Electronic Supplementary Material (ESI) for ChemComm.

Nucleophilic *Halo*-Michael Addition under Lewis-Base Activation

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1. General methods and starting materials.

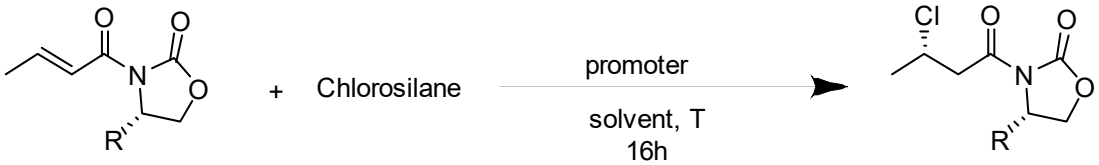
All solvents were dried using activated 4Å molecular sieves and stored under nitrogen. 4Å molecular sieves, 1.6-2.5 mm of particle size, were activated by microwave (700W) (3 x 60 sec) and subsequent cycles of vacuum/nitrogen. For thin layer chromatography (TLC) silica gel plates with fluorescence indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of potassium permanganate in water followed by heating. Flash column chromatography was performed using Geduran® Silica Gel 60 (0.040-0.063 nm) or Iatrobeads 6RS-8060 silica gel and compressed air. Cyclohexane and ethyl acetate for flash chromatography were acquired from commercial sources and were used without previous purification. Optical rotation was recorded on a Perkin-Elmer 241 MC Polarimeter in cells with 10 cm path length; the specific solvents and concentrations (in g/100 mL) are indicated. NMR spectra were acquired on a *Bruker Avance 300 MHz spectrometer*, running at 300, 75 and 282 MHz for ^{1}H, ^{13}C and ^{19}F respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR respectively). ^{13}C and ^{19}F spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), bs (broad singlet). Electrospray ionization has been used for measuring the exact mass (indicated for each case): MS (ESI) (Electrospray ionization mass spectroscopy) was acquired with an *Agilent Technologies 6120 Quadrupole LC/MS*. In this technique, *MassWorks software ver. 4.0.0.0 (Cerno Bioscience*) was used for the formula identification. *MassWorks* is a MS calibration software which calibrates for isotope profile as well as for mass accuracy, allowing highly accurate comparisons between calibrated and theoretical spectra.[1]

Crystal of compound **4e** was mounted at low temperature in inert oil on a glass fiber. Data were collected on a *Bruker X8 APPEX II* CCD-based diffractometer, equipped with a graphite monochromated MoKα (radiation source λ = 0.71073 Å).

[1] a) Y. Wang and M. Gu, *Anal. Chem.*, 2010, **82**, 7055; b) Y. Wang, Methods for Operating MS Instrument Systems, United States Patent No. 6,983,213, **2006**; c) N. Ochiaia, K. Sasamoto, K. MacNamara *Journal of Chromatography A*, 2012, **1270**, 296; d) H.-P. Ho, R.-Y. Lee, C.-Y. Chen, S.-R. Wang, Z.-G. Li and M.-R. Lee, *Rapid Commun. Mass Spectrom.* 2011, **25**, 25.

2. Optimization of the reaction conditions.

2.1. Optimization of the β-chlorination reaction.[a]

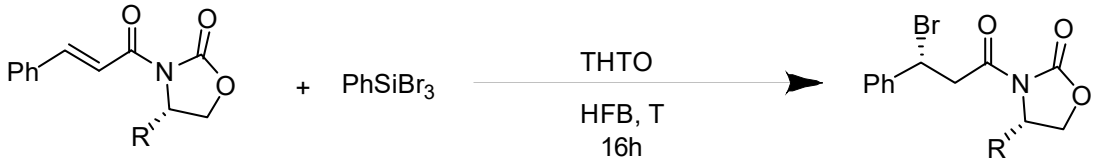


Entry	R	Chlorosilane	Promoter	Solvent	T (°C)	Conversion (%)	*d.r.*
1	*i*Pr	Allyl	-	DCM	25	<10	-
2	*i*Pr	Allyl	$Yb(OTf)_3$	DCM	25	57	60:40
3	*i*Pr	Allyl	$Yb(OTf)_3$	THF	25	n.r.	-
4	*i*Pr	Allyl	$Yb(OTf)_3$	Toluene	25	n.r.	-
5	*i*Pr	Allyl	$Yb(OTf)_3$	MeCN	25	30	60:40
6	*i*Pr	Allyl	$Yb(OTf)_3$	$CHCl_3$	25	-	-
7	*i*Pr	Allyl	$Yb(OTf)_3$	HFB	25	20	87:13
8	*i*Pr	Allyl[b]	$Yb(OTf)_3$	HFB	25	50	87:13
9	*i*Pr	Allyl	THTO	HFB	25	48	87:13
10	*i*Pr	Allyl	PPh_3 oxide	HFB	25	n.r.	-
11	*i*Pr	Allyl	Phenol	HFB	25	n.r.	-
12	*i*Pr	Allyl	PPh_3	HFB	25	n.r.	-
13	*i*Pr	Allyl	DMSO	HFB	25	21	85:15
14	*i*Pr	TMSCl	THTO	HFB	25	10	-
15	*i*Pr	TMS-$SiMe_2Cl$	THTO	HFB	25	n.r.	-
16	*i*Pr	TBACl	THTO	HFB	25	n.r.	-
17	*i*Pr	$PhSiCl_3$	THTO	HFB	25	47	86:14
18	*i*Pr	$SiCl_4$	THTO	HFB	25	25	86:14
19	*i*Pr	Allyl[b]	THTO	HFB	4	87	80:20
20	*i*Pr	Allyl[b]	THTO	HFB	25	100	80:20
21	*i*Pr	Allyl[b]	THTO	Hexane	25	100	66:34
22	*i*Pr	Allyl[b]	THTO	1,2-DCB	25	100	60:40
23	*i*Pr	Allyl[b]	THTO	DCM	-78	15	60:40
24	*i*Pr	Allyl[b]	THTO	DCM:HFB (3:1)	-78	80	70:30
25	Ph	Allyl[b]	THTO	HFB	25	100	80:20
26	Ph	Allyl[b]	$Yb(OTf)_3$	HFB	25	50	80:20
27	*t*Bu	Allyl[b]	THTO	HFB	25	100	87:13
28	*t*Bu	Allyl[b]	THTO + $Yb(OTf)_3$	HFB	25	100	91:9
29	*t*Bu	Allyl[b]	$Yb(OTf)_3$	HFB	25	22	93:7
30	*t*Bu	Allyl[b]	THTO	HFB[c]	25	80	95:5
31	*t*Bu	Allyl[b]	$Yb(OTf)_3$	HFB[c]	25	20	95:5
32	*t*Bu	Allyl[d]	THTO	HFB	25	78	95:5
33	*t*Bu	Allyl[d]	THTO	HFB[e]	25	82	94:6
34	*t*Bu	Allyl[d]	THTO	HFB[f]	25	81	92:8
35	***t*Bu**	**Allyl[g]**	**THTO**	**HFB[c]**	**25**	**94 (82)**	**96:4**
36	*t*Bu	Allyl[g]	THTO	DCM[c]	25	95	92:8

37	*t*Bu	Allyl[g]	THTO	THF[c]	25	n.r.	-
38	*t*Bu	Allyl[g]	THTO	Toluene[c]	25	82	95:5
39	*t*Bu	Allyl[g]	THTO	MeCN[c]	25	80	75:25
40	*t*Bu	Allyl[g]	-	HFB[c]	25	n.r.	-

[a] Standard conditions: 0.1 mmol of Michael acceptor, 0.1 mmol of silane and $Yb(OTf)_3$ (20mol%) or THTO (0.1 mmol) in 1.2 mL of solvent were used. [b] 3 equivalents of silane and THTO were used. [c] 2.5 mL of solvent were used. [d] 2 equivalents of allyltrichlorosilane and THTO were used. [e] 0.9 mL of HFB were used. [f] 0.6 mL of HFB were used. [g] 4 equivalents of silane and THTO were used.

2.2. Optimization of the β-bromination reaction.[a]

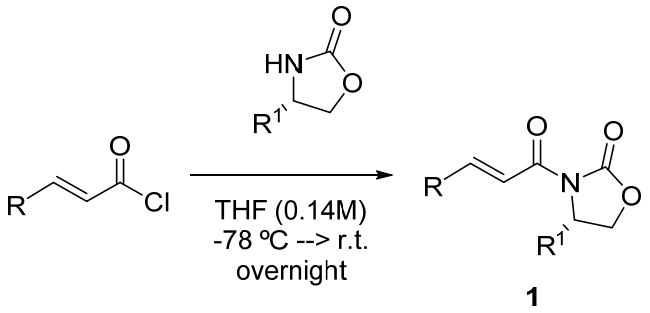


Entry	R	$PhSiBr_3$ (eq.)	HFB (mL)	T (°C)	Conversion (%)	d.r.
1	*i*Pr	3	2.5	25	82	80:20
2	***t*Bu**	**4**	**2.5**	**25**	**95 (81)**	**90:10**
3	*t*Bu	3	2.5	25	97	87:13
4	*t*Bu	3	2.5	4	17	>95:5
5	*t*Bu	2	2.5	25	50	91:9
6	*t*Bu	2	1.8	25	60	91:9

[a] Standard conditions: 0.1 mmol of Michael acceptor, 0.3 mmol of tribromo(phenyl)silane and THTO (0.3 mmol) in 2.5 mL of hexafluorobenzene were used.

3. Synthesis and characterization data of *α,β*-unsaturated *N*-acyloxazolidinones 1.

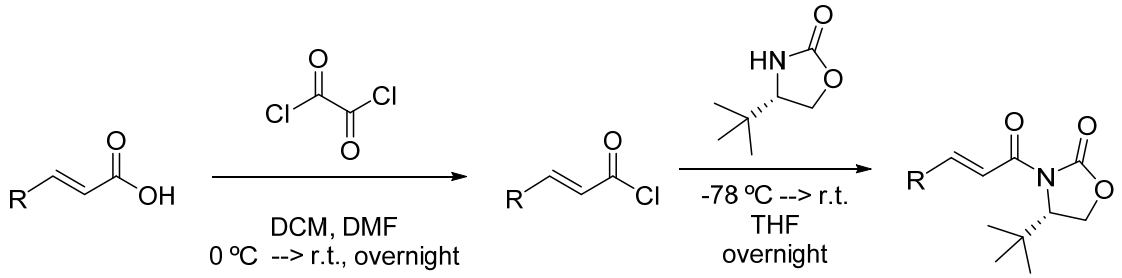
3.1. General procedure A: Synthesis of *α,β*-unsaturated *N*-acyloxazolidinones 1.



1

A previously oven-dried round bottom flask was charged with a magnetic stirrer and the corresponding oxazolidinone (1.4 mmol, 1.0 eq.)[2] under nitrogen atmosphere. Then, anhydrous THF (5 mL) was added. The reaction mixture was cooled to -78 °C and *n*-BuLi (2.5M in hexanes, 1.1 eq.) was added dropwise. The reaction mixture was allowed to get room temperature and stirred for 1h. The solution was cooled again to -78 °C and another solution of the corresponding α,β-unsaturated acyl chloride (1.4 mmol, 1.0 eq.) in anhydrous THF (5 mL) was added dropwise under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. The mixture was quenched with saturated NH_4Cl (aq) and the aqueous phases were extracted with EtOAc (2 x 5 mL). The organic phases were combined and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography using silica gel and the eluent indicated in each case.

3.2. General procedure B: Synthesis of *α,β*-unsaturated *N*-acyloxazolidinones 1.



1

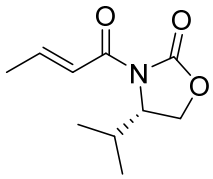
It was prepared following a modified procedure described in the literature:[3] A previously oven-dried round bottom flask was charged with a magnetic stirrer and the corresponding α,β-

[2] They were prepared following a procedure described in the literature: A.-R. Silva, V. Guimaraes, A.-P. Carvalho and J. Pires, *Catal. Sci. Technol.* 2013, **3**, 659.

[3] W. Zhi, J. Li, D. Zou, Y. Wu and Y. Wu, *J. Org. Chem.* 2017, **82**, 12286.

unsaturated carboxylic acid (1.2 eq.) under nitrogen atmosphere. Then, DCM (3 mL) was added and the reaction mixture was cooled to 0 °C. Oxalylchloride (1.2 eq.) was added dropwise, followed by the addition of two drops of DMF, and the reaction mixture was stirred overnight at room temperature. Then, the solvent was evaporated under reduced pressure and the crude mixture was redissolved in anhydrous THF (5 mL). Another round bottom flask previously oven-dried was charged with a magnetic stirrer and the (*S*)-4-(*tert*-butyl)oxazolidin-2-one (1.0 eq.) under nitrogen atmosphere. Then, anhydrous THF (5 mL) was added, the reaction mixture was cooled to -78 °C and *n*-BuLi (2.5M in hexanes, 1.1 eq.) was added dropwise. The reaction mixture was allowed to get room temperature and stirred for 1h. The solution was cooled again to -78 °C and another solution of the corresponding α,β-unsaturated acyl chloride solution previously prepared (1.2 eq.) was added dropwise under nitrogen atmosphere and the reaction mixture was stirred overnight at room temperature. The mixture was quenched with saturated NH_4Cl (aq) and the aqueous phases were extracted with EtOAc (2 x 5 mL). The organic phases were combined and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography using silica gel and the eluent indicated in each case.

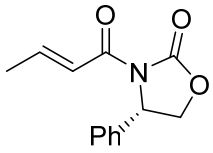
(*S,E*)-3-(But-2-enoyl)-4-isopropyloxazolidin-2-one (1a)[3]



Following general procedure A, crotonoyl chloride (0.13 mL, 1.4 mmol, 1.0 eq.), (*S*)-4-isopropyloxazolidin-2-one (181 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1a** as a yellow oil (88% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 7.26 (m, 1H), 7.12 (m, 1H), 4.47 (m, 1H), 4.29 (t, *J* = 8.8 Hz, 1H), 4.22 (dd, *J* = 7.2, 3.2 Hz, 1H), 2.40 (m, 1H), 1.95 (dd, *J* = 6.8, 1.6 Hz, 3H), 0.92 (dd, *J* = 17.6, 7.2 Hz, 6H) ppm.

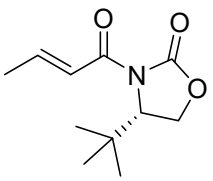
(*S,E*)-3-(But-2-enoyl)-4-phenyloxazolidin-2-one (SI1)[3]



Following general procedure A, crotonoyl chloride (0.13 mL, 1.4 mmol, 1.0 eq.), (*S*)-4-phenyloxazolidin-2-one (228 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **SI1** as a white solid (77% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 2:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 7.43 – 7.25 (m, 6H), 7.10 (dq, *J* = 15.2, 6.8 Hz, 1H), 5.49 (dd, *J* = 8.7, 3.9 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 1H), 4.28 (dd, *J* = 8.9, 3.9 Hz, 1H), 1.94 (dd, *J* = 6.8, 1.5 Hz, 3H) ppm.

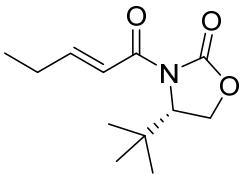
(*S,E*)-3-(But-2-enoyl)-4-(tert-butyl)oxazolidin-2-one (1b)[3]



Following general procedure A, crotonoyl chloride (0.13 mL, 1.4 mmol, 1.0 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1b** as a white solid (81% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 2:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 7.31 – 7.25 (m, 1H), 7.21 – 7.07 (m, 1H), 4.51 (dd, *J* = 7.2, 2.1 Hz, 1H), 4.32 – 4.20 (m, 2H), 1.96 (dd, *J* = 6.6, 1.4 Hz, 3H), 0.93 (s, 9H) ppm.

(*S,E*)-4-(*tert*-Butyl)-3-(pent-2-enoyl)oxazolidin-2-one (1c)



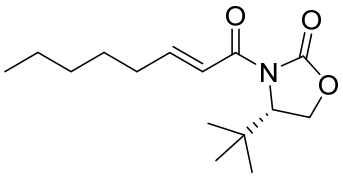
Following general procedure B, (*E*)-pent-2-enoic acid (0.14 mL, 1.25 mmol, 1.2 eq.), oxalyl chloride (0.11 mL, 1.25 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (150 mg, 1.05 mmol, 1.0 eq.) and *n*-BuLi (0.5 mL, 1.15 mmol, 1.1 eq.), gave **1c** as a yellow oil (56% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 2:1. **$[\alpha]^{20}_{D}$** = +85.3 (*c* 1.07, $CHCl_3$).

^{1}H-NMR: δ 7.31 – 7.13 (m, 2H), 4.52 (dd, *J* = 7.2, 2.1 Hz, 1H), 4.33 – 4.20 (m, 2H), 2.39 – 2.24 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H), 0.95 (s, 9H) ppm.

^{13}C-NMR: δ 165.5, 154.7, 152.9, 119.6, 65.2, 60.8, 35.9, 25.8, 25.6, 12.2 ppm.

HRMS (ESI^{+}): calculated for $C_{12}H_{20}NO_3$ $[M+H]^{+}$: 226.1438; found: 226.1451.

(*S,E*)-4-(*tert*-Butyl)-3-(oct-2-enoyl)oxazolidin-2-one (1d)



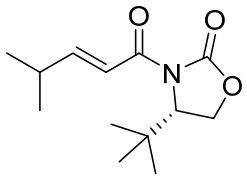
Following general procedure B, (*E*)-oct-2-enoic acid (0.19 mL, 1.25 mmol, 1.2 eq.), oxalyl chloride (0.11 mL, 1.25 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (150 mg, 1.05 mmol, 1.0 eq.) and *n*-BuLi (0.5 mL, 1.15 mmol, 1.1 eq.), gave **1d** as a yellow oil (90% yield). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_{D}$** = +69.9 (*c* 1.21, $CHCl_3$).

^{1}H-NMR: δ 7.30 – 7.09 (m, 2H), 4.52 (dd, *J* = 7.2, 2.0 Hz, 1H), 4.33 – 4.19 (m, 2H), 2.33 – 2.23 (m, 2H), 1.57 – 1.43 (m, 2H), 1.39 – 1.27 (m, 4H), 0.95 (s, 9H), 0.92 – 0.86 (m, 3H) ppm.

^{13}C-NMR: δ 165.5, 154.7, 151.8, 120.3, 65.2, 60.8, 35.9, 32.7, 31.4, 27.7, 25.6, 22.4, 13.9 ppm.

HRMS (ESI$^+$): calculated for $C_{15}H_{26}NO_3$ $[M+H]^+$: 268.1907; found: 268.1920.

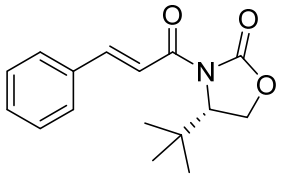
(*S,E*)-4-(*tert*-Butyl)-3-(4-methylpent-2-enoyl)oxazolidin-2-one (1e)[3]



Following general procedure B, (*E*)-4-methylpent-2-enoic acid (0.15 mL, 1.25 mmol, 1.2 eq.), oxalyl chloride (0.11 mL, 1.25 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (150 mg, 1.05 mmol, 1.0 eq.) and *n*-BuLi (0.5 mL, 1.15 mmol, 1.1 eq.), gave **1e** as a yellow oil (62% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 2:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 7.26 – 7.05 (m, 2H), 4.52 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.33 – 4.19 (m, 2H), 2.62 – 2.47 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 6H), 0.95 (s, 9H) ppm.

(*S*)-4-(*tert*-Butyl)-3-cinnamoyloxazolidin-2-one (1f)



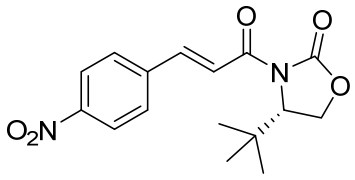
Following general procedure A, cinnamoyl chloride (233 mg, 1.4 mmol, 1.0 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1f** as a yellow solid (97% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. **$[\alpha]^{20}_D$** = +117.2 (*c* 1.07, $CHCl_3$).

^{1}H-NMR: δ 7.95 (d, *J* = 15.7 Hz, 1H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.43 – 7.34 (m, 3H), 4.59 (dd, *J* = 7.0, 2.2 Hz, 1H), 4.38 – 4.23 (m, 2H), 0.97 (s, 9H) ppm.

^{13}C-NMR: δ 165.5, 154.7, 146.3, 134.6, 130.6, 128.8, 128.6, 117.1, 65.2, 61.0, 36.0, 25.6 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1438; found: 274.1451.

(*S,E*)-4-(*tert*-Butyl)-3-(3-(4-nitrophenyl)acryloyl)oxazolidin-2-one (1g)



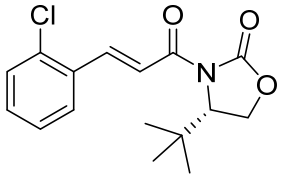
Following general procedure A, (*E*)-3-(4-nitrophenyl)acryloyl chloride (296 mg, 1.4 mmol, 1.0 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1g** as a yellow solid (93% yield). Eluent: cyclohexane: ethyl acetate 7:3. **$[\alpha]^{20}_D$** = +114.4 (*c* 1.03, $CHCl_3$).

^{1}H-NMR: δ 8.24 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 15.7 Hz, 1H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 4.58 (dd, *J* = 6.9, 2.3 Hz, 1H), 4.40 – 4.27 (m, 2H), 0.97 (s, 9H) ppm.

^{13}C-NMR: δ 164.7, 154.7, 148.6, 142.9, 140.7, 129.0, 124.1, 121.4, 65.4, 61.1, 36.0, 25.6 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{19}N_2O_5$ $[M+H]^+$: 319.1288; found: 319.1262.

(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(2-chlorophenyl)acryloyl)oxazolidin-2-one (1h)



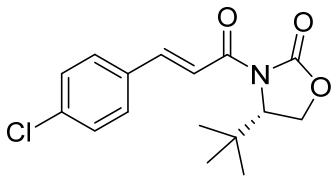
Following general procedure A, (*E*)-3-(2-chlorophenyl)acryloyl chloride (281 mg, 1.4 mmol, 1.0 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1h** as a yellow oil (87% yield). Eluent: cyclohexane: ethyl acetate 7:3. **$[\alpha]^{20}_D$** = +100.1 (*c* 1.05, $CHCl_3$).

^{1}H-NMR: δ 8.25 (d, *J* = 15.7 Hz, 1H), 7.94 (d, *J* = 15.7 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.44 – 7.38 (m, 1H), 7.36 – 7.24 (m, 2H), 4.59 (dd, *J* = 6.7, 2.6 Hz, 1H), 4.38 – 4.27 (m, 2H), 0.98 (s, 9H) ppm.

^{13}C-NMR: δ 164.9, 154.6, 141.5, 135.1, 132.7, 131.2, 130.0, 128.0, 127.0, 119.6, 65.2, 60.9, 35.8, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{19}ClNO_3$ $[M+H]^+$: 308.1048; found: 308.1065.

(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(4-chlorophenyl)acryloyl)oxazolidin-2-one (1i)



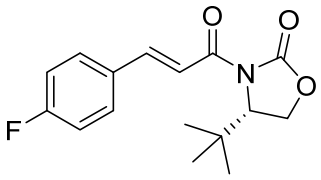
Following general procedure B, (*E*)-3-(4-chlorophenyl)acrylic acid (307 mg, 1.68 mmol, 1.2 eq.), oxalyl chloride (0.15 mL, 1.68 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1i** as a yellow solid (66% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. **$[\alpha]^{20}_D$** = +111.8 (*c* 1.46, $CHCl_3$).

^{1}H-NMR: δ 7.93 (d, *J* = 15.7 Hz, 1H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.59 (dd, *J* = 7.0, 2.3 Hz, 1H), 4.39 – 4.22 (m, 2H), 0.98 (s, 9H) ppm.

^{13}C-NMR: δ 165.3, 154.7, 144.8, 136.5, 133.1, 129.7, 129.1, 117.7, 65.3, 61.0, 36.0, 25.6 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{19}ClNO_3$ $[M+H]^+$: 308.1048; found: 308.1061.

(*S,E*)-4-(*tert*-Butyl)-3-(3-(4-fluorophenyl)acryloyl)oxazolidin-2-one (1j)



Following general procedure A, (*E*)-3-(4-fluorophenyl)acryloyl chloride (260 mg, 1.4 mmol, 1.0 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1j** as a yellow solid (59% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. $\mathbf{[\alpha]^{20}_D}$ = +113.1 (*c* 0.64, $CHCl_3$).

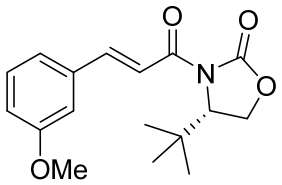
^{1}H-NMR: δ 7.88 (d, *J* = 15.7 Hz, 1H), 7.79 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.13 – 7.02 (m, 2H), 4.58 (dd, *J* = 7.1, 2.2 Hz, 1H), 4.41 – 4.21 (m, 2H), 0.98 (s, 9H) ppm.

^{13}C-NMR: δ 165.4, 164.1 (d, *J* = 251.8 Hz), 154.7, 145.0, 130.9 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 8.6 Hz), 116.9 (d, *J* = 2.5 Hz), 116.0 (d, *J* = 22.0 Hz), 65.3, 61.0, 36.0, 25.6 ppm.

^{19}F-NMR: δ -109.0 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{19}FNO_3$ $[M+H]^+$: 292.1343; found: 292.1360.

(*S,E*)-4-(*tert*-Butyl)-3-(3-(3-methoxyphenyl)acryloyl)oxazolidin-2-one (1k)



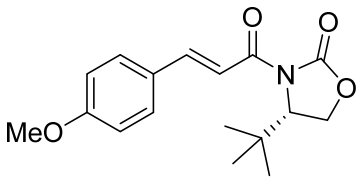
Following general procedure B, (*E*)-3-(3-methoxyphenyl)acrylic acid (299 mg, 1.68 mmol, 1.2 eq.), oxalyl chloride (0.15 mL, 1.68 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1k** as a yellow oil (88% yield). Eluent: cyclohexane: ethyl acetate 7:3. $\mathbf{[\alpha]^{20}_D}$ = +87.9 (*c* 1.04, $CHCl_3$).

^{1}H-NMR: δ 7.93 (d, *J* = 15.7 Hz, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.36 – 7.18 (m, 2H), 7.14 – 7.09 (m, 1H), 6.99 – 6.89 (m, 1H), 4.58 (dd, *J* = 7.0, 2.3 Hz, 1H), 4.37 – 4.21 (m, 2H), 3.84 (s, 3H), 0.97 (s, 9H) ppm.

^{13}C-NMR: δ 165.5, 159.9, 154.7, 146.3, 136.0, 129.8, 121.3, 117.4, 116.6, 113.3, 65.3, 61.0, 55.3, 36.0, 25.7 ppm.

HRMS (ESI$^+$): calculated for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1543; found: 304.1564.

(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(4-methoxyphenyl)acryloyl)oxazolidin-2-one (1l)



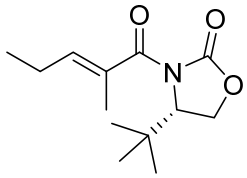
Following general procedure B, (*E*)-3-(4-methoxyphenyl)acrylic acid (299 mg, 1.68 mmol, 1.2 eq.), oxalyl chloride (0.15 mL, 1.68 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1l** as a yellow oil (68% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. $[\alpha]^{20}_{D}$ = +122.2 (*c* 0.93, $CHCl_3$).

^{1}H-NMR: δ 7.81 (s, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.58 (dd, *J* = 7.0, 2.3 Hz, 1H), 4.35 – 4.22 (m, 2H), 3.84 (s, 3H), 0.97 (s, 9H) ppm.

^{13}C-NMR: δ 165.7, 161.7, 154.8, 146.2, 130.4, 127.4, 114.6, 114.3, 65.2, 60.9, 55.4, 36.0, 25.6 ppm.

HRMS (ESI$^+$): calculated for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1543; found: 304.1552.

(*S*,*E*)-4-(*tert*-Butyl)-3-(2-methylpent-2-enoyl)oxazolidin-2-one (1m)



Following general procedure B, (*E*)-2-methylpent-2-enoic acid (192 mg, 1.68 mmol, 1.2 eq.), oxalyl chloride (0.15 mL, 1.68 mmol, 1.2 eq.), (*S*)-4-(*tert*-butyl)oxazolidin-2-one (200 mg, 1.4 mmol, 1.0 eq.) and *n*-BuLi (0.61 mL, 1.54 mmol, 1.1 eq.), gave **1m** as a yellow oil (79% yield). Eluent: cyclohexane: ethyl acetate 4:1. $[\alpha]^{20}_{D}$ = +16.6 (*c* 0.31, $CHCl_3$).

^{1}H-NMR: δ 6.27 – 6.17 (m, 1H), 4.57 (dd, *J* = 6.6, 4.6 Hz, 1H), 4.32 – 4.24 (m, 2H), 2.29 – 2.19 (m, 2H), 1.95 – 1.90 (m, 3H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.94 (s, 9H) ppm.

^{13}C-NMR: δ 172.3, 154.0, 142.9, 130.0, 64.7, 60.3, 35.8, 25.4, 21.9, 13.5, 12.8 ppm.

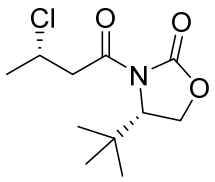
HRMS (ESI$^+$): calculated for $C_{13}H_{21}NO_3Na$ $[M+Na]^+$: 262.1413; found: 262.1419.

4. General procedure C for the nucleophilic halogenation of *α,β*-unsaturated *N*-acyloxazolidinones. Synthesis of 3 and 4.

3 and **4**

The corresponding *α,β*-unsaturated *N*-acyloxazolidinone **1** (0.1 mmol, 1.0 eq.) was dissolved in hexafluorobenzene (2.5 mL) in a vial. Then, tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and the corresponding halosilane[4] (0.4 mmol, 4.0 eq.) were sequentially added and the reaction was stirred for 16 hours. Finally, the crude mixture was purified by flash column chromatography using Iatrobeads silica gel and eluting with the solvent indicated in each case.

(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chlorobutanoyl)oxazolidin-2-one (3b)



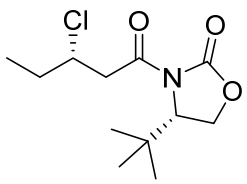
Following general procedure C, (*S,E*)-3-(but-2-enoyl)-4-(*tert*-butyl)oxazolidin-2-one **1b** (21.1 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and allyltrichlorosilane (60 μL, 0.4 mmol, 0.4 eq.), gave **3b** as a colorless oil (82% yield). Eluent: cyclohexane: ethyl acetate 4:1. $[\alpha]^{20}_{D}$ = +53.9 (*c* 0.98, $CHCl_3$).

^{1}H-NMR: δ 4.63 – 4.50 (m, 1H), 4.46 (dd, *J* = 7.1, 2.0 Hz, 1H), 4.37 – 4.21 (m, 2H), 3.44 (dd, *J* = 16.8, 8.8 Hz, 1H), 3.30 (dd, *J* = 16.7, 4.5 Hz, 1H), 1.62 (d, *J* = 6.5 Hz, 3H), 0.94 (s, 9H) ppm.

^{13}C-NMR: δ 169.6, 154.6, 65.6, 61.1, 52.9, 45.7, 35.8, 25.7, 25.2 ppm.

HRMS (ESI^{+}): calculated for $C_{11}H_{19}NO_3Cl$ $[M+H]^{+}$: 248.1048; found: 248.1058.

(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chloropentanoyl)oxazolidin-2-one (3c)



Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(pent-2-enoyl)oxazolidin-2-one **1c** (22.5 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and

[4] Tribromo(phenyl)silane was prepared following a reported procedure: A. Iwataa, Y. Toyoshimaa, T. Hayashidaa, T. Ochia, A. Kunaia and J. Ohshita, *J. Organomet. Chem.*, 2003, **667**, 90.

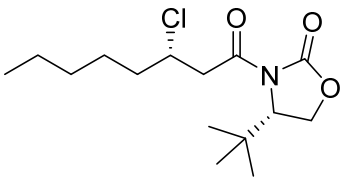
allyltrichlorosilane (60 μL, 0.4 mmol, 0.4 eq.), gave **3c** as a yellow oil (76% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 3:1. $[\alpha]^{20}_{D}$ = +49.1 (*c* 0.35, $CHCl_3$).

^{1}H-NMR: δ 4.46 (dd, *J* = 7.1, 2.1 Hz, 1H), 4.44 – 4.34 (m, 1H), 4.34 – 4.22 (m, 2H), 3.44 (dd, *J* = 16.6, 9.2 Hz, 1H), 3.30 (dd, *J* = 16.6, 4.0 Hz, 1H), 1.98 – 1.75 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H), 0.95 (s, 9H) ppm.

^{13}C-NMR: δ 169.8, 154.7, 65.6, 61.1, 59.4, 43.9, 35.8, 31.4, 25.7, 10.8 ppm.

HRMS (ESI$^+$): calculated for $C_{12}H_{21}NO_3Cl$ $[M+H]^+$: 262.1205; found: 262.1215.

(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chlorooctanoyl)oxazolidin-2-one (3d)



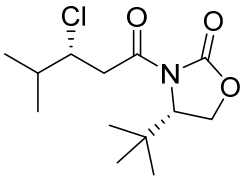
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(oct-2-enoyl)oxazolidin-2-one **1d** (26.7 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and allyltrichlorosilane (60 μL, 0.4 mmol, 0.4 eq.), gave **3d** as a yellow oil (83% yield, 92:8 *dr*). Eluent: cyclohexane: ethyl acetate 4:1. $[\alpha]^{20}_{D}$ = +25.8 (*c* 0.78, $CHCl_3$).

^{1}H-NMR: δ 4.51 – 4.38 (m, 2H), 4.34 – 4.22 (m, 2H), 3.44 (dd, *J* = 16.6, 9.2 Hz, 1H), 3.29 (dd, *J* = 16.6, 4.0 Hz, 1H), 1.87 – 1.74 (m, 2H), 1.66 – 1.40 (m, 2H), 1.40 – 1.24 (m, 4H), 0.95 (s, 9H), 0.93 – 0.86 (m, 3H) ppm.

^{13}C-NMR: δ 169.8, 154.7, 65.6, 61.1, 58.0, 44.2, 38.2, 35.8, 31.2, 25.7, 25.6, 22.5, 13.9 ppm.

HRMS (ESI$^+$): calculated for $C_{15}H_{27}NO_3Cl$ $[M+H]^+$: 292.0543; found: 292.0531.

(*S*)-4-(*tert*-butyl)-3-((*R*)-3-chloro-4-methylpentanoyl)oxazolidin-2-one (3e)



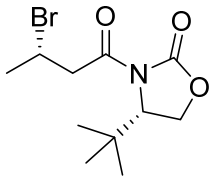
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(4-methylpent-2-enoyl)oxazolidin-2-one **1e** (23.9 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and allyltrichlorosilane (60 μL, 0.4 mmol, 0.4 eq.), gave **3e** as a yellow oil (70% yield). Eluent: cyclohexane: ethyl acetate from 9:1 to 3:1. $[\alpha]^{20}_{D}$ = +77.3 (*c* 1.00, $CHCl_3$).

^{1}H-NMR: δ 4.55 – 4.37 (m, 2H), 4.35 – 4.22 (m, 2H), 3.47 (dd, *J* = 16.4, 10.2 Hz, 1H), 3.29 – 3.17 (m, 1H), 2.05 (ddd, *J* = 13.4, 6.7, 4.2 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.95 (s, 9H) ppm.

^{13}C-NMR: δ 170.1, 154.7, 65.6, 64.1, 61.2, 41.8, 35.8, 34.3, 25.7, 19.7, 17.3 ppm.

HRMS (ESI$^+$): calculated for $C_{13}H_{23}NO_3Cl$ $[M+H]^+$: 276.1361; found: 276.1325.

(*S*)-3-((*S*)-3-Bromobutanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4a)



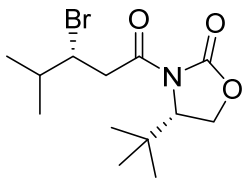
Following general procedure C, (*S,E*)-3-(but-2-enoyl)-4-(*tert*-butyl)oxazolidin-2-one **1b** (21.1 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4a** as a yellow oil (86% yield). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_D$** = +57.1 (*c* 0.30, $CHCl_3$).

^{1}H-NMR: δ 4.65 – 4.51 (m, 1H), 4.45 (dd, *J* = 7.0, 2.2 Hz, 1H), 4.35 – 4.23 (m, 2H), 3.61 (dd, *J* = 17.1, 8.9 Hz, 1H), 3.39 (dd, *J* = 17.1, 4.6 Hz, 1H), 1.80 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 9H) ppm.

^{13}C-NMR: δ 169.7, 154.6, 65.6, 61.1, 46.2, 43.4, 35.8, 26.3, 25.7 ppm.

HRMS (ESI$^+$): calculated for $C_{11}H_{19}NO_3Br$ $[M+H]^+$: 292.0543; found: 292.0531.

(*S*)-3-((*R*)-3-Bromo-4-methylpentanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4b)



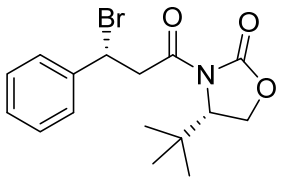
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(4-methylpent-2-enoyl)oxazolidin-2-one **1e** (23.9 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4b** as a yellow oil (78% yield). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_D$** = +59.2 (*c* 0.45, $CHCl_3$).

^{1}H-NMR: δ 4.56 – 4.43 (m, 2H), 4.34 – 4.23 (m, 2H), 3.68 (dd, *J* = 16.8, 10.3 Hz, 1H), 3.31 (dd, *J* = 16.8, 3.2 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 9H) ppm.

^{13}C-NMR: δ 170.2, 154.7, 65.6, 61.2, 58.2, 42.2, 35.8, 34.5, 25.7, 20.8, 18.2 ppm.

HRMS (ESI$^+$): calculated for $C_{13}H_{23}NO_3Br$ $[M+H]^+$: 320.0856; found: 320.0843.

(*S*)-3-((*R*)-3-Bromo-3-phenylpropanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4c)



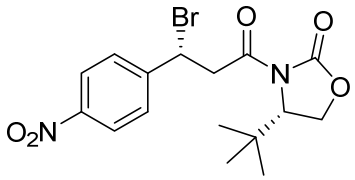
Following general procedure C, (*S*)-4-(*tert*-butyl)-3-cinnamoyloxazolidin-2-one **1f** (27.3 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4c** as a dark yellow oil (81% yield). Eluent: cyclohexane: ethyl acetate 4:1. $[\alpha]^{20}_{D}$ = +45.8 (*c* 0.35, $CHCl_3$).

^{1}H-NMR: δ 7.52 – 7.46 (m, 2H), 7.38 – 7.27 (m, 3H), 5.53 (dd, *J* = 8.9, 5.8 Hz, 1H), 4.44 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.36 – 4.21 (m, 2H), 4.03 (dd, *J* = 17.0, 8.9 Hz, 1H), 3.86 (dd, *J* = 17.0, 5.8 Hz, 1H), 0.83 (s, 9H) ppm.

^{13}C-NMR: δ 169.4, 154.6, 140.8, 128.8, 128.7, 127.4, 65.6, 61.2, 48.0, 44.8, 35.7, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{21}NO_3Br$ $[M+H]^+$: 354.0700; found: 354.0714.

(*S*)-3-((*R*)-3-Bromo-3-(4-nitrophenyl)propanoyl)-4-(tert-butyl)oxazolidin-2-one (4d)



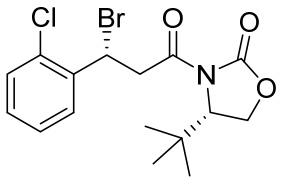
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(3-(4-nitrophenyl)acryloyl)oxazolidin-2-one **1g** (31.8 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4d** and **4d'** as a yellow oil (85% yield, 90:10 *dr*). Eluent: cyclohexane: ethyl acetate from 9:1 to 4:1. $[\alpha]^{20}_{D}$ = +67.2 (*c* 1.25, $CHCl_3$).

^{1}H-NMR: δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 5.54 (dd, *J* = 8.2, 6.5 Hz, 1H), 4.42 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.36 – 4.26 (m, 2H), 3.98 (dd, *J* = 17.2, 8.2 Hz, 1H), 3.88 (dd, *J* = 17.2, 6.5 Hz, 1H), 0.83 (s, 9H) ppm.

^{13}C-NMR: δ 168.7, 154.5, 147.8, 147.7, 128.5, 124.0, 65.7, 61.2, 45.1, 44.8, 35.7, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{20}N_2O_5Br$ $[M+H]^+$: 399.0550; found: 399.0563.

(*S*)-3-((*R*)-3-Bromo-3-(2-chlorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4e)



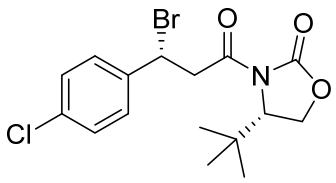
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(3-(2-chlorophenyl)acryloyl)oxazolidin-2-one **1h** (30.8 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4e** as a white solid (72% yield). Eluent: cyclohexane: ethyl acetate from 95:5 to 3:1. **$[\alpha]^{20}_D$** = +39.3 (*c* 1.51, $CHCl_3$).

^{1}H-NMR: δ 7.64 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.42 – 7.18 (m, 3H), 5.98 (dd, *J* = 8.8, 5.8 Hz, 1H), 4.44 (dd, *J* = 6.3, 2.8 Hz, 1H), 4.34 – 4.24 (m, 2H), 4.13 (dd, *J* = 17.4, 8.8 Hz, 1H), 3.84 (dd, *J* = 17.4, 5.8 Hz, 1H), 0.85 (s, 9H) ppm.

^{13}C-NMR: δ 169.0, 154.6, 138.1, 133.0, 130.0, 129.7, 128.7, 127.5, 65.6, 61.2, 43.6, 43.0, 35.7, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{20}NO_3BrCl$ $[M+H]^+$: 388.0310; found: 388.0325.

(*S*)-3-((*R*)-3-Bromo-3-(4-chlorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4f)



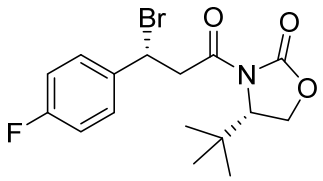
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(3-(4-chlorophenyl)acryloyl)oxazolidin-2-one **1i** (30.8 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4f** and **4f'** as a yellow oil (71% yield, 90:10 *dr*). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_D$** = +49.1 (*c* 0.51, $CHCl_3$).

^{1}H-NMR: δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.49 (dd, *J* = 8.7, 6.0 Hz, 1H), 4.43 (dd, *J* = 6.9, 2.2 Hz, 1H), 4.34 – 4.26 (m, 2H), 3.97 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.84 (dd, *J* = 16.8, 6.2 Hz, 1H), 0.84 (s, 9H) ppm.

^{13}C-NMR: δ 169.1, 154.6, 139.4, 134.5, 129.0, 128.8, 65.6, 61.2, 46.7, 44.8, 35.7, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{20}NO_3BrCl$ $[M+H]^+$: 388.0310; found: 388.0322.

(*S*)-3-((*R*)-3-Bromo-3-(4-fluorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4g)



Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(3-(4-fluorophenyl)acryloyl)oxazolidin-2-one **1j** (29.1 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4g** and **4g'** as a yellow oil (79% yield, 95:5 *dr*). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_D$** = +95.7 (*c* 0.94, $CHCl_3$).

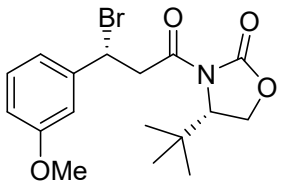
^{1}H-NMR: δ 7.53 – 7.43 (m, 2H), 7.12 – 6.97 (m, 2H), 5.51 (dd, *J* = 8.6, 6.1 Hz, 1H), 4.43 (dd, *J* = 6.7, 2.4 Hz, 1H), 4.34 – 4.25 (m, 2H), 3.98 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.86 (dd, *J* = 17.0, 6.2 Hz, 1H), 0.83 (s, 9H) ppm.

^{13}C-NMR: δ 169.2, 162.6 (d, *J* = 248.4 Hz), 154. 6, 136.8 (d, *J* = 3.4 Hz), 129.3 (d, *J* = 8.4 Hz), 115.7 (d, *J* = 21.8 Hz), 65.6, 61.1, 46.9, 45.0, 35.7, 25.5 ppm.

^{19}F-NMR: δ -112.6 ppm.

HRMS (ESI$^+$): calculated for $C_{16}H_{20}NO_3BrF$ $[M+H]^+$: 372.0605; found: 372.0618.

(*S*)-3-((*R*)-3-Bromo-3-(3-methoxyphenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4h)



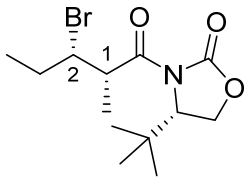
Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(3-(3-methoxyphenyl)acryloyl)oxazolidin-2-one **1k** (30.3 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4h** as a yellow oil (61% yield). Eluent: cyclohexane: ethyl acetate from 98:2 to 3:1. **$[\alpha]^{20}_D$** = +99.9 (*c* 1.01, $CHCl_3$).

^{1}H-NMR: δ 7.29 – 7.21 (m, 1H), 7.10 – 7.01 (m, 2H), 6.86 – 6.80 (m, 1H), 5.49 (dd, *J* = 8.8, 5.8 Hz, 1H), 4.44 (dd, *J* = 6.6, 2.5 Hz, 1H), 4.33 – 4.23 (m, 2H), 3.99 (dd, *J* = 16.9, 8.8 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.82 (s, 3H), 0.84 (s, 9H) ppm.

^{13}C-NMR: δ 169.3, 159.8, 154.6, 142.2, 129.8, 119.6, 114.5, 112.9, 65.5, 61.2, 55.3, 47.9, 44.7, 35.7, 25.5 ppm.

HRMS (ESI$^+$): calculated for $C_{17}H_{23}NO_4Br$ $[M+H]^+$: 384.0805; found: 384.0798.

(*S*)-3-((*2S,3S*)-3-Bromo-2-methylpentanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4i)



Following general procedure C, (*S,E*)-4-(*tert*-butyl)-3-(2-methylpent-2-enoyl)oxazolidin-2-one **1m** (23.9 mg, 0.1 mmol, 1.0 eq.), tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and tribromo(phenyl)silane (75 μL, 0.4 mmol, 0.4 eq.), gave **4i** as a yellow oil (55% yield). Eluent: cyclohexane: ethyl acetate 4:1. **$[\alpha]^{20}_D$** = +23.4 (*c* 0.14, $CHCl_3$).

^{1}H-NMR: δ 4.55 – 4.45 (m, 2H), 4.37 – 4.23 (m, 2H), 3.95 (qd, *J* = 6.7, 3.7 Hz, 1H), 2.05 – 1.87 (m, 2H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.10 (t, *J* = 7.3 Hz, 3H), 0.97 (s, 9H) ppm.

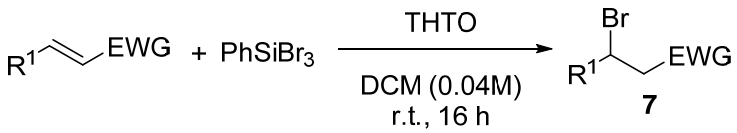
^{13}C-NMR: δ 173.3, 154.6, 65.4, 61.1, 60.2, 43.7, 35.8, 26.9, 25.7, 12.5, 12.1 ppm.

HRMS (ESI$^+$): calculated for $C_{13}H_{22}NO_3BrNa$ $[M+Na]^+$: 342.0675; found: 342.0667.

The relative stereochemistry between the bromide and the methyl substituents was determined as *syn*. The coupling constant of 3.7 Hz between H_1 and H_2 can only be assumed if both hydrogens are in a *syn* disposition.[5]

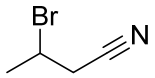
[5] Following Karplus equation: $^3J_{gauche}$= 2-5 Hz and $^3J_{anti}$ = 8 – 15 Hz

5. General procedure D for the nucleophilic bromination to diverse Michael acceptors.



The corresponding Michael acceptor (0.1 mmol, 1.0 eq.) was dissolved in dichloromethane (2.5 mL) in a vial. Then, tetrahydrothiophene 1-oxide (40 μL, 0.4 mmol, 4.0 eq.) and the tribromo(phenyl)silane (75 μL, 0.4 mmol, 4 eq.) were added and the reaction was stirred for 16 hours. Finally, the crude mixture was purified by flash column chromatography using Iatrobeads silica gel and eluting with the solvent indicated in each case.

3-Bromobutanenitrile (7a)[6]

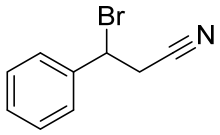


Following general procedure D, (*E*)-but-2-enenitrile (8 μL, 0.1 mmol, 1 eq.) gave **7a** as a yellow oil (92% yield). Eluent: cyclohexane: ethyl acetate 9:1. The NMR is in accordance with the literature.

^{1}H-NMR: δ 4.29 – 4.17 (m, 1H), 2.95 (d, *J* = 6.7, Hz, 2H), 1.84 (dd, *J* = 6.7, 1.0 Hz, 3H) ppm.

^{13}C-NMR: δ 116.5, 40.0, 29.7, 25.4 ppm.

3-Bromo-3-phenylpropanenitrile (7b)



Following general procedure D, cinnamonitrile (13 μL, 0.1 mmol, 1 eq.) gave **7b** as a yellow oil (70% yield). Eluent: cyclohexane: ethyl acetate 9:1.

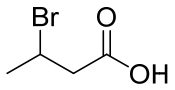
^{1}H-NMR: δ 7.65 – 7.29 (m, 5H), 5.14 (t, *J* = 7.1 Hz, 1H), 3.29 (dd, *J* = 17.0, 7.1 Hz, 1H), 3.22 (dd, *J* = 17.0, 7.1 Hz, 1H) ppm.

^{13}C-NMR: δ 138.7, 129.5, 129.1, 127.0, 116.4, 45.3, 29.4 ppm.

The desired mass for HRMS was not detected.

[6] National Institute of Advanced Industrial Science and Technology (AIST).

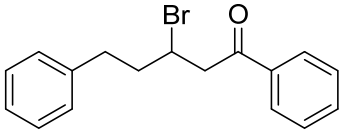
3-Bromobutanoic acid (7c)[7]



Following general procedure D, methyl crotonate (11 μL, 0.1 mmol, 1.0 eq.) gave **7c** as a yellow oil (55% yield). Eluent: cyclohexane: ethyl acetate 4:1. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 4.53 – 4.37 (m, 1H), 3.08 – 2.83 (m, 2H), 1.78 (d, *J* = 6.7 Hz, 3H) ppm.

3-Bromo-1,5-diphenylpentan-1-one (7d)



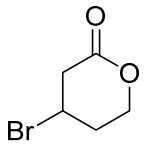
Following general procedure D, (*E*)-1,5-diphenylpent-2-en-1-one (23.6 mg, 0.1 mmol, 1 eq.) gave **7d** as a yellow oil (80% yield). Eluent: cyclohexane: ethyl acetate 4:1.

^{1}H-NMR: δ 7.96 – 7.91 (m, 2H), 7.68 – 7.53 (m, 1H), 7.52 – 7.41 (m, 2H), 7.37 – 7.15 (m, 5H), 4.59 4.65 – 4.53 (m, 1H), 3.75 (dd, *J* = 17.4, 7.3 Hz, 1H), 3.43 (dd, *J* = 17.4, 6.1 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.88 – 2.76 (m, 1H), 2.35 – 2.09 (m, 2H) ppm.

^{13}C-NMR: δ 196.5, 140.6, 136.5, 133.5, 128.7, 128.7, 128.5, 128.1, 126.2, 49.3, 47.7, 40.5, 33.8 ppm.

HRMS (ESI$^+$): calculated for $C_{17}H_{17}BrONa$ $[M+Na]^+$: 339.0354; found: 339.0341.

4-Bromotetrahydro-2H-pyran-2-one (7e)



Following general procedure D, 5,6-dihydro-2H-pyran-2-one (9 μL, 0.1 mmol, 1 eq.) gave **7e** as a yellow oil (65% yield). Eluent: cyclohexane: ethyl acetate 7:3.

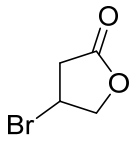
^{1}H-NMR: δ 4.67 (ddd, *J* = 11.9, 7.8, 4.3 Hz, 1H), 4.52 – 4.43 (m, 1H), 4.43 – 4.34 (m, 1H), 3.23 (dd, *J* = 18.2, 5.6, 1H), 3.03 (ddd, *J* = 18.2, 6.3, 1.1 Hz, 1H), 2.45 – 2.30 (m, 1H), 2.31 – 2.17 (m, 1H) ppm.

^{13}C-NMR: δ 167.20, 66.7, 41.0, 40.8, 32.3 ppm.

The desired mass for HRMS was not detected.

[7] G.-A. Olah, R. Karpeles and S.-C. Narang, *Synthesis*, 1982, **11**, 963.

4-Bromodihydrofuran-2(3H)-one (7f)[8]

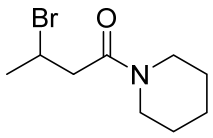


Following general procedure D, furan-2(5H)-one (8 μL, 0.1 mmol, 1 eq.) gave **7f** as a yellow oil (60% yield). Eluent: cyclohexane: ethyl acetate 4:1. The NMR is in accordance with the literature.

^{1}H-NMR: δ 4.73 – 4.60 (m, 1H), 4.59 – 4.51 (m, 1H), 3.23 – 3.06 (m, 1H), 2.98 – 2.88 (m, 1H), 2.89 – 2.85 (m, 1H) ppm.

^{13}C-NMR: δ 173.5, 75.5, 39.8, 39.3 ppm.

3-Bromo-1-(piperidin-1-yl)butan-1-one (7g)



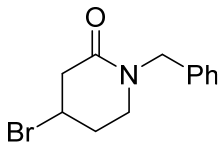
Following general procedure D, (*E*)-1-(piperidin-1-yl)but-2-en-1-one (15 mg, 0.1 mmol, 1 eq.) gave **7g** as a yellow oil (40% yield). Eluent: cyclohexane: ethyl acetate 4:1.

^{1}H-NMR: δ 4.61 (h, *J* = 6.7 Hz, 1H), 3.69 – 3.56 (m, 1H), 3.56 – 3.46 (m, 1H), 3.49 – 3.33 (m, 2H), 3.06 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.75 (dd, *J* = 15.6, 6.7 Hz, 1H), 1.78 (d, *J* = 6.7 Hz, 3H), 1.71 – 1.50 (m, 6H) ppm.

^{13}C-NMR: δ 167.8, 46.8, 45.5, 44.1, 42.9, 26.6, 26.5, 25.5, 24.5 ppm.

HRMS (ESI$^+$): calculated for $C_9H_{16}NOBrNa$ $[M+Na]^+$: 256.0307; found: 256.0309.

4-Bromo-1-ethylpiperidin-2-one (7h)



Following general procedure D, 1-benzyl-5,6-dihydropyridin-2(1H)-one (19 mg, 0.1 mmol, 1 eq.) gave **7h** as a yellow oil (70% yield). Eluent: cyclohexane: ethyl acetate 4:1.

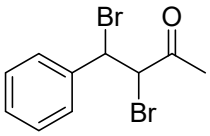
^{1}H-NMR: δ 7.38 – 7.22 (m, 1H), 4.68 (d, *J* = 14.7 Hz, 1H), 4.58 (d, *J* = 14.7 Hz, 1H), 4.48 – 4.40 (m, 1H), 3.48 (ddd, *J* = 12.6, 7.4, 5.1 Hz, 1H), 3.27 – 3.08 (m, 2H), 3.00 – 2.92 (m, 1H), 2.39 – 2.09 (m, 1H) ppm.

^{13}C-NMR: δ 166.4, 136.5, 128.7, 128.1, 127.6, 50.1, 44.4, 43.5, 42.4, 32.2 ppm.

HRMS (ESI$^+$): calculated for $C_{12}H_{14}NOBrNa$ $[M+Na]^+$: 290.0151; found: 290.0145.

[8] N.-J. Van Zee and V. Dragojlovic, *Org. Lett.*, 2009, **11**, 3190.

3,4-Dibromo-4-phenylbutan-2-one (8a)[9]

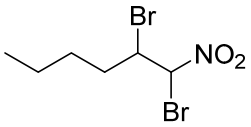


Following general procedure D, (*E*)-4-phenylbut-3-en-2-one (14.6 mg, 0.1 mmol, 1 eq.) gave **8a** as a brown solid (75% yield). Eluent: cyclohexane: ethyl acetate 90:10. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 7.51 – 7.34 (m, 5H), 5.32 (d, *J* = 11.7 Hz, 1H), 4.93 (d, *J* = 11.7 Hz, 1H), 2.48 (s, 3H) ppm.

^{13}C-NMR: δ 198.3, 137.8, 129.3, 128.9, 128.1, 52.8, 49.5, 26.9 ppm.

1,2-Dibromo-1-nitrohexane (8b)



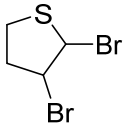
Following general procedure D, (*E*)-1-nitrohex-1-ene (13.0 mg, 0.1 mmol, 1 eq.) gave **8b** as a yellow oil (55% yield). Eluent: cyclohexane: ethyl acetate 95:5.

^{1}H-NMR: δ 5.97 (d, *J* = 10.1 Hz, 1H), 4.52 (ddd, *J* = 10.1, 9.3, 2.8 Hz, 1H), 2.24 – 2.08 (m, 1H), 1.93 – 1.79 (m, 1H), 1.65 – 1.29 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR: δ 80.6, 50.9, 33.6, 28.3, 21.8, 13.7 ppm.

The desired mass for HRMS was not detected.

2,3-Dibromotetrahydrothiophene (SI2)



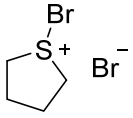
Following general procedure D, **SI2** was obtained as an impurity in all the cases.

^{1}H-NMR: δ 5.86 – 5.79 (m, 1H), 5.03 (d, *J* = 3.9 Hz, 1H), 3.51 – 3.40 (m, 1H), 3.39 – 3.29 (m, 1H), 2.96 – 2.80 (m, 1H), 2.58 – 2.46 (m, 1H) ppm.

^{13}C-NMR: δ 65.1, 58.8, 36.1, 31.8 ppm.

The desired mass for HRMS was not detected.

1-Bromotetrahydro-1H-thiophen-1-ium bromide (SI3)[10]



THTO (30 μL, 0.3 mmol, 1.0 eq.) and 2.5 mL of HFB were added in a vial. Then, the tribromo(phenyl)silane (56 μL, 0.3 mmol, 1.0 eq.) was added and the reaction mixture was stirred for 5 min. The mixture was filtrated through a Buchner funnel

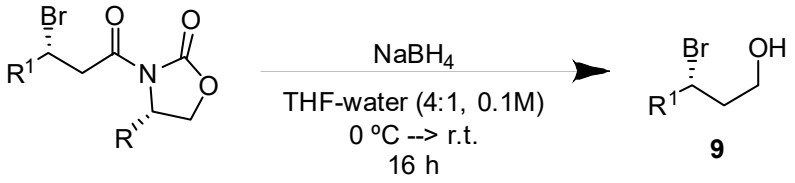
[9] K.-M. Kim and I.-H. Park, *Synthesis*, 2004, **16**, 2641.
[10] G. E. Wilson Jr. and R. Albert*, J. Org. Chem*., 1973, **38**, 2156.

and a yellow solid **SI3** was isolated and immediately stored under nitrogen atmosphere. The ^{1}H-NMR is in accordance with the literature.

^{1}H-NMR: δ 3.37 (bs, 4H), 2.30 (bs, 4H) ppm.

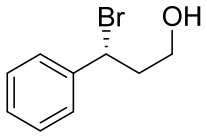
6. General procedures for the removal of the chiral auxiliary.

6.1. General procedure E: removal of the chiral auxiliary to the alcohol.



The corresponding β-halogenated oxazolidinone (0.1 mmol, 1.0 eq.) was dissolved in THF (0.8 mL) and water (0.2 mL) in a vial. Then, the mixture was cooled to 0 ^{o}C and $NaBH_4$ (15.1 mg, 0.4 mmol, 4.0 eq.) was added. The reaction was stirred for 16 h at room temperature. After that, the THF was evaporated under reduced pressure and the residue was diluted with water and extracted with AcOEt (3 x 3 mL). The organic phases were combined and dried over $MgSO_4$, filtered and evaporated. Finally, the crude mixture was purified by flash column chromatography using Iatrobeads silica gel and eluting with the solvent indicated in each case.

(*R*)-3-Bromo-3-phenylpropan-1-ol (9a)



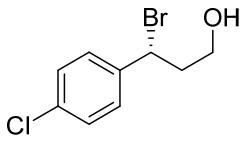
Following general procedure E, (*S*)-3-((*R*)-3-bromo-3-phenylpropanoyl)-4-(tert-butyl)oxazolidin-2-one **4c** (35.4 mg, 0.1 mmol, 1.0 eq.) gave **9a** as a yellow oil (58% yield). Eluent: cyclohexane: ethyl acetate 3:1. $[\alpha]^{20}_{D}$ = -2.7 (*c* 1.1, $CHCl_3$).

^{1}H-NMR: 7.46 – 7.28 (m, 5H), 5.23 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.91 – 3.81 (m, 1H), 3.80 – 3.70 (m, 1H), 2.59 – 2.43 (m, 1H), 2.40 – 2.27 (m, 1H) ppm.

^{13}C-NMR: δ 141.8, 128.8, 128.4, 127.3, 60.7, 52.0, 42.2 ppm.

The desired mass for HRMS was not detected.

(*R*)-3-Bromo-3-(4-chlorophenyl)propan-1-ol (9b)



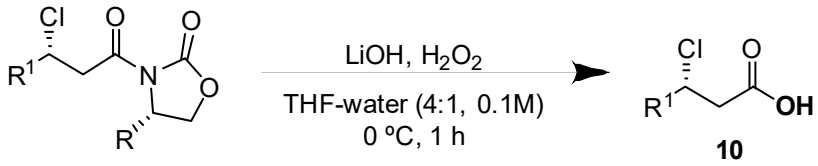
Following general procedure E, (*S*)-3-((*R*)-3-bromo-3-(4-chlorophenyl)propanoyl)-4-(tert-butyl)oxazolidin-2-one **4f** (38.8 mg, 0.1 mmol, 1.0 eq.) gave **9b** as a yellow oil (60% yield). Eluent: cyclohexane: ethyl acetate 3:1. $[\alpha]^{20}_{D}$ = -2.9 (*c* 0.99, $CHCl_3$).

^{1}H-NMR: δ 7.36 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 5.19 (dd, *J* = 9.2, 5.7 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.78 – 3.69 (m, 1H), 2.53 – 2.40 (m, 1H), 2.36 – 2.25 (m, 1H) ppm.

^{13}C-NMR: δ 140.4, 134.2, 128.9, 128.7, 60.4, 50.7, 42.1 ppm.

The desired mass for HRMS was not detected.

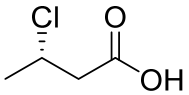
6.2. General procedure F: removal of the chiral auxiliary to the carboxylic acid.



10

The corresponding β-halogenated oxazolidinone (0.1 mmol, 1.0 eq.) was dissolved in THF (0.8 mL) and water (0.2 mL) in a vial. Then, the mixture was cooled to 0 ^{o}C and H_2O_2 (aq. solution 30%, 40 μL, 0.4 mmol, 4.0 eq.) was added and the mixture was stirred for 5 minutes. LiOH (6.3 mg, 0.15 mmol, 1.5 eq.) was then added and the reaction was stirred for 1h at 0 ^{o}C. After that, the THF was evaporated under reduced pressure and the residue was diluted with water and extracted with Et_2O (3 x 3 mL). The organic phases were combined and dried over $MgSO_4$, filtered and evaporated. Finally, the crude mixture was purified by flash column chromatography using Iatrobeads silica gel and eluting with the solvent indicated in each case.

(*S*)-3-Chlorobutanoic acid (10a)[11]

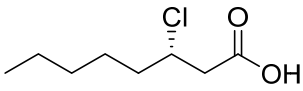


Following general procedure F, (*S*)-4-(tert-butyl)-3-((*S*)-3-chlorobutanoyl)oxazolidin-2-one **3b** (24.7 mg, 0.1 mmol, 1.0 eq.) gave **10a** as a yellow oil (45% yield) after distillation under reduced pressure (102 ^{o}C, 14 mmHg). $[\alpha]^{20}_{D}$ = -2.0 (*c* 1.48, $CHCl_3$). The NMR is in accordance with the literature.

^{1}H-NMR: δ 4.50 – 4.35 (m, 1H), 2.86 (dd, *J* = 16.3, 7.9 Hz, 1H), 2.76 (dd, *J* = 16.3, 6.0 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C-NMR: δ 175.3, 52.2, 44.7, 24.9 ppm.

(*S*)-3-Chlorooctanoic acid (10b)



Following general procedure F, (*S*)-4-(tert-butyl)-3-((*S*)-3-chlorooctanoyl)oxazolidin-2-one **3d** (31 mg, 0.1 mmol, 1.0 eq.) gave **10b** as a yellow oil (55% yield) after distillation under reduced pressure (154 ^{o}C, 22 mmHg). $[\alpha]^{20}_{D}$ = +1.1 (*c* 0.50, $CHCl_3$).

^{1}H-NMR: δ 4.35 – 4.22 (m, 1H), 2.81 (d, *J* = 6.9 Hz, 2H), 1.66 – 1.40 (m, 3H), 1.40 – 1.22 (m, 5H), 0.90 (t, *J* = 6.6 Hz, 3H) ppm.

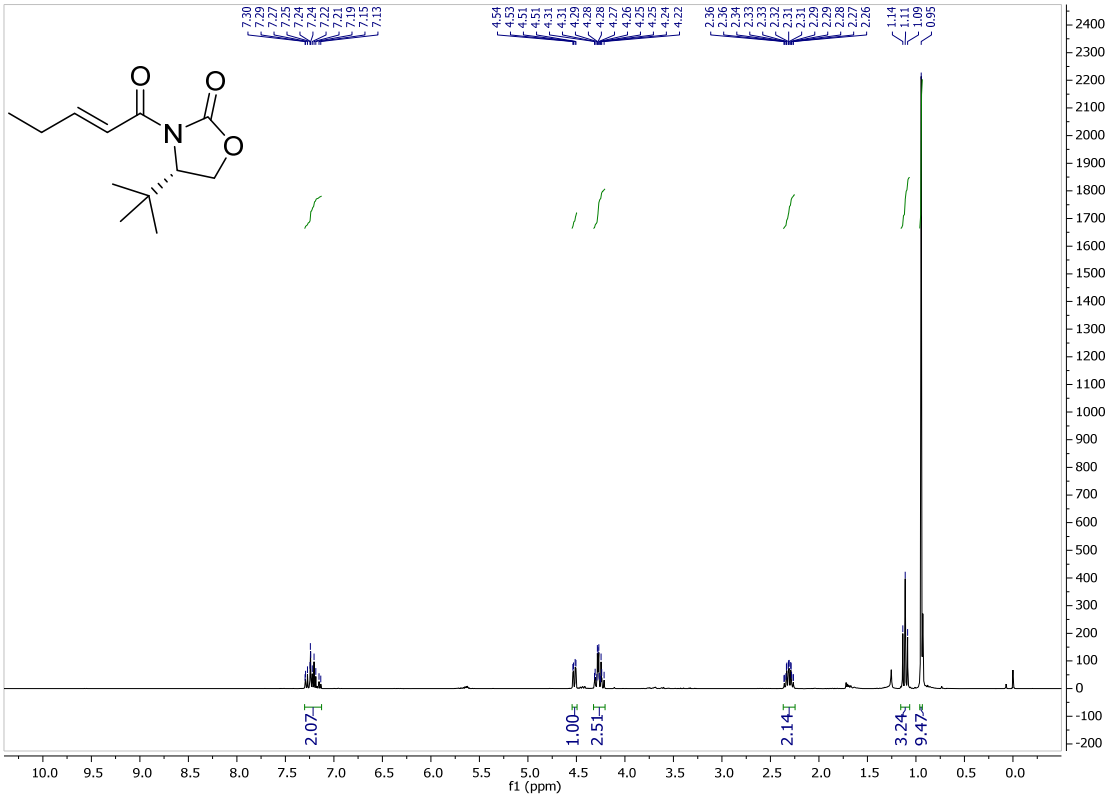
[11] Y. Tanaka, H. Sakuraba and H. Nakanishi, *J. Org. Chem.*, 1990, **55**, 564.

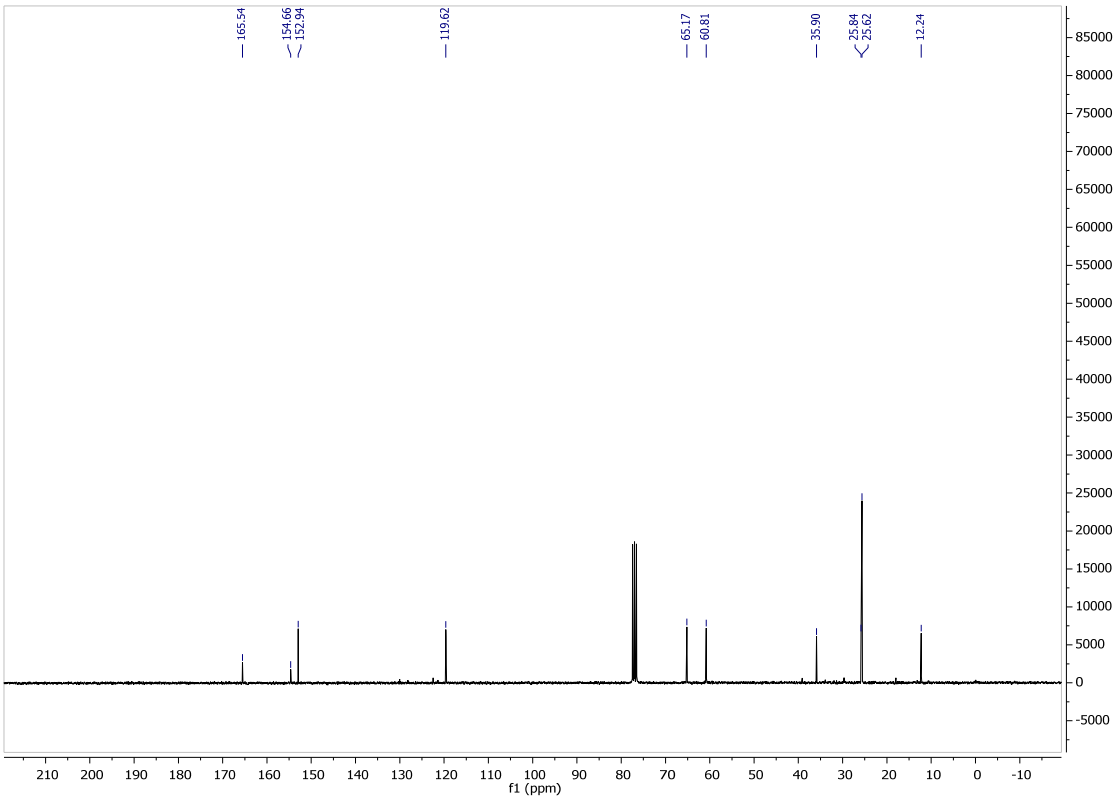
^{13}C-NMR: δ 152.8, 57.4, 37.9, 31.1, 25.9, 22.5, 22.5, 13.9 ppm.

HRMS (ESI$^+$): calculated for $C_8H_{16}ClO_2$ $[M+H]^+$: 179.0834; found: 179.0847.

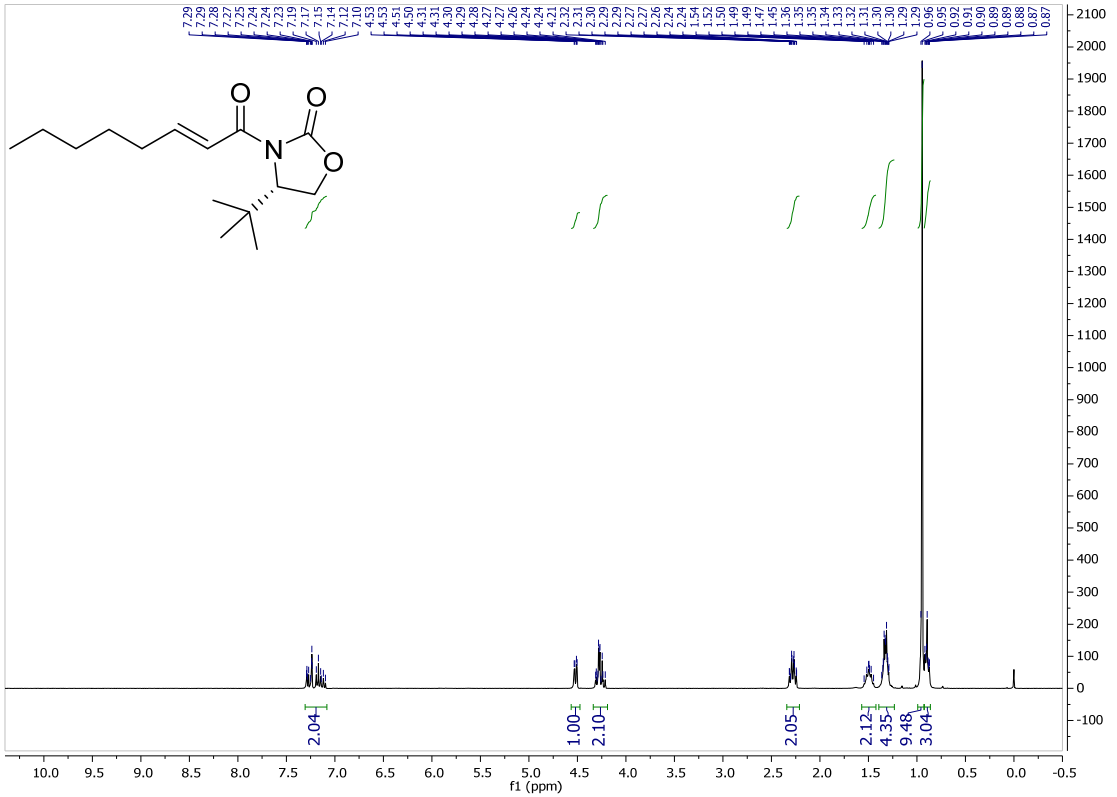
7. NMR spectra.

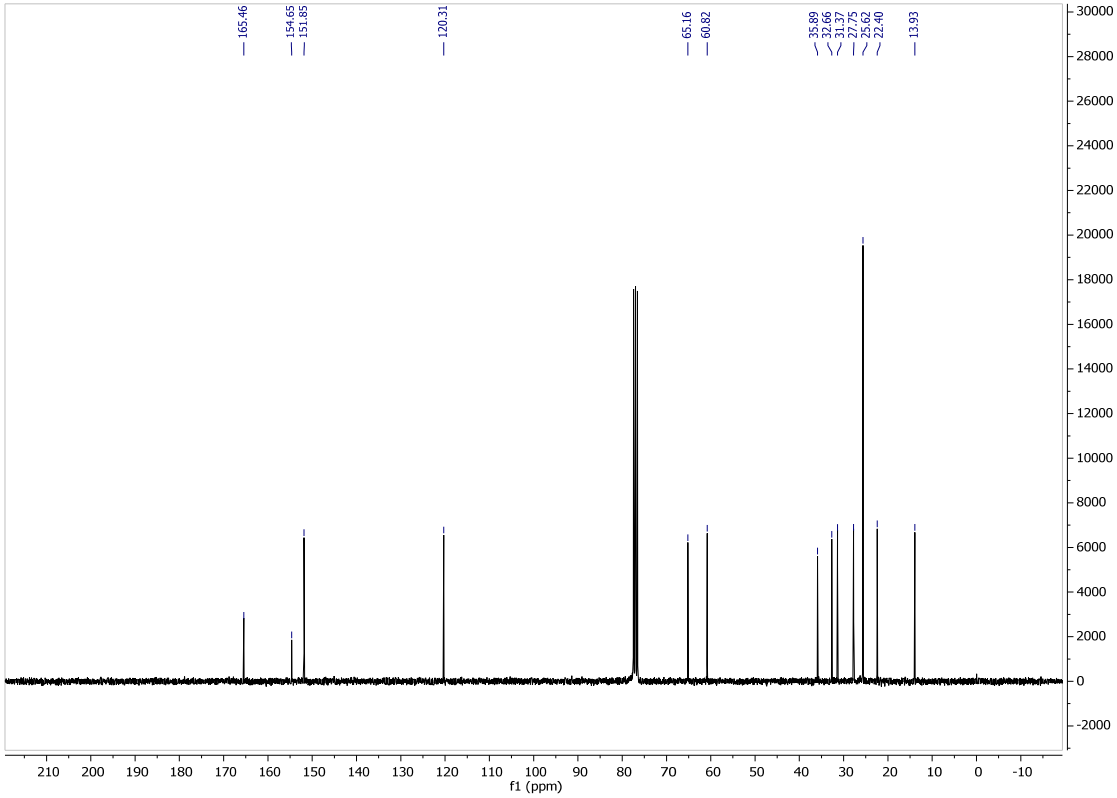
(*S,E*)-4-(*tert*-Butyl)-3-(pent-2-enoyl)oxazolidin-2-one (1c)



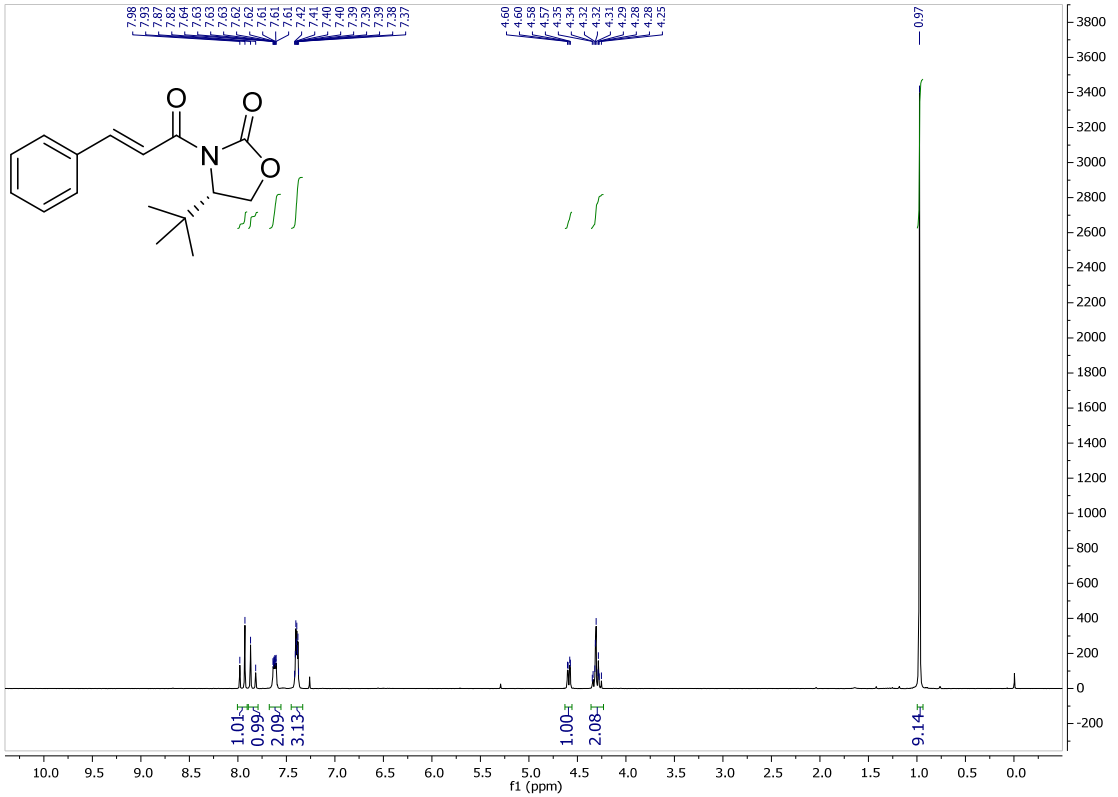


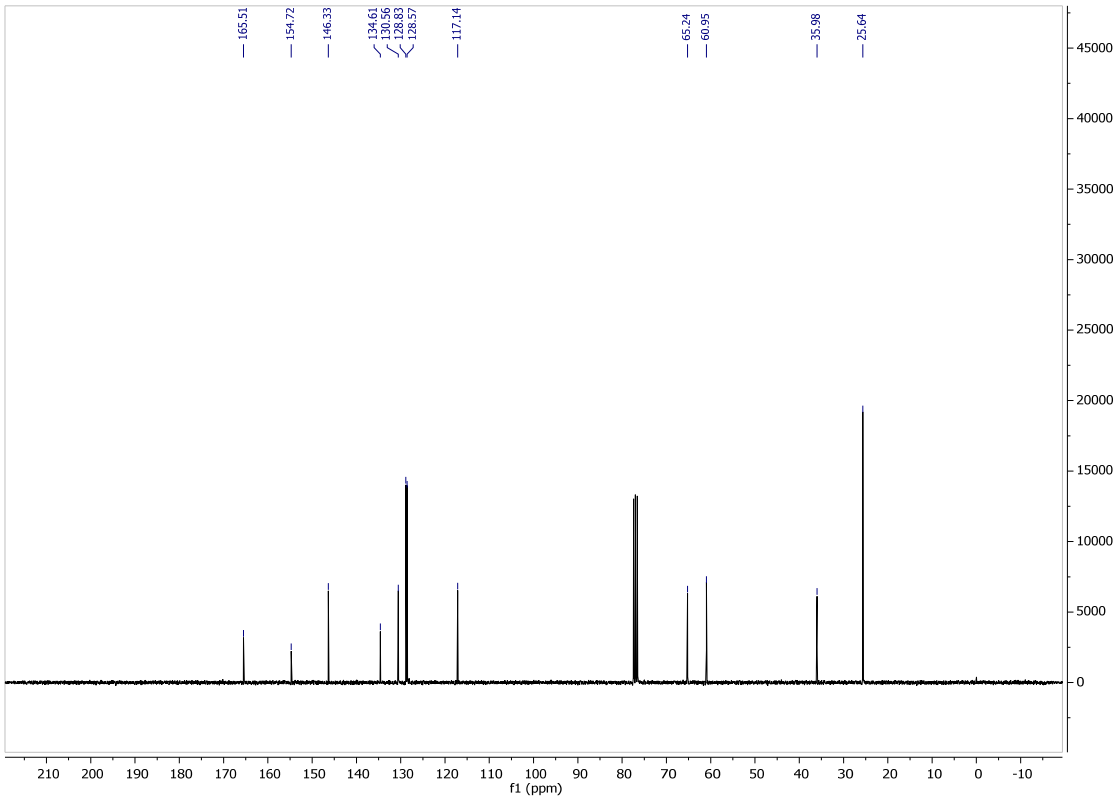
(*S*,*E*)-4-(*tert*-Butyl)-3-(oct-2-enoyl)oxazolidin-2-one (1d)



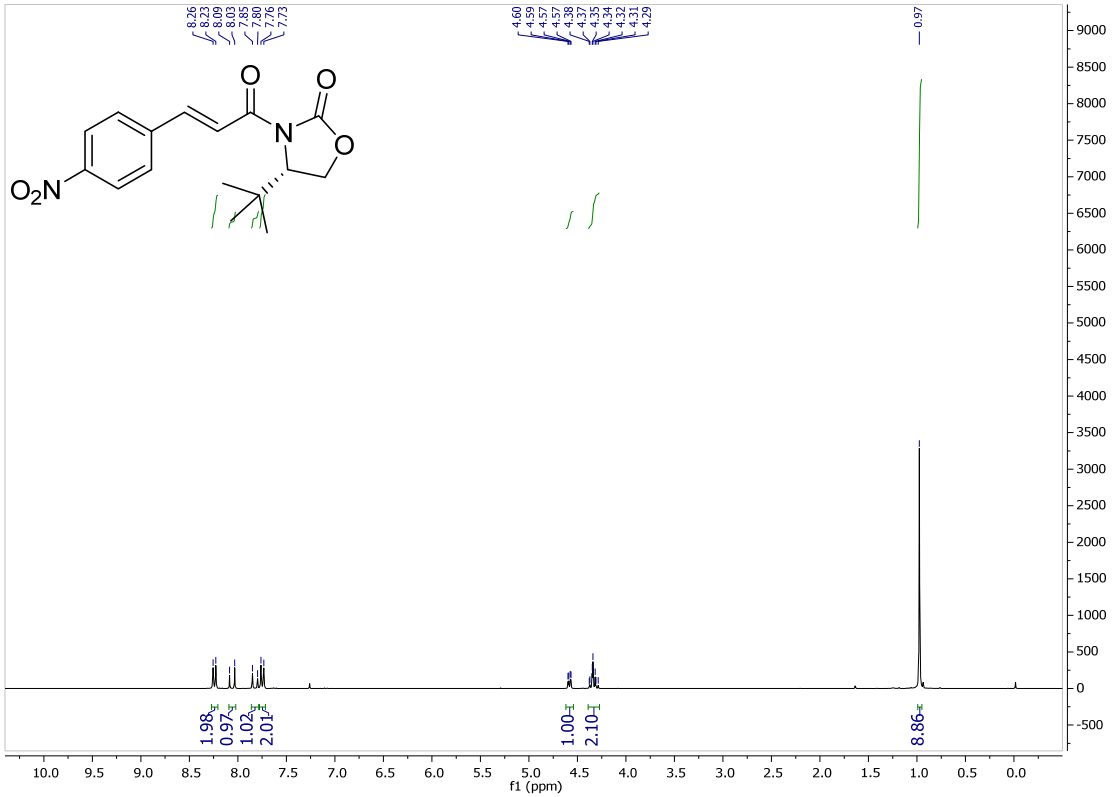


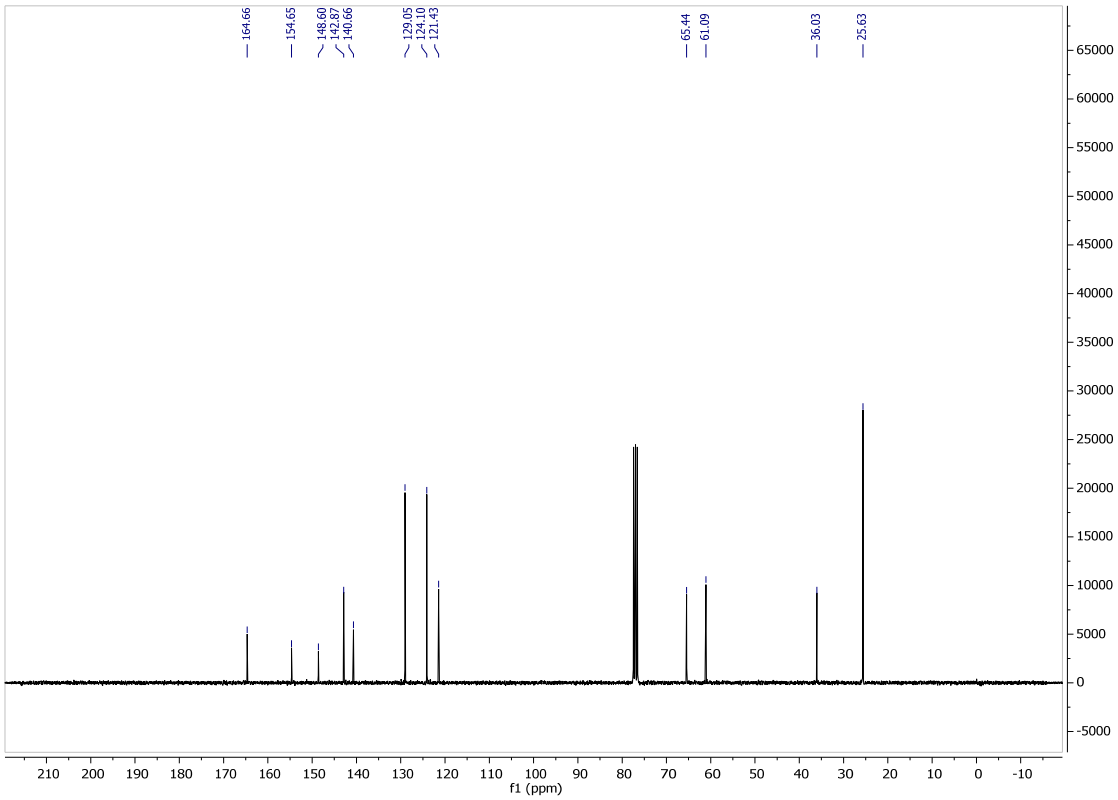
(*S*)-4-(*tert*-Butyl)-3-cinnamoyloxazolidin-2-one (1f)



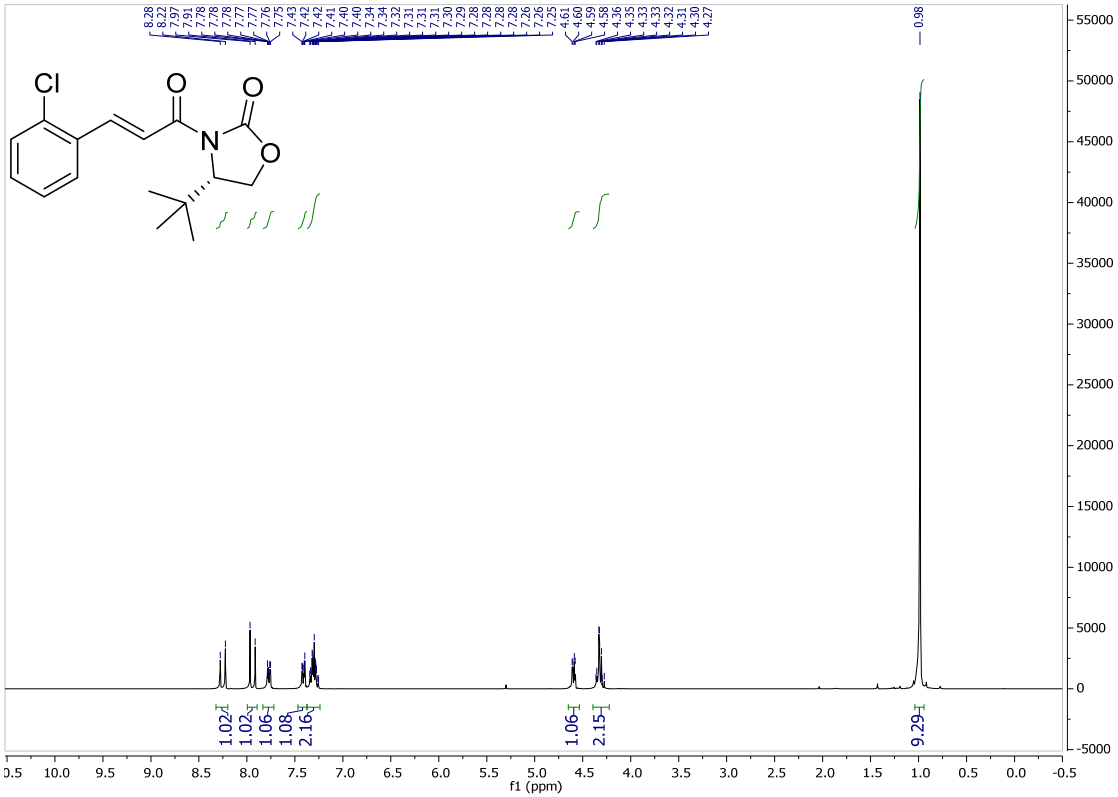


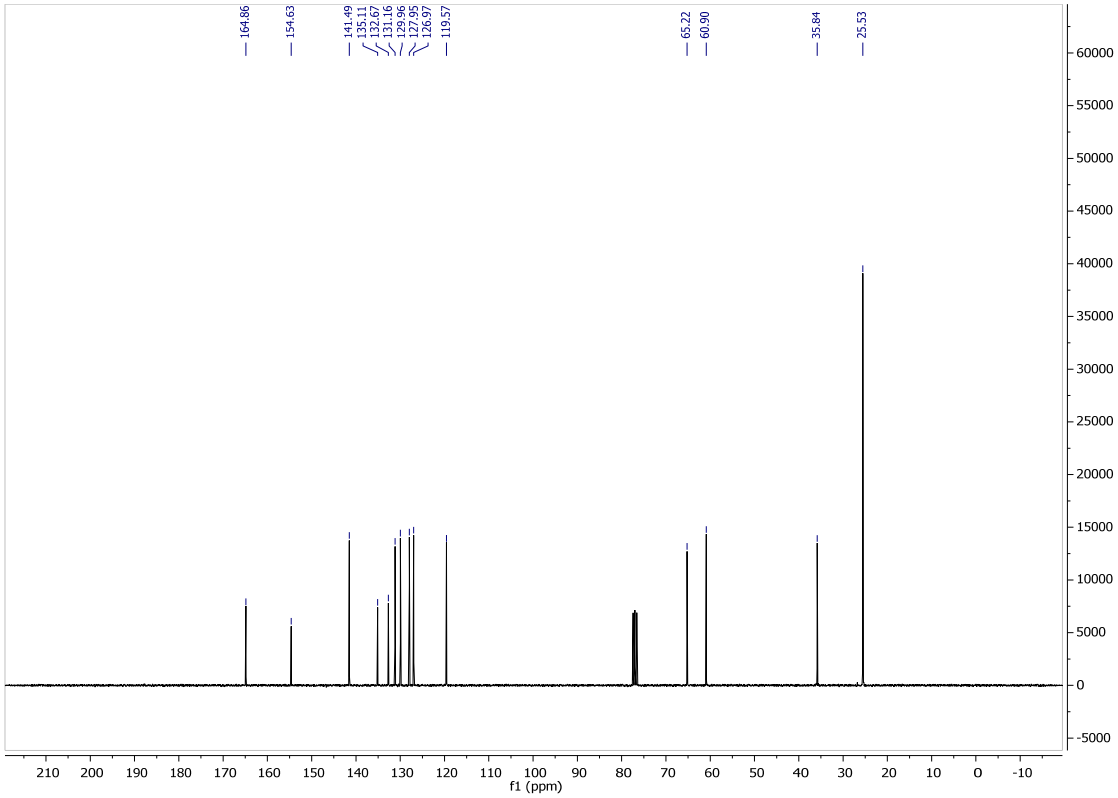
(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(4-nitrophenyl)acryloyl)oxazolidin-2-one (1g)



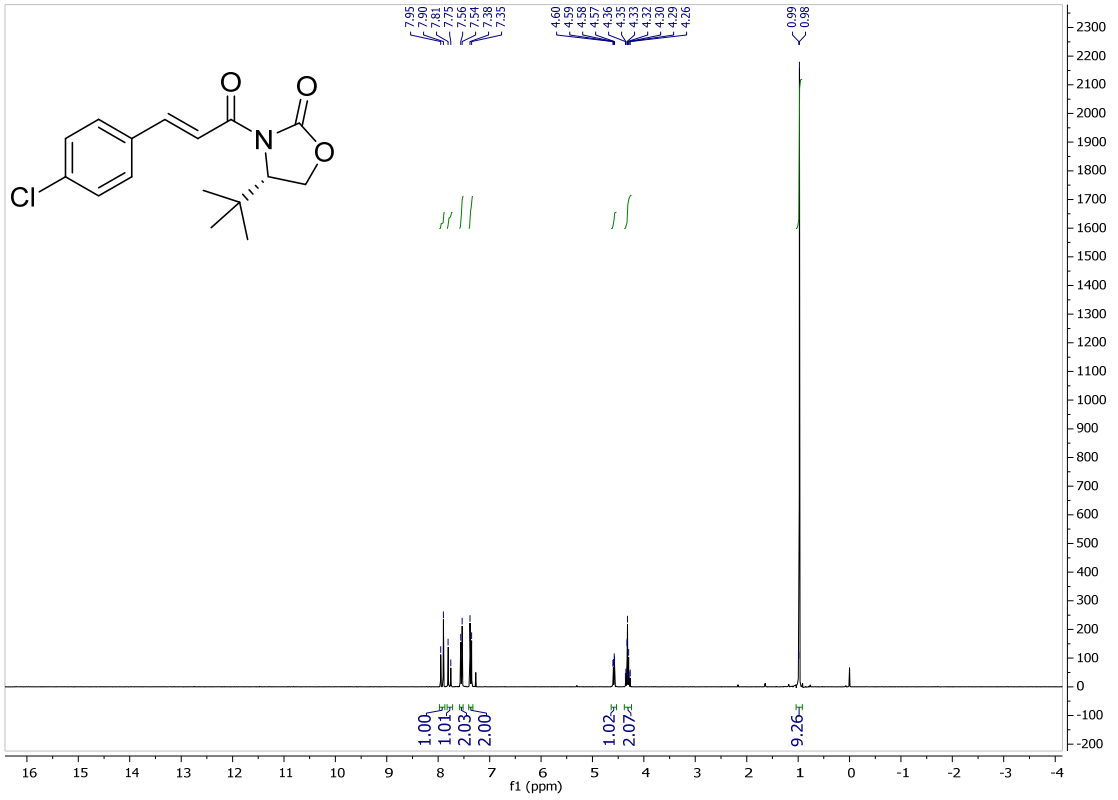


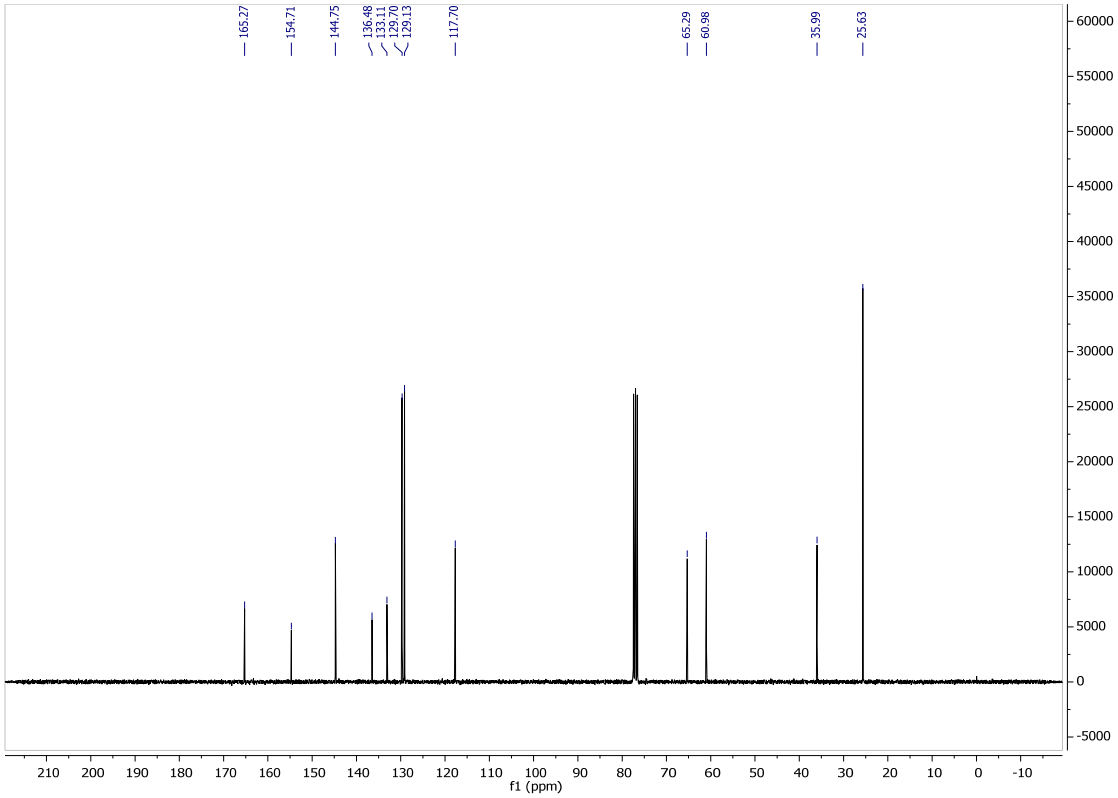
(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(2-chlorophenyl)acryloyl)oxazolidin-2-one (1h)



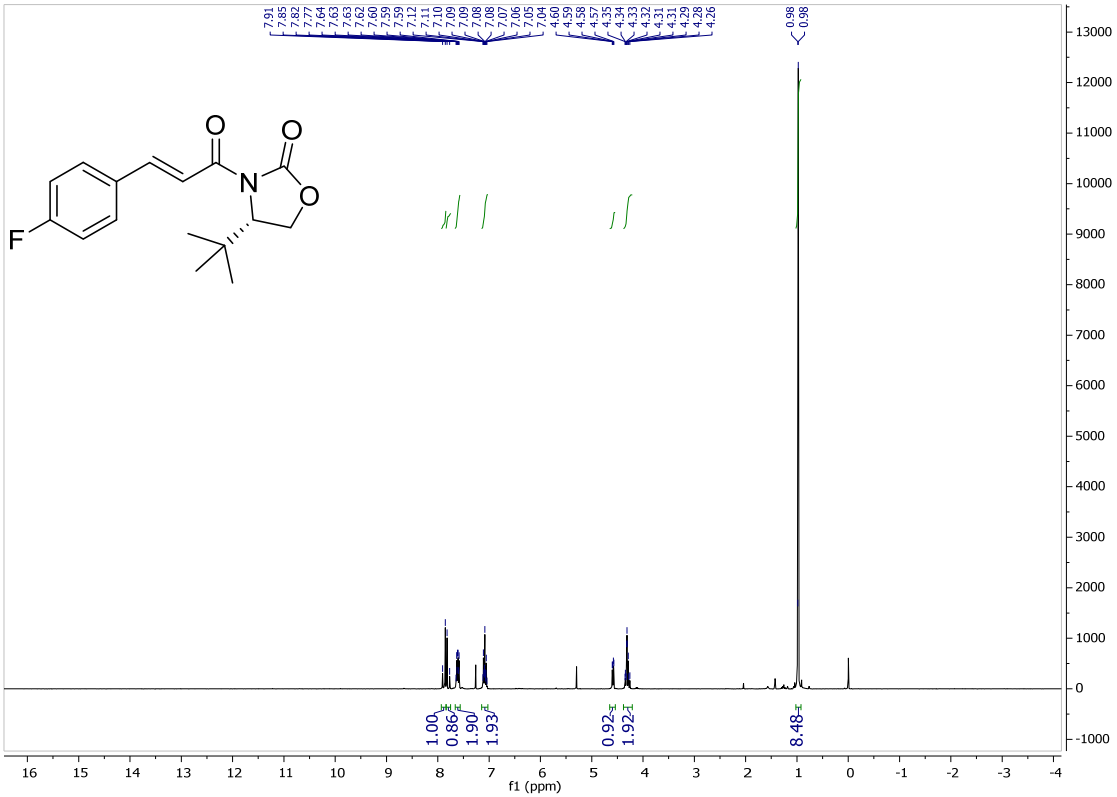


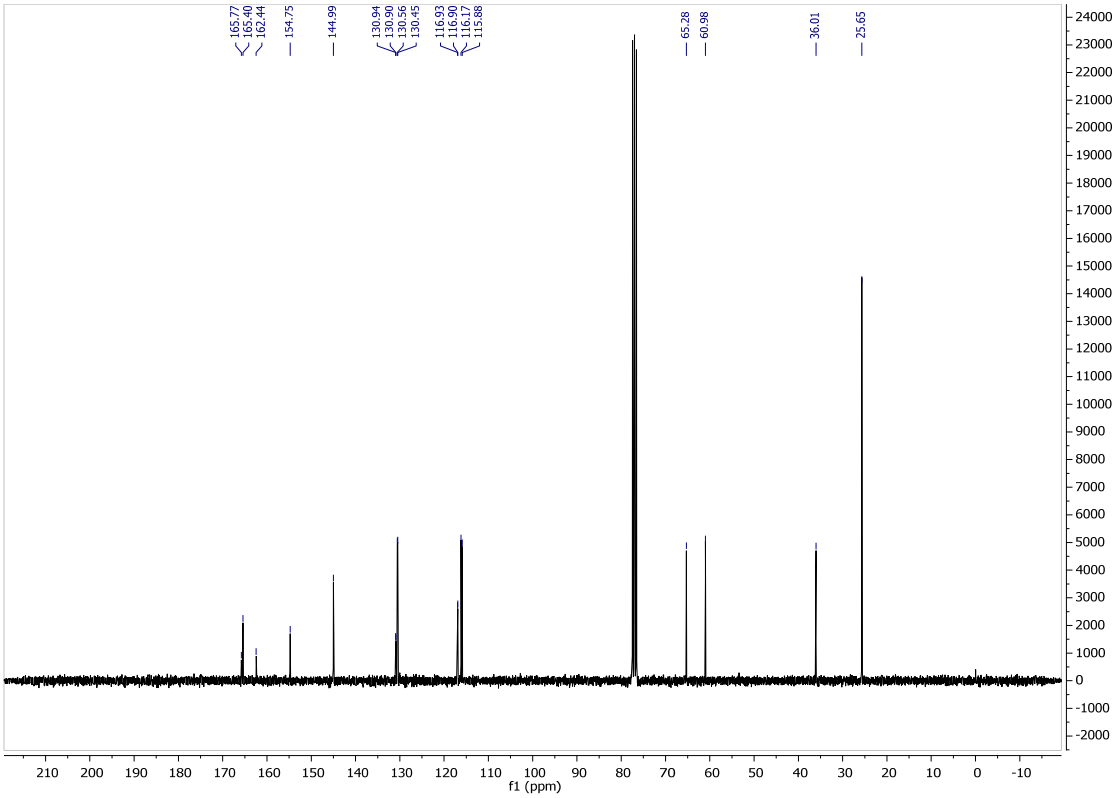
(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(4-chlorophenyl)acryloyl)oxazolidin-2-one (1i)

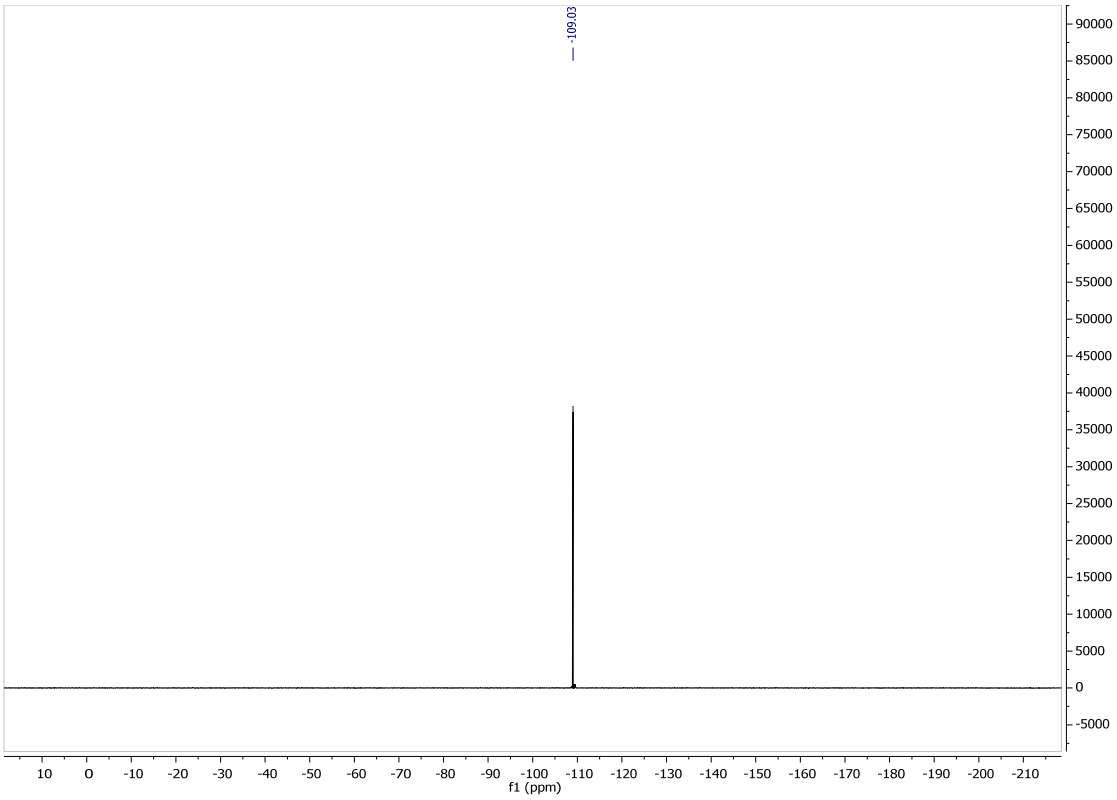




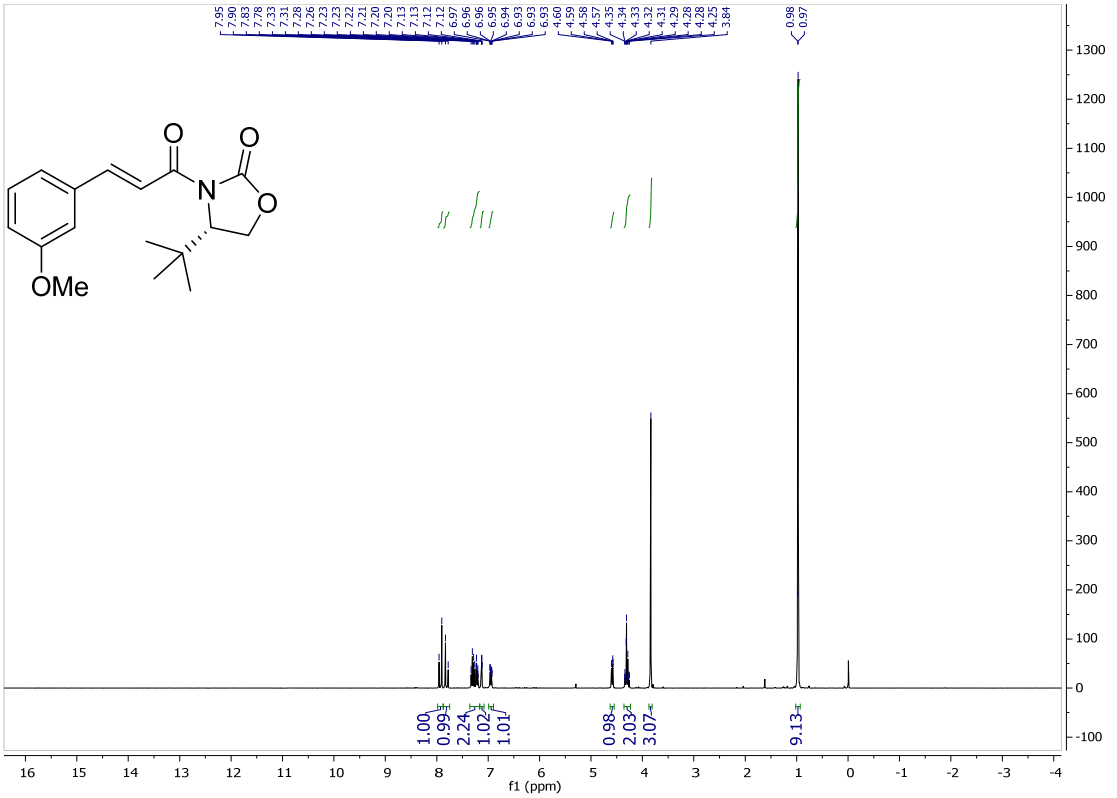
(*S,E*)-4-(*tert*-Butyl)-3-(3-(4-fluorophenyl)acryloyl)oxazolidin-2-one (1j)

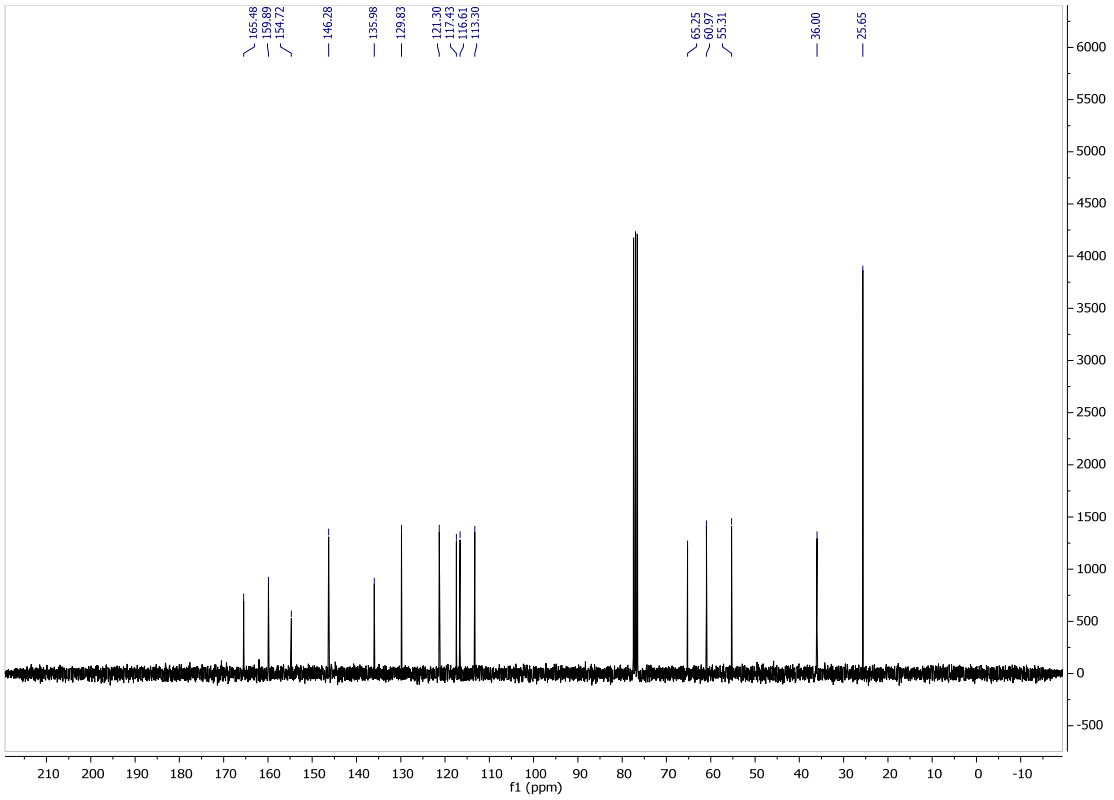




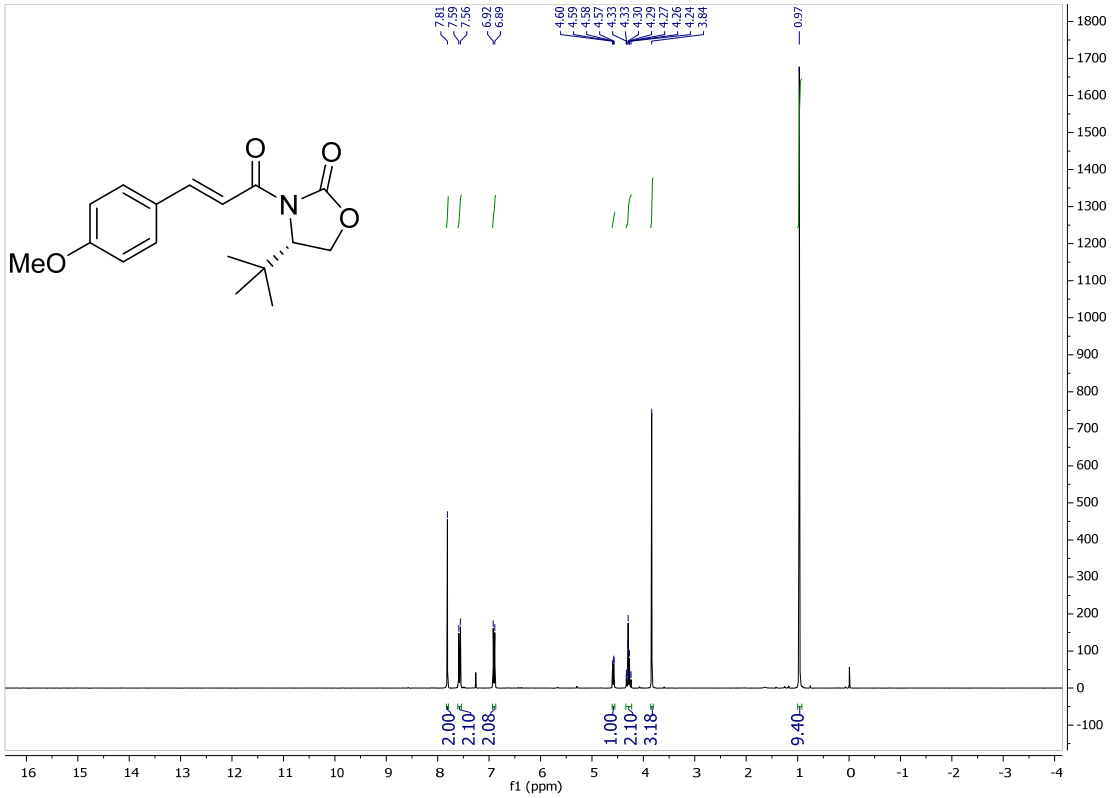


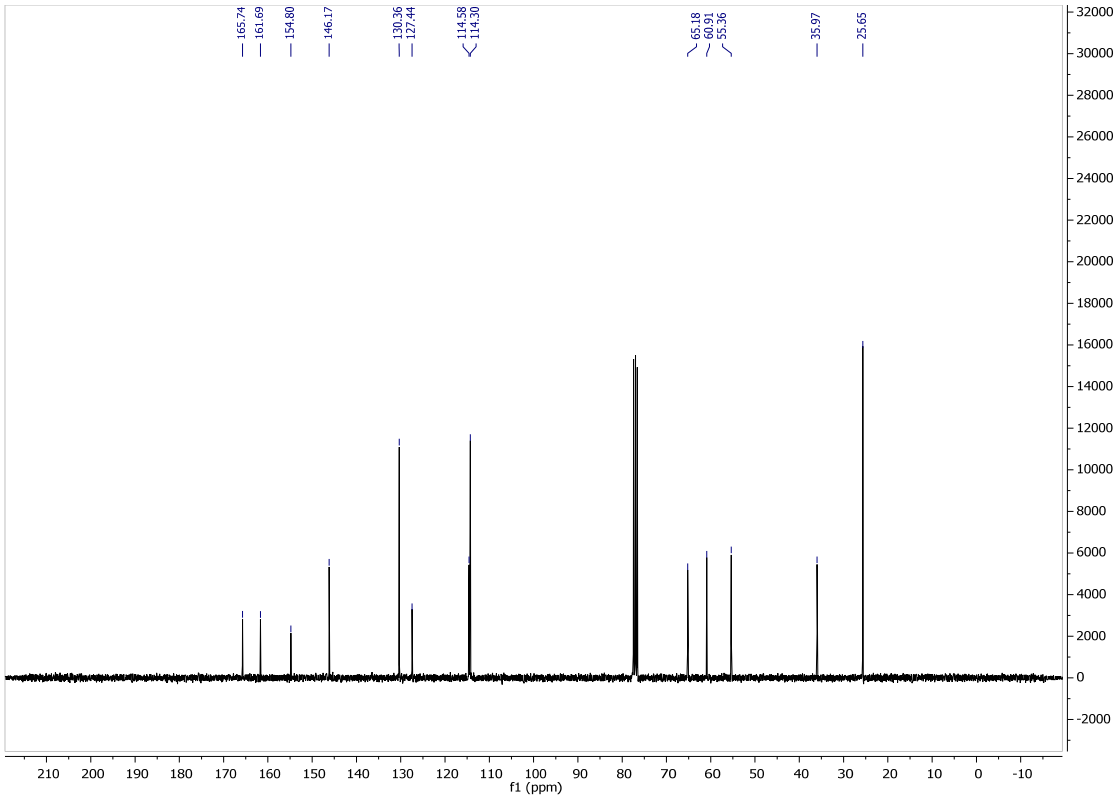
(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(3-methoxyphenyl)acryloyl)oxazolidin-2-one (1k)



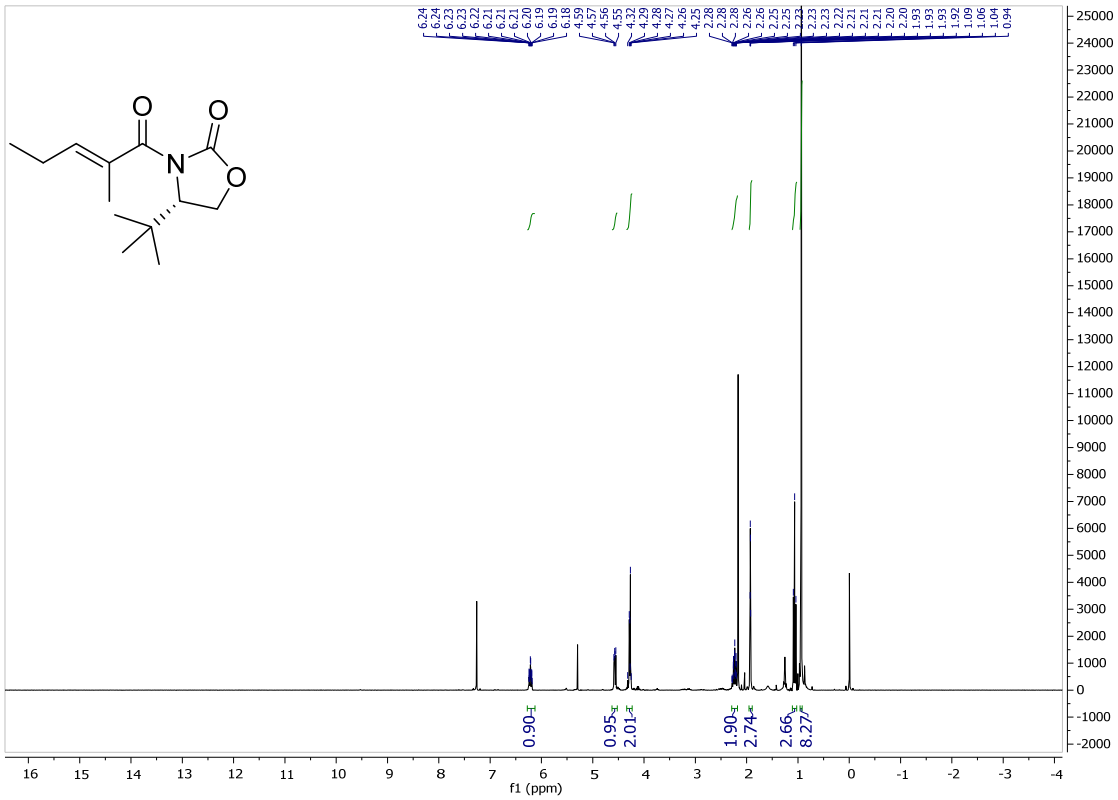


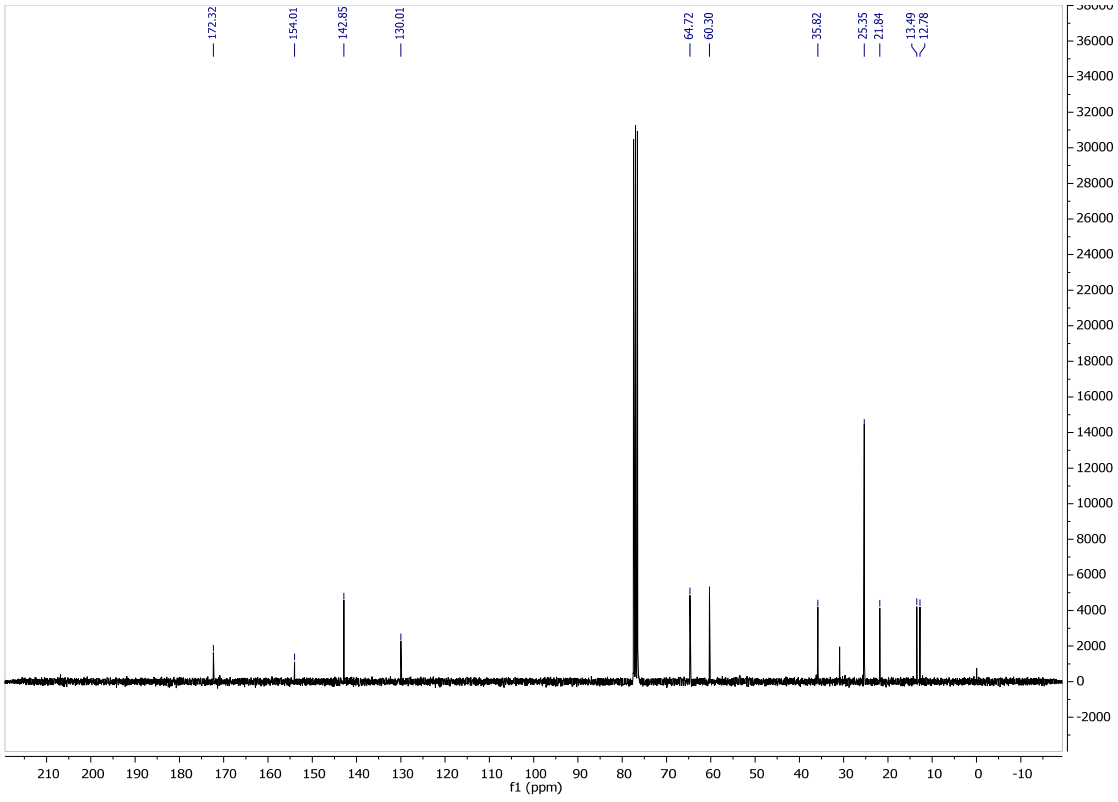
(*S*,*E*)-4-(*tert*-Butyl)-3-(3-(4-methoxyphenyl)acryloyl)oxazolidin-2-one (1l)



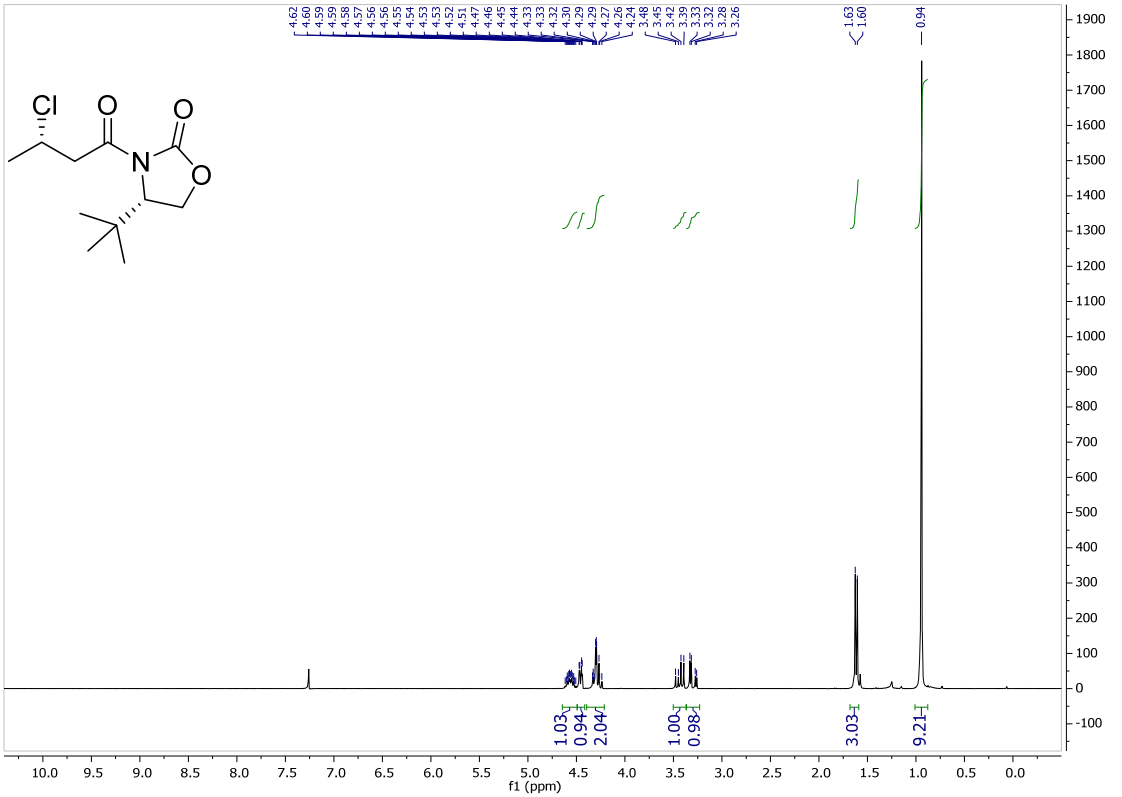


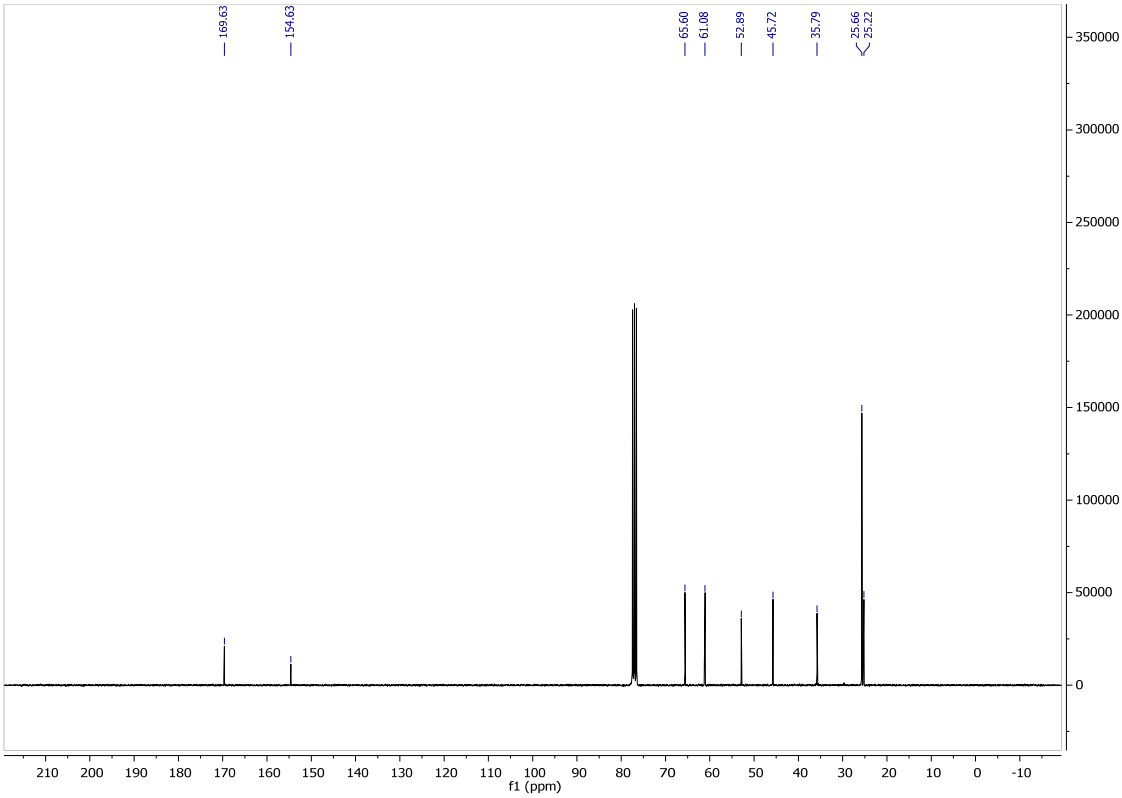
(*S*,*E*)-4-(*tert*-Butyl)-3-(2-methylpent-2-enoyl)oxazolidin-2-one (1m)



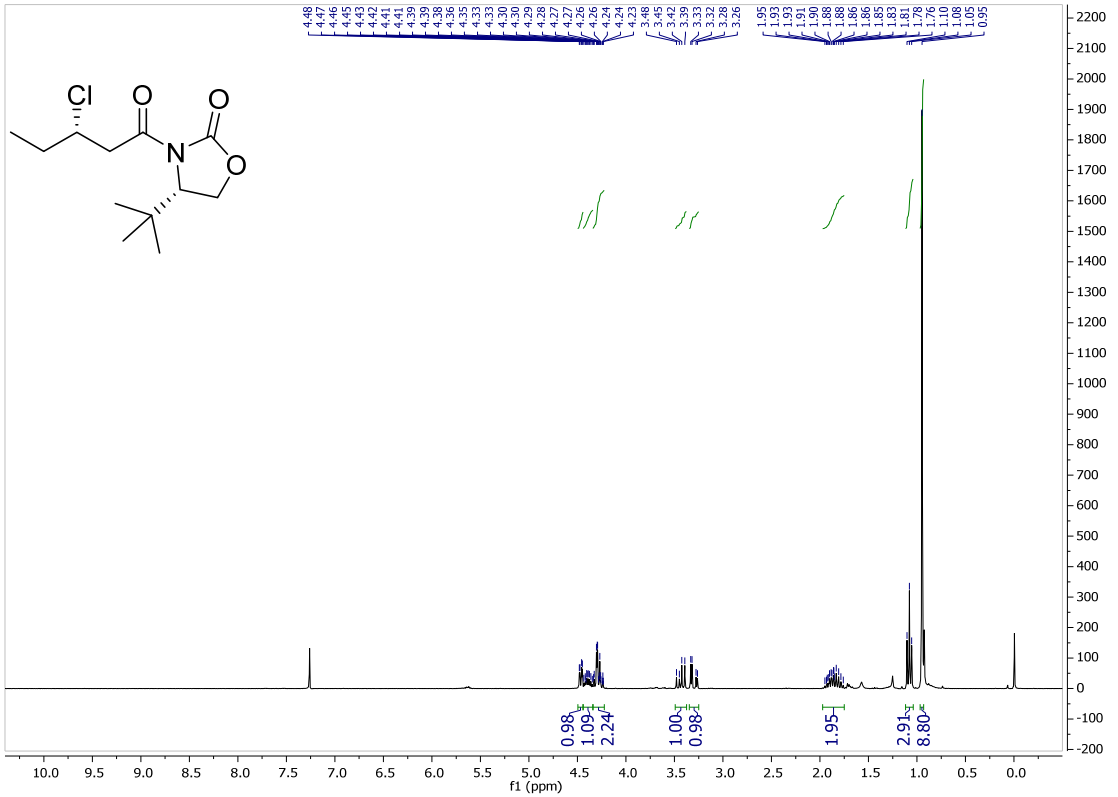

172.32
154.01
142.85
130.01
64.72
60.30
35.82
25.35
21.84
13.49
12.78
f1 (ppm)

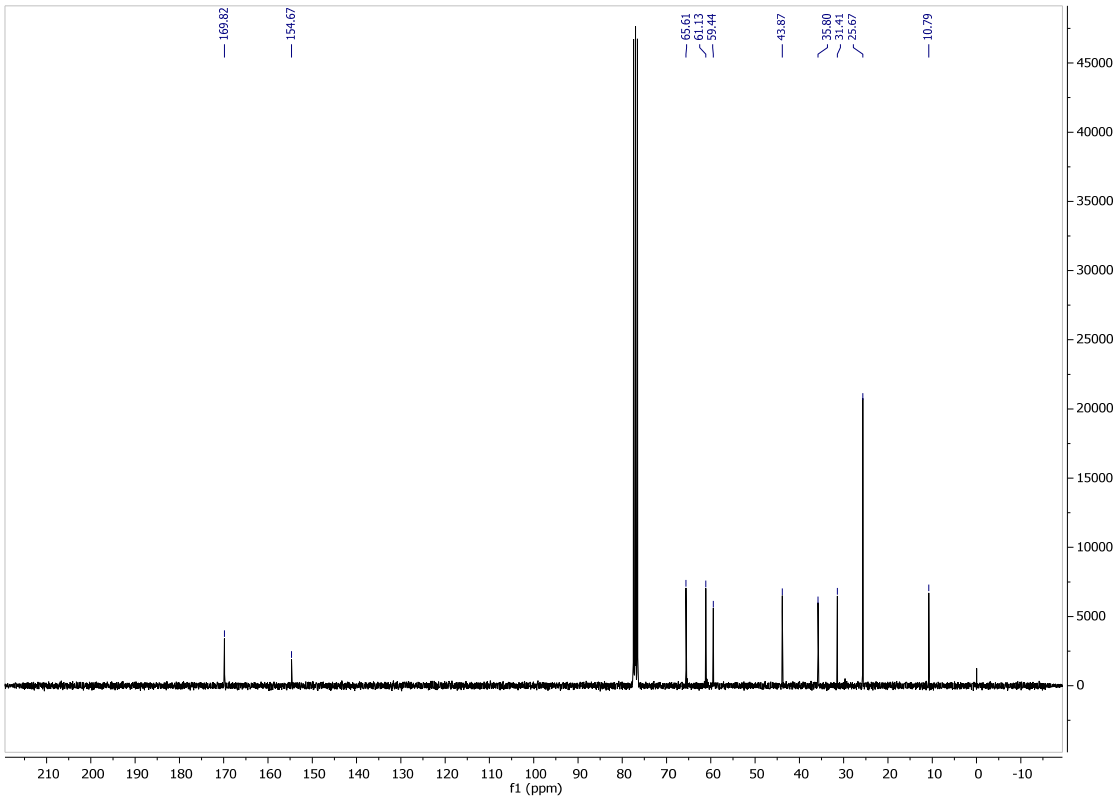
(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chlorobutanoyl)oxazolidin-2-one (3b)



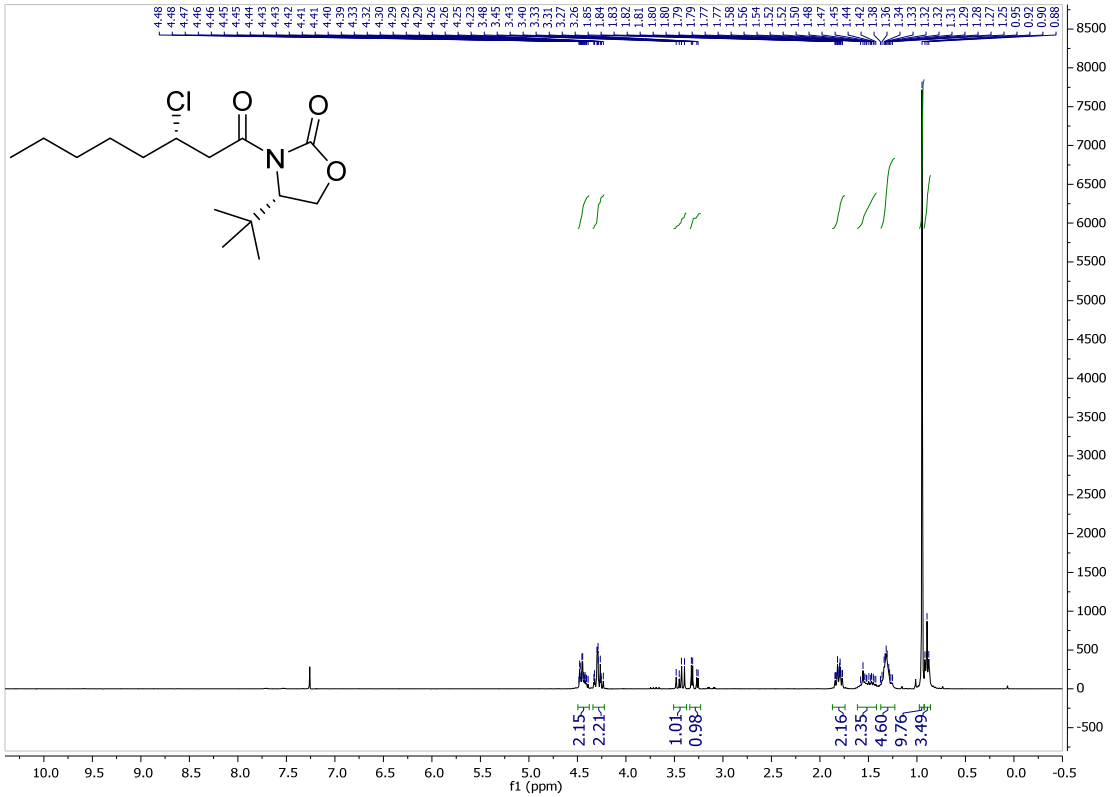


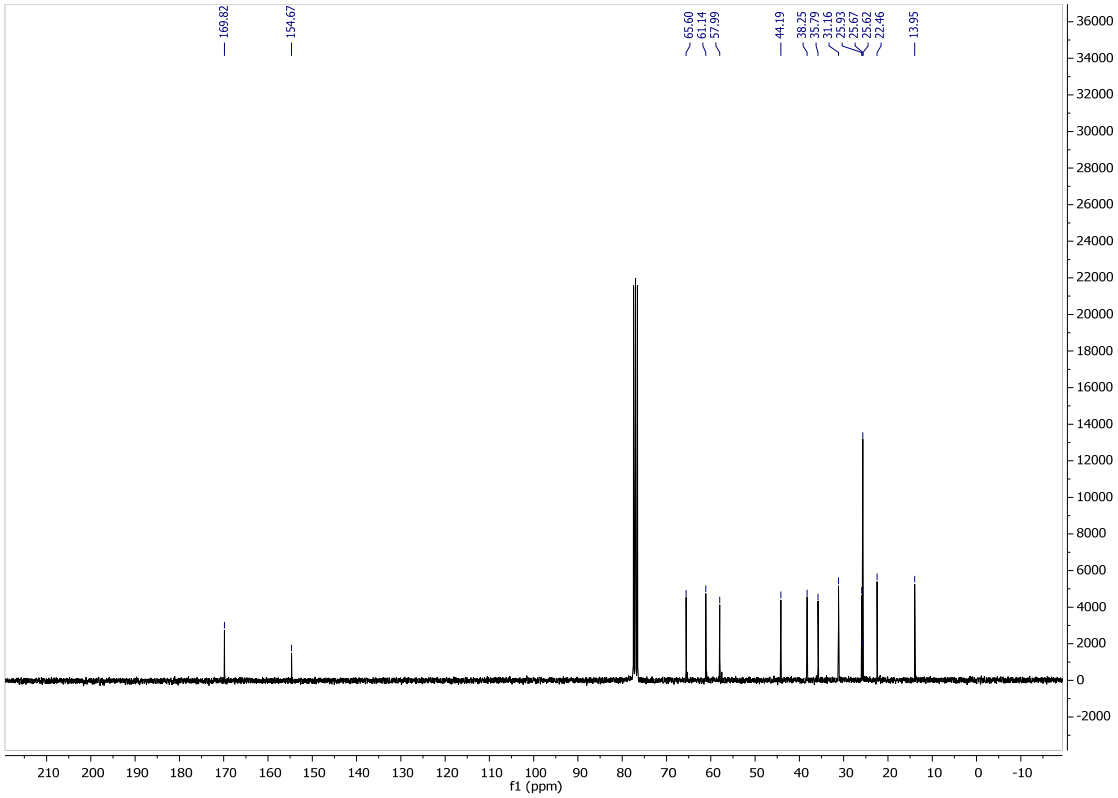
(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chloropentanoyl)oxazolidin-2-one (3c)



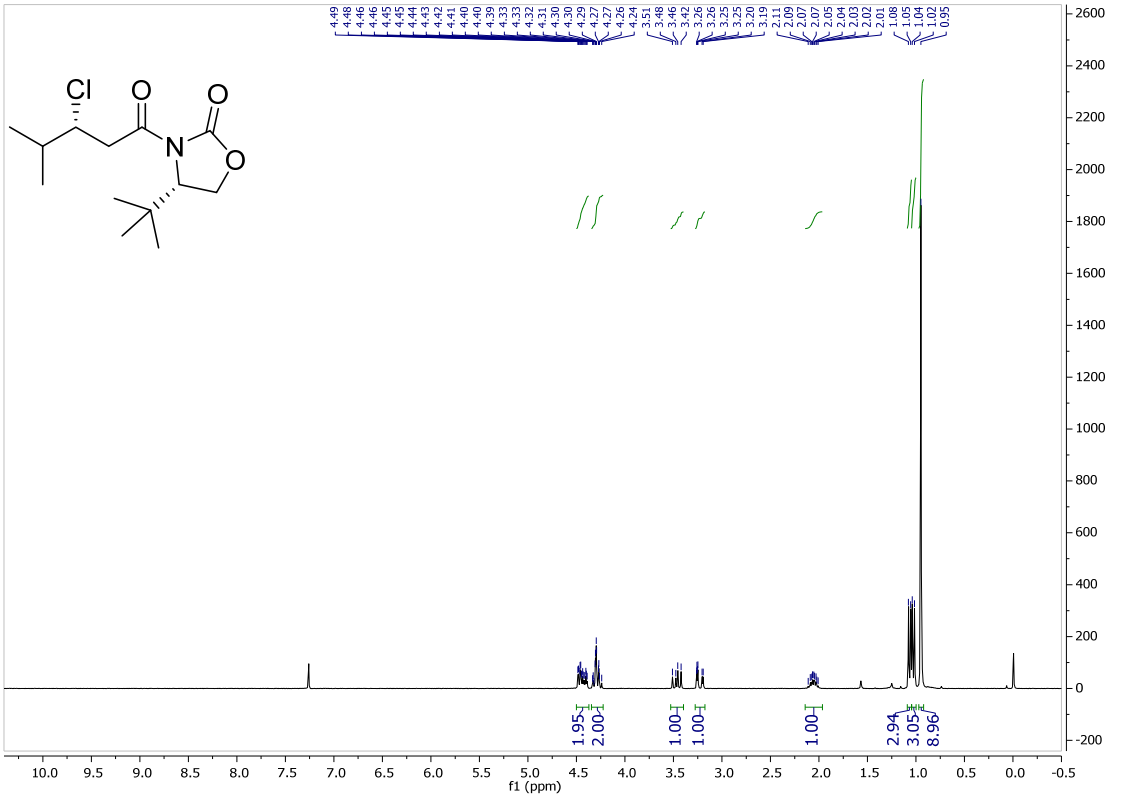


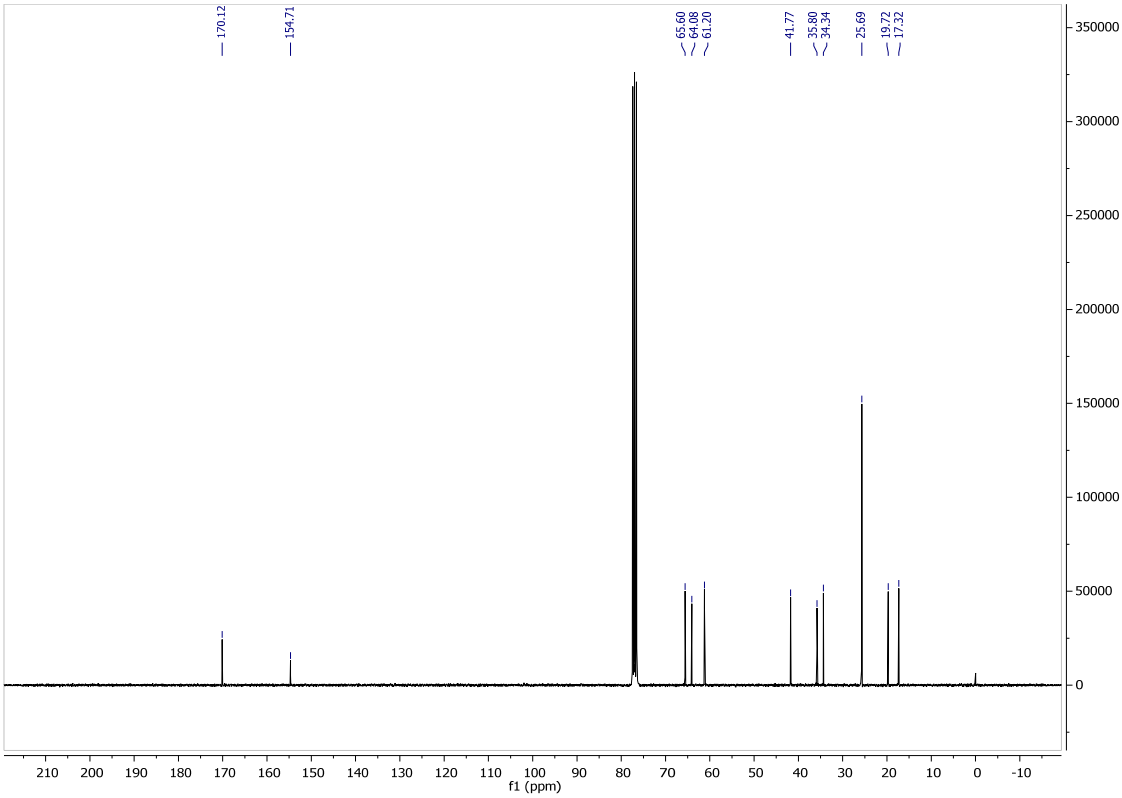
(*S*)-4-(*tert*-Butyl)-3-((*S*)-3-chlorooctanoyl)oxazolidin-2-one (3d)



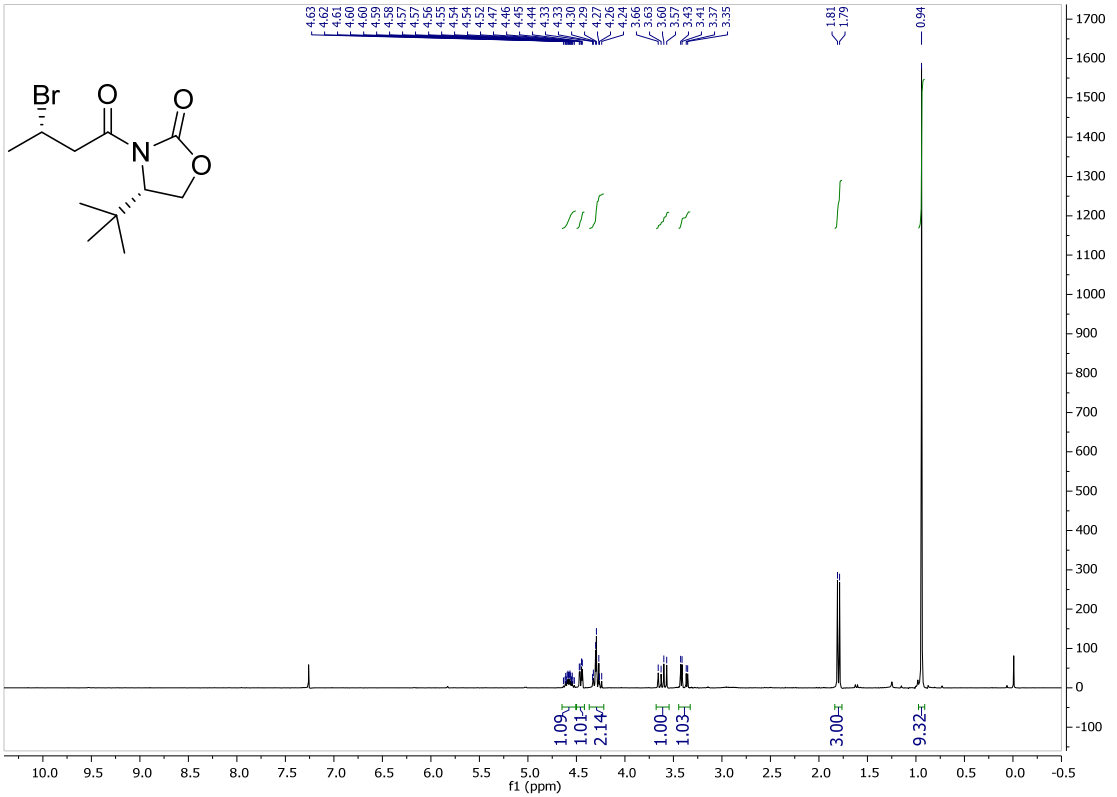


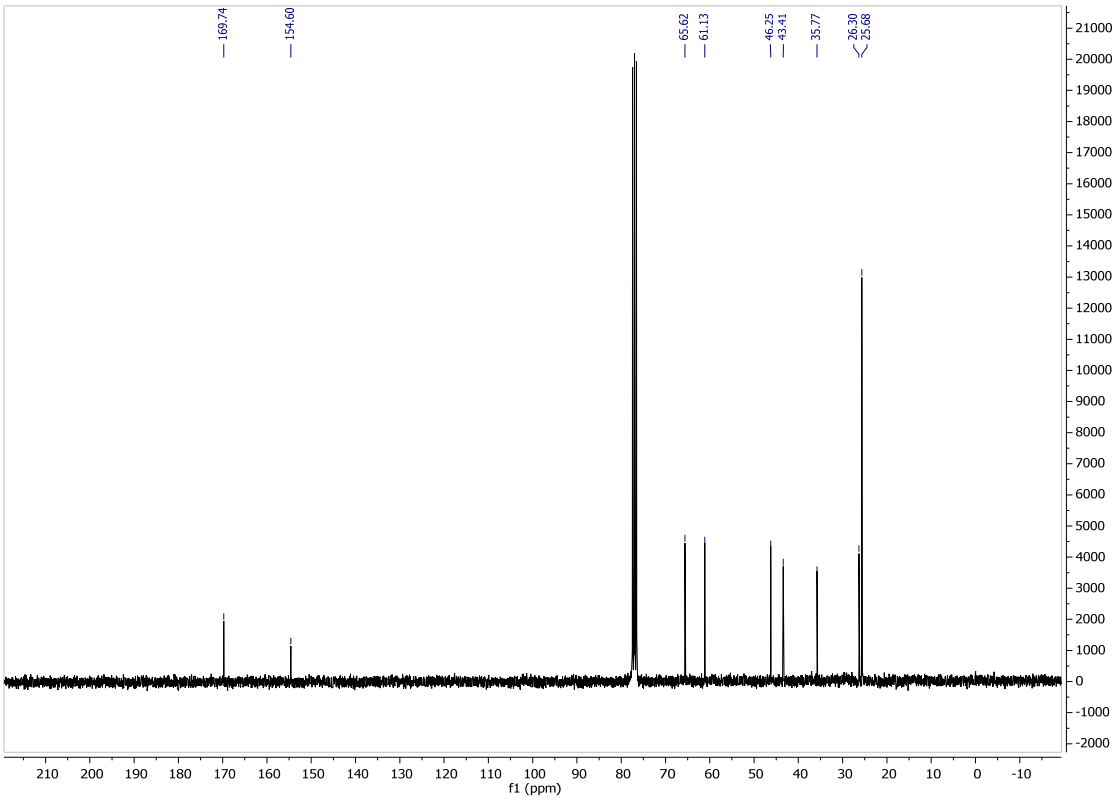
(*S*)-4-(*tert*-butyl)-3-((*R*)-3-chloro-4-methylpentanoyl)oxazolidin-2-one (3e)



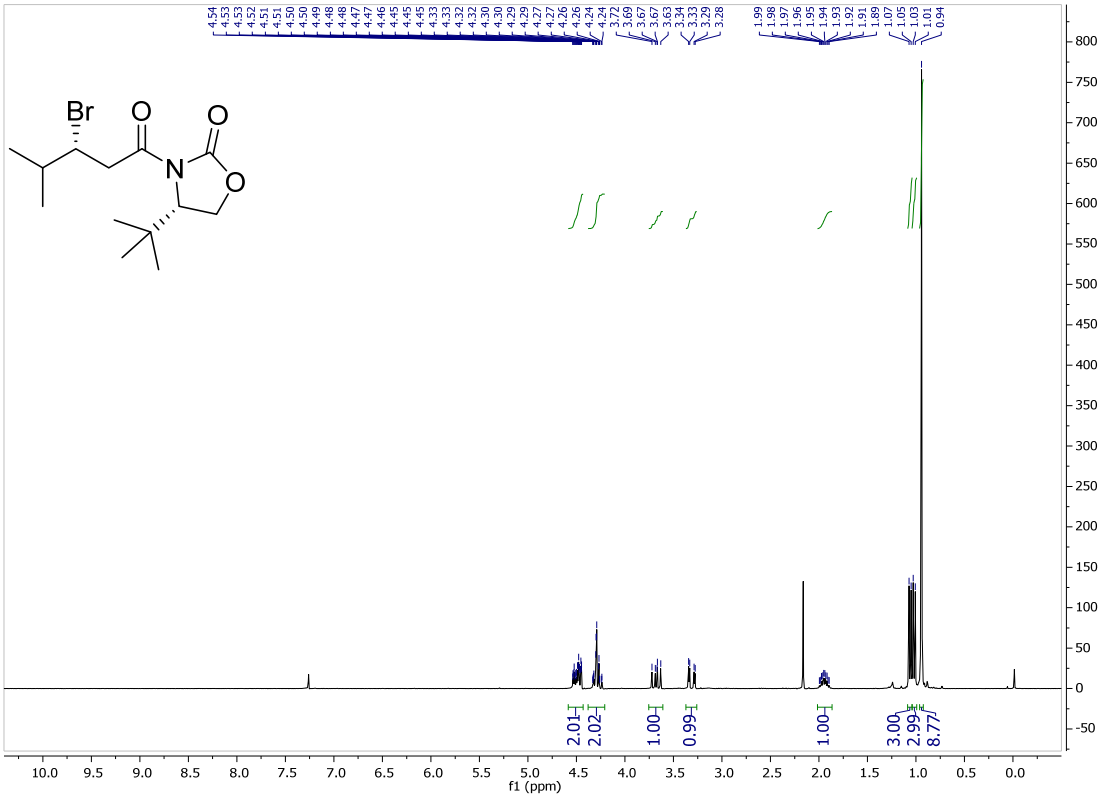


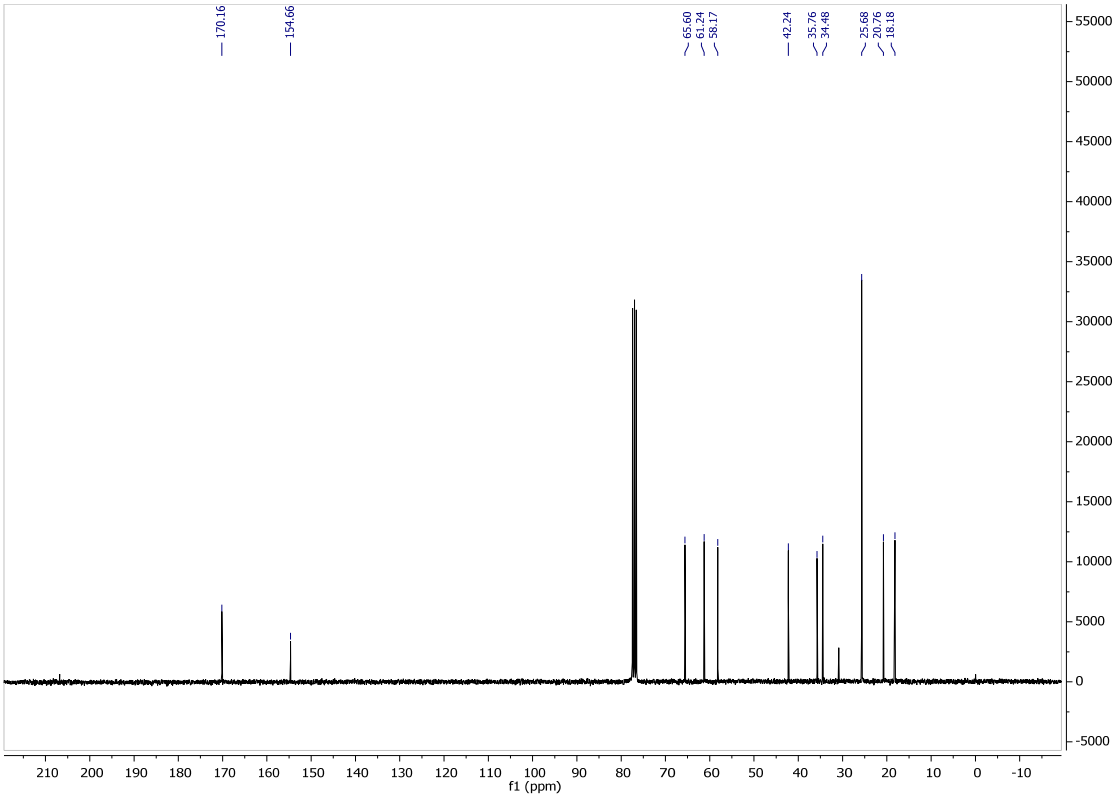
(*S*)-3-((*S*)-3-Bromobutanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4a)



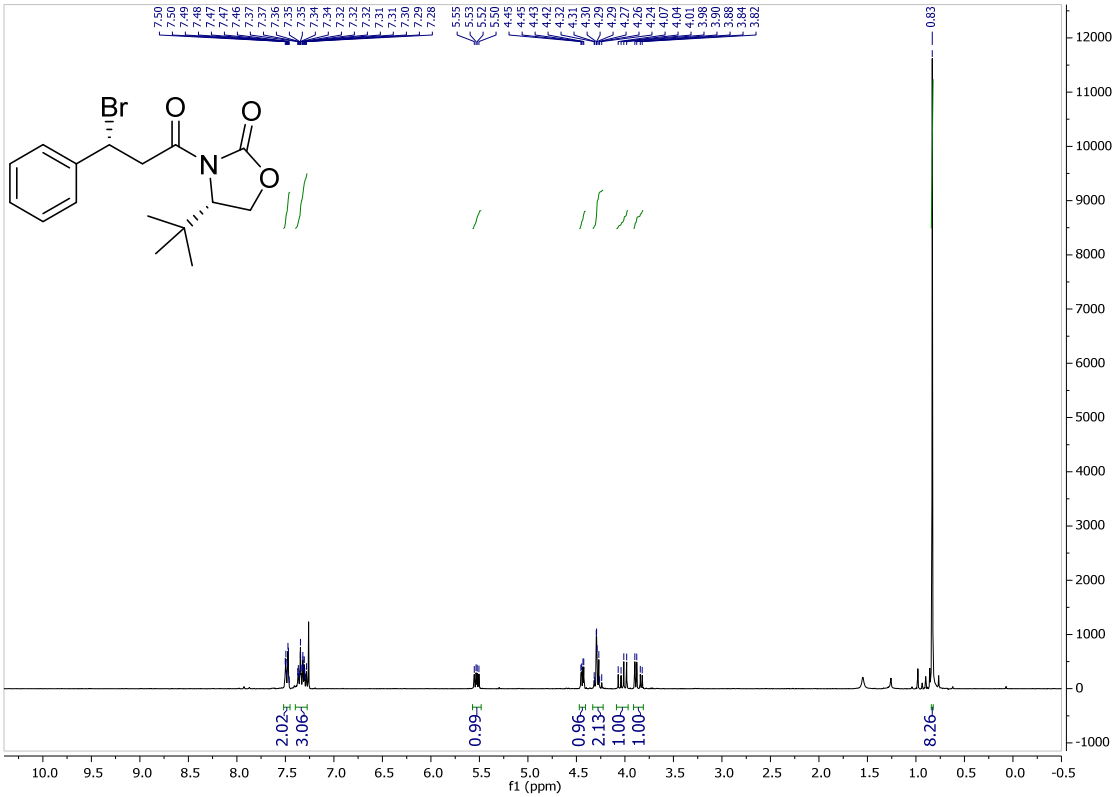


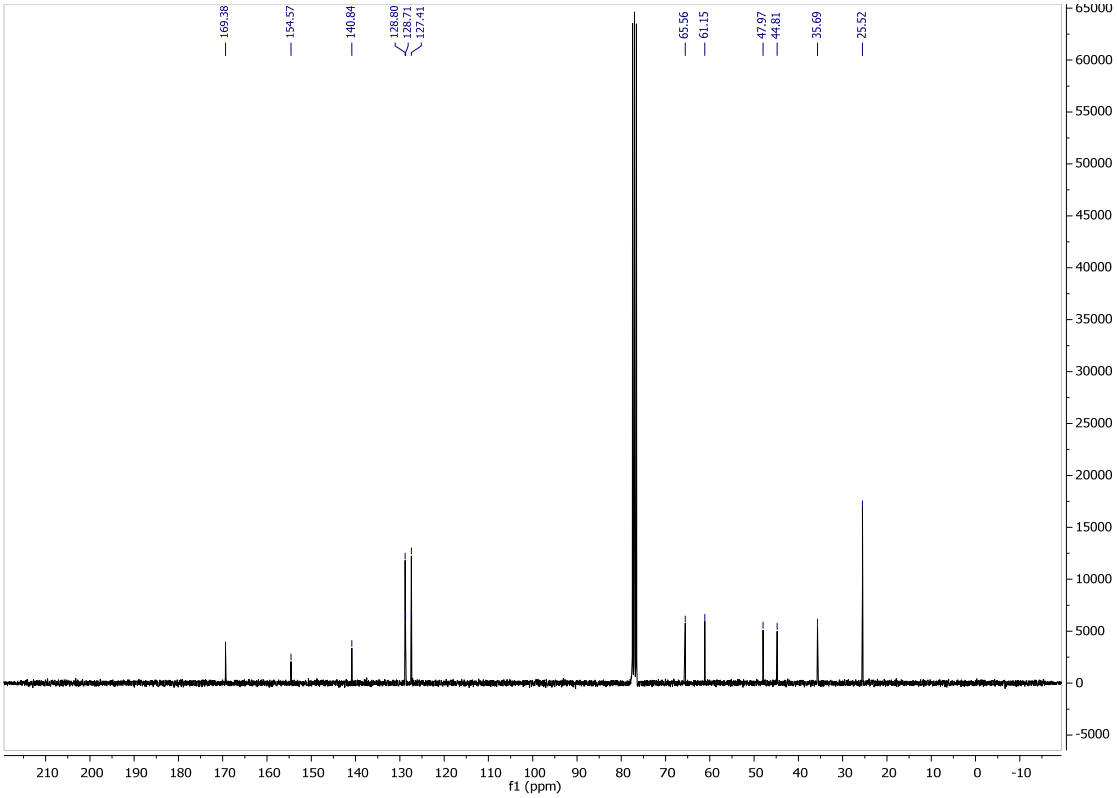
(*S*)-3-((*R*)-3-Bromo-4-methylpentanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4b)



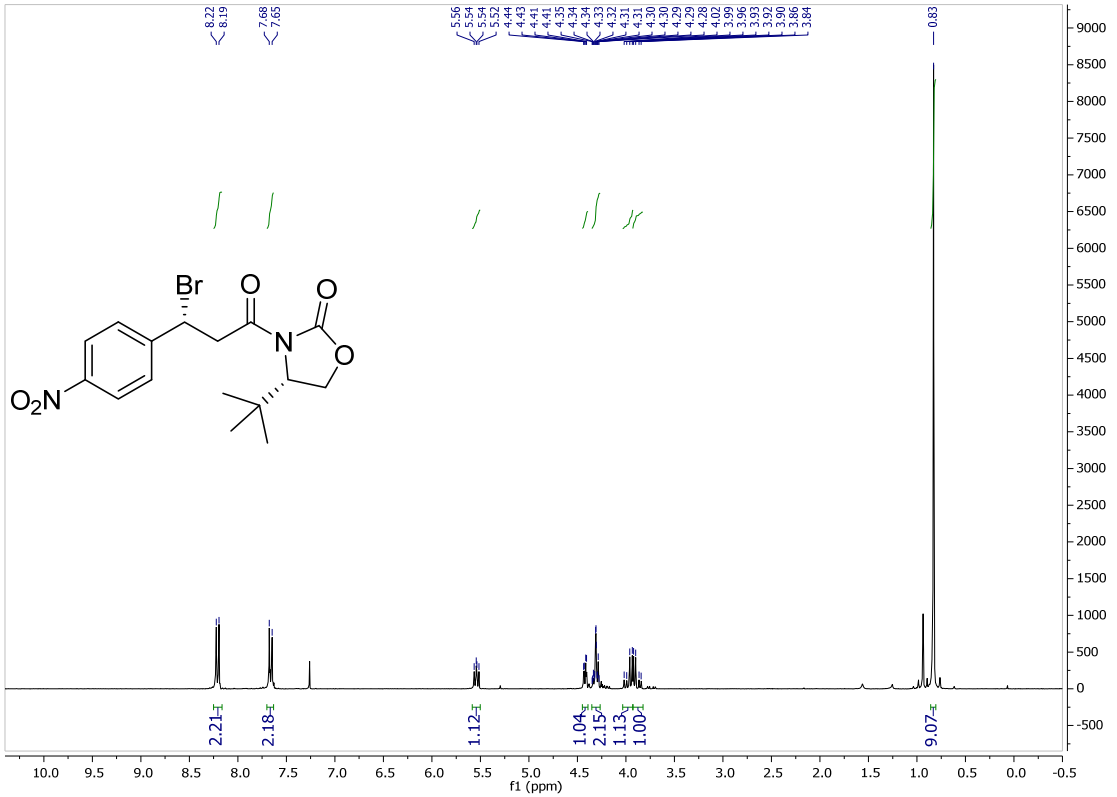


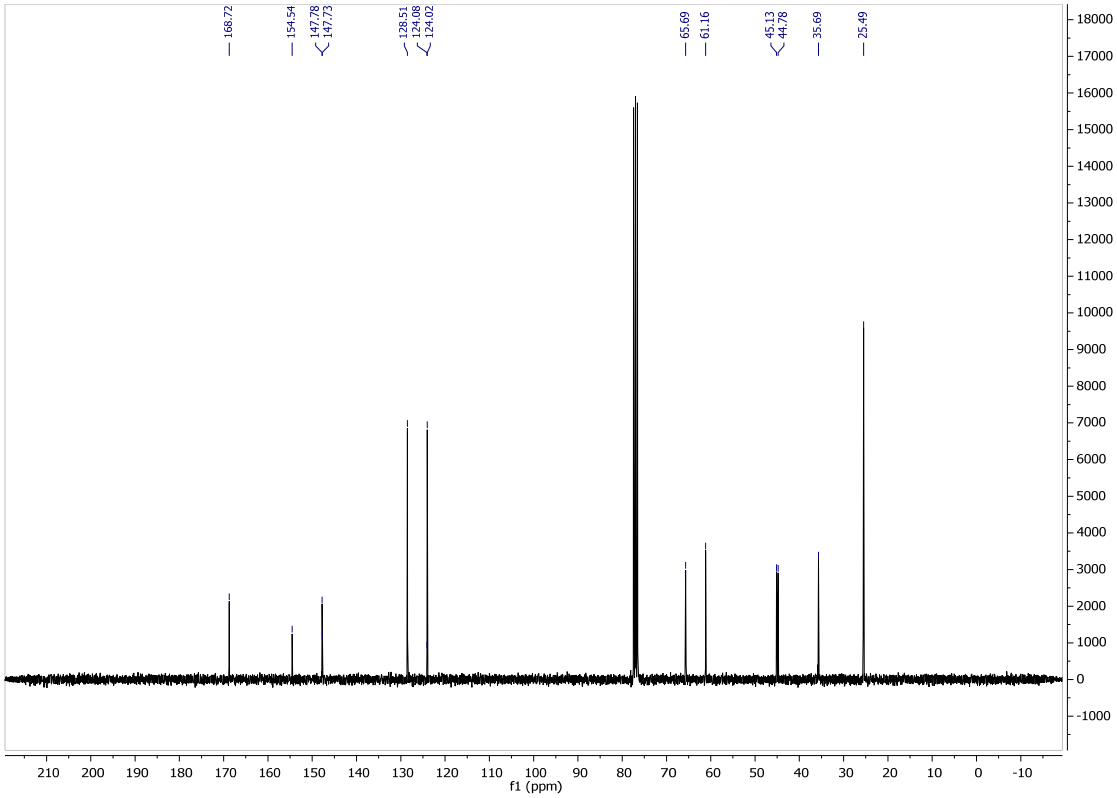
(*S*)-3-((*R*)-3-Bromo-3-phenylpropanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4c)



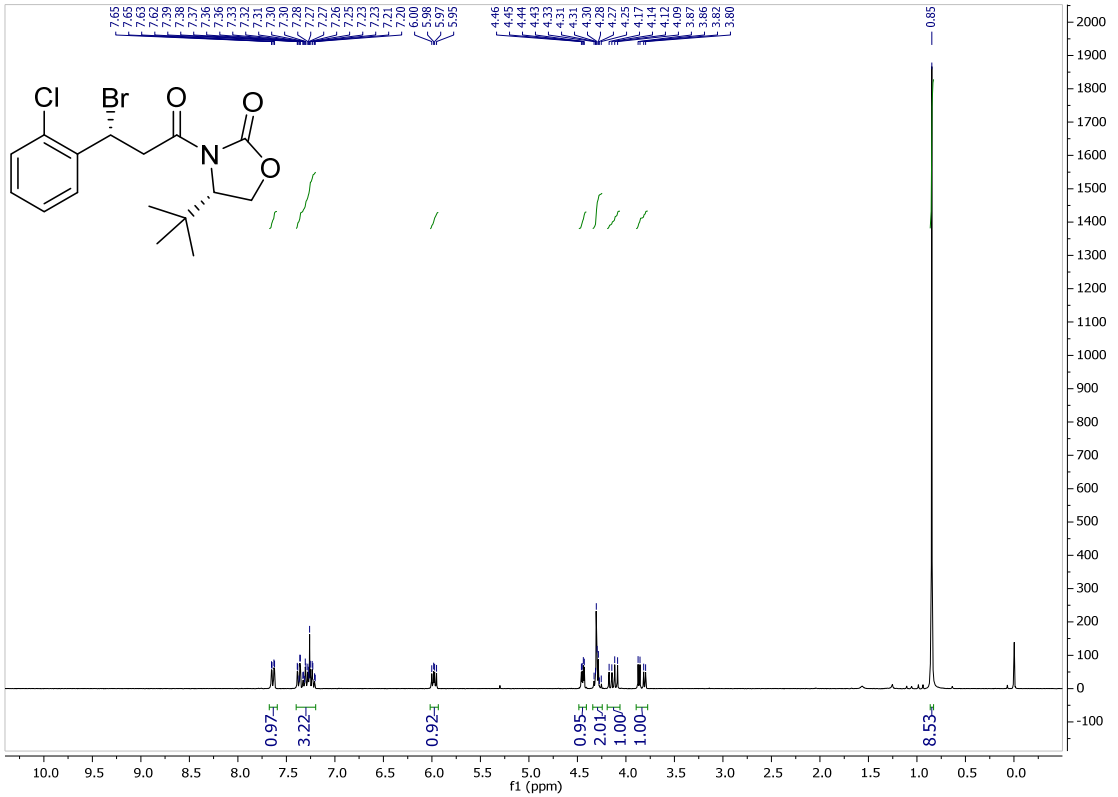


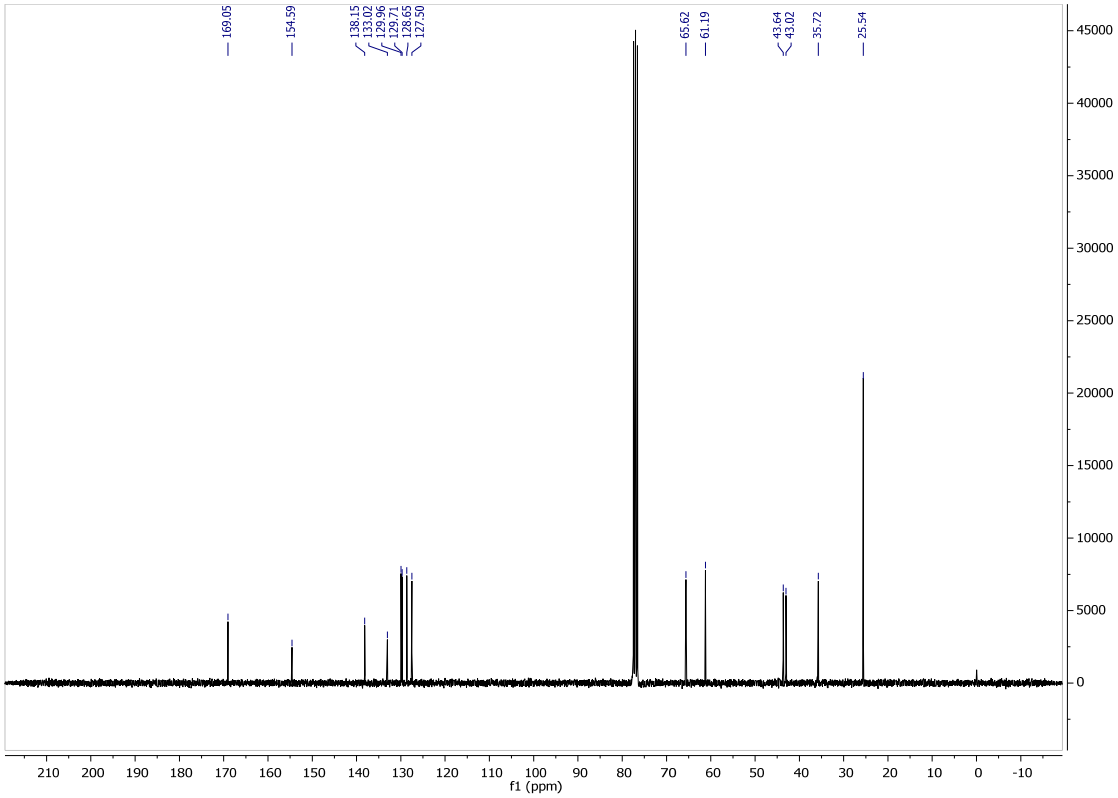
(*S*)-3-((*R*)-3-Bromo-3-(4-nitrophenyl)propanoyl)-4-(tert-butyl)oxazolidin-2-one (4d)



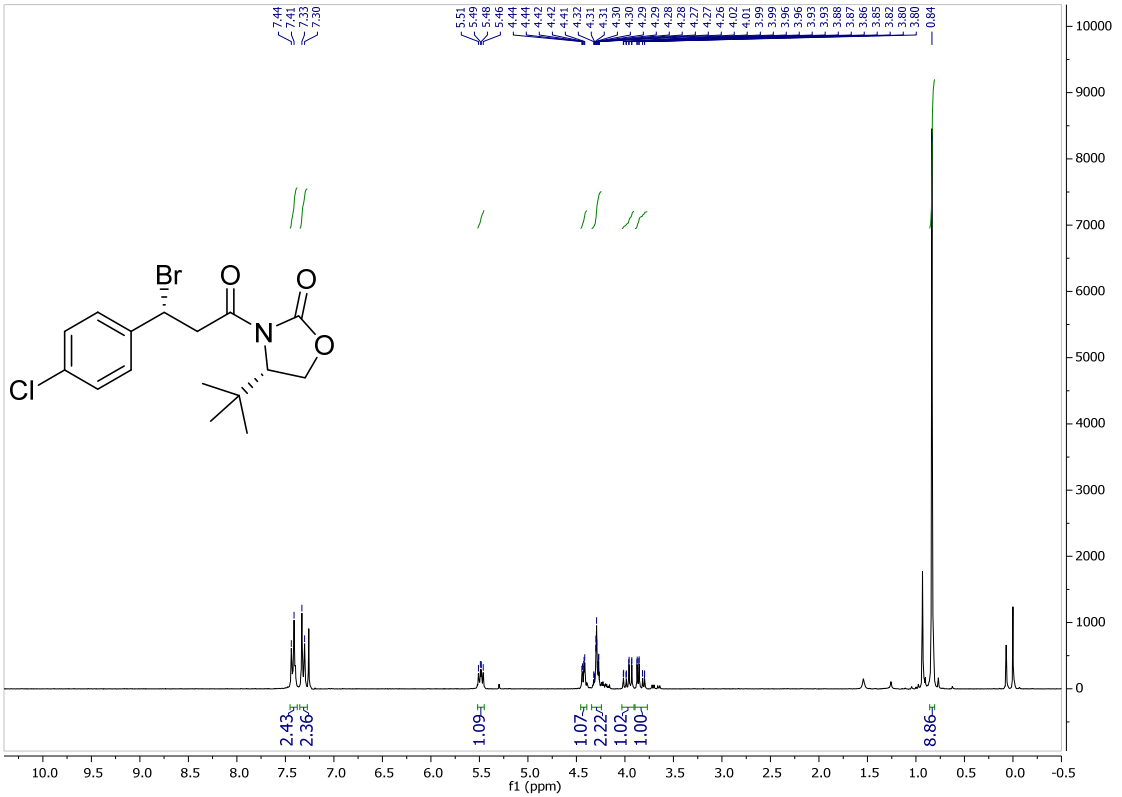


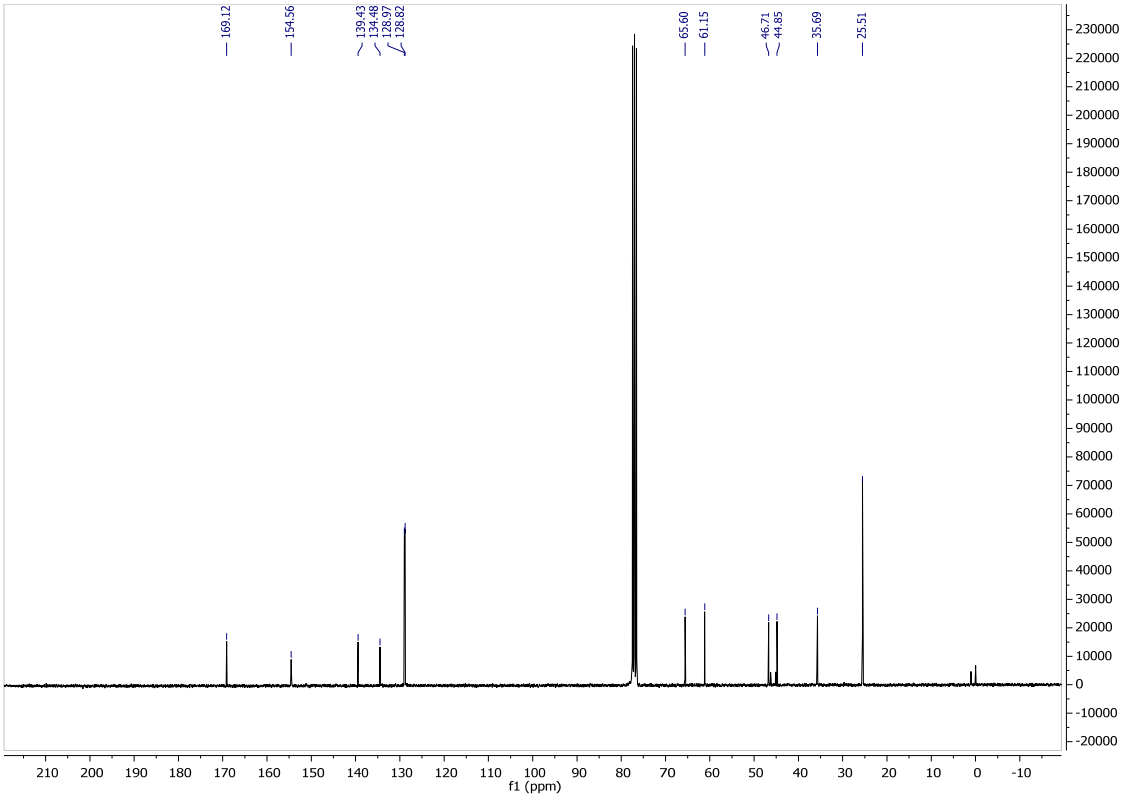
(*S*)-3-((*R*)-3-Bromo-3-(2-chlorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4e)



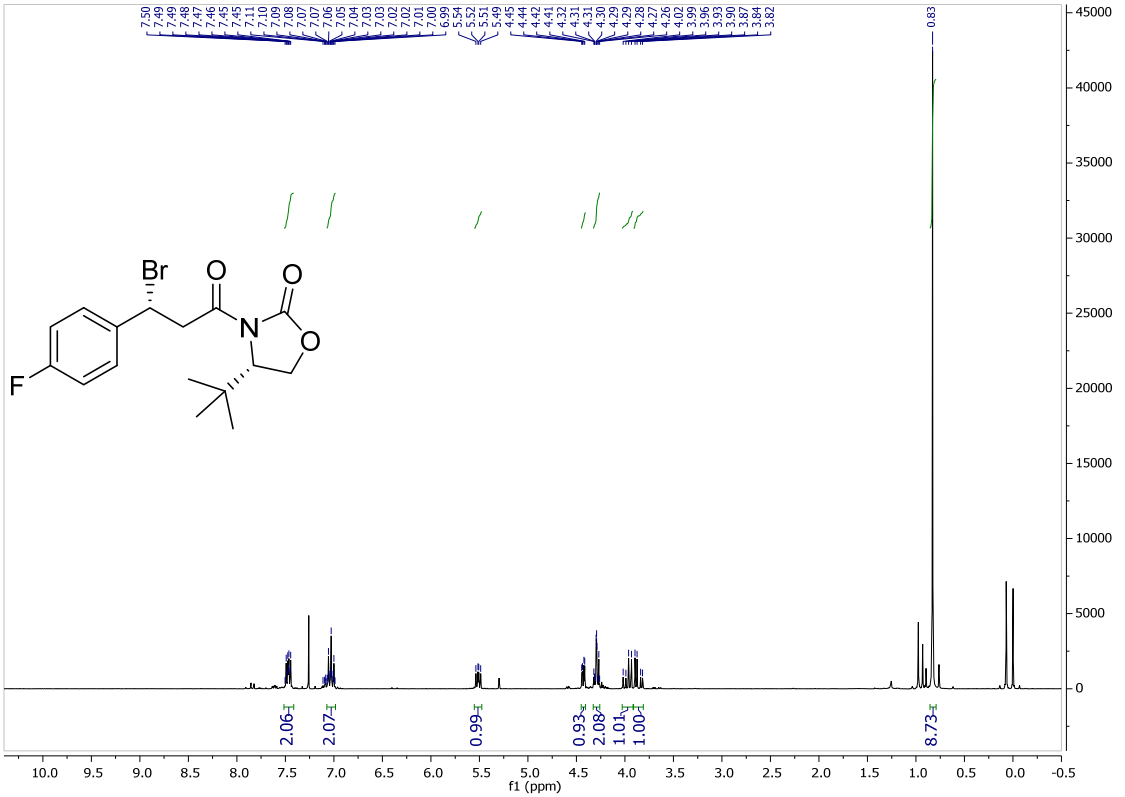


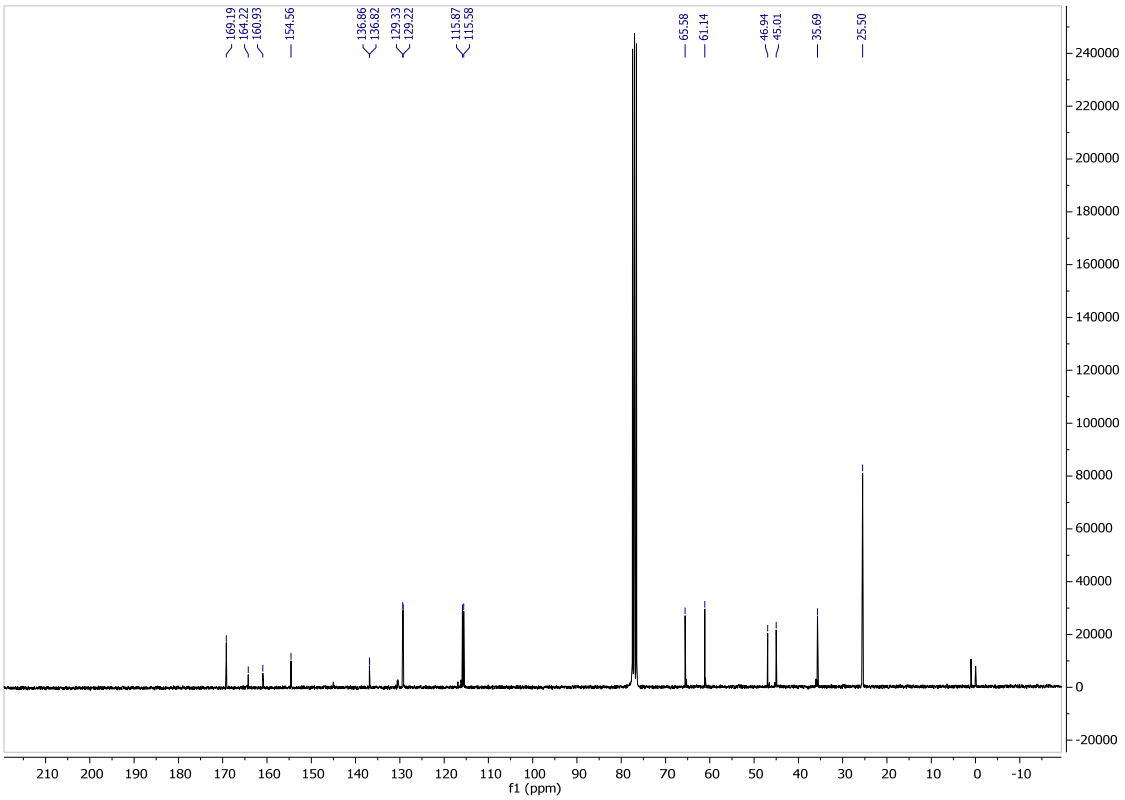
(*S*)-3-((*R*)-3-Bromo-3-(4-chlorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4f)

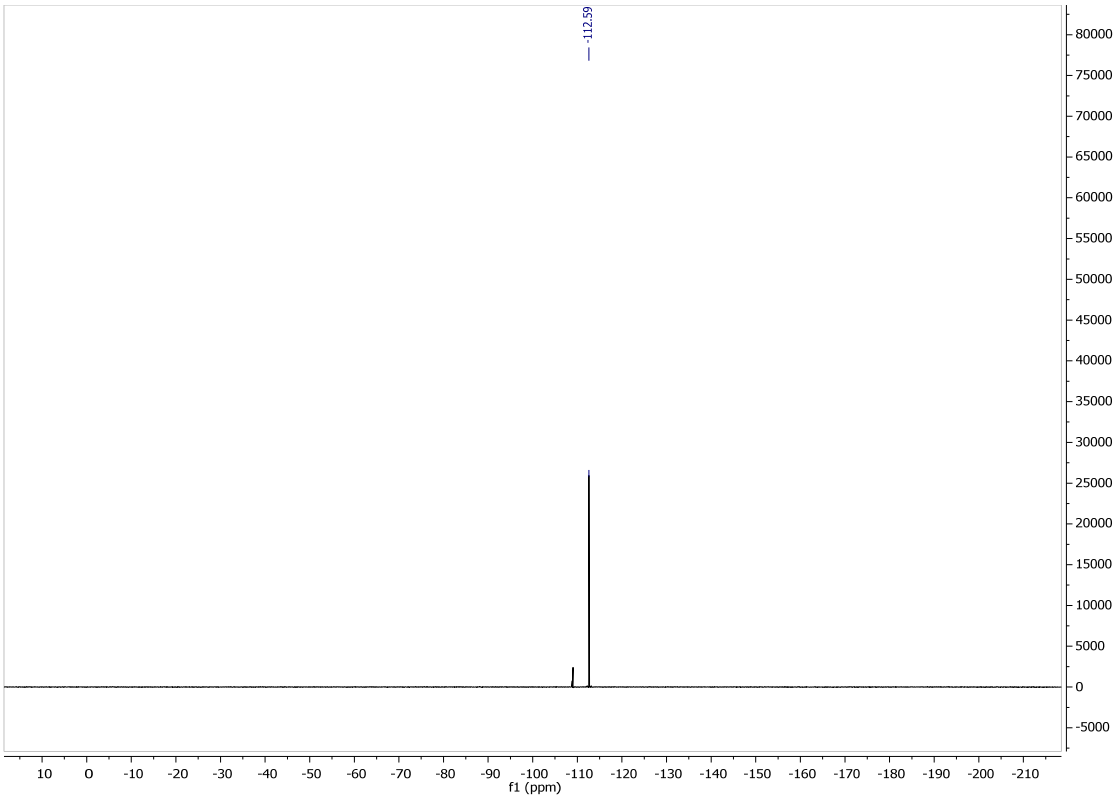




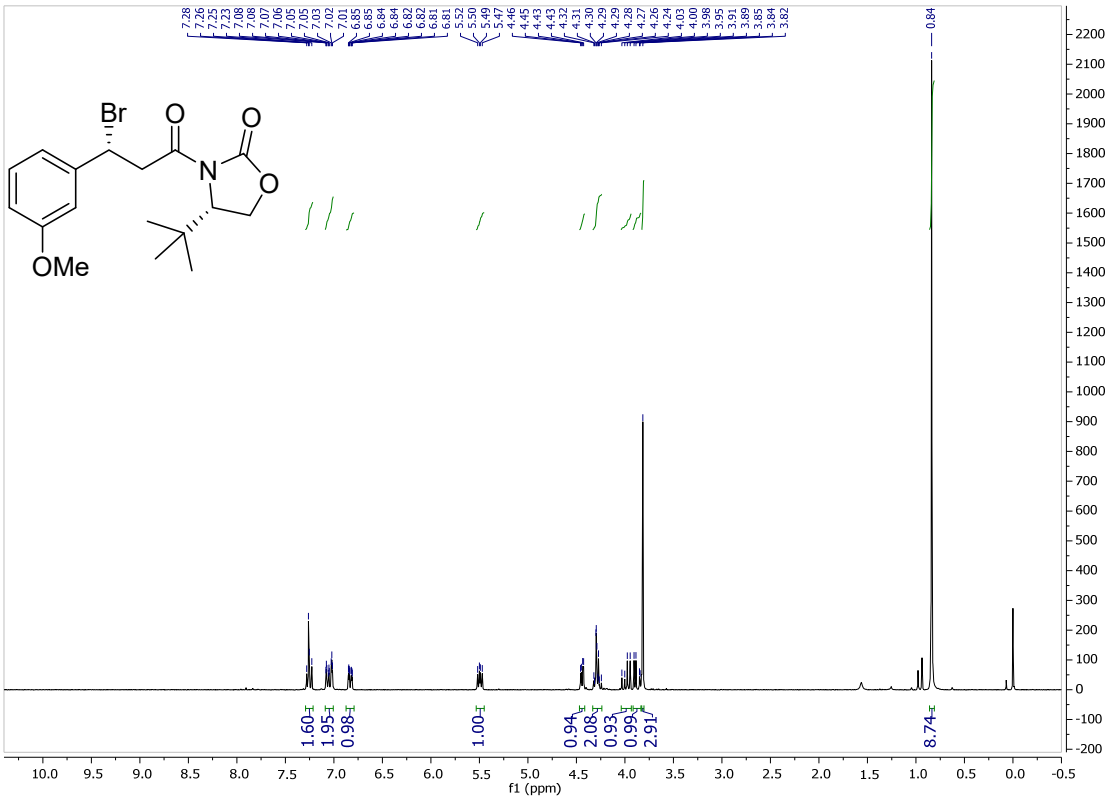
(*S*)-3-((*R*)-3-Bromo-3-(4-fluorophenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4g)

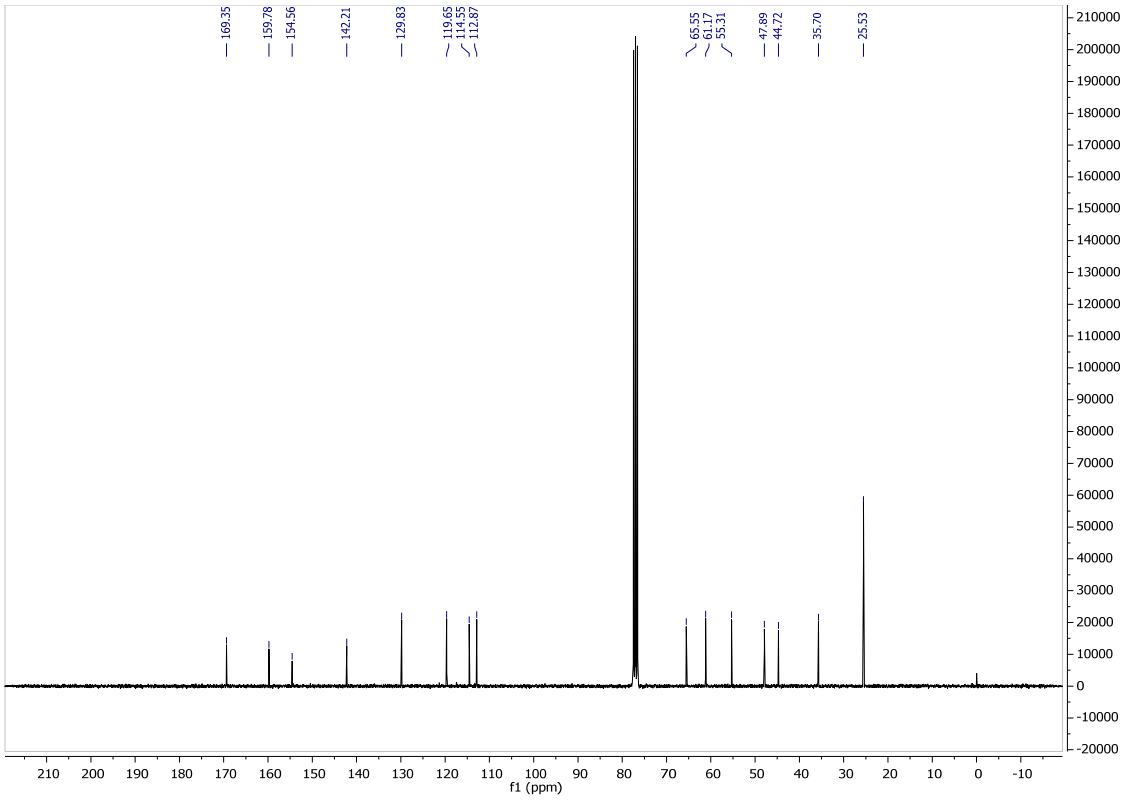




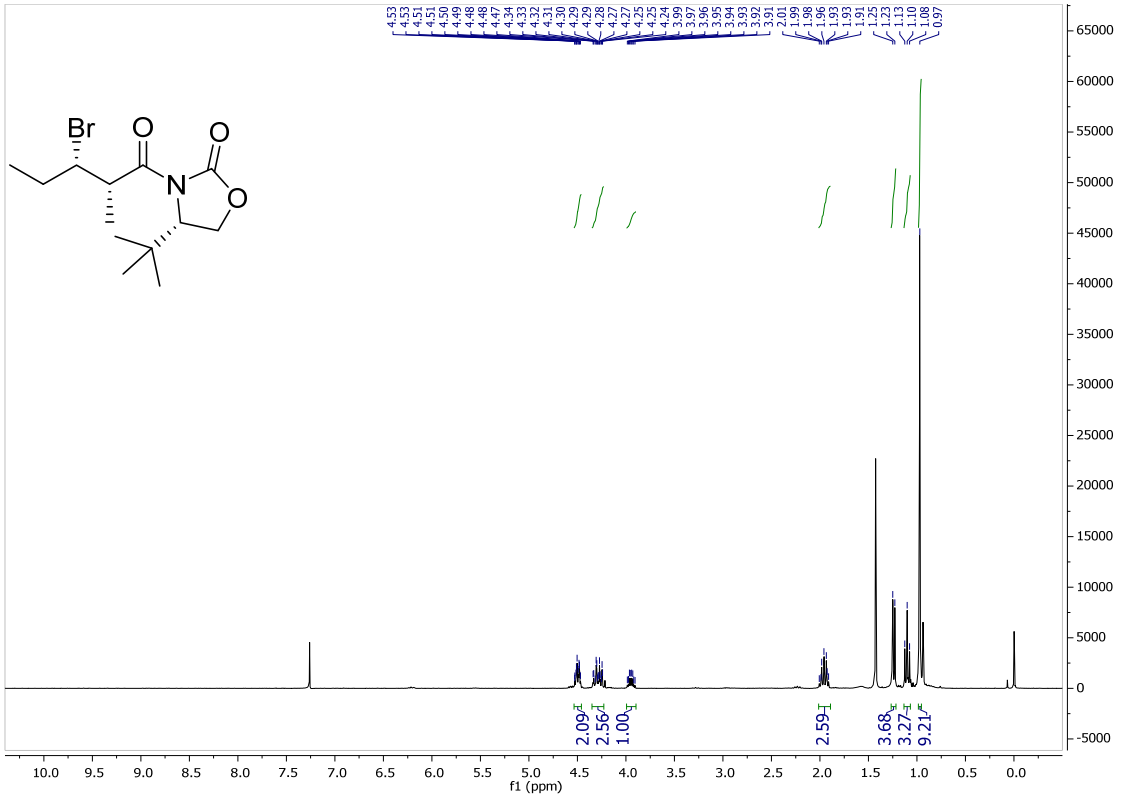


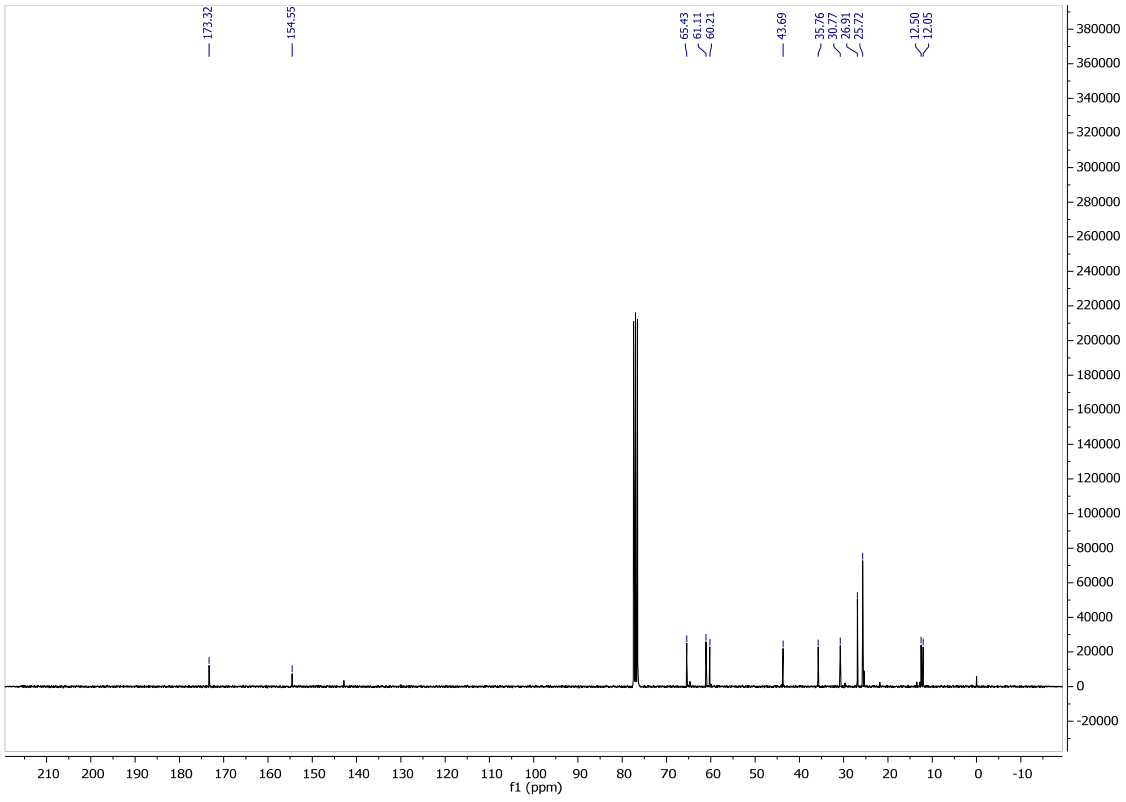
(*S*)-3-((*R*)-3-Bromo-3-(3-methoxyphenyl)propanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4h)



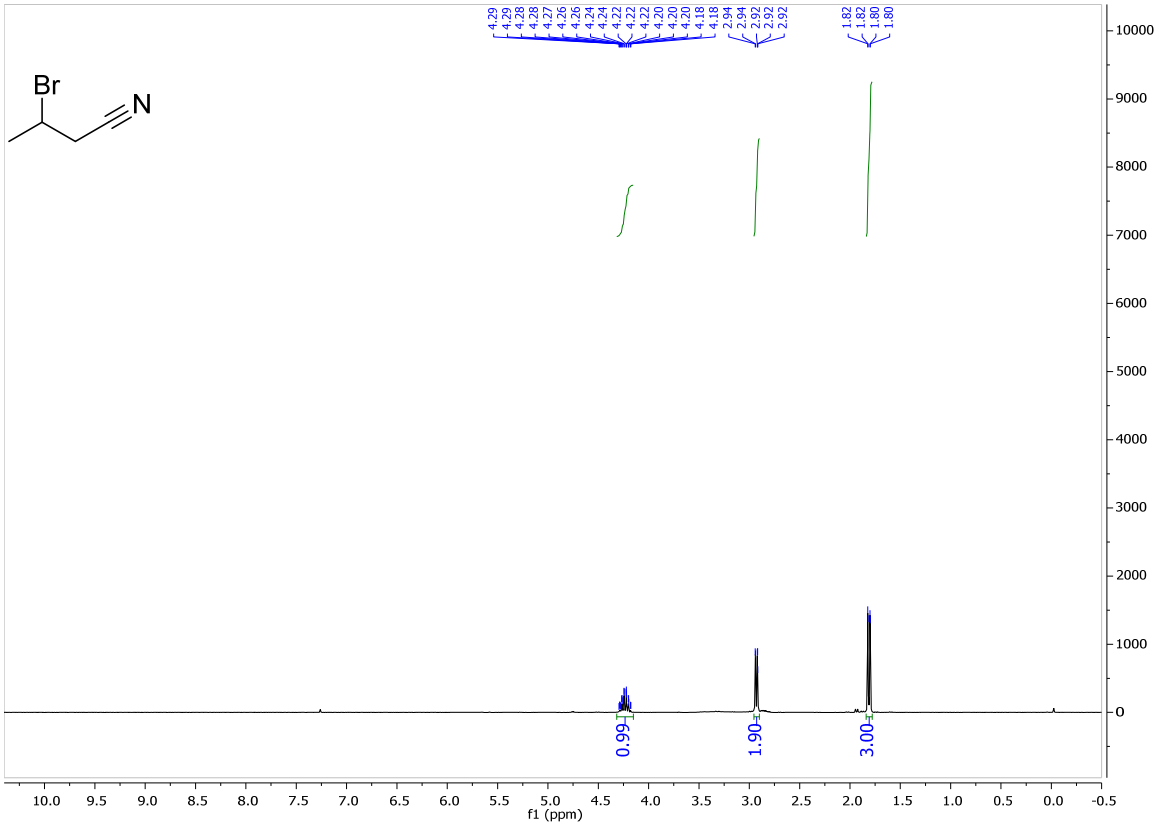


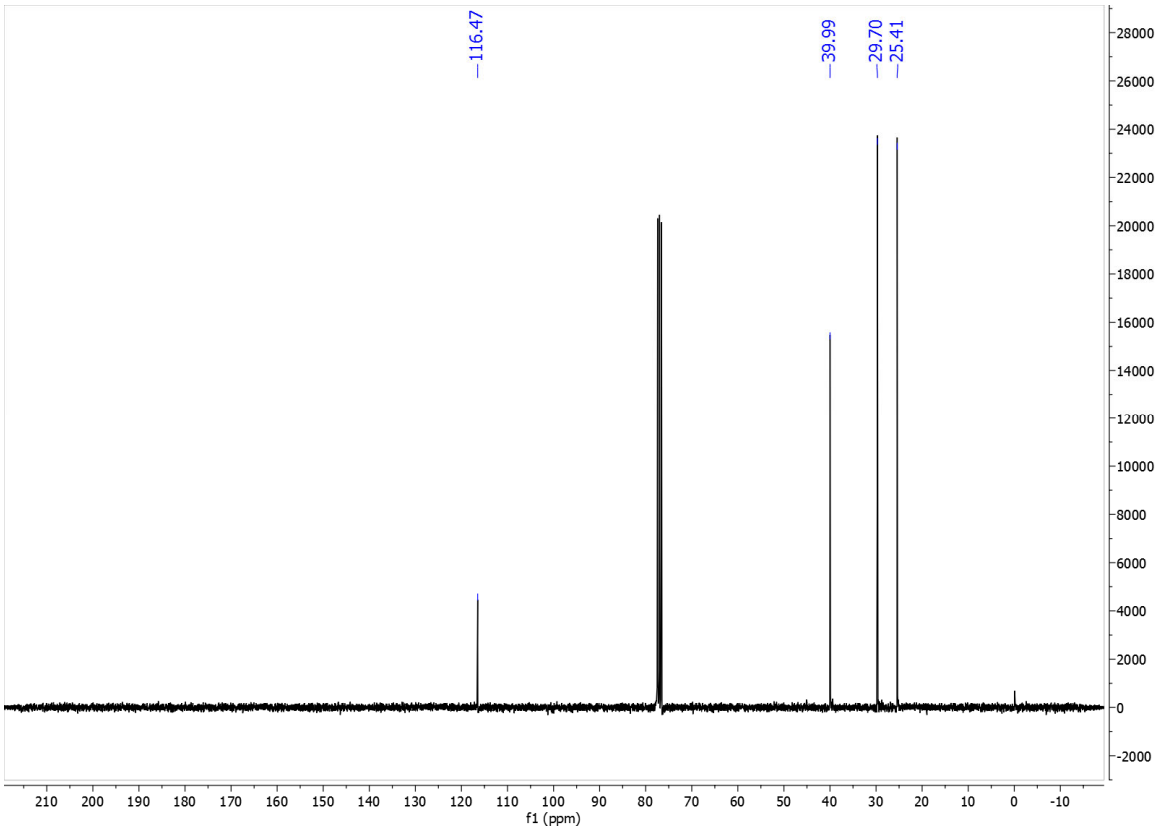
(*S*)-3-((*2S,3S*)-3-Bromo-2-methylpentanoyl)-4-(*tert*-butyl)oxazolidin-2-one (4i)



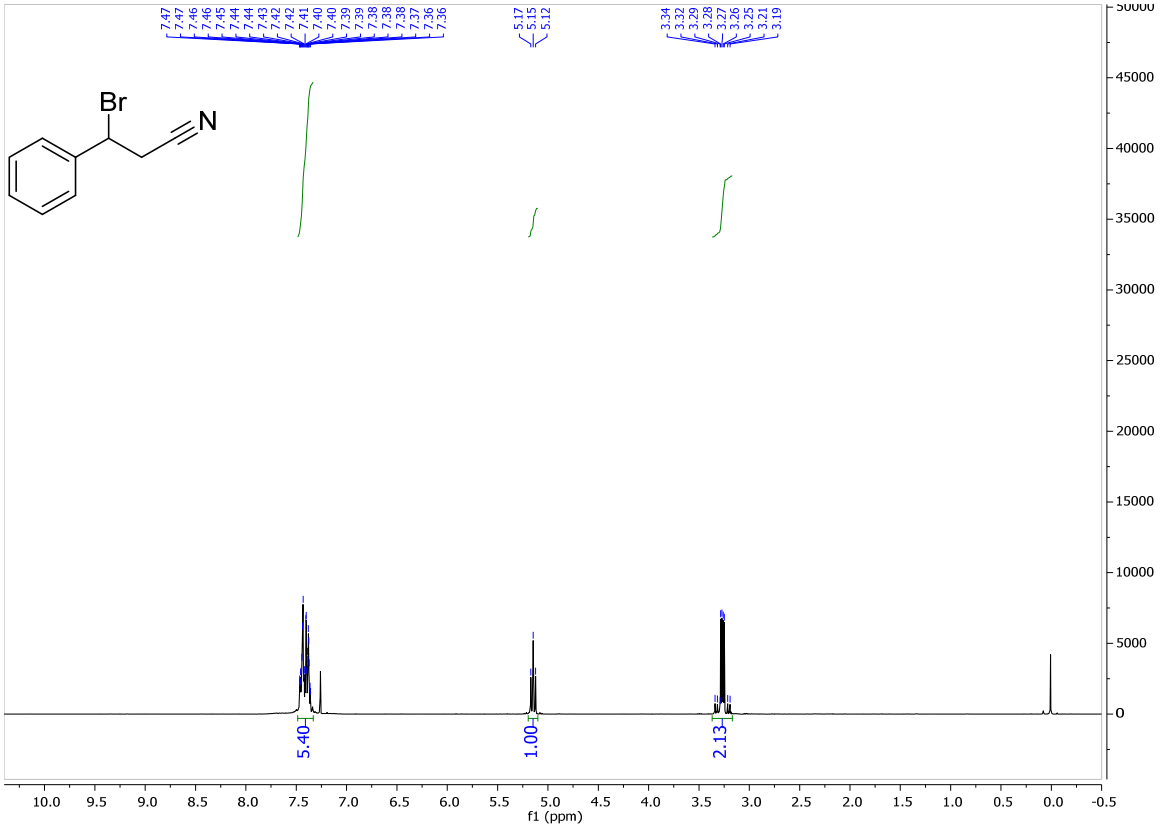

173.32
154.55
65.43
61.11
60.21
43.69
35.76
30.77
26.91
25.72
12.50
12.05
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

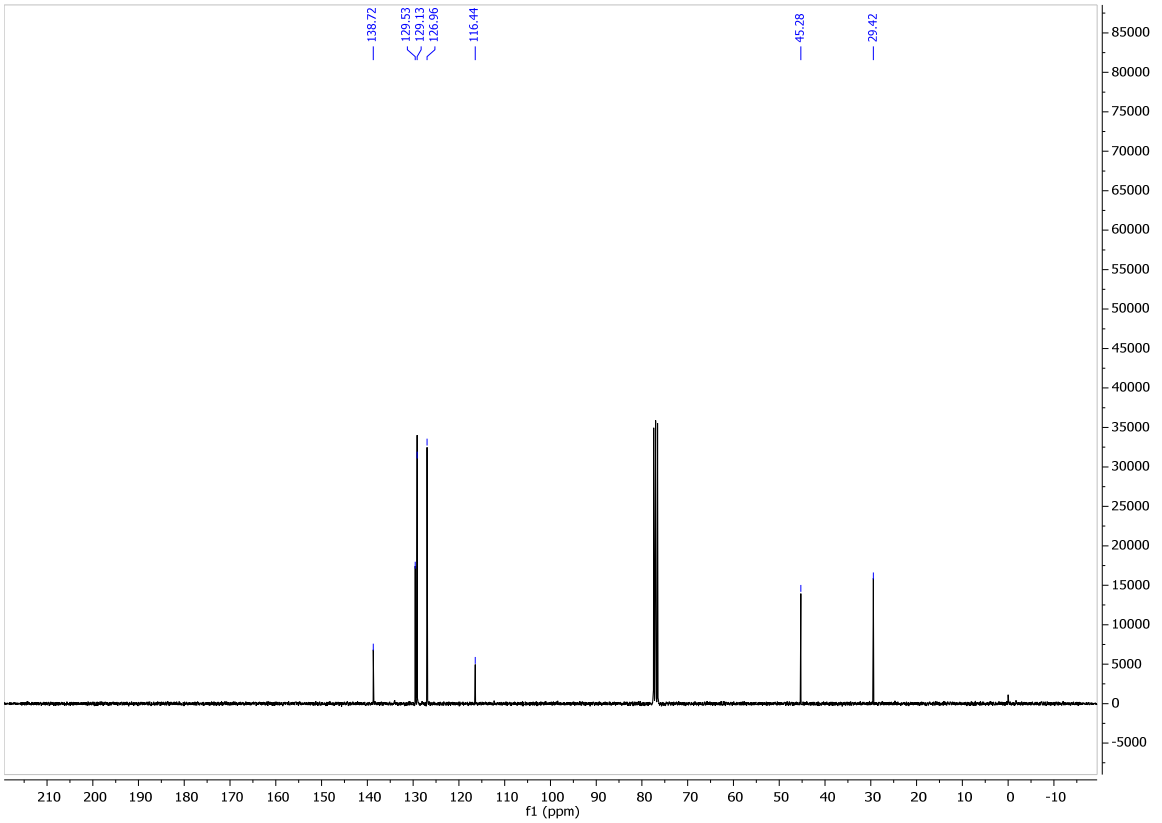
3-Bromobutanenitrile (7a)



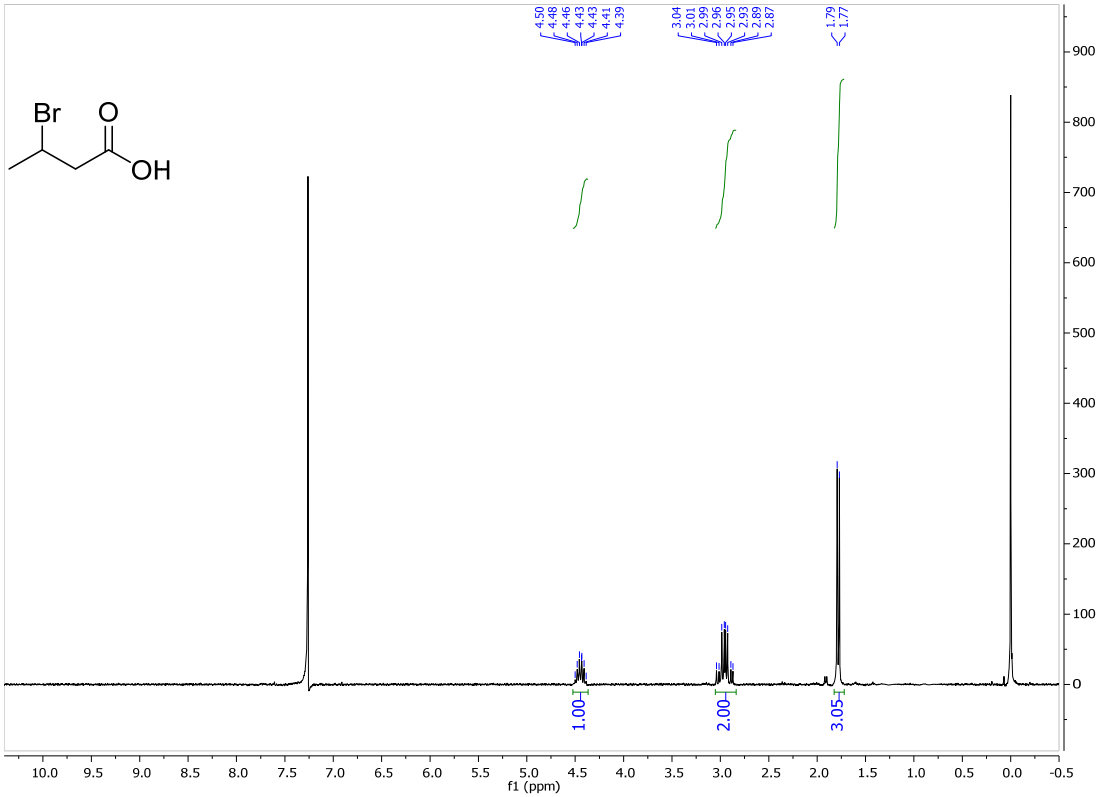


3-Bromo-3-phenylpropanenitrile (7b)

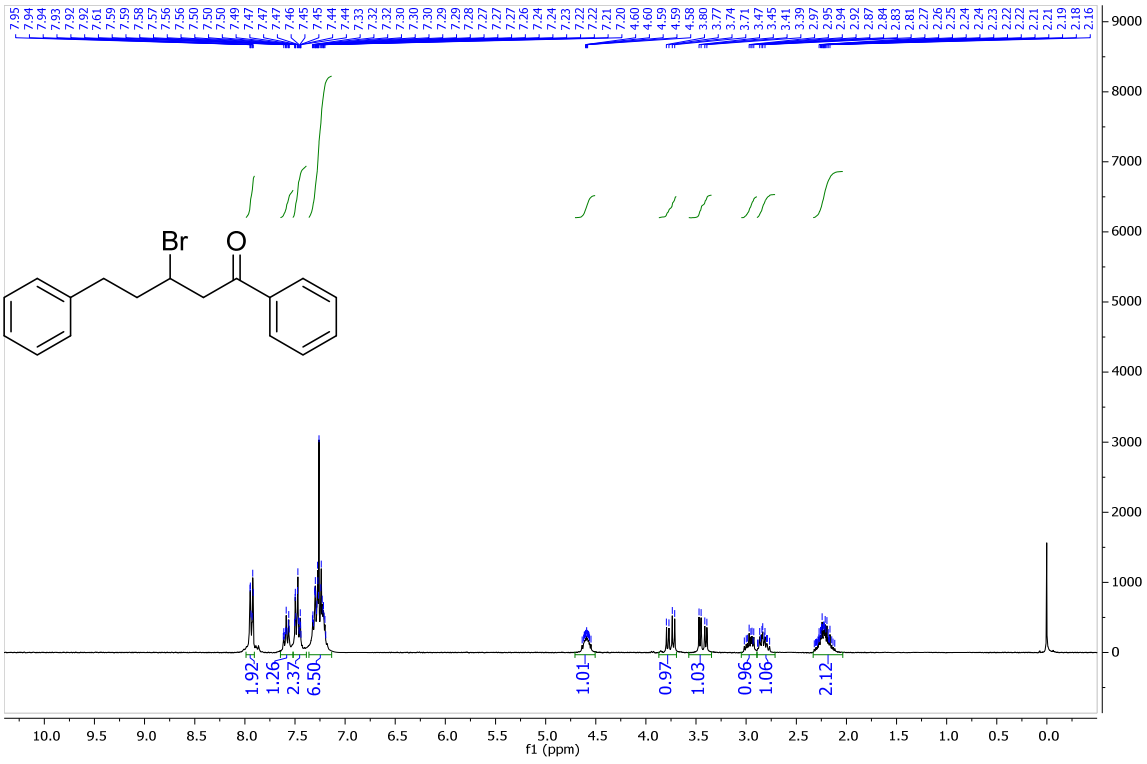


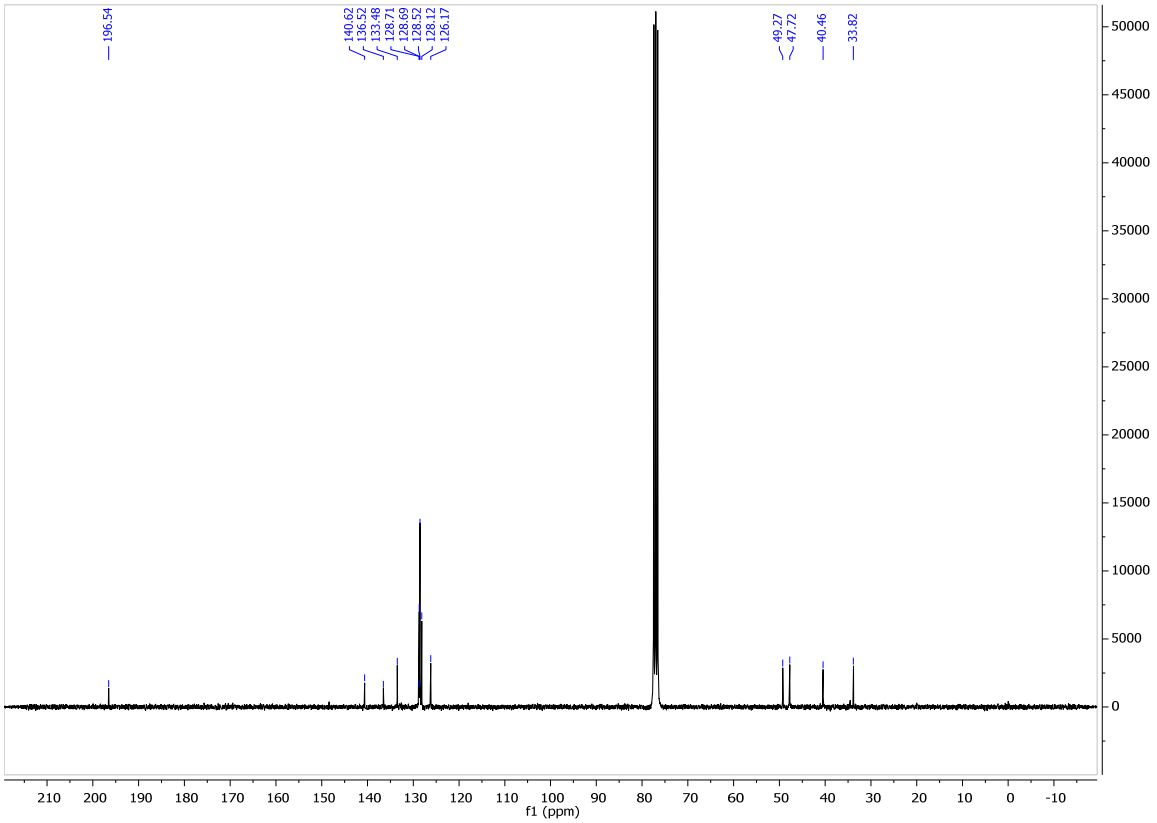


3-Bromobutanoic acid (7c)

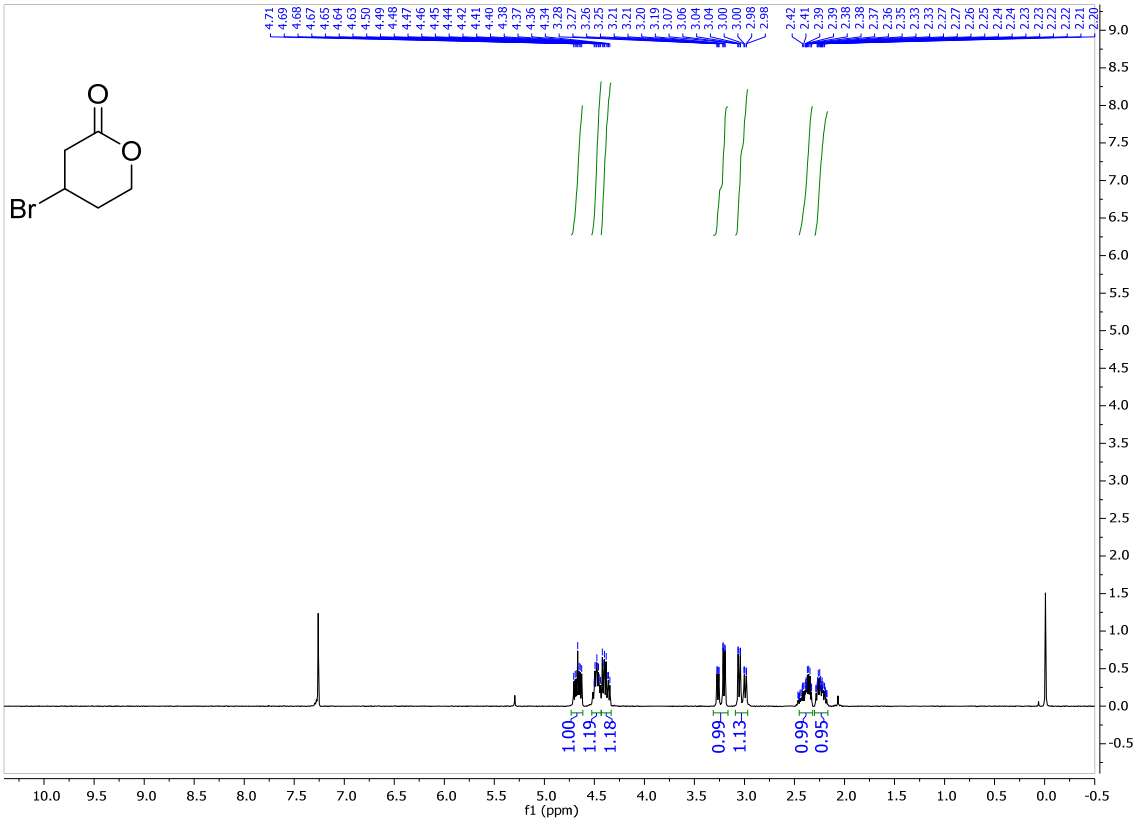


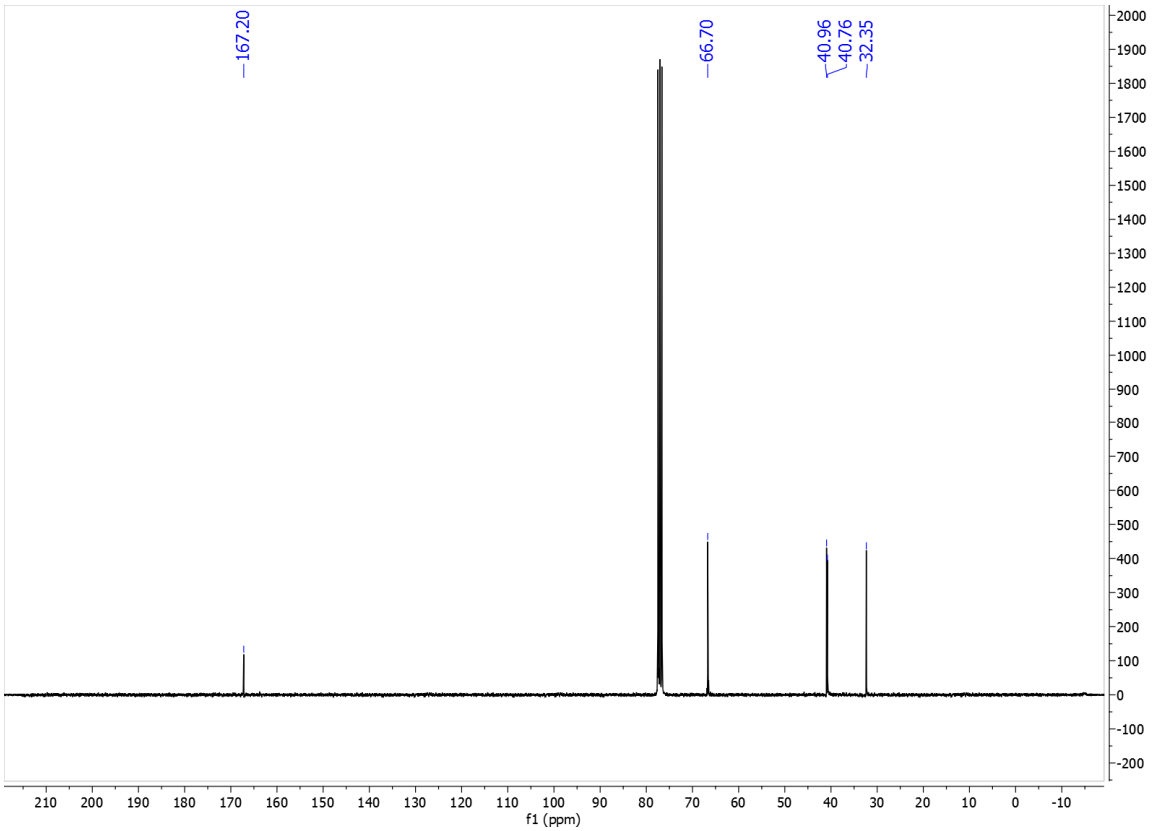
3-Bromo-1,5-diphenylpentan-1-one (7d)



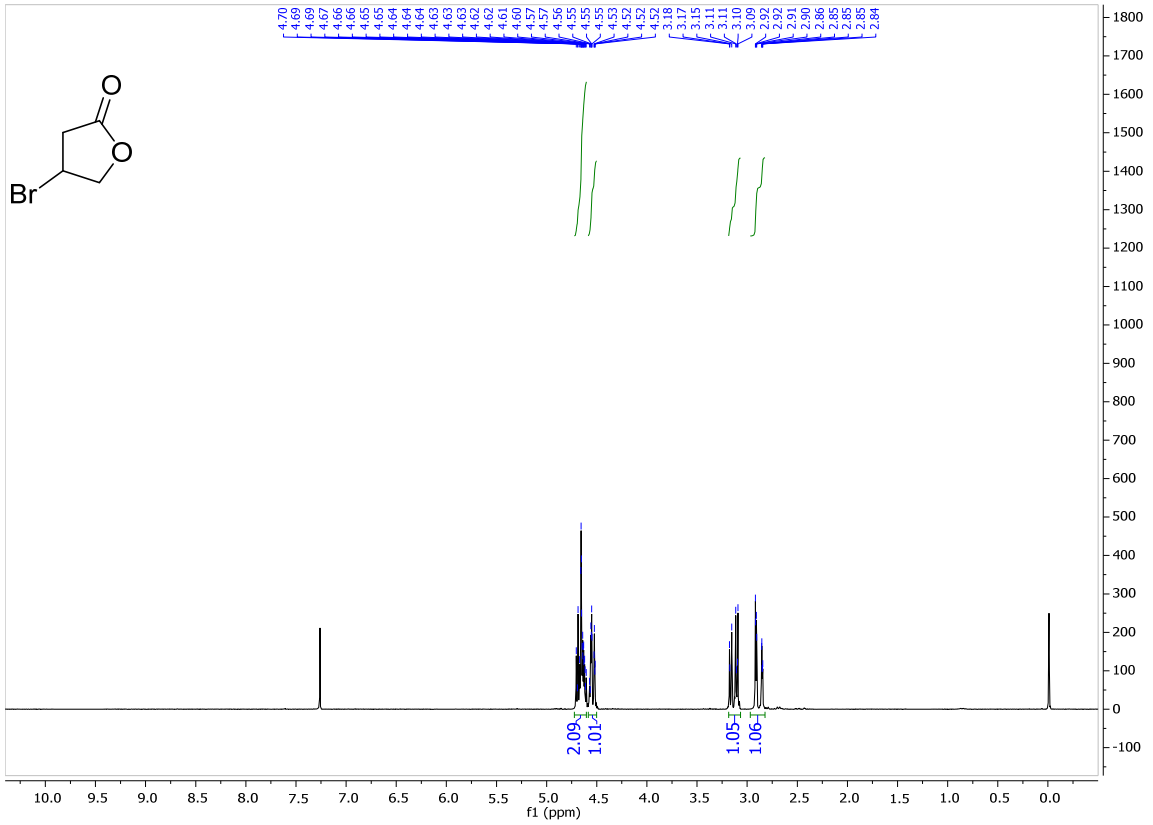


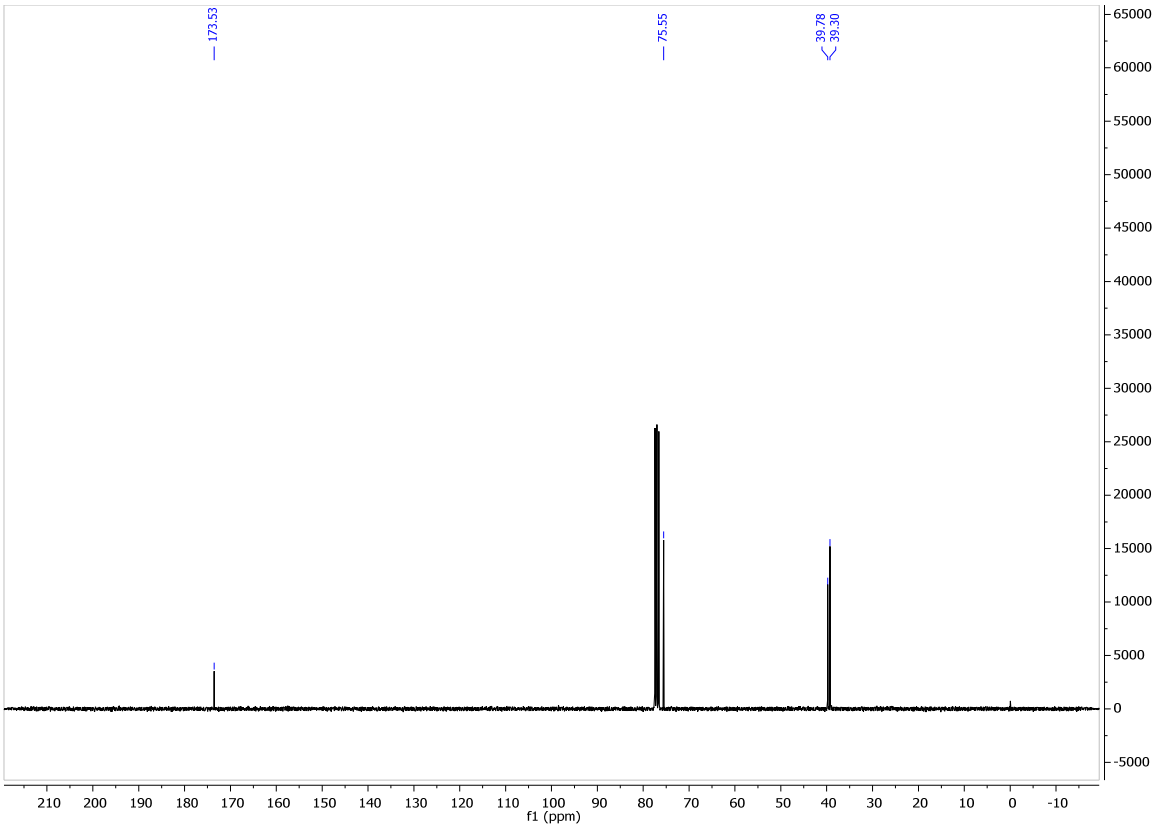
4-Bromotetrahydro-2H-pyran-2-one (7e)



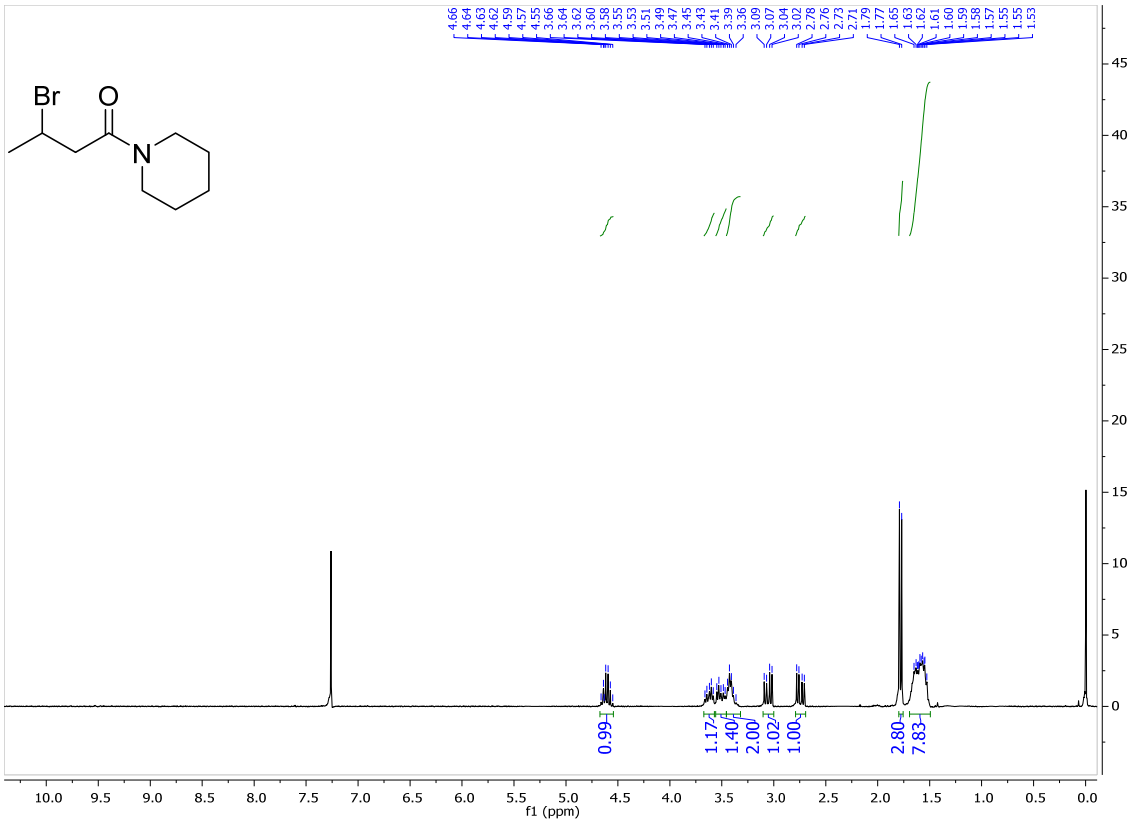


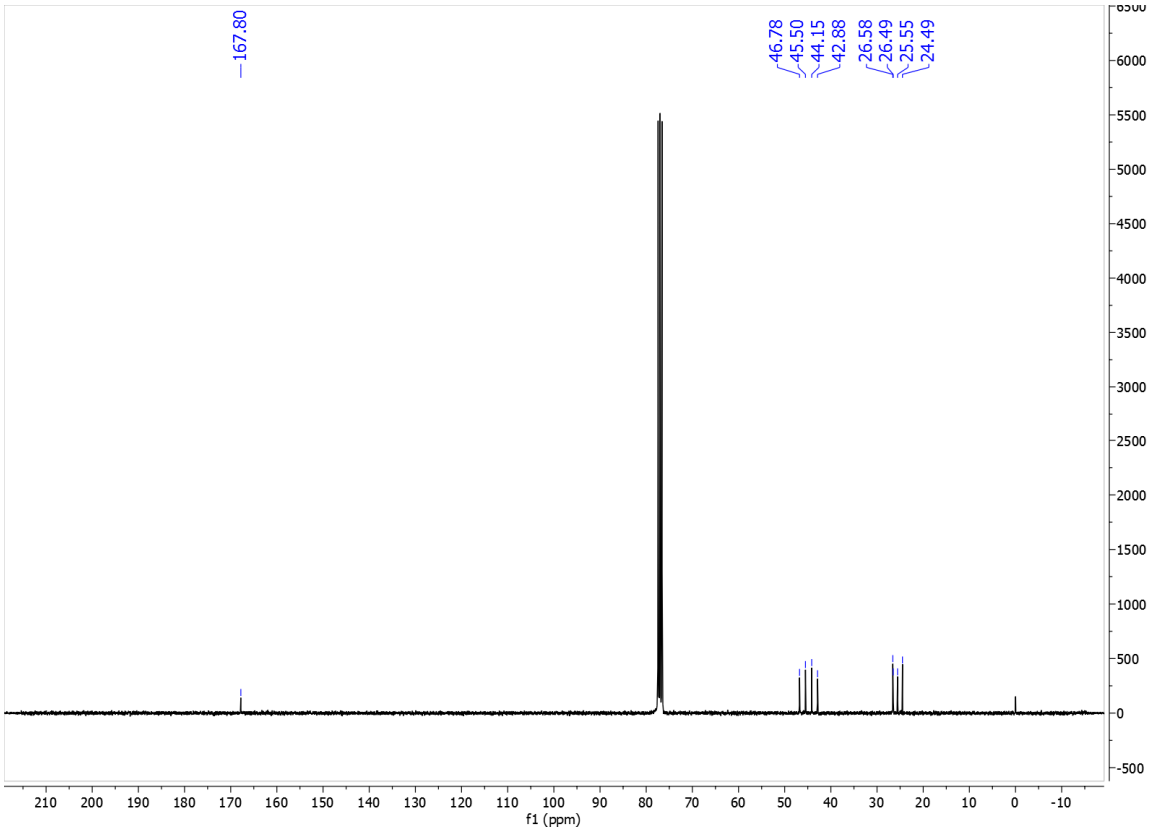
4-Bromodihydrofuran-2(3H)-one (7f)



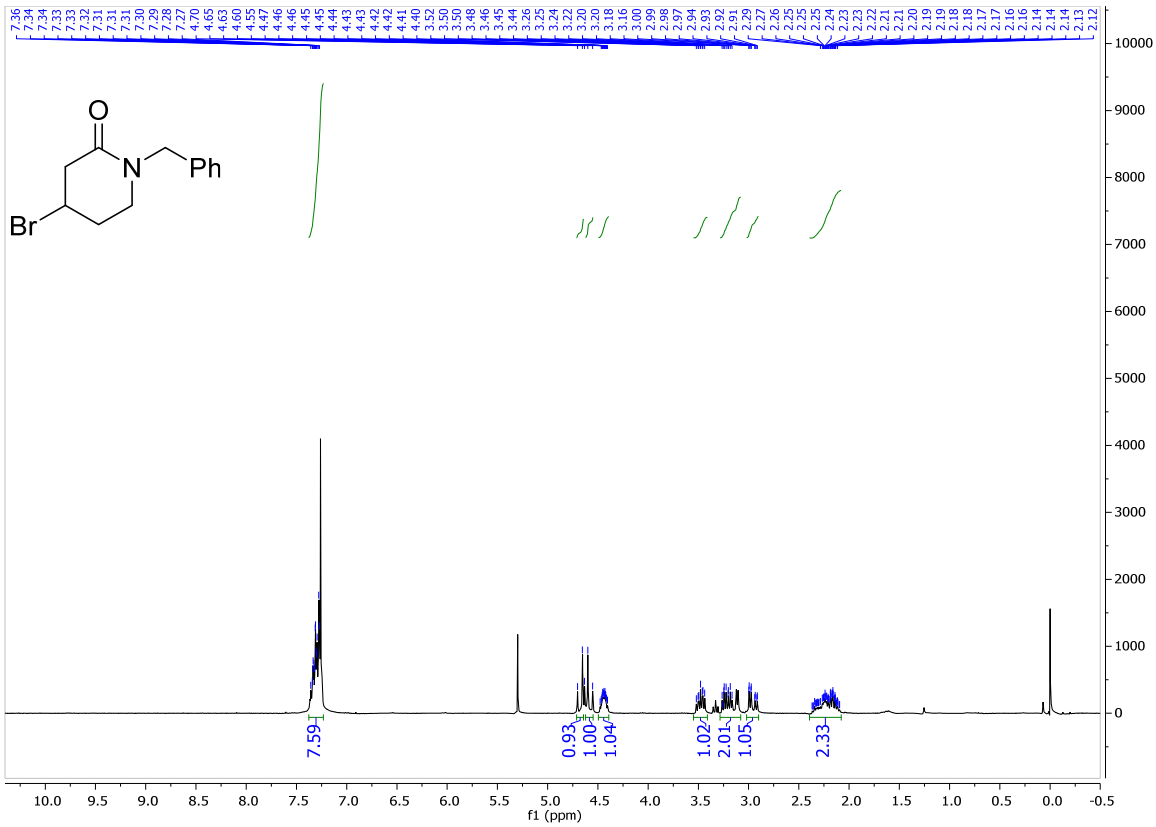


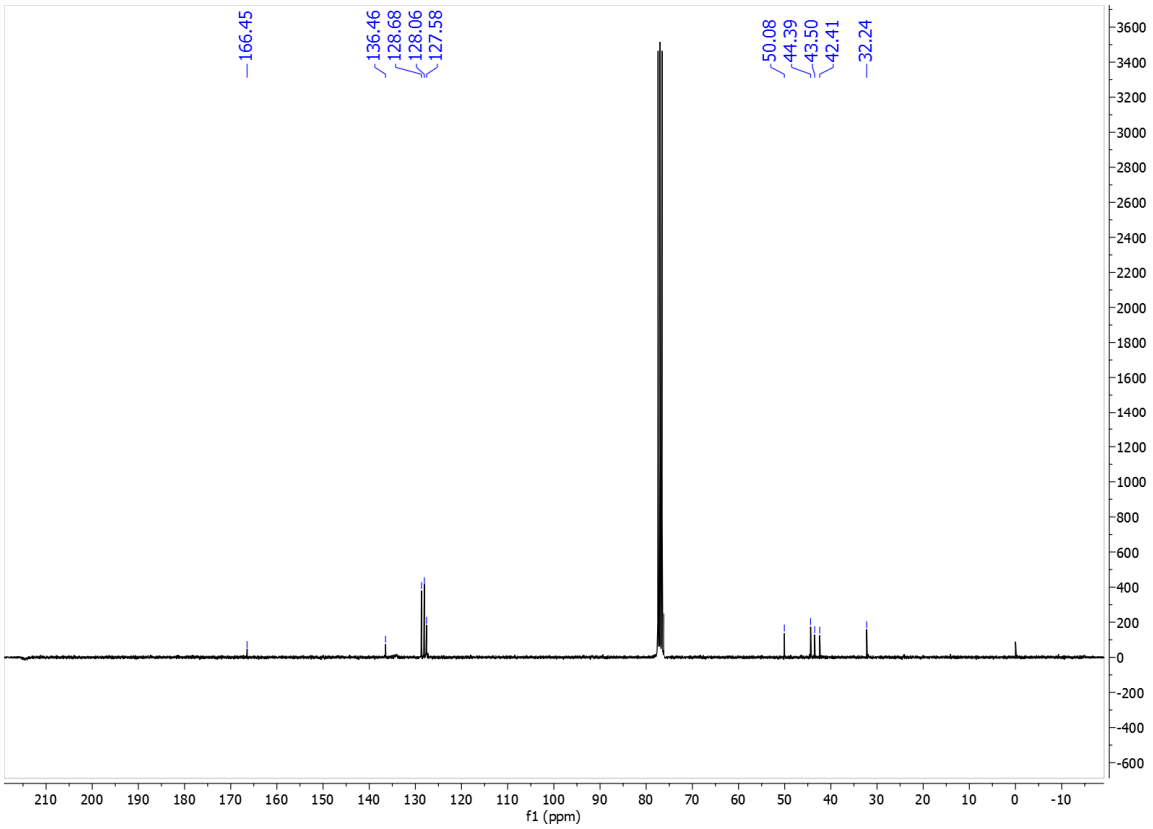
3-Bromo-1-(piperidin-1-yl)butan-1-one (7g)



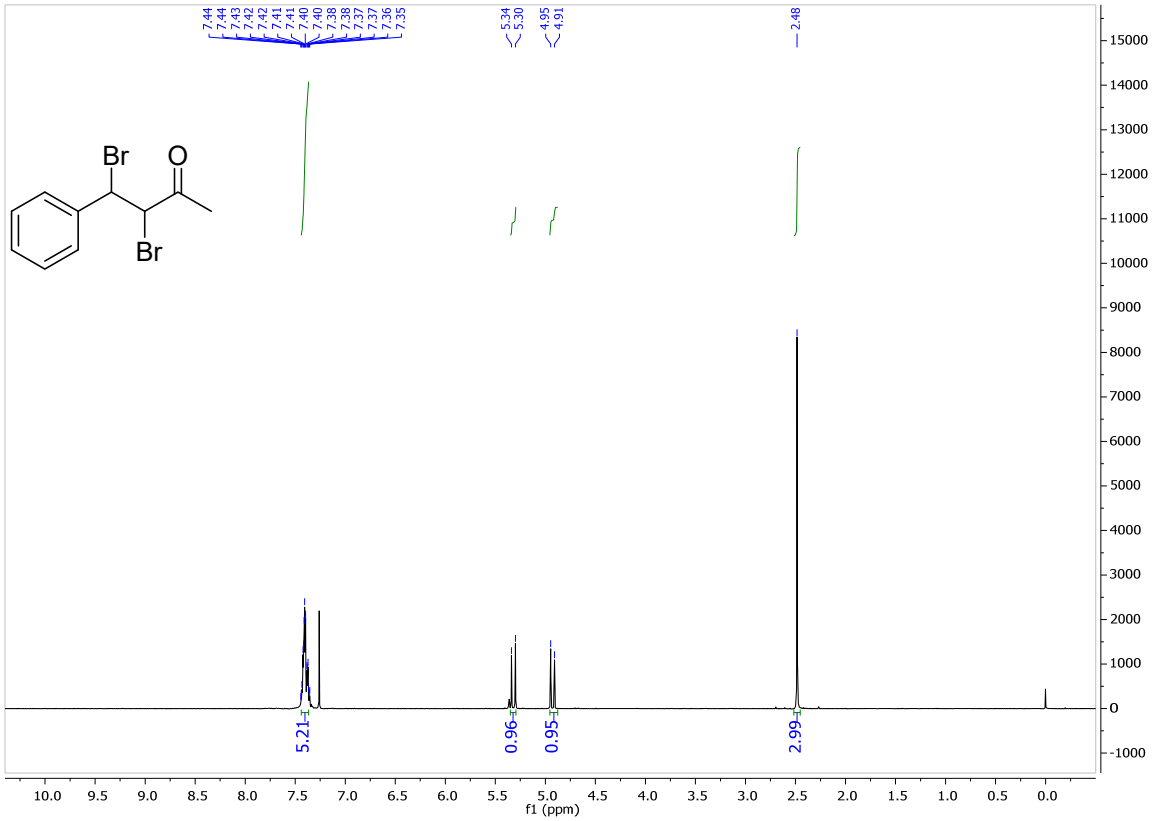


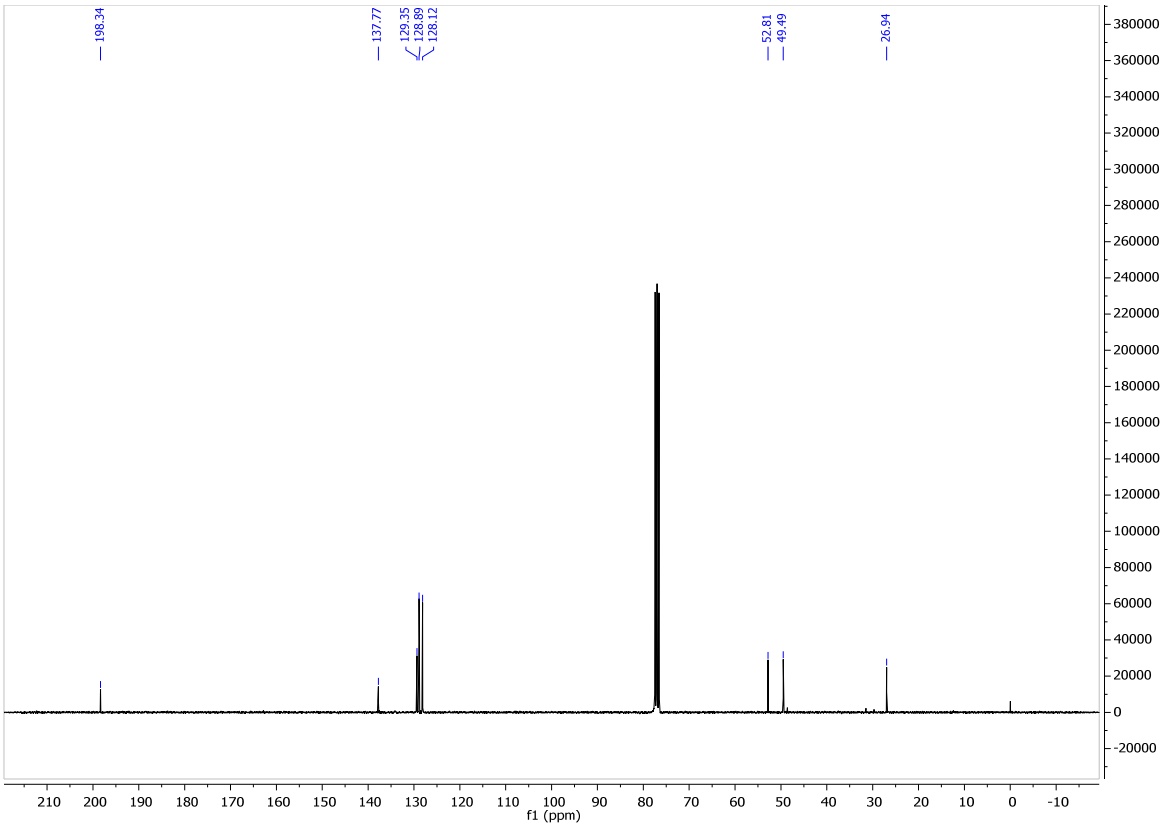
4-Bromo-1-ethylpiperidin-2-one (7h)



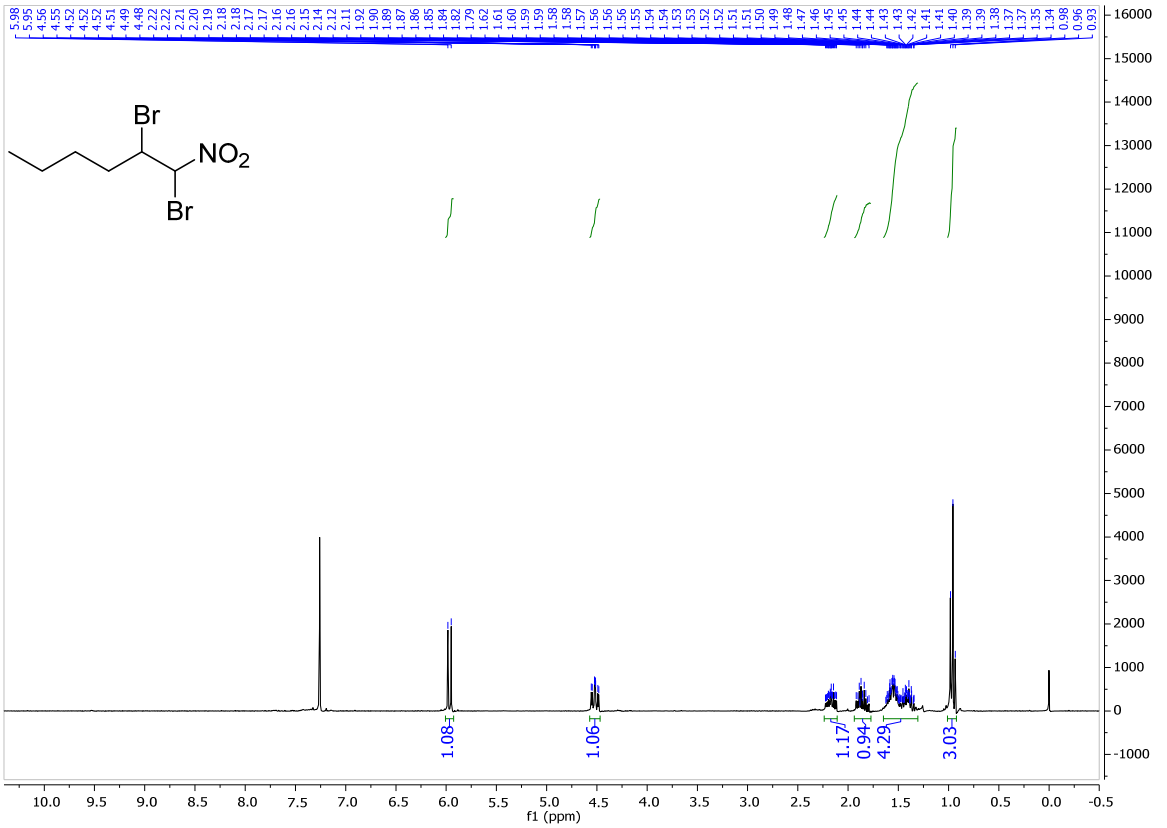


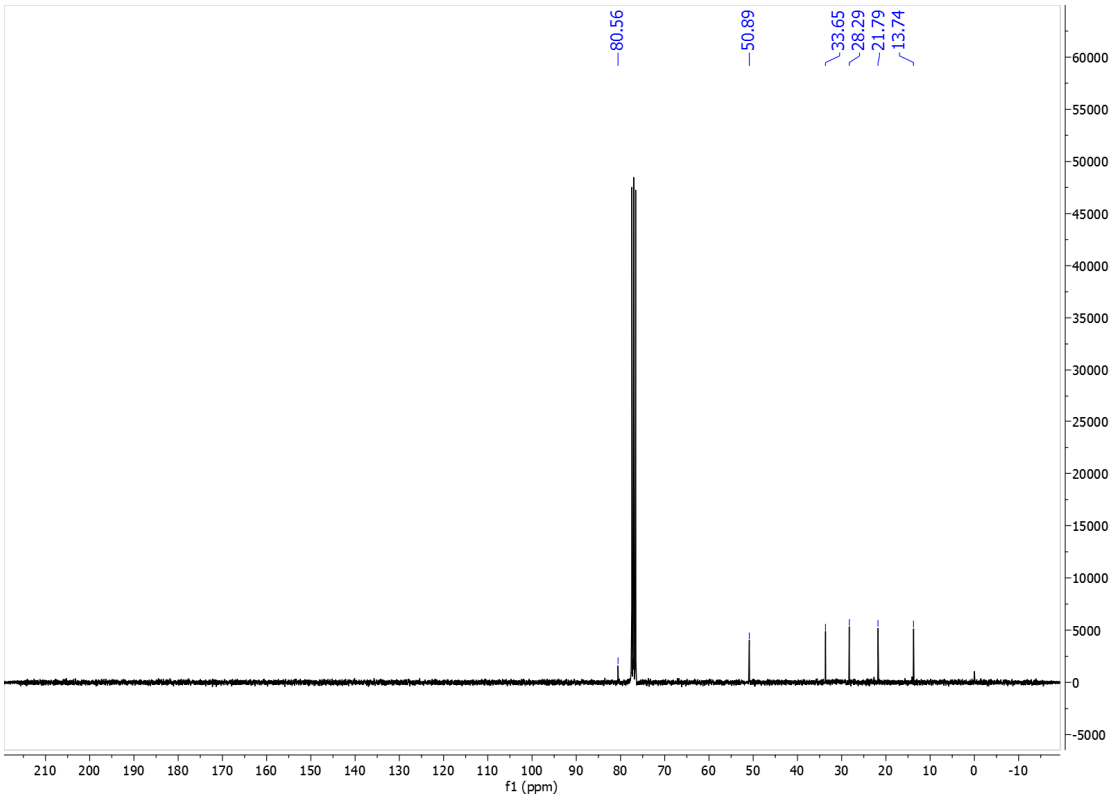
3,4-Dibromo-4-phenylbutan-2-one (8a)



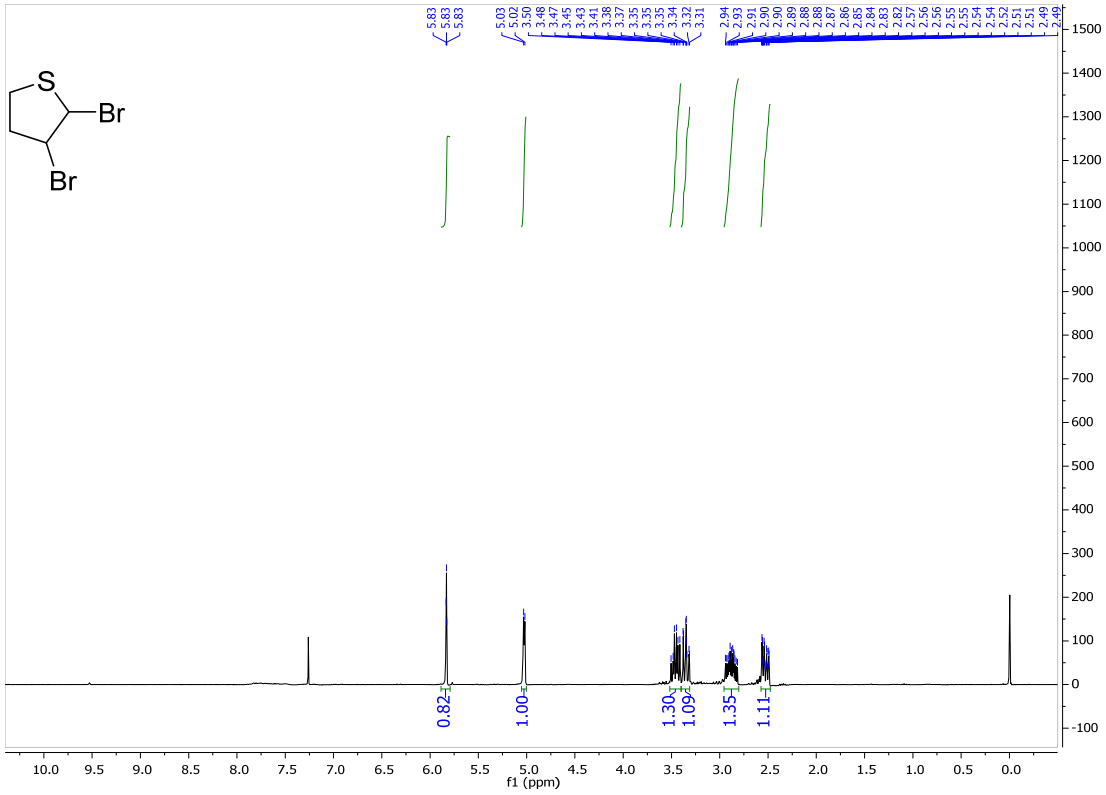


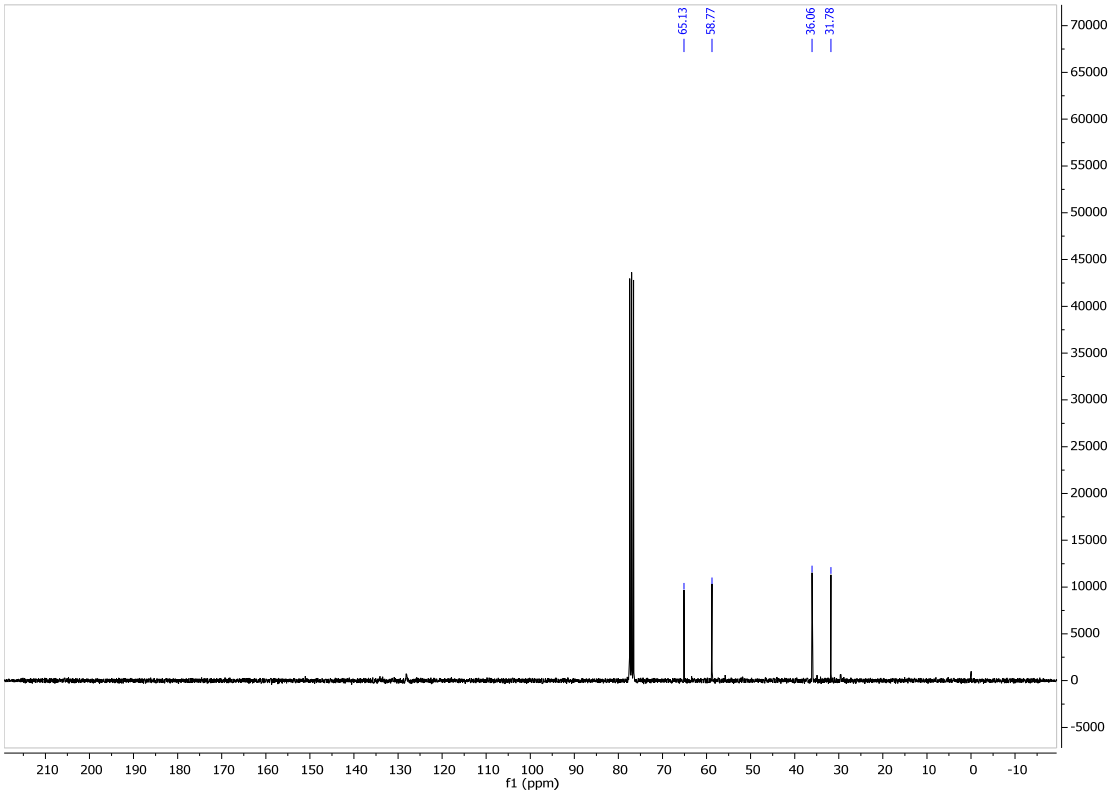
1,2-Dibromo-1-nitrohexane (8b)



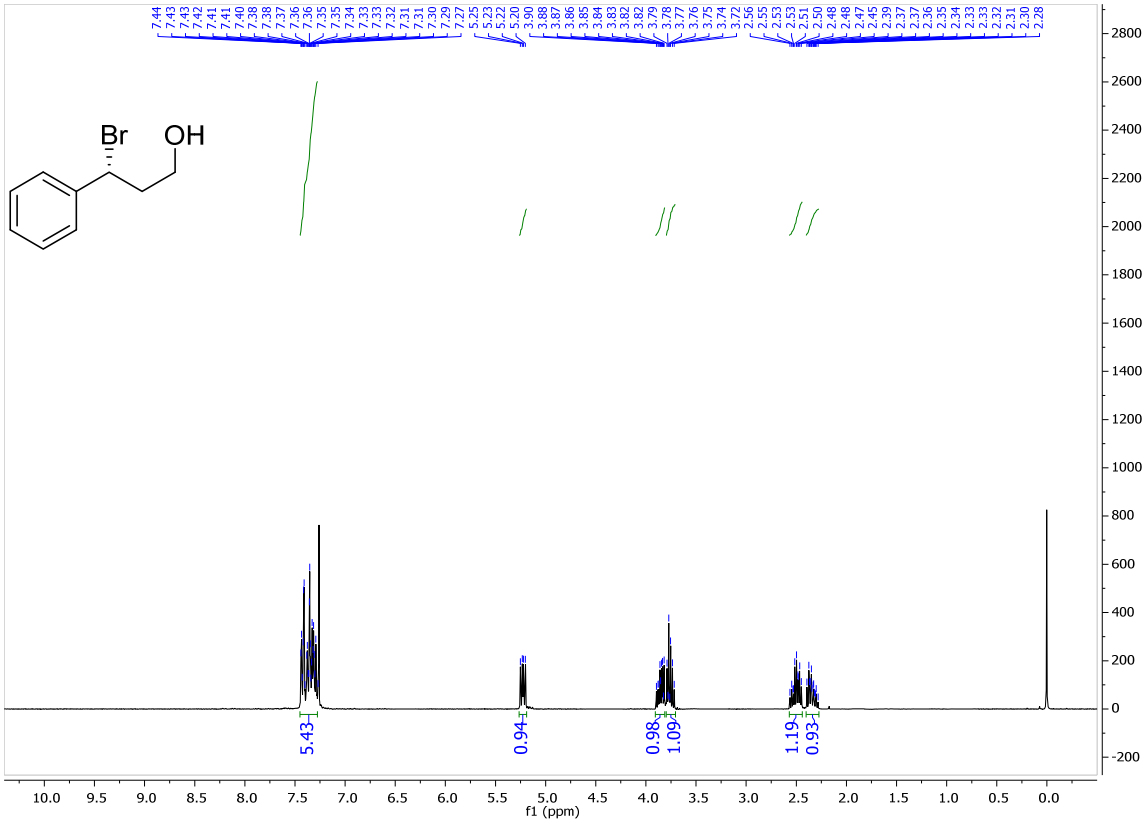


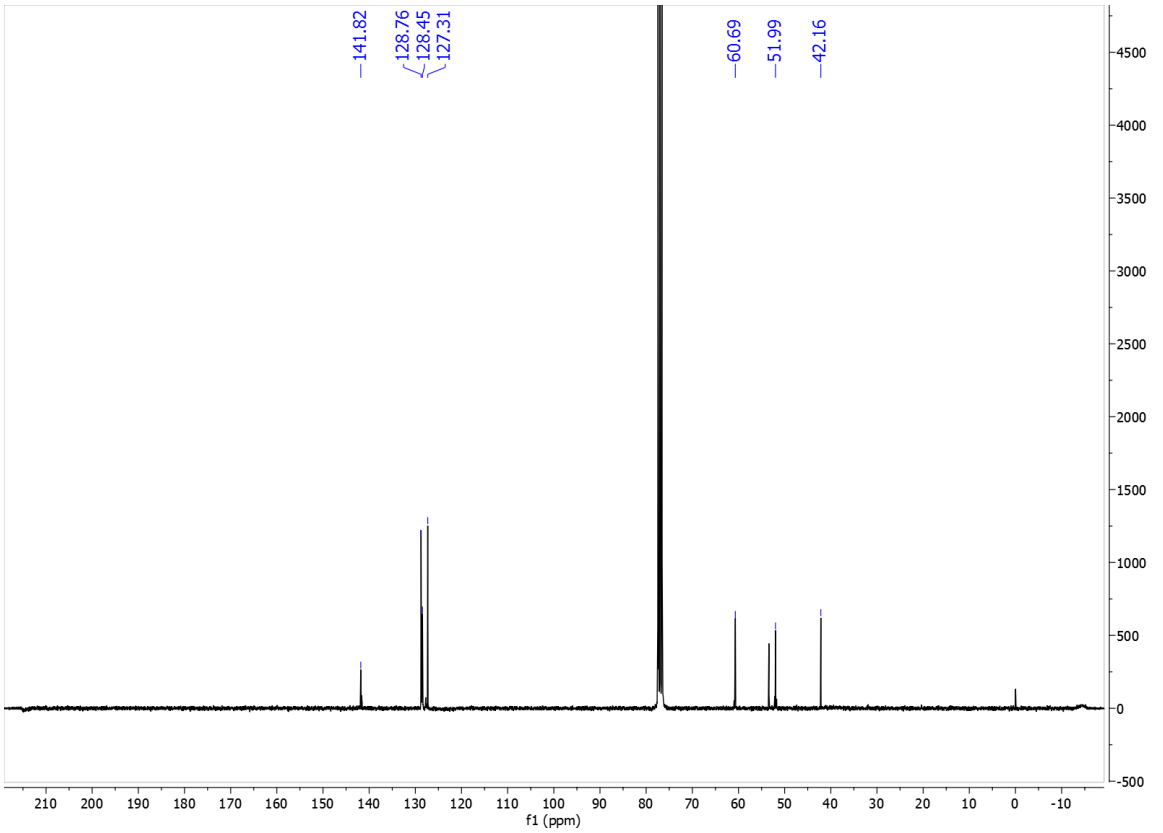
2,3-Dibromotetrahydrothiophene SI2



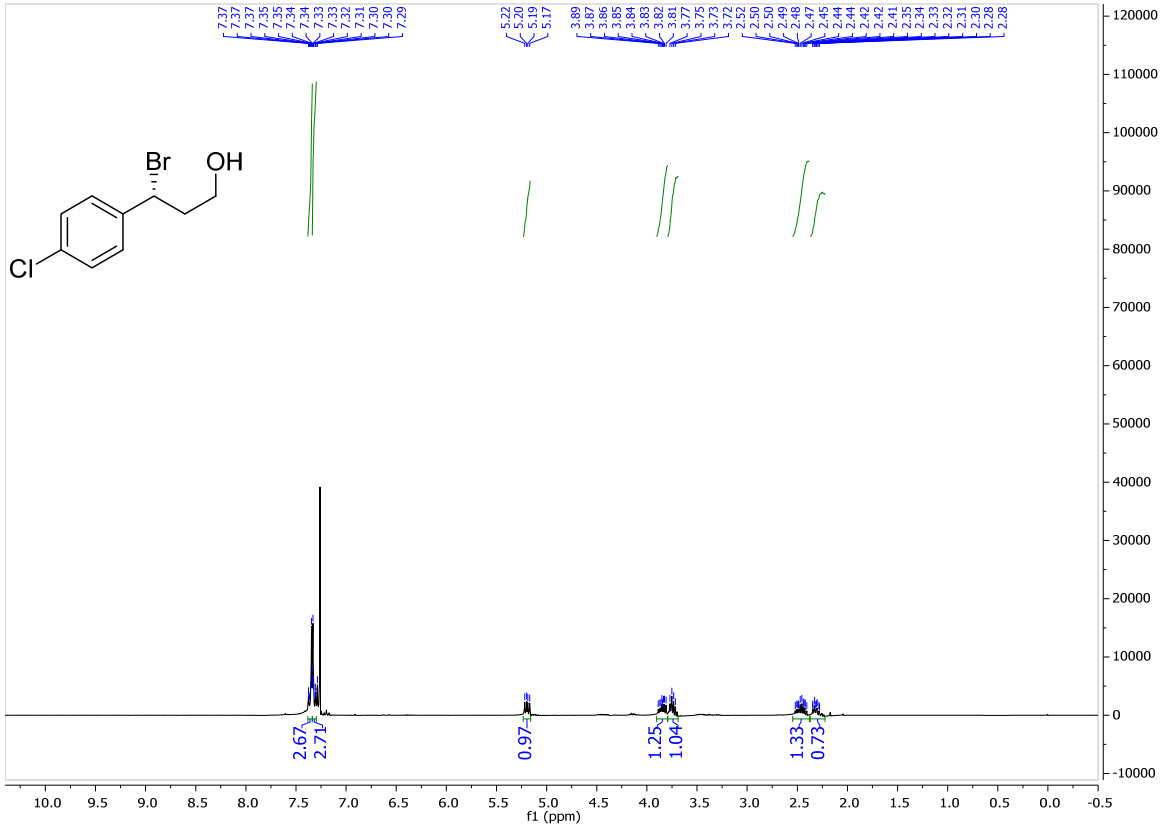


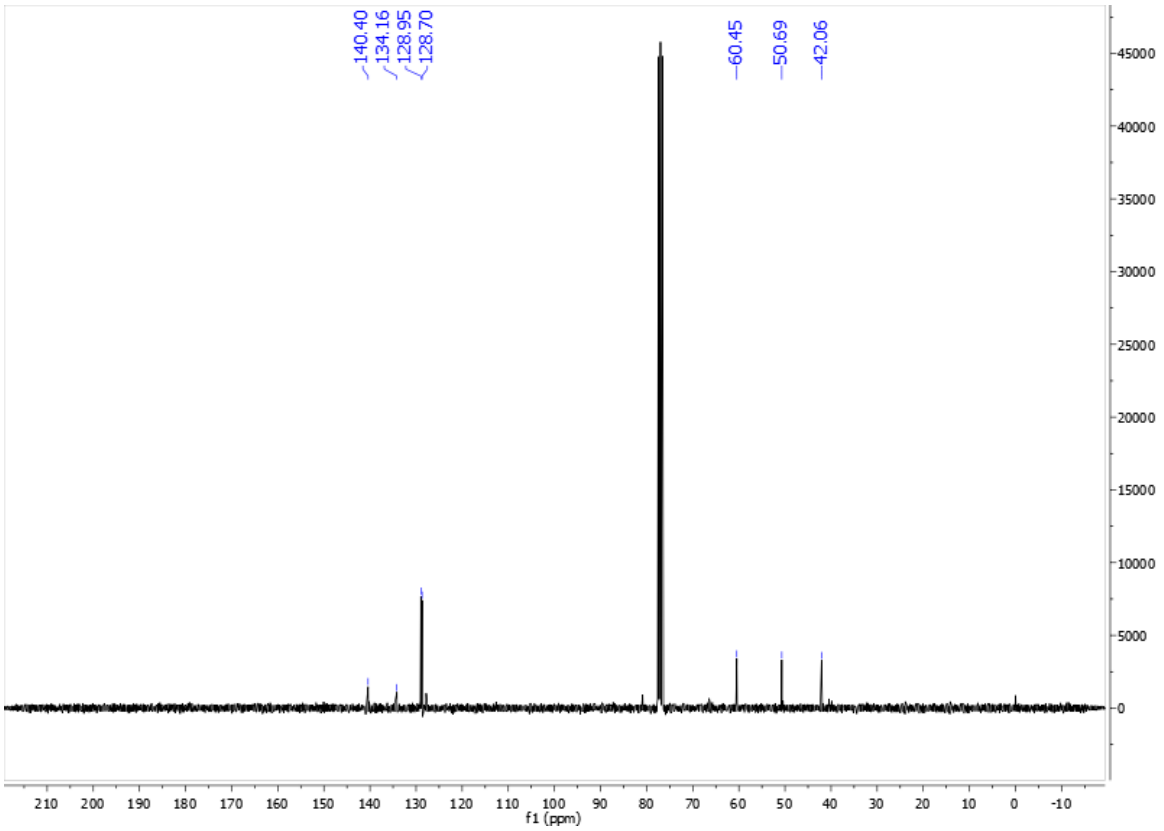
(*R*)-3-Bromo-3-phenylpropan-1-ol (9a)



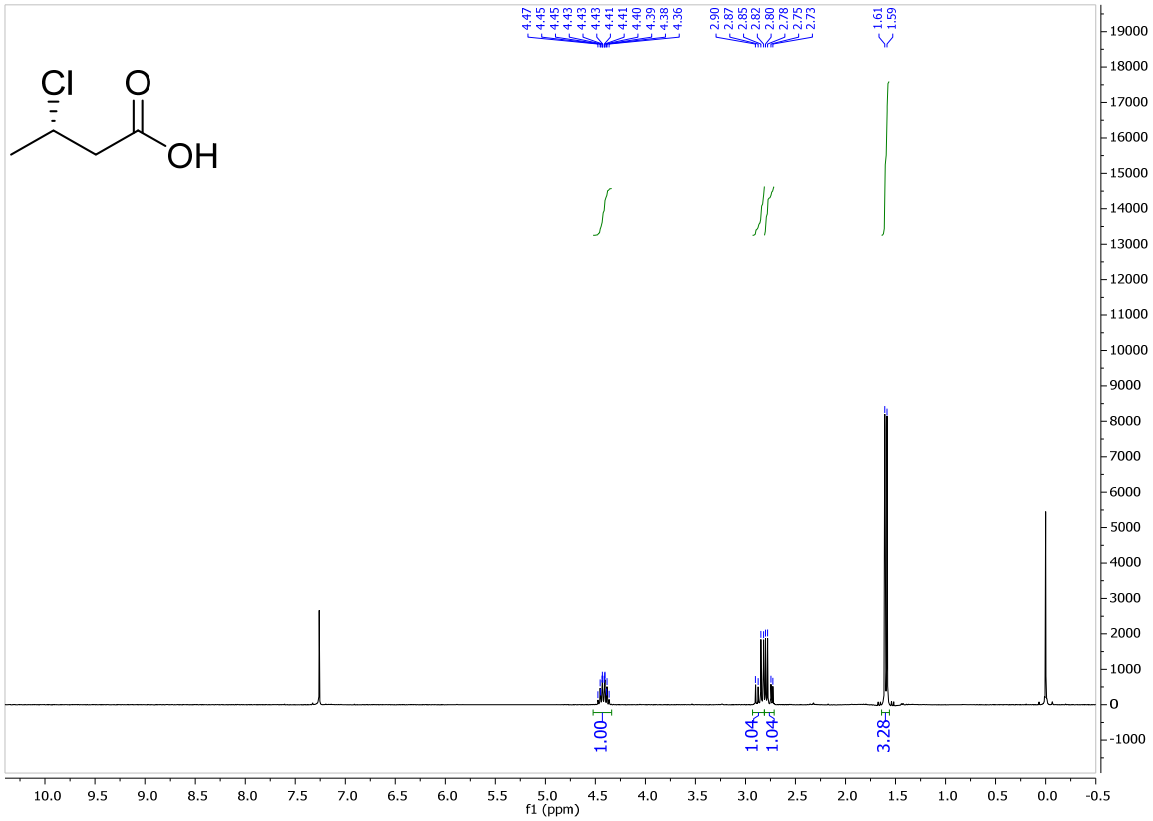


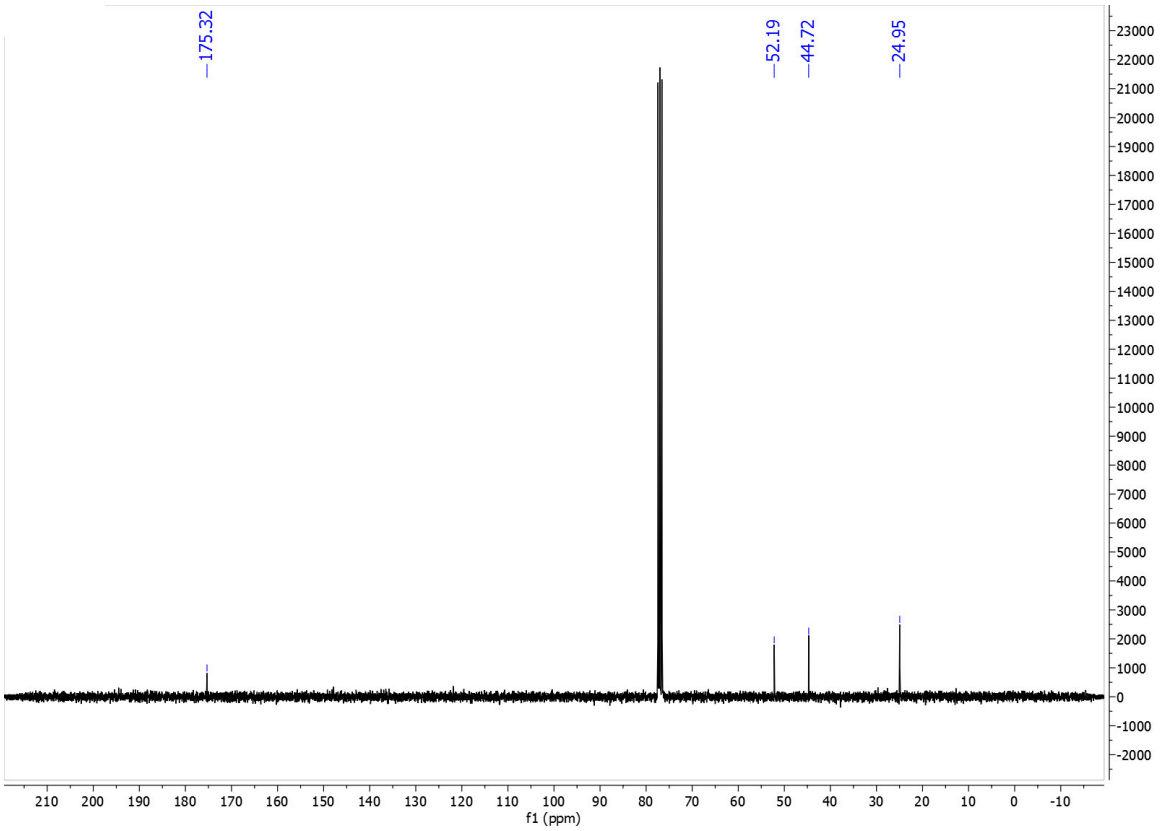
(*R*)-3-Bromo-3-(4-chlorophenyl)propan-1-ol (9b)



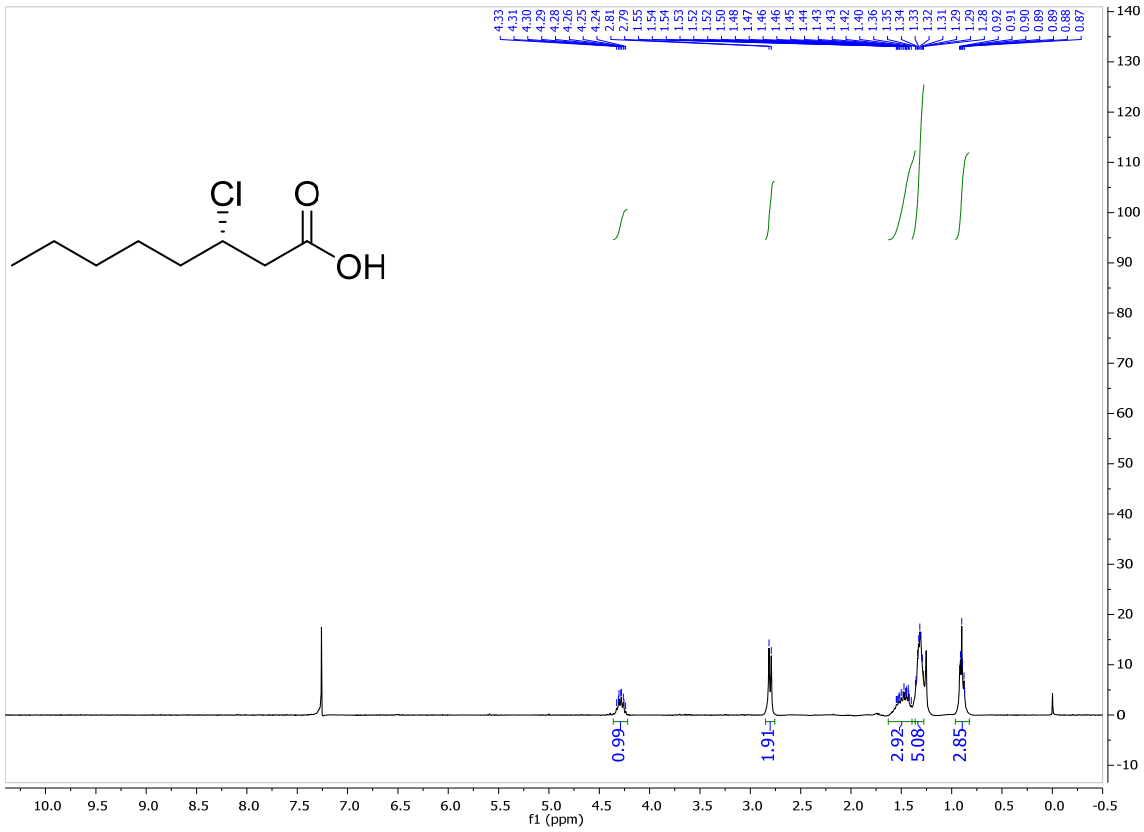


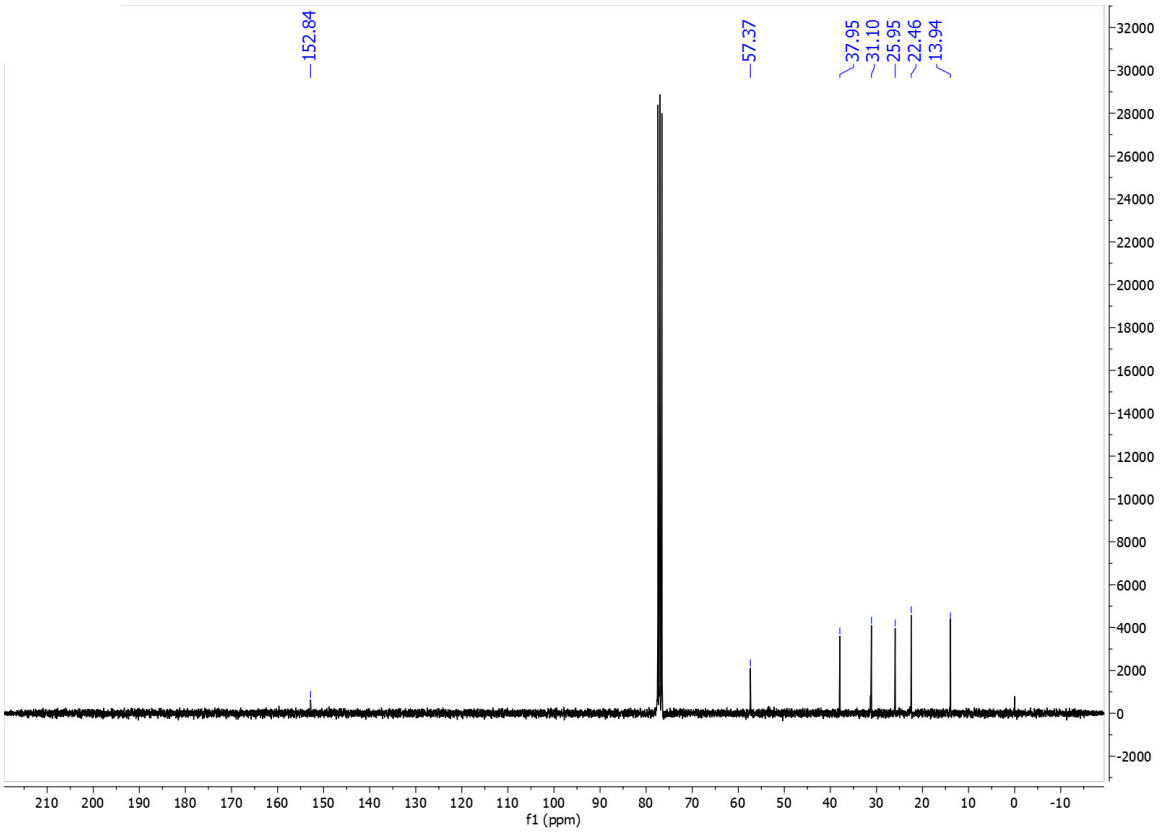
(*S*)-3-Chlorobutanoic acid (10a)



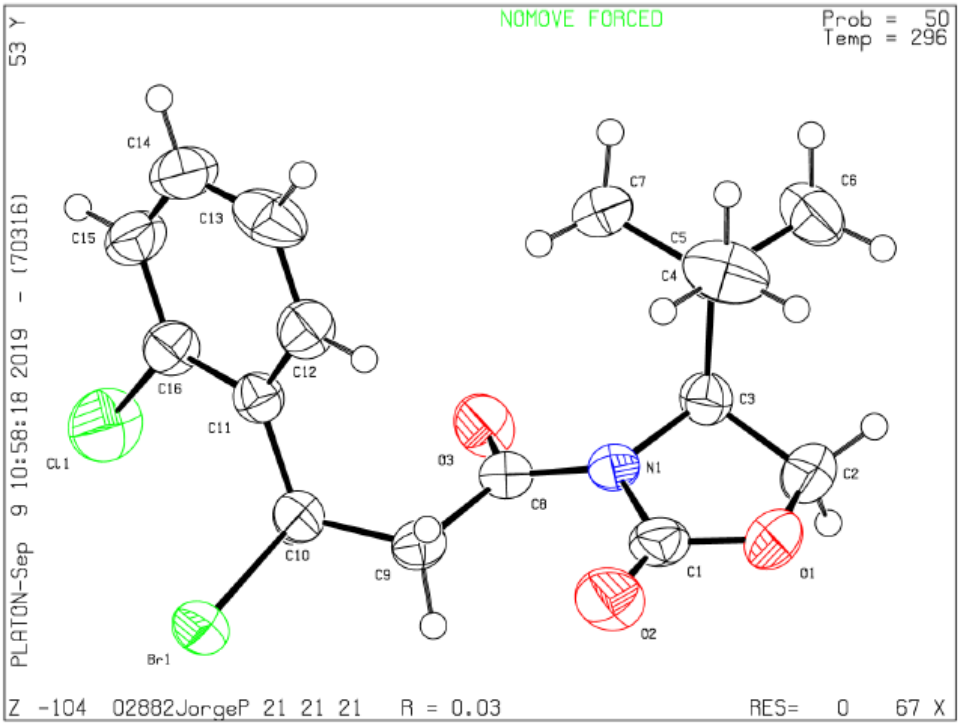


(*S*)-3-Chlorooctanoic acid (10b)




152.84
57.37
37.95
31.10
25.95
22.46
13.94
f1 (ppm)

8. Single Crystal X-Ray Structure of compound 4e.



A clear colourless prismatic-like specimen of $C_{16}H_{19}BrClNO_3$, approximate dimensions 0.219 mm x 0.355 mm x 0.429 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 1.67 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 56068 reflections to a maximum θ angle of 25.34° (0.83 Å resolution), of which 3131 were independent (average redundancy 17.907, completeness = 100.0%, R_{int} = 3.75%, R_{sig} = 1.52%) and 2946 (94.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.0480(2) Å, b = 12.9076(3) Å, c = 18.7303(5) Å, volume = 1703.95(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 9803 reflections above 20 σ(I) with 5.374° < 2θ < 46.00°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.734. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4040 and 0.6020.

The final anisotropic full-matrix least-squares refinement on F^2 with 202 variables converged at R1 = 2.84%, for the observed data and wR2 = 8.58% for all data. The goodness-of-fit was 1.192.

The largest peak in the final difference electron density synthesis was 0.457 $e^-/Å^3$ and the largest hole was -0.220 $e^-/Å^3$ with an RMS deviation of 0.063 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.515 g/cm^3 and F(000), 792 e^-.

Table 1. Sample and crystal data.

Identification code	02882JorgeHumbrias	
Chemical formula	$C_{16}H_{19}BrClNO_3$	
Formula weight	388.68 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.219 x 0.355 x 0.429 mm	
Crystal habit	clear colourless prismatic	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.0480(2) Å	α = 90°
	b = 12.9076(3) Å	β = 90°
	c = 18.7303(5) Å	γ = 90°
Volume	1703.95(8) $Å^3$	
Z	4	
Density (calculated)	1.515 g/cm^3	
Absorption coefficient	2.580 mm^{-1}	
F(000)	792	

Table 2. Data collection and structure refinement.

Theta range for data collection	1.92 to 25.34°
Index ranges	-8<=h<=8, -15<=k<=15, -22<=l<=22
Reflections collected	56068
Independent reflections	3131 [R(int) = 0.0375]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.6020 and 0.4040
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3131 / 0 / 202
Goodness-of-fit on F^2	1.192
Δ/σ_{max}	0.001

Final R indices	2946 data; I>2σ(I)	R1 = 0.0284, wR2 = 0.0740
	all data	R1 = 0.0320, wR2 = 0.0858
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0458P)^2+0.5981P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	0.457 and -0.220 eÅ^{-3}	
R.M.S. deviation from mean	0.063 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2).

U(eq) is defined as one third of the trace of the U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Br1	0.45685(8)	0.44691(4)	0.70546(2)	0.05026(17)
C1	0.4494(9)	0.2521(3)	0.4466(3)	0.0477(11)
C2	0.3411(10)	0.2662(4)	0.3328(3)	0.0665(17)
C3	0.3983(7)	0.3749(4)	0.3555(2)	0.0407(10)
C4	0.5785(6)	0.4166(3)	0.3186(2)	0.0373(10)
C5	0.7478(9)	0.3477(5)	0.3294(4)	0.0701(17)
C6	0.5369(9)	0.4285(5)	0.2391(3)	0.0616(14)
C7	0.6249(10)	0.5244(4)	0.3482(3)	0.0676(17)
C8	0.3786(7)	0.4325(3)	0.4829(2)	0.0393(10)
C9	0.4202(8)	0.4053(3)	0.5600(2)	0.0457(12)
C10	0.4278(7)	0.5007(4)	0.6061(2)	0.0415(11)
C11	0.5854(6)	0.5751(3)	0.5908(2)	0.0369(10)
C12	0.7525(8)	0.5463(4)	0.5566(3)	0.0489(11)
C13	0.8943(8)	0.6169(5)	0.5411(3)	0.0611(15)
C14	0.8693(9)	0.7198(5)	0.5596(3)	0.0600(14)
C15	0.7083(9)	0.7496(4)	0.5934(3)	0.0544(14)
C16	0.5705(7)	0.6788(3)	0.6092(2)	0.0434(11)
Cl1	0.3676(3)	0.72412(11)	0.65196(10)	0.0750(5)
N1	0.4227(5)	0.3583(3)	0.43263(18)	0.0356(8)
O1	0.4141(7)	0.1992(3)	0.3868(2)	0.0692(12)
O2	0.4970(7)	0.2116(3)	0.5007(2)	0.0640(12)
O3	0.3163(6)	0.5149(3)	0.46474(18)	0.0530(9)

Table 4. Bond lengths (Å).

Br1-C10	1.996(4)	C1-O2	1.188(6)
C1-O1	1.335(6)	C1-N1	1.408(6)
C2-O1	1.426(7)	C2-C3	1.521(7)
C2-H2A	0.97	C2-H2B	0.97
C3-N1	1.470(5)	C3-C4	1.543(6)
C3-H3	0.98	C4-C5	1.502(7)
C4-C6	1.526(7)	C4-C7	1.532(7)
C5-H5A	0.96	C5-H5B	0.96
C5-H5C	0.96	C6-H6A	0.96
C6-H6B	0.96	C6-H6C	0.96
C7-H7A	0.96	C7-H7B	0.96
C7-H7C	0.96	C8-O3	1.200(5)
C8-N1	1.378(6)	C8-C9	1.515(6)
C9-C10	1.505(6)	C9-H9A	0.97
C9-H9B	0.97	C10-C11	1.496(6)
C10-H10	0.98	C11-C16	1.387(6)
C11-C12	1.391(7)	C12-C13	1.384(8)
C12-H12	0.93	C13-C14	1.383(9)
C13-H13	0.93	C14-C15	1.355(9)
C14-H14	0.93	C15-C16	1.366(7)
C15-H15	0.93	C16-Cl1	1.740(5)

Table 5. Bond angles (°).

O2-C1-O1	122.8(4)	O2-C1-N1	128.7(5)
O1-C1-N1	108.5(4)	O1-C2-C3	105.3(4)
O1-C2-H2A	110.7	C3-C2-H2A	110.7
O1-C2-H2B	110.7	C3-C2-H2B	110.7
H2A-C2-H2B	108.8	N1-C3-C2	99.9(4)
N1-C3-C4	113.2(4)	C2-C3-C4	114.5(4)
N1-C3-H3	109.6	C2-C3-H3	109.6
C4-C3-H3	109.6	C5-C4-C6	110.1(4)
C5-C4-C7	108.7(5)	C6-C4-C7	107.6(4)
C5-C4-C3	112.7(4)	C6-C4-C3	108.3(4)
C7-C4-C3	109.3(4)	C4-C5-H5A	109.5
C4-C5-H5B	109.5	H5A-C5-H5B	109.5
C4-C5-H5C	109.5	H5A-C5-H5C	109.5
H5B-C5-H5C	109.5	C4-C6-H6A	109.5
C4-C6-H6B	109.5	H6A-C6-H6B	109.5
C4-C6-H6C	109.5	H6A-C6-H6C	109.5

H6B-C6-H6C	109.5	C4-C7-H7A	109.5
C4-C7-H7B	109.5	H7A-C7-H7B	109.5
C4-C7-H7C	109.5	H7A-C7-H7C	109.5
H7B-C7-H7C	109.5	O3-C8-N1	120.4(4)
O3-C8-C9	123.1(4)	N1-C8-C9	116.5(4)
C10-C9-C8	111.4(4)	C10-C9-H9A	109.3
C8-C9-H9A	109.3	C10-C9-H9B	109.3
C8-C9-H9B	109.3	H9A-C9-H9B	108.0
C11-C10-C9	116.2(4)	C11-C10-Br1	109.0(3)
C9-C10-Br1	104.8(3)	C11-C10-H10	108.9
C9-C10-H10	108.9	Br1-C10-H10	108.9
C16-C11-C12	115.8(4)	C16-C11-C10	121.1(4)
C12-C11-C10	123.0(4)	C13-C12-C11	122.2(5)
C13-C12-H12	118.9	C11-C12-H12	118.9
C14-C13-C12	119.2(5)	C14-C13-H13	120.4
C12-C13-H13	120.4	C15-C14-C13	119.8(5)
C15-C14-H14	120.1	C13-C14-H14	120.1
C14-C15-C16	120.4(5)	C14-C15-H15	119.8
C16-C15-H15	119.8	C15-C16-C11	122.6(5)
C15-C16-Cl1	117.3(4)	C11-C16-Cl1	120.0(4)
C8-N1-C1	125.4(4)	C8-N1-C3	122.9(4)
C1-N1-C3	109.9(4)	C1-O1-C2	110.6(4)

Table 6. Torsion angles (°).

O1-C2-C3-N1	-23.3(6)	O1-C2-C3-C4	98.0(5)
N1-C3-C4-C5	56.9(6)	C2-C3-C4-C5	-56.8(6)
N1-C3-C4-C6	178.9(4)	C2-C3-C4-C6	65.2(5)
N1-C3-C4-C7	-64.1(5)	C2-C3-C4-C7	-177.8(5)
O3-C8-C9-C10	-16.3(7)	N1-C8-C9-C10	161.4(4)
C8-C9-C10-C11	-65.3(6)	C8-C9-C10-Br1	174.4(3)
C9-C10-C11-C16	155.9(4)	Br1-C10-C11-C16	-86.0(5)
C9-C10-C11-C12	-22.9(6)	Br1-C10-C11-C12	95.2(5)
C16-C11-C12-C13	-0.8(7)	C10-C11-C12-C13	178.1(4)
C11-C12-C13-C14	-0.4(8)	C12-C13-C14-C15	0.8(8)
C13-C14-C15-C16	0.0(8)	C14-C15-C16-C11	-1.3(8)
C14-C15-C16-Cl1	-179.5(4)	C12-C11-C16-C15	1.6(7)
C10-C11-C16-C15	-177.2(4)	C12-C11-C16-Cl1	179.8(4)
C10-C11-C16-Cl1	0.9(6)	O3-C8-N1-C1	-162.8(5)
C9-C8-N1-C1	19.5(7)	O3-C8-N1-C3	0.4(7)
C9-C8-N1-C3	-177.3(4)	O2-C1-N1-C8	-25.4(9)

O1-C1-N1-C8	155.4(5)	O2-C1-N1-C3	169.5(6)
O1-C1-N1-C3	-9.7(6)	C2-C3-N1-C8	-145.2(5)
C4-C3-N1-C8	92.5(5)	C2-C3-N1-C1	20.3(6)
C4-C3-N1-C1	-102.0(5)	O2-C1-O1-C2	174.0(6)
N1-C1-O1-C2	-6.8(6)	C3-C2-O1-C1	19.7(7)

Table 7. Anisotropic atomic displacement parameters (Å^2).

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0588(3)	0.0549(3)	0.0371(2)	0.0052(2)	0.0008(2)	-0.0084(2)
C1	0.059(3)	0.032(2)	0.052(3)	0.005(2)	0.013(3)	-0.002(2)
C2	0.086(5)	0.063(4)	0.051(3)	-0.005(3)	-0.005(3)	-0.031(3)
C3	0.039(2)	0.046(3)	0.037(2)	0.0009(19)	-0.0021(18)	-0.003(2)
C4	0.038(3)	0.038(2)	0.036(2)	0.0007(17)	0.0022(18)	-0.0032(18)
C5	0.051(3)	0.084(4)	0.076(4)	0.026(4)	0.010(3)	0.015(3)
C6	0.057(3)	0.087(4)	0.041(2)	0.004(3)	0.003(3)	-0.002(3)
C7	0.085(4)	0.055(3)	0.062(3)	-0.008(3)	0.020(3)	-0.031(3)
C8	0.041(2)	0.038(2)	0.039(2)	0.0028(19)	0.0033(18)	-0.005(2)
C9	0.063(3)	0.033(2)	0.041(2)	0.0058(18)	-0.001(2)	-0.009(2)
C10	0.048(3)	0.042(2)	0.035(2)	0.0019(18)	-0.001(2)	-0.004(2)
C11	0.038(2)	0.038(2)	0.034(2)	0.0027(17)	-0.0023(17)	0.0003(18)
C12	0.055(3)	0.041(3)	0.050(3)	0.000(2)	0.001(2)	0.004(2)
C13	0.036(3)	0.094(4)	0.053(3)	0.013(3)	0.009(2)	0.002(3)
C14	0.061(3)	0.059(3)	0.061(3)	0.011(3)	-0.002(3)	-0.020(3)
C15	0.066(4)	0.043(3)	0.054(3)	0.008(2)	-0.007(3)	-0.015(3)
C16	0.049(3)	0.035(2)	0.046(2)	0.0026(18)	0.002(2)	0.005(2)
Cl1	0.0721(10)	0.0544(8)	0.0987(12)	-0.0142(8)	0.0230(9)	0.0128(7)
N1	0.040(2)	0.0309(17)	0.0363(18)	0.0037(14)	0.0009(15)	-0.0017(16)
O1	0.106(4)	0.0376(18)	0.064(2)	-0.0078(17)	0.011(2)	-0.020(2)
O2	0.094(3)	0.0376(17)	0.061(2)	0.0126(16)	0.009(2)	0.0099(19)
O3	0.072(3)	0.0392(18)	0.0481(19)	0.0030(15)	0.0071(18)	0.0144(17)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²).

	x/a	y/b	z/c	U(eq)
H2A	0.2042	0.2602	0.3297	0.08
H2B	0.3954	0.2492	0.2866	0.08
H3	0.2926	0.4227	0.3473	0.049
H5A	0.7724	0.3403	0.3796	0.105
H5B	0.8564	0.3778	0.3065	0.105
H5C	0.7227	0.2808	0.3090	0.105
H6A	0.6415	0.4628	0.2163	0.092
H6B	0.4238	0.4689	0.2329	0.092
H6C	0.5194	0.3613	0.2182	0.092
H7A	0.6631	0.5185	0.3972	0.101
H7B	0.5144	0.5677	0.3450	0.101
H7C	0.7260	0.5545	0.3209	0.101
H9A	0.3223	0.3592	0.5777	0.055
H9B	0.5406	0.3692	0.5627	0.055
H10	0.3065	0.5374	0.6024	0.05
H12	0.7695	0.4773	0.5438	0.059
H13	1.0050	0.5955	0.5185	0.073
H14	0.9627	0.7683	0.5489	0.072
H15	0.6915	0.8188	0.6058	0.065

Table 9. Hydrogen bond distances (Å) and angles (°).

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C15-H15···O3	0.93	2.67	3.316(6)	127.2