

**Diastereodivergent Reductive Cross Coupling of Alkynes
Through Tandem Catalysis: *Z*- and *E*-Selective
Hydroarylation of Terminal Alkynes**

Megan K. Armstrong[†], Madison B. Goodstein[†] and Gojko Lalic*

Department of Chemistry, University of Washington, Seattle, Washington 98195, United States

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1. General Information

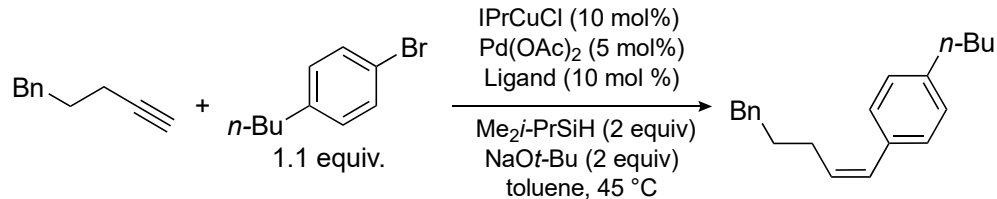
All reactions were performed under a nitrogen atmosphere with flame-dried or oven-dried (120 °C) glassware, using standard Schlenk techniques, or in a glovebox (Nexus II from Vacuum Atmospheres). Column chromatography was performed using a Biotage Iso-1SV flash purification system with silica gel from Agela Technologies Inc. (60Å, 40-60 µm, 230-400 mesh). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer. IR peak absorbencies are represented as follows: s = strong, m = medium, w = weak, br = broad. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ¹H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual solvent peak (CDCl₃ (7.26 ppm)). ¹³C NMR chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.2 ppm). ¹⁹F NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to the internal standard, hexafluorobenzene. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet), coupling constants in Hertz (Hz), integration. Mass spectra were collected on a JEOL HX-110 mass spectrometer. GC analysis was performed on a Shimadzu GC-2010 instrument with a flame ionization detector and a SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 µm film thickness). The following temperature program was used: 2 min @ 60 °C, 13 °C/min to 160 °C, 30 °C/min to 250 °C, 5.5 min @ 250 °C.

Materials: THF, CH₂Cl₂, Ether, benzene, and toluene were degassed and dried by passing through columns of neutral alumina. Anhydrous methanol was purchased from Millipore Sigma, and was subsequently degassed and stored over 4Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were stored over 4Å molecular sieves prior to use. Commercial reagents were purchased from Millipore Sigma, TCI America, GFS-Chemicals, Ark-Pharm, Combi-Blocks, Oakwood Chemicals, Strem Chemicals and Alfa Aesar. Dimethylisopropylsilane (Me₂i-PrSiH) was purchased from Gelest Inc and was degassed and stored over 4Å molecular sieves.

2. Reaction Development

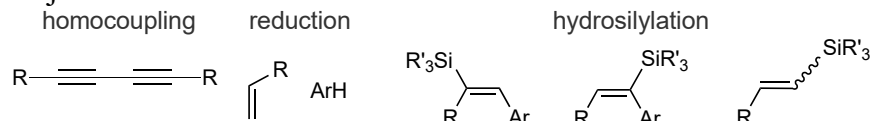
All reactions were performed on a 0.05 mmol scale with the stoichiometry shown in Tables S1-S3. In a nitrogen-filled glovebox a dram vial was charged with a stir bar, NaOt-Bu, 5-phenyl-1-pentyne, 1,3,5-trimethoxy benzene (TMB, used as an internal standard for GC), Pd(OAc)₂, IPrCuCl, ligand (Table S1), 1-bromo-4-butylbenzene, silane (Table S2) and toluene. The reaction mixture was stirred at 45 °C and monitored by Gas Chromatography for reaction completion. Aliquots were taken at 4 h, 8 h, and 24 h time points.

Table S1.
Ligand screen



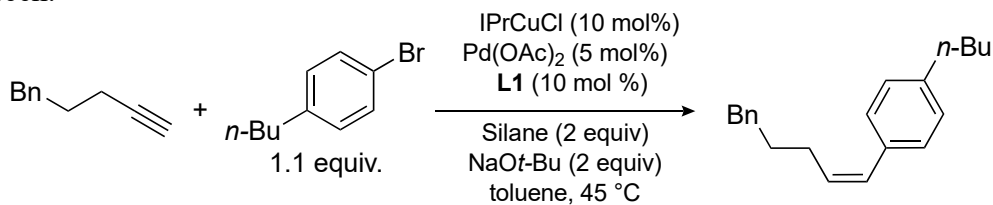
Entry	Ligand	Temperature (°C)	Time (h)	Yield (%)
1	Xphos	45	24	8
2	L1	45	24	47
3	L1	25	24	0
4	Ruphos	45	24	1
5	PCy ₃	45	24	0
6	dppf	45	24	0
7	dppp	45	24	0
8	Segphos	45	24	0
9	Davephos	45	24	21
10	BINAP	45	24	0
11	Xyl-MeOBIPHEP	45	24	0
12	DACH Trost	45	24	0
13	Sphos	45	24	26
14	Qphos	45	24	13

Major Side Products^a



^aSide products determined by GC-MS analysis of the aliquots and known palladium chemistry.

Table S2.
Silane screen.



Entry	Silane	Time (h)	Sonogashira Yield (%)	Z-alkene Yield (%)
1	Me ₂ PhSiH	24	5	27
2	MePh ₂ SiH	24	5	18
3	Ph ₃ SiH	24	9	10
4	Ph ₂ SiH ₂	24	0	0
5	PhSiH ₃	24	0	0
6	Et ₃ SiH	24	3	0
7	<i>t</i> -Bu ₂ SiH ₂	24	0	6
8	Me ₂ <i>i</i> -PrSiH	24	91	0
9	<i>t</i> -Bu ₂ MeSiH	24	86	0

10	(<i>O</i> - <i>t</i> -Bu) ₂ MeSiH	24	0	25
11	(OEt) ₃ SiH	24	2	0
12	(OMe) ₂ MeSiH	24	0	0
13	(OEt) ₂ MeSiH	24	0	0
14	TMDSO	24	10	12
15	PMHS	24	1	6

Table S3.

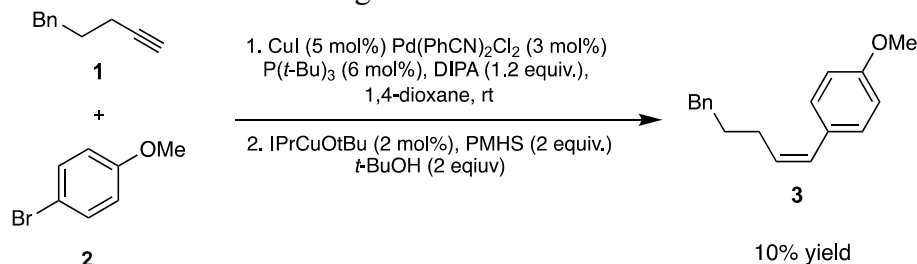
Alcohol additive screen.

Entry	Alcohol	Time (h)*	Sonogashira Yield (%)	Z-alkene Yield (%)	Z:E Ratio
1	MeOH	4	0	100	33/1
2	<i>i</i> -BuOH	4	0	100	25/1
3	Neopentanol	4	0	100	21/1
4	<i>t</i> -BuOH	4	73	27	--
5	<i>i</i> -PrOH	4	17	58	--

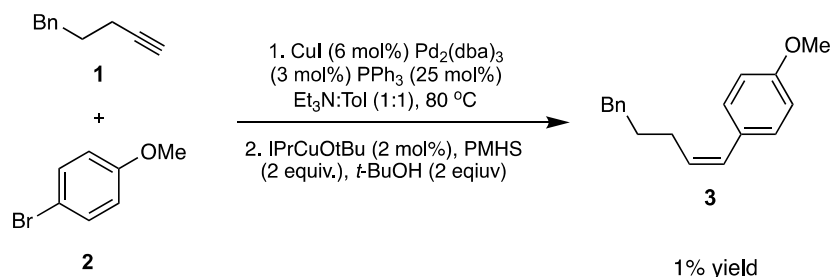
3. Standard Sonogashira Coupling Followed by in Situ Semireduction

General Procedure

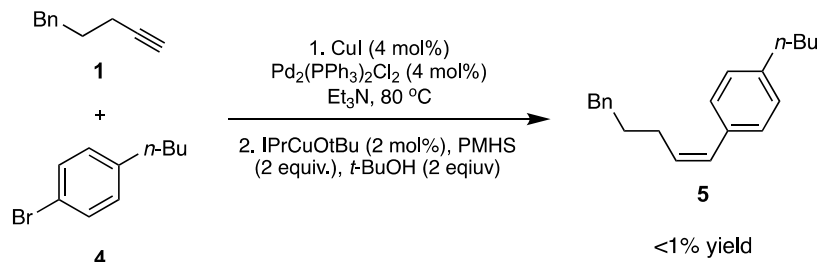
All manipulations were performed in a nitrogen-filled glovebox. Each Sonogashira coupling was performed according to the procedure reported in the literature. Reactions were performed on a 0.05 mmol scale and monitored by GC. Sonogashira coupling was determined to be complete upon full consumption of the aryl bromide. Standard semireduction conditions¹¹ were then applied, and reactions were allowed to stir at 25 °C for 1 h, at which point a 30 μL aliquot was taken, pushed through a plug of silica with EtOAc, and analyzed by GC. Every reaction was heated to 45 °C, 60 °C and 90 °C to encourage semireduction. At each temperature, reactions were monitored by GC, and if no change was seen after 1 h, reactions were moved to the next temperature. Reactions were monitored at 90 °C until no further change occurred.



Sonogashira coupling¹² determined complete at 16 h. Semireduction was stopped at 20 h. Yield determined by GC.



Sonogashira coupling¹³ determined complete at 24 h. Semireduction was stopped at 24 h. Yield determined by GC.

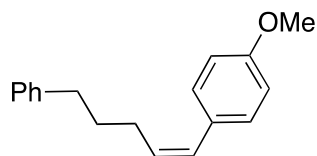


Sonogashira coupling¹⁴ determined complete at 16 h. Semireduction was stopped at 24 h. Yield determined by GC.

4. General Procedure for the Hydroarylation of Terminal Alkynes: Synthesis of Z-Alkenes

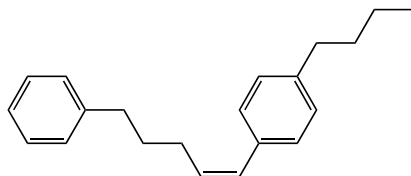
In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaOt-Bu (96.1 mg, 1.00 mmol, 2.0 equiv). To this was added alkyne (0.50 mmol, 1.0 equiv), Pd(OAc)₂ (2.8 mg, 0.025 mmol, 0.100 equiv) IPrCuCl (24.4 mg, 0.050 mmol, 0.10 equiv), **L1** (19 mg, 0.050 mmol, 0.10 equiv), aryl bromide (0.550 mmol, 1.10 equiv), Me₂*i*-PrSiH (102.3 mg, 1.00 mmol, 2.00 equiv), and toluene (5 mL). The reaction mixture was stirred at 45 °C, and the reaction progress was monitored by TLC. When the starting alkyne was fully consumed, methanol (24.0 mg, 0.750 mmol, 1.5 equiv) was added and stirring was continued at 45 °C. Upon consumption of the internal alkyne (as monitored by TLC), the reaction mixture was diluted with diethyl ether and filtered through a pad of silica gel. An aliquot was analyzed by GC to obtain the diastereoselectivity of the reactions. The crude reaction mixture was concentrated under reduced pressure and the product was purified by silica gel chromatography. The ratio of stereoisomers for each product was again determined by GC analysis of the isolated product.

5. Characterization of Hydroarylation Products: Z-alkenes

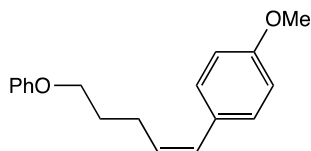


1-methoxy-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (3), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 20:1). The compound was purified by silica gel chromatography (EtOAc/Hex 0→10%) and a filtration through a short

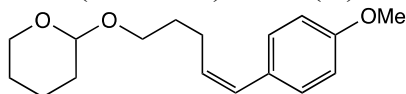
plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (110.0 mg, 87% yield, Z:E = 28:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.44 – 7.17 (m, 7H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 11.7 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.88 (s, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.27 (dt, *J* = 7.6, 7.2 Hz, 2H), 1.87 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.6, 142.7, 131.3, 130.7, 130.3, 129.0, 128.8, 128.6, 126.1, 113.9, 55.6, 35.9, 32.1, 28.5. GCMS (EI) calculated for [M]⁺ 252.15, found 252.3. FTIR (neat, cm⁻¹): 3028(m), 3006(m), 2924(m), 2857(m), 1605(s), 1508(s), 1247(s), 673(s).



1-butyl-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (5), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (100% Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 19:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 5%) and isolated as a colorless oil (113 mg, 81% yield, Z:E = 19:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 6.99 (m, 11H), 6.41 (d, *J* = 11.6 Hz, 1H), 5.65 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.81 – 2.49 (m, 5H), 2.49 – 2.30 (m, 3H), 1.93-1.69 (m, 2H), 1.69 – 1.52 (m, 2H), 1.47 – 1.28 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 141.3, 135.3, 131.9, 129.4, 128.8, 128.6, 128.4, 128.3, 125.8, 35.7, 35.5, 33.7, 31.8, 28.3, 22.5, 14.1. GCMS (EI) calculated for [M]⁺ 278.20, found 278.3. FTIR (neat, cm⁻¹): 3062(m), 2955(m), 2929(m), 2857(m), 1604(s), 1454(s), 844(s), 752(s) 699(s).

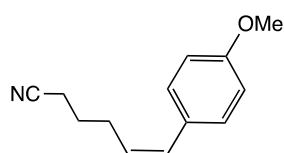


1-methoxy-4-[(1Z)-5-phenoxy-pent-1-en-1-yl]benzene (6), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 3 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 80:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 10%) and isolated as a colorless oil (105 mg, 78% yield, Z:E > 100:1). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.27 – 7.20 (m, 2H), 6.98 – 6.90 (m, 1H), 6.92 – 6.82 (m, 4H), 6.41 (d, *J* = 11.5 Hz, 1H), 5.68 – 5.55 (m, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.53 (q, *J* = 7.3 Hz, 2H), 1.95 (p, *J* = 6.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.1, 158.4, 130.3, 130.1, 129.5, 129.3, 120.7, 120.1, 114.7, 113.7, 67.3, 55.4, 29.7, 25.3. GCMS (EI) calculated for [M]⁺ 268.15, found 268.1. FTIR (neat, cm⁻¹): 3005 (m), 2937(m), 2863(m), 2172(m), 1601(s), 1510(s), 837(s), 753(s) 691(s).

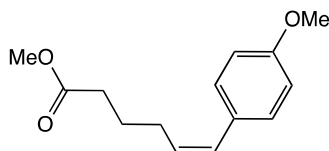


2-[[4-(1Z)-5-(4-methoxyphenyl)pent-4-en-1-yl]oxy]oxane (7), compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC

in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 9:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 30%) and isolated as a colorless oil (104 mg, 75% yield, Z:E = 10:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 11.4 Hz, 1H), 5.58 (dt, *J* = 11.4, 7.3 Hz, 1H), 4.55 (s, 1H), 3.87 – 3.73 (m, 5H), 3.52 – 3.37 (m, 2H), 2.53 – 2.23 (m, 2H), 1.89 – 1.41 (m, 8H). ¹³C NMR (75 MHz, CDCl₃) δ 158.3, 130.8, 130.5, 130.1, 128.8, 113.7, 98.95, 67.0, 62.4, 55.4, 30.9, 30.2, 25.6, 25.4, 19.7. GCMS (EI) calculated for [M]⁺ 276.17, found 276.3. FTIR (neat, cm⁻¹): 3006(m), 2942(m), 2869(m), 2246(s), 1608(s), 1511(s), 839(s), 734(m).

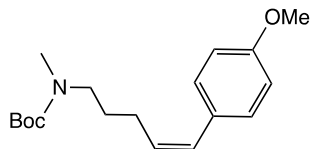


(5Z)-6-(4-methoxyphenyl)hex-5-enitrile (8), compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 3 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 16:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a colorless oil (72 mg, 72% yield, Z:E = 16:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 11.6 Hz, 1H), 5.49 (dt, *J* = 11.6, 7.1 Hz, 1H), 3.82 (s, 3H), 2.55 – 2.40 (m, 2H), 2.42 – 2.27 (m, 2H), 1.91 – 1.72 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 158.6, 130.5, 130.0, 129.8, 128.3, 119.7, 113.9, 55.4, 27.6, 25.9, 16.8. GCMS (EI) calculated for [M]⁺ 201.12, found 201.2. FTIR (neat, cm⁻¹): 3054(m), 2985(m), 2924(m), 2838(m), 2305(s), 2248(s), 1608(s), 1266(m) 895(s) 839(9).

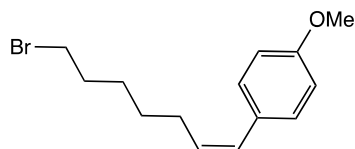


methyl (5Z)-6-(4-methoxyphenyl)hex-5-enoate (9), compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 45:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a colorless oil (111 mg, 94% yield, Z:E = 48:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 11.6 Hz, 1H), 5.70 - 5.38 (m, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 2.45 - 2.27 (m, 4H), 1.88 - 1.68 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 174.0, 158.4, 130.2, 130.1, 130.0, 129.3, 113.7, 55.3, 51.5, 33.6,

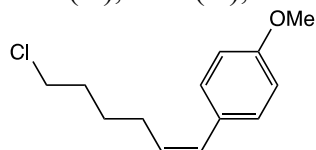
28.0, 25.2. GCMS (EI) calculated for [M]⁺ 234.13, found 234.2. FTIR (neat, cm⁻¹): 3005(m), 2949(m), 2836(m), 2255(m), 1736(s), 1608(s), 836(s), 734(s).



tert-butyl N-[(4Z)-5-(4-methoxyphenyl)pent-4-en-1-yl]-N-methylcarbamate (10), compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 3 h. After the addition of 2 equiv of NaO*t*-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 30:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a pale yellow oil (119 mg, 82% yield, Z:E = 32:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 11.6 Hz, 1H), 5.56 (dt, *J* = 11.6, 7.1 Hz, 1H), 3.81 (s, 3H), 3.22 (t, *J* = 7.3 Hz, 2H), 2.82 (s, 3H), 2.46 – 2.21 (m, 2H), 1.75 – 1.56 (m, 2H), 1.45 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 158.3, 155.9, 130.5, 130.0, 128.9, 127.1, 113.7, 79.3, 55.3, 48.7, 34.3, 28.6, 26.0. GCMS (EI) calculated for [M]⁺ 305.20, found 305.1. FTIR (neat, cm⁻¹): 3005(m), 2974(m), 2932(m), 2836(m), 1694(s), 1608(s), 1511(s), 883(s).

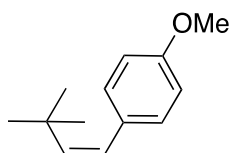


1-[(1Z)-7-bromohept-1-en-1-yl]-4-methoxybenzene (11), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 1 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 90:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (85 mg, 60% yield, Z:E > 100:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 11.6 Hz, 1H), 5.55 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.82 (s, 3H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.50 – 2.18 (m, 2H), 2.00 – 1.72 (m, 2H), 1.53 – 1.33 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 158.2, 131.1, 130.4, 130.0, 128.6, 113.6, 55.4, 34.1, 32.8, 29.3, 28.5, 28.0. GCMS (EI) calculated for [M]⁺ 282.06, found 282.1. FTIR (neat, cm⁻¹): 3003(m), 2926(m), 2852(m), 2172(m), 1609(s), 1511(s), 835(s), 734(s) 678(s).

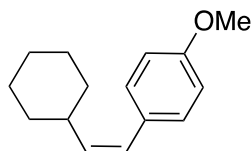


1-[(1Z)-6-chlorohex-1-en-1-yl]-4-methoxybenzene (12), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 2 h. An aliquot of

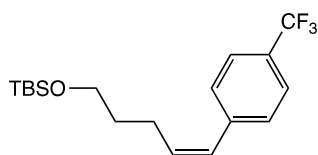
the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 90:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (99.3 mg, 88% yield, Z:E = 99:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 11.5 Hz, 1H), 5.72 – 5.41 (m, 1H), 3.82 (s, 3H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.48 – 2.26 (m, 2H), 1.89 – 1.74 (m, 2H), 1.68 – 1.55 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 158.4, 130.7, 130.4, 130.0, 129.0, 113.7, 55.4, 45.0, 32.3, 27.9, 27.3. GCMS (EI) calculated for [M]⁺ 224.10, found 224.2. FTIR (neat, cm⁻¹): 3054(m), 2958(m), 2864(m), 2305(m), 1608(s), 1511(s), 896(s), 741(s).



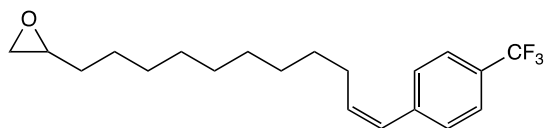
1-[(1Z)-3,3-dimethylbut-1-en-1-yl]-4-methoxybenzene (13) compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 15:1). The compound was purified by silica gel chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (69.0 mg, 73% yield, Z:E = 16:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 12.5 Hz, 1H), 5.56 (d, *J* = 12.5 Hz, 1H), 3.80 (s, 3H), 0.99 (s, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.2, 142.7, 131.8, 130.2, 126.9, 113.1, 55.3, 34.2, 31.4. GCMS (EI) calculated for [M]⁺ 190.29, found 190.5. FTIR (neat, cm⁻¹): 2927 (s), 2852 (s), 1605(s), 1509(s), 1245(s), 6774(m).



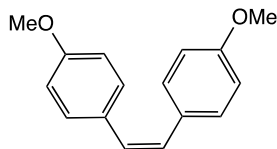
1-[(Z)-2-cyclohexylethenyl]-4-methoxybenzene (14) compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 15:1). The compound was purified by silica gel chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (88.0 mg, 81% yield, Z:E = 17:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.92 (d, 8.8 Hz, 2H), 6.30 (d, *J* = 11.7 Hz, 1H), 5.50 – 5.40 (t, *J* = 11.7, 1H), 3.86 (s, 3H), 2.72 – 2.54 (m, 1H), 1.88 – 1.68 (m, 5H), 1.45 – 1.16 (m, 5H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.3, 137.7, 130.7, 129.9, 126.4, 113.7, 55.4, 37.0, 33.5, 26.2, 25.9. GCMS (EI) calculated for [M]⁺ 216.32, found 216.5. FTIR (neat, cm⁻¹): 2925 (s), 2850 (s), 1608(s), 1511(s), 1245(s), 677(m).



tert-butyl dimethyl {[(5Z)-6-[4-(trifluoromethyl)phenyl]hex-5-en-1-yl]oxy} silane (15), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 23:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (148 mg, 86% yield, Z:E = 23:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 11.8 Hz, 1H), 5.95 – 5.63 (m, 1H), 3.63 (t, *J* = 6.2 Hz, 2H), 2.58 – 2.21 (m, 2H), 1.83 – 1.58 (m, 2H), 0.02 (s, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 141.4, 134.9, 129.1, 128.6 (q, *J* = 31.9 Hz), 128.1, 125.2 (q, *J* = 4.1 Hz), 124.4 (q, *J* = 271.7 Hz), 62.5, 33.0, 26.0, 25.2, 18.4, -5.2. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.5. GCMS (EI) calculated for [M]⁺ 358.19, found 358.3. FTIR (neat, cm⁻¹): 3013(m), 2930(m), 2865(m), 2175(m), 1919(s), 1616(m), 1473(s), 836(s), 775(s).

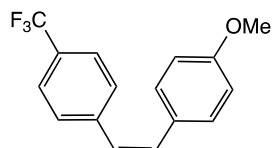


2-[(9Z)-10-[4-(trifluoromethyl)phenyl]dec-9-en-1-yl]oxirane (16), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 22:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (143 mg, 87% yield, Z:E = 22:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.42 (d, *J* = 11.7 Hz, 1H), 5.77 (dt, *J* = 11.7, 7.3 Hz, 1H), 3.03 – 2.82 (m, 1H), 2.74 (t, *J* = 4.5 Hz, 1H), 2.56 – 2.39 (m, 1H), 2.39 – 2.20 (m, 2H), 1.72 – 1.03 (m, 21H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 141.5, 135.5, 131.9, 129.0, 128.5 (q, *J* = 32.3 Hz), 125.1 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.0 Hz), 52.5, 47.2, 32.6, 29.9, 29.5, 29.4, 29.2, 29.0, 28.7, 26.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4. GCMS (EI) calculated for [M]⁺ 326.19, found 326.3. FTIR (neat, cm⁻¹): 3055(m), 2929(m), 2855(m), 2305(m), 1613(s), 1422(s), 896(s), 740(s).

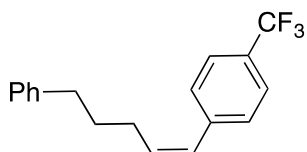


1-methoxy-4-[(Z)-2-(4-methoxyphenyl)ethenyl]benzene (17), compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After

the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 16:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 45%) and isolated as a white solid (105 mg, 87% yield, Z:E = 16:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.7 Hz, 4H), 6.77 (d, *J* = 8.7 Hz, 4H), 6.44 (s, 2H), 3.79 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 158.6, 130.2, 130.1, 128.5, 113.7, 55.3. GCMS (EI) calculated for [M]⁺ 240.12, found 240.2. FTIR (neat, cm⁻¹): 3054(m), 2958(m), 2937(m), 2838(m), 1607(s), 1511(s), 836(s), 740(s).

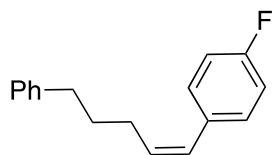


1-[(Z)-2-(4-methoxyphenyl)ethenyl]-4-(trifluoromethyl)benzene (18), compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 31:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a pale yellow oil (133 mg, 96% yield, Z:E = 32:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 12.2 Hz, 1H), 6.50 (d, *J* = 12.2 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 159.2, 141.5, 132.0, 130.3, 129.2, 128.9 (q, *J* = 32.1 Hz), 128.5, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.6 Hz), 113.9, 55.3. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.5. GCMS (EI) calculated for [M]⁺ 278.09, found 278.1. FTIR (neat, cm⁻¹): 3010(m), 2956(m), 2837(m), 1607(s), 1508(s), 882(s), 830(s) 730(s).

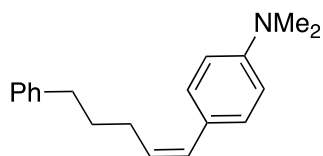


1-[(1Z)-5-phenylpent-1-en-1-yl]-4-(trifluoromethyl)benzene (19), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by TLC (100% Hex) revealed that the internal alkyne intermediate was consumed after 2 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 20:1). The compound was purified by silica gel column chromatography (100% Hex) and a filtration through a short plug of alumina (100% Hex). The compound was isolated as a clear colorless oil (107 mg, 73% yield, Z:E = 22:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.05 (m, 8H), 6.46 (d, *J* = 11.6 Hz, 1H), 5.81 (dt, *J* = 11.7, 7.4 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.35 (dt, *J* = 7.6, 7.3 Hz, 2H), 1.81 (p, *J* = 7.6Hz, 2H). GCMS (EI) calculated for [M]⁺ 290.13, found 290.5. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -65.2. ¹³C NMR (126 MHz, Chloroform-*d*) δ 142.1, 141.1, 134.8, 129.0, 128.6 (q, *J* = 35.2 Hz), 128.5, 128.2, 127.7, 126.0, 125.5 (q, *J* = 3.0 Hz), 124.4

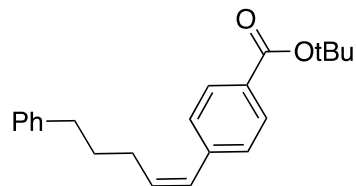
(q, $J = 276.5$ Hz), 35.6, 31.6, 28.1. FTIR (neat, cm^{-1}): 3088(w), 3065(w), 3028(m), 2931(m), 2849(w), 1612(w), 1478(w), 1322(s), 1165(s), 1120(s), 1068(s), 673(s).



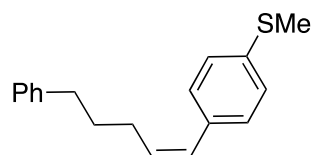
1-fluoro-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (20), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (100% Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 9:1). The compound was purified by silica gel column chromatography (100% Hex) and a filtration through a short plug of alumina. The compound was isolated as a clear colorless oil (105 mg, 83% yield, Z:E = 10:1). ^1H NMR (500 MHz, Chloroform- d) δ 7.35 – 7.23 (m, 3H), 7.23 – 7.13 (m, 4H), 7.04 – 6.95 (m, 2H), 6.39 (d, $J = 11.7$ Hz, 1H), 5.68 (dt, $J = 11.6, 7.3$ Hz, 1H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.33 (dt, $J = 7.6, 7.3$ Hz, 2H), 1.79 (p, $J = 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 161.5 (d, $J = 246.1$ Hz), 142.3, 133.8 (d, $J = 3.1$ Hz), 132.5, 130.4 (d, $J = 7.9$ Hz), 128.6, 128.4, 128.3, 125.9, 115.1 (d, $J = 21.3$ Hz), 35.6, 31.7, 28.1. ^{19}F NMR (471 MHz, Chloroform- d) δ -123.5. GCMS (EI) calculated for $[\text{M}]^+$ 240.13, found 240.2. FTIR (neat, cm^{-1}): 3058(w), 3028(w), 2931(m), 1597(m), 1500(m), 1456(m), 1225(s), 1158(s), 857(m).



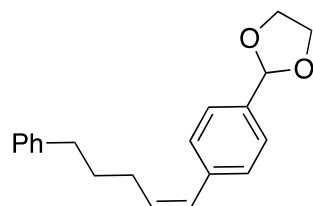
N,N-dimethyl-4-[(1Z)-5-phenylpent-1-en-1-yl]aniline (21), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, the reaction mixture was then moved to 0 °C to slow the rate of isomerization, and the reaction progress was monitored progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 6 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 12:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (10% Et₂O/Hex). Compound was isolated as a clear colorless liquid (85 mg, 65% yield, Z:E = 12:1). ^1H NMR (500 MHz, Chloroform- d) δ 7.16 (t, $J = 7.5$ Hz, 2H), 7.11 – 7.05 (m, 5H), 6.59 (d, $J = 8.7$ Hz, 2H), 6.25 (d, $J = 11.6$ Hz, 1H), 5.42 (dt, $J = 11.5, 7.2$ Hz, 1H), 2.84 (s, 6H), 2.56 (t, $J = 7.8$ Hz, 2H), 2.31 (dt, $J = 7.6, 7.2$ Hz, 2H), 1.69 (p, $J = 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 149.3, 142.6, 129.8, 129.1, 128.6, 128.4, 126.5, 125.8, 112.3, 40.6, 35.7, 32.0, 28.5. GCMS (EI) calculated for $[\text{M}]^+$ 265.18, found 265.3. FTIR (neat, cm^{-1}): 3088(w), 3036(m), 2924(m), 2849(m), 2797(w), 1605(s), 1515(s), 1351(m), 1158(m), 679(s).



tert-butyl 4-[(1Z)-5-phenylpent-1-en-1-yl]benzoate (22), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *t*-BuOH to prevent transesterification, monitoring the reaction progress by GC revealed that the internal alkyne intermediate was consumed after 75 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 9:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→15%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil. (128 mg, 79% yield, Z:E = 10:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.10 (m, 5H), 7.12 – 7.00 (m, 2H), 6.36 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.53 (t, *J* = 7.5, 2H), 2.27 (dt, *J* = 7.5, 7.3 Hz, 2H), 1.68 (p, *J* = 7.5 Hz, 2H), 1.50 (s, 9H). ¹³C NMR (126 MHz, Chloroform-d) δ 165.7, 142.2, 141.9, 134.5, 130.1, 129.4, 128.7, 128.6, 128.5, 128.4, 125.9, 80.9, 35.5, 31.6, 28.3, 28.3. GCMS (EI) calculated for [M]⁺ 322.19, found 322.4. FTIR (neat, cm⁻¹): 3058(w), 3028(m), 2976(s), 2931(s), 2849(m), 1709(s), 1597(s), 1456(s), 1292(s), 1165(s), 1105(s), 852(m), 740(m), 695(s), 681(m).

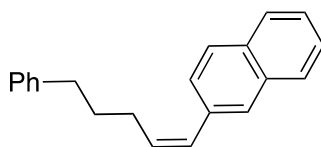


1-(methylsulfanyl)-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (23), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 1 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 80:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (118 mg, 88% yield, Z:E = 80:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.19 – 7.12 (m, 3H), 7.12 – 7.02 (m, 6H), 6.27 (d, *J* = 11.7 Hz, 1H), 5.56 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 2.26 (dt, *J* = 7.6, 7.3 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.3, 136.6, 134.7, 132.5, 129.3, 128.7, 128.6, 128.4, 126.5, 125.8, 35.6, 31.8, 28.3 16.0. GCMS (EI) calculated for [M]⁺ 268.13, found 268.3. FTIR (neat, cm⁻¹): 3088(w), 3065(w), 3021(m), 2924(s), 2849(m), 1597(m), 1493(s), 1090(m), 830(m), 673(s)

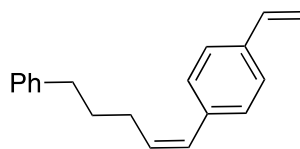


2-{4-[(1Z)-5-phenylpent-1-en-1-yl]phenyl}-1,3-dioxolane (24), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was

consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 45 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 18:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→15%). The compound was isolated as a clear colorless oil (102 mg, 69% yield, Z:E = 18:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 4H), 7.17 (dd, *J* = 14.7, 7.4 Hz, 3H), 6.45 (d, *J* = 11.7 Hz, 1H), 5.81 (s, 1H), 5.71 (dt, *J* = 11.6, 7.3 Hz, 1H), 4.18 – 4.06 (m, 2H), 4.06 – 3.97 (m, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.37 (dt, *J* = 7.6, 7.3 Hz, 2H), 1.78 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.3, 138.7, 136.2, 133.1, 129.0, 128.8, 128.5, 128.4, 126.3, 125.8, 103.8, 65.4, 35.6, 31.7, 28.2. GCMS (EI) calculated for [M]⁺ 294.16, found 294.4. FTIR (neat, cm⁻¹): 3058(w), 3028(m), 2924(s), 2887(s), 2857(w), 1605(m), 1381(m), 1217(m), 1083(s), 941(m), 703(s), 681(s).

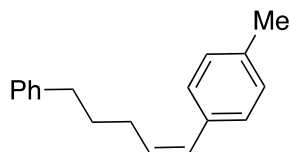


2-[(1Z)-5-phenylpent-1-en-1-yl]naphthalene (25), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by TLC (5% Et₂O in Hex) revealed that the internal alkyne intermediate was consumed after 20 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 29:1). The compound was purified by silica gel column chromatography (Et₂O/Hex 0→5%) and a filtration through a short plug of alumina (5% Et₂O/Hex). The compound was isolated as a clear colorless oil (109 mg, 80% yield, Z:E = 29:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.73 – 7.64 (m, 3H), 7.59 (s, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.17 – 7.11 (m, 2H), 7.09 – 7.03 (m, 3H), 6.49 (d, *J* = 11.6 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.61 – 2.52 (m, 2H), 2.37 (dt, *J* = 7.5, 7.3 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.4, 135.4, 133.5, 133.1, 132.4, 129.5, 128.6, 128.6, 128.4, 127.7, 127.7, 127.5, 127.4, 126.1, 125.9, 125.8, 35.6, 31.8, 28.4. GCMS (EI) calculated for [M]⁺ 272.16, found 272.3. FTIR (neat, cm⁻¹): 3051(m), 3021(m), 2924(s), 2849(m), 1597(m), 1493(m), 1448(m), 822(s), 748(s), 695(s).

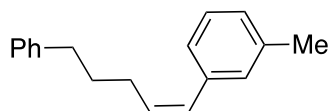


1-ethenyl-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (26), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% Et₂O//Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 19:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→5%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (105 mg, 85% yield, Z:E = 20:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.26 – 7.13 (m, 7H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.40 (d, *J* = 11.7 Hz, 1H), 5.82 – 5.58 (m, 2H), 5.22 (d, *J* = 10.9 Hz, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.37 (dt, *J* = 7.7, 7.2 Hz, 2H), 1.78 (p, *J* = 7.6

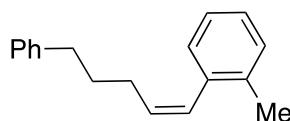
Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 142.4, 137.5, 136.8, 136.0, 132.8, 129.1, 129.1, 128.6, 128.4, 126.2, 125.9, 113.6, 35.6, 31.8, 28.4. GCMS (EI) calculated for $[\text{M}]^+$ 248.16, found 248.2. FTIR (neat, cm^{-1}): 3080(w), 3058(w), 3021(m), 3006(m), 2924(s), 2857(m), 1620(m), 1605(m), 1500(s), 1456(s), 986(m), 904(m), 845(s), 678(s).



1-methyl-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (27), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 9:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0 \rightarrow 10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (116 mg, 98% yield, Z:E = 10:1). ^1H NMR (300 MHz, Chloroform- d) δ 7.35 – 7.05 (m, 9H), 6.41 (d, J = 11.6 Hz, 1H), 5.65 (dt, J = 11.6, 7.3 Hz, 1H), 2.69 – 2.60 (m, 2H), 2.45 – 2.30 (m, 5H), 1.79 (p, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 142.4, 136.2, 134.9, 131.9, 129.2, 128.8, 128.6, 128.4, 128.4, 125.8, 35.6, 31.9, 28.3, 21.3. GCMS (EI) calculated for $[\text{M}]^+$ 236.16, found 236.2. FTIR (neat, cm^{-1}): 3058(w), 3021(m), 2924(s), 2857(m), 1597(w), 1508(w), 1448(m), 830(m), 695(s), 681(s).

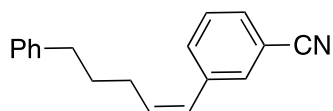


1-methyl-3-[(1Z)-5-phenylpent-1-en-1-yl]benzene (28), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 9:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0 \rightarrow 10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (102 mg, 86% yield, Z:E = 10:1). ^1H NMR (500 MHz, Chloroform- d) δ 7.19 – 7.02 (m, 6H), 6.99 – 6.90 (m, 3H), 6.31 (d, J = 11.7 Hz, 1H), 5.57 (dt, J = 11.9, 7.3 Hz, 1H), 2.54 (t, J = 7.8 Hz, 2H), 2.32 – 2.21 (m, 5H), 1.68 (p, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 142.5, 137.8, 132.5, 129.6, 129.5, 128.6, 128.4, 128.2, 127.4, 125.9, 125.8, 123.3, 35.6, 31.8, 28.3, 21.6. GCMS (EI) calculated for $[\text{M}]^+$ 236.16, found 236.2. FTIR (neat, cm^{-1}): 3065(w), 3028(m), 2924(s), 2849(m), 1605(m), 1582(w), 1493(m), 1456(m), 792(m), 748(m), 675(s).

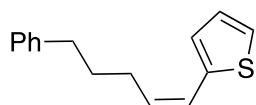


1-methyl-2-[(1Z)-5-phenylpent-1-en-1-yl]benzene (29), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex)

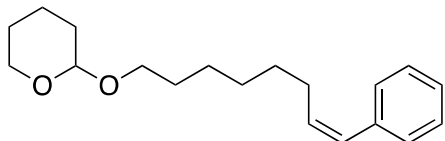
revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 35:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (110 mg, 93% yield, Z:E = 35:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.20 – 6.96 (m, 9H), 6.36 (d, *J* = 11.4 Hz, 1H), 5.63 (dt, *J* = 11.5, 7.4 Hz, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.04 (m, 5H), 1.62 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 136.9, 136.3, 132.4, 129.9, 129.1, 128.5, 128.4, 126.9, 125.8, 125.5, 120.1, 35.6, 31.8, 28.1, 20.0. GCMS (EI) calculated for [M]⁺ 236.16, found 236.2. FTIR (neat, cm⁻¹): 3058(w), 3021(m), 2924(s), 2857(m), 1597(m), 1485(m), 1448(s), 1031(m), 740(s), 695(s).



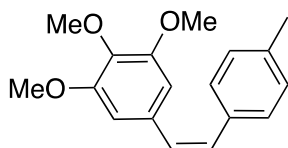
3-[(1Z)-5-phenylpent-1-en-1-yl]benzonitrile (30), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by GC revealed that the internal alkyne intermediate was consumed after 2 h. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 20:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→5%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (114 mg, 92% yield, Z:E = 24:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.35 (m, 4H), 7.21 – 6.99 (m, 5H), 6.30 (d, *J* = 11.7 Hz, 1H), 5.71 (dt, *J* = 11.7, 7.4 Hz, 1H), 2.58 – 2.49 (t, *J* = 7.6 Hz, 2H), 2.27 – 2.15 (m, 2H), 1.69 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 141.9, 139.8, 135.1, 133.1, 132.1, 130.0, 129.0, 128.8, 128.4, 127.2, 125.9, 119.0, 112.4, 35.4, 31.4, 28.0. GCMS (EI) calculated for [M]⁺ 247.14 found 247.3. FTIR (neat, cm⁻¹): 3058(m), 3021(m), 2924(s), 2857(m), 2223(s), 1597(m), 1448(m), 904(m), 800(s), 740(m), 695(s).



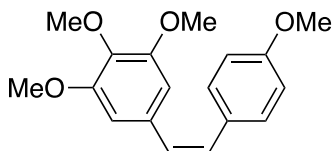
2-[(1Z)-5-phenylpent-1-en-1-yl]thiophene (31), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% Et₂O//Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 50:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→5%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (82 mg, 72% yield, Z:E = 52:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.42 (s, 1H), 7.39 – 7.27 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 3H), 7.09 – 6.96 (m, 2H), 6.62 (d, *J* = 11.1 Hz, 1H), 5.67 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.53 (dt, *J* = 7.5, 7.2 Hz, 2H), 1.90 (p, *J* = 7.5 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.4, 140.9, 130.7, 128.6, 128.5, 127.2, 126.8, 125.9, 125.1, 122.3, 35.8, 31.4, 29.0. GCMS (EI) calculated for [M]⁺ 228.10, found 228.3. FTIR (neat, cm⁻¹): 3058(m), 3021(s), 2924(s), 2849(s), 1597(m), 1493(s), 1446(s), 1031(m), 845(m), 730(m), 740(s), 695(s).



2-((7Z)-8-phenyloct-7-en-1-yl)oxane (32) compound was prepared according to the general procedure, TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv MeOH, the reaction was moved to 60 °C and monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 16:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→40%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (117 mg, 81% yield, Z:E = 16:1). This compound has been previously synthesized and spectra matches literature values.⁹

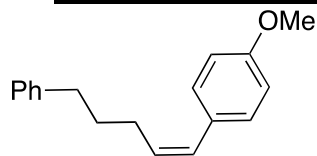


1,2,3-trimethoxy-5-((Z)-2-(4-methylphenyl)ethenyl)benzene (34) compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2.5 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 20 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 31:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 25%) and isolated as a pale yellow oil (120 mg, 85% yield, Z:E = 31:1). This compound has been previously synthesized and spectra matches literature values.¹⁰



1,2,3-trimethoxy-5-((Z)-2-(4-methoxyphenyl)ethenyl)benzene (35) compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOt-Bu and 4 equiv of MeOH the reaction was moved to 60 °C and, monitoring the reaction progress by TLC (20% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 10 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = >100:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 25%) and isolated as a pale yellow oil (131 mg, 87% yield, Z:E = >100:1). This compound has been previously synthesized and spectra matches literature values.¹⁰

6. Gram Scale Reaction



1-methoxy-4-[(1Z)-5-phenylpent-1-en-1-yl]benzene (3), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne intermediate was consumed after 15 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 18:1). The compound was purified by silica gel chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (1.1247 g, 75% yield, Z:E = 20:1).

7. Selectivity Studies (Table 3)

In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaOt-Bu (9.6 mg, 0.10 mmol, 2.0 equiv). To this was added 5-phenyl-1-pentyne (7.2 mg, 0.05 mmol, 1.0 equiv), Pd(OAc)₂ (0.6 mg, 0.0025 mmol, 0.05 equiv) IPrCuCl (2.4 mg, 0.005 mmol, 0.10 equiv), **L1** (1.9 mg, 0.0050 mmol, 0.10 equiv), aryl bromide (0.055 mmol, 1.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.00 equiv), and toluene (0.5 mL). The reaction mixture was stirred at 45 °C, and the reaction progress was monitored by TLC. When the starting alkyne was fully consumed, methanol (2.4 mg, 0.0750 mmol, 1.5 equiv) was added and stirring was continued at 45 °C. 30 μL aliquots were taken at 20 min, 25 min, 30 min, 35 min and 40 min passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S4.

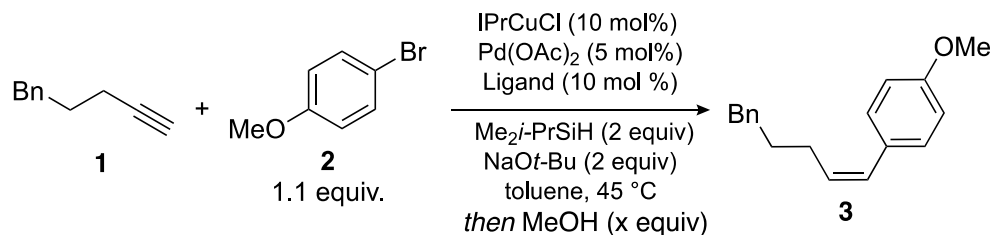
Ar =						Yield Range
	20 min ^b	25 min	30 min	35 min	40 min	
	20:1	18:1	13:1	10:1	10:1	92 - 95
	>100:1 ^d	18:1	18:1	17:1	13:1	70 - 79
	28:1	28:1	27:1	26:1	25:1	84 - 89

^aSelectivity determined by GC analysis of crude reaction mixture. ^bTime after the addition of alcohol. ^c*i*-BuOH used instead of MeOH. ^dReaction mixture contains <10% internal alkyne.

8. Optimization of *E*-Selective Hydroarylation (Table 4)

In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaOtBu (9.6 mg, 0.100 mmol, 2 equiv). To this was added **1** (7.20 mg 0.050 mmol, 1.0 equiv), Pd(OAc)₂ (0.6 mg, 0.0025 mmol, 0.05 equiv) IPrCuCl (2.4 mg, 0.0050 mmol, 0.10 equiv), ligand (0.10 equiv), **2** (0.0550 mmol, 1.10 equiv), Me₂iPrSiH (10.2 mg, 0.10 mmol, 2.00 equiv), and toluene (0.5 mL). The reaction mixture was stirred at 45 °C, and the reaction progress was monitored by TLC. When the starting alkyne was fully consumed, methanol was added and stirring was continued at 45 °C. The reaction progress was monitored by GC for complete isomerization to the *E*-alkene. The reaction mixture was diluted with diethyl ether and filtered through a pad of silica gel. The crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography. The ratio of stereoisomers for each product was determined by GC analysis of a crude reaction mixture.

Table S5



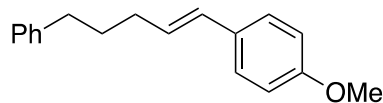
Entry	Ligand	Yield 20 min (E:Z)
1	Qphos	100% (1.9:1)
2	Davephos	81% (1:2.5)
3	Ruphos	69% (1:2.8)
4	Sphos	81% (1:1.2)
5	L1	90% (1:29)
6	L1 (6 days)	95% (2:1)
7	L1 (5 equiv MeOH)	94% (>100:1)

^aCombined yields and E:Z selectivity determined by GC

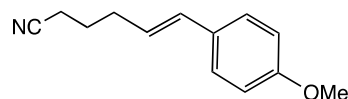
9. General Procedure for the Hydroarylation of Terminal Alkynes: Synthesis of *E*-Alkenes

In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaOtBu (96.1 mg, 1.00 mmol, 2 equiv). To this was added alkyne (0.50 mmol, 1.0 equiv), Pd(OAc)₂ (2.8 mg, 0.025 mmol, 0.100 equiv) IPrCuCl (24.4 mg, 0.050 mmol, 0.10 equiv), **L1** (19 mg, 0.050 mmol, 0.10 equiv), aryl bromide (0.550 mmol, 1.10 equiv), Me₂iPrSiH (102.3 mg, 1.00 mmol, 2.00 equiv), and toluene (5 mL). The reaction mixture was stirred at 45 °C, and the reaction progress was monitored by TLC. When the starting alkyne was fully consumed, methanol (80.1 mg, 2.50 mmol, 5.00 equiv) was added and stirring was continued at 45 °C. The reaction progress was monitored by GC for complete isomerization to the *E*-alkene (usually less than 24 h). The reaction mixture was diluted with diethyl ether and filtered through a pad of silica gel. The crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography. The ratio of stereoisomers for each product was determined by GC analysis of a purified reaction mixture.

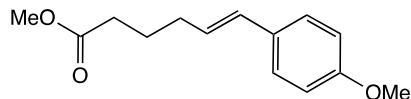
10. Characterization of Hydroarylation Products: *E*-alkenes



1-methoxy-4-[(1*E*)-5-phenylpent-1-en-1-yl]benzene (36), compound was prepared according to the general procedure. After 2 h TLC in 100% hexane showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 12 h a 30 μ L aliquot was taken and analysis by GC for confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 \rightarrow 10%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (118 mg, 94% yield, 1 isomer). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.12 (m, 8H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.80 (p, *J* = 7.5 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.8, 142.6, 130.8, 129.7, 128.6, 128.5, 128.4, 127.1, 125.8, 114.0, 55.4, 35.5, 32.7, 31.3. GCMS (EI) calculated for [M]⁺ 252.15, found 252.3. FTIR (neat, cm⁻¹): 3088(w), 3021(m), 2924(m), 1605(s), 1500(s), 1478(w), 1247(s), 1165(s), 1038(s), 964(m), 733(m), 673(s).

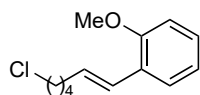


(5*E*)-6-(4-methoxyphenyl)hex-5-enenitrile (37), compound was prepared according to an altered general procedure. LiOtBu was used in place of NaOtBu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOtBu and 4 equiv of MeOH, the reaction mixture was stirred at 60 °C. After 12 hours a 30 μ L was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 \rightarrow 45%) and isolated as a pale yellow oil (96 mg, 95% yield, E:Z = 44:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.98 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.34 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 159.1, 131.4, 130.0, 127.2, 125.4, 119.7, 114.0, 55.3, 31.7, 25.2, 16.4. GCMS (EI) calculated for [M]⁺ 201.12, found 201.2. FTIR (neat, cm⁻¹): 3004(m), 2935(m), 2836(m), 2245(m), 1607(s), 1512(s), 836(s), 736(s).

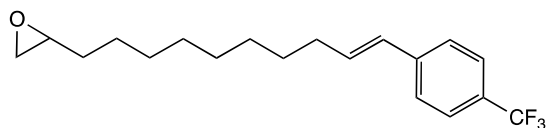


methyl (5*E*)-6-(4-methoxyphenyl)hex-5-enoate (38), compound was prepared according to an altered general procedure. LiOtBu was used in place of NaOtBu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOtBu and 4 equiv of MeOH, the reaction mixture was stirred at 60 °C. After 12 hours a 30 μ L was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 \rightarrow 40%) and isolated as a clear oil (81 mg, 70% yield, E:Z = >100:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.11 – 5.95 (m, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.45 – 2.30 (m, 2H), 2.34 – 2.14 (m, 2H), 1.81 (p, *J* = 7.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 174.1, 158.9, 130.5, 130.2, 127.4, 127.1, 114.0, 55.3, 51.5, 33.5, 32.4, 24.7. GCMS

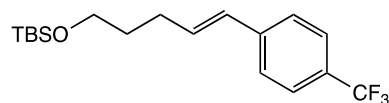
(EI) calculated for [M]⁺ 234.13, found 234.2. FTIR (neat, cm⁻¹): 3000(m), 2951(m), 2057(m), 1736(s), 1607(s), 1512(s), 839(s).



1-[(1E)-6-chlorohex-1-en-1-yl]-2-methoxybenzene (39), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 hours a 30 μL was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (91 mg, 85% yield, E:Z = 10:1) ¹H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 1.92 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 158.9, 130.6, 129.9, 127.2, 127.2, 114.1, 55.4, 45.1, 32.3, 32.2, 26.8. GCMS (EI) calculated for [M]⁺ 224.10, found 224.2. FTIR (neat, cm⁻¹): 3055(m), 2986(m), 2937(m), 2305(m), 1608(s), 1511(s), 896(s), 740(s).

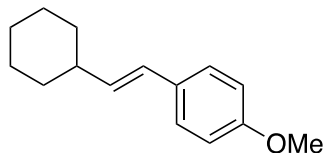


2-[(9E)-10-[4-(trifluoromethyl)phenyl]dec-9-en-1-yl]oxirane (40), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 12 hours a 30 μL was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (154 mg, 95% yield, E:Z = 16:1). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 6.48 – 6.26 (m, 2H), 2.96 – 2.84 (m, 1H), 2.79 – 2.70 (m, 1H), 2.50 – 2.42 (m, 1H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.67 – 1.10 (m, 20H). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4. ¹³C NMR (126 MHz, Chloroform-*d*) δ 141.5, 134.2, 128.7, 128.7 (q, *J* = 32.1 Hz), 125.6, 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.6 Hz), 52.5, 47.2, 33.2, 32.6, 29.6, 29.5, 29.3, 29.2, 26.1. GCMS (EI) calculated for [M]⁺ 326.19, found 326.3. FTIR (neat, cm⁻¹): 3044(m), 2928(m), 2855(m), 1740(m), 1615(m), 1465(s), 834(s), 757(s),

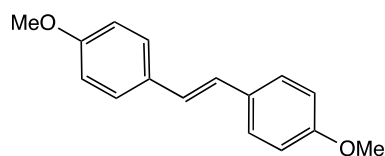


tert-butyl dimethyl{(4E)-5-[4-(trifluoromethyl)phenyl]pent-4-en-1-yl}oxy silane (41), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 12 hours a 30 μL was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (148 mg, 86% yield, E:Z = 16:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.59 – 6.16 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.31 (q, *J* = 6.9 Hz, 2H), 1.79 – 1.58 (m, 2H), 0.91 (s, 9H), 0.06

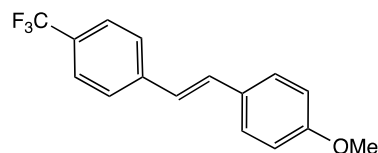
(s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.5, 133.6, 129.2, 128.7 (q, $J = 32.2$ Hz), 126.2, 125.6 (q, $J = 3.7$ Hz), 124.5 (q, $J = 271.7$ Hz), 62.5, 32.4, 29.6, 26.1, 18.2, -5.2. ^{19}F NMR (471 MHz, CDCl_3) δ -62.4. GCMS (EI) calculated for $[\text{M}]^+$ 358.19, found 358.3. FTIR (neat, cm^{-1}): 2930(m), 2895(m), 2858(m), 1915(m), 1615(s), 1473(s), 835(s), 735(s).



1-[(Z)-2-cyclohexylethenyl]-4-methoxybenzene (42) compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography ($\text{Et}_2\text{O}/\text{Hex}$ 0 \rightarrow 10%) and filtration through a short plug of alumina (10% $\text{Et}_2\text{O}/\text{Hex}$). The compound was isolated as a clear colorless oil (118 mg, 94% yield, E:Z = 10:1). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.28 (d, $J = 9.1$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.29 (d, $J = 15.9$ Hz, 1H), 6.03 (dd, $J = 16.0, 6.9$ Hz, 1H), 3.80 (s, 3H), 2.17 – 2.01 (m, 1H), 1.89 – 1.61 (m, 5H), 1.42 – 1.06 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.7, 134.8, 131.0, 127.1, 126.7, 114.0, 55.4, 41.2, 33.2, 26.3, 26.2. GCMS (EI) calculated for $[\text{M}]^+$ 216.32, found 216.5. FTIR (neat, cm^{-1}): 2923 (s), 2845 (s), 1605(s), 1511(s), 1246(s), 678(m).

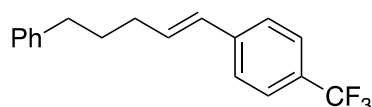


1-methoxy-4-[(E)-2-(4-methoxyphenyl)ethenyl]benzene (43), compound was prepared according to an altered general procedure. LiOtBu was used in place of NaOtBu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOtBu and 4 equiv of MeOH, the reaction mixture was stirred at 60 °C. After 12 hours a 30 μL was taken and analysis by GC confirmed complete isomerization to the E-alkene. The compound was purified by trituration with Hex and isolated as a white solid (109 mg, 91% yield, E:Z = 32:1). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.43 (d, $J = 8.4$ Hz, 4H), 7.06 – 6.71 (m, 6H), 3.83 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.6, 130.2, 130.1, 128.5, 113.7, 55.3. GCMS (EI) calculated for $[\text{M}]^+$ 240.12, found 240.2. FTIR (neat, cm^{-1}): 3055(m), 2987(m), 2305(m), 1609(s), 1514(s), 896(s), 740(s).

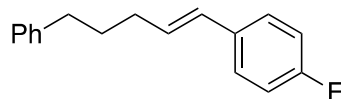


1-methoxy-4-[(E)-2-[4-(trifluoromethyl)phenyl]ethenyl]benzene (44), compound was prepared according to an altered general procedure. LiOtBu was used in place of NaOtBu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaOtBu and 6 equiv of *i*BuOH, the reaction mixture was stirred at 60 °C. After 12 hours a 30 μL was taken and analysis by GC confirmed complete isomerization to

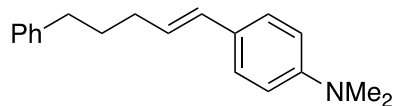
the E-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a pale yellow solid (115 mg, 83% yield, E:Z = 22:1). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 16.4 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 160.0, 141.3, 130.9, 129.6, 129.0 (q, *J* = 32.1 Hz), 126.4, 125.7 (q, *J* = 4.3 Hz), 125.1, 124.4 (q, *J* = 271.4 Hz), 114.4, 55.5. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.4. GCMS (EI) calculated for [M]⁺ 278.09, found 278.1. FTIR (neat, cm⁻¹): 3053(s), 2986(m), 2839(m), 2305(m), 1603(s), 1510(s), 835(s), 740(s).



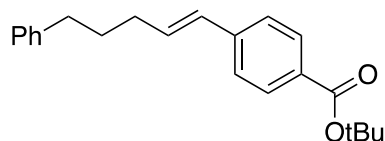
1-[(1E)-5-phenylpent-1-en-1-yl]-4-(trifluoromethyl)benzene (45), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of *i*BuOH were added and the reaction mixture was stirred at 45 °C. After 1 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Hex 100%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (120 mg, 83% yield, E:alkane = 11:1). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.14 (s, 3H), 7.10 (d, *J* = 7.1 Hz, 3H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.3, 6.6 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.25 – 2.13 (m, 2H), 1.73 (p, *J* = 7.7 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 142.3, 141.4, 133.6, 129.3, 128.7 (q, *J* = 19.5 Hz), 128.6, 128.5, 125.7, 125.6, 125.4 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 271.2 Hz), 35.5, 32.7, 30.9. GCMS (EI) calculated for [M]⁺ 290.12, found 290.5. FTIR (neat, cm⁻¹): 3028(m), 2934(m), 2858(w), 1615(m), 1454(w), 1326(s), 1164(s), 1122(s), 1068.2(s), 1016(w), 747(w), 699(m).



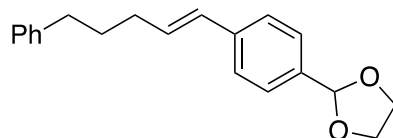
1-fluoro-4-[(1E)-5-phenylpent-1-en-1-yl]benzene (46), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Hex 100%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (103 mg, 86% yield, 1 isomer). ¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.17 (m, 5H), 7.14 (d, *J* = 6.7 Hz, 3H), 6.99 – 6.86 (m, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.19 (dt, *J* = 8.2, 7.6, 6.2 Hz, 2H), 1.85 – 1.66 (m, 2H). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -123.85. ¹³C NMR (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.6 Hz), 142.4, 134.1 (d, *J* = 2.7 Hz), 130.4, 129.2, 128.6 (d, *J* = 17.5 Hz), 127.4 (d, *J* = 7.8 Hz), 125.9, 115.5, 115.4, 35.5, 32.6, 31.1. GCMS (EI) calculated for [M]⁺ 240.13, found 240.2. FTIR (neat, cm⁻¹): 3058(w), 3021(m), 2924(s), 2849(m), 1597(m), 1508(s), 1448(w), 1225(s), 1158(m), 956(m), 837(m), 748(m), 688(s).



N,N-dimethyl-4-[(1E)-5-phenylpent-1-en-1-yl]aniline (47), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH and 0.50 equiv Me₂iPrSiH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →15%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (124 mg, 93% yield, E:Z = 14:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.24 – 7.01 (m, 8H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 15.8 Hz, 1H), 5.92 (dt, *J* = 15.7, 6.9 Hz, 1H), 2.84 (s, 6H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.21 – 2.04 (m, 2H), 1.68 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 149.8, 142.7, 130.1, 128.6, 128.4, 126.9, 126.7, 126.4, 125.7, 112.7, 40.7, 35.5, 32.7, 31.5. GCMS (EI) calculated for [M]⁺ 265.18, found 265.3. FTIR (neat, cm⁻¹): 3085(w), 3028(m), 2934(m), 2854(m), 1615(s), 1512(s), 1351(m), 1146(m), 672(s).

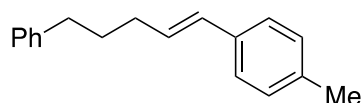


tert-butyl 4-[(1E)-5-phenylpent-1-en-1-yl]benzoate (48), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of *t*BuOH (used to prevent transesterification) were added and the reaction mixture was stirred at 60 °C. After 30 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (125 mg, 78% yield, E:alkane = 10:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 4H), 6.44 (d, *J* = 16.1 Hz, 1H), 6.36 (dt, *J* = 14.6, 6.5 Hz, 1H), 2.69 (t, *J* = 7.9 Hz, 2H), 2.33 – 2.25 (m, 2H), 1.84 (p, *J* = 7.1 Hz, 2H), 1.60 (s, 13H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.3, 142.0, 133.3, 129.8, 129.7, 128.6, 128.5, 125.9, 125.7, 120.1, 80.9, 35.7, 32.7, 30.9, 28.4. GCMS (EI) calculated for [M]⁺ 322.19, found 322.4. FTIR (neat, cm⁻¹): 3027(w), 2977(m), 2932(m), 2857(m), 1710(s), 1606(s), 1455(m), 1367(m), 1293(s), 1165(s), 1118(s), 747(m), 699(m).

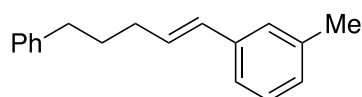


2-{4-[(1E)-5-phenylpent-1-en-1-yl]phenyl}-1,3-dioxolane (49), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →15%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a

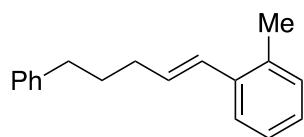
clear colorless oil (126 mg, 86% yield, 1 isomer). ^1H NMR (300 MHz, Chloroform- d) δ 7.43 – 7.20 (m, 7H), 7.17 (d, J = 7.1 Hz, 3H), 6.37 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 15.8, 6.6 Hz, 1H), 5.77 (s, 1H), 4.21 – 3.89 (m, 4H), 2.65 (t, J = 7.6 Hz, 2H), 2.31 – 2.13 (m, 2H), 1.79 (p, J = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 142.4, 138.8, 136.5, 131.3, 129.9, 128.5, 128.4, 126.7, 126.0, 125.8, 103.7, 65.3, 35.5, 32.6, 31.0. GCMS (EI) calculated for $[\text{M}]^+$ 294.16, found 294.4. FTIR (neat, cm^{-1}): 3088(w), 3027(m), 2931(s), 2887(m), 2857(m), 1479(m), 1426(w), 1390(m), 1081(s), 969(s), 678(s).



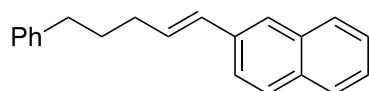
1-methyl-4-[(1E)-5-phenylpent-1-en-1-yl]benzene (50), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography ($\text{Et}_2\text{O}/\text{Hex}$ 0 \rightarrow 5%) and filtration through a short plug of alumina (10% $\text{Et}_2\text{O}/\text{Hex}$). The compound was isolated as a clear colorless oil (101 mg, 85% yield, E:alkane = 22:1). ^1H NMR (300 MHz, Chloroform- d) δ 7.40 – 7.20 (m, 7H), 7.15 (d, J = 7.9 Hz, 2H), 6.42 (d, J = 15.9 Hz, 1H), 6.23 (dt, J = 15.8, 6.8 Hz, 1H), 2.81 – 2.67 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H), 2.36 – 2.23 (m, 2H), 1.86 (p, J = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 1542.5 136.6, 135.2, 130.2, 129.6, 129.3, 128.6, 128.4, 126.0, 125.8, 35.5, 32.7, 31.2, 21.5. GCMS (EI) calculated for $[\text{M}]^+$ 236.16, found 236.2. FTIR (neat, cm^{-1}): 3080(w), 3021(m), 2924(s), 2849(m), 1605(w), 1508(m), 1453(m), 1032(w), 966(s), 735(m), 678(s).



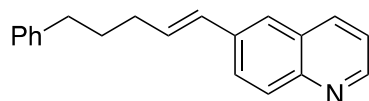
1-methyl-3-[(1E)-5-phenylpent-1-en-1-yl]benzene (51), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography ($\text{Et}_2\text{O}/\text{Hex}$ 0 \rightarrow 5%) and filtration through a short plug of alumina (10% $\text{Et}_2\text{O}/\text{Hex}$). The compound was isolated as a clear colorless oil (103 mg, 87% yield, 1 isomer). ^1H NMR (500 MHz, Chloroform- d) δ 7.35 – 7.24 (m, 2H), 7.24 – 7.12 (m, 6H), 7.03 (d, J = 7.3 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.2, 6.8 Hz, 1H), 2.68 (t, J = 7.8 Hz, 2H), 2.35 (s, 3H), 2.31 – 2.18 (m, 2H), 1.82 (p, J = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform- d) δ 142.3, 136.4, 134.9, 129.9, 129.3, 129.0, 128.3, 128.2, 125.7, 125.6, 35.3, 32.4, 31.0, 21.0. GCMS (EI) calculated for $[\text{M}]^+$ 236.16, found 236.2. FTIR (neat, cm^{-1}): 3059(w), 3022(m), 2931(s), 2849(m), 1603(w), 1502(m), 1454(m), 1031(w), 965(s), 738(m), 691(s).



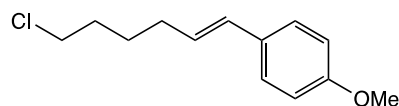
1-methyl-2-[(1E)-5-phenylpent-1-en-1-yl]benzene (52), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH and 0.50 equiv Me₂iPrSiH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →5%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (95 mg, 80% yield, E:Z = 24:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.31 (d, *J* = 5.9 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.15 – 6.99 (m, 6H), 6.50 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.00 (dt, *J* = 15.4, 6.9 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.29 – 2.11 (m, 5H), 1.73 (p, *J* = 7.7 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 137.1, 135.0, 132.0, 130.3, 128.6, 127.0, 126.1, 125.9, 125.6, 35.5, 33.0, 31.5, 20.0. GCMS (EI) calculated for [M]⁺ 236.16, found 236.2. FTIR (neat, cm⁻¹): 3062(w), 3026(m), 2931(s), 2856(m), 1602(w), 1495(m), 1454(m), 1031(w), 964(s), 743(s), 698(s).



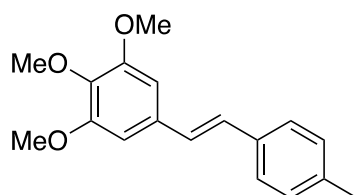
2-[(1E)-5-phenylpent-1-en-1-yl]naphthalene (53), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of *i*BuOH were added and the reaction mixture was stirred at 45 °C. After 30 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (121 mg, 89% yield, E:alkane = 37:1). ¹H NMR (300 MHz, Chloroform-d) δ 7.73 – 7.61 (m, 3H), 7.62 – 7.43 (m, 2H), 7.39 – 7.26 (m, 2H), 7.24 – 7.04 (m, 6H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.21 (m, 2H), 1.77 (p, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 135.4, 133.9, 132.8, 131.2, 130.5, 128.6, 128.5, 128.2, 127.9, 127.8, 126.3, 125.9, 125.6, 125.5, 123.7, 35.6, 32.8, 31.2. GCMS (EI) calculated for [M]⁺ 272.16, found 272.3. FTIR (neat, cm⁻¹): 3058(m), 3028(m), 2931(m), 2855(m), 1598(m), 1496(m), 1478(m), 1453(m), 962(m), 745(s), 678(s).



6-[(1E)-5-phenylpent-1-en-1-yl]quinolone (54), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 1 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et₂O/Hex 0 →25%) and filtration through a short plug of alumina (10% Et₂O/Hex). The compound was isolated as a clear colorless oil (103 mg, 75% yield, E:alkane = 14:1). ¹H NMR (500 MHz, Chloroform-d) δ 8.87 (s, 1H), 8.09 (dd, *J* = 16.2, 8.5 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.65 (s, 1H), 7.44 – 7.30 (m, 4H), 7.25 (q, *J* = 10.7 Hz, 4H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.43 (dt, *J* = 15.3, 6.8 Hz, 1H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.41 – 2.31 (m, 2H), 1.89 (p, *J* = 7.2 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d) δ 149.8, 147.9, 142.3, 136.1, 135.8, 132.4, 129.7, 129.6, 128.6, 128.5, 128.4, 127.3, 125.9, 124.8, 121.4, 35.5, 32.7, 31.0. GCMS (EI) calculated for [M]⁺ 273.15, found 273.3. FTIR (neat, cm⁻¹): 3062(w), 3025(m), 2930(s), 1590(w), 1497(s), 1454(m), 1118(w), 962(m), 839(m), 747(m), 699(s).

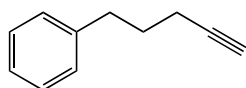


1-[(1E)-6-chlorohex-1-en-1-yl]-4-methoxybenzene (55), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of *i*BuOH were added and the reaction mixture was stirred at 45 °C. After 12 hours a 30 μ L was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 \rightarrow 15%) and isolated as a colorless oil (99 mg, 88% yield, E:Z = >100:1) ^1H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.05 (dt, J = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.56 (t, J = 6.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 1.92 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.9, 130.6, 129.9, 128.0, 127.2, 114.1, 55.4, 45.1, 32.3, 32.2, 26.8. GCMS (EI) calculated for $[\text{M}]^+$ 224.10, found 224.2. FTIR (neat, cm^{-1}): 3055(m), 2986(m), 2937(m), 2305(m), 1608(s), 1511(s), 896(s), 740(s).

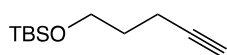


1,2,3-trimethoxy-5-[(E)-2-(4-methylphenyl)ethenyl]benzene (57) compound was prepared according to an altered general procedure. LiOt-Bu was used in place of NaOt-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 4 h. After the addition of 2 equiv of NaOt-Bu and 5 equiv of MeOH. The reaction mixture was stirred at 60 °C. After 24 hours a 30 μ L was taken and analysis by GC confirmed complete isomerization to the *E*-alkene. The compound was purified by trituration with Hex and isolated as a white solid (115 mg, 85% yield, 1 isomer). This compound has been previously synthesized and spectra matches literature values.¹⁰

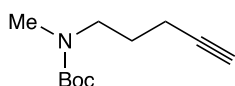
11. Alkyne Starting Materials



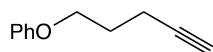
5-phenyl-1-pentyne (1) was purchased from GFS Chemical and distilled over calcium hydride under reduced pressure before use.



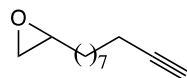
tert-butyl dimethyl (pent-4-yn-1-yloxy)silane (S1) was prepared according to a known procedure and has been previously characterized.¹



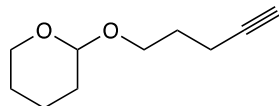
tert-butyl N-methyl-N-(pent-4-yn-1-yl)carbamate (S2) was prepared according to a known procedure and has been previously characterized.²



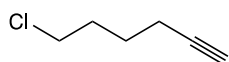
(pent-4-yn-1-yloxy)benzene (S3) was prepared according to a known procedure and has been previously characterized.³



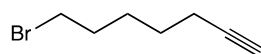
2-(dec-9-yn-1-yl)oxirane (S4) was prepared according to a known procedure and has been previously characterized.⁴



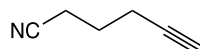
2-(pent-4-yn-1-yloxy)tetrahydro-2H-pyran (S5) has been previously characterized and spectral data match literature values.⁵



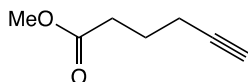
6-chlorohex-1-yne (S6) was purchased from TCI America and distilled over calcium hydride under reduced pressure before use.



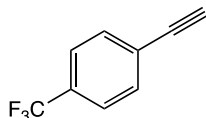
7-bromohept-1-yne (S7) was prepared according to a known procedure and has been previously characterized.⁶



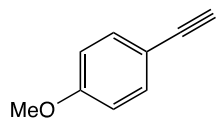
hex-5-ynenitrile (S8) was purchased from Oakwood Chemical and distilled over calcium hydride under reduced pressure before use.



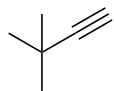
methyl hex-5-ynoate (S9) was purchased from Fischer Scientific and distilled over calcium hydride under reduced pressure before use.



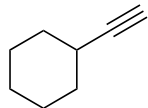
1-ethynyl-4-(trifluoromethyl)benzene (S10) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



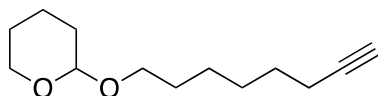
1-ethynyl-4-methoxybenzene (S11) was purchase from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



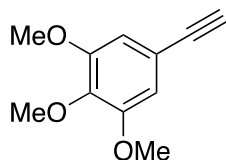
3,3-dimethylbut-1-yne (S12) was purchased from Milipore Sigma and distilled over calcium hydride under reduced pressure before use.



ethynylcyclohexane (S13) was purchased from Milipore Sigma and distilled over calcium hydride under reduced pressure before use.

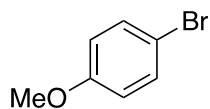


2-(oct-7-yn-1-yloxy)oxane (S14) was prepared according to a known literature procedure and has been previously characterized.⁷

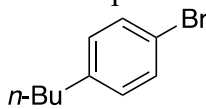


5-ethynyl-1,2,3-trimethoxybenzene (S15) was prepared according to a known literature procedure and has been previously characterized.⁸

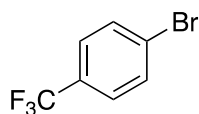
12. Aryl Bromide Starting Materials



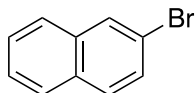
4-bromoanisole (2) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



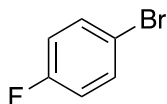
1-bromo-4-butylbenzene (4) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



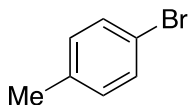
4-bromobenzotrifluoride (S16) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



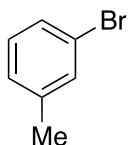
2-bromonaphthalene (S17) was purchased from Ark-Pharm and used without purification.



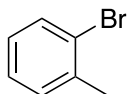
1-bromo-4-fluorobenzene (S18) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



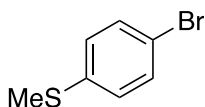
4-bromotoluene (S19) was purchased from Alfa Aesar and used without purification.



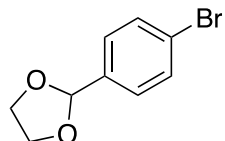
3-bromotoluene (S20) was purchased from TCI America and distilled over calcium hydride under reduced pressure before use.



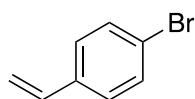
2-bromotoluene (S21) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



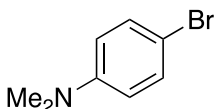
1-bromo-4-(methylsulfanyl)benzene (S22) was purchased from Oakwood Chemicals and used without purification.



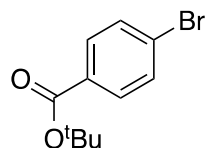
1-bromo-4-phenyl-1,3-dioxolane (S23) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.



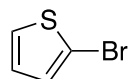
4-bromostyrene (S24) was purchased from TCI America and degassed before use.



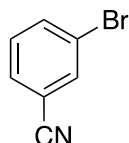
4-bromo-N,N-dimethylaniline (S25) was purchased from Oakwood Chemicals and used without purification.



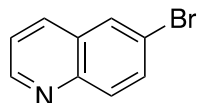
tert-butyl-4-bromobenzoate (S26) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.



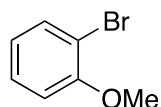
2-bromothiophene (S27) was purchased from Combi-Blocks and distilled over calcium hydride under reduced pressure before use.



3-bromobenzonitrile (S28) was purchased from Ark-Pharm and used without purification.

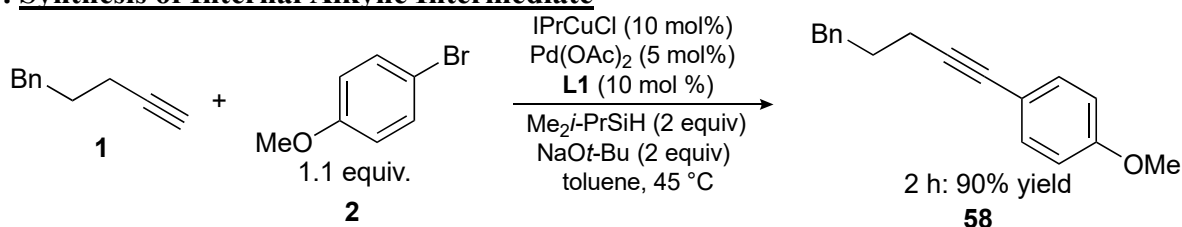


6-bromoquinoline (S29) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.

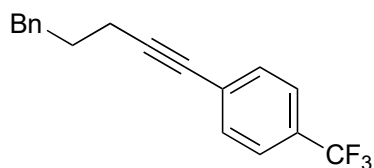


2-bromoanisole (S30) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.

13. Synthesis of Internal Alkyne Intermediate



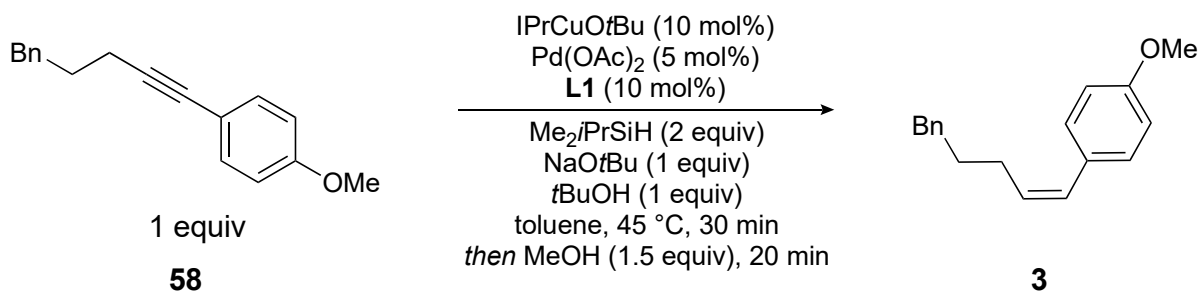
In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaO*t*-Bu (96.1 mg, 1.00 mmol, 2 equiv). To this was added alkyne (**1**) (0.50 mmol, 1.0 equiv), Pd(OAc)₂ (2.8 mg, 0.025 mmol, 0.100 equiv) IPrCuCl (24.4 mg, 0.050 mmol, 0.10 equiv), L1 (19 mg, 0.050 mmol, 0.10 equiv), aryl bromide (**2**) (102.9 mg, 0.550 mmol, 1.10 equiv), Me₂*i*-PrSiH (102.3 mg, 1.00 mmol, 2.00 equiv), and toluene (5 mL). The reaction mixture was stirred at 45 °C, and monitored by TLC until starting alkyne was fully consumed, 2h. TLC 100% Hex. Compound was purified by silica gel column chromatography (Et₂O/Hex 0→10%) and passed through a short plug of alumina (10% Et₂O/Hex) **58** was isolated as a clear colorless liquid (113 mg, 90% yield). This compound has been previously synthesized and spectra matches literature values.¹⁵



1-(5-phenylpent-1-yn-1-yl)-4-(trifluoromethyl)benzene (59), was synthesized according to the above procedure, but has previously been synthesized and spectra matches literature values.¹⁵

14. Mechanistic Studies: Semireduction (Scheme 5)

Catalytic Semireduction: Contribution of Pd and Cu catalysts



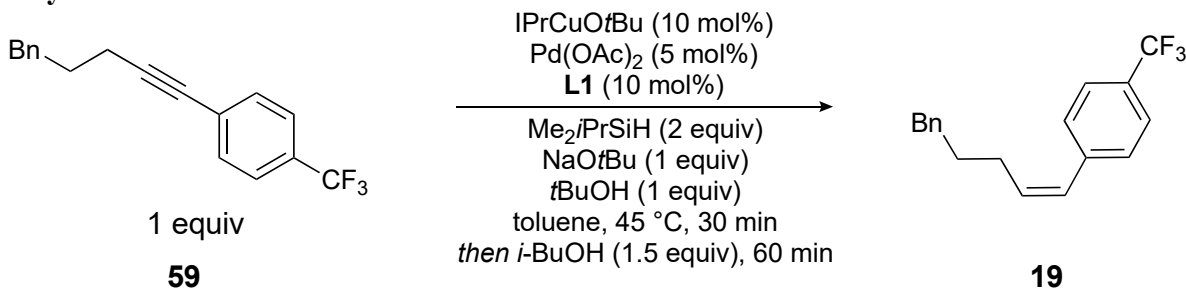
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then MeOH (2.4 mg, 0.075 mmol, 1.5 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 10 min, 20 min, 30 min and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S6.

Reaction Conditions	yield (10 min)	yield (20 min)	yield (30 min)	yield (24 h)
Above Conditions	78%	86% (18:1) *	86% (18:1) *	80% (3:1) *
No Cu	38%	39%	40%	41%
No Pd/L	64%	70%	71%	99% (48:1) *

*Z:E diastereoselectivity determine by GC analysis. Yield of major isomer is reported

Catalytic Semireduction: EWG with *i*-BuOH



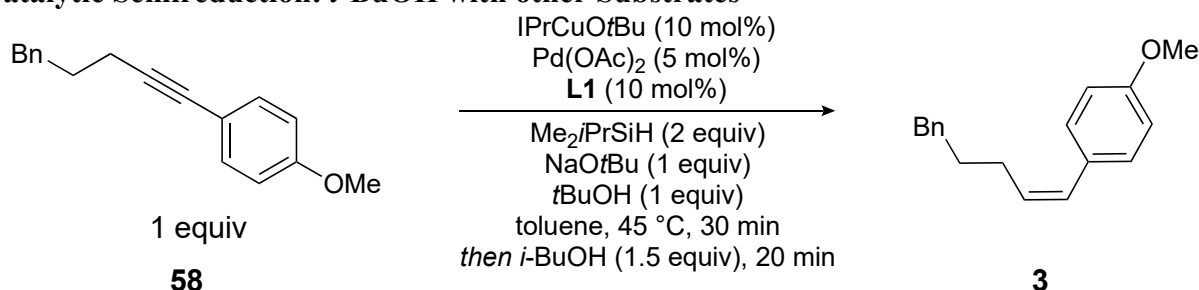
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **59** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then *i*-BuOH (4.1 mg, 0.075 mmol, 1.5 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 30 min, 60 min and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S7.

Reaction Conditions	yield (30 min)	yield (60 min)	yield (24 h)
Above Conditions	58%	76% (38:1) *	36% (2:1) *
No Cu	1%	5%	11%
No Pd/L	40%	52%	74%

*Z:E diastereoselectivity determined by GC analysis. Yield of major isomer is reported

Catalytic Semireduction: *i*-BuOH with other Substrates



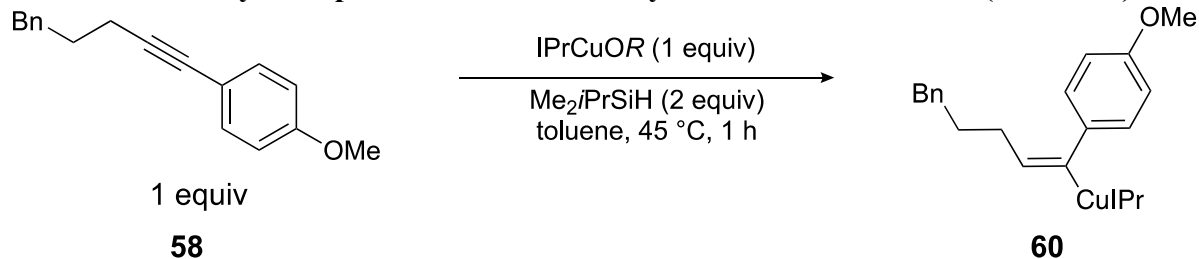
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then *i*-BuOH (4.1 mg, 0.075 mmol, 1.5 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 10 min, 20 min, 30 min and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S8.

Reaction Conditions	yield (10 min)	yield (20 min)	yield (30 min)	yield (24 h)
Above Conditions	39%	57%	66%	74%
No Cu	1%	2%	6%	9%
No Pd/L	26%	39%	49%	56%

*Z:E diastereoselectivity determine by GC analysis. Yield of major isomer is reported

Stoichiometric Hydrocupration of Internal Alkyne: Effect of IPrCuOR (Scheme 6)



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, IPrCuOR (0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Me₂i-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C and 15 μL aliquots were taken every min for 10 min, and then every 5 min for 1 hour and passed through a short plug of silica in the glovebox with 1.5 mL of Ether and analyzed by Gas Chromatography. The reported yield of **60** is based on the yield of alkene obtained after quenching of the reaction mixture.

Table S9a

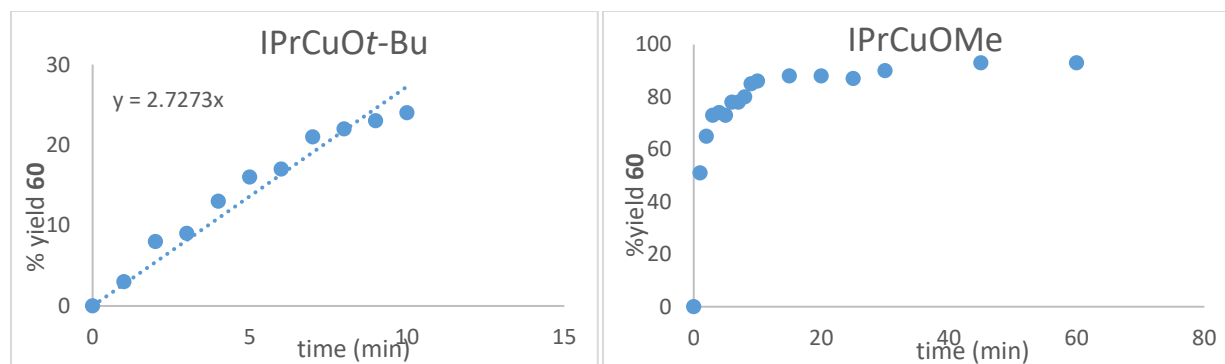
IPrCuOt-Bu

Time (min)	% 58	% yield (60)
0	96	0
1	93	3
2	91	8
3	86	9
4	83	13
5	78	16
6	82	17
7	72	21
8	71	22
9	70	23
10	70	24
15	60	27
20	54	36
25	0	48
30	37	45
45	29	68
60	20	74

Table S9b

IPrCuOMe

Time (min)	% 58	% yield (60)
0	100	0
1	47	51
2	28	65
3	26	73
4	23	74
5	20	73
6	18	78
7	19	78
8	17	80
9	15	85
10	15	86
15	13	88
20	13	88
25	13	87
30	10	90
45	10	93
60	8	93



Control Experiments for Quenching Alkenyl Copper with Dibromotetrachloroethane

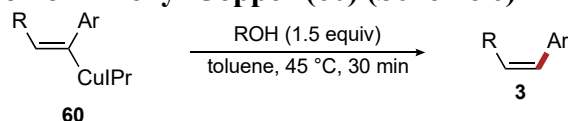
Quenching of *IPrCuOt-Bu*

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, *IPrCuOt-Bu* (2.6 mg, 0.0050 mmol, 0.1 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), *Me*₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), Na*Ot*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv), MeOH (2.4 mg, 0.075 mmol, 1.5 equiv), Br₂Cl₄C₂ (65.1 mg, 0.2 mmol, 4 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C and 15 μL aliquots were taken at 20 min 1 hour and 2 hours, passed through a short plug of silica with 1.5 mL of EtOAc and analyzed by Gas Chromatography. Over the course of the reaction there was no formation of alkenyl copper or vinyl bromide product and quantitative recovery of the internal alkyne. This indicated that in the presence of 4 equivalents of dibromotetrachloroethane the catalyst could not turnover, thus confirming it as an effective quenching method.

Quenching of Alkenyl Copper

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, **58** (12.5 mg, 0.050 mmol, 1.0 equiv). To this was added **60** (3.5 mg, 0.0050 mmol, 0.1 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), *Me*₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), Na*Ot*-Bu (4.8 mg, 0.050 mmol, 1 equiv), MeOH (2.4 mg, 0.075 mmol, 1.50 equiv), Br₂Cl₄C₂ (65.1 mg, 0.2 mmol, 4 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C and 15 μL aliquots were taken at 20 min 1 hour and 2 hours, passed through a short plug of silica with 1.5 mL of EtOAc and analyzed by Gas Chromatography. Over the course of the reaction we observe only the formation of 1 equivalent of alkenyl bromide (relative to the amount of **60** used in the reaction) and the quantitative recovery of the internal alkyne. This indicated that in the presence of 4 equivalents of dibromotetrachloroethane the alkenyl copper could not turnover and regenerate the active catalyst, thus confirming it as an effective quenching method.

Stoichiometric Protonation of Alkenyl Copper (**60**) (Scheme 6)



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, alkenyl copper **60** (17.6 mg, 0.050 mmol, 1.00 equiv). To this was added TMB (2.8 mg, 0.017 mmol, 0.33 equiv), alcohol (0.075 mmol, 1.5 equiv) and toluene (0.50 mL). The reaction was placed at 45 °C and 15 μL aliquots were taken every min for the first 5 min and then every 5 min for 20 min. Aliquots were quenched into Br₂Cl₄C₂ (1.6 mg, 0.005 mmol, 0.04 equiv) and passed through a short plug of silica with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

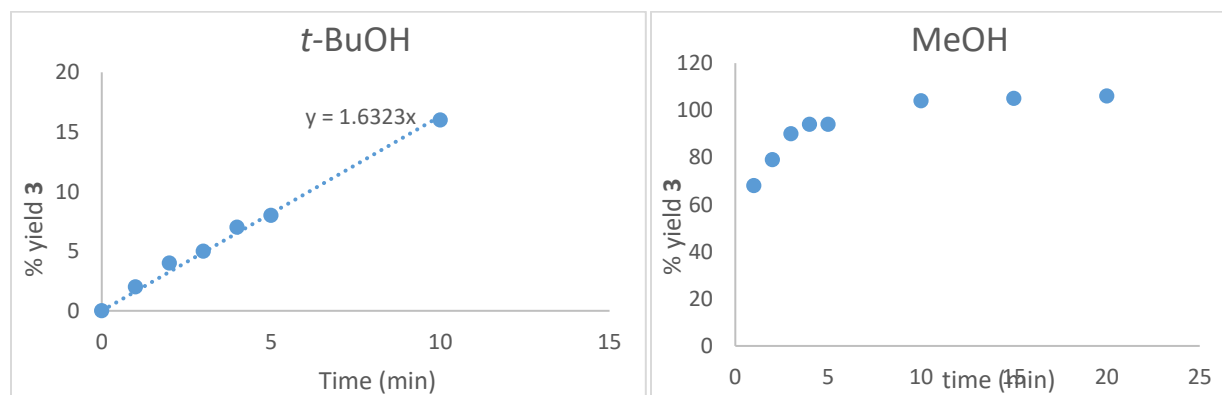
Table S10a

<i>t</i> -BuOH			
Time (min)	alkenyl copper (60)	% yield 3	% yield 3 (corrected)
0	86	5	0
1	85	7	2
2	86	9	4
3	85	10	5
4	82	12	7
5	84	13	8
10	70	21	16
15	67	25	20
20	61	27	22

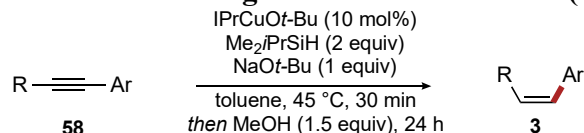
Table S10b

MeOH		
Time (min)	alkenyl copper (60)	% yield 3
0	100	0
1	34	68
2	22	79
3	0	90
4	0	94
5	0	94
10	0	104
15	0	105
20	0	106

Yields for *t*-BuOH are corrected to 0 based on initial formation of alkene before alcohol was added



Copper-Catalyzed Semireduction of Sonogashira: Effect of ROH (Scheme 6)



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), alcohol (0.075 mmol, 1.5 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C 15 μ L aliquots were taken, and quenched into Br₂Cl₄C₂ (3.4 mg, 0.004 mmol, 0.04 equiv) and diluted with 0.50 mL of Ether, passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S11a

MeOH

Time (min)	% yield 3
0	0
10	37
20	61
30	72
2 h	79
7 h	80
24 h	82

Table S11b*t*-BuOH

Time (min)	% 58	% yield 3
1	98	0
5	100	0
10	100	0
20	95	0
30	95	2
60	90	1
90	96	4
5 h	83	8
8 h	69	16
24 h	73	23

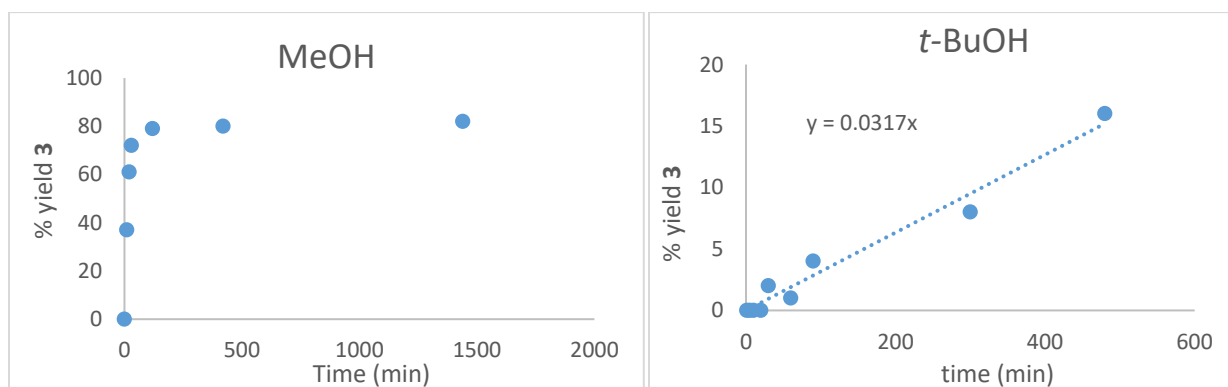


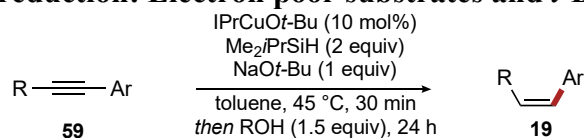
Table S11c

1.5 MeOH and No NaOt-Bu

Time (min)	% 58	% yield 3	% alkenyl copper 60
0	100	0	0
1	73	22	4
2	70	30	4
3	60	35	4
4	54	40	4
5	44	52	4
10	43	52	4
20	36	63	4
30	33	66	4
45	30	63	2
60	31	66	3
3 h	29	66	0
8 h	28	63	0
24 h	28	67	0

Table S11d1 equiv *t*-BuOH with 1.5 equiv MeOH

Time (min)	% 58	% yield 3	% alkenyl copper 60
0	90	0	4
1	72	18	5
2	66	22	7
3	71	22	5
4	64	27	5
5	65	29	5
8	58	37	5
10	52	41	5
15	50	44	5
20	34	62	5
25	25	65	5
30	22	75	4
45	13	84	3
60	12	88	0
75	15	84	0
90	10	93	0
2 h	10	93	0
7 h	4	96	0
24h	11	90	0

Copper Catalyzed Semireduction: Electron poor substrates and *i*-BuOH (Scheme 7)

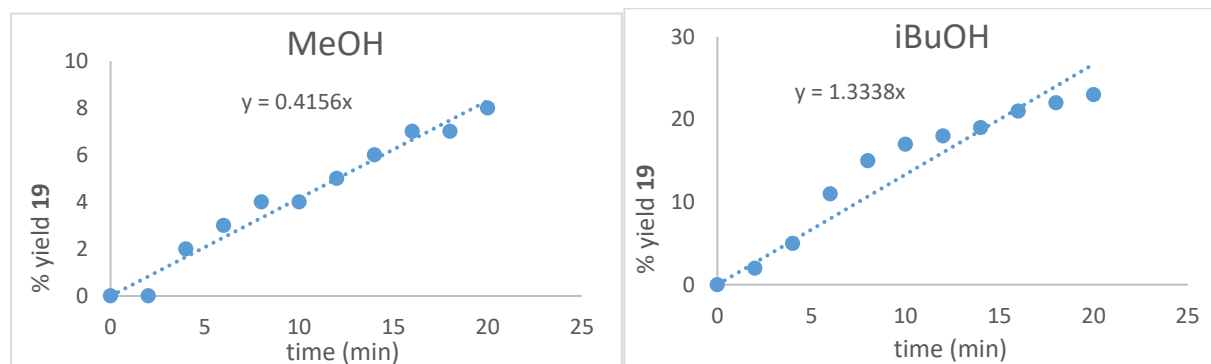
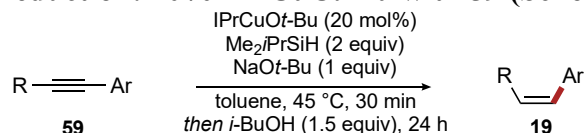
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **59** (14.4 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), alcohol (0.075 mmol, 1.5 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C 15 μL aliquots were taken, and quenched into Br₂Cl₄C₂ (3.4 mg, 0.004 mmol, 0.04 equiv) and diluted with 0.50 mL of Ether, passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Table S12a

Time (min)	% 59	% yield 19	alkenyl copper
0	97	0	0
2	92	0	4
4	91	2	6
6	90	3	6
8	91	4	6
10	86	4	7
12	93	5	8
14	89	6	8
16	88	7	9
18	87	7	10
20	88	8	10

Table S12b

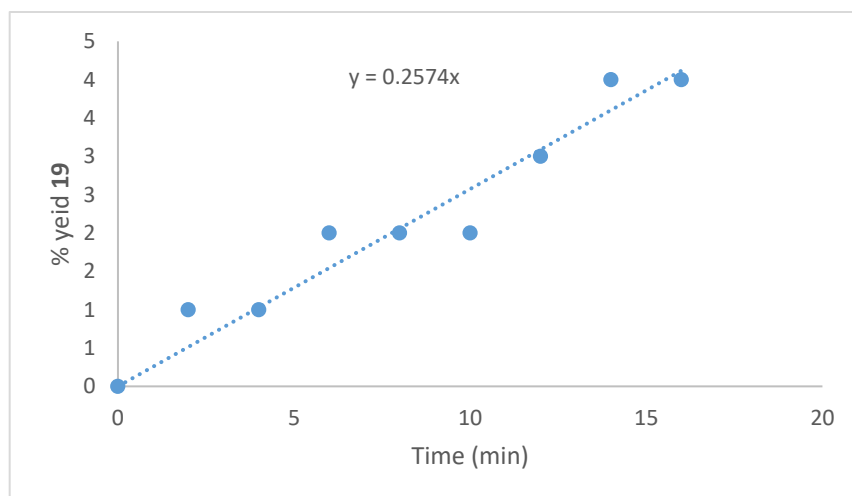
Time (min)	% 59	% yield 19	alkenyl copper (61)
0	100	0	0
2	95	2	5
4	88	5	10
6	83	11	10
8	80	15	9
10	75	17	8
12	74	18	10
14	69	19	10
16	69	21	10
18	69	22	10
20	70	23	10

**Copper-Catalyzed Semireduction: 20% IPrCuOt-Bu with 59 (Scheme 7)**

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **59** (14.4 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), IPrCuOt-Bu (5.2 mg, 0.01 mmol, 0.20 equiv), Me₂i-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *i*-BuOH (0.075 mmol, 1.5 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C 15 μ L aliquots were taken, and quenched into Br₂Cl₄C₂ (3.4 mg, 0.004 mmol, 0.04 equiv) and diluted with 0.50 mL of Ether, passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

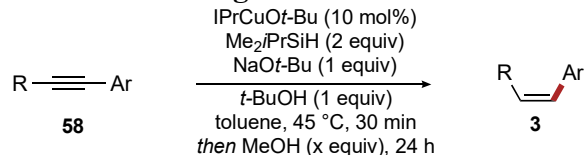
Table S13

Time (min)	% 59	% yield 19	alkenyl copper (61)
0	100	0	0
2	84	1	20
4	85	1	18
6	82	2	19
8	78	2	20
10	79	2	21
12	89	3	18
14	82	4	18
16	82	4	19
18	78	4	20
20	78	4	20
25	75	5	20
30	71	5	21
45	72	7	18
60	75	8	18
90	68	10	19
120	64	11	20



15. Effect of MeOH Stoichiometry on Copper-Catalyzed Semireduction

Copper-catalyzed Semireduction of Sonogashira intermediate: Effect of MeOH (Scheme 8)

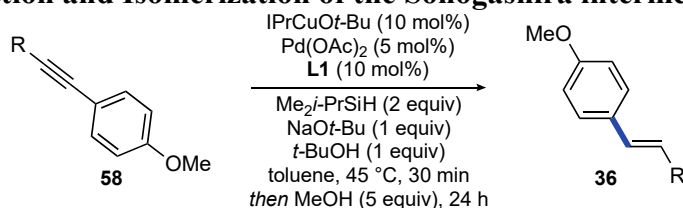


equiv of MeOH	Yield (30 min)	yield (4 h)	yield (7 h)	yield (24 h)
1	65%	70%	86%	89%
2	50%	66%	73%	75%
3	32%	33%	33%	35%
4	16%	16%	17%	17%
5	10%	10%	10%	10%

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then MeOH (x equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 30 min, 4 h, 7 h and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

16. Mechanistic Studies: Isomerization

Catalytic Semireduction and Isomerization of the Sonogashira intermediate to the *E*-alkene

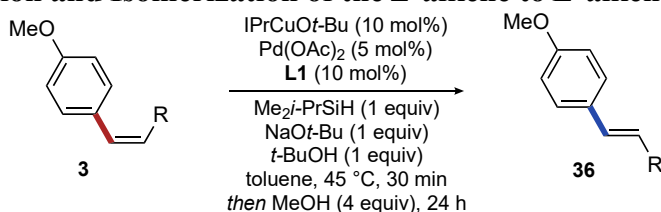


In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then MeOH (8.0 mg, 0.25 mmol, 5 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 20 min, 4 h, 7 h, and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Reaction Conditions	yield (20 min)	yield (4 h)	yield (7 h)	yield (24 h)
Above Conditions	20%	50%	60%	88%
No Cu	0% (83%) ^a	0% (33%) ^a	40%	60%
No Pd/L	0% (97%) ^a	0% (95%) ^a	0% (95%) ^a	0% (90%) ^a
No MeOH	0% (100%) ^a	0% (97%) ^a	0% (92%) ^a	0% (87%) ^a

^aYield of Sonogashira starting material, mass balance is *Z* alkene.

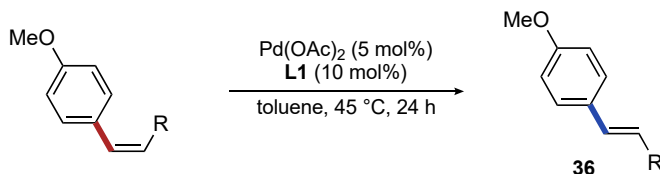
Catalytic Semireduction and Isomerization of the *Z*-alkene to *E*-alkene



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaOt-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **3** (12.6 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), L1 (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuOt-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (5.1 mg, 0.05 mmol, 1.0 equiv), *t*-BuOH (3.7 mg, 0.050, 1.0 equiv) and toluene (0.50 mL). The reaction mixture was stirred at 45 °C for 30 min, then MeOH (8.0 mg, 0.25 mmol, 4.0 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 20 min, 4 h, 7 h, and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

Reaction Conditions	Yield (20 min)	Yield (4 h)	Yield (7 h)	Yield (12 h)	yield (24 h)
Above Conditions	80% (74:1)	85% (76:1)	88% (81:1)	88% (100:1)	88% (100:1)
No Me ₂ <i>i</i> -PrSiH	0%	0%	2%	3%	8%
No Pd/L	0%	0%	1%	1%	5%

Conditions for the Isomerization of *Z*-alkenes to *E*-alkenes



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, **3** (12.6 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg, 0.017 mmol, 0.33 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), L1 (1.9 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (0.50 mg, 0.005 mmol, 0.10 equiv) and toluene (0.50 mL) and the appropriate additive. The reaction mixture was stirred at 45 °C for 30 min, then MeOH (8.0 mg, 0.25 mmol, 4.0 equiv) was added. The reaction mixture was stirred at 45 °C and 30 μL aliquots were taken at 20 min, 4 h, 7 h, and 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography.

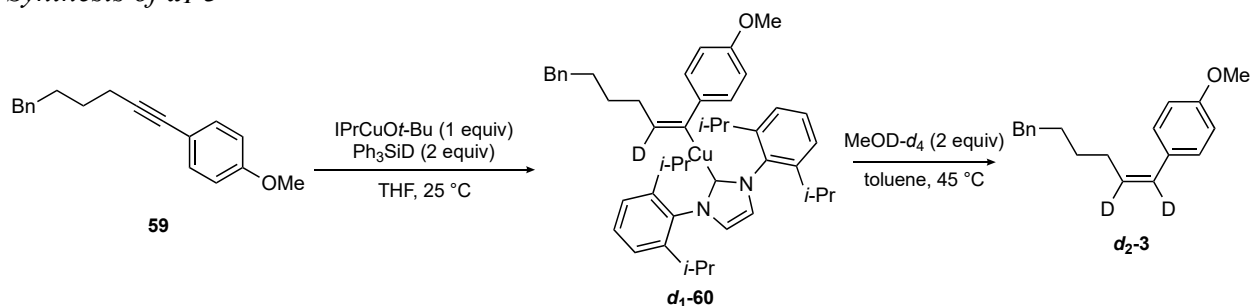
Reaction Conditions	Yield (20 min)	yield (4 h)	yield (7 h)	yield (24 h)
10 mol% Me ₂ <i>i</i> -PrSiH	18%	47%	69%	88% ^a
10 mol% Me ₂ <i>i</i> -PrSiH w/ 4 equiv MeOH	9%	15%	46%	82% ^a
Pd ₂ dba ₃ instead of Pd(OAc) ₂	0%	0%	0%	2%
1 equiv Me ₂ <i>i</i> -PrSiH	34%	73%	80%	82% ^a
1 equiv Me ₂ <i>i</i> -PrSiH w/ 4 equiv MeOH	15%	23%	63%	85% ^a
2 equiv Me ₂ <i>i</i> -PrSiH	28%	95% ^b	82%	78%

2 equiv Me ₂ <i>i</i> -PrSiH w/ 4 equiv MeOH	11%	85%	93 ^b	81%
Pd ₂ dba ₃ w/ 1 equiv Me ₂ <i>i</i> - PrSiH	8%	14%	18%	44% ^c
Pd ₂ dba ₃ w/ 2 equiv Me ₂ <i>i</i> - PrSiH	8%	9%	20%	45% ^c

^aRemaining material is overreduction to alkane. ^bFull isomerization complete, extended reaction times result in increased reduction to alkane. ^cRemaining material is *Z*-alkene.

17. Mechanistic Studies: Deuterium Incorporation Experiments

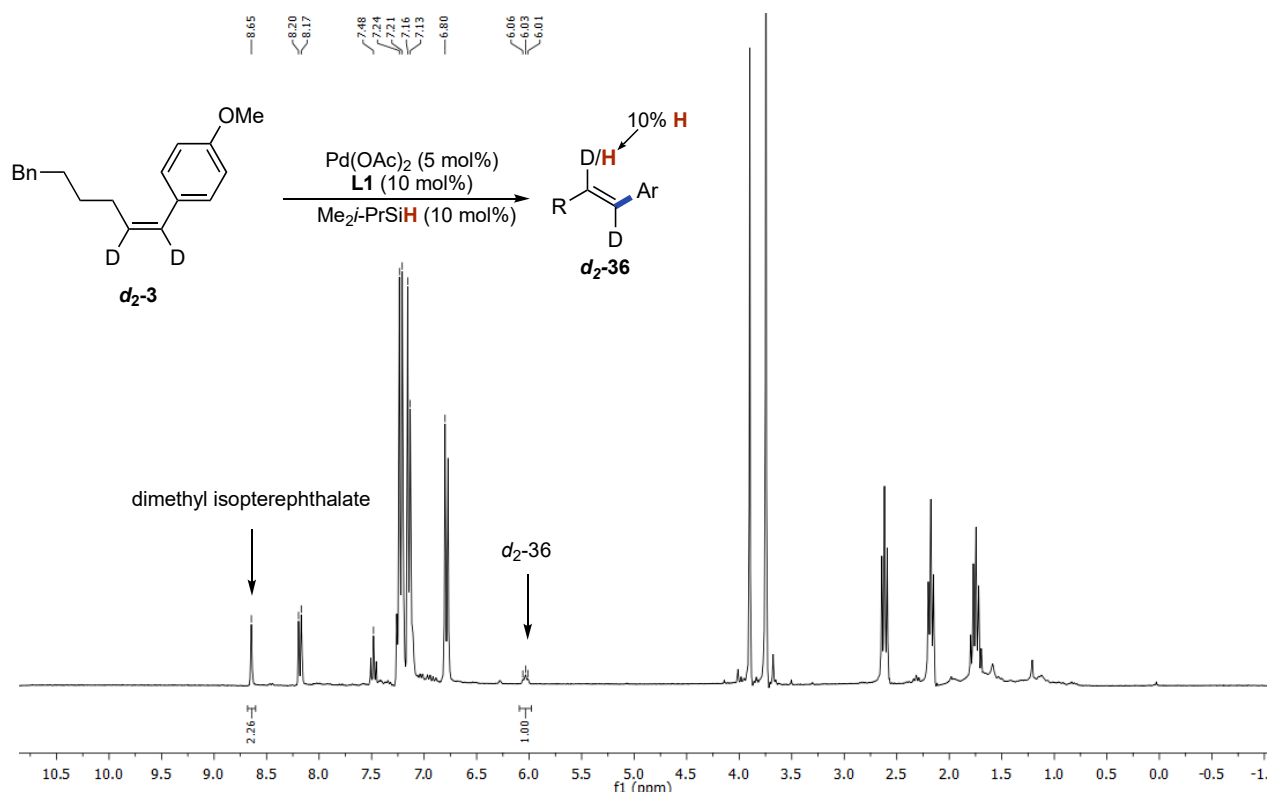
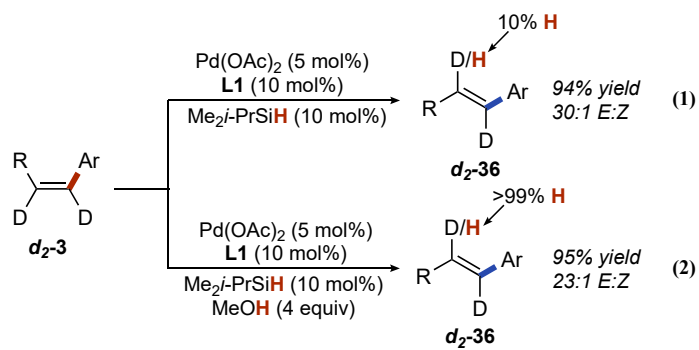
Synthesis of *d*₁-3

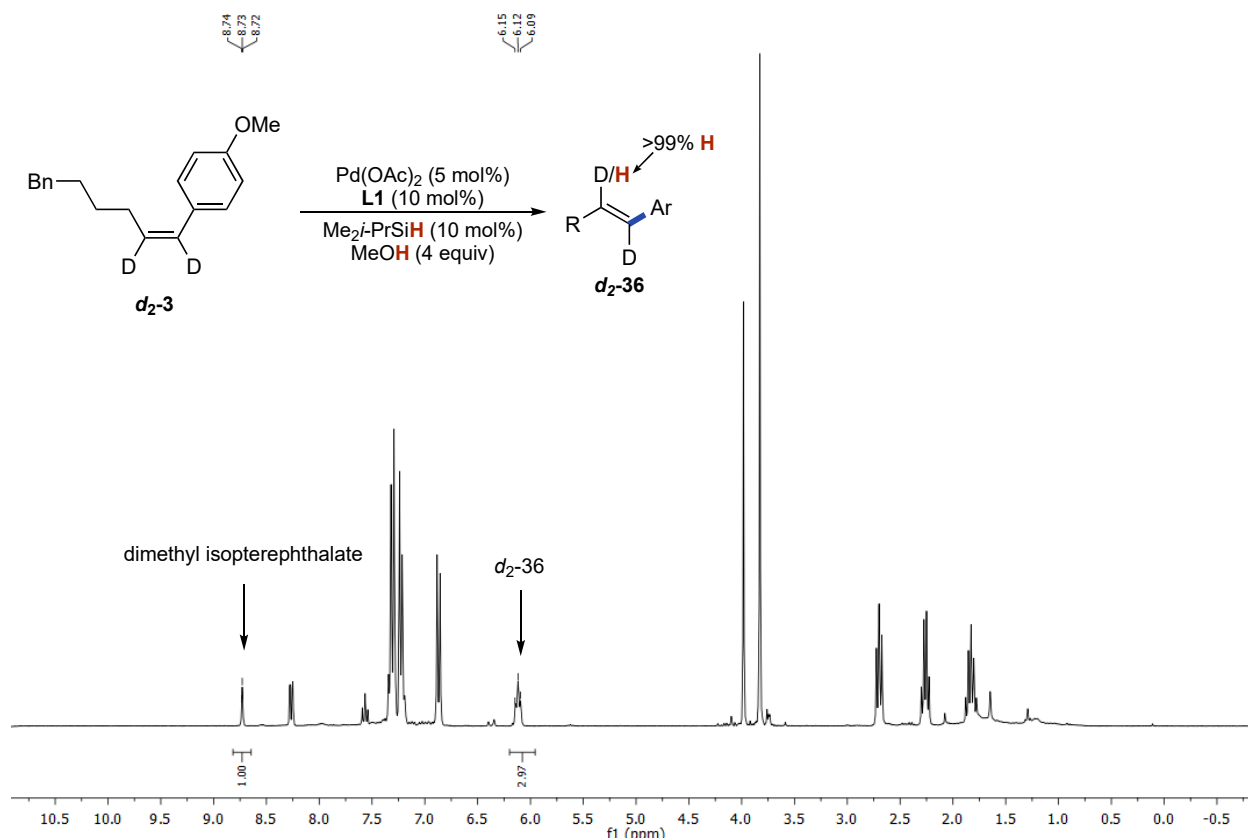


In a nitrogen filled glovebox, IPrCuOt-Bu (394.7 mg, 0.750 mmol, 1.0 equiv) was weighed in a 20 mL scintillation vial, followed by 1000 μ L THF. **58** (225.3 mg, 0.90 mmol, 1.2 equiv) was weighed out and transferred to the reaction with 3 aliquots of 500 μ L of THF and reaction mixture was allowed to stir at 25 $^{\circ}$ C for 1 min resulting in a orange solution. TriphenylSilane-*d*₁¹⁶ (391.7 mg, 1.5 mmol, 2.00 equiv) was weighed into a shell vial and transferred to the reaction with 3 aliquots of 500 μ L THF at which point the reaction turned red. The reaction was vigorously stirred (1500 rpm) at 25 $^{\circ}$ C for 30 min after which the reaction turned back to a light orange. The reaction was concentrated in vacuo, dissolved in minimal dichloromethane, layered with pentane and recrystallized at -35 $^{\circ}$ C. ***d*₁-60** was then filtered and washed with cold pentane. ***d*₁-60** was then dissolved in 2 ml of toluene and MeOD-*d*₄ (54.1 mg, 1.5 mmol, 2.0 equiv) was added. The reaction mixture was stirred until all the solids had dissolved, \sim 10 min. The reaction was then pushed through a plug of silica with excess EtOAc and purified by silica gel column chromatography. (0 \rightarrow 5% EtOAc in hexanes).

Deuterium Labeling

All glassware was washed with D₂O and then placed in an oven overnight. In a nitrogen filled glovebox, a dram vial was charged with a stir bar ***d*₂-3** (12.5 mg, 0.050 mmol, 1.0 equiv), Pd(OAc)₂ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), Me₂*i*-PrSiH (0.50 mg, 0.010 mmol, 0.1 equiv), and *d*₈-toluene (0.50 mL). The reaction mixture was stirred at 45 $^{\circ}$ C for 30 min, then MeOH (x equiv) was added. The reaction mixture was stirred at 45 $^{\circ}$ C and 30 μ L aliquots were taken at 24 h passed through a short plug of silica, washed with 1.5 mL of EtOAc and analyzed by Gas Chromatography to ensure completion. Then dimethyl isophterphthalate (2.6 mg, 0.017 mmol, 0.33 equiv) was added as internal standard and proton incorporation was determined by ¹HNMR in CDCl₃.





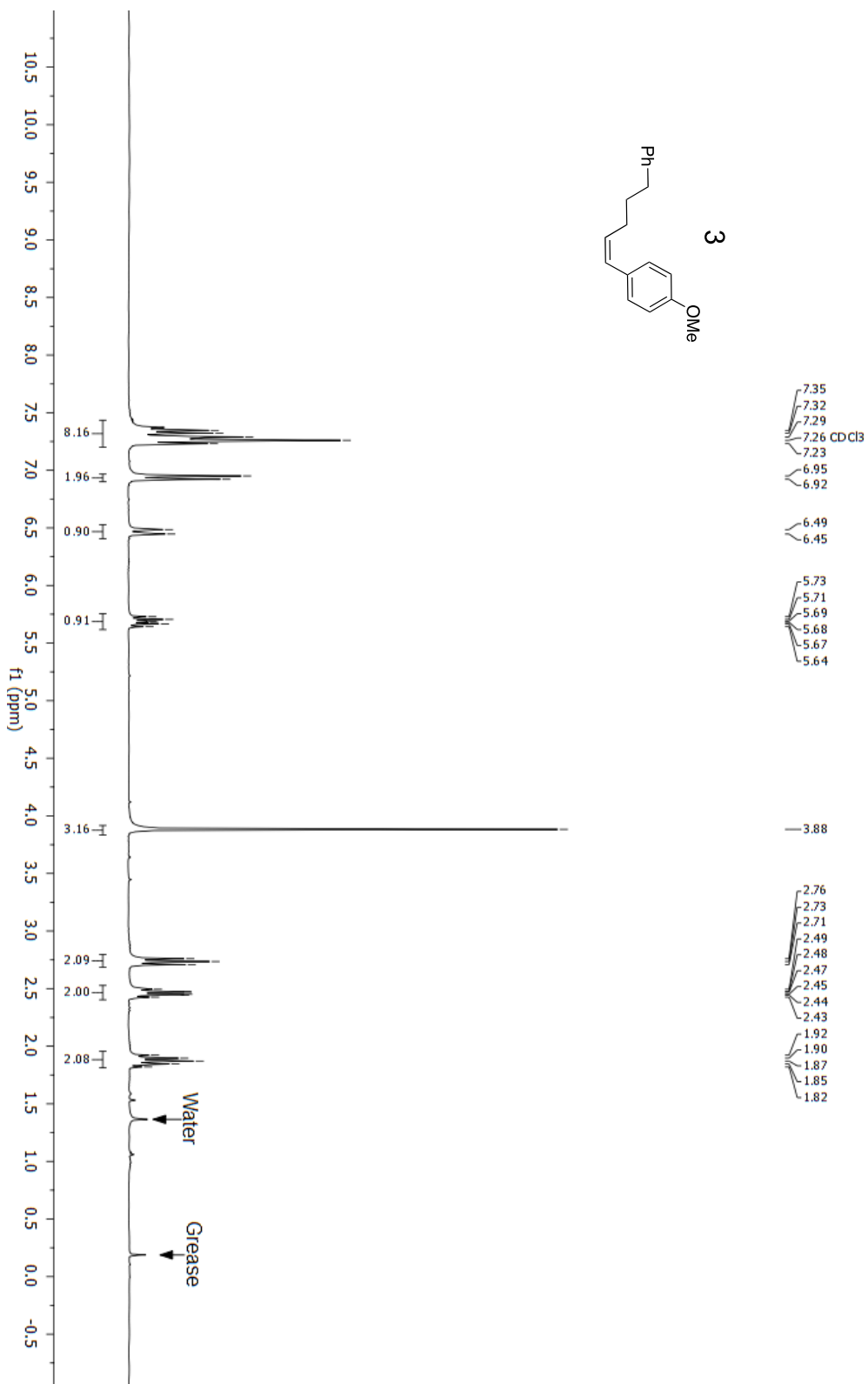
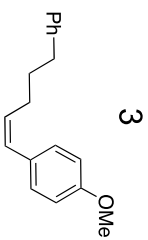
18. References

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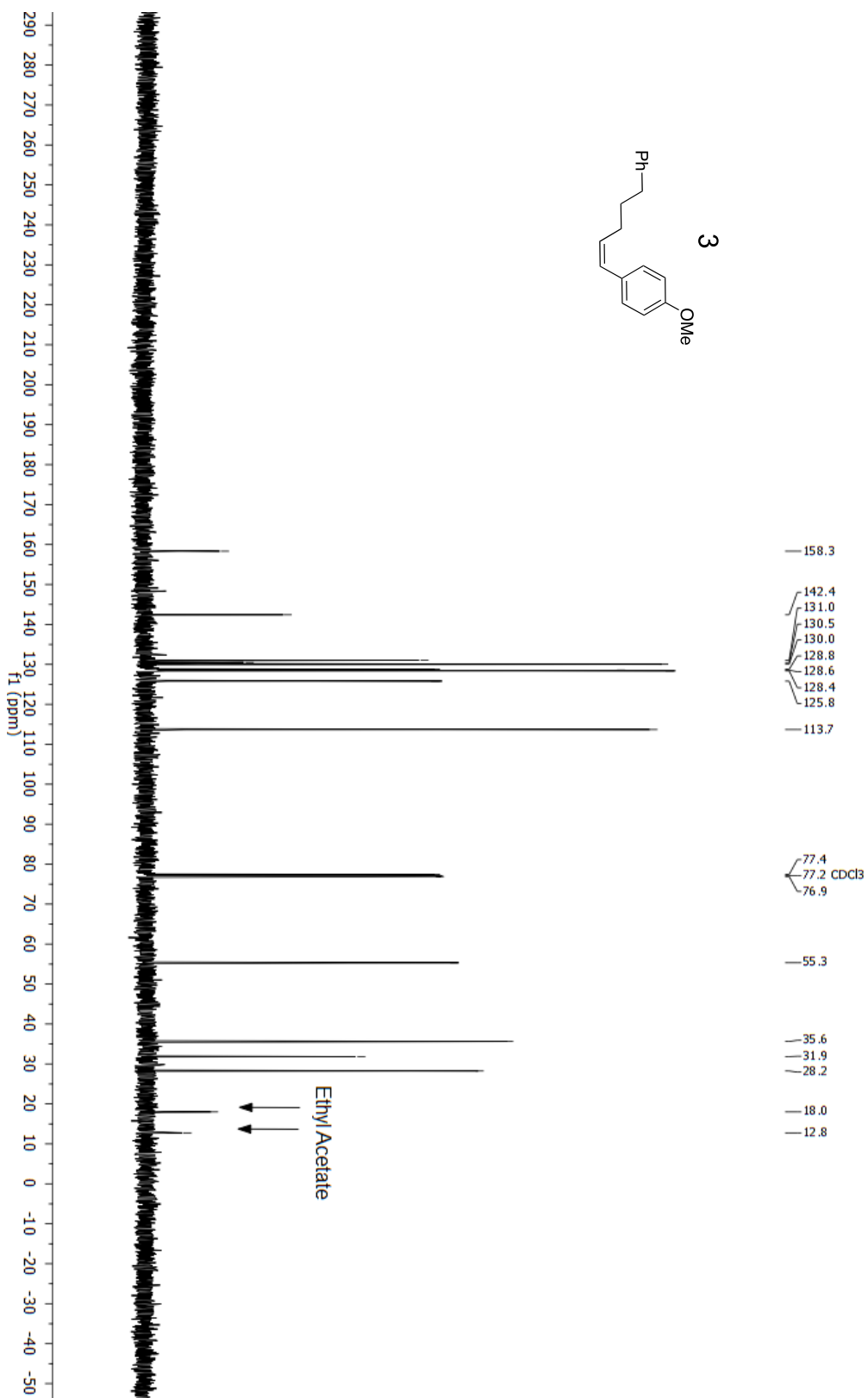
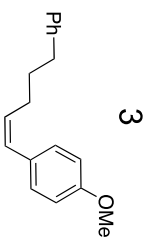
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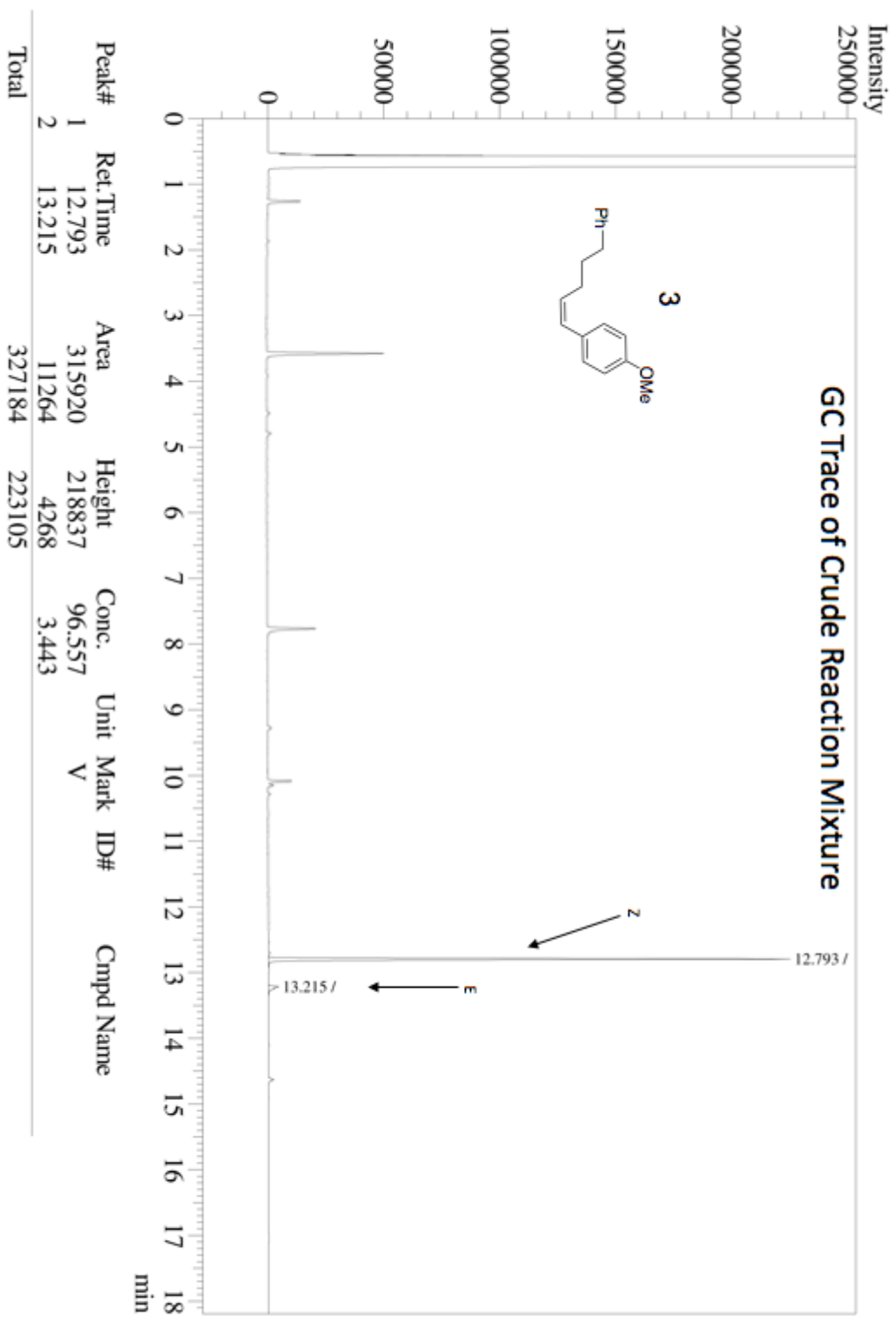
19. Spectral Data

¹H NMR (300 MHz, Chloroform-*d*) 8.744 – 7.117 (m, 7H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 11.7 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.88 (s, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.27 (dt, *J* = 7.6, 7.2 Hz, 2H), 1.87 (p, *J* = 7.6 Hz, 2H).

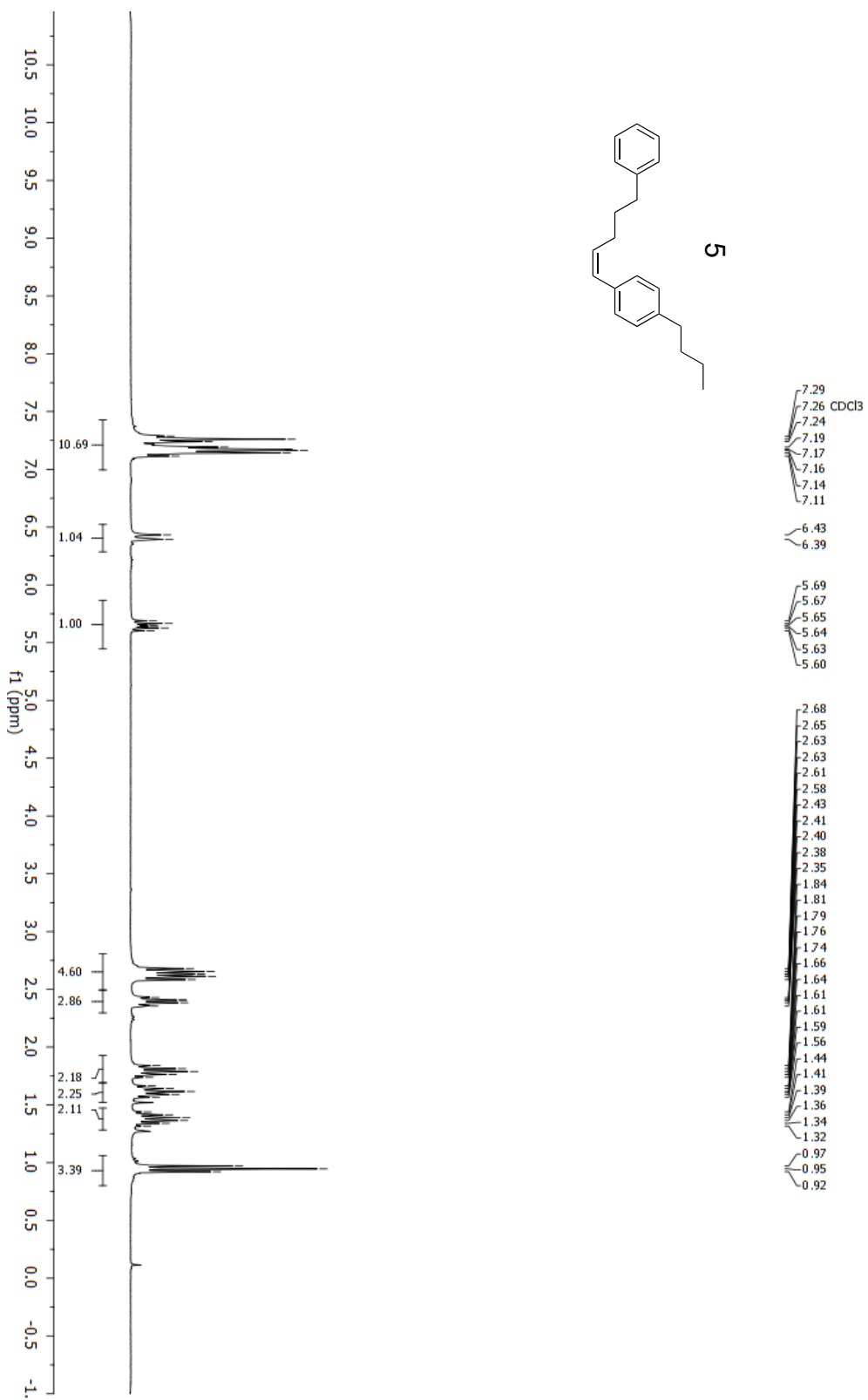
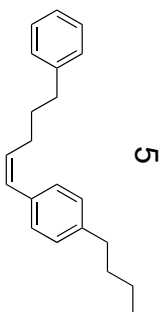


¹³C NMR (126 MHz, Chloroform-d) δ 158.6, 142.7, 131.3, 130.7, 130.3, 129.0, 128.8, 128.6, 126.1, 113.9, 55.6, 35.9, 32.1, 28.5.

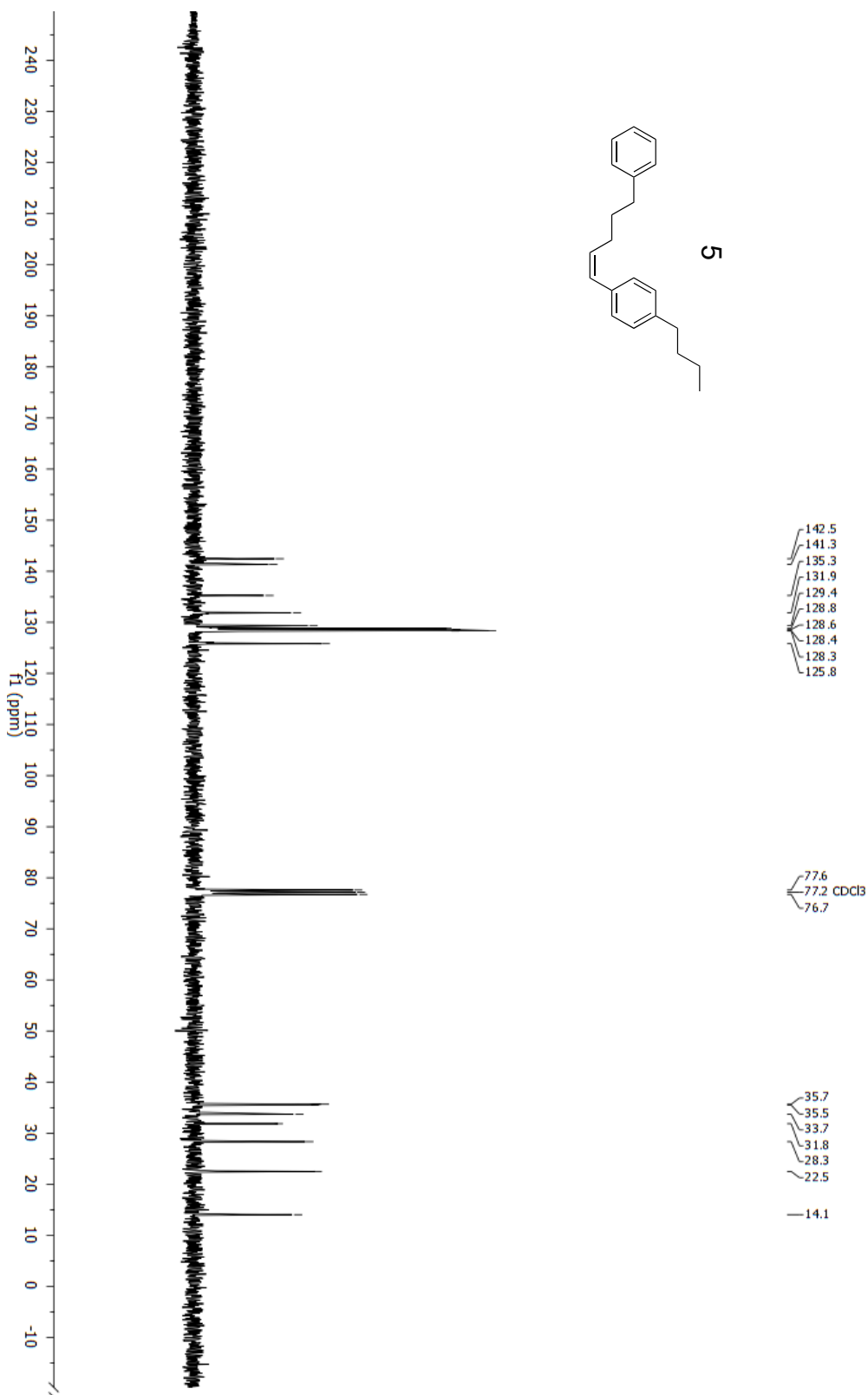
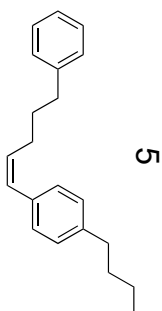




¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 6.99 (m, 11H), 6.41 (d, *J* = 11.6 Hz, 1H), 5.65 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.81 – 2.49 (m, 5H), 2.49 – 2.30 (m, 3H), 1.93–1.69 (m, 2H), 1.69 – 1.52 (m, 2H), 1.47 – 1.28 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

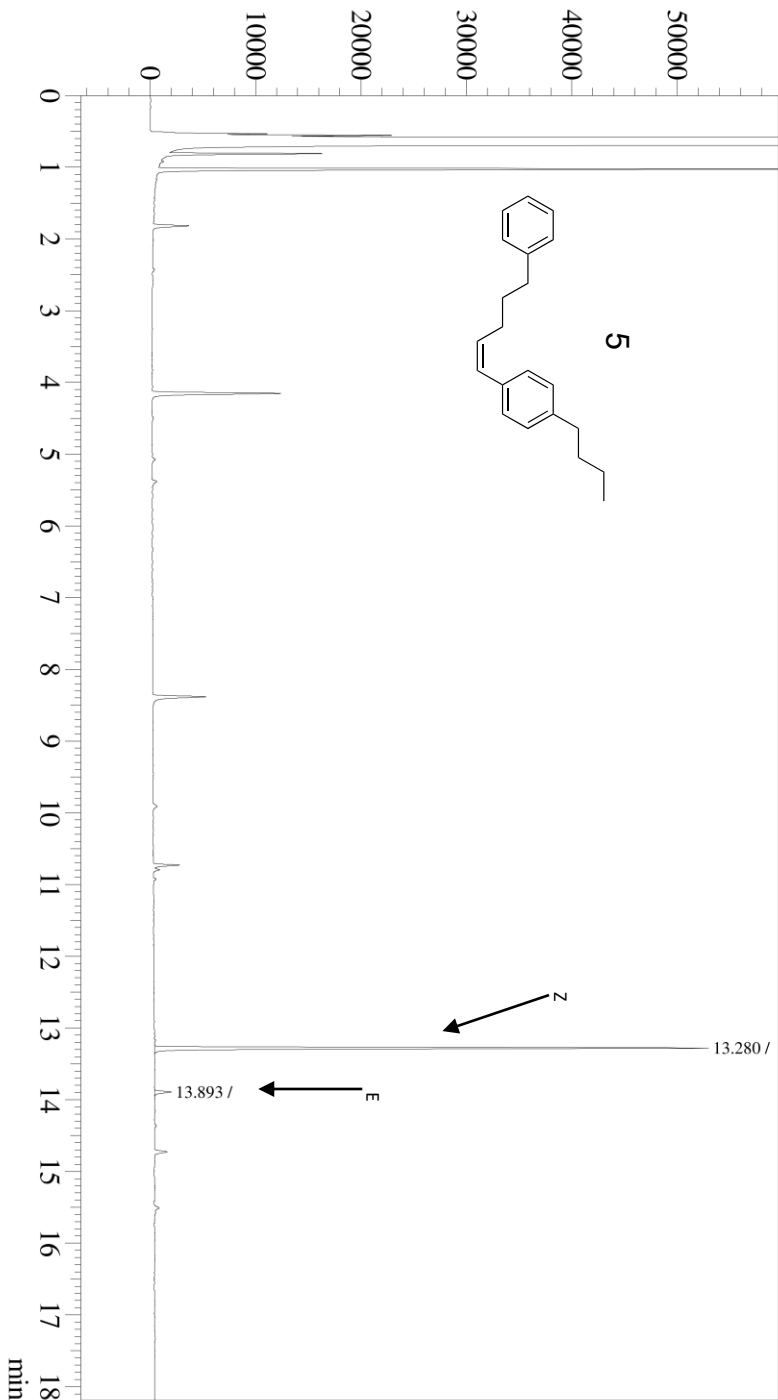


^{13}C NMR (75 MHz, CDCl_3) δ 142.5, 141.3, 135.3, 131.9, 129.4, 128.8, 128.6, 128.4, 128.3, 125.8, 35.7, 35.5, 33.7, 31.8, 28.3, 22.5, 14.1.



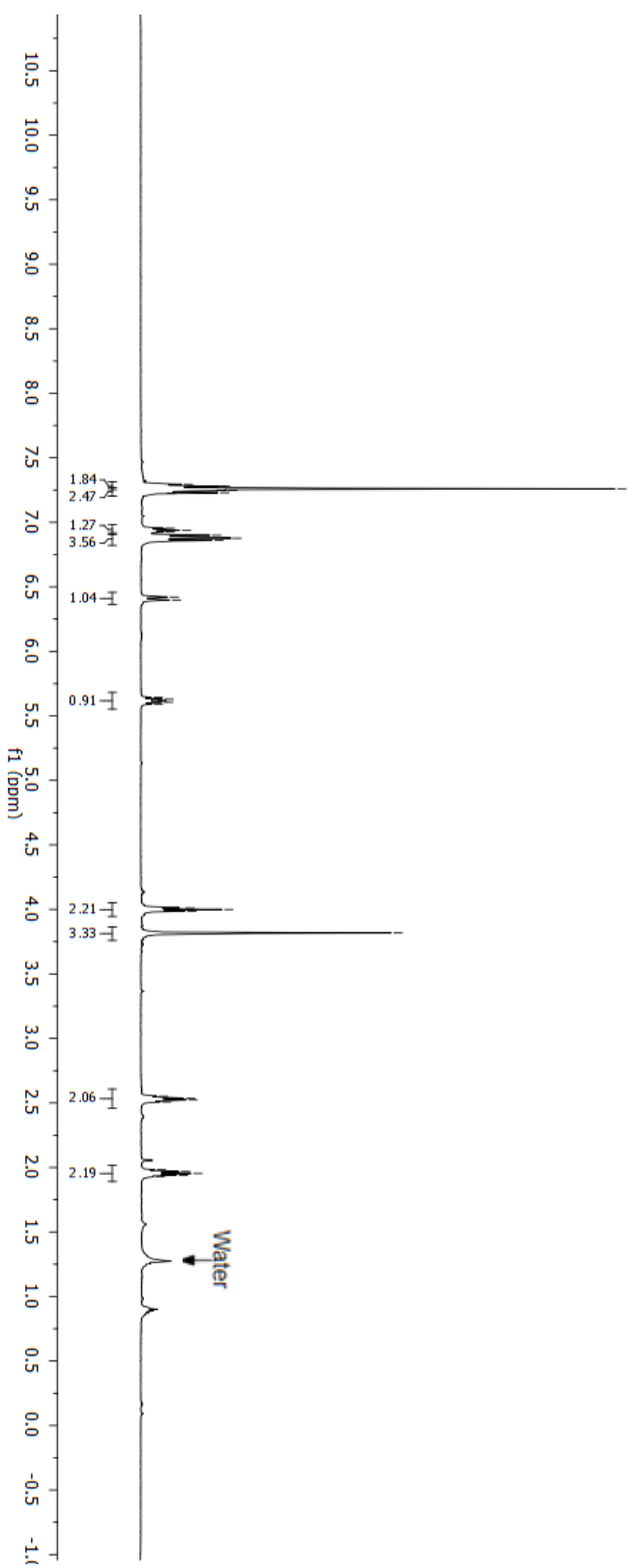
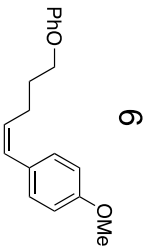
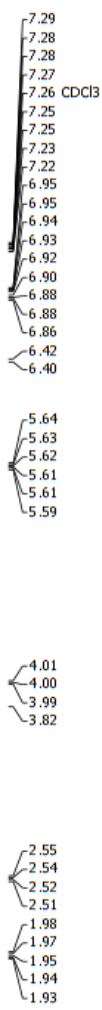
Intensity

GC Trace of Crude Reaction Mixture

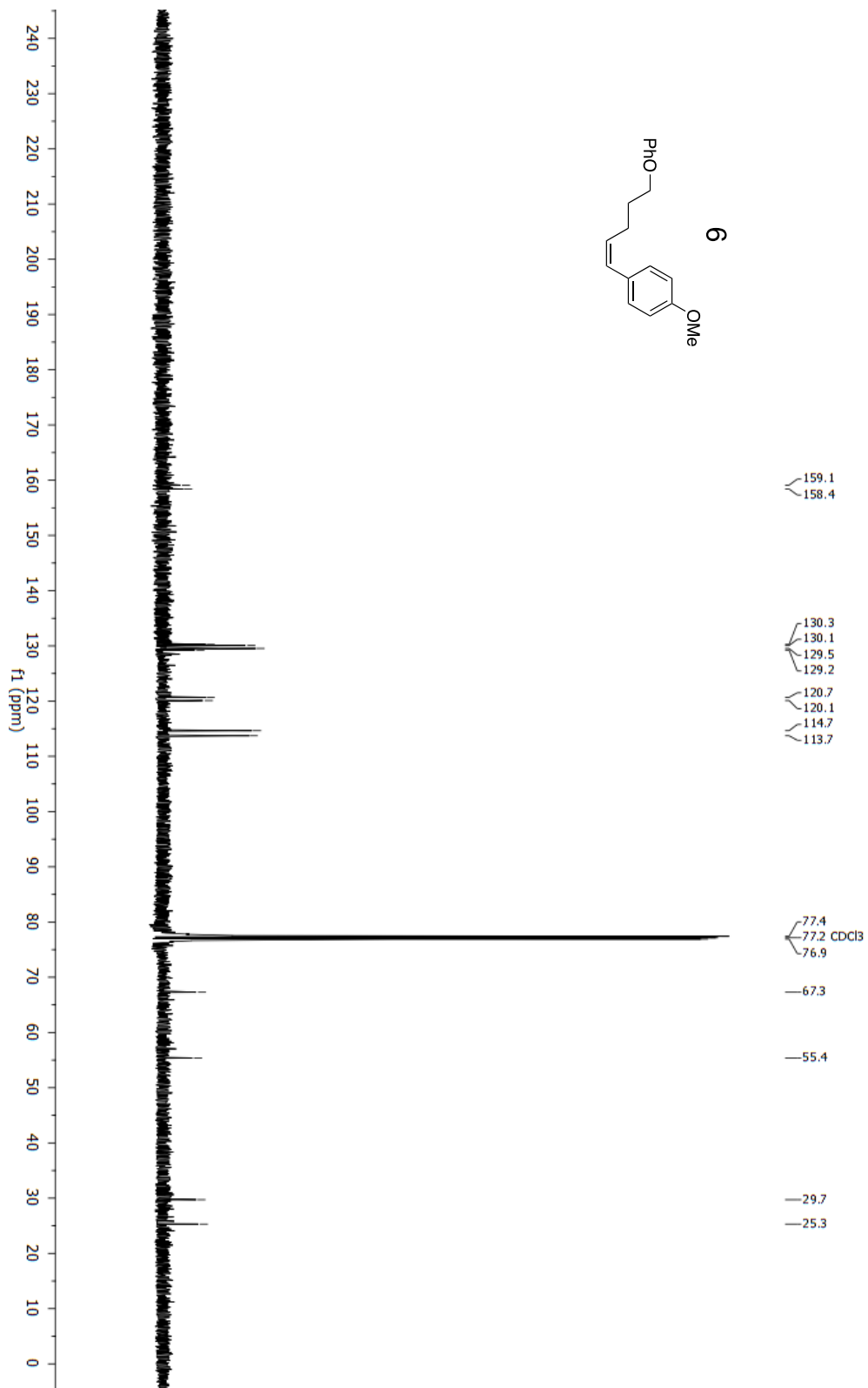
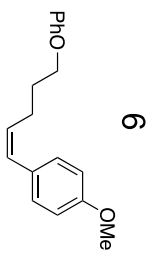


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Total		83170	53614					

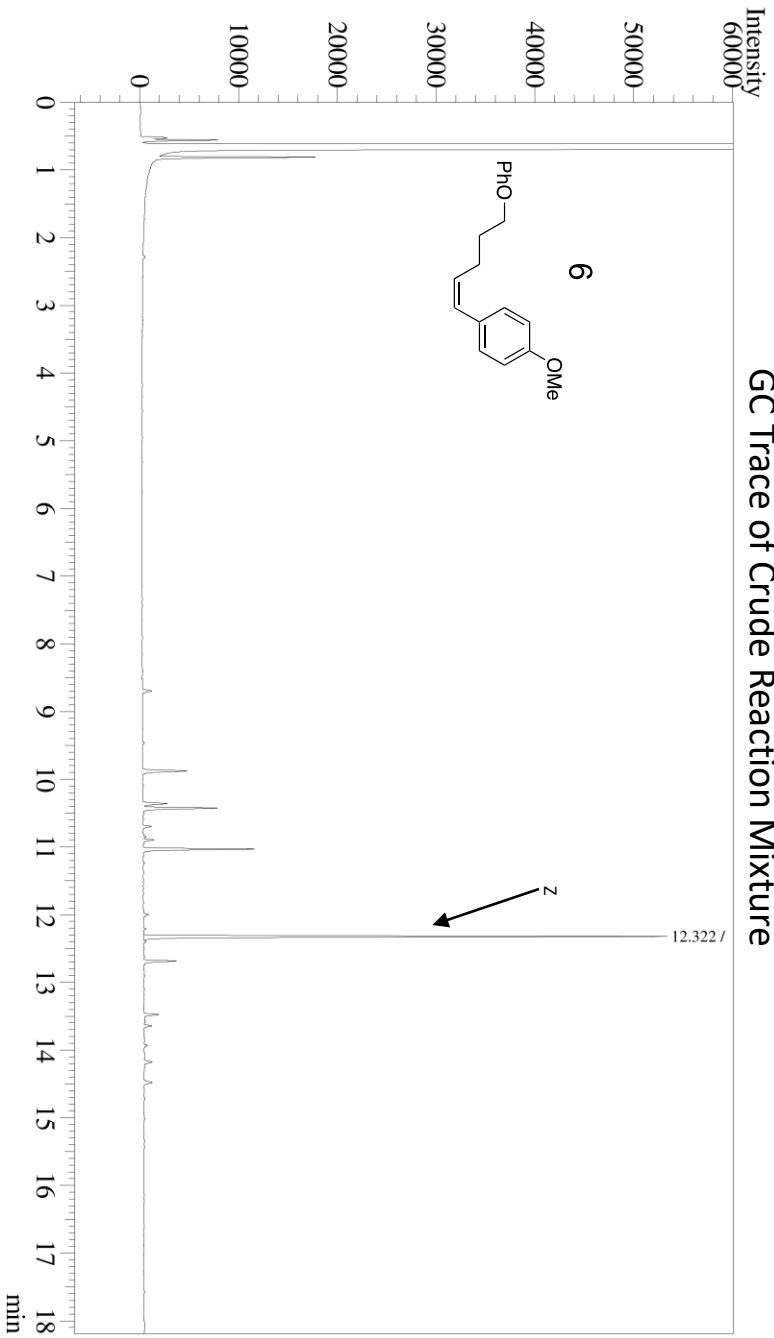
¹H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.27 – 7.20 (m, 2H), 6.98 – 6.90 (m, 1H), 6.92 – 6.82 (m, 4H), 6.41 (d, J = 11.5 Hz, 1H), 5.68 – 5.55 (m, 1H), 4.00 (t, J = 6.4 Hz, 2H), 3.82 (s, 3H), 2.53 (q, J = 7.3 Hz, 2H), 1.95 (p, J = 6.9 Hz, 2H).



^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 158.4, 130.3, 130.1, 129.5, 129.3, 129.2, 120.7, 120.1, 114.7, 113.7, 67.3, 55.4, 29.7, 25.3.

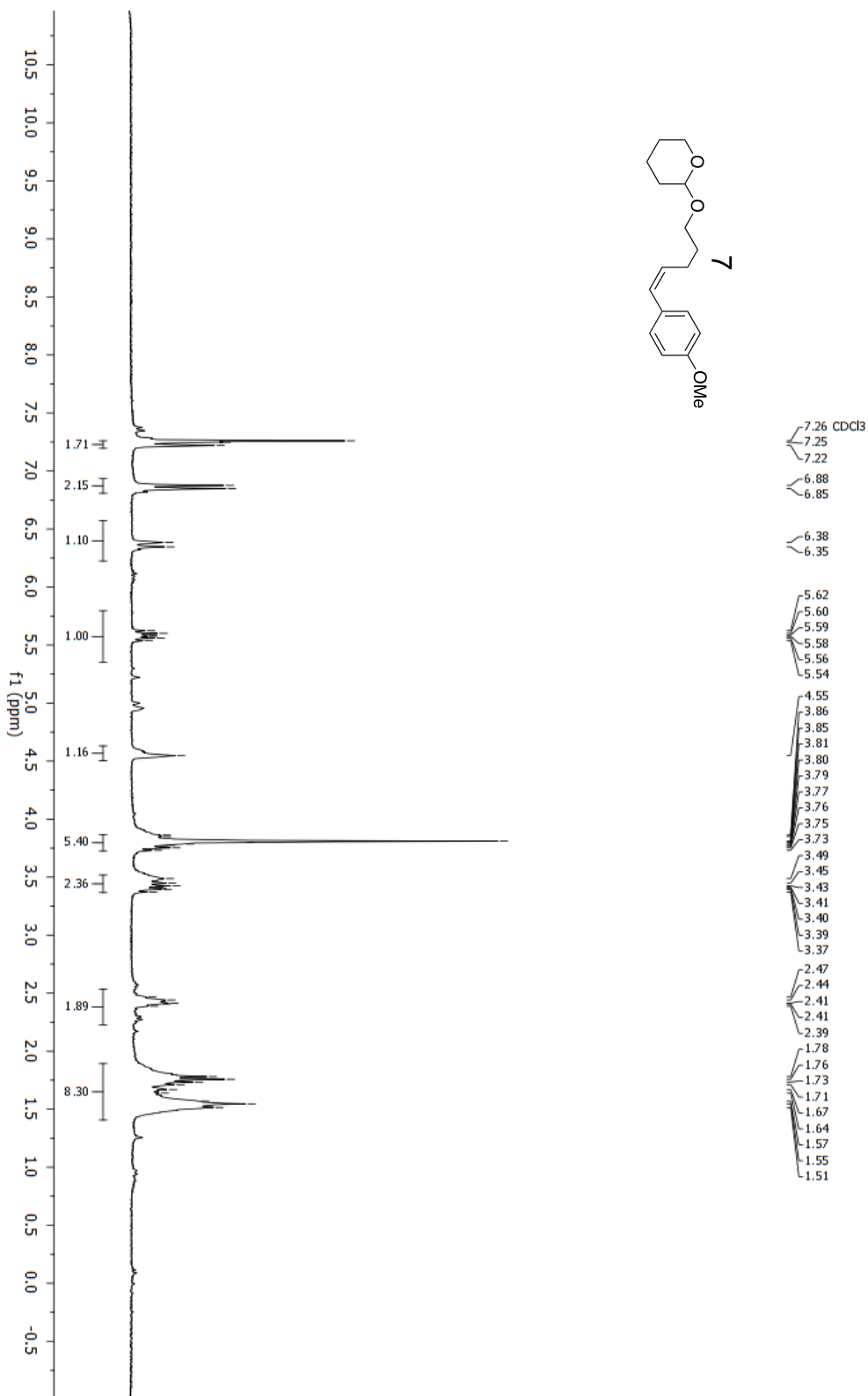
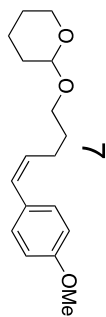


GC Trace of Crude Reaction Mixture

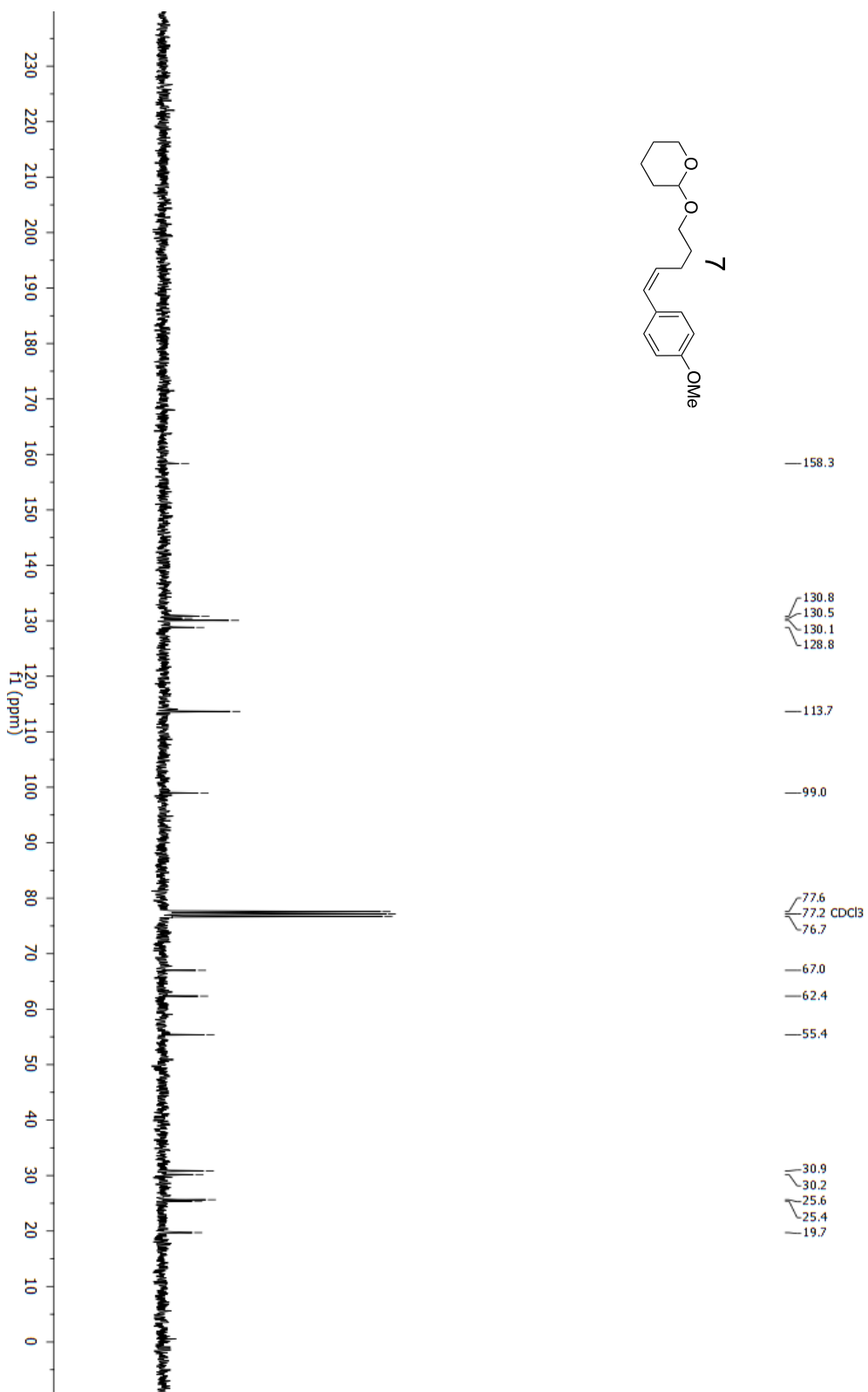
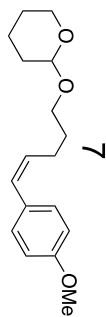


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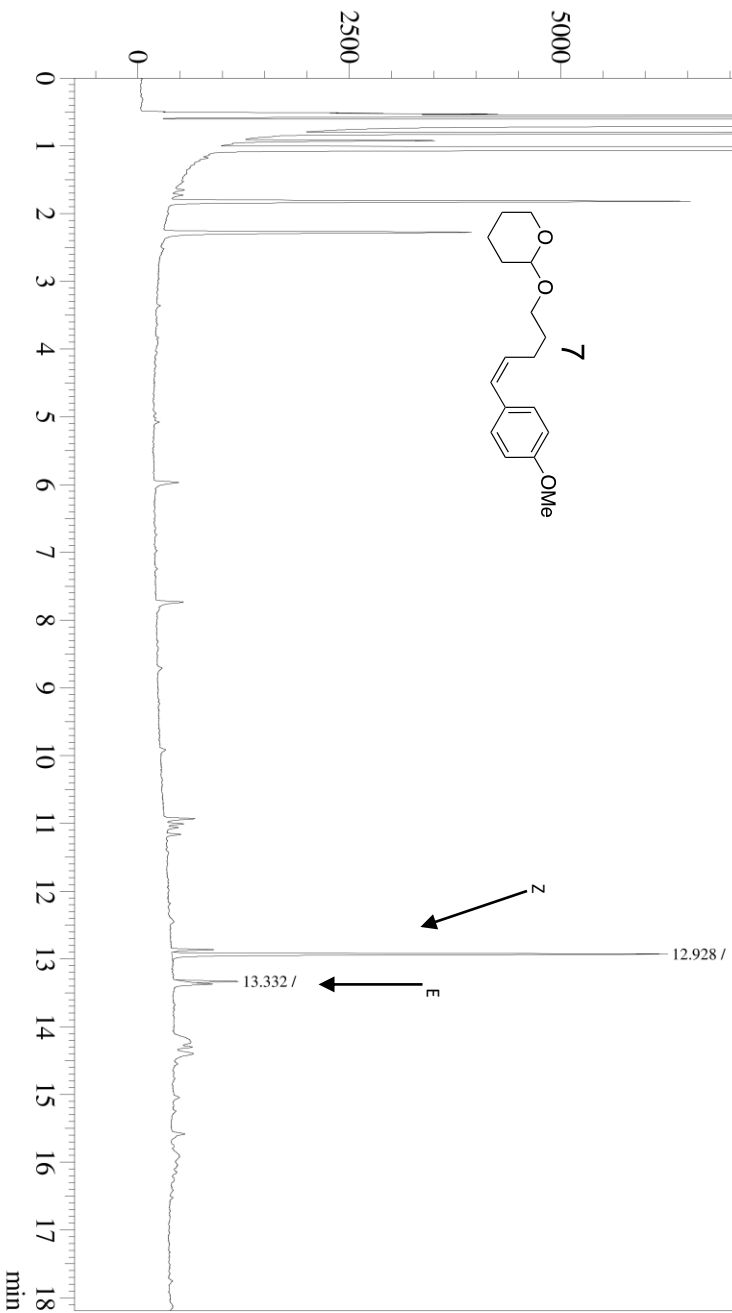
¹H NMR (300 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 11.4 Hz, 1H), 5.58 (dt, *J* = 11.4, 7.3 Hz, 1H), 4.55 (s, 1H), 3.87 – 3.73 (m, 5H), 3.52 – 3.37 (m, 2H), 2.53 – 2.23 (m, 2H), 1.89 – 1.41 (m, 8H).



¹³C-NMR (75 MHz, CDCl₃) δ 158.3, 130.8, 130.5, 130.1, 128.8, 113.7, 99.0, 67.0, 62.4, 55.4, 30.9, 30.2, 25.6, 25.4, 19.7.

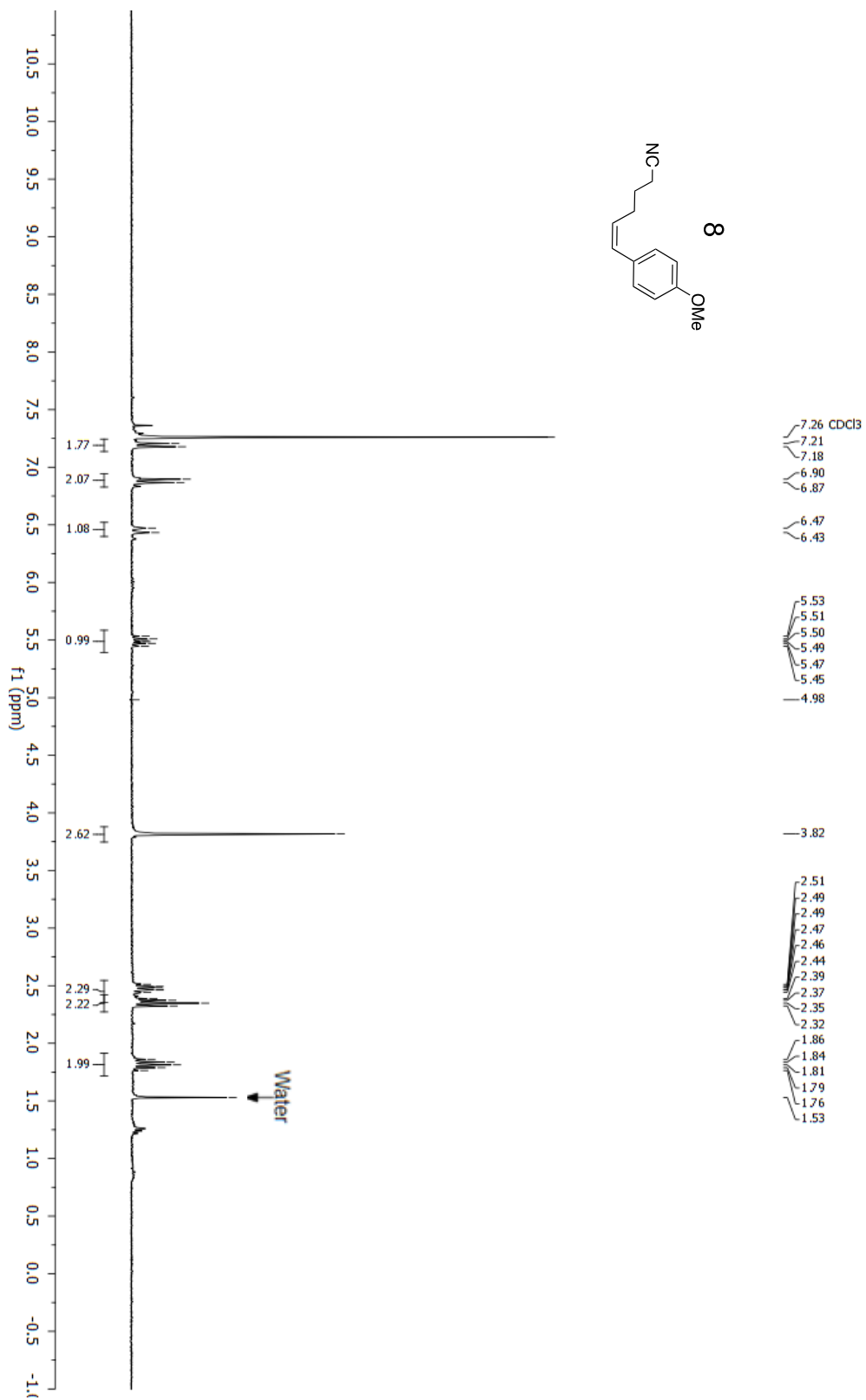
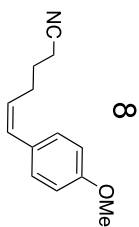


GC Trace of Crude Reaction Mixture

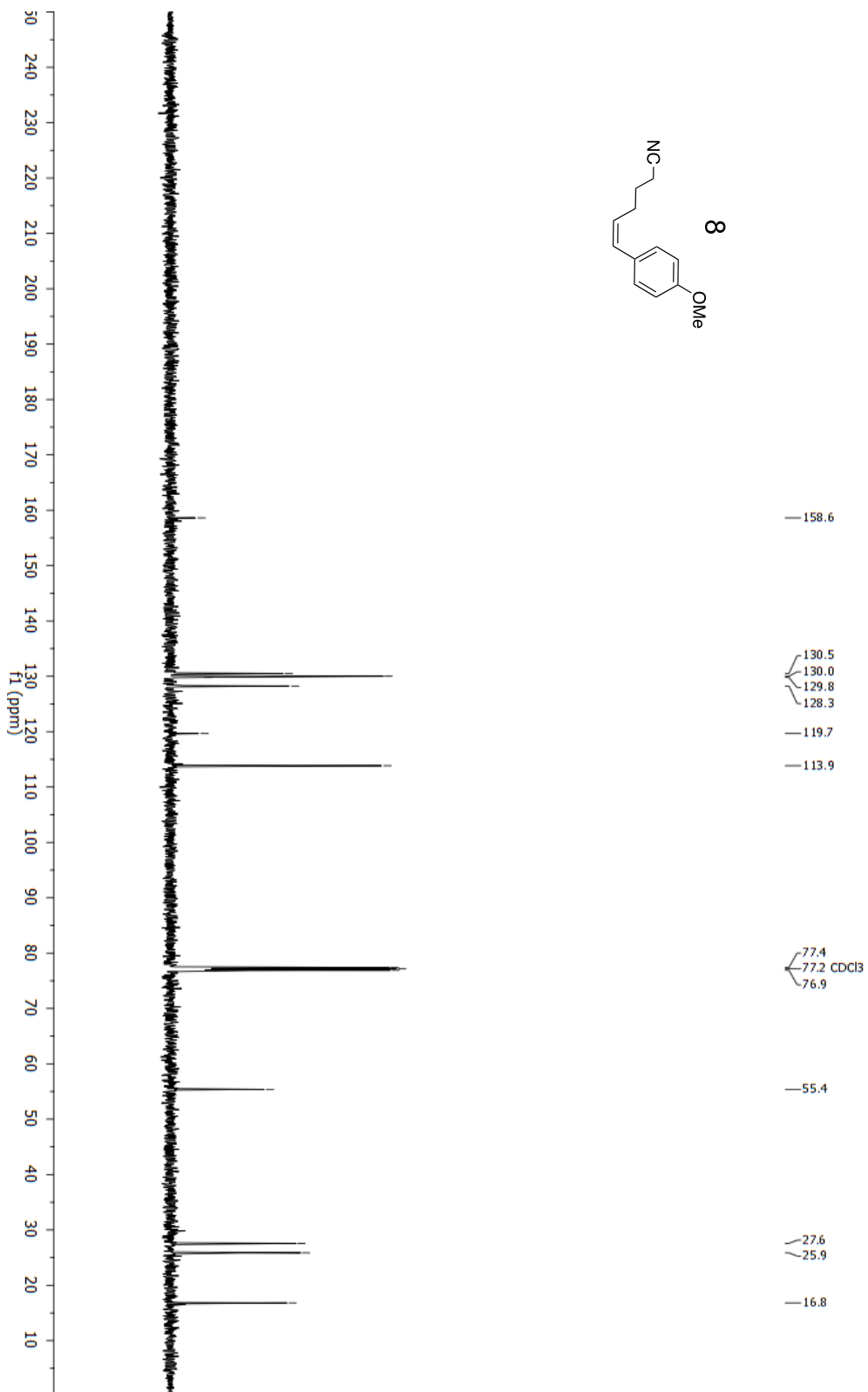
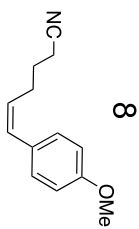


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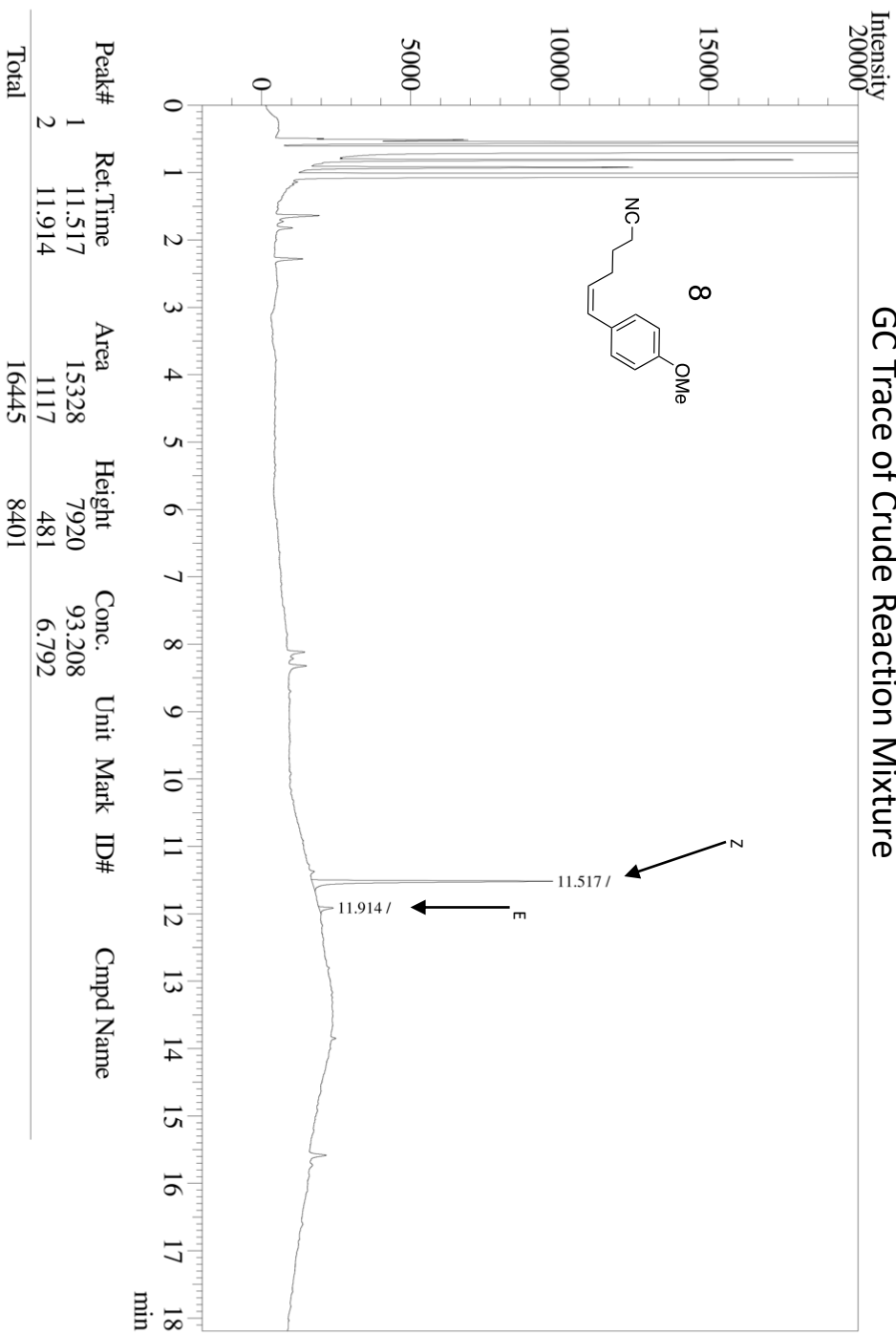
¹H NMR (300 MHz, Chloroform-*d*) δ 7.19 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 11.6 Hz, 1H), 5.49 (dt, J = 11.6, 7.1 Hz, 1H), 3.82 (s, 3H), 2.55 – 2.40 (m, 2H), 2.42 – 2.27 (m, 2H), 1.91 – 1.72 (m, 2H).



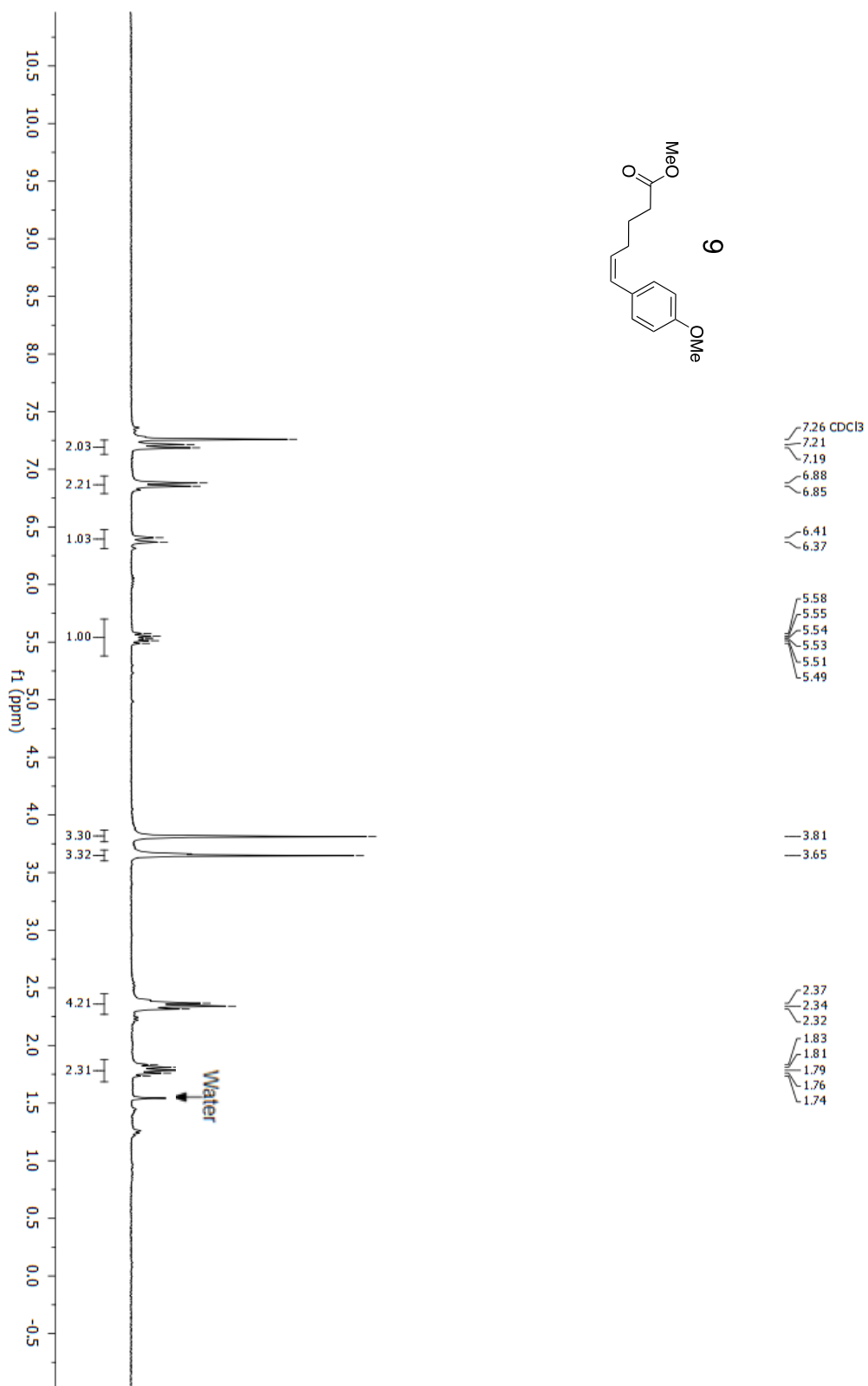
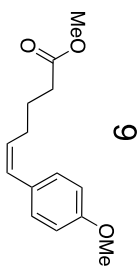
¹³C-NMR (126 MHz, CDCl₃) δ 158.6, 130.5, 130.0, 129.8, 129.8, 128.3, 119.7, 113.9, 55.4, 27.6, 25.9, 16.8.



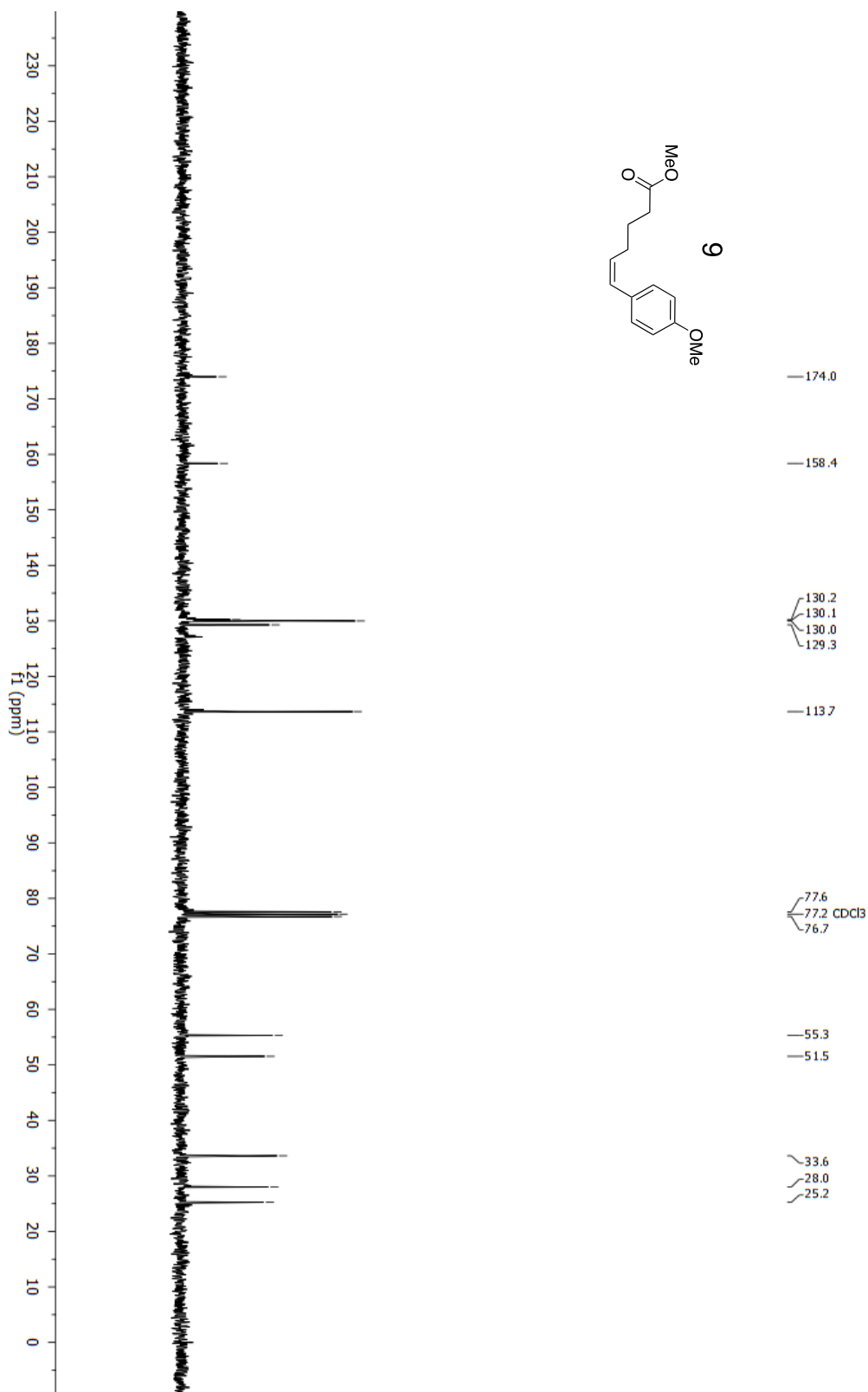
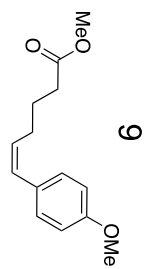
GC Trace of Crude Reaction Mixture



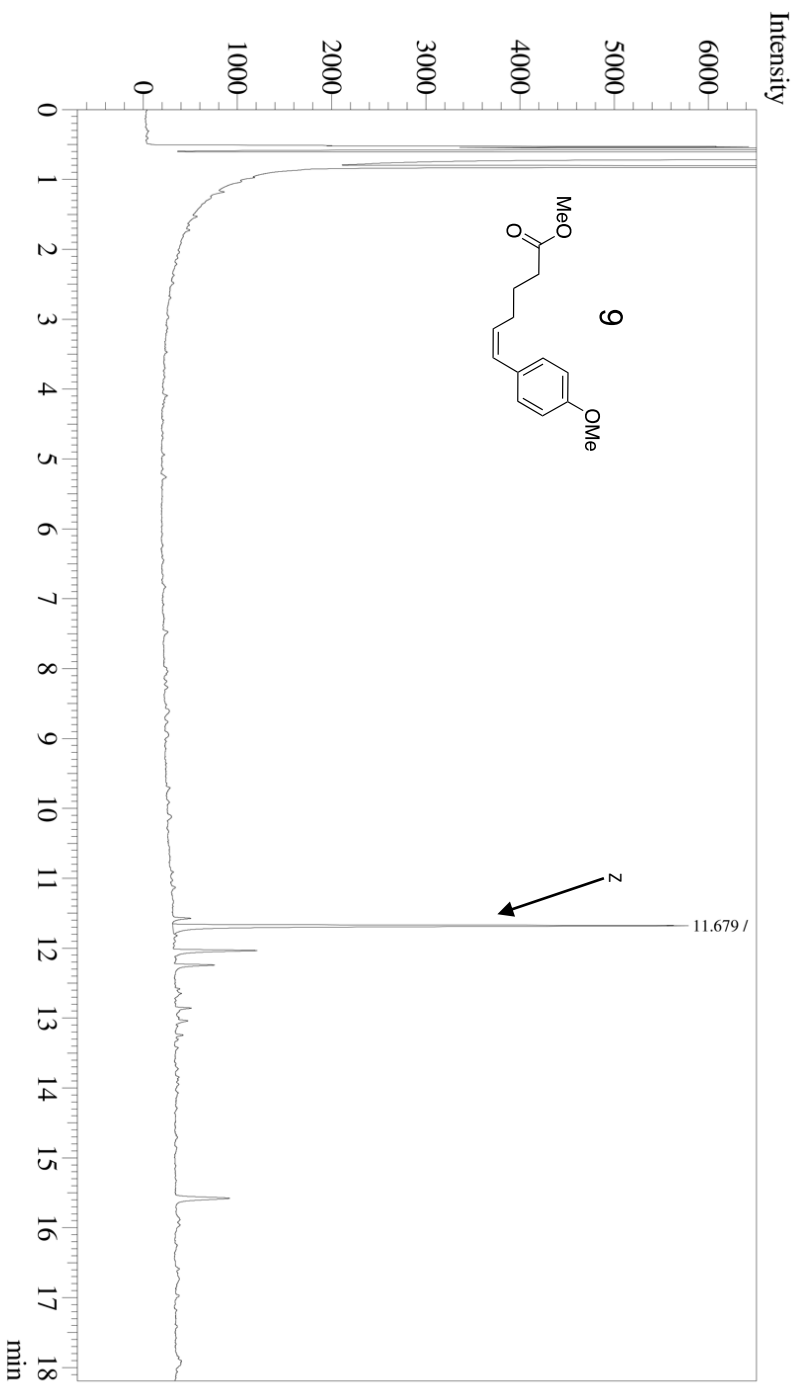
¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 11.6 Hz, 1H), 5.70 - 5.58 (m, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 2.45 - 2.27 (m, 4H), 1.88 - 1.68 (m, 2H).



^{13}C NMR (75 MHz, CDCl_3) δ 174.0, 158.4, 130.2, 130.1, 130.0, 129.3, 113.7, 55.3, 51.5, 33.6, 28.0, 25.2.

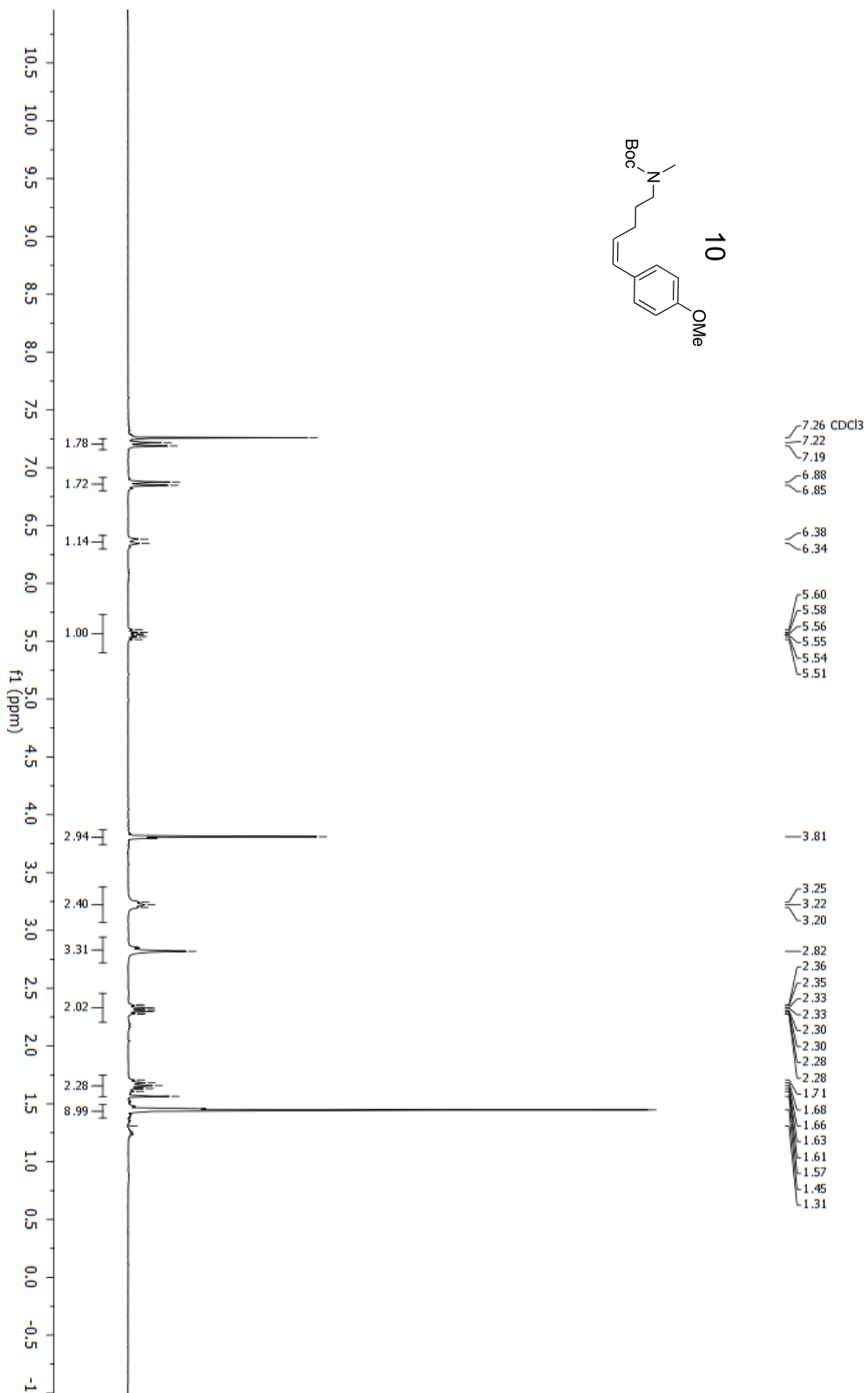
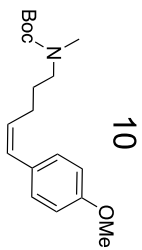


GC Trace of Crude Reaction Mixture

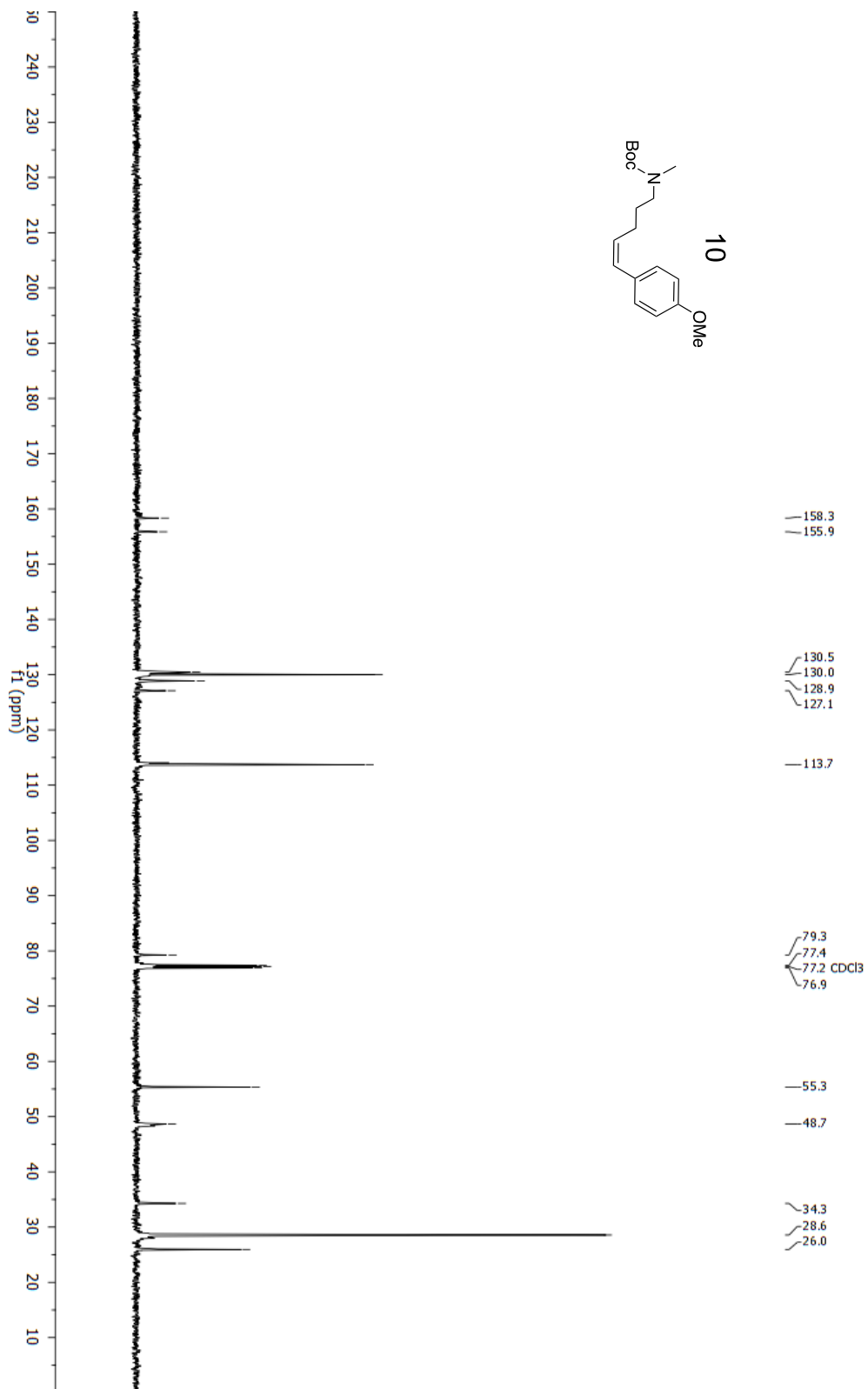
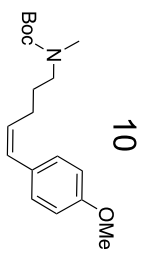


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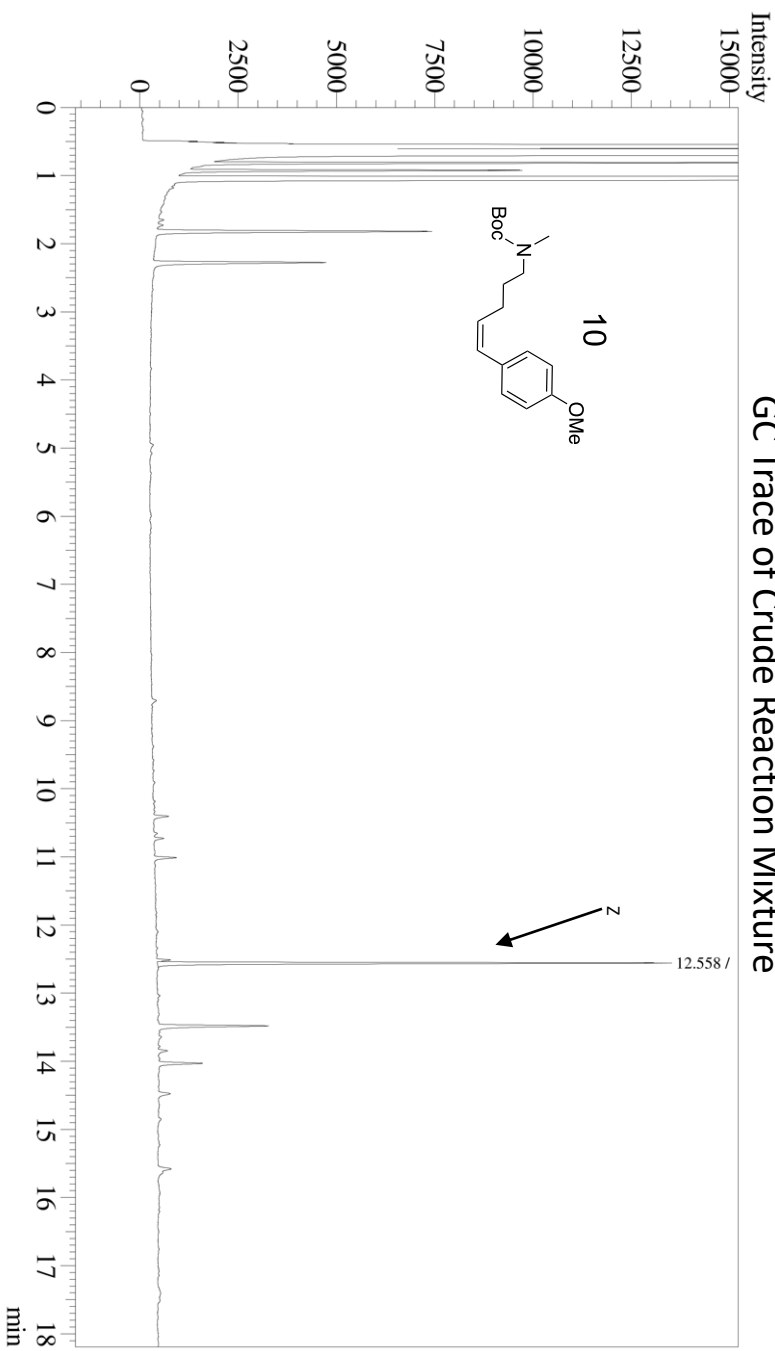
¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 11.6 Hz, 1H), 5.56 (dt, *J* = 11.6, 7.1 Hz, 1H), 3.81 (s, 3H), 3.22 (t, *J* = 7.3 Hz, 2H), 2.82 (s, 3H), 2.46 – 2.21 (m, 2H), 1.75 – 1.56 (m, 2H), 1.45 (s, 9H).



¹³C-NMR (126 MHz, CDCl₃) δ 158.3, 155.9, 130.5, 130.0, 128.9, 127.1, 113.7, 79.3, 55.3, 48.7, 34.3, 28.6, 26.0.

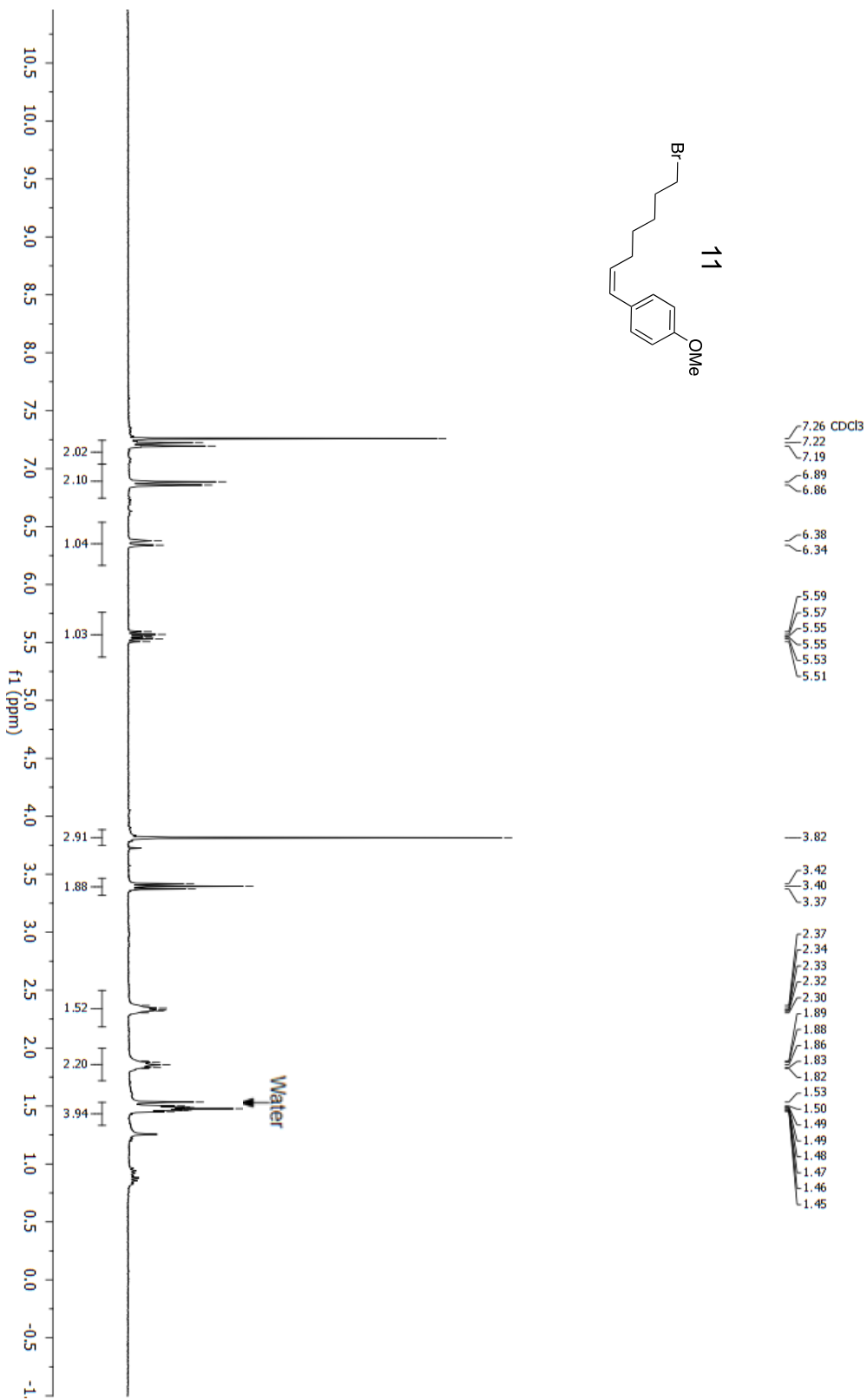
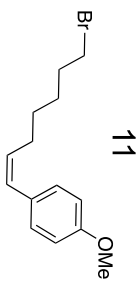


GC Trace of Crude Reaction Mixture

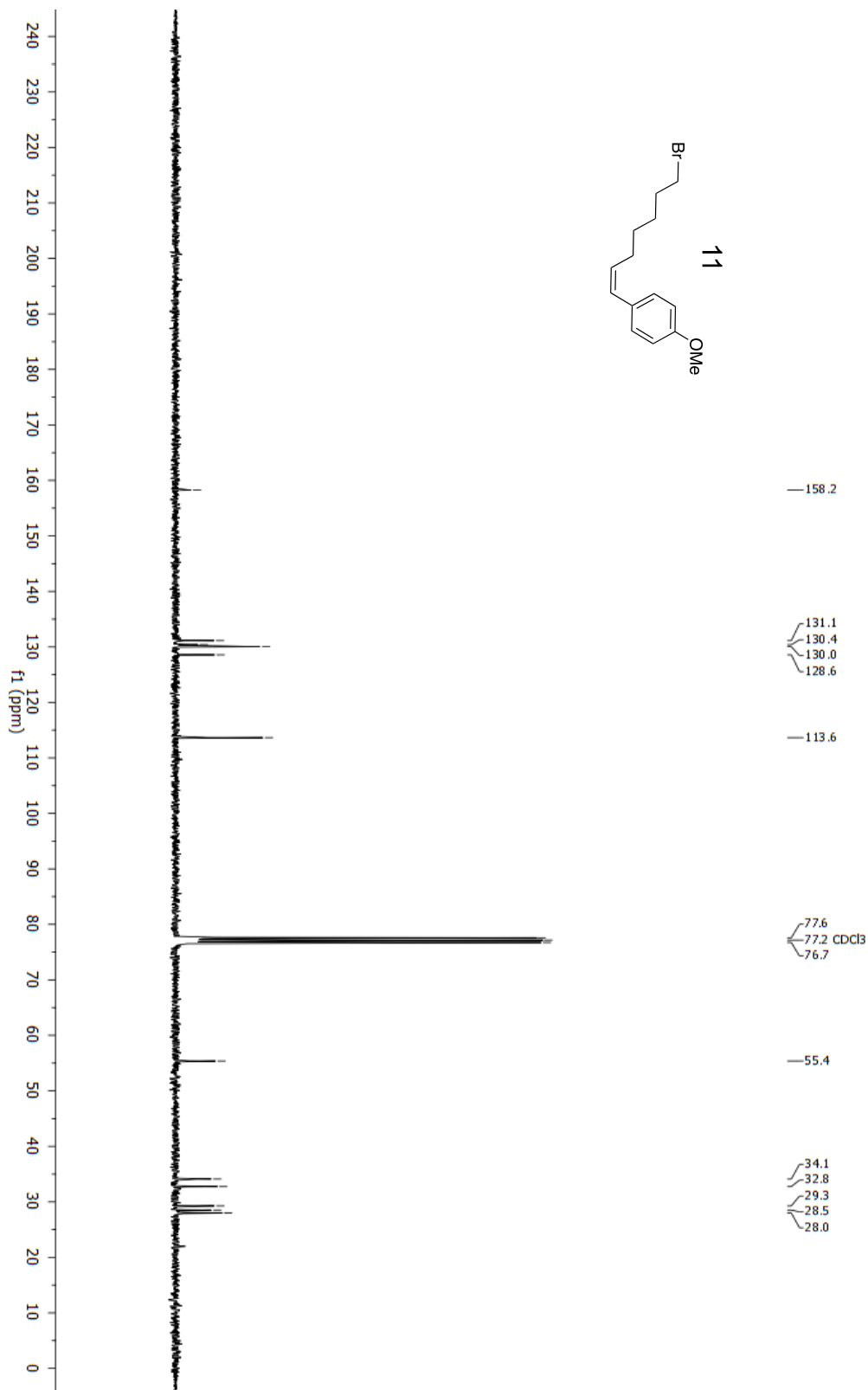
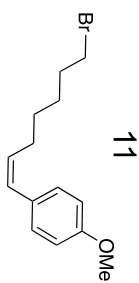


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Total		18785	12699					

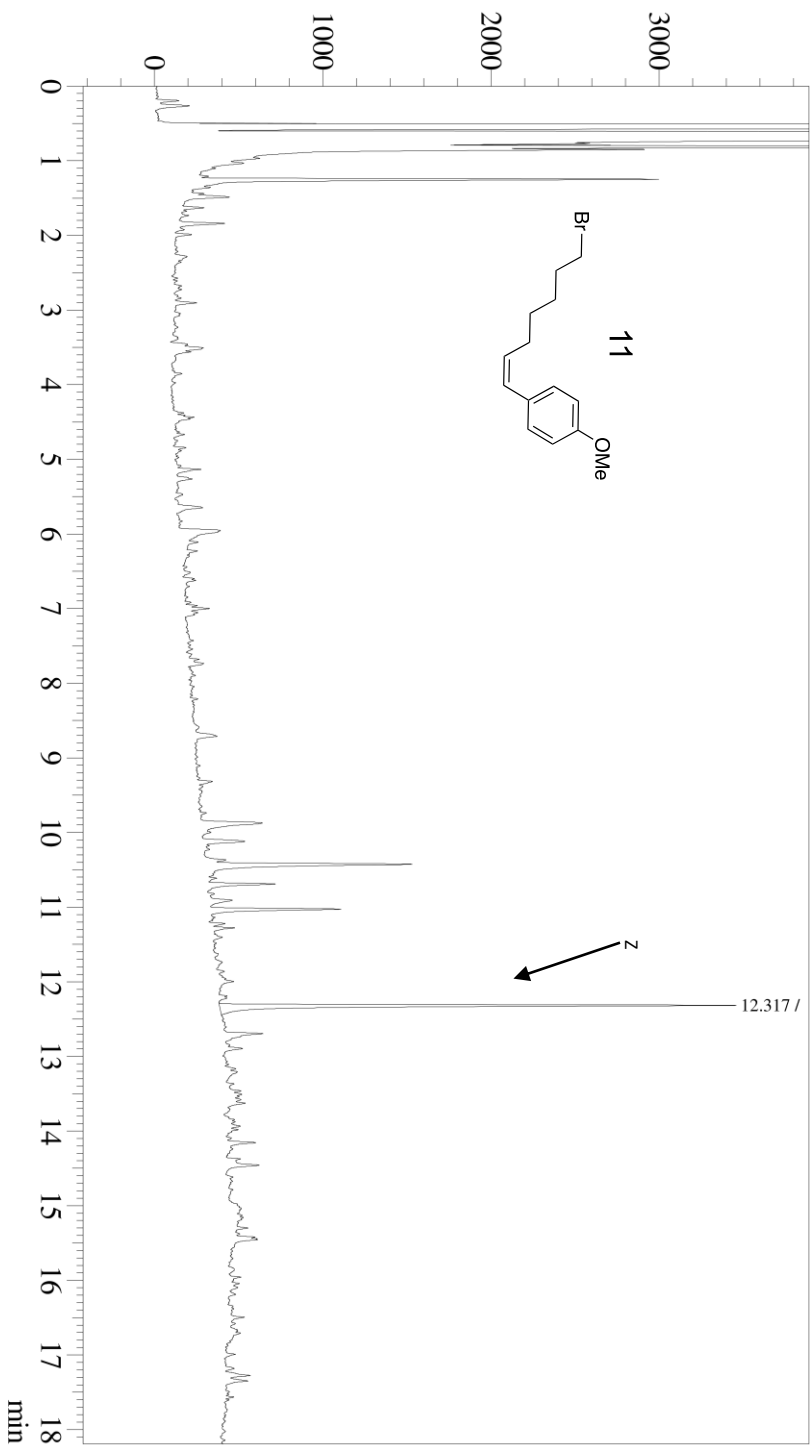
¹H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.36 (d, J = 11.6 Hz, 1H), 5.55 (dt, J = 11.6, 7.2 Hz, 1H), 3.82 (s, 3H), 3.40 (t, J = 6.8 Hz, 2H), 2.50 – 2.18 (m, 2H), 2.00 – 1.72 (m, 2H), 1.53 – 1.33 (m, 4H).



¹³C NMR (75 MHz, CDCl₃) δ 158.2, 131.1, 130.4, 130.0, 128.6, 113.6, 55.4, 34.1, 32.8, 29.3, 28.5, 28.0.

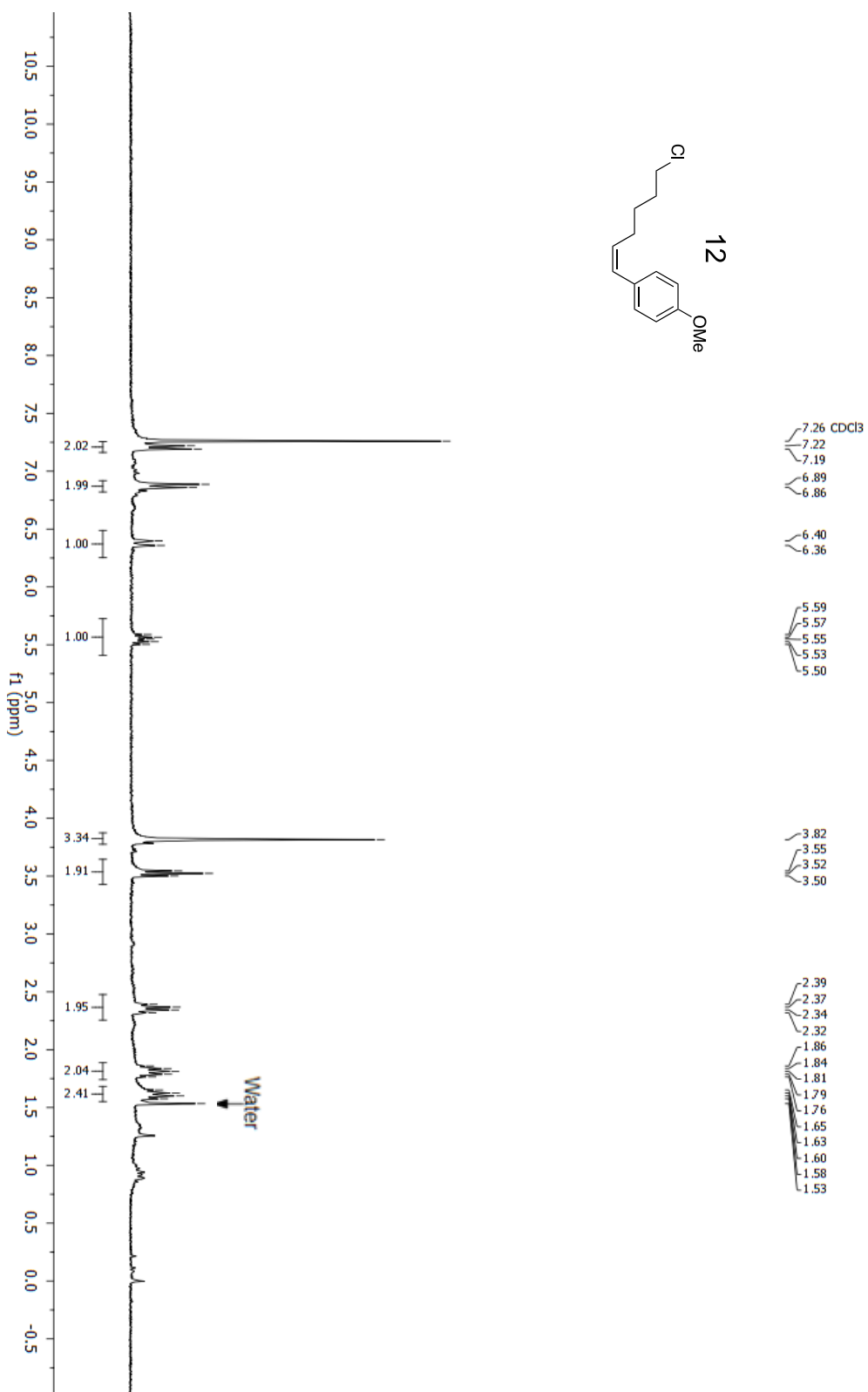
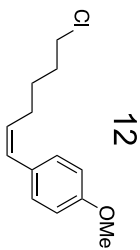


GC Trace of Crude Reaction Mixture

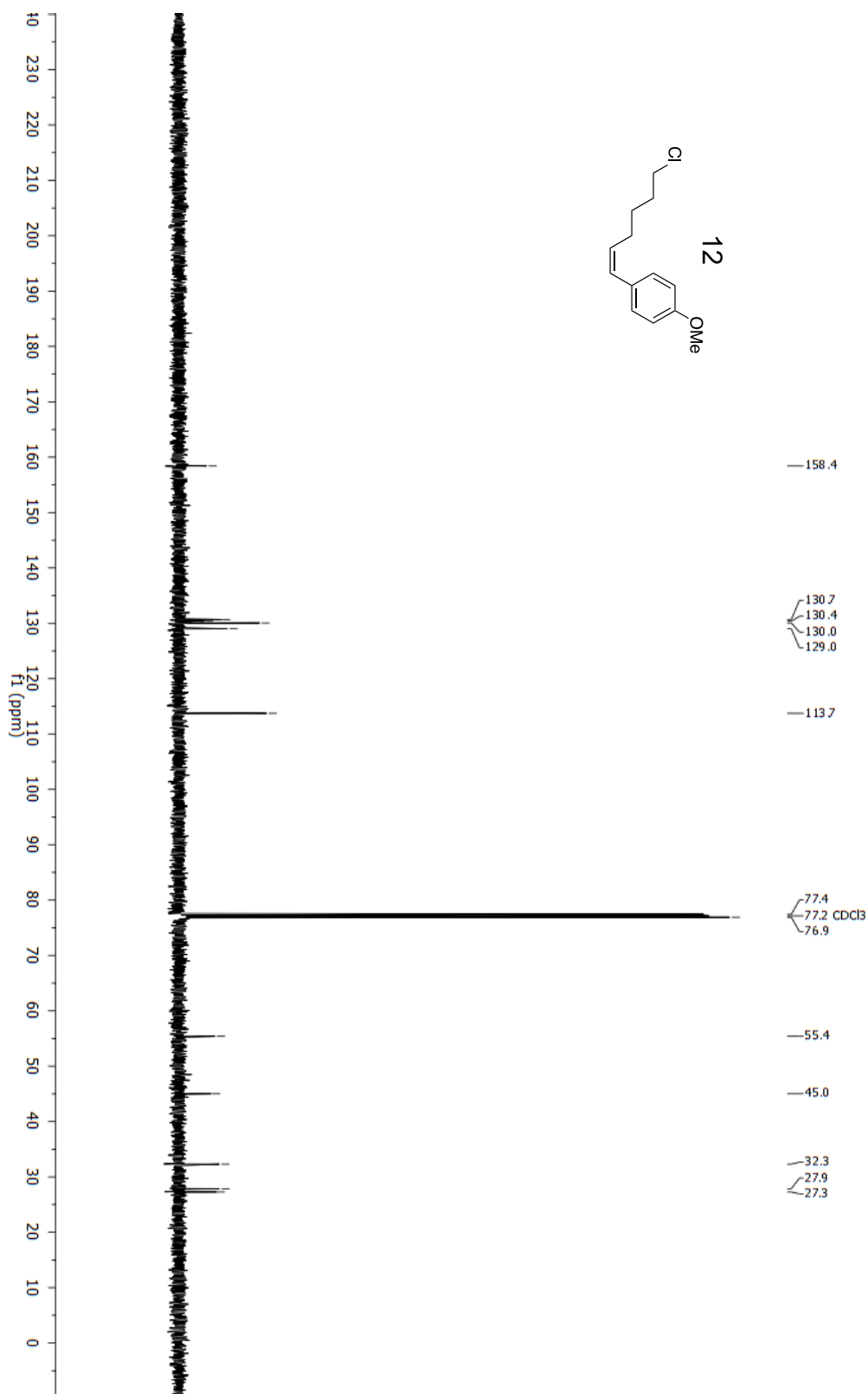
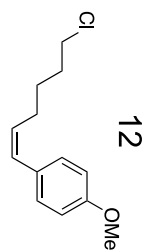


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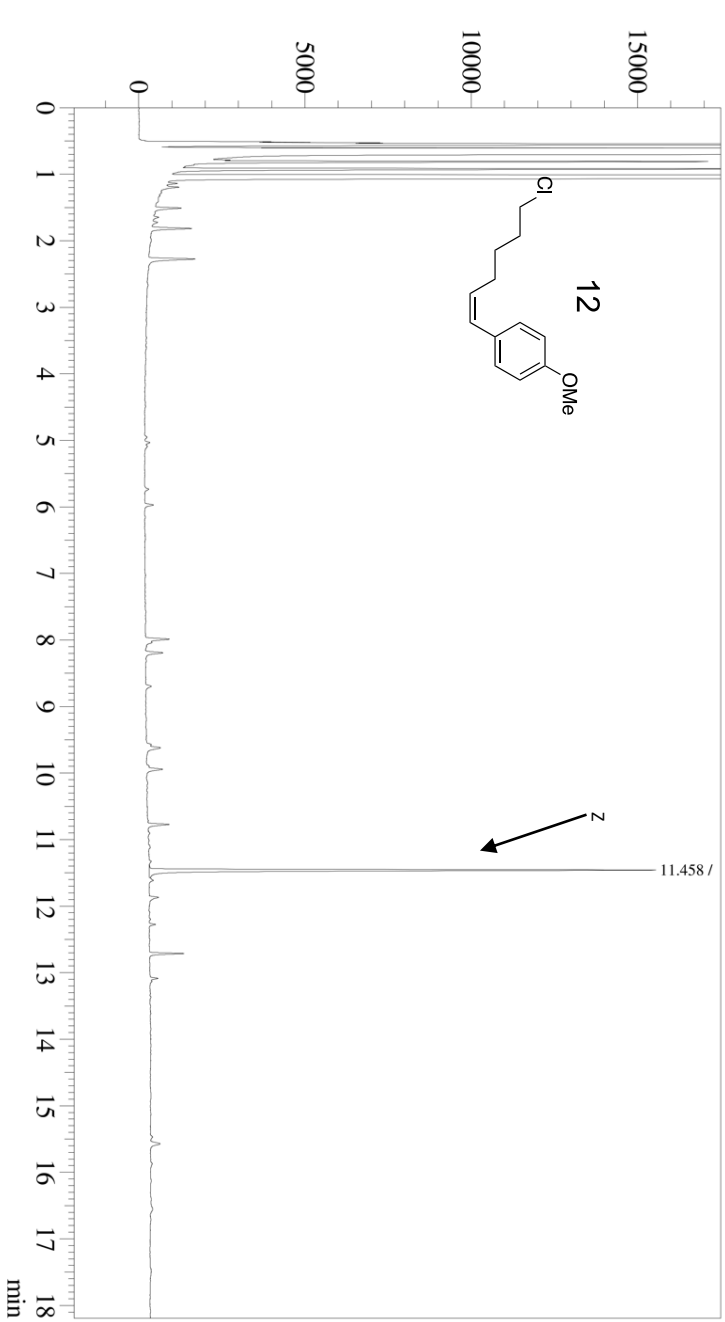
¹H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 11.5 Hz, 1H), 5.72 – 5.41 (m, 1H), 3.82 (s, 3H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.48 – 2.26 (m, 2H), 1.89 – 1.74 (m, 2H), 1.68 – 1.55 (m, 2H).



^{13}C NMR (126 MHz, CDCl_3) δ 158.4, 130.7, 130.4, 130.0, 129.0, 113.7, 55.4, 45.0, 32.3, 27.9, 27.3.

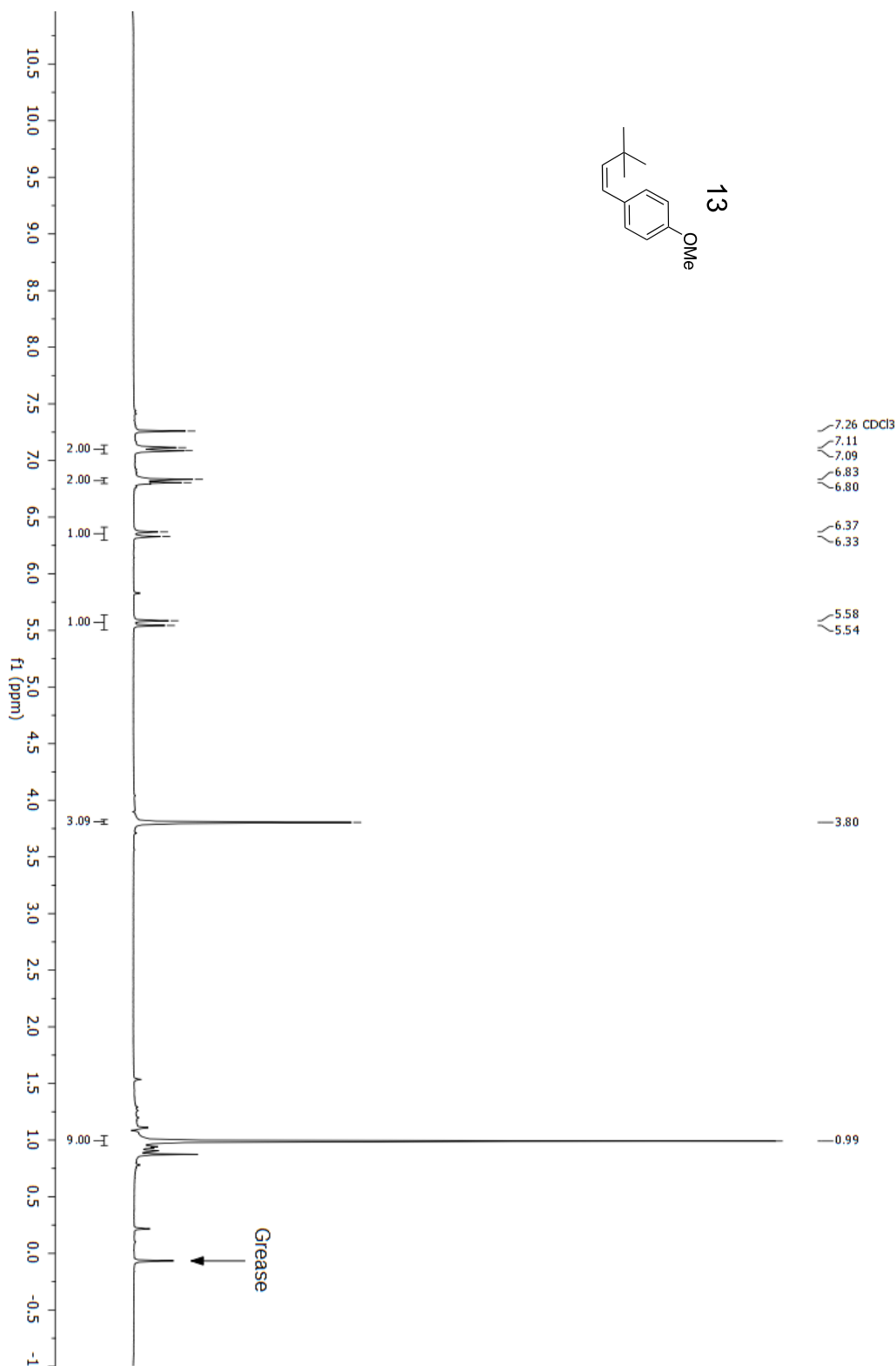
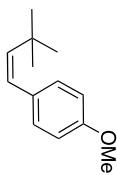


GC Trace of Crude Reaction Mixture

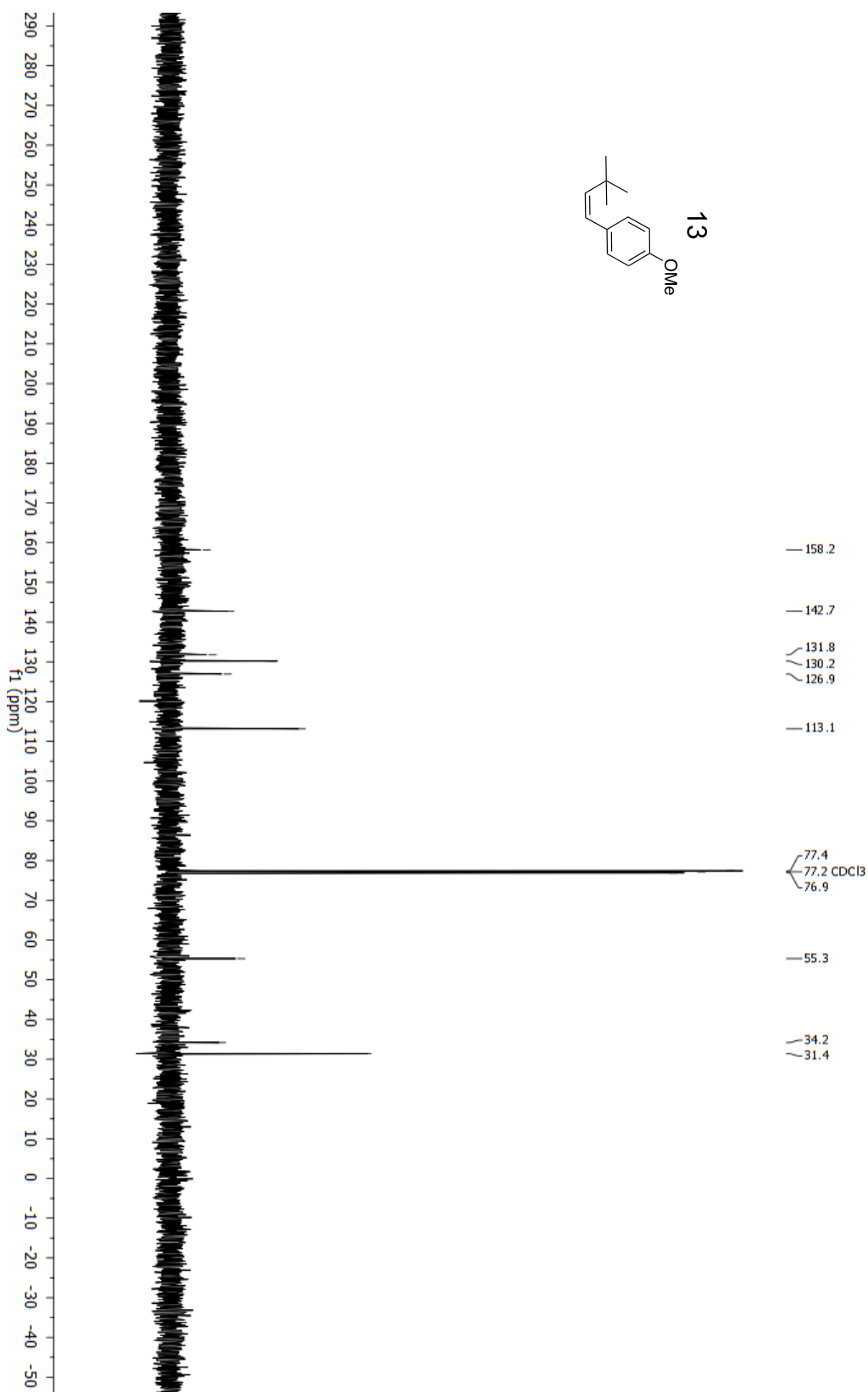
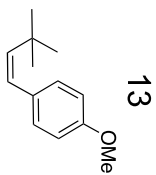


Peak#	Ret. Time	Area	Height	Conc.	Unit Mark	ID#	Crmpd Name
1	11.458	24227	14800	100.000	V		
Total		24227	14800				

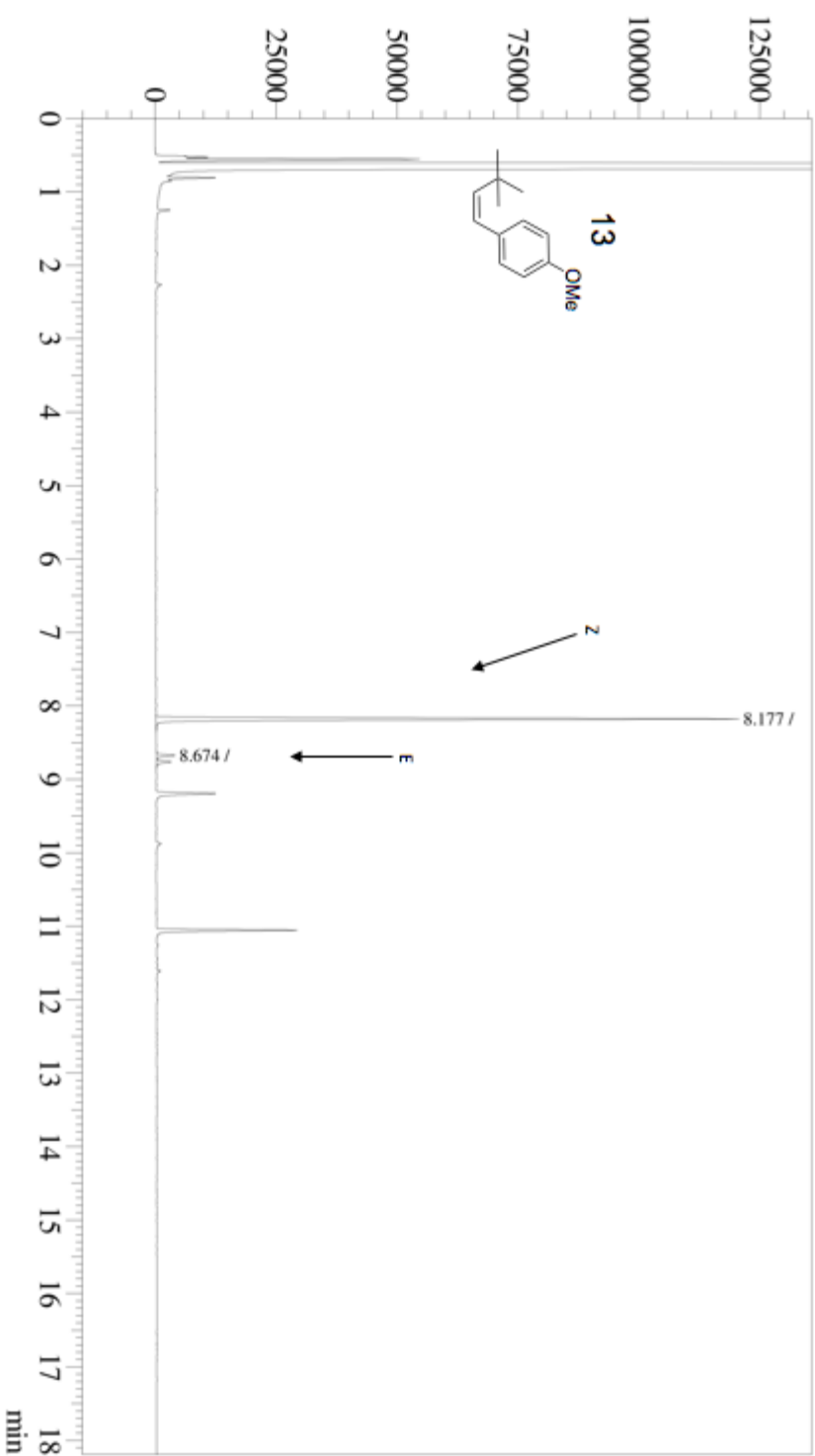
¹H NMR (300 MHz, Chloroform-d) δ 7.10 (d, J = 8.1 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.35 (d, J = 12.5 Hz, 1H), 5.56 (d, J = 12.5 Hz, 1H), 3.80 (s, 3H), 0.99 (s, 9H).



^{13}C NMR (126 MHz, Chloroform- d_3) δ 158.2, 142.7, 131.8, 130.2, 126.9, 113.1, 55.3, 34.2, 31.4.

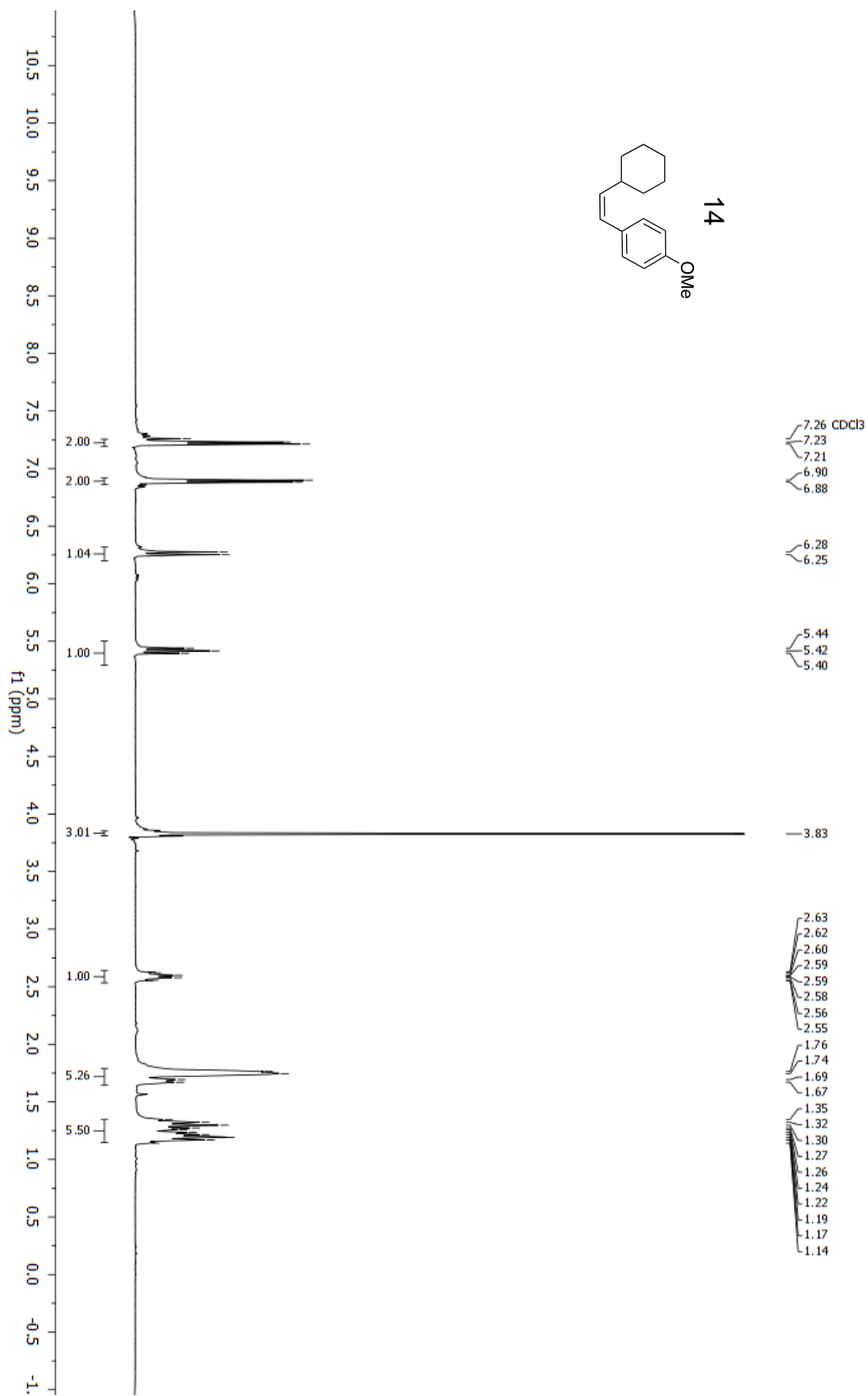
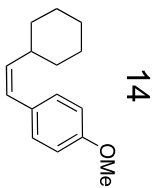


GC Trace of Crude Reaction Mixture

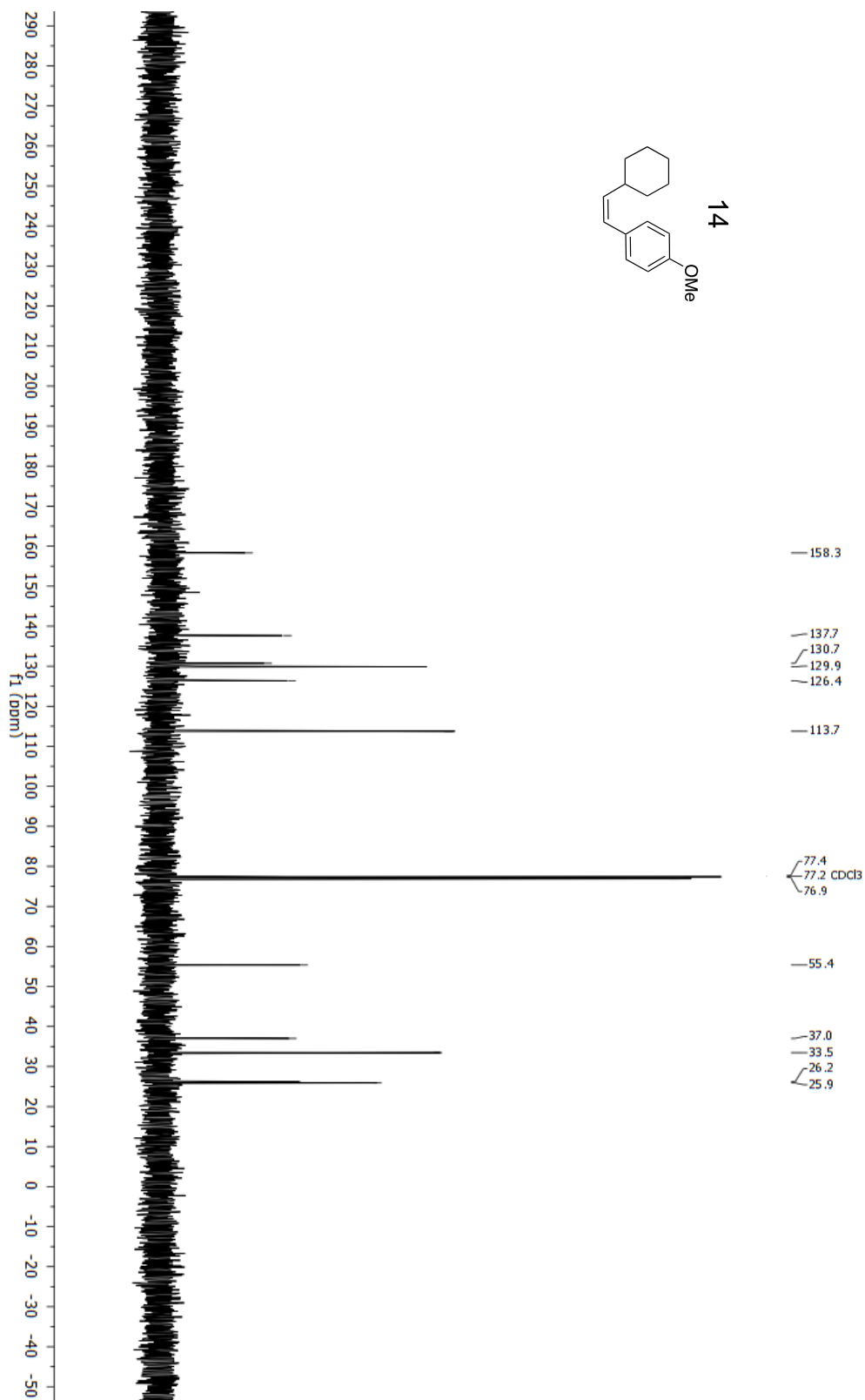
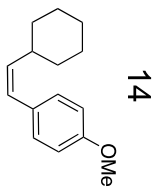


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	8.177	216002	118486	94.188				
2	8.674	13328	3772	5.812		S		
Total		229330	122258					

¹H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 11.7 Hz, 1H), 5.44 – 5.40 (t, *J* = 11.7 Hz, 1H), 3.83 (s, 3H), 2.63 – 2.55 (m, 1H), 1.76 – 1.67 (m, 5H), 1.35 – 1.14 (m, 5H).

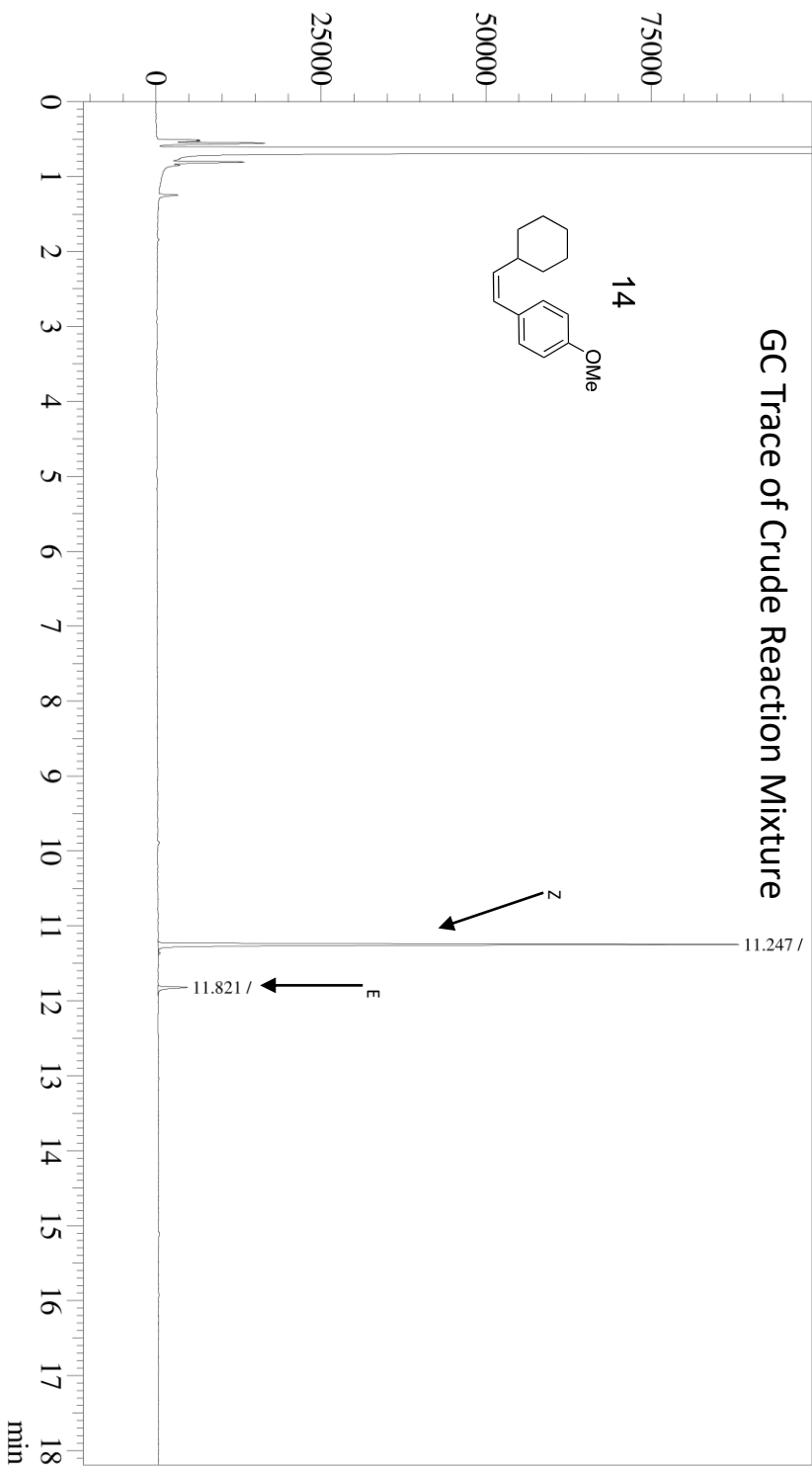


^{13}C NMR (126 MHz, Chloroform- d_3) δ 158.3, 137.7, 130.7, 129.9, 126.4, 113.7, 55.4, 37.0, 33.5, 26.2, 25.9.



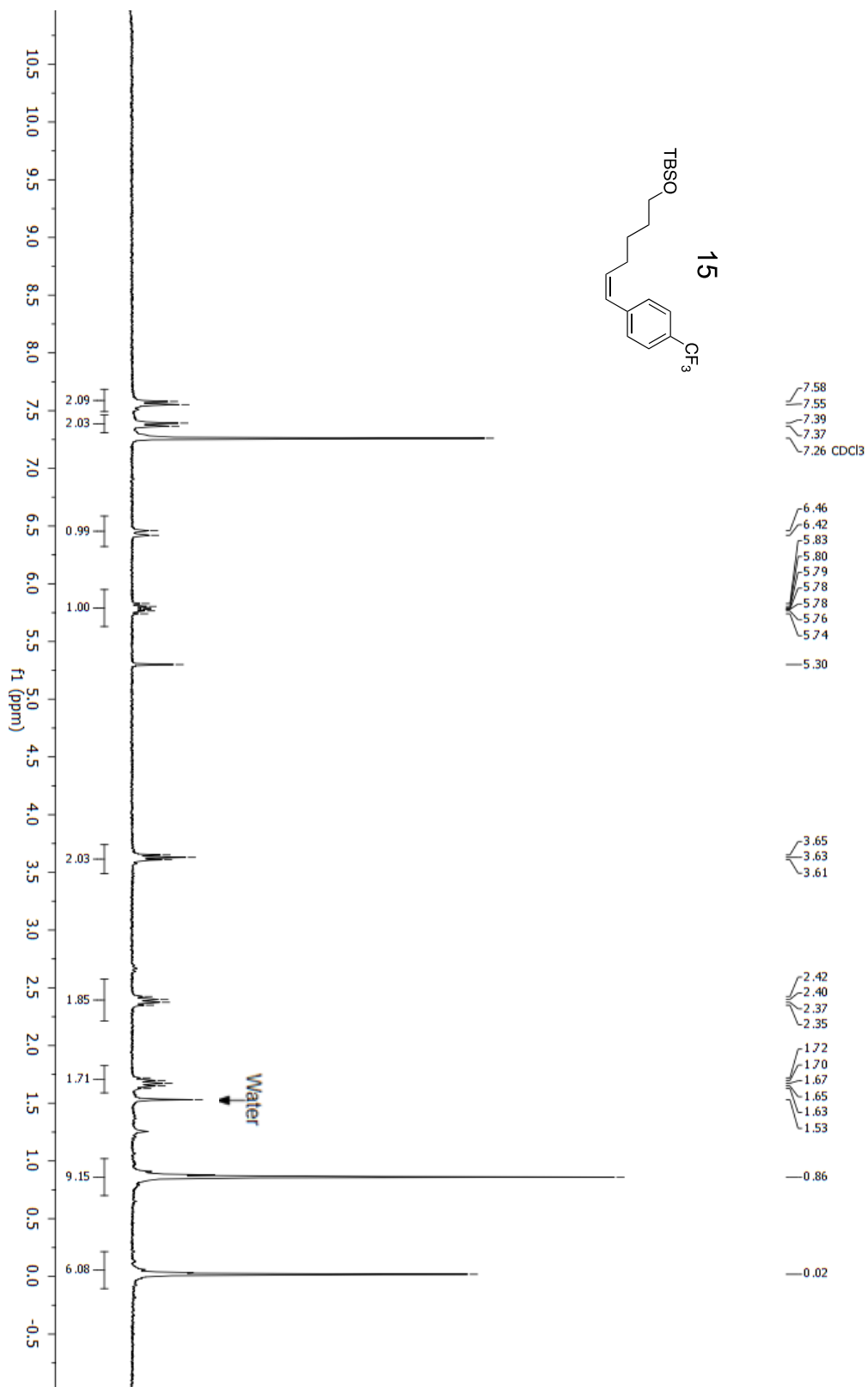
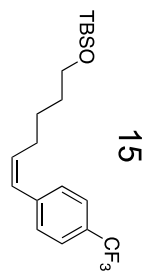
Intensity

GC Trace of Crude Reaction Mixture

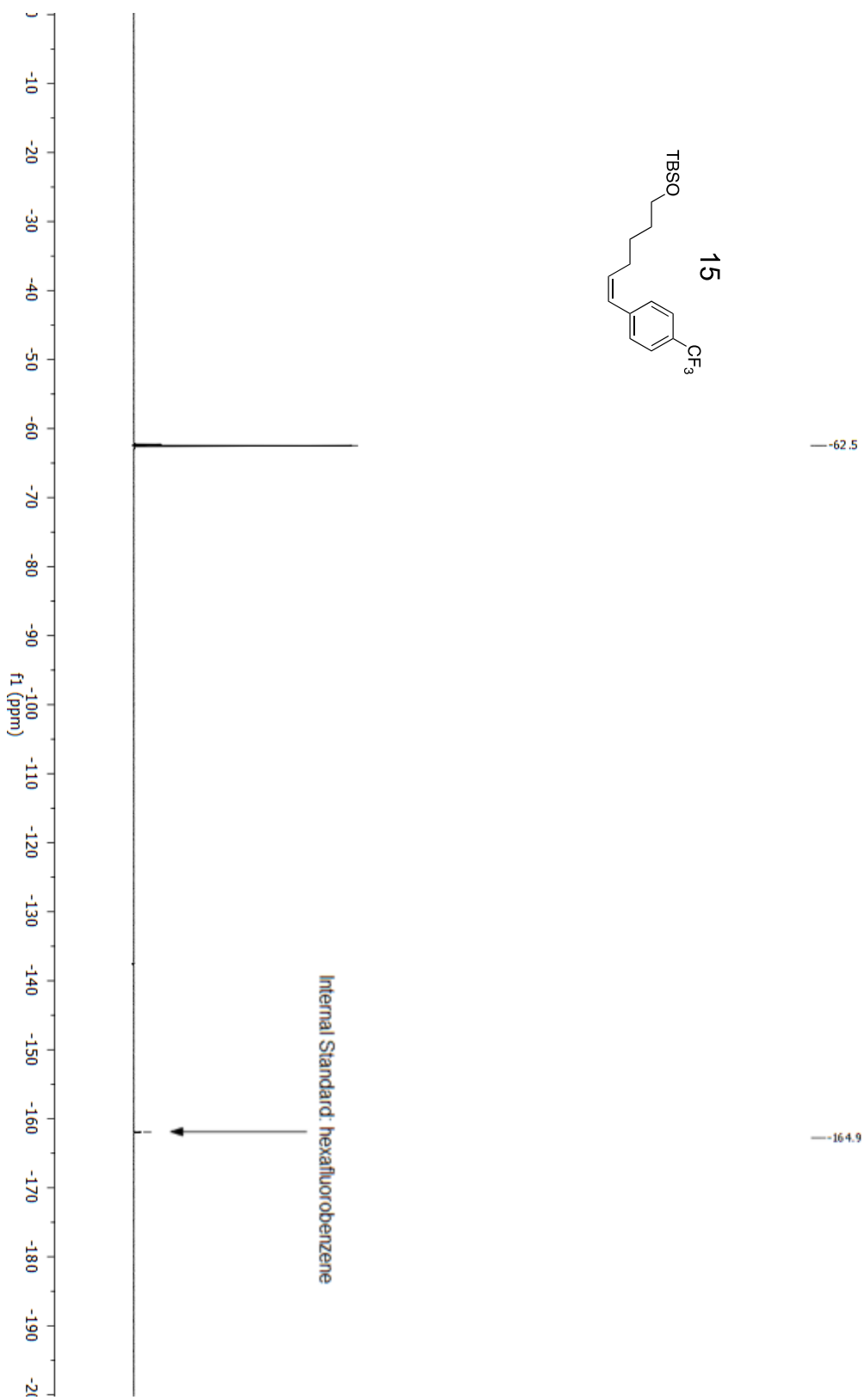
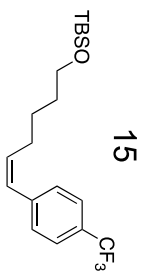


Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	11.247	127283	84442	94.320	S		
2	11.821	7666	4321	5.680			
Total		134949	88763				

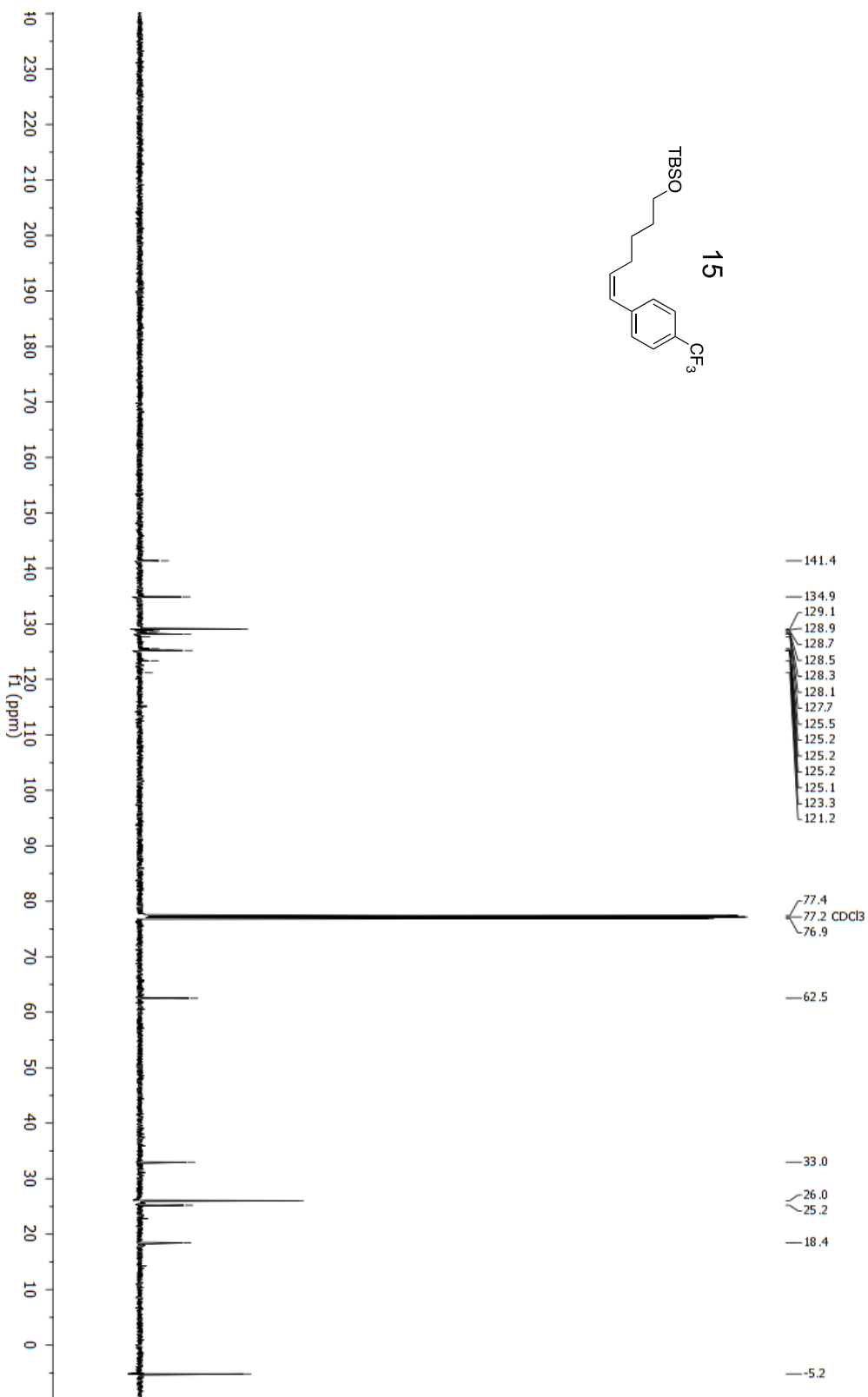
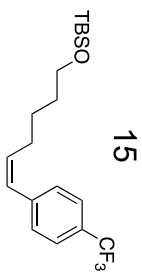
¹H NMR (300 MHz, Chloroform-d) δ 7.57 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.44 (d, J = 11.8 Hz, 1H), 5.95 – 5.63 (m, 1H), 3.63 (t, J = 6.2 Hz, 2H), 2.58 – 2.21 (m, 2H), 1.83 – 1.58 (m, 2H), 0.02 (s, 6H).



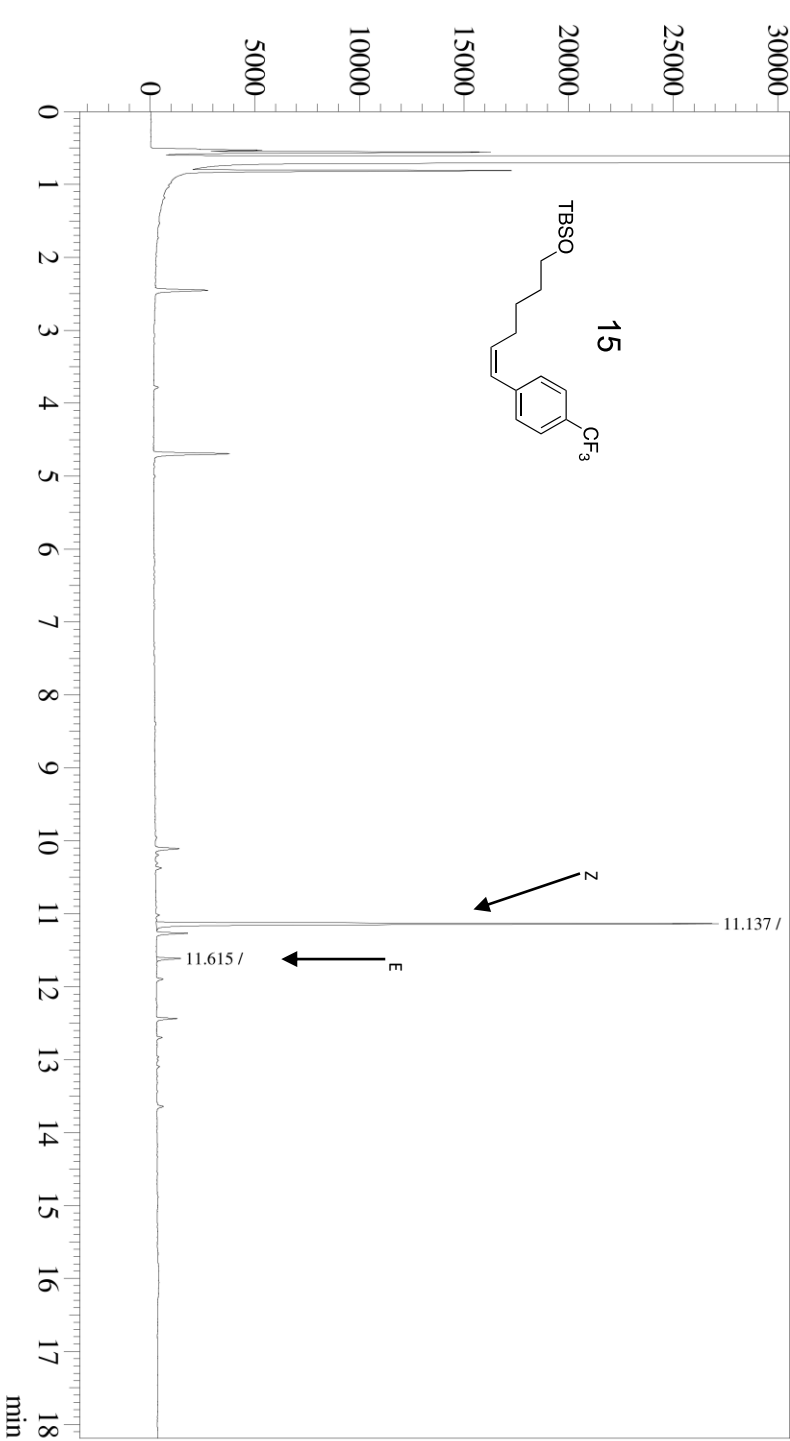
^{19}F NMR (471 MHz, CDCl_3) δ -62.5.



^{13}C NMR (126 MHz, Chloroform- d) δ 141.4, 134.9, 129.1, 128.9, 128.7, 128.6 (q, $J = 31.9$ Hz), 128.1, 125.2 (q, $J = 4.1$ Hz), 124.4 (q, $J = 271.7$ Hz), 62.5, 33.0, 26.0, 25.2, 18.4, -5.2.

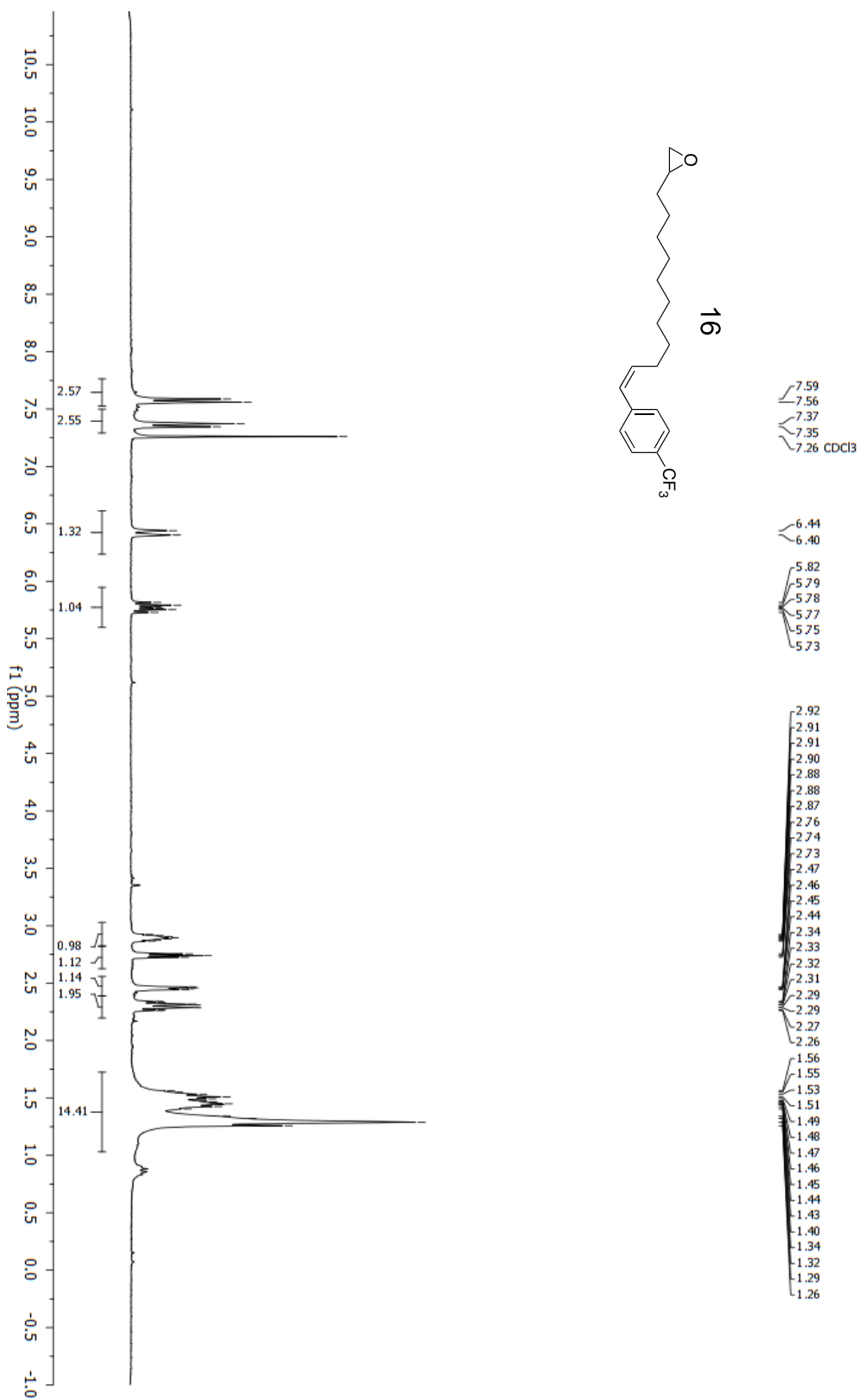
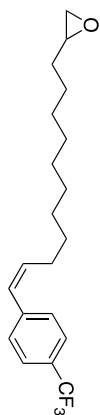


GC Trace of Crude Reaction Mixture

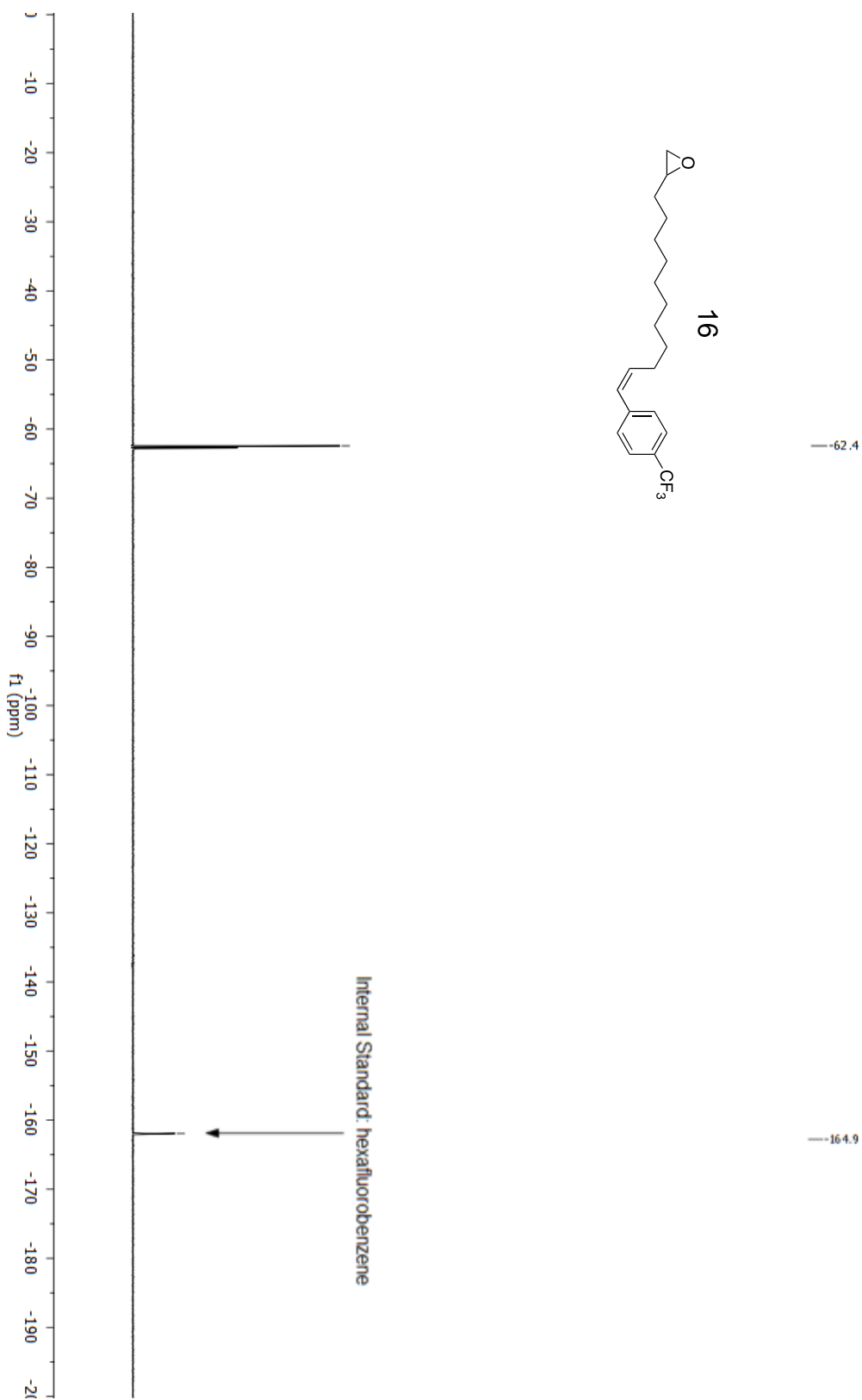
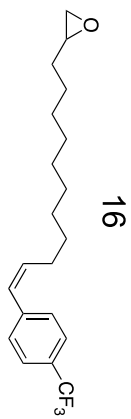


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.137	40699	26357	95.853		V		
2	11.615	1761	1140	4.147				
Total		42460	27497					

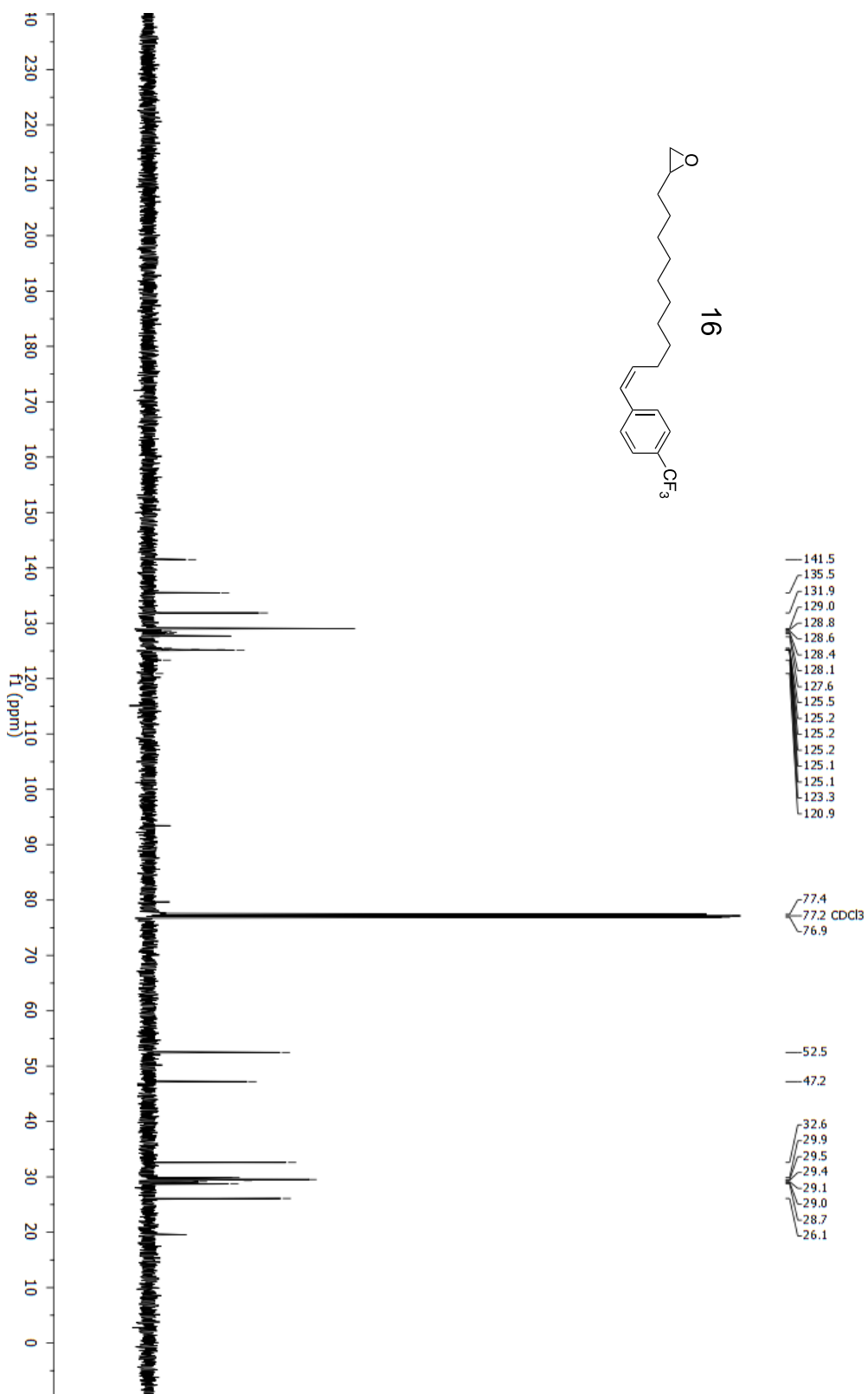
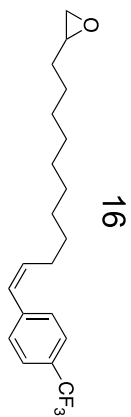
¹H NMR (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.42 (d, *J* = 11.7 Hz, 1H), 5.77 (dt, *J* = 11.7, 7.3 Hz, 1H), 3.03 – 2.82 (m, 1H), 2.74 (t, *J* = 4.5 Hz, 1H), 2.56 – 2.39 (m, 1H), 2.39 – 2.20 (m, 2H), 1.72 – 1.03 (m, 21H).



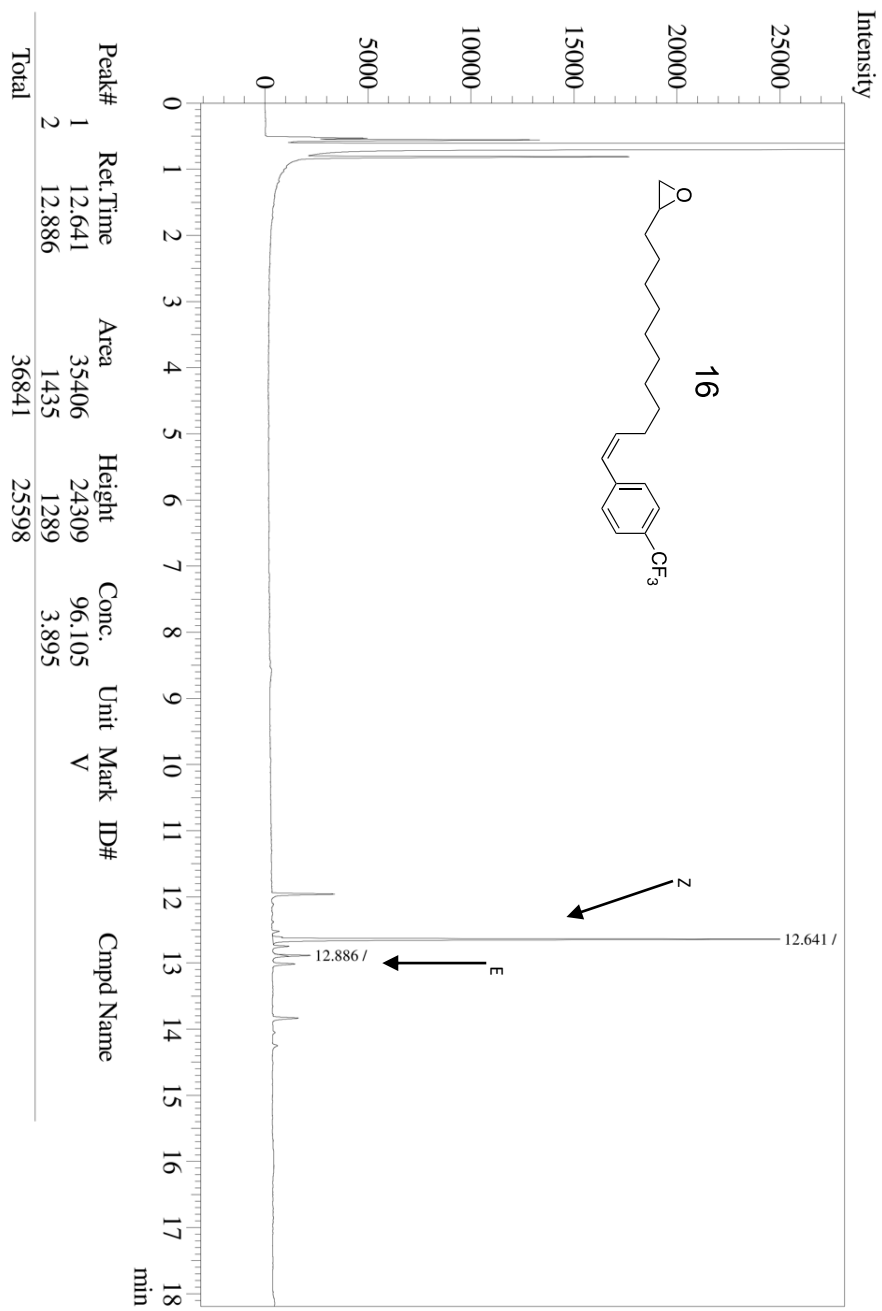
^{19}F NMR (471 MHz, CDCl_3) δ -62.4.



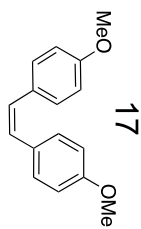
¹³C NMR (126 MHz, Chloroform-*d*) δ 141.5, 135.5, 131.9, 131.9, 129.0, 128.5 (q, *J* = 32.3 Hz), 125.1 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.0 Hz), 52.5, 47.2, 32.6, 29.9, 29.5, 29.4, 29.2, 29.0, 28.7, 26.1.



GC Trace of Crude Reaction Mixture



¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.7 Hz, 4H), 6.77 (d, *J* = 8.7 Hz, 4H), 6.44 (s, 2H), 3.79 (s, 6H).

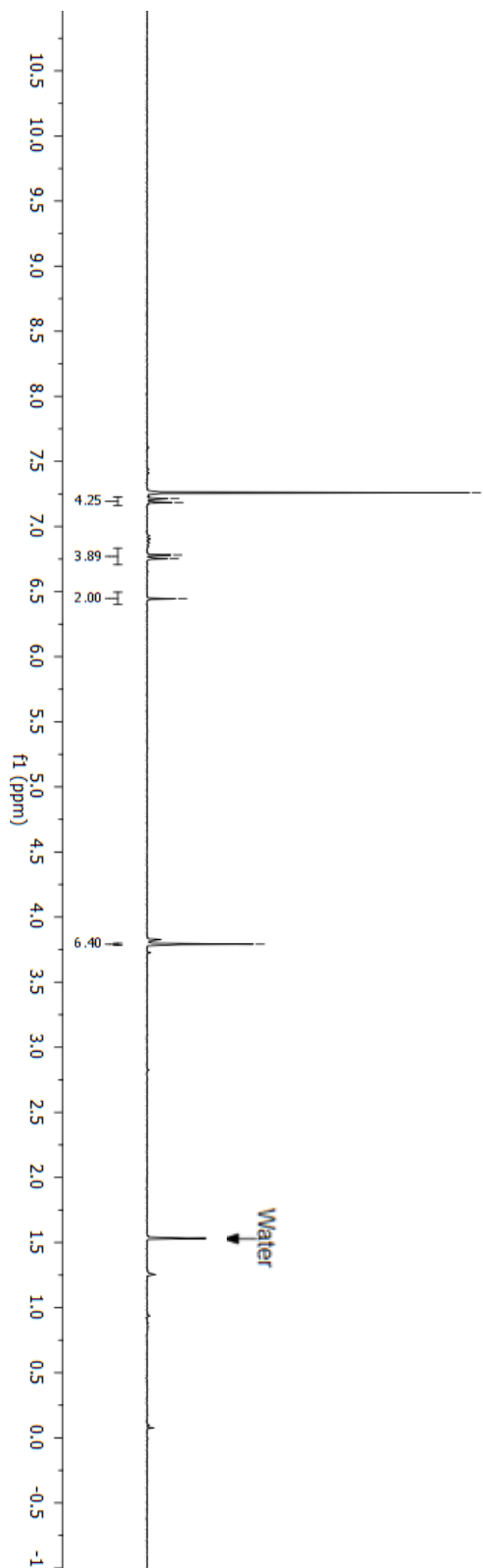


7.26 CDCl₃
7.21
7.18

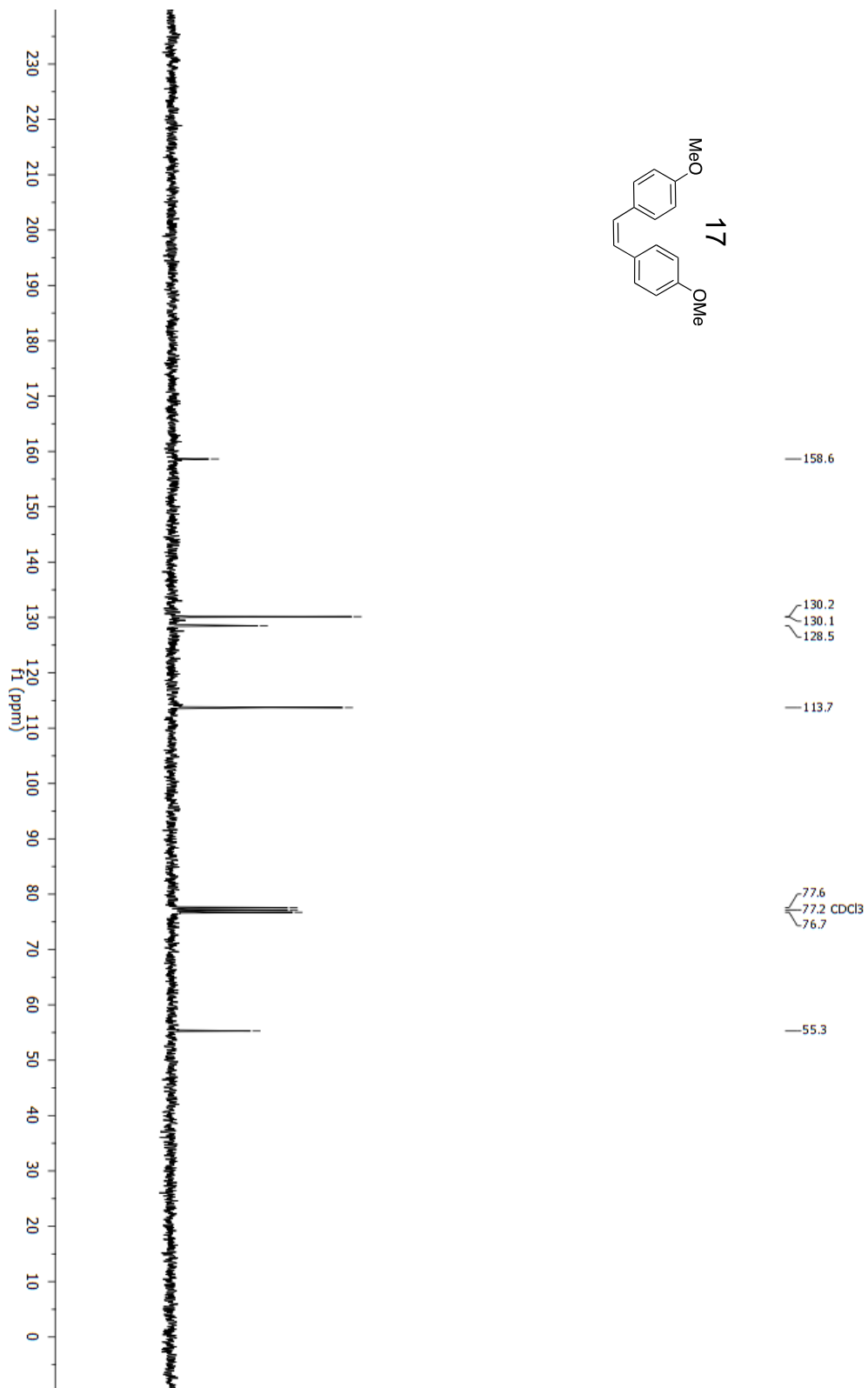
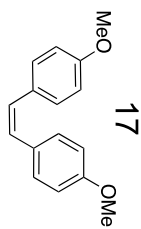
6.78
6.75

6.44

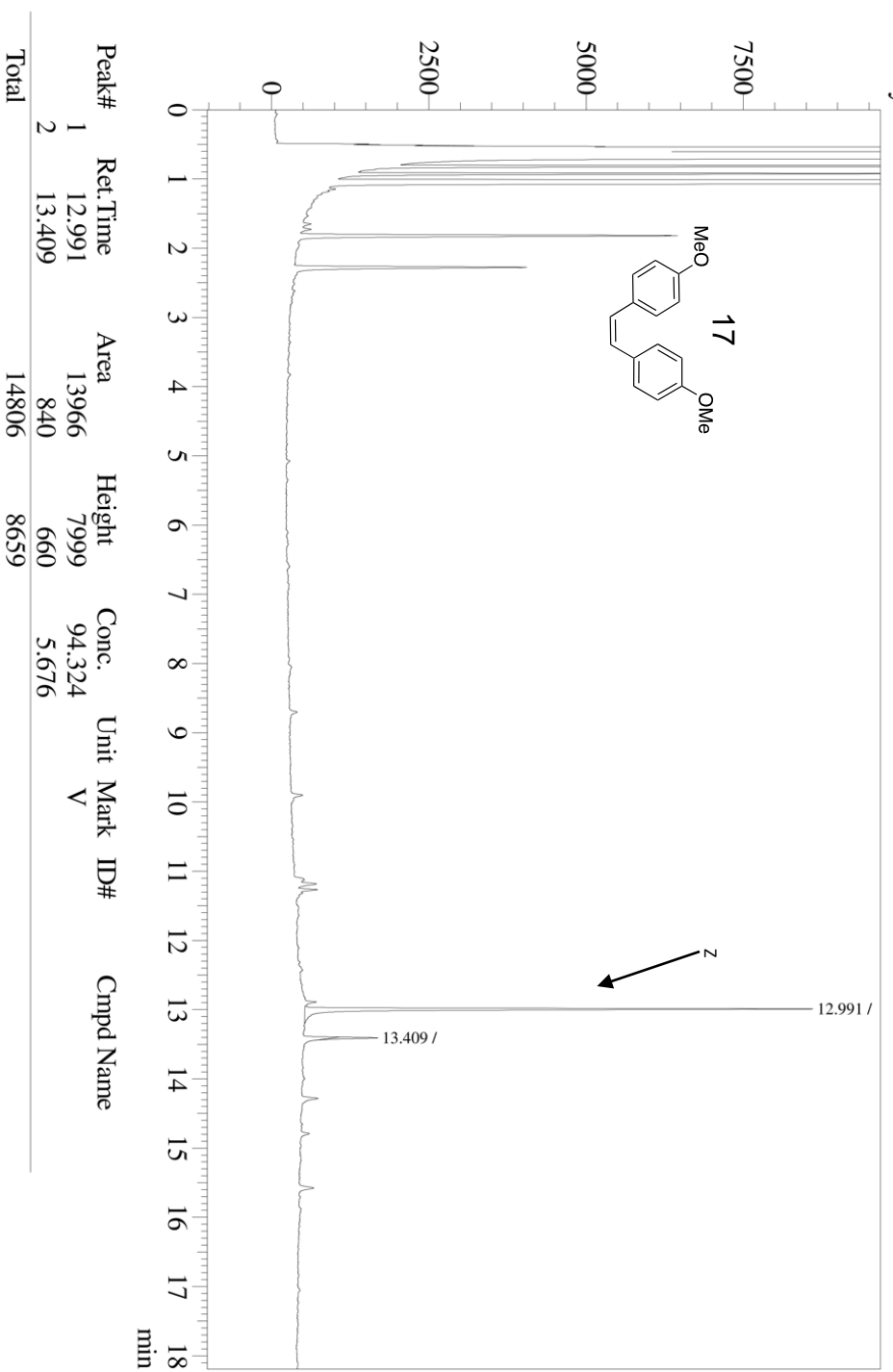
3.79



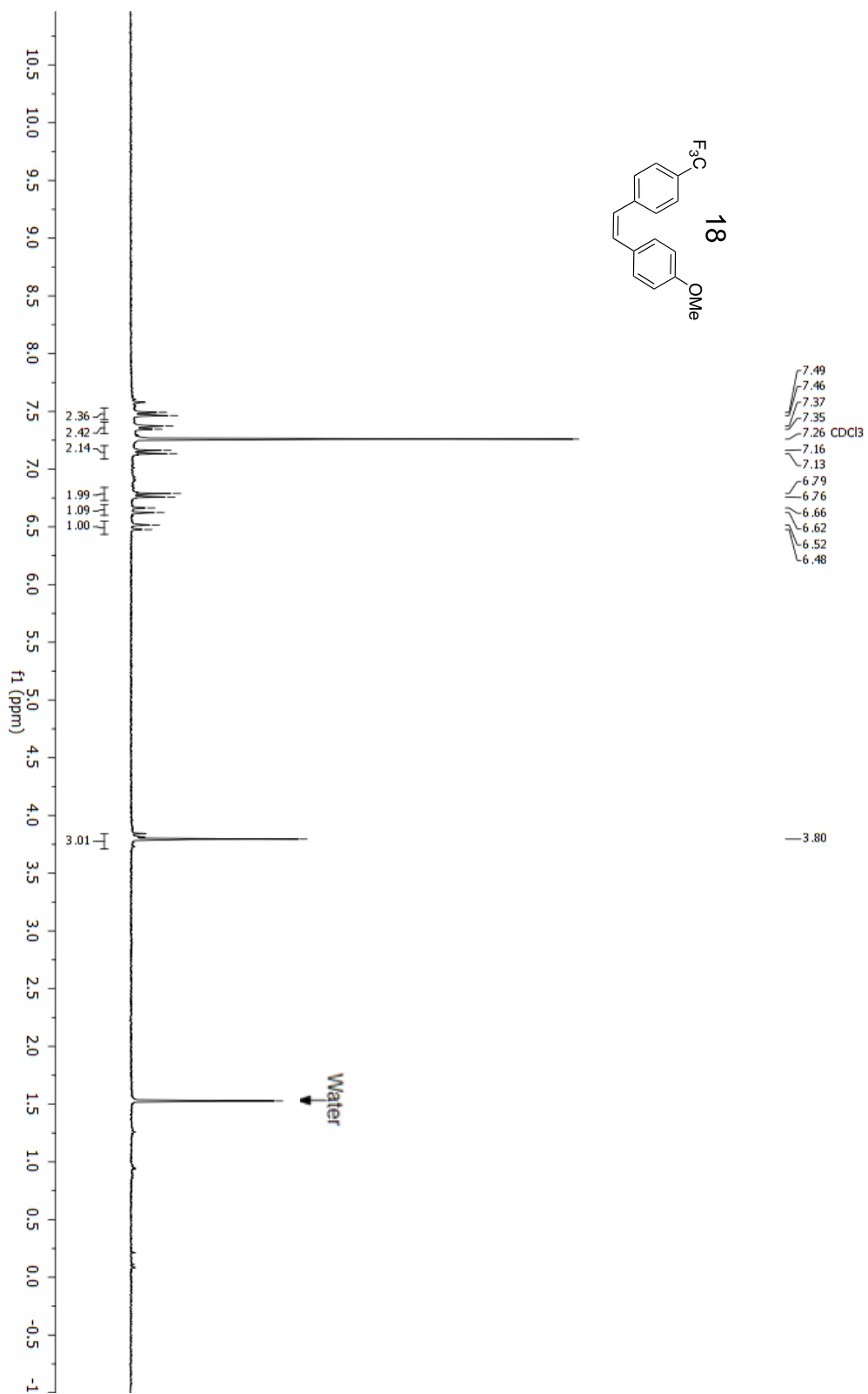
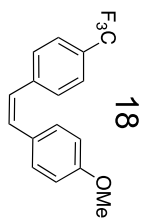
^{13}C -NMR (75 MHz, CDCl_3) δ 158.6, 130.2, 130.1, 128.5, 113.7, 55.3.



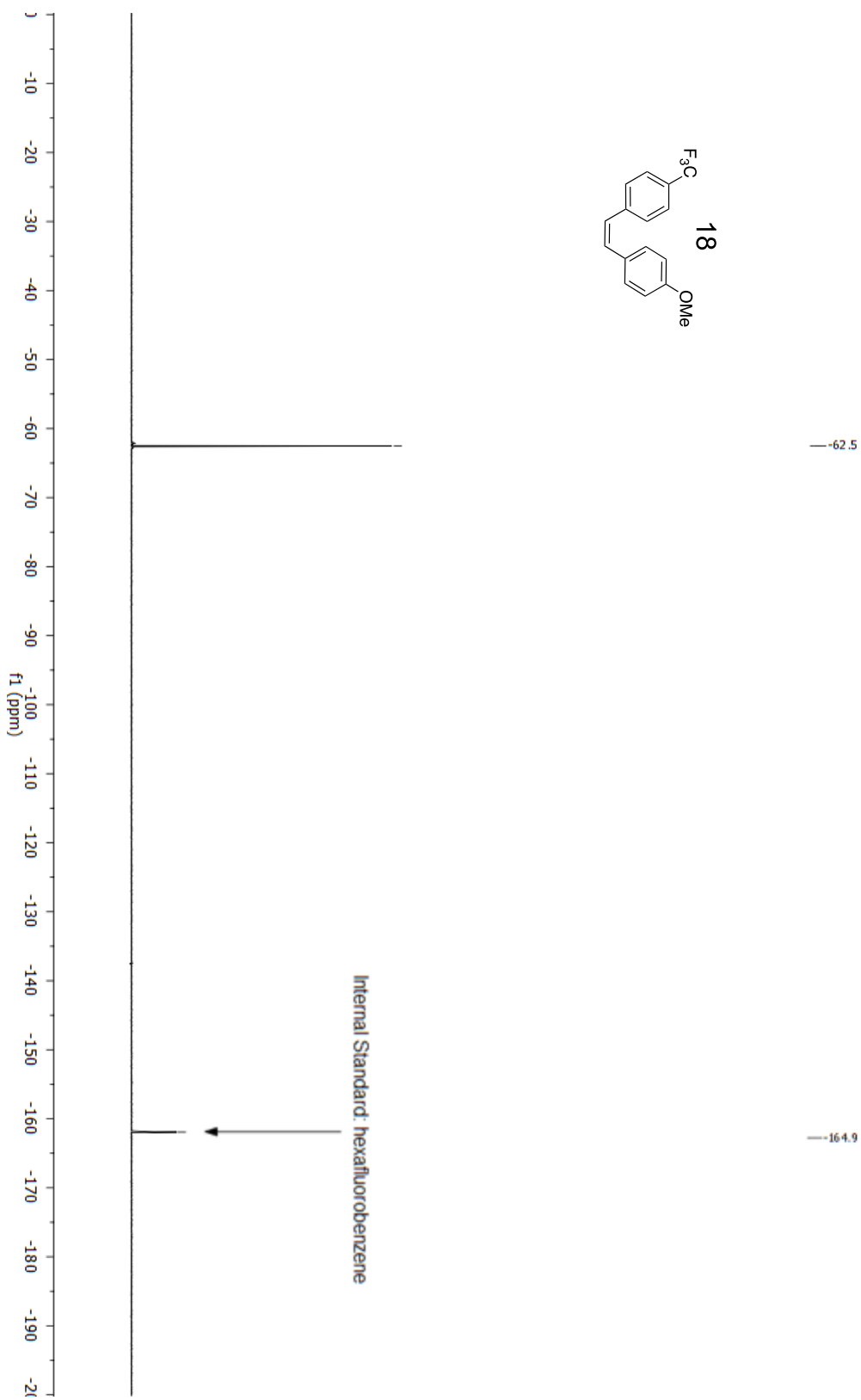
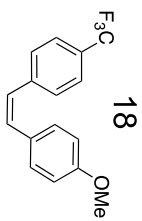
GC Trace of Crude Reaction Mixture



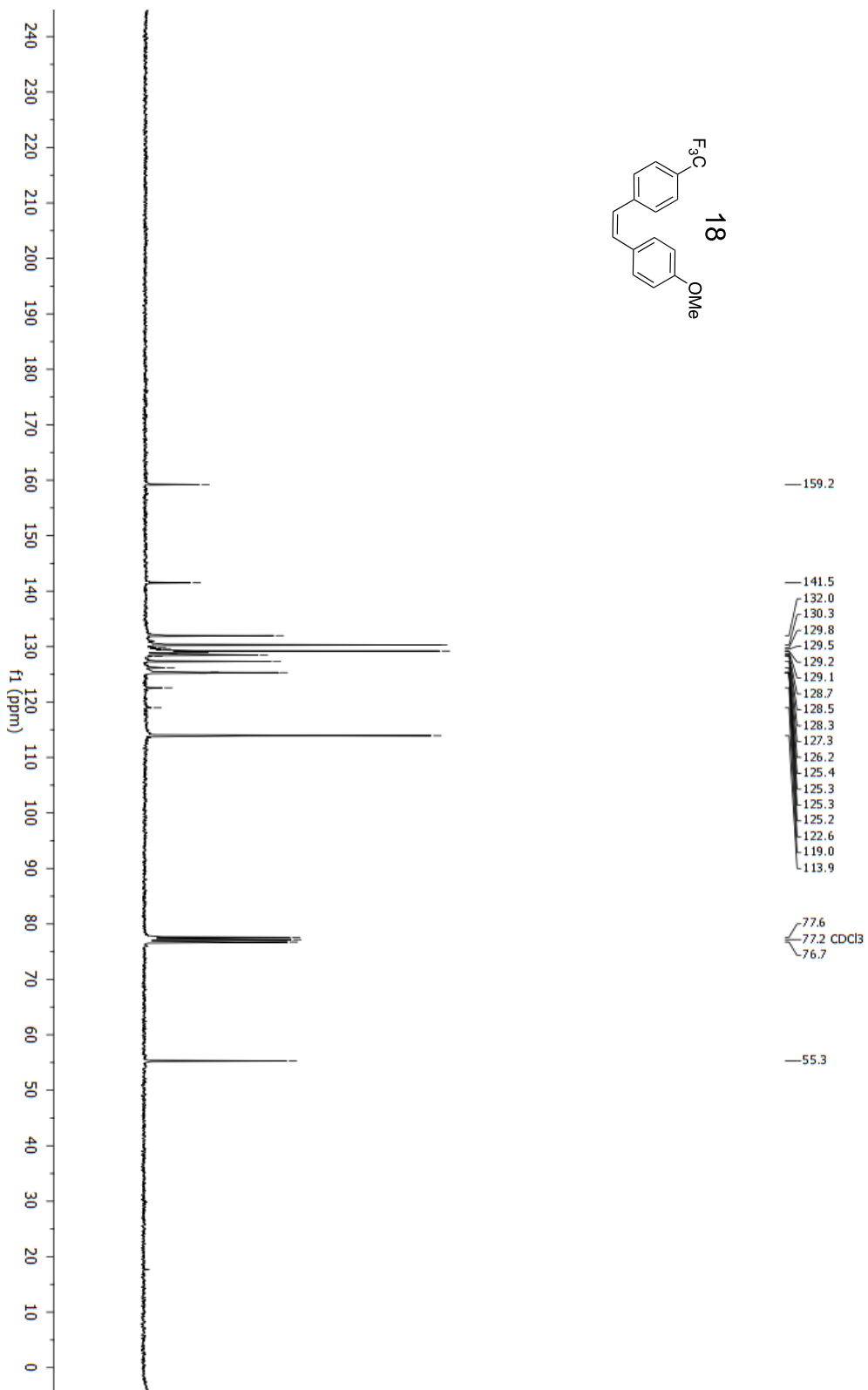
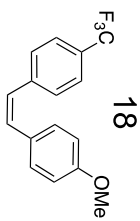
¹H NMR (300 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 12.2 Hz, 1H), 6.50 (d, J = 12.2 Hz, 1H), 3.80 (s, 3H).



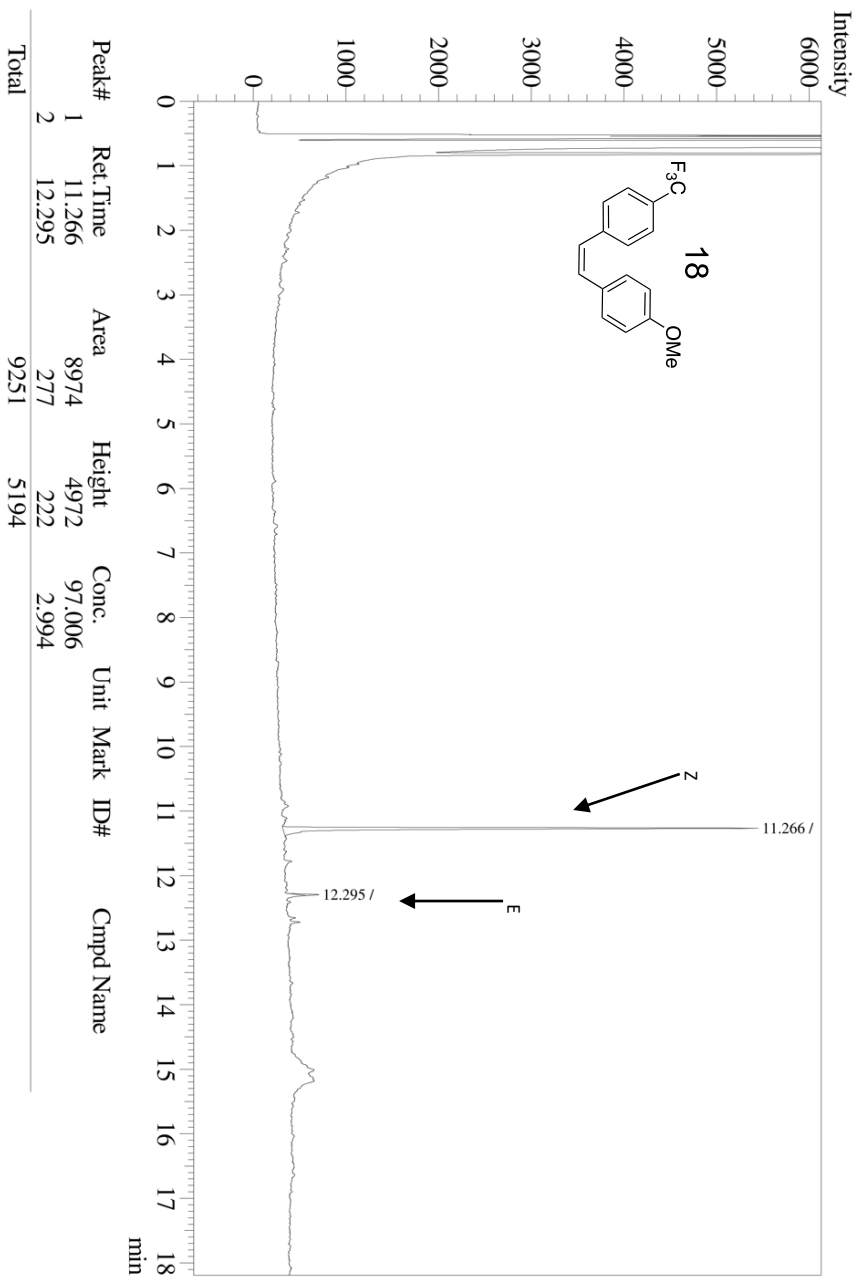
^{19}F NMR (471 MHz, CDCl_3) δ -62.5.



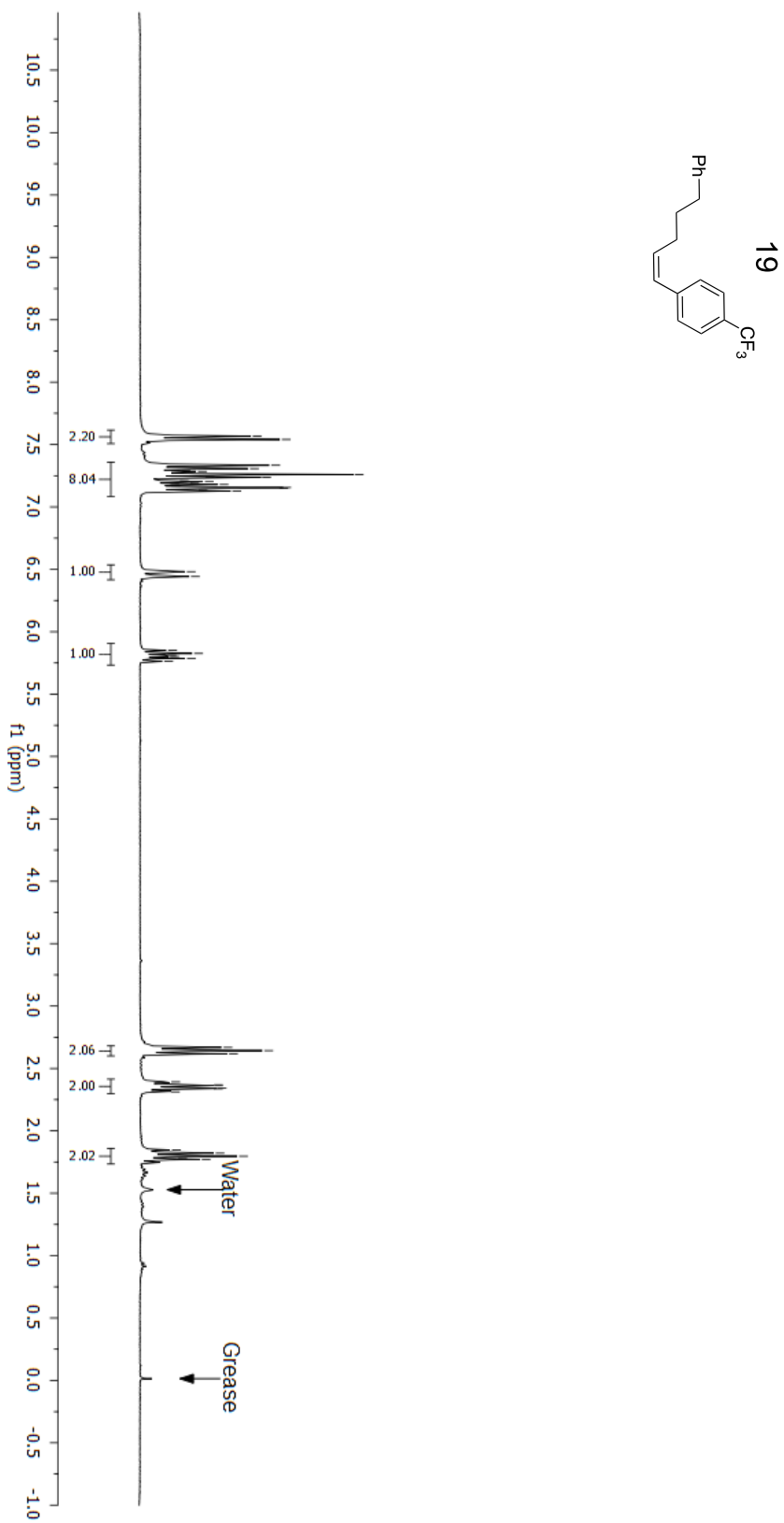
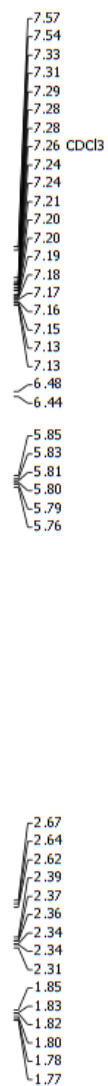
^{13}C NMR (75 MHz, Chloroform- d_3) δ 159.2, 141.5, 132.0, 130.3, 130.3, 129.8, 129.2, 128.9 (q, $J = 32.1$ Hz), 128.5, 127.3, 125.3 (q, $J = 3.8$ Hz), 124.4 (q, $J = 271.6$ Hz), 113.9, 55.3.



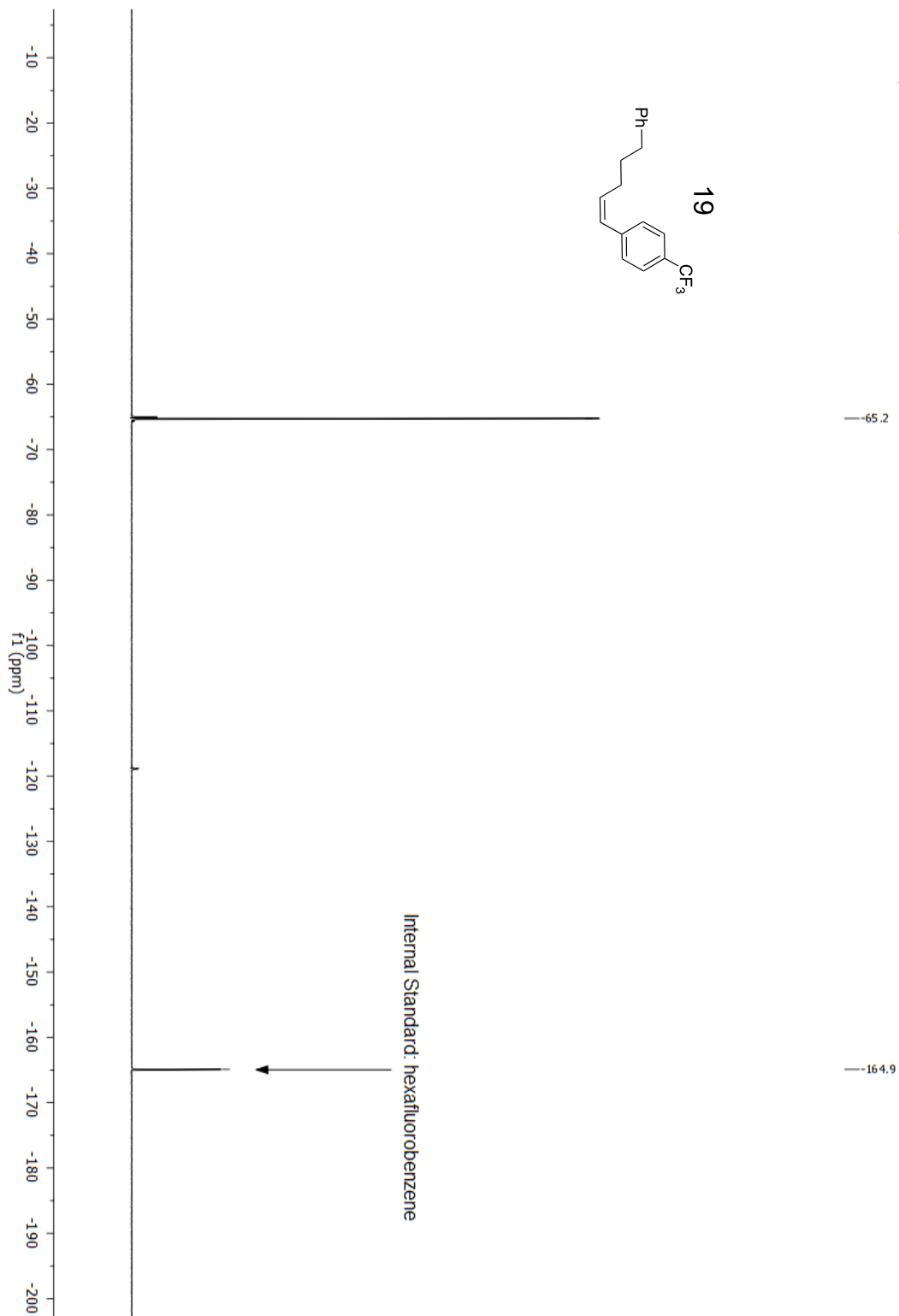
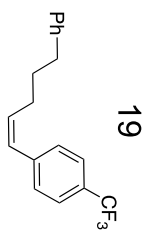
GC Trace of Crude Reaction Mixture



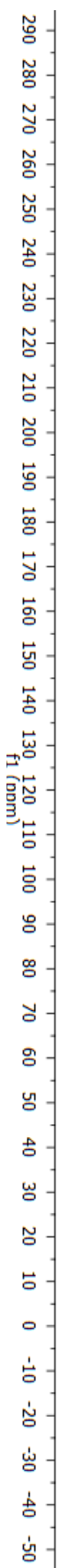
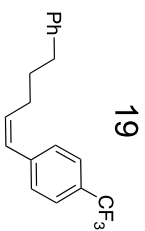
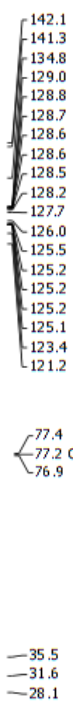
¹H NMR (300 MHz, Chloroform-*d*) δ 7.55 (d, J = 8.1 Hz, 2H), 7.41 – 7.05 (m, 8H), 6.46 (d, J = 11.6 Hz, 1H), 5.81 (dt, J = 11.7, 7.4 Hz, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.35 (dt, J = 7.6, 7.3 Hz, 2H), 1.81 (q, J = 7.6 Hz, 2H).

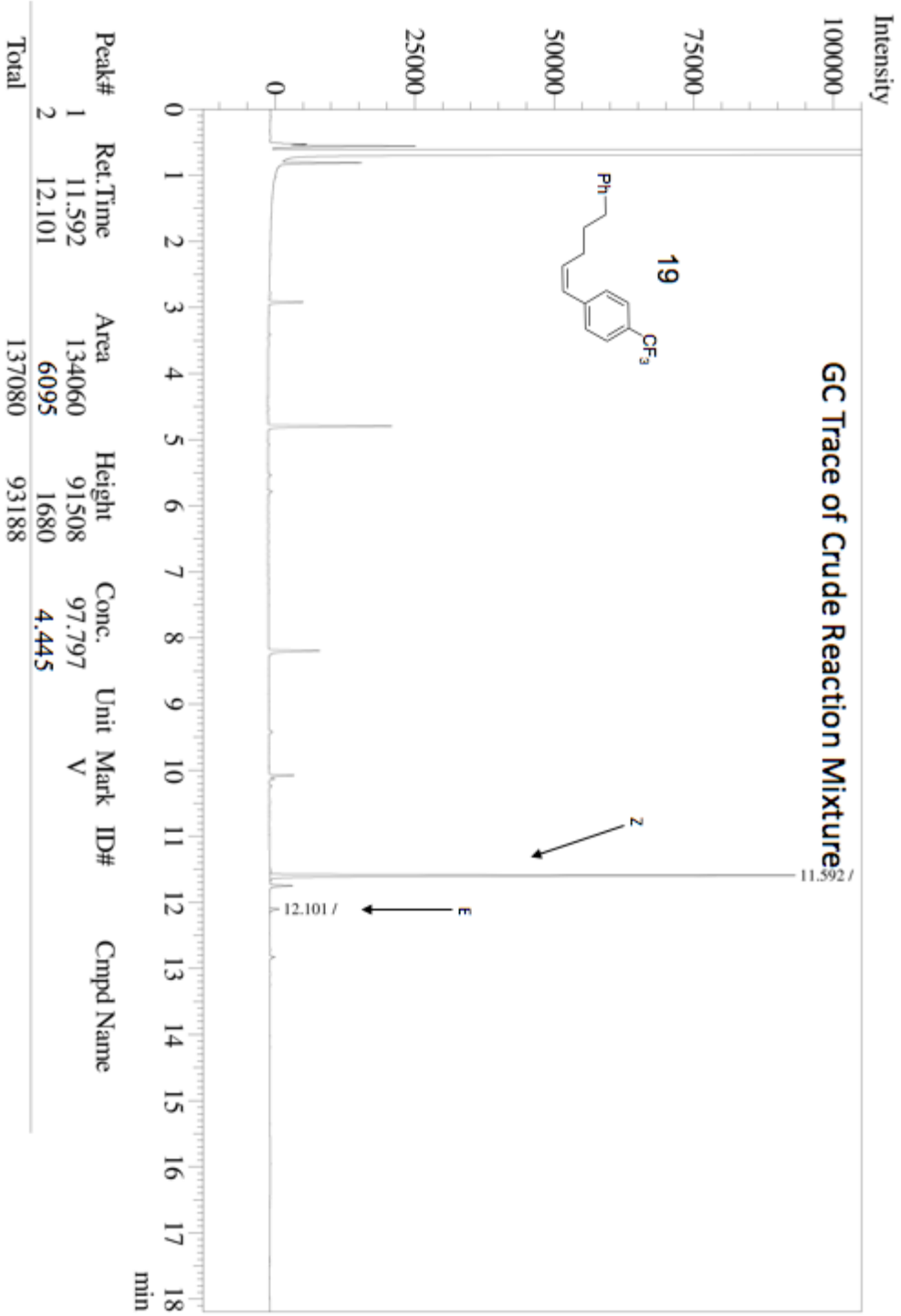


^{19}F NMR (471 MHz, Chloroform- d_3) δ -65.2.



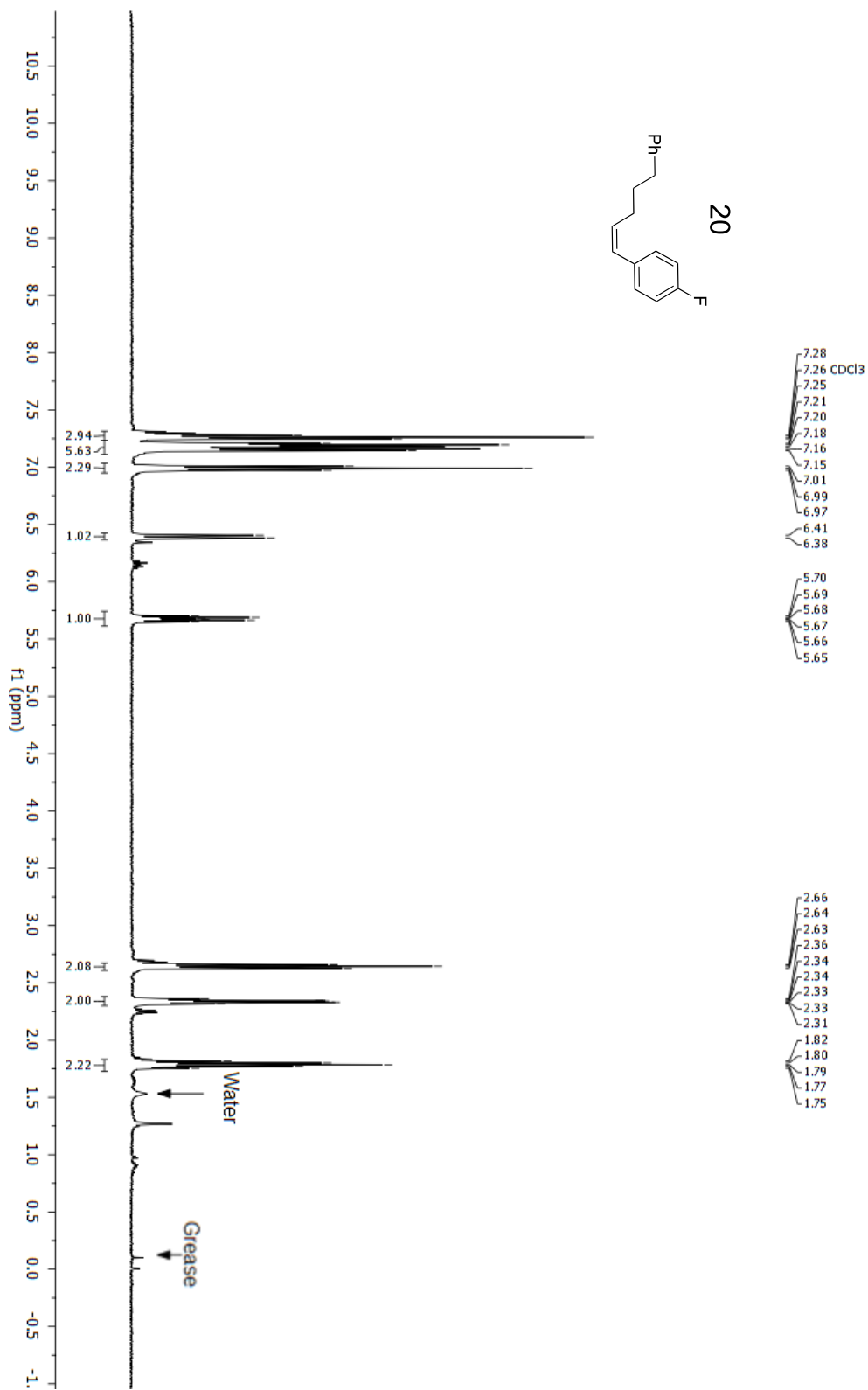
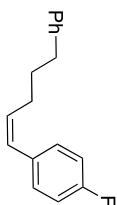
^{13}C NMR (126 MHz, Chloroform- d_3) δ 142.1, 141.3, 134.8, 129.0, 128.6 (q, $J = 35.2$ Hz), 128.5, 128.2, 127.7, 126.0, 125.5 (q, $J = 3.0$ Hz), 124.4 (q, $J = 276.5$ Hz), 35, 31.6, 28.1



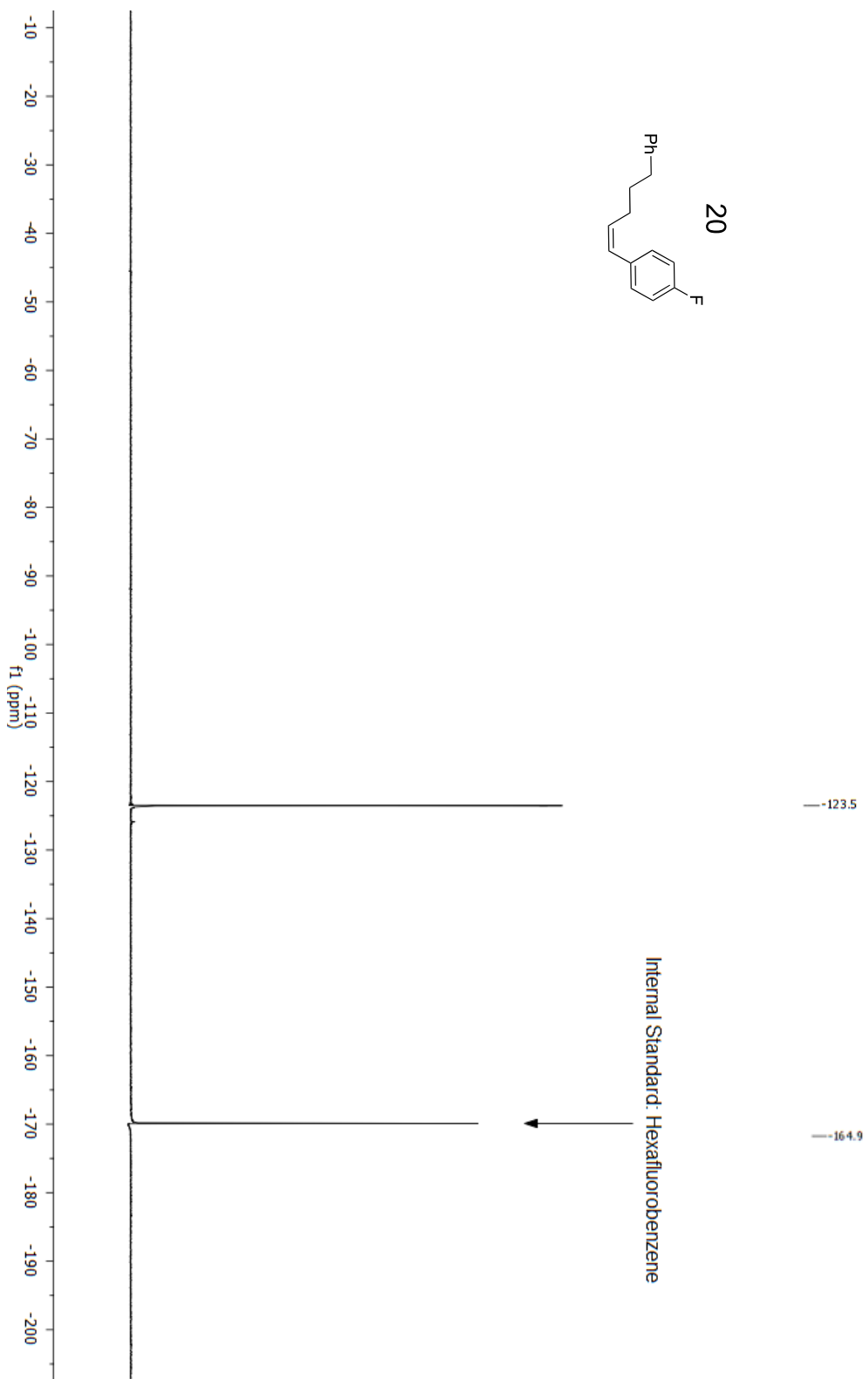
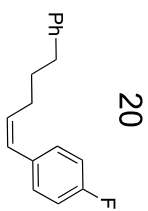


¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.23 (m, 3H), 7.23 – 7.13 (m, 4H), 7.04 – 6.95 (m, 2H), 6.39 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.33 (dt, *J* = 7.6, 7.3 Hz, 2H), 1.79 (p, *J* = 7.6 Hz, 2H).

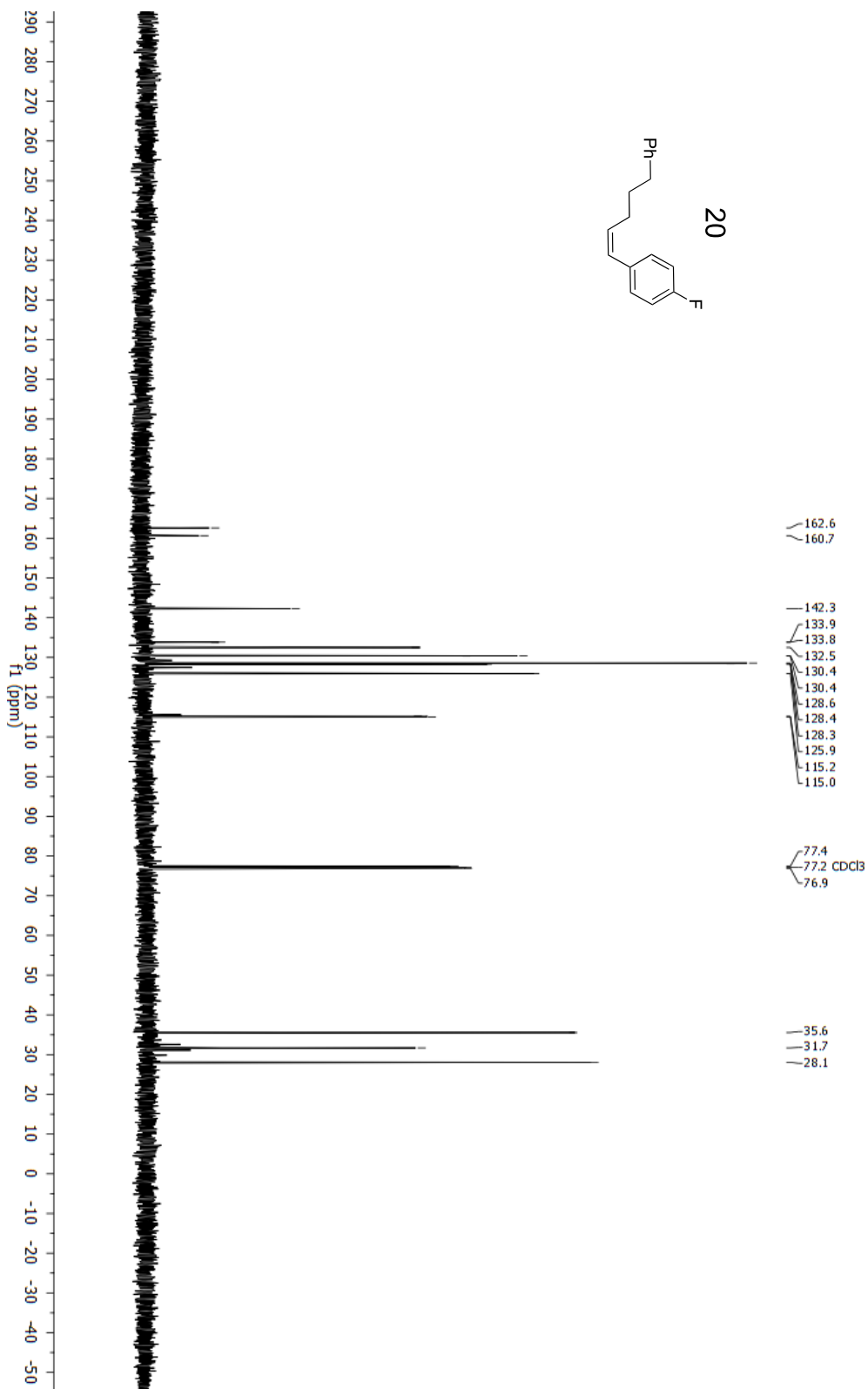
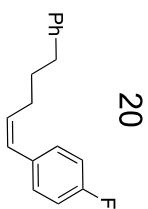
20

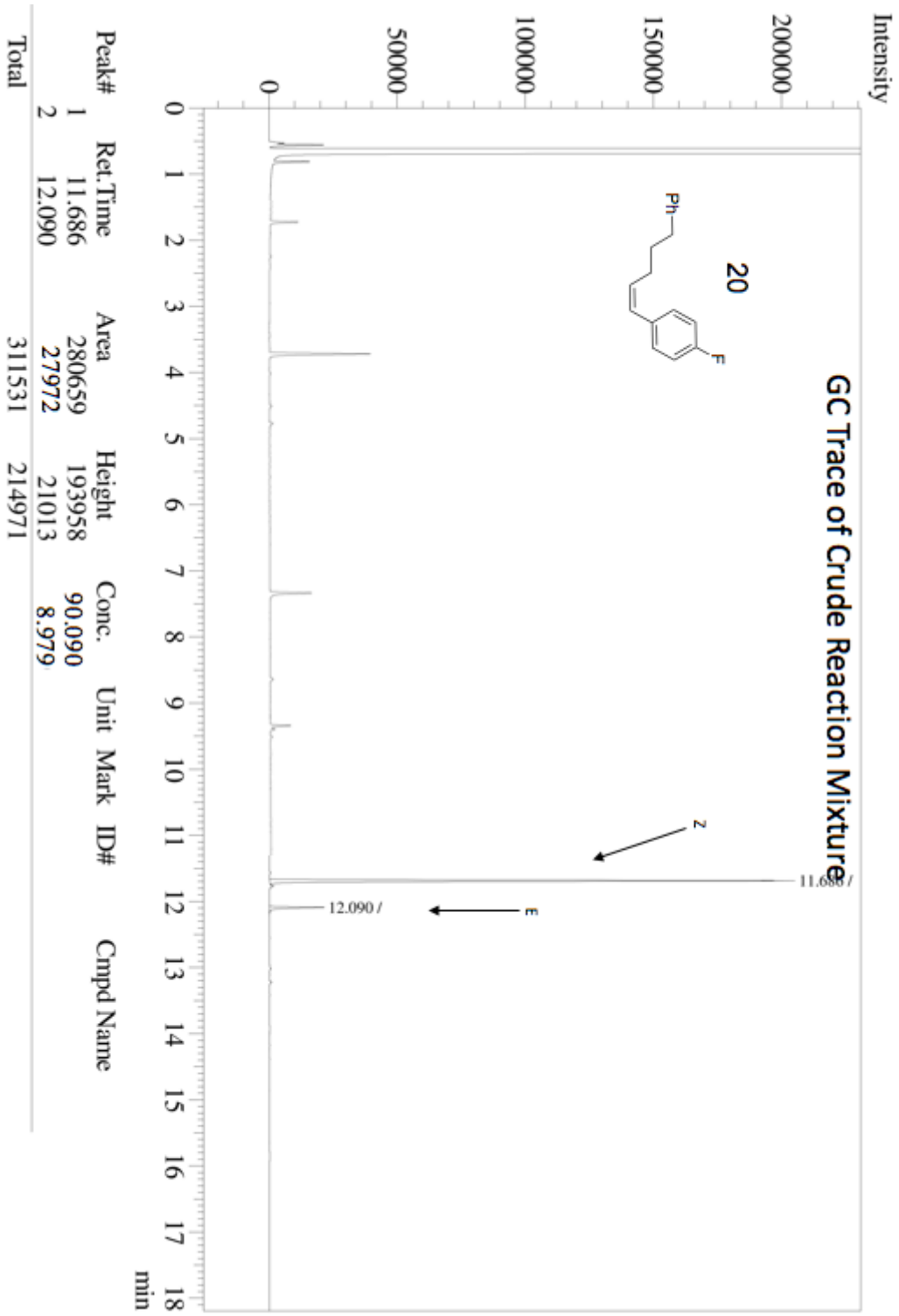


¹⁹F NMR (471 MHz, Chloroform-*d*) δ -123.5.



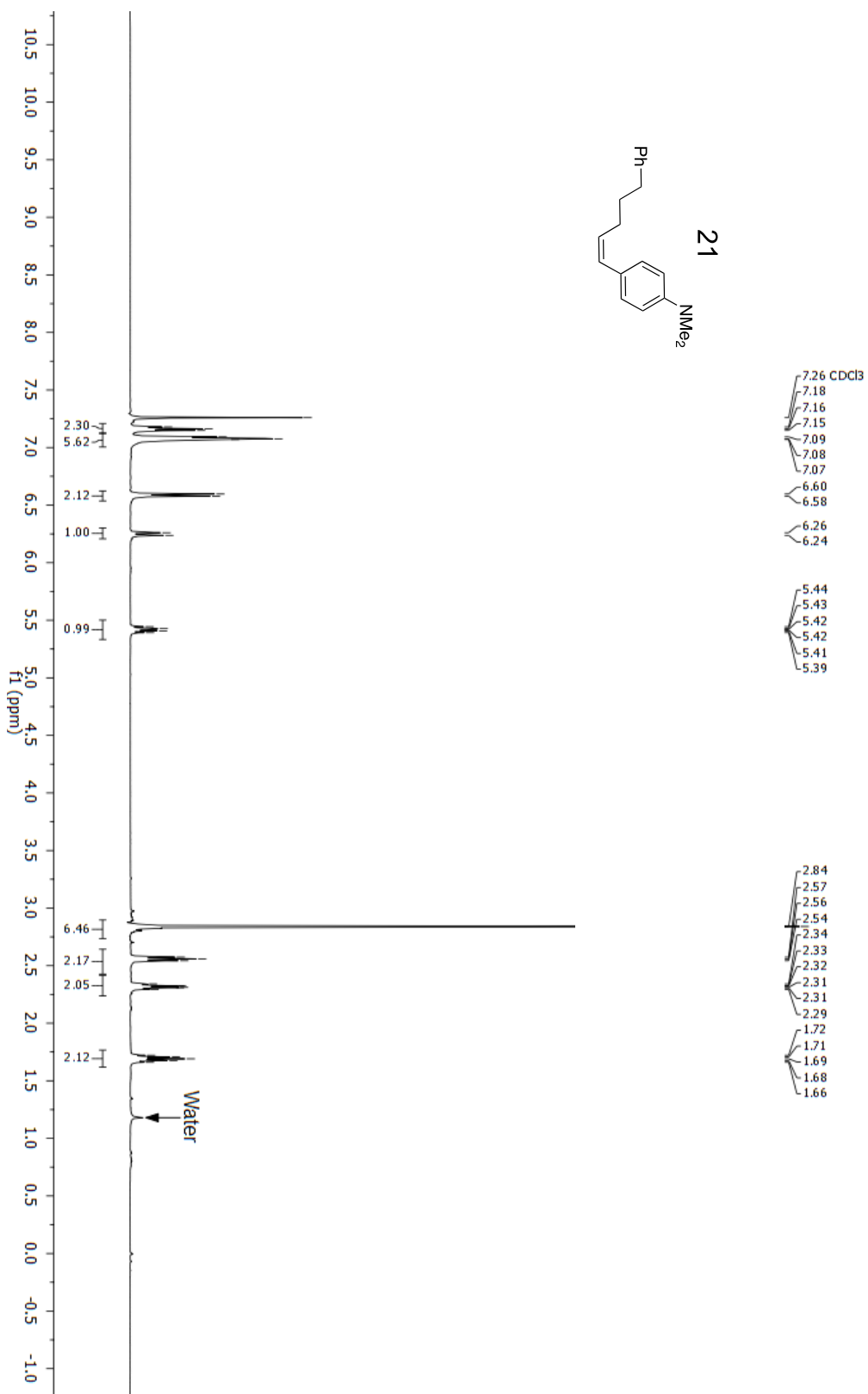
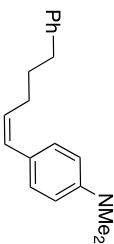
^{13}C NMR (126 MHz, Chloroform- d_3) δ 161.5 (d, $J = 246.1$ Hz), 142.3, 133.8 (d, $J = 3.1$ Hz), 132.5, 130.4 (d, $J = 7.9$ Hz), 128.6, 128.4, 128.3, 125.9, 125.1 (d, $J = 21.3$ Hz), 35.6, 31.7, 27.1.



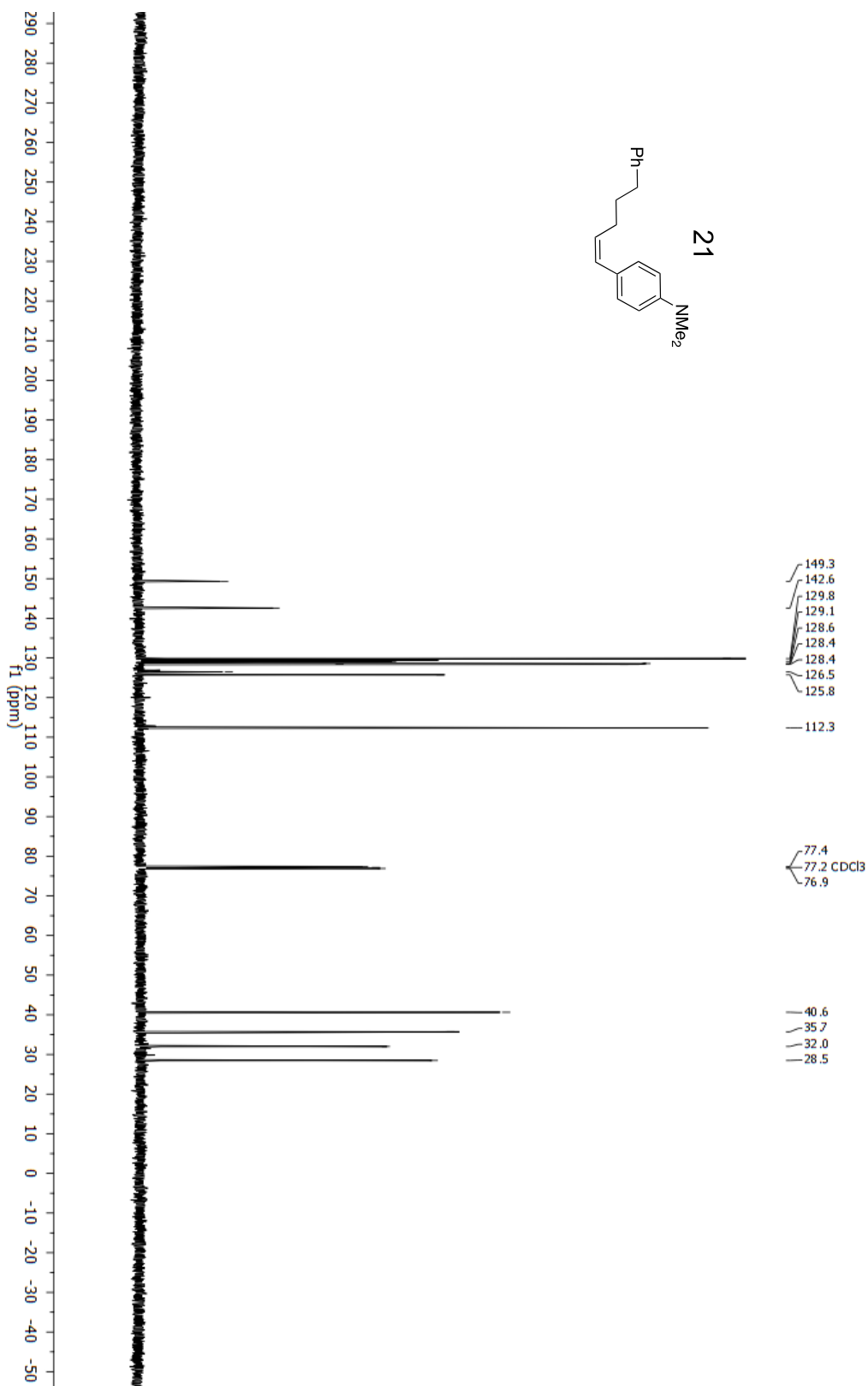
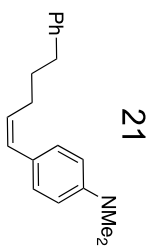


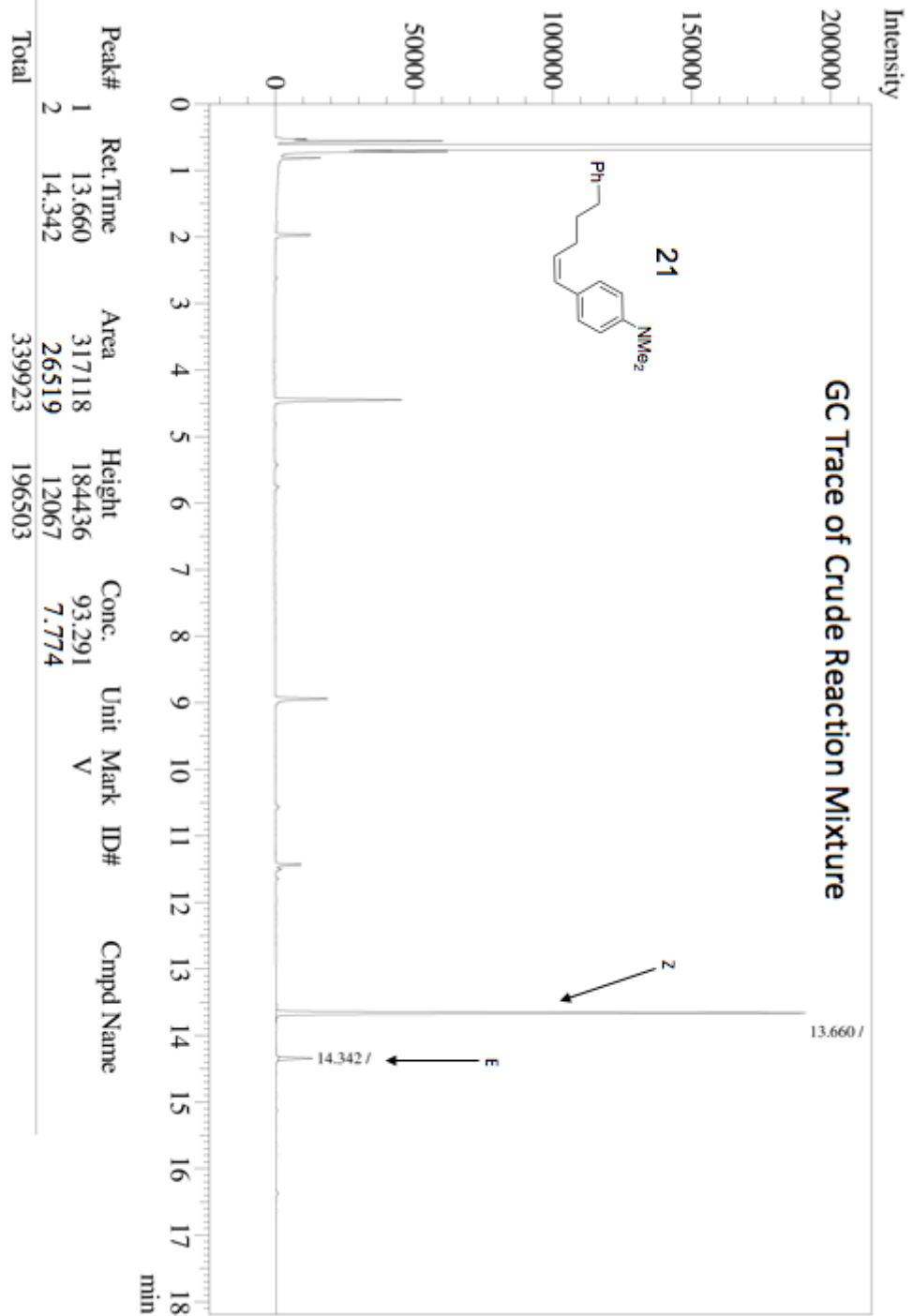
¹H NMR (300 MHz, Chloroform-*d*) δ 7.16 (t, *J* = 7.5 Hz, 2H), 7.11 – 7.05 (m, 5H), 6.59 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 11.6 Hz, 1H), 5.42 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.84 (s, 6H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.31 (dt, *J* = 7.2 Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H).

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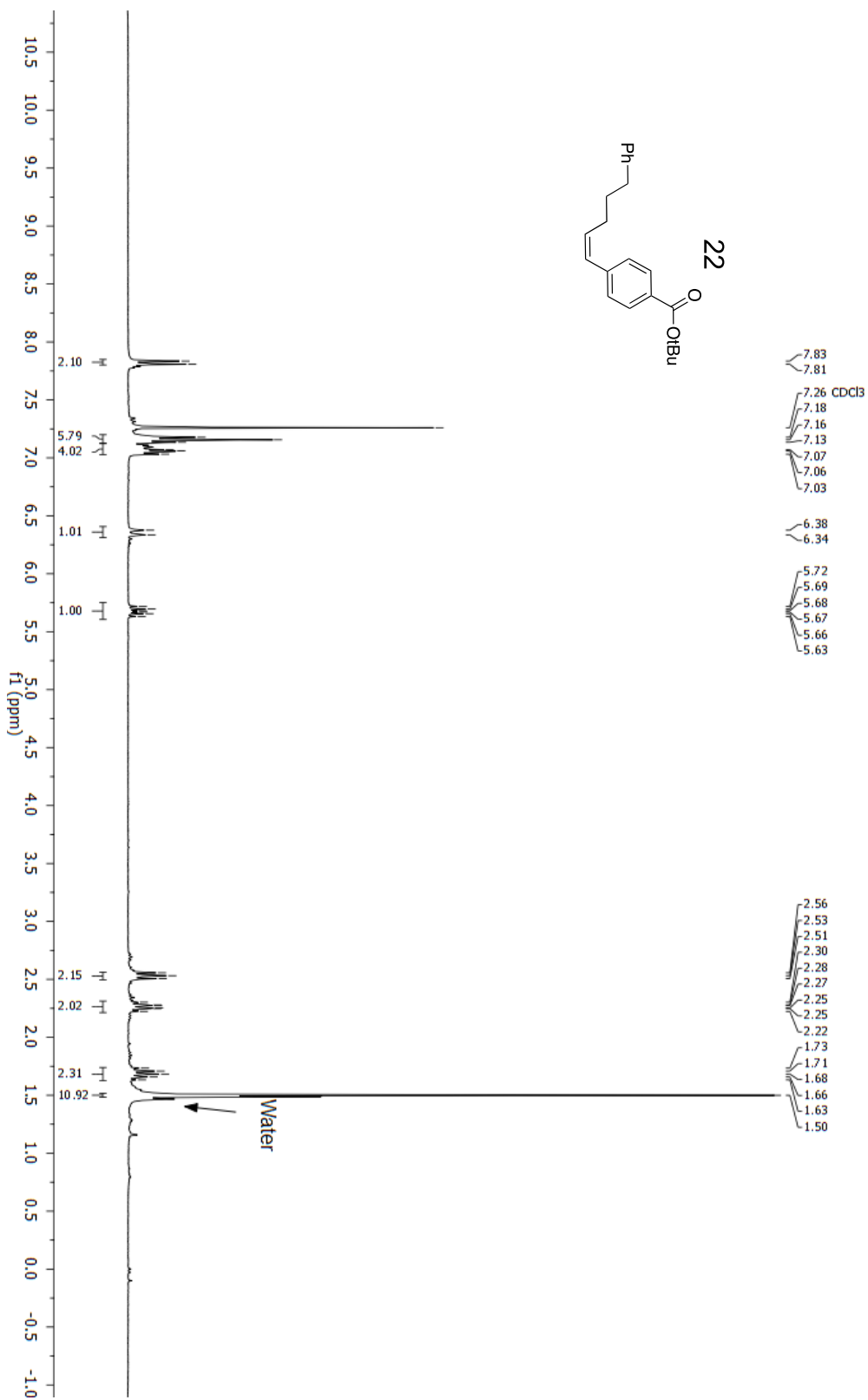
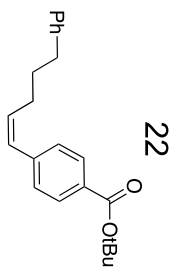


¹³C NMR (126 MHz, Chloroform-*d*) δ 149.3, 142.6, 129.8, 129.1, 128.6, 128.4, 126.5, 125.8, 112.3, 40.6, 35.7, 32.0, 28.5.

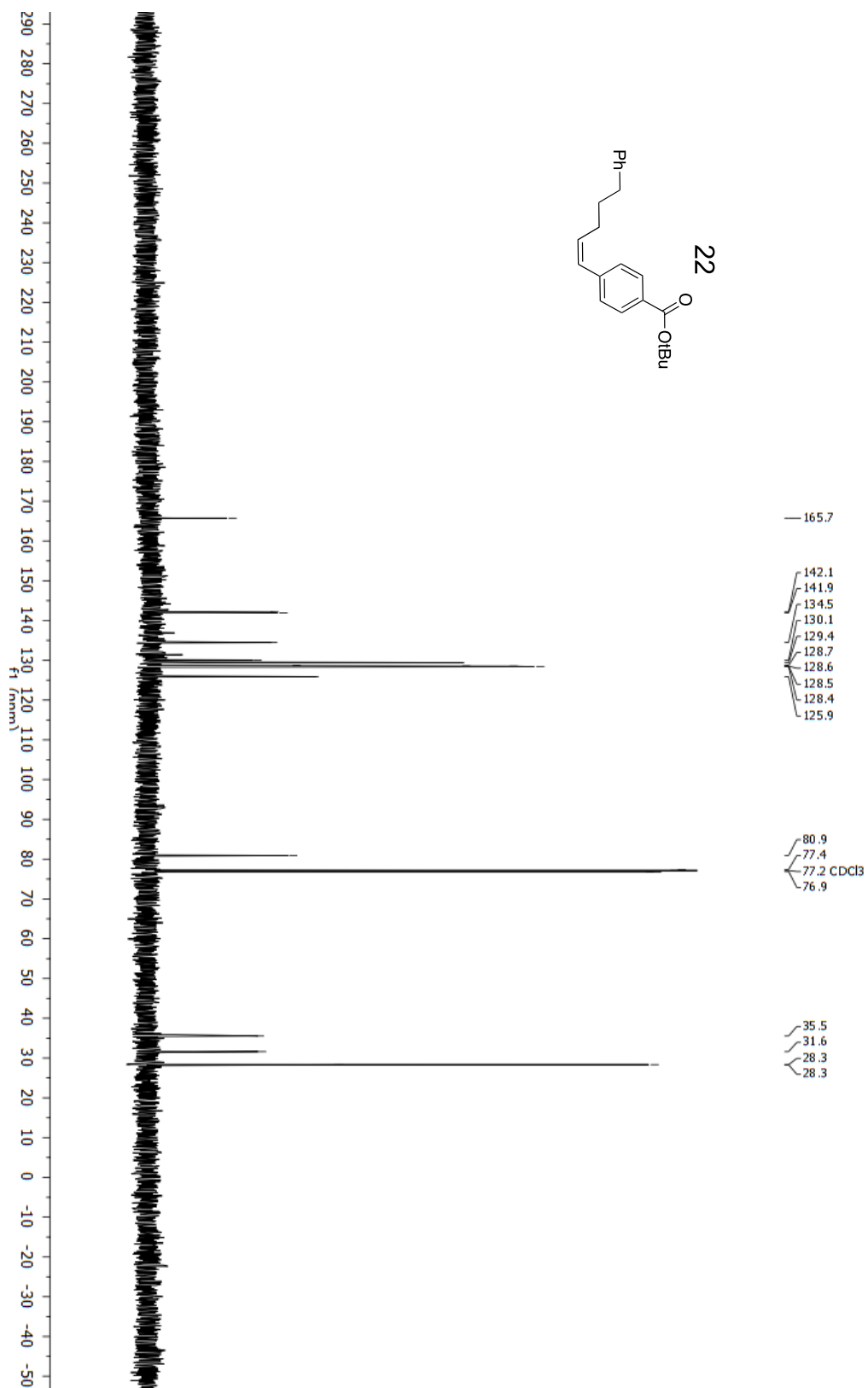
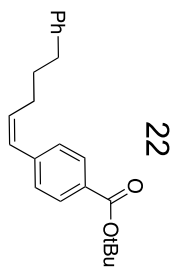




¹H NMR (300 MHz, Chloroform-*d*) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.21 – 7.10 (m, 5H), 7.12 – 7.00 (m, 2H), 6.36 (d, $J = 11.7$ Hz, 1H), 5.68 (dt, $J = 11.7, 7.3$ Hz, 1H), 2.53 (t, $J = 7.5, 2H$), 2.27 (dt, $J = 7.5, 7.3$ Hz, 2H), 1.68 (p, $J = 7.5$ Hz, 2H), 1.50 (s, 9H).

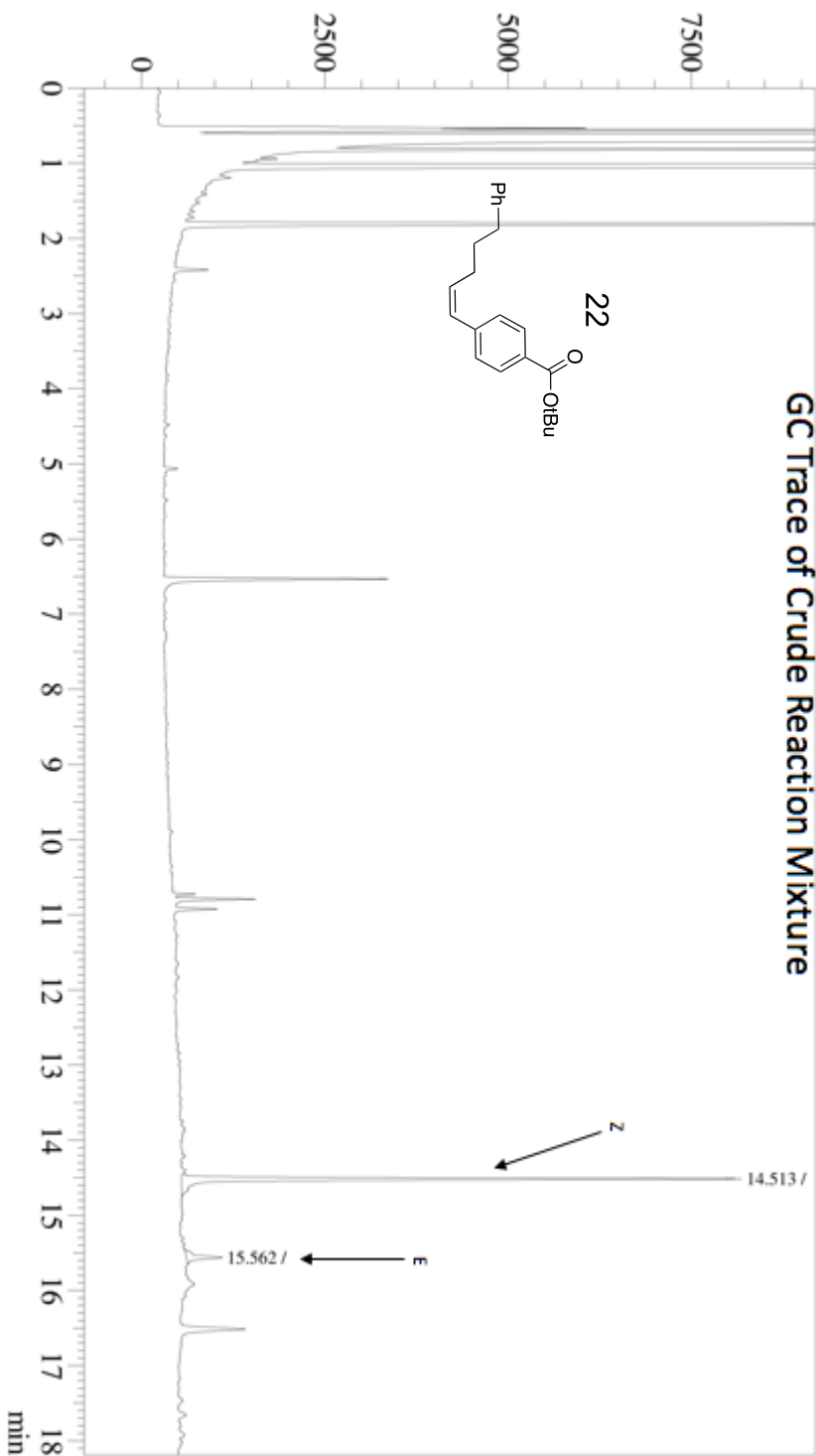


¹³C NMR (126 MHz, Chloroform-d) δ 165.7, 142.2, 141.9, 134.5, 130.1, 129.4, 128.7, 128.6, 128.5, 128.4, 125.9, 80.9, 77.4, 77.2, 76.9, 35.5, 31.6, 28.3, 28.3.



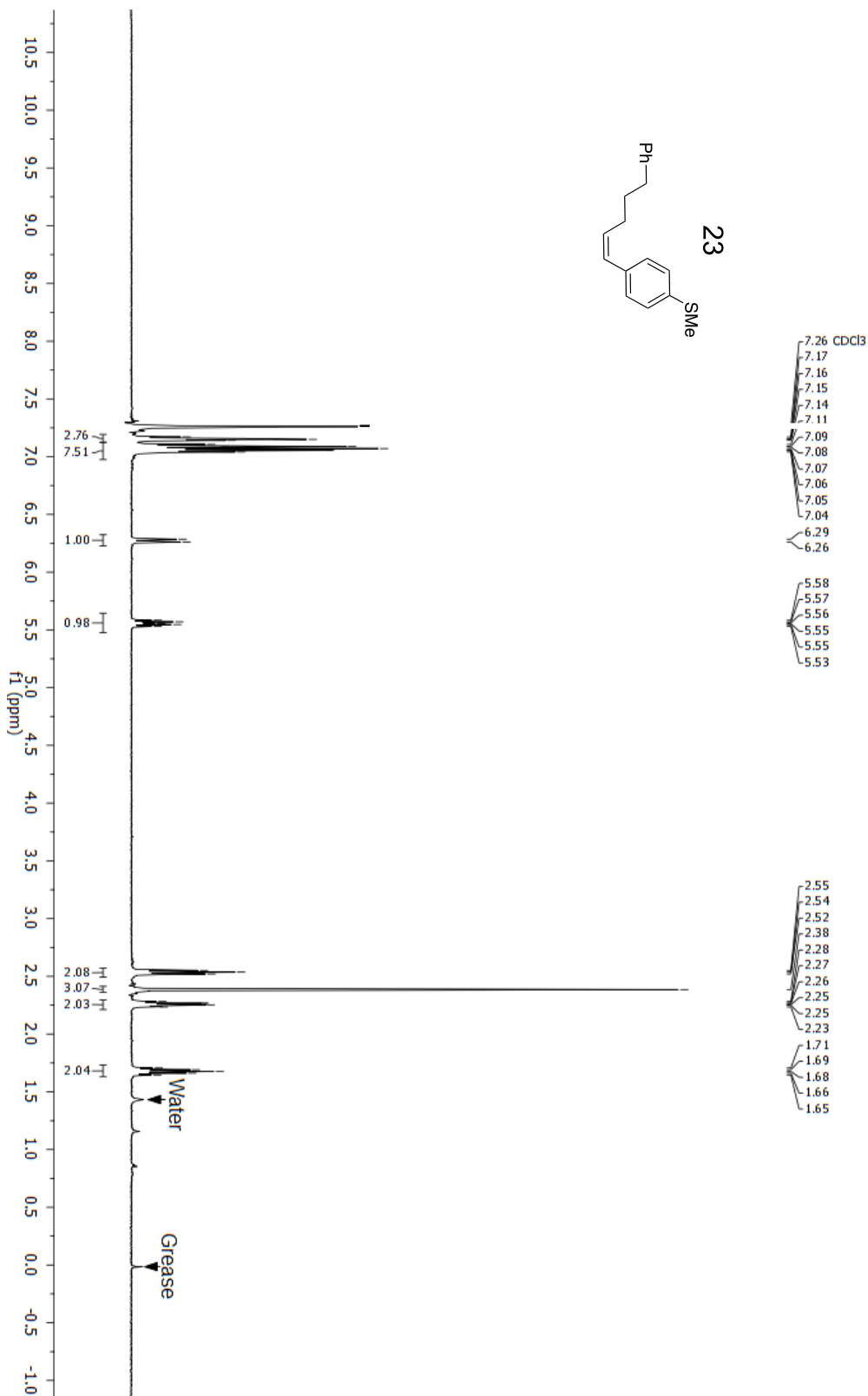
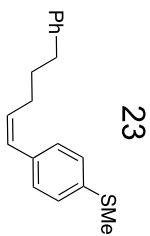
Intensity

GC Trace of Crude Reaction Mixture

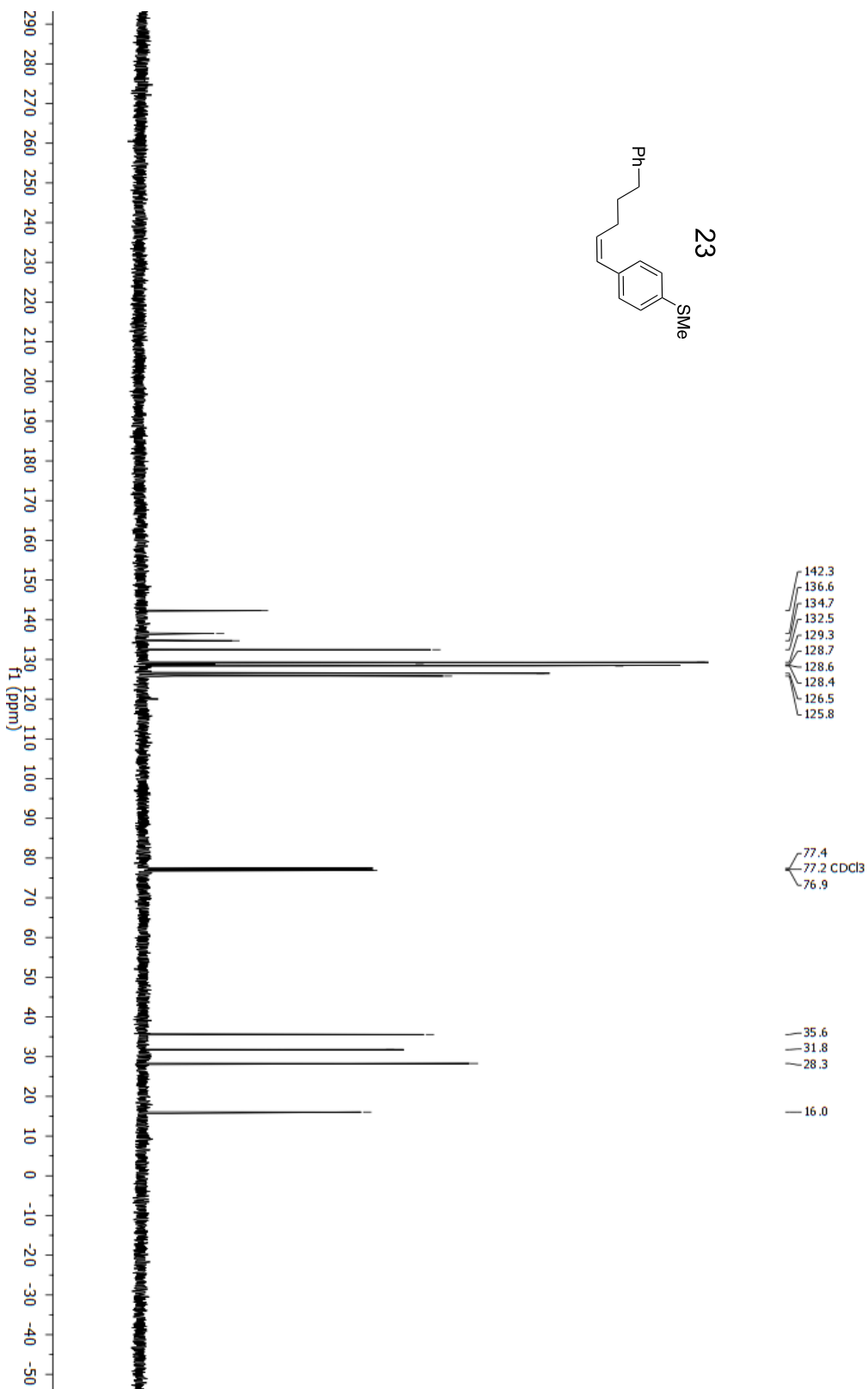
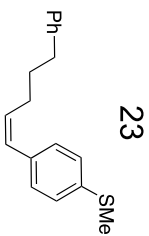


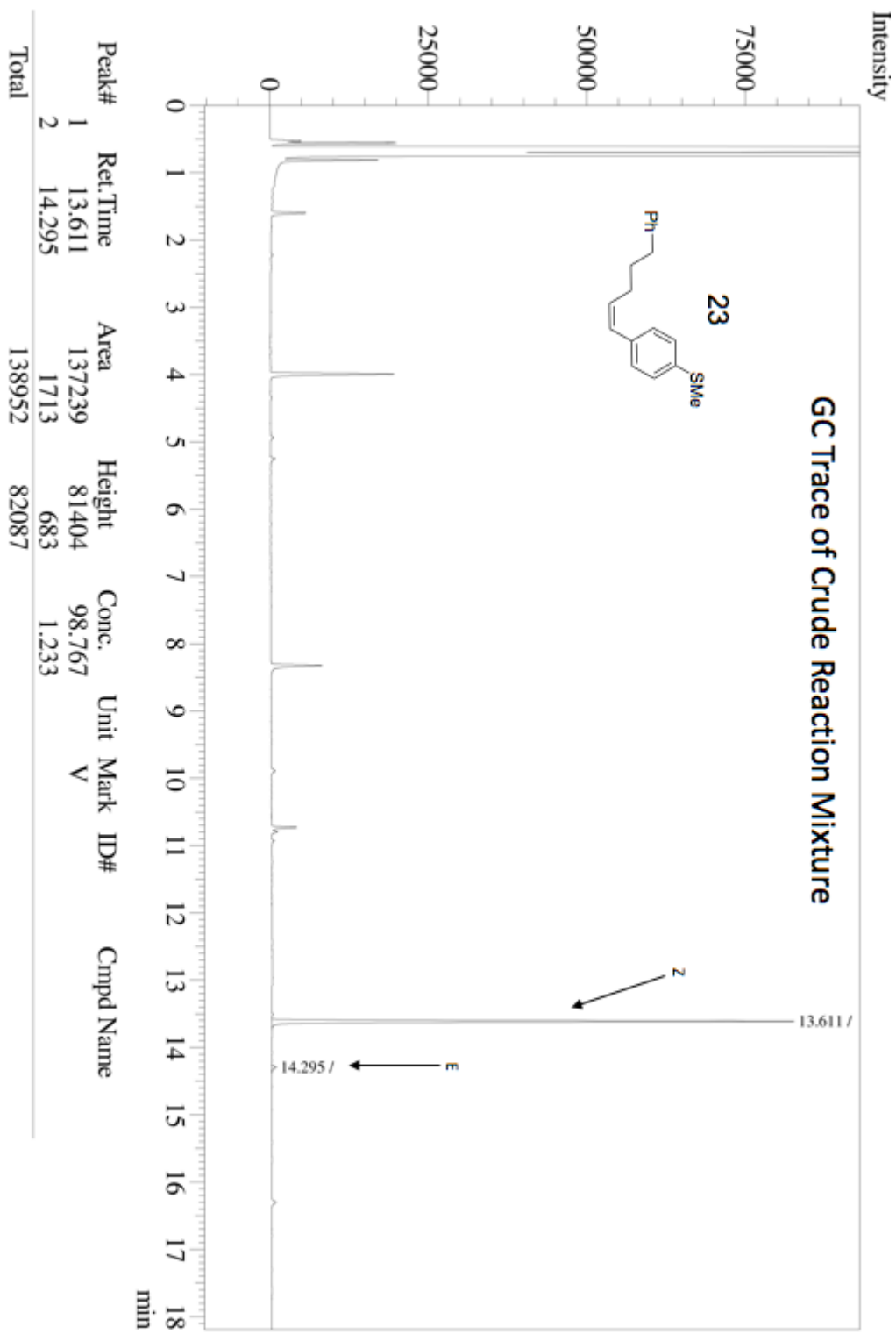
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.513	17273	7559	91.108		SV		
2	15.562	1686	491	8.892				
Total		18959	8050					

¹H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 3H), 7.12 – 7.02 (m, 6H), 6.27 (d, *J* = 11.7 Hz, 1H), 5.56 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 2.26 (dt, *J* = 7.3 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 2H).

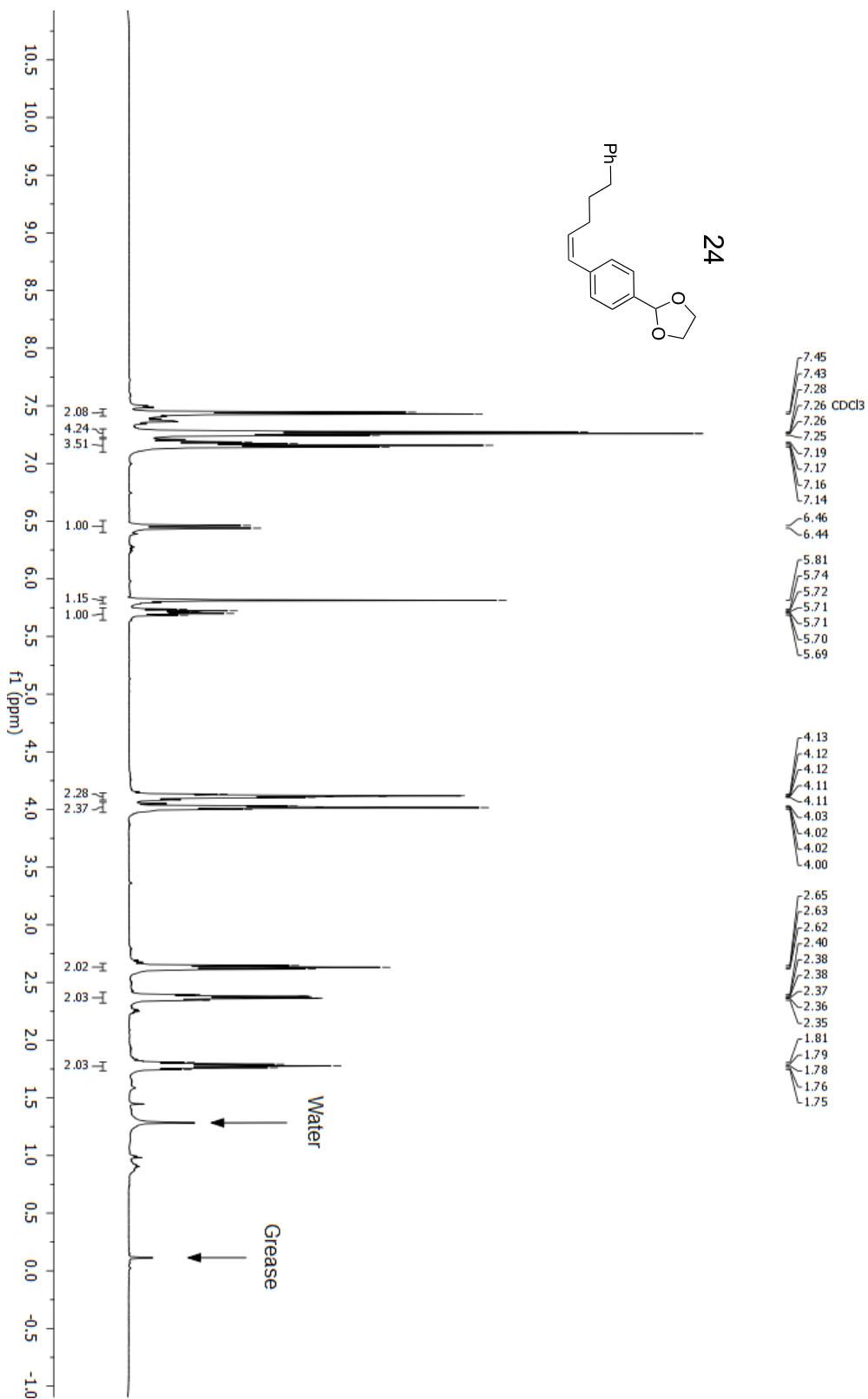


^{13}C NMR (126 MHz, Chloroform- d) δ 142.3, 136.6, 134.7, 132.5, 129.3, 128.7, 128.6, 128.4, 126.5, 125.8, 35.6, 31.8, 28.3, 16.0.



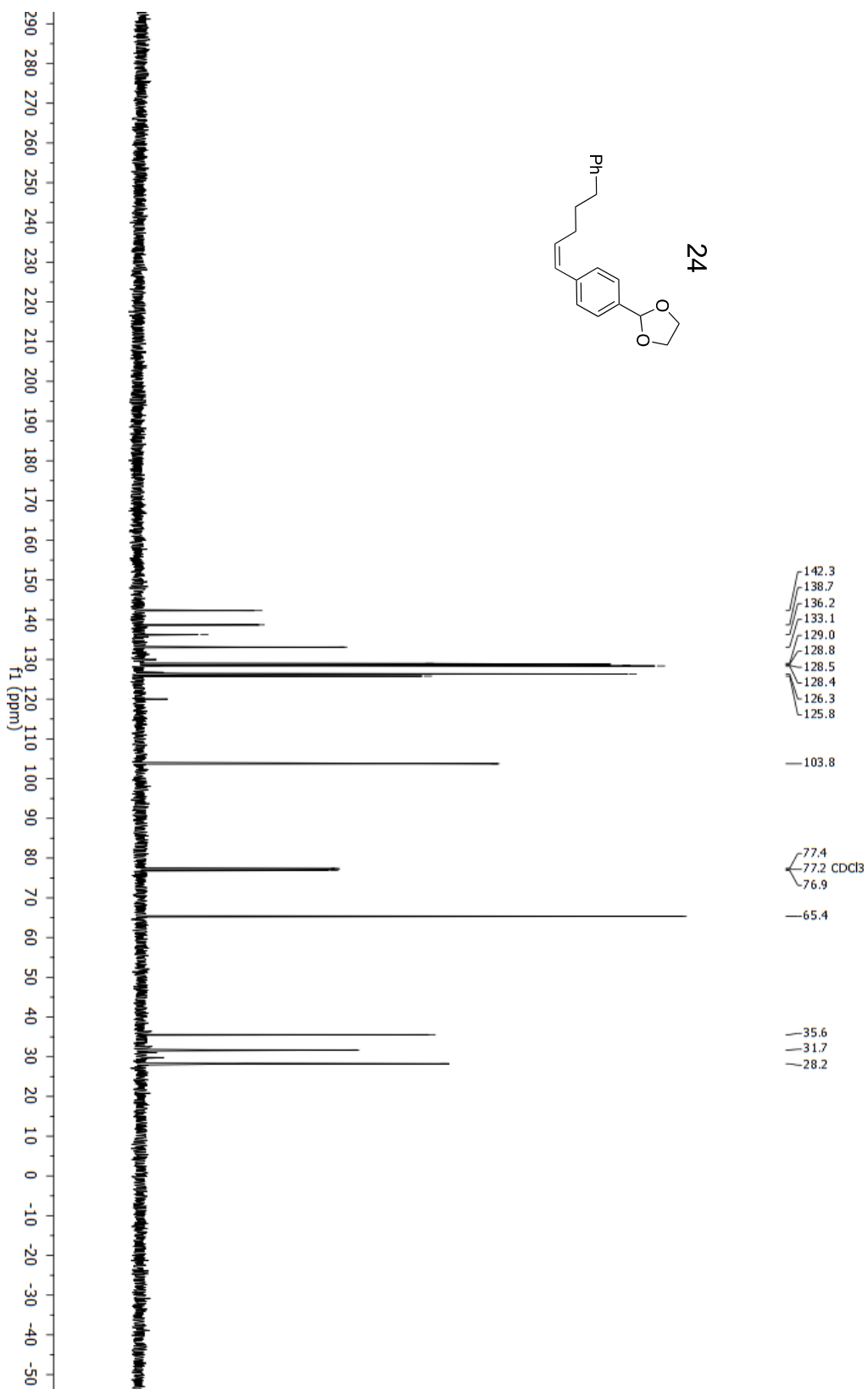
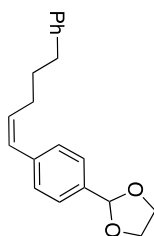


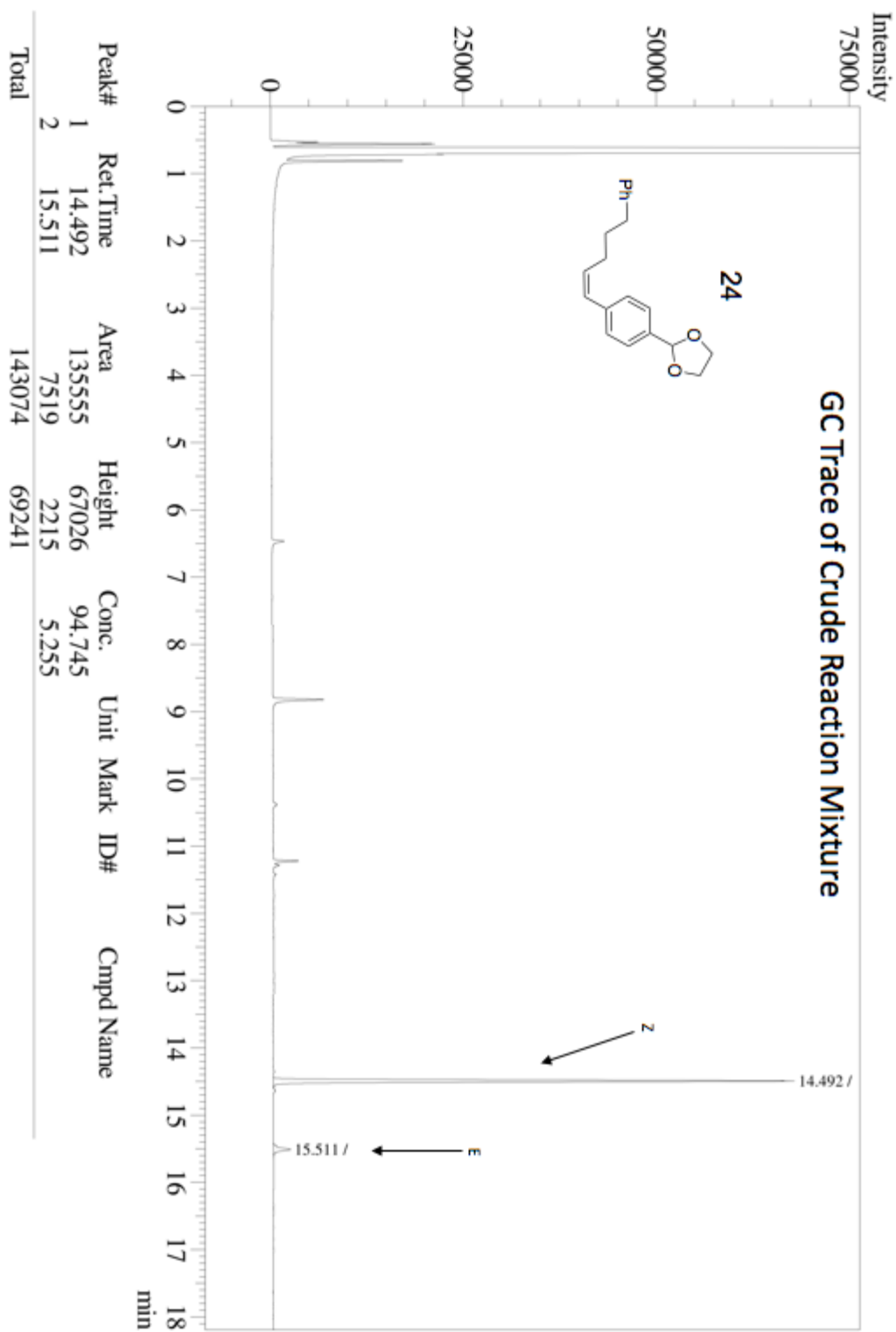
¹H NMR (500 MHz, Chloroform-*d*) 8.744 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 4H), 7.17 (dd, *J* = 14.7, 7.4 Hz, 3H), 6.45 (d, *J* = 11.7 Hz, 1H), 5.81 (s, 1H), 5.71 (dt, *J* = 11.6, 7.3 Hz, 1H), 4.18 – 4.06 (m, 2H), 4.06 – 3.97 (m, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.37 (dt, *J* = 7.3 Hz, 2H), 1.78 (q, *J* = 7.6 Hz, 2H).



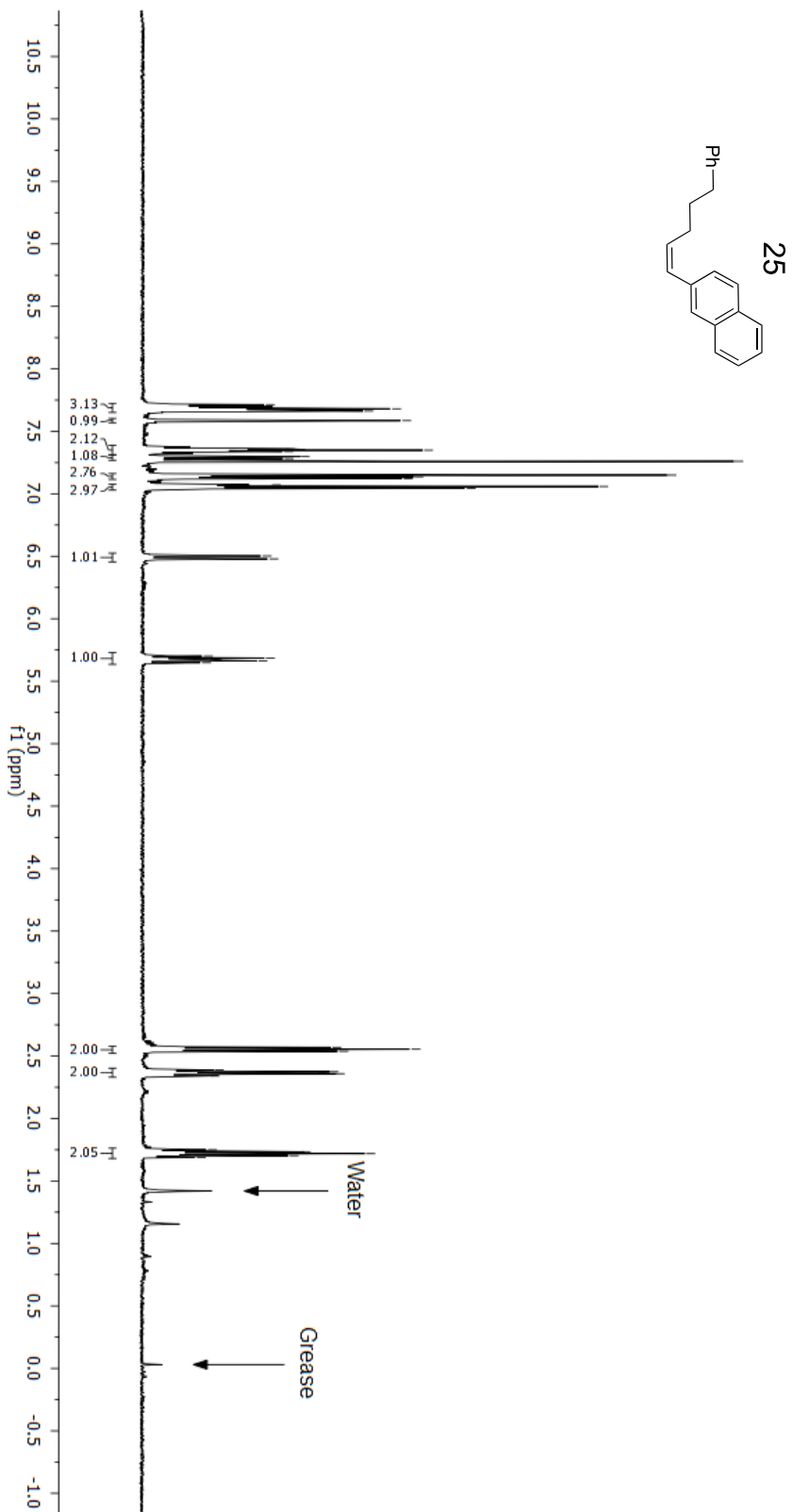
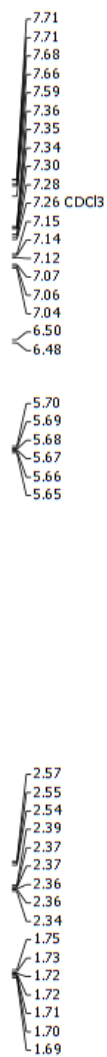
^{13}C NMR (126 MHz, Chloroform- d) δ 142.3, 138.7, 136.2, 133.1, 129.0, 128.8, 128.5, 128.4, 126.3, 125.8, 125.8, 103.8, 65.4, 35.6, 31.7, 28.2.

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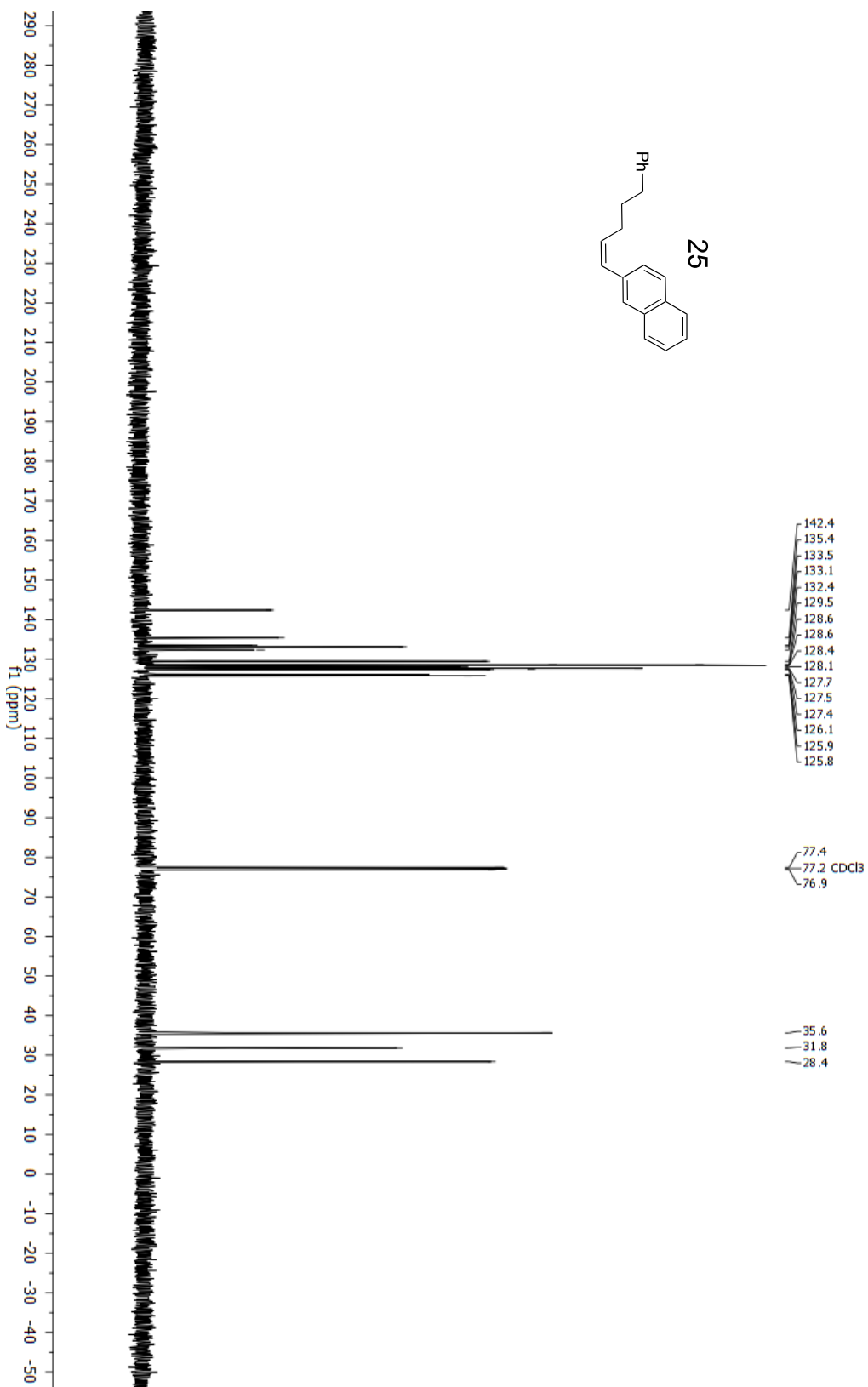
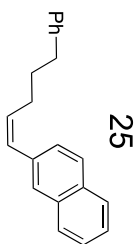


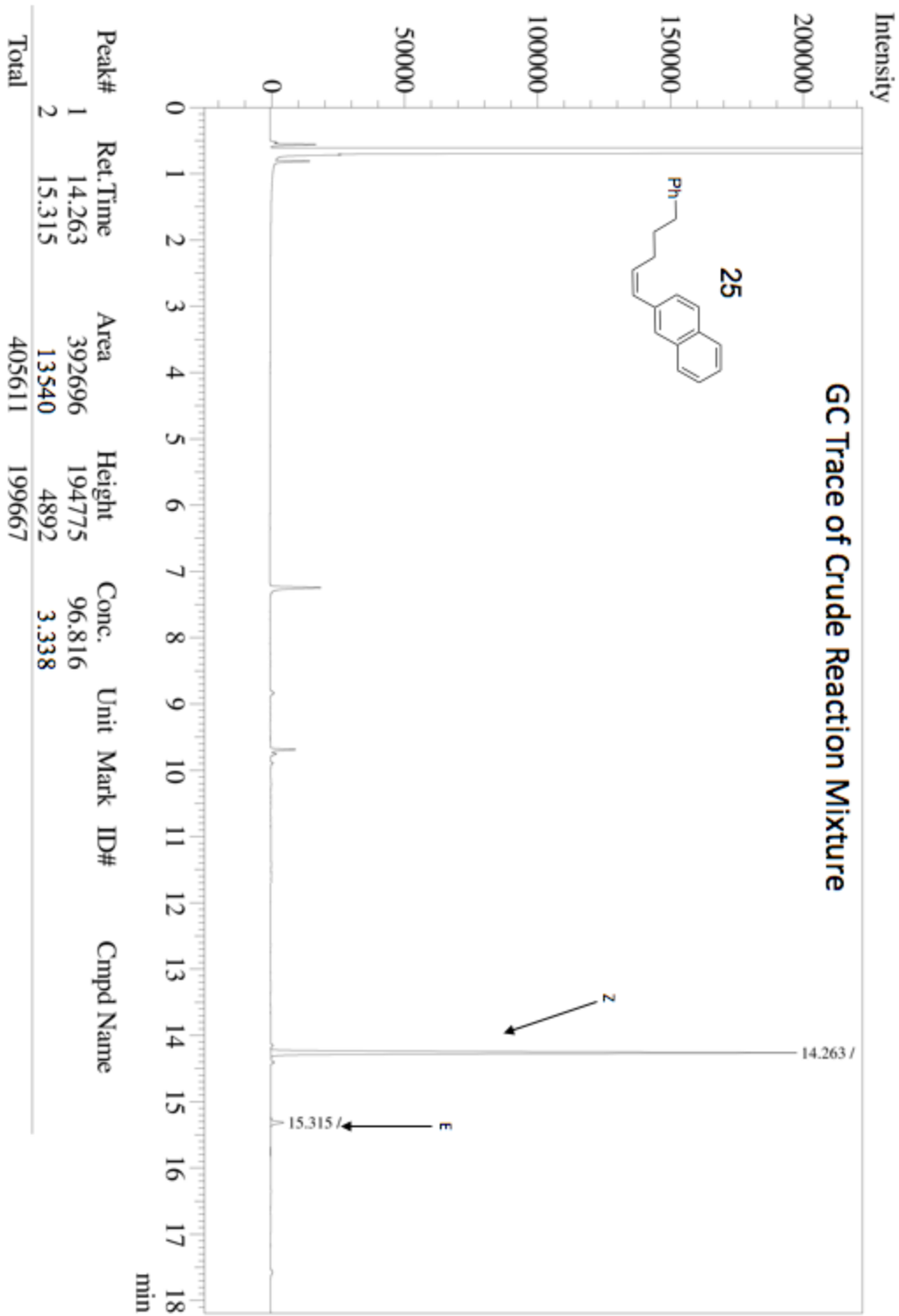


¹H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.64 (m, 3H), 7.59 (s, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.17 – 7.11 (m, 2H), 7.09 – 7.03 (m, 3H), 6.49 (d, *J* = 11.6 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.61 – 2.52 (m, 2H), 2.37 (dt, *J* = 7.3 Hz, 2H), 1.72 (p, *J* = 7.3 Hz, 2H).

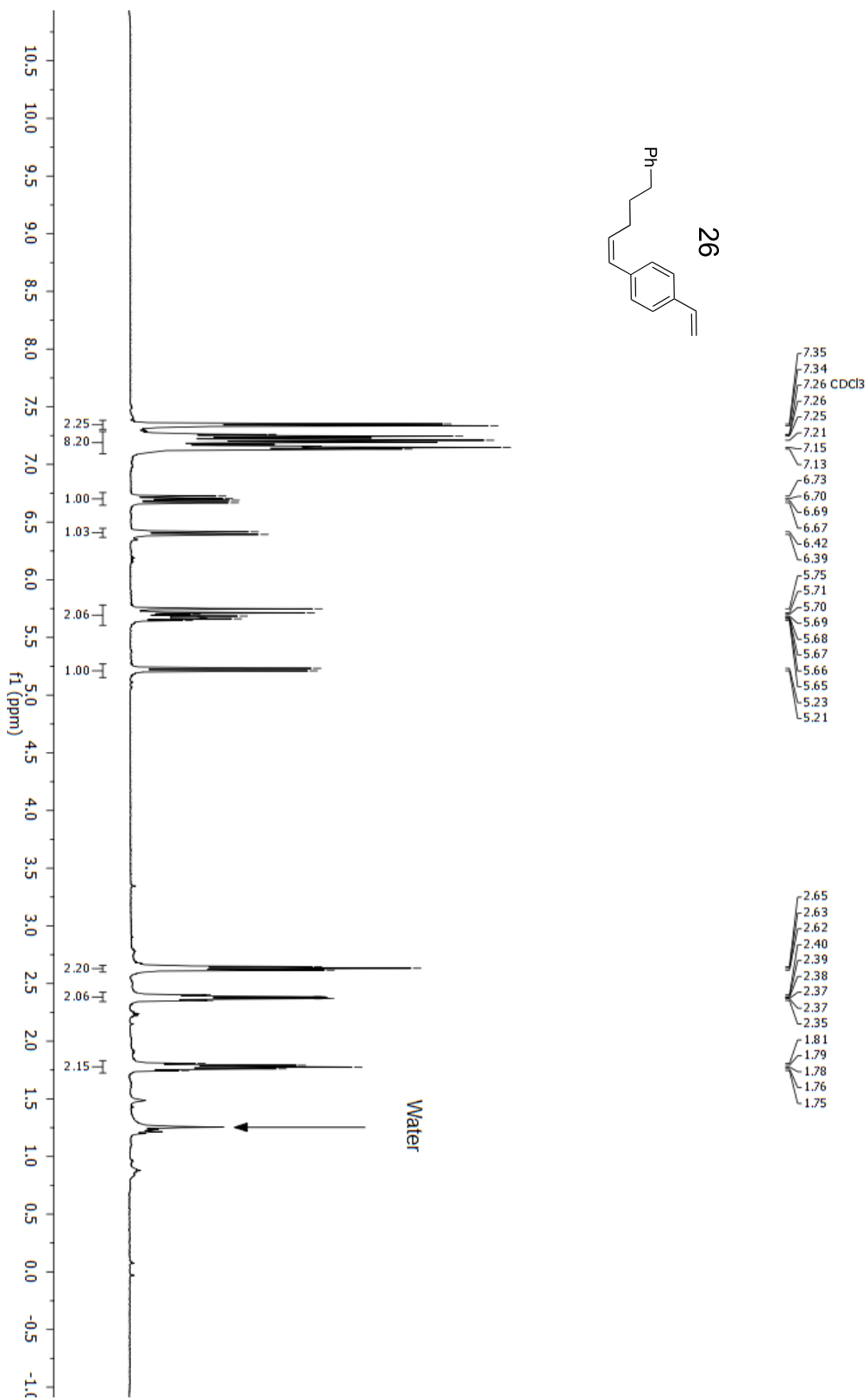
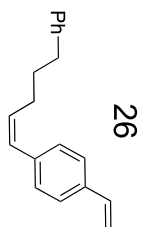


¹³C NMR (126 MHz, Chloroform-d) δ 142.4, 135.4, 133.5, 133.1, 132.4, 129.5, 128.6, 128.6, 128.4, 127.7, 127.7, 127.5, 127.4, 126.1, 125.9, 125.8, 35.6, 31.8, 28.4.

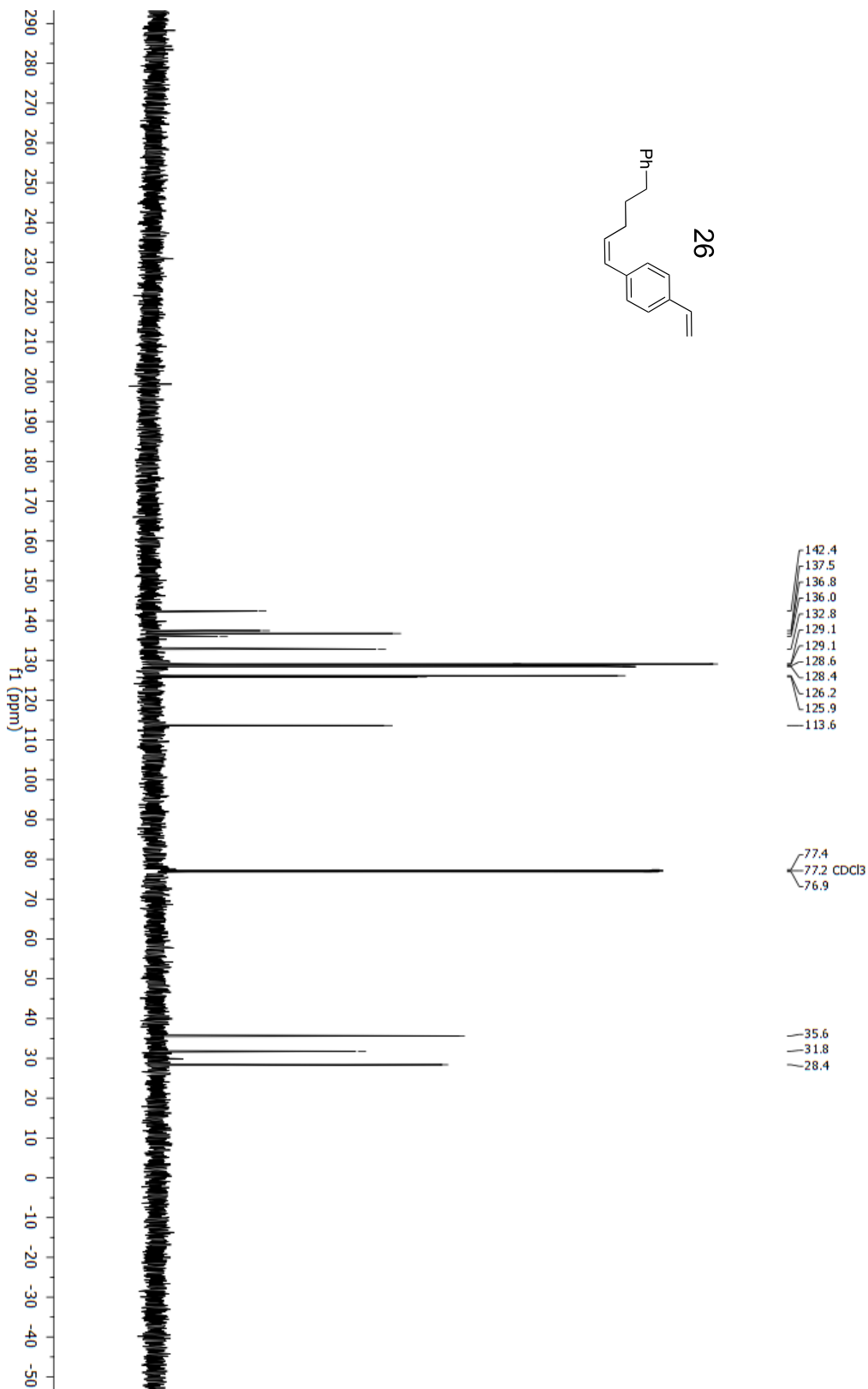
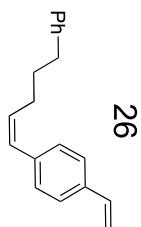


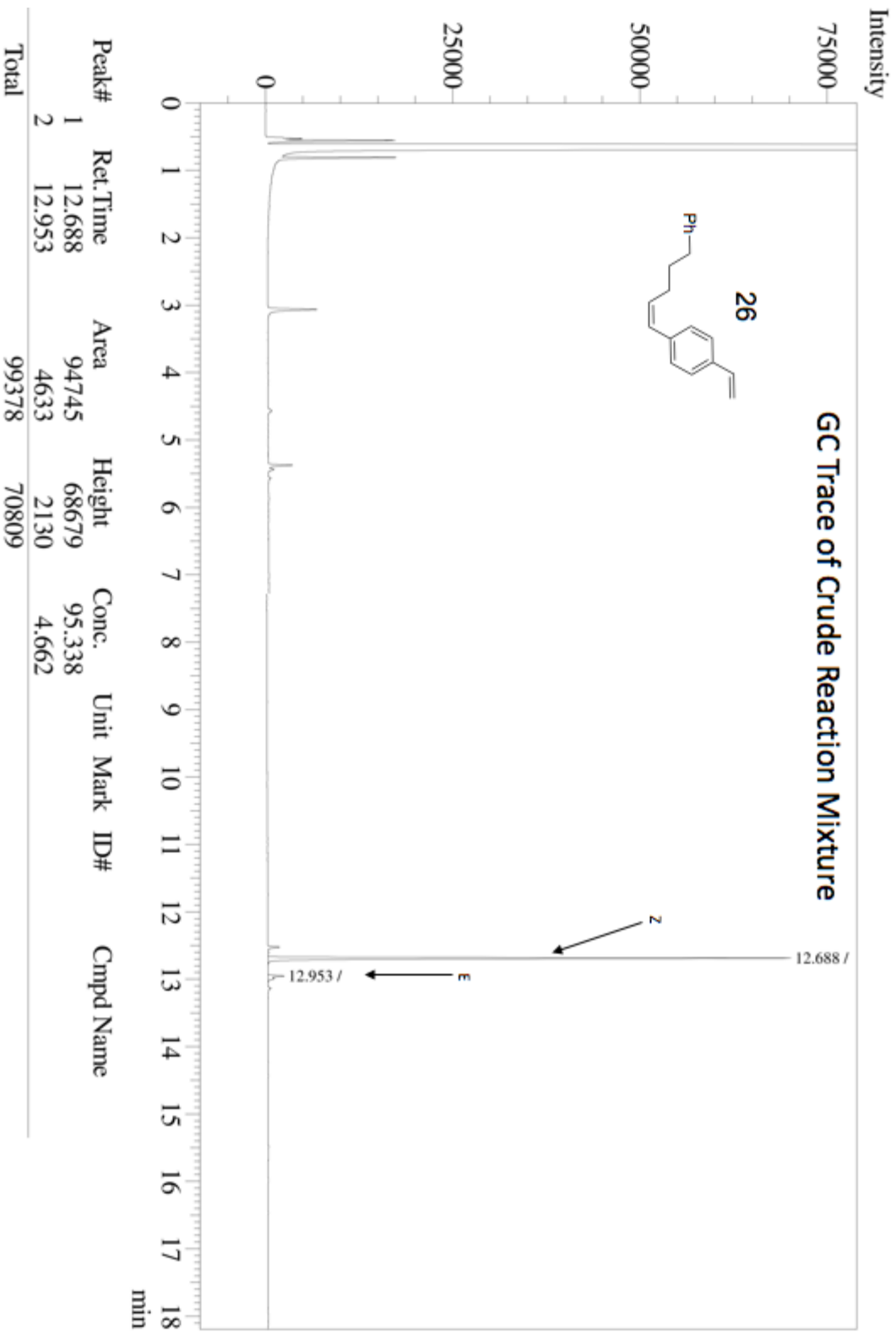


¹H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, $J = 7.7$ Hz, 2H), 7.26 – 7.13 (m, 7H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 6.40 (d, $J = 11.7$ Hz, 1H), 5.82 – 5.58 (m, 2H), 5.22 (d, $J = 10.9$ Hz, 1H), 2.63 (t, $J = 7.7$ Hz, 2H), 2.37 (dt, $J = 7.7$ Hz, 2H), 1.78 (q, $J = 7.6$ Hz, 2H).

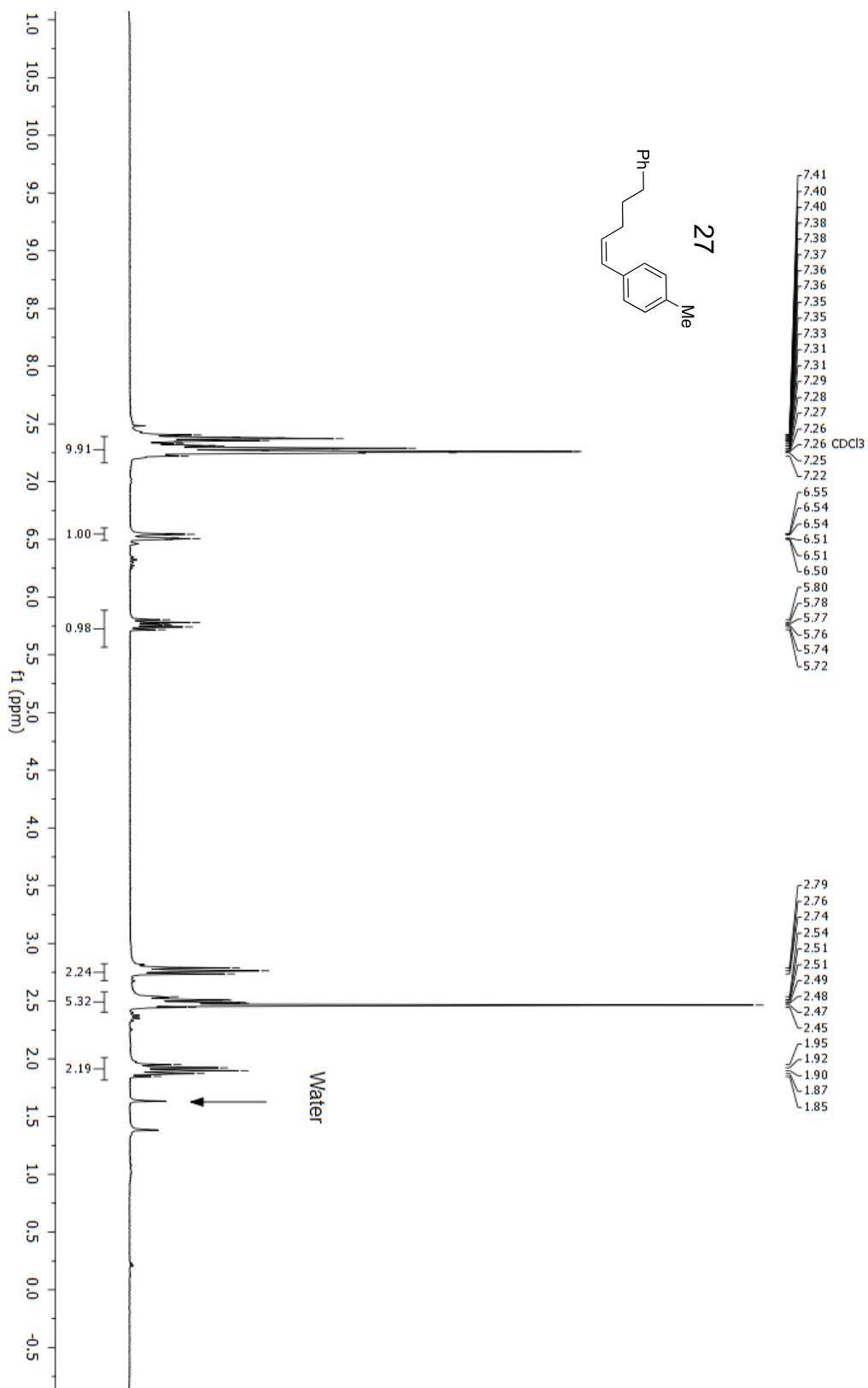
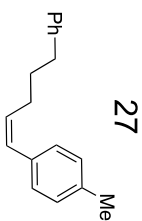


¹³C NMR (126 MHz, Chloroform-d) δ 142.4, 137.5, 136.8, 136.0, 132.8, 129.1, 129.1, 128.6, 128.4, 126.2, 125.9, 125.9, 113.6, 35.6, 31.8, 28.4.

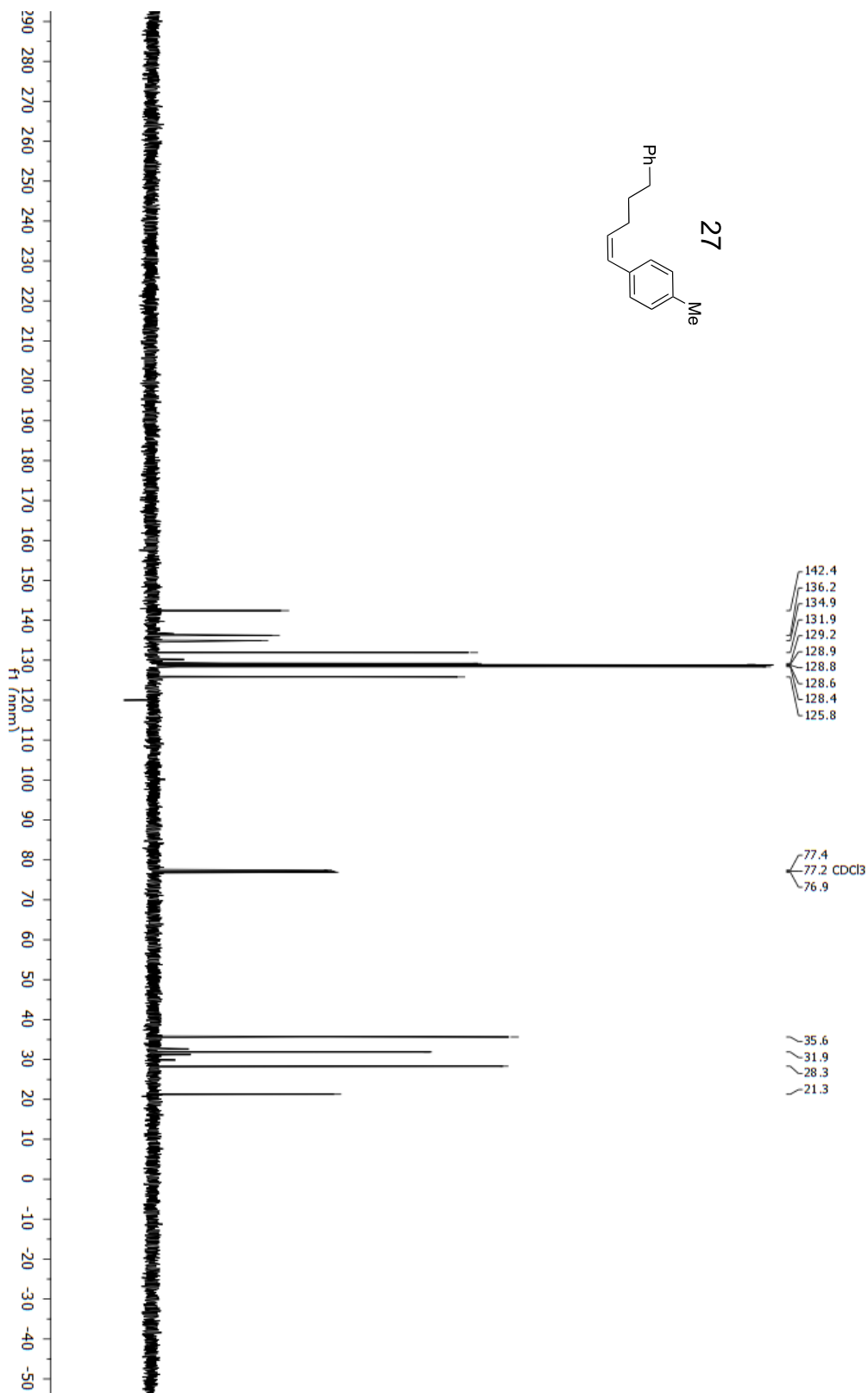
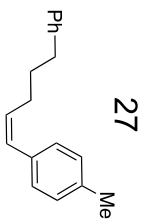


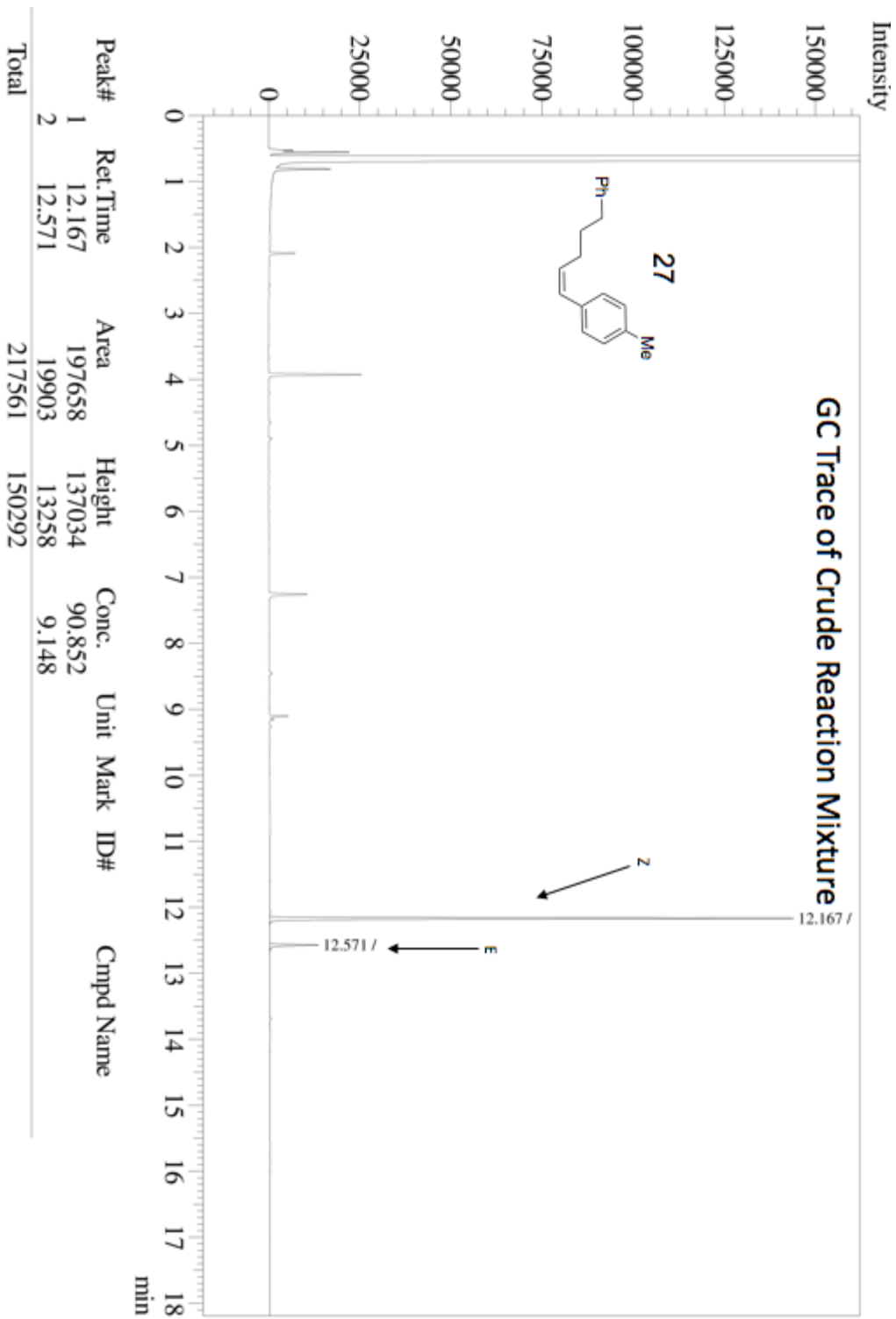


¹H NMR (300 MHz, Chloroform-*d*) δ 7.61 – 7.17 (m, 9H), 6.53 (dd, *J* = 11.6, 1.9 Hz, 1H), 5.76 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.76 (t, 2H), 2.57 – 2.41 (m, 3H), 1.90 (q, *J* = 7.7 Hz, 2H).

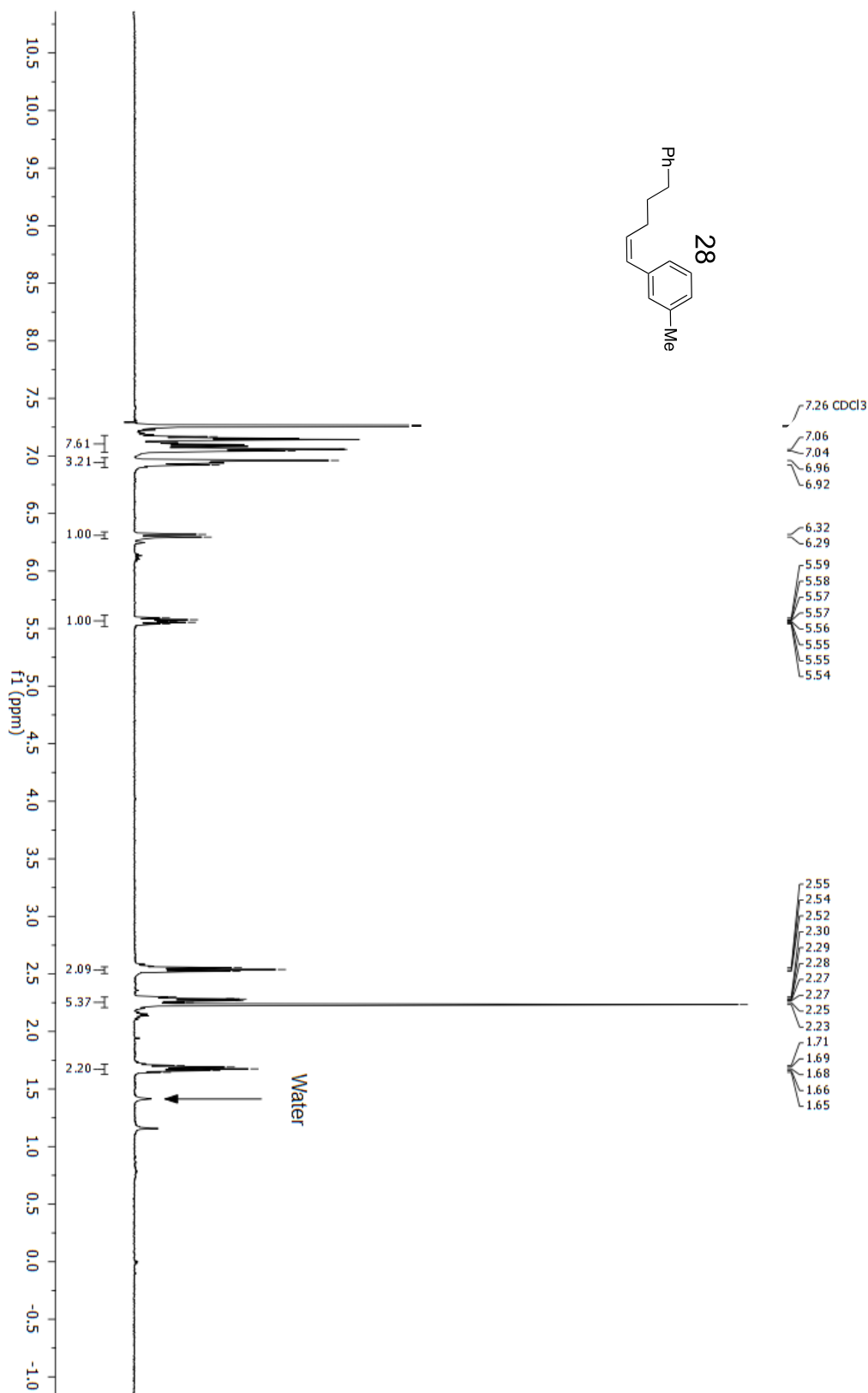
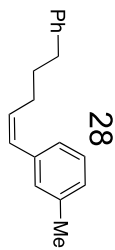


^{13}C NMR (126 MHz, Chloroform- d_3) δ 142.4, 136.2, 134.9, 131.9, 129.2, 128.8, 128.6, 128.4, 128.4, 125.8, 35.6, 31.9, 28.3, 21.3.

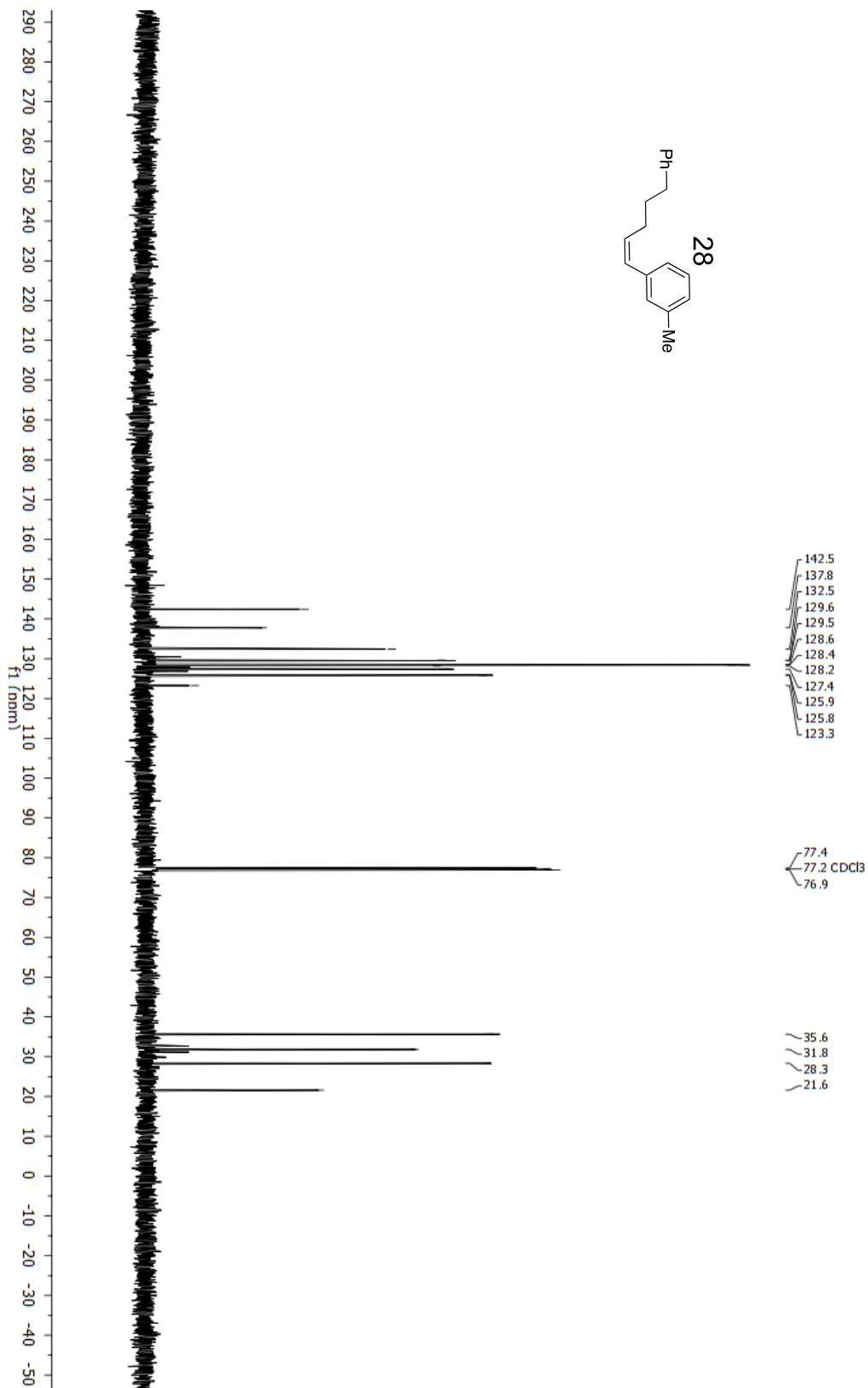
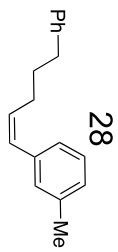


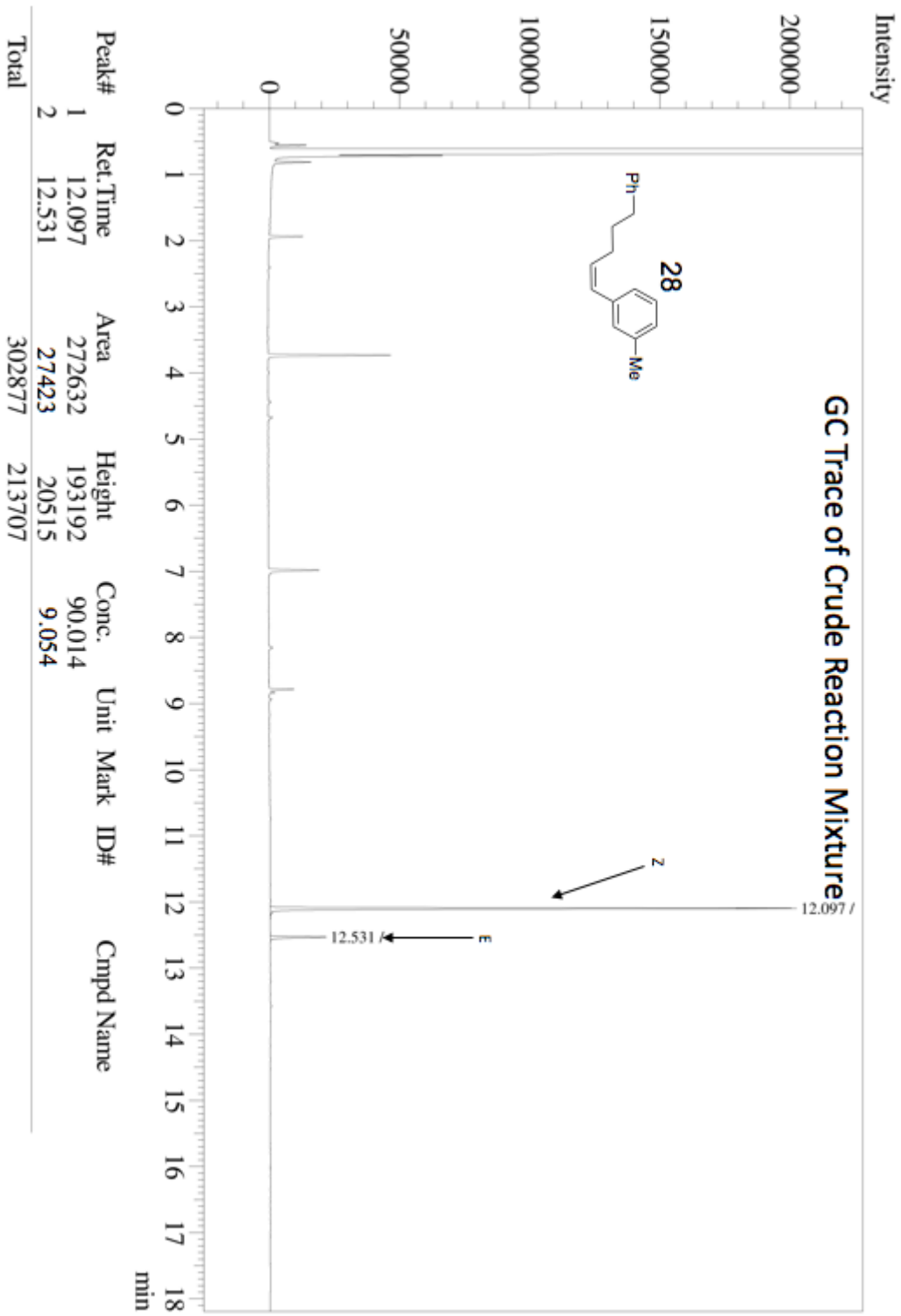


¹H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.02 (m, 6H), 6.99 – 6.90 (m, 3H), 6.31 (d, *J* = 11.7 Hz, 1H), 5.57 (dt, *J* = 11.9, 7.3 Hz, 1H), 2.54 (t, *J* = 7.8 Hz, 2H), 2.32 – 2.21 (m, 5H), 1.68 (q, *J* = 7.5 Hz, 2H).

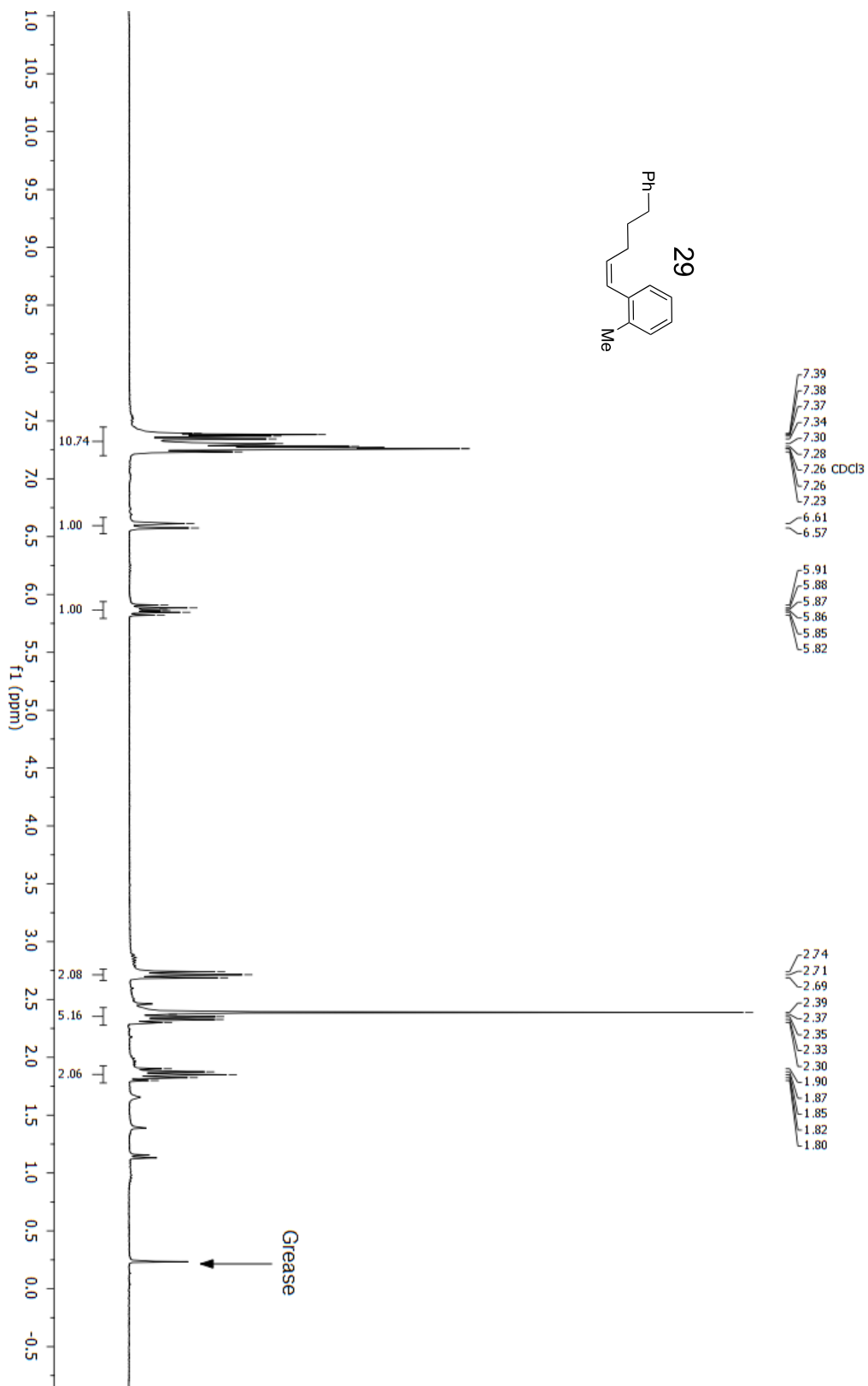
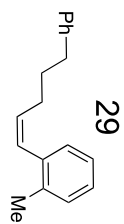


¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 137.8, 132.5, 129.6, 129.5, 128.6, 128.4, 128.2, 127.4, 125.9, 125.8, 123.3, 35.6, 31.8, 28.3, 21.6.

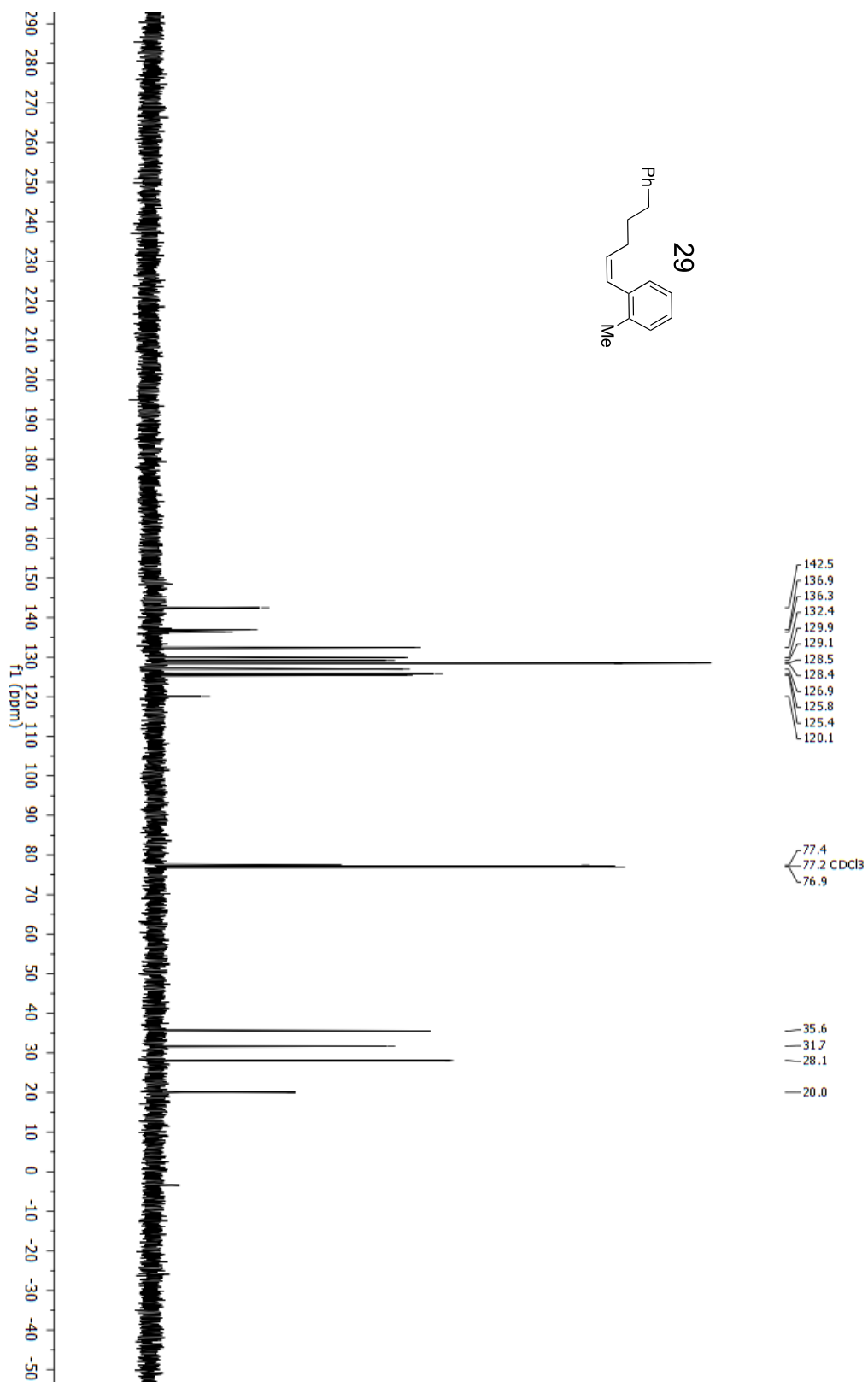
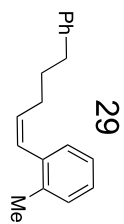


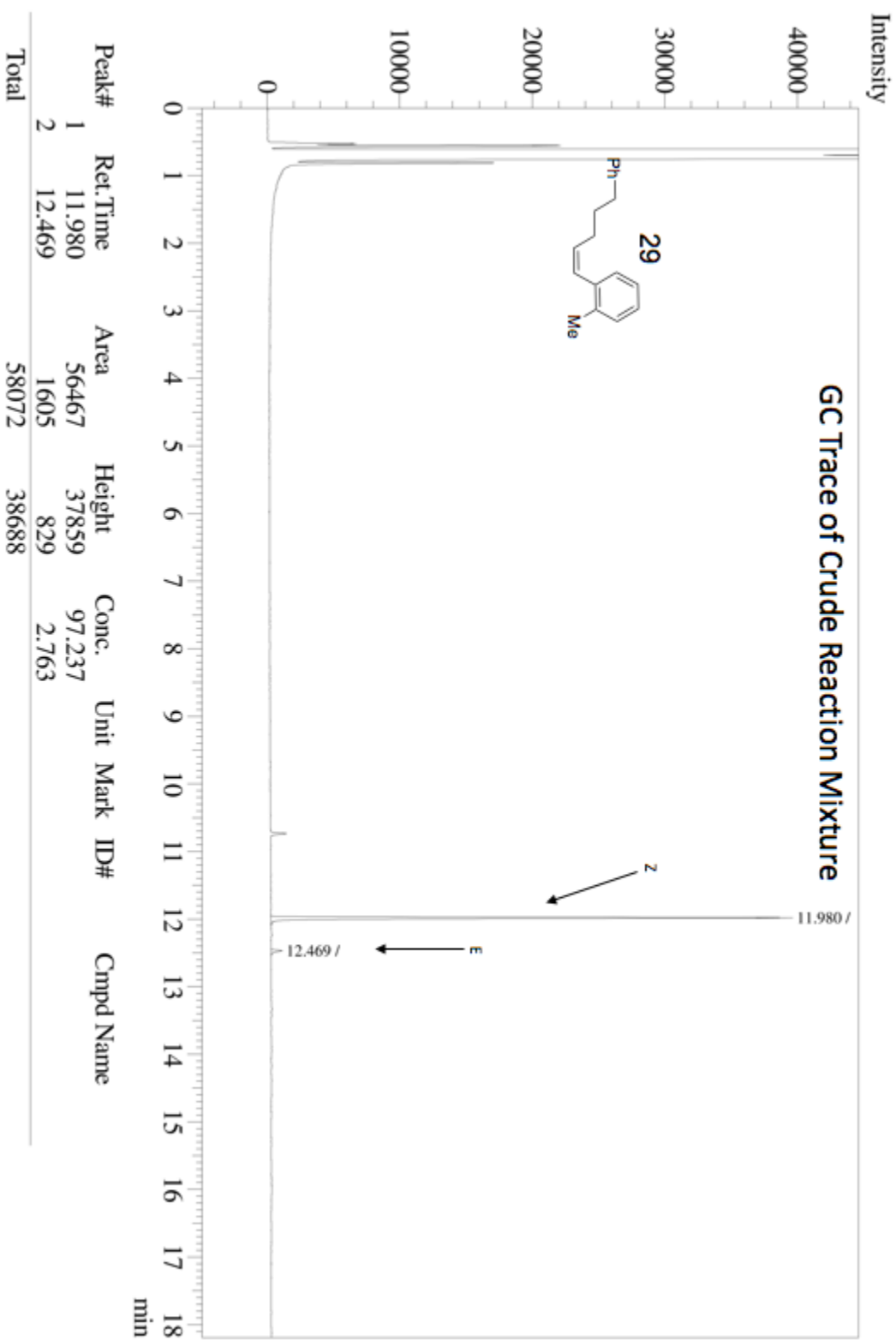


¹H NMR (300 MHz, Chloroform-d) δ 7.20 – 6.96 (m, 9H), 6.36 (d, J = 11.4 Hz, 1H), 5.63 (dt, J = 11.5, 7.4 Hz, 1H), 2.48 (t, J = 7.6 Hz, 2H), 2.22 – 2.04 (m, 5H), 1.62 (q, J = 7.6 Hz, 2H).

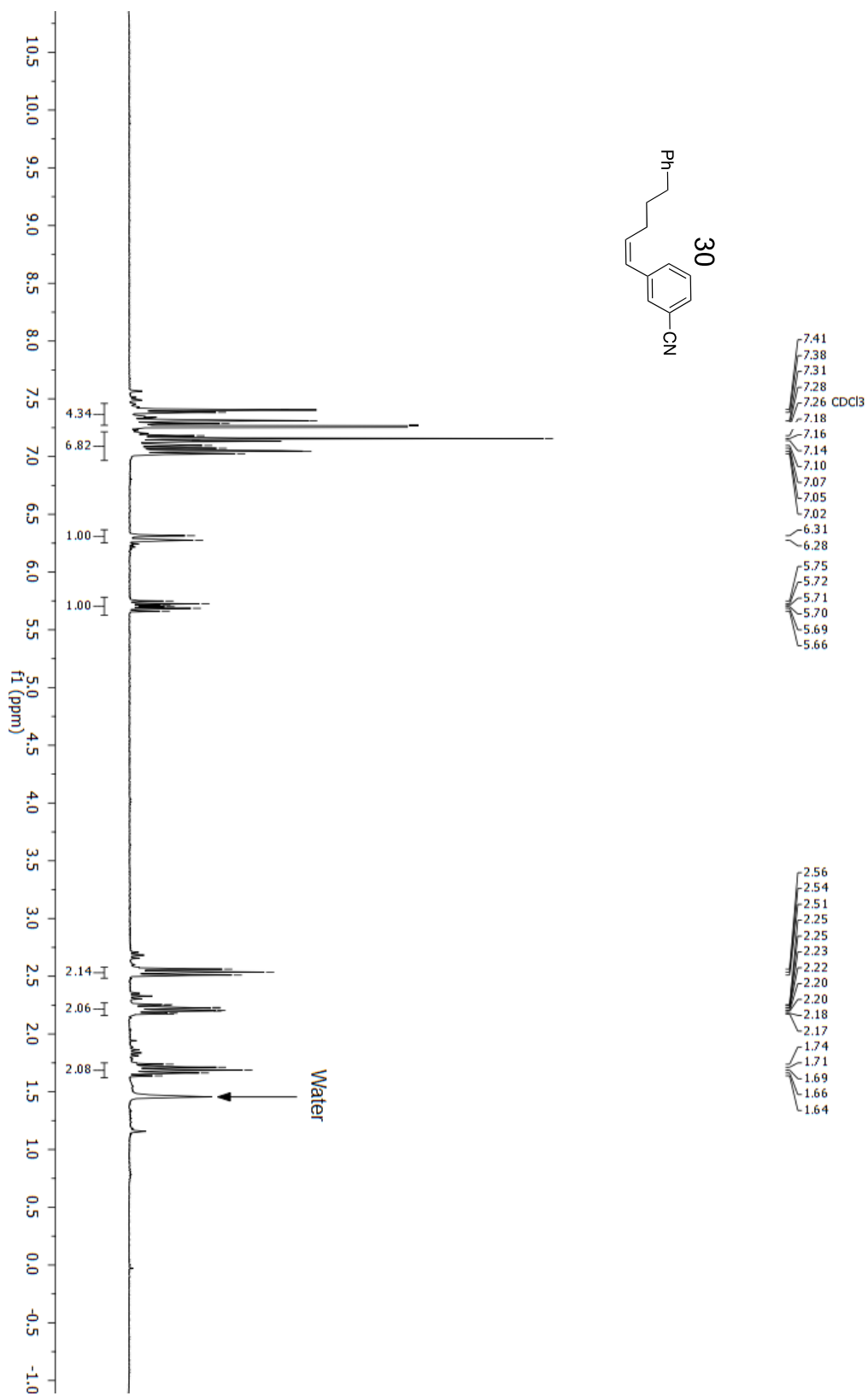
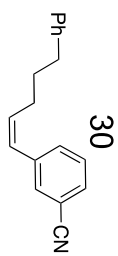


¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 136.9, 136.3, 132.4, 129.9, 129.1, 128.5, 128.4, 126.9, 125.8, 125.4, 120.1, 35.6, 31.7, 28.1, 20.0.

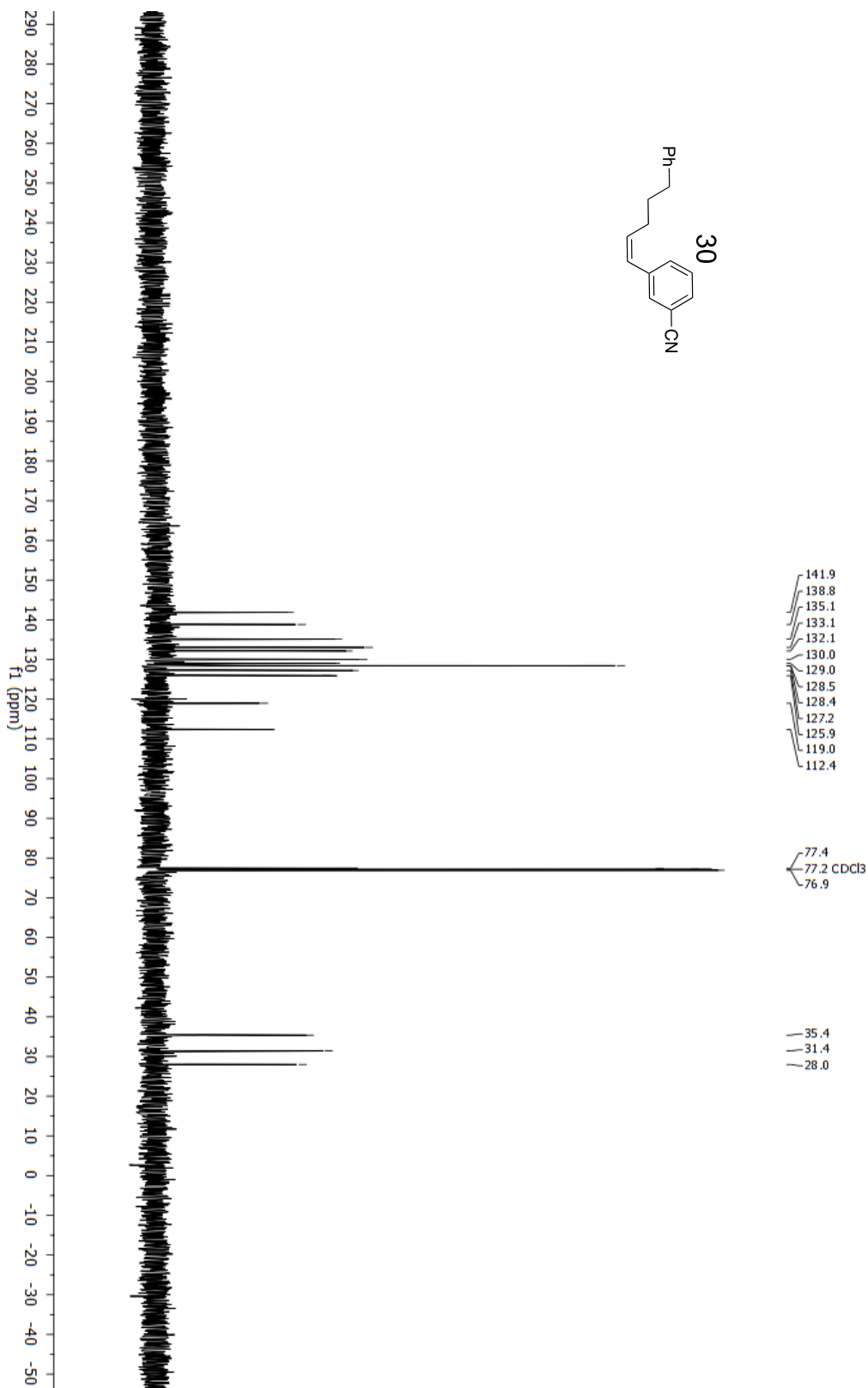
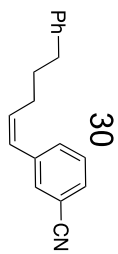


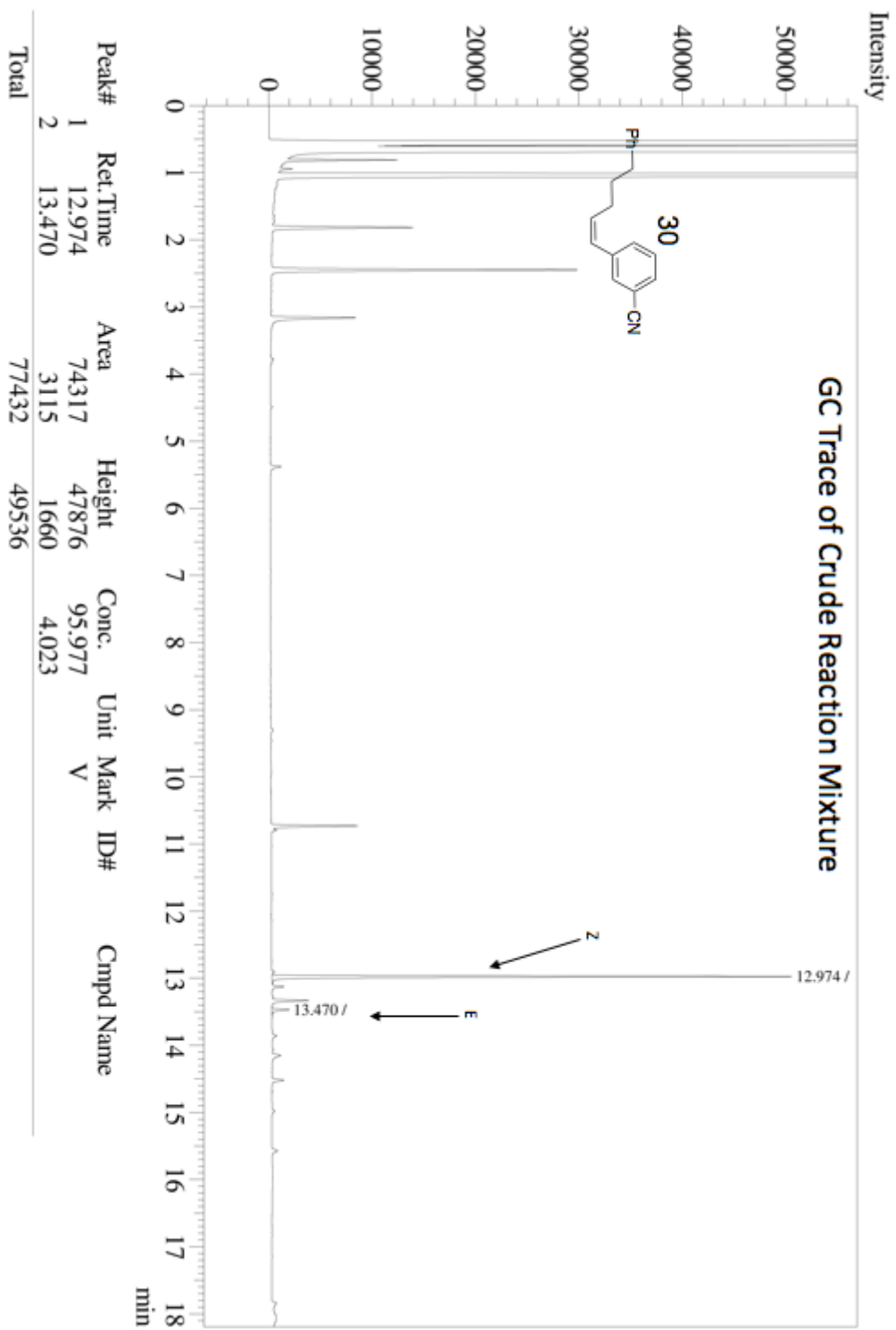


¹H NMR (300 MHz, Chloroform-*d*) δ 7.35 (m, 4H), 7.21 – 6.99 (m, 5H), 6.30 (d, *J* = 11.7 Hz, 1H), 5.71 (dt, *J* = 11.7, 7.4 Hz, 1H), 2.58 – 2.49 (t, *J* = 7.6 Hz, 2H), 2.27 – 2.15 (m, 2H), 1.69 (p, *J* = 7.6 Hz, 2H).

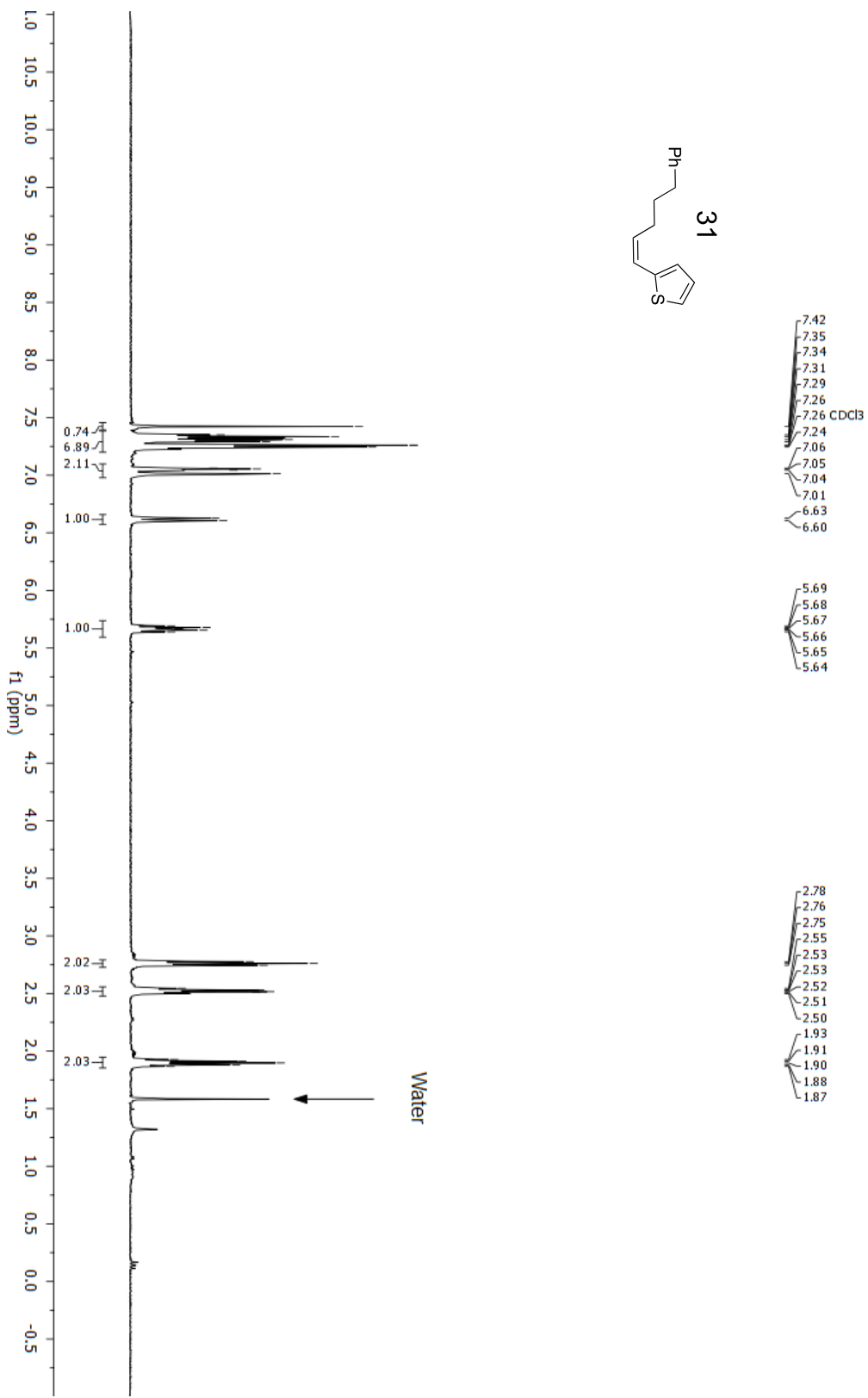
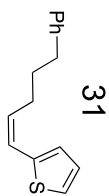


¹³C-NMR (126 MHz, Chloroform-d) δ 141.9, 139.8, 135.1, 133.1, 132.1, 130.0, 129.0, 128.8, 128.4, 127.2, 125.9, 119.0, 112.4, 35.4, 31.4, 28.0.

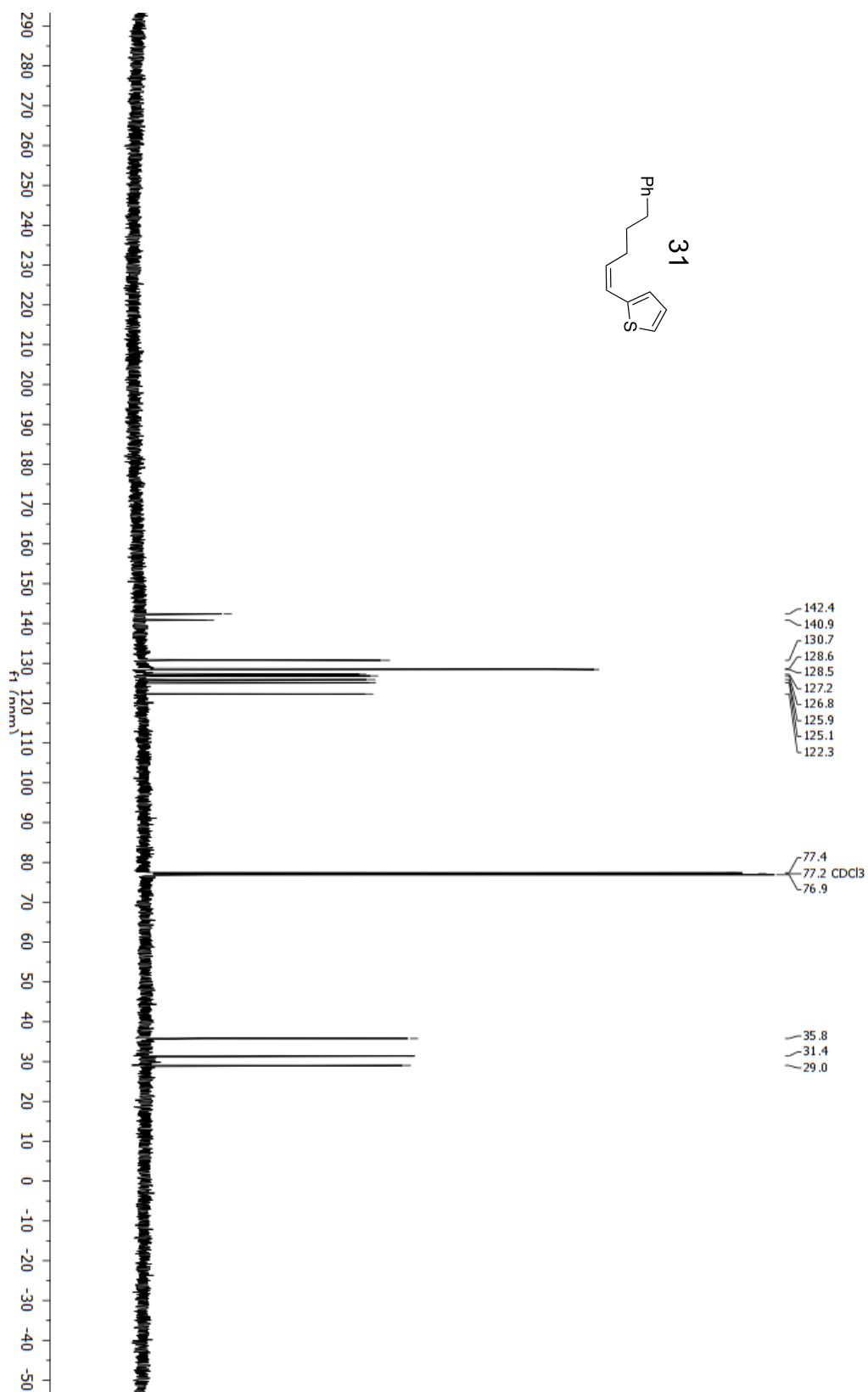
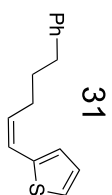


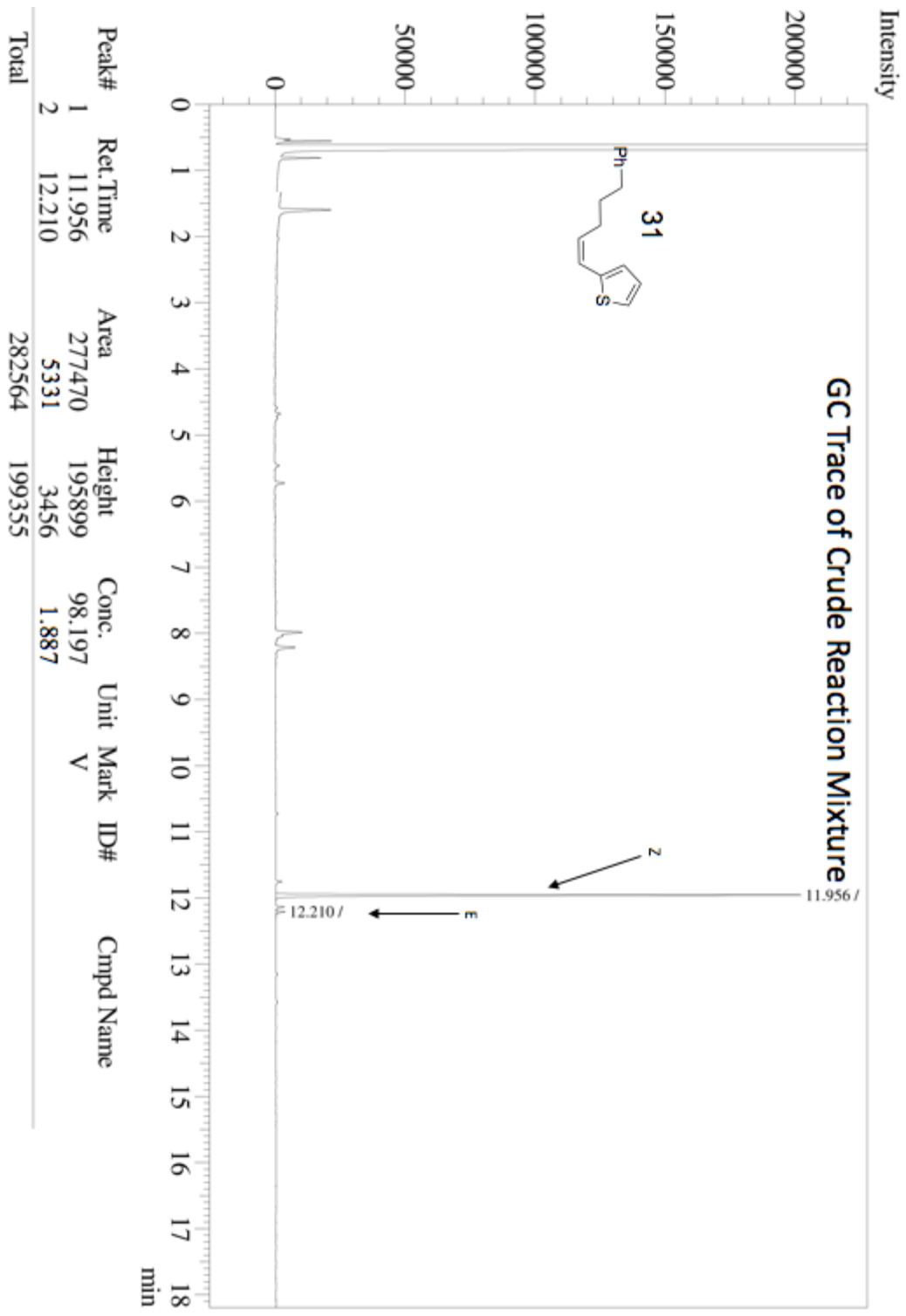


¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.39 – 7.27 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 3H), 7.09 – 6.96 (m, 2H), 6.62 (d, *J* = 11.1 Hz, 1H), 5.67 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.53 (dt, *J* = 7.5, 7.2 Hz, 2H), 1.90 (q, *J* = 7.5 Hz, 2H).

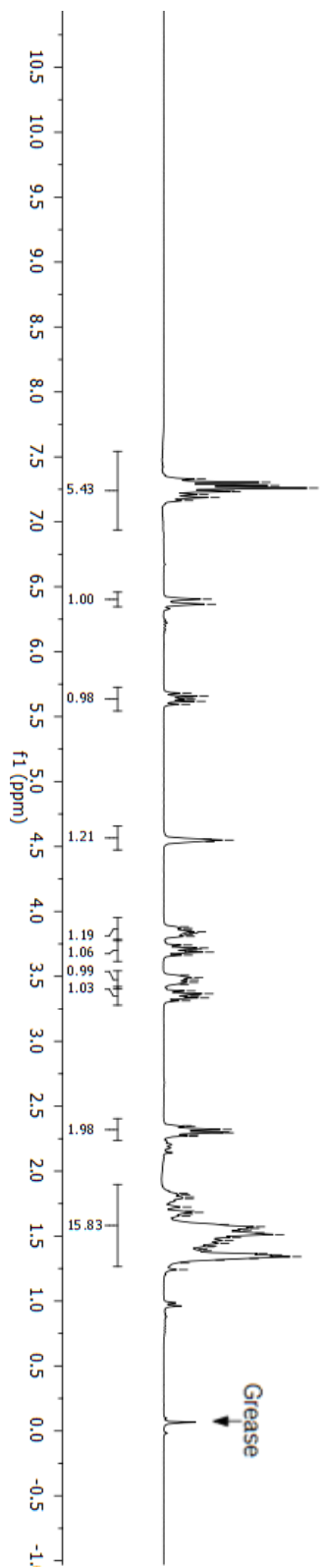
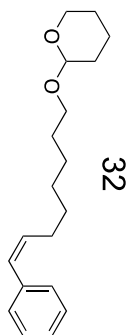
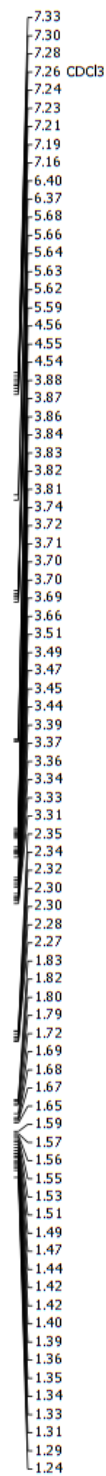


^{13}C NMR (126 MHz, Chloroform- d) δ 142.4, 140.9, 130.7, 128.6, 128.5, 127.2, 126.8, 125.9, 125.1, 122.3, 35.8, 31.4, 29.0.

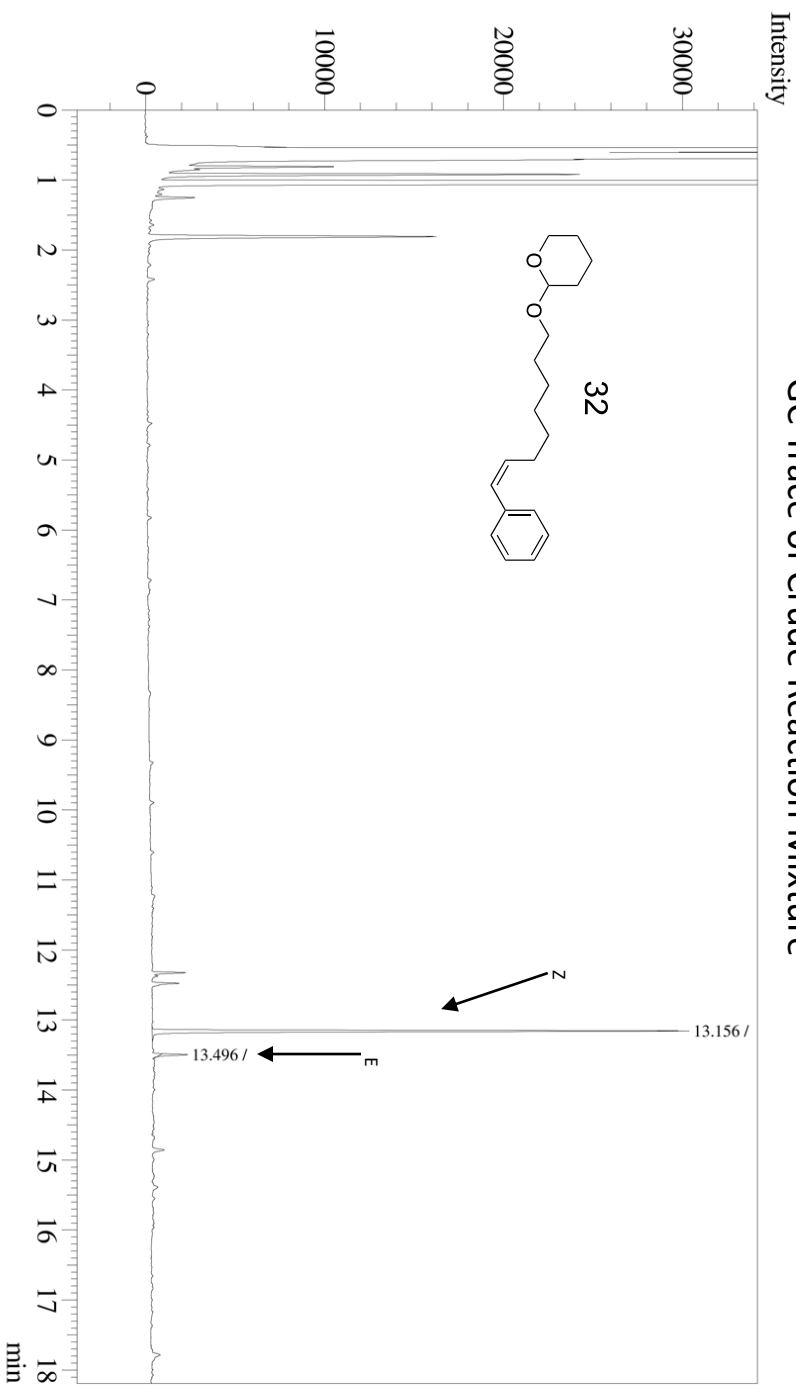




¹H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 6.94 (m, 5H), 6.38 (d, *J* = 11.5 Hz, 1H), 5.73 – 5.54 (m, 1H), 4.57 – 4.53 (m, 1H), 3.95 – 3.77 (m, 1H), 3.78 – 3.61 (m, 1H), 3.54 – 3.40 (m, 1H), 3.42 – 3.28 (m, 1H), 2.40 – 2.24 (m, 2H), 1.90 – 1.27 (m, 16H).

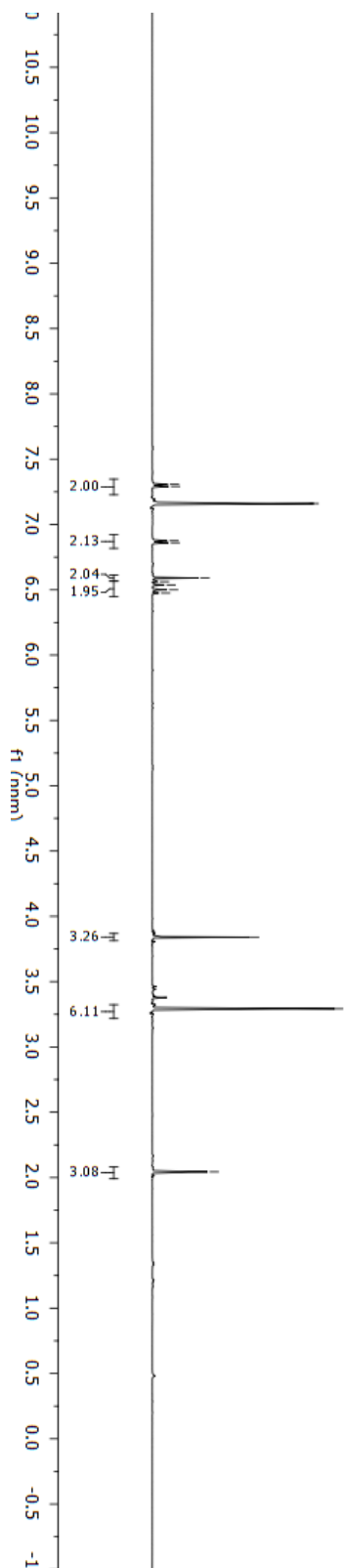
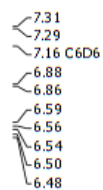
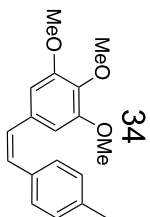


GC Trace of Crude Reaction Mixture



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Compd Name
1	13.156	46101	29080	95.817				
2	13.496	2013	1490	4.183		S		
Total		48114	30570					

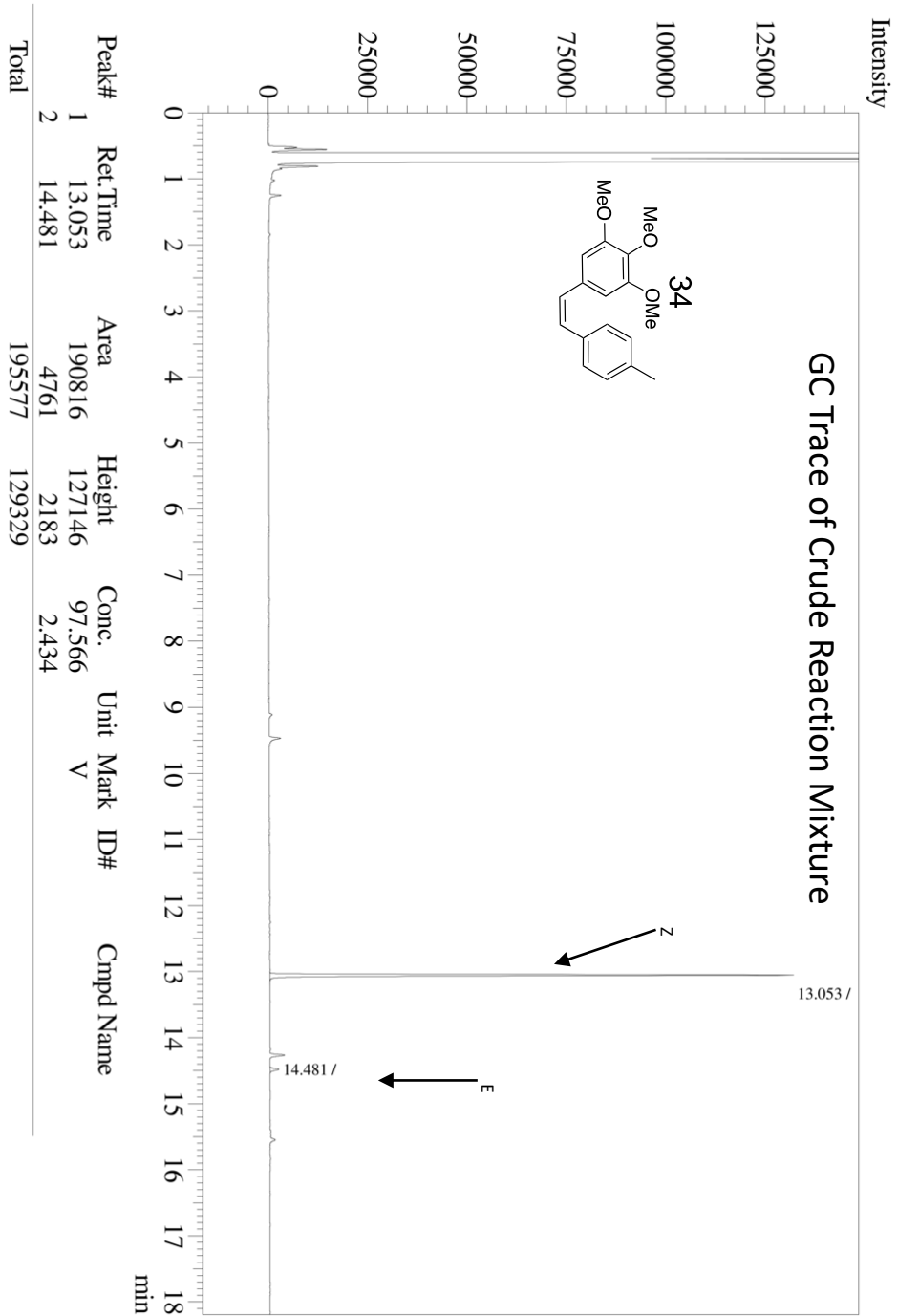
¹H NMR (500 MHz, Benzene-d₆) δ 7.30 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.59 (s, 2H), 6.57 – 6.45 (m, 2H), 3.84 (s, 3H), 3.29 (s, 6H), 2.04 (s, 3H).



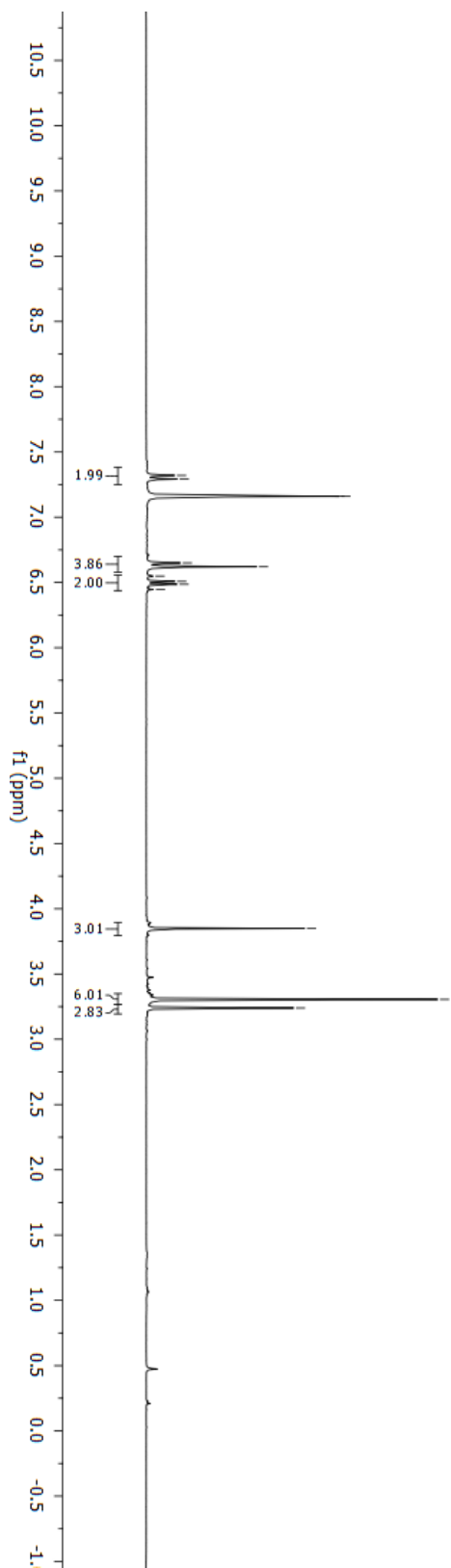
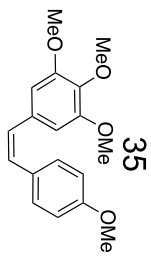
— 3.84

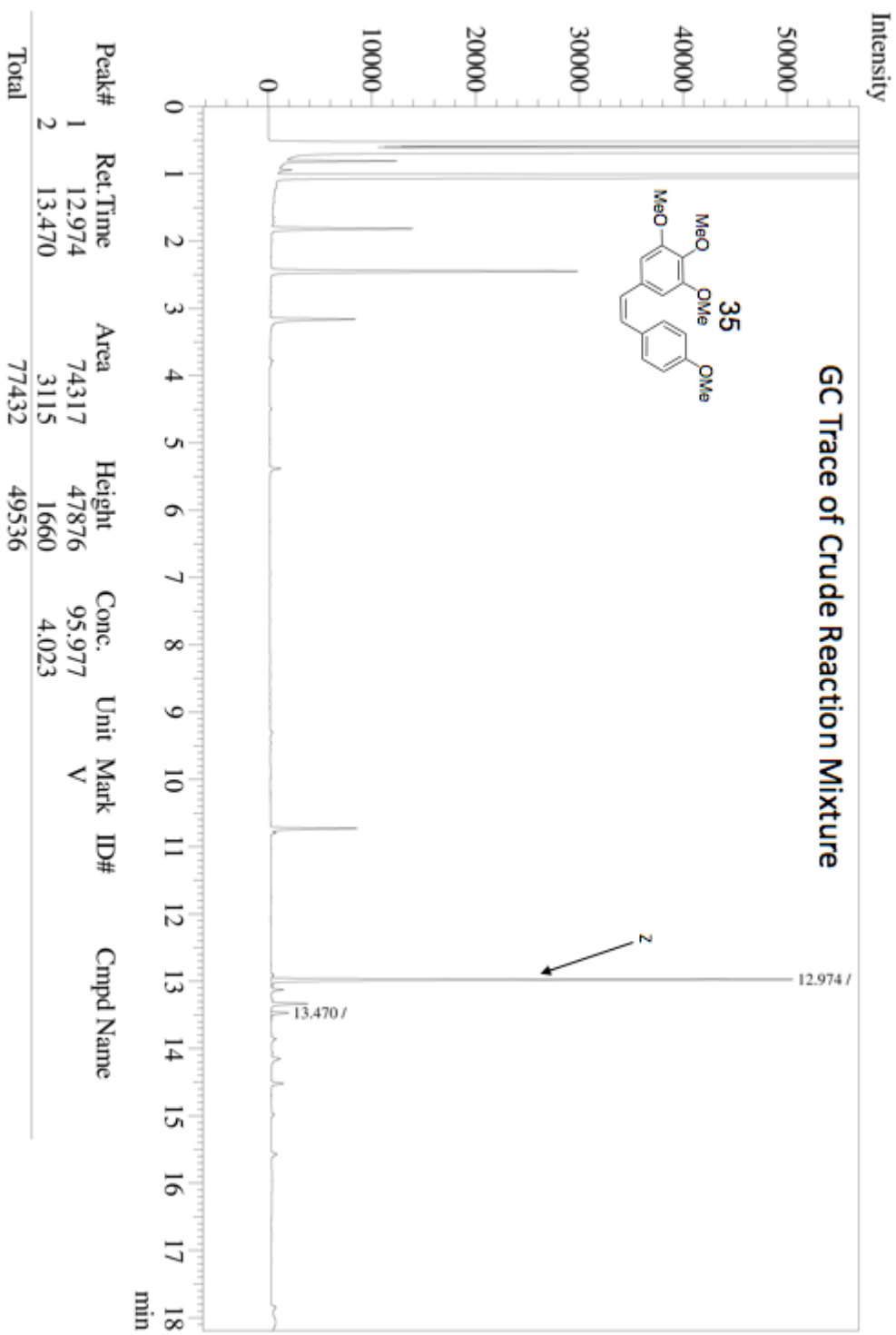
— 3.29

— 2.04

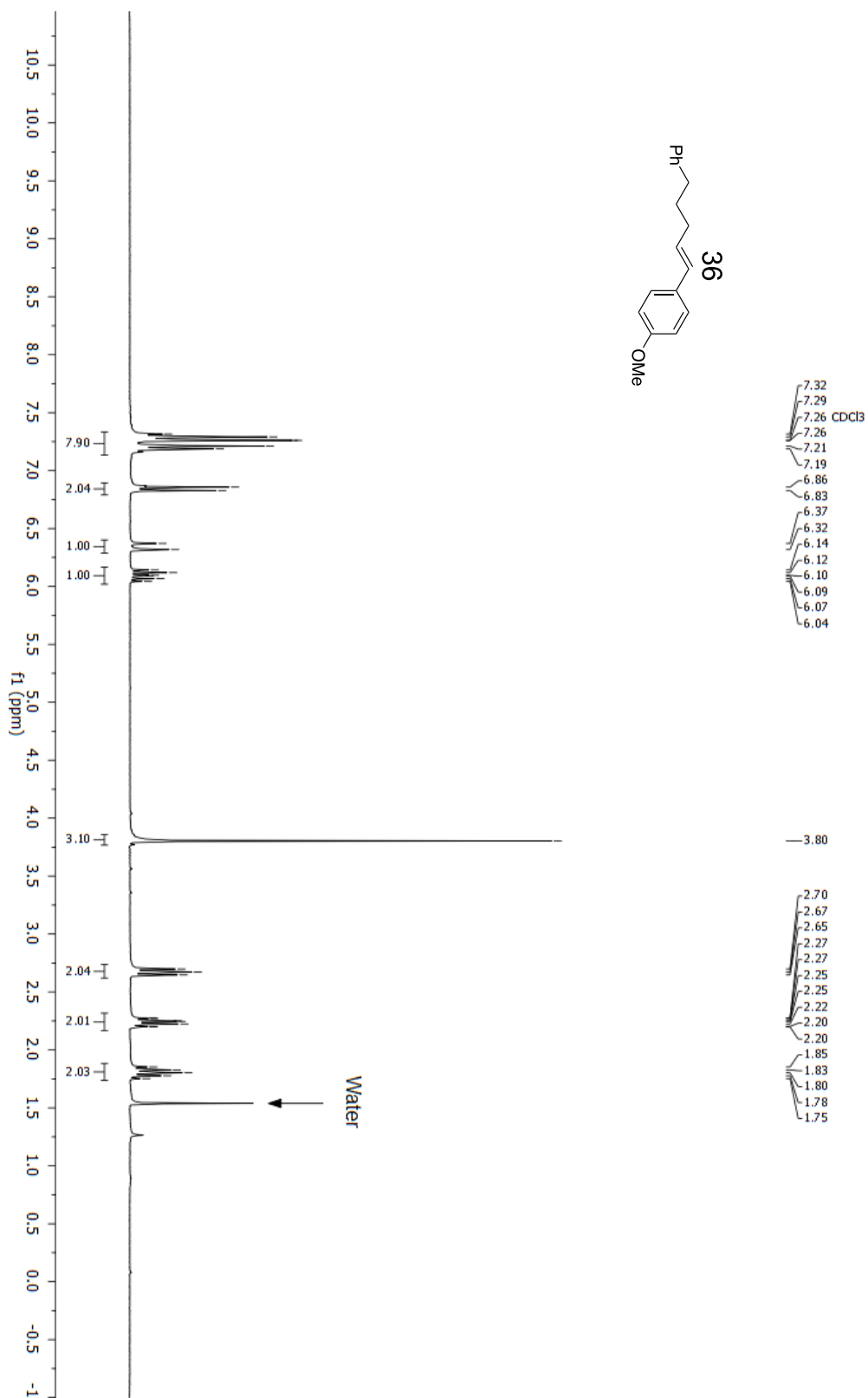
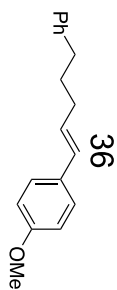


¹H NMR (300 MHz, Benzene-d₆) δ 7.31 (d, J = 8.6 Hz, 2H), 6.68 – 6.58 (m, 4H), 6.56 – 6.42 (m, 2H), 3.85 (s, 3H), 3.31 (s, 6H), 3.24 (s, 3H).

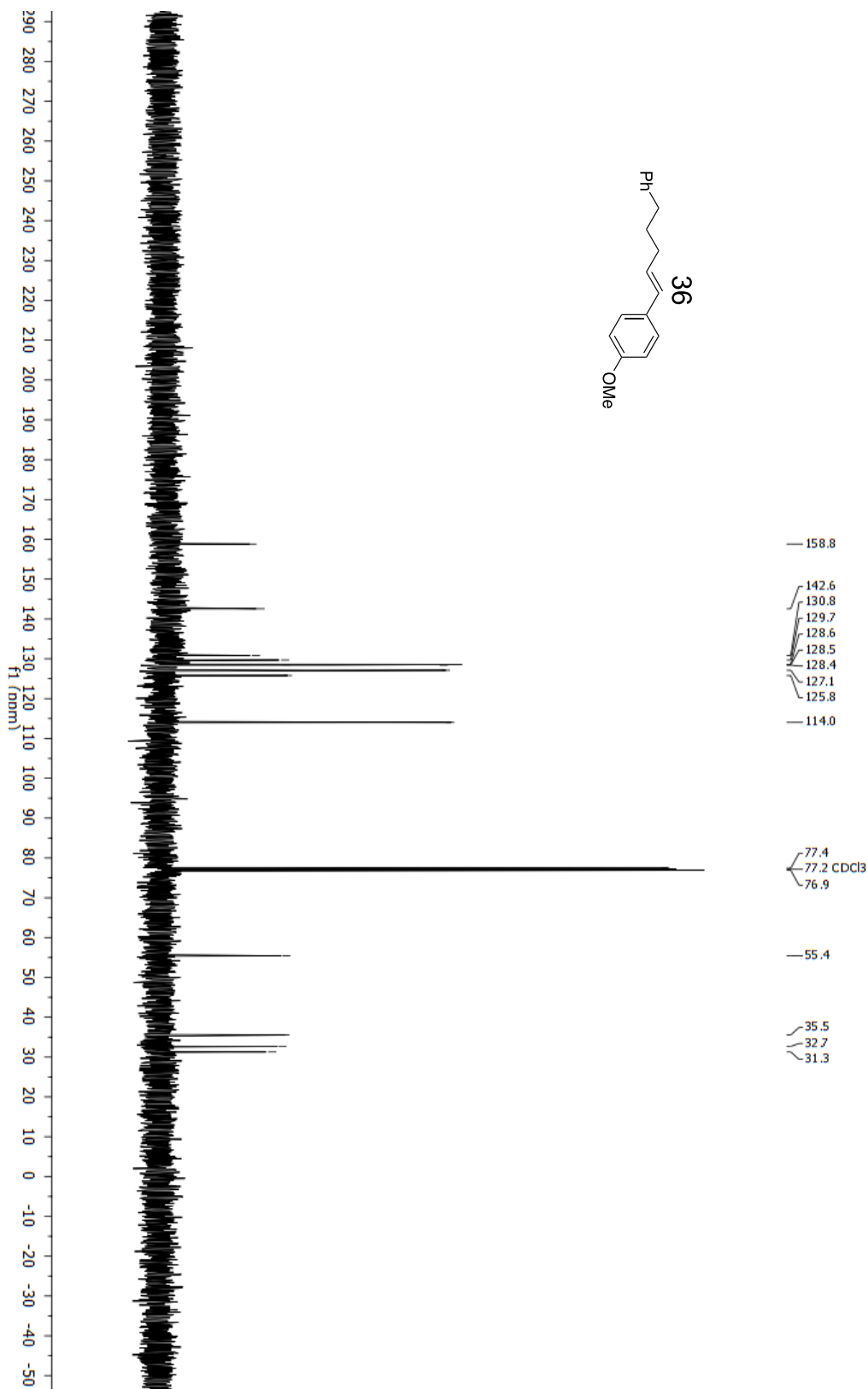
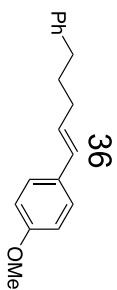


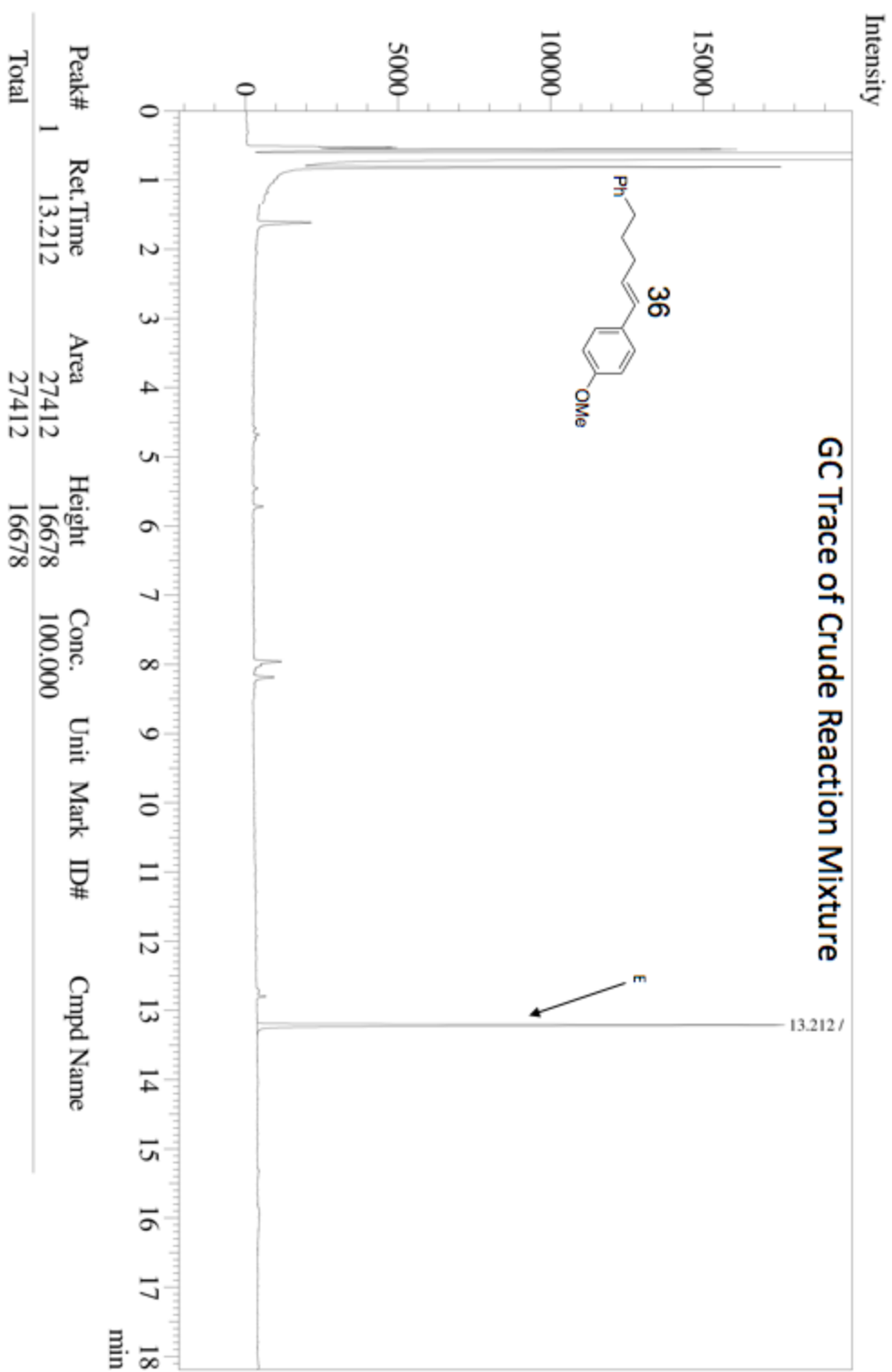


¹H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.12 (m, 5H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.80 (s, 3H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.80 (q, *J* = 7.5 Hz, 2H).

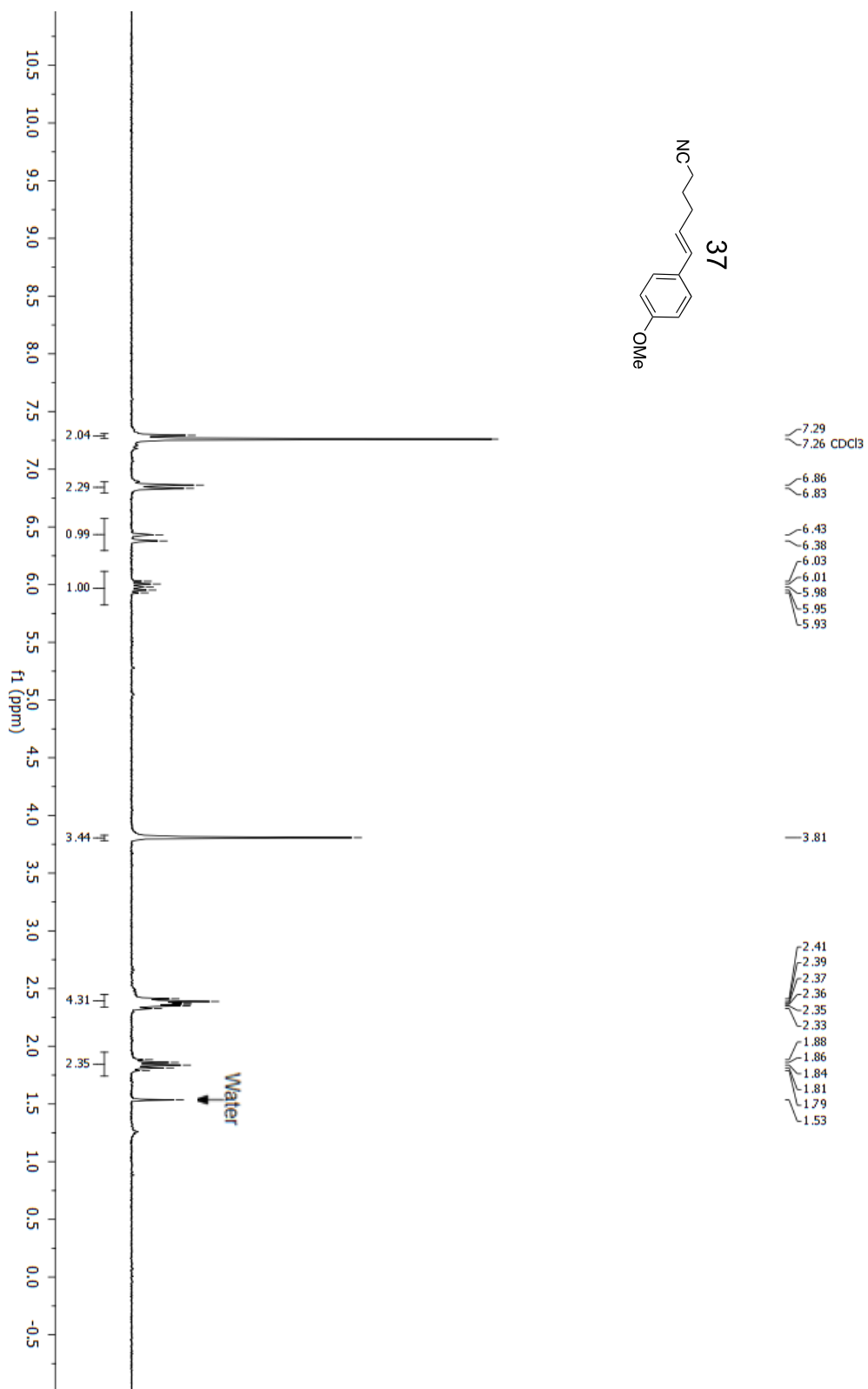
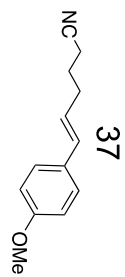


¹³C NMR (126 MHz, Chloroform-d) δ 158.8, 142.6, 130.8, 129.7, 128.6, 128.5, 128.4, 127.1, 125.8, 125.8, 114.0, 55.4, 35.5, 32.7, 31.3.

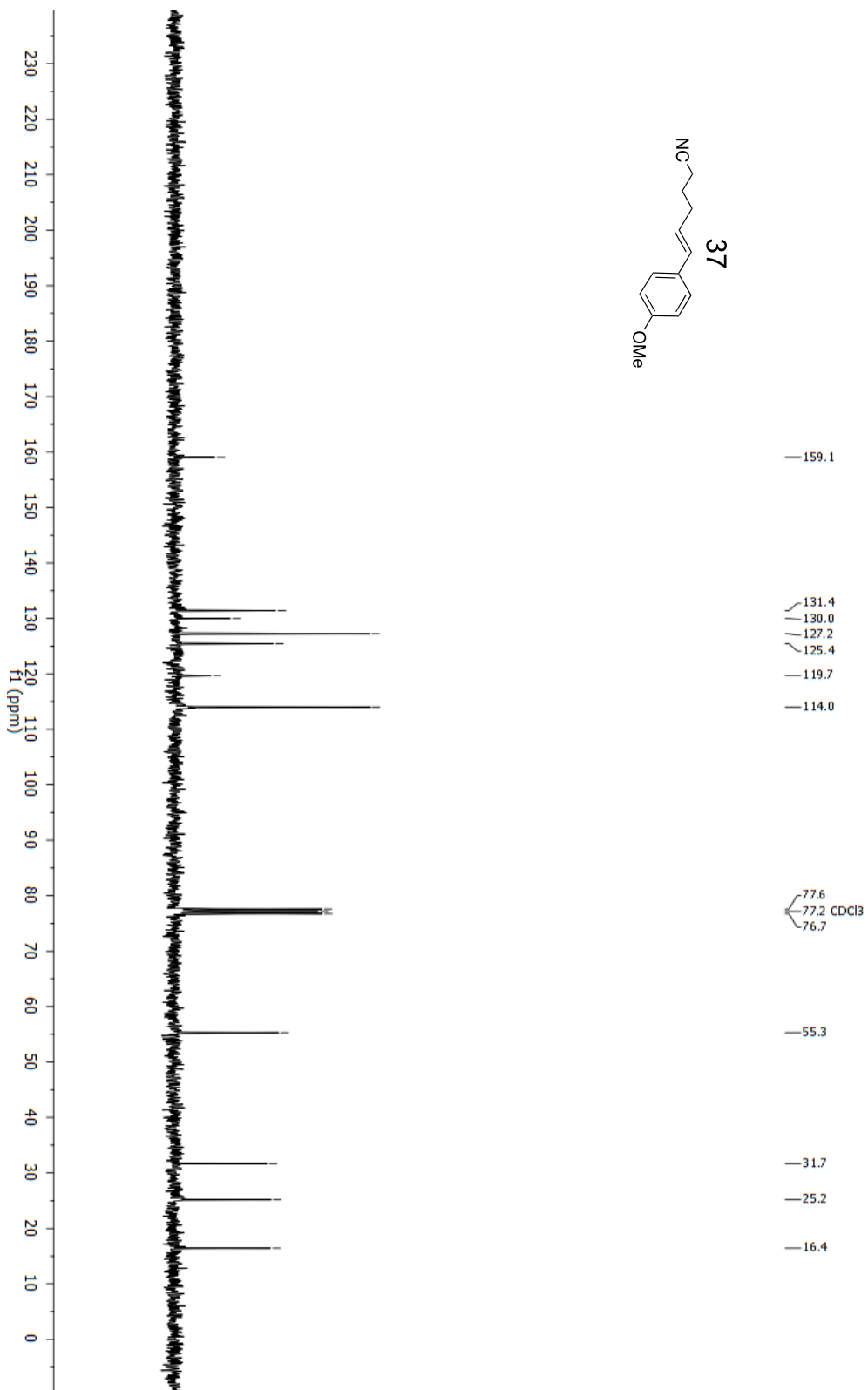
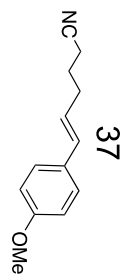




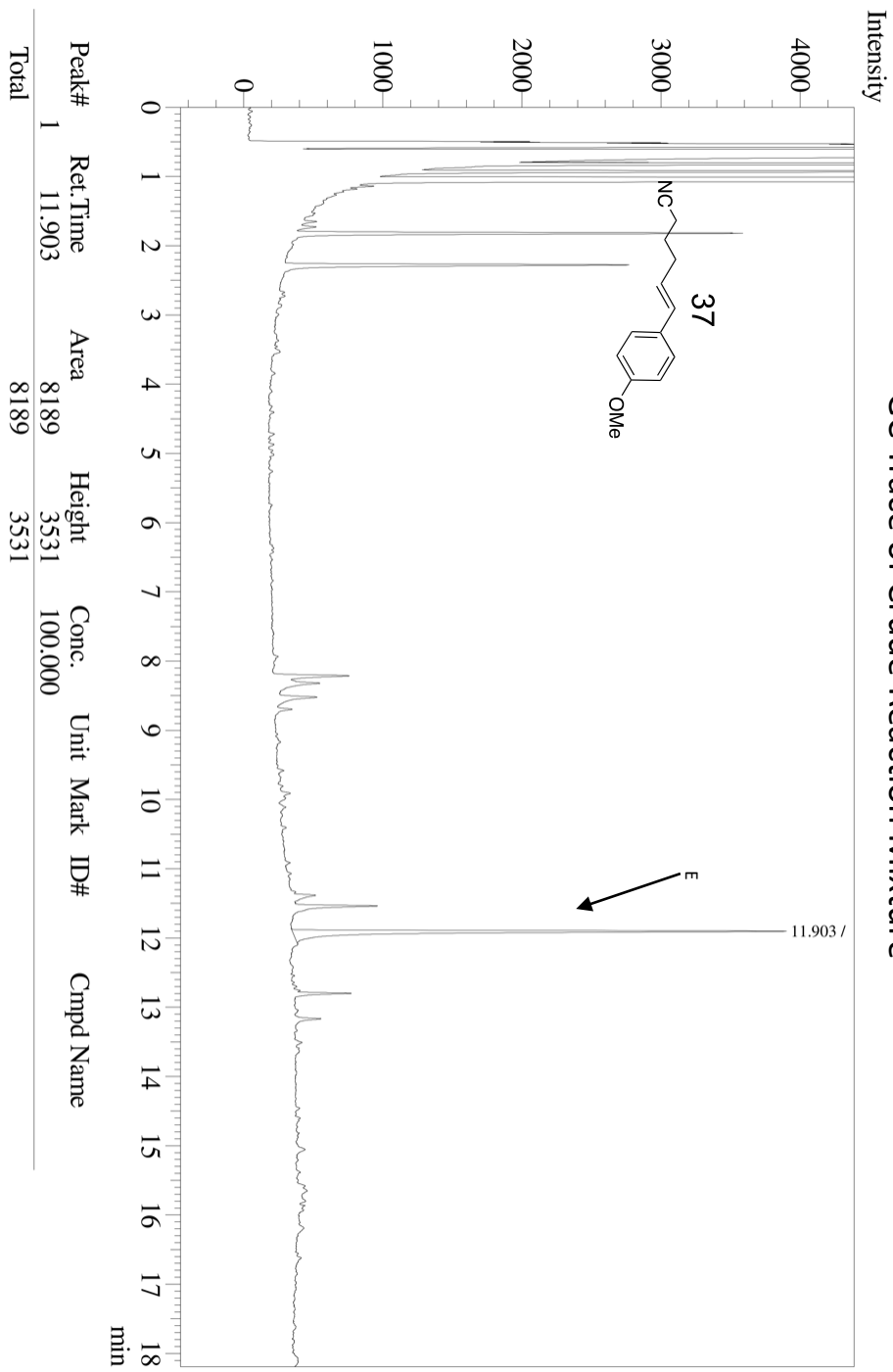
¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.98 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.34 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H).



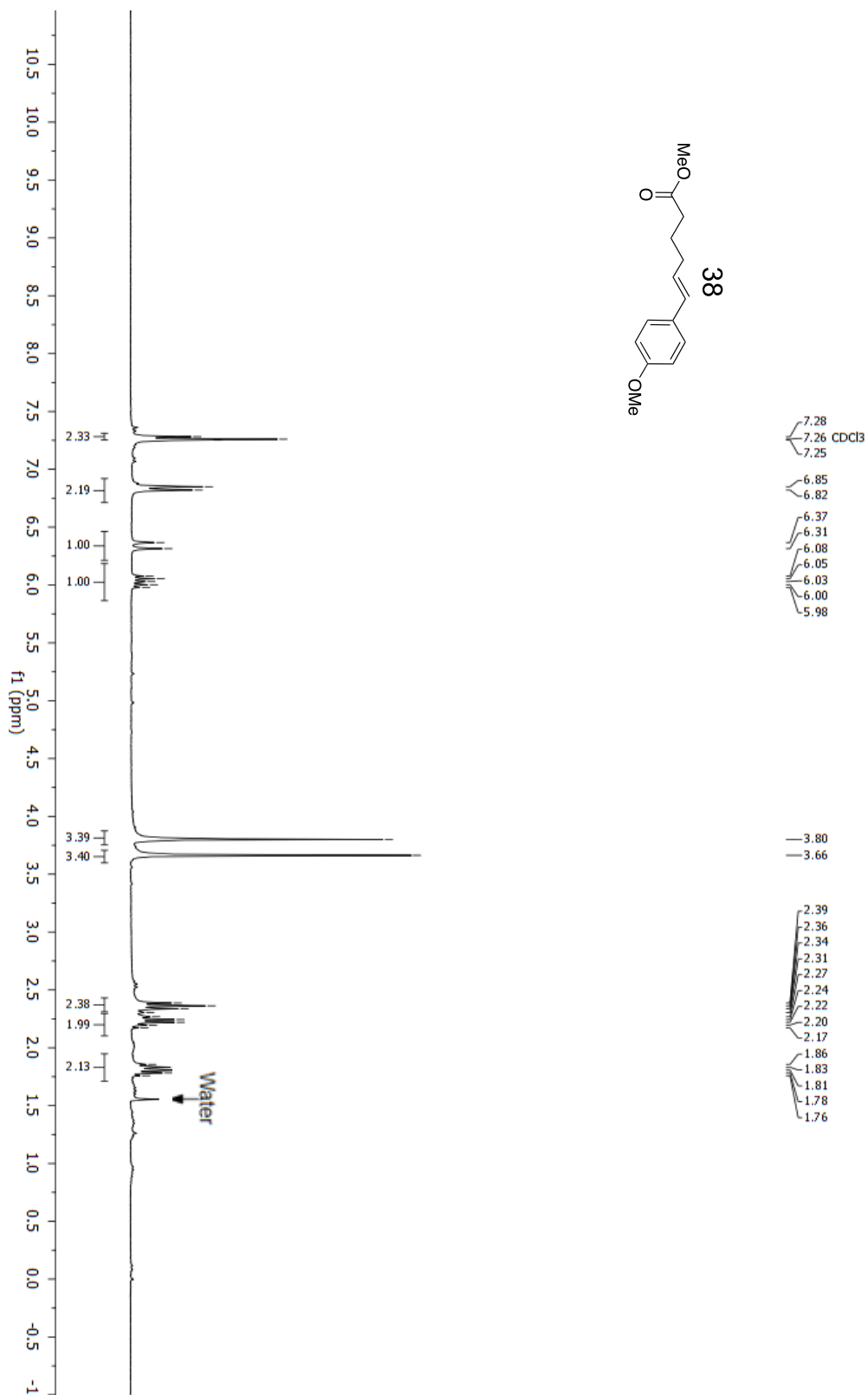
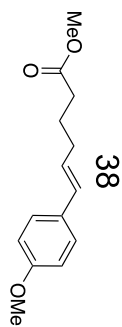
¹³C NMR (75 MHz, CDCl₃) δ 159.1, 131.4, 130.0, 127.2, 125.4, 119.7, 114.0, 55.3, 31.7, 25.2, 16.4.



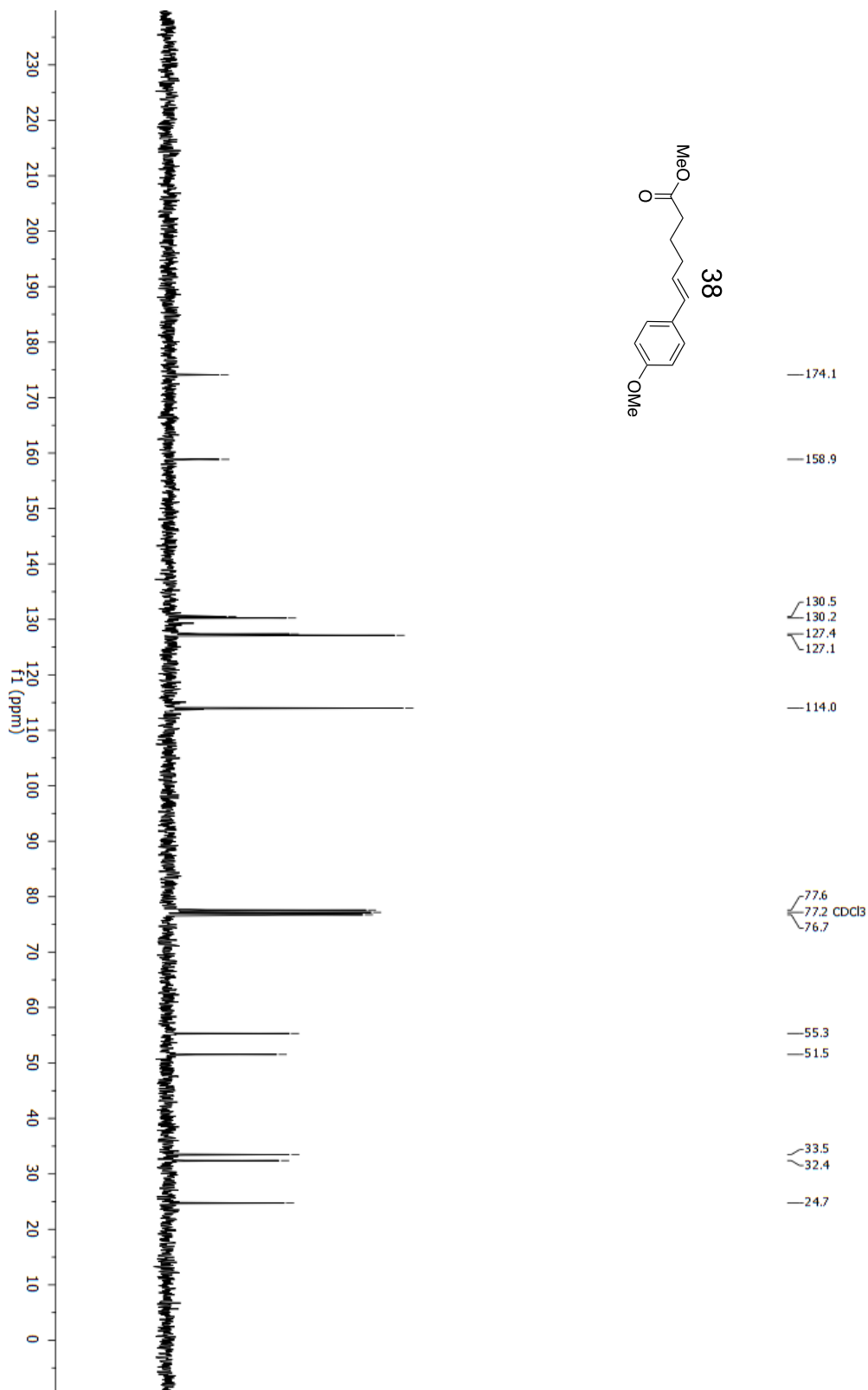
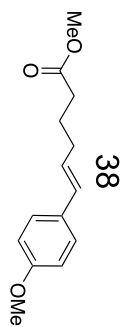
GC Trace of Crude Reaction Mixture



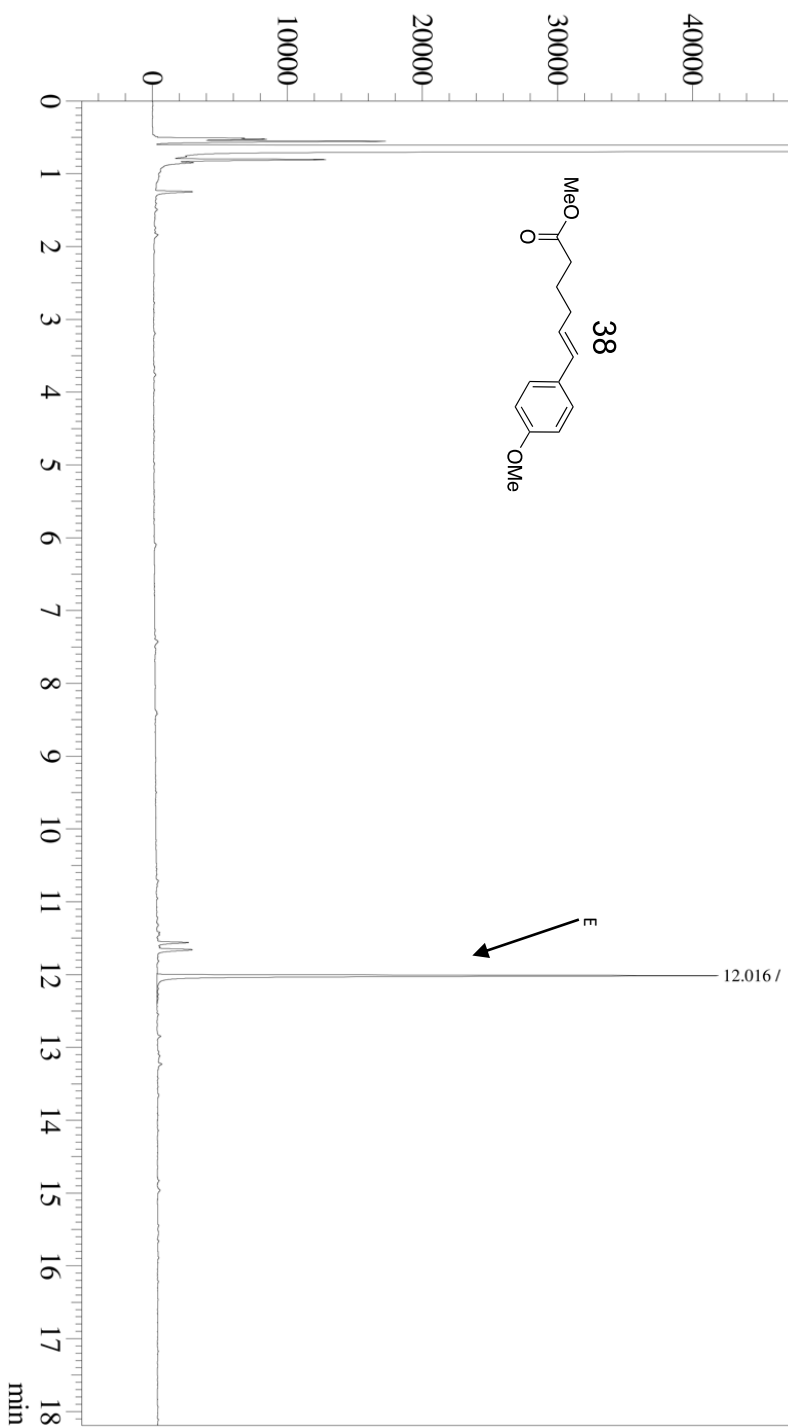
¹H NMR (300 MHz, Chloroform-d) δ 7.27 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.11 – 5.95 (m, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.45 – 2.30 (m, 2H), 2.34 – 2.14 (m, 2H), 1.81 (p, J = 7.3 Hz, 2H).



¹³C NMR (75 MHz, CDCl₃) δ 174.1, 158.9, 130.5, 130.2, 127.4, 127.1, 114.0, 55.3, 51.5, 33.5, 32.4, 24.7.

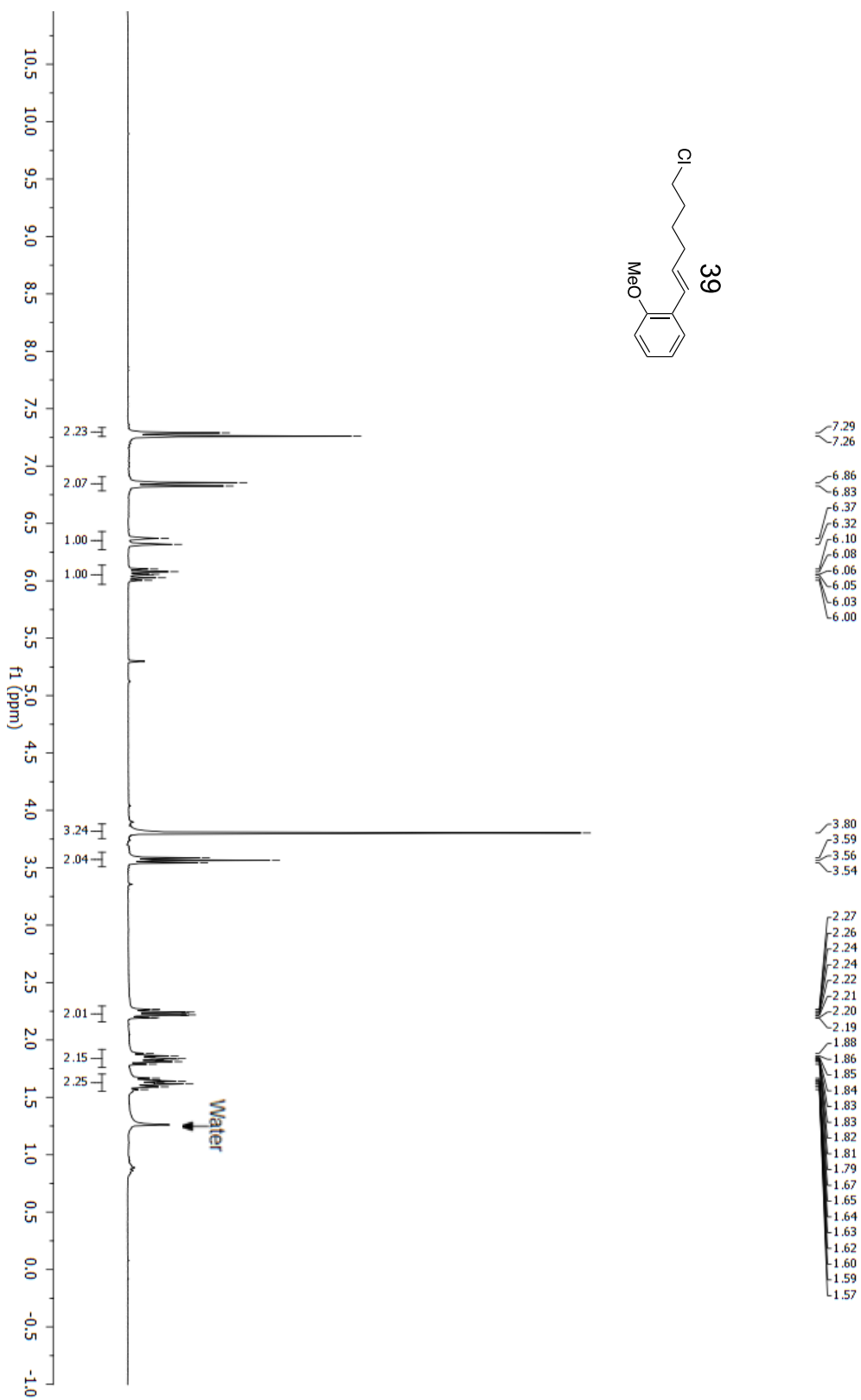
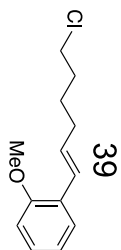


GC Trace of Crude Reaction Mixture

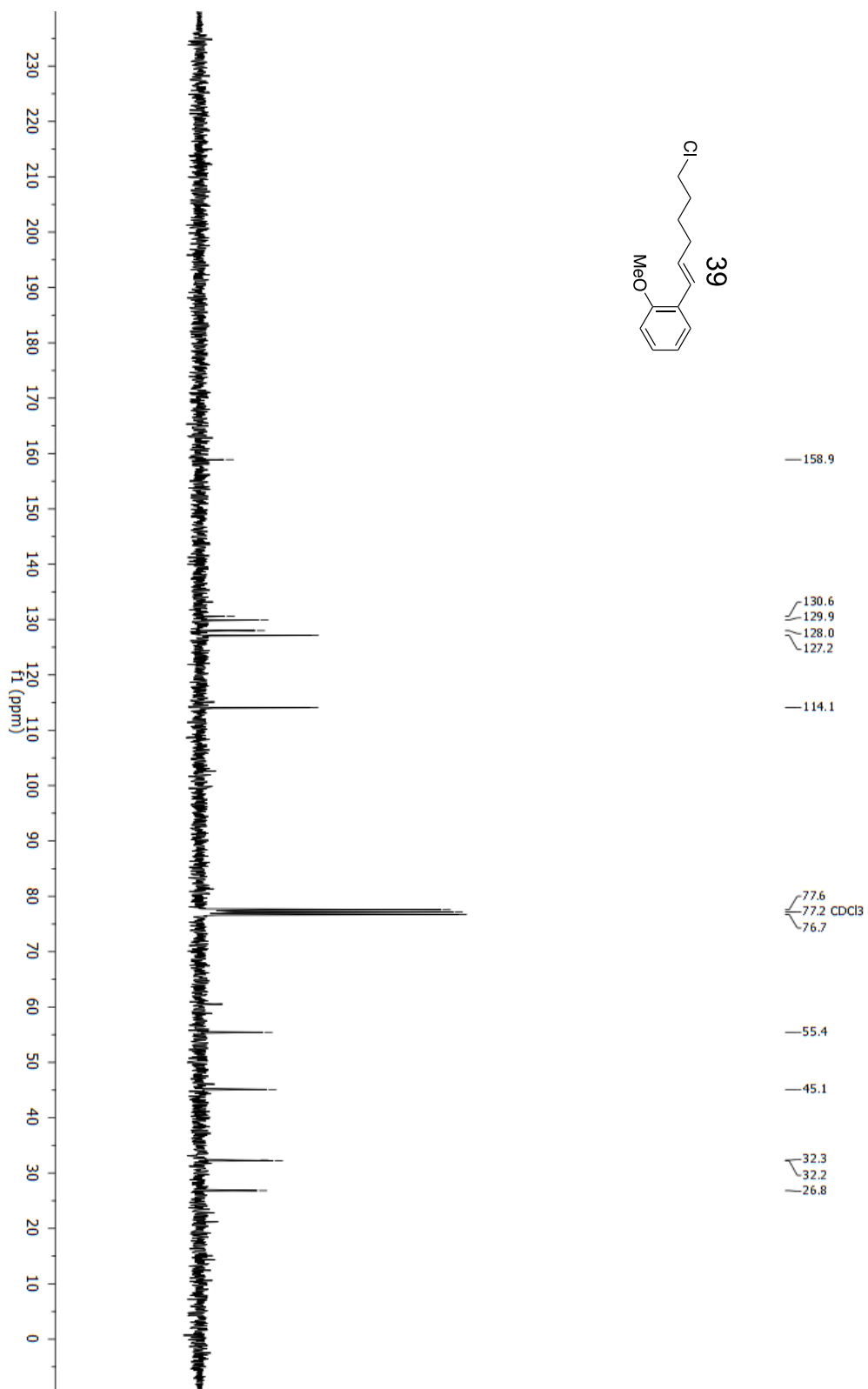
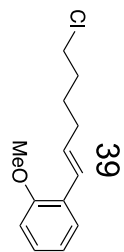


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.016	62340	41073	100.000	S			
Total		62340	41073					

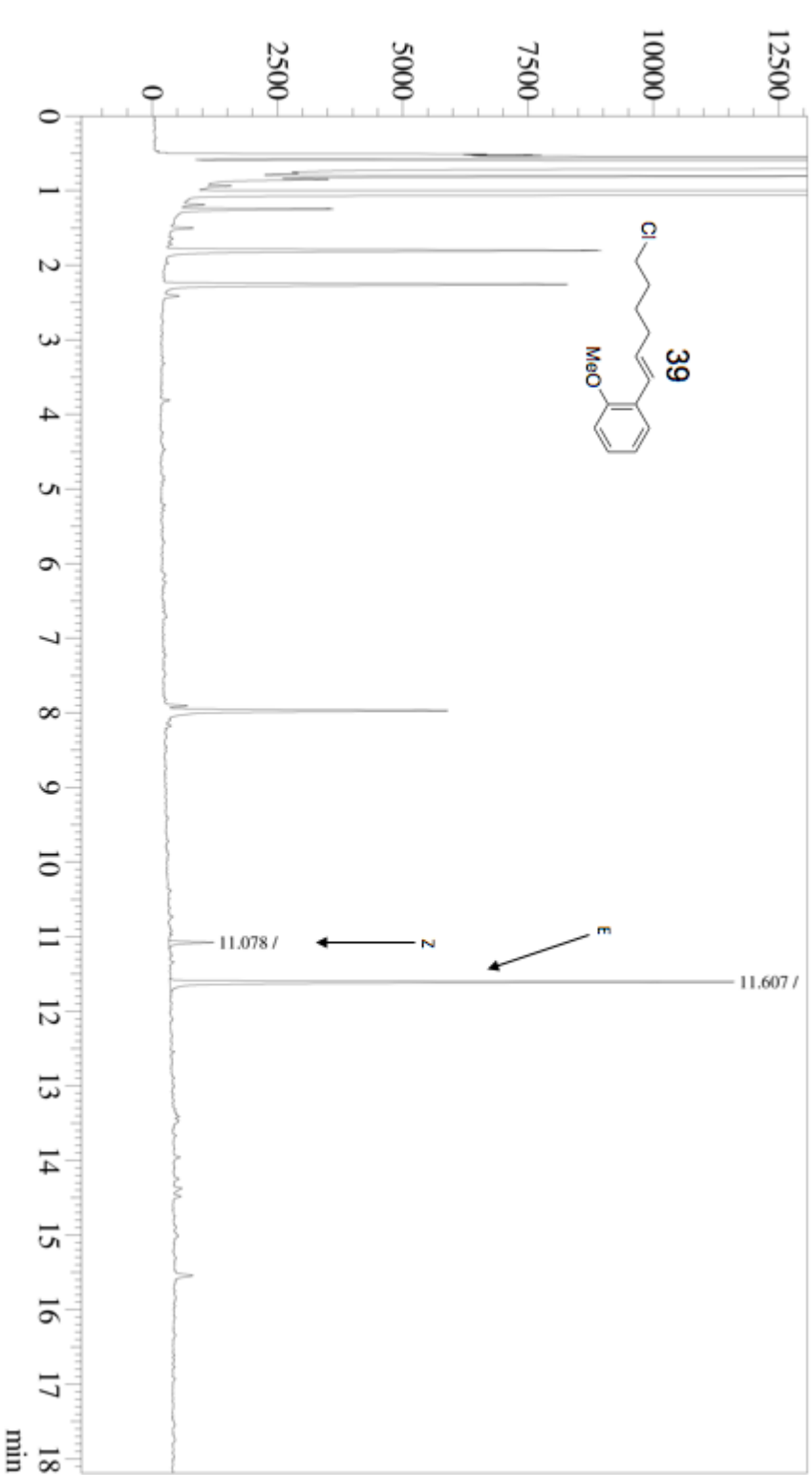
¹H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 1.92 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H).



¹³C-NMR (75 MHz, CDCl₃) δ 158.9, 130.6, 129.9, 127.2, 127.2, 114.1, 55.4, 45.1, 32.3, 32.2, 26.8.

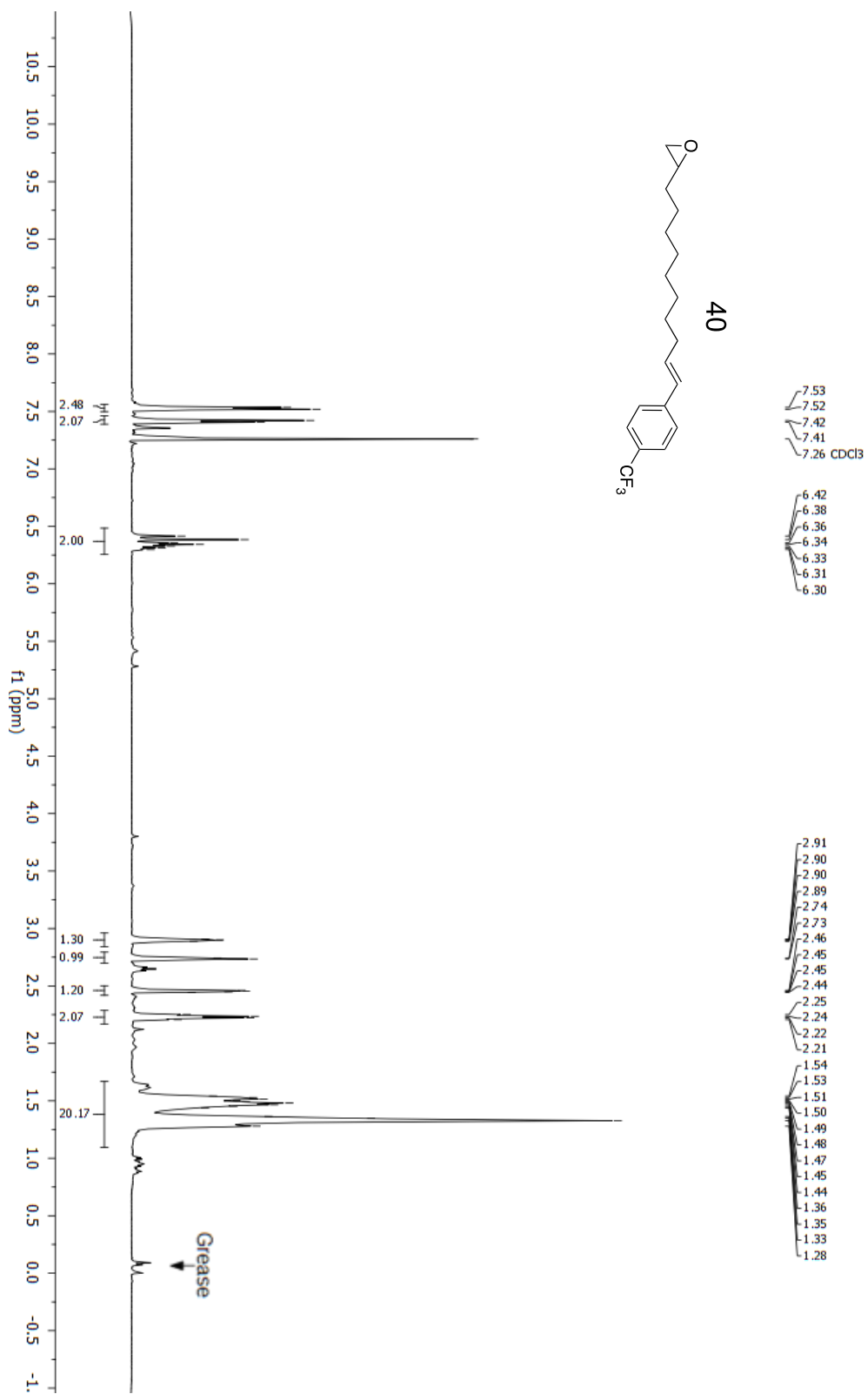
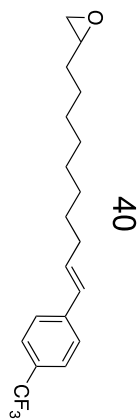


GC Trace of Crude Reaction Mixture

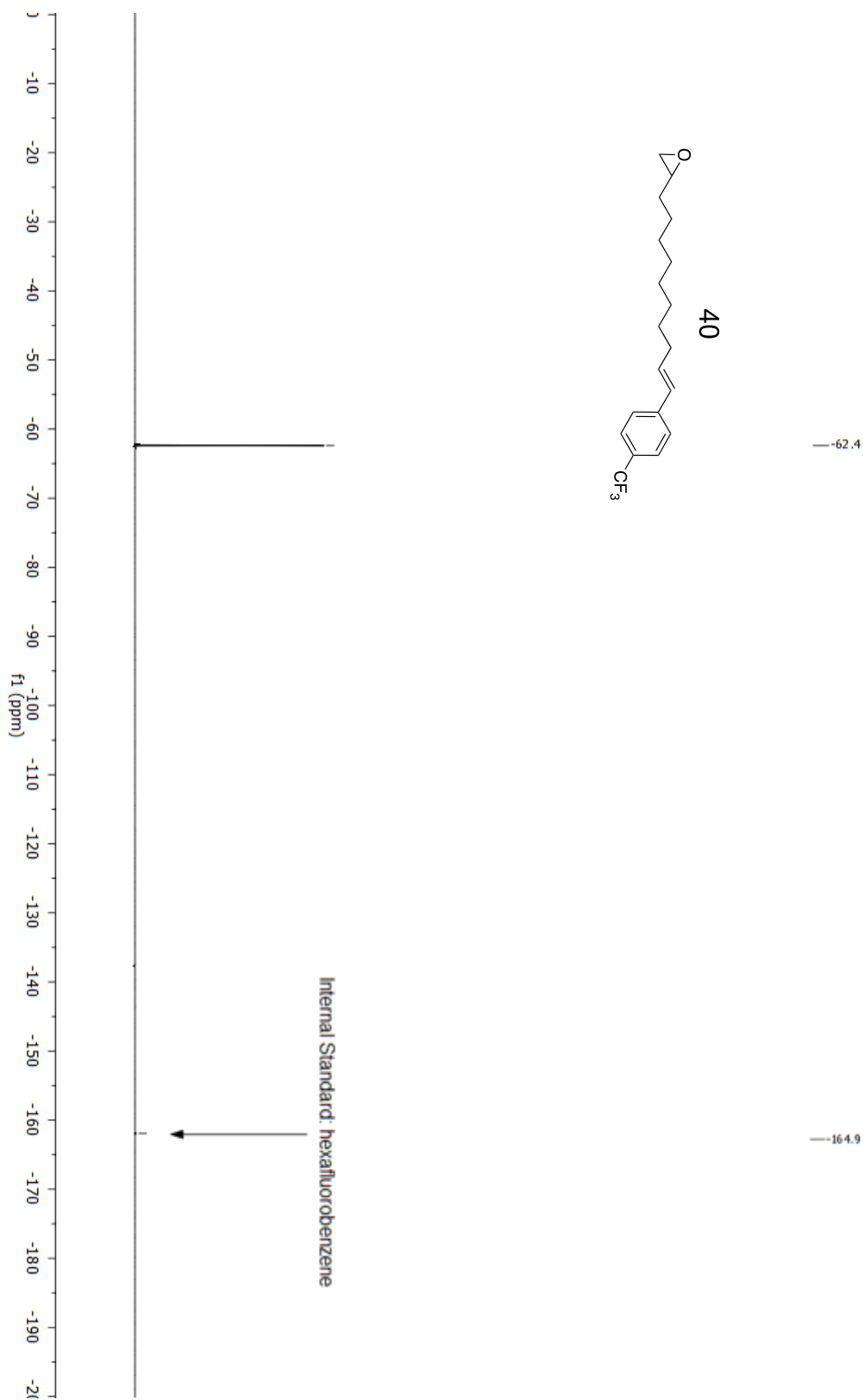
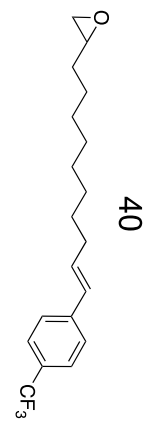


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.078	1789	885	8.336				
2	11.607	18345	10929	91.664				
Total		20013	11814					

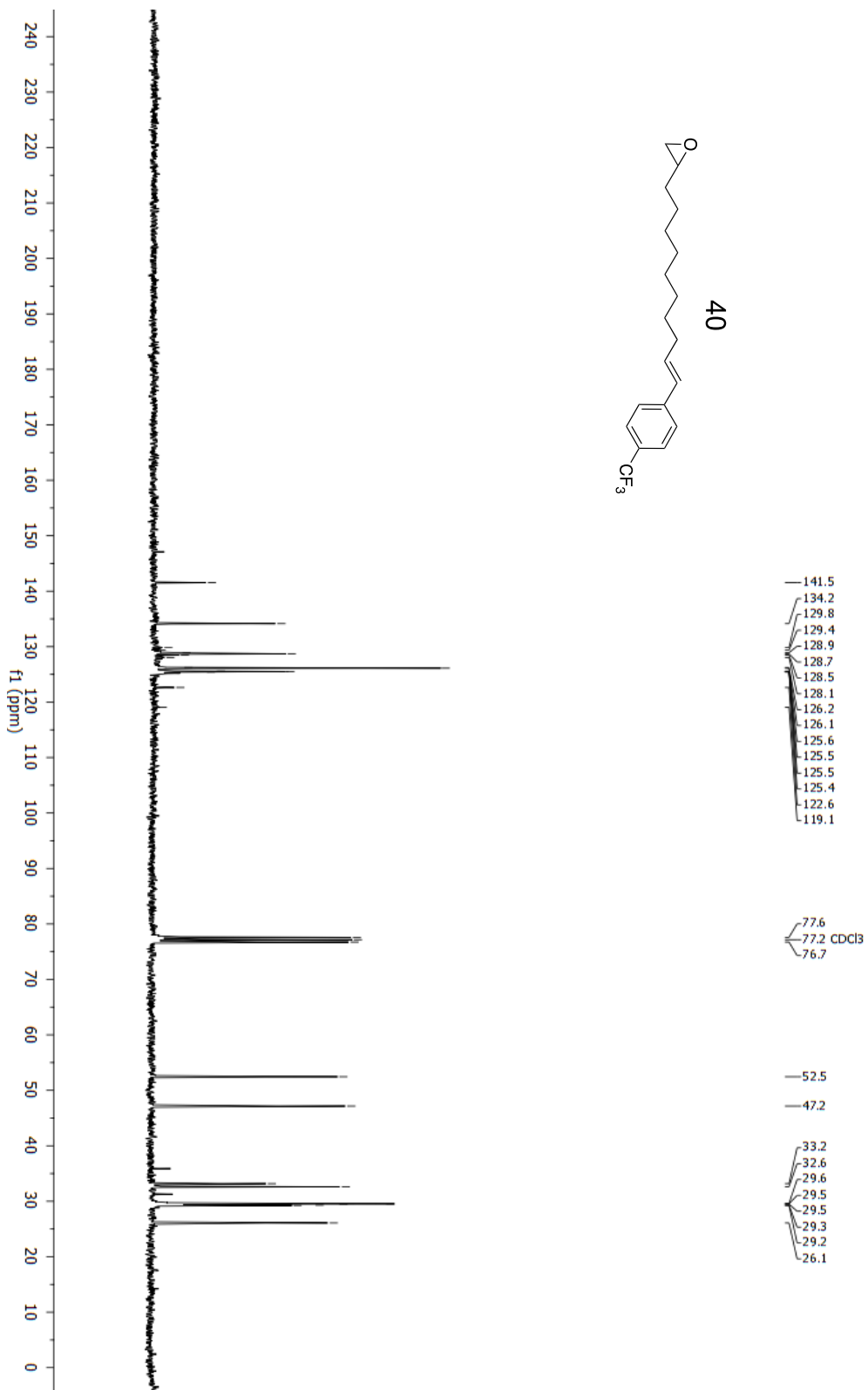
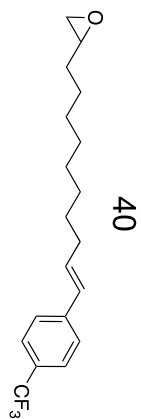
¹H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 6.48 – 6.26 (m, 2H), 2.96 – 2.84 (m, 1H), 2.79 – 2.70 (m, 1H), 2.50 – 2.42 (m, 1H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.67 – 1.10 (m, 20H).



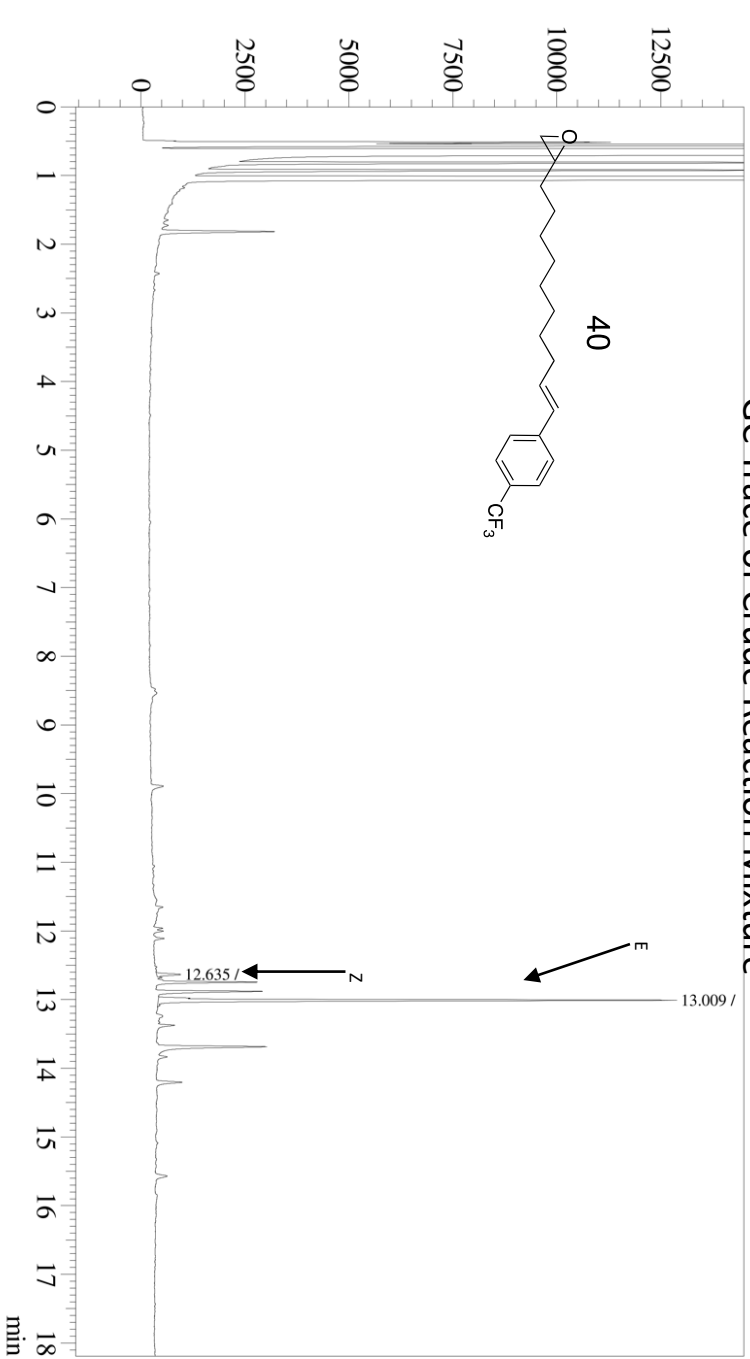
¹⁹F NMR (471 MHz, CDCl₃) δ -62.4.



¹³C NMR (75 MHz, Chloroform-*d*) δ 141.5, 134.2, 128.7, 128.7 (q, *J* = 32.1 Hz), 125.6, 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.6 Hz), 52.5, 47.2, 33.2, 32.6, 29.6, 29.5, 29.3, 29.2, 26.1.

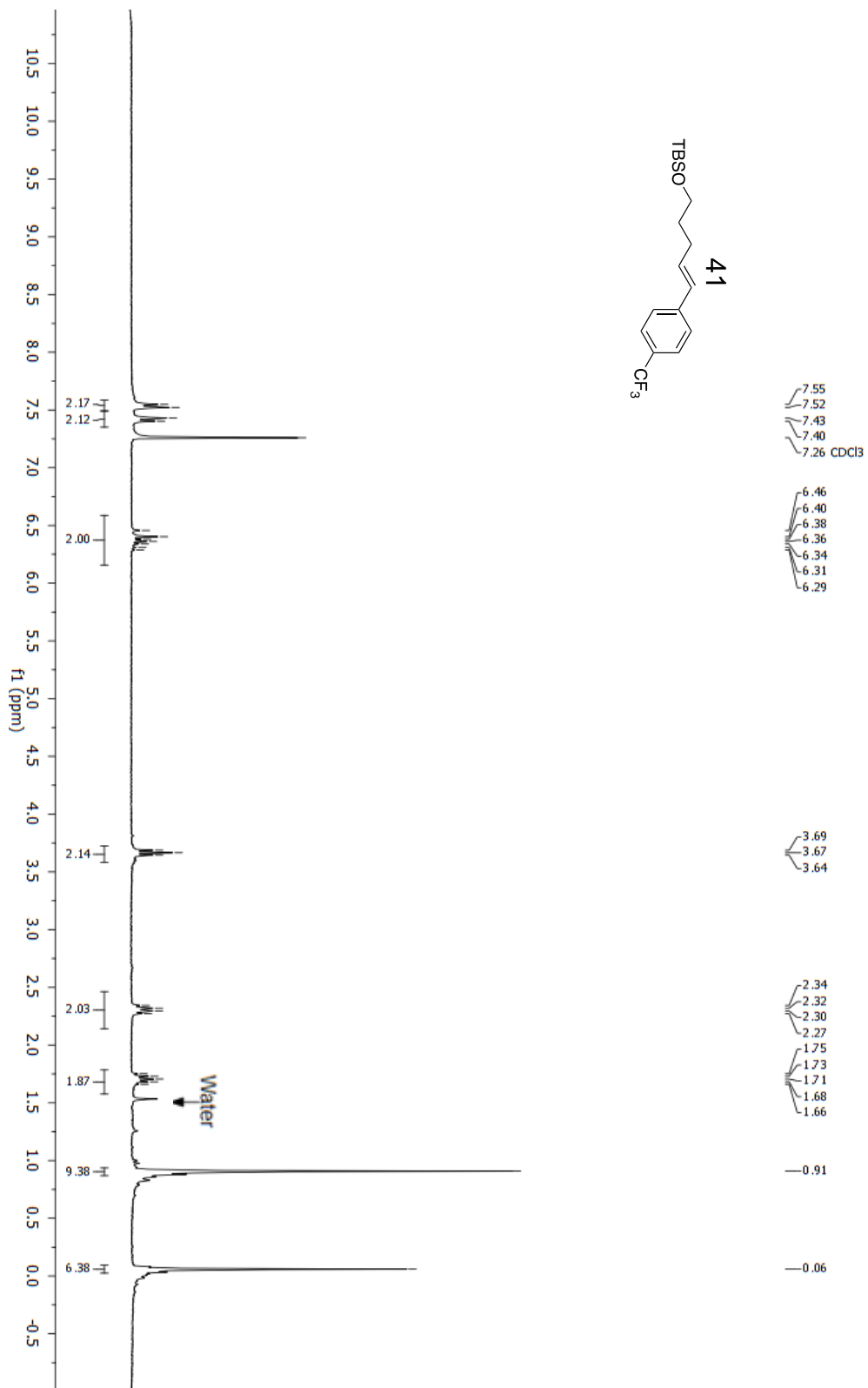
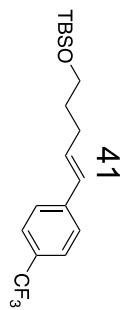


GC Trace of Crude Reaction Mixture

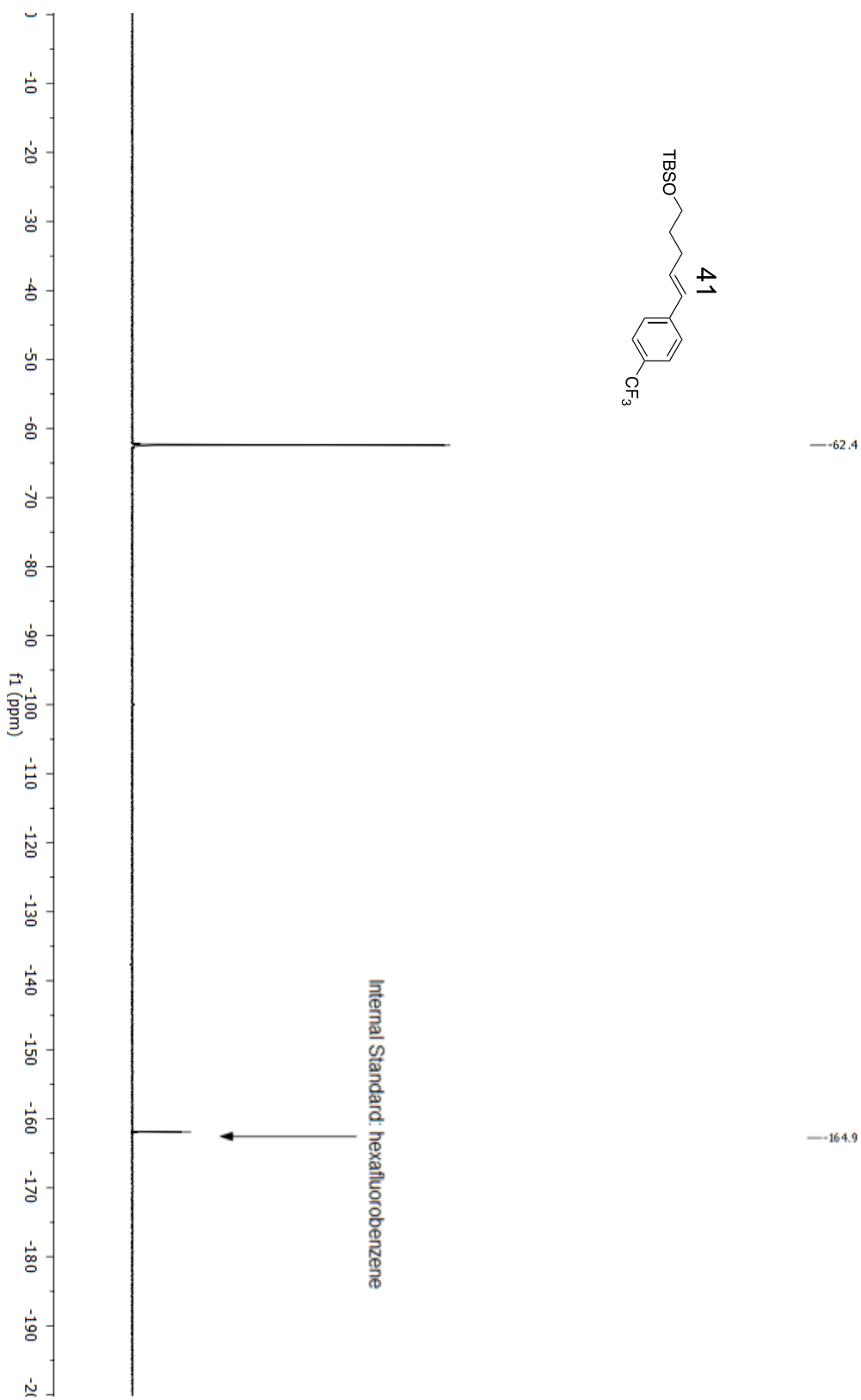
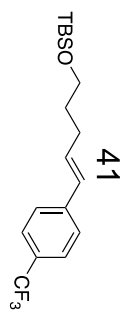


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.635	1112	571	5.343				
2	13.009	19701	12346	94.657		S		
Total		20813	12917					

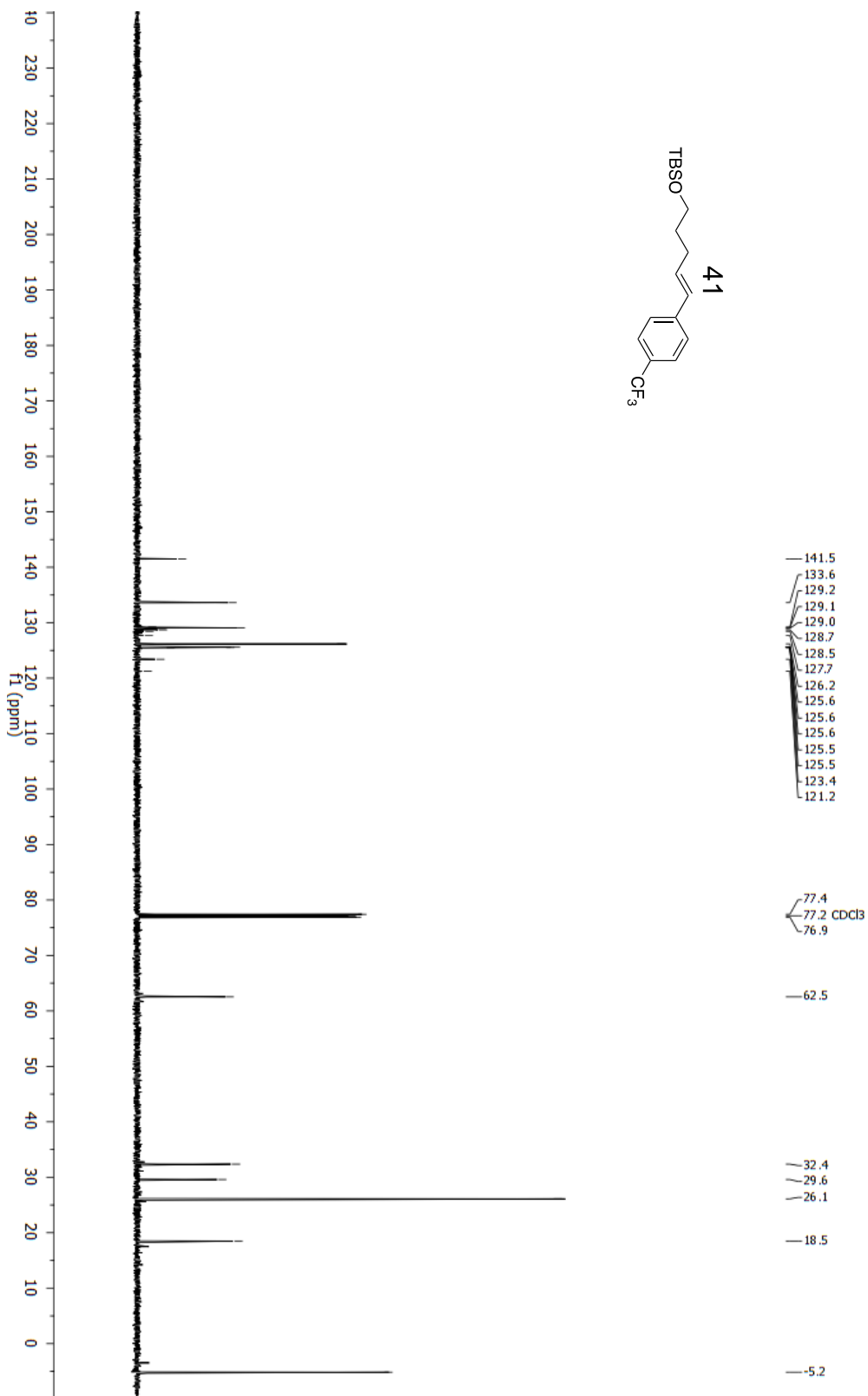
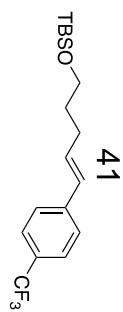
¹H NMR (300 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.59 – 6.16 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.31 (q, *J* = 6.9 Hz, 2H), 1.79 – 1.58 (m, 2H), 0.91 (s, 9H), 0.06 (s, 6H).



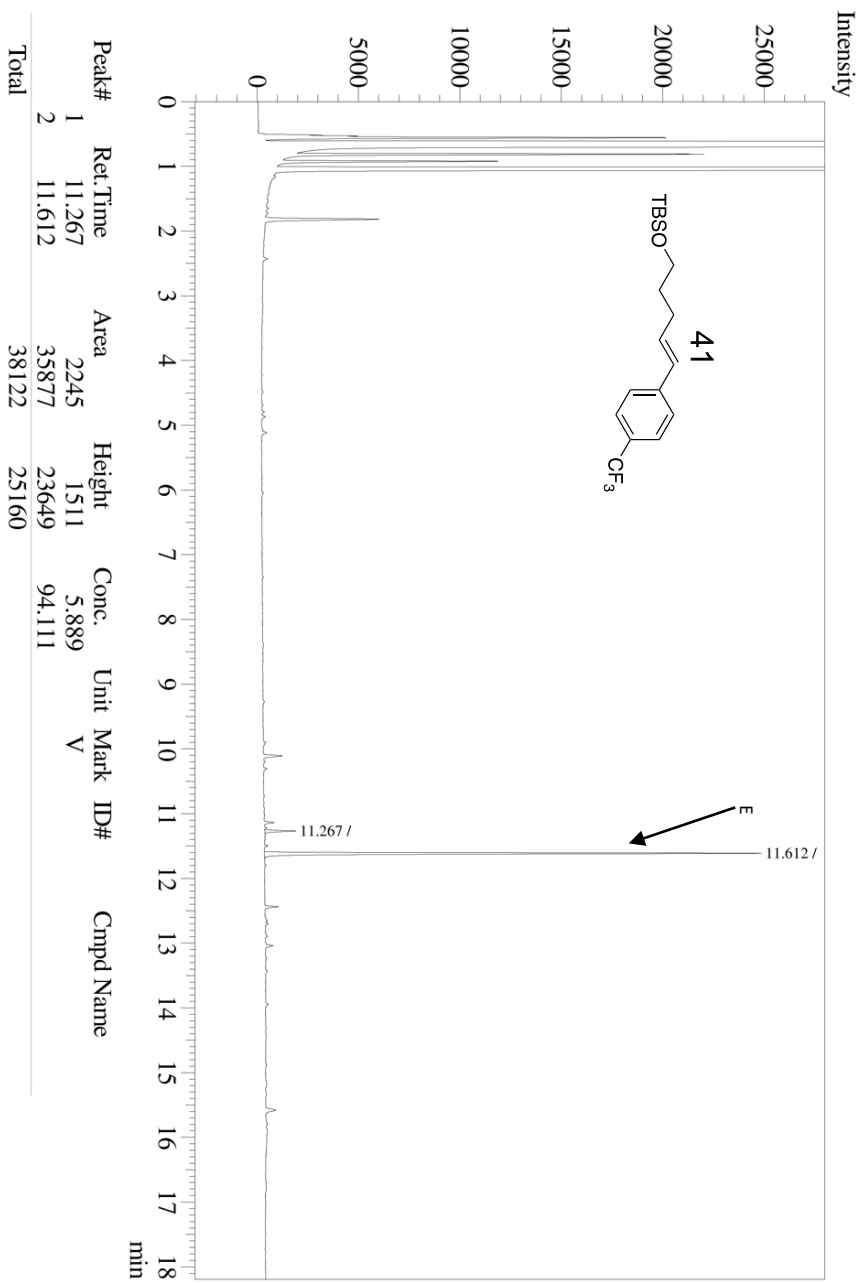
¹⁹F NMR (471 MHz, CDCl₃) δ -62.4.



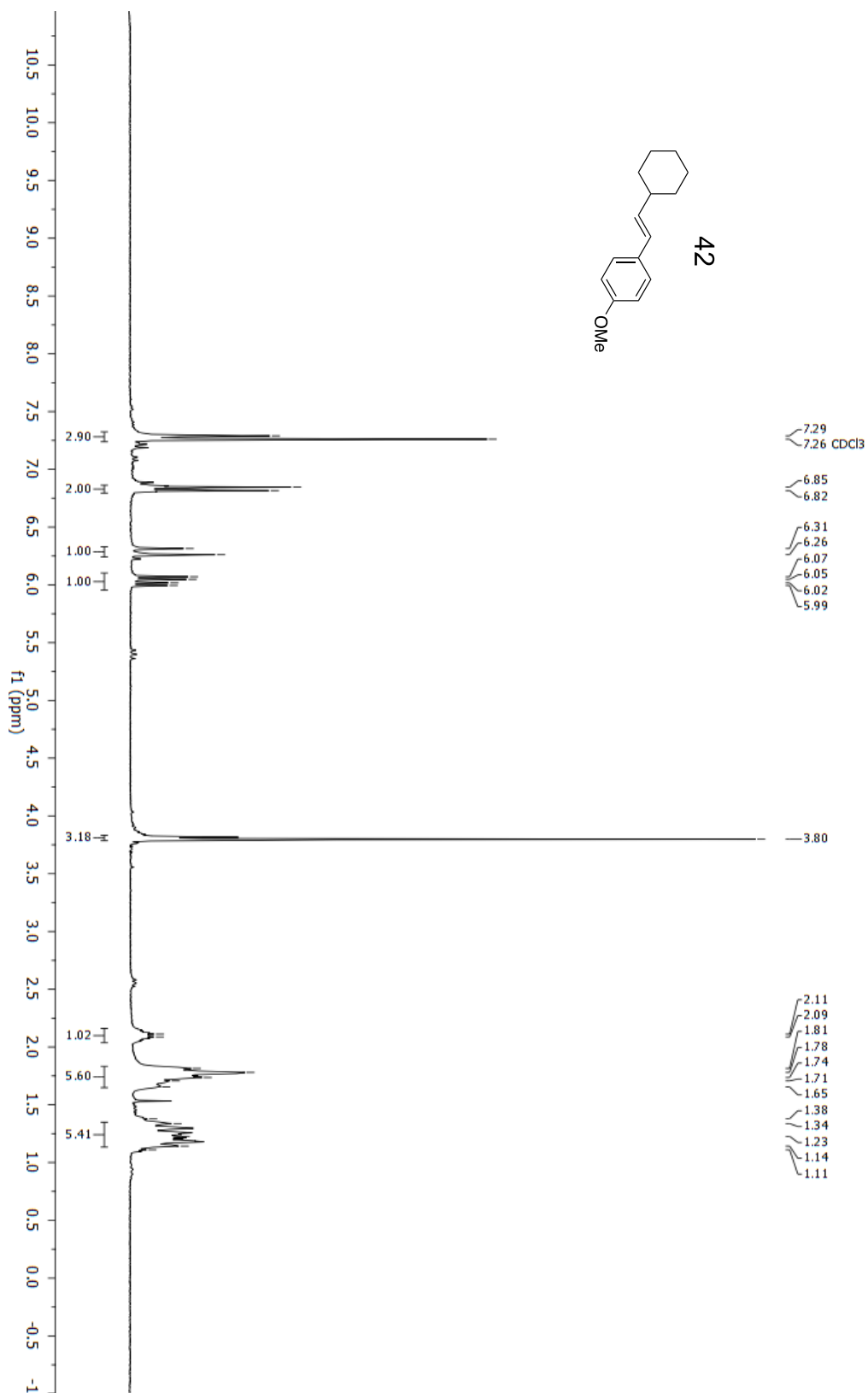
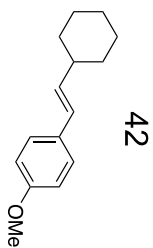
¹³C NMR (126 MHz, Chloroform-*d*) δ 141.5, 133.6, 129.2, 128.7 (q, *J* = 32.2 Hz), 126.2, 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.7 Hz), 62.5, 32.4, 29.6, 26.1, 18.2, -5.2.



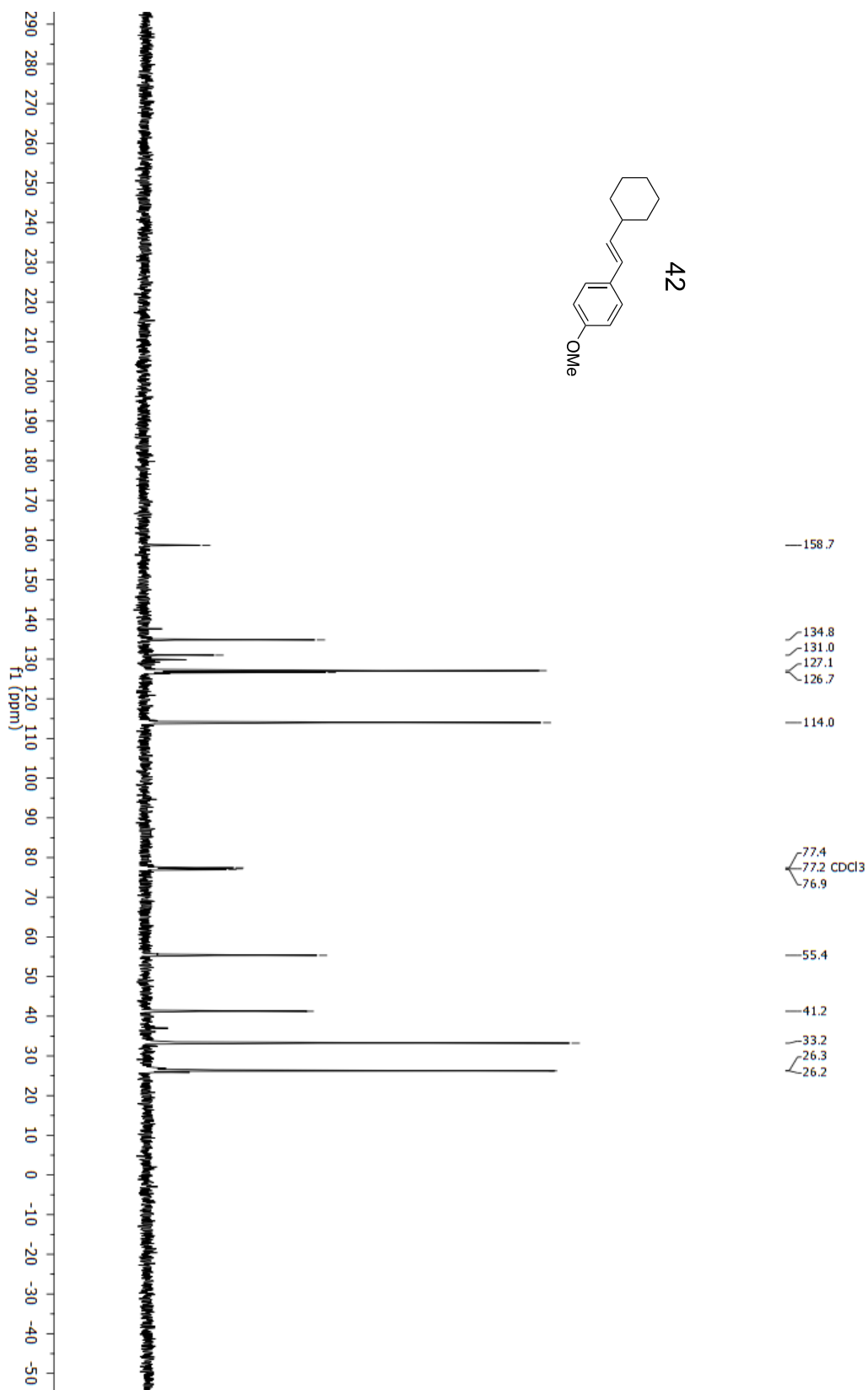
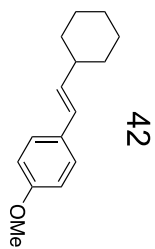
GC Trace of Crude Reaction Mixture

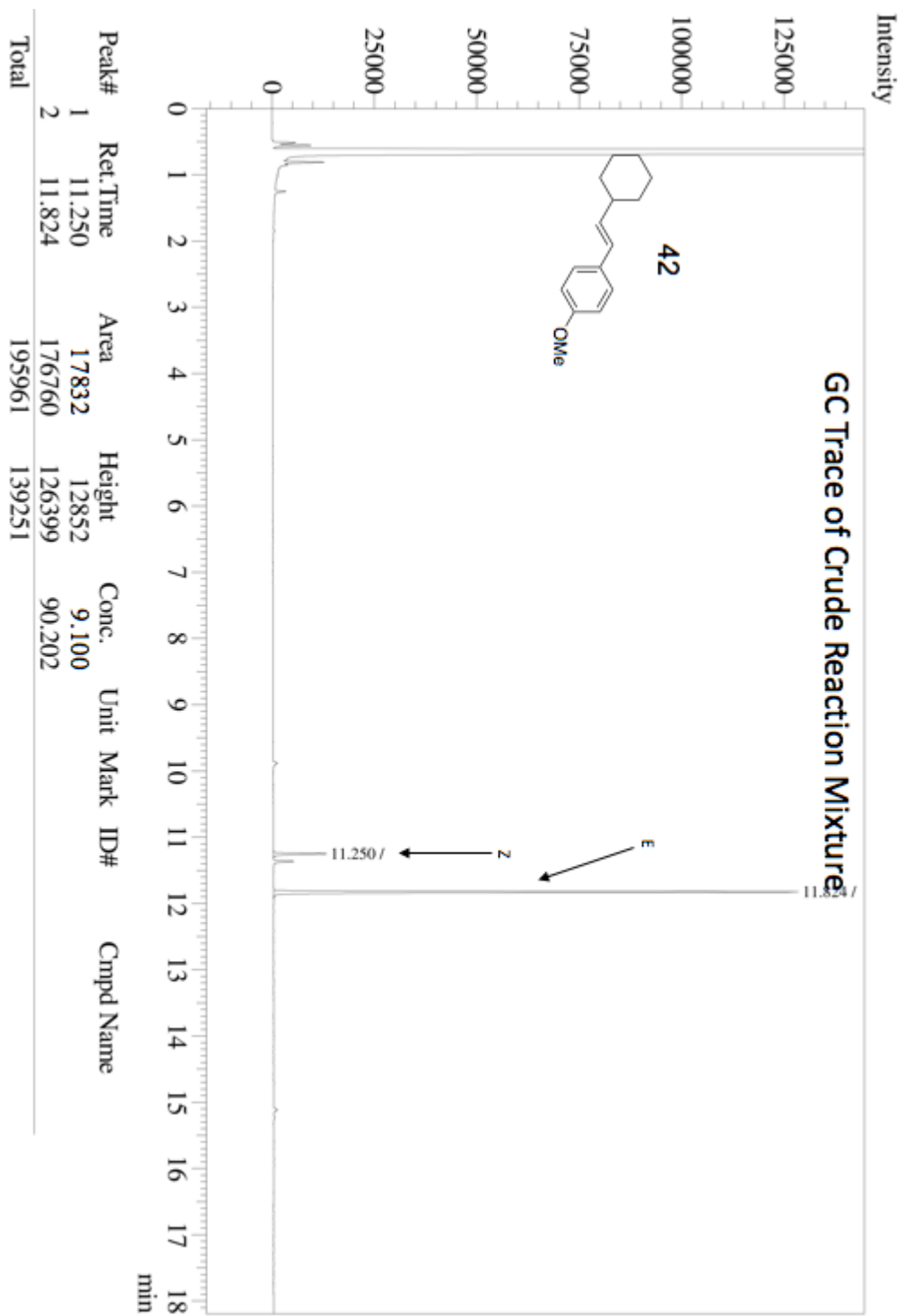


¹H NMR (300 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 16.0, 6.9 Hz, 1H), 3.80 (s, 3H), 2.17 – 2.01 (m, 1H), 1.89 – 1.61 (m, 5H), 1.42 – 1.06 (m, 5H).



^{13}C NMR (126 MHz, Chloroform- d) δ 158.7, 134.8, 131.0, 127.1, 126.7, 114.0, 55.4, 41.2, 33.2, 26.2, 26.2.

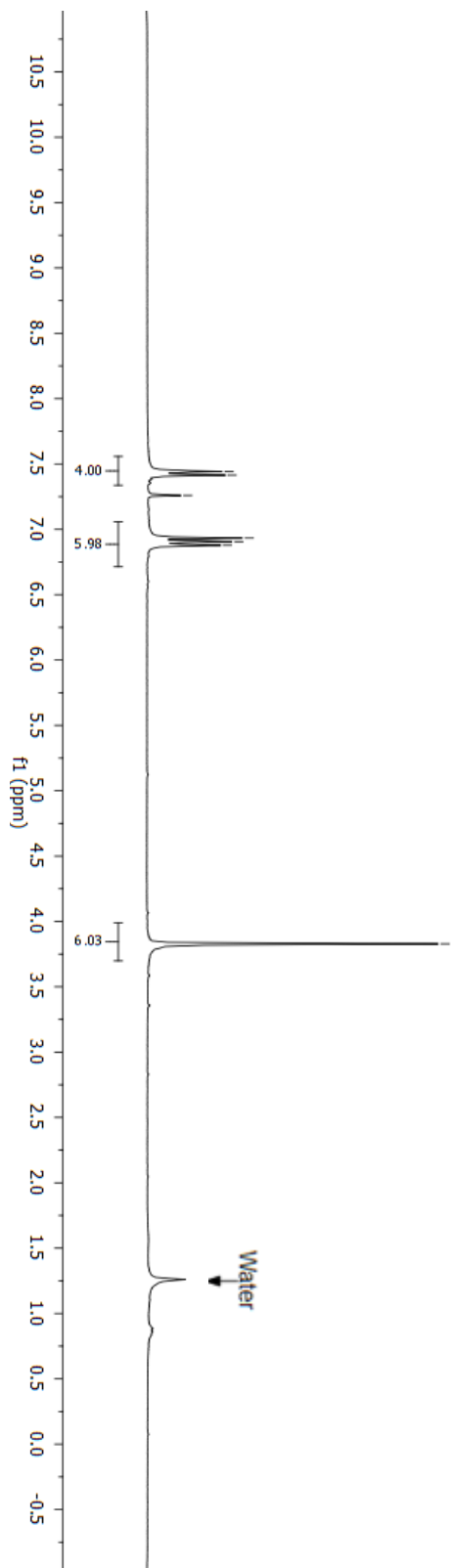
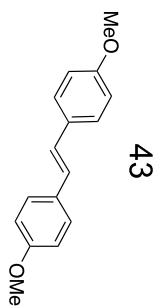




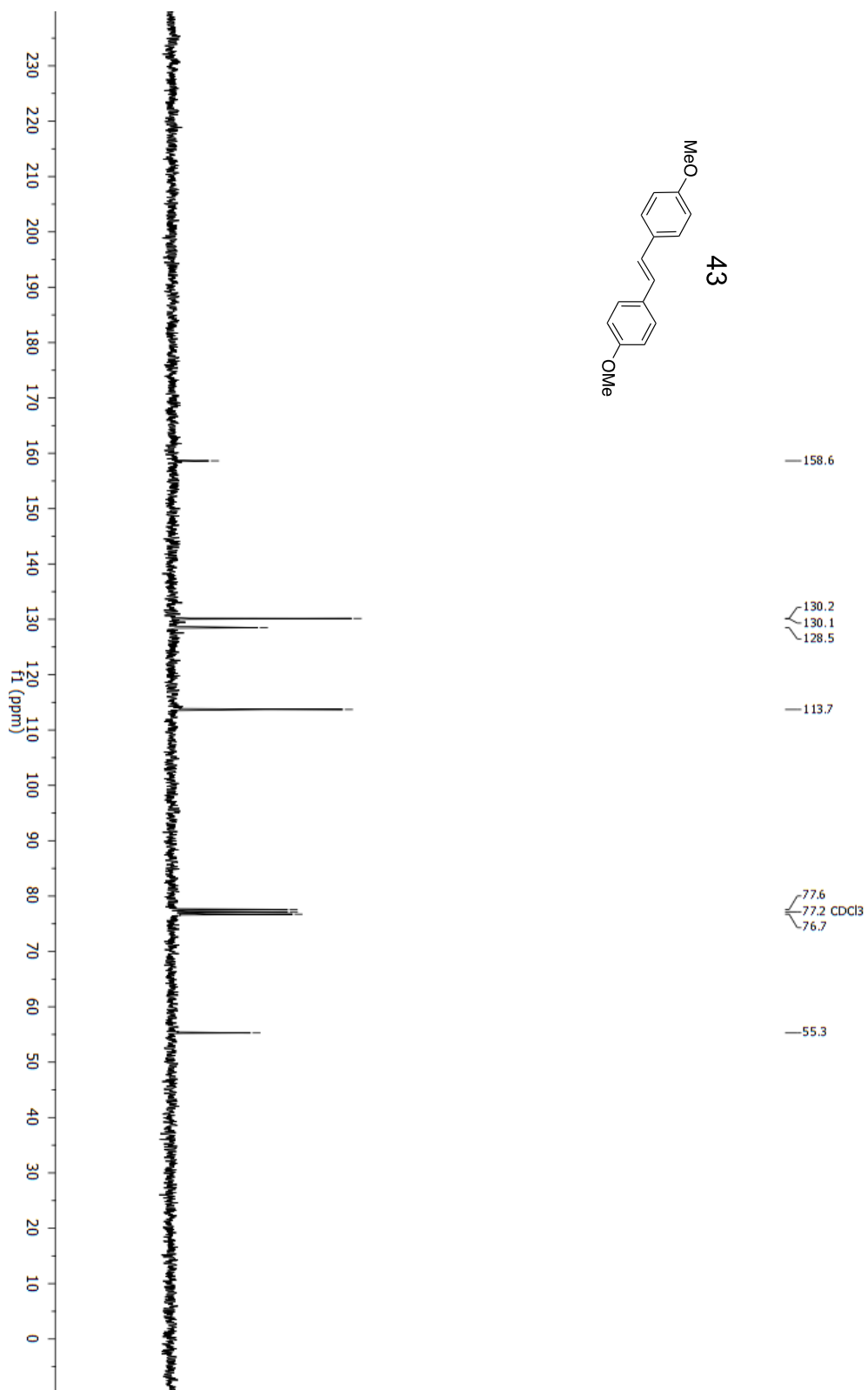
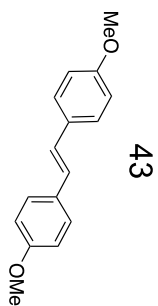
¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.4 Hz, 4H), 7.06 – 6.71 (m, 6H), 3.83 (s, 6H).

7.44
7.42
7.26 CDCl₃
6.93
6.91
6.88

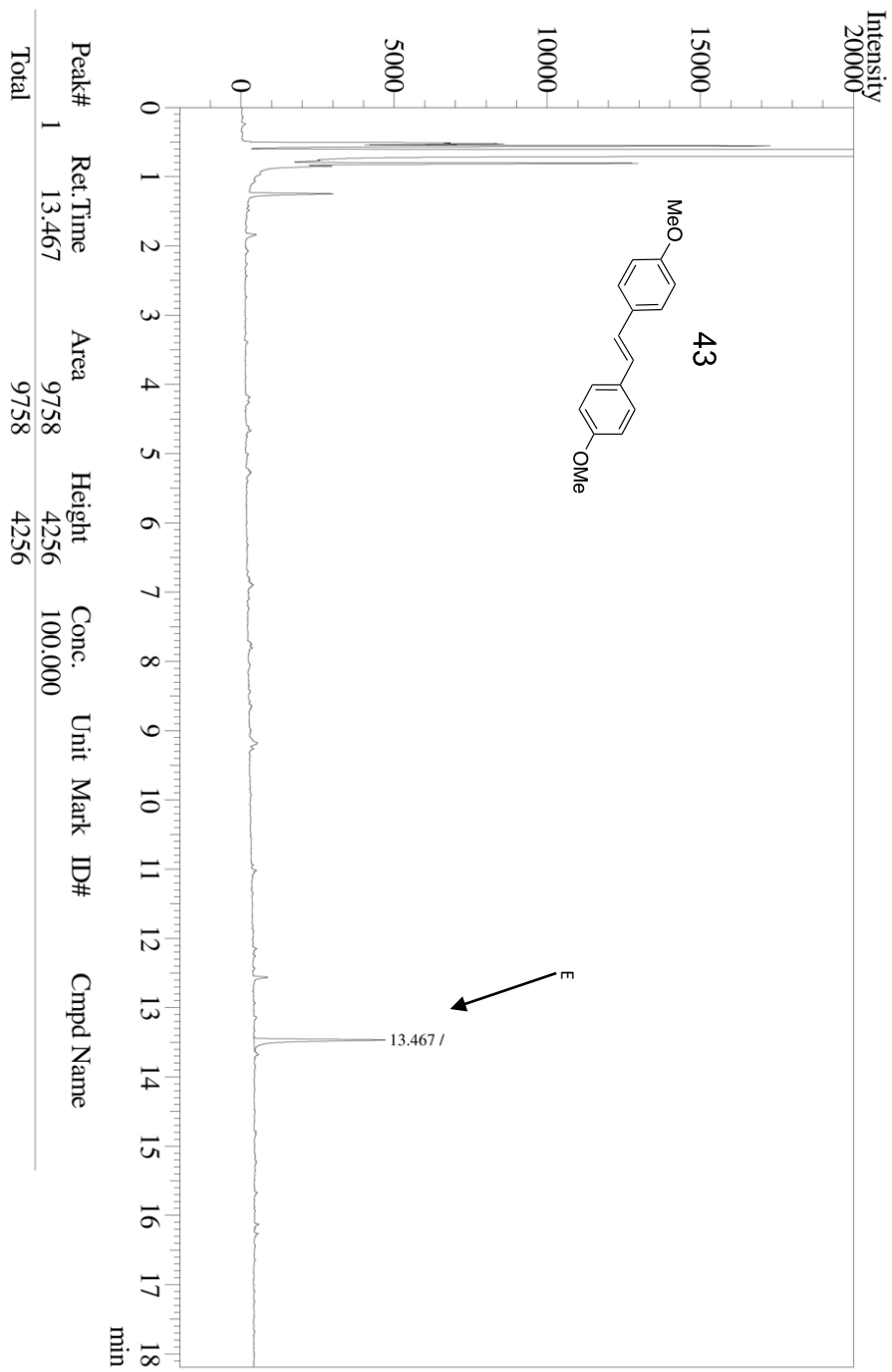
3.83



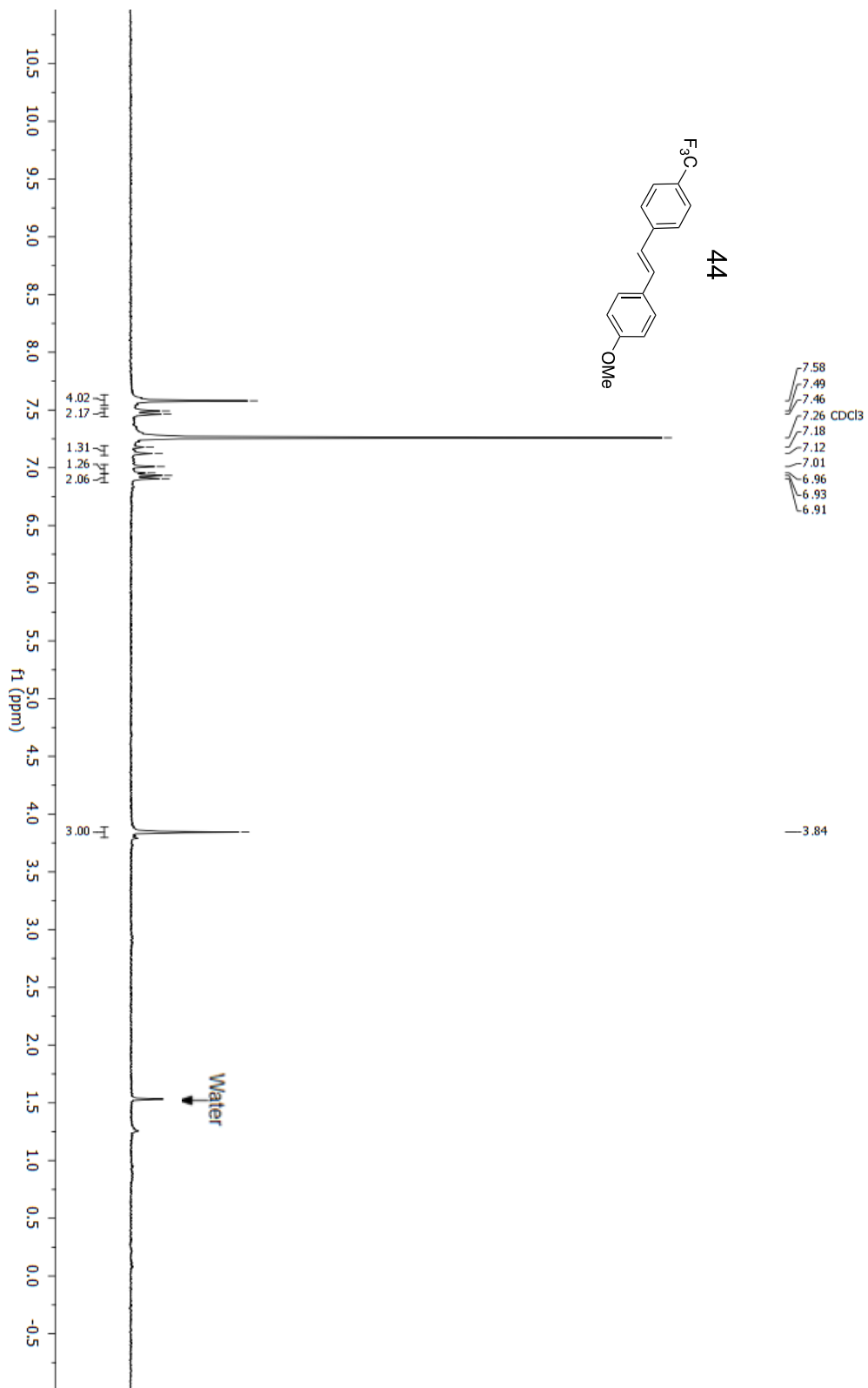
¹³C-NMR (75 MHz, CDCl₃) δ 158.6, 130.2, 130.1, 128.5, 113.7, 55.3.



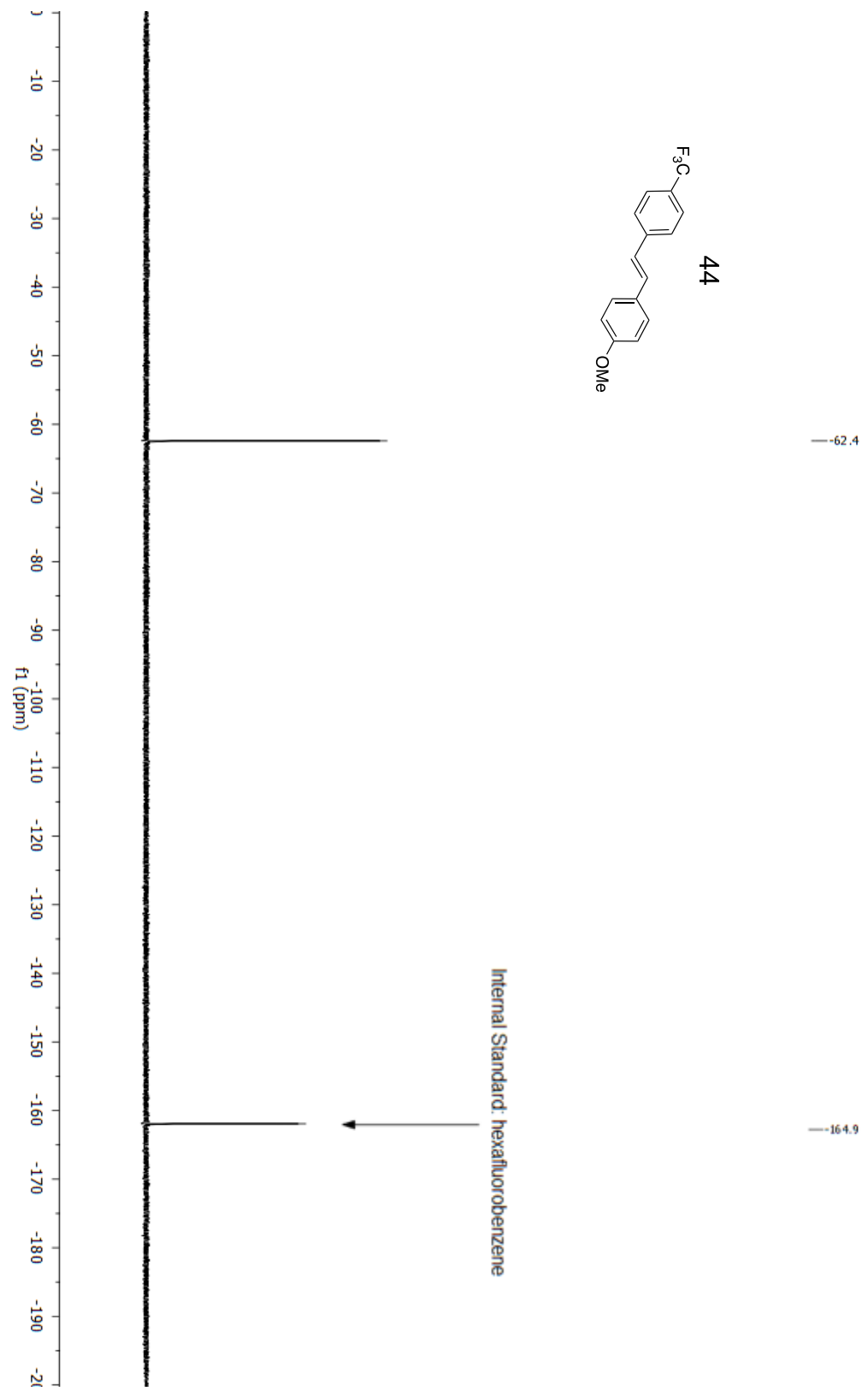
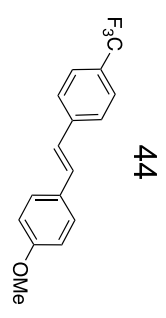
GC Trace of Crude Reaction Mixture



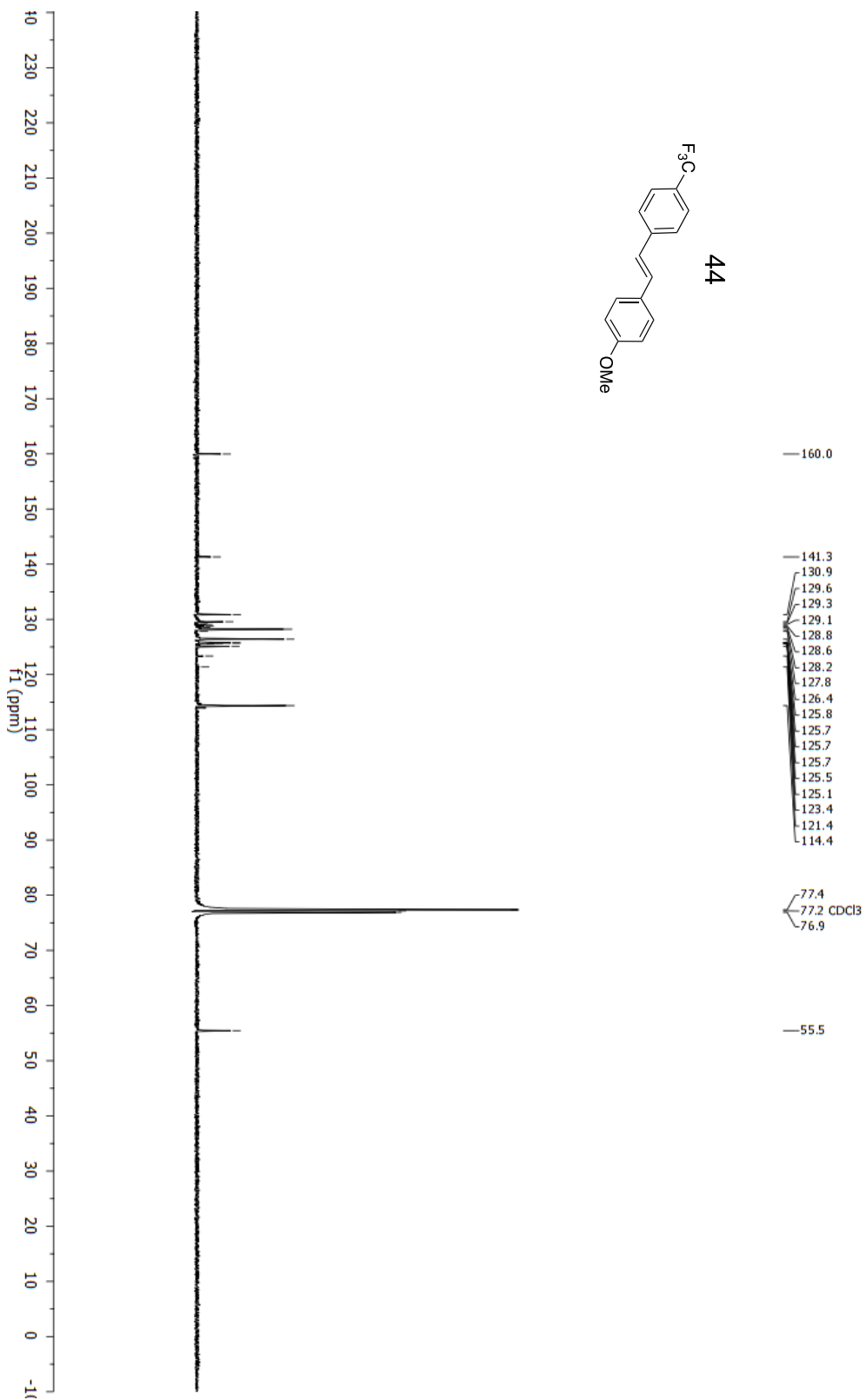
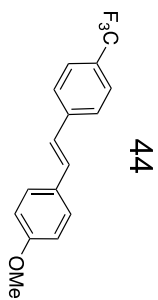
¹H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 16.4 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H).



¹⁹F NMR (471 MHz, CDCl₃) δ -62.4.

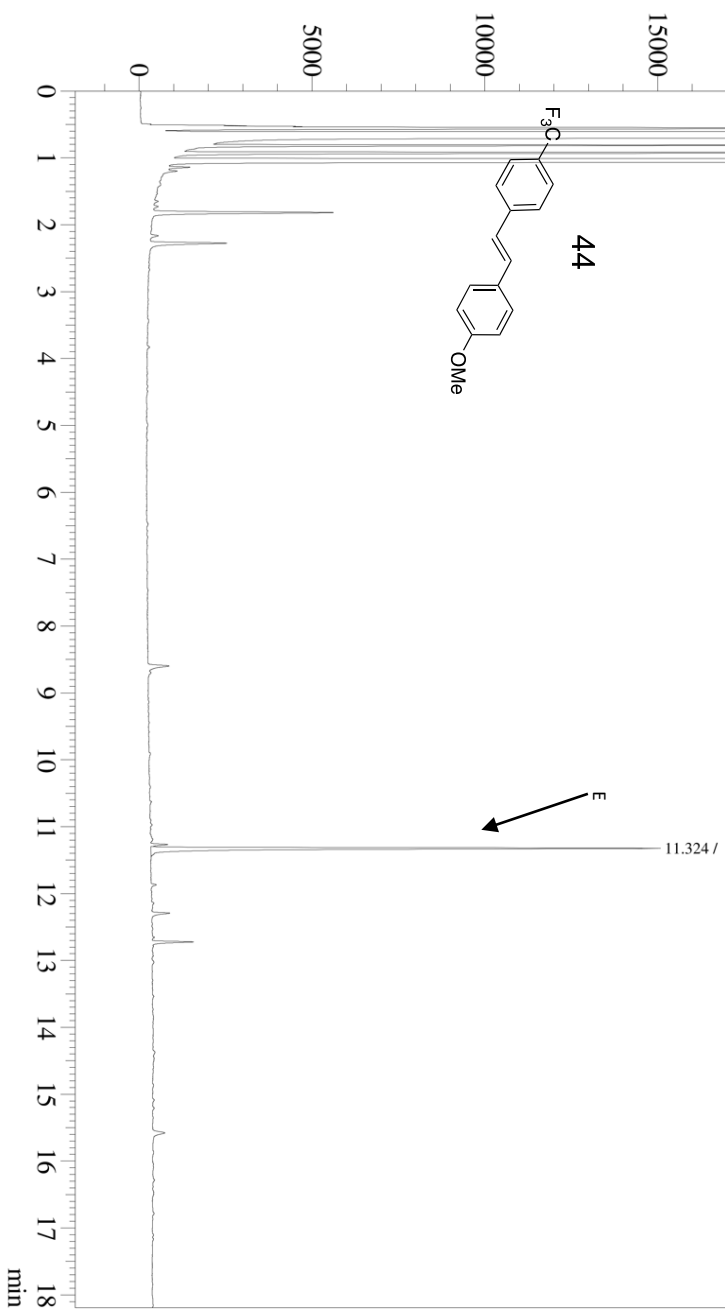


^{13}C NMR (126 MHz, Chloroform- d) δ 160.0, 141.3, 130.9, 129.6, 129.0 (q, $J = 32.1$ Hz), 126.4, 125.7 (q, $J = 4.3$ Hz), 125.1, 124.4 (q, $J = 271.4$ Hz), 114.4, 55.5.



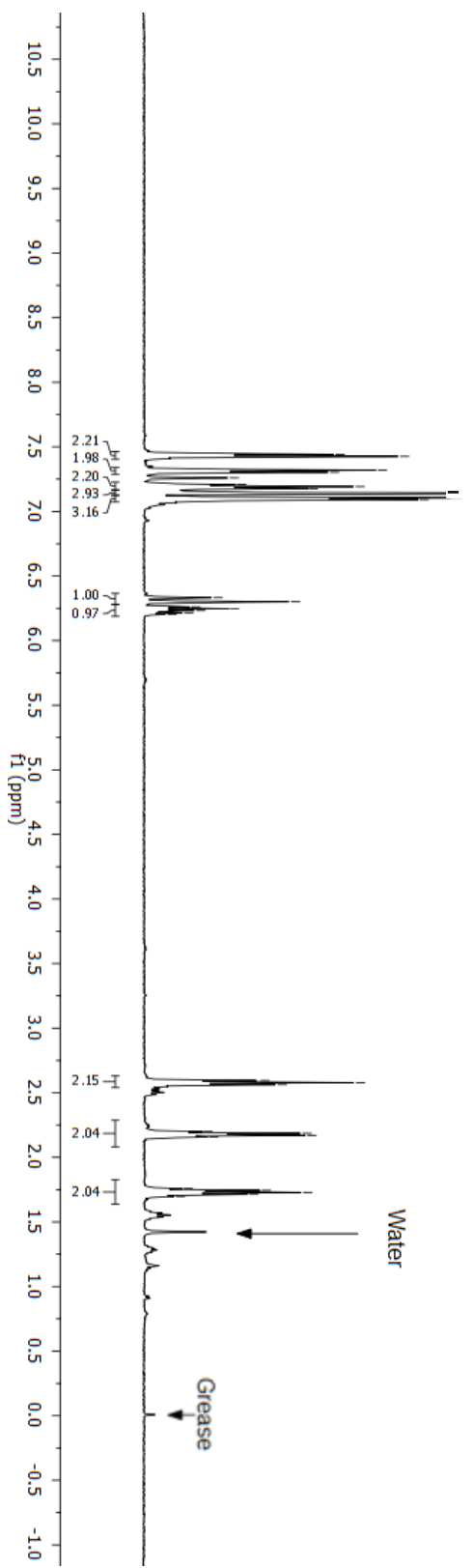
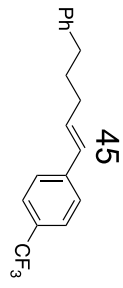
Intensity

GC Trace of Crude Reaction Mixture

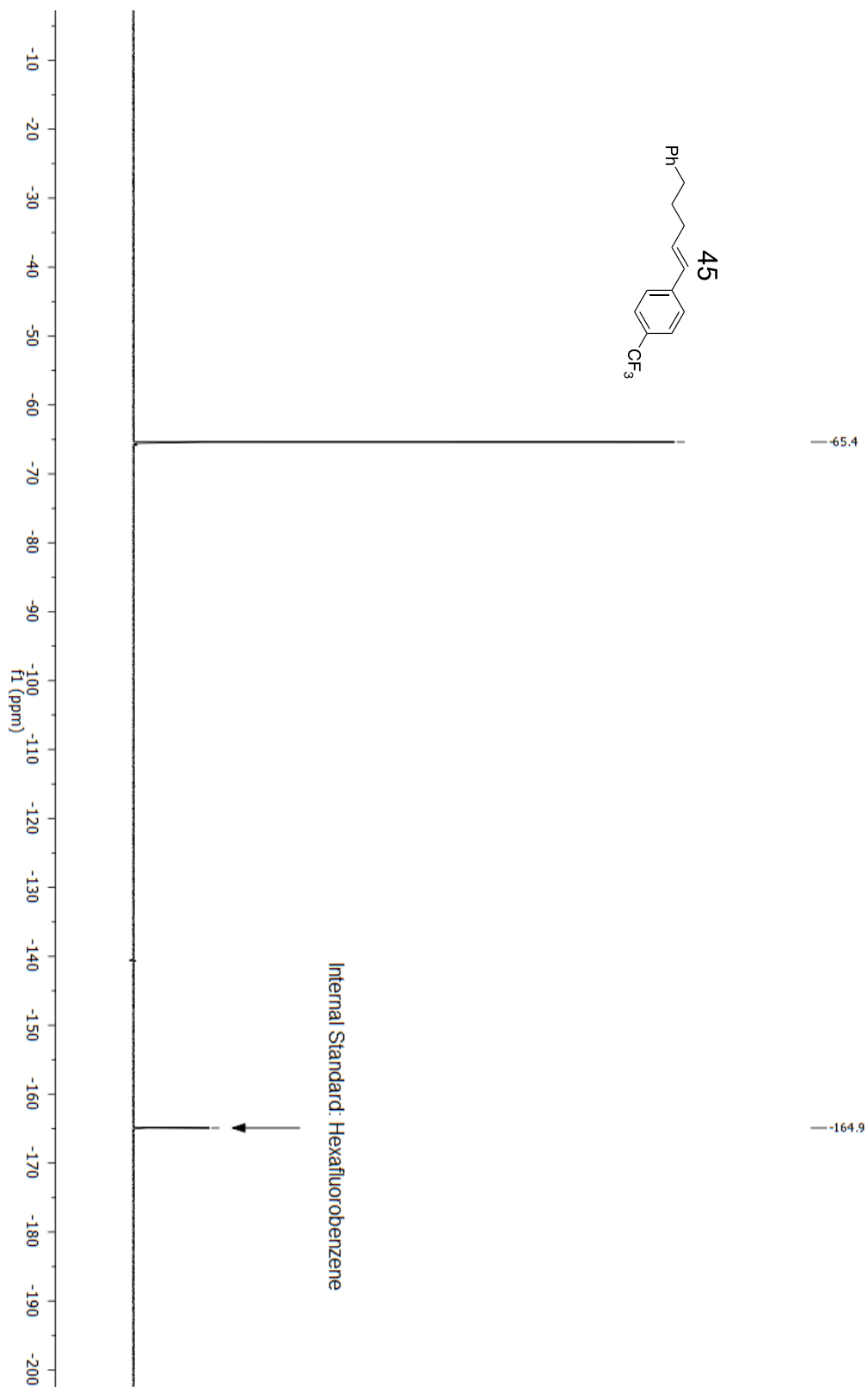
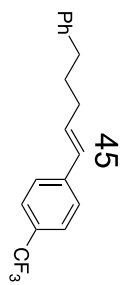


Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.324	24744	14558	100.000		V		
Total		24744	14558					

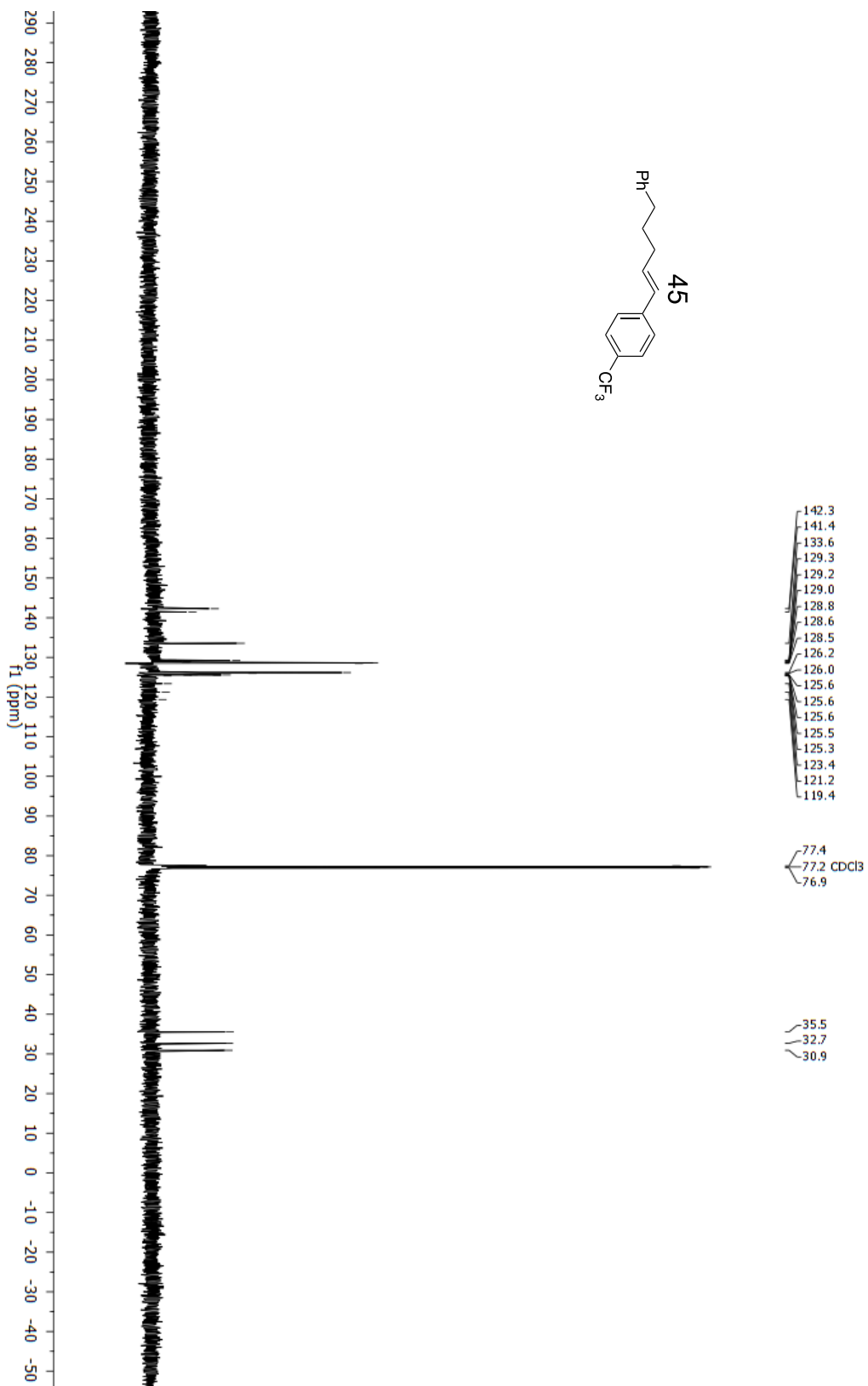
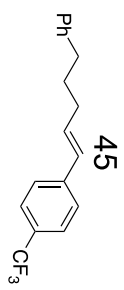
¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.14 (s, 3H), 7.10 (d, *J* = 7.1 Hz, 3H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.3, 6.6 Hz, 1H), 2.58

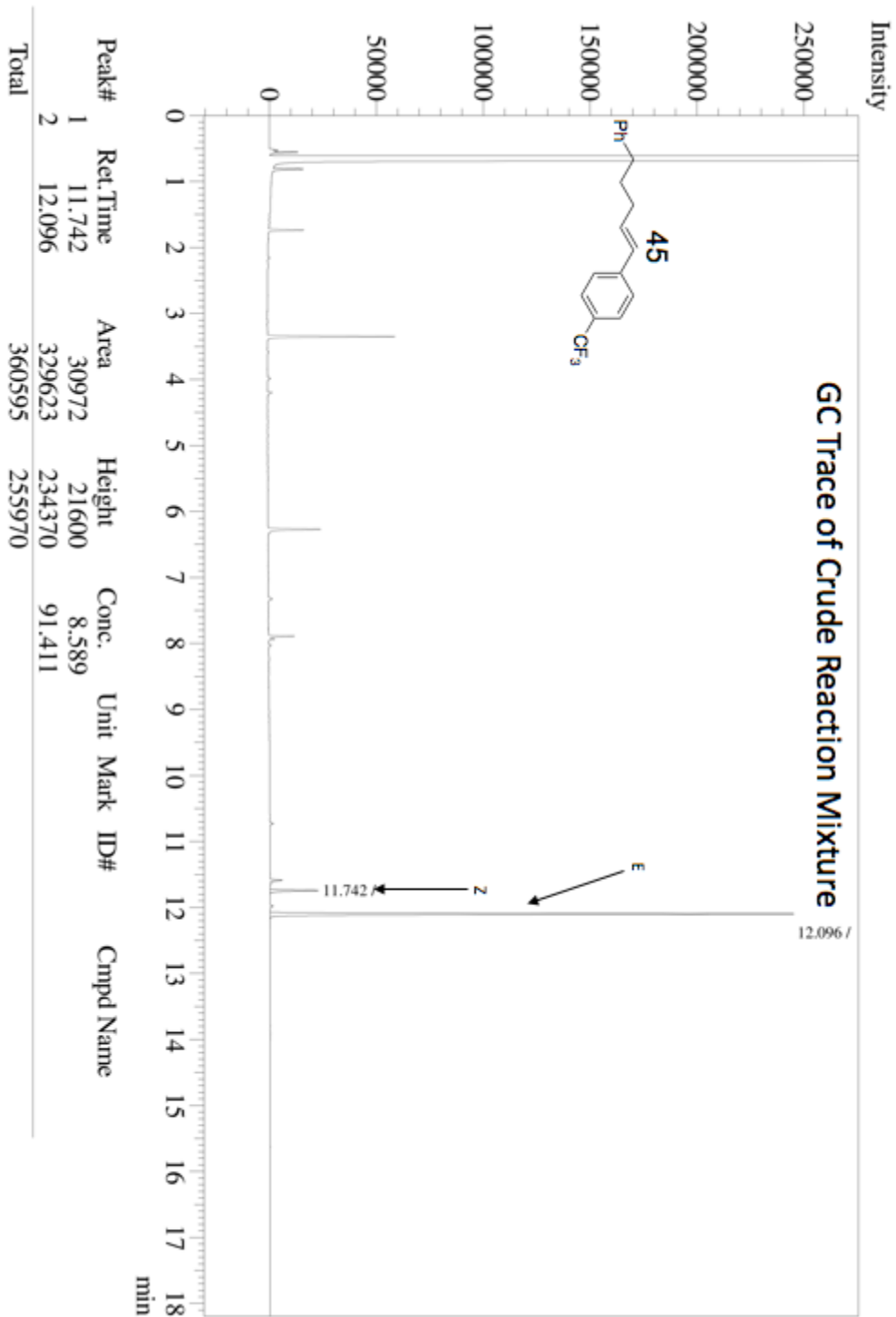


¹⁹F NMR (471 MHz, Chloroform-d) δ -65.4.

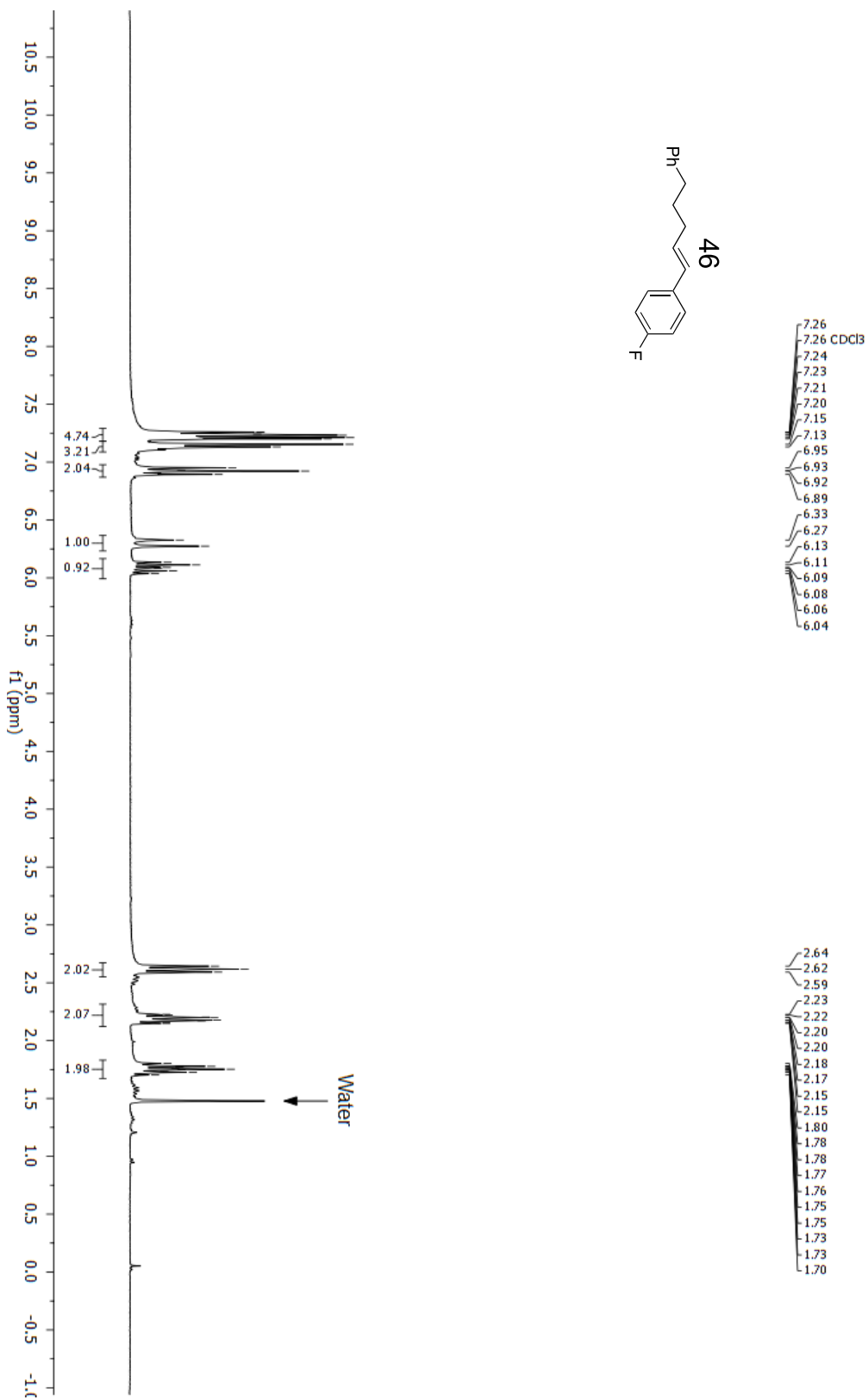
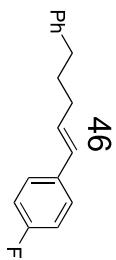


¹³C NMR (126 MHz, Chloroform-*d*) δ 142.3, 141.4, 133.6, 129.3, 128.7 (q, *J* = 19.5 Hz), 128.6, 128.5, 126.0, 125.6, 125.4 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 271.2 Hz), 35.5, 32.7, 30.9.

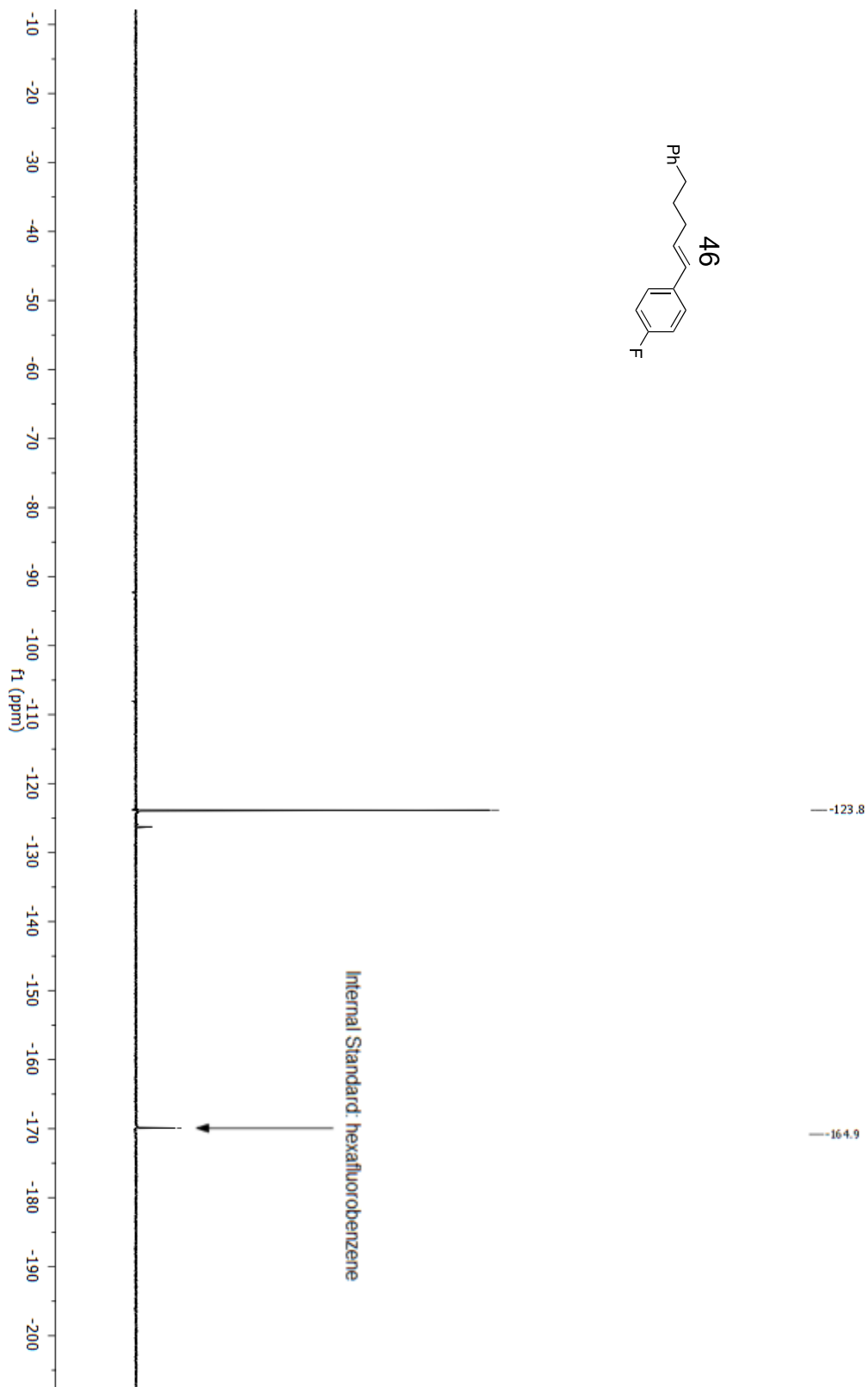
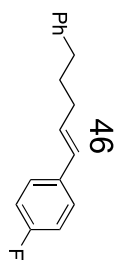




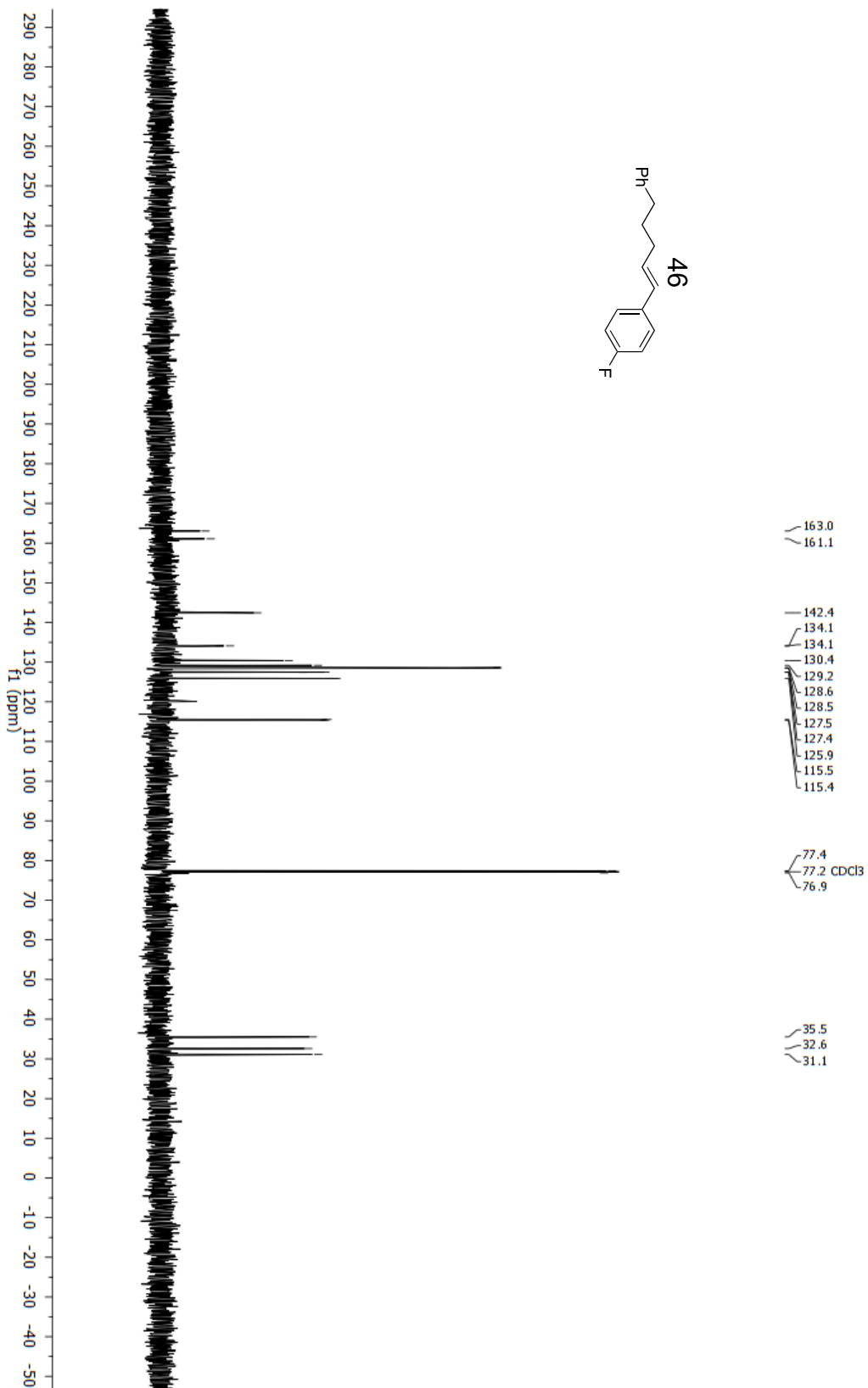
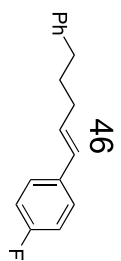
¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.17 (m, 5H), 7.14 (d, *J* = 6.7 Hz, 2H), 6.99 – 6.86 (m, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.19 (dt, *J* = 8.2, 7.6, 6.2 Hz, 2H), 1.85 – 1.66 (m, 2H).

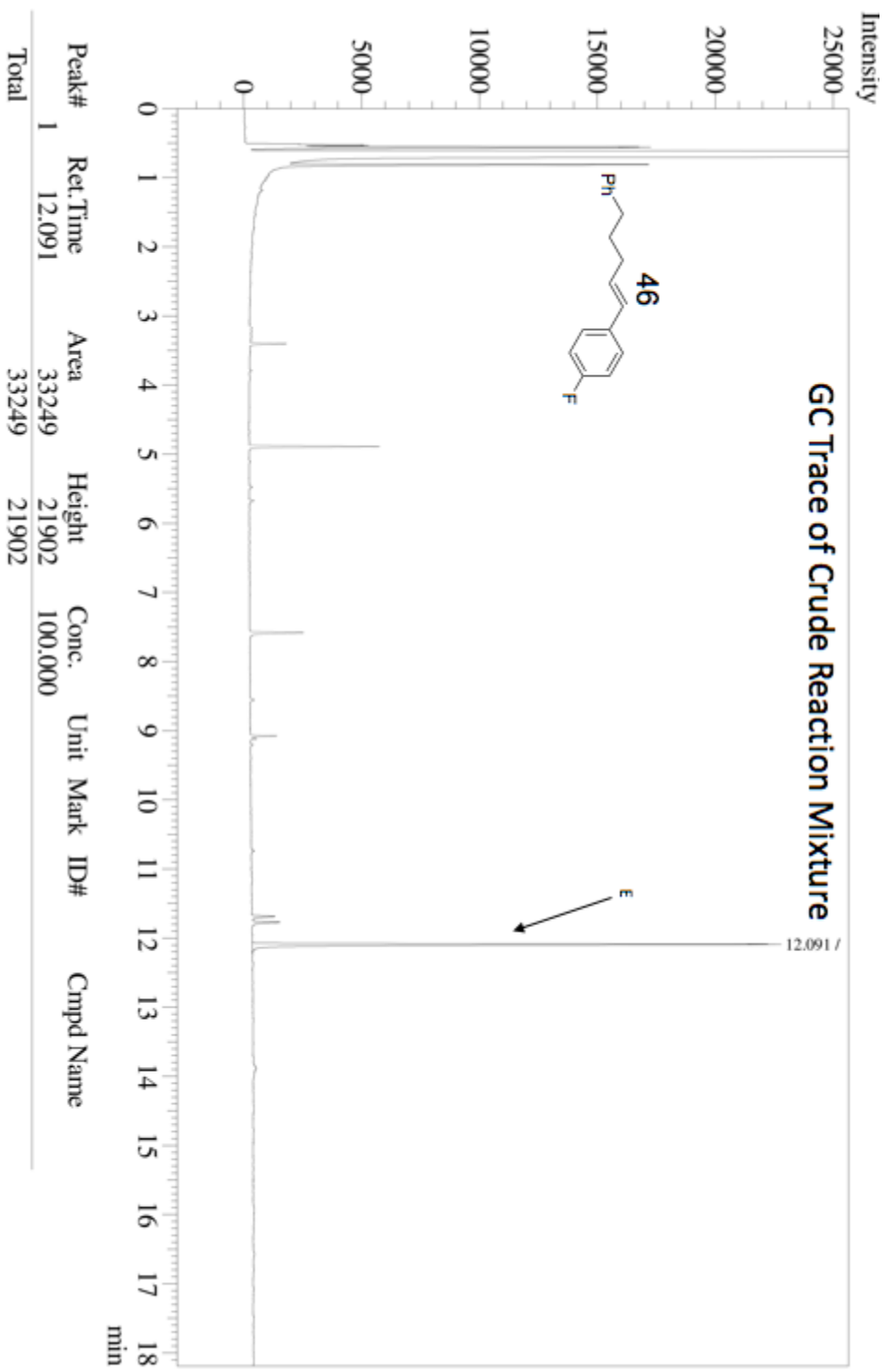


¹⁹F NMR (471 MHz, Chloroform-d) δ -123.8.

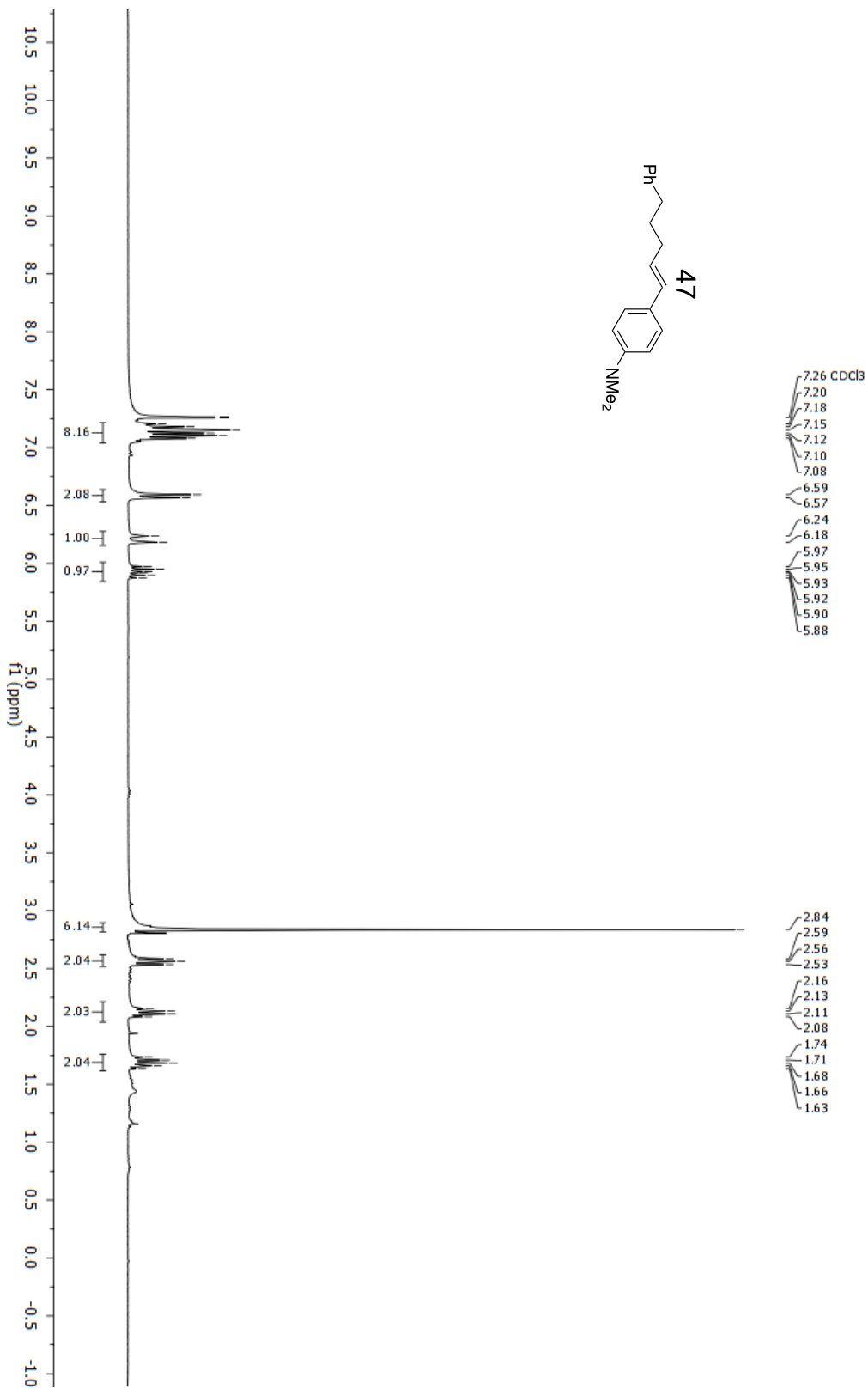
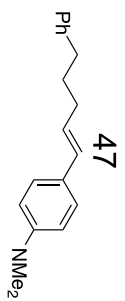


¹³C NMR (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.6 Hz), 142.4, 134.1 (d, *J* = 2.7 Hz), 130.4, 129.2, 128.6 (d, *J* = 17.5 Hz), 127.4 (d, *J* = 7.8 Hz), 125.9, 115.5, 115.4, 35.5, 32.6, 31.1.

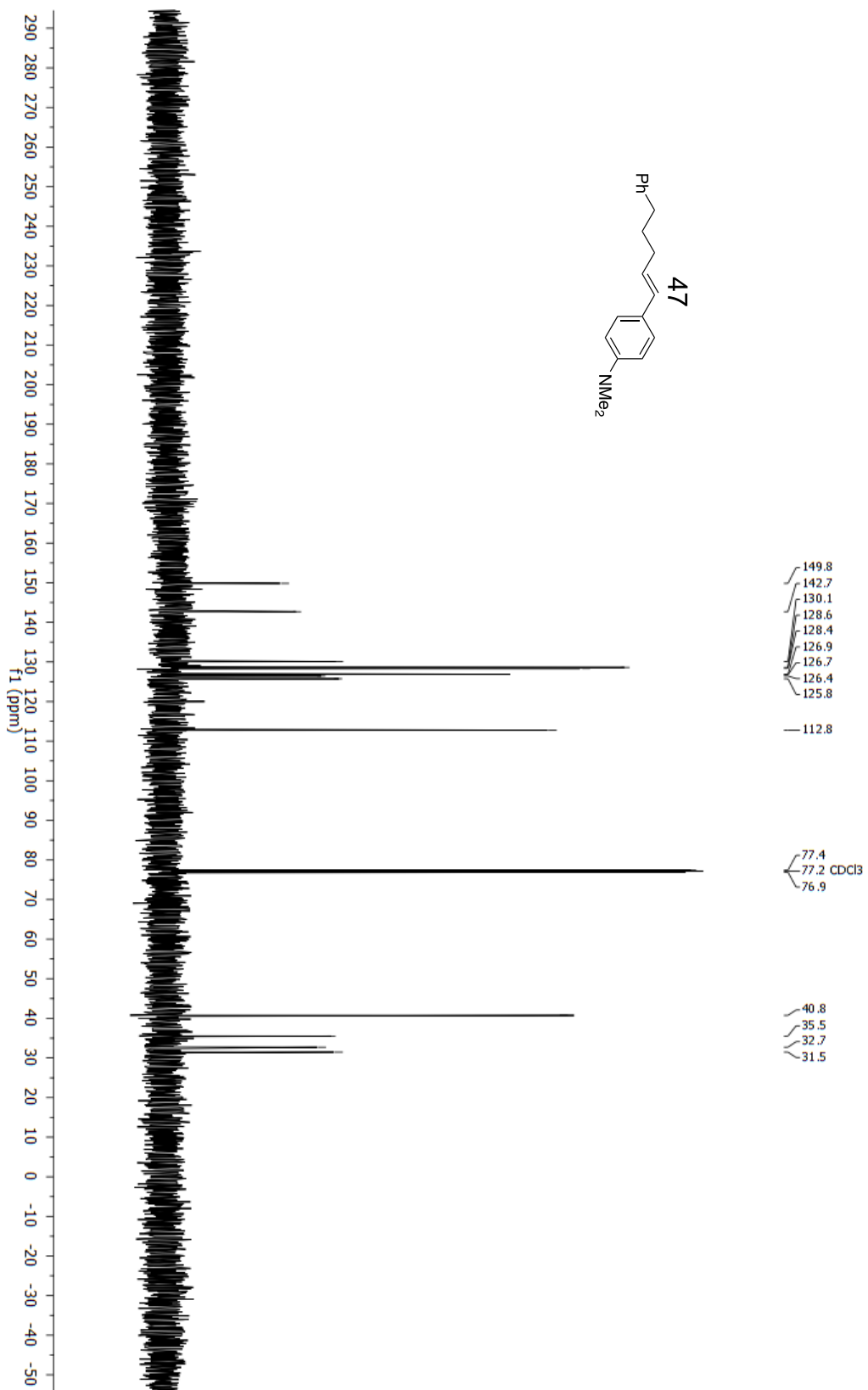
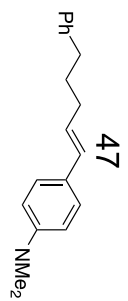


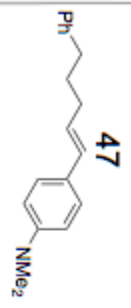
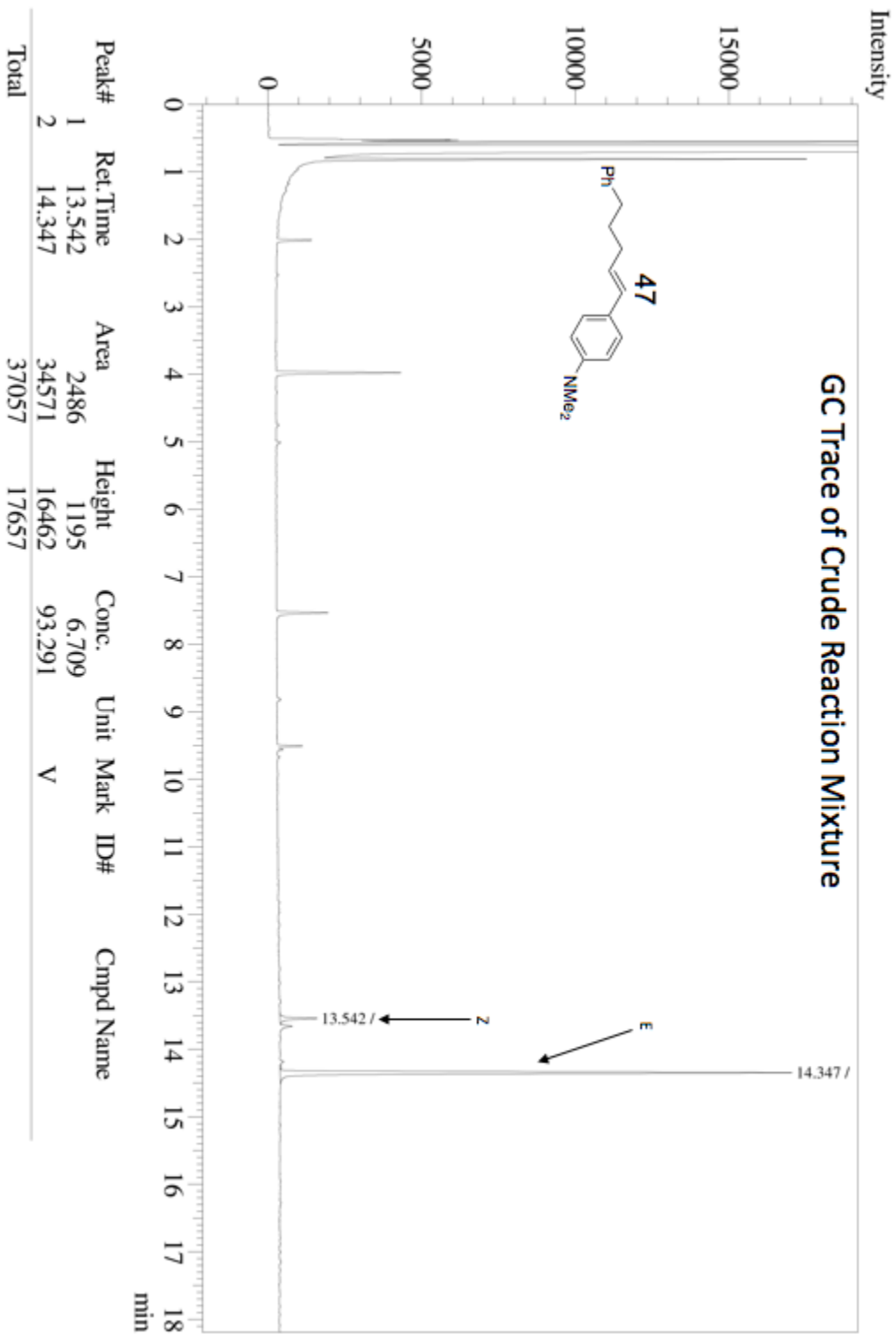


¹H NMR (300 MHz, Chloroform-d) δ 7.24–7.01 (m, 8H), 6.58 (d, J = 8.8 Hz, 2H), 6.21 (d, J = 15.8 Hz, 1H), 5.92 (dt, J = 15.7, 6.9 Hz, 1H), 2.84 (s, 6H), 2.56 (t, J = 7.6 Hz, 2H), 2.21–2.04 (m, 2H), 1.68 (p, J = 7.6 Hz, 2H).

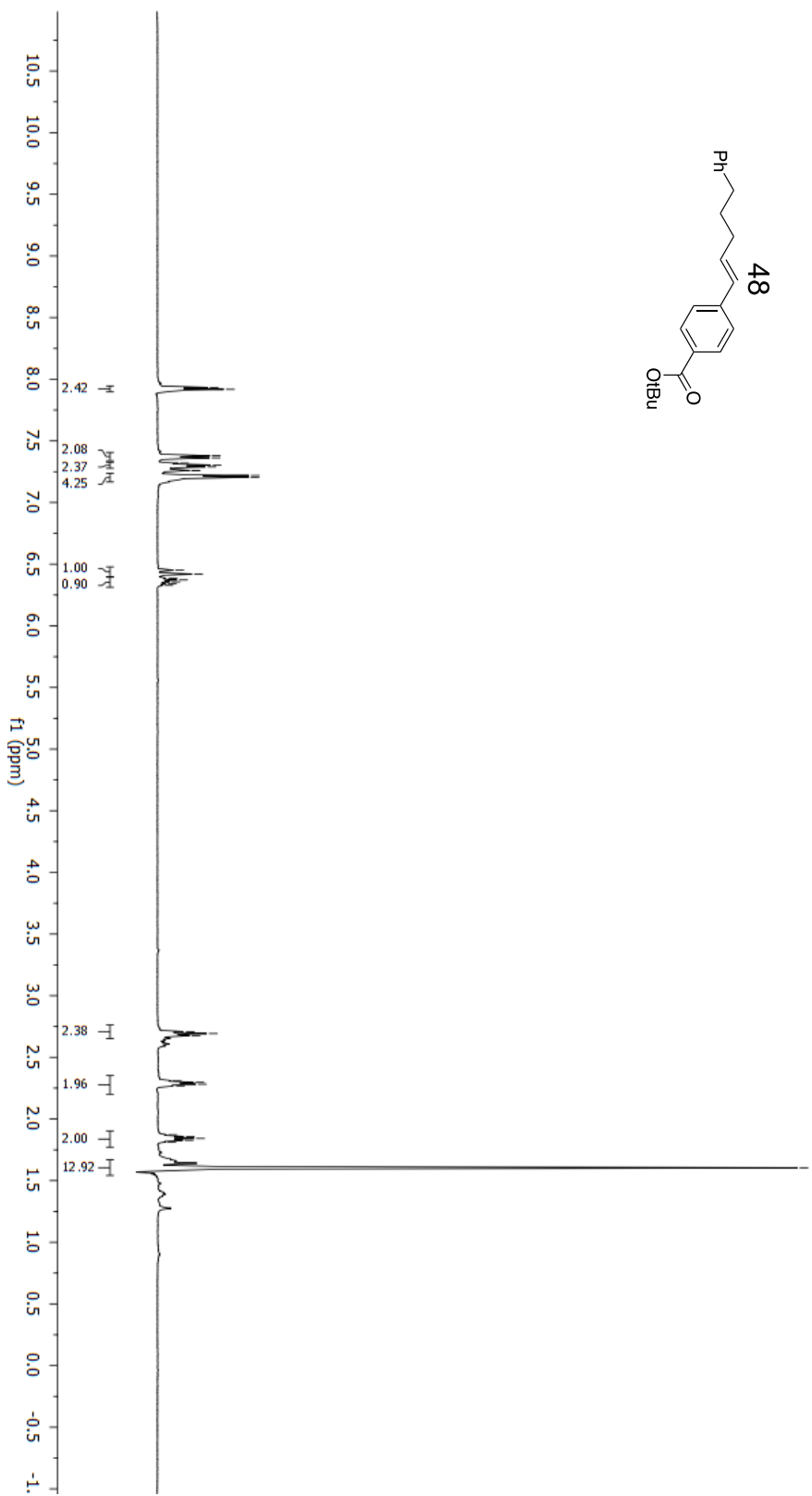
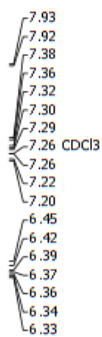


^{13}C NMR (126 MHz, Chloroform- d_3) δ 149.8, 142.7, 130.1, 128.6, 128.4, 126.9, 126.7, 126.4, 125.7, 125.8, 112.7, 40.7, 35.5, 32.7, 31.5.

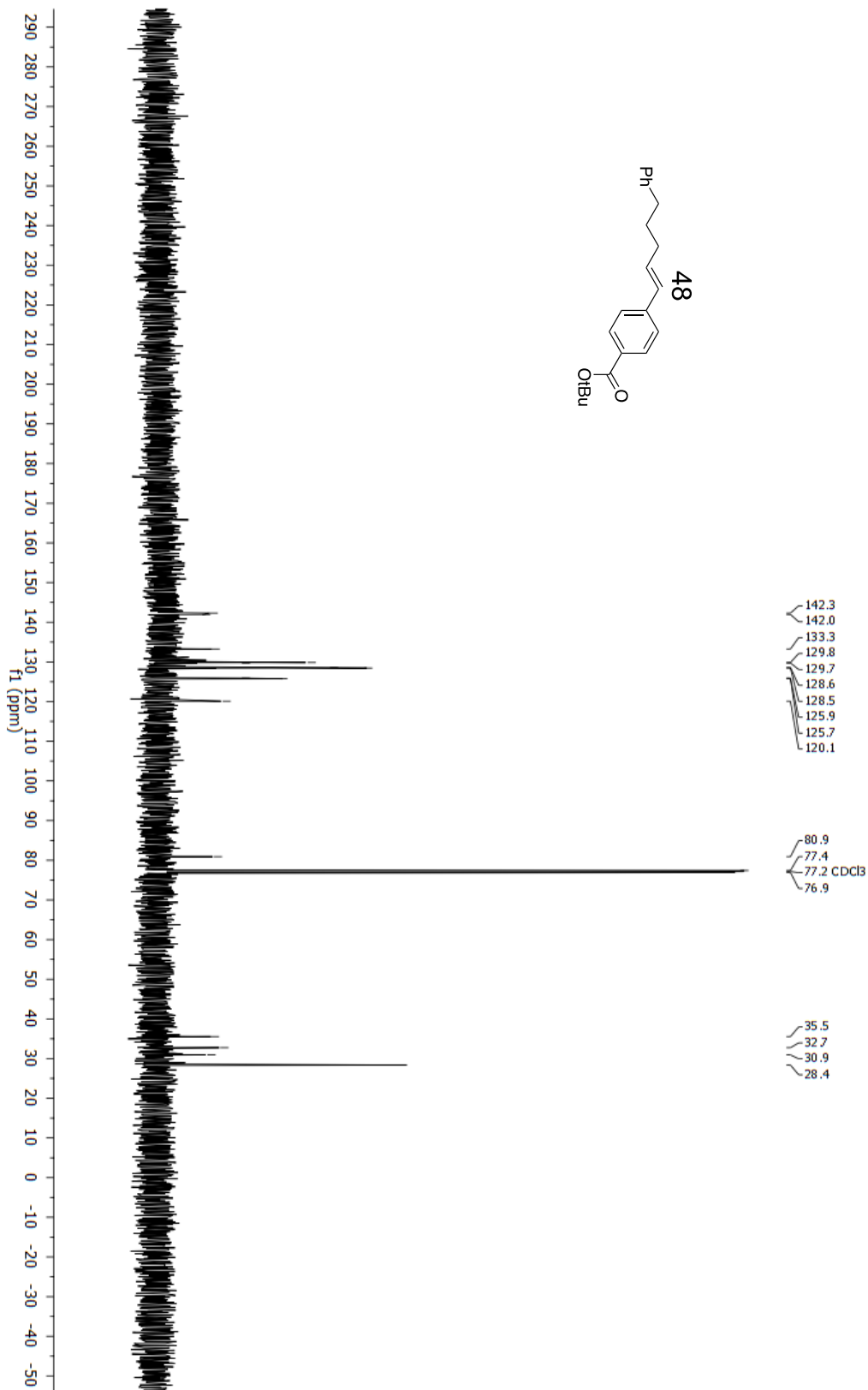
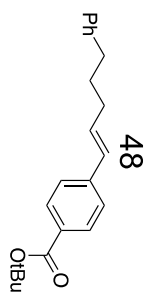


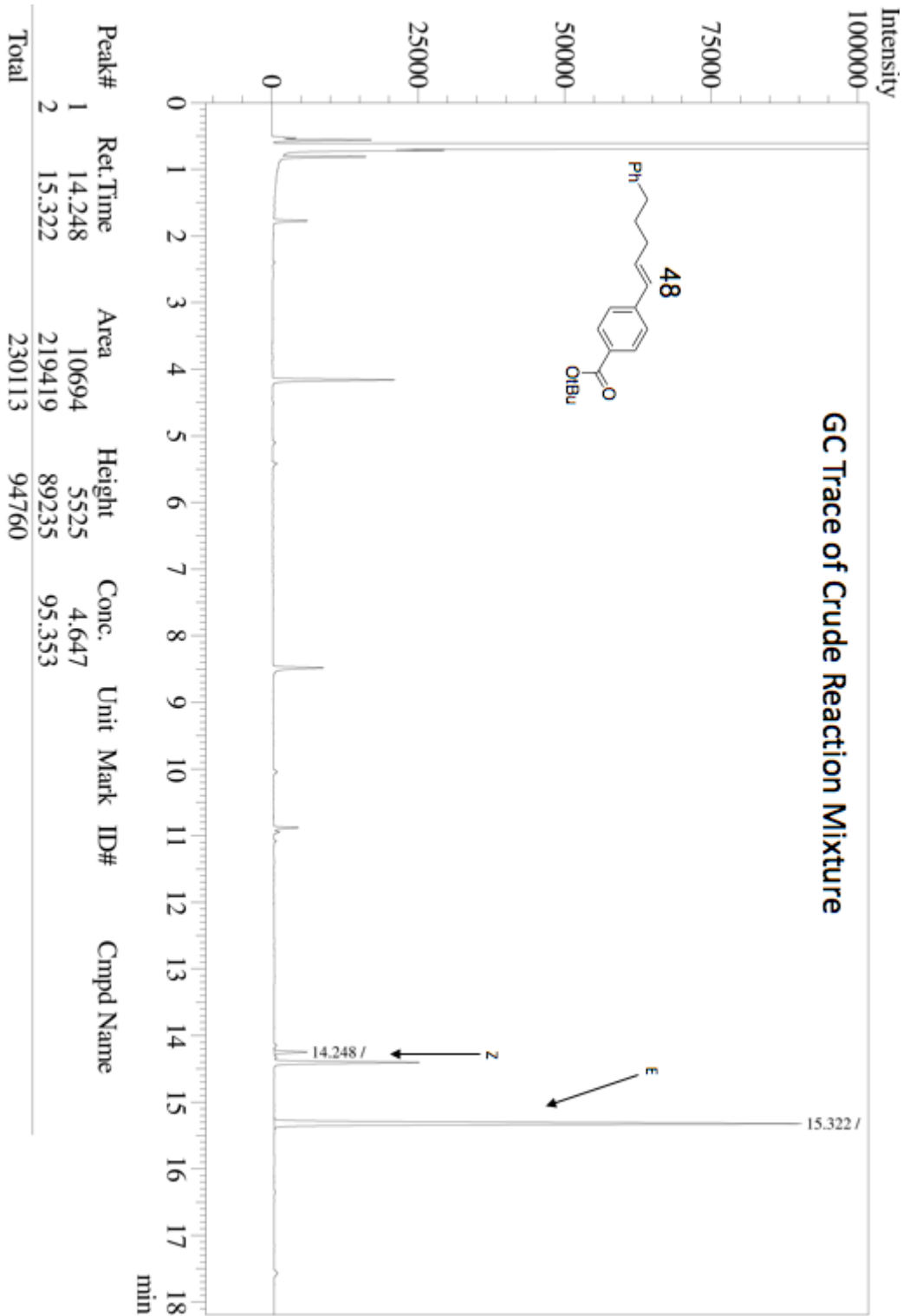


¹H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 4H), 6.44 (d, *J* = 16.1 Hz, 1H), 6.36 (dt, *J* = 14.6, 6.5 Hz, 1H), 2.69 (t, *J* = 7.9 Hz, 2H), 2.33 – 2.25 (m, 2H), 1.84 (p, *J* = 7.1 Hz, 2H), 1.60 (s, 13H).

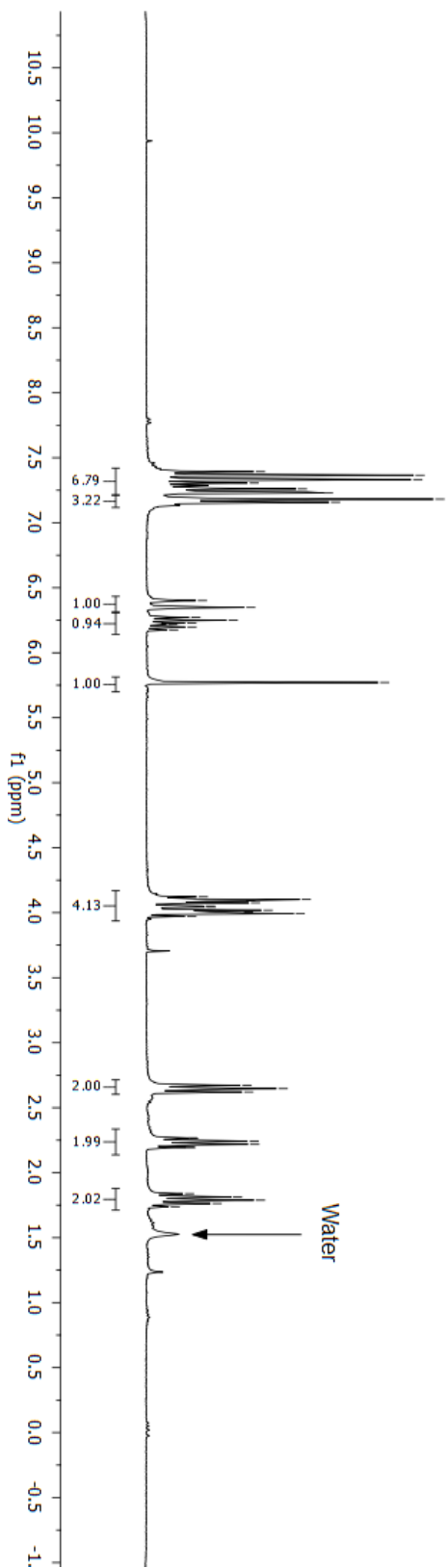
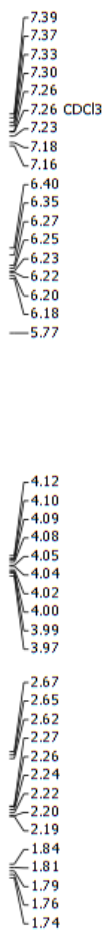


¹³C NMR (126 MHz, Chloroform-d) δ 142.3, 142.0, 133.3, 129.8, 129.7, 128.6, 128.5, 125.9, 125.7, 120.1, 80.9, 35.5, 32.7, 30.9, 28.4.

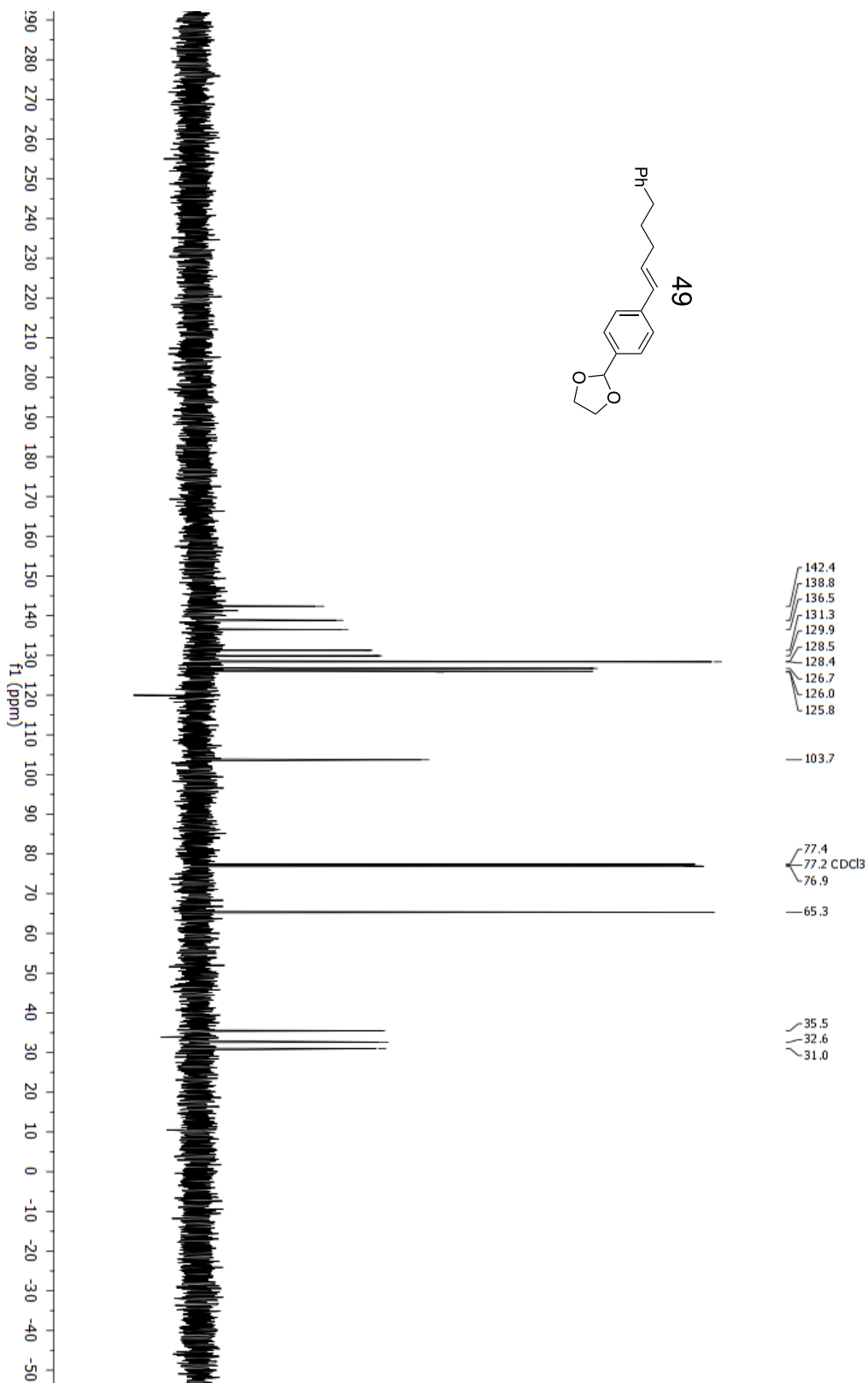
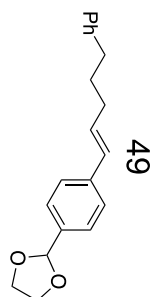


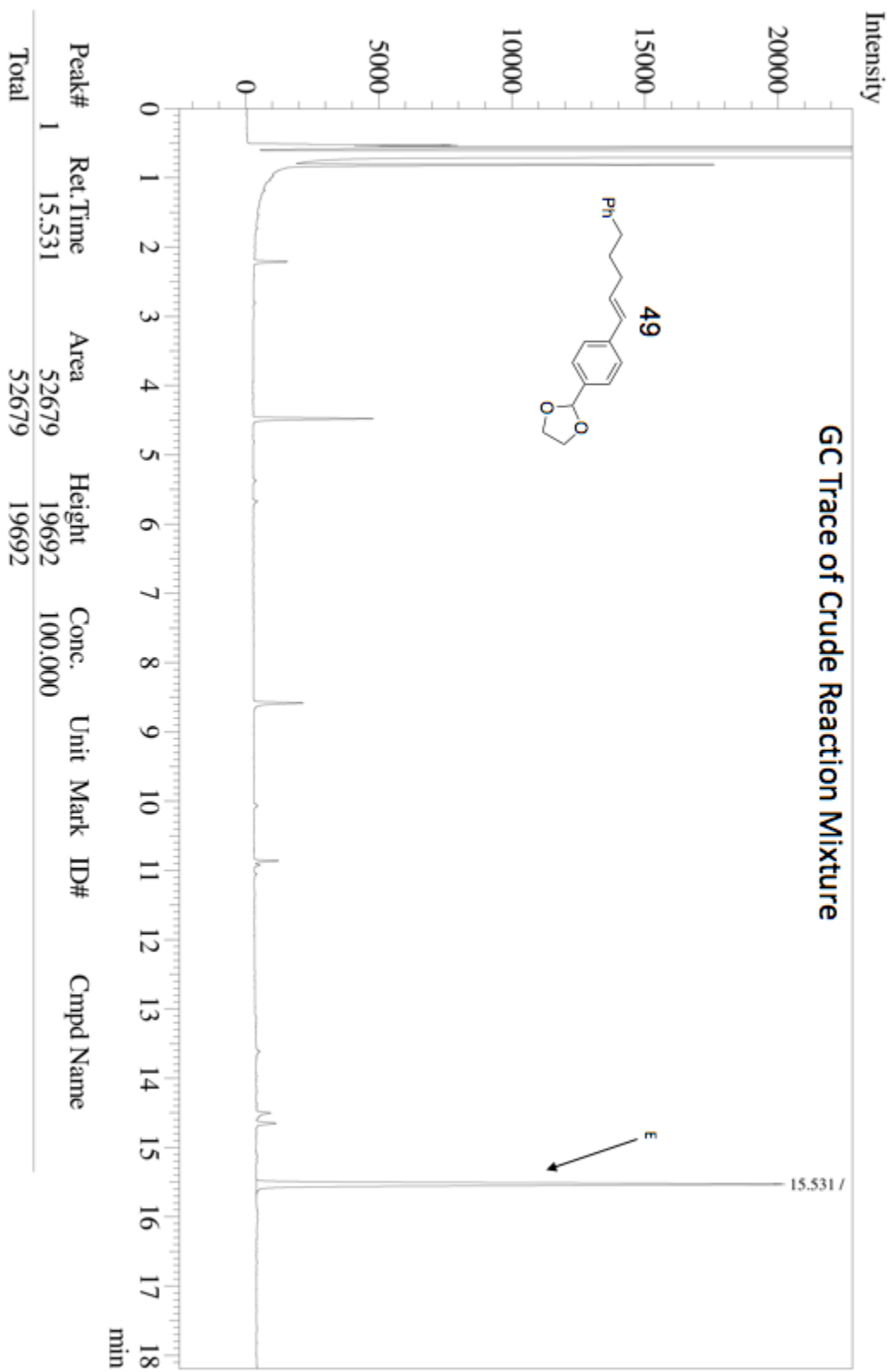


¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.20 (m, 7H), 7.17 (d, $J = 7.1$ Hz, 3H), 6.37 (d, $J = 15.9$ Hz, 1H), 6.22 (dt, $J = 15.8, 6.6$ Hz, 1H), 5.77 (s, 1H), 4.21 – 3.89 (m, 4H), 2.65 (t, $J = 7.6$ Hz, 2H), 2.31 – 2.13 (m, 2H), 1.79 (q, $J = 7.6$ Hz, 2H)

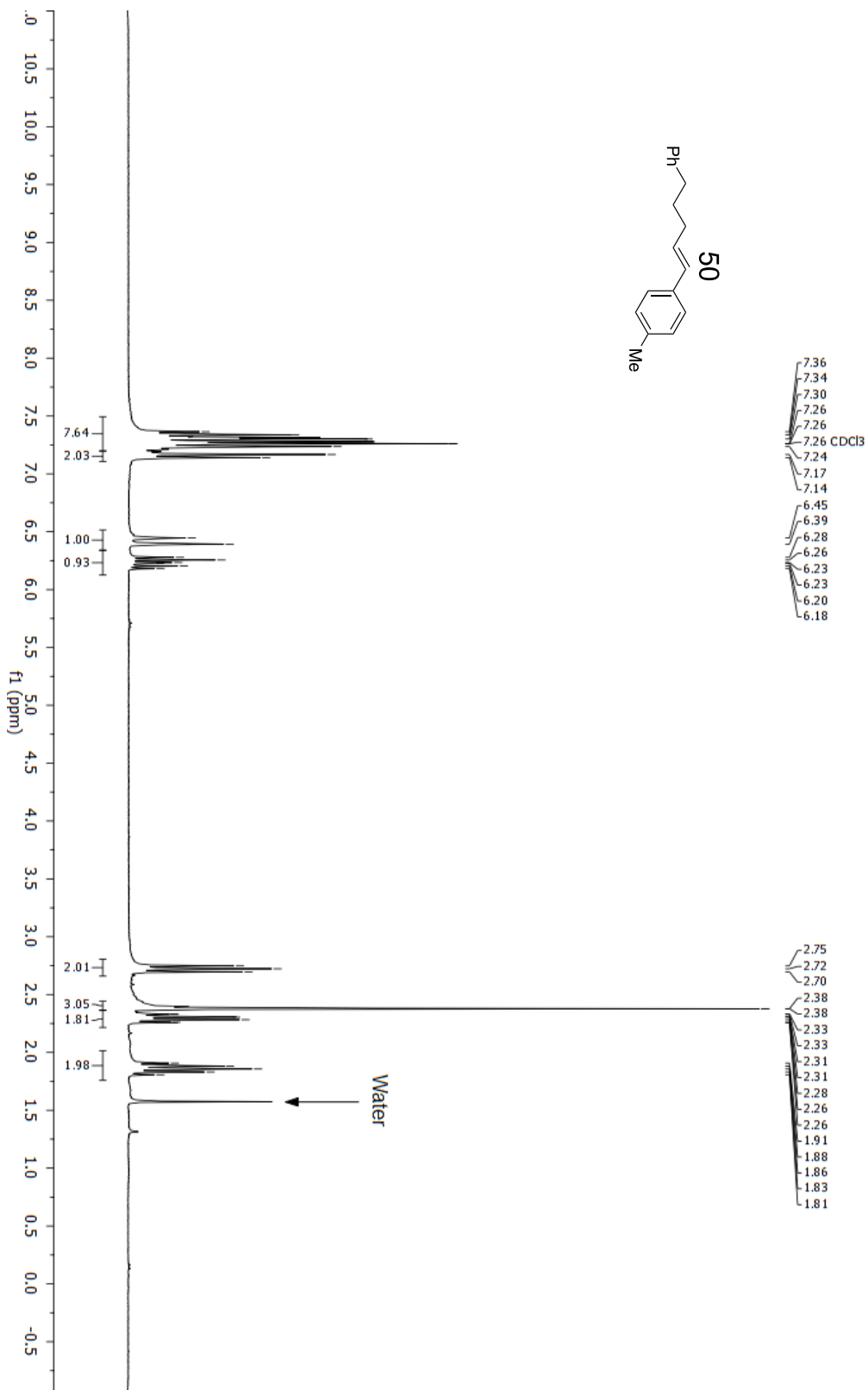
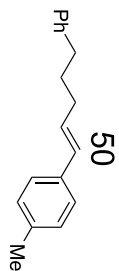


¹³C NMR (126 MHz, Chloroform-*d*) δ 142.4, 138.8, 136.5, 131.3, 129.9, 128.5, 128.4, 126.7, 126.0, 125.8, 125.8, 103.7, 65.3, 35.5, 32.6, 31.0.

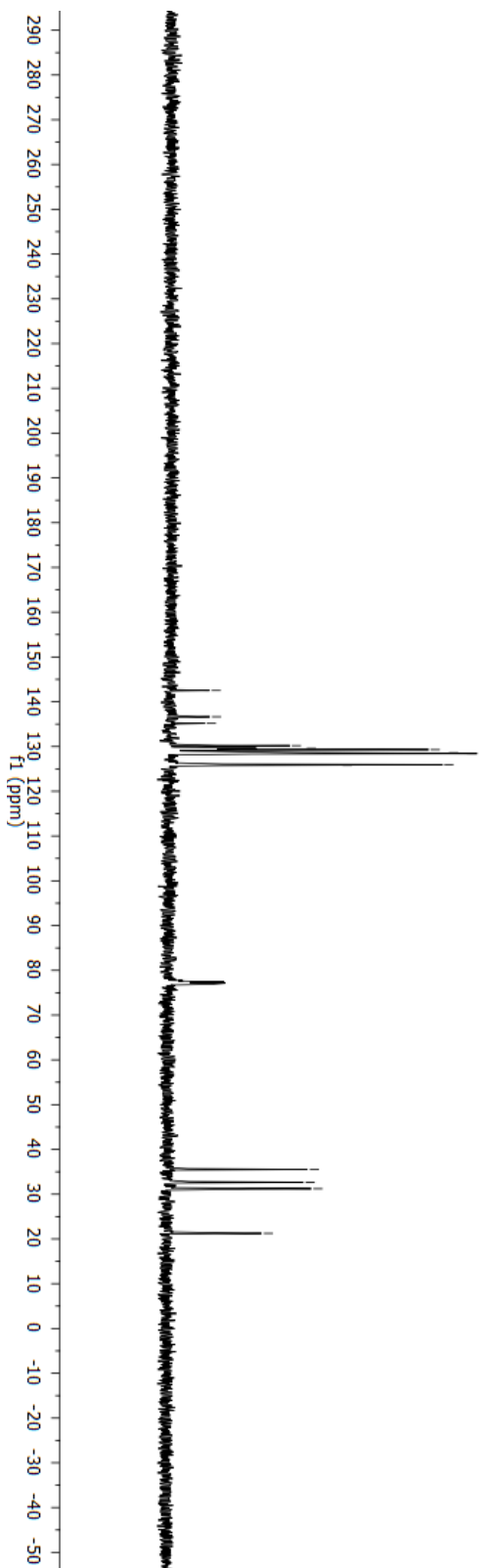
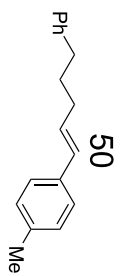
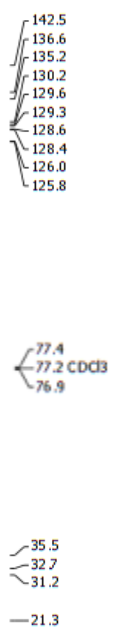


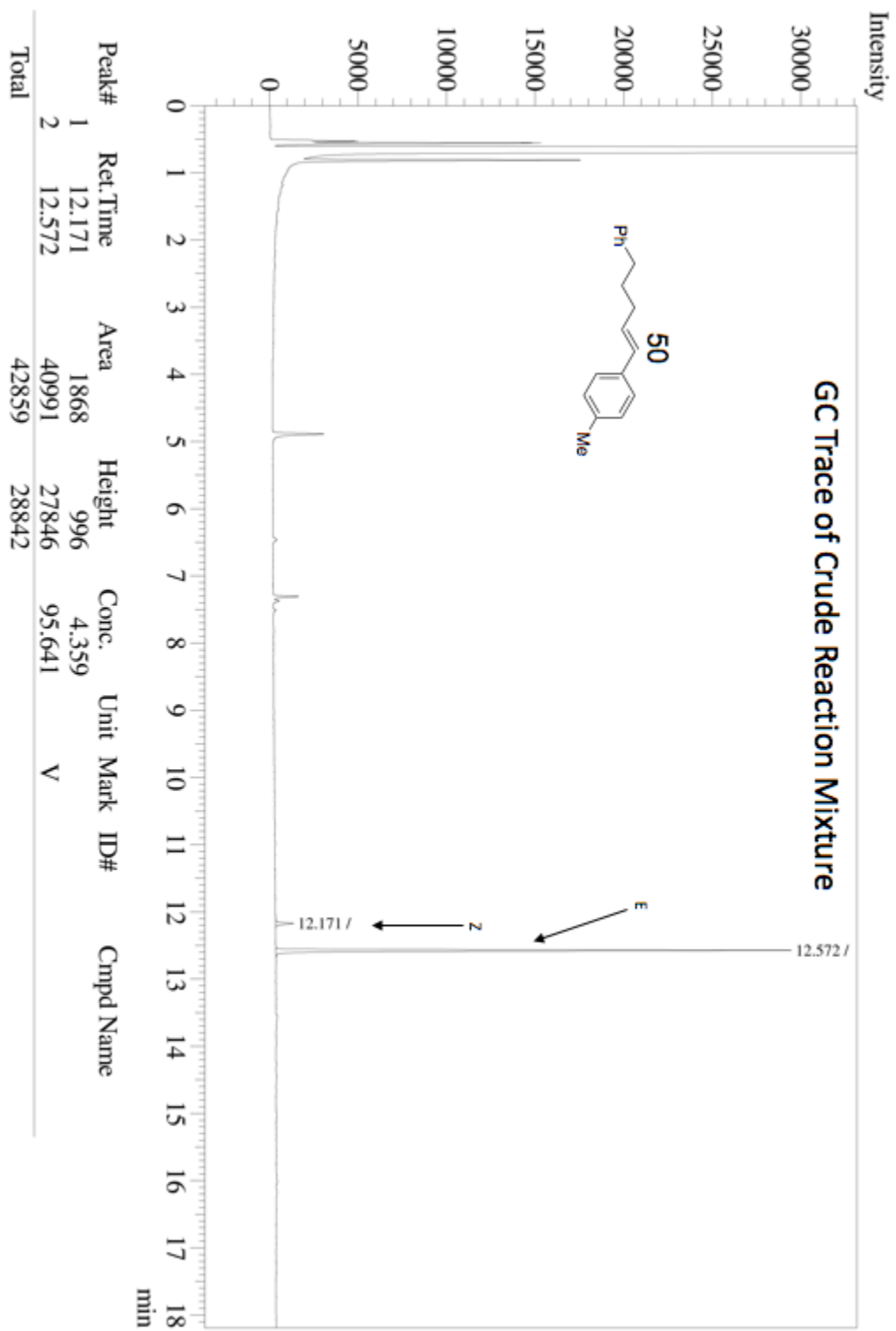


¹H NMR (300 MHz, Chloroform-d) δ 7.40 – 7.20 (m, 7H), 7.15 (d, J = 7.9 Hz, 2H), 6.42 (d, J = 15.9 Hz, 1H), 6.23 (dt, J = 15.8, 6.8 Hz, 1H), 2.81 – 2.67 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H), 2.36 – 2.23 (m, 2H), 1.86 (p, J = 7.6 Hz, 2H).

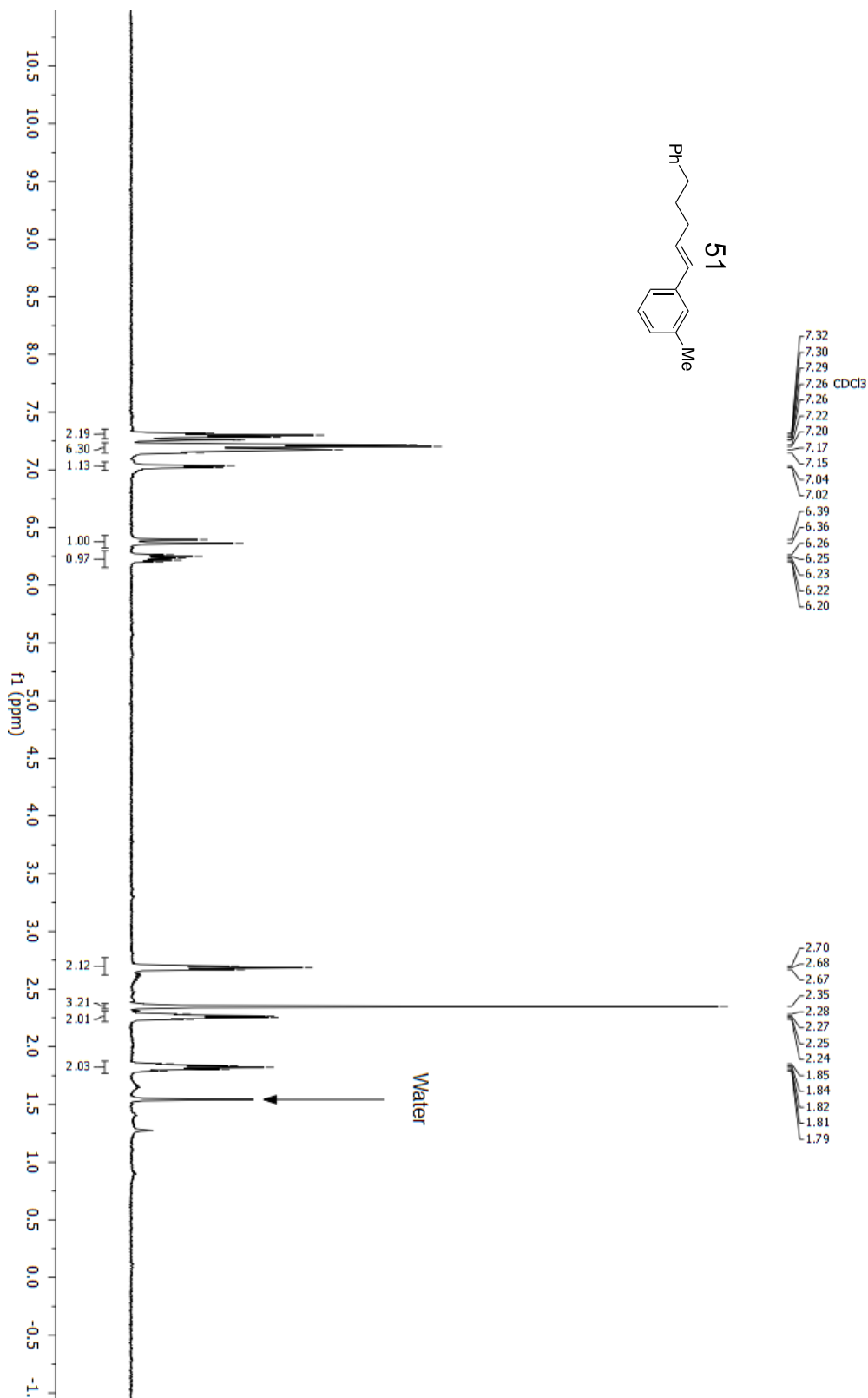
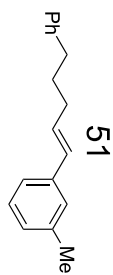


¹³C NMR (126 MHz, Chloroform-*d*) δ 142.5, 136.6, 135.2, 130.2, 129.6, 129.3, 128.6, 128.4, 126.0, 125.8, 125.8, 35.5, 32.7, 31.2, 21.3.

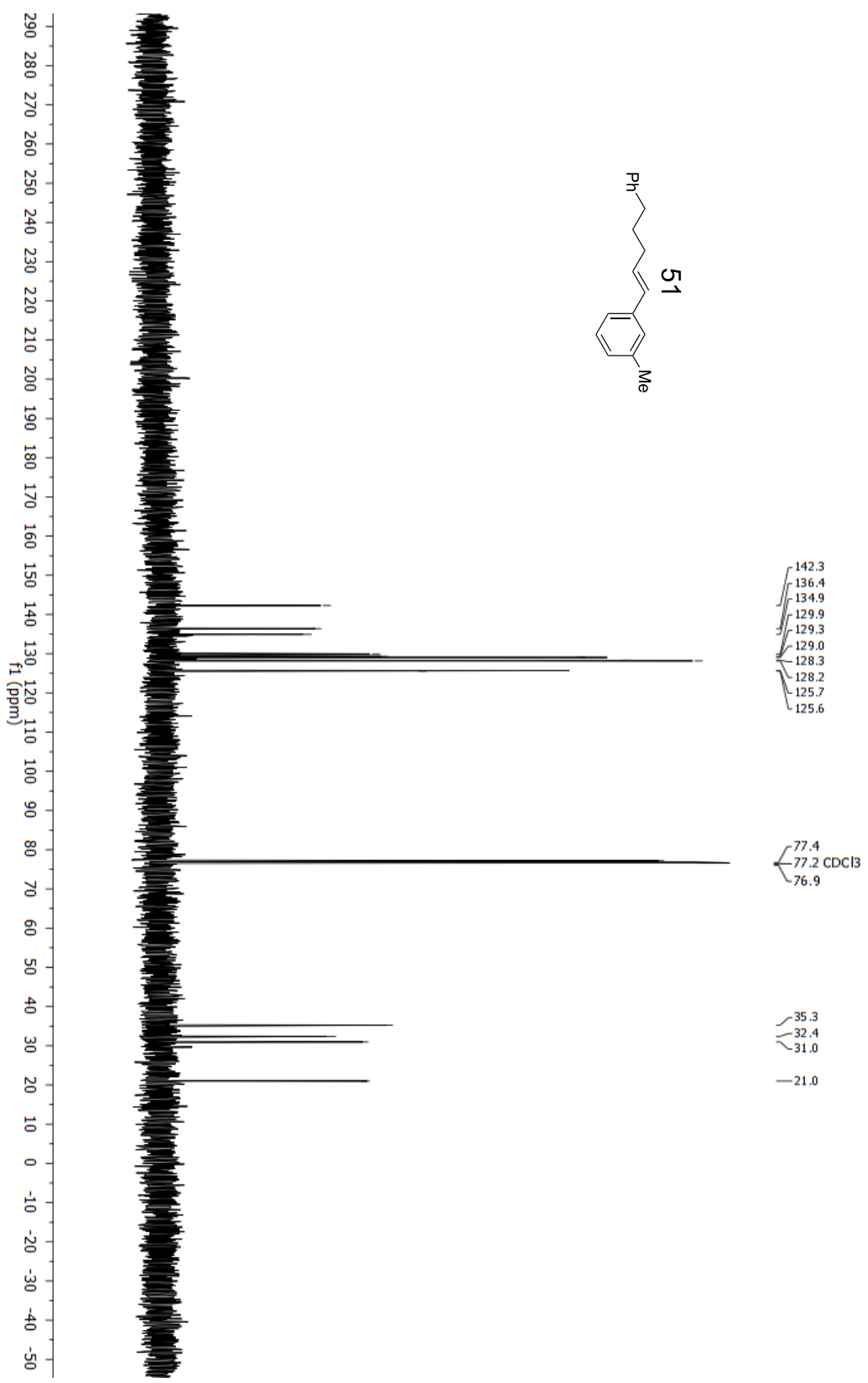
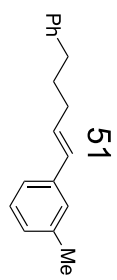


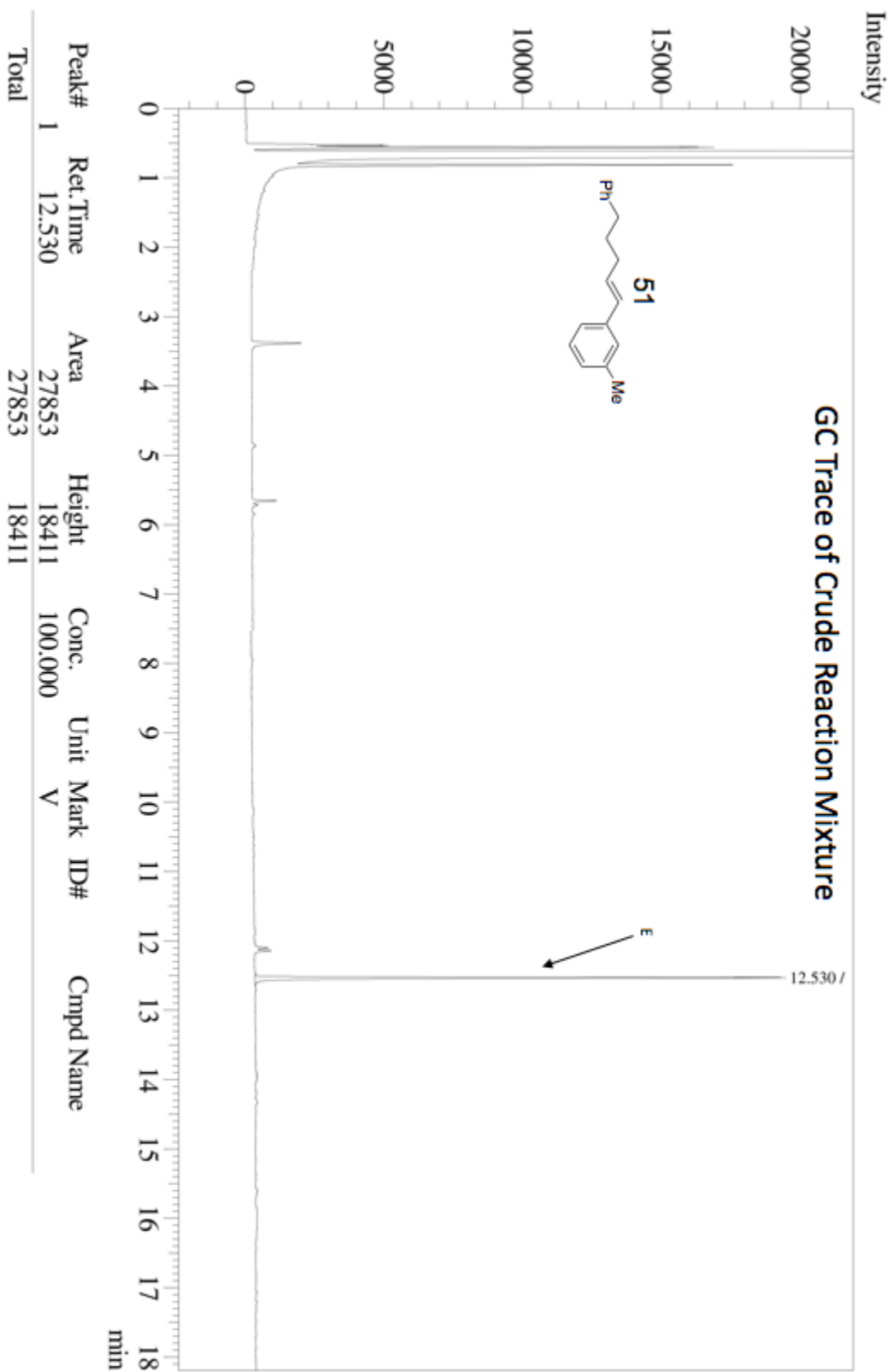


¹H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.24 (m, 2H), 7.24 – 7.12 (m, 6H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.2, 6.8 Hz, 1H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.35 (s, 3H), 2.31 – 2.18 (m, 2H), 1.82 (p, *J* = 7.4 Hz, 2H).

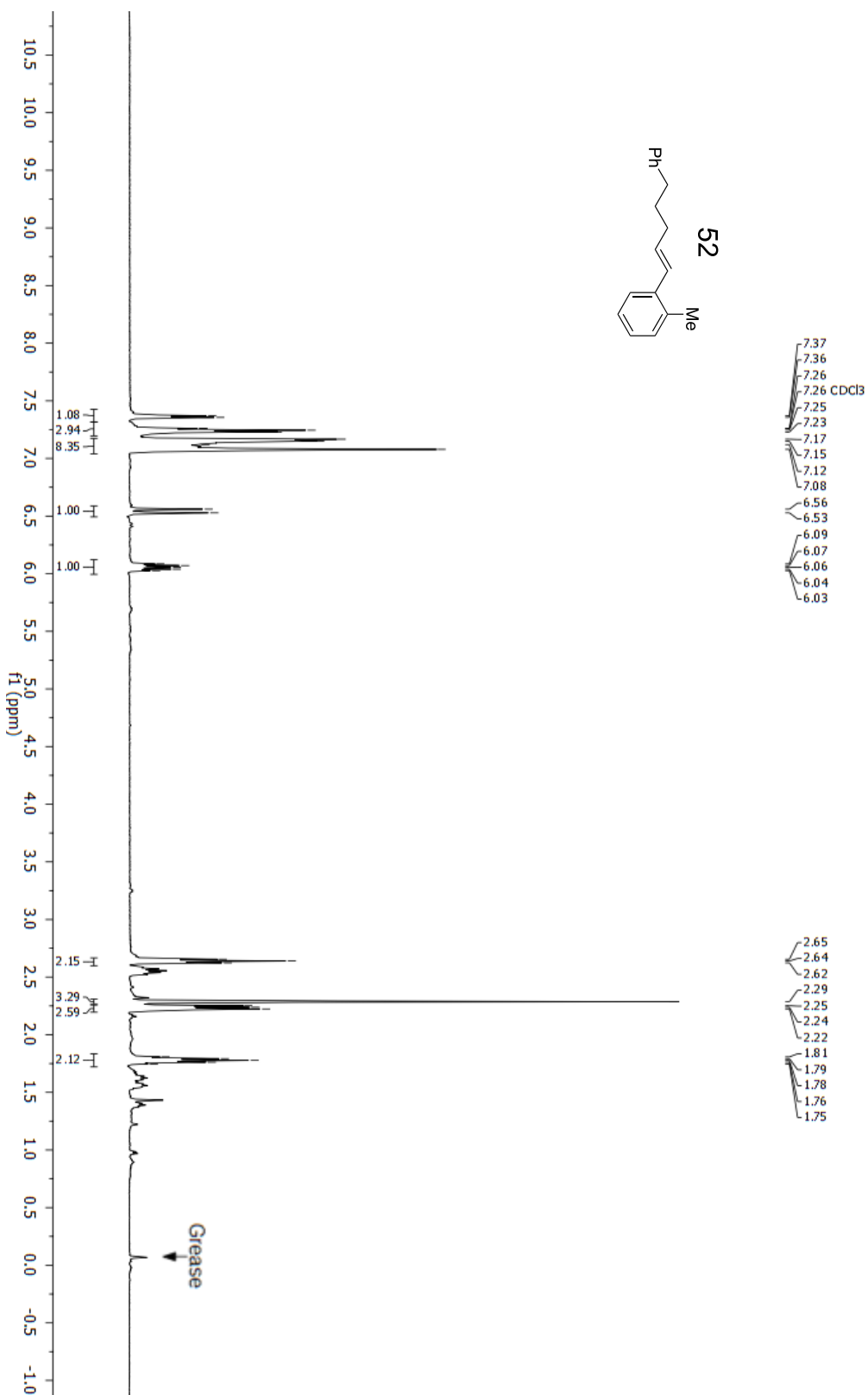
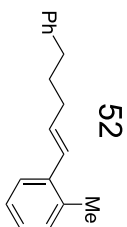


¹³C NMR (126 MHz, Chloroform-*d*) δ 142.3, 136.4, 134.9, 129.9, 129.3, 129.0, 128.3, 128.2, 125.7, 125.6, 35.3, 32.4, 31.0, 21.0.

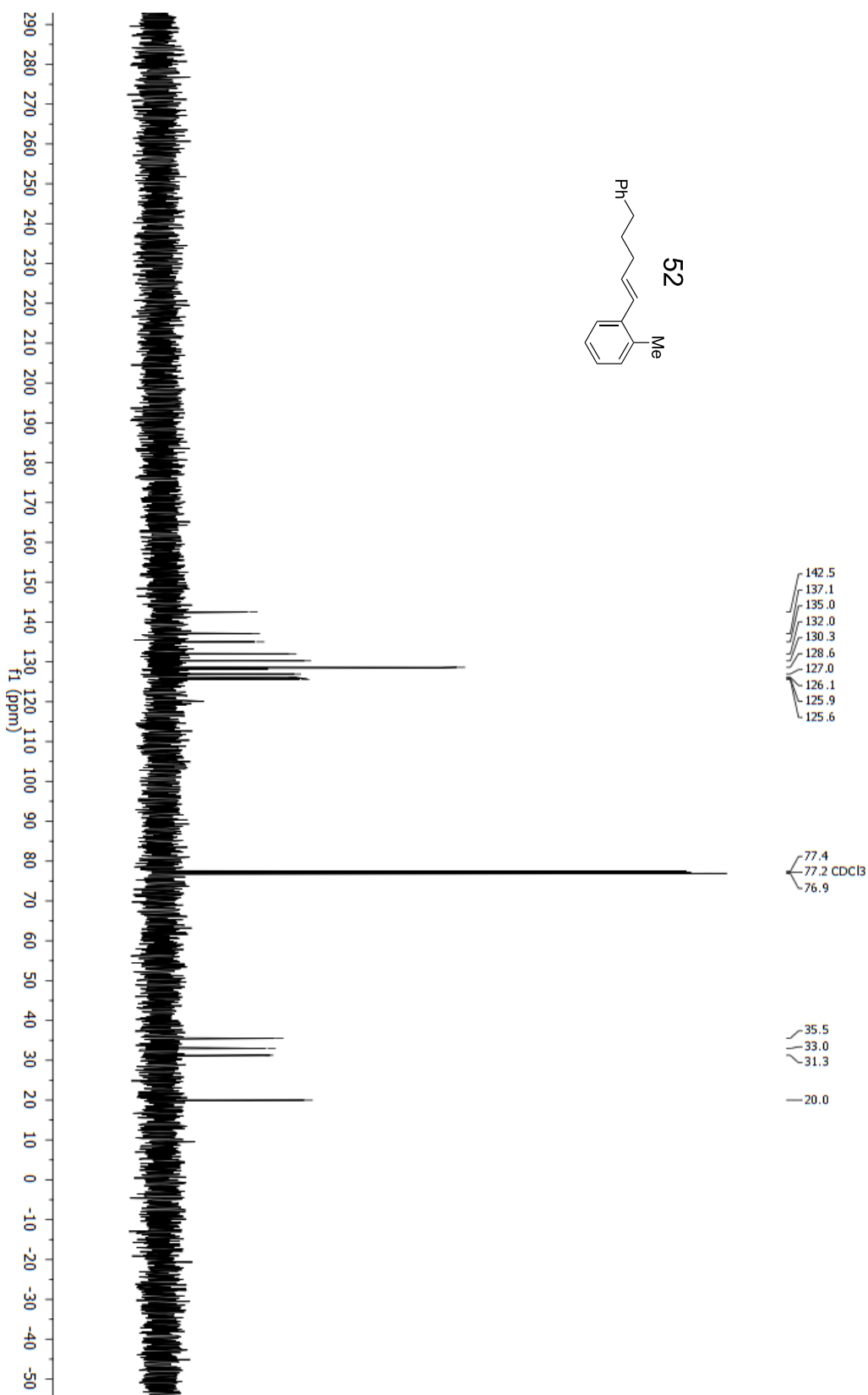
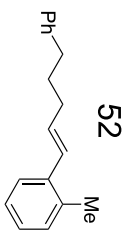


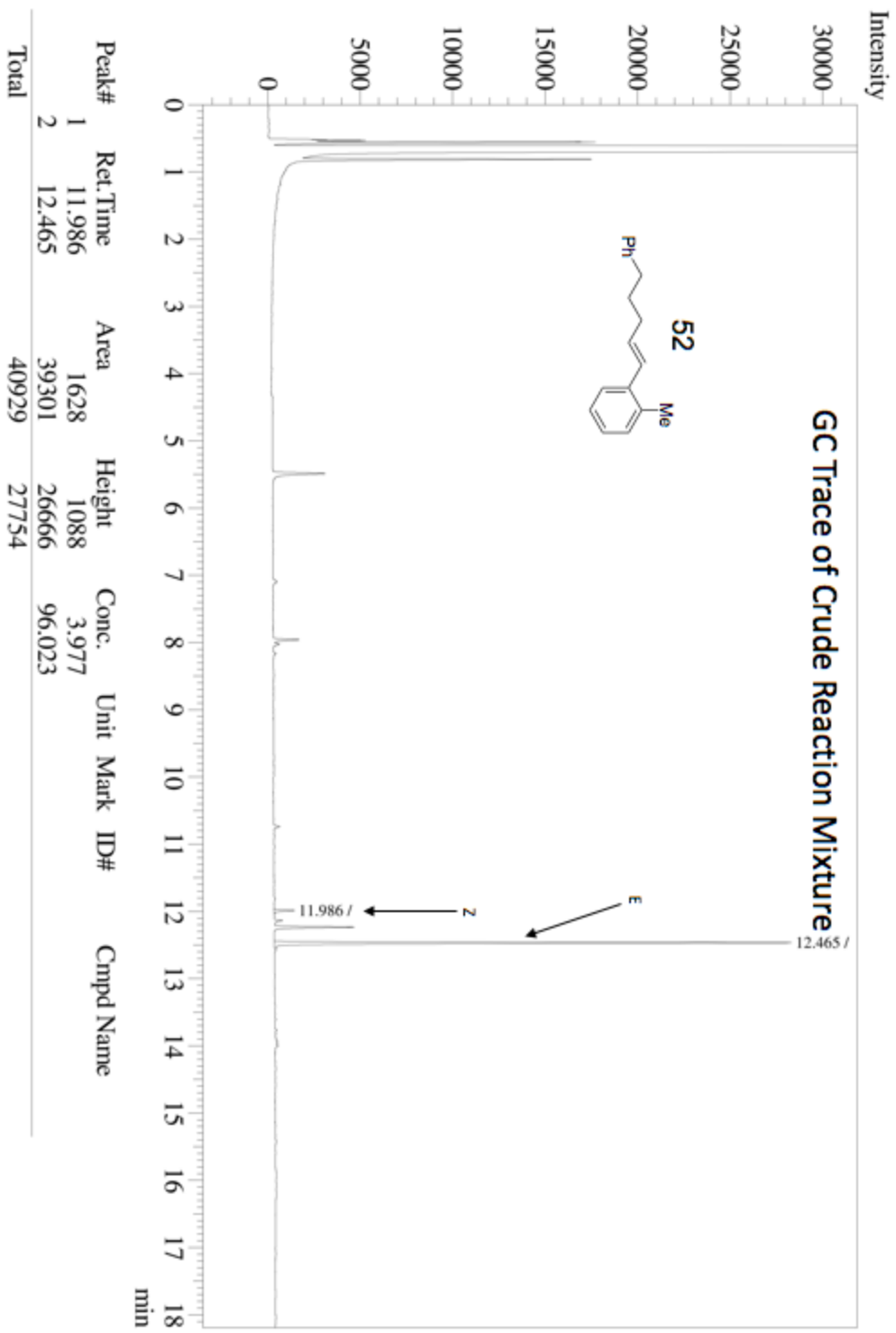


¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, J = 7.2 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.19 – 7.04 (m, 8H), 6.54 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 15.0, 7.0 Hz, 1H), 2.64 (t, J = 7.7 Hz, 2H), 2.29 (s, 3H), 2.26 – 2.19 (m, 2H), 1.78 (p, J = 7.6 Hz, 2H).

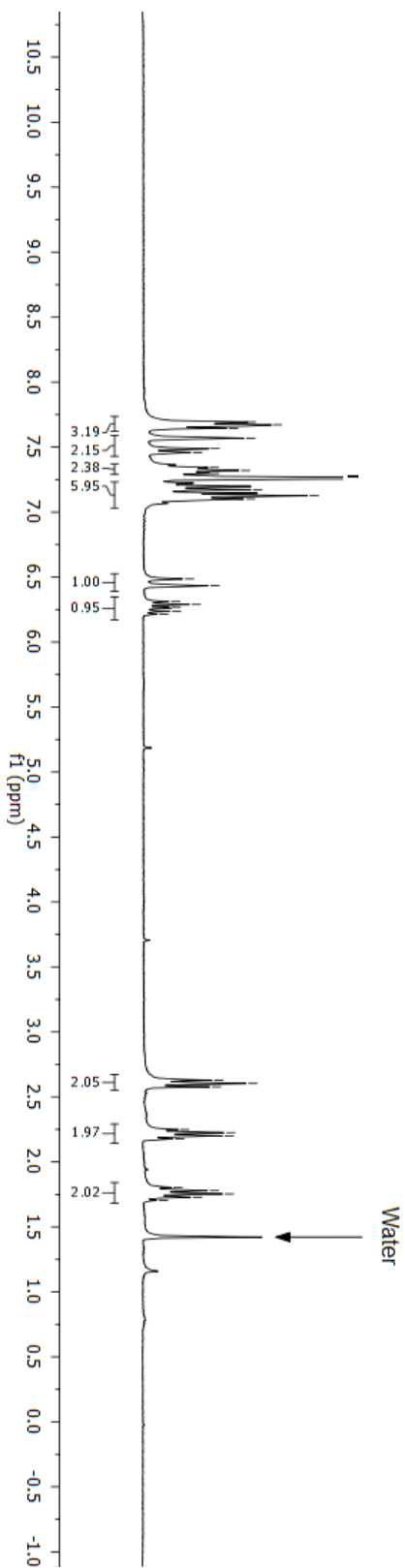
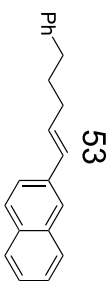


¹³C NMR (126 MHz, Chloroform-d) δ 142.5, 137.1, 135.0, 132.0, 130.3, 128.6, 127.0, 126.1, 125.9, 125.6, 35.5, 33.0, 31.5, 20.0.

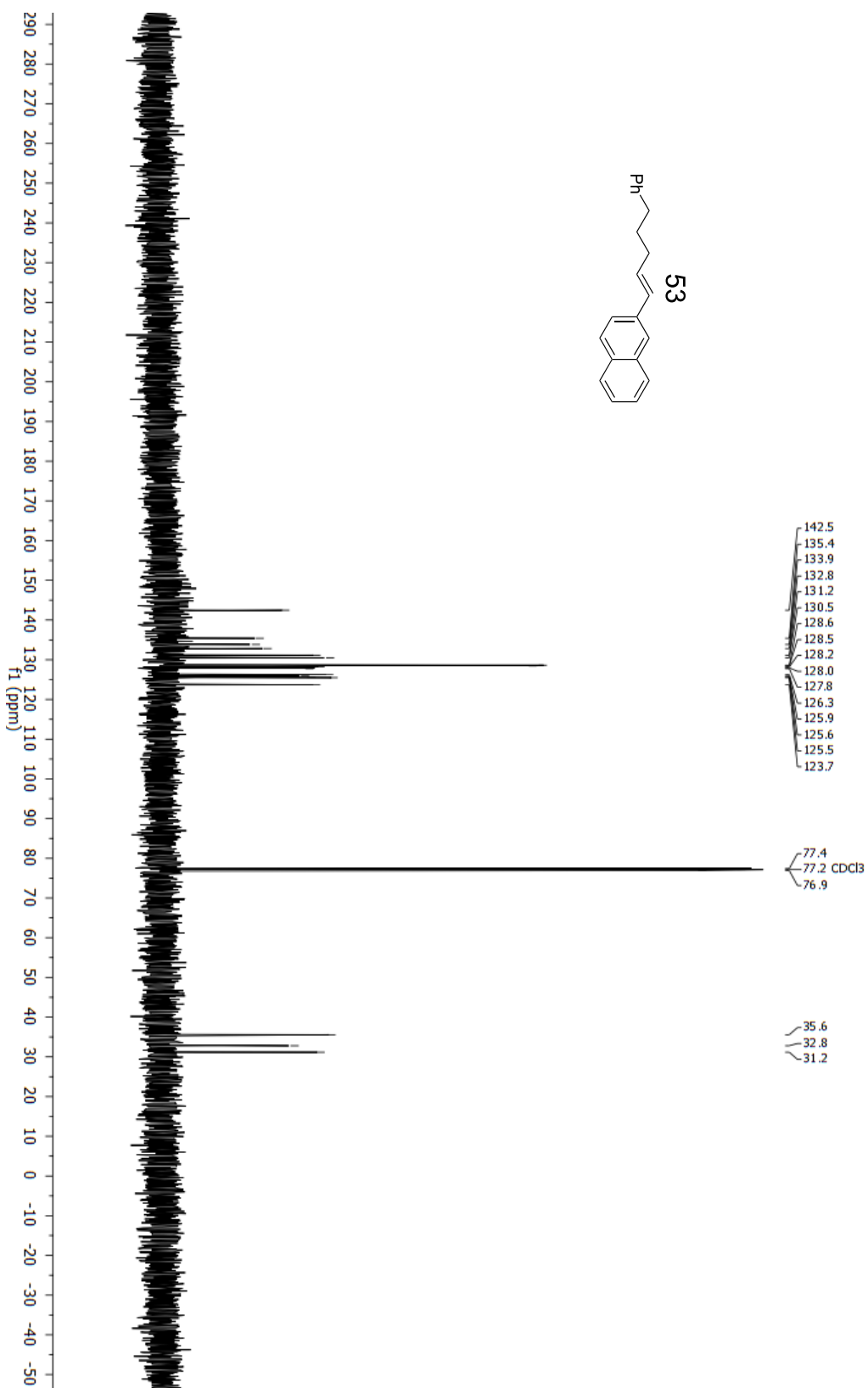
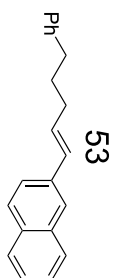


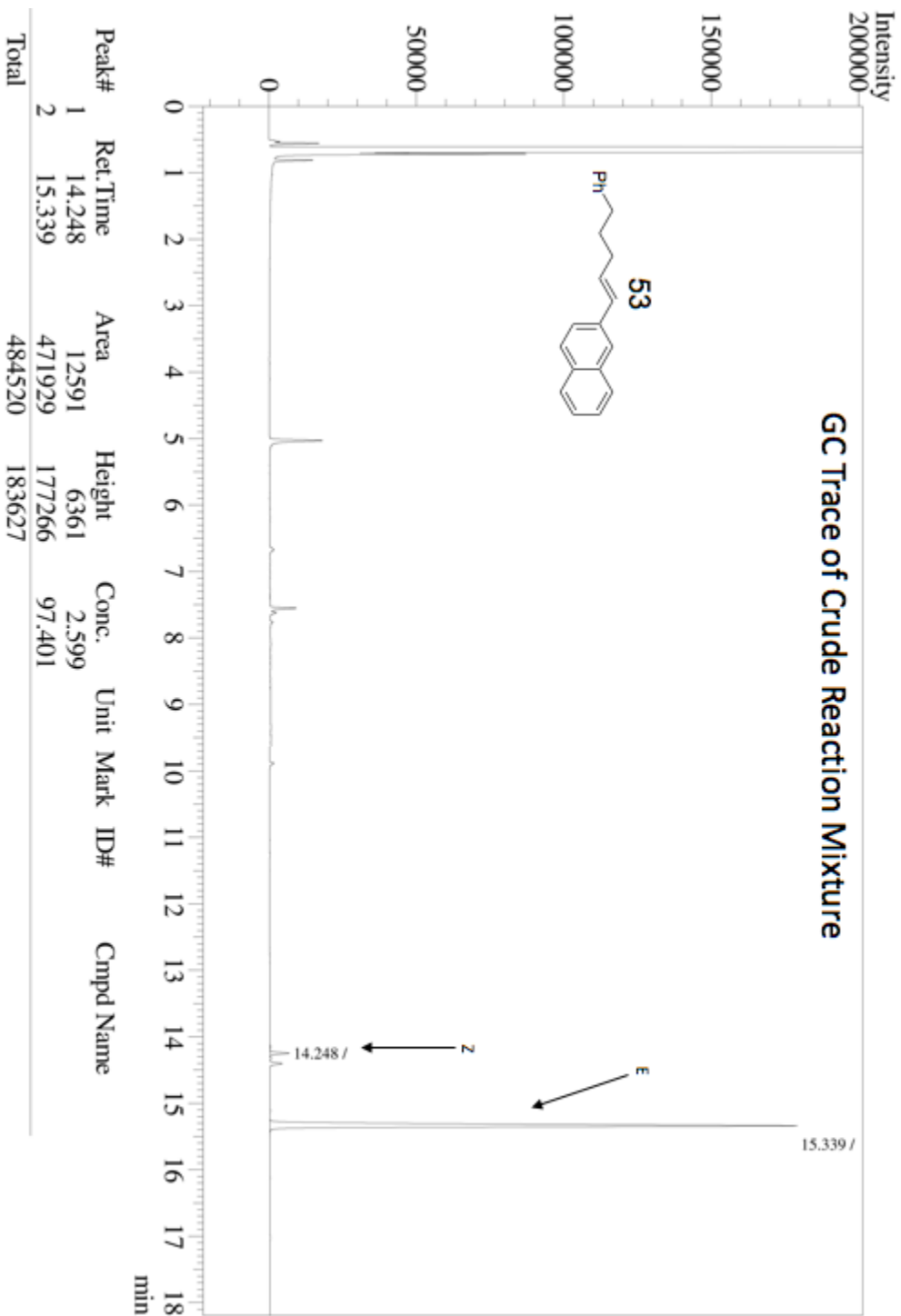


¹H NMR (300 MHz, Chloroform-*d*) δ 7.73 – 7.61 (m, 3H), 7.62 – 7.43 (m, 2H), 7.39 – 7.26 (m, 2H), 7.24 – 7.04 (m, 6H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.21 (m, 2H), 1.77 (p, *J* = 7.6 Hz, 2H).



¹³C NMR (126 MHz, Chloroform-*d*) δ 142.5, 135.4, 133.9, 132.8, 131.2, 130.5, 128.6, 128.5, 128.2, 127.9, 127.8, 126.3, 125.9, 125.6, 125.5, 123.7, 35.6, 32.8, 31.2.

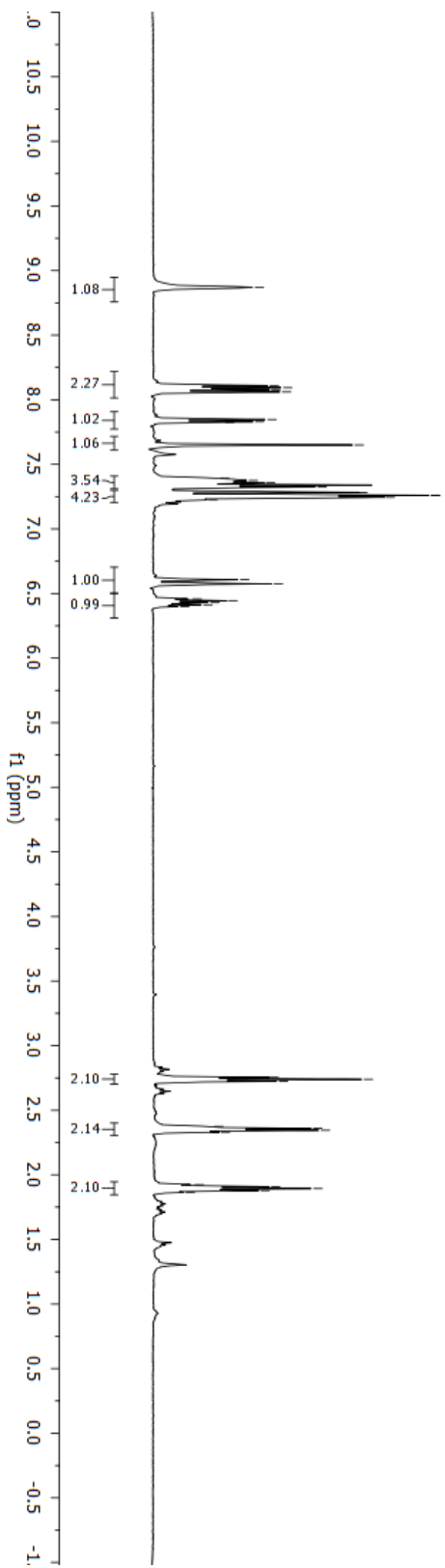
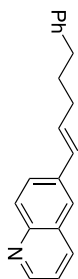




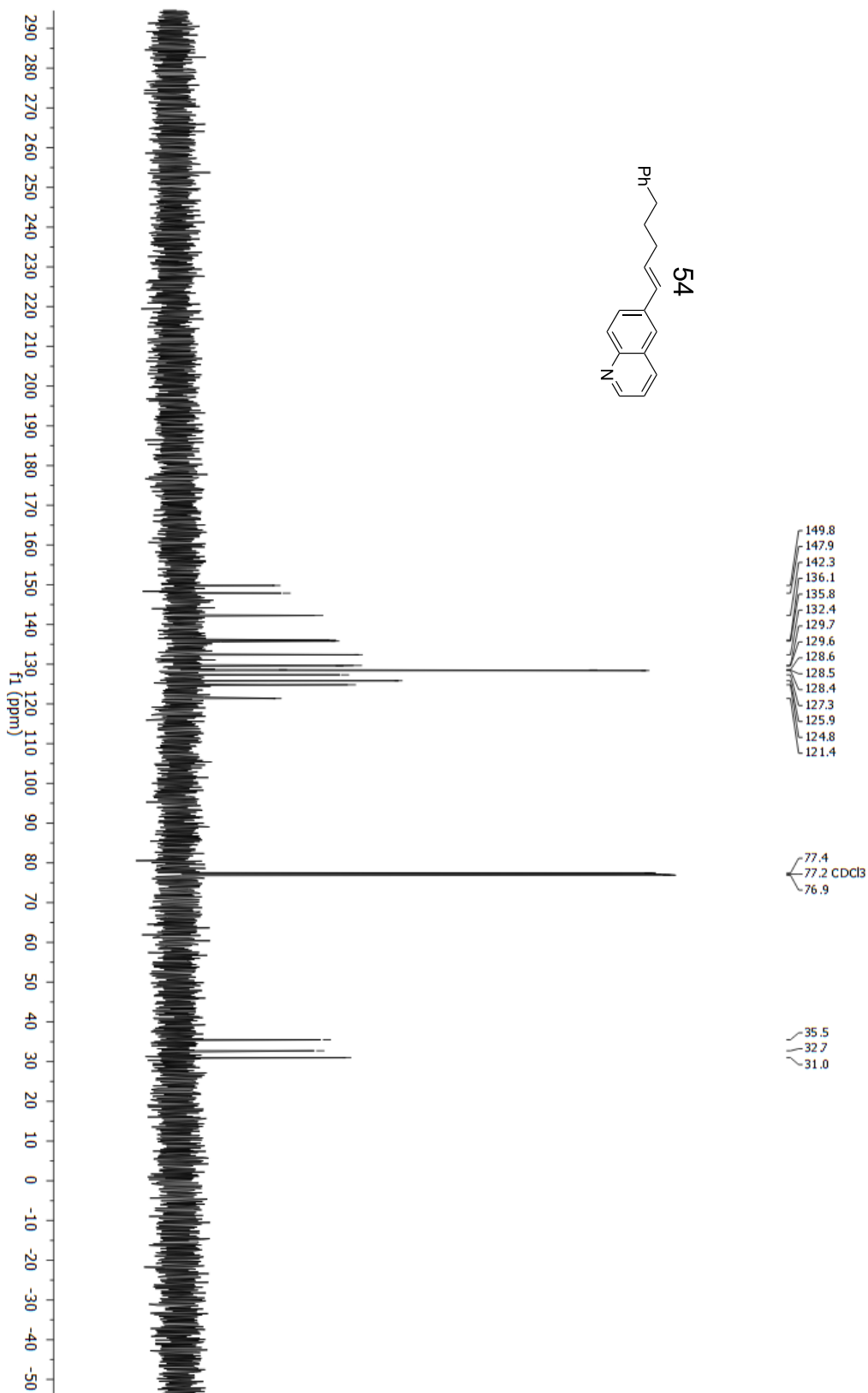
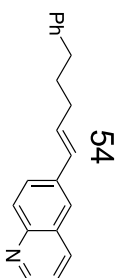
¹H NMR (300 MHz, Chloroform-*d*) 8.87 (s, 1H), 8.09 (dd, *J* = 16.2, 8.5 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.65 (s, 1H), 7.44 – 7.30 (m, 4H), 7.25 (q, *J* = 10.7 Hz, 4H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.43 (dt, *J* = 15.3, 6.8 Hz, 1H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.41 – 2.31 (m, 2H), 1.89 (q, *J* = 7.2 Hz, 2H).

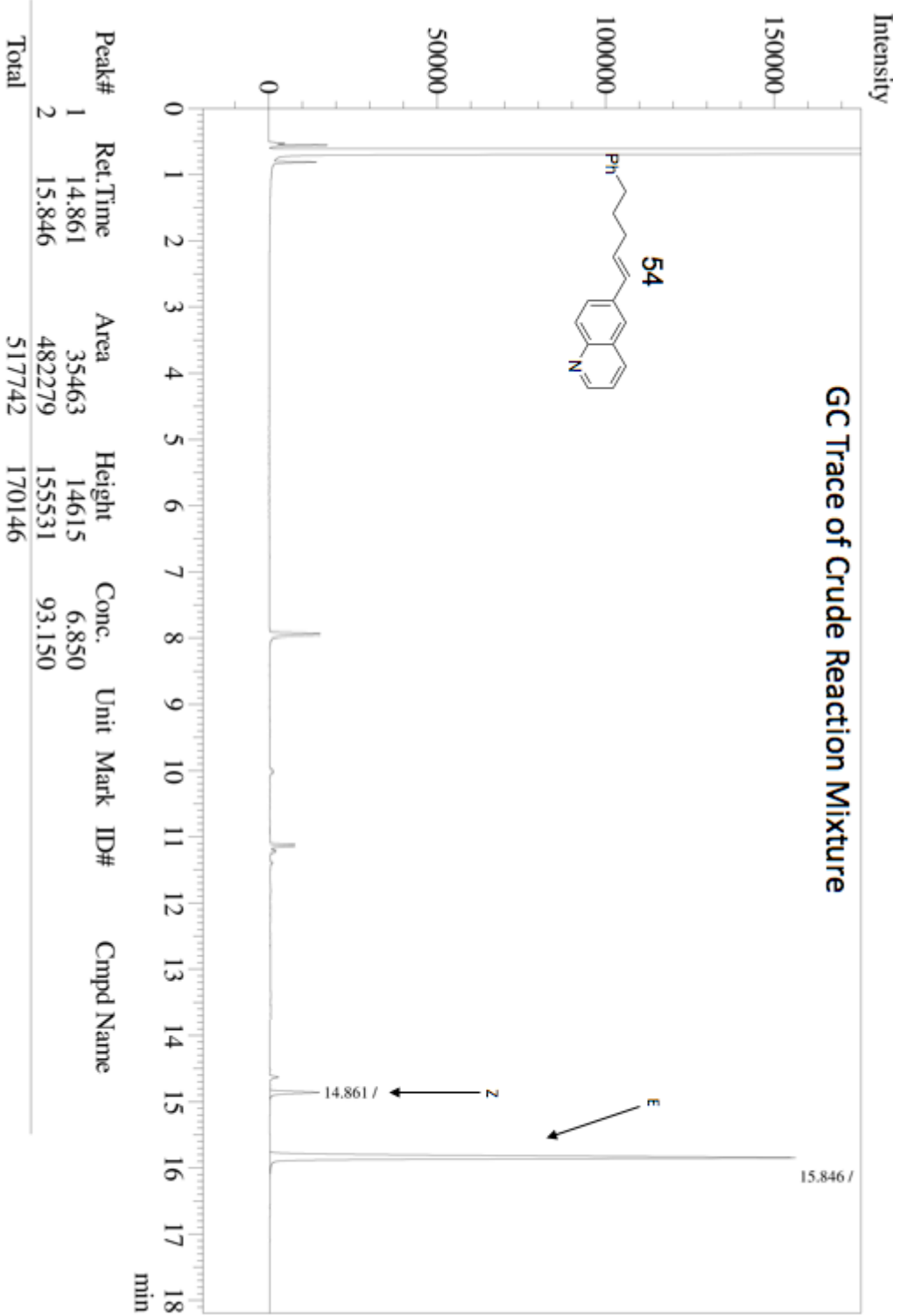


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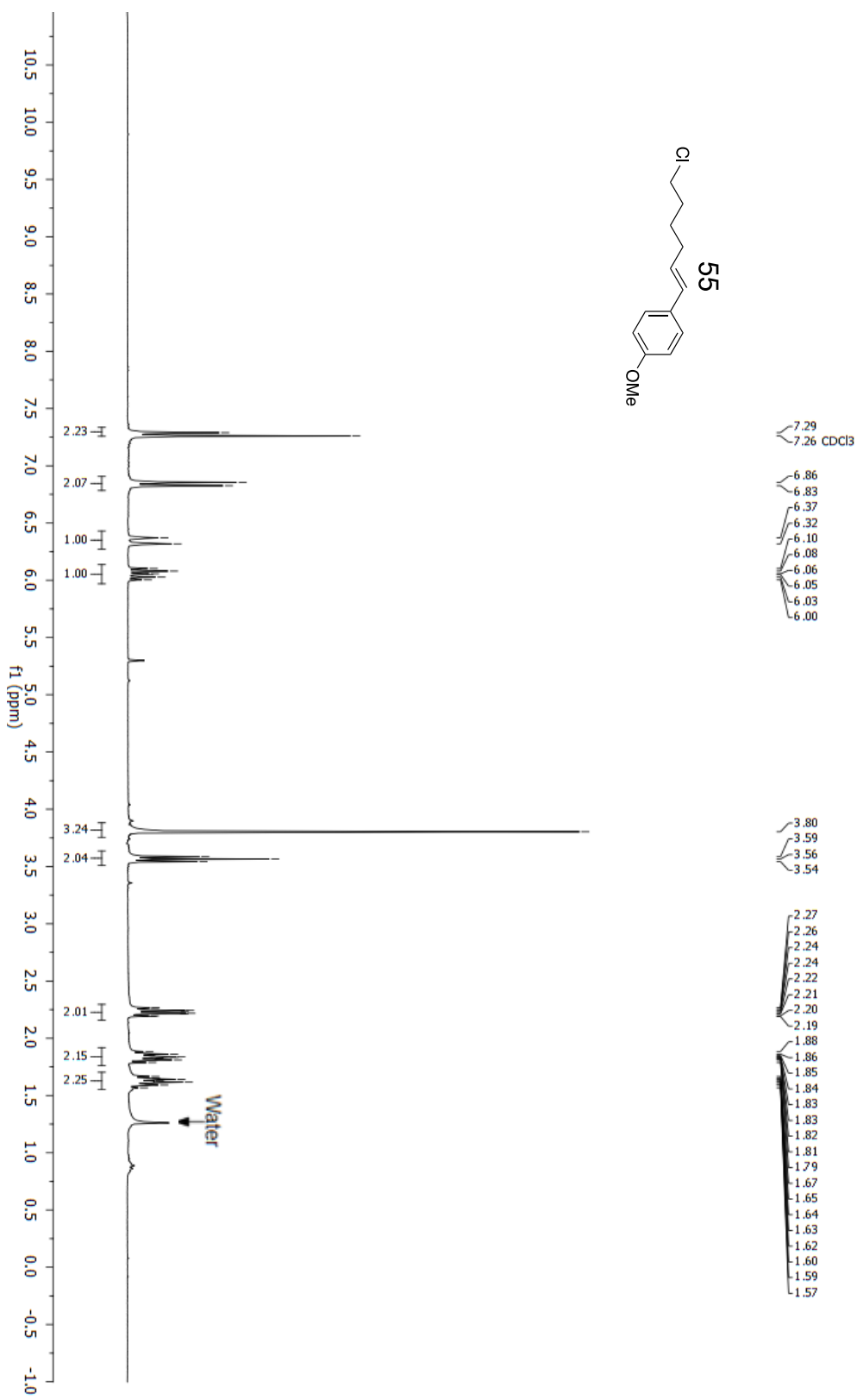
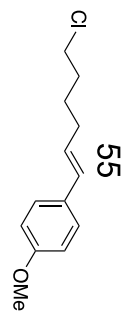


¹³C NMR (126 MHz, Chloroform-d) δ 159.8, 147.9, 142.3, 136.1, 135.8, 132.4, 129.7, 129.6, 128.6, 128.5, 128.4, 127.3, 125.9, 124.8, 121.4, 35.5, 32.7, 31.0.

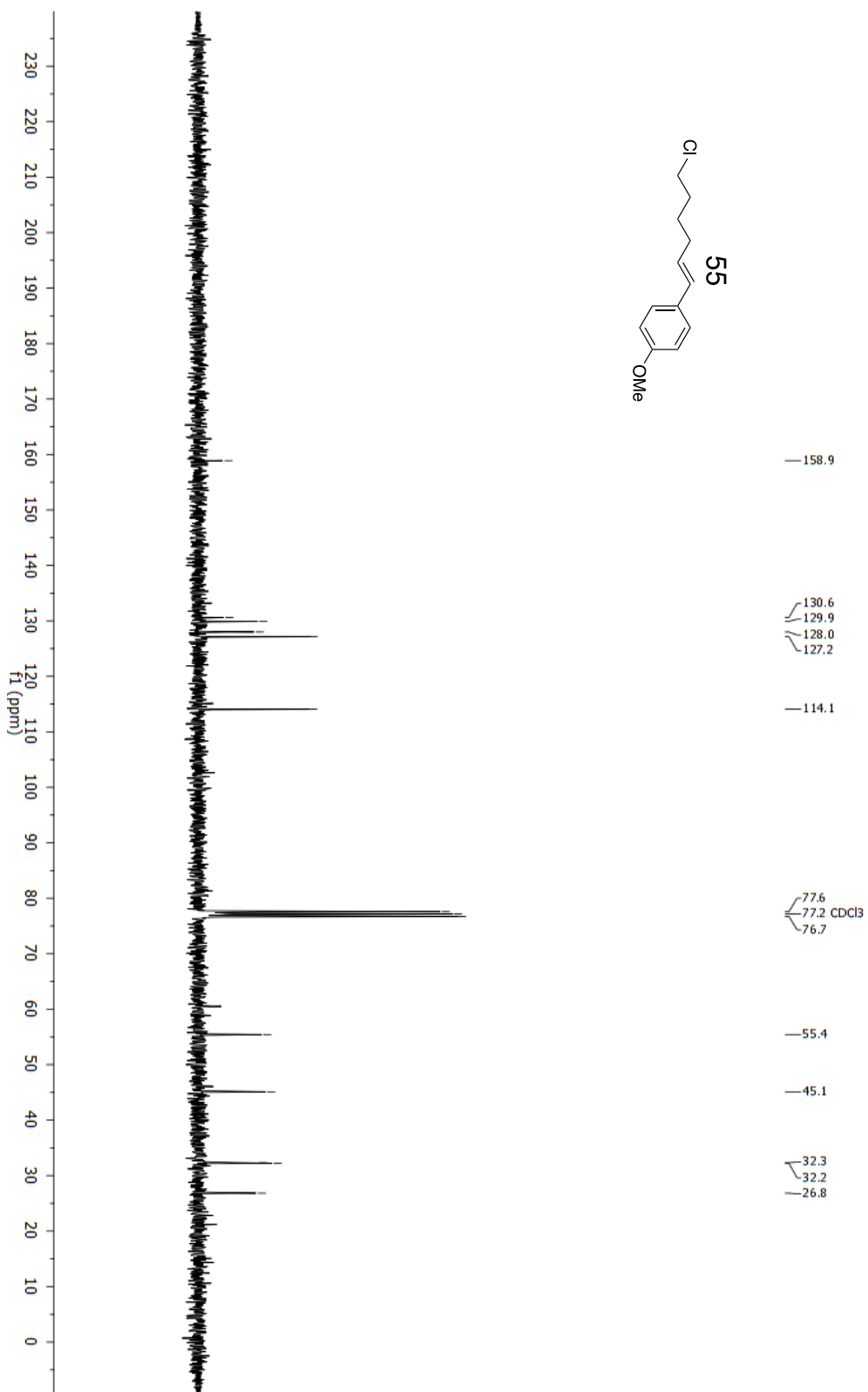
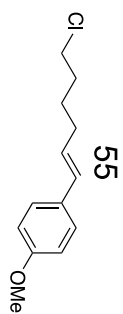


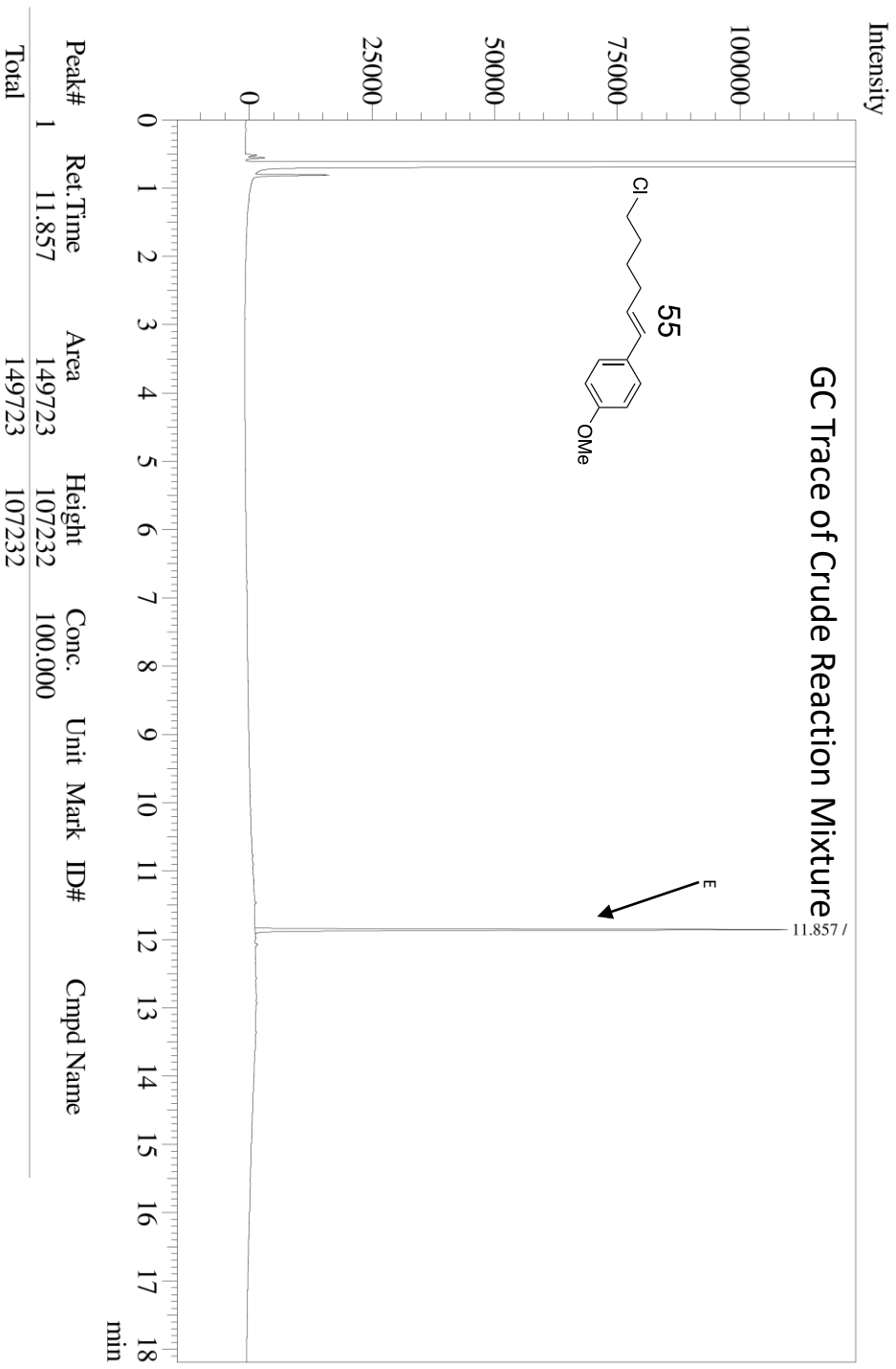


¹H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.05 (dt, J = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.56 (t, J = 6.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 1.92 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H).



^{13}C -NMR (75 MHz, CDCl_3) δ 158.9, 130.6, 129.9, 127.2, 127.2, 114.1, 55.4, 45.1, 32.3, 32.2, 26.8.



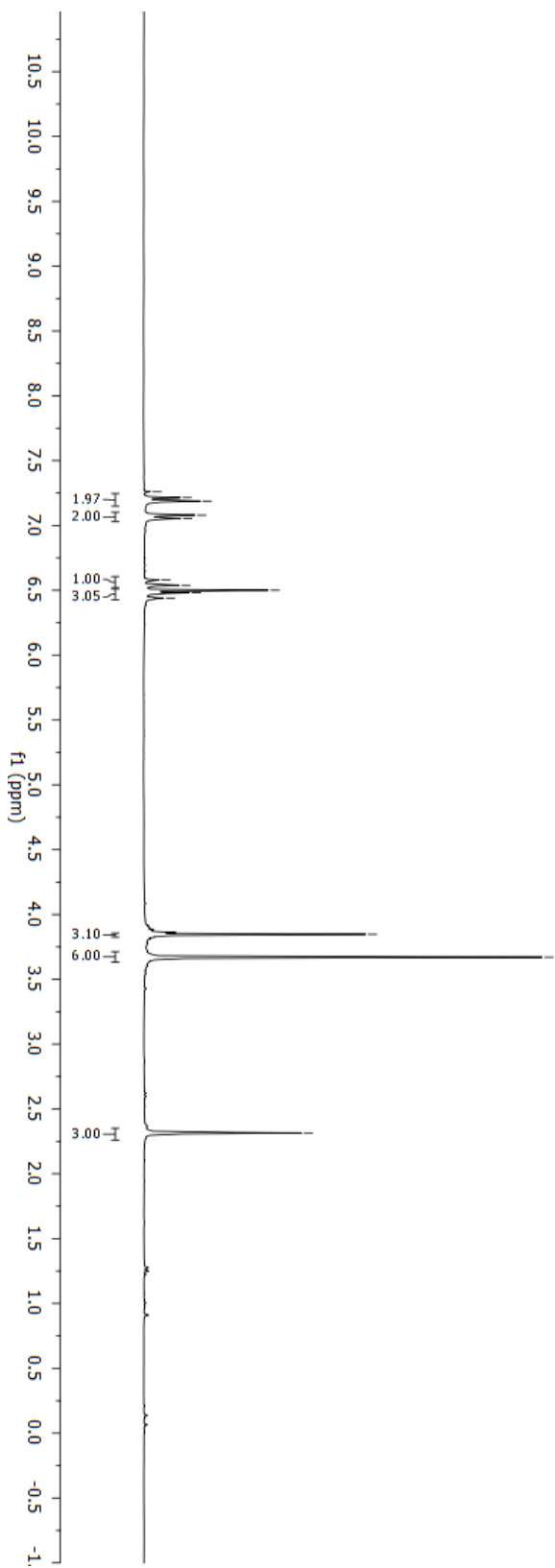
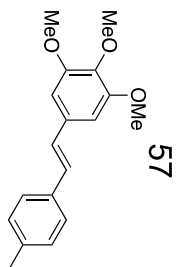


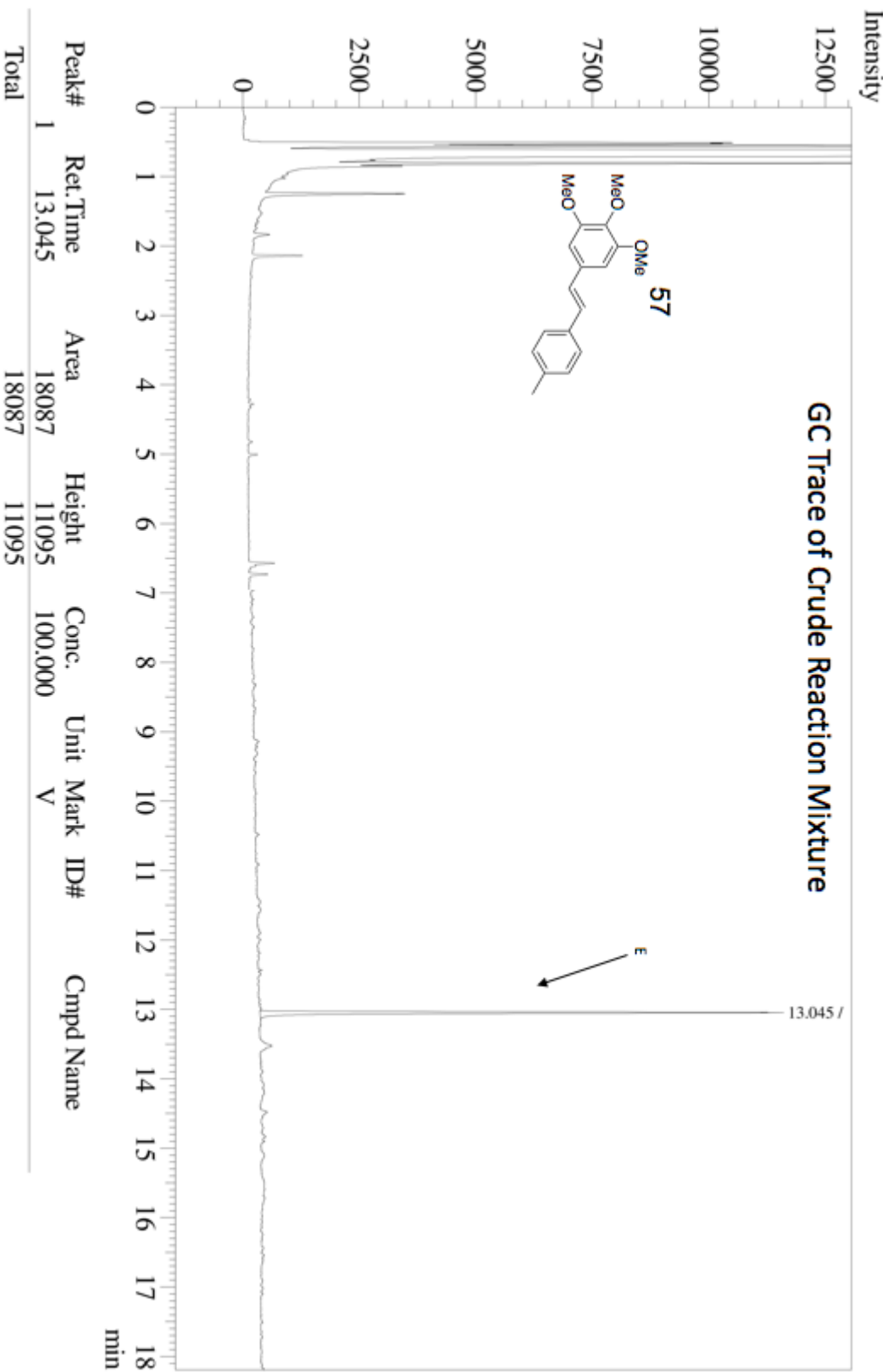
¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 12.2 Hz, 1H), 6.52 – 6.43 (m, 3H), 3.85 (s, 3H), 3.67 (s, 6H), 2.31 (s, 3H).

7.26 CDCl₃
7.21
7.19
7.08
7.05
6.58
6.54
6.50
6.48
6.44

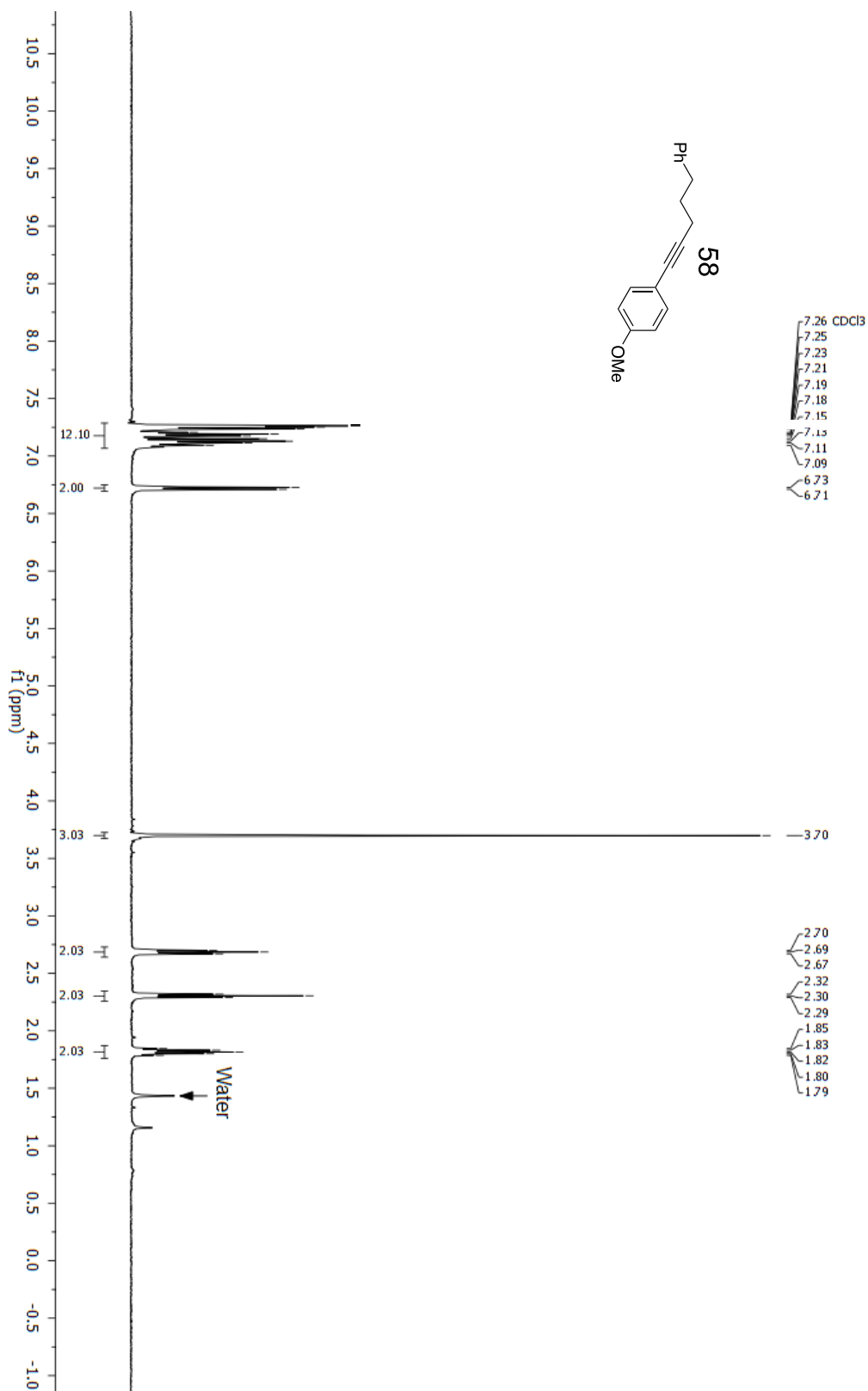
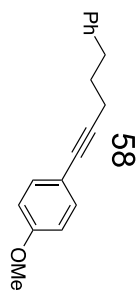
3.85
3.67

2.31





¹H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.07 (m, 7H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.70 (s, 3H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.82 (p, *J* = 7.1 Hz, 2H).



^1H NMR (300 MHz, Chloroform- d_3) δ 7.61 – 7.43 (m, 4H), 7.26 (s, 5H), 2.80 (t, J = 7.6 Hz, 2H), 2.45 (t, J = 7.0 Hz, 2H), 1.95 (p, J = 7.3 Hz, 2H).

7.56
7.54
7.51
7.49
7.26 CDCl₃

2.81
2.80
2.78
2.46
2.45
2.43
1.98
1.97
1.95
1.94
1.92

