

— SUPPORTING INFORMATION —

NXS, Morpholine, and HFIP: The Ideal Combination for Biomimetic Haliranium- induced Polyene Cyclizations

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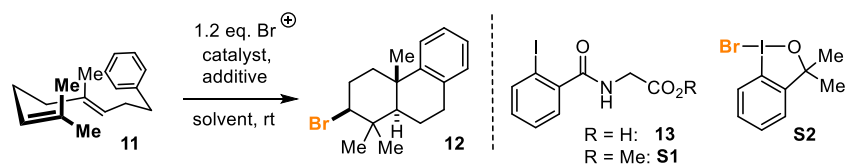
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1. General Information

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Anhydrous dichloromethane, diethylether and THF were obtained from a MBraun MB-SPS 800 solvent purification system. Other dry solvents were obtained from Fluka and Acros in the highest purity available and used without further purification. 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) was purchased from Fluorochem with a purity >99% and dried over activated 3Å molecular sieve for at least 48 h before use. *N*-Bromosuccinimide (NBS) was purchased from Carbolution Chemicals and recrystallized from water. *N*-Iodosuccinimide (NIS) was purchased from Carbolution Chemicals, 1,3-Dichloro-5,5-dimethyl hydantoin (DCDMH) and BDSB (**17**) were purchased from Sigma-Aldrich, respectively, and used as received. Other reagents were purchased at the highest commercial quality and used without further purification. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on Merck silica gel aluminium plates with F-254 indicator using UV light as the visualizing agent (UV), basic potassium permanganate solution (KMnO₄), ceric ammonium molybdate (CAN), and heat as developing agents. Silica gel Merck 60 (particle size 40 – 63 μm) was used for flash column chromatography. Solvent mixtures are understood as volume/volume. NMR spectra were recorded on Bruker AV300, Bruker AV400, Bruker AV500, or Bruker AV500-cryo spectrometers. The spectra were calibrated using residual undeuterated solvent as an internal reference (CDCl₃ @ 7.26 ppm, D₂O @ 4.79 ppm ¹H NMR, CDCl₃ @ 77.16 ppm ¹³C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, p = pentet, quint = quintet (with 1:2:3:2:1 intensity), hept = heptet, m = multiplet, br = broad. In addition, the following abbreviations were used: EtOAc = ethyl acetate, MeCN = acetonitrile, DCM = dichloromethane, PFTB = perfluoro-*tert*-butanol, TFE = 1,1,1-trifluoroethanol, PFNP = 2,2,3,3,3-pentafluoro-1-propanol, TFA = trifluoroacetic acid, Oxone = potassium peroxydisulfate triple salt, FA = formic acid, TLC = thin layer chromatography, rt = room temperature, sat. = saturated. Melting points were measured on a Büchi 510 and are not calibrated. IR spectra were recorded on a JASCO FT-IR-4100 (ATR) and are reported in terms of frequency of absorption (cm⁻¹). Mass spectra were conducted on a Finnigan MAT SSQ 7000 (MS-EI, 70 eV; CI, 100 eV), or a Thermo Scientific LTQ-FT ultra and ThermoFisher Scientific LTQ Orbitrap XL spectrometer (ESI HRMS).

2. Optimization of the Reaction Conditions

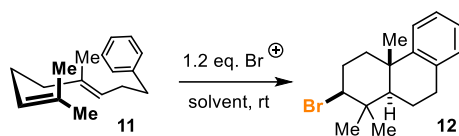


22.8 mg Homogeranyl benzene (**11**, 100 μ mol, 1.0 eq), 10.0 μ mol additive (0.1 eq) and 10.0 μ mol catalyst (0.1 eq) were mixed in 1.0 mL solvent. Then, 120 μ mol electrophilic bromine source (1.2 eq) was added to the mixture at room temperature.

Table S1. Hypervalent Iodane catalyzed bromiranium-induced cyclizations of **11**.

Entry	Br ⁺ source	Solvent	Catalyst	Additive	Yield 12 ^a	d.r. ^b
1 ^c	NBS	DCM	13	NH ₄ Cl _{solid}	<5% ^d	n.d.
2	NBS	DCM	13	NH ₄ Cl _{aq}	<5% ^d	n.d.
3	NBS	DCM	S1	NH ₄ Cl _{aq}	<5% ^d	n.d.
4	NBS	HFIP	13	–	33%	80:20
5 ^e	KBr (3.0 eq)/oxone (1.1 eq.)	HFIP	13	–	<5%	n.d.
6	S2	HFIP	–	–	41%	77:23
7	NBS	HFIP	–	–	42%	79:21

^ayield determined by ¹H-NMR spectroscopy using an internal standard. ^bdetermined from the ¹H-NMR spectrum of the crude mixture. ^c48 h reaction time. ^dcomplex product mixture. ^e1 drop of water was added to enhance solubility of KBr and oxone.

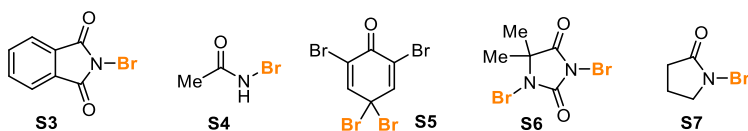


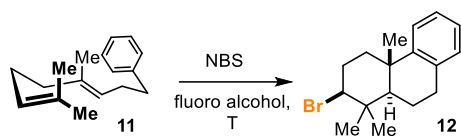
22.8 mg Homogeranyl benzene (**11**, 100 μmol , 1.0 eq) was dissolved in 1.0 mL solvent. Then, 120 μmol electrophilic bromine source (1.2 eq) was added to the mixture at room temperature.

Table S2. Screening of various Br^+ sources and solvents.

Entry	Br^+ source	Solvent	Yield 12 ^a	d.r. ^b
1	NBS	HFIP	42%	79:21
2	S3	HFIP	27%	78:22
3	S4	HFIP	17%	77:23
4	S5	HFIP	21%	73:27
5	S6	HFIP	32%	79:21
6	S7	HFIP	39%	80:20
7	NBS	<i>i</i> PrOH	<5% ^c	n.d.
8	NBS	DCM	8% ^c	n.d.
9	NBS	MeCN	12% ^d	n.d.

^ayield determined by $^1\text{H-NMR}$ spectroscopy using an internal standard. ^bdetermined from the $^1\text{H-NMR}$ spectrum of the crude mixture. ^creaction stirred for 24 h. Mainly acyclic *i*PrO/Br addition product observed. ^dreaction stirred for 24 h. Monocyclic product observed as the main product.



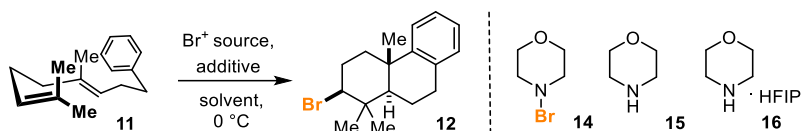


22.8 mg Homogeranyl benzene (**11**, 100 μmol , 1.0 eq) was dissolved in 1.0 mL solvent. Then, 21.4 mg NBS (120 μmol , 1.2 eq) was added to the mixture at the given temperature.

Table S3. Variation of fluorinated alcohols as solvent at different temperatures.

Entry	Solvent	T	Yield 12 ^a	d.r. ^b
1	HFIP	rt	42%	79:21
2	TFE	rt	18%	n.d.
3	TFE	-20 °C	<5%	n.d.
4	PFTB	0 °C	<5%	n.d.
5	PFNP	0 °C	17%	n.d.
6 ^c	HFIP	0 °C	68%	79:21

^ayield determined by ¹H-NMR spectroscopy using an internal standard. ^bdetermined from the ¹H-NMR spectrum of the crude mixture. ^creaction was terminated after 1 minute.

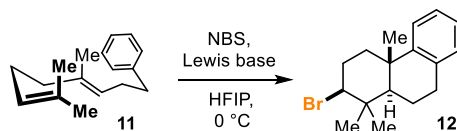


22.8 mg Homogeranyl benzene (**11**, 100 μmol, 1.0 eq) and 140 μmol additive (1.4 eq) were mixed in 1.0 mL solvent. Then, 120 μmol of the electrophilic bromine source (1.2 eq) was added to the mixture at 0 °C.

Table S4. Screening of different *N*-bromo reagents at 0 °C.

Entry	Br ⁺ source	Solvent	Additive	Yield 12 ^a	d.r. ^b
1	NBS	HFIP	–	68%	79:21
2	14	HFIP	–	62%	>95:5
3	14	DCM	–	23%	>95:5
4	14	MeNO ₂	–	27%	>95:5
5 ^c	NBS	HFIP	15	72%	>95:5
6 ^d	NBS	HFIP	15	78%	>95:5
7 ^d	NBS	HFIP	16	78% (76%) ^e	>95:5
8 ^d	NBS	HFIPMe	15	<5%	n.d.
9 ^d	NBS	TFE	15	35%	>95:5
10 ^d	NBS	PFTB	15	13%	>95:5

^ayield determined by ¹H-NMR spectroscopy using an internal standard. ^bdetermined from the ¹H-NMR spectrum of the crude mixture. ^cadditive was mixed with NBS for 1 min at 0 °C prior to the addition of **11**. ^dadditive was mixed with NBS for 10 min at 0 °C prior to the addition of **11**. ^eisolated yield.

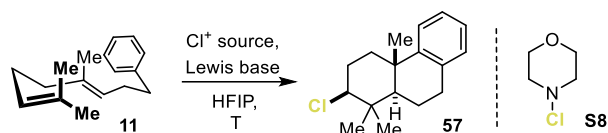


120 μmol bromine source (1.2 eq) and 140 μmol Lewis base (1.4 eq) were mixed in 1.0 mL HFIP. After 10 min, 22.8 mg homoogeranyl benzene (**11**, 100 μmol , 1.0 eq) was added to the mixture at 0 °C.

Table S5. Screening of different *N*-bromo reagents.

Entry	Additive	Conversion	Yield 12 ^a	d.r. ^b
1	Pyrrolidine	>95%	62%	91:9
2	Pyridine	71%	40%	78:22
3	Pyrrrole	>95%	<5%	n.d.
4	2,2,6,6-Tetramethylpiperidine	75%	42%	80:20
5	1,4-Diazabicyclo[2.2.2]octan (DABCO)	78%	37%	79:21
6	(<i>S</i>)-Proline	64%	33%	81:19
7	AcONa	>95%	50%	77:23
8	2,4,6-Trimethylaniline	>95%	<5%	n.d.
9	<i>N,O</i> -Dimethylhydroxylamine · HCl	>95%	7%	83:17
10	<i>n</i> -Butylamine	89%	51%	86:14
11	PPh ₃	<5%	<5%	n.d.
12	Piperidine	>95%	63%	>95:5
13	<i>N</i> -Methylmorpholine	59%	45%	86:14
14	15	>95%	78%	>95:5
15	16	>95%	78%	>95:5
16	Morpholine HCl salt	>95%	35%	90:10
17	Morpholine TFA salt	>95%	40%	84:16

^ayield determined by ¹H-NMR spectroscopy using an internal standard. ^bdetermined from the ¹H-NMR spectrum of the crude mixture.



The electrophilic chlorine reagent and **16** were mixed in 1.0 mL HFIP at temperature T_1 . After stirring for 1 h, 22.8 mg homogeranyl benzene (**11**, 100 μmol , 1.0 eq) were added at temperature T_2 and stirred for the time given.

Table S6. Screening of chlorination conditions.

Entry	Cl ⁺ source	16 (eq)	T_1	T_2	t	Conversion	Yield ^a	d.r. ^b
1	DCDMH (0.60 eq)	0	– ^c	rt	5 min	>95%	16%	50:50
2	NCS (1.20 eq)	1.4	0 °C ^d	0 °C	30 min	81%	19%	56:44
3	S8 (3.00 eq)	1.4	– ^c	0 °C	30 min	78%	22%	66:34
4	DCDMH (0.60 eq)	1.4	rt	rt	30 min	>95%	25%	65:35
5	DCDMH (0.65 eq)	1.4	rt	0 °C	1 h	>95%	39%	72:28
6	DCDMH (1.34 eq)	1.7	rt	0 °C	30 min	>95%	43% (32%) ^e	76:24

^ayield determined by ¹H-NMR spectroscopy using an internal standard. ^bdetermined from the ¹H-NMR spectrum of the crude mixture. ^cCl reagent was added directly to a solution of **11** in HFIP without **16** at temperature T_2 . ^dNCS was stirred for 10 min at 0 °C with **16**. ^eisolated yield of the major isomer.

3. NMR Investigations on the in-situ Formation of NBM (14)

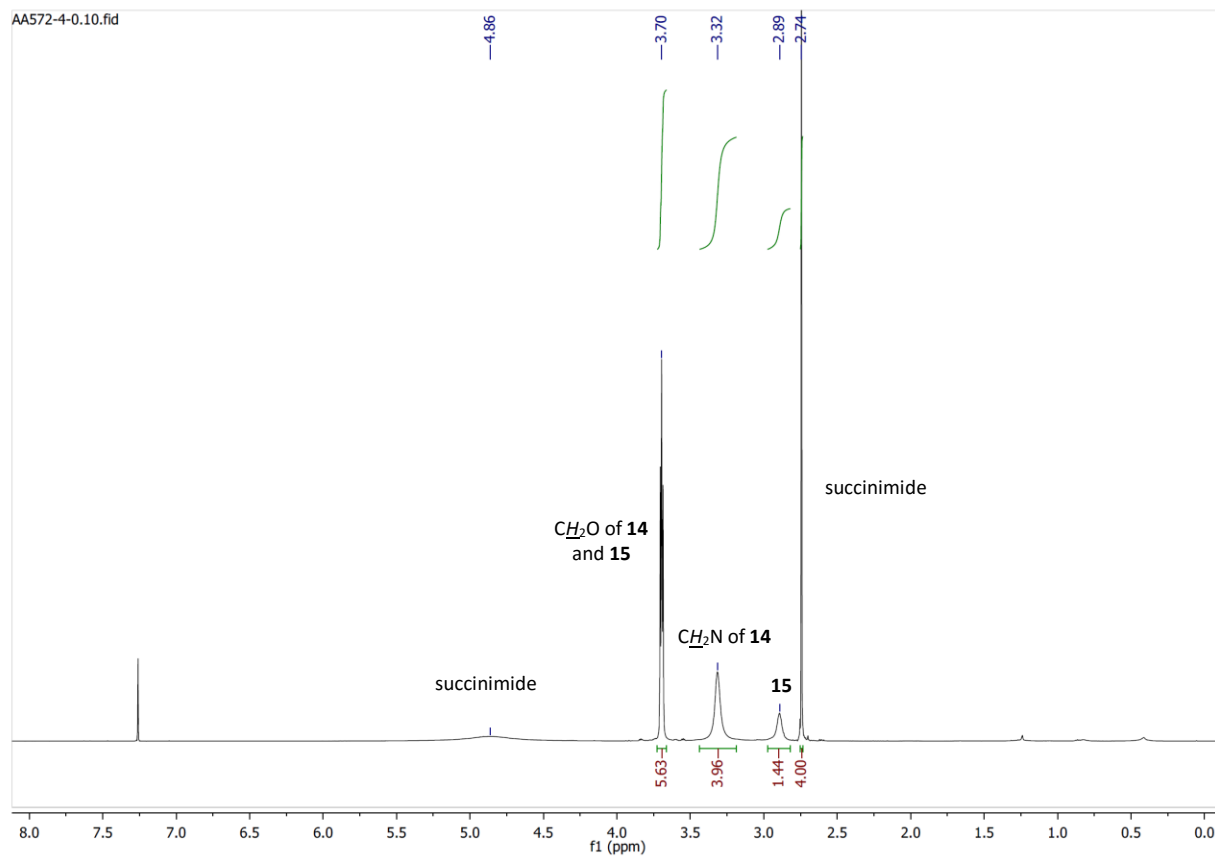


Figure S1. ^1H -NMR spectrum of 1.35 eq. morpholine (15) and 1.00 eq. NBS in CDCl_3 .

4. NMR Investigations on the Interaction of HFIP with NBS

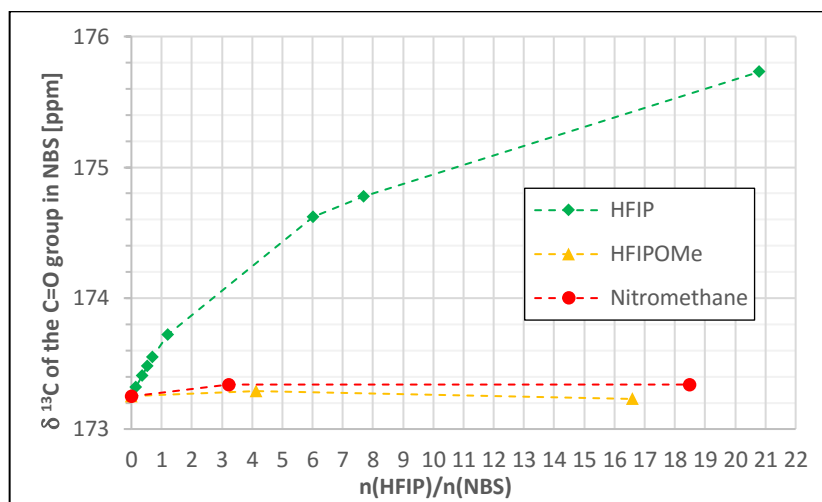


Figure S2. NMR titration curves of NBS with HFIP in CDCl_3 at 300 K.

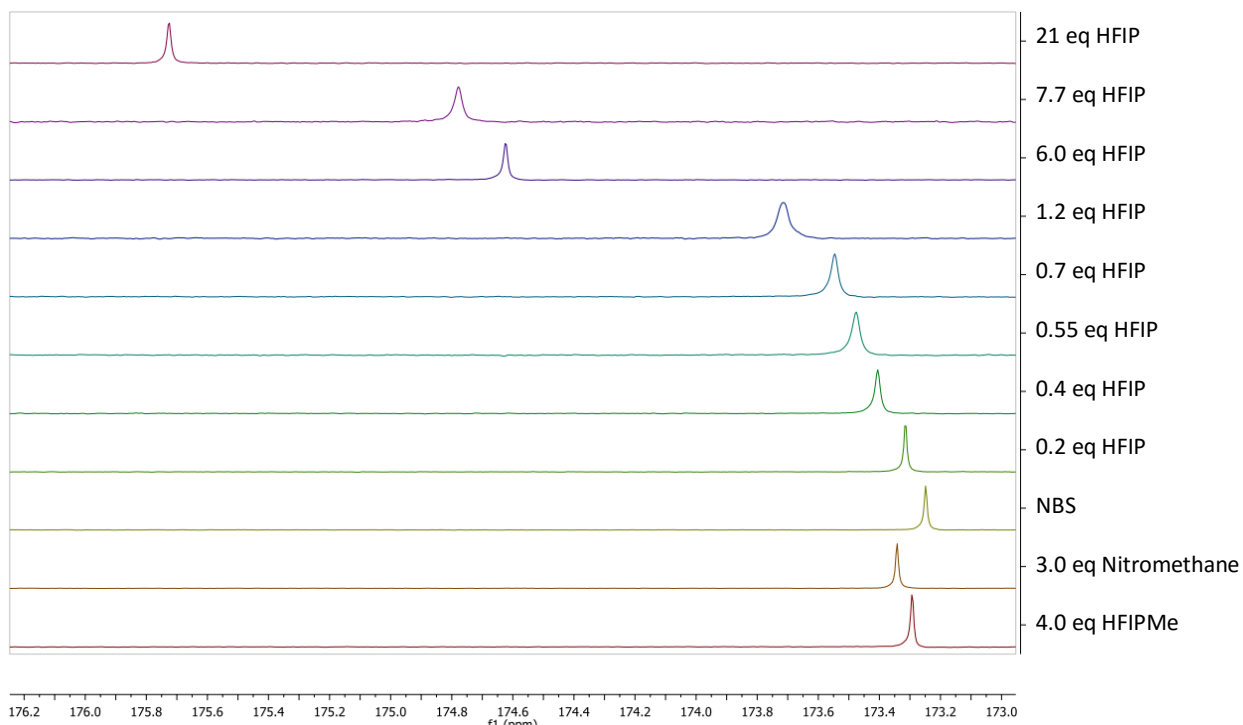


Figure S3. ^{13}C -shift of the NBS C=O group (0.1 M NBS in CDCl_3) upon addition of HFIP, nitromethane and HFIPMe, respectively, at 300 K, recorded with 125 MHz. The precise molar ratio of the mixtures was determined from the ^1H -NMR spectrum (500 MHz).

5. NMR Investigations on the Interaction of HFIP with NBM (**14**)

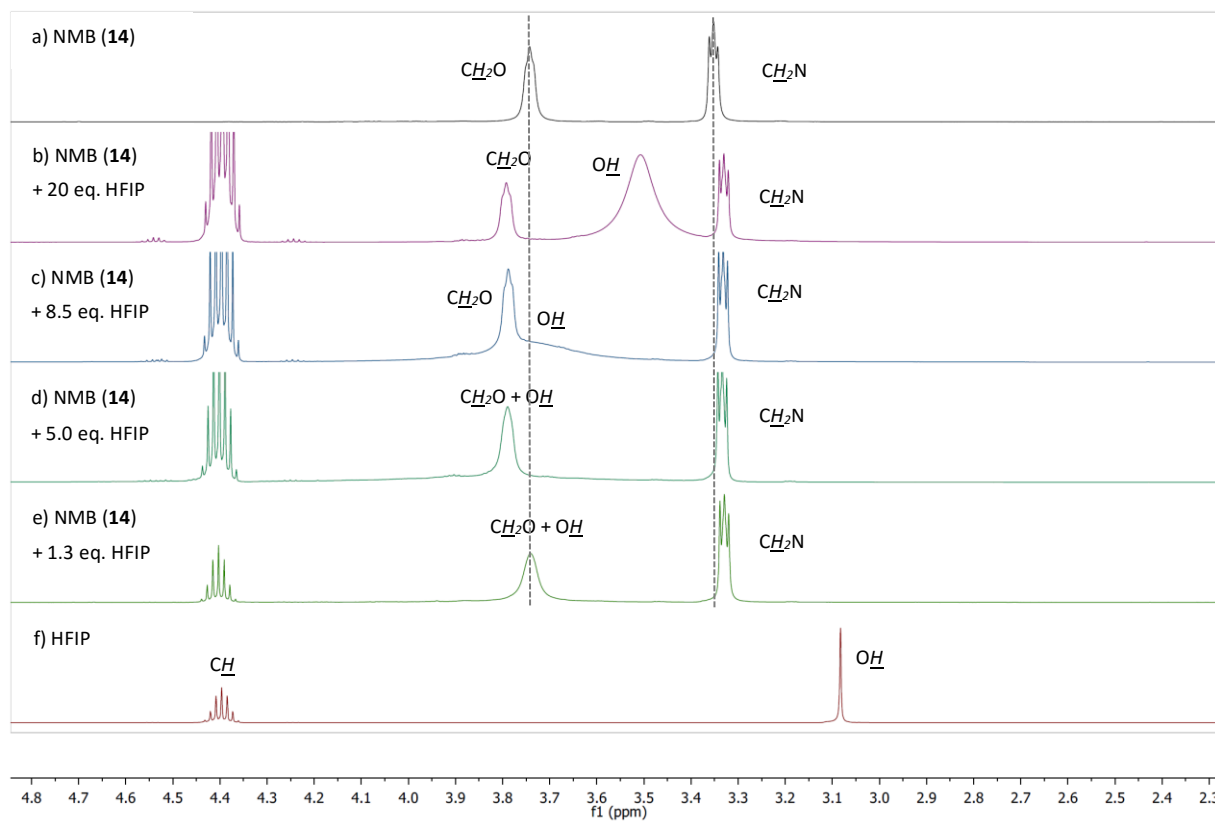


Figure S4. NMR study of 0.3 M *N*-bromo morpholine (**14**) mixtures with increasing amounts of HFIP in CDCl₃ (0.6 mL) at 300 K, recorded with 500 MHz. In entry d and e the signal of the HFIP-OH group overlapped with that of the CH₂O-moiety of **14**.

6. Determination of Halogenating Ability of *N*-Chloro Morpholine (**S8**)

In order to investigate the halogenating ability of *N*-chloro morpholine (**S8**) in comparison with other chlorinating agents,^[1] 0.5 mL of a 0.1 M solution of collidine (**S9**, 50.0 μmol , 1.0 eq) were added to 50.0 μmol (1.0 eq) halogen source in abs. CDCl_3 in an NMR tube. A ^1H NMR spectrum was recorded (Figure S5).

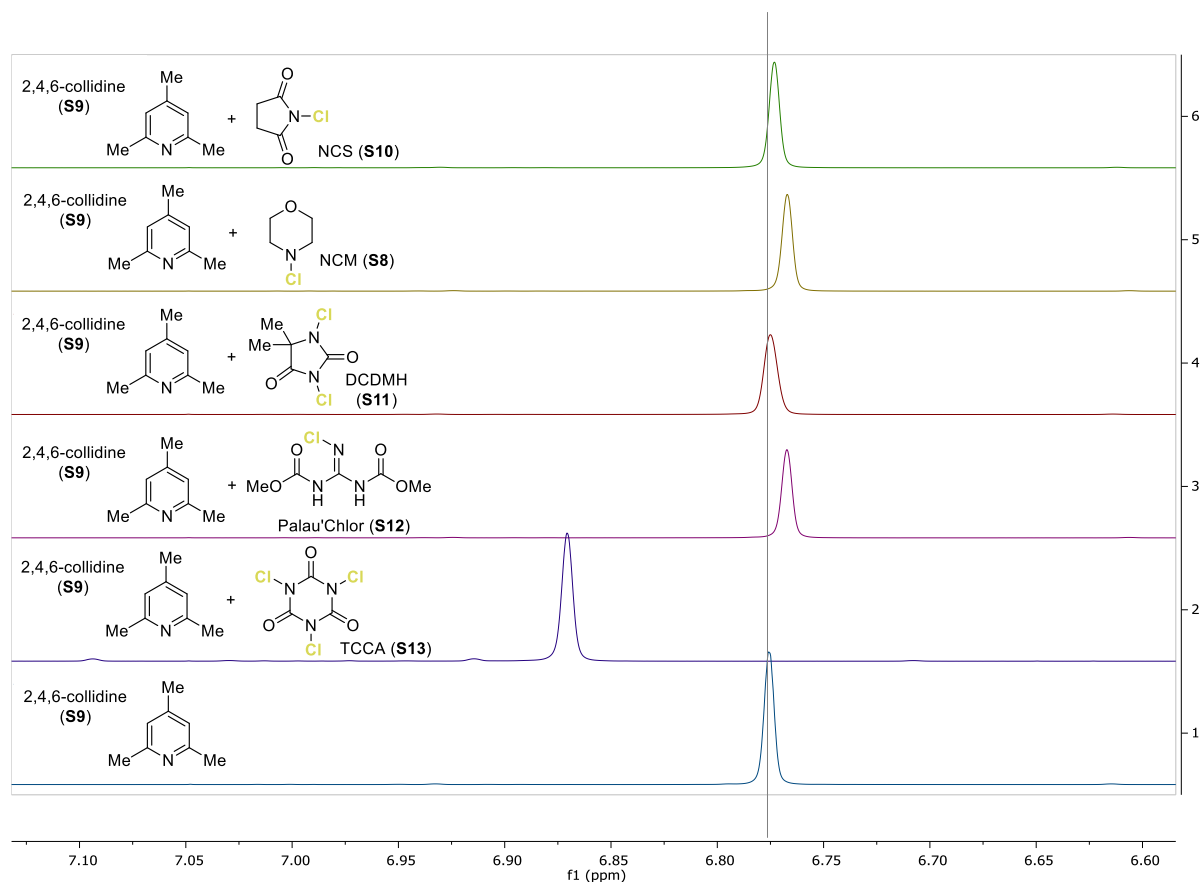


Figure S5. ^1H -NMR study of *N*-chloro reagents (0.1 M, 1.0 eq.) with 1.0 eq 2,4,6-collidine (**S9**) in CDCl_3 .

In order to test the influence of the solvent HFIP on the chlorinating ability of **S8** compared to other common electrophilic halogenation reagents, increasing equivalents of HFIP were added to the NMR tube next, followed by subsequent ^1H -NMR measurements. As standard, the same series of experiments has been conducted without adding any chloro reagent (Figure S6).

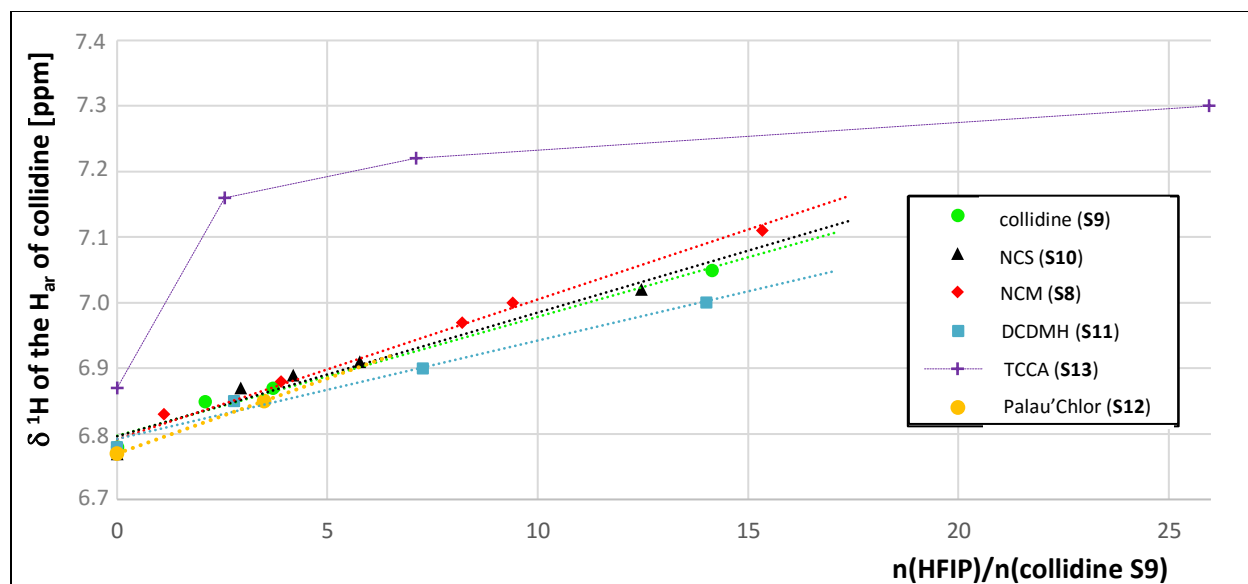


Figure S6. Titration of 1.0 eq chlorinating reagent **S8**, **S10** – **S13**, 1.0 eq collidine (**S9**) and increasing equivalents of HFIP.

In CDCl_3 the resonance of the aryl proton in collidine (**S9**) was significantly shifted to higher field upon addition of *N*-chloro morpholine (**S8**), indicating a halogen bonding interaction of **S8** and **S9** rather than a complete chlorenium ion transfer. In contrast, the collidine-aryl-H signal displayed a downfield shift in a mixture of HFIP/ CDCl_3 , which enhanced with increasing amounts of HFIP. This effect nicely corroborates the decisive impact of HFIP on the halogenating ability of **S8**. In HFIP, **S8** is more activated than other commonly used chlorenium sources and, as a consequence, it becomes more productive (selective) as observed in the described chloro cyclization.

7. General Procedures

7.1 Cyclization Procedure GP-A using NBS or NIS

119 mg Morpholine-HFIP salt (**16**, 280 μmol , 1.4 eq) were dissolved in HFIP (2.0 mL) and the mixture cooled to 0 °C. 42.7 mg NBS (240 μmol , 1.2 eq) and 54.0 mg NIS (240 μmol , 1.2 eq), respectively, were added in one portion and the solution stirred for 10 minutes (NBS) or 5 min (NIS). Next, 200 μmol substrate (1.0 eq) were added to the solution and the mixture stirred for further 20 min (NBS) or 10 min (NIS). The reaction was terminated by the addition of freshly prepared 10% aq. Na_2SO_3 solution (2.0 mL), the suspension stirred for 5 minutes, poured into water (20 mL) and extracted with EtOAc/*n*-hexane (1:1, 10 mL, 2 \times). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , and filtered. The solvent was removed under reduced pressure, the d.r. determined by ^1H NMR from the crude sample (where applicable), and the combined crude product purified by column chromatography.

7.2 Cyclization Procedure GP-B using NBS or NIS

119 mg Morpholine-HFIP salt (**16**, 280 μmol , 1.4 eq) were dissolved in HFIP (1.0 mL) and the mixture cooled to 0 °C. 42.7 mg NBS (240 μmol , 1.2 eq) and 54.0 mg NIS (240 μmol , 1.2 eq), respectively, were added in one portion and the solution stirred for 10 minutes (NBS) or 5 min (NIS). This solution was then added dropwise to a stirring emulsion of 200 μmol substrate (1.0 eq) in HFIP (1.0 mL) at 0 °C. After stirring for another 20 min (NBS) or 10 min (NIS) at 0 °C, the reaction was terminated by the addition of freshly prepared 10% aq. Na_2SO_3 solution (2.0 mL). The suspension was stirred for 5 minutes, poured into water (20 mL) and extracted with EtOAc/*n*-hexane (1:1, 10 mL, 2 \times). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , and filtered. The solvent was removed under reduced pressure, the d.r. determined by ^1H NMR from the crude sample, and the combined crude product purified by column chromatography.

7.3 Cyclization Procedure GP-C using NBS or NIS

102 mg Morpholine-HFIP salt (**16**, 240 μmol , 1.2 eq) were dissolved in HFIP (1.0 mL) and the mixture cooled to 0 °C. 33.8 mg NBS (190 μmol , 0.95 eq) and 42.8 mg NIS (190 μmol , 0.95 eq), respectively, were added in one portion and the solution stirred for 10 minutes (NBS) or 5 min (NIS). This solution was then added

dropwise to a stirring emulsion of 200 μmol substrate (1.0 eq) in HFIP (1.0 mL) at 0 °C. After stirring for another 20 min (NBS) or 10 min (NIS) at 0 °C, the reaction was terminated by the addition of freshly prepared 10% aq. Na_2SO_3 solution (2.0 mL). The suspension was stirred for 5 minutes, poured into water (20 mL) and extracted with EtOAc/*n*-hexane (1:1, 10 mL, 2 \times). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , and filtered. The solvent was removed under reduced pressure, the d.r. determined by ^1H NMR from the crude sample, and the combined crude product purified by column chromatography.

7.4 Cyclization Procedure GP-D using NBS (10 mmol scale)

1.22 g Morpholine (**15**, 14.0 mmol, 1.4 eq) were placed in a 250 mL round bottom flask and dissolved in 70 mL abs. HFIP. The mixture was cooled to 0 °C and 2.14 g NBS (12.0 mmol, 1.2 eq.) were added in 3 portions over 30 seconds. After 10 minutes, 1.54 g geraniol (**34**, 10.0 mmol, 1.0 eq.) were added dropwise and the reaction mixture stirred for 30 minutes at 0 °C. The reaction was terminated by the addition of freshly prepared 10% aq. Na_2SO_3 solution (50 mL), the mixture stirred for 5 minutes, and the phases separated. The lower HFIP phase was withdrawn and recycled by distillation (62 mL recovered), and the residue diluted with EtOAc/*n*-hexane (1:1, 70 mL) and poured back into the separation funnel. The phases were separated, the aqueous phase extracted with EtOAc/*n*-hexane (2:1, 70 mL, $\times 2$), the combined organic layers then washed with brine (70 mL), dried over MgSO_4 , and filtered. The solvent was removed under reduced pressure and the crude product purified by column chromatography.

7.5 Cyclization Procedure GP-E using DCDMH

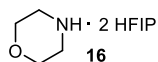
71.4 mg Morpholine-HFIP salt (**16**, 280 μmol , 1.4 eq) were dissolved in HFIP (1.0 mL) at rt. 23.6 mg DCDMH (120 μmol , 0.6 eq) were added in one portion and the solution stirred for 1 h at rt. This solution was then added dropwise to a stirring emulsion of 200 μmol substrate (1.0 eq) in HFIP (1.0 mL) at 0 °C. After the addition the mixture was stirred for another 30 min. The reaction was terminated by the addition of freshly prepared 10% aq. Na_2SO_3 solution (2.0 mL), the inhomogeneous mixture stirred for 5 min., poured into water (20 mL) and extracted with EtOAc/*n*-hexane (1:1, 10 mL, 2 \times). The combined organic layers were washed with brine (20 mL), dried over MgSO_4 , and filtered. The solvent was removed under reduced

pressure, the d.r. determined by ^1H NMR from the crude sample, and the combined crude product purified by column chromatography.

7.6 Cyclization Procedure (GP-F) using BDSB (17)

According to the literature procedure,^[2] 54.9 mg BDSB (100 μmol , 1.0 eq) were dissolved in 0.5 mL abs. MeNO_2 . The solution was added quickly to 100 μmol of the substrate (1.0 eq) dissolved in 1.5 mL abs. MeNO_2 at $-25\text{ }^\circ\text{C}$. After stirring for 5 min, the reaction was stopped by the addition of freshly prepared 5% aq. NaHCO_3 /5% aq. Na_2SO_3 solution (1:1, 5 mL), the mixture stirred for 15 min and then poured into water (5 mL). After extraction with DCM (5 mL, $\times 3$), the combined organic layers were dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product subjected to NMR analysis.

7.7 Preparation of Morpholine-HFIP Salt (**16**)



Morpholine-HFIP salt (16**):** 11.5 g abs. HFIP (7.2 mL, 68.2 mmol, 2.5 eq) were quickly added to 2.38 g neat morpholine (**15**, 27.3 mmol, 1.0 eq) in a round bottom flask under argon. A crystalline solid formed, which was, upon complete crystallization, suspended in abs. DCM (10 mL) and cooled to 0 °C for 10 minutes for further precipitation. The solid was then filtered, washed with cold DCM (10 mL) and dried for 1 h under vacuum at 40 °C to afford the product **16** as colorless crystals (6.57 g, 15.5 mmol, 57%); **m.p.** = 57 – 58 °C (DCM); ¹H NMR (300 MHz, D₂O) δ 4.72 (dt, *J* = 13.2, 6.6 Hz, 2H, CH), 3.82 – 3.75 (m, 4H, CH₂), 3.02 – 2.96 (m, 4H, CH₂) ppm [Note: Due to signal overlap with the solvent, integration was performed for half the dt of HFIP resulting in an integral of 1.02]; ¹H NMR (500 MHz, CDCl₃) δ 4.41 (br s, 1H, OH, NH), 4.34 (hept, *J* = 6.2 Hz, 1H, CH), 3.77 – 3.66 (m, 4H, CH₂), 2.94 – 2.82 (m, 4H, CH₂); **Anal. Calcd.** for C₁₀H₁₃F₁₂NO₂: C: 28.38; H: 3.10, N: 3.31. Found: C: 28.22; H: 3.09; N: 3.33.

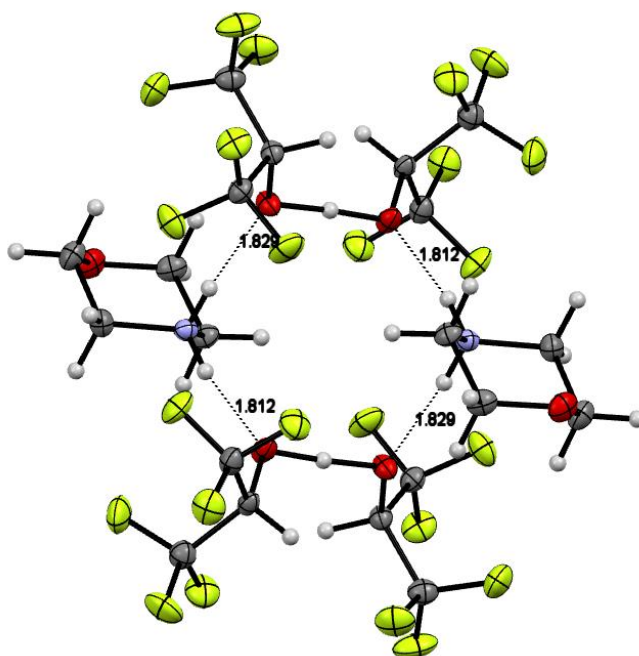
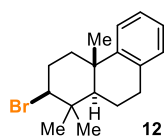


Figure S7. H-Bonding network with 4 molecules HFIP and 2 molecules morpholine in **16** (CCDC 1584440).

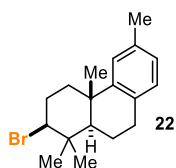
8. Physical and Spectroscopic Data of Bromocyclized Products



2-Bromo-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (12), prepared from **11** (43.4 mg, 190 μmol) by GP-A; colorless solid (44.4 mg, 144 μmol , 76%; d.r. >95:5);

TLC: $R_f = 0.32$ (silica gel, *n*-hexane); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.21 (d, $J = 7.4$ Hz, 1H), 7.16 – 7.05 (m, 3H), 4.06 (dd, $J = 12.7, 4.2$ Hz, 1H), 3.02 – 2.83 (m, 2H), 2.45 – 2.22 (m, 3H), 1.98 (dt, $J = 12.1, 4.7$ Hz, 1H), 1.89 – 1.76 (m, 1H), 1.65 – 1.54 (m, 1H), 1.48 (dd, $J = 12.2, 2.2$ Hz, 1H), 1.26 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.08 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 148.8, 134.9, 129.2, 126.0, 125.7, 124.6, 69.01, 51.36, 40.17, 40.02, 38.02, 31.68, 30.92, 30.68, 25.04, 20.74, 18.40 ppm.

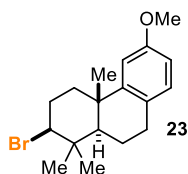
The spectroscopic data are in accordance to those reported in the literature.^[2]



2-Bromo-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (22), prepared from **18** (48.9 mg, 202 μmol) by GP A; colorless solid (46.7 mg, 145 μmol , 72%;

d.r. >95:5); **TLC:** $R_f = 0.29$ (silica gel, *n*-hexane); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.86 – 6.83 (m, 1H), 6.82 – 6.73 (m, 2H), 3.88 (dd, $J = 12.6, 4.1$ Hz, 1H), 2.71 (qdd, $J = 18.1, 16.8, 9.2, 4.5$ Hz, 2H), 2.23 – 2.14 (m, 2H), 2.13 (s, 3H, CH_3), 2.12 – 2.04 (m, 1H), 1.79 (ddt, $J = 13.3, 7.0, 2.2$ Hz, 1H), 1.63 (dtd, $J = 13.3, 11.6, 6.7$ Hz, 1H), 1.46 – 1.37 (m, 1H), 1.29 (dd, $J = 12.0, 2.2$ Hz, 1H), 1.08 (d, $J = 0.8$ Hz, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.90 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 148.7, 135.3, 131.7, 129.1, 126.6, 125.1, 69.15, 51.52, 40.23, 40.05, 37.98, 31.72, 30.72, 30.55, 25.01, 21.41, 20.83, 18.41 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[3]

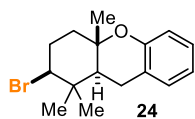


2-Bromo-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (23), prepared from **19** (42.2 mg, 163 μmol) by GP-B; colorless solid (46.6 mg, 138

μmol , 85%; d.r. >95:5), **TLC:** $R_f = 0.65$ (silica gel, *n*-hexane/EtOAc; 9:1); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 6.97 (dd, $J = 8.3, 1.0$ Hz, 1H), 6.74 (d, $J = 2.6$ Hz, 1H), 6.72 – 6.64 (m, 1H), 4.04 (dd, $J = 12.3, 4.1$ Hz, 1H), 3.77 (s, 3H), 2.96 – 2.71 (m, 2H), 2.44 – 2.19 (m, 3H), 1.95 (ddt, $J = 13.4, 6.8, 2.3$ Hz, 1H), 1.88 – 1.71 (m, 1H), 1.69 – 1.53 (m, 1H), 1.45 (dd, $J = 11.9, 2.3$ Hz, 1H), 1.25 (s, 3H, CH_3), 1.16

(s, 3H, CH₃), 1.06 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 157.9, 150.1, 130.0, 127.1, 111.3, 110.3, 68.97, 55.41, 51.37, 40.18, 40.02, 38.21, 31.66, 30.69, 30.09, 24.93, 20.87, 18.42 ppm.

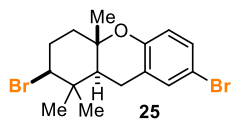
The spectroscopic data are in accordance to those reported in the literature.^[2]



2-Bromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (24), prepared from **20** (46.6 mg, 202 μmol) by GP-B; colorless solid (48.1 mg, 156 μmol, 77%; d.r. >95:5);

TLC: *R*_f = 0.57 (silica gel, *n*-hexane/EtOAc; 19:1); ¹H NMR (300 MHz, CDCl₃) δ 7.14 – 7.03 (m, 2H), 6.85 (td, *J* = 7.5, 1.3 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.06 (dd, *J* = 12.4, 4.2 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.30 (dtd, *J* = 13.8, 4.3, 3.4 Hz, 1H), 2.24 – 2.10 (m, 1H), 2.02 (dt, *J* = 13.2, 3.5 Hz, 1H), 1.91 – 1.76 (m, 2H, CH), 1.25 (s, 3H, CH₃), 1.19 (s, 3H, CH₃), 1.05 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 152.8, 129.5, 127.5, 121.8, 120.2, 117.2, 75.87, 66.13, 48.21, 40.85, 39.35, 31.66, 29.76, 24.72, 19.98, 17.06 ppm.

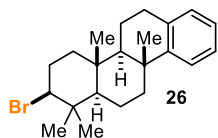
The spectroscopic data are in accordance to those reported in the literature.^[4]



2,7-dibromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (25),

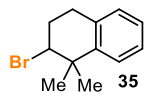
prepared from **20** (41.2 mg, 179 μmol) by GP-B but employing 70.1 mg NBS (394 μmol, 2.2 eq) and 197 mg morpholine HFIP salt (**16**, 465 μmol, 2.6 eq); colorless solid (61.2 mg, 158 μmol, 88%; d.r. >95:5); **TLC:** *R*_f = 0.78 (silica gel, *n*-hexane/EtOAc; 19:1); ¹H NMR (300 MHz, CDCl₃) δ 7.21 – 7.13 (m, 2H), 6.67 – 6.60 (m, 1H), 4.03 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.81 – 2.68 (m, 2H), 2.28 (dtd, *J* = 13.9, 4.2, 3.4 Hz, 1H), 2.20 – 2.08 (m, 1H), 1.99 (dt, *J* = 13.2, 3.5 Hz, 1H), 1.83 – 1.69 (m, 2H, CH), 1.22 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 1.02 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 152.0, 132.2, 130.4, 124.1, 119.0, 112.2, 76.29, 65.69, 47.89, 40.70, 39.33, 31.58, 29.73, 24.61, 19.91, 17.03 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[4]

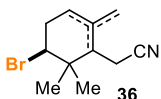


2-Bromo-1,1,4a,10b-tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysene (26), prepared from **21** (33.6 mg, 113 μmol) by GP-A. After 20 min, the mixture was diluted with 2.00 mL *i*PrNO₂ and cooled to $-25\text{ }^{\circ}\text{C}$. 75.1 μL ClSO₃H (1.13 mmol, 10.0 eq) was added and stirred for 40 min at that temperature before the reaction was terminated; colorless solid (17.0 mg, 45.2 μmol , 40%; d.r. >95:5); **TLC**: $R_f = 0.27$ (silica gel, *n*-hexane); **¹H NMR** (300 MHz, CDCl₃) δ 7.23 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.16 – 6.98 (m, 3H), 4.01 (dd, $J = 12.6, 4.5$ Hz, 1H), 2.94 (ddd, $J = 17.3, 6.6, 2.3$ Hz, 1H), 2.81 (ddd, $J = 17.4, 11.2, 7.2$ Hz, 1H), 2.41 (dt, $J = 12.6, 3.1$ Hz, 1H), 2.26 (qd, $J = 13.3, 3.9$ Hz, 1H), 2.17 – 2.04 (m, 1H), 1.89 – 1.59 (m, 5H), 1.55 – 1.45 (m, 1H), 1.26 (dd, $J = 11.7, 2.7$ Hz, 1H), 1.20 (s, 3H, CH₃), 1.13 – 1.01 (m, 2H), 1.08 (s, 3H, CH₃), 0.99 (s, 3H, CH₃), 0.98 (s, 3H, CH₃) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 149.9, 135.0, 129.0, 125.9, 125.4, 124.7, 69.96, 56.75, 55.17, 41.51, 40.72, 39.92, 37.98, 37.85, 31.10, 30.83, 30.62, 26.14, 20.73, 18.23 (2C), 16.41 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[2]



2-Bromo-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (35), prepared from **27** (30.0 mg, 187 μmol) by GP-A; colorless oil (37.1 mg, 155 μmol , 83%); **TLC**: $R_f = 0.31$ (silica gel, *n*-hexane); **¹H NMR** (300 MHz, CDCl₃) δ 7.36 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.23 – 7.10 (m, 2H), 7.06 (ddq, $J = 7.1, 1.5, 0.8$ Hz, 1H), 4.44 (dd, $J = 9.2, 3.4$ Hz, 1H), 3.14 – 2.87 (m, 2H), 2.53 – 2.31 (m, 2H), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 143.2, 133.8, 129.0, 126.9, 126.5, 126.2, 64.97 (CHBr), 39.78, 30.49, 30.11, 29.41, 28.88 ppm; **MS** (EI, 70 eV): m/z (%) = 240/238 (17) [M]⁺, 225/223 (26) [M-Me]⁺, 159 (26) [M-Br]⁺, 143 (100) [M-Me-Br]⁺, 128 (51) [M-2 \times Me-Br]⁺, 91 (11) [PhCH₂]⁺, 77 (9) [Ph]⁺; **IR** (film) $\tilde{\nu}_{\text{max}} = 1489, 1387, 1364, 1207, 1161, 1043, 884, 790, 758, 733, 705\text{ cm}^{-1}$; **HRMS** (EI) calcd. for C₁₂H₁₅Br [M]⁺ 238.0352, found 238.0315.

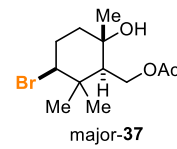


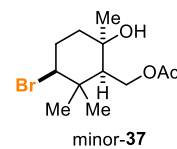
2-(5-Bromo-2,6,6-trimethylcyclohexen-1-yl)acetonitrile (36), prepared from **28** (33.0 mg, 202 μmol) by GP-C, isolated as a 12:53:35 mixture of inseparable elimination products (di-, tri- and tetrasubstituted alkenes); colorless oil (24.0 mg, 99.2 μmol , 52%); **TLC**: $R_f = 0.34$ (silica gel, *n*-hexane/EtOAc 9:1); **¹H NMR** (300 MHz, CDCl₃; *disubstituted isomer*) δ 5.07 (s, 1H), 4.81 (s, 1H), 1.22 (s, 3H), 0.89 (s, 3H) ppm (the other signals overlap with the signals of the other isomers); **¹H**

NMR (300 MHz, CDCl₃; *trisubstituted isomer*) δ 5.43 (br s, 1H), 4.16 – 4.10 (m, 1H), 2.73 (dd, $J = 17.4, 5.0$ Hz, 2H), 2.46 (dd, $J = 17.4, 5.7$ Hz, 1H), 1.82 (td, $J = 2.0, 0.9$ Hz, 3H), 1.18 (s, 3H), 1.05 (s, 3H) ppm; **¹H NMR** (300 MHz, CDCl₃; *tetrasubstituted isomer*) δ 4.24 – 4.18 (m, 1H), 3.15 – 2.95 (m, 2H), 1.74 (s, 3H), 1.27 (s, 3H), 1.19 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃; *trisubstituted isomer*) δ 132.7, 123.5, 120.0, 62.09, 46.88, 38.57, 34.84, 28.58, 21.79, 17.35, 16.90 ppm; **¹³C NMR** (75 MHz, CDCl₃; *other isomers*) δ 133.2, 125.7, 118.6, 64.58, 63.82, 49.43, 40.33, 32.50, 31.74, 29.88, 28.50, 26.99, 24.28, 22.80, 19.99, 17.23, 14.27 ppm.

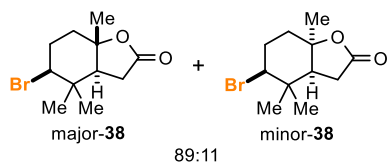
The spectroscopic data are in accordance to those reported in the literature.^[2]

(3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl acetate (37), prepared from **29** (40.4 mg, 206 μ mol) by GP-C, a 82:18 mixture of separable diastereomers;

 *major diastereomer*: colorless solid (31.5 mg, 107 μ mol, 52%); **TLC**: $R_f = 0.50$ (silica gel, *n*-hexane/EtOAc; 1:1); **¹H NMR** (300 MHz, CDCl₃) δ 4.43 (dd, $J = 11.9, 5.1$ Hz, 1H), 4.32 (dd, $J = 11.9, 5.0$ Hz, 1H), 3.98 (dd, $J = 12.4, 4.1$ Hz, 1H), 2.50 (s, 1H), 2.19 (dq, $J = 13.9, 4.0$ Hz, 1H), 2.07 (s, 3H), 2.12 – 1.94 (m, 1H), 1.81 (dt, $J = 13.4, 3.5$ Hz, 1H), 1.72 (t, $J = 5.2$ Hz, 1H), 1.67 – 1.50 (m, 1H), 1.24 (s, 3H), 1.17 (s, 3H), 1.00 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 171.2, 71.90, 66.03, 63.59, 55.70, 43.12, 39.94, 32.15, 30.43, 23.95, 21.34, 17.82 ppm.

 *minor diastereomer*: colorless solid (6.1 mg, 20.8 μ mol, 10%); **TLC**: $R_f = 0.84$ (silica gel, *n*-hexane/EtOAc; 1:1); **¹H NMR** (300 MHz, CDCl₃) δ 4.47 (dd, $J = 12.3, 4.7$ Hz, 1H), 4.35 (dd, $J = 12.3, 2.9$ Hz, 1H), 3.99 (dd, $J = 12.8, 3.8$ Hz, 1H), 2.43 (qd, $J = 13.3, 4.0$ Hz, 1H), 2.08 – 2.04 (m, 4H), 1.73 – 1.64 (m, 1H), 1.56 (td, $J = 14.0, 4.1$ Hz, 1H), 1.54 (br s, 1H), 1.41 (dd, $J = 4.7, 2.9$ Hz, 1H), 1.24 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H) ppm; **¹³C NMR** (75 MHz, CDCl₃) δ 170.7, 71.84, 67.47, 63.44, 53.12, 42.24, 39.94, 30.67, 30.50, 29.97, 21.34, 17.89 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[2]

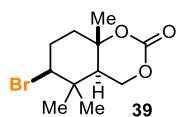


5-Bromo-4,4,7a-trimethylhexahydrobenzofuran-2(3H)-one (38),

prepared from **30** (24.2 mg, 133 μmol) by GP-A; colorless solid (20.0 mg, 76.6 μmol , 58%; d.r. = 89:11); **TLC:** R_f = 0.39 (silica gel, *n*-hexane/EtOAc; 4:1); *major diastereomer:* $^1\text{H NMR}$ (300 MHz, CDCl_3) δ

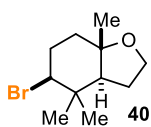
3.92 (dd, J = 12.4, 4.6 Hz, 1H, CHBr), 2.52 (dd, J = 16.3, 14.5 Hz, 1H), 2.45 – 2.28 (m, 2H), 2.13 – 1.95 (m, 3H), 1.86 – 1.73 (m, 1H), 1.37 (d, J = 0.8 Hz, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.5, 84.71, 62.90, 54.57, 38.66, 38.51, 32.44, 30.34, 30.11, 20.59, 17.18 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[2]



6-Bromo-5,5,8a-trimethylhexahydro-4H-benzo[d][1,3]dioxin-2-one (39), prepared from **31** (41.6 mg, 164 μmol) by GP-B and from **32** (48.2 mg, 189 μmol) by GP-A; colorless solid (25.7 mg, 92.7 μmol , 57%; d.r. >95:5 and 20.0 mg, 72.2 μmol , 38%; d.r. >95:5, respectively); **TLC:** R_f = 0.60 (silica gel, *n*-hexane/EtOAc; 1:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.49 (dd, J = 10.8, 5.7 Hz, 1H), 4.42 (dd, J = 12.7, 10.8 Hz, 1H), 3.96 (dd, J = 12.5, 4.1 Hz, 1H), 2.30 (dtd, J = 13.9, 4.0, 3.0 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.98 (dt, J = 13.2, 3.4 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.52 (d, J = 1.0 Hz, 3H, CH_3), 1.15 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.5, 80.81, 67.72, 62.83, 47.23, 39.53, 38.11, 31.13, 29.31, 20.93, 17.35 ppm.

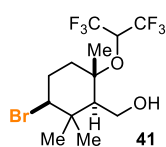
The spectroscopic data are in accordance to those reported in the literature.^[2]



5-Bromo-4,4,7a-trimethyloctahydrobenzofuran (40), prepared from **33** (29.1 mg, 173

μmol) by GP-A; colorless oil (33.2 mg, 134 μmol , 78%; d.r. >95:5); **TLC:** R_f = 0.24 (silica gel, *n*-hexane/EtOAc; 19:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.98 – 3.80 (m, 3H), 2.25 (dtd, J = 14.3, 4.4, 3.0 Hz, 1H), 2.06 (tdd, J = 14.1, 12.6, 4.0 Hz, 1H), 1.93 – 1.81 (m, 3H), 1.57 – 1.45 (m, 2H, CH), 1.13 (d, J = 0.9 Hz, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.96 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 79.02, 65.99, 65.13, 56.13, 39.43, 38.92, 32.98, 30.52, 24.97, 20.18, 17.16 ppm; **MS** (EI, 70 eV): m/z (%) = 233/231 (100/99) $[\text{M}-\text{CH}_3]^+$, 166 (3) $[\text{M}-\text{HBr}]^+$, 151 (29) $[\text{M}-\text{CH}_3-\text{HBr}]^+$, 107 (13) $[\text{M}-\text{CH}_3-\text{HBr}-\text{CH}_2\text{CH}_2\text{O}]^+$; **IR** (film) $\tilde{\nu}_{\text{max}}$

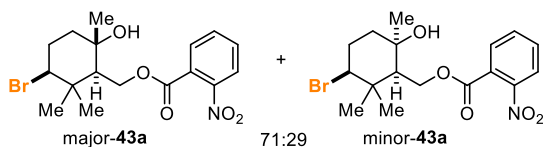
= 2960, 2873, 1456, 1378, 1153, 1068, 1009, 987, 925, 901, 783, 701 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{11}\text{H}_{20}\text{BrO}^+$ $[\text{M}+\text{H}]^+$ 247.0692, found 247.0694.



(3-Bromo-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2,2,6-trimethylcyclohexyl)

methanol (41), prepared from **34** (17.0 mg, 175 μmol and 1.54 g, 10.0 mmol) by GP-A and GP-D; colorless solid (45.3 mg, 113 μmol , 65%; d.r. >95:5 and 2.31 g, 5.75 mmol, 58%,

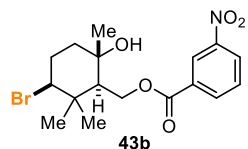
d.r. >95:5, respectively); **m.p.** = 117 – 119 $^{\circ}\text{C}$ (EtOAc); **TLC**: R_f = 0.52 (silica gel, *n*-hexane/EtOAc; 4:1); **^1H NMR** (300 MHz, CDCl_3) δ 4.35 (hept, J = 5.7 Hz, 1H, $\text{CH}(\text{CF}_3)_2$), 4.05 – 3.95 (m, 1H, CHBr), 4.01 – 3.91 (m, 1H, CH_2O), 3.78 (d, J = 11.8 Hz, 1H, CH_2O), 2.27 (dq, J = 13.8, 3.9 Hz, 1H), 2.24 (br s, 1H, OH) 2.06 – 1.87 (m, 1H), 1.85 – 1.78 (m, 2H), 1.79 – 1.70 (m, 1H), 1.37 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 0.94 (s, 3H, CH_3) ppm; **^{13}C NMR** (126 MHz, CDCl_3) δ 121.4 (q, J = 287.0, 285.5 Hz, $2\times\text{CF}_3$), 85.60, 68.54 (hept, J = 32.6 Hz, $\text{CH}(\text{CF}_3)_2$), 64.62, 61.55, 58.45, 40.03, 38.61 (d, J = 2.4 Hz), 31.56, 30.59, 19.14 (t, J = 2.4 Hz), 18.43 ppm; **^{19}F NMR** (376 MHz, CDCl_3) δ -72.60 – -72.90 (m, $2\times\text{CF}_3$) ppm; **IR** (neat) $\tilde{\nu}_{\text{max}}$ = 3539, 1369, 1274, 1216, 1184, 1098, 1023, 906, 890, 686 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{13}\text{H}_{19}\text{BrF}_6\text{O}_2$ $[\text{M}+\text{FA}-\text{H}]^-$ 447.0434, found 447.0435.



(3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl

2-nitrobenzoate (43a), prepared from **42a** (41.7 mg, 137 μmol) by GP-A; colorless oil (33.2 mg, 82.9 μmol , 60 %;

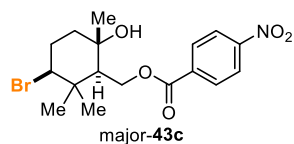
d.r. = 71:29); **TLC**: R_f = 0.56-0.59 (silica gel, *n*-hexane/EtOAc 1:1); **^1H NMR** (300 MHz, CDCl_3 ; *major diastereomer*) δ 8.01 – 7.87 (m, 1H), 7.80 – 7.52 (m, 3H), 4.77 (dd, J = 11.8, 4.3 Hz, 1H), 4.51 (dd, J = 11.8, 4.9 Hz, 1H), 3.99 (dd, J = 12.2, 4.3 Hz, 1H), 2.39 – 2.10 (m, 1H), 2.11 – 1.95 (m, 1H), 1.88 – 1.74 (m, 2H), 1.71 – 1.45 (m, 1H), 1.26 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm; **^1H NMR** (300 MHz, CDCl_3 ; *minor diastereomer*) δ 7.85 (dd, J = 7.6, 1.6 Hz, 1H), 7.80 – 7.52 (m, 3H), 4.08 – 4.01 (m, 1H), 3.98 – 3.91 (m, 1H), 3.83 (dd, J = 11.7, 2.2 Hz, 1H), 3.03 (dt, J = 15.1, 3.4 Hz, 1H), 2.34 – 2.20 (m, 1H), 2.16 – 1.95 (m, 3H), 1.82 (s, 3H, CH_3), 1.32 (dd, J = 4.7, 2.2 Hz, 1H), 1.19 (s, 3H, CH_3), 0.81 (s, 3H, CH_3) ppm; **^{13}C NMR** (75 MHz, CDCl_3 , *major and minor diastereomer*) δ 165.6, 164.5, 133.6, 133.2, 132.0, 131.3, 130.1, 129.9, 129.2, 127.7, 124.2, 124.1, 86.85, 71.84, 66.50, 65.69, 65.41, 60.74, 59.75, 55.83, 43.33, 40.04, 39.87, 36.52, 32.21, 30.41, 30.34, 29.91, 24.61, 23.69, 17.98 ppm; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 3428, 1726, 1532, 1349, 1296, 1255, 1126, 1073, 911, 730 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{BrNO}_7$ $[\text{M}+\text{FA}-\text{H}]^-$ 444.0663, found 444.0665.



(3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl 3-nitrobenzoate (43b),

prepared from **42b** (59.0 mg, 194 μmol) by GP-A; colorless solid (50.5 mg, 126 μmol , 65%; d.r. >95:5); **m.p.** = 117 – 118 $^{\circ}\text{C}$ (DCM); **TLC**: R_f = 0.58 (silica gel, *n*-hexane/EtOAc; 1:1); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 8.82 (dd, J = 2.2, 1.6 Hz, 1H), 8.42 (ddd, J = 8.2, 2.4, 1.1 Hz, 1H), 8.33 (dt, J = 7.8, 1.4 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 4.84 (dd, J = 11.9, 3.4 Hz, 1H), 4.54 (dd, J = 11.9, 5.7 Hz, 1H), 4.02 (dd, J = 12.4, 4.1 Hz, 1H), 2.29 – 2.18 (m, 1H), 2.07 (tdd, J = 13.9, 11.6, 3.6 Hz, 1H), 1.91 – 1.81 (m, 2H), 1.63 (tdd, J = 13.4, 4.4, 1.1 Hz, 1H), 1.29 (d, J = 0.8 Hz, 3H), 1.25 (s, 3H), 1.09 (s, 3H) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 164.7, 148.5, 135.3, 132.0, 129.9, 127.7, 124.7, 71.86, 65.53, 64.59, 56.18, 43.55, 40.18, 32.22, 30.65, 23.99, 18.02 ppm; **IR** (neat) $\tilde{\nu}_{\text{max}}$ = 3550, 2969, 1723, 1533, 1350, 1296, 1260, 1140, 1072, 796, 718 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{BrN}_2\text{O}_9$ $[\text{M}+\text{FA}-\text{H}]^-$ 444.0663, found 444.0659.

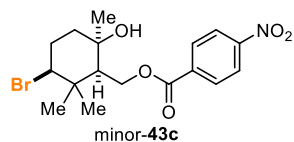
3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl 4-nitrobenzoate (43c), prepared from **42c** (60.0 mg, 198 μmol) by GP-A; produced as a 78:22 mixture of separable diastereomers;



major diastereomer: colorless solid (37.4 mg, 93.4 μmol , 47%);

m.p. = 147 – 148 $^{\circ}\text{C}$ (EtOAc); **TLC**: R_f = 0.71 (silica gel, *c*-hexane/EtOAc; 1:1);

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.32 – 8.26 (m, 2H), 8.21 – 8.15 (m, 2H), 4.84 (dd, J = 11.9, 3.5 Hz, 1H), 4.53 (dd, J = 11.9, 5.7 Hz, 1H), 4.01 (dd, J = 12.4, 4.0 Hz, 1H, CHBr), 2.23 (dq, J = 13.7, 4.0 Hz, 1H), 2.04 (s, 1H, OH), 2.16 – 1.98 (m, 1H), 1.91 – 1.81 (m, 2H), 1.63 (td, J = 13.6, 4.5 Hz, 1H), 1.30 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.09 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 164.9, 150.8, 135.5, 130.8 (2C), 123.8 (2C), 71.88, 65.50, 64.63, 56.14, 43.52, 40.16, 32.20, 30.67, 24.06, 18.01 ppm; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 3554, 1719, 1515, 1343, 1292, 1109, 920, 720 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{BrNO}_7$ $[\text{M}+\text{FA}-\text{H}]^-$ 444.0663, found 444.0663.

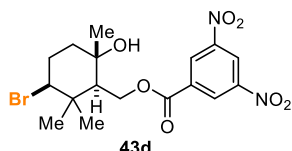


minor diastereomer: colorless solid (10.5 mg, 26.2 μmol , 13%); **m.p.** =

128 – 130 $^{\circ}\text{C}$ (EtOAc); **TLC**: R_f = 0.39 (silica gel, *c*-hexane/EtOAc; 4:1); **$^1\text{H NMR}$**

(300 MHz, CDCl_3) δ 8.30 – 8.23 (m, 2H), 8.18 – 8.12 (m, 2H), 4.12 – 4.04 (m, 2H),

4.01 – 3.89 (m, 1H), 2.75 – 2.66 (m, 1H), 2.34 – 2.21 (m, 2H), 2.21 – 2.01 (m, 2H), 1.70 (s, 3H, CH₃), 1.31 (s, 3H, CH₃), 1.07 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 163.5, 150.6, 137.2, 130.7 (2C), 123.7 (2C), 87.37, 65.00, 61.47, 56.93, 40.47, 38.32, 31.58, 30.67, 20.73, 18.93 ppm; IR (neat) $\tilde{\nu}_{\max}$ = 3566, 1709, 1521, 1280, 1106, 875, 839, 719 cm⁻¹; HRMS (ESI) calcd. for C₁₈H₂₃BrNO₇ [M+FA-H]⁻ 444.0663, found 444.0663.

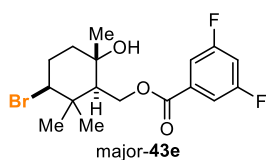


(3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl 3,5-dinitrobenzoate

(43d), prepared from **42d** (69.6 mg, 195 μmol) by GP-A; colorless solid (44.5 mg, 100 μmol, 51%; d.r. >95:5); m.p. = 178 – 180 °C (CHCl₃); TLC: R_f = 0.61

(silica gel, *n*-hexane/EtOAc; 1:1); ¹H NMR (300 MHz, CDCl₃) δ 9.23 (t, *J* = 2.2 Hz, 1H), 9.13 (d, *J* = 2.1 Hz, 2H), 4.91 (dd, *J* = 11.8, 3.4 Hz, 1H), 4.60 (dd, *J* = 11.8, 5.7 Hz, 1H), 4.03 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.26 (dq, *J* = 14.0, 4.0 Hz, 1H), 2.17 – 2.01 (m, 1H), 1.95 – 1.82 (m, 2H), 1.70 (s, 1H), 1.62 (ddd, *J* = 13.4, 4.2, 1.0 Hz, 1H), 1.30 (s, 3H, CH₃), 1.25 (s, 3H, CH₃), 1.10 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 162.7, 148.9 (2x C), 134.0, 129.5 (2x C), 122.6, 71.90, 65.46, 65.12, 56.02, 43.73, 40.17, 32.20, 30.65, 24.04, 18.08 ppm; IR (film) $\tilde{\nu}_{\max}$ = 3555, 2934, 1717, 1515, 1341, 1280, 1104, 852, 720 cm⁻¹; HRMS (ESI) calcd. for C₁₈H₂₂BrN₂O₉⁻ [M+FA-H]⁻ 489.0514, found 489.0509.

(3-Bromo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl 3,5-difluorobenzoate (43e), prepared from **42e** (55.6 mg, 190 μmol) by GP-A; produced as a 71:29 mixture of separable diastereoisomes;

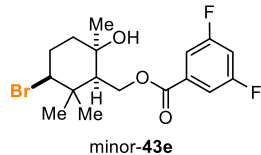


major diastereomer: colorless solid (29.4 mg, 75.2 μmol, 40%); m.p. = 88 – 89 °C

(DCM); TLC: R_f = 0.68 (silica gel, *n*-hexane/EtOAc; 1:1); ¹H NMR (300 MHz, CDCl₃) δ 7.55 – 7.46 (m, 2H), 7.02 (tt, *J* = 8.5, 2.4 Hz, 1H), 4.79 (dd, *J* = 11.9, 3.6 Hz, 1H),

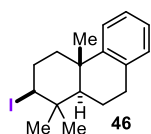
4.48 (dd, *J* = 11.9, 5.7 Hz, 1H), 4.00 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.22 (dq, *J* = 13.9, 4.0 Hz, 1H), 2.15 (br s, 1H), 2.06 (tdd, *J* = 13.8, 12.4, 3.6 Hz, 1H), 1.88 – 1.79 (m, 2H), 1.61 (tdd, *J* = 13.4, 4.3, 1.1 Hz, 1H), 1.28 (d, *J* = 0.9 Hz, 3H, CH₃), 1.23 (s, 3H, CH₃), 1.07 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 164.8 – 164.4 (m), 161.3 (d, *J* = 11.9 Hz, 2x C), 133.3 (t, *J* = 9.1 Hz), 113.0 – 112.5 (m), 108.8 (t, *J* = 25.2 Hz, 2x C), 71.84, 65.59, 64.46, 56.15, 43.47, 40.13, 32.20, 30.63, 23.99, 17.98 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -108.19 (s) ppm; IR (neat) $\tilde{\nu}_{\max}$ = 3491, 2961, 1703, 1595, 1442, 1329, 1236, 1123, 987, 974, 890, 862, 768, 661 cm⁻¹; HRMS (ESI) calcd. for C₁₈H₂₂BrF₂O₅⁻ [M+FA-H]⁻ 435.0624, found 435.0628.

Minor diastereomer: colorless solid [contained 16% of an impurity that could not be removed] (12.2 mg



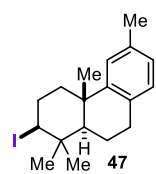
total, 10.5 mg of desired product alone, 26.8 μmol , 14%); **TLC**: $R_f = 0.79$ (silica gel, *n*-hexane/EtOAc; 1:1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.51 – 7.47 (m, 2H), 7.03 – 6.96 (m, 1H), 4.06 (ddd, $J = 11.6, 5.7, 2.4$ Hz, 2H), 3.94 (dt, $J = 11.4, 5.0$ Hz, 1H), 2.72 – 2.62 (m, 1H), 2.34 – 2.24 (m, 1H), 2.20 (t, $J = 4.1$ Hz, 1H), 2.15 – 1.96 (m, 2H), 1.67 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.06 (s, 3H, CH_3); **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 164.1 – 163.8 (m, 1C), 163.2 – 163.1 (m, 1C), 162.0 – 161.8 (m, 1C), 135.1 (t, $J = 8.9$ Hz, 1C), 112.8 – 112.5 (m, 1C), 108.7 – 108.1 (m, 2C), 87.06, 71.65, 67.08, 65.14, 61.44, 42.36, 40.42, 31.55, 31.02, 30.66, 30.04, 29.86, 20.68, 17.84 ppm; **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -108.5 (s, 2F) ppm; **IR** (film) $\tilde{\nu}_{\text{max}} = 3470, 1718, 1597, 1444, 1329, 1239, 1123, 989, 768$ cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{BrF}_2\text{O}_5^-$ [$\text{M}+\text{FA}-\text{H}$] $^-$ 435.0624, found 435.0628.

9. Physical and Spectroscopic Data of Iodocyclized Products



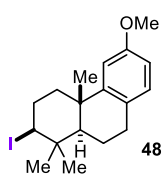
2-Iodo-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (46), prepared from **11** (26.6 mg, 117 μmol) by GP-A; colorless solid (32.1 mg, 90.6 μmol , 78%; d.r. >95:5); **TLC**: $R_f = 0.37$ (silica gel, *n*-hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.13 (ddd, $J = 7.7, 6.9, 1.9$ Hz, 1H), 7.11 – 7.07 (m, 1H), 7.07 – 7.03 (m, 1H), 4.29 (dd, $J = 12.9, 4.2$ Hz, 1H), 2.90 (ddd, $J = 10.6, 7.0, 1.8$ Hz, 2H), 2.58 (qd, $J = 13.4, 3.6$ Hz, 1H), 2.46 (dq, $J = 13.9, 3.9$ Hz, 1H), 2.18 (dt, $J = 13.3, 3.5$ Hz, 1H), 2.05 – 1.95 (m, 1H), 1.83 (dddd, $J = 13.2, 12.0, 10.5, 7.6$ Hz, 1H), 1.64 – 1.54 (m, 2H), 1.26 (d, $J = 0.7$ Hz, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.10 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.9, 134.8, 129.2, 126.0, 125.7, 124.6, 53.59, 50.03, 41.97, 39.69, 38.32, 34.53, 33.22, 31.03, 25.04, 21.82, 21.32 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[5]



2-Iodo-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (47), prepared from **18** (44.2 mg, 182 μmol) by GP-A; colorless crystals (59.9 mg, 163 μmol , 90%; d.r. >95:5); **TLC**: $R_f = 0.34$ (silica gel, *n*-hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.02 – 7.00 (m, 1H_r), 6.98 – 6.91 (m, 2H), 4.29 (dd, $J = 12.9, 4.2$ Hz, 1H), 2.92 – 2.83 (m, 2H), 2.59 (qd, $J = 13.4, 3.6$ Hz, 1H), 2.47 (dq, $J = 13.9, 3.9$ Hz, 1H), 2.31 (s, 3H, CH_3), 2.18 (dt, $J = 13.3, 3.5$ Hz, 1H), 2.01 (ddt, $J = 15.6, 5.5, 2.5$ Hz, 1H), 1.88 – 1.76 (m, 1H), 1.66 – 1.51 (m, 2H), 1.27 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.11 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.7, 135.3, 131.6, 129.1, 126.6, 125.1, 53.75, 50.16, 41.99, 39.69, 38.24, 34.56, 33.24, 30.65, 25.01, 21.89, 21.41, 21.33 ppm.

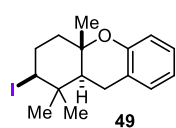
The spectroscopic data are in accordance to those reported in the literature.^[3]



2-Iodo-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (48), prepared from **19** (53.1 mg, 205 μmol) by GP-B; colorless solid (61.1 mg, 159 μmol , 77%; d.r. >95:5); **TLC**: $R_f = 0.65$ (silica gel, *n*-hexane/EtOAc; 9:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.98 (dd, $J = 8.3, 1.0$ Hz, 1H), 6.74 (d, $J = 2.6$ Hz, 1H), 6.69 (dd, $J = 8.3, 2.7$ Hz, 1H), 4.28 (dd,

$J = 12.7, 4.4 \text{ Hz}$, 1H), 3.78 (s, 3H), 2.89 – 2.78 (m, 2H), 2.57 (qd, $J = 13.3, 3.6 \text{ Hz}$, 1H), 2.45 (dq, $J = 13.9, 4.1 \text{ Hz}$, 1H), 2.13 (dt, $J = 13.3, 3.5 \text{ Hz}$, 1H), 2.00 (ddq, $J = 13.2, 5.6, 2.6 \text{ Hz}$, 1H), 1.81 (dddd, $J = 13.2, 11.9, 10.7, 7.4 \text{ Hz}$, 1H), 1.58 (qd, $J = 12.7, 12.0, 2.9 \text{ Hz}$, 2H), 1.26 (d, $J = 0.8 \text{ Hz}$, 3H, CH₃), 1.14 (s, 3H, CH₃), 1.10 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 157.9, 150.1, 130.0, 126.9, 111.2, 110.3, 55.38, 53.52, 50.00, 41.92, 39.65, 38.45, 34.48, 33.20, 30.19, 24.91, 21.92, 21.32 ppm.

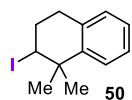
The spectroscopic data are in accordance to those reported in the literature.^[3]



2-Iodo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (49), prepared from **20**

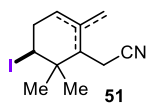
(53.1 mg, 205 μmol) by GP-B; colorless solid (61.1 mg, 159 μmol , 78%; d.r. >95:5); **TLC**: $R_f = 0.65$ (silica gel, *n*-hexane/EtOAc; 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.16 – 7.01 (m, 2H), 6.91 – 6.71 (m, 2H), 4.26 (dd, $J = 12.7, 4.0 \text{ Hz}$, 1H), 2.91 – 2.69 (m, 2H), 2.47 (dtd, $J = 14.0, 4.2, 3.4 \text{ Hz}$, 1H), 2.41 – 2.24 (m, 1H), 1.94 – 1.85 (m, 2H), 1.80 (ddd, $J = 13.4, 4.4, 1.0 \text{ Hz}$, 1H), 1.25 (d, $J = 0.9 \text{ Hz}$, 3H, CH₃), 1.15 (s, 3H, CH₃), 1.07 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 152.7, 129.6, 127.5, 122.0, 120.1, 117.2, 76.07, 49.64, 46.75, 42.59, 39.05, 34.37, 32.28, 25.69, 19.97, 19.82 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[6]



2-Iodo-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (50), prepared from **27** (23.1 mg,

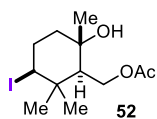
144 μmol) by GP-A; colorless to beige oil (30.3 mg, 106 μmol , 74%); **TLC**: $R_f = 0.51$ (silica gel, *n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.39 – 7.33 (m, 1H), 7.21 – 7.10 (m, 2H), 7.08 – 7.02 (m, 1H), 4.64 (dd, $J = 8.0, 4.8 \text{ Hz}$, 1H), 2.96 (ddd, $J = 7.4, 6.5, 1.0 \text{ Hz}$, 2H), 2.58 – 2.43 (m, 2H), 1.50 (s, 3H, CH₃), 1.48 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 133.9, 129.1, 127.2, 126.4, 126.2, 48.43, 39.36, 32.60, 32.37, 31.25 (2x C) ppm.; **MS** (EI, 70 eV): m/z (%) = 286 (1) [M]⁺, 159 (100) [M-I]⁺, 143 (19) [M-Me-I]⁺, 128 (28) [M-2xMe-I]⁺, 91 (9) [PhCH₂]⁺, 77 (4) [Ph]⁺; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 2967, 1489, 1446, 1218, 1194, 1143, 1042, 881, 757, 729 cm⁻¹; **HRMS** (EI) calcd. for C₁₂H₁₅I⁺ [M]⁺ 286.0213, found 286.0214.



2-(5-Iodo-2,6,6-trimethylcyclohexen-1-yl)acetonitrile (51), prepared from **28** (32.6 mg, 200 μmol) by GP-C, isolated as an 51:40:9 mixture of inseparable elimination products (di-, tri- and tetrasubstituted alkene); colorless oil (42.9 mg, 148 μmol , 74%); **TLC**: R_f = 0.38 (silica gel, *n*-hexane/EtOAc 9:1);

$^1\text{H NMR}$ (300 MHz, CDCl_3 ; *disubstituted isomer*) δ 5.06 (t, J = 1.3 Hz, 1H), 4.78 (s, 1H), 1.22 – 1.21 (m, 3H), 0.88 (s, 3H, CH_3) ppm; **$^1\text{H NMR}$** (300 MHz, CDCl_3 ; *trisubstituted isomer*) δ 5.32 (s, 1H), 4.37 – 4.27 (m, 2H), 2.72 (dd, J = 17.1, 4.7 Hz, 2H), 2.47 (dd, J = 22.2, 5.2 Hz, 3H), 1.80 (dq, J = 2.7, 1.4 Hz, 3H), 1.18 (s, 3H, CH_3), 1.04 (s, 3H, CH_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3 ; *tetrasubstituted isomer*) δ 4.41 (dd, J = 8.8, 4.8 Hz, 1H), 3.07 (q, J = 17.5 Hz, 4H), 1.74 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.23 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3 ; *trisubstituted isomer*) δ 132.7, 125.2, 119.5, 46.92, 45.41, 37.72, 34.16, 28.08, 21.64, 18.09, 18.05 ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3 ; *other isomers*) δ 143.7, 110.6, 48.13, 47.80, 44.73, 41.27, 38.57, 38.11, 38.05, 31.90, 31.18, 27.63, 20.01, 18.27, 17.49, 16.38 ppm.

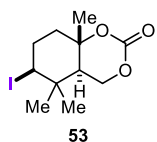
The spectroscopic data are in accordance to those reported in the literature.^[5]



6-Hydroxy-3-iodo-2,2,6-trimethylcyclohexyl)methyl acetate (52), prepared from **29** (38.6 mg, 197 μmol) by GP-C, colorless solid (32.0 mg, 94.0 μmol , 50%, d.r. >95:5); **TLC**: R_f = 0.50 (silica gel, *n*-hexane/EtOAc 1:1);

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.45 (dd, J = 11.9, 4.8 Hz, 1H), 4.30 (dd, J = 11.9, 5.1 Hz, 1H), 4.16 (dd, J = 12.8, 4.0 Hz, 1H), 2.53 (s, 1H), 2.36 (dq, J = 14.1, 4.0 Hz, 1H), 2.19 (ddd, J = 27.2, 13.4, 4.0 Hz, 1H), 2.05 (s, 3H, CH_3), 1.76 (t, J = 4.9 Hz, 1H), 1.66 (dt, J = 13.3, 3.7 Hz, 1H), 1.56 (dddd, J = 14.3, 13.3, 4.2, 1.0 Hz, 1H), 1.22 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 171.1, 72.04, 64.16, 54.37, 49.54, 44.98, 39.62, 34.92, 32.97, 23.84, 21.33, 20.54 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[5]

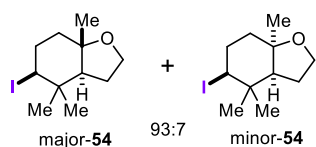


6-Iodo-5,5,8a-trimethylhexahydro-4H-benzo[d][1,3]dioxin-2-one (53), prepared from **31** (47.5 mg, 188 μmol) by GP-B and from **32** (50.6 mg, 199 μmol) by GP-A; colorless solid (43.6 mg, 135 μmol , 72%; d.r. >95:5 and 55.8 mg, 172 μmol , 87%; d.r. >95:5, respectively);

TLC: R_f = 0.68 (silica gel, *n*-hexane/EtOAc; 1:1); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 4.50 (dd, J = 10.8, 5.9 Hz, 1H),

4.40 (dd, $J = 12.5, 10.8$ Hz, 1H), 4.13 (dd, $J = 12.8, 4.0$ Hz, 1H, CHI), 2.46 (dtd, $J = 14.4, 4.2, 3.3$ Hz, 1H), 2.32 – 2.15 (m, 1H), 2.10 (dd, $J = 12.5, 5.8$ Hz, 1H), 1.90 – 1.69 (m, 2H), 1.51 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 1.00 (s, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 148.3, 80.97, 68.42, 45.64, 45.14, 41.17, 37.79, 33.78, 31.64, 20.88, 20.05 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[5]

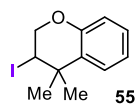


5-Iodo-4,4,7a-trimethyloctahydrobenzofuran (54), prepared from **33**

(30.7 mg, 182 μmol) by GP-A; colorless oil (35.3 mg, 120 μmol, 66%; d.r. = 93:7); TLC: $R_f = 0.21$ (silica gel, *n*-hexane/EtOAc; 19:1); major diastereomer:

¹H NMR (400 MHz, CDCl₃) δ 4.07 (dd, $J = 12.9, 4.4$ Hz, 1H), 3.94 – 3.78 (m, 2H), 2.40 (dtd, $J = 14.3, 4.4, 3.0$ Hz, 1H), 2.22 (dtd, $J = 14.3, 13.2, 4.0$ Hz, 1H), 2.00 – 1.81 (m, 2H), 1.72 (ddd, $J = 12.4, 4.0, 3.0$ Hz, 1H), 1.56 (dd, $J = 12.7, 7.2$ Hz, 1H), 1.49 (dddd, $J = 13.4, 12.5, 4.4, 1.0$ Hz, 1H), 1.12 (d, $J = 0.9$ Hz, 3H, CH₃), 1.03 (s, 3H, CH₃), 0.96 (s, 3H, CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 79.08, 64.75, 54.45, 49.06, 41.07, 38.86, 35.64, 32.64, 25.88, 20.13, 19.79 ppm.

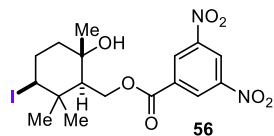
The spectroscopic data are in accordance to those reported in the literature.^[7]



3-Iodo-4,4-dimethylchromane (55), prepared from prenylphenyl ether (36.1 mg, 222 μmol)

by GP-B; slightly beige solid (38.2 mg, 133 μmol, 60%); m.p. = 47 – 48 °C (CHCl₃); TLC:

$R_f = 0.21$ (silica gel, *n*-hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dt, $J = 7.9, 1.6$ Hz, 1H, H_{ar}), 7.13 (ddd, $J = 8.2, 7.3, 1.6$ Hz, 1H, H_{ar}), 6.92 (ddd, $J = 7.8, 7.2, 1.3$ Hz, 1H, H_{ar}), 6.79 (dd, $J = 8.2, 1.3$ Hz, 1H, H_{ar}), 4.56 (dd, $J = 10.7, 3.6$ Hz, 1H, CHI), 4.49 (dd, $J = 11.2, 3.7$ Hz, 1H), 4.39 (d, $J = 11.3, 10.7$ Hz, 1H), 1.47 (s, 3H, CH₃), 1.43 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 128.0, 127.6, 127.6, 121.3, 117.0, 69.11, 40.64, 36.34, 31.81, 29.57 ppm; MS (EI, 70 eV): m/z (%) = 286 (1) [M]⁺, 159 (100) [M-I]⁺, 143 (19) [M-Me-I]⁺, 128 (28) [M-2×Me-I]⁺, 91 (9) [PhCH₂]⁺, 77 (4) [Ph]⁺; IR (film) $\tilde{\nu}_{max} = 2968, 1488, 1446, 1284, 1221, 1042, 1011, 797, 755, 722$ cm⁻¹; HRMS (EI) calcd. for C₁₁H₁₃IO⁺ [M]⁺ 288.0006, found 287.9961.

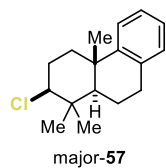


(3-Iodo-6-hydroxy-2,2,6-trimethylcyclohexyl)methyl 3,5-dinitrobenzoate (56),

prepared from **42d** (68.4 mg, 196 μmol) by GP-A; faint yellow crystals (66.1 mg,

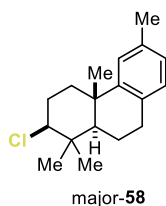
135 μmol , 69%; d.r. >95:5); **m.p.** = 122 – 123 $^{\circ}\text{C}$ (EtOAc, *n*-hexane); **TLC**: R_f = 0.70 (silica gel, *n*-hexane/EtOAc; 1:1); **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 9.22 (dt, J = 3.3, 2.1 Hz, 1H, H_{ar}), 9.11 (dd, J = 3.1, 2.0 Hz, 2H, H_{ar}), 4.93 (ddd, J = 11.8, 3.2, 1.6 Hz, 1H), 4.59 (ddd, J = 11.8, 5.8, 1.3 Hz, 1H), 4.21 (dd, J = 12.7, 4.0 Hz, 1H, CHI), 2.49 – 2.36 (m, 1H), 2.35 – 2.15 (m, 1H), 1.97 (dd, J = 5.8, 3.2 Hz, 1H), 1.81 (br s, 1H), 1.77 – 1.68 (m, 1H), 1.62 (td, J = 13.3, 4.4 Hz, 1H), 1.30 (s, 3H), 1.21 (s, 3H, CH_3), 1.11 (s, 3H, CH_3) ppm; **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 162.7, 148.8 (2x C), 134.0, 129.5 (2xC), 122.6, 72.07, 66.02, 54.66, 48.29, 45.55, 39.85, 34.94, 33.18, 23.90, 20.69 ppm; **IR** (neat) $\tilde{\nu}_{\text{max}}$ = 3574, 3100, 1723, 1541, 1344, 1269, 1164, 920, 719 cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_9^-$ [$\text{M}+\text{FA}-\text{H}$] $^-$ 537.0375, found 537.0373.

10. Physical and Spectroscopic Data of Chlorocyclized Products

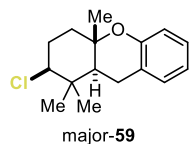


2-Chloro-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (57), prepared from **11** (33.2 mg, 146 μmol) by GP-E; produced as a 76:24 mixture of separable diastereomes; *major diastereomer*: colorless solid (12.4 mg, 47.2 μmol , 32%); **TLC**: R_f = 0.38 (silica gel, *n*-hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.24 – 7.18 (m, 1H), 7.16 – 7.02 (m, 3H), 3.81 (dd, J = 11.5, 5.3 Hz, 1H), 2.36 (dt, J = 13.1, 3.6 Hz, 1H), 2.22 – 2.08 (m, 2H), 1.99 – 1.90 (m, 1H), 1.84 – 1.74 (m, 1H), 1.58 (d, J = 5.8 Hz, 3H), 1.42 (dd, J = 12.0, 2.4 Hz, 1H), 1.23 (d, J = 0.7 Hz, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 148.9, 134.9, 129.2, 126.0, 125.7, 124.6, 72.80, 51.42, 40.10, 38.87, 37.87, 30.84, 30.36, 29.37, 25.03, 20.06, 16.88 ppm.

The spectroscopic data are in accordance to those reported in the literature.^[5]

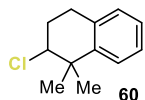


2-Chloro-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (58), prepared from **18** (34.1 mg, 141 μmol) by GP-E; produced as a 76:24 mixture of separable diastereoisomes; *major diastereomer*: colorless solid (11.8 mg, 42.6 μmol , 30%); **TLC**: R_f = 0.28 (silica gel, *n*-hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.15 – 6.95 (m, 2H), 6.92 (dd, J = 10.2, 8.5 Hz, 2H), 3.80 (dd, J = 12.2, 4.6 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.83 (ddd, J = 17.5, 11.6, 7.2 Hz, 1H), 2.35 (dt, J = 13.3, 3.5 Hz, 1H), 2.29 (s, 3H, CH_3), 2.22 – 2.14 (m, 1H), 2.14 – 2.06 (m, 1H), 1.93 (ddt, J = 13.3, 7.3, 2.1 Hz, 1H), 1.78 (dtd, J = 13.3, 11.8, 6.6 Hz, 1H), 1.57 (td, J = 13.3, 3.9 Hz, 1H), 1.40 (dd, J = 12.1, 2.2 Hz, 1H), 1.23 (d, J = 0.8 Hz, 3H), 1.14 (s, 3H), 1.01 (s, 3H) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 148.8, 135.3, 131.8, 129.1, 126.6, 125.1, 72.89, 51.58, 40.12, 38.93, 37.82, 30.47, 30.40, 29.40, 25.01, 21.42, 20.16, 16.89 ppm; **MS** (EI, 70 eV): m/z (%) = 278/276 (8/25) $[\text{M}]^+$, 263/261 (13/31) $[\text{M-Me}]^+$, 240 (33) $[\text{M-HCl}]^+$, 225 (100) $[\text{M-Me-HCl}]^+$, 210 (3) $[\text{M-2Me-HCl}]^+$, 77 (6) $[\text{Ph}]^+$; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 2946, 1501, 1454, 1377, 1269, 1180, 970, 880, 870, 807, 767, 728 cm^{-1} ; **HRMS** (EI) calcd. for $\text{C}_{18}\text{H}_{25}\text{Cl}^+$ $[\text{M}]^+$ 276.1639, found 276.1634.



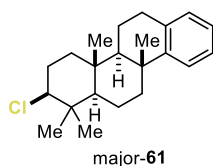
2-Chloro-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (59), prepared from **20** (23.2 mg, 101 μmol) by GP-E; colorless oil (12.1 mg, 45.7 μmol , 45%; d.r. = 82:18);

TLC: R_f = 0.53 (silica gel, *n*-hexane/EtOAc; 19:1); *major diastereomer*: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.11 – 7.03 (m, 2H), 6.84 (td, J = 7.4, 1.2 Hz, 1H), 6.76 (dd, J = 8.1, 1.2 Hz, 1H), 3.85 (dd, J = 12.3, 4.0 Hz, 1H, CHCl), 2.85 – 2.67 (m, 2H), 2.19 – 2.08 (m, 1H), 2.08 – 2.00 (m, 1H), 1.99 – 1.91 (m, 1H), 1.79 – 1.74 (m, 2H), 1.24 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 152.9, 129.7, 127.5, 121.8, 120.2, 117.2, 75.88, 70.86, 48.44, 39.66, 39.48, 30.50, 28.49, 24.14, 20.01, 15.63 ppm; **MS** (EI, 70 eV): m/z (%) = 266/264 (9/27) $[\text{M}]^+$, 228 (20) $[\text{M}-\text{HCl}]^+$, 159 (17) $[\text{M}-\text{CH}_2\text{C}_6\text{H}_4\text{OH}]^+$, 107 (100) $[\text{CH}_2\text{C}_6\text{H}_4\text{OH}]^+$, 91 (21) $[\text{PhCH}_2]^+$, 77 (21) $[\text{Ph}]^+$; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 2927, 2357, 1584, 1488, 1455, 1239, 913, 754 cm^{-1} ; **HRMS** (EI) calcd. for $\text{C}_{16}\text{H}_{21}\text{ClO}^+ [\text{M}]^+$ 264.1275, found 264.1256.



2-Chloro-1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (60), prepared from **27** (26.0 mg, 162 μmol) by GP-E; colorless oil (16.0 mg, 82.2 μmol , 51%); **TLC:** R_f = 0.45 (silica gel, *n*-hexane);

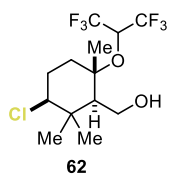
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.35 (dd, J = 7.8, 1.6 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.13 (td, J = 7.3, 1.6 Hz, 1H), 7.09 – 7.03 (m, 1H), 4.23 (dd, J = 9.2, 3.3 Hz, 1H), 3.05 (dt, J = 17.2, 6.0 Hz, 1H), 2.98 – 2.83 (m, 1H), 2.40 – 2.15 (m, 2H), 1.44 (s, 3H, CH_3), 1.40 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.6, 133.9, 129.0, 126.9, 126.4, 126.1, 69.38, 39.97, 29.86, 28.99, 28.35, 27.01 ppm; **MS** (EI, 70 eV): m/z (%) = 196/194 (6/19) $[\text{M}]^+$, 181/179 (27/9) $[\text{M}-\text{CH}_3]^+$, 158 (19) $[\text{M}-\text{HCl}]^+$, 143 (100) $[\text{M}-\text{Me}-\text{HCl}]^+$, 128 (44) $[\text{M}-2\text{Me}-\text{HCl}]^+$; **IR** (film) $\tilde{\nu}_{\text{max}}$ = 1490, 1364, 1044, 890, 761 cm^{-1} ; **HRMS** (EI) calcd. for $\text{C}_{12}\text{H}_{15}\text{Cl} [\text{M}]^+$ 194.0857, found 194.0856.



2-Chloro-1,1,4a,10b-tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysene (61), prepared from **21** (53.4 mg, 180 μmol) by GP-E. After 30 min, the mixture was diluted with 2.00 mL *i*PrNO₂ and cooled to -25 $^{\circ}\text{C}$. 120 μL ClSO_3H (1.80

mmol, 10.0 eq) was added and stirred for 40 min at that temperature before the reaction was terminated; produced as a 85:15 mixture of separable diastereomes; *major diastereomer*: colorless semisolid (17.6 mg, 53.2 μmol , 30%); **TLC:** R_f = 0.24 (silica gel, *n*-hexane); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.24 (d, J = 7.9 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.07 (td, J = 7.3, 1.3 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 3.75 (dd, J = 12.4, 4.5 Hz, 1H), 2.94 (ddd, J = 17.1, 6.6, 1.8 Hz, 1H), 2.82 (ddd, J = 17.5, 11.5, 7.3 Hz, 1H),

2.42 (dt, $J = 12.7, 3.3$ Hz, 1H), 2.06 (qd, $J = 13.3, 3.8$ Hz, 1H), 1.96 (dq, $J = 13.7, 3.9$ Hz, 1H), 1.89 (dt, $J = 13.2, 3.7$ Hz, 1H), 1.84 – 1.75 (m, 2H), 1.75 – 1.60 (m, 2H), 1.56 – 1.47 (m, 1H), 1.30 – 1.26 (m, 1H), 1.20 (s, 3H), 1.07 (s, 3H), 1.06 – 1.01 (m, 1H), 0.97 (s, 3H), 0.96 – 0.92 (m, 1H), 0.94 (s, 3H) ppm; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.9, 135.0, 129.0, 125.9, 125.4, 124.7, 73.38, 56.81, 55.14, 40.66, 40.20, 39.96, 38.01, 37.65, 30.85, 29.72, 29.26, 26.17, 20.05, 18.21, 16.76, 16.42 ppm; **IR** (film) $\tilde{\nu}_{\text{max}} = 2944, 1451, 1379, 1175, 876, 760, 723$ cm^{-1} ; **HRMS** (EI) calcd. for $\text{C}_{22}\text{H}_{31}\text{Cl}^+ [\text{M}]^+$ 330.2109, found 330.2100.



(3-Chloro-6-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2,2,6-trimethylcyclohexyl) methanol (62), prepared from **34** (28.9 mg, 187 μmol) by GP-E; colorless crystalline solid (12.2 mg, 34.2 μmol , 18%, d.r. >95:5); **m.p.** = 100 – 101 $^\circ\text{C}$ (EtOAc); **TLC**: $R_f = 0.63$ (silica gel, *n*-hexane/EtOAc 4:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.35 (hept, $J = 5.7$ Hz, 1H), 3.98

(ddd, $J = 12.1, 6.3, 1.4$ Hz, 1H), 3.83 – 3.73 (m, 2H), 2.22 (br d, $J = 9.0$ Hz, 1H), 2.18 – 2.10 (m, 1H), 1.89 – 1.69 (m, 4H), 1.38 (t, $J = 1.1$ Hz, 3H, CH_3), 1.28 (s, 3H, CH_3), 0.90 (s, 3H, CH_3) ppm; $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 124.8 – 118.1 (m, 2C), 85.64, 69.64, 68.57 (hept, $J = 32.3$ Hz) 61.13, 58.50, 40.13, 37.33, 30.38, 29.38, 19.18 (t, $J = 2.6$ Hz), 16.96 ppm; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -72.61 – -72.88 (m, 2x CF_3) ppm; **IR** (film) $\tilde{\nu}_{\text{max}} = 3541, 2964, 1397, 1276, 1229, 1187, 1102, 909, 687$ cm^{-1} ; **HRMS** (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{ClF}_6\text{O}_4^- [\text{M}+\text{FA}-\text{H}]^-$ 401.0960, found 401.0957.

11. X-Ray Crystal Structure Analysis of Compound 16 (CCDC 1584440)

A suitable crystal of compound **16** was obtained by letting a clean sample stand for 1 week in a screw capped vial at ambient conditions. Crystals collected at the top of the vial via sublimation. A clear colourless fragment-like specimen of $C_{10}H_{13}F_{12}NO_3$, approximate dimensions 0.170 mm x 0.356 mm x 0.476 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Kappa-Apex II system equipped with a Triumph optic monochromator and a Mo fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$).

A total of 2304 frames were collected. The total exposure time was 3.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 16008 reflections to a maximum θ angle of 25.01° (0.84 \AA resolution), of which 2795 were independent (average redundancy 5.727, completeness = 99.9%, $R_{\text{int}} = 2.54\%$, $R_{\text{sig}} = 1.63\%$) and 2561 (91.63%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 9.5076(11) \text{ \AA}$, $b = 9.6913(11) \text{ \AA}$, $c = 9.7530(11) \text{ \AA}$, $\alpha = 103.771(5)^\circ$, $\beta = 91.642(5)^\circ$, $\gamma = 113.628(4)^\circ$ volume = $791.84(16) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 92 reflections above $20 \sigma(I)$ with $10.67^\circ < 2\theta < 58.82^\circ$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9040 and 0.9640.

The final anisotropic full-matrix least-squares refinement on F^2 with 248 variables converged at $R1 = 2.42\%$, for the observed data and $wR2 = 6.30\%$ for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was $0.270 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.277 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.039 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.775 g/cm^3 and $F(000)$, 424 e^- .

Table S7. Sample and crystal data for compound **16** (CCDC 1584440).

Chemical formula	C ₁₀ H ₁₃ F ₁₂ NO ₃	
Formula weight	423.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.170 x 0.356 x 0.476 mm	
Crystal habit	clear colourless fragment	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5076(11) Å	α = 103.771(5)°
	b = 9.6913(11) Å	β = 91.642(5)°
	c = 9.7530(11) Å	γ = 113.628(4)°
Volume	791.84(16) Å ³	
Z	2	
Density (calculated)	1.775 g/cm ³	
Absorption coefficient	0.217 mm ⁻¹	
F(000)	424	

Table S8. Data collection and structure refinement for compound **16** (CCDC 1584440).

Diffractometer	Bruker D8 Kappa-Apex II
Theta range for data collection	2.17 to 25.01°
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected	16008
Independent reflections	2795 [R(int) = 0.0254]
Coverage of independent reflections	99.9%
Absorption correction	multi-Scan
Max. and min. transmission	0.9640 and 0.9040
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2795 / 0 / 248
Goodness-of-fit on F²	1.063
Δ/σ_{\max}	0.001
Final R indices	2561 data; $l > 2\sigma(l)$ R1 = 0.0242, wR2 = 0.0613 all data R1 = 0.0267, wR2 = 0.0630
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.2313P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.270 and -0.277 eÅ ⁻³
R.M.S. deviation from mean	0.039 eÅ ⁻³

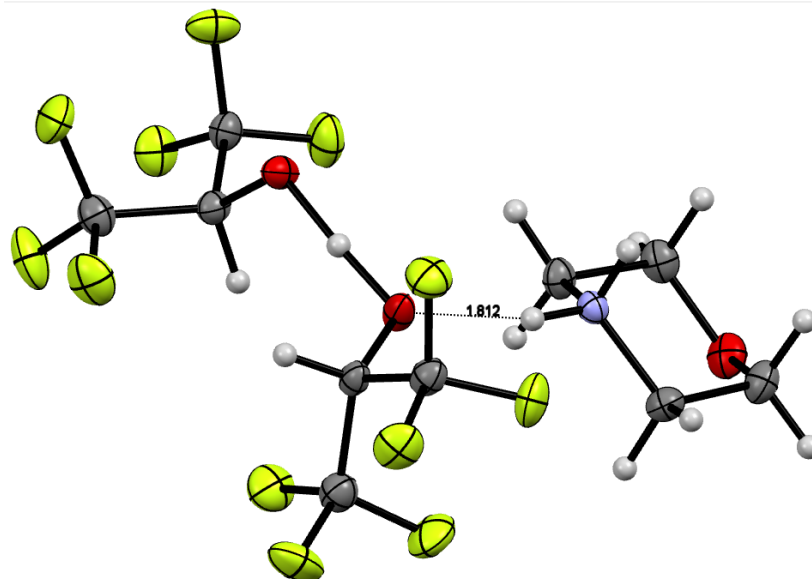


Figure S8. Crystal structure of **16** (CCDC 1584440).

12. X-Ray Crystal Structure Analysis of Compound 41 (CCDC 1571223)

A suitable crystal of compound **41** was grown by vapor-diffusion method using EtOAc/Et₂O. A clear colourless block-like specimen of C₁₃H₁₉BrF₆O₂, approximate dimensions 0.135 mm x 0.155 mm x 0.369 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Kappa-Apex II system equipped with a Triumph optic monochromator.

A total of 2917 frames were collected. The total exposure time was 16.21 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38407 reflections to a maximum θ angle of 25.02° (0.84 Å resolution), of which 2729 were independent (average redundancy 14.074, completeness = 100.0%, $R_{\text{int}} = 3.71\%$, $R_{\text{sig}} = 2.09\%$) and 2396 (87.80%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 7.071(2)$ Å, $\underline{b} = 21.450(8)$ Å, $\underline{c} = 10.258(3)$ Å, $\beta = 95.885(15)^\circ$, volume = 1547.7(9) Å³, are based upon the refinement of the XYZ-centroids of 99 reflections above $20 \sigma(I)$ with $6.622^\circ < 2\theta < 46.88^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.828. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4330 and 0.7100.

The final anisotropic full-matrix least-squares refinement on F^2 with 205 variables converged at $R1 = 4.40\%$, for the observed data and $wR2 = 11.85\%$ for all data. The goodness-of-fit was 1.087. The largest peak in the final difference electron density synthesis was 1.389 e⁻/Å³ and the largest hole was -0.554 e⁻/Å³ with an RMS deviation of 0.105 e⁻/Å³. On the basis of the final model, the calculated density was 1.722 g/cm³ and $F(000)$, 808 e⁻.

Table S9. Sample and crystal data for compound **41** (CCDC 1571223).

Chemical formula	C ₁₃ H ₁₉ BrF ₆ O ₂	
Formula weight	401.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.135 x 0.155 x 0.369 mm	
Crystal habit	clear colourless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 7.071(2) Å	α = 90°
	b = 21.450(8) Å	β = 95.885(15)°
	c = 10.258(3) Å	γ = 90°
Volume	1547.7(9) Å ³	
Z	4	
Density (calculated)	1.722 g/cm ³	
Absorption coefficient	2.723 mm ⁻¹	
F(000)	808	

Table S10. Data collection and structure refinement for compound **41** (CCDC 1571223).

Diffractometer	Bruker D8 Kappa-Apex II
Theta range for data collection	2.21 to 25.02°
Index ranges	-8 ≤ h ≤ 8, -25 ≤ k ≤ 25, -12 ≤ l ≤ 12
Reflections collected	38407
Independent reflections	2729 [R(int) = 0.0371]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7100 and 0.4330
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2729 / 1 / 205
Goodness-of-fit on F²	1.087
Δ/σ_{\max}	0.001
Final R indices	2396 data; $l > 2\sigma(l)$ R1 = 0.0440, wR2 = 0.1157 all data R1 = 0.0495, wR2 = 0.1185
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 1.7780P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.389 and -0.554 eÅ ⁻³
R.M.S. deviation from mean	0.105 eÅ ⁻³

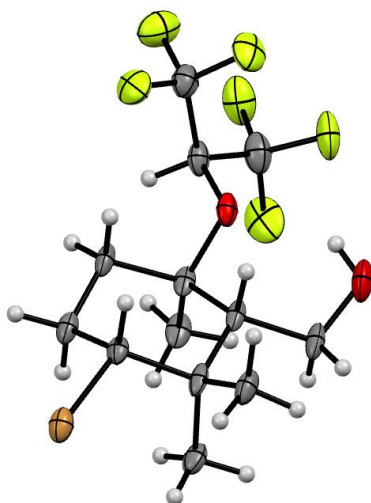


Figure S9. Crystal structure of **41** (CCDC 1571223).

13. X-ray Crystal Analysis of Compound 56 (CCDC 1584439)

A suitable crystal of compound **56** was grown by vapor-diffusion method using EtOAc/Et₂O. A clear colourless block-like specimen of C₁₇H₂₁IN₂O₇, approximate dimensions 0.063 mm x 0.138 mm x 0.158 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture TXS system equipped with a Helios optic monochromator and a Mo TXS rotating anode ($\lambda = 0.71073 \text{ \AA}$)

A total of 286 frames were collected. The total exposure time was 4.77 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33831 reflections to a maximum θ angle of 25.40° (0.83 Å resolution), of which 3593 were independent (average redundancy 9.416, completeness = 99.8%, $R_{\text{int}} = 7.30\%$, $R_{\text{sig}} = 3.21\%$) and 2572 (71.58%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 18.1478(7) \text{ \AA}$, $\underline{b} = 6.6216(3) \text{ \AA}$, $\underline{c} = 17.9704(7) \text{ \AA}$, $\beta = 114.684(2)^\circ$, volume = 1962.14(14) Å³, are based upon the refinement of the XYZ-centroids of 246 reflections above $20 \sigma(I)$ with $4.880^\circ < 2\theta < 38.63^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.848. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7780 and 0.9020.

The final anisotropic full-matrix least-squares refinement on F^2 with 250 variables converged at $R1 = 5.59\%$, for the observed data and $wR2 = 13.48\%$ for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was $0.971 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-1.128 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.087 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.666 g/cm^3 and $F(000)$, 984 e⁻.

Table S11. Sample and crystal data for compound **56** (CCDC 1584439).

Chemical formula	C ₁₇ H ₂₁ IN ₂ O ₇	
Formula weight	492.26	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.063 x 0.138 x 0.158 mm	
Crystal habit	clear colourless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 18.1478(7) Å	α = 90°
	b = 6.6216(3) Å	β = 114.684(2)°
	c = 17.9704(7) Å	γ = 90°
Volume	1962.14(14) Å ³	
Z	4	
Density (calculated)	1.666 g/cm ³	
Absorption coefficient	1.673 mm ⁻¹	
F(000)	984	

Table S12. Data collection and structure refinement for compound **56** (CCDC 1571223).

Diffractometer	Bruker D8 Venture TXS
Theta range for data collection	2.27 to 25.40°
Index ranges	-21 ≤ h ≤ 21, -7 ≤ k ≤ 7, -21 ≤ l ≤ 21
Reflections collected	33831
Independent reflections	3593 [R(int) = 0.0730]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9020 and 0.7780
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3593 / 2 / 250
Goodness-of-fit on F²	1.026
Δ/σ_{\max}	0.001
Final R indices	2572 data; $l > 2\sigma(l)$ R1 = 0.0559, wR2 = 0.1195 all data R1 = 0.0849, wR2 = 0.1348
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0401)^2 + 8.9023P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.971 and -1.128 eÅ ⁻³
R.M.S. deviation from mean	0.087 eÅ ⁻³

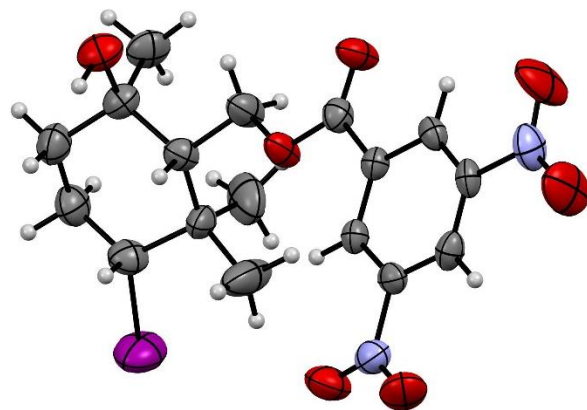
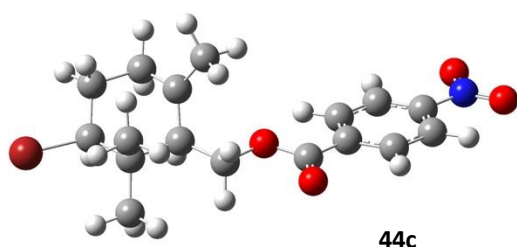


Figure S10. Crystal structure of **56** (CCDC 1584439).

14. Computational Details

All calculations have been performed with the software package Gaussian 09.E.03.^[8] The level of theory consisted of the hybrid density functional B3LYP^[9-12] and the basis set 6-311+G**.^[13-14] All energy values reported are free energies (ΔG) taken from a frequency calculation after optimization of the relevant structure in gas-phase. The number of imaginary frequencies were used to determine an intermediate or ground state (NIMag=0) from a transition state (NIMag=1). In the following section, you find all optimized structures with graphical representation and absolute energies.

a) Starting cationic compounds **44** and water



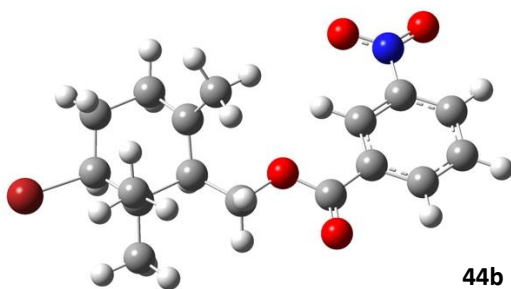
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2	6	0	2.087219	-2.202168	0.510732
3	6	0	1.392593	-0.959303	0.845528
4	6	0	1.461368	0.111340	-0.147556
5	6	0	3.040472	0.628114	-0.130116
6	6	0	3.862927	-0.644529	-0.462992
7	1	0	1.816960	-2.546906	-0.491076
8	1	0	1.923950	-2.996662	1.238238
9	1	0	3.974125	-1.592196	1.487398
10	1	0	4.159528	-2.706801	0.140901
11	1	0	1.358500	-0.331392	-1.143372
12	1	0	3.652656	-0.940515	-1.491563
13	35	0	5.815766	-0.293348	-0.482838
14	6	0	3.408396	1.260670	1.219573
15	1	0	4.418089	1.668578	1.160990
16	1	0	2.741720	2.090233	1.460627
17	1	0	3.391417	0.557165	2.054898
18	6	0	3.175049	1.665925	-1.253087
19	1	0	2.827412	1.280445	-2.214810
20	1	0	2.635819	2.585849	-1.026175
21	1	0	4.230731	1.927058	-1.356384
22	6	0	0.781491	-0.798955	2.164956
23	1	0	1.240195	-1.438805	2.921220
24	1	0	0.687295	0.233396	2.498455
25	1	0	-0.251843	-1.172962	2.029717

26	6	0	0.442182	1.236115	0.005975
27	1	0	0.545991	1.793198	0.937837
28	1	0	0.530233	1.947419	-0.814162
29	8	0	-0.852959	0.609281	-0.045375
30	6	0	-1.912069	1.475800	0.114287
31	8	0	-1.735620	2.643762	0.343001
32	6	0	-3.231912	0.806972	-0.013052
33	6	0	-3.365075	-0.524696	-0.427383
34	6	0	-4.369338	1.567292	0.287716
35	6	0	-4.625787	-1.098138	-0.534221
36	1	0	-2.489167	-1.106138	-0.681052
37	6	0	-5.633560	1.000845	0.188279
38	1	0	-4.250971	2.597877	0.596787
39	6	0	-5.736603	-0.324302	-0.218820
40	1	0	-4.761835	-2.120977	-0.857166
41	1	0	-6.527941	1.563706	0.417558
42	7	0	-7.088295	-0.940784	-0.325714
43	8	0	-8.046025	-0.237101	-0.049218
44	8	0	-7.141911	-2.108774	-0.680432

HF= -3590.1601101 / NImag=0

Sum of electronic and thermal Enthalpies= -3589.780697

Sum of electronic and thermal Free Energies= -3589.860782



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			X	Y	Z
1	6	0	-3.163423	1.813690	0.376101
2	6	0	-1.599262	2.080639	0.394015
3	6	0	-1.000969	0.816376	0.822847
4	6	0	-1.156190	-0.316315	-0.090719
5	6	0	-2.766060	-0.706853	-0.042758
6	6	0	-3.487201	0.596251	-0.477429
7	1	0	-1.298644	2.329122	-0.627738
8	1	0	-1.375405	2.911548	1.062251
9	1	0	-3.529367	1.690458	1.396319
10	1	0	-3.625465	2.714250	-0.029444
11	1	0	-1.018656	0.046825	-1.114306
12	1	0	-3.252823	0.797179	-1.523622
13	35	0	-5.461428	0.393799	-0.486621
14	6	0	-3.181840	-1.201481	1.350260

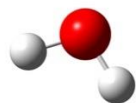
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17	1	0	-3.107658	-0.438957	2.128863
18	6	0	-2.980679	-1.816175	-1.081881
19	1	0	-2.604683	-1.534462	-2.068569
20	1	0	-2.511679	-2.753225	-0.780715
21	1	0	-4.052887	-2.004807	-1.170925
22	6	0	-0.399419	0.711395	2.151773
23	1	0	-0.829890	1.421651	2.861119
24	1	0	-0.354061	-0.299504	2.553027
25	1	0	0.648582	1.034380	1.999270
26	6	0	-0.218664	-1.499548	0.136135
27	1	0	-0.366894	-1.998505	1.095630
28	1	0	-0.345020	-2.245214	-0.647097
29	8	0	1.111341	-0.955471	0.072164
30	6	0	2.127144	-1.883644	0.052837
31	8	0	1.906734	-3.064026	0.119448
32	6	0	3.465421	-1.250197	-0.051340
33	6	0	4.597546	-2.076803	-0.045712
34	6	0	3.614444	0.133306	-0.154316
35	1	0	4.464908	-3.148708	0.032742
36	6	0	4.892496	0.661929	-0.242586
37	1	0	2.765539	0.798106	-0.174304
38	6	0	6.029285	-0.139634	-0.242405
39	1	0	7.007400	0.316322	-0.318053
40	7	0	5.035577	2.135755	-0.337183
41	8	0	4.009771	2.804840	-0.263675
42	8	0	6.159228	2.585915	-0.477176
43	6	0	5.869365	-1.520684	-0.142582
44	1	0	6.741763	-2.162048	-0.139766

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Sum of electronic and thermal Free Energies= -3589.864445

Water



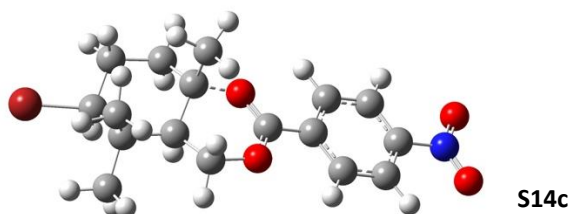
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3	1	0	-0.000000	-0.764045	-0.467984

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Sum of electronic and thermal Free Energies= -76.454836

b) Ester stabilized cations **S14**



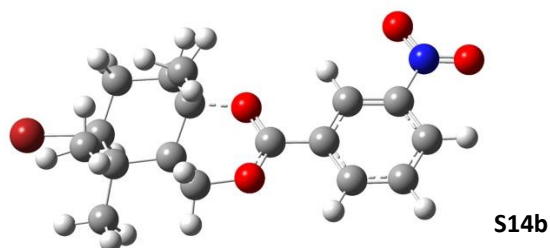
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3	6	0	-0.865133	0.581927	0.802703
4	6	0	-1.339475	-0.661305	0.031342
5	6	0	-2.899242	-0.881517	-0.024453
6	6	0	-3.457333	0.459895	-0.588703
7	1	0	-1.097409	1.960615	-0.820937
8	1	0	-1.177812	2.720371	0.767143
9	1	0	-3.423782	1.714010	1.178873
10	1	0	-3.422797	2.595482	-0.327252
11	1	0	-1.049145	-0.474710	-1.011292
12	1	0	-3.155955	0.542095	-1.634797
13	35	0	-5.441879	0.467962	-0.705044
14	6	0	-3.521055	-1.264141	1.332239
15	1	0	-4.560446	-1.556160	1.183585
16	1	0	-3.009489	-2.119791	1.780461
17	1	0	-3.522151	-0.451532	2.057657
18	6	0	-3.179750	-2.018334	-1.030070
19	1	0	-2.681631	-1.846446	-1.989132
20	1	0	-2.860044	-2.988955	-0.643373
21	1	0	-4.250763	-2.089159	-1.220597
22	6	0	-0.908923	0.567279	2.326480
23	1	0	-1.931202	0.691557	2.677888
24	1	0	-0.513843	-0.352629	2.760751
25	1	0	-0.323437	1.405202	2.709182
26	6	0	-0.539342	-1.866654	0.486221
27	1	0	-0.716141	-2.162776	1.518684
28	1	0	-0.652215	-2.729966	-0.163334
29	8	0	0.911955	-1.568272	0.406306
30	6	0	1.369190	-0.361203	0.356205
31	8	0	0.637528	0.684166	0.479561
32	6	0	2.802508	-0.191181	0.140884
33	6	0	3.619473	-1.319318	-0.049859
34	6	0	3.352998	1.102301	0.123336
35	6	0	4.980513	-1.154772	-0.259012
36	1	0	3.191695	-2.312579	-0.035359
37	6	0	4.713777	1.267635	-0.086189
38	1	0	2.720096	1.966735	0.271891
39	6	0	5.498998	0.135380	-0.273743
40	1	0	5.638521	-1.999435	-0.410685

41	1	0	5.171260	2.247296	-0.105713
42	7	0	6.966326	0.313230	-0.500966
43	8	0	7.391150	1.455706	-0.488547
44	8	0	7.622236	-0.698162	-0.681259

HF= -3590.1909292 / NImag=0

Sum of electronic and thermal Enthalpies= -3589.808349

Sum of electronic and thermal Free Energies= -3589.882918



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.600881	-1.735635	0.232173
2	6	0	1.061604	-1.672765	0.194591
3	6	0	0.583324	-0.336800	0.744554
4	6	0	1.235960	0.817930	-0.033839
5	6	0	2.812513	0.846891	-0.022371
6	6	0	3.226667	-0.566771	-0.530502
7	1	0	0.713922	-1.776191	-0.837713
8	1	0	0.632447	-2.497698	0.767776
9	1	0	2.963516	-1.755517	1.262547
10	1	0	2.922258	-2.674350	-0.220694
11	1	0	0.970705	0.636283	-1.083897
12	1	0	2.962135	-0.641318	-1.586992
13	35	0	5.199055	-0.817262	-0.556732
14	6	0	3.417468	1.188797	1.352549
15	1	0	4.488672	1.357105	1.243801
16	1	0	2.989287	2.107402	1.761887
17	1	0	3.295165	0.398910	2.092374
18	6	0	3.270911	1.913161	-1.039770
19	1	0	2.795133	1.775595	-2.015712
20	1	0	3.055823	2.925596	-0.689567
21	1	0	4.349609	1.848514	-1.183906
22	6	0	0.567733	-0.286938	2.268341
23	1	0	1.547321	-0.541813	2.667756
24	1	0	0.286084	0.689607	2.665950
25	1	0	-0.142485	-1.026676	2.642296
26	6	0	0.568508	2.124129	0.352940
27	1	0	0.739947	2.432026	1.382824
28	1	0	0.808872	2.945645	-0.315897
29	8	0	-0.905186	2.000389	0.222644
30	6	0	-1.502294	0.855123	0.191225
31	8	0	-0.905688	-0.266160	0.361530

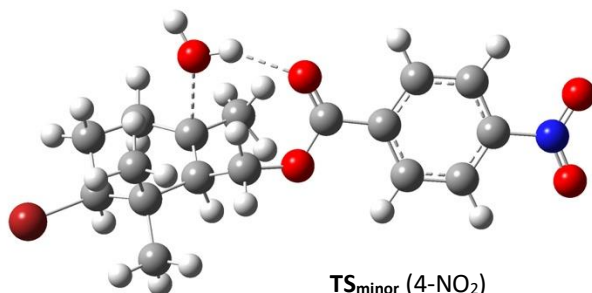
32	6	0	-2.938910	0.847236	-0.054978
33	6	0	-3.624823	2.046203	-0.323500
34	6	0	-3.629529	-0.373071	-0.013618
35	1	0	-3.085492	2.983751	-0.353013
36	6	0	-4.992164	-0.360044	-0.243543
37	1	0	-3.129475	-1.308867	0.191868
38	6	0	-5.691161	0.813258	-0.511839
39	1	0	-6.758797	0.767836	-0.683907
40	7	0	-5.731684	-1.653142	-0.195497
41	8	0	-5.077517	-2.655675	0.045510
42	8	0	-6.931664	-1.611184	-0.399907
43	6	0	-4.994064	2.021013	-0.551156
44	1	0	-5.525069	2.941091	-0.759430

HF= HF=-3590.193267 / NImag=0

Sum of electronic and thermal Enthalpies= -3589.810605

Sum of electronic and thermal Free Energies= -3589.884348

c) Transition states **TS** and water adducts **45**



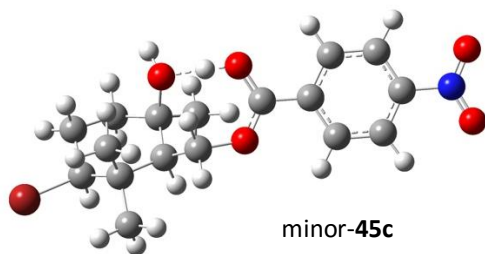
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.893975	-0.360837	-0.099019
2	6	0	4.953741	-1.336998	-0.407247
3	6	0	3.614864	-1.076141	-0.145276
4	6	0	3.238012	0.152068	0.416913
5	6	0	4.208680	1.116632	0.723173
6	6	0	5.548498	0.862799	0.463618
7	6	0	1.826341	0.472138	0.724320
8	8	0	1.453407	1.495637	1.266683
9	7	0	7.331254	-0.638796	-0.383073
10	8	0	7.601712	-1.724409	-0.871395
11	8	0	0.958731	-0.490386	0.310346
12	6	0	-0.381692	-0.459357	0.830726
13	6	0	-1.488489	-0.263583	-0.242415
14	6	0	-1.417780	0.990541	-1.048014
15	6	0	-2.638547	1.645684	-1.540589
16	6	0	-3.953438	1.295921	-0.855897

17	6	0	-3.998667	-0.207820	-0.627331
18	6	0	-2.897975	-0.710924	0.345459
19	6	0	-0.153507	1.402282	-1.708770
20	8	0	-1.137668	2.537512	0.846856
21	6	0	-3.105789	-0.161806	1.772342
22	6	0	-2.924428	-2.254573	0.370566
23	35	0	-5.832934	-0.718241	-0.063487
24	8	0	8.132419	0.239759	-0.108744
25	1	0	-2.662710	1.313419	-2.599040
26	1	0	-2.451727	2.721337	-1.630131
27	1	0	-4.050992	1.833960	0.088433
28	1	0	-4.781060	1.611613	-1.491535
29	1	0	-1.244898	-0.990130	-1.046366
30	1	0	-3.894472	-0.729268	-1.582077
31	1	0	-4.121452	-0.378177	2.103195
32	1	0	-2.432900	-0.644452	2.483102
33	1	0	-2.941708	0.914489	1.835763
34	1	0	-2.841639	-2.674842	-0.636758
35	1	0	-2.122654	-2.673788	0.980748
36	1	0	-3.865046	-2.602611	0.796684
37	1	0	-0.463407	0.307143	1.593032
38	1	0	-0.532680	-1.435932	1.282100
39	1	0	2.867459	-1.825004	-0.368298
40	1	0	3.904941	2.055419	1.167754
41	1	0	5.277145	-2.274924	-0.837154
42	1	0	6.319297	1.586686	0.689595
43	1	0	0.516961	1.852474	-0.974226
44	1	0	0.369848	0.532150	-2.112698
45	1	0	-0.334097	2.134432	-2.495079
46	1	0	-1.455334	3.421354	1.063704
47	1	0	-0.236576	2.453585	1.207482

HF= -3666.6295511 / NImag=1 (-137.9295 cm⁻¹)

Sum of electronic and thermal Enthalpies= -3666.223273

Sum of electronic and thermal Free Energies= -3666.305256



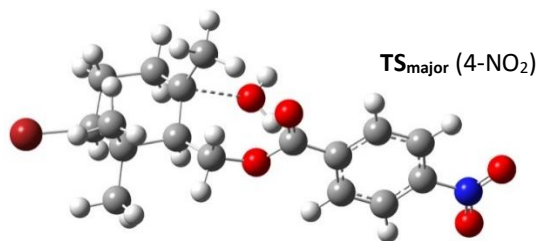
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.958717	1.517333	-0.290190
2	6	0	-2.706263	2.037924	-0.988638
3	6	0	-1.391266	1.353570	-0.590219
4	6	0	-1.509037	-0.195297	-0.407656
5	6	0	-2.894727	-0.778888	0.150930
6	6	0	-4.040443	0.018144	-0.527217

7	1	0	-2.828600	1.905906	-2.068236
8	1	0	-2.593060	3.119245	-0.842145
9	1	0	-3.953973	1.741017	0.779111
10	1	0	-4.833926	2.012921	-0.712488
11	1	0	-1.388096	-0.619515	-1.409347
12	1	0	-4.027743	-0.185130	-1.599965
13	35	0	-5.853601	-0.625275	-0.000263
14	6	0	-2.988616	-0.684715	1.690957
15	1	0	-3.998239	-0.938144	2.013962
16	1	0	-2.320534	-1.399220	2.176920
17	1	0	-2.754754	0.311320	2.070630
18	6	0	-2.997328	-2.257944	-0.280512
19	1	0	-2.984711	-2.358243	-1.369749
20	1	0	-2.190387	-2.871598	0.125476
21	1	0	-3.931939	-2.687306	0.079935
22	6	0	-0.410397	-0.785295	0.488167
23	1	0	-0.449012	-0.390489	1.499139
24	1	0	-0.499306	-1.865653	0.525782
25	8	0	0.987380	-0.618963	0.007815
26	6	0	1.795830	0.241111	0.546529
27	8	0	1.387088	1.235121	1.235551
28	6	0	3.223489	0.050077	0.331659
29	6	0	3.691570	-1.098221	-0.331681
30	6	0	4.124024	1.023949	0.799058
31	6	0	5.052841	-1.270182	-0.530834
32	1	0	2.994233	-1.846181	-0.683921
33	6	0	5.486029	0.851195	0.603931
34	1	0	3.755552	1.903277	1.310254
35	6	0	5.921133	-0.291448	-0.058701
36	1	0	5.448866	-2.140037	-1.036669
37	1	0	6.207621	1.578194	0.950571
38	7	0	7.389653	-0.476542	-0.273502
39	8	0	8.123459	0.399064	0.151458
40	8	0	7.737851	-1.488166	-0.857828
41	6	0	-0.334048	1.742141	-1.637076
42	1	0	0.663731	1.363994	-1.425133
43	1	0	-0.623460	1.352377	-2.614897
44	1	0	-0.273480	2.830505	-1.721438
45	8	0	-0.970284	1.877222	0.735350
46	1	0	-1.154939	2.824454	0.789968
47	1	0	0.376213	1.503778	1.096181

HF= -3666.6526602 / NImag=0

Sum of electronic and thermal Enthalpies= -3666.242911

Sum of electronic and thermal Free Energies= -3666.321177



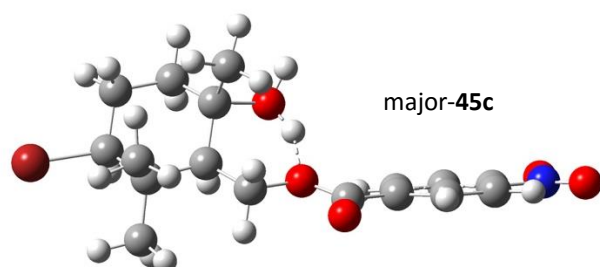
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.008164	0.375503	0.678234
2	6	0	1.478686	0.062960	0.149411
3	6	0	1.522330	-1.142615	-0.704603
4	6	0	2.317964	-1.031603	-1.934725
5	6	0	3.805880	-0.787206	-1.491598
6	6	0	3.887013	0.440775	-0.599342
7	6	0	0.458876	0.055860	1.295371
8	8	0	-0.873532	0.244025	0.769111
9	6	0	-1.824255	-0.688499	1.081073
10	8	0	-1.557816	-1.741483	1.608975
11	6	0	1.060077	-2.457470	-0.252466
12	8	0	-0.571168	-0.533159	-2.121392
13	35	0	5.806009	0.745249	-0.181115
14	6	0	3.473641	-0.688803	1.682776
15	6	0	2.987536	1.757922	1.354385
16	6	0	-3.186760	-0.268516	0.661846
17	6	0	-3.463826	1.030400	0.211916
18	6	0	-4.756251	1.373205	-0.168038
19	6	0	-5.751046	0.405837	-0.088639
20	6	0	-5.505608	-0.885512	0.364719
21	6	0	-4.212377	-1.220057	0.743881
22	7	0	-7.135585	0.769291	-0.503921
23	8	0	-7.991748	-0.094376	-0.403629
24	8	0	-7.312606	1.904273	-0.918107
25	1	0	1.990425	-0.163192	-2.510417
26	1	0	2.251580	-1.924124	-2.555068
27	1	0	4.204829	-1.669521	-0.988068
28	1	0	4.390072	-0.645693	-2.401470
29	1	0	1.260527	0.911199	-0.507568
30	1	0	3.614154	1.331162	-1.167717
31	1	0	4.427827	-0.387539	2.115937
32	1	0	2.764808	-0.791263	2.506791
33	1	0	3.624091	-1.674492	1.237382
34	1	0	2.521137	2.516841	0.720770
35	1	0	2.477162	1.742622	2.317365
36	1	0	4.016806	2.066859	1.545677
37	1	0	1.820690	-2.810029	0.468732
38	1	0	0.132707	-2.421380	0.323507
39	1	0	1.007083	-3.184137	-1.060722
40	1	0	0.485531	-0.858066	1.884928
41	1	0	0.636178	0.903807	1.951995

42	1	0	-2.679002	1.774312	0.178724
43	1	0	-3.985874	-2.213552	1.108926
44	1	0	-5.003139	2.367731	-0.513405
45	1	0	-6.316275	-1.599305	0.416704
46	1	0	-0.972755	-0.934824	-2.901034
47	1	0	-1.275079	-0.033502	-1.690390

HF=-3666.6325721 / NImag=1 (-20.5178 cm⁻¹)

Sum of electronic and thermal Enthalpies= -3666.226140

Sum of electronic and thermal Free Energies= -3666.310108



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.750999	1.660478	0.638172
2	6	0	-2.302801	2.172525	0.727548
3	6	0	-1.352402	1.019720	0.992750
4	6	0	-1.482102	-0.092786	-0.075523
5	6	0	-2.964333	-0.645211	-0.259218
6	6	0	-3.868501	0.606982	-0.458476
7	1	0	-2.029041	2.644789	-0.220088
8	1	0	-2.217228	2.929304	1.512591
9	1	0	-4.089732	1.261069	1.597244
10	1	0	-4.402763	2.504389	0.409508
11	1	0	-1.247887	0.398860	-1.027662
12	1	0	-3.627232	1.058657	-1.422585
13	35	0	-5.791051	0.139839	-0.664303
14	6	0	-3.432697	-1.527206	0.914932
15	1	0	-4.385597	-1.990908	0.660867
16	1	0	-2.725755	-2.335158	1.113815
17	1	0	-3.589691	-0.975086	1.841996
18	6	0	-2.994199	-1.491791	-1.550902
19	1	0	-2.563774	-0.953179	-2.400360
20	1	0	-2.461570	-2.437067	-1.434401
21	1	0	-4.025870	-1.738849	-1.801535
22	6	0	-1.253399	0.611876	2.451025
23	1	0	-2.216794	0.231488	2.789808
24	1	0	-0.510524	-0.166307	2.629711
25	1	0	-1.018536	1.477060	3.077894
26	6	0	-0.464625	-1.224875	0.103632
27	1	0	-0.550922	-1.744804	1.055392
28	1	0	-0.541243	-1.955988	-0.696443

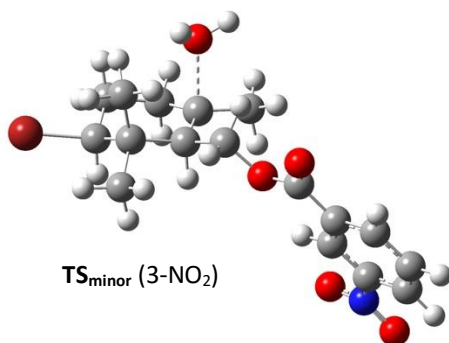
S55

29	8	0	0.878988	-0.632165	0.026099
30	6	0	1.952493	-1.511973	0.241811
31	8	0	1.748706	-2.642292	0.571323
32	6	0	3.269414	-0.867418	0.031245
33	6	0	3.423171	0.305409	-0.721707
34	6	0	4.388519	-1.498659	0.591068
35	6	0	4.686265	0.856006	-0.900420
36	1	0	2.571814	0.768414	-1.204407
37	6	0	5.652944	-0.948595	0.424314
38	1	0	4.257895	-2.414979	1.152592
39	6	0	5.775670	0.222111	-0.314853
40	1	0	4.840154	1.751451	-1.486855
41	1	0	6.533527	-1.409547	0.850604
42	7	0	7.129908	0.820359	-0.495377
43	8	0	8.068836	0.233624	0.015491
44	8	0	7.197191	1.856413	-1.137846
45	8	0	0.097250	1.631883	0.639384
46	1	0	0.458517	2.170753	1.362383
47	1	0	0.697390	0.829511	0.430186

HF= -3666.6411339 / NImag=0

Sum of electronic and thermal Enthalpies= -3666.231312

Sum of electronic and thermal Free Energies= -3666.311522



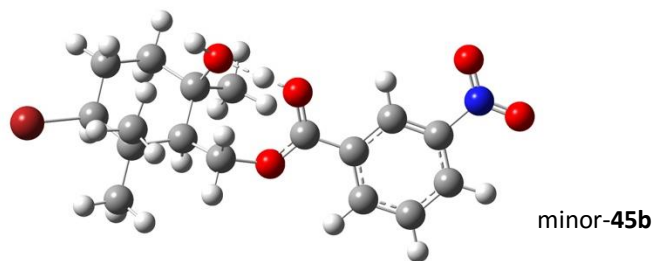
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.606620	1.159783	1.170085
2	6	0	-2.281116	1.407411	1.892779
3	6	0	-1.216404	0.397159	1.657460
4	6	0	-1.133829	-0.240056	0.302870
5	6	0	-2.483865	-0.467126	-0.497940
6	6	0	-3.363718	0.796743	-0.289342
7	1	0	-1.822429	2.340241	1.518771
8	1	0	-2.418631	1.567855	2.963543
9	1	0	-4.166167	0.373241	1.680231
10	1	0	-4.216486	2.061658	1.231379
11	1	0	-0.630399	0.588434	-0.234216
12	1	0	-2.894777	1.636780	-0.806050
13	35	0	-5.128259	0.652402	-1.192220
14	6	0	-3.207920	-1.758105	-0.057374

15	1	0	-3.967113	-2.025434	-0.792152
16	1	0	-2.520837	-2.605379	0.010939
17	1	0	-3.743821	-1.646034	0.890129
18	6	0	-2.123768	-0.581573	-1.995677
19	1	0	-1.561792	0.291425	-2.340552
20	1	0	-1.534094	-1.472616	-2.214404
21	1	0	-3.034667	-0.646553	-2.590199
22	6	0	-0.148401	-1.418521	0.213599
23	1	0	-0.201185	-2.071884	1.087490
24	1	0	-0.352644	-2.033343	-0.659122
25	8	0	1.176541	-0.872709	0.102393
26	6	0	2.172765	-1.796411	-0.102330
27	8	0	1.944018	-2.978169	-0.135566
28	6	0	3.505998	-1.164152	-0.262312
29	6	0	3.671931	0.220466	-0.207210
30	6	0	4.615895	-1.994261	-0.472853
31	6	0	4.946013	0.744802	-0.358310
32	1	0	2.838710	0.888509	-0.055728
33	6	0	5.882855	-1.441082	-0.629053
34	1	0	4.469561	-3.066452	-0.514085
35	6	0	6.060214	-0.059847	-0.572485
36	1	0	7.035000	0.394386	-0.689682
37	7	0	5.112788	2.217587	-0.282638
38	8	0	6.228812	2.668963	-0.474027
39	8	0	4.114812	2.882782	-0.027581
40	6	0	0.007892	0.525108	2.496558
41	1	0	-0.235122	0.840596	3.511629
42	1	0	0.634735	-0.364183	2.498866
43	1	0	0.613029	1.323899	2.046440
44	8	0	-2.091544	-1.112190	2.825233
45	1	0	-1.544595	-1.501151	3.521556
46	1	0	-2.553157	-1.837935	2.381312
47	1	0	6.737781	-2.084685	-0.794346

HF= -3666.6305032 / NImag=1 (-116.1735 cm⁻¹)

Sum of electronic and thermal Enthalpies= -3666.223806

Sum of electronic and thermal Free Energies= -3666.306644



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.685232	1.660138	-0.334485
2	6	0	-2.428014	1.974017	-1.142806
3	6	0	-1.182055	1.161182	-0.765108

4	6	0	-1.475953	-0.351402	-0.471707
5	6	0	-2.880197	-0.721721	0.210557
6	6	0	-3.966611	0.170726	-0.448275
7	1	0	-2.641578	1.773648	-2.197127
8	1	0	-2.168680	3.034991	-1.082939
9	1	0	-3.599146	1.959615	0.715350
10	1	0	-4.519793	2.232952	-0.740781
11	1	0	-1.484681	-0.846159	-1.447914
12	1	0	-4.056972	-0.102578	-1.501201
13	35	0	-5.801552	-0.199187	0.242812
14	6	0	-2.863951	-0.534075	1.744966
15	1	0	-3.869857	-0.671681	2.141192
16	1	0	-2.230617	-1.275215	2.236438
17	1	0	-2.527042	0.456392	2.062311
18	6	0	-3.192467	-2.200061	-0.110665
19	1	0	-3.254782	-2.366782	-1.189801
20	1	0	-2.445020	-2.884582	0.295731
21	1	0	-4.150954	-2.484687	0.323146
22	6	0	-0.392790	-1.020166	0.386248
23	1	0	-0.319199	-0.575617	1.374640
24	1	0	-0.597153	-2.080741	0.490625
25	8	0	0.979679	-1.034190	-0.181674
26	6	0	1.916084	-0.255829	0.270800
27	8	0	1.676124	0.809493	0.931513
28	6	0	3.293157	-0.630185	-0.008229
29	6	0	3.596658	-1.868442	-0.605545
30	6	0	4.319020	0.264252	0.336021
31	6	0	4.918504	-2.207818	-0.856783
32	1	0	2.799503	-2.552970	-0.863637
33	6	0	5.623641	-0.107857	0.073006
34	1	0	4.112245	1.221213	0.794643
35	6	0	5.945848	-1.326663	-0.517358
36	1	0	6.984721	-1.568632	-0.701293
37	7	0	6.719186	0.836169	0.434200
38	8	0	6.390441	1.897156	0.939855
39	8	0	7.858701	0.476209	0.196403
40	6	0	-0.157293	1.349515	-1.891977
41	1	0	0.807686	0.885136	-1.701532
42	1	0	-0.545985	0.915309	-2.814549
43	1	0	0.007998	2.415252	-2.059206
44	8	0	-0.561778	1.775038	0.430370
45	1	0	0.710533	1.208978	0.826494
46	1	0	-1.223319	2.060729	1.072223
47	1	0	5.156667	-3.159532	-1.314344

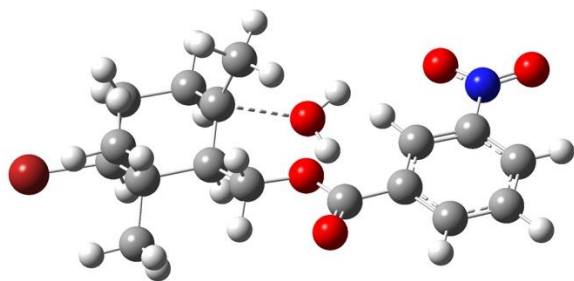
HF= -3666.6525511 / NImag=0

Sum of electronic and thermal Enthalpies=

-3666.242936

Sum of electronic and thermal Free Energies=

-3666.320996



TS_{major} (3-NO₂)

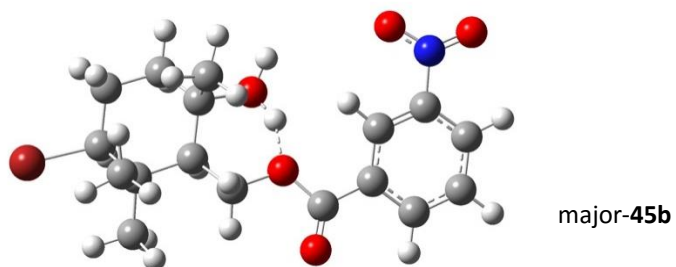
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.990385	0.392731	-0.402090
2	6	0	-4.910573	-0.444351	-0.141690
3	6	0	-3.635999	0.047680	0.082060
4	6	0	-3.412585	1.420441	0.003730
5	6	0	-4.484455	2.284442	-0.255652
6	6	0	-5.762919	1.767892	-0.454141
7	6	0	-2.046014	1.977681	0.186446
8	8	0	-1.769281	3.134448	0.351599
9	7	0	-5.096044	-1.912822	-0.110253
10	8	0	-4.078230	-2.607378	-0.086234
11	8	0	-1.089602	0.987896	0.127948
12	6	0	0.265773	1.409217	0.378031
13	6	0	1.206827	0.277606	-0.045627
14	6	0	1.027047	-1.025551	0.635301
15	6	0	1.811547	-2.155935	0.111584
16	6	0	3.332491	-1.794401	0.203658
17	6	0	3.596909	-0.470847	-0.495401
18	6	0	2.784716	0.724973	0.068964
19	6	0	0.351832	-1.155540	1.933555
20	8	0	-0.893859	-1.836555	-0.807786
21	6	0	3.162797	1.075513	1.516593
22	6	0	2.978621	1.957802	-0.831333
23	35	0	5.557412	-0.147396	-0.444100
24	8	0	-6.232657	-2.343676	-0.120443
25	1	0	1.559537	-2.297961	-0.942429
26	1	0	1.603412	-3.081317	0.647416
27	1	0	3.655627	-1.761482	1.245747
28	1	0	3.884418	-2.602865	-0.276618
29	1	0	1.076956	0.088803	-1.117134
30	1	0	3.390964	-0.564151	-1.562789
31	1	0	4.197302	1.419317	1.545416
32	1	0	2.544600	1.887540	1.902862
33	1	0	3.086911	0.231783	2.206032
34	1	0	2.612003	1.783851	-1.846609
35	1	0	2.488667	2.844409	-0.428923
36	1	0	4.044762	2.182120	-0.893951
37	1	0	1.132169	-0.943786	2.688007
38	1	0	-0.446917	-0.435025	2.089113
39	1	0	0.011965	-2.174058	2.117819
40	1	0	0.366340	1.663463	1.434824
41	1	0	0.466582	2.308064	-0.199475

42	1	0	-2.841732	-0.635964	0.329676
43	1	0	-4.303788	3.351285	-0.304170
44	1	0	-6.974389	-0.027672	-0.562653
45	1	0	-1.591895	-2.495066	-0.676072
46	1	0	-1.356318	-1.044285	-1.107485
47	1	0	-6.589002	2.437609	-0.657931

HF= / NImag=1 (-57.9055 cm⁻¹)

Sum of electronic and thermal Enthalpies= -3666.230203

Sum of electronic and thermal Free Energies= -3666.313463



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.293314	-1.802818	-0.323880
2	6	0	1.821120	-2.101341	-0.655254
3	6	0	0.898095	-1.197856	0.143561
4	6	0	1.229162	0.300267	-0.068131
5	6	0	2.750293	0.674400	0.220917
6	6	0	3.604741	-0.335455	-0.598862
7	1	0	1.650328	-1.923228	-1.720751
8	1	0	1.594228	-3.152495	-0.454923
9	1	0	3.525962	-2.061793	0.711788
10	1	0	3.923872	-2.436863	-0.948138
11	1	0	1.098569	0.467496	-1.144142
12	1	0	3.462362	-0.126900	-1.660901
13	35	0	5.560524	-0.061151	-0.359240
14	6	0	3.109786	0.662720	1.719849
15	1	0	4.115911	1.060416	1.851363
16	1	0	2.438174	1.299770	2.298445
17	1	0	3.105545	-0.331752	2.167482
18	6	0	2.994054	2.097560	-0.329079
19	1	0	2.656706	2.196331	-1.365206
20	1	0	2.494752	2.860396	0.270553
21	1	0	4.060475	2.321545	-0.304338
22	6	0	0.613192	-1.678236	1.554353
23	1	0	1.538929	-1.686917	2.128990
24	1	0	-0.101077	-1.046267	2.083064
25	1	0	0.237684	-2.705374	1.543685
26	6	0	0.265820	1.256528	0.650280
27	1	0	0.334367	1.198497	1.735888
28	1	0	0.427204	2.284471	0.340615
29	8	0	-1.111757	0.895066	0.293278

30	6	0	-2.065374	1.921767	0.223864
31	8	0	-1.752452	3.067727	0.342338
32	6	0	-3.425955	1.388755	-0.023624
33	6	0	-3.726271	0.041212	0.168536
34	6	0	-4.429585	2.269091	-0.453597
35	6	0	-5.004715	-0.412231	-0.108314
36	1	0	-3.009315	-0.661511	0.561720
37	6	0	-5.712665	1.792761	-0.706569
38	1	0	-4.191541	3.317036	-0.587903
39	6	0	-6.014529	0.441163	-0.537596
40	1	0	-7.004304	0.049877	-0.733310
41	7	0	-5.271903	-1.860927	0.059522
42	8	0	-6.425312	-2.236569	-0.017276
43	8	0	-4.298650	-2.587730	0.253671
44	8	0	-0.507264	-1.324451	-0.629235
45	1	0	-0.984418	-2.147216	-0.423684
46	1	0	-1.044625	-0.505313	-0.353008
47	1	0	-6.484239	2.474510	-1.041482

HF= -3666.6459769 / NImag=0

Sum of electronic and thermal Enthalpies= -3666.235923

Sum of electronic and thermal Free Energies= -3666.316067

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