

Supplementary information

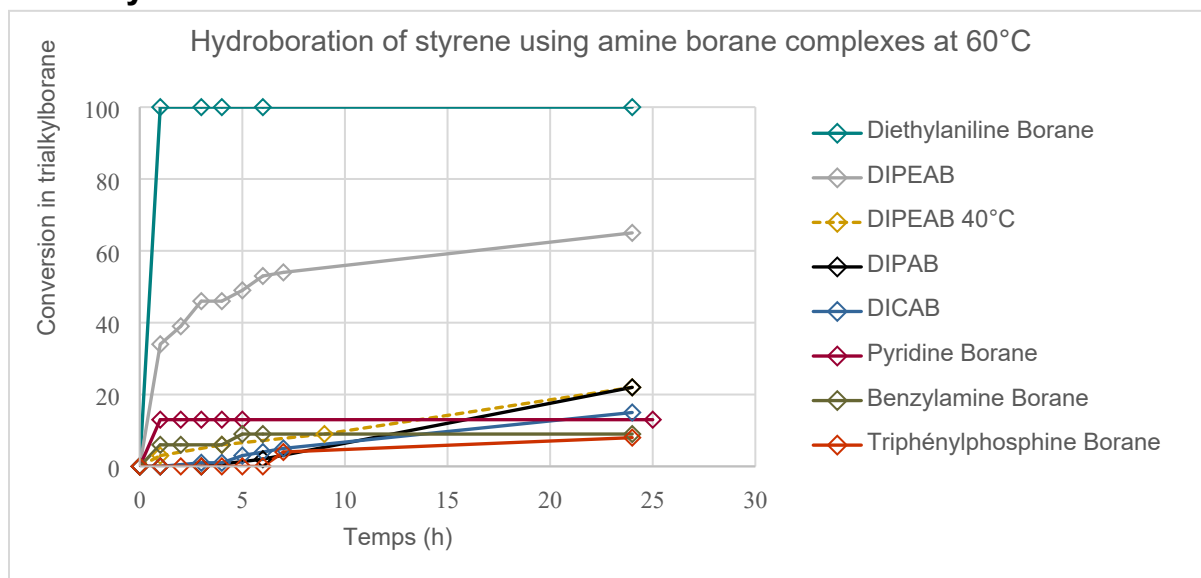
***In situ* generation of radical initiators: Air stable Amine-borane complexes promote Atom Transfer Radical Additions of alkyl halides to alkenes**

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1. Generalities

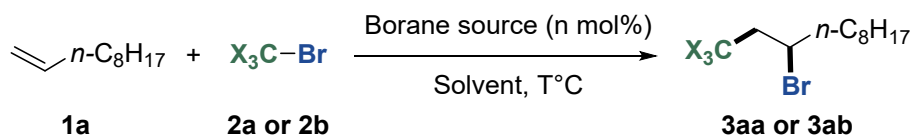
All reactions were carried out in oven dried reaction vessels. NMR spectra were recorded on Bruker Avance 300 FT and Avance 400 FT spectrometers using CDCl_3 as internal reference. The chemical shifts (δ) are reported in ppm relative to residual chloroform ($^1\text{H} = 7.26$ or $^{13}\text{C} = 77.2$). Coupling constants (J) are reported in Hertz (Hz). Reaction solvents were dried using distillation over an appropriate drying agent: MTBE (Na), Hexane (CaH_2), d_6 -Benzene (CaH_2). Column chromatography was carried out using 230-400 mesh silica gel. Routine TLC analysis was carried out on aluminum sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were observed using a 254 mm ultraviolet lamp or stained using a KMnO_4 solution. All other chemicals were used as purchased. NMR spectra were recorded on Bruker Avance 300 FT and Avance 400 FT spectrometers using CDCl_3 as internal reference. The chemical shifts (δ) are reported in ppm relative to residual chloroform ($^1\text{H} = 7.26$ or $^{13}\text{C} = 77.2$). Coupling constants (J) are reported in Hertz (Hz). ^{11}B NMR spectra were recorded at 25°C and chemical shifts (δ) are given in ppm relative to $\text{BF}_3\cdot\text{OEt}_2$ (internal standard). GC-MS analyses were performed on HP 6890 series GC-system equipped with a J&W Scientific DB-1701 capillary column, a HP 5973 mass selective detector (EI) using the following method: 70°C for 1 min then $20^\circ\text{C}/\text{min}$ until 230°C then 6 min at 230°C . Infrared spectra (IR) were recorded on a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer as neat films on NaCl windows or as solids with KBr pellets. The melting points (Mp) were recorded on a Mettler Toledo DSC1-star system using the following method: 30°C to 300°C at $10^\circ\text{C}/\text{min}$. HRMS were recorded on a Qstar ABSciex spectrometer in the electrospray ionization (ESI) mode at the CESAMO (Université de Bordeaux) or a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) mode at the CRMPO (Université de Rennes 1).

2. hydroboration kinetics



3. Reaction condition Optimization

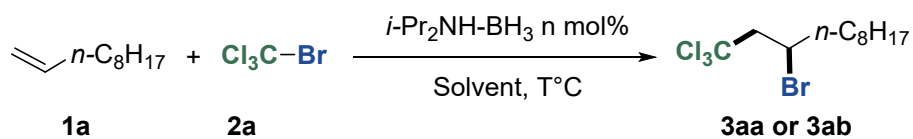
Table 1 : Optimization of amine borane structure for ATRA reaction



Entry	Borane	R-X	Loading	Solvent	Temperature	Time	Conv ^a
1	BEt ₃ 1M in hex	CCl ₃ Br	10%	C ₆ D ₆	60°C	1h	26-71%
2	neat BEt ₃	CCl ₃ Br	3.3%	C ₆ D ₆	60°C	1h	60%
3	DIPAB	CCl ₃ Br	3.3%	C ₆ D ₆	60°C	1h	51%
4	DIPAB	CCl ₃ Br	3.3%	C ₆ D ₆	60°C	3h	90%
5	DICAB	CCl ₃ Br	3.3%	C ₆ D ₆	60°C	3h	0%
6	DICAB	CCl ₃ Br	3.3%	C ₆ D ₆	90°C	16h	100%
7	DICAB	CCl ₃ Br	3.3%	MTBE	90°C	3h	100%
8	DICAB	CCl ₃ Br	3.3%	MTBE	60°C	3h	88%
9	DIPAB	CCl ₃ Br	3.3%	MTBE	60°C	3h	100%
10	TMP-BH ₃	CCl ₃ Br	3.3%	MTBE	60°C	3h	98%
11	piperidine-BH ₃	CCl ₃ Br	3.3%	MTBE	60°C	3h	94%
12	morpholine-BH ₃	CCl ₃ Br	3.3%	MTBE	60°C	3h	87%
13	Bn ₂ NH-BH ₃	CCl ₃ Br	3.3%	MTBE	60°C	3h	57%
14	Et ₃ N-BH ₃	CCl ₃ Br	3.3%	MTBE	60°C	3h	87%
15	DICAB	CBr ₄	1.1%	MTBE	60°C	3h	41%
16	DIPAB	CBr ₄	1.1%	MTBE	60°C	3h	41%
17	TMP-BH ₃	CBr ₄	1.1%	MTBE	60°C	3h	12%
18	piperidine-BH ₃	CBr ₄	1.1%	MTBE	60°C	3h	45%
19	morpholine-BH ₃	CBr ₄	1.1%	MTBE	60°C	3h	34%
20	Et ₃ N-BH ₃	CBr ₄	1.1%	MTBE	60°C	3h	0%

^a Measured by ¹H NMR

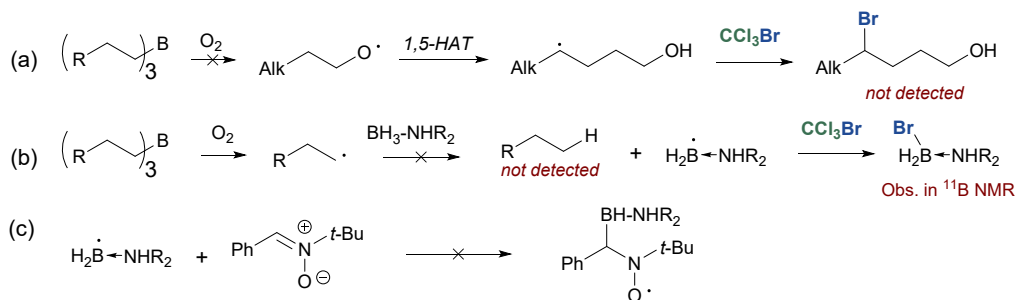
Table 2 : Optimization of solvent and temperature for ATRA reaction

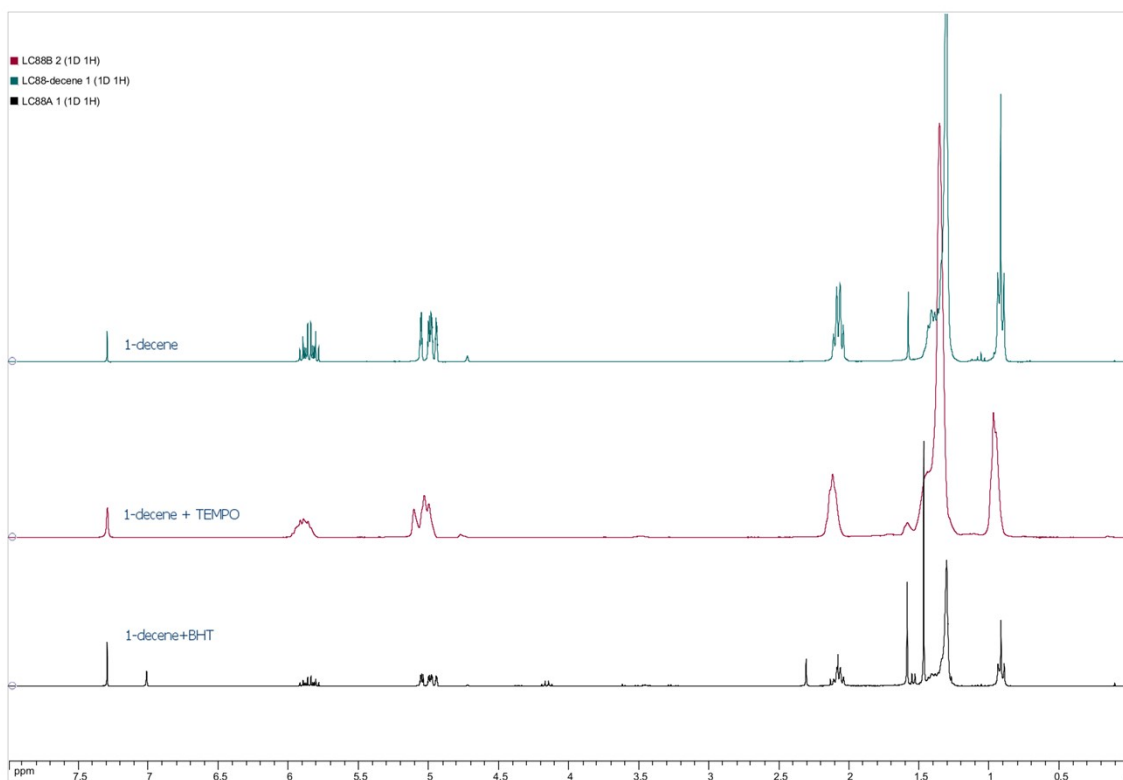
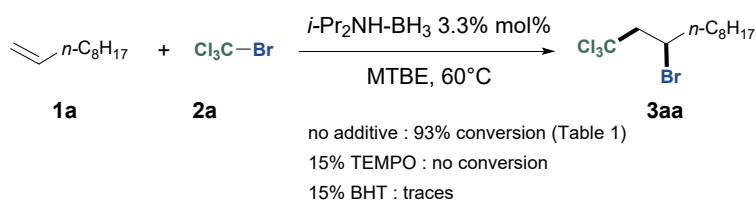


Entry	Solvent	Loading	Temperature	Time	Conv ^a
1	C ₆ D ₆	3.3%	60°C	1h	51%
2	C ₆ D ₆	3.3%	60°C	3h	90%
3	C ₆ D ₆	3.3%	90°C	1h	72%
4	C ₆ D ₆	3.3%	90°C	3h	96%
5	C ₆ H ₆	3.3%	60°C	1h	66%
6	C ₆ H ₆	3.3%	60°C	3h	88%
7	CH ₃ CN	3.3%	60°C	1h	67%
8	CH ₃ CN	3.3%	60°C	3h	80%
9	1,2-dichloroethane	3.3%	60°C	1h	76%
10	1,2-dichloroethane	3.3%	60°C	3h	91%
11	Cyclohexane	3.3%	60°C	1h	55%
12	Cyclohexane	3.3%	60°C	3h	88%
13	dioxane	3.3%	60°C	1h	84%
14	dioxane	3.3%	60°C	3h	96%
15	MTBE	3.3%	60°C	1h	80%
16	MTBE	3.3%	60°C	3h	93%
17	MTBE (0.3M)	3.3%	60°C	3h	87%
18	MTBE	1.1%	60°C	3h	75%
19	MTBE	1.1%	90°C	6h	100%
20	tBuOH	1.1%	60°C	3h	62%
21	H ₂ O	1.1%	60°C	3h	57%

^a Measured by ¹H NMR

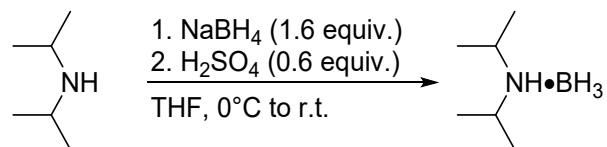
4. Mechanistic investigations





5. Product analysis

N,N-diisopropylamine-borane complex [105416-38-4]



To a stirred solution of diisopropylamine (70.6 mL, 0.5 mol) and NaBH₄ (30 g, 0.79 mol) in THF (500 mL) was added at 0°C over a period of 45 minutes sulfuric acid (16 mL, 0.3 mol). The mixture was allowed to warm to room temperature and stirred for 3 hours. The crude product was concentrated under vacuum and the residue was taken with CH₂Cl₂, and then filtrated to eliminate all solid residues. The filtrate was washed with water (4x100 mL). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to give the product obtained as a colorless oil which solidified upon cooling (50.8 g, 90%).

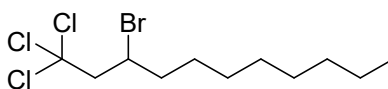
^1H NMR (400 MHz, CDCl_3) δ (ppm) 2.72 – 2.90 (m, 2H), 1.91 (q, $J = 91\text{Hz}$, 3H), 1.05 (d, $J = 6.6\text{Hz}$, 6H), 0.96 (d, $J = 6.6\text{Hz}$, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 52.1, 21.1, 19.0.

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) -21.3 (q, $J_{\text{H-B}} = 91,4$ Hz).

m.p. 20-25 °C .

3-bromo-1,1,1-trichloroundecane (**3aa**). [95382-86-8] ¹



Chemical Formula: $\text{C}_{11}\text{H}_{20}\text{BrCl}_3$

Molecular Weight: 338,54

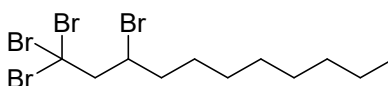
To a solution of trichlorobromomethane (3.3 mmol, 1.1 equiv., 325 μL) in MTBE (300 μL) was added 11 μg of DIPAB (0.1 mmol, 3.3 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μL). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 3-bromo-1,1,1-trichloroundecane **3aa** (909 mg, 89%) as a colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 4.32 (dq, $J = 9.8, 5.1$ Hz, 1H), 3.45 (dd, $J = 15.9, 5.1$ Hz, 1H), 3.22 (dd, $J = 15.8, 5.2$ Hz, 1H), 2.14-1.82 (m, 2H), 1.66-1.43 (m, 3H), 1.41 – 1.10 (m, 11H), 0.88 (t, $J = 6.7$ Hz, 11H).

^{13}C NMR (76 MHz, CDCl_3) δ 97.4, 62.8, 49.4, 47.9, 39.7, 32.0, 29.5, 29.3, 28.9, 27.4, 22.8, 19.5, 14.2.

GC: rt = 9.4 min.

1,1,1,3-tetrabromoundecane **3ab** [1123200-04-3]²



Chemical Formula: $\text{C}_{11}\text{H}_{20}\text{Br}_4$

Molecular Weight: 471,90

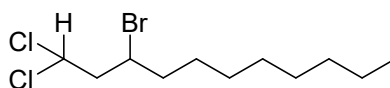
To a solution of Br_4C (3.3 mmol, 1.1 equiv., 1.09g) in MTBE (300 μL) was added 35 μg of DIPAB (0.3 mmol, 10 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μL). After 3h at 90°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 1,1,1,3-tetrabromoundecane **3ab** (1.45g, 93%) as a colorless oil

^1H NMR (300 MHz, CDCl_3) δ 4.23 (dq, $J = 9.0, 4.6$ Hz, 1H), 3.86 (dd, $J = 16.2, 4.5$ Hz, 1H), 3.57 (dd, $J = 16.2, 4.9$ Hz, 1H), 2.19-1.90 (m, 2H), 1.71-1.48 (m, 2H), 1.46-1.22 (m, 12H), 0.91 (t, $J = 6.7$ Hz, 3H).

^{13}C NMR (76 MHz, CDCl_3) δ 67.0, 52.2, 39.9, 36.5, 32.0, 29.5, 29.4, 28.9, 27.5, 22.8, 14.3.

GC : rt = 9.0 min.

3-bromo-1,1-dichloroundecane **3ad**



Chemical Formula: C₁₁H₂₁BrCl₂

Molecular Weight: 304,09

To a solution of dichlorobromomethane (3.3 mmol, 1.1 equiv., 273 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 90°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 3-bromo-1,1-dichloroundecane **3ad** (652 mg, 71%) as a colorless oil.

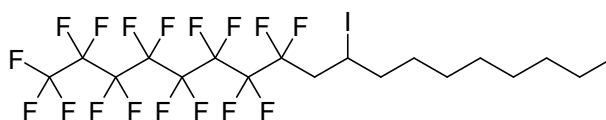
¹H NMR (300 MHz, CDCl₃): δ 6.02-5.97 (m, 1H), 4.17-4.08 (m, 2H), 2.62 (dd, *J* = 3.7, 4.7 Hz, 1H), 2.59 (dd, *J* = 3.2, 4.7 Hz, 1H), 2.01-1.70 (m, 2H), 1.64-1.13 (m, 14H), 0.89 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (76 MHz, CDCl₃) δ 72.0, 52.6, 52.2, 38.9, 32.0, 29.5, 29.3, 29.0, 27.3, 22.8, 14.3.

GC: rt = 9.0 min;

HRMS Found: [M-H] 301.0119. C₁₁H₂₀BrCl₃ Theo. M = 301.0125.

9-iodo-11,11,12,12,13,13,14,15,15,15,16,16,17,17,18,18,18-heptafluoro-octadecane **3ae** [176979-17-2]³⁻⁴



Chemical Formula: C₁₈H₂₀F₇I

Molecular Weight: 686,24

To a solution of 1-iodoperfluorooctane (3.3 mmol, 1.1 equiv., 1.8 g) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 cyclohexane/ethylacetate to give 9-iodo-11,11,12,12,13,13,14,15,15,15,16,16,17,17,18,18,18-heptafluoro-octadecane **3ae** (1.89 g, 92%) as a colorless oil.

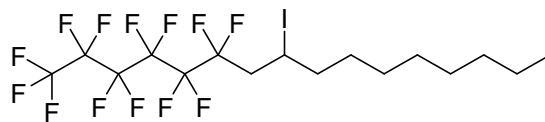
¹H NMR (300 MHz, CDCl₃) δ 4.36 (tt, *J* = 8.2, 5.4 Hz, 1H), 2.65 (s, 2H), 1.98-1.70 (m, 2H), 1.66-1.17 (m, 14H), 0.91 (t, *J* = 6.7 Hz, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -80.74 (t, *J* = 9.9 Hz), -113.15 (dd, *J* = 804.6, 260.3 Hz), -121.57 (s), -121.88 (s), -122.69 (s), -123.58 (s), -126.07 (s).

¹³C NMR (151 MHz, CDCl₃) δ 121.47 – 115.95 (m), 115.0 – 105.4 (m), 42.0 (t, *J* = 20.8 Hz), 40.6, 32.0, 29.8, 29.6, 29.4, 28.7, 22.9, 20.9, 14.1.

GC: rt = 8.1 min.

8-iodo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-hexadecane **3ag** [207122-00-7]⁴⁻⁶



Chemical Formula: C₁₆H₂₀F₁₃I
Molecular Weight: 586,22

To a solution of 1-iodoperfluorohexane (3.3 mmol, 1.1 equiv., 713 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 cyclohexane/ethylacetate to give 8-iodo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-hexadecane **3ag** (1.80 g, 89%) as a colorless oil.

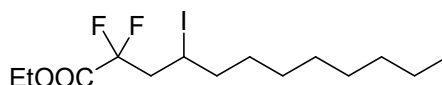
¹H NMR (300 MHz, CDCl₃) δ 4.41 – 4.24 (m, 1H), 3.07 – 2.62 (m, 2H), 1.93 – 1.67 (m, 2H), 1.63 – 1.16 (m, 14H), 0.89 (t, *J* = 6.7 Hz, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -80.78 (t, *J* = 9.9 Hz), -113.19 (ddd, *J* = 282.4, 270.2, 14.1 Hz), -121.77 (m), -122.85 (brs), -123.61 (d, *J* = 12.5 Hz), -125.67 – -126.70 (m).

¹³C NMR (76 MHz, CDCl₃) δ 123.9 – 103.6 (m), 42.0 (t, *J* = 20.9 Hz), 40.6 (d, *J* = 1.9 Hz), 32.0, 29.8, 29.6, 29.5, 28.8, 22.9, 20.9, 14.1.

GC: rt = 7.6 min.

Ethyl 4-iodo-2,2-difluorododecanoate **3ah** [2088203-14-7]⁷



Chemical Formula: C₁₄H₂₅F₂IO₂
Molecular Weight: 390,25

To a solution of ethyl-2-difluoro-2-iodoacetate (3.3 mmol, 1.1 equiv., 485 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 90°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 cyclohexane/ethylacetate to give ethyl 4-iodo-2,2-difluorododecanoate **3ah** (1.09 g, 91%) as a colorless oil.

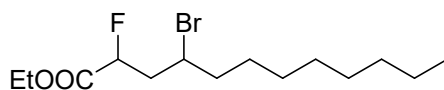
¹H NMR (300 MHz, CDCl₃) δ 4.37 (q, *J* = 7.2 Hz, 2H), 4.32 – 4.17 (m, 1H), 3.01 – 2.65 (m, 2H), 1.91 – 1.63 (m, 2H), 1.63 (m, 17H), 0.91 (t, *J* = 6.7 Hz, 3H).

¹⁹F NMR (282 MHz, CDCl₃) δ -102.12 (ddd, *J* = 262, 18.0, 12.8 Hz), -106.80 (dt, *J* = 262, 17.0 Hz).

¹³C NMR (76 MHz, CDCl₃) δ 163.6 (t, *J* = 32.3 Hz), 115.3 (dd, *J* = 254.6, 253.8 Hz), 63.3, 45.5 (t, *J* = 23.2 Hz), 40.6, 31.9, 29.6, 29.4, 29.3, 28.6, 23.45 (t, *J* = 4.0 Hz), 22.8, 14.2, 14.1.

GC: rt = 10.0 min.

Ethyl 4-bromo-1-fluorododecanoate **3ai**



Chemical Formula: C₁₄H₂₆BrFO₂

Molecular Weight: 325,26

To a solution of ethyl-2-fluoro-2-bromoacetate (3.3 mmol, 1.1 equiv., 390 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 90°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 cyclohexane/ethylacetate to give ethyl 4-bromo-1-fluorododecanoate **3ai** as mixture of diastereoisomers (667 mg, 68%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 5.36 – 5.00 (m, 1H), 4.27 (q, *J* = 7.1Hz, 1H d1), 4.26 (q, *J* = 7.1Hz, 1H d2), 4.21-4.12 (m, 1H), 2.56 – 2.15 (m, 2H), 1.98 – 1.72 (m, 2H), 1.58 – 1.14 (m, 18H), 0.87 (t, *J* = 6.7 Hz, 3H).

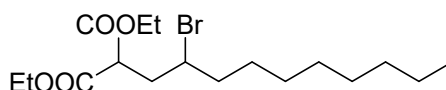
¹⁹F NMR (282 MHz, CDCl₃) δ -190.64 (dt, *J* = 48.3, 21.6 Hz), -194.57 – -195.17 (m).

¹³C NMR (76 MHz, CDCl₃) δ 169.6 (d, *J* = 22.3 Hz), 169.3 (d, *J* = 22.3 Hz), 87.5 (d, *J* = 186.2 Hz), 87.2 (d, *J* = 186.9 Hz), 52.16, 52.13, 51.11, 51.06, 61.92, 61.88, 52.2 (d, *J* = 1.9 Hz), 51.1 (d, *J* = 4.1 Hz), 41.9 (d, *J* = 20.5 Hz), 41.5 (d, *J* = 21.3 Hz), 39.5, 38.5, 31.9, 29.5, 29.3, 29.03, 28.99, 27.6, 27.5, 22.8, 14.3, 14.2.

GC: rt = 10.0, 10.2 min

HRMS; m/z (CI⁺) Found: [M]⁺ 325.1179. C₁₄H₂₇BrFO₂ Theo. M = 325.1178.

Diethyl (2-bromodecyl)propandioate **3aj** [156001-85-3] ⁸⁻⁹



Chemical Formula: C₁₇H₃₁BrO₄

Molecular Weight: 379,34

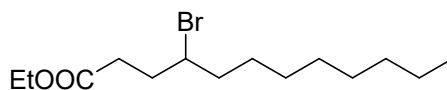
To a solution of ethyl-bromomalonate (3.3 mmol, 1.1 equiv., 563 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 cyclohexane/ethylacetate to give 4-bromo-diethyldodecandioate **3aj** (1.035 g, 91%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 4.30-4.13 (m, 4H), 4.06-3.91 (m, 1H), 3.78 (dd, *J* = 10.2, 4.3 Hz, 1H), 2.46 (ddd, *J* = 14.8, 10.2, 3.1 Hz, 1H), 2.24 (ddd, *J* = 14.9, 10.6, 4.3 Hz, 1H), 1.90-1.78 (m, 2H), 1.35-1.17 (m, 16H), 0.87 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (76 MHz, CDCl₃) δ 169.2, 169.0, 61.8, 61.7, 55.2, 50.8, 39.60, 38.0, 32.0, 29.5, 29.3, 29.1, 27.6, 22.8, 14.2, 14.2, 14.2.

GC: rt = 12.8 min.

Ethyl 4-bromododecanoate **3ak** [156001-82-0]⁸



Chemical Formula: C₁₄H₂₇BrO₂

Molecular Weight: 307,27

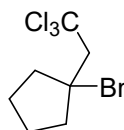
To a solution of ethylbromoacetate (3.3 mmol, 1.1 equiv., 391 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by 1-decene (3 mmol, 1 equiv., 568 μ L). After 6h at 90°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 97/3 cyclohexane/ethylacetate to give Ethyl 4-bromododecanoate **3ak** (467 mg, 51%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 4.14 (q, *J* = 7.1 Hz, 2H), 4.12-3.98 (m, 1H), 2.66-2.43 (m, 2H), 2.19 (dddd, *J* = 15.4, 8.5, 6.9, 3.6 Hz, 1H), 2.31 – 2.11 (m, 1H), 2.10-1.73 (m, 2H), 1.71-1.37 (m, 2H), 1.29-1.24 (m, 15H), 0.88 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (76 MHz, CDCl₃) δ 173.05, 60.67, 57.48, 39.42, 34.14, 32.56, 31.99, 29.56, 29.36, 29.15, 27.68, 22.80, 14.37, 14.26.

GC: rt = 9.9 min.

1-bromo-1-(2,2,2-trichloroethyl)cyclopentane **3ba**



Chemical Formula: C₇H₁₀BrCl₃

Molecular Weight: 280,4110

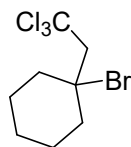
To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.3 mmol, 3.3 mol%), followed by methylene cyclopentane (3 mmol, 1 equiv., 82 μ g). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 1-bromo-1-(2,2,2-trichloroethyl)cyclopentane **3ba** (703 mg, 87%) as pale yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 3.61 (s, 2H), 2.46-2.30 (m, 2H), 2.20-1.93 (m, 3H), 1.71 (s, 2H).

¹³C NMR (76 MHz, CDCl₃) δ 96.6, 73.5, 64.7, 43.7, 22.6.

GC: rt = 7.8 min (2,2,2-trichloroethyl)cyclopentene observed in GC (rt = 5.7min) formed upon heating in the GC oven).

1-bromo-1-(2,2,2-trichloroethyl)cyclohexane **3ca** [2412926-56-6]¹⁰



Chemical Formula: C₈H₁₂BrCl₃

Molecular Weight: 294,44

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.3 mmol, 3.3 mol%), followed by methylene cyclohexane (3 mmol, 1 equiv., 360 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 1-bromo-1-(2,2,2-trichloroethyl)cyclohexane **3ca** (967 mg, 79%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 3.61 (s, 2H), 2.30-2.14 (s, 2H), 2.06-1.62 (s, 7H), 1.33 – 1.12 (m, 1H).

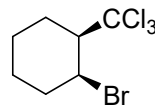
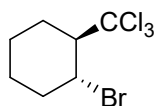
¹³C NMR (76 MHz, CDCl₃) δ 96.1, 72.5, 68.0, 40.5, 25.0, 23.2.

GC: rt = 8.6 min.

HRMS m/z (CI+) Found: (M + H)⁺ 292.9266. C₈H₁₃BrCl₃ requires M, 292.9266.

trans-1-bromo-2-trichloromethylcyclohexane **3da** [17831-06-0]¹¹⁻¹³

cis-1-bromo-1-trichloromethylcyclohexane **3da'** [17831-07-1]^{11, 13}



Chemical Formula: C₇H₁₀BrCl₃ Chemical Formula: C₇H₁₀BrCl₃

Molecular Weight: 280,41

Molecular Weight: 280,41

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by cyclohexene (3 mmol, 1 equiv., 304 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 2-bromo-1-trichloromethylcyclohexane **3da** (121 mg, 14%) as a colorless oil and **3da'** (105 mg, 0.37 mmol, 12%) as a colorless oil.

3da: ¹H NMR (300 MHz, CDCl₃) δ 4.50-4.42 (m, 1H), 3.06 (dd, *J* = 6, 3.6 Hz, 1H), 3.04 (dd, *J* = 6.3, 3.6 Hz, 1H), 2.46-2.25 (m, 2H), 2.09-1.74 (m, 4H), 1.70-1.49 (m, 2H).

¹³C NMR (76 MHz, CDCl₃) δ 103.0, 62.0, 50.5, 32.7, 24.9, 20.8, 20.6.

GC : rt = 8.0 min.

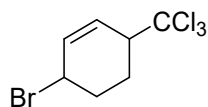
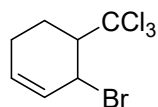
3da': ¹H NMR (300 MHz, CDCl₃) δ 5.06-5.00 (m, 1H), 2.5 (ddd, *J* = 11.1, 2.7, 2.4 Hz, 1H), 2.36-2.10 (m, 2H), 2.08-1.79 (m, 4H), 1.70-1.53 (m, 1H), 1.53-1.34 (m, 1H).

¹³C NMR (76 MHz, CDCl₃) δ 103.0, 61.2, 51.8, 36.5, 25.6, 24.5, 20.3.

GC : rt = 8.4 min.

1-bromo-2-trichloromethylcyclohex-5-ene **3ea** [1093613-07-0]¹⁴

1-bromo-3-trichloromethylcyclohex-2-ene **3ea'** [55005-81-7]¹⁴



Chemical Formula: C₇H₈BrCl₃ Chemical Formula: C₇H₈BrCl₃

Molecular Weight: 278,40 Molecular Weight: 278,40

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by cyclohex-1,3-diene (3 mmol, 1 equiv., 304 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give a mixture of 1-bromo-2-trichloromethylcyclohex-5-ene **3ea** (123 mg, 15%) as a colorless oil and 1-bromo-3-trichloromethylcyclohex-2-ene **3ea'** (162 mg, 19%) as a colorless oil.

3ea ¹H NMR (300 MHz, CDCl₃) δ 6.21 (dtd, J = 10.3, 2.7, 1.0 Hz, 1H), 6.02 (ddd, J = 10.3, 3.9, 1.7 Hz, 1H), 4.77 – 4.67 (m, 0.85H D1), 4.61 – 4.52 (m, 0.15H D2), 3.40 – 3.26 (m, 1H), 2.63-2.30 (m, 2H), 2.09 (dddd, J = 13.5, 11.9, 8.8, 3.1 Hz, 1H), 1.85 (dddd, J = 15.1, 13.7, 8.7, 3.0 Hz, 1H).

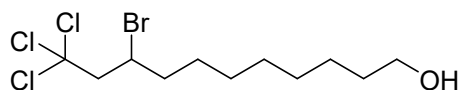
¹³C NMR (76 MHz, CDCl₃) δ 134.36 (D1), 133.99 (D2), 127.30 (D2), 127.21 (D1), 103.28, 55.92 (D2), 55.51(D2), 54.29 (D1), 45.45 (D2), 32.68 (D1), 32.41 (D2), 26.21 (D1), 25.86 (D2).

GC : rt = 8.0 min.

3ea' ¹H NMR (300 MHz, CDCl₃) δ 6.24 - 6.15 (m, 1H), 6.04 (dt, J = 10.1, 1.5 Hz, 1H), 4.85-4.80 (m, 1H), 3.46-3.33 (m, 1H), 2.42-2.01 (m, 4H). ¹³C NMR (76 MHz, CDCl₃) δ 132.5 (D1), 131.5 (D2), 128.2 (D2), 127.5 (D1), 103.4 (D2), 56.8(D1), 52.8 (D2), 45.6, 31.1 (D1), 30.7 (D2), 21.6 (D1), 21.0 (D2).

GC : rt = 8.4 min.

1,1,1-trichloro-3-bromoundecan-11-ol **3fa**



Chemical Formula: C₁₁H₂₀BrCl₃O

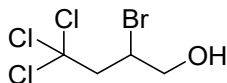
Molecular Weight: 354,53

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by 9-decen-1-ol (3 mmol, 1 equiv., 589 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 8/2 cyclohexane/ethylacetate to give 1,1,1-trichloro-3-bromo-undecan-11-ol **3fa** (856 mg, 81%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 4.34 (dt, J = 9.6, 5.1 Hz, 1H), 3.66 (t, J = 6.6 Hz, 2H), 3.47 (dd, J = 15.8, 5.1 Hz, 1H), 3.24 (dd, J = 15.8, 5.3 Hz, 1H), 2.13-1.87 (m, 2H), 1.69-1.247 (m, 13H).

^{13}C NMR (76 MHz, CDCl_3) δ 97.3, 63.2, 62.8, 49.3, 39.7, 32.9, 29.5, 29.4, 28.8, 27.4, 25.8.

2-bromo-4,4,4-trichlorobutan-1-ol **3ga** [15344-05-5]¹⁵



Chemical Formula: $\text{C}_4\text{H}_6\text{BrCl}_3\text{O}$

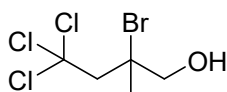
Molecular Weight: 256,35

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μL) in MTBE (300 μL) was added 35 μg of DIPAB (0.3 mmol, 10 mol%), followed by allyl alcohol (3 mmol, 1 equiv., 204 μL). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 80/20 cyclohexane/ethylacetate gave 2-bromo-4,4,4-trichlorobutan-1-ol **3ga** (274 mg, 65%) as a colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 4.50-4.42 (m, 1H), 3.97 (dd, J = 6.6 Hz, 1H), 3.95 (dd, J = 6.6, 0.9 Hz, 1H), 3.39 (dq, J = 15.9 Hz, 5.22, 1H), 2.13 (t, J = 6.9 Hz, 1H).

^{13}C NMR (76 MHz, CDCl_3) δ 96.7, 66.8, 58.7, 50.4.

2-bromo-4,4,4-trichloro-2-methylbutan-1-ol **3ha**



Chemical Formula: $\text{C}_5\text{H}_8\text{BrCl}_3\text{O}$

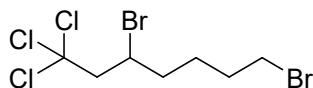
Molecular Weight: 270,37

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μL) in MTBE (300 μL) was added 35 μg of DIPAB (0.3 mmol, 10 mol%), followed by 2-methylpropenol (3 mmol, 1 equiv., 252 μL). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 80/20 cyclohexane/ethylacetate to give 2-bromo-4,4,4-trichloro-2-methylbutan-1-ol **3ha** (733 mg, 93%) as a colorless oil.

^1H NMR (300 MHz, CDCl_3) δ 3.99 (dd, J = 12.6, 8.2 Hz, 1H), 3.84 (dd, J = 12.6, 6.2 Hz, 1H), 3.69 (d, J = 15.9 Hz, 1H), 3.54 (d, J = 15.9 Hz, 1H), 2.22 (dd, J = 8.2, 6.3 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (76 MHz, CDCl_3) δ 95.8, 71.5, 69.5, 61.6, 27.5.

1,5-dibromo-7,7,7-trichloroheptane **3ia**



Chemical Formula: C₇H₁₁Br₂Cl₃

Molecular Weight: 361,32

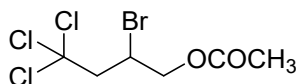
To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (3.3 mol%), followed by 1-bromohex-5-ene (3 mmol, 1 equiv., 503 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 1,5-dibromo-7,7,7-trichloroheptane **3ia** (752 mg, 92%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 4.32 (dq, *J* = 9.6, 5.1 Hz, 1H), 3.47 (dd, *J* = 15.9, 5.1 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 3.22 (dd, *J* = 15.8, 5.4 Hz, 1H), 1.80 (s, 4H), 1.26 (s, 7H).

¹³C NMR (76 MHz, CDCl₃) δ 97.3, 62.8, 49.1, 39.5, 33.9, 32.7, 28.0, 28.0, 27.2.

GC: rt = 11.6 min

2-bromo-4,4,4-trichlorobutyl methanoate **3ja** [81932-47-0] ¹⁶



Chemical Formula: C₆H₈BrCl₃O₂

Molecular Weight: 298,38

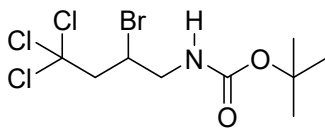
To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 3x 11 μ g of DIPAB (0.3 mmol, 10 mol%), followed by allylacetate (3 mmol, 1 equiv., 324 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 96/4 cyclohexane/ethylacetate to give 2-bromo-4-trichlorobutyl methanoate **3ja** (475 mg, 53%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 4.54 – 4.32 (m, 3H), 3.37 (d, *J* = 4.9 Hz, 2H), 2.13 (s, 3H).

¹³C NMR (76 MHz, CDCl₃) δ 170.2, 96.7, 66.9, 59.1, 42.9, 20.8.

GC: rt = 7.8 min

N-tert-butoxycarbonyl-2-bromo-4,4,4-trichlorobutyl-1-amine **3ka**



Chemical Formula: C₉H₁₅BrCl₃NO₂

Molecular Weight: 355,48

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by *tert*-butyl allylcarbamate (3 mmol, 1 equiv., 503 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 98/2 toluene/ethylacetate gave (3-bromo-1-trichlorobutyl)*tert*-butylcarbamate **3ka** (421 mg, 39%) as a white solid.

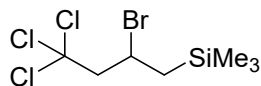
¹H NMR (300 MHz, CDCl₃) δ 5.00 (brs, 1H), 4.40 (dq, J = 4.9, 6.7 Hz, 1H), 3.73 (ddd, J = 5.1, 6.5, 14.5 Hz, 1H), 3.63-3.48 (m, 1H), 3.41-3.26 (m, 2H), 1.46 (m, 9H).

¹³C NMR (76 MHz, CDCl₃) δ 155.3, 96.9, 80.3, 56.0, 47.8, 28.2.

GC: rt = 10.2 min;

HRMS [M – CH₃]⁺ found 339.9093. C₈H₁₂BrCl₃NO Theo. M = 339.9096.

(2-bromo-4,4,4-trichlorobut-1-yl)trimethylsilane **3la** [35070-72-5] ¹⁷



Chemical Formula: C₇H₁₄BrCl₃Si

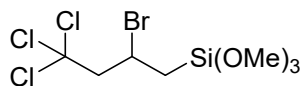
Molecular Weight: 312,53

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by allyltrimethylsilane (3 mmol, 1 equiv., 503 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give (2-bromo-4,4,4-trichlorobut-1-yl)trimethylsilane **3la** (814 mg, 87%) as a pale yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 4.50 (dtd, J = 9.2, 5.7, 4.9 Hz, 1H), 3.49 (dd, J = 15.8, 5.6 Hz, 1H), 3.21 (dd, J = 15.8, 4.9 Hz, 1H), 1.68 (dd, J = 15.0, 5.8 Hz, 1H), 1.54 (dd, J = 15.0, 9.2 Hz, 1H), 0.20 – 0.04 (m, 9H).

¹³C NMR (76 MHz, CDCl₃) δ 97.2, 65.5, 46.2, 30.8, -0.7.

(2-bromo-4,4,4-trichlorobut-1-yl)trimethoxysilane **3ma**



Chemical Formula: C₇H₁₄BrCl₃O₃Si

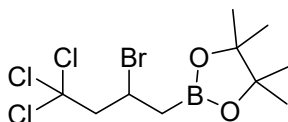
Molecular Weight: 360,53

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by allyltrimethoxysilane (3 mmol, 1 equiv., 507 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give (2-bromo-4,4,4-trichlorobut-1-yl)trimethoxysilane **3ma** (1.05 g, 98%) as a pale yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 4.64 – 4.52 (m, 1H), 3.64 (s, 9H), 3.44 (d, *J* = 0.9 Hz, 1H), 3.42 (s, 1H), 1.72 (qd, *J* = 15.4, 7.3 Hz, 2H).

¹³C NMR (76 MHz, CDCl₃) δ 97.2, 63.8, 50.9, 43.5, 24.2.

1-(4,4,5,5-tetramethyl-1,3-dioxabor-2-yl)-2-bromo-4,4,4-trichlorobutane



Chemical Formula: C₁₀H₁₇BBBrCl₃O₂

Molecular Weight: 366,31

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 11 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by allylpinacol borane (3 mmol, 1 equiv., 562 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 1-(4,4,5,5-tetramethyl-1,3-dioxabor-2-yl)-2-bromo-4,4,4-trichlorobutane **3na** (1.02 g, 2.8 mmol, 93%) as a pale yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 4.60 (dq, *J* = 8.4, 5.5 Hz, 1H), 3.48 (dd, *J* = 15.8, 5.4 Hz, 1H), 3.33 (dd, *J* = 15.8, 5.7 Hz, 1H), 1.91 (dd, *J* = 15.9, 5.3 Hz, 1H), 1.77 (dd, *J* = 15.9, 8.4 Hz, 1H), 1.28 (s, 12H).

¹¹B NMR (96 MHz, CDCl₃) δ 32.5.

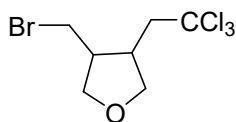
¹³C NMR (76 MHz, CDCl₃) δ 97.2, 83.9, 63.7, 44.8, 25.0, 24.8.

GC: 9.3 min;

HRMS *m/z* (Cl⁺) Found: [M]⁺ 364.9586. C₁₃H₁₇BBBrCl₃O₂ Theo. M = 364.9586.

3-(bromomethyl)-4-(2,2,2-trichloroethyl)tetrahydrofuran [54711-89-6]¹⁶

Cis isomer **3oa** [172091-12-2]¹⁸ trans isomer **3oa'** [138972-07-3]¹⁹



Chemical Formula: C₇H₁₀BrCl₃O

Molecular Weight: 296,41

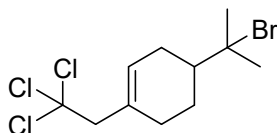
To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 5 x 3 μ g of DIPAB (0.15 mmol, 5 mol%), followed by diallylether (3 mmol, 1 equiv., 405 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to 9/1 cyclohexane/ethylacetate gave 3-(bromomethyl)-4-(2,2,2-trichloroethyl)tetrahydrofuran **3oa** (518 mg, 68%) as a colorless oily mixture of cis/trans diastereoisomers (60/40). Cis isomer **3oa** [172091-12-2]¹⁸ trans isomer **3oa'** [138972-07-3]¹⁹

¹H NMR (300 MHz, CDCl₃) δ 4.29 (dd, *J* = 9.1, 7.1 Hz, 0.4H d1), 4.16 (dd, *J* = 8.7, 7.4 Hz, 0.6H d2), 4.02-3.94 (m, 1H d1d2), 3.88 (dd, *J* = 9.1, 3.5 Hz, 0.6H d2), 3.75-3.61 (m, 1.6H d1d2), 3.61-3.48 (m, 1H d1d2), 3.41 (dd, *J* = 10.2, 8.0 Hz, 0.4H d1), 3.33 (t, *J* = 9.9 Hz, 0.6H d2), 3.06 (dd, *J* = 4.8, 3.3 Hz, 0.4H d1), 3.01 (dd, *J* = 3.7, 3.3 Hz, 0.6H d2), 2.94– 2.79 (m, 1.4H d1d2), 2.74 (dd, *J* = 14.4, 7.7 Hz, 0.6H d2) 2.55-2.38 (m, 0.8H d1).

¹³C NMR (76 MHz, CDCl₃) δ 98.8 (d2), 98.6 (d1), 74.6 (d1), 72.1 (d1), 72.03 (d2), 71.99 (d2), 58.6 (d1), 53.0(d2), 48.0 (d1), 44.8 (d2), 43.0 (d1), 40.8 (d2), 33.9 (d1), 31.3 (d2).

GC: rt = 9.228, 9.432 min.

4-(1-bromo-1-methylethyl)-1-(2,2,2-trichloroethyl)cyclohex-1-ene **3pa** [19876-32-5]²⁰



Chemical Formula: C₁₁H₁₆BrCl₃

Molecular Weight: 334,50

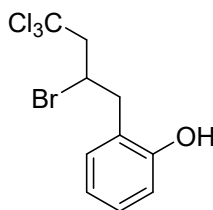
To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.1 mmol, 3.3 mol%), followed by β -pinene (3 mmol, 1 equiv., 568 μ L). After 3h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to give 4-(1-bromo-1-methylethyl)-1-(2,2,2-trichloroethyl)cyclohex-1-ene **3pa** (967 mg, 96%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 5.85 – 5.74 (m, 1H), 3.35 (s, 2H), 2.50 – 2.23 (m, 3H), 2.15 – 1.99 (m, 2H), 1.78 (d, *J* = 15.0 Hz, 6H), 1.74 – 1.60 (m, 1H), 1.50-1.34 (m, 1H).

¹³C NMR (76 MHz, CDCl₃) δ 131.4, 130.7, 99.2, 72.7, 62.0, 47.0, 32.6, 31.9, 30.7, 28.8, 26.1.

GC : rt = 8.32 min.

2-(2-bromo-3,3,3-trichlorobutyl)phenol **3qa**



Chemical Formula: C₁₀H₁₀BrCl₃O
Molecular Weight: 332,44

To a solution of bromotrichloromethane (3.3 mmol, 1.1 equiv., 325 μ L) in MTBE (300 μ L) was added 35 μ g of DIPAB (0.3 mmol, 10 mol%), followed by allyl phenol (3 mmol, 1 equiv., 392 μ L). After 6h at 60°C, reaction mixture was concentrated under reduced pressure. Crude mixture was purified by chromatography on silica gel, eluting with 100% cyclohexane to 98/2 toluene/ethylacetate to give 2-(2-bromo-3,3,3-trichlorobutyl)phenol **3qa** (283 mg, 28%) as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.22 – 7.07 (m, 2H), 6.92 (td, J = 7.4, 1.2 Hz, 1H), 6.75 (dd, J = 10.5, 5.0 Hz, 1H), 5.03 (s, 1H), 4.76 – 4.63 (m, 1H), 3.53 – 3.12 (m, 4H).

¹³C NMR (76 MHz, CDCl₃) δ 153.8, 132.0, 128.8, 124.2, 121.1, 115.7, 97.3, 61.9, 47.5, 41.2.

GC: 9.117 min;

HRMS m/z (EI+) Found: [M] 329.8981. C₁₀H₁₀BrCl₃O Found M = 329.8981.

6. References for already described products

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