Cyclizative Atmospheric CO_2 Fixation by Unsaturated Amines With *t*-BuOI Leading to Cyclic Carbamates

Supporting Information

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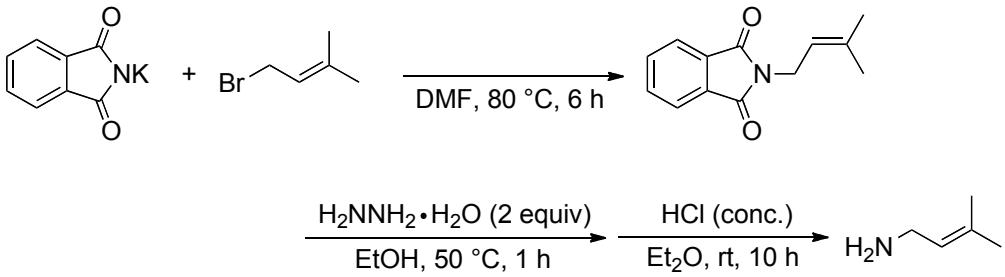
General Methods

Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System and are uncorrected. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC–908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or NH-silica gel (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on precoated silica gel glass plates (Merck silica gel 60 F_{254}, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

Typical procedures for the preparation of unsaturated amines

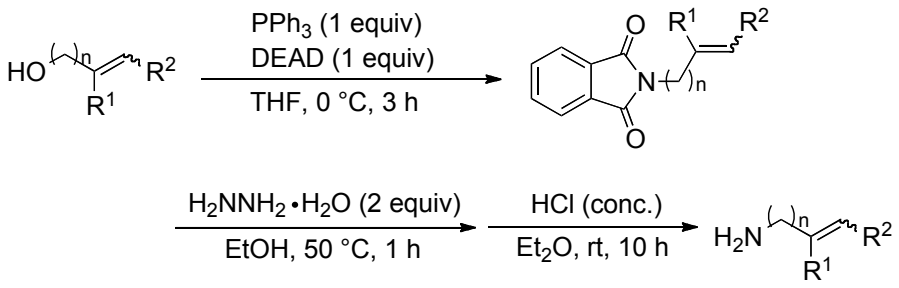
Procedure for the preparation of unsaturated amine 1c



A mixture of potassium phthalimide (30 mmol) and prenyl bromide (30 mmol) in DMF was stirred at 80 °C for 6 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was poured into an ice-water, and the solid was collected on a filter funnel. The crude product was used without further purification. To a mixture of *N*-prenylphthalimide and ethanol (200 mL) was added hydrazine monohydrate (60 mmol) at 50 °C. The mixture was stirred for 1 h and quenched with aq. HCl (6.0 M, 20 mL). The forming solids were removed by filtration. The filtrate was dried over Na_2SO_4 and concentrated under vacuum to give prenylamine hydrochloride. Aqueous NaOH (6.0 M, 10 mL) was added to the amine salt, and the resulting solution was extracted with diethyl ether (50 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated

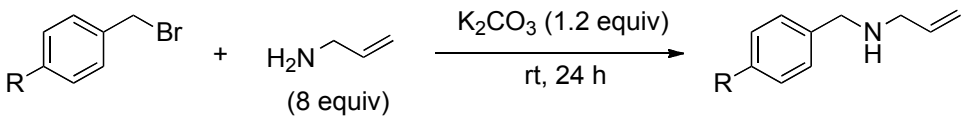
under vacuum to give amine **1c** (1.35 g, 53%). The spectroscopic data for this compound were in agreement with the reported data.[S1]

Procedure for the preparation of unsaturated amines 1d, 1e and 1n



To a mixture of triphenylphosphine (25 mmol) and the corresponding allyl alcohol (25 mmol) in THF (30 mL) was slowly added diethyl azodicarboxylate (DEAD) (25 mmol) at 0 °C under N_2 atmosphere. The mixture was stirred at 0 °C for 3 h. After the reaction completion, *n*-hexane was added to the reaction mixture and filtered. The filtrate was dried over Na_2SO_4 and concentrated under vacuum to give the crude product, which was used without further purification. To a mixture of phthalimide product and ethanol (100 mL) was added hydrazine monohydrate (50 mmol) at 50 °C. The mixture was stirred for 1 h and quenched with HCl (6.0 M, 20 mL) to produce precipitates. The forming solids were removed by filtration, and the filtrate was dried over Na_2SO_4 and concentrated under vacuum to give an unsaturated amine hydrochloride. Aqueous NaOH (6.0 M, 10 mL) was added to the amine salt, and the resulting solution was extracted with diethyl ether (50 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give unsaturated amine (**1d**: 1.58 g, 64%; **1e**: 1.63 g, 66%; **1n**: 0.75 g, 35%). The spectroscopic data for **1d**[S2] and **1n**[S3] were in agreement with the reported data.

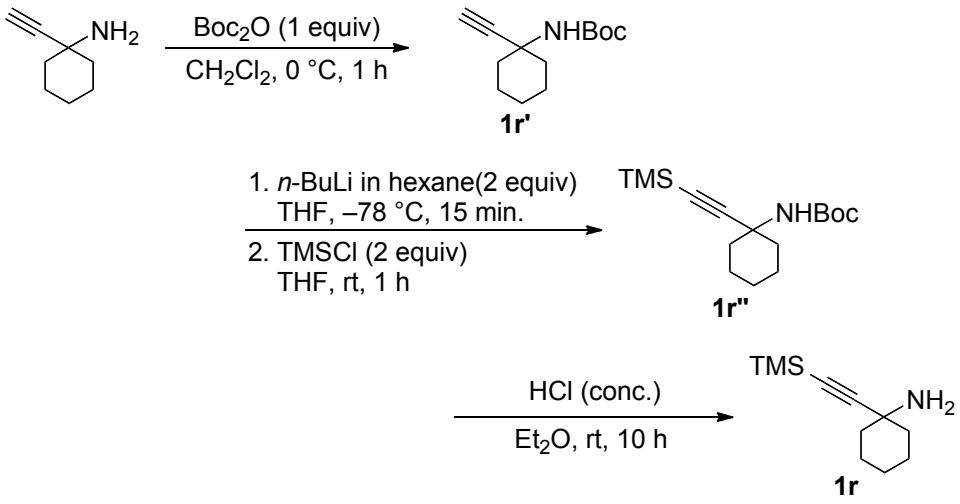
Procedure for the preparation of N-benzyl allyl amines 1i–1t[S4]



To a mixture of K_2CO_3 (16.1 mmol) and allyl amine (107 mmol) was added the corresponding benzyl bromide (13.4 mmol) over 15 min under N_2 atmosphere. The mixture was stirred at room temperature for 24 h. The extra K_2CO_3 was filtered and washed with CH_2Cl_2. The filtrate was concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate/hexane) gave

N-benzyl allyl amine (**1i**: 1.77 g, 90%; **1j**: 2.21 g, 93%; **1k**: 1.53 g, 60%; **1l**: 2.61 g, 95%). The spectroscopic data for all compounds were in agreement with the reported data (**1i**[S4], **1j**[S5], **1k**,[S6] and **1l**[S7]).

Procedure for the preparation of 1-((trimethylsilyl)ethynyl)cyclohexylamine (1r)[S8,S9]



To a CH_2Cl_2 solution (20 mL) of 1-ethynylcyclohexylamine (10 mmol) was added di-*tert*-butyl dicarbonate (10 mmol) at 0 °C under N_2 atmosphere. The mixture was stirred for 1 h, and the solvent was removed under vacuum to give *N*-Boc protected crude product **1r'**. To a solution of **1r'** in THF (60 mL) was added *n*-BuLi (20 mmol, 1.65 M hexane solution) at –20 °C under N_2 atmosphere. After 15 min stirring, TMSCl (20 mmol) was added dropwise to the mixture over 30 min. The solution was allowed to warm up to room temperature and stirred for 1 h, quenched with aqueous HCl (2 M, 15 mL), and extracted with diethyl ether (50 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product **1r''**. To a solution of **1r''** in Et_2O (30 mL) was added aqueous HCl (12 M, 3 mL) at 0 °C, and the resulting mixture was allowed to warm up to room temperature. After 10 h stirring, the solution was quenched with aqueous Na_2CO_3 (sat. 20 mL) and extracted with Et_2O (30 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product **1r**. Purification by flash column chromatography on silica gel (eluent: ethyl acetate/hexane) gave propargyl amine **1r** (1.38 g, 70%).

* Other unsaturated amines **1a**, **1b**, **1f–1h**, **1m** and **1o–1q** were purchased from a commercial supplier.

Typical procedure for CO_2 fixation by unsaturated amines

To a mixture of NaI (0.5 mmol, 75.0 mg) and unsaturated amine (0.5 mmol) in an appropriate solvent (3 mL) was added *t*-BuOCl (0.5 mmol, 54.3 mg) at –20 °C under CO_2 atmosphere. The mixture was stirred for 24 h in dark and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the resulting mixture was extracted with diethyl ether (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate/hexane) gave cyclic carbamate **2** (for example, **2a**: 103.2 mg, 91%).

Procedures for the synthesis of AMOZ

Gram scale preparation of cyclic carbamates 2a

To a mixture of NaI (5.0 mmol, 750 mg) and allyl amine (**1a**) (5.0 mmol, 286 mg) in acetonitrile (30 mL) was added *t*-BuOCl (5.0 mmol, 543 mg) at –20 °C under CO_2 atmosphere. The mixture was stirred for 24 h in dark and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 30 mL), and the resulting mixture was extracted with diethyl ether (50 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography on silica gel (eluent: ethyl acetate/hexane) gave **2a** (1.0 g, 88%).

Procedure for the prepartion of 3 through nucleophilic substitution of iodo group[S10]

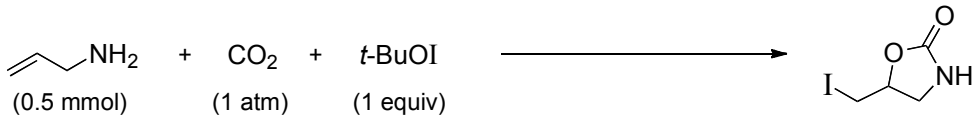
A mixture of **2a** (2 mmol, 454 mg), K_2CO_3 (2 mmol, 276 mg), morpholine (10 mmol, 872 mg), and THF (10 mL) was refluxed for 18 h. After the reaction completion, the extra K_2CO_3 was filtered and washed with THF. The filtrate was concentrated under vacuum to give the crude product. Purification by flash column chromatography on NH-silica gel (eluent: ethyl acetate) gave **3** (261 mg, 70%).

Procedure for the preparation of AMOZ through N-amination of 3[S11]

To a solution of **3** (0.5 mmol, 93.2 mg) in DMF (3 mL) was added NaH (0.75 mmol, 18.0 mg) at room temperature under nitrogen atmosphere. The mixture was stirred at 80 °C for 2 h. *O*-(diphenylphoshinyl)hydroxylamine* ($DppONH_2$) (0.75 mmol, 172.6 mg) was added to the mixture, which was stirred at 80 °C for 48 h. Insoluble solids were filtered, and the filtrate was concentrated under vacuum to give the crude product. Purification by flash column chromatography on NH-silica gel (eluent: ethyl acetate) gave AMOZ (70.5 mg, 70%).

**O*-(diphenylphoshinyl)hydroxylamine ($DppONH_2$) was prepared by reported method.[S12]

Table S1. Optimization study of reaction parameters



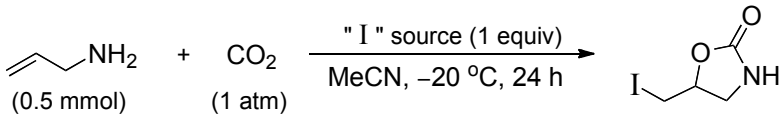
entry	solvent	temp. (°C)	time (h)	yield (%)[a]
1	MeCN	–20	24	91[b]
2	THF	–20	24	27
3	DMF	–20	24	23
4	toluene	–20	24	48
5	CH_2Cl_2	–20	24	67
6	MeCN	rt	24	47
7	MeCN	0	24	71[b]
8	MeCN	–40	24	84

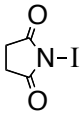
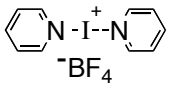
[a] ^{1}H NMR yields. [b] Isolated yield.

Comparative study of CO_2 fixation reaction by allyl amine using various iodinating reagents

To a solution of allyl amine **1a** (0.5 mmol) in MeCN (3 mL) was added iodinating reagent (0.5 mmol) at –20 °C under CO_2 atmosphere. The mixture was stirred for 24 h in dark and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 10 mL), and the resulting mixture was extracted with diethyl ether (20 mL × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. The product yield was calculated by ^{1}H NMR integration of the crude product.

Table S2. Comparison of iodinating reagents

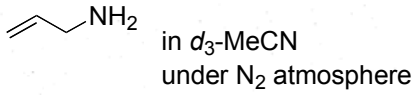


entry	oxidant	yield (%)[a]
1	*t*-BuOI	91[b]
2	I_2	17
3	I_2 + Et_3N	0
4		5
5		1

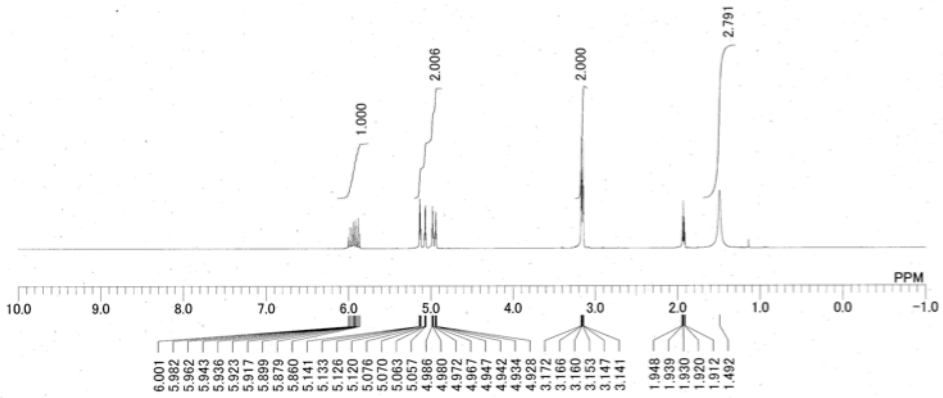
[a] ^{1}H NMR yields. [b] Isolated yield.

^{1}H NMR monitoring of reaction of allyl amine 1a with *t*-BuOI under N_2 atmosphere

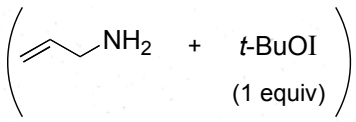
a)



in d_3-MeCN
under N_2 atmosphere



b)

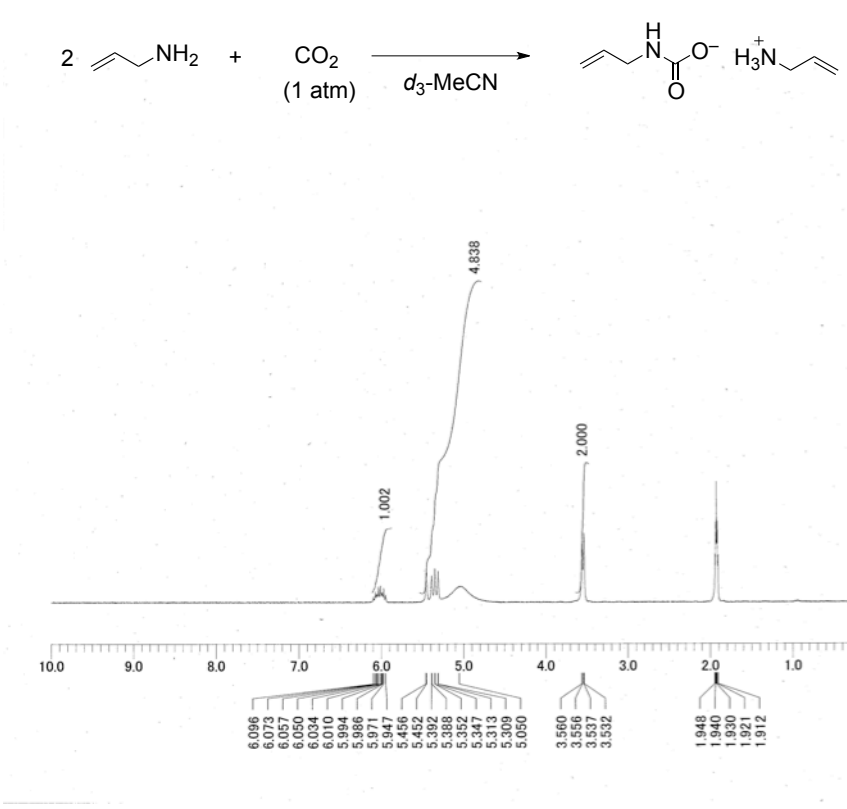


in d_3-MeCN
under N_2 atmosphere

Figure S1. ^{1}H NMR spectra of a) the d_3-MeCN solution of allyl amine (0.1 mmol, 5.7 mg) and NaI (0.1 mmol, 15.0 mg) under N_2 atmosphere; b) the d_3-MeCN solution after the treated with *t*-BuOCl (0.1 mmol, 10.9 mg).

^{1}H NMR monitoring of reaction of allyl amine 1a with *t*-BuOI under CO_2 atmosphere

a)



b)

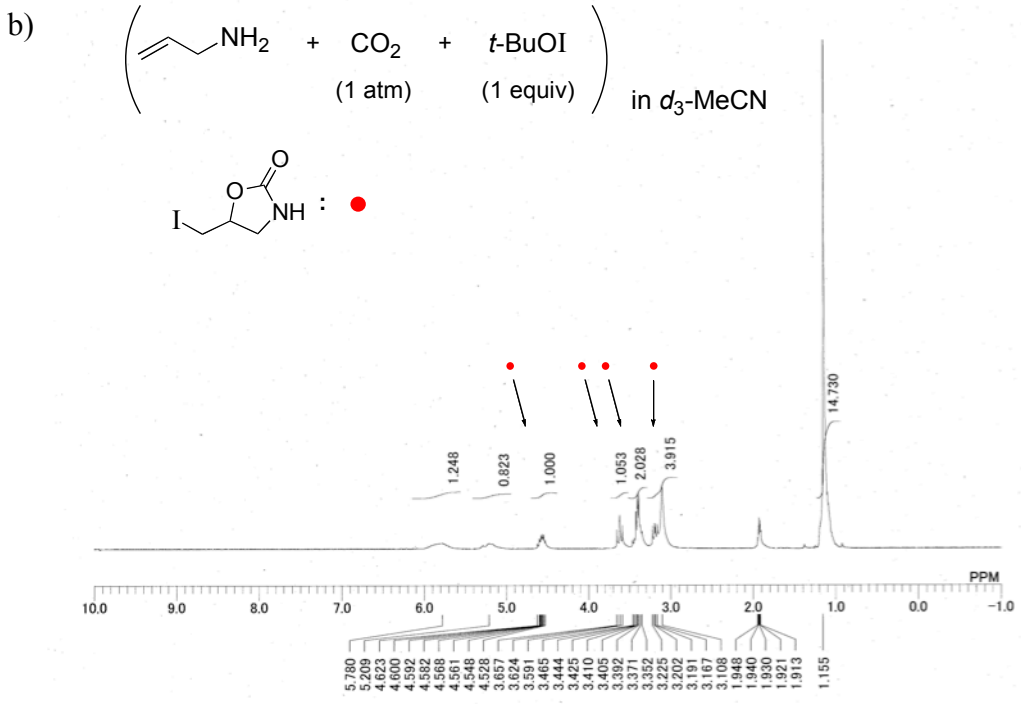


Figure S2. ^{1}H NMR spectra of a) the d_3-MeCN solution of allyl amine (0.1 mmol, 5.7 mg) and NaI (0.1 mmol, 15.0 mg) under CO_2 atmosphere; b) the d_3-MeCN solution after treated with *t*-BuOCl (0.1 mmol, 10.9 mg).

^{13}C NMR monitoring of reaction of allyl amine 1a and CO_2

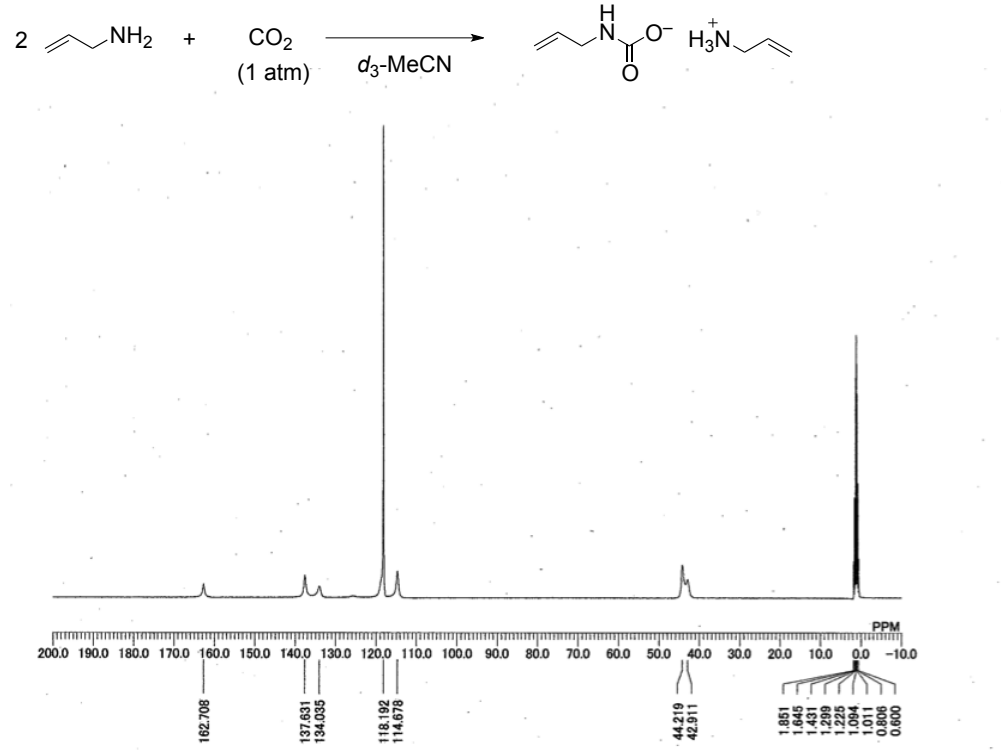


Figure S3. ^{1}H NMR spectra of a d_3-MeCN solution of allyl amine (0.1 mmol, 5.7 mg) and NaI (0.1 mmol, 15.0 mg) under CO_2 atmosphere.

FT-IR monitoring of reaction of allyl amine 1a and CO_2

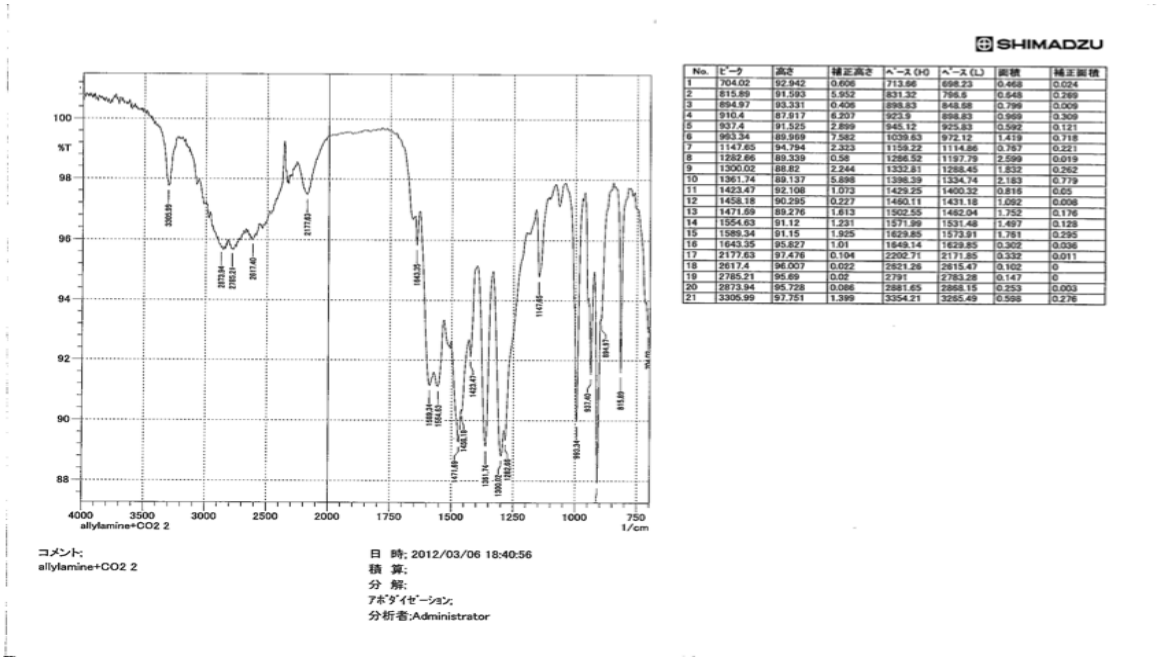


Figure S4. FT-IR spectra of the precipitates that formed from d_3-MeCN solution of allyl amine and NaI under CO_2 atmosphere (ν 3006, 2874, 2785, 2617, 2178, 1648, 1589, 1555, 1472, 1458, 1362, 1300, 1283, 1148, 993, 937, 910, 816, 704 cm^{-1}).[S13]

The exclusive formation of allylammonium allylcarbamate (**IP**) from allyl amine and CO_2 suggested the existence of possible reaction pathways leading to intermediate **B** other than the one shown in Figure 3 (Figure S5), although the clarification of precise mechanism awaits further study. The first feasible route is that the resulting **IP** directly undergoes *O*-iodination with *t*-BuOI to generate **B** (*path a*) and allyl amine. Since ammonium alkylcarbamates and carbamic acids are reportedly in equilibrium (*Chem. Commun.* **2002**, 1450; *Tetrahedron* **2003**, *59*, 9619), another possible route to **B** is proton-iodine exchange of carbamic acid **A** that is formed as the result of the equilibrium (*path b*).

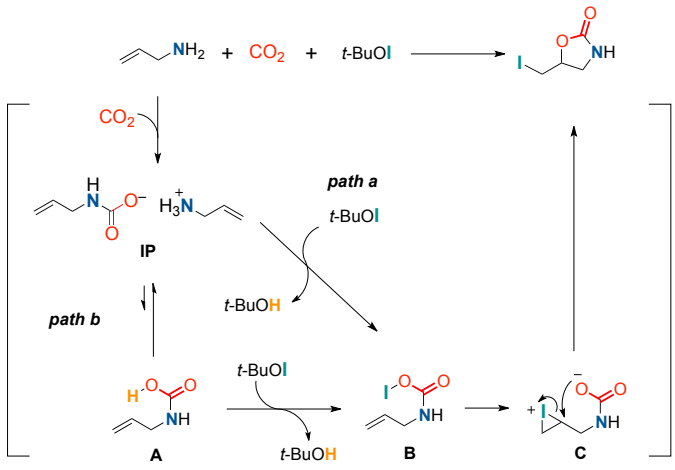
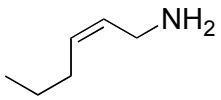


Figure S5. Other possible reaction mechanisms.

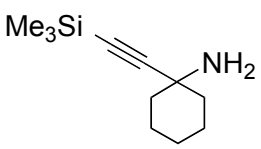
Spectra data of compounds

(*Z*)-Hex-2-en-1-amine (1e)



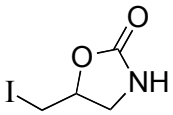
colorless oil; R_f 0.08 (hexane/EtOAc 1:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (m, 3H), 1.30–1.45 (m, 4H), 2.02 (q, 2H, J = 6.8 Hz), 3.30 (dd, 2H, J = 1.1, 5.7 Hz), 5.38–5.53 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.4, 22.5, 29.0, 38.5, 130.2, 130.8; IR (KBr) ν 3290, 3008, 2959, 2872, 1574, 1464, 1377, 1366, 1301 cm^{-1}; MS (CI, isobutane): *m/z* (relative intensity, %) 100 ([M+H]$^+$, 100); HRMS (CI, isobutane): *m/z* calcd for $C_6H_{14}N$ (M+H) 100.1126, found 100.1126.

1-((Trimethylsilyl)ethynyl)cyclohexylamine (1r)



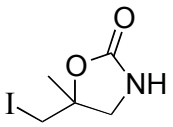
colorless oil; R_f 0.2 (hexane/EtOAc 7:3); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.01 (s, 9H), 0.97–1.75 (m, 12H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 0.09, 23.2, 25.3, 40.2, 49.9, 86.1, 112.6; IR (KBr) ν 3360, 3285, 2933, 2900, 2857, 2158, 1447, 1250, 968, 840, 760 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 195 ([M]$^+$, 10), 152 (100); HRMS (EI): *m/z* calcd for $C_{11}H_{21}NSi$ (M) 195.1443, found 195.1448.

5-(Iodomethyl)-oxazolidin-2-one (2a)



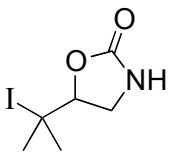
Purified by silica gel column chromatography (hexane/EtOAc 1:1). colorless solid; mp: 117.6–118.5 °C; R_f 0.38 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.27–3.44 (m, 3H), 3.77 (dd, 1H, J = 8.6, 8.6 Hz), 4.73 (m, 1H), 6.24 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 5.8, 46.4, 75.1, 159.2; IR (KBr) ν 3256, 3151, 1780, 1739, 1242, 1092, 958 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 227 ([M]$^+$, 76), 100 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_4H_6INO_2$ (M) 226.9443, found 226.9439.

5-(Iodomethyl)-5-methyloxazolidin-2-one (2b)



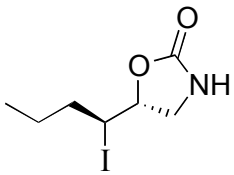
Purified by silica gel column chromatography (hexane/EtOAc 1:1). yellow solid; dec: 84.7–87.2 °C; R_f 0.11 (hexane/EtOAc 6:4); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.69 (s, 3H), 3.35 (d, 1H, J = 8.9 Hz), 3.42 (dd, 2H, J = 10.5, 17.0 Hz), 3.63 (d, 1H, J = 8.9 Hz), 5.96 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.6, 25.2, 51.2, 80.7, 158.9; IR (KBr) ν 3232, 3146, 1728, 1481, 1305, 1222, 1095, 987, 764 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 241 ([M]$^+$, 29), 100 ([M]$^+$ – I – CH_2, 100); HRMS (EI): *m/z* calcd for $C_5H_8INO_2$ (M) 240.9600, found 240.9603.

5-(2-Iodopropane-2-yl)oxazolidin-2-one (2c)



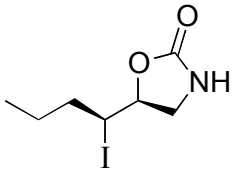
Purified by silica gel column chromatography (hexane/EtOAc 1:1). yellow solid; dec: 118.7–120.5 °C; R_f 0.24 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.58 (s, 3H), 3.71 (m, 2H), 4.19 (dd, 1H, *J* = 5.7, 8.4 Hz), 7.37 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.1, 24.8, 27.7, 47.1, 80.6, 153.8; IR (ATR) *ν* 1692, 1313, 1136, 1111, 1066 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 255 ([M]$^+$, 30), 212 (27), 154 (70), 128 ([M]$^+$-I, 100); HRMS (EI): *m/z* calcd for $C_6H_{10}INO_2$ (M) 254.9756, found 254.9760.

(*R*)-5-((*S*)-1-Iodobutyl)oxazolidin-2-one (2d)



Purified by silica gel column chromatography (hexane/EtOAc 1:1). colorless solid; mp: 97.2–99.8 °C; R_f 0.14 (hexane/EtOAc 6:4); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, 3H, *J* = 7.0 Hz), 1.32–1.98 (m, 4H), 3.43 (dd, 1H, *J* = 7.3, 7.3 Hz), 3.79 (dd, 1H, *J* = 7.3, 7.3 Hz), 4.11 (td, 1H, *J* = 3.2, 8.6 Hz), 4.63 (ddd, 1H, *J* = 7.3, 7.3, 8.6 Hz), 6.36 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.1, 22.2, 37.1, 37.7, 47.3, 79.0, 159.4; IR (ATR) *ν* 1719, 1242, 1092, 1005 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 269 ([M]$^+$, 29), 142 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_7H_{12}INO_2$ (M) 268.9913, found 268.9911.

(*S*)-5-((*S*)-1-Iodobutyl)oxazolidin-2-one (2e)



Purified by silica gel column chromatography (EtOAc). colorless solid; mp: 123.2–125.5 °C; R_f 0.33 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, 3H, *J* = 7.0 Hz), 1.35–1.93 (m, 4H), 3.54 (dd, 1H, *J* = 6.5, 8.9 Hz), 3.76 (dd, 1H, *J* = 8.9, 8.9 Hz), 4.11 (td, 1H, *J* = 3.5, 10.5 Hz), 4.65 (m, 1H), 5.74 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.0, 22.7, 35.5, 36.6, 44.8, 78.2, 159.7; IR (ATR) *ν* 1751, 1719, 1248, 1087, 953 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 269 ([M]$^+$, 12), 142 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_7H_{12}INO_2$ (M) 268.9913, found 268.9912.

*The Stereochemistry of compounds **2d** and **2e** were determined by nOe difference spectra. Reaction yielding **2d** and **2e** proceeded stereospecifically as observed in our previous work where CO_2 fixation by unsaturated alcohols.[S14]

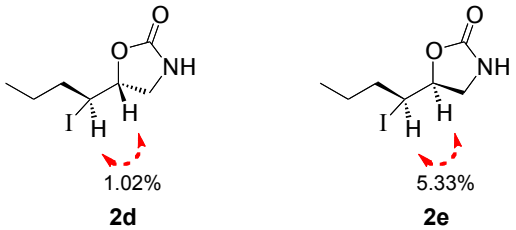
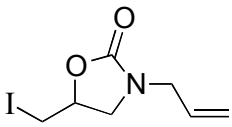


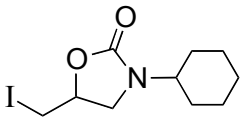
Figure S6. Schematic nOe difference of **2d** and **2e**

3-Allyl-5-(iodomethyl)oxazolidin-2-one (2f)



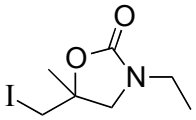
Purified by silica gel column chromatography (hexane/EtOAc 7:3). brown oil; R_f 0.26 (hexane/EtOAc 6:4); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.21–3.43 (m, 3H), 3.68 (t, 1H, *J* = 9.2 Hz), 3.87 (m, 2H), 4.58 (m, 1H), 5.26 (m, 2H), 5.71–5.84 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.88, 46.7, 49.7, 71.5, 118.9, 131.5, 156.8; IR (ATR) ν 1740, 1440, 1254, 1074, 1009, 912, 727 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 267 ([M]$^+$, 41), 140 ([M]$^+$-I, 62), 96 ([M]$^+$ – I – CO_2, 54), 41(C_3H_5, 100); HRMS (EI): *m/z* calcd for $C_7H_{10}INO_2$ (M) 266.9756, found 266.9749.

3-Cyclohexyl-5-(iodomethyl)oxazolidin-2-one (2g)



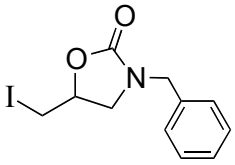
Purified by silica gel column chromatography (hexane/EtOAc 7:3). yellow solid; mp: 75.6–77.9 °C; R_f 0.33 (hexane/EtOAc 6:4); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.06–1.82 (m, 10H), 3.26 (m, 2H), 3.39 (dd, 1H, *J* = 3.8, 10.3 Hz), 3.66 (t, 1H, *J* = 8.9 Hz), 3.69 (m, 1H), 4.56 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.78, 25.25,25.30, 30.2, 30.3, 46.5, 52.6, 71.8, 77.2, 156.4; IR (ATR) ν 2924, 2855, 1726, 1433, 1248, 1067 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 309 ([M]$^+$, 80), 266 (62), 228 (100), 187 ([M]$^+$ – I, 66); HRMS (EI): *m/z* calcd for $C_{10}H_{16}INO_2$ (M) 309.0226, found 309.0223.

3-Ethyl-5-(iodomethyl)-5-methyloxazolidin-2-one (2h)



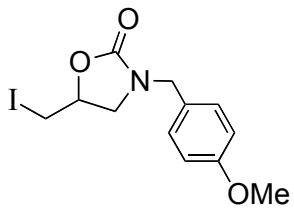
Purified by silica gel column chromatography (hexane/EtOAc 1:1). colorless solid; mp: 39.2–42.9 °C; R_f 0.08 (hexane/EtOAc 8:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18 (t, 3H, *J* = 7.8 Hz), 1.66 (s, 3H), 3.29–3.45 (m, 5H), 3.54 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.3, 13.2, 25.1, 38.5, 54.4, 76.5, 156.1; IR (ATR) ν 3493, 2978, 1746, 1450, 1303, 1051, 960, 801, 662 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 269 ([M]$^+$, 100), 128 ([M]$^+$ – I – CH_2, 78); HRMS (EI): *m/z* calcd for $C_7H_{12}INO_2$ (M) 268.9913, found 268.9915.

3-Benzyl-5-(iodomethyl)oxazolidin-2-one (2i)



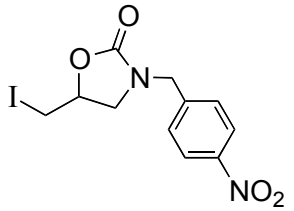
Purified by silica gel column chromatography (hexane/EtOAc 1:1). yellow oil; R_f 0.4 (hexane/EtOAc 1:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.11–3.37 (m, 3H), 3.55 (dd, 1H, *J* = 8.9, 8.9 Hz), 4.36 (d, 1H, *J* = 14.9 Hz), 4.47 (d, 1H, *J* = 14.9 Hz), 4.54 (m, 1H), 7.27–7.40 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.6, 48.0, 49.5, 71.5, 127.9, 128.0, 128.7, 135.1, 157.0; IR (ATR) ν 1739, 1485, 1429, 1254, 1087, 1064, 1008 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 317 ([M]$^+$, 15), 190 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_{11}H_{12}INO_2$ (M) 316.9913, found316.9914.

5-(Iodomethyl)-3-(4-methoxybenzyl)oxazolidin-2-one (2j)



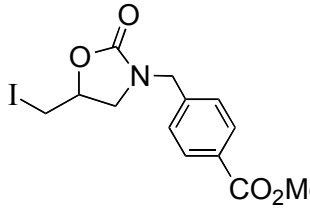
Purified by silica gel column chromatography (hexane/EtOAc 1:1). yellow oil; R_f 0.38 (hexane/EtOAc 5:5); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.10–3.26 (m, 2H), 3.33 (dd, 1H, *J* = 4.1, 10.5 Hz), 3.53 (dd, 1H, *J* = 8.6, 8.6 Hz), 3.80 (s, 3H), 4.31 (d, 1H, *J* = 14.9 Hz), 4.40 (d, 1H, *J* = 14.9 Hz), 4.52 (m, 1H), 6.88 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.5, 47.5, 49.4, 55.2, 71.6, 114.1, 127.2, 129.5, 157.0, 159.2; IR (ATR) *ν* 2931, 1740, 1610, 1510, 1437, 1242, 1010 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 347 ([M]$^+$, 24), 220 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_{12}H_{14}INO_3$ (M) 347.0018, found 347.0018.

5-(Iodomethyl)-3-(4-nitrobenzyl)oxazolidin-2-one (2k)



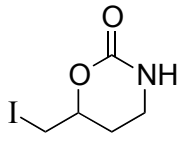
Purified by silica gel column chromatography (hexane/EtOAc 1:1). colorless solid; dec: 130.4–131.6 °C; R_f 0.2 (hexane/EtOAc 1:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.20–3.43 (m, 3H), 3.64 (dd, 1H, *J* = 8.6, 8.6 Hz), 4.56 (d, 2H, *J* = 9.5 Hz), 4.62 (m, 1H), 7.50 (d, 2H, *J* = 8.6 Hz), 8.23 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.5, 47.6, 50.0, 71.7, 124.1, 128.8, 142.7, 147.7, 157.2; IR (ATR) *ν* 1748, 1728, 1514, 1444, 1339, 1267, 1076, 1011 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 362 ([M]$^+$, 14), 235 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_{11}H_{11}IN_2O_4$ (M) 361.9763, found 361.9765.

Methyl 4-((5-(iodomethyl)-2-oxooxazolidin-3-yl)methyl)benzoate (2l)



Purified by silica gel column chromatography (hexane/EtOAc 1:1). colorless solid; dec: 97.6–98.8 °C; R_f 0.28 (hexane/EtOAc 1:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.19 (dd, 1H, *J* = 6.5, 8.9 Hz), 3.67–3.40 (m, 2H), 3.60 (dd, 1H, *J* = 8.9, 8.9 Hz), 3.92 (s, 3H), 4.49 (d, 2H, *J* = 3.2 Hz), 4.57 (m, 1H), 7.38 (d, 2H, *J* = 8.4 Hz), 8.03 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 6.7, 47.7, 49.6, 52.0, 71.5, 127.8, 129.7, 129.9, 140.3, 157.0, 166.3; IR (ATR) *ν* 1719, 1269, 1107, 1074, 1005 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 375 ([M]$^+$, 18), 248 ([M]$^+$ – I, 100); HRMS (EI): *m/z* calcd for $C_{13}H_{14}INO_4$ (M) 374.9968, found 374.9970.

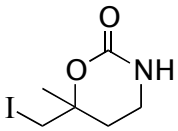
6-(Iodomethyl)-1,3-oxazinan-2-one (2m)



Purified by silica gel column chromatography (EtOAc). colorless solid; dec: 141.4–143.6 °C; R_f 0.11 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.90 (m, 1H), 2.28 (m, 1H), 3.28 (dd, 1H, *J* = 7.6, 10.5 Hz), 3.39–3.44 (m, 3H), 4.32 (m, 1H), 6.15 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 5.4, 26.2, 38.4, 76.2, 153.9; IR (ATR) ν 1686, 1668, 1479, 1300, 1200, 1130, 1047 cm^{-1}; MS (EI): m/z (relative

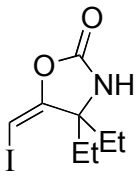
intensity, %) 241 ([M]$^+$, 100), 114 ([M]$^+$ – I, 55), 100 ([M]$^+$ – I – CH_2, 56); HRMS (EI): m/z calcd for $C_5H_8INO_2$ (M) 240.9600, found 240.9607.

6-(Iodomethyl)-1,3-oxazinan-2-one (2n)



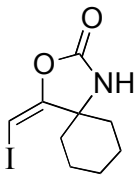
Purified by silica gel column chromatography (EtOAc). colorless solid; dec: 137.6−138.5 °C; R_f 0.11 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.94 (m, 1H), 2.18 (m, 1H), 3.35 (m, 4H), 6.93 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.9, 24.9, 29.4, 36.5, 78.6, 153.8; IR (ATR) ν 1702, 1655, 1321, 1111, 1020 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 255 ([M]$^+$, 5), 128 ([M]$^+$ – I, 16), 114 ([M]$^+$ – I – CH_2, 100); HRMS (EI): *m/z* calcd for $C_6H_{10}INO_2$ (M) 254.9756, found 254.9758.

(*E*)-4,4-Diethyl-5-(iodomethylene)oxazolidin-2-one (2p)



Purified by Preparative gel permeation liquid chromatography. yellow oil; R_f 0.49 (hexane/EtOAc 8:2); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, 6H, *J* = 7.3 Hz), 1.66 (dddd, 2H, *J* = 7.3, 7.3, 7.3, 14.6 Hz), 2.28 (dddd, 2H, *J* = 7.3, 7.3, 7.3, 14.6 Hz), 5.80 (s, 1H), 7.01 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 7.6, 29.6, 47.7, 68.1, 153.5, 155.3; IR (ATR) ν 1772, 1651, 1352, 1080, 968 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 281 ([M]$^+$, 15), 252 ([M]$^+$ – C_2H_5, 100); HRMS (EI): *m/z* calcd for $C_8H_{12}INO_2$ (M) 280.9913, found 280.9918.

(*E*)-4-(Iodomethylene)-3-oxa-1-azaspiro[4.5]decan-2-one (2q)



Purified by Preparative gel permeation liquid chromatography. yellow solid; dec: 178.8 °C; R_f 0.33 (hexane/EtOAc 7:3); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.22–1.84 (m, 8H), 2.51 (td, 2H, *J* = 4.1, 13.2 Hz), 5.70 (s, 1H), 7.89 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.8, 24.5, 33.5, 46.6, 63.4, 155.0, 155.9; IR (ATR) ν 1780, 1744, 1647, 1043 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 293 ([M]$^+$, 100), 166 ([M]$^+$ – I, 84); HRMS (EI): *m/z* calcd for $C_8H_{12}INO_2$ (M) 292.9913, found 292.9911.

*The product **2q** was recrystallized from its dichloromethane/hexane solution to give the suitable crystal for X-ray crystallographic analysis.

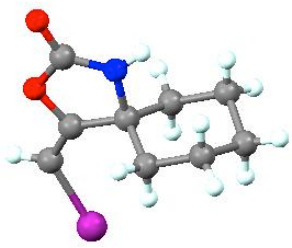
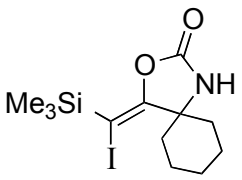


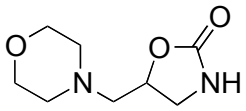
Figure S7. Molecular structure of **2q**

(*E*)-4-(Iodo(trimethylsilyl)methylene)-3-oxa-1-azaspiro[4.5]decan-2-one (2r)



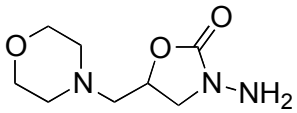
Purified by Preparative gel permeation liquid chromatography. yellow solid; dec: 213.0–214.5 °C; R_f 0.45 (hexane/EtOAc 7:3); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.28 (s, 9H), 1.26-1.83 (m, 8H), 2.82 (td, 2H, *J* = 13.2, 3.8 Hz), 5.70 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 0.53, 22.1, 22.4, 33.0, 65.2, 72.0, 154.7, 159.4; IR (ATR) ν 1769, 1609, 1352, 1327, 1246, 1177, 1036, 1016, 978, 840 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 365 ([M]$^+$, 100), 240 (73); HRMS (EI): *m/z* calcd for $C_{12}H_{20}INO_2Si$ (M) 365.0308, found 365.0306.

5-(Morpholinomethyl)oxazolidin-2-one (3)



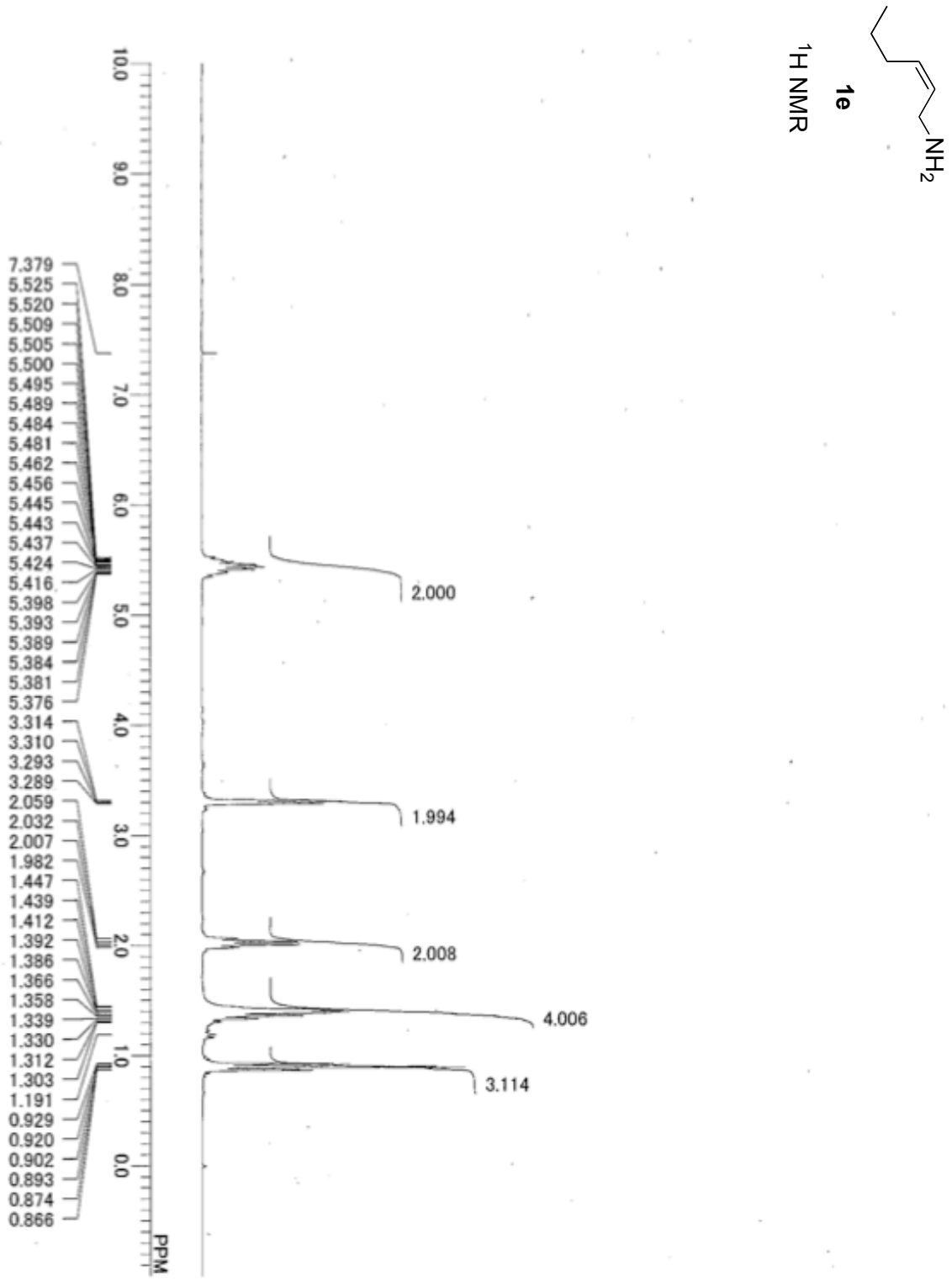
Purified by NH-silica gel column chromatography (EtOAc). yellow solid; dec: 113.7 °C; R_f 0.55 ($CHCl_3$/MeOH 99:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.48–2.75 (m, 6H), 3.36 (dd, 1H, *J* = 8.1, 8.1 Hz), 3.64–3.72 (m, 5H), 4.79 (m, 1H), 6.70 (br, s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 44.3, 54.2, 61.7, 66.8, 75.0, 159.9; IR (ATR) ν 1740, 1234, 1112, 1084 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 186 ([M]$^+$, 4), 100 ([M]$^+$ – C_4H_8NO, 100); HRMS (EI): *m/z* calcd for $C_8H_{14}N_2O_3$ (M) 186.1004, found 180.1006.

3-Amino-5-(morpholinomethyl)oxazolidin-2-one (AMOZ)

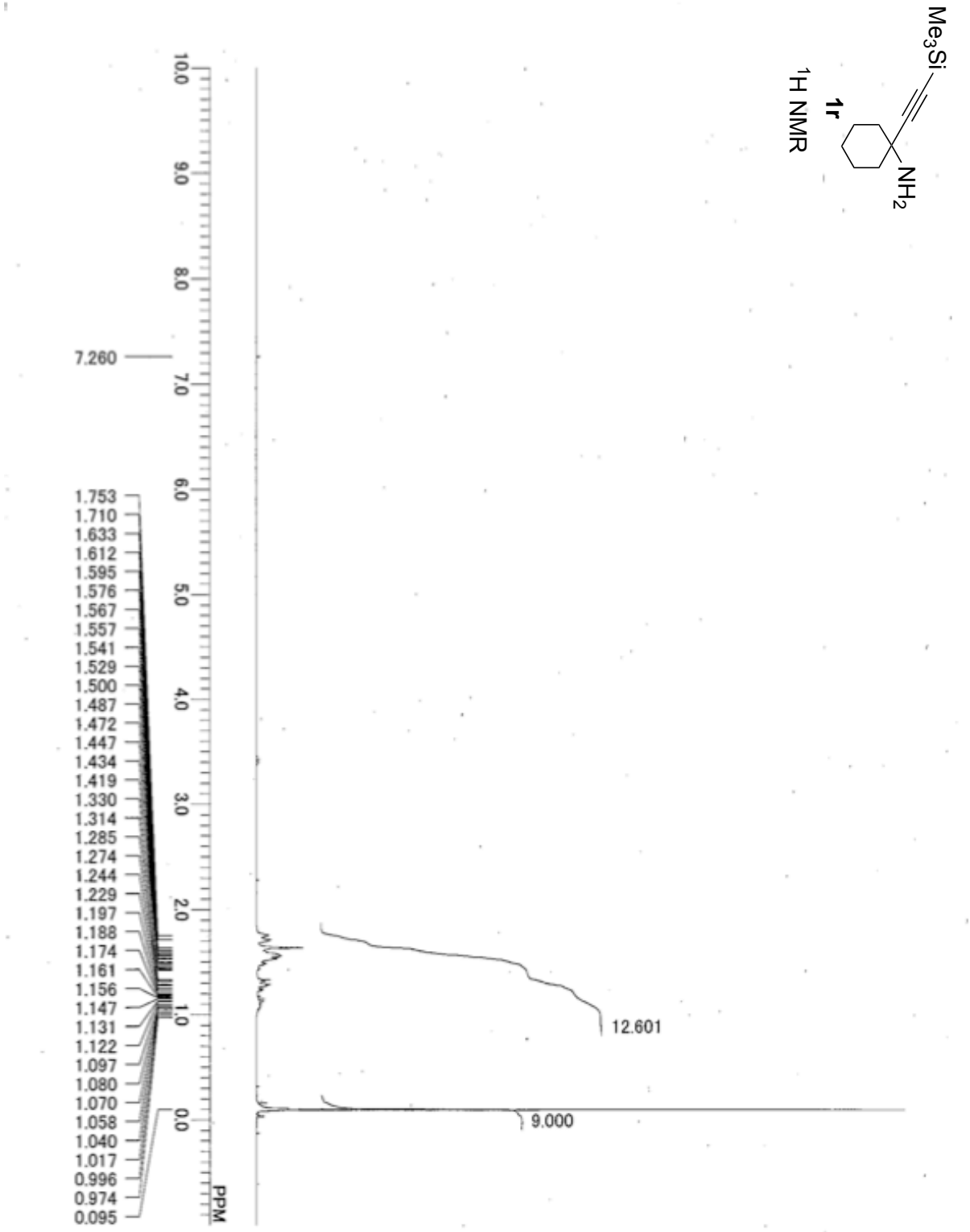


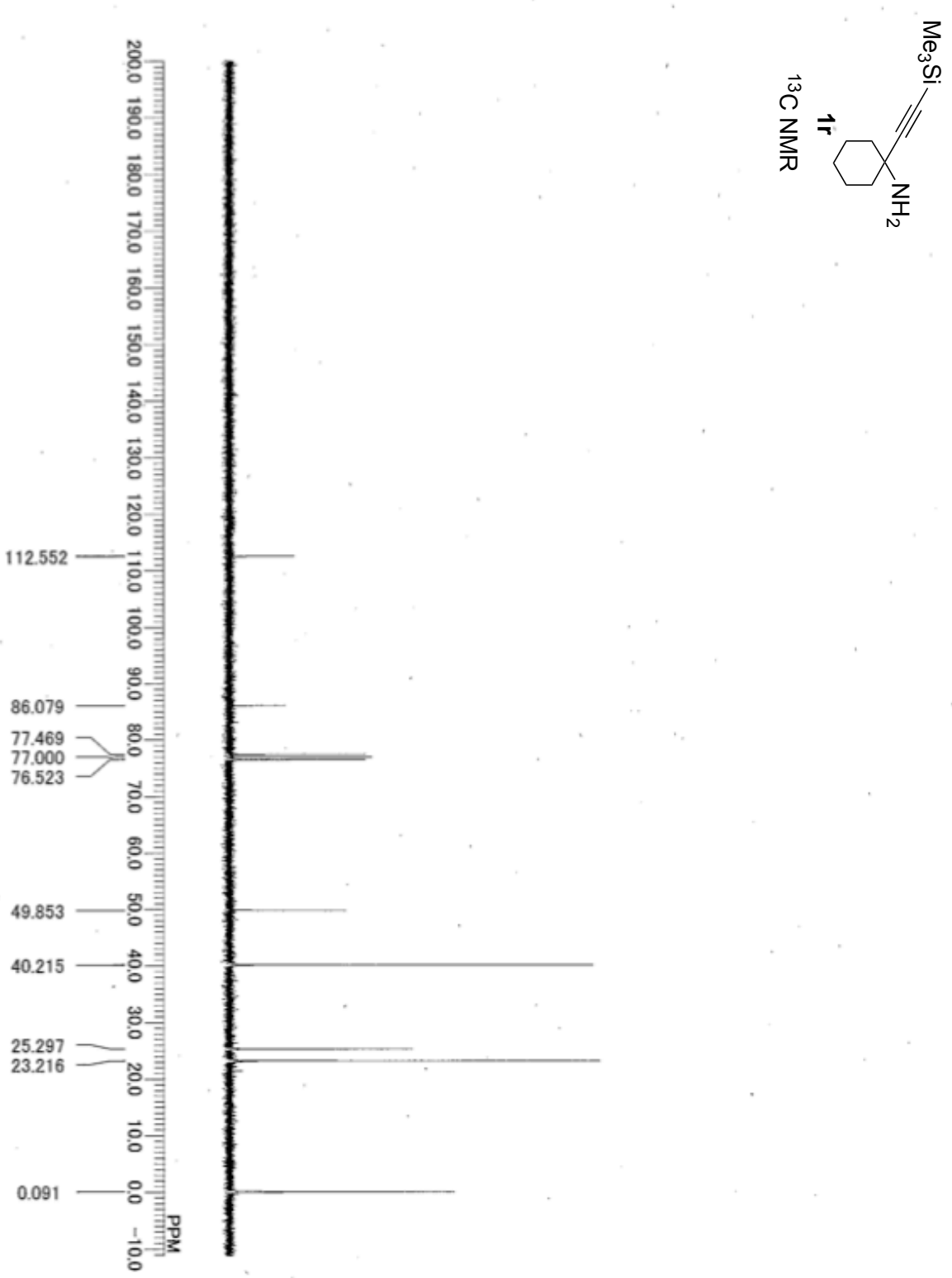
Purified by NH-silica gel column chromatography (EtOAc). yellow solid; dec: 110.6–112.9 °C; R_f 0.43 ($CHCl_3$/MeOH 99:1); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.50–2.74 (m, 6H), 3.43 (dd, 1H, *J* = 8.1, 8.1 Hz), 3.70–3.79 (m, 5H), 4.00 (br, s, 2H), 4.65 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 52.0, 54.2, 61.3, 66.7, 71.2, 158.9; IR (ATR) ν 1748, 1128, 1112, 964, 758 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 201 ([M]$^+$, 1), 185 ([M]$^+$ – NH_2, 1), 100, ([M]$^+$ – C_4H_8NO – NH_2, 100); HRMS (EI): *m/z* calcd for $C_8H_{15}N_3O_2$ (M) 201.1113, found 201.1117.

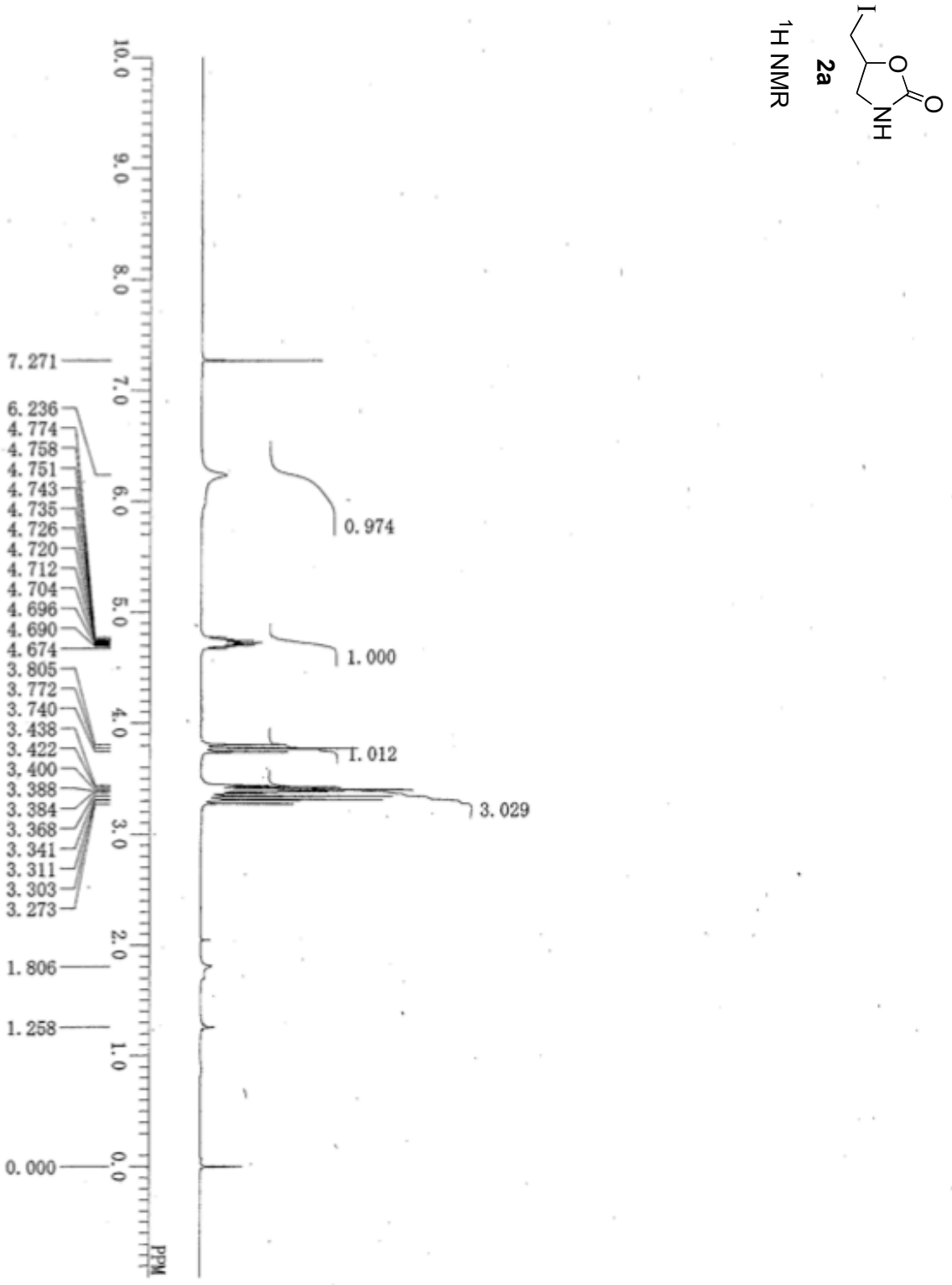
^{1}H and ^{13}C NMR charts of compounds

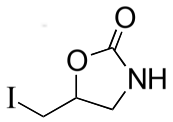


NH2
1e
13C NMR
130.792
130.184
77.477
77.000
76.531
38.521
29.006
22.525
13.413
PPM


Me3Si
NH2
1r
1H NMR
7.260
1.753
1.710
1.633
1.612
1.595
1.576
1.567
1.557
1.541
1.529
1.500
1.487
1.472
1.447
1.434
1.419
1.330
1.314
1.285
1.274
1.244
1.229
1.197
1.188
1.174
1.161
1.156
1.147
1.131
1.122
1.097
1.080
1.070
1.058
1.040
1.017
0.996
0.974
0.095
12.601
9.000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

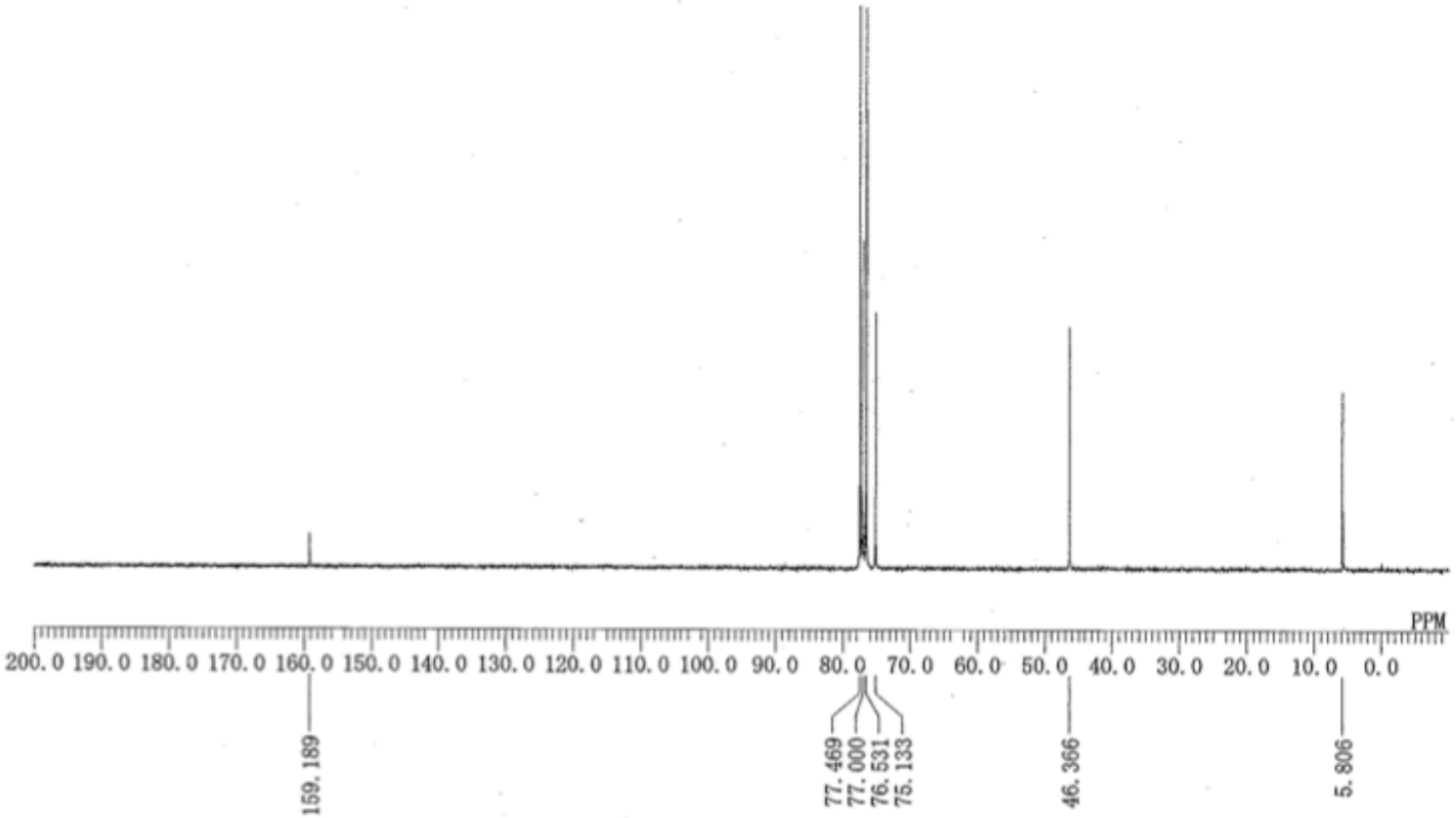

Me3Si
NH2
1r
13C NMR
112.552
86.079
77.469
77.000
76.523
49.853
40.215
25.297
23.216
0.091
PPM

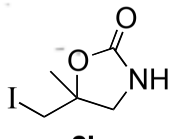

I
O
O
NH
2a
^{1}H NMR
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.271
6.236
4.774
4.758
4.751
4.743
4.735
4.726
4.720
4.712
4.704
4.696
4.690
4.674
3.805
3.772
3.740
3.438
3.422
3.400
3.388
3.384
3.368
3.341
3.311
3.303
3.273
1.806
1.258
0.000
0.974
1.000
1.012
3.029


O
O
NH
I

2a

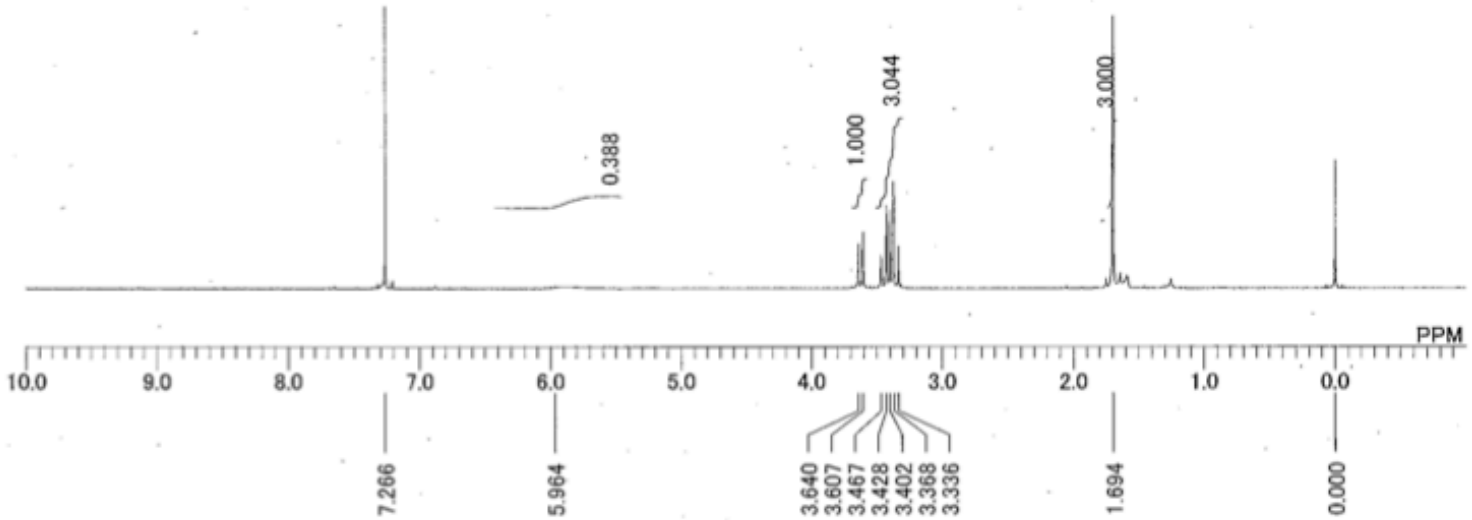
^{13}C NMR

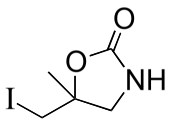

PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
159.189
77.469
77.000
76.531
75.133
46.366
5.806


O
O
NH
I

2b

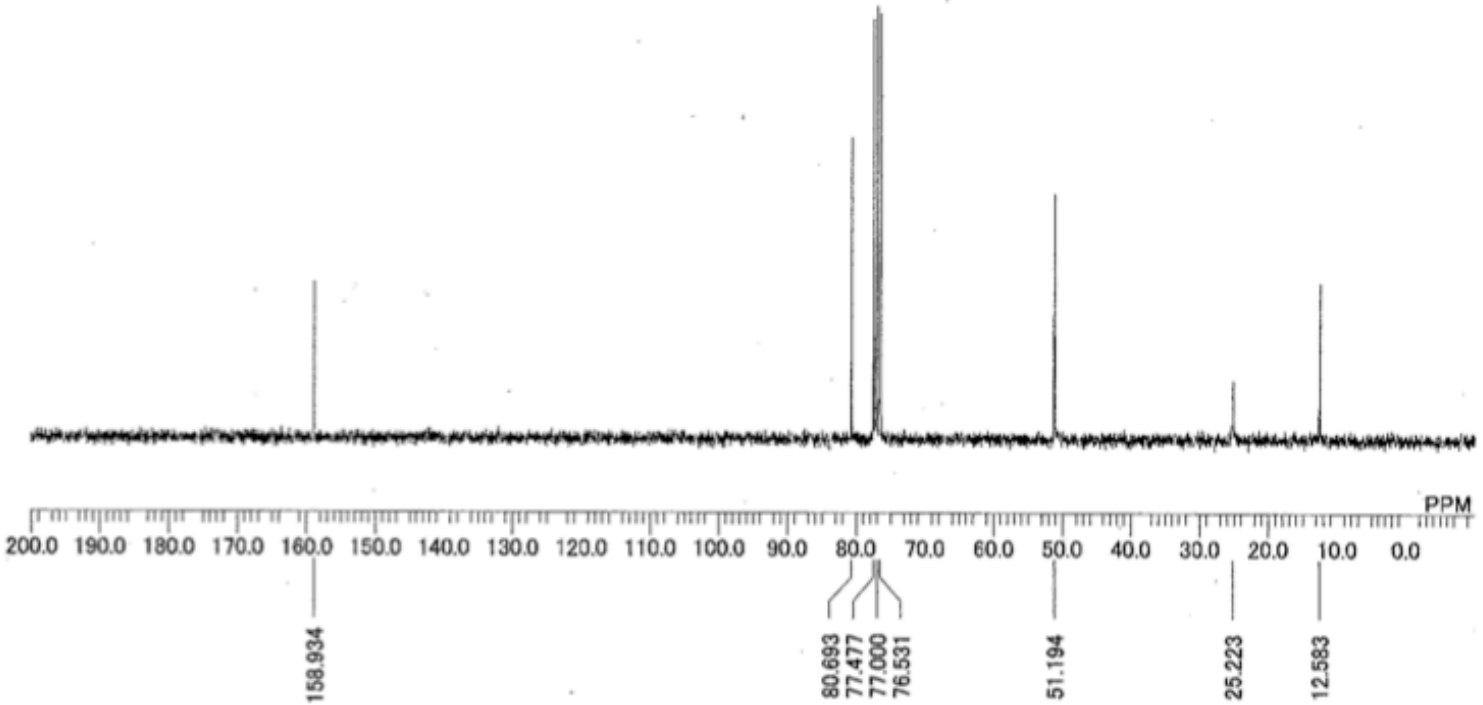
^{1}H NMR


0.388
1.000
3.044
3.000
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.266
5.964
3.640
3.607
3.467
3.428
3.402
3.368
3.336
1.694
0.000


O
O
NH
I

2b

^{13}C NMR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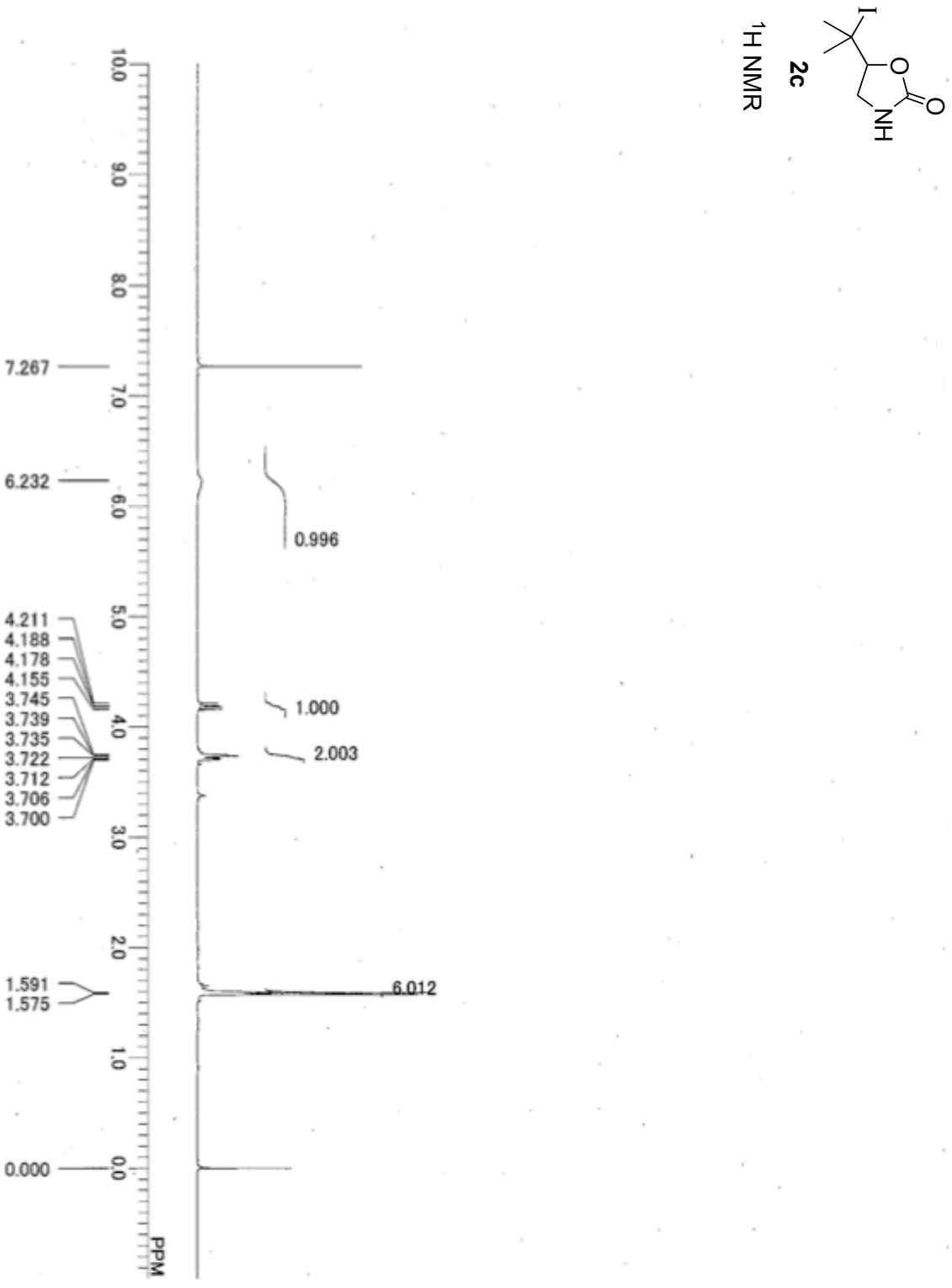
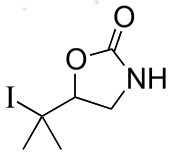
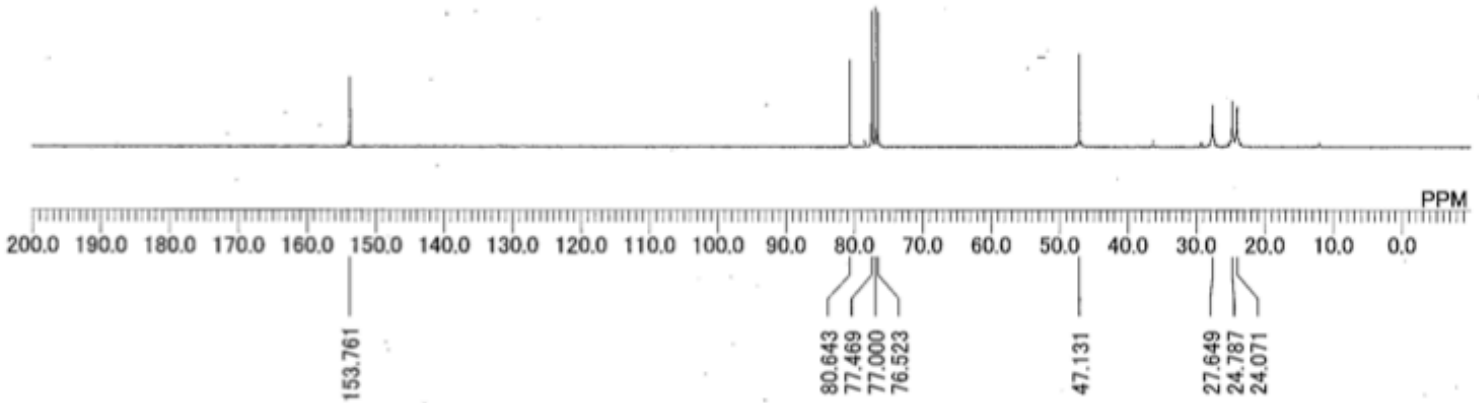
158.934
80.693
77.477
77.000
76.531
51.194
25.223
12.583

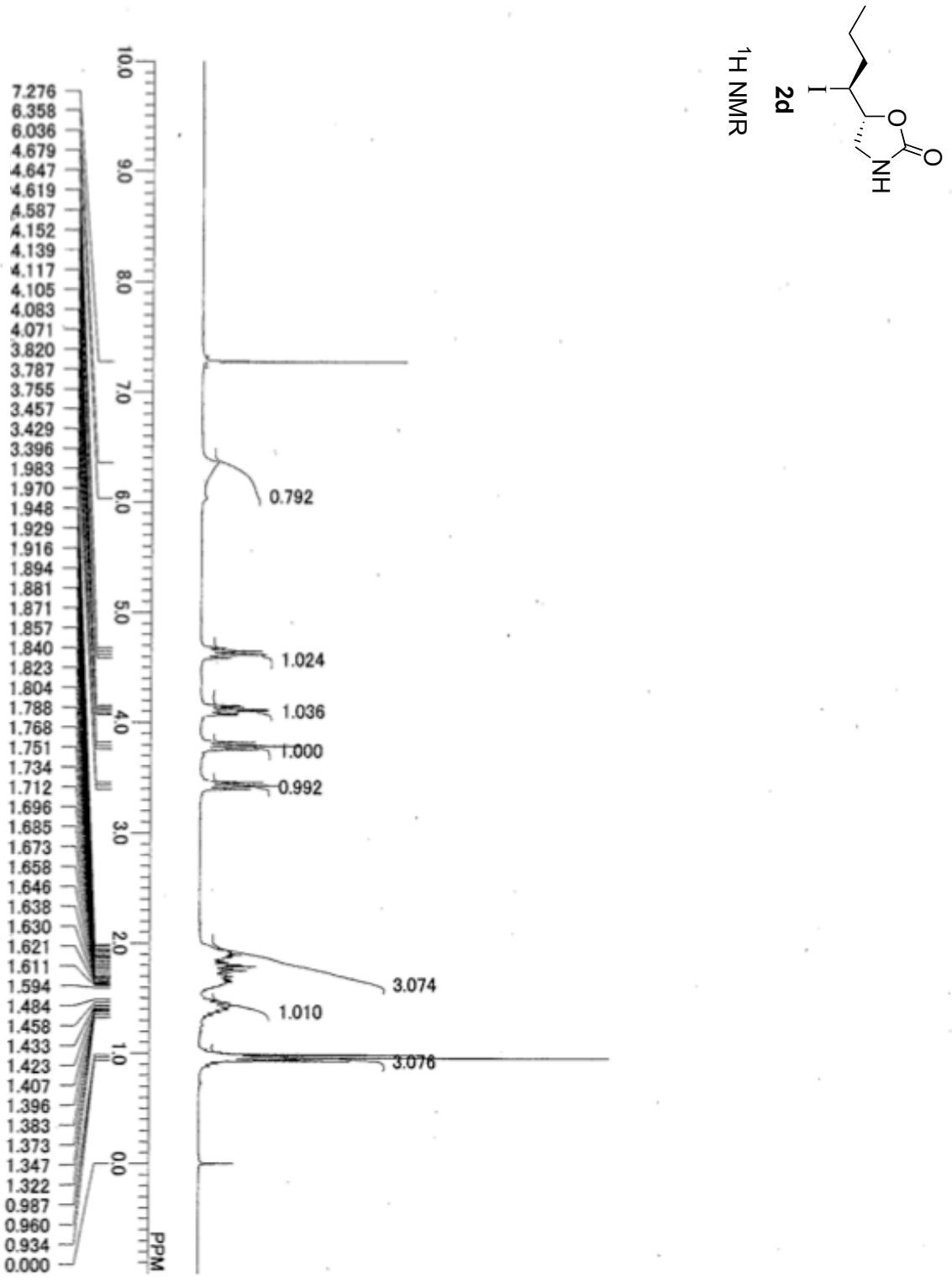

2c
^{1}H NMR
I
O
O
NH
7.267
6.232
4.211
4.188
4.178
4.155
3.745
3.739
3.735
3.722
3.712
3.706
3.700
1.591
1.575
0.000
0.996
1.000
2.003
6.012
PPM

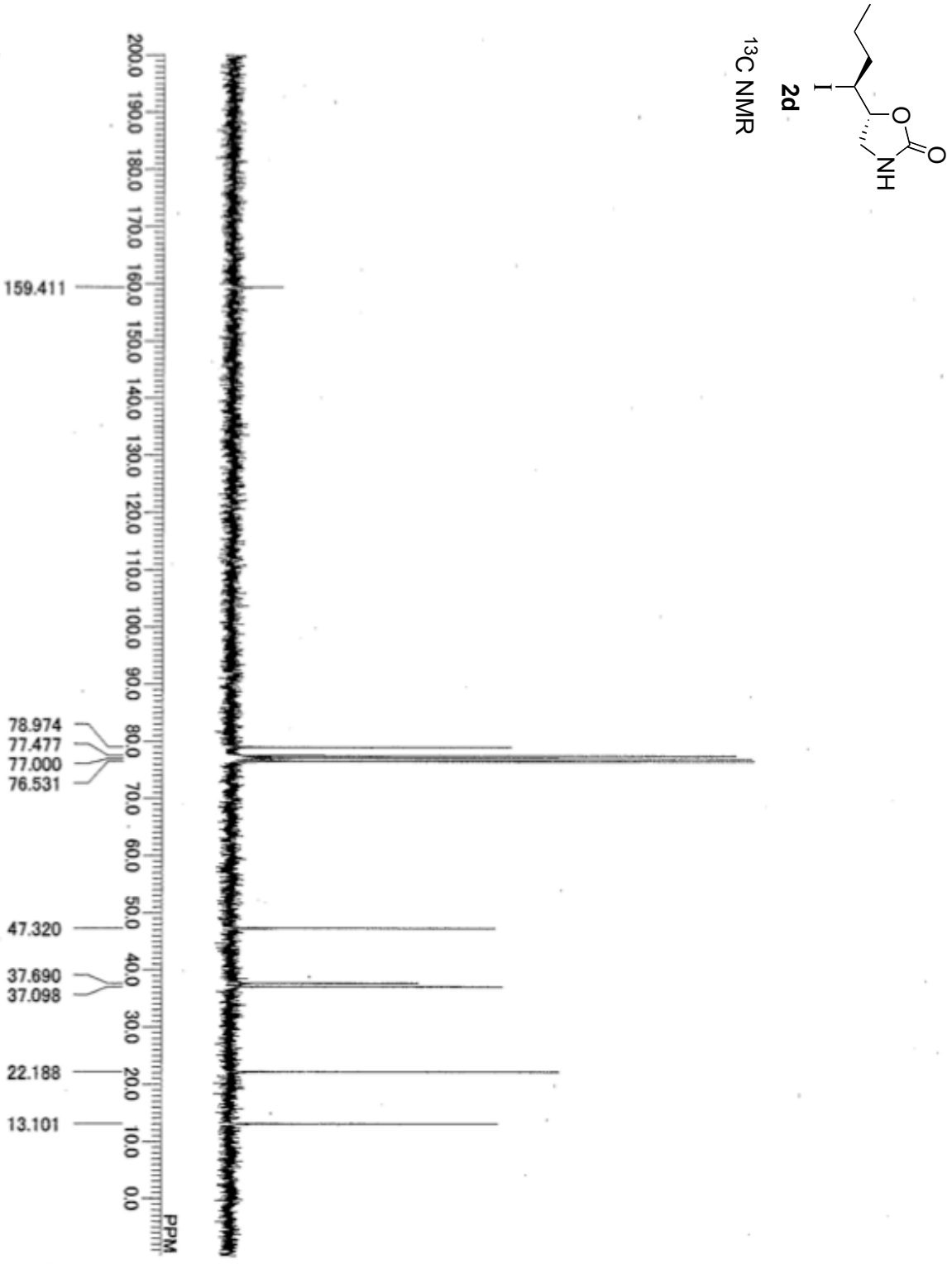

O
O
NH
I

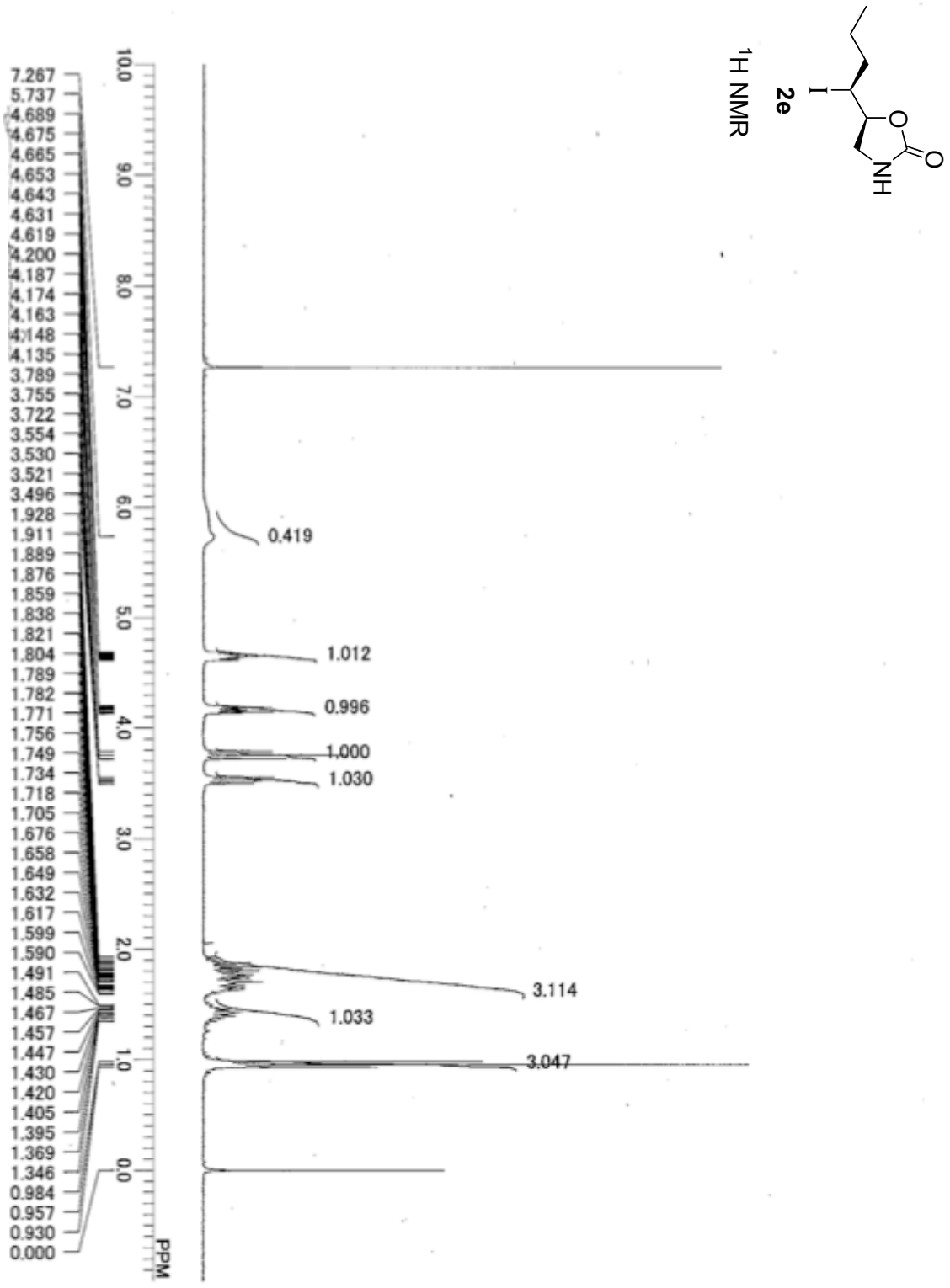
2c

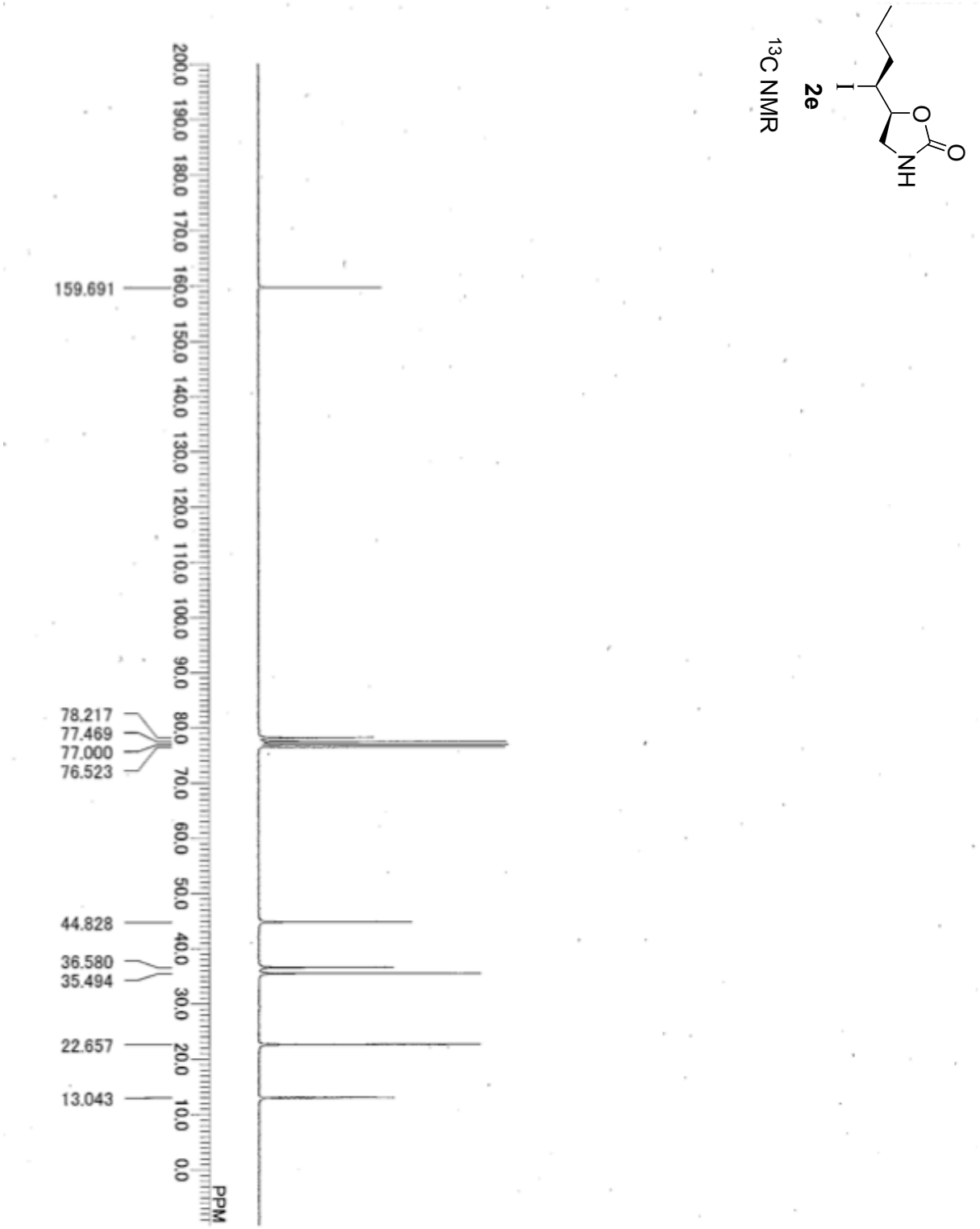
^{13}C NMR

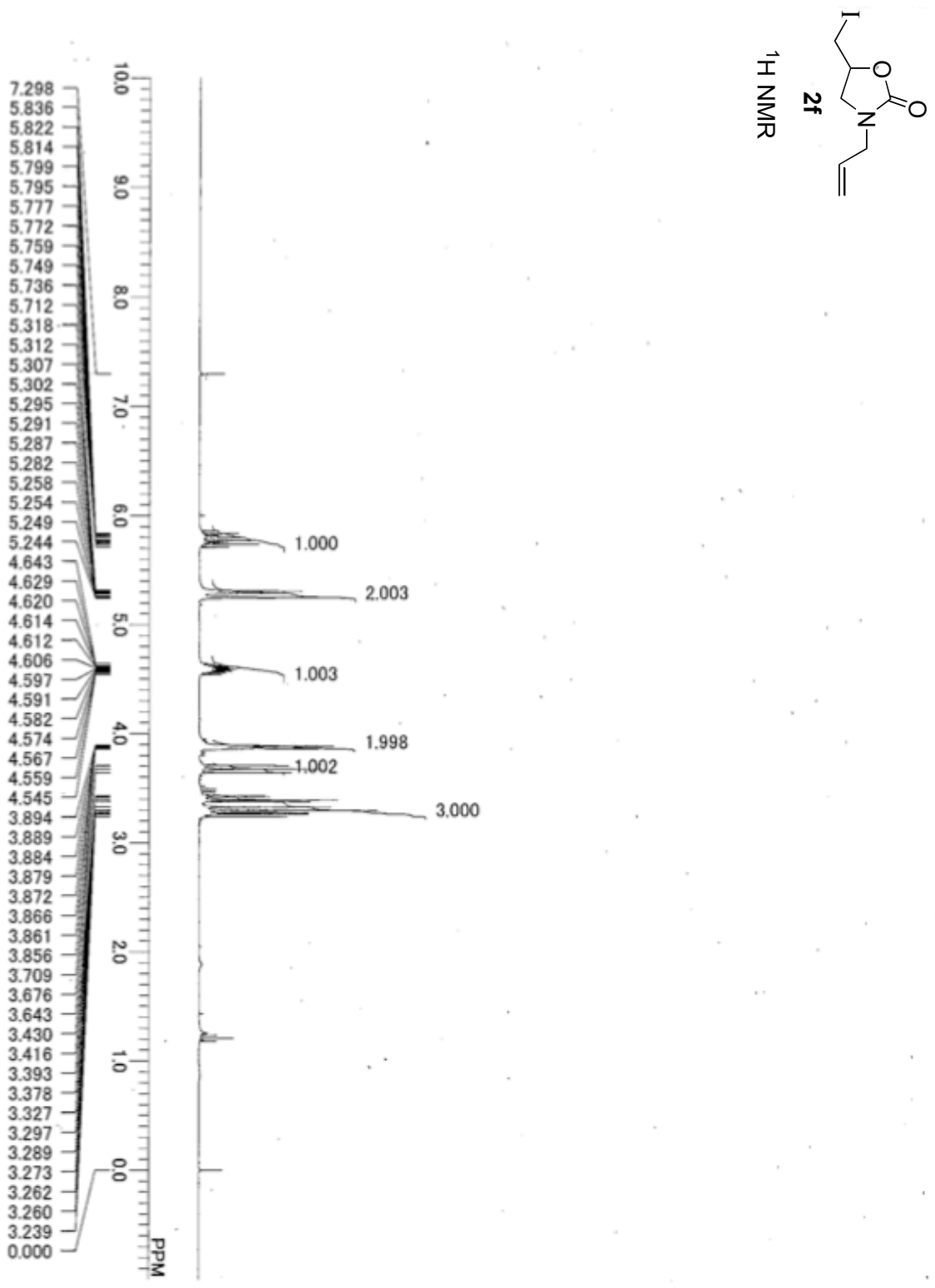

PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
153.761
80.643
77.469
77.000
76.523
47.131
27.649
24.787
24.071

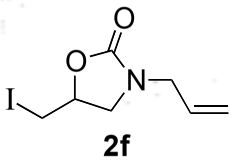

2d
^{1}H NMR
NH
O
O
I
7.276
6.358
6.036
4.679
4.647
4.619
4.587
4.152
4.139
4.117
4.105
4.083
4.071
3.820
3.787
3.755
3.457
3.429
3.396
1.983
1.970
1.948
1.929
1.916
1.894
1.881
1.871
1.857
1.840
1.823
1.804
1.788
1.768
1.751
1.734
1.712
1.696
1.685
1.673
1.658
1.646
1.638
1.630
1.621
1.611
1.594
1.484
1.458
1.433
1.423
1.407
1.396
1.383
1.373
1.347
1.322
0.987
0.960
0.934
0.000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
0.792
1.024
1.036
1.000
0.992
3.074
1.010
3.076


2d
^{13}C NMR
159.411
78.974
77.477
77.000
76.531
47.320
37.690
37.098
22.188
13.101
PPM


2e
^{1}H NMR
7.267
5.737
4.689
4.675
4.665
4.653
4.643
4.631
4.619
4.200
4.187
4.174
4.163
4.148
4.135
3.789
3.755
3.722
3.554
3.530
3.521
3.496
1.928
1.911
1.889
1.876
1.859
1.838
1.821
1.804
1.789
1.782
1.771
1.756
1.749
1.734
1.718
1.705
1.676
1.658
1.649
1.632
1.617
1.599
1.590
1.491
1.485
1.467
1.457
1.447
1.430
1.420
1.405
1.395
1.369
1.346
0.984
0.957
0.930
0.000
0.419
1.012
0.996
1.000
1.030
3.114
1.033
3.047
PPM

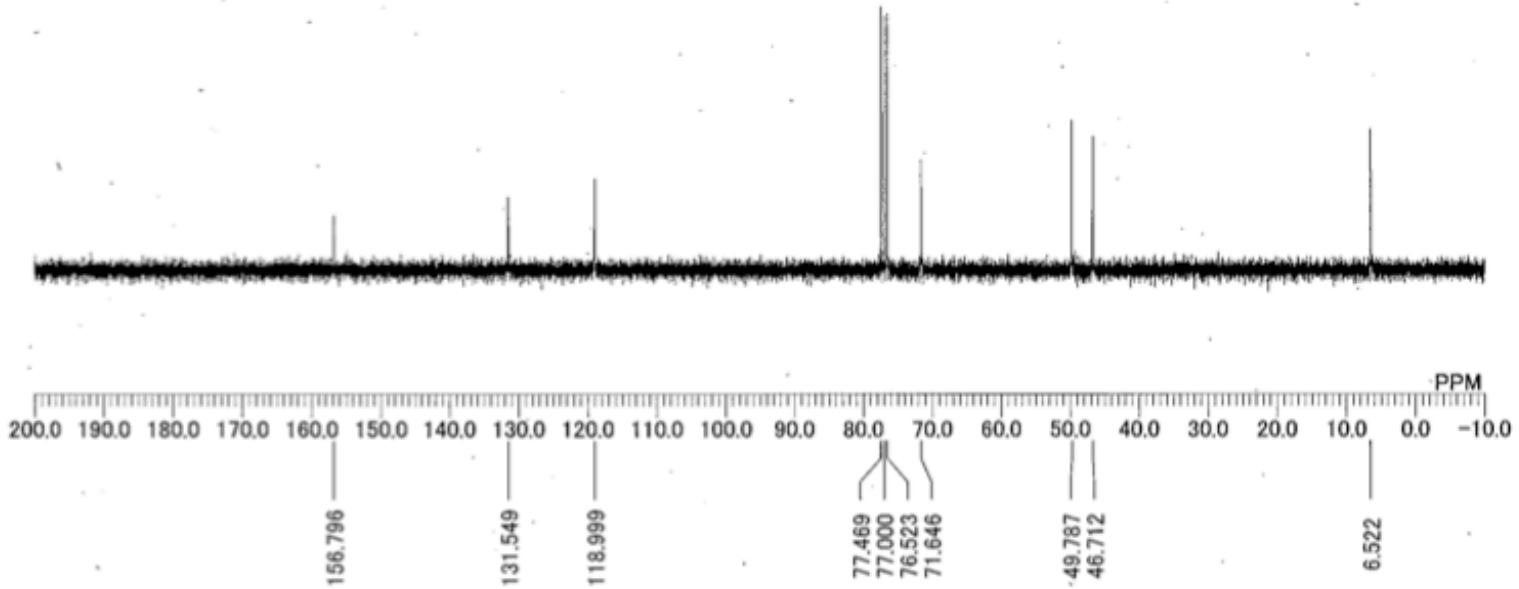

2e
^{13}C NMR
159.691
78.217
77.469
77.000
76.523
44.828
36.580
35.494
22.657
13.043
PPM

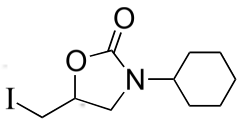

2f
^{1}H NMR
7.298
5.836
5.822
5.814
5.799
5.795
5.777
5.772
5.759
5.749
5.736
5.712
5.318
5.312
5.307
5.302
5.295
5.291
5.287
5.282
5.258
5.254
5.249
5.244
4.643
4.629
4.620
4.614
4.612
4.606
4.597
4.591
4.582
4.574
4.567
4.559
4.545
3.894
3.889
3.884
3.879
3.872
3.866
3.861
3.856
3.709
3.676
3.643
3.430
3.416
3.393
3.378
3.327
3.297
3.289
3.273
3.262
3.260
3.239
0.000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
1.000
2.003
1.003
1.998
1.002
3.000


O
O
N
I

2f

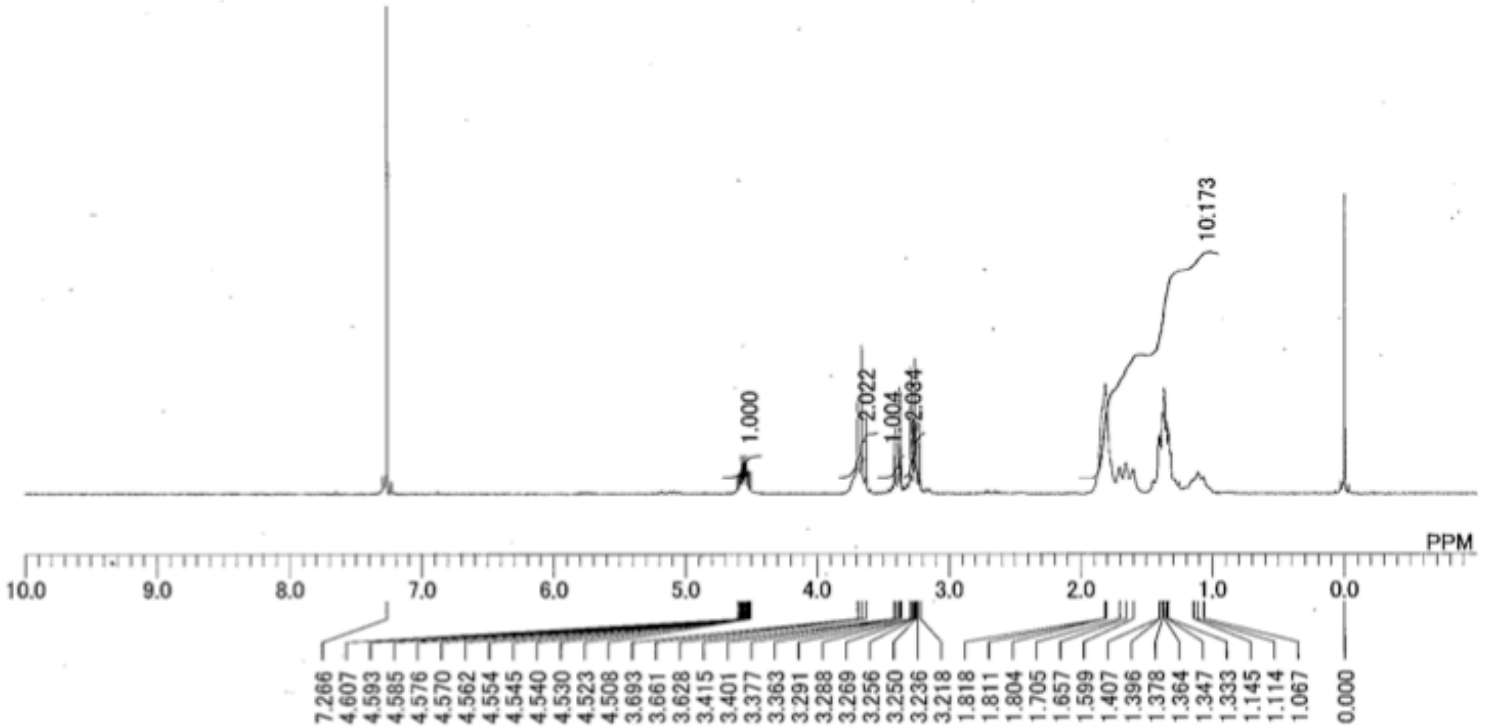
^{13}C NMR


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 −10.0
156.796
131.549
118.999
77.469
77.000
76.523
71.646
49.787
46.712
6.522



2g

^{1}H NMR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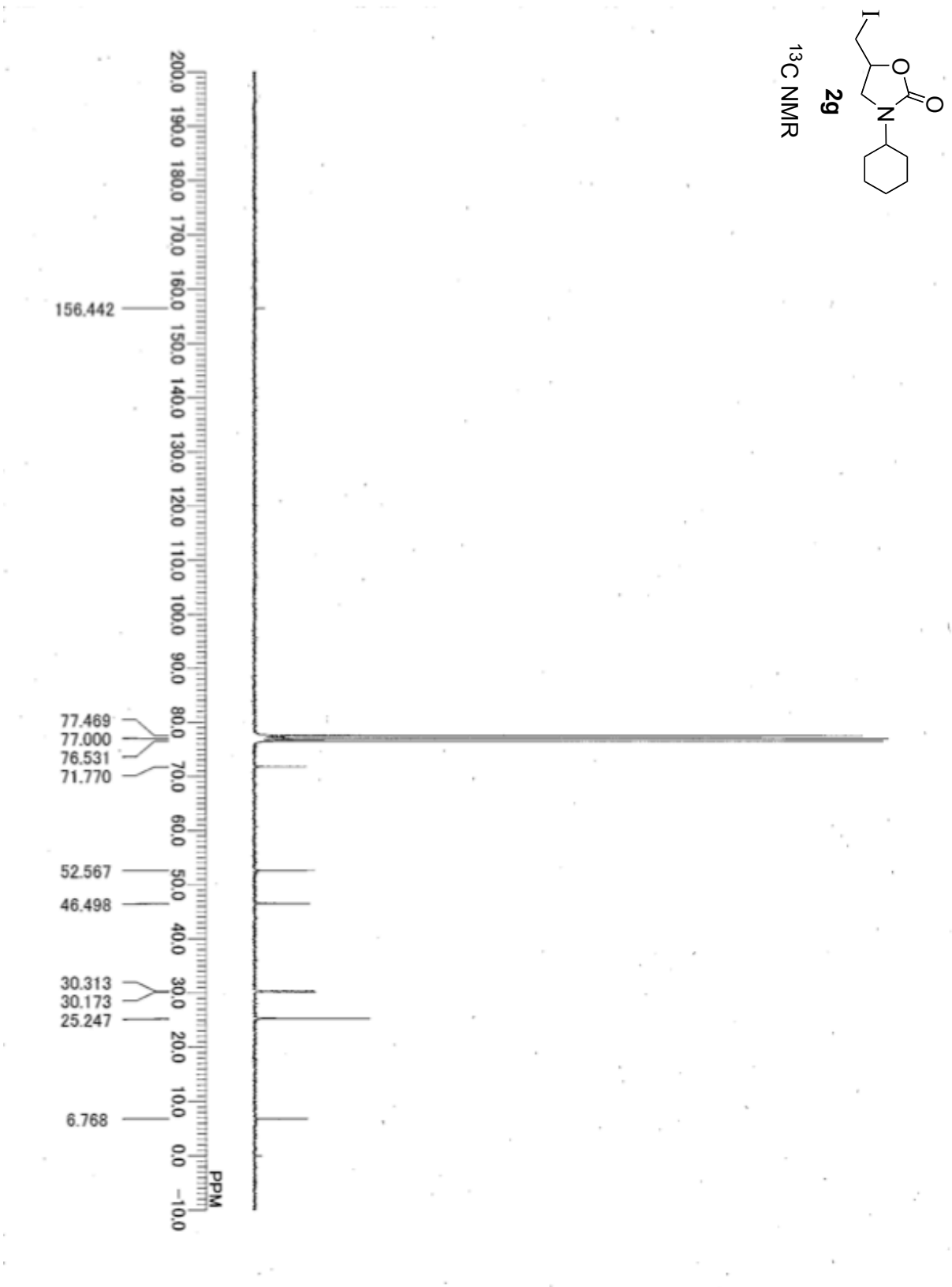
2.022
1.004
2.084
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.266
4.607
4.593
4.585
4.576
4.570
4.562
4.554
4.545
4.540
4.530
4.523
4.508
3.693
3.661
3.628
3.415
3.401
3.377
3.363
3.291
3.288
3.269
3.256
3.250
3.236
3.218
1.818
1.811
1.804
1.705
1.657
1.599
1.407
1.396
1.378
1.364
1.347
1.333
1.145
1.114
1.067
0.000


2g
13C NMR
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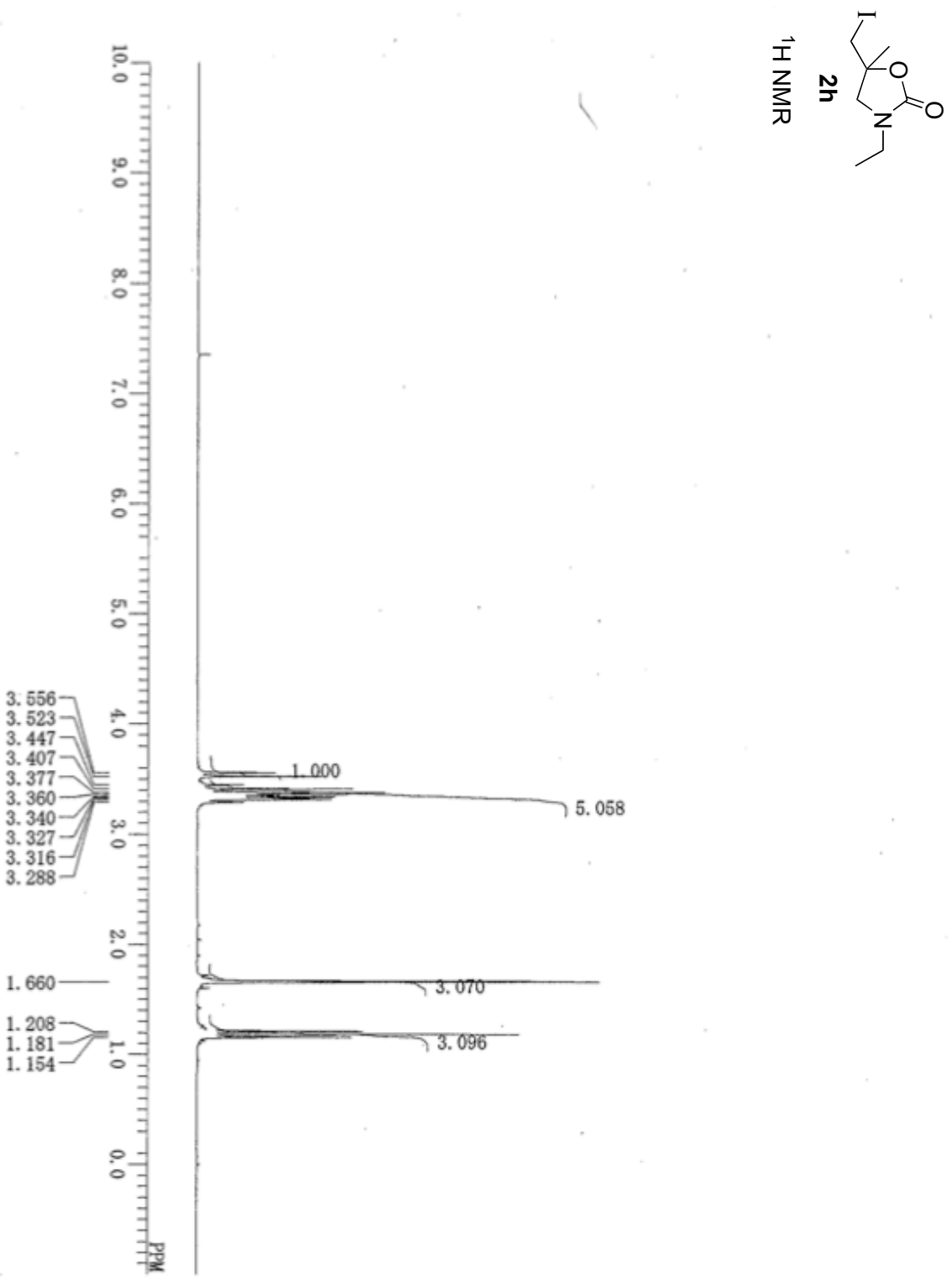
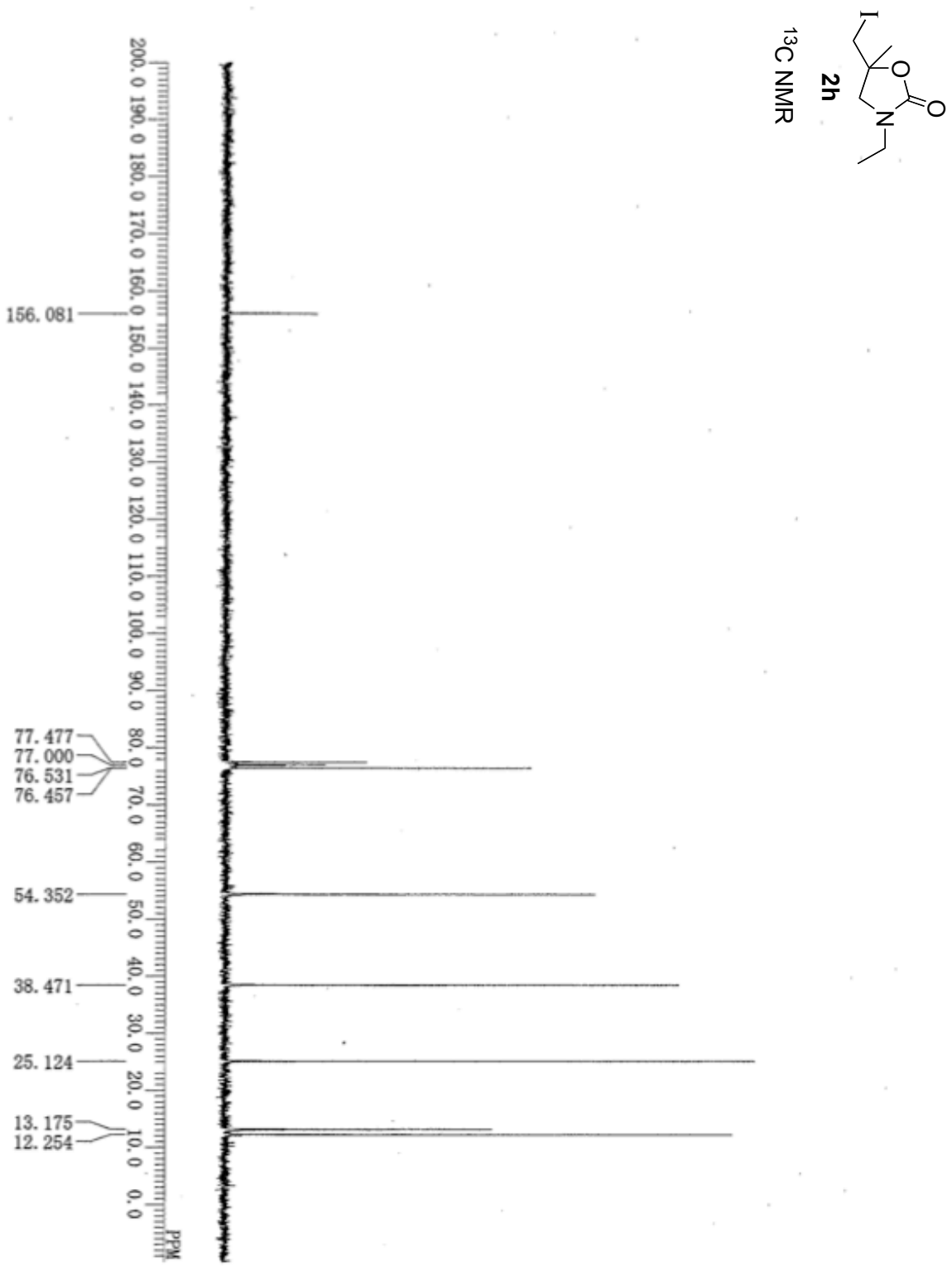
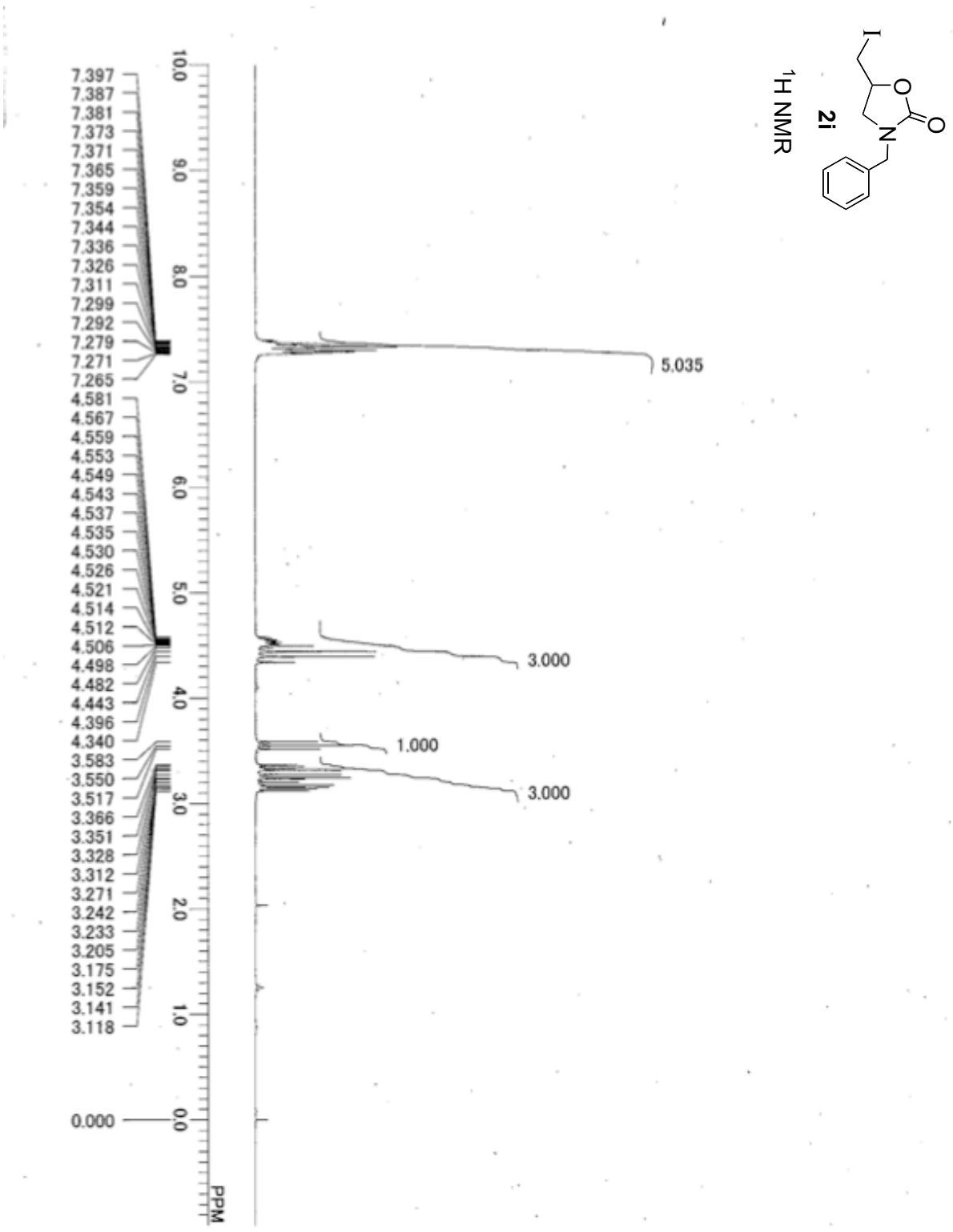
77.000
76.531
71.770
52.567
46.498
30.313
30.173
25.247
6.768
PPM


2h
^{1}H NMR
3.556
3.523
3.447
3.407
3.377
3.360
3.340
3.327
3.316
3.288
1.660
1.208
1.181
1.154
1.000
5.058
3.070
3.096
PPM


2h
^{13}C NMR
156.081
77.477
77.000
76.531
76.457
54.352
38.471
25.124
13.175
12.254
PPM


2i
^{1}H NMR
7.397
7.387
7.381
7.373
7.371
7.365
7.359
7.354
7.344
7.336
7.326
7.311
7.299
7.292
7.279
7.271
7.265
4.581
4.567
4.559
4.553
4.549
4.543
4.537
4.535
4.530
4.526
4.521
4.514
4.512
4.506
4.498
4.482
4.443
4.396
4.340
3.583
3.550
3.517
3.366
3.351
3.328
3.312
3.271
3.242
3.233
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3.175
3.152
3.141
3.118
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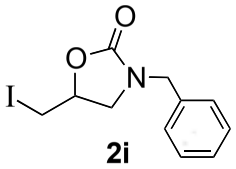
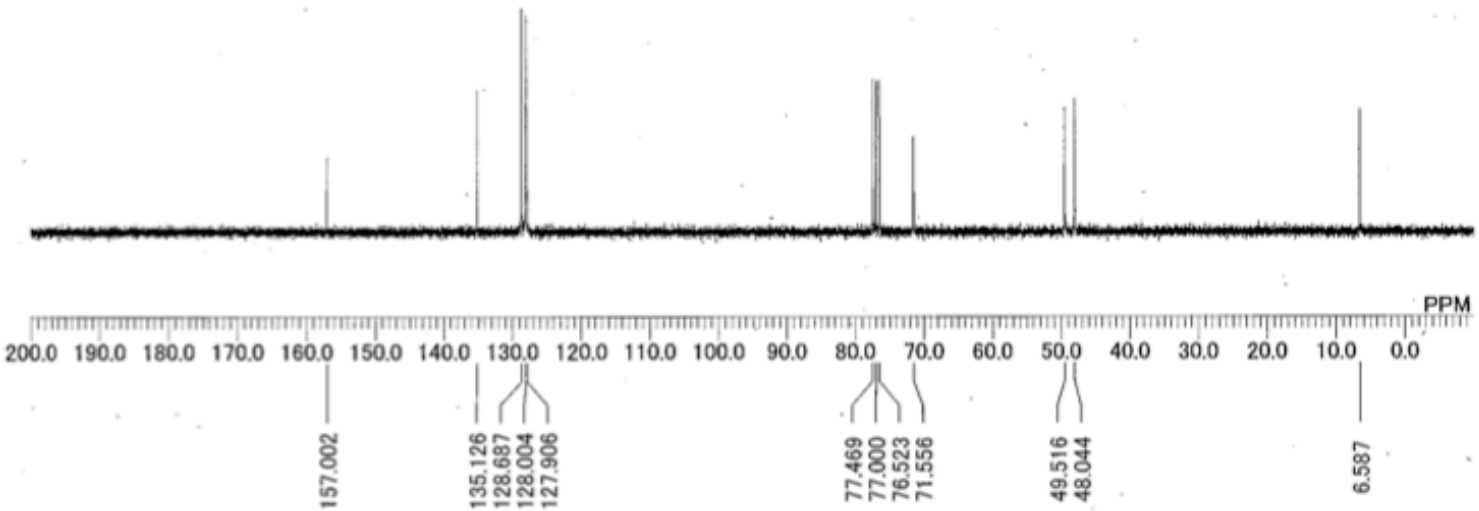
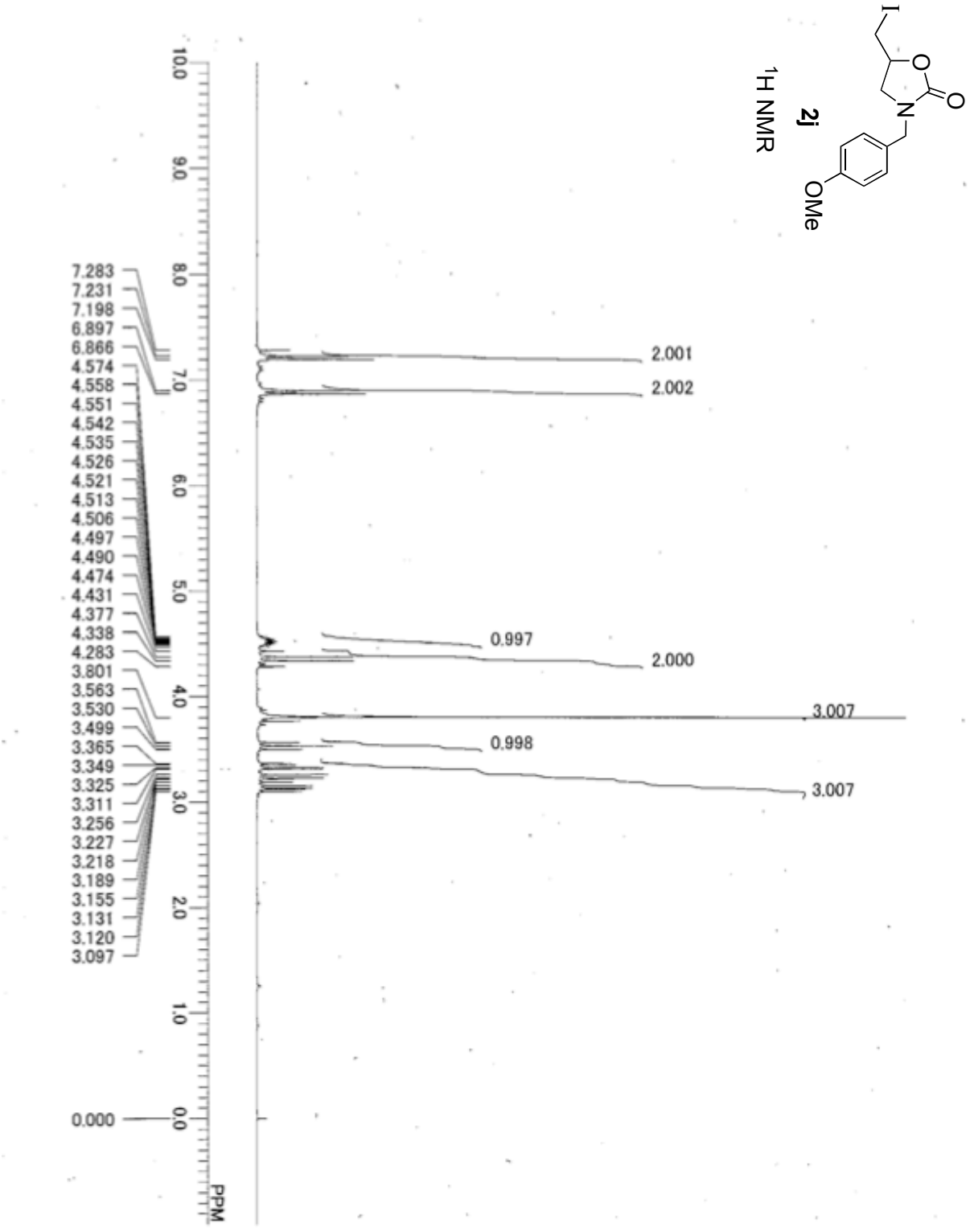
5.035
3.000
1.000
3.000
PPM



2i

^{13}C NMR


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
157.002
135.126
128.687
128.004
127.906
77.469
77.000
76.523
71.556
49.516
48.044
6.587


2j
^{1}H NMR
I
O
O
N
OMe
7.283
7.231
7.198
6.897
6.866
4.574
4.558
4.551
4.542
4.535
4.526
4.521
4.513
4.506
4.497
4.490
4.474
4.431
4.377
4.338
4.283
3.801
3.563
3.530
3.499
3.365
3.349
3.325
3.311
3.256
3.227
3.218
3.189
3.155
3.131
3.120
3.097
0.000
2.001
2.002
0.997
2.000
3.007
0.998
3.007
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7.0
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3.0
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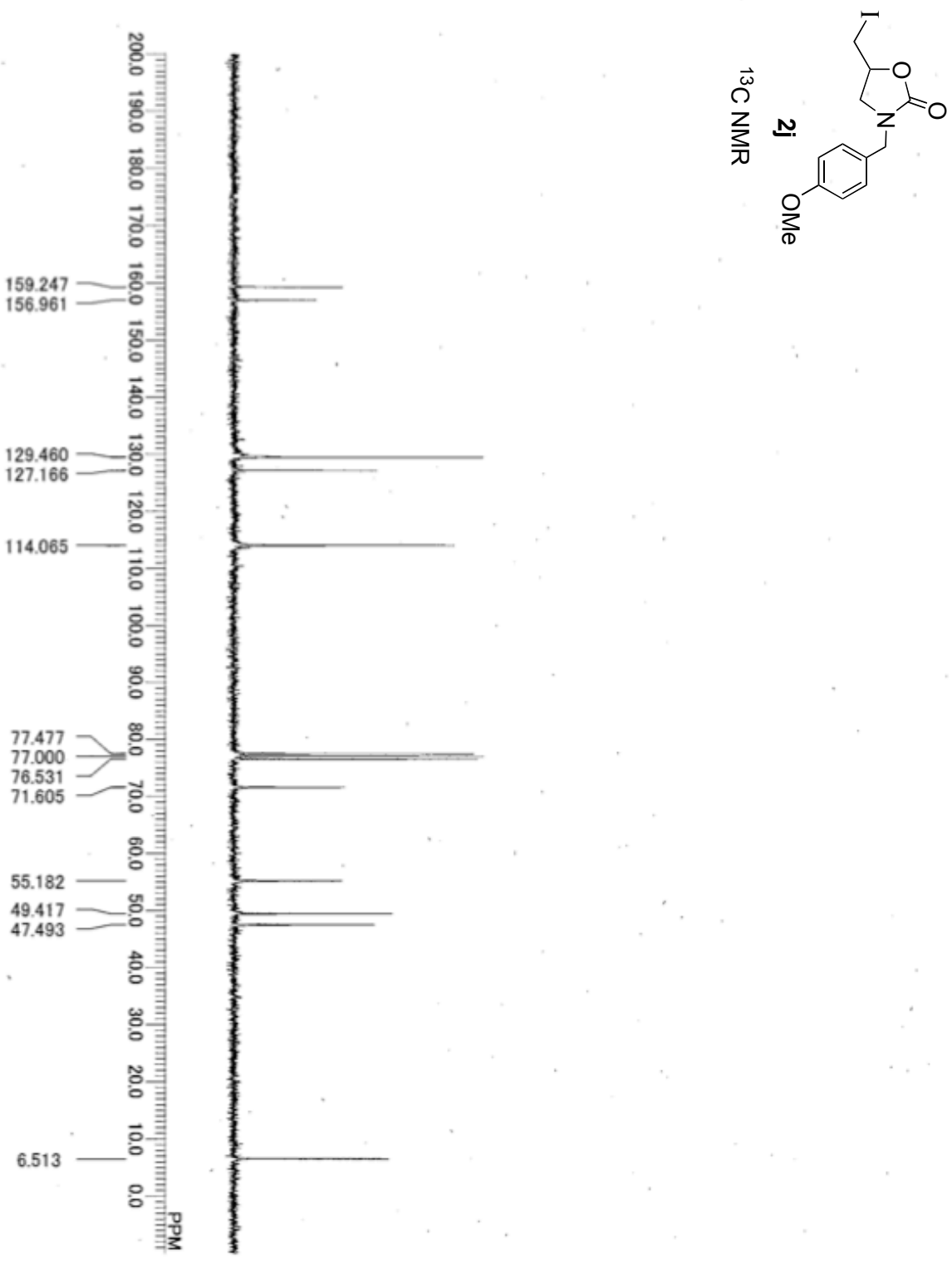
PPM


2j
^{13}C NMR
OMe
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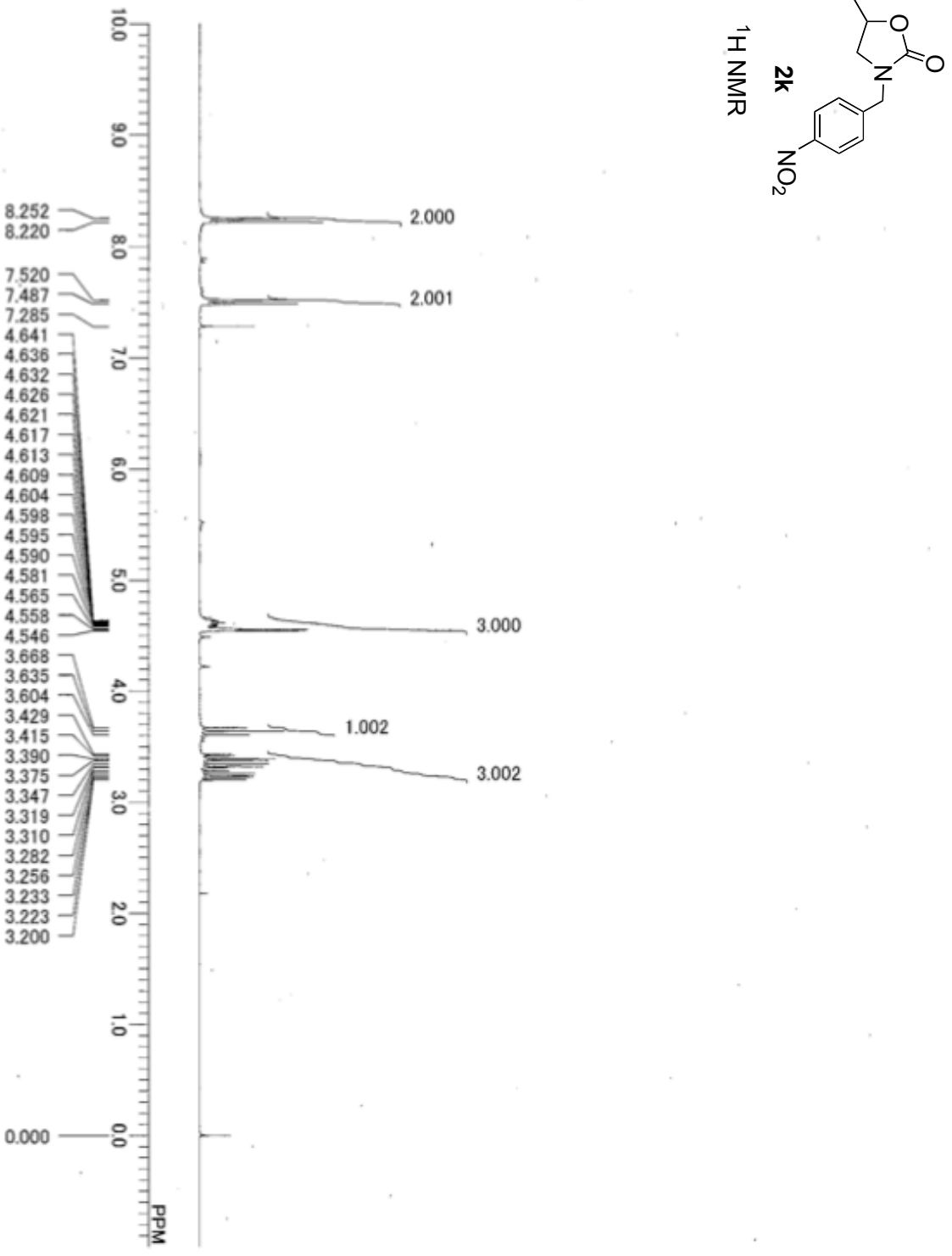
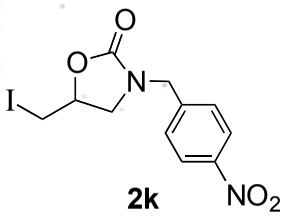
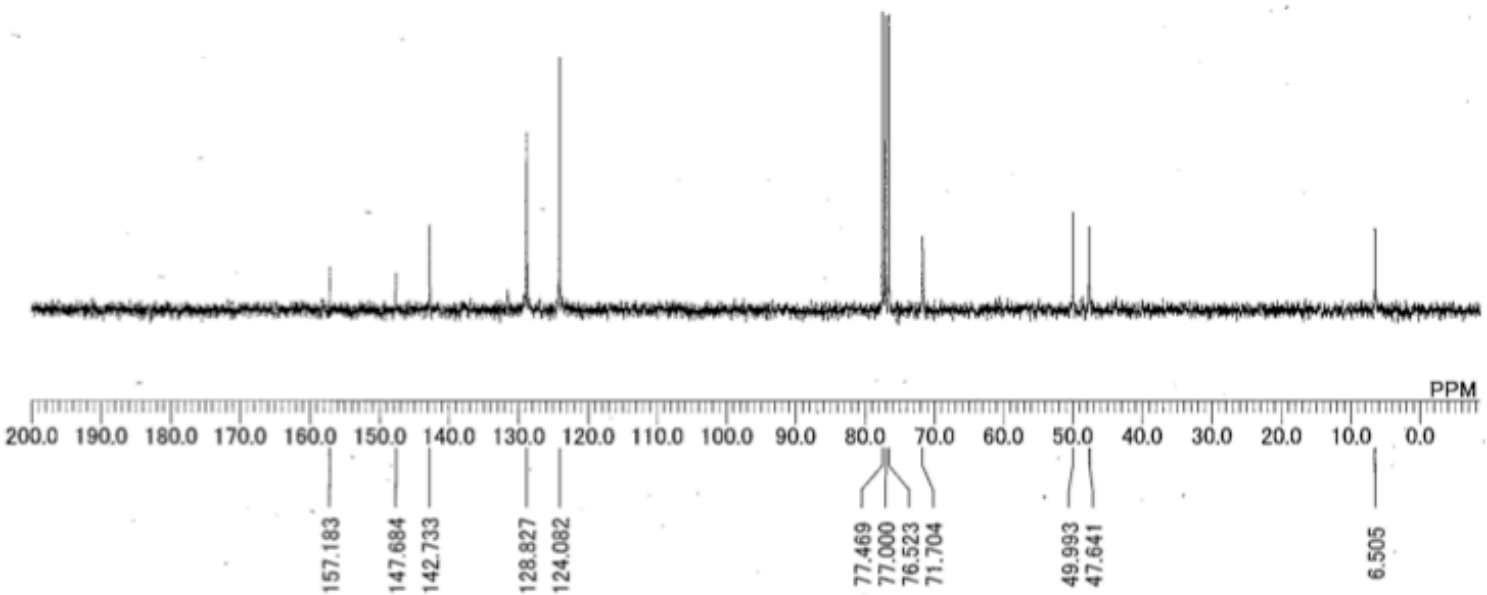
114.065
77.477
77.000
76.531
71.605
55.182
49.417
47.493
6.513
PPM

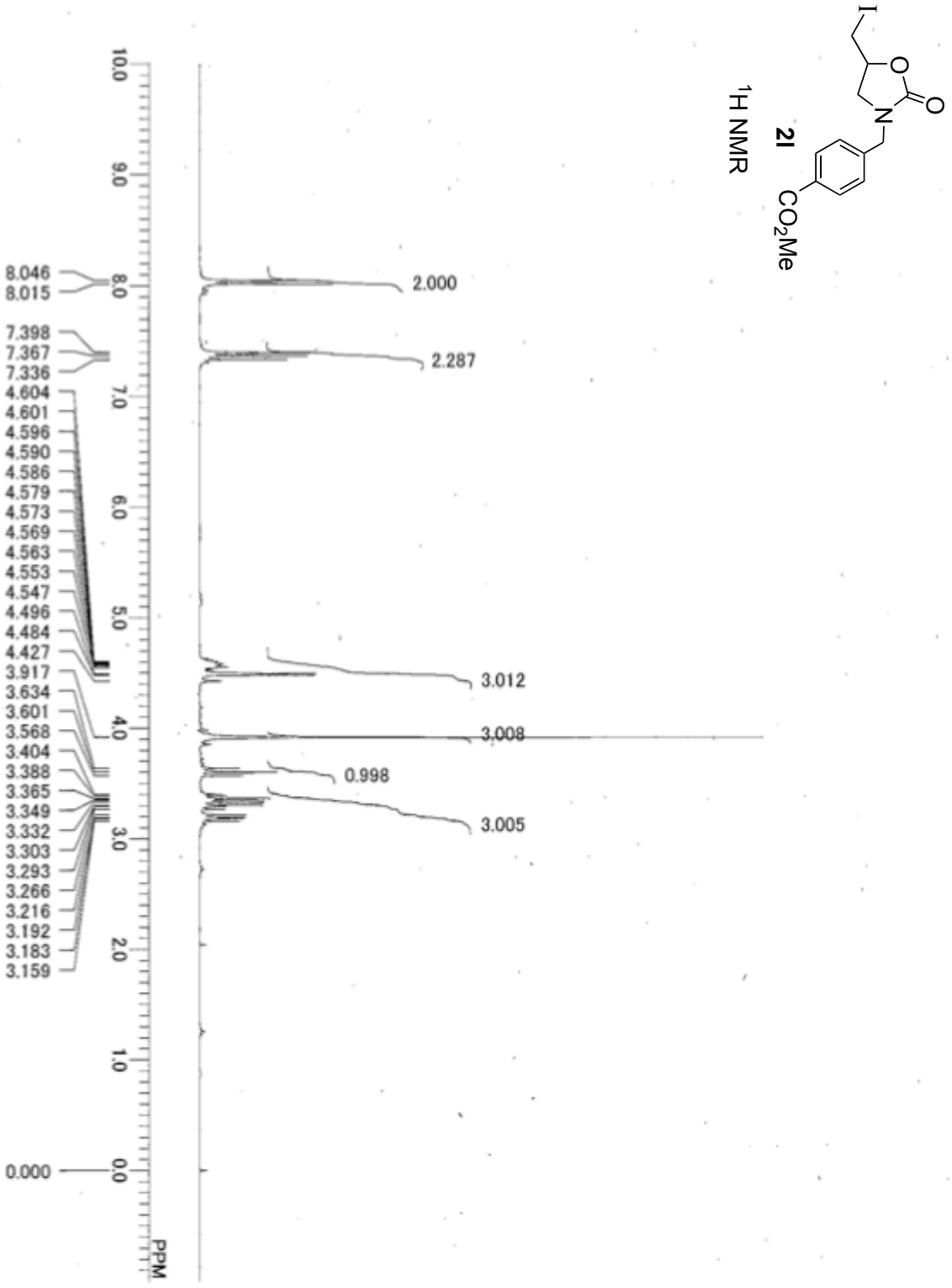

2k
^{1}H NMR
I
O
O
N
NO_2
8.252
8.220
7.520
7.487
7.285
4.641
4.636
4.632
4.626
4.621
4.617
4.613
4.609
4.604
4.598
4.595
4.590
4.581
4.565
4.558
4.546
3.668
3.635
3.604
3.429
3.415
3.390
3.375
3.347
3.319
3.310
3.282
3.256
3.233
3.223
3.200
0.000
2.000
2.001
3.000
1.002
3.002
PPM

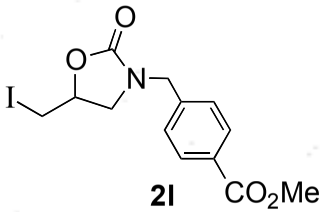

O
O
N
I
NO2

2k

^{13}C NMR

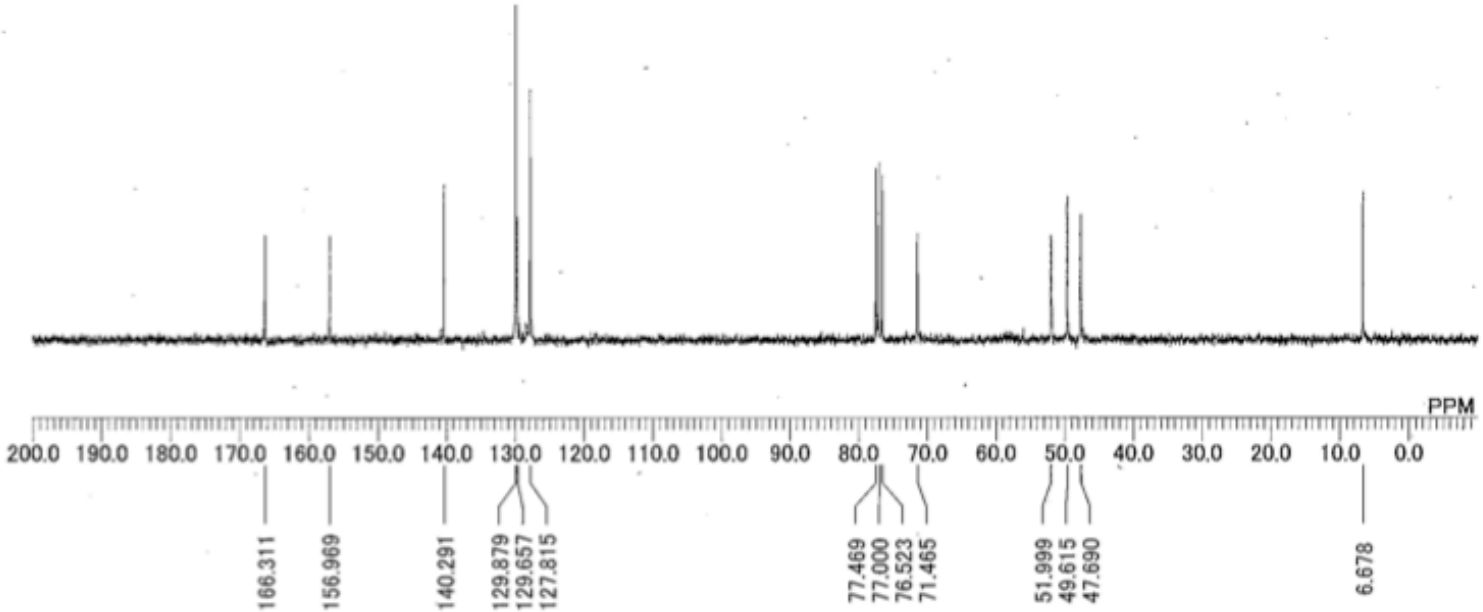

PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
157.183
147.684
142.733
128.827
124.082
77.469
77.000
76.523
71.704
49.993
47.641
6.505

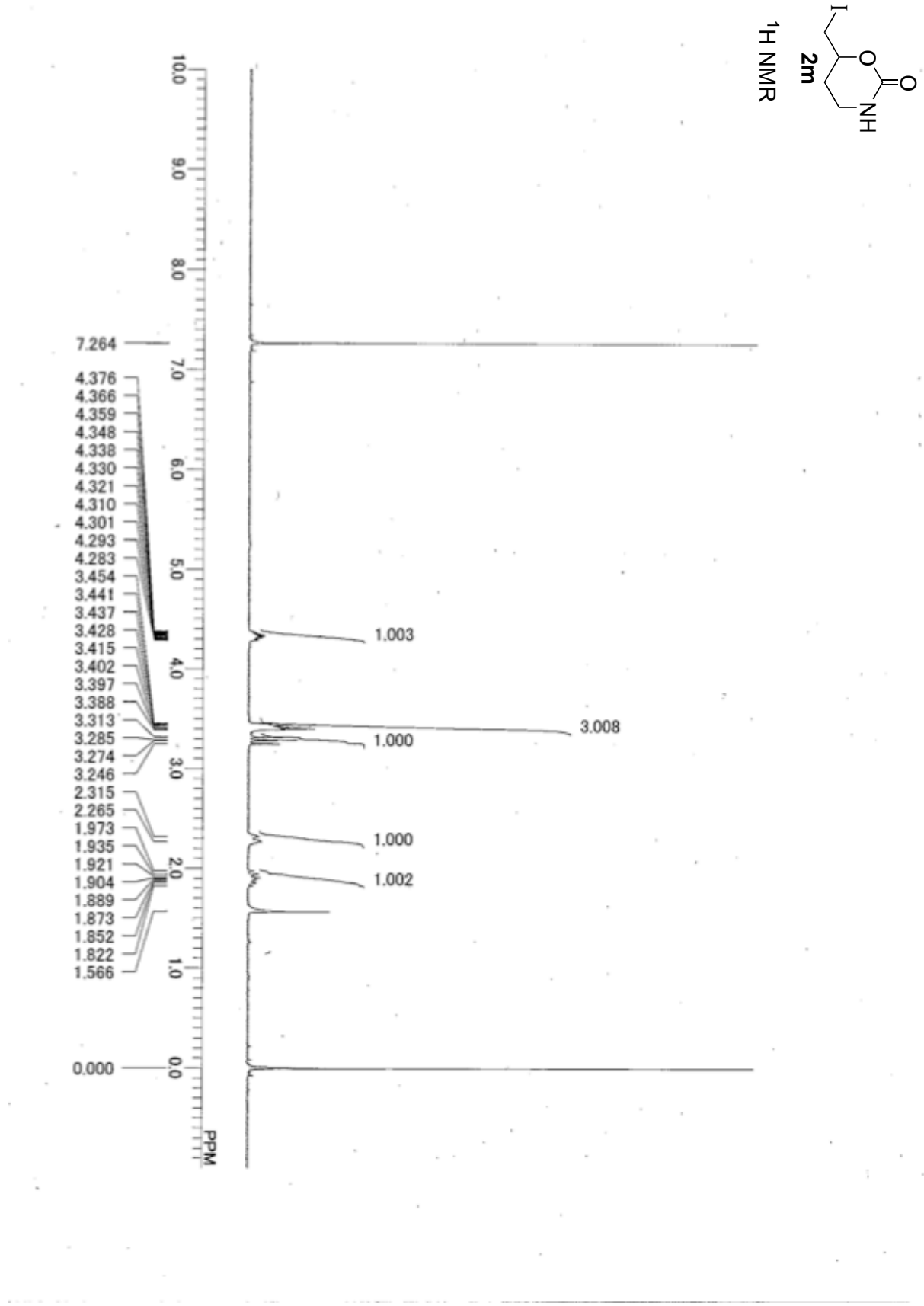

2l
^{1}H NMR
CO$_2$Me
I
O
O
N
8.046
8.015
7.398
7.367
7.336
4.604
4.601
4.596
4.590
4.586
4.579
4.573
4.569
4.563
4.553
4.547
4.496
4.484
4.427
3.917
3.634
3.601
3.568
3.404
3.388
3.365
3.349
3.332
3.303
3.293
3.266
3.216
3.192
3.183
3.159
0.000
2.000
2.287
3.012
3.008
0.998
3.005
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

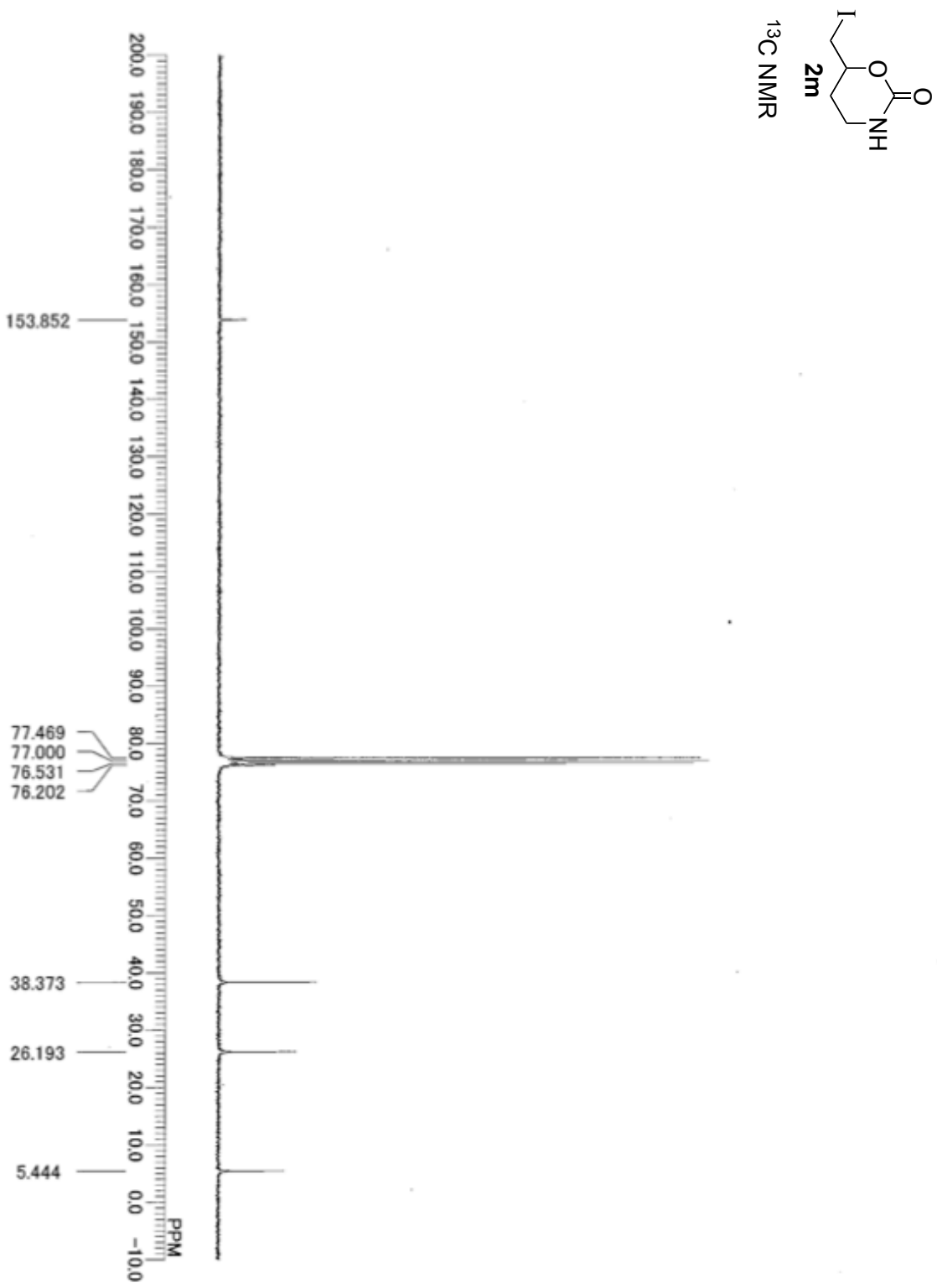

O
O
N
I
CO2Me

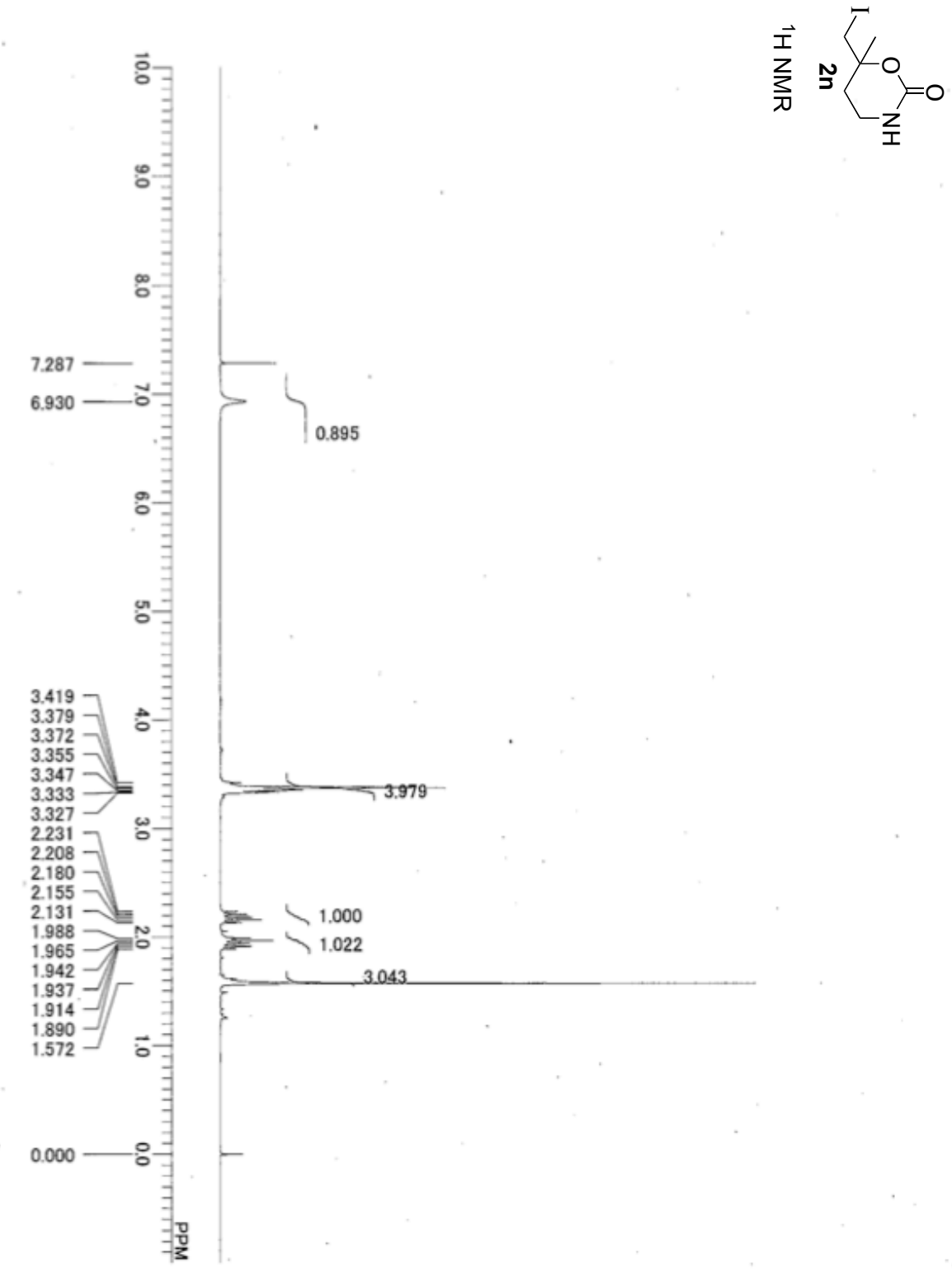
2l

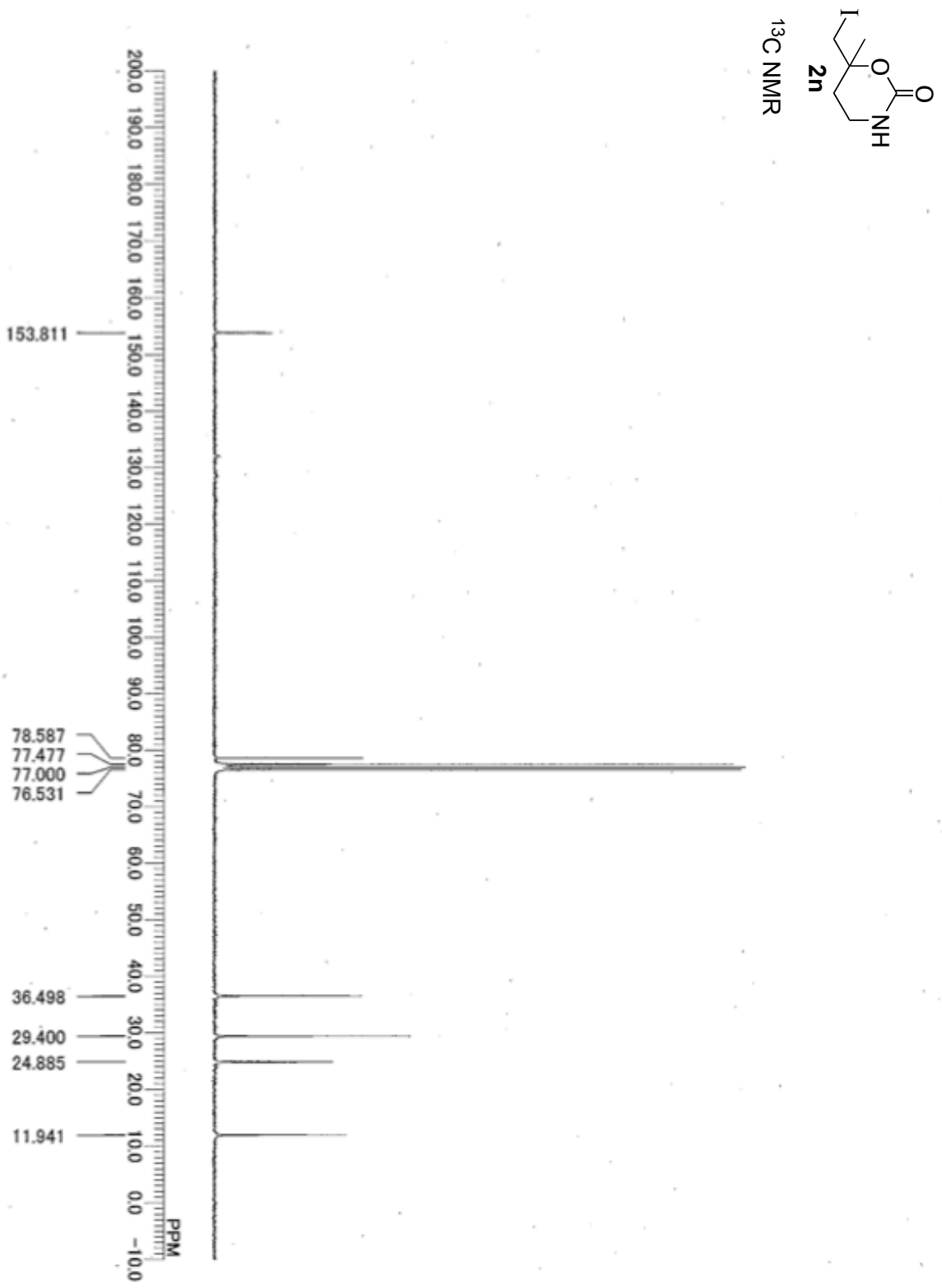
^{13}C NMR

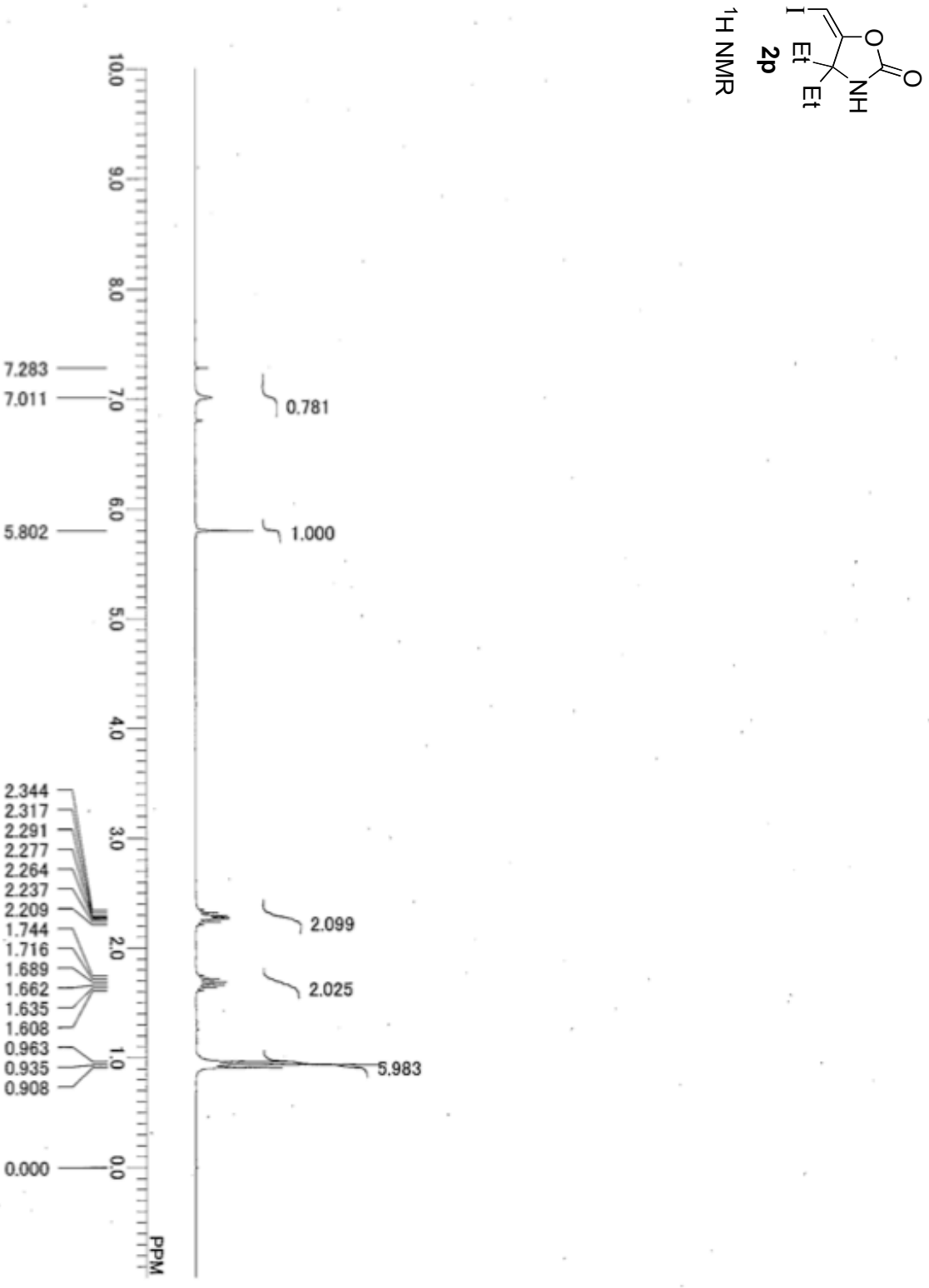

PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
166.311
156.969
140.291
129.879
129.657
127.815
77.469
77.000
76.523
71.465
51.999
49.615
47.690
6.678

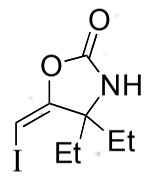

2m
^{1}H NMR
I
O
O
NH
7.264
4.376
4.366
4.359
4.348
4.338
4.330
4.321
4.310
4.301
4.293
4.283
3.454
3.441
3.437
3.428
3.415
3.402
3.397
3.388
3.313
3.285
3.274
3.246
2.315
2.265
1.973
1.935
1.921
1.904
1.889
1.873
1.852
1.822
1.566
0.000
1.003
3.008
1.000
1.000
1.002
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


2m
^{13}C NMR
153.852
77.469
77.000
76.531
76.202
38.373
26.193
5.444
PPM


2n
^{1}H NMR
I
O
O
NH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.287
6.930
0.895
3.419
3.379
3.372
3.355
3.347
3.333
3.327
3.979
2.231
2.208
2.180
2.155
2.131
1.988
1.965
1.942
1.937
1.914
1.890
1.572
1.000
1.022
3.043
0.000

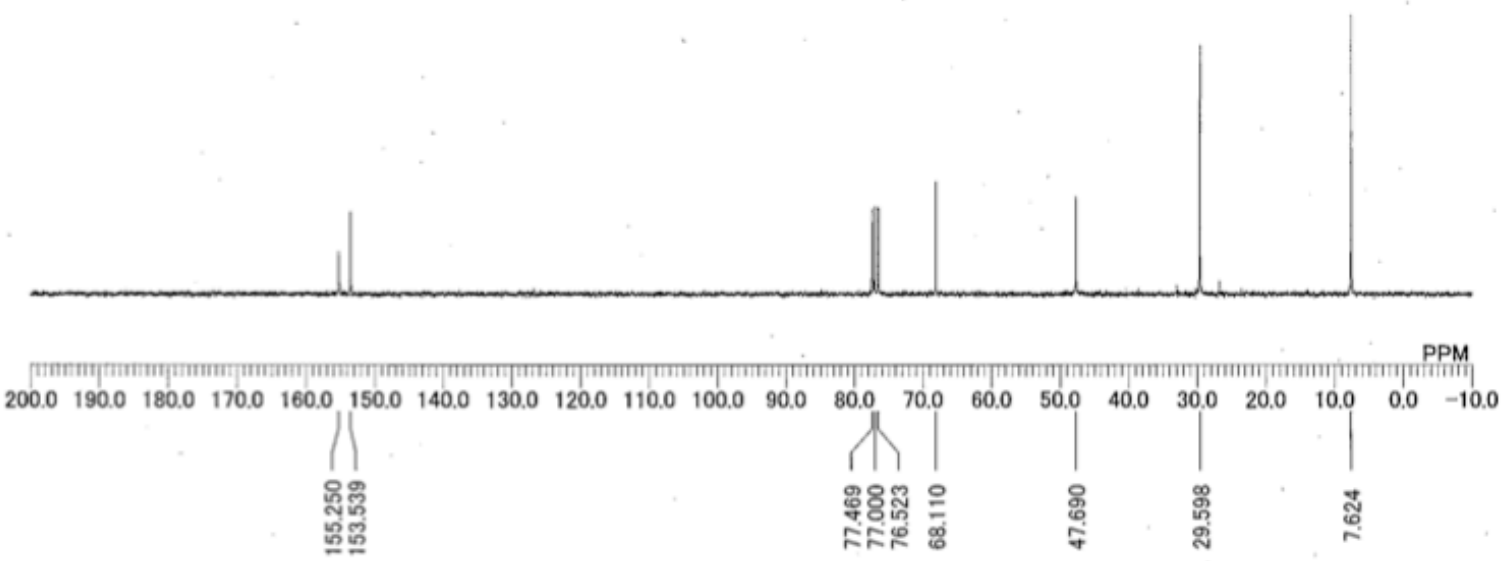

I
O
O
NH
2n
^{13}C NMR
153.811
78.587
77.477
77.000
76.531
36.498
29.400
24.885
11.941
PPM

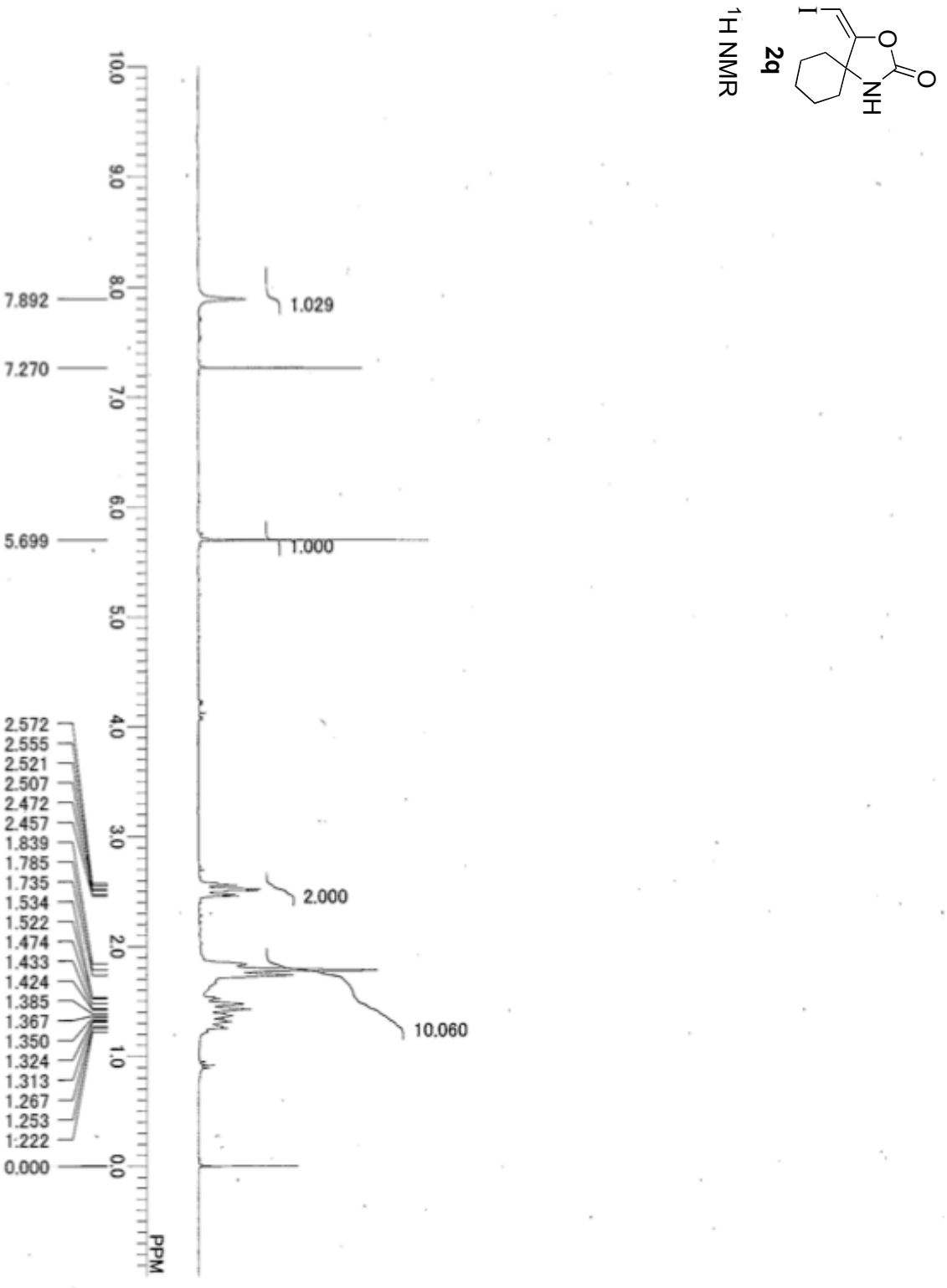

2p
^{1}H NMR
I
Et
Et
NH
O
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.283
7.011
5.802
2.344
2.317
2.291
2.277
2.264
2.237
2.209
1.744
1.716
1.689
1.662
1.635
1.608
0.963
0.935
0.908
0.000
0.781
1.000
2.099
2.025
5.983

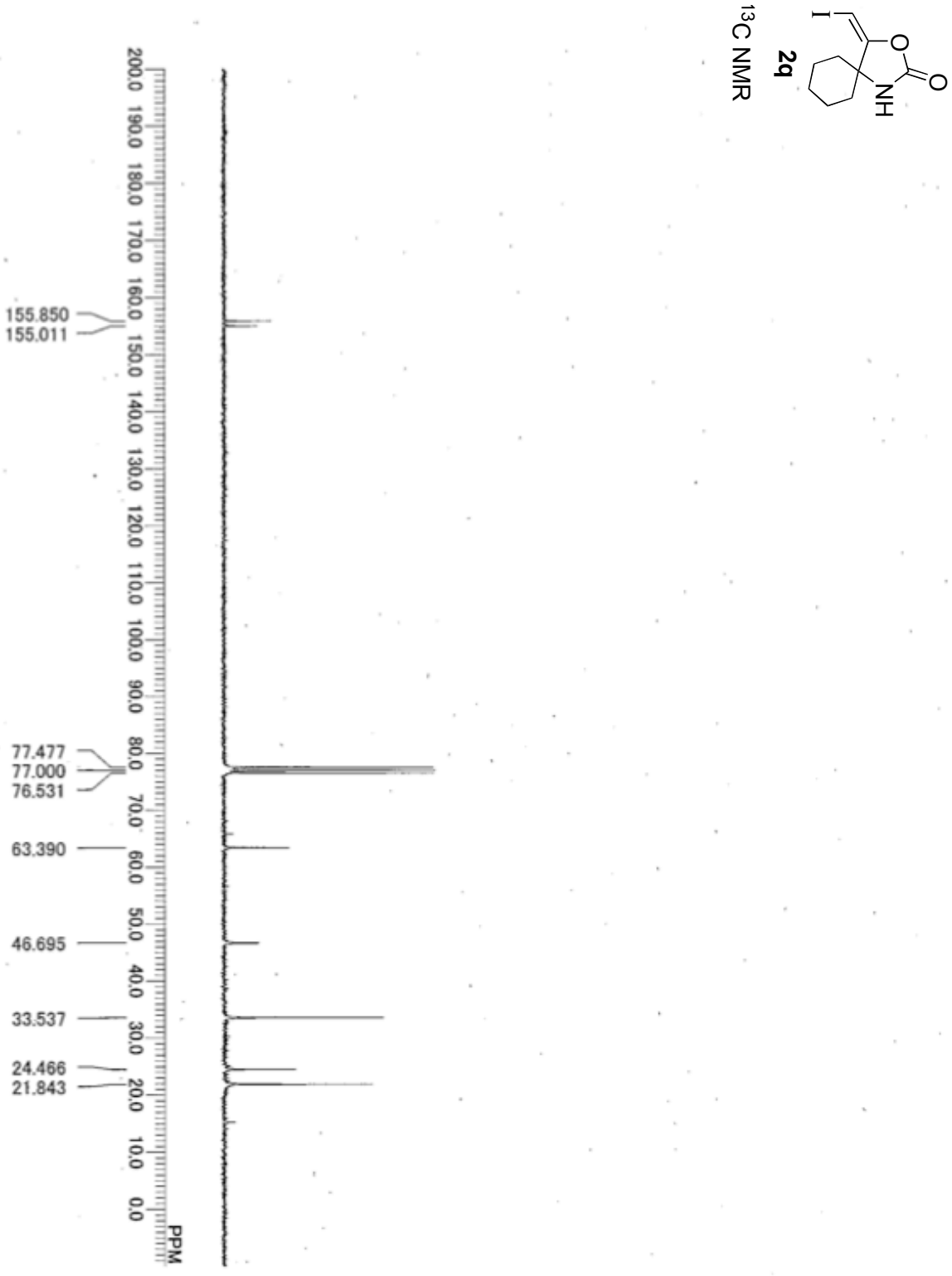

O
O
NH
I
Et
Et

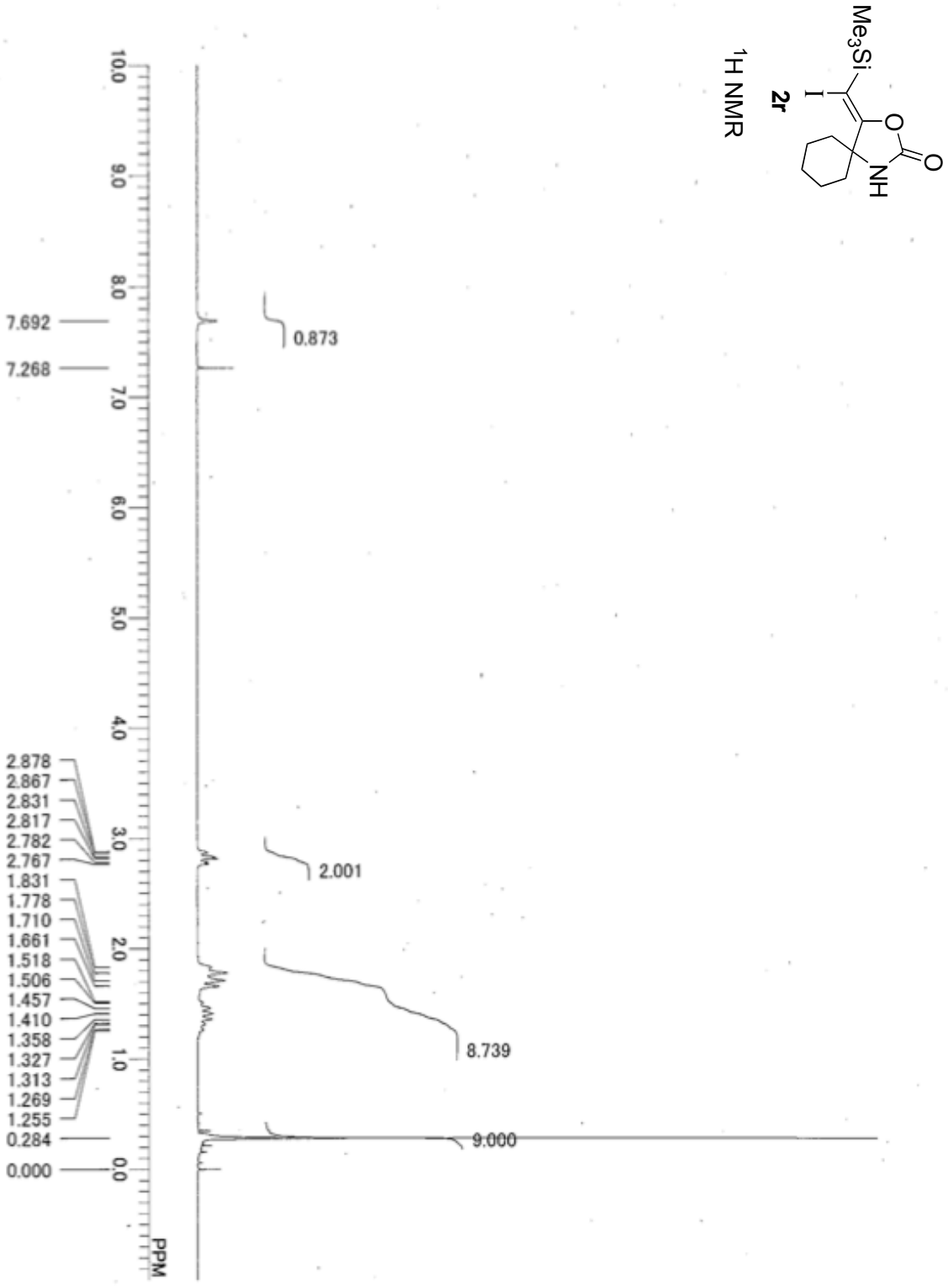
2p

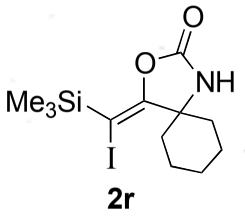
^{13}C NMR


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 −10.0
155.250
153.539
77.469
77.000
76.523
68.110
47.690
29.598
7.624


2q
1H NMR
I
O
O
NH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.892
7.270
5.699
2.572
2.555
2.521
2.507
2.472
2.457
1.839
1.785
1.735
1.534
1.522
1.474
1.433
1.424
1.385
1.367
1.350
1.324
1.313
1.267
1.253
1.222
0.000
1.029
1.000
2.000
10.060

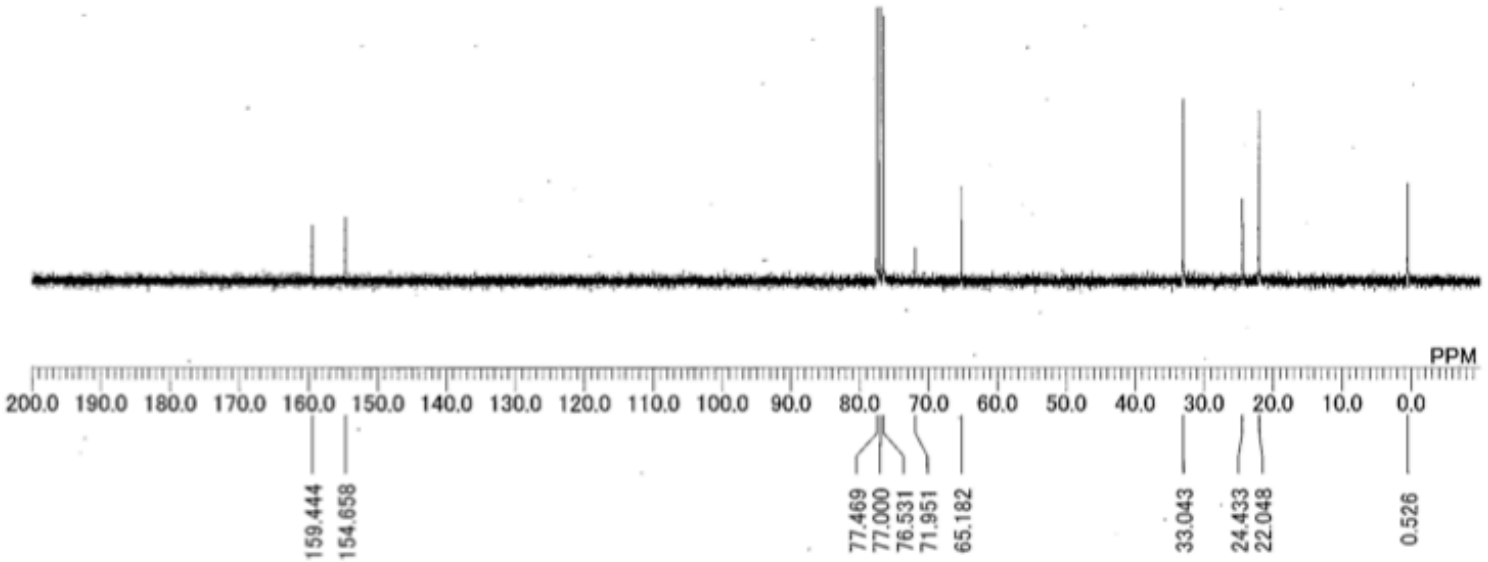

155.850
155.011
77.477
77.000
76.531
63.390
46.695
33.537
24.466
21.843
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
I
O
O
NH
2q
13C NMR

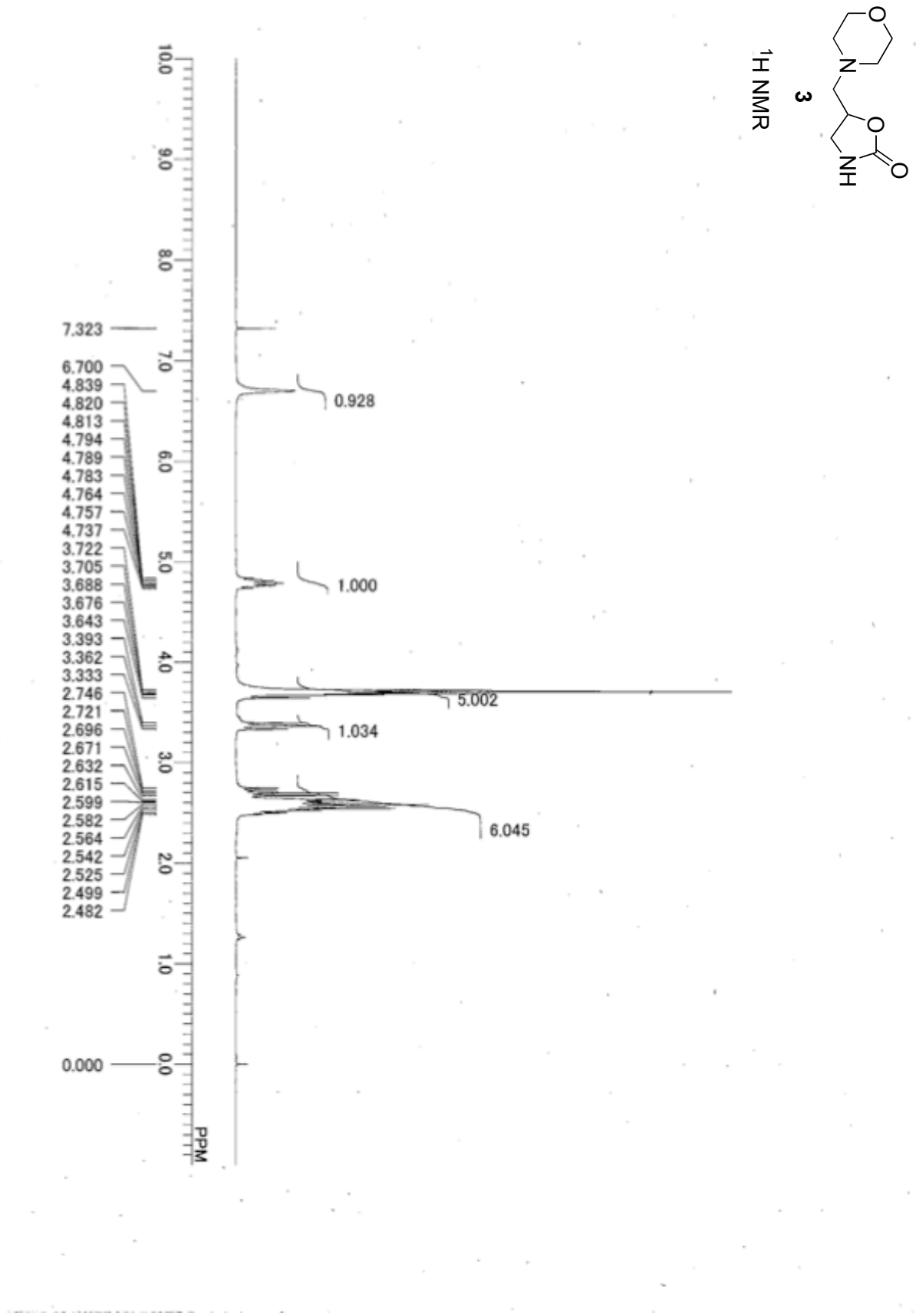

Me3Si
I
O
O
NH
2r
1H NMR
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.692
7.268
2.878
2.867
2.831
2.817
2.782
2.767
1.831
1.778
1.710
1.661
1.518
1.506
1.457
1.410
1.358
1.327
1.313
1.269
1.255
0.284
0.000
0.873
2.001
8.739
9.000


O
O
NH
Me3Si
I

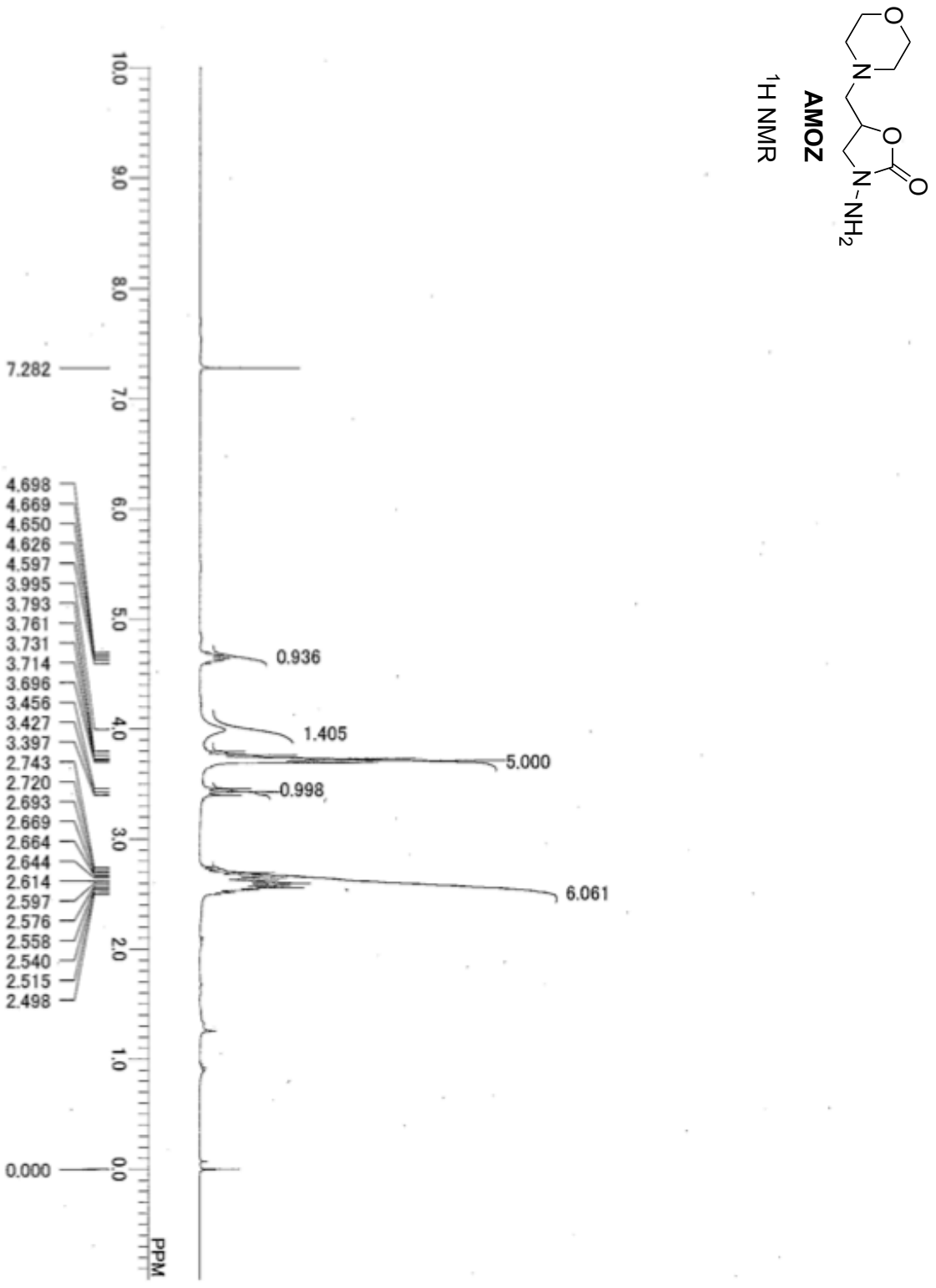
2r

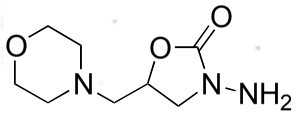
^{13}C NMR


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
159.444
154.658
77.469
77.000
76.531
71.951
65.182
33.043
24.433
22.048
0.526


3
^{1}H NMR
7.323
6.700
4.839
4.820
4.813
4.794
4.789
4.783
4.764
4.757
4.737
3.722
3.705
3.688
3.676
3.643
3.393
3.362
3.333
2.746
2.721
2.696
2.671
2.632
2.615
2.599
2.582
2.564
2.542
2.525
2.499
2.482
0.000
0.928
1.000
5.002
1.034
6.045
PPM

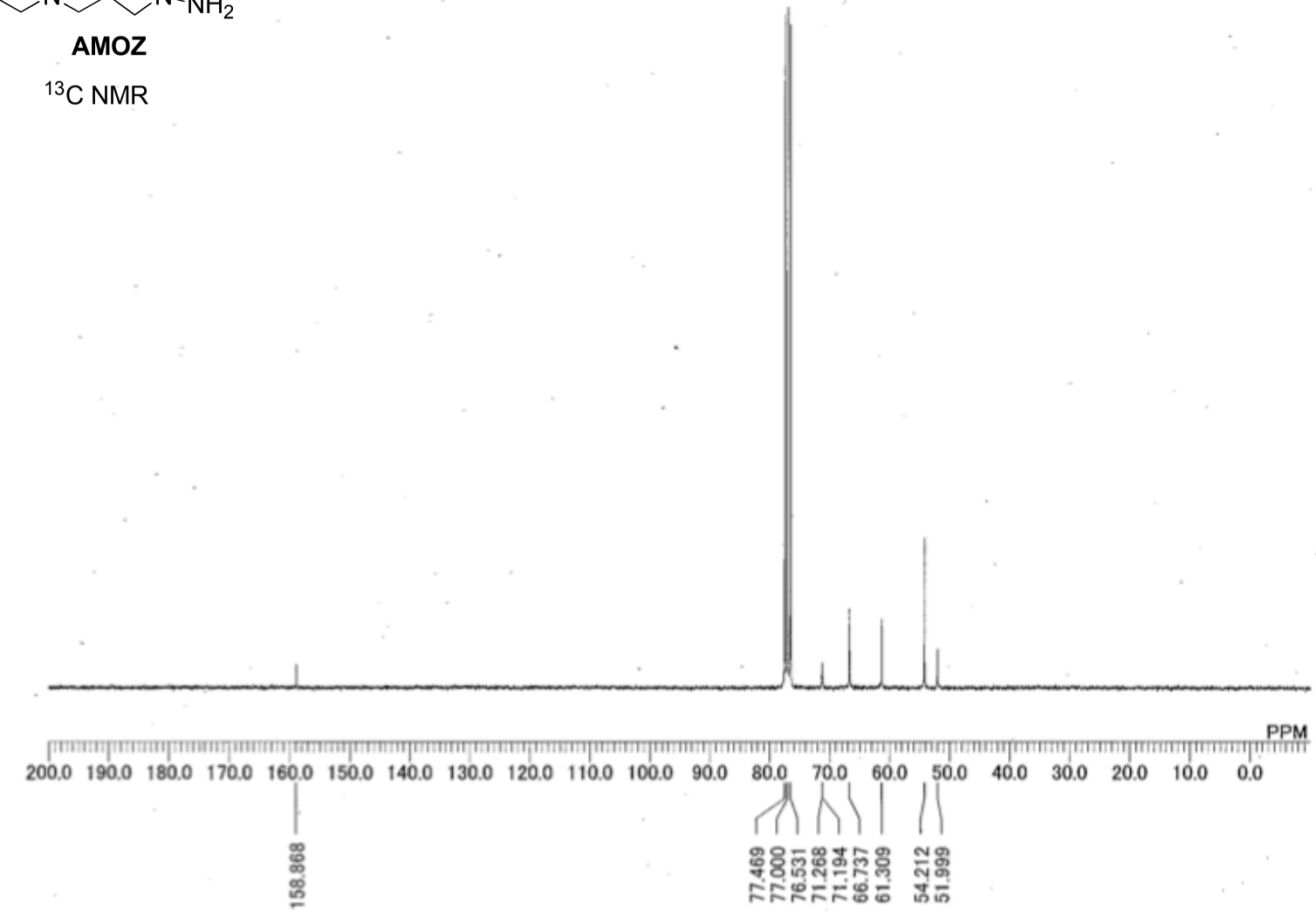
3
^{13}C NMR
159.896
77.469
77.000
76.531
75.010
66.761
61.695
54.179
44.286
PPM


AMOZ
^{1}H NMR
7.282
4.698
4.669
4.650
4.626
4.597
3.995
3.793
3.761
3.731
3.714
3.696
3.456
3.427
3.397
2.743
2.720
2.693
2.669
2.664
2.644
2.614
2.597
2.576
2.558
2.540
2.515
2.498
0.000
0.936
1.405
5.000
0.998
6.061
PPM

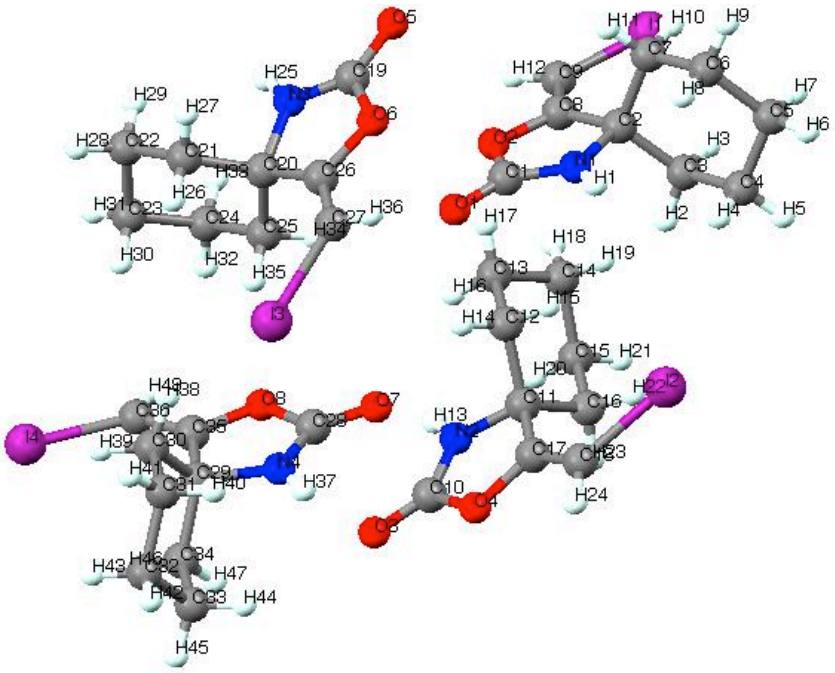

O
O
O
N
N
NH2

AMOZ

^{13}C NMR


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
158.868
77.469
77.000
76.531
71.268
71.194
66.737
61.309
54.212
51.999

X-ray crystallographic analysis of 2q



Non-hydrogen atoms except iodine (I1–I4) were refined with isotropic displacement parameters, and the analysis was completed to optimize the structure. Although a level A alert still remain, this structure should be justified because of the excellent level of the structure refinement.

Experimental

Data Collection

A colorless prism crystal of $C_9H_{12}INO_2$ having approximate dimensions of 0.100 × 0.100 × 0.050 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Ka radiation.

The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions:

a	=	9.2914(2) Å	α	=	73.2150(8)°
b	=	13.5608(3) Å	β	=	82.1360(9)°
c	=	17.0451(3) Å	γ	=	80.3700(9)°
V	=	2018.25(7) Å^3			

For Z = 8 and F.W. = 293.10, the calculated density is 1.929 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P–1 (#2)

The data were collected at a temperature of –150±1 ˚C to a maximum 2θ value of 143.4˚. A total of 90 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0˚ in 10.0˚ step, at χ=54.0˚ and ϕ = 0.0˚. The exposure rate was 30.0 [sec./˚]. A second sweep was performed using ω scans from 80.0 to 260.0˚ in 10.0˚ step, at χ=54.0˚ and ϕ = 90.0˚. The exposure rate was 30.0 [sec./˚]. Another sweep was performed using ω scans from 80.0 to 260.0˚ in 10.0˚ step, at χ=54.0˚ and ϕ = 180.0˚. The exposure rate was 30.0 [sec./˚]. Another sweep was performed using w scans from 80.0 to 260.0˚ in 10.0˚ step, at χ = 54.0˚ and ϕ = 290.0˚. The exposure rate was 30.0 [sec./˚]. Another sweep was performed using w scans from 80.0 to 260.0˚ in 10.0˚ step, at χ=15.0˚ and ϕ = 0.0˚. The exposure rate was 30.0 [sec./˚]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 23493 reflections that were collected, 7498 were unique (R_{int} = 0.1630); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Ka radiation is 246.895 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.156 to 0.291. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F was based on 6157 observed reflections (I > 1.00σ(I)) and 277 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o| = 0.0818$$

$$Rw = [\, \Sigma \, w \, (|F_o| - |F_c|)^2 \, / \, \Sigma \, w \, F_o^{\,2}]^{1/2} = 0.1158$$

The standard deviation of an observation of unit weight[3] was 1.00. A Sheldrick weighting scheme was used. Plots of $\Sigma \, w \, (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 9.11 and –10.30 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[4]. Anomalous dispersion effects were included in Fcalc[5]; the values for Δf' and Δf'' were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8,9] crystallographic software package.

References

(1) SIR2008: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(2) Least Squares function minimized:

$$\Sigma\, w\, (|F_o| - |F_c|)^2 \qquad \text{where } w = \text{Least Squares weights.}$$

(3) Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations
N_v = number of variables

(4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr. 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W. J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(9) CRYSTALS Issue 11: Carruthers, J.R., Rollett,J.S., Betteridge, P.W., Kinna, D., Pearce, L., Larsen, A., and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_9H_{12}INO_2$
Formula Weight	293.10
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.100 × 0.100 × 0.050 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.2914(2) Å
	b = 13.5608(3) Å
	c = 17.0451(3) Å
	α = 73.2150(8)˚
	β = 82.1360(9)˚
	γ = 80.3700(9)˚
	V = 2018.25(7) Å^3
Space Group	P–1 (#2)
Z value	8
Dcalc	1.929 g/cm^3
F000	1136.00
m(CuKa)	246.895 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKa (l = 1.54187 Å) graphite monochromated
Voltage, Current	50kV, 100mA
Temperature	–150.0 ˚C
Detector Aperture	460 × 256 mm
Data Images	90 exposures
ω oscillation Range (χ = 54.0, ϕ = 0.0)	80.0 – 260.0˚
Exposure Rate	30.0 sec./˚
ω oscillation Range (χ = 54.0, ϕ = 90.0)	80.0 – 260.0˚
Exposure Rate	30.0 sec./˚
ω oscillation Range (χ = 54.0, ϕ = 180.0)	80.0 – 260.0˚
Exposure Rate	30.0 sec./˚
ω oscillation Range (χ = 54.0, ϕ = 290.0)	80.0 – 260.0˚
Exposure Rate	30.0 sec./˚
ω oscillation Range (χ = 15.0, ϕ = 0.0)	80.0 – 260.0˚

Exposure Rate	30.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	143.4°
No. of Reflections Measured	Total: 23493 Unique: 7498 (R_{int} = 0.1630)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.156 – 0.291)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\, w\, (\|F_o\| - \|F_c\|)^2$
Least Squares Weights	$1/[0.0034F_o^2+1.0000\sigma(F_o^2)]$
$2\theta_{max}$ cutoff	143.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>1.00σ(I))	6157
No. Variables	277
Reflection/Parameter Ratio	22.23
Residuals: R (I>2.00σ(I))	0.0818
Residuals: R (I>1.00σ(I))	0.0915
Residuals: wR (I>1.00σ(I))	0.1158
Goodness of Fit Indicator	1.001
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	9.11 $e^-/Å^3$
Minimum peak in Final Diff. Map	–10.30 $e^-/Å^3$

Table S3. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
I1	0.10581(8)	0.33904(5)	1.10952(4)	2.31(2)
I2	0.73065(8)	0.43289(5)	0.80607(4)	1.85(2)
I3	0.35030(8)	0.07477(5)	0.68695(4)	1.86(2)
I4	-0.18284(8)	0.15875(5)	0.38864(4)	1.96(2)
O1	0.5719(8)	0.0739(5)	0.9068(4)	2.0(2)
O2	0.3685(8)	0.1470(5)	0.9659(4)	1.9(2)
O3	0.4509(8)	0.3671(5)	0.5024(5)	1.8(2)
O4	0.6032(8)	0.3902(5)	0.5868(4)	1.6(2)
O5	-0.1098(8)	0.1268(5)	0.9974(5)	2.1(2)
O6	0.0925(8)	0.1090(5)	0.9104(4)	1.6(2)
O7	0.0657(8)	0.4203(5)	0.5894(4)	1.9(2)
O8	-0.0766(8)	0.3486(5)	0.5311(4)	1.8(2)
N1	0.580(1)	0.1690(6)	0.9984(5)	1.9(2)
N2	0.3643(9)	0.4077(5)	0.6241(5)	1.4(2)
N3	-0.118(1)	0.0883(6)	0.8734(5)	1.5(2)
N4	0.163(1)	0.3229(6)	0.4995(5)	1.9(2)
C1	0.521(2)	0.1256(7)	0.9528(7)	1.7(2)
C2	0.473(1)	0.2295(7)	1.0445(6)	1.4(2)
C3	0.493(1)	0.3442(7)	1.0190(6)	1.6(2)
C4	0.640(2)	0.3597(7)	1.0417(7)	1.9(2)
C5	0.650(2)	0.3171(8)	1.1330(7)	2.3(2)
C6	0.634(2)	0.1994(7)	1.1607(7)	2.1(2)
C7	0.490(1)	0.1820(7)	1.1369(6)	1.6(2)
C8	0.333(1)	0.2093(7)	1.0195(6)	1.4(2)
C9	0.194(2)	0.2390(8)	1.0372(7)	2.2(2)
C10	0.467(2)	0.3872(7)	0.5660(7)	1.5(2)
C11	0.428(1)	0.4224(6)	0.6948(6)	1.0(2)
C12	0.392(1)	0.3358(7)	0.7733(6)	1.3(2)
C13	0.227(2)	0.3491(7)	0.8006(7)	2.1(2)
C14	0.178(2)	0.4550(7)	0.8147(7)	1.8(2)
C15	0.207(1)	0.5402(7)	0.7351(6)	1.6(2)
C16	0.368(1)	0.5306(7)	0.7053(6)	1.5(2)
C17	0.586(1)	0.4126(7)	0.6636(6)	1.4(2)
C18	0.711(2)	0.4167(7)	0.6913(6)	1.6(2)
C19	-0.054(2)	0.1091(7)	0.9308(7)	1.7(2)
C20	-0.010(1)	0.0775(7)	0.8017(6)	1.4(2)
C21	-0.008(1)	-0.0297(7)	0.7882(6)	1.5(2)

Table S3. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C22	-0.150(2)	-0.0428(7)	0.7587(7)	2.0(2)
C23	-0.186(2)	0.0475(7)	0.6795(7)	2.0(2)
C24	-0.197(2)	0.1528(7)	0.6964(7)	1.8(2)
C25	-0.055(1)	0.1650(7)	0.7259(6)	1.5(2)
C26	0.127(1)	0.0901(7)	0.8335(6)	1.5(2)
C27	0.268(2)	0.0857(7)	0.8050(6)	1.7(2)
C28	0.059(2)	0.3693(7)	0.5439(7)	1.8(2)
C29	0.108(1)	0.2628(7)	0.4510(6)	1.2(2)
C30	0.169(1)	0.1471(7)	0.4793(7)	1.7(2)
C31	0.335(1)	0.1279(7)	0.4566(6)	1.6(2)
C32	0.372(2)	0.1727(7)	0.3647(7)	1.9(2)
C33	0.311(2)	0.2904(7)	0.3381(7)	2.0(2)
C34	0.146(1)	0.3089(7)	0.3604(6)	1.7(2)
C35	-0.055(1)	0.2849(7)	0.4783(6)	1.4(2)
C36	-0.174(2)	0.2577(7)	0.4595(6)	1.7(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\ \gamma + 2U_{13}(aa^*cc^*)\cos\ \beta + 2U_{23}(bb^*cc^*)\cos\ \alpha)$

Table S4. Atomic coordinates and B_{iso} involving hydrogen atoms/B_{eq}

atom	x	y	z	B_{iso}
H1	0.6807	0.1629	1.0009	2.23
H2	0.4902	0.3721	0.9599	1.92
H3	0.4149	0.3817	1.0471	1.92
H4	0.7216	0.3240	1.0142	2.28
H5	0.6497	0.4330	1.0276	2.29
H6	0.7430	0.3311	1.1444	2.72
H7	0.5707	0.3572	1.1584	2.72
H8	0.7135	0.1602	1.1347	2.56
H9	0.6351	0.1746	1.2201	2.57
H10	0.4111	0.2157	1.1676	1.92
H11	0.4847	0.1080	1.1522	1.93
H12	0.1274	0.2123	1.0156	2.60
H13	0.2641	0.4111	0.6220	1.65
H14	0.4235	0.2687	0.7625	1.60
H15	0.4456	0.3414	0.8167	1.61
H16	0.1701	0.3454	0.7581	2.48
H17	0.2023	0.2973	0.8513	2.48
H18	0.0748	0.4585	0.8353	2.11
H19	0.2350	0.4575	0.8573	2.11
H20	0.1530	0.5348	0.6921	1.92
H21	0.1772	0.6076	0.7456	1.92
H22	0.4212	0.5445	0.7453	1.79
H23	0.3811	0.5825	0.6530	1.79
H24	0.7964	0.4127	0.6558	1.98
H25	-0.2173	0.0830	0.8762	1.77
H26	0.0751	-0.0393	0.7488	1.80
H27	0.0069	-0.0806	0.8406	1.80
H28	-0.1363	-0.1080	0.7440	2.35
H29	-0.2306	-0.0428	0.8014	2.35
H30	-0.1064	0.0475	0.6361	2.38
H31	-0.2766	0.0432	0.6592	2.39
H32	-0.2210	0.2062	0.6464	2.18
H33	-0.2779	0.1553	0.7388	2.18
H34	-0.0653	0.2306	0.7396	1.75
H35	0.0219	0.1636	0.6816	1.76
H36	0.3348	0.0890	0.8398	2.07
H37	0.2623	0.3265	0.4993	2.23

Table S4. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} (continued)

atom	x	y	z	B_{eq}
H38	0.1470	0.1223	0.5384	2.00
H39	0.1191	0.1110	0.4520	2.00
H40	0.3890	0.1616	0.4839	1.94
H41	0.3724	0.0545	0.4689	1.94
H42	0.4769	0.1587	0.3518	2.26
H43	0.3224	0.1348	0.3387	2.26
H44	0.3608	0.3282	0.3641	2.41
H45	0.3325	0.3138	0.2788	2.41
H46	0.0975	0.2767	0.3295	2.08
H47	0.1154	0.3834	0.3453	2.07
H48	-0.2627	0.2882	0.4802	2.01

Table S5. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	0.0285(5)	0.0384(4)	0.0252(5)	0.0014(4)	0.0046(4)	-0.0217(4)
I2	0.0268(5)	0.0352(4)	0.0124(4)	-0.0073(4)	-0.0008(4)	-0.0119(3)
I3	0.0243(5)	0.0359(4)	0.0122(4)	-0.0037(4)	0.0040(4)	-0.0122(3)
I4	0.0290(5)	0.0308(4)	0.0219(5)	-0.0048(3)	-0.0023(4)	-0.0179(3)

The general temperature factor expression: $\exp(-2\pi^2(a^*2U_{11}h^2 + b^*2U_{22}k^2 + c^*2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S6. Fragment Analysis

fragment: 1

I(1)	O(1)	O(2)	N(1)	C(1)
C(2)	C(3)	C(4)	C(5)	C(6)
C(7)	C(8)	C(9)		

fragment: 2

I(2)	O(3)	O(4)	N(2)	C(10)
C(11)	C(12)	C(13)	C(14)	C(15)
C(16)	C(17)	C(18)		

fragment: 3

I(3)	O(5)	O(6)	N(3)	C(19)
C(20)	C(21)	C(22)	C(23)	C(24)
C(25)	C(26)	C(27)		

fragment: 4

I(4)	O(7)	O(8)	N(4)	C(28)
C(29)	C(30)	C(31)	C(32)	C(33)
C(34)	C(35)	C(36)		

Table S7. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
I1	C9	2.085(11)	I2	C18	2.065(12)
I3	C27	2.090(11)	I4	C36	2.065(12)
O1	C1	1.198(13)	O2	C1	1.399(13)
O2	C8	1.387(13)	O3	C10	1.223(15)
O4	C10	1.372(14)	O4	C17	1.410(13)
O5	C19	1.252(13)	O6	C19	1.359(13)
O6	C26	1.392(13)	O7	C28	1.193(14)
O8	C28	1.391(14)	O8	C35	1.391(13)
N1	C1	1.320(16)	N1	C2	1.474(13)
N2	C10	1.334(13)	N2	C11	1.489(14)
N3	C19	1.329(16)	N3	C20	1.500(13)
N4	C28	1.335(13)	N4	C29	1.502(15)
C2	C3	1.528(13)	C2	C7	1.539(14)
C2	C8	1.507(16)	C3	C4	1.529(16)
C4	C5	1.506(15)	C5	C6	1.554(14)
C6	C7	1.523(17)	C8	C9	1.310(15)
C11	C12	1.543(11)	C11	C16	1.532(13)
C11	C17	1.489(14)	C12	C13	1.540(14)
C13	C14	1.509(14)	C14	C15	1.534(12)
C15	C16	1.509(14)	C17	C18	1.328(16)
C20	C21	1.535(14)	C20	C25	1.535(12)
C20	C26	1.495(16)	C21	C22	1.528(16)
C22	C23	1.570(13)	C23	C24	1.519(15)
C24	C25	1.525(16)	C26	C27	1.335(15)
C29	C30	1.534(12)	C29	C34	1.506(13)
C29	C35	1.527(14)	C30	C31	1.533(14)
C31	C32	1.521(14)	C32	C33	1.557(13)
C33	C34	1.522(15)	C35	C36	1.331(16)

Table S8. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
N1	H1	0.930	N2	H13	0.930
N3	H25	0.930	N4	H37	0.930
C3	H2	0.970	C3	H3	0.970
C4	H4	0.970	C4	H5	0.970
C5	H6	0.970	C5	H7	0.970
C6	H8	0.970	C6	H9	0.970
C7	H10	0.970	C7	H11	0.970
C9	H12	0.930	C12	H14	0.970
C12	H15	0.970	C13	H16	0.970
C13	H17	0.970	C14	H18	0.970
C14	H19	0.970	C15	H20	0.970
C15	H21	0.970	C16	H22	0.970
C16	H23	0.970	C18	H24	0.930
C21	H26	0.970	C21	H27	0.970
C22	H28	0.970	C22	H29	0.970
C23	H30	0.970	C23	H31	0.970
C24	H32	0.970	C24	H33	0.970
C25	H34	0.970	C25	H35	0.970
C27	H36	0.930	C30	H38	0.970
C30	H39	0.970	C31	H40	0.970
C31	H41	0.970	C32	H42	0.970
C32	H43	0.970	C33	H44	0.970
C33	H45	0.970	C34	H46	0.970
C34	H47	0.970	C36	H48	0.930

Table S9. Bond angles (˚)

atom	atom	atom	angle	atom	atom	atom	angle
C1	O2	C8	109.3(9)	C10	O4	C17	108.4(8)
C19	O6	C26	108.3(9)	C28	O8	C35	109.1(8)
C1	N1	C2	114.0(9)	C10	N2	C11	112.4(9)
C19	N3	C20	110.9(9)	C28	N4	C29	114.6(9)
O1	C1	O2	118.7(11)	O1	C1	N1	133.1(11)
O2	C1	N1	108.2(9)	N1	C2	C3	111.8(8)
N1	C2	C7	108.1(7)	N1	C2	C8	99.3(9)
C3	C2	C7	110.3(9)	C3	C2	C8	113.7(8)
C7	C2	C8	113.1(8)	C2	C3	C4	111.6(8)
C3	C4	C5	110.5(9)	C4	C5	C6	110.3(10)
C5	C6	C7	110.4(8)	C2	C7	C6	112.5(8)
O2	C8	C2	109.1(8)	O2	C8	C9	117.6(11)
C2	C8	C9	133.4(11)	I1	C9	C8	126.9(10)
O3	C10	O4	121.5(9)	O3	C10	N2	128.5(11)
O4	C10	N2	109.9(10)	N2	C11	C12	109.7(8)
N2	C11	C16	109.1(7)	N2	C11	C17	99.5(8)
C12	C11	C16	111.7(8)	C12	C11	C17	113.1(7)
C16	C11	C17	113.0(8)	C11	C12	C13	110.3(7)
C12	C13	C14	110.6(9)	C13	C14	C15	110.2(9)
C14	C15	C16	110.7(8)	C11	C16	C15	112.5(8)
O4	C17	C11	109.7(9)	O4	C17	C18	114.3(9)
C11	C17	C18	136.0(10)	I2	C18	C17	124.9(8)
O5	C19	O6	119.3(11)	O5	C19	N3	129.3(10)
O6	C19	N3	111.4(9)	N3	C20	C21	109.0(8)
N3	C20	C25	108.1(7)	N3	C20	C26	99.4(9)
C21	C20	C25	111.2(9)	C21	C20	C26	114.3(8)
C25	C20	C26	114.0(8)	C20	C21	C22	113.7(8)
C21	C22	C23	109.4(8)	C22	C23	C24	110.8(10)
C23	C24	C25	110.7(8)	C20	C25	C24	113.1(8)
O6	C26	C20	109.9(8)	O6	C26	C27	115.9(10)
C20	C26	C27	134.3(11)	I3	C27	C26	124.9(9)
O7	C28	O8	120.3(9)	O7	C28	N4	131.2(11)
O8	C28	N4	108.5(10)	N4	C29	C30	110.5(8)
N4	C29	C34	109.7(8)	N4	C29	C35	97.1(8)
C30	C29	C34	112.0(8)	C30	C29	C35	113.0(8)
C34	C29	C35	113.6(8)	C29	C30	C31	111.9(8)
C30	C31	C32	110.6(9)	C31	C32	C33	110.3(9)

Table S9. Bond angles (˚) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C32	C33	C34	111.5(8)	C29	C34	C33	111.1(8)
O8	C35	C29	110.7(9)	O8	C35	C36	116.8(9)
C29	C35	C36	132.5(10)	I4	C36	C35	127.3(8)

Table S10. Bond angles involving hydrogens (˚)

atom	atom	atom	angle	atom	atom	atom	angle
C1	N1	H1	123.2	C2	N1	H1	122.7
C10	N2	H13	124.4	C11	N2	H13	123.2
C19	N3	H25	125.0	C20	N3	H25	124.1
C28	N4	H37	122.7	C29	N4	H37	122.7
C2	C3	H2	109.8	C2	C3	H3	108.7
C4	C3	H2	108.6	C4	C3	H3	108.7
H2	C3	H3	109.5	C3	C4	H4	111.3
C3	C4	H5	110.7	C5	C4	H4	107.7
C5	C4	H5	107.2	H4	C4	H5	109.4
C4	C5	H6	107.1	C4	C5	H7	105.5
C6	C5	H6	112.9	C6	C5	H7	111.5
H6	C5	H7	109.1	C5	C6	H8	110.7
C5	C6	H9	108.9	C7	C6	H8	108.2
C7	C6	H9	109.3	H8	C6	H9	109.5
C2	C7	H10	108.2	C2	C7	H11	110.3
C6	C7	H10	107.4	C6	C7	H11	108.9
H10	C7	H11	109.5	I1	C9	H12	116.6
C8	C9	H12	116.5	C11	C12	H14	109.3
C11	C12	H15	108.3	C13	C12	H14	110.6
C13	C12	H15	108.8	H14	C12	H15	109.5
C12	C13	H16	111.1	C12	C13	H17	111.8
C14	C13	H16	106.0	C14	C13	H17	107.9
H16	C13	H17	109.3	C13	C14	H18	108.0
C13	C14	H19	105.1	C15	C14	H18	112.8
C15	C14	H19	111.2	H18	C14	H19	109.2
C14	C15	H20	110.4	C14	C15	H21	109.0
C16	C15	H20	108.2	C16	C15	H21	109.1
H20	C15	H21	109.4	C11	C16	H22	109.1
C11	C16	H23	109.7	C15	C16	H22	108.0
C15	C16	H23	108.0	H22	C16	H23	109.5
I2	C18	H24	117.9	C17	C18	H24	117.2
C20	C21	H26	106.8	C20	C21	H27	106.9
C22	C21	H26	111.0	C22	C21	H27	108.9
H26	C21	H27	109.4	C21	C22	H28	109.1
C21	C22	H29	110.8	C23	C22	H28	107.9
C23	C22	H29	110.1	H28	C22	H29	109.5
C22	C23	H30	110.7	C22	C23	H31	112.3

Table 10. Bond angles involving hydrogens (˚) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C24	C23	H30	105.0	C24	C23	H31	108.5
H30	C23	H31	109.3	C23	C24	H32	108.2
C23	C24	H33	106.6	C25	C24	H32	111.7
C25	C24	H33	110.2	H32	C24	H33	109.4
C20	C25	H34	108.0	C20	C25	H35	107.8
C24	C25	H34	110.4	C24	C25	H35	108.0
H34	C25	H35	109.5	I3	C27	H36	117.4
C26	C27	H36	117.7	C29	C30	H38	108.8
C29	C30	H39	106.9	C31	C30	H38	110.1
C31	C30	H39	109.6	H38	C30	H39	109.5
C30	C31	H40	112.0	C30	C31	H41	112.3
C32	C31	H40	106.2	C32	C31	H41	106.2
H40	C31	H41	109.2	C31	C32	H42	109.0
C31	C32	H43	105.0	C33	C32	H42	113.2
C33	C32	H43	109.7	H42	C32	H43	109.4
C32	C33	H44	109.5	C32	C33	H45	106.7
C34	C33	H44	109.8	C34	C33	H45	109.8
H44	C33	H45	109.5	C29	C34	H46	108.9
C29	C34	H47	110.4	C33	C34	H46	108.9
C33	C34	H47	108.0	H46	C34	H47	109.5
I4	C36	H48	117.4	C35	C36	H48	115.2

Table S11. Torsion Angles (˚)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C1	O2	C8	C2	-0.8(8)	C1	O2	C8	C9	178.5(6)
C8	O2	C1	O1	-178.7(7)	C8	O2	C1	N1	2.2(8)
C10	O4	C17	C11	1.2(8)	C10	O4	C17	C1	179.3(6)
C17	O4	C10	O3	-178.6(7)	C17	O4	C10	N2	0.9(8)
C19	O6	C26	C20	0.3(8)	C19	O6	C26	C27	-178.9(6)
C26	O6	C19	O5	-178.6(7)	C26	O6	C19	N3	2.0(9)
C28	O8	C35	C29	-1.7(8)	C28	O8	C35	C36	-179.9(6)
C35	O8	C28	O7	-177.8(7)	C35	O8	C28	N4	1.5(8)
C1	N1	C2	C3	-118.0(8)	C1	N1	C2	C7	120.4(8)
C1	N1	C2	C8	2.3(8)	C2	N1	C1	O1	178.2(9)
C2	N1	C1	O2	-2.9(9)	C10	N2	C11	C12	-115.7(7)
C10	N2	C11	C16	121.7(7)	C10	N2	C11	C17	3.2(8)
C11	N2	C10	O3	176.7(8)	C11	N2	C10	O4	-2.7(9)
C19	N3	C20	C21	123.1(8)	C19	N3	C20	C25	-115.9(8)
C19	N3	C20	C26	3.3(8)	C20	N3	C19	O5	177.2(8)
C20	N3	C19	O6	-3.4(9)	C28	N4	C29	C30	-118.1(8)
C28	N4	C29	C34	117.9(8)	C28	N4	C29	C35	-0.3(8)
C29	N4	C28	O7	178.4(8)	C29	N4	C28	O8	-0.7(9)
N1	C2	C3	C4	-65.5(11)	N1	C2	C7	C6	68.9(10)
N1	C2	C8	O2	-0.8(8)	N1	C2	C8	C9	-179.9(8)
C3	C2	C7	C6	-53.6(10)	C7	C2	C3	C4	54.9(10)
C3	C2	C8	O2	118.1(8)	C3	C2	C8	C9	-61.0(12)
C8	C2	C3	C4	-176.9(7)	C7	C2	C8	O2	-115.2(8)
C7	C2	C8	C9	65.7(11)	C8	C2	C7	C6	177.8(7)
C2	C3	C4	C5	-58.7(10)	C3	C4	C5	C6	58.8(10)
C4	C5	C6	C7	-56.9(11)	C5	C6	C7	C2	54.5(11)
O2	C8	C9	I1	-176.2(6)	C2	C8	C9	I1	2.8(15)
N2	C11	C12	C13	-68.4(9)	N2	C11	C16	C15	69.1(9)
N2	C11	C17	O4	-2.5(7)	N2	C11	C17	C18	179.9(8)
C12	C11	C16	C15	-52.3(11)	C16	C11	C12	C13	52.7(11)
C12	C11	C17	O4	113.7(9)	C12	C11	C17	C18	-63.8(13)
C17	C11	C12	C13	-178.5(8)	C16	C11	C17	O4	-118.1(8)
C16	C11	C17	C18	64.4(12)	C17	C11	C16	C15	178.7(7)
C11	C12	C13	C14	-57.2(11)	C12	C13	C14	C15	60.1(11)
C13	C14	C15	C16	-58.6(12)	C14	C15	C16	C11	54.7(12)
O4	C17	C18	I2	-173.6(6)	C11	C17	C18	I2	3.9(15)
N3	C20	C21	C22	67.7(9)	N3	C20	C25	C24	-68.4(10)

Table S11. Torsion angles (˚) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
N3	C20	C26	O6	-2.0(8)	N3	C20	C26	C27	176.9(8)
C21	C20	C25	C24	51.3(10)	C25	C20	C21	C22	-51.4(10)
C21	C20	C26	O6	-118.0(8)	C21	C20	C26	C27	61.0(12)
C26	C20	C21	C22	177.9(7)	C25	C20	C26	O6	112.7(8)
C25	C20	C26	C27	-68.3(12)	C26	C20	C25	C24	-177.9(7)
C20	C21	C22	C23	54.1(10)	C21	C22	C23	C24	-57.2(10)
C22	C23	C24	C25	58.1(10)	C23	C24	C25	C20	-55.6(10)
O6	C26	C27	I3	-173.0(6)	C20	C26	C27	I3	8.0(14)
N4	C29	C30	C31	-68.2(10)	N4	C29	C34	C33	68.8(9)
N4	C29	C35	O8	1.2(7)	N4	C29	C35	C36	179.0(8)
C30	C29	C34	C33	-54.3(11)	C34	C29	C30	C31	54.4(12)
C30	C29	C35	O8	117.1(9)	C30	C29	C35	C36	-65.1(12)
C35	C29	C30	C31	-175.8(8)	C34	C29	C35	O8	-113.9(9)
C34	C29	C35	C36	63.9(12)	C35	C29	C34	C33	176.2(8)
C29	C30	C31	C32	-55.3(11)	C30	C31	C32	C33	56.0(11)
C31	C32	C33	C34	-56.8(12)	C32	C33	C34	C29	55.7(12)
O8	C35	C36	I4	-176.6(6)	C29	C35	C36	I4	5.7(14)

Table S12. Possible hydrogen bonds

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A
N1	H1	O5[1]	2.840(12)	0.93	1.92	168.50
N2	H13	O7	2.882(12)	0.93	1.97	166.27
N3	H25	O1[2]	2.887(11)	0.93	1.97	167.44
N4	H37	O3	2.846(12)	0.93	1.93	166.05

Symmetry Operators:

(1) X+1,Y,Z (2) X–1,Y,Z

Table S13. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C2	3.526(13)	O1	C8	3.389(12)
O2	C3	3.470(14)	O2	C7	3.446(14)
O3	C11	3.540(13)	O3	C17	3.420(14)
O4	C12	3.451(11)	O4	C16	3.477(12)
O5	C20	3.559(13)	O5	C26	3.411(12)
O6	C21	3.485(14)	O6	C25	3.437(13)
O7	C29	3.558(13)	O7	C35	3.389(14)
O8	C30	3.495(12)	O8	C34	3.453(12)
N1	C4	3.039(15)	N1	C6	3.030(16)
N1	C9	3.576(14)	N2	C13	3.036(13)
N2	C15	3.043(13)	N2	C18	3.599(15)
N3	C22	3.069(15)	N3	C24	3.047(14)
N4	C31	3.075(13)	N4	C33	3.020(14)
N4	C36	3.596(16)	C1	C3	3.425(15)
C1	C7	3.403(16)	C1	C9	3.492(15)
C2	C5	2.962(18)	C3	C6	2.944(14)
C3	C9	3.272(16)	C4	C7	2.936(13)
C7	C9	3.295(16)	C10	C12	3.394(14)
C10	C16	3.426(16)	C10	C18	3.466(17)
C11	C14	2.945(14)	C12	C15	2.955(12)
C12	C18	3.318(14)	C13	C16	2.935(13)
C16	C18	3.312(14)	C19	C21	3.425(16)
C19	C25	3.355(15)	C19	C27	3.461(14)
C20	C23	2.974(17)	C21	C24	2.954(12)
C21	C27	3.304(16)	C22	C25	2.969(14)
C25	C27	3.346(15)	C28	C30	3.453(15)
C28	C34	3.417(16)	C28	C36	3.499(17)
C29	C32	2.952(14)	C30	C33	2.932(13)
C30	C36	3.307(14)	C31	C34	2.967(12)
C34	C36	3.293(15)			

Table S14. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
I1	H3	3.013	I1	H10	3.170
I2	H15	3.070	I2	H22	3.176
I3	H26	3.112	I3	H35	3.091
I4	H39	3.045	I4	H46	3.179
O1	H1	2.651	O2	H1	3.095
O2	H2	3.399	O2	H11	3.362
O2	H12	2.402	O3	H13	2.629
O4	H13	3.106	O4	H14	3.343
O4	H23	3.405	O4	H24	2.380
O5	H25	2.664	O6	H25	3.110
O6	H27	3.372	O6	H34	3.307
O6	H36	2.416	O7	H37	2.627
O8	H37	3.100	O8	H38	3.386
O8	H47	3.363	O8	H48	2.390
N1	H2	2.656	N1	H3	3.304
N1	H4	2.751	N1	H8	2.744
N1	H10	3.266	N1	H11	2.588
N2	H14	2.620	N2	H15	3.301
N2	H16	2.730	N2	H20	2.750
N2	H22	3.291	N2	H23	2.589
N3	H26	3.282	N3	H27	2.565
N3	H29	2.828	N3	H33	2.751
N3	H34	2.576	N3	H35	3.282
N4	H38	2.632	N4	H39	3.304
N4	H40	2.811	N4	H44	2.737
N4	H46	3.289	N4	H47	2.594
C1	H2	3.344	C1	H11	3.312
C2	H4	2.747	C2	H5	3.367
C2	H7	3.248	C2	H8	2.768
C2	H9	3.371	C2	H12	3.366
C3	H1	2.834	C3	H6	3.313
C3	H7	2.636	C3	H8	3.295
C3	H10	2.721	C3	H11	3.356
C4	H1	2.900	C4	H8	2.738
C4	H9	3.337	C4	H10	3.264
C5	H1	3.445	C5	H2	3.320
C5	H3	2.680	C5	H10	2.712

Table S14. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C5	H11	3.360	C6	H1	2.871
C6	H3	3.262	C6	H4	2.687
C6	H5	3.335	C7	H1	2.766
C7	H2	3.354	C7	H3	2.726
C7	H4	3.246	C7	H6	3.383
C7	H7	2.741	C8	H1	3.175
C8	H2	2.723	C8	H3	2.755
C8	H10	2.749	C8	H11	2.724
C9	H2	3.445	C9	H3	3.098
C9	H10	3.118	C9	H11	3.483
C10	H14	3.272	C10	H23	3.331
C11	H16	2.737	C11	H17	3.384
C11	H19	3.200	C11	H20	2.748
C11	H21	3.353	C11	H24	3.381
C12	H13	2.834	C12	H18	3.333
C12	H19	2.626	C12	H20	3.289
C12	H22	2.783	C12	H23	3.374
C13	H13	2.903	C13	H20	2.705
C13	H21	3.326	C13	H22	3.296
C14	H13	3.469	C14	H14	3.347
C14	H15	2.699	C14	H22	2.711
C14	H23	3.328	C15	H13	2.902
C15	H15	3.285	C15	H16	2.632
C15	H17	3.323	C16	H13	2.794
C16	H14	3.370	C16	H15	2.766
C16	H16	3.209	C16	H18	3.360
C16	H19	2.699	C17	H13	3.175
C17	H14	2.708	C17	H15	2.735
C17	H22	2.726	C17	H23	2.713
C18	H14	3.488	C18	H15	3.139
C18	H22	3.132	C18	H23	3.506
C19	H27	3.296	C19	H34	3.207
C20	H28	3.380	C20	H29	2.831
C20	H30	3.229	C20	H32	3.395
C20	H33	2.771	C20	H36	3.388
C21	H25	2.809	C21	H30	2.721
C21	H31	3.384	C21	H33	3.246

Table S14. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C21	H34	3.351	C21	H35	2.758
C22	H25	2.930	C22	H32	3.372
C22	H33	2.695	C22	H35	3.304
C23	H25	3.489	C23	H26	2.772
C23	H27	3.365	C23	H34	3.344
C23	H35	2.698	C24	H25	2.924
C24	H26	3.326	C24	H28	3.359
C24	H29	2.777	C25	H25	2.814
C25	H26	2.771	C25	H27	3.340
C25	H29	3.334	C25	H30	2.638
C25	H31	3.332	C26	H25	3.189
C26	H26	2.707	C26	H27	2.696
C26	H34	2.693	C26	H35	2.741
C27	H26	3.071	C27	H27	3.461
C27	H34	3.512	C27	H35	3.160
C28	H38	3.338	C28	H47	3.309
C29	H40	2.787	C29	H41	3.390
C29	H43	3.220	C29	H44	2.736
C29	H45	3.329	C29	H48	3.386
C30	H37	2.837	C30	H42	3.343
C30	H43	2.649	C30	H44	3.283
C30	H46	2.744	C30	H47	3.358
C31	H37	2.937	C31	H44	2.750
C31	H45	3.336	C31	H46	3.305
C32	H37	3.473	C32	H38	3.348
C32	H39	2.722	C32	H46	2.752
C32	H47	3.368	C33	H37	2.891
C33	H39	3.264	C33	H40	2.705
C33	H41	3.340	C34	H37	2.815
C34	H38	3.342	C34	H39	2.721
C34	H40	3.296	C34	H42	3.400
C34	H43	2.727	C35	H37	3.177
C35	H38	2.695	C35	H39	2.742
C35	H46	2.753	C35	H47	2.721
C36	H38	3.452	C36	H39	3.104
C36	H46	3.115	C36	H47	3.481
H1	H2	3.030	H1	H4	2.357

Table S14. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H1	H8	2.332	H1	H11	2.929
H2	H4	2.373	H2	H5	2.373
H2	H7	3.506	H3	H4	2.850
H3	H5	2.352	H3	H6	3.541
H3	H7	2.457	H3	H10	2.574
H4	H6	2.285	H4	H7	2.774
H4	H8	2.557	H4	H9	3.568
H5	H6	2.260	H5	H7	2.248
H6	H8	2.432	H6	H9	2.439
H7	H8	2.889	H7	H9	2.401
H7	H10	2.572	H8	H10	2.807
H8	H11	2.306	H9	H10	2.297
H9	H11	2.361	H13	H14	3.001
H13	H16	2.335	H13	H20	2.355
H13	H23	2.929	H14	H16	2.411
H14	H17	2.425	H14	H19	3.514
H15	H16	2.859	H15	H17	2.388
H15	H18	3.557	H15	H19	2.453
H15	H22	2.656	H16	H18	2.293
H16	H19	2.758	H16	H20	2.477
H16	H21	3.512	H17	H18	2.266
H17	H19	2.277	H17	H20	3.570
H18	H20	2.421	H18	H21	2.407
H18	H22	3.597	H19	H20	2.868
H19	H21	2.395	H19	H22	2.551
H19	H23	3.594	H20	H22	2.801
H20	H23	2.275	H21	H22	2.285
H21	H23	2.339	H25	H27	2.918
H25	H29	2.434	H25	H33	2.368
H25	H34	2.963	H26	H28	2.331
H26	H29	2.863	H26	H30	2.613
H26	H35	2.646	H27	H28	2.396
H27	H29	2.326	H28	H30	2.392
H28	H31	2.429	H28	H33	3.573
H29	H30	2.890	H29	H31	2.429
H29	H33	2.575	H30	H32	2.279
H30	H33	2.770	H30	H34	3.528

Table S14. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H30	H35	2.467	H31	H32	2.296
H31	H33	2.310	H31	H35	3.560
H32	H34	2.413	H32	H35	2.350
H33	H34	2.374	H33	H35	2.832
H37	H38	2.998	H37	H40	2.414
H37	H44	2.355	H37	H47	2.968
H38	H40	2.397	H38	H41	2.437
H38	H43	3.537	H39	H40	2.867
H39	H41	2.380	H39	H42	3.594
H39	H43	2.499	H39	H46	2.589
H40	H42	2.297	H40	H43	2.768
H40	H44	2.574	H40	H45	3.568
H41	H42	2.286	H41	H43	2.246
H42	H44	2.424	H42	H45	2.403
H43	H44	2.866	H43	H45	2.359
H43	H46	2.582	H44	H46	2.833
H44	H47	2.314	H45	H46	2.317
H45	H47	2.366			

Table S15. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	O1[1]	3.458(9)	O1	O2[1]	3.164(8)
O1	N3[2]	2.887(11)		O1	C1[1] 3.204(11)
O1	C27	3.469(14)		O2	O1[1] 3.164(8)
O2	O6	3.020(11)		O2	C1[1] 3.578(10)
O2	C12	3.538(10)		O2	C13 3.538(11)
O2	C27	3.371(14)		O3	O4[3] 3.187(8)
O3	N4	2.846(12)		O3	C10[3] 3.378(11)
O3	C17[3]	3.478(10)		O4	O3[3] 3.187(8)
O4	O8[2]	3.008(9)	O4	C10[3]	3.403(10)
O4	C24[2]	3.573(10)		O4	C36[2] 3.465(12)
O5	O6[4]	3.116(8)	O5	N1[5]	2.840(12)
O5	C19[4]	3.267(10)		O5	C26[4] 3.480(10)
O6	O2	3.020(11)		O6	O5[4] 3.116(8)
O6	C9	3.461(15)		O6	C13 3.586(11)
O6	C19[4]	3.415(10)		O7	O7[6] 3.433(9)
O7	O8[6]	3.222(8)	O7	N2	2.882(12)
O7	C18[5]	3.506(12)		O7	C28[6] 3.242(11)
O8	O4[5]	3.008(9)	O8	O7[6]	3.222(8)
O8	C18[5]	3.400(13)		O8	C24 3.473(11)
O8	C25	3.536(10)		N1	O5[2] 2.840(12)
N1	N3[2]	3.505(12)		N1	C19[2] 3.475(14)
N2	O7	2.882(12)		N2	N4 3.542(14)
N2	C28	3.489(15)		N3	O1[5] 2.887(11)
N3	N1[5]	3.505(12)		N3	C1[5] 3.451(13)
N4	O3	2.846(12)		N4	N2 3.542(14)
N4	C10	3.502(16)		C1	O1[1] 3.204(11)
C1	O2[1]	3.578(10)		C1	N3[2] 3.451(13)
C1	C1[1]	3.384(13)		C9	O6 3.461(15)
C10	O3[3]	3.378(11)		C10	O4[3] 3.403(10)
C10	N4	3.502(16)		C10	C10[3] 3.329(12)
C12	O2	3.538(10)		C13	O2 3.538(11)
C13	O6	3.586(11)		C13	C27 3.507(14)
C17	O3[3]	3.478(10)		C18	O7[2] 3.506(12)
C18	O8[2]	3.400(13)		C18	C24[2] 3.516(13)
C19	O5[4]	3.267(10)		C19	O6[4] 3.415(10)
C19	N1[5]	3.475(14)		C19	C19[4] 3.310(12)
C24	O4[5]	3.573(10)		C24	O8 3.473(11)

Table S15. Intermolecular contacts less than 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C24	C18[5]	3.516(13)		C25	O8 3.536(10)
C26	O5[4]	3.480(10)		C27	O1 3.469(14)
C27	O2	3.371(14)		C27	C13 3.507(14)
C28	O7[6]	3.242(11)		C28	N2 3.489(15)
C28	C28[6]	3.476(12)		C36	O4[5] 3.465(12)

Symmetry Operators:

(1) –X+1,-Y,–Z+2 (2) X+1,Y,Z
(3) –X+1,–Y+1,–Z+1 (4) –X,–Y,–Z+2
(5) X–1,Y,Z (6) –X,-Y+1,–Z+1

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
I1	H6[1]	3.357	I1	H18[2]	3.280
I1	H21[2]	3.486	I1	H28[3]	3.393
I1	H46[4]	3.591	I2	H2	3.211
I2	H4	3.422	I2	H18[5]	3.391
I2	H34[5]	3.445	I2	H45[6]	3.305
I2	H47[6]	3.374	I3	H9[7]	3.282
I3	H11[7]	3.459	I3	H14	3.440
I3	H31[5]	3.406	I3	H38	3.218
I3	H40	3.308	I3	H42[8]	3.501
I4	H9[9]	3.466	I4	H21[10]	3.333
I4	H26[11]	3.181	I4	H28[11]	3.572
I4	H42[1]	3.306	O1	H11[7]	3.063
O1	H14	3.298	O1	H15	3.570
O1	H25[5]	1.972	O1	H29[5]	2.978
O1	H33[5]	2.993	O1	H36	2.569
O2	H14	3.390	O2	H15	3.192
O2	H17	2.797	O2	H36	2.565
O3	H23[6]	2.846	O3	H37	1.935
O3	H40	3.048	O3	H44	2.818
O3	H48[5]	2.715	O4	H32[5]	2.749
O4	H33[5]	3.595	O4	H48[5]	2.651
O5	H1[1]	1.923	O5	H4[1]	2.933
O5	H8[1]	2.773	O5	H12	2.747
O5	H27[3]	2.907	O6	H12	2.652
O6	H17	2.771	O7	H13	1.970
O7	H16	2.998	O7	H20	2.917
O7	H24[1]	2.607	O7	H34	3.323
O7	H35	3.448	O7	H47[10]	3.295
O8	H24[1]	2.589	O8	H32	2.710
O8	H34	3.459	O8	H35	3.142
N1	H15	3.539	N1	H25[5]	2.973
N2	H37	2.982	N3	H1[1]	2.960
N4	H13	3.003	N4	H35	3.462
C1	H14	3.418	C1	H15	3.206
C1	H25[5]	2.654	C1	H36	2.950
C3	H5[12]	3.014	C3	H15	3.548
C4	H3[12]	3.375	C4	H5[12]	3.600

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C5	H19[12]	3.456	C5	H21[12]	3.252
C5	H22[12]	3.117	C5	H45[4]	3.585
C6	H26[7]	3.413	C6	H27[7]	3.455
C6	H42[4]	3.312	C7	H29[3]	3.187
C7	H42[4]	3.572	C7	H43[4]	3.501
C7	H45[4]	3.441	C8	H15	3.509
C8	H17	3.100	C8	H29[3]	3.358
C9	H17	3.030	C9	H27[3]	3.183
C9	H29[3]	3.240	C10	H37	2.689
C10	H48[5]	3.042	C12	H36	3.319
C13	H36	3.395	C14	H6[12]	3.388
C15	H6[12]	3.176	C15	H7[12]	3.596
C15	H46[10]	3.509	C15	H47[10]	3.348
C16	H6[12]	3.544	C16	H7[12]	3.275
C16	H44[6]	3.300	C16	H48[10]	3.541
C17	H32[5]	3.128	C17	H33[5]	3.435
C17	H44[6]	3.517	C18	H32[5]	3.108
C18	H33[5]	3.388	C18	H34[5]	2.978
C18	H44[6]	3.289	C18	H47[6]	3.246
C19	H1[1]	2.669	C19	H12	3.084
C21	H8[7]	3.221	C22	H10[3]	3.511
C22	H11[3]	3.407	C22	H43[11]	3.075
C23	H39[11]	3.461	C23	H43[11]	3.068
C24	H24[1]	3.383	C25	H24[1]	3.345
C26	H8[7]	3.391	C26	H16	3.399
C26	H17	3.113	C27	H8[7]	3.176
C27	H11[7]	3.170	C27	H14	2.940
C27	H16	3.371	C27	H17	3.132
C28	H13	2.688	C28	H24[1]	2.970
C28	H34	3.470	C28	H35	3.119
C30	H30	3.567	C30	H35	3.588
C31	H31[11]	3.597	C31	H41[8]	3.465
C32	H9[13]	3.225	C32	H10[13]	3.220
C32	H28[11]	3.418	C32	H31[11]	3.344
C33	H10[13]	3.313	C33	H22[6]	3.503
C34	H20[10]	3.263	C34	H21[10]	3.572
C35	H20[10]	3.336	C35	H32	3.050

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C35	H35	3.495	C36	H20^{10}	3.238
C36	H21^{10}	3.447	C36	H23^{10}	3.047
C36	H30	3.542	C36	H32	3.043
H1	O5^{5}	1.923	H1	N3^{5}	2.960
H1	C19^{5}	2.669	H1	H25^{5}	2.651
H2	I2	3.211	H2	H3^{12}	3.558
H2	H5^{12}	2.796	H2	H15	2.689
H2	H19	3.011	H3	C4^{12}	3.375
H3	H2^{12}	3.558	H3	H5^{12}	2.479
H4	I2	3.422	H4	O5^{5}	2.933
H5	C3^{12}	3.014	H5	C4^{12}	3.600
H5	H2^{12}	2.796	H5	H3^{12}	2.479
H5	H5^{12}	3.156	H5	H19^{12}	3.161
H6	I1^{5}	3.357	H6	C14^{12}	3.388
H6	C15^{12}	3.176	H6	C16^{12}	3.544
H6	H19^{12}	2.900	H6	H21^{12}	2.499
H6	H22^{12}	2.982	H7	C15^{12}	3.596
H7	C16^{12}	3.275	H7	H19^{12}	3.262
H7	H21^{12}	3.204	H7	H22^{12}	2.409
H7	H45^{4}	2.820	H8	O5^{5}	2.773
H8	C21^{7}	3.221	H8	C26^{7}	3.391
H8	C27^{7}	3.176	H8	H26^{7}	2.933
H8	H27^{7}	2.681	H8	H36^{7}	3.380
H9	I3^{7}	3.282	H9	I4^{14}	3.466
H9	C32^{4}	3.225	H9	H26^{7}	3.013
H9	H27^{7}	3.486	H9	H42^{4}	2.485
H9	H43^{4}	3.333	H9	H45^{4}	3.320
H10	C22^{3}	3.511	H10	C32^{4}	3.220
H10	C33^{4}	3.313	H10	H28^{3}	3.138
H10	H29^{3}	2.991	H10	H42^{4}	3.130
H10	H43^{4}	2.861	H10	H45^{4}	2.578
H11	I3^{7}	3.459	H11	O1^{7}	3.063
H11	C22^{3}	3.407	H11	C27^{7}	3.170
H11	H28^{3}	3.470	H11	H29^{3}	2.600
H11	H36^{7}	2.885	H11	H43^{4}	3.417
H12	O5	2.747	H12	O6	2.652
H12	C19	3.084	H12	H17	2.743

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H12	H27[3]	2.852	H12	H29[3]	3.446
H13	O7	1.970	H13	N4	3.003
H13	C28	2.688	H13	H37	2.663
H14	I3	3.440	H14	O1	3.298
H14	O2	3.390	H14	C1	3.418
H14	C27	2.940	H14	H33[5]	2.975
H14	H36	2.621	H15	O1	3.570
H15	O2	3.192	H15	N1	3.539
H15	C1	3.206	H15	C3	3.548
H15	C8	3.509	H15	H2	2.689
H16	O7	2.998	H16	C26	3.399
H16	C27	3.371	H16	H34	2.986
H16	H36	3.517	H17	O2	2.797
H17	O6	2.771	H17	C8	3.100
H17	C9	3.030	H17	C26	3.113
H17	C27	3.132	H17	H12	2.743
H17	H36	2.936	H18	I1[2]	3.280
H18	I2[1]	3.391	H19	C5[12]	3.456
H19	H2	3.011	H19	H5[12]	3.161
H19	H6[12]	2.900	H19	H7[12]	3.262
H20	O7	2.917	H20	C34[10]	3.263
H20	C35[10]	3.336	H20	C36[10]	3.238
H20	H46[10]	3.129	H20	H47[10]	2.638
H20	H48[10]	3.369	H21	I1[2]	3.486
H21	I4[10]	3.333	H21	C5[12]	3.252
H21	C34[10]	3.572	H21	C36[10]	3.447
H21	H6[12]	2.499	H21	H7[12]	3.204
H21	H46[10]	3.002	H21	H47[10]	3.277
H22	C5[12]	3.117	H22	C33[6]	3.503
H22	H6[12]	2.982	H22	H7[12]	2.409
H22	H44[6]	2.973	H22	H45[6]	3.139
H23	O3[6]	2.846	H23	C36[10]	3.047
H23	H44[6]	2.806	H23	H48[10]	2.678
H24	O7[5]	2.607	H24	O8[5]	2.589
H24	C24[5]	3.383	H24	C25[5]	3.345
H24	C28[5]	2.970	H24	H32[5]	2.883
H24	H33[5]	3.514	H24	H34[5]	2.682

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H24	H44^{6}	3.510	H24	H47^{6}	3.007
H25	O1^{1}	1.972	H25	N1^{1}	2.973
H25	C1^{1}	2.654	H25	H1^{1}	2.651
H26	I4^{11}	3.181	H26	C6^{7}	3.413
H26	H8^{7}	2.933	H26	H9^{7}	3.013
H27	O5^{3}	2.907	H27	C6^{7}	3.455
H27	C9^{3}	3.183	H27	H8^{7}	2.681
H27	H9^{7}	3.486	H27	H12^{3}	2.852
H28	I1^{3}	3.393	H28	I4^{11}	3.572
H28	C32^{11}	3.418	H28	H10^{3}	3.138
H28	H11^{3}	3.470	H28	H39^{11}	3.333
H28	H43^{11}	2.505	H28	H46^{11}	2.862
H29	O1^{1}	2.978	H29	C7^{3}	3.187
H29	C8^{3}	3.358	H29	C9^{3}	3.240
H29	H10^{3}	2.991	H29	H11^{3}	2.600
H29	H12^{3}	3.446	H29	H43^{11}	3.257
H30	C30	3.567	H30	C36	3.542
H30	H38	2.846	H30	H39	3.497
H30	H39^{11}	2.981	H30	H43^{11}	3.337
H31	I3^{1}	3.406	H31	C31^{11}	3.597
H31	C32^{11}	3.344	H31	H39^{11}	3.257
H31	H41^{11}	3.148	H31	H43^{11}	2.509
H32	O4^{1}	2.749	H32	O8	2.710
H32	C17^{1}	3.128	H32	C18^{1}	3.108
H32	C35	3.050	H32	C36	3.043
H32	H24^{1}	2.883	H32	H48	2.784
H33	O1^{1}	2.993	H33	O4^{1}	3.595
H33	C17^{1}	3.435	H33	C18^{1}	3.388
H33	H14^{1}	2.975	H33	H24^{1}	3.514
H34	I2^{1}	3.445	H34	O7	3.323
H34	O8	3.459	H34	C18^{1}	2.978
H34	C28	3.470	H34	H16	2.986
H34	H24^{1}	2.682	H35	O7	3.448
H35	O8	3.142	H35	N4	3.462
H35	C28	3.119	H35	C30	3.588
H35	C35	3.495	H35	H38	2.725
H36	O1	2.569	H36	O2	2.565

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H36	C1	2.950	H36	C12	3.319
H36	C13	3.395	H36	H8^{7}	3.380
H36	H11^{7}	2.885	H36	H14	2.621
H36	H16	3.517	H36	H17	2.936
H37	O3	1.935	H37	N2	2.982
H37	C10	2.689	H37	H13	2.663
H38	I3	3.218	H38	H30	2.846
H38	H35	2.725	H39	C23^{11}	3.461
H39	H28^{11}	3.333	H39	H30	3.497
H39	H30^{11}	2.981	H39	H31^{11}	3.257
H40	I3	3.308	H40	O3	3.048
H40	H41^{8}	3.332	H41	C31^{8}	3.465
H41	H31^{11}	3.148	H41	H40^{8}	3.332
H41	H41^{8}	2.746	H42	I3^{8}	3.501
H42	I4^{5}	3.306	H42	C6^{13}	3.312
H42	C7^{13}	3.572	H42	H9^{13}	2.485
H42	H10^{13}	3.130	H43	C7^{13}	3.501
H43	C22^{11}	3.075	H43	C23^{11}	3.068
H43	H9^{13}	3.333	H43	H10^{13}	2.861
H43	H11^{13}	3.417	H43	H28^{11}	2.505
H43	H29^{11}	3.257	H43	H30^{11}	3.337
H43	H31^{11}	2.509	H44	O3	2.818
H44	C16^{6}	3.300	H44	C17^{6}	3.517
H44	C18^{6}	3.289	H44	H22^{6}	2.973
H44	H23^{6}	2.806	H44	H24^{6}	3.510
H45	I2^{6}	3.305	H45	C5^{13}	3.585
H45	C7^{13}	3.441	H45	H7^{13}	2.820
H45	H9^{13}	3.320	H45	H10^{13}	2.578
H45	H22^{6}	3.139	H46	I1^{13}	3.591
H46	C15^{10}	3.509	H46	H20^{10}	3.129
H46	H21^{10}	3.002	H46	H28^{11}	2.862
H47	I2^{6}	3.374	H47	O7^{10}	3.295
H47	C15^{10}	3.348	H47	C18^{6}	3.246
H47	H20^{10}	2.638	H47	H21^{10}	3.277
H47	H24^{6}	3.007	H48	O3^{1}	2.715
H48	O4^{1}	2.651	H48	C10^{1}	3.042
H48	C16^{10}	3.541	H48	H20^{10}	3.369

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H48	H23[10]	2.678	H48	H32	2.784

Symmetry Operators:

(1)	X–1,Y,Z	(2)	–X,–Y+1,–Z+2
(3)	–X,–Y,–Z+2	(4)	X,Y,Z+1
(5)	X+1,Y,Z	(6)	–X+1,–Y+1,–Z+1
(7)	–X+1,–Y,–Z+2	(8)	–X+1,–Y,–Z+1
(9)	X–1,Y,Z–1	(10)	–X,–Y+1,–Z+1
(11)	–X,–Y,–Z+1	(12)	–X+1,–Y+1,–Z+2
(13)	X,Y,Z–1	(14)	X+1,Y,Z+1

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