Supporting Information

Palladium-Catalyzed Allylic C–H Fluorination

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I. General information

General Procedures. Unless otherwise noted, reactions were performed without the exclusion of air or moisture. Screens and reactions were performed in polypropylene vials. Flasks were sealed with rubber septa or polyethylene caps. Stainless steel cannulae or syringes were used to transfer air- and moisture-sensitive reagents. Reactions using silver(I) fluoride were performed with the exclusion of light by wrapping reaction vessels in aluminum foil. Reactions were monitored by gas chromatography (GC, see below) or thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates, visualizing with fluorescence quenching, potassium permanganate ($KMnO_4$), or ceric ammonium molybdate (CAM). Organic solutions were concentrated under reduced pressure using a rotary evaporator with an ice-water bath for volatile compounds. Manual column chromatography was performed using SiliCycle SiliaFlash F60 (40-53 µm, 60 Å). Automated column chromatography was performed using pre-packed silica gel cartridges on a Biotage SP4 (40–53 µm, 60 Å).

Materials. Commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Strem, and TCI, and used as received with the following exceptions. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, and benzene were dried by passing through activated alumina columns. Silver(I) fluoride, (1*R*,2*R*)-(-)-[1,2-Cyclohexanediamino-*N,N'*-bis(3,5-di-t-butylsalicylidene)]chromium(III) chloride were purchased from Strem and used as received. Palladium(II) trifluoroacetate was purchased from Sigma-Aldrich and used as received. Deuterated solvents were purchased from Sigma-Aldrich or Cambridge Isotope Laboratories and used as received. 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate was purchased from Aldrich and stored at –30 °C. Methyl 10-undecenoate (96%) and 8-Bromo-1-octene (97%) were purchased from Aldrich. Palladium(II) acetate was recrystallized according to literature procedures.[1]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for proton are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26, d_8-toluene = δ 7.09, d_8-THF = δ 1.72 ppm). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16, d_8-toluene = δ 137.48, d_8-THF = δ 25.31 ppm). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker AVANCE 300 (282 MHz) spectrometer; chemical shifts are reported in parts per millions and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. High-resolution mass spectra (HRMS) were obtained on an Agilent 6220 LC/MS using electrospray ionization time-of-flight (ESI-TOF) or Agilent 7200 GC/MS spectrometer using electron impact time-of-flight (EI-TOF). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum 100 and are reported in terms of frequency of absorption (cm^{-1}) and intensity (s = strong, m = moderate, w = weak, br = broad). Gas chromatography (GC) was performed on an Agilent 7890A series instrument equipped with a split-mode capillary injection system and flame ionization detectors.

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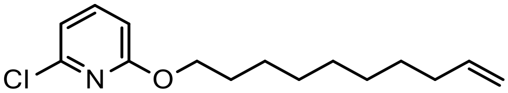
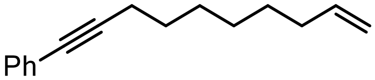
[1] 1,2-bis(benzylsulfinyl)ethane was prepared according literature procedures : Young, A. J.; White, M. C.; *Angew. Chem., Int. Ed.* **2011**, *50*, 6824–6827.

II. Synthesis of terminal alkenes



2-chloro-6-(dec-9-en-1-yloxy)pyridine (S1).[2]

To 9-decen-1-ol (3.56 mL, 20 mmol), was added sodium (138 mg, 6.0 mmol) and the mixture was heated at 70 °C for 1 h. To this solution was added 2,6-dichloropyridine (740 mg, 5.0 mmol) and the reaction was heated at 80 °C. After stirring at 80 °C for 12 h, the reaction mixture was quenched with water, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (100 g silica gel, 0→5% ether in hexanes) to afford 2-chloro-6-(dec-9-en-1-yloxy)pyridine (1.34 g, 4.1 mmol, 82% yield) as a colorless oil. FTIR (thin film, cm^{-1}) 2926 (m), 2855 (w), 1640 (w), 1590 (s), 1559 (s), 1441 (s), 1407 (m), 1298 (s), 1262 (m), 1159 (s), 985 (s), 907 (s), 786 (s), 725 (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, J = 8.2, 7.5 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.63 (10.2 Hz, 1H), 5.81 (ddt, J = 17.0, 10.2, 6.6 Hz, 1H), 5.00 (dm, J= 17.0 Hz, 1H), 4.93 (dm, J = 10.2 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 2.04 (q, J = 7.1 Hz, 2H), 1.75 (p, J = 6.8 Hz, 2H), 1.24–1.46 (m, 10H). ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.84, 148.39, 140.60, 139.32, 116.11, 114.28, 109.25, 66.87, 33.94, 29.53, 29.44, 29.19, 29.02, 28.97, 26.10; HRMS (ESI+) calculated for $C_{15}H_{23}ClNO$ ($[M+H]^+$): 268.1462, found: 268.1468.



dec-9-en-1-yn-1-ylbenzene (S2).[3]

To a solution of dec-1-en-9-yne[4] (340 mg, 2.5 mmol) in DMSO (25 mL) was added iodobenzene (280 µL, 2.5 mmol), copper iodide (23.8 mg, 0.125 mmol), triphenylphosphine (0.25 mmol, 66 mg) and potassium carbonate (518 mg, 3.75 mmol). The reaction mixture was heated at 120 °C. After stirring for 12 h at this temperature, the reaction mixture was quenched with aqueous sodium bicarbonate (saturated). The aqueous layer was extracted with ether three times and washed with water, then brine. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by automated column chromatography (10 g silica gel, 0→3% ether in pentanes) to afford dec-9-en-1-yn-1-ylbenzene (451 mg, 2.13 mmol, 85% yield) as a colorless oil. FTIR (thin film, cm^{-1}) 2928 (m), 2856 (m), 1640 (w), 1599 (w), 1490 (m), 1442 (m), 1070 (w), 994 (w), 909 (s), 754 (s), 690 (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 6.7, 2.6 Hz, 2H), 7.23–7.33 (m, 3H), 5.81 (ddt, J = 17.0, 10.1, 6.7 Hz, 1H), 5.03 (dm, J = 17.0 Hz, 1H), 4.95 (dm, J = 10.1 Hz, 1H), 2.40 (t, J = 7.1 Hz, 2H), 2.06 (q, J = 7.1 Hz, 2H), 1.60 (p, J = 7.1 Hz, 2H), 1.30–1.53 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.20, 131.64, 128.29, 127.58, 124.14, 114.39, 90.50, 80.69, 33.90, 28.92,

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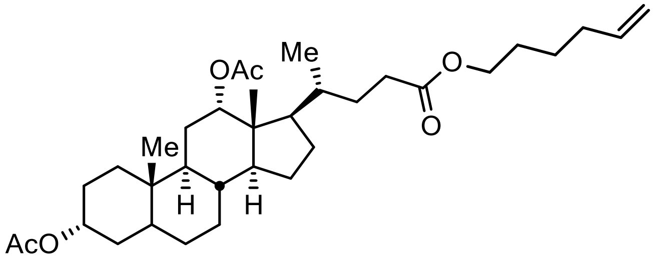
[2] Charrier, N.; Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* **2008**, *130*, 8898–8899.

[3] Okuro, K.; Furuune, M.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **1992**, *33*, 5363–5364.

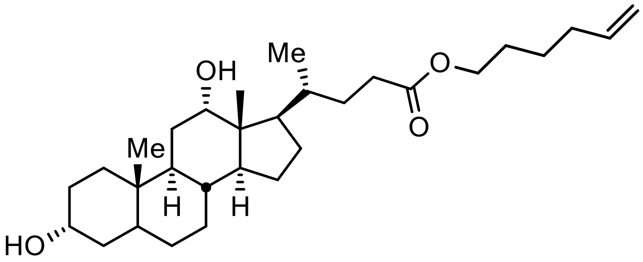
[4] Homsi, F.; Rousseau, G. *J. Org. Chem.* **1998**, *63*, 5255–5258.

28.88, 28.82, 28.77, 18.52; HRMS (EI+) calculated for $C_{16}H_{20}$ ($[M^{\bullet}]^{+}$): 212.1565, found: 212.1515.



(3*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-(hex-5-en-1-yloxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diyl diacetate (16).

To a solution of (4*R*)-4-((3*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,12-diacetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid[5] (4.76 g, 10 mmol) in CH_2Cl_2 (10 mL) was added 5-hexen-1-ol (2.4 mL, 20 mmol) and 4-(dimethylamino)pyridine (123 mg, 1.0 mmol). The reaction mixture was then cooled to 0 °C, and dicyclohexylcarbodiimide solution (1M in CH_2Cl_2, 20 mL, 20 mmol) was added dropwise. The reaction mixture was allowed to warm at 23 °C, stirred for 3 hours at this temperature, filtered. The filtrate was concentrated under reduced pressure. The residue was purified by automated chromatography (100 g silica gel, 5→10% ethyl acetate in hexanes) to afford the title compound (4.41 g, 7.9 mmol, 79% yield). FTIR (thin film, cm^{-1}) 2943 (m), 2869 (m), 1734 (s), 1450 (w), 1364 (w), 1243 (s), 1169 (w), 1027 (m), 971 (w), 912 (w) ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.07 (s, 1H), 5.00 (dm, J = 16.9 Hz, 1H), 4.95 (dm, J = 10.2 Hz, 1H), 4.69 (tt, J = 10.8, 4.6 Hz, 1H), 4.05 (t, J = 6.7 Hz, 2H), 2.29–2.35 (m, 1H), 2.15–2.21 (m, 1H), 2.09 (s, 3H), 2.02–2.09 (m, 4H), 2.02 (s, 3H) 0.97–1.90 (m, 26H), 0.97 (s, 3H), 0.79 (d, J = 6.4 Hz, 3H), 0.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.40, 170.73, 170.65, 138.46, 114.95, 76.02, 74.32, 64.37, 49.53, 47.74, 45.10, 41.92, 35.76, 34.82, 34.80, 34.49, 34.15, 33.42, 32.35, 31.36, 30.96, 28.18, 27.47, 26.99, 26.74, 25.97, 25.75, 25.30, 23.54, 23.21, 21.63, 21.55, 17.60, 12.53 ; HRMS (ESI+) calculated for $C_{34}H_{54}O_6Na$ ($[M+Na]^{+}$): 581.3818, found: 581.3825.



hex-5-en-1-yl 4-((3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,12-dihydroxy-10,13-dimethylhexa decahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (S3).

To a solution of deoxycholic acid ((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,12-dihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid) (1.96 g, 5.00 mmol) in CH_2Cl_2 (10 mL) was added 5-hexen-1-ol (1.2 mL, 10 mmol) and DMAP (4-(*N*,*N*-dimethylamino)pyridine) (70 mg, 0.57 mmol) under nitrogen. The reaction mixture was then

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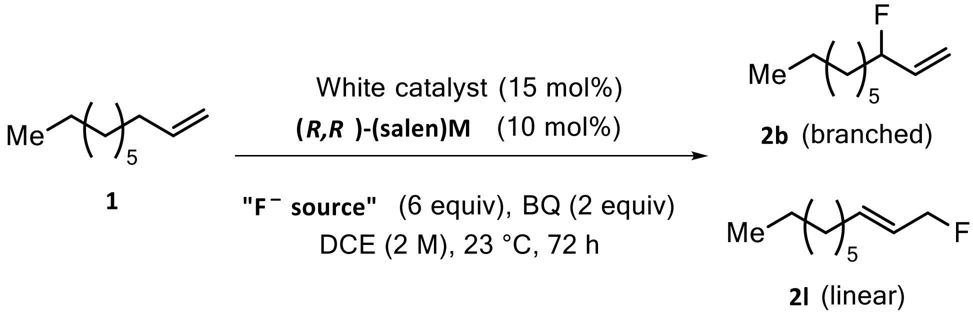
[5] Balasubramanian, R.; Maitra, U. *J. Org. Chem.* **2001**, *66*, 3035–3040.

cooled to 0 °C, and dicyclohexylcarbodiimide solution (1M in CH_2Cl_2, 10 mL, 10 mmol) was added dropwise. The reaction mixture was allowed to warm to 23 °C. After stirring for three hours at this temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by hand column chromatography (50 g silica gel, 20→50% ethyl acetate in hexanes) to afford the title compound, a white crystalline solid (2.02 g, 4.25 mmol, 85% yield). FTIR (thin film, cm^{-1}) 3383 (br), 2931 (s), 2864 (m), 1735 (s), 1641 (w), 1449 (m), 1377 (w), 1311 (w), 1252 (w), 1170 (m), 1092 (w), 1065 (w), 1043 (s), 1014 (w), 968 (w), 944 (w), 912 (m), 851 (w); ^1H NMR (500 MHz, $CDCl_3$): δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.03 (dm, J = 17.2 Hz, 1H), 4.98 (dm, J = 10.2 Hz, 1H), 4.07 (t, J = 6.6 Hz, 2H), 3.99 (m, 1H), 3.59–3.66 (m, 1H), 2.34–2.40 (m, 1H), 2.20–2.26 (m, 1H), 2.09 (q, J = 7.0 Hz, 2H), 1.01–1.92 (m, 29H), 0.98 (d, J = 6.4 Hz, 4H), 0.92 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.42, 138.39, 114.85, 73.14, 71.77, 64.24, 48.25, 47.31, 46.48, 42.05, 36.40, 36.01, 35.21, 35.14, 34.12, 33.62, 33.33, 31.35, 30.91, 30.45, 28.64, 28.08, 27.49, 27.13, 26.13, 25.21, 23.67, 23.18, 17.29, 12.76; HRMS (ESI+) calculated for $C_{30}H_{51}O_4$ ($[M+H]^+$): 475.3782, found: 475.3779.

III. Details for fluorine source and co-catalyst optimization (Table 1)



Procedure for screening fluorine source and co-catalyst:

A 2 M stock solution was prepared in DCE (100 µL/rxn), containing 1-decene 96% (39.5 µL/rxn, 0.2 mmol/rxn, 1.0 equiv) and dodecane (18.2 µL/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by GC. To undried 2.5 mL polypropylene vials was sequentially added a stir bar, 1,2-Bis(phenylsulfinyl)ethane palladium(II) acetate (15 mol%, 0.03 mmol), the appropriate Lewis acid (10 mol%, 0.02 mmol) and benzoquinone (2.0 equiv, 0.8 mmol), followed by 157.8 µL stock solution and the appropriate fluorine source[6] (6.0 equiv, 1.2 mmol/rxn).[7] No precautions were taken to exclude air or moisture. After stirring at 600 rpm at 23 °C for 72 h, the crude reaction mixture was then diluted with Et_2O and the Et_2O layer was removed by glass pipette. The remaining mixture was extracted with Et_2O (3X). The combined Et_2O layers were filtered through a short plug of silica gel, eluting with ether. Conversion, yields and regioselectivities were determined by GC using commercial columns.

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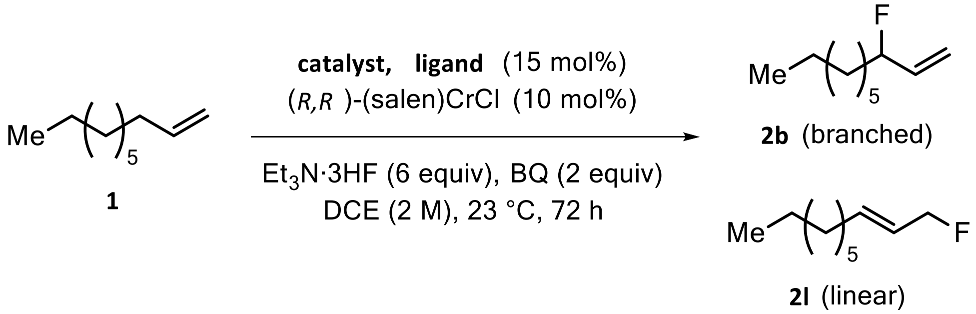
[6] When the fluoride source is a solid, it was added first in the vial.

[7] For KF, DCE (100 µL) was added so that the reaction mixture was able to stir.

IV. Details for catalyst and ligand optimization (Table 2)



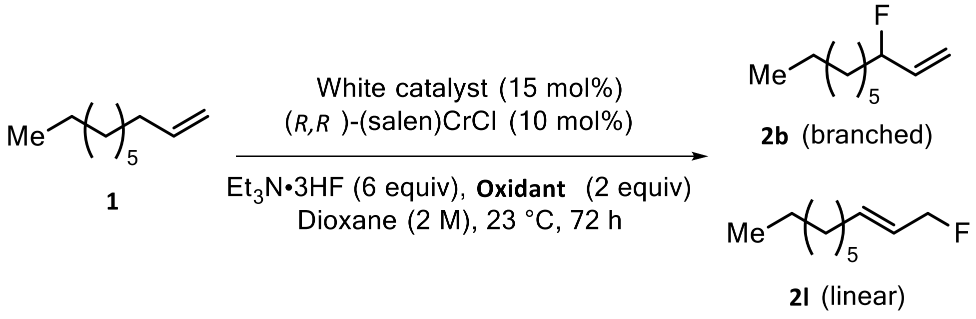
Procedure for screening ligand and catalyst:

A 2 M stock solution was prepared in DCE (100 µL/rxn), containing 1-decene 96% (39.5 µL/rxn, 0.2 mmol/rxn, 1.0 equiv) and dodecane (18.2 µL/rxn, 0.4 equiv). An aliquot was reserved for measurement of the initial ratio by GC. To undried 2.5 mL polypropylene vials was sequentially added a stir bar, the appropriate catalyst (15 mol%, 0.03 mmol), the appropriate catalyst (15 mol%, 0.03 mmol), (*R,R*)-Cr(salen)Cl (10 mol%, 0.02 mmol) and benzoquinone (2.0 equiv, 0.8 mmol), followed by 157.8 µL stock solution and Et_3N•3HF (6.0 equiv, 1.2 mmol/rxn). No precautions were taken to exclude air or moisture. After stirring at 600 rpm at 23 °C for 72 h, the crude reaction mixture was then diluted with Et_2O and the Et_2O layer was removed by glass pipette. The remaining Pd(II) catalyst/Cr(III) co-catalyst and Et_3N•3HF was extracted with Et_2O (3X). The combined Et_2O layers were filtered through a short plug of silica gel, eluting with ether. Conversion, yields and regioselectivities were determined by GC using commercial columns.

V. Additional reaction optimization

For the reactions in this section, procedures similar to those in section **IV** were used.

Table S1. Influence of the oxidant for the C–H fluorination of **1**

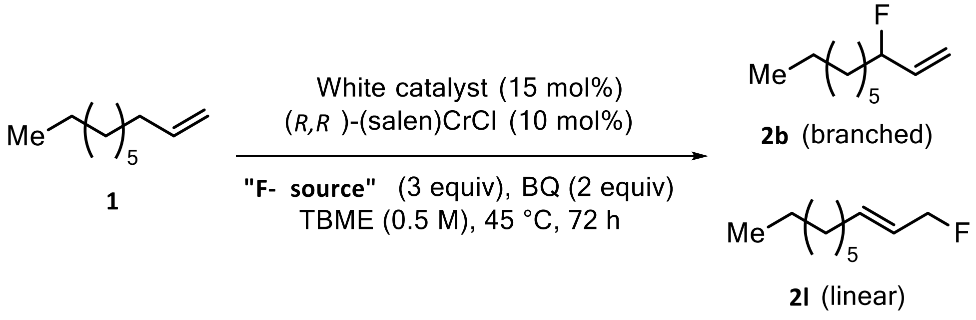


entry	Oxidant	conv (%)[a]	yield (%)[b]	2b:2l[c]
1	BQ	87	39	7.7:1
2	PhBQ	43	11	8.1:3
3	2,6-DMBQ	34	3	nd
4	Duroquinone	16	4	nd
5	DDQ	8	0	nd

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

Note: Use of $Cu(OAc)_2$, MnO_2, O_2, $K_2S_2O_8$ as oxidants did not provide any products.

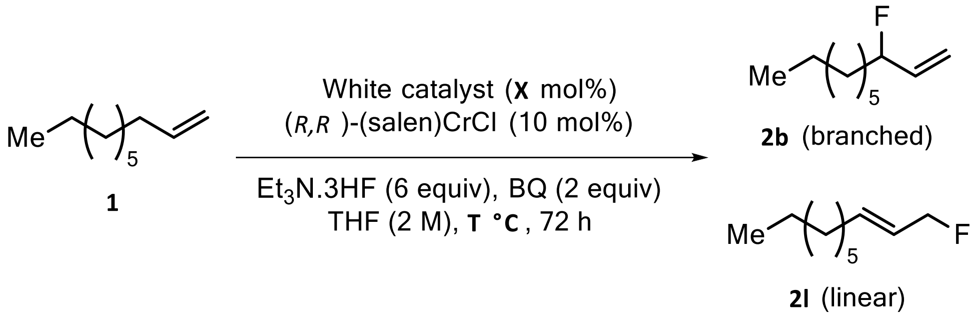
Table S2. Screening of fluorine source for the C–H fluorination of **1**



entry	“F^- source”	conv (%)[a]	yield (%)[b]	2b:2l[c]
1	Et_3N•3HF	39	17	6:1
2	AgF	100	4	3:1
3	Pyr•9HF	45	3	nd
4	TBAF.4*tert*-BuOH	25	0	-
5	TASF[d]	27	0	-
6	TBABF[e]	37	10	8:1

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations. [d] Tris(dimethylamino)sulfonium difluorotrimethylsilicate. [e] Tetrabutylammonium hydrogen difluoride solution.

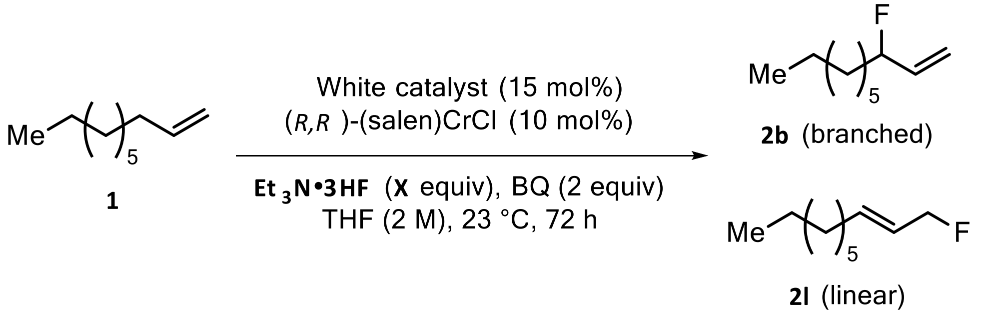
Table S3. Screening of catalyst loading and temperature for the C–H fluorination of **1**



entry	X (mol%)	Temperature (°C)	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	10	42	45	17	6.4:1	7
2	15	42	58	23	6.2:1	6
3	15	30	78	37	6.5:1	2
4	15	23	85	44	6.4:1	2

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

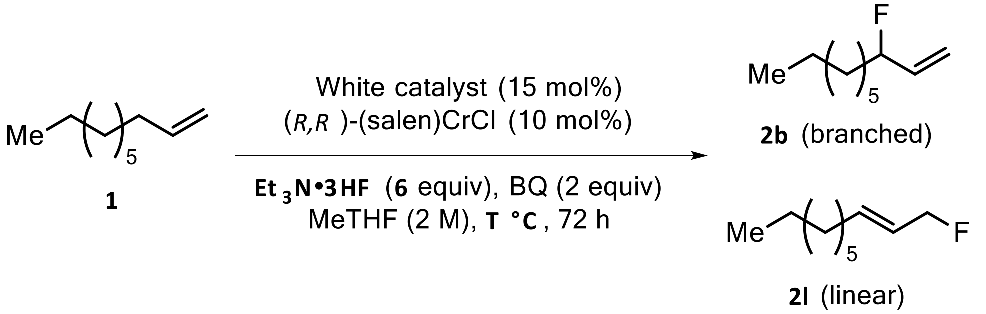
Table S4. Screening of equivalents of $Et_3N•3HF$ for the C–H fluorination of **1**



entry	X (equiv)	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	3	66	48	6.6:1	1
2	6	61	56	6.5:1	2
3	7.5	60	55	6.5:1	2
4	9.0	64	53	6.9:1	2
5	10.5	58	44	6.8:1	2
6	12	62	44	6.9:1	2
7	15	60	43	6.8:1	2

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

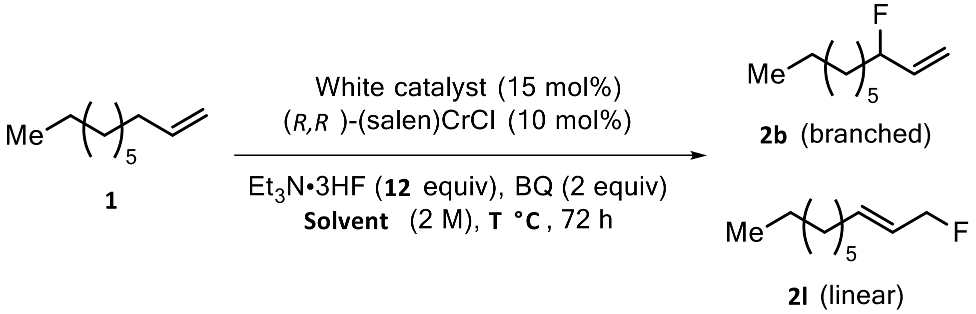
Table S5. Screening of temperature for the C–H fluorination of **1**



Entry	T (°C)	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	42	58	23	4.2:1	6
2	30	78	37	6.5:1	2
3	23	85	45	6.4:1	2

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

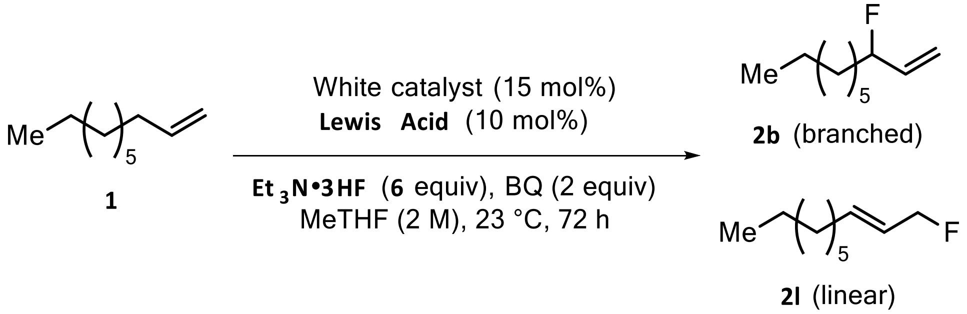
Table S6. Screening of solvent for the C–H fluorination of **1**



Entry	Solvent	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	Dioxane	98	61	6.0:1	4
2	DCE	92	62	6.4:1	2
3	2-MeTHF	64	40	6.8:1	2
4	THF	62	44	6.9:1	2
5	EtOAc	26	19	6.6:1	2
6	Et_2O	67	30	6.9:1	3

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

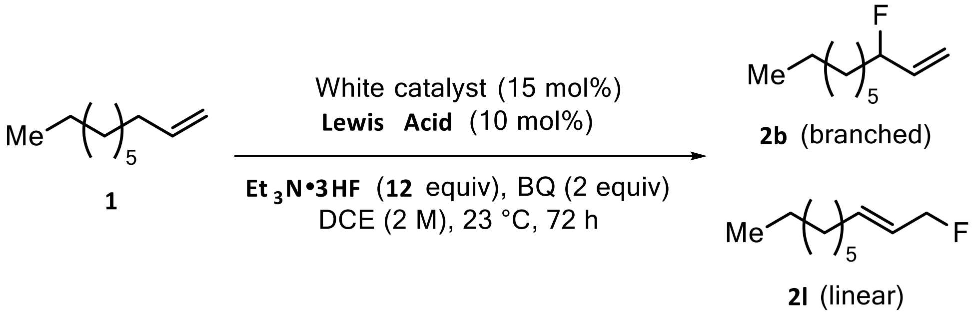
Table S7. Additional Screening of Lewis Acid for the C–H fluorination of **1**



entry	Lewis Acid	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	None	34	10	6.8:1	1
2	CrF_3	22	14	6.4:1	1
3	CoF_3	27	14	6.3:1	2
4	(*R,R*)-(salen)CrOAc	32	26	6.6:1	2

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

Table S8. Additional Screening of Lewis Acid for the C–H fluorination of **1**

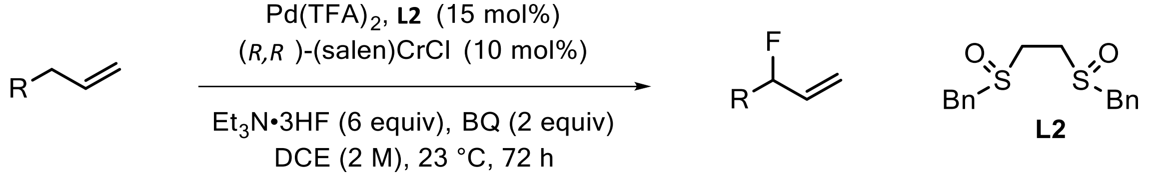


entry	Lewis Acid	conv (%)[a]	yield (%)[b]	2b:2l[c]	diene[a]
1	(*R,R*)-Cr(salen)Cl	92	62	6.4:1	2
2	(*R,R*)-Cr(salen)BF_4	78	44	5.0:1	4
3	(*R,R*)-Cr(salen)I	25	4	2.5:1	1

[a] Determined by GC using dodecane as an internal standard for reactions carried out on a 0.2 mmol scale in a polypropylene vial. [b] Combined GC yield of **2b** and **2l**. [c] Ratio based on GC analysis of unpurified reaction mixture; not corrected for small response variations.

VI. Procedure for C–H allylic fluorination (Table 3)

General procedure for the palladium-catalyzed regioselective fluorination of terminal alkenes.



A 2.5 mL polypropylene vial was sequentially charged with a stir bar, the olefin (1 equiv, 0.4 mmol), palladium(II)trifluoroacetate (15 mol%, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane[1] **L2** (15 mol%, 0.06 mmol), (*R,R*)-Cr(salen)Cl (10 mol%, 0.04 mmol) and benzoquinone (2.0 equiv, 0.8 mmol), 1,2-dichloroethane (2M, 200 μL) and Et_3N•3HF (6.0 equiv, 2.4 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 1000 rpm at 23 °C for 72 hours. After 72 hours, the reaction mixture was directly purified by hand column chromatography.[8] Yields and regioselectivities are averages values for two reactions. Regioselectivities were determined by ^{19}F NMR.

Note: When the olefin is commercially available, it was added after addition of the solvent.

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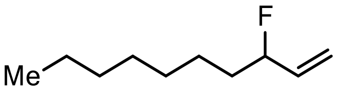
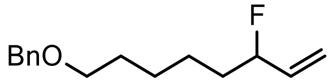
[8] Sand has to be deposited on the top of the column to prevent exothermic reaction with silica.



2b:2l = 7.0:1

3-fluorodec-1-ene (2b). The general procedure was followed, using 1-decene (79 µL, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→2% ether in hexanes) afforded the title compound (34 mg, 0.21 mmol, 54% yield) as a colorless oil with spectral data in agreement with literature values.[9] The regioselectivity was determined to be 7.0:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 36 mg, 0.23 mmol, 57% yield and the b:l ratio was: 7.0:1; average yield was 56% and average b:l ratio was 7.0:1. FTIR (thin film, cm^{-1}) 2925 (s), 2854 (m), 1462 (w), 1378 (w), 1222 (w), 1170 (w), 972 (w), 929 (w), 766 (w); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 5.50–5.95 (m, 1H, 2H*), 5.28 (dm, J= 17.2 Hz, 1H), 5.19 (dm, J = 10.7 Hz, 1H), 4.84 (dm, J = 48.5 Hz, 1H), 4.77 (dd, J= 47.5, 6.2 Hz, 2H*), 2.04–2.08 (m, J = 6.5 Hz, 2H*), 1.15–1.80 (m, 12H, 10H*), 0.88 (t, J= 5.5 Hz, 3H, 3H*); ^{19}F NMR (282 MHz, $CDCl_3$, linear isomer indicated by *) –176.78 (m), –207.50* (m).



3b:3l = 6.9:1

(((6-fluorooct-7-en-1-yl)oxy)methyl)benzene (3b). The general procedure was followed, using ((oct-7-en-1-yloxy)methyl)benzene (87.3 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by column chromatography (silica gel, 0→5% ether in hexanes) afforded the title compound (55 mg, 0.23 mmol, 58% yield) as a colorless oil. The regioselectivity was determined to be 6.6:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 57 mg, 0.24 mmol, 60% yield and the b:l ratio was 7.2:1; average yield was 59% and average b:l ratio was 6.9:1. The enantiomeric excess was determined to be 4% by chiral HPLC analysis (Chiralpak AS-H, 99.5% hexanes/isopropanol, 1 mL/min, t_R = 5.56 min and t_R = 5.94 min). FTIR (thin film, cm^{-1}) 2937 (m), 2859 (m), 1496 (w), 1454 (m), 1428 (w), 1363 (w), 1275 (w), 1204 (w), 1100 (s), 1028 (m), 987 (m), 931 (m), 735 (s), 697 (s); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *) δ 7.27–7.42 (m, 5H, 5H*), 5.79–5.96 (m, 1H, 2H*), 5.32 (ddt, J = 17.3, 3.3, 1.4, 1H), 5.23 (dm, J = 10.6 Hz, 1H), 4.88 (dm, J = 49.7 Hz, 1H), 4.82 (dd, J = 47.3, 6.5 Hz, 2H*), 4.53 (s, 2H, 2H*), 3.33 (t, J = 5.3 Hz, 2H), 3.32 (t, J = 5.3 Hz, 2H*), 2.04–2.08 (m, 2H*), 1.57–1.79 (m, 4H, 2H*), 1.37–1.52 (m, 4H, 4H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 138.70, 138.70*, 137.71* (d, J = 12.0 Hz), 136.80 (d, J = 19.6 Hz), 128.50, 128.50*, 127.77, 127.77*, 127.66, 127.66*, 124.69* (d, J = 16.3 Hz), 117.02 (d, J = 11.9 Hz), 93.82 (d, J = 166.5 Hz), 83.91* (d, J = 159.9 Hz), 73.05*, 73.03, 70.43*, 70.37, 35.28 (d, J = 22.1 Hz), 32.27* (d, J = 2.2 Hz), 29.76, 29.71*, 28.73* (d, J = 3.2 Hz), 26.13, 25.85*, 24.65 (d, J = 4.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$; linear isomer indicated by *) δ –177.48 (m),

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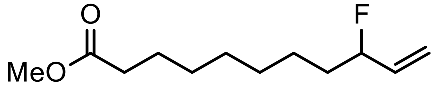
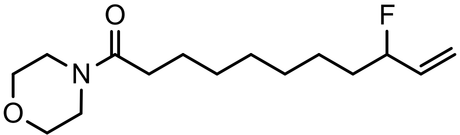
[9] Umemoto, T; Singh, R. P.; Xu, Y.; Saito, N. *J. Am. Chem. Soc.* **2010**, *132*, 18199–18205.

–208.03* (m); HRMS (ESI+) calculated for $C_{15}H_{21}O$ ($[M–F]^+$): 217.1592, found: 217.1590.



4b:4l = 7.5:1

methyl 9-fluoroundec-10-enoate (4b). The general procedure was followed, using methyl 10-undecenoate 96% (93.7 μL, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 μL) and Et_3N•3HF (400 μL, 2.4 mmol). Purification by column chromatography (silica gel, 0→2→5→8% ether in pentanes) afforded the title compound (45 mg, 0.21 mmol, 52% yield) as a colorless oil. The regioselectivity was determined to be 7.3:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 46 mg, mmol, 53% yield and the b:l ratio was 7.7:1; average yield was 53% and average b:l ratio was 7.5:1. FTIR (thin film, cm^{-1}) 2931 (m), 2857 (w), 1739 (s), 1436 (m), 1362 (w), 248 (w), 1198 (m), 1169 (s), 968 (m), 933 (m), 749 (w); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 5.80 (dddd, J = 17.0, 13.9, 10.6, 6.0 Hz, 1H), 5.72–5.77 (m, 1H*), 5.54–5.64 (m, 1H*), 5.32 (dm, J = 17.3 Hz, 1H), 5.14 (dm, J = 10.6 Hz, 1H), 4.78 (dm, J = 48.7 Hz, 1H), 4.71 (dd, J = 47.5 6.3 Hz , 2H*), 3.60 (s, 3H, 3H*), 2.23 (t, J = 7.5 Hz, 2H, 2H*), 1.97–2.03 (m, 2H*), 1.47–1.69 (m, 4H, 2H*), 1.20–1.36 (m, 8H, 8H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 174.41, 174.41*, 137.77* (d, J = 12.0 Hz), 136.86 (d, J = 19.6 Hz), 124.63* (d, J = 16.5 Hz), 116.90 (d, J = 11.9 Hz), 93.83 (d, J = 166.6 Hz), 83.86* (d, J = 160.0 Hz), 51.60, 51.60*, 35.29 (d, J = 22.0 Hz), 34.19, 34.19*, 32.26* (d, J = 2.2 Hz), 29.29, 29.28*, 29.23, 29.17*, 29.14, 29.03*, 28.80* (d, J = 3.1 Hz), 25.02, 25.02*, 24.71 (d, J = 4.5 Hz) ; ^{19}F NMR (282 MHz, $CDCl_3$, linear isomer indicated by *) –177.56 (m), –208.07* (m); HRMS (ESI+) calculated for $C_{12}H_{21}FNaO_2$ ($[M+Na]^+$): 239.1423, found: 239.1415.



5b:5l = 7.0:1

9-fluoro-1-morpholinoundec-10-en-1-one (5b)

The general procedure was followed, using 1-morpholinoundec-10-en-1-one[10] (101 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 μL) and Et_3N•3HF (400 μL, 2.4 mmol). Purification by hand column chromatography (silica gel, 10→30→50→75% ethyl acetate in hexanes) afforded the title compound (55 mg, 0.20 mmol, 51% yield) as a colorless oil. The regioselectivity was determined to be 6.8:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 59 mg, 0.22 mmol, 54% yield and the b:l ratio was 7.2:1; average yield was 53% and average b:l ratio was 7.0:1. FTIR (thin film, cm^{-1}) 2929 (m), 2856 (m), 1630 (s), 1512 (m), 1460 (s), 1431 (s), 1361 (m), 1271 (m), 1232 (s), 1125 (s), 1032 (m), 961 (m), 848 (m), 762 (m), 701 (m); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *) δ 5.77–5.90 (m, 1H, 1H*), 5.65–5.73 (m, 1H*),

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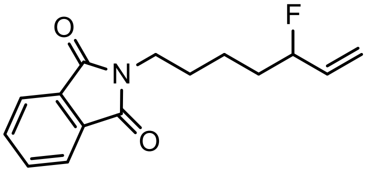
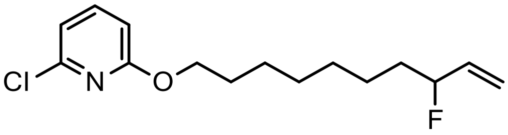
[10] Kirchhoff, J. H.; Netherton, M. R.; Hills I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662–13663.

5.29 (dm, J = 17.3 Hz, 1H), 5.19 (dm, J = 10.7 Hz, 1H), 4.85 (dq, J = 48.7, 6.2 Hz, 1H), 4.78 (dd, J = 47.4 Hz, 6.5 Hz, 2H*), 3.64–3.66 (m, 4H, 4H*), 3.59–3.61 (m, 2H, 2H*), 3.44–3.46 (m, 2H, 2H*), 3.45 (t, J = 4.7 Hz, 2H, 2H*), 2.03–2.08 (m, 2H*), 1.52–1.73 (m, 4H, 2H*), 1.26–1.44 (m, 8H, 8H*); ^{13}C NMR (125 MHz, CDCl$_3$; linear isomer indicated by *) δ 171.94, 171.94*, 137.83* (d, J = 12.0 Hz), 136.79 (d, J = 19.6 Hz), 124.55* (d, J = 16.4 Hz), 116.94 (d, J = 11.9 Hz), 93.85 (d, J = 166.5 Hz), 83.80* (d, J =159.8 Hz), 67.05, 67.05*, 66.78, 66.78*, 46.11, 46.11*, 41.93, 41.93*, 35.35 (d, J = 22.0 Hz), 33.20*, 33.19, 32.26* (d, J = 3.2 Hz), 29.48*, 29.44, 29.38, 29.34*, 29.30, 29.05*, 28.78* (d, J = 3.2 Hz), 25.29*, 25.27, 24.70 (d, J = 4.5 Hz); ^{19}F NMR (282 MHz, CDCl$_3$, linear isomer indicated by *) –177.55 (m), –207.79*; δ HRMS (ESI+) calculated for ($C_{15}H_{26}NO_2$ $[M–F]^+$): 252.1964, found: 252.1960.



6b:6l = 6.7:1

2-(5-fluorohept-6-en-1-yl)isoindoline-1,3-dione (6b). The general procedure was followed, using 2-(hept-6-en-1-yl)isoindoline-1,3-dione[11] (97.3 mg, 0.4 mmol), palladium(II) trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (26.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 μL) and Et$_3$N•3HF (400 μL, 2.4 mmol). Purification by hand column chromatography (silica gel, 5→40% ether in hexanes), followed by a second hand column chromatography (silica gel, 0→30% ether in toluene) afforded the title compound (54 mg, 0.21 mmol, 52 % yield) as a colorless oil. The regioselectivity was determined to be 6.6:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 52 mg, 0.2 mmol, 50% yield and the b:l ratio was 6.8:1; average yield was 51% and average b:l ratio was 6.7:1. FTIR (thin film, cm^{-1}) 2942 (w), 1771 (m), 1705 (s), 1467 (w), 1437 (m), 1395 (s),1368 (m), 104((w), 969 (m), 935 (m), 718 (s); ^{1}H NMR (500 MHz, CDCl$_3$; linear isomer indicated by *): δ 7.80–7.89 (m, 2H, 2H*), 7.69–7.73 (m, 2H, 2H*), 5.74–5.91 (m, 1H, 1H*), 5.62–5.72 (m, 1H*), 5.29 (ddt, J = 17.3, 3.3, 1.5 Hz, 1H), 5.20 (dt, J = 10.7, 1.4 Hz, 1H), 4.86 (dm, J = 48.6 Hz, 1H), 4.77 (dd, J = 47.4, 6.3 Hz, 2H*), 3.69 (t, *J* = 7.3 Hz, 2H, 2H*), 2.10–2.14 (m, 2H*), 1.59–1.83 (m, 4H, 2H*), 1.36–1.57 (m, 2H, 2H*); ^{13}C NMR (125 MHz, CDCl$_3$) δ 168.54, 169.54*, 136.77* (d, J = 11.9 Hz), 136.51 (d, J = 19.6 Hz), 134.04, 134.04*, 132.18, 132.18*, 125.18*(d, J = 16.5 Hz), 123.32, 123.32*, 117.18 (d, J = 11.9 Hz), 93.50 (d, J =167.2 Hz), 83.70* (d, J =160.3 Hz), 37.84, 37.84*, 34.77 (d, J = 22.3 Hz), 31.81* (d, J = 2.2 Hz), 28.44, 28.18*, 26.07* (d, J = 3.3 Hz), 22.12 (d, J = 4.5 Hz); ^{19}F NMR (282 MHz, CDCl$_3$, linear isomer indicated by *) δ –177.63 (m), –208.24 (m); HRMS (ESI+) calculated for $C_{15}H_{16}NO_2$ ($[M–F]^+$): 242.1181, found: 242.1177.



7b:7l = 7.8:1

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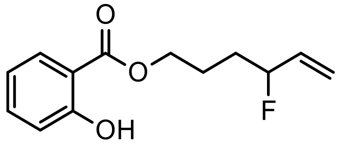
[11] Yang, H.; Carter, R. G. *Org. Lett.* **2010**, *12*, 3108–3111.

2-chloro-6-((8-fluorodec-9-en-1-yl)oxy)pyridine (7b). The general procedure was followed, using 2-chloro-6-(dec-9-en-1-yloxy)pyridine (107 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (15 mol%, 0.06 mmol), (*R,R*)-Cr(salen)Cl (10 mol%, 0.04 mmol), benzoquinone (88 mg equiv, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→2% ether in hexanes) afforded the title compound (62 mg, 0.22 mmol, 54% yield) as a colorless oil. The regioselectivity was determined to be 7.7:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 62 mg, 0.22 mmol, 54% yield and the b:l ratio was 7.8:1; average yield was 54% and average b:l ratio was 7.8:1. FTIR (thin film, cm^{-1}) 2933 (m), 2858 (w), 1590 (s), 1559 (s), 1441 (s), 1407 (m), 1382 (m), 1298 (s), 1262 (m), 1159 (s), 985 (s), 933 (m), 788 (s), 726 (m); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 7.50 (dd, J = 8.2, 7.4 Hz, 1H, 1H*), 6.87 (d, J = 7.4 Hz, 1H, 1H*), 6.63 (d, J = 8.2 Hz, 1H, 1H*), 5.78–5.92 (m, 1H, 1H*), 5.64–5.71 (m, 1H*), 5.30 (ddt, J = 17.3, 3.4, 1.5 Hz, 1H), 5.21 (dt, J = 10.6, 1.3 Hz, 1H), 4.74–4.93 (m, 1H, 2H*), 4.27 (t, J = 6.7 Hz, 2H, 2H*), 2.05–2.11 (m, 2H*), 1.52–1.80 (m, 4H, 2H*), 1.29–1.48 (m, 8H, 8H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 163.82, 163.82*, 148.39, 148.39*, 140.64, 140.64*, 137.89* (d, J = 11.9 Hz), 136.84 (d, J = 19.6 Hz), 124.58* (d, J =16.5 Hz), 116.97 (d, J = 11.8 Hz), 116.14, 116.14*, 109.25*, 109.25, 93.89 (d, J = 166.5 Hz), 83.92* (d, J =159.9 Hz), 66.80, 66.80*, 35.29 (d, J = 22.0 Hz), 32.30* (d, J = 1.9 Hz), 29.41, 29.33, 29.29*, 29.16*, 28.93, 28.93*, 28.81* (d, J = 3.2 Hz), 26.01*, 26.01, 24.73 (d, J = 4.6 Hz); ^{19}F NMR (282 MHz, $CDCl_{3,}$ linear isomer indicated by *) δ –178.10 (m), –208.64* (m); HRMS (ESI+) calculated for $(C_{15}H_{21}ClNO[M–F]^+)$: 266.1312, found: 266.1303.



8b:8l = 7.4:1

4-fluorohex-5-en-1-yl 2-hydroxybenzoate (8b). The general procedure was followed, using hex-5-en-1-yl 2-hydroxybenzoate[12] (88.1 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by column chromatography (silica gel, 0→2→5% ether in hexanes) afforded the title compound (67 mg, 0.28 mmol, 70% yield) as a colorless oil. The regioselectivity was determined to be 7.6:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 62 mg, 0.26 mmol, 65% yield and the b:l ratio was 7.2:1; average yield was 68% and average b:l ratio was 7.4:1. FTIR (thin film, cm^{-1}) 3175 (br), 2946 (w), 1673 (s), 1614 (m), 1486 (m), 1397 (w), 1325 (m), 1300 (s), 1250 (s), 1213 (s), 1158 (s), 1090 (s), 965 (m), 757 (s), 701 (s); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *) δ 10.79 (s, 1H, 1H*), 7.84 (dd, J = 8.0, 1.8 Hz, 1H, 1H*), 7.46 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H, 1H*), 6.98 (dd, J = 8.4, 1.1 Hz, 1H, 1H*), 6.89 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H, 1H*), 5.90 (dddd, J = 17.0, 14.3, 10.7, 5.9 Hz, 1H), 5.71–5.79 (m, 2H*), 5.36 (dm, J = 17.0 Hz, 1H), 5.26 (dm, J = 10.7 Hz, 1H), 4.81 (dd, J = 46.9, 6.4 Hz, 1H), 4.84 (dd, J = 47.4, 6.3 Hz, 2H*), 4.35– 4.42 (m, 2H, 2H*), 2.24–2.30 (m, 2H*), 1.76–2.01 (m, 4H, 2H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ

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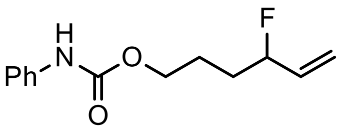
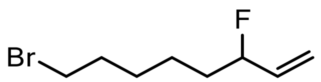
[12] Breit, B.; Seiche, W. *J. Am. Chem. Soc.* **2003**, *125*, 6608–6609.

170.25, 170.25*, 161.78, 161.78*, 136.14 (d, J = 19.6 Hz), 135.87, 135.87*, 135.43* (d, ^{2}J = 12.0 Hz), 129.93, 129.93*, 125.86* (d, J = 16.5 Hz), 119.29*, 119.29, 117.73, 117.73*, 117.56 (d, J = 11.8 Hz), 112.51, 112.51*, 93.10 (d, J = 168.0 Hz), 83.48* (d, J = 161.1 Hz), 65.00, 64.69*, 31.81 (d, J = 22.7 Hz), 28.76* (d, J = 3.0 Hz), 27.99* (d, J = 3.2 Hz), 24.12 (d, J = 4.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$; linear isomer indicated by *) δ –177.56 (m), –208.08* (m); HRMS (ESI+) calculated for $C_{13}H_{15}FNaO_3$ ([M+Na]$^+$): 261.2903, found: 261:2908.



9b:9l = 6.5:1

4-fluorohex-5-en-1-yl phenylcarbamate (9b). The general procedure was followed, using hex-5-en-1-yl phenylcarbamate[13] (87.7 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→30% ether in hexanes), followed by a second hand column chromatography (silica gel, 0→15% ether in toluene) afforded the title compound (60 mg, 0.25 mmol, 63% yield) as a colorless oil. The regioselectivity was determined to be 6.6:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 66 mg, mmol, 70% yield and the b:l ratio was 6.4:1; average yield was 67% and average b:l ratio was 6.5:1. FTIR (thin film, cm^{-1}) 3319 (br), 2956 (w), 1706 (s), 1600 (s), 1534 (s), 1502 (m), 1445 (s), 1314 (m), 1222 (s); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 7.30–7.33 (m, 2H, 2H*), 7.22–7.25 (m, 2H, 2H*), 6.99 (t, J = 7.4 Hz, 1H, 1H*), 6.61 (brs, 1H, 1H*), 5.74–5.87 (m, 1H, 1H*), 5.59–5.71 (m, 1H*), 5.27 (ddt, J = 17.3, 3.3, 1.5 Hz, 1H), 5.17 (ddd, J = 10.6, 1.4, 1.4 Hz, 1H), 4.86 (dqd, J = 48.7, 5.8, 1.5 Hz, 1H), 4.72 (dd, J = 47.3 Hz, 6.3 Hz, 2H*), 4.10–4.17 (m, 2H, 2H*), 2.10–2.16 (m, 2H*), 1.64–1.79 (m, 4H, 2H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 153.65, 153.65*, 137.92, 137.92*, 136.24 (d, J = 19.6 Hz), 135.99* (d, J = 12.2 Hz), 129.18[14], 129.18[14]*, 125.52* (d, J = 16.4 Hz), 123.55, 123.55*, 117.34 (d, J = 11.9 Hz), 93.22 (d, J = 167.7 Hz), 83.61* (d, J = 160.5 Hz), 64.82, 64.62*, 31.73 (d, J = 22.6 Hz), 28.72* (d, J =2.1 Hz), 28.13* (d, J = 3.1 Hz), 24.42 (d, J =4.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, linear isomer indicated by *) δ –178.55 (m), –208.86* (m); (HRMS (ESI+) calculated for $C_{13}H_{16}NO_2$ ([M–F]$^+$): 218.1181, found: 218.1174.



10b:10l = 7.0:1

8-bromo-3-fluorooct-1-ene (10b).[15] The general procedure was followed, using 8-bromo-1-octene 97% (69.2 µL, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→2% ether in pentanes)

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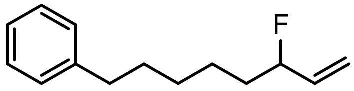
[13] Breit, B.; Seiche, W. *J. Am. Chem. Soc.* **2003**, *125*, 6608–6609.

[14] The four CH of the aromatic ring are overlapping.

[15] Katcher, M. H.; Sha, A.; Doyle, A. G. *J. Am. Chem. Soc.* **2011**, *133*, 15902–15905.

afforded the title compound (46 mg, 0.22 mmol, 55 % yield) as a colorless oil with spectral data in agreement with literature values.[16] The regioselectivity was determined to be 6.8:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 44 mg, 0.21 mmol, 53% yield and the b:l ratio was 7.1:1; average yield was 54% and average b:l ratio was 7.0:1. ^{1}H NMR (500 MHz, CDCl$_3$, linear isomer indicated by *): δ 5.77–5.92 (m, 1H, 1H*), 5.65–5.72 (m, 1H*), 5.32 (ddd, J = 17.3, 2.7, 1.3 Hz, 1H), 5.23 (ddd, 10.7, 2.2, 1.1 Hz, 1H), 4.79–4.95 (dm, J = 48.7 Hz, 1H), 4.81 (dd, J = 47.4, 6.3 Hz, 2H*), 3.42 (t, J = 6.8 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H*), 2.09–2.12 (m, 2H*), 1.84–1.91 (m, 2H), 1.58–1.79 (m, 2H, 2H*), 1.36–1.53 (m, 4H, 4H*); ^{13}C NMR (125 MHz, CDCl$_3$, linear isomer indicated by *) δ 137.65 (d, J = 19.6 Hz), 137.19* (d, J = 12.0 Hz), 124.96* (d, J = 16.4 Hz), 117.16 (d, J = 11.9 Hz), 93.65 (d, J = 166.9 Hz), 83.79* (d, J = 160.1 Hz), 35.12 (d, J = 22.2 Hz), 33.97*, 33.93, 33.69* (d, J = 4.1 Hz), 32.72, 32.70*, 32.09* (d, J = 2.2 Hz), 28.01, 27.75*, 24.00 (d, J = 4.5 Hz); ^{19}F NMR (282 MHz, CDCl$_3$, linear isomer indicated by *) δ –177.94 (m), –208.38* (m).



11b:11l = 7.0:1

6-fluorooct-7-en-1-yl)benzene (11b). The general procedure was followed, using oct-7-en-1-ylbenzene[17] (73.3 mg, 0.4 mmol), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (2.0 equiv, 0.8 mmol), 1,2-dichloroethane (200 μL) and Et$_3$N•3HF (400 μL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→2% ether in pentanes) afforded the title compound (54 mg, 0.26 mmol, 65% yield) as a colorless oil. The regioselectivity was determined to be 6.9:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 52 mg, 0.25 mmol, 63% yield and the b:l ratio was 7.0:1; average yield was 64% and average b:l ratio was 7.0:1. FTIR (thin film, cm^{-1}) 2923 (s), 2854 (s), 1496 (w), 1459 (m), 1377 (w), 1275 (w), 980 (m), 929 (m), 747 (s), 698 (s) ; ^{1}H NMR (500 MHz, CDCl$_3$, linear isomer indicated by *): δ 7.27–7.30 (m, 2H, 2H*), 7.18–7.20 (m, 3H, 3H*), 5.79–5.92 (m, 1H, 1H*), 5.64–5.72 (m, 1H*), 5.31 (ddt, J = 17.3, 3.3, 1.4 Hz, 1H), 5.22 (dm, J = 10.6 Hz, 1H), 4.80 (dq, J = 48.7, 6.5 Hz, 1H), 4.48 (dd, J = 47.6, 6.3 Hz, 2H*), 2.60–2.63 (t, J = 7.6 Hz, 2H, 2H*), 2.06–2.11 (m, 2H*), 1.36–1.78 (m, 8H, 6H*); ^{13}C NMR (125 MHz, CDCl$_3$, linear isomer indicated by *) δ 142.83, 142.75*, 137.79* (d, J = 11.9 Hz), 136.81 (d, J = 19.6 Hz), 128.51, 128.51*, 128.38, 128.38*, 125.77, 125.77*, 124.63* (d, J = 16.4 Hz), 116.99 (d, J = 11.9 Hz), 93.86 (d, J = 166.5 Hz), 83.91* (d, J = 159.9 Hz), 36.00*, 35.95, 35.24* (d, J = 22.1 Hz), 32.24 (d, J = 2.2 Hz), 31.49, 31.47*, 29.12, 28.90*, 28.76* (d, J = 3.3 Hz), 24.67 (d, J = 4.6 Hz); ^{19}F NMR (282 MHz, CDCl$_3$, linear isomer indicated by *) δ –177.59 (m), –208.08* (m); HRMS (EI+) calculated for $C_{14}H_{19}F$ ([M$^{\bullet}$]$^+$): 206.1471, found: 206.1469.

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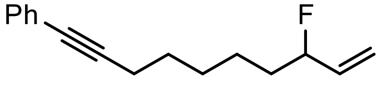
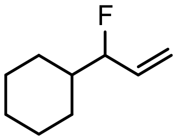
[16] Umemoto, T; Singh, R. P.; Xu, Y.; Saito, N. *J. Am. Chem. Soc.* **2010**, *132*, 18199–18205.

[17] Nagano, T.; Hayashi, T. *Org. Lett.* **2004**, *6*, 1297–1299.



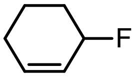
12b:12l = 7.5:1

(8-fluorodec-9-en-1-yn-1-yl)benzene (12b). The general procedure was followed, using dec-9-en-1-yn-1-ylbenzene (84.9 mg, 0.4 mmol),), palladium(II)trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL) and $Et_3N•3HF$ (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→2% ether in pentanes) afforded the title compound (46 mg, 0.2 mmol, 50% yield) as a colorless oil. The regioselectivity was determined to be 7.6:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 40 mg, 0.17 mmol, 43% yield and the b:l ratio was 7.4:1; average yield was 47% and average b:l ratio was 7.5:1. FTIR (thin film, cm^{-1}) 2934 (m), 2860 (m), 1640 (w), 1599 (w), 1490 (m), 1442 (w), 1276 (w), 1070 (w), 977 (m), 932 (w), 909 (s), 756 (s), 692 (s); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 7.38–7.40 (m, 2H, 2H*), 7.26–7.30 (m, 3H, 3H*), 5.81–5.93 (m, 1H, 1H*), 5.66–5.74 (m, 1H*), 5.32 (dm, J = 17.3 Hz, 1H), 5.22 (dm, J = 10.6 Hz, 1H), 4.88 (dq, J = 48.7, 6.2 Hz, 1H), 4.78 (dd, J = 47.4 Hz, 6.9 Hz, 2H*), 2.42 (t, J = 7.0 Hz, 2H), 2.41 (t, J = 7.0 Hz, 2H*), 2.09–2.14 (m, 2H*), 1.40–1.81 (m, 8H, 6H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 137.64* (d, J = 11.7 Hz), 136.77 (d, J = 19.6 Hz), 131.65, 131.65*, 128.33, 128.33*, 127.66, 127.66*, 125.67, 125.67*, 124.06, 124.06*, 117.62* (d, J =11.9 Hz), 117.06 (d, J =11.9 Hz), 93.83 (d, J = 166.6 Hz), 90.25*, 90.27, 83.69* (d, J = 160.0 Hz), 80.82, 80.82*, 35.22 (d, J = 22.1 Hz), 32.21* (d, J = 3.0 Hz), 29.86, 28.75, 28.70, 28.66*, 28.49*, 28.41* (d, J = 3.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, linear isomer indicated by *) –177.58, –208.02*. HRMS (ESI+) calculated for $C_{16}H_{19}$ ($[M–F]^+$): 211.1487, found: 211.1484.



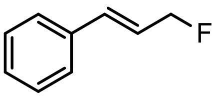
13b:13l = 2.0:1

(1-fluoroallyl)cyclohexane (13b).[15] For this product, a NMR yield was obtained : a 2.5 mL polypropylene vial was sequentially charged with a stir bar, palladium(II)trifluoroacetate (20 mg 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,4-dioxane (400 µL), allylcyclohexane (61.9 µL, 0.4 mmol), fluorobenzene (30 µL, 0.8 equiv) as internal ^{19}F NMR standard and $Et_3N•3HF$ (6.0 equiv, 2.4 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 600 rpm at 23 °C for 72 hours. After 72 h, the reaction mixture was filtered through a short plug of silica gel, eluting with ether. The yield and the regioselectivity were determined to be respectively 30% and 2:1 b:l by ^{19}F NMR analysis of the crude compound. After a second run, the yield and the regioselectivity were determined to be respectively 35% and 2.0:1 b:l by GC analysis; average yield was 33% and average b:l ratio was 2.0:1. ^{19}F NMR (282 MHz, $CDCl_3$,; linear isomer indicated by *) δ –180.52 (m), –206.26* (m).



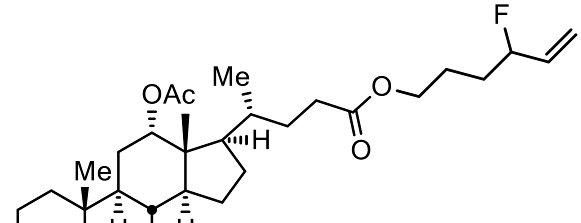
14

3-fluorocyclohex-1-ene (14).[18] For this product, a NMR yield was obtained : a 2.5 mL polypropylene vial was sequentially charged with a stir bar, palladium(II)trifluoroacetate (20 mg 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (400 µL), cyclohexene (40.5 µL, 0.4 mmol), fluorobenzene (30 µL, 0.8 equiv) as internal ^{19}F NMR standard, and Et_3N•3HF (400 µL, 2.4 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 600 rpm at 23 °C for 72 hours. After 72 h, the reaction mixture was filtered through a short plug of silica gel, eluting with ether. The yield was determined to be 17% by ^{19}F NMR analysis of the crude compound. After a second run, the yield was determined to be 15%; average yield was 16%. ^{19}F NMR (282 MHz, $CDCl_3$) δ –166.34 (m).



15

(*E*)-(3-fluoroprop-1-en-1-yl)benzene (15).[18] For this product, a NMR yield was obtained: A 2.5 mL polypropylene vial was sequentially charged with a stir bar, palladium(II)trifluoroacetate (20 mg 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (400 µL), allylbenzene 98% (54 µL, 0.4 mmol), fluorobenzene (30 µL, 0.8 equiv) as internal ^{19}F NMR standard, and Et_3N•3HF (400 µL, 2.4 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 600 rpm at 23 °C for 72 hours. After 72 h, the reaction mixture was filtered through a short plug of silica gel, eluting with ether. The yield and the regioselectivity were determined to be respectively 18% and 1:20 b:l by ^{19}F NMR analysis of the crude compound.[19] After a second run, the yield and the regioselectivity were determined to be respectively 17% and 1:20 b:l; average yield was 18% and average b:l ratio was 1:20 b:l. ^{19}F NMR (282 MHz, $CDCl_3$, linear product) δ –212.51 (m).



17b:17l = 8.0:1

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-((-4-fluorohex-5-en-1-yl)oxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,12-diyl diacetate (17b). The general procedure was followed, using **16** (223.5 mg, 0.4 mmol), palladium(II)

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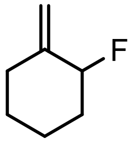
[18] Katcher, M. H.; Doyle, A. G. *J. Am. Chem. Soc.* **2010**, *132*, 17402–17404.

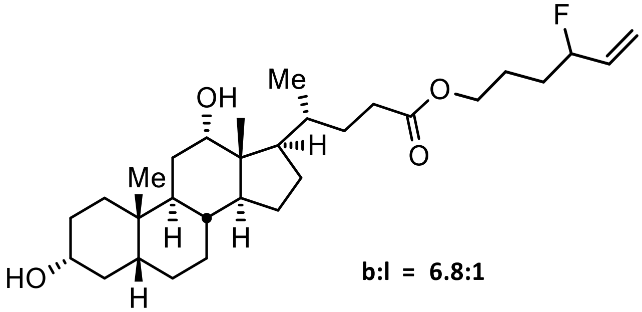
[19] The yields are determined by comparing integration of the ^{19}F NMR (282 MHz, $CDCl_3$, 23 ºC) resonance of fluorobenzene (–115.3 ppm)

trifluoroacetate (20 mg, 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (15 mol%, 0.06 mmol), (*R,R*)-Cr(salen)Cl (10 mol%, 0.04 mmol), benzoquinone (2.0 equiv, 0.8 mmol), 1,2-dichloroethane (200 µL) and Et_3N•3HF (400 µL, 2.4 mmol). Purification by hand column chromatography (silica gel, 0→10→20% ether in hexanes) afforded the title compound (138 mg, 0.24 mmol, 60% yield) as a colorless oil. The regioselectivity was determined to be 8.0:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 131 mg, 0.23 mmol, 57% yield and the b:l ratio was 7.9:1; average yield was 59% and average b:l ratio was 8.0:1. FTIR (thin film, cm^{-1})) 2940 (m), 2868 (m), 1731 (s), 1449 (w), 1377 (m), 1362 (w), 1239 (s), 1168 (w), 1025 (s), 971 (m), 911 (w), 750 (w); ^{1}H NMR (500 MHz, $CDCl_3$; linear isomer indicated by *): δ 5.79–5.92 (m, 1H, 1H*), 5.65–5.71 (m, 1H*), 5.33 (dm, J = 17.4 Hz, 1H), 5.24 (dm, J = 10.2 Hz, 1H), 5.08 (t, J = 2.9 Hz, 1H, 1H*), 4.91 (dm, J = 48.8 Hz, 1H), 4.85 (t, J = 6.2 Hz, 1H, 1H*), 4.66–4.78 (m, 1H, 3H*), 4.05–4.13 (m, 2H, 2H*), 2.14–2.36 (m, 3H, 3H*), 2.10 (s, 3H, 3H*), 2.04 (s, 3H, 3H*),0.97–1.90 (m, 26H, 26H*), 0.90 (s, 3H, 3H*), 0.80 (d, J = 6.4 Hz, 3H, 3H*), 0.72 (s, 3H, 3H*); ^{13}C NMR (125 MHz, $CDCl_3$; linear isomer indicated by *) δ 174.34, 174.34*, 170.76, 170.76*, 170.69, 170.69*, 136.26 (d, *J* = 19.6 Hz), 135.78* (d, *J* = 12.0 Hz), 125.52* (d, *J* = 16.5 Hz), 117.44 (d, *J* = 11.9 Hz), 93.22 (d, *J* = 167.7 Hz), 83.52* (d, *J* = 160.9 Hz), 76.03, 76.03*, 74.34, 74.34*, 63.97, 63.66*, 49.54, 49.54*, 47.75, 47.75*, 45.11, 45.11*, 41.93, 41.93*, 35.77, 35.77*, 34.83, 34.83*,34.82, 34.82*, 34.51, 34.51*, 34.16, 34.16*, 32.37, 32.37*, 31.82 (d, *J* = 22.6 Hz), 31.34, 31.34*, 30.95, 30.95*, 28.68* (d, *J* = 2.0 Hz), 27.82* (d, *J* = 3.1 Hz), 27.49, 27.49*, 27.00, 27.00*,26.76, 26.76*, 25.98, 25.98*, 25.77, 25.77*, 24.15 (d, *J* = 4.4 Hz), 23.55, 23.55*, 23.23, 23.23*, 21.66, 21.66*, 21.58, 21.58*, 17.62, 17.62*, 12.55, 12.55*; ^{19}F NMR (282 MHz, $CDCl_{3,}$ linear isomer indicated by *) –171.27, –202.08; HRMS (ESI+) calculated for $C_{34}H_{53}FNaO_6$ ($[M+Na]^+$): 599.3724, found: 599.3711.

VII. Fluorination with additional substrates

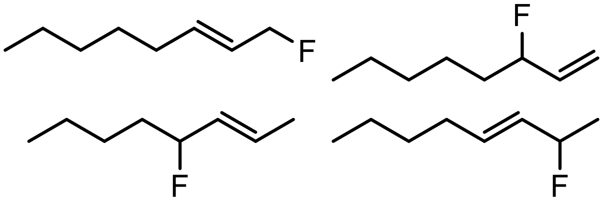


1-fluoro-2-methylenecyclohexane (P1).[18] For this product, a NMR yield was obtained : a 2.5 mL polypropylene vial was sequentially charged with a stir bar, palladium(II)trifluoroacetate (20 mg 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18.4 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25.2 mg, 0.04 mmol), benzoquinone (88 mg, 0.8 mmol), 1,2-dichloroethane (200 µL), methylenecyclohexane (48.1 µL, 0.4 mmol), fluorobenzene (30 µL, 0.8 equiv) as internal ^{19}F NMR standard, and Et_3N•3HF (400 µL, 2.4 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 600 rpm at 23 °C for 72 hours. After 72 h, the reaction mixture was filtered through a short plug of silica gel, eluting with ether. The yield was determined to be 8% by ^{19}F NMR analysis of the crude compound. ^{19}F NMR (282 MHz, $CDCl_3$, linear product) δ –178.05 (m).



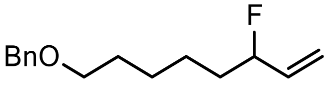
b:l = 6.8:1

4-fluorohex-5-en-1-yl (4R)-4-((3R,5R,8R,9S,10S,12S,13R,14S,17R)-3,12-dihydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (P2). The general procedure was followed using olefin **S3**, palladium(II)trifluoroacetate (15 mol%), 1,2-bis(benzylsulfinyl)ethane **L2** (15 mol%), (*R,R*)-Cr(salen)Cl (10 mol%), benzoquinone (2.0 equiv), 1,2-dichloroethane (2 M) and Et_3N•3HF (6 equiv). However, the hygroscopic nature of substrate **S3** required that it be introduced to the reaction vials in solution followed by removal of solvent *in vacuo*, resulting in a variable amount of starting material. The quantities of all other reagents were adjusted accordingly. Two runs were conducted using the following quantities of substrate **S3**: 101 mg (0.213 mmol) and 96 mg (0.202 mmol). Purification by automated column chromatography (50 g silica gel, 50→80% ethyl acetate in hexanes) afforded the title compound (43 mg, 0.087 mmol, 41% yield) as a white solid. The regioselectivity was determined to be 6.8:1 b:l by ^{19}F NMR analysis of the isolated compound. A second run provided 44 mg, 0.089 mmol, 44% yield and the b:l ratio was 6.7:1; average yield was 43% and average b:l ratio was 6.8:1. The product was acetylated to obtain the previously characterized compound **17b**: To a solution of **P2** (43 mg, 0.087 mmol) in pyridine (4 mL) was added DMAP (5 mg, 0.04 mmol) and acetic anhydride (20 µL, 0.21 mmol). The reaction mixture was stirred at 500 rpm for 24 hours under nitrogen and at 23 °C. The pyridine was removed under vacuum and the residue was purified by automated chromatography (50 g silica gel, 5→20% ethyl acetate in hexanes) to yield the white crystalline solid **17** (35 mg, 70% yield). Comparison of the ^{1}H, ^{13}C, and ^{19}F NMR spectra confirmed the product identity.

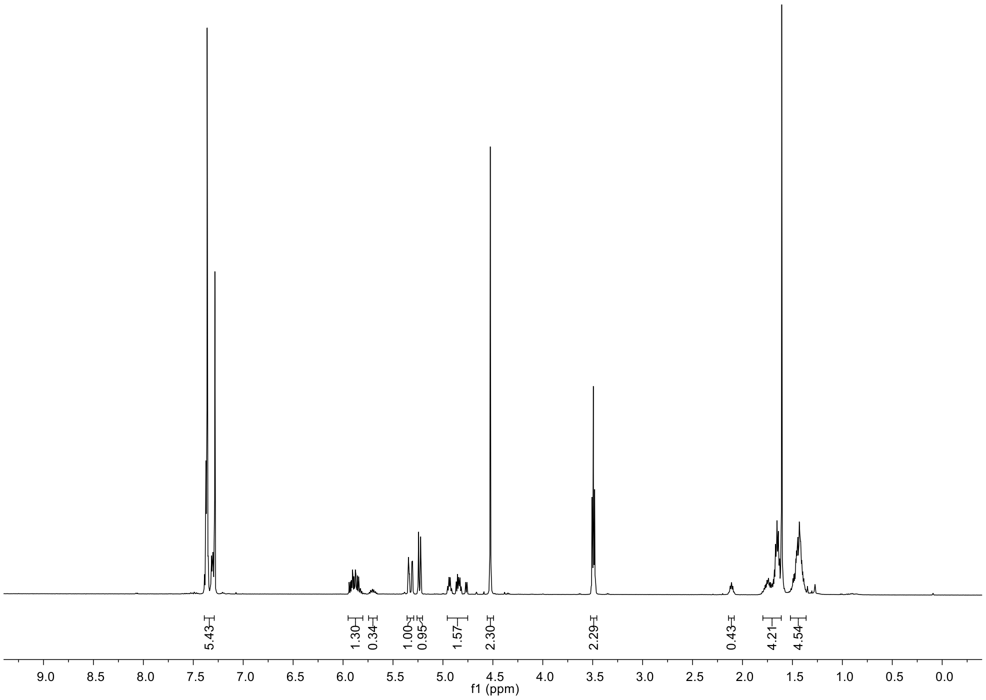


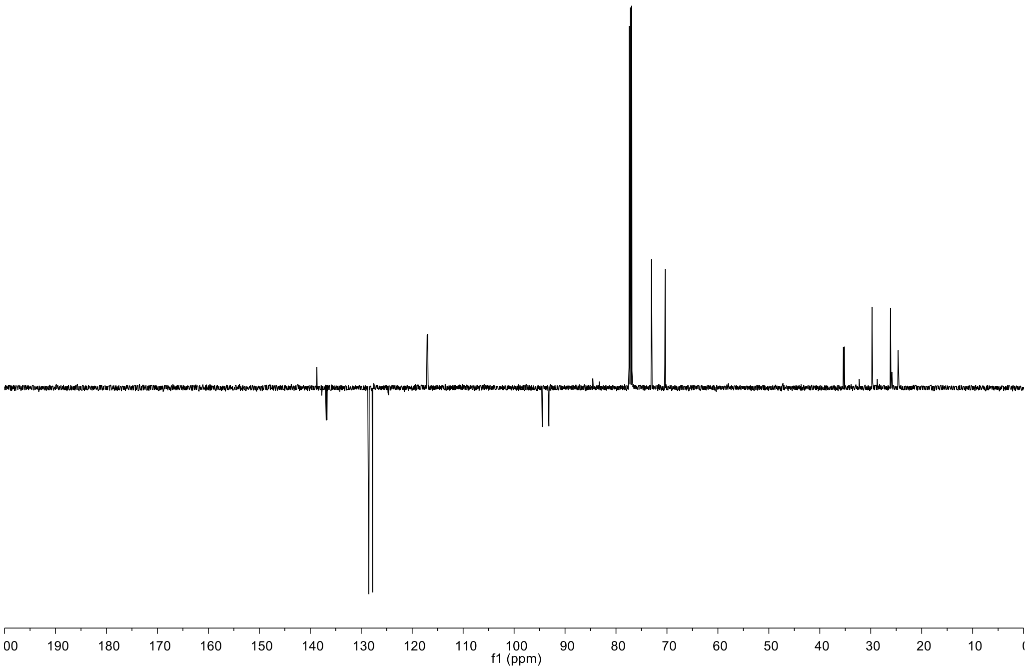
(*E*)-1-fluorooct-2-ene, (*E*)-2-fluorooct-3-ene, (*E*)-4-fluorooct-2-ene and/or **3-fluorooct-1-ene (P3).** For this product, a NMR yield was obtained: a 2.5 mL polypropylene vial was sequentially charged with a stir bar, palladium(II)trifluoroacetate (20 mg 0.06 mmol), 1,2-bis(benzylsulfinyl)ethane **L2** (18 mg, 0.06 mmol), (*R,R*)-Cr(salen)Cl (25 mg, 0.04 mmol), benzoquinone (86 mg, 0.8 mmol), 1,2-dichloroethane (200 µL), 2-octene (44.5 mg, 0.397 mmol), fluorobenzene (19.0 mg, 0.499 equiv) as internal ^{19}F NMR standard, and Et_3N•3HF (390 µL, 2.38 mmol). No precautions were taken to exclude air or moisture. The reaction vial was capped and stirred at 1000 rpm at 23 °C for 72 hours. After 72 h, the reaction mixture was filtered through a short plug of silica gel, eluting with ether. The yield was determined to be less than 1% by ^{19}F NMR analysis of the crude compound. ^{19}F NMR (376 MHz, C_6D_6, isomer not determined) δ –179.75 (m).

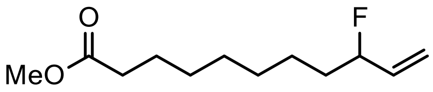
VIII. NMR Spectra



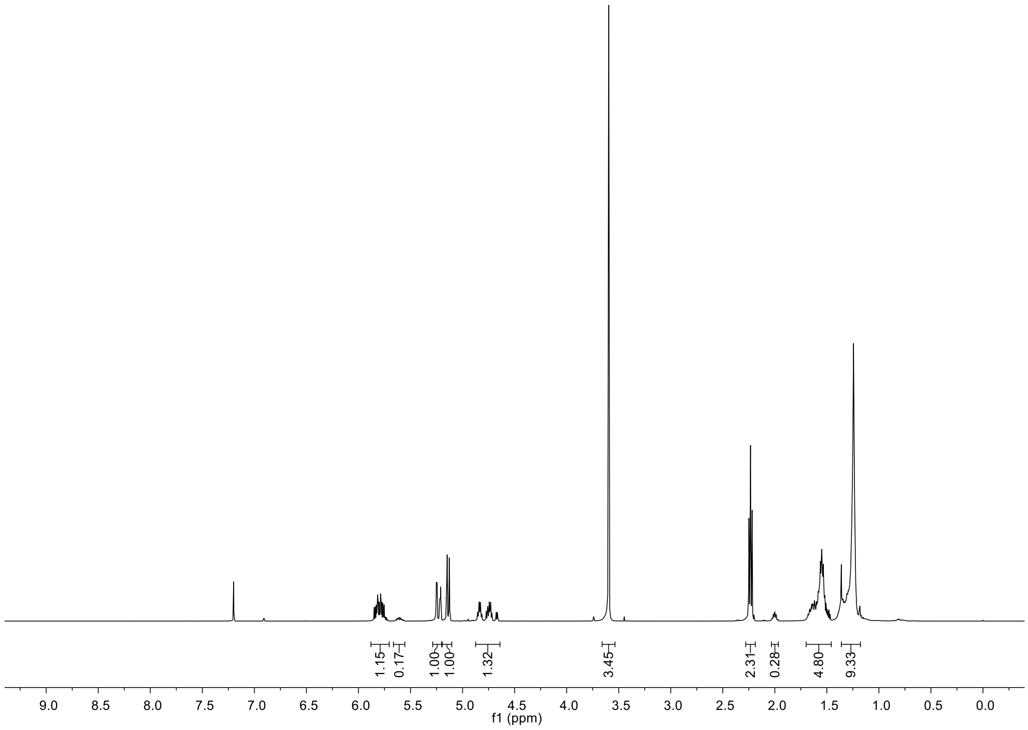
3b:3l = 6.9:1






O
MeO
F

4b:4l = 7.5:1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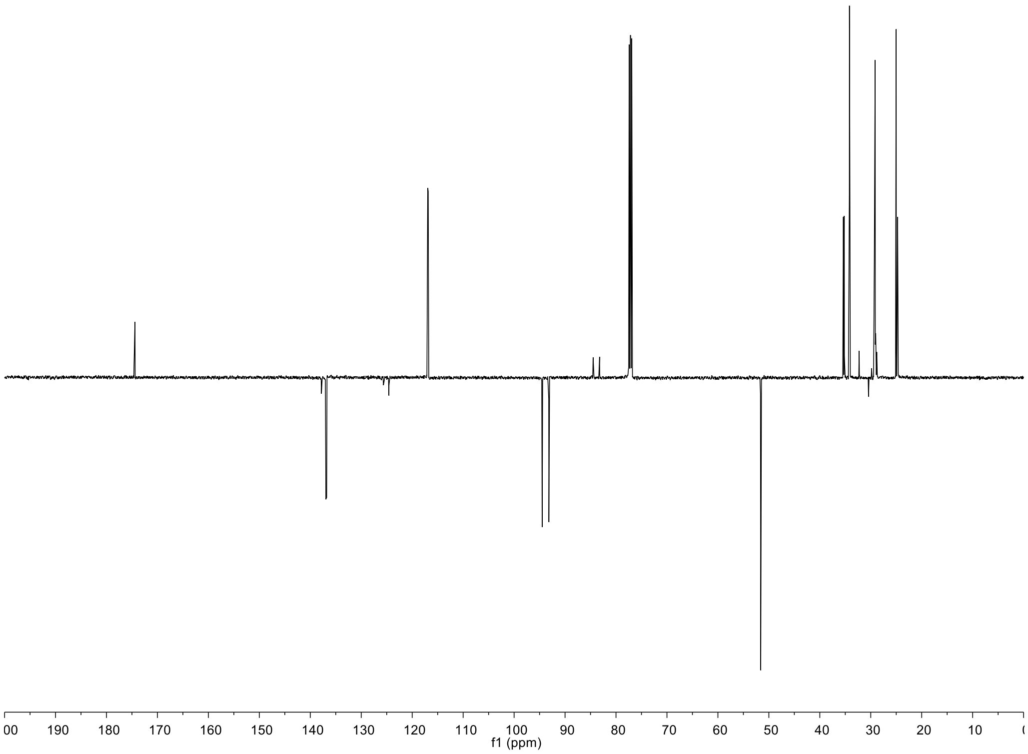
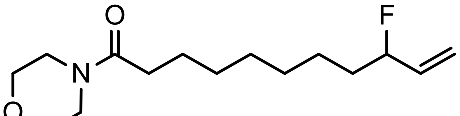
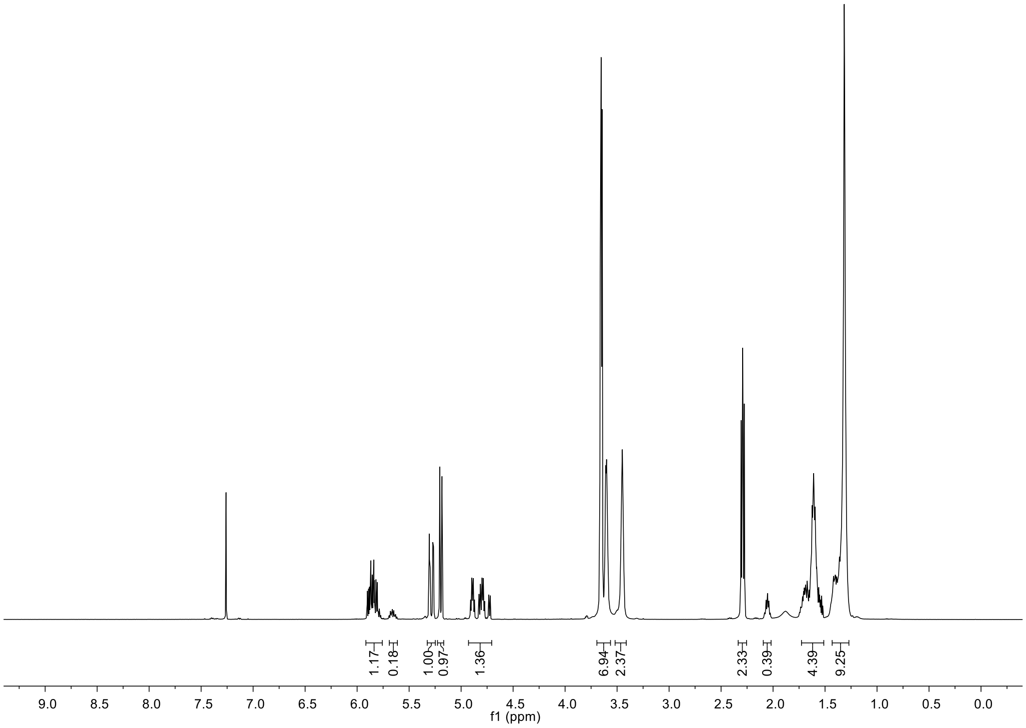
1.00
1.00
1.32
3.45
2.31
0.28
4.80
9.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
F
N
O

5b:5l = 7.0:1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1.00
0.97
1.36
6.94
2.37
2.33
0.39
4.39
9.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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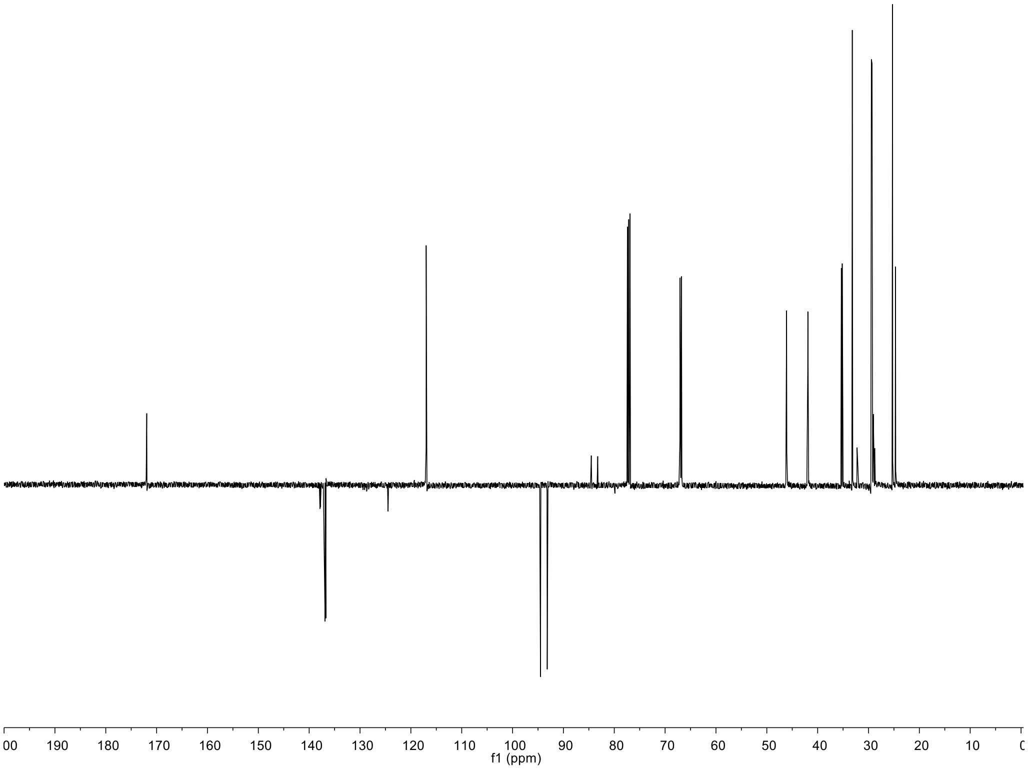
0.5
0.0
f1 (ppm)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180
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160
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140
130
120
110
100
90
80
70
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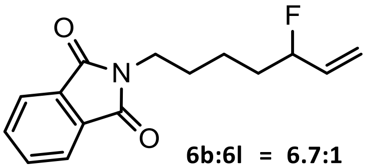
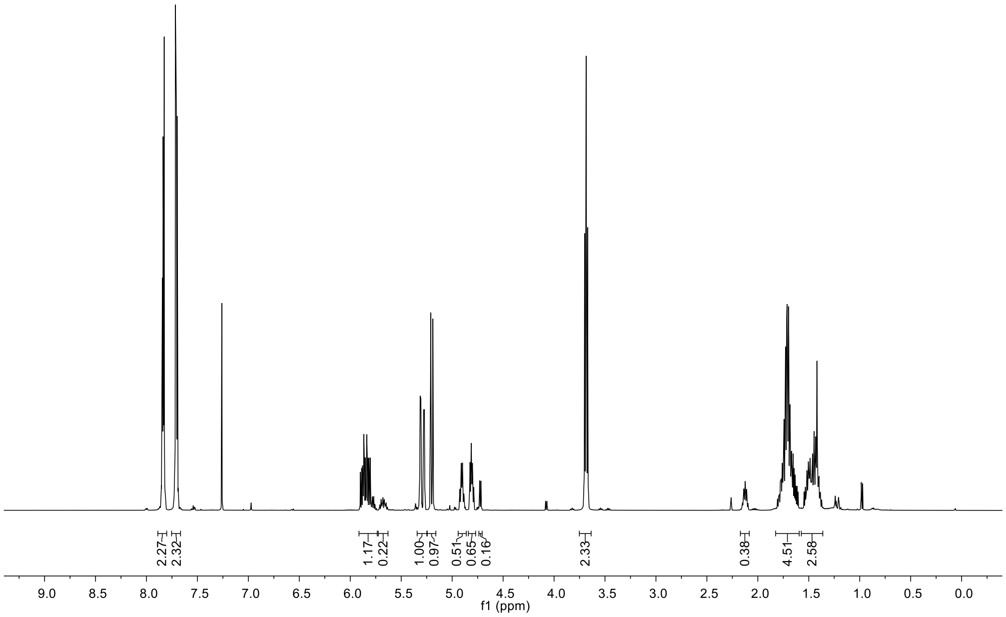
50
40
30
20
10
0
f1 (ppm)


O
N
O
F

6b:6l = 6.7:1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2.32
1.17
0.22
1.00
0.97
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0.65
0.16
2.33
0.38
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2.58
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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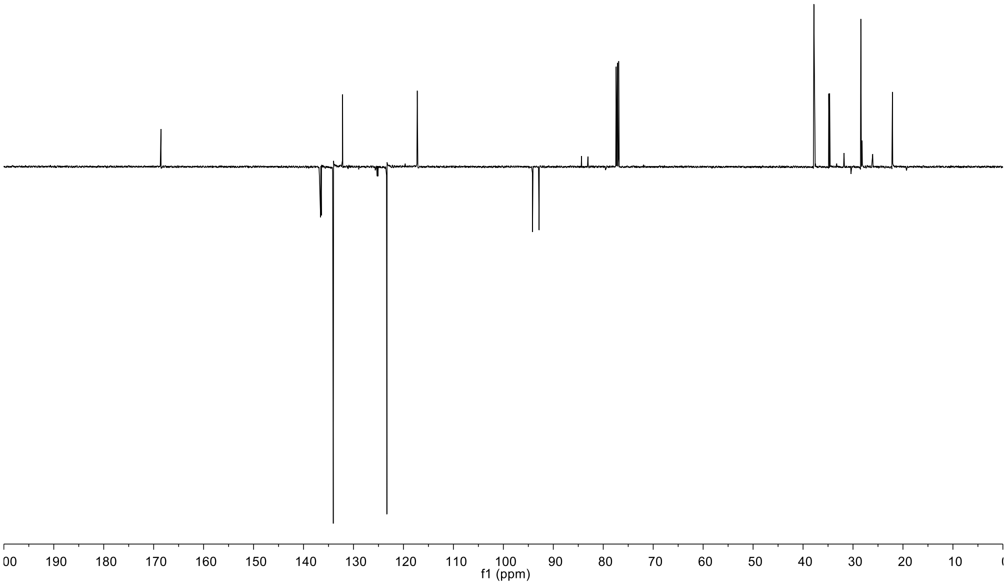
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


00
190
180
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160
150
140
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120
110
100
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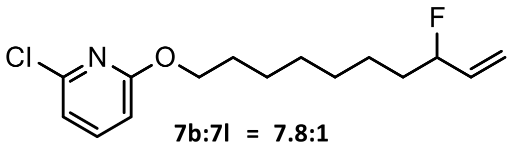
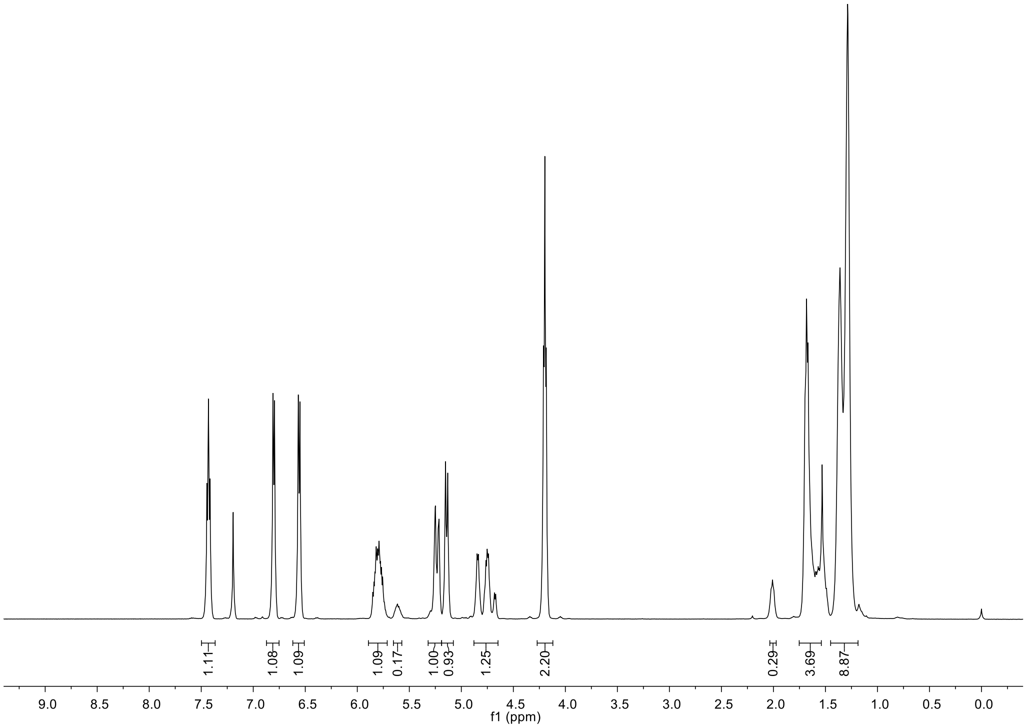
80
70
60
50
40
30
20
10
f1 (ppm)


F
Cl
N
O

7b:7l = 7.8:1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1.08
1.09
1.09
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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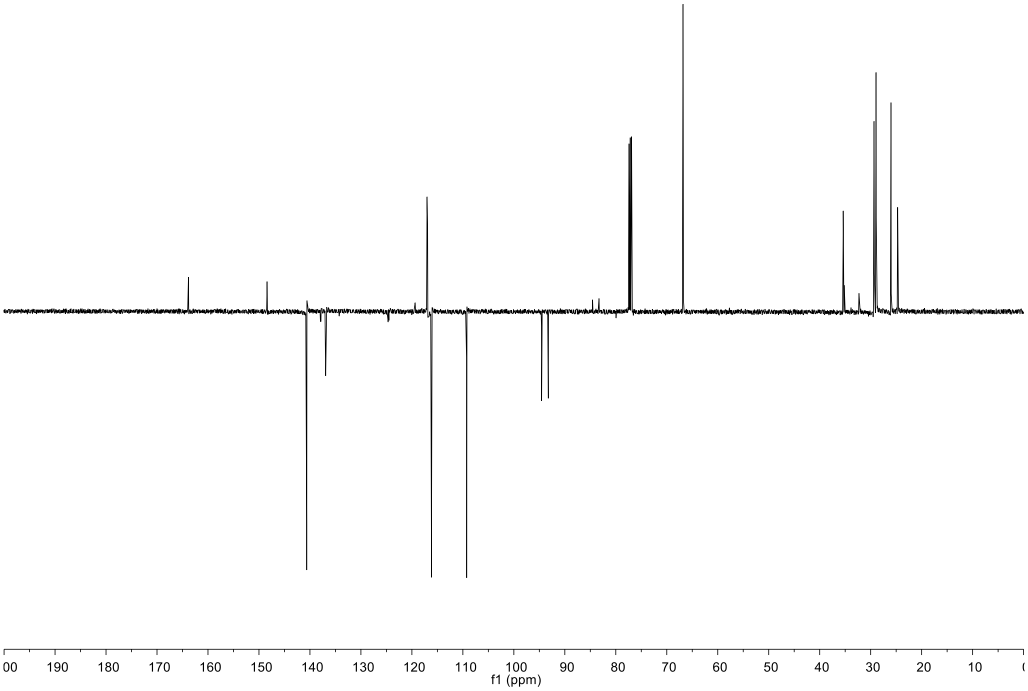
1.0
0.5
0.0
f1 (ppm)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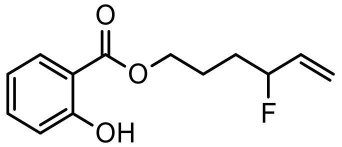
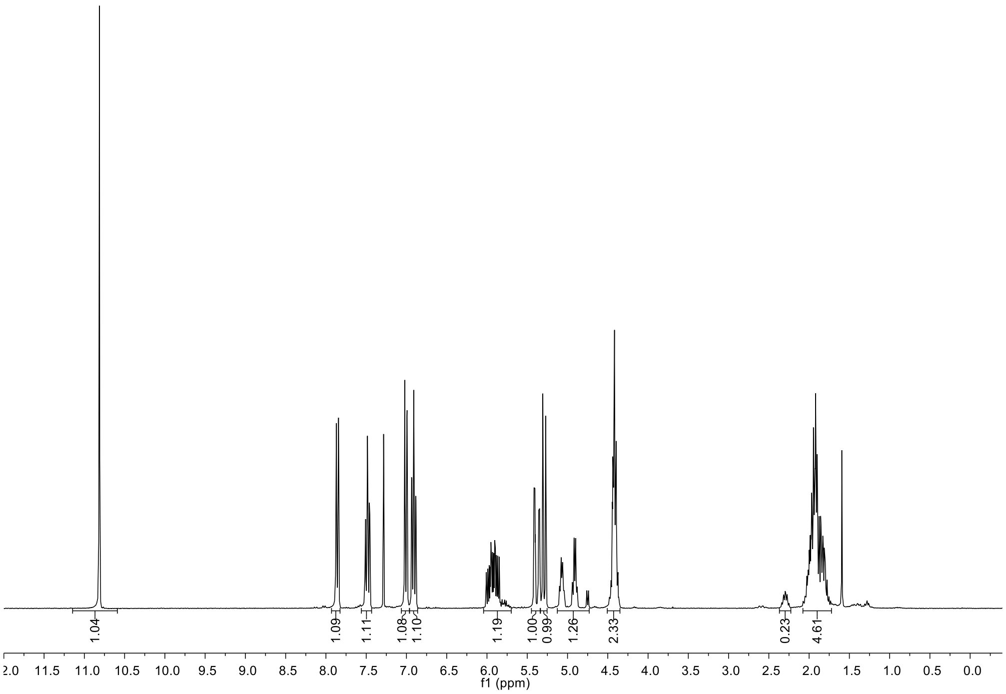
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
O
OH
F

8b:8l = 7.4:1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1.09
1.11
1.08
1.10
1.19
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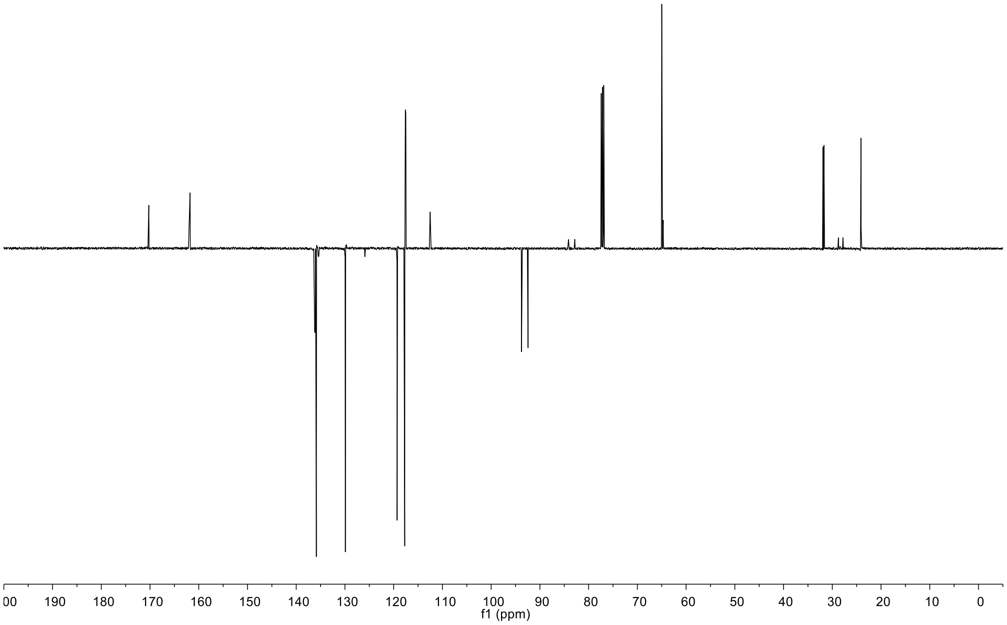
0.99
1.26
2.33
0.23
4.61
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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180
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140
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100
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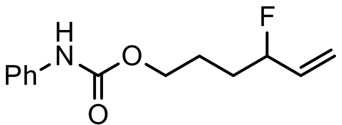
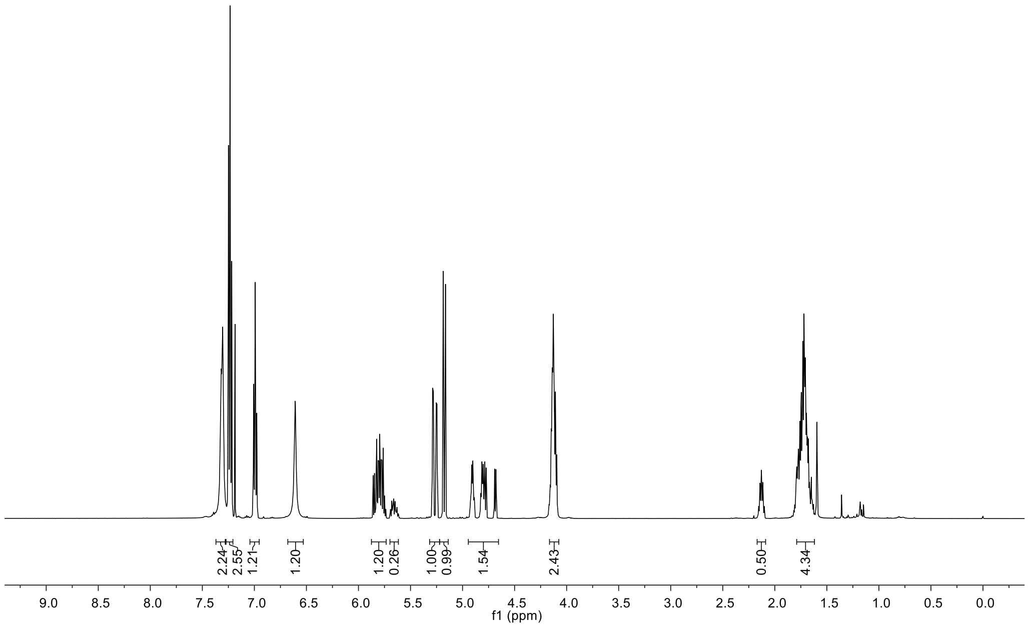
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
H
N
Ph
O
O

9b:9l = 6.5:1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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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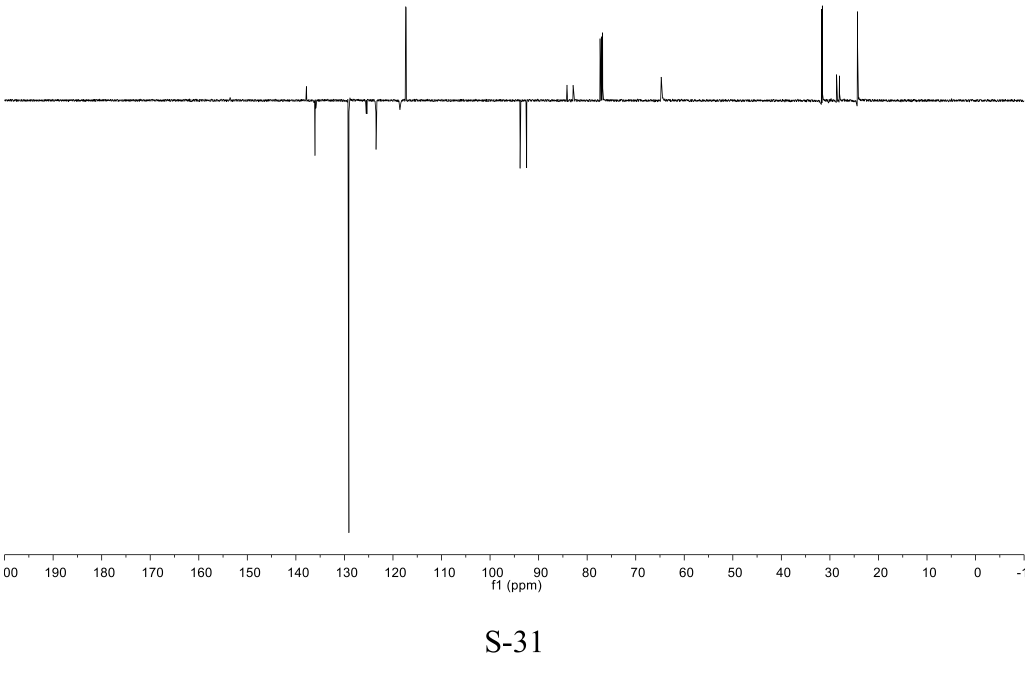
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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180
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140
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120
110
100
90
80
70
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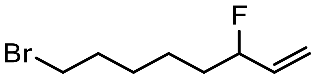
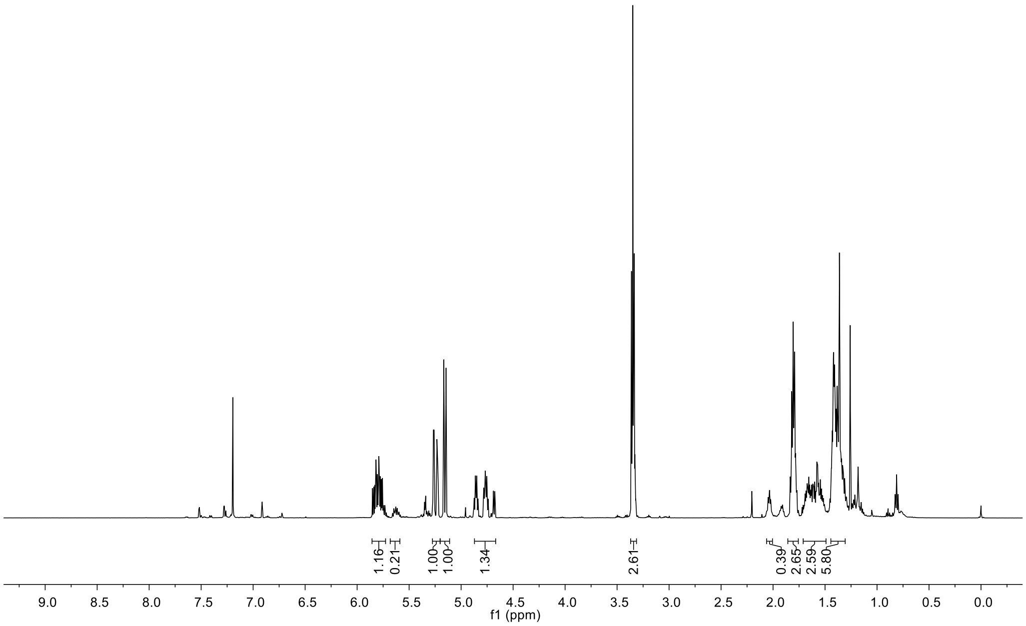
50
40
30
20
10
0
f1 (ppm)


F
Br

10b:10l = 7.0:1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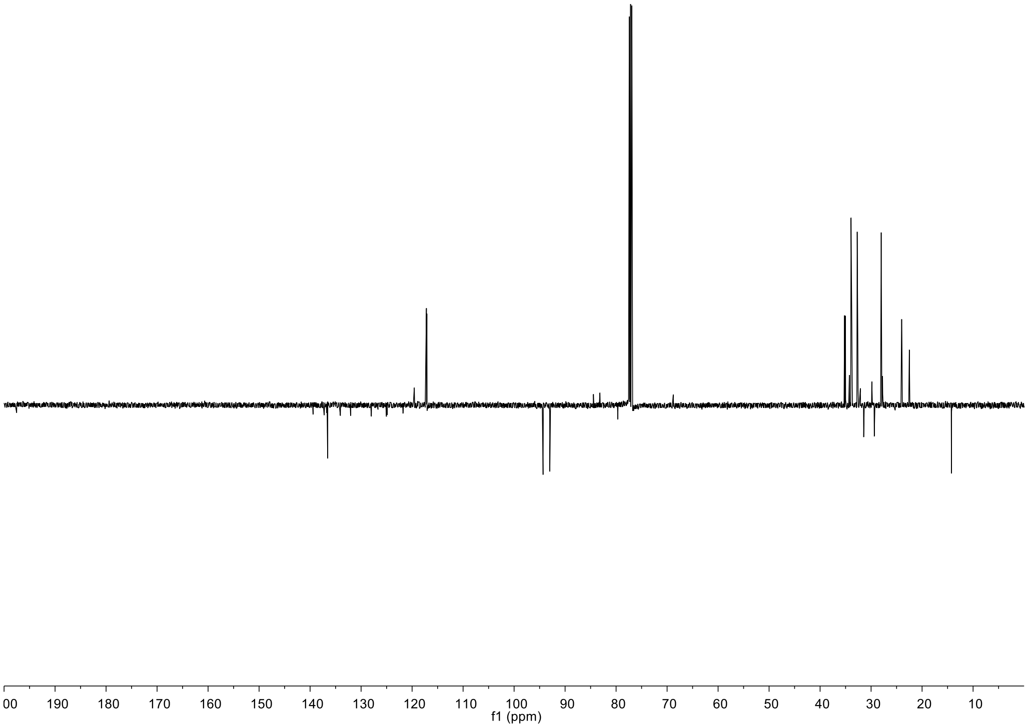
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


00
190
180
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160
150
140
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120
110
100
90
80
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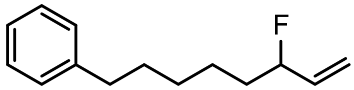
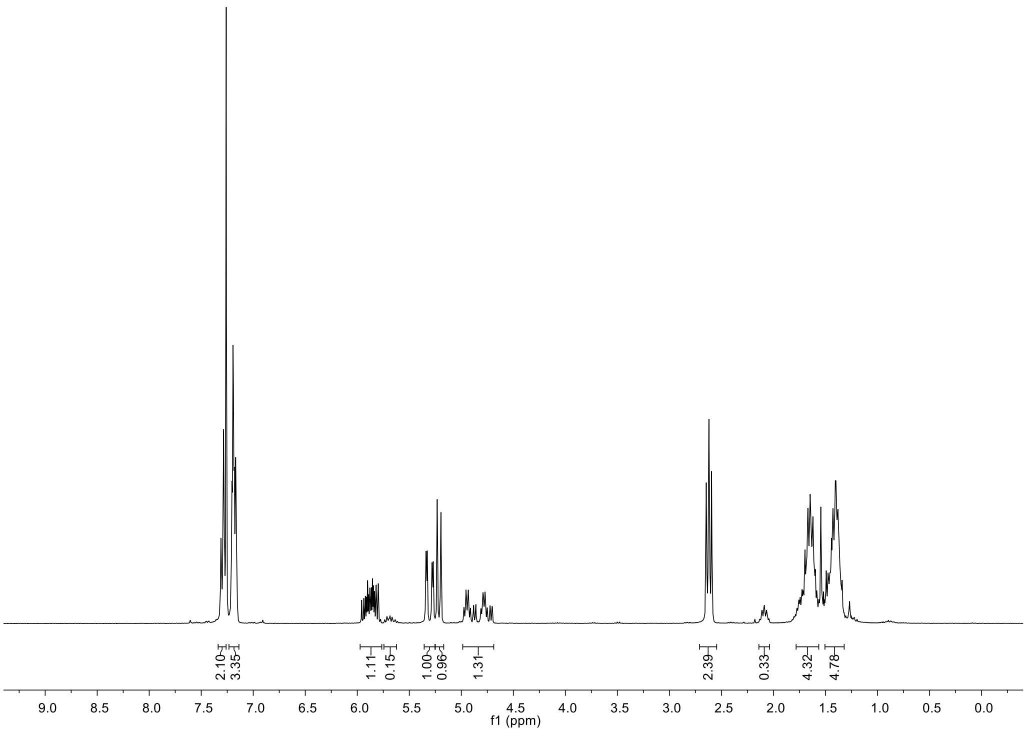
50
40
30
20
10
f1 (ppm)


F

11b:11l = 7.0:1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8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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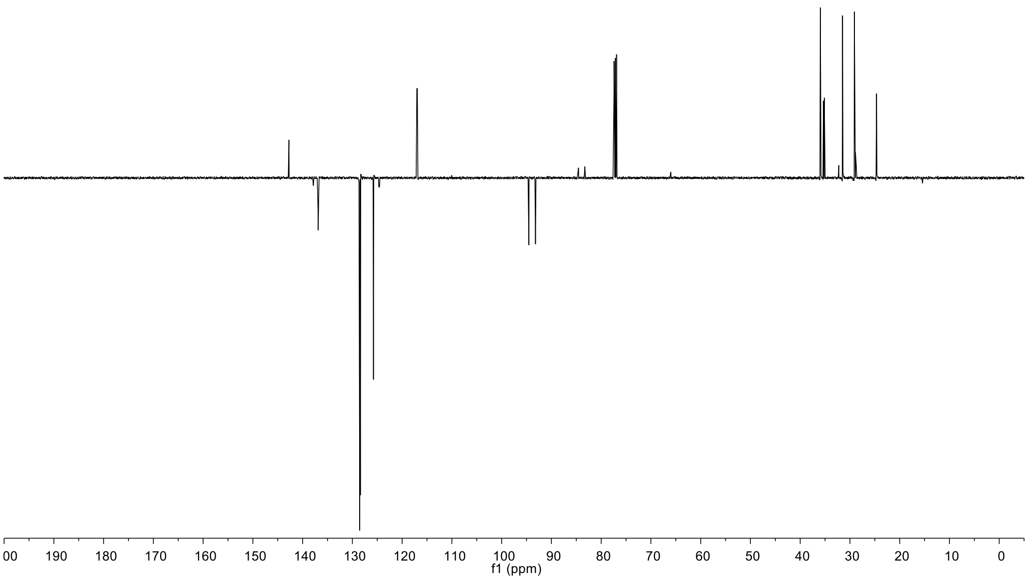
0.0
f1 (ppm)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110
100
90
80
70
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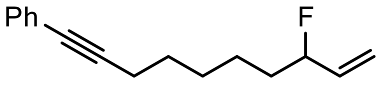
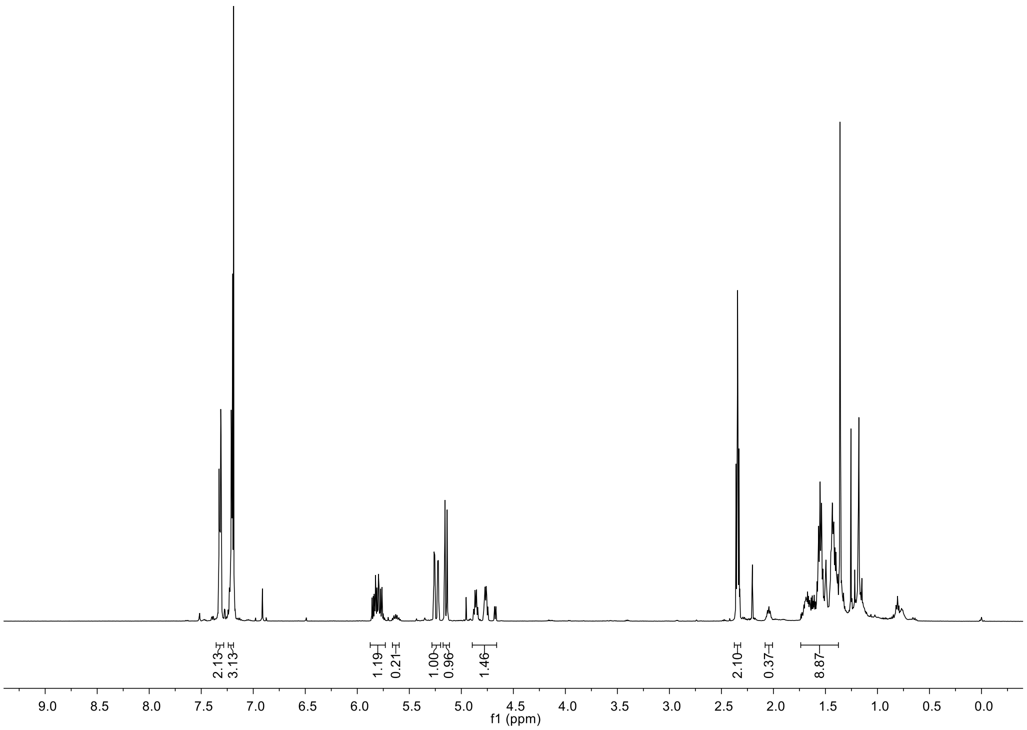
50
40
30
20
10
0
f1 (ppm)


Ph
F

12b:12l = 7.5:1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8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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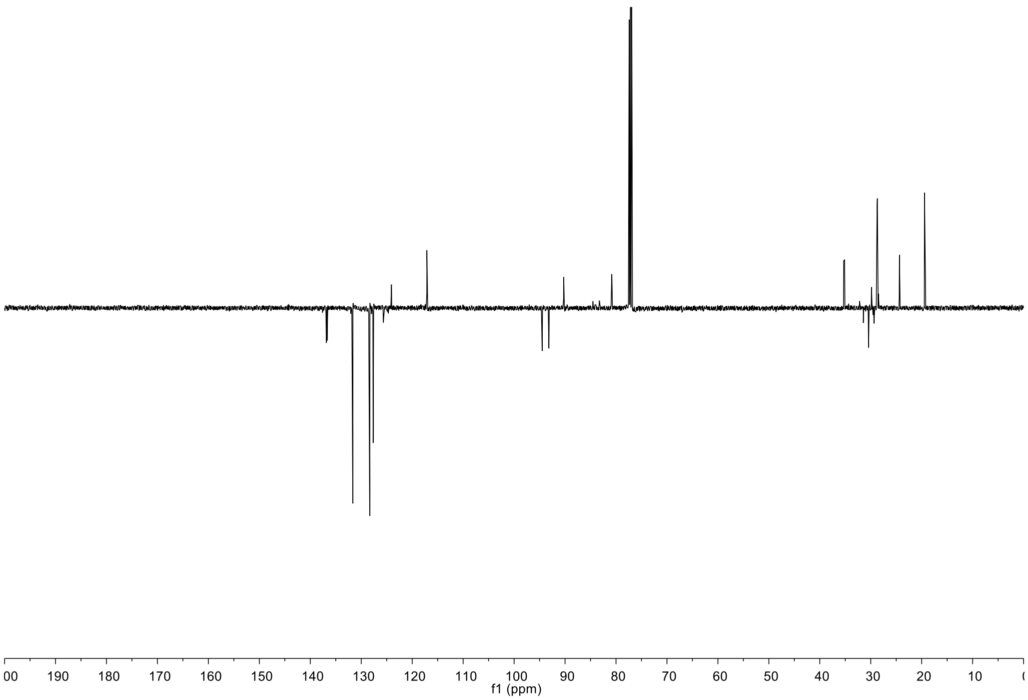
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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100
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80
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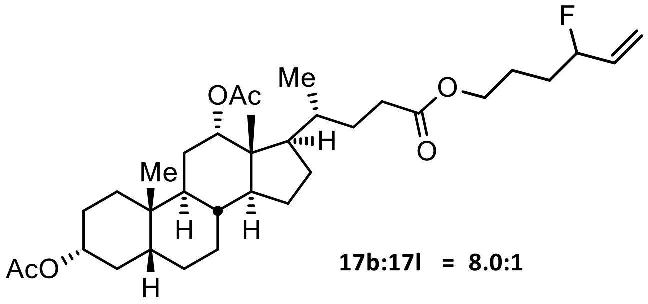
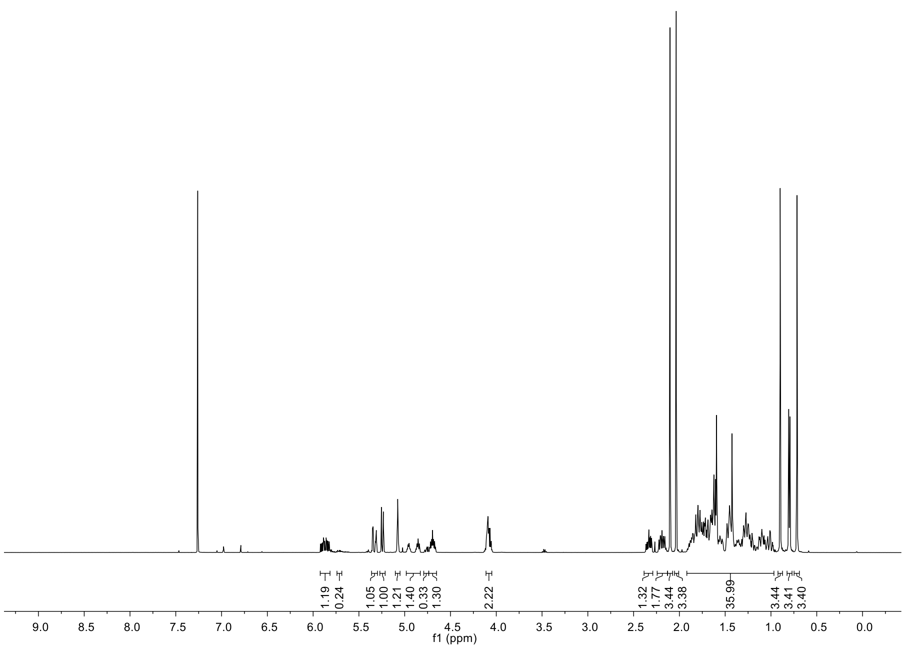
20
10
f1 (ppm)


F
Me
OAc
O
O
Me
H
H
H
AcO
H

17b:17l = 8.0:1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35.99
3.44
3.41
3.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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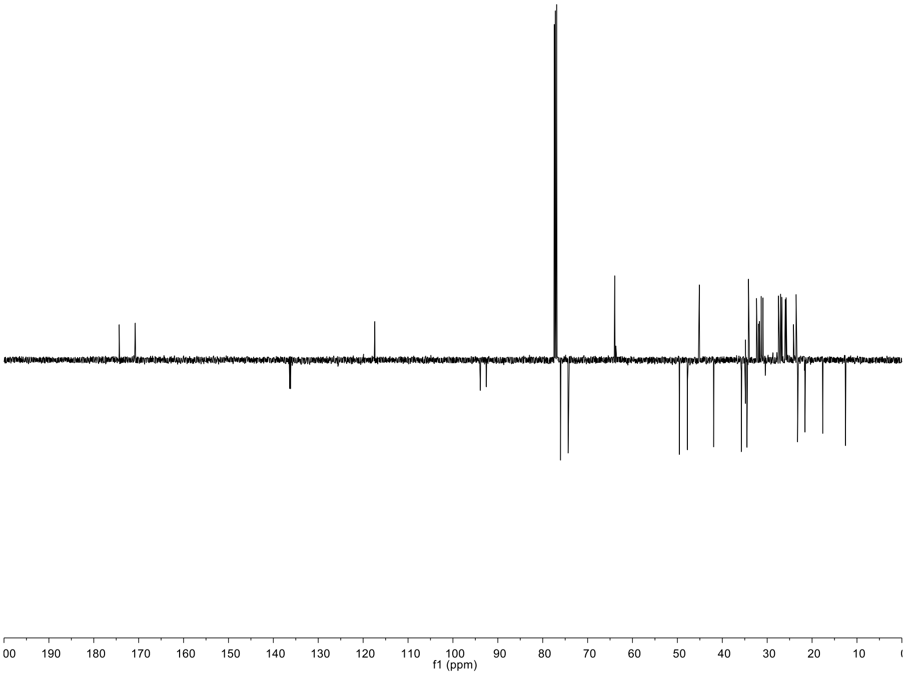
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


00
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)