Supplementary Information

Catalytic fluoride triggers dehydrative oxazolidinone synthesis from CO_2

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General

^{1}H NMR spectra were measured on JEOL ECA-600 (600 MHz), JEOL ECA-500 (500 MHz) or JEOL ECA-400 (400 MHz) at room temperature. Data were recorded as follows: Chemical shifts are presented in ppm δ relative to tetramethylsilane (for $CDCl_3$, 0 ppm) or solvent residual signal (for DMSO-d_6, 2.49 ppm; methanol-d_4, 3.31 ppm), coupling constants (J) in Hz, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), and integrations are based on the internal standard (anisole). ^{13}C NMR spectra were measured on JEOL ECA-600 (150 MHz), JEOL ECA-500 (125 MHz) or JEOL ECA-400 (100 MHz) at room temperature. Chemical shifts were recorded in ppm based on the solvent residual signals (chloroform-d_1, 77.06 ppm; DMSO-d_6, 39.52 ppm; methanol-d_4, 49.00 ppm). High-resolution mass spectra (HRMS) were obtained from JEOL JMS-700 (FAB) and Bruker micrOTOF-QII (ESI). Organic element analyzer MT-6 (YANACO Co., Ltd.,) was used for elemental analysis. For GC-MS analysis, Agilent GC-MS was used (GC: Agilent 6850 series GC system; MS: Agilent 5975 network Mass Selective Detector; Column: J&W 19091J-413 (HP-5, 30 m x 319 μm x 0.25 μm); Carrier gas: H_2). Chiral GC-MS analysis was performed on the another Agilent GC-MS machine (GC: Agilent 6890 series GC system; MS: Agilent 5973 network Mass Selective Detector; Chiral column: J&W 112-2532 (Cyclodex-B, 30 m x 250 μm x 0.25 nominal); Carrier gas: **2c**, **2d**, **2e**, **2g** and **2h** (obtained from the reaction with TBAT) = H_2, other oxazolidinones including **2a** and **2p** (obtained from the reaction with TBAT or TBAF and $(Me_2SiO)_3$) and **2c**, **2d**, **2e**, **2g** and **2h** (obtained from the reaction with TBAF and $(Me_2SiO)_3$)) = He). HPLC (Shimadzu HPLC system. Detector: SPD-M20A) was equipped with chiral column (DAICEL CHIRALCEL OJ-RH) for chirality determination. For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254 0.25mm) were used and products were observed under UV light or stain in iodine chamber or phosphomolybdic acid

solution. The products were purified by preparative column chromatography on silica gel 60 (230–400 mesh; Merck) or automated flash column chromatography (YAMAZEN WPrep2XY, column: Ultra Pack A. Biotage Isorela, column: column filled with silica gel 60 (230–400 mesh; Merck)). All 1 atm reactions were carried out in oven-dried glass tube connected with CO_2 balloon. Whereas, reactions more than 1 atm were carried out in oven-dried Teflon tube fitted into autoclave (Taiatsu Techno).

Materials

All starting materials including catalysts, Si–O agents, **1b**, (*S*)-**1d,** (*S*)-**1g**, (*S*)-**1k**•HCl, (*R*)-**1k**•HCl, (*S*)-**1l, 1m**, *rac*-**1n**, **1o**, and (*R*)-**1p** were purchased from commercial suppliers and were directly used without further purification, unless otherwise stated. DMSO-d_6 (99.9%D) was distilled over CaH_2 before use. Several commercial amino acids were reduced by $LiAlH_4$ or combination of $NaBH_4$ and I_2 and purified in laboratory according to the reported methods in literatures,[1] i.e., L-valinol ((*S*)-**1a**), L-alaninol ((*S*)-**1c**), L-isoleucinol ((*S*)-**1e**), L-phenylalaninol((*S*)-**1f**), L-*tert*-leucinol ((*S*)-**1h**), L-phenyglycinol ((*S*)-**1i**), (*R*)-2-amino-3-(benzylthio)-1-propanol ((*R*)-**1j**) and D-tryptophanol ((*R*)-**1l**). **2b** is commercially available.

Typical procedure for oxazolidinone synthesis:

using carbon dioxide pressure of P_{CO2} = 1 atm (catalyst: TBAT, Table 1, entry 9)

To a DMSO-d_6 (0.5 mL) solution of tetrabutylammonium difluorotriphenylsilicate (TBAT) (54.0 mg, 0.1 mmol) was added (*S*)-**1a** (55.7 μL, 0.5 mmol). A dried glass Schlenk tube containing the reaction mixture was frozen with liquid nitrogen (–196 ºC) under vacuum for air removal, and then purged with CO_2 gas from a balloon (1 L) filled with CO_2 fitted to the glass tube and thawed at 25 °C. The glass tube was stirred at 150 °C for 12 h. Upon completion, the reaction mixture was subjected to ^{1}H NMR for determining crude product yield (94%), which was calculated based on an integral ratio between product and internal standard (anisole). After that, DMSO-d_6 was removed through distillation under vacuum conditions (1 mmHg, 50 °C); the syrupy product was then purified by column chromatography on silica gel (hexane/ethyl acetate 1:3) to give the product (*S*)-4-isopropyloxazolidin-2-one ((*S*)-**2a**) as white solids with an isolated yield of 90% (58.5 mg, 0.45 mmol).

using carbon dioxide pressure of P_{CO2} = 5 atm (catalyst: TBAT, Table 2, entry 9)

To a DMSO-d_6 (1 mL) solution of TBAT (108.0 mg, 0.2 mmol) in a Teflon tube was added (*S*)-**1i** (81.6 mg, 0.5 mmol). The Teflon tube containing the reaction mixture was fitted into a 30 mL autoclave. The vessel was purged six times with CO_2 gas (9 atm), and then pressurized with CO_2 (5 atm). The autoclave was stirred at 150 °C for 12 h. Upon completion, the reaction mixture was subjected to ^{1}H NMR for determining crude product yield (85%), which was calculated based on an integral ratio between product and internal standard (anisole). After that, DMSO-d_6 was removed through distillation under vacuum conditions (1 mmHg, 50 °C); the syrupy product was then purified by column chromatography on silica gel (hexane/ethyl acetate 1:3) to give the product (*S*)-4-phenyloxazolidin-2-one ((*S*)-**2i**) as colorless solid with an isolated yield of 76% (62.0 mg, 0.38 mmol).

using carbon dioxide pressure of P_{CO2} = 1 atm (catalyst: TBAF and siloxane, Table 3, entry 4)

To a DMSO-d_6 (1.0 mL) solution of hexamethylcyclotrisiloxane (7.4 mg, 0.033 mmol) and tetrabutylammonium fluoride (TBAF) (0.1 mmol, prepared from a commercial THF solution of TBAF by azeotropic removal of THF and H_2O for three times with dimethoxyethane–toluene, followed by evaporation under oil pump vacuum (0.01 mmHg) at r.t.) was added (*S*)-**1a** (0.111 mL, 1.0 mmol). A dried glass Schlenk tube containing the reaction mixture was frozen with liquid nitrogen (–196 ºC) under vacuum for air removal, and then purged with CO_2 gas from a balloon (1 L) filled with CO_2 fitted to the glass tube and thawed at 25 °C. The glass tube was stirred at 150 °C for 24 h. Upon completion, the reaction mixture was subjected to ^{1}H NMR for determining crude product yield (91%), which was calculated based on an integral ratio between product and internal standard (anisole).

Preparation of 1k from 1k·HCl

To a **1k**·HCl (101.2 mg, 0.5 mmol) was added NaH (60%, dispersion in paraffin liquid, 20 mg, 0.5 mmol) in THF (1 mL) and stirred at room temperature for 8 h. The mixture was filtrated through a celite pad. The filtrate was used for oxazolidinone synthesis after the removal of THF.

Typical procedure for observation of the carbamic acid[2]

A 30 mL glass Schlenk tube equipped with a two-way cock was charged with (*S*)-**1a** (111.4 μL, 1.0 mmol) and DMSO-d_6 (1 mL) under nitrogen atmosphere at room temperature. The mixture was frozen using liquid nitrogen prior to connecting to a vacuum line for air removal. After the mixture was evaporated under vacuum at –196 ºC and warmed up to room temperature, a 1 L balloon filled with CO_2 was fitted to the Schlenk tube and CO_2 was introduced to the vessel by opening the cock of the Schlenk tube. The reaction mixture was monitored by ^{1}H and ^{13}C NMR at room temperature and then stirred under CO_2 (1 atm) for 3 h at 150 °C followed by monitoring by ^{1}H and ^{13}C NMR after cooling down to room temperature.

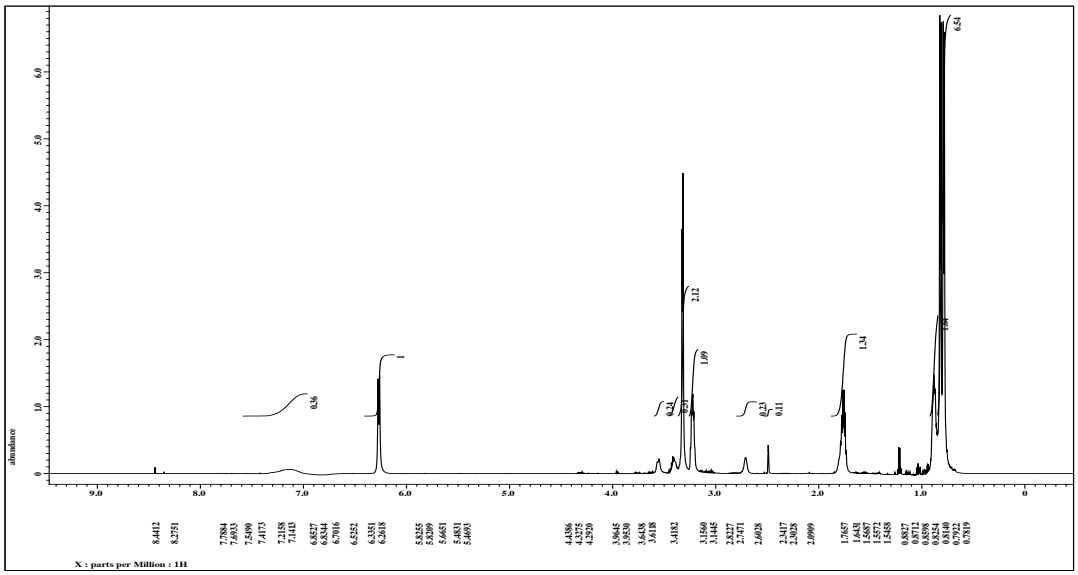


Figure S1. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of a reaction mixture of (*S*)-**1a** and CO_2 at room temperature (P_{CO2} = 1 atm).[2]

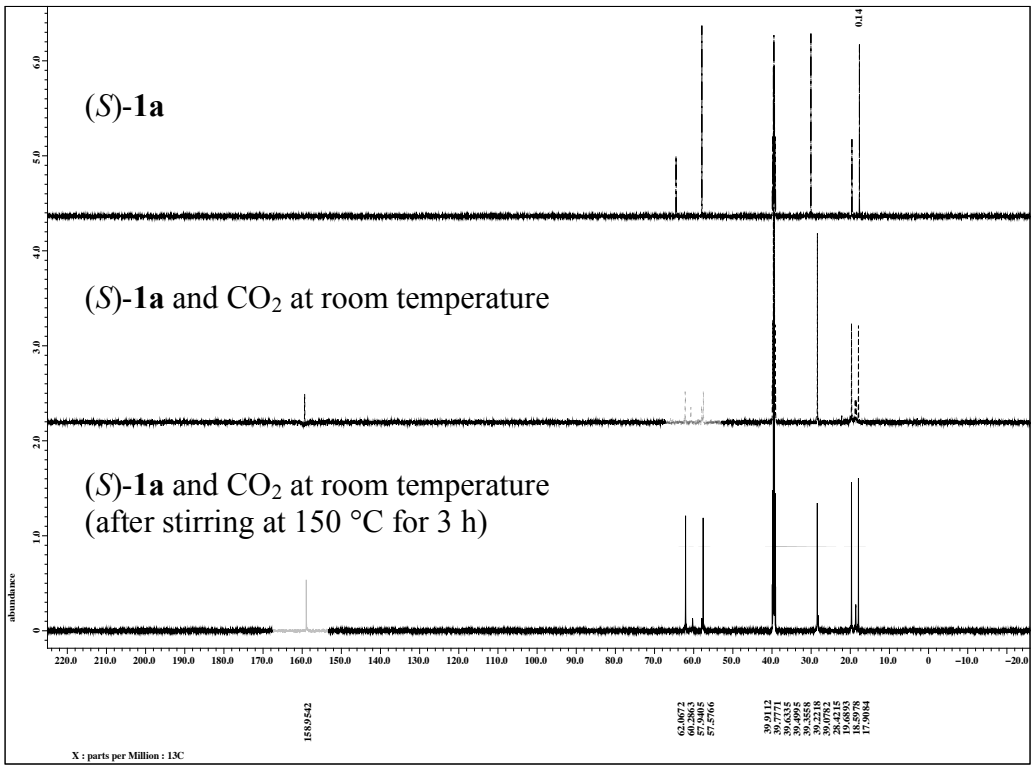


Figure S2. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of (*S*)-**1a** (above), a reaction mixture of (*S*)-**1a** and CO_2 at room temperature (P_{CO2} = 1 atm) (middle) and a reaction mixture of (*S*)-**1a** and CO_2 at room temperature, obtained after stirring at 150 °C for 3 h and cooling down to room temperature, while keeping P_{CO2} = 1 atm (below).[2]

Control experiment: reaction of TBAT in the absence of valinol

TBAT solution in DMSO-d_6 was heated to 150 °C for 3 h under N_2 in the absence of valinol and reaction mixture was analyzed by GC-MS (Figure S3). Low-resolution mass spectroscopy of benzene region on gas chromatography showed generation of benzene-d_1 (C_6H_5D).

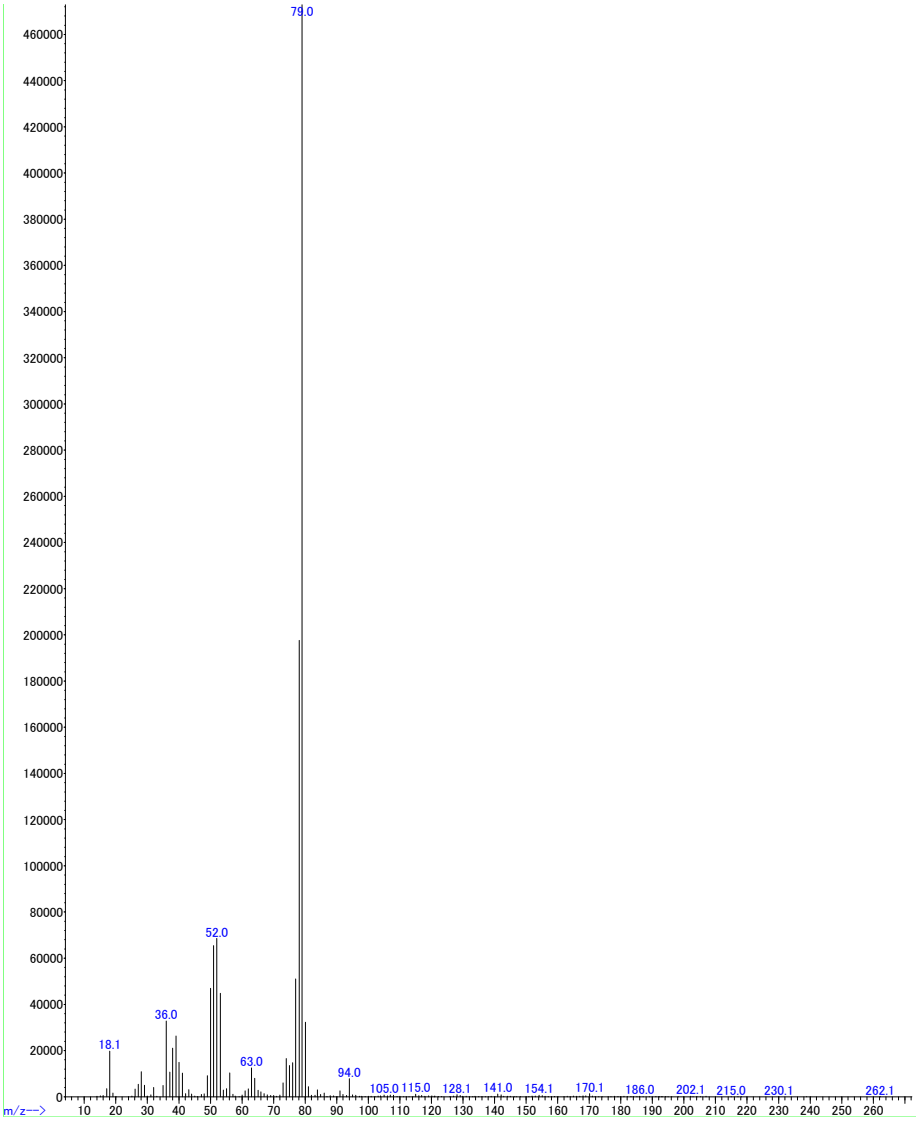


Figure S3. Low-resolution mass spectrum of benzene-d_1 (C_6H_5D) obtained from GC-MS analysis of a $CHCl_3$ solution of TBAT in DMSO-d_6 heated at 150 °C for 3 h under N_2.

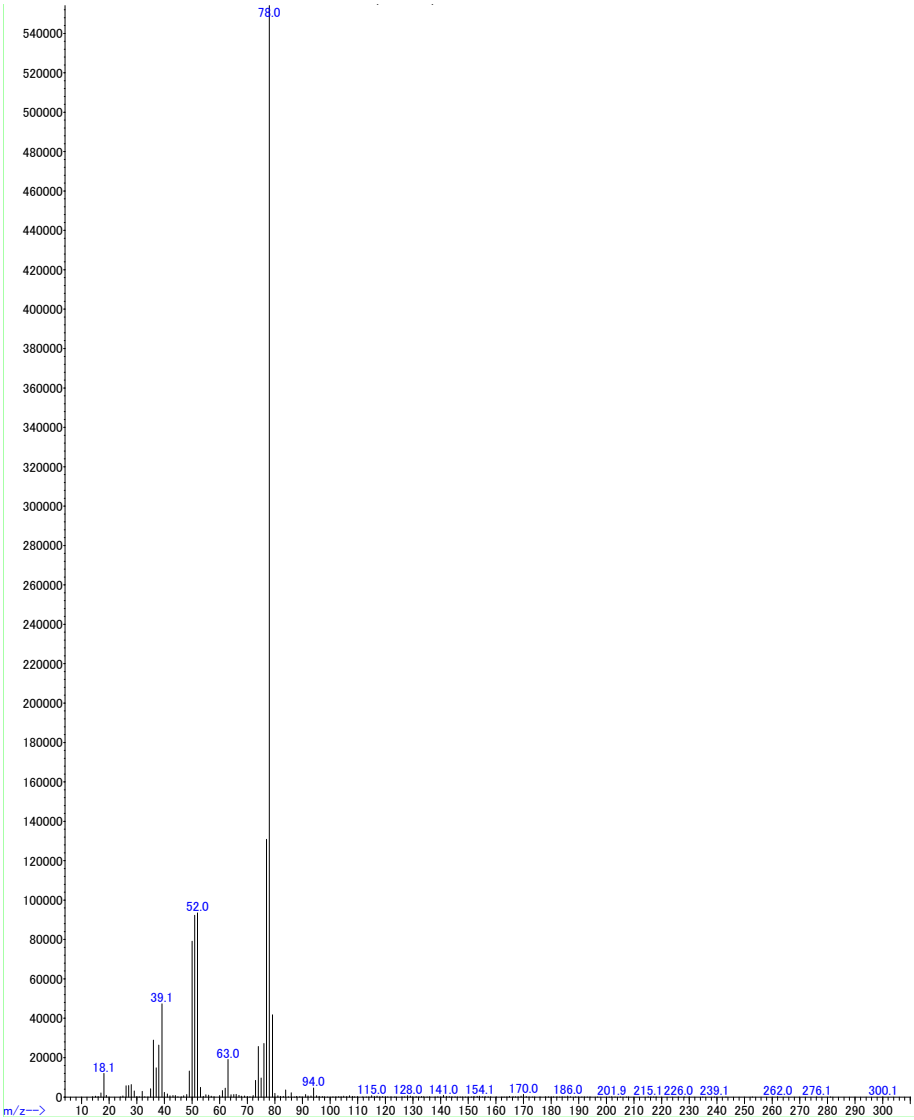


Figure S4. Gas chromatography–Low-resolution mass spectrum of a $CHCl_3$ solution of commercially available benzene (C_6H_6).

^{19}F NMR spectra of the reaction mixture during oxazolidione synthesis using TBAT as catalyst

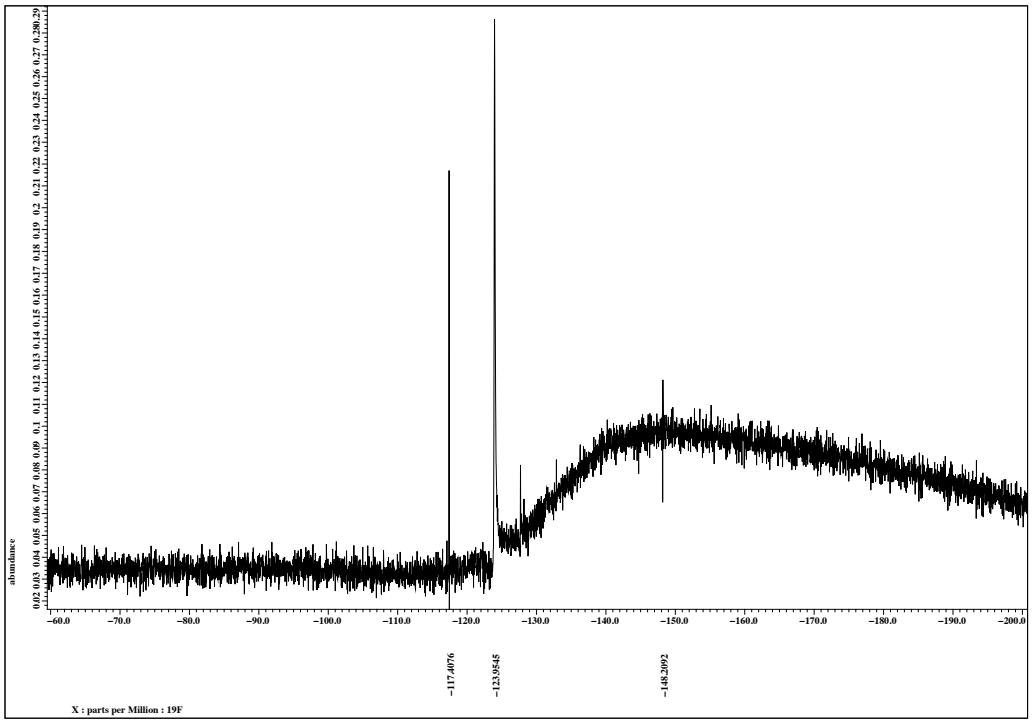


Figure S5. ^{19}F NMR spectrum of the reaction mixture of (*S*)-**1a** and TBAT in DMSO-d_6 heated at 150 °C for 5 h under CO_2.

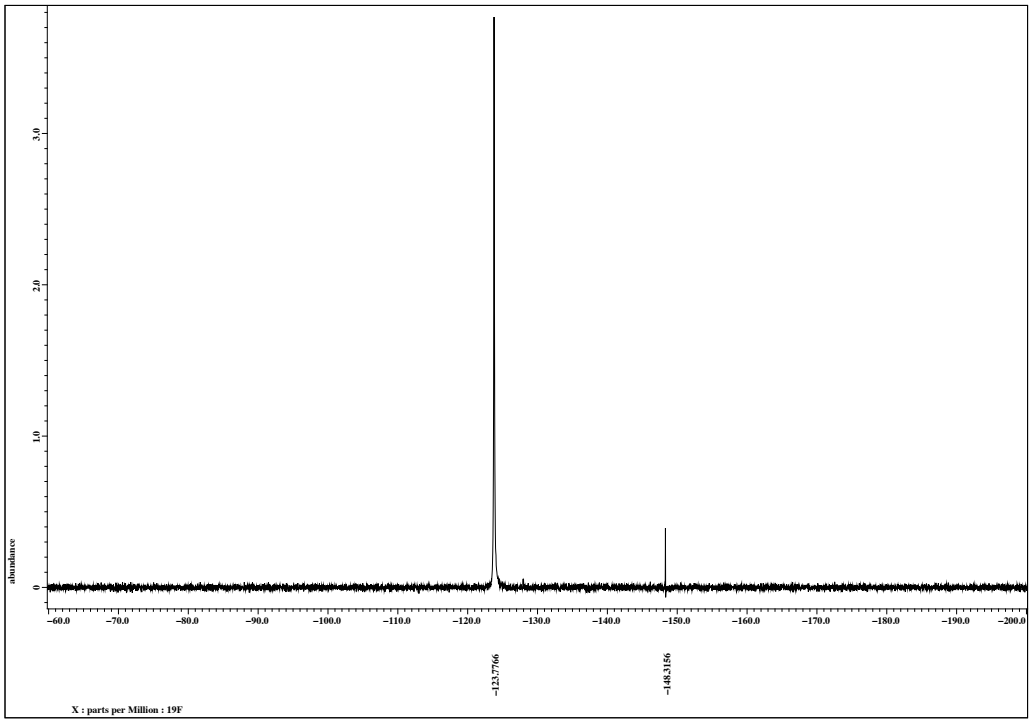
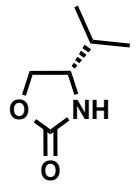


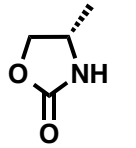
Figure S6. ^{19}F NMR spectrum of the reaction mixture of (*S*)-**1a** and TBAT in DMSO-d_6 heated at 150 °C for 12 h under CO_2.

Spectral and analytical data for compounds

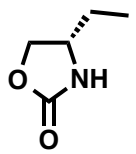
Obtained from reaction with TBAT



(*S*)-4-isopropyloxazolidin-2-one ((*S*)-**2a**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 1:3) yielded (*S*)-**2a** (58.5 mg, 0.45 mmol, 90% (Table 1, entry 9)). R_f (hexane/ethyl acetate = 1:3) 0.55. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (bs, 1H), 4.44 (t, J = 8.6 Hz, 1H), 4.10 (dd, J = 8.6, 6.3 Hz, 1H), 3.65–3.61 (m, 1H), 1.73 (oct, J = 6.8 Hz, 1H), 0.97 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 68.1, 57.9, 32.2, 17.4, 17.1. HRMS (FAB) calcd for $C_6H_{12}NO_2^+$ ($M+H^+$): 130.0863; Found: 130.0882. $[\alpha]_D^{20}$ = +10.7 (*c* 1.0, $CHCl_3$) (lit.[3] $[\alpha]_D^{16}$ = +8.9 (*c* 1.1, $CHCl_3$)). GC retention time: t_R [(*S*)-**2a**] = 15.47 min; t_R [(*R*)-**2a**] = 15.63 min; t_R [*rac*-**2a**] = 15.47 min, 15.64 min.

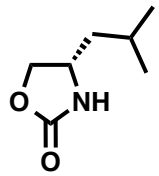


(*S*)-4-methyloxazolidin-2-one ((*S*)-**2c**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 2:3 to 1:49) yielded (*S*)-**2c** (35.0 mg, 0.34 mmol, 69% (Table 2, entry 2)). R_f (hexane/ethyl acetate = 1:3) 0.55. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.62 (bs, 1H), 4.50 (t, J = 8.6 Hz, 1H), 4.04–3.99 (m, 1H), 3.94 (dd, J = 8.6, 6.3 Hz, 1H), 1.29 (d, J = 6.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 71.5, 48.1, 20.6. HRMS (FAB) calcd for $C_4H_8NO_2^+$ ($M+H^+$): 102.0550; Found: 102.0573. $[\alpha]_D^{19}$ = +9.5 (*c* 1.0, $CHCl_3$) (lit.[4] $[\alpha]_D^{20}$ = +9.2 (*c* 2.0, $CHCl_3$)). GC retention time: t_R [(*S*)-**2c**] = 8.88 min; t_R [*rac*-**2c**] = 8.89 min, 9.02 min.

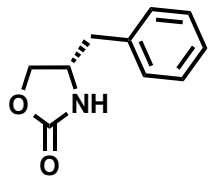


(*S*)-4-ethyloxazolidin-2-one ((*S*)-**2d**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2d** (53.7 mg, 0.47 mmol, 93% (Table 2, entry 3)). R_f (hexane/ethyl acetate = 1:3) 0.35 ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (bs, 1H), 4.48 (t, J = 8.6 Hz, 1H), 4.03 (dd, J = 8.6, 6.3 Hz, 1H), 3.84–3.80 (m, 1H), 1.67–1.54

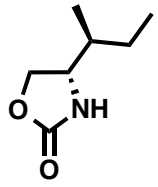
(m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 69.9, 53.8, 28.1, 9.1. HRMS (FAB) calcd for $C_5H_{10}NO_2^+$ ($M+H^+$): 116.0706; Found: 116.0721. $[\alpha]_D^{20}$ = –5.0 (c 0.9, $CHCl_3$) (lit.[5] $[\alpha]_D^{30}$ = –5.3 (c 0.6, $CHCl_3$)). GC retention time: t_R [(*S*)-**2d**] = 10.71 min; t_R [*rac*-**2d**] = 10.76 min, 11.00 min.



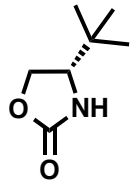
(*S*)-4-isobutyloxazolidin-2-one ((*S*)-**2e**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 1:1) yielded (*S*)-**2e** (55.7 mg, 0.39 mmol, 77% (Table 2, entry 4)). R_f (hexane/ethyl acetate = 1:1) 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (bs, 1H), 4.49 (t, J = 6.9 Hz, 1H), 4.00–3.93 (m, 2H), 1.70–1.62 (m, 1H), 1.60–1.55 (m, 1H), 1.40–1.35 (m, 1H), 0.95–0.91 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 70.7, 50.9, 44.4, 24.9, 22.8, 22.0. HRMS (FAB) calcd for $C_7H_{14}NO_2^+$ ($M+H^+$): 144.1019; Found: 144.1017. $[\alpha]_D^{21}$ = –12.2 (c 1.1, $CHCl_3$) (lit.[3] $[\alpha]_D^{16}$ = –11.6 (c 1.0, $CHCl_3$)). GC retention time: t_R [(*S*)-**2e**] = 15.51 min; t_R [*rac*-**2e**] = 15.51 min, 15.61 min.



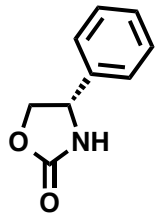
(*S*)-4-benzyloxazolidin-2-one ((*S*)-**2f**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2f** (56.4 mg, 0.032 mmol, 64%, (Table 2, entry 5)). R_f (hexane/ethyl acetate = 3:1) 0.04. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.27–7.24 (m, 1H), 7.18–7.14 (m, 2H), 6.36 (bs, 1H), 4.44 (t, J = 8.6 Hz, 1H), 4.15 (dd, J = 8.6, 5.8 Hz, 1H), 4.11–4.06 (m, 1H), 2.97–2.83 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 135.9, 129.0 (2C), 128.9 (2C), 127.1, 69.5, 53.7, 41.3. HRMS (FAB) calcd for $C_{10}H_{12}NO_2^+$ ($M+H^+$): 178.0863; Found: 178.0876. $[\alpha]_D^{22}$ = –63.3 (c 1.0, $CHCl_3$) (lit.[3] $[\alpha]_D^{23}$ = –63 (c 1.0, $CHCl_3$)). HPLC retention time (acetonitrile/water = 1:4, 1 mL/min): t_R [(*S*)-**2f**] = 6.82 min; t_R [(*R*)-**2f**] = 6.30 min; t_R [*rac*-**2f**] = 6.36 min, 6.99 min.



(*S*)-4-((*S*)-*sec*-butyl)oxazolidin-2-one ((*S*)-**2g**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 2:3 to 1:49) yielded (*S*)-**2g** (65.8 mg, 0.46 mmol, 92% (Table 2, entry 6)). R_f (hexane/ethyl acetate = 1:4) 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (bs, 1H), 4.43 (t, J = 8.9 Hz, 1H), 4.10 (dd, J = 8.7, 6.9 Hz, 1H), 3.73–3.69 (m, 1H), 1.57–1.47 (m, 2H), 1.18–1.11 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 68.3, 57.1, 38.9, 24.9, 13.6, 10.9. HRMS (FAB) calcd for $C_7H_{14}NO_2^+$ ($M+H^+$): 144.1019; Found: 144.1021. $[\alpha]_D^{21}$ = +5.8 (*c* 1.0, $CHCl_3$) (lit.[6] $[\alpha]_D^{27}$ = +6 (*c* 6.5, $CHCl_3$)). GC retention time: t_R - [(*S*)-**2g**] = 15.65 min; t_R [*rac*-**2g**] = 15.61 min, 15.76 min.

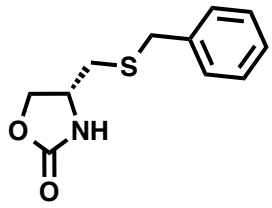


(*S*)-4-(*tert*-butyl)oxazolidin-2-one ((*S*)-**2h**):[2] After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2h** (57.7 mg, 0.403 mmol, 81% (Table 2, entry 7)). R_f (hexane/ethyl acetate = 1:3) 0.49. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (bs, 1H), 4.36 (t, J = 8.9 Hz, 1H), 4.18 (dd, J = 8.9, 5.5 Hz, 1H), 3.62–3.59 (m, 1H), 0.91 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 66.4, 61.4, 33.2, 24.6 (3C). HRMS (FAB) calcd for $C_7H_{14}NO_2^+$ ($M+H^+$): 144.1019; Found: 144.1021. $[\alpha]_D^{21}$ = +12.8 (*c* 1.0, $CHCl_3$) (lit.,[6] $[\alpha]_D^{25}$ = +12 (*c* 1.8, $CHCl_3$)). GC retention time: t_R [(*S*)-**2h**] = 13.24 min; t_R [*rac*-**2h**] = 13.20 min, 13.33 min.

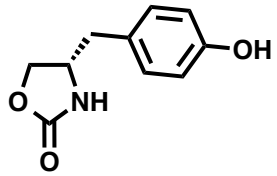


(*S*)-4-phenyloxazolidin-2-one ((*S*)-**2i**):[3] After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2i** (62.0 mg, 0.38 mmol, 76% (Table 2, entry 9)). R_f (hexane/ethyl acetate = 1:3) 0.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.30 (m,

5H), 6.63 (bs, 1H), 4.91–4.88 (m, 1H), 4.67 (t, J = 8.3 Hz, 1H), 4.12 (dd, J = 8.2, 6.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 139.6, 129.1 (2C), 128.6, 125.9 (2C), 72.3, 56.2. HRMS (ESI) calcd for $C_9H_{10}NO_2^+$ ($M+H^+$): 164.0706; Found: 164.0719. $[\alpha]_D^{19}$ = +45.4 (c 1.0, $CHCl_3$) (lit.[3] $[\alpha]_D^{20}$ = +49.5 (c 1.0, $CHCl_3$)). HPLC retention time (acetonitrile/water = 1:4, 1 mL/min): t_R [(*R*)-**2i**] = 5.92 min, t_R [(*S*)-**2i**] = 6.52 min; t_R [*rac*-**2i**] = 5.94 min, 7.03 min;

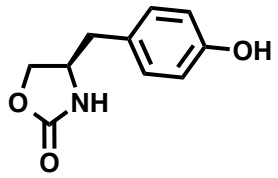


(*R*)-4-((benzylthio)methyl)oxazolidin-2-one ((*R*)-**2j**): After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*R*)-**2j** (48.1 mg, 0.21 mmol, 42% (Table 2, entry 10)). R_f (hexane/ethyl acetate = 1:4) 0.68. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.31–7.28 (m, 2H), 7.28–7.25 (m, 1H), 6.48 (bs, 1H), 4.38 (t, J = 8.9 Hz, 1H), 4.04 (dd, J = 8.9, 4.8 Hz, 1H), 3.86–3.81 (m, 1H), 3.73 (s, 2H), 2.61–2.52 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 137.5, 128.7 (2C), 128.7 (2C), 127.4, 69.4, 51.7, 36.5, 35.9. HRMS (ESI) calcd for $C_{11}H_{14}NO_2S^+$ ($M+H^+$): 224.0740; Found: 224.0763. $[\alpha]_D^{20}$ = –29.4 (c 1.0, $CHCl_3$). Elemental analysis Found: C, 59.24; H, 5.96; N, 6.13. Calc. for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27%. HPLC retention time (acetonitrile/water = 1:15, 1 mL/min): t_R [(*R*)-**2j**] = 75.32 min; t_R [*Rac*-**2j**] = 73.91 min, 78.14 min.

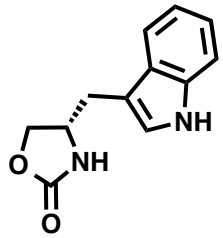


(*S*)-4-(4-hydroxybenzyl)oxazolidin-2-one ((*S*)-**2k**): After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2k** (36.8 mg, 0.19 mmol, 38% (Table 2, entry 12)). R_f (hexane/ethyl acetate = 1:3) 0.51. ^{1}H NMR (600 MHz, CD_3OD) δ 7.04 (d, J = 8.3 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 4.36 (t, J = 8.3 Hz, 1H), 4.12–4.09 (m, 1H), 4.08–4.05 (m, 1H), 2.78 (dd, J = 6.2, 13.7 Hz, 1H), 2.72 (dd, J = 6.9, 13.7 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD) δ 162.2, 157.4, 131.4 (2C), 128.2, 116.5 (2C), 70.7, 55.1, 41.0. HRMS (FAB) calcd for $C_{10}H_{12}NO_3^+$ ($M+H^+$): 194.0812;

Found: 194.0791. Elemental analysis Found: C, 62.10; H, 5.97; N, 6.85. Calc. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25%. $[\alpha]_D^{20}$ = –2.9 (*c* 1.0, MeOH). HPLC retention time (acetonitrile/water = 1:9, 1 mL/min): t_R [(*S*)-**2k**] = 7.08 min; t_R [*rac*-**2k**] = 5.81 min, 7.05 min.

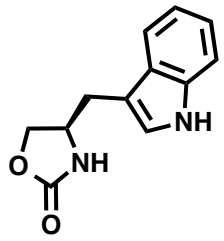


(*R*)-4-(4-hydroxybenzyl)oxazolidin-2-one ((*R*)-**2k**): After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2k** (30.8 mg, 0.16 mmol, 32% (Table 2, entry 15)) R_f (hexane/ethyl acetate = 1:3) 0.50. ^{1}H NMR (600 MHz, CD_3OD) δ 7.04 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 4.35 (t, *J* = 8.3 Hz, 1H), 4.12–4.09 (m, 1H), 4.09–4.05 (m, 1H), 2.77 (dd, *J* = 6.2, 14.4 Hz, 1H), 2.71 (dd, *J* = 6.9, 13.7 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD) δ 162.2, 157.5, 131.4 (2C), 128.2, 116.5 (2C), 70.7, 55.1, 41.0. HRMS (FAB) calcd for $C_{10}H_{12}NO_3^+$ ($M+H^+$): 194.0812; Found: 194.0828. $[\alpha]_D^{21}$ = +2.4 (*c* 1.0, MeOH). HPLC retention time (acetonitrile/water = 1:9, 1 mL/min): t_R [(*R*)-**2k**] = 5.89 min; t_R [*rac*-**2k**] = 5.81 min, 7.05 min.

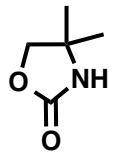


(*S*)-4-((1*H*-indol-3-yl)methyl)oxazolidin-2-one ((*S*)-**2l**):[6] After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*S*)-**2l** (75.4 mg, 0.35 mmol, 69% (Table 2, entry 16)). R_f (hexane/ethyl acetate = 1:4) 0.61. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (bs, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.18 (dd, *J* = 6.6, 15.0 Hz, 1H). 7.10 (dd, *J* = 6.6, 15.0 Hz, 1H), 7.00 (s, 1H), 6.21 (bs 1H), 4.39–4.36 (m, 1H), 4.13–4.12 (m, 1H), 4.12–4.10 (m, 1H), 2.99 (dd, *J* = 6.6, 14.4 Hz, 1H), 2.94 (dd, *J* = 6.6, 14.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 139.6, 127.0, 122.9, 121.9, 119.3, 118.1, 111.5, 109.5, 69.7, 52.7, 31.0. HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2^+$ ($M+H^+$): 217.0972; Found: 217.098. $[\alpha]_D^{19}$ = +3.8 (*c* 1.0,

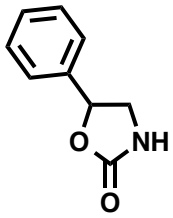
MeOH) (lit.[6] $[\alpha]_D^{28}$ = +4 (*c* 2.6, MeOH)). HPLC retention time (acetonitrile/water = 3:7, 1 mL/min): t_R [(*S*)-**2l**] = 6.25 min; t_R [*rac*-**2l**] = 5.44 min, 6.43 min.



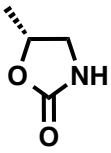
(*R*)-4-((1*H*-indol-3-yl)methyl)oxazolidin-2-one ((*R*)-**2l**): After column chromatography on silica gel (hexane/ethyl acetate = 3:1) yielded (*R*)-**2l** (58.6 mg, 0.27 mmol, 54% (Table 2, entry 18)). R_f (hexane/ethyl acetate = 1:3) 0.46. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (bs, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 6.9, 13.8 Hz, 1H). 7.13 (dd, J = 6.9, 13.8 Hz, 1H), 7.00 (s, 1H), 5.85 (bs 1H), 4.44–4.40 (m, 1H), 4.15–4.14 (m, 1H), 4.14–4.13 (m, 1H), 2.95 (dd, J = 6.7, 14.5 Hz, 1H), 2.89 (dd, J = 6.7, 14.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 136.8, 127.5, 123.3, 122.8, 120.2, 118.7, 112.0, 110.4, 70.4, 53.3, 31.6. HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2^+$ ($M+H^+$): 217.0972; Found: 217.0992. $[\alpha]_D^{19}$ = –4.2 (*c* 1.0, MeOH) (lit.[6] (*S*)-isomer: $[\alpha]_D^{28}$ = +4 (*c* 2.6, MeOH)). HPLC retention time (acetonitrile/water = 3:7, 1 mL/min): t_R [(*R*)-**2l**] = 5.39 min; t_R [*rac*-**2l**] = 5.44 min, 6.43 min.



4-dimethyloxazolidin-2-one ((**2m**):[7] After column chromatography on silica gel (hexane/ethyl acetate = 2:3 to 1:49) yielded **2m** (13.18 mg, 0.114 mmol, 23% (Table 2, entry 19)). R_f (hexane/ethyl acetate = 1:4) 0.53. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.12 (bs, 1H), 4.09 (s, 2H), 1.37 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 77.2, 55.2, 27.5(2C). HRMS (ESI) calcd for $C_5H_{10}NO_2^+$ ($M+H^+$): 116.0706; Found: 116.0733.

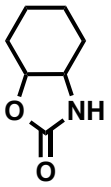


***rac*-5-phenyloxazolidin-2-one** (*rac*-**2n**):[8] After column chromatography on silica gel (hexane/ethyl acetate = 1:3) yielded *rac*-**2n** (29.5 mg, 0.18 mmol, 36% (Table 2, entry 20)). R_f (hexane/ethyl acetate = 1:3) 0.41. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.35 (m, 5H), 6.44 (bs, 1H), 5.61 (t, J = 9.0 Hz, 1H), 3.97 (t, J = 9.0 Hz, 1H), 3.54 (t, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 138.9, 129.4 (3C), 126.2 (2C), 77.8, 48.8. HRMS (FAB) calcd for $C_9H_{10}NO_2^+$ ($M+H^+$): 164.0706; Found: 164.0702.



(*R*)-5-methyloxazolidin-2-one ((*R*)-**2p**):[9] After column chromatography on silica gel (hexane/ethyl acetate = 2:3 to 1:49) yielded (*R*)-**2p** (18.3 mg, 0.18 mmol, 36% (Scheme 2)). R_f (hexane/ethyl acetate = 1:4) 0.67. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.21 (bs, 1H), 4.80–4.75 (m, 1H), 3.71 (dd, J = 9.0, 9.0 Hz, 1H), 3.20 (dd, J = 8.9, 7.8 Hz, 1H), 1.46 (d, J = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 73.5, 47.4. 20.5. HRMS (FAB) calcd for $C_4H_8NO_2^+$ ($M+H^+$): 102.0550; Found: 102.0545. $[\alpha]_D^{20}$ = +7.9 (*c* 1.0, $CHCl_3$) (lit.[9] (*S*)-isomer: $[\alpha]_D^{rt}$ = –8.9 (*c* 1.0, $CHCl_3$) for 99% ee (rt = room temperature)). GC retention time: t_R [(*R*)-**2p**] = 16.77 min; t_R [(*S*)-**2p**] = 16.90 min; t_R [*rac*-**2p**] = 16.68 min, 16.99 min.

<u>Obtained from the reaction with TBAF and $(Me_2SiO)_3$</u>



***rac*-hexahydrobenzo[*d*]oxazol-2(3*H*)-one** (*rac*-**2o**):[10] After column chromatography on silica gel (hexane/ethyl acetate = 2:3 to 1:49) yielded *rac*-**2o** (48.5 mg, 0.34 mmol, 68% (Table 4, entry 6)). R_f (hexane/ethyl acetate = 1:4) 0.39. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.35 (bs, 1H), 4.59 (dt, J = 4.8, 6.2 Hz, 1H), 3.74–3.78 (m, 1H), 1.96–2.02 (m, 1H), 1.80–1.87 (m, 1H), 1.72–1.80 (m, 1H), 1.59–1.66 (m, 1H), 1.51–1.59 (m,

2H), 1.42–1.49 (m, 1H), 1.25–1.33 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 75.9, 51.7, 28.5, 26.6, 19.7, 19.4. HRMS (ESI) calcd for $C_7H_{12}NO_2^+$ ($M+H^+$): 142.0862; Found: 142.0848.

Data collections for Table 4

GC and HPLC retention time of (*S*)-**2a**, (*S*)-**2c**, (*S*)-**2f**, (*R*)-**2j**, (*S*)-**2k**, (*S*)-**2l** and (*R*)-**2p** obtained from the reaction with TBAF and $(Me_2SiO)_3$.

(*S*)-**2a**: GC retention time: t_R [(*S*)-**2a**] = 14.97 min; t_R [*rac*-**2a**] = 14.96 min, 15.20 min.

(*S*)-**2c**: GC retention time: t_R [(*S*)-**2c**] = 10.40 min; t_R [*rac*-**2c**] = 10.38 min, 10.55 min.

(*S*)-**2f**: HPLC retention time (acetonitrile/water = 1:5, 1 mL/min): t_R [(*S*)-**2f**] = 4.93 min; t_R [*rac*-**2f**] = 4.60 min, 4.92 min.

(*R*)-**2j**: HPLC retention time (acetonitrile/water = 1.1:8.9, 1 mL/min): t_R [(*R*)-**2j**] = 18.52 min; t_R [*rac*-**2j**] = 17.69 min, 18.60 min.

(*S*)-**2l**: HPLC retention time (acetonitrile/water = 1:1, 1 mL/min): t_R [(*S*)-**2l**] = 2.73 min; t_R [*rac*-**2l**] = 2.55 min, 2.72 min.

(*R*)-**2p**: GC retention time: t_R [(*R*)-**2p**] = 10.48 min; t_R [*rac*-**2p**] = 10.48 min, 10.56 min.

References

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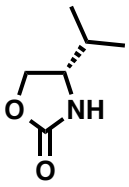
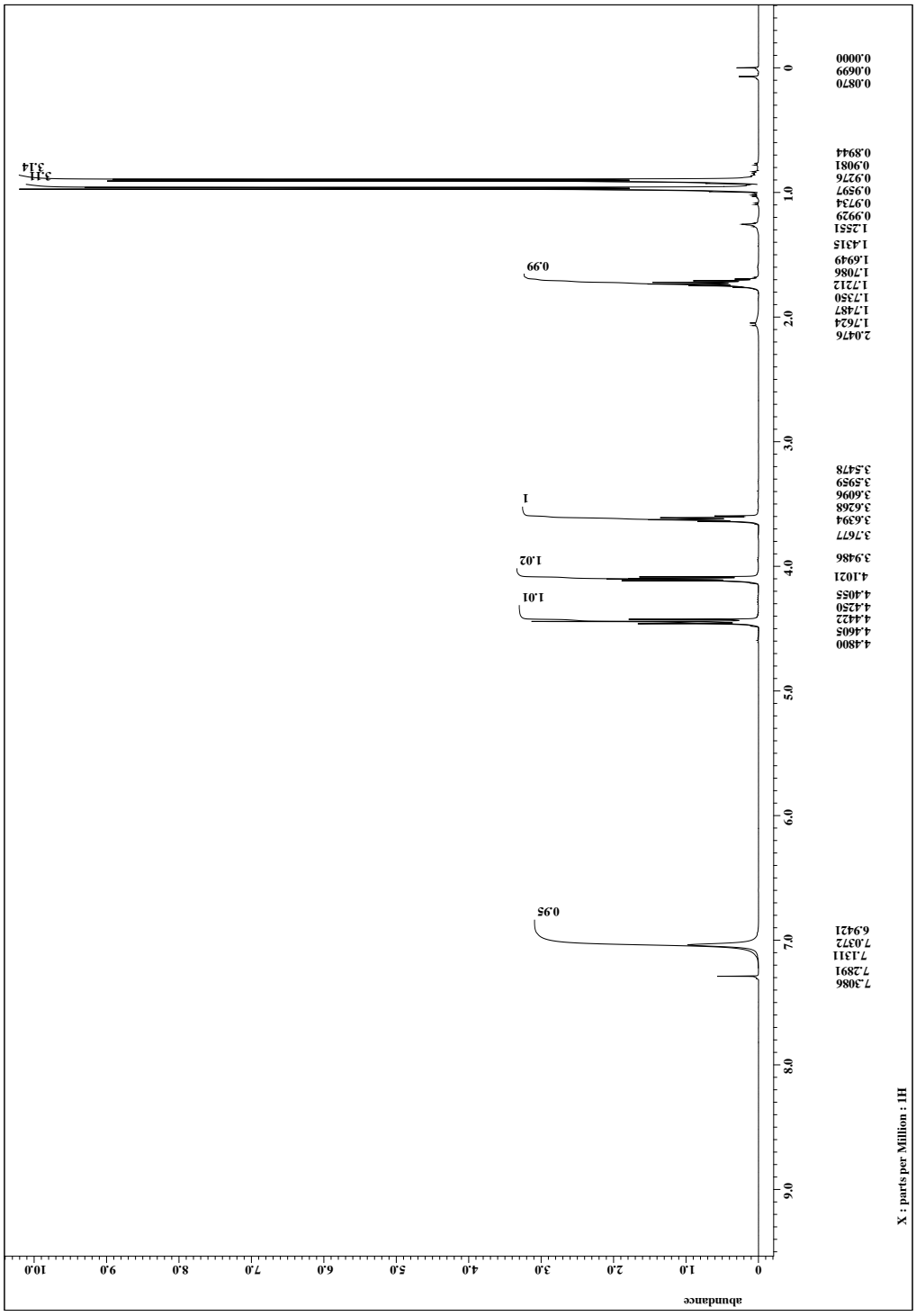
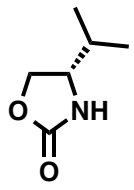
Appendix: ^{1}H NMR and ^{13}C NMR Spectra of oxazolidinones (isolated)

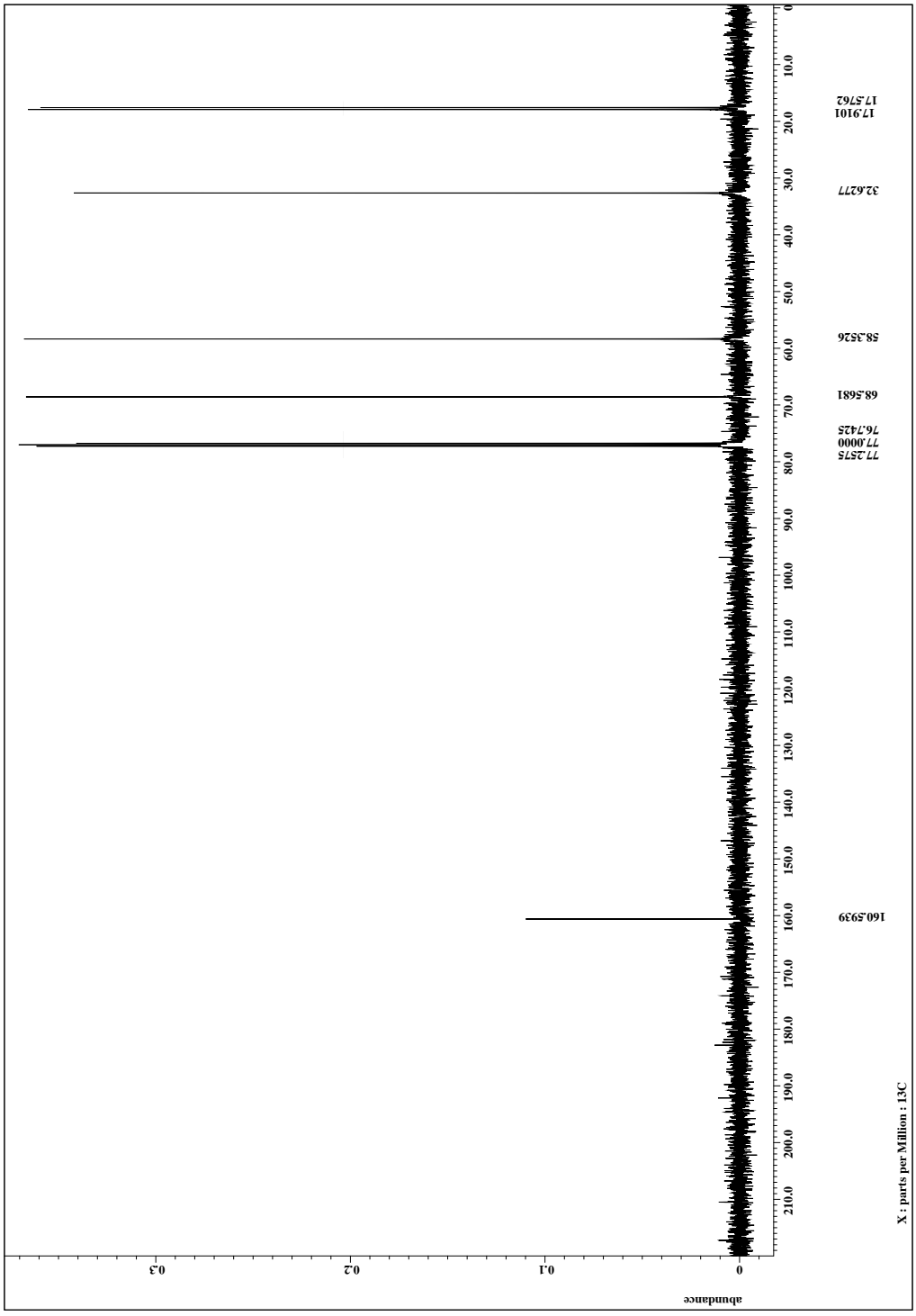
(*S*)-**2a** (^{1}H NMR)



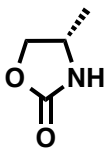


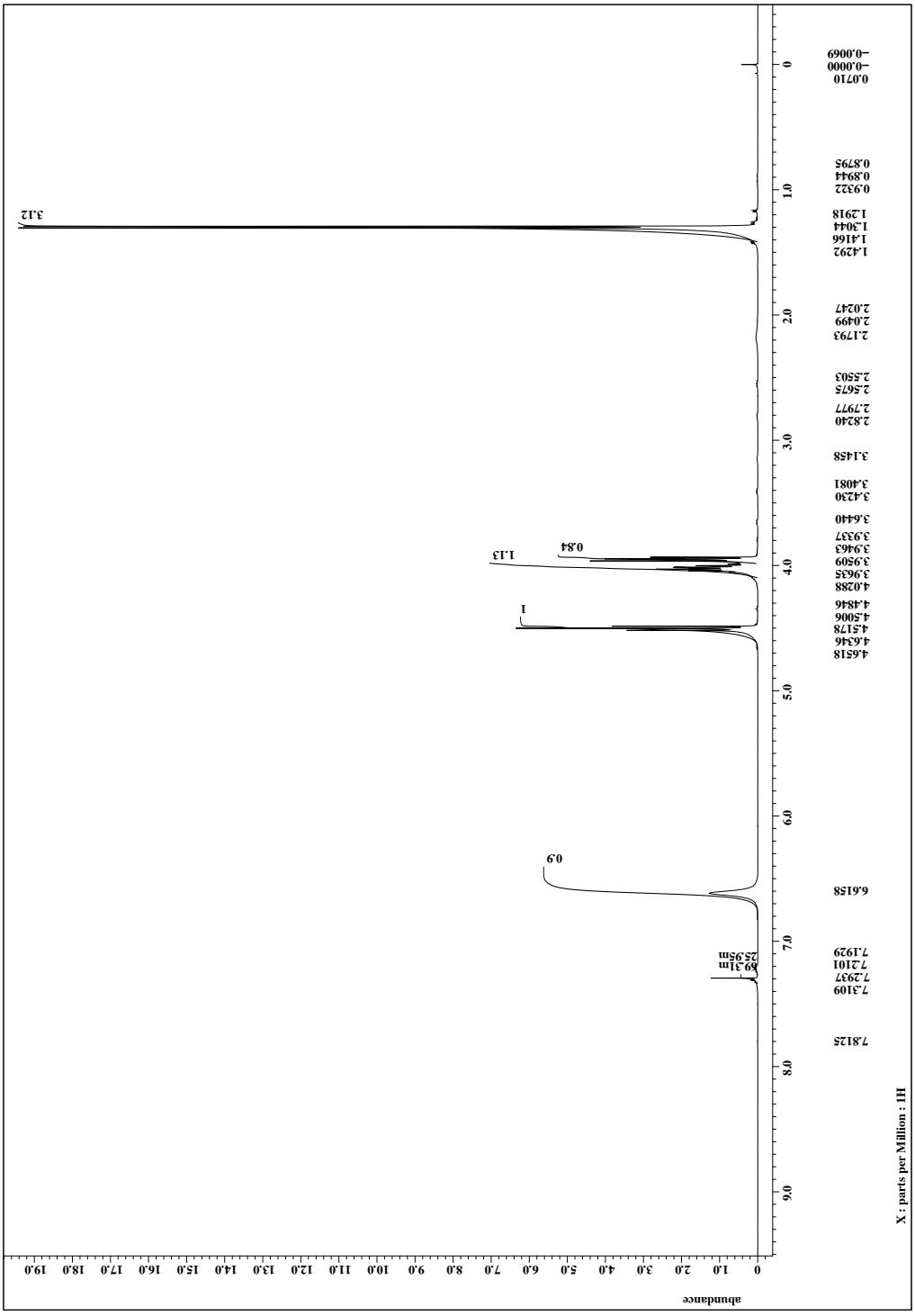
(*S*)-**2a** (^{13}C NMR)


O
NH
O


17.9101
17.5762
32.6277
58.3526
68.5681
77.2575
77.0000
76.7425
160.5939
X : parts per Million : 13C
abundance

(*S*)-**2c** (^{1}H NMR)


O
NH
O


X : parts per Million : 1H
abundance
7.8125
7.3109
7.2937
7.2101
7.1929
89.31m
25.95m
6.6158
0.9
4.6518
4.6346
4.5178
4.5006
4.4846
1
4.0288
3.9635
3.9509
3.9463
3.9337
3.6440
3.4230
3.4081
3.1458
2.8240
2.7977
2.5675
2.5503
2.1793
2.0499
2.0247
1.4292
1.4166
1.3044
1.2918
3.12
0.9322
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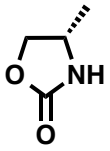
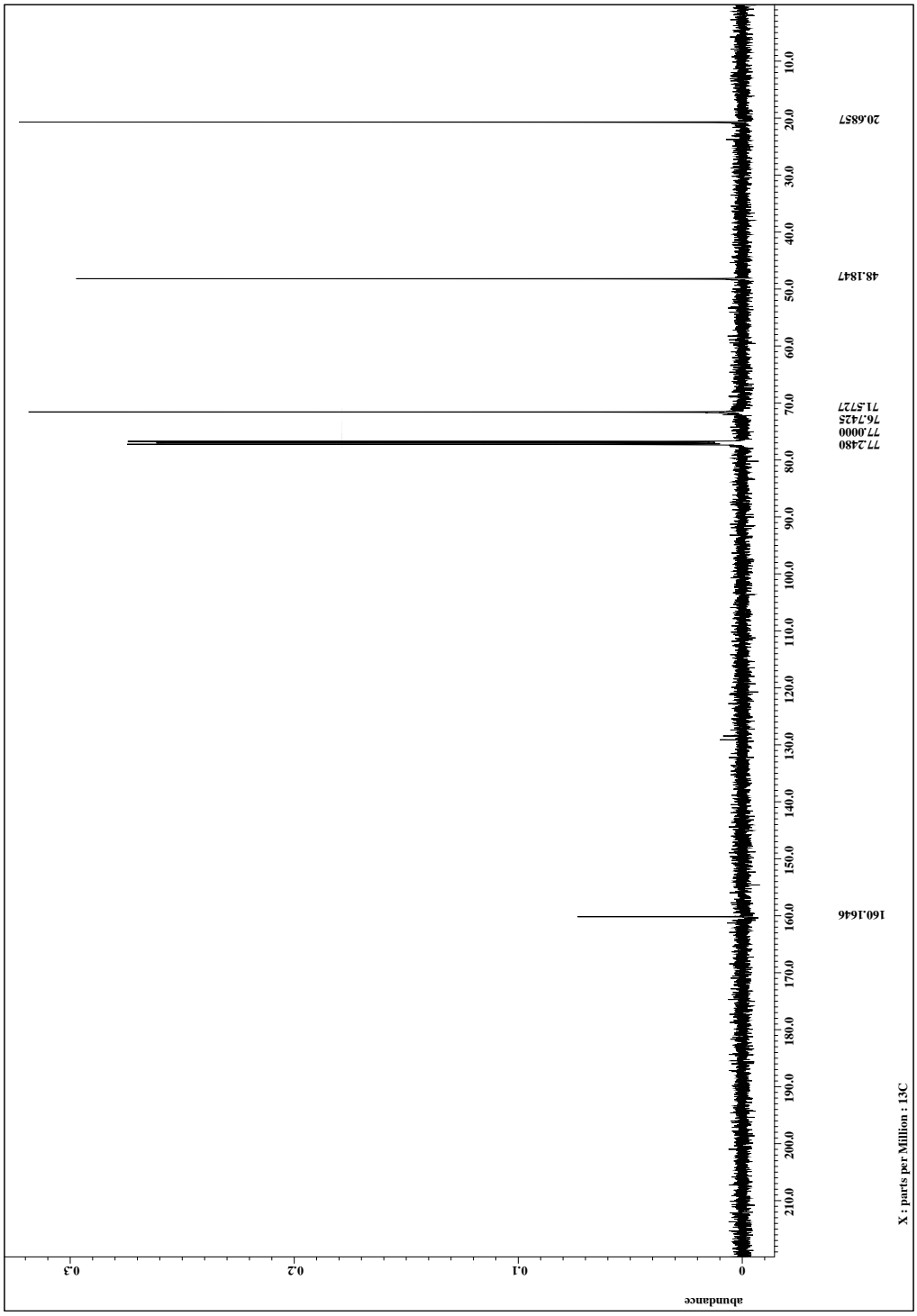
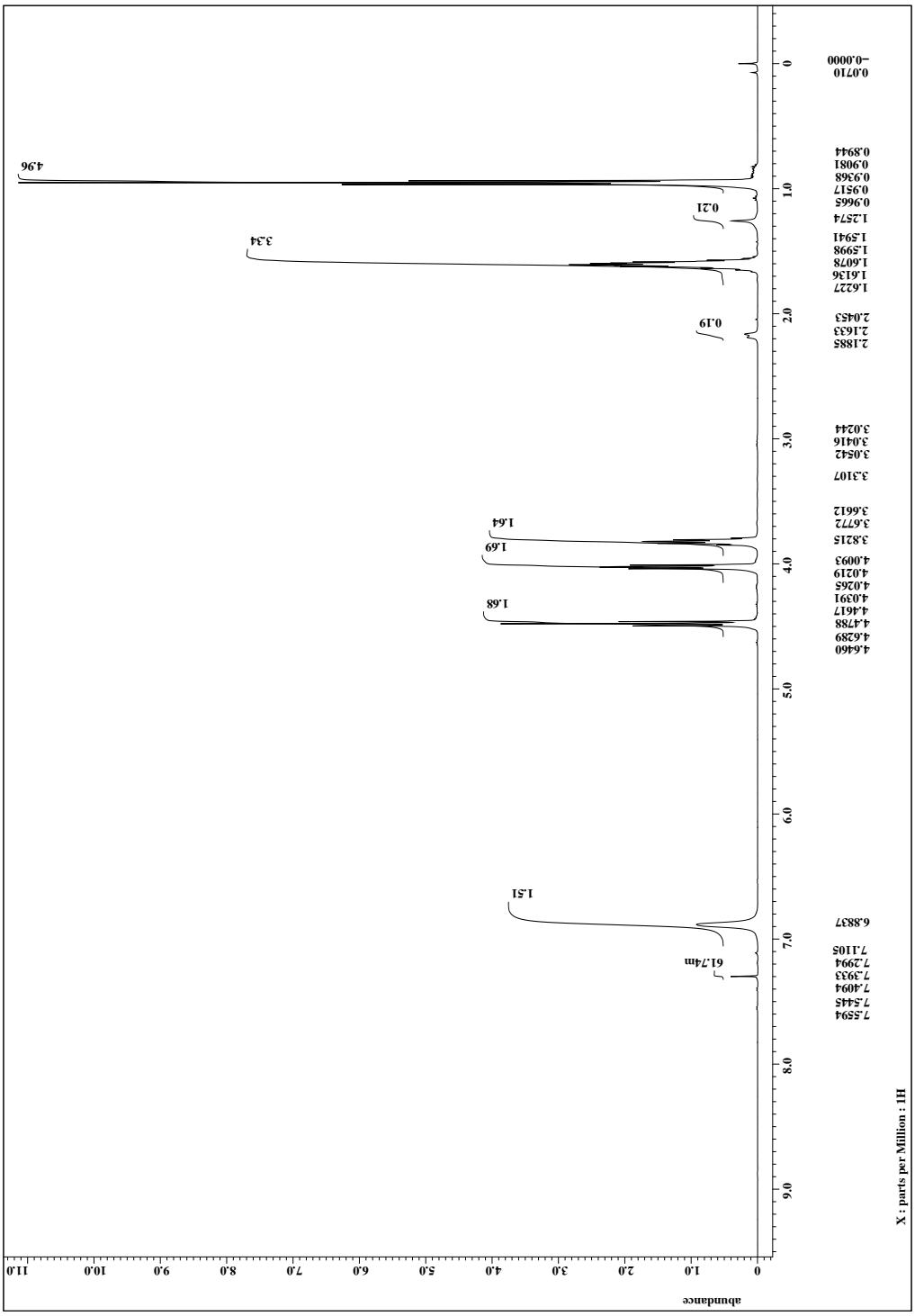
0.84
1.13
0.0710
-0.0000
-0.0069

(*S*)-**2c** (^{13}C NMR)


O
NH
O


abundance
0
0.1
0.2
0.3
X : parts per Million : 13C
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
210.0
20.6857
48.1847
77.2480
77.0000
76.7425
71.5727
160.1646

(*S*)-**2d** (^{1}H NMR)


X : parts per Million : 1H
abundance
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7.1105
6.8837
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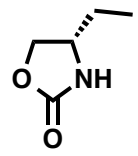
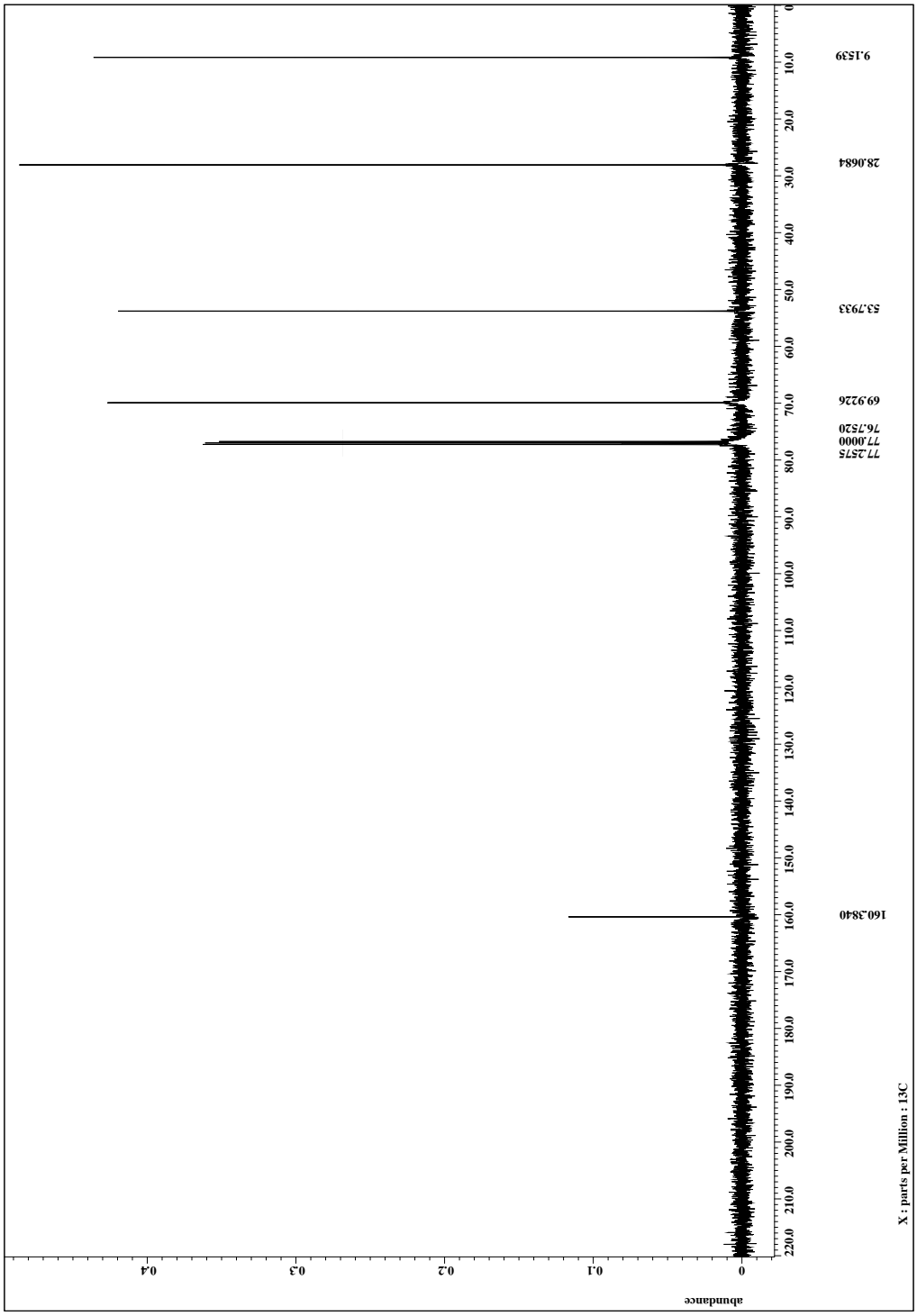
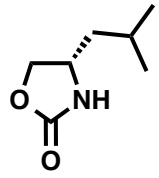
4.6289
4.4788
4.4617
4.0391
4.0265
4.0219
4.0093
3.8215
3.6772
3.6612
3.3107
3.0542
3.0416
3.0244
2.1885
2.1633
2.0453
1.6227
1.6136
1.6078
1.5998
1.5941
1.2574
0.9665
0.9517
0.9368
0.9081
0.8944
0.0710
−0.0000
61.74m
1.51
1.68
1.69
1.64
0.19
3.34
0.21
4.96

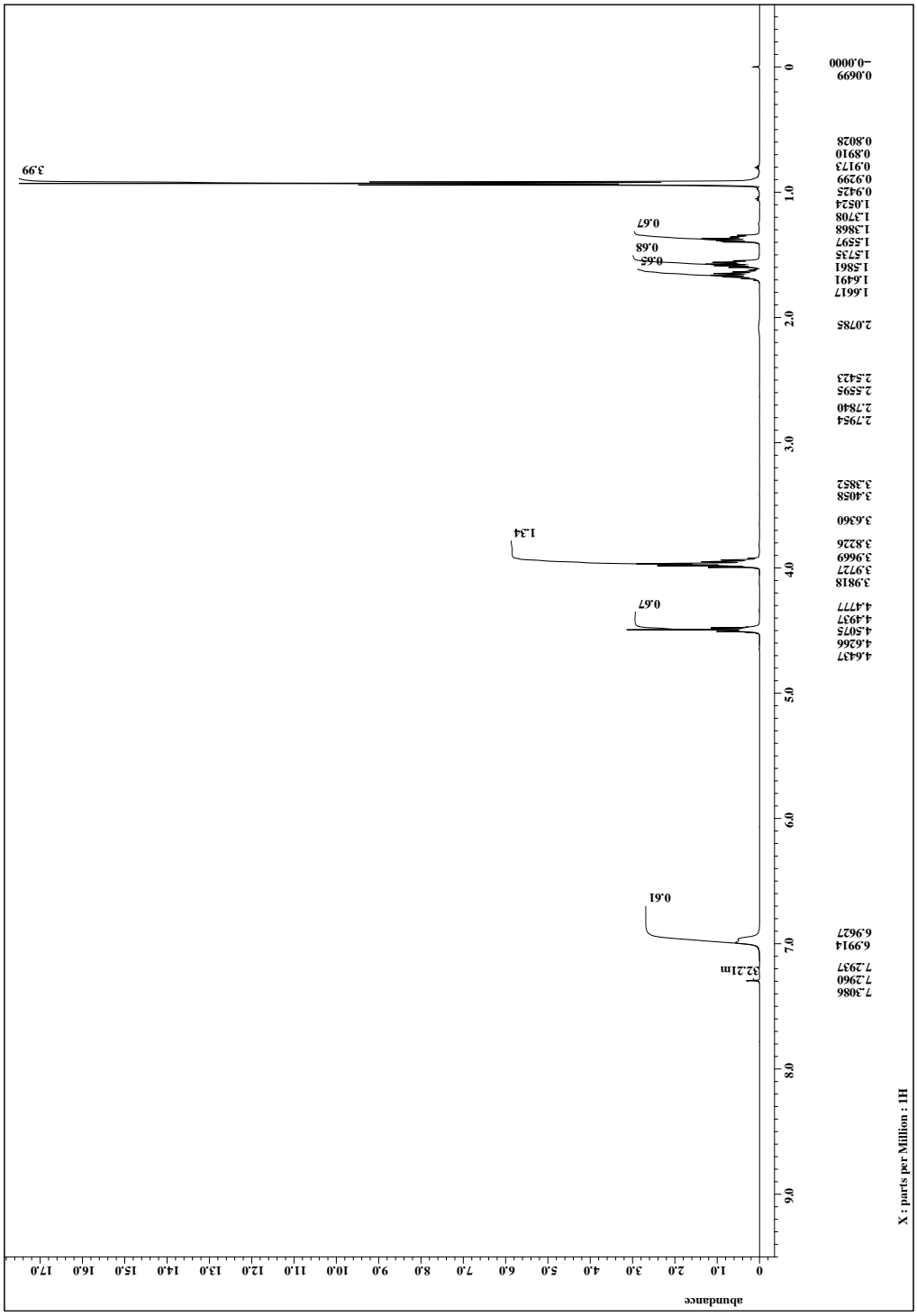
(*S*)-**2d** (^{13}C NMR)


O
NH
O

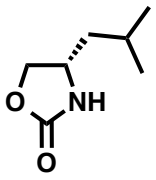

9.1539
28.0684
53.7933
69.9226
76.7520
77.0000
77.2575
160.3840
X : parts per Million : 13C
abundance

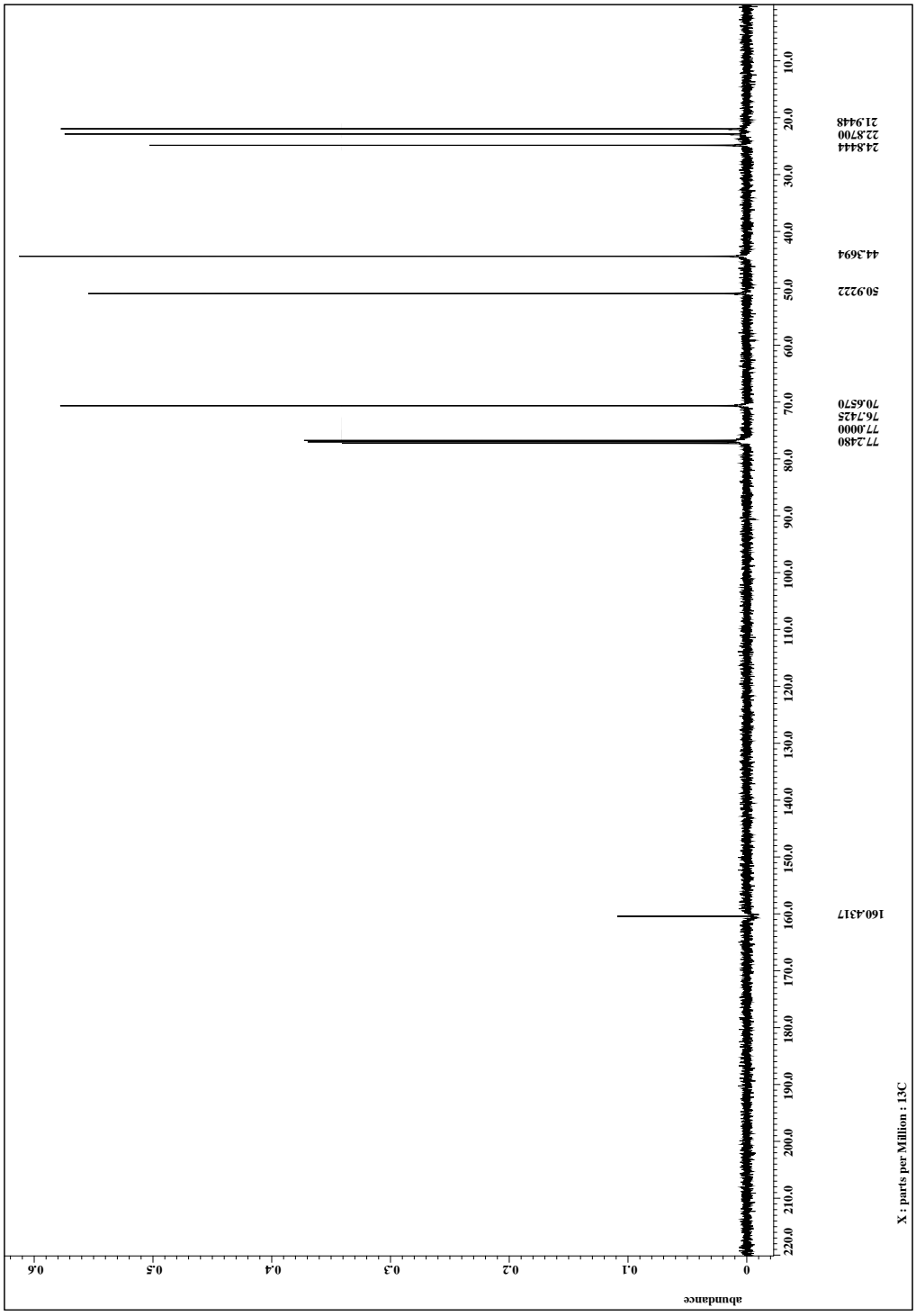
(*S*)-**2e** (^{1}H NMR)


O
NH
O

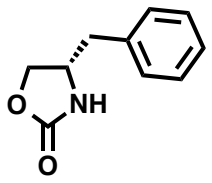

abundance
X : parts per Million : 1H
3.99
1.34
0.67
0.61
0.67
0.65
0.68
0.67
32.21m

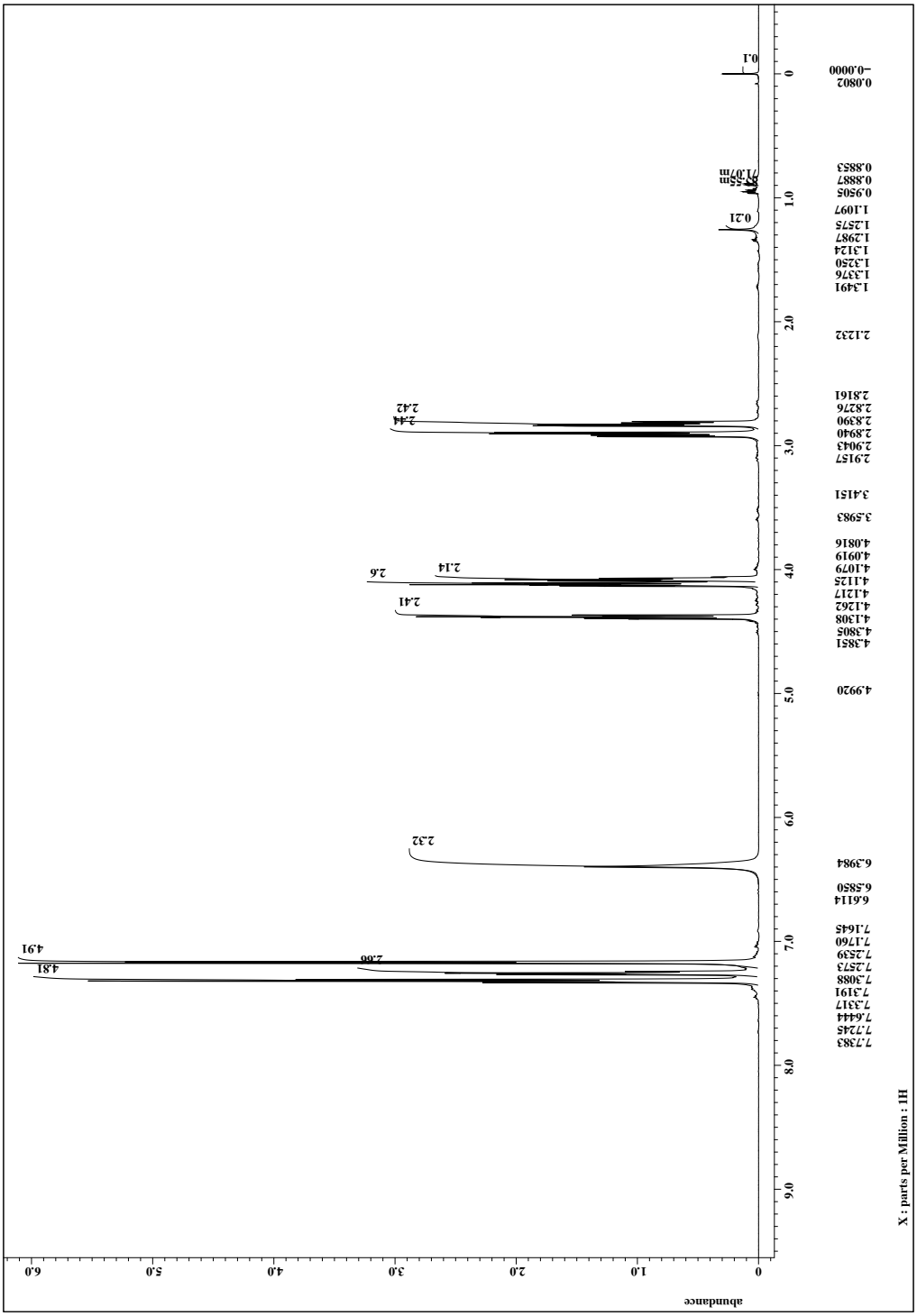
(*S*)-**2e** (^{13}C NMR)


O
NH
O

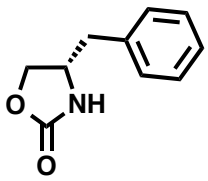

160.4317
77.2480
77.0000
76.7425
70.6570
50.9222
44.3694
24.8444
22.8700
21.9448
X : parts per Million : 13C
abundance

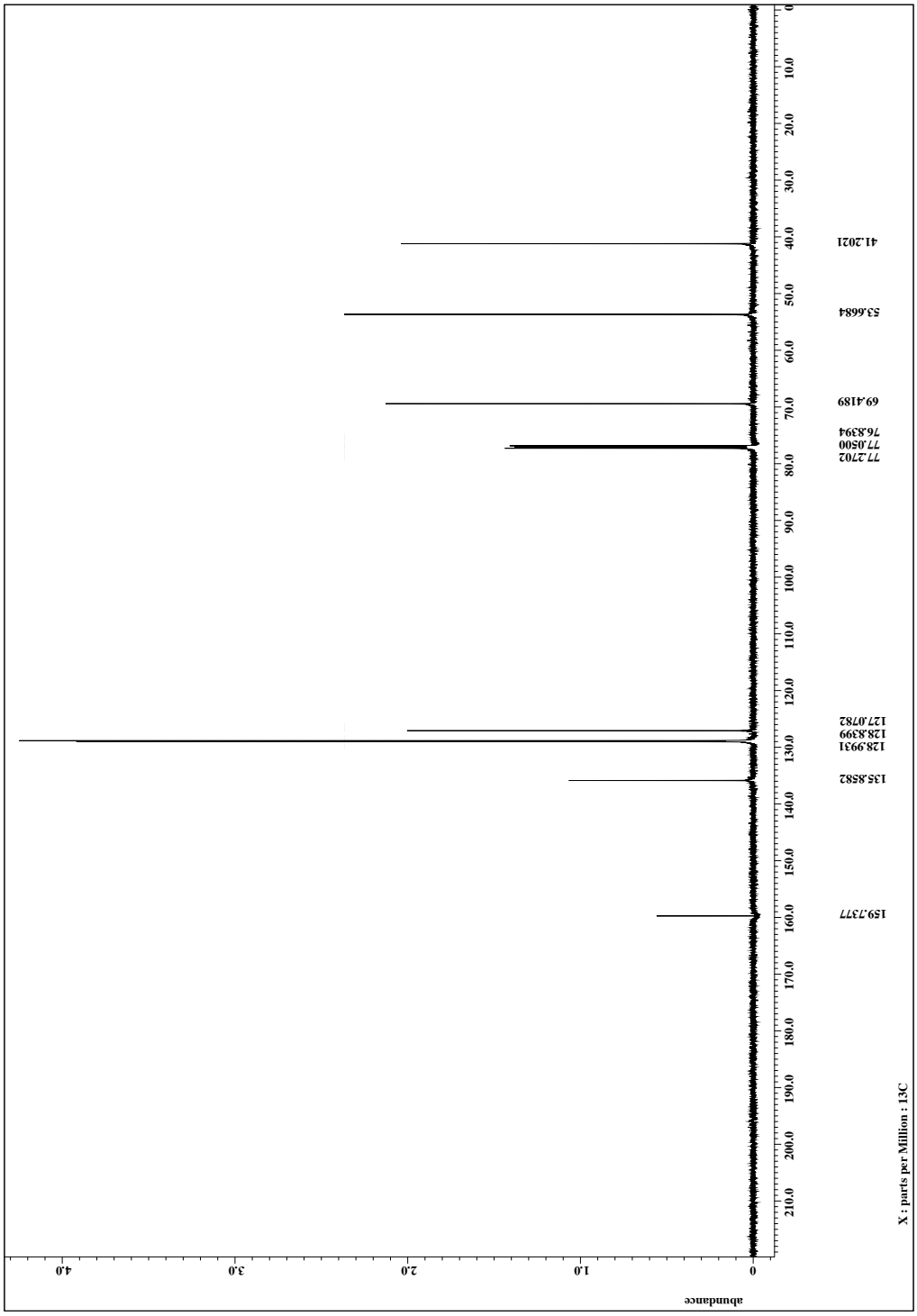
(*S*)-**2f** (^{1}H NMR)


O
NH
O

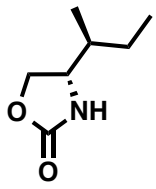

abundance
X : parts per Million : 1H
4.81
4.91
2.32
2.41
2.14
2.6
2.44
2.42
0.21
0.1

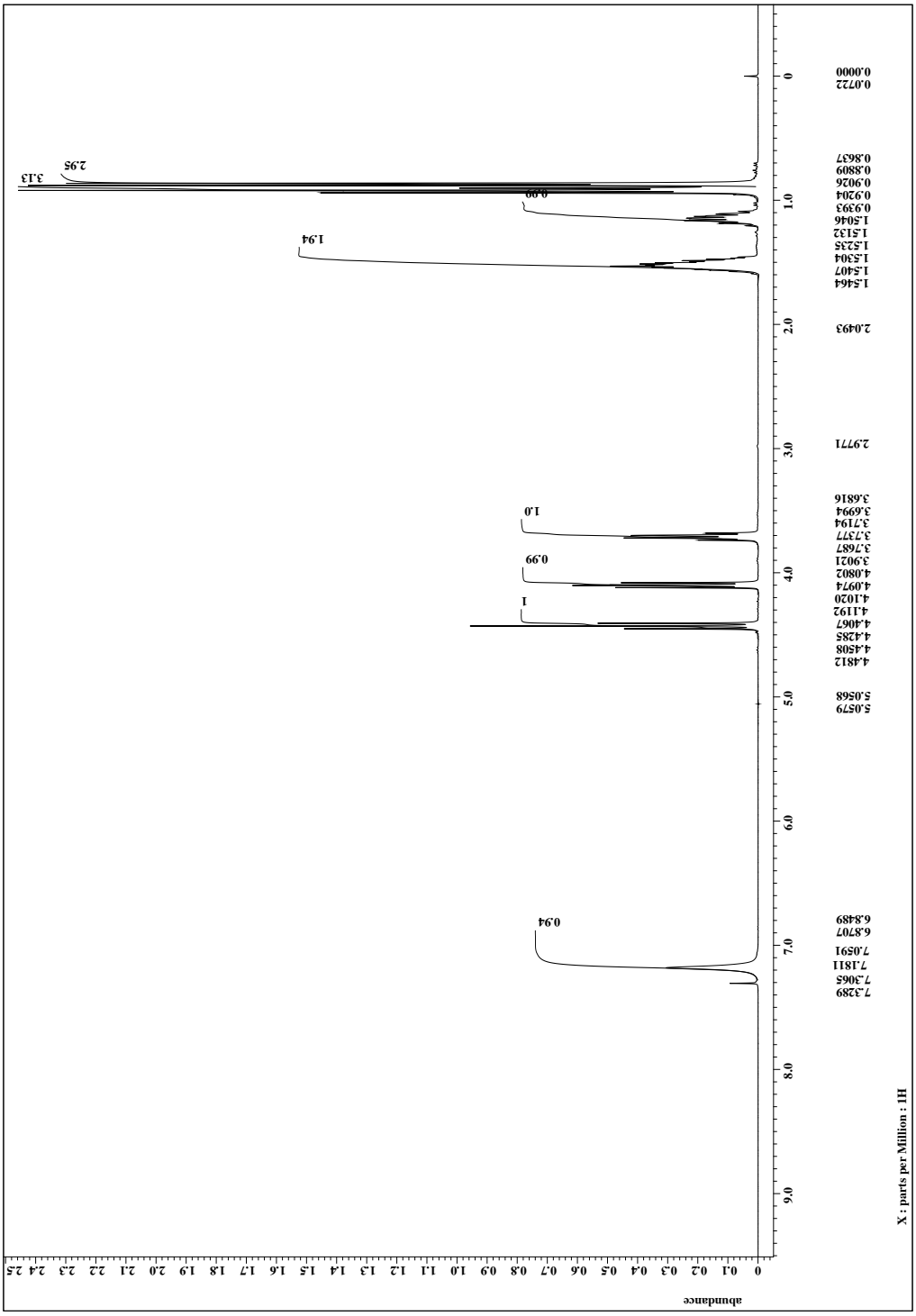
(*S*)-**2f** (^{13}C NMR)


O
NH
O

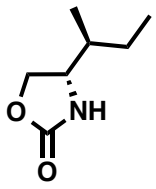

41.2021
53.6684
69.4189
77.2702
77.0500
76.8394
127.0782
128.8399
128.9931
135.8582
159.7377
X : parts per Million : 13C
abundance

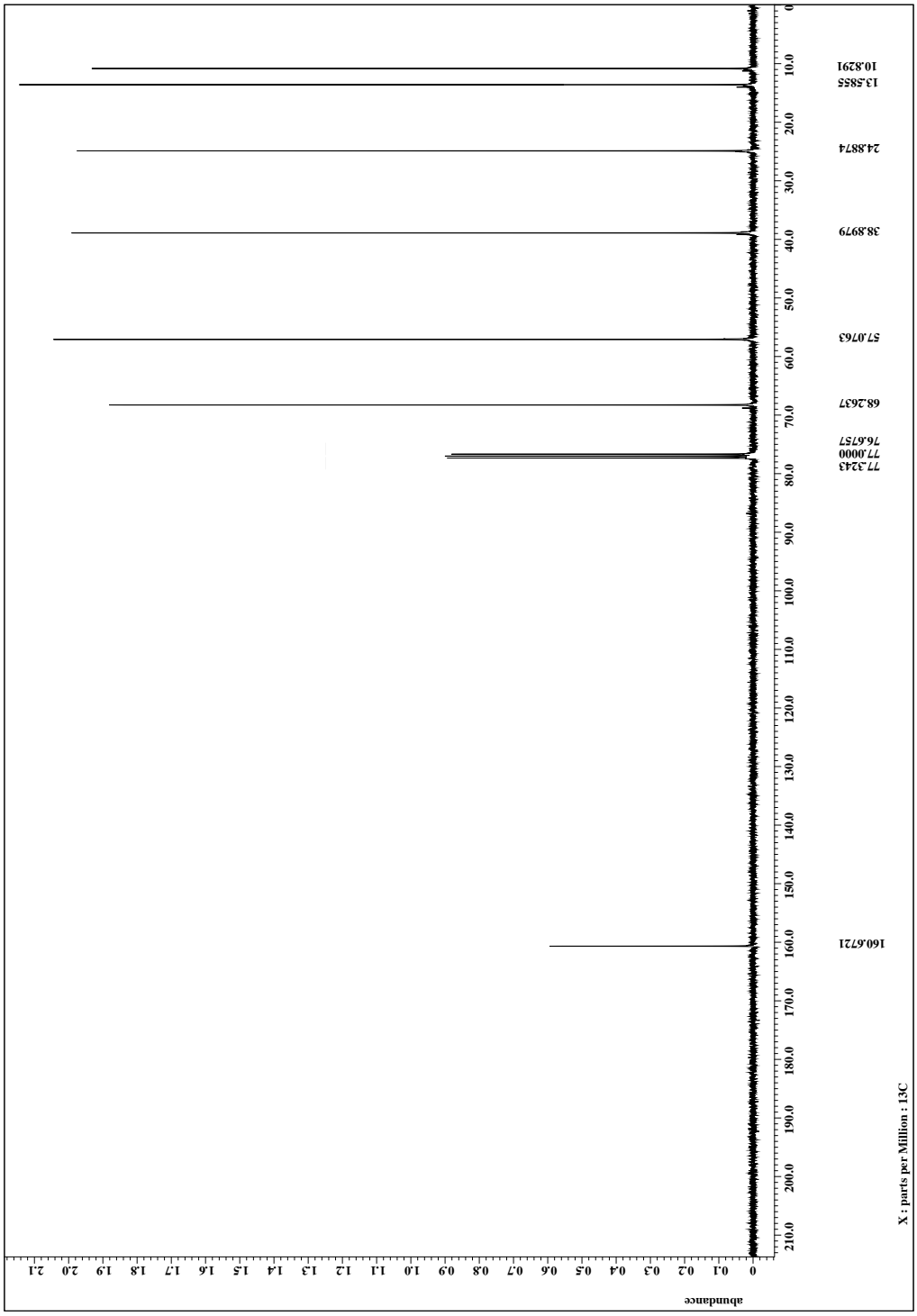
(*S*)-**2g** (^{1}H NMR)


O
NH
O

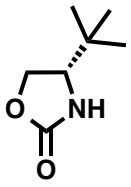

X : parts per Million : 1H
abundance
0.0722
0.0000
0.8637
0.8809
0.9026
0.9204
0.9393
1.5046
1.5132
1.5235
1.5304
1.5407
1.5464
2.0493
2.9771
3.6816
3.6994
3.7194
3.7377
3.7687
3.9021
4.0802
4.0974
4.1020
4.1192
4.4067
4.4285
4.4508
4.4812
5.0568
5.0579
6.8489
6.8707
7.0591
7.1811
7.3065
7.3289
0.94
1.0
0.99
1
0.99
1.94
2.95
3.13

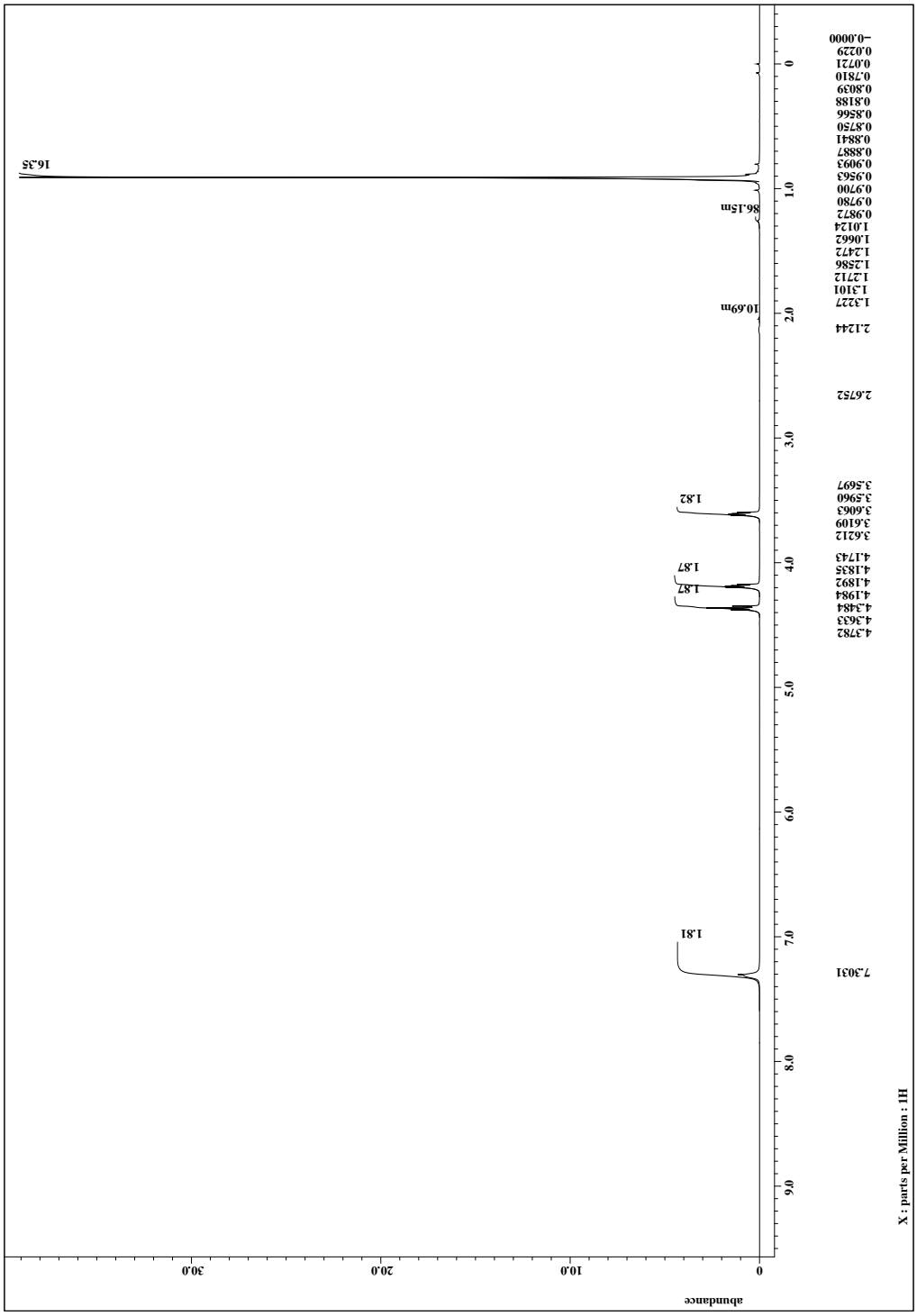
(*S*)-**2g** (^{13}C NMR)


O
NH
O

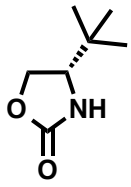

10.8291
13.5855
24.8874
38.8979
57.0763
68.2637
76.6757
77.0000
77.3243
160.6721
X : parts per Million : 13C
abundance

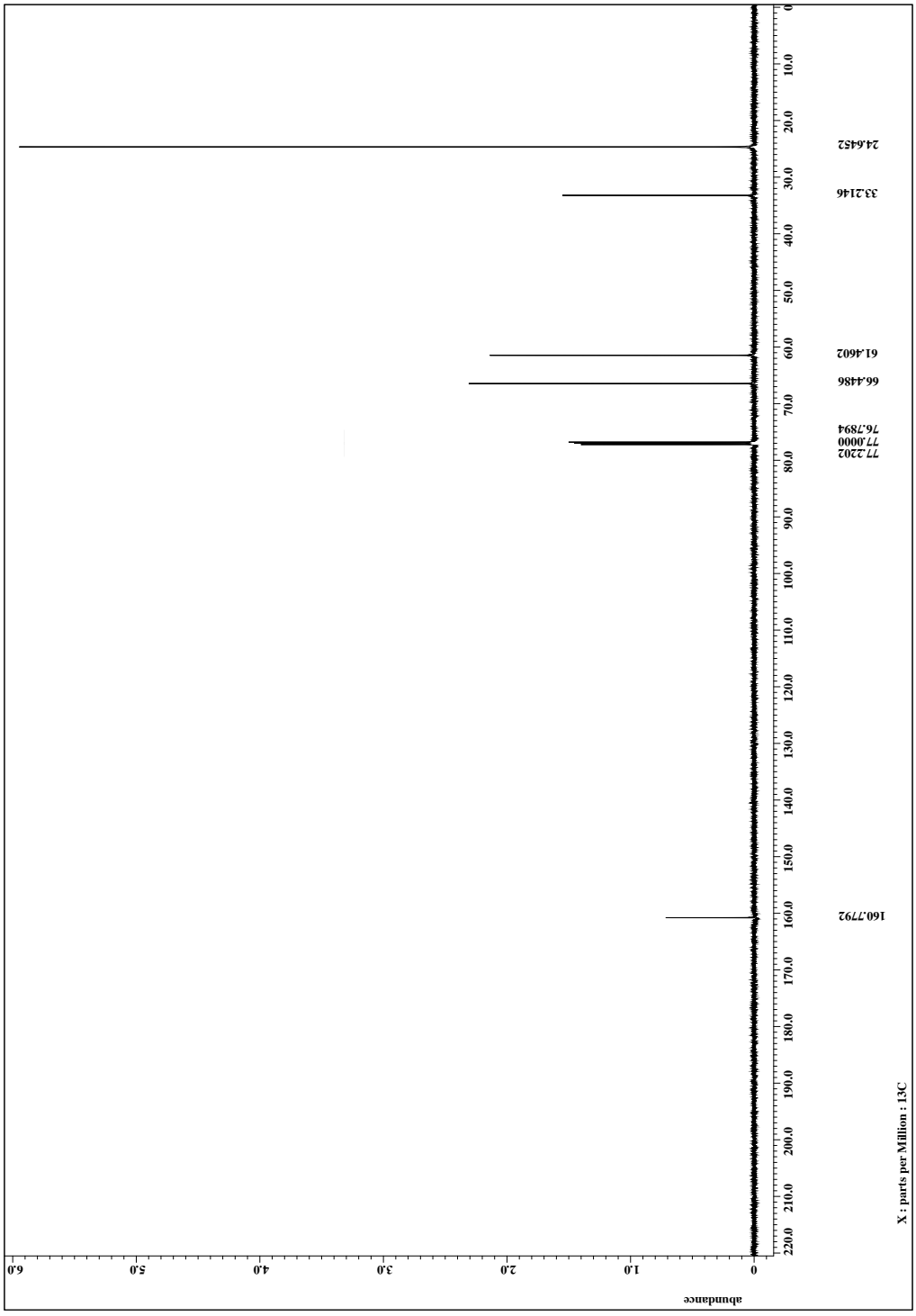
(*S*)-**2h** (^{1}H NMR)


O
NH
O

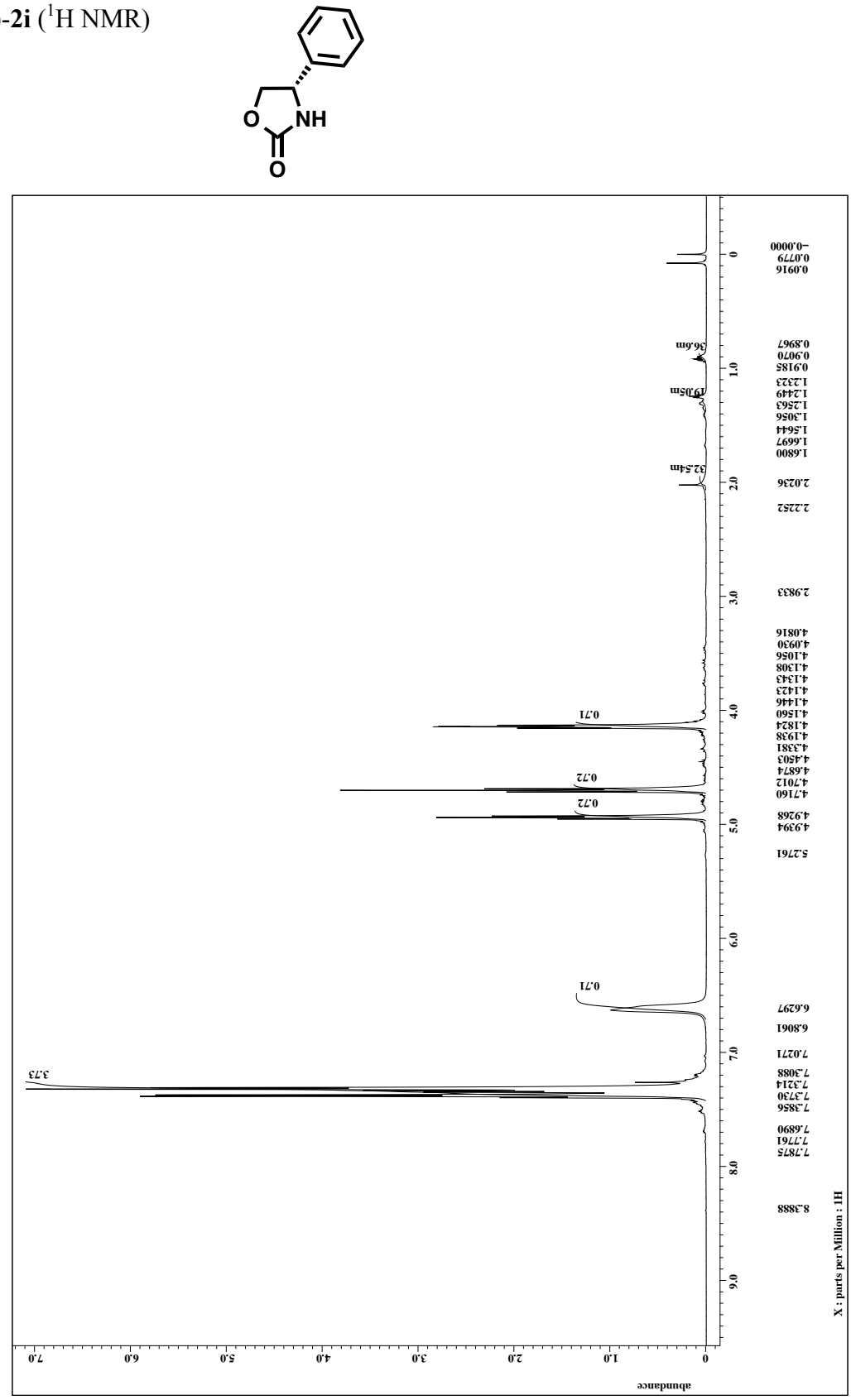

16.35
10.69m
1.82
1.87
1.87
1.81
7.3031
4.3782
4.3633
4.3484
4.1984
4.1892
4.1835
4.1743
3.6212
3.6109
3.6063
3.5960
3.5697
2.6752
2.1244
1.3227
1.3101
1.2712
1.2586
1.2472
1.0662
1.0124
0.9872
0.9780
0.9700
0.9563
0.9093
0.8887
0.8841
0.8750
0.8566
0.8188
0.8039
0.7810
0.0721
0.0229
−0.0000
abundance
X : parts per Million : 1H

(*S*)-**2h** (^{13}C NMR)

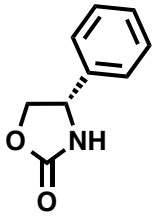

O
NH
O

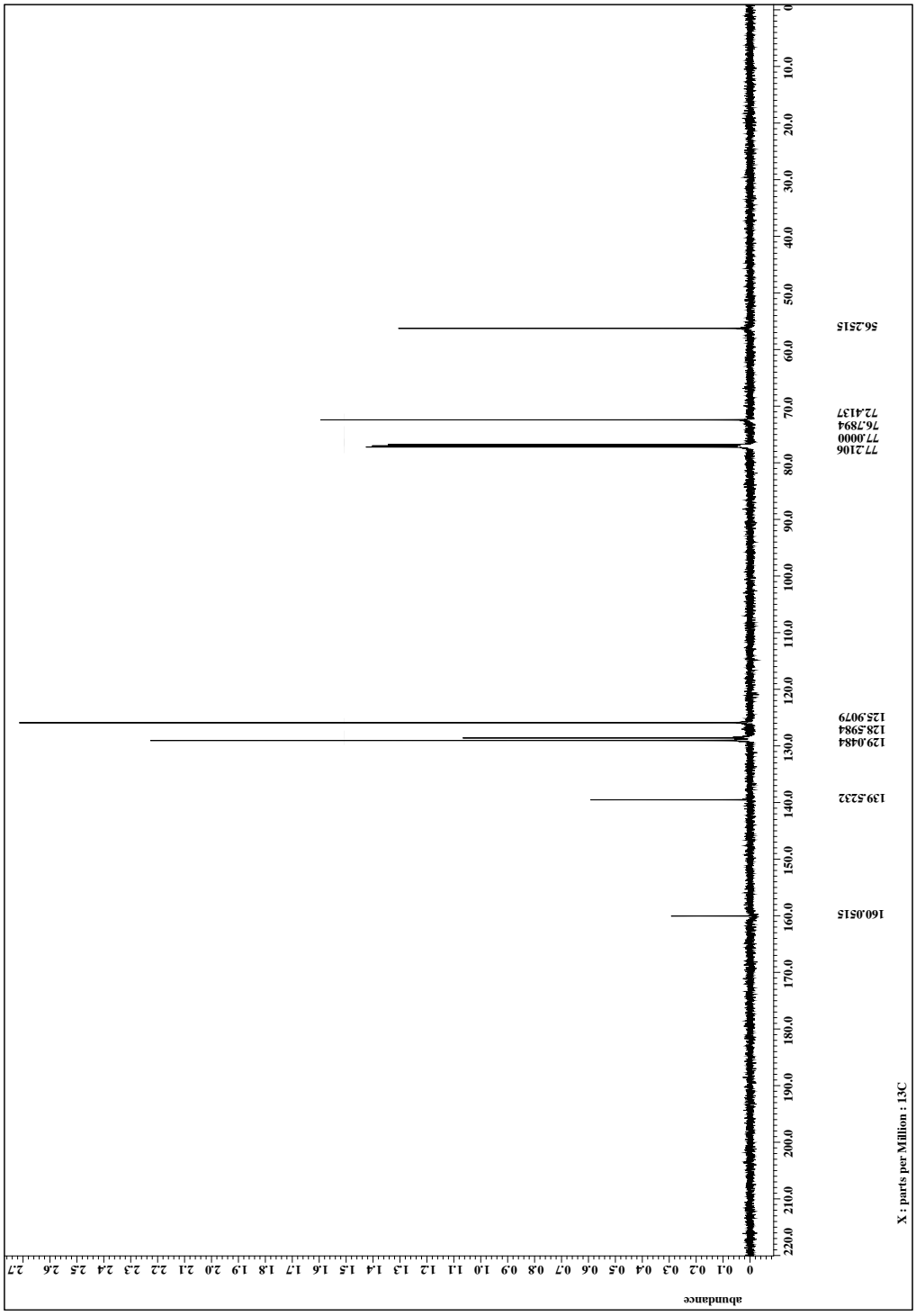

24.6452
33.2146
61.4602
66.4486
77.2202
77.0000
76.7894
160.7792
X : parts per Million : 13C
abundance

(*S*)-**2i** (^{1}H NMR)

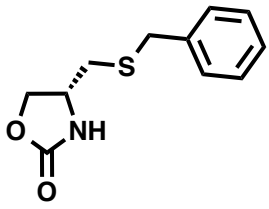

O
NH
O
3.73
0.71
0.72
0.72
0.71
32.54m
19.05m
36.6m
X : parts per Million : 1H
abundance

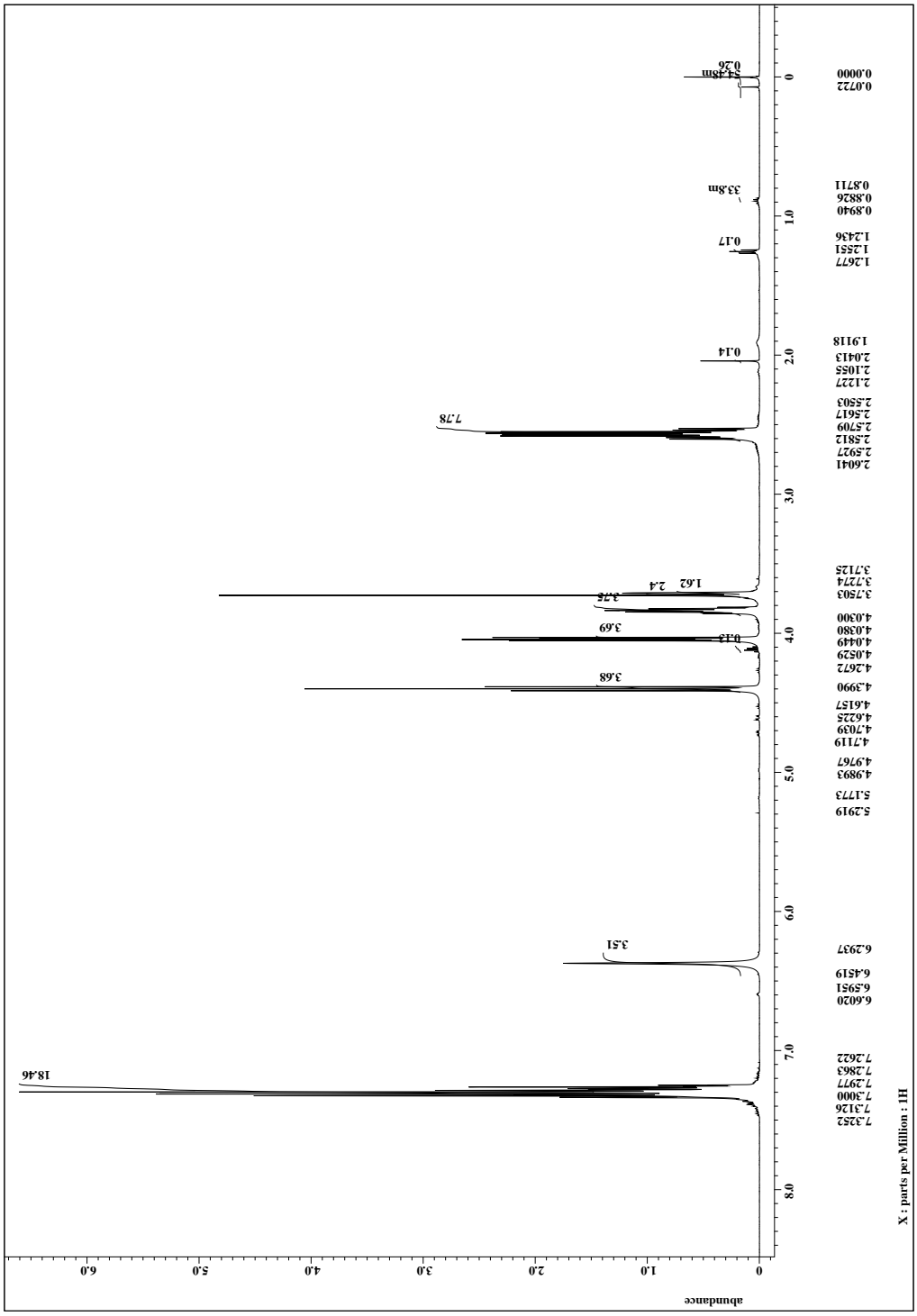
(*S*)-**2i** (^{13}C NMR)


O
NH
O

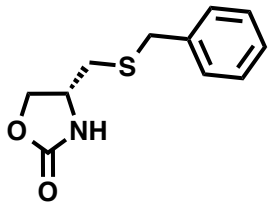

56.2515
72.4137
76.7894
77.0000
77.2106
125.9079
128.5984
129.0484
139.5232
160.0515
X : parts per Million : 13C
abundance

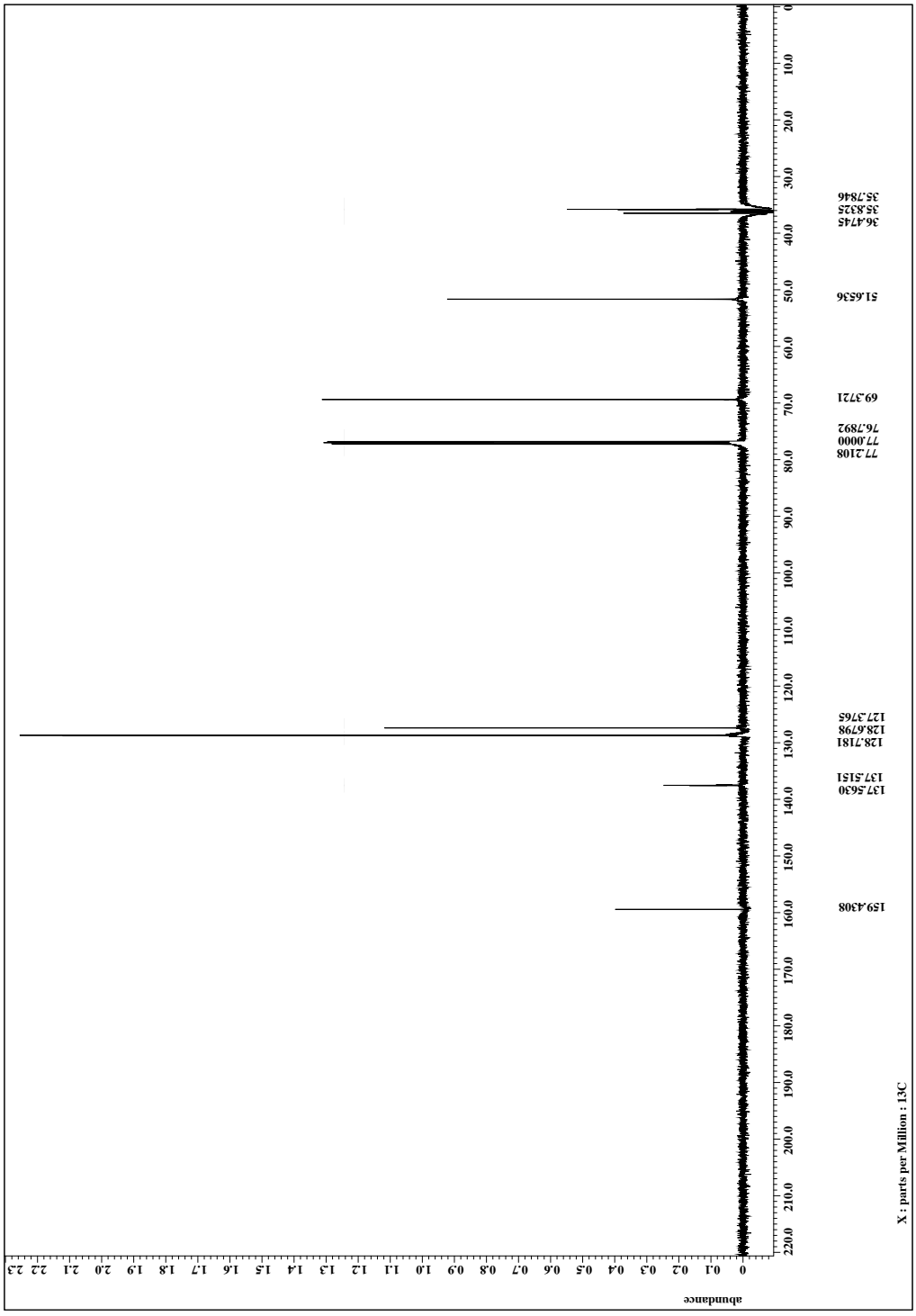
(*R*)-**2j** (^{1}H NMR)


S
O
NH
O

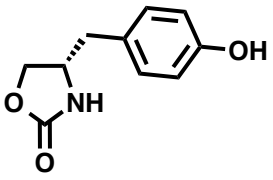

abundance
X : parts per Million : 1H
18.46
7.78
3.78
3.69
3.68
3.51
2.4
1.62
0.26
33.8m
0.17
0.14
0.0000
0.0722
7.3252
7.3126
7.3000
7.2977
7.2863
7.2622
6.6020
6.5951
6.4519
6.2937
5.2919
5.1773
4.9893
4.9767
4.7119
4.7039
4.6228
4.6157
4.3990
4.2672
4.0529
4.0449
4.0380
4.0300
3.7503
3.7274
3.7125
2.6041
2.5927
2.5812
2.5709
2.5617
2.5503
2.1227
2.1055
2.0413
1.9118
1.2677
1.2551
1.2436
0.8940
0.8826
0.8711

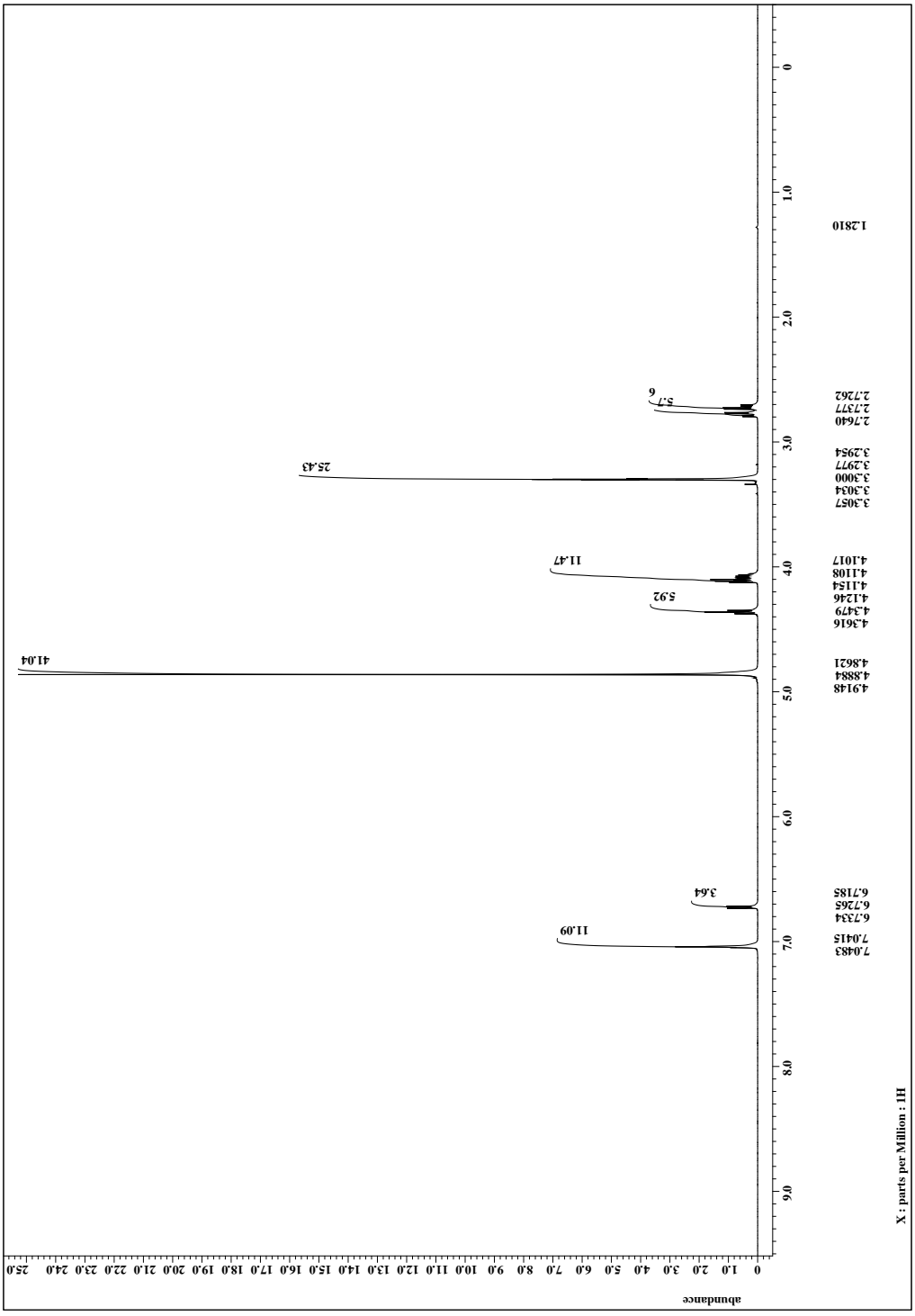
(*R*)-**2j** (^{13}C NMR)


S
O
NH
O

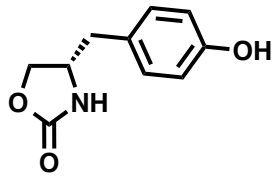

159.4308
137.5630
137.5151
128.7181
128.6798
127.3765
77.2108
77.0000
76.7892
69.3721
51.6536
36.4745
35.8325
35.7846
X : parts per Million : 13C
abundance

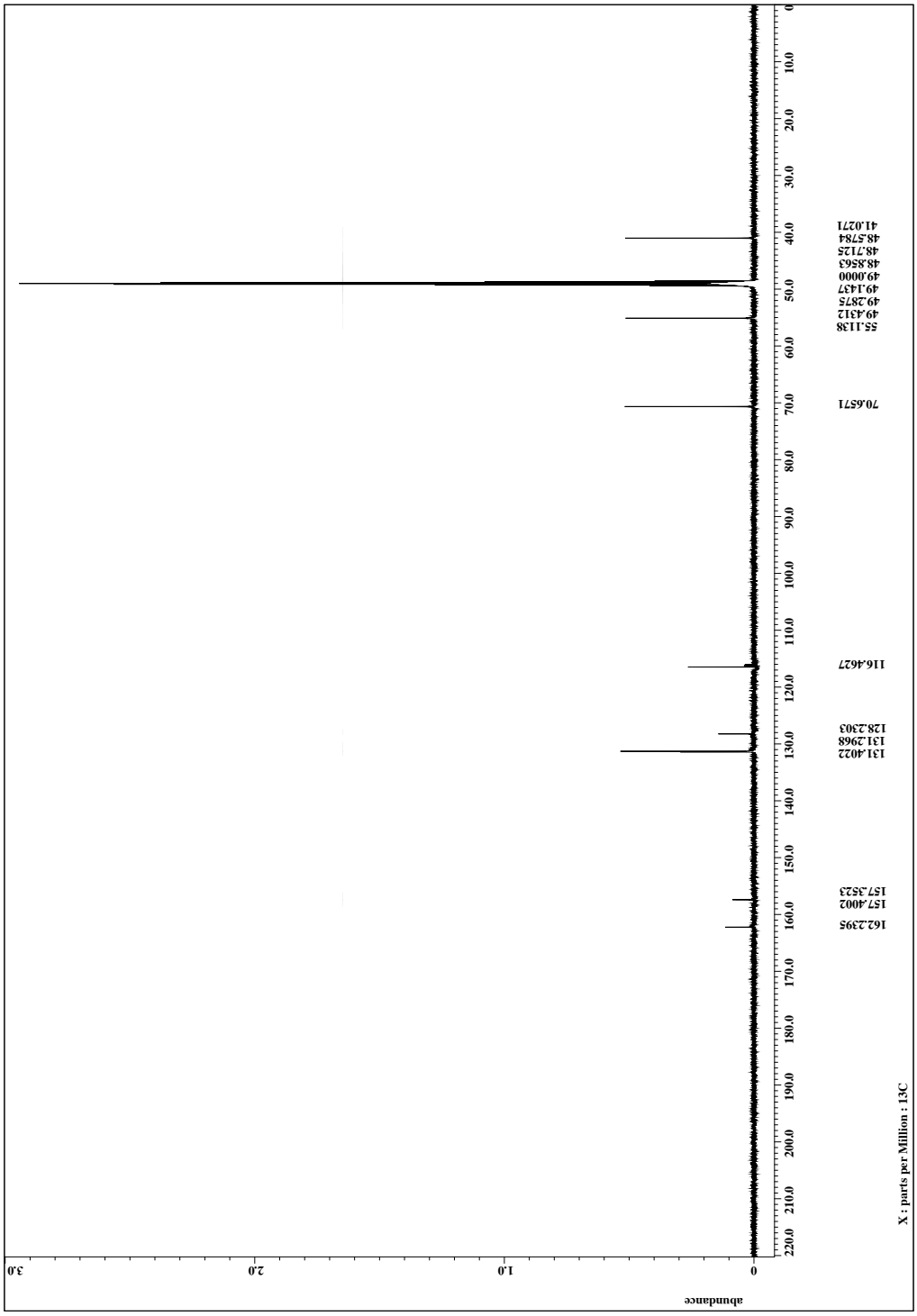
(*S*)-**2k** (^{1}H NMR in methanol-d_4)



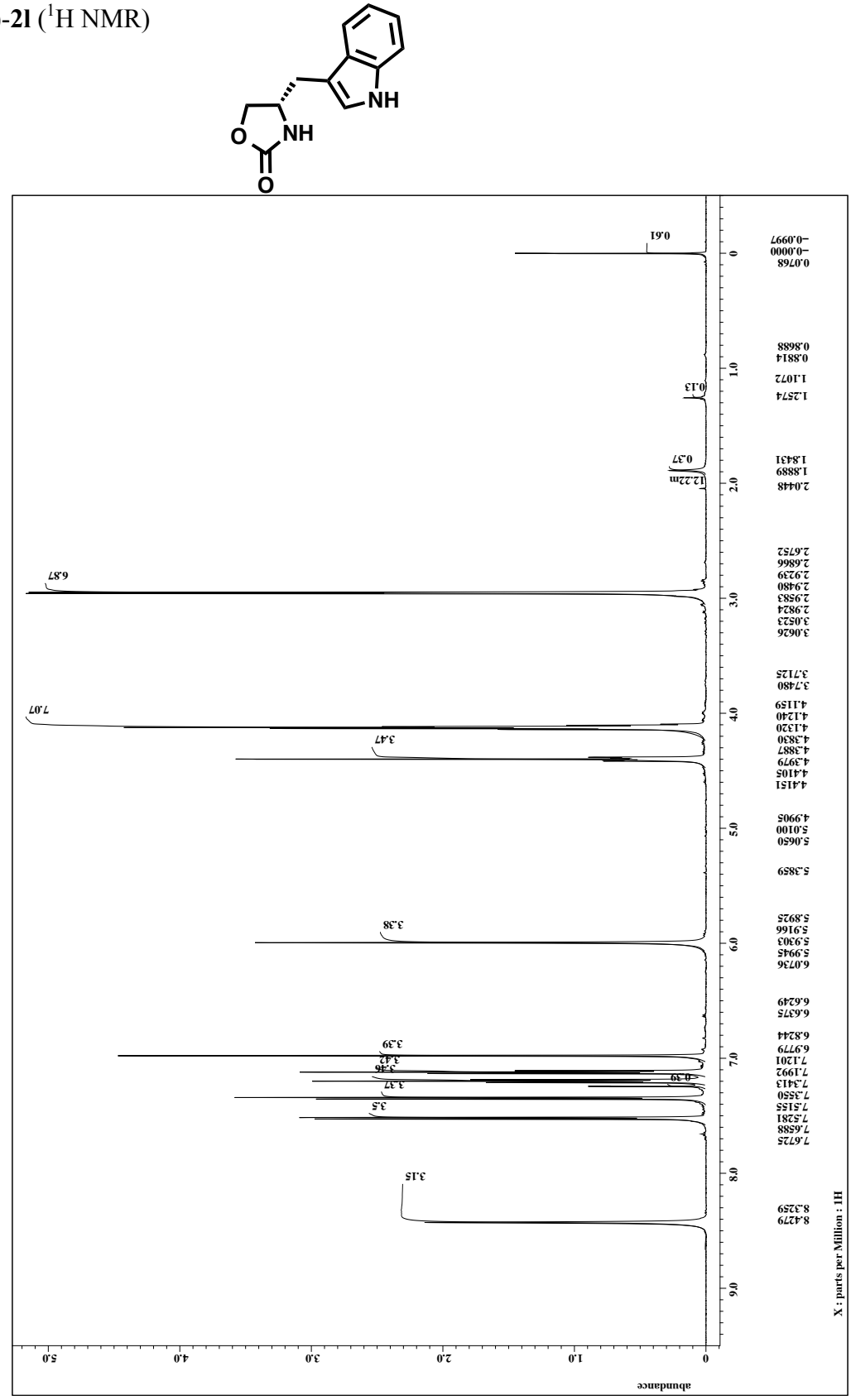


(*S*)-**2k** (^{13}C NMR in methanol-d_4)

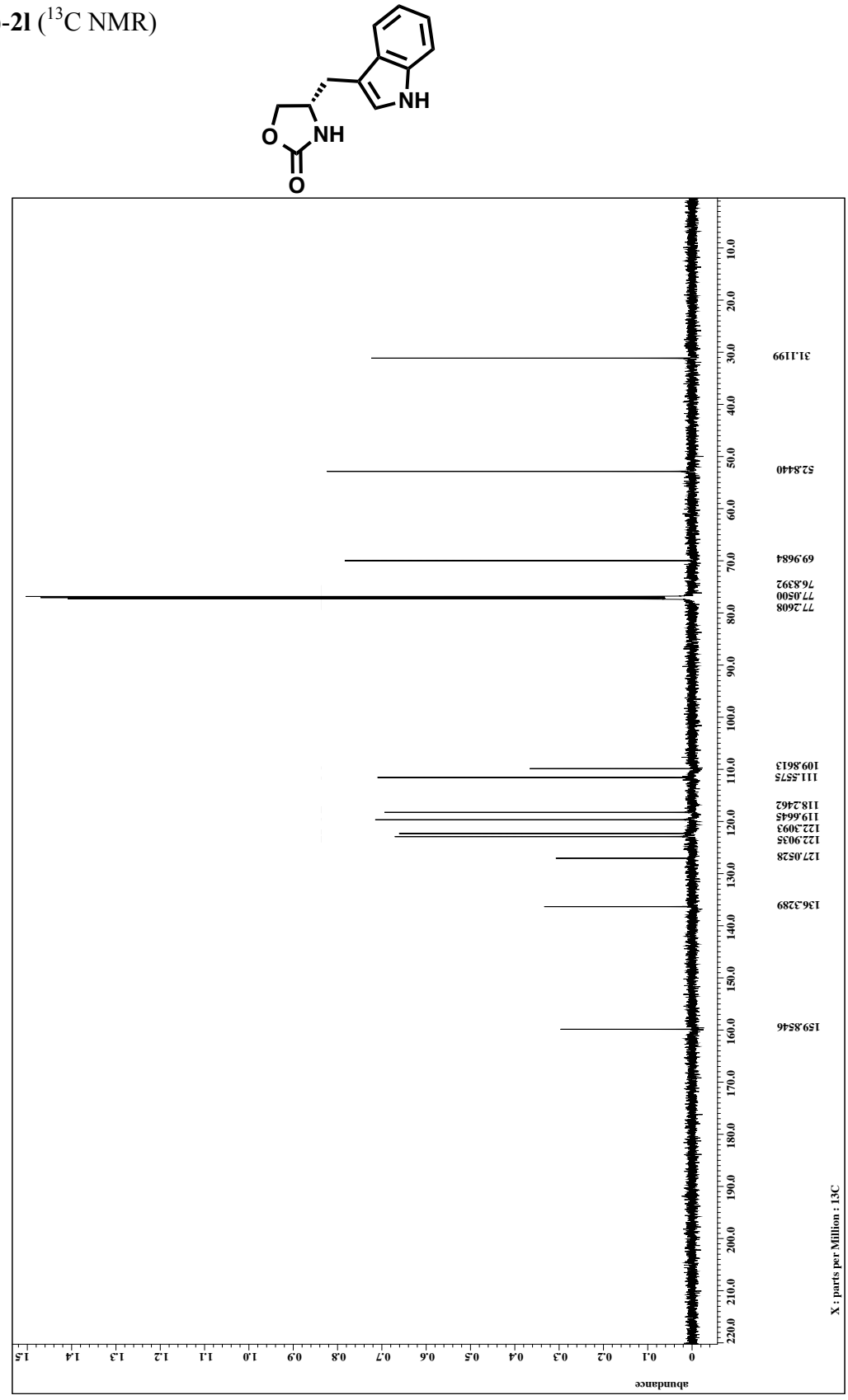




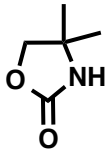
(*S*)-**21** (^{1}H NMR)

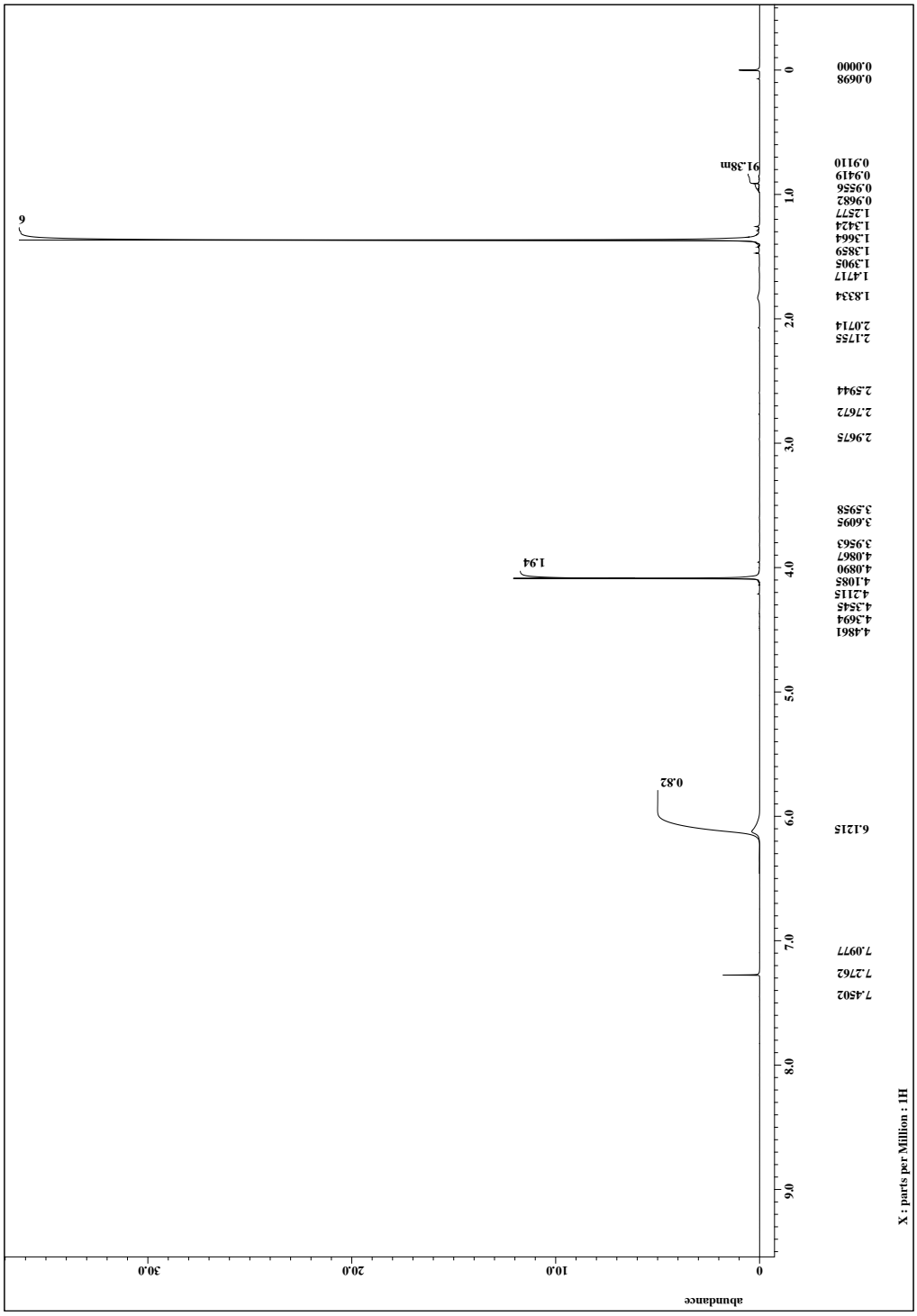


(*S*)-**21** (^{13}C NMR)

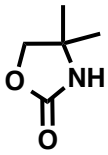

NH
O
NH
O
31.1199
52.8440
69.9684
76.8392
77.0500
77.2608
109.8613
111.5575
118.2462
119.6645
122.3093
122.9035
127.0528
136.3289
159.8546
X : parts per Million : 13C
abundance

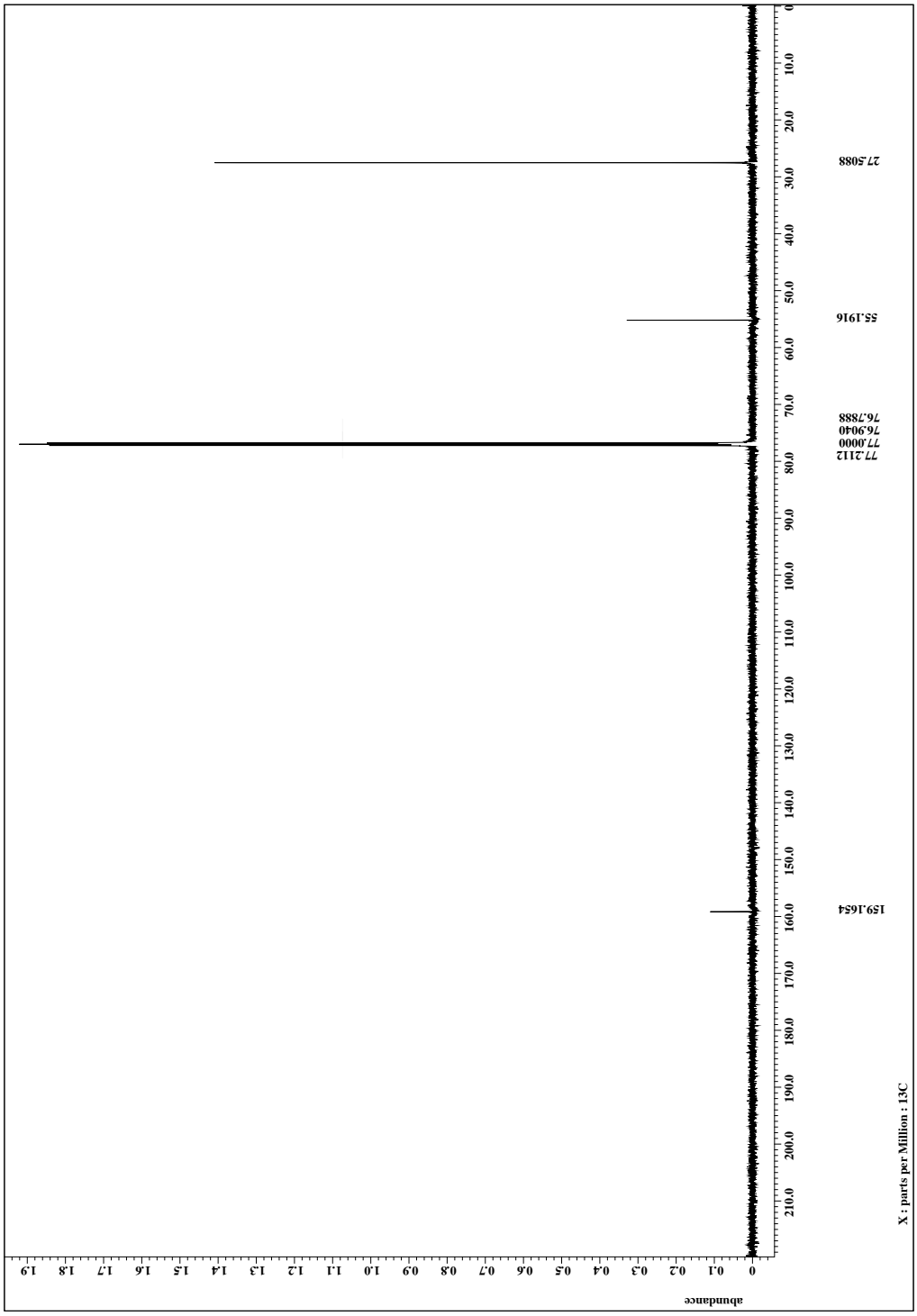
2m (^{1}H NMR)


O
NH
O

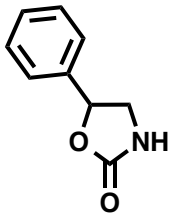

abundance
0
10.0
20.0
30.0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.82
1.94
6
91.38m
0.0000
0.0698
0.9110
0.9419
0.9556
0.9682
1.2577
1.3424
1.3664
1.3859
1.3905
1.4717
1.8334
2.0714
2.1755
2.5944
2.7672
2.9675
3.5958
3.6095
3.9563
4.0867
4.0890
4.1085
4.2115
4.3545
4.3694
4.4861
6.1215
7.0977
7.2762
7.4502

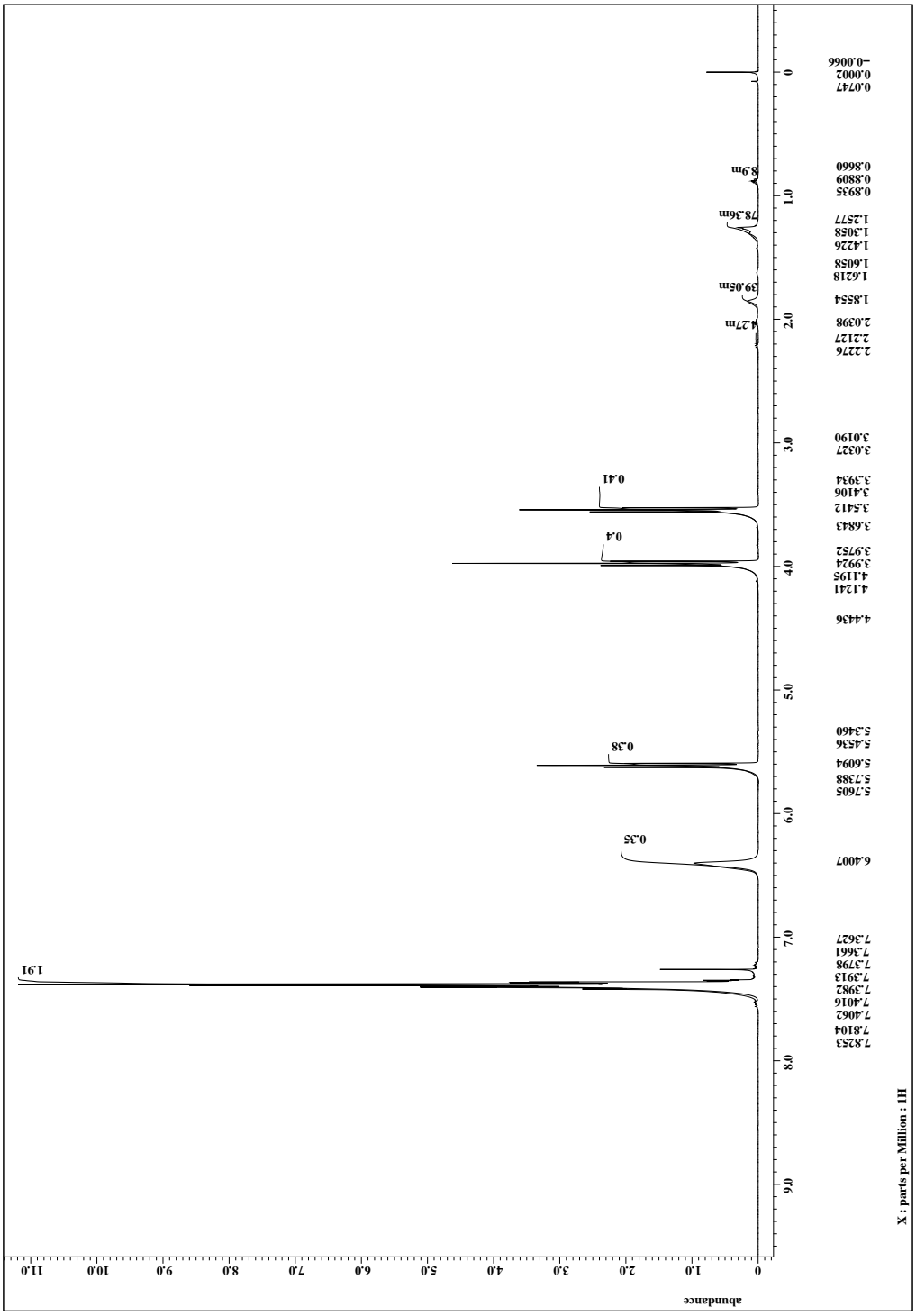
2m (^{13}C NMR)


O
NH
O

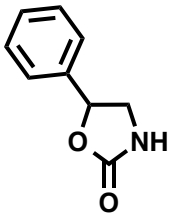

159.1654
77.2112
77.0000
76.9040
76.7888
55.1916
27.5088
X : parts per Million : 13C
abundance

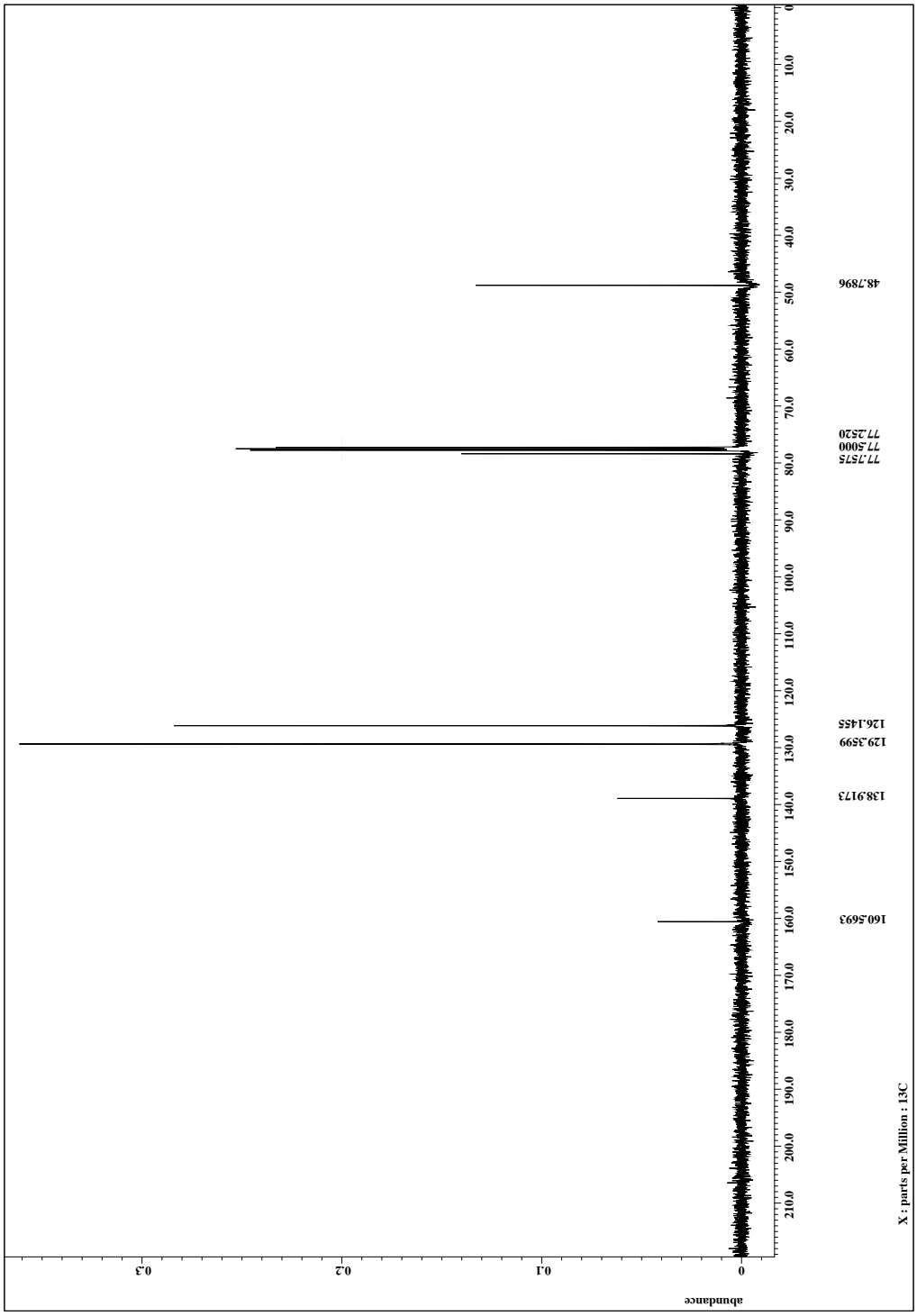
rac-**2n** (^{1}H NMR)


O
NH
O

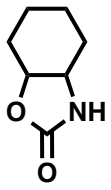

abundance
X : parts per Million : 1H
1.91
0.35
0.38
0.4
0.41
4.27m
39.05m
78.36m
8.9m

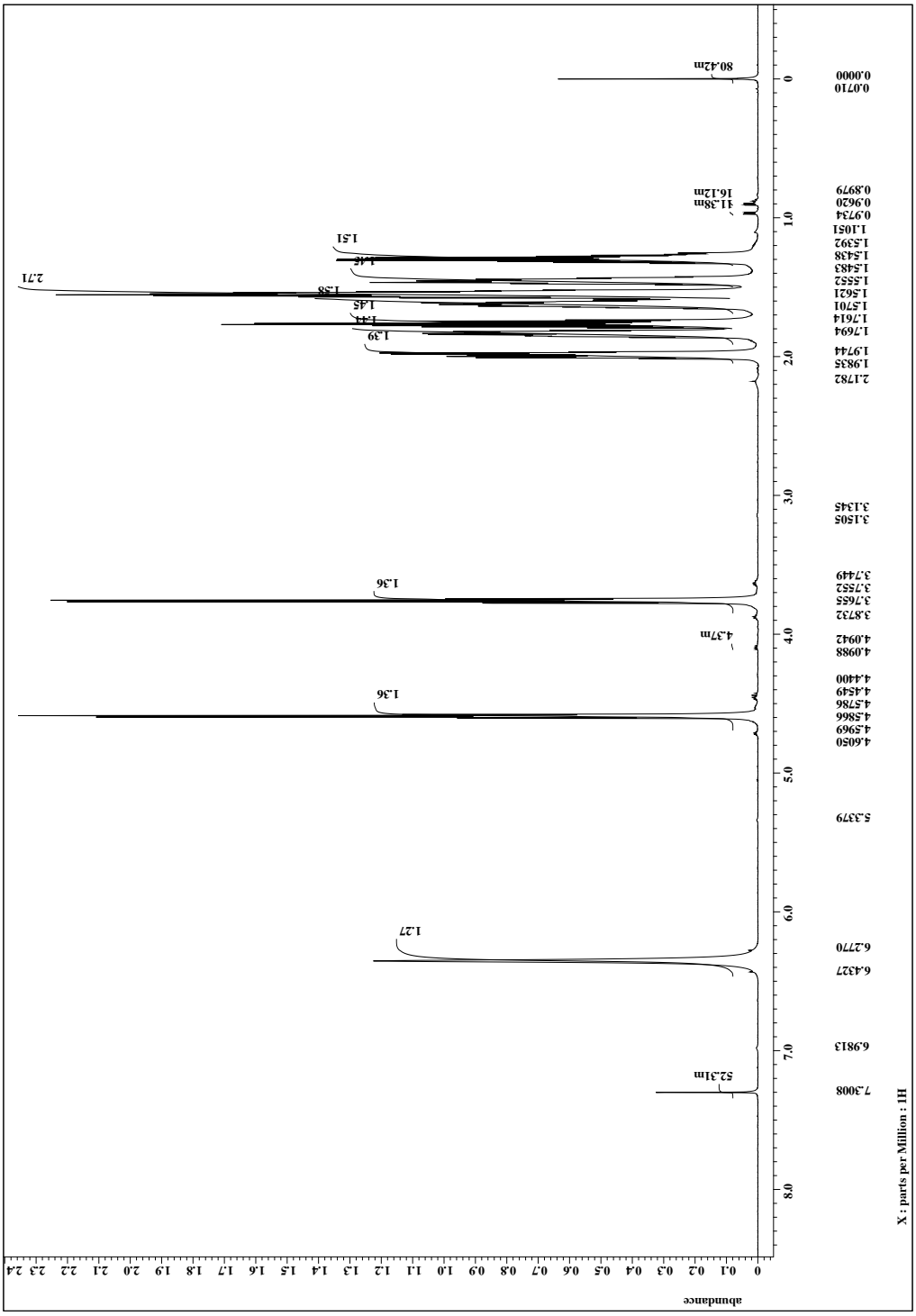
rac-**2n** (^{13}C NMR)



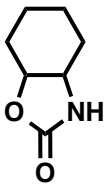


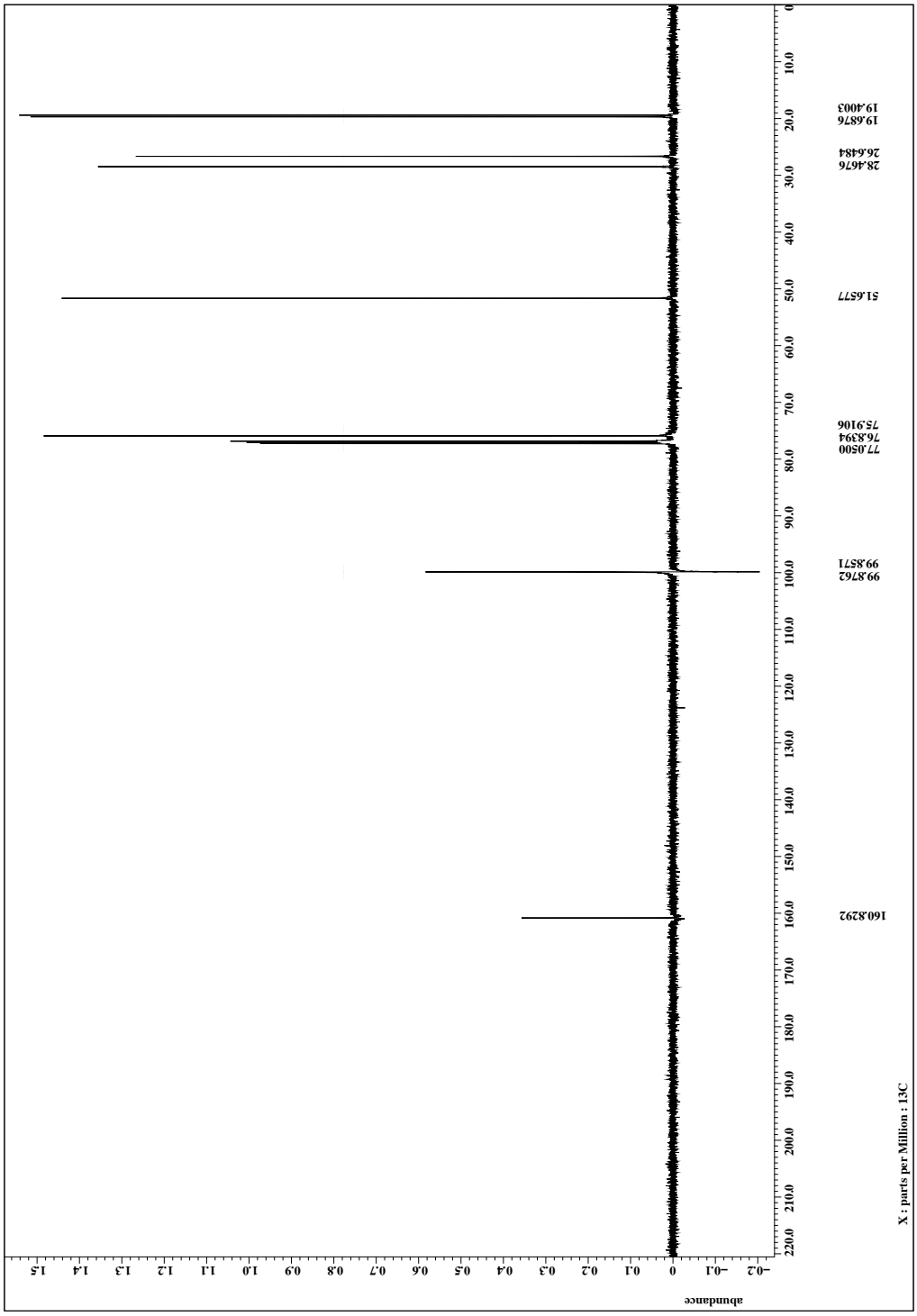
***rac*-2o** (^{1}H NMR)


O
NH
O

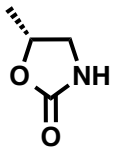

abundance
X : parts per Million : 1H
7.3008
6.9813
6.4327
6.2770
5.3379
4.6050
4.5969
4.5866
4.5786
4.4549
4.4400
4.0988
4.0942
3.8732
3.7655
3.7552
3.7449
3.1505
3.1345
2.1782
1.9835
1.9744
1.7694
1.7614
1.5701
1.5621
1.5552
1.5483
1.5438
1.5392
1.1051
0.9734
0.9620
0.8979
0.0710
0.0000
52.31m
1.27
1.36
4.37m
1.36
80.42m
16.12m
31.38m
1.51
1.46
1.58
2.71
1.45
1.41
1.39

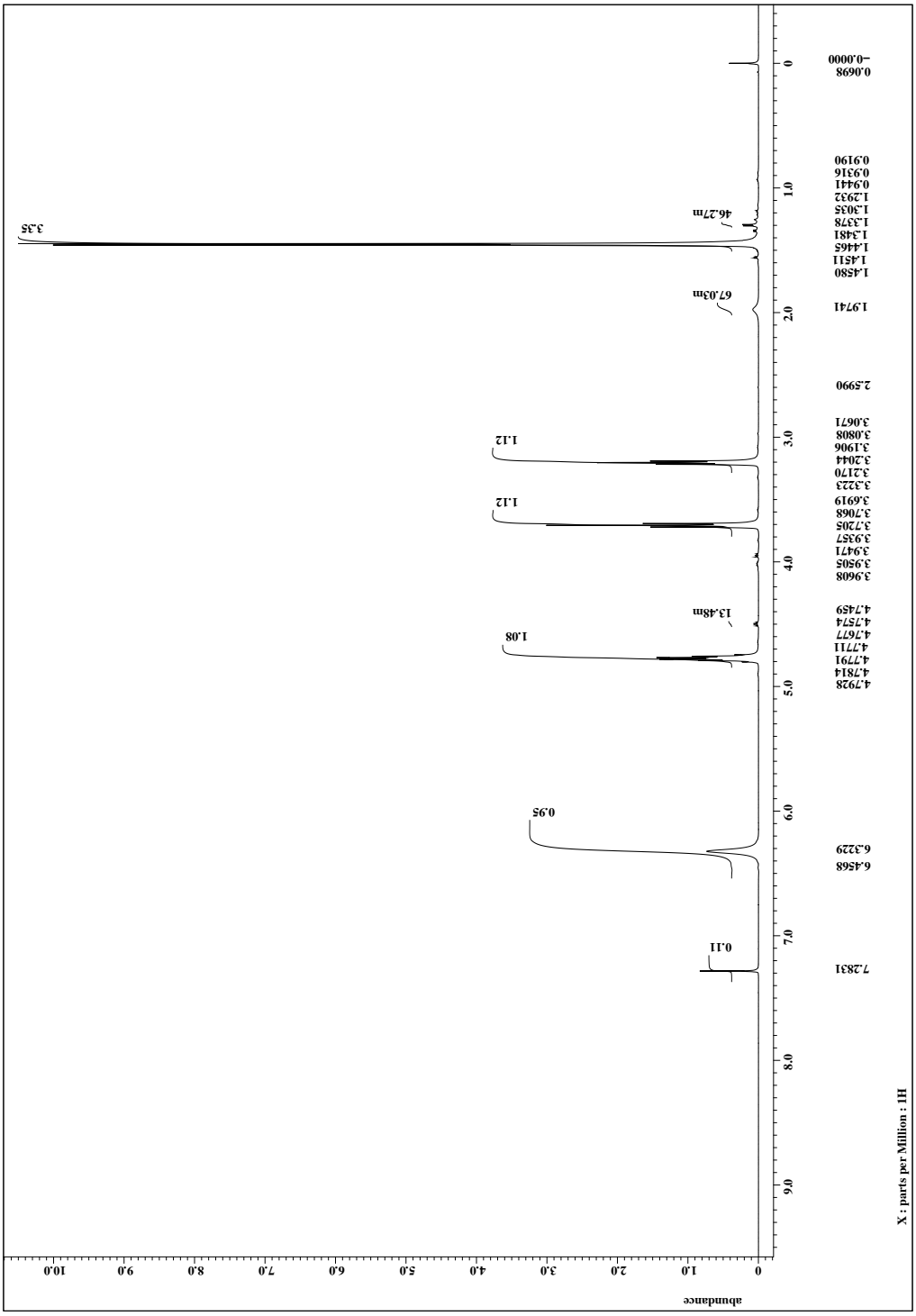
***rac*-2o** (^{13}C NMR)



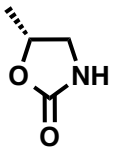


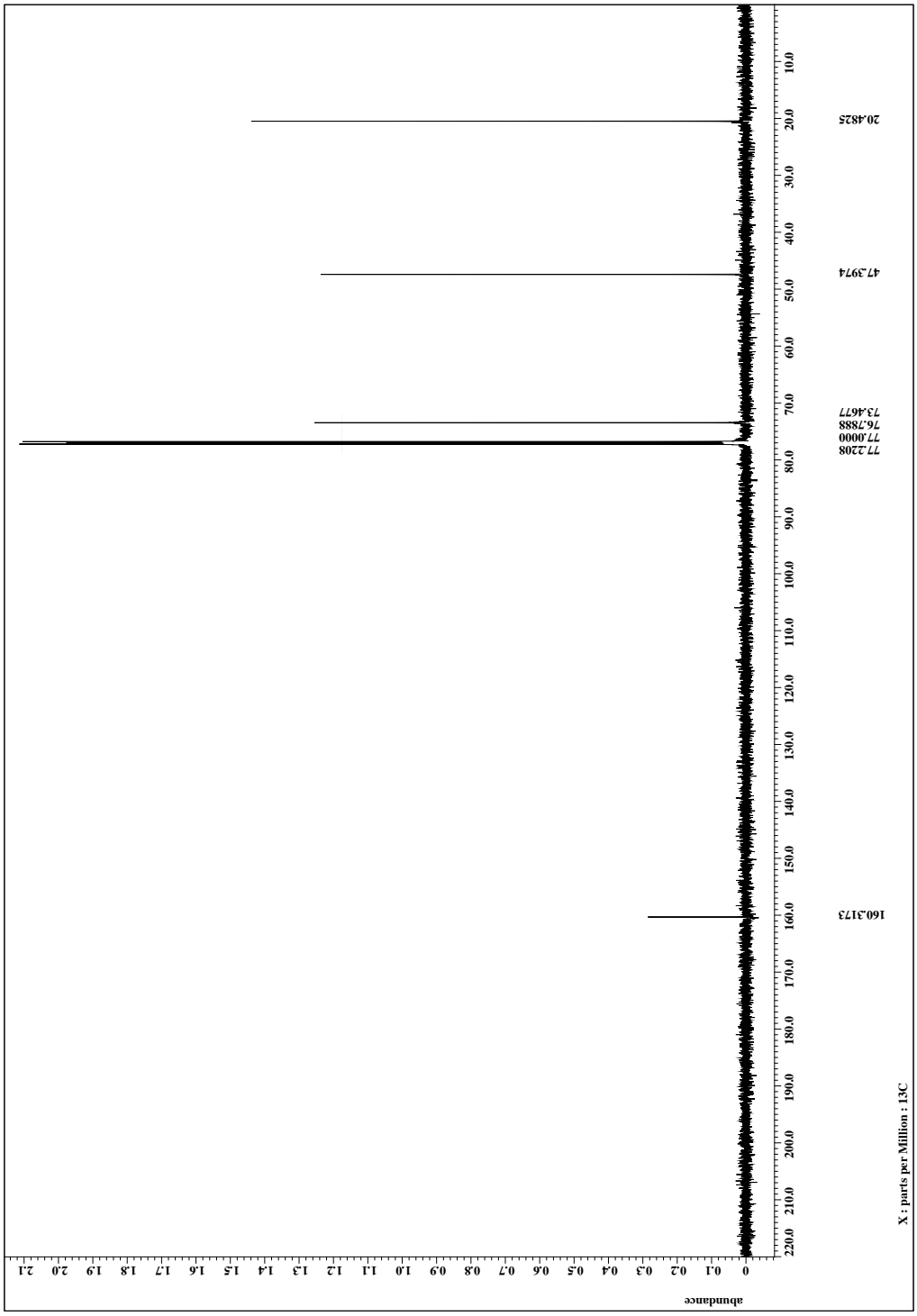
(*R*)-**2p** (^{1}H NMR)


O
NH
O


X : parts per Million : 1H
abundance
0.0698
-0.0000
7.2831
6.4568
6.3229
4.7928
4.7814
4.7791
4.7711
4.7677
4.7574
4.7459
3.9608
3.9505
3.9471
3.9357
3.7205
3.7068
3.6919
3.3223
3.2170
3.2044
3.1906
3.0808
3.0671
2.5990
1.9741
1.4580
1.4511
1.4465
1.3481
1.3378
1.3035
1.2932
0.9441
0.9316
0.9190
0.11
0.95
1.08
13.48m
1.12
1.12
67.03m
46.27m
3.35

(*R*)-**2p** (^{13}C NMR)


O
NH
O


20.4825
47.3974
73.4677
76.7888
77.0000
77.2208
160.3173
X : parts per Million : 13C
abundance