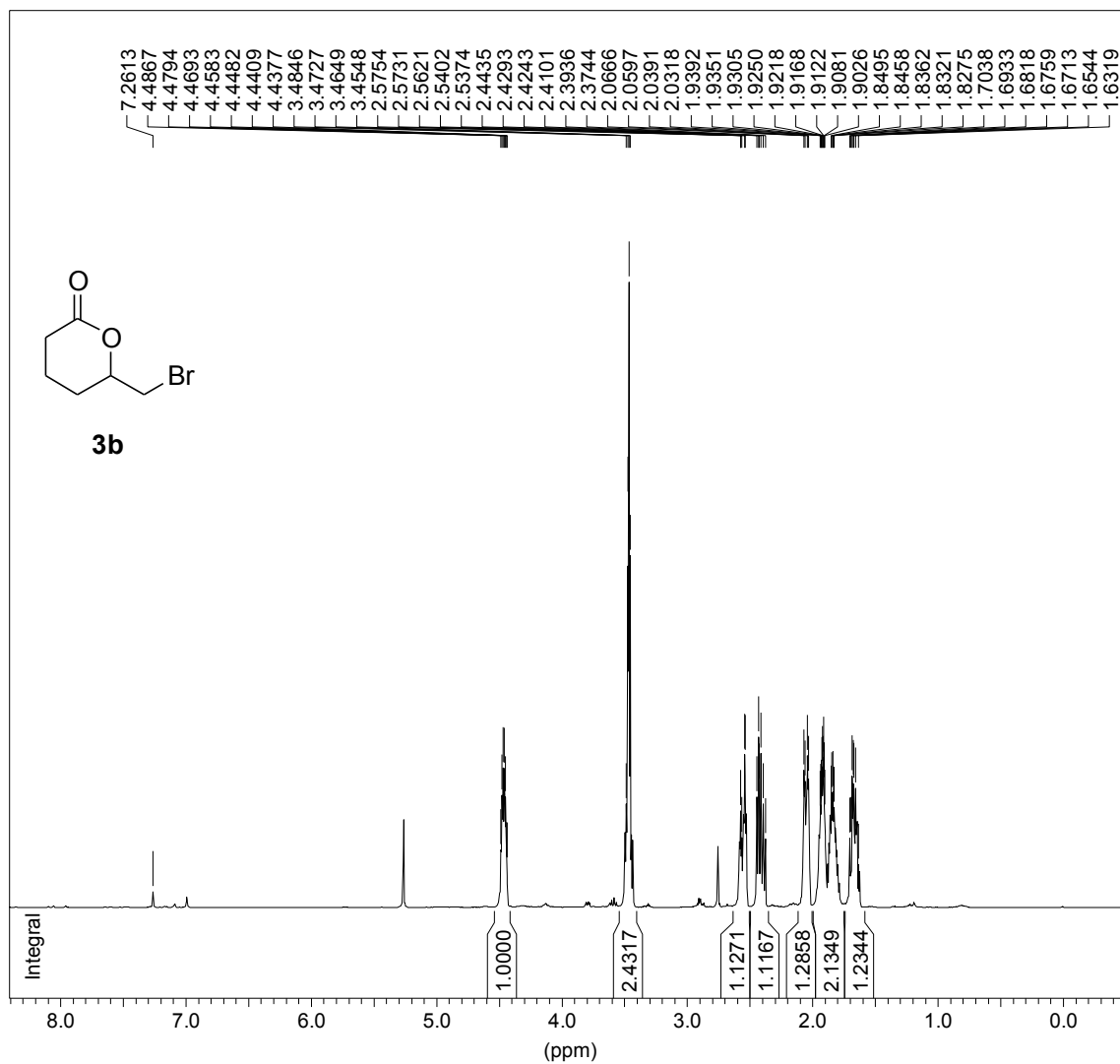
INSTRUM : spect
LOCNUC : 2H
NS : 22
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0513
EXPNO : 4
PROCNO : 1

*** Acquisition Parameters ***

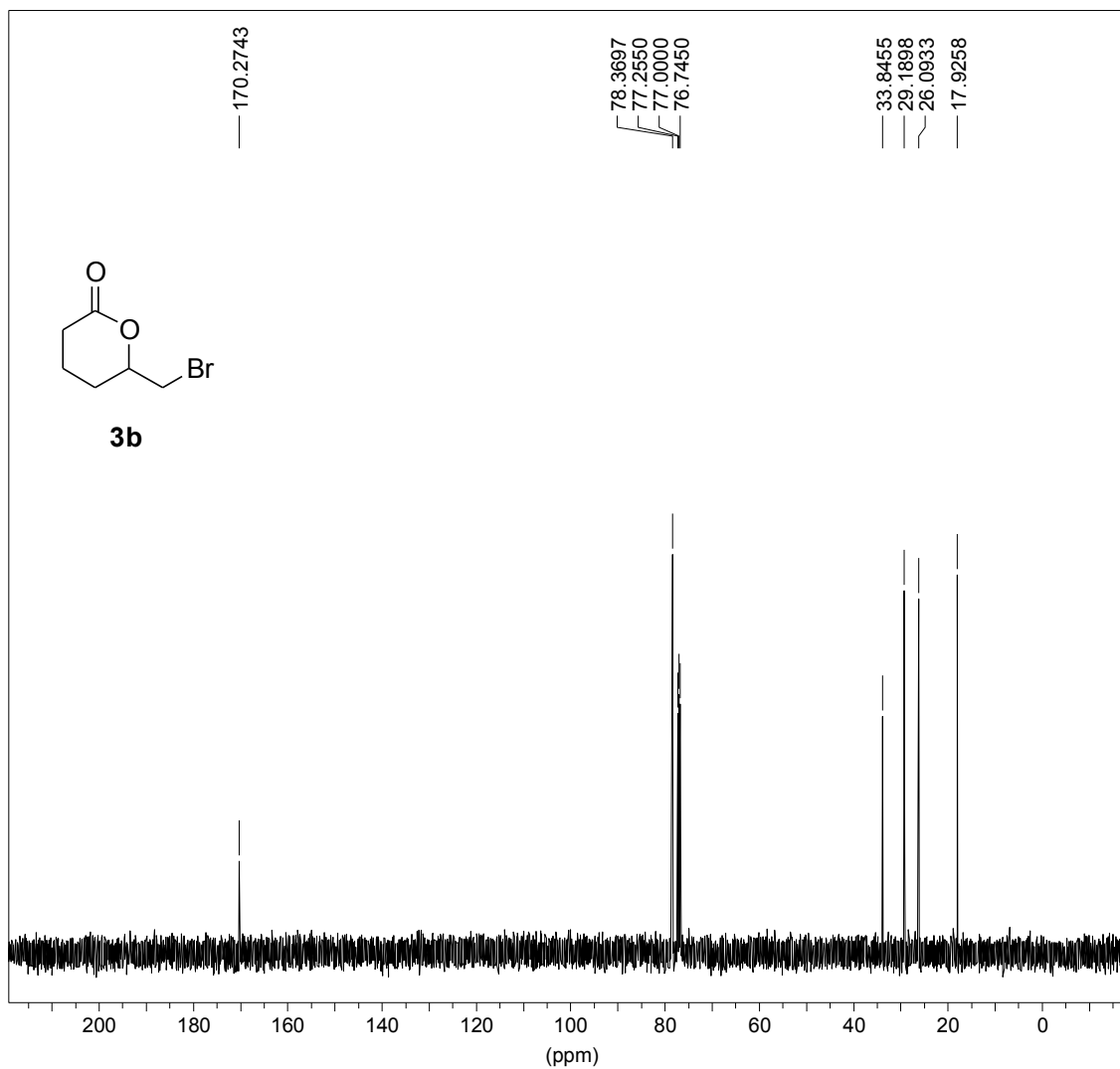
INSTRUM : spect
LOCNUC : 2H
NS : 16
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0513
EXPNO : 5
PROCNO : 1

*** Acquisition Parameters ***

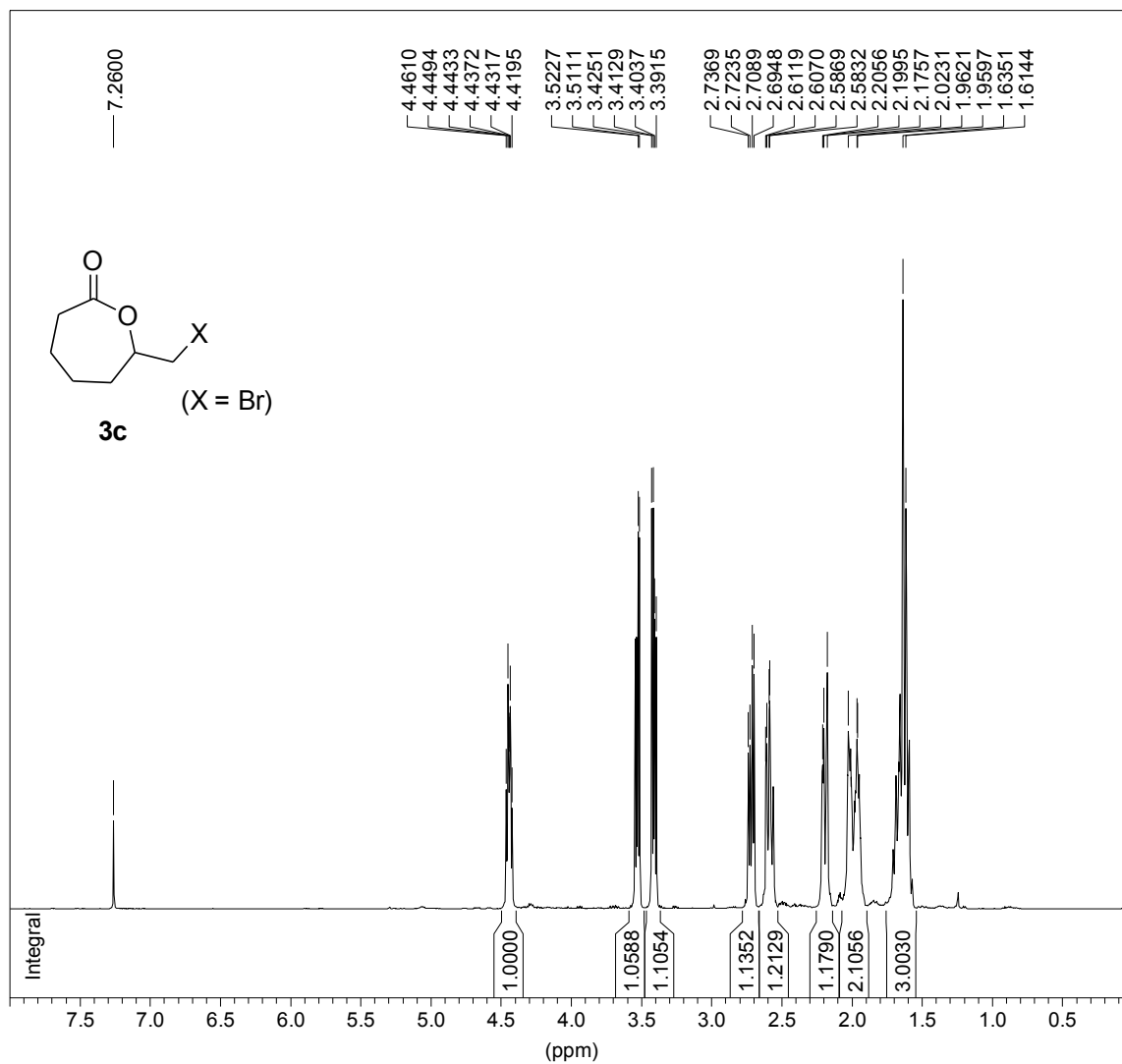
INSTRUM : spect
LOCNUC : 2H
NS : 17
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

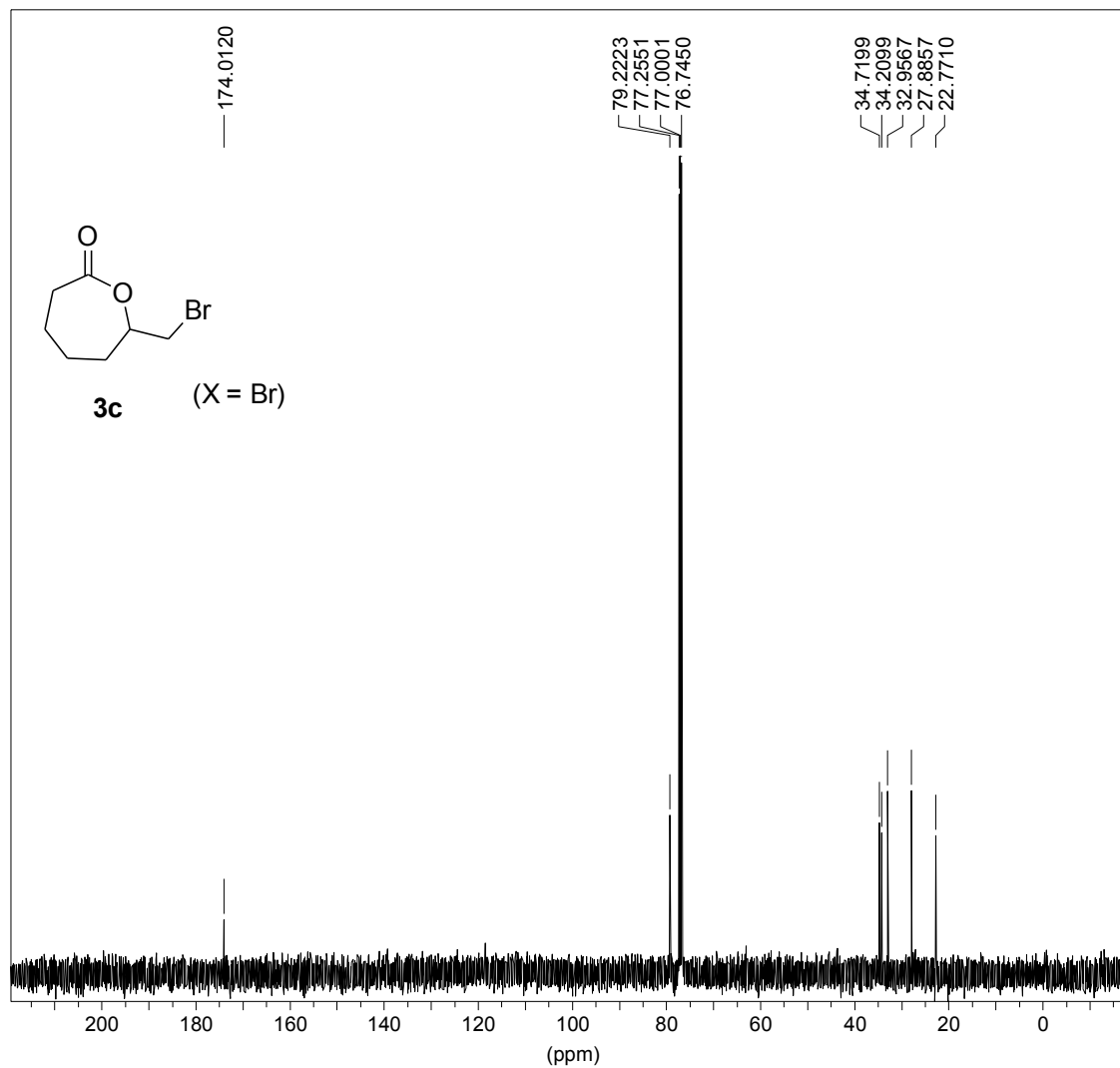
NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0303
 EXPNO : 1
 PROCNO : 1
 *** Acquisition Parameters ***
 INSTRUM : spect
 LOCNUC : 2H
 NS : 24
 NUCLEUS : off
 O1 : 4251.96 Hz
 PULPROG : zg
 SFO1 : 500.2342520 MHz
 SOLVENT : CDCl3
 SW : 19.9906 ppm
 TD : 32768
 *** Processing Parameters ***
 LB : 0.10 Hz
 *** 1D NMR Plot Parameters ***
 NUCLEUS : off

7-membered ring (Br)



*** Current Data Parameters ***

NAME : ya0303
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

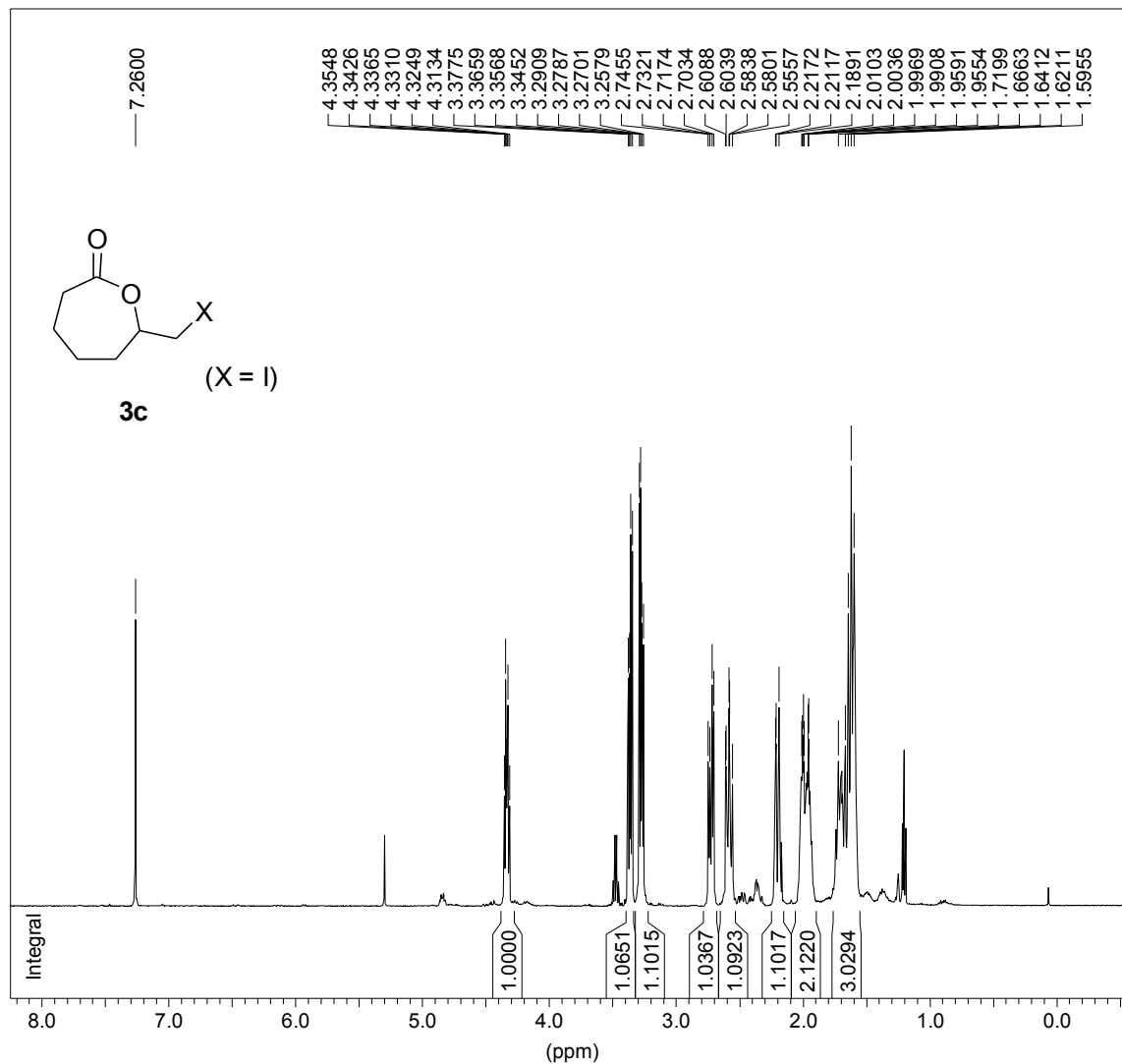
INSTRUM : spect
LOCNUC : 2H
NS : 127
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0303

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 16

NUCLEUS : off

O1 : 4251.96 Hz

PULPROG : zg

SFO1 : 500.2342520 MHz

SOLVENT : CDCl₃

SW : 19.9906 ppm

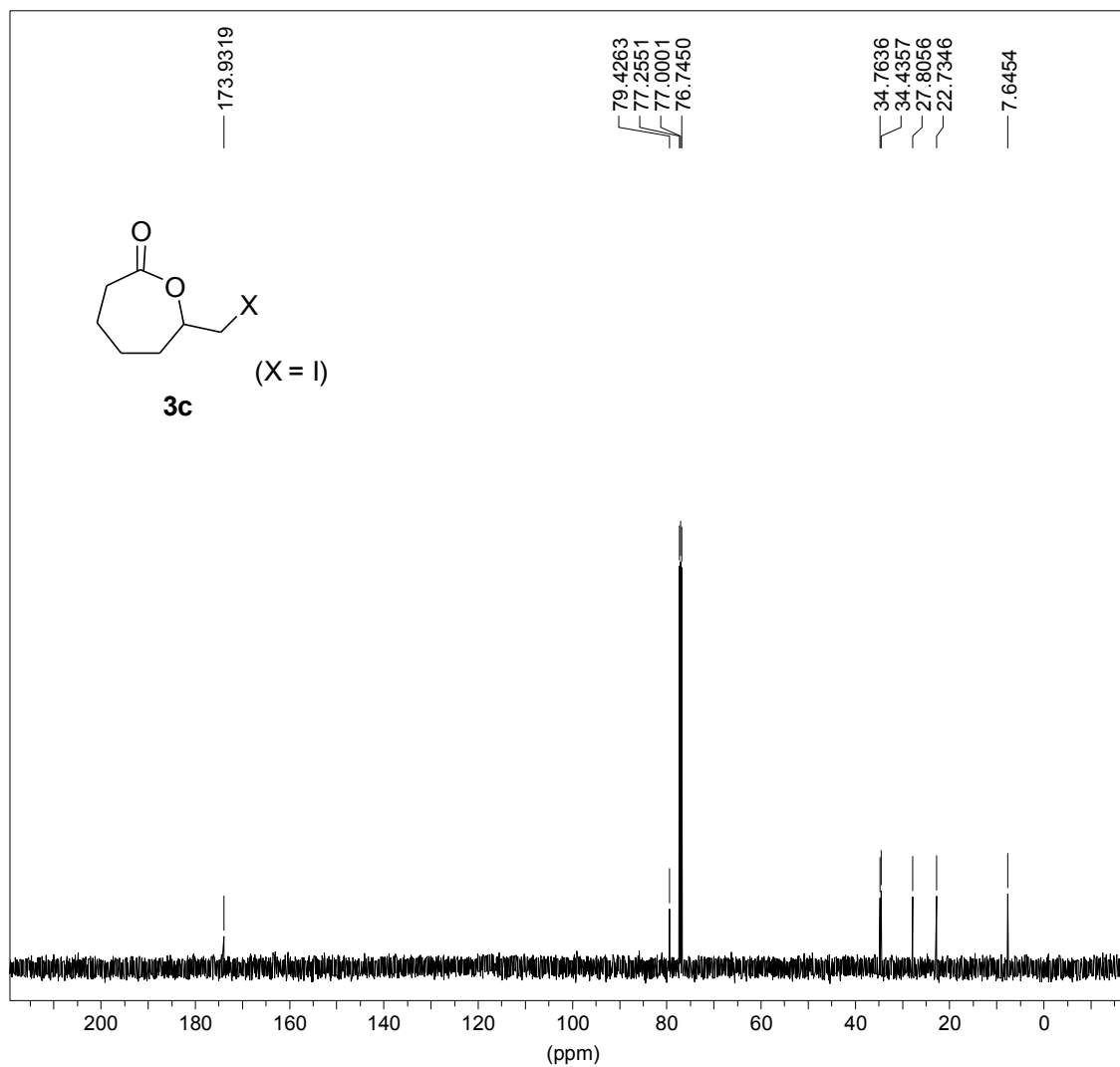
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0304
EXPNO : 6
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 89
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

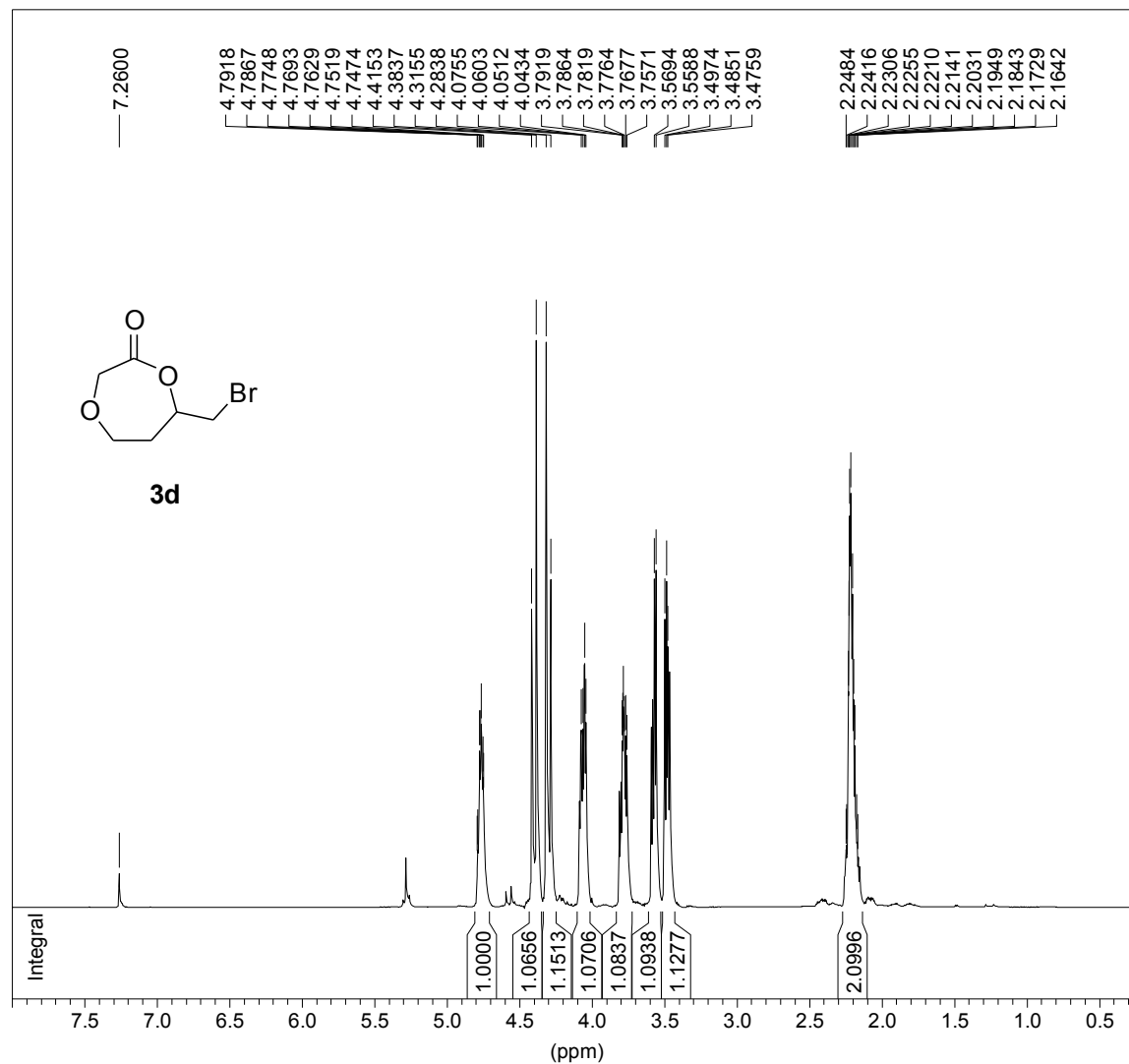
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

7-0b lactone (7-membered ether-bromolactone)



*** Current Data Parameters ***

NAME : ya0524
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

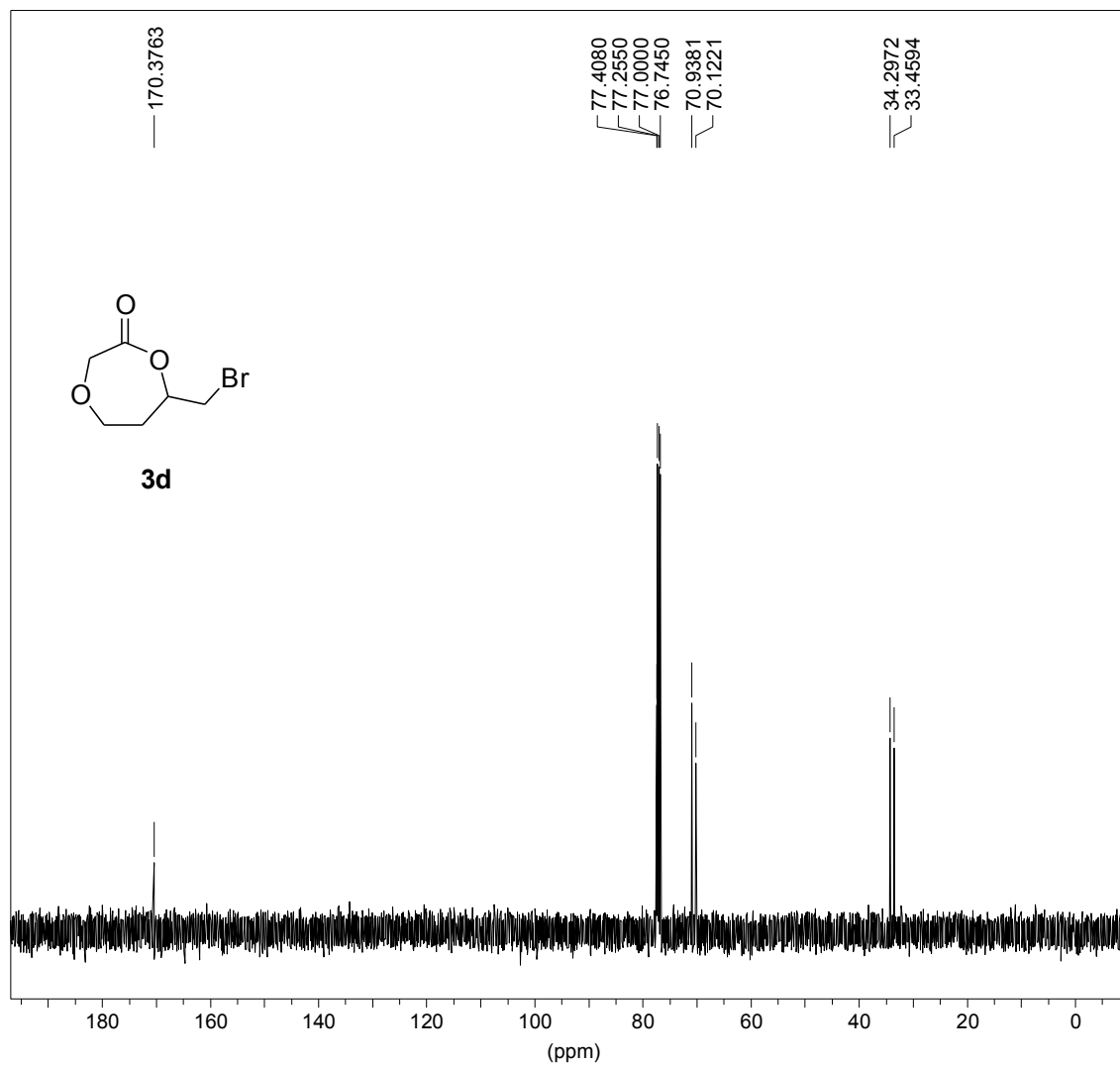
*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

7-Ob lactone (7-membered ether-lactone)



*** Current Data Parameters ***

NAME : ya0524

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 33

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

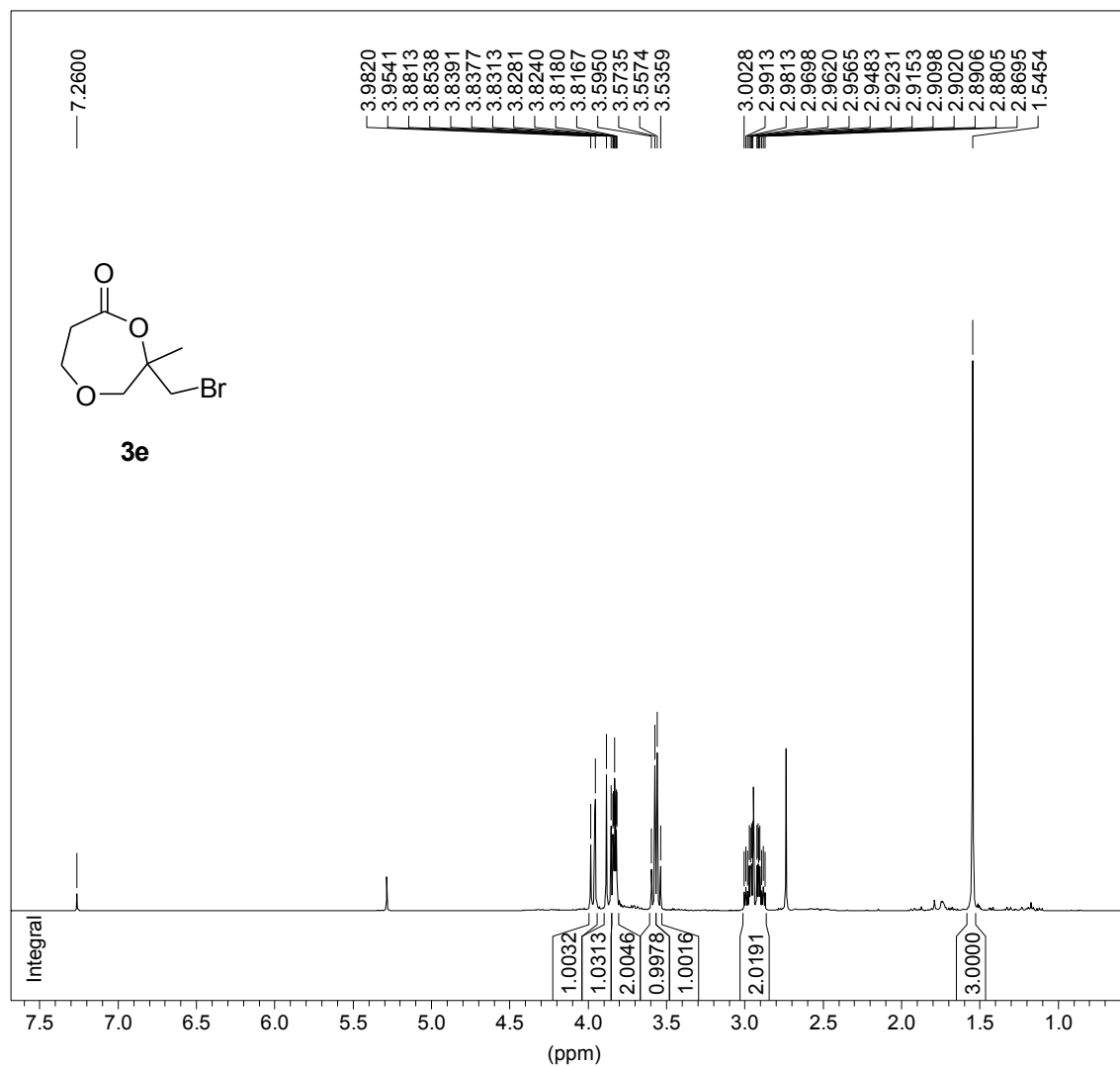
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

S58



*** Current Data Parameters ***

NAME : ya0603

EXPNO : 6

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 24

NUCLEUS : off

O1 : 2751.27 Hz

PULPROG : zg

SFO1 : 500.2327513 MHz

SOLVENT : CDCl₃

SW : 15.0080 ppm

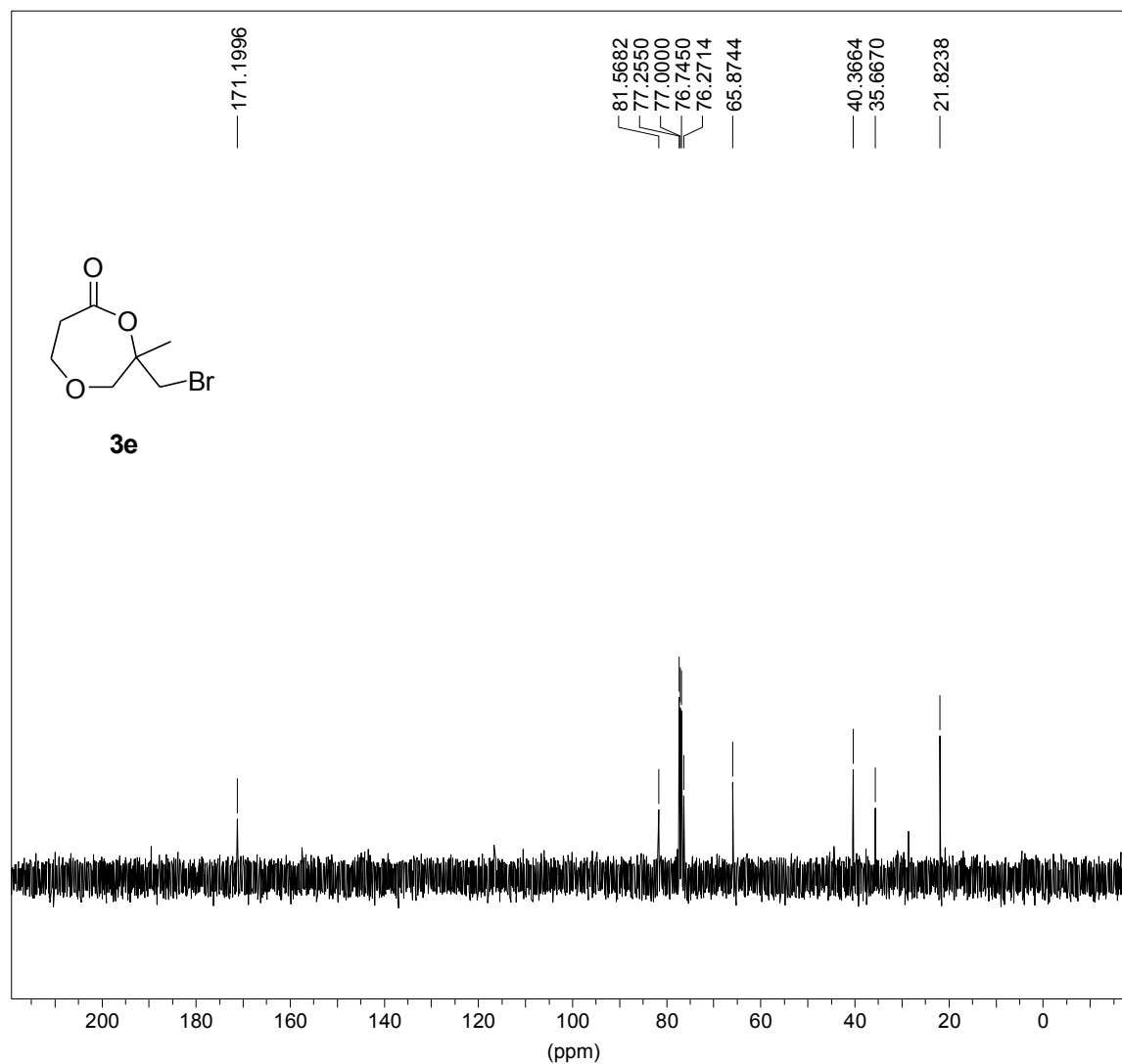
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0603

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 35

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

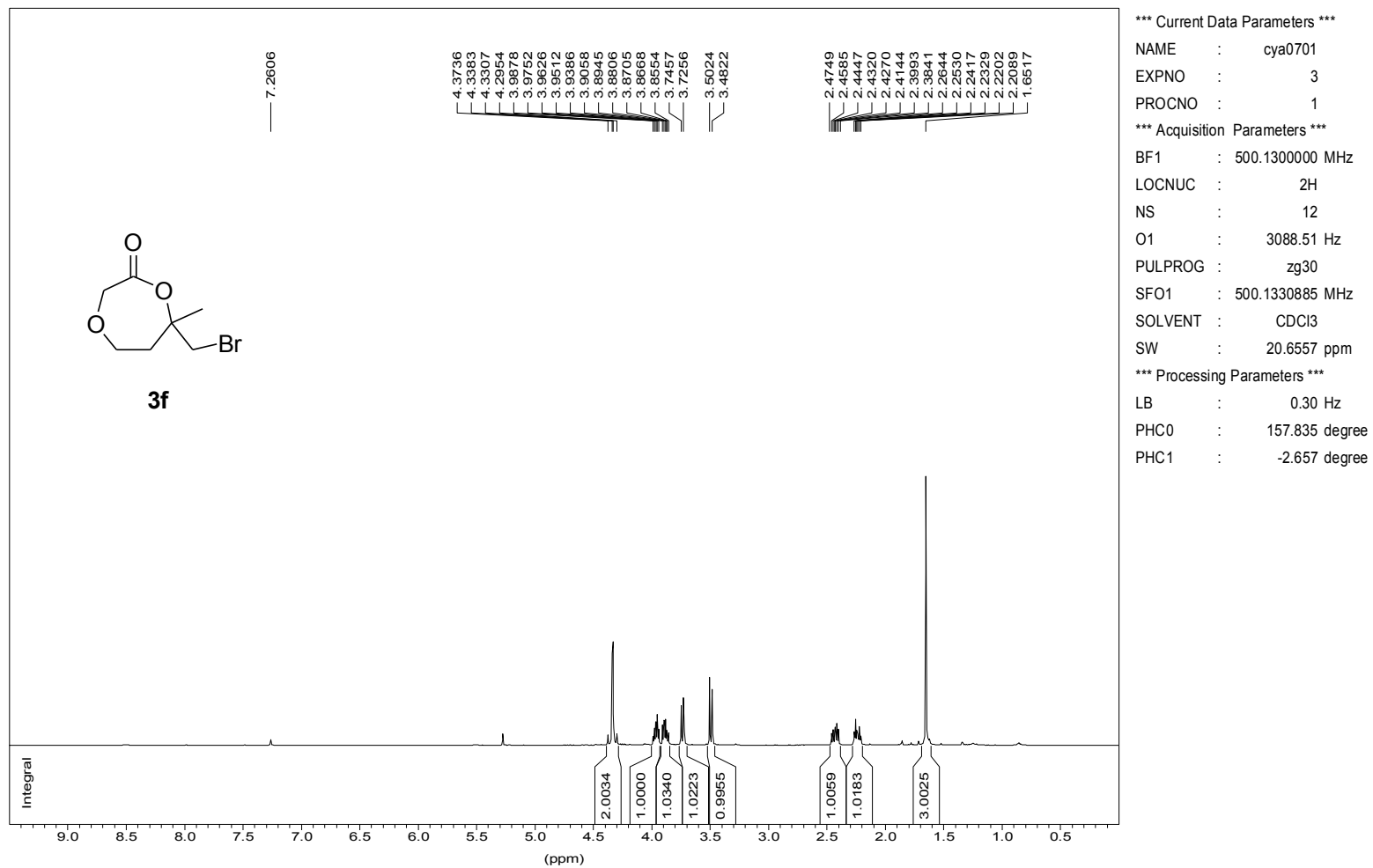
*** Processing Parameters ***

LB : 1.00 Hz

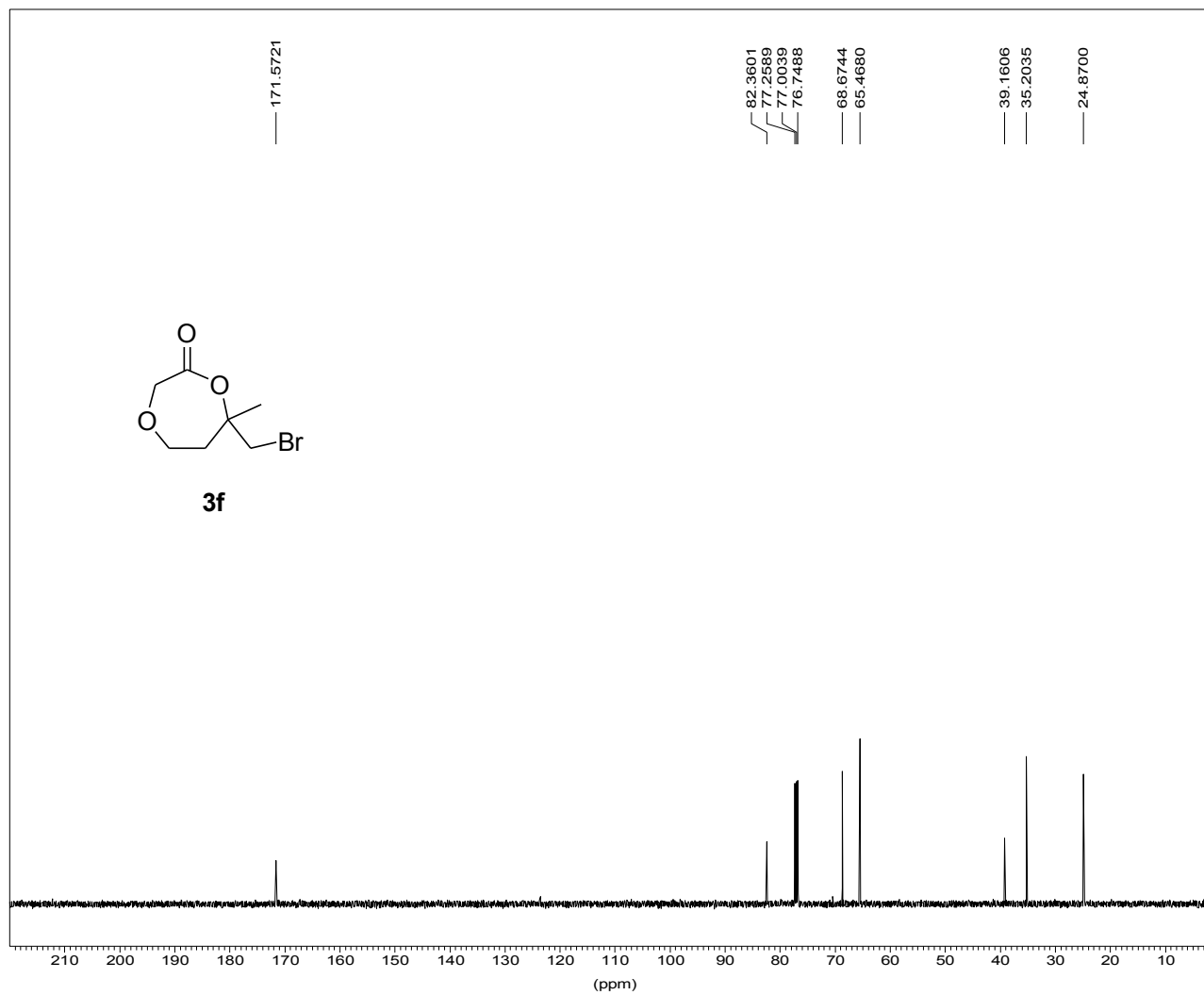
*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500
7-Me 2 lactam



¹³C AMX500



*** Current Data Parameters ***

NAME : cya0701
EXPNO : 4
PROCNO : 1

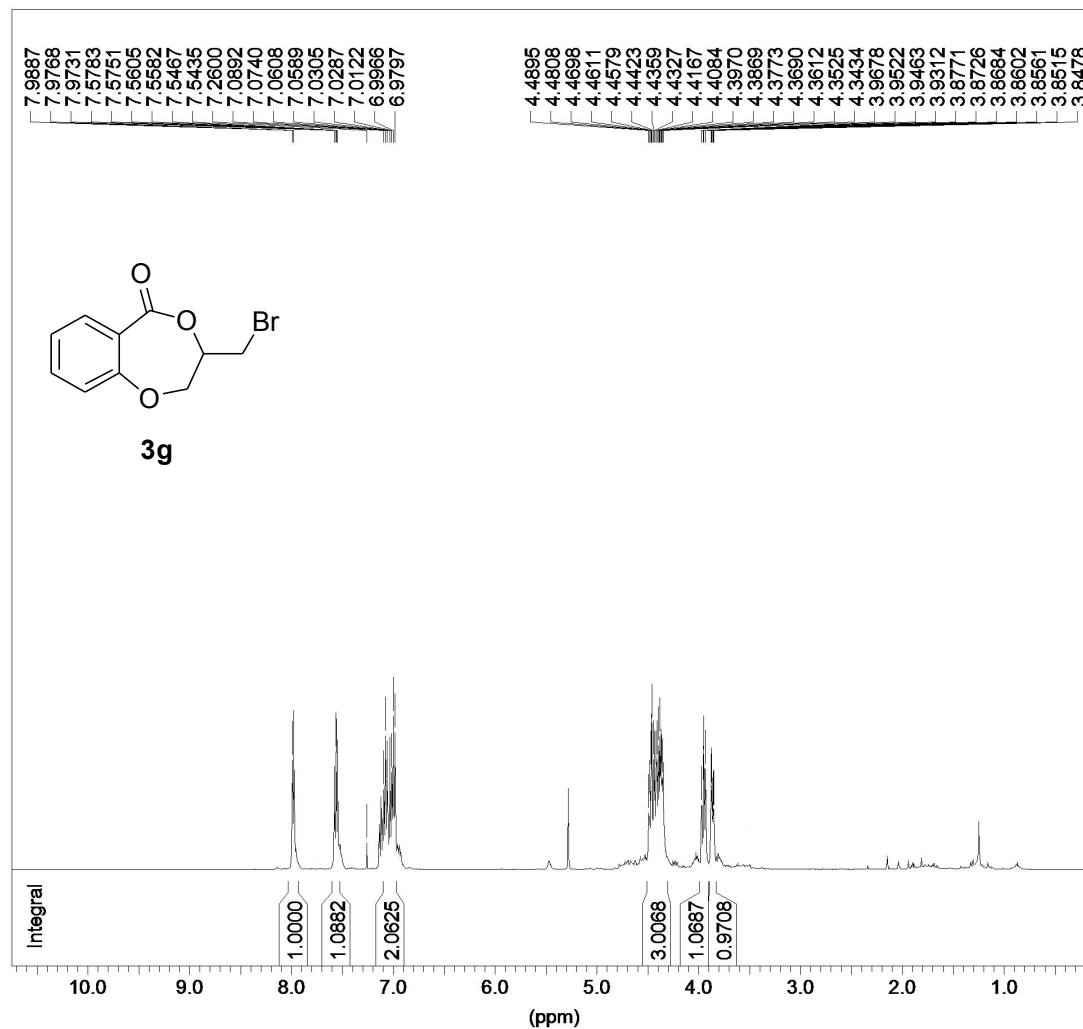
*** Acquisition Parameters ***

BF1 : 125.7577890 MHz
LOCNUC : 2H
NS : 11
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl₃
SW : 238.7675 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 18.494 degree
PHC1 : 31.757 degree

phenyl-lactone (7)



*** Current Data Parameters ***

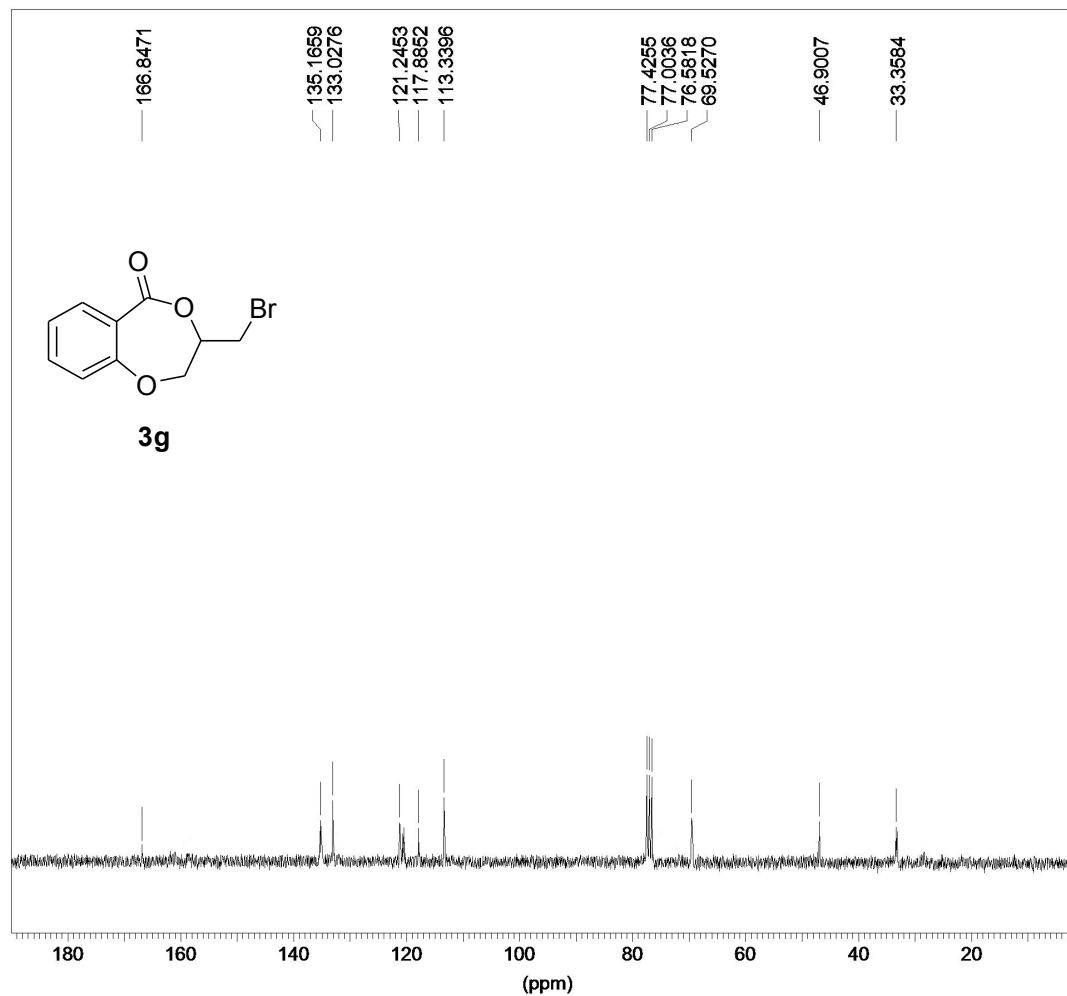
NAME : ya0610
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
INSTRUM : spect
LOCNUC : 2H
NS : 8
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ju13cya
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 199
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
SW : 238.2968 ppm
TD : 32768

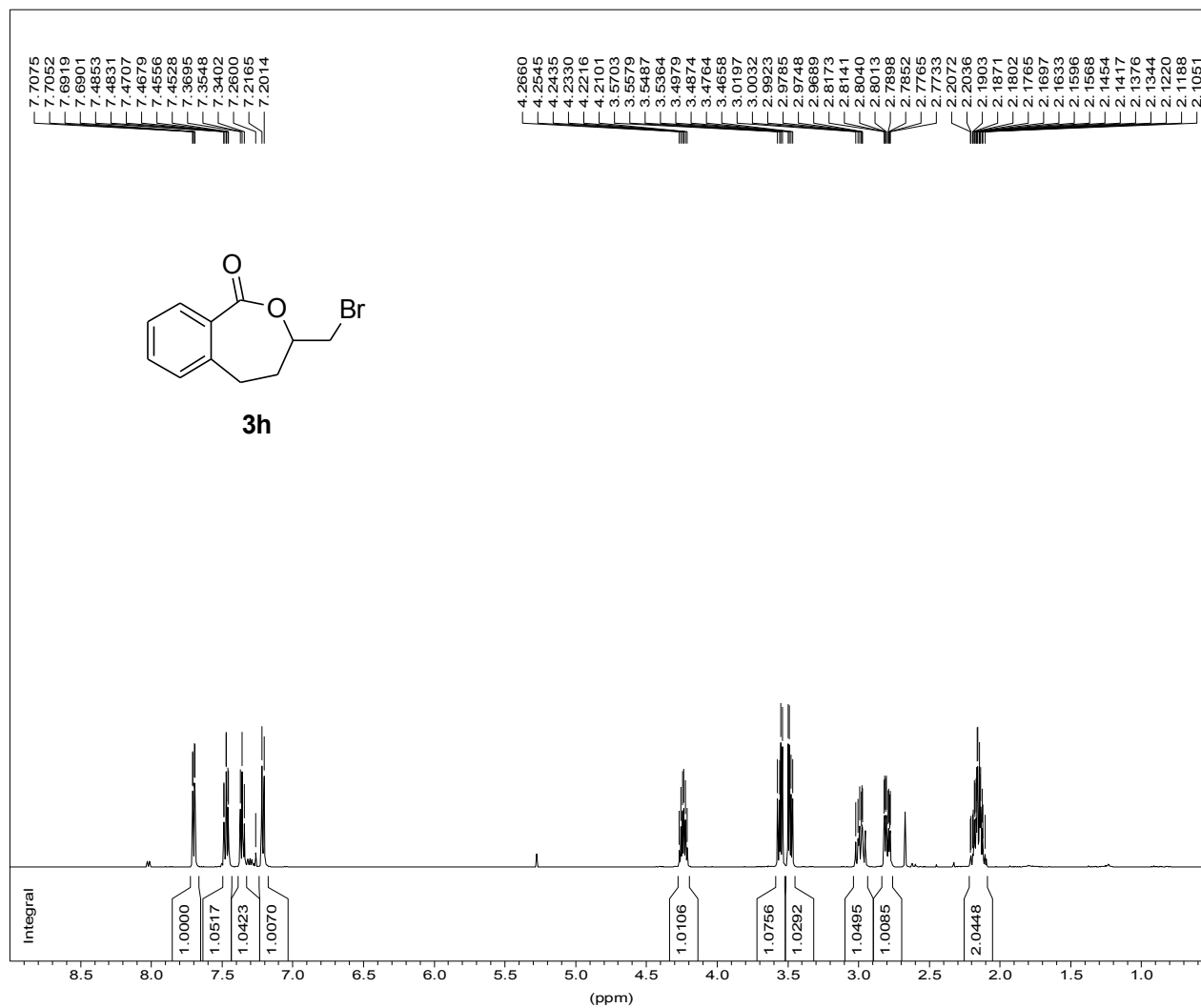
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

Ph 7-0 lactone



*** Current Data Parameters ***

NAME : ya1018
EXPNO : 1
PROCNO : 1

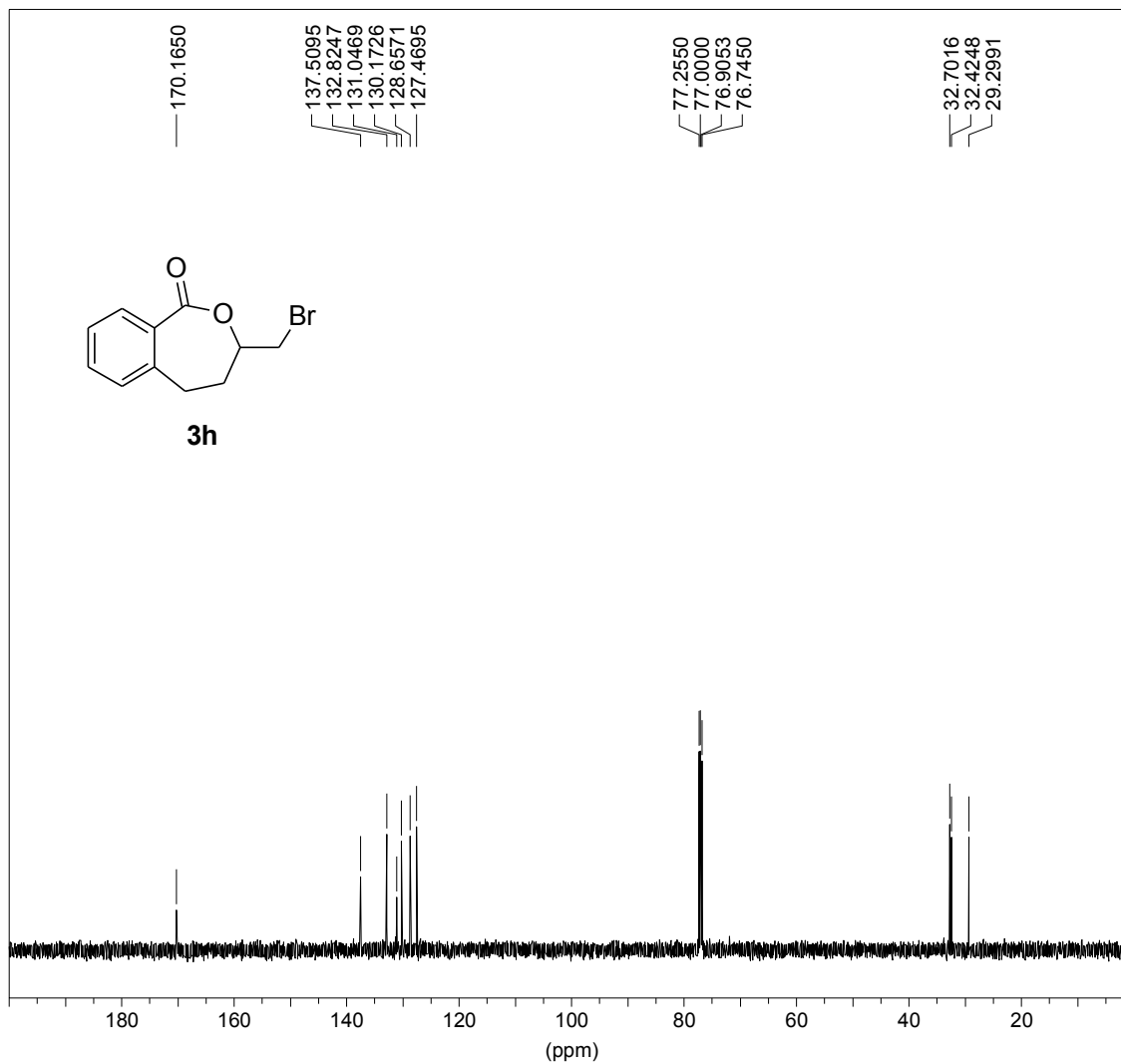
*** Acquisition Parameters ***

BF1 : 500.2300000 MHz
LOCNUC : 2H
NS : 32
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl₃
SW : 15.0080 ppm

*** Processing Parameters ***

LB : 0.10 Hz
PHC0 : 309.027 degree
PHC1 : -12.978 degree

Ph 7-0 lactone



*** Current Data Parameters ***

NAME : ya1018

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 18

NUCLEUS : off

O1 : 12577.84 Hz

PULPROG : zgpg30

SFO1 : 125.7955118 MHz

SOLVENT : CDCl3

SW : 238.7210 ppm

TD : 65536

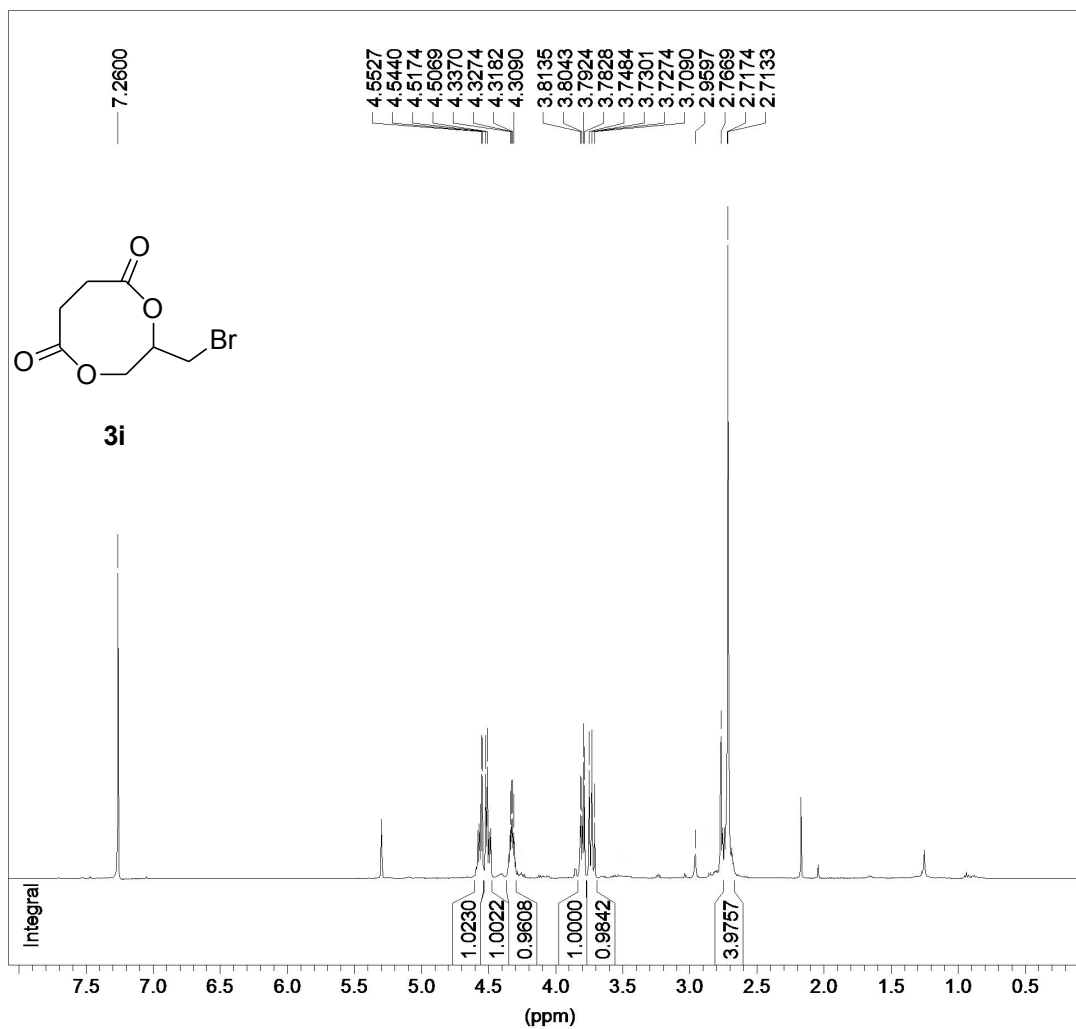
TE : 298.1 K

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya1215b
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

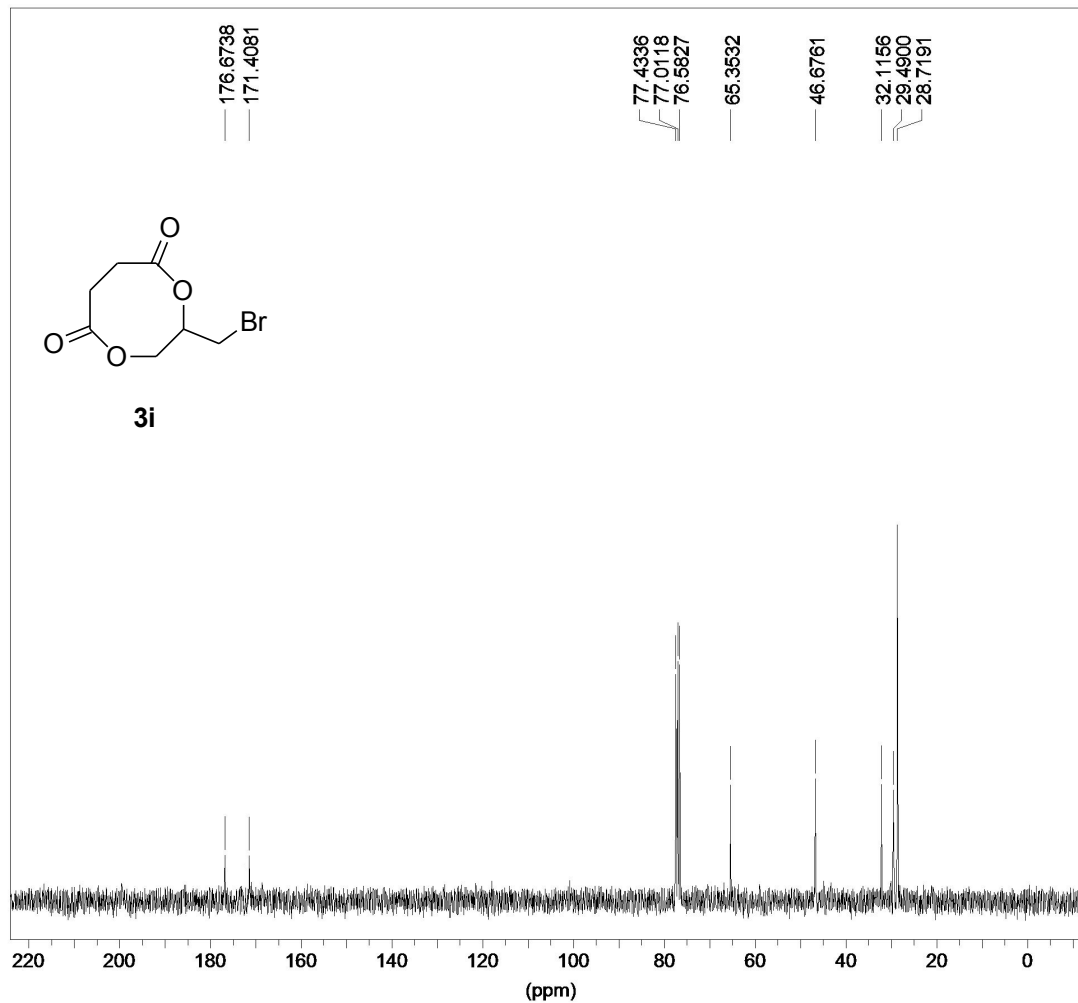
INSTRUM : spect
LOCNUC : 2H
NS : 12
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl₃
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : junjie~1
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 188
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
SW : 238.2968 ppm
TD : 32768

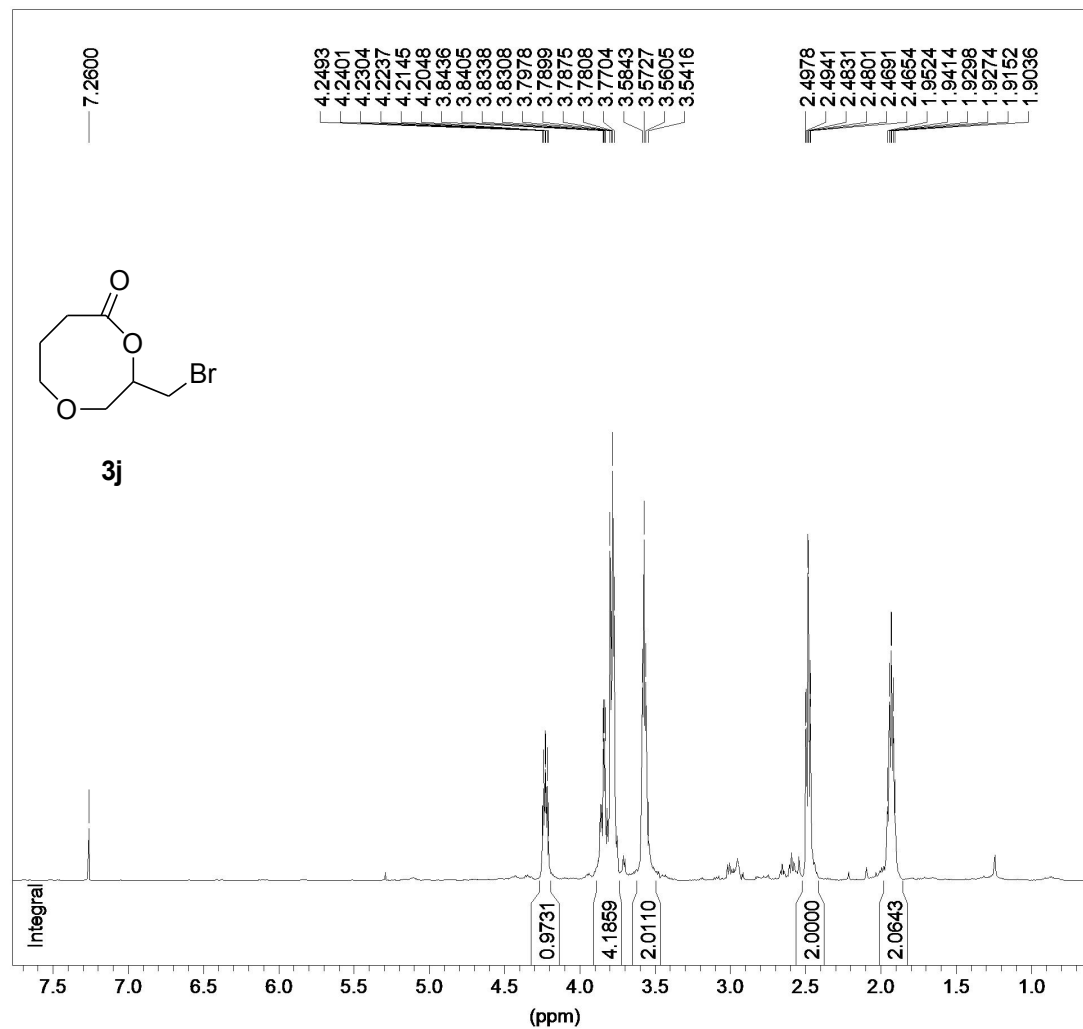
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

8-0b



*** Current Data Parameters ***

NAME : ya0310
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

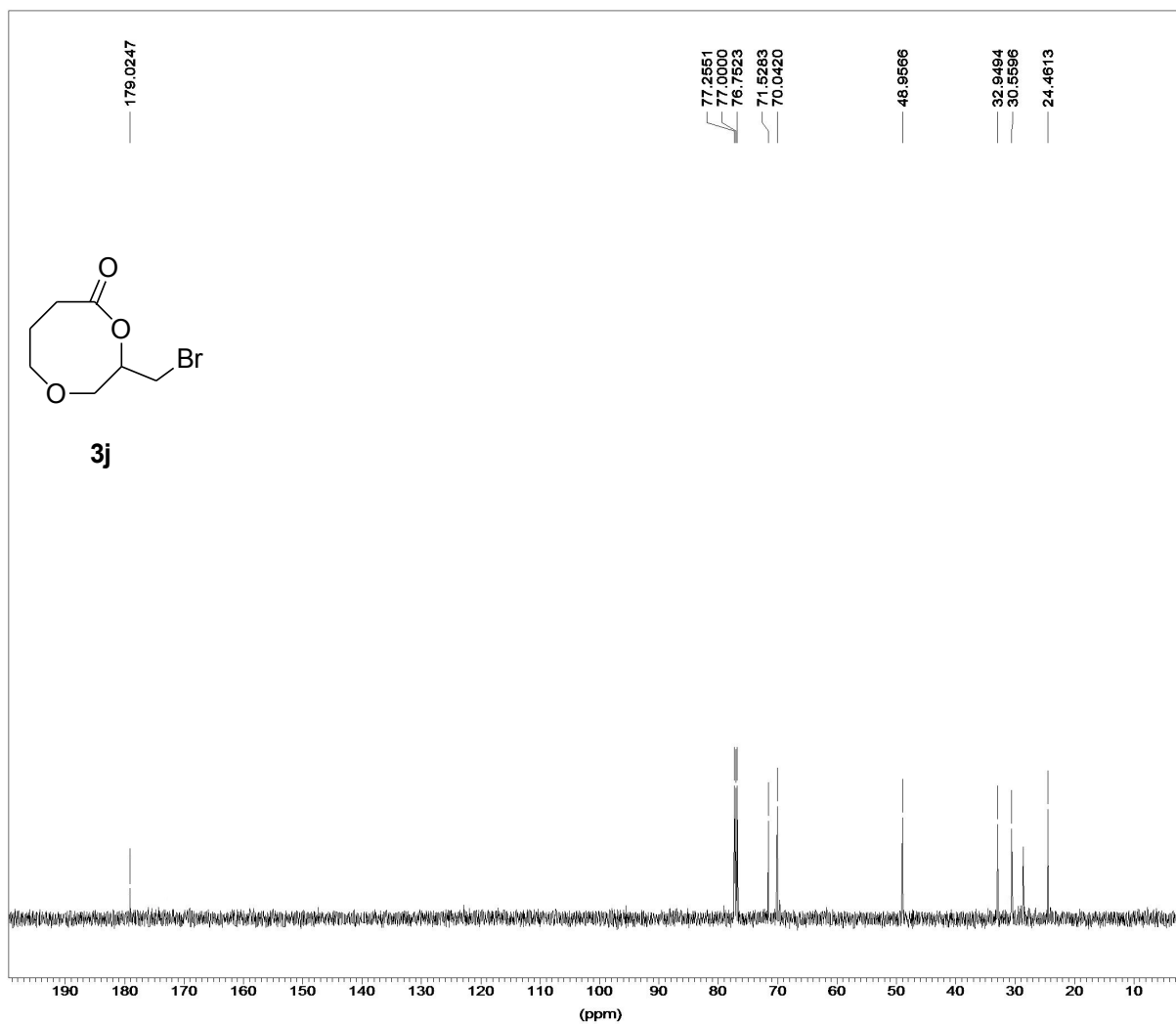
INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 4251.96 Hz
PULPROG : zg
SFO1 : 500.2342520 MHz
SOLVENT : CDCl3
SW : 19.9906 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

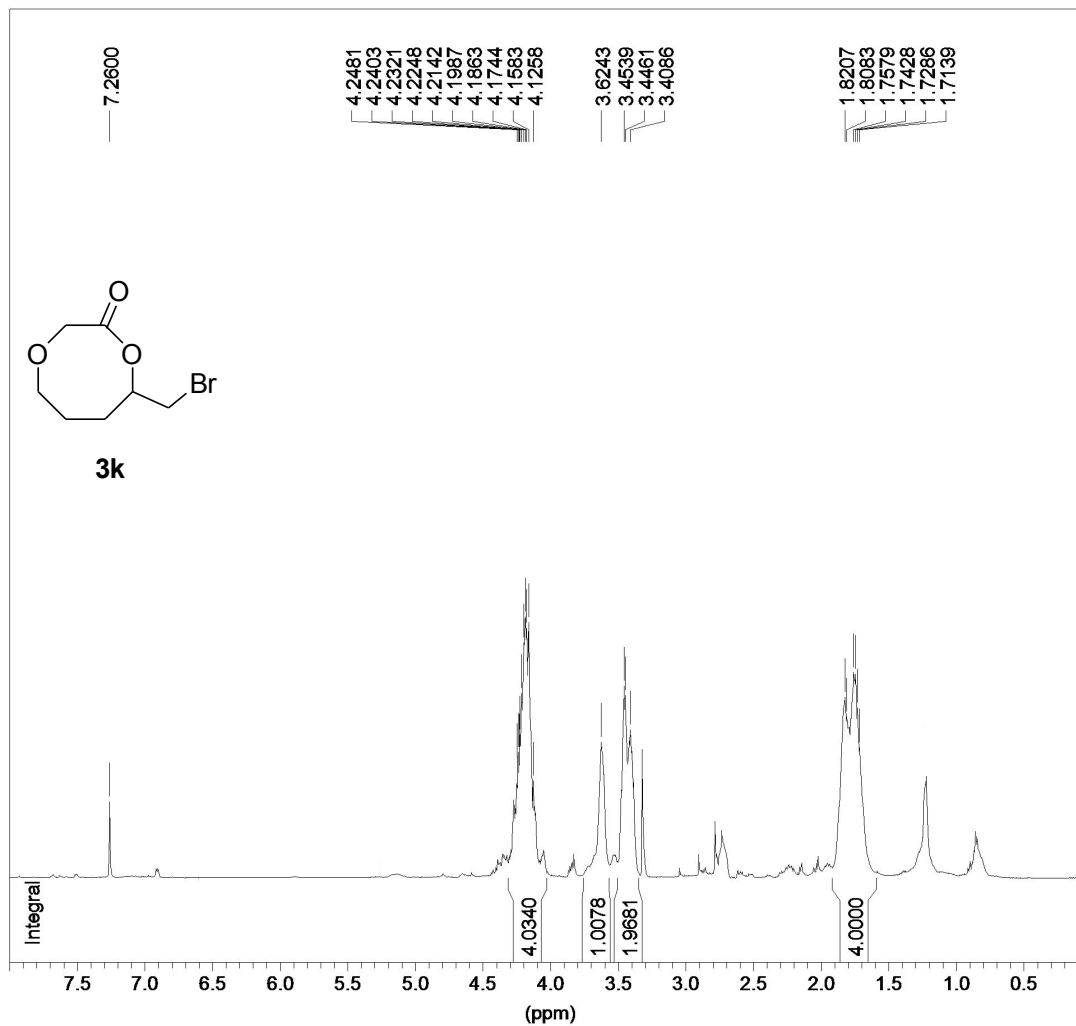
NAME : ya0310
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

BF1 : 125.7829340 MHz
LOCNUC : 2H
NS : 64
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm

*** Processing Parameters ***

LB : 1.00 Hz
PHC0 : 122.480 degree
PHC1 : 40.755 degree



*** Current Data Parameters ***

NAME : ya1223
EXPNO : 4
PROCNO : 1

*** Acquisition Parameters ***

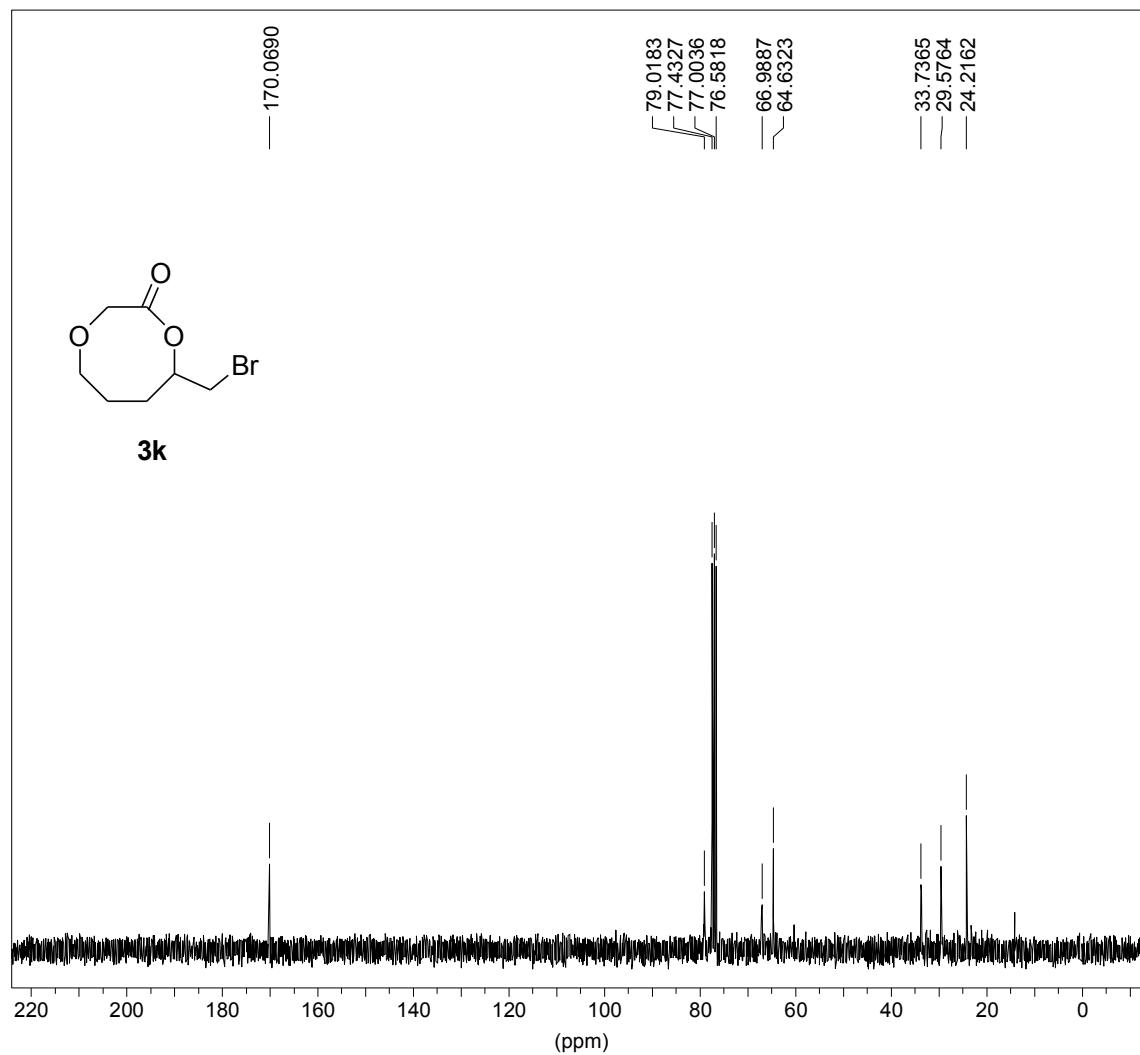
INSTRUM : spect
LOCNUC : 2H
NS : 24
NUCLEUS : off
O1 : 2352.00 Hz
PULPROG : zgpr
SFO1 : 500.2323520 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ja12cya
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 148
NUCLEUS : off
O1 : 7924.11 Hz
PULPROG : zgpg30
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
SW : 238.2968 ppm
TD : 32768

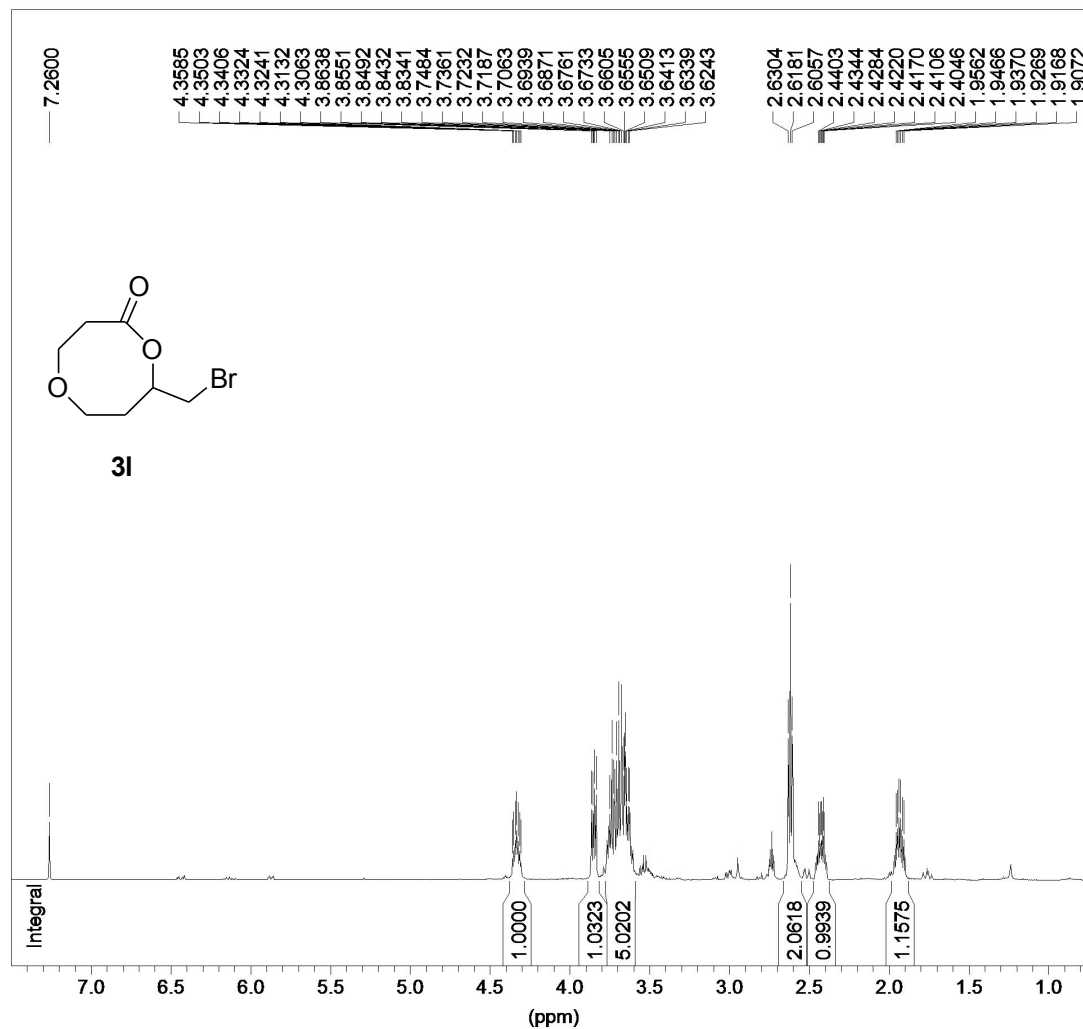
*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

8-Oc lactone (8-membered ether lactone)



*** Current Data Parameters ***

NAME : ya0525b

EXPNO : 7

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 32

NUCLEUS : off

O1 : 2751.27 Hz

PULPROG : zg

SFO1 : 500.2327513 MHz

SOLVENT : CDCl3

SW : 15.0080 ppm

TD : 32768

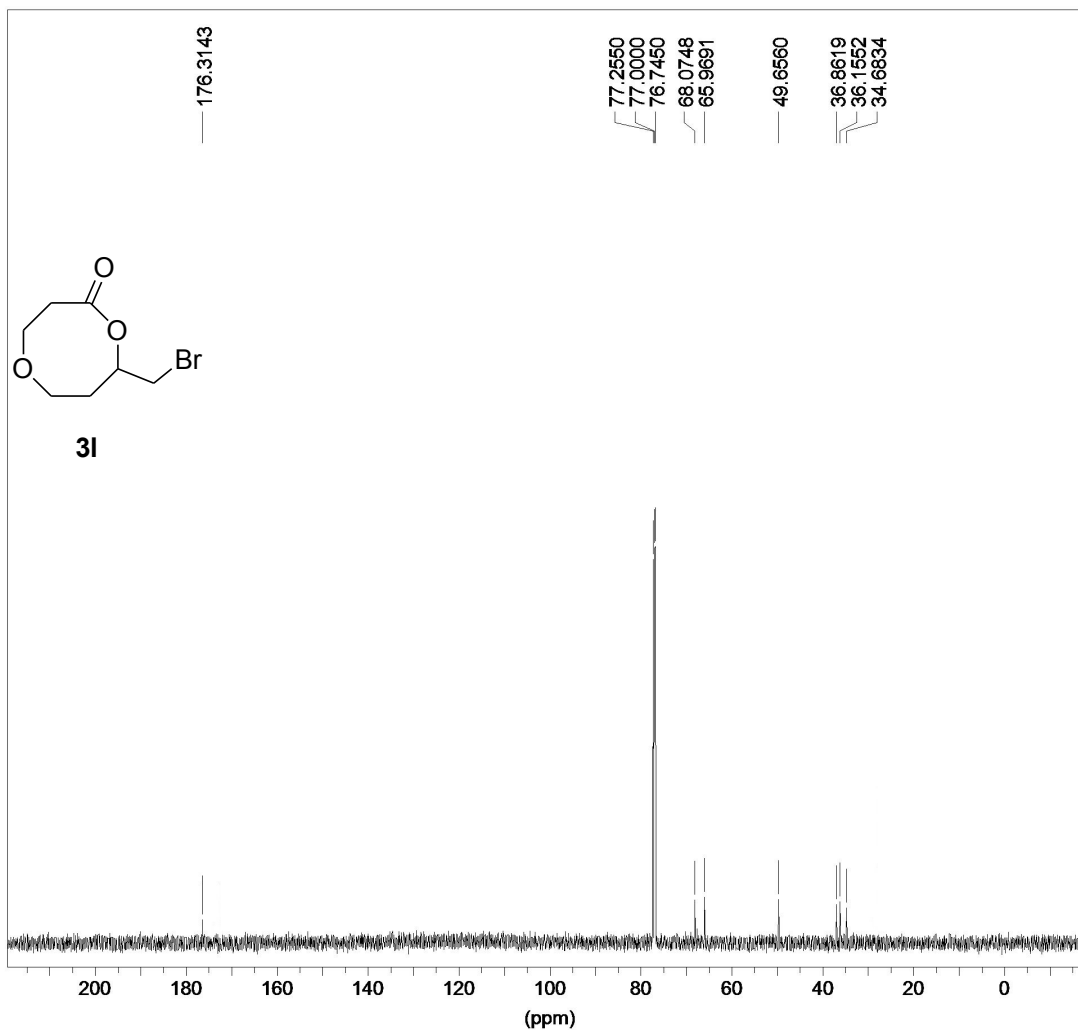
*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

8-Oc lactone (8-membered ether lactone)



*** Current Data Parameters ***

NAME : ya0525b
EXPNO : 8
PROCNO : 1

*** Acquisition Parameters ***

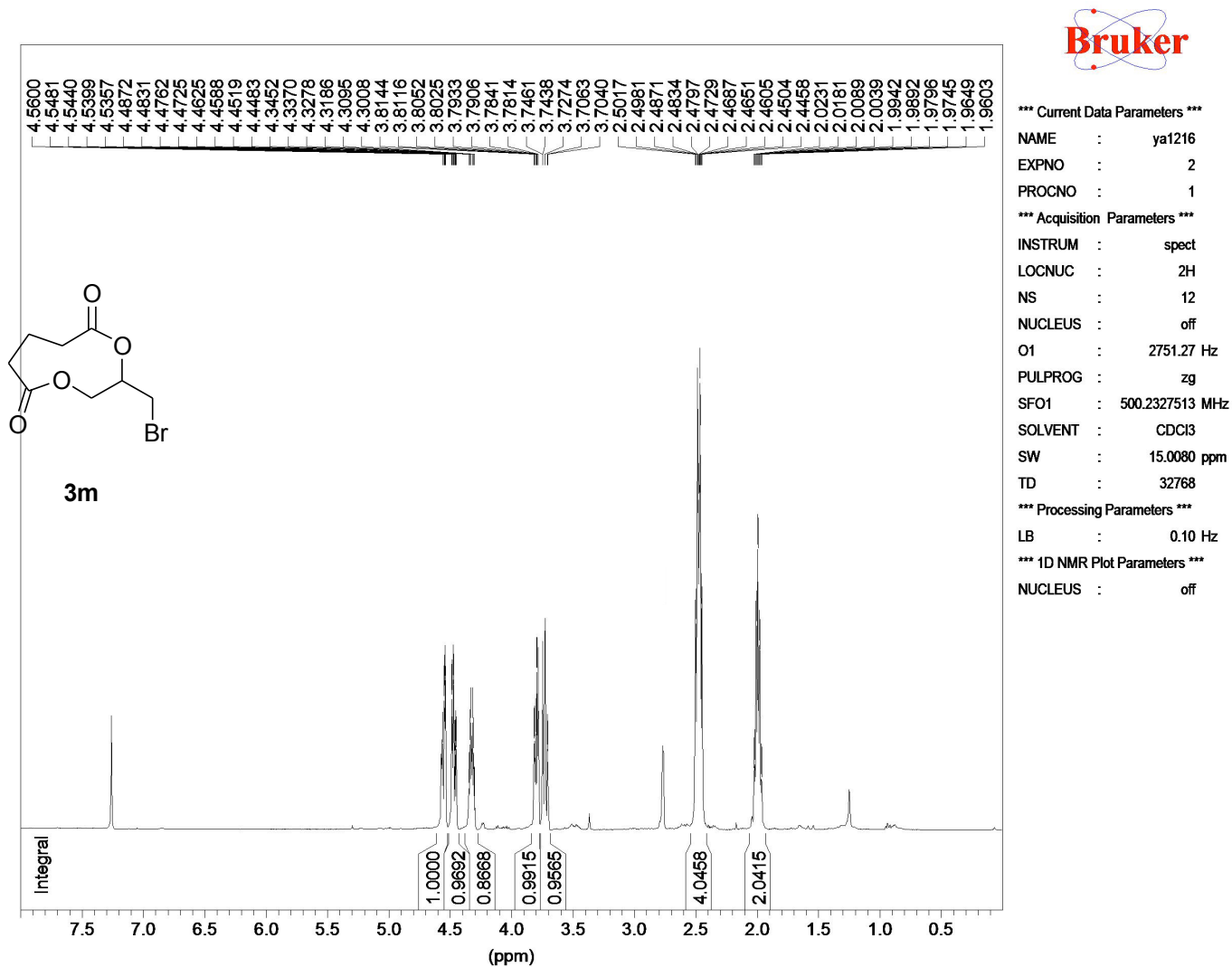
INSTRUM : spect
LOCNUC : 2H
NS : 122
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl₃
SW : 238.7210 ppm
TD : 65536

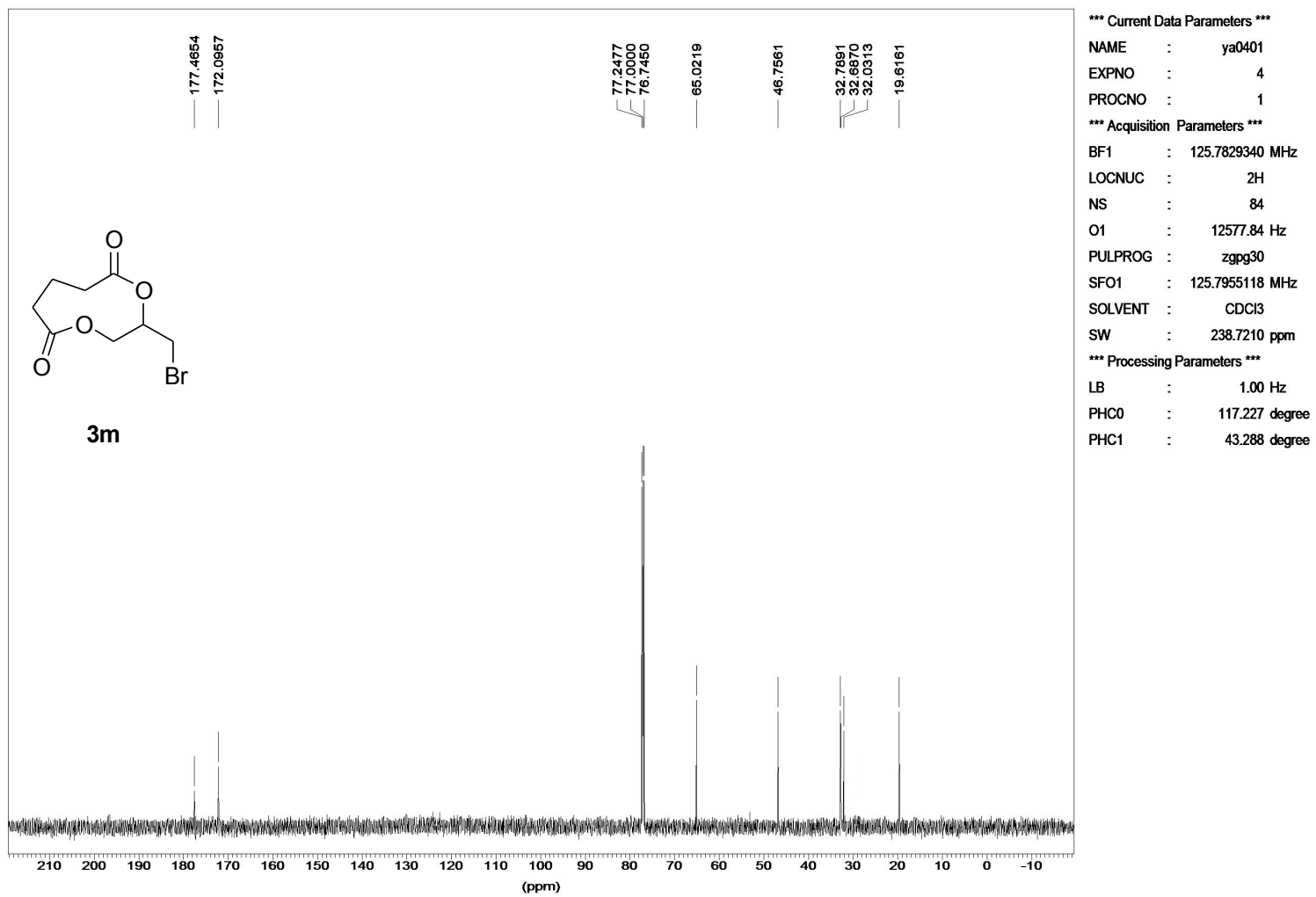
*** Processing Parameters ***

LB : 1.00 Hz

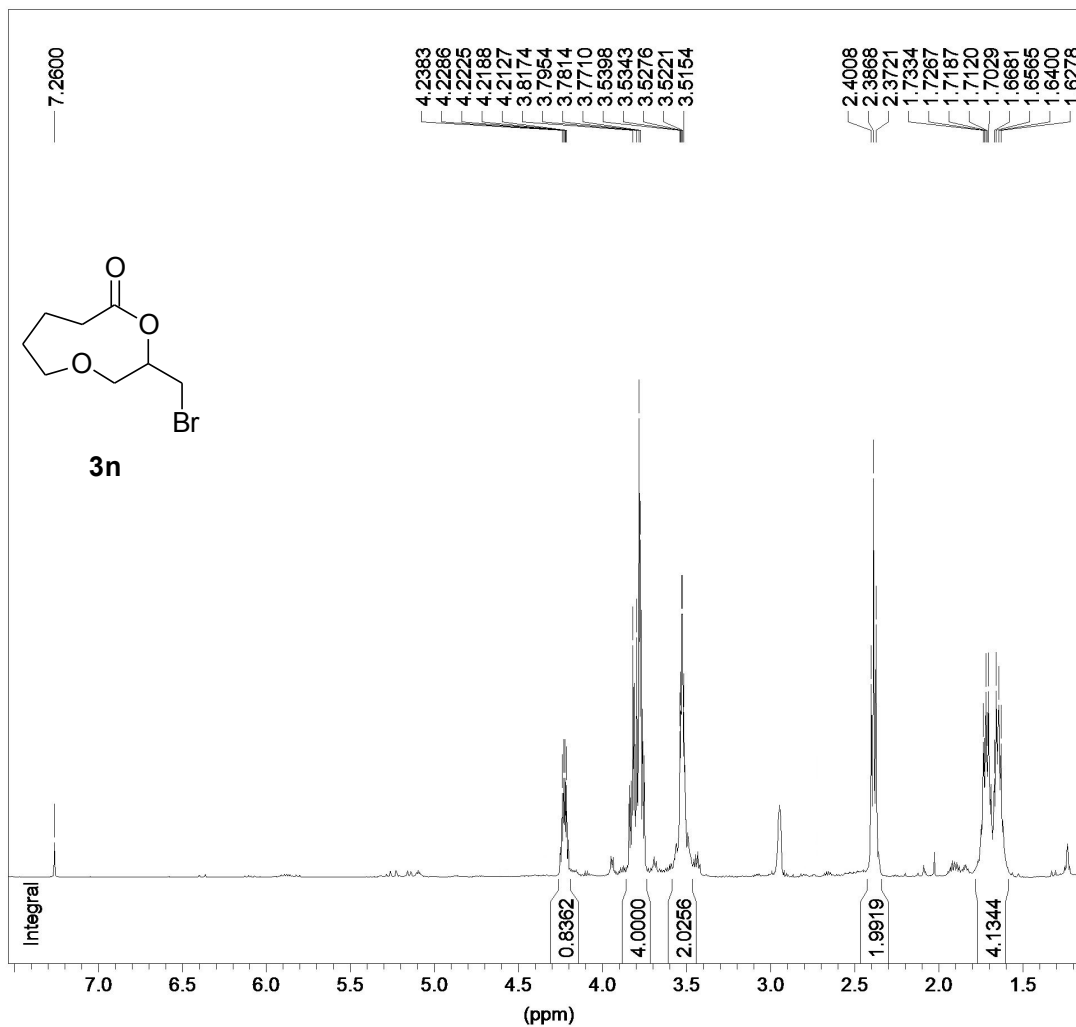
*** 1D NMR Plot Parameters ***

NUCLEUS : off





9-0a (ether-lactone 9a)



*** Current Data Parameters ***

NAME : ya0330b

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect

LOCNUC : 2H

NS : 24

NUCLEUS : off

O1 : 4251.96 Hz

PULPROG : zg

SFO1 : 500.2342520 MHz

SOLVENT : CDCl3

SW : 19.9906 ppm

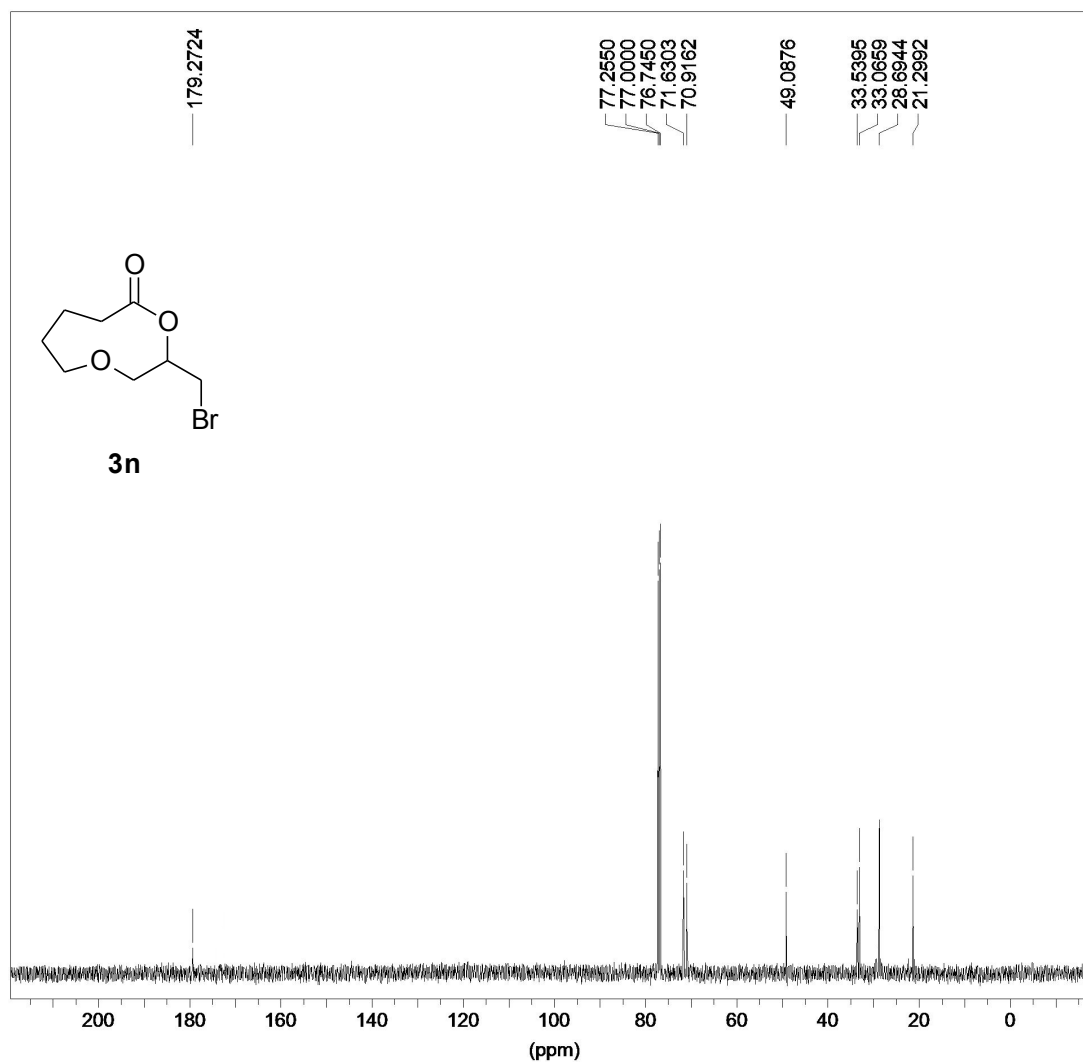
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0330b
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

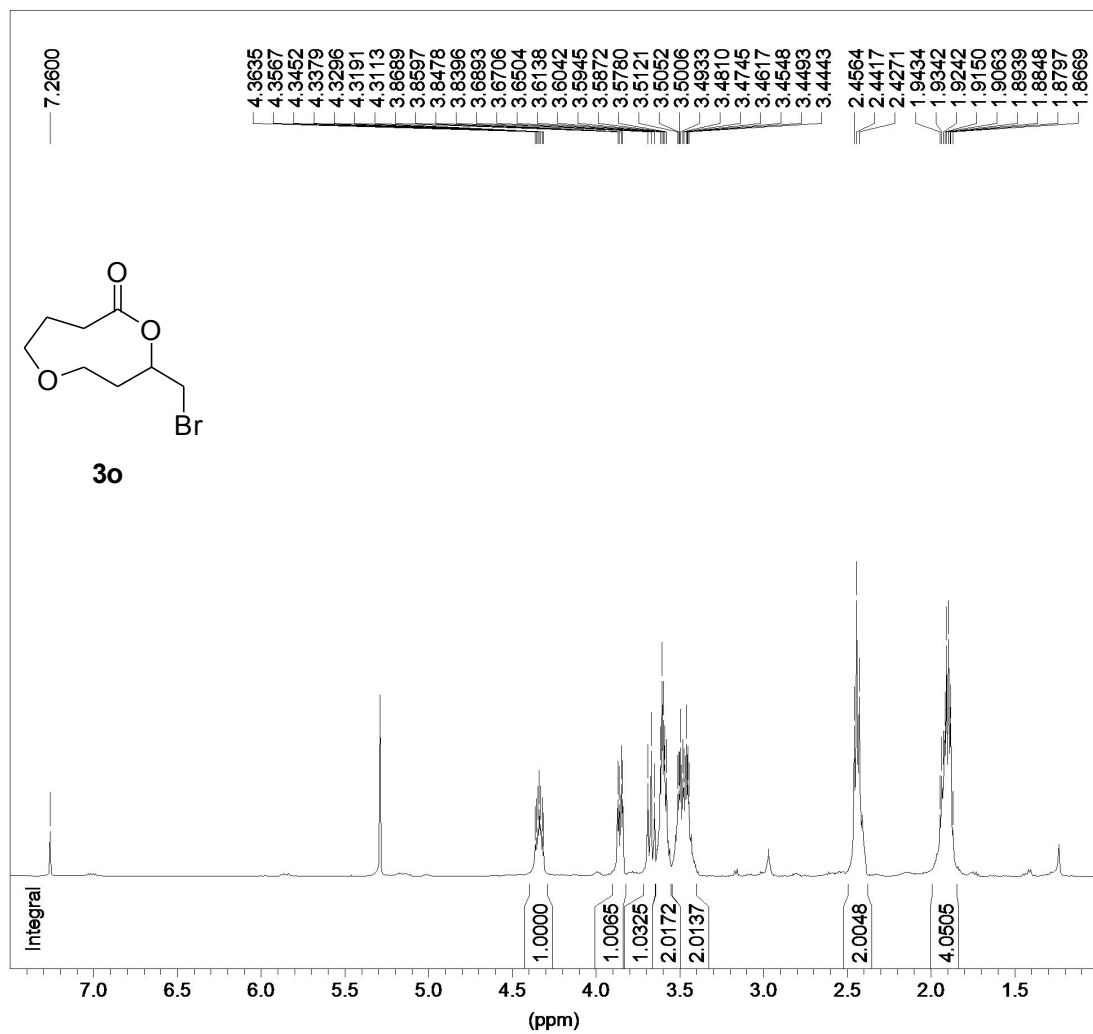
INSTRUM : spect
LOCNUC : 2H
NS : 120
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl₃
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0601
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

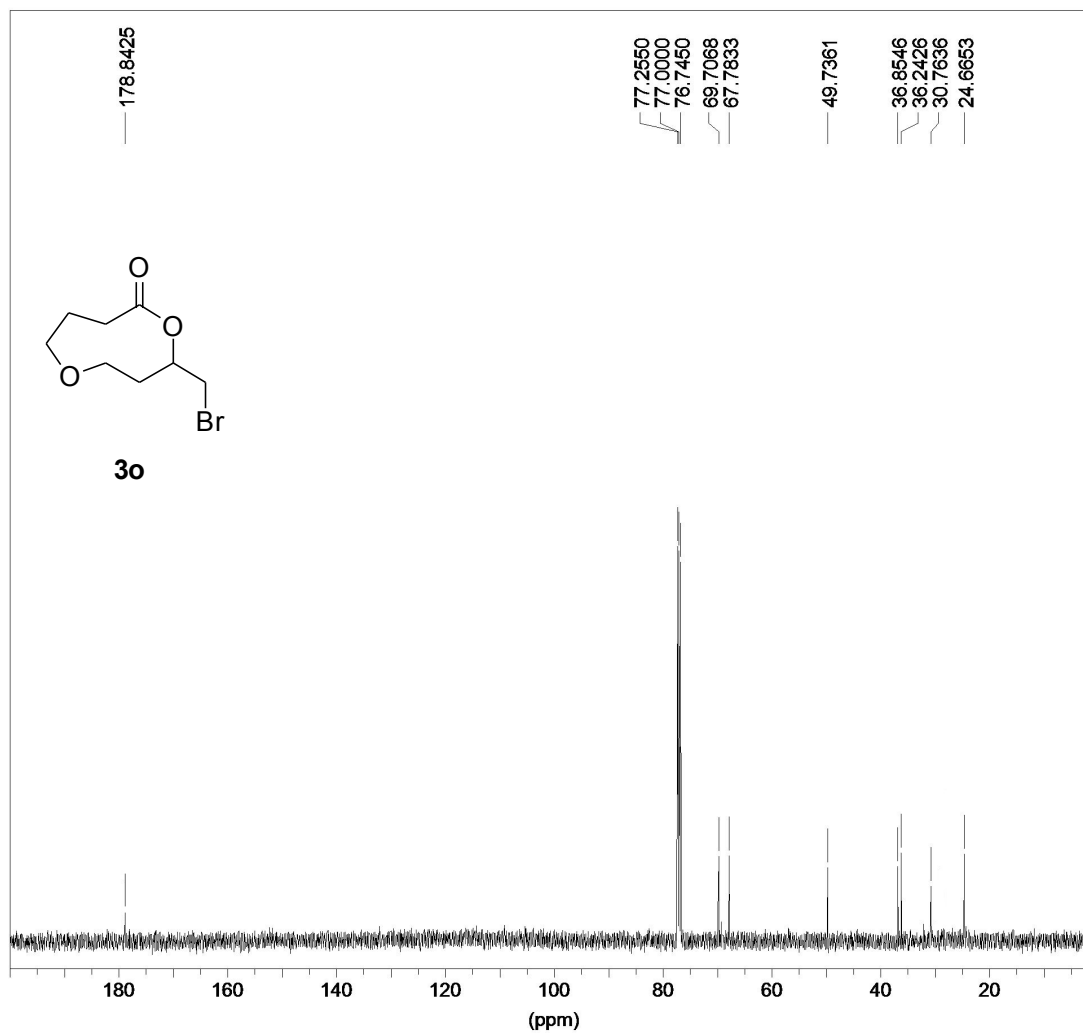
INSTRUM : spect
LOCNUC : 2H
NS : 32
NUCLEUS : off
O1 : 2751.27 Hz
PULPROG : zg
SFO1 : 500.2327513 MHz
SOLVENT : CDCl3
SW : 15.0080 ppm
TD : 32768

*** Processing Parameters ***

LB : 0.10 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



*** Current Data Parameters ***

NAME : ya0601
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

INSTRUM : spect
LOCNUC : 2H
NS : 276
NUCLEUS : off
O1 : 12577.84 Hz
PULPROG : zgpg30
SFO1 : 125.7955118 MHz
SOLVENT : CDCl3
SW : 238.7210 ppm
TD : 65536

*** Processing Parameters ***

LB : 1.00 Hz

*** 1D NMR Plot Parameters ***

NUCLEUS : off