

Supporting information

Catalytic *Vicinal* Dichlorination of Unactivated Alkenes

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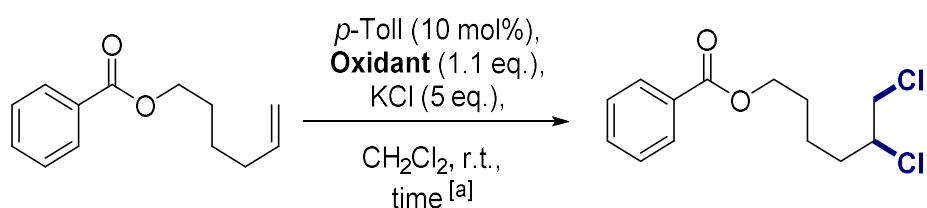
I. General information

All chemicals were purchased as reagent grade and used as received except for 4-chlorostyrene and 11-bromo-1-undecene which were filtered through silica using 100% *n*-pentane prior to use. Dry solvents were dried by a Grubbs purification system including columns packed with molecular sieves and aluminium oxide. Solvents for extraction or purification were purchased as technical grade and distilled on the rotary evaporator prior to use (exception: diethyl ether was used as purchased). Column chromatography was performed using silica gel (40-63 μm ; *VWR Chemicals*) as stationary phase. Reaction monitoring was achieved by analytical thin layer chromatography (TLC) on aluminum foil pre-coated with silica gel 60 F₂₅₄ (*Merck*). Compounds were visualised with UV light (254 nm) or by chemical staining using solution of KMnO_4 (KMnO_4 (10 g), K_2CO_3 (65 g), NaOH (1 N, 15 mL) in water (1 L)) or of CAM ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (50 g), $\text{Ce}(\text{SO}_4)_2$ (10 g), conc. H_2SO_4 (100 mL) in water (900 mL)) followed by heating. Concentration in *vacuo* was performed at ~10 mbar at 40 °C unless otherwise stated. NMR spectra were measured by the NMR service in the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a *Bruker Avance II 300*, a *Bruker Avance II 400*, an *Agilent DD2 500* or an *Agilent DD2 600* spectrometer at 298 K. ^1H NMR chemical shifts are given relative to TMS and are referenced to the residual solvent peak as internal standard. Spectra of other nuclides as ^{13}C and ^{19}F are referenced according to the proton resonance of TMS as the primary reference for the unified chemical shift scale. ^1H NMR spectra are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant J_{PH} , J_{FH} and J_{HH} in Hz, number of protons, assignment of proton). ^{13}C NMR spectra are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant J_{PC} , J_{FC} in Hz, number of carbons, assignment of carbon). ^{19}F NMR spectra are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant J_{FH} in Hz, number of fluorines, assignment

of fluorine). The resonance multiplicity is abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) or m (multiplet). Assignments of unknown compounds are based on COSY, HMBC and HSQC spectra. Melting points were measured on a *Büchi B-545* melting point apparatus in open capillaries and are uncorrected. IR spectra were recorded on a *Perkin-Elmer 100 FT-IR* spectrometer. Absorption bands are reported in wave numbers (cm^{-1}) and the intensities are reported as w (weak), m (medium), s (strong). Mass spectra were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität on a *Bruker Daltonics MicroTof* (HRMS-ESI), a *Triplequad TSQ 7000* (MS-EI), *Triplequad Quattro Micro GC* (GC-EI-MS), a *Qp5050 Single Quad* (GC-EI-MS) or a *LTQ Orbitap LTQ XL* (HRMS-APCI). Enantiomeric ratios were determined on an Agilent Infinity 1260 HPLC system using a diode array detector (DAD). The chiral stationary phases were OJ, OM and AM. The eluent of *n*-hexane and *i*-propanol is specified for each compound. The column temperature measured 25 to 35°C.

II. Reaction optimisation

a. Table S1: Exploring alternative oxidants.



Entry	Oxidant	MCI	time (h)	Yield ^[a]
1	Ground oxone [®]	KCl	15	67%
2 ^[b]	<i>Ground oxone[®]</i>	<i>KCl</i>	<i>15</i>	<i>70%</i>
3	<i>m</i> CPBA	KCl	15	5% ^[c]
4	aq. NaOCl 10%	KCl	15	<5%
5	NaIO ₄	KCl	15	<5%
6	CAN	KCl	15	<5%
7	<i>t</i> -BuOOH	KCl	15	<5%
8	aq. H ₂ O ₂ 30%	KCl	15	<5%
9	K ₂ S ₂ O ₈	KCl	15	<5%
10	CH ₃ CO ₃ H	KCl	15	<5%
11	CH ₃ CO ₃ H	TMSCl	15	40%
12 ^[b]	<i>CH₃CO₃H</i>	<i>TMSCl</i>	<i>15</i>	<i>46%</i>
13	Selectfluor [®]	KCl	15	<5%
14 ^[d]	Selectfluor [®]	KCl	3	59%
15 ^{[b][d]}	<i>Selectfluor[®]</i>	<i>KCl</i>	<i>3</i>	<i><5%</i>

[a] ¹H NMR yield using DMF as internal standard. [b] Control experiment without catalyst. [c] Epoxidation of the alkene was observed. The analytic data of the isolated product are in agreement with the literature.¹ [d] HFIP instead of CH₂Cl₂.

b. Table S2: Interrogating the role of HFIP as an additive.

$$\begin{array}{c}
 p\text{-Toll (10 mol\%),} \\
 \text{Selectfluor}^{\text{®}} (1.1 \text{ eq.}), \\
 \text{CsCl (3 eq.)}, \\
 \text{HFIP (X eq.)}, \\
 \xrightarrow{\text{CH}_2\text{Cl}_2, 0\text{ }^{\circ}\text{C}, 8 \text{ h [a]}}
 \end{array}$$

Entry	HFIP (X eq.)	Yield ^[a]
1	0	0%
2	4	45%
3	6	56%
4	8	81%
5	9	84%
6	10	84%

[a] ¹H NMR yield using DMF as internal standard.

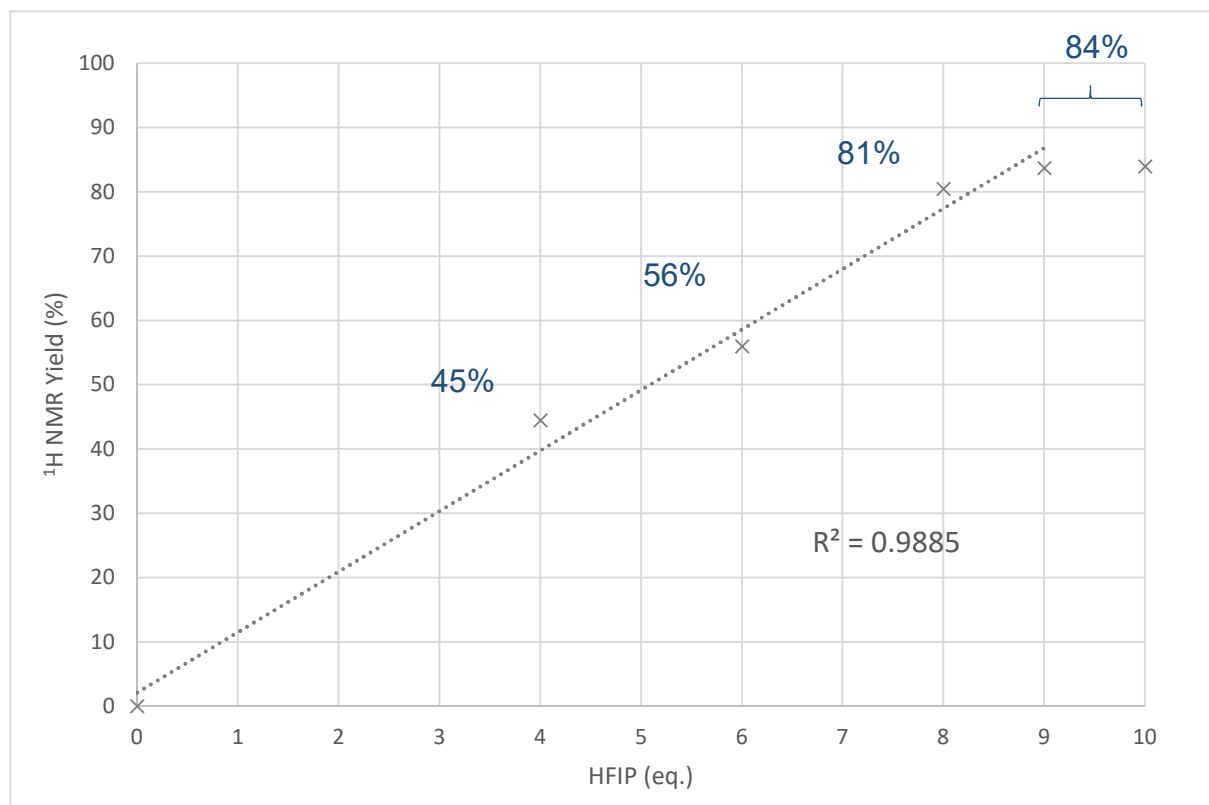


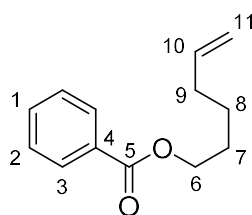
Figure S1: Dependency of the ¹H NMR yield in function of HFIP.

III. Synthesis of starting materials

General procedure A for the esterification of acyl chlorides with alkenols

The corresponding alkenol (1.0 eq.) and acyl chloride (1.1-2.0 eq.) were dissolved in diethyl ether. Then NEt_3 (1.1-2.0 eq.) was added slowly and the reaction mixture was stirred for the indicated time (monitored by TLC) at ambient temperature. The reaction mixture was diluted with ethyl acetate and water, and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were washed with water and brine, dried over MgSO_4 and filtered. The solvent was removed in *vacuo* and the crude mixture was purified by column chromatography.

Hex-5-en-1-yl benzoate (**1**)



According **General Procedure A** hex-5-en-1-ol (2.0 mL, 17 mmol, 1.0 eq.) and benzoyl chloride (2.1 mL, 18 mmol, 1.1 eq.) were dissolved in diethyl ether (16 mL). NEt_3 (2.6 mL, 18 mmol, 1.1 eq.)

was added slowly and the reaction mixture was stirred for 19 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford hex-5-en-1-yl benzoate (**1**) as a colourless oil (3.1 g, 15 mmol, 92%).

Rf: (cyclohexane:ethyl acetate 95:5) 0.32;

^1H NMR (400 MHz, CDCl_3) δ = 8.05 (m, 2H, H^3), 7.55 (m, 1H, H^1), 7.44 (m, 2H, H^2), 5.82 (ddt, $^3J_{\text{HH}} = 16.9, 10.3, 6.7$ Hz, 1H, H^{10}), 5.04 (td, $^3J_{\text{HH}} = 16.9$ Hz, $^2J_{\text{HH}} = 1.8$ Hz, 1H, $\text{H}^{11\text{E}}$), 4.98 (td, $^3J_{\text{HH}} = 10.3$ Hz, $^2J_{\text{HH}} = 1.8$ Hz, 1H, $\text{H}^{11\text{Z}}$), 4.33 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, H^6), 2.14 (td, $^3J_{\text{HH}} = 7.6, 6.7$ Hz, 2H, H^9), 1.82 (tt, $^3J_{\text{HH}} = 7.4, 6.6$ Hz, 2H, H^7), 1.58 (tt, $^3J_{\text{HH}} = 7.6, 7.4$ Hz, 2H, H^8) ppm;

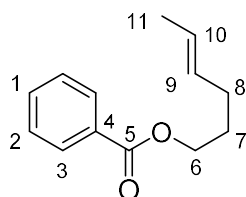
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 166.8 (1C, C^5), 138.5 (1C, C^{10}), 132.9 (1C, C^1), 130.6 (1C, C^4), 129.7 (2C, C^3), 128.4 (2C, C^2), 115.0 (1C, C^{11}), 65.0 (1C, C^6), 33.4 (1C, C^9), 28.3 (1C, C^7), 25.4 (1C, C^8) ppm;

IR (ATR) $\tilde{\nu}$ = 3075 (w), 2936 (w), 2860 (w), 1716 (s), 1640 (w), 1602 (w), 1585 (w), 1451 (m), 1385 (w), 1314 (m), 1268 (s), 1175 (m), 1109 (s), 1069 (m), 1026 (m), 993 (m), 910 (m), 805 (w), 707 (s), 686 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}^+$: 227.1043, found: 227.1040.

The analytic data are in agreement with the literature.²

(E)-Hex-4-en-1-yl benzoate (S1**)**



According **General Procedure A** (*E*)-hex-4-en-1-ol (2.0 mL, 17 mmol, 1.0 eq.) and benzoyl chloride (2.2 mL, 18 mmol, 1.1 eq.) were dissolved in diethyl ether (16 mL). Then NEt_3 (2.6 mL, 18

mmol, 1.1 eq.) was added slowly and the reaction mixture was stirred for 19 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford (*E*)-hex-4-en-1-yl benzoate (**S1**) as a colourless oil (3.2 g, 16 mmol, 94%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.69;

^1H NMR (599 MHz, CDCl_3) δ = 8.05 (m, 2H, H^3), 7.55 (m, 1H, H^1), 7.44 (m, 2H, H^2), 5.53 – 5.39 (m, 2H, H^9 , H^{10}), 4.32 (t, $^3J_{\text{HH}}$ = 6.7 Hz, 2H, H^6), 2.15 (tdd, $^3J_{\text{HH}}$ = 7.7, 6.1 Hz, $^4J_{\text{HH}}$ = 1.5 Hz, 2H, H^8), 1.83 (tt, $^3J_{\text{HH}}$ = 7.7, 6.7 Hz, 2H, H^7), 1.67 – 1.64 (m, 3H, H^{11}) ppm;

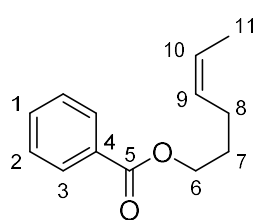
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ = 166.8 (1C, C^5), 132.9 (1C, C^1), 130.6 (1C, C^4), 130.1 (1C, C^9), 129.7 (2C, C^3), 128.4 (2C, C^2), 126.0 (1C, C^{10}), 64.6 (1C, C^6), 29.1 (1C, C^8), 28.7 (1C, C^7), 18.0 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 2937 (w), 1716 (s), 1602 (w), 1585 (w), 1450 (m), 1385 (w), 1314 (m), 1268 (s), 1175 (m), 1109 (s), 1069 (m), 1026 (m), 965 (m), 927 (w), 806 (w), 707 (s), 686 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}^+$: 227.1043, found: 227.1049.

The analytic data are in agreement with the literature.³

(Z)-Hex-4-en-1-yl benzoate (**S2**)



According **General Procedure A** (Z)-hex-4-en-1-ol (1.0 mL, 8.3 mmol, 1.0 eq.) and benzoyl chloride (1.1 mL, 9.2 mmol, 1.1 eq.) were dissolved in diethyl ether (8 mL). Then NEt_3 (1.3 mL, 9.2 mmol, 1.1 eq.) was added slowly and the reaction mixture was

stirred for 19 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford (Z)-hex-4-en-1-yl benzoate (**S2**) as a colourless oil (1.0 g, 5.1 mmol, 61%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.69;

^1H NMR (599 MHz, CDCl_3) δ = 8.06 (m, 2H, H^3), 7.56 (m, 1H, H^1), 7.44 (m, 2H, H^2), 5.52 (dqt, $^3J_{\text{HH}} = 10.8$, 6.6 Hz, $^4J_{\text{HH}} = 1.5$ Hz, 1H, H^{10}), 5.42 (dtq, $^3J_{\text{HH}} = 10.8$, 7.2 Hz, $^4J_{\text{HH}} = 1.7$ Hz, 1H, H^9), 4.33 (t, $^3J_{\text{HH}} = 6.6$ Hz, 2H, H^6), 2.22 (tddq, $^3J_{\text{HH}} = 7.4$, 7.2 Hz, $^4J_{\text{HH}} = 1.6$ Hz, $^5J_{\text{HH}} = 0.9$ Hz, 2H, H^8), 1.85 (tt, $^3J_{\text{HH}} = 7.4$, 6.6 Hz, 2H, H^7), 1.62 (ddt, $^3J_{\text{HH}} = 6.8$ Hz, $^4J_{\text{HH}} = 1.7$ Hz, $^5J_{\text{HH}} = 0.9$ Hz, 3H, H^{11}) ppm;

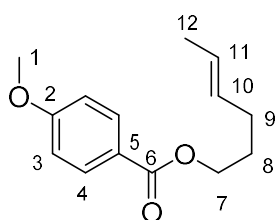
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ = 166.8 (1C, C^5), 132.9 (1C, C^1), 130.6 (1C, C^4), 129.7 (2C, C^3), 129.2 (1C, C^9), 128.5 (2C, C^2), 125.2 (1C, C^{10}), 64.6 (1C, C^6), 28.7 (1C, C^7), 23.4 (1C, C^8), 12.9 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 3014 (w), 2953 (w), 1716 (s), 1602 (w), 1585 (w), 1451 (m), 1386 (w), 1314 (m), 1268 (s), 1175 (m), 1109 (s), 1069 (m), 1026 (m), 997 (w), 966 (w), 806 (w), 707 (s), 686 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}^+$: 227.1043, found: 227.1039.

The analytic data are in agreement with the literature.⁴

(*E*)-Hex-4-en-1-yl 4-methoxybenzoate (S3**)**



According **General Procedure A** (*E*)-hex-4-en-1-ol (0.59 mL, 5.0 mmol, 1.0 eq.) and 4-methoxybenzoyl chloride (0.78 mL, 5.5 mmol, 1.1 eq.) were dissolved in diethyl ether (6 mL). Then NEt_3 (0.77 mL, 5.5 mmol, 1.1 eq.) was added slowly and the

reaction mixture was stirred for 19 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford (*E*)-hex-4-en-1-yl 4-methoxybenzoate (**S3**) as a colourless oil (0.82 g, 3.5 mmol, 63%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.41;

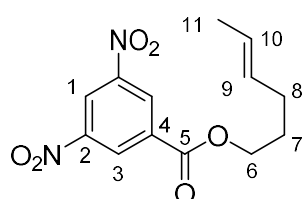
^1H NMR (599 MHz, CDCl_3) δ = 8.01 (m, 2H, H^4), 6.91 (m, 2H, H^3), 5.52 – 5.41 (m, 2H, $\text{H}^{10}, \text{H}^{11}$), 4.28 (t, $^3J_{\text{HH}}$ = 6.6 Hz, 2H, H^7), 3.85 (s, 3H, H^1), 2.17 – 2.07 (m, 2H, H^9), 1.81 (tt, $^3J_{\text{HH}}$ = 7.9, 6.6 Hz, 2H, H^8), 1.68 – 1.62 (m, 3H, H^{12}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ = 166.5 (1C, C^6), 163.4 (1C, C^5), 131.7 (2C, C^4), 130.2 (1C, C^{10}), 126.0 (1C, C^{11}), 123.1 (1C, C^2), 113.7 (2C, C^3), 64.3 (1C, C^7), 55.5 (1C, C^1), 29.2 (1C, C^9), 28.7 (1C, C^8), 18.0 (1C, C^{12}) ppm;

IR (ATR) $\tilde{\nu}$ = 2937 (w), 2284 (w), 1708 (s), 1605 (s), 1510 (m), 1457 (w), 1385 (w), 1315 (w), 1271 (s), 1250 (s), 1100 (s), 1028 (s), 965 (m), 846 (m), 768 (s), 695 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}^+$: 257.1148, found: 257.1158.

(E)-Hex-4-en-1-yl 3,5-dinitrobenzoate (S4)



According **General Procedure A** (*E*)-hex-4-en-1-ol (0.94 mL, 8.0 mmol, 1.0 eq.) and 3,5-dinitrobenzoyl chloride (3.6 g, 16 mmol, 2.0 eq.) were dissolved in diethyl ether (30 mL). Then

NEt_3 (2.2 mL, 16 mmol, 2.0 eq.) was added slowly and the reaction mixture was stirred for 5 days. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford (*E*)-hex-4-en-1-yl 3,5-dinitrobenzoate (**S4**) as a yellow solid (1.7 g, 5.7 mmol, 71%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.34;

M.p. 36-38 $^{\circ}\text{C}$;

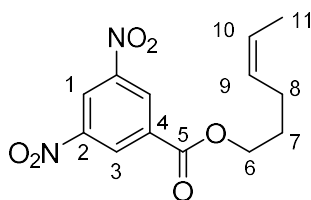
^1H NMR (400 MHz, CDCl_3) δ = 9.21 (m, 1H, H^1), 9.14 (m, 2H; H^3), 5.61 – 5.34 (m, 2H, H^9 , H^{10}), 4.45 (t, $^3J_{\text{HH}}$ = 6.6 Hz, 2H, H^6), 2.16 (tdd, $^3J_{\text{HH}}$ = 7.0, 6.6, Hz, $^4J_{\text{HH}}$ = 1.5 Hz, 2H, H^8), 1.89 (tt, $^3J_{\text{HH}}$ = 7.0, 6.6 Hz, 2H, H^7), 1.65 (d, $^3J_{\text{HH}}$ = 5.5 Hz, 3H, H^{11}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 162.6 (1C, C^5), 148.8 (2C, C^2), 134.2 (1C, C^4), 129.5 (3C, C^3 , C^9), 126.6 (1C, C^{10}), 122.4 (1C, C^1), 66.7 (1C, C^6), 29.0 (1C, C^8), 28.4 (1C, C^7), 18.0 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 3097 (m), 1723 (s), 1628 (m), 1595 (w), 1539 (s), 1461 (w), 1459 (w), 1341 (s), 1278 (s), 1168 (s), 1079 (w), 1023 (w), 959 (s), 919 (m), 855 (w), 825 (w), 777 (w), 719 (s) cm^{-1} ;

HRMS (ESI) m/z $[M+Ag]^+$, calcd. for $C_{13}H_{14}N_2O_6Ag^+$: 400.9897, found 400.9903.

(Z)-Hex-4-en-1-yl 3,5-dinitrobenzoate (S5)



According **General Procedure A** (Z)-hex-4-en-1-ol (0.47 mL, 4.0 mmol, 1.0 eq.) and 3,5-dinitrobenzoyl chloride (1.8 g, 8.0 mmol, 2.0 eq.) were dissolved in diethyl ether (15 mL).

Then NEt_3 (1.1 mL, 8.0 mmol, 2.0 eq.) was added slowly and the reaction mixture was stirred for 5 days. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford (Z)-hex-4-en-1-yl 3,5-dinitrobenzoate (**S5**) as a yellow solid (0.82 g, 2.8 mmol, 69%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.34;

M.p. 26-28 °C;

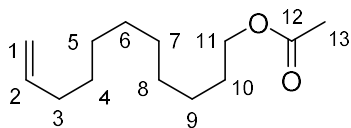
1H NMR (400 MHz, $CDCl_3$) δ = 9.21 (m, 1H, H^1), 9.15 (m, 2H, H^3), 5.55 (dq, $^3J_{HH}$ = 10.8, 5.9 Hz, 1H, H^{10}), 5.42 (dtq, $^3J_{HH}$ = 10.8, 7.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H^9), 4.46 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H^6), 2.23 (tdq, $^3J_{HH}$ = 7.4, 7.0 Hz, $^5J_{HH}$ = 0.9 Hz, 2H, H^8), 1.91 (tt, $^3J_{HH}$ = 7.4, 6.7 Hz, 2H, H^7), 1.63 (ddt, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 1.8 Hz, $^5J_{HH}$ = 0.9 Hz, 3H, H^{11}) ppm;

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 162.6 (1C, C^5), 148.8 (2C, C^2), 134.2 (1C, C^4), 129.5 (2C, C^3), 128.7 (1C, C^9), 125.5 (1C, C^{10}), 122.4 (1C, C^1), 66.6 (1C, C^6), 28.4 (1C, C^7), 23.3 (1C, C^8), 12.9 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 3098 (m), 1842 (w), 1719 (s), 1629 (m), 1541 (s), 1464 (m), 1346 (s), 1284 (m), 1171 (m), 1075 (m), 1022 (m), 922 (m), 882 (m), 827 (m), 773 (m), 718 (s), 680 (m) cm^{-1} ;

HRMS (ESI) m/z $[M+Ag]^+$, calcd. for $C_{13}H_{14}N_2O_6Ag^+$: 400.9897, found 400.9902.

Undec-10-en-1-yl acetate (**S6**)



10-Undecen-1-ol (1.00 mL, 5.0 mmol, 1.0 eq.) and pyridine (0.60 mL, 7.5 mmol, 1.5 eq.) were diluted in CH_2Cl_2 (1 mL). The mixture was cooled down to 0°C and

acetyl chloride (0.39 mL, 5.5 mmol, 1.1 eq.) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 and was washed with 1N HCl, water, and brine. The organic layer was dried over MgSO_4 , filtered and the solvent was removed in *vacuo*. The crude mixture was purified by column chromatography using *n*-pentane: CH_2Cl_2 1:1 to afford undec-10-en-1-yl acetate (**S6**) as a colourless oil (0.99 g, 4.7 mmol, 93%).

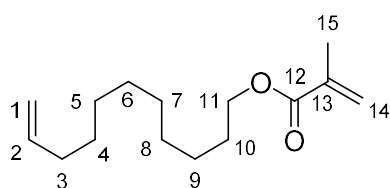
Rf: (*n*-pentane: CH_2Cl_2 1:1) 0.48;

^1H NMR (400 MHz, CDCl_3) δ = 5.80 (ddt, J_{HH} = 16.9, 10.2, 6.7 Hz, 1H, H^2), 4.98 (dq, J_{HH} = 17.2, 1.7 Hz, 1H, $\text{H}^{1\text{E}}$), 4.92 (ddt, J_{HH} = 10.2, 2.4, 1.2 Hz, 1H, $\text{H}^{1\text{Z}}$), 4.04 (t, J_{HH} = 6.8 Hz, 2H, H^{11}), 2.04 (s, 3H, H^{13}), 2.08 – 1.99 (m, 2H, H^3), 1.65 – 1.55 (m, 2H, H^{10}), 1.42 – 1.23 (m, 12H, $\text{H}^4\text{-H}^9$) ppm;

HRMS (ESI) m/z [$\text{M}+\text{Na}$] $^+$ calcd. for $\text{C}_{13}\text{H}_{24}\text{NaO}_2^+$: 235.1669, found: 235.1678.

The analytic data are in agreement with the literature.⁵

Undec-10-en-1-yl methacrylate (**S7**)



According to **General Procedure A**, 10-undecen-1-ol (1.00 mL, 5.0 mmol, 1.0 eq.) and methacryloyl chloride (0.97 mL, 10.0 mmol, 2.0 eq.) were dissolved in diethyl ether (5 mL). Then NEt_3 (1.4 mL, 10.0 mmol, 2.0 eq.) was added slowly and the reaction mixture was stirred for 24 h. The crude mixture was purified by column chromatography using *n*-pentane: CH_2Cl_2 3:1 to afford undec-10-en-1-yl methacrylate (**S7**) as a colourless oil (1.01 g, 4.2 mmol, 85%).

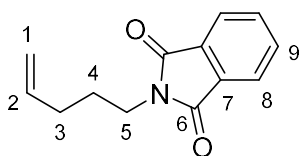
Rf: (*n*-pentane: CH_2Cl_2 3:1) 0.42;

^1H NMR (400 MHz, CDCl_3) δ = 6.09 (br s, 1H), 5.81 (ddt, J_{HH} = 16.9, 10.2, 6.7 Hz, 1H), 5.54 (m, 1H), 4.99 (m, 1H), 4.93 (m, 1H), 4.13 (t, J_{HH} = 6.7 Hz, 2H), 2.04 (q, J_{HH} = 6.9 Hz, 2H), 1.94 (br s, J_{HH} = 1.4 Hz, 3H), 1.66 (p, J_{HH} = 6.7 Hz, 2H), 1.41 – 1.25 (m, 12H) ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{26}\text{NaO}_2^+$: 261.1825, found: 261.1830.

The analytic data are in agreement with the literature.⁶

2-(Pent-4-en-1-yl)isoindoline-1,3-dione (**S8**)



5-Bromopent-1-ene (0.30 mL, 2.5 mmol, 1.0 eq.) and potassium phthalimide (1.4 g, 7.5 mmol, 3.0 eq.) were suspended in DMF (20 mL). The reaction mixture was stirred at 60°C for 16 h. The reaction mixture was diluted with ethyl acetate and washed with water (5x). The organic layer was dried over MgSO_4 , filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using *n*-pentane:ethyl acetate 15:1 to afford 2-(pent-4-en-1-yl)isoindoline-1,3-dione (**S8**) as a colourless oil (441 mg, 2.0 mmol, 82%).

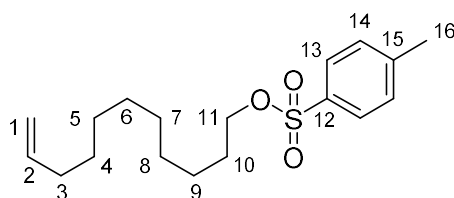
Rf: (*n*-pentane:ethyl acetate 15:1) 0.24;

¹H NMR (300 MHz, CDCl₃) δ = 7.84 (dd, J_{HH} = 5.4, 3.1 Hz, 2H), 7.71 (dd, J_{HH} = 5.5, 3.0 Hz, 2H), 5.82 (ddt, J_{HH} = 16.8, 10.2, 6.5 Hz, 1H), 5.05 (dq, J_{HH} = 17.1, 1.7 Hz, 1H), 4.98 (dq, J_{HH} = 10.2, 1.4 Hz, 1H), 3.70 (t, J_{HH} = 7.3 Hz, 2H), 2.18 – 2.06 (m, 2H), 1.87 – 1.71 (m, 2H);

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₃NNaO₂⁺: 238.0838, found: 238.0845.

The analytic data are in agreement with the literature.⁵

Undec-10-en-1-yl 4-methylbenzenesulfonate (**S9**)



p-Toluenesulfonyl chloride (1.43 g, 7.5 mmol, 1.5 eq.) was dissolved in pyridine (2.50 mL) and cooled down to 0°C. 10-Undecen-1-ol (1.00 mL,

5.0 mmol, 1.0 eq.) was added dropwise to the mixture which was then stirred for 2 h. Upon completion, the reaction mixture was poured on a mixture ice/HCl_{conc.} and was extracted with ethyl acetate (3x). The combined organic layers were washed with water and brine, dried over MgSO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using a gradient *n*-pentane:CH₂Cl₂ 1:9 to 3:7 to afford undec-10-en-1-yl 4-methylbenzenesulfonate (**S9**) as a colourless oil (1.05 g, 3.2 mmol, 65%).

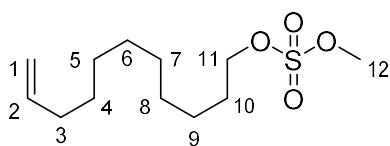
Rf: (*n*-pentane:CH₂Cl₂ 9:1) 0.27;

¹H NMR (400 MHz, CDCl₃) δ = 7.79 (m, 2H), 7.34 (m, 2H), 5.80 (ddt, J_{HH} = 17.0, 10.2, 6.6 Hz, 1H), 4.99 (m, 1H), 4.93 (m, 1H), 4.02 (t, J_{HH} = 6.5 Hz, 2H), 2.45 (s, 3H), 2.03 (m, 2H), 1.63 (m, 2H), 1.40 – 1.31 (m, 2H), 1.31 – 1.16 (m, 10H) ppm;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₈H₂₈NaO₃S⁺: 347.1651, found: 347.1658.

The analytic data are in agreement with the literature.⁵

Methyl undec-10-en-1-yl sulfate (**S10**)



This compound was prepared according to a modified procedure from *Ooi et al.*⁷ Sulfur trioxide pyridine complex (0.56 g, 3.5 mmol, 3.5 eq.) was suspended in tetrahydrofuran (15 mL). 10-Undecen-1-ol (0.20 mL, 1.0 mmol, 1.0 eq.) was added dropwise to the mixture which was then stirred at ambient temperature for 18 h. The reaction mixture was diluted with ethyl acetate and washed with water (1x) and brine (2x). The organic layer was dried over MgSO₄, filtered and evaporated under *vacuo*. The crude mixture (0.20 g) was suspended in CH₂Cl₂ (20 mL). The round-bottom flask was wrapped in aluminium foil, proton-sponge (1.07 g, 5.0 mmol, 5.0 eq.) was added in one portion and trimethyloxonium tetrafluoroborate (0.74 g, 5.0 mmol, 5.0 eq.) was added in two portions. The reaction mixture was stirred at ambient temperature for 5 h. Upon completion, the reaction mixture was treated with 1N HCl and extracted with CH₂Cl₂ (3x). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed in *vacuo*. The crude mixture was purified by column chromatography using a gradient of *n*-pentane:CH₂Cl₂ 4:1 to 3:2 to afford methyl undec-10-en-1-yl sulfate (**S10**) as a colourless oil (0.14 g, 0.5 mmol, 54% over two steps).

Rf: (*n*-pentane:CH₂Cl₂ 4:1) 0.11;

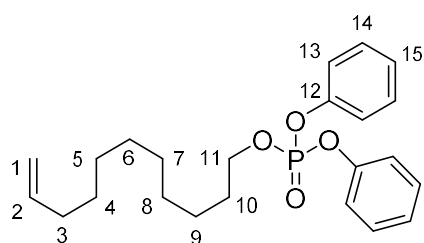
¹H NMR (400 MHz, CDCl₃) δ = 5.80 (dddd, ³*J*_{HH} = 17.1, 12.5, 6.7, 3.3 Hz, 1H, H²), 4.99 (ddt, ³*J*_{HH} = 17.1 Hz, ²*J*_{HH} = 2.4 Hz, ⁴*J*_{HH} = 1.6 Hz, 1H, H^{1Z}), 4.93 (ddt, ³*J*_{HH} = 10.2 Hz, ²*J*_{HH} = 2.5 Hz, ⁴*J*_{HH} = 1.3 Hz, 1H, H^{1E}), 4.26 (t, ³*J*_{HH} = 6.6 Hz, 2H, H¹¹), 3.95 (s, 3H, H¹²), 2.04 (qd, ³*J*_{HH} = 8.1, 6.8 Hz, 2H, H³), 1.76 (p, ³*J*_{HH} = 6.7 Hz, 2H, H¹⁰), 1.45 – 1.25 (m, 12H, H⁴⁻⁹) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 139.3 (1C, C^2), 114.3 (1C, C^1), 73.8 (1C, C^{11}), 58.4 (1C, C^{12}), 33.9 (1C, C^3), 29.5 (2C), 29.2 (1C), 29.1 (1C), 29.0 (1C, C^4), 28.9 (1C), 25.5 (1C, C^9) ppm;

IR (ATR) $\tilde{\nu}$ = 2926 (m), 2855 (m), 1641 (w), 1463 (w), 1397 (m), 1194 (s), 997 (m), 946 (m), 914 (m), 826 (m), 799 (m), 772 (m), 723 (w) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{24}\text{NaO}_4\text{S}^+$: 287.1288, found: 287.1291.

Diphenyl undec-10-en-1-yl phosphate (**S11**)



This compound was prepared according to a modified procedure from *Dieter et al.*⁸ 10-Undecen-1-ol (0.20 mL, 1.0 mmol, 1.0 eq.) and NEt_3 (0.28 mL, 2.0 mmol, 2.0 eq.) were diluted in dry tetrahydrofuran (5 mL) and the resulting solution was cooled to 0°C . Diphenyl phosphorochloridate (0.31 mL, 1.5 mmol, 1.5 eq.) was added dropwise into the reaction mixture which was allowed to warm to ambient temperature and was stirred for 24 h. The reaction mixture was diluted with ethyl acetate and water, and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were washed with water and brine, dried over MgSO_4 , filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using *n*-pentane: CH_2Cl_2 1:1 to afford diphenyl undec-10-en-1-yl phosphate (**S11**) as a light yellow oil (0.27 g, 0.7 mmol, 68%).

Rf: (CH_2Cl_2 100%) 0.54;

^1H NMR (400 MHz, CDCl_3) δ = 7.34 (m, 4H, H^{14}), 7.21 (m, 6H, H^{13} , H^{15}), 5.81 (ddt, $^3J_{\text{HH}}$ = 16.8, 9.9, 6.7 Hz, 1H, H^2), 4.99 (dq, $^3J_{\text{HH}}$ = 17.1 Hz, $^2J_{\text{HH}}$ = 1.8 Hz, 1H, $\text{H}^{1\text{E}}$), 4.93 (dd, $^3J_{\text{HH}}$ = 10.1 Hz, $^2J_{\text{HH}}$ = 2.3 Hz, 1H, $\text{H}^{1\text{Z}}$), 4.24 (td, $^3J_{\text{PH}}$ = 7.7 Hz, $^3J_{\text{HH}}$ = 6.9 Hz, 2H,

H¹¹), 2.04 (q, ³J_{HH} = 7.1 Hz, 2H, H³), 1.69 (p, ³J_{HH} = 6.9 Hz, 2H, H¹⁰), 1.43 – 1.19 (m, 12H, H⁴⁻⁹) ppm;

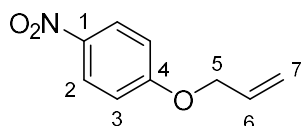
¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 150.8 (d, ²J_{PC} = 7.2 Hz, 2C, C¹²), 139.3 (1C, C²), 129.9 (4C, C¹⁴), 125.4 (2C, C¹⁵), 120.2 (d, ³J_{PC} = 4.9 Hz, 4C, C¹³), 114.3 (1C, C¹), 69.6 (d, ²J_{PC} = 6.6 Hz, 1C, C¹¹), 33.9 (1C, C³), 30.3 (d, ³J_{PC} = 6.8 Hz, 1C, C¹⁰), 29.5 (2C), 29.2 (1C), 29.1 (1C), 29.0 (1C, C⁴), 25.4 (1C, C⁹) ppm;

³¹P NMR (162 MHz, CDCl₃) δ = -11.81 (t, ³J_{PH} = 7.7 Hz) ppm;

IR (ATR) $\tilde{\nu}$ = 3075 (w), 2926 (m), 2855 (w), 1640 (w), 1591 (m), 1489 (m), 1457 (w), 1394 (w), 1287 (m), 1221 (m), 1189 (s), 1163 (m), 1023 (m), 1008 (m), 940 (s), 904 (m), 823 (w), 753 (m), 687 (s) cm⁻¹;

HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₂₃H₃₁NaO₄P⁺: 425.1852, found: 425.1845.

1-(Allyloxy)-4-nitrobenzene (**S12**)



This compound was prepared according to a modified procedure from *Jana et al.*⁹ 4-Nitrophenol (1.0 g, 7.2 mmol, 1.0 eq.) and K₂CO₃ (2.0 g, 14.4 mmol, 2.0 eq.) were combined in DMF (15 mL). To this suspension was added allyl bromide (623 μ L, 7.2 mmol, 1.0 eq.) and the mixture was stirred at ambient temperature for 16 h. The reaction mixture was diluted with ethyl acetate, washed with a saturated solution of NH₄Cl (1x) as well as with water (5x). The resulting organic layer was dried over MgSO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 4:1 to afford 1-(allyloxy)-4-nitrobenzene (**S12**) as a yellow oil (1.1 g, 6.1 mmol, 84%).

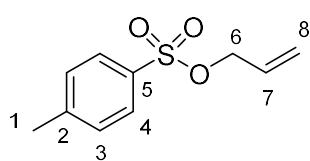
Rf: (cyclohexane:ethyl acetate 4:1) 0.55;

¹H NMR (400 MHz, CDCl₃) δ = 8.19 (m, 2H), 6.97 (m, 2H), 6.04 (ddt, ³J_{HH} = 17.3, 10.6, 5.3 Hz, 1H, H⁶), 5.43 (dq, ³J_{HH} = 17.2, ⁴J_{HH} = 1.5 Hz, 1H, H^{7E}), 5.35 (dq, ³J_{HH} = 10.6, ⁴J_{HH} = 1.4 Hz, 1H; H^{7Z}), 4.63 (dt, ³J_{HH} = 5.3 Hz, ⁴J_{HH} = 1.5 Hz, 2H, H⁵) ppm;

HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₉H₉NNaO₃⁺: 202.0475, found: 202.0477.

The analytic data are in agreement with the literature.¹⁰

Allyl 4-methylbenzenesulfonate (**S13**)



NaH (480 mg, 12 mmol, 1.2 eq., 60% in mineral oil) was suspended in diethyl ether and cooled down to 0°C. Allyl alcohol (680 μ L, 10 mmol, 1.0 eq.) was added and the mixture was stirred at 0°C for 30 min. Finally, a solution of *p*-toluenesulfonyl chloride (1.91 g, 10 mmol, 1.0 eq.) in diethyl ether (20 mL) was added dropwise to the mixture which was then stirred for 3 h. Upon completion, the reaction mixture was diluted with diethyl ether, washed with a saturated solution of NH₄Cl, water and brine, dried over MgSO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using *n*-pentane:ethyl acetate 95:5 to afford allyl 4-methylbenzenesulfonate (**S13**) as a colourless oil (1.62 g, 7.6 mmol, 76%).

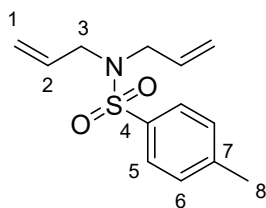
Rf: (*n*-pentane:ethyl acetate 9:1) 0.37;

¹H NMR (300 MHz, CDCl₃) δ = 7.78 (m, 2H), 7.34 (m, 2H), 5.80 (ddt, *J*_{HH} = 17.1, 10.3, 5.9 Hz, 1H, H⁷), 5.31 (dq, *J*_{HH} = 17.1, 1.4 Hz, 1H, H^{8E}), 5.24 (dq, *J*_{HH} = 10.3, 1.2 Hz, 1H, H^{8Z}), 4.51 (dt, *J*_{HH} = 5.9, 1.3 Hz, 2H, H⁶), 2.44 (s, 3H, H¹) ppm;

MS (EI) *m/z* (%) = 212.0 (5) [M]⁺, 155.0 (46) [M-C₃H₅O]⁺, 91.1 (100) [M-C₃H₅O₃S]⁺.

The analytic data are in agreement with the literature.¹¹

***N,N*-diallyl-4-methylbenzenesulfonamide (S14)**



This compound was prepared according to a modified procedure from Hayashi *et al.*¹² *p*-Toluenesulfonyl chloride (1.91 g, 10 mmol, 1.0 eq.) was dissolved in CH₂Cl₂ (35 mL). To this solution was added diallylamine (1.23 mL, 10 mmol, 1.0 eq.) and NEt₃ (1.53 mL, 11 mmol, 1.1 eq.) and the mixture was stirred at ambient temperature for 4 h. Upon completion, the reaction mixture was poured on a saturated solution of NH₄Cl and was extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried over MgSO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using *n*-pentane:ethyl acetate 9:1 to afford *N,N*-diallyl-4-methylbenzenesulfonamide (**S14**) as a colourless oil (2.34 g, 9.3 mmol, 93%).

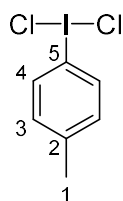
R_f: (*n*-pentane:ethyl acetate 9:1) 0.48;

¹H NMR (300 MHz, CDCl₃) δ = 7.71 (m, 2H), 7.29 (m, 2H), 5.60 (ddt, J_{HH} = 17.5, 9.8, 6.4 Hz, 2H, H²), 5.16 (m, 2H, H^{1a}), 5.11 (m, 2H, H^{1b}), 3.80 (dt, J_{HH} = 6.2, 1.3 Hz, 4H, H³), 2.42 (s, 3H, H⁸) ppm;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₇NNaO₂S⁺: 274.0872, found: 274.0878.

The analytic data are in agreement with the literature.¹²

Dichloro(*p*-tolyl)- λ^3 -iodane (**S15**)¹⁴



This compound was prepared according to a modified procedure from *Tao et al.*¹³ 4-Iodotoluene (1.0 g, 4.6 mmol, 1.0 eq.) was dissolved in acetonitrile (4.6 mL). water (3.5 mL) and aq. NaOCl (10%, 3.5 mL) were added slowly to the solution. Dropwise addition of aq. HCl (37%, 2.3 mL) led to a yellow precipitate. The residue was filtered and washed with water and *n*-pentane. Dichloro(*p*-tolyl)- λ^3 -iodane (**S15**) was obtained as a yellow solid (1.2 g, 4.1 mmol, 89%).

M.p. 102-105 °C;

¹H NMR (400 MHz, CDCl₃) δ = 8.05 (m, 2H, H⁴), 7.27 (m, 2H, H³), 2.47 (s, 3H, H¹) ppm;

¹³C NMR (101 MHz, CDCl₃) δ = 143.4 (1C, C²), 134.0 (2C, C⁴), 132.5 (2C, C³), 122.1 (1C, C⁵), 21.6 (1C, C¹) ppm;

IR (ATR) $\tilde{\nu}$ = 3774 (w), 3327 (s), 2942 (w), 2808 (m), 1598 (s), 1484 (m), 1481 (m), 1467 (m), 1389 (w), 1299 (w), 1207 (m), 1179 (m), 1006 (s), 994 (m), 794 (m) cm⁻¹;

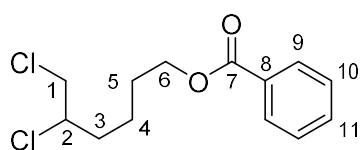
MS (EI) *m/z*: 287.9 (2) [M]⁺, 218.0 (100) [M-Cl₂]⁺, 91.0 (54) [M-ICl₂].

The analytic data are in agreement with the literature.¹⁴

IV. General procedure B for the catalytic dichlorination of terminal alkenes

The corresponding alkene (0.20 mmol, 1.0 eq.), *p*-iodotoluene (8.7 mg, 0.04 mmol, 0.2 eq.), cesium chloride (101 mg, 0.60 mmol, 3.0 eq.) and Selectfluor® (78.0 mg, 0.22 mmol, 1.1 eq.) were dissolved in a solution of HFIP (302 mg, 1.80 mmol, 9.0 eq.) in CH₂Cl₂ (0.9 mL). The mixture was cooled and stirred at 0°C (ice bath). After 8 h, the reaction mixture was quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR. The sample was then evaporated under *vacuo* and purified by column chromatography using the indicated solvent ratio.

5,6-Dichlorohexyl benzoate (**2**)



According to **General Procedure B** using hex-5-en-1-yl benzoate (41 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 95:5 to afford 5,6-dichlorohexyl benzoate (**2**) as a colourless oil (41 mg, 0.15 mmol, 75%).

For 1 mmol scale, according to **General Procedure B**: hex-5-en-1-yl benzoate (204 mg, 1.0 mmol, 1.0 eq.), *p*-iodotoluene (44 mg, 0.2 mmol, 0.2 eq.), cesium chloride (505 mg, 3.0 mmol, 3.0 eq.) and Selectfluor® (390 mg, 1.1 mmol, 1.1 eq.) were dissolved in a solution of HFIP (1.51 g, 9.0 mmol, 9.0 eq.) in CH₂Cl₂ (4.5 mL). The reaction mixture was stirred at 0°C for 8h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford 5,6-dichlorohexyl benzoate as a colourless oil (213 mg, 0.77 mmol, 77%).

Rf: (cyclohexane:ethyl acetate 95:5) 0.28;

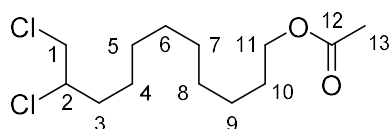
¹H NMR (500 MHz, CDCl₃) δ = 8.05 (m, 2H, H⁹), 7.56 (m, 1H, H¹¹), 7.44 (m, 2H, H¹⁰), 4.35 (td, ³J_{HH} = 6.4 Hz, J_{HH} = 1.7 Hz, 2H; H⁶), 4.06 (tdd, ³J_{HH} = 8.8, 5.0, 3.5 Hz, 1H, H²), 3.78 (dd, ³J_{HH} = 11.3, 5.0 Hz, 1H, H^{1a}), 3.66 (dd, ³J_{HH} = 11.3, 7.7 Hz, 1H, H^{1b}), 2.10 (m, 1H, H^{3a}), 1.92 – 1.67 (m, 4H, H^{3b}, H^{4a}, H⁵), 1.60 (m, 1H, H^{4b}) ppm;

¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 166.7 (1C, C⁷), 133.1 (1C, C¹¹), 130.5 (1C, C⁸), 129.7 (2C, C⁹), 128.5 (2C, C¹⁰), 64.7 (1C, C⁶), 60.9 (1C, C²), 48.2 (1C, C¹), 34.8 (1C, C³), 28.3 (1C, C⁵), 22.7 (1C, C⁴) ppm;

IR (ATR) $\tilde{\nu}$ = 2954 (w), 2870 (w), 1714 (s), 1602 (w), 1585 (w), 1492 (w), 1451 (m), 1386 (w), 1314 (m), 1270 (s), 1219 (m), 1193 (m), 1176 (m), 1114 (m), 1070 (m), 1026 (m), 971 (w), 936 (w), 900 (w), 806 (w), 708 (s), 687 (m), 675 (m), 661 (m) cm⁻¹;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₆Cl₂NaO₂⁺: 297.0420, found: 297.0420.

10,11-Dichloroundecyl acetate (**3**)



According to **General Procedure B** using undec-10-en-1-yl acetate (42 mg, 0.20 mmol, 1.0 eq.). The reaction

mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 98:2 to afford 10,11-dichloroundecyl acetate (**3**) as a colourless oil (38 mg, 0.13 mmol, 66%).

Rf: (*n*-pentane:CH₂Cl₂ 1:1) 0.45;

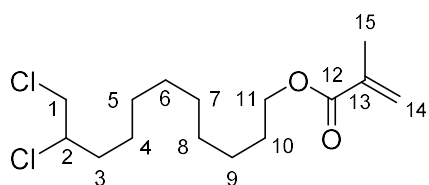
¹H NMR (400 MHz, CDCl₃) δ = 4.04 (t, ³J_{HH} = 6.8 Hz, 2H, H¹¹), 4.06 – 3.98 (m, 1H, H²), 3.75 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 5.1 Hz, 1H, H^{1a}), 3.64 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 7.4 Hz, 1H, H^{1b}), 2.04 (s, 3H, H¹³), 1.96 (m, 1H, H^{3a}), 1.71 (m, 1H, H^{3b}), 1.61 (p, ³J_{HH} = 6.9, 2H, H¹⁰), 1.53 (m, 1H, H^{4a}), 1.41 (m, 1H, H^{4b}), 1.30 (m, 10H, H⁵⁻⁹) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 171.4 (1C, C^{12}), 64.7 (1C, C^{11}), 61.4 (1C, C^2), 48.4 (1C, C^1), 35.2 (1C, C^3), 29.5 (1C), 29.4 (1C), 29.3 (1C), 29.1 (1C, C^5), 28.7 (1C, C^{10}), 26.0 (1C, C^9), 25.9 (1C, C^4), 21.2 (1C, C^{13}) ppm;

IR (ATR) $\tilde{\nu}$ = 2928 (m), 2856 (m), 1737 (s), 1464 (w), 1435 (w), 1387 (w), 1365 (w), 1235 (s), 1036 (m), 969 (w), 912 (w), 726 (m), 662 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{24}\text{Cl}_2\text{NaO}_2^+$: 305.1046, found: 305.1055.

10,11-Dichloroundecyl methacrylate (**4**)



According to **General Procedure B** using undec-10-en-1-yl methacrylate (48 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude

mixture was purified by column chromatography using a gradient *n*-pentane: CH_2Cl_2 9:1 to 4:1 to afford 10,11-dichloroundecyl methacrylate (**4**) as a colourless oil (43 mg, 0.14 mmol, 70%).

Rf: (*n*-pentane: CH_2Cl_2 1:1) 0.48;

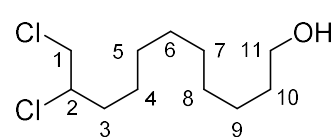
^1H NMR (400 MHz, CDCl_3) δ = 6.09 (m, 1H, H^{14a}), 5.54 (m, 1H, H^{14b}), 4.13 (t, $^3J_{\text{HH}}$ = 6.7 Hz, 2H, H^{11}), 4.03 (dddd, $^3J_{\text{HH}}$ = 8.9, 7.3, 5.2, 3.7 Hz, 1H, H^2), 3.76 (dd, $^2J_{\text{HH}}$ = 11.3 Hz, $^3J_{\text{HH}}$ = 5.2 Hz, 1H, H^{1a}), 3.65 (dd, $^2J_{\text{HH}}$ = 11.2 Hz, $^3J_{\text{HH}}$ = 7.4 Hz, 1H, H^{1b}), 1.98 (m, 1H, H^{3a}), 1.94 (m, 3H, H^{15}), 1.76 – 1.61 (m, 3H, H^{3b} , H^{10}), 1.53 (m, 1H, H^{4a}), 1.46 – 1.22 (m, 11H, H^{4b} , H^{5-9}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 167.7 (1C, C^{12}), 136.7 (1C, C^{13}), 125.3 (1C, C^{14}), 64.9 (1C, C^{11}), 61.4 (1C, C^2), 48.4 (1C, C^1), 35.2 (1C, C^3), 29.5 (1C), 29.4 (1C), 29.3 (1C), 29.1 (1C, C^5), 28.7 (1C, C^{10}), 26.1 (1C, C^9), 25.9 (1C, C^4), 18.5 (1C, C^{15}) ppm;

IR (ATR) $\tilde{\nu}$ = 2928 (m), 2856 (w), 1716 (s), 1638 (w), 1455 (w), 1403 (w), 1376 (w), 1321 (m), 1296 (m), 1161 (s), 1012 (w), 939 (m), 815 (m), 726 (m), 661 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{26}\text{Cl}_2\text{NaO}_2^+$: 331.1202, found: 331.1202.

10,11-Dichloroundecan-1-ol (**5**)

 According to **General Procedure B** using undec-10-en-1-ol (34 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using CH_2Cl_2 100% to afford 10,11-dichloroundecan-1-ol (**5**) as a colourless oil (36 mg, 0.15 mmol, 75%).

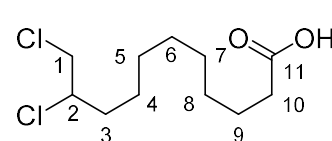
R_f: (CH_2Cl_2 100%) 0.24;

^1H NMR (400 MHz, CDCl_3 , 299 K) δ = 4.02 (dddd, J_{HH} = 9.0, 7.3, 5.2, 3.8 Hz, 1H, H^2), 3.74 (dd, J_{HH} = 11.3, 5.2 Hz, 1H, H^{1a}), 3.66 – 3.59 (m, 3H, H^{1b} , H^{11}), 1.96 (dddd, J_{HH} = 14.2, 9.9, 5.7, 3.8 Hz, 1H, H^{3a}), 1.69 (dtd, J_{HH} = 14.2, 9.4, 4.6 Hz, 1H, H^{3b}), 1.59 – 1.50 (m, 4H), 1.37 – 1.25 (m, 10H) ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{22}\text{Cl}_2\text{NaO}^+$: 263.0940, found: 263.0938.

The analytic data are in agreement with the literature.¹⁵

10,11-Dichloroundecanoic acid (**6**)

 According to **General Procedure B** using undec-10-enoic acid (37 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:ethyl acetate 7:3 to afford 10,11-dichloroundecanoic acid (**6**) as a colourless oil (34 mg, 0.13 mmol, 66%).

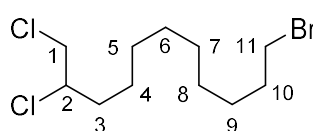
R_f: (cyclohexane:ethyl acetate 1:1) 0.44;

¹H NMR (300 MHz, CDCl₃) δ = 11.29 (s, 1H, COOH), 4.03 (dddd, J_{HH} = 8.9, 7.3, 5.1, 3.8 Hz, 1H), 3.76 (dd, J_{HH} = 11.3, 5.2 Hz, 1H), 3.65 (dd, J_{HH} = 11.3, 7.4 Hz, 1H), 2.35 (t, J_{HH} = 7.5 Hz, 2H), 1.98 (dddd, J_{HH} = 14.1, 9.9, 5.6, 3.7 Hz, 1H), 1.78 – 1.21 (m, 13H) ppm;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₁H₂₀Cl₂NaO₂⁺: 277.0733, found: 277.0703.

The analytic data are in agreement with the literature.¹⁶

11-Bromo-1,2-dichloroundecane (7)



According to **General Procedure B** using 11-bromoundec-1-ene (47 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using *n*-pentane 100% to afford 11-bromo-1,2-dichloroundecane (**7**) as a colourless oil (43 mg, 0.14 mmol, 71%).

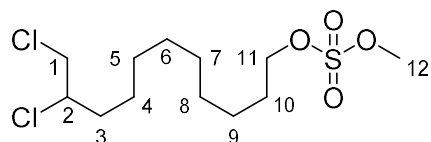
R_f: (cyclohexane 100%) 0.45;

¹H NMR (400 MHz, CDCl₃) δ = 4.03 (m, 1H), 3.76 (dd, J_{HH} = 11.3, 5.2, 1H), 3.65 (dd, J_{HH} = 11.2, 7.4, 1H), 3.41 (t, J_{HH} = 6.8, 2H), 1.98 (m, 1H), 1.85 (m, 2H), 1.71 (m, 1H), 1.61 – 1.48 (m, 1H), 1.48 – 1.26 (m, 11H) ppm;

MS (EI) m/z (%) = 302.0 (52), 304.0 (100), 306.1 (38), 308.0 (12) [M]⁺, calcd. for [M]⁺: 302.0 (62), 304.0 (100), 306.0 (46), 308.0 (8).

The analytic data are in agreement with the literature.¹⁵

10,11-Dichloroundecyl methyl sulfate (8)



According to **General Procedure B** using methyl undec-10-en-1-yl sulfate (53 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by

column chromatography using cyclohexane:ethyl acetate 9:1 to afford 10,11-dichloroundecyl methyl sulfate as a colourless oil (35 mg, 0.10 mmol, 52%).

Rf: (cyclohexane:ethyl acetate 9:1) 0.35;

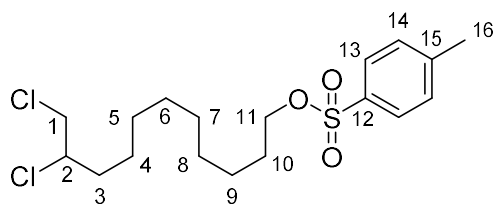
¹H NMR (599 MHz, CDCl₃) δ = 4.26 (t, ³J_{HH} = 6.6 Hz, 2H, H¹¹), 4.03 (dddd, ³J_{HH} = 8.9, 7.3, 5.1, 3.7 Hz, 1H, H²), 3.94 (s, 3H, H¹²), 3.76 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 5.2 Hz, 1H, H^{1a}), 3.65 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 7.4 Hz, 1H, H^{1b}), 1.98 (dddd, ²J_{HH} = 14.2 Hz, ³J_{HH} = 10.3, 5.8, 3.8 Hz, 1H, H^{3a}), 1.76 (m, 2H, H¹⁰), 1.70 (m, 1H, H^{3b}), 1.55 (m, 1H, H^{4a}), 1.41 (m, 3H, H^{4b}, H⁹), 1.36 – 1.26 (m, 8H, H⁵⁻⁸) ppm;

¹³C{¹H} NMR (151 MHz, CDCl₃) δ = 73.7 (1C, C¹¹), 61.3 (1C, C²), 58.4 (1C, C¹²), 48.4 (1C, C¹), 35.1 (1C, C³), 29.4 (1C), 29.4 (1C), 29.0 (2C), 28.8 (1C, C¹⁰), 25.9 (1C, C⁴), 25.5 (1C, C⁹) ppm;

IR (ATR) $\tilde{\nu}$ = 2928 (m), 2856 (w), 1462 (w), 1396 (m), 1385 (m), 1296 (w), 1264 (w), 1194 (s), 998 (m), 947 (s), 826 (m), 799 (m), 772 (m), 724 (m), 661 (m) cm⁻¹;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₂H₂₄Cl₂NaO₄S⁺: 357.0665, found: 357.0668.

10,11-Dichloroundecyl 4-methylbenzenesulfonate (**9**)



According to **General Procedure B** using undec-10-en-1-yl 4-methylbenzenesulfonate (65 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was

stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:CH₂Cl₂ 4:1 to afford 10,11-dichloroundecyl 4-methylbenzenesulfonate (**9**) as a colourless oil (57 mg, 0.14 mmol, 72%).

Rf: (*n*-pentane:CH₂Cl₂ 1:1) 0.36;

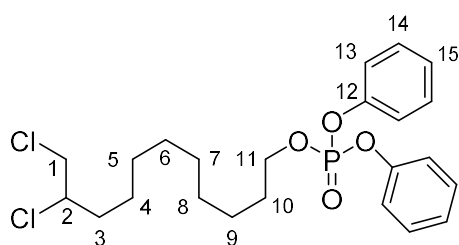
¹H NMR (500 MHz, CDCl₃) δ = 7.79 (m, 2H, H¹³), 7.34 (m, 2H, H¹⁴), 4.03 (m, 1H, H²), 4.02 (t, ³J_{HH} = 7.7 Hz, 2H, H¹¹), 3.76 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 5.2 Hz, 1H, H^{1a}), 3.65 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 7.4 Hz, 1H, H^{1b}), 2.45 (s, 3H, H¹⁶), 1.97 (dddd, ²J_{HH} = 14.1 Hz, ³J_{HH} = 10.2, 5.8, 3.8 Hz, 1H, H^{3a}), 1.70 (m, 1H; H^{3b}), 1.63 (m, 2H, H¹⁰), 1.55 (m, 1H, H^{4a}), 1.39 (m, 1H, H^{4b}), 1.35 – 1.18 (m, 10H, H⁵⁻⁹) ppm;

¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 144.8 (1C, C¹⁵), 133.4 (1C, C¹²), 129.9 (2C, C¹⁴), 128.0 (2C, C¹³), 70.8 (1C, C¹¹), 61.4 (1C, C²), 48.4 (1C, C¹), 35.2 (1C, C³), 29.4 (2C), 29.0 (2C), 25.5 (1C), 28.9 (1C, C¹⁰), 25.9 (1C, C⁴), 21.8 (1C, C¹⁶) ppm;

IR (ATR) $\tilde{\nu}$ = 2927 (m), 2857 (w), 1599 (w), 1464 (w), 1357 (m), 1289 (w), 1262 (w), 1219 (w), 1188 (m), 1174 (s), 1098 (m), 1020 (m), 952 (m), 813 (m), 777 (w), 724 (w), 688 (w), 662 (s) cm⁻¹;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₈H₂₈Cl₂NaO₃S⁺: 417.1028, found: 417.1031.

10,11-Dichloroundecyl diphenyl phosphate (**10**)



According to **General Procedure B** using diphenyl undec-10-en-1-yl phosphate (80 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column

chromatography using a gradient *n*-pentane:CH₂Cl₂ 1:1 to 100% CH₂Cl₂ to afford 10,11-dichloroundecyl diphenyl phosphate (**10**) as a pale yellow oil (72 mg, 0.15 mmol, 76%).

R_f: (*n*-pentane:CH₂Cl₂ 1:1) 0.1;

¹H NMR (500 MHz, CDCl₃) δ = 7.34 (m, 4H, H¹⁴), 7.22 (m, 4H, H¹³), 7.19 (m, 2H, H¹⁵), 4.25 (dt, ³J_{PH} = 7.6 Hz, ³J_{HH} = 6.5 Hz, 2H, H¹¹), 4.03 (dddd, ³J_{HH} = 9.0, 7.4, 5.2, 3.8 Hz, 1H, H²), 3.76 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 5.2 Hz, 1H, H^{1a}), 3.65 (dd, ²J_{HH} = 11.3 Hz,

$^3J_{\text{HH}} = 7.4$ Hz, 1H, H^{1b}), 1.98 (dddd, $J = 14.2, 10.3, 5.8$ Hz, $^3J_{\text{HH}} = 3.8$ Hz, 1H, H^{3a}), 1.70 (m, 3H, H^{3b}, H¹⁰), 1.53 (m, 1H, H^{4a}), 1.41 (m, 1H, H^{4b}), 1.37 – 1.22 (m, 10H) ppm;

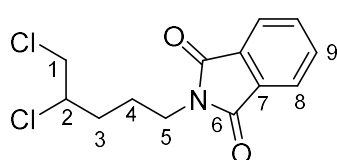
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl₃) $\delta = 150.8$ (d, $^2J_{\text{PC}} = 7.2$ Hz, 2C, C¹²), 129.9 (d, $^4J_{\text{PC}} = 0.7$ Hz, 4C, C¹⁴), 125.4 (d, $J_{\text{PC}} = 1.2$ Hz, 2C, C¹⁵), 120.2 (d, $^3J_{\text{PC}} = 5.0$ Hz, 4C, C¹³), 69.6 (d, $J_{\text{PC}} = 6.6$ Hz, 1C, C¹¹), 61.4 (1C, C²), 48.4 (1C, C¹), 35.2 (1C, C³), 30.3 (d, $J_{\text{PC}} = 6.8$ Hz, 1C, C¹⁰), 29.4 (2C), 29.1 (2C), 25.9 (1C, C⁴), 25.4 (1C, C⁹) ppm;

^{31}P NMR (202 MHz, CDCl₃) $\delta = -11.85$ (t, $^3J_{\text{PH}} = 7.6$ Hz) ppm;

IR (ATR) $\tilde{\nu} = 2927$ (w), 2856 (w), 1591 (w), 1488 (m), 1457 (w), 1287 (m), 1220 (m), 1189 (s), 1162 (m), 1023 (m), 1008 (m), 941 (s), 903 (m), 824 (w), 754 (m), 724 (w), 688 (m), 660 (w) cm⁻¹;

HRMS (ESI) m/z [M+H]⁺ calcd. for C₂₃H₃₂O₄PCl₂⁺: 473.1410, found: 473.1411.

2-(4,5-Dichloropentyl)isoindoline-1,3-dione (**11**)



According to **General Procedure B** using 2-(pent-4-en-1-yl)isoindoline-1,3-dione (43 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture

was purified by column chromatography using *n*-pentane:ethyl acetate 9:1 to afford 2-(4,5-dichloropentyl)isoindoline-1,3-dione (**11**) as a white solid (34 mg, 0.12 mmol, 59%).

Rf: (*n*-pentane:CH₂Cl₂ 1:1) 0.36;

M.p.: 53-55°C;

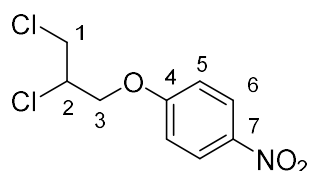
^1H NMR (400 MHz, CDCl₃) $\delta = 7.85$ (m, 2H, H⁸), 7.72 (m, 2H, H⁹), 4.09 (dddd, $^3J_{\text{HH}} = 10.9, 8.3, 5.0, 3.0$ Hz, 1H, H²), 3.74 (m, 3H, H^{1a}, H⁵), 3.64 (m, 1H, H^{1b}), 2.02 (m, 2H, H^{3a}, H^{4a}), 1.79 (m, 2H, H^{3b}, H^{4b}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 168.5 (2C, C^6), 134.2 (2C, C^9), 132.2 (2C, C^7), 123.4 (2C, C^8), 60.4 (1C, C^2), 48.2 (1C, C^1), 37.2 (1C, C^5), 32.3 (1C, C^3), 25.3 (1C, C^4) ppm;

IR (ATR) $\tilde{\nu}$ = 2949 (w), 1771 (m), 1703 (s), 1615 (w), 1467 (w), 1436 (w), 1395 (s), 1362 (m), 1288 (w), 1219 (w), 1189 (m), 1122 (w), 1102 (w), 1088 (w), 1021 (m), 960 (w), 889 (m), 879 (m), 794 (w), 716 (s), 693 (m), 662 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{13}\text{NCl}_2\text{NaO}_2^+$: 308.0216, found: 308.0213.

1-(2,3-dichloropropoxy)-4-nitrobenzene (**12**)



According to **General Procedure B** using 1-(allyloxy)-4-nitrobenzene (36 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 9:1 to afford 1-(2,3-dichloropropoxy)-4-nitrobenzene (**12**) as a light yellow oil (33 mg, 0.13 mmol, 66%).

Rf: (cyclohexane:ethyl acetate 95:5) 0.23;

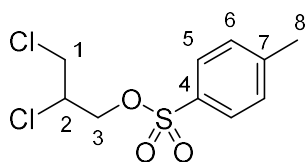
^1H NMR (400 MHz, CDCl_3) δ = 8.23 (m, 2H, H^6), 7.01 (m, 2H, H^5), 4.39 (m, 2H, H^3), 4.32 (m, 1H, H^2), 3.94 (m, 2H, H^1) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 162.9 (1C, C^4), 142.4 (1C, C^7), 126.2 (2C, C^6), 114.8 (2C, C^5), 68.7 (1C, C^3), 56.7 (1C, C^2), 44.5 (1C, C^1) ppm;

IR (ATR) $\tilde{\nu}$ = 2956 (w), 1609 (w), 1593 (m), 1514 (m), 1497 (m), 1455 (w), 1365 (m), 1341 (s), 1299 (m), 1256 (s), 1190 (m), 1175 (s), 1112 (m), 1097 (s), 1020 (m), 1002 (m), 980 (m), 932 (m), 862 (m), 845 (m), 830 (m), 814 (m), 792 (m), 752 (m), 688 (m), 667 (m) cm^{-1} ;

HRMS (ESI) m/z $[M+Na]^+$ calcd. for $C_9H_9Cl_2NNaO_3^+$: 271.9852, found: 271.9856.

2,3-Dichloropropyl 4-methylbenzenesulfonate (**13**)



According to **General Procedure B** using allyl 4-methylbenzenesulfonate (43 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at 0°C for 8 h. The crude mixture

was purified by column chromatography using *n*-pentane:ethyl acetate 95:5 to afford 2,3-dichloropropyl 4-methylbenzenesulfonate (**13**) as a colourless oil (30 mg, 0.11 mmol, 53%).

Rf: (*n*-pentane:ethyl acetate 95:5) 0.17;

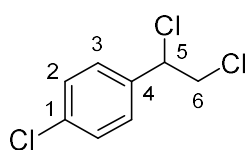
1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (m, 2H, H^5), 7.37 (m, 2H, H^6), 4.32 (dd, $^2J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H^{3a}), 4.26 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, H^{3b}), 4.21 (dq, $^3J_{HH}$ = 6.7, 5.1 Hz, 1H, H^2), 3.78 (dd, $^2J_{HH}$ = 11.8 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H^{1a}), 3.74 (dd, $^2J_{HH}$ = 11.8 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, H^{1b}), 2.46 (s, 3H, H^8) ppm;

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 145.6 (1C, C^7), 132.3 (1C, C^4), 130.2 (2C, C^6), 128.2 (2C, C^5), 68.7 (1C, C^3), 55.9 (1C, C^2), 44.3 (1C, C^1), 21.8 (1C, C^8) ppm;

IR (ATR) $\tilde{\nu}$ = 2958 (w), 1598 (w), 1495 (w), 1453 (w), 1362 (m), 1308 (w), 1293 (w), 1212 (w), 1190 (m), 1174 (s), 1096 (m), 1039 (w), 978 (m), 933 (m), 828 (m), 812 (m), 792 (m), 745 (w), 681 (m), 666 (m) cm^{-1} ;

HRMS (ESI) m/z $[M+Na]^+$ calcd. for $C_{10}H_{12}Cl_2NaO_3S^+$: 304.9776, found: 304.9783.

1-chloro-4-(1,2-dichloroethyl)benzene (**14**)



According to **General Procedure B** using 1-chloro-4-vinylbenzene (139 mg, 1.0 mmol, 1.0 eq.), *p*-iodotoluene (44 mg, 0.2 mmol, 0.2 eq.), cesium chloride (505 mg, 3.0 mmol, 3.0 eq.) and Selectfluor® (390 mg, 1.1 mmol, 1.1 eq.) were dissolved in a solution of HFIP (1.51 g, 9.0 mmol, 9.0 eq.) in CH₂Cl₂ (4.5 mL). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using 100% cyclohexane to afford 1-chloro-4-(1,2-dichloroethyl)benzene (**14**) as a colourless oil (112 mg, 0.53 mmol, 53%).

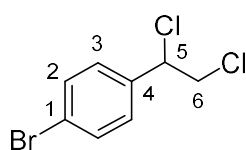
Rf: (cyclohexane 100%) 0.44;

¹H NMR (300 MHz, CDCl₃) δ = 7.36 (m, 4H), 4.97 (dd, ³*J*_{HH} = 8.4, 6.2 Hz, 1H), 3.99 (dd, ²*J*_{HH} = 11.3 Hz, ³*J*_{HH} = 6.2 Hz, 1H), 3.88 (dd, ²*J*_{HH} = 11.3 Hz, ³*J*_{HH} = 8.4 Hz, 1H).

MS (EI) *m/z*: 207.98 (40) [M]⁺, 173.03 (100) [M-Cl]⁺.

The analytic data are in agreement with the literature.¹⁵

1-bromo-4-(1,2-dichloroethyl)benzene (**15**)



According to **General Procedure B** using 1-bromo-4-vinylbenzene (183 mg, 1.0 mmol, 1.0 eq.), *p*-iodotoluene (44 mg, 0.2 mmol, 0.2 eq.), cesium chloride (505 mg, 3.0 mmol, 3.0 eq.) and Selectfluor® (390 mg, 1.1 mmol, 1.1 eq.) were dissolved in a solution of HFIP (1.51 g, 9.0 mmol, 9.0 eq.) in CH₂Cl₂ (4.5 mL). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using 100% cyclohexane to afford 1-bromo-4-(1,2-dichloroethyl)benzene (**15**) as a colourless oil (146 mg, 0.57 mmol, 57%).

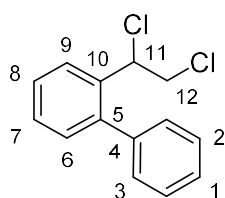
Rf: (cyclohexane 100%) 0.45;

¹H NMR (300 MHz, CDCl₃) δ = 7.53 (m, 2H), 7.29 (m, 2H), 4.95 (dd, ³J_{HH} = 8.4, 6.1 Hz, 1H), 3.98 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 6.2 Hz, 1H), 3.88 (dd, ²J_{HH} = 11.3 Hz, ³J_{HH} = 8.4 Hz, 1H).

MS (EI) *m/z*: 251.94 (12), 253.93 (22), 255.93 (8) [M]⁺, 202.94 (77), 204.94 (100), 206.95 (24) [M-CH₂Cl]⁺.

The analytic data are in agreement with the literature.¹⁷

2-(1,2-dichloroethyl)-1,1'-biphenyl (**16**)



According to **General Procedure B** using 2-vinyl-1,1'-biphenyl (180 mg, 1.0 mmol, 1.0 eq.), *p*-iodotoluene (44 mg, 0.2 mmol, 0.2 eq.), cesium chloride (505 mg, 3.0 mmol, 3.0 eq.) and Selectfluor® (390 mg, 1.1 mmol, 1.1 eq.) were dissolved in a solution of HFIP (1.51 g, 9.0 mmol, 9.0 eq.) in CH₂Cl₂ (4.5 mL). The reaction mixture was stirred at 0°C for 8 h. The crude mixture was purified by column chromatography using 100% cyclohexane to afford 2-(1,2-dichloroethyl)-1,1'-biphenyl (**16**) as a colourless oil (147 mg, 0.59 mmol, 59%).

Rf: (cyclohexane 100%) 0.28;

¹H NMR (500 MHz, CDCl₃) δ = 7.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.49 – 7.35 (m, 7H), 7.28 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.16 (t, ³J_{HH} = 7.5 Hz, 1H), 3.97 – 3.92 (m, 2H).

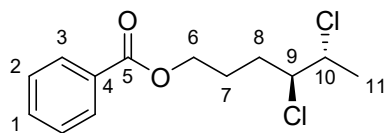
MS (EI) *m/z*: 250.01 (100), 252.07 (65), 254.04 (10) [M]⁺

The analytic data are in agreement with the literature.¹⁸

V. General procedure C for the catalytic dichlorination of internal alkenes

The corresponding alkene (0.20 mmol, 1.0 eq.), *p*-iodotoluene (8.7 mg, 0.04 mmol, 0.2 eq.) cesium chloride (101 mg, 0.60 mmol, 3.0 eq.) and Selectfluor® (78.0 mg, 0.22 mmol, 1.1 eq.) were dissolved in a solution of HFIP (302 mg, 1.80 mmol, 9.0 eq.) in CH₂Cl₂ (0.9 mL) and stirred at ambient temperature. After 8 h, the reaction mixture was quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR. The sample was then evaporated under *vacuo* and purified by column chromatography using the indicated solvent ratio.

4,5-Dichlorohexyl benzoate (17)



According to **General Procedure C** using (*E*)-hex-4-en-

1-yl benzoate (41 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at ambient temperature for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:diethyl ether 40:1 to afford 4,5-dichlorohexyl benzoate (**17**) as a colourless oil (30 mg, 0.11 mmol, 54%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.39;

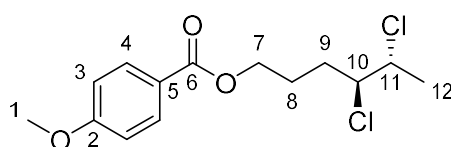
¹H NMR (400 MHz, CDCl₃) δ = 8.04 (m, 2H, H³), 7.56 (m, 1H, H¹), 7.45 (m, 2H, H²), 4.37 (m, 2H, H⁶), 4.11 (qd, ³J_{HH} = 6.9, 6.6 Hz, 1H, H¹⁰), 4.00 (ddd, ³J_{HH} = 9.6, 6.9, 2.9 Hz, 1H, H⁹), 2.26 – 2.18 (m, 1H, H^{8a}), 2.15 – 2.07 (m, 1H, H^{7a}), 1.97 – 1.87 (m, 2H, H^{7b}, H^{8b}), 1.65 (d, ³J_{HH} = 6.5 Hz, 3H, H¹¹) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ = 166.7 (1C, C^5), 133.1 (1C, C^1), 130.3 (1C, C^4), 129.7 (2C, C^3), 128.5 (2C, C^2), 66.7 (1C, C^9), 64.2 (1C, C^6), 60.1 (1C, C^{10}), 31.9 (1C, C^8), 25.7 (1C, C^7), 22.3 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 3069 (w), 2937 (w), 2860 (w), 1716 (s), 1640 (w), 1602 (w), 1585 (w), 1451 (m), 1385 (w), 1268 (s), 1175 (m), 1109 (s), 1069 (m), 1026 (m), 993 (m), 910 (m), 847 (w), 707 (s), 686 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Cl}_2\text{Na}^+$: 297.0420, found: 297.0426.

4,5-Dichlorohexyl 4-methoxybenzoate (**18**)



According to **General Procedure C** using (*E*)-hex-4-en-1-yl 4-methoxybenzoate (47 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at ambient

temperature for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:diethyl ether 40:1 to afford 4,5-dichlorohexyl 4-methoxybenzoate (**18**) as a colourless oil (35 mg, 0.11 mmol, 57%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.19;

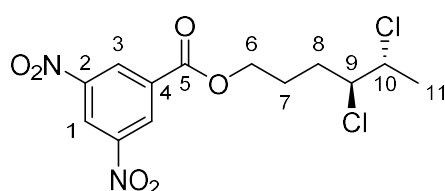
^1H NMR (400 MHz, CDCl_3) δ = 7.99 (m, 2H, H^4), 6.92 (m, 2H, H^3), 4.34 (m, 2H, H^7), 4.11 (dq, $^3J_{\text{HH}}$ = 6.9, 6.6 Hz, 1H, H^{11}), 4.00 (ddd, $^3J_{\text{HH}}$ = 9.5, 6.9, 2.9 Hz, 1H, H^{10}), 3.86 (s, 3H, H^1), 2.26 – 2.03 (m, 2H, H^{8a} , H^{9a}), 1.95 – 1.83 (m, 2H, H^{8b} , H^{9b}), 1.64 (d, J_{HH} = 6.6 Hz, 3H, H^{12}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 166.4 (1C, C^6), 163.5 (1C, C^2), 131.7 (2C, C^4), 122.7 (1C, C^5), 113.8 (2C, C^3), 66.8 (1C, C^{10}), 63.9 (1C, C^7), 60.2 (1C, C^{11}), 55.6 (1C, C^1), 31.9 (1C, C^9), 25.7 (1C, C^8), 22.3 (1C, C^{12}) ppm;

IR (ATR) $\tilde{\nu}$ = 3673 (w), 2966 (w), 1708 (s), 1605 (s), 1510 (m), 1444 (w), 1420 (w), 1381 (w), 1273 (s), 1251 (s), 1165 (s), 1110 (s), 1027 (s), 968 (w), 920 (w), 846 (m), 768 (s), 695 (m) cm^{-1} ;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Cl}_2\text{Na}^+$: 327.0525, found: 327.0530.

4,5-Dichlorohexyl 3,5-dinitrobenzoate (**19**)



According to **General Procedure C** using (*E*)-hex-4-en-1-yl 3,5-dinitrobenzoate (59 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at ambient

temperature for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:diethyl ether 10:1 to afford 4,5-dichlorohexyl 3,5-dinitrobenzoate (**19**) as a yellow solid (41 mg, 0.11 mmol, 56%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.13;

M.p. 51-53 °C;

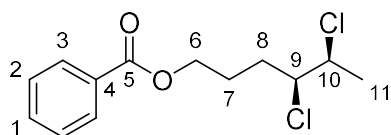
^1H NMR (400 MHz, CDCl_3) δ = 9.23 (t, $^4J_{\text{HH}}$ = 2.1 Hz, 1H, H^1), 9.16 (d, $^4J_{\text{HH}}$ = 2.1 Hz, 2H, H^3), 4.51 (t, $^3J_{\text{HH}}$ = 6.2 Hz, 2H, H^6), 4.11 (dq, $^3J_{\text{HH}}$ = 7.5, 6.5 Hz, 1H, H^{10}), 3.98 (ddd, $^3J_{\text{HH}}$ = 8.9, 7.5, 2.5 Hz, 1H, H^9), 2.33 – 2.10 (m, 2H, H^{7a} , H^{8a}), 2.08 – 1.87 (m, 2H, H^{7b} , H^{8b}), 1.67 (d, $^3J_{\text{HH}}$ = 6.5 Hz, 3H, H^{11}) ppm;

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ = 162.6 (1C, C^5), 148.9 (2C, C^2), 134.0 (1C, C^4), 129.6 (2C, C^3), 122.6 (1C, C^1), 66.3 (1C, C^9), 66.2 (1C, C^6), 60.0 (1C, C^{10}), 31.7 (1C, C^8), 25.4 (1C, C^7), 22.7 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 3095 (w), 1726 (s), 1628 (m), 1597 (w), 1542 (s), 1462 (m), 1343 (s), 1278 (s), 1197 (w), 1169 (m), 1159 (m), 1076 (w), 985 (w), 883 (m), 827 (w), 730 (m), 718 (s) cm^{-1} ;

HRMS (ESI) m/z $[M+Na]^+$ calcd. for $C_{13}H_{14}N_2O_2Cl_2Na^+$: 387.0121, found: 387.0118.

4,5-Dichlorohexyl benzoate (**20**)



According to **General Procedure C** using (Z)-hex-4-en-

1-yl benzoate (41 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at ambient temperature for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:diethyl ether 40:1 to afford 4,5-dichlorohexyl benzoate (**20**) as a colourless oil (25 mg, 0.09 mmol, 45%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.29;

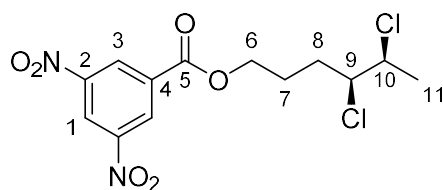
1H NMR (400 MHz, $CDCl_3$) δ = 8.04 (m, 2H, H^3), 7.56 (m, 1H, H^1), 7.45 (m, 2H, H^2), 4.38 (m, 2H, H^6), 4.28 (qd, $^3J_{HH}$ = 6.7, 3.0 Hz, 1H, H^{10}), 4.09 (td, $^3J_{HH}$ = 10.4, 3.0 Hz, 1H, H^9), 2.18 – 2.04 (m, 2H, H^{7a} , H^{8a}), 1.97 – 1.83 (m, 2H, H^{7b} , H^{8b}), 1.60 (d, $^3J_{HH}$ = 6.7 Hz, 3H, H^{11}) ppm;

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 166.7 (1C, C^5), 133.1 (1C, C^1), 130.3 (1C, C^4), 129.7 (2C, C^3), 128.5 (2C, C^2), 65.7 (1C, C^9), 64.2 (1C, C^6), 60.0 (1C, C^{10}), 30.6 (1C, C^8), 26.2 (1C, C^7), 20.8 (1C, C^{11}) ppm;

IR (ATR) $\tilde{\nu}$ = 2956 (m), 1715 (s), 1602 (w), 1584 (w), 1451 (m), 1380 (w), 1314 (m), 1269 (s), 1176 (m), 1108 (s), 1069 (m), 1026 (m), 981 (w), 915 (w), 806 (w), 708 (s), 687 (m) cm^{-1} ;

HRMS (ESI) m/z $[M+Na]^+$ calcd. for $C_{13}H_{16}O_2Cl_2Na^+$: 297.0420, found: 297.0421.

4,5-Dichlorohexyl 3,5-dinitrobenzoate (**21**)



According to **General Procedure C** using (Z)-hex-4-en-1-yl 3,5-dinitrobenzoate (59 mg, 0.20 mmol, 1.0 eq.). The reaction mixture was stirred at ambient

temperature for 8 h. The crude mixture was purified by column chromatography using *n*-pentane:diethyl ether 10:1 to afford 4,5-dichlorohexyl 3,5-dinitrobenzoate (**21**) as a yellow solid (41 mg, 0.11 mmol, 57%).

Rf: (*n*-pentane:diethyl ether 10:1) 0.06;

¹H NMR (400 MHz, CDCl₃) δ = 9.24 (t, $^4J_{\text{HH}}$ = 2.2 Hz, 1H, H¹), 9.16 (d, $^4J_{\text{HH}}$ = 2.2 Hz, 2H, H³), 4.51 (m, 2H, H⁶), 4.30 (qd, $^3J_{\text{HH}}$ = 6.7, 3.0 Hz, 1H, H¹⁰), 4.10 (dt, $^3J_{\text{HH}}$ = 10.1, 3.0 Hz, 1H, H⁹), 2.26 – 2.06 (m, 2H, H^{7a}, H^{8a}), 2.04 – 1.82 (m, 2H, H^{7b}, H^{8b}), 1.61 (d, $^3J_{\text{HH}}$ = 6.7 Hz, 3H, H¹¹) ppm;

¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 162.6 (1C, C⁵), 148.9 (2C, C²), 134.0 (1C, C⁴), 129.6 (2C, C³), 122.6 (1C, C¹), 66.2 (1C, C⁶), 65.3 (1C, C⁹), 59.8 (1C, C¹⁰), 30.1 (1C, C⁸), 26.1 (1C, C⁷), 20.5 (1C, C¹¹) ppm;

IR (ATR) $\tilde{\nu}$ = 3102 (w), 2928 (w), 1731 (s), 1629 (m), 1540 (s), 1342 (s), 1273 (s), 1163 (s), 1074 (m), 1011 (w), 989 (w), 919 (m), 772 (m), 718 (s), 694 (m) cm⁻¹;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₄N₂O₂Cl₂Na⁺: 387.0121, found: 387.0120.

VI. Mechanistic studies on the dichlorination of terminal alkenes

a. Table S3: Exploring the role of HFIP in the dichlorination.

$ \begin{array}{c} \text{p-Toll (20 mol\%),} \\ \text{Selectfluor}^{\text{®}} \text{ (1.1 eq.),} \\ \text{CsCl (3 eq.),} \\ \text{Additive (9 eq.),} \\ \text{CH}_2\text{Cl}_2, 0\text{ }^{\circ}\text{C, 8 h [a]} \end{array} $		
Entry	Additive	Yield ^[a]
1	1,1,1,3,3,3-hexafluoro-2-methoxypropane:	<5%
2	<i>i</i> -propanol:	<5%

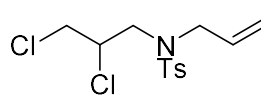
[a] According to **General Procedure B** using the corresponding additive instead of HFIP. ¹H NMR yield using DMF as internal standard.

b. Table S4: Radical clock experiments.

	22	23	24
Conditions	Yield 22	Yield 23	Yield 24
<i>p</i> -Toll (20 mol%), Selectfluor [®] (1.1 eq.), CsCl (3.0 eq.), HFIP (9.0 eq.), CH ₂ Cl ₂ , 0°C, 8 h	62%	20%	<5%
<i>p</i> -Toll (40 mol%), Selectfluor [®] (2.2 eq.), CsCl (6.0 eq.), HFIP (18.0 eq.), CH ₂ Cl ₂ , 0°C, 8 h	<5%	77%	<5%
Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 eq.), LiClO ₄ (1.75 eq.), AcOH/MeCN, C(+)/Pt(-), E _{cell} = 2.3 V, 40°C ¹⁵	<5%	<5%	71%

¹H NMR yield using DMF as internal standard.

***N*-allyl-*N*-(2,3-dichloropropyl)-4-methylbenzenesulfonamide (**22**)**

 *N,N*-diallyl-4-methylbenzenesulfonamide (50 mg, 0.20 mmol, 1.0 eq.), *p*-iodotoluene (8.7 mg, 0.04 mmol, 0.2 eq.), cesium chloride (101 mg, 0.60 mmol, 3.0 eq.) and Selectfluor® (78 mg, 0.22 mmol, 1.1 eq.) were dissolved in a solution of HFIP (302 mg, 1.80 mmol, 9.0 eq.) in CH₂Cl₂ (0.9 mL). The mixture was cooled and stirred at 0°C (ice bath). After 8 h, the reaction mixture was quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR (yield **19**: 62%, yield **20**: 20%). The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 95:5 to afford *N*-allyl-*N*-(2,3-dichloropropyl)-4-methylbenzenesulfonamide (**22**) as a white solid (28 mg, 0.09 mmol, 43%).

Rf: (cyclohexane:ethyl acetate 95:5) 0.12;

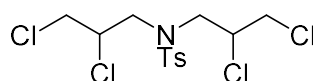
M.p. 69-71 °C;

¹H NMR (400 MHz, CDCl₃) δ = 7.71 (m, 2H), 7.33 (m, 2H), 5.55 (ddt, J_{HH} = 16.8, 10.1, 6.6 Hz, 1H), 5.19 (m, 2H), 4.44 (tt, J_{HH} = 7.0, 5.0 Hz, 1H), 3.94 (ddt, J_{HH} = 15.5, 6.4, 1.4 Hz, 1H), 3.86 (d, J_{HH} = 5.0 Hz, 2H), 3.82 (m, 1H), 3.56 (dd, J_{HH} = 15.0, 7.3 Hz, 1H), 3.27 (dd, J_{HH} = 15.0, 6.6 Hz, 1H), 2.44 (s, 3H) ppm;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₇Cl₂NNaO₂S⁺: 344.0249, found: 344.0265.

The analytic data are in agreement with the literature.¹⁵

***N,N*-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide (23)**



N,N-diallyl-4-methylbenzenesulfonamide (50 mg, 0.20 mmol, 1.0 eq.), *p*-iodotoluene (17 mg, 0.08 mmol, 0.4 eq.), cesium chloride (202 mg, 1.20 mmol, 6.0 eq.) and Selectfluor® (156 mg, 0.44 mmol, 2.2 eq.) were dissolved in a solution of HFIP (604 mg, 3.60 mmol, 18.0 eq.) in CH₂Cl₂ (1.8 mL). The mixture was cooled and stirred at 0°C (ice bath). After 8 h, the reaction mixture was quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR (yield **20**: 77%). The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 9:1 to afford *N,N*-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide (**23**) as a colourless oil (49 mg, 0.13 mmol, 62%).

Rf: (cyclohexane:ethyl acetate 9:1) 0.21;

¹H NMR (400 MHz, CDCl₃) δ = 7.73 (m, 2H), 7.37 (m, 2H), 4.51 (m, 2H), 3.86 (m, 3H), 3.78 (m, 3H), 3.38 (dd, J_{HH} = 15.3, 8.0 Hz, 1H), 3.16 (dd, J_{HH} = 15.1, 7.3 Hz, 1H), 2.46 (s, 3H) ppm;

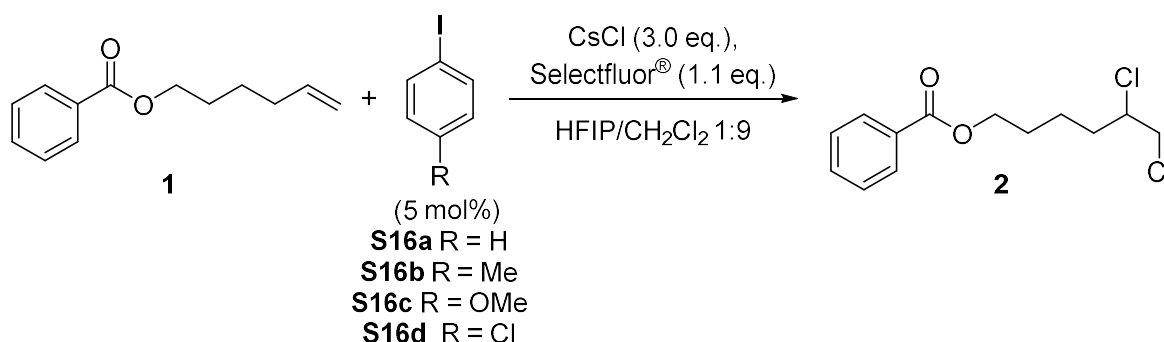
HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₃H₁₇Cl₄NNaO₂S⁺: 413.9626, found: 413.9630.

The analytic data are in agreement with the literature.¹⁵

c. Hammett correlation

General Procedure E for kinetic studies on the dichlorination of terminal alkenes generating the Hammett plot

Hex-5-en-1-yl benzoate (**1**) (41 mg, 0.20 mmol, 1.0 eq.), cesium chloride (101 mg, 0.60 mmol, 3.0 eq.) and the iodine catalyst (10 μ mol, 5 mol%) were dissolved in CH_2Cl_2 (0.9 mL) and HFIP (0.1 mL). Selectfluor[®] (78.0 mg, 0.22 mmol, 1.1 eq.) was added and the reaction mixture was stirred for 5, 10, 15 or 20 min. The reaction mixture was diluted with CH_2Cl_2 and a solution of saturated $\text{Na}_2\text{S}_2\text{O}_3$. The aqueous layer was extracted with CH_2Cl_2 , dried over MgSO_4 , filtered and the solvent was removed in *vacuo*. The NMR yield was obtained by adding DMF (7.7 μ L, 0.10 mmol) as internal standard to the crude mixture.



Each experiment was repeated thrice and an average of the obtained yield at each time was formed. The yield was plotted in a diagram *versus* the time. The slope of the linear equation corresponds to the initial rate constant k_R of the reaction. Using the Hammett equation a Hammett plot was generated by plotting the logarithm of the rate constants k_R/k_H *versus* the substitution constant σ_p . The slope of the linear equation then corresponds to the reaction constant ρ .

$$\log(k_R/k_H) = \sigma_p \rho$$

d. Kinetic studies with 4-iodobenzene (S16a)

Table S5: ¹H NMR yield of the dichlorination of hex-5-en-1-yl benzoate (**1**) with 4-iodobenzene (**S16a**).

Time [min]	¹ H NMR Yield (%)			
	1. Exp.	2. Exp.	3. Exp.	Average
0	0	0	0	0
5	0	1	2	1
10	4	7	5	5
15	7	7	6	7
20	13	20	13	15

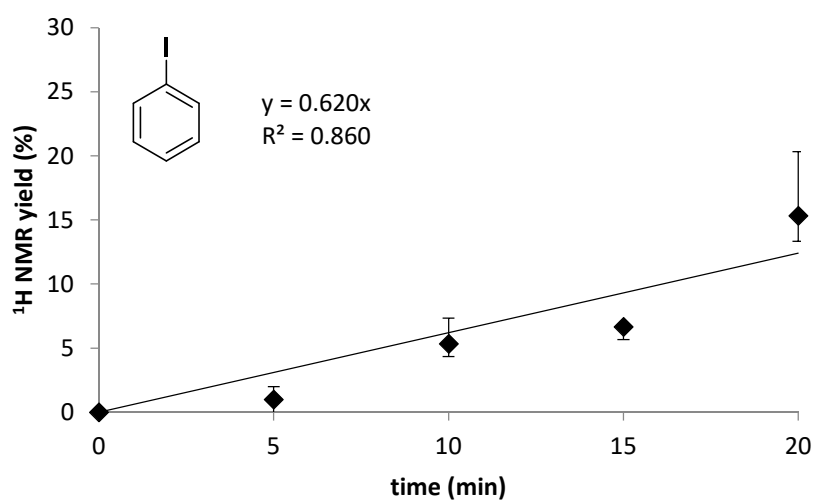


Figure S2: Kinetic data for the dichlorination of hex-5-en-1-yl benzoate (**1**) with 4-iodobenzene (**S16a**) plotting the ¹H NMR yield *versus* the time.

e. Kinetic studies with 4-iodotoluene (**S16b**)

Table S6: ¹H NMR yield of the dichlorination of hex-5-en-1-yl benzoate (**1**) with 4-iodotoluene (**S16b**).

Time [min]	¹ H NMR Yield (%)			
	1. Exp.	2. Exp.	3. Exp.	Average
0	0	0	0	0
5	1	4	2	2
10	5	8	7	7
15	12	10	12	11
20	18	25	20	20

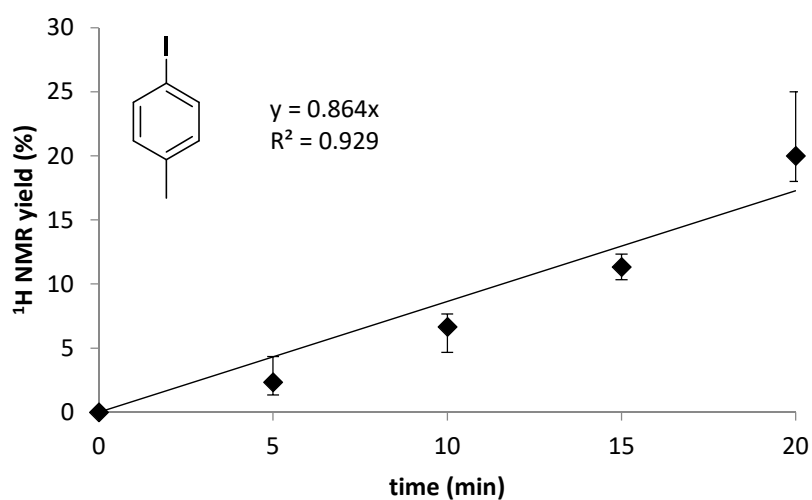


Figure S3: Kinetic data for the dichlorination of hex-5-en-1-yl benzoate (**1**) with 4-iodotoluene (**S16b**) plotting the ¹H NMR yield *versus* the time.

f. Kinetic studies with 1-iodo-4-methoxybenzene (S16c)

Table S7: ^1H NMR yield of the dichlorination of hex-5-en-1-yl benzoate (**1**) with 1-iodo-4-methoxybenzene (**S16c**).

Time [min]	^1H NMR Yield (%)			
	1. Exp.	2. Exp.	3. Exp.	Average
0	0	0	0	0
5	4	4	4	4
10	9	10	16	12
15	15	16	16	16
20	28	18	25	24

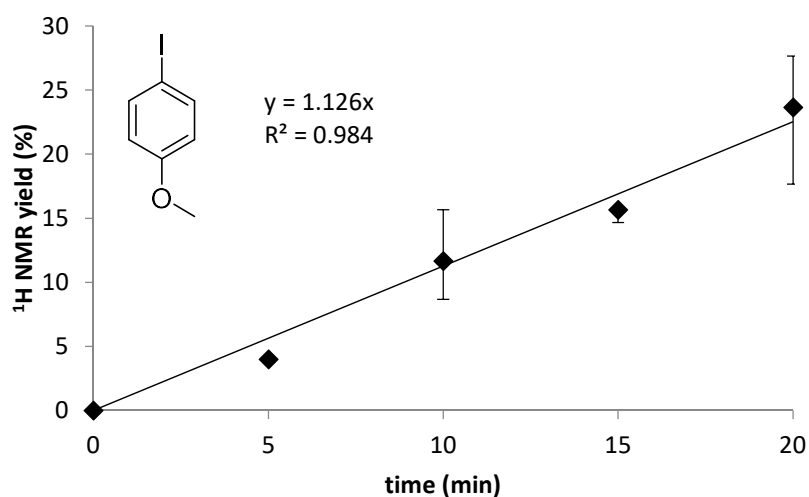


Figure S4: Kinetic data for the dichlorination of hex-5-en-1-yl benzoate (**1**) with 1-iodo-4-methoxybenzene (**S16c**) plotting the ^1H NMR yield *versus* the time.

g. Kinetic studies for 1-chloro-4-iodobenzene (S16d)

Table S8: ¹H NMR yield of the dichlorination of hex-5-en-1-yl benzoate (**1**) with 1-chloro-4-iodobenzene (**S16d**).

Time [min]	¹ H NMR Yield (%)			
	1. Exp.	2. Exp.	3. Exp.	Average
0	0	0	0	0
5	0	0	0	0
10	2	3	2	2
15	4	6	3	4
20	12	8	6	9

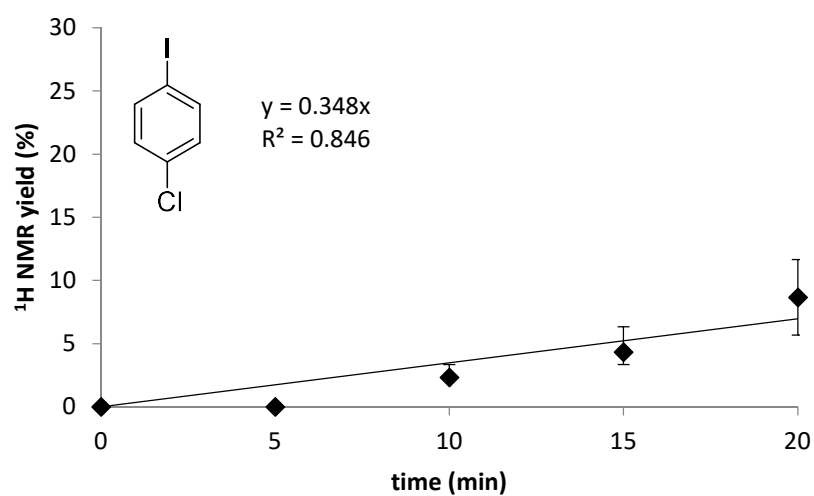


Figure S5: Kinetic data for the dichlorination of hex-5-en-1-yl benzoate (**1**) with 1-chloro-4-iodobenzene (**S16d**) plotting the ¹H NMR yield *versus* the time.

h. Kinetic studies: Hammett plot

Table S9: Kinetic data for the Hammett plot of the dichlorination with different iodoarenes as catalyst.

Substituent	σ_p^{61}	k_R	k_R/k_H	$\log(k_R/k_H)$
OMe	-0.27	1.13	1.82	0.26
Me	-0.14	0.86	1.39	0.14
H	0.00	0.62	1.00	0.00
Cl	0.24	0.35	0.56	-0.25

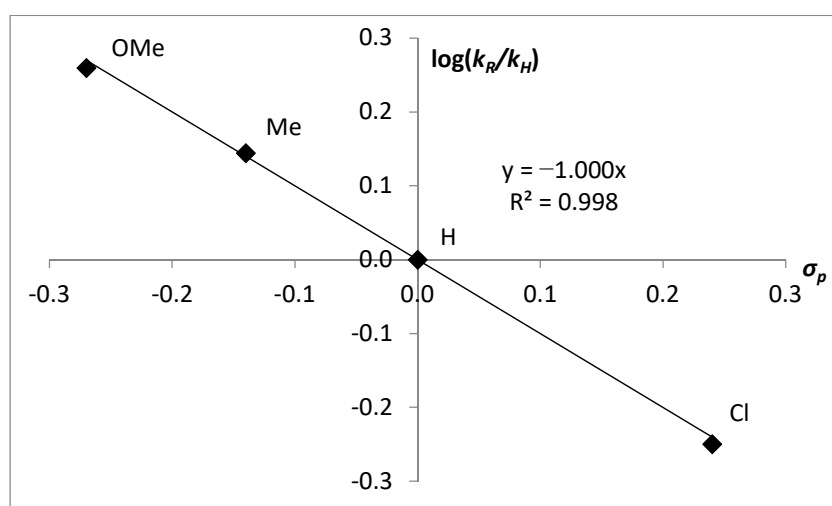
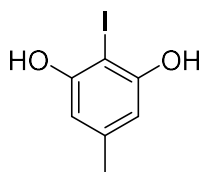


Figure S6: Kinetic data for the Hammett plot of the dichlorination of hex-5-en-1-yl benzoate (**1**) plotting the logarithm of the initial rate constant k versus the substituent constants σ_p .

VII. Preliminary validation of an enantioselective variant

2-Iodo-5-methylbenzene-1,3-diol¹⁹ (**S17**)



This compound was prepared according to a modified procedure from *Uchida et al.*¹⁹ 5-Methylbenzene-1,3-diol (1.24 g, 10 mmol, 1.0 eq.) was dissolved in acetonitrile (20 mL) and the resulting solution was cooled to 0°C. *N*-iodosuccinimide (2.25 g, 10 mmol, 1.0 eq.) was added in one portion and the reaction mixture was stirred at 0°C for 15 min. The reaction mixture was quenched with a saturated solution of sodium thiosulfate and extracted with ethyl acetate (3x). The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by filtration through column chromatography using cyclohexane:ethyl acetate 1:1 (15 g of silica) to afford 2-iodo-5-methylbenzene-1,3-diol (**S17**) as a white solid (2.2 g, 8.8 mmol, 88%).

Rf: (cyclohexane:ethyl acetate 1:1) 0.66;

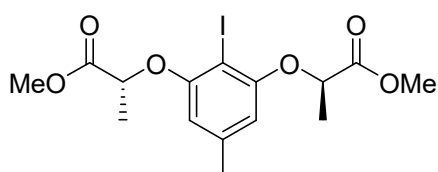
M.p. 101-104 °C;

¹H NMR (300 MHz, CDCl₃) δ = 6.40 (m, 2H), 5.20 (s, 2H), 2.26 (s, 3H) ppm;

HRMS (ESI) m/z [M-H]⁻ calcd. for C₇H₆IO₂⁻: 248.9418, found: 248.9443.

The analytic data are in agreement with the literature.²⁰

Dimethyl 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))(2*R*,2'*R*)- dipropionate (**S18**)



This compound was prepared according to a modified procedure from *Fujita et al.*²¹ 2-Iodo-5-methylbenzene-1,3-diol (1.0 g, 4.0 mmol, 1.0 eq.), *L*-

methyl lactate (840 μ L, 8.8 mmol, 2.2 eq.) and triphenylphosphine (2.4 g, 9.2 mmol, 2.3 eq.) were dissolved in tetrahydrofuran (15 mL) and the resulting solution was cooled to 0°C. Diisopropyl azodicarboxylate (1.8 mL, 9.2 mmol, 2.3 eq.) was added dropwise. The reaction mixture was then allowed to slowly warm up to ambient temperature and was stirred for 16 h. The crude reaction mixture was evaporated under *vacuo* and directly purified by column chromatography using a gradient cyclohexane:ethyl acetate 95:5 to 9:1 to afford dimethyl 2,2'-((2-iodo-5-methyl-1,3-phenylene) bis(oxy)) (2*R*,2'*R*)- dipropionate (**S18**) as a light yellow solid (1.4 g, 3.2 mmol, 81%).

Rf: (cyclohexane:ethyl acetate 4:1) 0.39;

M.p. 54-56 °C;

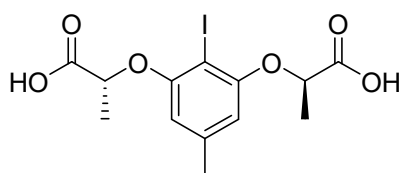
ORD (CHCl₃, c 1.00): $[\alpha]_D^{25} = -2.3^\circ$;

¹H NMR (300 MHz, CDCl₃) δ = 6.19 (s, 2H), 4.75 (q, $J_{HH} = 6.8$ Hz, 2H), 3.75 (s, 6H), 2.25 (s, 3H), 1.69 (d, $J_{HH} = 6.8$ Hz, 6H) ppm;

HRMS (ESI) m/z [M+Na]⁺ calcd. for C₁₅H₁₉INaO₆⁺: 445.0119, found: 445.0133.

The analytic data are in agreement with the literature.²⁰

(2*R*,2'*R*)-2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))dipropionic acid (**S19**)



This compound was prepared according to a modified procedure from *Uyanik et al.*²² Dimethyl 2,2'-((2-iodo-5-methyl-1,3-phenylene) bis(oxy))(2*R*,2'*R*)-dipropionate

(968 mg, 2.0 mmol, 1.0 eq.) was dissolved in tetrahydrofuran (5 mL) and methanol (5 mL). Then, an aqueous solution of NaOH 2N (5 mL) was added to the reaction mixture and the solution was stirred at ambient temperature for 16 h. The reaction

mixture was treated with an aqueous solution of HCl 1N (10 mL) and extracted with ethyl acetate (2x). The combined organic layers were washed with water, brine, dried over MgSO₄, filtered and evaporated under *vacuo* to afford (2*R*,2'*R*)-2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))dipropionic acid (**S19**) as a white solid (673 mg, 1.7 mmol, 85%).

M.p. 148-150 °C;

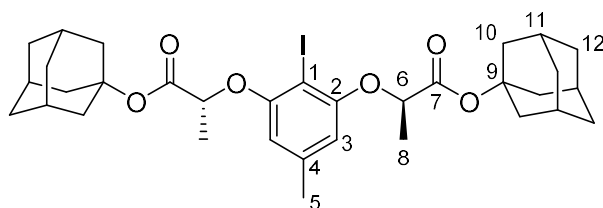
ORD (CHCl₃, c 1.00): $[\alpha]_D^{26} = -43.5^\circ$;

¹H NMR (300 MHz, DMSO-*d*₆) δ = 13.05 (s, 2H), 6.28 (s, 2H), 4.83 (q, $J_{HH} = 6.7$ Hz, 2H), 2.21 (s, 3H), 1.53 (d, $J_{HH} = 6.7$ Hz, 6H).

HRMS (ESI) m/z [M-H]⁻ calcd. for C₁₃H₁₄IO₆⁻: 392.9841, found: 392.9864.

The analytic data are in agreement with the literature.²⁰

(Di((3*S*,5*S*,7*S*)-adamantan-1-yl) 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy)) - (2*R*,2'*R*)-dipropionate (S20**)**



This compound was prepared according to a modified procedure from *Uyanik et al.*²³ (2*R*,2'*R*)-2,2'-((2-iodo-5-methyl-1,3-

phenylene)bis(oxy))dipropionic acid (500 mg, 1.27 mmol, 1.0 eq.), 1-adamantanol (487 mg, 3.17 mmol, 2.5 eq.) and 4-(dimethylamino)-pyridine were dissolved in CH₂Cl₂ (8 mL) and the resulting solution was cooled down to 0°C. Then, a solution of *N,N'*-dicyclohexylcarbodiimide (681 mg, 3.30 mmol, 2.6 eq.) in CH₂Cl₂ (2 mL) was added dropwise. The reaction mixture was allowed to warm up slowly to ambient temperature and was stirred for 16 h. The reaction mixture was treated with an aqueous solution of HCl 1N and extracted with CH₂Cl₂ (3x). The combined organic layers were dried over

MgSO₄, filtered and evaporated under *vacuo*. The crude mixture was purified by column chromatography using cyclohexane:ethyl acetate 95:5 to afford (di((3*S*,5*S*,7*S*)-adamantan-1-yl) 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))-(2*R*,2'*R*)-dipropionate (**S20**) as a white foam (520 mg, 0.78 mmol, 62%).

Rf: (cyclohexane:ethyl acetate 9:1) 0.47;

M.p. 52-56 °C;

ORD (CHCl₃, c 1.00): $[\alpha]_D^{26} = -8.6^\circ$;

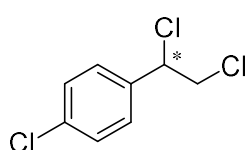
¹H NMR (400 MHz, CDCl₃) δ = 6.20 (s, 2H, H³), 4.60 (q, ³*J*_{HH} = 6.8 Hz, 2H, H⁶), 2.25 (s, 3H, H⁵), 2.15 (m, 6H, H¹¹), 2.07 (m, 12H, H¹⁰), 1.64 (d, ³*J*_{HH} = 6.7 Hz, 6H, H⁸), 1.64 (m, 12H, H¹²) ppm;

¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 170.8 (2C, C⁷), 158.1 (2C, C²), 139.7 (1C, C⁴), 107.9 (2C, C³), 82.0 (2C, C⁹), 76.5 (1C, C¹), 74.5 (2C, C⁶), 41.3 (6C, C¹⁰), 36.2 (6C, C¹²), 31.0 (6C, C¹¹), 22.0 (1C, C⁵), 18.7 (2C, C⁸).

IR (ATR) $\tilde{\nu}$ = 2909 (m), 2852 (w), 1748 (m), 1726 (m), 1579 (m), 1455 (m), 1418 (w), 1374 (w), 1354 (w), 1315 (w), 1272 (m), 1239 (m), 1196 (m), 1135 (s), 1102 (s), 1073 (s), 1051 (s), 1022 (m), 966 (w), 941 (w), 917 (w), 897 (w), 878 (w), 856 (w), 812 (w), 778 (w), 754 (w), 725 (w), 705 (w), 663 (w) cm⁻¹;

HRMS (ESI) *m/z* [M+Na]⁺ calcd. for C₃₃H₄₃IO₆Na⁺: 685.1997, found: 685.1999.

1-Chloro-4-(1,2-dichloroethyl)benzene¹⁵ (**14**)



Reaction time of 3 days:

4-Chlorostyrene (28 mg, 0.20 mmol, 1.0 eq.), (di((3*S*,5*S*,7*S*)-adamantan-1-yl) 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))-(2*R*,2'*R*)-dipropionate (27 mg, 0.04 mmol, 0.2 eq.), cesium chloride (101 mg,

0.60 mmol, 3.0 eq.) and Selectfluor® (78 mg, 0.22 mmol, 1.1 eq.) were dissolved in a solution of HFIP (302 mg, 1.80 mmol, 9.0 eq.) in CH₂Cl₂ (0.9 mL). The mixture was cooled to -40°C and stirred for 3 days using a mechanical stirring. The reaction mixture was then quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic layers were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The *e.r.* of the product was determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and *n*-hexane:*i*-propanol (99.5:0.5, 0.5 mL/min) as the eluent. The detection was at 230 nm. *t_R* = 17.91 min (major enantiomer), *t_R* = 17.29 min (minor enantiomer); ***e.r.*: 64:36**. The sample was combined with the crude and evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR (**yield: 29%**).

Reaction time of 24 h:

4-Chlorostyrene (28 mg, 0.20 mmol, 1.0 eq.), di((3*S*,5*S*,7*S*)-adamantan-1-yl) 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy))-(2*R*,2'*R*)-dipropionate (27 mg, 0.04 mmol, 0.2 eq.), cesium chloride (101 mg, 0.60 mmol, 3.0 eq.) and Selectfluor® (78.0 mg, 0.22 mmol, 1.1 eq.) were dissolved in a solution of HFIP (302 mg, 1.80 mmol, 9.0 eq.) in CH₂Cl₂ (0.9 mL). The mixture was cooled to -40°C and stirred for 24 h using a mechanical stirring. The reaction mixture was then quenched with a saturated solution of Na₂S₂O₃ and extracted with CH₂Cl₂ (3x). The combined organic layers were dried over MgSO₄, filtered and the solvent was evaporated under *vacuo*. The *e.r.* of the product was determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and *n*-hexane:*i*-propanol (99.5:0.5, 0.5 mL/min) as the eluent. The detection was at 230 nm. *t_R* = 17.90 min (major enantiomer), *t_R* = 17.36 min (minor enantiomer), ***e.r.*: 64:36**. The sample was combined with the crude and

evaporated under *vacuo*. The residue was dissolved in 0.6 mL of CDCl₃ containing 0.1 mmol of DMF (stock solution) and analysed by ¹H NMR (**yield: 23%**). The crude was then purified by column chromatography using cyclohexane 100% to afford 1-chloro-4-(1,2-dichloroethyl)benzene (**14**) as a colourless oil (6 mg, 0.03 mmol, 14%). The *e.r.* of the purified product was determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and *n*-hexane : *i*-propanol (99.5 : 0.5, 0.5 mL/min) as the eluent. The detection was at 230 nm. *t_R* = 18.66 min (major enantiomer), *t_R* = 18.08 min (minor enantiomer), ***e.r.*: 64:36**.

R_f: (100% cyclohexane) 0.44;

ORD (CHCl₃, c 0.50): [α]_D²⁶ = +14.5° for an *e.r.* 64:36;

¹H NMR (300 MHz, CDCl₃) δ = 7.36 (m, 4H), 4.97 (dd, ³*J*_{HH} = 8.4, 6.2 Hz, 1H), 3.99 (dd, ³*J*_{HH} = 11.3, 6.2 Hz, 1H), 3.88 (dd, ³*J*_{HH} = 11.4, 8.4 Hz, 1H).

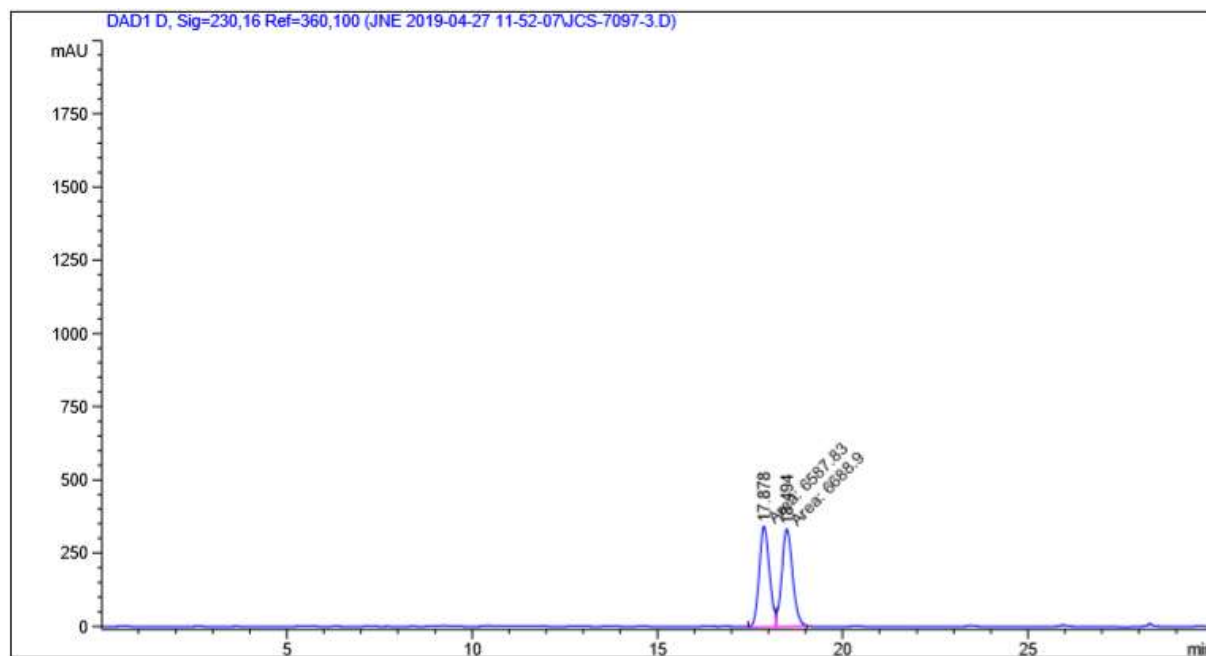
MS (EI) *m/z* (%) = 208.0 (12), 210.0 (12), 212.0 (4) [M]⁺, 173.0 (26) [M-Cl]⁺, 159.0 (100) [M-CH₂Cl]⁺.

The analytic data are in agreement with the literature.¹⁵

VIII. HPLC traces

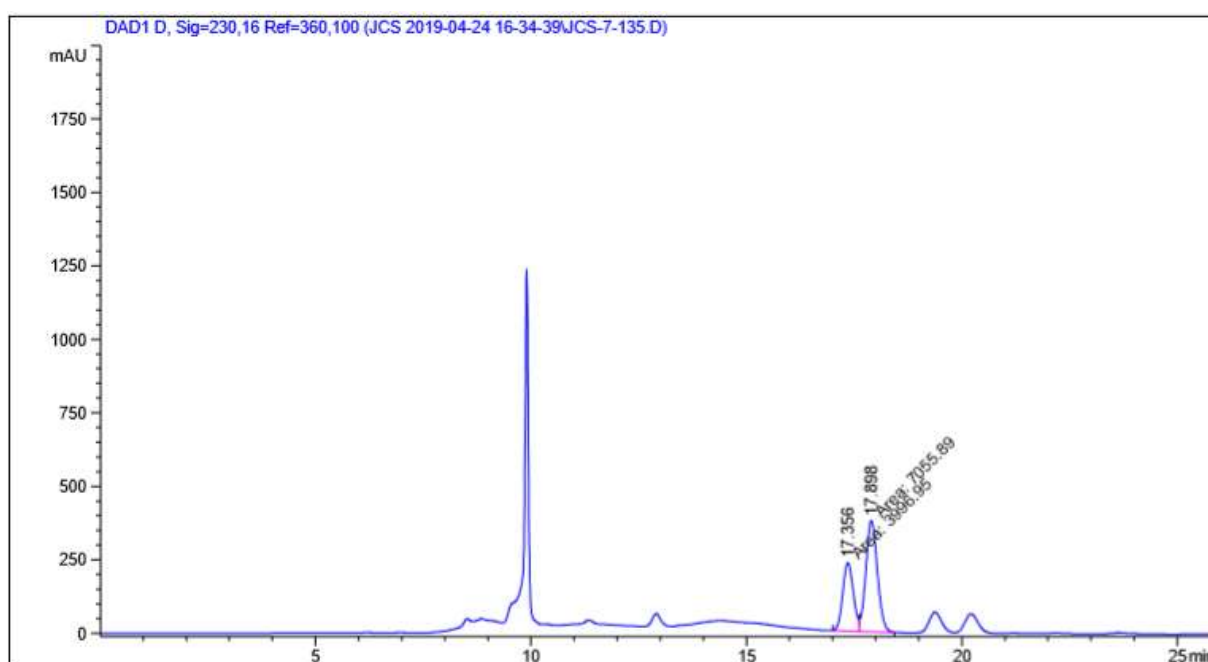
1-Chloro-4-(1,2-dichloroethyl)benzene (14)

HPLC trace: racemic sample.



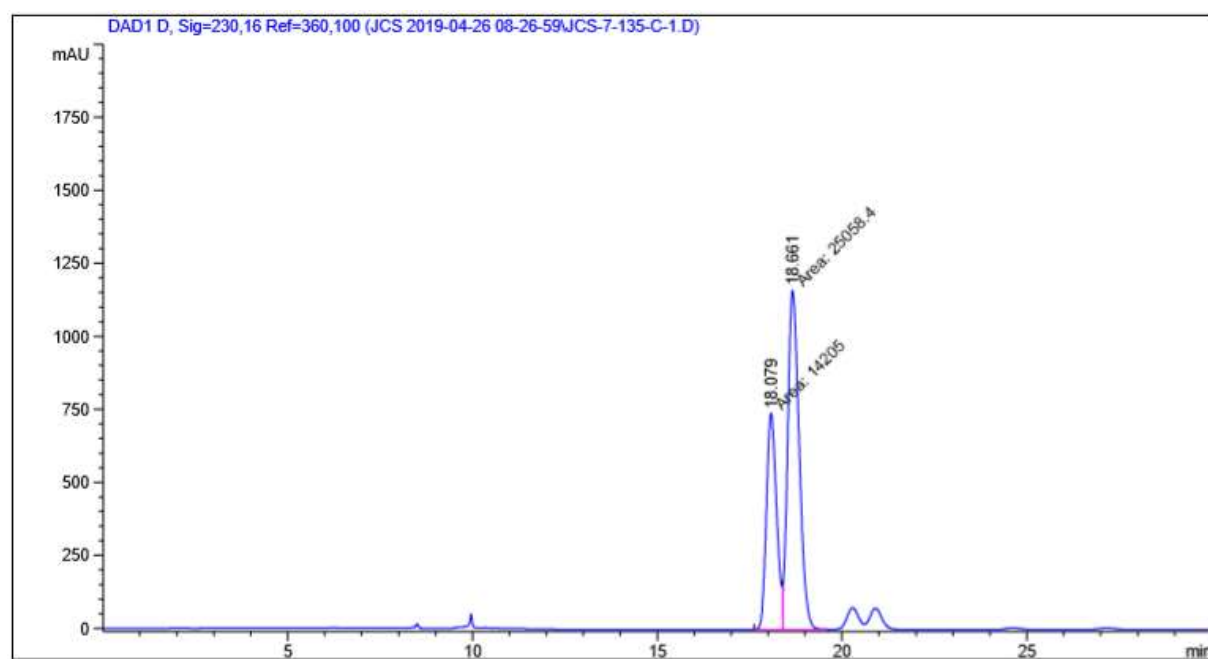
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.878	MF	0.3212	6587.82764	341.87112	49.6194
2	18.494	FM	0.3372	6688.89600	330.62091	50.3806

HPLC trace: crude reaction mixture using catalyst **S20** after a reaction time of 24 h.



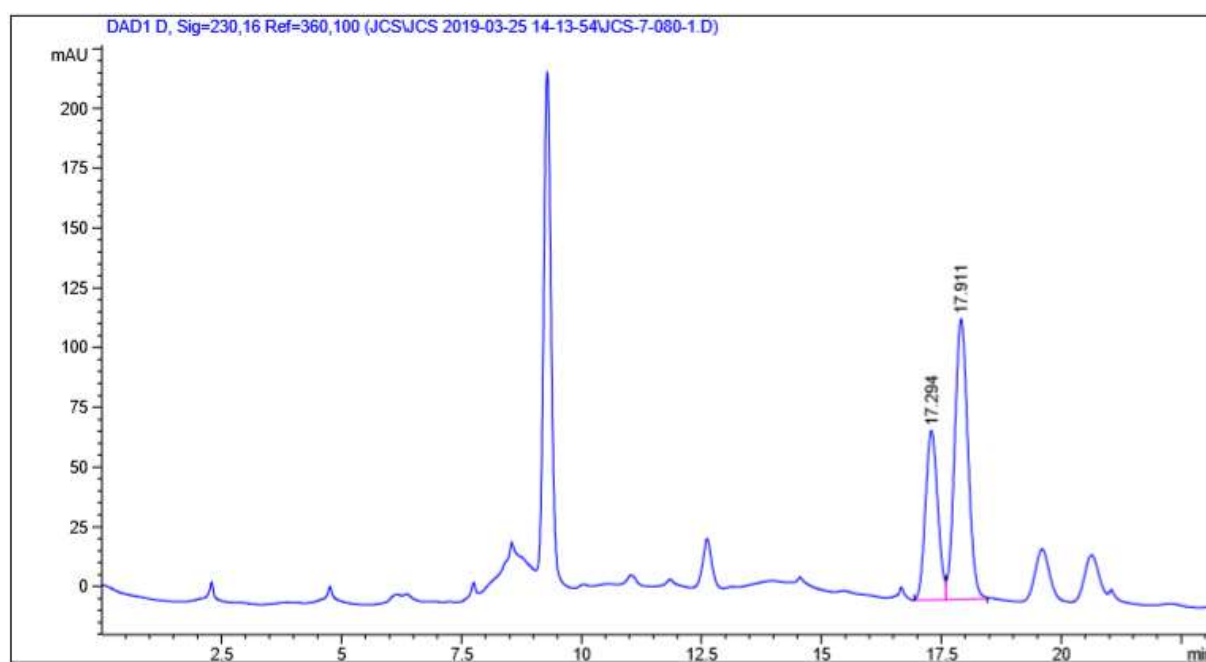
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.356	MF	0.2855	3996.95239	233.30226	36.1622
2	17.898	FM	0.3105	7055.88574	378.70444	63.8378

HPLC trace: product **23** after column chromatography.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.079	MF	0.3200	1.42050e4	739.83081	36.1787
2	18.661	FM	0.3596	2.50584e4	1161.32532	63.8213

HPLC trace: crude reaction mixture using catalyst **S20** after a reaction time of 3 days.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.294	BV	0.2797	1259.91699	70.77761	35.9425
2	17.911	VB	0.2996	2245.45142	117.18168	64.0575

IX. X-Ray Crystallographic Data

X-Ray diffraction: Data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, A71, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, C71 (1), 3-8) and graphics, *XP* (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *wR*² values are given for all reflections.

Exceptions and special features: For compound **19** the chlorinated alkyl chain was found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR, DFIX and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of *p*-Toll(III)Cl₂ (S15, gil8779): A pale yellow prism-like specimen of C₇H₇Cl₂l, approximate dimensions 0.065 mm x 0.109 mm x 0.114 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1138 frames were collected. The total exposure time was 15.81 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 7283 reflections to a maximum θ angle of 27.54° (0.77 Å resolution), of which 1050 were independent (average redundancy 6.936, completeness = 99.2%, *R*_{int} = 3.35%, *R*_{sig} = 2.12%) and 1026 (97.71%) were greater than 2 σ (*F*²). The final cell constants of *a* = 9.0964(5) Å, *b* = 13.1668(7) Å, *c* = 7.9041(4) Å, β = 107.089(2)°, volume = 904.88(8) Å³, are based upon the refinement of the XYZ-centroids of 5927 reflections above 20 σ (*I*) with 5.614° < 2 θ < 55.07°. Data were corrected for absorption

effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.812. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6550 and 0.7790. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $C2/c$, with $Z = 4$ for the formula unit, $C_7H_7Cl_2I$. The final anisotropic full-matrix least-squares refinement on F^2 with 49 variables converged at $R1 = 1.76\%$, for the observed data and $wR2 = 4.46\%$ for all data. The goodness-of-fit was 1.142. The largest peak in the final difference electron density synthesis was $0.912 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.972 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.107 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 2.121 g/cm^3 and $F(000)$, 544 e^- . CCDC number: 1555066.

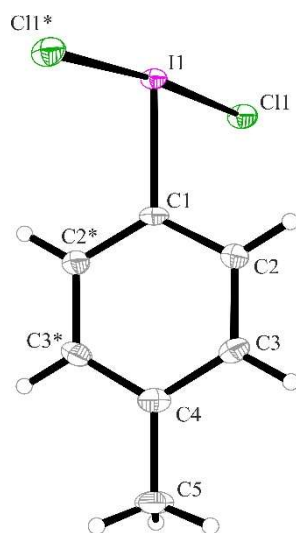


Figure S10: Crystal structure of compound ***p*-Toll(III)Cl₂ (S15)**.

Thermal ellipsoids are set at 50% probability.

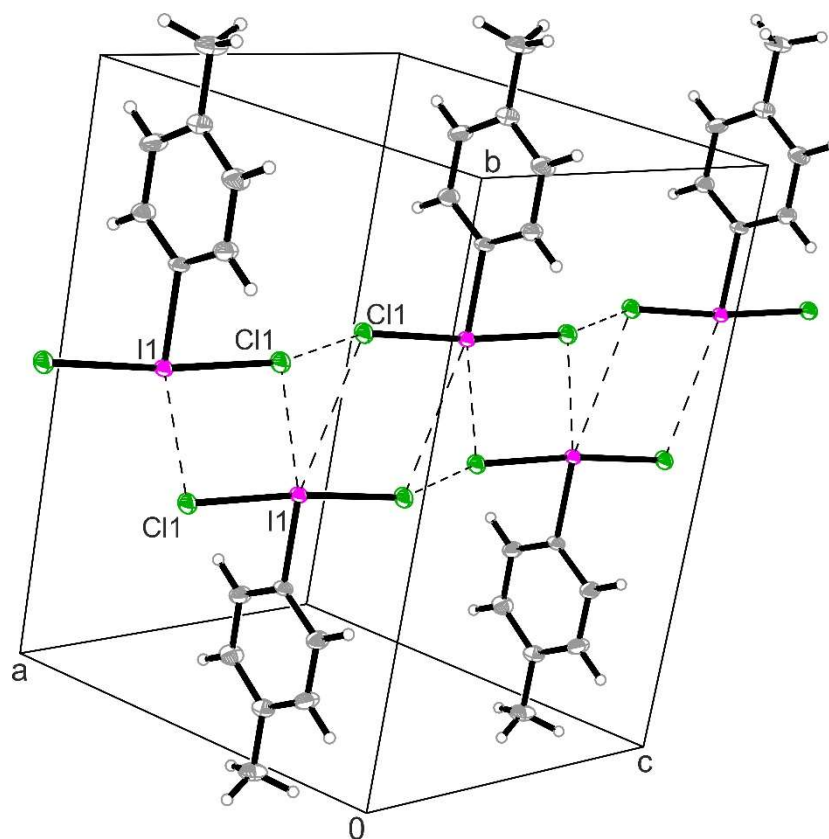


Figure S11: Excerpt of the packing diagram of compound ***p*-Toll(III)Cl₂ (S15)** representing the formation of a supramolecular chain along the *ac*-diagonal involving

non-covalent intermolecular interactions I...Cl and Cl...Cl

(I...Cl 3.608 Å^{#1} and Cl...Cl 3.234 Å^{#2})

Symmetry transformations used to generate equivalent atoms: ^{#1} $-x+1, -y+2, -z+1$; ^{#2} $x, -y+2, z-1/2$.

X-ray crystal structure analysis of 19 (gil9203): A colourless plate-like specimen of $C_{13}H_{14}Cl_2N_2O_6$, approximate dimensions 0.051 mm x 0.122 mm x 0.208 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1254 frames were collected. The total exposure time was 21.44 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 18112 reflections to a maximum θ angle of 68.35° (0.83 Å resolution), of which 2869 were independent (average redundancy 6.313, completeness = 99.6%, $R_{int} = 5.68\%$, $R_{sig} = 3.99\%$) and 2419 (84.32%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 14.7104(4)$ Å, $b = 6.5032(2)$ Å, $c = 17.3354(5)$ Å, $\beta = 109.6840(10)^\circ$, volume = $1561.48(8)$ Å³, are based upon the refinement of the XYZ-centroids of 7806 reflections above $20 \sigma(I)$ with $10.56^\circ < 2\theta < 136.6^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.846. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4860 and 0.8200. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $C_{13}H_{14}Cl_2N_2O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 290 variables converged at $R1 = 4.94\%$, for the observed data and $wR2 = 12.23\%$ for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was $0.272 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.401 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.049 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.553 g/cm^3 and $F(000)$, 752 e^- . CCDC number: 1905463.

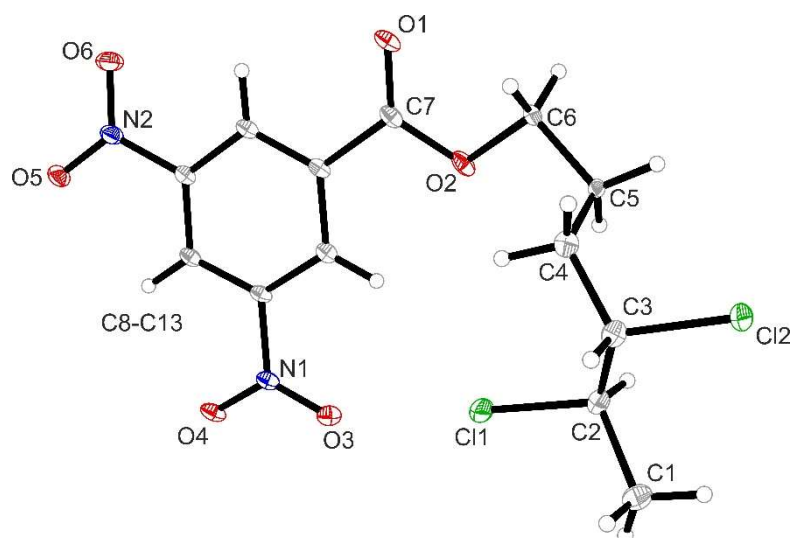


Figure S12: Crystal structure of compound **19**.
Thermal ellipsoids are set at 15% probability.

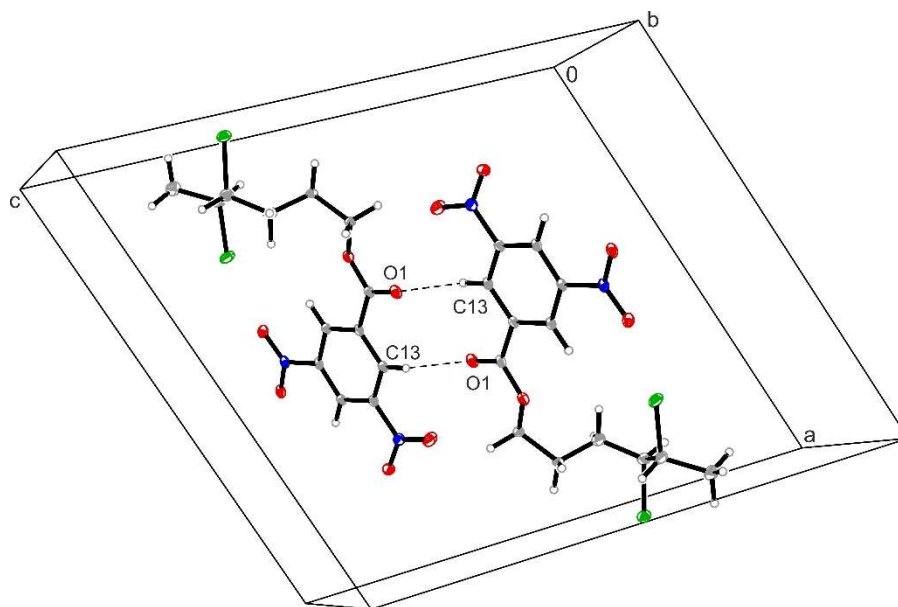


Figure S13: Dimer formation involving C-H...O interaction in compound **19**.

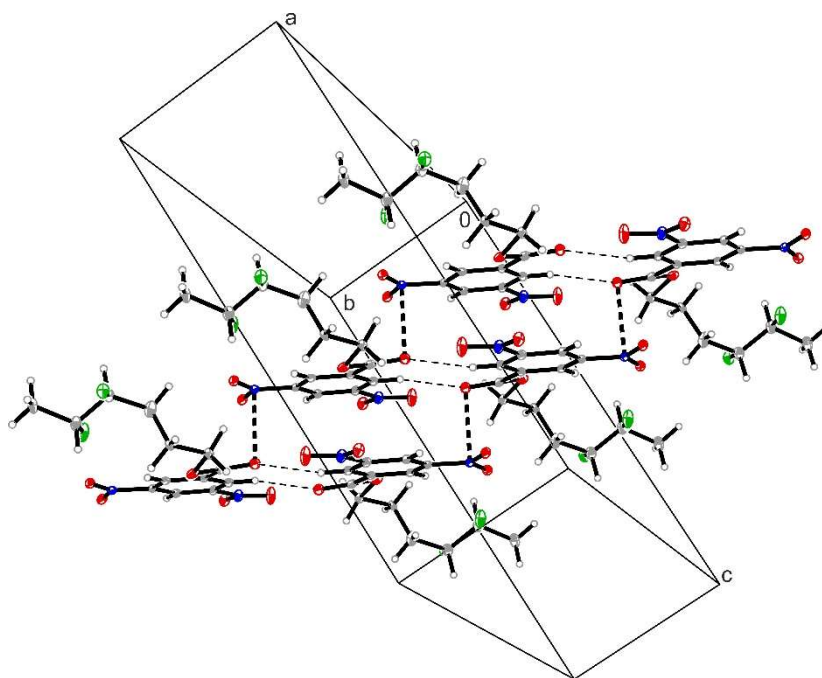


Figure S14: Excerpt of the packing diagram of compound **19** representing the formation of a linear stairs chain along the *b*-axis trough non-covalent intermolecular $\pi\cdots\pi$ interactions (shortest distance between the dimeric units: N1 \cdots O1 2.918 Å^{#1})

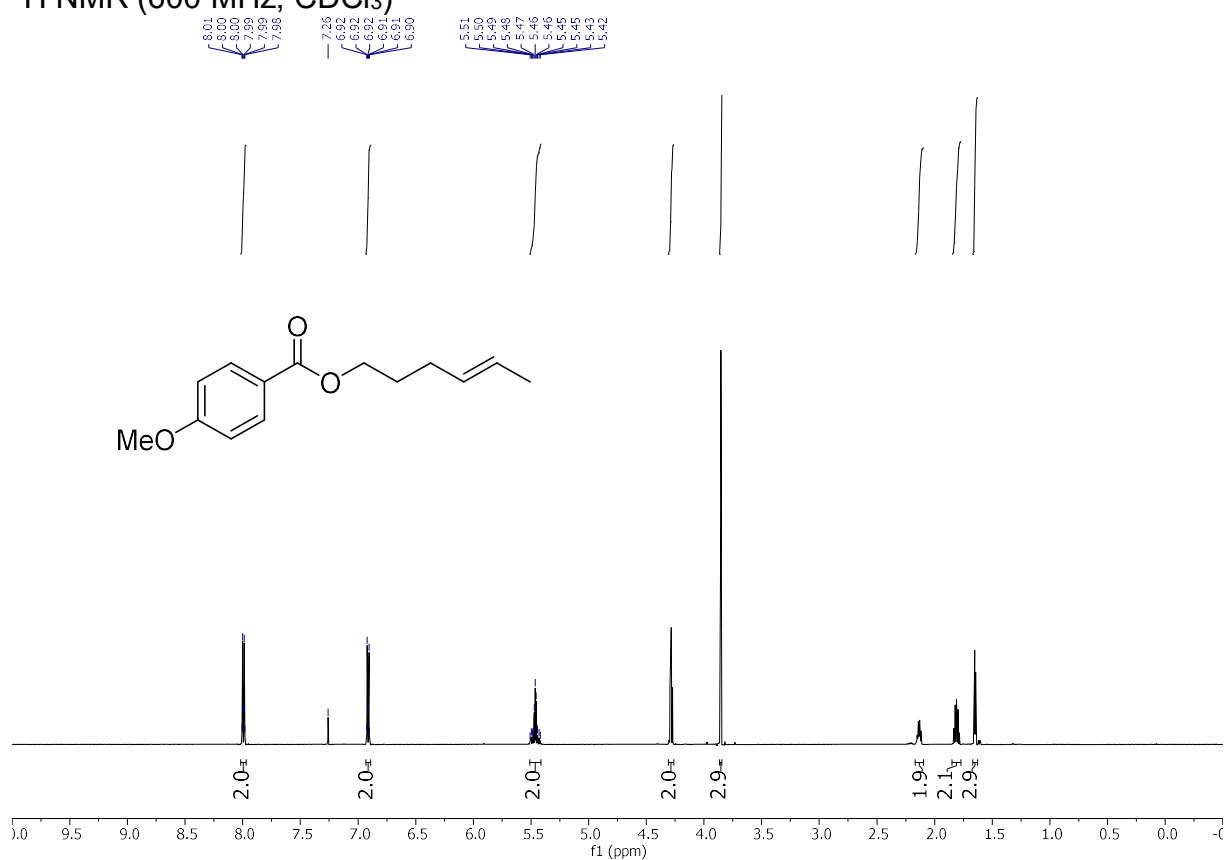
Symmetry transformations used to generate equivalent atoms: ^{#1} *x*, *y*+1, *z*.

1. *APEX3* (2016), *SAINT* (2015) and *SADABS* (2015), Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M., *SHELXT – Integrated space-group and crystal-structure determination*, *Acta Cryst.*, **2015**, A71, 3-8.
3. Sheldrick, G.M., *Crystal structure refinement with SHELXL*, *Acta Cryst.*, **2015**, C71 (1), 3-8.
4. *XP – Interactive molecular graphics, Version 5.1*, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**.

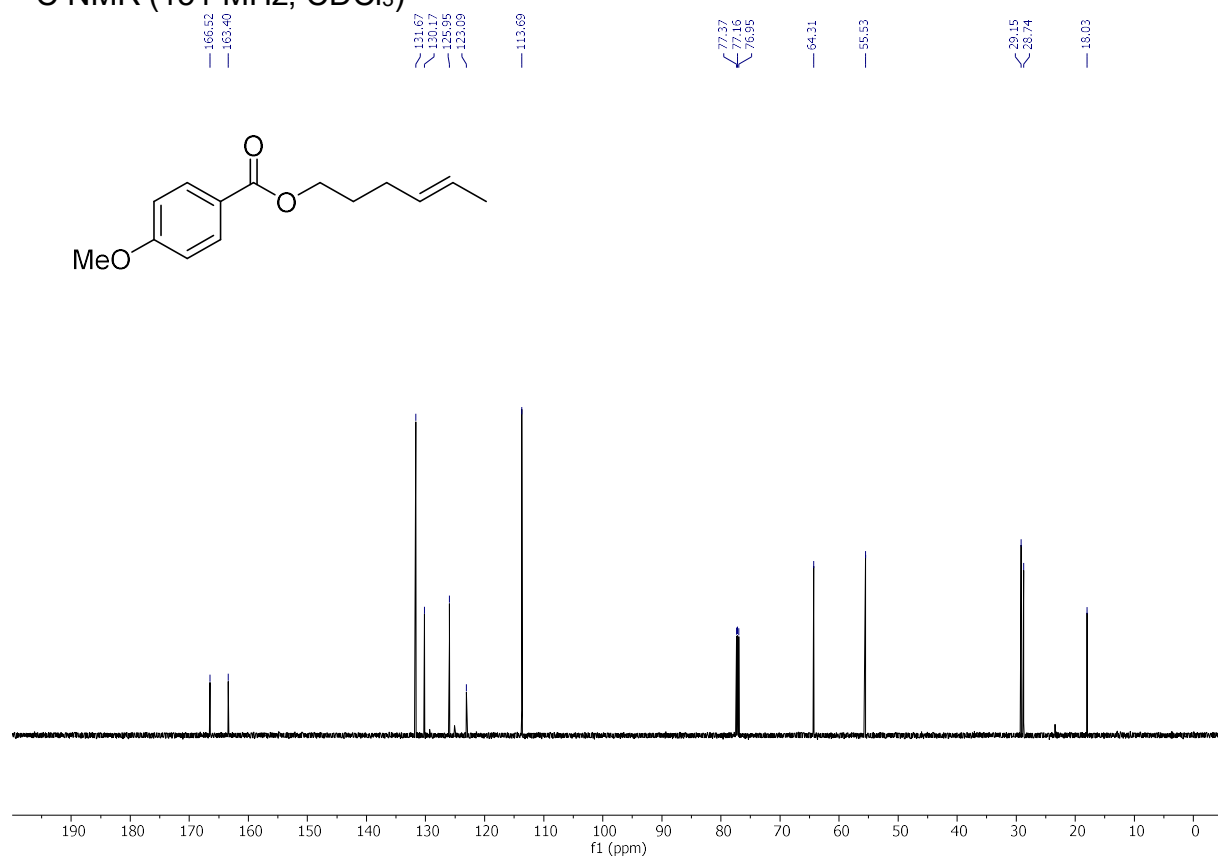
X. NMR Spectra of unreported starting materials

(E)-Hex-4-en-1-yl 4-methoxybenzoate (S3)

^1H NMR (600 MHz, CDCl_3)

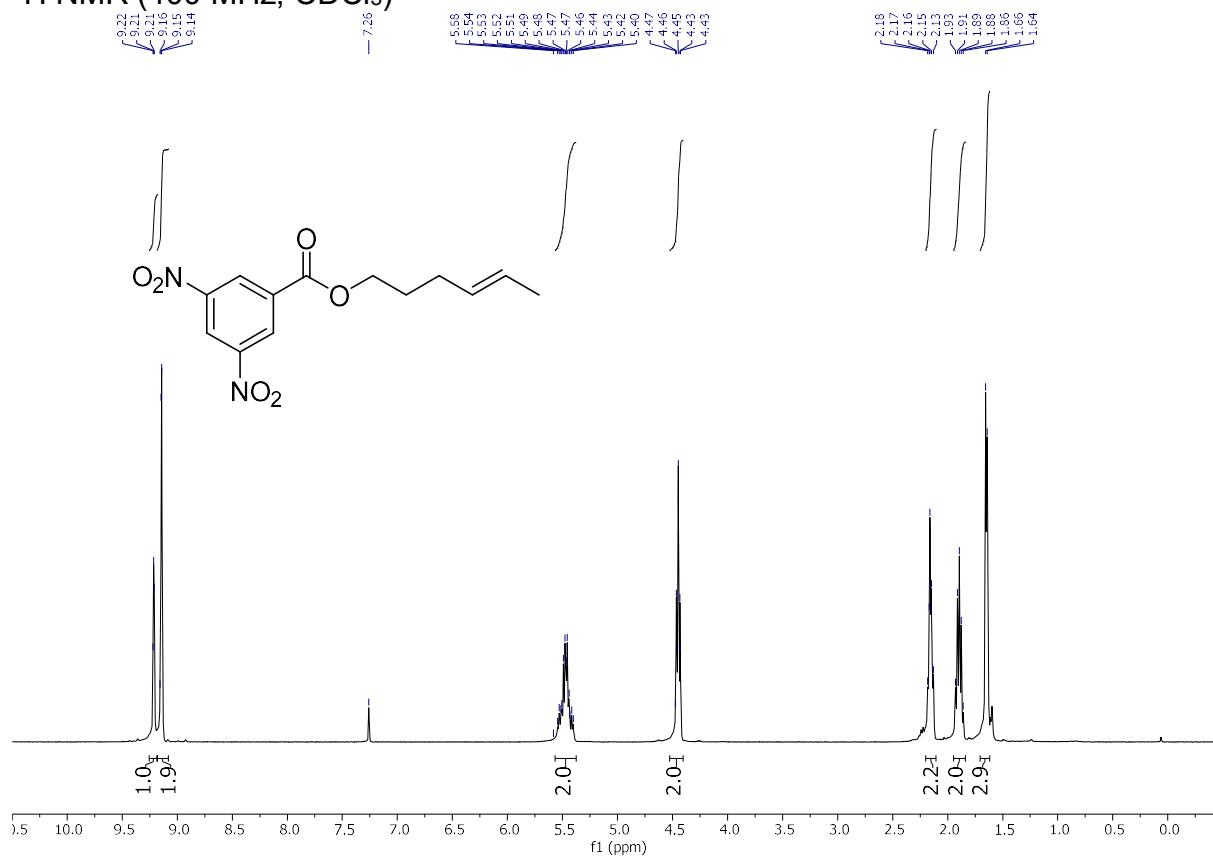


^{13}C NMR (151 MHz, CDCl_3)

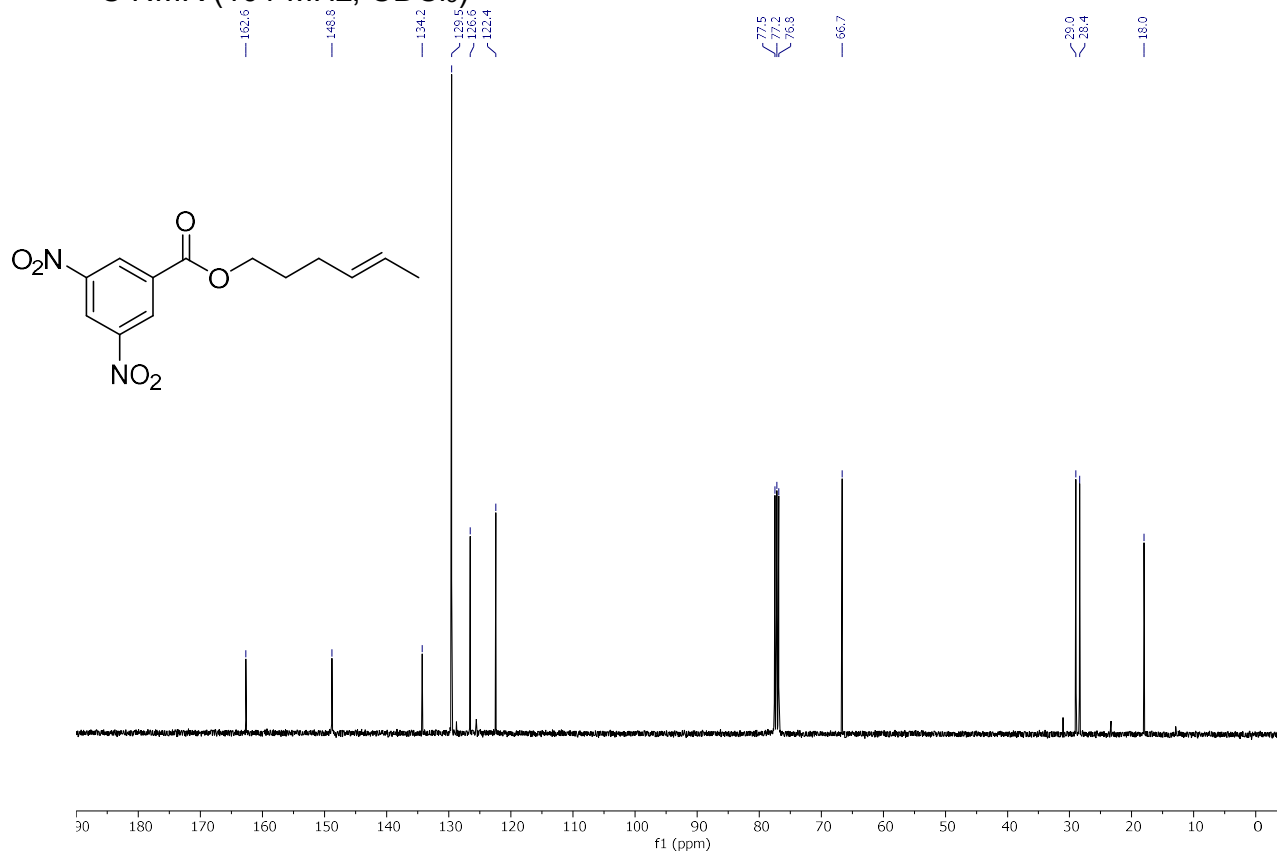


(E)-Hex-4-en-1-yl 3,5-dinitrobenzoate (S4)

^1H NMR (400 MHz, CDCl_3)

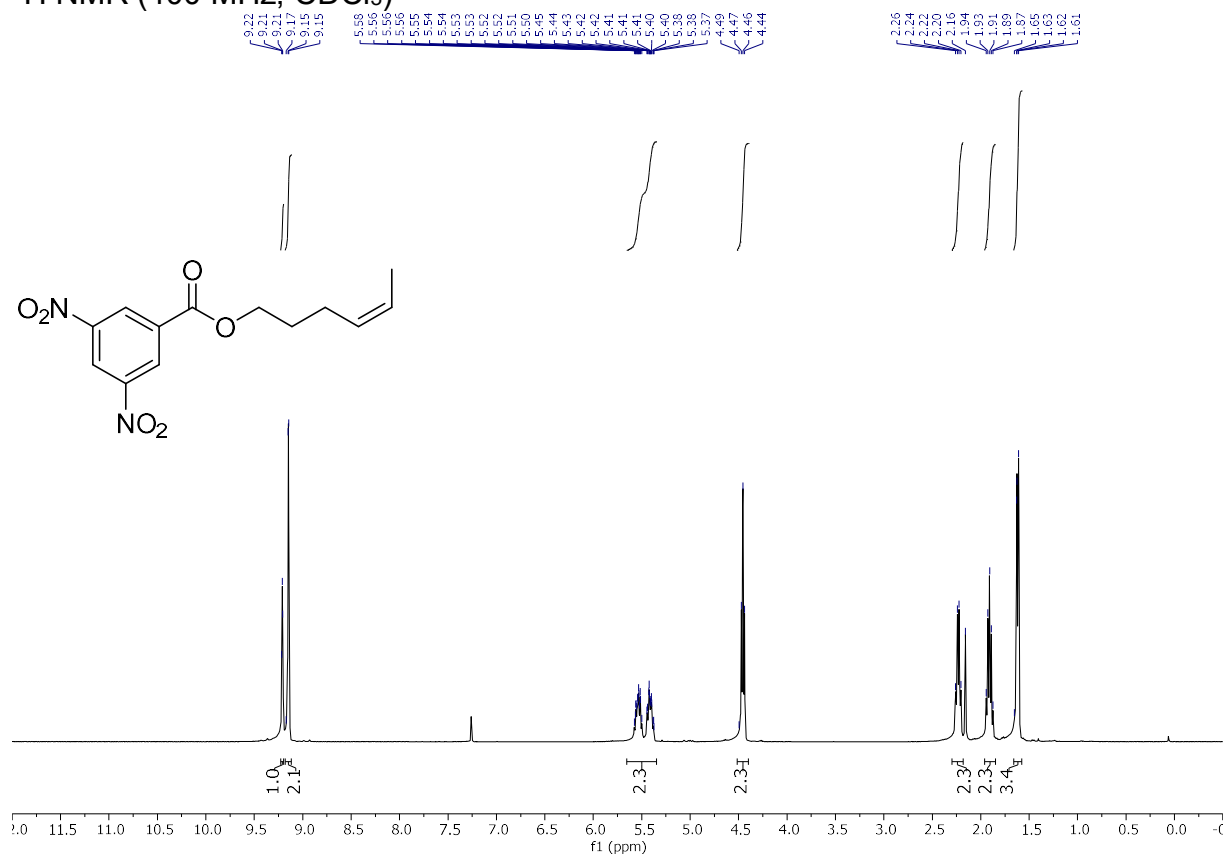


^{13}C NMR (101 MHz, CDCl_3)

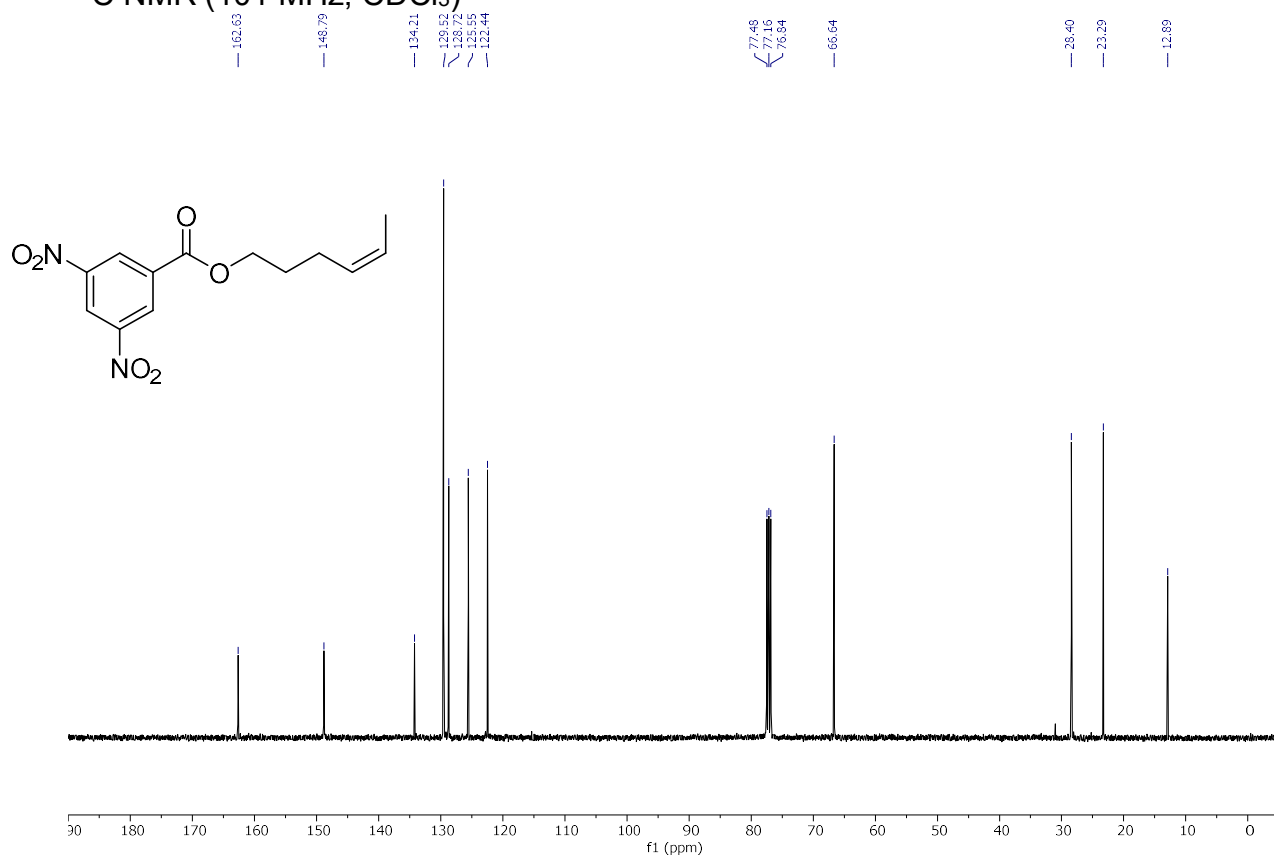


(Z)-Hex-4-en-1-yl 3,5-dinitrobenzoate (S5)

¹H NMR (400 MHz, CDCl₃)

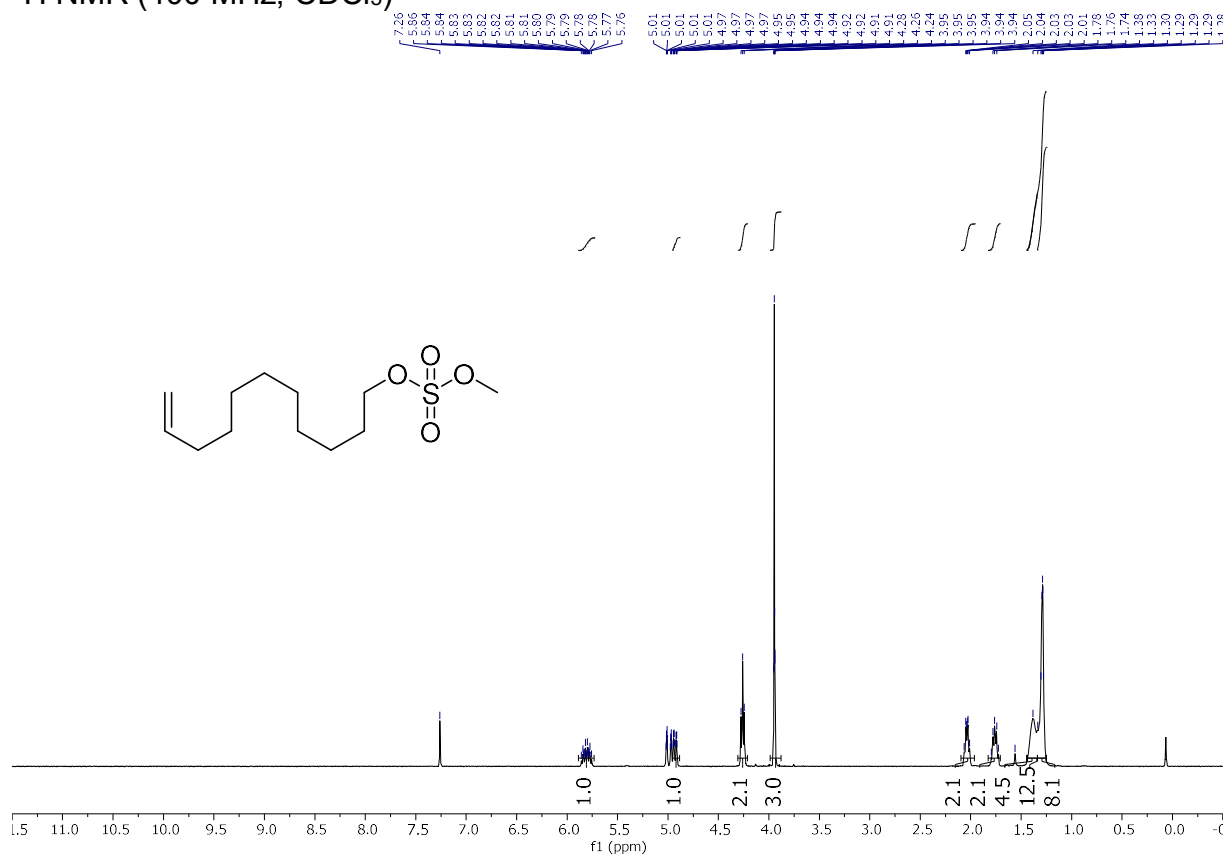


¹³C NMR (101 MHz, CDCl₃)

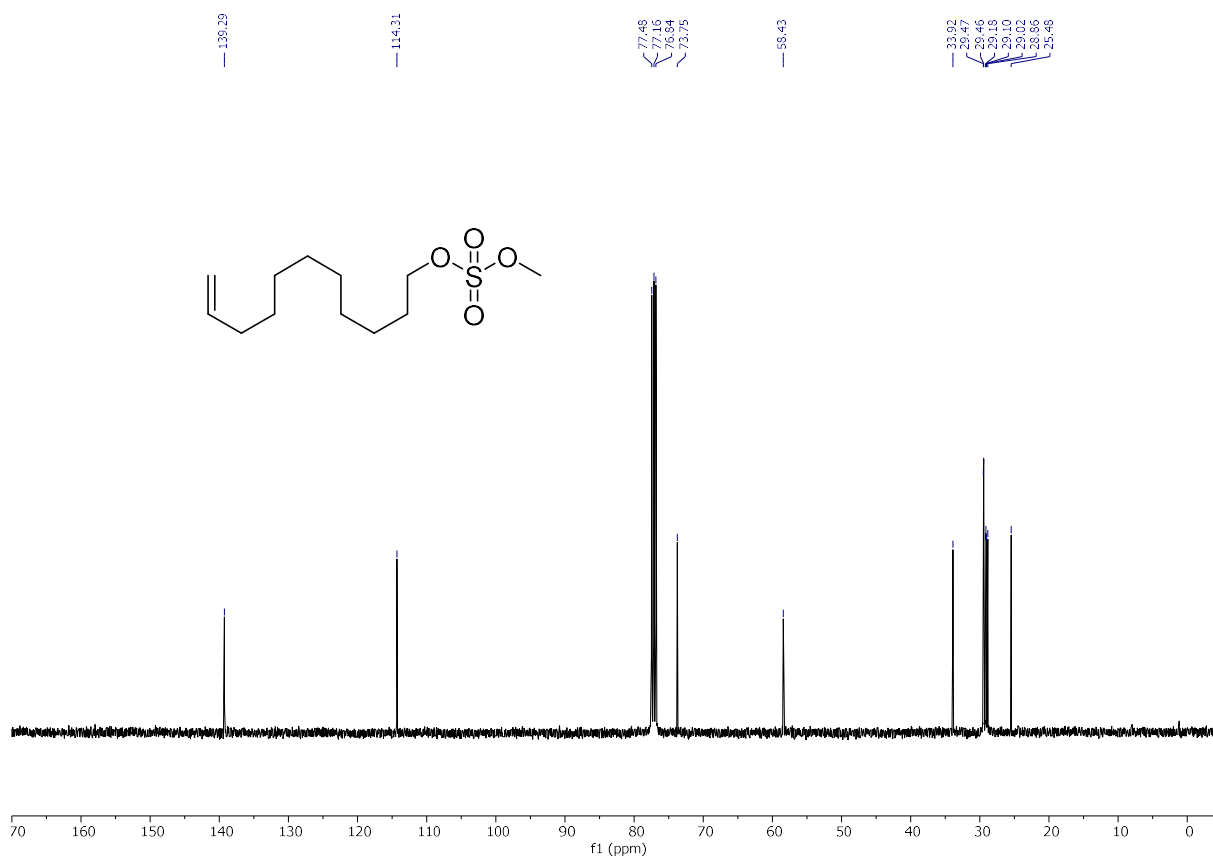


Methyl undec-10-en-1-yl sulfate (S10)

^1H NMR (400 MHz, CDCl_3)

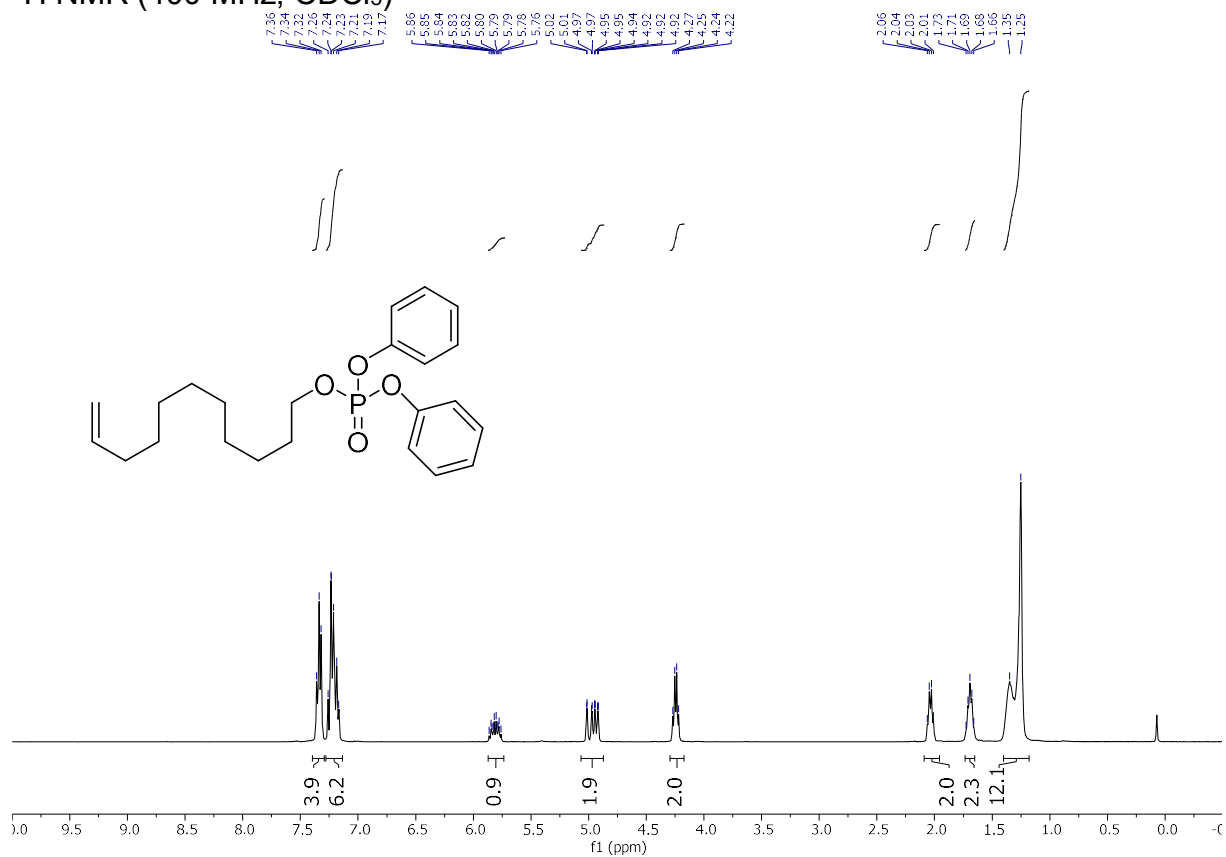


^{13}C NMR (101 MHz, CDCl_3)

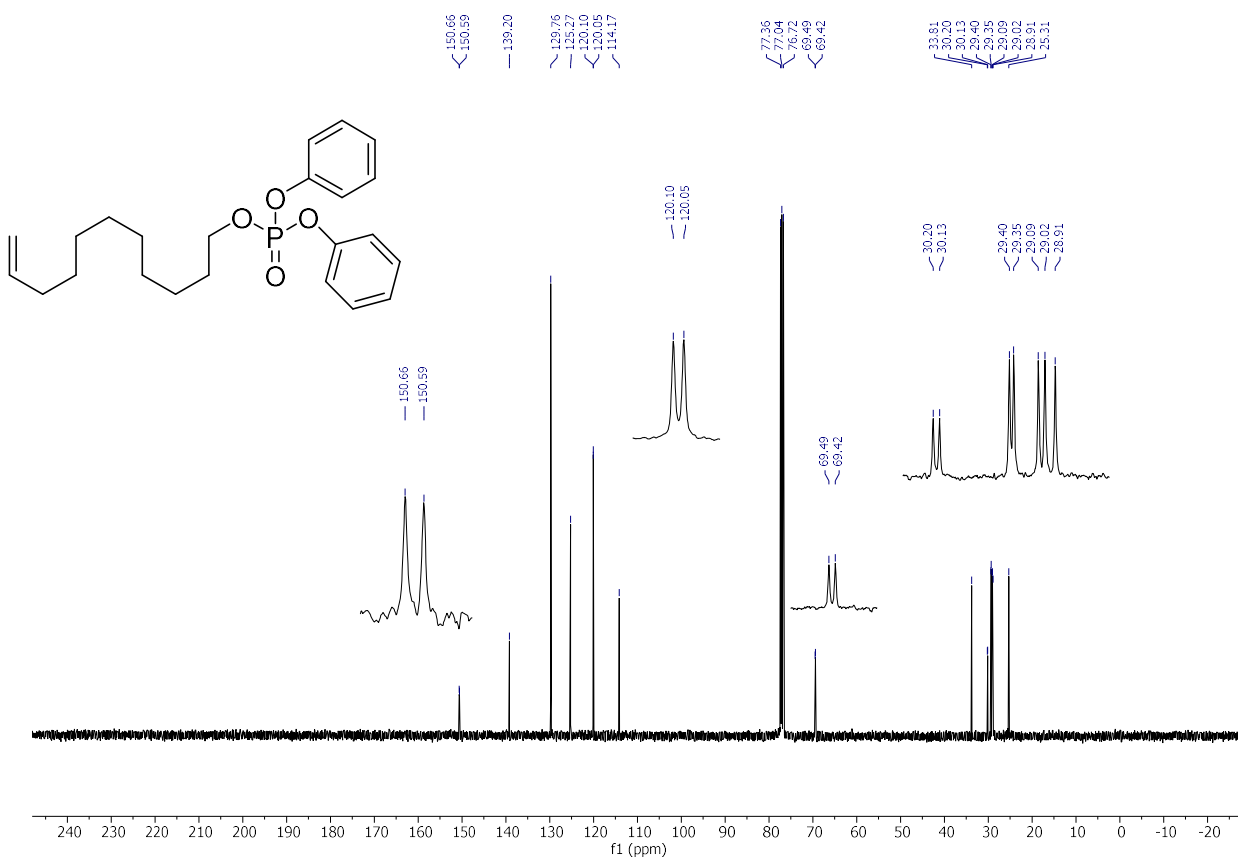


Diphenyl undec-10-en-1-yl phosphate (S11)

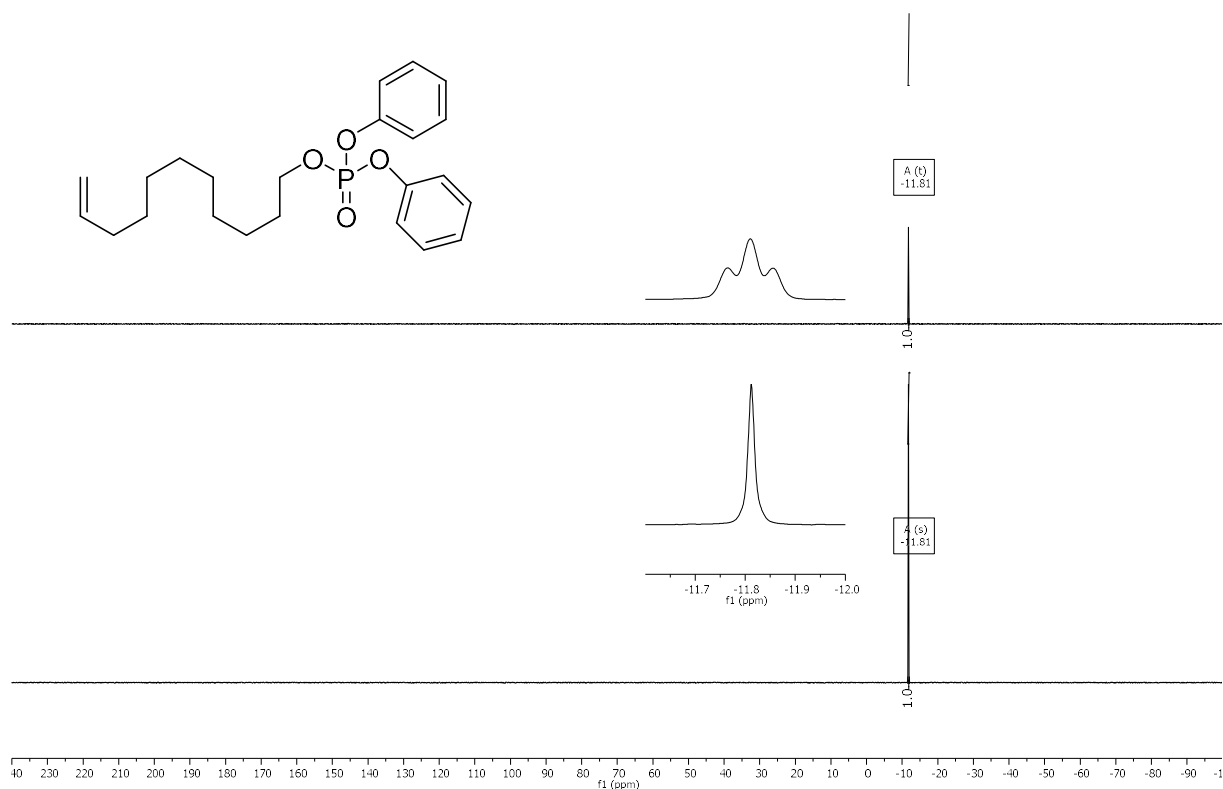
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

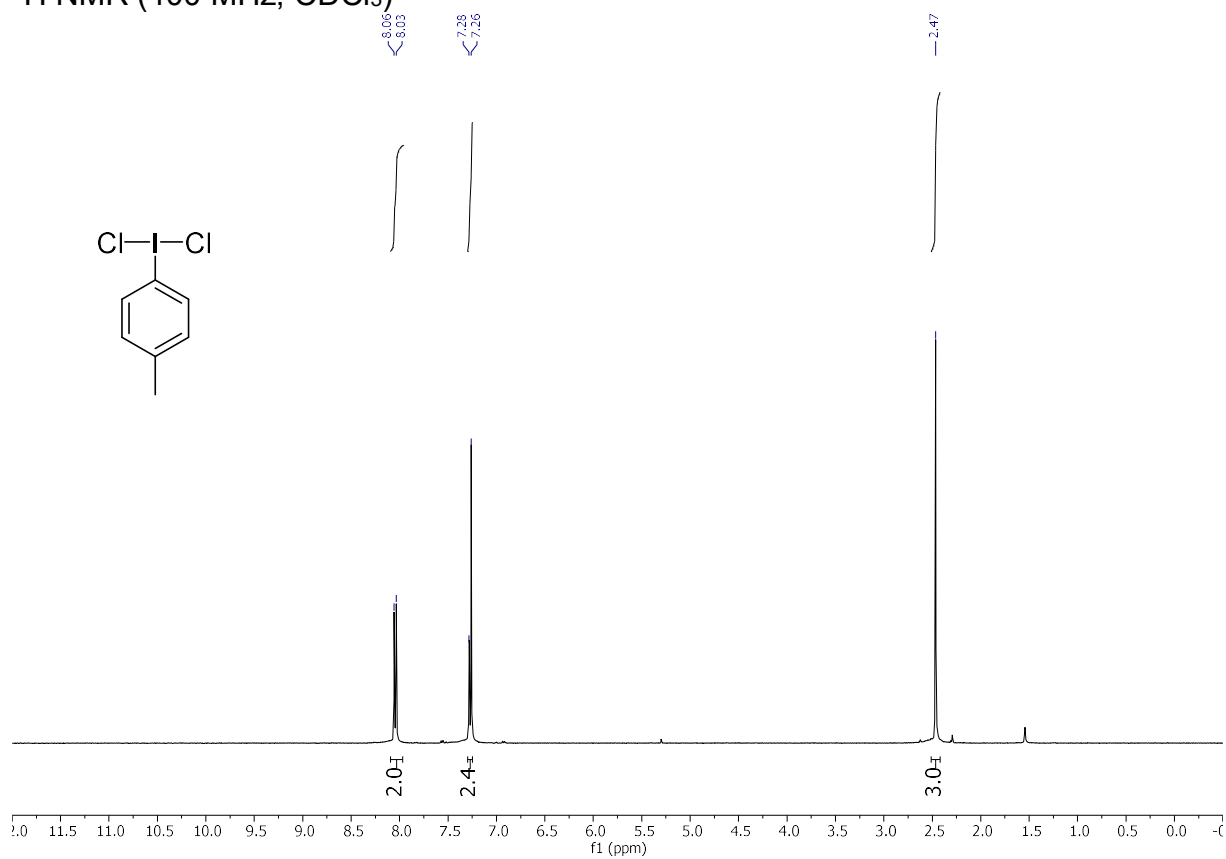


^{31}P NMR (162 MHz, CDCl_3)



Dichloro(*p*-tolyl)- λ^3 -iodane (S15)

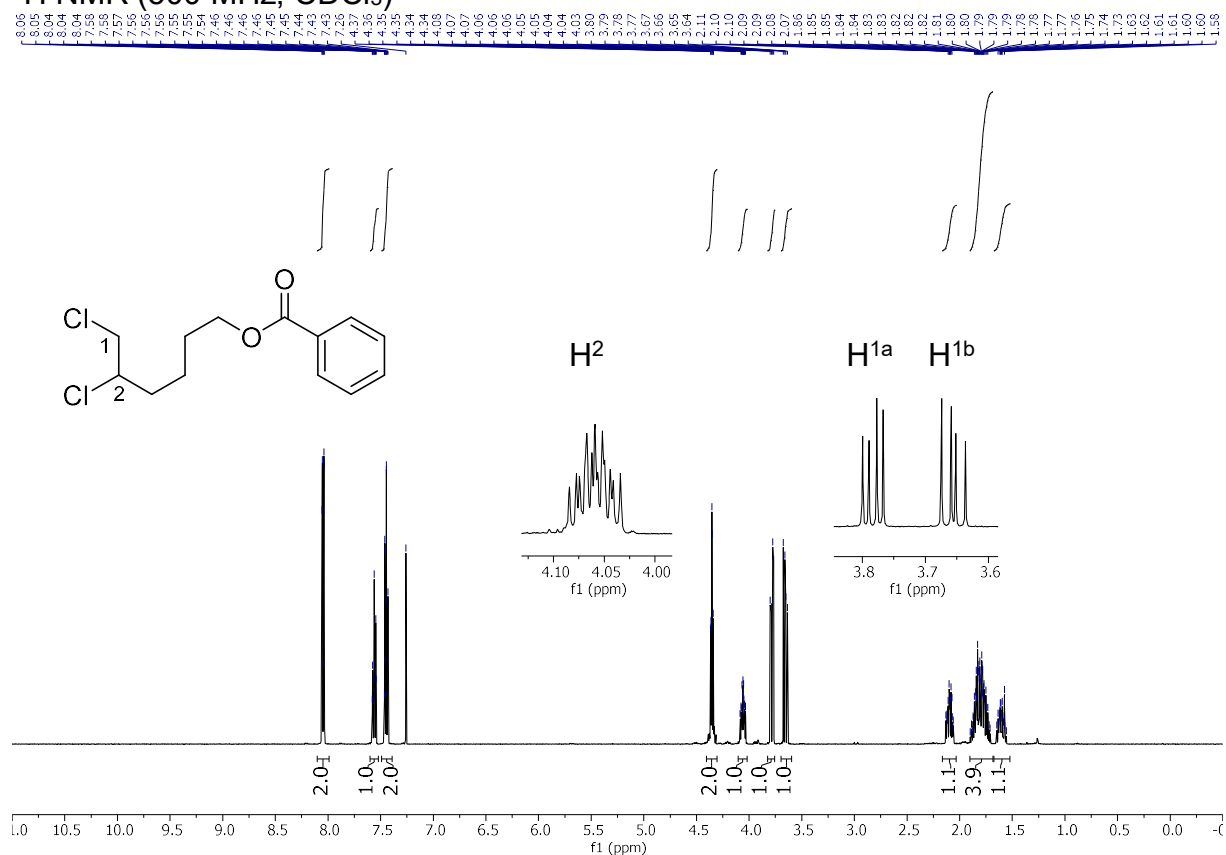
^1H NMR (400 MHz, CDCl_3)



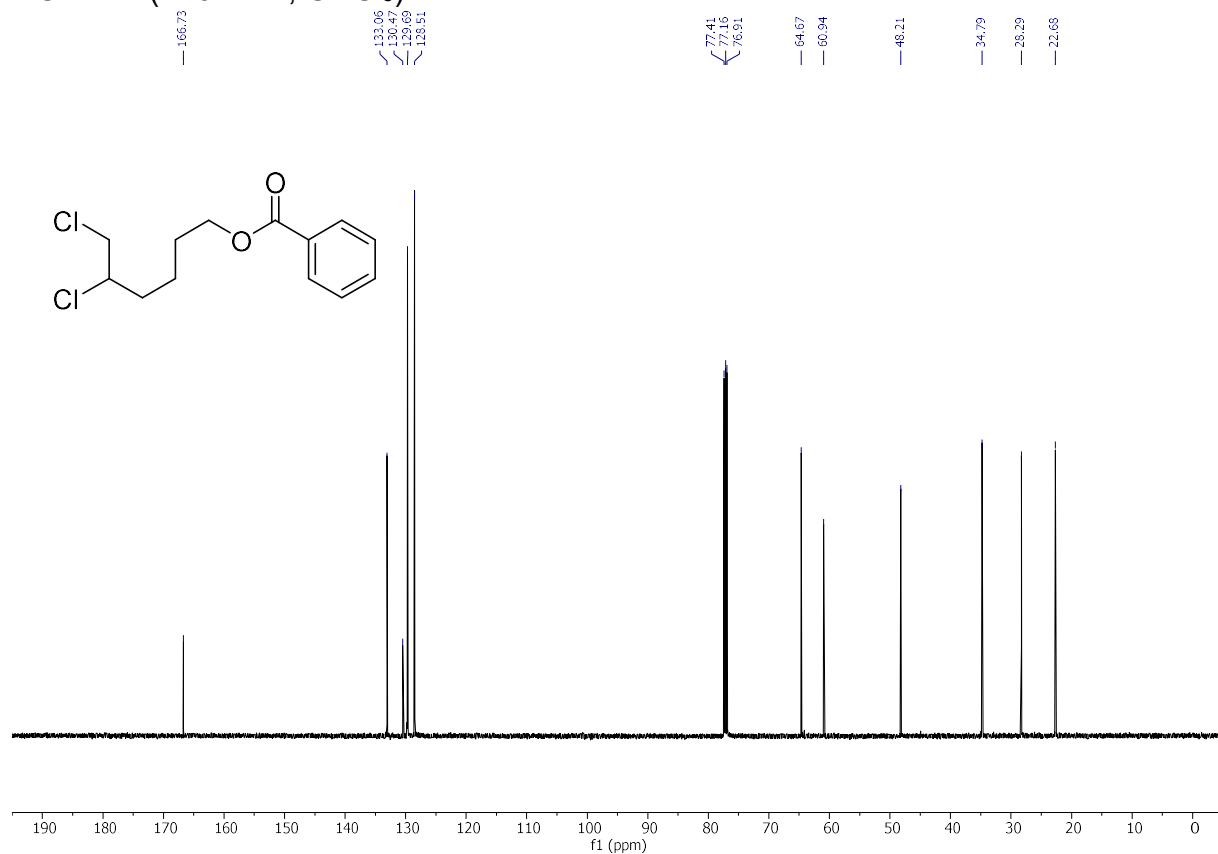
XI. NMR Spectra of products

5,6-Dichlorohexyl benzoate (2)

¹H NMR (500 MHz, CDCl₃)

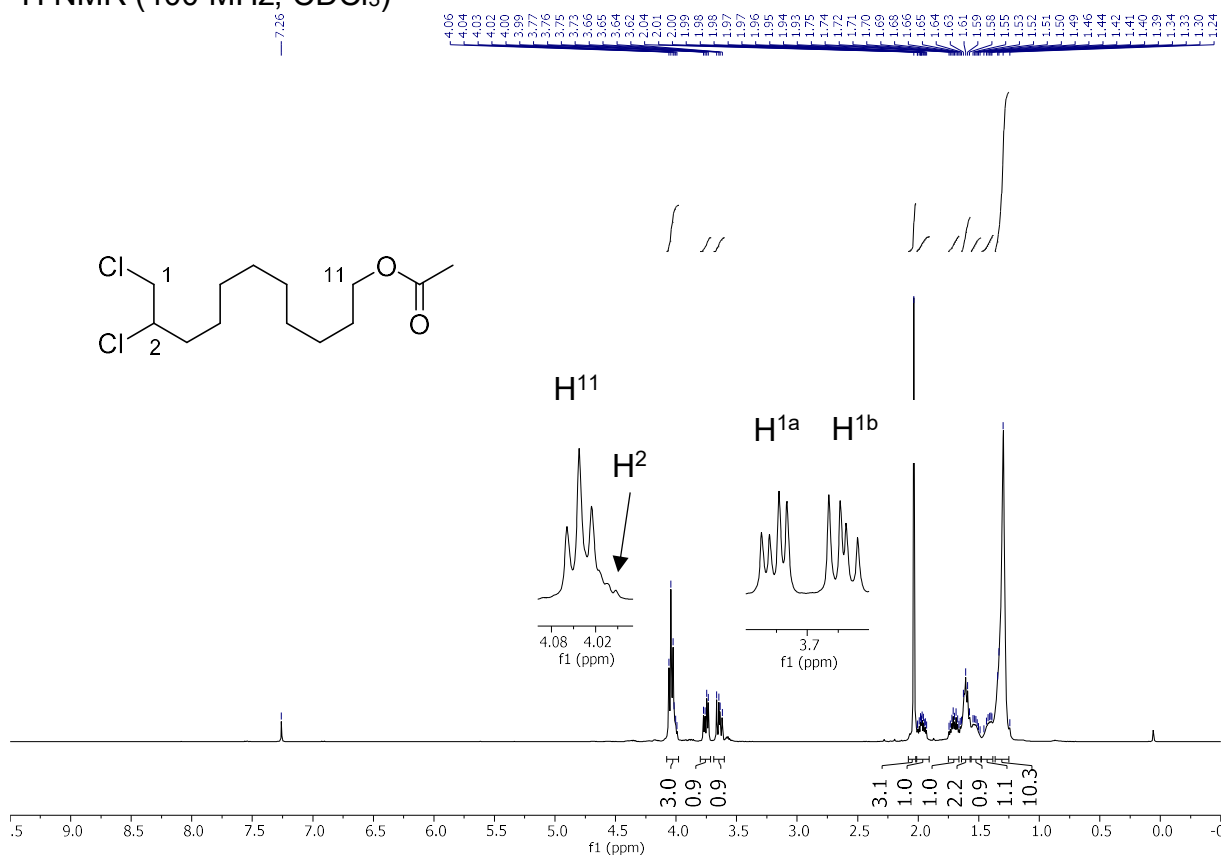


¹³C NMR (126 MHz, CDCl₃)



10,11-Dichloroundecyl acetate (3)

^1H NMR (400 MHz, CDCl_3)

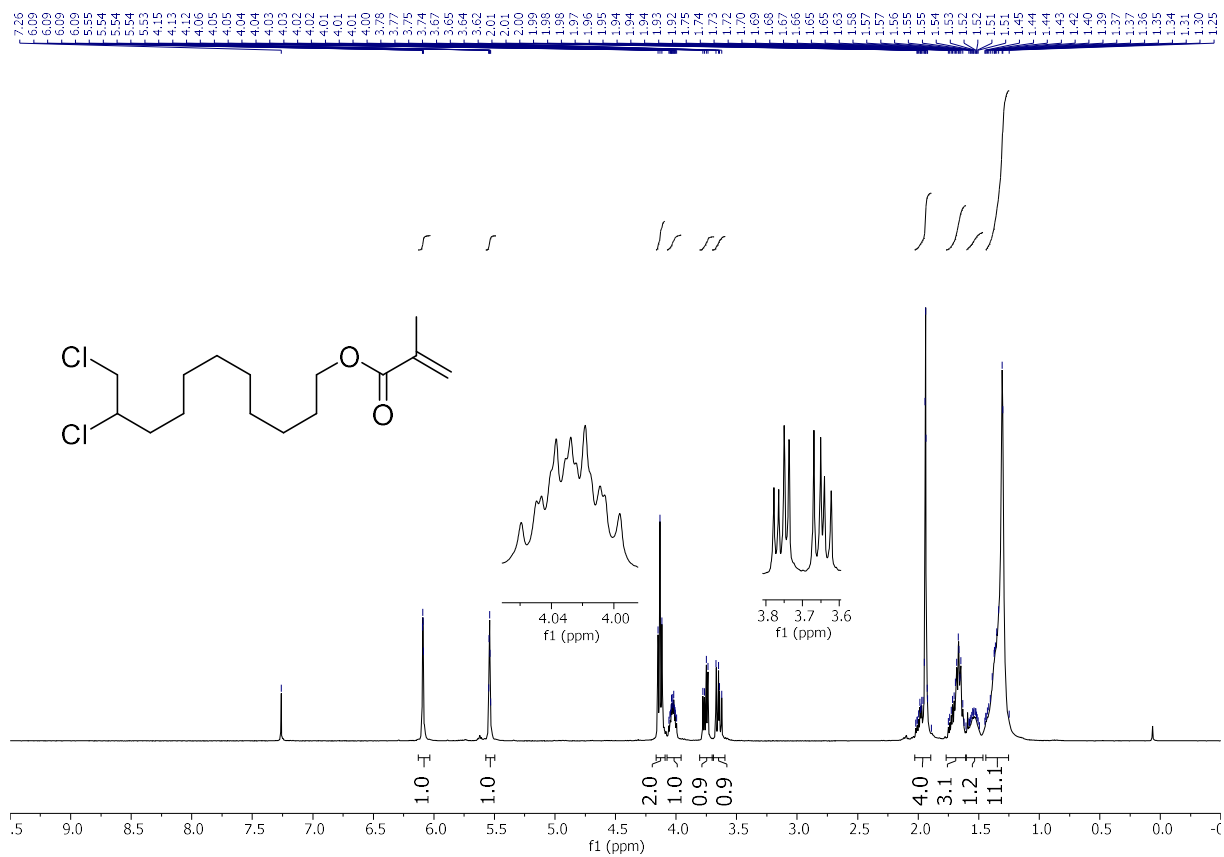


^{13}C NMR (101 MHz, CDCl_3)

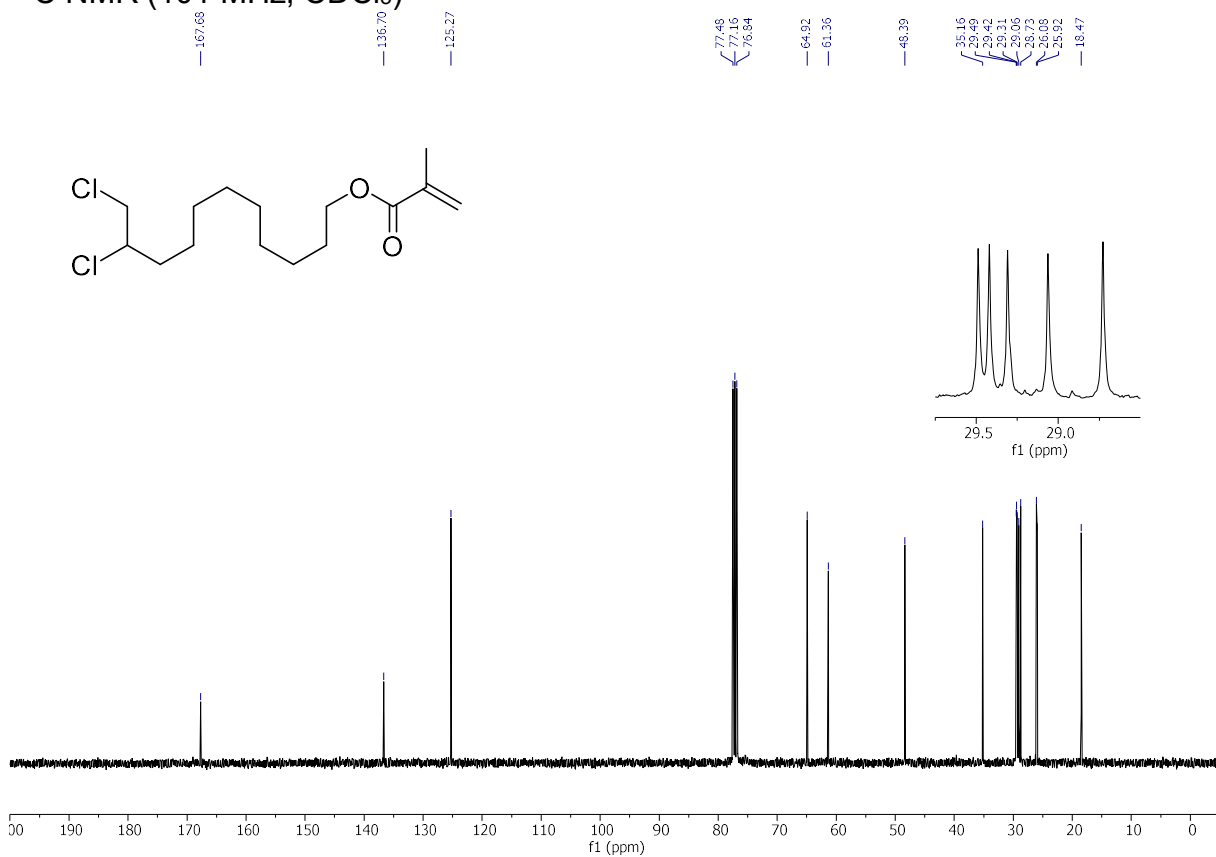


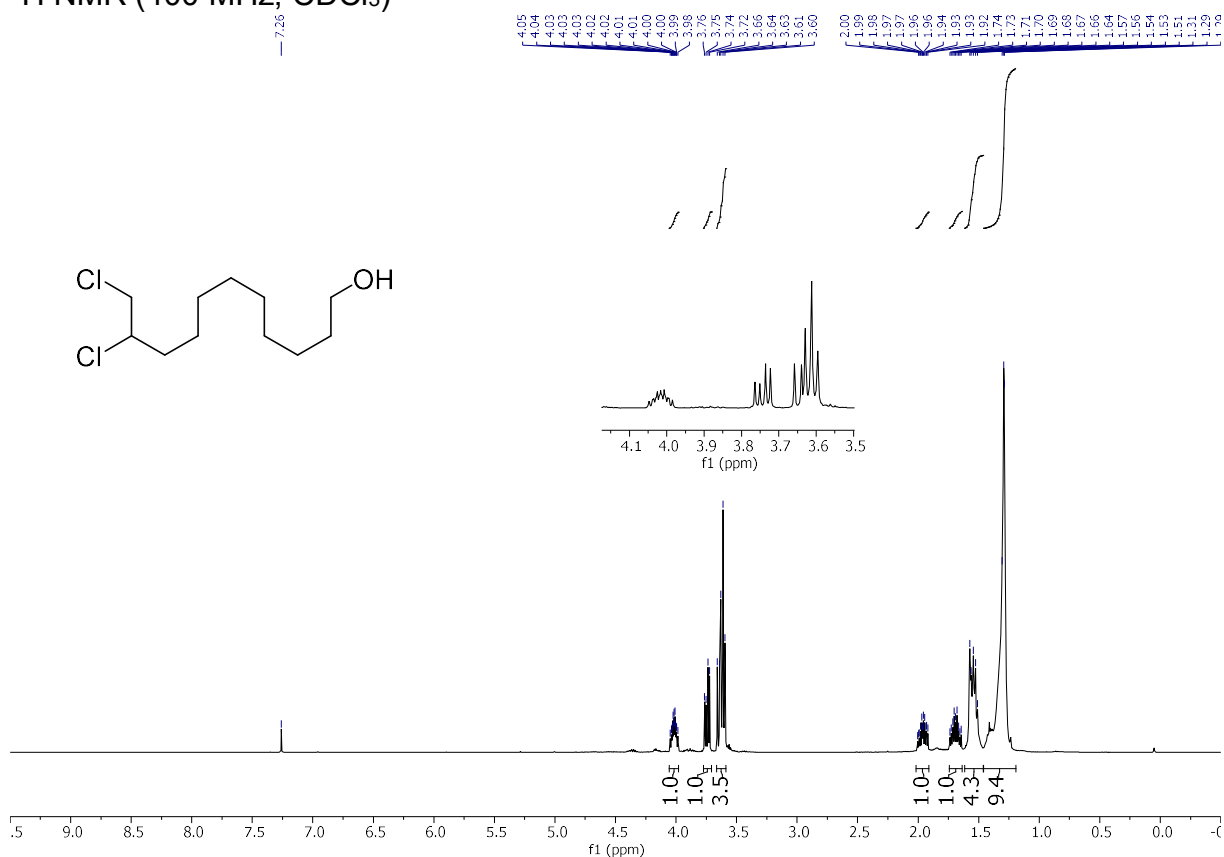
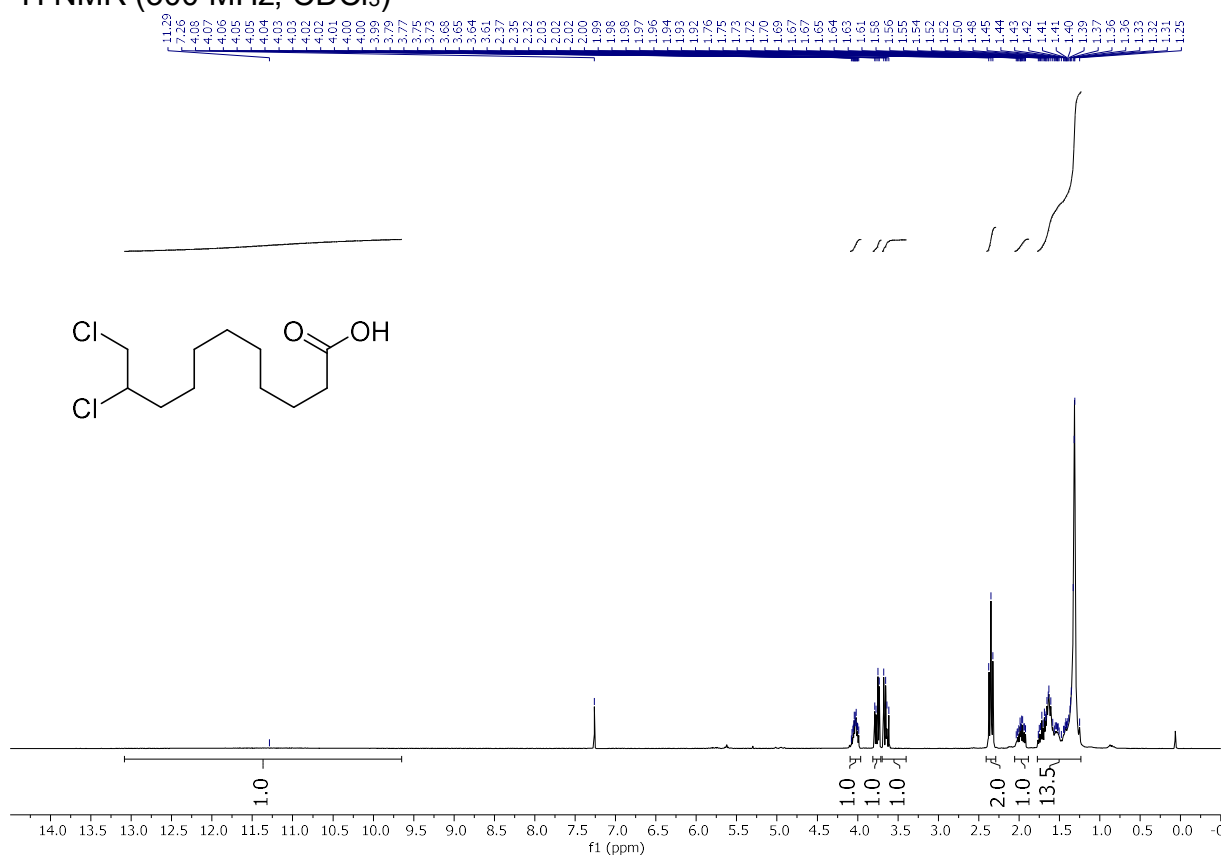
10,11-Dichloroundecyl methacrylate (4)

^1H NMR (400 MHz, CDCl_3)



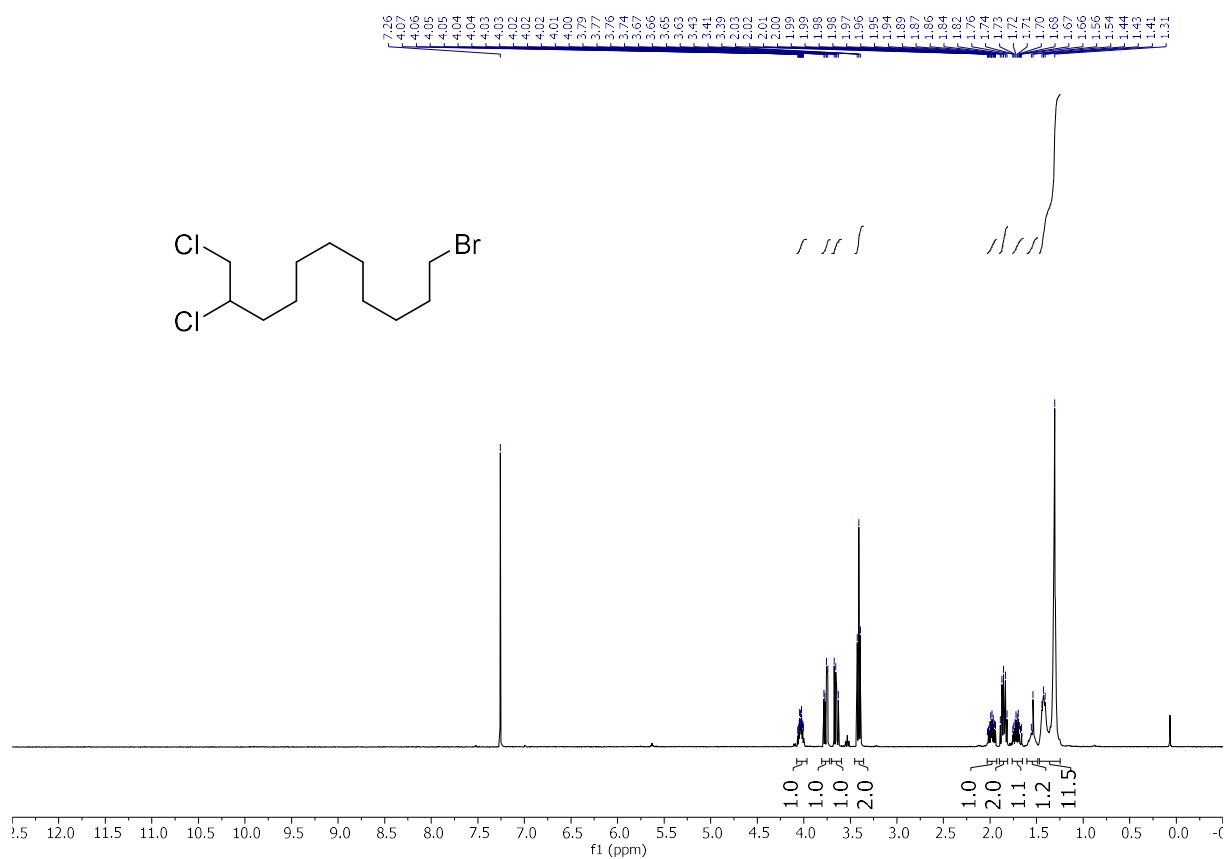
^{13}C NMR (101 MHz, CDCl_3)



10,11-Dichloroundecan-1-ol (5)¹H NMR (400 MHz, CDCl₃)**10,11-Dichloroundecanoic acid (6)**¹H NMR (300 MHz, CDCl₃)

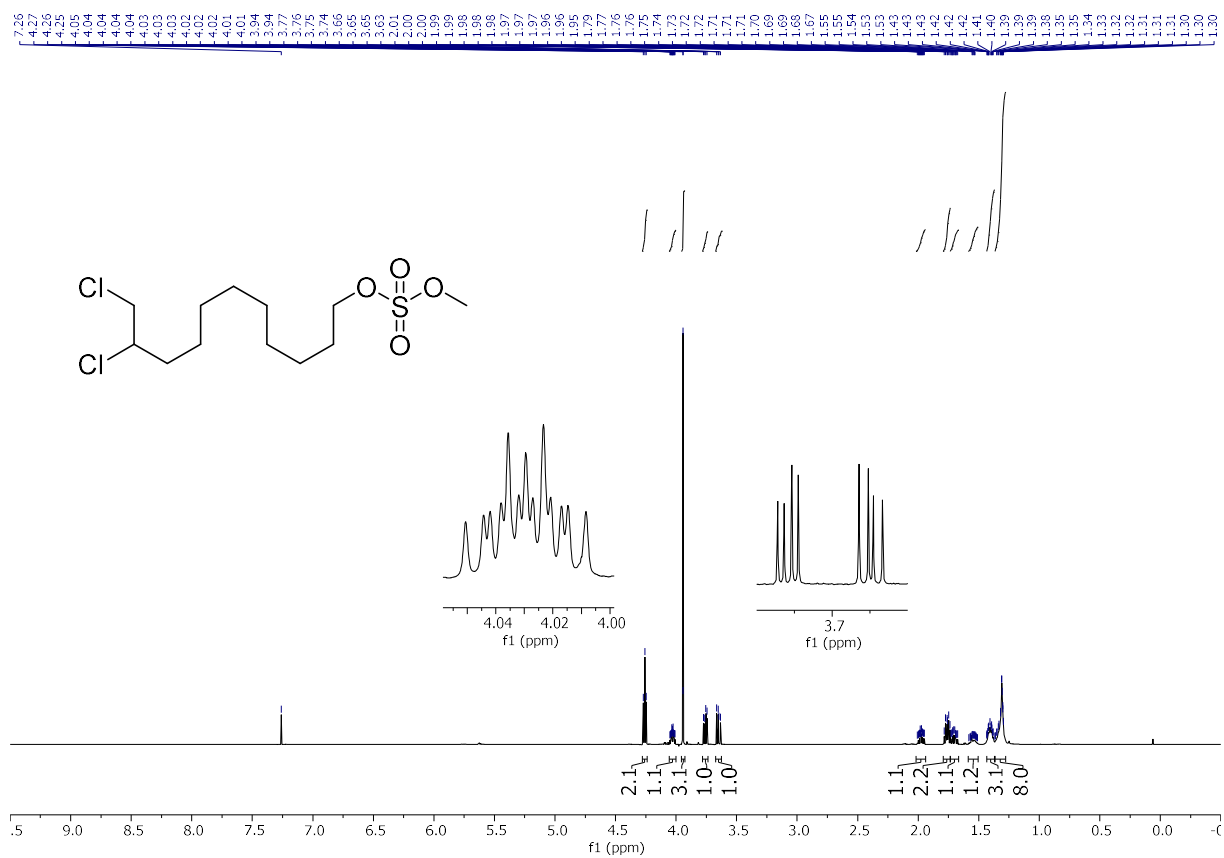
11-Bromo-1,2-dichloroundecane (7)

^1H NMR (400 MHz, CDCl_3)

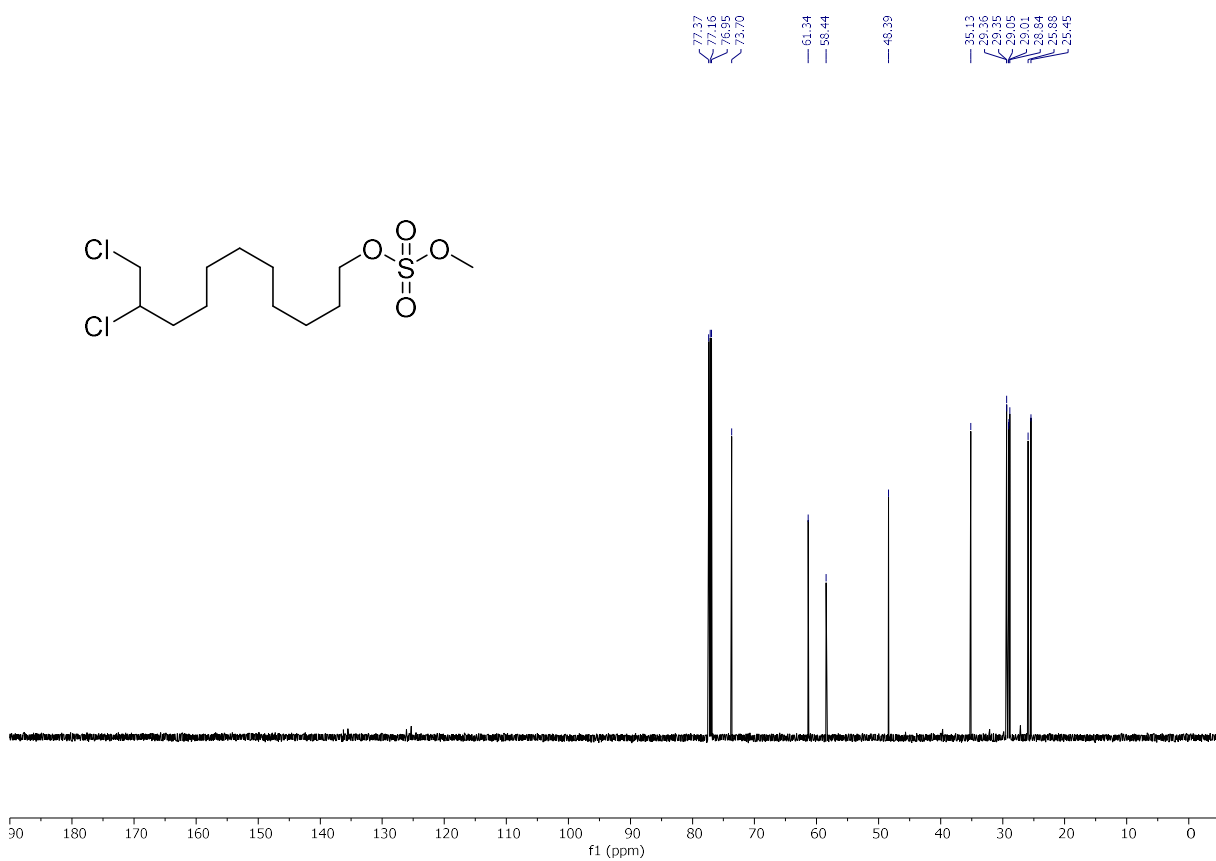


10,11-Dichloroundecyl methyl sulfate (8)

¹H NMR (599 MHz, CDCl₃)

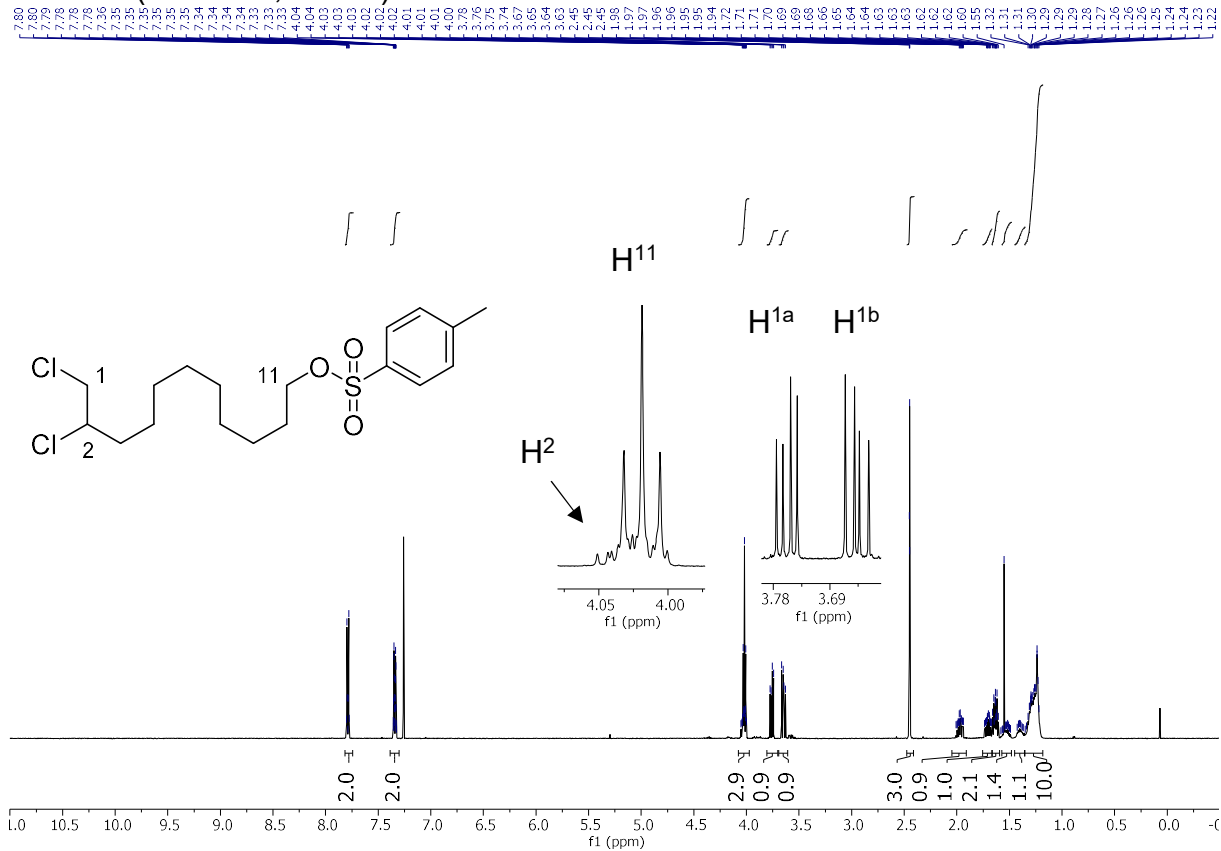


¹³C NMR (151 MHz, CDCl₃)



10,11-Dichloroundecyl 4-methylbenzenesulfonate (9)

¹H NMR (500 MHz, CDCl₃)

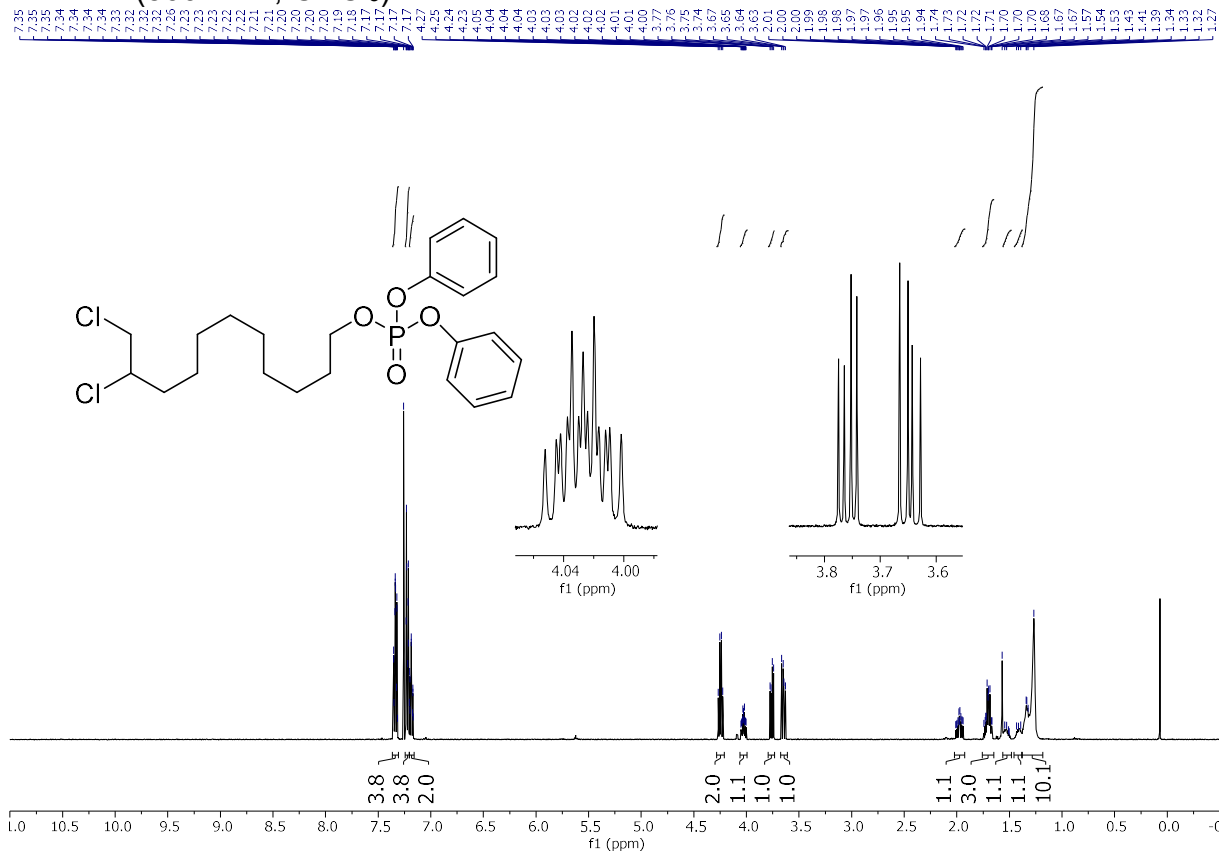


¹³C NMR (126 MHz, CDCl₃)

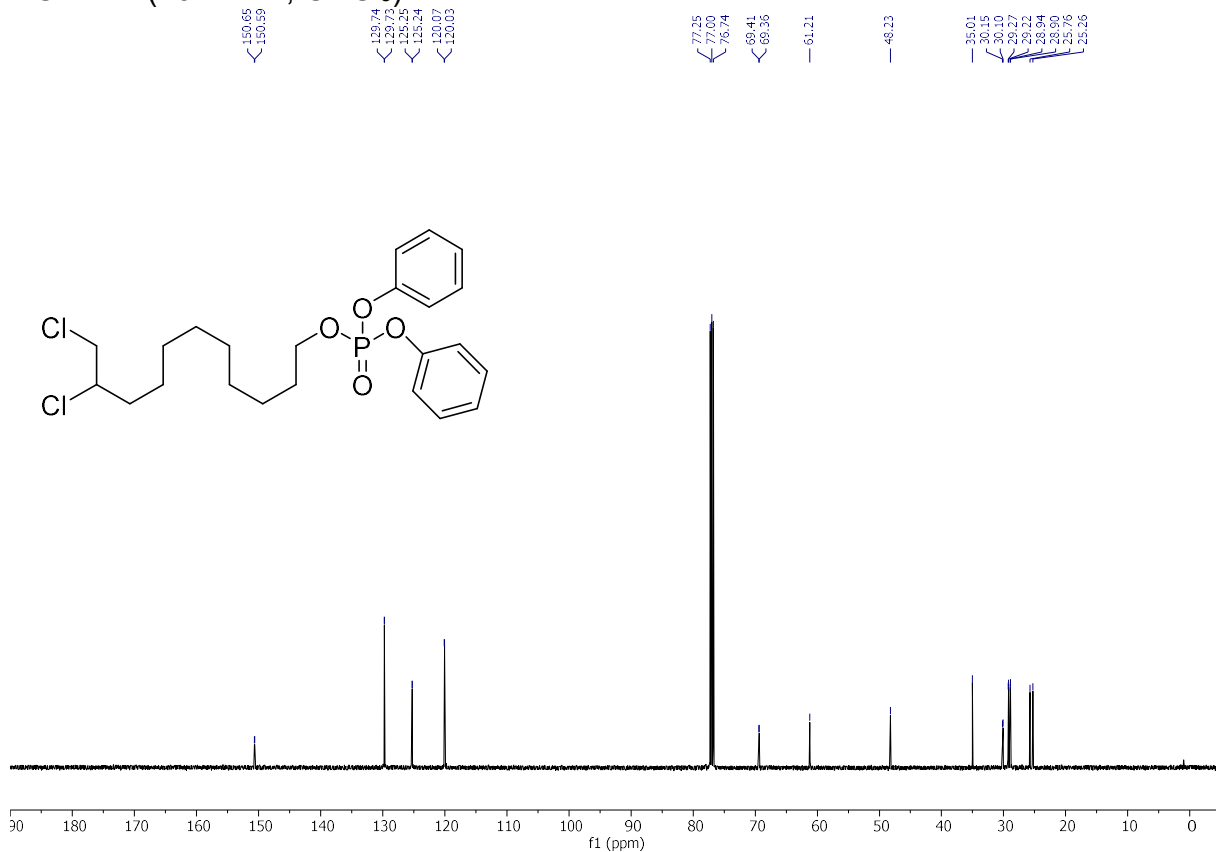


10,11-Dichloroundecyl diphenyl phosphate (10)

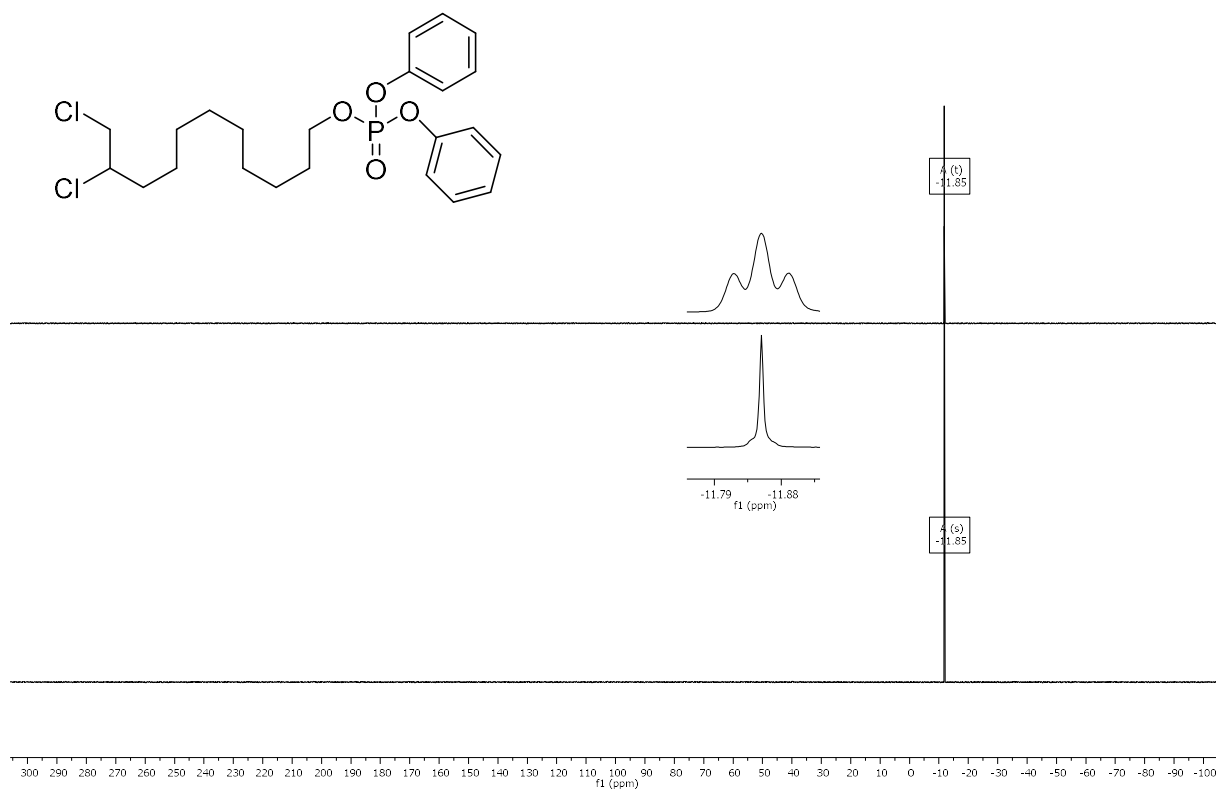
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

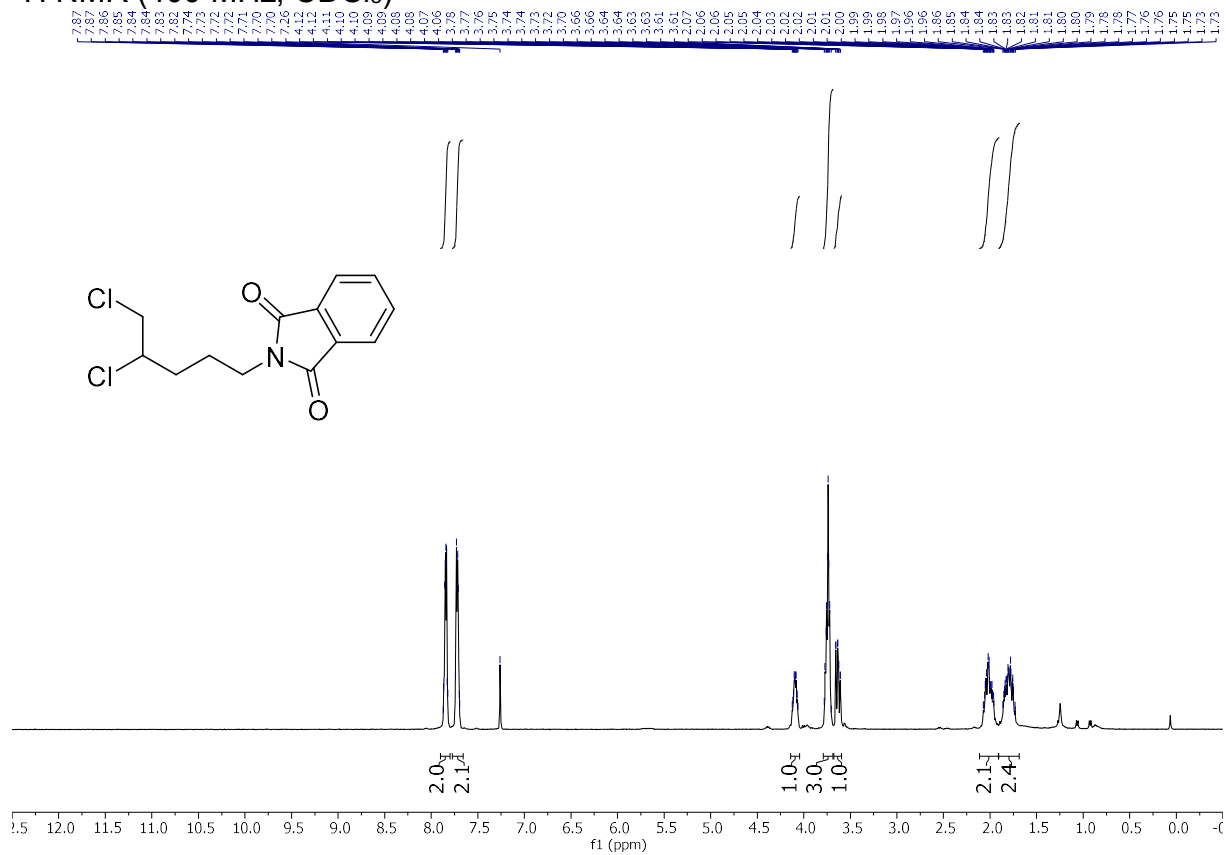


^{31}P NMR (202 MHz, CDCl_3)

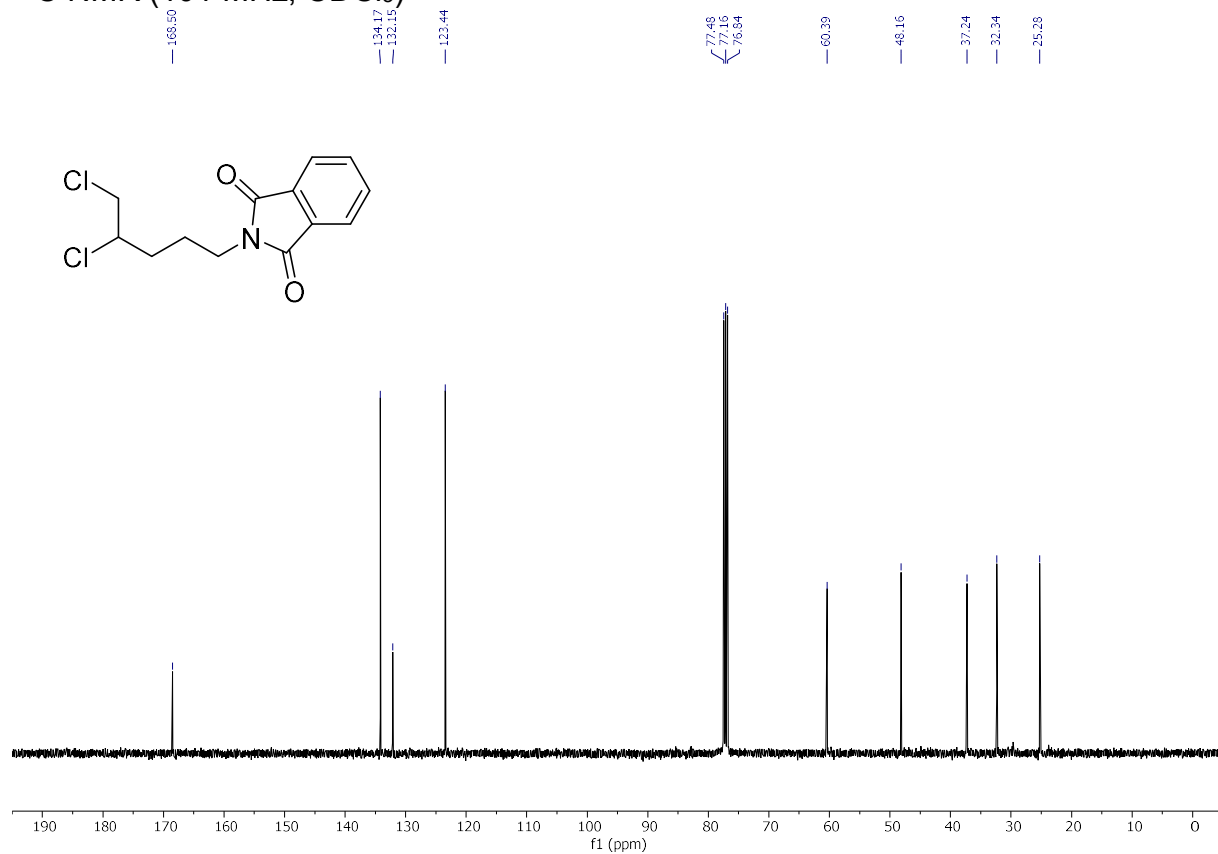


2-(4,5-Dichloropentyl)isoindoline-1,3-dione (11)

^1H NMR (400 MHz, CDCl_3)

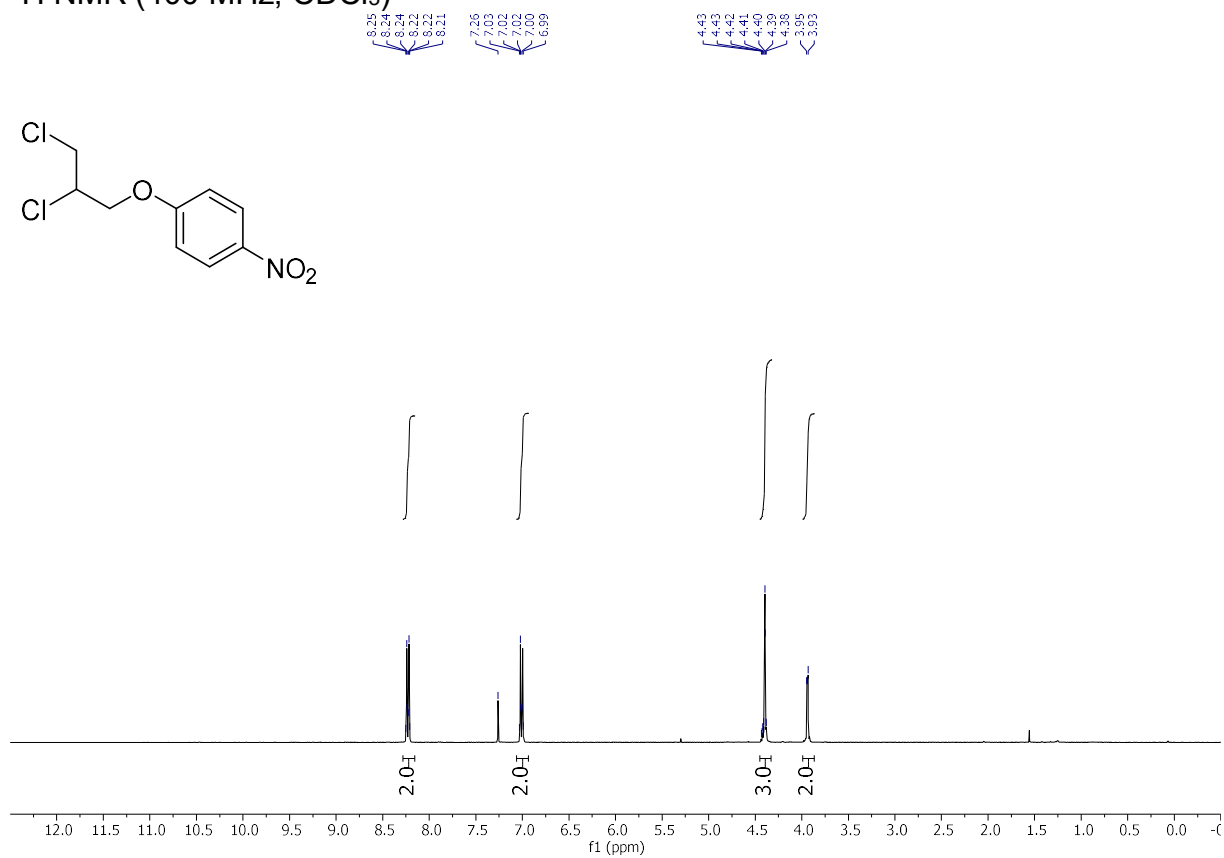


^{13}C NMR (101 MHz, CDCl_3)

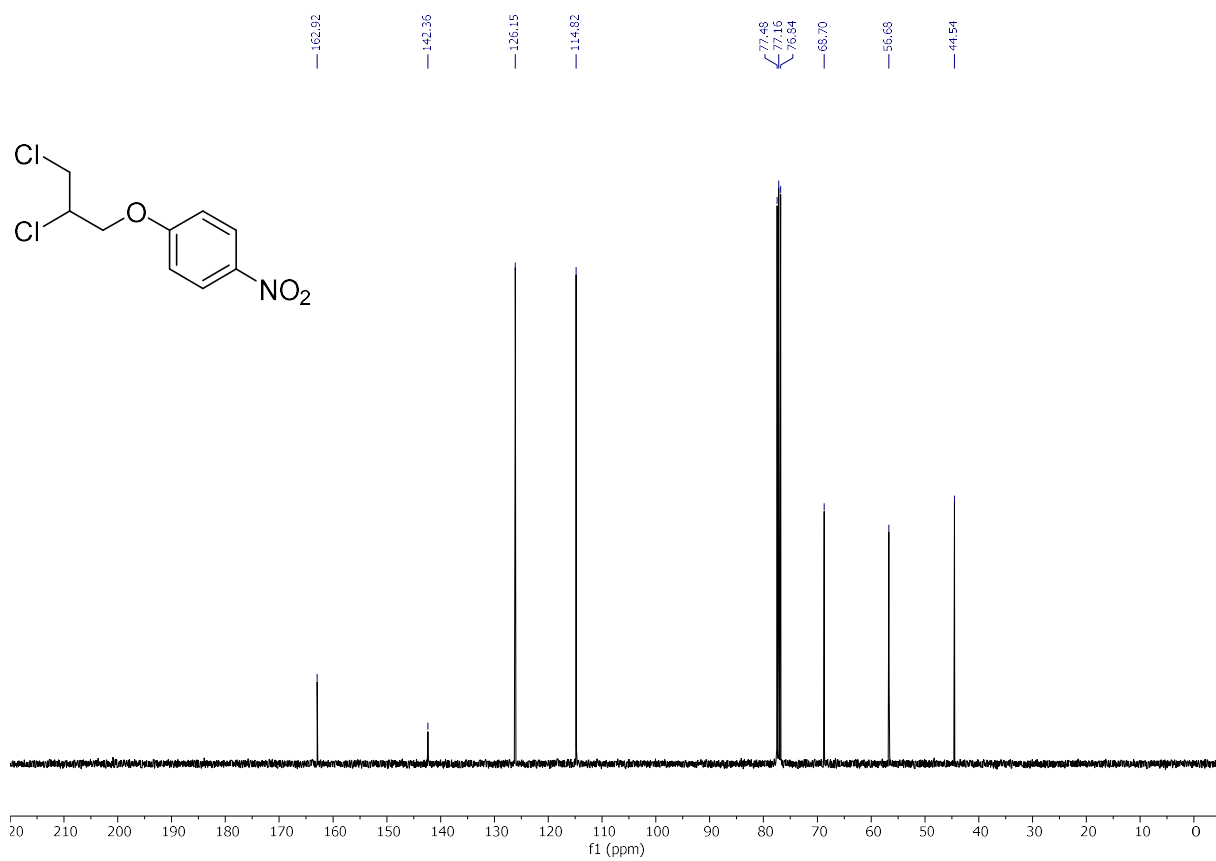


1-(2,3-Dichloropropoxy)-4-nitrobenzene (12)

^1H NMR (400 MHz, CDCl_3)

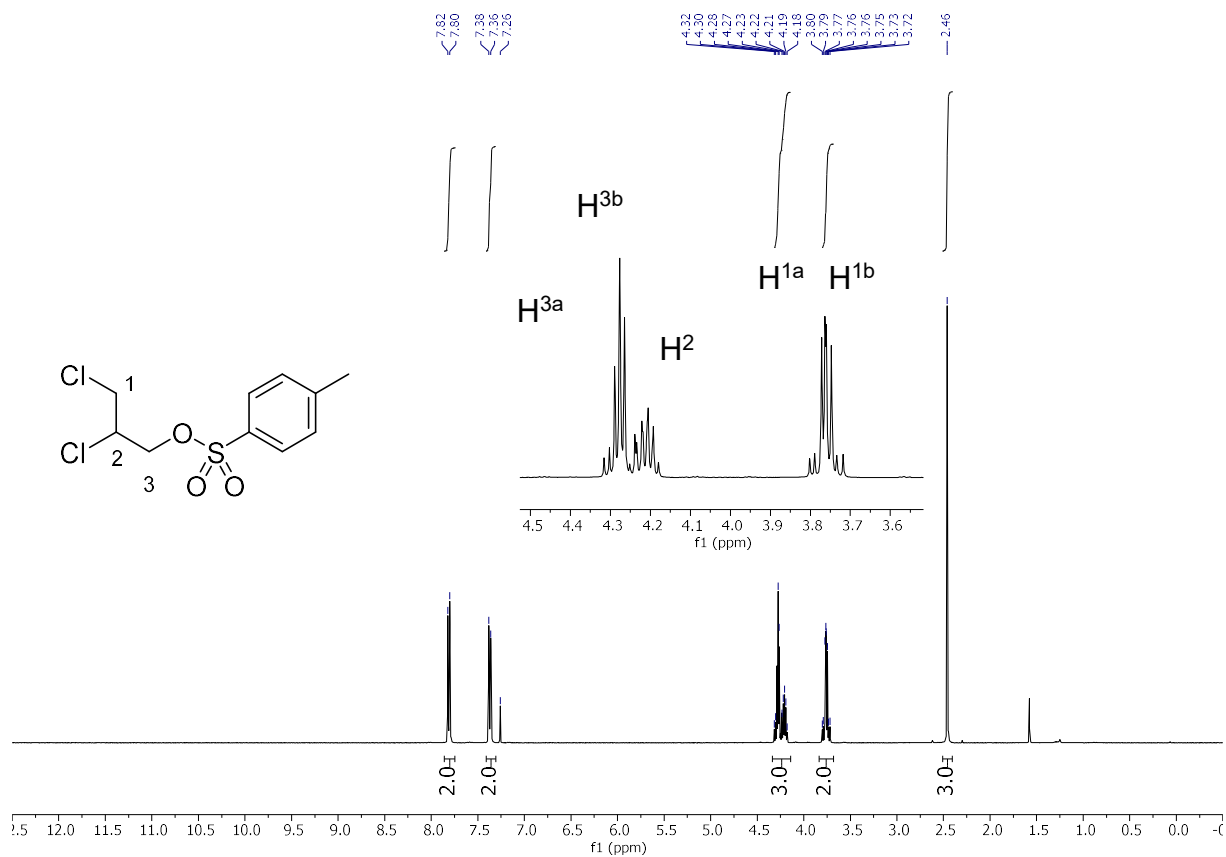


^{13}C NMR (101 MHz, CDCl_3)

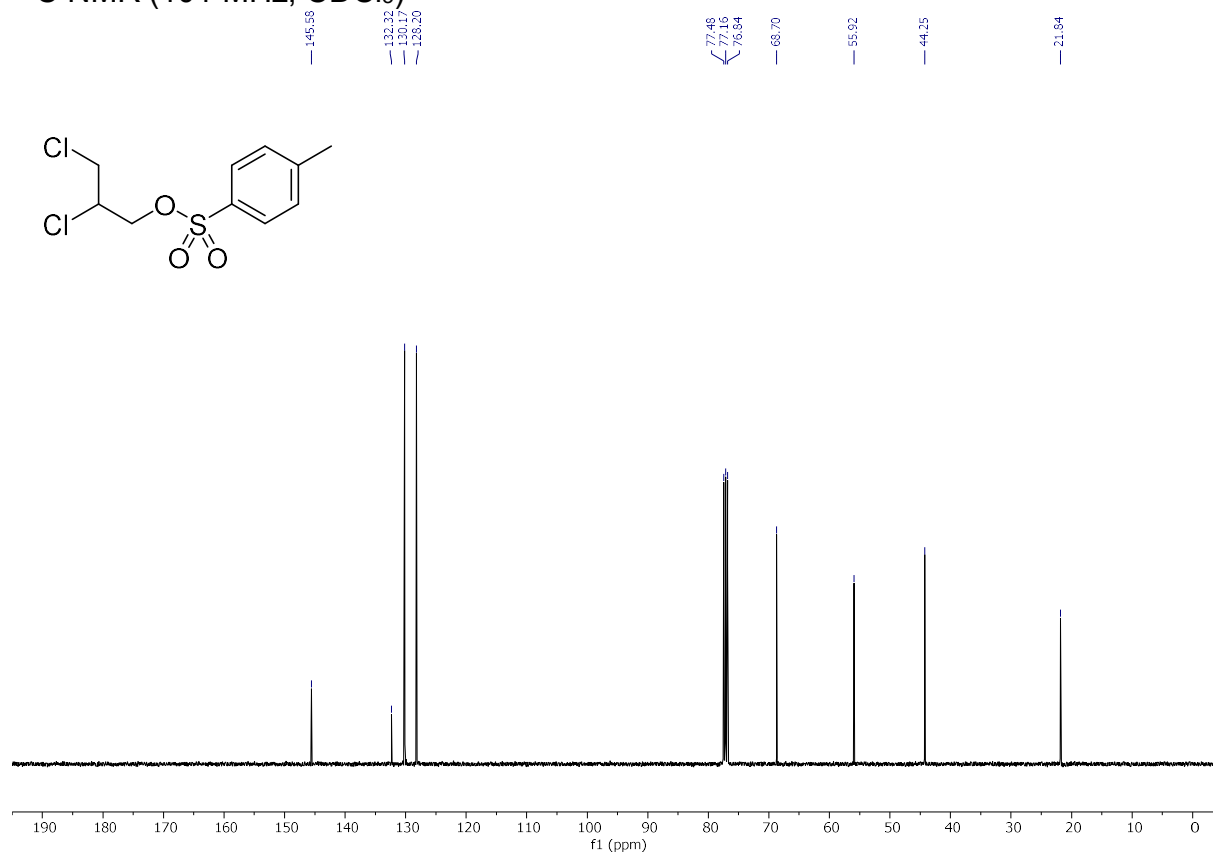


2,3-Dichloropropyl 4-methylbenzenesulfonate (13)

^1H NMR (400 MHz, CDCl_3)

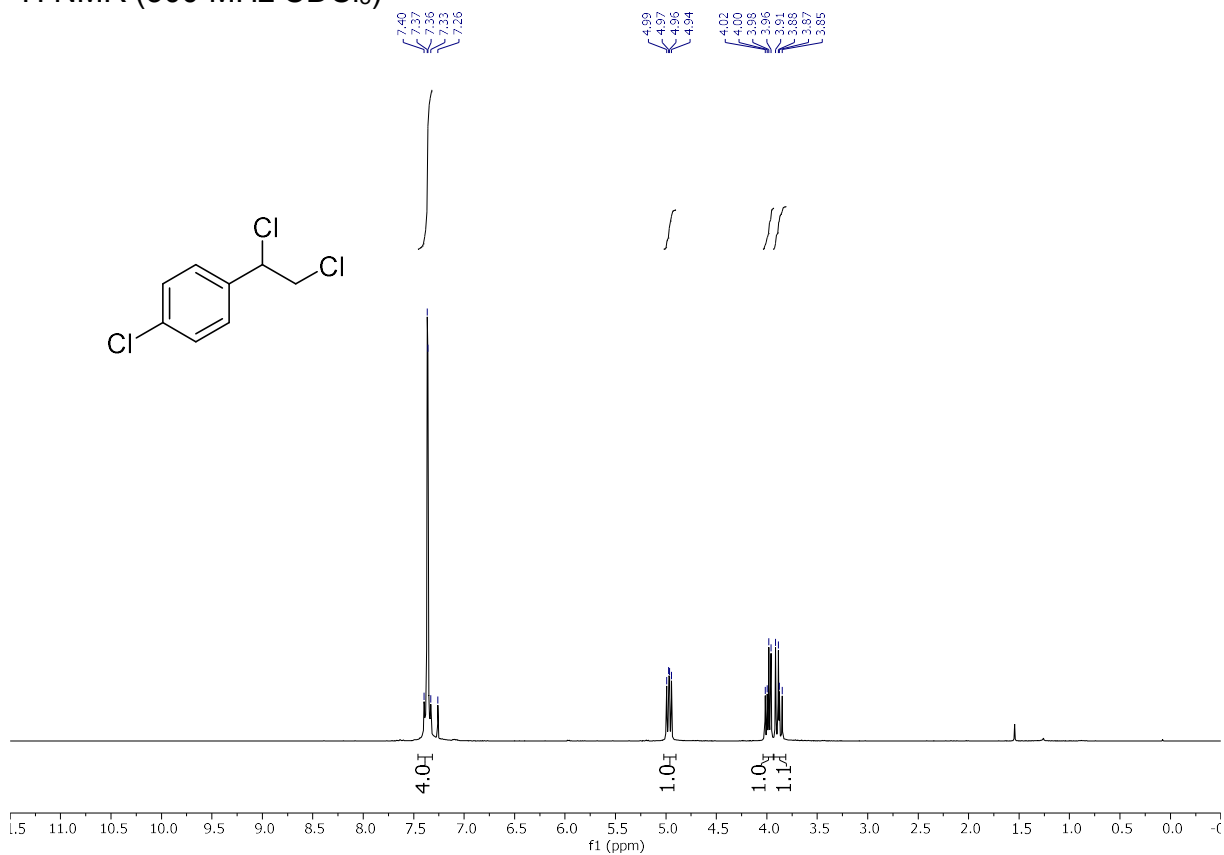


^{13}C NMR (101 MHz, CDCl_3)



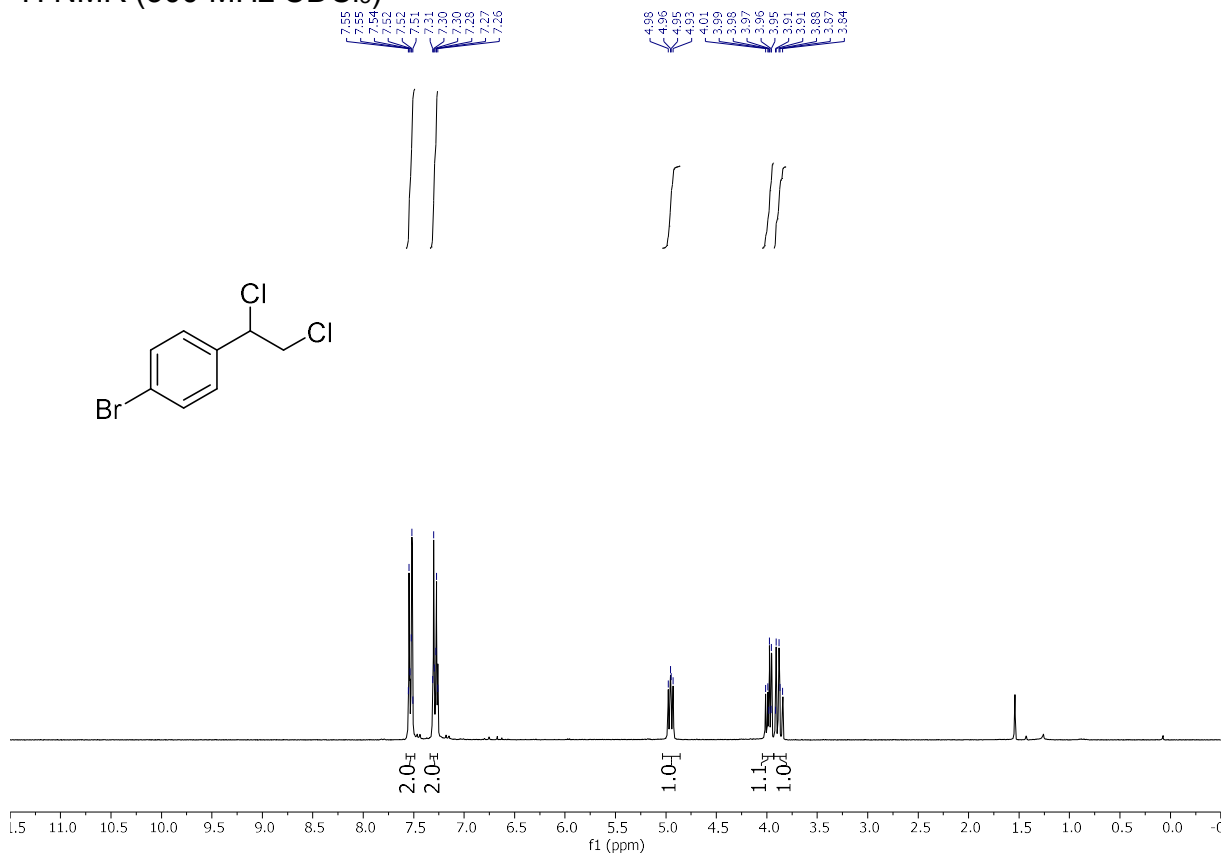
1-Chloro-4-(1,2-dichloroethyl)benzene (14)

^1H NMR (300 MHz CDCl_3)

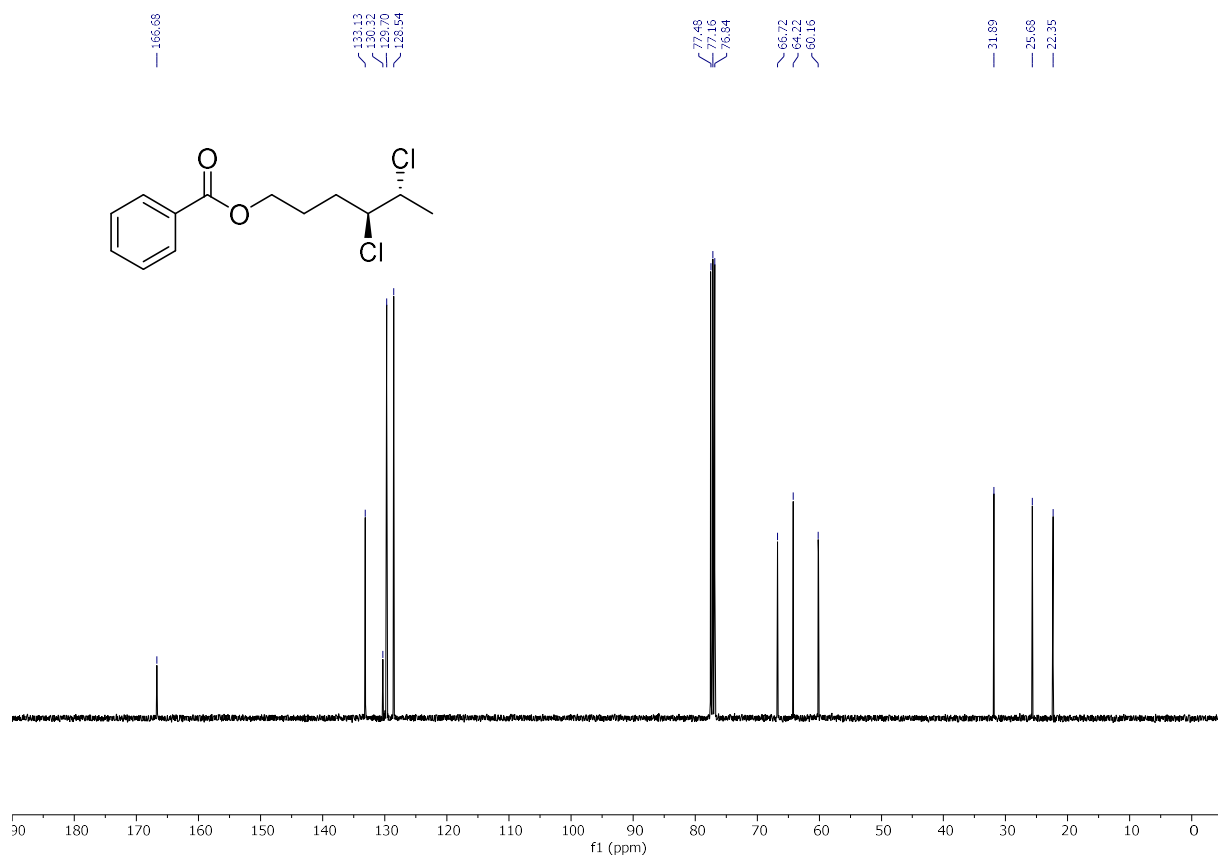
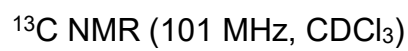


1-Bromo-4-(1,2-dichloroethyl)benzene (15)

^1H NMR (300 MHz CDCl_3)

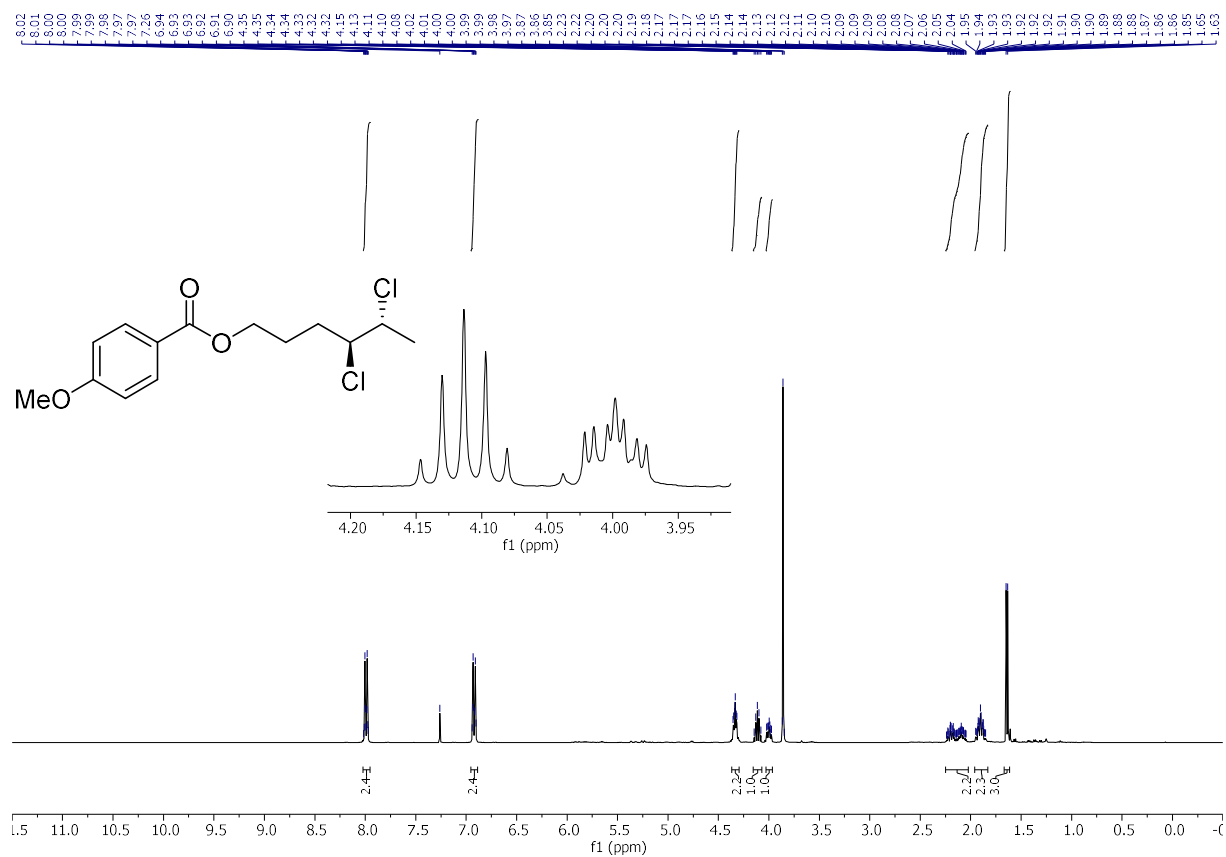


¹H NMR (300 MHz CDCl₃)

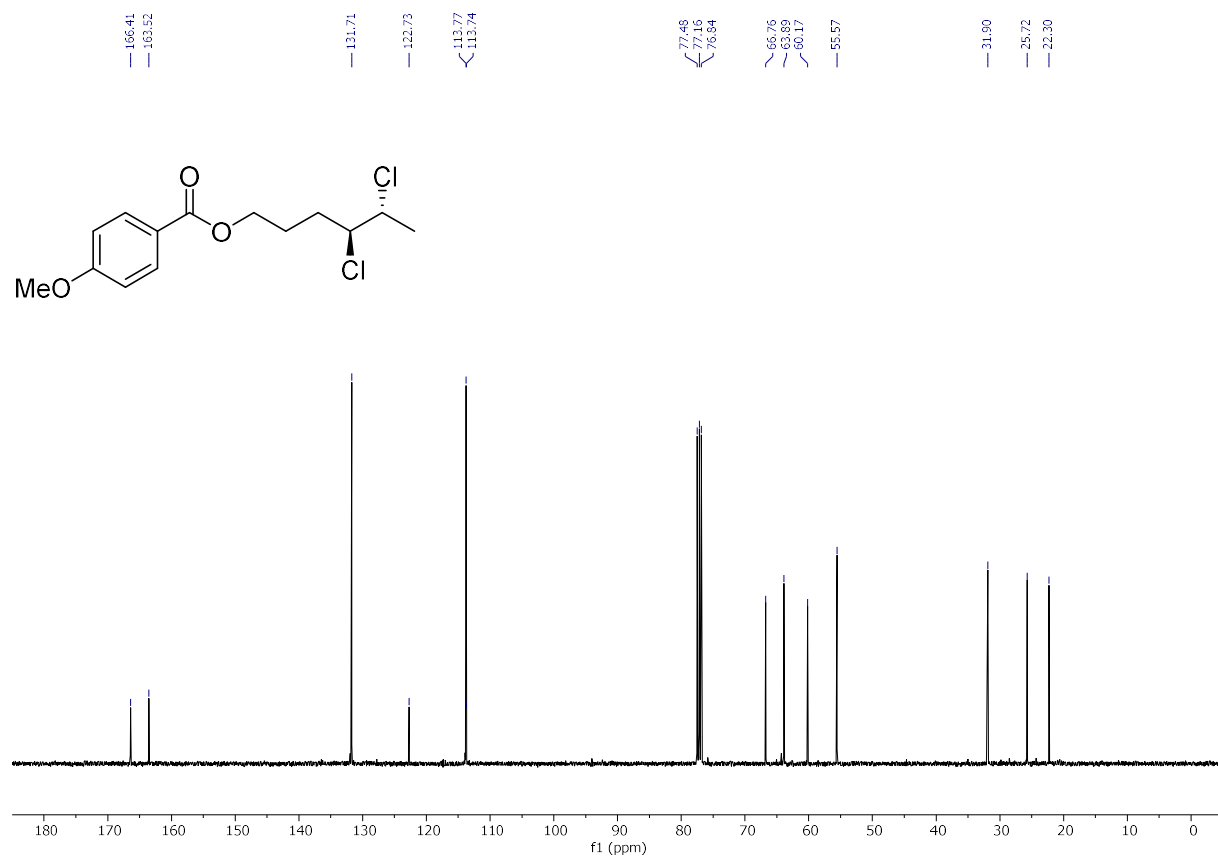
¹H NMR (400 MHz CDCl₃)

4,5-Dichlorohexyl 4-methoxybenzoate (18)

¹H NMR (400 MHz CDCl₃)

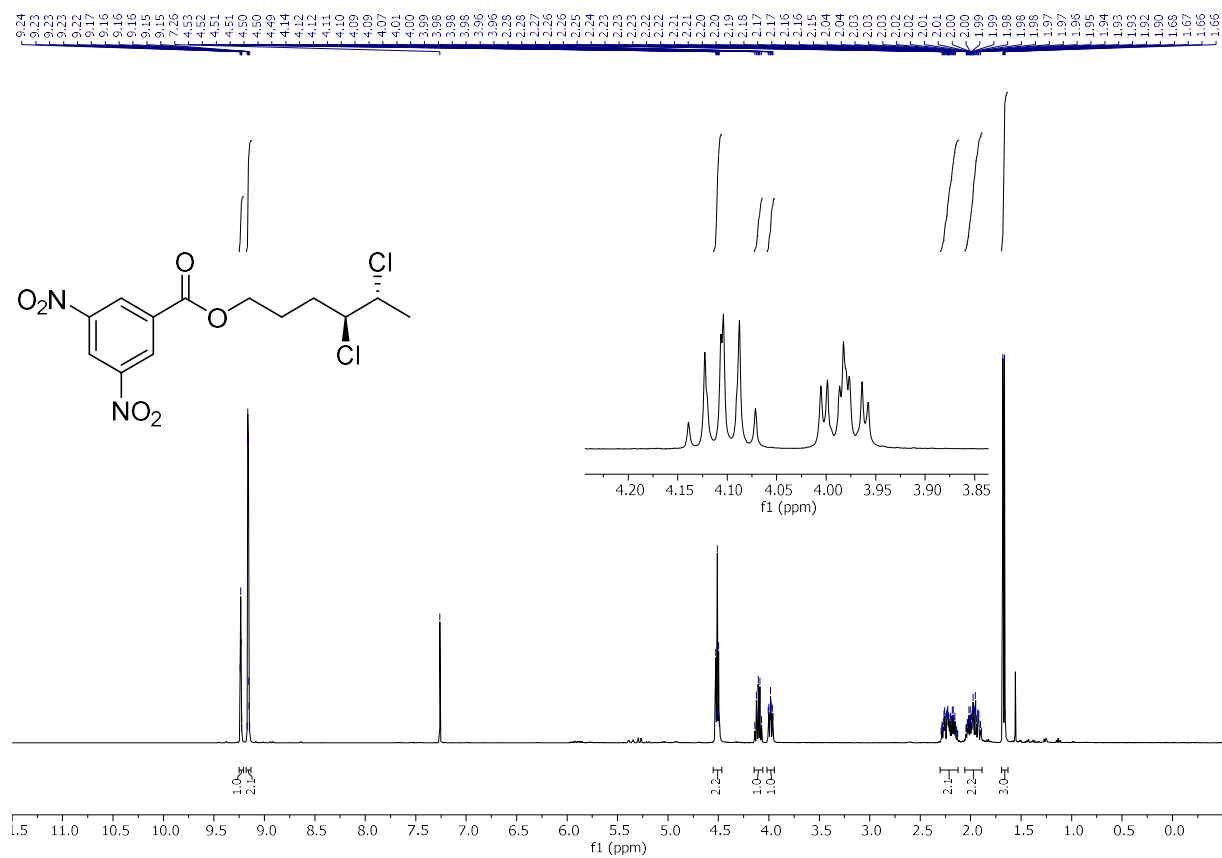


¹³C NMR (101 MHz, CDCl₃)

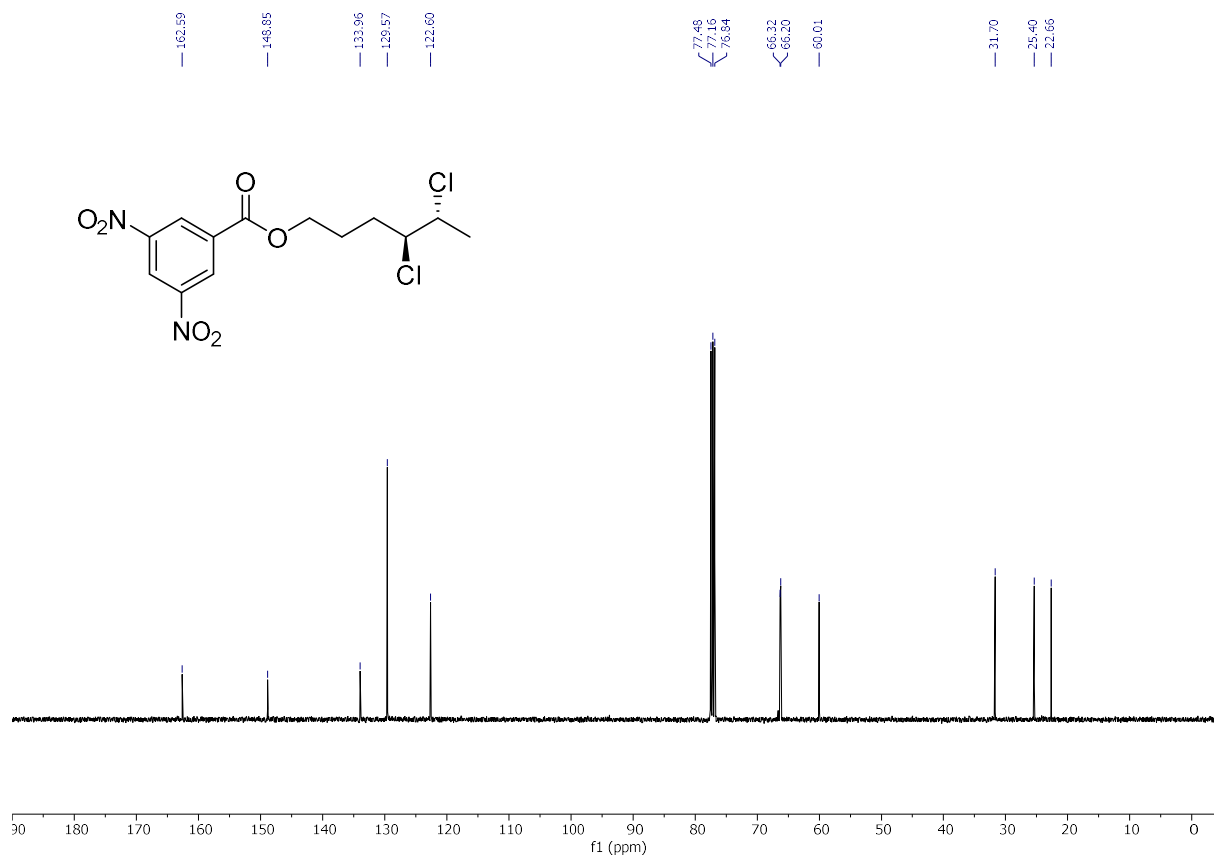


4,5-Dichlorohexyl 3,5-dinitrobenzoate (19)

^1H NMR (400 MHz CDCl_3)

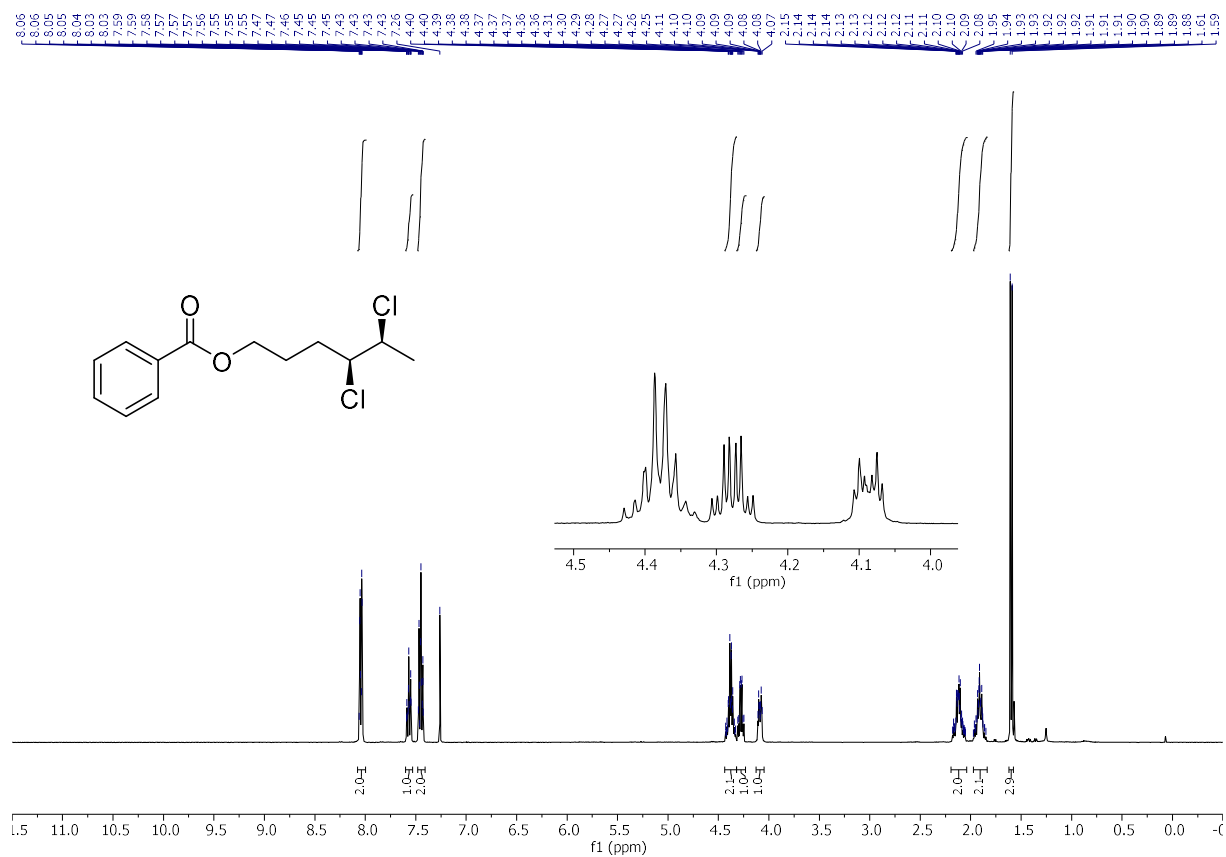


^{13}C NMR (101 MHz, CDCl_3)

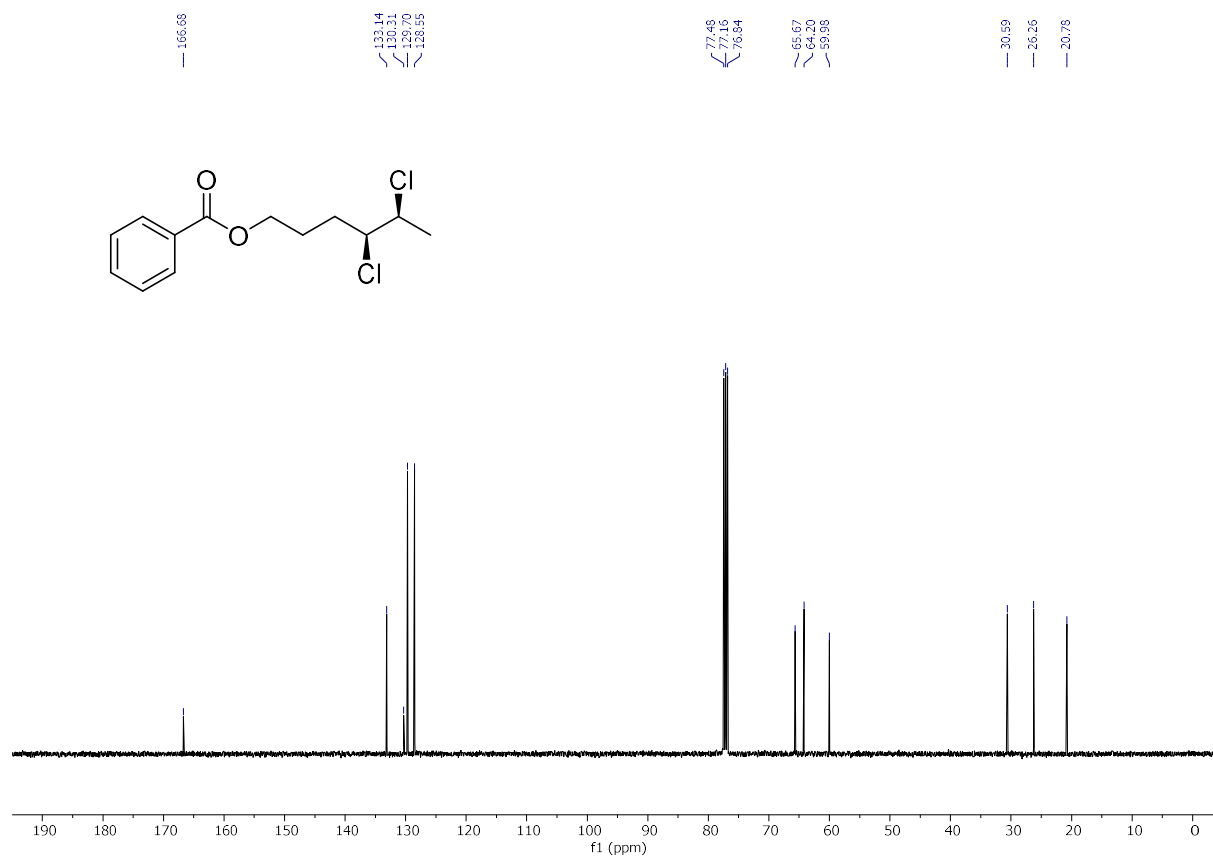


4,5-Dichlorohexyl benzoate (20)

^1H NMR (400 MHz CDCl_3)

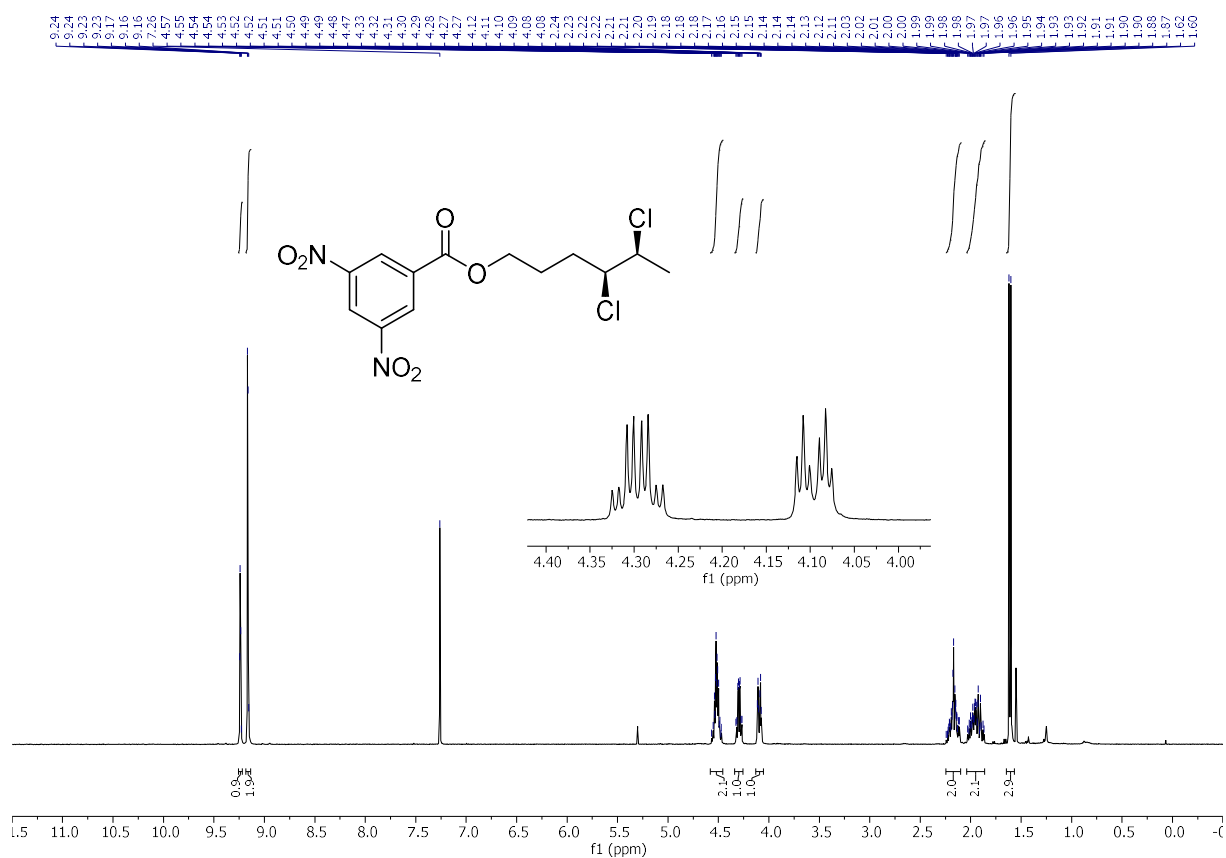


^{13}C NMR (101 MHz, CDCl_3)

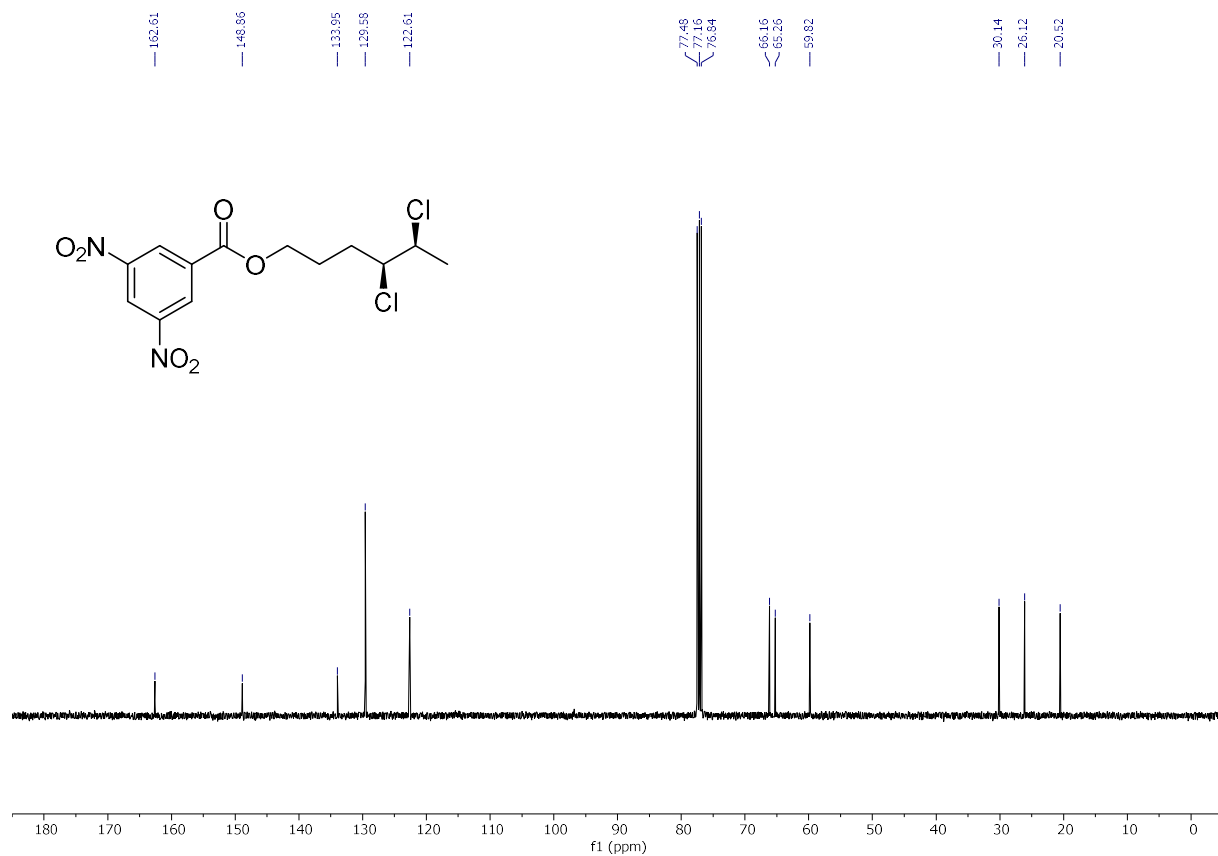


4,5-Dichlorohexyl 3,5-dinitrobenzoate (21)

^1H NMR (400 MHz CDCl_3)

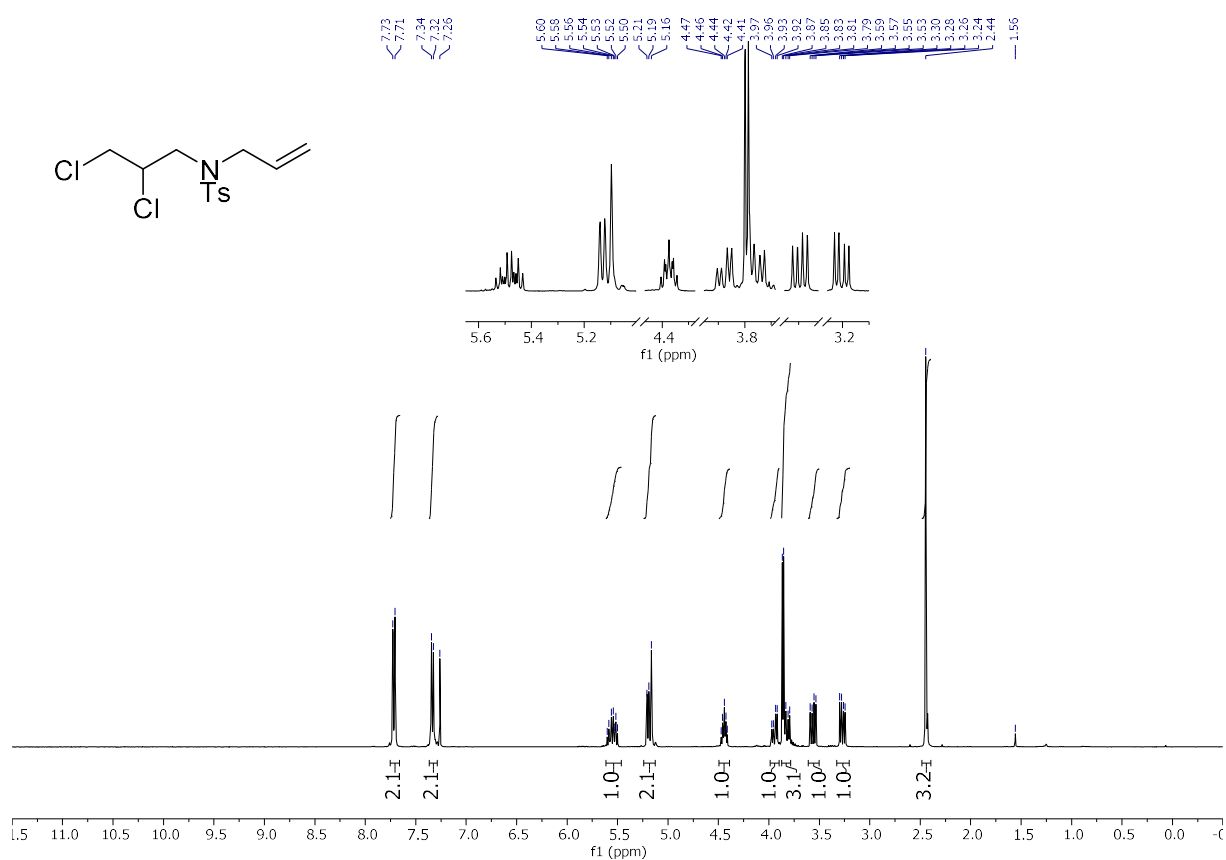


^{13}C NMR (101 MHz, CDCl_3)



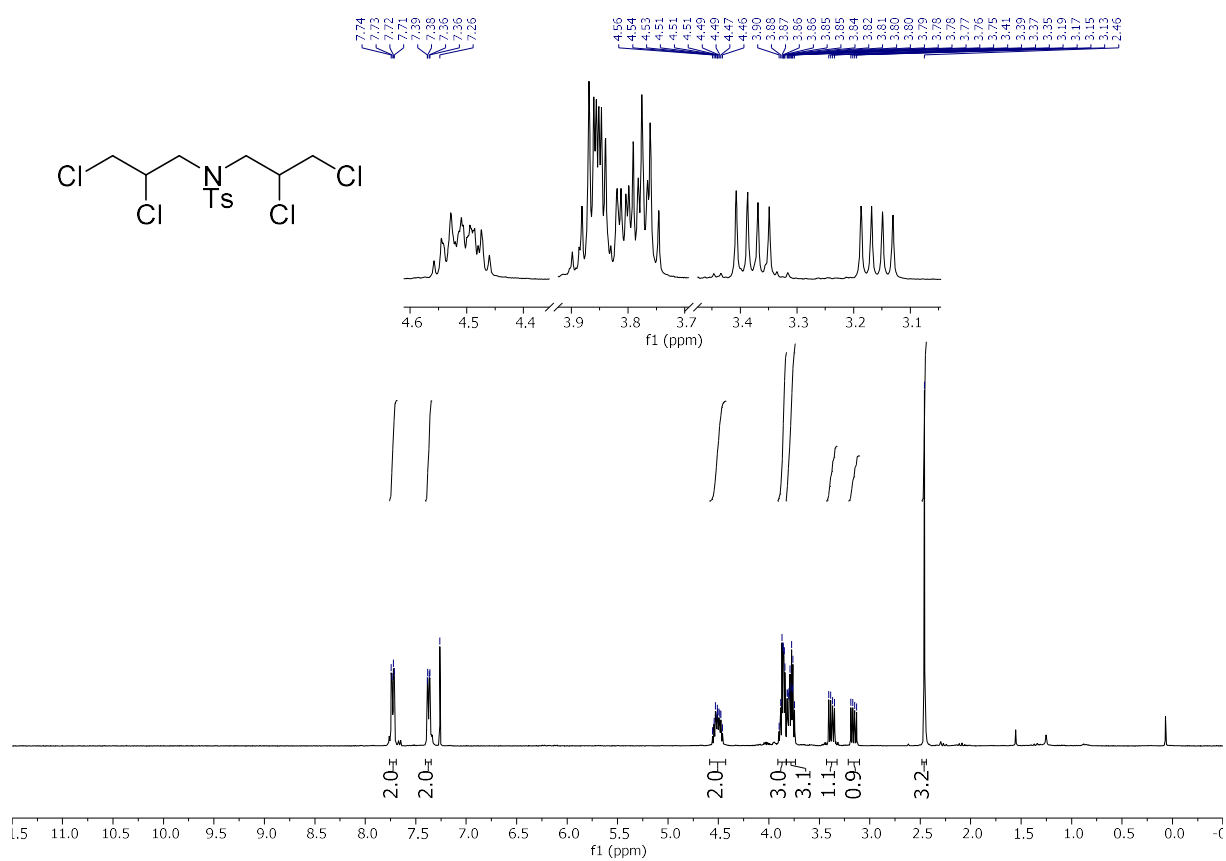
***N*-allyl-*N*-(2,3-dichloropropyl)-4-methylbenzenesulfonamide (22)**

¹H NMR (400 MHz, CDCl₃)



***N,N*-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide (23)**

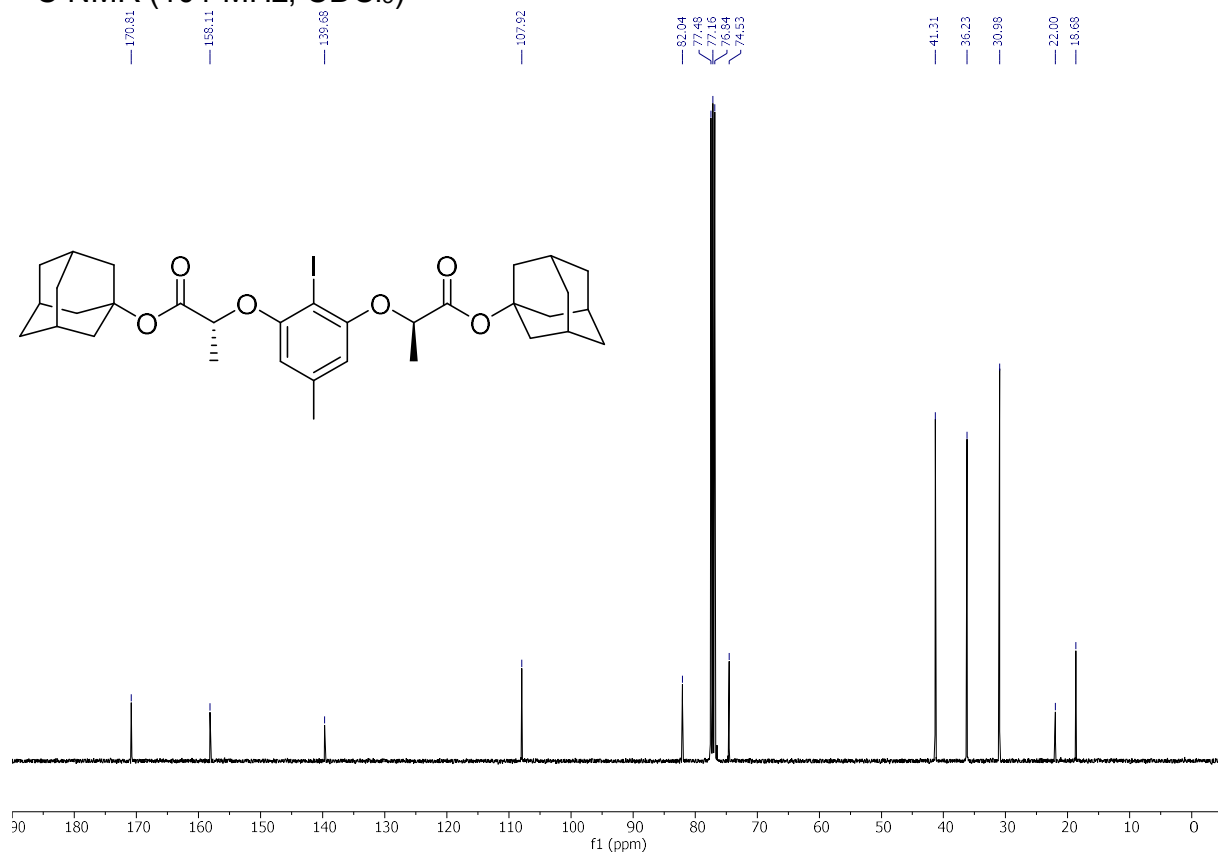
¹H NMR (400 MHz, CDCl₃)



XII. NMR Spectra: preliminary validation of an enantioselective variant
(Di((3*S*,5*S*,7*S*)-adamantan-1-yl) 2,2'-((2-iodo-5-methyl-1,3-phenylene)bis(oxy)) -
(2*R*,2'*R*)-dipropionate (S20)
¹H NMR (400 MHz CDCl₃)



¹³C NMR (101 MHz, CDCl₃)



XIII. References

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