

Supplementary Materials for
Electrocatalytic Radical Dichlorination of Alkenes with
Nucleophilic Chlorine Sources

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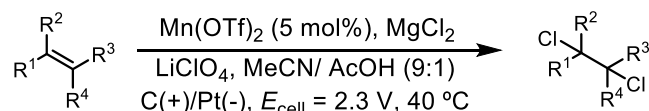
Section 1. General information

All reactions were performed in oven-dried two-neck glass tubes unless otherwise noted. The tubes were fitted with a rubber septum and a threaded Teflon cap with airtight, electrical feed-throughs. The reactions were conducted under a nitrogen atmosphere. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SiliCycle. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI, AK Scientific, and Oakwood and used as received with the following exceptions: toluene, dichloromethane, tetrahydrofuran, diethyl ether, and acetonitrile were dried by passing through columns of activated alumina; dimethylformamide was dried by passing through columns of activated molecular sieves. Triethylamine were distilled from CaH_2 at 760 torr. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz) and Inova-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($\text{CHCl}_3 = \delta$ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($\text{CDCl}_3 = \delta$ 77.0). Data are represented as follows: chemical shift, multiplicity (br. s = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Bruker Hyperion Tensor 27 FTIR spectrometer. Cyclic voltammetry data were measured with a BASi Epsilon potentiostat. The mass spectral (MS) data were obtained on a Thermo Fisher Scientific Exactive series DART Mass Spectrometer.

Electrolysis experiments were performed using a BASi EC Epsilon potentiostat/galvanostat or a DC power supply. Reticulated vitreous carbon was purchased from ERG Aerospace. The carbon was cut into $1 \times 0.5 \times 0.6 \text{ cm}^3$ pieces before use, and was connected to electrical feed-through on the Teflon cap of the electrochemical cell via a piece of graphite (2B pencil lead, 2 mm in diameter). Ag/AgNO_3 reference electrodes were obtained from CH Instruments and stored in an acetonitrile solution with 0.01 M AgNO_3 and 0.1 M LiClO_4 before use.

Abbreviations: ^tBu —*tert*-butyl, DCM—dichloromethane, EtOAc—ethyl acetate, HOAc—acetic acid, MeCN—acetonitrile, MeOH—methanol, NEt_3 —triethylamine, RVC—reticulated vitreous carbon, TBA—tetrabutylammonium.

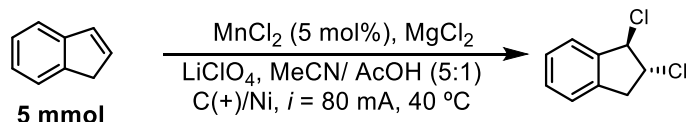
Section 2. General procedures for electrochemical dichlorination of alkenes



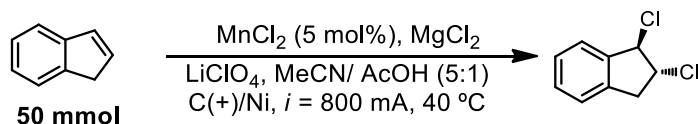
Method A: An oven-dried, 10 mL two-neck glass tube was equipped with a magnetic stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feed-throughs, a 100 PPI RVC anode ($0.5 \times 1.0 \times 0.6 \text{ cm}^3$, connected to the electrical feed-through via a 9 cm in length, 2 mm in diameter graphite rod), and a platinum foil cathode ($0.5 \times 1.0 \text{ cm}^2$), maintaining a distance of 0.3 cm between the closest point of the two electrodes. To this reaction vessel was added $\text{Mn}(\text{OTf})_2$ (3.5-3.6 mg, 5 mol%) and MgCl_2 (57.0 mg, 0.6 mmol, 3.0 equiv). The cell was sealed and flushed with nitrogen gas for 5 minutes, followed by the sequential addition via syringe of olefin substrate (0.20 mmol, 1 equiv), electrolyte solution (0.10 M LiClO_4 in MeCN, 3.5 mL), and acetic acid (0.40 mL). The reaction mixture was then purged with nitrogen gas for another 5 minutes. A nitrogen-filled balloon was adapted through the septum to sustain a nitrogen atmosphere. Electrolysis was initiated at a cell potential of 2.3 V at 40 °C (oil bath temperature). Upon full consumption of olefin starting material as determined by thin-layer chromatography analysis, the electrical input was removed. The entire reaction mixture was then transferred to a short silica gel column (7-10 cm in length, ca. 10 g) and flushed through with 100 mL of a mixture of hexanes and ethyl acetate to eliminate the inorganic salts, and the product solution was concentration *in vacuo*. In many cases, the crude product was spectroscopically pure. Otherwise, the residue was subjected to flash column chromatography on silica gel (eluted with hexanes/ethyl acetate) to yield the purified product.



Fig. S1. Setup for the small-scale electrosynthesis of 1,2-*trans*-dichloroindane (needle on the right is connected to a N_2 balloon).



Method B: To an oven-dried three-neck round bottom flask (100 mL) equipped with a magnetic stirbar was added MgCl_2 (0.950 g, 10 mmol, 2.0 equiv) and MnCl_2 (32 mg, 0.25 mmol, 5 mol%). Each neck was fitted with a rubber septum. The septa on the side necks were fitted with a 80 PPI RVC anode (1.0 cm in diameter and 2.0 cm in length, connected to a 9 cm in length, 2 mm in diameter graphite rod), and a nickel foam cathode ($2.0 \times 2.0 \text{ cm}^2$), respectively, maintaining a distance of 1.0 cm between the closest point of the two electrodes. The cell was sealed and flushed with nitrogen gas for 5 minutes, followed by addition via syringe of electrolyte solution (0.10 M LiClO_4 in MeCN, 50 mL), indene (580 mg, 5.0 mmol, 1 equiv), and acetic acid (10.0 mL). The reaction mixture was then purged with nitrogen gas for another 5 minutes. A nitrogen-filled balloon was adapted through a septum to sustain a nitrogen atmosphere. Electrolysis was initiated at a constant current of 80 mA at $40 \text{ }^\circ\text{C}$ (oil bath temperature). The reaction was allowed to proceed for 3 h and 21 min before the current was withdrawn (2 F of total charge passed, assuming that the overall reaction is a 2-electron oxidation process). The entire reaction mixture was then transferred to a short silica gel column (7-10 cm in length, ca. 50 g) and flushed through with a mixture of hexanes and ethyl acetate to eliminate the inorganic salts. After concentration in vacuo, the residue was then dissolved in EtOAc and washed with NaHCO_3 (aq.) ($3 \times 50 \text{ mL}$), and then brine (50 mL). The organic layer was dried over Na_2SO_4 and then concentrated in vacuo to yield the pure product (0.81 g, 87% yield, >19:1 dr).



Method C: To an oven-dried three neck round bottom flask (1000 mL) equipped with a magnetic stirbar was added MgCl_2 (9.50 g, 100 mmol, 2 equiv) and MnCl_2 (315 mg, 2.5 mmol, 5 mol%). Each neck was fitted with a rubber septum. The septa on the side necks were fitted with a carbon felt anode ($3.0 \times 5.0 \text{ cm}^2$, connected to a platinum wire), and a nickel foam cathode ($3.0 \times 5.0 \text{ cm}^2$), respectively, maintaining a distance of ca. 4.0 cm between the closest point of the two electrodes. The cell was sealed and flushed with nitrogen gas for 5 minutes, followed by the addition of electrolyte solution (0.10 M LiClO_4 in MeCN, 500 mL), indene (5.8 g, 50.0 mmol, 1 equiv), and acetic acid (100 mL). The reaction mixture was then purged with nitrogen gas for another 5 minutes. A nitrogen-filled balloon was adapted through a septum to sustain a nitrogen atmosphere. Electrolysis was initiated at a constant current of 800 mA at $40 \text{ }^\circ\text{C}$ (oil bath temperature). The reaction was allowed to proceed for 3 h 21 min before the current was withdrawn (2 F of total charge passed, assuming that the overall reaction is a 2-electron oxidation process). The entire reaction mixture was then concentrated in vacuo. The residue was then dissolved in EtOAc and washed with NaHCO_3 (aq.) ($3 \times 100 \text{ mL}$), and then brine (100 mL). The organic layer was dried over Na_2SO_4 and then concentrated in vacuo to yield the pure product (9.06 g, 97% yield, >19:1 dr). No chromatographic purification was needed.

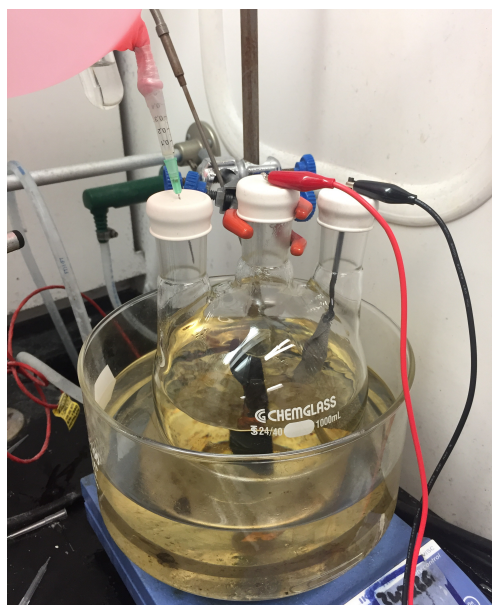
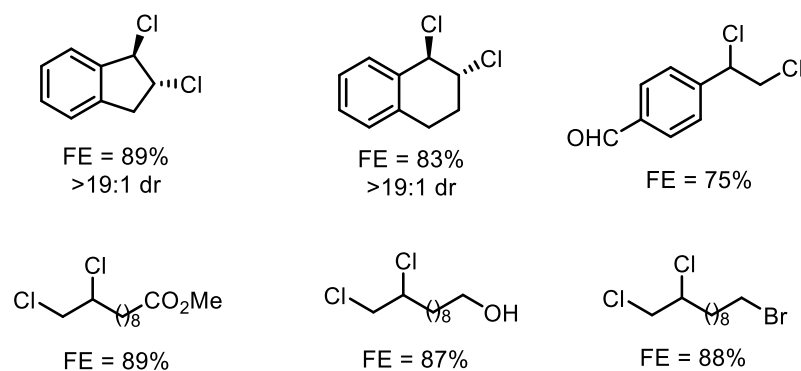


Fig. S2. Setup for the gram-scale electroynthesis of 1,2-*trans*-dichloroindane.

Section 3. Current efficiency of reaction with representative substrates

General information: Current efficiencies (Faradaic efficiencies) were measured using Method A with the following modifications. A constant current of 8 mA was applied and the reaction was allowed to proceed for 80 min before the current was withdrawn (this corresponds to a total of 2 F of charge passed). Assuming that the overall reaction is a 2-electron oxidation process, the Faradaic efficiency thus equals the percentage yield.



Section 4. Stereochemical assignment of the dichlorination products

Product	Assignment	References
2	Comparison with reported ^1H NMR	S2, S3
10	Comparison with reported ^1H NMR	S2
11	Coupling constant ($J = 8.5 \text{ Hz}$) ^a	S4
12	Comparison with reported ^1H NMR	S2, S5
13	Comparison with reported ^1H NMR	S6
17	Coupling constant ($J = 7.7 \text{ Hz}$) ^a	S4
21	Comparison with reported ^1H NMR	S2, S7, S8

^aThe vicinal α -protons of linear *trans*- and *cis*-1,2-dichloroalkanes exhibit distinct coupling constants. The *trans* isomers typically have a J value of larger than 6 Hz, while the *cis* isomers typically have a J value of smaller than 3.5 Hz. See ref. S3.

Section 5. Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a Ag/AgNO₃ reference electrode, and a platinum wire counter electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection.

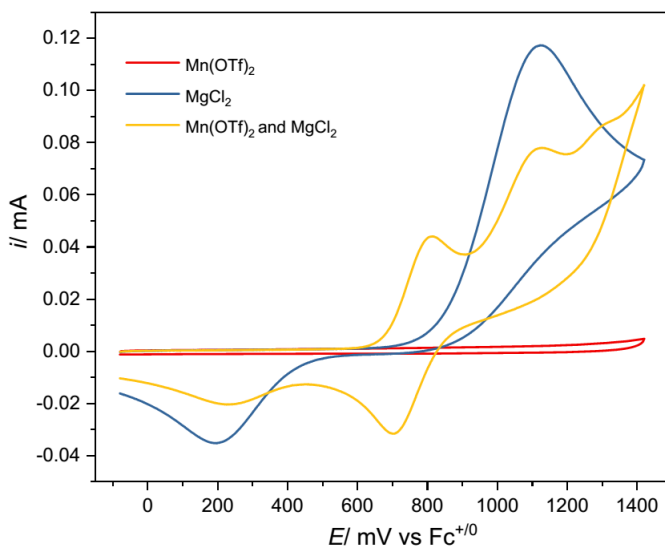


Fig. S3. Cyclic voltammogram of Mn(OTf)₂, MgCl₂, and their mixture in MeCN/HOAc. Conditions: LiClO₄ (0.10 M in MeCN), HOAc (60 mM), and with (a) Mn(OTf)₂ (2.0 mM), (b) MgCl₂ (8.0 mM), or (c) Mn(OTf)₂ (2.0 mM) and MgCl₂ (8.0 mM). **Scan rate: 100 mV/s.**

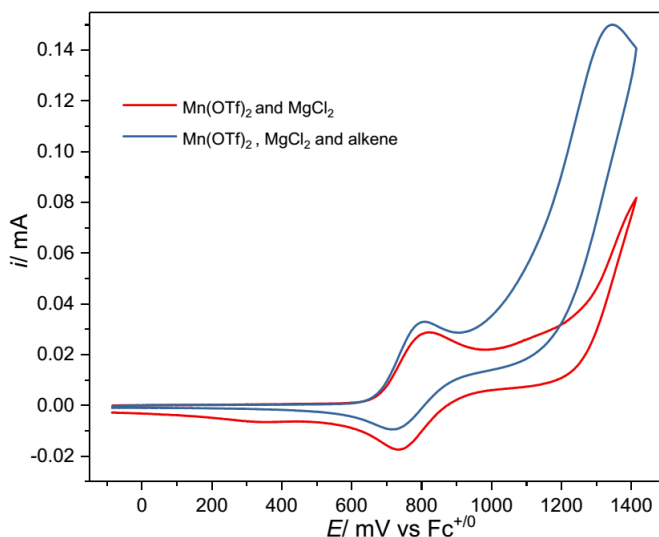
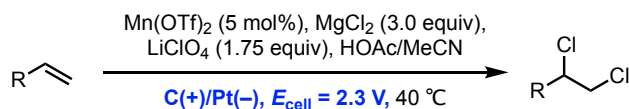
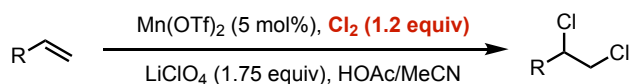


Fig. S4. Cyclic voltammogram of Mn(OTf)₂, MgCl₂, and/or 4-*tert*-butylstyrene in MeCN/HOAc. Conditions: LiClO₄ (0.10 M in MeCN), HOAc (60 mM), and with (a) Mn(OTf)₂ (2.0 mM), MgCl₂ (8.0 mM), (b) Mn(OTf)₂ (2.0 mM), MgCl₂ (8.0 mM) and 4-*tert*-butylstyrene (4.0 mM). **Scan rate: 50 mV/s.**

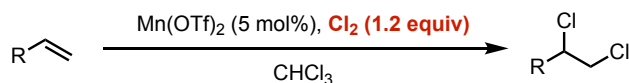
Section 6. Control experiments: electrocatalytic vs Cl₂-mediated chlorination



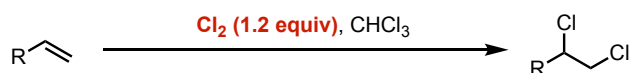
Method A (electrocatalytic protocol): see Section 2.



Method D: Under N₂, an oven-dried 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with LiClO₄ (1.0 mmol, 106 mg) and CH₃CN was added via syringe, then the bottle was sealed with a rubber septum and weighed and connected to a cylinder containing Cl₂ gas, using Tygon® tubing and a Pasteur pipet. Cl₂ gas was gently bubbled into the solution over 2 min, with stirring, which gave a yellow solution almost immediately. The Cl₂ gas inlet was then disconnected, and the flask was re-weighed to measure the amount of Cl₂ gas dissolved in the solution, thus allowing calculation of the concentration (ca. 0.338 M). An oven-dried vial was then charged with the alkene substrate (0.20 mmol, 1.0 equiv), Mn(OTf)₂ (0.01 mmol, 3.5-3.6 mg), 0.1 M LiClO₄ in CH₃CN (2.79-2.08 mL) and AcOH (0.4 mL). The Cl₂ solution (0.71-1.42 mL, 1.2-2.4 equiv) was then added dropwise via syringe to the reaction mixture with shaking. The resultant mixture was shaken for 5 min and subsequently subjected to a short column to remove any polar impurities, concentrated, and analyzed by ¹H NMR.



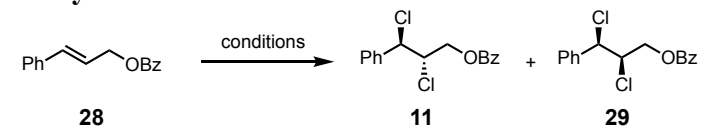
Method E: Under N₂, an oven-dried 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with CHCl₃ was added via syringe, then the bottle was sealed with a rubber septum and weighed and connected to a cylinder containing Cl₂ gas, using Tygon® tubing and a Pasteur pipet. Cl₂ gas was gently bubbled into the solution over 1 min, with stirring, which gave a yellow solution almost immediately. The Cl₂ gas inlet was then disconnected, and the flask was re-weighed to measure the amount of Cl₂ gas dissolved in the solution, thus allowing calculation of the concentration (ca. 0.16 M). An oven-dried vial was then charged with the alkene substrate (0.20 mmol, 1.0 equiv) and Mn(OTf)₂ (0.01 mmol, 3.5-3.6 mg). The Cl₂ solution (1.5-3.0 mL, 1.2-2.4 equiv) was then added dropwise via syringe to the reaction mixture with shaking. The resultant mixture was shaken for 5 min and subsequently subjected to a short column to remove any polar impurities, concentrated, and analyzed by ¹H NMR.



Method F (Cl₂-mediated method in CHCl₃ without Mn): This method made use of the same Cl₂/CHCl₃ solution (ca. 0.16 M) prepared following the procedure in Method E. An oven-dried vial was charged with the alkene substrate (0.20 mmol, 1.0 equiv). The Cl₂ solution (1.5-3.0 mL, 1.2-2.4 equiv) was then added dropwise via syringe to the

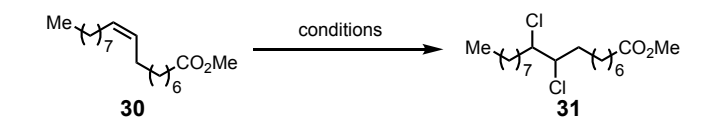
reaction mixture with shaking. At the end of the addition, a pale yellow solution was observed. At the end of the addition, a pale yellow solution was observed. The resultant mixture was shaken for 5 min and subsequently subjected to a short column to remove any polar impurities, concentrated, and analyzed by ^1H NMR.

A. Diastereoselectivity test



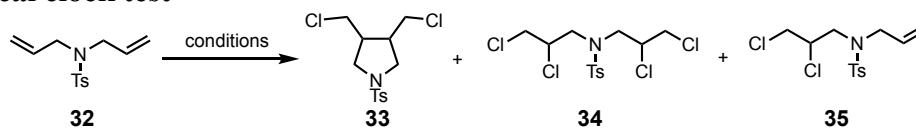
Entry	conditions	yield (%)	dr (11:29)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-) , $E_{\text{cell}} = 2.3 \text{ V}$, 40 °C	87	12:1
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , LiClO ₄ (1.75 equiv), HOAc/MeCN	<5	— ^a
3	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	73	1:8
4	Cl₂ (1.2 equiv) , CHCl ₃	70	1:5

^aNot determined.



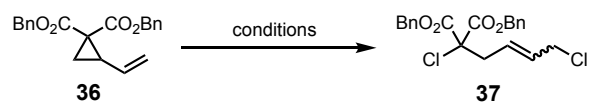
Entry	conditions	yield (%)	dr (<i>syn:anti</i>)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-) , $E_{\text{cell}} = 2.3 \text{ V}$, 40 °C	91	1:2
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	90	>19:1
3	Cl₂ (1.2 equiv) , CHCl ₃	70	>19:1

B. Radical clock test



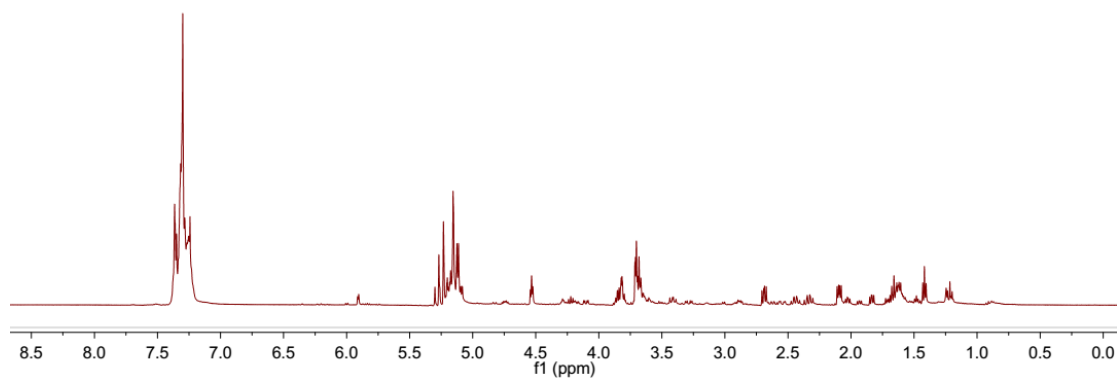
Entry	conditions	33 yield (%)	34+35 yield(%)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-) , $E_{\text{cell}} = 2.3 \text{ V}$, 40 °C	71^a	<5
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	<5	70^b
3	Mn(OTf) ₂ (5 mol%), Cl₂ (2.4 equiv) , CHCl ₃	<5	77^c
4	Cl₂ (2.4 equiv) , CDCl ₃	<5	79^c

^a*trans/cis* = 2:1. ^b34:35 = 1:1.5. ^cOnly 34 observed.

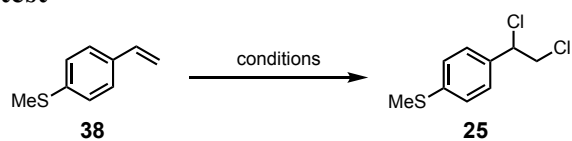


Entry	conditions	37 yield (%)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-), E_{cell} = 2.3 V, 40 °C	86^a
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	<5^b
3	Cl₂ (1.2 equiv) , CHCl ₃	<5^b

^aE/Z = 8:1. ^bMultiple unidentified products observed by ¹H NMR (the crude NMR spectrum from entry 2 is shown below). See page S53 for product NMR from entry 1 for comparison.

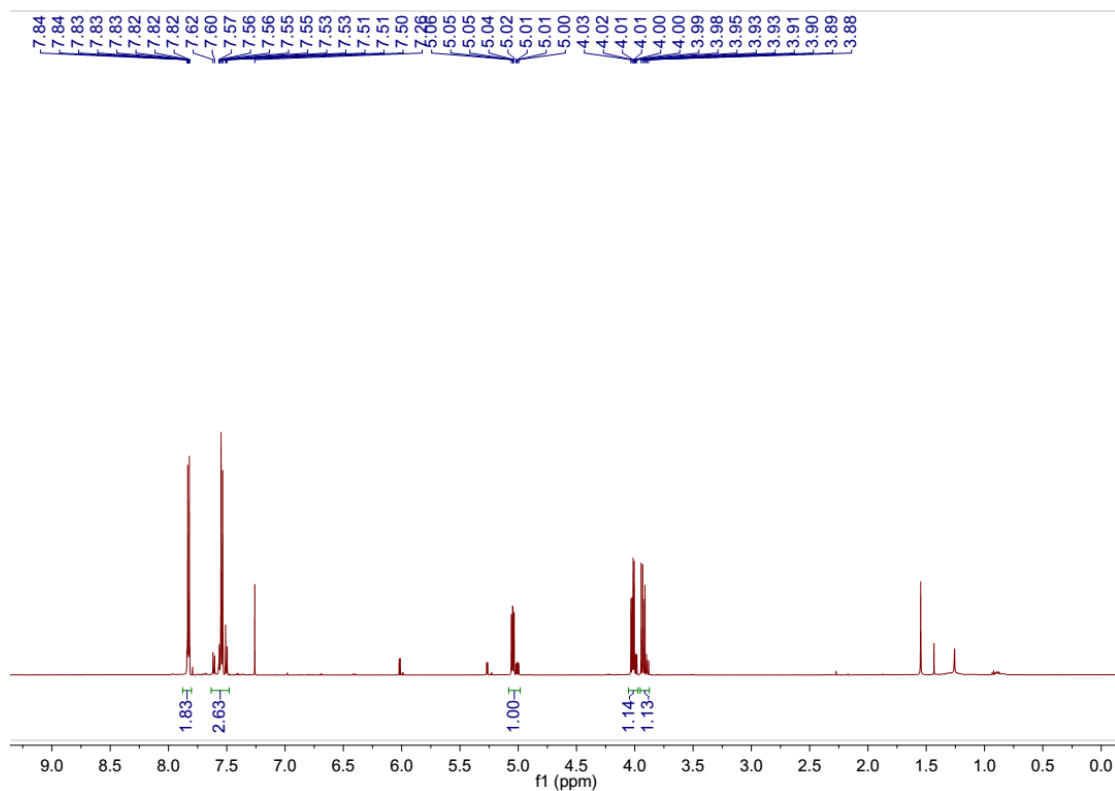


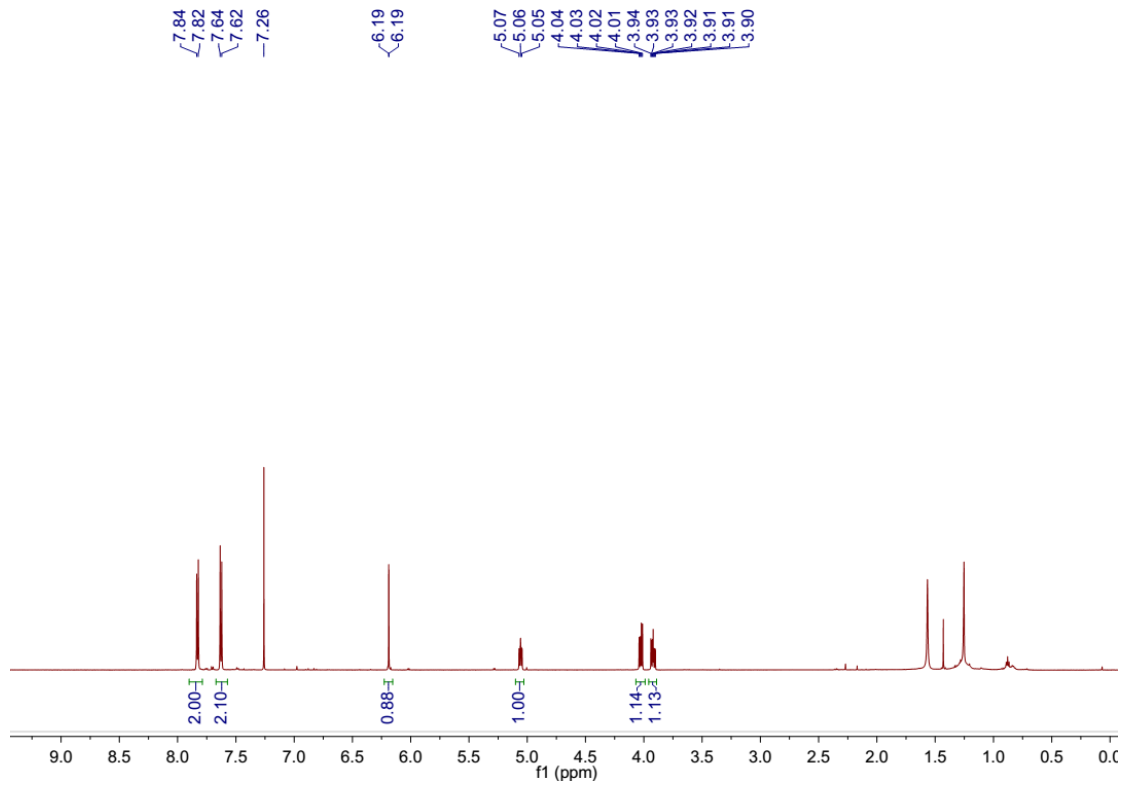
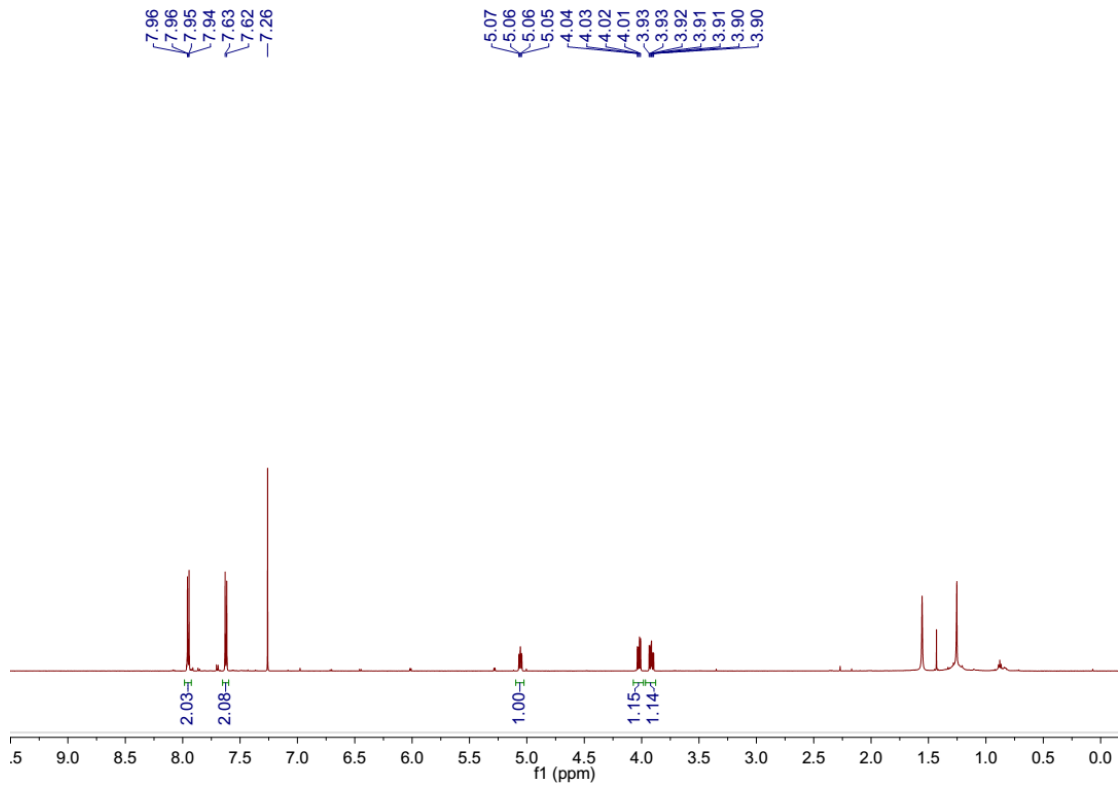
C. Chemoselectivity test

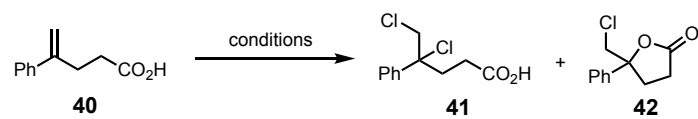


Entry	conditions	25 yield (%)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-), E_{cell} = 2.3 V, 40 °C	71
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	50^{a,b}
3	Mn(OTf) ₂ (5 mol%), Cl₂ (2.0 equiv) , CHCl ₃	<5^a
4	Cl₂ (1.2 equiv) , CHCl ₃	46^{a,b}

^aFull conversion; at least three unidentified byproducts observed by ¹H NMR. The spectra of some of these byproducts (purified) from entry 4 are shown below. ^bFreshly prepared Cl₂/CHCl₃ solution required to observe any formation of **25**.

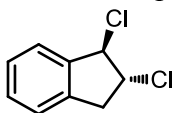




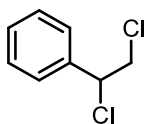


Entry	conditions	41 yield (%)	42 yield (%)
1	Mn(OTf) ₂ (5 mol%), MgCl ₂ (3.0 equiv), LiClO ₄ (1.75 equiv), HOAc/MeCN, C(+)/Pt(-), E_{cell} = 2.3 V, 40 °C	77	10
2	Mn(OTf) ₂ (5 mol%), Cl₂ (1.2 equiv) , CHCl ₃	16	68
3	Cl₂ (1.2 equiv) , CHCl ₃	15	68

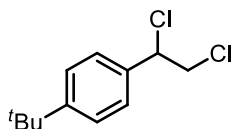
Section 7. Spectral Data for Products



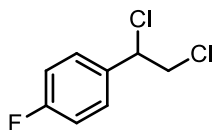
trans-1,2-dichloro-2,3-dihydro-1H-indene (2). Followed Method A from indene (23.2 mg, 0.20 mmol), for 2.0 h, and purified using silica gel chromatography to give 32.5 mg (90% yield, >19:1 dr) of **2** as a pale yellow oil. IR (Film): 2961, 1464, 1426, 1310, 1280, 1248, 1199, 947, 741, 657 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.47-7.44 (m, 1 H), 7.37-7.28 (m, 3 H), 5.35 (d, $J = 3.0$ Hz, 1 H), 4.66 (dt, $J = 6.3, 3.3$ Hz, 1 H), 3.71 (dd, $J = 16.7, 6.1$ Hz, 1 H), 3.19 (dd, $J = 16.7, 3.4$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 139.79, 129.66, 127.89, 125.45, 125.06, 67.58, 64.45, 40.71; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_8\text{Cl}_2^+ - \text{Cl}]$: 151.0309, found 151.0308.



(1,2-dichloroethyl)benzene (3). Followed Method A from styrene (20.8 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 29.8 mg (85% yield) of **3** as a pale yellow oil. IR (Film): 2958, 2923, 1454, 1257, 1234, 1209, 1077, 1046, 772, 733, 697 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.46-7.33 (m, 5 H), 5.00 (dd, $J = 7.8, 6.7$ Hz, 1 H), 4.00 (dd, $J = 11.3, 6.6$ Hz, 1 H), 3.93 (dd, $J = 11.3, 8.0$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 137.98, 129.14, 128.80, 127.38, 61.74, 48.33; MS (DART) exact mass calculated for $[\text{C}_8\text{H}_8\text{Cl}_2^+ - \text{Cl}]$: 139.0309, found 139.0311.

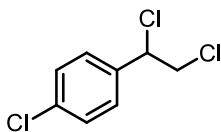


1-(tert-butyl)-4-(1,2-dichloroethyl)benzene (4). Followed Method A from 1-tert-butylstyrene (32.0 mg, 0.20 mmol), for 2.5 h, and purified using silica gel chromatography to give 42.5 mg (91% yield) of **4** as a colorless oil. IR (Film): 2964, 2904, 2869, 1512, 1414, 1365, 1269, 1109, 943, 922, 838, 764, 699 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.45-7.37 (m, 2 H), 7.37-7.30 (m, 2 H), 5.00 (t, $J = 7.2$ Hz, 1 H), 3.96 (ddd, $J = 19.1, 11.3, 7.2$ Hz, 2 H), 1.33 (s, 9 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 152.25, 134.95, 127.01, 125.75, 61.81, 48.40, 34.68, 31.23; MS (DART) exact mass calculated for $[\text{C}_{12}\text{H}_{16}\text{Cl}_2^+ - \text{Cl}]$: 195.0935, found 195.0941.

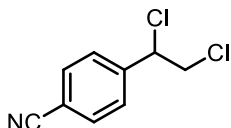


1-(1,2-dichloroethyl)-4-fluorobenzene (5). Followed Method A from 1-fluoro-4-vinylbenzene (24.4 mg, 0.20 mmol), for 3.5 h, and purified using silica gel chromatography to give 36.7 mg (95% yield) of **5** as a colorless oil. IR (Film): 2957, 2924, 2853, 1606, 1512, 1232, 1160, 839, 729 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.43-7.33 (m, 2 H), 7.08 (t, $J = 8.6$ Hz, 2 H), 4.99 (dd, $J = 8.2, 6.4$ Hz, 1 H), 3.99 (dd, $J = 11.3,$

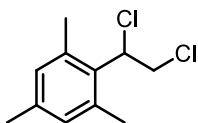
6.2 Hz, 1 H), 3.89 (dd, $J = 11.3, 8.4$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 163.90, 161.92, 133.87, 133.85, 129.30, 129.23, 115.89, 115.72, 60.77, 48.21; MS (EI) calculated for $[\text{C}_8\text{H}_7\text{Cl}_2\text{F}]$: 192.0, found 191.9.



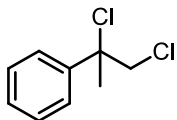
1-chloro-4-(1,2-dichloroethyl)benzene (6). Followed Method A from 1-chloro-4-vinylbenzene (27.7 mg, 0.20 mmol), for 3.5 h, and purified using silica gel chromatography to give 38.5 mg (92% yield) of **6** as a colorless oil. IR (Film): 2952, 2926, 2654, 1598, 1493, 1410, 1092, 1015, 923, 831, 790, 758, 724, 693 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.42-7.31 (m, 4 H), 4.97 (dd, $J = 8.3, 6.2$ Hz, 1 H), 3.98 (dd, $J = 11.3, 6.2$ Hz, 1 H), 3.88 (dd, $J = 11.3, 8.4$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 136.46, 135.02, 129.01, 128.81, 60.64, 48.02; MS (EI) calculated for $[\text{C}_8\text{H}_7\text{Cl}_3^+ - \text{Cl}]$: 207.9, 209.9, found 207.9, 209.9.



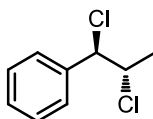
4-(1,2-dichloroethyl)benzonitrile (7). Followed Method A from 4-vinylbenzonitrile (25.8 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 32.0 mg (80% yield) of **7** as a colorless oil. IR (Film): 2956, 2922, 2851, 2231, 1610, 1504, 1392, 1288, 1207, 1020, 945, 843, 770, 732, 709 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.74-7.67 (m, 2 H), 7.54 (d, $J = 8.3$ Hz, 2 H), 5.01 (dd, $J = 8.7, 5.8$ Hz, 1 H), 4.01 (dd, $J = 11.4, 5.8$ Hz, 1 H), 3.89 (dd, $J = 11.4, 8.7$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 142.83, 132.56, 128.36, 118.14, 113.05, 59.97, 47.55; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_8\text{Cl}_2\text{N}^+]$: 200.0028, found 200.0031.



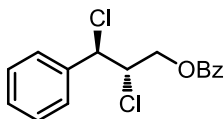
2-(1,2-dichloroethyl)-1,3,5-trimethylbenzene (8). Followed Method A from 1,3,5-trimethyl-2-vinylbenzene (29.2 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 37.3 mg (86% yield) of **8** as a pale yellow oil. IR (Film): 2953, 2922, 2868, 1611, 1483, 1462, 1451, 1428, 1378, 1031, 853, 717 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 6.88 (s, 2 H), 5.56 (t, $J = 7.9$ Hz, 1 H), 4.21-4.07 (m, 2 H), 2.62-2.36 (m, 6 H), 2.28 (s, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 138.62, 137.11, 132.56, 131.68, 130.47, 129.41, 57.99, 46.52, 20.83, 20.78; MS (DART) exact mass calculated for $[\text{C}_{11}\text{H}_{14}\text{Cl}_2^+ - \text{Cl}]$: 181.0779, found 181.0779.



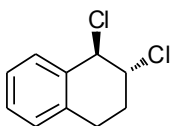
(1,2-dichloropropan-2-yl)benzene (9). Followed Method A from prop-1-en-2-ylbenzene (23.6 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 32.9 mg (87% yield) of **9** as a colorless oil. IR (Film): 2955, 2924, 2853, 1447, 1379, 1279, 1047, 769, 720, 695, 657 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.59-7.55 (m, 2 H), 7.43-7.37 (m, 2 H), 7.37-7.32 (m, 1 H), 4.03 (dd, $J = 27.0, 11.3$ Hz, 2 H), 2.11 (s, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 141.45, 128.39, 128.37, 126.39, 70.52, 54.59, 28.20; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_{10}\text{Cl}_2^+ - \text{Cl}]$: 153.0466, found 153.0471.



trans-1,2-dichloropropylbenzene (10). Followed Method A from (*E*)-prop-1-en-1-ylbenzene (23.6 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 33.6 mg (89% yield, 11:1 dr) of **10** as a pale yellow oil. IR (Film): 2986, 2932, 2850, 1494, 1451, 1379, 1225, 1192, 1079, 1013, 826, 767, 735, 696, 666 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.45-7.30 (m, 5 H), 4.91 (d, $J = 7.8$ Hz, 1 H), 4.39 (dq, $J = 13.0, 6.5$ Hz, 1 H), 1.71 (d, $J = 6.5$ Hz, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 138.64, 128.77, 128.50, 127.73, 67.41, 60.18, 22.15; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_{10}\text{Cl}_2^+ - \text{Cl}]$: 153.0466, found 153.0465.

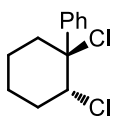


trans-2,3-dichloro-3-phenylpropyl benzoate (11). Followed Method A from cinnamyl benzoate (47.6 mg, 0.20 mmol), for 2.5 h, and purified using silica gel chromatography to give 53.8 mg (87% yield, 12:1 dr) of **11** as a colorless oil. IR (Film): 2958, 2919, 1721, 1452, 1268, 1177, 1118, 1070, 1027, 709, 697 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 8.14-8.03 (m, 2 H), 7.65-7.55 (m, 1 H), 7.51-7.45 (m, 4 H), 7.43-7.36 (m, 3 H), 5.17 (d, $J = 8.5$ Hz, 1 H), 4.85-4.77 (m, 2 H), 4.67-4.63 (m, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 165.85, 137.48, 133.37, 129.74, 129.43, 129.10, 128.66, 128.49, 127.89, 65.49, 62.06, 61.62; MS (DART) exact mass calculated for $[\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_2^+ - \text{N}_2]$: 273.0677, found 273.0679.

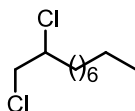


trans-1,2-dichloro-1,2,3,4-tetrahydronaphthalene (12). Followed Method A from 1,2-dihydronaphthalene (26.0 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 34.2 mg (85% yield, >19:1 dr) of **12** as a colorless oil. IR (Film): 2970, 2924, 2901, 1233, 1066, 814, 738, 679, 647 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.27 (dd, $J = 7.6, 1.2$ Hz, 1 H), 7.22-7.12 (m, 2 H), 7.07 (d, $J = 7.4$ Hz, 1 H), 5.16 (d, $J = 2.6$ Hz, 1 H), 4.62-4.52 (m, 1 H), 3.11-3.04 (m, 1 H), 2.82-2.77 (m, 1 H), 2.63-2.55 (m, 1

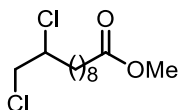
H), 2.10-2.03 (m, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 134.85, 132.32, 131.01, 129.04, 128.79, 126.66, 59.71, 59.42, 24.96, 23.83; MS (DART) exact mass calculated for $[\text{C}_{10}\text{H}_{10}\text{Cl}_2^+ - \text{Cl}]$: 165.0466, found 165.0462.



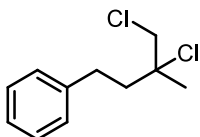
(trans-1,2-dichlorocyclohexyl)benzene (13). Followed Method A from 2,3,4,5-tetrahydro-1,1'-biphenyl (31.6 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 35.3 mg (77% yield, 8:1 dr) of **13** as a colorless oil. IR (Film): 2941, 2866, 1446, 1437, 1150, 1007, 915, 746, 693, 647, 616 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.57-7.45 (m, 2 H), 7.44-7.34 (m, 2 H), 7.34-7.27 (m, 1 H), 4.78 (d, $J = 2.1$ Hz, 1 H), 2.70-2.61 (m, 2 H), 2.31-2.28 (m, 1 H), 2.09-1.93 (m, 2 H), 1.90-1.75 (m, 2 H), 1.69-1.59 (m, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 143.98, 128.24, 128.08, 125.97, 73.68, 64.90, 30.93, 29.90, 21.27, 18.48; MS (DART) exact mass calculated for $[\text{C}_{12}\text{H}_{14}\text{Cl}_2^+ - \text{Cl}]$: 193.0779, found 193.0784.



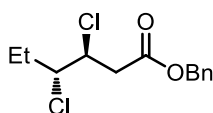
1,2-dichlorodecane (14). Followed Method A from dec-1-ene (28.0 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 38.0 mg (90% yield) of **14** as a colorless oil. IR (Film): 2955, 2925, 2855, 1466, 1443, 1298, 1056, 920, 730, 664, 625 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 4.06-4.01 (m, 1 H), 3.76 (dd, $J = 11.3, 5.2$ Hz, 1 H), 3.65 (dd, $J = 11.3, 7.4$ Hz, 1 H), 2.03-1.93 (m, 1 H), 1.77-1.64 (m, 1 H), 1.62-1.49 (m, 1 H), 1.47-1.37 (m, 1 H), 1.35-1.25 (m, 10 H), 0.88 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 61.27, 48.27, 35.05, 31.82, 29.36, 29.18, 28.98, 25.81, 22.64, 14.09; MS (EI) calculated for $[\text{C}_{10}\text{H}_{20}\text{Cl}_2]$: 210.1, found 210.1.



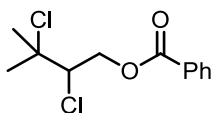
methyl 10,11-dichloroundecanoate (15). Followed Method A from methyl undec-10-enoate (39.6 mg, 0.20 mmol), for 4.0 h, at 40 $^\circ\text{C}$, with 5 mol % $\text{Mn}(\text{OTf})_2$, using LiClO_4 as the electrolyte, with 0.4 mL HOAc, using Pt plate counter electrode, and purified using silica gel chromatography to give 49.0 mg (91% yield) of **15** as a colorless oil. IR (Film): 2928, 2856, 1736, 1435, 1366, 1231, 1197, 1171, 1107, 725, 662 cm^{-1} ; ^1H NMR: (300 MHz, CDCl_3) δ 4.14-3.92 (m, 1 H), 3.75 (dd, $J = 11.3, 5.2$ Hz, 1 H), 3.70-3.57 (m, 4 H), 2.29 (t, $J = 7.5$ Hz, 2 H), 2.02-1.89 (m, 1 H), 1.76-1.25 (m, 13 H); ^{13}C NMR: (75 MHz, CDCl_3) δ 174.26, 61.17, 51.45, 48.21, 34.95, 34.02, 29.13, 29.06, 29.01, 28.83, 25.72, 24.85; MS (DART) exact mass calculated for $[\text{C}_{12}\text{H}_{23}\text{Cl}_2\text{O}_2^+]$: 269.1070, found 269.1072.



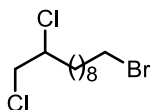
(3,4-dichloro-3-methylbutyl)benzene (16). Followed Method A from (3-methylbut-3-en-1-yl)benzene (29.2 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 38.2 mg (88% yield) of **16** as a pale yellow oil. IR (Film): 2953, 2930, 2865, 1498, 1454, 1439, 1380, 1057, 1032, 748, 725, 698, 626 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.35-7.32 (m, 2 H), 7.29-7.21 (m, 3 H), 3.85 (d, $J = 11.2$ Hz, 1 H), 3.76 (d, $J = 11.2$ Hz, 1 H), 2.88-2.79 (m, 2 H), 2.27-2.10 (m, 2 H), 1.73 (s, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 141.07, 128.51, 128.41, 126.11, 70.96, 52.35, 42.58, 30.73, 28.14; MS (EI) calculated for $[\text{C}_{11}\text{H}_{14}\text{Cl}_2]$: 216.0, found 216.0.



Benzyl-*trans*-3,4-dichlorohexanoate (17). Followed Method A from benzyl (*E*)-hex-3-enoate (40.8 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 40.7 mg (74% yield, 5:1 dr) of **17** as a colorless oil. IR (Film): 2971, 2935, 1737, 1455, 1386, 1267, 1231, 1215, 1158, 993, 908, 813, 739, 697, 653 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.42-7.30 (m, 5 H), 5.19 (s, 2 H), 4.42 (ddd, $J = 9.5, 7.7, 3.4$ Hz, 1 H), 4.04-3.96 (m, 1 H), 3.20 (dd, $J = 16.4, 3.3$ Hz, 1 H), 2.87 (dd, $J = 16.4, 9.5$ Hz, 1 H), 2.13-2.05 (m, 1 H), 1.86-1.75 (m, 1 H), 1.08 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 169.73, 135.42, 128.58, 128.39, 128.29, 66.90, 66.46, 59.34, 40.70, 28.16, 10.29; MS (DART) exact mass calculated for $[\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{O}_2]^+$: 275.0600, found 275.0607.

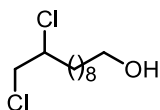


2,3-dichloro-3-methylbutyl benzoate (18). Followed Method A from 3-methylbut-2-en-1-yl benzoate (38.0 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 50.1 mg (96% yield, 5:1 dr) of **18** as a colorless oil. IR (Film): 2985, 2936, 1721, 1602, 1451, 1390, 1373, 1315, 1269, 1177, 1113, 1070, 1027, 973, 709, 686, 630 cm^{-1} ; ^1H NMR: (300 MHz, CDCl_3) δ 8.13-8.03 (m, 2 H), 7.59 (t, $J = 7.4$ Hz, 1 H), 7.46 (t, $J = 7.5$ Hz, 2 H), 5.00 (dd, $J = 11.9, 3.0$ Hz, 1 H), 4.56 (dd, $J = 11.8, 8.4$ Hz, 1 H), 4.34 (dd, $J = 8.4, 3.0$ Hz, 1 H), 1.80 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR: (75 MHz, CDCl_3) δ 166.11, 133.28, 129.72, 129.52, 128.44, 69.17, 67.08, 66.02, 31.72, 27.77; MS (DART) exact mass calculated for $[\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{O}_2]^+$: 261.0444, found 261.0446.

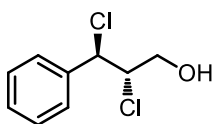


11-bromo-1,2-dichloroundecane (19). Followed Method A from 11-bromoundec-1-ene (46.6 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 51.1 mg (84% yield) of **19** as a colorless oil. IR (Film): 2926, 2854, 1462, 1440, 1371, 1238, 1035, 724, 662 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 4.05-4.00 (m, 1 H), 3.76 (dd,

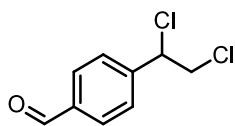
$J = 11.3, 5.2$ Hz, 1 H), 3.65 (dd, $J = 11.3, 7.4$ Hz, 1 H), 3.40 (t, $J = 6.9$ Hz, 2 H), 2.01-1.93 (m, 1 H), 1.88-1.82 (m, 2 H), 1.76-1.65 (m, 1 H), 1.59-1.49 (m, 1 H), 1.46-1.27 (m, 11 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 61.19, 48.23, 34.99, 34.00, 32.76, 29.25, 29.23, 28.88, 28.66, 28.10, 25.75; MS (EI) mass calculated for $[\text{C}_{11}\text{H}_{21}\text{BrCl}_2]$: 302.0, 304.0, found 301.9 and 304.0.



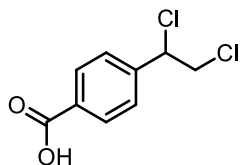
10,11-dichloroundecan-1-ol (20). Followed Method A from undec-10-en-1-ol (34.0 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 39.0 mg (81% yield) of **20** as a colorless oil. IR (Film): 3346, 2926, 2854, 1462, 1433, 1370, 1054, 920, 724, 662, 623 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 4.06-4.00 (m, 1 H), 3.75 (dd, $J = 11.3, 5.2$ Hz, 1 H), 3.68-3.60 (m, 3 H), 2.01-1.93 (m, 1 H), 1.79-1.64 (m, 2 H), 1.58-1.53 (m, 2 H), 1.45-1.26 (m, 12 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 62.99, 61.21, 48.23, 34.99, 32.72, 29.41, 29.32, 29.27, 28.90, 25.75, 25.67; MS (DART) exact mass calculated for $[\text{C}_{11}\text{H}_{23}\text{Cl}_2\text{O}^+]$: 241.1120, found 241.1122.



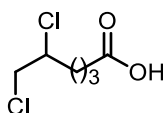
trans-2,3-dichloro-3-phenylpropan-1-ol (21). Followed Method A from (*E*)-3-phenylprop-2-en-1-ol (26.8 mg, 0.20 mmol), for 2.5 h, and purified using silica gel chromatography to give 32.0 mg (78% yield, 10:1 dr) of **21** as a colorless oil. IR (Film): 3379, 3033, 2928, 1454, 1236, 1187, 1077, 1059, 969, 696, 678, 634 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.48-7.32 (m, 5 H), 5.10 (d, $J = 9.5$ Hz, 1 H), 4.43 (ddd, $J = 9.5, 4.8, 3.1$ Hz, 1 H), 4.18 (dd, $J = 12.4, 4.8$ Hz, 1 H), 4.09 (dd, $J = 12.4, 3.0$ Hz, 1 H), 2.13 (s, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 138.14, 128.97, 128.62, 127.84, 66.03, 64.19, 61.35; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_{10}\text{Cl}_2\text{O}^+ - \text{Cl}]$: 169.0415, found 169.0416.



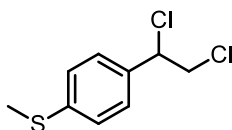
4-(1,2-dichloroethyl)benzaldehyde (22). Followed Method A from 4-vinylbenzaldehyde (26.4 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 30.8 mg (76% yield) of **22** as a colorless oil. IR (Film): 2958, 2920, 2850, 1703, 1608, 1580, 1426, 1391, 1306, 1209, 1171, 834, 803, 748, 727 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 10.04 (s, 1 H), 7.92 (d, $J = 8.2$ Hz, 2 H), 7.59 (d, $J = 8.2$ Hz, 2 H), 5.05 (dd, $J = 8.5, 6.0$ Hz, 1 H), 4.03 (dd, $J = 11.4, 6.0$ Hz, 1 H), 3.93 (dd, $J = 11.4, 8.5$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 191.40, 144.16, 136.75, 130.08, 128.25, 60.43, 47.74; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_9\text{Cl}_2\text{O}^+]$: 203.0025, found 203.0028.



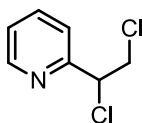
4-(1,2-dichloroethyl)benzoic acid (23). Followed Method A from 4-vinylbenzoic acid (29.6 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 32.9 mg (75% yield) of **23** as a white solid. IR (Film): 2955, 2668, 2546, 1682, 1611, 1422, 1318, 1284, 1183, 1127, 944, 926, 862, 741, 714, 703 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.3$ Hz, 2 H), 7.54 (d, $J = 8.3$ Hz, 2 H), 5.05 (dd, $J = 8.3, 6.2$ Hz, 1 H), 4.02 (dd, $J = 11.4, 6.1$ Hz, 1 H), 3.93 (dd, $J = 11.4, 8.4$ Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 171.37, 143.59, 130.68, 129.97, 127.70, 60.55, 47.84; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_8\text{Cl}_2\text{O}_2^+ - \text{Cl}]$: 218.9969, found 218.9974.



5,6-dichlorohexanoic acid (24). Followed Method A from hex-5-enoic acid (22.8 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 30.7 mg (83% yield) of **24** as a pale yellow oil. IR (Film): 3084, 2958, 2919, 1704, 1432, 1412, 1279, 1233, 1210, 1146, 1066, 935, 918, 867, 734, 663, 624 cm^{-1} ; ^1H NMR: (300 MHz, CDCl_3) δ 4.07-3.96 (m, 1 H), 3.78 (dd, $J = 11.3, 5.0$ Hz, 1 H), 3.65 (dd, $J = 11.4, 7.6$ Hz, 1 H), 2.43 (t, $J = 6.7$ Hz, 2 H), 2.11-1.88 (m, 2 H), 1.84-1.66 (m, 2 H); ^{13}C NMR: (75 MHz, CDCl_3) δ 179.12, 60.43, 47.93, 34.16, 33.23, 21.02; MS (DART) exact mass calculated for $[\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}_2^+ - \text{Cl}]$: 149.0364, found 149.0366.

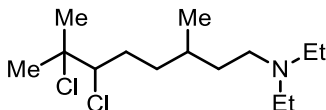


(4-(1,2-dichloroethyl)phenyl)(methyl)sulfane (25). Followed Method A from methyl(4-vinylphenyl)sulfane (30.0 mg, 0.20 mmol), for 4.0 h, with 10 mol % $\text{Mn}(\text{OTf})_2$, and purified using silica gel chromatography to give 34.0 mg (77% yield) of **25** as a yellow oil. IR (Film): 2919, 2850, 1493, 1437, 1397, 1092, 989, 906, 826, 755, 724, 691 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.25 (d, $J = 8.4$ Hz, 2 H), 7.18 (d, $J = 8.3$ Hz, 2 H), 4.89 (dd, $J = 8.0, 6.6$ Hz, 1 H), 3.91 (dd, $J = 11.3, 6.4$ Hz, 1 H), 3.83 (dd, $J = 11.3, 8.2$ Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 140.10, 134.46, 127.81, 126.33, 61.37, 48.12, 15.43; MS (DART) exact mass calculated for $[\text{C}_9\text{H}_{10}\text{Cl}_2\text{S}^+ - \text{Cl}]$: 185.0186, found 185.0189.

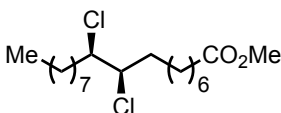


2-(1,2-dichloroethyl)pyridine (26). Followed Method A from 2-vinylpyridine (21.0 mg, 0.20 mmol), for 3.0 h, and purified using silica gel chromatography to give 22.9 mg (65% yield) of **26** as a pale yellow oil. IR (Film): 3056, 3013, 1589, 1473, 1437, 996, 827, 787, 751, 702, 671 cm^{-1} ; ^1H NMR: (300 MHz, CDCl_3) δ 8.61 (d, $J = 4.6$ Hz, 1 H), 7.72 (td, $J =$

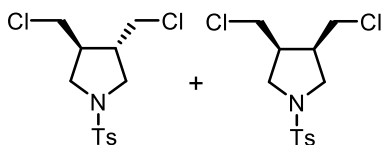
7.7, 1.6 Hz, 1 H), 7.43 (d, $J = 7.8$ Hz, 1 H), 7.26 (dd, $J = 7.0, 5.3$ Hz, 1 H), 5.09 (dd, $J = 7.8, 5.8$ Hz, 1 H), 4.25 (dd, $J = 11.1, 8.0$ Hz, 1 H), 4.04 (dd, $J = 11.1, 5.8$ Hz, 1 H); ^{13}C NMR: (75 MHz, CDCl_3) δ 156.10, 149.62, 137.02, 123.69, 123.01, 61.05, 46.71; MS (DART) exact mass calculated for $[\text{C}_7\text{H}_8\text{Cl}_2\text{N}^+]$: 176.0028, found 176.0031.



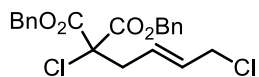
6,7-dichloro-*N,N*-diethyl-3,7-dimethyloctan-1-amine (27). Followed Method A from *N,N*-diethyl-3,7-dimethyloct-6-en-1-amine (42.2 mg, 0.20 mmol), for 4.0 h, and purified using silica gel chromatography to give 50.2 mg (89% yield) of **27** as a yellow oil. IR (Film): 2967, 2932, 2873, 2802, 1457, 1386, 1372, 1109, 795, 670, 623 cm^{-1} ; ^1H NMR: (300 MHz, CDCl_3) δ 3.88-3.82 (m, 1 H), 2.57-2.38 (m, 6 H), 2.31-2.12 (m, 1 H), 1.70 (s, 3 H), 1.60 (s, 3 H), 1.54-1.11 (m, 6 H), 1.01 (t, $J = 7.1$ Hz, 6 H), 0.90 (t, $J = 5.3$ Hz, 3 H); ^{13}C NMR: (75 MHz, CDCl_3) δ 72.04, 72.00, 71.80, 71.48, 50.63, 50.52, 46.79, 34.86, 34.54, 34.07, 33.26, 31.71, 31.68, 31.07, 30.96, 30.76, 26.60, 26.52, 20.02, 19.44, 11.54; MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{30}\text{Cl}_2\text{N}^+]$: 282.1750, found 282.1754.



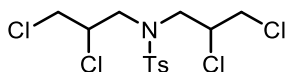
methyl 9,10-dichlorooctadecanoate (31). Followed Method E or F from methyl oleate (59.3 mg, 0.20 mmol), for 5 min, and purified using silica gel chromatography to give 66.1-67.6 mg (90-92% yield) of **31** as a colorless oil. IR (Film): 2926, 2856, 1738, 1458, 1436, 1249, 1196, 1171, 724, 647 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 4.09-3.97 (m, 2 H), 3.65 (s, 3 H), 2.29 (t, $J = 7.5$ Hz, 2 H), 1.92-1.86 (m, 2 H), 1.80-1.73 (m, 3 H), 1.67-1.45 (m, 4 H), 1.45-1.16 (m, 17 H), 0.87 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 174.18, 65.55, 65.50, 51.41, 34.38, 34.34, 34.00, 31.79, 29.35, 29.16, 28.99, 28.95, 28.77, 26.68, 26.60, 24.83, 22.61, 14.06; MS (EI) calculated for $[\text{C}_{19}\text{H}_{37}\text{Cl}_2\text{O}_2^+]$: 367.2165, found 367.2167.



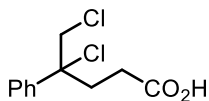
3,4-bis(chloromethyl)-1-tosylpyrrolidine (33). Followed Method A from *N,N*-diallyl-4-methylbenzenesulfonamide (50.2 mg, 0.20 mmol), for 6.0 h, and purified using silica gel chromatography to give 45.7 mg (71% yield, 2:1 dr) of **33** as a colorless oil. IR (Film): 2957, 2917, 1587, 1442, 1344, 1161, 1092, 1038, 815, 737, 664 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.72 (t, $J = 8.8$ Hz, 2 H), 7.36-7.34 (m, 2 H), 3.94-3.72 (m, 1 H), 3.55-3.37 (m, 4 H), 3.33-3.04 (m, 3 H), 2.71-2.55 (m, 1 H), 2.44 (s, 3 H), 2.40-2.32 (m, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 143.95, 143.84, 133.30, 132.45, 129.80, 129.79, 127.75, 127.50, 51.09, 50.52, 45.12, 43.79, 43.18, 41.81, 21.55; MS (DART) exact mass calculated for $[\text{C}_{13}\text{H}_{18}\text{Cl}_2\text{NO}_2\text{S}^+]$: 322.0430, found 322.0431.



dibenzyl (*E*)-2-chloro-2-(4-chlorobut-2-en-1-yl)malonate (37). Followed Method A from dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate (67.2 mg, 0.20 mmol), for 5.0 h, and purified using silica gel chromatography to give 70.0 mg (86% yield, *E*:*Z* = 8:1) of **37** as a yellow oil. IR (Film): 3034, 2960, 1746, 1455, 1376, 1262, 1233, 1214, 1184, 1139, 987, 936, 905, 736, 695 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.47-7.20 (m, 10 H), 5.86-5.79 (m, 1 H), 5.32 (d, J = 16.9 Hz, 1 H), 5.20 (d, J = 2.3 Hz, 2 H), 5.17 (d, J = 5.0 Hz, 2 H), 5.13 (d, J = 10.1 Hz, 1 H), 4.74 (dd, J = 13.9, 7.7 Hz, 1 H), 2.96 (dd, J = 15.3, 7.6 Hz, 1 H), 2.88 (dd, J = 15.3, 5.7 Hz, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 165.66, 136.79, 134.33, 134.25, 128.64, 128.59, 128.54, 128.34, 128.24, 117.80, 68.85, 68.66, 68.58, 57.34, 44.66; MS (DART) exact mass calculated for $[\text{C}_{21}\text{H}_{21}\text{Cl}_2\text{O}_4]^+$: 407.0811, found 407.0812.



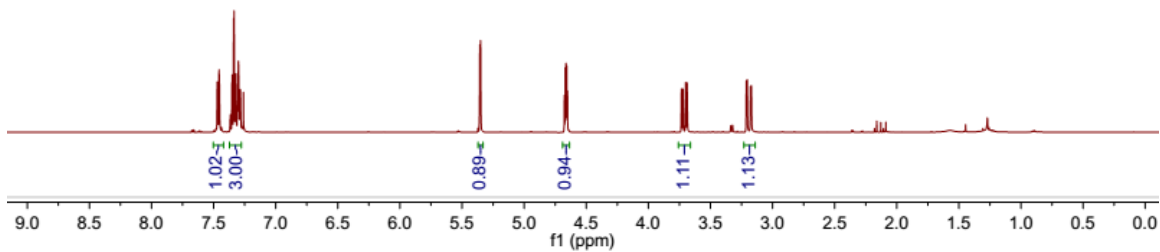
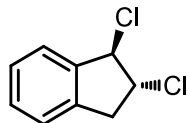
***N,N*-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide (34).** Followed Method E or F from *N,N*-diallyl-4-methylbenzenesulfonamide (50.2 mg, 0.20 mmol), for 5 min, and purified using silica gel chromatography to give 60.5-62.1 mg (77-79% yield) of **34** as a colorless oil. IR (Film): 2988, 2922, 1598, 1347, 1159, 1088, 1057, 815, 733, 673, 654 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.76-7.69 (m, 2 H), 7.37 (dd, J = 8.2, 3.2 Hz, 2 H), 4.57-4.45 (m, 2 H), 3.88-3.75 (m, 6 H), 3.38 (dd, J = 15.3, 8.0 Hz, 1 H), 3.16 (dd, J = 15.1, 7.3 Hz, 1 H), 2.46 (s, 3 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 144.68, 144.57, 134.54, 134.01, 130.13, 130.08, 127.62, 127.59, 58.51, 58.22, 54.65, 54.59, 46.37, 46.28, 21.59.; MS (EI) calculated for $[\text{C}_{13}\text{H}_{18}\text{Cl}_4\text{NO}_2\text{S}]^+$: 393.9777, found 393.9770.



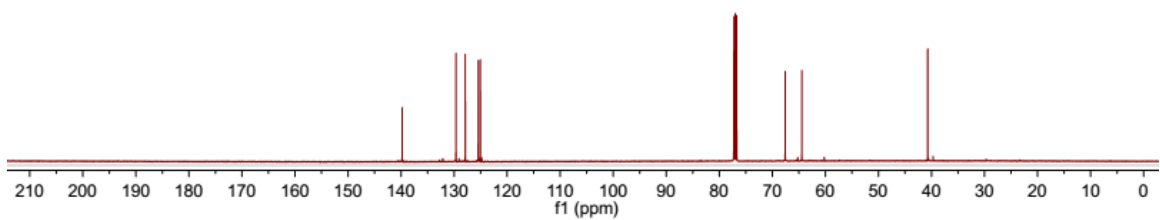
4,5-dichloro-4-phenylpentanoic acid (41). Followed Method A from 4-phenylpent-4-enoic acid (35.2 mg, 0.20 mmol), for 2.5 h, and purified using silica gel chromatography to give 38 mg (77% yield) of **35** as a colorless oil. IR (Film): 3662, 2988, 2901, 1710, 1447, 1408, 1291, 1242, 1075, 1057, 697 cm^{-1} ; ^1H NMR: (500 MHz, CDCl_3) δ 7.58-7.50 (m, 2 H), 7.43-7.32 (m, 3 H), 3.99 (s, 2 H), 2.75-2.59 (m, 3 H), 2.45-2.36 (m, 1 H); ^{13}C NMR: (126 MHz, CDCl_3) δ 178.50, 139.07, 128.60, 128.51, 126.77, 74.97, 54.02, 34.69, 29.62; MS (EI) calculated for $[\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{O}_2^+ - \text{Cl}]$: 211.0520, found 211.0515.

***trans*-1,2-Dichloro-2,3-dihydro-1H-indene (2)**

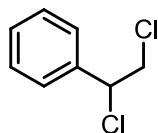
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3.21
3.20
3.18
3.17



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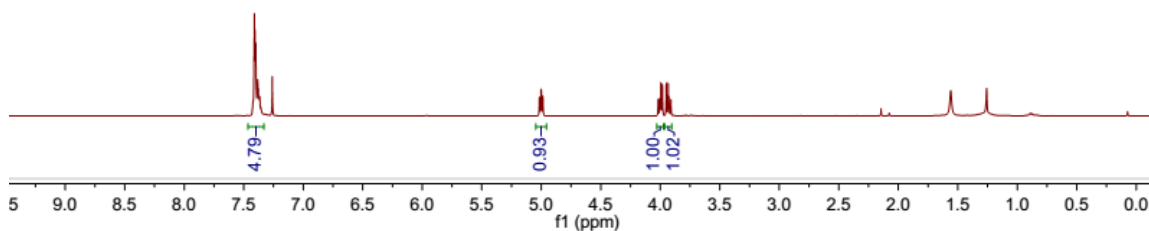


(1,2-Dichloroethyl)benzene (3)

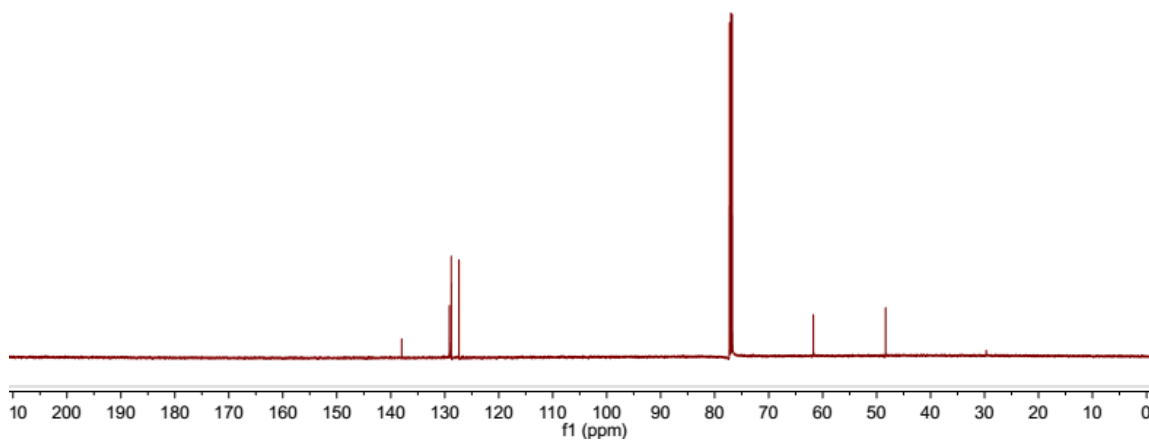


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7.26

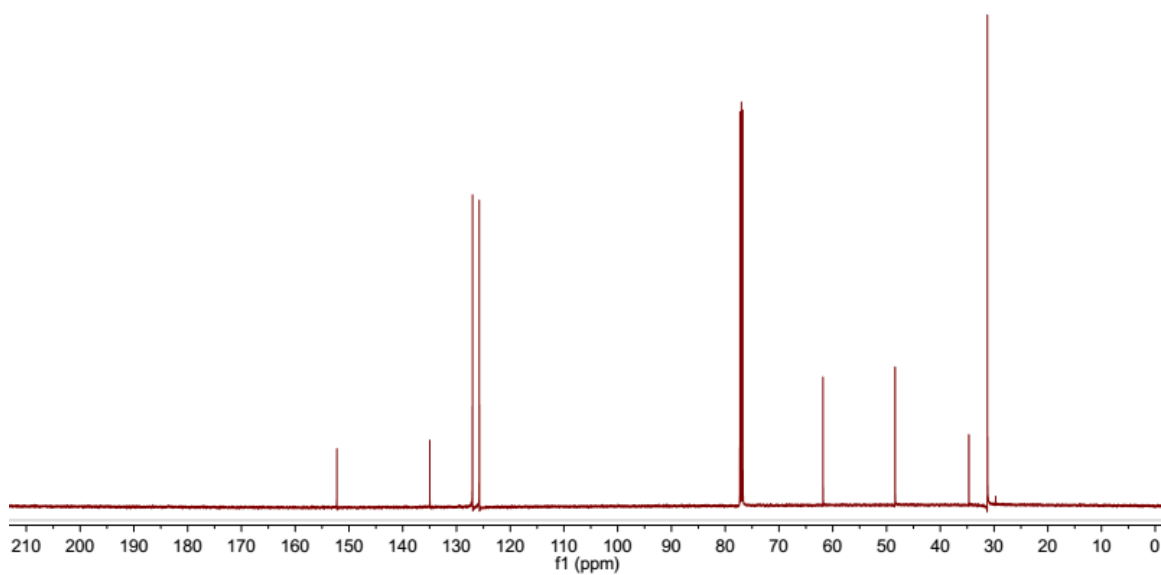
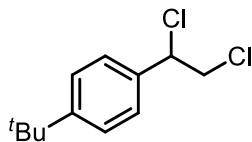
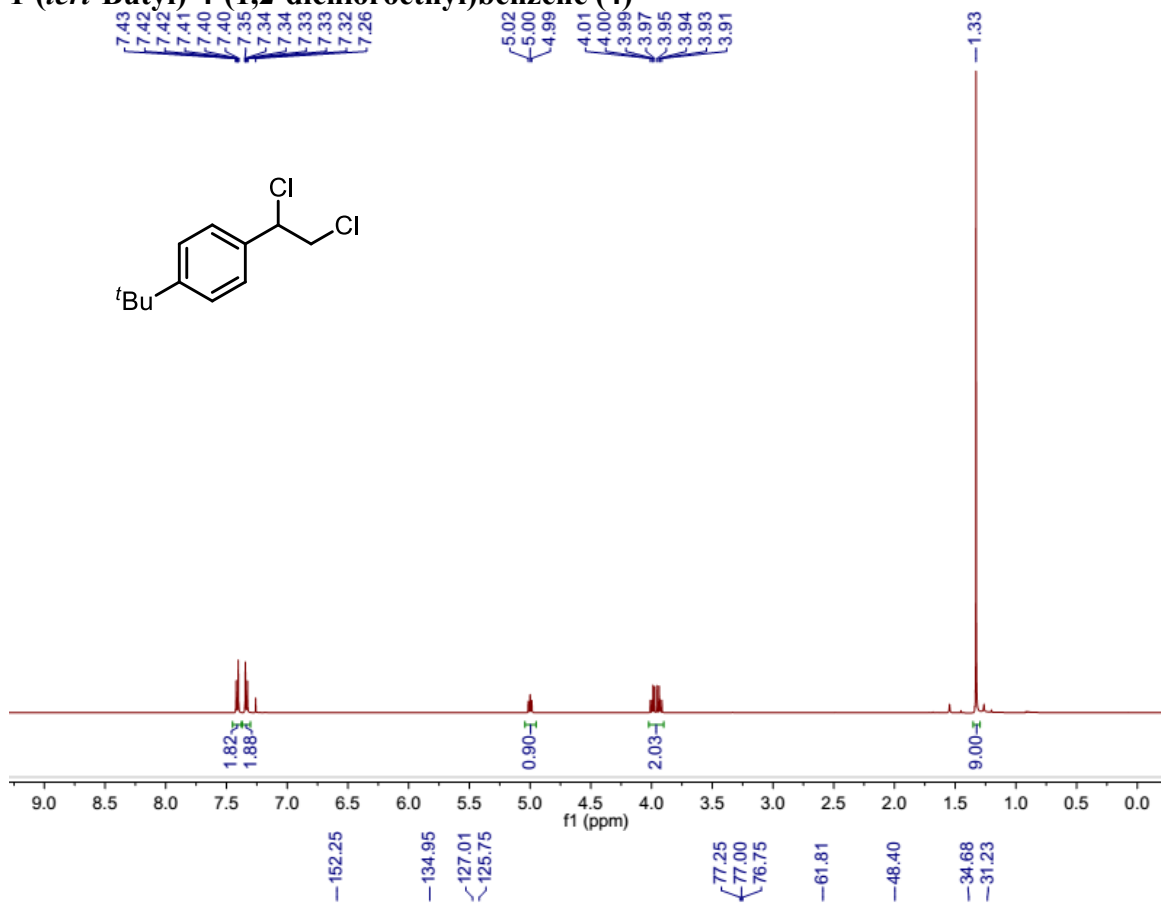
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3.98
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3.93
3.91



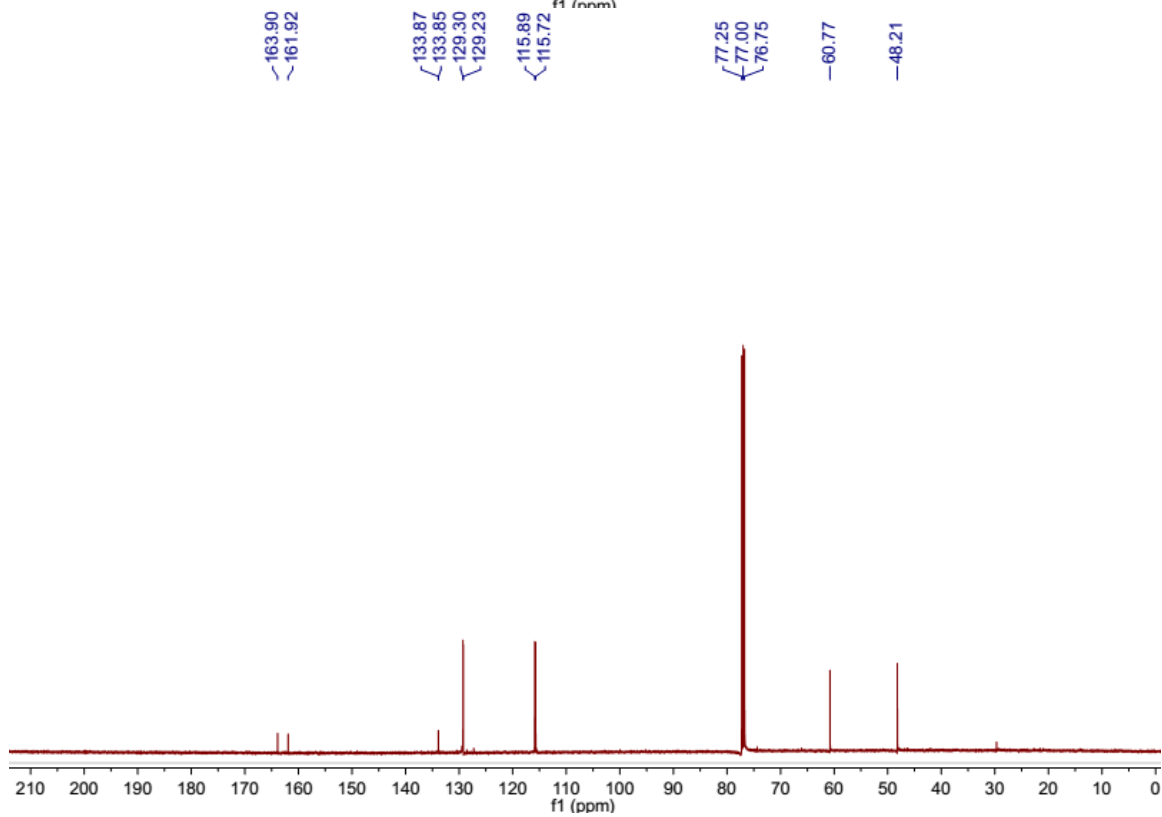
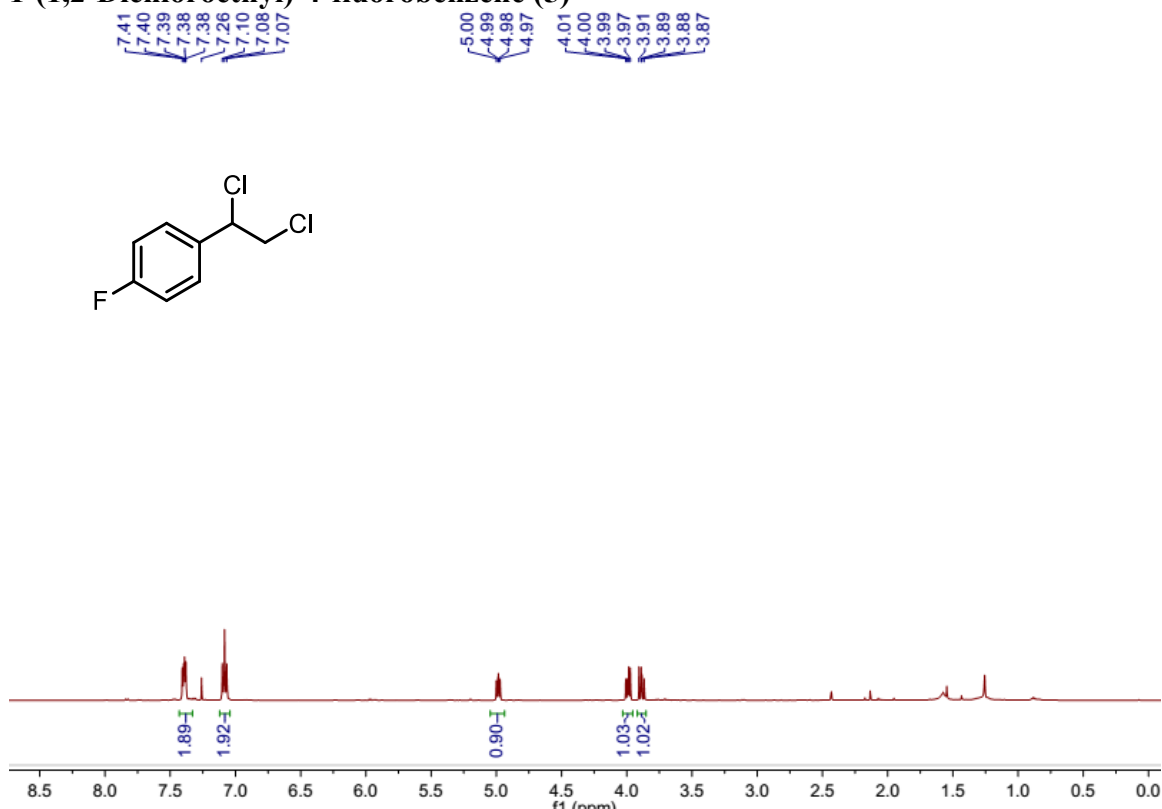
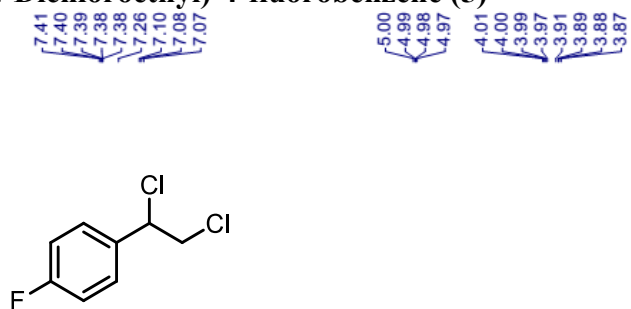
137.98
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76.75
61.74
48.33



1-(*tert*-Butyl)-4-(1,2-dichloroethyl)benzene (4)

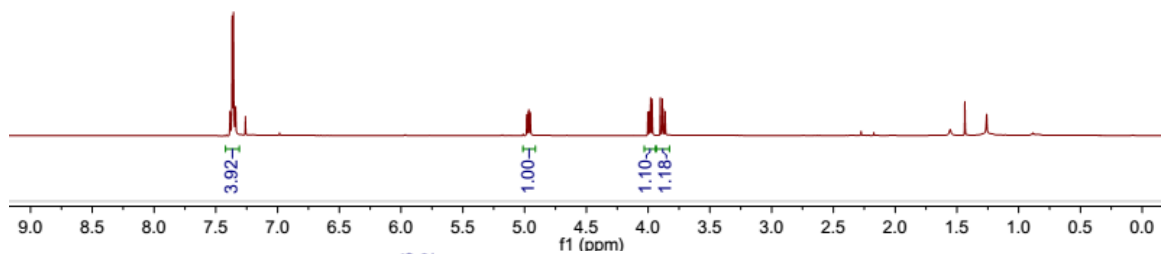
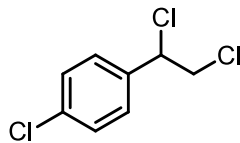


1-(1,2-Dichloroethyl)-4-fluorobenzene (5)

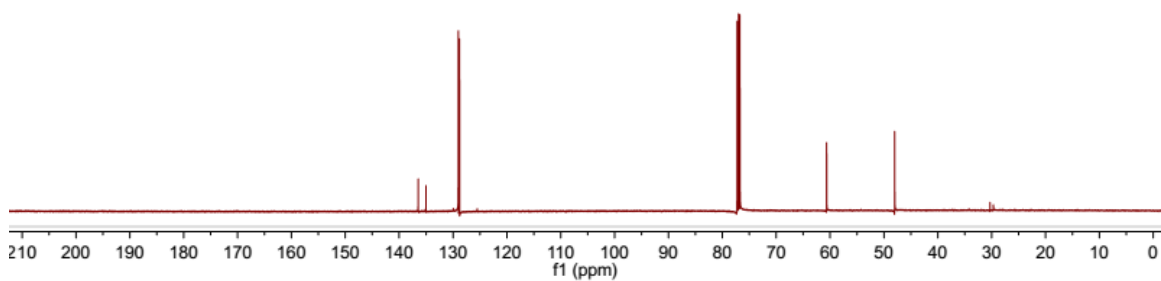


1-Chloro-4-(1,2-dichloroethyl)benzene (6)

7.39, 7.38, 7.37, 7.37, 7.36, 7.34, 7.34, 7.26, 4.98, 4.97, 4.97, 4.95, 4.00, 3.99, 3.98, 3.97, 3.90, 3.88, 3.88, 3.86



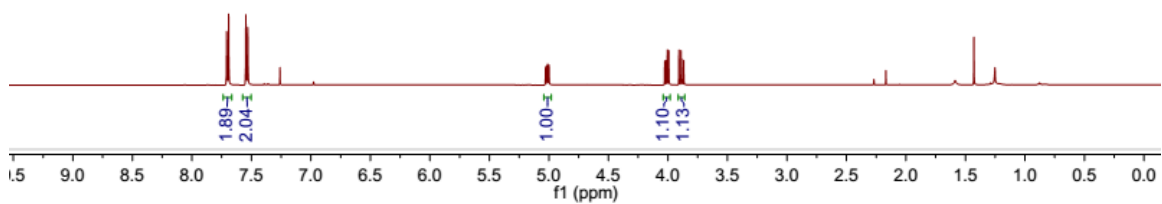
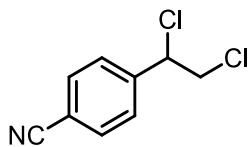
136.46, 135.02, 129.01, 128.81, 77.25, 77.00, 76.75, 60.64, 48.02



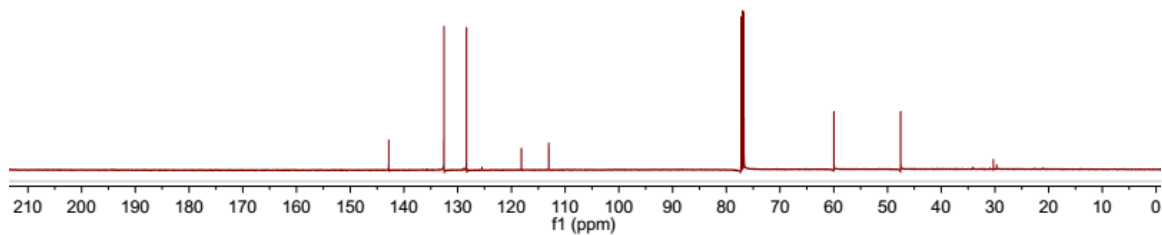
4-(1,2-Dichloroethyl)benzonitrile (7)

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7.26

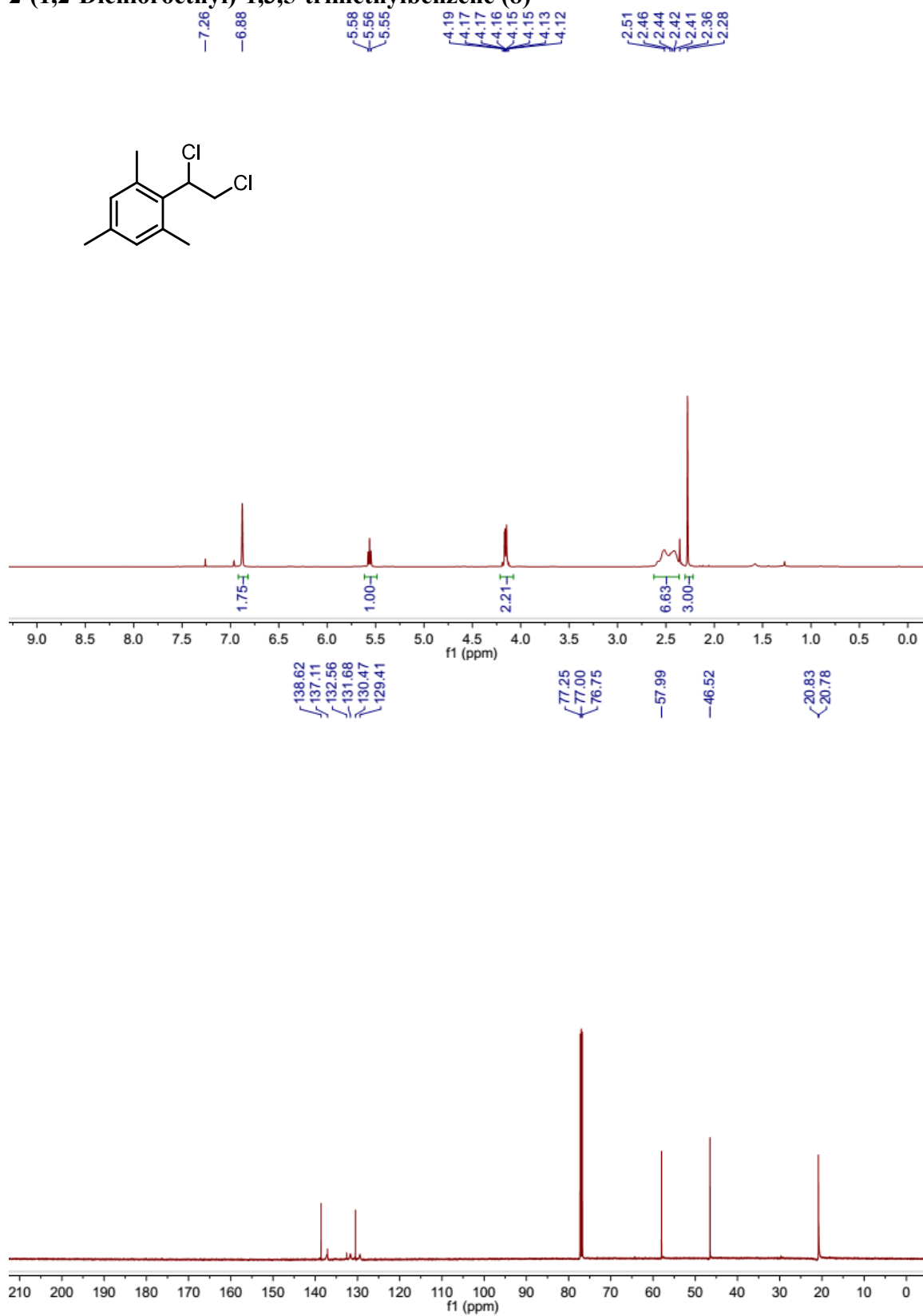
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4.03
4.02
4.00
3.99
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3.88
3.87



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132.56
128.36
118.14
113.05
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77.00
76.75
59.97
47.55



2-(1,2-Dichloroethyl)-1,3,5-trimethylbenzene (8)

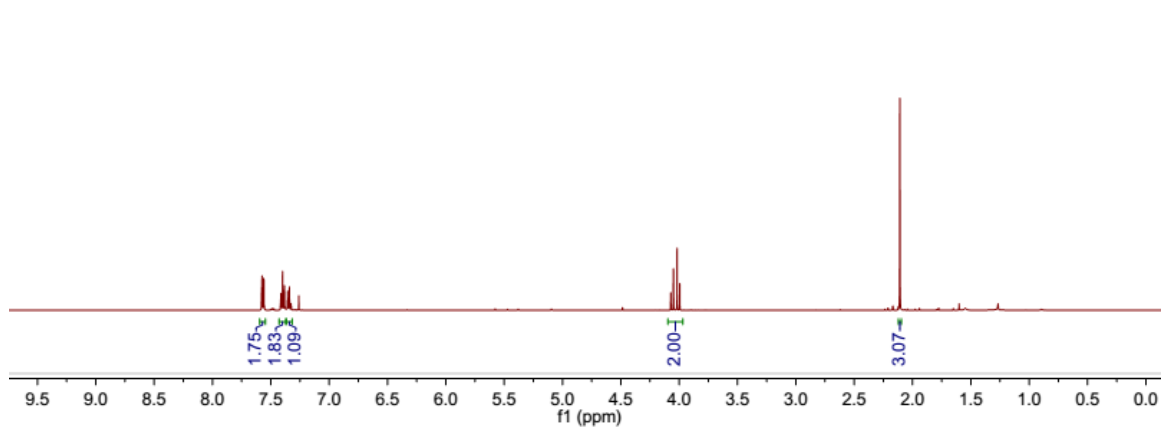
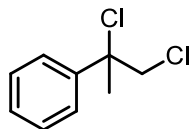


(1,2-Dichloropropan-2-yl)benzene (9)

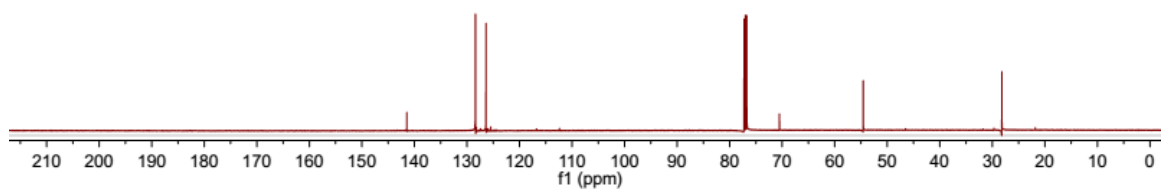
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4.07, 4.05, 4.02, 4.00

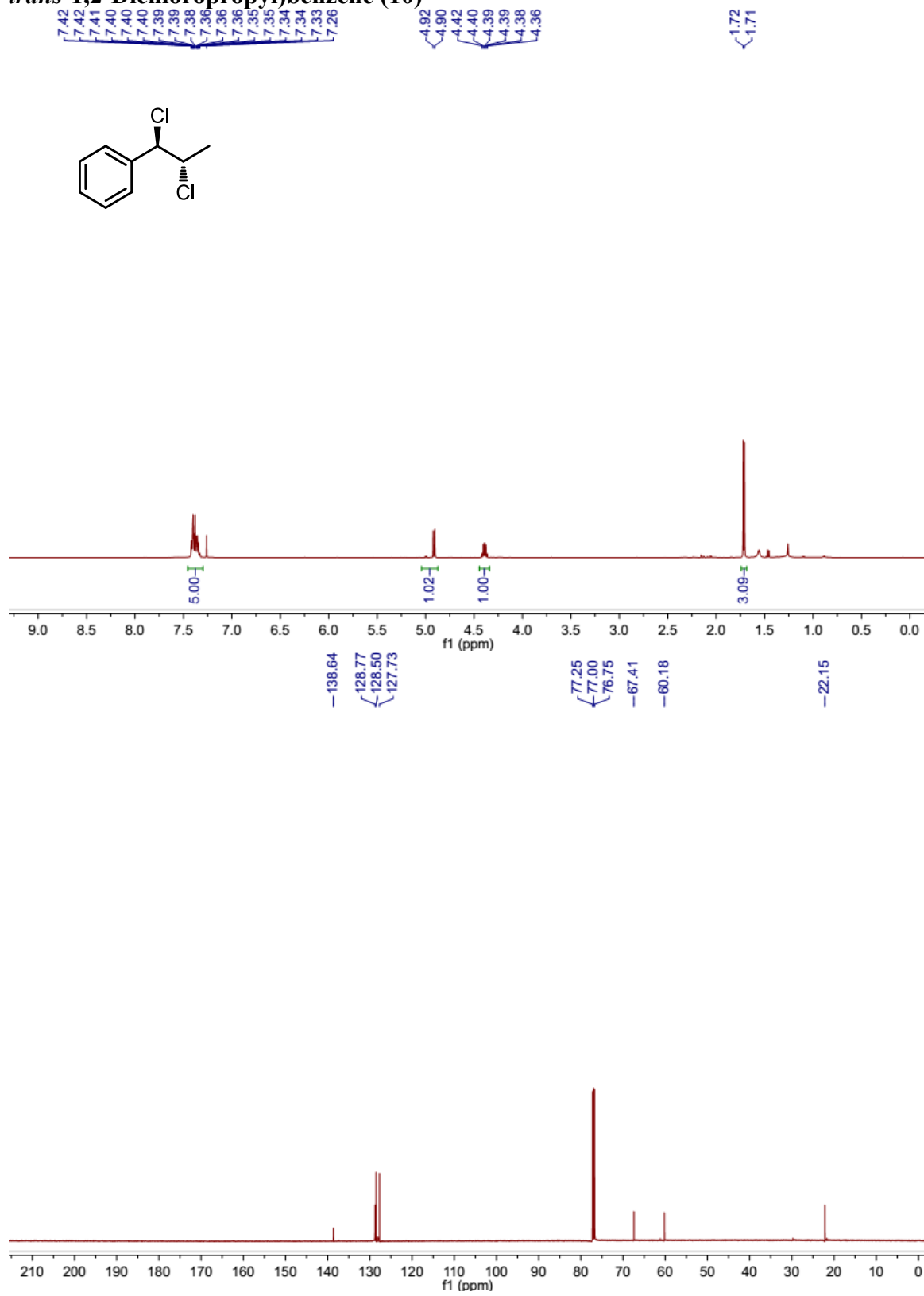
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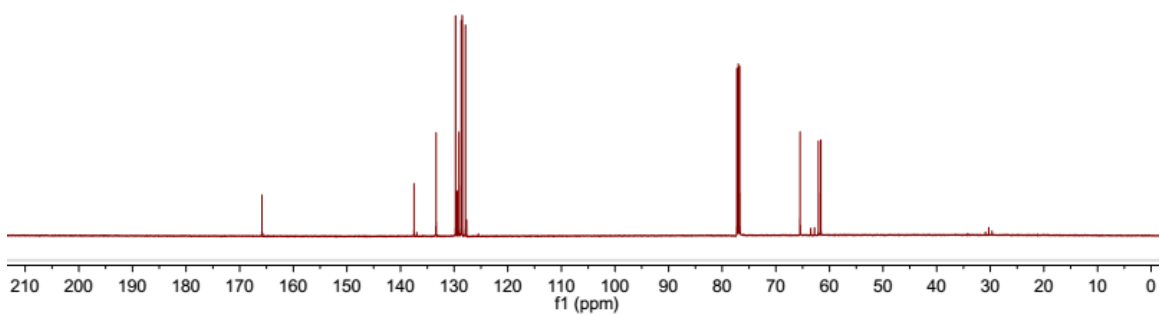
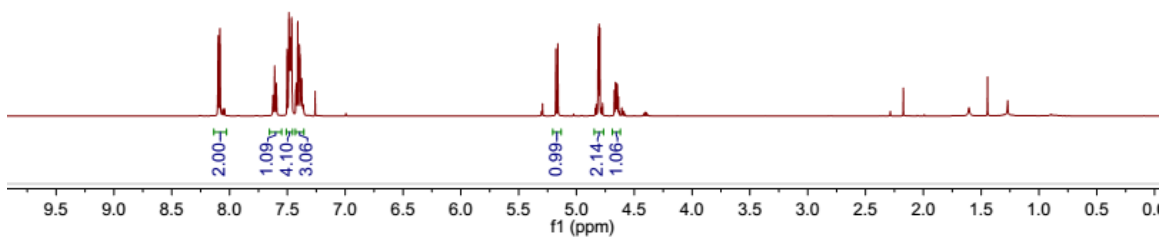
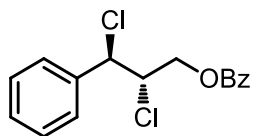
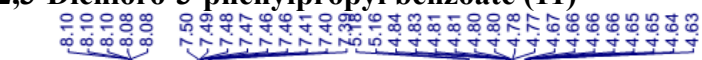
141.45, 128.39, 128.37, 126.39, 77.25, 77.00, 76.75, 70.52, 54.59, 28.20



***trans*-1,2-Dichloropropylbenzene (10)**

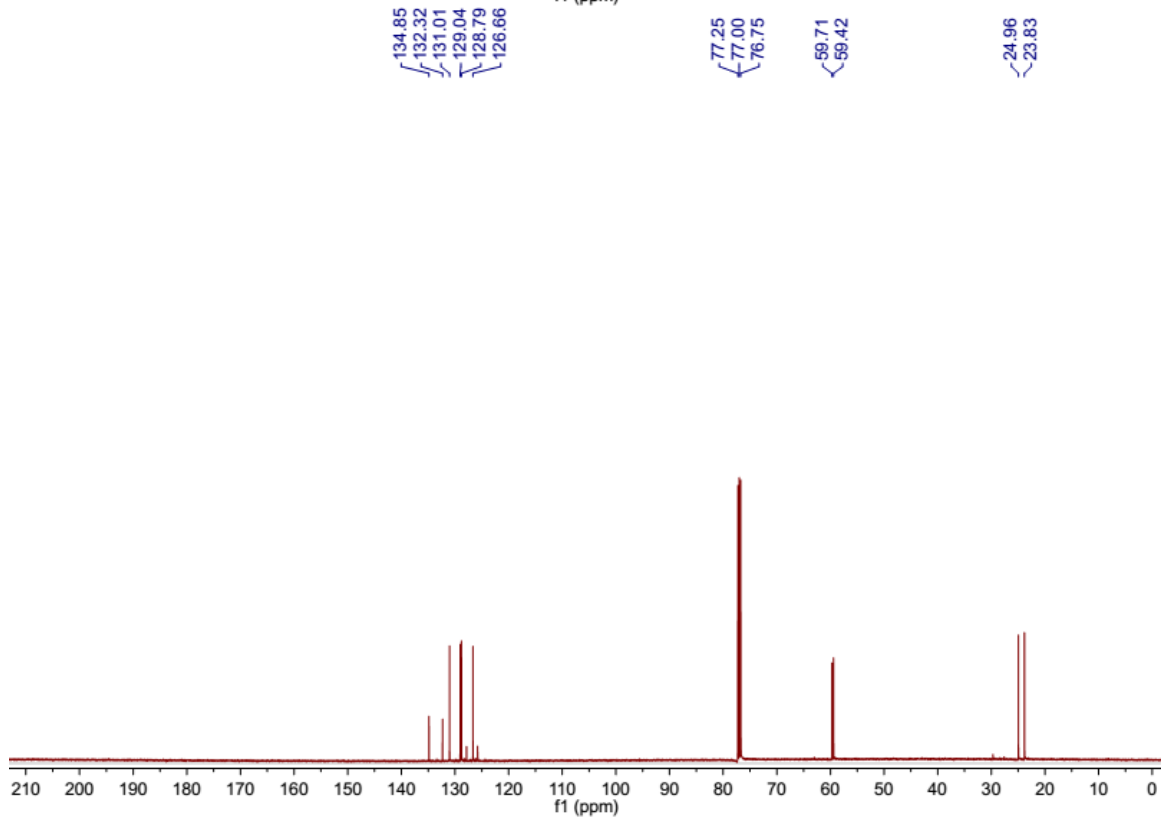
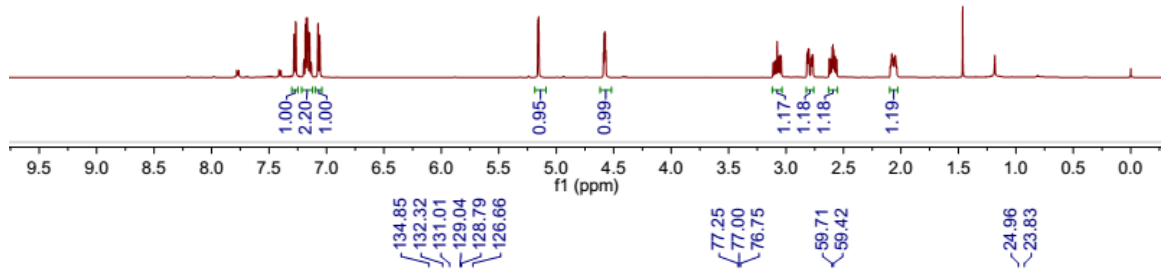
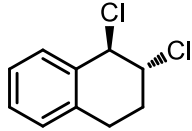


***trans*-2,3-Dichloro-3-phenylpropyl benzoate (11)**



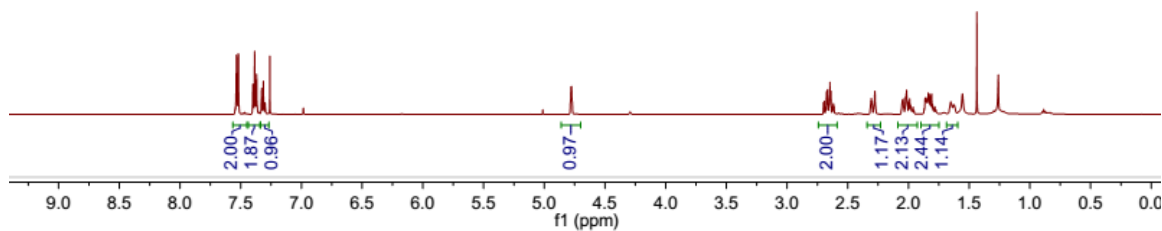
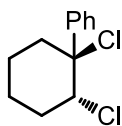
***trans*-1,2-Dichloro-1,2,3,4-tetrahydronaphthalene (12)**

7.28
7.28
7.27
7.27
7.20
7.20
7.18
7.18
7.18
7.17
7.17
7.16
7.15
7.07
7.06
5.16
5.15
4.58
4.58
4.57
4.57
3.10
3.09
3.08
3.07
3.05
3.04
2.82
2.81
2.81
2.80
2.78
2.78
2.77
2.77
2.63
2.62
2.61
2.61
2.60
2.60
2.59
2.59
2.58
2.57
2.57
2.56
2.56
2.08
2.08
2.08
2.07
2.06
2.06
2.05
2.05
2.04

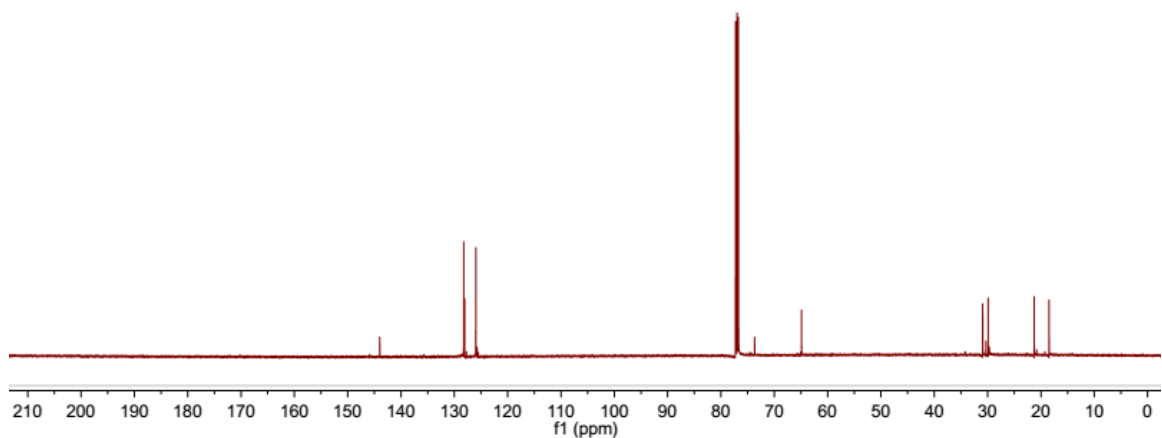


(trans-1,2-Dichlorocyclohexyl)benzene (13)

7.54, 7.53, 7.53, 7.52, 7.52, 7.40, 7.40, 7.39, 7.38, 7.37, 7.37, 7.33, 7.33, 7.33, 7.32, 7.31, 7.31, 7.30, 7.26, 4.78, 4.78, 2.70, 2.69, 2.67, 2.67, 2.67, 2.65, 2.65, 2.64, 2.64, 2.64, 2.64, 2.62, 2.62, 2.31, 2.31, 2.30, 2.28, 2.05, 2.05, 2.04, 2.02, 2.02, 2.02, 2.01, 2.00, 1.99, 1.86, 1.86, 1.85, 1.85, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.65, 1.65

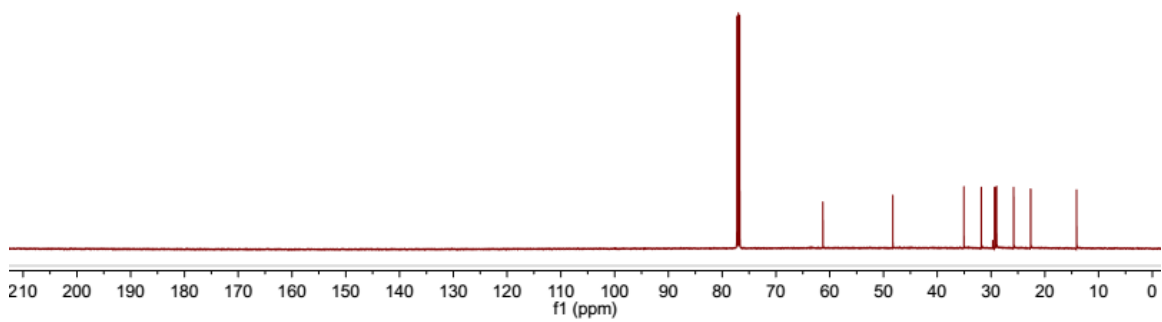
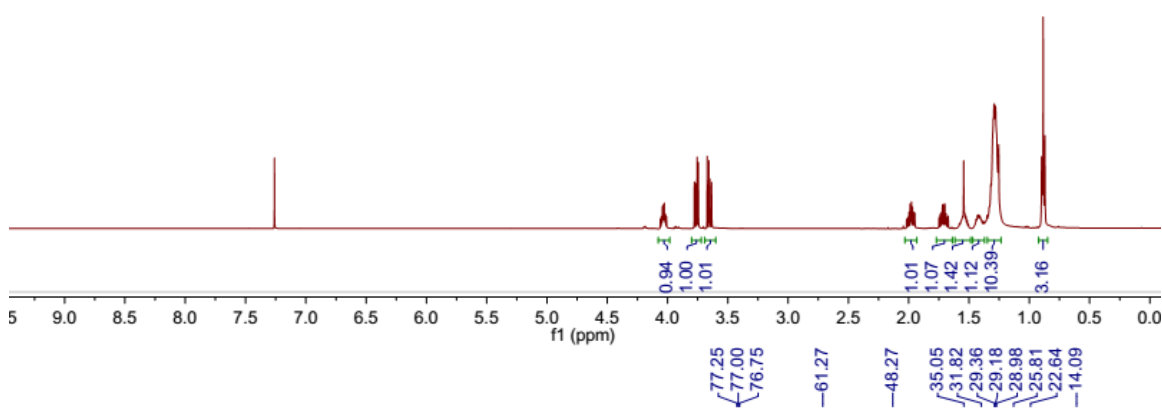
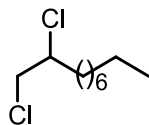


143.98, 128.24, 128.08, 125.97, 77.25, 77.00, 76.75, 73.68, 64.90, 30.93, 29.90, 21.27, 18.48

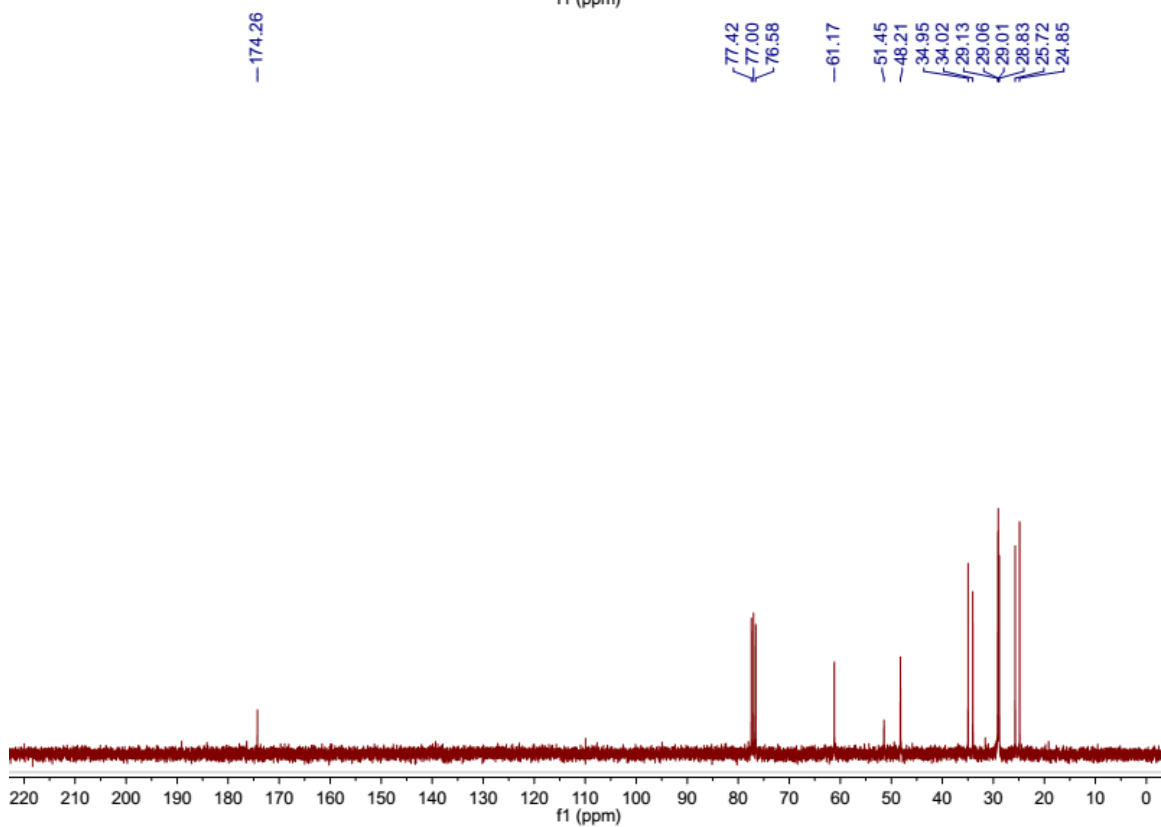
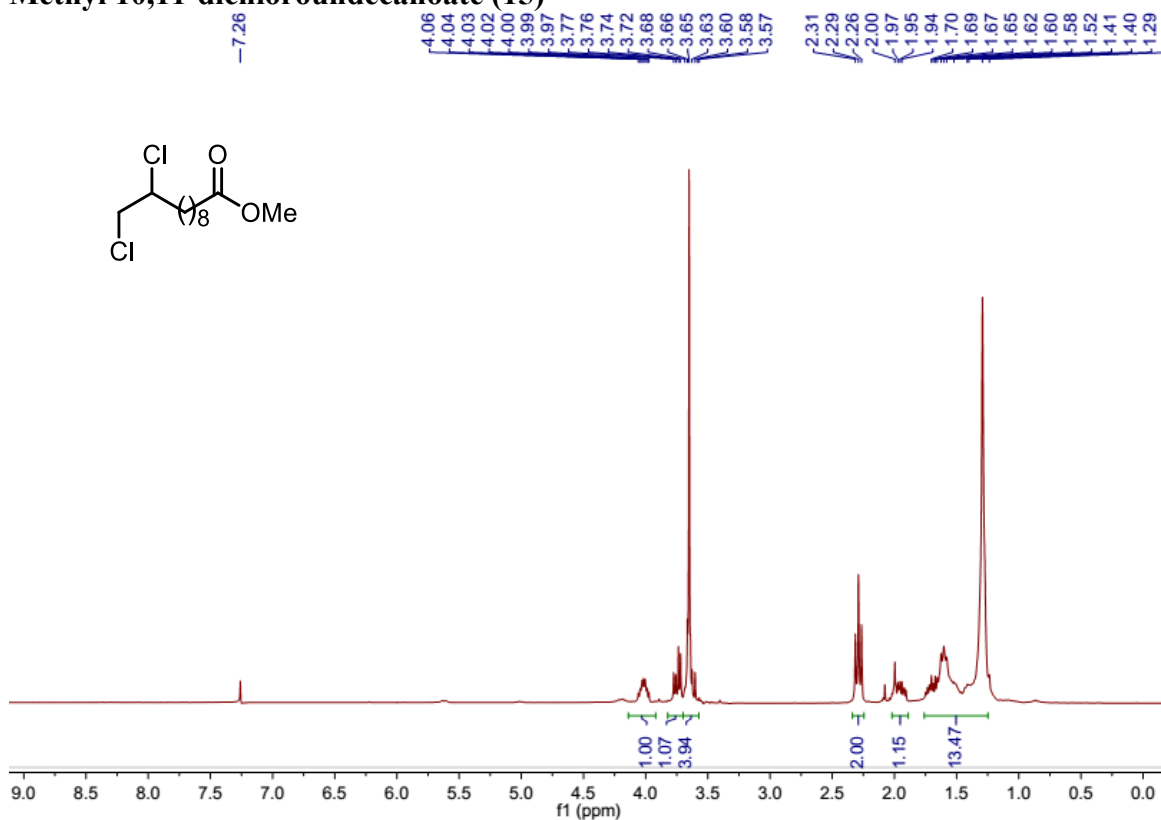


1,2-Dichlorodecane (14)

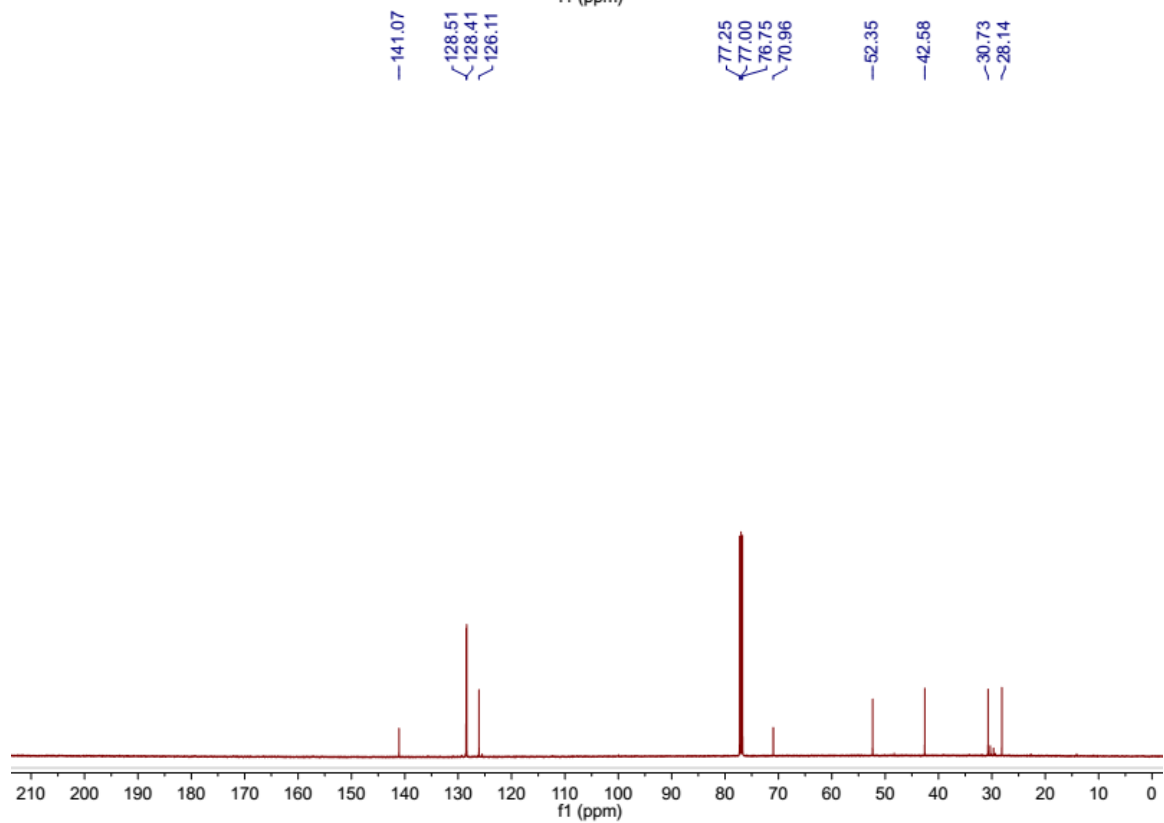
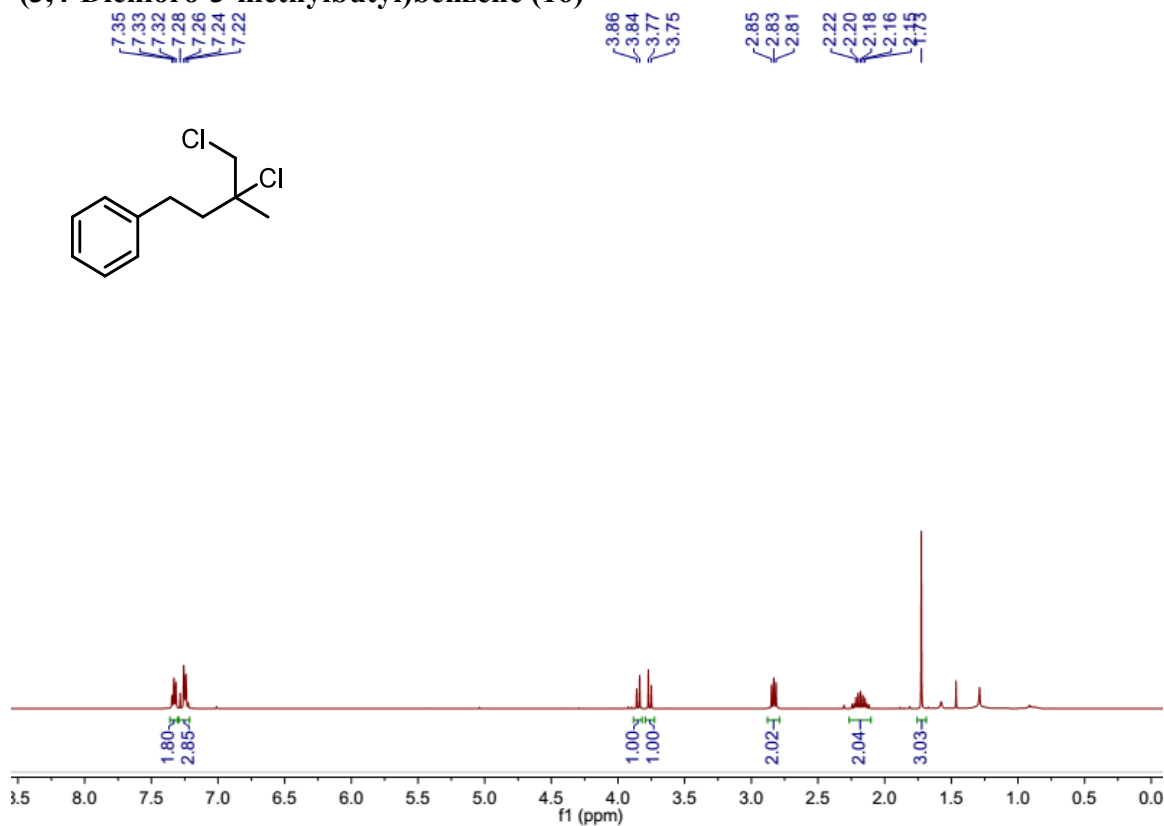
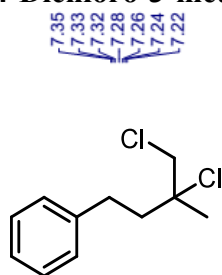
7.26, 4.05, 4.05, 4.05, 4.04, 4.04, 4.03, 4.03, 4.02, 4.02, 4.01, 3.78, 3.77, 3.76, 3.74, 3.67, 3.66, 3.65, 3.63, 2.00, 1.99, 1.99, 1.98, 1.97, 1.96, 1.96, 1.95, 1.95, 1.74, 1.73, 1.73, 1.72, 1.71, 1.70, 1.69, 1.69, 1.67, 1.67, 1.55, 1.54, 1.54, 1.53, 1.43, 1.42, 1.41, 1.35, 1.33, 1.32, 1.30, 1.29, 1.29, 1.28, 1.26, 1.25, 0.90, 0.88, 0.87



Methyl 10,11-dichloroundecanoate (15)

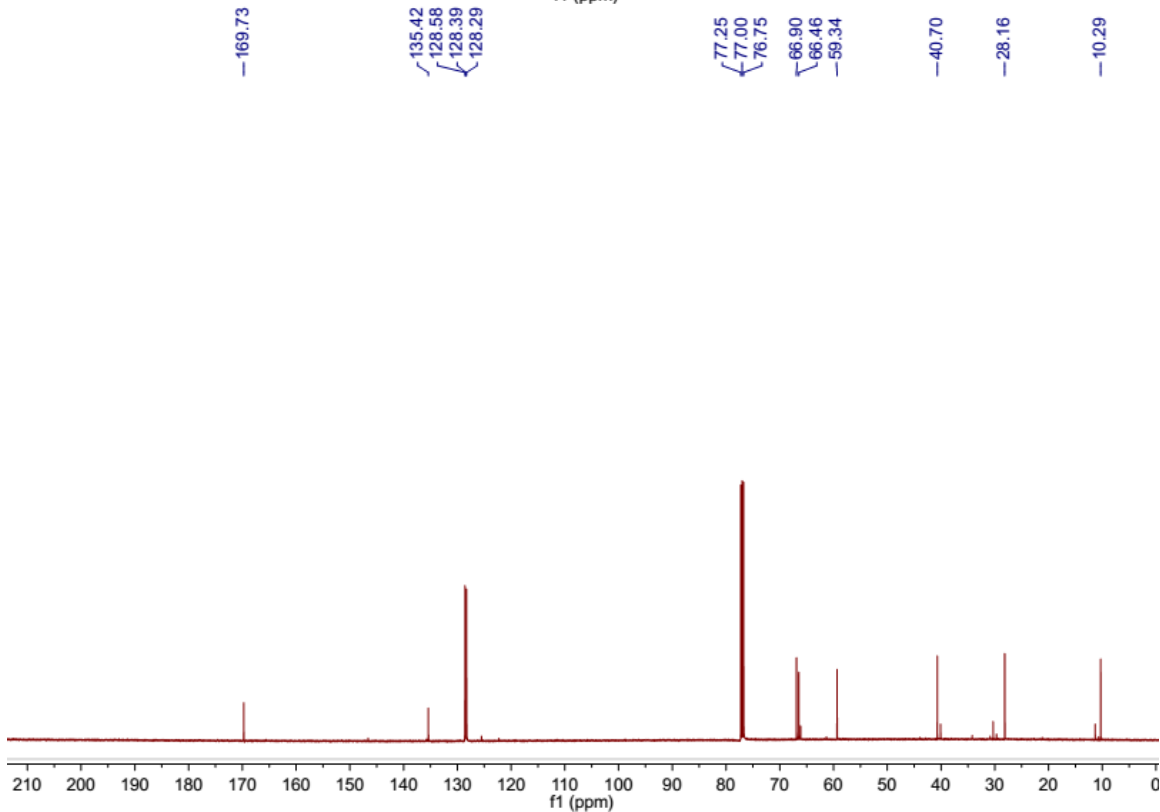
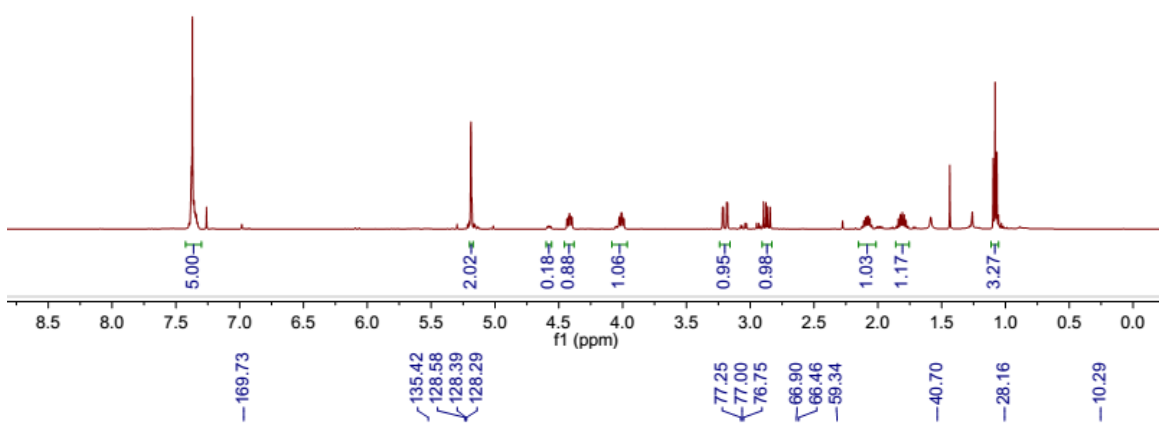
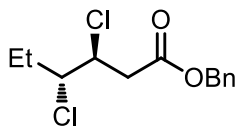


(3,4-Dichloro-3-methylbutyl)benzene (16)

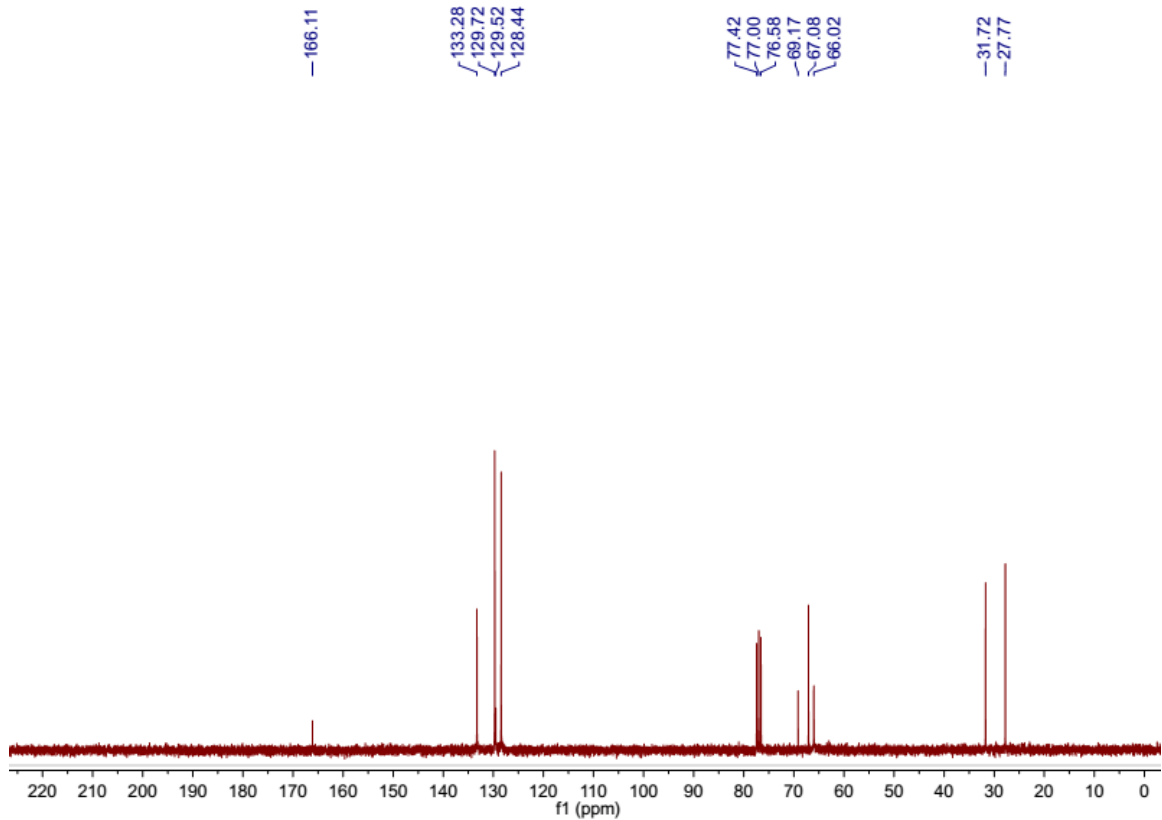
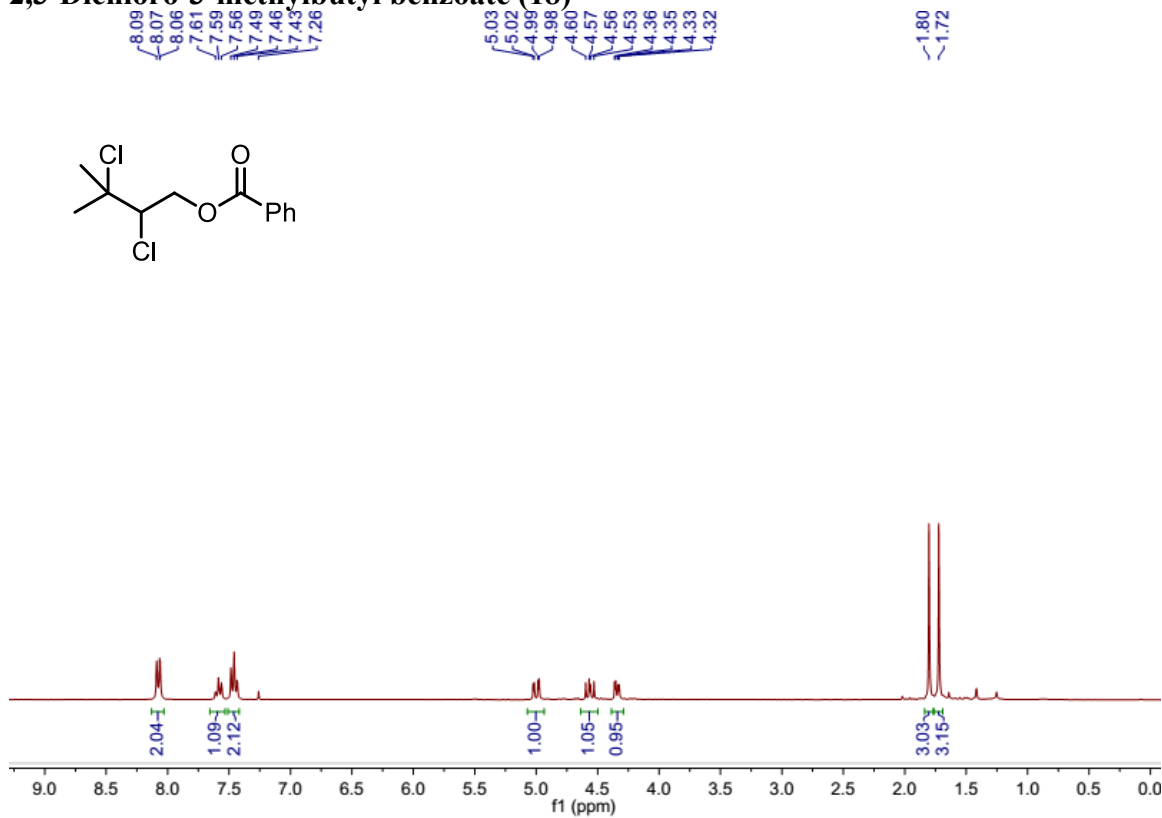
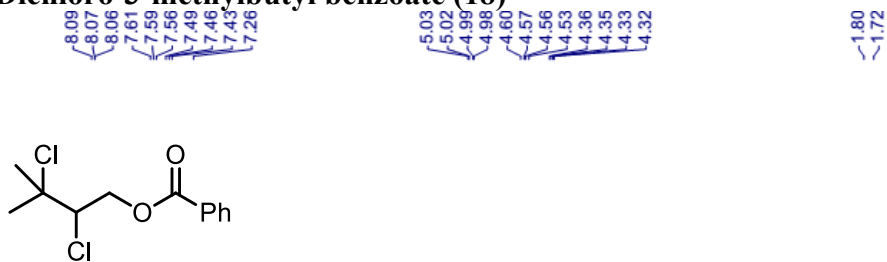


Benzyl-*trans*-3,4-dichlorohexanoate (17)

7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.26, 5.19, 5.18, 4.44, 4.43, 4.42, 4.42, 4.41, 4.41, 4.40, 4.40, 4.40, 4.03, 4.02, 4.01, 4.01, 3.99, 3.99, 3.22, 3.21, 3.18, 3.18, 2.90, 2.88, 2.86, 2.84, 2.11, 2.10, 2.10, 2.09, 2.08, 2.08, 2.07, 2.06, 2.05, 2.05, 1.85, 1.84, 1.83, 1.82, 1.81, 1.81, 1.80, 1.79, 1.78, 1.10, 1.08, 1.07

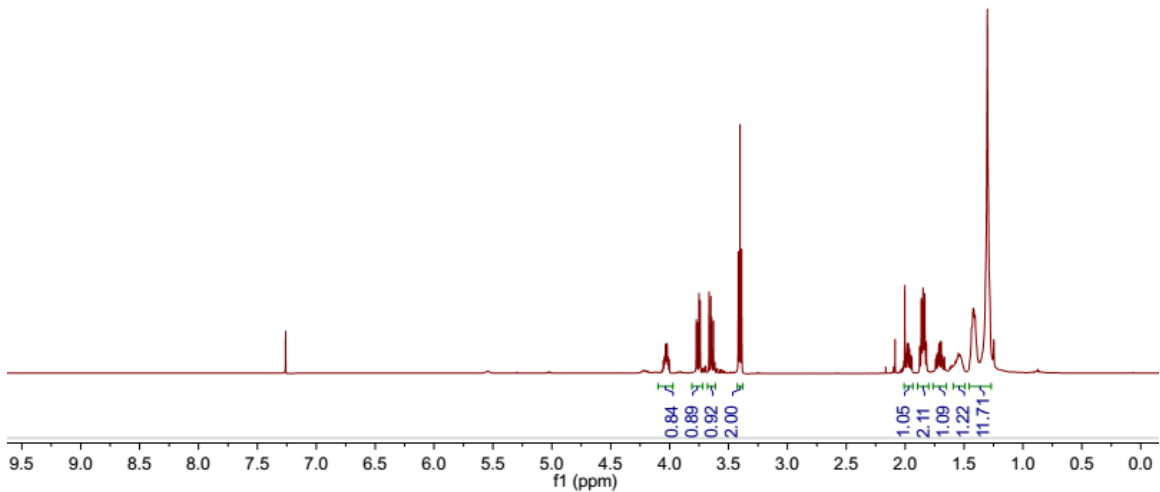
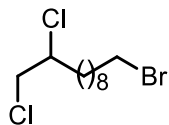


2,3-Dichloro-3-methylbutyl benzoate (18)

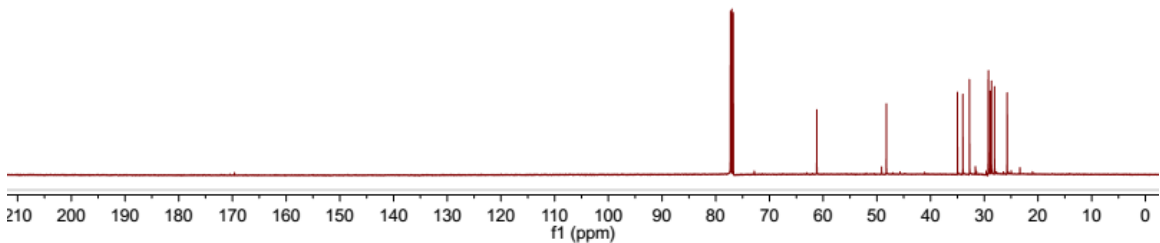


11-Bromo-1,2-dichloroundecane (19)

7.26
4.04
4.04
4.04
4.03
4.03
4.02
4.02
4.01
3.77
3.76
3.75
3.74
3.67
3.65
3.64
3.63
3.42
3.40
3.39
2.00
1.99
1.98
1.98
1.98
1.97
1.96
1.96
1.95
1.94
1.88
1.86
1.86
1.85
1.83
1.82
1.73
1.72
1.71
1.70
1.69
1.69
1.68
1.67
1.55
1.55
1.54
1.54
1.53
1.53
1.44
1.43
1.42
1.42
1.41
1.35
1.30
1.25

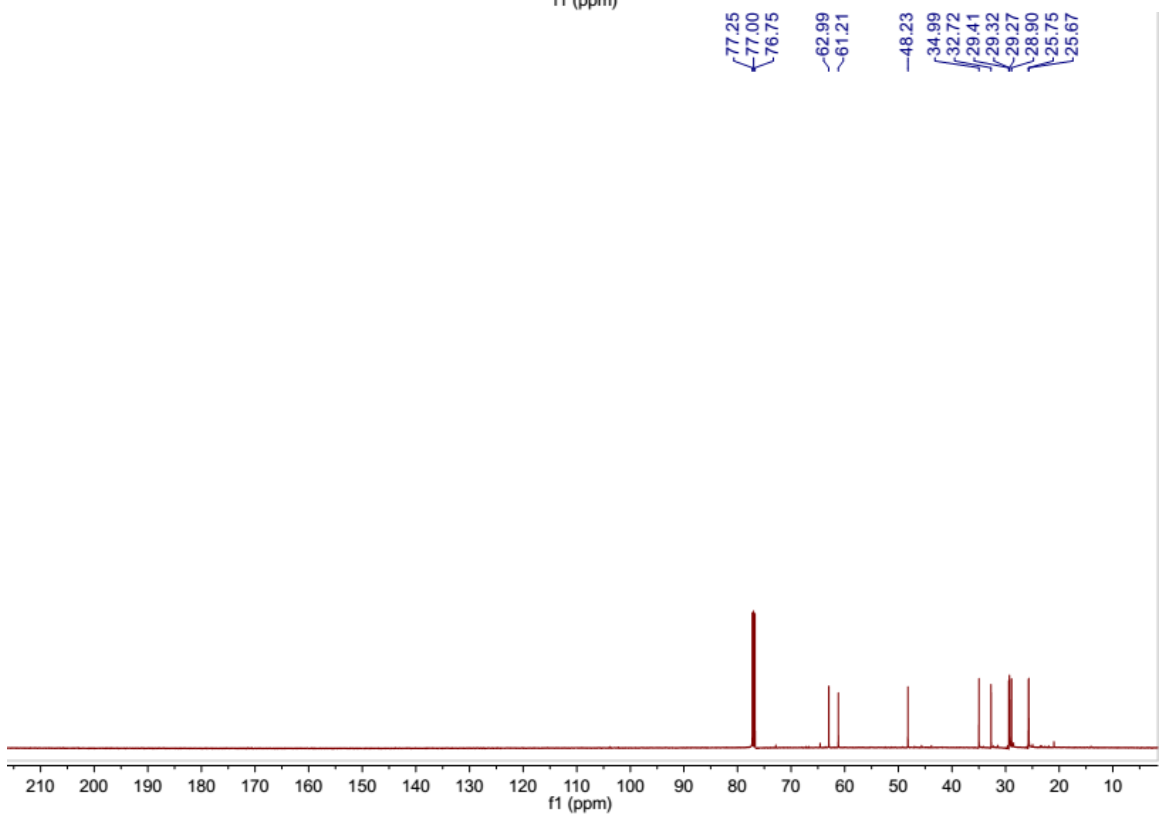
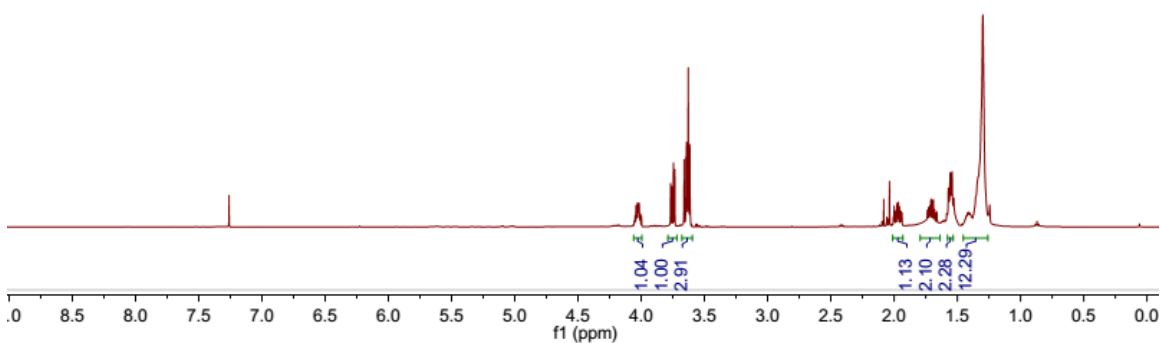
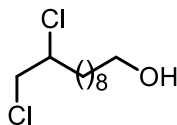


77.25
77.00
76.75
-61.19
-48.23
-34.99
-34.00
-32.76
-29.25
-29.23
-28.88
-28.66
-28.10
-25.75



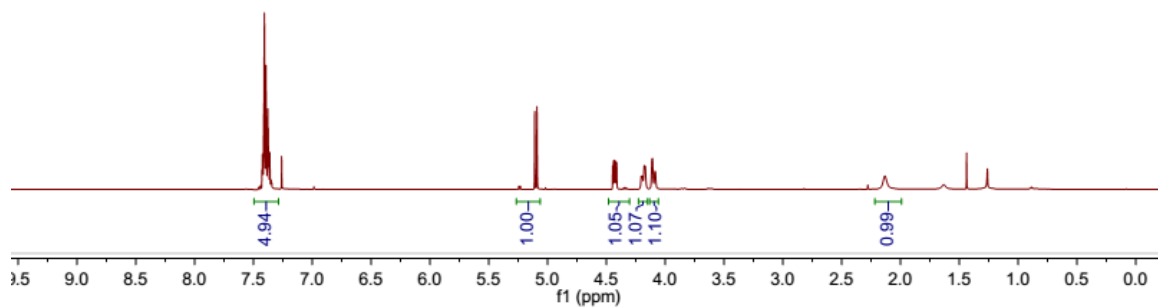
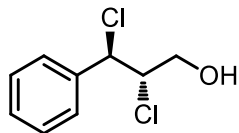
10,11-Dichloroundecan-1-ol (20)

7.26
4.04
4.04
4.03
4.03
4.02
4.02
4.01
4.01
4.01
3.77
3.76
3.75
3.73
3.66
3.65
3.64
3.63
3.62
2.00
1.99
1.99
1.98
1.97
1.97
1.97
1.96
1.96
1.94
1.94
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.58
1.57
1.55
1.54
1.53
1.42
1.41
1.40
1.39
1.33
1.30
1.24

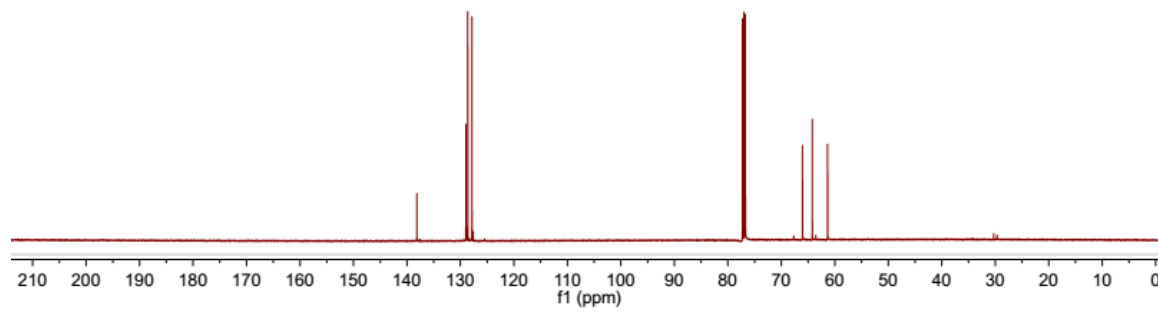


***trans*-2,3-Dichloro-3-phenylpropan-1-ol (21)**

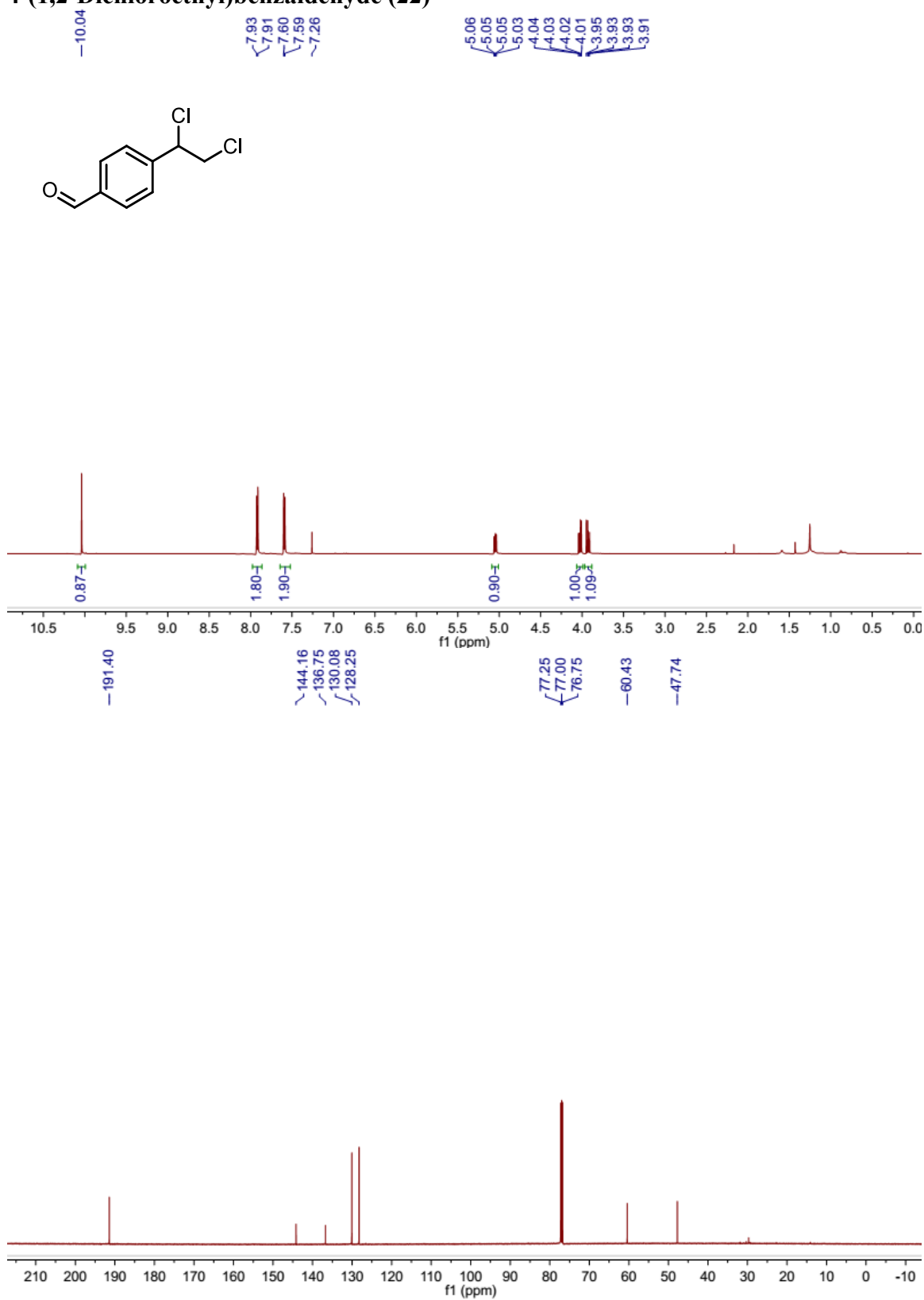
7.45, 7.44, 7.44, 7.43, 7.42, 7.42, 7.41, 7.38, 7.38, 7.37, 7.37, 7.36, 7.36, 7.35, 7.35, 7.35, 7.34, 7.26, 5.11, 5.08, 4.45, 4.44, 4.44, 4.43, 4.43, 4.42, 4.42, 4.41, 4.20, 4.18, 4.18, 4.17, 4.11, 4.11, 4.08, 4.08, -2.13



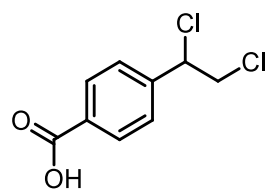
138.15, 128.98, 128.63, 127.84, 77.25, 77.00, 76.75, 66.05, 64.21, 61.36



4-(1,2-Dichloroethyl)benzaldehyde (22)



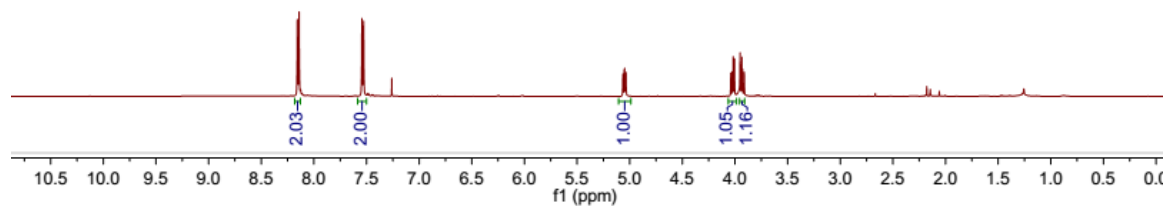
4-(1,2-Dichloroethyl)benzoic acid (23)



8.16
8.14

7.54
7.53
7.26

5.06
5.05
5.05
5.04
4.04
4.03
4.02
4.00
3.95
3.93
3.91



171.37

143.59

130.68

129.97

127.70

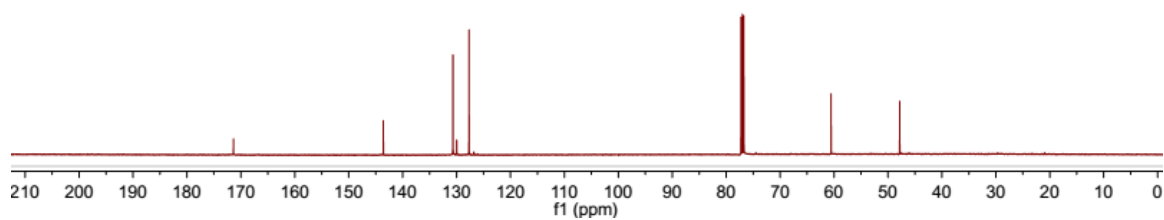
77.25

77.00

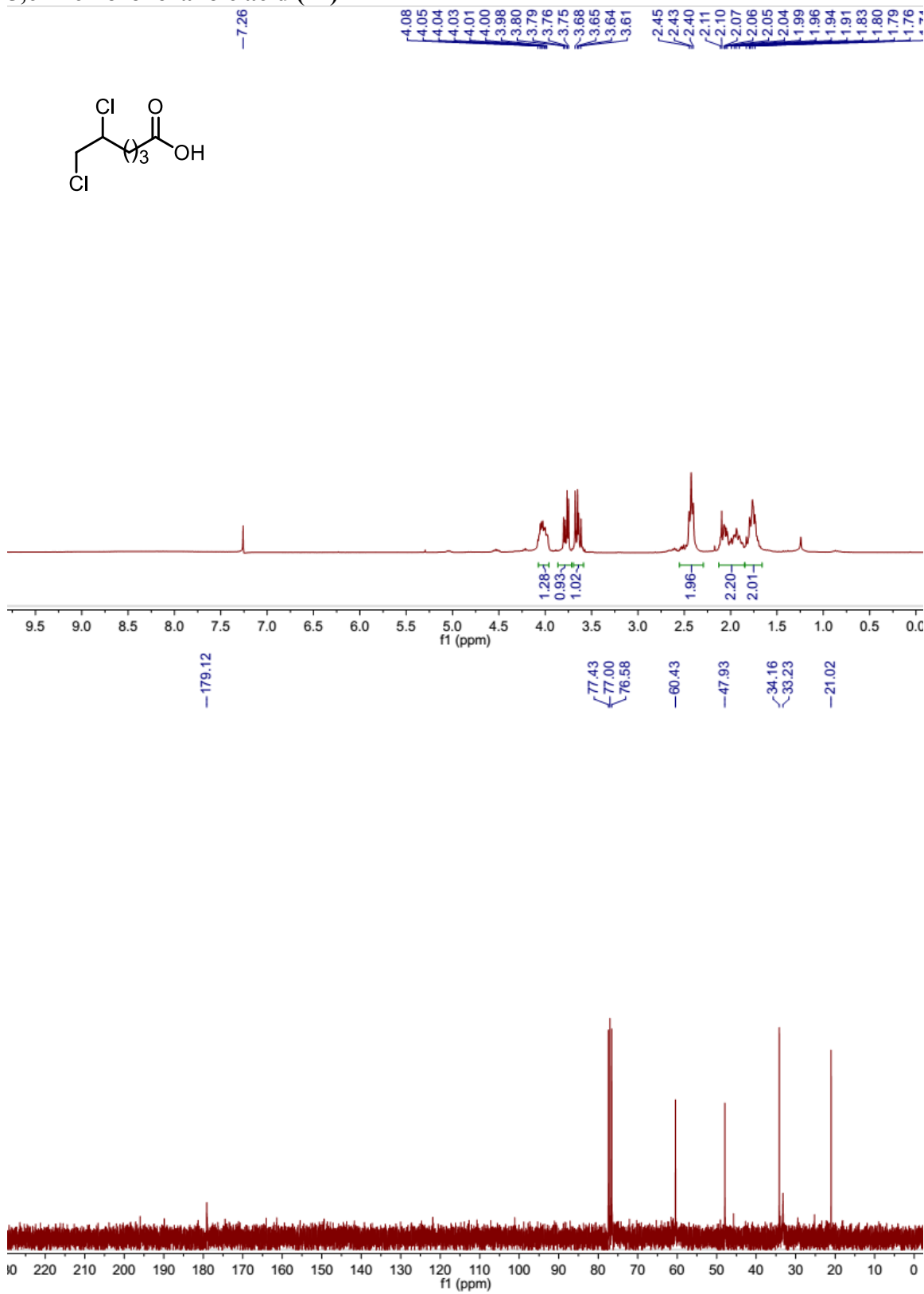
76.75

60.55

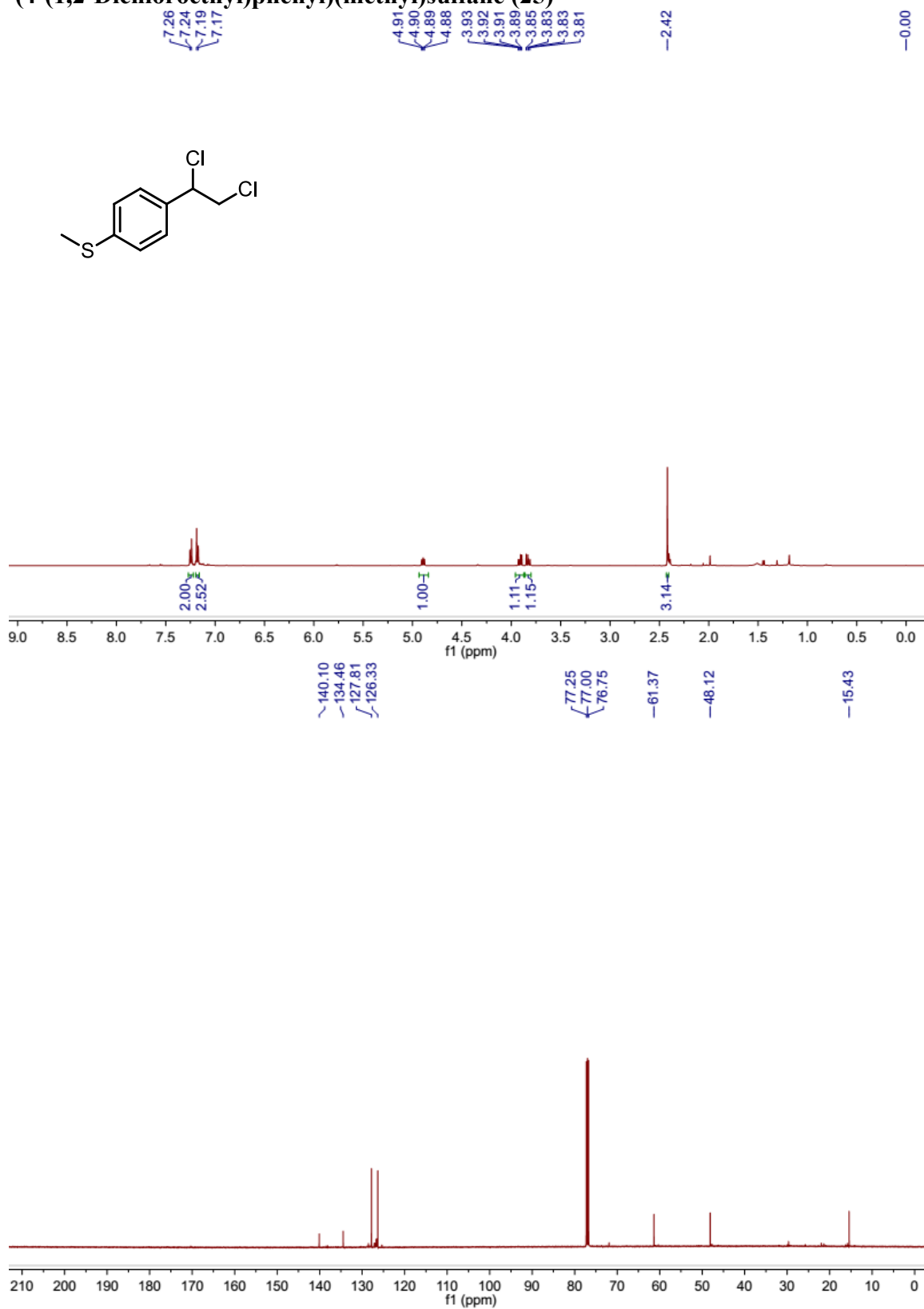
47.84



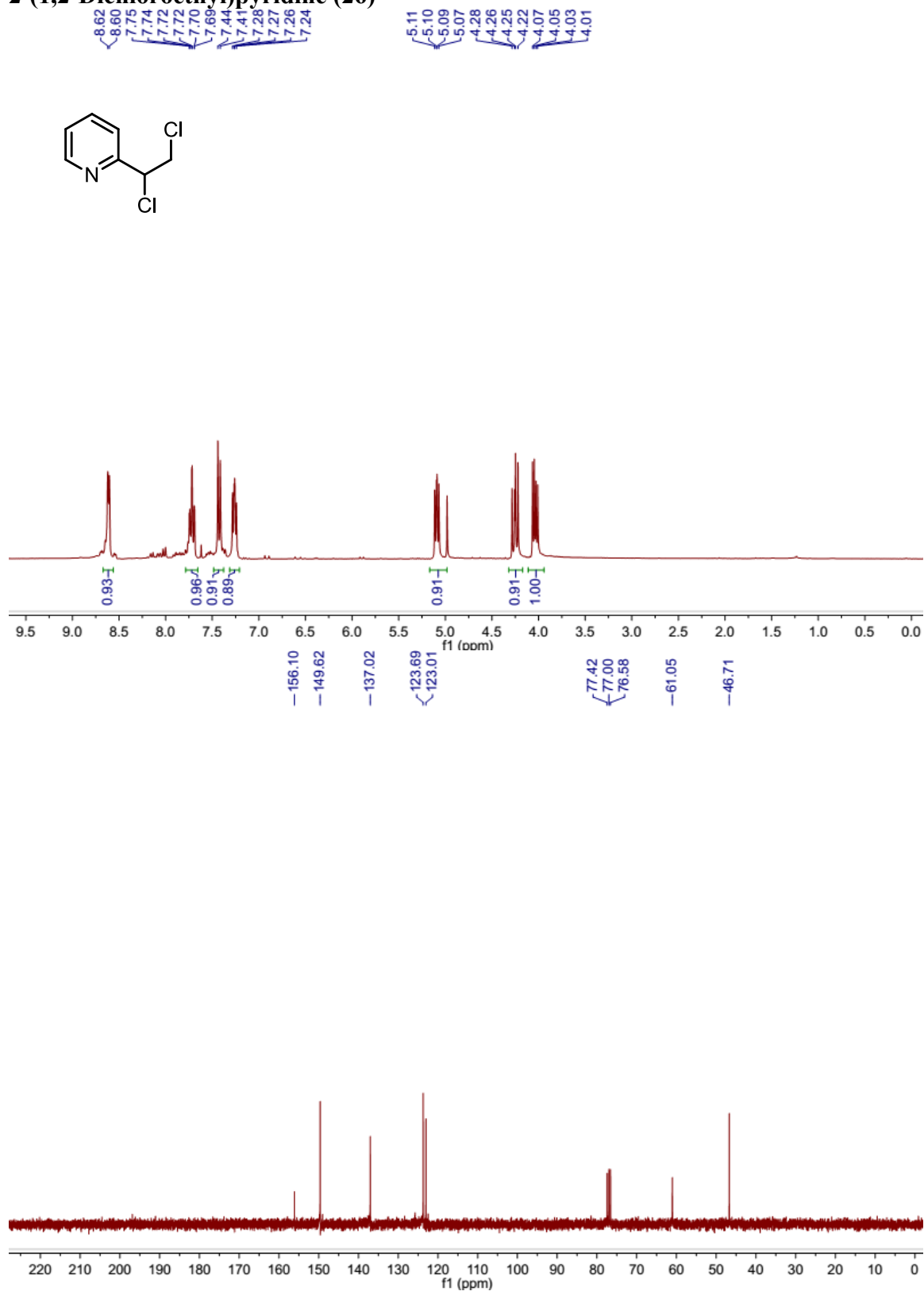
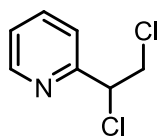
5,6-Dichlorohexanoic acid (24)



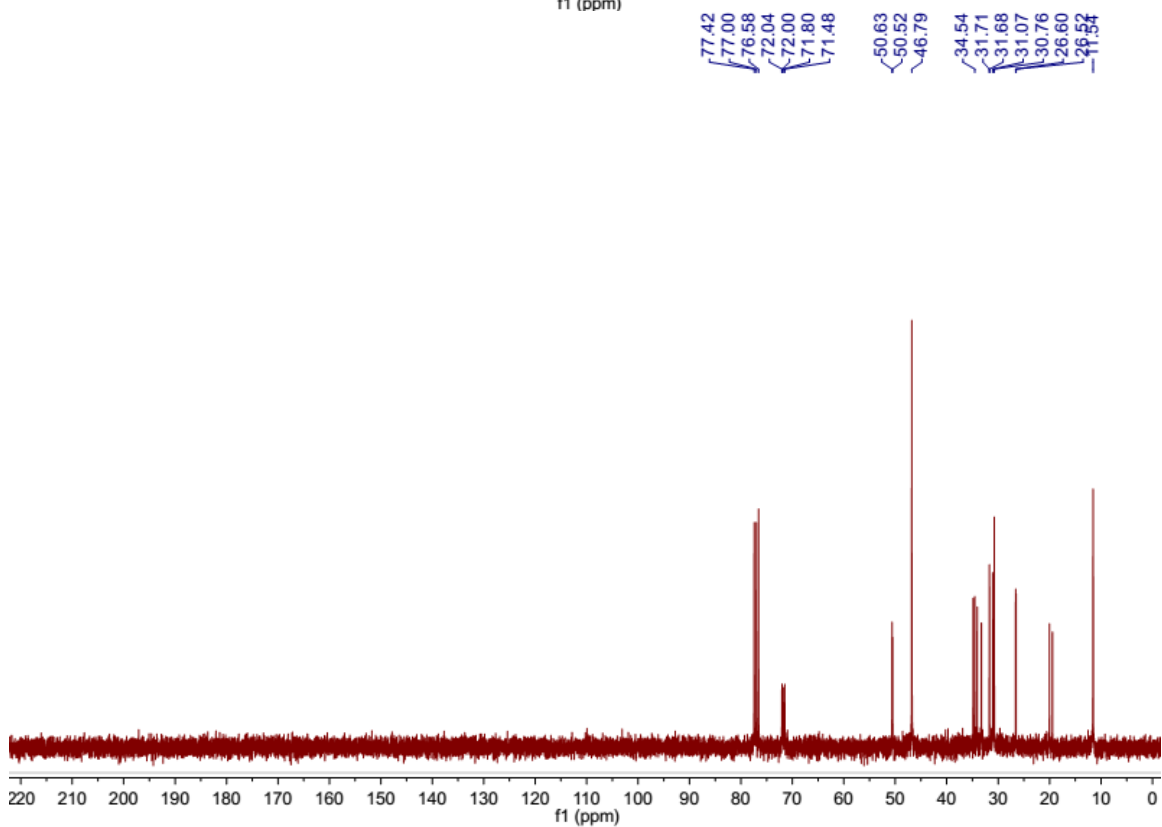
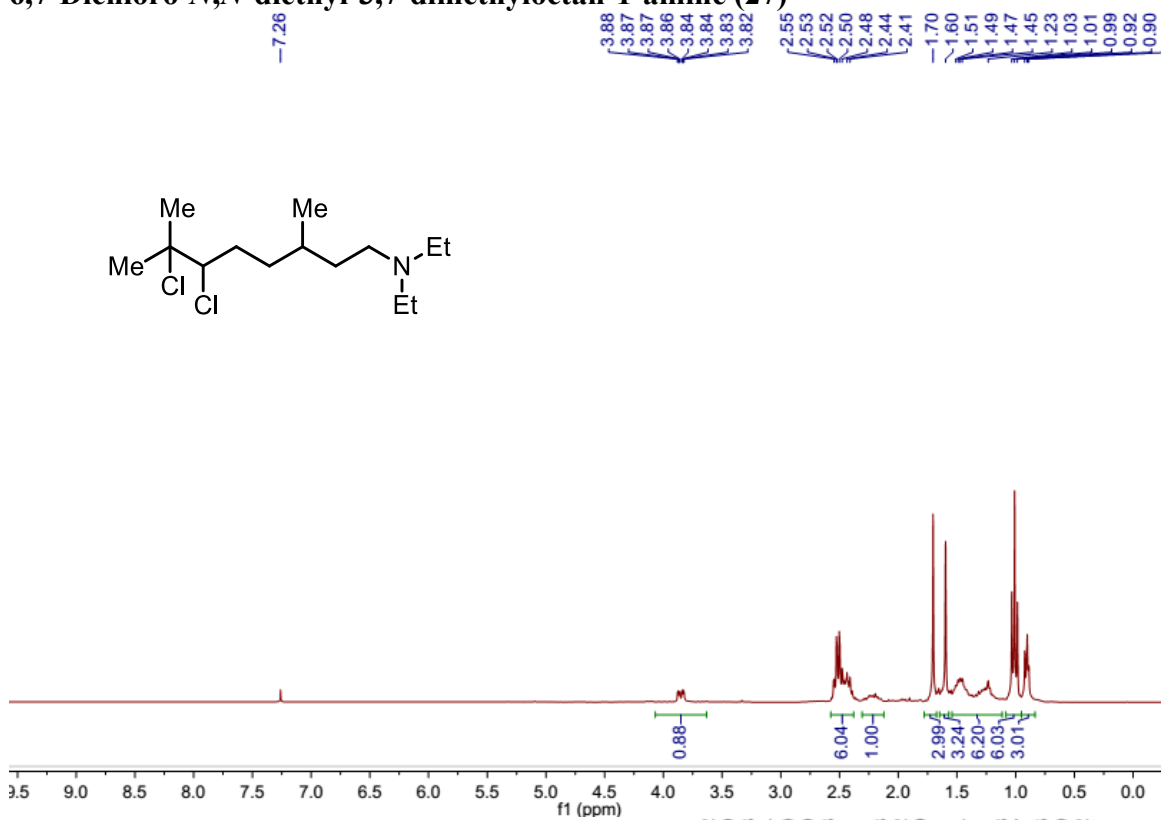
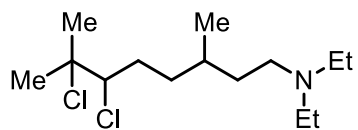
(4-(1,2-Dichloroethyl)phenyl)(methyl)sulfane (25)



2-(1,2-Dichloroethyl)pyridine (26)

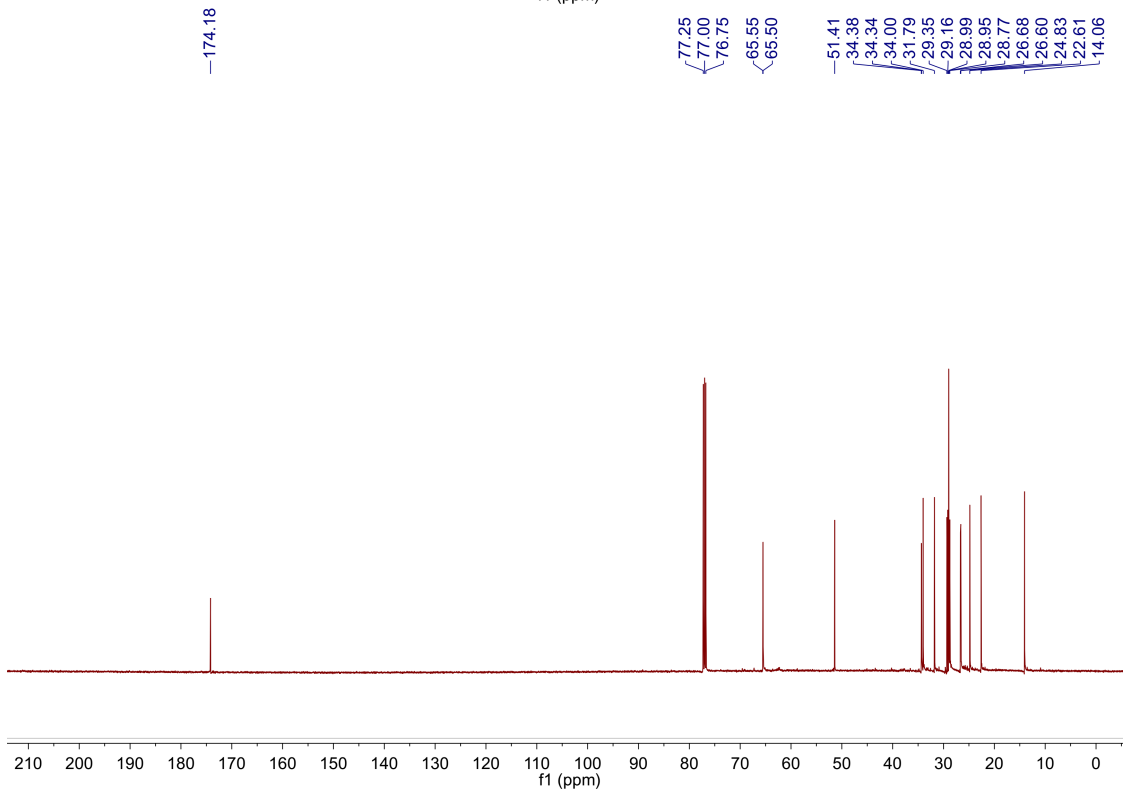
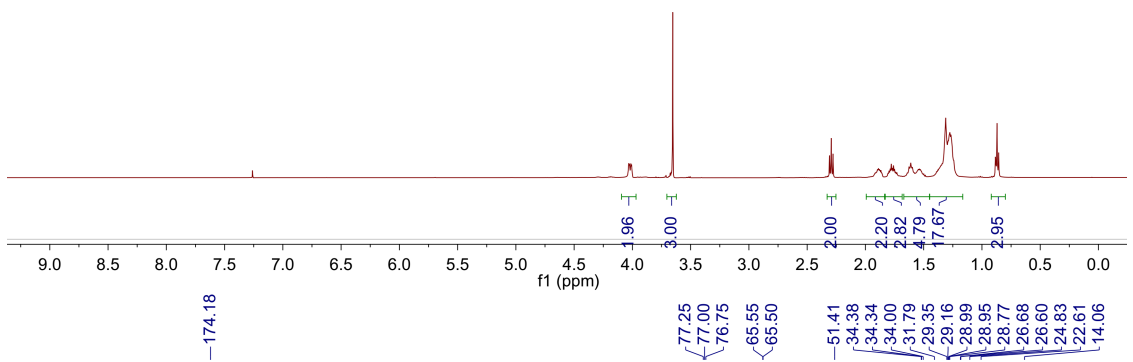
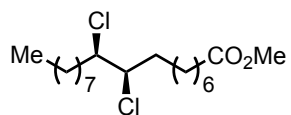


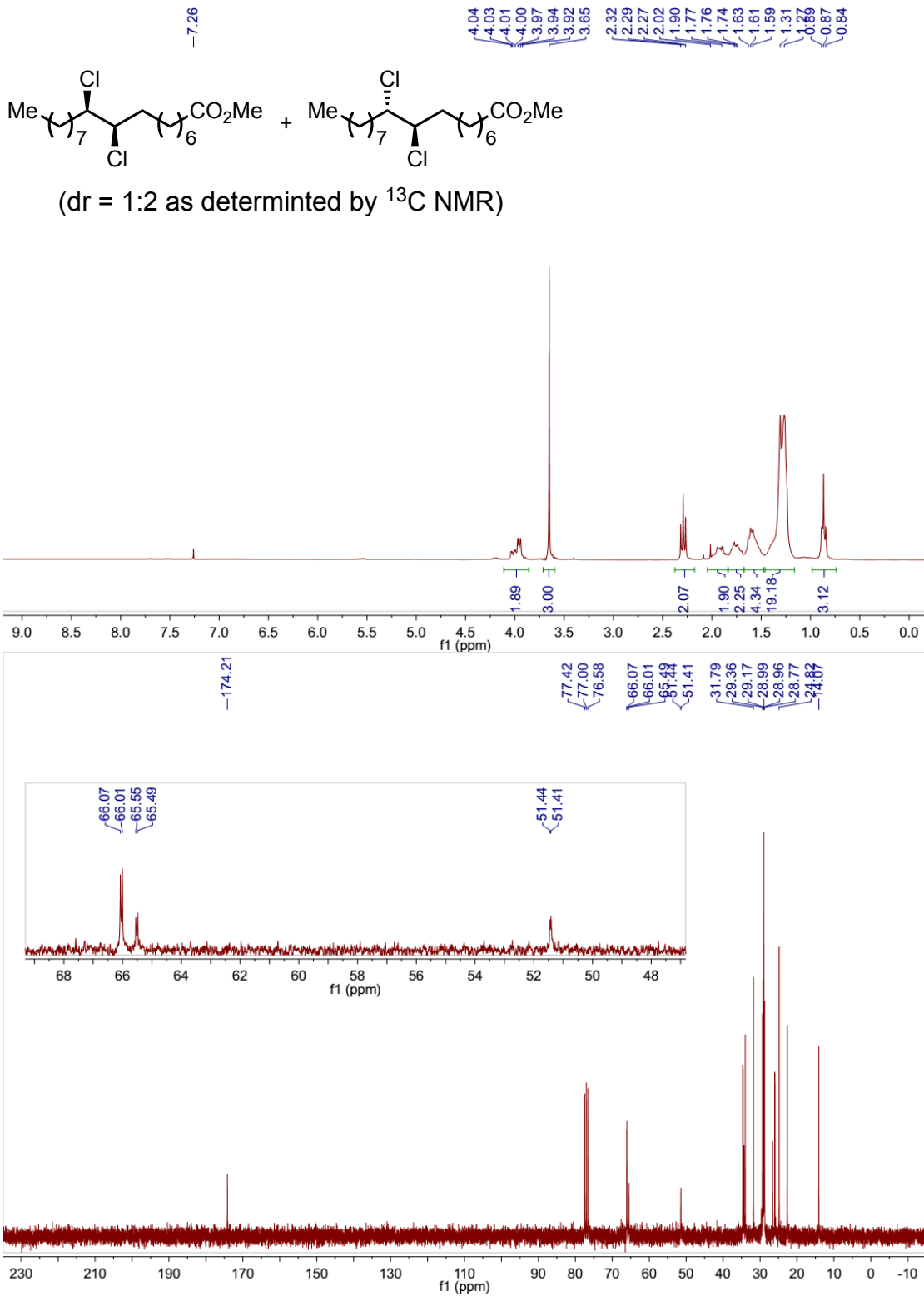
6,7-Dichloro-*N,N*-diethyl-3,7-dimethyloctan-1-amine (27)



Methyl 9,10-dichlorooctadecanoate (31)

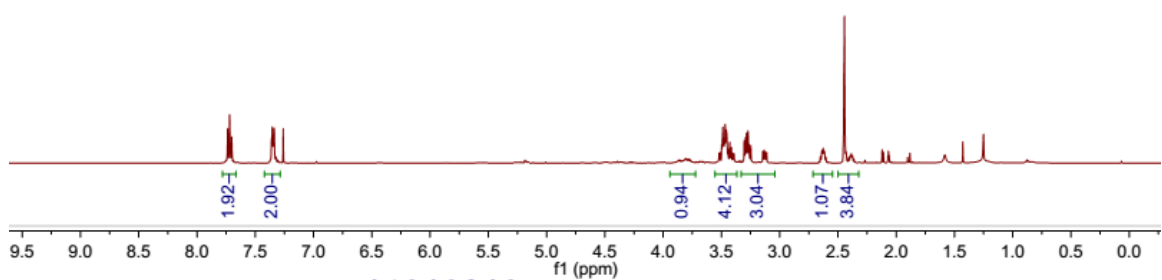
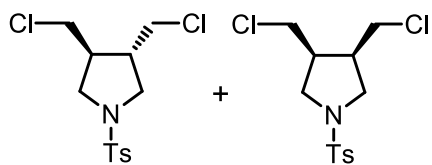
7.26
4.03
4.03
4.02
4.01
4.01
3.65
2.31
2.29
2.28
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.79
1.78
1.77
1.76
1.75
1.62
1.61
1.61
1.60
1.55
1.55
1.54
1.54
1.53
1.38
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1.35
1.34
1.34
1.32
1.32
1.31
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.27
1.26
1.26
1.24
1.24
0.88
0.87
0.86



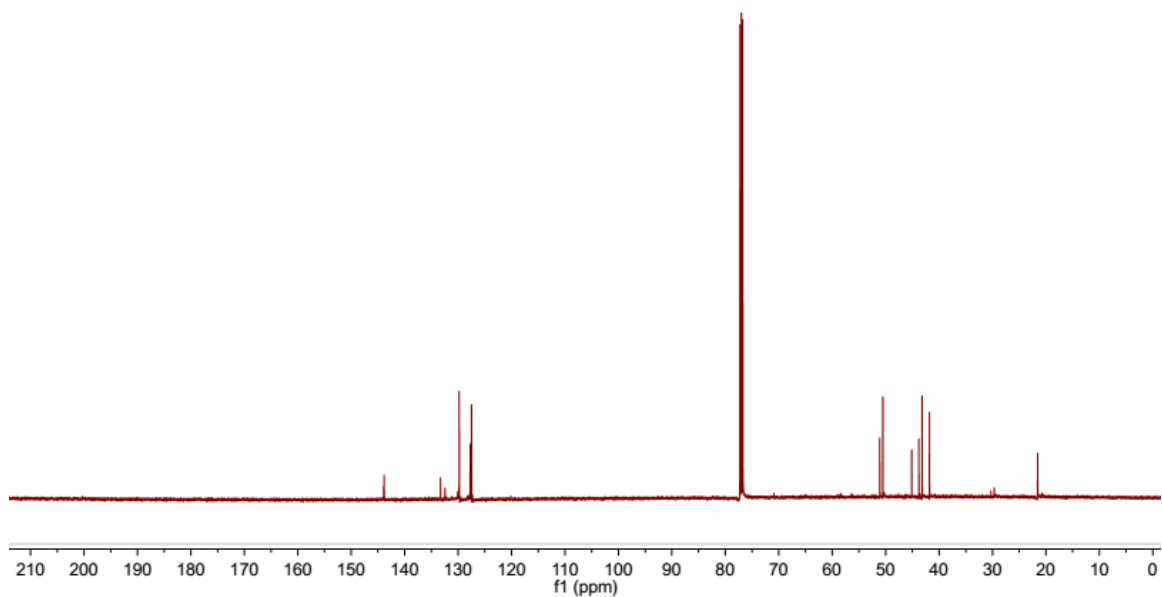


3,4-Bis(chloromethyl)-1-tosylpyrrolidine (33)

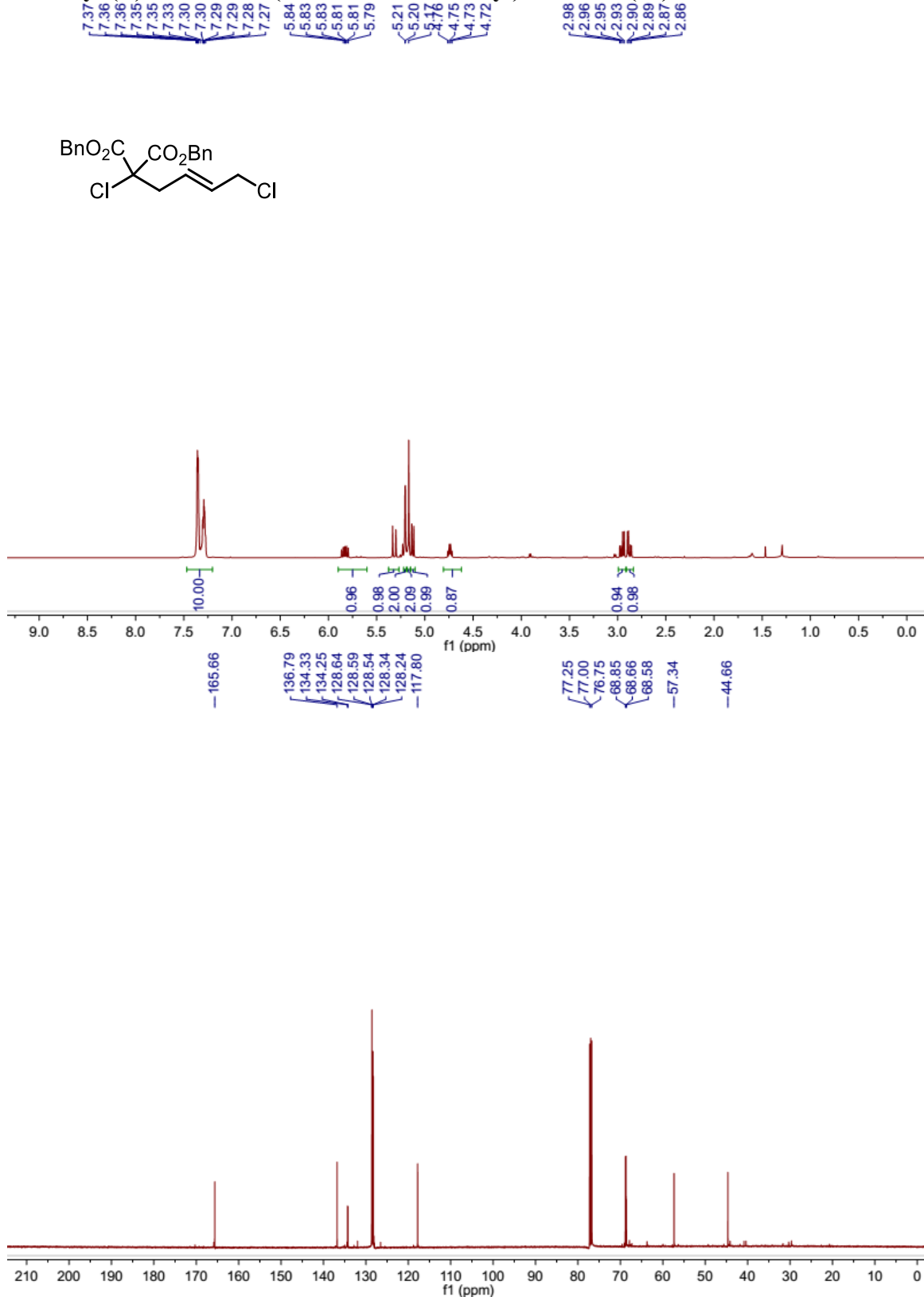
7.74, 7.72, 7.70, 7.36, 7.35, 7.34, 7.26, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.47, 3.46, 3.45, 3.44, 3.43, 3.41, 3.41, 3.39, 3.39, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.14, 3.13, 3.12, 3.11, 2.65, 2.64, 2.63, 2.62, 2.60, 2.44, 2.43, 2.41, 2.39, 2.38, 2.36



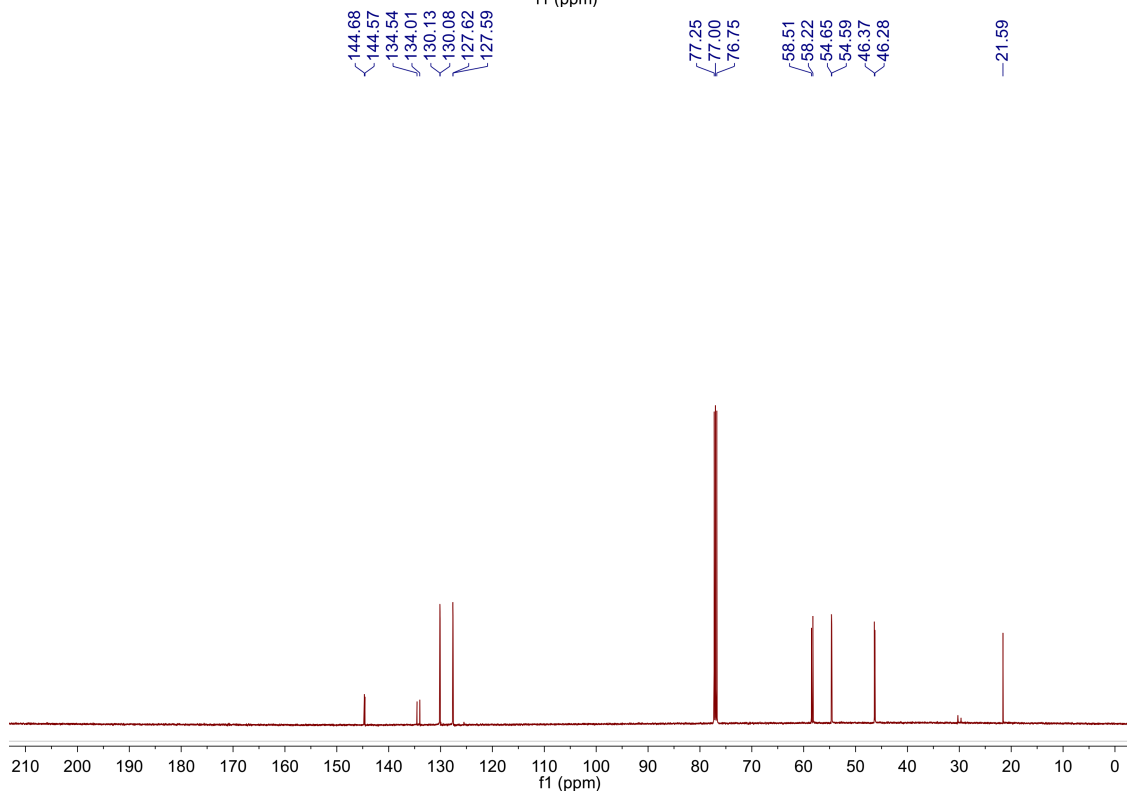
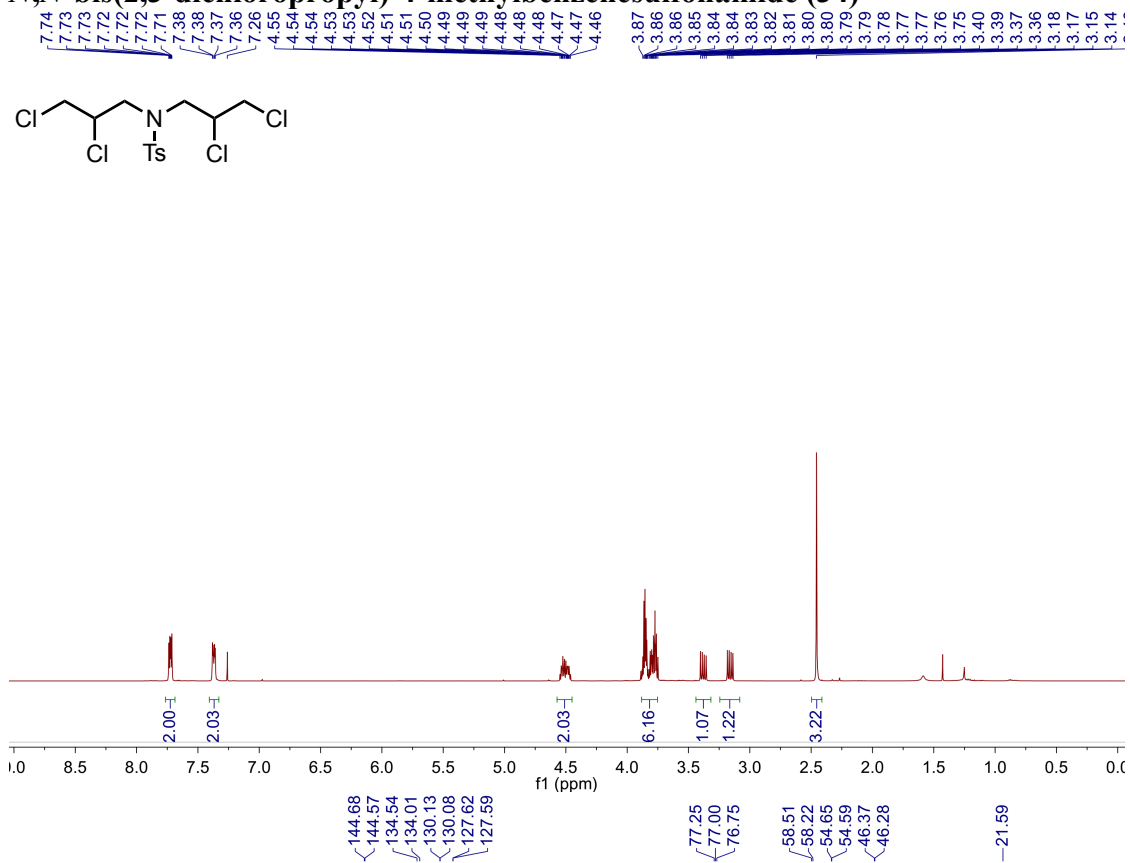
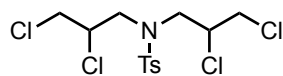
143.95, 143.84, 133.30, 132.45, 129.80, 129.79, 127.75, 127.50, 77.25, 77.00, 76.75, 51.09, 50.52, 45.12, 43.79, 43.18, 41.81, -21.55



Dibenzyl (*E*)-2-chloro-2-(4-chlorobut-2-en-1-yl)malonate (37)

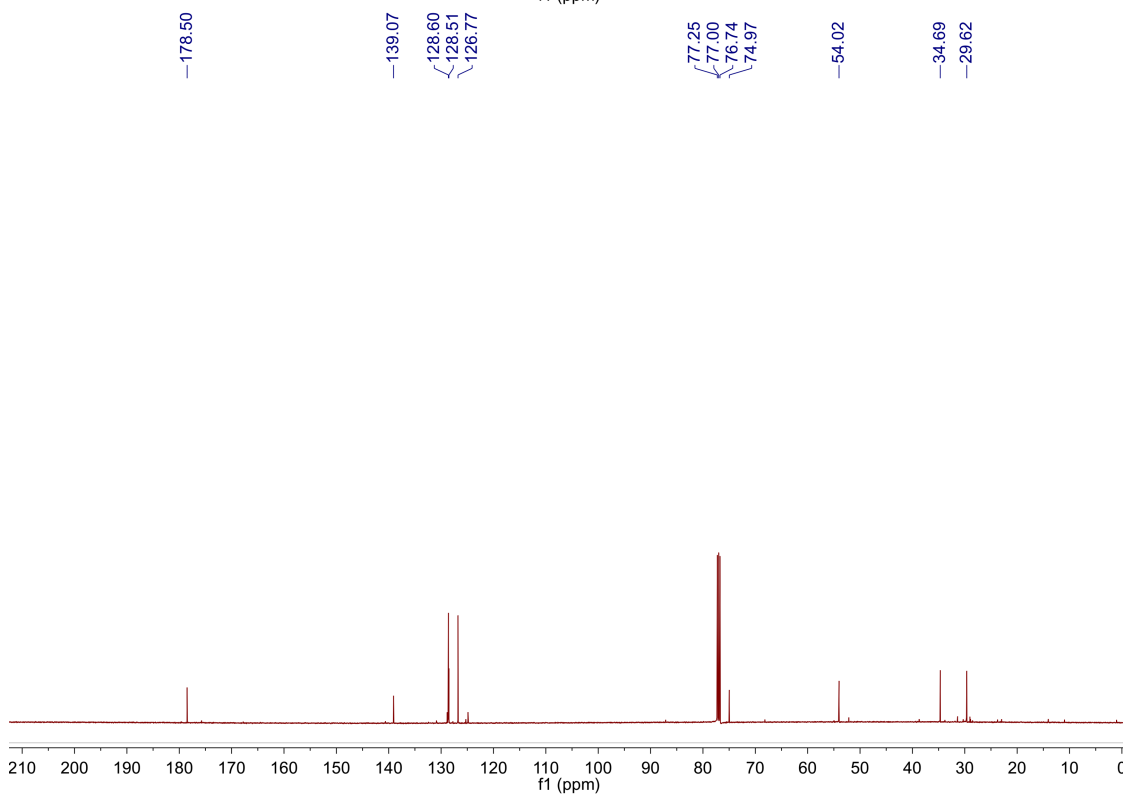
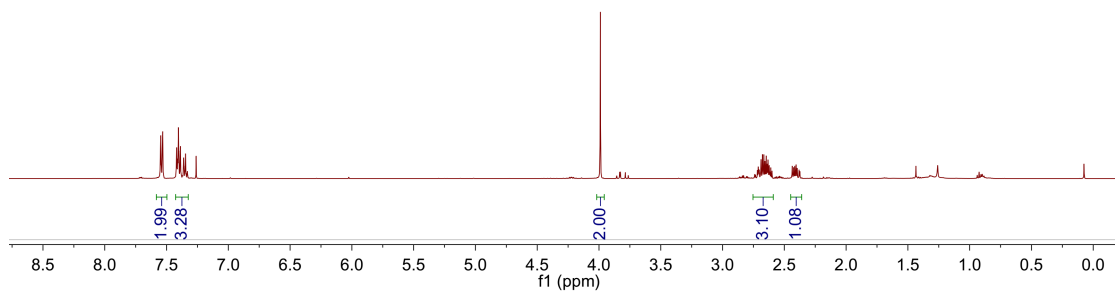
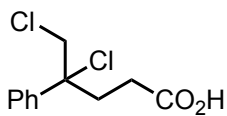


N,N-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide (34)



4,5-Dichloro-4-phenylpentanoic acid (41)

7.55, 7.54, 7.54, 7.53, 7.53, 7.42, 7.41, 7.41, 7.40, 7.40, 7.39, 7.39, 7.38, 7.36, 7.36, 7.36, 7.35, 7.35, 7.34, 7.33, 7.26, -3.99, 2.74, 2.72, 2.71, 2.71, 2.70, 2.69, 2.69, 2.68, 2.67, 2.66, 2.66, 2.65, 2.64, 2.63, 2.62, 2.62, 2.61, 2.60, 2.44, 2.42, 2.41, 2.40, 2.38



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