Supporting Information for

Rhodium(II)-catalysed tandem aziridination and ring-opening: stereoselective synthesis of functionalised tetrahydrofurans

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Procedure for cross metathesis between allyl carbamate (1) & alkenes 2–5

To a solution of allyl carbamate (**1**, 4*x* mmol) and alkene (**2**–**5**, *x* mmol) in degassed dichloromethane (10*x* mL) was added Grubbs' 2nd generation catalyst (0.05*x* mmol) and the mixture was heated to reflux under argon for 45 min. The reaction mixture was opened to the air, cooled to rt, and passed through a short plug of silica to remove the bulk of the ruthenium residues and the insoluble homodimer of **1**. The solution was concentrated *in vacuo* and the residue purified by column chromatography (petrol/ethyl acetate/methanol, 10:5:1) to furnish the cross-metathesis product (**6**–**9**).

(*E*)-6-Hydroxyhex-2-enyl carbamate (6)

The *title compound* was obtained as a colourless oil (134 mg, 88%) as a mixture of geometrical isomers (*E*:*Z* = 7:1). R_f 0.32 (petrol/ethyl acetate/methanol, 5:5:1); ν_{max} (thin film)/cm^{-1} 3352br,

1707s, 1607w, 1407m, 1340s, 1097w, 1048m, 974w, 785w; δ_H (400 MHz, $CDCl_3$) 1.66 (4 H, quin, *J* 6.9, CH_2CH_2OH, *E* & *Z*), 1.93 (2 H, br t, *J* 5.2, OH, *E* & *Z*), 2.15 (4 H, q, *J* 6.9, =CHCH_2, *E* & *Z*), 3.60–3.67 (4 H, m, CH_2OH, *E* & *Z*), 4.49 (2 H, dd, *J* 6.3, 0.8, OCH_2, *E*), 4.66 (2 H, d, *J* 5.0, OCH_2, *Z*), 4.93 (2 H, br s, NH_2, *E*), 5.00 (2 H, br s, NH_2, *Z*), 5.55–5.82 (4 H, m, CH=CH, *E* & *Z*); δ_C (125 MHz, $CDCl_3$) data for *E*-isomer: 28.6 (CH_2), 31.7 (CH_2), 62.1 (CH_2), 65.7 (CH_2), 124.7 (CH), 135.3 (CH), 157.0 (C); HRMS (ESI^+) found 182.0781, $C_7H_{13}NNaO_3$ (MNa^+) requires 182.0788.

(*E*)-6-Hydroxyhept-2-enyl carbamate (7)

The *title compound* was obtained as a pale brown oil (206 mg, 60%) as a mixture of geometrical isomers (*E*:*Z* ~ 4:1). R_f 0.28 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3355br, 1707s, 1607w, 1406m, 1336s, 1050m, 974w; δ_H (400 MHz, $CDCl_3$) 1.18 (3 H, d, *J* 6.1, CH_3), 1.47–1.57 (2 H, m, CH_2CHOH), 2.05–2.21 (2 H, m, =CHCH_2), 3.75–3.82 (1 H, m, C*H*OH), 4.48 (2 H, d, *J* 6.3, OCH_2), 5.51–5.63 (1 H, m, OCH_2C*H*=), 5.77 (1 H, dt, *J* 15.2, 6.7, =C*H*CH_2); δ_C (100 MHz, $CDCl_3$) 23.4 (CH_3), 28.6 (CH_2), 38.2 (CH_2), 65.7 (CH_2), 67.5 (CH), 124.5 (CH), 135.6 (CH), 157.0 (C); HRMS (ESI^+) found 196.0947, $C_8H_{15}NNaO_3$ (MNa^+) requires 196.0944.

(*E*)-6-Hydroxy-6-methylhept-2-enyl carbamate (8)

The *title compound* was obtained as a pale brown oil (115 mg, 44%) as a mixture of geometrical isomers (*E*:*Z* ~ 5.5:1). R_f 0.34 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3355br, 1707s, 1617w, 1405m, 1338s, 1102w, 1047m, 973w, 908w, 786w; δ_H (400 MHz, $CDCl_3$) 1.23 (6 H, s, 2 × CH_3), 1.52–1.63 (3 H, m, CH_2C$(CH_3)_2$O*H*), 2.12–2.20 (2 H, m, =CHCH_2), 4.50 (2 H, d, *J* 6.3, OCH_2), 4.72 (2 H, br s, NH_2), 5.57–5.65 (1 H, m, OCH_2C*H*=), 5.81 (1 H, dt, *J* 15.4, 6.6, =C*H*CH_2); δ_C (100 MHz, $CDCl_3$) 27.2 (CH_2), 29.3 (CH_3), 42.7 (CH_2), 65.8 (CH_2), 70.8 (C), 124.2 (CH), 136.2 (CH), 156.8 (C); HRMS (ESI^+) found 210.1101, $C_9H_{17}NNaO_3$ (MNa^+) requires 210.1101.

7-Hydroxyhept-2-enyl carbamate (9)

The *title compound* was obtained as a colourless oil (92 mg, 46%) as a mixture of geometrical isomers (*E*:*Z* = 4:1). R_f 0.33 (petrol/ethyl acetate/methanol, 5:5:1); ν_{max} (thin film)/cm^{-1} 3411br, 2936w, 1684s, 1615w, 1422m, 1346m, 1099w, 1056s, 967w, 781w; δ_H (400 MHz, $CDCl_3$) 1.28 (1 H, t, *J* 5.2, OH, *E*), 1.42 (1 H, t, *J* 5.4, OH, *Z*), 1.45–1.52 and 1.55–1.63 (8 H, CH_2CH_2, *E* & *Z*), 2.10 (2 H, app q, *J* 7.1, =CHCH_2, *E*), 2.14–2.16 (2 H, m, =CHCH_2, *Z*), 3.62–3.69 (4 H, m, CH_2OH, *E* & *Z*), 4.51 (2 H, d, *J* 6.3, OCH_2, *E*), 4.60 (4 H, br s, NH_2, *E* & *Z*), 4.63 (2 H, d, *J* 6.8, OCH_2, *Z*), 5.54–5.68 (3 H, m, OCH_2C*H*=, *E* & CH=CH, *Z*), 5.78 (1 H, dt, *J* 15.3, 6.8, OCH_2CH=C*H*, *E*); δ_C

(125 MHz, $CDCl_3$) data for *E*-isomer: 25.0 (CH_2), 32.0 (CH_2), 32.2 (CH_2), 62.8 (CH_2), 65.9 (CH_2), 124.6 (CH), 135.9 (CH), 156.7 (C); HRMS (ESI^+) found 196.0935, $C_8H_{15}NNaO_3$ (MNa^+) requires 196.0944.

General procedure for Rh(II)-mediated aziridination and *O*-cyclisation

A solution of the carbamate (*x* mmol) in dichloromethane (6*x* mL) was placed in a sealable tube and purged with argon. MgO (3.3*x* mmol), diacetoxyiodobenzene (1.7*x* mmol) and the catalyst [$Rh_2(oct)_4$ or $Rh_2(OAc)_4$, 0.05*x* mmol] were added sequentially maintaining the flow of argon. The tube was sealed and the reaction mixture was heated to 50 °C and stirred vigorously for 18 h. The mixture was cooled to rt, the solvent was removed *in vacuo*, and the resulting residue was purified by column chromatography through a short plug of silica (petrol → petrol/ethyl acetate, 3:1 → 1:1).

(*R)-4-[(*S**)-Tetrahydrofuran-2-yl]oxazolidin-2-one (10)**

Procedure 1: Application of the general procedure from carbamate **6** afforded the *title compound* as a colourless oil (38 mg, 48%) with a dr = 9:1 (A:B).

Procedure 2: To a solution of (*E*)-6-hydroxyhex-2-enyl *N-para*-toluenesulfonyloxycarbamate (82 mg, 0.25 mmol) in degassed acetone (5.0 mL) was added $Rh_2(OAc)_4$ (5.5 mg, 0.013 mmol) and finely ground K_2CO_3 (242 mg, 1.75 mmol). The resulting suspension was stirred at 25 °C for 18 h. The mixture was cooled and dichloromethane (50 mL) was added; the insoluble residues were removed by filtration, the solution was concentrated *in vacuo*, and the residue was purified by column chromatography (petrol/ethyl acetate, 3:1) to give the *title compound* as a colourless oil (27 mg, 68%) with a dr of >10:1 (A:B).

Procedure 3: To a solution of (*E*)-6-hydroxyhex-2-enyl *N-para*-toluenesulfonyloxycarbamate (20 mg, 0.061 mmol) in degassed acetone (1.2 mL) under argon, was added finely ground K_2CO_3 (59 mg, 0.428 mmol) and $Cu(pyridine)_4{\cdot}(BF_4)_2$ (2.0 mg, 3.62 μmol). The resulting suspension was stirred at 25 ºC for 18 h then cooled to rt and filtered, concentrated *in vacuo*, and purified by column chromatography (ethyl acetate) to give the *title compound* as a colourless oil (4.0 mg, 42%), with a dr of >10:1 (A:B).

The product (from Procedure 1) was characterised as a 9:1 (A:B) mixture of diastereoisomers. R_f 0.14 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3283br, 2877w, 1750s, 1411w, 1239m, 1069m, 929w, 770w; δ_H (500 MHz, $CDCl_3$) 1.46–1.53 (1 H, m, CH_2CHH', B), 1.60–1.70 (1 H, m, CH_2CHH', A), 1.91–1.97 (4 H, m, CH_2CH_2, A & B), 2.02–2.09 (2 H, m, CH_2CHH', A & B), 3.62–3.67 (1H, m, $OCHH'CH_2$, B), 3.74–3.79 (1 H, m, $OCHH'CH_2$, A), 3.83–3.91 (6 H, m, OCH, CHNH and $OCHH'CH_2$, A & B,), 4.12 (1 H, dd, *J* 8.7, 5.5, $OCHH'CHN$, B), 4.25 (1 H, dd, *J* 8.8, 4.9,

OC*H*H′CHN, A), 4.43 (1 H, app t, *J* 8.7, OCH*H*′CHN, B), 4.49 (1 H, app t, *J* 8.8, OCH*H*′CHN, A), 6.19 (1 H, br s, NH, B), 6.37 (1 H, br s, NH, A); δ_C (125 MHz, $CDCl_3$) 25.7 (CH_2, A), 25.8 (CH_2, B), 27.5 (CH_2, B), 27.5 (CH_2, A), 55.4 (CH, A), 56.2 (CH, B), 66.6 (CH_2, B), 67.8 (CH_2, A), 68.6 (CH_2, B), 68.7 (CH_2, A), 80.1 (CH, A), 80.4 (CH, B), 159.7 (C, B), 160.2 (C, A); HRMS (ESI^+) found 180.0629, $C_7H_{11}NNaO_3$ (MNa^+) requires 180.0631.

(*R)-4-[(2*S**,5*S**)- and (2*S**,5*R**)- and (2*R**,5*R**)- and (2*R**,5*S**)-5-Methyltetrahydrofuran-2-yl]oxazolidin-2-one (11)**

Application of the general procedure from carbamate **7** afforded the *title compound* as a mixture of four diastereoisomers (A:B:C:D, 1:0.8:0.2:0.15), as a pale yellow oil (30.5 mg, 54%); R_f 0.23 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3286br, 1748s, 1410w, 1237m, 1080w; δ_H (500 MHz, $CDCl_3$) 1.20–1.25 (12 H, m, CH_3, all), 1.45–1.60, 1.65–1.76, 1.95–2.14 (16 H, m, CH_2CH_2, all), 3.75–4.25 (20 H, m, $OCH_2CHCHOCH$, all), 4.70–4.84 (2 H, br m, NH, C & D), 5.62–5.71 (2 H, br m, NH, A & B); δ_C (125 MHz, $CDCl_3$) 20.9 (CH_3, D), 20.9 (CH_3, B), 21.1 (CH_3, C), 21.1 (CH_3, A), 26.7 (CH_2, B), 27.5 (CH_2, C), 28.0 (CH_2, A), 28.3 (CH_2, D), 32.6 (CH_2, B), 32.7 (CH_2, C), 33.6 (CH_2, D), 33.6 (CH_2, A), 54.4 (CH, A), 55.2 (CH, B), 56.4 (CH, D), 56.7 (CH, C), 66.5 (CH_2, D), 66.6 (CH_2, C), 67.6 (CH_2, B), 67.8 (CH_2, A), 75.9 (CH, D), 76.2 (CH, C), 76.2 (CH, B), 76.3 (CH, A), 79.5 (CH, A), 80.0 (CH, B), 80.1 (CH, C), 80.6 (CH, D), 159.3 (C, C), 159.3 (C, D), 159.7 (C, B), 159.8 (C, A); HRMS (ESI^+) found 194.0791, $C_8H_{13}NNaO_3$ (MNa^+) requires 194.0788.

(*R)-4-[(*S**)-5,5-Dimethyltetrahydrofuran-2-yl]oxazolidin-2-one (12)**

Application of the general procedure from carbamate **8** afforded the *title compound* with a *dr* of 3:1 (A:B), as a colourless oil (29 mg, 51%); a sample of pure diastereoisomer A was separated and used for characterisation. R_f 0.20 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3286br, 1748s, 1408m, 1336w, 1240s, 1134w, 1060s, 952w, 925w, 768w; δ_H (500 MHz, $CDCl_3$) 1.24 (3 H, s, CH_3), 1.26 (3 H, s, CH_3), 1.75–1.83 and 2.02–2.10 (4 H, m, CH_2CH_2), 3.90–4.00 (2 H, m, NHC*H*C*H*O), 4.21 (1 H, dd, *J* 8.8, 5.2) and 4.50 (1 H, t, 8.8, OCH_2), 5.48 (1 H, br s, NH); δ_C (125 MHz, $CDCl_3$) 27.1 (CH_2), 27.6 (CH_3), 28.7 (CH_3), 38.1 (CH_2), 55.2 (CH), 67.6 (CH_2), 79.3 (CH), 81.9 (C), 159.8 (C); HRMS (ESI^+) found 208.0942, $C_9H_{15}NNaO_3$ (MNa^+) requires 208.0944.

(*R)-4-[(*S**)-Tetrahydro-2*H*-pyran-2-yl]oxazolidin-2-one (13)**

Application of the general procedure from carbamate **9** afforded the *title compound* as a colourless oil (12 mg, 20%) with a *dr* of >10:1. R_f 0.16 (ethyl acetate); ν_{max} (thin film)/cm^{-1} 3298br, 2853w, 1751s, 1410w, 1238m, 1092s, 1049s, 940w, 770w; δ_H (500 MHz, $CDCl_3$) 1.23–1.95 (6 H, m,

C_3H_6), 3.26 (1 H, ddd, *J* 11.2, 6.5, 2.1, OCH), 3.42 (1 H, td, *J* 11.2, 3.9, OC*H*H′CH_2), 3.71–3.79 (1 H, m, C*H*NH), 3.95–4.02 (1 H, m, OCH*H*′CH_2), 4.32 (1 H, dd, *J* 8.7, 5.0) and 4.43 (1 H, t, *J* 8.7, OC*H*$_2$CHN), 5.78 (1 H, br s, NH); δ_C (125 MHz, $CDCl_3$) 22.6 (CH_2), 25.7 (CH_2), 27.1 (CH_2), 56.0 (CH), 67.5 (CH_2), 68.6 (CH_2), 78.6 (CH), 159.9 (C); HRMS (ESI^+) found 194.0788, $C_8H_{13}NNaO_3$ (MNa^+) requires 194.0788.

(*S*,*E*)-1-(*tert*-Butyldimethylsilyloxy)-4-{(4*R*,5*S*)-5-[(*S*)-1-hydroxybenzyl]-2,2-dimethyl-1,3-dioxolan-4-yl}but-3-en-2-yl carbamate (16)

To a solution of (*S*,*E*)-4-[(4*R*,5*R*)-5-benzoyl-2,2-dimethyl-1,3-dioxolan-4-yl]-1-(*tert*-butyldimethylsilyloxy)but-3-en-2-yl carbamate (14.0 mg, 0.031 mmol) in dichloromethane (1.25 mL) at –78 °C was slowly added $ZnCl_2$ (0.042 mL, 1.0 M solution in ether, 0.042 mmol). After stirring for 30 min, L-Selectride (0.107 mL, 1.0 M solution in THF, 0.107 mmol) was added slowly and stirring was continued at the same temperature for 90 min. The reaction was quenched by the careful addition, sequentially, of methanol (0.2 mL), water (0.1 mL), 30% aq H_2O_2 solution (0.1 mL), and 6.0 M aq NaOH solution (0.1 mL). Stirring was continued while the mixture was warmed to rt, then water (5 mL) was added and the solution extracted with dichloromethane (3 × 15 mL). The extracts were washed with saturated aq $NaHCO_3$ solution (10 mL) then saturated aq Na_2CO_3 solution (10 mL) then brine (10 mL) and dried over $MgSO_4$. The solution was concentrated *in vacuo* to afford the *title compound* as a colourless oil (14.0 mg, quant) which could be used in crude form for the next reaction. R_f 0.66 (petrol/ethyl acetate, 1:3); $[\alpha]_D^{23}$ –116 (*c* 0.3, $CDCl_3$); ν_{max} (thin film)/cm^{-1} 3353br, 1716s, 1601w, 1382s, 1256m, 1063s, 838s, 779m, 700w; δ_H (500 MHz, $CDCl_3$) 0.08 (6 H, s, $Si(CH_3)_2$), 0.90 (9 H, s, $C(CH_3)_3$), 1.29 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 3.75 (1 H, dd, *J* 11.4, 6.3) and 3.79 (1 H, dd, *J* 11.4, 4.4, CH_2OSi), 4.25 (1 H, dd, *J* 9.1, 6.7 C*H*CHPh), 4.60 (1 H, d, *J* 9.1, C*H*Ph), 4.72 (2 H, br s, NH_2), 4.80 (1 H, app t, *J* 6.7, C*H*CHCHPh), 5.12–5.17 (1 H, m, C*H*OCONH$_2$), 5.89 (1 H, dd, *J* 15.7, 6.7, =C*H*CHOCONH$_2$), 6.07 (1 H, dd, *J* 15.7, 6.3, =C*H*CH(OR)CH(OR)), 7.25–7.41 (5 H, m, Ph); δ_C (125 MHz, $CDCl_3$) –5.3 (CH_3), 18.4 (C), 25.1 (CH_3), 25.9 (CH_3), 27.8 (CH_3), 64.7 (CH_2), 71.4 (CH), 76.4 (CH), 77.5 (CH), 81.3 (CH), 108.9 (C), 127.1 (CH), 127.6 (CH), 128.1 (CH), 128.5 (CH), 129.7 (CH), 141.7 (C), 156.7 (C); HRMS (ESI^+) found 474.2275, $C_{23}H_{37}NNaO_6Si$ (MNa^+) requires 474.2282.

(4*R*,5*S*)-5-[(*tert*-Butyldimethylsilyloxy)methyl]-4-[(3a*R*,4*R*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl]oxazolidin-2-one (17) and (4*S*,5*S*)-5-[(*tert*-Butyldimethylsilyloxy)methyl]-4-[(3a*R*,4*S*,6*S*,6a*S*)-2,2-dimethyl-6-phenyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl]oxazolidin-2-one (18)

Application of the general procedure to three batches of crude carbamate **16** (1 x 195 mg, 0.432 mmol; 2 x 420 mg, 2 x 0.930) and purification of the combined crude products from these three reactions by column chromatography (petrol/ethyl acetate, 10:1 → 6:1 → 3:1) afforded the *title compound* as a pale yellow oil (620 mg, 60%) as a mixture of diastereoisomers (A:B, 1.3:1). R*f* 0.26 (petrol/ethyl acetate, 2:1); δ_H (500 MHz, $CDCl_3$) 0.08–0.12 (12 H, m, $Si(CH_3)_2$, A & B), 0.91 (9 H, s, $C(CH_3)_3$, B), 0.92 (9 H, s, $C(CH_3)_3$, A), 1.34 (3 H, s, CH_3, A), 1.37 (3 H, s, CH_3, B), 1.57 (3 H, s, CH_3, B), 1.60 (3 H, s, CH_3, A), 3.80 (1 H, dd, *J* 11.4, 3.5) and 3.95 (1 H, dd, *J* 11.4, 3.0, CH_2, B), 4.00–4.15 (3 H, m), 4.33–4.37 (1 H, m), 4.54–4.60 (2 H, m), 4.65–4.69 (1 H, m) and 4.73–4.82 (3 H, m, CH_2, A and C*H*(OCO)C*H*(NH)C*H*(OR)C*H*(OR), A & B) 4.95 (1 H, dd, *J* 6.3, 1,4, C*H*Ph, A), 5.20 (1 H, s, C*H*Ph, B), 5.42 (1 H, br s, NH, B), 5.71 (1 H, br s, NH, A), 7.27–7.42 (10 H, m, Ph, A & B); δ_C (125 MHz, $CDCl_3$) –5.5 (two peaks) and –5.4 (two peaks, 4 x CH_3, A & B), 18.2 (two peaks, C, A & B), 24.7 (CH_3, B), 25.3 (CH_3, A), 25.7 (CH_3, B), 25.8 (CH_3, B), 25.9 (CH_3, A), 26.0 (CH_3, A), 53.0 (CH, B), 55.8 (CH, A), 61.0 (CH_2, A), 63.6 (CH_2, B), 78.4, 80.7 (two peaks), 81.6, 82.3, 82.4, 84.8, 85.3, 87.0 and 87.3 (5 x CH, A & B), 113.6 (C, B), 115.9 (C, A), 125.4, 125.7, 127.9, 128.2, 128.6 and 128.8 (3 × CH, A & B), 137.9 (C, B), 138.6 (C, A), 158.7 (C, B), 158.8 (C, A); HRMS (ESI^+) found 472.2125, $C_{23}H_{35}NNaO_6Si$ (MNa^+) requires 472.2126.

(*S*)-4-{(3a*S*,4*R*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl}oxazolidin-2-one (21) and (*R*)-4-{(3a*S*,4*S*,6a*R*)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl}oxazolidin-2-one (22)

Application of the general procedure [with $Rh_2(OAc)_4$ as catalyst] to allylic carbamate **20** (300 mg, 1.30 mmol) afforded the *title compound* **21** as a white powder (181 mg, 61%; 52% corrected for EtOAc present (NMR)). R_f 0.26 (ethyl acetate); mp 120–122 °C; $[\alpha]_D^{25}$ –5.2 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3313br, 2987w, 1755s, 1382w, 1210m, 1167w, 1105m, 1020m, 986w, 916m, 858m; δ_H (400 MHz, $CDCl_3$) 1.24 (3 H, s, CH_3-*exo*), 1.41 (3 H, s, CH_3-*endo*), 3.46 (1 H, dd, *J* 7.0, 4.0, C*H*OCH_2), 3.51 (1 H, dd, *J* 11.0, 3.5, CHOC*H*H′-*exo*), 4.01 (1 H, d, *J* 11.0, CHOCH*H*′-*endo*), 4.05 (1 H, app q, *J* 7.0, C*H*NH), 4.11 (1 H, app t, *J* 7.0) and 4.43–4.52 (1 H, m, CH_2CHN) 4.64 (1 H, dd, *J* 6.0, 4.0 CH_2OCHC*H*O), 4.76 (1 H, dd, *J* 6.0, 3.5, OCH_2C*H*O), 6.03 (1 H, br, NH); δ_C (100 MHz, $CDCl_3$) 24.3 (CH_3), 25.8 (CH_3), 52.3 (CH), 66.7 (CH_2), 72.7 (CH_2), 79.9 (CH), 81.1 (CH), 83.4 (CH), 112.7 (C), 159.4 (C); HRMS (ESI^+) found 230.1024, $C_{10}H_{16}NO_5$ (MH^+) requires 230.1028. Structure confirmed by single crystal X-ray crystallography. The second diastereomer (**22**) was obtained in impure form as a yellow oil (109 mg of which ~50% comprised **22**, ~18%). R_f 0.23 (ethyl acetate); $[\alpha]_D^{25}$ –37.8 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3302br, 2986w, 1751s, 1376w, 1211m, 1161w, 1089m, 1057m, 858w; δ_H (400 MHz, $CDCl_3$) 1.35 (3 H, s, CH_3-*exo*), 1.52 (3 H, s, CH_3-*endo*), 3.88 (1 H, m, C*H*NH), 3.90 (1 H, dd, *J* 7.0, 3.0, C*H*OCH_2), 4.00 (2 H, app d, *J*

3.5, CHOCH_2), 4.27 (1 H, dd, *J* 8.5, 5.5, C*H*H′CHN), 4.43 (1 H, dd, *J* 6.5, 3.0 CH_2OCHC*H*O), 4.48 (1 H, app t, *J* 8.5, C H*H*′CHN), 4.85 (1 H, dt, *J* 6.5, 3.5, OCH_2C*H*O), 6.36 (1 H, br s, NH); δ_C (100 MHz, $CDCl_3$) 25.1 (CH_3), 26.8 (CH_3), 52.3 (CH), 66.2 (CH_2), 73.2 (CH_2), 81.0 (CH), 81.9 (CH), 85.9 (CH), 114.0 (C), 159.6 (C); HRMS (ESI^+) found 252.0842, $C_{10}H_{15}NNaO_5$ (MNa^+) requires 252.0848.

(*R*)-4-{(3a*S*,4*R*,6a*R*)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl}oxazolidin-2-one (25) and (*S*)-4-{(3a*S*,4*S*,6a*R*)-2,2-Dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl}oxazolidin-2-one (26)

Application of the general procedure [with $Rh_2(OAc)_4$ as catalyst] to allyl carbamate **24** (306 mg, 1.32 mmol) afforded the *title compounds*, **26** as a yellow solid (81 mg, 27%; 22% corrected for EtOAc present (NMR)) and **25** as a white powder (138 mg, 46%). Data for **26**: R_f 0.25 (ethyl acetate); mp 78–79 °C; $[\alpha]_D^{25}$ –68.2 (*c* 1.0, $CHCl_3$); ν_{max} (thin film, cm^{-1}) 3305br, 2987w, 1751s, 1375w, 1216m, 1089m, 914w, 858w; δ_H (400 MHz, $CDCl_3$) 1.36 (3 H, s, CH_3-*exo*), 1.53 (3 H, s, CH_3-*endo*), 3.88 (1 H, dd, *J* 6.5, 3.5, C*H*OCH_2), 3.94 (1 H, dd, *J* 10.5, 3.0, CHOC*H*H′-*endo*), 3.98 (1 H, m, C*H*NH), 4.02 (1 H, dd, *J* 10.5, 5.0, CHOCH*H*′-*exo*), 4.32 (1 H, dd, *J* 9.0, 5.5) and 4.50 (1 H, app t, *J* 9.0, CH_2CHN), 4.60 (1 H, dd, *J* 6.5, 3.5, CH_2OCHC*H*O), 4.84 (1 H, ddd, *J* 6.5, 5.0, 3.0, OCH_2C*H*O), 5.92 (1 H, br s, NH); δ_C (100 MHz, $CDCl_3$) 25.1 (CH_3), 27.0 (CH_3), 51.2 (CH), 67.0 (CH_2), 73.1 (CH_2), 80.8 (CH), 80.9 (CH), 85.4 (CH), 114.4 (C), 159.6 (C); HRMS (ESI^+) found 252.0843, $C_{10}H_{15}NNaO_5$ (MNa^+) requires 252.0848. Structure confirmed by single crystal X-ray crystallography. Data for **25**: R_f 0.22 (ethyl acetate); mp 181–183 °C; $[\alpha]_D^{25}$ –17.4 (*c* 1.0, $CHCl_3$); ν_{max} (thin film)/cm^{-1} 3275br, 2986w, 1736m, 1706s, 1373w, 1241m, 1206m, 1022m, 852w; δ_H (400 MHz, $CDCl_3$) 1.32 (3 H, s, CH_3-*exo*), 1.46 (3 H, s, CH_3-*endo*), 3.56 (1 H, dd, *J* 11.0, 3.5, CHOC*H*H′-*exo*) overlapping 3.57 (1 H, dd, *J* 7.5, 4.0, C*H*OCH_2), 4.07 (1 H, d, *J* 11.0, CHOCH*H*′-*endo*), 4.12 (1 H, m, C*H*NH), 4.44 (1 H, dd, *J* 9.0, 5.0) and 4.53 (1 H, app t, *J* 9.0, CH_2CHN), 4.70 (1 H, dd, *J* 6.0, 4.0, CH_2OCHC*H*O), 4.81 (1 H, dd, *J* 6.0, 3.5, OCH_2C*H*O), 5.75 (1 H, br, NH); δ_C (100 MHz, $CDCl_3$) 24.3 (CH_3), 25.7 (CH_3), 51.7 (CH), 69.8 (CH_2), 72.9 (CH_2), 80.1 (CH), 81.0 (CH), 83.2 (CH), 112.8 (C), 159.3 (C); HRMS (ESI^+) found 252.0843, $C_{10}H_{15}NNaO_5$ (MNa^+) requires 252.0848. Structure confirmed by single crystal X-ray crystallography.

***trans*-Octahydro-1*H*-pyrano[3,2-d][1,2,3]oxathiazepine-2,2-dioxide (28)**

To a stirred solution of sulfamate *E*-**27** (19.8 mg, 0.095 mmol) in dichloromethane (0.8 mL) were added MgO (9.0 mg, 0.223 mmol) and $Rh_2(OAc)_4$ (2.0 mg, 0.0045 mmol). The mixture was cooled to 0 °C, diacetoxyiodobenzene (40 mg, 0.124 mmol) was added and the resulting suspension was

allowed to warm to rt over 2 h. After stirring for a further 2.5 h the reaction mixture was filtered through Celite and concentrated *in vacuo*. Purification by column chromatography (ether/petrol, 3:2 → 4:1) afforded the *title compound* as a pale brown oil (9.5 mg, 48%). R_f 0.22 (petrol/ethyl acetate, 1:1); ν_{max} (thin film)/cm^{-1} 2960w, 1573w, 1445m, 1349m, 1263w, 1179s, 1096m, 1034m; δ_H (500 MHz, C_6D_6) 0.60 (1 H, qd, *J* 13.0, 4.5, C*H*H′CHN), 1.00–1.05 (1 H, m) and 1.18 (1 H, qt, *J* 13.0, 4.5, C*H*$_2$CH$_2$OCH), 1.56 (1 H, dtd, *J* 15.0, 4.5, 1.0, C*H*H′CH$_2$OS), 1.60–1.67 (1 H, m, CH*H*′CHN), 1.76–1.86 (1 H, m, CH*H*′CH$_2$OS), 2.35 (1 H, td, *J* 10.0, 4.5, C*H*OCH$_2$), 2.80 (1 H, ddd, *J* 12.5, 11.5, 2.5, C*H*H′OCH), 2.95 (1 H, dtd, *J* 12.0, 10.0, 4.5, C*H*NH), 3.57 (1 H, ddt, *J* 11.5, 4.5, 1.5, CH*H*′OCH), 3.59 (1 H, dt, *J* 13.0, 3.5) and 3.78 (1 H, td, *J* 13.0, 1.0, CH$_2$OS), 3.84 (1 H, br d, *J* 10.0, NH); δ_C (125 MHz, C_6D_6) 25.5 (CH$_2$), 30.5 (CH$_2$), 35.5 (CH$_2$), 52.8 (CH), 66.4 (CH$_2$), 66.9 (CH$_2$), 79.7 (CH); HRMS (ESI$^+$) found 230.0462, $C_7H_{13}NNaO_4S$ (MNa$^+$) requires 230.0457.

cis-Octahydro-1*H*-pyrano[3,2-d][1,2,3]oxathiazepine-2,2-dioxide (29) and (*R)-4-[(*R**)-tetrahydrofuran-2-yl]-1,2,3-oxathiazinane-2,2-dioxide (30)**

To a stirred solution of sulfamate *Z*-**27** (54 mg, 0.258 mmol) in dichloromethane (2.0 mL) were added MgO (24 mg, 0.596 mmol) and $Rh_2(OAc)_4$ (5,5 mg, 0.012 mmol). The mixture was cooled to 0 °C, diacetoxyiodobenzene (108 mg, 0.335 mmol) was added and the resulting suspension was allowed to warm to rt over 2 h. After stirring for a further 2 h the reaction mixture was filtered through Celite and concentrated *in vacuo*. Purification by column chromatography (ether/petrol, 3:2 → 4:1, then ethyl acetate) afforded the *title compounds* as a mixture (**29**/**30**, 1.25:1), and as a pale brown oil (24 mg, 44%). R_f 0.27 (petrol/ethyl acetate, 2:3); ν_{max} (thin film)/cm^{-1} 3271w, 2955w, 1418w, 1349m, 1180s, 1091m, 1056m, 1008m; δ_H (500 MHz, acetone-d_6) 1.41–1.47 (1 H, m, C*H*H′CH$_2$OCH, **29**), 1.76 (1 H, dtd, *J* 14.5, 2.5, 1.5, C*H*H′CH$_2$OS, **30**), 1.82–2.11 (9 H, m, C*H*H′CH$_2$OS, **29** and CH*H*′CH$_2$OS, **30** and C*H*$_2$CH$_2$CH$_2$OCH, **29** & **30**, C*H*$_2$CH$_2$OCH, **30** and CH*H*′CH$_2$OCH, **29**), 2.19 (1 H, dddd, *J* 16.0, 12.0, 4.0, 3.0, CH*H*′CH$_2$OS, **29**), 3.56 (1 H, td, *J* 11.5, 3.0, C*H*H′OCH, **29**), 3.61 (1 H, dt, *J* 11.0, 3.5, CHN, **29**), 3.67–3.73 (2 H, m, CHO and CH*H*′OCH, **29**), 3.74 (1 H, dt, *J* 10.0, 3.0, CHN, **30**), 3.86–3.91 (1 H, m, C*H*H′OCH, **30**), 3.93–4.00 (2 H, m, CHO and CH*H*′OCH, **30**), 4.12 (1 H, dt, *J* 12.5, 3.5) and 4.50 (1 H, t, *J* 12.5, CH$_2$OS, **29**), 4.59 (1 H, ddd, *J* 11.5, 5.5, 1.5) and 4.65 (1 H, ddd, *J* 13.0, 11.5, 2.5, CH$_2$OS, **30**), 5.56 (1 H, br d, *J* 10.0, NH, **30**), 6.85 (1 H, br d, *J* 10.0, NH, **29**); δ_C (125 MHz, acetone-d_6) 20.7 (CH$_2$, **29**), 27.9 (CH$_2$, **30**), 26.5, 28.2 and 29.5 (CH$_2$, **29** and 2 x CH$_2$, **30**), 35.6 (CH$_2$, **29**), 51.0 (CH, **29**), 59.4 (CH, **30**), 65.8 (CH$_2$, **29**), 69.1 (CH$_2$, **29**), 69.2 (CH$_2$, **30**), 72.6 (CH$_2$, **30**), 76.3 (CH, **29**), 80.3 (CH, **30**); HRMS (ESI$^+$) found 230.0454, $C_7H_{13}NNaO_4S$ (MNa$^+$) requires 230.0457.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 21

```
Bond precision:  C-C = 0.0021 A          Wavelength=0.71073

Cell:             a=5.5980(1)     b=13.2848(3)     c=14.6114(4)
                  alpha=90        beta=90          gamma=90
Temperature:      150 K
```

	Calculated	Reported
Volume	1086.63(4)	1086.63(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C10 H15 N O5	C10 H15 N1 O5
Sum formula	C10 H15 N O5	C10 H15 N1 O5
Mr	229.23	229.23
Dx,g cm-3	1.401	1.401
Z	4	4
Mu (mm-1)	0.113	0.113
F000	488.0	488.0
F000'	488.30	
h,k,lmax	7,17,18	7,17,18
Nref	2487[1465]	1449
Tmin,Tmax	0.958,0.971	0.610,0.970
Tmin'	0.958	

```
Correction method= MULTI-SCAN

Data completeness= 0.99/0.58      Theta(max)= 27.450

R(reflections)= 0.0273( 1350)     wR2(reflections)= 0.0704( 1448)

S = 0.943                 Npar= Npar = 145
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Why ?
PLAT791_ALERT_4_G The Model has Chirality at C3      .............          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C9      .............          S Verify
PLAT791_ALERT_4_G The Model has Chirality at C10     .............          R Verify
PLAT791_ALERT_4_G The Model has Chirality at C11     .............          S Verify
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found     Please Check
```

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: 25

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=5.8112(2) b=7.6935(2) c=23.7155(7)
alpha=90 beta=90 gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1060.28(6)	1060.28(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C10 H15 N O5	C10 H15 N1 O5
Sum formula	C10 H15 N O5	C10 H15 N1 O5
Mr	229.23	229.23
Dx,g cm-3	1.436	1.436
Z	4	4
Mu (mm-1)	0.116	0.116
F000	488.0	488.0
F000'	488.30	
h,k,lmax	7,9,30	7,9,30
Nref	2433[1445]	1419
Tmin,Tmax	0.983,0.988	0.790,0.990
Tmin'	0.933	

Correction method= MULTI-SCAN

Data completeness= 0.98/0.58 Theta(max)= 27.453

R(reflections)= 0.0395(1190) wR2(reflections)= 0.0989(1418)

S = 0.991 Npar= Npar = 145

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Why ?
PLAT791_ALERT_4_G The Model has Chirality at C3 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C9 ..... S Verify
PLAT791_ALERT_4_G The Model has Chirality at C10 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C11 ..... R Verify
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found Please Check

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: 26

Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=5.7625(2) b=8.6145(3) c=21.3435(8)
alpha=90 beta=90 gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1059.51(7)	1059.51(7)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C10 H15 N O5	C10 H15 N1 O5
Sum formula	C10 H15 N O5	C10 H15 N1 O5
Mr	229.23	229.23
Dx,g cm-3	1.437	1.437
Z	4	4
Mu (mm-1)	0.116	0.116
F000	488.0	488.0
F000'	488.30	
h,k,lmax	7,11,27	7,11,27
Nref	2441[1445]	1428
Tmin,Tmax	0.983,0.988	0.930,0.990
Tmin'	0.955	

Correction method= MULTI-SCAN

Data completeness= 0.99/0.59 Theta(max)= 27.474

R(reflections)= 0.0650(1262) wR2(reflections)= 0.1851(1428)

S = 0.960 Npar= Npar = 145

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0041 Ang.

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Why ?
PLAT791_ALERT_4_G The Model has Chirality at C3 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C9 ..... S Verify
PLAT791_ALERT_4_G The Model has Chirality at C10 ..... S Verify
PLAT791_ALERT_4_G The Model has Chirality at C11 ..... S Verify
PLAT808_ALERT_5_G No Parseable SHELXL Style Weighting Scheme Found Please Check

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

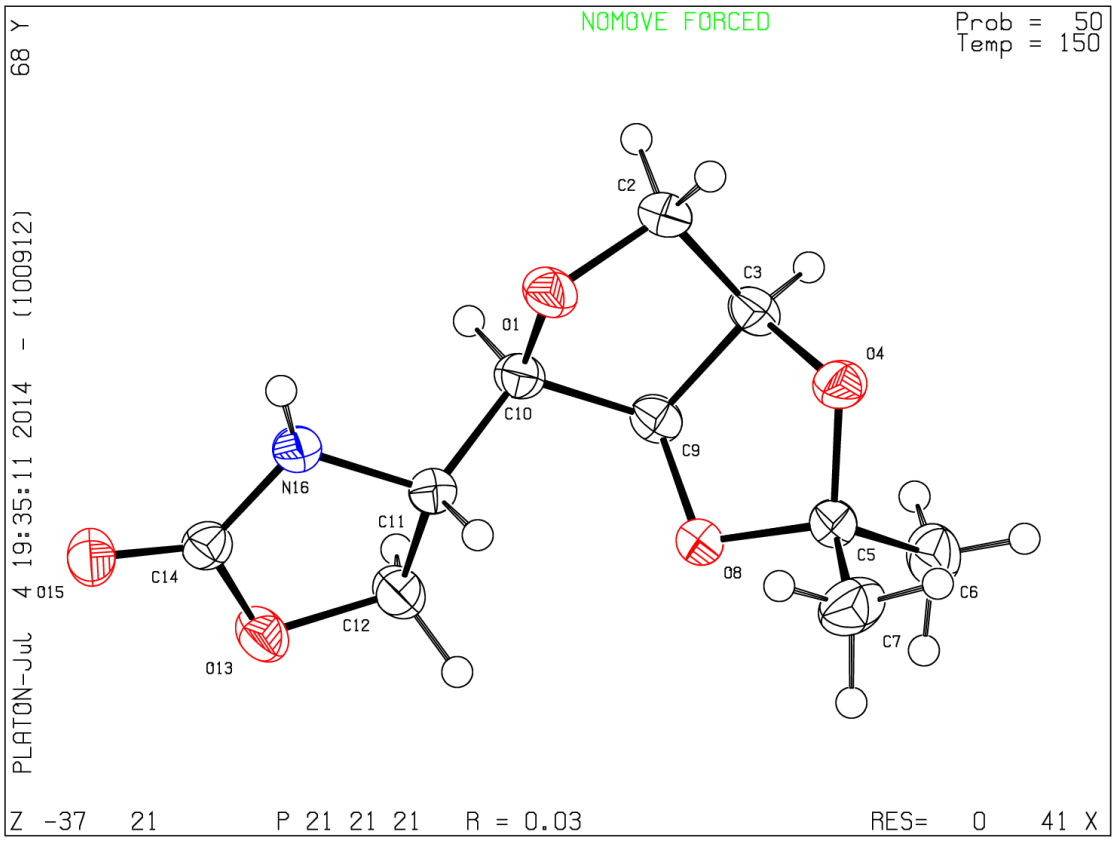
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

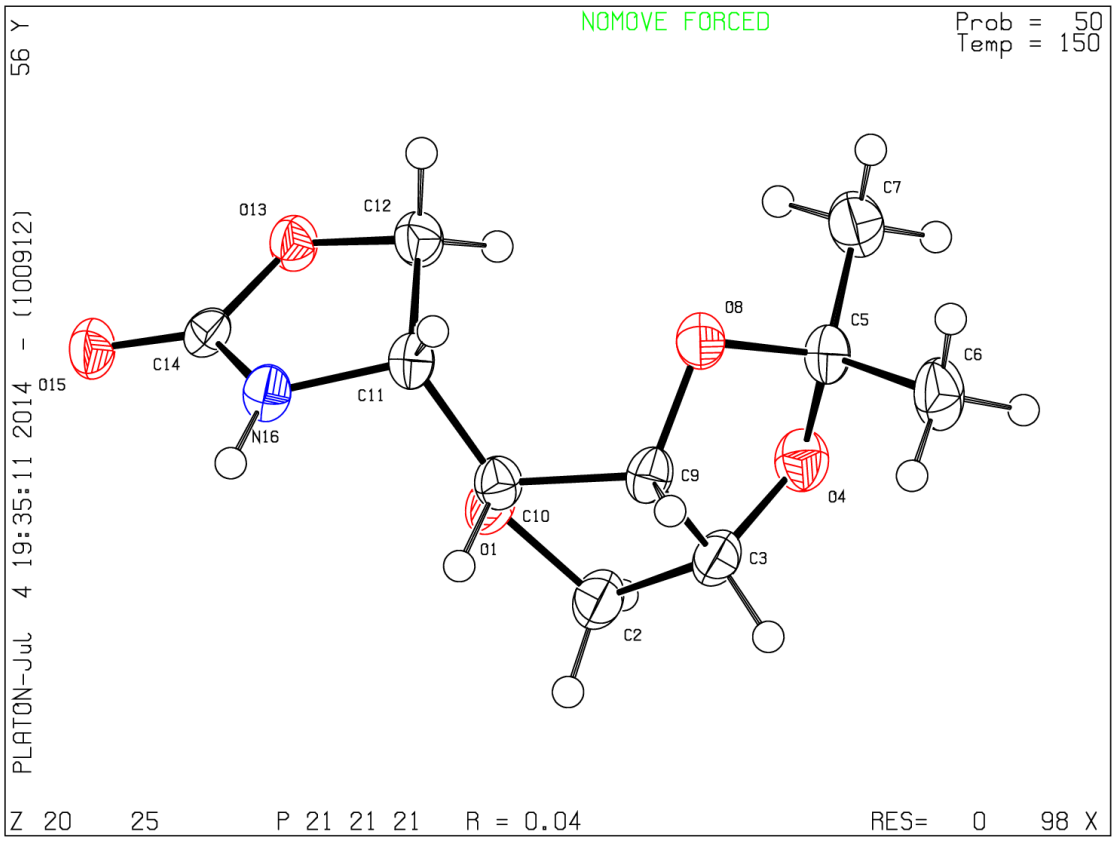
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/02/2014; check.def file version of 05/02/2014

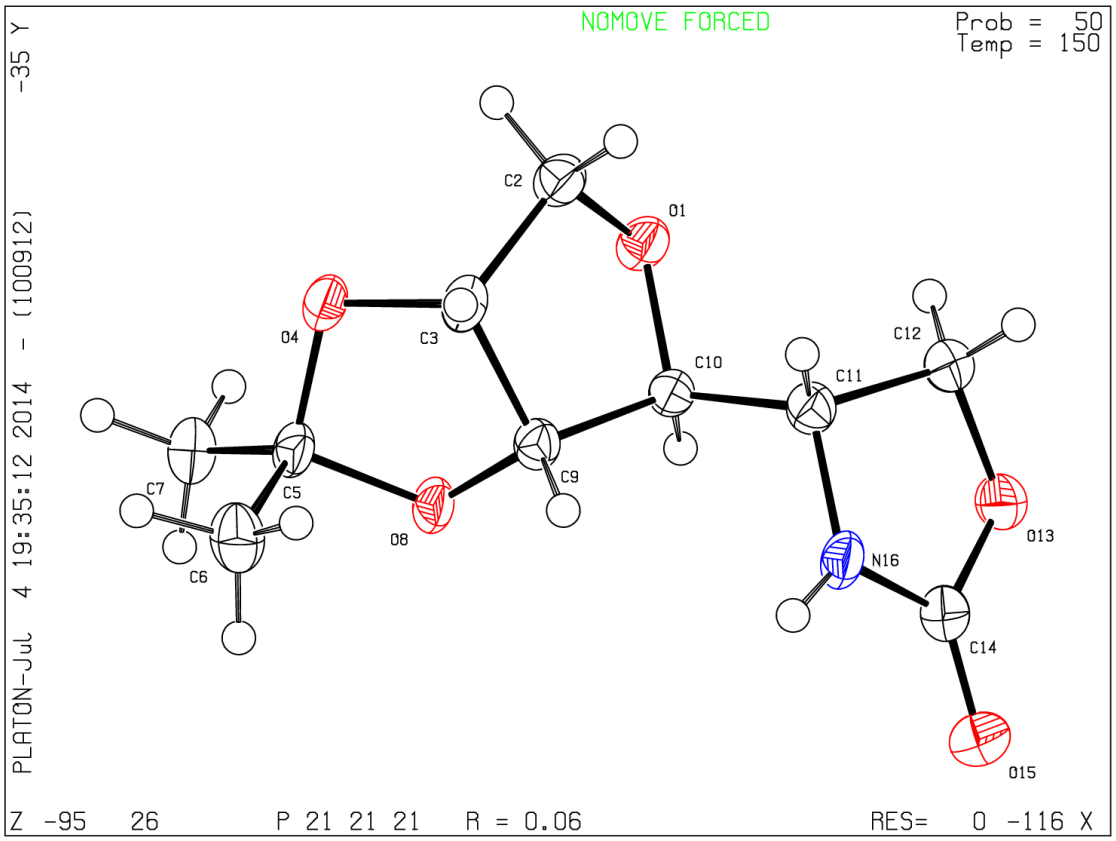
Datablock 21 - ellipsoid plot



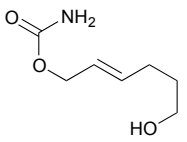
Datablock 25 - ellipsoid plot



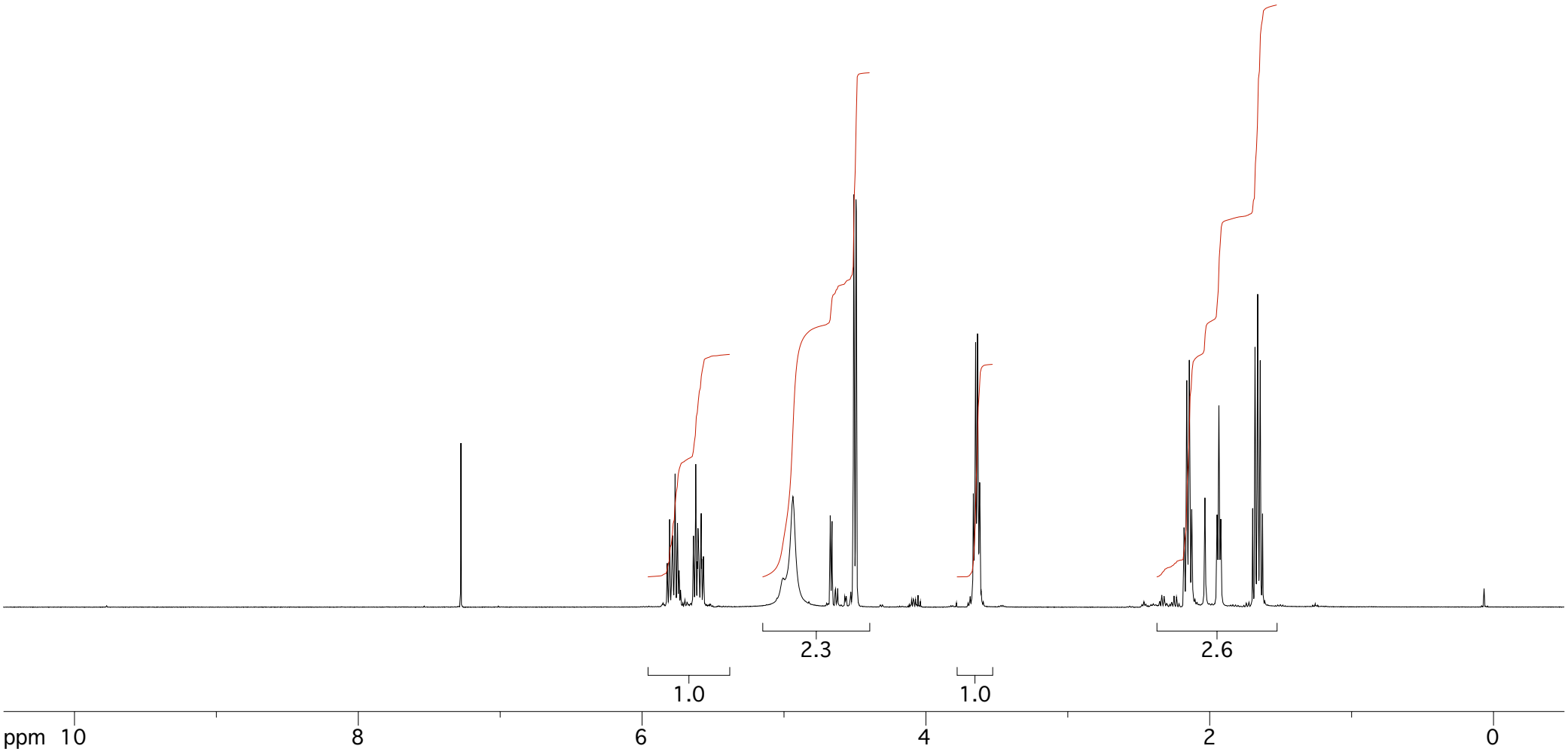
Datablock 26 - ellipsoid plot



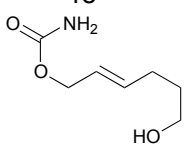
17



6 (*E*/*Z* ~7:1)



18



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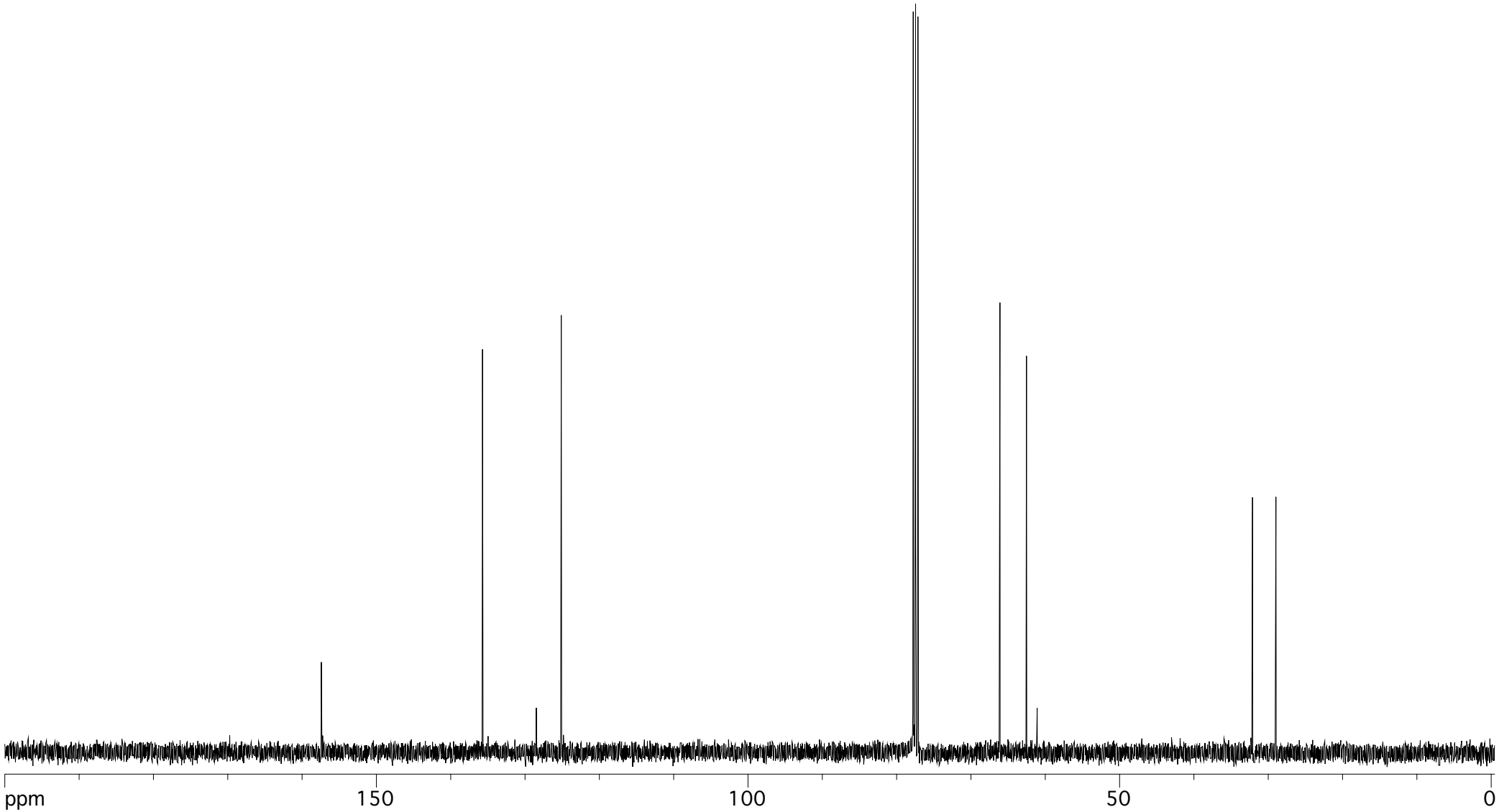
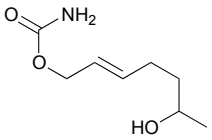
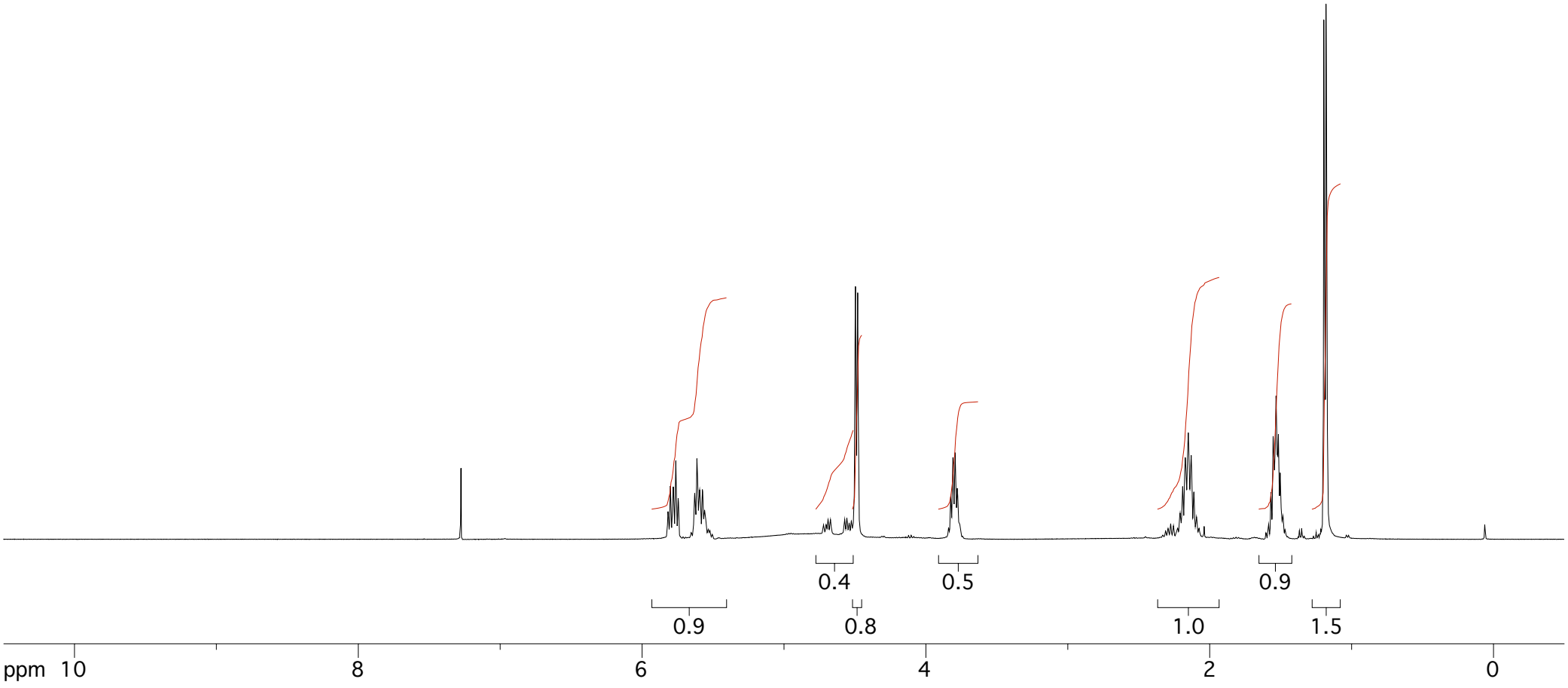


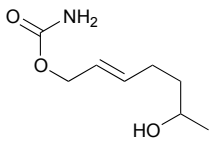
19



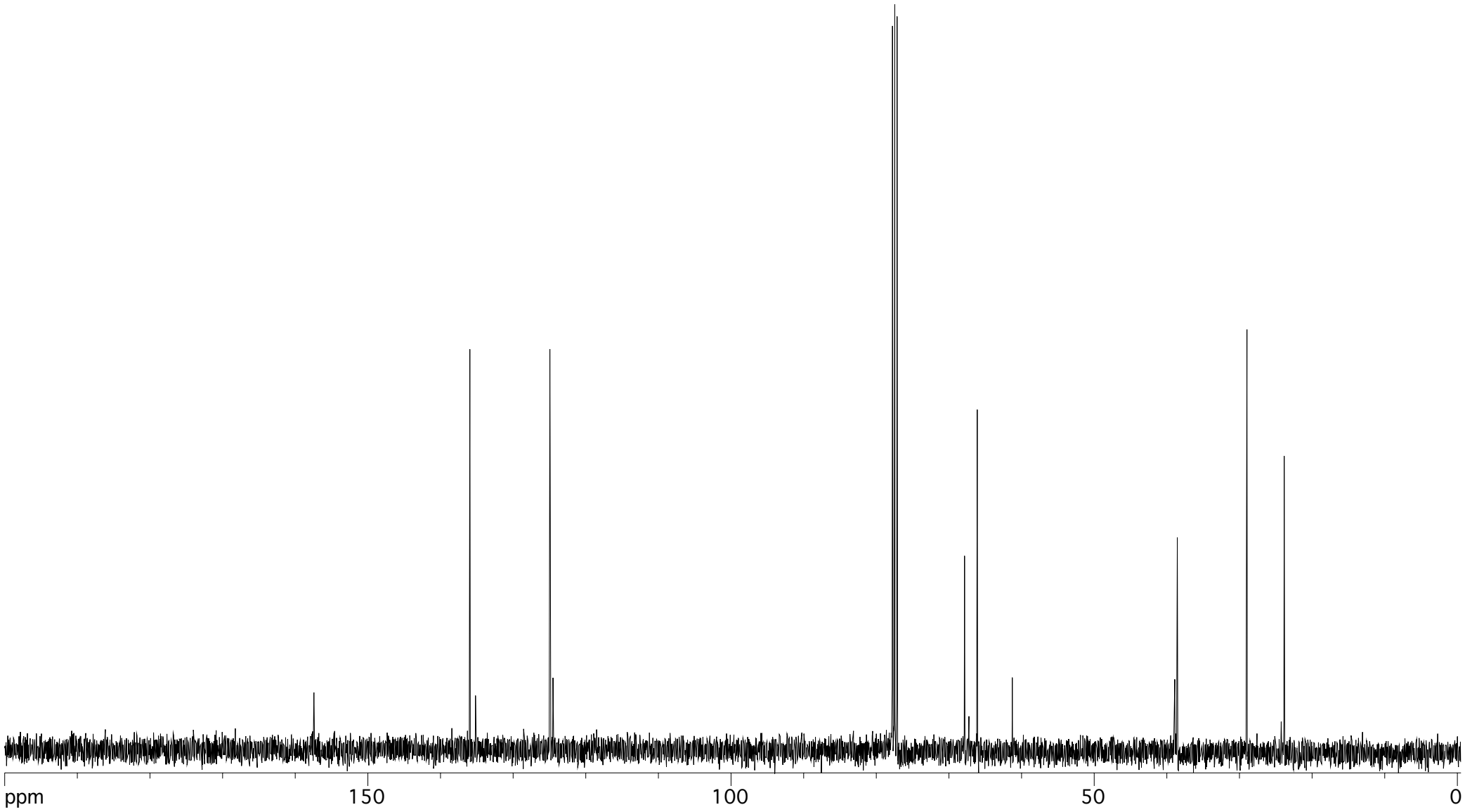
7 (*E*/*Z* ~4:1)



20



7 (*E*/*Z* ~4:1)



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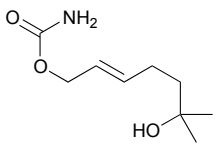
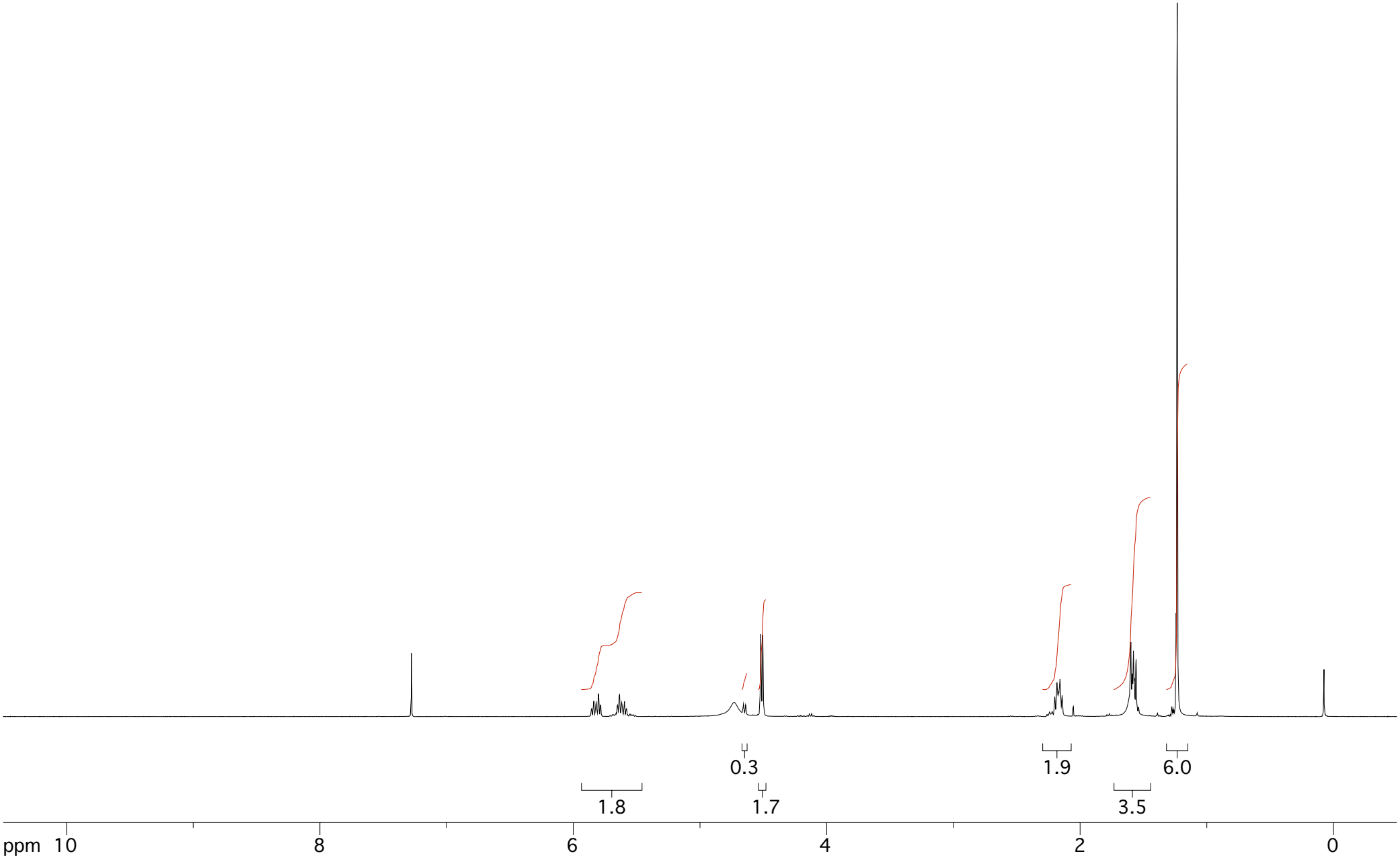


8 (*E*/*Z* ~5.5:1)



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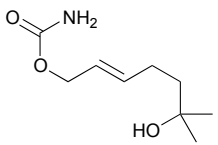
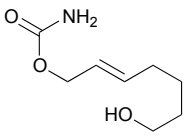


8 (*E*/*Z* ~5.5:1)

23



9 (*E*/*Z* ~4:1)

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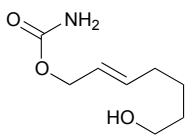
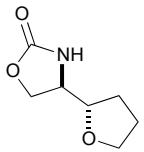
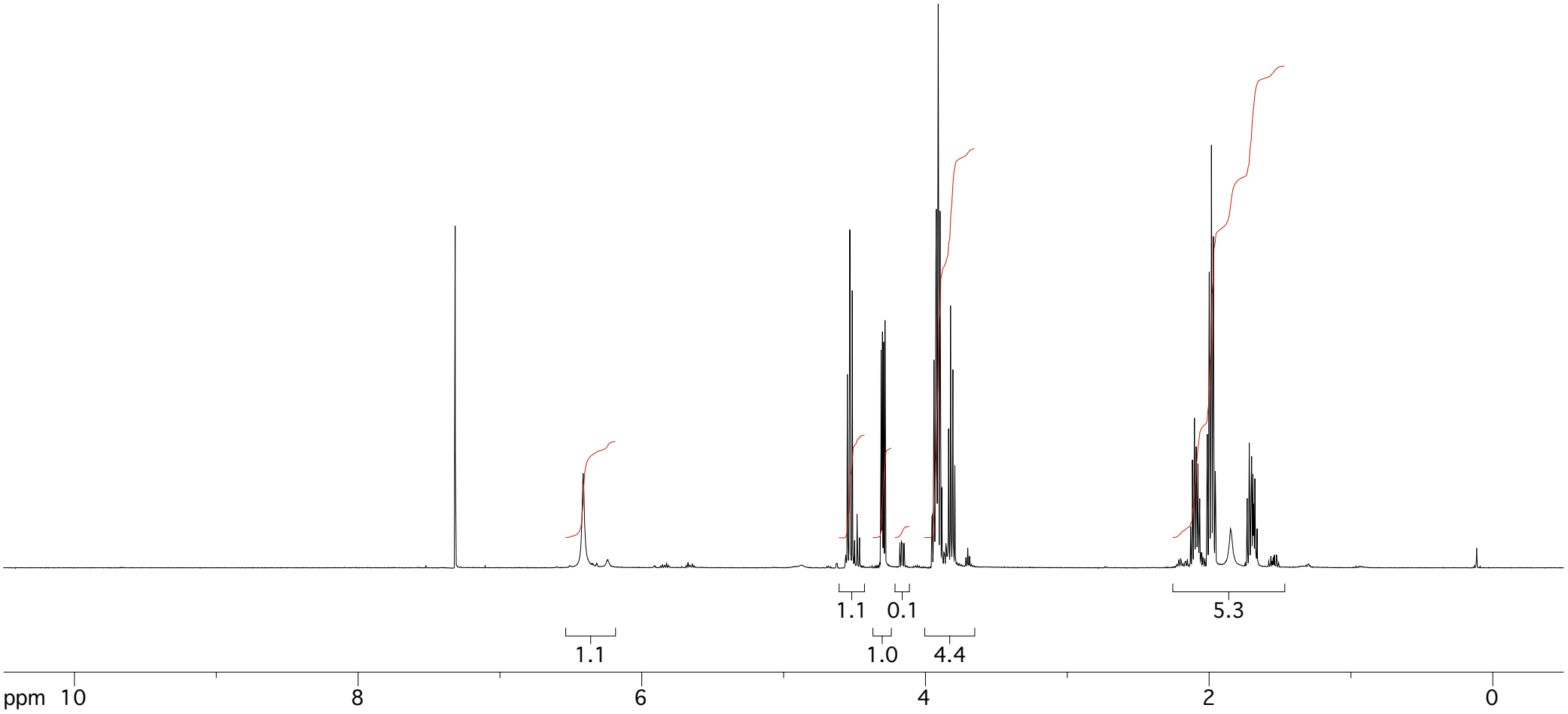


9 (*E*/*Z* ~4:1)



10 (dr ~9:1)



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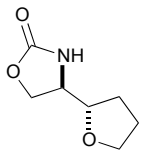

10 (dr ~9:1)

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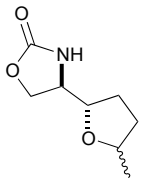
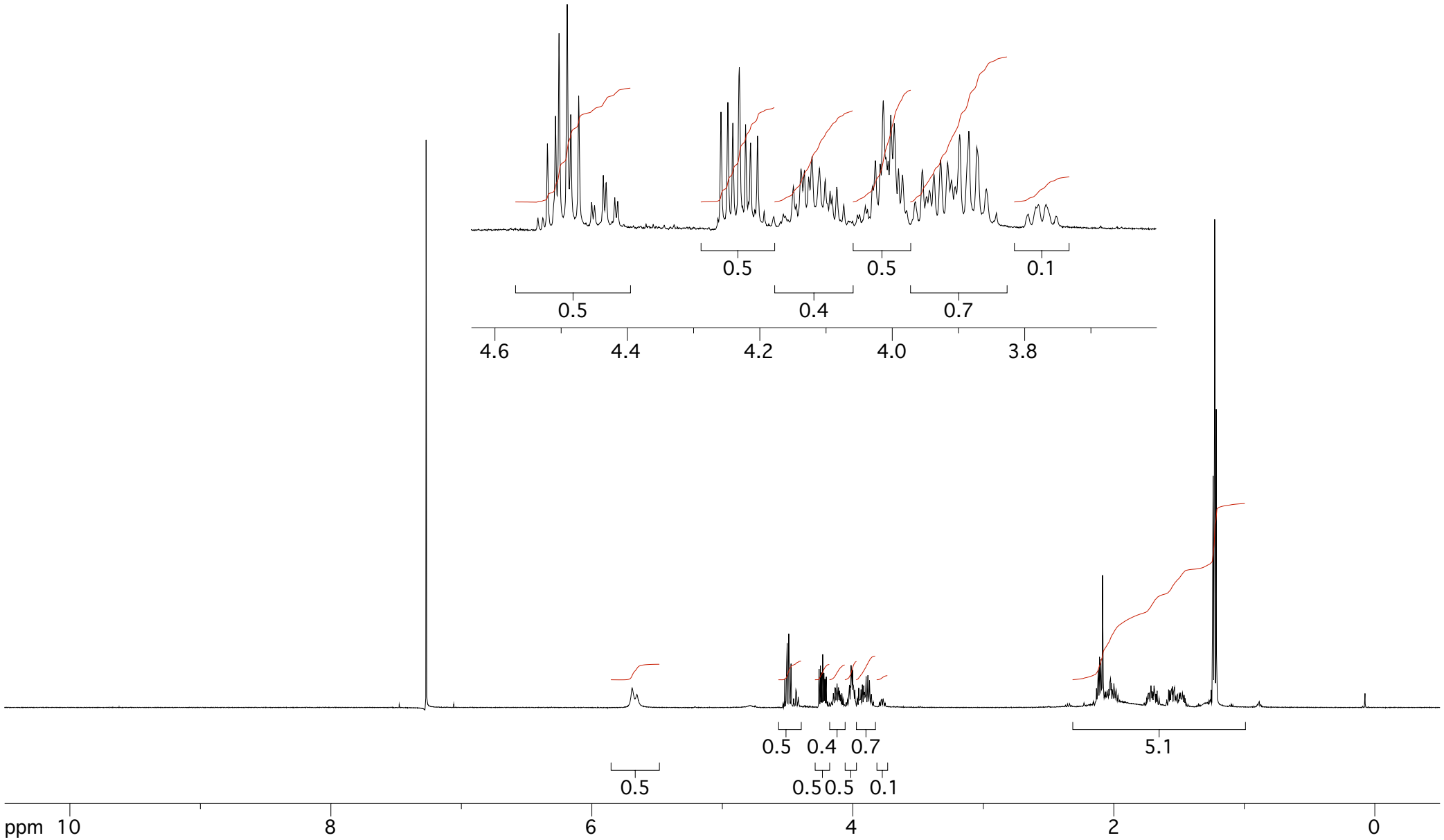
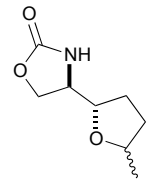
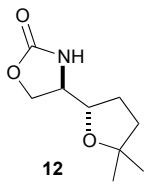


11 (dr ~6.5 : 5.5 : 1.5 : 1)





11 (dr ~6.5 : 5.5 : 1.5 : 1)



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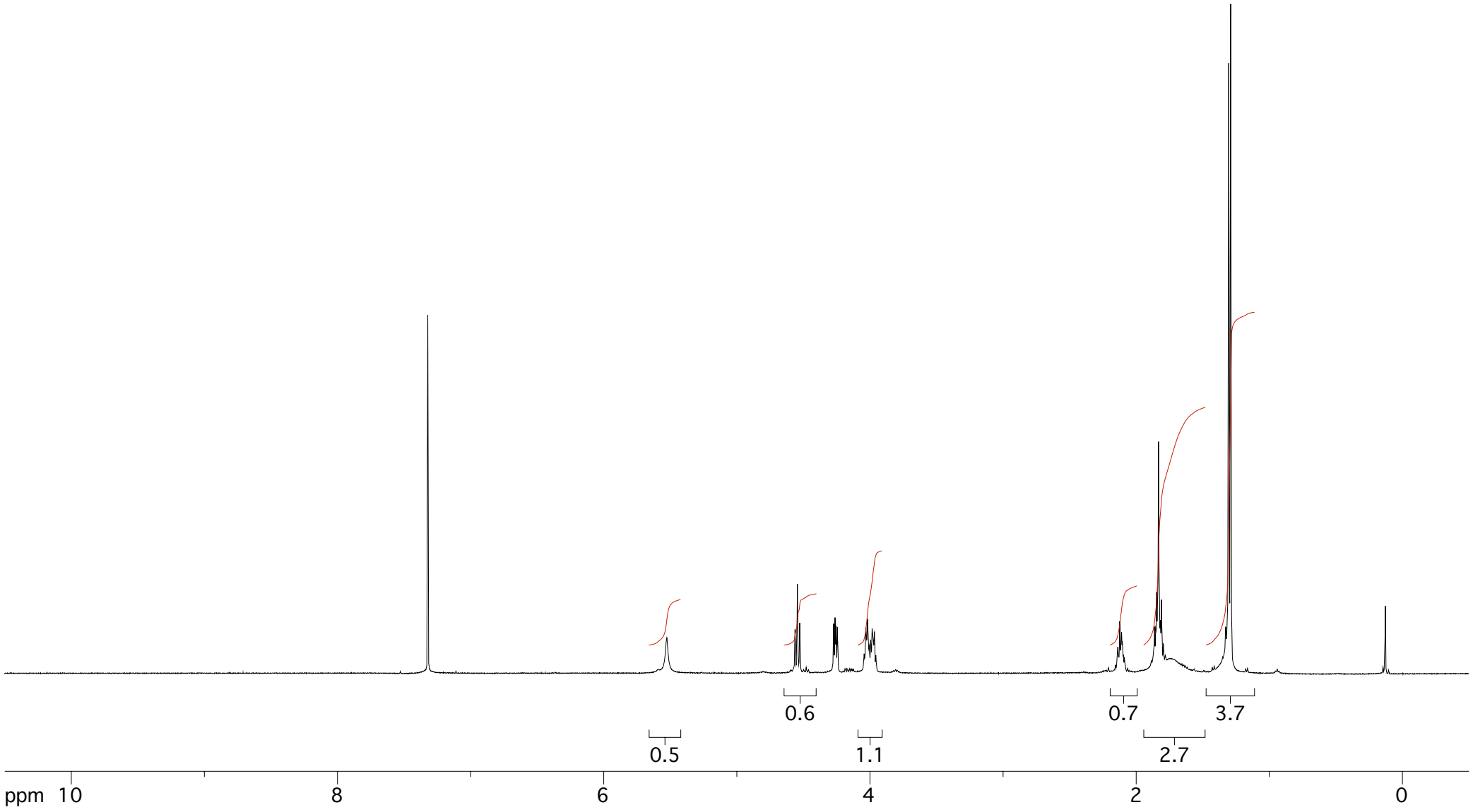

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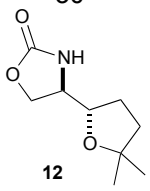

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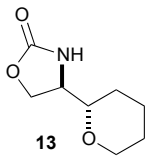

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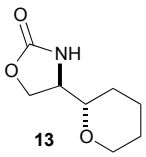

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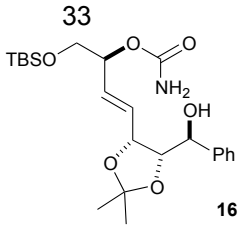
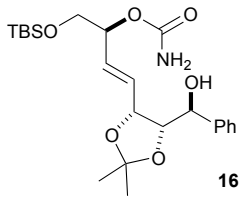

TBSO
O
O
NH2
OH
Ph
O
O

16

0.2
0.4
0.2
1.4
0.7
0.1
0.1
1.1
0.8
Hz 5000
4000
3000
2000
1000
0

34



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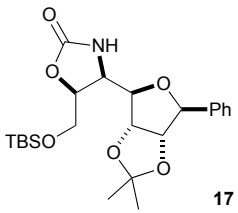
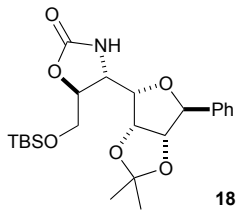

O
NH
O
O
O
Ph
TBSO
O
O

17


O
NH
O
O
O
Ph
TBSO
O
O

18

1.1
0.4
3.0
2.8
5.0
4.5
4.0
1.1
0.4
9.3
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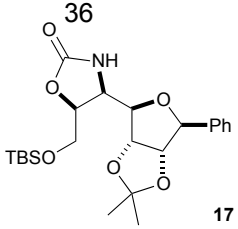
7.2
3.0
2.8
3.0
6.0
ppm 10
8
6
4
2
0

36



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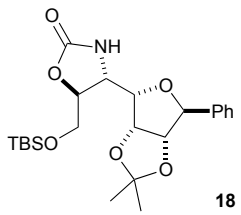

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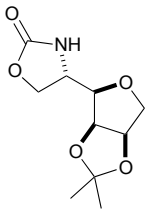

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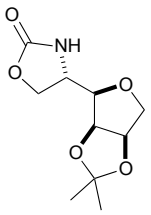

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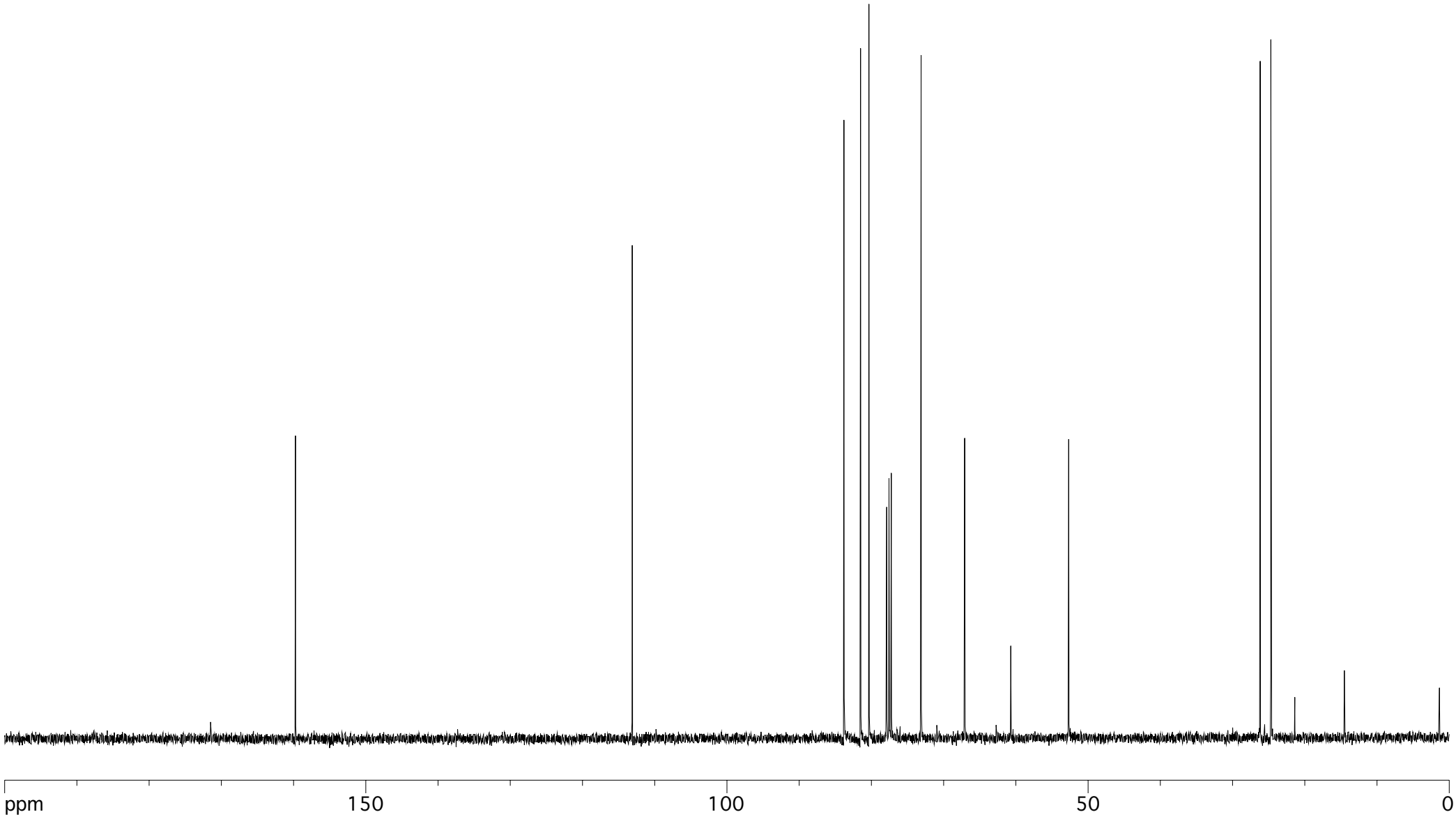
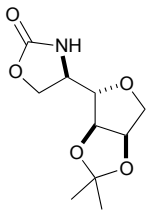
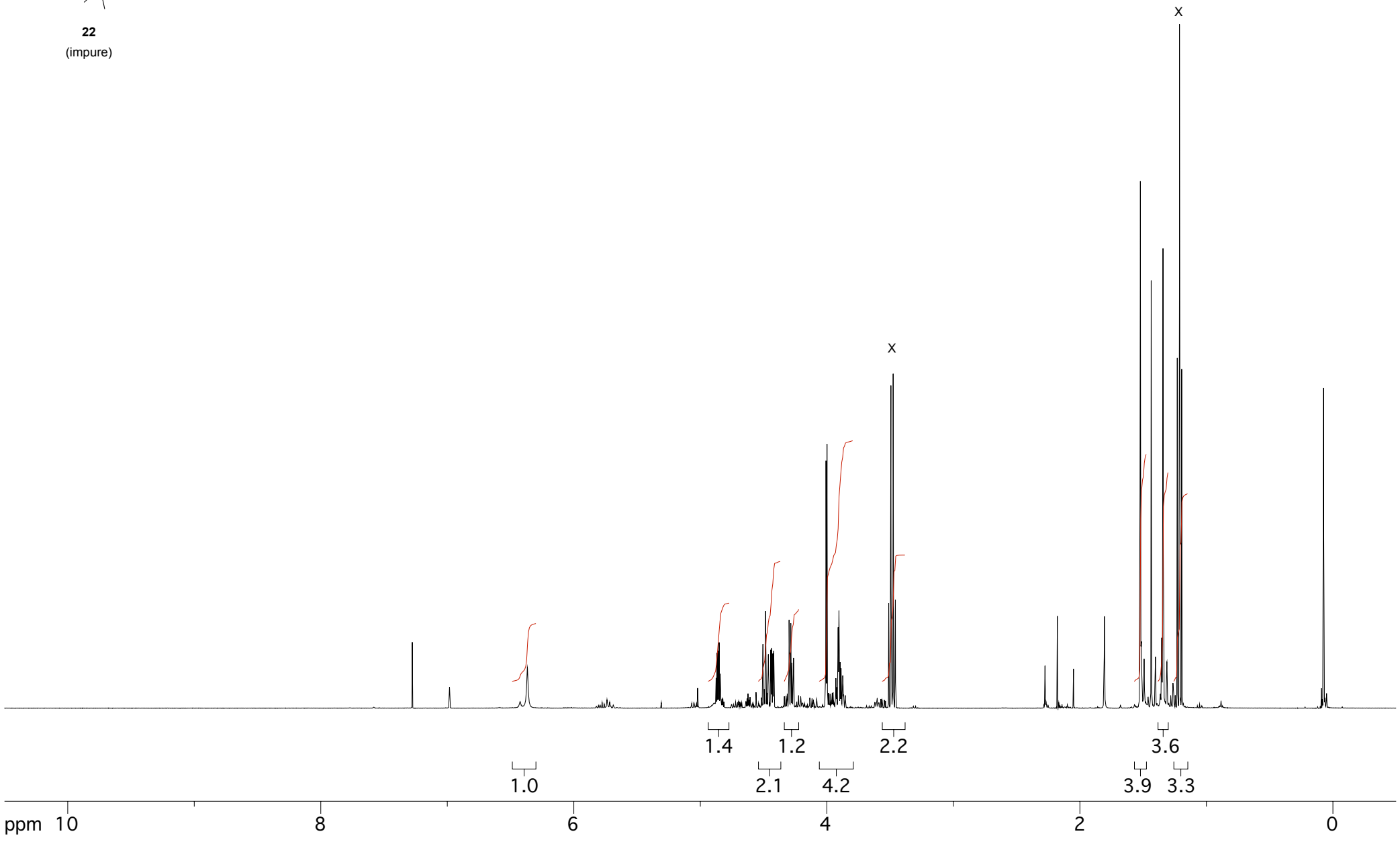




22
(impure)



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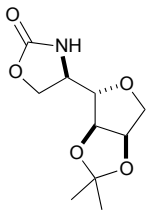
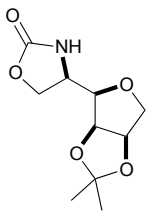


22
(impure)

41



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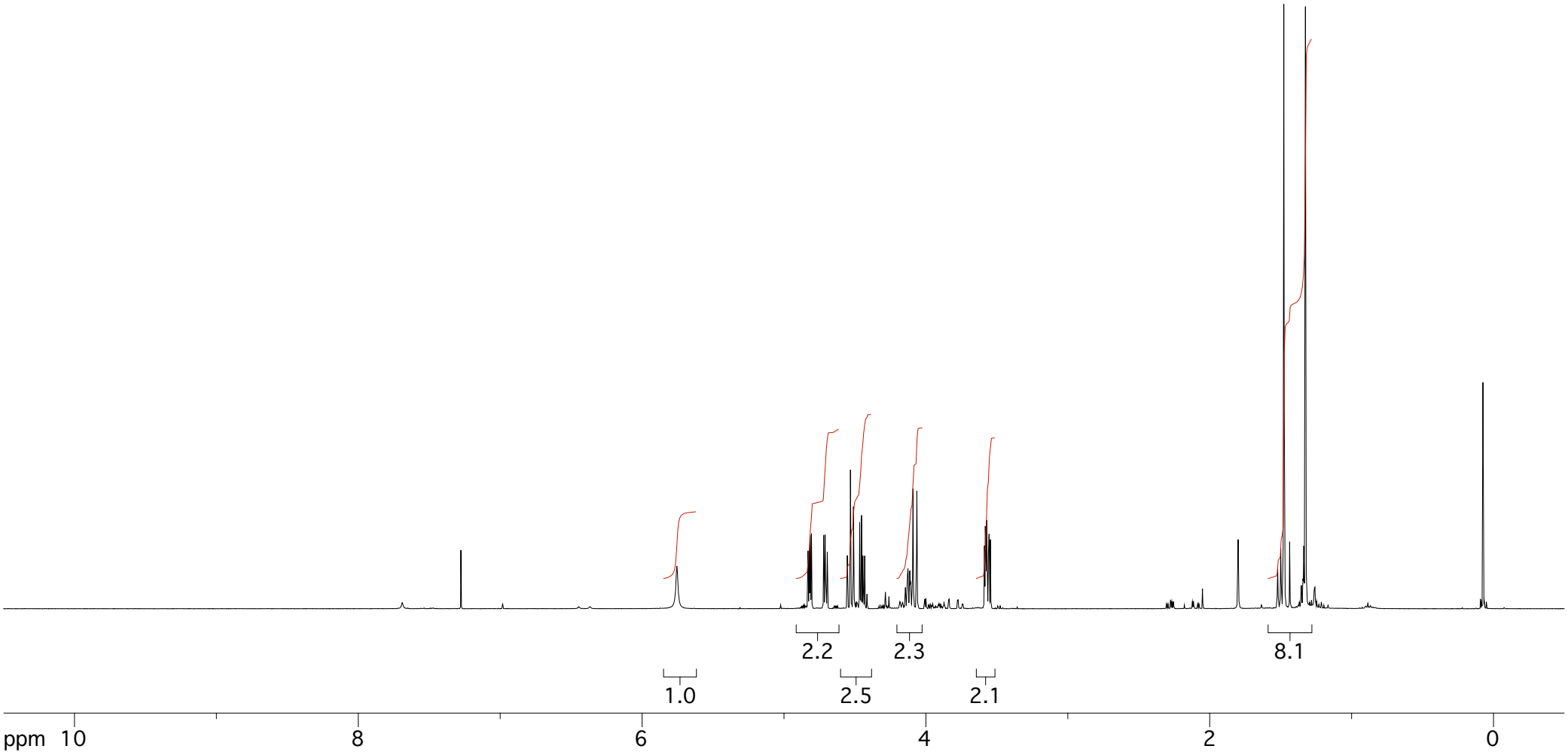

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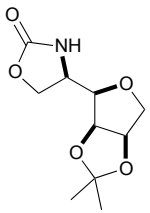

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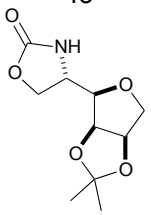

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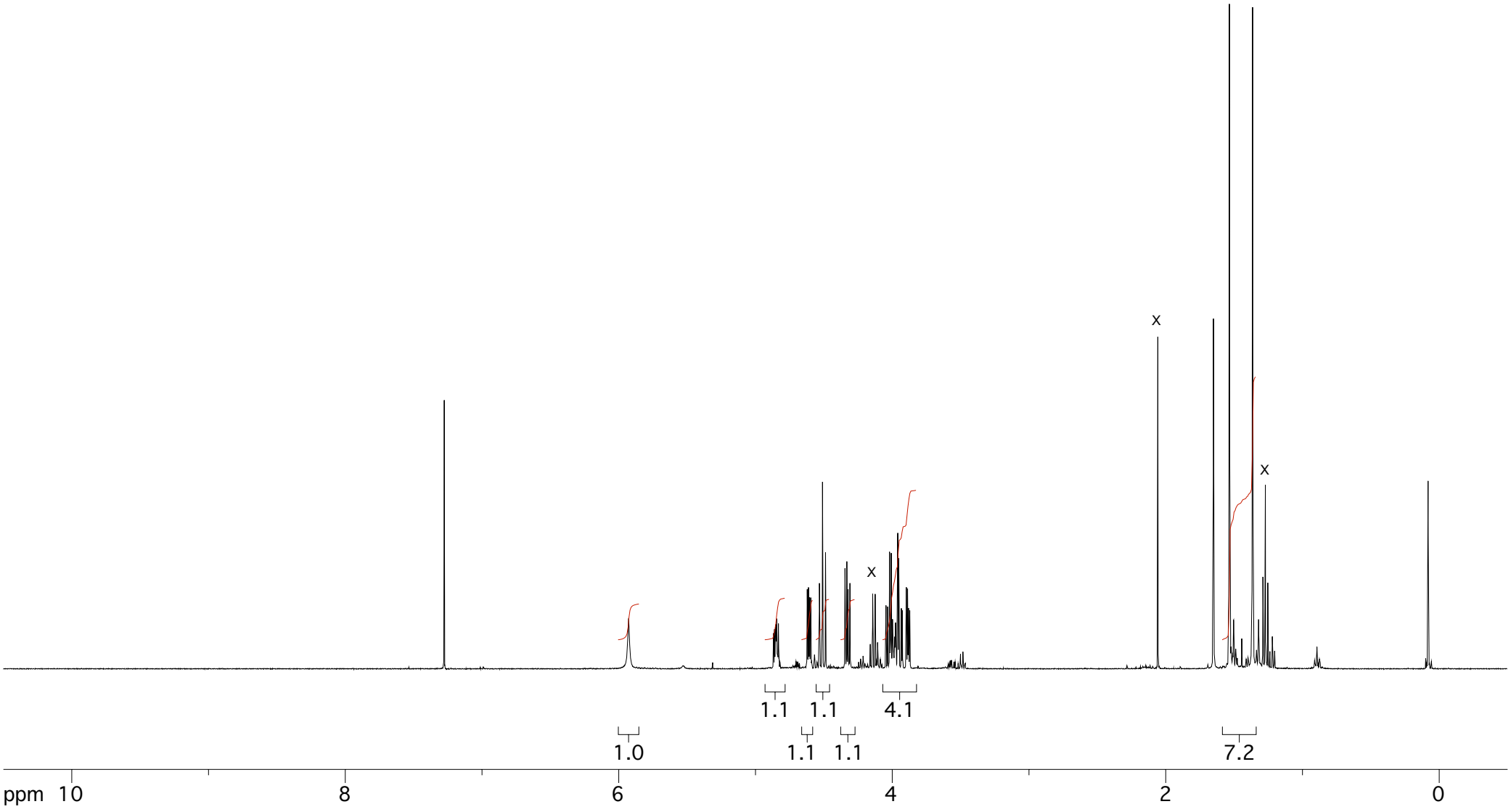

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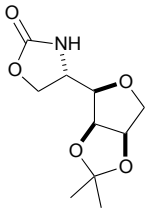

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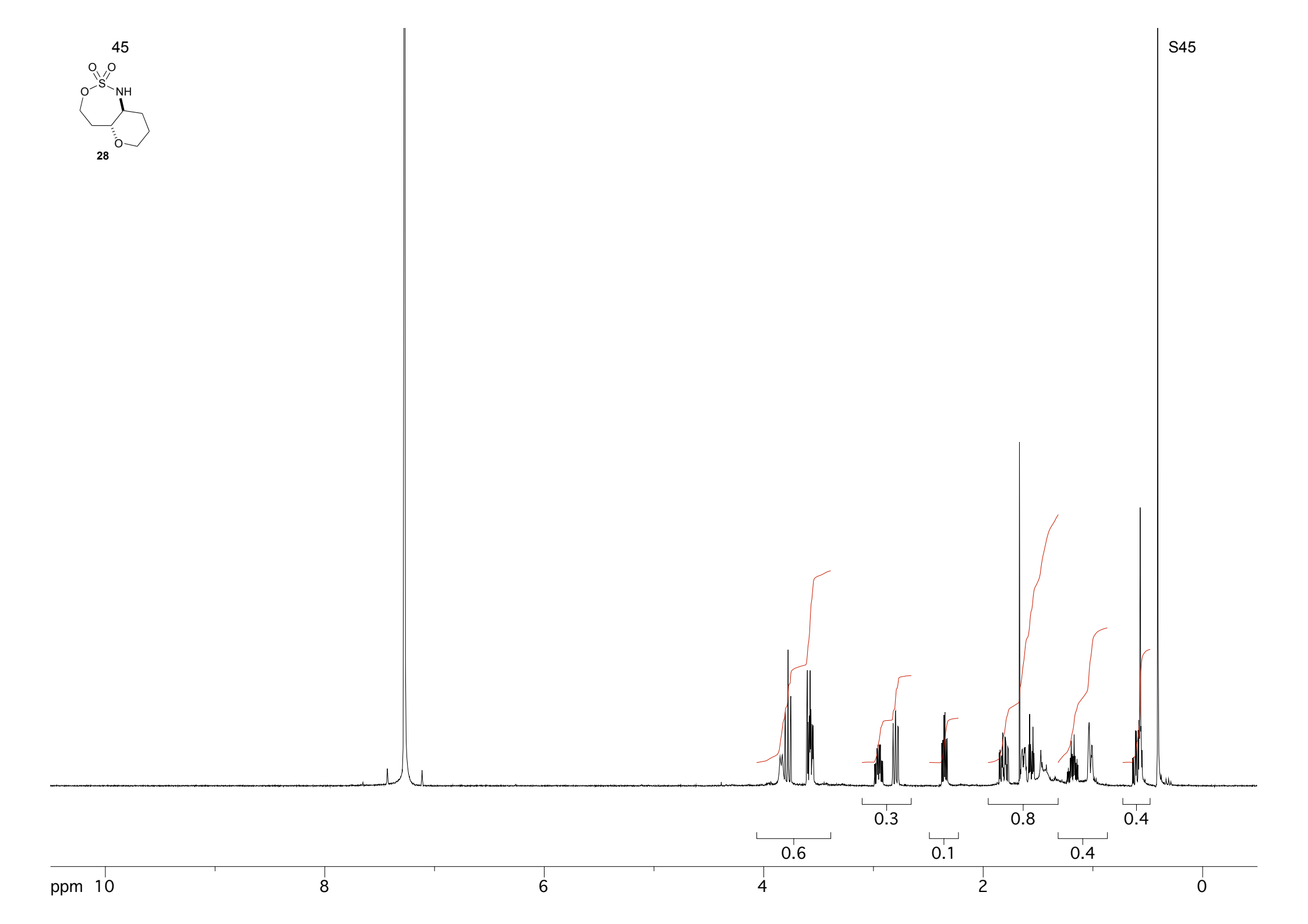
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O
O
S
NH
O
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S45
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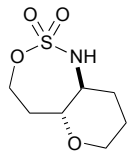
0.8
0.4
0.6
0.1
0.4
ppm 10
8
6
4
2
0

46



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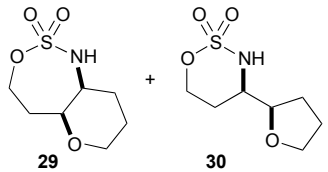
O
O
S
NH
O
O
29
+
O
O
S
NH
O
O
30

2.0
1.7
5.3
7.0
8.5
20.5
2.0
ppm 10
8
6
4
2
0

48