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Controlling Regioselectivity of Bromolactonization Reaction in HFIP

Tuong Anh To,[†a] Nhu T. A. Phan,[†a] Binh Khanh Mai,*[b] Thanh Vinh Nguyen*[a]

[a] School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia.

E-mail: t.v.nguyen@unsw.edu.au

[b] Department of Chemistry, University of Pittsburgh, Pennsylvania 15260, United States.

E-mail: binh.mai@pitt.edu

[†] Contributed equally

Supporting Information

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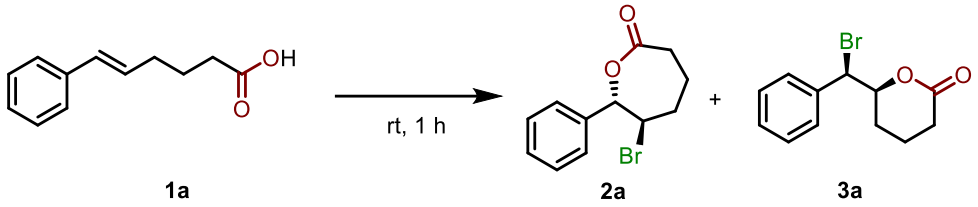
General Methods

Reactions, unless otherwise stated, were conducted in screw-cap vials under ambient air. Commercially available solvents reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using silica gel plates pre-coated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using either a Bruker Avance III 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C; BBFO probe), an Avance I 300 (300.13 MHz, ^{1}H; 75.5 MHz, ^{13}C; BBFO probe) or an Avance III 400 (400.13 MHz, ^{1}H; 100.6 MHz, ^{13}C; BBFO probe or Prodigy cryoprobe). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a ThermoNicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

Optimization Studies



1a 2a 3a

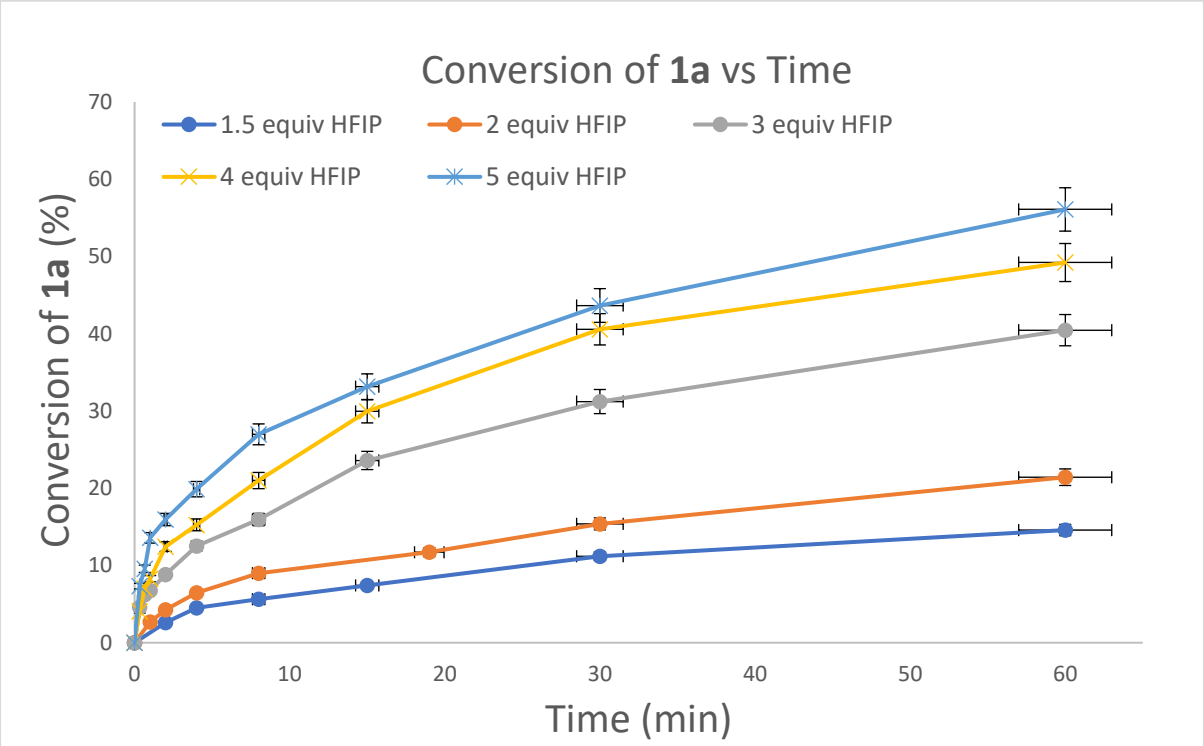
Entry[a]	Catalyst	NBS	Solvent	Yield of **2a**[b]	Yield of **3a**[b]
1	**no cat**	**1.1 equiv**	**HFIP (0.1 M)**	**91%**	**7%**
2	no cat	1.1 equiv	TFE (0.1 M)	29%	60%
3	no cat	1.1 equiv	*i*PrOH (0.1 M)	-	-
4	no cat	1.1 equiv	DCE (0.1 M)	-	-
5	no cat	1.1 equiv	$MeNO_2$ (0.1 M)	Trace	Trace
6	no cat	1.1 equiv	HFIP (0.05 M)	91%	6%
7	no cat	1.1 equiv	HFIP (0.2 M)	86%	12%
8	no cat	1.1 equiv	HFIP (0.5 M)	68%	14%
9	no cat	1.1 equiv	HFIP (1 M)	51%	15%
10	no cat	1.1 equiv	9DCE:HFIP (0.1 M)	71%	Trace
11	no cat	1.1 equiv	7DCE:3HFIP (0.1 M)	85%	9%
12	no cat	1.1 equiv	5DCE:5HFIP (0.1 M)	85%	8%
13	no cat	1.1 equiv	3DCE:7HFIP (0.1 M)	88%	10%
14	no cat	1 equiv	HFIP (0.1 M)	86%	7%
15	no cat	1.2 equiv	HFIP (0.1 M)	90%	7%
16	no cat	1.5 equiv	HFIP (0.1 M)	91%	8%
17	no cat	2 equiv	HFIP (0.1 M)	85%	8%
18	TfOH (10 mol%)	1.1 equiv	HFIP (0.1 M)	-	86%
19	TfOH (10 mol%)	1.1 equiv	TFE (0.1 M)	18%	12%
20	TfOH (10 mol%)	1.1 equiv	*i*PrOH (0.1 M)	22%	29%
21	TfOH (10 mol%)	1.1 equiv	DCE (0.1 M)	-	25%
22	TfOH (10 mol%)	1.1 equiv	$MeNO_2$ (0.1 M)	-	45%
23	*p*TSA (10 mol%)	1.1 equiv	HFIP (0.1 M)	-	89%
24	TFA (10 mol%)	1.1 equiv	HFIP (0.1 M)	67%	20%
25	AcOH (10 mol%)	1.1 equiv	HFIP (0.1 M)	88%	10%

26	*p*TSA (1 mol%)	1.1 equiv	HFIP (0.1 M)	-	77%
27	*p*TSA (2 mol%)	1.1 equiv	HFIP (0.1 M)	-	79%
28	***p*TSA (5 mol%)**	**1.1 equiv**	**HFIP (0.1 M)**	**-**	**87%**
29	*p*TSA (20 mol%)	1.1 equiv	HFIP (0.1 M)	-	84%
30	*p*TSA (5 mol%)	1.1 equiv	HFIP (0.05 M)	-	87%
31	*p*TSA (5 mol%)	1.1 equiv	HFIP (0.2 M)	-	81%
32	*p*TSA (5 mol%)	1.1 equiv	HFIP (0.5 M)	-	67%
33	*p*TSA (5 mol%)	1.1 equiv	HFIP (1 M)	-	54%
34	*p*TSA (5 mol%)	1.1 equiv	9DCE:HFIP (0.1 M)	43%	12%
35	*p*TSA (5 mol%)	1.1 equiv	7DCE:3HFIP (0.1 M)	9%	38%
36	*p*TSA (5 mol%)	1.1 equiv	5DCE:5HFIP (0.1 M)	-	70%
37	*p*TSA (5 mol%)	1.1 equiv	3DCE:7HFIP (0.1 M)	-	83%
38	*p*TSA (5 mol%)	1 equiv	HFIP (0.1 M)	-	82%
39	*p*TSA (5 mol%)	1.2 equiv	HFIP (0.1 M)	-	83%
40	*p*TSA (5 mol%)	1.5 equiv	HFIP (0.1 M)	-	85%
41	*p*TSA (5 mol%)	2 equiv	HFIP (0.1 M)	-	85%
42	*p*TSA (5 mol%)	1.1 equiv	TFE (0.1 M)	22%	12%
43	*p*TSA (5 mol%)	1.1 equiv	*i*PrOH (0.1 M)	13%	5%
44	*p*TSA (5 mol%)	1.1 equiv	DCE (0.1 M)	11%	5%
45	*p*TSA (5 mol%)	1.1 equiv	$MeNO_2$ (0.1 M)	17%	20%

[a] Reaction was carried out on 0.2 mmol scale of substrate **1a**; [b] Yields were determined by ^{1}H NMR integration using methyl benzoate as an internal standard.

Kinetic Studies and Reaction Order in HFIP Solvent

Kinetic studies were carried out by monitoring the reaction of substrate **1a** (0.1 mmol) and NBS (1.1 equiv, 39.2 mg) with varying amount of HFIP from 1.5 – 5 equivalents in CD_2Cl_2 within 60 minutes. The volume of CD_2Cl_2 was adjusted with the changing volume of HFIP so that the total volume of the reaction was fixed at 1.0 mL (the initial concentration of substrate **1a** was 0.1 M for all kinetic runs). Conversion of substrate **1a** was quantified by ^{1}H NMR spectroscopy analysis of aliquots of the reaction mixture in $CDCl_3$ with methyl benzoate as internal standard. We applied a standard error range of ±5% for conversion to all figures, as this is the commonly accepted error for ^{1}H NMR integration. We also applied a ± 5% error range for reaction time.



Initial rates were approximated within the range of the first 10% conversion. The following assumptions are made:

- The difference in polarity of the reaction medium was negligible and did not alter the reaction profile when the amount of HFIP was varied. Indeed, with the amount of CD_2Cl_2 being 18 – 62 times the volume of HFIP, the overall polarity of the reaction mixture does not change significantly.
- The reaction rate can be calculated as:

$$rate = k[\text{HFIP}]^x[\mathbf{1a}]^y[\text{NBS}]^z$$

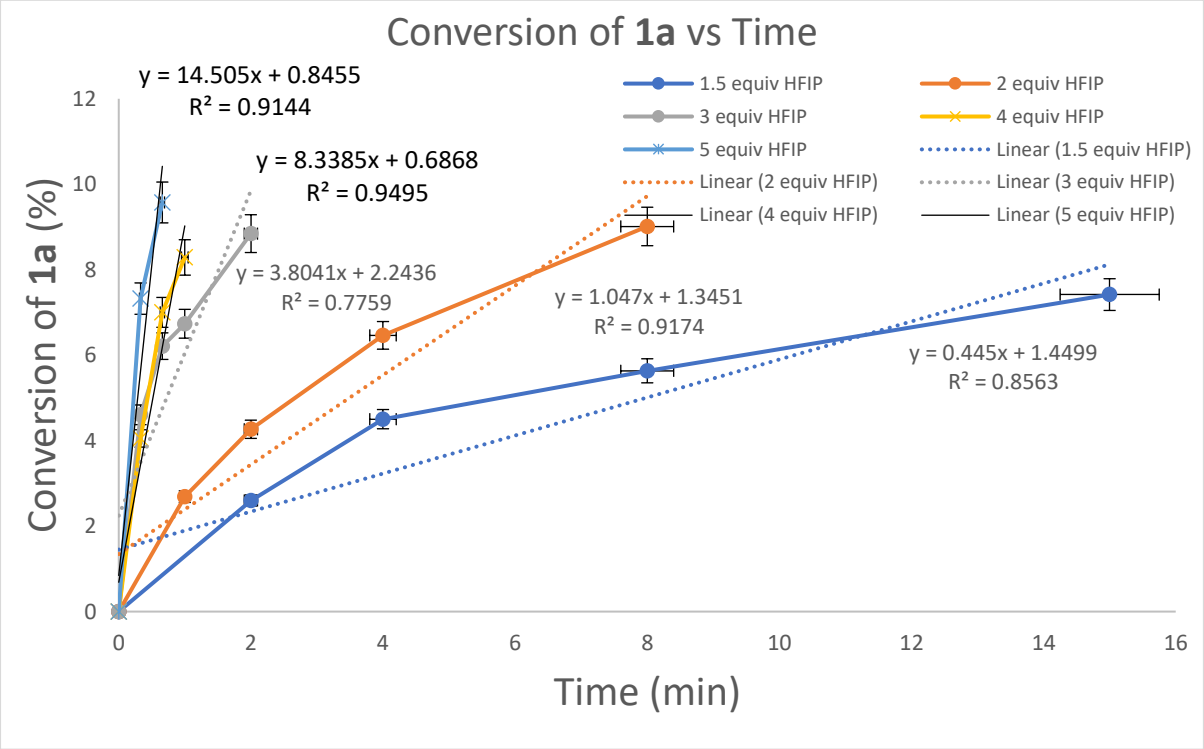
[**1a**] and [NBS] can be approximated as negligibly changed in the first 10% conversion range, we can assume that:

$$rate = k'[\text{HFIP}]^x$$

or

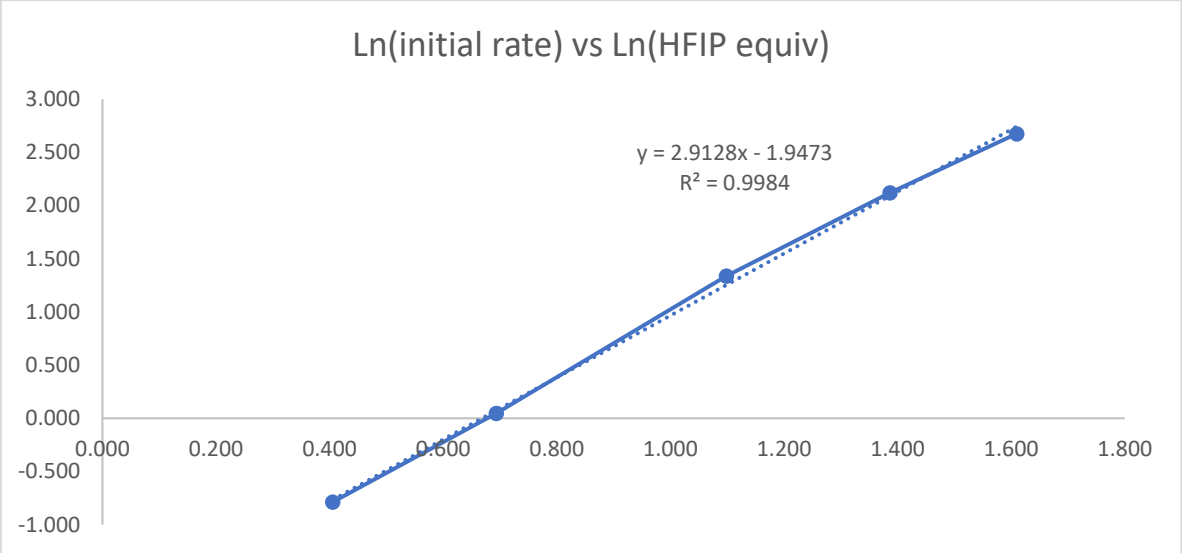
$$\ln[rate] = x*\ln[\text{HFIP}] + \ln k' = x*\ln[\text{HFIP equivalent}] + \text{constant}$$

with [HFIP] = 0.1*[HFIP equivalent] M. Therefore, a plot of ln[$rate$] vs. ln[HFIP equivalent] should give the slope x, which is the reaction order in HFIP.



HFIP equiv	Initial rate	ln(HFIP equiv)	ln(initial rate)
1.5	0.445	0.405	-0.787
2	1.047	0.693	0.046
3	3.8041	1.099	1.336
4	8.3385	1.386	2.121
5	14.505	1.609	2.674

ln(initial rate) was plotted against ln(HFIP equivalent) to give the reaction order in HFIP:



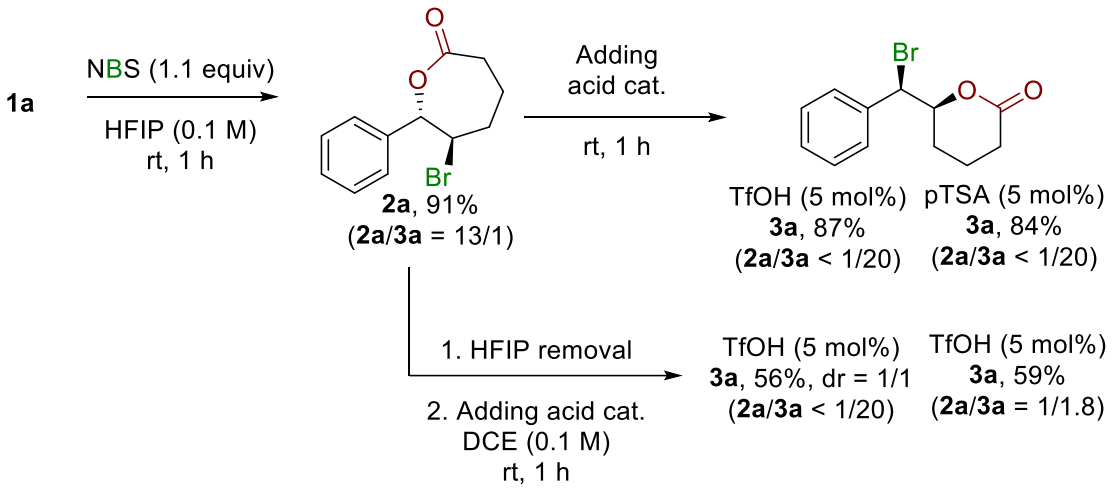
The reaction order in HFIP is approximately 2.9.

Control Experiments

Experiment to confirm *endo*-product **2a** is convertible to *exo*-product **3a**

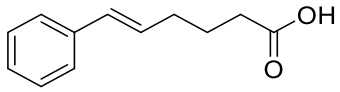
To a solution of **1a** (0.2 mmol) in HFIP (0.1 M) in a screw-cap vial equipped with a stirrer bar was added NBS (1.1 equiv, 39.2 mg). The vial was capped, and the reaction was stirred at room temperature for 1 h. After the *endo*-bromolactonization step was finished, methyl benzoate as an internal standard (0.33 equiv) was added. Aliquots withdrawn from the reaction was analyzed by ^{1}H NMR to determine yield of **2a** and **3a**. TfOH or pTSA (5 mol%) was then added, and the reaction mixture was stirred at room temperature for 1 h. After the next step finished, ^{1}H NMR analysis was performed again to observe the conversion of *endo*-product **2a** to *exo*-product **3a**. NMR yields of products were showed as below.

For the experiments carried out in DCE, after the *endo*-bromolactonization step was finished, HFIP was remove under reduced pressure prior to DCE (0.1 M) was added as the solvent for isomerization step.



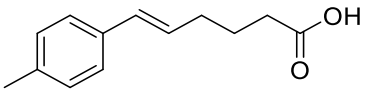
Synthesis of Starting Materials

Alkenoic acid **1a**, **1b**, **1c**, **1d**, **1e**, **1g**, **1h**, **1i**, **2j**, **1l**, and **1m** were synthesized through the ring-opening olefination of cyclic ketone ketals according to our previous work.[1] **1o** was acquired from our previous work.[1]



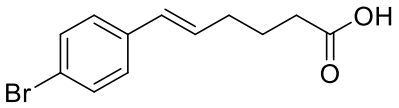
(*E*)-6-phenylhex-5-enoic acid (1a): Prepared from benzaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.25 – 7.16 (m, 1H), 6.42 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 6.9 Hz, 1H), 2.42 (t, J = 7.4 Hz, 2H), 2.29 (qd, J = 7.2, 1.5 Hz, 2H), 1.83 (p, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 137.7, 131.1, 129.4, 128.6 (2C), 127.2, 126.1 (2C), 33.4, 32.4, 24.4.



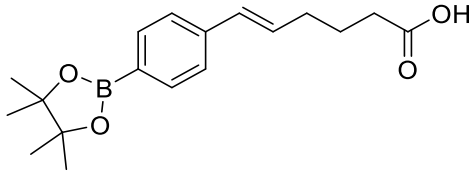
(*E*)-6-(*p*-tolyl)hex-5-enoic acid (1b): Prepared from 4-methylbenzaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.10 (d, J = 7.7 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.12 (dt, J = 15.8, 7.0 Hz, 1H), 2.41 (t, J = 7.5 Hz, 2H), 2.33 (s, 3H), 2.27 (qd, J = 7.2, 1.4 Hz, 2H), 1.83 (p, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 136.9, 134.9, 131.0, 129.3 (2C), 128.4, 126.0 (2C), 33.4, 32.4, 24.4, 21.3.



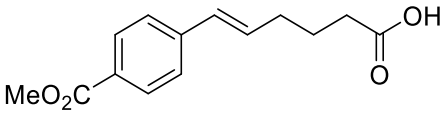
(*E*)-6-(4-bromophenyl)hex-5-enoic acid (1c): Prepared from 4-bromobenzaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.22 – 7.17 (m, 2H), 6.34 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.27 (qd, *J* = 7.2, 1.4 Hz, 2H), 1.82 (p, *J* = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 136.6, 131.7 (2C), 130.4, 130.0, 127.7 (2C), 120.8, 33.4, 32.4, 24.2.



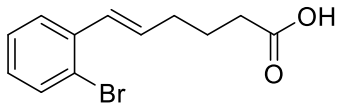
(*E*)-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-5-enoic acid (1d): Prepared from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.36 – 7.31 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.83 (p, *J* = 7.4 Hz, 2H), 1.34 (s, 12H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 140.4, 135.2 (2C), 131.2, 130.6, 125.5 (2C), 83.9, 33.4, 32.4, 25.0 (4C), 24.3;
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.



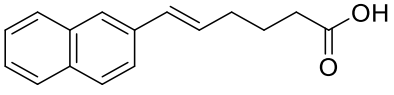
(*E*)-6-(4-(methoxycarbonyl)phenyl)hex-5-enoic acid (1e): Prepared from methyl 4-formylbenzoate and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.41 – 7.36 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.90 (s, 3H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.84 (p, *J* = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 167.1, 142.1, 132.4, 130.3 (2C), 130.0 (2C), 128.6, 126.0, 52.2, 33.4, 32.4, 24.1.



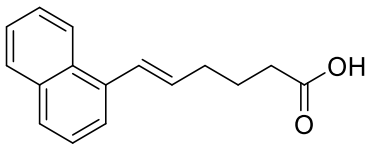
(*E*)-6-(2-bromophenyl)hex-5-enoic acid (1g): Prepared from 2-bromobenzaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.47 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.07 (td, *J* = 7.8, 1.7 Hz, 1H), 6.74 (d, *J* = 15.7 Hz, 1H), 6.12 (dt, *J* = 15.7, 7.0 Hz, 1H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.33 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.86 (p, *J* = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 137.5, 133.0, 132.6, 130.0, 128.5, 127.6, 127.0, 123.4, 33.4, 32.4, 24.2.



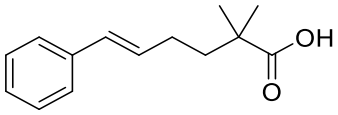
(*E*)-6-(naphthalen-2-yl)hex-5-enoic acid (1h): Prepared from 2-naphthaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, J = 7.8 Hz, 3H), 7.68 (s, 1H), 7.57 (dd, J = 8.6, 1.7 Hz, 1H), 7.48 – 7.39 (m, 2H), 6.58 (d, J = 15.8 Hz, 1H), 6.31 (dt, J = 15.8, 7.0 Hz, 1H), 2.42 (t, J = 7.4 Hz, 2H), 2.33 (qd, J = 7.2, 1.4 Hz, 2H), 1.86 (p, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 135.1, 133.8, 132.9, 131.2, 129.9, 128.2, 128.0, 127.8, 126.3, 125.7, 125.7, 123.7, 33.4, 32.5, 24.4.



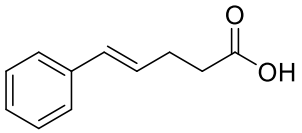
(*E*)-6-(naphthale*n*-1-yl)hex-5-enoic acid (1i): Prepared from 1-naphthaldehyde and cyclopentanone pinacol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 1H), 7.84 (dd, J = 7.9, 1.6 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.57 – 7.40 (m, 4H), 7.16 (d, J = 15.6 Hz, 1H), 6.20 (dt, J = 15.5, 7.0 Hz, 1H), 2.49 (t, J = 7.4 Hz, 2H), 2.42 (qd, J = 7.2, 1.6 Hz, 2H), 1.92 (p, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 135.5, 133.7, 132.8, 131.2, 128.6, 128.4, 127.6, 126.0, 125.8, 125.8, 124.0, 123.8, 33.5, 32.8, 24.4.



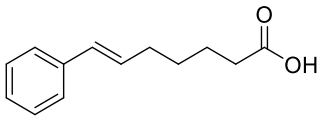
(*E*)-2,2-dimethyl-6-phenylhex-5-enoic acid (1j): Prepared from benzaldehyde and 2,2-dimethylcyclopentanone neopentyl glycol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.21 – 7.16 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 6.8 Hz, 1H), 2.26 – 2.19 (m, 2H), 1.77 – 1.71 (m, 2H), 1.25 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 137.8, 130.3, 130.3, 128.6 (2C), 127.1, 126.1 (2C), 42.1, 40.1, 28.7, 25.2 (2C).



(*E*)-5-phenylpent-4-enoic acid (1l): Prepared from benzaldehyde and cyclobutanone ethylene glycol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

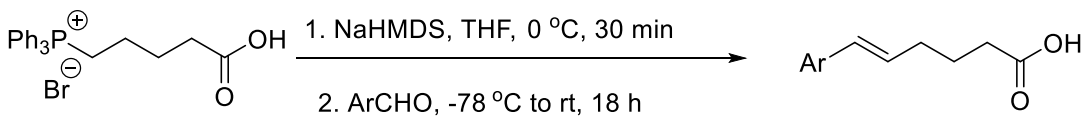
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.27 – 6.17 (m, 1H), 2.56 (d, *J* = 2.5 Hz, 4H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 137.4, 131.4, 128.7 (2C), 128.1, 127.4, 126.2 (2C), 33.9, 28.0.



(*E*)-7-phenylhept-6-enoic acid (1m): Prepared from benzaldehyde and cyclohexanone ethylene glycol ketal. The reaction yield was comparable to previously reported synthetic method and spectral data were in accordance with those previously reported.[1]

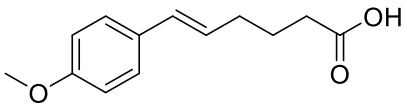
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.22 – 7.17 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.25 (qd, *J* = 7.2, 1.4 Hz, 2H), 1.71 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.59 – 1.50 (m, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 137.8, 130.4, 130.3, 128.6 (2C), 127.0, 126.1 (2C), 34,0 32.7, 28.8, 24.3.

1f and **1k** were synthesized by Wittig olefination according to the following procedure:



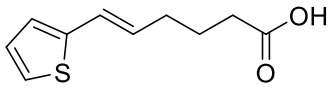
To an oven-dried round bottom flask equipped with a sir bar was added (4-carboxypropyl)triphenylphosphonium bromide (1.2 equiv). The flask was sealed by a septum,

evacuated, and backfilled with nitrogen for three times. Dry THF (20 mL) was added before the resulting suspension was cooled to 0 °C. Sodium bis(trimethylsilyl)amide 1 M solution in THF (2.4 equiv, 24 mL) was added dropwise. The mixture was stirred for 30 min until an orange suspension formed. The mixture was then cooled to -78 °C, and aromatic aldehyde (10 mmol) was added over 20 min. After addition was complete, the reaction was warmed up to room temperature and stirred for 18 h. The reaction was then quenched with HCl (1M) to pH = 2, extracted by Et_2O (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to dryness. The alkenoic acid was purified over silica gel eluting with hexanes/ethyl acetate/formic acid (4/1/0.04) to afford alkenoic acid.



(*E*)-6-(4-methoxyphenyl)hex-5-enoic acid (1f): Prepared according to the general procedure from 4-methoxylbenzaldehyde. Spectral data were in accordance with those previously reported.[2]

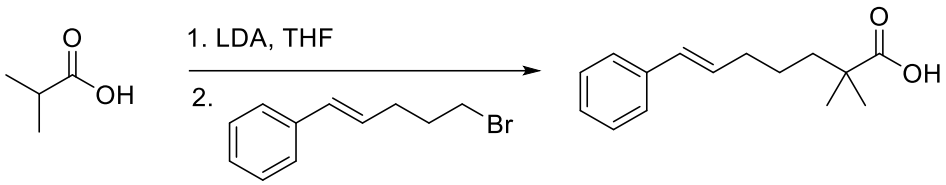
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 6.86 – 6.82 (m, 2H), 6.35 (d, J = 15.8 Hz, 1H), 6.03 (dt, J = 15.8, 7.0 Hz, 1H), 3.80 (s, 3H), 2.41 (t, J = 7.5 Hz, 2H), 2.26 (qd, J = 7.2, 1.5 Hz, 2H), 1.82 (p, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 158.9, 130.5, 130.5, 127.3, 127.2 (2C), 114.1 (2C), 55.4, 33.4, 32.4, 24.5.



(*E*)-6-(thiophen-2-yl)hex-5-enoic acid (1k): Prepared according to the general procedure from thiophene-2-carbaldehyde, yielding **1k** as an inseparable mixture of *E* and *Z* isomers (E/Z = 6/1). Spectral data were in accordance with those previously reported.[2] Due to the low intensity of signals of the minor Z isomer, only signals of the major E isomer were reported below.

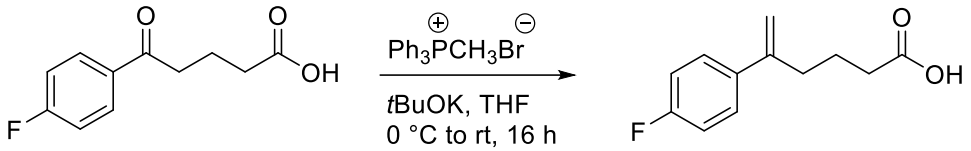
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 5.1 Hz, 1H), 6.93 (dd, J = 5.1, 3.5 Hz, 1H), 6.88 (d, J = 3.0 Hz, 1H), 6.54 (ddq, J = 15.7, 1.6, 0.8 Hz, 1H), 6.02 (dt, J = 15.6, 7.0 Hz, 1H), 2.41 (t, J = 7.5 Hz, 2H), 2.25 (qd, J = 7.2, 1.5 Hz, 2H), 1.82 (t, J = 7.4 Hz, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 142.8, 129.4, 127.4, 124.7, 124.4, 123.5, 33.4, 32.1, 24.3.

(*E*)-2,2-dimethyl-7-phenylhept-6-enoic acid (1n):



To an oven-dried round-bottom flask equipped with a stir bar was added isobutyric acid (5 mmol) and dry THF (10 mL) under nitrogen atmosphere. The resulting solution was cooled to 0 °C, added lithium diisopropylamide 2 M solution in THF (2.2 equiv, 5.5 mL) dropwise, then stirred for 30 minutes. The resulting mixture was cooled to -78 °C before adding (*E*)-(5-bromopent-1-en-1-yl)benzene[3] (1.1 equiv) dropwise. The reaction was then warmed up to room temperature and stirred overnight. The reaction was quenched by adding water (10 mL), acidified to pH 2 by HCl (1 M). Organic compounds were extracted to diethyl ether (3 × 10 mL), washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluting hexanes/ethyl acetate/formic acid (4/1/0.04) to afford the title compound (904 mg, 78% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 6.41 (dt, J = 15.8, 1.6 Hz, 1H), 6.23 (dt, J = 15.8, 6.8 Hz, 1H), 2.24 (qd, J = 7.1, 1.5 Hz, 2H), 1.69 – 1.59 (m, 2H), 1.55 – 1.45 (m, 2H), 1.24 (s, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 137.8, 130.4, 130.2, 128.5, 126.9, 126.0, 125.9, 42.1, 40.1, 33.4, 25.0, 24.7;
ESI-HRMS: calcd for $C_{15}H_{20}O_2Na^+$: m/z = 255.1356, found: m/z = 255.1349;
FTIR (neat): 3022, 2983, 2905, 1689, 1476 1447, 1404, 1284, 1205 cm^{-1}.



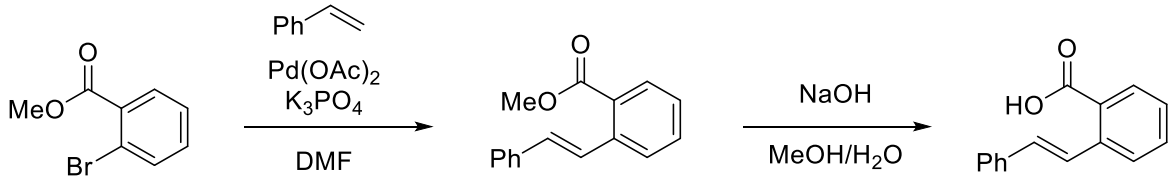
(*E*)-6-(4-fluorophenyl)hex-5-enoic acid (1p): To an oven-dried round bottom flask equipped with a stir bar was added methyltriphenylphosphosphonium bromide (1.3 equiv) and potassium *tert*-butoxide (2.6 equiv). The flask was sealed by a septum then evacuated and backfilled with nitrogen for three times. Dry THF (20 mL) was added by syringe at 0 °C, and the resulting yellow reaction mixture was and stirred for 30 min. 5-(4-fluorophenyl)-5-oxopentanoic acid (10 mmol, 2100 mg) in dry THF was added dropwise and the reaction mixture was stirred at 0 °C for 1 h and at room temperature for 16 h. The reaction was then quenched with HCl (1M) to pH = 2, extracted by Et_2O (3 × 20 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to dryness. The crude residue was purified by silica gel chromatography eluting hexanes/ethyl acetate/formic acid (4/1/0.04) to afford the title compound (686 mg, 33% yield) as a yellow solid. Spectral data were in accordance with those previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.30 – 7.22 (m, 2H), 5.51 (d, J = 1.3 Hz, 1H), 5.31 (d, J = 1.3 Hz, 1H), 2.83 – 2.76 (m, 2H), 2.63 (t, J = 7.4 Hz, 2H), 2.03 (p, J = 7.5 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 162.5 (d, $^1J_{C–F}$ = 247.3 Hz), 146.5, 136.9 (d, $^4J_{C–F}$ = 3.3 Hz), 127.8 (d, $^3J_{C–F}$ = 7.8 Hz, 2C), 115.3 (d, $^2J_{C–F}$ = 21.3 Hz, 2C), 113.2 (d, $^6J_{C–F}$ = 1.4 Hz), 34.7, 33.3, 23.1;

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1 (tt, J = 8.8, 5.4 Hz).

(*E*)-2-styrylbenzoic acid (1q):



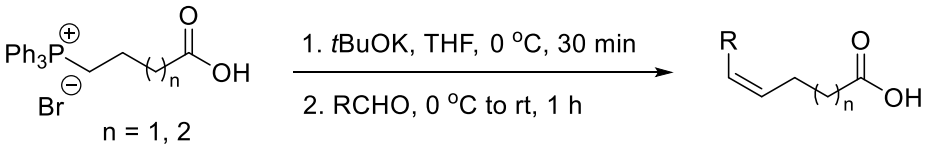
To a two-neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added methyl 2-bromobenzoate (5 mmol, 1.08 g), K_3PO_4 (1.5 equiv, 1.59 g), and $Pd(OAc)_2$

(5 mol%, 56 mg). The flask was sealed by a septum, vacuumed and backfilled with nitrogen for three times. DMF (0.5 M, 10 mL) and styrene (2 equiv, 1.15 mL) were added by syringes. The resulting mixture was vigorously stirred at 80 °C overnight. Upon the completion of the reaction was confirmed by TLC, the reaction mixture was cooled to room temperature and filtered through celite. The resulting filtrate was diluted by adding water (50 mL). Organic components were extracted to diethyl ether (3 × 20 mL), washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was used directly in the next step without further purification.

To a solution of the crude product obtained in the previous step in MeOH (10 mL) was added aqueous NaOH solution (5 M, 3 equiv, 3 mL). The resulting mixture was stirred at room temperature until the hydrolysis step was complete as confirming by TLC. After the reaction was complete, the reaction mixture was acidified to pH 2 by adding aqueous HCl (1 M). Organic components was extracted by ethyl acetate (3 × 20 mL), washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexanes/ethyl acetate/acid formic (4/1/0.04) as eluent to obtain the titled compound (1001 mg, 90% yield) as a white solid. Spectral data were in accordance with those previously reported.[5]

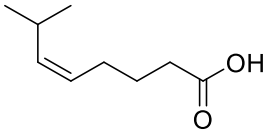
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.06 (m, 2H), 7.82 – 7.75 (m, 1H), 7.64 – 7.56 (m, 3H), 7.40 (td, *J* = 7.4, 1.1 Hz, 3H), 7.35 – 7.29 (m, 1H), 7.07 (d, *J* = 16.2 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 140.2, 137.4, 133.2, 131.9, 131.7, 128.7 (2C), 127.98, 127.6, 127.4, 127.30, 127.27, 127.0 (2C).

1r, **1s**, and **1t** were synthesized by Wittig olefination according to the following procedure:



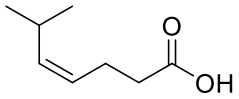
To an oven-dried round bottom flask equipped with a sir bar was added phosphonium salt (5 mmol) and dry THF (20 mL). The resulting suspension was cooled to 0 °C. Potassium *tert*-butoxide (2 equiv) was added in portion for 5 minutes. The mixture was warmed to room temperature and stirred for 30 min. The reaction was cooled again to 0 °C before adding aliphatic aldehyde (1.5 equiv) dropwise. After addition was complete, the reaction was warmed up to room temperature and stirred for 1 h. The reaction was then quenched with HCl (1M) to

pH = 2, extracted by Et_2O (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to dryness. The alkenoic acid was purified over silica gel eluting with hexanes/ethyl acetate/formic acid (9/1/0.05) to afford alkenoic acid.



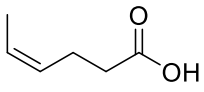
(*Z*)-7-methyloct-5-enoic acid (1r): Prepared according to the general procedure from (4-carboxybutyl)triphenylphosphonium bromide and isobutyraldehyde, yielding a mixture of *Z* (major) and *E* (minor) isomers. A fraction of pure *Z* isomer was characterized and used as a substrate for bromolactonization. Spectral data were in accordance with those previously reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 – 5.16 (m, 2H), 2.66 – 2.52 (m, 1H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.77 – 1.67 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 138.8, 125.8, 33.3, 26.5, 26.5, 24.7, 23.2.



(*Z*)-6-methylhept-4-enoic acid (1s): Prepared according to the general procedure from (3-carboxypropyl)triphenylphosphonium bromide and isobutyraldehyde, yielding a mixture of *Z* (major) and *E* (minor) isomers. A fraction of pure *Z* isomer was characterized and used as a substrate for bromolactonization. Spectral data were in accordance with those previously reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.19 (m, 2H), 2.70 – 2.57 (m, 1H), 2.47 – 2.36 (m, 4H), 0.97 (d, *J* = 6.6 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 139.4, 124.5, 34.3, 26.5, 23.1, 22.6.



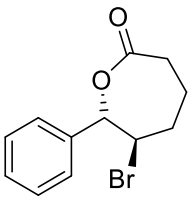
(*Z*)-hex-4-enoic acid (1t): Prepared according to the general procedure from (3-carboxypropyl)triphenylphosphonium bromide and acetaldehyde, yielding a mixture of *Z*

(major) and *E* (minor) isomers. A fraction with *E*/*Z* = 10/1 was characterized and used as a substrate for bromolactonization. Spectral data were in accordance with those previously reported.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 – 5.50 (m, 1.1 H), 5.50 – 5.45 (m, 0.1 H), 5.44 – 5.35 (m, 1H), 2.46 – 2.39 (m, 4.4H), 1.69 – 1.63 (m, 3.3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 127.9, 125.7, 34.0, 22.2, 12.7; (Signals of *Z* isomer)
^{13}C NMR (101 MHz, $CDCl_3$) 128.8, 126.5, 34.1, 27.5, 17.9. (Signals of *E* isomer)

General Procedure for the Regioselective *endo*-Bromolactonization (General Procedure A):

To a solution of unsaturated carboxylic acids (0.2 mmol) in HFIP or DCM/HFIP (0.1 M) in a screw-cap vial equipped with a stirrer bar was then added NBS (1.1 equiv, 39.2 mg). The reaction mixture was stirred at room temperature for 1 h. The solvent was then evaporated off and the residue was directly purified by flash column chromatography (silica gel, hexanes/ethyl acetate) to obtain the bromolactone product.



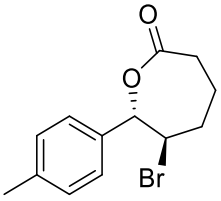
6-bromo-7-phenyloxepan-2-one (2a): Prepared according to the general procedure A from **1a** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided an inseparable mixture of **2a** and **3a** (53.6 mg, 86% yield, 12.5/1 ratio) as a white solid. Due to the low intensity of signals of the minor regioisomer, only signals of the major regioisomer were reported below.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 5.37 (d, J = 9.4 Hz, 1H), 4.43 (dt, J = 9.3, 4.6 Hz, 1H), 2.98 (dt, J = 14.7, 8.7 Hz, 1H), 2.79 (ddd, J = 14.7, 7.8, 4.0 Hz, 1H), 2.55 – 2.42 (m, 1H), 2.28 (dddd, J = 15.4, 6.5, 5.2, 3.6 Hz, 1H), 2.15 (dddt, J = 14.5, 10.7, 7.9, 3.8 Hz, 1H), 1.97 – 1.87 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 137.5, 129.3, 128.7 (2C), 127.5 (2C), 84.2, 53.9, 34.7, 32.5, 17.7;

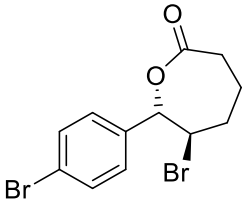
ESI-HRMS: calcd for $C_{12}H_{13}{}^{79}BrO_2Na^+$: m/z = 290.9991, found: m/z = 290.9995;

FTIR (neat): 3032, 2922, 2852, 2647, 2104, 1712, 1450, 1344, 1265, 1218 cm^{-1}.



6-bromo-7-(*p*-tolyl)oxepan-2-one (2b): Prepared according to the general procedure A from **1b** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2b** (38.9 mg, 69% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.19 (d, J = 7.7 Hz, 2H), 5.34 (d, J = 9.5 Hz, 1H), 4.43 (dt, J = 9.3, 4.5 Hz, 1H), 2.98 (dt, J = 14.4, 8.7 Hz, 1H), 2.78 (ddd, J = 14.7, 7.9, 4.0 Hz, 1H), 2.48 (ddt, J = 14.9, 10.8, 3.9 Hz, 1H), 2.37 (s, 3H), 2.27 (dddd, J = 15.3, 6.4, 5.0, 3.5 Hz, 1H), 2.20 – 2.08 (m, 1H), 1.96 – 1.85 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 139.2, 134.6, 129.4 (2C), 127.4 (2C), 84.1, 54.1, 34.7, 32.5, 21.4, 17.7;
ESI-HRMS: calcd for $C_{13}H_{15}{}^{79}BrO_2Na^+$: m/z = 305.0148, found: m/z = 305.0148;
FTIR (neat): 2922, 2644, 2322, 1717, 1517, 1441, 1350, 1264 cm^{-1}.



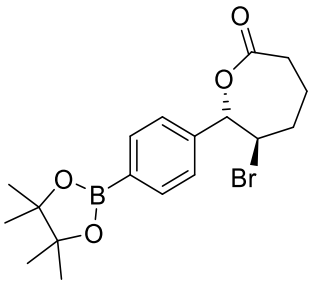
6-bromo-7-(4-bromophenyl)oxepan-2-one (2c): Prepared according to the general procedure A from **1c** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2c** (62.5 mg, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.34 – 7.29 (m, 2H), 5.32 (d, J = 9.5 Hz, 1H), 4.33 (dt, J = 9.5, 4.7 Hz, 1H), 2.95 (dt, J = 14.7, 8.7 Hz, 1H), 2.79 (ddd, J = 14.8, 7.7, 4.0 Hz, 1H), 2.48 (ddt, J = 14.6, 10.4, 3.9 Hz, 1H), 2.27 (dddd, J = 15.5, 6.6, 5.3, 3.5 Hz, 1H), 2.14 (tdd, J = 14.4, 7.8, 3.8 Hz, 1H), 1.97 – 1.85 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 136.6, 131.8 (2C), 129.2 (2C), 123.3, 83.4, 53.6, 34.9, 32.5, 17.8;

ESI-HRMS: calcd for $C_{12}H_{12}{}^{79}Br_2O_2Na^+$: m/z = 368.9096, found: m/z = 368.9098;

FTIR (neat): 3054, 2947, 1912, 1719, 1593, 1487, 1328, 1260, 1226 cm^{-1}.



6-bromo-7-(4-(4,4,5,5 tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)oxepan-2-one (2d): Prepared according to the general procedure A from **1d** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2d** (67 mg, 85% yield) as a white solid.

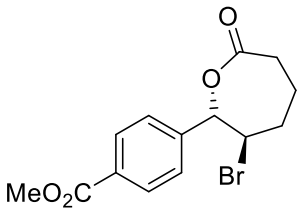
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.47 – 7.41 (m, 2H), 5.37 (d, J = 9.4 Hz, 1H), 4.41 (dt, J = 9.3, 4.6 Hz, 1H), 2.97 (dt, J = 14.7, 8.6 Hz, 1H), 2.78 (ddd, J = 14.7, 7.8, 4.0 Hz, 1H), 2.48 (ddt, J = 14.8, 10.7, 3.9 Hz, 1H), 2.27 (dddd, J = 15.3, 6.5, 5.1, 3.5 Hz, 1H), 2.15 (tdd, J = 14.7, 7.9, 3.8 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.34 (s, 12H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 135.1 (2C), 126.8 (2C), 84.1 (2C), 53.7, 34.7, 32.5, 25.0 (4C), 17.7;

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6;

ESI-HRMS: calcd for $C_{18}H_{24}B^{79}BrO_4Na^+$: m/z = 417.08465, found: m/z = 417.08416;

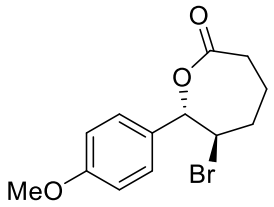
FTIR (neat): 2974, 1728, 1611, 1515, 1442, 1356, 1267, 1215 cm^{-1}.



Methyl 4-(3-bromo-7-oxooxepan-2-yl)benzoate (2e): Prepared according to the general procedure A from **1e** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room

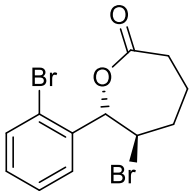
temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2e** (33.3 mg, 51% yield) as a pale-pink solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.55 – 7.50 (m, 2H), 5.41 (d, *J* = 9.5 Hz, 1H), 4.39 – 4.33 (m, 1H), 3.92 (s, 3H), 2.97 (dt, *J* = 14.8, 8.4 Hz, 1H), 2.81 (ddd, *J* = 14.8, 7.5, 4.1 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.28 (dddd, *J* = 15.6, 6.9, 5.5, 3.6 Hz, 1H), 2.15 (tdd, *J* = 14.3, 7.9, 3.8 Hz, 1H), 1.92 (dddd, *J* = 16.4, 14.5, 7.3, 3.7 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.6, 142.3, 131.0, 130.0 (2C), 127.6 (2C), 83.5, 53.3, 52.4, 35.1, 32.5, 18.0;
ESI-HRMS: calcd for $C_{14}H_{15}{}^{79}BrO_4Na^+$: m/z = 349.0046, found: m/z = 349.0047;
FTIR (neat): 2952, 2916, 2084, 1710, 1612, 1437, 1346, 1279, 1226 cm^{-1}.



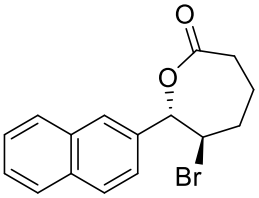
6-bromo-7-(4-methoxyphenyl)oxepan-2-one (2f): Prepared according to the general procedure A from **1f** using NBS (1.1 equiv, 39.2 mg) and HFIP/DCM (1/4, 0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2f** as a mixture of diastereomers (47.1 mg, 79% yield, 17/1 ratio) as a white solid. Due to the low intensity of signals of the minor diastereomer, only signals of the major diastereomer were reported below.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 6.93 – 6.88 (m, 2H), 5.32 (d, *J* = 9.5 Hz, 1H), 4.42 (dt, *J* = 9.3, 4.5 Hz, 1H), 3.82 (s, 3H), 2.97 (dt, *J* = 14.7, 8.7 Hz, 1H), 2.78 (ddd, *J* = 14.8, 8.0, 4.0 Hz, 1H), 2.47 (ddt, *J* = 14.9, 10.7, 3.9 Hz, 1H), 2.27 (dddd, *J* = 15.4, 6.5, 5.0, 3.5 Hz, 1H), 2.14 (tdd, *J* = 14.5, 8.0, 3.7 Hz, 1H), 1.96 – 1.85 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 160.2, 129.7, 128.8 (2C), 114.0 (2C), 83.9, 55.4, 54.4, 34.7, 32.5, 17.6;
ESI-HRMS: calcd for $C_{13}H_{15}{}^{79}BrO_3Na^+$: m/z = 321.0097, found: m/z = 321.0098;
FTIR (neat): 2940, 2650, 1894, 1716, 1611, 1511, 1440, 1303, 1247 cm^{-1}.



6-bromo-7-(2-bromophenyl)oxepan-2-one (2g): Prepared according to the general procedure A from **1g** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2g** (54.8 mg, 79% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 5.94 (d, *J* = 9.8 Hz, 1H), 4.51 (ddd, *J* = 10.2, 6.4, 4.2 Hz, 1H), 3.03 (ddd, *J* = 15.0, 9.2, 7.4 Hz, 1H), 2.83 (ddd, *J* = 15.0, 6.8, 4.6 Hz, 1H), 2.57 (ddt, *J* = 15.2, 9.4, 3.8 Hz, 1H), 2.34 (dddd, *J* = 15.0, 8.2, 6.4, 3.5 Hz, 1H), 2.21 – 2.10 (m, 1H), 1.92 (ddddd, *J* = 14.9, 9.9, 8.2, 6.8, 3.4 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 136.9, 133.0, 130.7, 128.7, 128.2, 124.8, 81.7, 51.5, 36.2, 32.7, 18.8;
ESI-HRMS: calcd for $C_{12}H_{12}{}^{79}Br_2O_2Na^+$: m/z = 368.9096, found: m/z = 368.9099;
FTIR (neat): 3439, 3053, 2922, 2115, 1929, 1723, 1590, 1463, 1438, 1346, 1257, 1209 cm^{-1}.



6-bromo-7-(naphthalen-2-yl)oxepan-2-one (2h): Prepared according to the general procedure A from **1h** using NBS (1.1 equiv, 39.2 mg) and HFIP/DCM (1/4, 0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2h** (50.9 mg, 80% yield) as a pale-yellow solid.

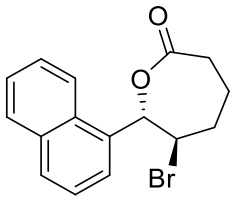
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 4H), 7.58 – 7.48 (m, 3H), 5.54 (d, *J* = 9.4 Hz, 1H), 4.53 (dt, *J* = 9.4, 4.6 Hz, 1H), 3.03 (dt, *J* = 14.4, 8.6 Hz, 1H), 2.82 (ddd, *J* = 14.7, 7.7, 4.0

Hz, 1H), 2.59 – 2.49 (m, 1H), 2.31 (dddd, *J* = 15.4, 6.6, 5.2, 3.6 Hz, 1H), 2.24 – 2.13 (m, 1H), 2.00 – 1.89 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 134.8, 133.7, 133.0, 128.7, 128.4, 127.9, 127.4, 126.8, 126.6, 124.4, 84.4, 53.8, 34.9, 32.6, 17.9;

ESI-HRMS: calcd for $C_{16}H_{15}{}^{79}BrO_2Na^+$: m/z = 341.0148, found: m/z = 341.0148;

FTIR (neat): 3053, 2944, 2322, 1723, 1509, 1443, 1344, 1257 cm^{-1}.



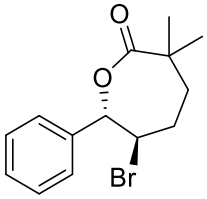
6-bromo-7-(naphthalen-1-yl)oxepan-2-one (2i): Prepared according to the general procedure A from **1i** using NBS (1.1 equiv, 39.2 mg) and HFIP/DCM (1/4, 0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2i** (50.9 mg, 80% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.62 – 7.46 (m, 4H), 6.02 (d, *J* = 9.5 Hz, 1H), 4.85 (dt, *J* = 9.2, 4.4 Hz, 1H), 3.15 (dt, *J* = 14.7, 8.7 Hz, 1H), 2.88 (ddd, *J* = 14.7, 8.1, 3.4 Hz, 1H), 2.62 (ddt, *J* = 14.9, 10.9, 3.9 Hz, 1H), 2.37 (dddd, *J* = 15.2, 6.1, 5.0, 3.6 Hz, 1H), 2.26 (dddt, *J* = 14.5, 10.8, 8.8, 3.6 Hz, 1H), 2.08 – 1.97 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 134.2, 132.8, 130.8, 130.3, 129.3, 127.2, 126.8, 126.0, 125.1, 123.9, 83.0, 53.3, 34.4, 32.3, 17.7;

ESI-HRMS: calcd for $C_{16}H_{15}{}^{79}BrO_2Na^+$: m/z = 341.01476, found: m/z = 341.01477;

FTIR (neat): 3041, 2937, 2875, 2050, 1717, 1596, 1510, 1461, 1344, 1265, 1203 cm^{-1}.



6-bromo-3,3-dimethyl-7-phenyloxepan-2-one (2j): Prepared according to the general procedure A from **1j** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room

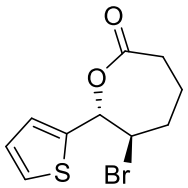
temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2j** (45 mg, 76% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.42 – 7.35 (m, 3H), 5.42 (d, *J* = 10.2 Hz, 1H), 4.35 (ddd, *J* = 10.3, 6.0, 4.5 Hz, 1H), 2.42 (dddd, *J* = 16.0, 9.8, 4.5, 1.7 Hz, 1H), 2.33 – 2.24 (m, 1H), 1.94 (ddd, *J* = 14.9, 9.8, 1.7 Hz, 1H), 1.84 (ddd, *J* = 14.9, 9.0, 1.8 Hz, 1H), 1.41 (s, 3H), 1.38 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 137.2, 129.3, 128.6 (2C), 127.8 (2C), 83.3, 54.4, 44.5, 35.2, 33.8, 29.6, 26.0;

ESI-HRMS: calcd for $C_{14}H_{17}{}^{79}BrO_2Na^+$: m/z = 319.0304, found: m/z = 319.0308;

FTIR (neat): 3036, 2970, 2931, 1716, 1458, 1390, 1293, 1249 cm^{-1}.



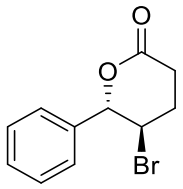
6-bromo-7-(thiophen-2-yl)oxepan-2-one (2k): Prepared according to the general procedure A from **1k** using NBS (1.1 equiv, 39.2 mg) and HFIP/DCM (1/99, 0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2k** as a mixture of diastereomers (11.5 mg, 21% yield, 17/1 ratio) as a colourless liquid. Due to the low intensity of signals of the minor diastereomer, only signals of the major diastereomer were reported below.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.18 (ddd, *J* = 3.5, 1.2, 0.6 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.69 (d, *J* = 9.2 Hz, 1H), 4.55 – 4.49 (m, 1H), 2.96 (dt, *J* = 14.2, 8.7 Hz, 1H), 2.77 (ddd, *J* = 14.8, 8.3, 4.0 Hz, 1H), 2.45 (ddt, *J* = 15.5, 11.5, 3.9 Hz, 1H), 2.27 (dddd, *J* = 15.6, 5.8, 4.4, 3.5 Hz, 1H), 2.14 (dddd, *J* = 15.1, 8.8, 7.4, 3.7 Hz, 1H), 1.96 – 1.85 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 139.8, 127.2, 126.7, 126.5, 79.8, 54.2, 33.9, 32.4, 17.1;

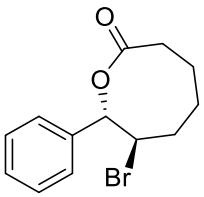
ESI-HRMS: calcd for $C_{10}H_{11}{}^{79}BrO_2SNa^+$: m/z = 296.9555, found: m/z = 296.9558;

FTIR (neat): 3434, 3140, 2923, 1717, 1440, 1350, 1262 cm^{-1}.



5-bromo-6-phenyltetrahydro-2*H*-pyran-2-one (2l): Prepared according to the general procedure A from **1l** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2l** (39.1 mg, 77% yield) as a white solid. Spectral data were in accordance with those previously reported.[9]

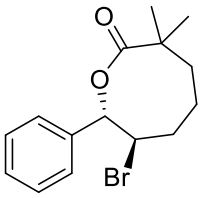
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 5.56 (d, J = 6.3 Hz, 1H), 4.39 (td, J = 6.6, 4.3 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.76 – 2.67 (m, 1H), 2.42 (dddd, J = 14.8, 8.5, 6.5, 4.3 Hz, 1H), 2.32 – 2.22 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 137.4, 129.2, 129.0 (2C), 126.5 (2C), 85.8, 47.3, 28.5, 27.8.



7-bromo-8-phenyloxocan-2-one (2m): Prepared according to the general procedure A from **1m** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2m** (16.3 mg, 23% yield) as a white solid.

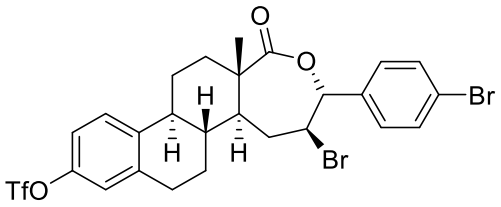
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.9, 1.7 Hz, 2H), 7.41 – 7.36 (m, 3H), 5.78 (d, J = 10.5 Hz, 1H), 4.30 (ddd, J = 10.8, 8.4, 2.7 Hz, 1H), 2.57 – 2.39 (m, 3H), 2.10 – 1.90 (m, 4H), 1.86 – 1.79 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 137.2, 129.2, 128.6 (2C), 128.0 (2C), 82.7, 56.4, 36.0, 33.8, 29.0, 25.5;
ESI-HRMS: calcd for $C_{13}H_{15}{}^{79}BrO_2Na^+$: m/z = 305.0148, found: m/z = 305.0148;

FTIR (neat): 3034, 2930, 2858, 1893, 1705, 1452, 1349, 1267 cm^{-1}.



7-bromo-3,3-dimethyl-8-phenyloxocan-2-one (2n): Prepared according to the general procedure A from **1n** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2n** (18.0 mg, 29% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.42 – 7.33 (m, 3H), 6.04 (d, J = 10.2 Hz, 1H), 4.13 (ddd, J = 11.4, 10.3, 2.4 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.04 – 1.93 (m, 1H), 1.86 – 1.74 (m, 3H), 1.66 (ddd, J = 14.1, 11.5, 2.3 Hz, 1H), 1.23 (d, J = 17.0 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 137.5, 129.0, 128.6 (2C), 128.0 (2C), 82.3, 56.6, 46.4, 41.7, 37.9, 25.6, 25.0, 22.4;
ESI-HRMS: calcd for $C_{15}H_{19}{}^{79}BrO_2H^+$: m/z = 311.0641, found: m/z = 311.0643;
FTIR (neat): 2966, 2923, 2669, 2083, 1721, 1605, 1452, 1391. 1345, 1303, 1210 cm^{-1}.



(5a*S*,5b*R*,11b*S*,13a*S*)-4-bromo-3-(4-bromophenyl)-13a-methyl-1-oxo 1,3,4,5,5a,5b,6,7,11b,12,13,13a-dodecahydrophenanthro[2,1-*c*]oxepin-9-yl trifluoromethanesulfonate (2o): Prepared according to the general procedure A from **1o** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2o** as a mixture of diastereomers (116.9 mg, 88% yield, 1/1 ratio) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.33 (ddd, J = 15.3, 8.6, 6.0 Hz, 3H), 7.07 (dd, J = 8.6, 2.8 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 5.43 (d, J = 8.8 Hz, 0.5H), 5.29 (d, J = 10.3 Hz, 0.5H), 4.46 (dt, J = 8.8, 5.2 Hz, 0.5H), 4.22 (ddd, J = 12.0, 10.3, 3.6 Hz, 0.5H), 3.03 – 2.79

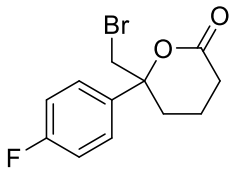
(m, 2.5H), 2.56 – 2.34 (m, 3H), 2.30 – 1.91 (m, 4.5H), 1.66 – 1.40 (m, 3H, overlapping with H_2O signal), 1.38 (s, 1.5H), 1.36 (s, 1.5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 179.7, 147.9, 147.9, 140.4, 140.3, 139.34, 139.29, 138.0, 137.9, 131.8, 131.7, 129.2, 128.7, 127.1, 127.0, 123.0, 121.1, 121.0, 118.9 (q, $^1J_{C–F}$ = 321.9 Hz), 118.7, 118.6, 85.4, 83.3, 77.4, 54.1, 53.3, 47.9, 47.4, 47.0, 43.19, 43.15, 41.8, 39.1, 39.0, 38.5, 36.6, 36.4, 35.3, 29.7, 29.6, 27.1, 26.6, 25.3, 25.0, 17.8, 16.3;

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.9 (d, J = 2.6 Hz);

ESI-HRMS: calcd for $C_{26}H_{25}{}^{79}Br_2F_3O_5SH^+$: m/z = 664.9814, found: m/z = 664.9809;

FTIR (neat): 2932, 1721, 1593, 1489, 1416, 1205 cm^{-1}.

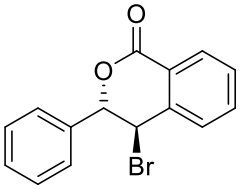


6-(bromomethyl)-6-(4-fluorophenyl)tetrahydro-2*H*-pyran-2-one (3p): Prepared according to the general procedure A from **1p** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3p** (38.9 mg, 95% yield) as a pale-pink solid. Spectral data were in accordance with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.13 – 7.06 (m, 2H), 3.65 (d, J = 11.1 Hz, 1H), 3.60 (d, J = 11.1 Hz, 1H), 2.56 – 2.31 (m, 4H), 1.90 – 1.81 (m, 1H), 1.59 (tddd, J = 11.9, 10.0, 7.2, 4.7 Hz, 1H);

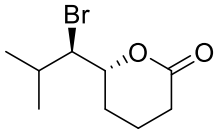
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 162.7 (d, $^1J_{C–F}$ = 249.7 Hz), 136.2 (d, $^4J_{C–F}$ = 3.2 Hz, 2C), 127.5 (d, $^3J_{C–F}$ = 8.3 Hz, 2C), 116.1 (d, $^2J_{C–F}$ = 21.7 Hz), 84.9, 41.5 (d, J = 1.41 Hz), 30.2, 29.2, 16.4;

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (tt, J = 8.2, 5.1 Hz).



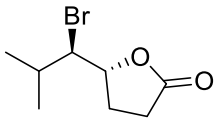
4-bromo-3-phenylisochroman-1-one (2q): Prepared according to the general procedure A from **1q** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (10/1) provided **2q** (46.1 mg, 76% yield) as a pale-yellow solid. Spectral data were in accordance with those previously reported.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.8, 1.4 Hz, 1H), 7.60 (td, J = 7.6, 1.4 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.34 – 7.30 (m, 3H), 7.30 – 7.26 (m, 2H), 5.91 (d, J = 4.6 Hz, 1H), 5.56 (d, J = 4.6 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 137.9, 136.5, 134.8, 130.6, 130.0, 129.1, 129.0 (2C), 128.5, 126.6 (2C), 124.3, 84.3, 46.3.



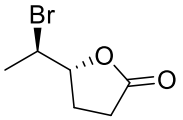
6-(1-bromo-2-methylpropyl)tetrahydro-2*H*-pyran-2-one (3r): Prepared according to the general procedure A from **1r** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (4/1) provided **3r** (44.5 mg, 95% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (ddd, J = 9.2, 4.8, 3.3 Hz, 1H), 3.79 (dd, J = 6.8, 3.4 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.53 – 2.42 (m, 1H), 2.18 (dq, J = 13.3, 6.7 Hz, 1H), 2.02 – 1.82 (m, 4H), 1.09 (dd, J = 11.0, 6.6 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 80.1, 66.0, 32.3, 29.8, 27.3, 21.3, 21.0, 18.6;
ESI-HRMS: calcd for $C_9H_{15}{}^{79}BrO_2Na^+$: m/z = 257.0148, found: m/z = 257.0148;
FTIR (neat): 2963, 2876, 2247. 1732, 1461, 1367, 1343, 1235 cm^{-1}.



5-(1-bromo-2-methylpropyl)dihydrofuran-2(3*H*)-one (3s): Prepared according to the general procedure A from **1s** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (4/1) provided **3s** (41.1 mg, 93% yield) as a colorless oil. Spectral data were in accordance with those previously reported.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (ddd, J = 7.7, 6.6, 3.5 Hz, 1H), 3.86 (dd, J = 6.1, 3.5 Hz, 1H), 2.71 (ddd, J = 17.9, 10.5, 5.1 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.37 (dddd, J = 12.9, 10.4, 7.7, 5.1 Hz, 1H), 2.21 – 2.06 (m, 2H), 1.09 (dd, J = 6.7, 1.2 Hz, 6H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 80.0, 67.0, 33.0, 28.4, 26.8, 21.3, 20.4.

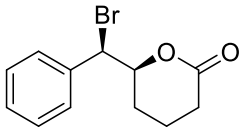


1-(bromoethyl)dihydrofuran-2(3*H*)-one (3t): Prepared according to the general procedure A from **1t** using NBS (1.1 equiv, 39.2 mg) and HFIP (0.1 M, 2 mL) at room temperature for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (3/1) provided **3t** (33.6 mg, 87% yield) as a colorless oil. Spectral data were in accordance with those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (ddd, J = 7.8, 6.5, 3.7 Hz, 1H), 4.22 (qd, J = 6.9, 3.7 Hz, 1H), 2.71 (ddd, J = 18.0, 10.4, 5.5 Hz, 1H), 2.58 (ddd, J = 18.0, 10.4, 7.9 Hz, 1H), 2.41 (dddd, J = 13.3, 10.4, 7.8, 5.4 Hz, 1H), 2.18 (dddd, J = 13.2, 10.5, 7.8, 6.4 Hz, 1H), 1.77 (d, J = 6.8 Hz, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 81.8, 50.2, 28.4, 25.0, 21.2.

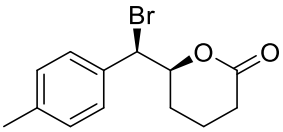
General Procedure for the Regioselective *exo*-Bromolactonization (General Procedure B):

To a solution of unsaturated carboxylic acid (0.2 mmol) in HFIP or DCM/HFIP (0.1 M) in a screw-cap vial equipped with a stirrer bar was added NBS (1.1 equiv, 39.2 mg). After stirring the resulting at room temperature for 2 minutes or 1 h, catalytic amount of *p*TSA or triflic acid was then added. The reaction mixture was stirred at room temperature for 1 h. The solvent was then evaporated off and the residue was directly purified by flash column chromatography (silica gel, hexanes/ethyl acetate) to obtain the product.



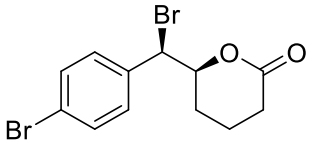
6-(bromo(phenyl)methyl)tetrahydro-2*H*-pyran-2-one (3a): Prepared according to the general procedure B from **1a** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL). After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3a** (45 mg, 84% yield) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 5.06 (d, *J* = 5.8 Hz, 1H), 4.64 (ddd, *J* = 10.5, 5.8, 3.4 Hz, 1H), 2.60 (dddd, *J* = 17.9, 6.5, 4.5, 1.3 Hz, 1H), 2.43 (ddd, *J* = 17.8, 9.7, 7.0 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.00 – 1.91 (m, 1H), 1.88 – 1.70 (m, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 137.2, 129.0, 128.8 (2C), 128.8 (2C), 82.4, 55.9, 29.6, 25.5, 18.3;
ESI-HRMS: calcd for $C_{12}H_{13}{}^{79}BrO_2H^+$: m/z = 269.0172, found: m/z = 269.0171;
FTIR (neat): 3033, 2961, 2110, 1713, 1497, 1452, 1233 cm^{-1}.



6-(bromo(*p*-tolyl)methyl)tetrahydro-2*H*-pyran-2-one (3b): Prepared according to the general procedure B from **1b** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL). After 1 h, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3b** (27.6 mg, 49% yield) as a yellow liquid.

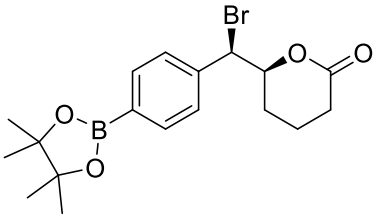
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.17 – 7.13 (m, 2H), 5.03 (d, *J* = 5.7 Hz, 1H), 4.63 (ddd, *J* = 10.5, 5.8, 3.4 Hz, 1H), 2.60 (dddd, *J* = 17.9, 6.5, 4.5, 1.3 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.34 (s, 3H), 2.25 – 2.18 (m, 1H), 1.99 – 1.90 (m, 1H), 1.88 – 1.70 (m, 2H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.0, 134.3, 129.5 (2C), 128.6 (2C), 82.5, 55.9, 29.6, 25.5, 21.3, 18.3;
ESI-HRMS: calcd for $C_{13}H_{15}{}^{79}BrO_2H^+$: m/z = 283.0328, found: m/z = 283.0328;
FTIR (neat): 3167, 3022, 2958, 2629, 2113, 1735, 1672, 1510, 1456, 1410, 1338, 1284, 1243 cm^{-1}.



6-(Bromo(4-bromophenyl)methyl)tetrahydro-2*H*-pyran-2-one (3c): Prepared according to the general procedure B from **1c** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3c** (61.6 mg, 89% yield) as a pale-yellow liquid. Spectral data were in accordance with those previously reported.[14]

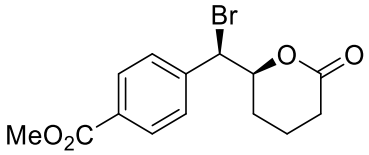
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.33 – 7.29 (m, 2H), 4.95 (d, *J* = 6.2 Hz, 1H), 4.63 (ddd, *J* = 10.9, 6.2, 3.4 Hz, 1H), 2.60 (dddd, *J* = 17.9, 6.6, 4.5, 1.3 Hz, 1H), 2.43 (ddd, *J* = 17.8, 9.8, 7.1 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.00 – 1.93 (m, 1H), 1.89 – 1.80 (m, 1H), 1.67 (dtd, *J* = 13.8, 11.2, 5.2 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 136.4, 132.0 (2C), 130.4 (2C), 123.1, 82.1, 54.4, 29.5, 25.8, 18.3.



6-(bromo(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)tetrahydro-2*H*-pyran-2-one (3d): Prepared according to the general procedure B from **1d** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3d** (67.8 mg, 86% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.45 – 7.40 (m, 2H), 5.05 (d, *J* = 5.7 Hz, 1H), 4.63 (ddd, *J* = 10.5, 5.7, 3.4 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.44 – 2.38 (m, 1H), 2.21 – 2.13 (m, 1H), 1.94 (ddt, *J* = 13.2, 7.0, 4.4 Hz, 1H), 1.84 – 1.69 (m, 2H), 1.33 (s, 11H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 128.0, 84.1 (2C), 82.3 (2C), 55.7, 29.6, 25.4, 25.0 (4C), 18.3;
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8;
ESI-HRMS: calcd for $C_{18}H_{24}B^{79}BrO_4H^+$: m/z = 395.1024, found: m/z = 395.1026;
FTIR (neat): 2975, 1727, 1612, 1518, 1448, 1357, 1251 cm^{-1}.



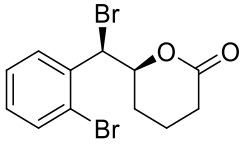
Methyl 4-(bromo(6-oxotetrahydro-2*H*-pyran-2-yl)methyl)benzoate (3e): Prepared according to the general procedure B from **1e** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3e** (58.2 mg, 85% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.55 – 7.47 (m, 2H), 5.03 (d, *J* = 6.3 Hz, 1H), 4.67 (ddd, *J* = 10.8, 6.3, 3.4 Hz, 1H), 3.91 (s, 3H), 2.65 – 2.55 (m, 1H), 2.42 (ddd, *J* = 17.9, 9.7, 7.0 Hz, 1H), 2.29 – 2.21 (m, 1H), 1.96 (ddq, *J* = 13.6, 6.9, 4.8 Hz, 1H), 1.91 – 1.77 (m, 1H), 1.69 (dtd, *J* = 13.9, 11.1, 5.2 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 166.5, 142.1, 130.7, 130.1 (2C), 128.8 (2C), 82.0, 54.5, 52.4, 29.5, 25.7, 18.3;

ESI-HRMS: calcd for $C_{14}H_{15}{}^{79}BrO_4Na^+$: m/z = 349.0046, found: m/z = 349.0040;

FTIR (neat): 3415, 2950, 2077, 1935, 1711, 1609, 1435, 1360, 1276, 1234 cm^{-1}.



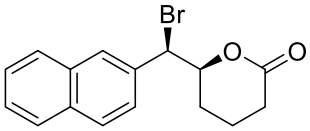
6-(bromo(2-bromophenyl)methyl)tetrahydro-2*H*-pyran-2-one (3g): Prepared according to the general procedure B from **1g** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) added and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3g** (51.9 mg, 75% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 5.64 (d, *J* = 5.7 Hz, 1H), 4.73 (ddd, *J* = 10.4, 5.7, 3.4 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.49 – 2.41 (m, 1H), 2.22 – 2.15 (m, 1H), 1.96 (dtd, *J* = 8.9, 4.4, 2.6 Hz, 1H), 1.88 – 1.71 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 136.3, 133.1, 131.5, 130.3, 128.2, 123.8, 81.2, 53.4, 29.6, 25.2, 18.3;

ESI-HRMS: calcd for $C_{12}H_{12}{}^{79}Br_2O_2H^+$: m/z = 346.9277, found: m/z = 346.9274;

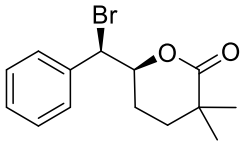
FTIR (neat): 3060, 2957, 2251, 1733, 1439, 1360, 1231 cm^{-1}.



6-(bromo(naphthalen-2-yl)methyl)tetrahydro-2*H*-pyran-2-one (3h): Prepared according to the general procedure B from **1h** using NBS (1.1 equiv, 39.2 mg) in HFIP/DCM (1/4, 0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added triflic acid (10 mol%, 3 mg)

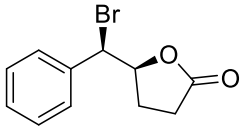
and further stirred for 1 h. Due to the product **3h** degraded after silica gel column chromatography, only NMR yield of 76% was reported.

ESI-HRMS: calcd for $C_{16}H_{15}{}^{79}BrO_2Na^+$: m/z = 341.0148, found: m/z = 341.0148 (result of crude reaction mixture);



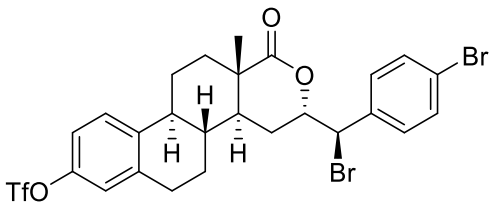
6-(bromo(phenyl)methyl)-3,3-dimethyltetrahydro-2*H*-pyran-2-one (3j): Prepared according to the general procedure B from **1j** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3j** (45 mg, 76% yield) as a pale-yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.38 – 7.30 (m, 3H), 5.10 (d, *J* = 5.1 Hz, 1H), 4.60 (dt, *J* = 10.1, 5.1 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.75 – 1.68 (m, 2H), 1.28 (s, 3H), 1.23 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 128.9, 128.8 (4C), 83.1, 56.6, 33.8, 27.8, 27.3, 22.9;
ESI-HRMS: calcd for $C_{14}H_{17}{}^{79}BrO_2Na^+$: m/z = 319.0304, found: m/z = 319.0305;
FTIR (neat): 3313, 2962, 2924, 2102, 1722, 1681, 1471, 1453, 1385, 1287 cm^{-1}.



5-(bromo(phenyl)methyl)dihydrofuran-2(3*H*)-one (3l): Prepared according to the general procedure B from **1l** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3l** (34.5 mg, 68% yield) as a white solid. Spectral data were in accordance with those previously reported.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 5.01 (d, J = 6.9 Hz, 1H), 4.95 – 4.89 (m, 1H), 2.57 – 2.49 (m, 3H), 2.33 – 2.23 (m, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 137.2, 129.2, 129.0 (2C), 128.4 (2C), 81.8, 55.6, 28.7, 26.5.

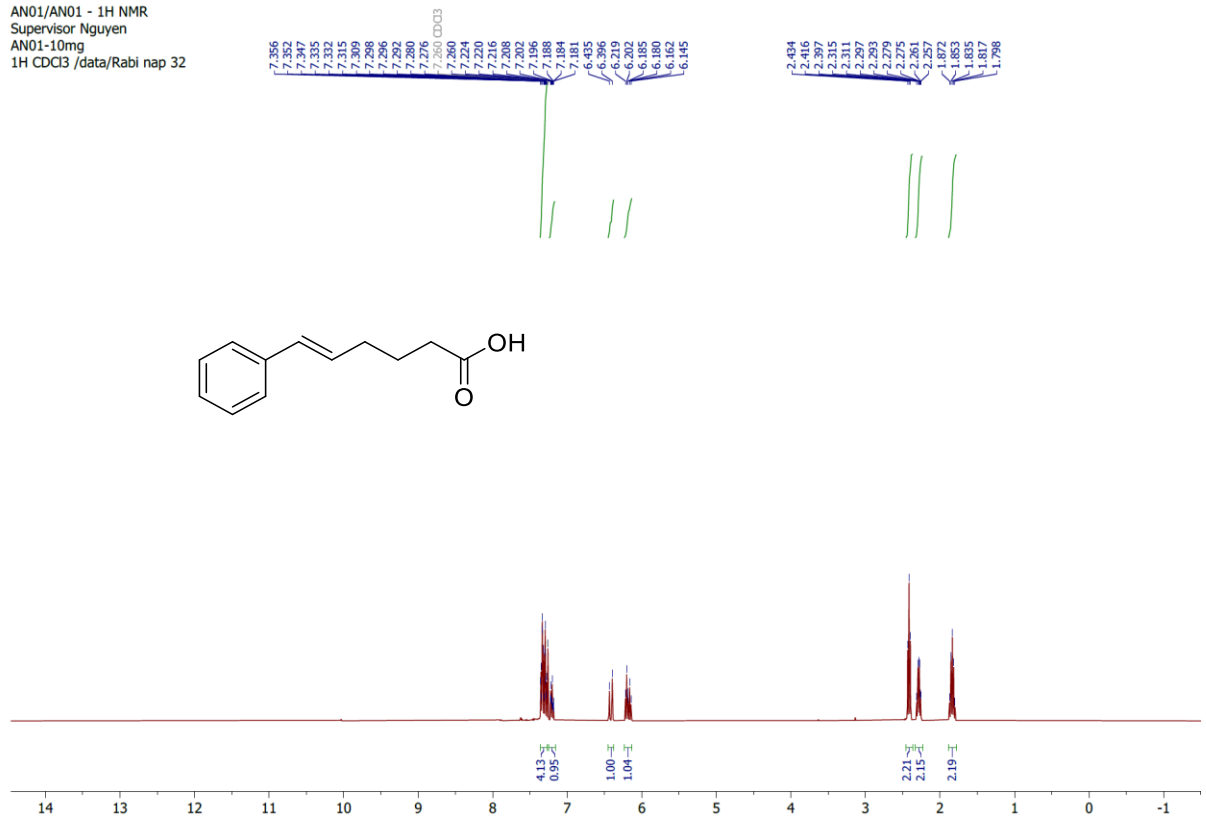


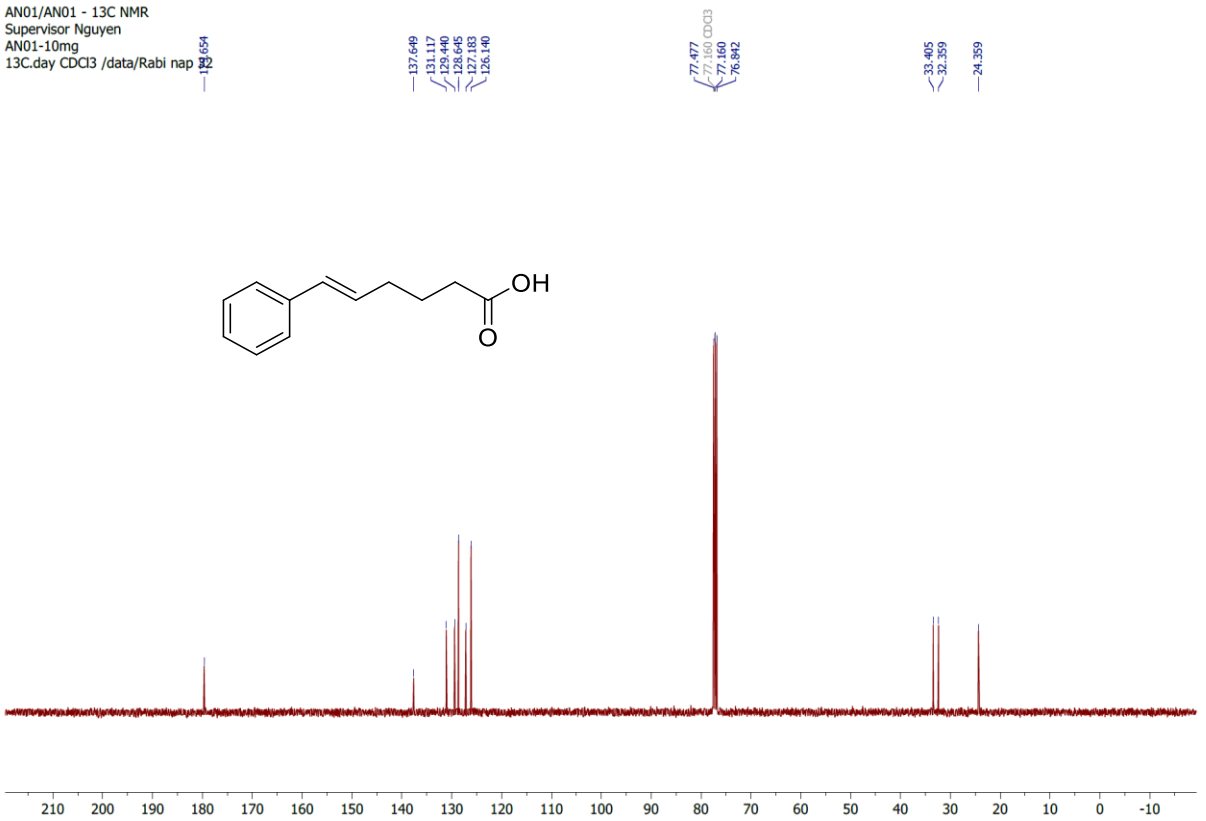
(4a*S*,4b*R*,10b*S*,12a*S*)-3-(bromo(4-bromophenyl)methyl)-12a-methyl-1-oxo-3,4,4a,4b,5,6,10b,11,12,12a-decahydro-1*H*-naphtho[2,1-*f*]isochromen-8-yl trifluoromethanesulfonate (3o): Prepared according to the general procedure B from **1o** using NBS (1.1 equiv, 39.2 mg) in HFIP (0.1 M, 2 mL) at room temperature. After 2 minutes, the reaction was added *p*TSA (5 mol%, 1.7 mg) and further stirred for 1 h. Purification by flash column chromatography eluting with hexanes/ethyl acetate (5/1) provided **3o** as a mixture of diastereomers (34.5 mg, 91% yield, 1/1 ratio) as a white solid. Spectral data were in accordance with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.38 – 7.30 (m, 3H), 7.04 (dd, J = 8.7, 2.7 Hz, 1H), 6.99 (dd, J = 2.7, 1.5 Hz, 1H), 5.09 (d, J = 4.7 Hz, 0.5H), 5.03 (d, J = 6.2 Hz, 0.5H), 4.89 (dt, J = 8.4, 5.9 Hz, 0.5H), 4.61 (dt, J = 10.9, 4.7 Hz, 0.5H), 2.98 – 2.83 (m, 2H), 2.44 – 2.26 (m, 3H), 2.26 – 2.10 (m, 1H), 2.10 – 1.93 (m, 1H), 1.87 – 1.61 (m, 3H), 1.65 – 1.23 (m, 3H, overlapping with H_2O signal), 1.21 (s, 1.5H), 1.15 (s, 1.5H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 175.7, 147.8, 139.9, 139.8, 139.0, 138.9, 136.4, 136.0, 132.1, 132.0, 130.5, 130.3, 127.3, 127.2f, 123.1, 121.22, 121.19, 118.8 (q, $^1J_{C–F}$ = 321.9 Hz), 118.6, 82.3, 77.4, 56.0, 55.7, 43.1, 42.9, 42.5, 41.2, 40.8, 40.3, 39.2, 37.3, 34.3, 34.2, 29.6, 29.5, 26.8, 25.9, 25.8, 25.28, 25.26, 24.6, 18.3, 15.6;
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.9.

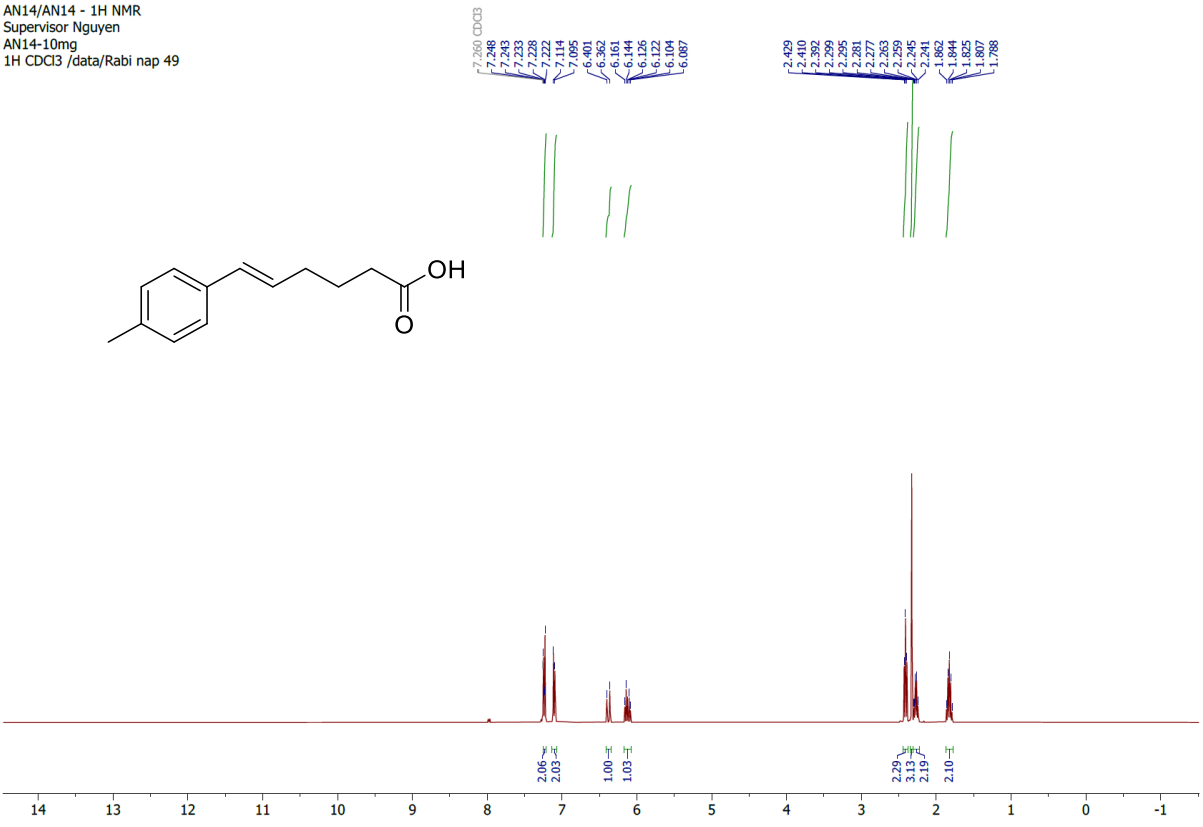
NMR Spectra

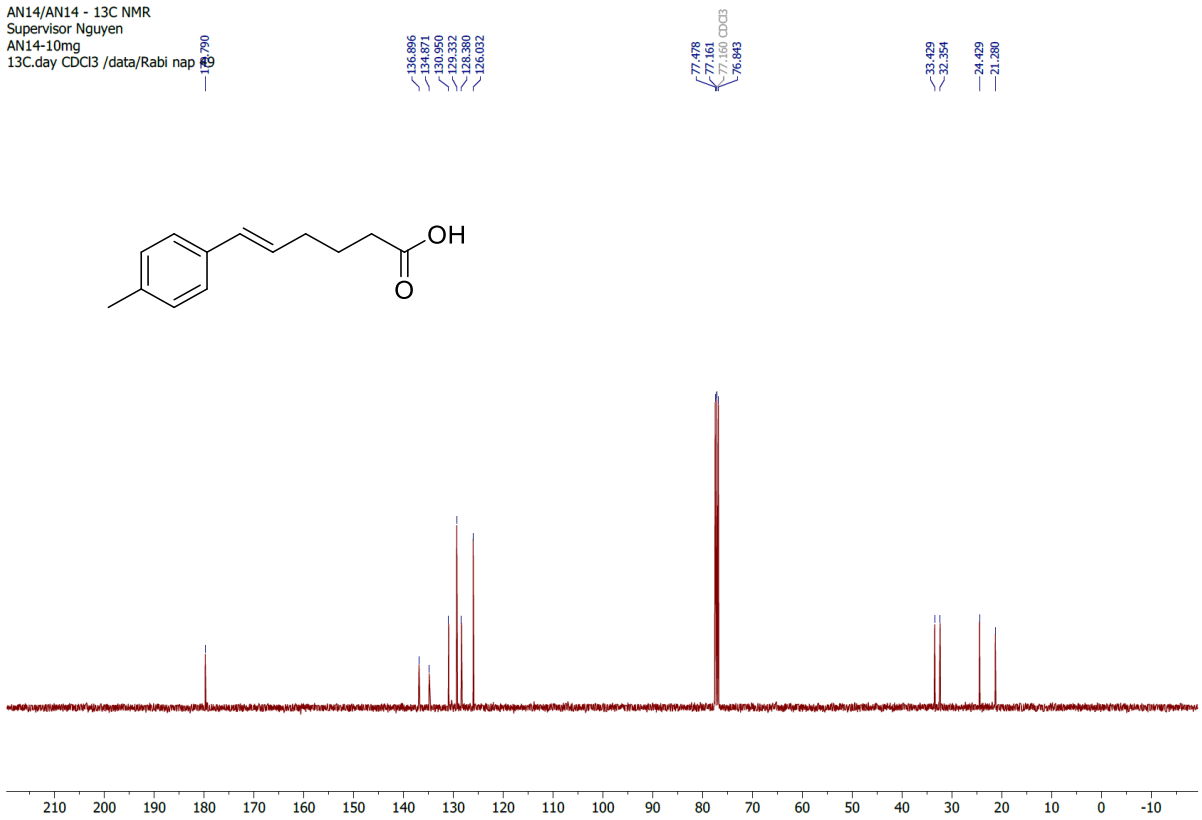
(*E*)-6-phenylhex-5-enoic acid (1a): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



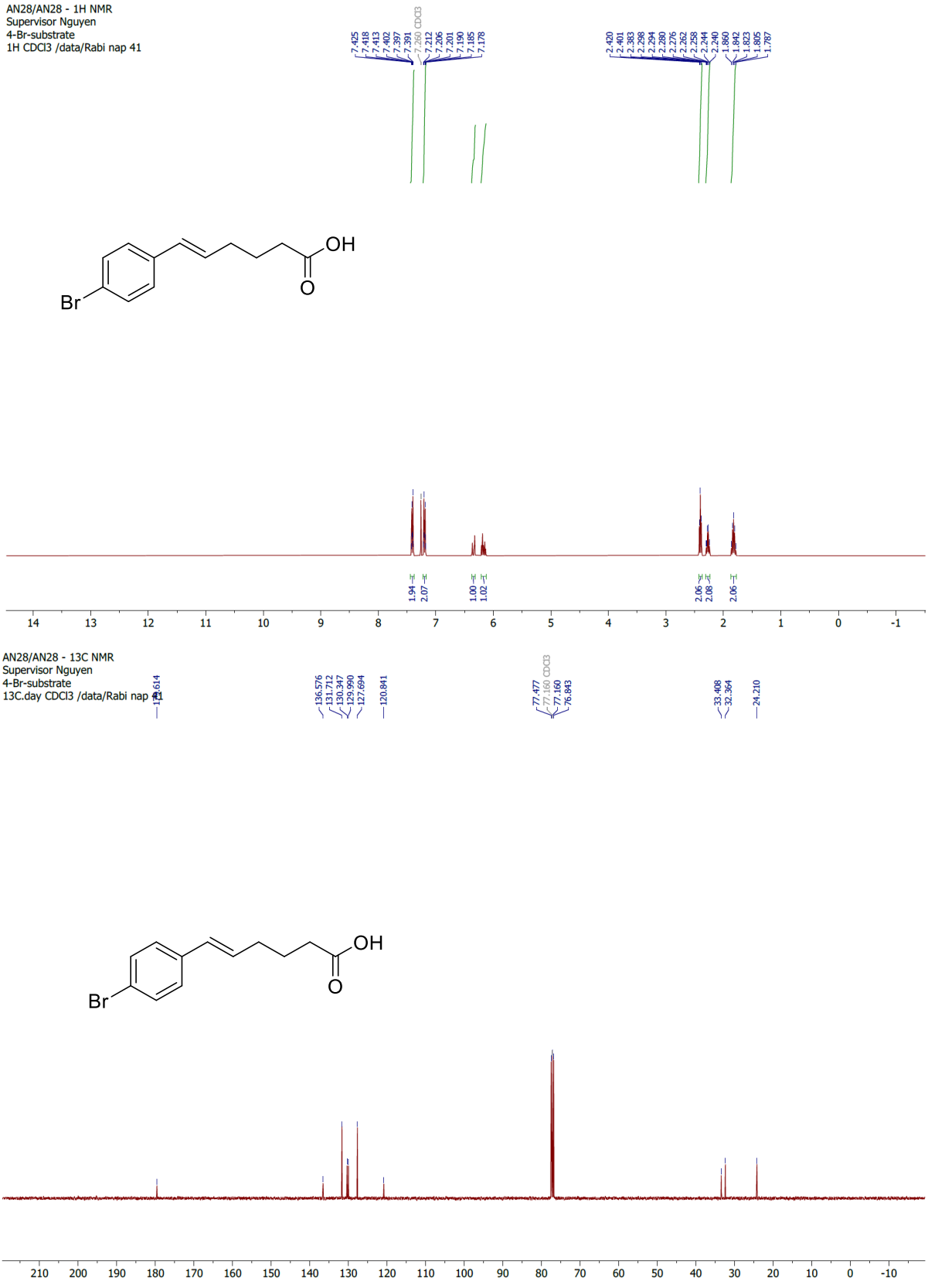


(*E*)-6-(*p*-tolyl)hex-5-enoic acid (1b): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

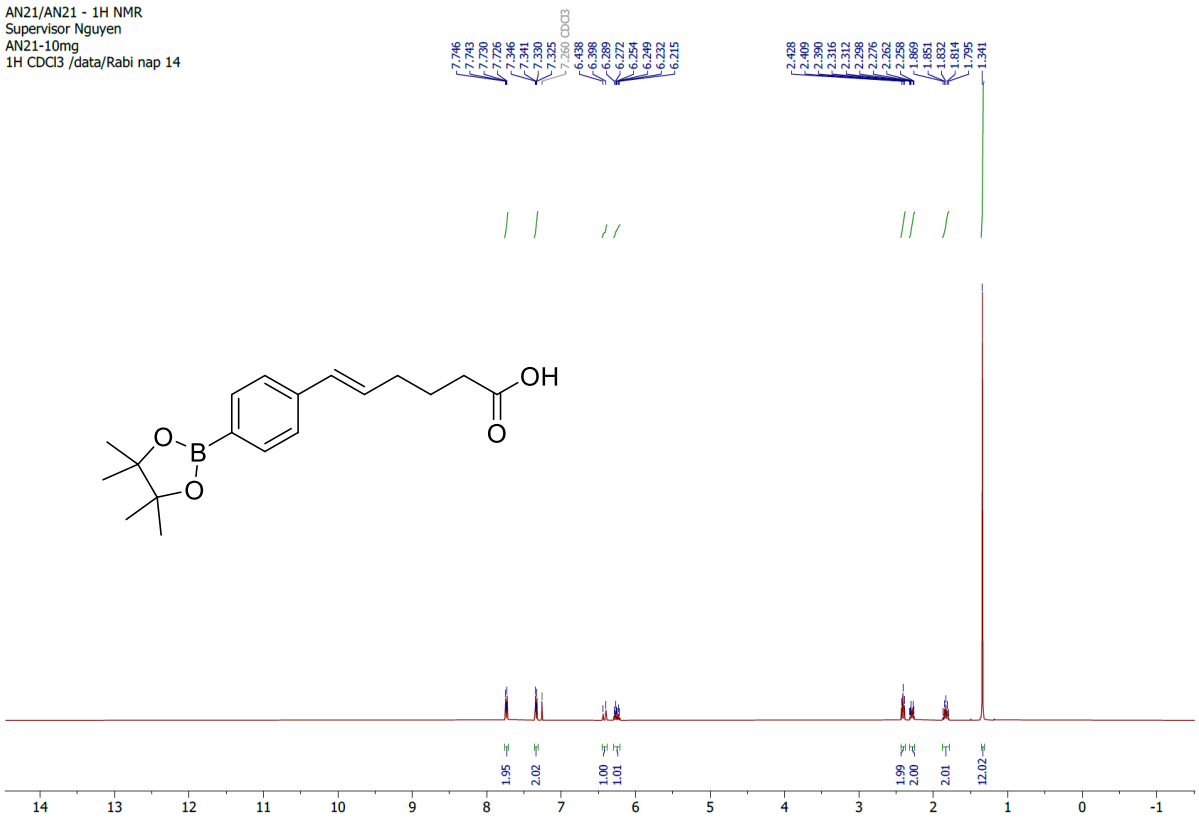


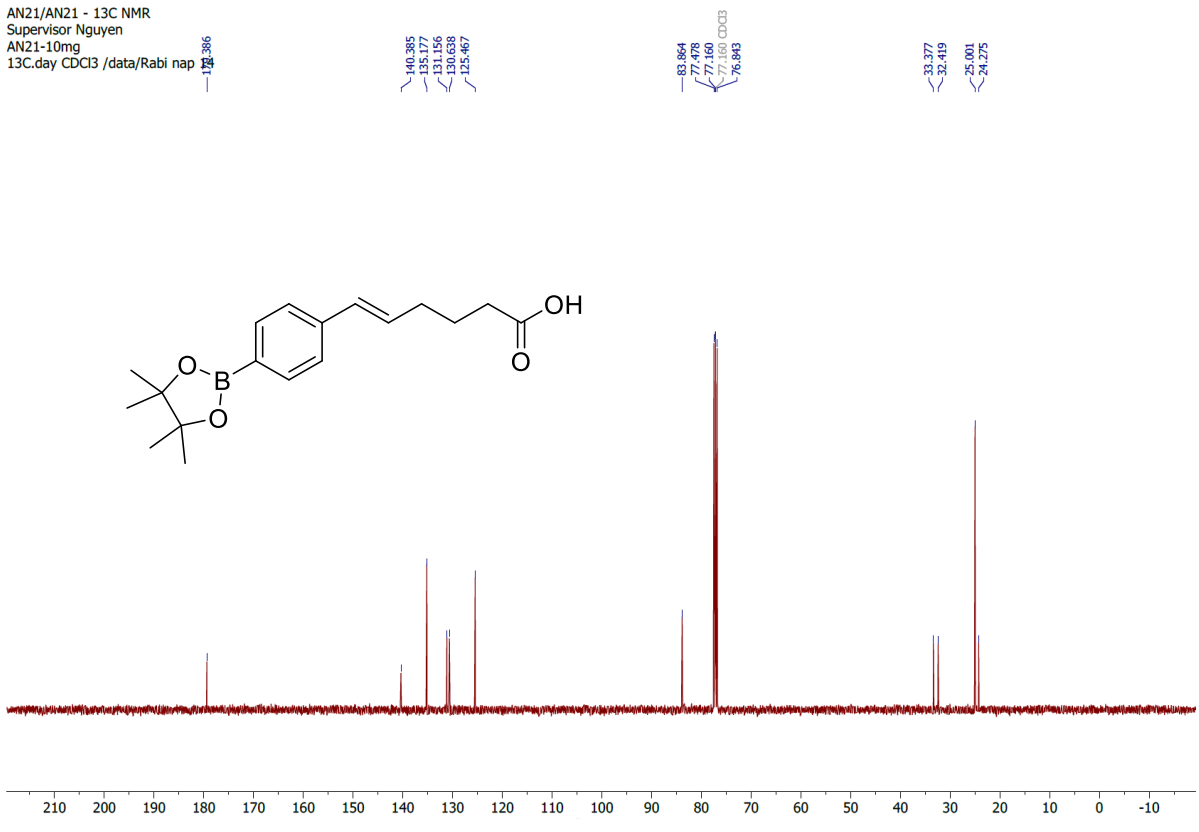


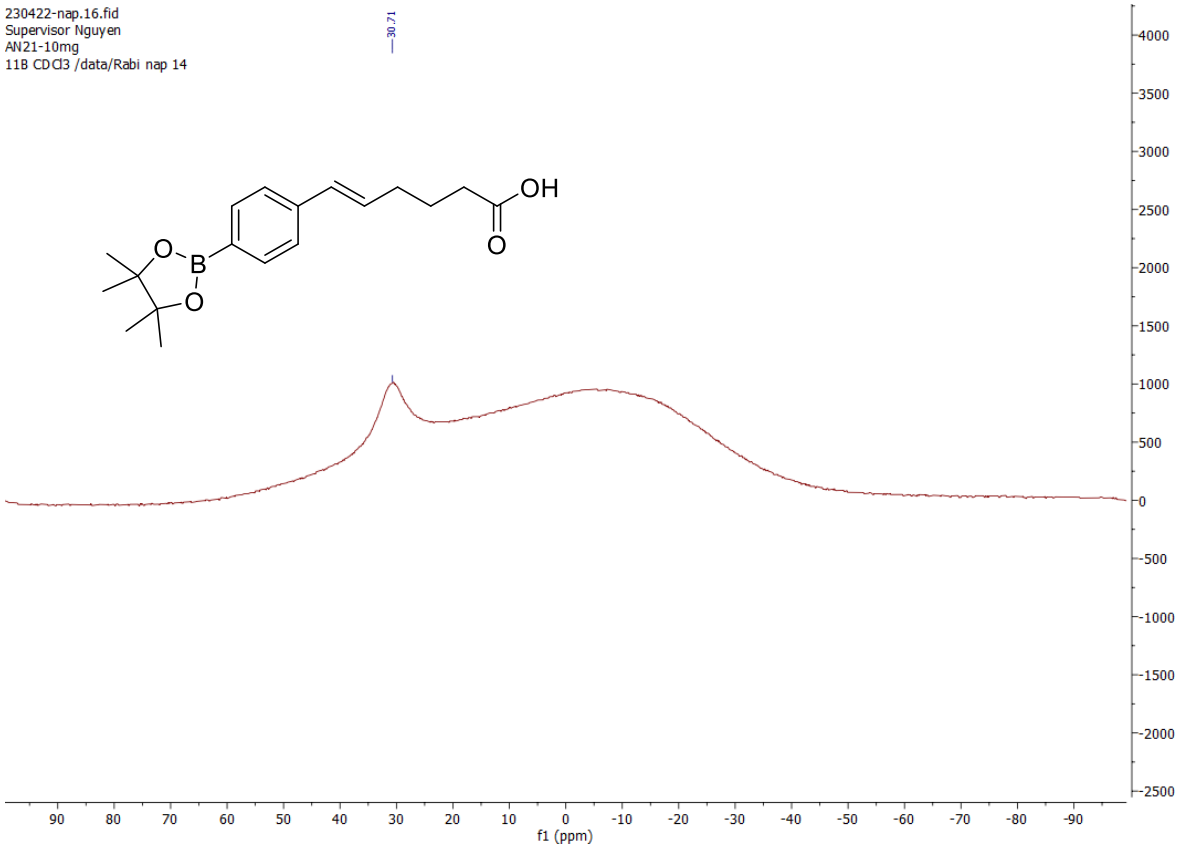
(*E*)-6-(4-bromophenyl)hex-5-enoic acid (1c): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



(*E*)-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-5-enoic acid (1d): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{11}B NMR (128 MHz, $CDCl_3$)



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Supervisor Nguyen
AN21-10mg
11B CDCl3 /data/Rabi nap 14
30.71
OH
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O
B
O
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3000
2500
2000
1500
1000
500
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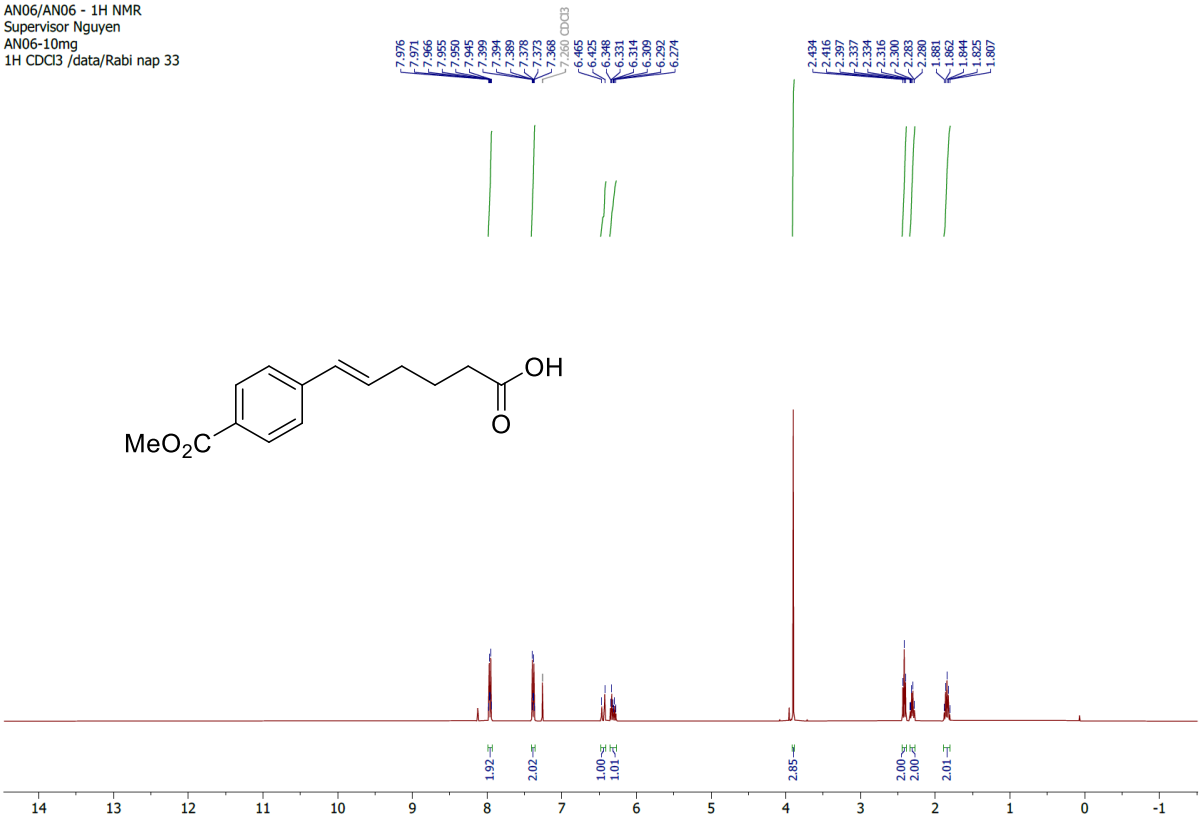
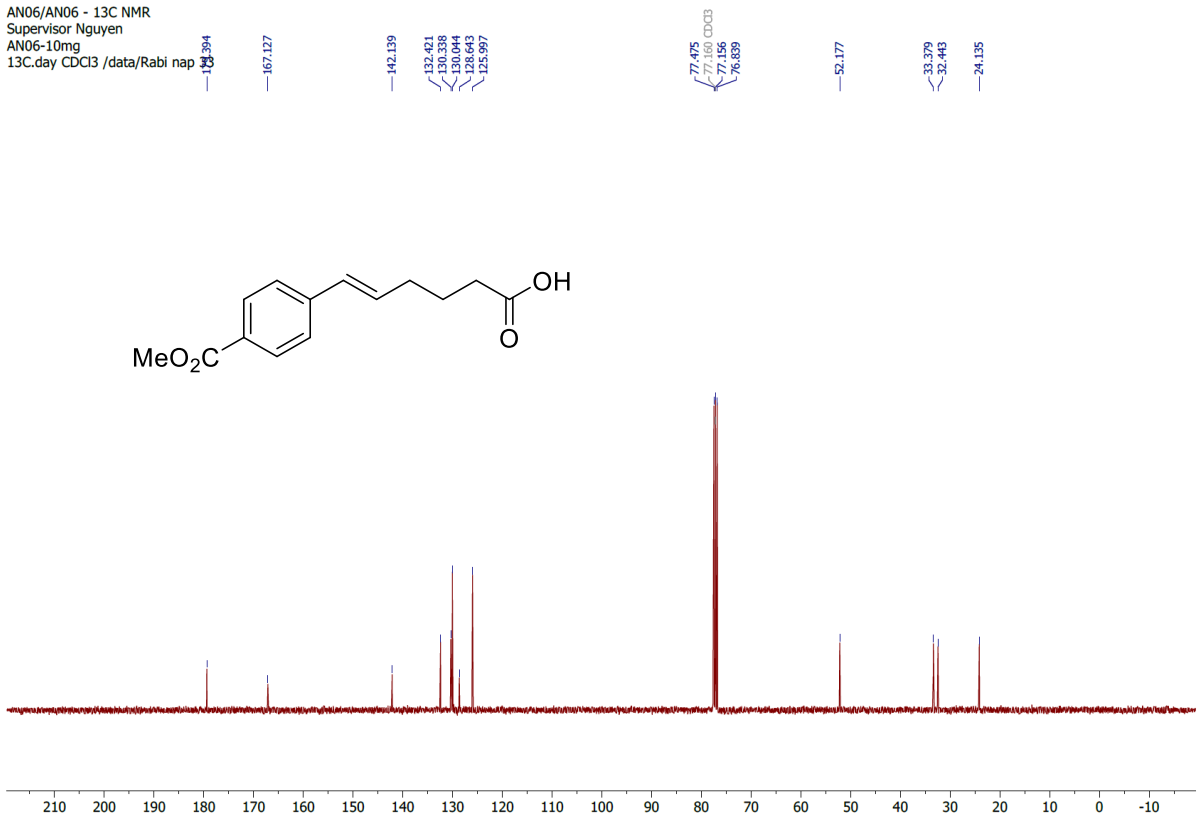
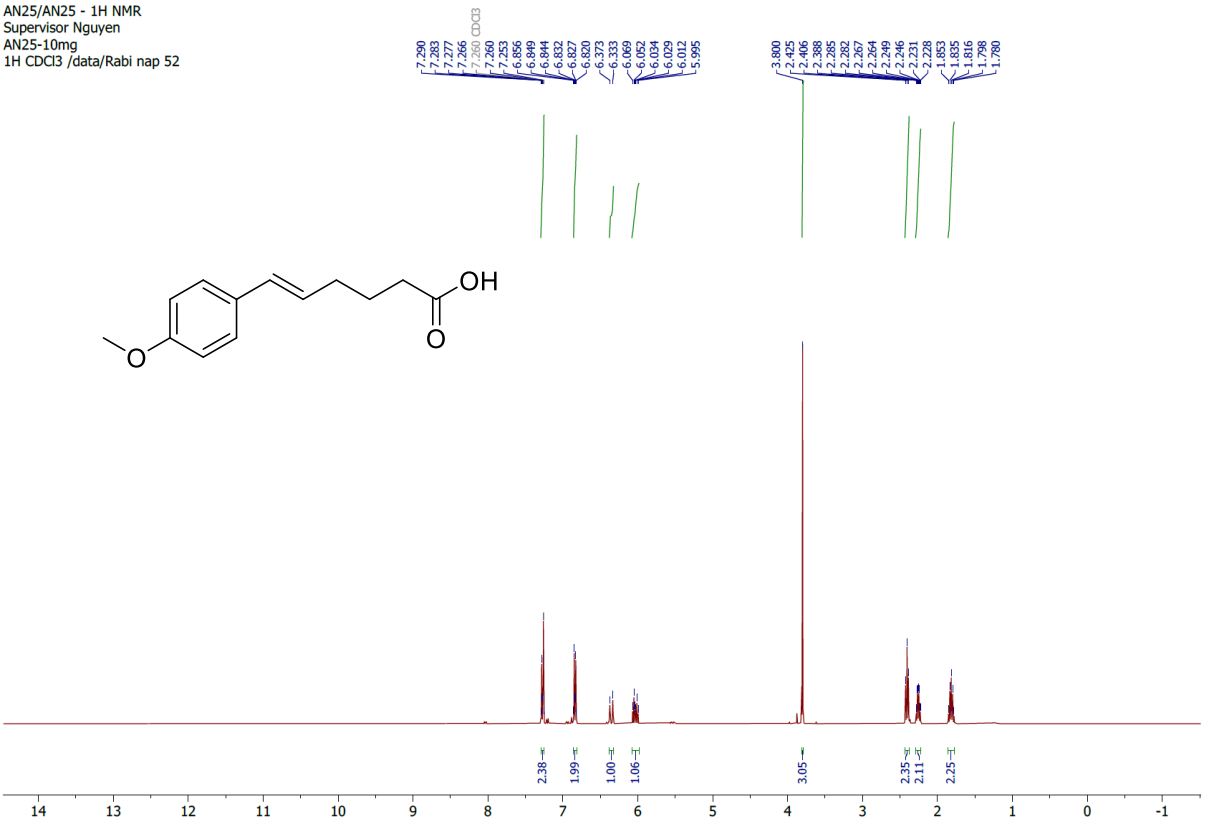
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

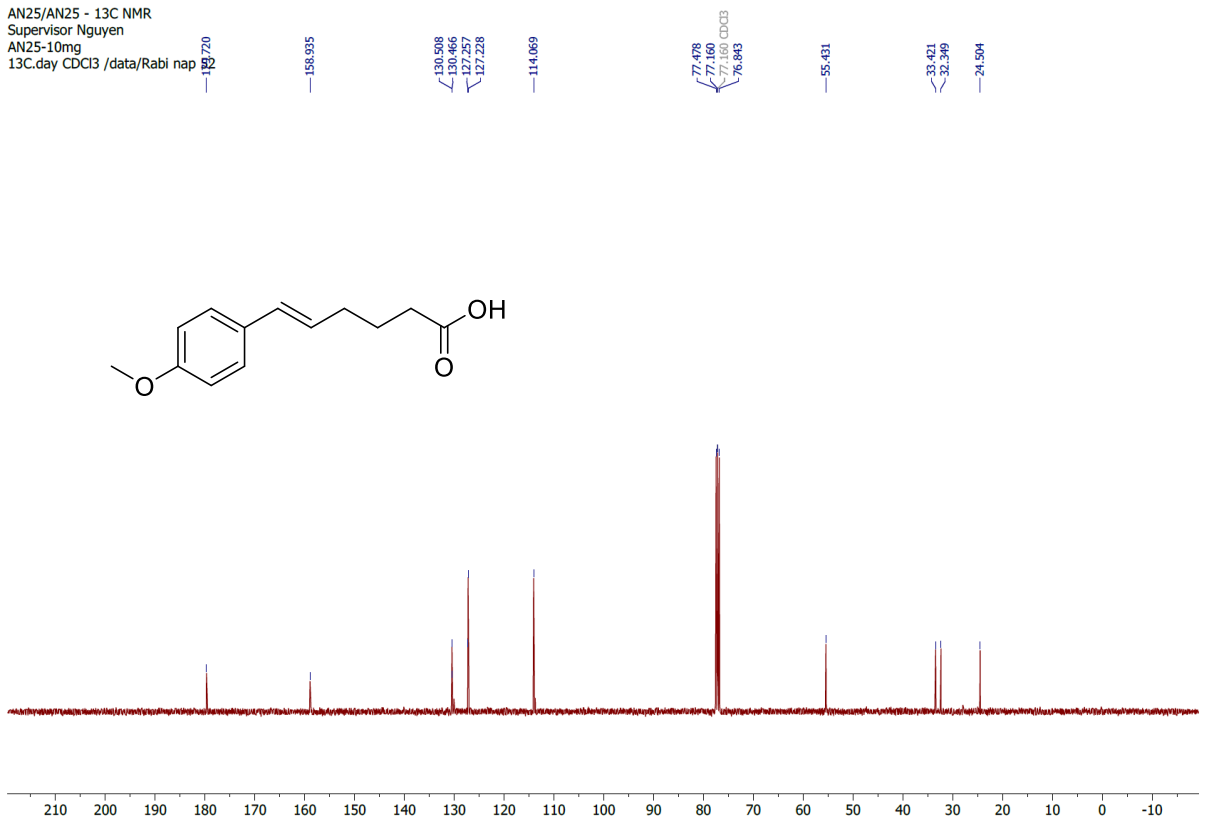
(*E*)-6-(4-(methoxycarbonyl)phenyl)hex-5-enoic acid (1e): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



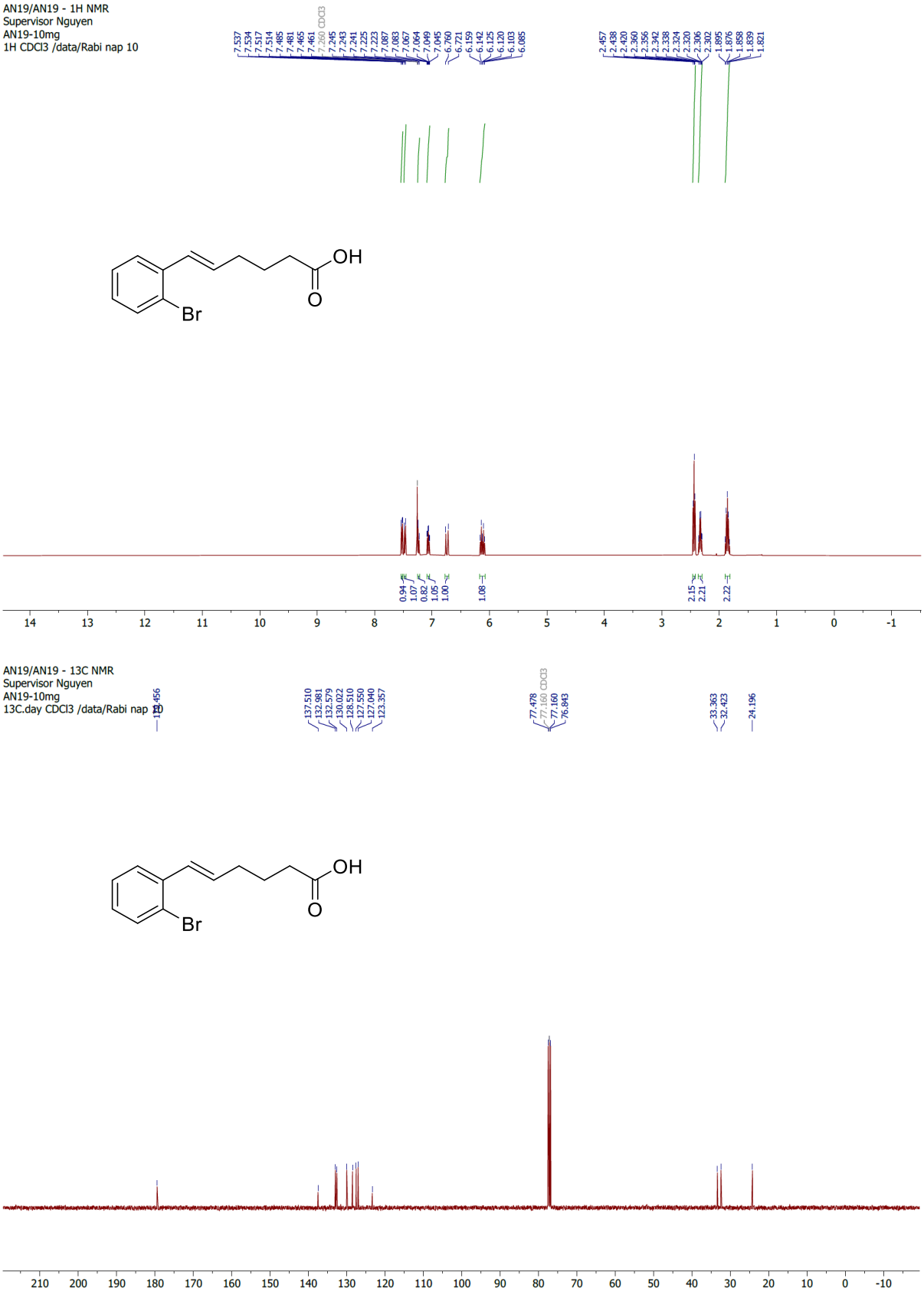


(*E*)-6-(4-methoxyphenyl)hex-5-enoic acid (1f): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

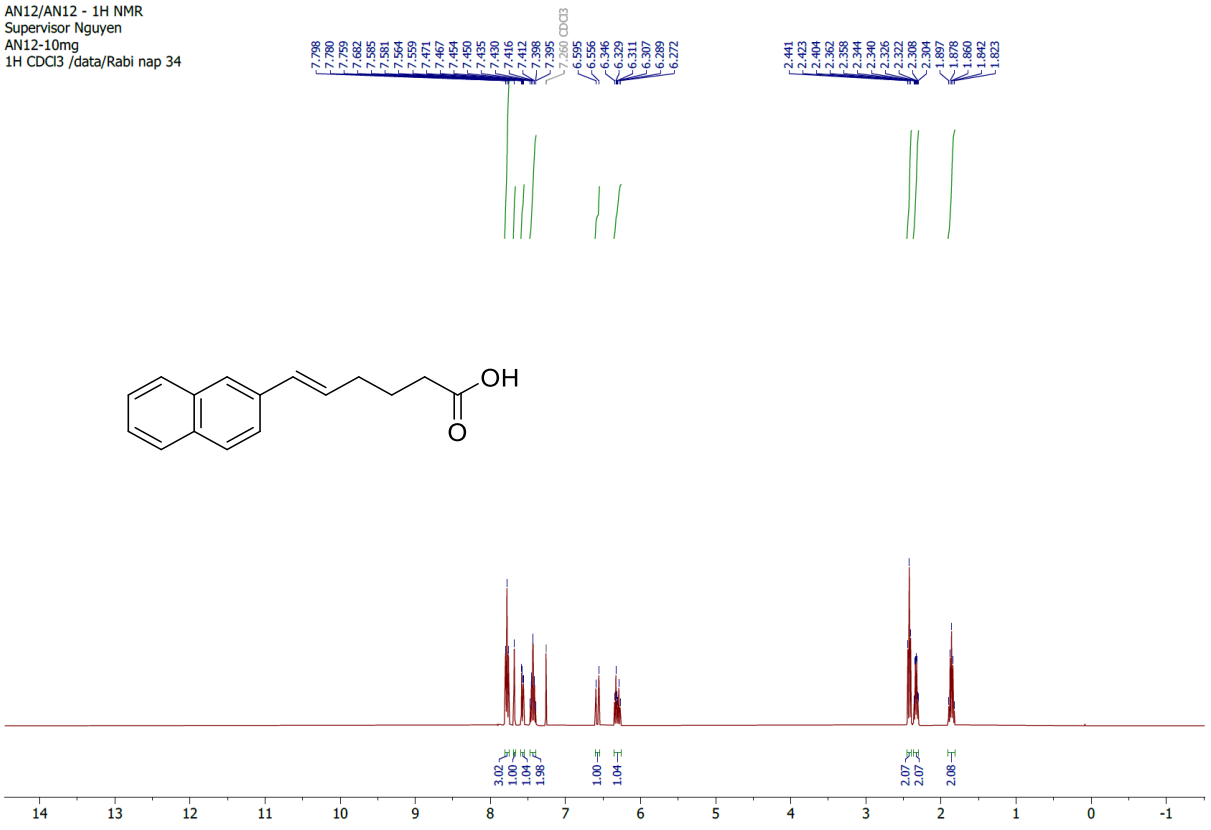


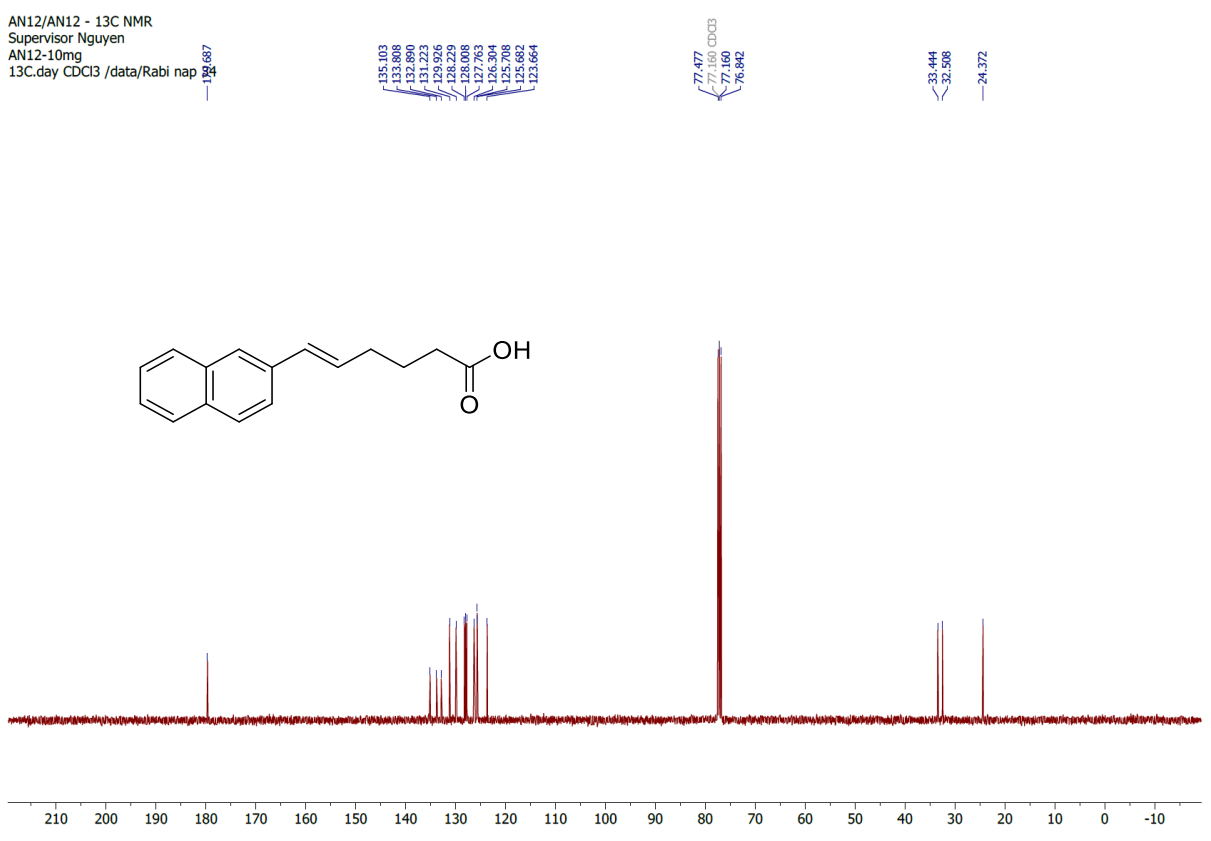


(*E*)-6-(2-bromophenyl)hex-5-enoic acid (1g): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

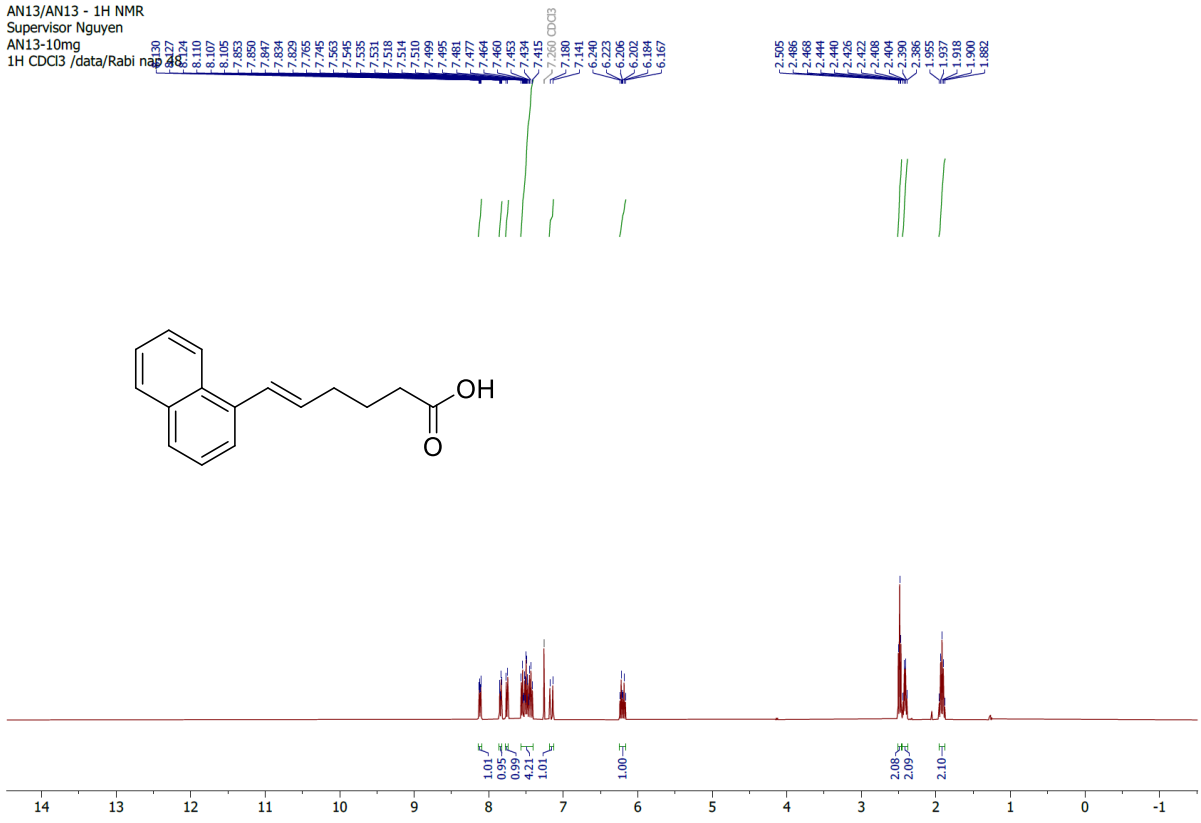


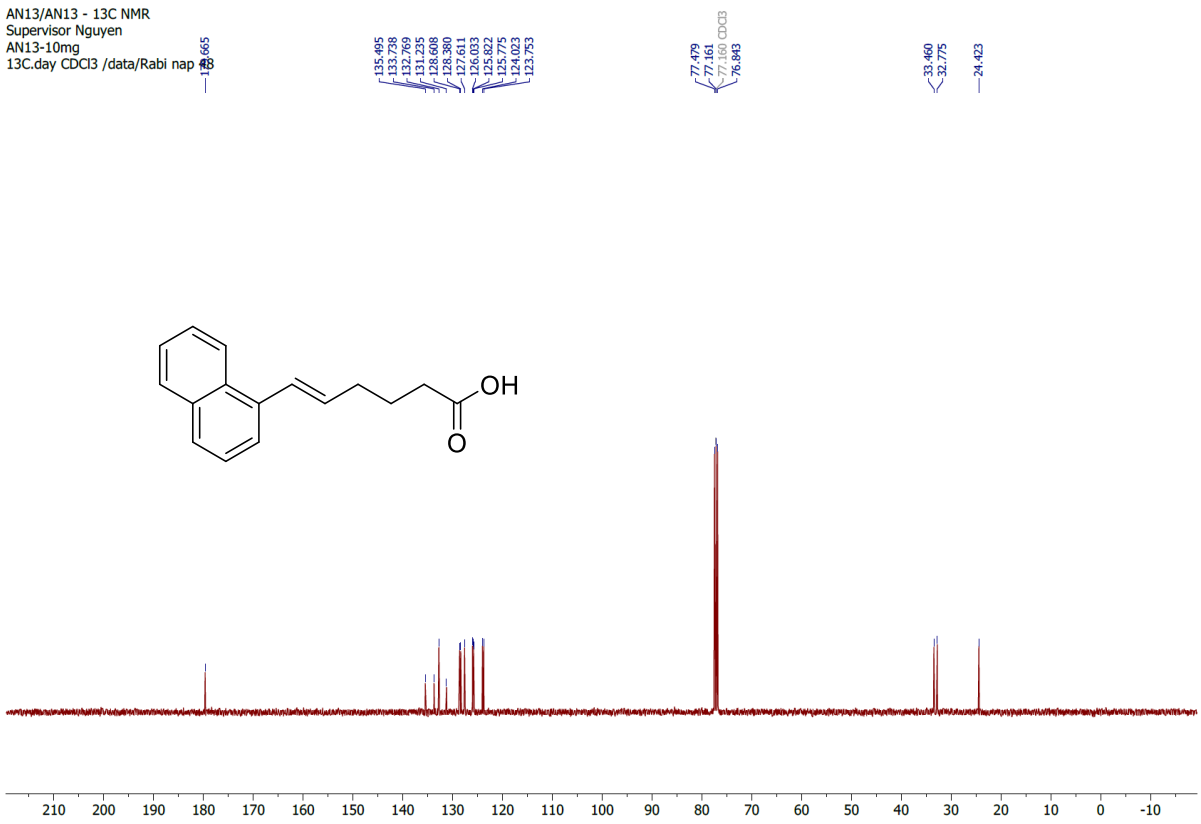
(*E*)-6-(naphthalen-2-yl)hex-5-enoic acid (1h): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



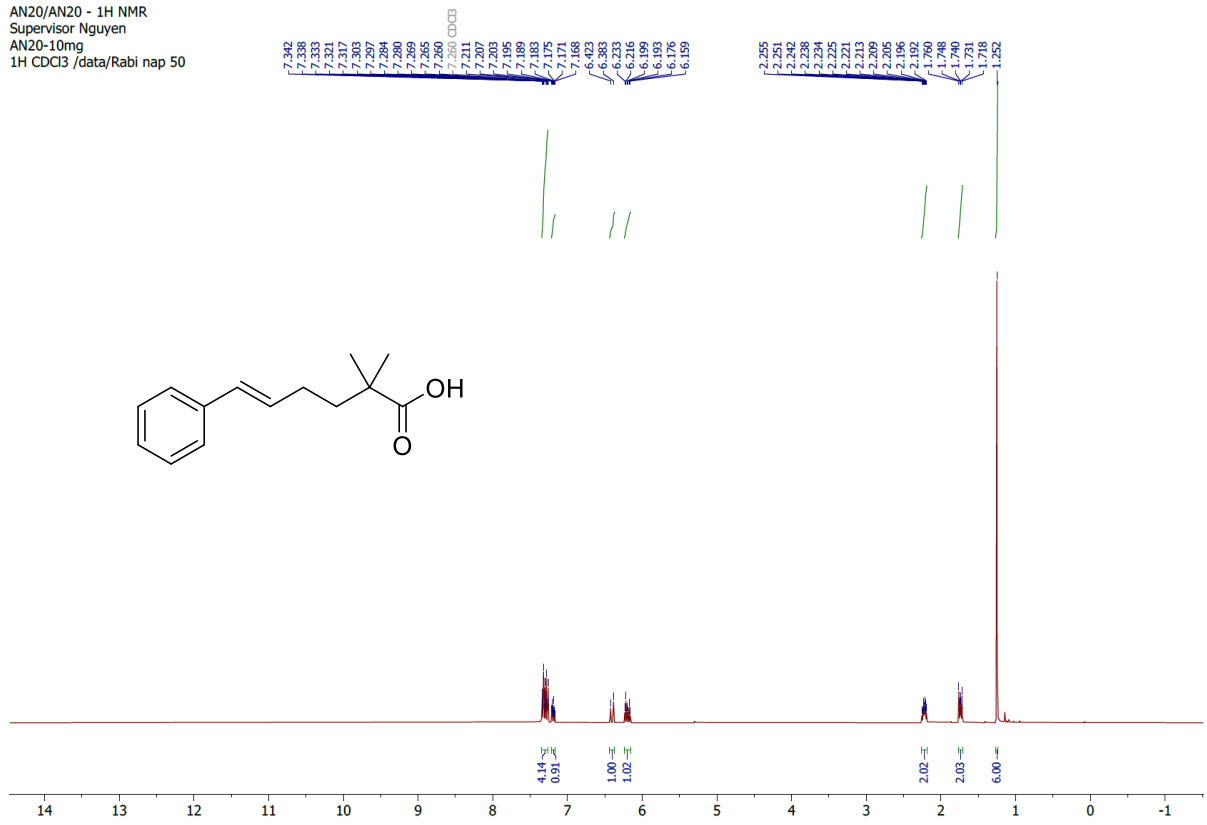


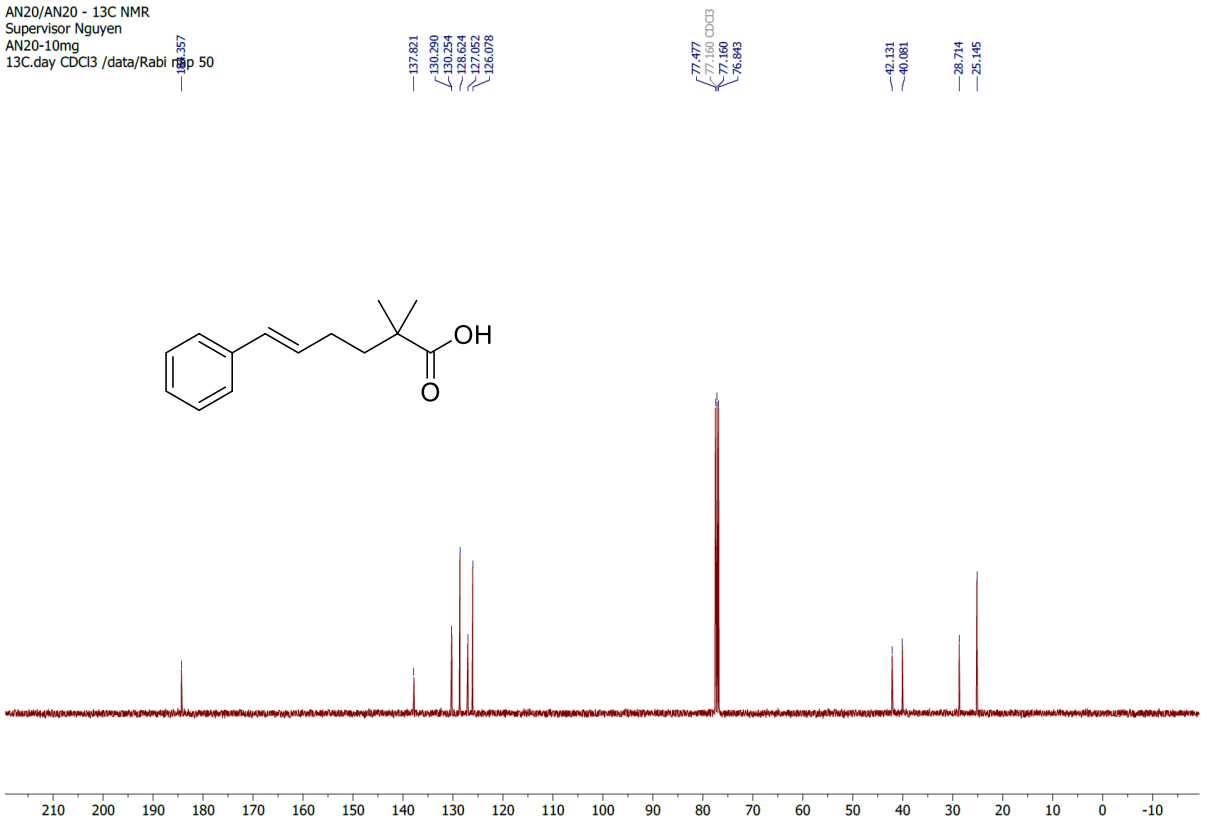
(*E*)-6-(naphthale*n*-1-yl)hex-5-enoic acid (1i): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



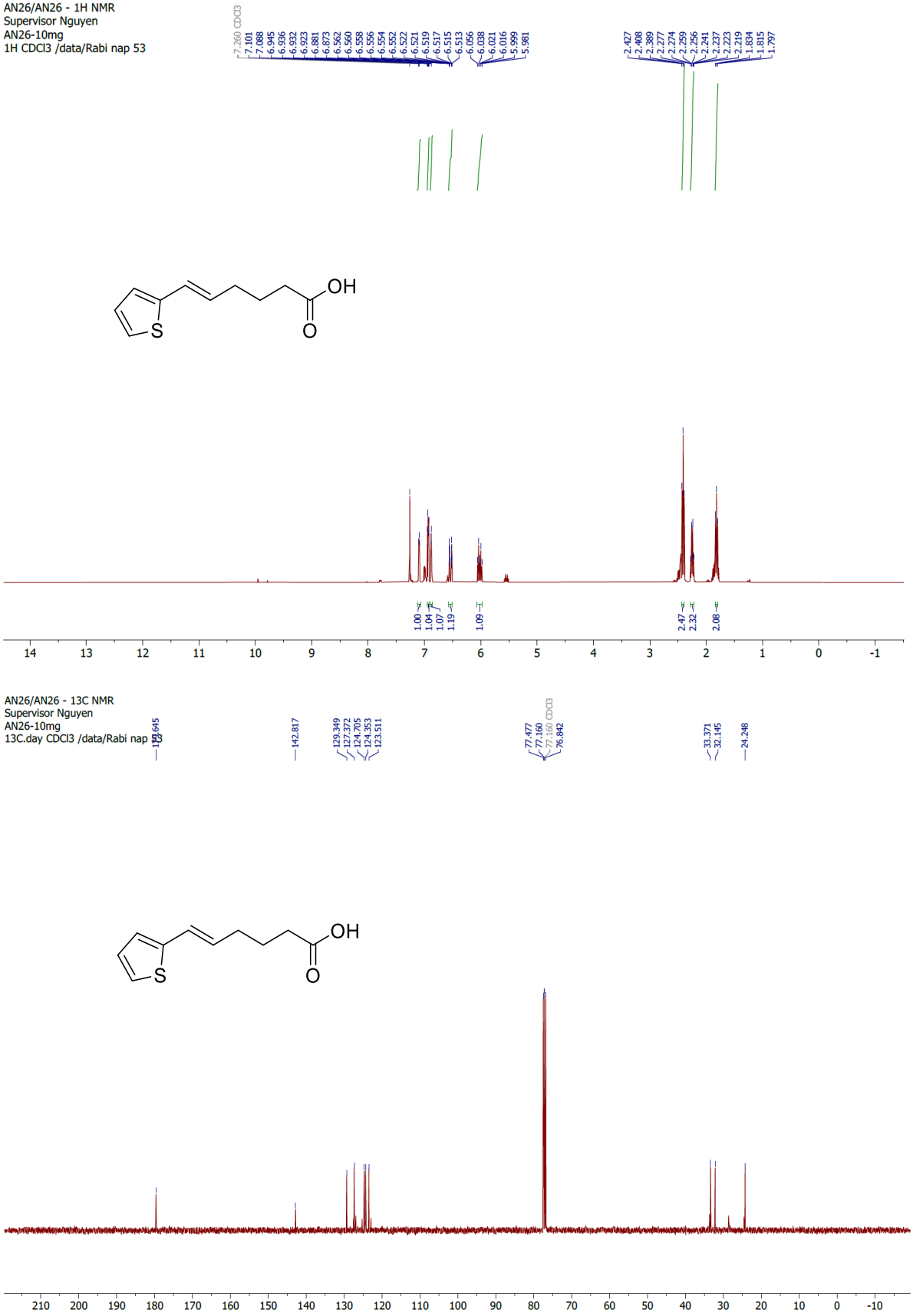


(*E*)-2,2-dimethyl-6-phenylhex-5-enoic acid (1j): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

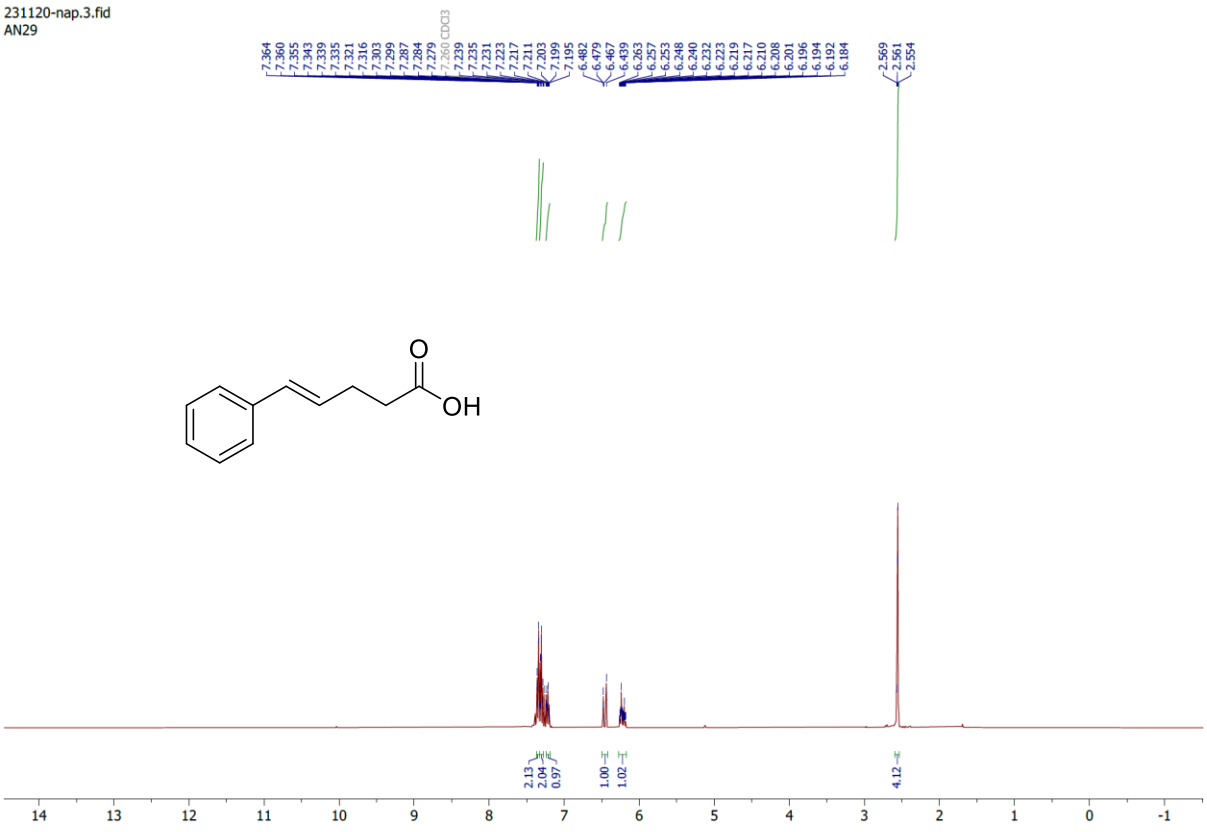


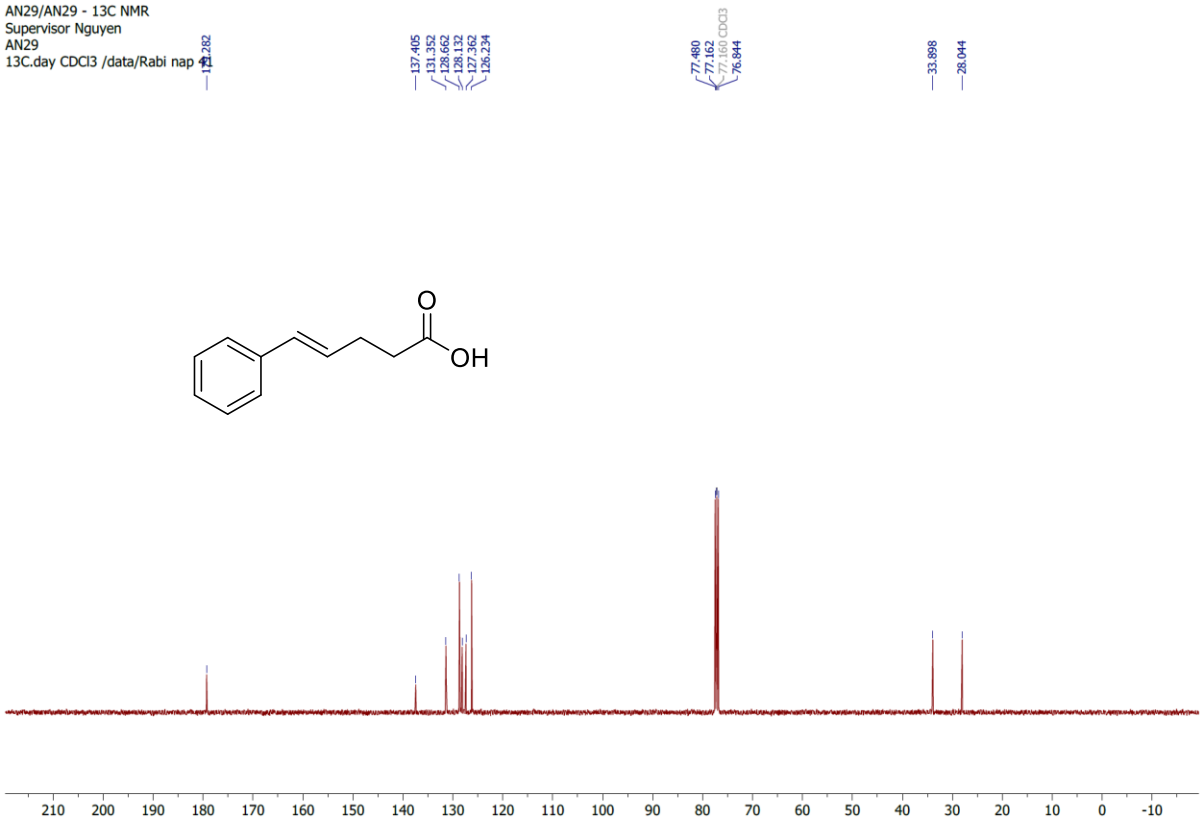


(*E*)-6-(thiophen-2-yl)hex-5-enoic acid (1k): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

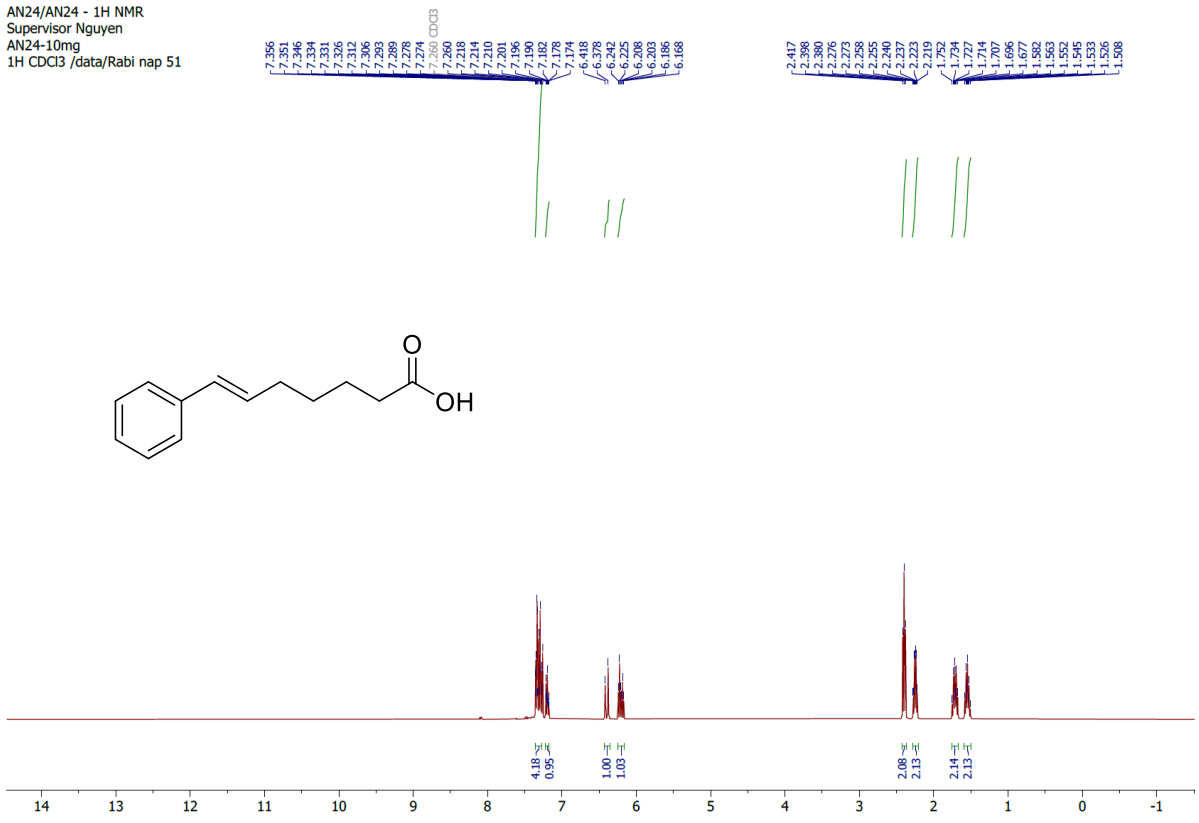


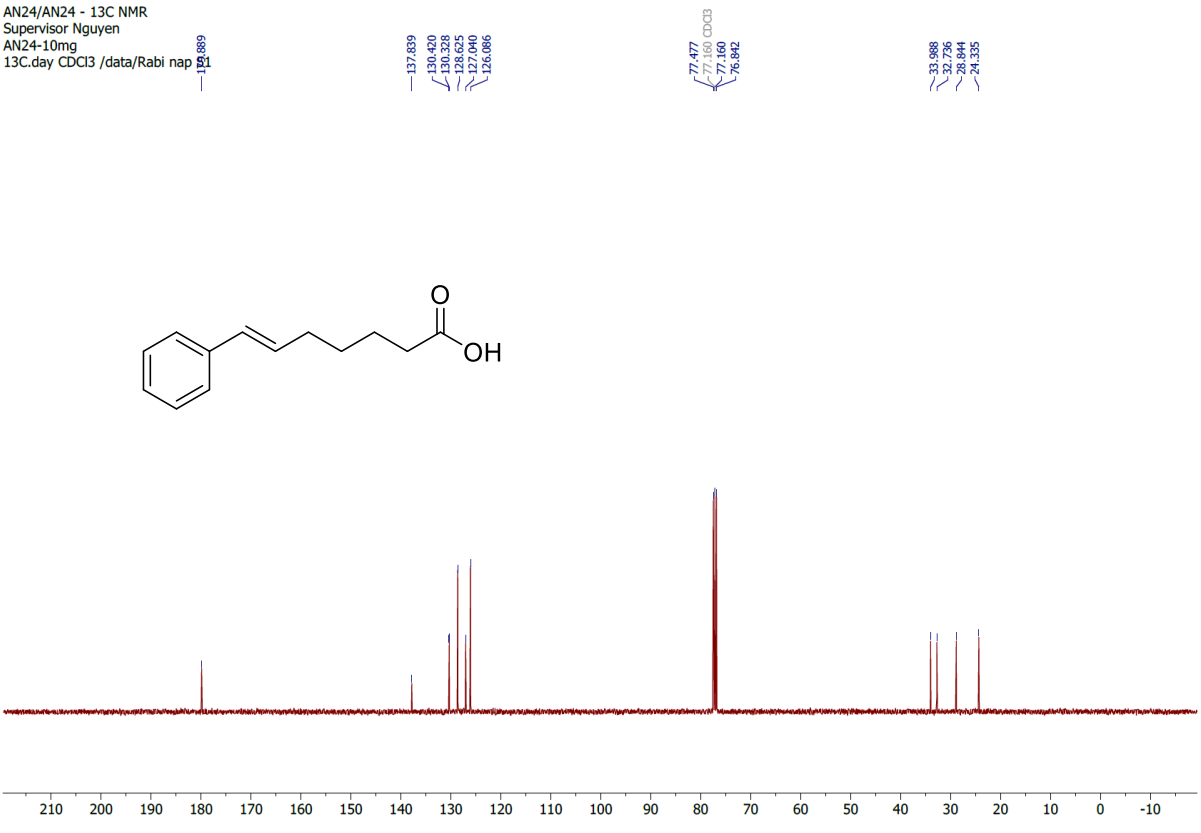
(*E*)-5-phenylpent-4-enoic acid (1l): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



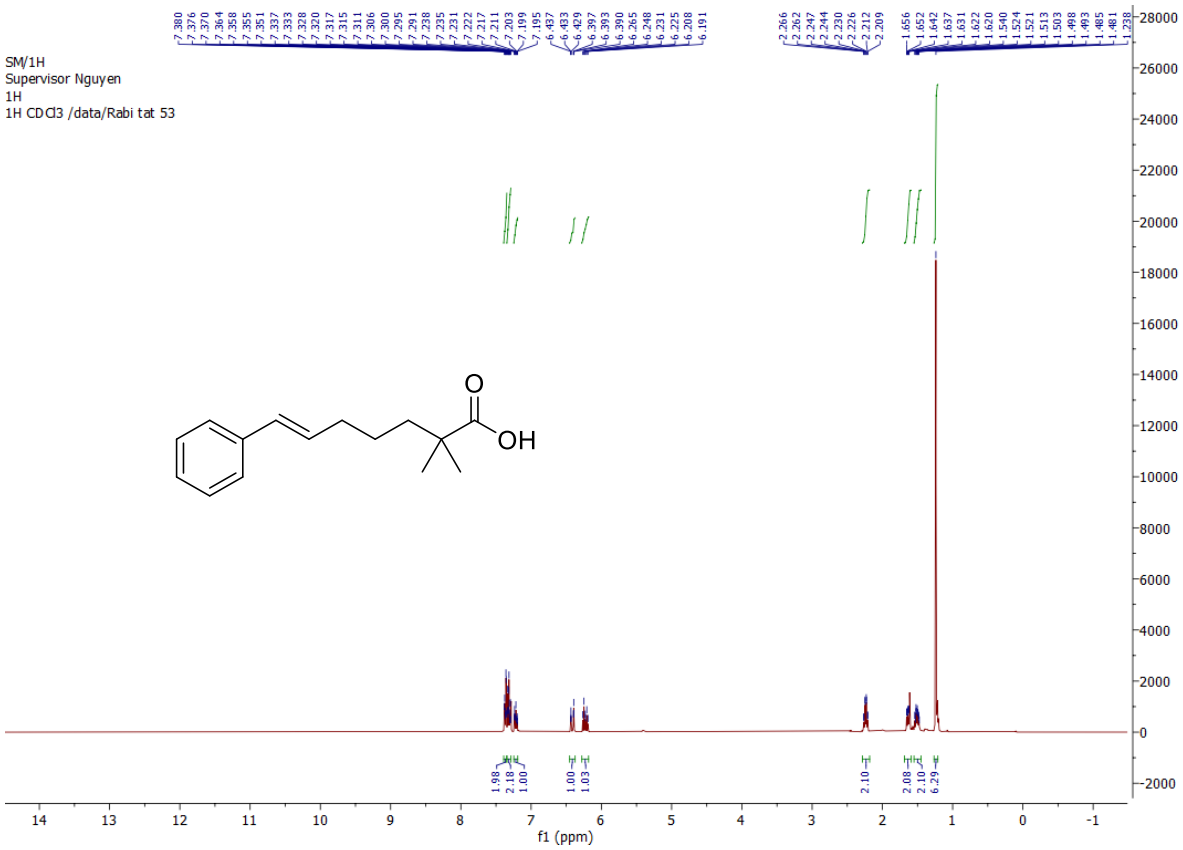


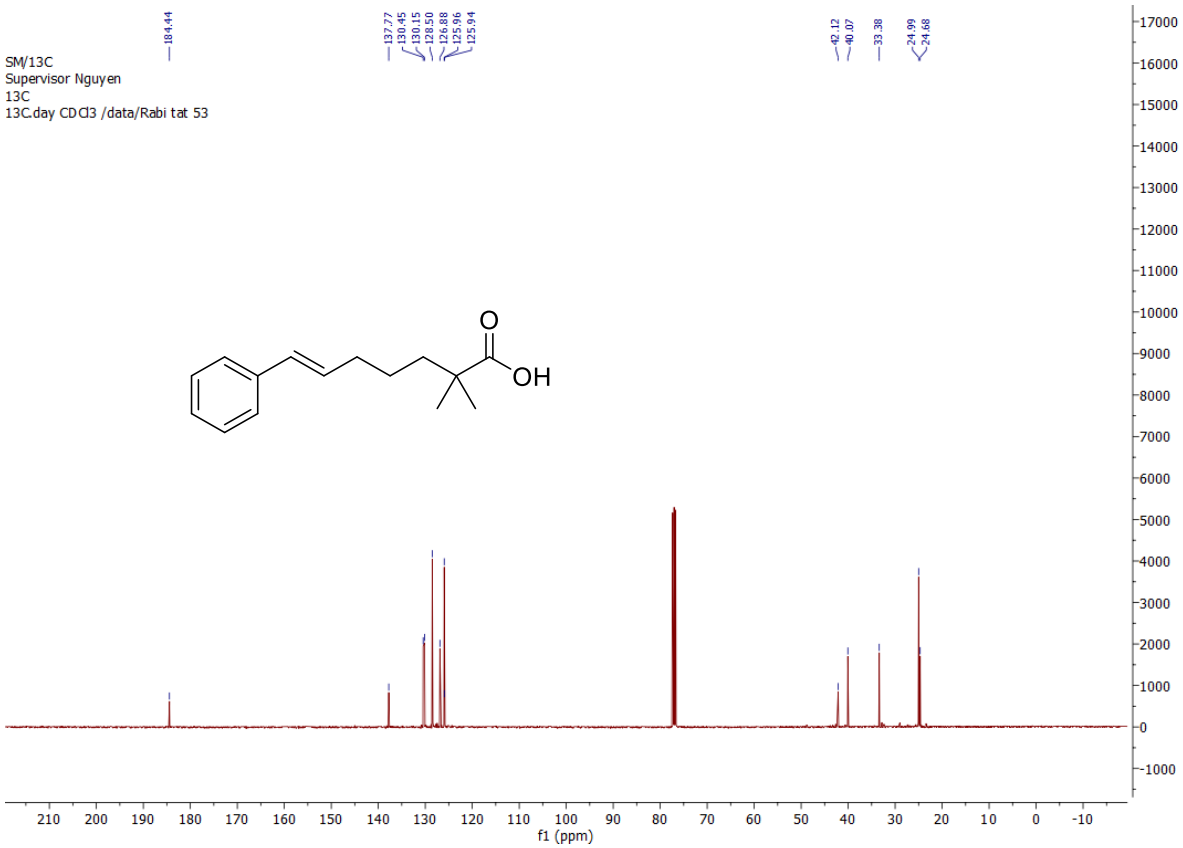
(*E*)-7-phenylhept-6-enoic acid (1m): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



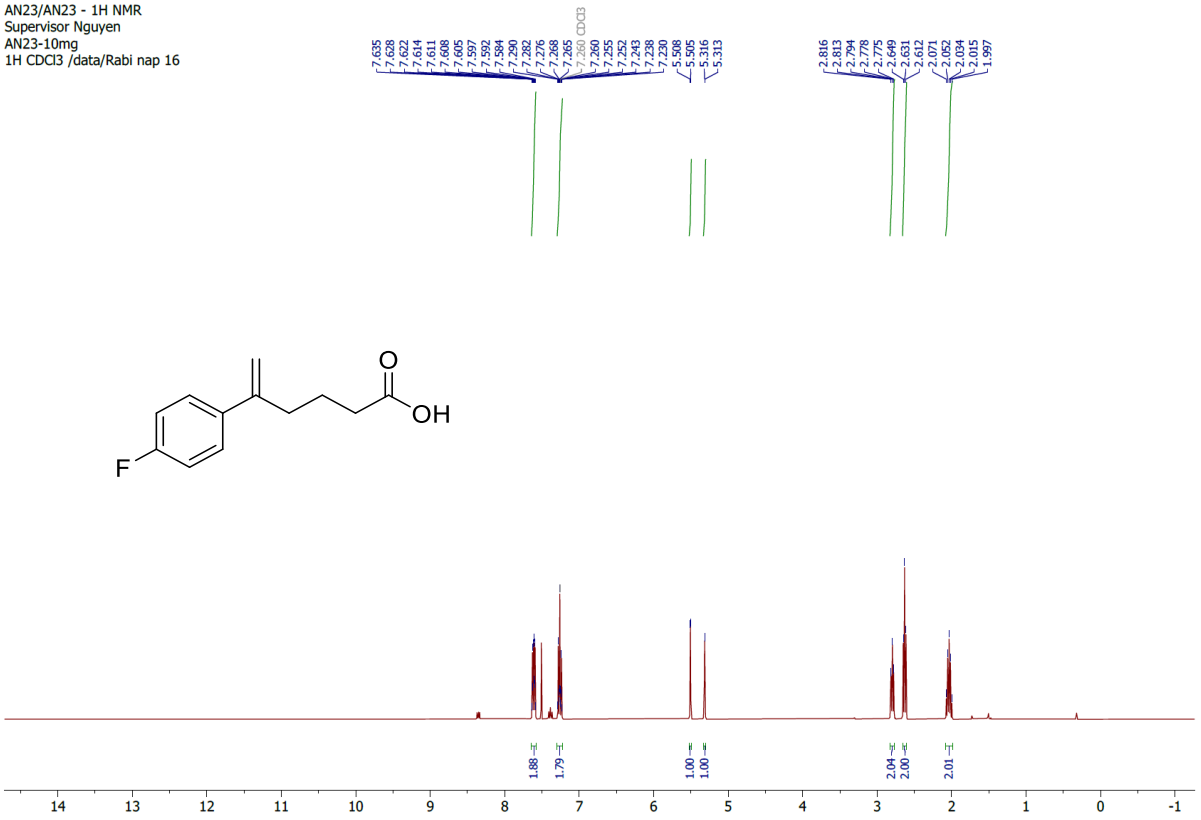


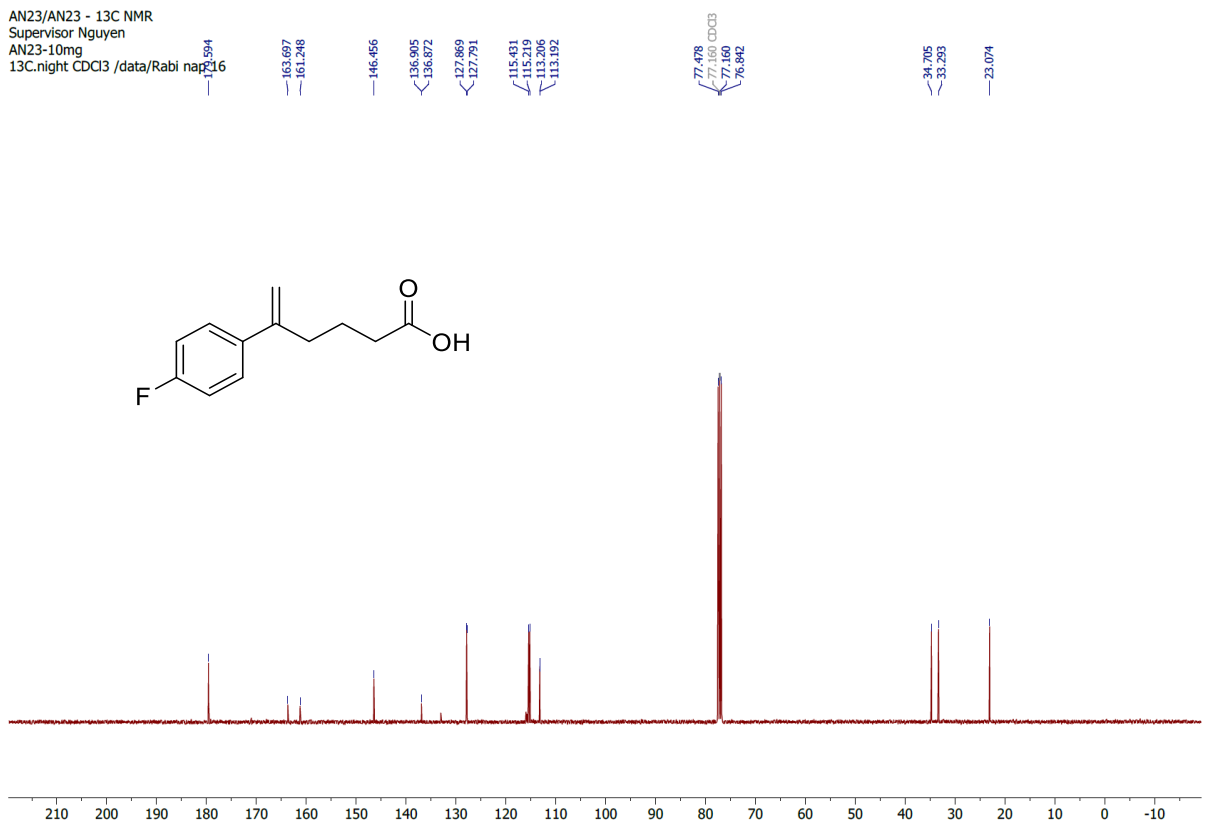
(*E*)-2,2-dimethyl-7-phenylhept-6-enoic acid (1n): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)





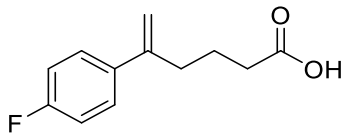
(*E*)-6-(4-fluorophenyl)hex-5-enoic acid (1p): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$)

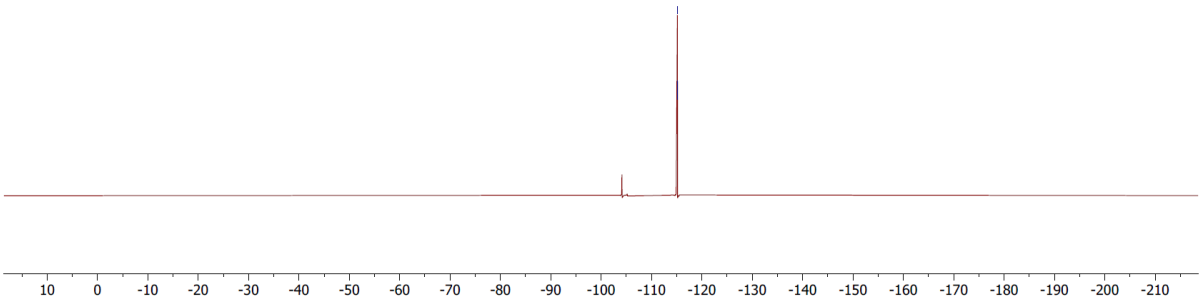




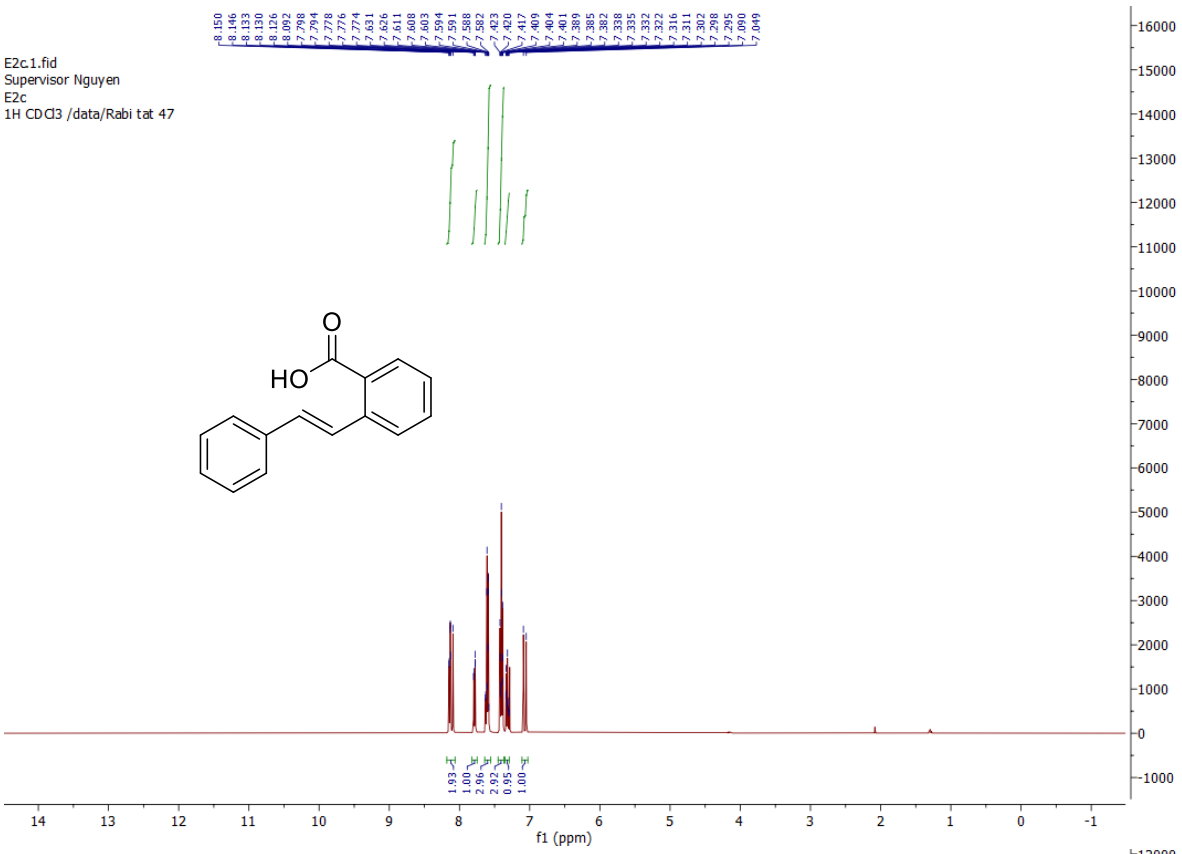
AN23/AN23 - 19F
Supervisor Nguyen
AN23-10mg
19F CDCl3 /data/Rabi nap 16

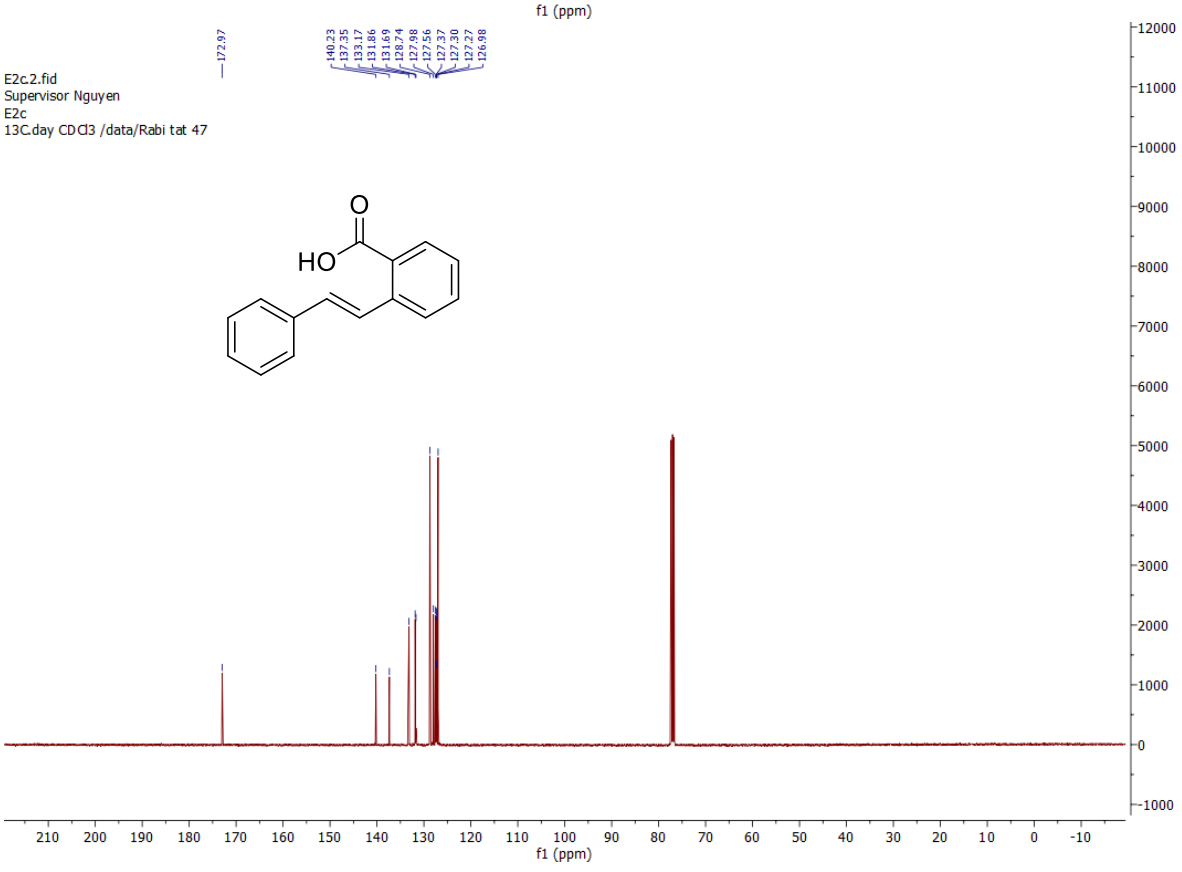
-115.114
-115.122
-115.136
-115.151
-115.159



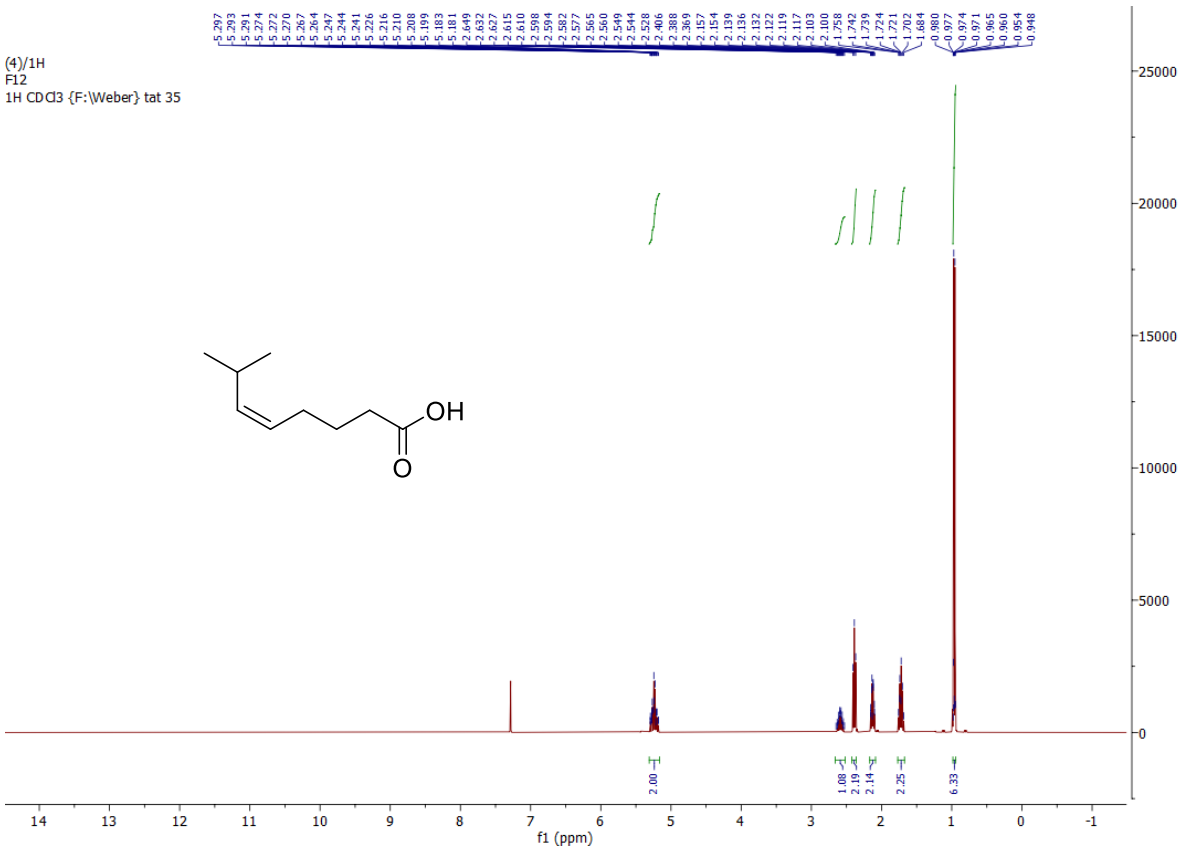


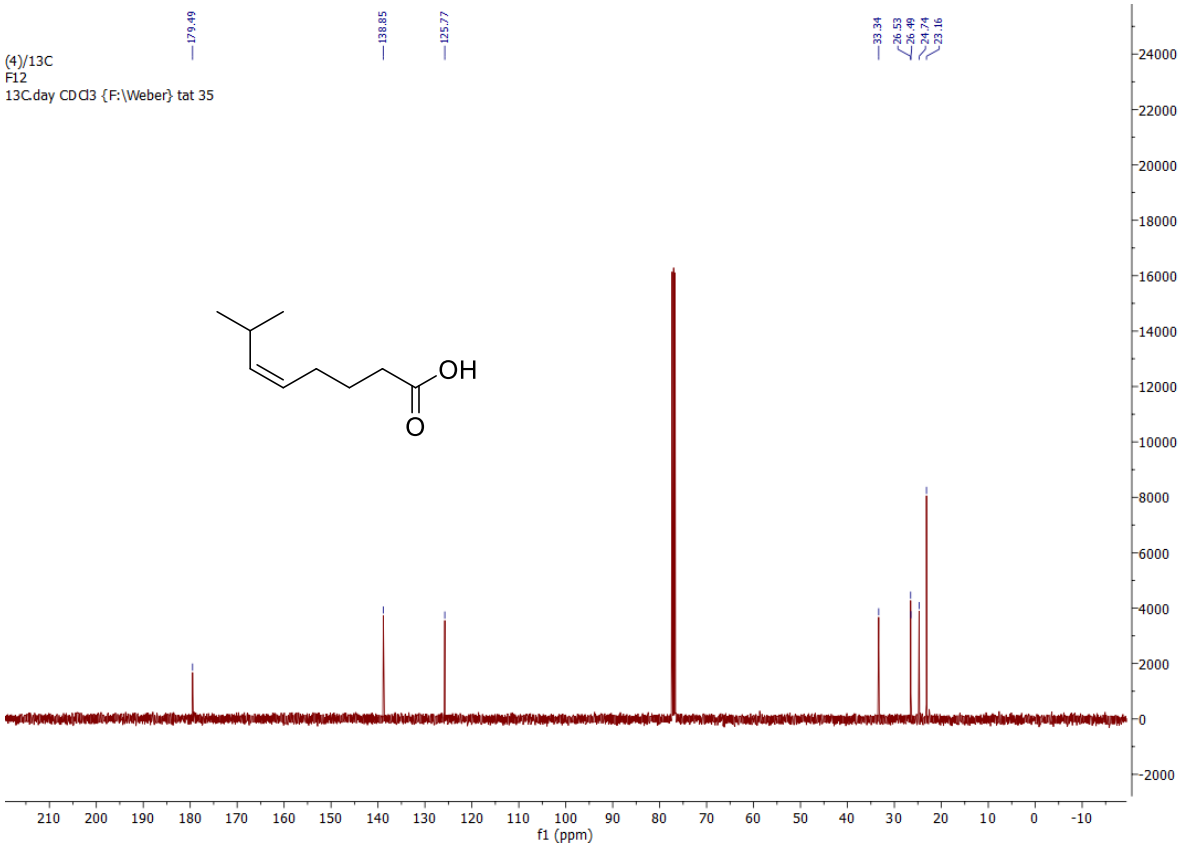
(*E*)-2-styrylbenzoic acid (1q): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$).



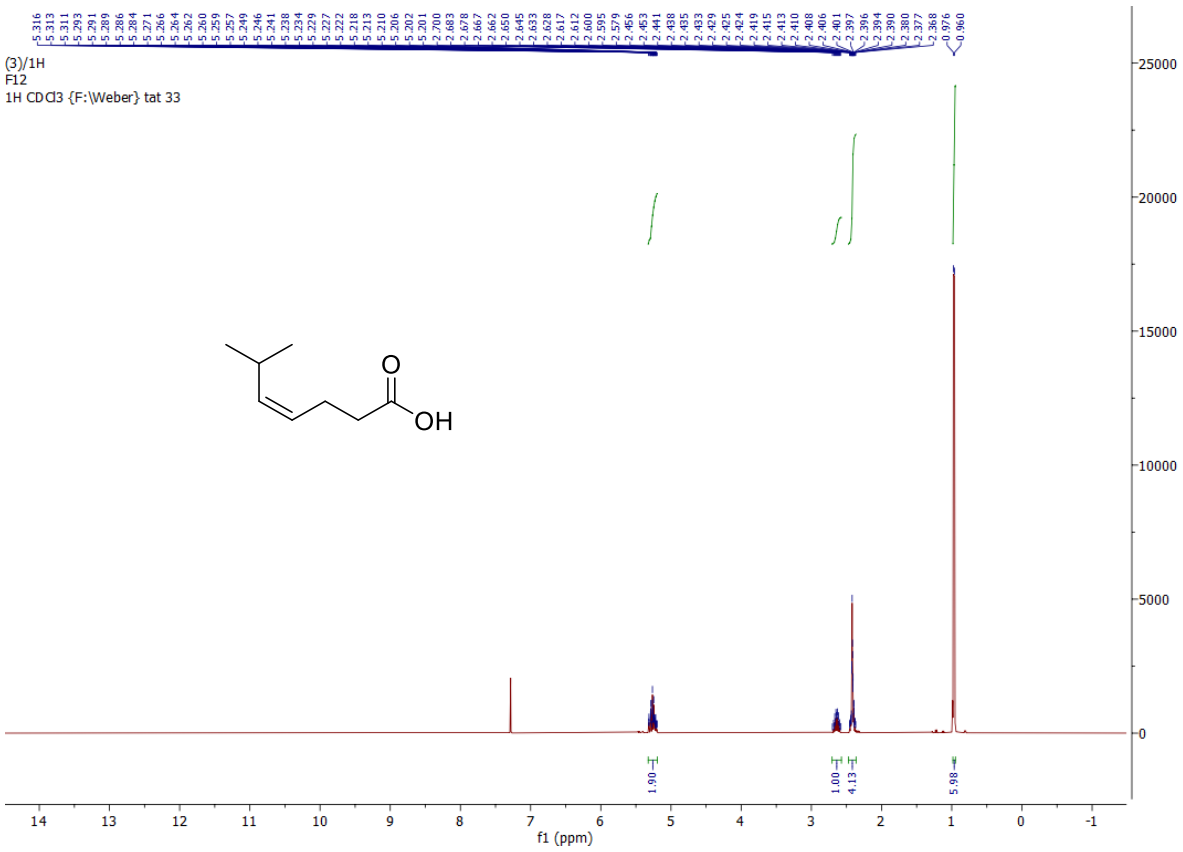


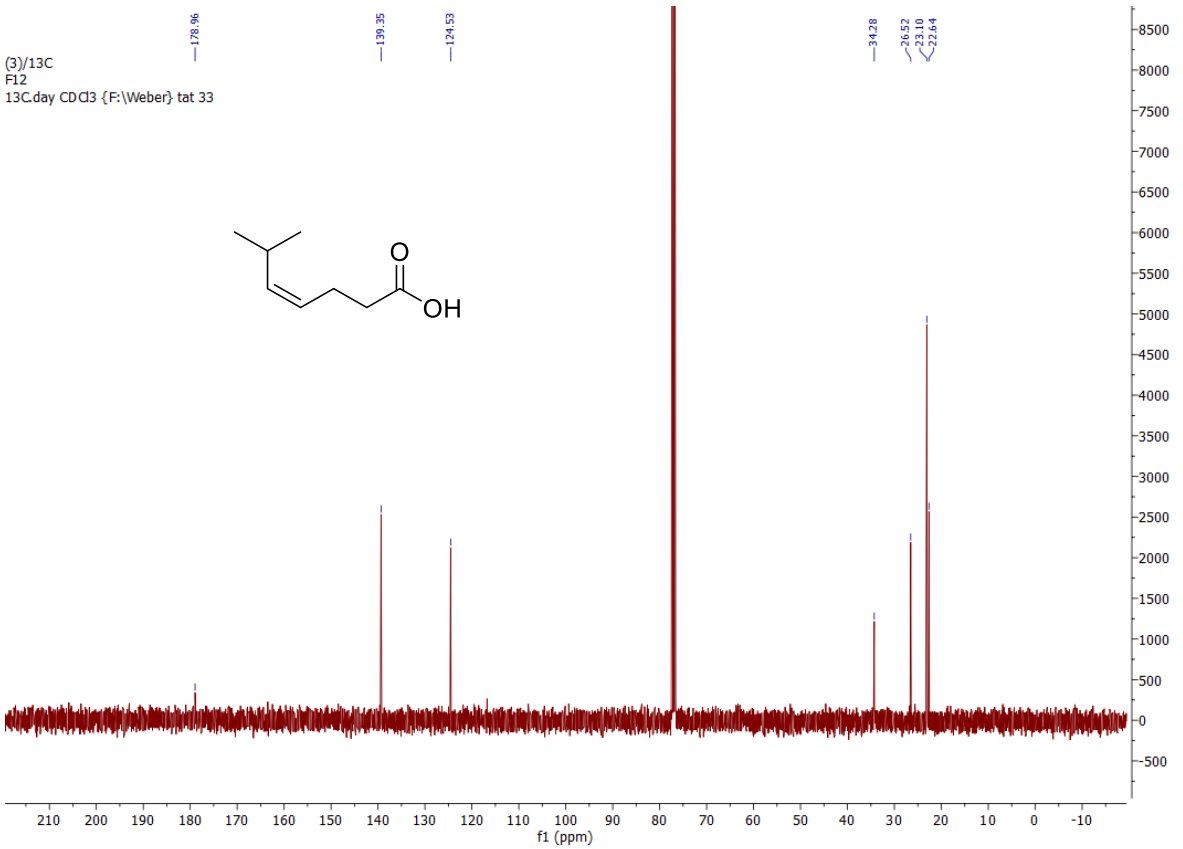
(*Z*)-7-methyloct-5-enoic acid (1r): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$).



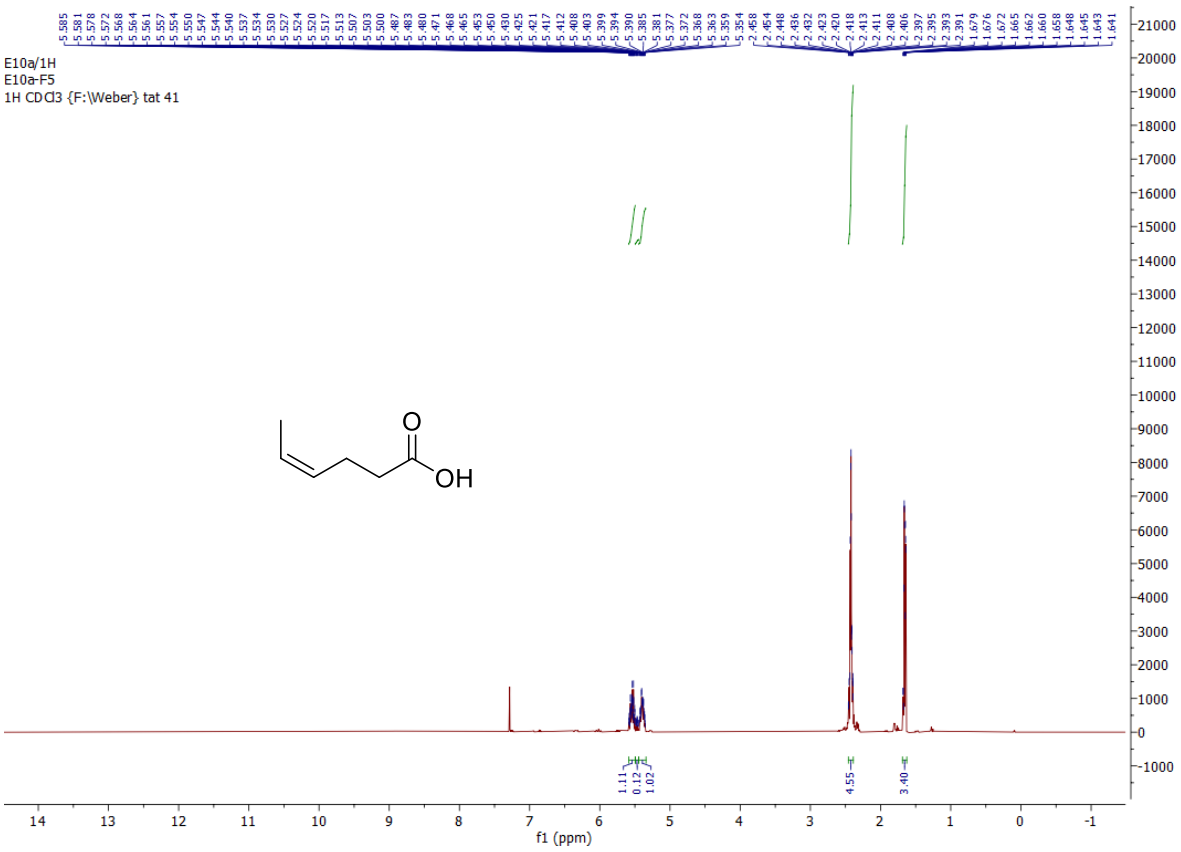


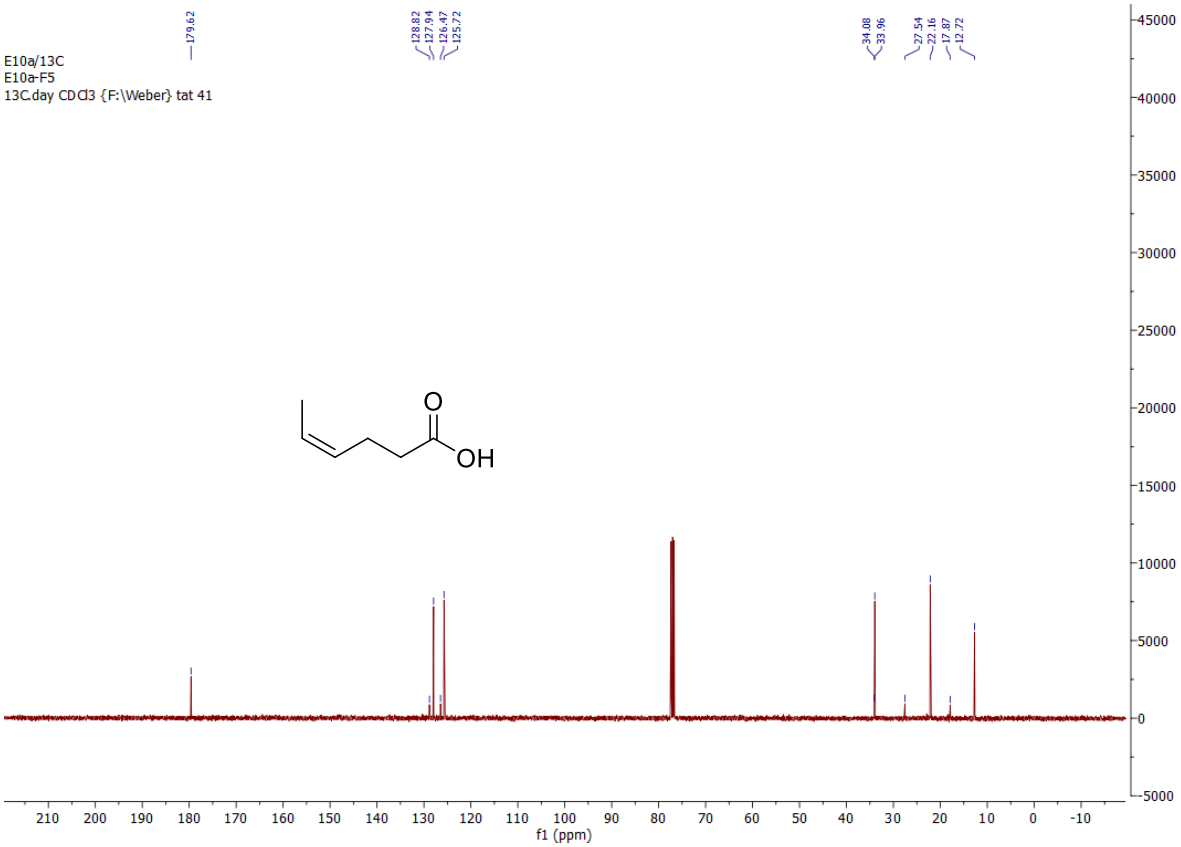
(*Z*)-6-methylhept-4-enoic acid (1s): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$).



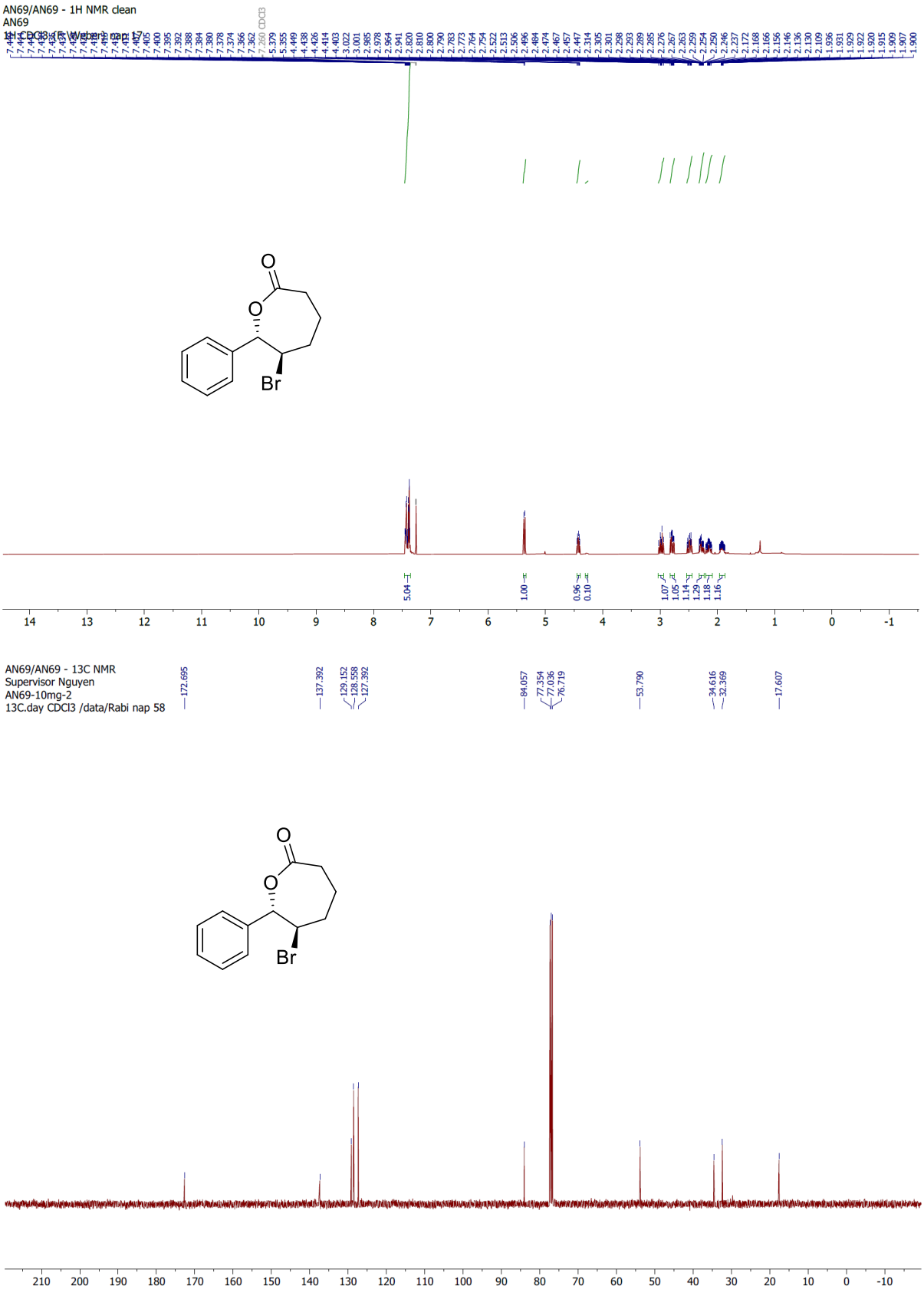


(Z)-hex-4-enoic acid (1t): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$).

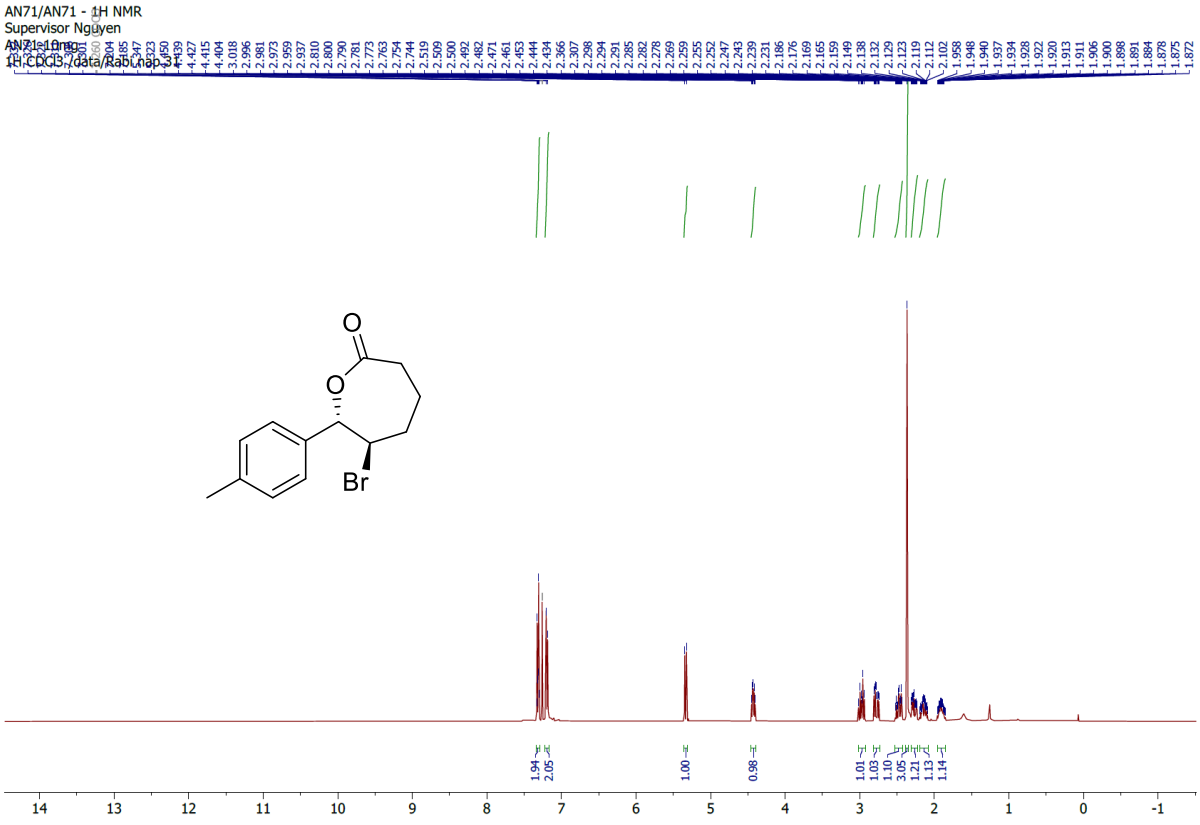


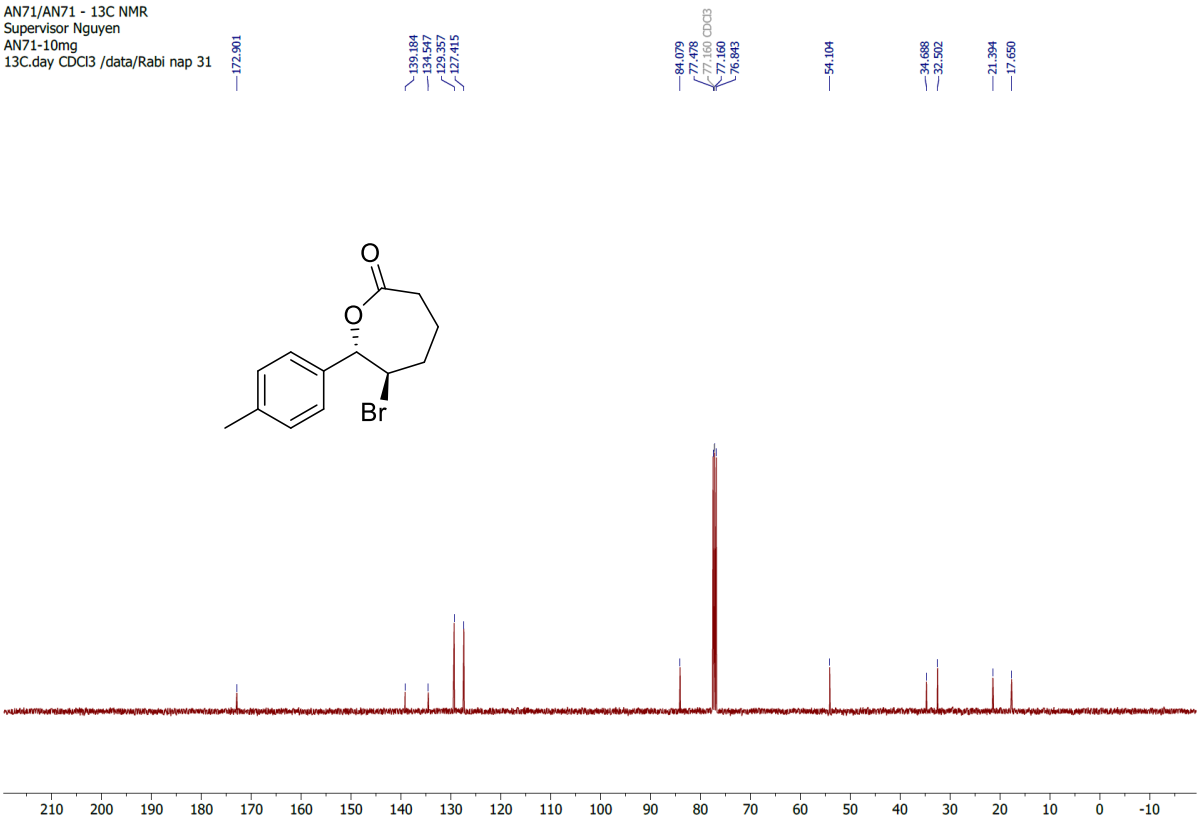


6-bromo-7-phenyloxepan-2-one (2a): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

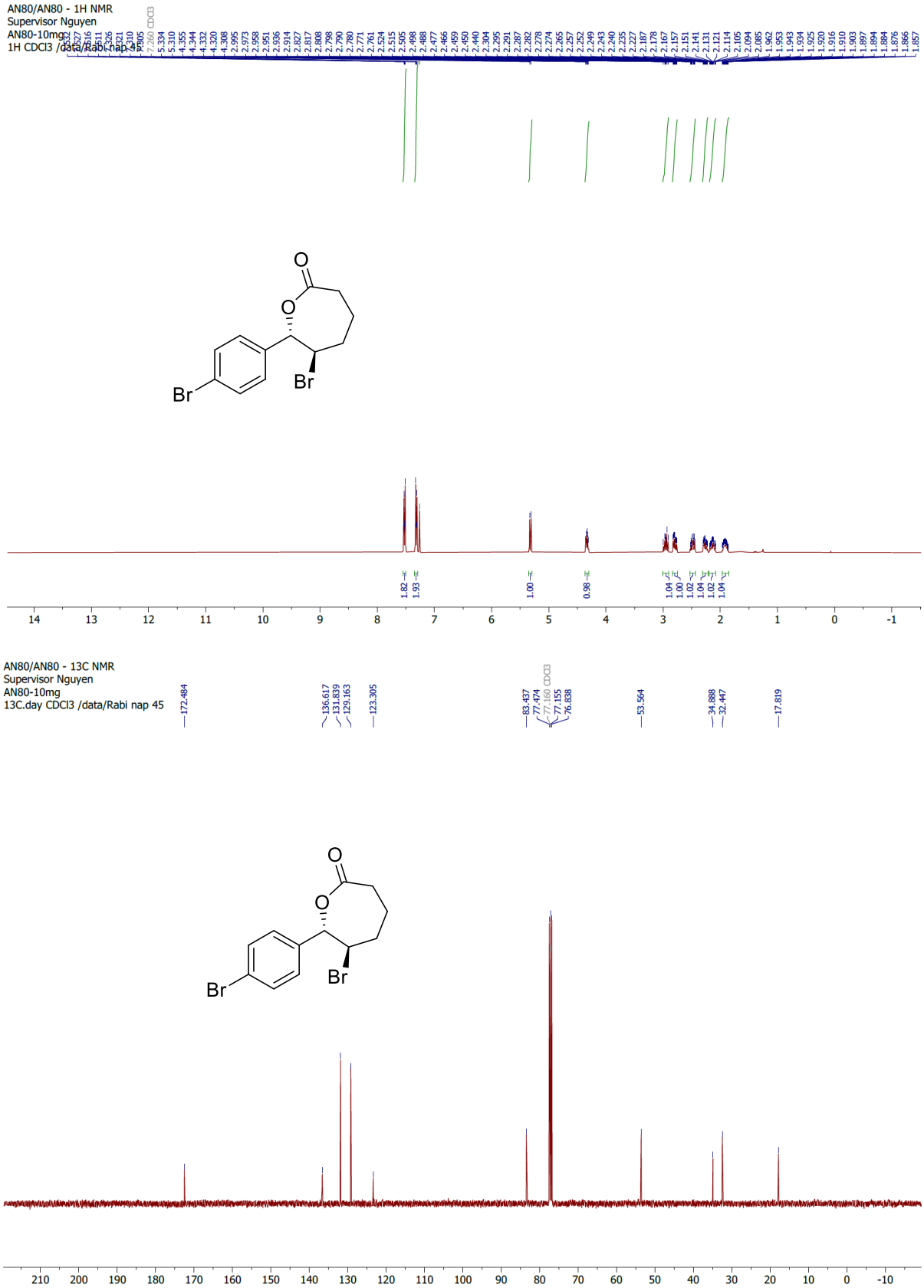


6-bromo-7-(*p*-tolyl)oxepan-2-one (2b): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

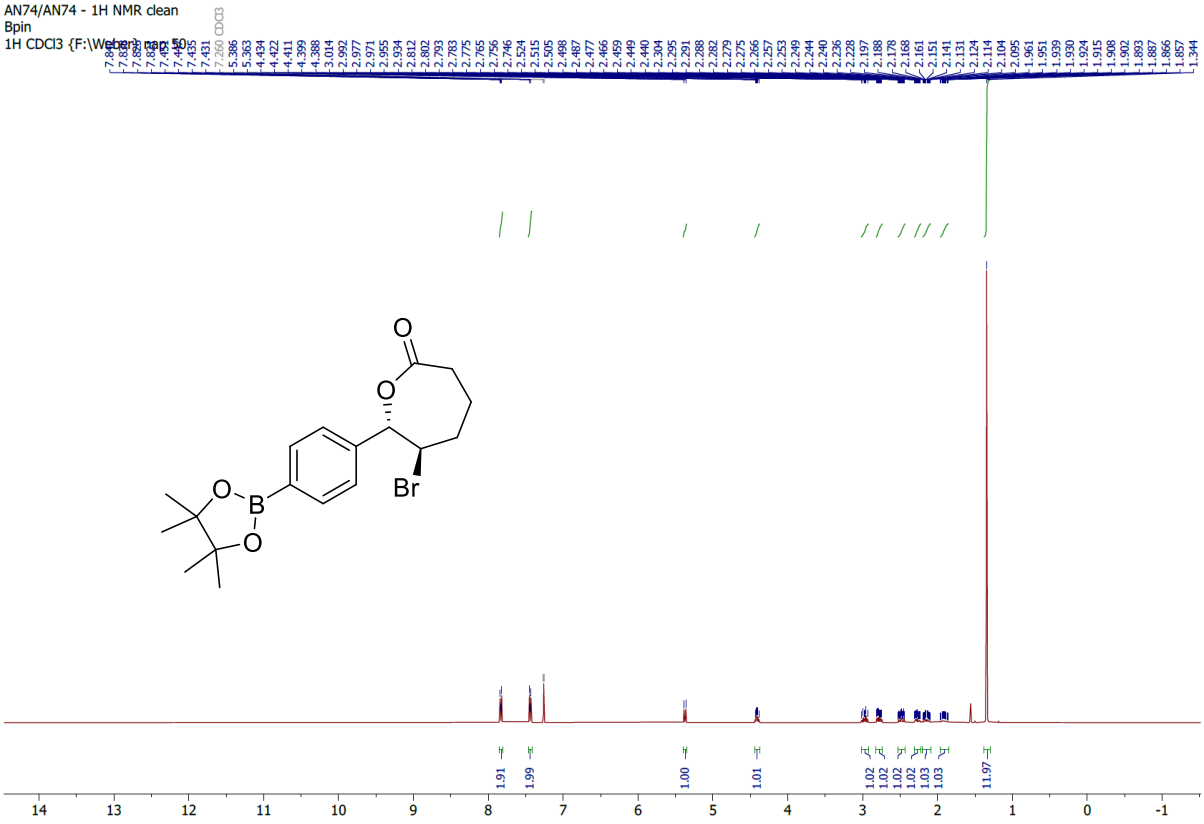


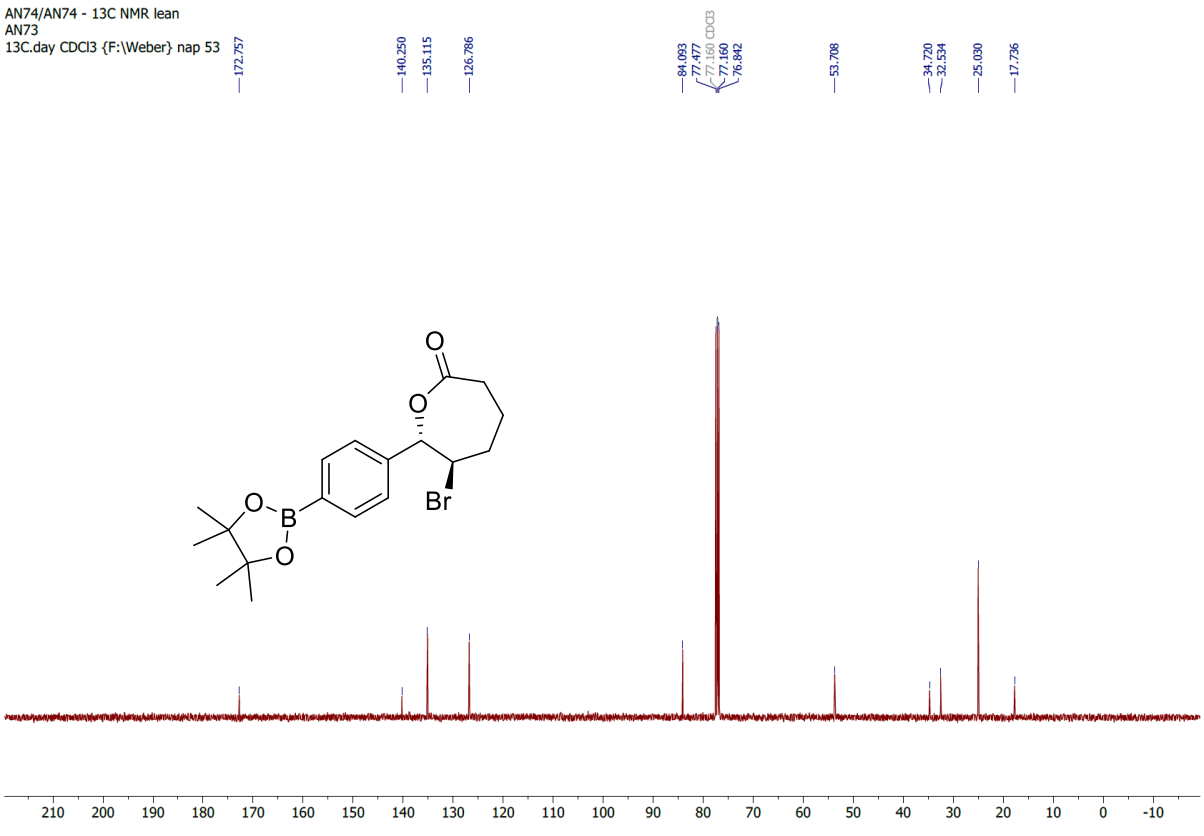


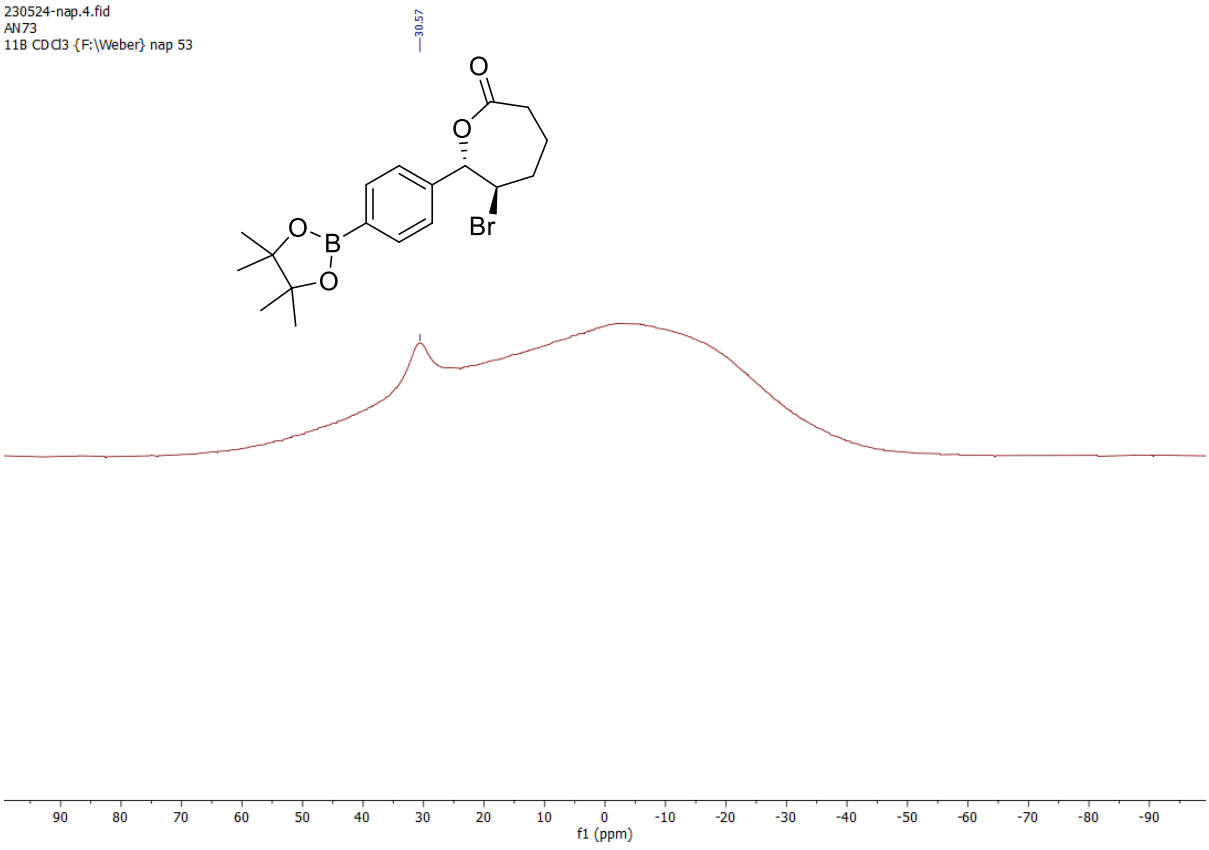
6-bromo-7-(4-bromophenyl)oxepan-2-one (2c): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



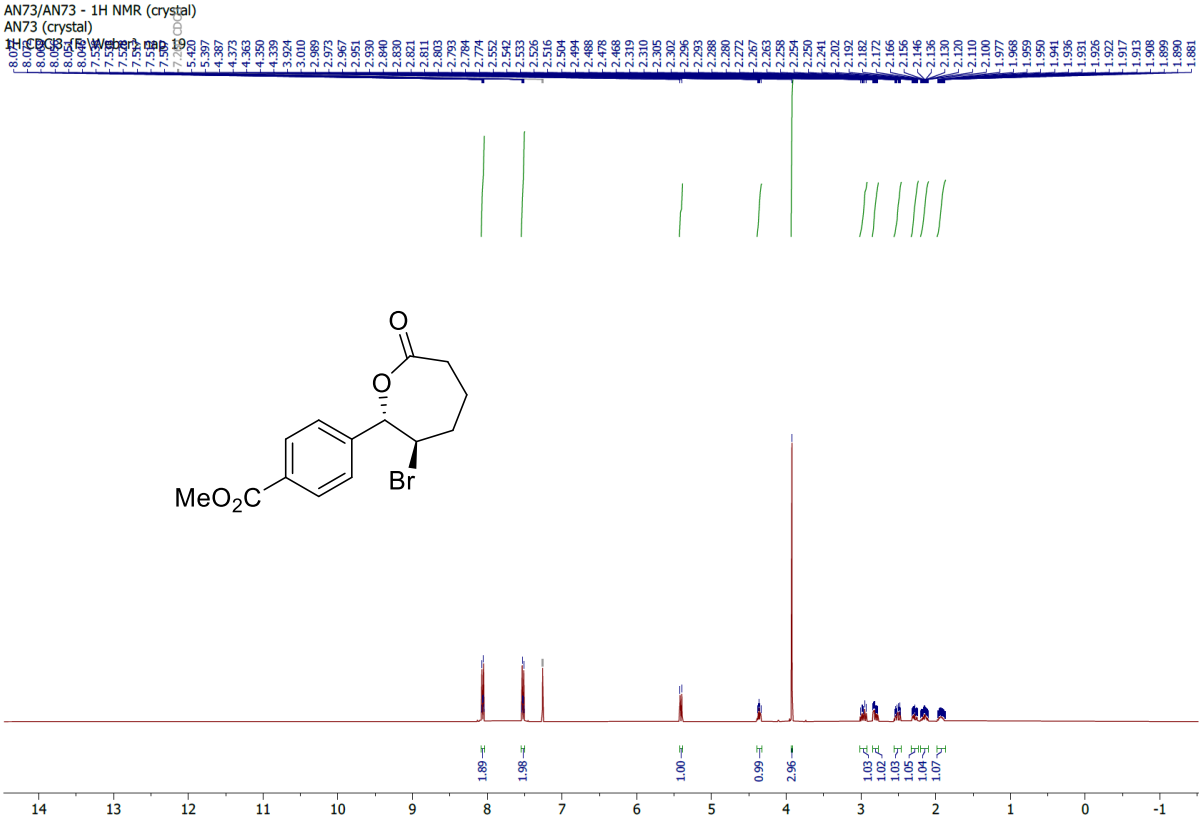
6-bromo-7-(4-(4,4,5,5 tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)oxepan-2-one (2d): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{11}B NMR (128 MHz, $CDCl_3$)

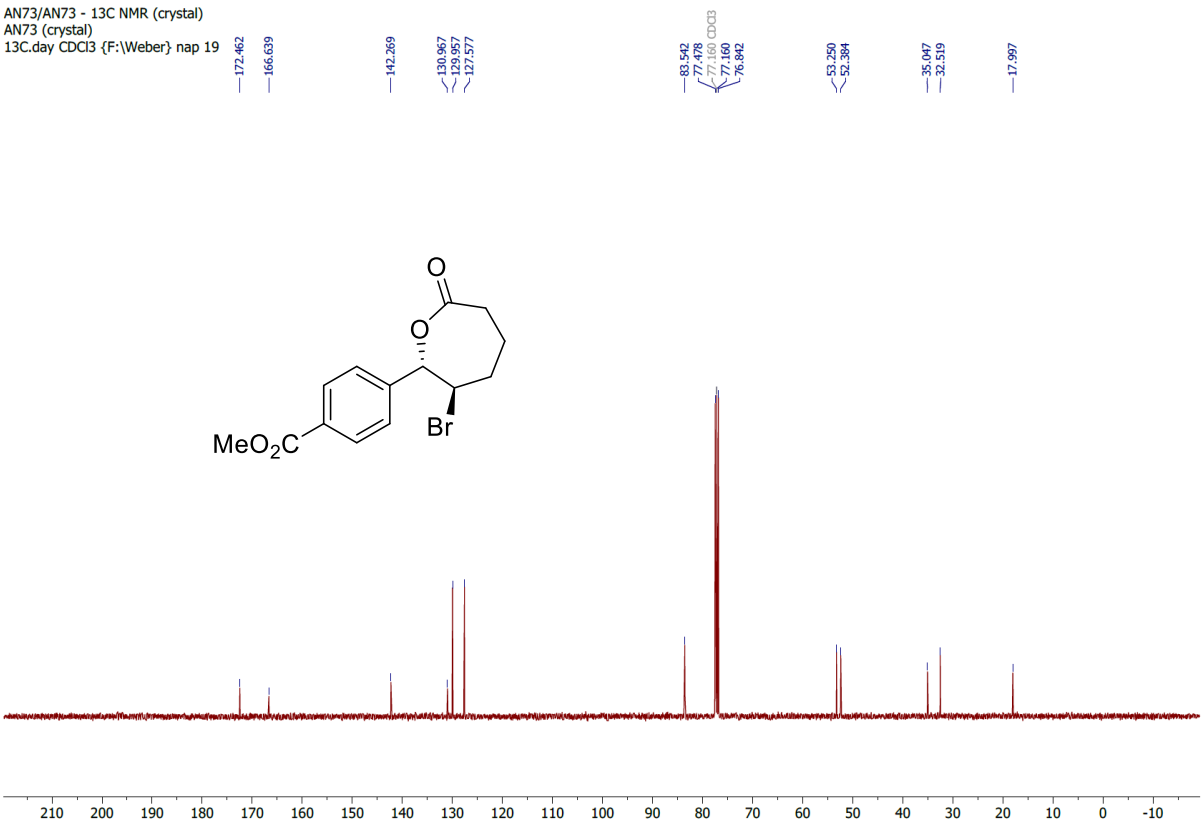




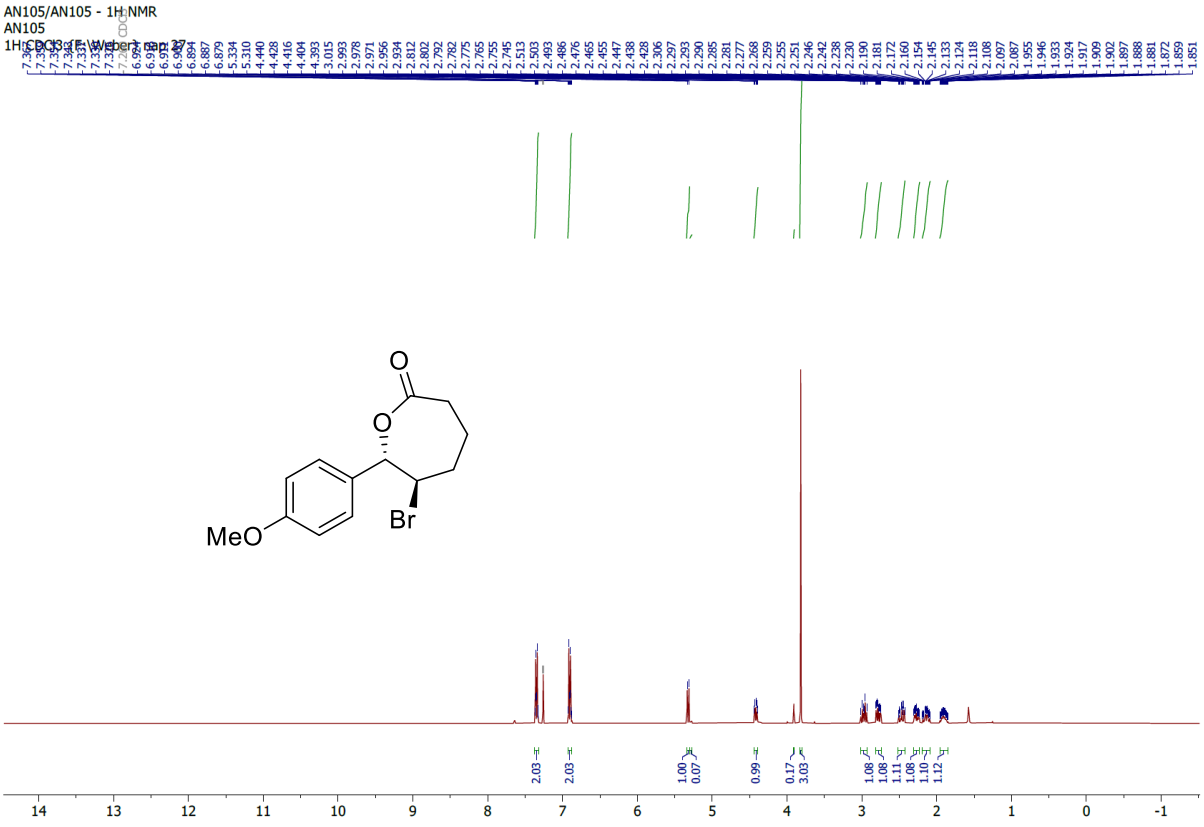

230524-nap.4.fid
AN73
11B CDCl3 {F:\Weber} nap 53
30.57
O
O
Br
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

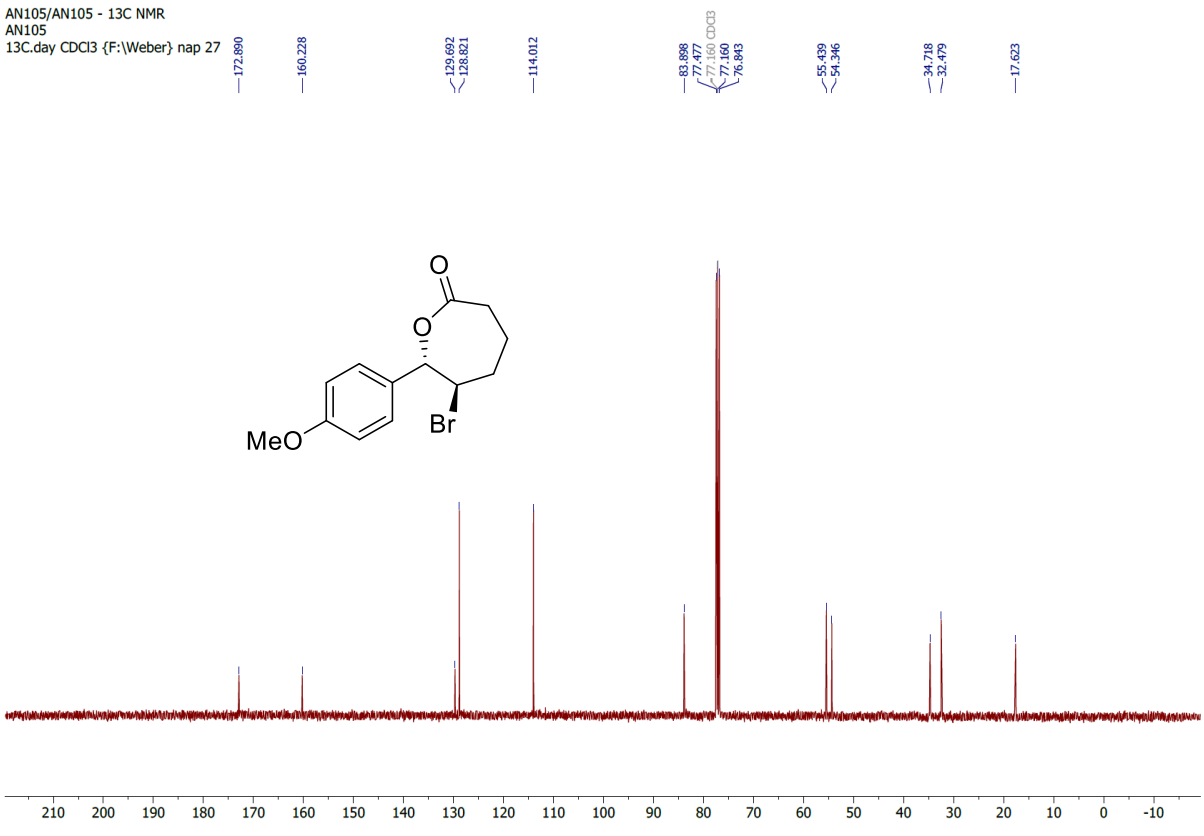
Methyl 4-(3-bromo-7-oxooxepan-2-yl)benzoate (2e): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



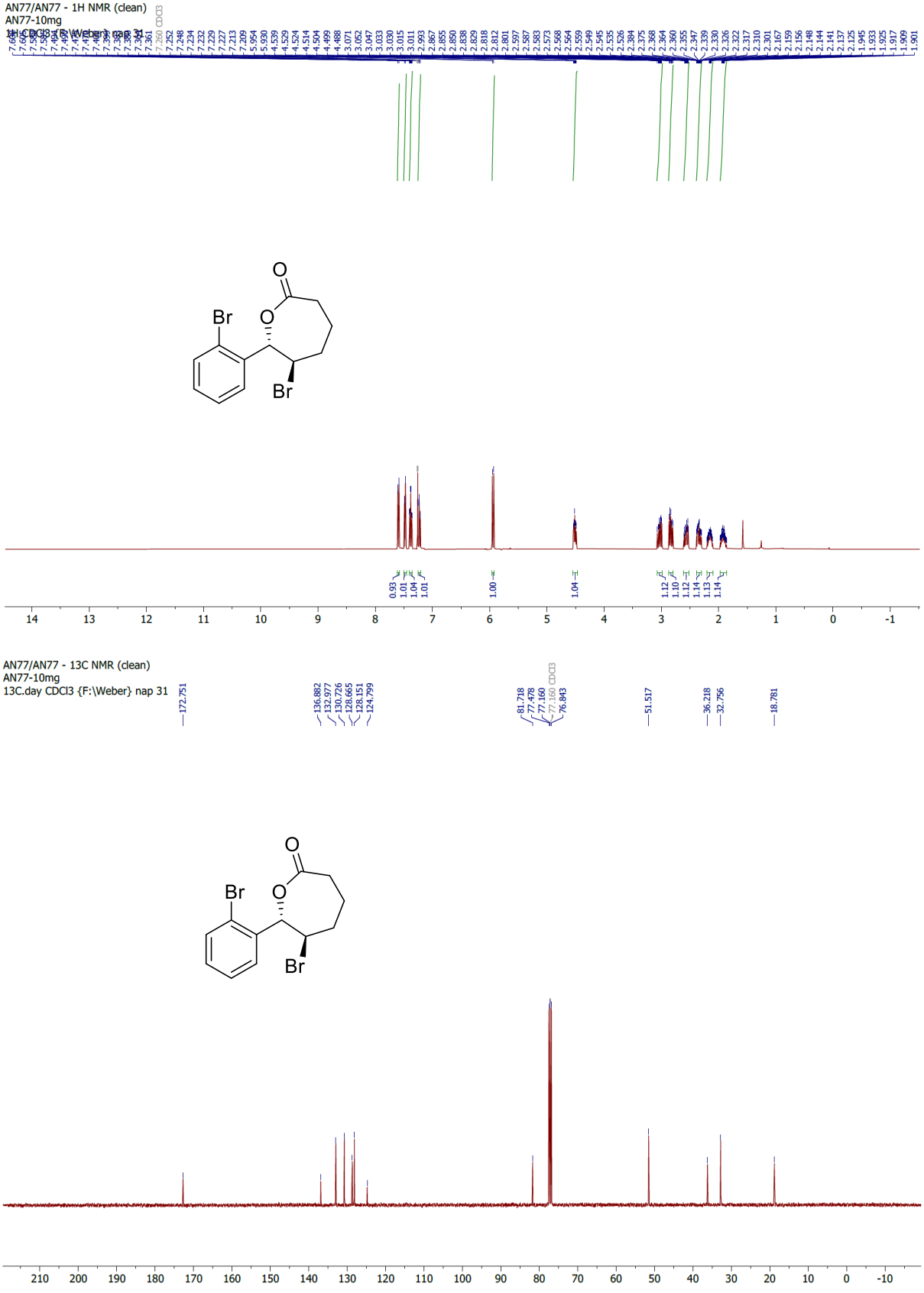


6-bromo-7-(4-methoxyphenyl)oxepan-2-one (2f): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

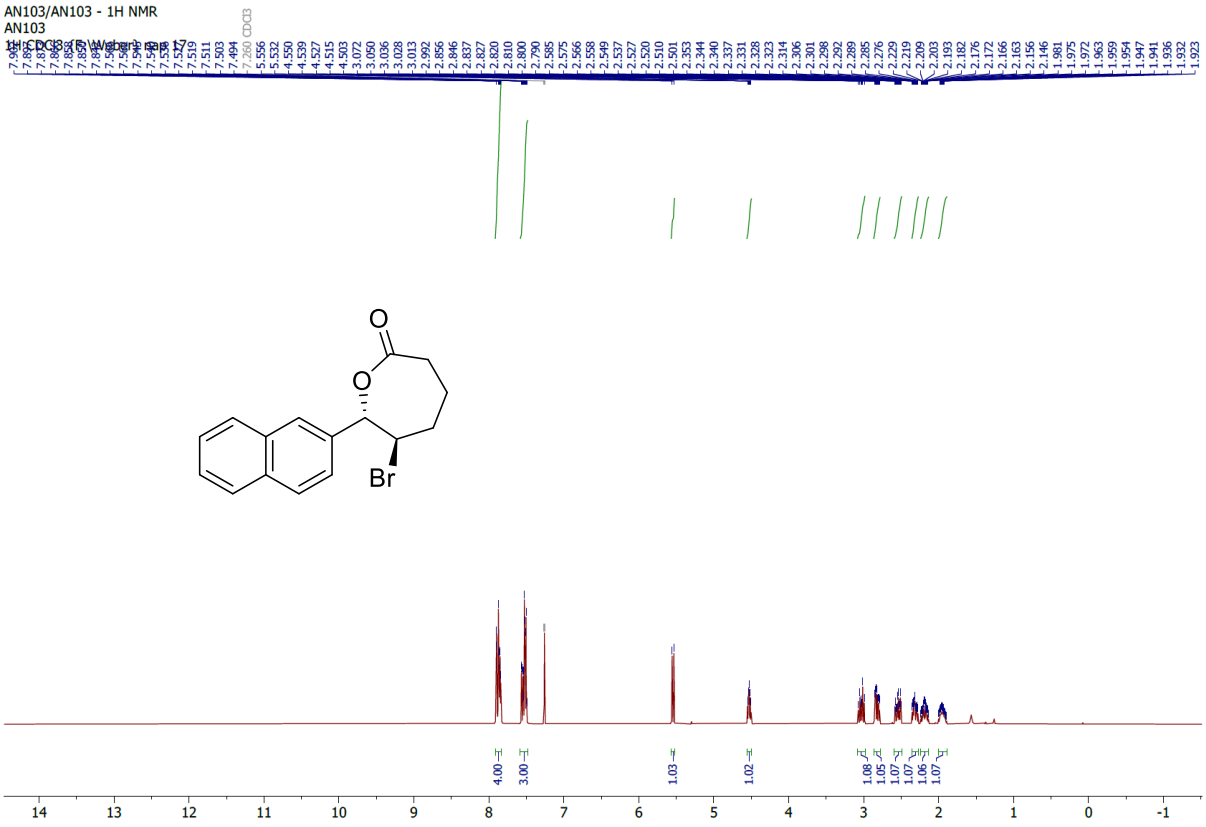


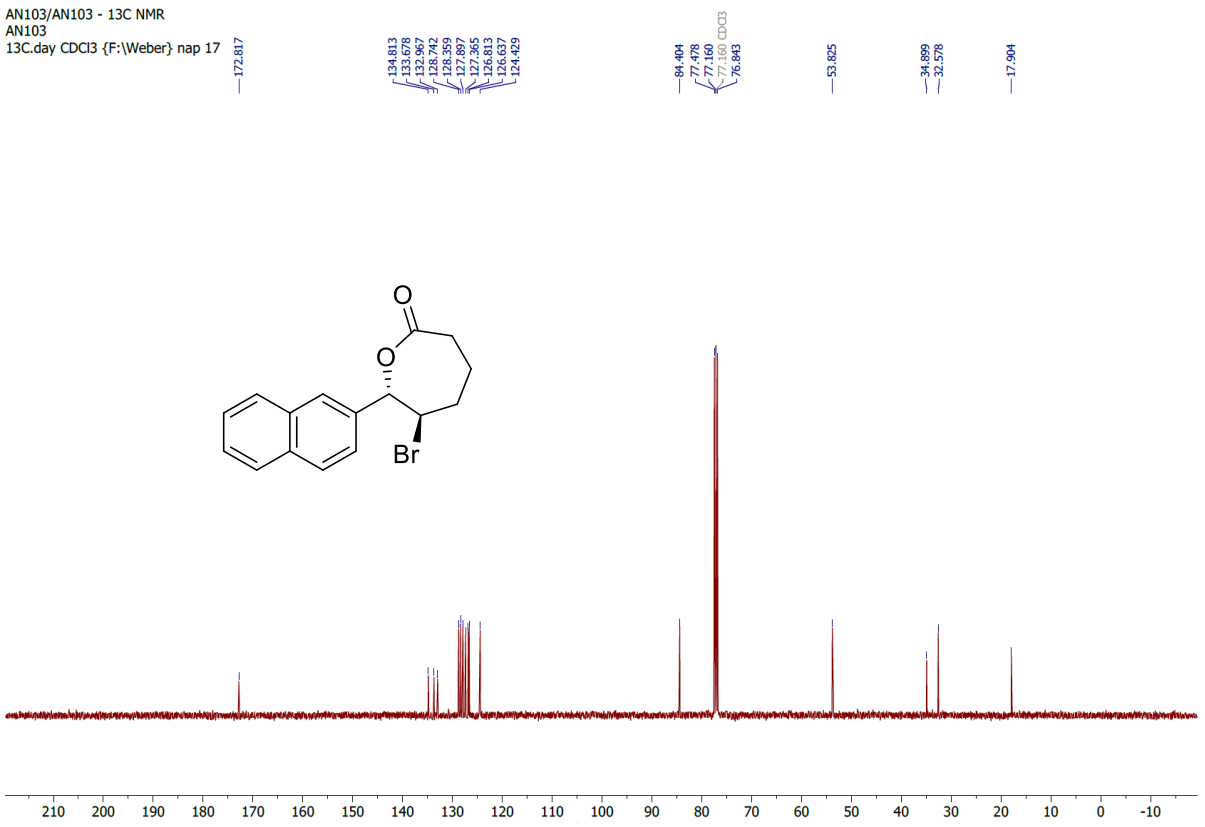


6-bromo-7-(2-bromophenyl)oxepan-2-one (2g): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

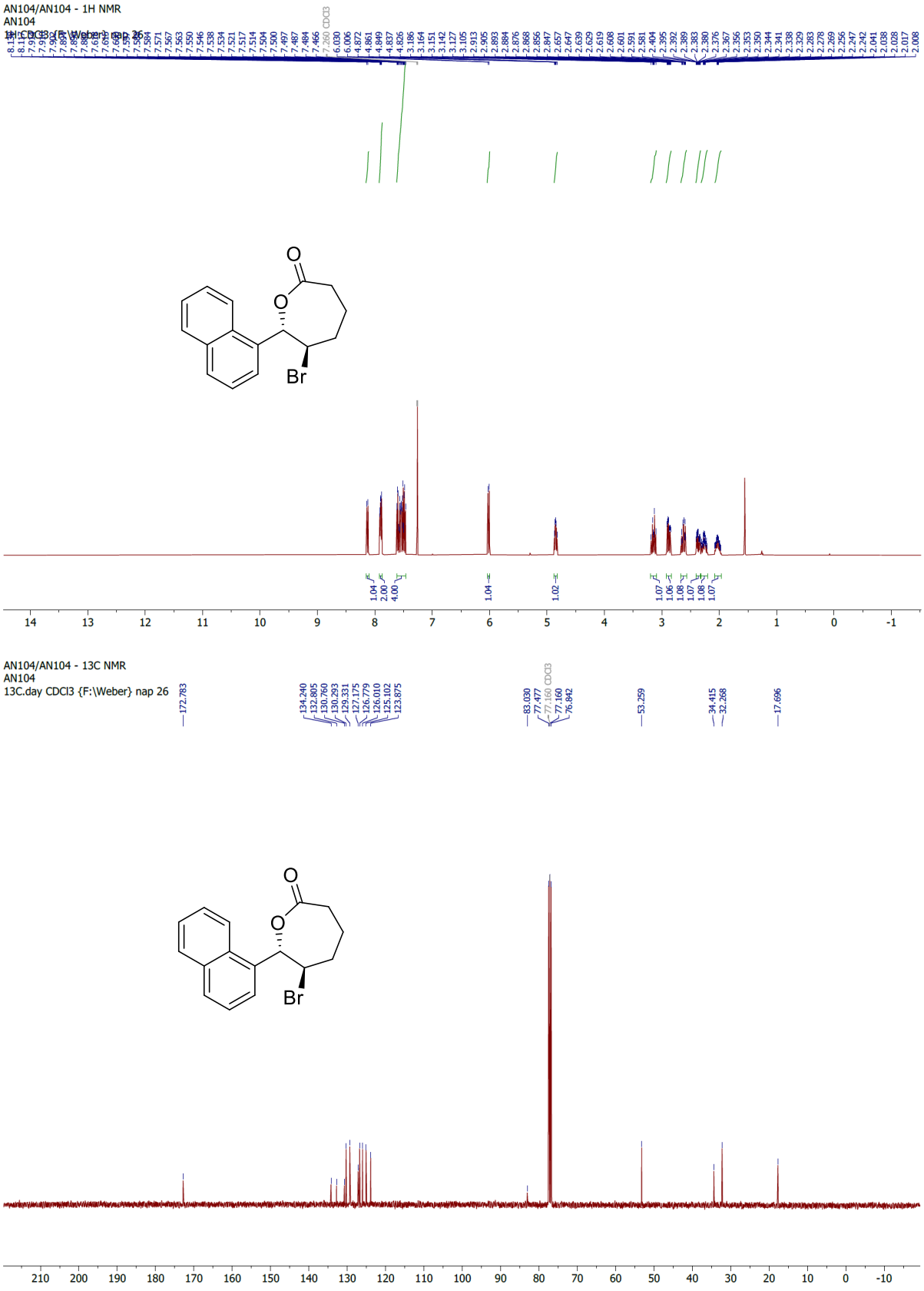


6-bromo-7-(naphthalen-2-yl)oxepan-2-one (2h): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

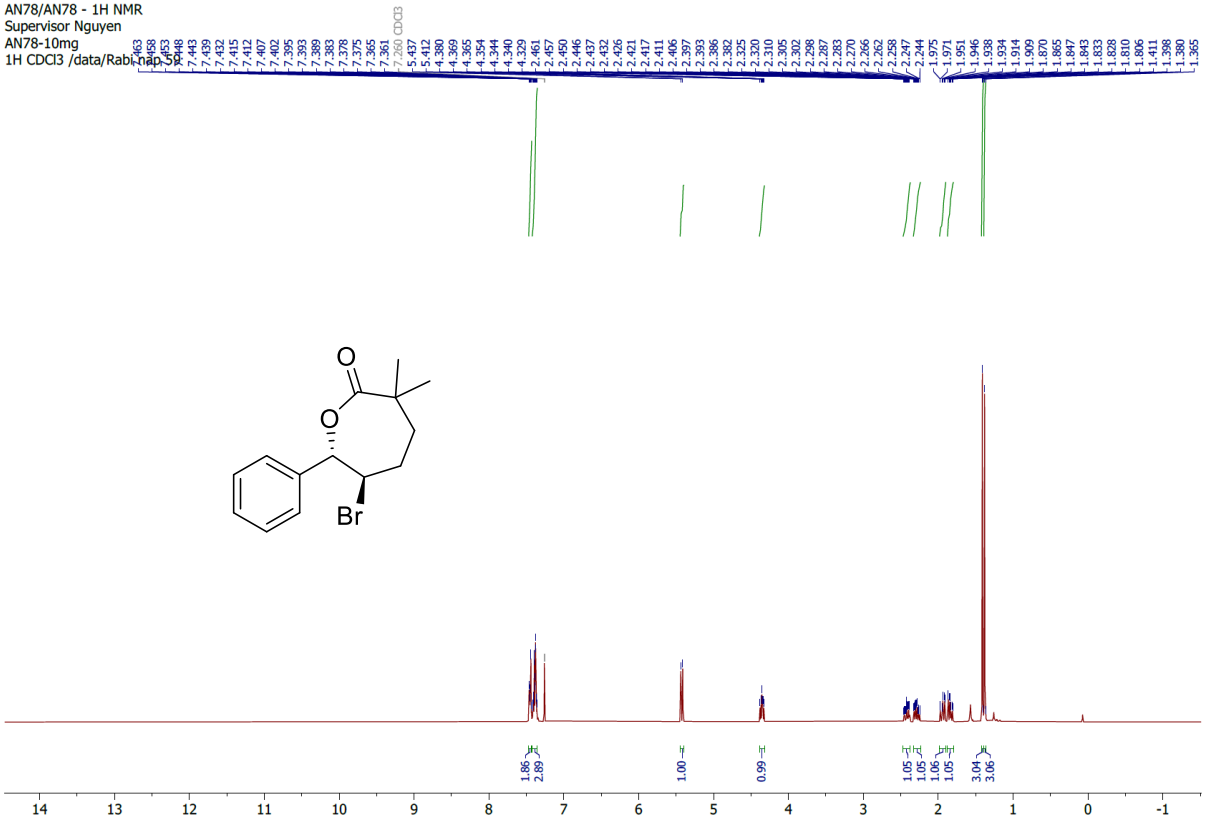


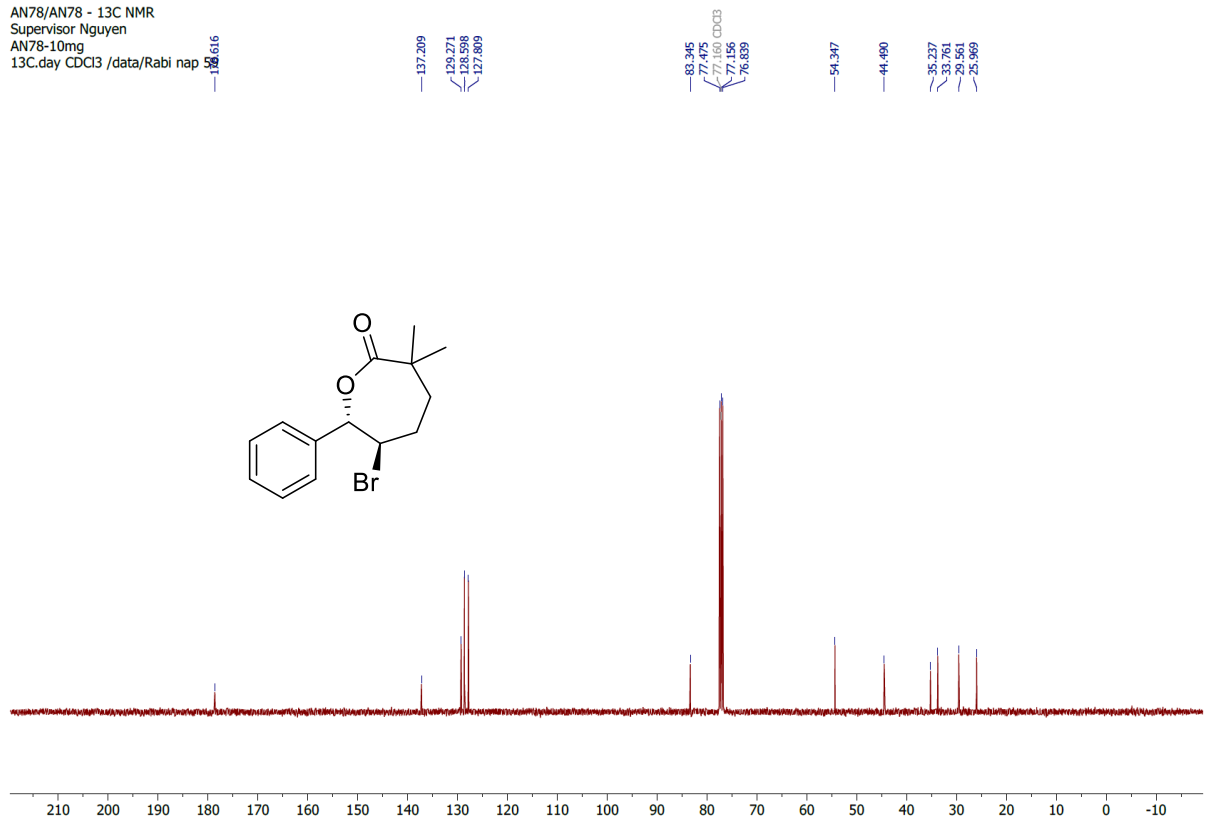


6-bromo-7-(naphthalen-1-yl)oxepan-2-one (2i): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

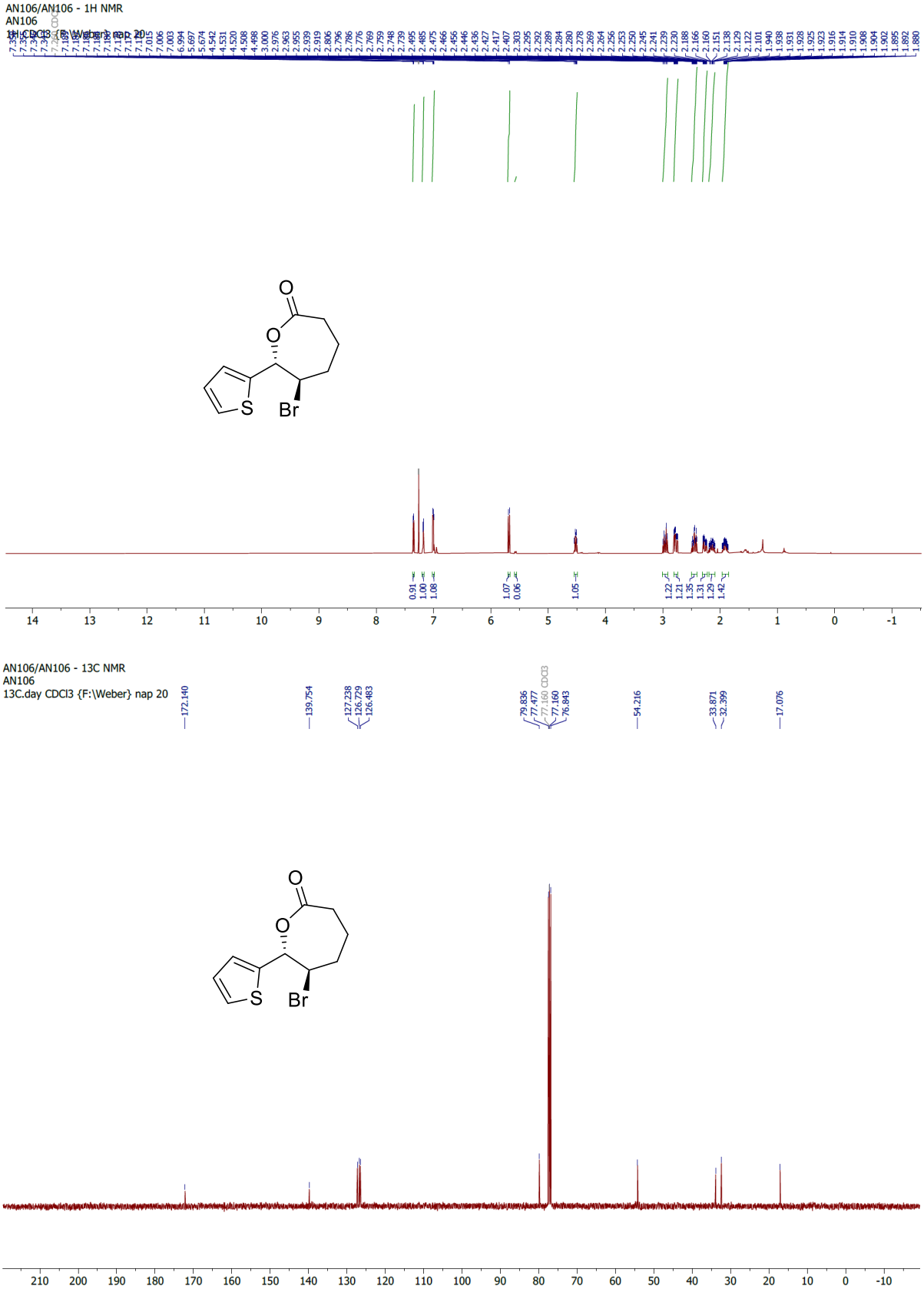


6-bromo-3,3-dimethyl-7-phenyloxepan-2-one (2j): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

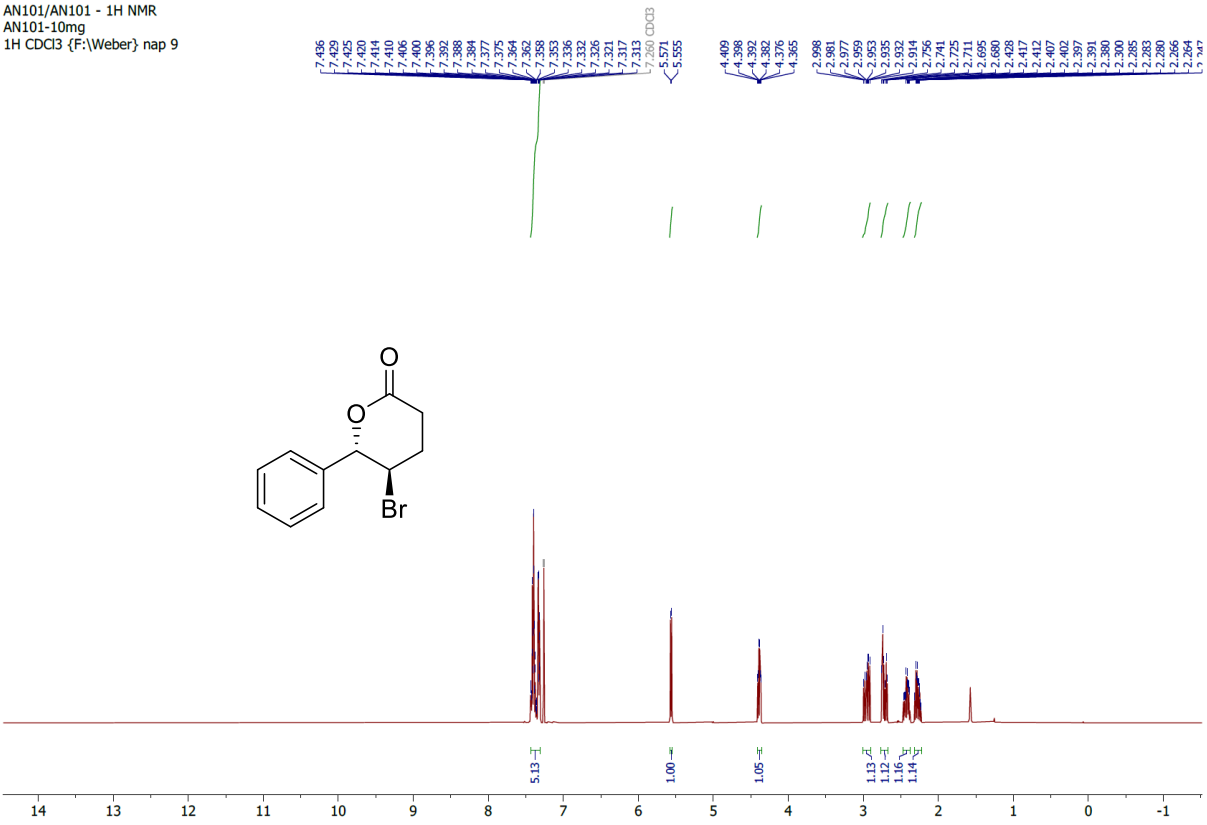


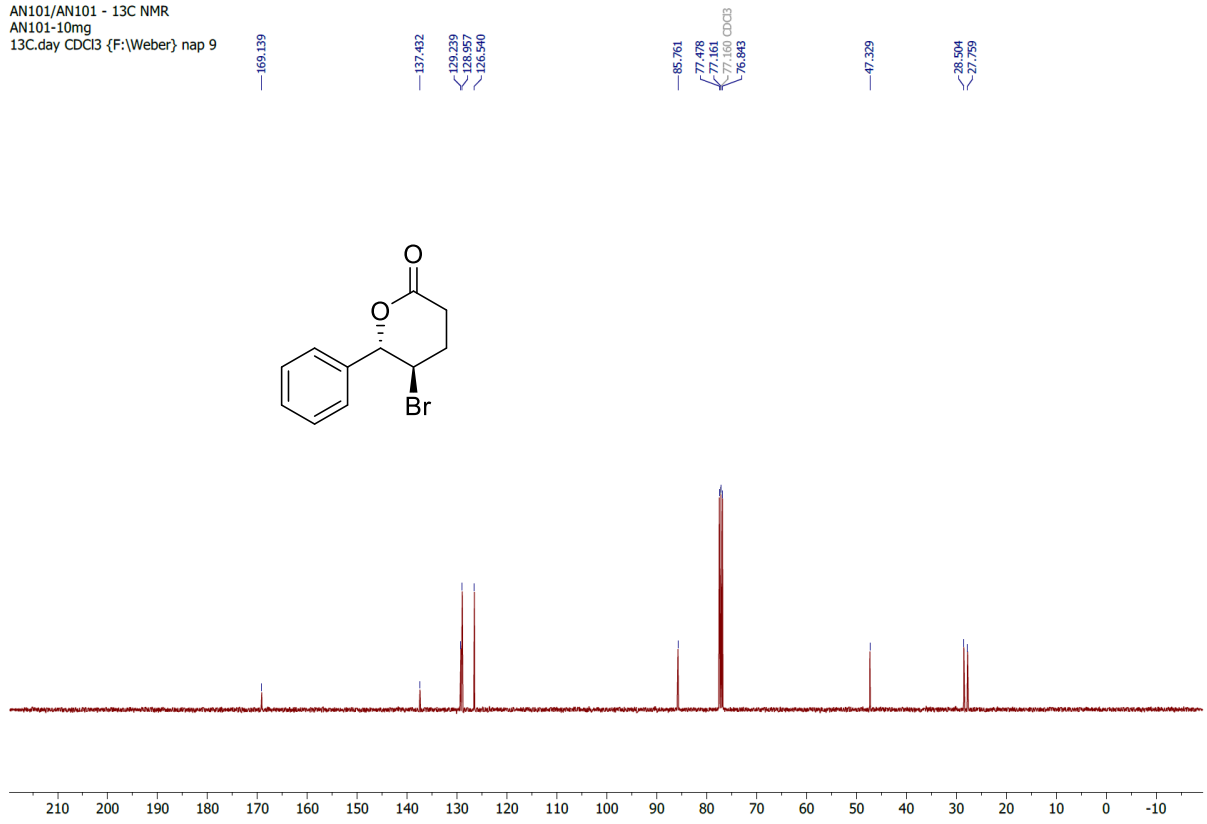


6-bromo-7-(thiophen-2-yl)oxepan-2-one (2k): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

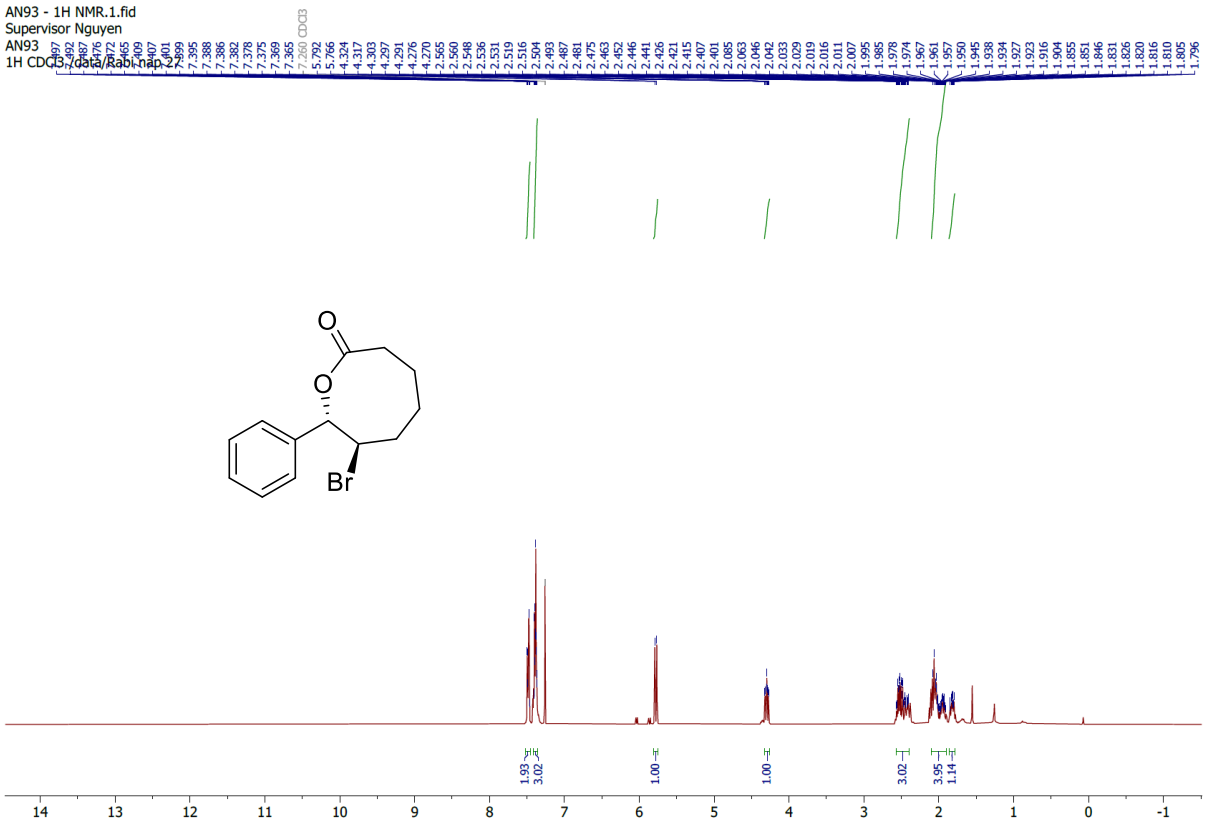


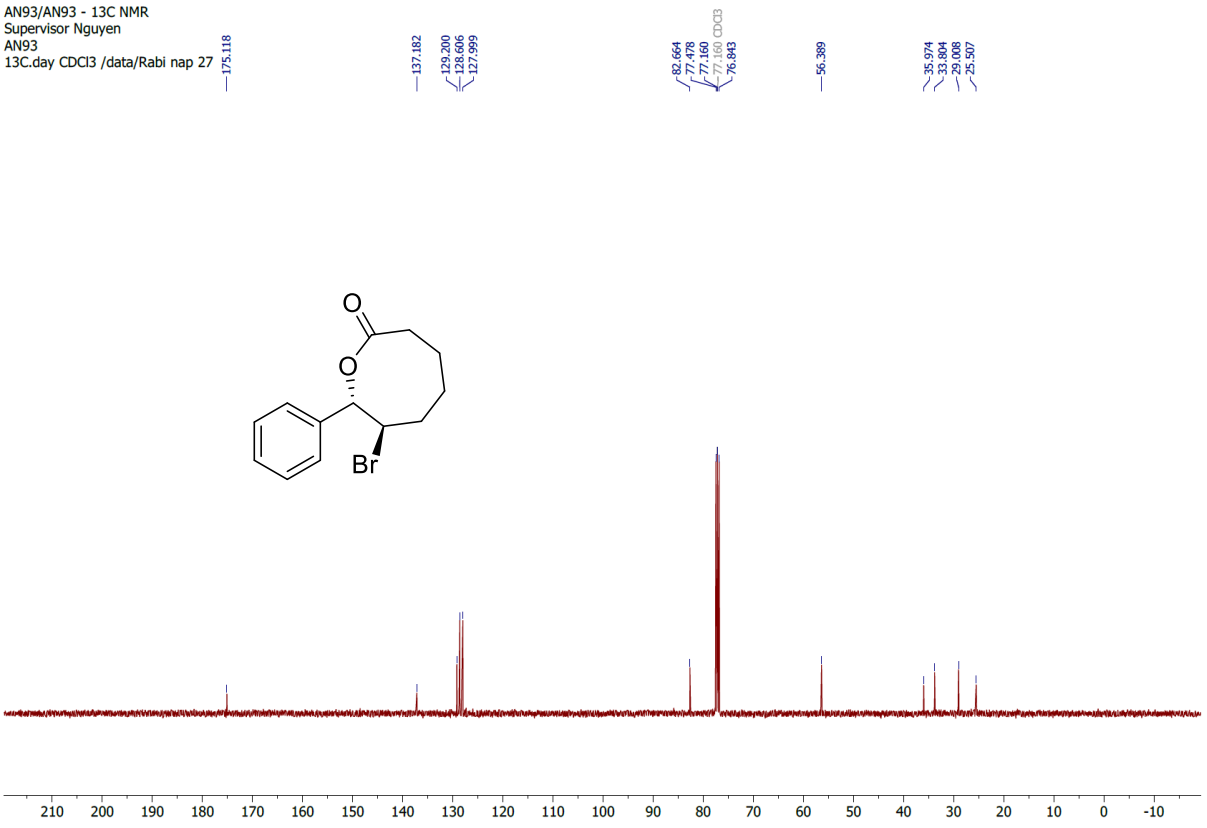
5-bromo-6-phenyltetrahydro-2*H*-pyran-2-one (2l): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



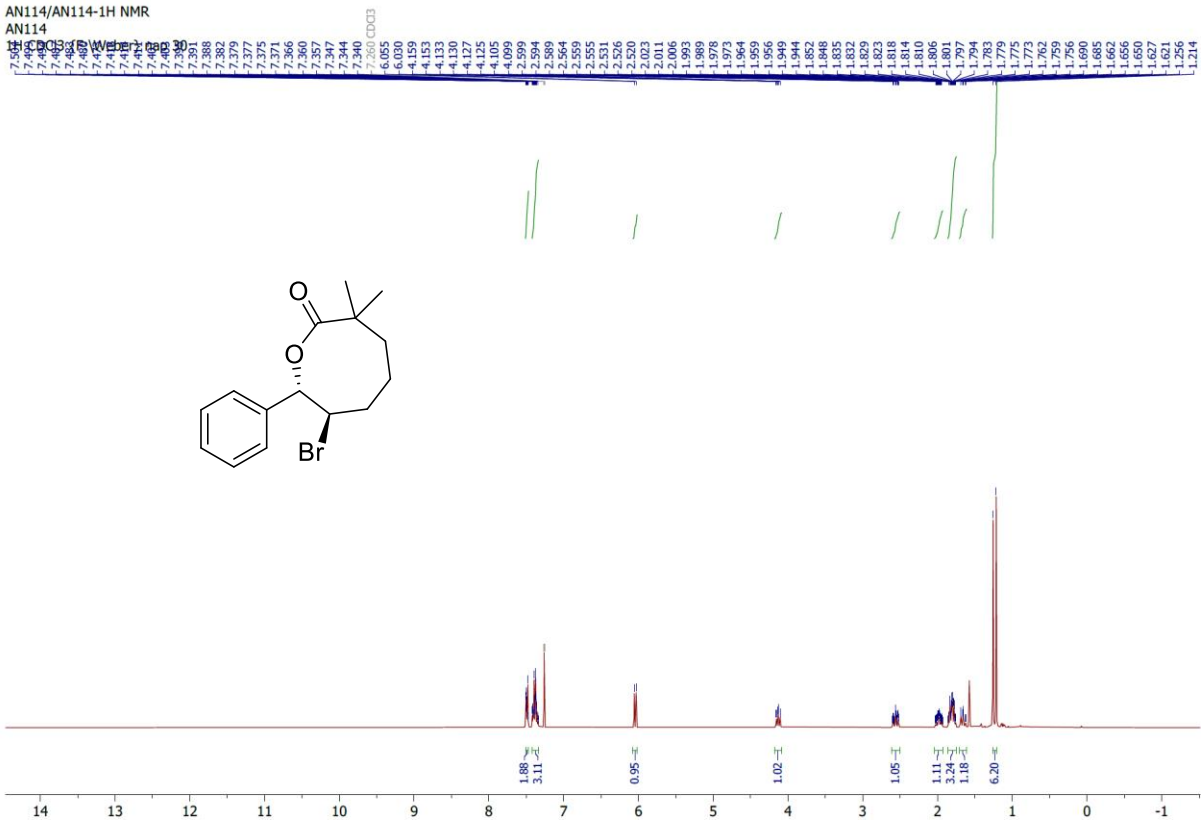


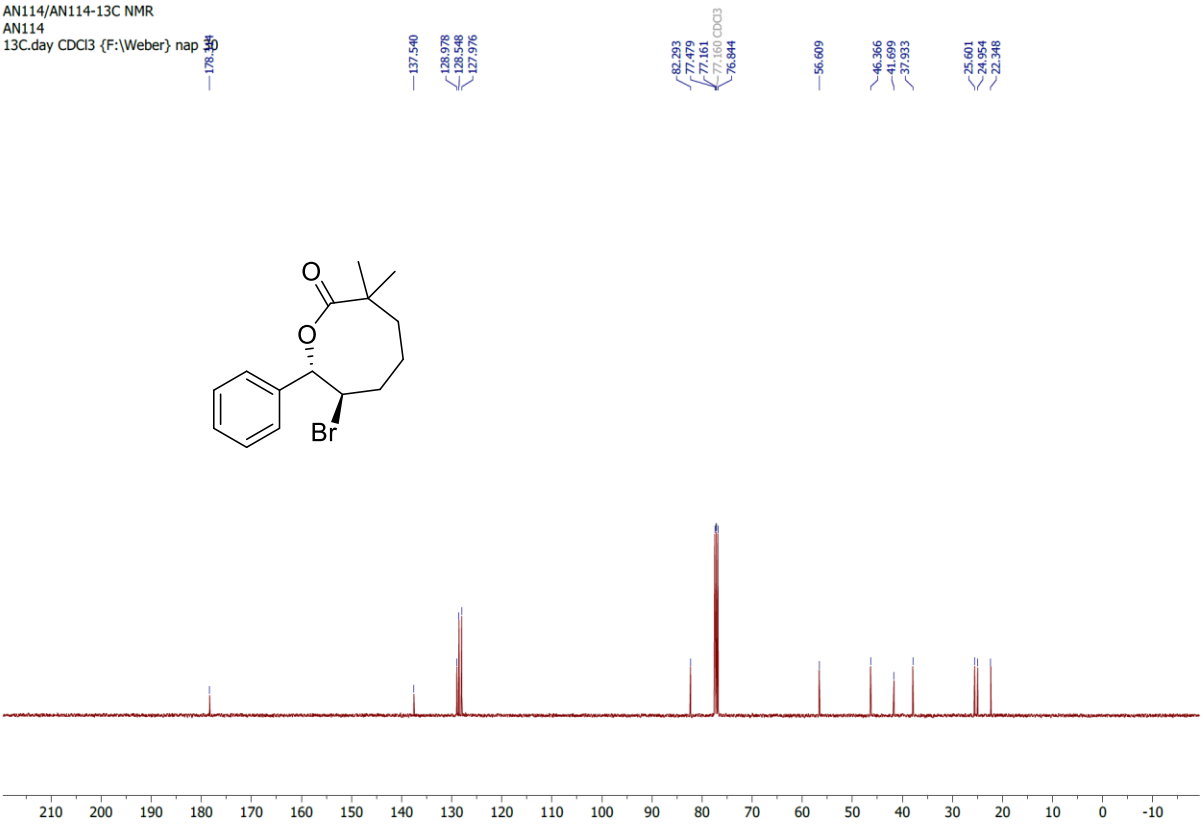
7-bromo-8-phenyloxocan-2-one (2m): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



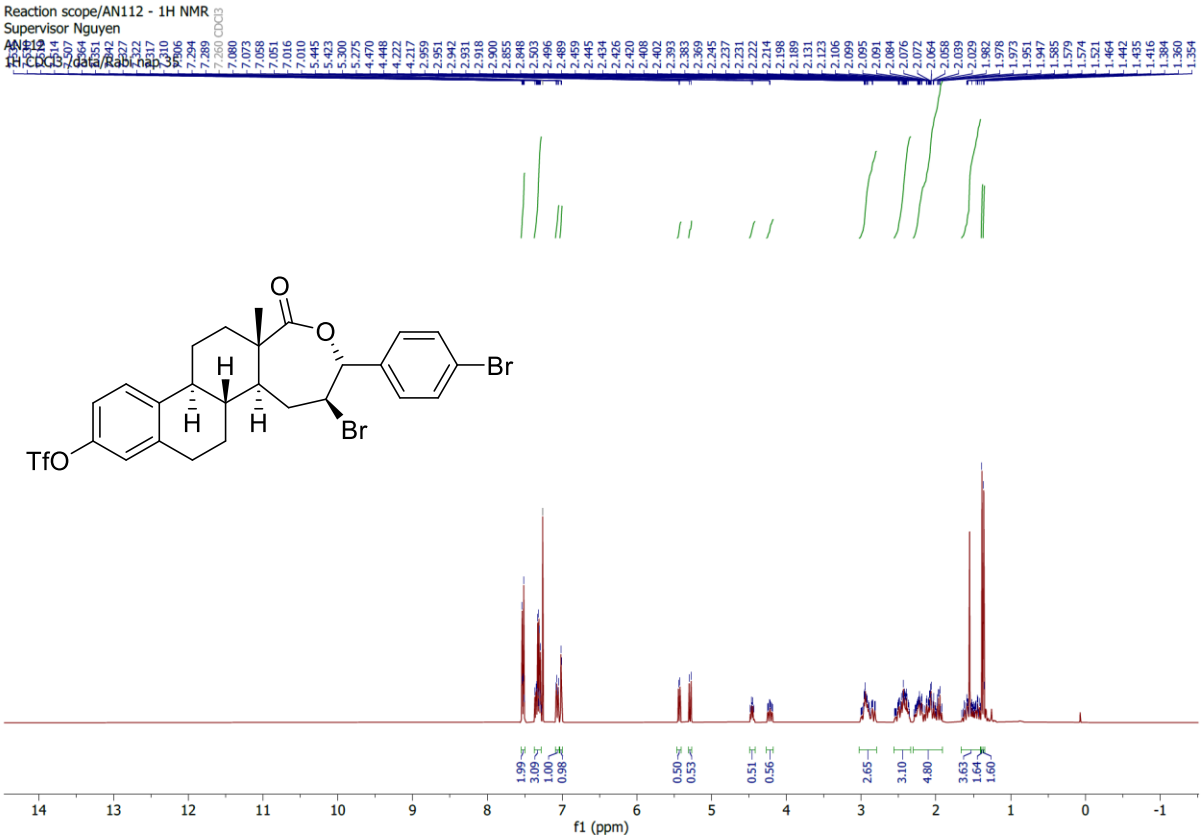


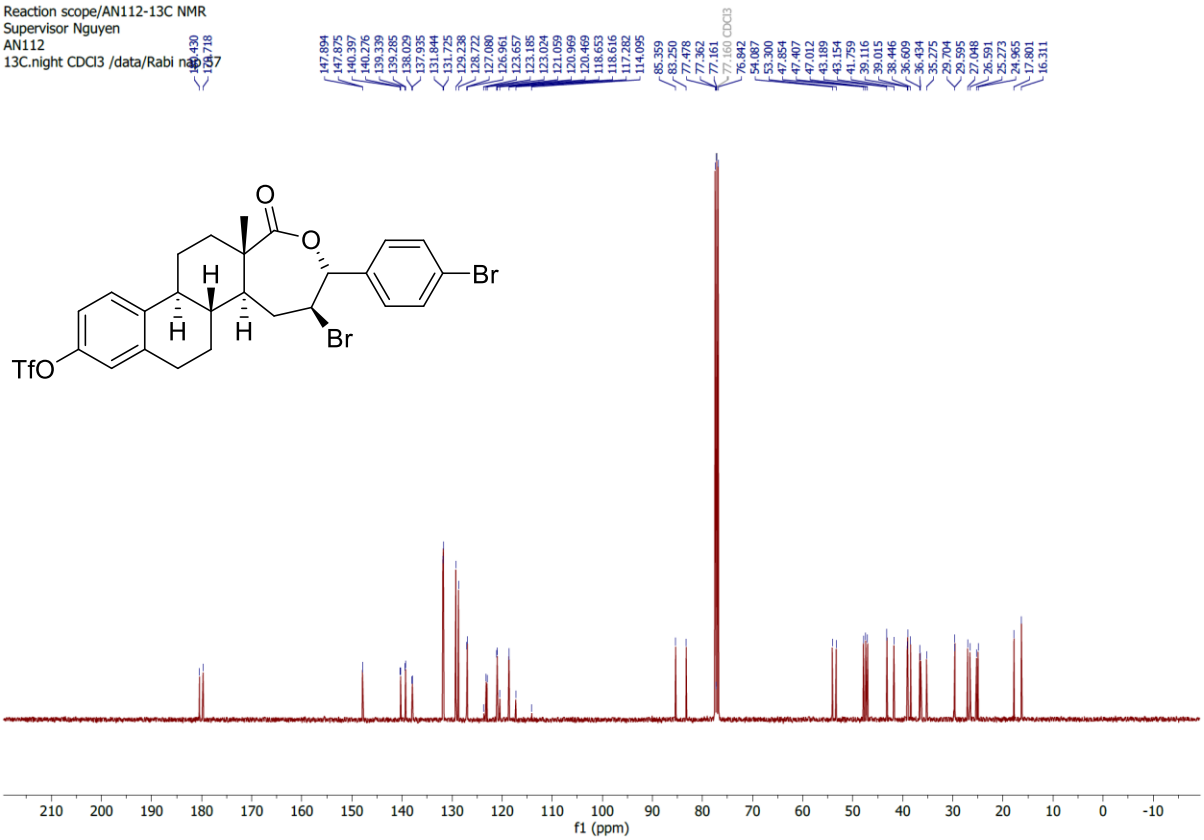
7-bromo-3,3-dimethyl-8-phenyloxocan-2-one (2n): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

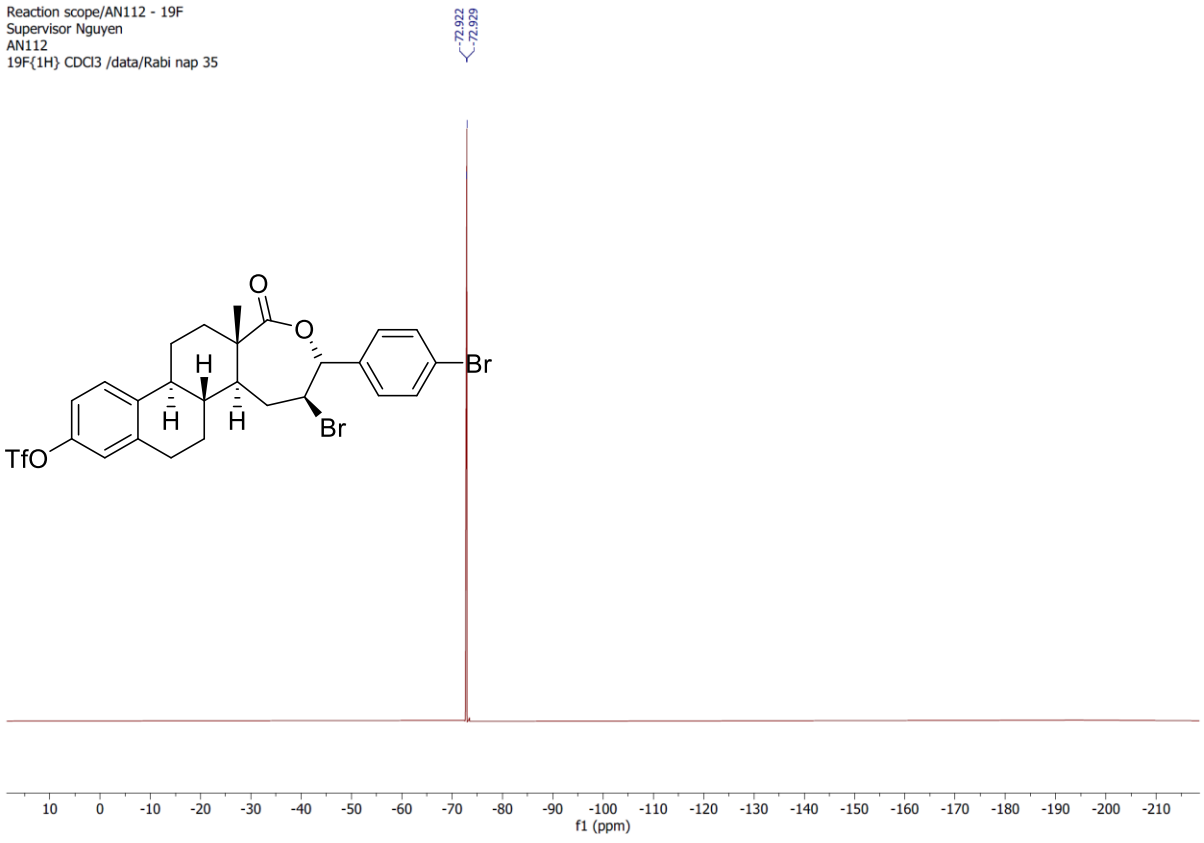




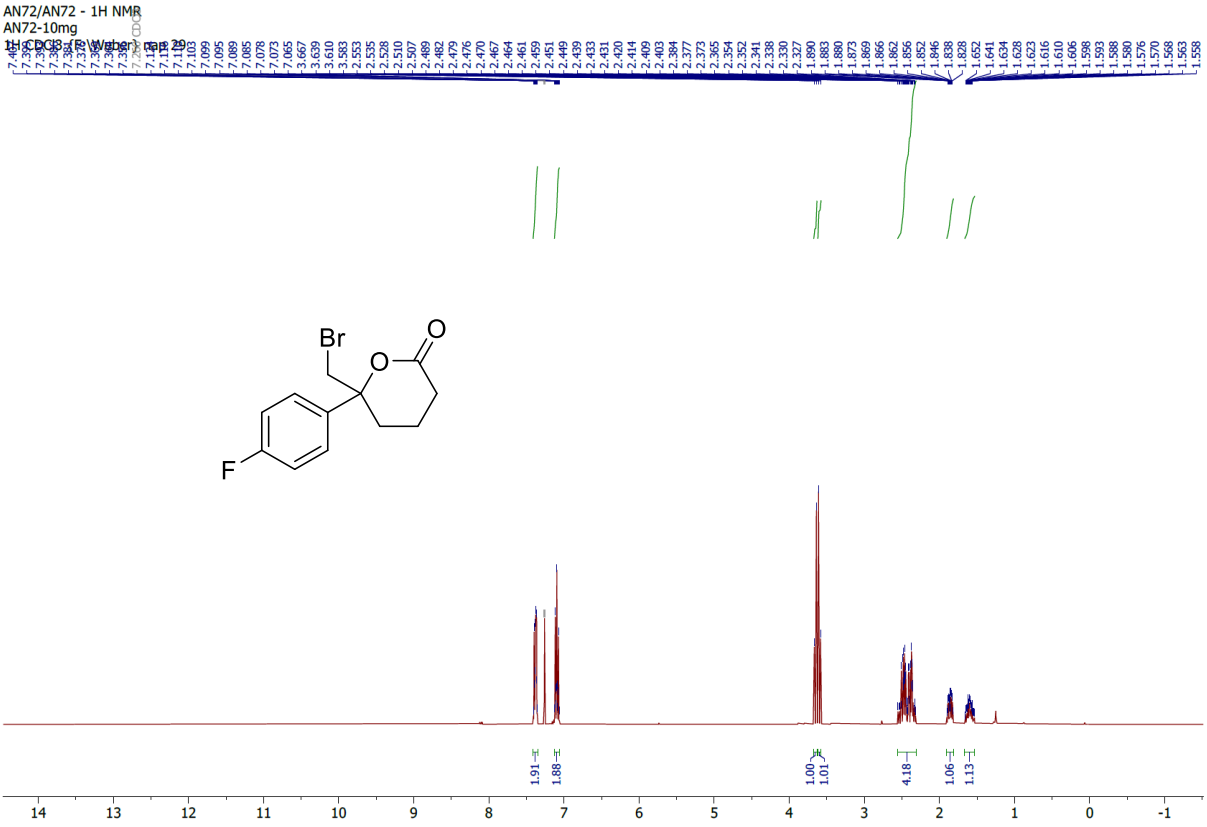
(5a*S*,5b*R*,11b*S*,13a*S*)-4-bromo-3-(4-bromophenyl)-13a-methyl-1-oxo 1,3,4,5,5a,5b,6,7,11b,12,13,13a-dodecahydrophenanthro[2,1-*c*]oxepin-9-yl trifluoromethanesulfonate (2o): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$)

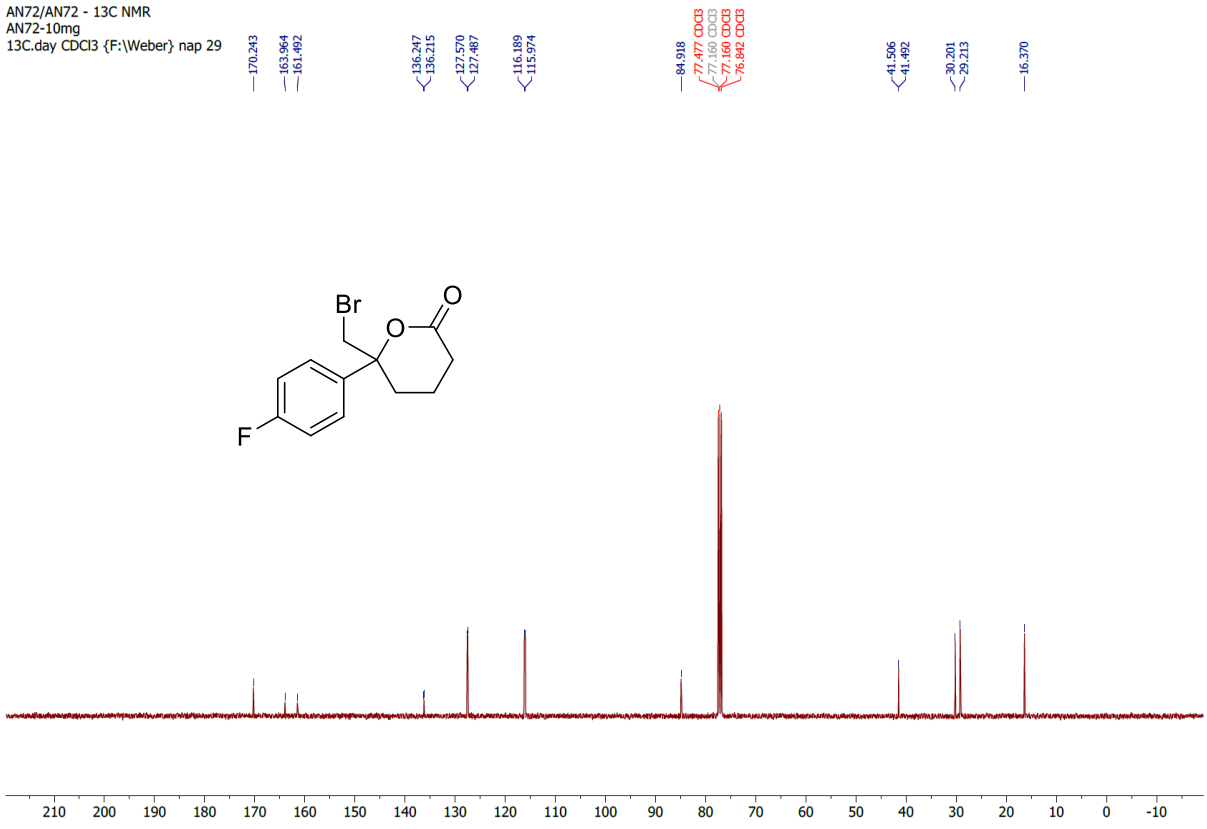



Reaction scope/AN112-13C NMR
Supervisor Nguyen
AN112
13C.night CDCl3 /data/Rabi nap 57
147.894
147.875
140.397
140.276
139.339
139.285
138.029
137.935
131.844
131.725
129.238
128.722
127.080
126.961
123.657
123.185
123.024
121.059
120.969
120.469
118.653
118.616
117.282
114.095
85.359
83.250
77.478
77.362
77.161
77.160 CDCl3
76.842
54.087
53.300
47.854
47.407
47.012
43.189
43.154
41.759
39.116
39.015
38.446
36.609
36.434
35.275
29.704
29.595
27.048
26.591
25.273
24.965
17.801
16.311
O
O
H
H
H
Br
Br
TfO
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)


Reaction scope/AN112 - 19F
Supervisor Nguyen
AN112
19F{1H} CDCl3 /data/Rabi nap 35
-72.922
-72.929
O
O
H
H
H
Br
Br
TfO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

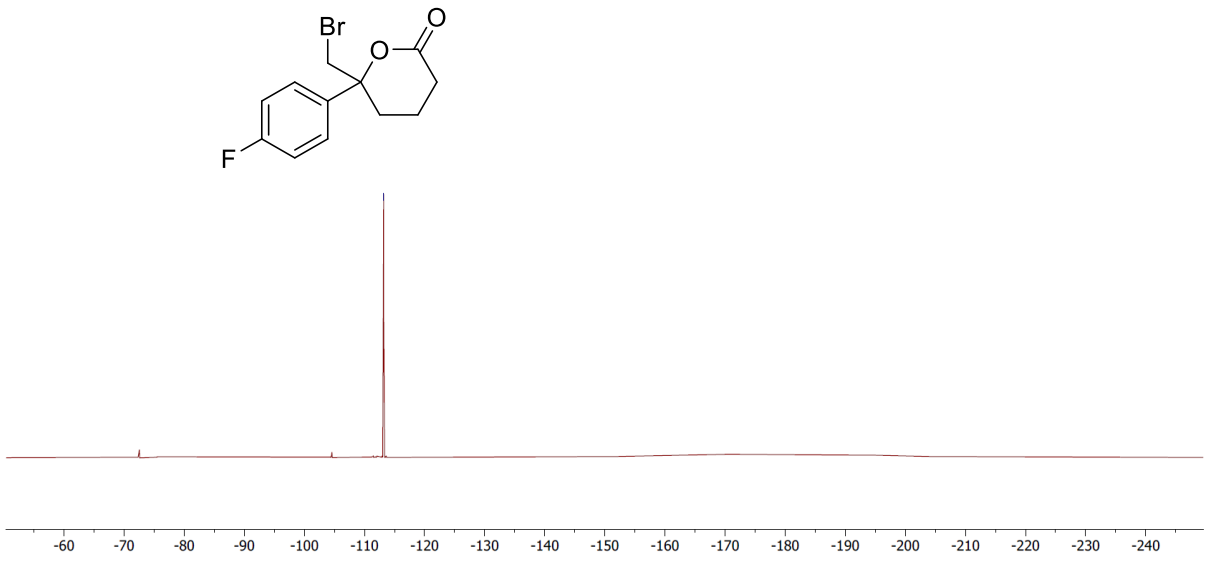
6-(bromomethyl)-6-(4-fluorophenyl)tetrahydro-2*H*-pyran-2-one (3p): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



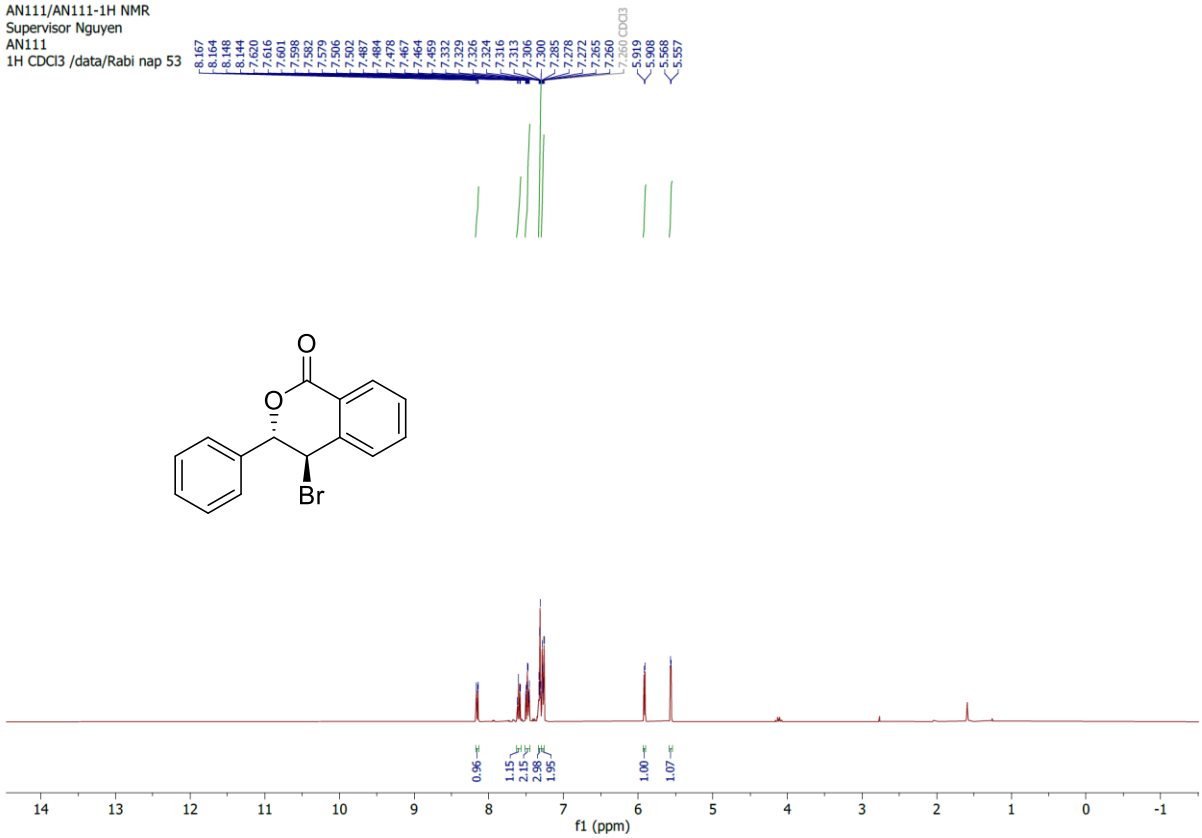


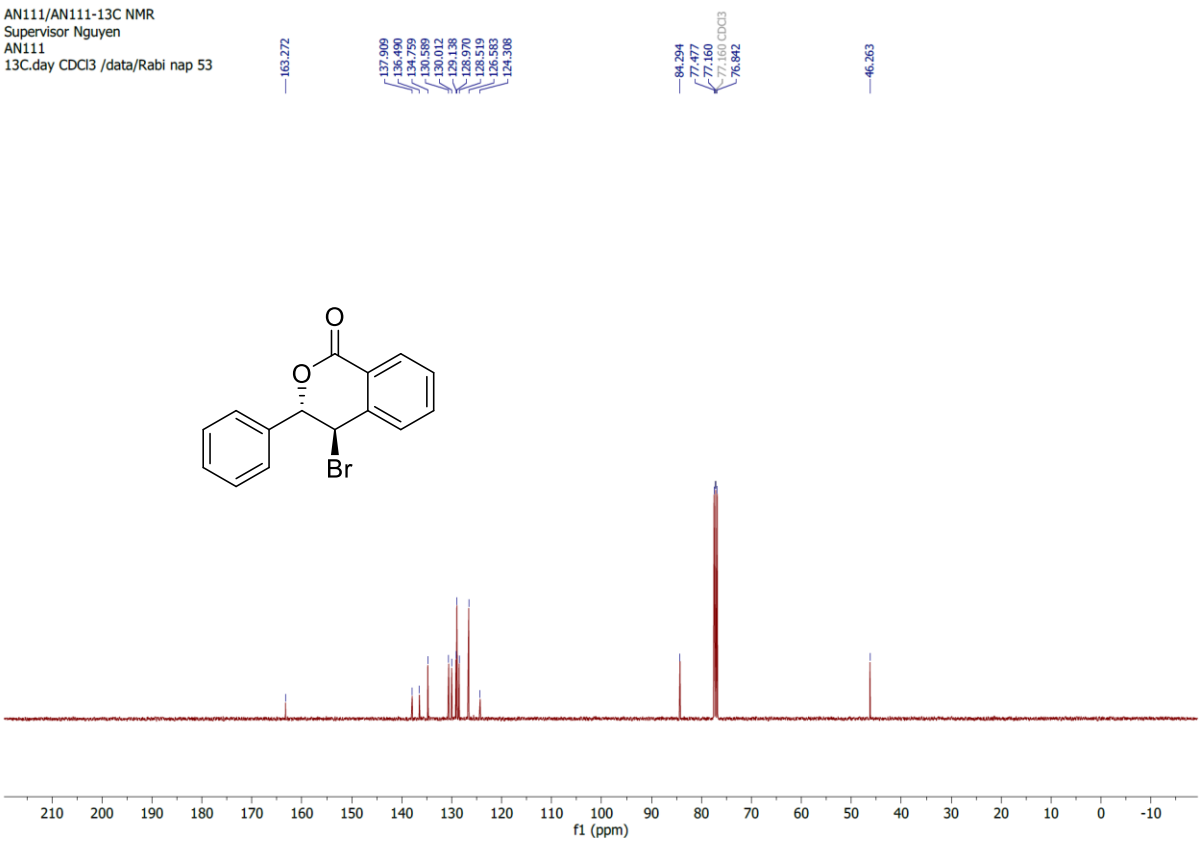
230427-nap.4.fid
AN72-10mg
19F CDCl3 {F:\Weber} nap 29

-113.19

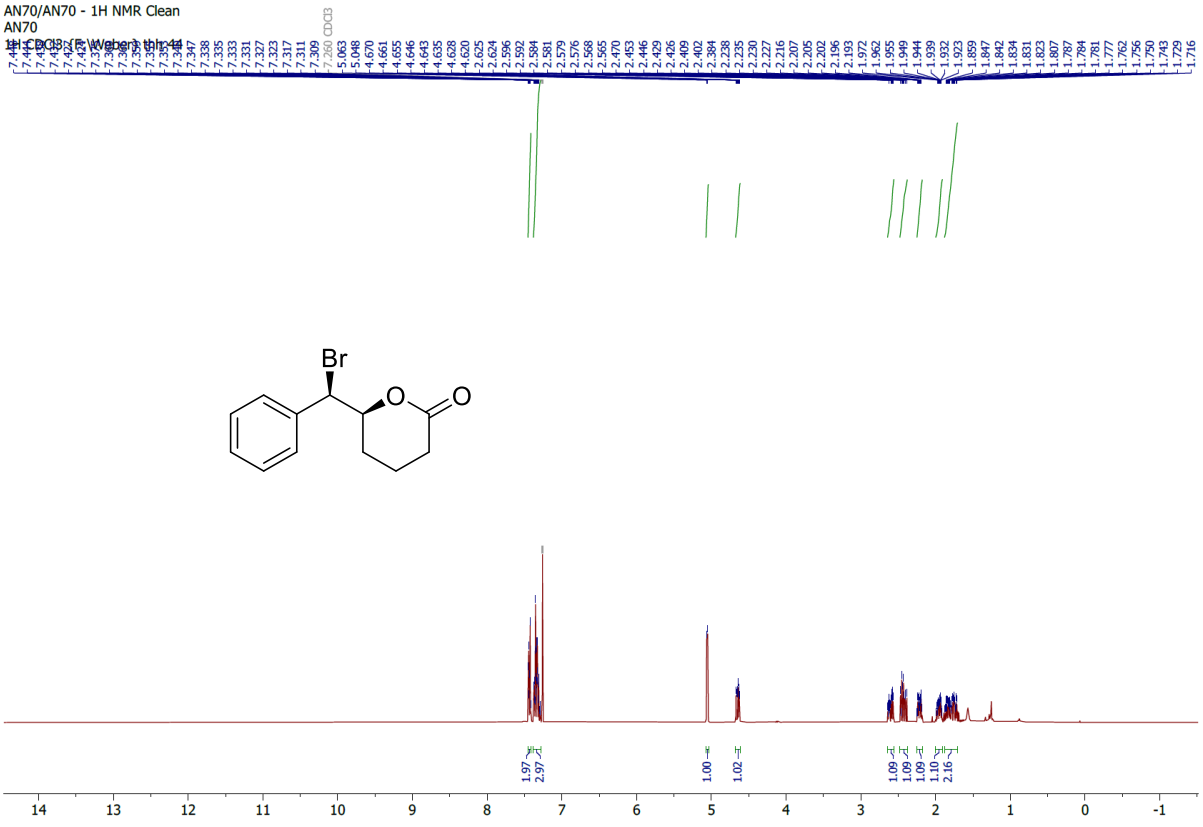


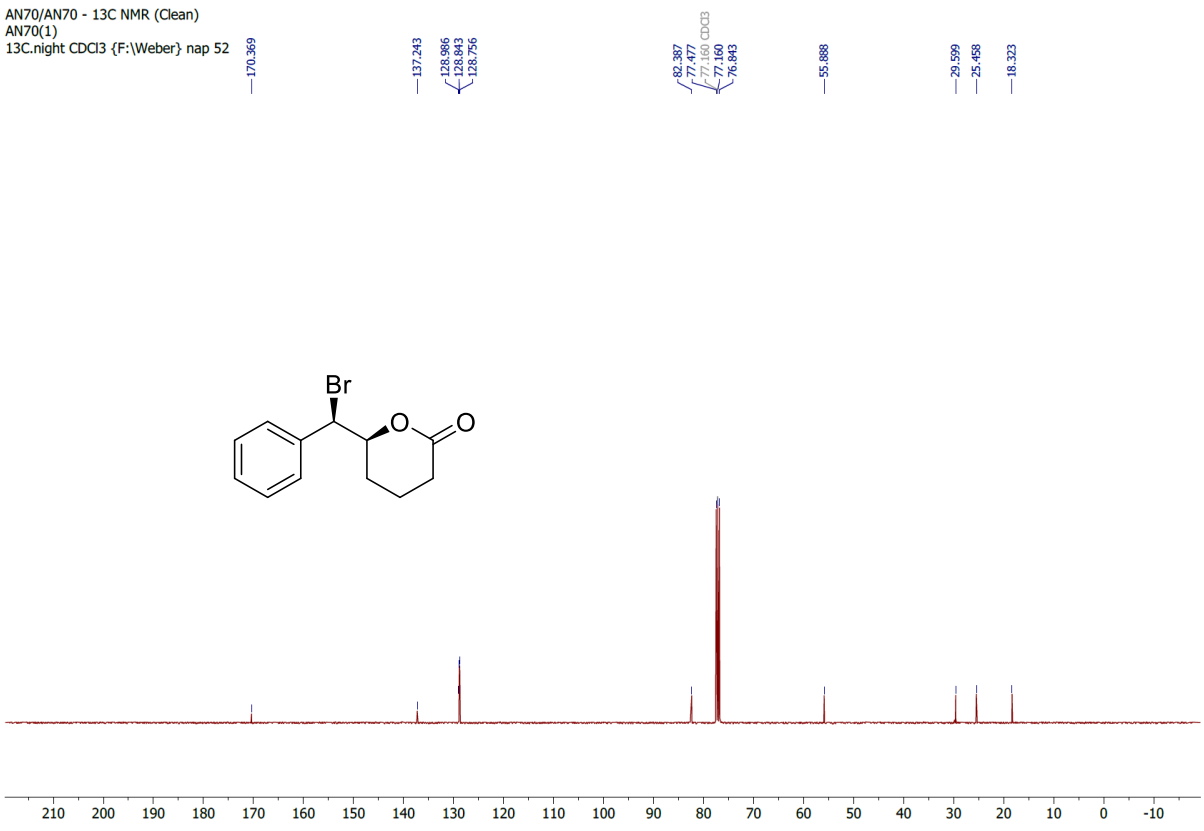
4-bromo-3-phenylisochroman-1-one (2q): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



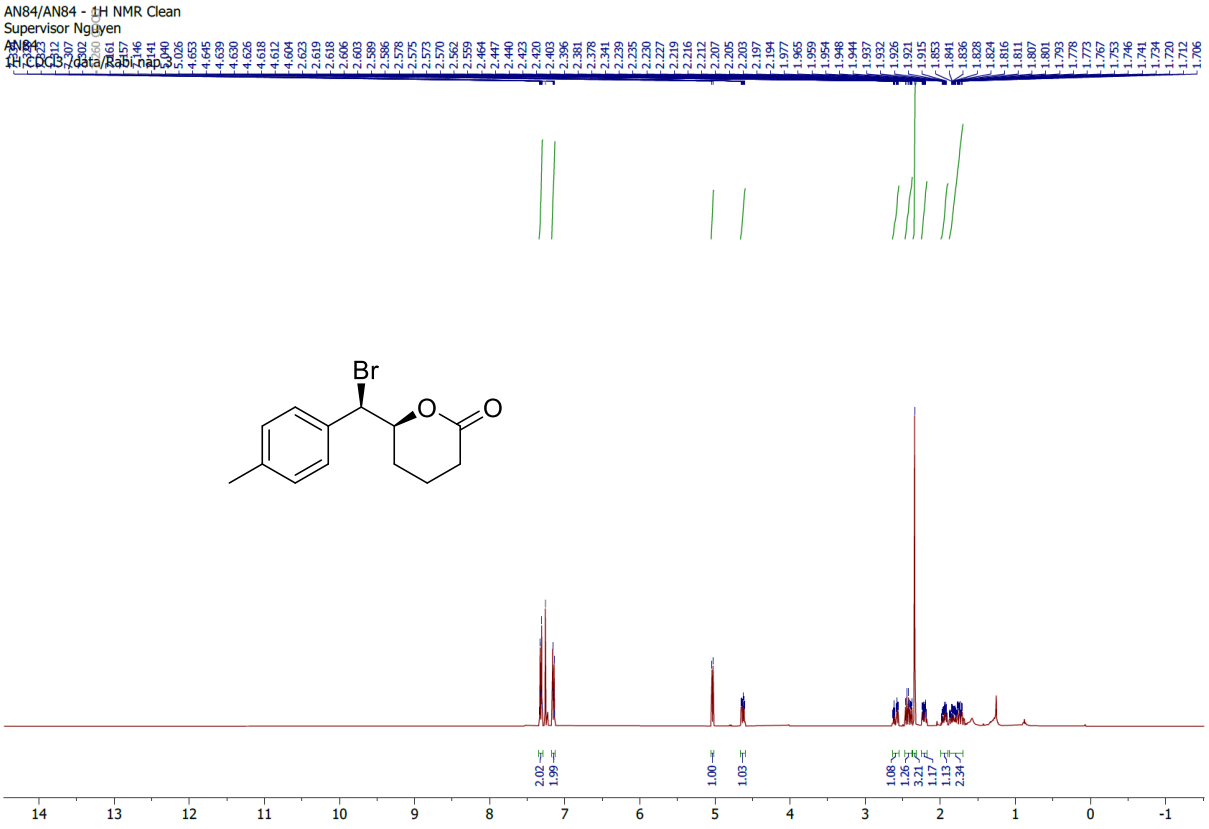


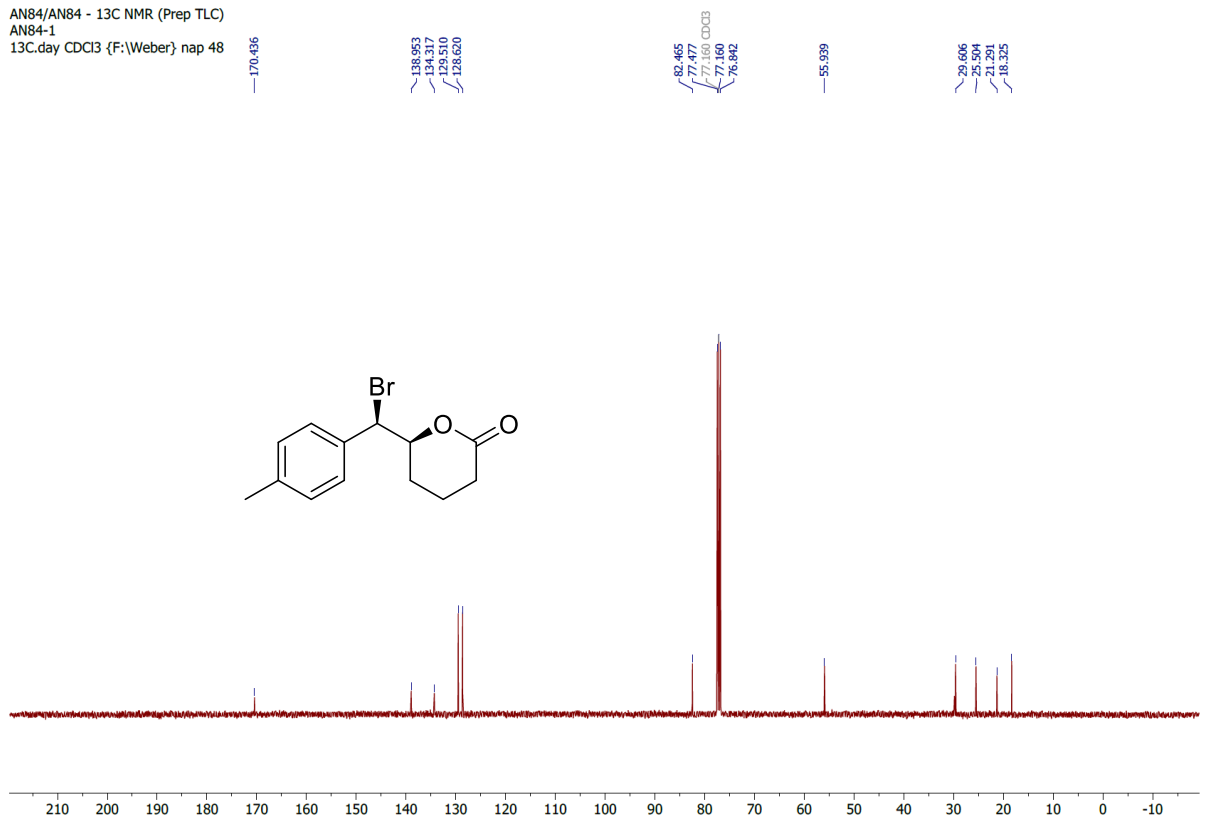
6-(bromo(phenyl)methyl)tetrahydro-2*H*-pyran-2-one (3a): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



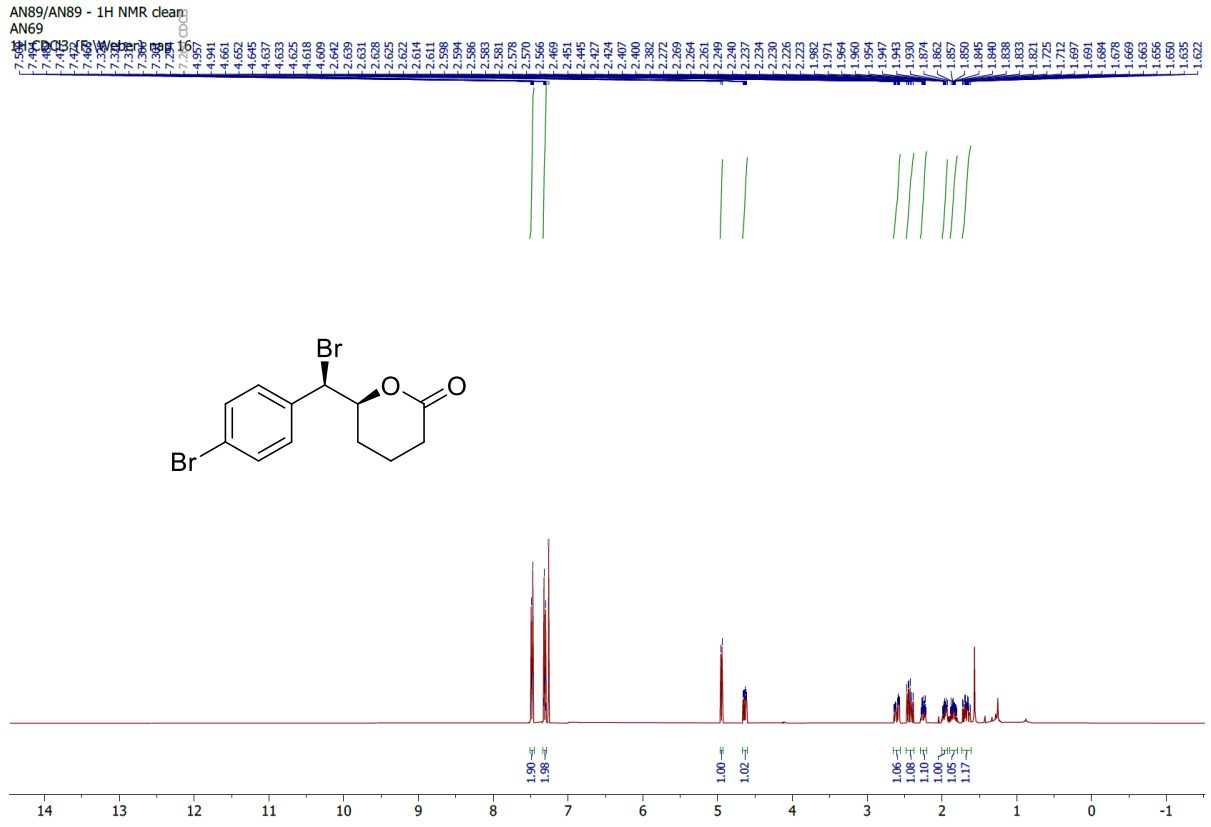


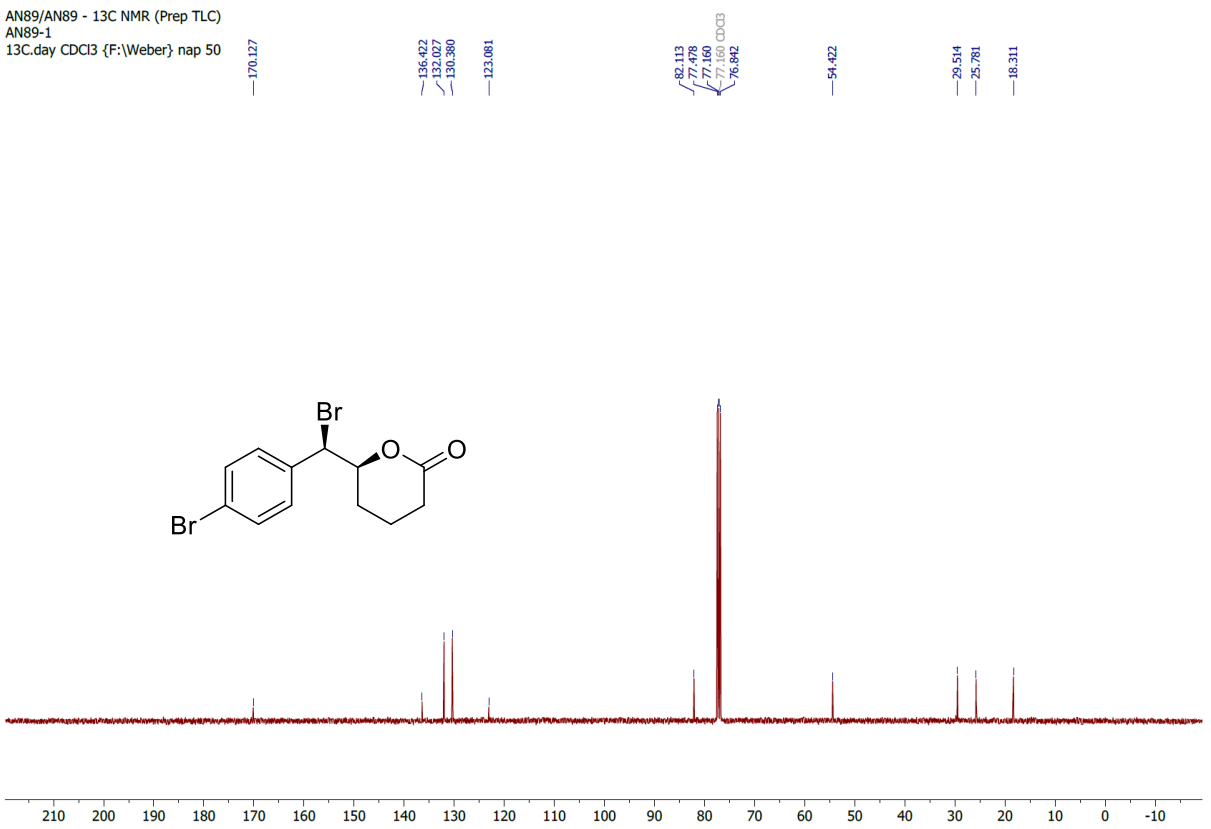
6-(bromo(p-tolyl)methyl)tetrahydro-2*H*-pyran-2-one (3b): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



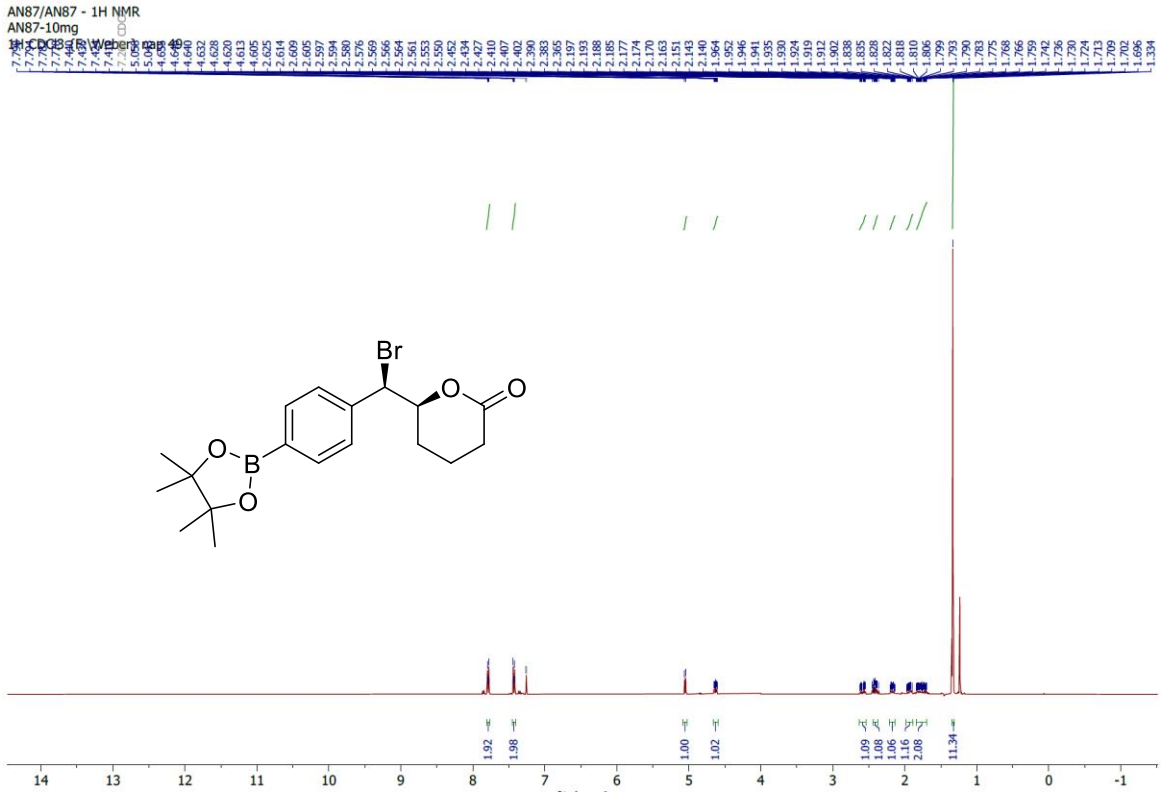


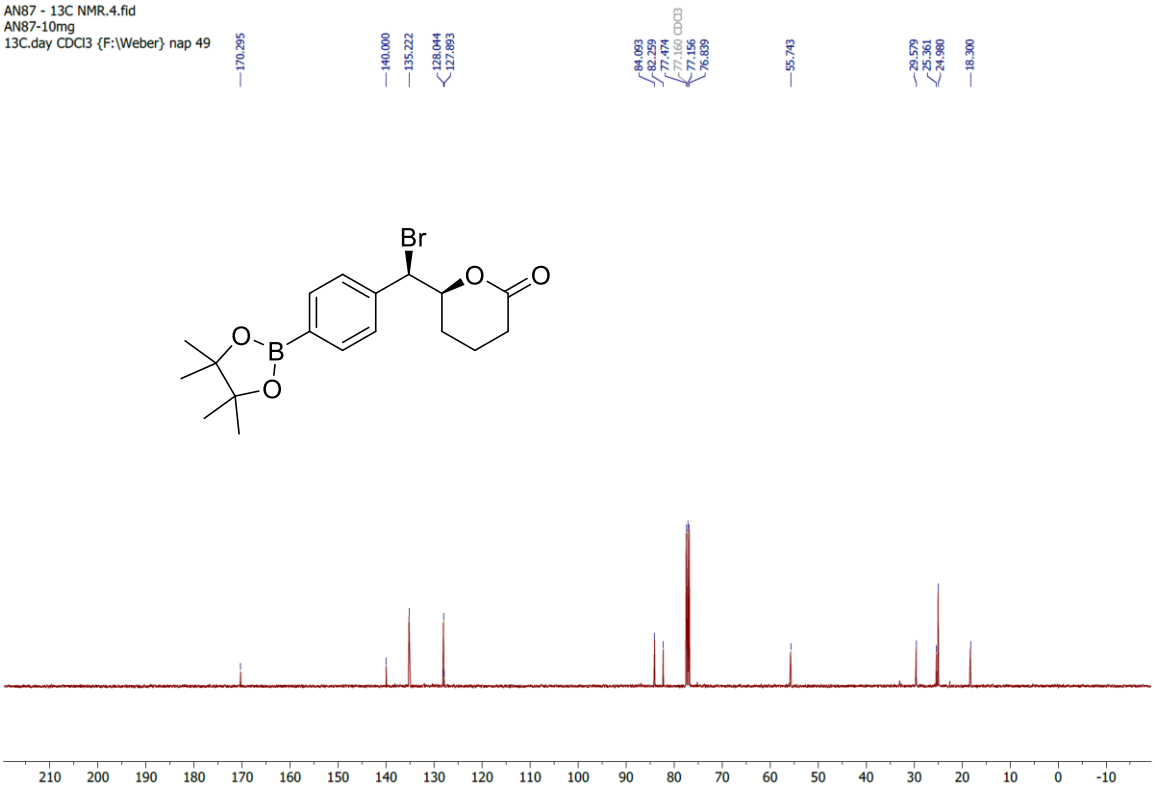
6-(bromo(4-bromophenyl)methyl)tetrahydro-2*H*-pyran-2-one (3c): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

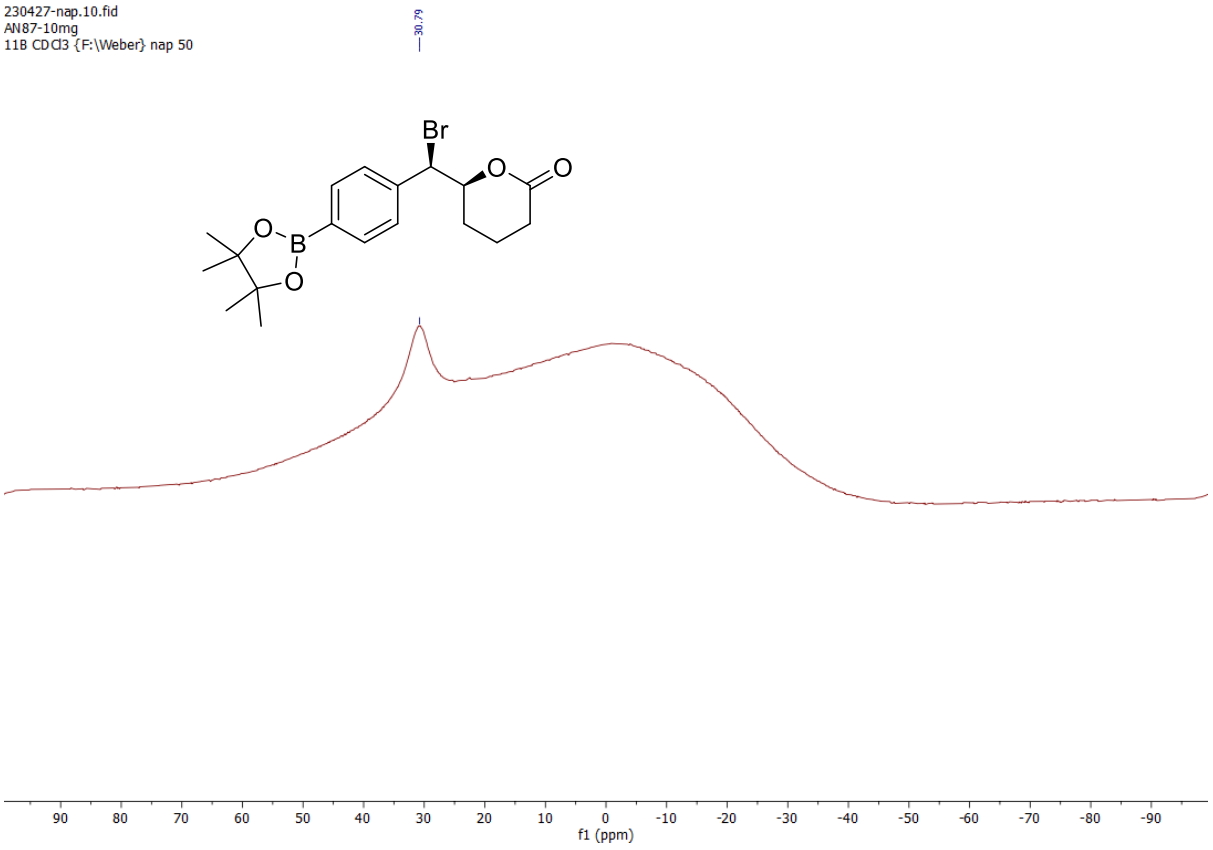




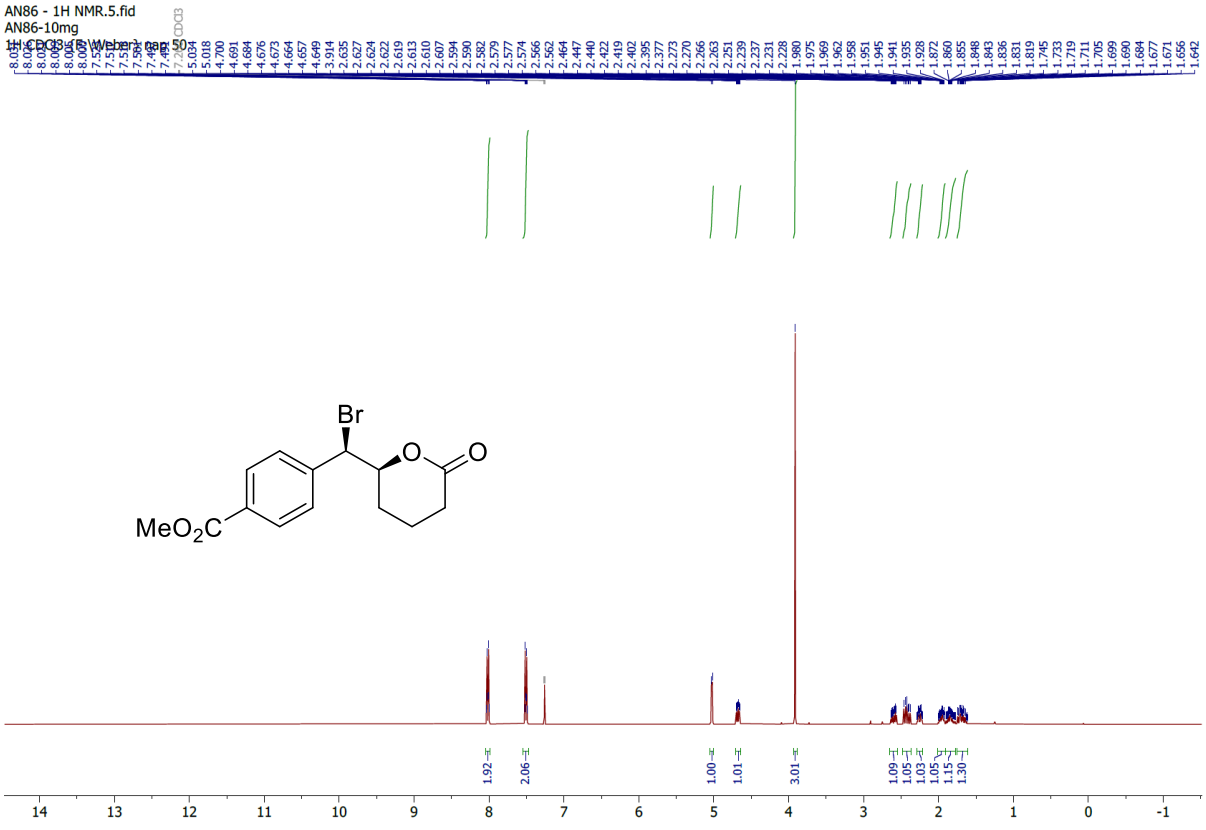
6-(bromo(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)tetrahydro-2*H*-pyran-2-one (3d): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{11}B NMR (128 MHz, $CDCl_3$)

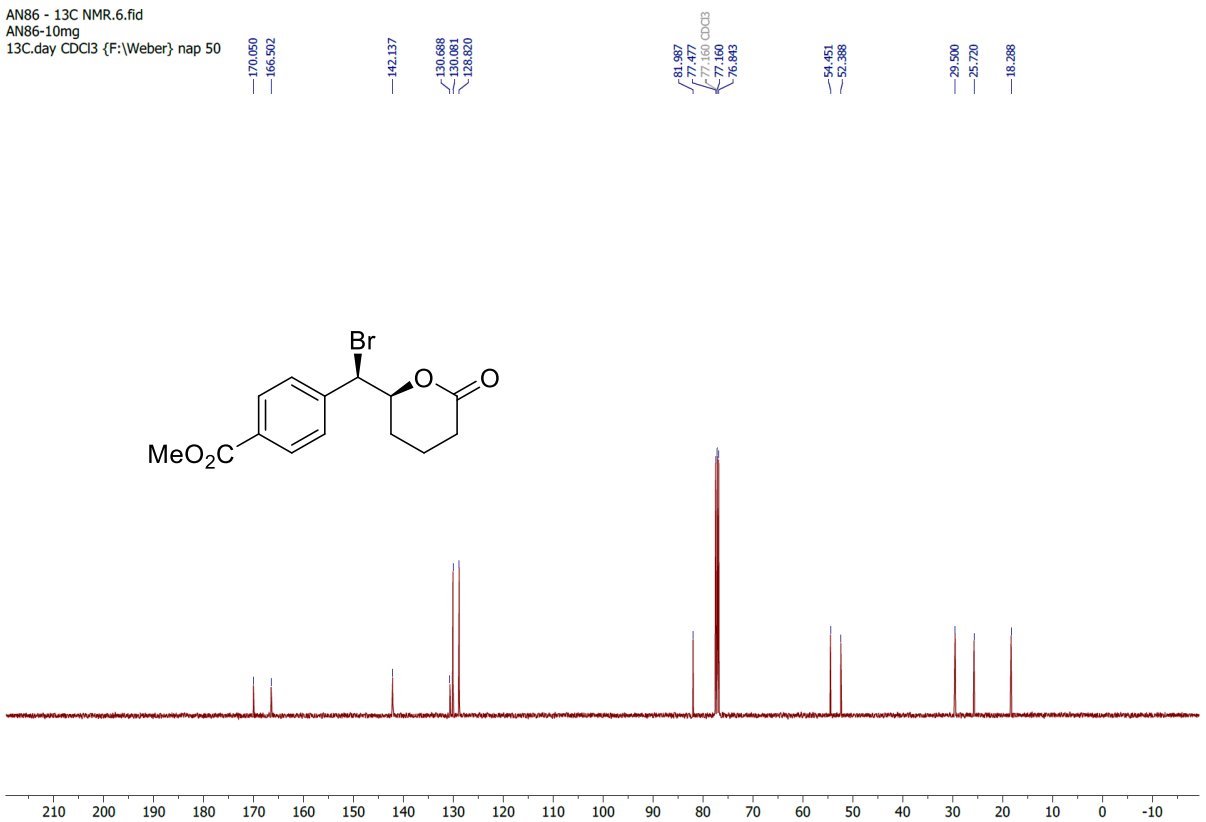




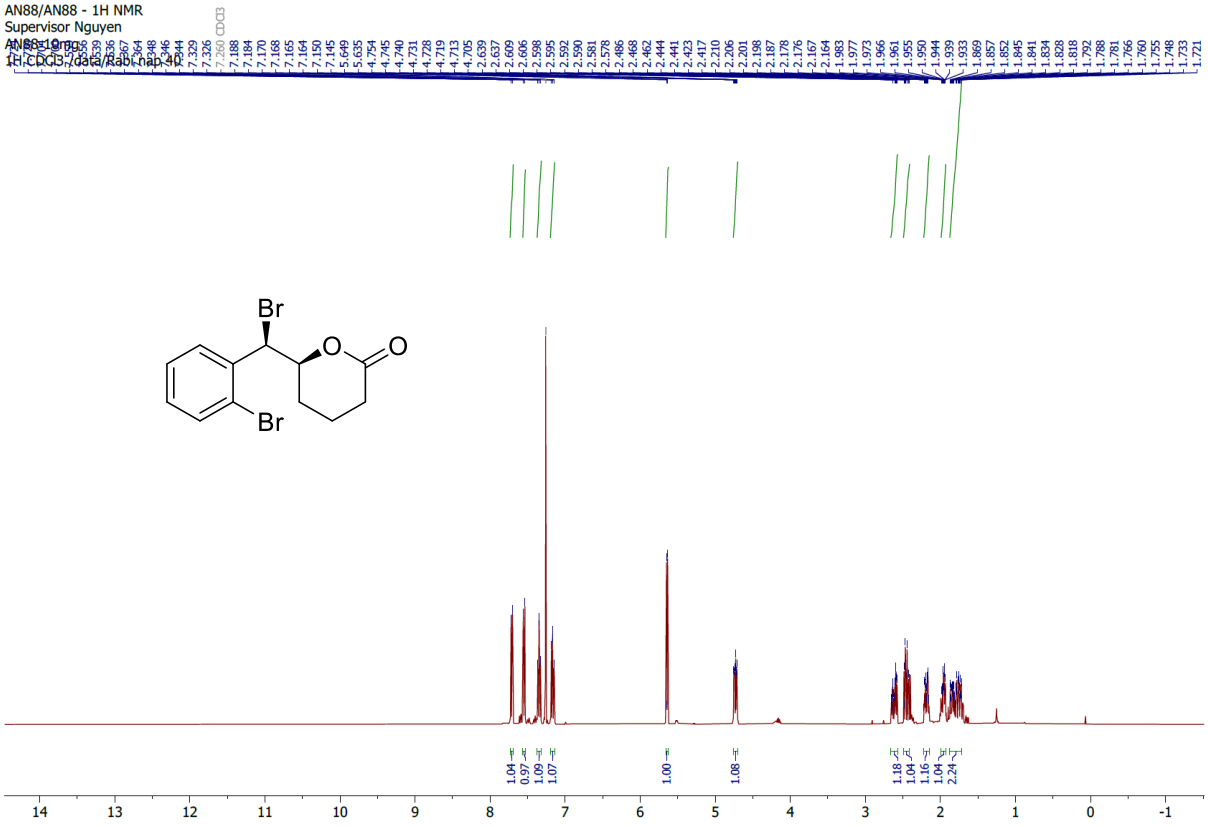

230427-nap.10.fid
AN87-10mg
11B CDCl3 {F:\Weber} nap 50
30.79
Br
O
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

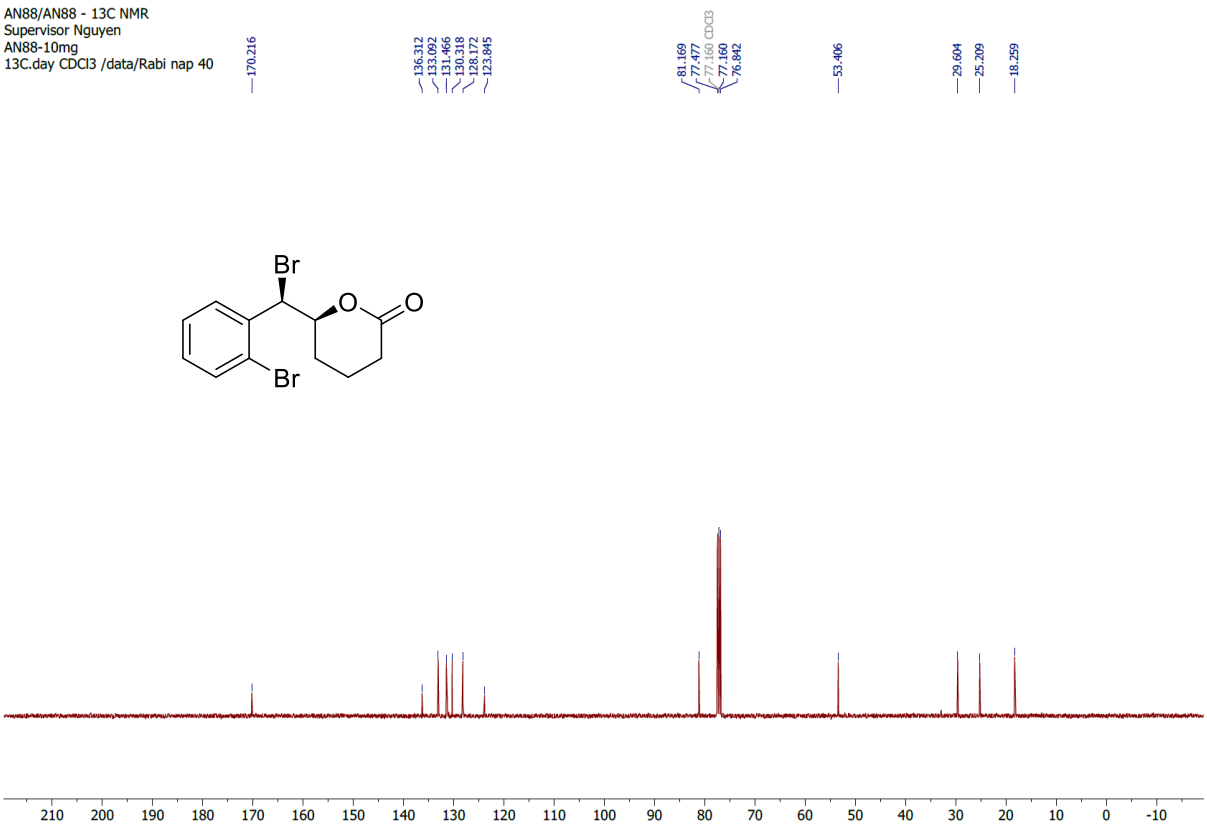
Methyl 4-(bromo(6-oxotetrahydro-2*H*-pyran-2-yl)methyl)benzoate (3e): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



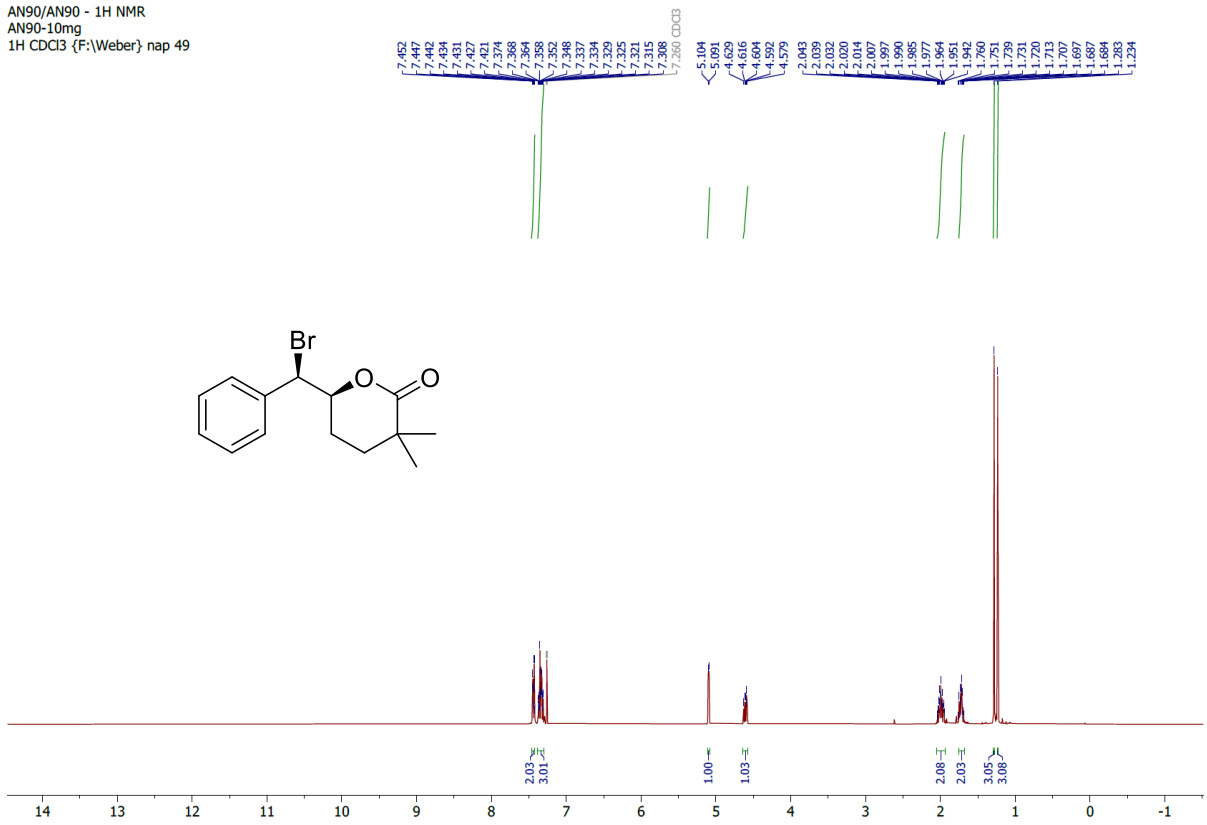


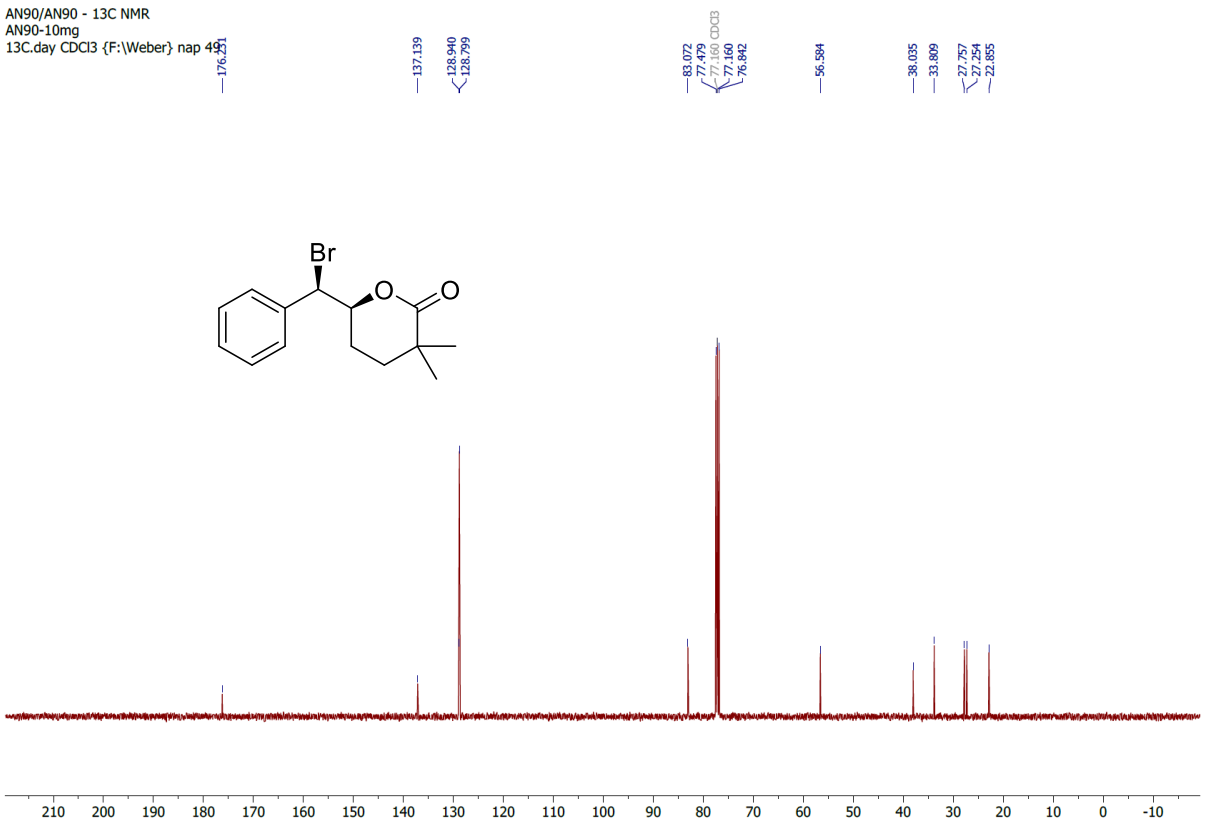
6-(bromo(2-bromophenyl)methyl)tetrahydro-2*H*-pyran-2-one (3g): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



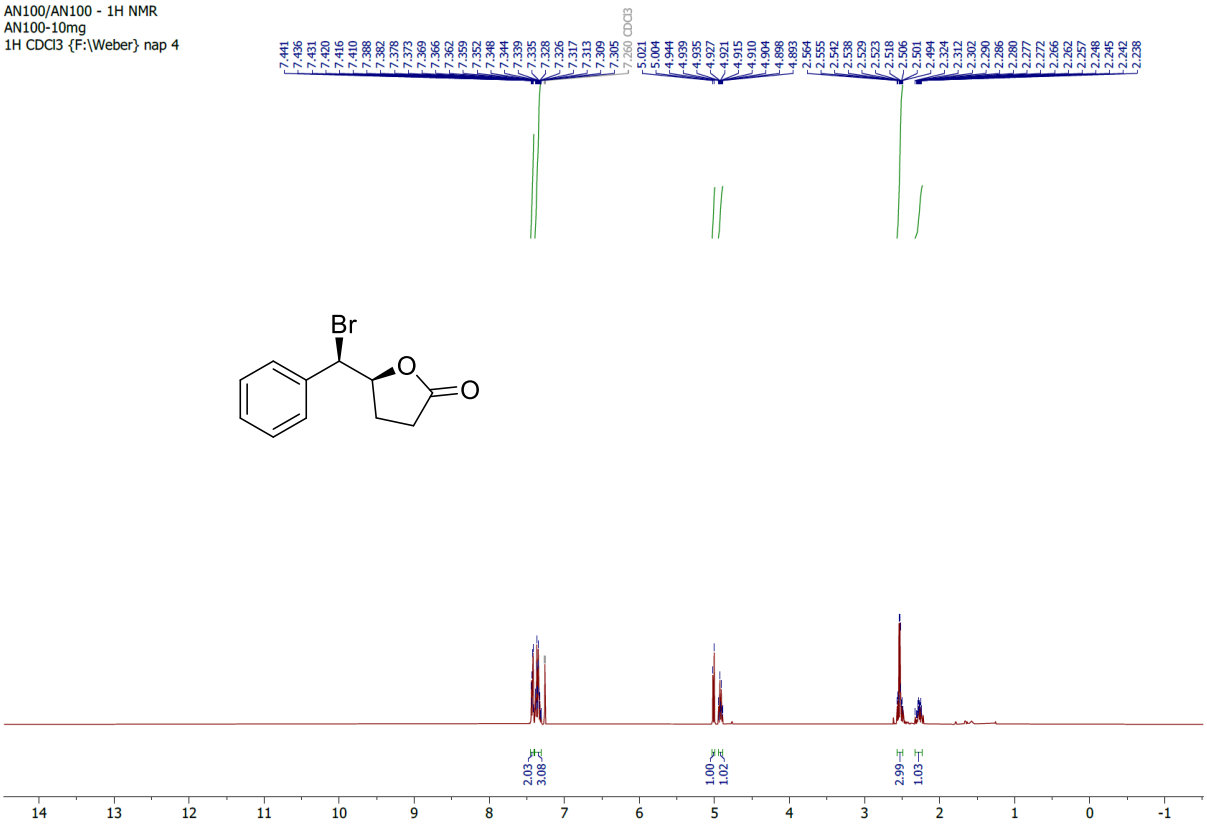


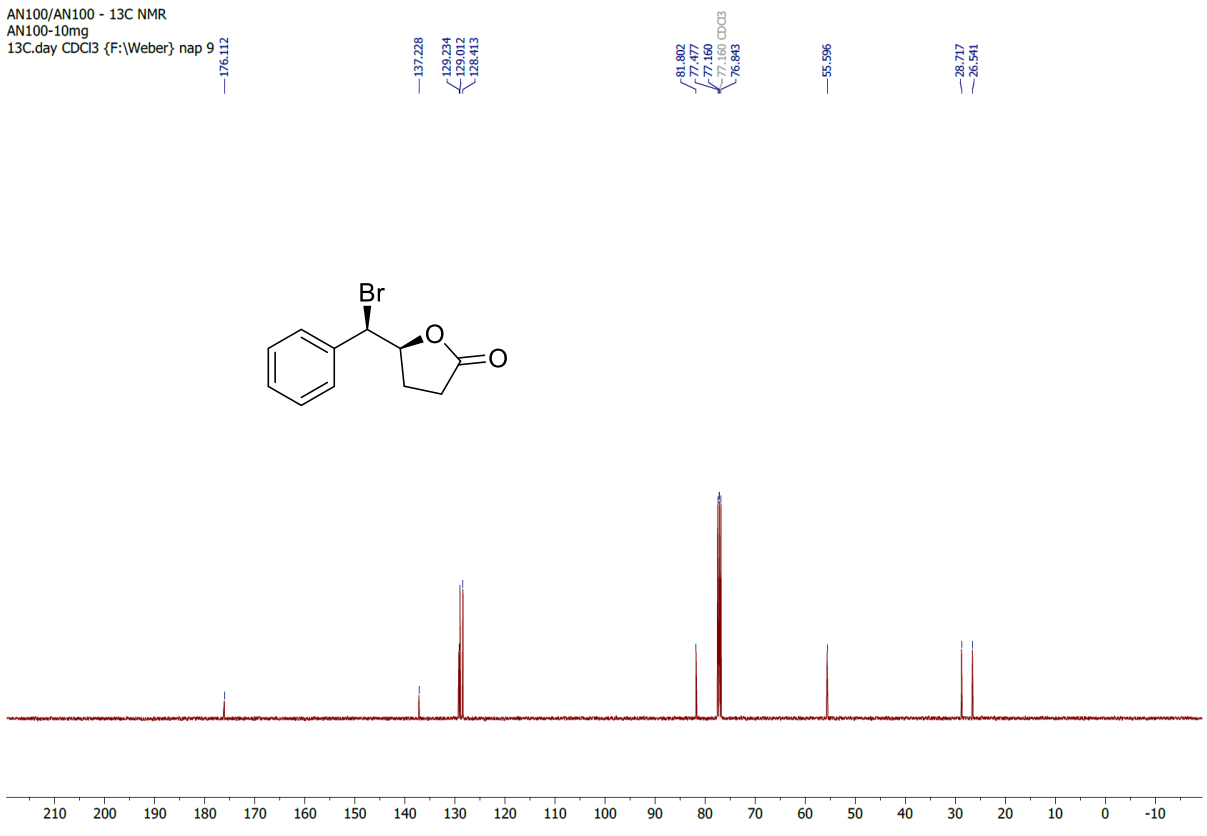
6-(bromo(phenyl)methyl)-3,3-dimethyltetrahydro-2*H*-pyran-2-one (3j): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



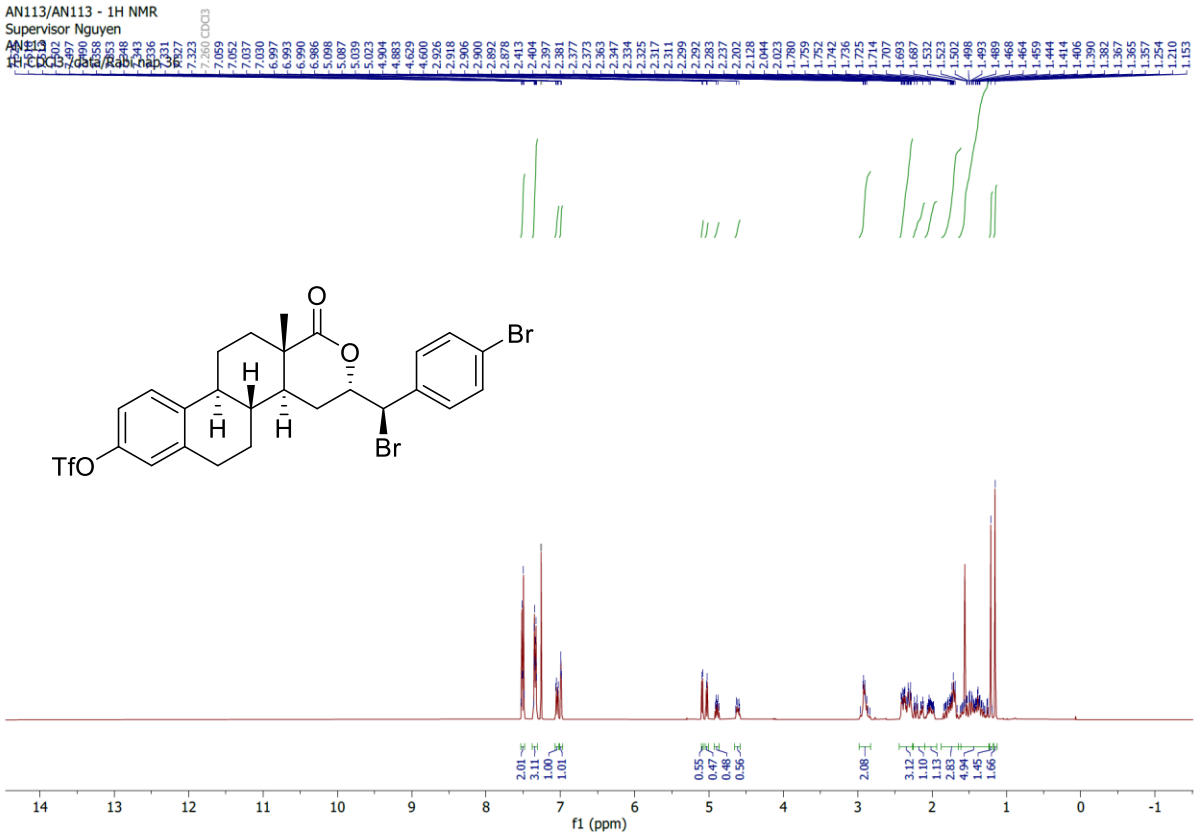


5-(bromo(phenyl)methyl)dihydrofuran-2(3*H*)-one (3l): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

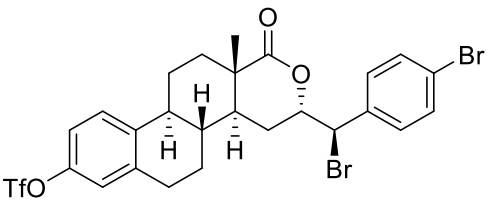


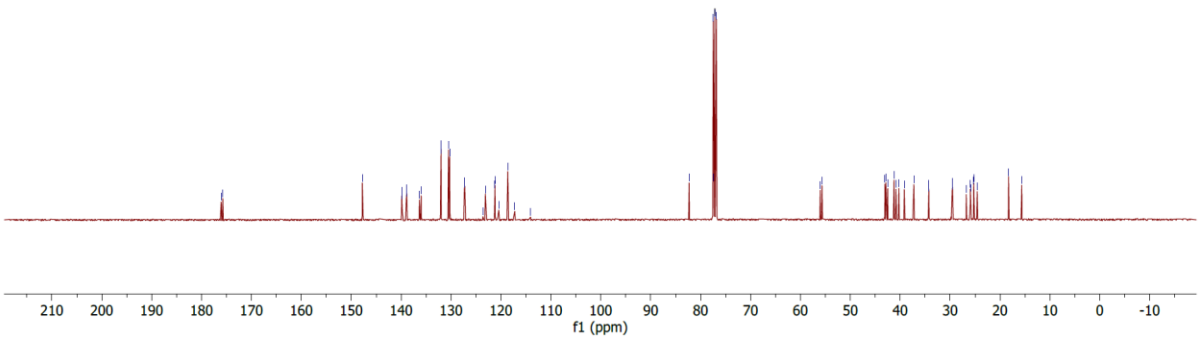


(4a*S*,4b*R*,10b*S*,12a*S*)-3-(bromo(4-bromophenyl)methyl)-12a-methyl-1-oxo-3,4,4a,4b,5,6,10b,11,12,12a-decahydro-1*H*-naphtho[2,1-*f*]isochromen-8-yl trifluoro methanesulfonate (3o): ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$)

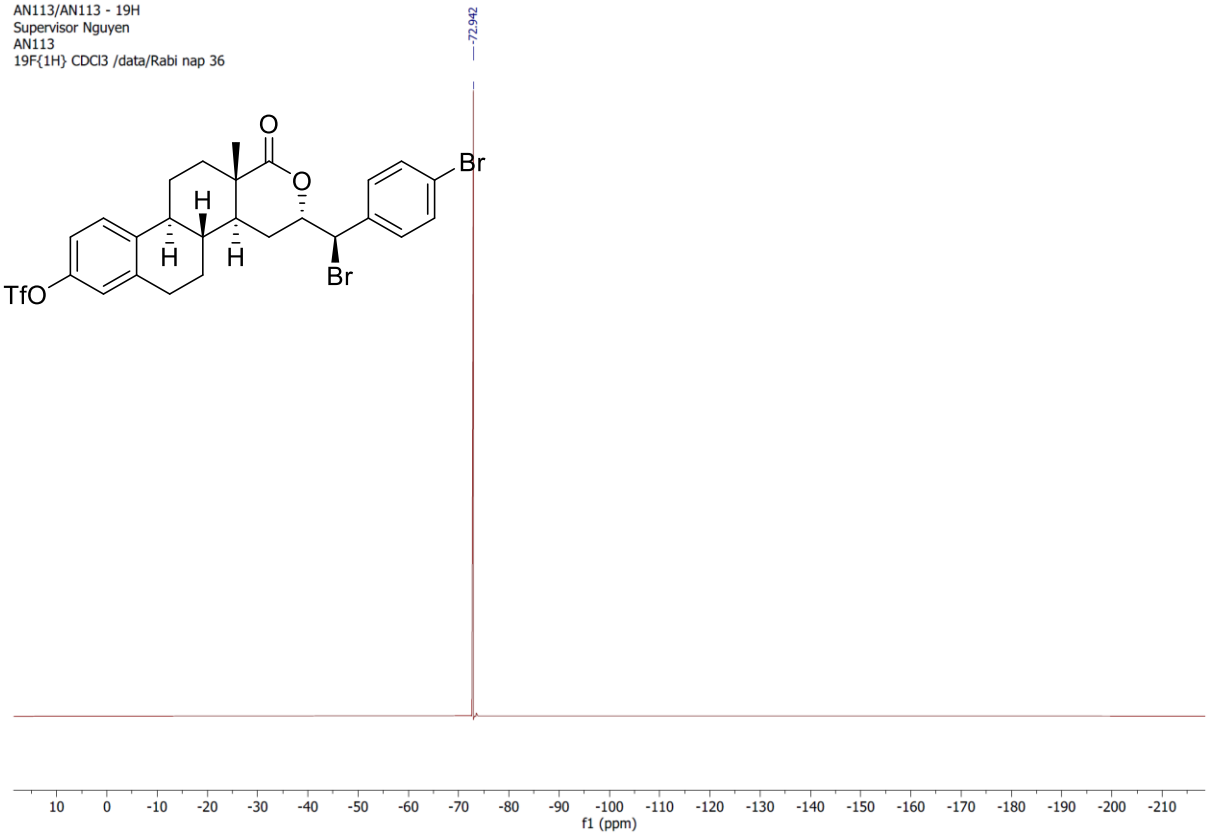


AN113/AN113 - 13C NMR
Supervisor Nguyen
AN113
13C.night CDCl3 /data/Rabi tat 36

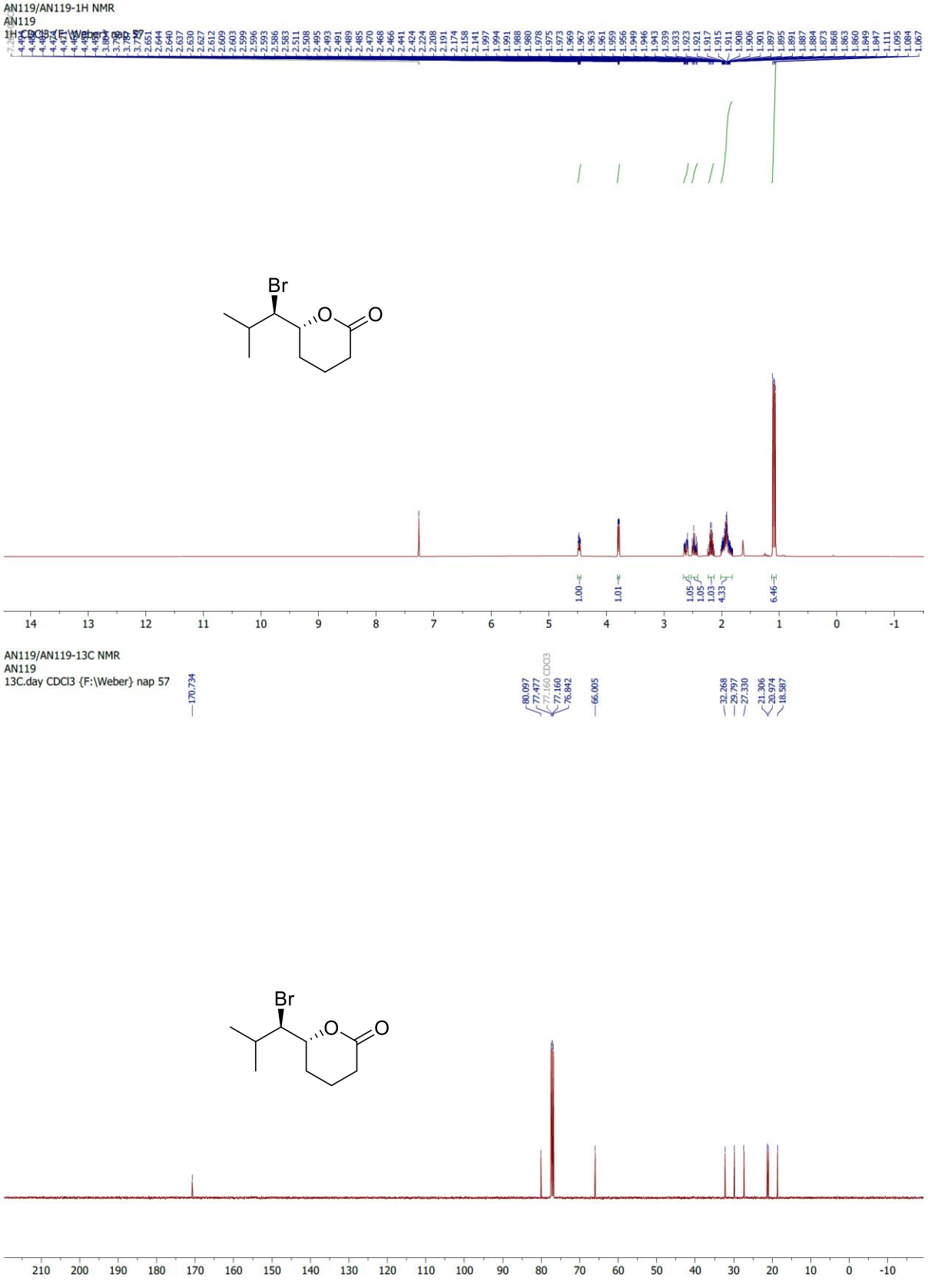




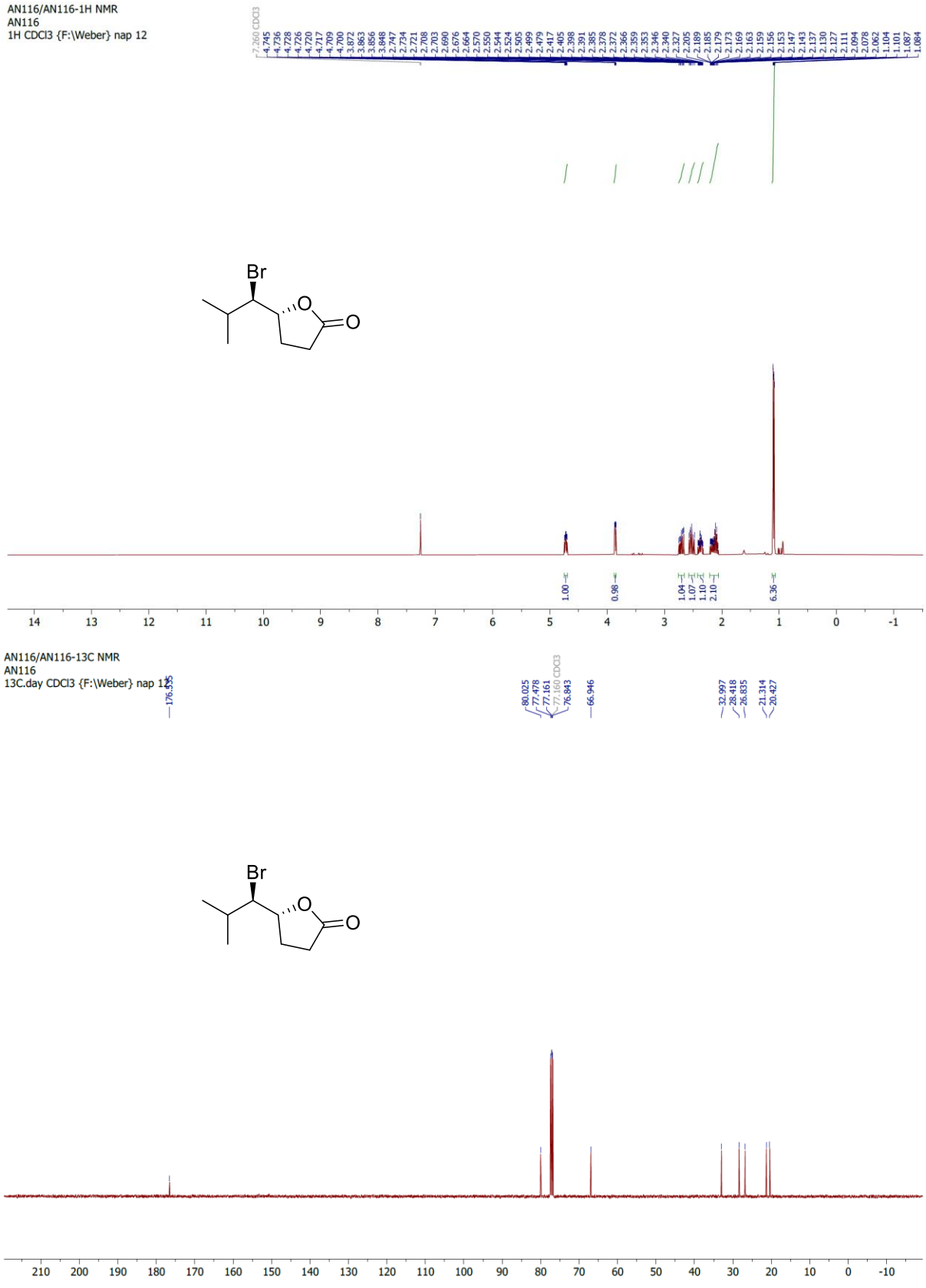
AN113/AN113 - 19H
Supervisor Nguyen
AN113
19F{1H} CDCl3 /data/Rabi nap 36



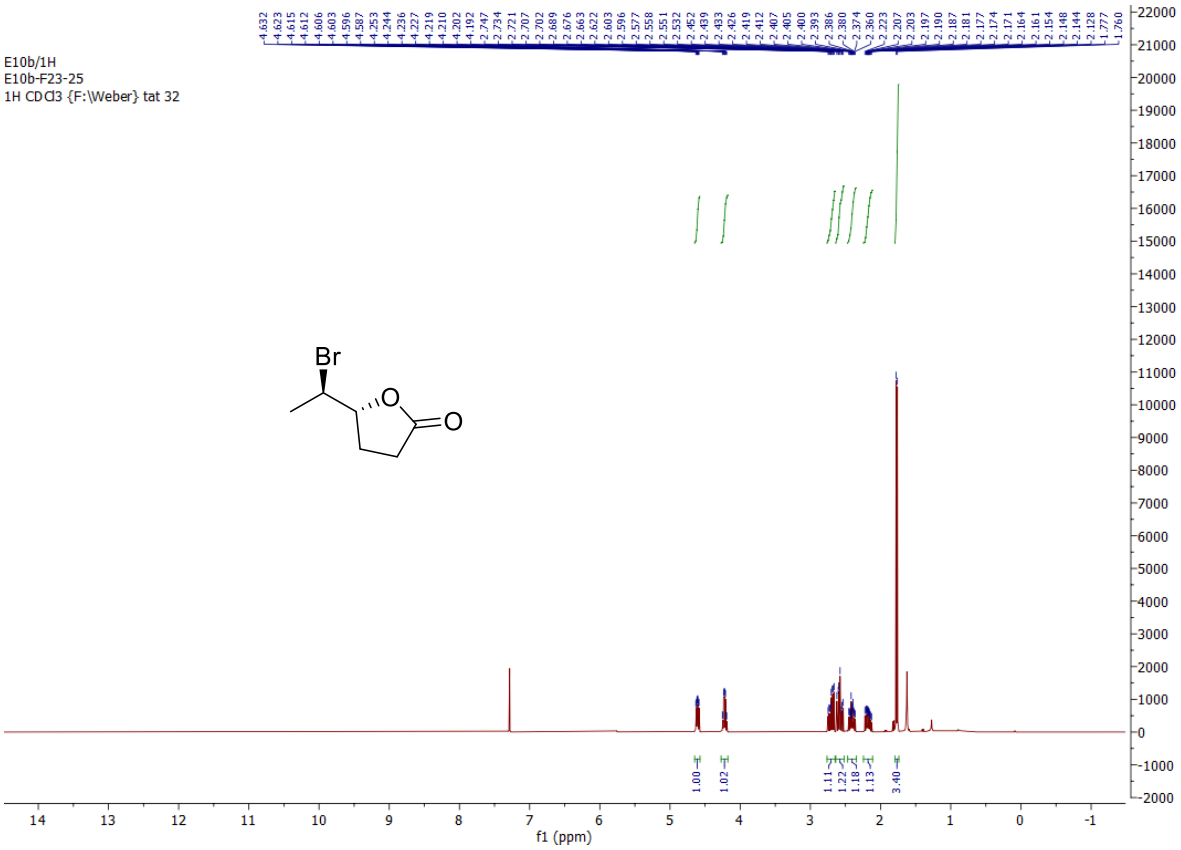
6-(1-bromo-2-methylpropyl)tetrahydro-2*H*-pyran-2-one (3r): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)

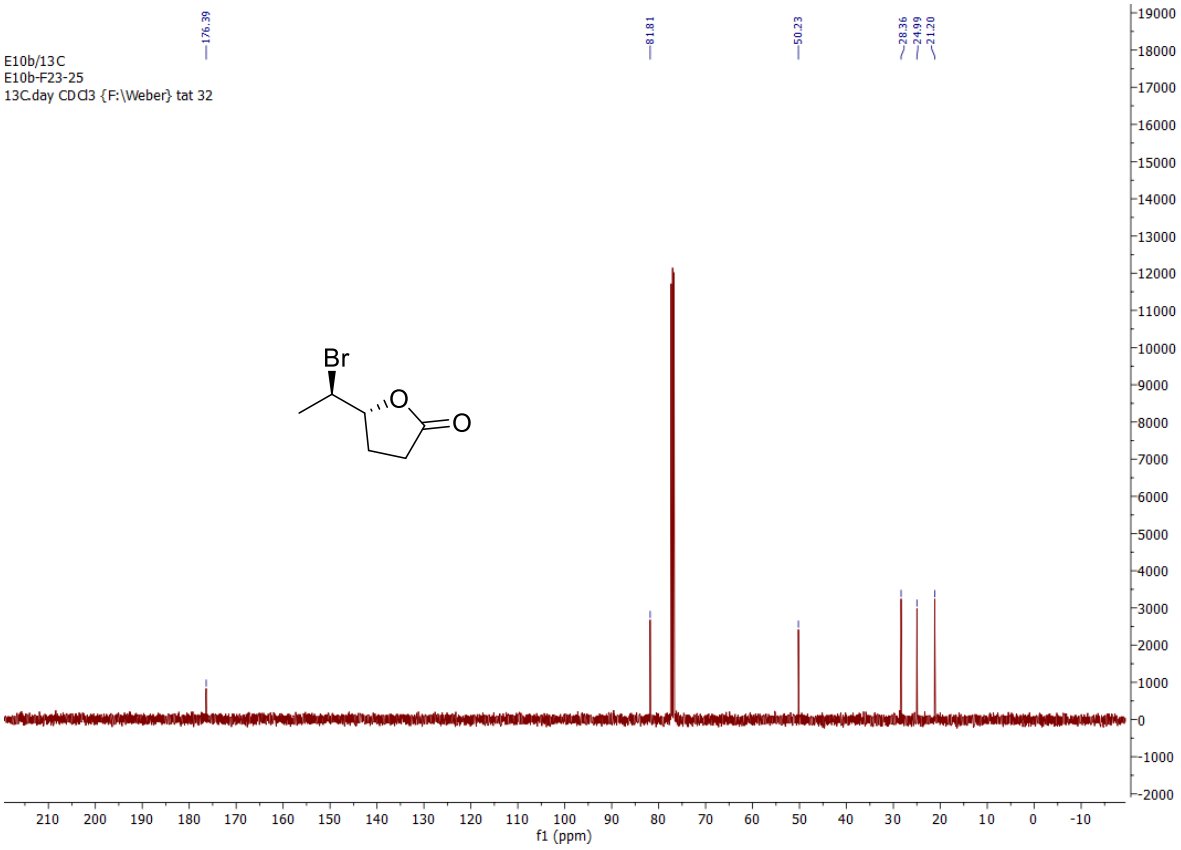


5-(1-bromo-2-methylpropyl)dihydrofuran-2(3*H*)-one (3s): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)



1-(bromoethyl)dihydrofuran-2(3*H*)-one (3t): ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz, $CDCl_3$)





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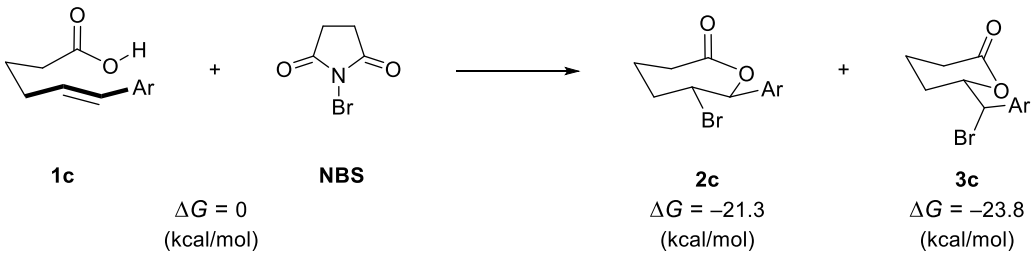
Computational Methods

DFT calculations were performed using the *Gaussian 16* program.[1] Geometries of all stationary points were fully optimized using the M06-2X functional[2] with 6-31G(d,p) basis set. Vibrational frequency calculations at the same level of theory of the geometry optimization were performed at 298.15 K to confirm if each structure is a local minimum or a transition state. Quasi-harmonic approximation with the Cramer and Truhlar approach[3] was performed using the GoodVibes package,[4] in which all vibrational frequencies below 100 cm^{-1} were shifted to 100 cm^{-1} in entropy calculations. To obtain higher accuracy for the electronic energies, single-point energy calculations were carried out using the MN15 functional[5] and 6-311+G(2d,2p) basis set. In geometry optimizations and single-point energy calculations, hexafluoroisopropanol (HFIP) and dichloroethane (DCE) are used as solvents using the SMD implicit solvation model.[6] Because the solvent parameters for HFIP are not available in *Gaussian 16*, the solvent parameters for HFIP were defined using reported literature values: the dielectric constant (the relative permittivity) of the solvent at 298 K was set to 16.7 (i.e. "Eps", ε);[7] the square of refractive index (i.e. "EpsInf", n^2) was set to 1.625625;[8] Abraham's hydrogen bond acidity (i.e. "HbondAcidity", α) and basicity (i.e. "HbondBasicity", β) were set to 0.77 and 0.10,[9] respectively; the macroscopic surface tension at a liquid-air interface at 298 K (i.e. "SurfaceTensionAtInterface", γ) was set to 23.23 (in $cal \cdot mol^{-1} \cdot Å^{-2}$);[10] the fraction of non-hydrogenic solvent atoms that are aromatic carbon atoms (i.e. "CarbonAromaticity", ϕ) was set to 0.00 because there is no aromatic carbon atoms in HFIP; the fraction of non-hydrogenic solvent atoms that are F, Cl, or Br (i.e. "ElectronegativeHalogenicity", ψ) was set to 0.60 (6 F atoms out of 10 non-hydrogenic atoms). In addition, to account for the hydrogen-bonding interactions between the HFIP solvent molecules and the template, a mixed explicit–implicit solvation protocol is applied where explicit HFIP molecules were added to the computational investigation. In these calculations, the outer-shell solvent molecules are treated using the implicit solvation model (SMD) described above. Reaction energies for the lactonization are calculated as follows (**Scheme S1**).



Scheme S1. Reaction energies for the bromolactonization.

Conformational sampling was carried out for each intermediate and transition state using metadynamics simulations and a genetic z-matrix crossing (iMTD-GC) approach in the gas phase with the conformer–rotamer ensemble sampling (CREST) algorithm.[11] In all conformational samplings, the semiempirical tight-binding based quantum chemistry method GFN2-xTB, implemented in the xTB code[12] was used. Conformers within 10.0 kcal/mol of the lowest-energy conformer were included in subsequent DFT calculations. Structural similarity of low-energy conformers was analyzed using root-mean-square deviation (RMSD), where conformers that have RMSD less than 0.5 Å were considered as duplicates and discarded. Initial DFT optimizations were carried out for intermediates and transition states to obtain geometry information for conformational samplings. During TS sampling, the forming/breaking bond distances were fixed to the values obtained from initial DFT-optimized TS geometries. In order to avoid the dissociation of HFIP molecules during conformational sampling, the hydrogen bond O···H distances were also fixed to the values obtained from initial DFT-optimized geometries. Each of the unique conformers was then re-optimized without constraint with DFT.

Additional Computational Results

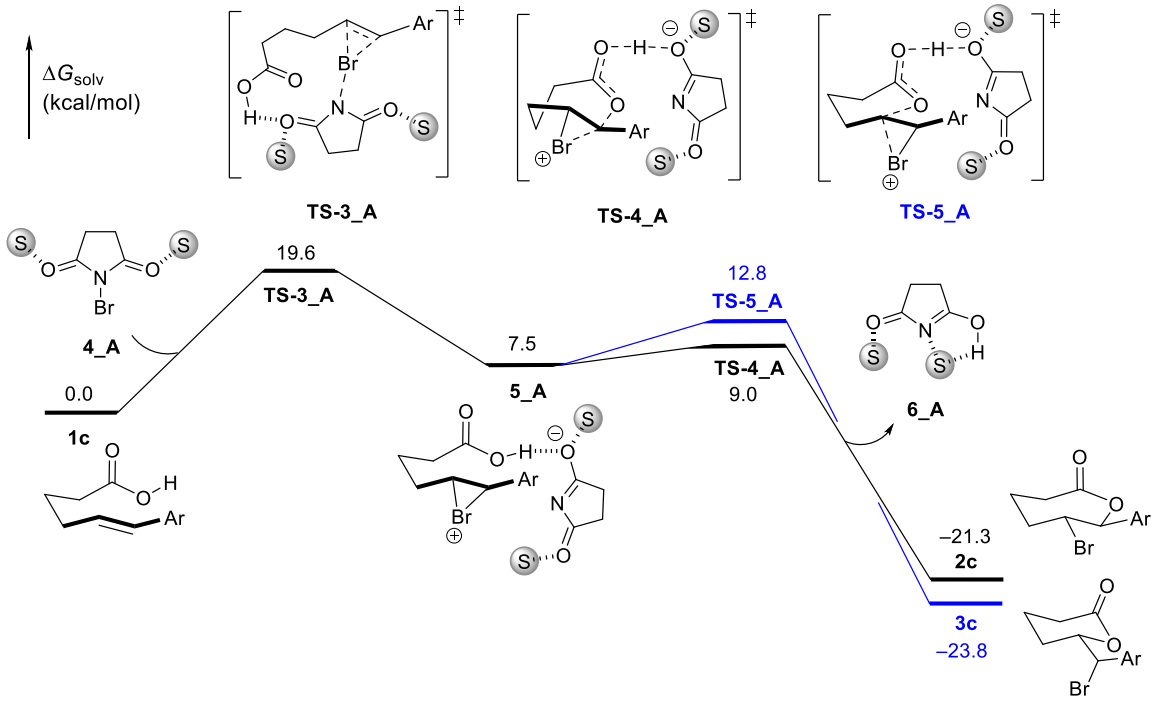


Figure S1. Computed free energy profile for the stepwise bromolactonization in HFIP. Two HFIP solvent molecules were included in DFT calculations.

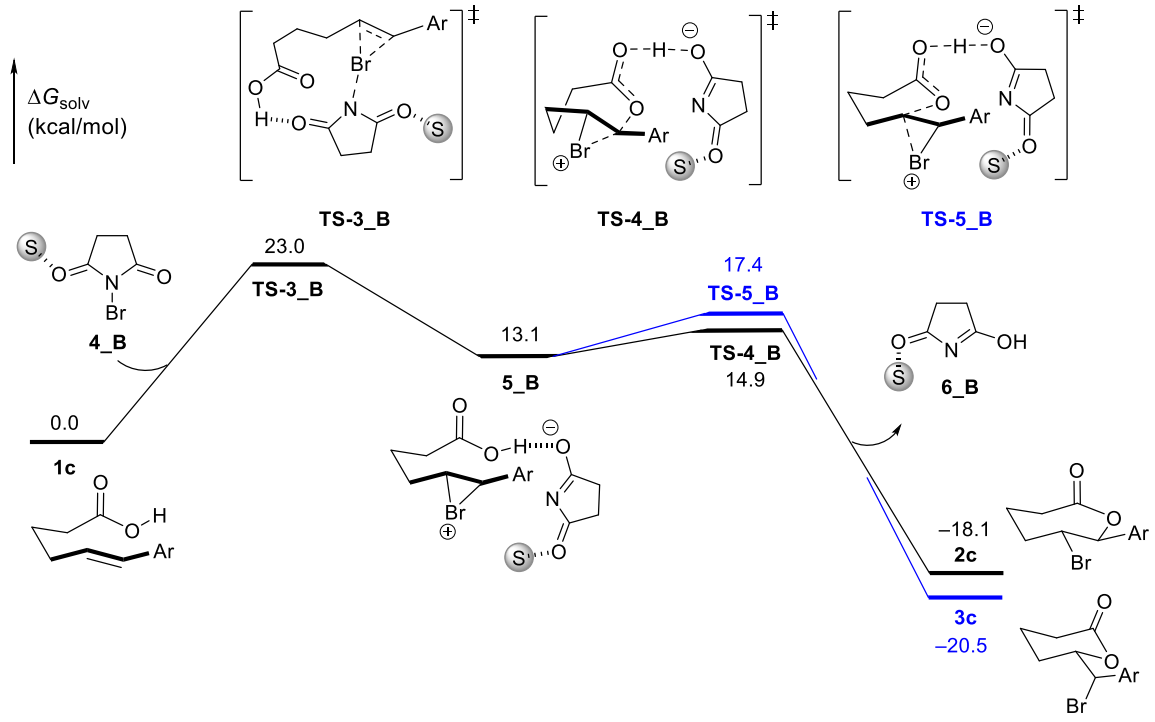


Figure S2 Computed free energy profile for the stepwise bromolactonization in HFIP. One HFIP solvent molecule was included in DFT calculations.

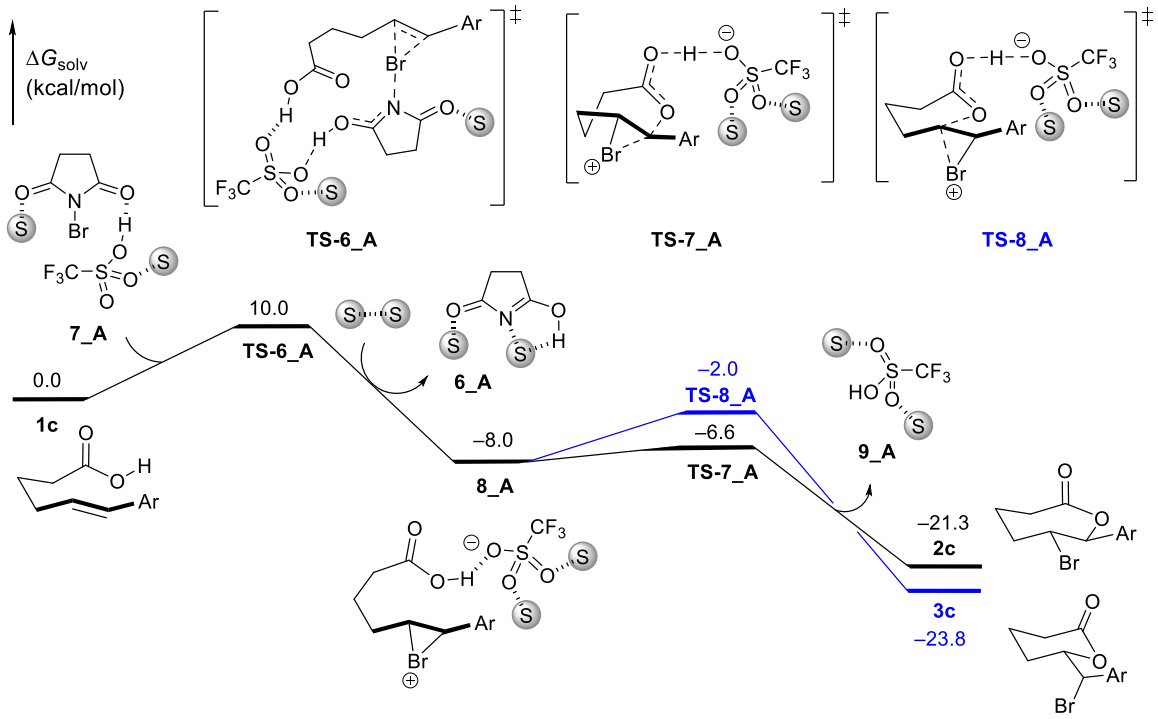


Figure S3. Computed free energy profile for the stepwise bromolactonization in HFIP catalyzed by TfOH. Two HFIP solvent molecules were included in DFT calculations.

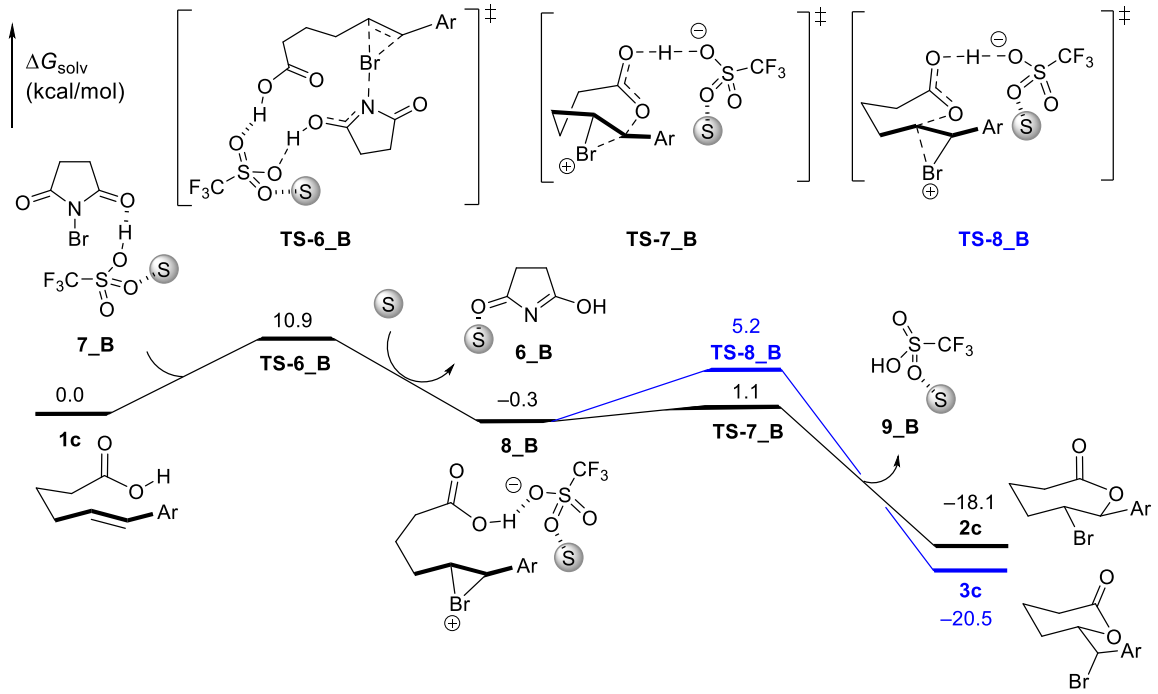


Figure S4. Computed free energy profile for the stepwise bromolactonization in HFIP catalyzed by TfOH. One HFIP solvent molecule was included in DFT calculations.

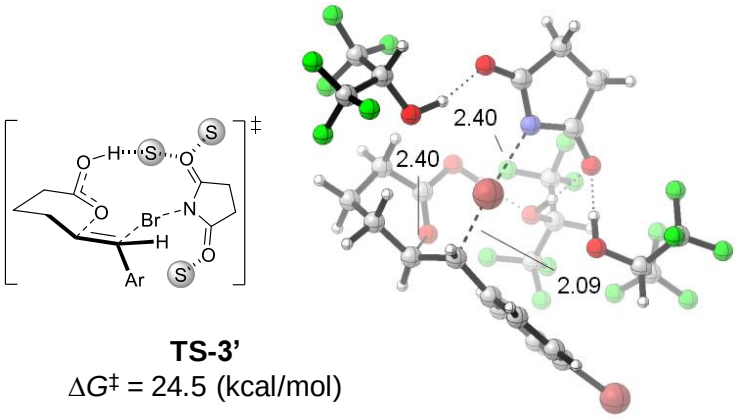


Figure S5. Optimized transition state for the concerted bromolactonization in HFIP leading to the *exo*-cyclic product.

Bromolactonization of 1l in HFIP

We turned our effort into calculating the preferred pathways for the bromolactonization of **1l** in HFIP. Similar to the reaction of **1c**, we could not locate the concerted transition state giving *endo*-cyclic product. Moreover, the bromine atom transition state **TS-9** giving six-membered ring product, i.e., *endo*-cyclization, is calculated to be 12.1 kcal/mol lower in energy than the *syn*-concerted addition pathway **TS-10**, which leads to five-membered ring product, i.e., *exo*-cyclization. This result indicates that the stepwise mechanism is also the favorable pathway for the reaction of **1l** in HFIP.

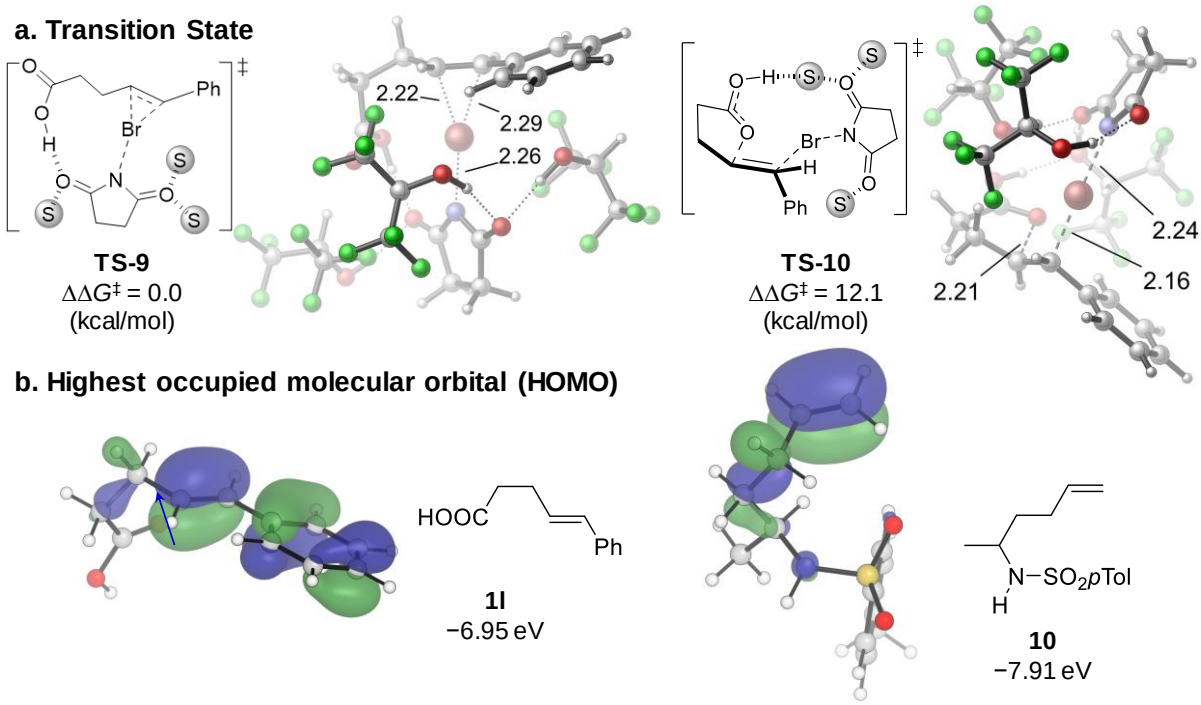


Figure S6. (a) Optimized transition state for the electrophilic addition of bromine atom, **TS-9**, and concerted bromolactonization, **TS-10**, leading to *exo*-cyclic product of **1l** and NBS in HFIP. Free energy values are relative to **TS-9**. (b) Highest occupied molecular orbital (HOMO) of **1l** and *N*-tosylaminoalkene **10** calculated at MN15/6-311+G(2d,2p)//M06-2X/6-31G(d,p) level of theory.

In a previous study, by using DFT calculation, Lebœuf and Gandon found that the reaction of *N*-tosylaminoalkene in HFIP takes place via a concerted mechanism giving five-membered ring product.[13] Our DFT calculations showed that *N*-tosylaminoalkene **10** has a low-energy HOMO; whereas the HOMO of **1l** is calculated to be much higher in energy than that of **10**. This result indicates that the C=C double bond in **1l** is prone to undergo electrophilic addition and, thus, the stepwise mechanism is expected to be more favorable than the concerted manner for **1l**.

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Energy and Cartesian Coordinate

1c
M06-2X SCF energy (au):   -3187.11248096
M06-2X enthalpy (au):   -3186.87051496
M06-2X free energy (au):   -3186.92944396
MN15 SCF energy (au):   -3189.57415899
MN15 enthalpy (au):   -3189.33219299
MN15 free energy (au):   -3189.39112199
MN15 free energy (quasi-harmonic) (au): -3189.38840203

Cartesian coordinates

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H	2.477866	-0.790766	-1.713484
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H	4.390331	-2.167079	0.284603
H	4.586407	-2.174708	-1.474576
C	5.080844	-0.292219	-0.542797
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C	-1.827174	-1.225255	0.900716
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Cartesian coordinates

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C    -0.160403    -0.666967     0.428685
C    -0.692067    -0.398930    -0.833147
C    -1.012389    -0.747170     1.530753
C    -2.062419    -0.215760    -0.994741
H    -0.036471    -0.337560    -1.694812
C    -2.383427    -0.562576     1.384545
H    -0.605515    -0.960529     2.516071
C    -2.891255    -0.298180     0.117727
H    -2.476010    -0.011224    -1.976181
H    -3.043501    -0.630854     2.242116
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3c
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MN15 free energy (quasi-harmonic) (au): -5763.35590235

Cartesian coordinates
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F     0.304036    -3.799506     2.625212
F     4.606658    -2.823703     1.052057
F     2.990832    -2.690803    -0.378766
F     3.641247    -4.622411     0.343446
O    -5.833617     1.192501     0.647391
H    -4.968646     0.754115     0.529093
C    -5.947182     2.248890    -0.255294
H    -6.921026     2.728090    -0.117490
C    -4.882443     3.307525     0.013723
C    -5.891705     1.722138    -1.684484
F    -3.645073     2.832809    -0.208324
F    -5.045991     4.386940    -0.756681
F    -4.938854     3.694973     1.289035
F    -5.945331     2.702824    -2.589887
F    -6.913544     0.893167    -1.906661
F    -4.760640     1.028624    -1.897357
O     2.869196    -0.466994    -2.171709
H     2.332500    -0.577578    -1.357796
C     3.895982     0.440080    -1.913326
H     4.542850     0.509242    -2.792794
C     3.324923     1.831538    -1.658428
C     4.748438    -0.055909    -0.749686
F     4.285113     2.750752    -1.523639
```

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F     2.545620     2.195467    -2.682990
F     2.568835     1.861304    -0.550953
F     5.729485     0.798965    -0.443101
F     5.301750    -1.230025    -1.059865
F     4.002992    -0.235065     0.351849

4_A
M06-2X SCF energy (au):     -4510.79338285
M06-2X enthalpy (au):       -4510.55074385
M06-2X free energy (au):    -4510.64754485
MN15 SCF energy (au):       -4513.15010732
MN15 enthalpy (au):         -4512.90746832
MN15 free energy (au):      -4513.00426932
MN15 free energy (quasi-harmonic) (au): -4512.99245647

Cartesian coordinates
ATOM   X             Y           Z
N    -0.019599    -0.226539    -1.346767
Br    -0.222121    -1.790661    -2.284084
C    -0.909391     0.835347    -1.465938
C    -0.455273     1.905175    -0.506037
C     0.683704     1.272231     0.301467
C     0.919765    -0.080864    -0.325977
O     1.724667    -0.937416    -0.044570
O    -1.858401     0.837228    -2.219660
H    -0.127288     2.764214    -1.097322
H    -1.311857     2.210599     0.098409
H     0.418049     1.105046     1.348859
H     1.611498     1.844122     0.272853
O     4.271290    -1.413598     0.957177
H     3.332052    -1.231929     0.757777
C     4.987262    -0.218305     0.963999
H     6.036720    -0.439009     1.180309
C     4.951905     0.465771    -0.400937
C     4.469926     0.693147     2.070720
F     5.242831    -0.414519    -1.359134
F     3.741277     0.980434    -0.678305
F     5.836177     1.465805    -0.471231
F     5.037397     1.902816     2.035016
F     4.715098     0.152226     3.265737
F     3.140464     0.859832     1.973294
O    -3.816526     1.569782    -0.413518
H    -3.332229     1.632900    -1.254999
C    -4.142591     0.227454    -0.196951
H    -3.884876    -0.423888    -1.039488
C    -3.368433    -0.259599     1.022318
C    -5.649635     0.150167     0.013162
F    -2.049216    -0.268770     0.751073
F    -3.551224     0.542281     2.073196
F    -3.712800    -1.499265     1.377738
F    -6.061788    -1.103846     0.226048
F    -6.279643     0.614032    -1.069282
F    -6.034391     0.892779     1.057655

4_B
M06-2X SCF energy (au):     -3721.23092289
M06-2X enthalpy (au):       -3721.06446689
M06-2X free energy (au):    -3721.13413489
MN15 SCF energy (au):       -3723.72299869
```

MN15 enthalpy (au):   -3723.55654269
MN15 free energy (au):   -3723.62621069
MN15 free energy (quasi-harmonic) (au): -3723.62061580

Cartesian coordinates

ATOM	X	Y	Z
N	-2.436986	0.679490	-0.294203
Br	-3.065594	0.292719	-1.974293
C	-3.100695	1.557005	0.573891
C	-2.285693	1.606762	1.844162
C	-1.093962	0.669832	1.612932
C	-1.274957	0.118517	0.218706
O	-0.587657	-0.665886	-0.396702
O	-4.123341	2.130940	0.298158
H	-1.990376	2.643763	2.017939
H	-2.926125	1.292063	2.670999
H	-1.064806	-0.171448	2.308857
H	-0.129917	1.179692	1.656232
O	1.912067	-1.828376	-0.576097
H	1.024891	-1.463265	-0.381820
C	2.880024	-1.075364	0.085777
H	3.868457	-1.478733	-0.153198
C	2.858188	0.374703	-0.387147
C	2.687550	-1.193305	1.592852
F	2.947822	0.420545	-1.717385
F	1.717449	0.993227	-0.038423
F	3.872344	1.080304	0.122656
F	3.552421	-0.439054	2.277130
F	2.846792	-2.461642	1.976360
F	1.446633	-0.820517	1.948816

5
M06-2X SCF energy (au):   -8487.49508747
M06-2X enthalpy (au):   -8486.93465447
M06-2X free energy (au):   -8487.08782647
MN15 SCF energy (au):   -8492.16983773
MN15 enthalpy (au):   -8491.60940473
MN15 free energy (au):   -8491.76257673
MN15 free energy (quasi-harmonic) (au): -8491.74317126

Cartesian coordinates

ATOM	X	Y	Z
C	2.716707	-2.355796	-0.596535
C	4.088102	-2.217781	-0.063931
H	2.314543	-3.369775	-0.559096
H	4.439178	-1.196778	0.065157
C	4.451637	-3.148577	1.083306
H	3.996300	-4.127997	0.896314
H	5.536315	-3.282979	1.077487
C	4.026886	-2.622235	2.460317
H	4.288192	-3.397967	3.184663
H	4.615286	-1.734724	2.711104
C	2.543278	-2.292967	2.595854
H	2.215214	-2.365668	3.638750
H	1.911139	-2.999786	2.042274
C	2.198445	-0.895702	2.138292
O	0.917305	-0.609518	2.247357
O	3.022634	-0.102144	1.704982
C	1.924103	-1.370111	-1.181791

C	0.695213	-1.782197	-1.779727
C	2.319705	-0.001377	-1.251982
C	-0.096473	-0.877582	-2.447365
H	0.393049	-2.822435	-1.716199
C	1.526392	0.903172	-1.915949
H	3.230853	0.345949	-0.776910
C	0.334473	0.452351	-2.505002
H	-1.034476	-1.177176	-2.900142
H	1.813152	1.947437	-1.976275
Br	-0.744642	1.698617	-3.386867
Br	4.936576	-2.883944	-1.746137
H	0.760012	0.339485	1.900399
N	-1.102426	0.547572	0.246661
C	-0.530264	1.700225	0.615474
C	-1.233560	2.931060	0.074640
C	-2.524791	2.333747	-0.481172
C	-2.200760	0.850374	-0.483805
O	-2.858055	-0.016663	-1.088180
O	0.507983	1.756118	1.324474
H	-1.362960	3.674133	0.863281
H	-0.606722	3.375087	-0.707810
H	-2.816969	2.678874	-1.473463
H	-3.372155	2.487750	0.194015
O	-2.157603	-2.508388	-0.307648
H	-2.363982	-1.584420	-0.598901
C	-1.486217	-2.466109	0.912721
H	-0.671447	-1.732955	0.938101
C	-2.446344	-2.105381	2.043911
C	-0.889097	-3.845181	1.135061
F	-3.343069	-3.077070	2.270661
F	-1.793802	-1.878821	3.191277
F	-3.128560	-0.999015	1.737312
F	-0.391575	-3.971057	2.372646
F	0.123944	-4.062856	0.275862
F	-1.778039	-4.822044	0.947585
O	2.806231	2.685327	0.258588
H	1.925635	2.384295	0.576256
C	3.613790	2.862552	1.381320
H	3.389699	2.155401	2.187840
C	5.045885	2.615840	0.938035
C	3.410354	4.271587	1.923059
F	5.911933	2.831123	1.934120
F	5.196567	1.348417	0.530461
F	5.390501	3.405177	-0.085397
F	2.116126	4.443343	2.221957
F	3.744332	5.208406	1.027669
F	4.123102	4.494461	3.033197
O	-5.148209	-0.207476	-2.373804
H	-4.283469	0.066473	-1.981744
C	-6.165323	-0.015641	-1.444538
H	-7.039356	-0.602206	-1.744717
C	-5.782066	-0.481317	-0.036490
C	-6.586520	1.450056	-1.428938
F	-5.051352	0.434077	0.620047
F	-6.874446	-0.711397	0.703079
F	-5.075485	-1.611040	-0.095983
F	-7.452169	1.706596	-0.439348
F	-7.170294	1.777571	-2.585345
F	-5.531835	2.263121	-1.272905

5_A
M06-2X SCF energy (au):   -7697.92906262
M06-2X enthalpy (au):   -7697.44382862
M06-2X free energy (au):   -7697.57044362
MN15 SCF energy (au):   -7702.74022612
MN15 enthalpy (au):   -7702.25499212
MN15 free energy (au):   -7702.38160712
MN15 free energy (quasi-harmonic) (au): -7702.36886950

Cartesian coordinates

ATOM	X	Y	Z
C	0.393576	-3.000379	0.060677
C	1.551834	-3.401837	0.883666
H	-0.487369	-3.637985	0.157655
H	2.355653	-2.668460	0.929463
C	1.194898	-4.000183	2.238199
H	0.339584	-4.672775	2.106472
H	2.041648	-4.603880	2.574988
C	0.880469	-2.943270	3.307050
H	0.564275	-3.487033	4.200922
H	1.793592	-2.399908	3.566626
C	-0.201290	-1.935683	2.924460
H	-0.660068	-1.503262	3.822087
H	-1.027232	-2.391954	2.366151
C	0.326776	-0.761641	2.132109
O	-0.618652	-0.044467	1.562941
O	1.518681	-0.504724	2.028397
C	0.294742	-1.897890	-0.779310
C	-0.997008	-1.613402	-1.308916
C	1.370163	-0.987331	-1.007029
C	-1.225872	-0.442338	-1.995167
H	-1.805273	-2.315530	-1.133464
C	1.147206	0.172268	-1.707165
H	2.368302	-1.206374	-0.640456
C	-0.151602	0.432864	-2.180605
H	-2.207584	-0.195362	-2.381486
H	1.943917	0.889550	-1.871686
Br	-0.458839	2.020363	-3.116077
Br	2.162462	-4.838300	-0.351554
H	-0.217203	0.780133	1.115929
N	-1.942651	2.296601	0.107012
C	-0.698095	2.778336	0.095461
C	-0.582762	4.200266	-0.420210
C	-2.000805	4.471724	-0.915473
C	-2.756774	3.234935	-0.447697
O	-3.981931	3.096960	-0.564822
O	0.296146	2.112059	0.488642
H	-0.289972	4.845913	0.413199
H	0.196782	4.266249	-1.183144
H	-2.074171	4.540433	-2.005239
H	-2.463973	5.366613	-0.495041
O	-4.732490	1.007759	0.888797
H	-4.484998	1.823442	0.371194
C	-3.991162	-0.054000	0.377413
H	-2.971623	0.241929	0.096203
C	-3.871560	-1.105534	1.466780
C	-4.692172	-0.590184	-0.864447
F	-5.060301	-1.610583	1.818868

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F    -3.102035    -2.134922     1.063816
F    -3.314603    -0.586647     2.561934
F    -4.066428    -1.659664    -1.389632
F    -4.711844     0.362687    -1.807673
F    -5.956699    -0.944574    -0.624137
O     2.796581     2.677580    -0.038529
H     1.817586     2.610982     0.108684
C     3.362184     1.620888     0.674798
H     2.740157     0.718933     0.682691
C     4.672781     1.273685    -0.004905
C     3.547284     2.018223     2.133456
F     5.366518     0.362548     0.688132
F     4.431326     0.760266    -1.221140
F     5.451903     2.346339    -0.168907
F     4.415406     3.029672     2.271317
F     3.987314     0.998147     2.880039
F     2.374606     2.419509     2.637386

5_B
M06-2X SCF energy (au):     -6908.35751154
M06-2X enthalpy (au):       -6907.94883154
M06-2X free energy (au):    -6908.05061754
MN15 SCF energy (au):       -6913.30323764
MN15 enthalpy (au):         -6912.89455764
MN15 free energy (au):      -6912.99634364
MN15 free energy (quasi-harmonic) (au): -6912.98820010

Cartesian coordinates
ATOM   X             Y           Z
C    -2.736574    -0.187317     0.347778
C    -3.834667    -0.303204    -0.633665
H    -2.741401    -0.940580     1.138486
H    -3.742847     0.345519    -1.502647
C    -4.236580    -1.729266    -0.983146
H    -4.249634    -2.324691    -0.063151
H    -5.256170    -1.706329    -1.376616
C    -3.311965    -2.377116    -2.022751
H    -3.645243    -3.411872    -2.137185
H    -3.447420    -1.885826    -2.990657
C    -1.828201    -2.363826    -1.663920
H    -1.300868    -3.184616    -2.163686
H    -1.650413    -2.518172    -0.591615
C    -1.113814    -1.098606    -2.086885
O     0.109222    -1.004957    -1.613646
O    -1.624278    -0.241481    -2.796373
C    -1.715946     0.754319     0.370469
C    -1.569693     1.772698    -0.618552
C    -0.729210     0.614263     1.390888
C    -0.478181     2.605173    -0.582359
H    -2.308584     1.897471    -1.401953
C     0.378878     1.426771     1.410213
H    -0.864040    -0.148173     2.149910
C     0.480966     2.419180     0.426993
H    -0.347918     3.383514    -1.324973
H     1.152447     1.308086     2.160414
Br     1.955702     3.565196     0.469909
Br    -5.219619     0.521610     0.534605
H     0.575376    -0.159886    -1.996113
N     2.649876     0.422128    -0.786871
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C     2.390429     1.116405    -1.907364
C     3.499905     2.080509    -2.299537
C     4.524439     1.869571    -1.188206
C     3.846152     0.831922    -0.302312
O     4.342251     0.402889     0.751298
O     1.333569     0.997061    -2.567228
H     3.866011     1.820140    -3.295878
H     3.096701     3.095701    -2.348044
H     4.745376     2.766021    -0.602898
H     5.476251     1.464016    -1.541171
O     3.130662    -1.854506     1.437949
H     3.483874    -0.957047     1.189944
C     1.858745    -2.051376     0.904807
H     1.469186    -1.172527     0.378933
C     1.939896    -3.187316    -0.106645
C     0.912012    -2.385459     2.044543
F     0.728508    -3.614028    -0.496476
F     2.606209    -2.789810    -1.194065
F     2.588559    -4.247253     0.396202
F    -0.366640    -2.466856     1.630996
F     0.963773    -1.425255     2.979846
F     1.214462    -3.543391     2.641997

6
M06-2X SCF energy (au):     -2729.21786467
M06-2X enthalpy (au):       -2728.88944067
M06-2X free energy (au):    -2729.00009467
MN15 SCF energy (au):       -2728.66429327
MN15 enthalpy (au):         -2728.33586927
MN15 free energy (au):      -2728.44652327
MN15 free energy (quasi-harmonic) (au): -2728.43569460

Cartesian coordinates
ATOM   X             Y           Z
N     0.307219     0.507705    -2.149176
C     1.139662     0.063620    -3.047558
C     0.571331    -0.828267    -4.108432
C    -0.910958    -0.834080    -3.728490
C    -0.919387    -0.072356    -2.418518
O    -1.863757     0.012508    -1.636355
O     2.412547     0.342791    -3.045988
H     0.788576    -0.419327    -5.097763
H     1.043025    -1.812561    -4.034933
H    -1.337007    -1.827761    -3.578895
H    -1.535369    -0.295522    -4.446870
H     2.645504     0.875627    -2.253881
O    -2.576499    -2.668284    -1.340988
H    -2.619074    -1.694279    -1.417913
C    -1.823050    -3.039113    -0.229474
H    -1.858209    -4.128746    -0.143219
C    -0.340343    -2.654694    -0.342822
C    -2.420429    -2.453598     1.046739
F     0.425144    -3.453407     0.402582
F     0.074750    -2.737300    -1.611320
F    -0.115870    -1.394960     0.069947
F    -3.606511    -3.006897     1.304431
F    -2.610538    -1.130460     0.933342
F    -1.619107    -2.667842     2.096921
O     2.184709     1.225259    -0.321051
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H     1.244542     1.189230    -0.601093
C     2.372382     0.300555     0.710406
H     1.429573    -0.062626     1.129273
C     3.141878    -0.898113     0.169974
C     3.116521     1.020846     1.823502
F     3.388268    -1.803766     1.120184
F     2.432646    -1.501368    -0.796851
F     4.310782    -0.530711    -0.367180
F     3.374632     0.212169     2.856488
F     2.371232     2.037945     2.270381
F     4.278612     1.526621     1.395875
O    -0.616853     1.092362     0.603722
H    -1.143893     0.703151    -0.132914
C    -1.120009     2.350226     0.923383
H    -0.541789     2.766164     1.753621
C    -0.968773     3.297083    -0.263169
C    -2.569410     2.216177     1.378467
F     0.319661     3.380481    -0.614711
F    -1.649500     2.857021    -1.330153
F    -1.398434     4.529964     0.019997
F    -3.321974     1.655794     0.420180
F    -3.112779     3.395755     1.692686
F    -2.636886     1.427276     2.453598

6_A
M06-2X SCF energy (au):     -1939.64871983
M06-2X enthalpy (au):       -1939.39709983
M06-2X free energy (au):    -1939.48584083
MN15 SCF energy (au):       -1939.23381343
MN15 enthalpy (au):         -1938.98219343
MN15 free energy (au):      -1939.07093443
MN15 free energy (quasi-harmonic) (au): -1939.06287060

Cartesian coordinates
ATOM   X             Y           Z
N    -0.556690     2.442713     0.163453
C     0.208454     3.449953    -0.135836
C    -0.146607     4.768773     0.479708
C    -1.397294     4.397020     1.281115
C    -1.503858     2.896765     1.072780
O    -2.282391     2.138114     1.633419
O     1.243902     3.350241    -0.923895
H     0.684574     5.116392     1.099152
H    -0.315979     5.508246    -0.306660
H    -2.305885     4.873297     0.903982
H    -1.319284     4.610400     2.348781
H     1.342264     2.420788    -1.232665
O    -1.102993    -0.306080     1.076425
H    -1.456312     0.551409     1.396474
C    -2.181819    -1.048362     0.594416
H    -3.152429    -0.637466     0.894884
C    -2.143941    -1.055160    -0.929625
C    -2.064300    -2.449055     1.176048
F    -1.046703    -1.663979    -1.400448
F    -3.207933    -1.671563    -1.453686
F    -2.131650     0.204570    -1.380409
F    -2.218724    -2.408007     2.502128
F    -0.861388    -2.983237     0.927186
F    -2.990240    -3.273892     0.674983
```

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O     0.818464     0.541870    -1.131478
H     0.081914     0.851072    -0.550790
C     1.570694    -0.426687    -0.463925
H     0.948720    -1.153028     0.069964
C     2.355662    -1.170127    -1.532436
C     2.479021     0.246626     0.558982
F     1.521972    -1.832458    -2.338049
F     3.068528    -0.330232    -2.291664
F     3.201006    -2.054643    -0.991899
F     3.171560    -0.641291     1.277265
F     1.735395     0.973935     1.402712
F     3.353942     1.079352    -0.021473

6_B
M06-2X SCF energy (au):     -1150.07664901
M06-2X enthalpy (au):       -1149.90113501
M06-2X free energy (au):    -1149.96577601
MN15 SCF energy (au):       -1149.80139012
MN15 enthalpy (au):         -1149.62587612
MN15 free energy (au):      -1149.69051712
MN15 free energy (quasi-harmonic) (au): -1149.68584811

Cartesian coordinates
ATOM   X             Y           Z
N     2.238848    -0.015447    -0.281013
C     3.385815    -0.548090     0.010509
C     4.387659     0.303929     0.728112
C     3.610754     1.611482     0.867331
C     2.284670     1.291875     0.200394
O     1.349701     2.073589     0.089745
O     3.712582    -1.781013    -0.285669
H     4.651310    -0.165022     1.679648
H     5.296943     0.384897     0.127054
H     4.075361     2.454986     0.351873
H     3.428666     1.906005     1.903331
H     2.982003    -2.225596    -0.752786
O    -0.658089     0.836424    -1.201315
H     0.090233     1.389388    -0.877983
C    -1.030748     0.011715    -0.141392
H    -0.195228    -0.243258     0.522081
C    -2.087162     0.719518     0.697298
C    -1.543552    -1.284561    -0.746198
F    -1.593730     1.882810     1.140230
F    -3.188563     0.991261    -0.012359
F    -2.455421    -0.001777     1.763226
F    -2.515646    -1.063935    -1.637893
F    -2.026176    -2.110703     0.190466
F    -0.551202    -1.918477    -1.380021

7
M06-2X SCF energy (au):     -6262.18965932
M06-2X enthalpy (au):       -6261.82139032
M06-2X free energy (au):    -6261.95494332
MN15 SCF energy (au):       -6264.27641486
MN15 enthalpy (au):         -6263.90814586
MN15 free energy (au):      -6264.04169886
MN15 free energy (quasi-harmonic) (au): -6264.02865154

Cartesian coordinates
```

ATOM	X	Y	Z
N	-1.037569	0.416510	2.720301
Br	0.414529	-0.559195	2.127622
C	-2.294656	-0.115356	2.830535
C	-3.261721	1.004597	3.096372
C	-2.447434	2.285931	2.889955
C	-1.040282	1.818800	2.632922
O	-0.056263	2.467741	2.366893
O	-2.572730	-1.306692	2.744765
H	-4.106312	0.903064	2.413173
H	-3.633113	0.890708	4.118448
H	-2.453299	2.958800	3.749528
H	-2.760788	2.847523	2.005891
S	-1.081688	-3.296772	0.521493
O	0.298549	-3.604740	0.192127
O	-1.746743	-2.160702	-0.083872
O	-1.296781	-3.315683	2.055479
H	-1.800697	-2.447870	2.387069
C	-2.037586	-4.787705	0.049978
F	-3.302465	-4.624778	0.401270
F	-1.953872	-4.942534	-1.262159
F	-1.534852	-5.848435	0.659664
O	-1.461900	1.016611	0.021149
H	-0.504940	1.001540	-0.170777
C	-2.177823	0.638869	-1.112104
H	-1.924803	-0.363843	-1.475234
C	-3.640634	0.626781	-0.697568
C	-1.913832	1.617135	-2.250563
F	-4.007537	1.790002	-0.143738
F	-4.438517	0.398610	-1.744275
F	-3.860718	-0.329933	0.211158
F	-2.463068	1.206656	-3.395899
F	-0.584358	1.704000	-2.439344
F	-2.367460	2.845711	-1.992452
O	1.268724	1.703520	0.064813
H	1.203478	1.964077	1.005691
C	1.714552	2.775740	-0.712169
H	1.568821	2.528960	-1.765979
C	0.914730	4.041575	-0.417081
C	3.209256	2.971621	-0.485072
F	1.228348	4.556778	0.779833
F	1.140321	4.981354	-1.337727
F	-0.390361	3.762627	-0.409909
F	3.491349	3.096131	0.816764
F	3.668244	4.052978	-1.118251
F	3.880064	1.904386	-0.939345
O	2.379672	-1.831513	0.838468
H	2.061087	-2.686632	0.498888
C	2.812088	-0.996390	-0.194813
H	2.910977	0.014025	0.207087
C	4.192768	-1.436513	-0.670219
C	1.818625	-0.922371	-1.357732
F	4.603492	-0.705716	-1.712399
F	5.079507	-1.293272	0.316767
F	4.200386	-2.723526	-1.036003
F	2.082047	0.128176	-2.142511
F	0.563383	-0.802019	-0.909249
F	1.860184	-2.021676	-2.121088

7_A
M06-2X SCF energy (au):   -5472.61572401
M06-2X enthalpy (au):   -5472.32435801
M06-2X free energy (au):   -5472.43428401
MN15 SCF energy (au):   -5474.84474851
MN15 enthalpy (au):   -5474.55338251
MN15 free energy (au):   -5474.66330851
MN15 free energy (quasi-harmonic) (au): -5474.65389350

Cartesian coordinates

ATOM	X	Y	Z
N	1.124404	2.325452	-0.109358
Br	0.281426	2.616590	1.493928
C	2.304516	1.651151	-0.254196
C	2.747513	1.769430	-1.684563
C	1.640098	2.557071	-2.390220
C	0.618303	2.859147	-1.321544
O	-0.425142	3.449563	-1.392569
O	2.920479	1.073859	0.638591
H	3.713065	2.281831	-1.688582
H	2.886433	0.762694	-2.079036
H	1.151298	1.990962	-3.184108
H	1.985003	3.509766	-2.798922
S	0.860345	-0.779518	2.340714
O	0.451482	-0.517535	0.973803
O	-0.127946	-0.780221	3.399801
O	2.070164	0.104144	2.734298
H	2.449489	0.606770	1.879582
C	1.636474	-2.440652	2.347523
F	0.712865	-3.346588	2.069655
F	2.593778	-2.476360	1.434838
F	2.149368	-2.680963	3.544506
O	-1.666352	0.997766	-0.313996
H	-2.258528	1.315781	-1.015805
C	-2.398132	0.427865	0.729117
H	-1.728521	0.273866	1.578783
C	-3.501081	1.378368	1.175368
C	-2.928269	-0.942725	0.318293
F	-4.279652	0.827152	2.108210
F	-2.967100	2.493996	1.679281
F	-4.277817	1.732691	0.141578
F	-1.927220	-1.678617	-0.182099
F	-3.871410	-0.848680	-0.628485
F	-3.447736	-1.601228	1.355032
O	0.385938	-0.035336	-1.768593
H	-0.348591	0.025980	-1.128154
C	0.408999	-1.278502	-2.391461
H	-0.575502	-1.753002	-2.466707
C	0.914741	-1.050758	-3.811615
C	1.335464	-2.228706	-1.624725
F	2.206882	-0.683575	-3.817276
F	0.799463	-2.145481	-4.565644
F	0.216685	-0.073798	-4.398189
F	0.701378	-2.762392	-0.575586
F	2.416080	-1.586794	-1.168632
F	1.756067	-3.241572	-2.395369

7_B
M06-2X SCF energy (au):   -4683.04649998

M06-2X enthalpy (au):   -4682.83101998
M06-2X free energy (au):   -4682.92003898
MN15 SCF energy (au):   -4685.41791317
MN15 enthalpy (au):   -4685.20243317
MN15 free energy (au):   -4685.29145217
MN15 free energy (quasi-harmonic) (au): -4685.28259019

Cartesian coordinates

ATOM	X	Y	Z
N	-0.272839	2.481750	0.523409
Br	-0.125472	2.720491	2.334659
C	-1.110526	1.622487	-0.064898
C	-1.067854	1.810752	-1.549426
C	0.178530	2.673292	-1.777540
C	0.571872	3.173285	-0.412379
O	1.404656	3.953226	-0.059631
O	-1.838403	0.855066	0.612585
H	-1.067029	0.855985	-2.074968
H	-1.990808	2.341998	-1.809725
H	0.014003	3.523298	-2.440478
H	1.016382	2.079512	-2.153770
S	-1.748858	-2.016899	-0.957743
O	-1.036298	-2.306647	0.282398
O	-0.924169	-1.916944	-2.169576
O	-2.733821	-0.887776	-0.831418
H	-2.336489	0.112949	0.007110
C	-2.856685	-3.441025	-1.263375
F	-3.658755	-3.611937	-0.222095
F	-3.583508	-3.220781	-2.349872
F	-2.122073	-4.531306	-1.437468
O	0.949029	-0.194989	-1.021894
H	0.545791	-0.827942	-1.646182
C	1.866268	-0.870579	-0.214017
H	1.587030	-1.912518	-0.018514
C	3.229516	-0.856894	-0.896192
C	1.880282	-0.137026	1.117357
F	3.152081	-1.511994	-2.059845
F	3.633934	0.390145	-1.162328
F	4.168380	-1.445988	-0.149717
F	2.751456	-0.670585	1.973912
F	0.664113	-0.184628	1.670464
F	2.199802	1.158362	0.958487

8
M06-2X SCF energy (au):   -9088.79319471
M06-2X enthalpy (au):   -9088.28039871
M06-2X free energy (au):   -9088.43569871
MN15 SCF energy (au):   -9093.50157941
MN15 enthalpy (au):   -9092.98878341
MN15 free energy (au):   -9093.14408341
MN15 free energy (quasi-harmonic) (au): -9093.12615870

Cartesian coordinates

ATOM	X	Y	Z
C	-0.670597	-2.179138	-2.915907
C	0.176280	-0.974685	-2.865235
H	-0.325665	-2.957175	-3.598558
H	-0.065523	-0.259140	-2.080143
C	1.664928	-1.182760	-3.084673

H	2.078235	-1.384556	-2.087092
H	1.824636	-2.082725	-3.687330
C	2.393218	-0.003437	-3.735319
H	3.465578	-0.214254	-3.710328
H	2.104043	0.066015	-4.787685
C	2.125262	1.353416	-3.072081
H	1.071184	1.636132	-3.132921
H	2.716247	2.123332	-3.577897
C	2.512637	1.347274	-1.620293
O	3.801945	1.072095	-1.437076
O	1.736708	1.539725	-0.700873
C	-1.867847	-2.410310	-2.230020
C	-2.362009	-1.525464	-1.236845
C	-2.584203	-3.596093	-2.538204
C	-3.539616	-1.812448	-0.585076
H	-1.795725	-0.648569	-0.950399
C	-3.765450	-3.884689	-1.889845
H	-2.194129	-4.272876	-3.292425
C	-4.226684	-2.986697	-0.921191
H	-3.920253	-1.150170	0.183880
H	-4.321869	-4.786119	-2.117694
Br	-5.823488	-3.377346	-0.019767
Br	-0.716065	-0.264361	-4.512957
H	4.003994	1.058480	-0.477484
S	2.786248	0.175116	1.726525
O	3.873358	1.130107	1.416461
O	2.705720	-0.931123	0.753489
O	1.495614	0.769691	2.106707
C	3.364129	-0.629160	3.264448
F	3.469432	0.271229	4.232842
F	2.491558	-1.564061	3.629127
F	4.546794	-1.195454	3.060651
O	0.371415	-1.868464	-0.165328
H	1.108946	-1.254037	0.025693
C	0.605943	-3.012908	0.594247
H	1.254638	-2.821983	1.456272
C	-0.722268	-3.524421	1.138643
C	1.298103	-4.046642	-0.284659
F	-1.410797	-2.519933	1.682189
F	-1.487050	-4.073788	0.181689
F	-0.529759	-4.457735	2.076330
F	2.536705	-3.636758	-0.578237
F	0.651206	-4.216141	-1.449076
F	1.381313	-5.239177	0.313067
O	-0.779687	0.788156	0.405257
H	0.078258	0.753582	0.873584
C	-1.103479	2.119279	0.146696
H	-0.245821	2.716870	-0.182441
C	-2.104729	2.107827	-0.997178
C	-1.683334	2.748537	1.409147
F	-1.550950	1.540830	-2.082587
F	-3.197450	1.394462	-0.693847
F	-2.493426	3.336866	-1.334166
F	-0.734297	2.801374	2.353648
F	-2.696324	2.022983	1.894860
F	-2.132431	3.989562	1.200603
O	3.446352	3.749426	0.719782
H	3.788986	2.860832	0.929286
C	2.202770	3.859789	1.346127

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H     1.602511     2.944683     1.278186
C     2.403777     4.166760     2.825043
C     1.458677     4.964372     0.618563
F     1.245357     4.268422     3.484295
F     3.114346     3.181081     3.389614
F     3.080734     5.306898     3.009590
F     0.272922     5.216360     1.184790
F     1.237377     4.602281    -0.653075
F     2.154651     6.104822     0.594949

8_A
M06-2X SCF energy (au):     -8299.22421974
M06-2X enthalpy (au):       -8298.78824074
M06-2X free energy (au):    -8298.92173674
MN15 SCF energy (au):       -8304.07022434
MN15 enthalpy (au):         -8303.63424534
MN15 free energy (au):      -8303.76774134
MN15 free energy (quasi-harmonic) (au): -8303.75180860

Cartesian coordinates
ATOM   X             Y           Z
C    -3.724320     0.655212    -1.385977
C    -3.459393     2.094492    -1.184346
H    -4.088371     0.382049    -2.378370
H    -2.927335     2.332578    -0.266041
C    -2.933646     2.869163    -2.386819
H    -3.464006     2.541525    -3.288604
H    -3.184778     3.920650    -2.223240
C    -1.414819     2.766442    -2.583932
H    -1.148816     3.507435    -3.342748
H    -0.905680     3.057436    -1.661243
C    -0.901819     1.406098    -3.046207
H     0.107482     1.502014    -3.465523
H    -1.525347     0.980646    -3.840065
C    -0.777142     0.392294    -1.940049
O    -0.700829    -0.854736    -2.392856
O    -0.760741     0.668113    -0.753032
C    -3.551444    -0.361982    -0.460089
C    -3.775717    -1.699267    -0.906190
C    -3.044031    -0.133961     0.856326
C    -3.460989    -2.765036    -0.098467
H    -4.166967    -1.862825    -1.906261
C    -2.756187    -1.196769     1.671432
H    -2.848218     0.871181     1.215424
C    -2.932098    -2.499584     1.171904
H    -3.587235    -3.785499    -0.439654
H    -2.351359    -1.044872     2.664567
Br    -2.381703    -3.928040     2.228534
Br    -5.362160     2.598184    -0.856873
H    -0.598387    -1.478777    -1.631564
S     0.655301    -2.066240     0.680065
O    -0.378950    -2.517865    -0.270550
O     0.152135    -1.675272     2.005427
O     1.646510    -1.141957     0.101376
C     1.613679    -3.584583     1.028428
F     2.598153    -3.306748     1.875895
F     0.827170    -4.511377     1.564026
F     2.133658    -4.056438    -0.099834
O    -0.257829     0.961277     2.554120
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H    -0.169580    -0.002761     2.402869
C     0.674202     1.607506     1.740589
H     0.727180     1.190003     0.729857
C     0.210771     3.051678     1.632405
C     2.071506     1.516935     2.342748
F     1.134498     3.829169     1.057434
F    -0.908860     3.130490     0.898097
F    -0.068649     3.569350     2.833053
F     2.355177     0.248220     2.650451
F     2.198444     2.242440     3.460915
F     3.000891     1.948113     1.473310
O     2.138305     0.032741    -2.307355
H     1.843260    -0.637715    -1.663476
C     3.088352     0.827076    -1.662537
H     3.205736     0.578156    -0.602216
C     4.433255     0.610159    -2.343172
C     2.629441     2.276205    -1.745292
F     4.364875     0.847253    -3.657872
F     5.383904     1.401338    -1.832131
F     4.820155    -0.659219    -2.182374
F     1.414323     2.396099    -1.192174
F     2.527303     2.694354    -3.013446
F     3.457031     3.103361    -1.102091

8_B
M06-2X SCF energy (au):     -7509.64738236
M06-2X enthalpy (au):       -7509.28738636
M06-2X free energy (au):    -7509.39704036
MN15 SCF energy (au):       -7514.63575681
MN15 enthalpy (au):         -7514.27576081
MN15 free energy (au):      -7514.38541481
MN15 free energy (quasi-harmonic) (au): -7514.37371545

Cartesian coordinates
ATOM   X             Y           Z
C     0.617251     1.787194     1.706629
C    -0.060259     3.045226     1.331606
H     0.425665     1.412168     2.707567
H     0.174658     3.382875     0.324669
C    -1.541774     3.172227     1.631618
H    -1.804753     4.221531     1.474595
H    -2.040392     2.606825     0.836599
C    -2.001837     2.687888     3.018716
H    -1.165551     2.311528     3.616510
H    -2.411501     3.528845     3.582641
C    -3.074905     1.610611     2.918714
H    -3.958884     1.983537     2.388310
H    -3.417933     1.286056     3.907181
C    -2.618128     0.387541     2.170886
O    -3.604120    -0.493146     2.007583
O    -1.493129     0.199100     1.737392
C     1.554685     1.095511     0.941903
C     2.223906     0.008393     1.568144
C     1.845825     1.412163    -0.415730
C     3.165752    -0.725501     0.882331
H     1.991677    -0.231480     2.600746
C     2.772735     0.668779    -1.107380
H     1.327580     2.218810    -0.923409
C     3.421763    -0.388164    -0.449742
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H     3.682970    -1.552058     1.354241
H     2.996661     0.888613    -2.144467
Br     4.680377    -1.397005    -1.402930
Br     1.002181     4.232671     2.533532
H    -3.314917    -1.184188     1.382603
S    -2.767681     0.508689    -1.122021
O    -3.019479    -0.896407    -0.765348
O    -1.333753     0.883444    -1.160566
O    -3.629556     1.486745    -0.447685
C    -3.269174     0.603220    -2.879055
F    -3.082369     1.837295    -3.340595
F    -2.547781    -0.241689    -3.609054
F    -4.555620     0.289251    -3.002324
O     0.318547    -1.223564    -0.577544
H    -0.273162    -0.468970    -0.786674
C    -0.452214    -2.301670    -0.158545
H    -1.385009    -2.004286     0.328315
C    -0.816117    -3.177432    -1.355327
C     0.370785    -3.068624     0.861411
F     0.234333    -3.889583    -1.794308
F    -1.790153    -4.043968    -1.050999
F    -1.235791    -2.421742    -2.372933
F     0.465934    -2.366359     1.998727
F     1.616161    -3.304261     0.432632
F    -0.192503    -4.248499     1.154037

9
M06-2X SCF energy (au):     -3330.48921480
M06-2X enthalpy (au):       -3330.21364880
M06-2X free energy (au):    -3330.32778180
MN15 SCF energy (au):       -3329.96642352
MN15 enthalpy (au):         -3329.69085752
MN15 free energy (au):      -3329.80499052
MN15 free energy (quasi-harmonic) (au): -3329.79378072

Cartesian coordinates
ATOM   X             Y           Z
S    -1.724872    -0.336089     1.791845
O    -2.972783    -0.299023     1.049063
O    -0.643083     0.557451     1.424805
O    -1.213171    -1.794085     1.930406
H    -0.201382    -1.873024     1.652971
C    -2.188703     0.034749     3.527004
F    -2.628307     1.282130     3.573011
F    -3.146354    -0.795077     3.905952
F    -1.138361    -0.101559     4.315852
O     1.110319    -1.827374     1.034281
H     1.028334    -1.189960     0.268919
C     2.306032    -1.658556     1.748231
H     2.364699    -2.429051     2.521450
C     3.485167    -1.849598     0.798308
C     2.324582    -0.295726     2.433845
F     3.385958    -3.028039     0.183370
F     3.509152    -0.895472    -0.141710
F     4.646684    -1.813100     1.453273
F     1.324681    -0.224884     3.318309
F     2.166810     0.695959     1.551898
F     3.470916    -0.094847     3.087536
O     0.540796    -0.283886    -1.007676
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H    -0.141247     0.377042    -0.771111
C     0.153108    -0.929885    -2.189108
H    -0.398342    -0.263264    -2.858764
C     1.427487    -1.357404    -2.901748
C    -0.754639    -2.115511    -1.867484
F     1.141635    -2.011985    -4.031257
F     2.158524    -0.285185    -3.208362
F     2.177925    -2.159527    -2.139238
F    -0.112620    -3.078866    -1.197918
F    -1.263364    -2.651788    -2.977768
F    -1.771460    -1.707110    -1.095325
O    -1.891402     1.014043    -1.234855
H    -2.624810     0.661069    -0.701248
C    -2.062832     2.382203    -1.464697
H    -3.093170     2.646421    -1.725613
C    -1.674655     3.175112    -0.219465
C    -1.174358     2.709562    -2.657146
F    -2.387428     2.738420     0.826628
F    -0.379021     3.035094     0.076674
F    -1.924634     4.478574    -0.372754
F    -1.125484     4.022012    -2.888164
F    -1.640679     2.105338    -3.753458
F     0.078685     2.273205    -2.463768

9_A
M06-2X SCF energy (au):     -2540.92033776
M06-2X enthalpy (au):       -2540.72094376
M06-2X free energy (au):    -2540.81107576
MN15 SCF energy (au):       -2540.53460000
MN15 enthalpy (au):         -2540.33520600
MN15 free energy (au):      -2540.42533800
MN15 free energy (quasi-harmonic) (au): -2540.41866124

Cartesian coordinates
ATOM   X             Y           Z
S    -2.389115     0.867386    -0.570186
O    -3.571703     0.054070    -0.390997
O    -1.309798     0.417095    -1.432655
O    -1.830716     1.340337     0.799871
H    -0.815091     1.098772     0.894274
C    -2.981288     2.469715    -1.238562
F    -1.976921     3.324957    -1.324089
F    -3.488779     2.254891    -2.442727
F    -3.916334     2.956186    -0.438677
O     0.539959     0.591920     0.889126
H     0.622073    -0.154837     0.233443
C     1.632073     1.468951     0.787967
H     1.484047     2.300280     1.481355
C     2.894229     0.717540     1.202005
C     1.709194     2.032251    -0.627866
F     3.093787    -0.348357     0.415203
F     3.974811     1.495647     1.130685
F     2.770817     0.281611     2.455443
F     2.757502     2.840100    -0.783296
F     0.599624     2.726129    -0.897124
F     1.801216     1.046928    -1.530739
O     0.757699    -1.472373    -0.791925
H     0.319520    -1.309177    -1.643676
C     0.334109    -2.692915    -0.243477
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H     0.385491    -3.517548    -0.961899
C     1.305601    -2.987029     0.892420
C    -1.110528    -2.564090     0.235104
F     2.546003    -3.084877     0.415322
F     1.291677    -2.002479     1.801257
F     1.001586    -4.128007     1.511182
F    -1.515974    -3.640647     0.905754
F    -1.919058    -2.392742    -0.813481
F    -1.257323    -1.493379     1.035175

9_B
M06-2X SCF energy (au):     -1751.34795854
M06-2X enthalpy (au):       -1751.22390354
M06-2X free energy (au):    -1751.29193254
MN15 SCF energy (au):       -1751.10295384
MN15 enthalpy (au):         -1750.97889884
MN15 free energy (au):      -1751.04692784
MN15 free energy (quasi-harmonic) (au): -1751.04193530

Cartesian coordinates
ATOM   X             Y           Z
S    -2.244935    -0.406374     0.959837
O    -1.561117     0.281616     2.038027
O    -3.451146    -1.164493     1.201012
O    -1.234501    -1.269468     0.141854
H    -0.277909    -1.144210     0.487653
C    -2.684832     0.864028    -0.288714
F    -1.615562     1.581829    -0.586950
F    -3.146894     0.269938    -1.375839
F    -3.619502     1.646269     0.227716
O     1.089626    -0.862897     1.103058
H     1.057269    -0.576315     2.030226
C     2.137534    -0.227661     0.412336
H     2.932796     0.086284     1.093131
C     2.707085    -1.260759    -0.551750
C     1.619992     1.014065    -0.314561
F     3.320591    -2.231878     0.125331
F     1.740575    -1.823173    -1.283450
F     3.589049    -0.700295    -1.382785
F     0.837952     0.697007    -1.353793
F     2.631945     1.753017    -0.772361
F     0.898876     1.758591     0.526794

HFIP_dimer
M06-2X SCF energy (au):     -1579.10982103
M06-2X enthalpy (au):       -1578.95960203
M06-2X free energy (au):    -1579.03002303
MN15 SCF energy (au):       -1578.84380226
MN15 enthalpy (au):         -1578.69358326
MN15 free energy (au):      -1578.76400426
MN15 free energy (quasi-harmonic) (au): -1578.75968723

Cartesian coordinates
ATOM   X             Y           Z
O    -0.681293    -1.178311     0.528966
H    -0.400430    -1.987101     0.076234
C    -2.004644    -0.858129     0.199374
H    -2.631009    -1.741662     0.041519
C    -2.555111    -0.096979     1.397763
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C    -2.024436    -0.025558    -1.079878
F    -2.564547    -0.887166     2.472819
F    -1.794445     0.967857     1.682407
F    -3.800721     0.328784     1.180056
F    -3.265043     0.345521    -1.408605
F    -1.525960    -0.742342    -2.091906
F    -1.280103     1.078912    -0.955666
O     0.988429     1.022364     0.970739
H     0.426621     0.228647     0.866711
C     2.176071     0.833296     0.265832
H     2.834398     1.689346     0.440608
C     2.892777    -0.412231     0.774395
C     1.900063     0.769528    -1.233485
F     4.048032    -0.628017     0.139829
F     3.151108    -0.289833     2.078084
F     2.128450    -1.506312     0.617596
F     1.096537    -0.260205    -1.540503
F     3.024489     0.632877    -1.944655
F     1.292037     1.888494    -1.632286

HFIP_monomer
M06-2X SCF energy (au):     -789.546847710
M06-2X enthalpy (au):       -789.472854710
M06-2X free energy (au):    -789.518084710
MN15 SCF energy (au):       -789.417726497
MN15 enthalpy (au):         -789.343733497
MN15 free energy (au):      -789.388963497
MN15 free energy (quasi-harmonic) (au): -789.388080787

Cartesian coordinates
ATOM   X             Y           Z
O    -0.010865     2.174661    -0.152203
H     0.789292     2.073874     0.380621
C    -0.458014     3.498343    -0.068189
H    -0.109438     4.026171     0.825618
C     0.039497     4.264367    -1.288691
C    -1.977352     3.436128    -0.006142
F     1.376062     4.228060    -1.326093
F    -0.412246     3.726573    -2.426684
F    -0.337665     5.547009    -1.261566
F    -2.482188     2.744689    -1.032872
F    -2.521782     4.657450    -0.023020
F    -2.360773     2.826578     1.119227

HFIP_trimer
M06-2X SCF energy (au):     -2368.67537517
M06-2X enthalpy (au):       -2368.44921517
M06-2X free energy (au):    -2368.54335217
MN15 SCF energy (au):       -2368.27081733
MN15 enthalpy (au):         -2368.04465733
MN15 free energy (au):      -2368.13879433
MN15 free energy (quasi-harmonic) (au): -2368.13141016

Cartesian coordinates
ATOM   X             Y           Z
O     1.436347    -1.285593     0.613362
H     0.617399    -0.756696     0.748141
C     1.121025    -2.545329     0.097604
H     2.048946    -3.102238    -0.059726
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C     0.279456    -3.332079     1.097966
C     0.433375    -2.401029    -1.255494
F     0.912218    -3.390110     2.272050
F    -0.910836    -2.755275     1.305855
F     0.062731    -4.581810     0.678017
F     1.240256    -1.763549    -2.108107
F    -0.697033    -1.683133    -1.151487
F     0.117576    -3.584725    -1.784783
O    -0.856746     0.085997     1.109905
H    -1.023939     0.215140     2.057432
C    -1.837429     0.699736     0.329040
H    -1.595436     0.533426    -0.722172
C    -3.196373     0.058699     0.587339
C    -1.825394     2.204633     0.572443
F    -4.132026     0.548796    -0.229301
F    -3.114675    -1.257897     0.388978
F    -3.603600     0.258490     1.848273
F    -2.032987     2.486696     1.866152
F    -2.764727     2.828269    -0.141790
F    -0.636904     2.711063     0.234515
O     3.343981     0.209950    -0.753793
H     2.710295    -0.352942    -0.260620
C     2.813088     1.489378    -0.910422
H     3.547925     2.118591    -1.421685
C     1.567206     1.447508    -1.788149
C     2.538228     2.126208     0.448230
F     0.594324     0.712618    -1.215319
F     1.068546     2.664049    -2.018968
F     1.851676     0.882766    -2.961928
F     2.045830     3.362700     0.332828
F     3.669337     2.192965     1.154766
F     1.661522     1.401278     1.161238

NBS
M06-2X SCF energy (au):     -2931.67105805
M06-2X enthalpy (au):       -2931.58070605
M06-2X free energy (au):    -2931.62268205
MN15 SCF energy (au):       -2934.29681925
MN15 enthalpy (au):         -2934.20646725
MN15 free energy (au):      -2934.24844325
MN15 free energy (quasi-harmonic) (au): -2934.24810020

Cartesian coordinates
ATOM   X             Y           Z
N    -1.829987     0.060265     0.059673
Br    -3.606645     0.518426     0.100762
C    -1.378439    -1.219982     0.388214
C     0.124808    -1.205175     0.231810
C     0.482215     0.212815    -0.229034
C    -0.828394     0.962421    -0.307414
O    -1.029928     2.110081    -0.619255
O    -2.098092    -2.126940     0.726787
H     0.568000    -1.470335     1.194252
H     0.398107    -1.976513    -0.491430
H     0.946197     0.239876    -1.217504
H     1.136108     0.741769     0.467626

NBS-H
M06-2X SCF energy (au):     -360.513272527
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M06-2X enthalpy (au):   -360.413913527
M06-2X free energy (au):   -360.450684527
MN15 SCF energy (au):   -360.371615037
MN15 enthalpy (au):   -360.272256037
MN15 free energy (au):   -360.309027037
MN15 free energy (quasi-harmonic) (au): -360.308933510

Cartesian coordinates

ATOM	X	Y	Z
N	-1.902882	0.074123	0.057057
C	-1.368128	-1.067922	0.340474
C	0.120924	-1.198197	0.226886
C	0.499840	0.208664	-0.227555
C	-0.843525	0.925929	-0.302460
O	-1.001864	2.085396	-0.627117
O	-2.050617	-2.124786	0.725186
H	0.538179	-1.484288	1.195907
H	0.366991	-1.984016	-0.491974
H	0.975112	0.237865	-1.210558
H	1.146780	0.736296	0.476880
H	-3.000632	-1.916522	0.768894

TS-1
M06-2X SCF energy (au):   -6118.76746712
M06-2X enthalpy (au):   -6118.43533312
M06-2X free energy (au):   -6118.51297012
MN15 SCF energy (au):   -6123.85011570
MN15 enthalpy (au):   -6123.51798170
MN15 free energy (au):   -6123.59561870
MN15 free energy (quasi-harmonic) (au): -6123.59002758

Cartesian coordinates

ATOM	X	Y	Z
C	0.265913	2.157437	0.438482
C	-0.914410	1.686662	1.187633
H	-0.633530	1.520233	2.231666
H	0.135876	3.038871	-0.182529
C	-2.144794	2.587555	1.093500
H	-2.972936	2.050073	1.565523
H	-1.940717	3.463435	1.721165
C	-2.570705	3.085929	-0.294982
H	-3.458683	3.703951	-0.133086
H	-1.809566	3.753466	-0.711818
C	-2.906148	2.024585	-1.343083
H	-3.501707	2.486394	-2.141387
H	-3.515354	1.214156	-0.934921
C	-1.689462	1.440143	-2.048746
O	-0.613898	2.028659	-2.070568
O	-1.862587	0.320286	-2.700568
C	1.555444	1.620459	0.491717
C	2.554983	2.245795	-0.300716
C	1.903779	0.510731	1.312695
C	3.857979	1.795148	-0.272181
H	2.279484	3.082267	-0.936050
C	3.203278	0.066264	1.351846
H	1.149107	0.007577	1.907309
C	4.164632	0.712928	0.557173
H	4.625561	2.264070	-0.875814
H	3.485581	-0.772511	1.976630

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Br     5.931140     0.091979     0.613118
Br    -1.346137    -0.143439     0.520892
N    -2.547001    -2.343154    -0.689700
C    -3.713759    -1.930239    -1.189094
C    -4.909362    -2.758369    -0.727945
C    -4.266434    -3.789142     0.188963
C    -2.778261    -3.407127     0.156446
O    -1.922961    -3.986660     0.806398
O    -3.879577    -0.957814    -1.967503
H    -5.625516    -2.101847    -0.226203
H    -5.409778    -3.185500    -1.600900
H    -4.377168    -4.818885    -0.160368
H    -4.623959    -3.749613     1.220909
H    -2.708647    -0.211047    -2.391725

TS-2
M06-2X SCF energy (au):     -6118.76678438
M06-2X enthalpy (au):       -6118.43575238
M06-2X free energy (au):    -6118.51358538
MN15 SCF energy (au):       -6123.84454870
MN15 enthalpy (au):         -6123.51351670
MN15 free energy (au):      -6123.59134970
MN15 free energy (quasi-harmonic) (au): -6123.58588232

Cartesian coordinates
ATOM   X             Y           Z
C    -0.047514    -1.532611     1.159461
C    -0.568039    -2.694811     0.515854
H    -0.208197    -1.562344     2.238601
H     0.055012    -3.207330    -0.212576
C    -1.635456    -3.502454     1.163772
H    -1.090950    -4.249472     1.759465
H    -2.204845    -2.878821     1.862510
C    -2.567693    -4.211546     0.177857
H    -1.972013    -4.719968    -0.587220
H    -3.143131    -4.973308     0.707742
C    -3.522384    -3.218782    -0.469935
H    -4.217451    -2.795633     0.263306
H    -4.134342    -3.689635    -1.247209
C    -2.786897    -2.074641    -1.109427
O    -1.548488    -2.057382    -1.183915
O    -3.541003    -1.128153    -1.568941
C     1.275848    -1.023292     0.719248
C     1.533688    -0.838476    -0.644425
C     2.269283    -0.703087     1.647188
C     2.769267    -0.372274    -1.077114
H     0.749697    -1.048407    -1.367694
C     3.508301    -0.226053     1.228550
H     2.077248    -0.830850     2.708872
C     3.744962    -0.071398    -0.131852
H     2.967439    -0.232884    -2.134114
H     4.278101     0.018108     1.952115
Br     5.433743     0.574162    -0.714467
Br    -1.469790     0.100155     0.804844
N    -2.719437     1.799778     0.219560
C    -2.918262     2.041201    -1.090036
C    -3.293762     3.493985    -1.330954
C    -3.322571     4.096005     0.072156
C    -2.863587     2.952563     0.976649
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O    -2.660994     3.029412     2.169252
O    -2.817234     1.211035    -2.008192
H    -2.538672     3.942509    -1.981939
H    -4.251175     3.532850    -1.854943
H    -4.321659     4.408666     0.385526
H    -2.648508     4.944710     0.204843
H    -3.057083    -0.227671    -1.759667

TS-3
M06-2X SCF energy (au):     -8487.50729783
M06-2X enthalpy (au):       -8486.94615083
M06-2X free energy (au):    -8487.09002083
MN15 SCF energy (au):       -8492.15791845
MN15 enthalpy (au):         -8491.59677145
MN15 free energy (au):      -8491.74064145
MN15 free energy (quasi-harmonic) (au): -8491.72807262

Cartesian coordinates
ATOM   X             Y           Z
C     0.438773     0.432155     2.672330
C    -0.142838     1.670051     2.967782
H    -1.227416     1.759191     2.918841
H     1.505006     0.317407     2.861220
C     0.587630     2.719998     3.749164
H     0.218441     2.591340     4.777155
H     1.658385     2.499160     3.763542
C     0.352996     4.170497     3.319634
H     0.755071     4.815086     4.104664
H     0.925031     4.379632     2.410234
C    -1.125958     4.527895     3.077270
H    -1.256898     5.608323     3.191032
H    -1.789175     4.021492     3.783315
C    -1.543226     4.181704     1.669027
O    -0.842398     4.865942     0.778462
O    -2.387333     3.352888     1.366969
C    -0.286361    -0.782320     2.310554
C    -1.621655    -0.755273     1.886898
C     0.399565    -1.999180     2.374813
C    -2.263947    -1.929529     1.529353
H    -2.157054     0.185209     1.794004
C    -0.238724    -3.185148     2.033199
H     1.442025    -2.015431     2.678116
C    -1.557546    -3.128857     1.599096
H    -3.288553    -1.910423     1.176060
H     0.291520    -4.129744     2.073853
Br    -2.401892    -4.725944     1.028248
Br     0.416086     1.789360     0.792902
N     0.631330     2.358326    -1.379617
C    -0.138773     3.194306    -2.120416
C     0.039626     2.950128    -3.603064
C     1.046282     1.804779    -3.653606
C     1.240642     1.453468    -2.194751
O     1.848801     0.453087    -1.796856
O    -0.931917     4.027469    -1.657999
H    -0.938317     2.688939    -4.017823
H     0.377732     3.872623    -4.080049
H     2.014210     2.095081    -4.071312
H     0.696005     0.920874    -4.189783
H    -0.985710     4.516015    -0.150524
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O     2.600294    -0.496902     0.625941
H     2.256362    -0.123064    -0.214116
C     3.930937    -0.117197     0.745196
H     4.524565    -0.297108    -0.160968
C     4.018019     1.374675     1.057896
C     4.512577    -0.976054     1.856812
F     3.471888     2.075065     0.056528
F     3.347277     1.690761     2.177542
F     5.279790     1.785837     1.211301
F     3.841284    -0.810857     3.008148
F     5.795718    -0.688268     2.090181
F     4.426029    -2.266688     1.526914
O    -3.184874     2.592921    -2.322281
H    -2.679948     3.398700    -2.116854
C    -2.995740     1.674410    -1.287238
H    -2.205516     1.959267    -0.580860
C    -4.293946     1.554411    -0.493326
C    -2.601636     0.351146    -1.930823
F    -4.132195     0.825199     0.621598
F    -4.728268     2.762387    -0.136353
F    -5.260216     0.973197    -1.217028
F    -3.413517     0.026516    -2.938715
F    -2.615116    -0.647675    -1.047305
F    -1.358922     0.447483    -2.438934
O     0.093812    -1.518296    -0.808546
H     0.625199    -0.839424    -1.265532
C     0.256626    -2.734849    -1.460425
H    -0.399143    -3.479083    -0.995151
C    -0.163528    -2.597596    -2.921274
C     1.696529    -3.224204    -1.311277
F     0.551183    -1.637385    -3.529836
F    -0.000848    -3.729917    -3.609543
F    -1.451681    -2.251002    -2.998781
F     1.899903    -4.388605    -1.936262
F     1.994661    -3.395419    -0.021057
F     2.562434    -2.331578    -1.813168

TS-3_A
M06-2X SCF energy (au):     -7697.93105768
M06-2X enthalpy (au):       -7697.44647868
M06-2X free energy (au):    -7697.56902368
MN15 SCF energy (au):       -7702.72261466
MN15 enthalpy (au):         -7702.23803566
MN15 free energy (au):      -7702.36058066
MN15 free energy (quasi-harmonic) (au): -7702.34958198

Cartesian coordinates
ATOM   X             Y           Z
C     0.982474    -0.306318     2.858498
C     0.361502     0.822424     3.425454
H    -0.719426     0.901655     3.324261
H     2.029402    -0.488891     3.099777
C     0.993446     1.652616     4.498947
H     0.582074     1.242369     5.432594
H     2.074602     1.485656     4.522898
C     0.682458     3.152082     4.434902
H     0.982003     3.592518     5.388598
H     1.295282     3.622296     3.659440
C    -0.798794     3.482322     4.168258
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H    -1.003125     4.499373     4.516641
H    -1.470387     2.796459     4.691230
C    -1.116246     3.455288     2.690883
O    -0.408986     4.351569     2.025002
O    -1.898363     2.683948     2.155368
C     0.273148    -1.378902     2.163866
C     0.943115    -2.588419     1.958974
C    -1.030377    -1.214736     1.676220
C     0.324904    -3.630195     1.277626
H     1.958391    -2.710046     2.326545
C    -1.652478    -2.243461     0.987800
H    -1.556428    -0.271729     1.796869
C    -0.960976    -3.436356     0.786580
H     0.844664    -4.567774     1.113952
H    -2.650994    -2.112003     0.588217
Br    -1.781880    -4.816443    -0.211573
Br     1.058045     1.469964     1.446040
N     1.368976     2.660968    -0.510938
C     0.509090     3.507766    -1.103308
C     0.784921     3.667593    -2.582970
C     1.948057     2.709955    -2.824059
C     2.211008     2.121934    -1.449125
O     3.063433     1.272752    -1.209565
O    -0.425270     4.097665    -0.521502
H    -0.125736     3.416531    -3.133369
H     1.023496     4.715233    -2.782883
H     2.856800     3.198883    -3.182728
H     1.711863     1.891900    -3.509077
H    -0.501157     4.224868     1.026710
O     3.112039    -0.950181     0.296151
H     3.165912    -0.047822    -0.093025
C     2.737714    -1.854103    -0.691297
H     2.514436    -2.811865    -0.213138
C     1.460741    -1.436678    -1.445060
C     3.879375    -2.125547    -1.663771
F     1.713981    -0.773666    -2.584229
F     0.728317    -2.508955    -1.773141
F     0.715082    -0.643639    -0.675004
F     4.884418    -2.740525    -1.030658
F     4.373157    -1.008927    -2.204043
F     3.468781    -2.923422    -2.661184
O    -2.560909     2.907652    -1.627042
H    -1.993056     3.598266    -1.233889
C    -2.347727     1.719848    -0.925155
H    -1.591696     1.802601    -0.132361
C    -3.663598     1.315510    -0.268749
C    -1.867784     0.682015    -1.932500
F    -4.154210     2.328530     0.443542
F    -4.583493     0.977830    -1.182388
F    -3.512351     0.266411     0.555837
F    -0.621009     0.983177    -2.332199
F    -2.639287     0.658769    -3.022295
F    -1.849464    -0.551619    -1.416765

TS-3_B
M06-2X SCF energy (au):     -6908.34915798
M06-2X enthalpy (au):       -6907.94138098
M06-2X free energy (au):    -6908.04561698
MN15 SCF energy (au):       -6913.28680346
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MN15 enthalpy (au):   -6912.87902646
MN15 free energy (au):   -6912.98326246
MN15 free energy (quasi-harmonic) (au): -6912.97231148

Cartesian coordinates

ATOM	X	Y	Z
C	0.017198	-0.555427	1.964278
C	-0.325586	-1.851852	2.427623
H	0.418780	-2.645172	2.370842
H	-0.680071	0.250786	2.192701
C	-1.442888	-2.041784	3.412852
H	-1.011245	-1.696548	4.363426
H	-2.267477	-1.357167	3.182761
C	-1.946571	-3.473864	3.613534
H	-1.094945	-4.148122	3.754000
H	-2.518190	-3.484882	4.545173
C	-2.838531	-4.010843	2.498561
H	-3.604438	-3.285233	2.207880
H	-3.370555	-4.904490	2.847435
C	-2.078105	-4.427286	1.263172
O	-2.821152	-4.376002	0.171169
O	-0.906542	-4.767624	1.267879
C	1.320245	-0.142855	1.439322
C	1.537472	1.226267	1.254569
C	2.331625	-1.057428	1.113414
C	2.752021	1.689706	0.763716
H	0.744971	1.929101	1.487494
C	3.547296	-0.605590	0.625299
H	2.178197	-2.126841	1.222416
C	3.743798	0.765124	0.459275
H	2.917798	2.750786	0.616575
H	4.332495	-1.308678	0.372065
Br	5.405019	1.377592	-0.208187
Br	-1.035297	-1.686214	0.382680
N	-1.804241	-2.092864	-1.834199
C	-1.649177	-3.227669	-2.559752
C	-1.520029	-2.937242	-4.045138
C	-1.623122	-1.416145	-4.114251
C	-1.717373	-1.010684	-2.653310
O	-1.708540	0.163118	-2.267338
O	-1.618236	-4.374399	-2.088841
H	-0.560975	-3.326321	-4.397069
H	-2.312885	-3.465080	-4.580121
H	-2.517244	-1.063307	-4.635029
H	-0.756399	-0.928190	-4.565620
H	-2.262254	-4.500135	-0.665440
O	-1.414613	1.471196	0.002769
H	-1.536782	0.810904	-0.723619
C	-1.637235	2.721874	-0.562925
H	-2.356764	2.697446	-1.391211
C	-2.213675	3.608969	0.528621
C	-0.336156	3.298109	-1.119961
F	-3.452819	3.218598	0.839318
F	-1.483161	3.546378	1.649919
F	-2.264554	4.890220	0.144162
F	-0.562231	4.357451	-1.905381
F	0.296909	2.370903	-1.842296
F	0.502370	3.697462	-0.148204

TS-3'
B3LYP-D3 SCF energy (au): -8487.48092408
B3LYP-D3 enthalpy (au): -8486.92196408
B3LYP-D3 free energy (au): -8487.07273208
M06 SCF energy (au): -8492.14091215
M06 enthalpy (au): -8491.58195215
M06 free energy (au): -8491.73272015
M06 free energy (quasi-harmonic) (au): -8491.71403107

Cartesian coordinates

ATOM	X	Y	Z
C	0.989380	-1.558051	1.986938
C	1.630710	-0.656881	2.904788
H	1.645496	-2.413406	1.793823
H	1.071904	-0.277038	3.756882
C	3.069645	-0.387871	2.848041
H	3.450982	-0.931299	3.732090
H	3.520482	-0.814388	1.948948
C	3.466387	1.094918	3.018291
H	3.008496	1.493308	3.928618
H	4.550241	1.125749	3.145096
C	3.085639	1.953864	1.818128
H	3.519034	1.563391	0.892645
H	3.456891	2.978135	1.939661
C	1.603211	2.023625	1.615140
O	0.794879	1.529300	2.394554
O	1.232275	2.629486	0.504710
C	-0.449986	-1.899974	2.155881
C	-0.874197	-3.212262	1.948378
C	-1.391198	-0.892381	2.391398
C	-2.231025	-3.523577	1.940652
H	-0.144022	-3.994823	1.761478
C	-2.745870	-1.194531	2.405754
H	-1.070938	0.138547	2.518900
C	-3.147161	-2.500669	2.149691
H	-2.564992	-4.538245	1.752325
H	-3.483797	-0.419897	2.571625
Br	-5.002964	-2.866291	1.989995
Br	1.183848	-0.619408	0.132541
N	1.222199	0.393574	-2.038042
C	0.099501	0.597336	-2.744701
C	0.382192	0.994962	-4.179132
C	1.908245	0.993887	-4.239816
C	2.311089	0.563656	-2.838419
O	3.478110	0.389362	-2.479544
O	-1.056344	0.478720	-2.282355
H	-0.089602	0.268602	-4.846312
H	-0.072197	1.970555	-4.370147
H	2.339632	1.977075	-4.444020
H	2.323495	0.287266	-4.962164
H	0.271195	2.437064	0.366045
O	-1.247332	1.649027	0.045444
H	-1.146766	1.074412	-0.762979
C	-2.318944	2.520063	-0.161116
H	-3.132459	2.066235	-0.737147
C	-2.851314	2.876424	1.219604
C	-1.844448	3.753213	-0.924975
F	-3.770364	3.844817	1.160170
F	-3.416289	1.804945	1.785912

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F    -1.868231     3.285379     2.029364
F    -0.946700     4.453517    -0.215196
F    -2.852833     4.571190    -1.233204
F    -1.248842     3.377701    -2.062512
O    -1.928340    -1.688903    -0.805031
H    -1.529634    -0.990085    -1.366983
C    -3.203765    -1.998085    -1.258385
H    -3.627150    -2.775252    -0.612785
C    -4.150724    -0.800956    -1.176695
C    -3.138988    -2.570816    -2.670799
F    -5.424376    -1.172857    -1.333865
F    -4.038678    -0.199181     0.011671
F    -3.878250     0.121851    -2.113685
F    -2.469910    -3.727164    -2.662027
F    -2.496417    -1.742369    -3.504442
F    -4.356890    -2.799396    -3.175812
O     4.417707    -0.339877    -0.136839
H     3.905298    -0.126029    -0.960916
C     5.769160    -0.196701    -0.425134
H     6.030864    -0.492033    -1.449324
C     6.193110     1.259287    -0.253527
C     6.515261    -1.115764     0.529489
F     5.398842     2.047275    -0.986510
F     6.092718     1.665267     1.022036
F     7.455256     1.464094    -0.645020
F     6.231519    -2.392317     0.256164
F     6.162155    -0.892157     1.803432
F     7.840430    -0.956246     0.439629

TS-4
M06-2X SCF energy (au):     -8487.49747763
M06-2X enthalpy (au):       -8486.93740363
M06-2X free energy (au):    -8487.08600763
MN15 SCF energy (au):       -8492.16872492
MN15 enthalpy (au):         -8491.60865092
MN15 free energy (au):      -8491.75725492
MN15 free energy (quasi-harmonic) (au): -8491.74064829

Cartesian coordinates
ATOM   X             Y           Z
C     2.090364     1.618626    -2.138109
C     1.467677     2.959999    -2.225669
H     0.597026     3.071709    -1.582537
H     3.145533     1.569462    -2.411775
C     2.423142     4.144169    -2.167526
H     3.106125     4.085415    -3.020706
H     1.820929     5.049227    -2.292944
C     3.247358     4.246833    -0.879915
H     3.996525     3.448089    -0.848447
H     3.795725     5.190770    -0.934647
C     2.441388     4.218667     0.415724
H     1.488562     4.755719     0.327497
H     2.988799     4.700608     1.231014
C     2.144487     2.815836     0.872282
O     2.303744     1.824352     0.157032
O     1.725204     2.724776     2.109842
C     1.420003     0.394572    -1.939432
C     0.094567     0.337122    -1.446250
C     2.143125    -0.798367    -2.159741
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C	-0.487933	-0.880585	-1.170569
H	-0.466274	1.245584	-1.259946
C	1.559482	-2.024659	-1.901473
H	3.160646	-0.745305	-2.534456
C	0.255217	-2.048094	-1.401921
H	-1.502014	-0.946800	-0.788784
H	2.102969	-2.946443	-2.070419
Br	-0.538650	-3.697944	-1.001304
Br	0.736331	2.837604	-4.069998
H	1.686629	1.736527	2.389266
N	-0.480687	0.301680	2.407607
C	0.687734	-0.343917	2.481183
C	0.579233	-1.847156	2.312604
C	-0.931072	-2.049176	2.259228
C	-1.453107	-0.622974	2.233563
O	-2.656428	-0.328350	2.092235
O	1.783273	0.246502	2.665512
H	1.089152	-2.143313	1.387484
H	1.080445	-2.356597	3.139010
H	-1.327356	-2.538992	3.153351
H	-1.290617	-2.605675	1.391912
O	-3.002764	2.344504	2.656178
H	-2.890603	1.377205	2.491972
C	-1.862883	3.003674	2.196430
H	-0.933366	2.484876	2.453028
C	-1.908323	3.096150	0.678386
C	-1.829092	4.372070	2.846416
F	-0.735360	3.525883	0.173340
F	-2.146315	1.881688	0.162377
F	-2.862009	3.915794	0.227989
F	-1.651711	4.252056	4.165351
F	-2.961938	5.057189	2.654835
F	-0.817560	5.105700	2.357933
O	3.829174	-1.333129	2.302496
H	3.116735	-0.746525	2.660205
C	3.874347	-1.077507	0.935036
H	2.906972	-0.755132	0.524270
C	4.879205	0.033630	0.640948
C	4.259133	-2.383881	0.258884
F	6.142407	-0.371164	0.830400
F	4.782097	0.469093	-0.625125
F	4.664720	1.072271	1.453564
F	5.319694	-2.948894	0.838950
F	4.551141	-2.207120	-1.039414
F	3.244990	-3.255875	0.334881
O	-3.342828	-1.926167	0.046234
H	-3.303890	-1.329195	0.828731
C	-4.405821	-2.813771	0.173989
H	-5.330520	-2.345219	0.533372
C	-4.684150	-3.359267	-1.218065
C	-4.044074	-3.916651	1.163009
F	-5.650659	-4.284429	-1.195442
F	-5.078350	-2.369252	-2.024686
F	-3.596816	-3.914218	-1.762841
F	-5.051290	-4.774465	1.353032
F	-3.744696	-3.364567	2.347746
F	-2.975670	-4.620517	0.766610

TS-4_A

M06-2X SCF energy (au):   -7697.93238391
M06-2X enthalpy (au):   -7697.44830791
M06-2X free energy (au):   -7697.57157291
MN15 SCF energy (au):   -7702.73924001
MN15 enthalpy (au):   -7702.25516401
MN15 free energy (au):   -7702.37842901
MN15 free energy (quasi-harmonic) (au): -7702.36648110

Cartesian coordinates

ATOM	X	Y	Z
C	0.223737	1.709821	1.330564
C	1.230547	2.405593	0.488148
H	1.545327	1.779367	-0.345937
H	-0.547867	2.343426	1.769717
C	0.838399	3.830813	0.100712
H	0.841959	4.442387	1.008772
H	1.620055	4.221082	-0.557685
C	-0.535446	3.978953	-0.570045
H	-1.332751	3.669106	0.114659
H	-0.681535	5.047242	-0.751740
C	-0.700865	3.237083	-1.888572
H	0.113820	3.445537	-2.588604
H	-1.626251	3.544156	-2.390742
C	-0.801028	1.747513	-1.715480
O	-0.893611	1.200726	-0.613590
O	-0.801307	1.071153	-2.834052
C	0.234440	0.368325	1.753151
C	1.170460	-0.589009	1.287028
C	-0.801309	-0.028438	2.631848
C	1.063709	-1.901586	1.698455
H	1.967546	-0.298595	0.609595
C	-0.923767	-1.343515	3.030652
H	-1.503590	0.715598	2.991463
C	0.022715	-2.259634	2.569121
H	1.779739	-2.645446	1.367275
H	-1.724531	-1.657863	3.689480
Br	-0.098326	-4.035707	3.155853
Br	2.824383	2.481399	1.659115
H	-0.733757	0.059130	-2.648578
N	-1.631966	-1.958263	-0.834956
C	-0.598681	-2.169722	-1.641150
C	0.068389	-3.521307	-1.469391
C	-0.832623	-4.192461	-0.439898
C	-1.783784	-3.067121	-0.052491
O	-2.613077	-3.145331	0.861531
O	-0.163652	-1.333106	-2.488122
H	0.120428	-4.031697	-2.433945
H	1.093858	-3.365527	-1.118513
H	-0.319593	-4.578589	0.441924
H	-1.426022	-5.010214	-0.859806
O	-4.359100	-1.147899	0.364200
H	-3.730955	-1.875145	0.607428
C	-3.660657	0.057270	0.381538
H	-2.574000	-0.079769	0.367388
C	-4.036868	0.833674	-0.874228
C	-4.033678	0.833548	1.637600
F	-3.599035	2.104765	-0.827720
F	-3.511834	0.267345	-1.963014
F	-5.364219	0.875838	-1.044854

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F    -5.309771     1.235647     1.632353
F    -3.266819     1.926994     1.800720
F    -3.861095     0.060863     2.719151
O     1.908836     0.059813    -1.622237
H     1.156631    -0.528050    -1.875360
C     2.647286     0.335301    -2.769358
H     2.030530     0.432965    -3.671689
C     3.328988     1.670974    -2.517280
C     3.646567    -0.792250    -2.997967
F     2.407329     2.647638    -2.483568
F     3.953659     1.684182    -1.334767
F     4.216586     1.973710    -3.465517
F     4.505575    -0.901284    -1.977559
F     4.355298    -0.622734    -4.117797
F     2.985706    -1.953057    -3.096673

TS-4_B
M06-2X SCF energy (au):     -6908.35513497
M06-2X enthalpy (au):       -6907.94812597
M06-2X free energy (au):    -6908.04784797
MN15 SCF energy (au):       -6913.30015606
MN15 enthalpy (au):         -6912.89314706
MN15 free energy (au):      -6912.99286906
MN15 free energy (quasi-harmonic) (au): -6912.98533309

Cartesian coordinates
ATOM   X             Y           Z
C     2.539130     0.826995     0.022313
C     3.149445    -0.510568     0.013577
H     2.502579    -1.320493     0.343199
H     3.099658     1.595355    -0.516053
C     4.084052    -0.880171    -1.129718
H     4.674621    -0.000324    -1.411422
H     4.781746    -1.619555    -0.727421
C     3.408318    -1.497836    -2.366156
H     4.192219    -2.029699    -2.912432
H     2.677323    -2.246674    -2.049843
C     2.754280    -0.513904    -3.330047
H     2.429460    -1.029387    -4.241677
H     3.454429     0.265779    -3.650689
C     1.541706     0.159540    -2.748389
O     1.091506    -0.159277    -1.647201
O     1.024239     1.109032    -3.481004
C     1.362451     1.240609     0.689596
C     0.449016     0.315210     1.246028
C     1.060738     2.618547     0.690464
C    -0.739912     0.760426     1.782082
H     0.653671    -0.749468     1.217308
C    -0.113647     3.075623     1.260829
H     1.757274     3.321620     0.243954
C    -0.999431     2.138305     1.789993
H    -1.463661     0.063244     2.187828
H    -0.346112     4.134174     1.280767
Br    -2.613020     2.747171     2.539008
Br     4.266944    -0.003965     1.610257
H     0.302919     1.633593    -2.927857
N    -2.054281     0.812076    -1.951917
C    -1.661314     2.088123    -1.811279
C    -2.732888     2.999312    -1.229177
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C    -3.859681     2.023030    -0.920187
C    -3.312079     0.709519    -1.456316
O    -3.961920    -0.348537    -1.419298
O    -0.537572     2.529139    -2.147053
H    -2.348854     3.537676    -0.358946
H    -2.996601     3.745302    -1.984288
H    -4.808220     2.254847    -1.409761
H    -4.054305     1.909234     0.150043
O    -2.399629    -2.375840    -1.843170
H    -3.029450    -1.596025    -1.785456
C    -1.379745    -2.162787    -0.920112
H    -1.039642    -1.118515    -0.882090
C    -1.870736    -2.554238     0.470330
C    -0.201521    -3.014687    -1.362331
F    -0.906565    -2.464117     1.405317
F    -2.864128    -1.737054     0.845492
F    -2.342912    -3.803747     0.505399
F     0.846281    -2.888460    -0.529389
F     0.201346    -2.661167    -2.585960
F    -0.517867    -4.315683    -1.407643

TS-5
M06-2X SCF energy (au):     -8487.49392992
M06-2X enthalpy (au):       -8486.93392292
M06-2X free energy (au):    -8487.08358192
MN15 SCF energy (au):       -8492.16476693
MN15 enthalpy (au):         -8491.60475993
MN15 free energy (au):      -8491.75441893
MN15 free energy (quasi-harmonic) (au): -8491.73650201

Cartesian coordinates
ATOM   X             Y           Z
C    -0.378171     2.463770     1.589147
C     0.880582     2.784214     0.935180
H    -1.214088     3.115528     1.336298
H     1.697302     2.071931     1.016280
C     1.048108     3.920555    -0.029022
H     1.842272     4.563510     0.359767
H     0.127336     4.511331    -0.078538
C     1.491960     3.453848    -1.430962
H     2.287094     2.709273    -1.327651
H     1.929141     4.323882    -1.926299
C     0.380041     2.906628    -2.315748
H    -0.425173     3.640142    -2.447248
H     0.755642     2.673861    -3.316946
C    -0.242137     1.662341    -1.751333
O     0.025264     1.251181    -0.626918
O    -1.100809     1.055929    -2.536539
C    -0.731985     1.154453     2.139166
C     0.207008     0.136691     2.362012
C    -2.085141     0.930373     2.409814
C    -0.204932    -1.083758     2.873916
H     1.263676     0.277637     2.158427
C    -2.508688    -0.290261     2.919087
H    -2.814502     1.711518     2.223584
C    -1.558108    -1.275598     3.156142
H     0.520840    -1.867610     3.061572
H    -3.558983    -0.465841     3.123786
Br    -2.122420    -2.929829     3.875219
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Br     0.770746     3.618217     2.959180
H     -1.586061     0.341174    -1.991203
N     -0.462198    -1.776848    -0.949339
C     -1.756118    -1.590710    -0.655773
C     -2.374944    -2.726247     0.138525
C     -1.172868    -3.631154     0.392533
C     -0.059412    -2.913701    -0.351018
O      1.117175    -3.337160    -0.394369
O     -2.403888    -0.584393    -1.035654
H     -3.147206    -3.193323    -0.479630
H     -2.860905    -2.348930     1.041612
H     -0.908998    -3.727044     1.449435
H     -1.282001    -4.640581    -0.012004
O      2.583393    -2.171133     1.608211
H      1.991561    -2.718373     1.053955
C      3.683888    -1.824872     0.824199
H      3.784152    -2.435916    -0.079548
C      4.931082    -2.043783     1.667937
C      3.554656    -0.371977     0.375034
F      4.832138    -1.447604     2.860763
F      6.024452    -1.567674     1.059678
F      5.112377    -3.349635     1.885849
F      4.473763    -0.044070    -0.534640
F      2.343893    -0.154757    -0.146461
F      3.686596     0.481562     1.410820
O     -4.447774     0.409146     0.321011
H     -3.663294    -0.003025    -0.127570
C     -4.921033     1.460866    -0.454196
H     -5.894033     1.780842    -0.068738
C     -3.979089     2.658936    -0.358440
C     -5.133491     1.061391    -1.916820
F     -2.703586     2.296076    -0.569149
F     -4.286631     3.613375    -1.242034
F     -4.030278     3.202812     0.865908
F     -5.676789    -0.154596    -1.987284
F     -3.984767     1.038279    -2.609587
F     -5.952436     1.920608    -2.535214
O      2.564823    -1.998745    -2.256759
H      2.032591    -2.486045    -1.576528
C      1.699839    -1.139459    -2.932599
H      0.975758    -0.659879    -2.267765
C      2.533367    -0.057167    -3.590039
C      0.894433    -1.917907    -3.970877
F      3.588534    -0.551240    -4.243288
F      1.796381     0.642915    -4.468810
F      2.996358     0.805225    -2.675940
F     -0.170359    -1.223455    -4.390997
F      0.455769    -3.067279    -3.446462
F      1.625498    -2.229659    -5.053480

TS-5_A
M06-2X SCF energy (au):     -7697.92563019
M06-2X enthalpy (au):       -7697.44242319
M06-2X free energy (au):    -7697.56711719
MN15 SCF energy (au):       -7702.73146922
MN15 enthalpy (au):         -7702.24826222
MN15 free energy (au):      -7702.37295622
MN15 free energy (quasi-harmonic) (au): -7702.36042403
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Cartesian coordinates

ATOM	X	Y	Z
C	-0.958115	0.390225	2.195014
C	-0.895851	1.843217	2.133646
H	-1.929441	-0.042006	1.965059
H	0.077771	2.318294	2.214317
C	-2.056787	2.725034	1.785601
H	-2.301819	3.317354	2.670828
H	-2.931083	2.115328	1.532275
C	-1.700451	3.711853	0.652197
H	-0.674219	4.064742	0.791810
H	-2.355292	4.579856	0.752672
C	-1.870880	3.136580	-0.747184
H	-2.922779	2.938540	-0.975276
H	-1.512114	3.841957	-1.505761
C	-1.113019	1.853876	-0.932089
O	-0.344500	1.423717	-0.071546
O	-1.337985	1.227789	-2.054817
C	0.196816	-0.499062	2.034024
C	1.519884	-0.044818	2.138715
C	-0.058321	-1.843362	1.748028
C	2.573760	-0.929831	1.988057
H	1.748870	0.995401	2.343016
C	0.994549	-2.742381	1.605439
H	-1.081438	-2.193476	1.642973
C	2.296131	-2.276070	1.748195
H	3.598077	-0.581838	2.058027
H	0.799659	-3.790585	1.406379
Br	3.733855	-3.490792	1.623207
Br	-1.179628	1.061112	4.186797
H	-0.922084	0.272791	-2.035069
N	1.514106	-0.892405	-1.457194
C	0.475943	-1.641741	-1.813597
C	0.791771	-3.117280	-1.971205
C	2.299348	-3.146399	-1.743144
C	2.606207	-1.704029	-1.355514
O	3.723841	-1.321001	-0.991808
O	-0.683247	-1.184894	-2.020308
H	0.475221	-3.455590	-2.960882
H	0.225824	-3.684298	-1.225299
H	2.630721	-3.818079	-0.948402
H	2.865663	-3.395084	-2.645264
O	3.866837	1.276024	-0.310411
H	3.851007	0.306097	-0.531736
C	2.654448	1.806890	-0.749874
H	1.799050	1.167777	-0.517075
C	2.653150	1.990655	-2.268331
C	2.445210	3.142641	-0.063048
F	3.320526	3.092985	-2.654898
F	1.402375	2.101081	-2.740435
F	3.235903	0.952308	-2.870591
F	1.414463	3.806441	-0.612593
F	2.165225	2.978671	1.241854
F	3.521745	3.930143	-0.129982
O	-3.099214	-2.249897	-2.063092
H	-2.126686	-2.079580	-2.085192
C	-3.717622	-1.004646	-2.162694
H	-3.149173	-0.277179	-2.755328
C	-5.053405	-1.222124	-2.854426

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C    -3.890917    -0.413254    -0.767196
F    -5.770136    -2.179306    -2.256415
F    -5.788279    -0.102671    -2.862446
F    -4.856921    -1.597550    -4.121428
F    -2.701771    -0.395951    -0.139233
F    -4.726496    -1.132441    -0.011610
F    -4.345857     0.846032    -0.796726

TS-5_B
M06-2X SCF energy (au):     -6908.35354453
M06-2X enthalpy (au):       -6907.94668053
M06-2X free energy (au):    -6908.04546753
MN15 SCF energy (au):       -6913.29632999
MN15 enthalpy (au):         -6912.88946599
MN15 free energy (au):      -6912.98825299
MN15 free energy (quasi-harmonic) (au): -6912.98127946

Cartesian coordinates
ATOM   X             Y           Z
C    -0.105304    -1.062214    -1.771122
C    -1.384946    -1.414921    -2.369909
H     0.288319    -0.089774    -2.064875
H    -1.886647    -2.318637    -2.036224
C    -2.097983    -0.539380    -3.352026
H    -2.295493    -1.144441    -4.241105
H    -1.458362     0.299588    -3.642026
C    -3.459632    -0.032240    -2.836252
H    -4.047608    -0.877423    -2.464256
H    -3.983769     0.369008    -3.706850
C    -3.373344     1.055927    -1.775801
H    -2.731522     1.878759    -2.106077
H    -4.358835     1.487784    -1.576726
C    -2.832251     0.537096    -0.472446
O    -2.295210    -0.571606    -0.392981
O    -2.974803     1.323115     0.556113
C     0.422707    -1.620065    -0.521047
C    -0.263219    -2.595430     0.216220
C     1.643909    -1.121284    -0.056628
C     0.275944    -3.073119     1.398913
H    -1.230813    -2.969676    -0.098450
C     2.201305    -1.607250     1.120719
H     2.160163    -0.341651    -0.609849
C     1.504830    -2.576675     1.832544
H    -0.253137    -3.819164     1.980895
H     3.146075    -1.217419     1.483301
Br     2.224765    -3.240879     3.449749
Br     0.375338    -2.269595    -3.435487
H    -2.635177     0.821781     1.424717
N    -0.175978     0.927759     1.994631
C    -0.995268     0.217917     2.787843
C    -0.300652    -0.393982     3.994392
C     1.091253     0.221092     3.906165
C     1.053962     0.926043     2.559843
O     2.054556     1.460732     2.049778
O    -2.220936     0.072020     2.574619
H    -0.292376    -1.484268     3.890082
H    -0.853099    -0.149571     4.904172
H     1.272083     0.974328     4.679065
H     1.914314    -0.495497     3.944313
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O     1.320565     3.246347     0.315833
H     1.599404     2.500939     0.926300
C     0.189813     2.876996    -0.404637
H    -0.224212     1.909792    -0.090160
C     0.569411     2.783997    -1.873046
C    -0.878213     3.933393    -0.156487
F     0.992745     3.948736    -2.370151
F    -0.455244     2.364571    -2.637426
F     1.564625     1.894716    -2.029203
F    -1.271242     3.899873     1.118936
F    -0.415663     5.165966    -0.404240
F    -1.964067     3.753295    -0.925373

TS-6
M06-2X SCF energy (au):     -9449.32270237
M06-2X enthalpy (au):       -9448.71102937
M06-2X free energy (au):    -9448.88272037
MN15 SCF energy (au):       -9453.86521935
MN15 enthalpy (au):         -9453.25354635
MN15 free energy (au):      -9453.42523735
MN15 free energy (quasi-harmonic) (au): -9453.40234598

Cartesian coordinates
ATOM   X             Y           Z
C     2.515659    -1.453581    -1.271386
C     1.877615    -0.857659    -2.339239
H     2.087164    -2.368086    -0.860855
H     2.321915     0.032212    -2.788336
C     0.726119    -1.493413    -3.062231
H     1.169319    -2.257126    -3.715793
H     0.086159    -2.034833    -2.352792
C    -0.088801    -0.538482    -3.940900
H     0.591047    -0.008886    -4.616728
H    -0.753887    -1.139134    -4.566699
C    -0.925915     0.498548    -3.187085
H    -1.513751     1.080330    -3.908802
H    -0.314130     1.207977    -2.627093
C    -1.932767    -0.105867    -2.241019
O    -2.455324    -1.236867    -2.708678
O    -2.282947     0.396483    -1.187765
C     3.798299    -1.022218    -0.702943
C     4.676307    -0.172051    -1.385874
C     4.140128    -1.480445     0.574487
C     5.870959     0.224001    -0.797600
H     4.446591     0.172018    -2.389609
C     5.328090    -1.085723     1.175789
H     3.459069    -2.140197     1.105638
C     6.177928    -0.231604     0.480967
H     6.557447     0.873236    -1.330008
H     5.586937    -1.435030     2.169093
Br     7.801298     0.318689     1.289729
Br     0.933819     0.113402    -0.384996
N    -0.366002     1.312142     0.711476
C    -1.360401     0.796261     1.394443
C    -2.536736     1.705959     1.531571
C    -2.145232     2.888348     0.639798
C    -0.786427     2.508220     0.098829
O    -0.128369     3.073700    -0.746328
O    -1.245754    -0.389846     1.878487
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H    -3.437509     1.186008     1.190543
H    -2.659651     1.964836     2.587253
H    -2.067107     3.835223     1.178748
H    -2.824283     3.017967    -0.204290
H    -3.153155    -1.551755    -2.090884
S    -3.349012    -2.378724     0.386941
O    -4.242841    -2.019825    -0.741592
O    -3.585611    -1.576459     1.601911
O    -1.944551    -2.548856    -0.004144
H    -2.119058    -0.759677     2.164597
C    -3.917466    -4.063049     0.831171
F    -3.776889    -4.863251    -0.218716
F    -3.198523    -4.542388     1.839953
F    -5.194899    -4.024658     1.186569
O    -5.098399     0.555549    -0.133299
H    -4.976201    -0.365330    -0.435519
C    -5.920495     1.253610    -1.012589
H    -6.832085     0.709397    -1.289023
C    -6.343055     2.514355    -0.272750
C    -5.177218     1.572258    -2.307261
F    -5.283438     3.184192     0.200022
F    -7.032565     3.342281    -1.063840
F    -7.113843     2.197277     0.770356
F    -4.128185     2.380813    -2.113423
F    -5.977828     2.155445    -3.205310
F    -4.715983     0.435409    -2.847212
O     2.568641     2.470022    -1.585567
H     1.639266     2.637147    -1.325466
C     3.417950     3.195587    -0.751945
H     4.454334     2.975354    -1.026877
C     3.198968     4.692549    -0.957938
C     3.237946     2.789160     0.709313
F     3.330234     4.992776    -2.252834
F     1.967121     5.062572    -0.579632
F     4.076849     5.431415    -0.272761
F     3.552400     1.506043     0.887186
F     1.966570     2.948460     1.106855
F     4.012732     3.519421     1.519406
O     0.600990    -2.641536     1.108628
H    -0.180760    -2.212846     0.715792
C     0.217008    -3.912966     1.532824
H    -0.535835    -4.378025     0.885974
C     1.463419    -4.781230     1.486969
C    -0.369346    -3.824594     2.938595
F     1.890026    -4.901473     0.224801
F     2.467142    -4.252510     2.198124
F     1.223125    -6.006248     1.964109
F    -0.872736    -4.994764     3.343012
F    -1.361926    -2.922104     2.954653
F     0.538349    -3.432584     3.838837

TS-6_A
M06-2X SCF energy (au):     -8659.75575246
M06-2X enthalpy (au):       -8659.22113646
M06-2X free energy (au):    -8659.36844546
MN15 SCF energy (au):       -8664.43190282
MN15 enthalpy (au):         -8663.89728682
MN15 free energy (au):      -8664.04459582
MN15 free energy (quasi-harmonic) (au): -8664.02629736
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Cartesian coordinates

ATOM	X	Y	Z
C	0.873589	-0.811735	1.828071
C	0.514341	0.505331	1.983825
H	1.858023	-1.128322	2.172182
H	-0.477927	0.811751	1.656104
C	1.343425	1.495491	2.744913
H	1.098909	1.323713	3.803330
H	2.405540	1.253331	2.631331
C	1.078021	2.975516	2.448670
H	0.025763	3.205902	2.646789
H	1.669731	3.559304	3.158806
C	1.423896	3.441538	1.033733
H	2.357582	3.007066	0.665043
H	1.559771	4.530565	1.024981
C	0.325265	3.171861	0.036948
O	0.766757	3.111908	-1.223308
O	-0.850918	3.062469	0.322177
C	-0.047560	-1.847048	1.325423
C	-1.428820	-1.737203	1.509655
C	0.461867	-2.933655	0.605689
C	-2.295637	-2.673017	0.956911
H	-1.841284	-0.908440	2.078201
C	-0.391624	-3.874134	0.043828
H	1.534323	-3.024571	0.456992
C	-1.764644	-3.723845	0.218447
H	-3.367458	-2.576492	1.095436
H	0.003345	-4.705930	-0.528816
Br	-2.940435	-4.990722	-0.562218
Br	1.557500	0.255560	-0.233766
N	2.296222	0.675415	-2.097025
C	2.007339	0.141311	-3.270740
C	2.841757	0.705957	-4.378772
C	3.675889	1.780504	-3.680474
C	3.329200	1.621845	-2.220071
O	3.829411	2.179280	-1.269238
O	1.141154	-0.759000	-3.508432
H	3.440859	-0.103562	-4.805192
H	2.176781	1.085943	-5.157582
H	3.402632	2.794110	-3.985807
H	4.753251	1.661367	-3.806734
H	0.025563	2.826087	-1.795472
S	-1.464652	0.116162	-1.758882
O	-1.772988	0.401737	-0.357374
O	-0.770185	-1.186464	-1.980593
O	-0.868386	1.214332	-2.530177
H	0.443402	-0.991562	-2.767579
C	-3.114994	-0.164496	-2.495676
F	-3.677449	-1.225369	-1.926561
F	-3.876767	0.901822	-2.273573
F	-3.013579	-0.368086	-3.802056
O	-4.088462	0.576308	1.044038
H	-3.365296	0.174465	0.531709
C	-3.877802	1.958622	1.021040
H	-3.139995	2.270592	0.273622
C	-5.205912	2.614520	0.677593
C	-3.357325	2.404921	2.382013
F	-5.135446	3.948167	0.774437

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F    -5.557838     2.308957    -0.575120
F    -6.188221     2.196416     1.483599
F    -3.011349     3.695749     2.389059
F    -2.271040     1.689204     2.711648
F    -4.261897     2.216223     3.351009
O     4.261610     0.978993     1.239137
H     4.162453     1.454783     0.392827
C     5.279319     0.035214     1.136475
H     6.191692     0.417893     0.662457
C     5.625733    -0.353126     2.566804
C     4.815668    -1.167937     0.318061
F     6.528533    -1.337786     2.606088
F     6.128997     0.699204     3.216130
F     4.541557    -0.761085     3.238560
F     3.776319    -1.796757     0.883651
F     5.792667    -2.063357     0.154049
F     4.424959    -0.761287    -0.899315

TS-6_B
M06-2X SCF energy (au):     -7870.18103749
M06-2X enthalpy (au):       -7869.72218349
M06-2X free energy (au):    -7869.84553349
MN15 SCF energy (au):       -7875.00211126
MN15 enthalpy (au):         -7874.54325726
MN15 free energy (au):      -7874.66660726
MN15 free energy (quasi-harmonic) (au): -7874.65368777

Cartesian coordinates
ATOM   X             Y           Z
C     0.379038    -0.176090     2.838092
C     0.738748     1.017425     2.255322
H     0.898210    -0.465533     3.752554
H     0.169195     1.402445     1.408274
C     1.732955     1.932904     2.916064
H     1.147568     2.493436     3.659356
H     2.455164     1.337538     3.488303
C     2.459245     2.964512     2.044547
H     1.725672     3.563957     1.497751
H     2.974462     3.643655     2.729534
C     3.487769     2.416685     1.057643
H     4.068805     1.583859     1.469295
H     4.212963     3.197518     0.796940
C     2.883923     1.971315    -0.247858
O     3.747339     1.291798    -1.008359
O     1.748700     2.210995    -0.607675
C    -0.754035    -1.029697     2.456477
C    -1.392440    -0.912644     1.214304
C    -1.205994    -1.986505     3.371014
C    -2.468972    -1.728585     0.897851
H    -1.040138    -0.194114     0.481387
C    -2.288637    -2.805483     3.067862
H    -0.710563    -2.089983     4.332338
C    -2.906929    -2.665354     1.831395
H    -2.958415    -1.638301    -0.065802
H    -2.639850    -3.542025     3.781799
Br    -4.376443    -3.782985     1.398241
Br     2.043639    -0.670792     1.097643
N     3.343596    -1.536138    -0.226041
C     3.071154    -2.277012    -1.271742
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C     4.291362    -2.739054    -1.999635
C     5.430296    -2.059062    -1.235225
C     4.746485    -1.334969    -0.095601
O     5.228395    -0.688722     0.794901
O     1.897463    -2.609003    -1.673961
H     4.327971    -3.831580    -1.972445
H     4.201715    -2.423770    -3.042617
H     5.959657    -1.316947    -1.837948
H     6.163204    -2.755553    -0.823959
H     3.275202     1.009436    -1.823448
S     0.678731     0.128344    -2.736837
O     0.031966     1.436098    -2.893835
O     0.202588    -0.649978    -1.566701
O     2.142059     0.091607    -2.915145
H     1.163650    -2.000457    -1.354107
C     0.066019    -0.828818    -4.172612
F     0.561420    -2.062025    -4.140543
F    -1.260109    -0.894808    -4.136781
F     0.440305    -0.239624    -5.302560
O    -1.104532     1.863765    -0.400364
H    -0.673793     1.958264    -1.272725
C    -2.004004     2.894948    -0.161491
H    -2.524667     3.245180    -1.060479
C    -3.048812     2.330480     0.790982
C    -1.269860     4.088442     0.443823
F    -2.486942     1.840647     1.903664
F    -3.936398     3.261631     1.156482
F    -3.711510     1.330958     0.202723
F    -2.086215     5.127968     0.647959
F    -0.293369     4.484491    -0.377950
F    -0.704073     3.779801     1.621515

TS-7
M06-2X SCF energy (au):     -9088.79557935
M06-2X enthalpy (au):       -9088.28402635
M06-2X free energy (au):    -9088.43605235
MN15 SCF energy (au):       -9093.50282394
MN15 enthalpy (au):         -9092.99127094
MN15 free energy (au):      -9093.14329694
MN15 free energy (quasi-harmonic) (au): -9093.12563759

Cartesian coordinates
ATOM   X             Y           Z
C     0.500264    -1.655470    -2.234271
C     1.243185    -2.946213    -2.136409
H     2.048779    -2.878853    -1.401170
H    -0.573626    -1.731787    -2.407762
C     0.355362    -4.176525    -1.968328
H    -0.227813    -4.305316    -2.885209
H     1.015605    -5.044346    -1.877819
C    -0.605507    -4.133495    -0.777765
H    -1.401159    -3.398694    -0.945941
H    -1.090615    -5.111667    -0.727709
C     0.056812    -3.848229     0.563040
H     1.019940    -4.363423     0.671330
H    -0.567408    -4.185934     1.396251
C     0.291187    -2.385570     0.793535
O     0.180675    -1.509590    -0.071378
O     0.608337    -2.095465     2.030017
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C     1.078202    -0.376807    -2.399508
C     2.471961    -0.142058    -2.299134
C     0.203442     0.696904    -2.677074
C     2.968613     1.127898    -2.493809
H     3.157795    -0.951981    -2.075485
C     0.696322     1.975038    -2.866760
H    -0.862715     0.505886    -2.744641
C     2.073349     2.169492    -2.774808
H     4.031655     1.323829    -2.426731
H     0.028648     2.802310    -3.078087
Br     2.769877     3.896598    -3.036734
Br     2.153050    -3.115102    -3.889963
H     0.634234    -1.113110     2.143751
S     0.048622     1.358521     1.004259
O     1.347289     1.374612     0.313325
O     0.033897     0.501719     2.218602
O    -1.128580     1.234668     0.136662
C    -0.096080     3.040107     1.708303
F     0.941003     3.288129     2.498684
F    -0.121158     3.936209     0.728111
F    -1.215756     3.136906     2.417069
O    -2.338432    -0.818972    -1.187112
H    -1.658700    -0.389794    -0.631888
C    -3.543376    -0.149479    -0.969612
H    -3.551402     0.424107    -0.037259
C    -3.779695     0.829017    -2.115128
C    -4.639769    -1.201627    -0.882327
F    -4.973643     1.424447    -2.030345
F    -2.841504     1.785426    -2.098964
F    -3.704229     0.220797    -3.305123
F    -4.364959    -2.071253     0.091799
F    -4.747013    -1.895602    -2.023432
F    -5.831108    -0.652924    -0.622048
O     2.870429    -0.865754     0.623191
H     2.298326    -0.079678     0.466257
C     3.987655    -0.498209     1.366021
H     4.597886    -1.388559     1.545322
C     4.848118     0.488438     0.582293
C     3.594154     0.050497     2.736879
F     4.175781     1.604720     0.276475
F     5.943680     0.841751     1.261576
F     5.238415    -0.069870    -0.572115
F     2.979197     1.236571     2.654737
F     4.665464     0.201457     3.523280
F     2.754520    -0.798177     3.341071
O    -1.832364    -0.062721     4.218567
H    -1.278383     0.264608     3.481284
C    -2.992865    -0.653855     3.724657
H    -3.582724    -1.026362     4.567297
C    -3.835685     0.381721     2.986199
C    -2.682934    -1.855560     2.834805
F    -4.835369    -0.178894     2.292634
F    -4.361899     1.256748     3.843800
F    -3.080031     1.074923     2.119402
F    -3.771562    -2.597789     2.616800
F    -1.767045    -2.632378     3.414557
F    -2.199281    -1.476759     1.635653
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TS-7_A

M06-2X SCF energy (au):   -8299.22768060
M06-2X enthalpy (au):   -8298.79274760
M06-2X free energy (au):   -8298.92033560
MN15 SCF energy (au):   -8304.06979028
MN15 enthalpy (au):   -8303.63485728
MN15 free energy (au):   -8303.76244528
MN15 free energy (quasi-harmonic) (au): -8303.74962168

Cartesian coordinates

ATOM	X	Y	Z
C	0.191681	-0.965093	-1.739661
C	1.267009	-1.987723	-1.551075
H	1.836103	-1.769569	-0.644604
H	-0.762981	-1.328359	-2.118970
C	0.792402	-3.434309	-1.643726
H	0.473160	-3.632166	-2.671656
H	1.658508	-4.072086	-1.441966
C	-0.347614	-3.795424	-0.690789
H	-1.280309	-3.318750	-1.010599
H	-0.504999	-4.874021	-0.772233
C	-0.080592	-3.446024	0.769912
H	0.975256	-3.580158	1.039416
H	-0.656677	-4.079614	1.449274
C	-0.445479	-2.028914	1.094120
O	-0.597450	-1.133408	0.258293
O	-0.622618	-1.811136	2.374928
C	0.383880	0.438989	-1.750011
C	1.618879	1.049053	-1.421425
C	-0.734431	1.247342	-2.044484
C	1.718603	2.421082	-1.360665
H	2.491677	0.441951	-1.218436
C	-0.644710	2.626062	-1.973412
H	-1.678576	0.778773	-2.307748
C	0.575016	3.190157	-1.610155
H	2.655783	2.898909	-1.100371
H	-1.508420	3.250055	-2.171239
Br	0.684274	5.058486	-1.426105
Br	2.555095	-1.702106	-3.026592
H	-0.882138	-0.866419	2.543841
S	-1.263541	1.573228	1.550952
O	0.137867	1.665509	1.113312
O	-1.460302	0.725063	2.746791
O	-2.269101	1.383152	0.492315
C	-1.614195	3.270802	2.133196
F	-1.394824	4.126288	1.138022
F	-2.878957	3.376103	2.526075
F	-0.817578	3.578676	3.151171
O	-3.011943	-0.804798	-1.015339
H	-2.623720	-0.111019	-0.439620
C	-4.203384	-1.246658	-0.444810
H	-4.905653	-0.437050	-0.208797
C	-4.856950	-2.144640	-1.483536
C	-3.913300	-1.986656	0.857704
F	-4.049930	-3.151792	-1.839074
F	-5.998644	-2.671871	-1.031713
F	-5.131854	-1.441040	-2.585239
F	-5.025721	-2.444748	1.436682
F	-3.309850	-1.154136	1.714187
F	-3.089887	-3.031191	0.672494

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O     1.877947    -0.476788     1.207494
H     1.367437     0.348644     1.342335
C     3.077169    -0.484763     1.910596
H     3.099514     0.198999     2.766193
C     3.253903    -1.902097     2.439825
C     4.199627    -0.086142     0.957581
F     3.283531    -2.796040     1.436897
F     4.382440    -2.038965     3.140076
F     2.228865    -2.224605     3.231400
F     4.040549     1.191004     0.585033
F     4.177458    -0.829486    -0.161236
F     5.409193    -0.209103     1.507574

TS-7_B
M06-2X SCF energy (au):     -7509.64972073
M06-2X enthalpy (au):       -7509.29143173
M06-2X free energy (au):    -7509.39883173
MN15 SCF energy (au):       -7514.63395691
MN15 enthalpy (au):         -7514.27566791
MN15 free energy (au):      -7514.38306791
MN15 free energy (quasi-harmonic) (au): -7514.37139818

Cartesian coordinates
ATOM   X             Y           Z
C     2.060442     0.745340    -1.831278
C     3.511239     0.940416    -1.539068
H     3.711961     0.819480    -0.472390
H     1.820768     0.248050    -2.771159
C     4.462916     0.150659    -2.433108
H     4.376793     0.538946    -3.452651
H     5.480292     0.362303    -2.090419
C     4.234741    -1.362138    -2.466917
H     3.295807    -1.595336    -2.980114
H     5.035813    -1.785779    -3.078317
C     4.245083    -2.047750    -1.106867
H     5.010752    -1.628463    -0.441274
H     4.471399    -3.113773    -1.200486
C     2.927040    -1.951694    -0.394311
O     2.015000    -1.186838    -0.713536
O     2.819200    -2.781693     0.616972
C     0.997103     1.359158    -1.144212
C     1.184102     2.061773     0.073016
C    -0.295135     1.271715    -1.714125
C     0.112223     2.663282     0.692138
H     2.166008     2.126959     0.529036
C    -1.370878     1.885938    -1.103926
H    -0.432756     0.721370    -2.639523
C    -1.150242     2.564407     0.095059
H     0.237026     3.192110     1.629852
H    -2.363576     1.830038    -1.533177
Br    -2.612249     3.367292     0.958126
Br     3.820628     2.864389    -1.913452
H     1.926218    -2.679992     1.059521
S     0.272229    -0.908003     1.902379
O     1.497091    -0.136322     2.125236
O     0.487353    -2.368084     1.747462
O    -0.679479    -0.347146     0.927147
C    -0.643132    -0.784649     3.479672
F     0.101769    -1.247004     4.479458
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F    -0.944355     0.488885     3.719694
F    -1.766624    -1.490432     3.416149
O    -0.725704    -1.763413    -1.386093
H    -0.680446    -1.246448    -0.548201
C    -1.973939    -2.365695    -1.502135
H    -1.997907    -2.951614    -2.426246
C    -2.227386    -3.340721    -0.354182
C    -3.072814    -1.313354    -1.613338
F    -2.358541    -2.715912     0.823083
F    -3.342274    -4.054093    -0.558722
F    -1.203990    -4.192337    -0.251120
F    -3.140782    -0.536908    -0.525248
F    -4.276049    -1.867526    -1.795611
F    -2.826076    -0.511386    -2.659114

TS-8
M06-2X SCF energy (au):     -9088.78961798
M06-2X enthalpy (au):       -9088.27898098
M06-2X free energy (au):    -9088.43501198
MN15 SCF energy (au):       -9093.49607318
MN15 enthalpy (au):         -9092.98543618
MN15 free energy (au):      -9093.14146718
MN15 free energy (quasi-harmonic) (au): -9093.12081420

Cartesian coordinates
ATOM   X             Y           Z
C    -1.860129     1.991278    -1.452596
C    -1.725020     2.378173    -0.046542
H    -1.412568     2.692702    -2.156699
H    -2.005639     1.667232     0.729252
C    -1.329564     3.760458     0.362148
H    -2.175712     4.176416     0.917217
H    -1.158523     4.382161    -0.522530
C    -0.113250     3.812851     1.299778
H    -0.283714     3.155802     2.159088
H    -0.055089     4.836680     1.674981
C     1.200767     3.463566     0.616480
H     1.324776     4.021533    -0.320547
H     2.059040     3.700897     1.249880
C     1.261926     2.007126     0.282016
O     0.255418     1.309040     0.161968
O     2.477489     1.533498     0.136107
C    -1.931431     0.593767    -1.920305
C    -2.313840    -0.454228    -1.079883
C    -1.604327     0.335361    -3.255637
C    -2.356757    -1.753947    -1.562949
H    -2.565406    -0.276028    -0.039430
C    -1.640102    -0.962813    -3.747513
H    -1.296723     1.149063    -3.905784
C    -2.014786    -1.992226    -2.890368
H    -2.631937    -2.572452    -0.907685
H    -1.370481    -1.168310    -4.776995
Br    -2.048879    -3.769359    -3.538012
Br    -3.769039     2.715884    -1.104725
H     2.464547     0.548440     0.058369
S     1.059699    -1.648862    -0.335589
O    -0.127905    -1.774383     0.520869
O     0.897478    -1.002278    -1.644260
O     2.256125    -1.169025     0.413608
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C     1.459740    -3.379303    -0.771544
F     1.646472    -4.092599     0.332779
F     2.563862    -3.417871    -1.507442
F     0.453057    -3.897878    -1.464819
O     1.010874     1.646127    -2.484336
H     0.848311     0.779721    -2.057704
C     2.197414     1.560347    -3.210203
H     2.950284     0.914953    -2.741250
C     2.761110     2.971723    -3.271618
C     1.895286     0.996194    -4.594453
F     1.847721     3.841169    -3.718289
F     3.828463     3.045673    -4.072048
F     3.131815     3.372472    -2.049921
F     1.325749    -0.208015    -4.468910
F     1.040459     1.777528    -5.268703
F     2.997514     0.856733    -5.337007
O    -1.216615     0.242643     2.105557
H    -0.620647    -0.342458     1.598333
C    -1.751311    -0.456020     3.182931
H    -1.117942    -1.283894     3.520424
C    -1.862836     0.550447     4.317454
C    -3.102995    -1.027071     2.774345
F    -2.533865     1.643221     3.932766
F    -2.479546     0.042918     5.388062
F    -0.639466     0.947227     4.694291
F    -3.933043    -0.064492     2.348734
F    -3.705975    -1.681594     3.769940
F    -2.933891    -1.886479     1.758569
O     1.220493    -1.122307     3.009885
H     1.719943    -1.217507     2.172423
C     2.027714    -0.535066     3.978450
H     1.440594    -0.391929     4.889355
C     3.192993    -1.460567     4.314538
C     2.523443     0.839235     3.532294
F     2.746886    -2.561645     4.923701
F     3.835780    -1.847623     3.204314
F     4.081389    -0.868051     5.120342
F     3.012452     1.543841     4.555623
F     1.514628     1.538019     2.993782
F     3.487093     0.742585     2.606116

TS-8_A
M06-2X SCF energy (au):     -8299.22004119
M06-2X enthalpy (au):       -8298.78540119
M06-2X free energy (au):    -8298.91763419
MN15 SCF energy (au):       -8304.06126703
MN15 enthalpy (au):         -8303.62662703
MN15 free energy (au):      -8303.75886003
MN15 free energy (quasi-harmonic) (au): -8303.74226084

Cartesian coordinates
ATOM   X             Y           Z
C     0.820631     0.643158    -2.560193
C     0.232695     1.926360    -2.170191
H     1.891210     0.668615    -2.766499
H    -0.804867     1.940493    -1.846603
C     1.045401     3.189337    -2.200505
H     0.384761     4.038081    -2.010895
H     1.458140     3.307476    -3.205568
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C     2.237868     3.195736    -1.223644
H     2.892751     4.009501    -1.543444
H     2.813082     2.268880    -1.316577
C     1.868807     3.427759     0.231303
H     2.763858     3.496796     0.853105
H     1.321356     4.371306     0.352224
C     0.992983     2.349945     0.793512
O     0.286501     1.616753     0.104002
O     1.027896     2.273224     2.104137
C     0.297237    -0.669801    -2.147658
C    -1.060344    -0.887994    -1.889951
C     1.213516    -1.717485    -2.008581
C    -1.498150    -2.139237    -1.486051
H    -1.789605    -0.091529    -2.010586
C     0.783278    -2.974455    -1.600620
H     2.268840    -1.545257    -2.200600
C    -0.569098    -3.166843    -1.343357
H    -2.547141    -2.309981    -1.272934
H     1.491305    -3.785925    -1.480485
Br   -1.173476    -4.869111    -0.785829
Br   -0.090088     1.289750    -4.319612
H     0.416897     1.558344     2.432673
S    -0.833974    -0.695281     1.848343
O    -2.000929    -0.343185     1.024991
O     0.353093    -1.189623     1.131160
O    -0.529559     0.277439     2.921234
C    -1.407427    -2.177679     2.751311
F    -1.708507    -3.134556     1.879807
F    -2.486101    -1.889325     3.471318
F    -0.450089    -2.614810     3.562691
O     2.575481     0.083914     0.184076
H     1.670951    -0.225612     0.400486
C     3.449913    -0.433120     1.138191
H     2.961928    -0.671377     2.090731
C     4.492019     0.643624     1.400274
C     4.067570    -1.716336     0.595650
F     5.488439     0.201203     2.172851
F     3.925387     1.686963     2.018310
F     5.024134     1.093468     0.257306
F     3.098783    -2.605036     0.344236
F     4.721085    -1.495972    -0.553188
F     4.924690    -2.275410     1.455187
O    -2.576206     1.678179    -0.693310
H    -2.264368     1.048703    -0.001970
C    -3.245117     2.751235    -0.110637
H    -3.578175     3.432849    -0.898831
C    -4.491466     2.271237     0.627699
C    -2.299985     3.529162     0.797829
F    -5.209305     3.295430     1.101128
F    -5.266410     1.572337    -0.205531
F    -4.180767     1.475812     1.658085
F    -1.274118     4.008942     0.078183
F    -1.788481     2.747066     1.757233
F    -2.903713     4.563901     1.387601

TS-8_B
M06-2X SCF energy (au):     -7509.64424739
M06-2X enthalpy (au):       -7509.28597939
M06-2X free energy (au):    -7509.39319239
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MN15 SCF energy (au):   -7514.62652162
MN15 enthalpy (au):   -7514.26825362
MN15 free energy (au):   -7514.37546662
MN15 free energy (quasi-harmonic) (au): -7514.36500023

Cartesian coordinates

ATOM	X	Y	Z
C	0.893566	-2.640659	0.998302
C	2.244525	-2.153912	0.748434
H	0.688484	-2.911934	2.033672
H	2.447549	-1.669554	-0.205764
C	3.340100	-2.196811	1.770070
H	4.061852	-2.947434	1.437691
H	2.938998	-2.525131	2.734766
C	4.112383	-0.873687	1.892502
H	4.344707	-0.496374	0.892505
H	5.065313	-1.107686	2.372259
C	3.422701	0.201128	2.717633
H	3.259004	-0.139855	3.747741
H	4.040830	1.101103	2.780728
C	2.084118	0.602600	2.175410
O	1.448315	-0.061324	1.362789
O	1.643381	1.743912	2.661532
C	-0.280054	-2.304865	0.180781
C	-0.176428	-1.917804	-1.162351
C	-1.537109	-2.418991	0.780218
C	-1.318969	-1.633941	-1.892276
H	0.787968	-1.842991	-1.656564
C	-2.689604	-2.146372	0.051810
H	-1.617351	-2.725942	1.819020
C	-2.563885	-1.756660	-1.275194
H	-1.244057	-1.326989	-2.929314
H	-3.665792	-2.233205	0.514324
Br	-4.123396	-1.385345	-2.277053
Br	1.883010	-4.300123	0.174929
H	0.751500	1.978165	2.284496
S	-1.744671	1.843052	1.075110
O	-2.936707	2.625953	0.759638
O	-1.347999	0.843047	0.072473
O	-0.614888	2.644135	1.607630
C	-2.225636	0.819154	2.514028
F	-2.587204	1.597439	3.529582
F	-1.197074	0.064497	2.900073
F	-3.244458	0.024410	2.199836
O	0.963806	0.920658	-1.375717
H	0.156174	0.714516	-0.861230
C	1.390845	2.184815	-0.967765
H	1.163435	2.409344	0.080946
C	0.700736	3.249835	-1.811872
C	2.901101	2.211613	-1.125041
F	-0.626659	3.141167	-1.668405
F	0.979790	3.108606	-3.113021
F	1.051890	4.488017	-1.448369
F	3.278570	1.849936	-2.354637
F	3.409108	3.421657	-0.875272
F	3.463322	1.348737	-0.262812

TfOH
M06-2X SCF energy (au):   -961.780651031

M06-2X enthalpy (au):   -961.732416031
M06-2X free energy (au):   -961.774214031
MN15 SCF energy (au):   -961.672607698
MN15 enthalpy (au):   -961.624372698
MN15 free energy (au):   -961.666170698
MN15 free energy (quasi-harmonic) (au): -961.665240667

Cartesian coordinates
ATOM   X   Y   Z
S   -2.207116   0.177469   -1.041031
O   -0.766047   0.181107   -1.031043
O   -2.984668   1.395184   -1.048480
O   -2.682559   -0.782054   0.121852
H   -3.576973   -0.560117   0.453584
C   -2.728998   -0.803506   -2.504417
F   -2.118650   -1.974172   -2.484670
F   -4.039301   -0.974011   -2.463709
F   -2.392931   -0.134321   -3.593384

1l
M06-2X SCF energy (au):   -576.627854649
M06-2X enthalpy (au):   -576.407377649
M06-2X free energy (au):   -576.460459649
MN15 SCF energy (au):   -576.345689165
MN15 enthalpy (au):   -576.125212165
MN15 free energy (au):   -576.178294165
MN15 free energy (quasi-harmonic) (au): -576.175727516

Cartesian coordinates
ATOM   X   Y   Z
C   -0.181059   0.930906   0.192119
C   0.740102   0.969688   -0.775863
H   0.105073   1.258843   1.192159
H   0.500046   0.606284   -1.775757
C   2.145951   1.457934   -0.578589
H   2.381296   2.214889   -1.334864
H   2.248452   1.928501   0.404071
C   3.167580   0.326242   -0.705549
H   3.038563   -0.238253   -1.634472
H   4.190915   0.720353   -0.717529
C   -1.570572   0.456500   0.058267
C   -2.312534   0.199468   1.219029
C   -2.189896   0.255116   -1.184780
C   -3.623789   -0.262463   1.145598
H   -1.848377   0.360891   2.188838
C   -3.498954   -0.206922   -1.258867
H   -1.650605   0.475948   -2.101344
C   -4.221783   -0.470721   -0.094856
H   -4.178470   -0.458372   2.058435
H   -3.961806   -0.354538   -2.230200
C   3.093057   -0.635827   0.449445
O   2.540337   -0.420513   1.507645
O   3.743776   -1.780312   0.198488
H   3.693620   -2.344485   0.989843
H   -5.245143   -0.827977   -0.156537

10
M06-2X SCF energy (au):   -1109.82740482
M06-2X enthalpy (au):   -1109.50411682

M06-2X free energy (au):   -1109.57095582
MN15 SCF energy (au):   -1109.45791665
MN15 enthalpy (au):   -1109.13462865
MN15 free energy (au):   -1109.20146765
MN15 free energy (quasi-harmonic) (au): -1109.19703383

Cartesian coordinates

ATOM	X	Y	Z
C	1.232096	1.291869	0.778886
C	2.494325	2.152595	0.726780
C	3.174157	2.127316	-0.647588
C	2.386644	2.884225	-1.679853
C	1.917722	2.372299	-2.815820
H	2.086556	1.331110	-3.080363
H	1.356241	2.977642	-3.522242
H	3.315776	1.089619	-0.972379
H	4.169412	2.579204	-0.553501
H	3.187014	1.800551	1.500496
H	2.223553	3.183954	0.984238
C	0.399454	1.548909	2.028376
N	1.631660	-0.133888	0.698402
H	0.632810	1.508725	-0.114346
H	-0.492540	0.915075	2.049174
H	0.079993	2.593904	2.061498
H	0.990886	1.345067	2.928183
S	0.834028	-1.128959	-0.339067
C	-0.893975	-1.073691	0.048815
C	-1.374388	-1.870856	1.088255
C	-1.720025	-0.181704	-0.627472
C	-2.710135	-1.764446	1.448449
H	-0.713824	-2.566600	1.597251
C	-3.567633	-0.872170	0.789405
H	-3.099418	-2.383267	2.252389
C	-3.056840	-0.089292	-0.249036
C	-5.014363	-0.781732	1.190336
H	-3.713247	0.600885	-0.771039
H	-1.327106	0.420625	-1.440849
H	-5.541675	-1.706645	0.934359
H	-5.111055	-0.640620	2.270796
H	-5.515146	0.046713	0.685176
O	0.995178	-0.566678	-1.678298
O	1.323218	-2.476356	-0.048734
H	2.192205	3.933583	-1.449885
H	1.756442	-0.585147	1.605265

TS-9
M06-2X SCF energy (au):   -5877.02450018
M06-2X enthalpy (au):   -5876.48539118
M06-2X free energy (au):   -5876.62403618
MN15 SCF energy (au):   -5878.93404320
MN15 enthalpy (au):   -5878.39493420
MN15 free energy (au):   -5878.53357920
MN15 free energy (quasi-harmonic) (au): -5878.52144102

Cartesian coordinates

ATOM	X	Y	Z
C	2.367518	2.234050	-1.987084
C	1.046571	2.256903	-2.458222
H	0.362385	2.974662	-2.012720

H	3.101769	1.673035	-2.564446
C	0.625875	1.661793	-3.769356
H	0.747531	2.464939	-4.507359
H	1.297328	0.847989	-4.058374
C	-0.840347	1.202208	-3.809094
H	-1.512723	1.996695	-3.481581
H	-1.088320	0.935847	-4.841177
C	2.881238	3.087164	-0.913308
C	2.027415	3.705744	0.012048
C	4.265788	3.244890	-0.798038
C	2.561510	4.473274	1.035973
H	0.953442	3.545200	-0.032483
C	4.795512	4.023989	0.226620
H	4.922591	2.753465	-1.510374
C	3.944942	4.632095	1.146656
H	1.900619	4.937900	1.760746
H	5.870439	4.148365	0.311193
Br	1.126557	0.595653	-0.987014
N	0.418635	-1.146859	0.266214
C	0.030294	-2.388774	-0.114779
C	-0.064739	-3.321914	1.076216
C	0.307056	-2.432546	2.260046
C	0.602942	-1.098485	1.612003
O	0.948564	-0.077254	2.219172
O	-0.228918	-2.731962	-1.276757
H	-1.078786	-3.727130	1.121512
H	0.626394	-4.154013	0.919003
H	1.194711	-2.763063	2.805010
H	-0.502861	-2.297337	2.981288
O	-0.590548	2.086850	1.353779
H	0.075024	1.424837	1.629240
C	-1.715842	1.422985	0.858631
H	-1.486016	0.534618	0.256396
C	-2.594360	0.993554	2.030265
C	-2.422192	2.412684	-0.052556
F	-1.948428	0.069546	2.756647
F	-2.865633	2.023340	2.838815
F	-3.759829	0.466335	1.640739
F	-1.618811	2.738268	-1.077979
F	-2.718914	3.546811	0.592863
F	-3.552313	1.918335	-0.556967
O	-2.656632	-3.975946	-1.018391
H	-1.707758	-3.857026	-1.214055
C	-3.320615	-2.836056	-1.482268
H	-2.719868	-2.233999	-2.172259
C	-4.557296	-3.313751	-2.228225
C	-3.676422	-1.941699	-0.298578
F	-5.323366	-2.292513	-2.628720
F	-4.192857	-4.005801	-3.312722
F	-5.310339	-4.119671	-1.471204
F	-4.482564	-2.565477	0.569398
F	-4.277312	-0.815775	-0.684418
F	-2.559820	-1.608694	0.374893
O	3.276278	1.279289	1.593920
H	2.451975	0.776180	1.762110
C	4.376624	0.431429	1.597430
H	5.283555	1.035276	1.487882
C	4.488419	-0.311392	2.925959
C	4.329422	-0.524107	0.409017

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F     3.454062    -1.144723     3.116064
F     5.611326    -1.033188     3.002622
F     4.489877     0.563989     3.933563
F     5.380948    -1.348630     0.385834
F     4.321105     0.164358    -0.737667
F     3.219751    -1.280116     0.427648
C    -1.087533    -0.015737    -2.952522
O    -1.871709    -0.058089    -2.021122
O    -0.335478    -1.049261    -3.314133
H    -0.344359    -1.731808    -2.585093
H     4.357557     5.228347     1.954684

TS-10
M06-2X SCF energy (au):     -5877.00011851
M06-2X enthalpy (au):       -5876.46155251
M06-2X free energy (au):    -5876.60395251
MN15 SCF energy (au):       -5878.91386848
MN15 enthalpy (au):         -5878.37530248
MN15 free energy (au):      -5878.51770248
MN15 free energy (quasi-harmonic) (au): -5878.50215597

Cartesian coordinates
ATOM   X             Y           Z
C     0.910323     2.700595    -1.601700
C     0.103473     2.045290    -2.567944
H     1.977649     2.533986    -1.760606
H    -0.746224     2.586949    -2.980795
C     0.503320     0.793428    -3.254637
H     1.031601     1.099580    -4.169385
H     1.199596     0.229992    -2.631770
C    -0.719908    -0.049747    -3.607915
H    -1.258091     0.354207    -4.473389
H    -0.461676    -1.086517    -3.825936
C     0.511862     4.063768    -1.161538
C     1.460489     5.079427    -1.031055
C    -0.826506     4.327606    -0.849286
C     1.071526     6.350351    -0.612884
H     2.502608     4.873908    -1.261399
C    -1.213827     5.598117    -0.438855
H    -1.562805     3.530676    -0.926291
C    -0.264621     6.613593    -0.318907
H     1.814828     7.136072    -0.517569
H    -2.255652     5.792701    -0.201710
Br     0.807928     1.385559     0.112255
N     0.686151     0.060281     1.913466
C    -0.385257    -0.741113     2.085279
C    -0.412389    -1.337772     3.477750
C     0.908995    -0.865495     4.085376
C     1.511186     0.011876     3.000956
O     2.605562     0.565942     3.067553
O    -1.206930    -0.985374     1.187097
H    -1.294274    -0.963845     4.004115
H    -0.503558    -2.422888     3.395988
H     1.606892    -1.682383     4.287439
H     0.797184    -0.280811     5.001204
O    -3.619869    -0.422334     0.226292
H    -2.895015    -0.923305     0.655940
C    -3.456566     0.919216     0.596131
H    -2.420026     1.259506     0.489380
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C	-4.341126	1.757032	-0.325248
C	-3.871511	1.115875	2.052101
F	-5.630321	1.701708	0.034233
F	-3.970779	3.042918	-0.300499
F	-4.264846	1.328536	-1.587805
F	-3.994266	2.416868	2.343632
F	-2.946018	0.598261	2.872119
F	-5.029766	0.515318	2.330156
O	0.342401	-1.574078	-0.943802
H	-0.318531	-1.234923	-0.293883
C	0.402737	-2.961438	-0.905440
H	1.243558	-3.282544	-1.527293
C	0.653295	-3.540037	0.498796
C	-0.861798	-3.586471	-1.487921
F	1.297505	-4.706814	0.418889
F	1.397010	-2.704353	1.236767
F	-0.479506	-3.757902	1.183013
F	-0.833562	-4.920298	-1.361606
F	-0.975665	-3.297530	-2.787393
F	-1.964367	-3.139777	-0.874482
O	4.044968	0.473576	0.772419
H	3.488202	0.706739	1.548478
C	3.520051	-0.674071	0.180887
H	2.435182	-0.783292	0.299744
C	3.786520	-0.575635	-1.313052
C	4.180622	-1.904975	0.791370
F	5.090537	-0.642510	-1.603300
F	3.167298	-1.554676	-1.987640
F	3.334513	0.591833	-1.790331
F	3.814420	-3.033789	0.164520
F	3.830798	-2.012318	2.079636
F	5.514468	-1.831898	0.745881
C	-1.656041	0.022044	-2.435441
O	-1.549759	0.928167	-1.615979
O	-2.587988	-0.898959	-2.368425
H	-3.129439	-0.754156	-1.555940
H	-0.565629	7.604515	0.006717