Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information:

Sulfoxide-mediated Umpolung of Alkali Halide Salts

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Part I: Experimental Part:

General Information

Unless otherwise stated, all glassware was oven dried and all reactions were carried out under an argon atmosphere using standard schlenk techniques. Dried acetonitrile was purchased from Acros Organics, and was stored under Argon. All commercially available reagents were purchased from Acros Organics, Alfa Aesar, Fluka AG or Sigma Aldrich and were used without further purification. Beta-Ketoesters[1] and unsaturated carboxylic acids[2] were prepared according to literature methods. Reaction progress was monitored by thin layer chromatography (TLC) performed on plastic plates coated with silica gel F_{254} with 0.2 mm thickness. Visualization was achieved by ultraviolet light (254 nm). Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 (^{1}H: 500.4 MHz; ^{13}C: 125.8 MHz) or on a Bruker DPX 300 (^{1}H: 300.1 MHz; ^{13}C: 75.5 MHz). All spectra were recorded in $CDCl_3$, chemical shifts were given in parts per million (ppm, δ), referenced to the peak of tetramethylsilane, using the solvent as internal standard ($CDCl_3$: ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm)[3]. Coupling constants were quoted in Hz (*J*). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (se), octet (o). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

Reaction Optimization:

Table 1: Optimisation of the chlorination reaction with NaCl.[a]

Entry:	Salt:	Additive:	Reaction time [h]:	Activating agent:	Conversion [%]:	Yield [%]:[b]
1	TBACl	---	28	TFAA 1.2 eq.	Very low	Traces
2	NaCl		26		88	29 [50][c]
3		15-crown-5 10 %	24		61	39 [53][c]
4	LiCl	---	25		100	44 [nd[d]][c]
5			19.5	TMSOTf 1.2 eq.		77
6	$FeCl_3$		18.5			72
7			20	TMSOTf 1.5 eq.		78
8	LiCl		2			84
9	NaCl		2			84
10	CsCl		7			88
11	$CaCl_2$		23			84
12	$MgCl_2$		24			84

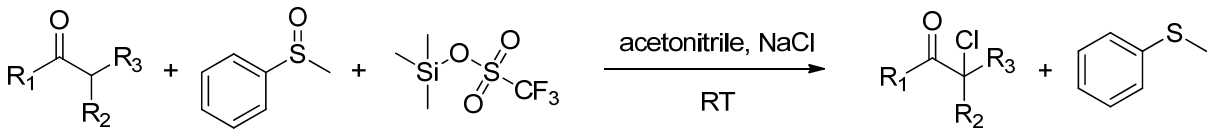
Table 2: Screening of different sulfoxides.[a]

Entry:	Sulfoxide:	Reaction time [h]:	Yield [%]:
1	Me_2SO	19.5	75
2	$(Ph)_2SO$	8	83[b]
3	PhMeSO	2	84
4	$(p\text{-}CF_3\text{-}C_6H_4)MeSO$	2	80
5	$(p\text{-}MeOC_6H_4)MeSO$	1	59

[a] – Reactions were carried out in dry acetonitrile, at room temperature. All yields refer to pure, isolated compounds. [b] – 90% conversion.

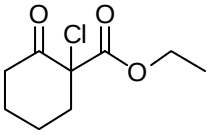
α-Functionlisation of carbonyl compounds:

General Procedure for the α-functionalisation of ketones:



A suspension of ketone (0.5 mmol), methyl phenyl sulfoxide (70.7 µl, 84.1 mg, 0.6 mmol), trimethylsilyl trifluoromethansulfonate (135.8 µl, 166.6 mg, 0.75 mmol) and the corresponding sodium halide (35.1 mg, 0.6 mmol (NaCl); 62.2 mg, 0.6 mmol (NaBr)) in acetonitrile (1 ml) was stirred for the mentioned time. The mixture was subsequently hydrolysed with water (10 ml), extracted with methyl *tert*-butyl ether (3 x 10 ml) and dried over Na_2SO_4. The resulting solution was evaporated *in vacuo*, and the crude product was purified by column chromatography on silica gel.

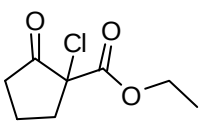
Ethyl 1-chloro-2-oxocyclohexanecarboxylate (4a):



The compound was prepared according to the general method using ethyl 2-oxocyclohexanecarboxylate (0.5 mmol, 85.11 mg, 80.3 µl). Stirring for 2 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f= 0.07, 86 mg, 0.42 mmol, 84%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 4.30 (2q, *J* = 7.1 Hz, 1H), 2.92 - 2.76 (m, 1H), 2.44 (ddd, *J* = 14.1, 8.6, 5.3 Hz, 1H), 2.18 - 2.10 (m, 1H), 2.00 - 1.83 (m, 2H), 1.80 - 1.71 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 2H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 199.85, 167.39, 73.64, 63.05, 39.76, 38.99, 26.84, 22.30, 14.0 ppm

The spectral data correlate to those reported in the literature.[4]

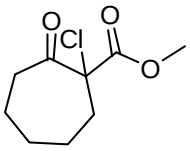
Ethyl 1-chloro-2-oxocyclopentanecarboxylate (4b):



The compound was prepared according to the general method using ethyl 2-oxocyclopentanecarboxylate (0.5 mmol, 78.09 mg, 74.4 µl). Stirring for 4.5 hours and purification by column chromatography using *n*-pentane / ether (10:1) as eluent, gave the title compound as a colourless oil (R_f= 0.1, 62.9 mg, 0.33 mmol, 66%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.28 (q, *J* = 7.1 Hz, 2H), 2.87 - 2.68 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.87 - 2.68 (m, 1H), 2.64 - 2.50 (m, 1H), 2.48 - 2.30 (m, 2H), 2.22 - 1.98 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 206.31, 167.38, 69.78, 63.28, 38.54, 35.50, 19.25, 14.15 ppm

The spectral data correlate to those reported in the literature.[4]

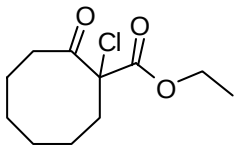
Methyl 1-chloro-2-oxocycloheptanecarboxylate (4c):



The compound was prepared according to the general method using methyl 2-oxocycloheptanecarboxylate (0.5 mmol, 85.11 mg, 78,1 µl). Stirring for 4 hours and purification by column chromatography using *n*-pentane / ether (10:1) as eluent, gave the title compound as a colourless oil (R_f= 0.13, 88.5 mg, 0.43 mmol, 86%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 3.82 (s, 3H), 2.84 (ddd, *J* = 12.7, 7.6, 4.1 Hz, 1H), 2.73 - 2.60 (m, 1H), 2.46 (ddd, *J* = 15.4, 9.8, 2.2 Hz, 1H), 2.30 (ddd, *J* = 15.5, 7.9, 2.1 Hz, 1H), 1.94 - 1.67 (m, 5H), 1.59 - 1.45 (m, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 202.52, 168.70, 76.11, 53.76, 40.72, 37.81, 29.23, 25.41, 24.83 ppm

The spectral data correlate to those reported in the literature.[4]

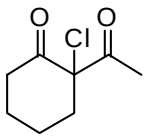
Ethyl 1-chloro-2-oxocyclooctanecarboxylate (4d):



The compound was prepared according to the general method using ethyl 2-oxocyclooctanecarboxylate (0.5 mmol, 99.13 mg, 95.3 µl). Stirring for 5.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.23, 101 mg, 0.44 mmol, 87%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.25 (2d, *J* = 7.1 Hz, 1H), 2.84 - 2.53 (m, 2H), 2.48 - 2.32 (m, 1H), 1.96 - 1.52 (m, 3H), 1.47 - 1.31 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 2H), 1.13 (tdd, *J* = 16.6, 8.5, 3.2 Hz, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 204.44, 167.76, 77.25, 63.06, 38.07, 34.13, 29.28, 25.68, 23.99, 22.93, 13.97 ppm

The spectral data correlate to those reported in the literature.[5]

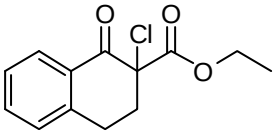
2-Acetyl-2-chlorocyclohexanone (4e):



The compound was prepared according to the general method using 2-acetylcyclohexanone (0.5 mmol, 70.1 mg, 65.9 µl). Stirring for 3.5 hours and purification by column chromatography using i-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.13, 56 mg, 0.32 mmol, 64%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 2.98 (ddd, J = 10.0, 9.2, 5.1 Hz, 1H), 2.67 - 2.53 (m, 1H), 2.41 - 2.29 (m, 1H), 2.36 (s, 3H), 2.18 - 2.05 (m, 1H), 2.04 - 1.91 (m, 2H), 1.89 - 1.74 (m, 2H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 203.18, 201.26, 76.88, 38.92, 37.86, 27.13, 26.95, 21.61 ppm

The spectral data correlate to those reported in the literature.[6]

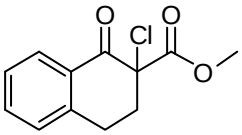
Ethyl 2-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4f):



The compound was prepared according to the general method using ethyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.5 mmol, 109.13 mg, 104 µl). Stirring for 3.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.09, 112 mg, 0.44 mmol, 89%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.10 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.29 (ddd, *J* = 14.9, 9.4, 4.6 Hz, 1H), 3.12 - 2.84 (m, 2H), 2.61 - 2.47 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 187.79, 167.60, 142.67, 134.53, 129.83, 129.14, 128.90, 127.43, 70.96, 63.25, 35.15, 25.74, 14.10 ppm

The spectral data correlate to those reported in the literature.[7]

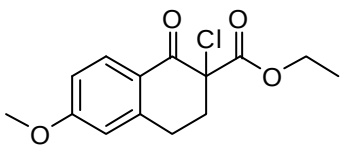
Methyl 2-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4g):



The compound was prepared according to the general method using methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.5 mmol, 102.11 mg). Stirring for 3 hours and purification by column chromatography, using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f = 0.09108 mg, 0.46 mmol, 91%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.10 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.29 (ddd, *J* = 15.0, 9.5, 4.6 Hz, 1H), 3.09 - 2.91 (m, 2H), 2.60 - 2.47 (m, 1H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 187.71, 168.17, 142.69, 134.62, 129.71, 129.20, 128.92, 127.47, 70.87, 53.98, 35.19, 25.71 ppm

The spectral data correlate to those reported in the literature.[7]

Ethyl 2-chloro-6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4h):

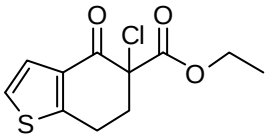


The compound was prepared according to the general method using ethyl 6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.5 mmol, 124.14 mg). Stirring for 2.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f= 0.11, 129 mg, 0.43 mmol, 86%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.06 (d, *J* = 8.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.26 (ddd, *J* = 13.5, 9.7, 4.5 Hz, 1H), 3.01 - 2.92 (m, 2H), 2.53 - 2.46 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.60, 167.83, 164.55, 145.29, 131.74, 123.14, 114.22, 112.62, 70.94, 63.18, 55.72, 35.27, 26.08, 14.12 ppm

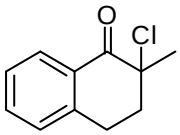
The spectral data correlate to those reported in the literature.[7]

Ethyl 5-chloro-4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carboxylate (4i):



The compound was prepared according to the general method using ethyl 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carboxylate (0.5 mmol, 112.14 mg, 92.4 µl). Stirring for 5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (20:1) as eluent, gave the title compound as a colourless oil (R_f= 0.13, 120 mg, 0.46 mmol, 93%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.44 (d, *J* = 5.3 Hz, 1H), 7.15 (d, *J* = 5.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.29 (ddd, *J* = 17.4, 9.3, 4.7 Hz, 1H), 3.17 (dt, *J* = 17.5, 4.7 Hz, 1H), 3.06 (ddd, *J* = 14.1, 9.3, 4.9 Hz, 1H), 2.60 (dt, *J* = 14.1, 4.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 4H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 182.40, 167.47, 154.84, 133.71, 126.04, 124.53, 70.41, 63.34, 36.77, 22.63, 14.12 ppm. **IR (neat):** ν = 3111, 2937 1756, 1731, 1679, 1523, 1400, 1274, 1243, 1223, 1086, 1035, 1014, 908, 712, 695. **MS (EI):** m/z (%) = 258 (10), 223 (57), 177 (13), 151 (29), 124 (100), 96 (36). **HRMS (ESIpos):** calc. for $C_{11}H_{11}O_3ClNaS$: 281.0009, found: 281.0008.

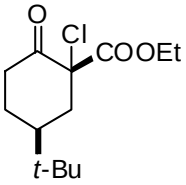
2-Chloro-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (4j):



The compound was prepared according to the general method using ethyl 2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (0.5 mmol, 80.1 mg, 75.8µl). Stirring for 3 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless solid (R_f= 0.26, 80.8 mg, 0.42 mmol, 84%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 3.46 - 3.32 (m, 1H), 2.94 - 2.85 (m, 1H), 2.50 (ddd, *J* = 14.5, 4.7, 3.1 Hz, 1H), 2.34 (ddd, *J* = 14.5, 11.3, 4.7 Hz, 1H), 1.84 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 191.54, 143.19, 133.94, 129.89, 129.08, 128.85, 127.14, 67.69, 38.59, 26.79, 26.14 ppm.

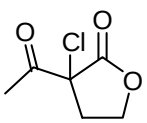
The spectral data correlate to those reported in the literature.[8]

Ethyl 5-(*tert*-butyl)-1-chloro-2-oxocyclohexanecarboxylate (4k):



The compound was prepared according to the general method using ethyl 5-(*tert*-butyl)-2-oxocyclohexanecarboxylate (0.5 mmol, 113.2 mg, 107.1µl). Stirring for 2 hours and purification by column chromatography using i-hexane / ethyl acetate (30:1) as eluent yielded the desired compounds. R_f= 0.17, *meso*, colourless oil that can be cystalized from pentane at -20°C (60 mg, 0.23 mmol, 46%). R_f= 0.1, colourless oil (15 mg, 0.07 mmol, 14%). ***Cis*-4k: ^{1}H NMR (500 MHz, $CDCl_3$):** δ = 4.31 (q, *J* = 7.1 Hz, 2H), 3.04 (td, *J* = 14.4, 6.2 Hz, 1H), 2.49 - 2.26 (m, 3H), 2.10 (ddd, *J* = 13.1, 6.1, 3.0 Hz, 1H), 1.96 (tt, *J* = 12.0, 3.4 Hz, 1H), 1.54 (ddd, *J* = 26.3, 13.2, 4.2 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 9H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 201.60, 167.83, 72.66, 63.06, 41.61, 39.48, 36.42, 32.26, 27.69, 27.56, 14.17 ppm. **IR (neat):** ν = 2947, 2866, 1738, 1368, 1251, 1011, 791. **MS (EI):** m/z (%) = 260 (23), 245 (10), 197 (54), 169 (31), 141 (15), 123 (10), 83 (15), 69 (13), 67 (15), 57 (100), 55 (47), 53 (10), 43 (15), 41 (52), 29 (49). **HRMS (ESIpos):** calc. for $C_{13}H_{21}O_3ClNa$: 283.1071, found: 283.1068. ***Trans*-4k: ^{1}H NMR (500 MHz, $CDCl_3$):** δ = 4.39 - 4.19 (m, 2H), 2.95 (dt, *J* = 13.1, 3.0 Hz, 1H), 2.70 (ddd, *J* = 14.3, 3.9, 2.7 Hz, 1H), 2.50 (td, *J* = 14.1, 6.1 Hz, 1H), 2.06 (ddd, *J* = 11.5, 5.6, 2.7 Hz, 1H), 1.78 (t, *J* = 12.8 Hz, 1H), 1.55 (tt, *J* = 12.1, 2.6 Hz, 1H), 1.46 (ddd, *J* = 26.3, 12.7, 4.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 199.00, 167.41, 74.28, 63.04, 45.79, 42.38, 39.97, 32.68, 27.86, 27.55, 13.99 ppm. **IR (neat):** ν = 2961, 2873, 1759, 1737, 1723, 1368, 1250, 1225, 1046, 1018, 742. **MS (EI):** m/z (%) = 260 (10), 197 (50), 169 (41), 140 (33), 123 (14), 95 (11), 83 (16), 67 (14), 57 (100), 55 (29), 41 (40), 27 (11) . **HRMS (ESIpos):** calc. for $C_{13}H_{21}O_3ClNa$: 283.1071, found: 283.1071.

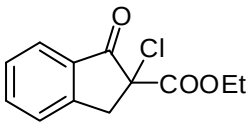
3-Acetyl-3-chlorodihydrofuran-2(3*H*)-one (4l):



The compound was prepared according to the general method using acetyldihydrofuran-2(3*H*)-one (0.5 mmol, 64.07 mg, 53.8 µl). Stirring for 5 hours and purification by column chromatography using n-pentane / ether (10:1) as eluent, gave the title compound as a colourless oil (R_f= 0.09, 54.3 mg, 0.33 mmol, 67%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.56 - 4.29 (m, 1H), 3.30 - 3.13 (m, 1H), 2.59 (s, 1H), 2.50 (ddd, J = 14.1, 6.9, 4.9 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 198.32, 170.14, 67.46, 66.10, 35.26, 26.06 ppm

The spectral data correlate to those reported in the literature.[5]

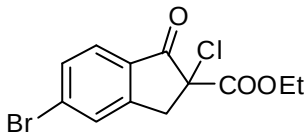
Ethyl 2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4m):



The compound was prepared according to the general method using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (0.5 mmol, 102.11 mg, 78.5 µl). Stirring for 5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f= 0.14, 94 mg, 0.40 mmol, 79%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.86 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.50 - 7.45 (m, 2H), 4.27 (2q, *J* = 7.1, 2H), 4.09 (d, *J* = 17.7 Hz, 1H), 3.56 (d, *J* = 17.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 4H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 195.27, 167.26, 150.73, 136.55, 132.66, 128.73, 126.44, 126.12, 68.12, 63.58, 43.55, 14.10 ppm

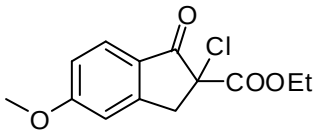
The spectral data correlate to those reported in the literature.[4]

Ethyl 5-bromo-2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4n):



The compound was prepared according to the general method using ethyl 5-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (0.5 mmol, 141.56 mg). Stirring for 6 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellow solid (R_f= 0.09, 130 mg, 0.41 mmol, 82%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.71 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 0.8 Hz, 1H), 7.62 - 7.60 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.07 (d, *J* = 17.9 Hz, 1H), 3.53 (d, *J* = 17.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 194.09, 166.81, 152.15, 132.46, 132.22, 131.47, 129.79, 127.14, 67.89, 63.73, 43.08, 14.08 ppm. **IR (neat):** ν = 3090, 2986, 2927, 1759, 1718, 1590, 1578, 1413, 1318, 1263, 1240, 1204, 1181, 1113, 1054, 1014, 885, 859, 818, 742, 708. **MS (EI):** m/z (%) =318 (5), 281 (88), 253 (22), 243 (20) , 235 (100), 225 (23), 209 (38), 136 (26), 101 (21), 74 (13), 29 (35) . **HRMS (ESIpos):** calc. for $C_{12}H_{10}O_3BrClNa$: 338.9394, found: 338.9391.

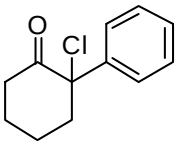
Ethyl 2-chloro-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4o):



The compound was prepared according to the general method using ethyl 5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (0.5 mmol, 117.5 mg, 104.9 µl). Stirring for 6 hours and purification by column chromatography using *i*-hexane / ethyl acetate (8:2) as eluent, gave the title compound as a yellow oil (R_f= 0.14, 78 mg, 0.29 mmol, 58%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.79 (d, *J* = 8.6 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.89 (d, *J* = 1.9 Hz, 1H), 4.27 (q, *J*

= 7.1 Hz, 2H), 4.05 (d, *J* = 17.8 Hz, 1H), 3.92 (s, 3H), 3.50 (d, *J* = 17.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 193.30, 167.46, 166.82, 153.94, 127.90, 125.67, 116.84, 109.57, 68.65, 63.51, 56.03, 43.51, 14.12 ppm. **IR (neat):** ν = 2981, 2944, 1755, 1712, 1595, 1491, 1446, 1304, 1256, 1179, 1075, 1019, 843, 659. **MS (EI):** m/z (%) = 268 (8), 233 (44), 195 (16), 187 (100), 177 (12), 161 (23), 29 (12). **HRMS (ESIpos):** calc. for $C_{13}H_{13}O_4ClNa$: 291.0394, found: 291.0390.

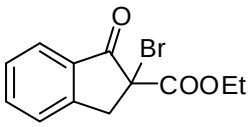
2-Chloro-2-phenylcyclohexanone (4p):



The compound was prepared according to the general method using 2-phenylcyclohexanone (0.5 mmol, 87.1 mg). Stirring for X hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f = 0.14, 77.2 mg, 0.37 mmol, 74%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.40 (d, J = 4.2 Hz, 1H), 7.35 (dd, J = 8.5, 4.0 Hz, 1H), 2.96 (ddd, J = 14.5, 7.0, 3.5 Hz, 1H), 2.91 - 2.82 (m, 1H), 2.51 - 2.39 (m, 1H), 2.09 - 1.98 (m, 1H), 1.92 (tt, J = 12.6, 6.2 Hz, 1H), 1.83 (ddd, J = 13.3, 8.6, 4.1Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 203.54, 138.72, 128.91, 128.72, 127.16, 76.82, 41.89, 39.17, 27.45, 22.83 ppm

The spectral data correlate to those reported in the literature.[8]

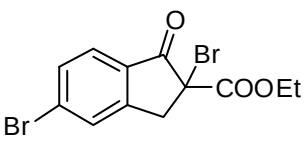
Ethyl 2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5a):



The compound was prepared according to the general method using ethyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (0.5 mmol, 102.11 mg, 78.5 µl). Stirring for 5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f = 0.07, 115.1 mg, 0.40 mmol, 80%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.87 (d, *J* = 8.0 Hz, 1H), 7.70 (td, *J* = 7.6, 1.1 Hz, 1H), 7.52 - 7.41 (m, 2H), 4.29 (2q, *J* = 7.1 Hz, 2H), 4.21 (d, *J* = 18.1 Hz, 1H), 3.68 (d, *J* = 18.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 195.30, 167.15, 150.30, 136.41, 132.39, 128.69, 126.43, 126.09, 63.69, 58.61, 43.99, 14.08 ppm

The spectral data correlate to those reported in the literature.[9]

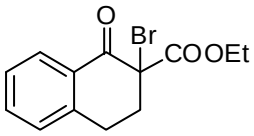
Ethyl 2,5-dibromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5b):



The compound was prepared according to the general method using ethyl 5-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (0.5

mmol, 141.6 mg). Stirring for 1.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless solid (R_f= 0.24, 168.1 mg, 0.46 mmol, 93%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.72 (d, *J* = 8.2 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 4.29 (2q, *J* = 7.1, 3.2 Hz, 2H), 4.19 (d, *J* = 18.2 Hz, 1H), 3.65 (d, *J* = 18.2 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 194.16, 166.75, 151.77, 132.44, 132.08, 131.24, 129.78, 127.17, 63.88, 58.16, 43.55, 14.09 ppm. **IR (neat):** ν = 3097, 2989, 1748, 1714, 1578, 1592 1414, 1317, 1260, 1235, 1206, 1182, 1032, 1013, 986, 910, 858, 837, 775, 731, 709, 680. **MS (EI):** m/z (%) =362 (1), 281 (55), 235 (100), 209 (31), 180 (13), 101 (23), 75 (23), 29 (44) . **HRMS (ESIpos):** calc. for $C_{12}H_{10}O_3Br_2Na$: 382.8889, found: 382.8888.

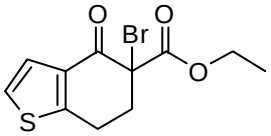
Ethyl 2-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5c):



The compound was prepared according to the general method using ethyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (0.5 mmol, 109.13 mg, 104 µl). Stirring for 3.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.07, 134.6 mg, 0.49 mmol, 90 %). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.10 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 9.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.29 - 3.16 (m, 1H), 3.11 - 2.90 (m, 2H), 2.57 (dt, *J* = 9.8, 4.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 187.69, 167.47, 142.49, 134.44, 129.66, 129.18, 128.88, 127.41, 65.25, 63.39, 35.80, 26.94, 14.07 ppm

The spectral data correlate to those reported in the literature.[7]

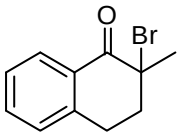
Ethyl 5-bromo-4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carboxylate (5d):



The compound was prepared according to the general method using ethyl 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-5-carboxylate (0.5 mmol, 112.14 mg, 92.4 µl). Stirring for 5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.08, 140.3 mg, 0.46 mmol, 92%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.44 (d, *J* = 5.3 Hz, 1H), 7.15 (d, *J* = 5.3 Hz, 1H), 4.32 (2q, *J* = 7.1 Hz, 2H), 3.29 - 3.11 (m, 2H), 3.05 (ddd, *J* = 14.1, 8.9, 5.1 Hz, 1H), 2.64 (dt, *J* = 14.2, 4.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 182.46, 167.32, 154.48, 133.57, 126.15, 124.47, 64.42, 63.49, 37.56, 23.79, 14.09 ppm. **IR (neat):** ν = 3082, 3119,

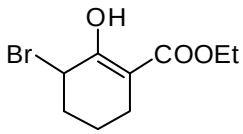
2979, 1746, 1674, 1526, 1401, 1277, 1240, 1227, 1187, 1123, 1087, 1026, 999, 907, 873, 718, 690. **MS (EI):** m/z (%) = 223 (63), 177 (31), 151 (64), 124 (100), 96 (47), 45 (11), 29 (15). **HRMS (ESIpos):** calc. for $C_{11}H_{11}O_3BrNaS$: 324.9505, found: 324.9508.

2-Bromo-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (5e):



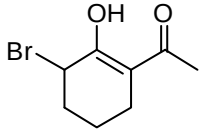
The compound was prepared according to the general method using ethyl 2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (0.5 mmol, 80.1 mg, 75.8µl). Stirring for 0.3 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a yellowish oil (R_f = 0.17 107.6 mg, 0.45 mmol, 90%).**^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 3.46 – 3.31 (m, 1H), 2.93 – 2.85 (m, 1H), 2.50 (ddd, *J* = 14.5, 4.7, 3.1 Hz, 1H), 2.34 (ddd, *J* = 14.5, 11.3 4.7 Hz, 1H), 1.84 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 191.54, 143.19, 133.94, 129.89, 129.08, 128.85, 127.14, 67.69, 38.59, 26.79, 26.14 ppm.
The spectral data correlate to those reported in the literature.[10]

Ethyl 3-bromo-2-hydroxycyclohex-1-enecarboxylate (7a):



The compound was prepared according to the general method using ethyl 2-oxocyclohexanecarboxylate (0.5 mmol, 85.11 mg, 80.3 µl). Stirring for 3.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.1, 65.6 mg, 0.26 mmol, 53 %). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 12.09 (s, 1H), 4.75 – 4.66 (m, 1H), 4.31 – 4.16 (m, 2H), 2.52 – 2.42 (m, 1H), 2.27 (td, *J* = 11.4, 6.0 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.12 -2.02 (m, 1H), 2.00 – 1.88 (m, 1H), 1.80 – 1.73 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 172.45, 166.63, 100.05, 61.10, 46.07, 32.34, 22.46, 17.97, 14.33 ppm.

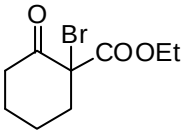
1-(3-Bromo-2-hydroxycyclohex-1-en-1-yl)ethanone (7b):



The compound was prepared according to the general method using ethyl 2-acetylcyclohexanone (0.5 mmol, 70.1 mg, 65.9 µl). Stirring for 3.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 0.09, 87.6 mg, 0.40 mmol, 80 %). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 15.18 (s, 1H), 4.68 (d, *J* = 3.5 Hz, 1H), 2.50 (ddd, *J* = 15.9, 5.5, 2.9 Hz, 1H), 2.46 – 2.35 (m, 1H), 2.26 – 2.17 (m, 1H), 2.19 (s,

3H), 2.15 – 1.94 (m, 2H), 1.88 – 1.74 (m, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 203.40, 172.40, 107.12, 46.47, 31.92, 26.33, 24.14, 18.42 ppm.

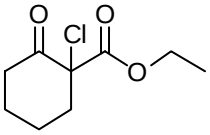
Ethyl 1-bromo-2-oxocyclohexanecarboxylate (8a):



The compound was prepared according to the general method using ethyl 2-oxocyclohexanecarboxylate (0.5 mmol, 85.11 mg, 80.3 µl). Stirring for 3.5 hours and purification by column chromatography using *i*-hexane / ethyl acetate (30:1) as eluent, gave the title compound as a colourless oil (R_f= 12, 99.0 mg, 0.40 mmol, 80 %). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 4.28 (q, *J* = 7.1 Hz, 2H), 2.97 – 2.80 (m, 2H), 2.44 (ddd, *J* = 14.5, 9.2, 5.1 Hz, 1H), 2.26 – 2.16 (m, 1H), 1.98 – 1.66 (m, 4), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 199.24, 167.62, 67.65, 63.05, 40.64, 38.96, 26.89, 23.26, 13.95 ppm.

The spectral data correlate to those reported in the literature.[9]

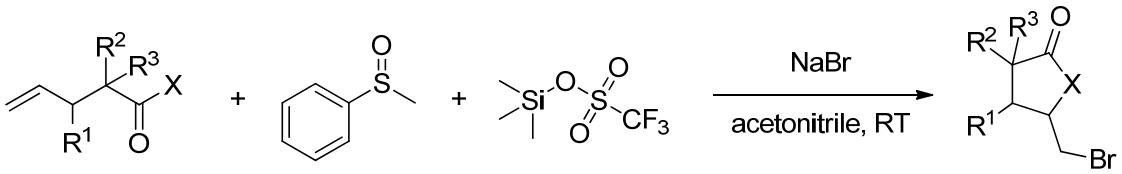
Large Scale preparation of 4a:



A suspension of ethyl 2-oxocyclohexanecarboxylate (10 mmol, 1.70 g, 1.61 ml), methyl phenyl sulfoxide (12 mmol, 1.68 g, 1.41 ml) and NaCl (12 mmol, 0.70g) in acetonitrile (20 ml), was treated with trimethylsilyl trifluoromethansulfonate (15 mmol, 3.33 g, 2.72 ml). The resulting reaction mixture was stirred at room temperature for 6.5 hours, and was subsequently hydrolised with water (75ml). The aqueous layer was separated and washed with MTBE (3 x 125 ml). The combined organic layers were dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. Column chromatography over silica using *i*-hexane : ethyl acetate 30 : 1 as eluent afforded the title compound as colourless oil (Rf = 0.07; 1.84 g, 8.99 mmol, 89%).

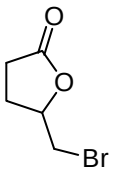
Bromolactonisation:

General Procedure for the bromolactonisation



A suspension of NaBr (0.6 mmol, 62 mg) and methyl phenyl sulfoxide (0.6 mmol, 84.12mg, 70.7 µl) in acetonitrile (2 ml) was treated with trimethylsilyl triflate (0.75 mmol, 166.6 mg, 135.8 µl). Subsequent dropwise addition of cyclisation precursor (0.5 mmol) yielded a colorless solution that was stirred until the formation of bromine, colour change to yellow, indicates the end of the reaction. The resulting solution was hydrolised with a 5% NaHCO3 – solution (10 ml), and extracted with ethyl acetate (3 x 10ml). The combined organic layers were dried over Na2SO4, and evaporated *in vacuo*. Further purification was carried out by colomn chromatography on silica gel, to yield the desired product.

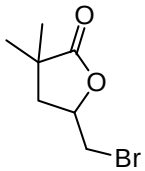
5-(bromomethyl)dihydrofuran-2(3*H*)-one (10a):



The compound was prepared according to the general method using 4-pentenoic acid (0.5 mmol, 50.1mg, 51.3 µl). Stirring for 25 minutes and purification by column chromatography using i-hexane / ethyl acetate (7:3) as eluent, gave the title compound as a colourless oil (R_f = 0.13, 85.0 mg, 0.47 mmol, 95%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 4.79 – 4.73 (m, 1H), 3.62 – 3.52 (m, 2H), 2.73 – 2.64 (m, 1H), 2.63 – 2.53 (m, 1H), 2.51 – 2.42 (m, 1H), 2.19 – 2.10 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 176.28, 77.96, 34.14, 28.49, 26.35 ppm.

The spectral data correlate to those reported in the literature.[11]

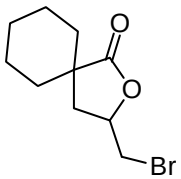
5-(bromomethyl)-3,3-dimethyldihydrofuran-2(3*H*)-one (10b):



The compound was prepared according to the general method using 2,2-dimethyl-4-pentenoic acid (0.5 mmol, 64.1mg, 68.7 µl). Stirring for 25 minutes and purification by column chromatography using i-hexane / ethyl acetate (9:1) as eluent, gave the title compound as a colourless oil (R_f = 0.11, 75.0 mg, 0.36 mmol, 73%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.63 (dt, *J* = 11.1, 6.3 Hz, 1H), 3.58 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.48 (dd, *J* = 10.6, 6.5 Hz, 1H), 2.28 (dd, *J* = 12.9, 6.3 Hz, 1H), 1.94 (dd, *J* = 12.9, 9.5 Hz, 1H), 1.31 (s, 3H), 1.29 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 181.03, 74.79, 42.09, 40.70, 33.69, 25.05, 25.03 ppm.

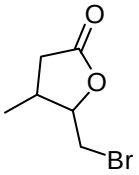
The spectral data correlate to those reported in the literature.[11]

3-(bromomethyl)-2-oxaspiro[4.5]decan-1-one (10c):



The compound was prepared according to the general method using 1-allylcyclohexanecarboxylic acid (0.5 mmol, 84.1 mg, 76.5 µl). Stirring for 20 minutes and purification by column chromatography using i-hexane / ethyl acetate (9:1) as eluent, gave the title compound as a colourless oil (R_f = 0.17, 105.0 mg, 0.42 mmol, 85%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.69 - 4.53 (m, 1H), 3.57 (dd, *J* = 10.6, 4.6 Hz, 1H), 3.48 (dd, *J* = 10.6, 6.4 Hz, 1H), 2.46 (dd, *J* = 13.1, 6.7 Hz, 1H), 1.87 - 1.78 (m, 3H), 1.74 (dd, *J* = 9.6, 4.3 Hz, 1H), 1.68 - 1.48 (m, 4H), 1.46 - 1.22 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 180.67, 75.12, 45.13, 38.19, 34.19, 34.07, 32.30, 25.32, 22.24, 22.16 ppm. **IR (neat):** ν = 2931, 2856, 1760, 1448, 1338, 1265, 1185, 1154, 1019, 936, 859, 656. **MS (EI):** m/z (%) = 246 (9), 191 (18), 178 (27), 167 (16), 153 (24), 123 (18), 107 (10), 81 (100), 69 (15), 67 (44), 55 (22), 53 (11), 41 (35), 39 (18), 27 (11). **HRMS (ESIpos):** calc. for $C_{10}H_{15}O_2BrNa$: 269.0147, found: 269.0148.

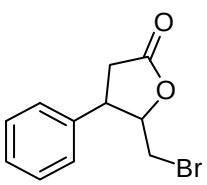
5-(bromomethyl)-4-methyldihydrofuran-2(3*H*)-one (10d):



The compound was prepared according to the general method using 3-methylpent-4-enoic acid (0.5 mmol, 57.1 mg, 60.7 µl). Stirring for 30 minutes and purification by column chromatography using i-hexane / ethyl acetate (8:2) as eluent, gave the title compound as a colourless oil (R_f =0.16, 80.7 mg, 0.42 mmol, 84 %) The compound appears as 1:1 mixture of diastereoisomers. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 4.69 (dt, *J* = 7.8, 5.6 Hz) and 4.27 (dt, *J* = 6.2, 4.8 Hz) (1H), 3.58 (2dd, *J* = 10.8, 7.1Hz, 1H), 3.52 (dd, *J* = 11.2, 4.5 Hz) and 3.43 (dd, *J* = 10.7, 7.8 Hz) (1H), 2.87 - 2.46 (m, 2H), 2.34 (dd, *J* = 16.7, 3.3 Hz) and 2.25 (dd, *J* = 17.7, 8.0 Hz) (1H), 1.23 (d, *J* = 6.8 Hz), 1.12 (d, *J* = 7.0 Hz) (3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 175.76, 175.44, 84.64, 81.00, 37.46, 36.76, 34.27, 32.66, 32.45, 28.63, 18.64, 13.19 ppm.

The spectral data correlate to those reported in the literature.[11]

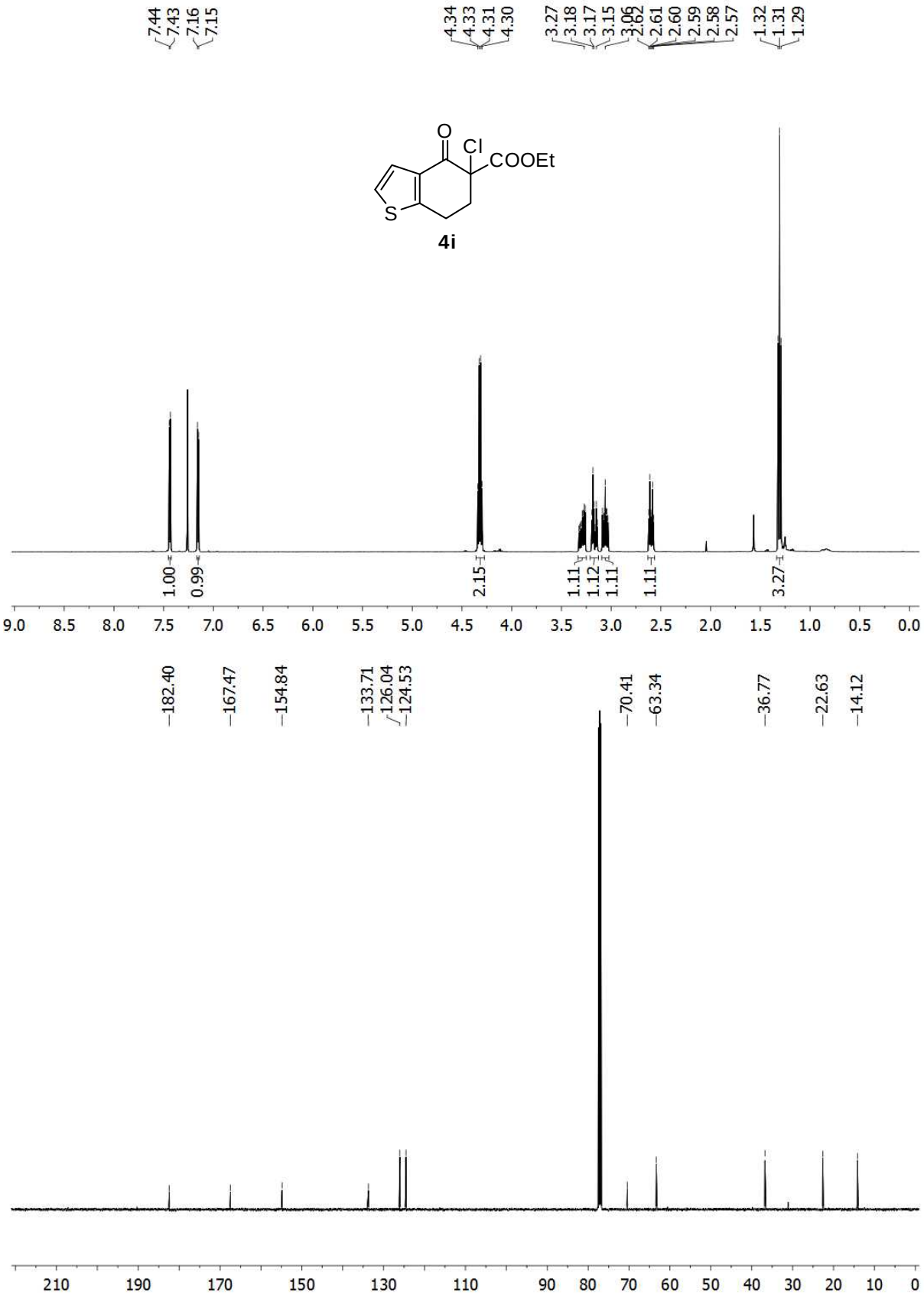
5-bromo-4-phenyldihydrofuran-2(3*H*)-one (10e):

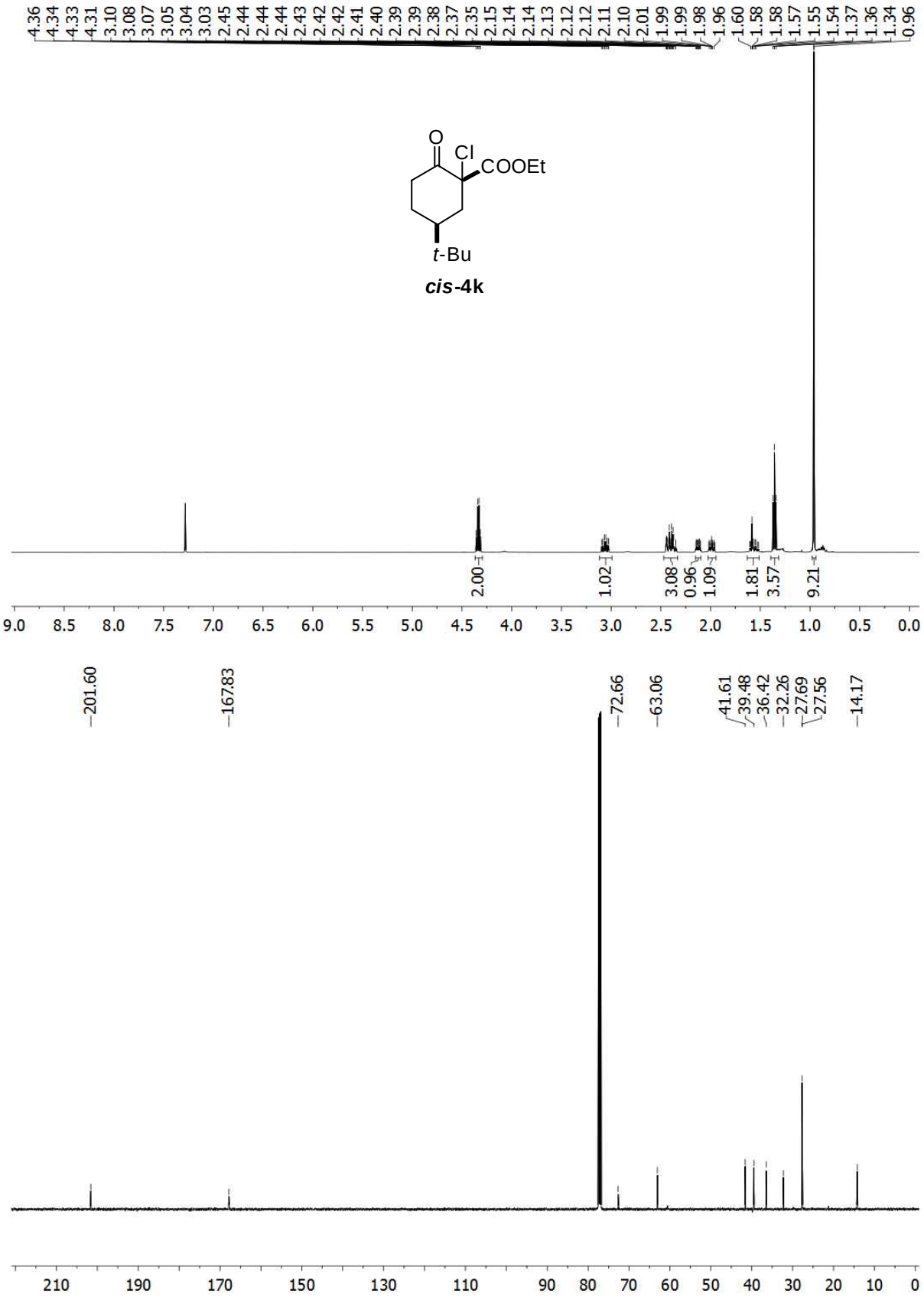


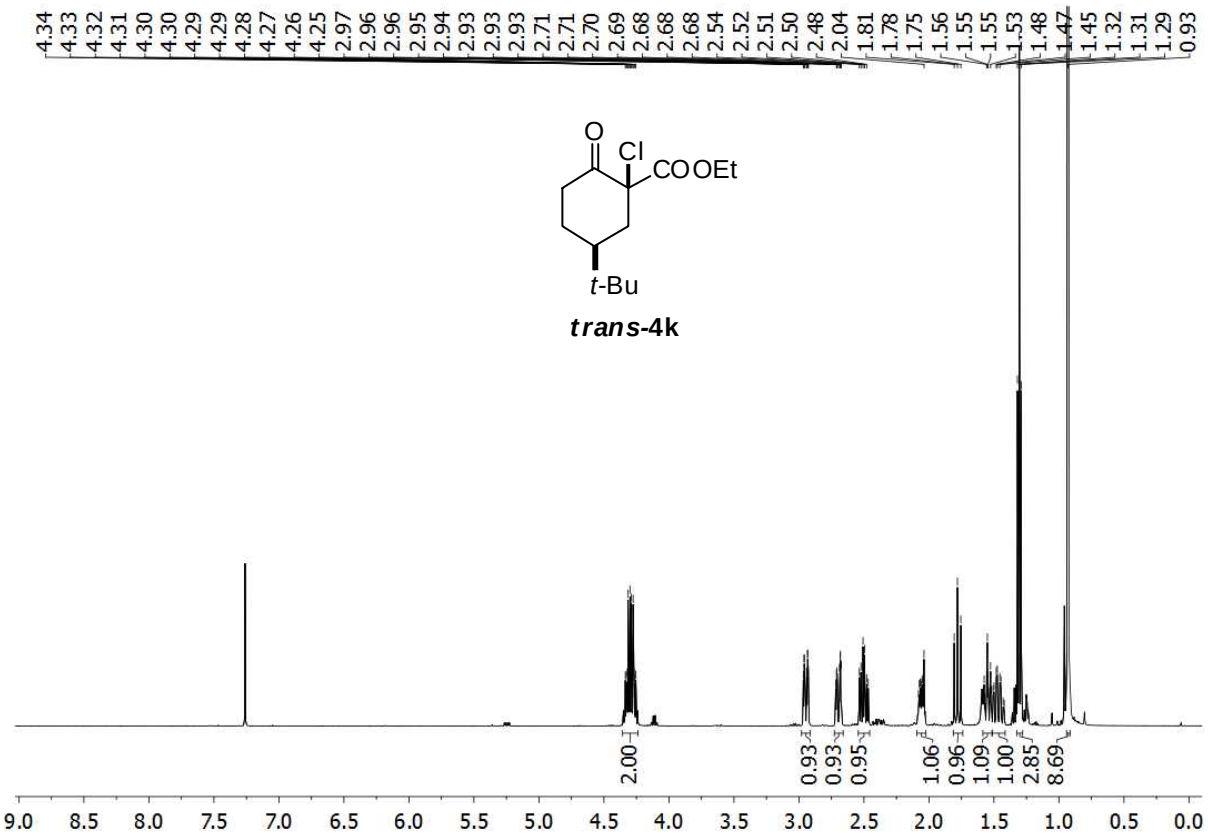
The compound was prepared according to the general method using 3-phenylpent-4-enoic acid (0.5 mmol, 88.1 mg, 79.1 µl). Stirring for 70 minutes and purification by column chromatography using i-hexane / ethyl acetate (8:2) as eluent, gave the title compound as a colourless (R_f = 0.26, 87 mg, 0.34 mmol, 68%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.47 – 7.14 (m, 5H), 4.95 (q)

and 4.67 – 4.60 (m)(1H), 3.90 (ddd, *J* = 8.8, 6.3, 3.8 Hz) and 3.73 – 3.46 (m)(2H), 3.31 – 2.73 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 175.77, 174.70, 138.73, 136.46, 129.51, 129.19, 128.35, 128.26, 128.06, 127.25, 84.33, 82.23, 45.26, 43.85, 37.00, 26.37, 32.76, 29.74 ppm. **IR (neat):** ν = 3031, 2924, 1778, 1603, 1497, 1455, 1419, 1327, 1274, 1188, 1165, 1140, 1030, 994, 970, 908, 807, 760, 700. **MS (EI):** m/z (%) = 254 (7), 104 (100). **HRMS (ESIpos):** calc. for $C_{11}H_{11}O_2BrNa$: 276.9834, found: 276.9836.

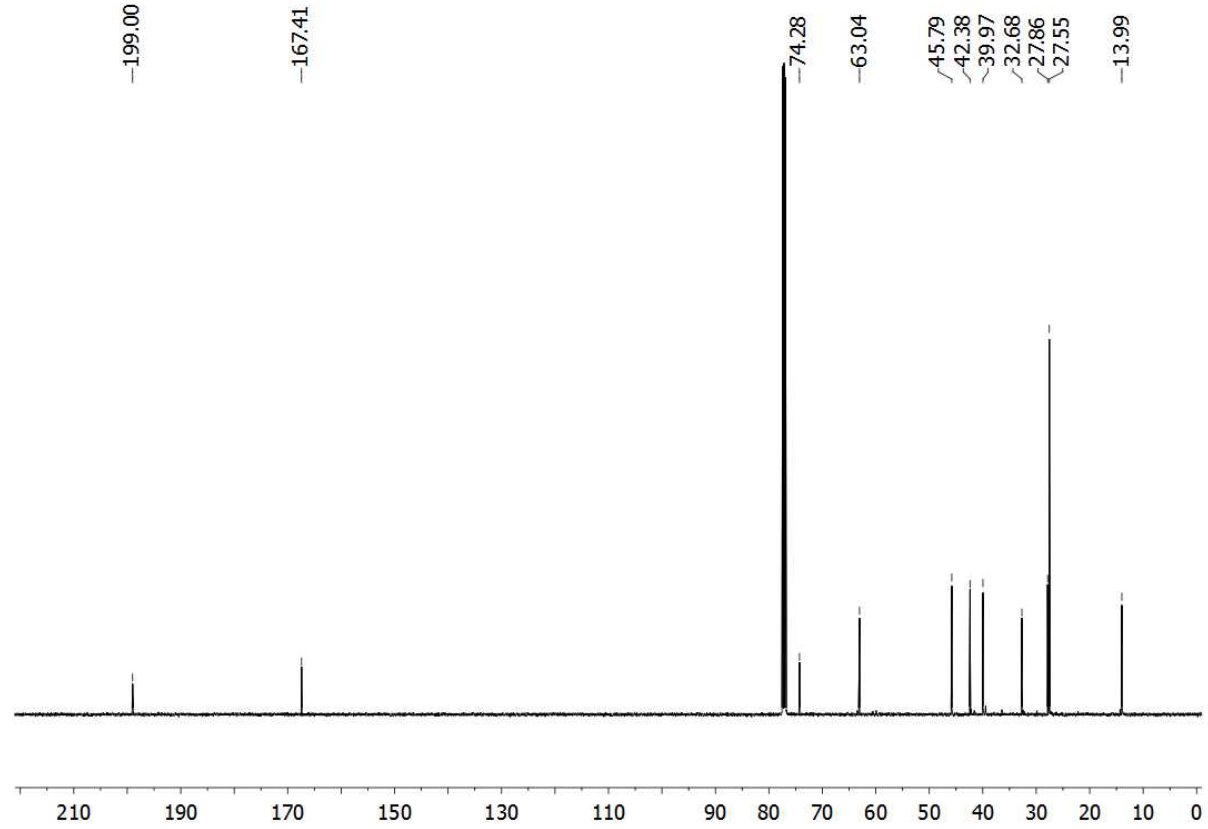
Part II: Spectral Data for new compounds

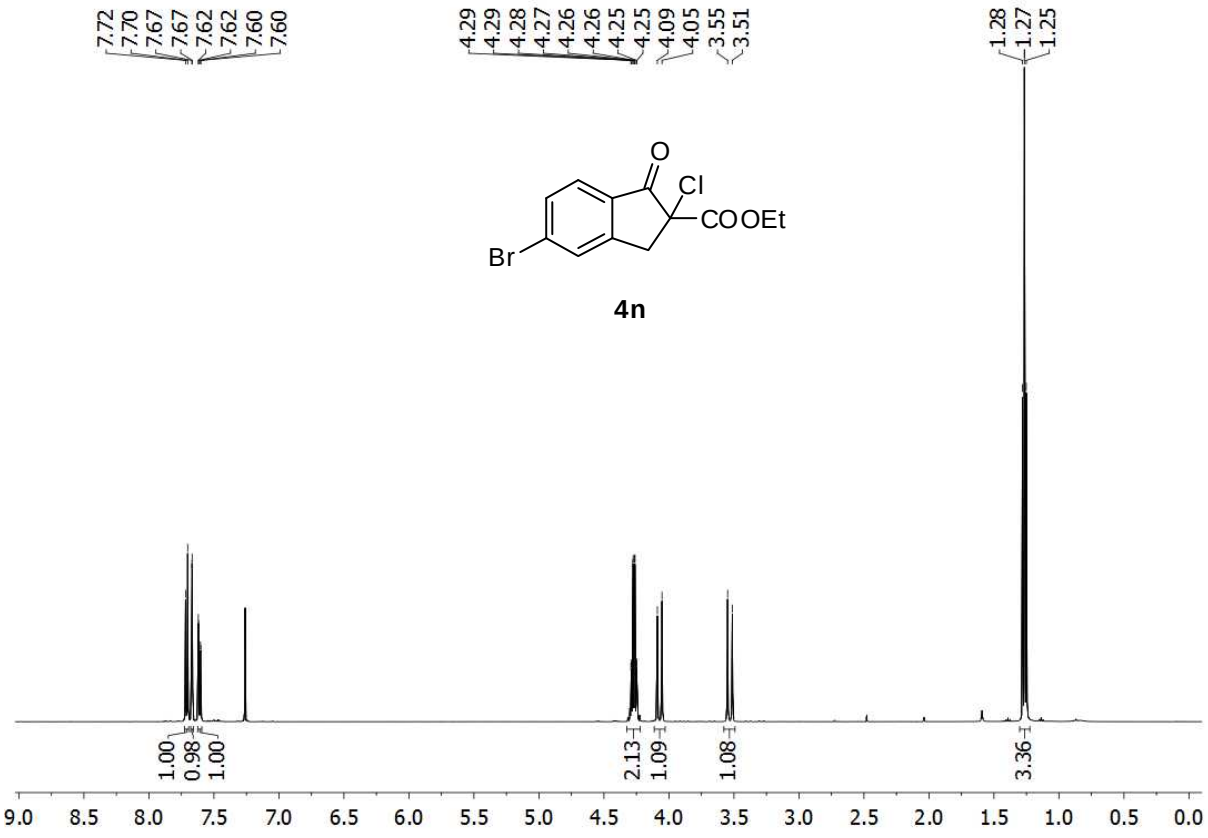




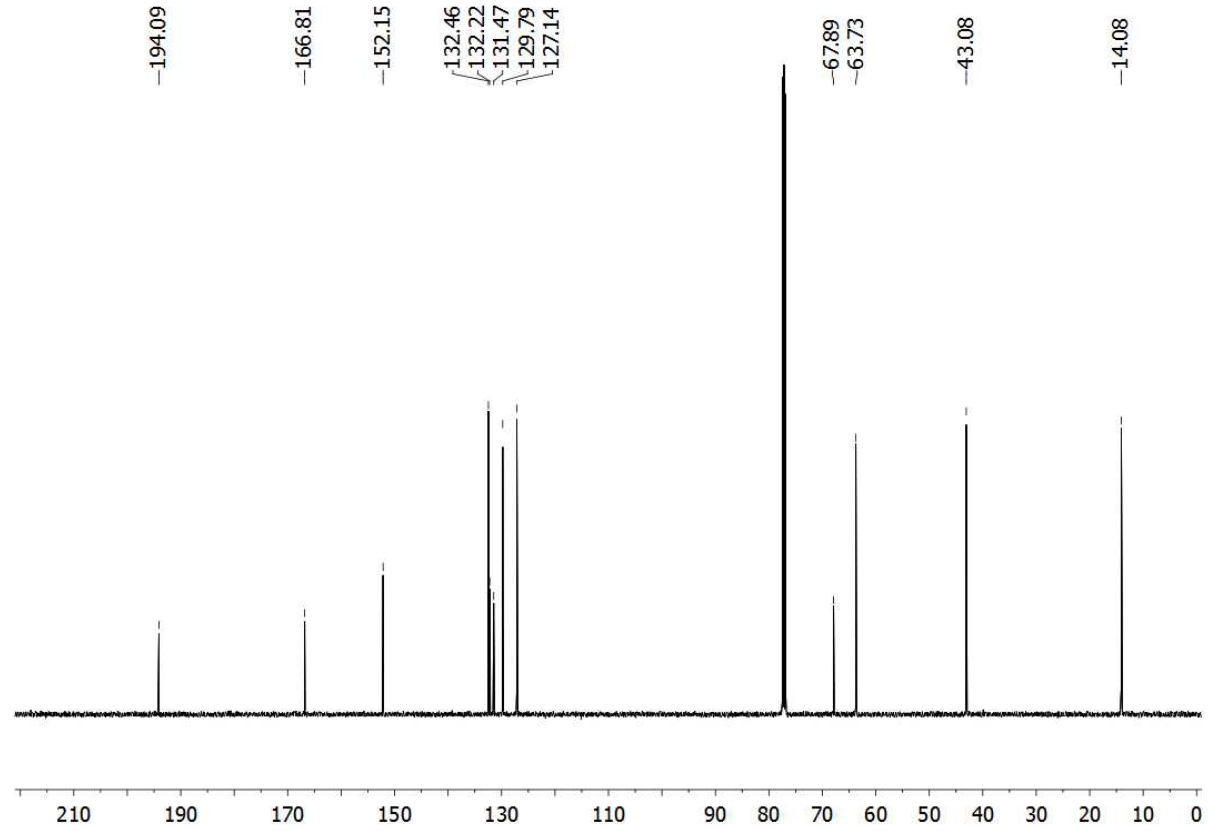


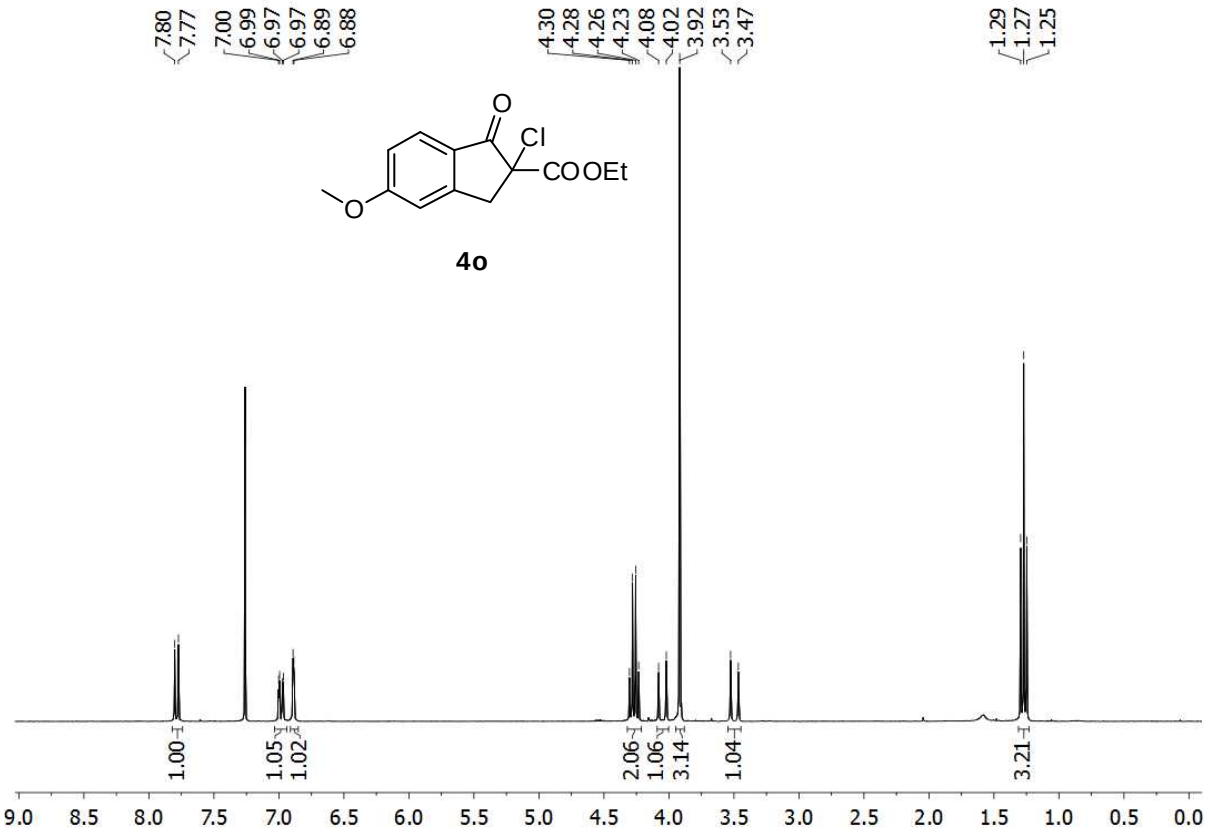
***trans*-4k**



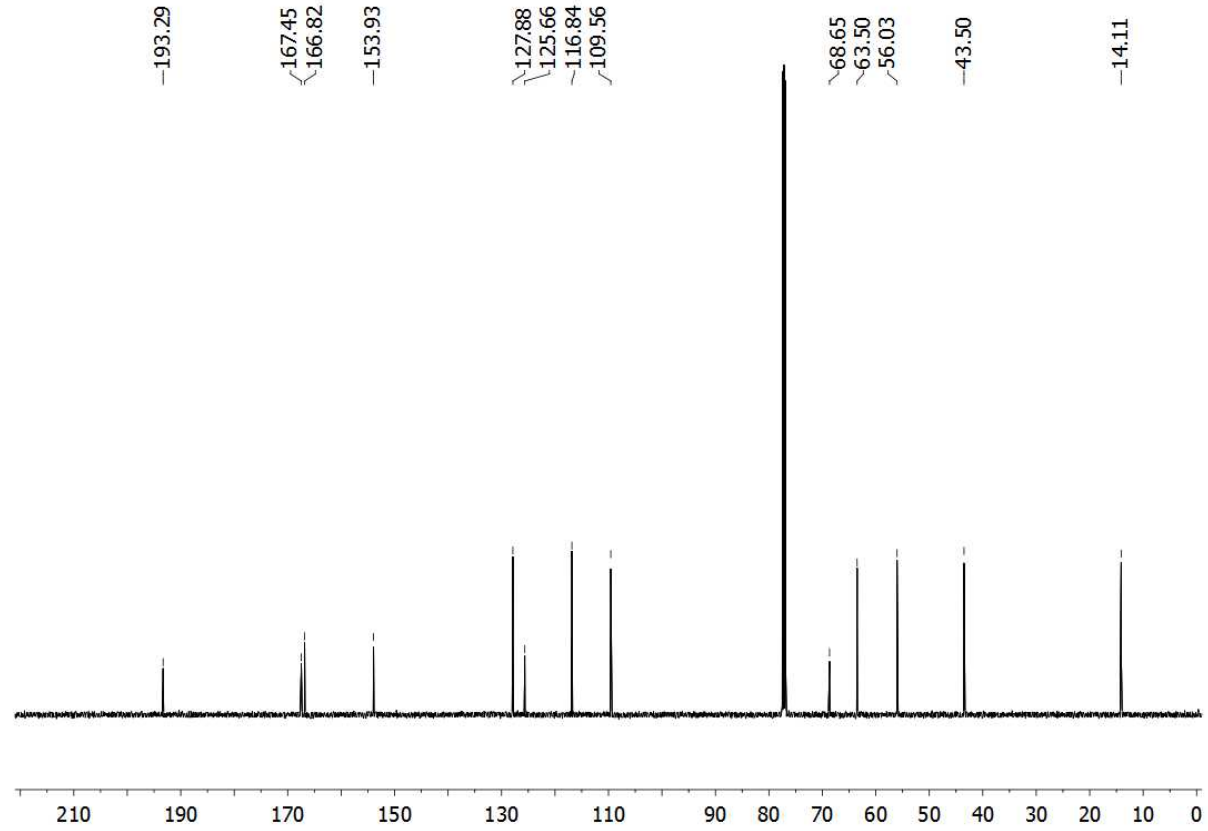


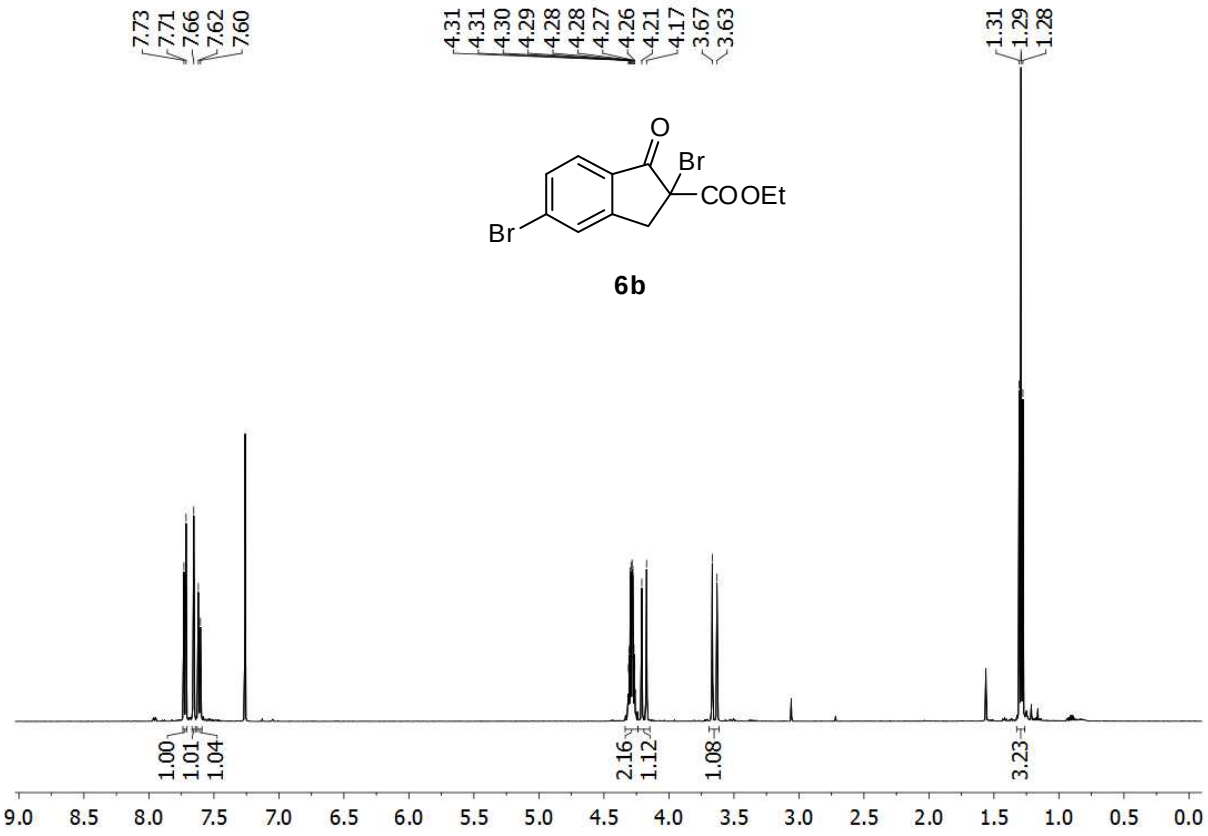
4n



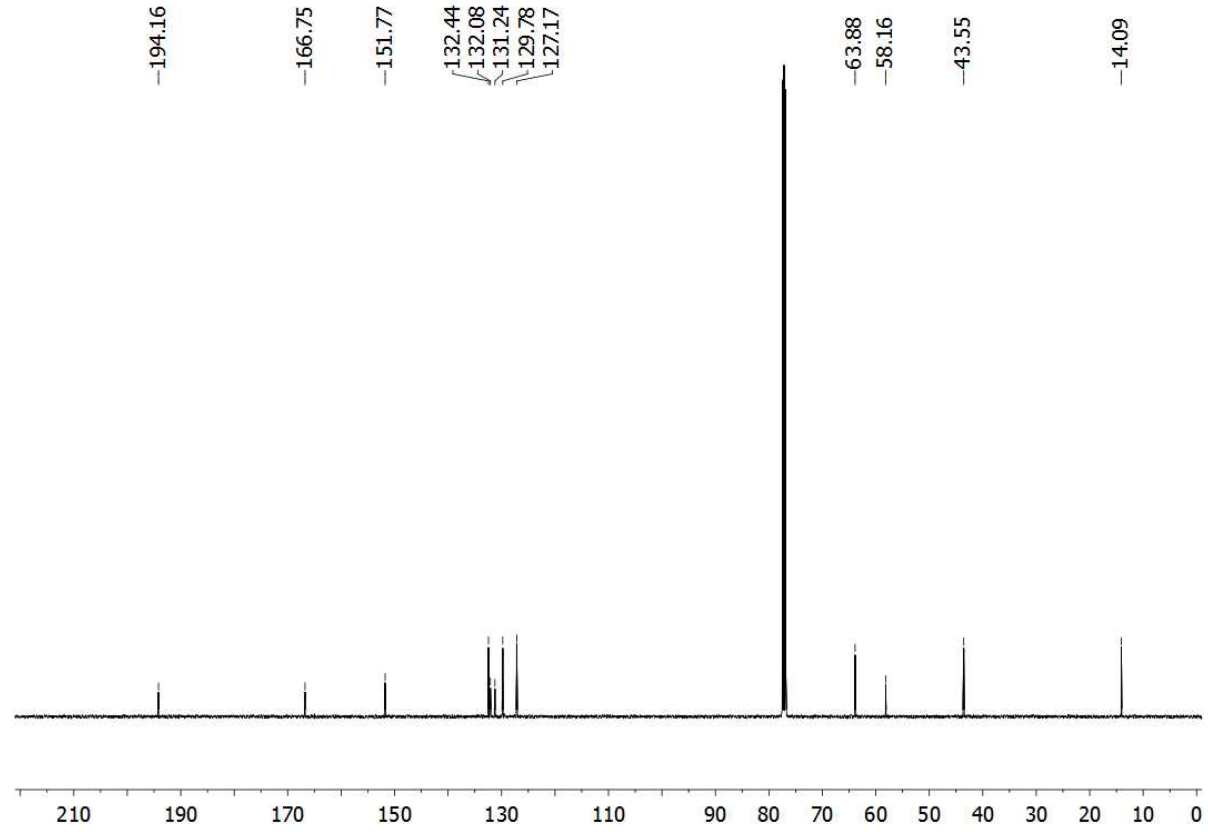


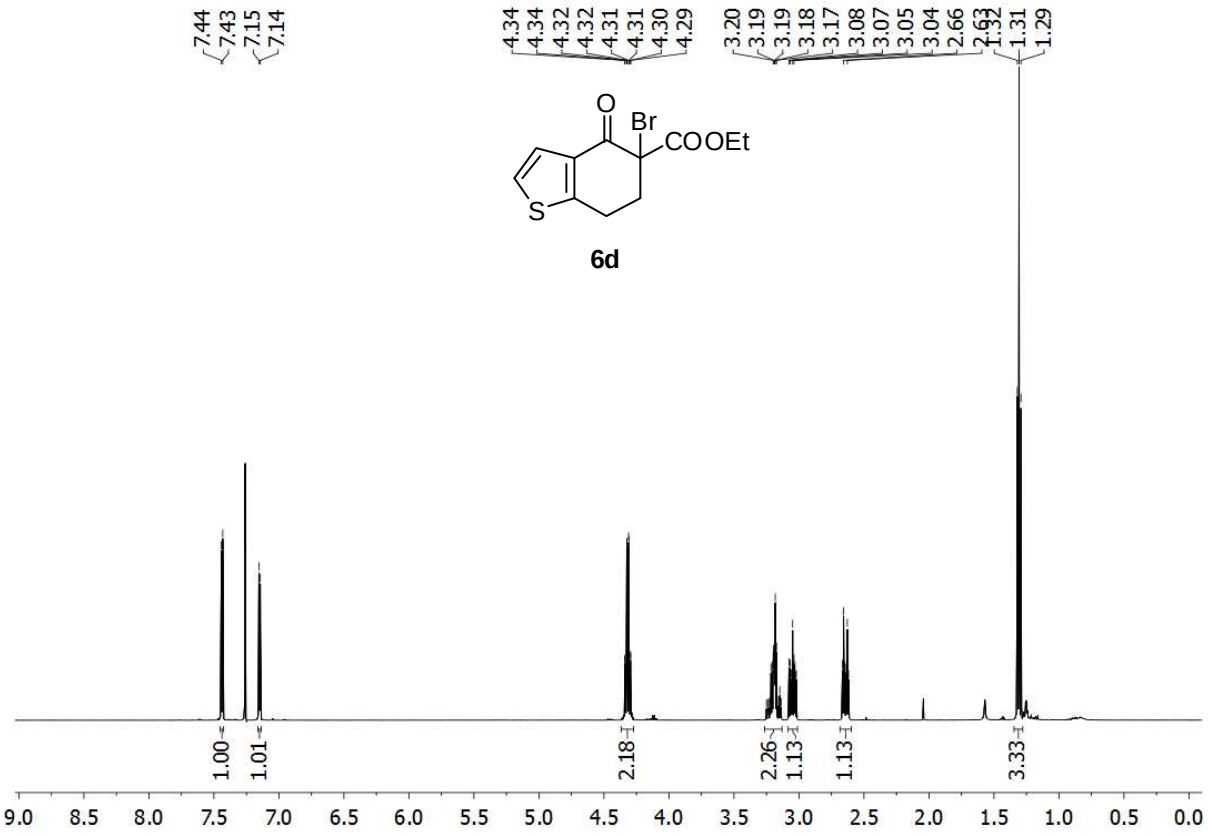
4o



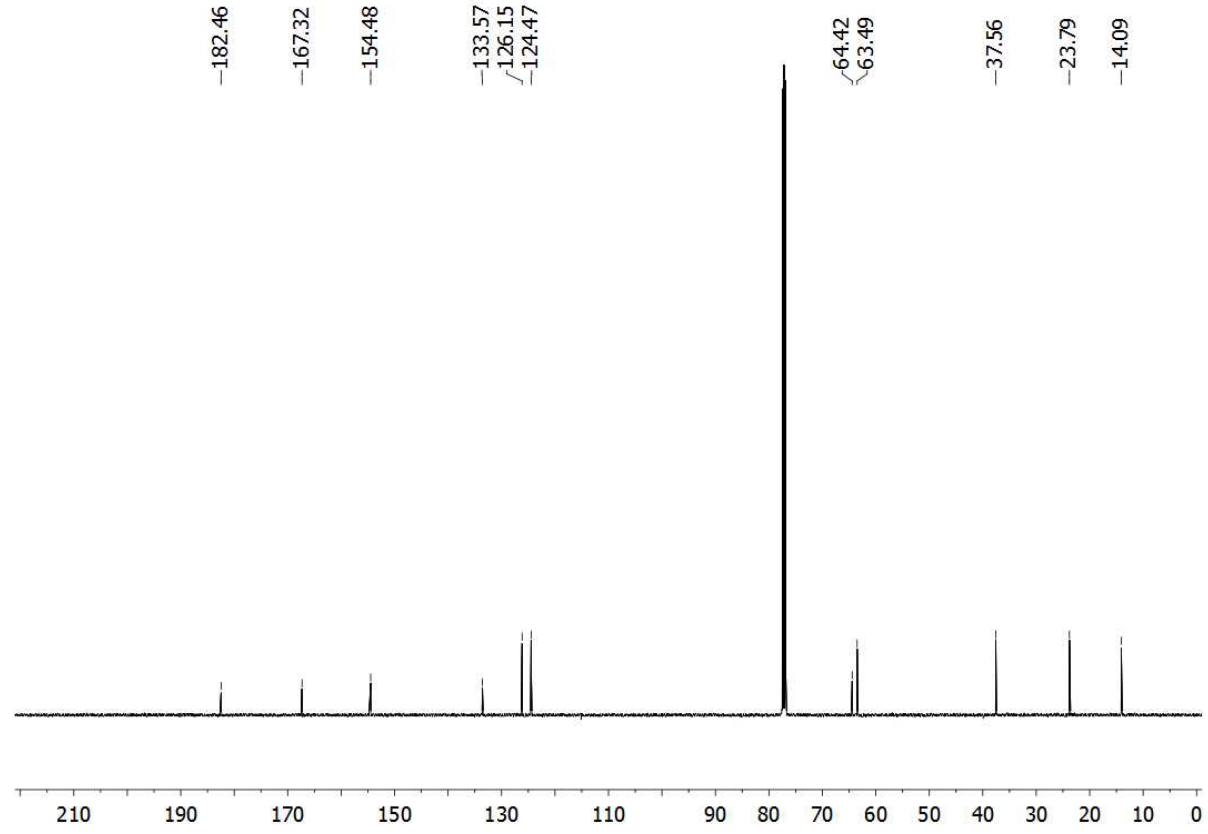


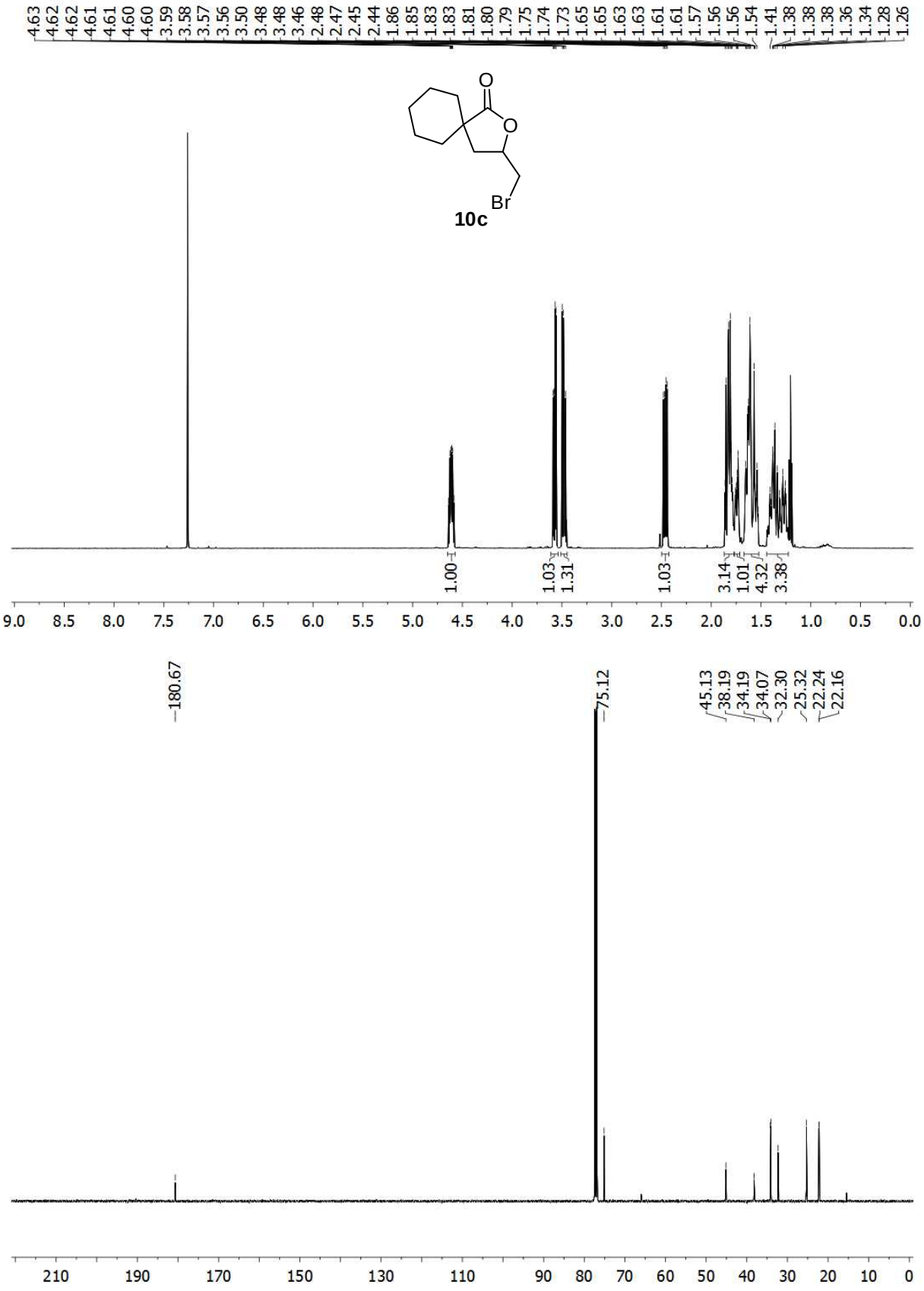
6b

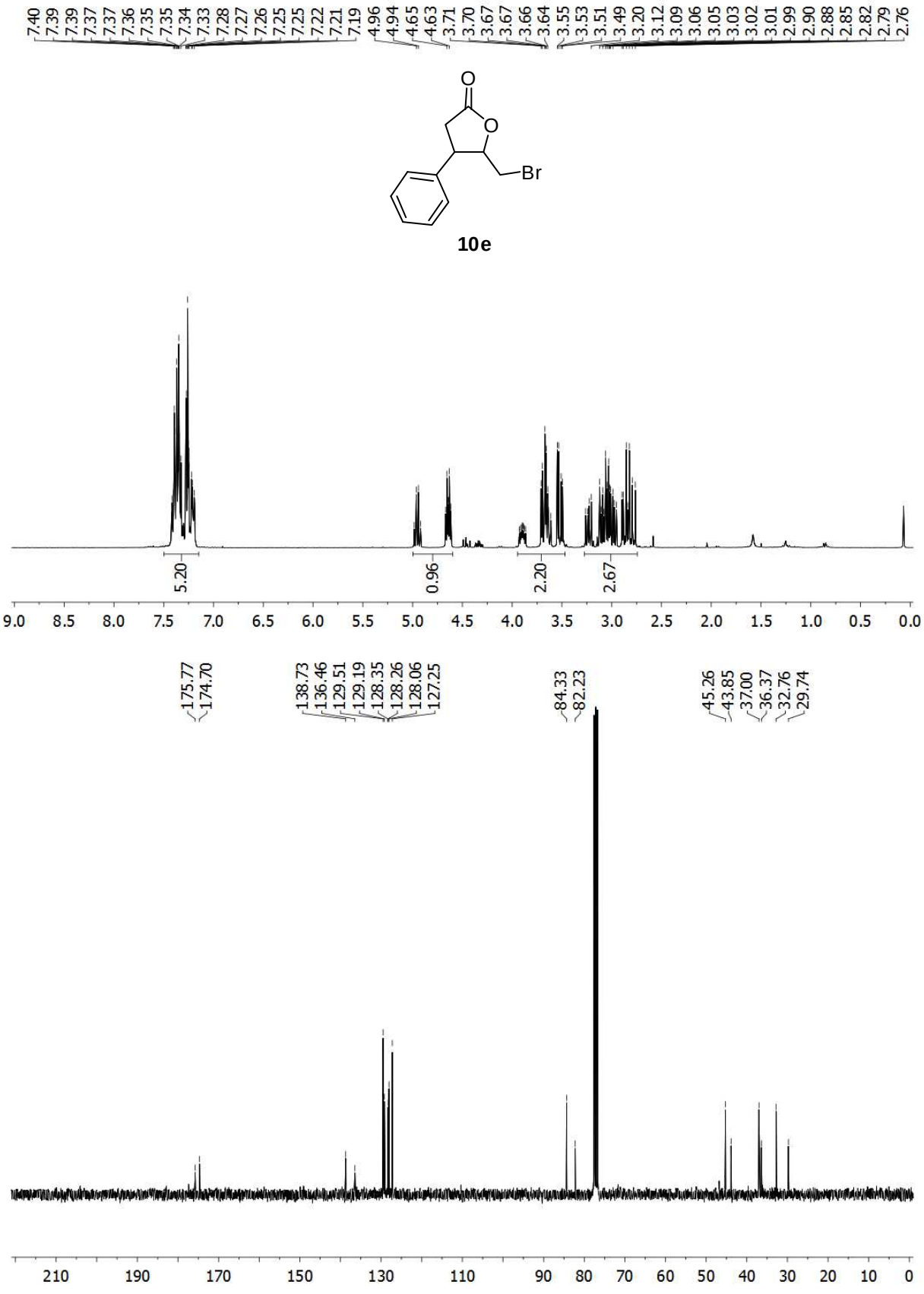




6d




4.63 4.62 4.62 4.61 4.61 4.60 4.60 3.59 3.58 3.57 3.56 3.50 3.48 3.48 3.46 2.48 2.47 2.45 2.44 1.86 1.85 1.83 1.83 1.81 1.80 1.79 1.75 1.74 1.73 1.65 1.65 1.63 1.63 1.61 1.61 1.57 1.56 1.56 1.54 1.41 1.38 1.38 1.38 1.36 1.34 1.28 1.26
O
O
Br
10c
1.00
1.03
1.31
1.03
3.14
1.01
4.32
3.38
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
180.67
75.12
45.13
38.19
34.19
34.07
32.30
25.32
22.24
22.16
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0



Part III: Crystallographic Information

Crystal Structure of *cis*-4k

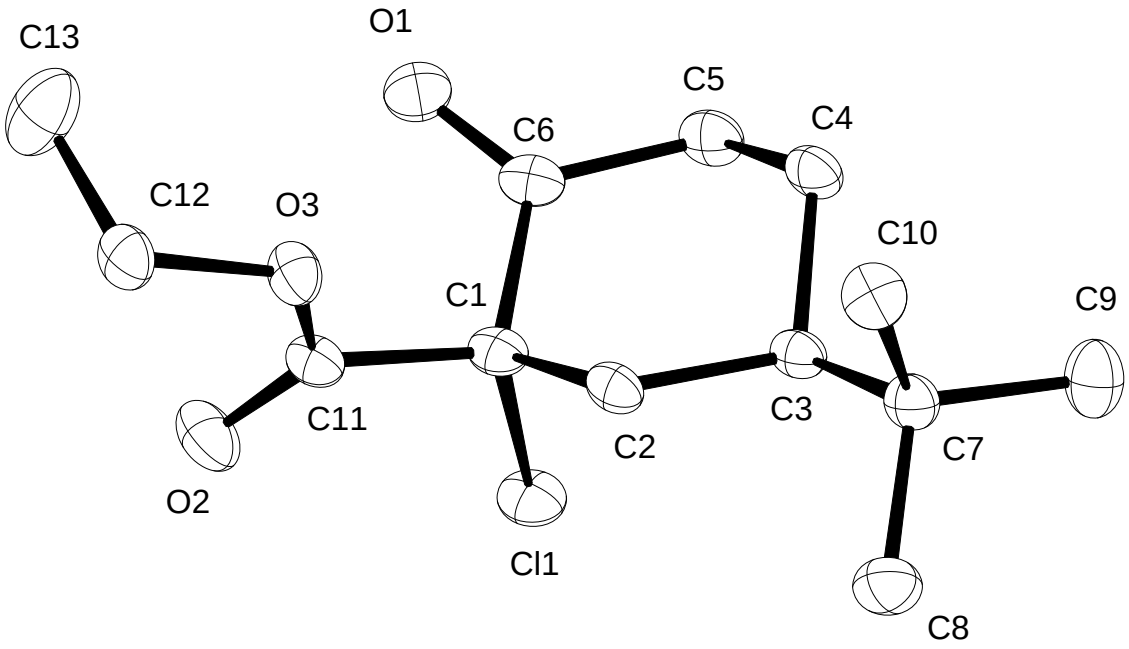


Table 1. Crystal data and structure refinement.

Identification code	7438	
Empirical formula	$C_{13}H_{21}ClO_3$	
Color	colourless	
Formula weight	260.75 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 6.176(2) Å	α= 80.717(6)°.
	b = 10.530(3) Å	β= 79.276(5)°.
	c = 10.911(3) Å	γ = 83.643(6)°.
Volume	685.8(4) Å^3	
Z	2	
Density (calculated)	1.263 Mg · m^{-3}	
Absorption coefficient	0.274 mm^{-1}	
F(000)	280 e	
Crystal size	0.23 x 0.11 x 0.05 mm^3	
θ range for data collection	1.92 to 31.51°.	

Index ranges	$-9 \le h \le 9$, $-15 \le k \le 15$, $-15 \le l \le 15$	
Reflections collected	12193	
Independent reflections	4407 [$R_{int} = 0.0595$]	
Reflections with $I>2\sigma(I)$	3055	
Completeness to $\theta = 27.50°$	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.47	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4407 / 0 / 158	
Goodness-of-fit on F^2	1.020	
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0527$	$wR^2 = 0.1113$
R indices (all data)	$R_1 = 0.0923$	$wR^2 = 0.1265$
Largest diff. peak and hole	0.526 and -0.646 e · $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	0.8979(2)	0.9475(2)	0.7481(1)	0.020(1)
C(2)	0.8259(2)	0.8239(2)	0.7164(1)	0.020(1)
C(3)	0.8472(2)	0.7056(2)	0.8171(1)	0.019(1)
C(4)	0.7136(3)	0.7398(2)	0.9430(1)	0.022(1)
C(5)	0.7997(3)	0.8553(2)	0.9833(1)	0.024(1)
C(6)	0.7983(2)	0.9720(2)	0.8841(1)	0.021(1)
C(7)	0.7832(3)	0.5815(2)	0.7765(1)	0.022(1)
C(8)	0.9298(3)	0.5561(2)	0.6512(2)	0.030(1)
C(9)	0.8246(3)	0.4647(2)	0.8752(2)	0.032(1)
C(10)	0.5391(3)	0.5932(2)	0.7603(2)	0.027(1)
C(11)	0.8395(2)	1.0663(2)	0.6553(1)	0.021(1)
C(12)	0.5365(3)	1.1766(2)	0.5637(2)	0.025(1)
C(13)	0.4446(4)	1.2805(2)	0.6407(2)	0.042(1)
Cl(1)	1.1919(1)	0.9336(1)	0.7447(1)	0.026(1)
O(1)	0.7278(2)	1.0797(1)	0.9049(1)	0.027(1)
O(2)	0.9629(2)	1.1466(1)	0.6026(1)	0.032(1)
O(3)	0.6295(2)	1.0660(1)	0.6417(1)	0.024(1)

Table 3. Bond lengths [Å] and angles [°].

C(1)-C(2)	1.531(2)	C(1)-C(11)	
1.532(2)	C(1)-C(6)	1.547(2)	C(1)-
Cl(1)	1.7999(15)	C(2)-C(3)	
1.534(2)	C(3)-C(4)	1.539(2)	C(3)-
C(7)	1.558(2)	C(4)-C(5)	
1.536(2)	C(5)-C(6)	1.502(2)	C(6)-
O(1)	1.210(2)	C(7)-C(9)	
1.531(2)	C(7)-C(8)	1.538(2)	C(7)-
C(10)	1.539(2)	C(11)-O(2)	
1.2042(19)	C(11)-O(3)	1.3330(18)	C(12)-
O(3)	1.457(2)	C(12)-C(13)	
1.486(3)			

C(2)-C(1)-C(11)111.93(12) C(2)-C(1)-C(6) 112.58(13) C(11)-C(1)-C(6) 109.23(14) C(2)-C(1)-Cl(1)110.31(11) C(11)-C(1)-Cl(1) 108.32(10) C(6)-C(1)-Cl(1)104.10(9) C(1)-C(2)-C(3)114.21(12) C(2)-C(3)-C(4) 107.86(14) C(2)-C(3)-C(7)111.82(12) C(4)-C(3)-C(7) 114.59(12) C(5)-C(4)-C(3)111.77(13) C(6)-C(5)-C(4) 111.68(13) O(1)-C(6)-C(5) 124.38(14) O(1)-C(6)-C(1)120.21(15) C(5)-C(6)-C(1) 115.41(15) C(9)-C(7)-C(8)107.29(15) C(9)-C(7)-C(10) 109.13(14) C(8)-C(7)-C(10) 108.87(13) C(9)-C(7)-C(3)109.77(13) C(8)-C(7)-C(3) 109.82(13) C(10)-C(7)-C(3)111.86(14) O(2)-C(11)-O(3) 125.41(15) O(2)-C(11)-C(1) 125.74(14) O(3)-C(11)-C(1)108.85(13) O(3)-C(12)-C(13)110.30(14) C(11)-O(3)-C(12)117.43(13)

Table 4. Anisotropic displacement parameters (Å^2).

The anisotropic 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}
C(1)	0.012(1)	0.027(1)	0.019(1)	-0.003(1)	-0.003(1)	-0.002(1)
C(2)	0.020(1)	0.026(1)	0.013(1)	-0.002(1)	-0.003(1)	-0.003(1)
C(3)	0.016(1)	0.026(1)	0.014(1)	-0.001(1)	-0.003(1)	0.000(1)
C(4)	0.023(1)	0.027(1)	0.014(1)	0.000(1)	-0.003(1)	-0.001(1)
C(5)	0.025(1)	0.032(1)	0.015(1)	-0.004(1)	-0.005(1)	-0.001(1)
C(6)	0.015(1)	0.031(1)	0.019(1)	-0.006(1)	-0.004(1)	-0.003(1)
C(7)	0.022(1)	0.024(1)	0.018(1)	-0.001(1)	-0.005(1)	0.000(1)
C(8)	0.032(1)	0.031(1)	0.025(1)	-0.009(1)	0.000(1)	-0.002(1)
C(9)	0.040(1)	0.027(1)	0.030(1)	0.000(1)	-0.015(1)	-0.002(1)
C(10)	0.024(1)	0.030(1)	0.028(1)	-0.004(1)	-0.009(1)	-0.004(1)
C(11)	0.019(1)	0.026(1)	0.017(1)	-0.002(1)	-0.002(1)	-0.003(1)
C(12)	0.025(1)	0.029(1)	0.022(1)	0.003(1)	-0.009(1)	-0.001(1)
C(13)	0.052(1)	0.036(1)	0.042(1)	-0.011(1)	-0.024(1)	0.012(1)
Cl(1)	0.013(1)	0.035(1)	0.028(1)	-0.004(1)	-0.004(1)	-0.002(1)
O(1)	0.027(1)	0.029(1)	0.026(1)	-0.008(1)	-0.004(1)	-0.002(1)
O(2)	0.024(1)	0.036(1)	0.031(1)	0.008(1)	-0.004(1)	-0.010(1)
O(3)	0.020(1)	0.025(1)	0.025(1)	0.004(1)	-0.008(1)	-0.003(1)

Crystal Structure of 4n

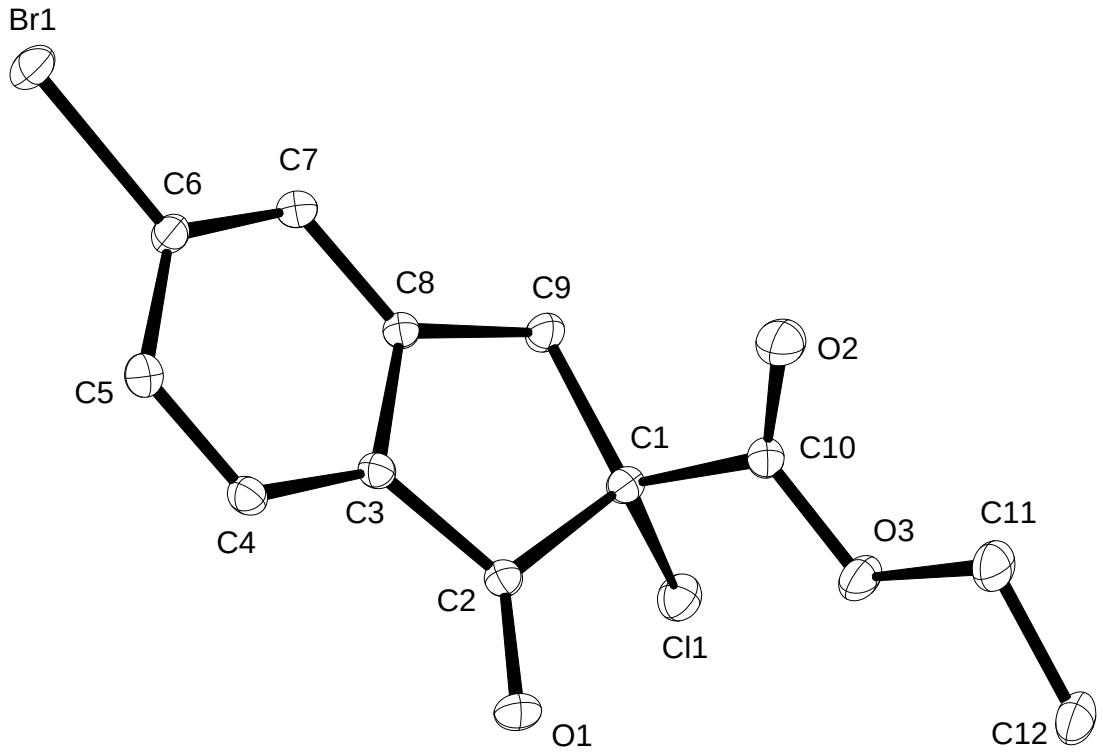


Table 1. Crystal data and structure refinement.

Identification code	7469	
Empirical formula	$C_{12}H_{10}BrClO_3$	
Color	yellow	
Formula weight	317.56 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 6.3627(2) Å	α= 84.098(4)°.
	b = 9.1546(4) Å	β= 83.470(3)°.
	c = 10.3192(3) Å	γ = 87.085(3)°.
Volume	593.54(4) Å^3	
Z	2	
Density (calculated)	1.777 Mg · m^{-3}	
Absorption coefficient	3.680 mm^{-1}	
F(000)	316 e	
Crystal size	0.21 x 0.16 x 0.08 mm^3	
θ range for data collection	2.85 to 35.01°.	
Index ranges	$-10 \le h \le 10$, $-14 \le k \le 14$, $-16 \le l \le 16$	

Reflections collected	18941	
Independent reflections	5224 [R_{int} = 0.0330]	
Reflections with I>2σ(I)	4775	
Completeness to θ = 27.50°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.75 and 0.48	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5224 / 0 / 155	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2σ(I)]	R_1 = 0.0243	wR^2 = 0.0576
R indices (all data)	R_1 = 0.0291	wR^2 = 0.0599
Largest diff. peak and hole	0.965 and -0.663 e · $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	0.1754(1)	0.9117(1)	0.3558(1)	0.017(1)
Cl(1)	0.6885(1)	0.1142(1)	0.2907(1)	0.016(1)
O(1)	0.9735(1)	0.3554(1)	0.3563(1)	0.018(1)
O(2)	0.7813(2)	0.4089(1)	0.0037(1)	0.023(1)
O(3)	0.9856(1)	0.2210(1)	0.0820(1)	0.018(1)
C(1)	0.6926(2)	0.3019(1)	0.2242(1)	0.012(1)
C(2)	0.8052(2)	0.3914(1)	0.3163(1)	0.012(1)
C(3)	0.6694(2)	0.5228(1)	0.3388(1)	0.012(1)
C(4)	0.7109(2)	0.6425(1)	0.4052(1)	0.013(1)
C(5)	0.5618(2)	0.7579(1)	0.4112(1)	0.014(1)
C(6)	0.3744(2)	0.7508(1)	0.3526(1)	0.013(1)
C(7)	0.3298(2)	0.6306(1)	0.2891(1)	0.014(1)
C(8)	0.4813(2)	0.5155(1)	0.2825(1)	0.012(1)
C(9)	0.4693(2)	0.3744(1)	0.2205(1)	0.014(1)
C(10)	0.8224(2)	0.3165(1)	0.0890(1)	0.014(1)
C(11)	1.1248(2)	0.2312(2)	-0.0413(1)	0.020(1)
C(12)	1.3041(2)	0.1213(2)	-0.0226(1)	0.020(1)

Table 3. Bond lengths [Å] and angles [°].

Br(1)-C(6)	1.8932(11)	Cl(1)-C(1)	1.7842(11)
O(1)-C(2)	1.1983(15)	O(2)-C(10)	1.4629(15)
O(3)-C(10)	1.4984(18)	O(3)-C(11)	1.5075(15)
C(9)-C(1)	1.3932(15)	C(12)-C(11)	1.3954(14)
C(2)-C(1)	1.4672(15)	C(8)-C(7)	1.3938(16)
C(5)-C(4)	1.4043(16)	C(8)-C(3)	1.5352(16)
C(3)-C(4)	1.3236(14)	C(9)-C(8)	1.5399(15)
C(7)-C(6)	1.3847(16)	C(2)-C(3)	1.5693(15)
C(1)-C(10)	1.4022(15)	C(5)-C(6)	1.4022(15)

C(10)-O(3)-C(11)	116.13(10)	O(3)-C(11)-C(12)	106.38(10)
C(8)-C(9)-C(1)	127.56(10)	C(7)-C(8)-C(9)	120.07(10)
C(3)-C(8)-C(9)	124.48(10)	O(1)-C(2)-C(1)	128.96(10)
C(3)-C(2)-C(1)	117.64(10)	C(8)-C(7)-C(6)	119.39(10)
C(9)-C(1)-Cl(1)	105.36(8)	C(9)-C(1)-C(2)	108.67(7)
C(10)-C(1)-Cl(1)	112.03(9)	C(10)-C(1)-C(9)	107.22(9)
C(8)-C(3)-C(2)	121.94(10)	C(8)-C(3)-C(4)	128.01(9)
C(5)-C(4)-C(3)	125.42(11)	O(2)-C(10)-O(3)	122.39(10)
O(3)-C(10)-C(1)	118.13(8)	C(7)-C(6)-Br(1)	122.61(10)
C(5)-C(6)-Br(1)	119.25(8)		

Table 4. Anisotropic displacement parameters (Å^2).

The anisotropic 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}
Br(1)	0.016(1)	0.014(1)	0.021(1)	-0.003(1)	-0.002(1)	0.004(1)
Cl(1)	0.018(1)	0.014(1)	0.017(1)	-0.001(1)	0.000(1)	0.000(1)
O(1)	0.012(1)	0.023(1)	0.020(1)	-0.005(1)	-0.006(1)	0.004(1)
O(2)	0.025(1)	0.025(1)	0.017(1)	0.000(1)	-0.002(1)	0.007(1)
O(3)	0.018(1)	0.020(1)	0.014(1)	0.001(1)	0.003(1)	0.007(1)
C(1)	0.012(1)	0.012(1)	0.014(1)	-0.002(1)	-0.002(1)	0.001(1)
C(2)	0.010(1)	0.015(1)	0.011(1)	-0.002(1)	-0.002(1)	0.001(1)
C(3)	0.010(1)	0.014(1)	0.011(1)	-0.002(1)	-0.002(1)	0.000(1)
C(4)	0.012(1)	0.015(1)	0.012(1)	-0.002(1)	-0.003(1)	-0.001(1)
C(5)	0.015(1)	0.014(1)	0.013(1)	-0.003(1)	-0.001(1)	-0.001(1)
C(6)	0.013(1)	0.013(1)	0.013(1)	-0.001(1)	0.000(1)	0.002(1)
C(7)	0.012(1)	0.015(1)	0.014(1)	-0.002(1)	-0.003(1)	0.002(1)
C(8)	0.010(1)	0.014(1)	0.011(1)	-0.003(1)	-0.002(1)	0.001(1)
C(9)	0.011(1)	0.016(1)	0.017(1)	-0.006(1)	-0.004(1)	0.002(1)
C(10)	0.013(1)	0.017(1)	0.014(1)	-0.005(1)	-0.003(1)	0.002(1)
C(11)	0.022(1)	0.023(1)	0.014(1)	-0.001(1)	0.003(1)	0.005(1)
C(12)	0.018(1)	0.022(1)	0.020(1)	-0.008(1)	0.001(1)	0.004(1)

Crystal Structure of 6d

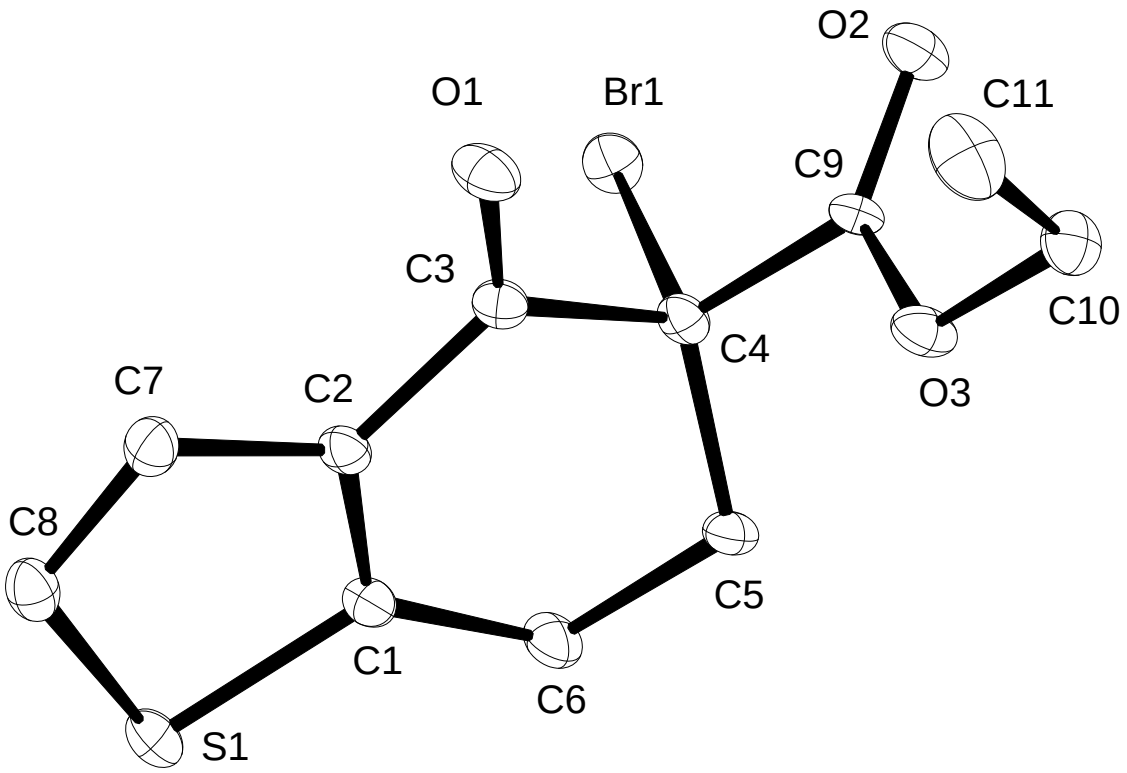


Table 1. Crystal data and structure refinement.

Identification code	7596	
Empirical formula	$C_{11}H_{11}BrO_3S$	
Color	colourless	
Formula weight	303.17 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 12.069(4) Å	α= 90°.
	b = 9.881(3) Å	β= 94.300(5)°.
	c = 9.854(3) Å	γ = 90°.
Volume	1171.9(6) Å^3	
Z	4	
Density (calculated)	1.718 Mg · m^{-3}	
Absorption coefficient	3.674 mm^{-1}	
F(000)	608 e	
Crystal size	0.253 x 0.090 x 0.063 mm^3	
θ range for data collection	2.67 to 35.75°.	
Index ranges	$-19 \le h \le 3$, $-3 \le k \le 12$, $-3 \le l \le 15$	

Reflections collected	2100	
Independent reflections	2010 [R_{int} = 0.0100]	
Reflections with I>2σ(I)	1848	
Completeness to θ = 27.50°	45.4 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.80 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2010 / 0 / 146	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2σ(I)]	R_1 = 0.0241	wR^2 = 0.0648
R indices (all data)	R_1 = 0.0272	wR^2 = 0.0668
Largest diff. peak and hole	0.297 and -0.220 e · $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	0.1121(1)	0.1725(1)	0.8140(1)	0.016(1)
S(1)	0.5211(1)	0.2579(1)	0.9638(1)	0.018(1)
O(1)	0.2827(1)	-0.0911(2)	0.7417(2)	0.019(1)
O(2)	0.0312(2)	-0.1104(2)	0.8432(2)	0.019(1)
O(3)	0.1633(2)	-0.1917(2)	0.9958(2)	0.017(1)
C(1)	0.3982(2)	0.1694(2)	0.9641(2)	0.014(1)
C(2)	0.3903(2)	0.0773(2)	0.8591(2)	0.013(1)
C(3)	0.2908(2)	-0.0051(2)	0.8304(2)	0.013(1)
C(4)	0.1922(2)	0.0274(2)	0.9154(2)	0.013(1)
C(5)	0.2297(2)	0.0750(2)	1.0596(2)	0.014(1)
C(6)	0.3110(2)	0.1946(2)	1.0614(2)	0.017(1)
C(7)	0.4852(2)	0.0773(2)	0.7797(2)	0.016(1)
C(8)	0.5609(2)	0.1705(2)	0.8226(2)	0.017(1)
C(9)	0.1165(2)	-0.0980(2)	0.9127(2)	0.012(1)
C(10)	0.1097(2)	-0.3245(2)	0.9912(2)	0.018(1)
C(11)	0.1651(2)	-0.4147(3)	0.8919(3)	0.028(1)

Table 3. Bond lengths [Å] and angles [°].

Br(1)-C(4)	1.961(2)	S(1)-C(1)	
1.722(2)	S(1)-C(8)	1.735(2)	O(1)-
C(3)	1.218(2)	O(2)-C(9)	
1.199(3)	O(3)-C(9)	1.333(3)	O(3)-
C(10)	1.462(3)	C(1)-C(2)	
1.376(3)	C(1)-C(6)	1.497(2)	C(2)-
C(3)	1.460(3)	C(2)-C(7)	
1.435(2)	C(3)-C(4)	1.539(2)	C(4)-
C(5)	1.533(3)	C(4)-C(9)	
1.539(3)	C(5)-C(6)	1.535(3)	C(7)-
C(8)	1.343(3)	C(10)-C(11)	
1.517(3)			
C(1)-S(1)-C(8)	92.26(10)	C(9)-O(3)-C(10)	
115.9(2)	C(2)-C(1)-S(1)	110.23(12)	C(2)-
C(1)-C(6)	125.37(19)	C(6)-C(1)-S(1)	
124.35(16)	C(1)-C(2)-C(3)	121.61(14)	C(1)-
C(2)-C(7)	113.33(18)	C(7)-C(2)-C(3)	
124.98(17)	O(1)-C(3)-C(2)	123.26(14)	O(1)-
C(3)-C(4)	120.80(19)	C(2)-C(3)-C(4)	
115.88(16)	C(3)-C(4)-Br(1)	104.30(12)	C(5)-
C(4)-Br(1)	110.35(14)	C(5)-C(4)-C(3)	
112.47(18)	C(5)-C(4)-C(9)	113.35(14)	C(9)-
C(4)-Br(1)	108.12(16)	C(9)-C(4)-C(3)	
107.78(15)	C(4)-C(5)-C(6)	112.99(14)	C(1)-
C(6)-C(5)	110.15(15)	C(8)-C(7)-C(2)	
112.39(17)	C(7)-C(8)-S(1)	111.77(13)	O(2)-
C(9)-O(3)	125.9(2)	O(2)-C(9)-C(4)	
125.1(2)	O(3)-C(9)-C(4)	108.9(2)	O(3)-
C(10)-C(11)	109.38(17)		

Table 4. Anisotropic displacement parameters (Å^2).

The anisotropic 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}
Br(1)	0.014(1)	0.014(1)	0.020(1)	0.003(1)	0.000(1)	0.003(1)
S(1)	0.016(1)	0.017(1)	0.021(1)	-0.002(1)	0.000(1)	-0.006(1)
O(1)	0.015(1)	0.020(1)	0.022(1)	-0.008(1)	0.000(1)	0.000(1)
O(2)	0.015(1)	0.016(1)	0.024(1)	0.003(1)	-0.005(1)	-0.002(1)
O(3)	0.018(1)	0.012(1)	0.020(1)	0.001(1)	-0.005(1)	-0.003(1)
C(1)	0.013(1)	0.016(1)	0.014(1)	0.000(1)	-0.001(1)	-0.002(1)
C(2)	0.010(1)	0.014(1)	0.014(1)	0.001(1)	-0.001(1)	0.001(1)
C(3)	0.010(1)	0.014(1)	0.014(1)	0.001(1)	-0.001(1)	0.003(1)
C(4)	0.009(1)	0.013(1)	0.016(1)	0.002(1)	-0.001(1)	0.001(1)
C(5)	0.013(1)	0.017(1)	0.012(1)	-0.003(1)	-0.001(1)	-0.002(1)
C(6)	0.016(1)	0.018(1)	0.018(1)	-0.007(1)	0.002(1)	-0.005(1)
C(7)	0.014(1)	0.019(1)	0.016(1)	0.003(1)	0.002(1)	0.002(1)
C(8)	0.013(1)	0.016(1)	0.021(1)	0.004(1)	0.001(1)	0.000(1)
C(9)	0.009(1)	0.014(1)	0.013(1)	-0.001(1)	-0.003(1)	0.000(1)
C(10)	0.021(1)	0.013(1)	0.021(1)	0.002(1)	0.001(1)	-0.002(1)
C(11)	0.026(1)	0.017(2)	0.041(1)	-0.008(1)	0.006(1)	-0.002(1)

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