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

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1. General Information

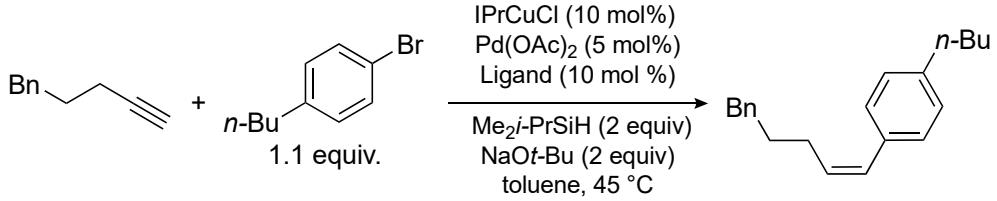
All reactions were performed under a nitrogen atmosphere with flame-dried or oven-dried (120 °C) glassware, using standard Schlenk techniques, or in a glovebox (Nexus II from Vacuum Atmospheres). Column chromatography was performed using a Biotage Iso-1SV flash purification system with silica gel from 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. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual solvent peak ($CDCl_3$ (7.26 ppm)). ^{13}C NMR chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.2 ppm). ^{19}F 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), intergration. 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, CH_2Cl_2, 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 (Me_2*i*-PrSiH) was purchased from Gelest Inc and was degassed and stored over 4Å molecular sieves.

2. Reaction Development

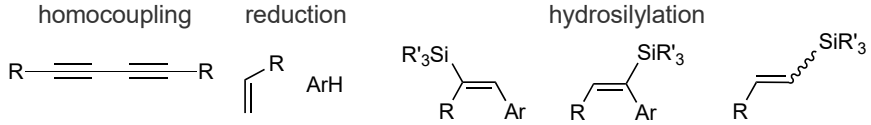
All reactions were performed on a 0.05 mmol scale with the stoichiometry shown in Tables S1-S3. In a nitrogen-filled glovebox a dram vial was charged with a stir bar, NaO*t*-Bu, 5-phenyl-1-pentyne, 1,3,5-trimethoxy benzene (TMB, used as an internal standard for GC), $Pd(OAc)_2$, IPrCuCl, ligand (Table S1), 1-bromo-4-butylbenzene, silane (Table S2) and toluene. The reaction mixture was stirred at 45 ºC 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



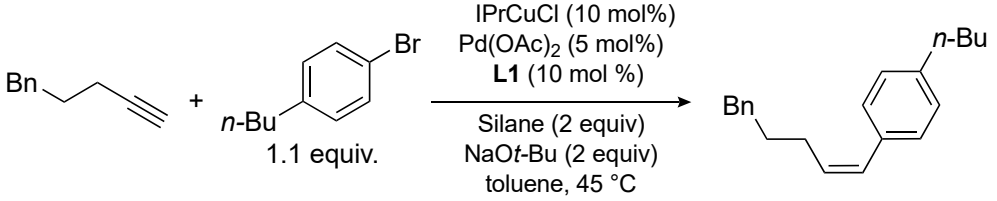
Entry	Ligand	Temperature (°C)	Time (h)	Yield (%)
1	Xphos	45	24	8
2	**L1**	45	24	47
3	**L1**	25	24	0
4	Ruphos	45	24	1
5	PCy_3	45	24	0
6	dppf	45	24	0
7	dppp	45	24	0
8	Segphos	45	24	0
9	Davephos	45	24	21
10	BINAP	45	24	0
11	Xyl-MeOBIPHEP	45	24	0
12	DACH Trost	45	24	0
13	Sphos	45	24	26
14	Qphos	45	24	13

Major Side Products[a]



[a]Side products determined by GC-MS analysis of the aliquots and known palladium chemistry.

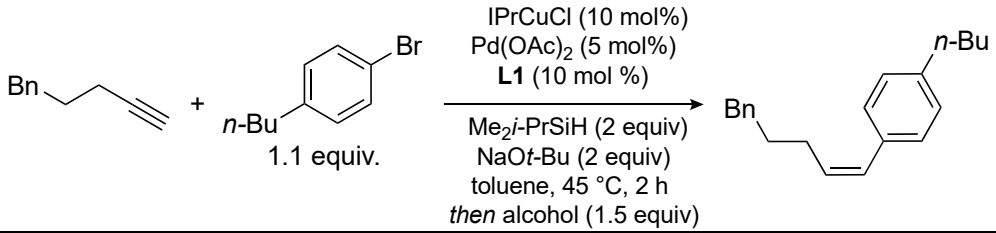
Table S2.
Silane screen.



Entry	Silane	Time (h)	Sonogashira Yield (%)	Z-alkene Yield (%)
1	Me_2PhSiH	24	5	27
2	$MePh_2SiH$	24	5	18
3	Ph_3SiH	24	9	10
4	Ph_2SiH_2	24	0	0
5	$PhSiH_3$	24	0	0
6	Et_3SiH	24	3	0
7	*t*-Bu_2SiH_2	24	0	6
8	Me_2*i*-PrSiH	24	91	0
9	*t*-Bu_2MeSiH	24	86	0

10	(O*t*-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

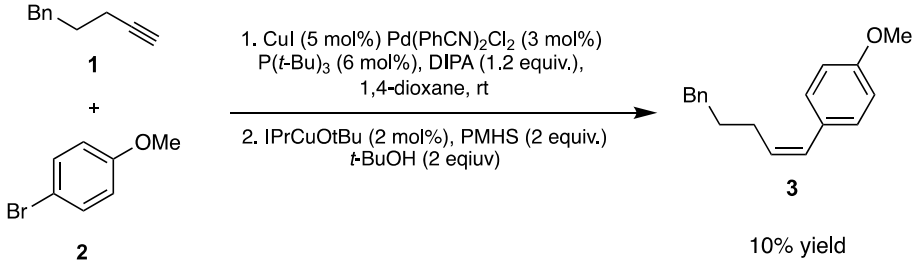
Table S3.
Alcohol additive screen.



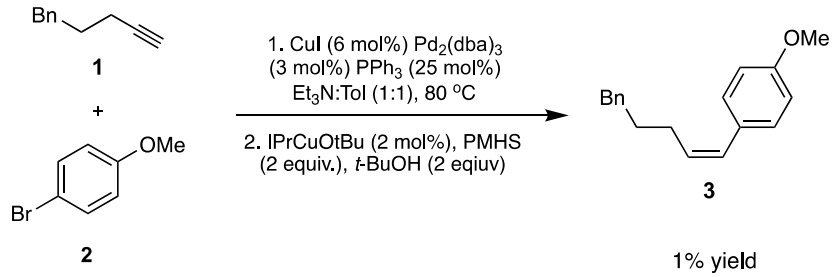
Entry	Alcohol	Time (h)*	Sonogashira Yield (%)	Z-alkene Yield (%)	Z:E Ratio
1	MeOH	4	0	100	33/1
2	*i*-BuOH	4	0	100	25/1
3	Neopentanol	4	0	100	21/1
4	*t*-BuOH	4	73	27	--
5	*i*-PrOH	4	17	58	--

3. Standard Sonogashira Coupling Followed by in Situ Semireduction

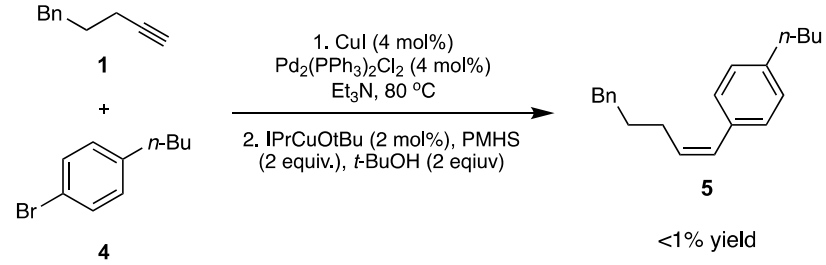
General Procedure
All manipulations were performed in a nitrogen-filled glovebox. Each Sonogashira coupling was performed according to the procedure reported in the literature. Reactions were performed on a 0.05 mmol scale and monitored by GC. Sonogashira coupling was determined to be complete upon full consumption of the aryl bromide. Standard semireduction conditions[11] were then applied, and reactions were allowed to stir at 25 ºC 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 ºC, 60 ºC and 90 ºC 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 ºC until no further change occurred.



Sonogashira coupling[12] determined complete at 16 h. Semireduction was stopped at 20 h. Yield determined by GC.



Sonogashira coupling[13] determine complete at 24 h. Semireduction was stopped at 24 h. Yield determined by GC.

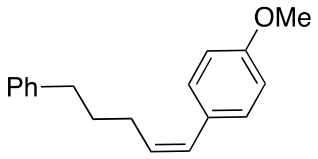


Sonogashira coupling[14] determined complete at 16 h. Semireduction was stopped at 24 h. Yield determined by GC.

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

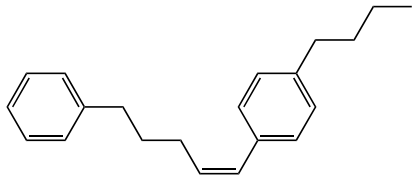
In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaO*t*-Bu (96.1 mg, 1.00 mmol, 2.0 equiv). To this was added alkyne (0.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.8 mg, 0.025 mmol, 0.100 equiv) IPrCuCl (24.4 mg, 0.050 mmol, 0.10 equiv), **L1** (19 mg, 0.050 mmol, 0.10 equiv), aryl bromide (0.550 mmol, 1.10 equiv), Me_2*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 dieastereoselectivity 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

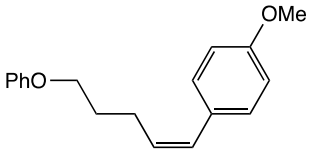


1-methoxy-4-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (3), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal 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

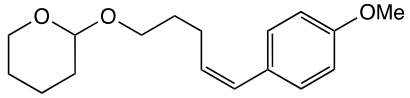
plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (110.0 mg, 87% yield, Z:E = 28:1). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.44 – 7.17 (m, 7H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 11.7 Hz, 1H), 5.69 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.88 (s, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.27 (dt, *J* = 7.6, 7.2 Hz, 2H), 1.87 (p, *J* = 7.6 Hz, 2H). ^{13}C 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-[(1*Z*)-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). ^{1}H 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. 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).

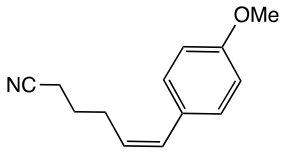


1-methoxy-4-[(1*Z*)-5-phenoxypent-1-en-1-yl]benzene (6), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 3 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that 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). ^{1}H 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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).

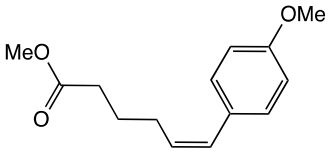


2-{[(4*Z*)-5-(4-methoxyphenyl)pent-4-en-1-yl]oxy}oxane (7), compound was prepared according to an altered general procedure. Li*O*t-Bu was used in place of Na*O*t-Bu as a turnover reagent. TLC

in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of 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 = 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). ^{1}H 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).^{13}C NMR (75 MHz, $CDCl_3$) 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).

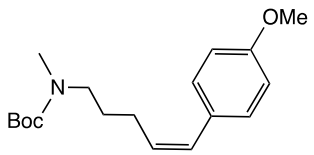


(5*Z*)-6-(4-methoxyphenyl)hex-5-enenitrile (8), compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 3 h. After the addition of 2 equiv of NaO*t*-Bu and 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 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). ^{1}H 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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).

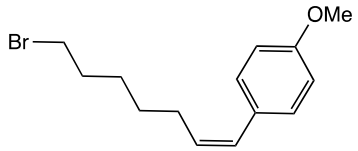


methyl (5*Z*)-6-(4-methoxyphenyl)hex-5-enoate (9), compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of NaO*t*-Bu and 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 = 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). ^{1}H 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). ^{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,

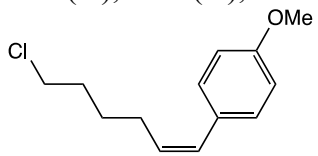
28.0, 25.2. GCMS (EI) calculated for [M]+ 234.13, found 234.2. FTIR (neat, cm^{-1}): 3005(m), 2949(m), 2836(m), 2255(m), 1736(s), 1608(s), 836(s), 734(s).



tert-butyl N-[(4*Z*)-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). ^{1}H 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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).

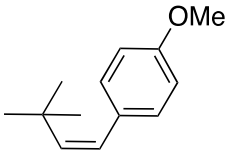


1-[(1*Z*)-7-bromohept-1-en-1-yl]-4-methoxybenzene (11), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that 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). ^{1}H 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). ^{13}C NMR (75 MHz, $CDCl_3$) 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).

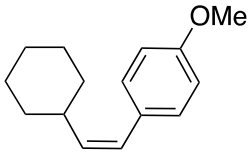


1-[(1*Z*)-6-chlorohex-1-en-1-yl]-4-methoxybenzene (12), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that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

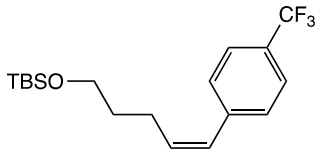
the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 90:1). The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 15%) and isolated as a colorless oil (99.3 mg, 88% yield, Z:E = 99:1). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 2H), 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. 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).



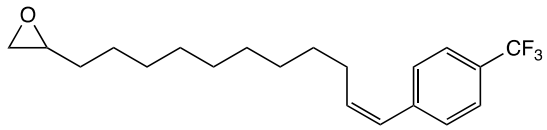
1-[(1Z)-3,3-dimethylbut-1-en-1-yl]-4-methoxybenzene (13) compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (69.0 mg, 73% yield, Z:E = 16:1). ^{1}H 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) 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).



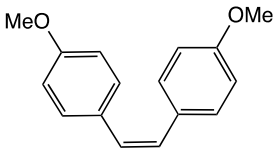
1-[(Z)-2-cyclohexylethenyl]-4-methoxybenzene (14) compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal alkyne 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (88.0 mg, 81% yield, Z:E = 17:1). ^{1}H 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). ^{13}C 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-butyldimethyl{[(5*Z*)-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). ^{1}H 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). ^{13}C 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. ^{19}F NMR (471 MHz, $CDCl_3$) 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).

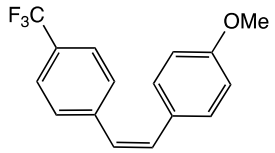


2-[(9*Z*)-10-[4-(trifluoromethyl)phenyl]dec-9-en-1-yl]oxirane (16), compound was prepared according to the general procedure, TLC in 10% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 1.5 equiv of MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed 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). ^{1}H 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). ^{13}C 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. ^{19}F NMR (471 MHz, $CDCl_3$) 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).

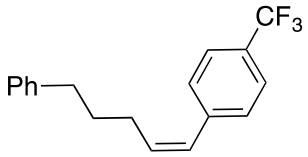


1-methoxy-4-[(*Z*)-2-(4-methoxyphenyl)ethenyl]benzene (17), compound was prepared according to an altered general procedure. Li*O*t-Bu was used in place of Na*O*t-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After

the addition of 2 equiv of 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 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). ^{1}H 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). ^{13}C NMR (75 MHz, $CDCl_3$) 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).

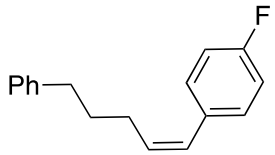


1-[(*Z*)-2-(4-methoxyphenyl)ethenyl]-4-(trifluoromethyl)benzene (18), compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv 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 = 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). ^{1}H 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). ^{13}C 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. ^{19}F NMR (471 MHz, $CDCl_3$) 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).

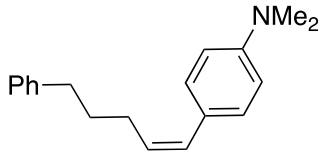


1-[(1*Z*)-5-phenylpent-1-en-1-yl]-4-(trifluoromethyl)benzene (19), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by TLC (100% Hex) revealed that 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). ^{1}H 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. ^{19}F NMR (471 MHz, Chloroform-d) δ -65.2. ^{13}C 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

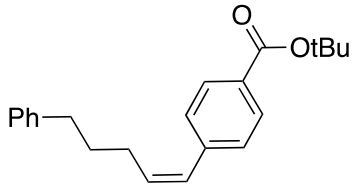
(q, J = 276.5 Hz), 35.6, 31.6, 28.1. FTIR (neat, cm^{-1}): 3088(w), 3065(w), 3028(m), 2931(m). 2849(w), 1612(w), 1478(w), 1322(s), 1165(s), 1120(s), 1068(s), 673(s).



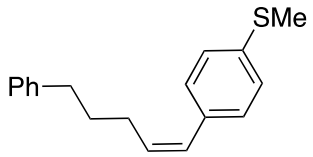
1-fluoro-4-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (20), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (100% Hex) revealed that the internal 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). ^{1}H 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 [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).



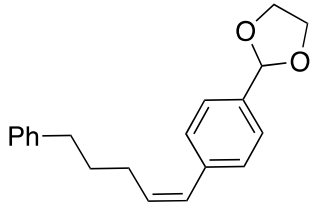
N,N-dimethyl-4-[(1*Z*)-5-phenylpent-1-en-1-yl]aniline (21), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, the reaction mixture was then moved to 0 ºC to slow the rate of isomerization, 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (10% Et_2O/Hex). Compound was isolated as a clear colorless liquid (85 mg, 65% yield, Z:E = 12:1). ^{1}H 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, 7.2Hz, 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 [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-[(1*Z*)-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% Et_2O/Hex). The compound was isolated as a clear colorless oil. (128 mg, 79% yield, Z:E = 10:1). ^{1}H 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). ^{13}C 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).

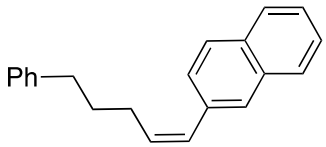


1-(methylsulfanyl)-4-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (23), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex) revealed that 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (118 mg, 88% yield, Z:E = 80:1). ^{1}H 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). ^{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. 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)

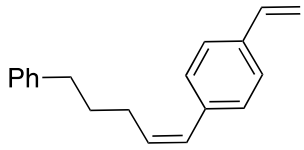


2-{4-[(1*Z*)-5-phenylpent-1-en-1-yl]phenyl}-1,3-dioxolane (24), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was

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). ^{1}H 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). ^{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, 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).

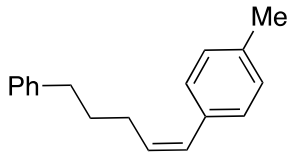


2-[(1*Z*)-5-phenylpent-1-en-1-yl]naphthalene (25), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by TLC (5% Et_2O in Hex) revealed that the internal 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 (Et_2O/Hex 0→5%) and a filtration through a short plug of alumina (5% Et_2O/Hex). The compound was isolated as a clear colorless oil (109 mg, 80% yield, Z:E = 29:1). ^{1}H 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). ^{13}C 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).

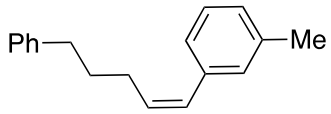


1-ethenyl-4-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (26), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% Et_2O//Hex) revealed that the internal 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (105 mg, 85% yield, Z:E = 20:1). ^{1}H 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

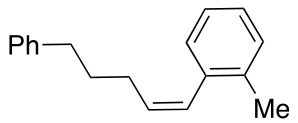
Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 142.4, 137.5, 136.8, 136.0, 132.8, 129.1, 129.1, 128.6, 128.4, 126.2, 125.9, 113.6, 35.6, 31.8, 28.4. GCMS (EI) calculated for [M]+ 248.16, found 248.2. FTIR (neat, cm^{-1}): 3080(w), 3058(w), 3021(m), 3006(m), 2924(s), 2857(m), 1620(m), 1605(m), 1500(s),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



1-methyl-4-[(1*Z*)-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→10%) and a filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (116 mg, 98% yield, Z:E = 10:1). ^{1}H 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 [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).

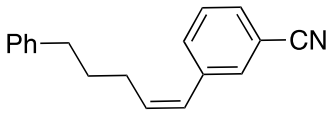


1-methyl-3-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (28), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex) revealed that the internal 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→10%) and a filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (102 mg, 86% yield, Z:E = 10:1). ^{1}H 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 [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).

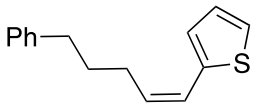


1-methyl-2-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (29), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (5% EtOAc/Hex)

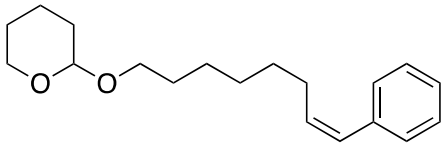
revealed that the internal alkyne intermediate was consumed after 30 min. An aliquot of the crude reaction mixture was analyzed by GC to obtain the isomeric ratio (Z:E = 35:1). The compound was purified by silica gel column chromatography (EtOAc/Hex 0→10%) and a filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (110 mg, 93% yield, Z:E = 35:1). ^{1}H 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). ^{13}C 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).



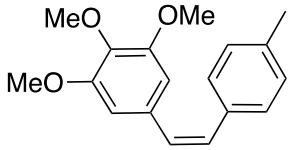
3-[(1*Z*)-5-phenylpent-1-en-1-yl]benzonitrile (30), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv *i*-BuOH, monitoring the reaction progress by GC revealed that the internal alkyne intermediate 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (114 mg, 92% yield, Z:E = 24:1). ^{1}H 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* = 7.6Hz, 2H), 2.27 – 2.15 (m, 2H), 1.69 (p, *J* = 7.6 Hz, 2H). ^{13}C 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).



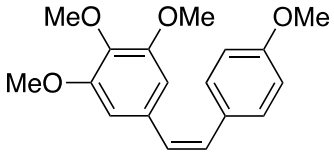
2-[(1*Z*)-5-phenylpent-1-en-1-yl]thiophene (31), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% Et_2O//Hex) revealed that the internal alkyne 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (82 mg, 72% yield, Z:E = 52:1). ^{1}H 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). ^{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. 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]oxy}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 ºC 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% Et_2O/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]

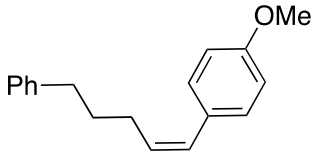


1,2,3-trimethoxy-5-[(Z)-2-(4-methylphenyl)ethenyl]benzene (34) compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2.5 h. After the addition of 2 equiv of NaO*t*-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. 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 2 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 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

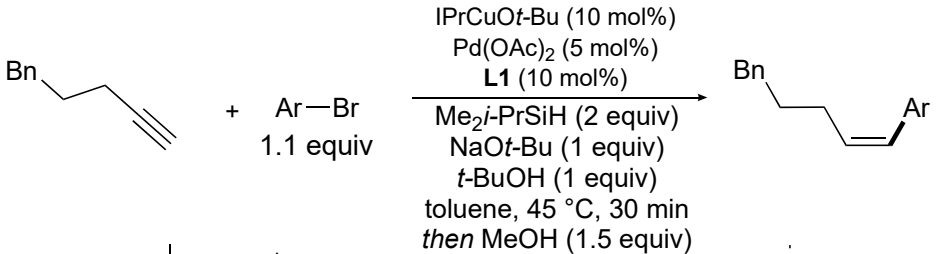


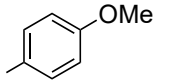
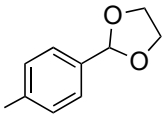
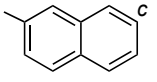
1-methoxy-4-[(1*Z*)-5-phenylpent-1-en-1-yl]benzene (3), compound was prepared according to the general procedure, TLC in 100% Hex showed that the starting alkyne was consumed after 2h. After the addition of 1.5 equiv MeOH, monitoring the reaction progress by TLC (10% EtOAc/Hex) revealed that the internal 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% Et_2O/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 NaO*t*-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), Me_2*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.



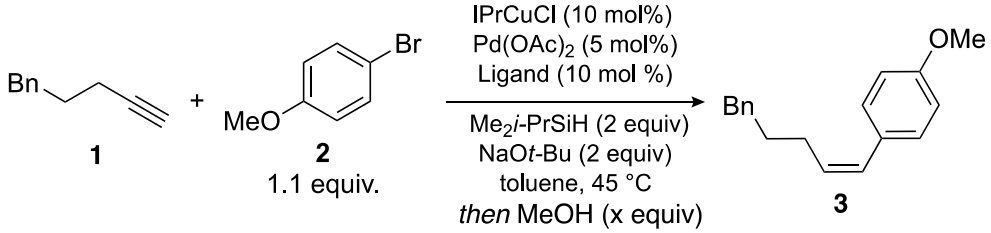
Ar =	20 min[b]	25 min	30 min	35 min	40 min	Yield Range
	20:1	18:1	13:1	10:1	10:1	92 - 95
	>100:1[d]	18:1	18:1	17:1	13:1	70 - 79
	28:1	28:1	27:1	26:1	25:1	84 - 89

[a]Selectivity determined by GC analysis of crude reaction mixture. [b]Time after the addition of alcohol. [c]*i*-BuOH used instead of MeOH. [d]Reaction 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 NaO*t*Bu (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), Me_2*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 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



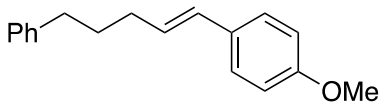
Entry	Ligand	Yield 20 min (E:Z)
1	Qphos	100% (1.9:1)
2	Davephos	81% (1:2.5)
3	Ruphos	69% (1:2.8)
4	Sphos	81% (1:1.2)
5	**L1**	90% (1:29)
6	**L1** (6 days)	95% (2:1)
7	**L1** (5 equiv MeOH)	94% (>100:1)

[a]Combined yields and E:Z selectivity determined by GC

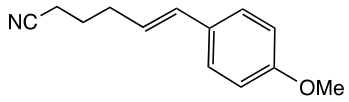
9. General Procedure for the Hydroarylation of Terminal Alkynes: Synthesis of *E*-Alkenes

In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaO*t*Bu (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), Me_2*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 (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.

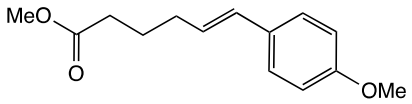
10. Characterization of Hydroarylation Products: *E*-alkenes



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 µL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et_2O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (118 mg, 94% yield, 1 isomer). ^{1}H 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). ^{13}C 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).

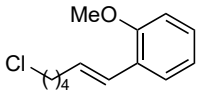


(5*E*)-6-(4-methoxyphenyl)hex-5-enenitrile (37), compound was prepared according to an altered general procedure. Li*O*t*Bu was used in place of Na*O*t*Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of Na*O*t*Bu and 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 silica gel chromatography with EtOAc/Hex (0 → 45%) and isolated as a pale yellow oil (96 mg, 95% yield, E:Z = 44:1). ^{1}H 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). ^{13}C NMR (75 MHz, $CDCl_3$) 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).

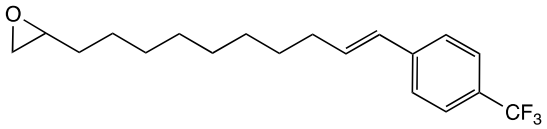


methyl (5*E*)-6-(4-methoxyphenyl)hex-5-enoate (38), compound was prepared according to an altered general procedure. Li*O*t*Bu was used in place of Na*O*t*Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of Na*O*t*Bu 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 silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a clear oil (81 mg, 70% yield, E:Z = >100:1). ^{1}H 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). ^{13}C NMR (75 MHz, $CDCl_3$) 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

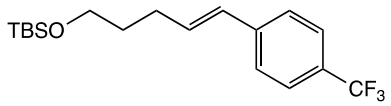
(EI) calculated for [M]+ 234.13, found 234.2. FTIR (neat, cm^{-1}): 3000(m), 2951(m), 2057(m), 1736(s), 1607(s), 1512(s), 839(s).



1-[(1*E*)-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) ^{1}H 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. 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).

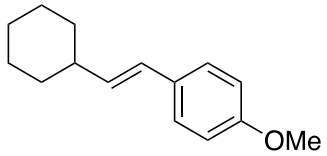


2-[(9*E*)-10-[4-(trifluoromethyl)phenyl]dec-9-en-1-yl]oxirane (40), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 12 hours a 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). ^{1}H 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). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4. ^{13}C 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),

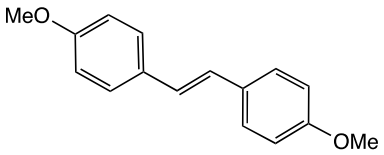


tert-butyldimethyl{[(4*E*)-5-[4-(trifluoromethyl)phenyl]pent-4-en-1-yl]oxy}silane (41), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °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). ^{1}H 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

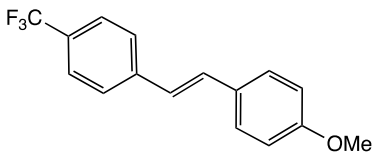
(s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.5, 133.6, 129.2, 128.7 (q, *J* = 32.2 Hz), 126.2, 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.7 Hz), 62.5, 32.4, 29.6, 26.1, 18.2, -5.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4. GCMS (EI) calculated for [M]+ 358.19, found 358.3. FTIR (neat, cm^{-1}): 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 (Et_2O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (118 mg, 94% yield, E:Z = 10:1). ^{1}H 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 [M]+ 216.32, found 216.5. FTIR (neat, cm-1): 2923 (s), 2845 (s), 1605(s), 1511(s), 1246(s), 678(m).

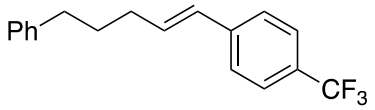


1-methoxy-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]benzene (43), compound was prepared according to an altered general procedure. Li*O*t*Bu was used in place of Na*O*t*Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of Na*O*t*Bu 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). ^{1}H 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 [M]+ 240.12, found 240.2. FTIR (neat, cm^{-1}): 3055(m), 2987(m), 2305(m), 1609(s), 1514(s), 896(s), 740(s).

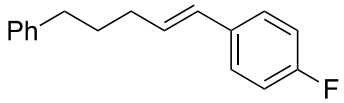


1-methoxy-4-[(*E*)-2-[4-(trifluoromethyl)phenyl]ethenyl]benzene (44), compound was prepared according to an altered general procedure. Li*O*t*Bu was used in place of Na*O*t*Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 2 h. After the addition of 2 equiv of Na*O*t*Bu 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

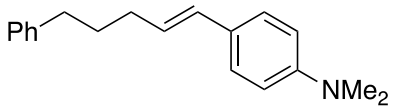
the E-alkene. The compound was purified by silica gel chromatography with EtOAc/Hex (0 → 40%) and isolated as a pale yellow solid (115 mg, 83% yield, E:Z = 22:1). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 16.4 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H). ^{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. ^{19}F NMR (471 MHz, $CDCl_3$) 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).



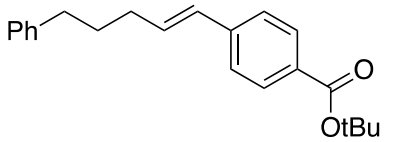
1-[(1*E*)-5-phenylpent-1-en-1-yl]-4-(trifluoromethyl)benzene (45), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of iBuOH were added and the reaction mixture was stirred at 45 °C. After 1 h a 30 μL aliquot 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (120 mg, 83% yield, E:alkane = 11:1). ^{1}H 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). ^{13}C 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).



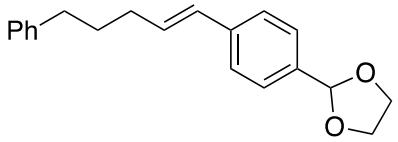
1-fluoro-4-[(1*E*)-5-phenylpent-1-en-1-yl]benzene (46), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken 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% Et_2O/Hex). The compound was isolated as a clear colorless oil (103 mg, 86% yield, 1 isomer). ^{1}H 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). ^{19}F NMR (471 MHz, Chloroform-d) δ -123.85. ^{13}C 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-[(1*E*)-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 Me2*i*PrSiH 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 (Et_2O/Hex 0 →15%) and filtration through a short plug of alumina (10% Et_2O/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). ^{13}C 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).

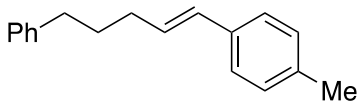


tert-butyl 4-[(1*E*)-5-phenylpent-1-en-1-yl]benzoate (48), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of *t*BuOH (used to prevent transesterification) were added and the reaction mixture was stirred 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 (Et_2O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et_2O/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). ^{13}C 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).

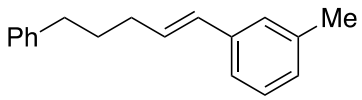


2-{4-[(1*E*)-5-phenylpent-1-en-1-yl]phenyl}-1,3-dioxolane (49), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 µL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et_2O/Hex 0 →15%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a

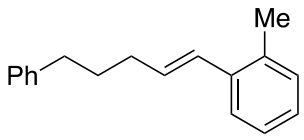
clear colorless oil (126 mg, 86% yield, 1 isomer). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.43 – 7.20 (m, 7H), 7.17 (d, *J* = 7.1 Hz, 3H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.77 (s, 1H), 4.21 – 3.89 (m, 4H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.31 – 2.13 (m, 2H), 1.79 (p, *J* = 7.6 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 [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).



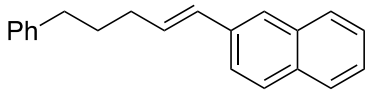
1-methyl-4-[(1*E*)-5-phenylpent-1-en-1-yl]benzene (50), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et_2O/Hex 0 →5%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (101 mg, 85% yield, E:alkane = 22:1). ^{1}H 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 [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).



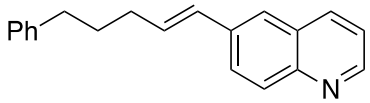
1-methyl-3-[(1*E*)-5-phenylpent-1-en-1-yl]benzene (51), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH were added and the reaction mixture was stirred at 45 °C. After 24 h a 30 μL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et_2O/Hex 0 →5%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (103 mg, 87% yield, 1 isomer). ^{1}H 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 [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).



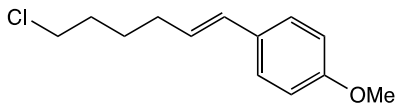
1-methyl-2-[(1*E*)-5-phenylpent-1-en-1-yl]benzene (52), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 5.0 equiv of MeOH and 0.50 equiv Me2*i*PrSiH were added and the reaction mixture was stirred at 45 °C. After 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 (Et_2O/Hex 0 →5%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (95 mg, 80% yield, E:Z = 24:1). ^{1}H 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). ^{13}C 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).



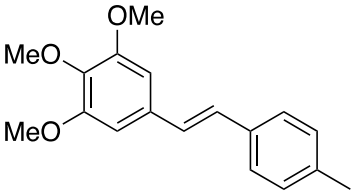
2-[(1*E*)-5-phenylpent-1-en-1-yl]naphthalene (53), compound was prepared according to the general procedure. After 2 h TLC in 100% Hex showed that the starting alkyne was fully consumed. 2.0 equiv of *i*BuOH were added and the reaction mixture was stirred at 45 °C. After 30 h a 30 µL aliquot was taken and analysis by GC for confirmed complete isomerization to the E-alkene. The compound was purified by silica gel chromatography (Et_2O/Hex 0 →10%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (121 mg, 89% yield, E:alkane = 37:1). ^{1}H 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). ^{13}C 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-[(1*E*)-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 (Et_2O/Hex 0 →25%) and filtration through a short plug of alumina (10% Et_2O/Hex). The compound was isolated as a clear colorless oil (103 mg, 75% yield, E:alkane = 14:1). ^{1}H 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). ^{13}C 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).

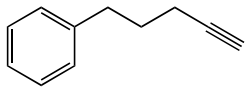


1-[(1*E*)-6-chlorohex-1-en-1-yl]-4-methoxybenzene (55), compound was prepared according to the general procedure. TLC in 10% EtOAc/Hex showed that the starting alkyne was fully consumed after 2 h. 5.0 equiv of *i*BuOH were added and the reaction mixture was stirred at 45 °C. After 12 hours a 30 µL was 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 (99 mg, 88% yield, E:Z = >100:1) ^{1}H 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 [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).

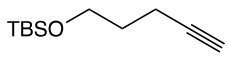


1,2,3-trimethoxy-5-[(E)-2-(4-methylphenyl)ethenyl]benzene (57) compound was prepared according to an altered general procedure. LiO*t*-Bu was used in place of NaO*t*-Bu as a turnover reagent. TLC in 20% EtOAc/Hex showed that the starting alkyne was consumed after 4 h. After the addition of 2 equiv of NaO*t*-Bu and 5 equiv of MeOH. The reaction mixture was stirred at 60 °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 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]

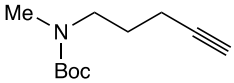
11. <u>Alkyne Starting Materials</u>



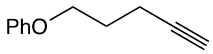
5-phenyl-1-pentyne (1) was purchased from GFS Chemical and distilled over calcium hydride under reduced pressure before use.



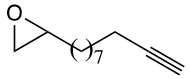
tert-butyldimethyl(pent-4-yn-1-yloxy)silane (S1) was prepared according to a known procedure and has been previously characterized.[1]



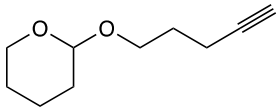
tert-butyl N-methyl-N-(pent-4-yn-1-yl)carbamate (S2) was prepared according to a known procedure and has been previously characterized.[2]



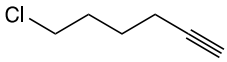
(pent-4-yn-1-yloxy)benzene (S3) was prepared according to a known procedure and has been previously characterized.[3]



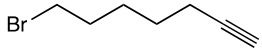
2-(dec-9-yn-1-yl)oxirane (S4) was prepared according to a known procedure and has been previously characterized.[4]



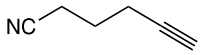
2-(pent-4-yn-1-yloxy)tetrahydra-2*H*-pyran (S5) has been previously characterized and spectral data match literature values.[5]



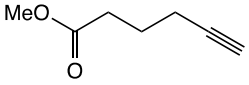
6-chlorohex-1-yne (S6) was purchased from TCI America and distilled over calcium hydride under reduced pressure before use.



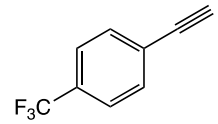
7-bromohept-1-yne (S7) was prepared according to a known procedure and has been previously characterized.[6]



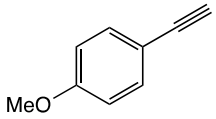
hex-5-ynenitrile (S8) was purchased from Oakwood Chemical and distilled over calcium hydride under reduced pressure before use.



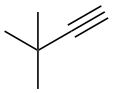
methyl hex-5-ynoate (S9) was purchased from Fischer Scientific and distilled over calcium hydride under reduced pressure before use.



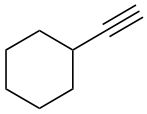
1-ethynyl-4-(trifluoromethyl)benzene (S10) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



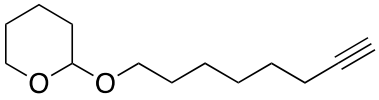
1-ethynyl-4-methoxybenzene (S11) was purchase from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



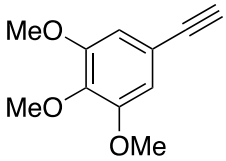
3,3-dimethylbut-1-yne (S12) was purchased from Milipore Sigma and distilled over calcium hydride under reduced pressure before use.



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

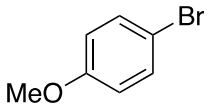


2-(oct-7-yn-1-yloxy)oxane (S14) was prepared according to a known literature procedure and has been previously characterized.[7]

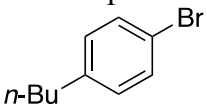


5-ethynyl-1,2,3-trimethoxybenzene (S15) was prepared according to a known literature procedure and has been previously characterized.[8]

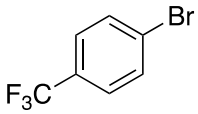
12. <u>Aryl Bromide Starting Materials</u>



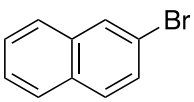
4-bromoanisole (2) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



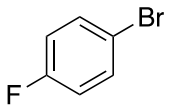
1-bromo-4-butylbenzene (4) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



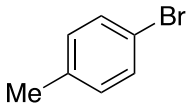
4-bromobenzotrifluoride (S16) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



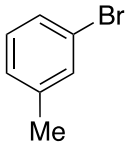
2-bromonaphthalene (S17) was purchased from Ark-Pharm and used without purification.



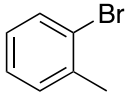
1-bromo-4-fluorobenzene (S18) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



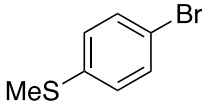
4-bromotoluene (S19) was purchased form Alfa Aesar and using without purification.



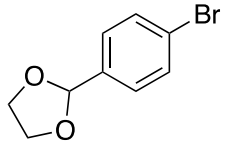
3-bromotoluene (S20) was purchased form TCI America and distilled over calcium hydride under reduced pressure before use.



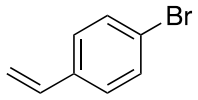
2-bromotoluene (S21) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.



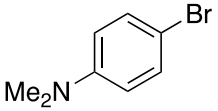
1-bromo-4-(methylsulfanyl)benzene (S22) was purchased from Oakwood Chemicals and used without purification.



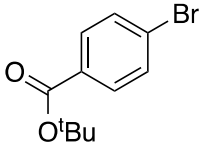
1-bromo-4-phenyl-1,3-dioxolane (S23) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.



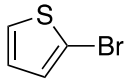
4-bromostyrene (S24) was purchased from TCI America and degassed before use.



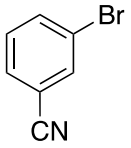
4-bromo-N,N-dimethylaniline (S25) was purchased from Oakwood Chemicals and used without purification.



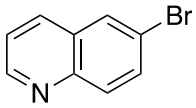
tert-butyl-4-bromobenzoate (S26) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.



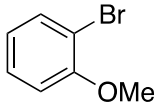
2-bromothiophene (S27) was purchased from Combi-Blocks and distilled over calcium hydride under reduced pressure before use.



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

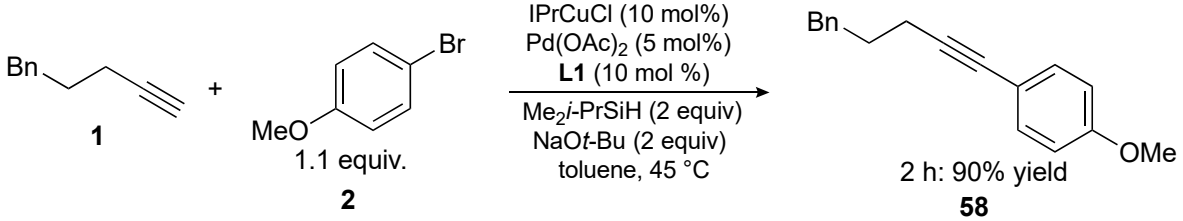


6-bromoquinoline (S29) was purchased from Ark-Pharm and distilled over calcium hydride under reduced pressure before use.

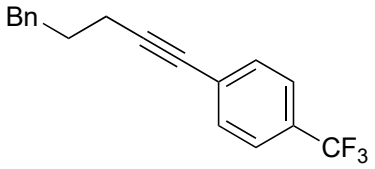


2-bromoanisole (S30) was purchased from Millipore Sigma and distilled over calcium hydride under reduced pressure before use.

13. Synthesis of Internal Alkyne Intermediate



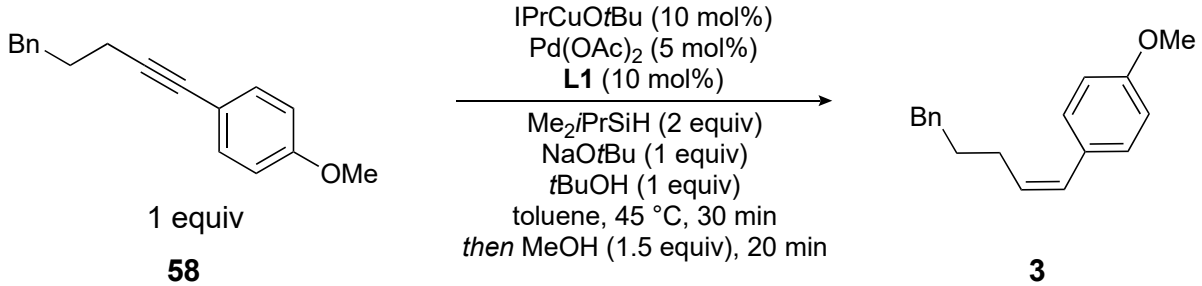
In a nitrogen filled glovebox, a scintillation vial was charged with a stir bar and NaO*t*-Bu (96.1 mg, 1.00 mmol, 2 equiv). To this was added alkyne (**1**) (0.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.8 mg, 0.025 mmol, 0.100 equiv) IPrCuCl (24.4 mg, 0.050 mmol, 0.10 equiv), **L1** (19 mg, 0.050 mmol, 0.10 equiv), aryl bromide (**2**) (102.9 mg, 0.550 mmol, 1.10 equiv), Me_2*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 (Et_2O/Hex 0→10%) and passed through a short plug of alumina (10% Et_2O/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



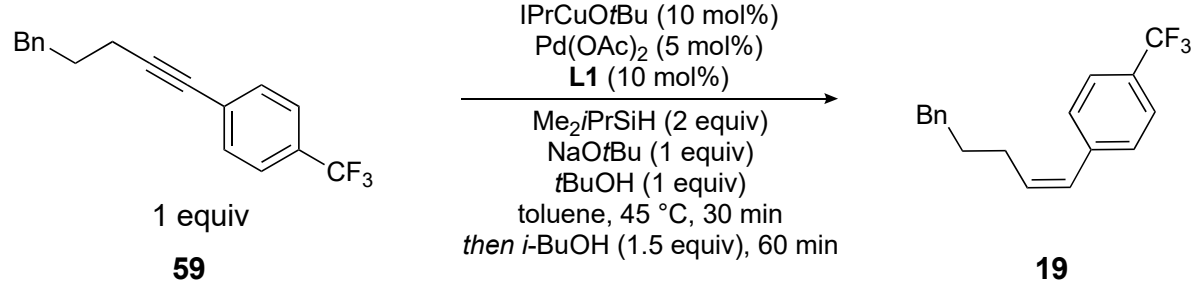
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg. 0.017 mmol, 0.33 equiv), $Pd(OAc)_2$ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuO*t*-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me_2*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



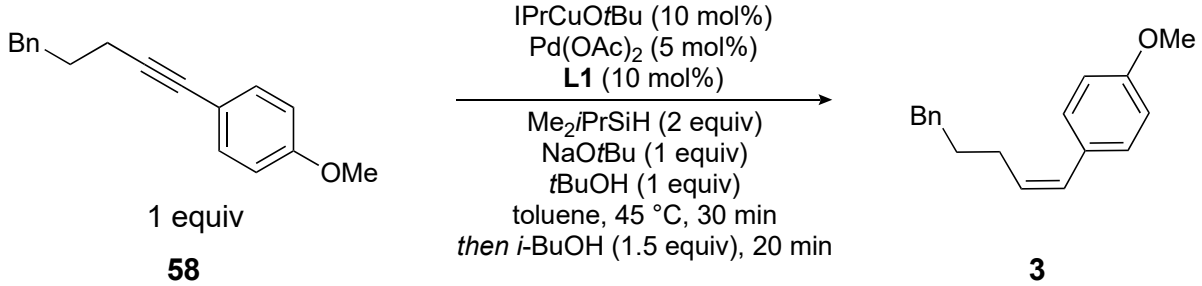
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **59** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg. 0.017 mmol, 0.33 equiv), $Pd(OAc)_2$ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuO*t*-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me_2*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



58 **3**

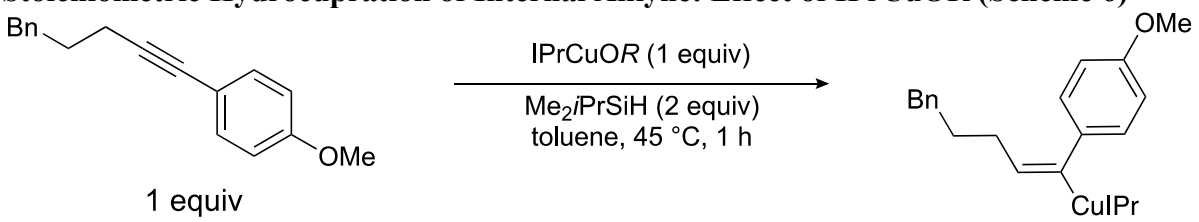
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg. 0.017 mmol, 0.33 equiv), $Pd(OAc)_2$ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuO*t*-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me_2*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)



1 equiv

58

60

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), Me2*i*-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

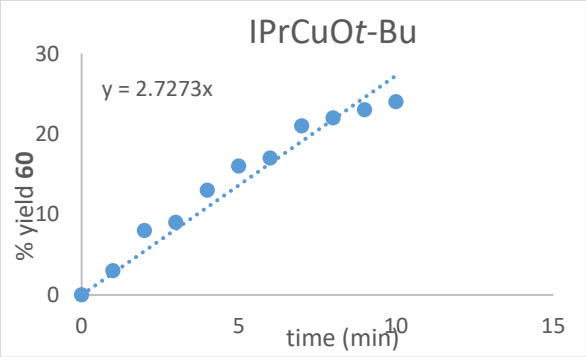
IPrCuO*t*-Bu

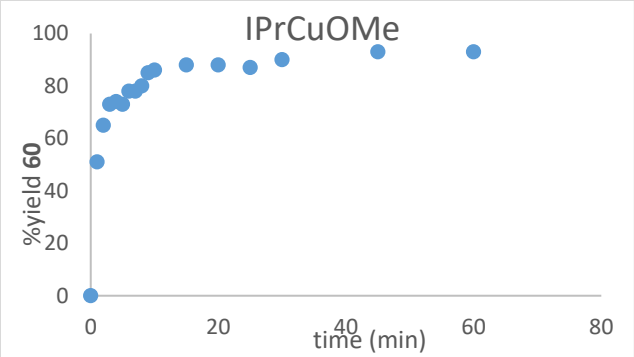
Time (min)	% **58**	% yield (**60**)
0	96	0
1	93	3
2	91	8
3	86	9
4	83	13
5	78	16
6	82	17
7	72	21
8	71	22
9	70	23
10	70	24
15	60	27
20	54	36
25	0	48
30	37	45
45	29	68
60	20	74

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

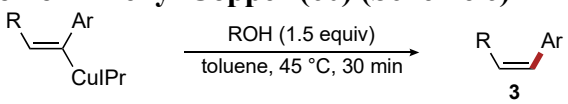
Quenching of IPrCuOt-Bu

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, IPrCuO*t*-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), Me2*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), NaO*t*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv), MeOH (2.4 mg, 0.075 mmol, 1.5 equiv), $Br_2Cl_4C_2$ (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 dibromotetrachloroehtane 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), Me2*i*-PrSiH (10.2 mg, 0.10 mmol, 2.0 equiv), NaO*t*-Bu (4.8 mg, 0.050 mmol, 1 equiv), MeOH (2.4 mg, 0.075 mmol, 1.50 equiv), $Br_2Cl_4C_2$ (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 dibromotetrachloroehtane 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)



60 **3**

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 $Br_2Cl_4C_2$ (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

t-BuOH

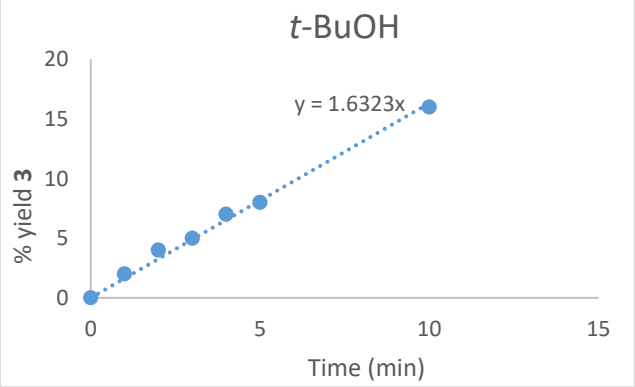
Time (min)	alkenyl copper (**60**)	% yield **3**	% yield **3** (corrected)
0	86	5	0
1	85	7	2
2	86	9	4
3	85	10	5
4	82	12	7
5	84	13	8
10	70	21	16
15	67	25	20
20	61	27	22

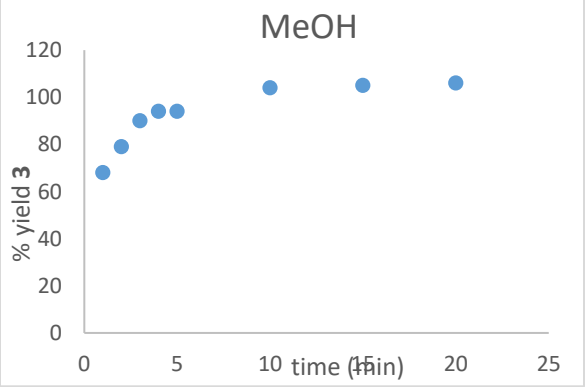
Table S10b

MeOH

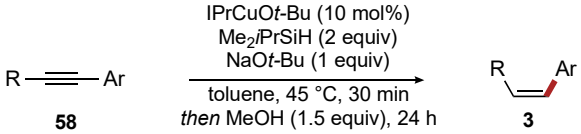
Time (min)	alkenyl copper (**60**)	% yield **3**
0	100	0
1	34	68
2	22	79
3	0	90
4	0	94
5	0	94
10	0	104
15	0	105
20	0	106

Yields for *t*-BuOH are corrected to 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, NaO*t*-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), IPrCuO*t*-Bu (2.6 mg, 0.005 mmol, 0.10 equiv), Me$_2$*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 $Br_2Cl_4C_2$ (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

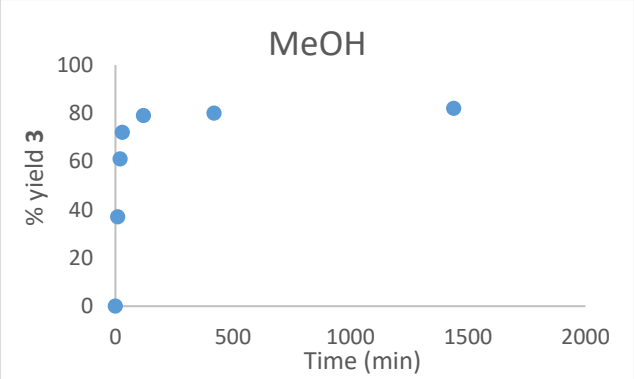
MeOH

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



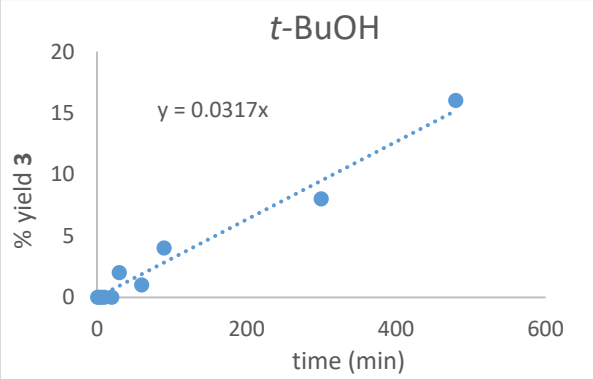


Table S11c

1.5 MeOH and No NaO*t*-Bu

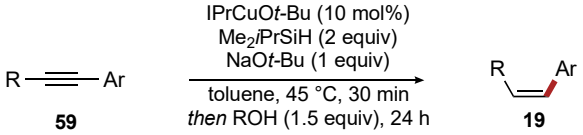
Time (min)	% **58**	% yield **3**	% alkenyl copper **60**
0	100	0	0
1	73	22	4
2	70	30	4
3	60	35	4
4	54	40	4
5	44	52	4
10	43	52	4
20	36	63	4
30	33	66	4
45	30	63	2
60	31	66	3
3 h	29	66	0
8 h	28	63	0
24 h	28	67	0

Table S11d

1 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, NaO*t*-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), IPrCuO*t*-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 $Br_2Cl_4C_2$ (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

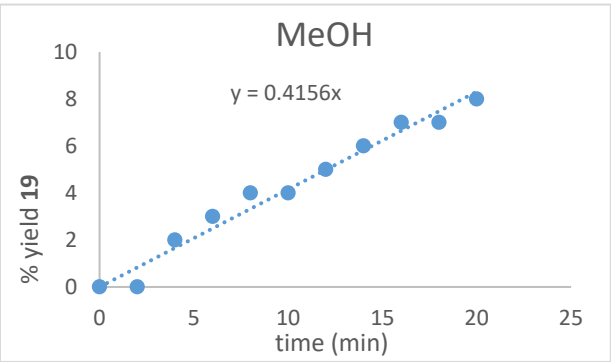
MeOH

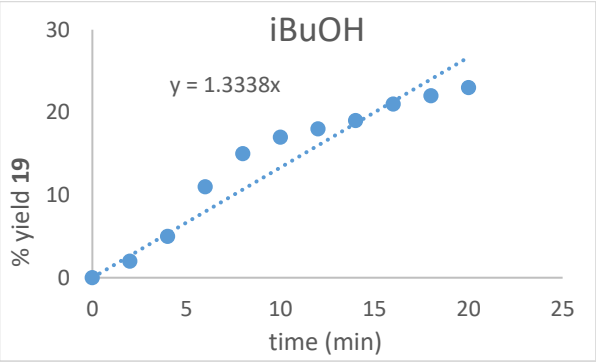
Time (min)	% **59**	% yield **19**	alkenyl copper
0	97	0	0
2	92	0	4
4	91	2	6
6	90	3	6
8	91	4	6
10	86	4	7
12	93	5	8
14	89	6	8
16	88	7	9
18	87	7	10
20	88	8	10

Table S12b

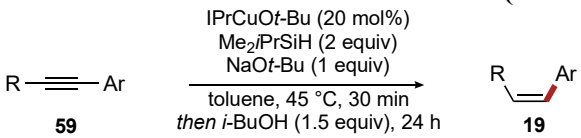
i-BuOH

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





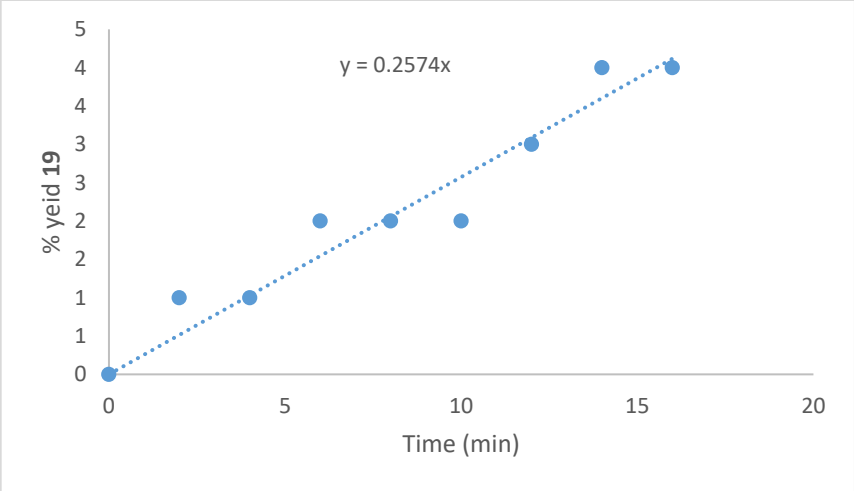
Copper-Catalyzed Semireduction: 20% IPrCuO*t*-Bu with 59 (Scheme 7)



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-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), IPrCuO*t*-Bu (5.2 mg, 0.01 mmol, 0.20 equiv), Me$_2$*i*-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 µL aliquots were taken, and quenched into $Br_2Cl_4C_2$ (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.

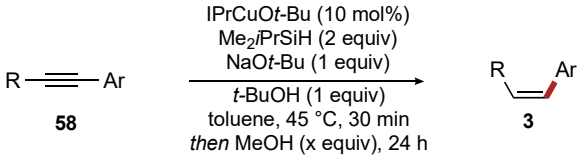
Table S13

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)

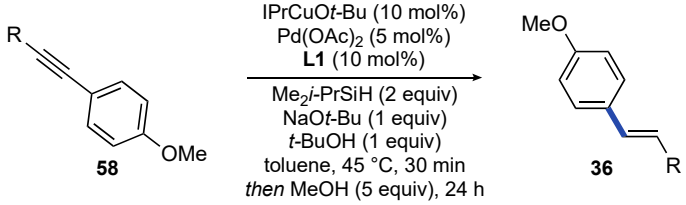


equiv of MeOH	Yield (30 min)	yield (4 h)	yield (7 h)	yield (24 h)
1	65%	70%	86%	89%
2	50%	66%	73%	75%
3	32%	33%	33%	35%
4	16%	16%	17%	17%
5	10%	10%	10%	10%

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-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), IPrCuO*t*-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

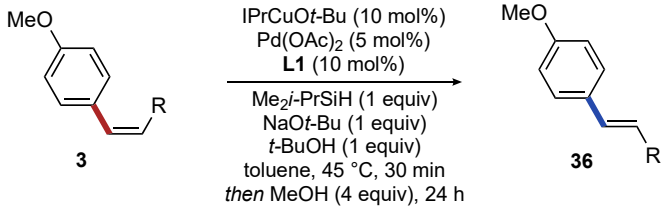


In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-Bu (4.8 mg, 0.050 mmol, 1.0 equiv). To this was added **58** (12.5 mg, 0.050 mmol, 1.0 equiv), TMB (2.8 mg. 0.017 mmol, 0.33 equiv), $Pd(OAc)_2$ (0.60 mg, 0.0025 mmol, 0.05 equiv), **L1** (1.9 mg, 0.005 mmol, 0.10 equiv), IPrCuO*t*-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]

[a]Yield of Sonogashira starting material, mass balance is Z alkene.

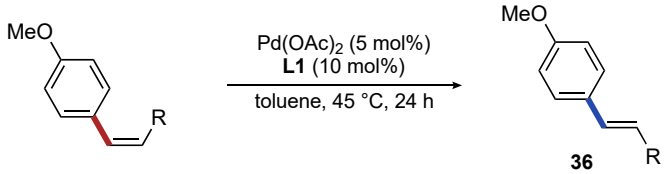
Catalytic Semireduction and Isomerization of the *Z*-alkene to *E*-alkene



In a nitrogen filled glovebox, a dram vial was charged with a stir bar, NaO*t*-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), IPrCuO*t*-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 Me2*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.

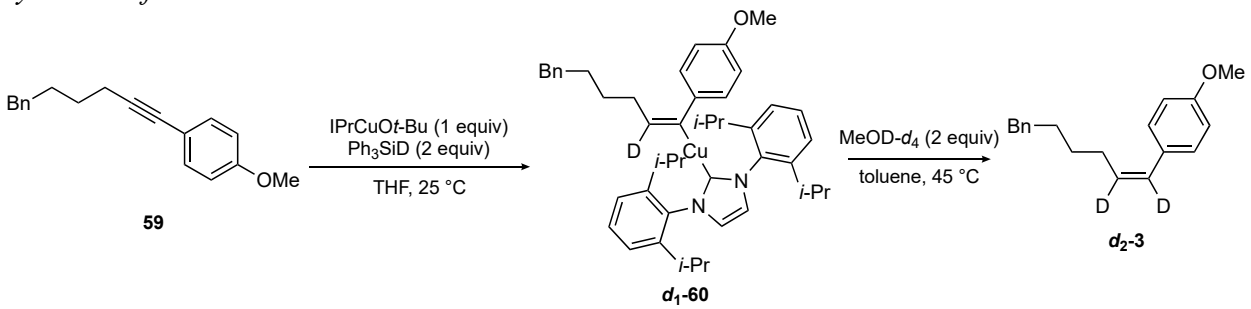
Reaction Conditions	**Yield (20 min)**	**yield (4 h)**	**yield (7 h)**	**yield (24 h)**
10 mol% Me2*i*-PrSiH	18%	47%	69%	88%[a]
10 mol% Me2*i*-PrSiH w/ 4 equiv MeOH	9%	15%	46%	82%[a]
Pd_2dba_3 instead of $Pd(OAc)_2$	0%	0%	0%	2%
1 equiv Me2*i*-PrSiH	34%	73%	80%	82%[a]
1 equiv Me2*i*-PrSiH w/ 4 equiv MeOH	15%	23%	63%	85%[a]
2 equiv Me2*i*-PrSiH	28%	95%[b]	82%	78%

2 equiv Me_2i-PrSiH w/ 4 equiv MeOH	11%	85%	93b[b]	81%
Pd_2dba_3 w/ 1 equiv Me_2i-PrSiH	8%	14%	18%	44%[c]
Pd_2dba_3 w/ 2 equiv Me_2i-PrSiH	8%	9%	20%	45%[c]

[a]Remaining material is overreduction to alkane. [b]Full isomerization complete, extended reaction times result in increased reduction to alkane. [c]Remaining material is *Z*-alkene.

17. Mechanistic Studies: Deuterium Incorporation Experiments

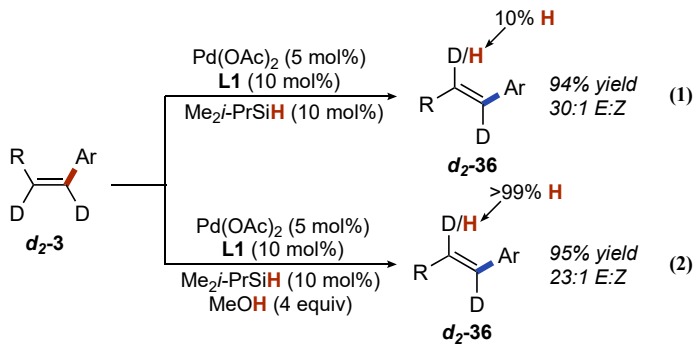
Synthesis of ***d*$_1$*-3***

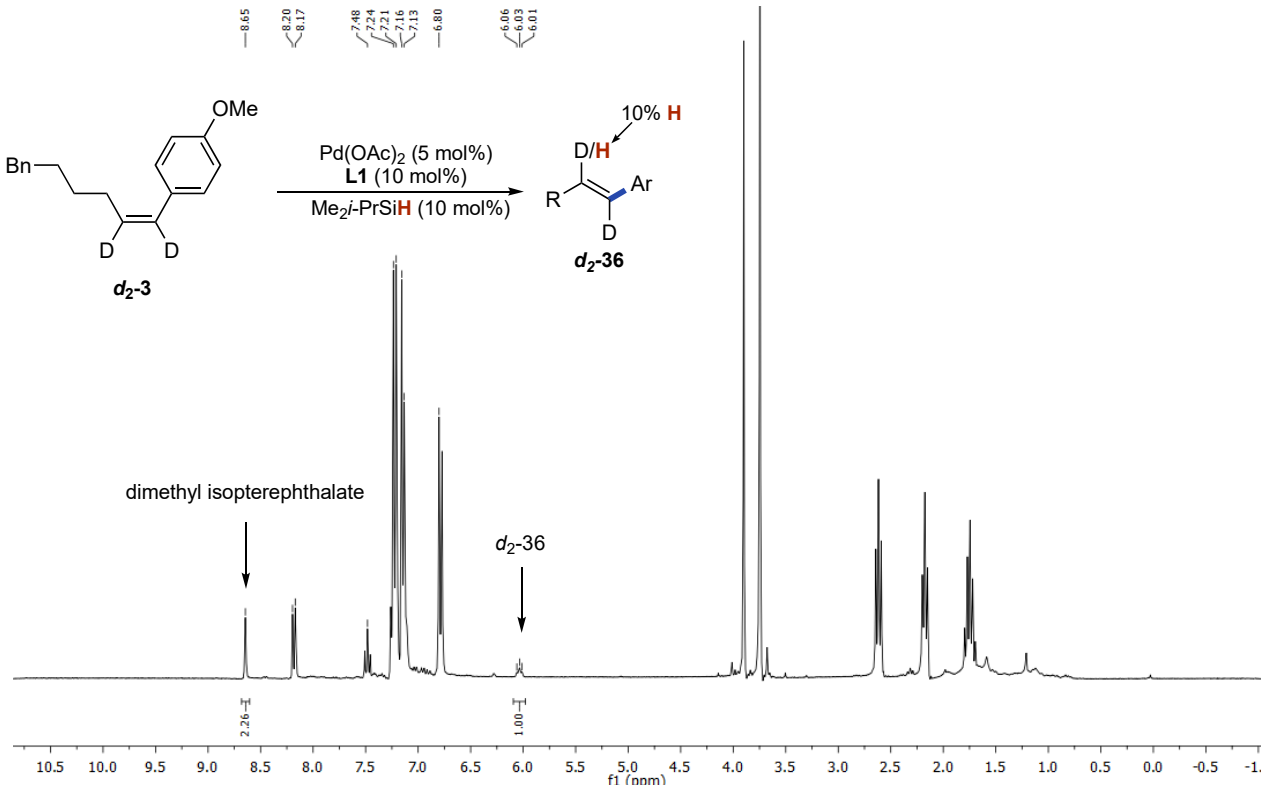


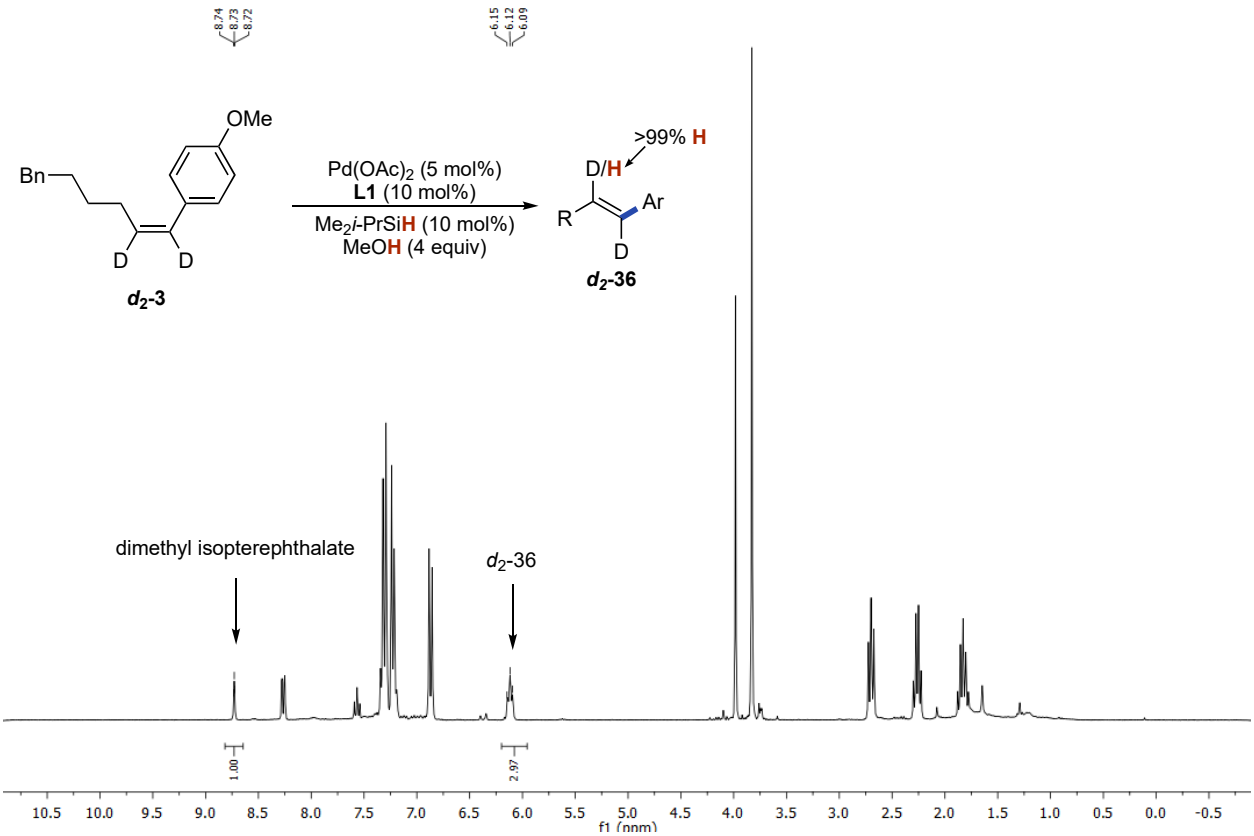
In a nitrogen filled glovebox, IPrCuO*t*-Bu (394.7 mg, 0.750 mmol, 1.0 equiv) was weighed in a 20 mL scintillation vial, followed by 1000 µL THF. **58** (225.3 mg, 0.90 mmol, 1.2 equiv) was weighed out and transferred to the reaction with 3 aliquots of 500 µL of THF and reaction mixture was allowed to stir at 25 °C for 1 min resulting in a orange solution. TriphenylSilane-d_1[16] (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 µL THF at which point the reaction turned red. The reaction was vigorously stirred (1500 rpm) at 25 °C for 30 min after which the reaction turned back to a light orange. The reaction was concentrated in vaccuo, dissolved in minimal dichloromethane, layered with pentane and recrystallized at -35 °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, ~10 min. The reaction was then pushed through a plug of silica with excess EtOAc and purified by silica gel column chromatography. (0→5% EtOAc in hexanes).

Deuterirum Labeling

All glassware was washed with D_2O 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), Me_2i-PrSiH (0.50 mg, 0.010 mmol, 0.1 equiv), and d_8-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 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 isopterephthalate (2.6 mg, 0.017 mmol, 0.33 equiv) was added as internal standard and proton incorporation was determined by ^{1}HNMR in $CDCl_3$.


10% H
D/H
R
Ar
D
d_2-36
94% yield
30:1 E:Z
(1)
R
Ar
D
D
d_2-3
Pd(OAc)$_2$ (5 mol%)
L1 (10 mol%)
Me$_2$i-PrSiH (10 mol%)
>99% H
D/H
R
Ar
D
d_2-36
95% yield
23:1 E:Z
(2)
Pd(OAc)$_2$ (5 mol%)
L1 (10 mol%)
Me$_2$i-PrSiH (10 mol%)
MeOH (4 equiv)


8.65
8.20
8.17
7.48
7.24
7.21
7.16
7.13
6.80
6.06
6.03
6.01
OMe
Bn
D
D
d_2-3
Pd(OAc)$_2$ (5 mol%)
L1 (10 mol%)
Me$_2$i-PrSiH (10 mol%)
10% H
D/H
R
Ar
D
d_2-36
dimethyl isopterephthalate
d_2-36
2.26
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



18. References

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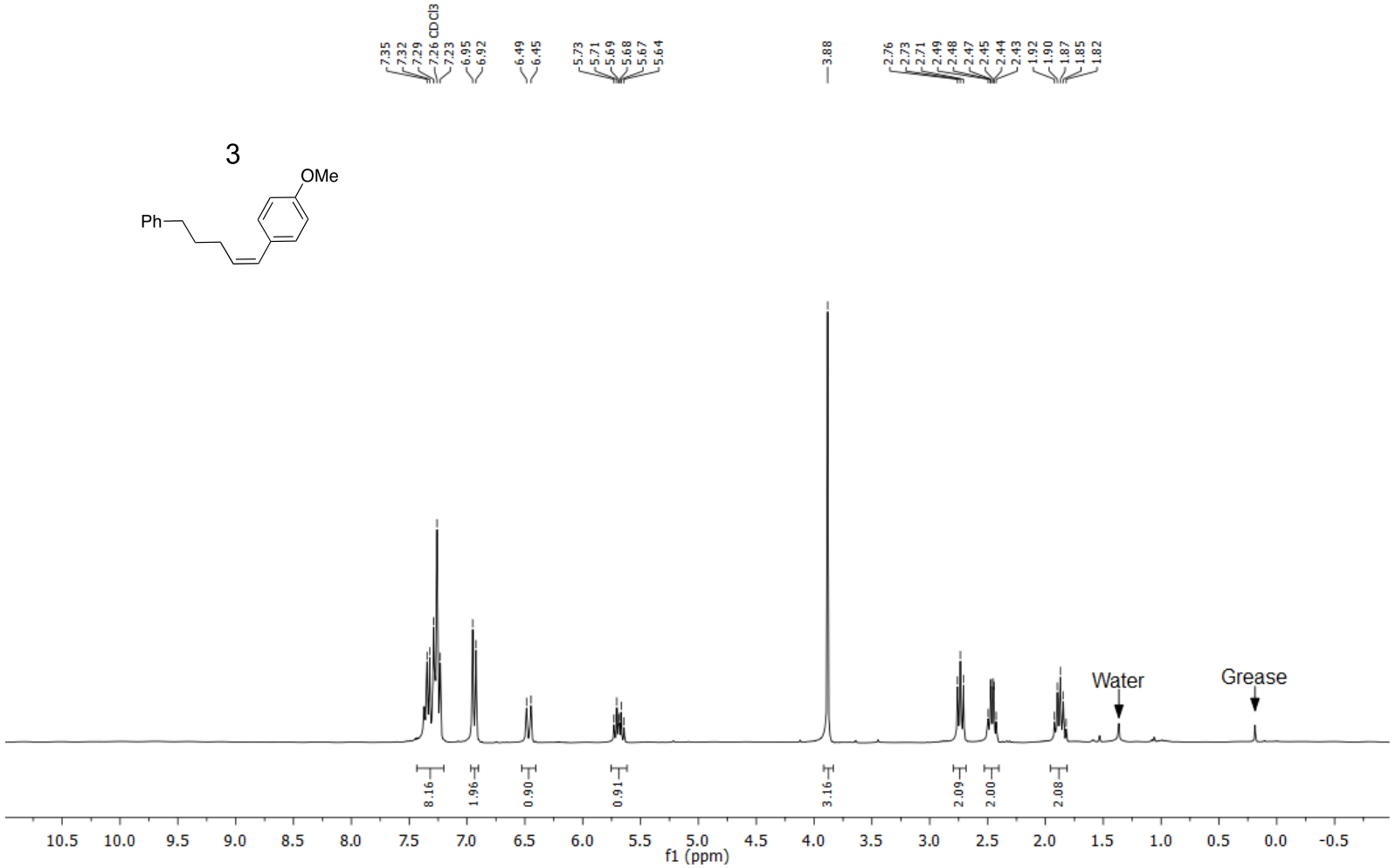
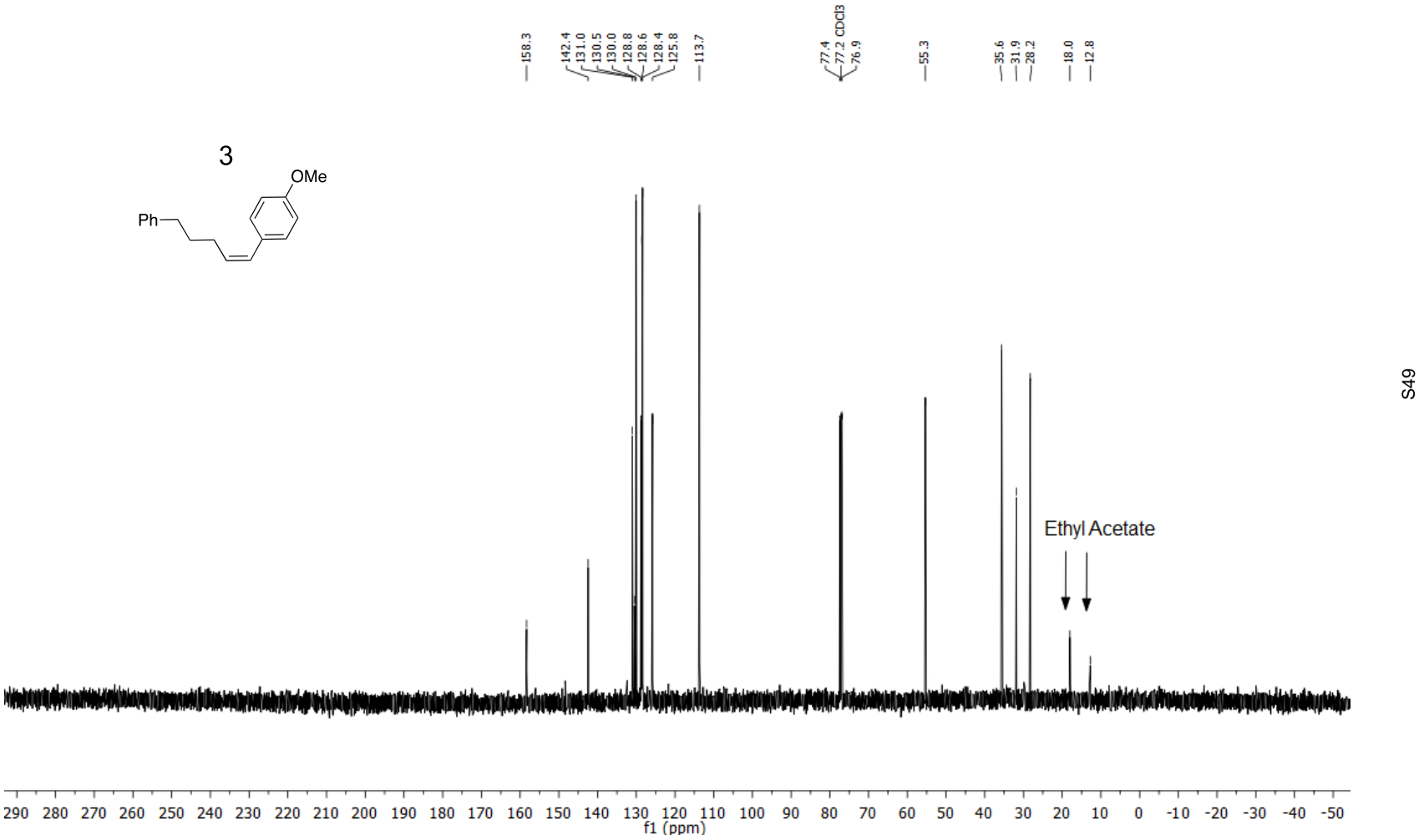
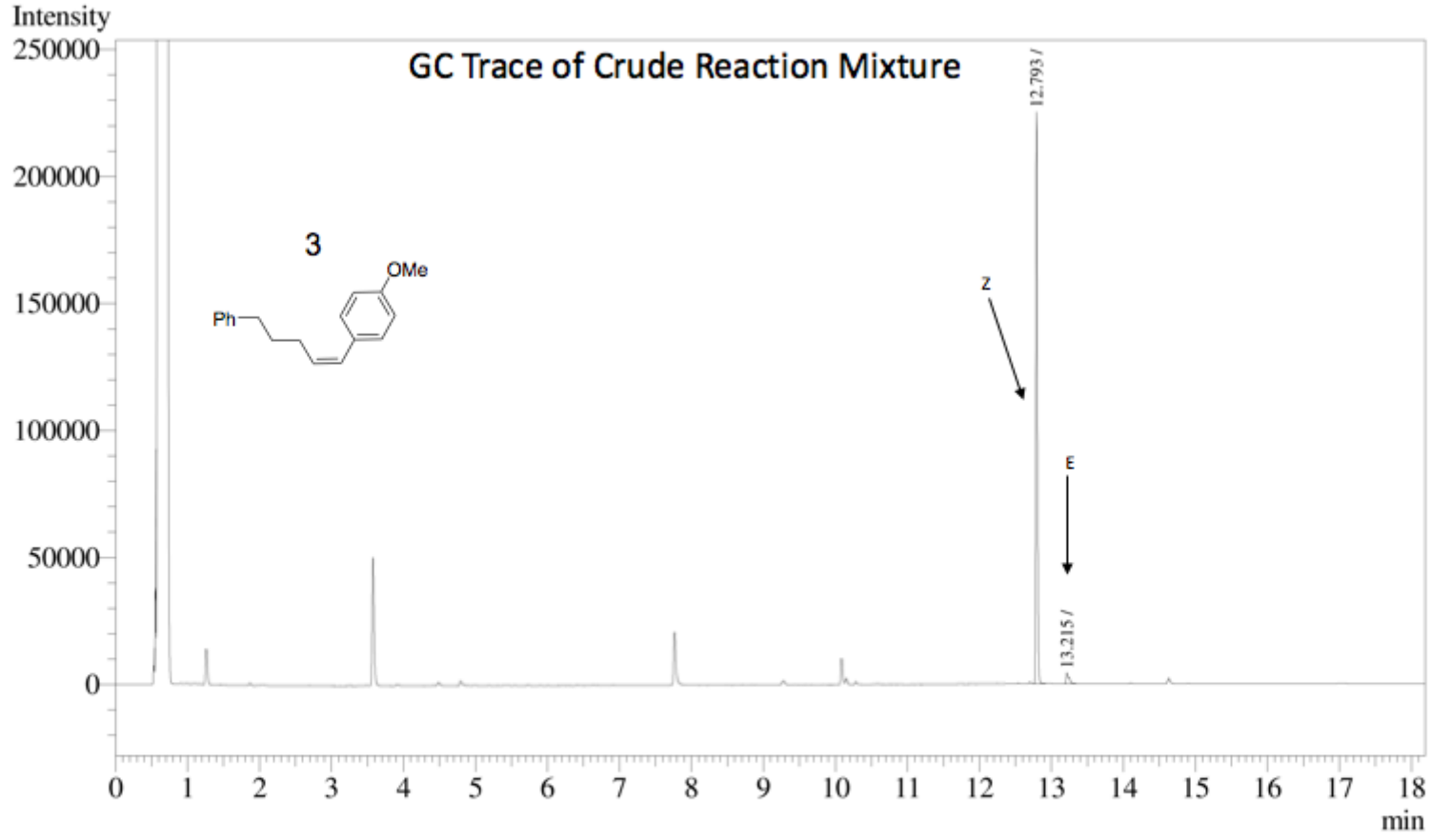
19. Spectral Data

^{1}H 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).



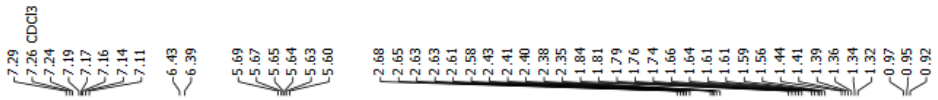
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.6 , 142.7 , 131.3 , 130.7 , 130.3 , 129.0 , 128.8 , 128.6 , 126.1 , 113.9 , 55.6 , 35.9 , 32.1 , 28.5 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.793	315920	218837	96.557		V		
2	13.215	11264	4268	3.443				
Total		327184	223105					

^{1}H 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).



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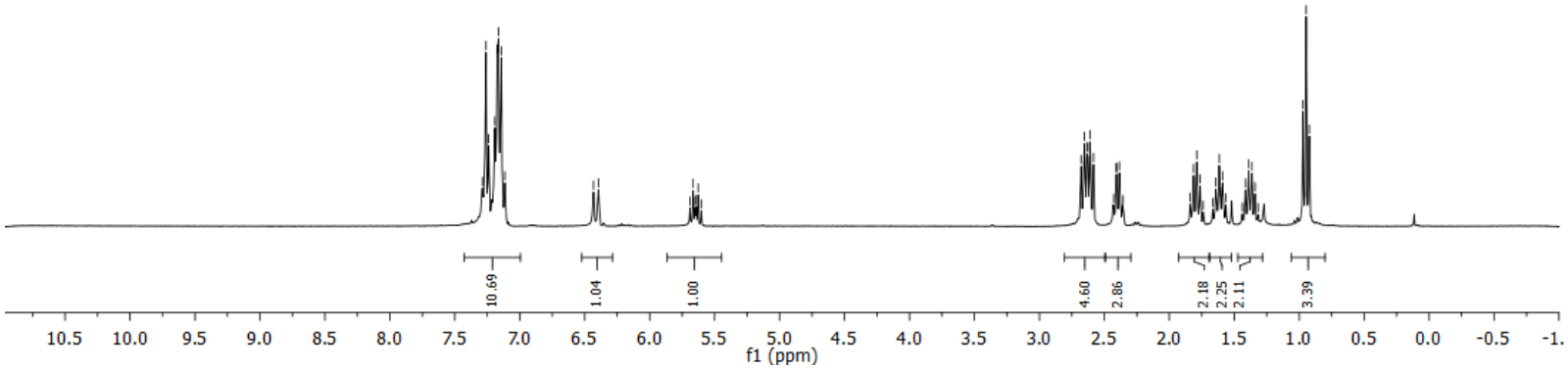
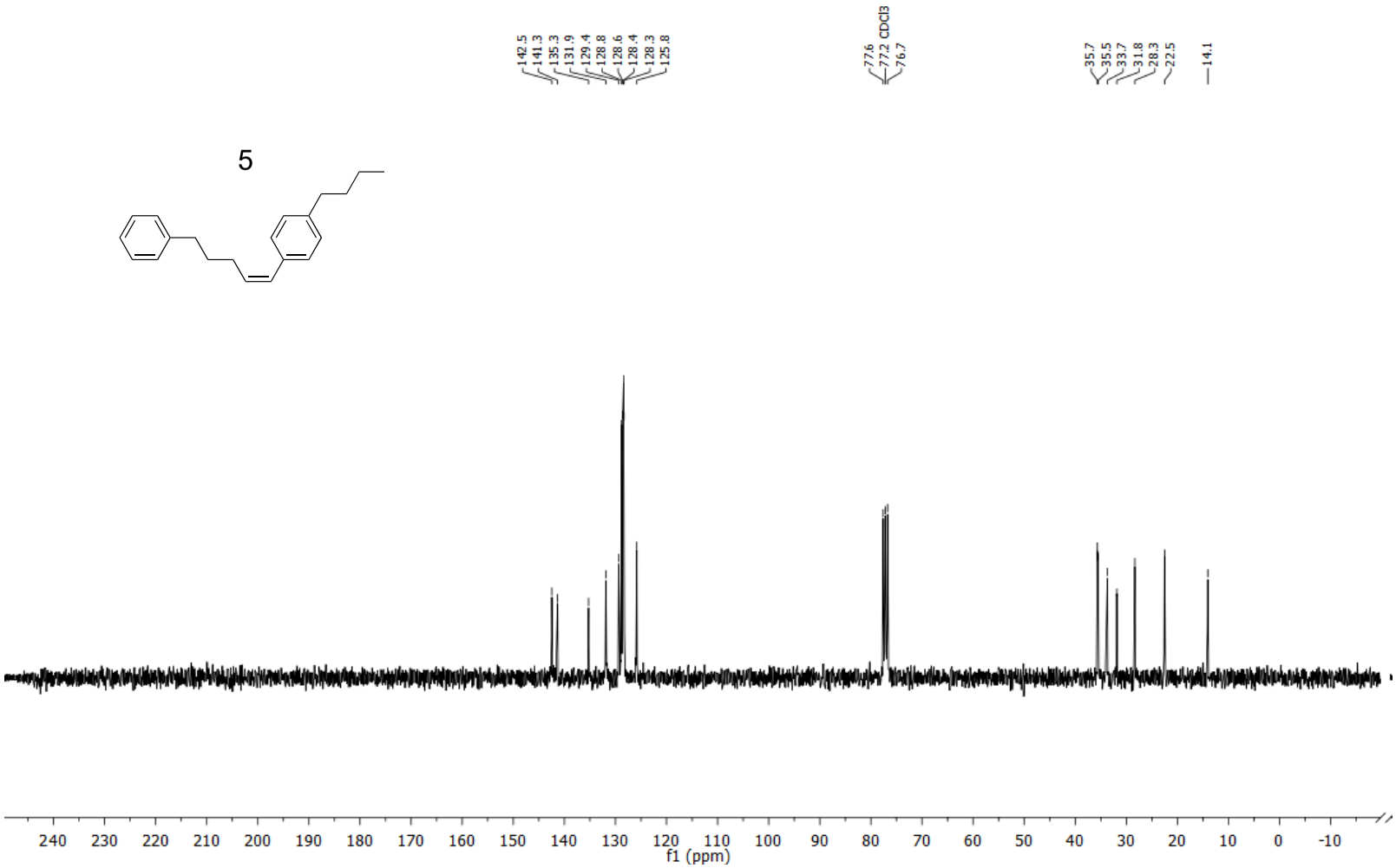
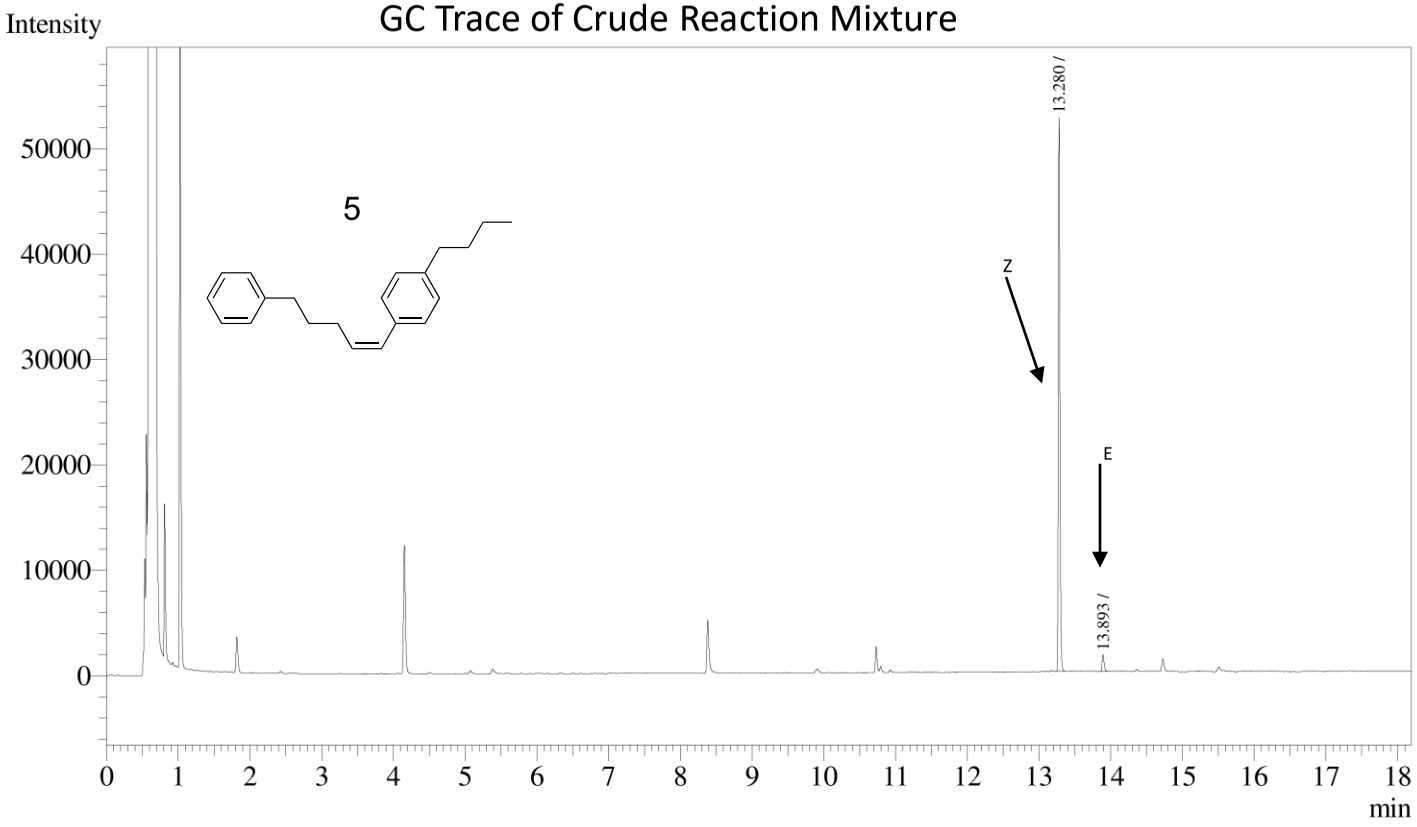


^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 141.3, 135.3, 131.9, 129.4, 128.8, 128.6, 128.4, 128.3, 125.8, 35.7, 35.5, 33.7, 31.8, 28.3, 22.5, 14.1.

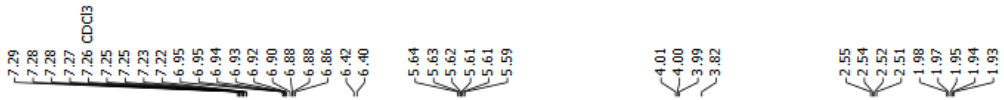


GC Trace of Crude Reaction Mixture

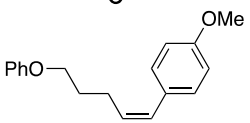


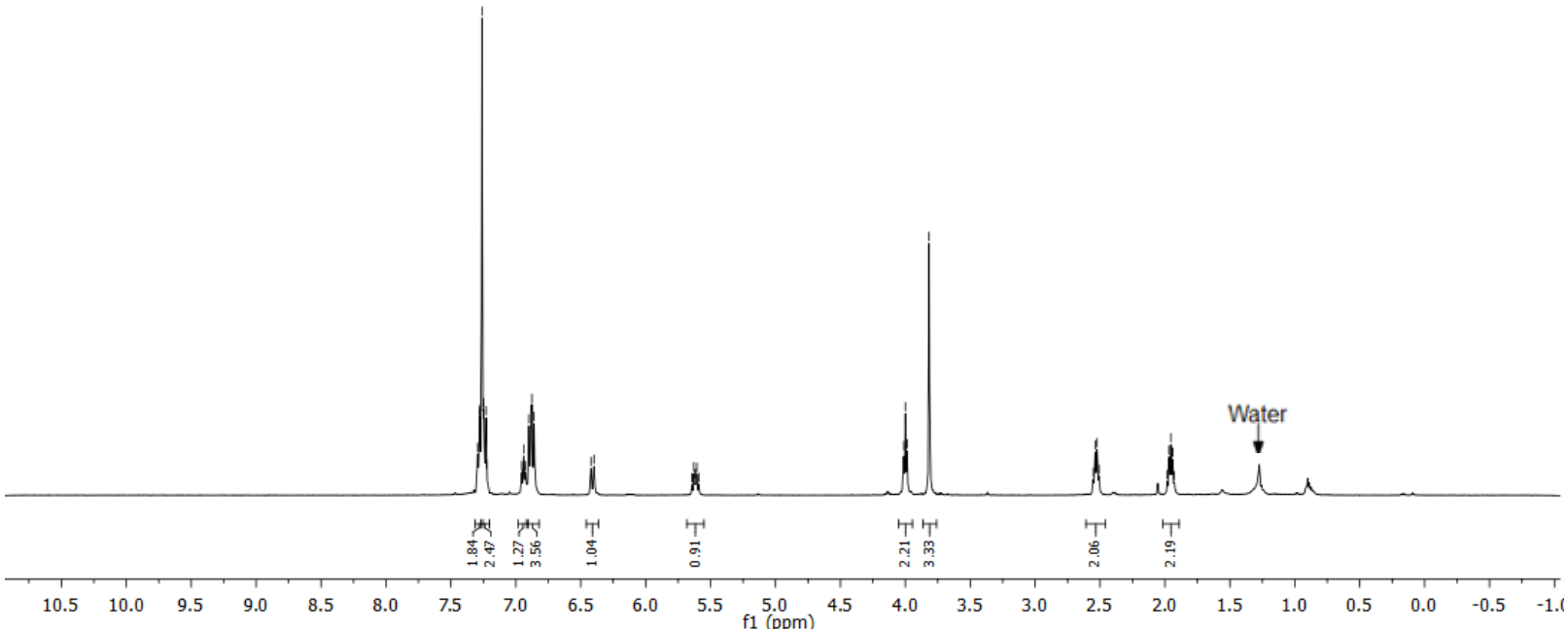
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.280	80126	52051	96.340		V		
2	13.893	3044	1563	3.660				
Total		83170	53614					

^{1}H 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).

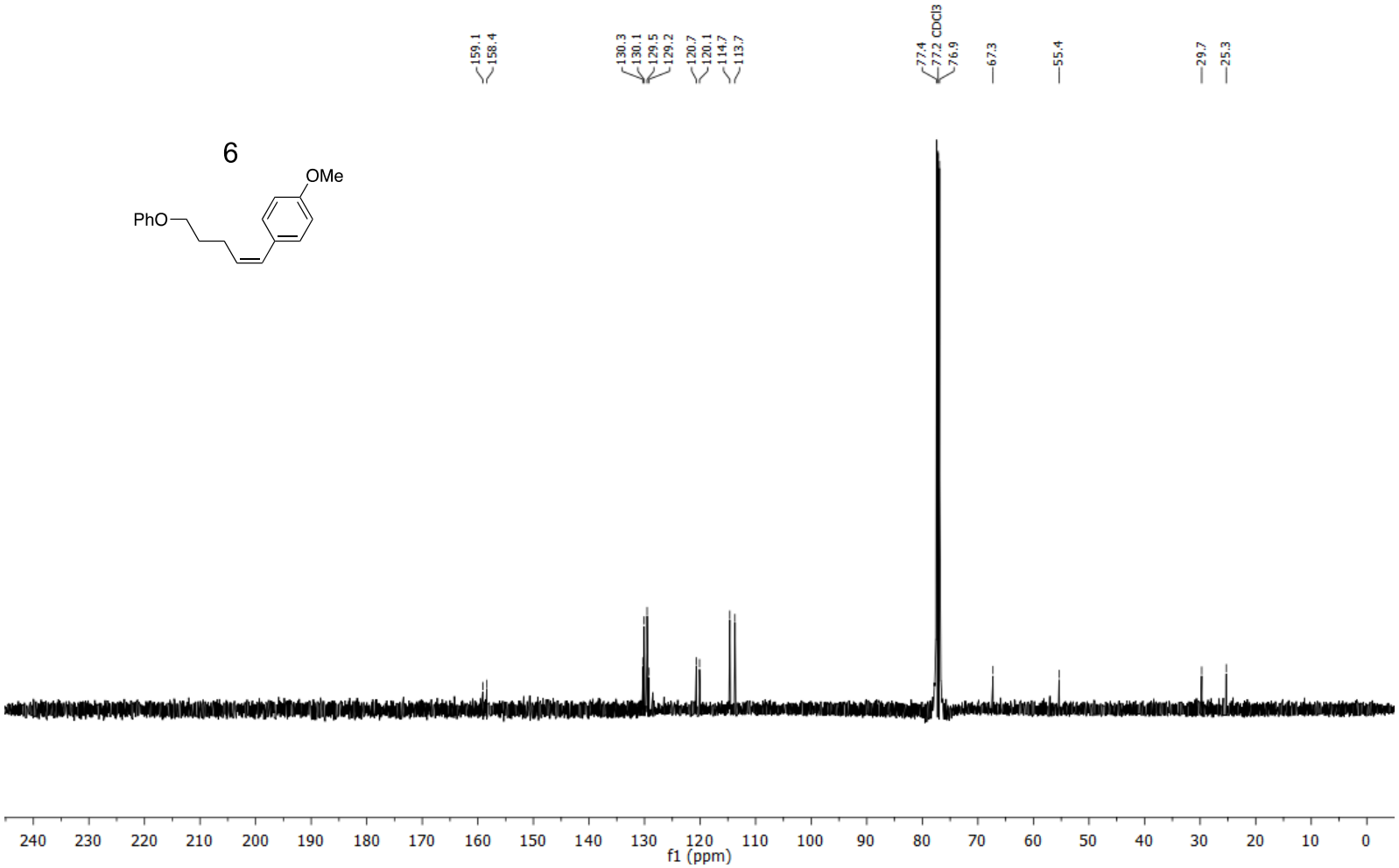


6

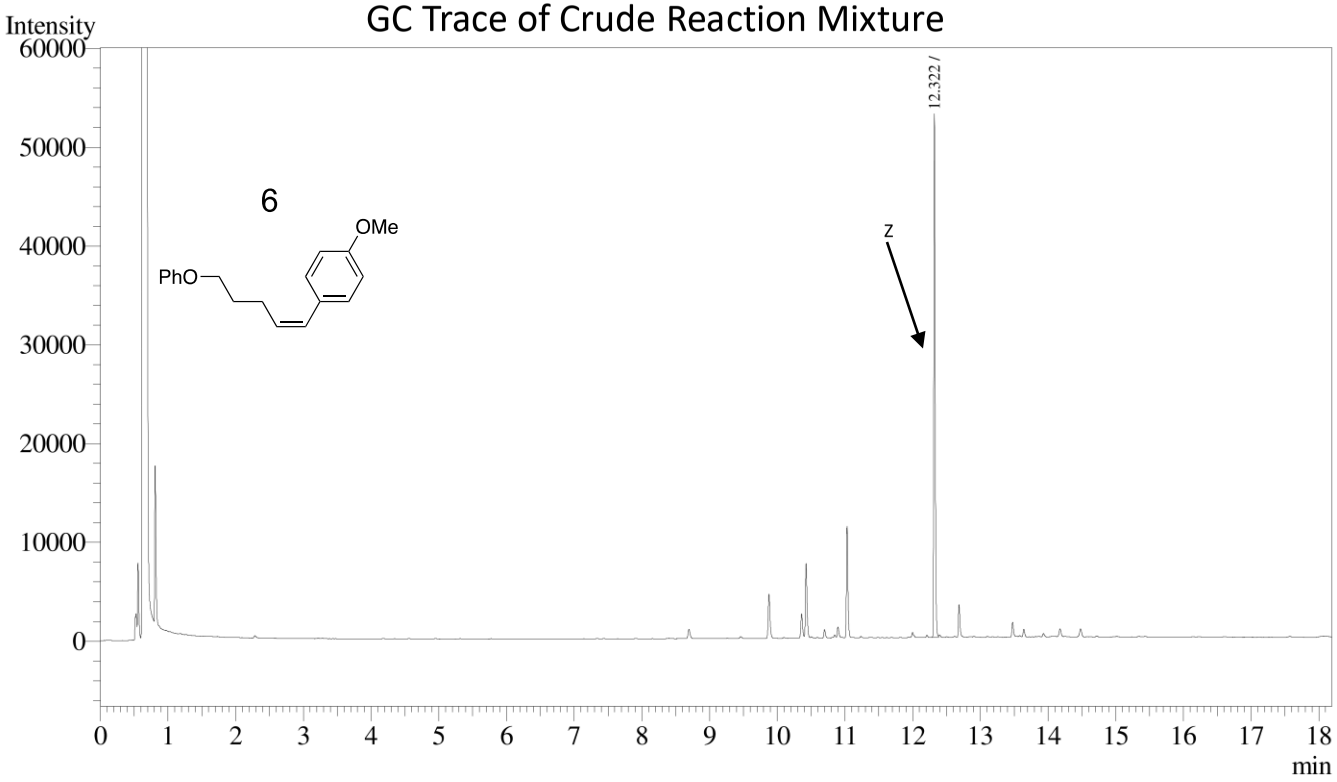




^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 158.4, 130.3, 130.1, 129.5, 129.3, 120.7, 120.1, 114.7, 113.7, 67.3, 55.4, 29.7, 25.3.

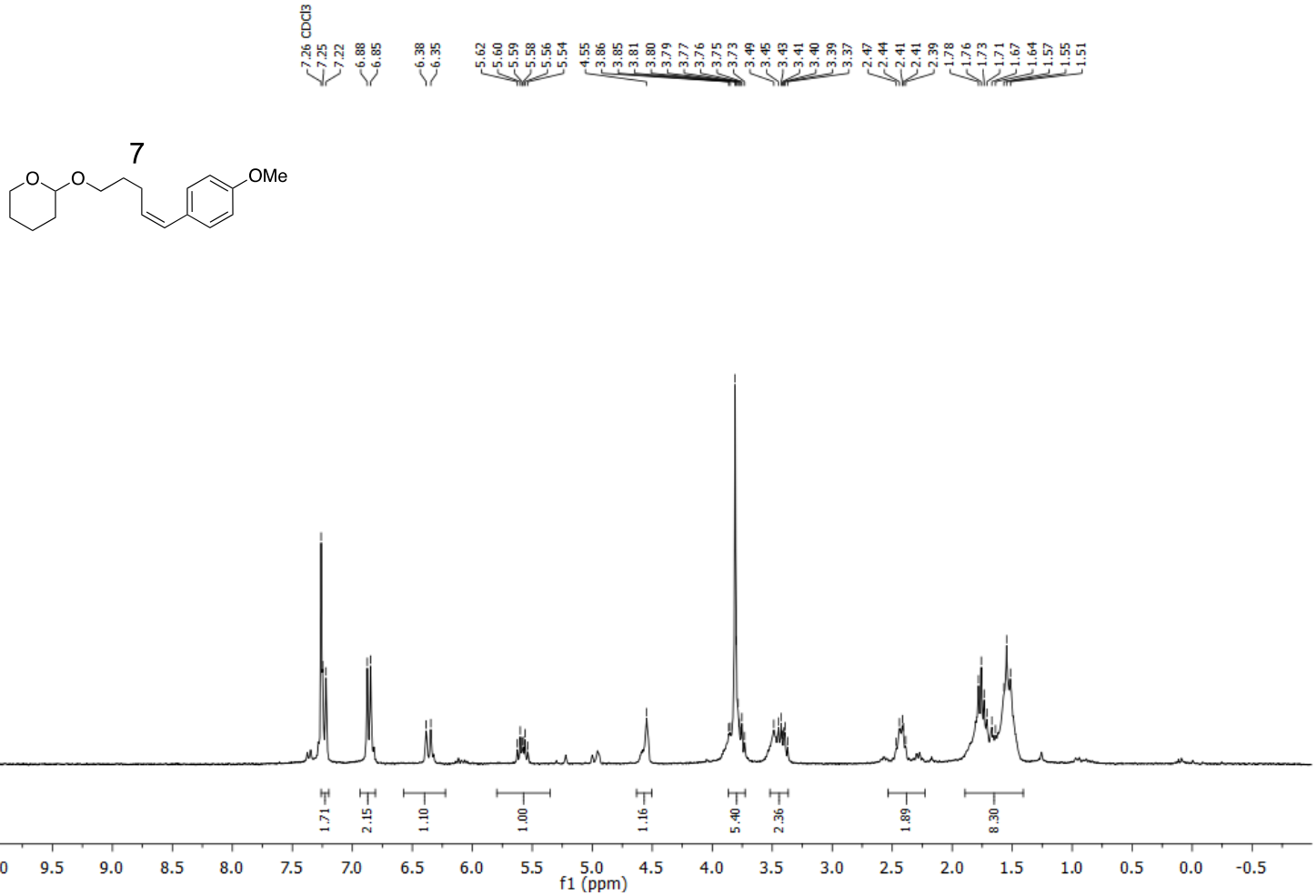


GC Trace of Crude Reaction Mixture

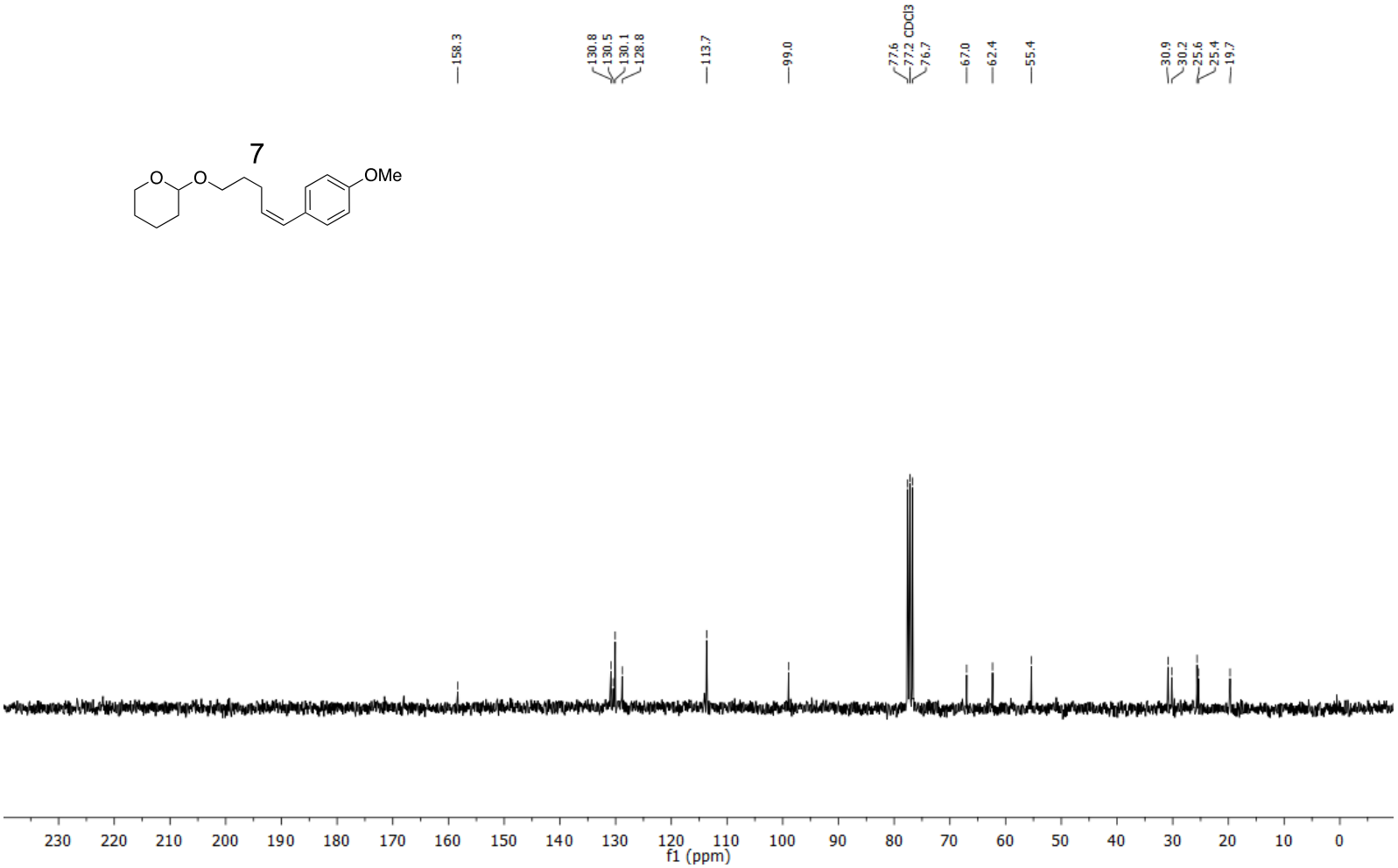


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.322	72532	51158	100.000				
Total		72532	51158					

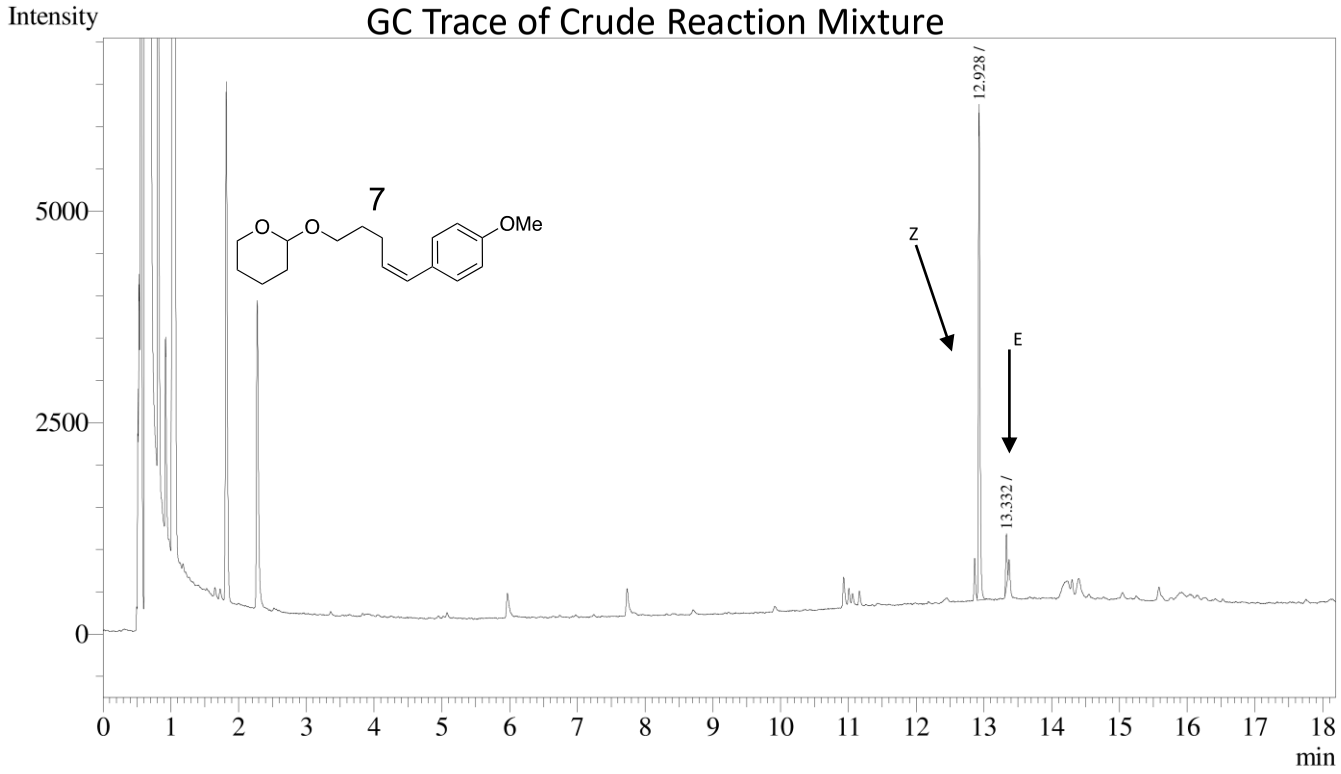
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 11.4 Hz, 1H), 5.58 (dt, *J* = 11.4, 7.3 Hz, 1H), 4.55 (s, 1H), 3.87 – 3.73 (m, 5H), 3.52 – 3.37 (m, 2H), 2.53 – 2.23 (m, 2H), 1.89 – 1.41 (m, 8H).



^{13}C NMR (75 MHz, $CDCl_3$) 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.

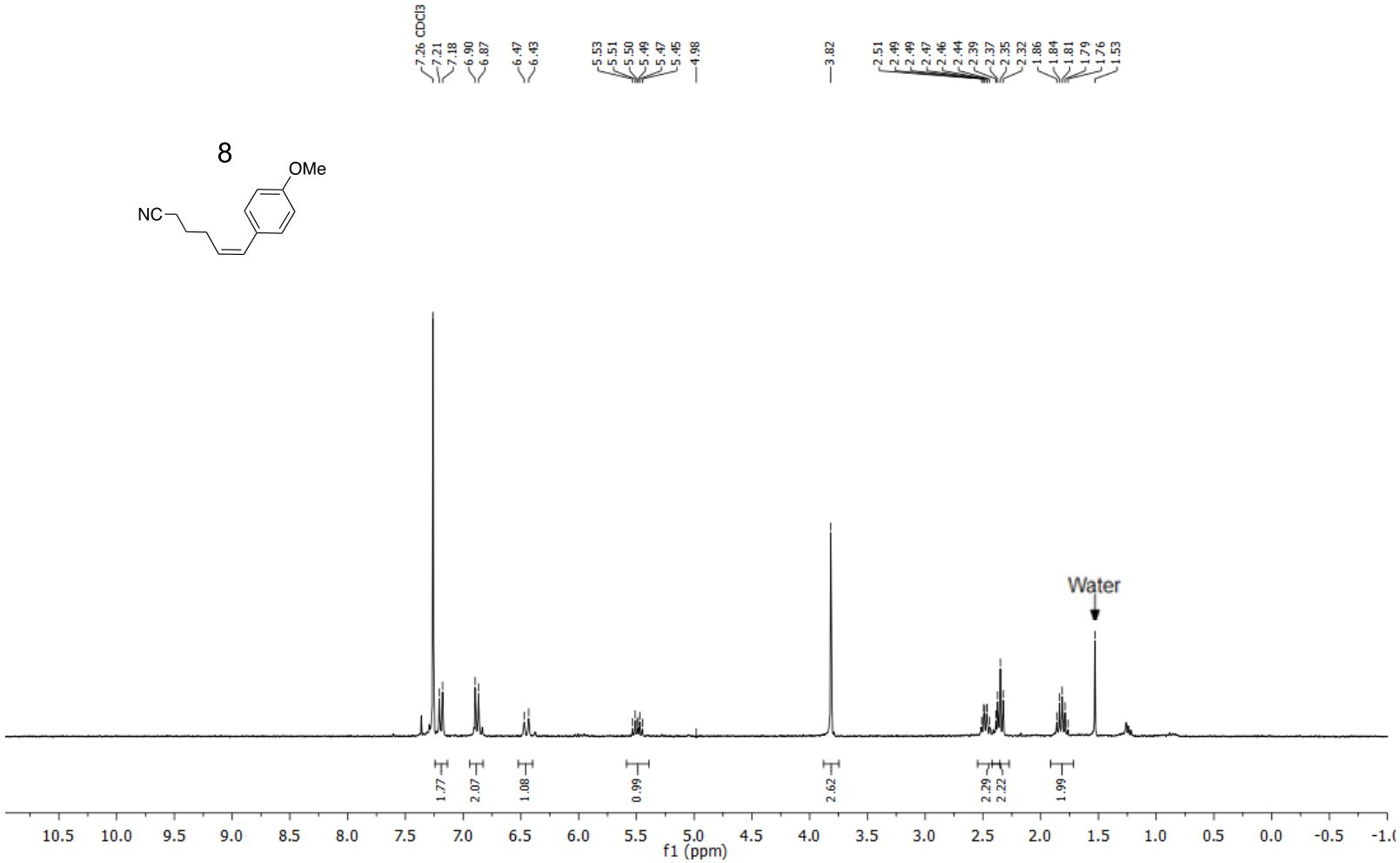


GC Trace of Crude Reaction Mixture

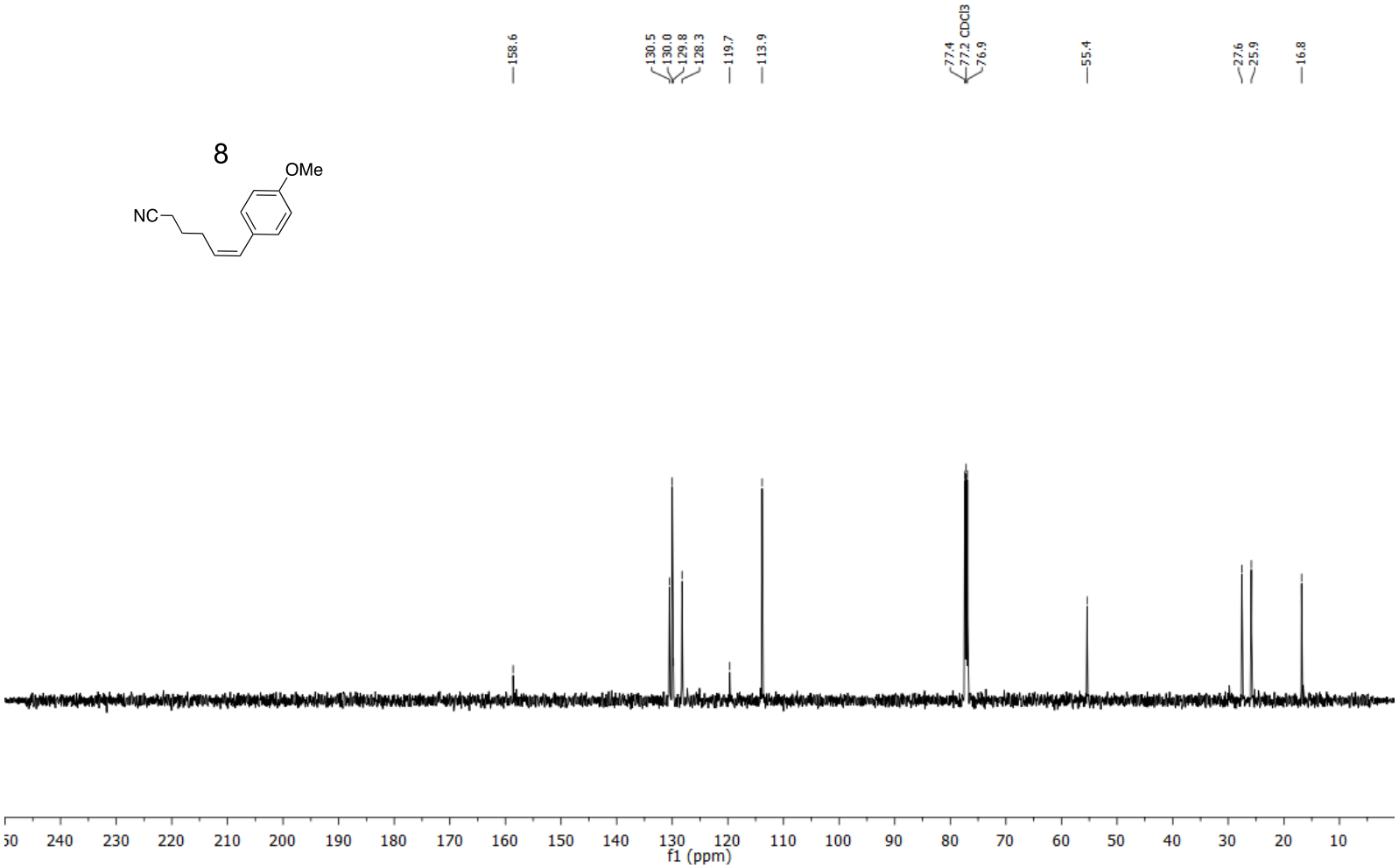


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.928	9151	5737	91.493		V		
2	13.332	851	614	8.507				
Total		10002	6351					

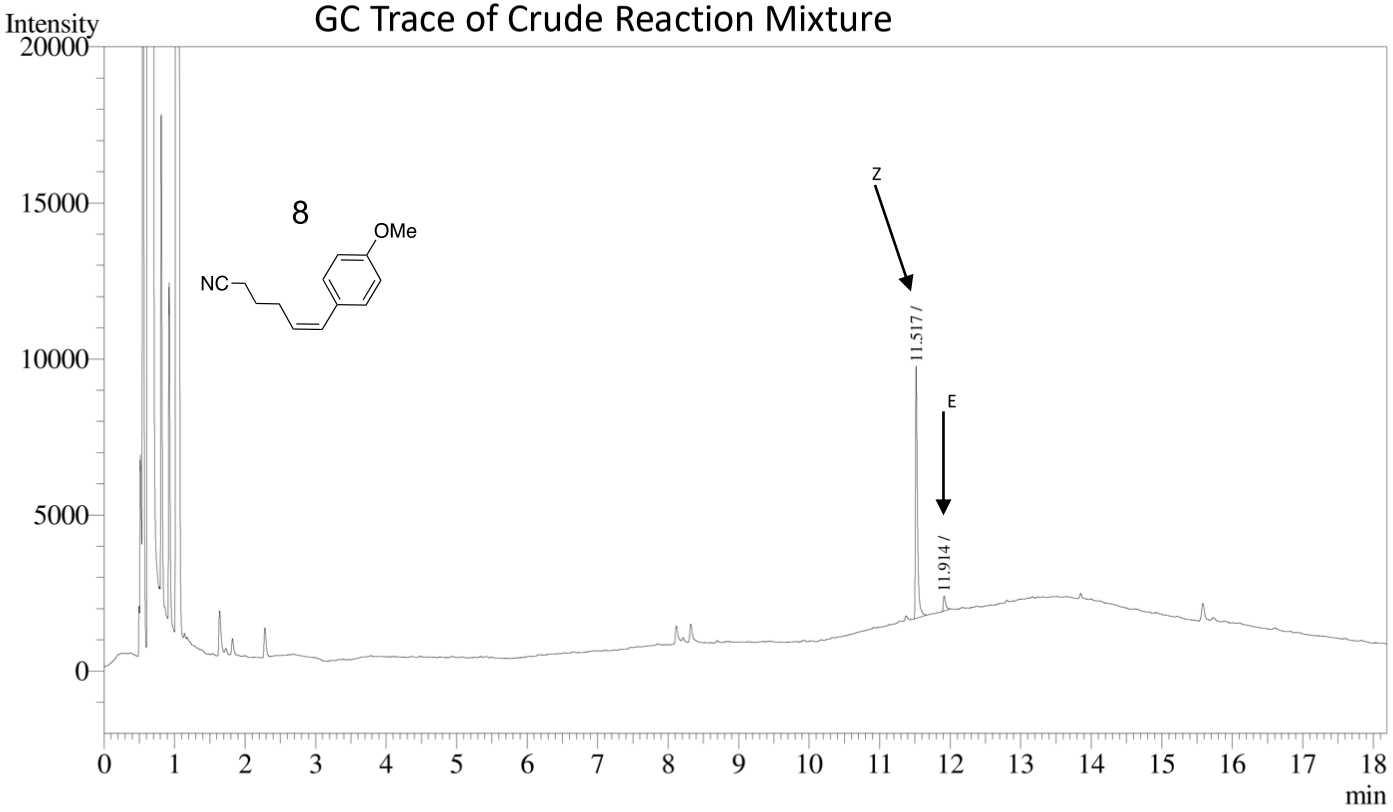
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 11.6 Hz, 1H), 5.49 (dt, *J* = 11.6, 7.1 Hz, 1H), 3.82 (s, 3H), 2.55 – 2.40 (m, 2H), 2.42 – 2.27 (m, 2H), 1.91 – 1.72 (m, 2H).



^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 130.5, 130.0, 129.8, 128.3, 119.7, 113.9, 55.4, 27.6, 25.9, 16.8.

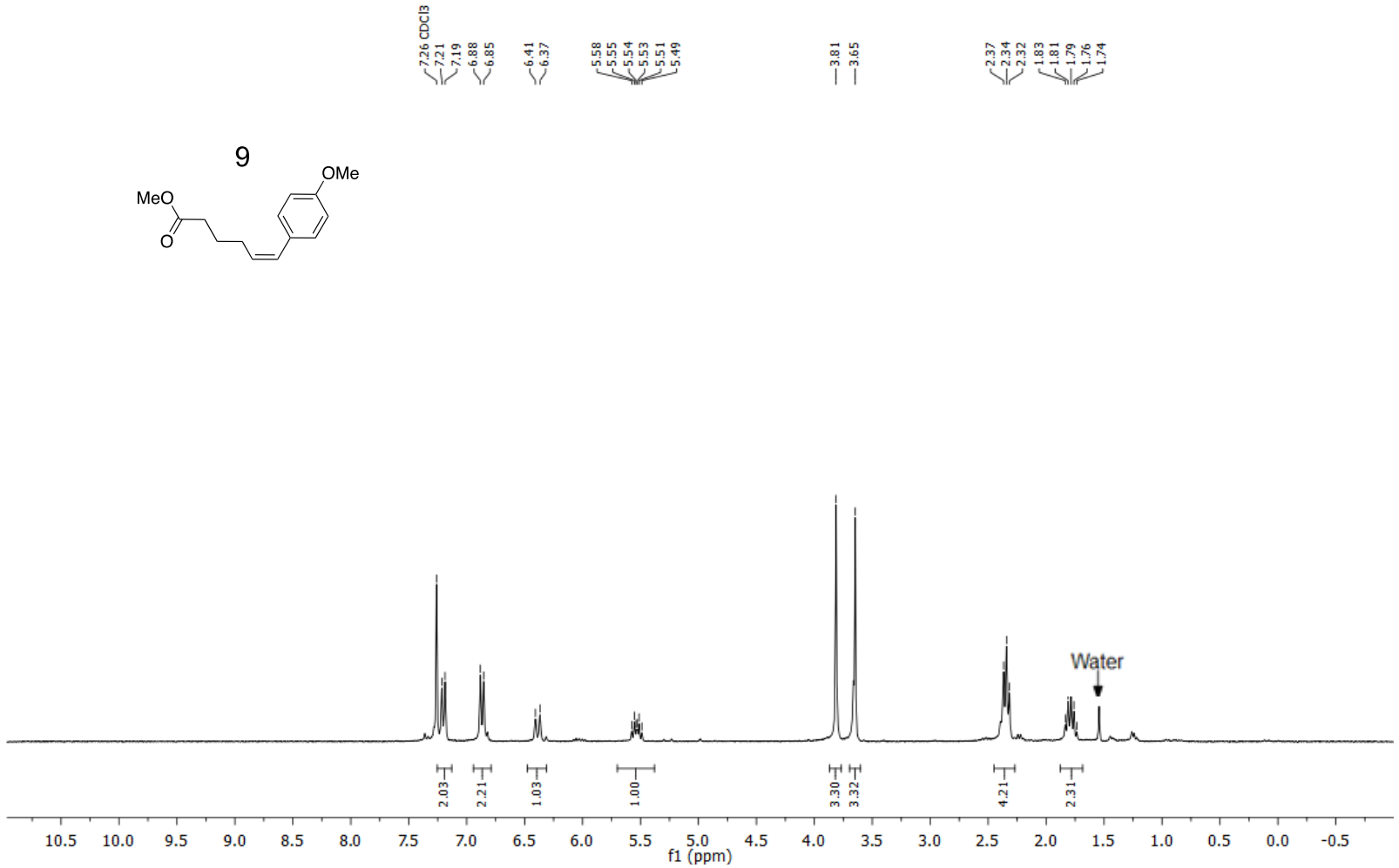


GC Trace of Crude Reaction Mixture

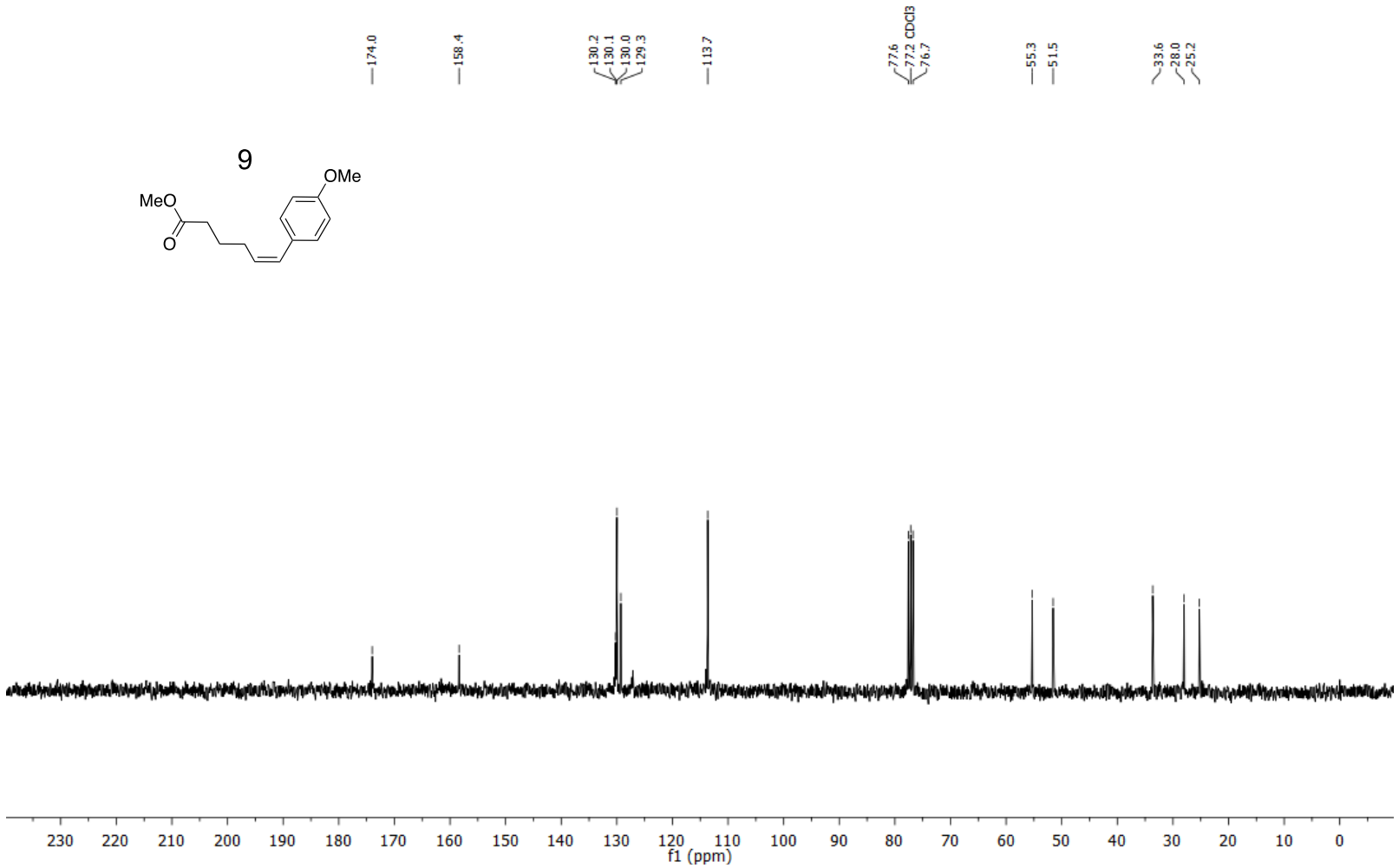


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.517	15328	7920	93.208				
2	11.914	1117	481	6.792				
Total		16445	8401					

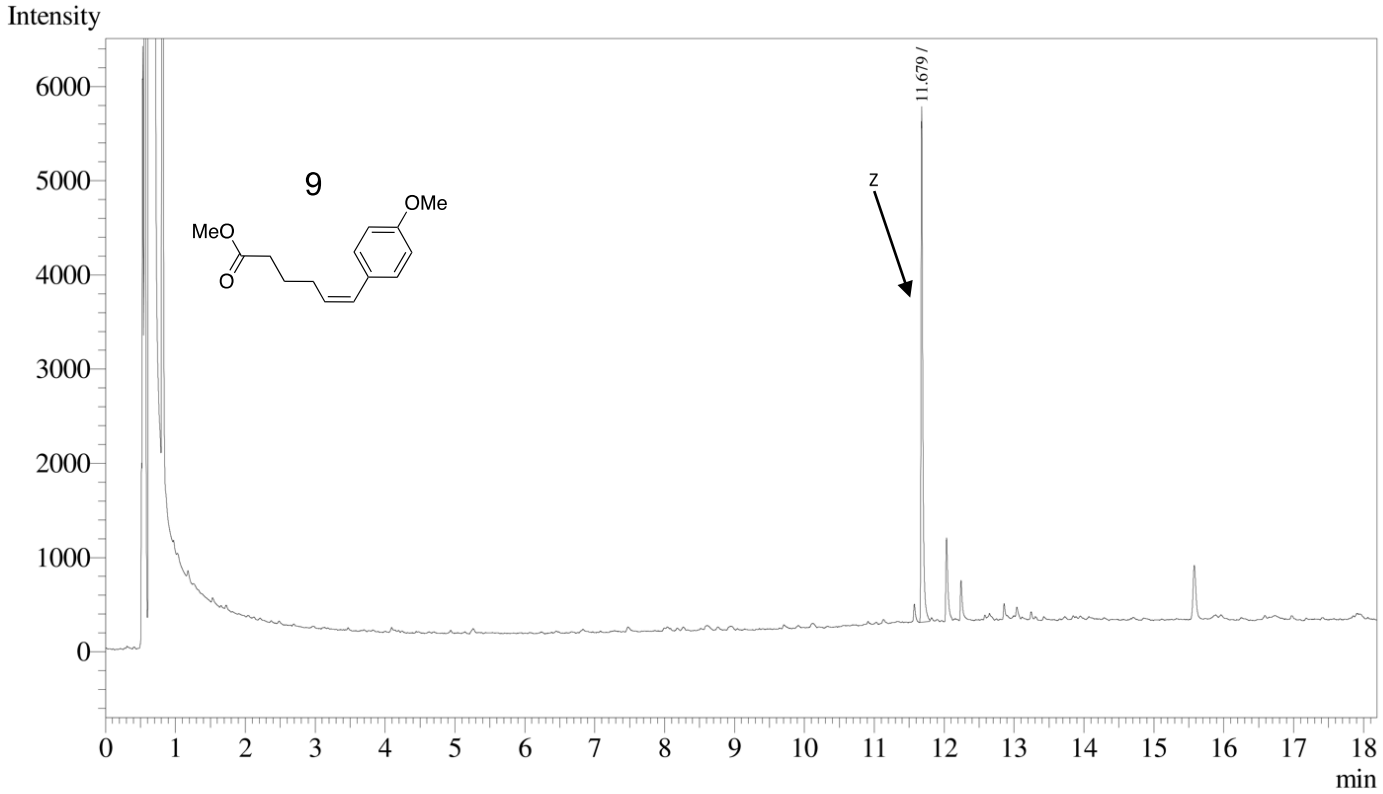
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 11.6 Hz, 1H), 5.70 - 5.38 (m, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 2.45 - 2.27 (m, 4H), 1.88 - 1.68 (m, 2H).



^{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.

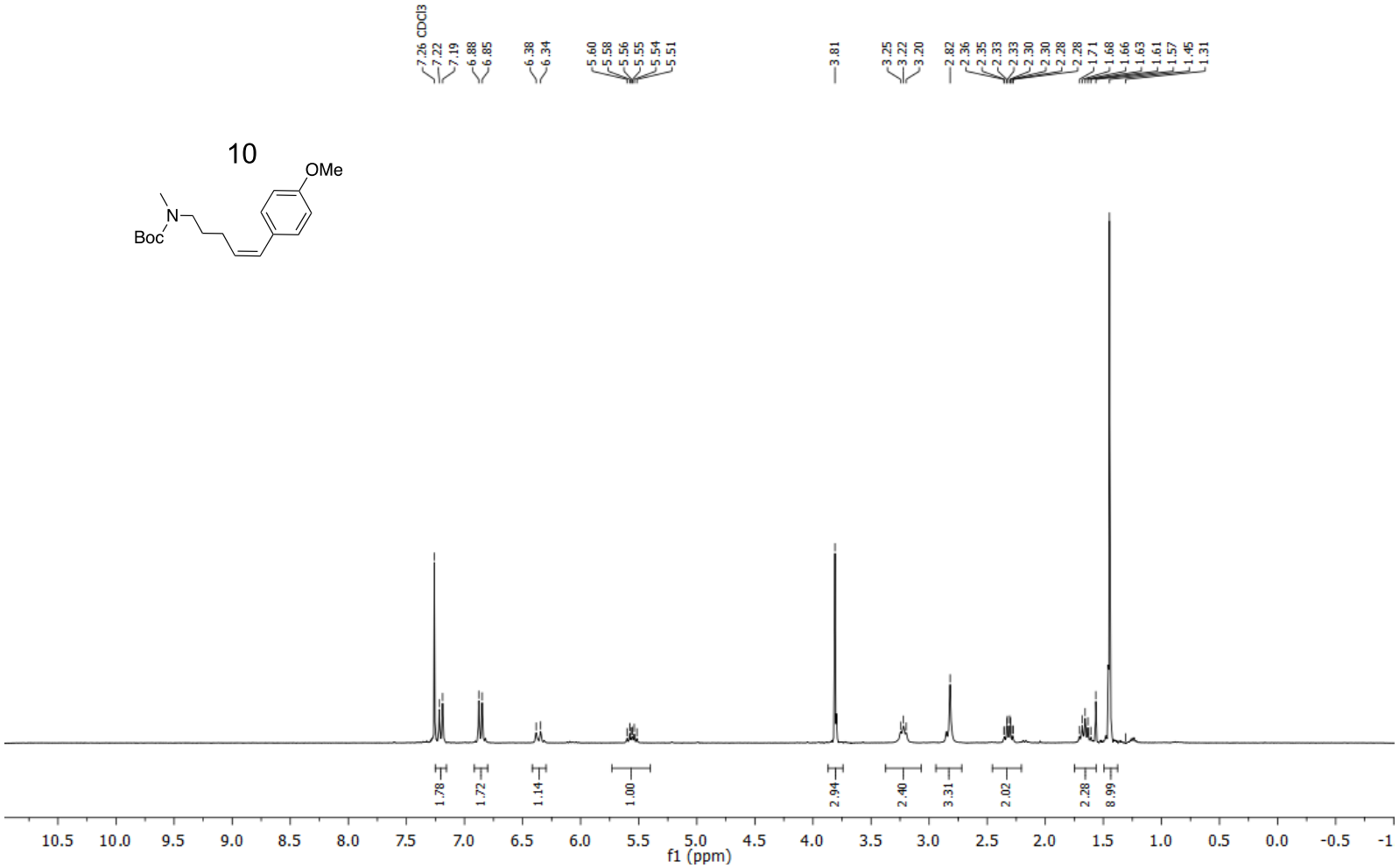


GC Trace of Crude Reaction Mixture

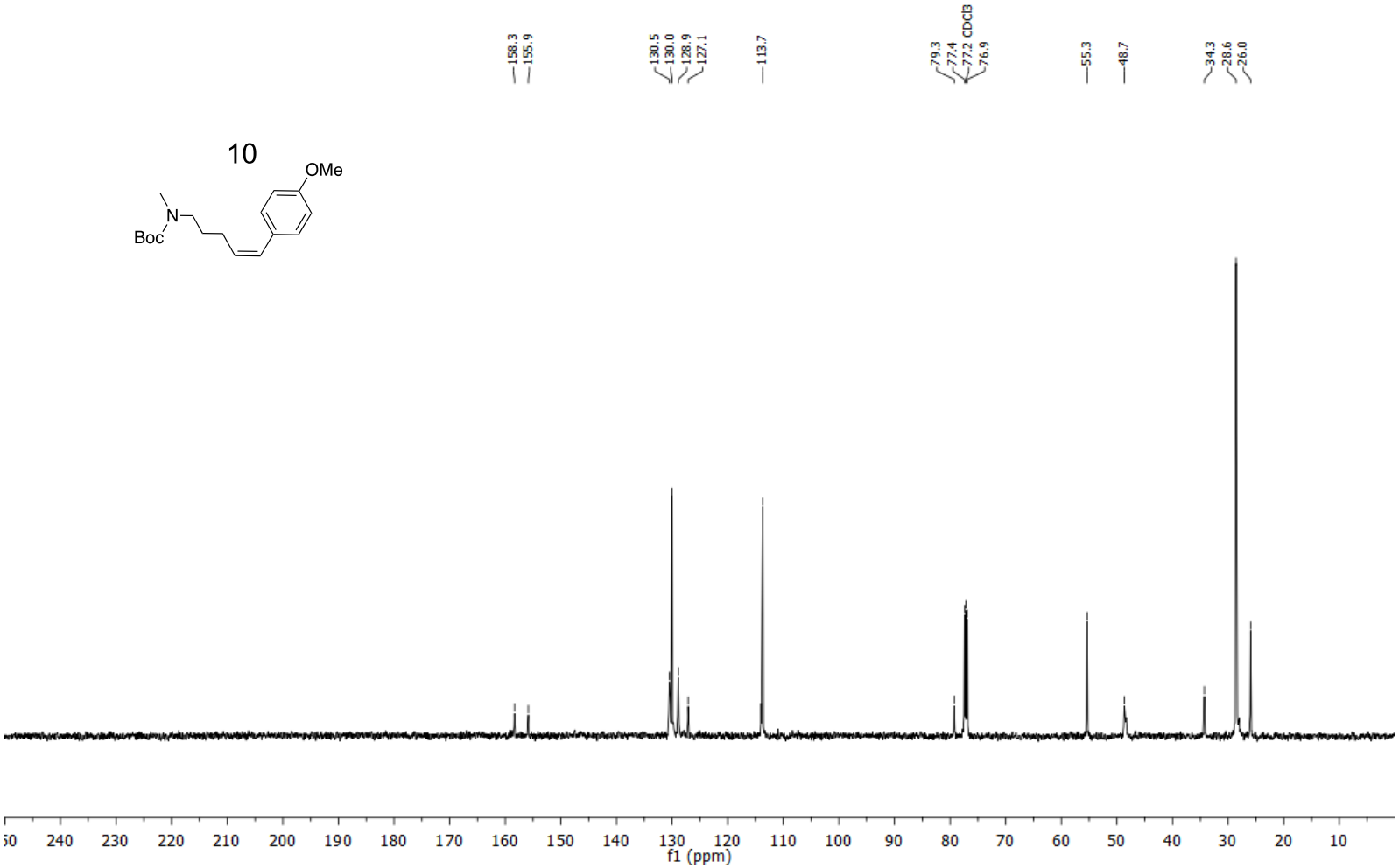


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.679	9564	5402	100.000				
Total		9564	5402					

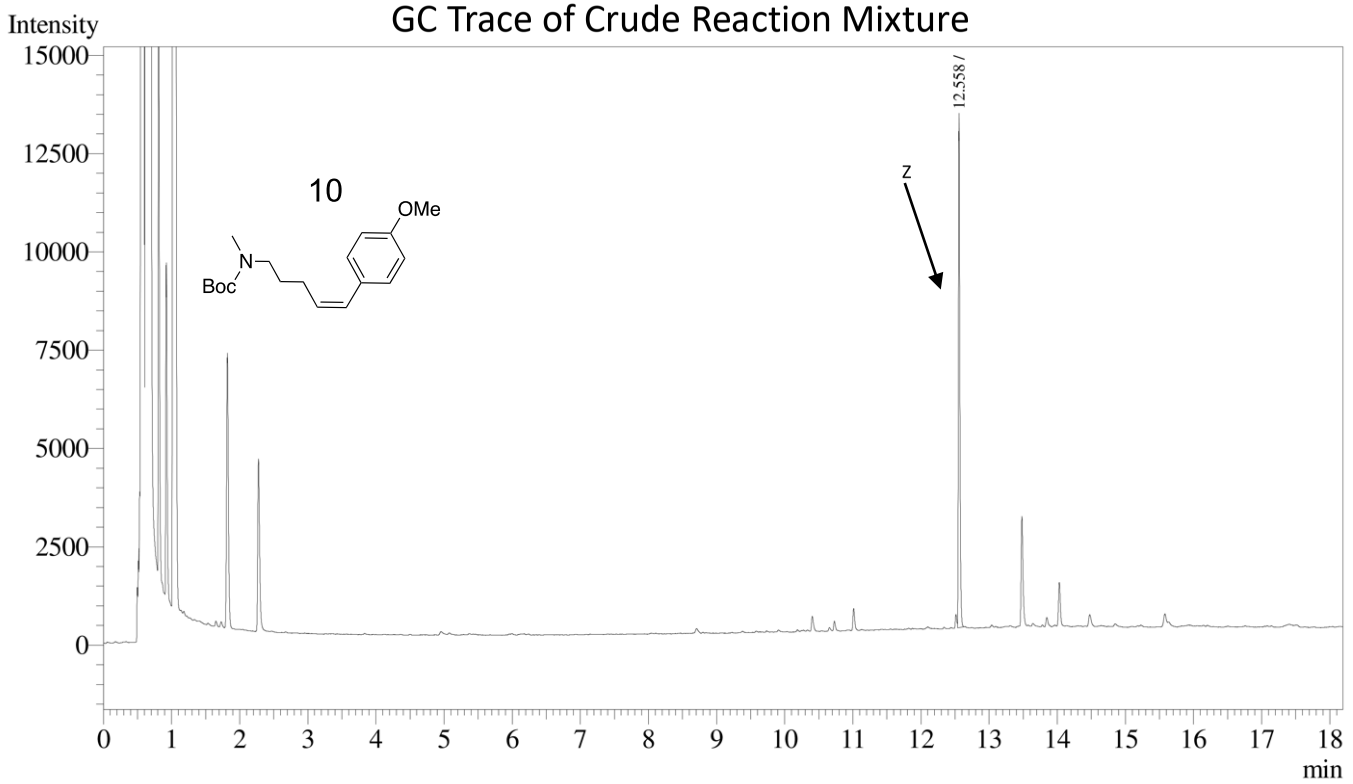
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.20 (**d**, *J* = 8.7 Hz, 2H), 6.86 (**d**, *J* = 8.7 Hz, 2H), 6.36 (**d**, *J* = 11.6 Hz, 1H), 5.56 (**dt**, *J* = 11.6, 7.1 Hz, 1H), 3.81 (**s**, 3H), 3.22 (**t**, *J* = 7.3 Hz, 2H), 2.82 (**s**, 3H), 2.46 – 2.21 (**m**, 2H), 1.75 – 1.56 (**m**, 2H), 1.45 (**s**,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



^{13}C NMR (126 MHz, $CDCl_3$) 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.

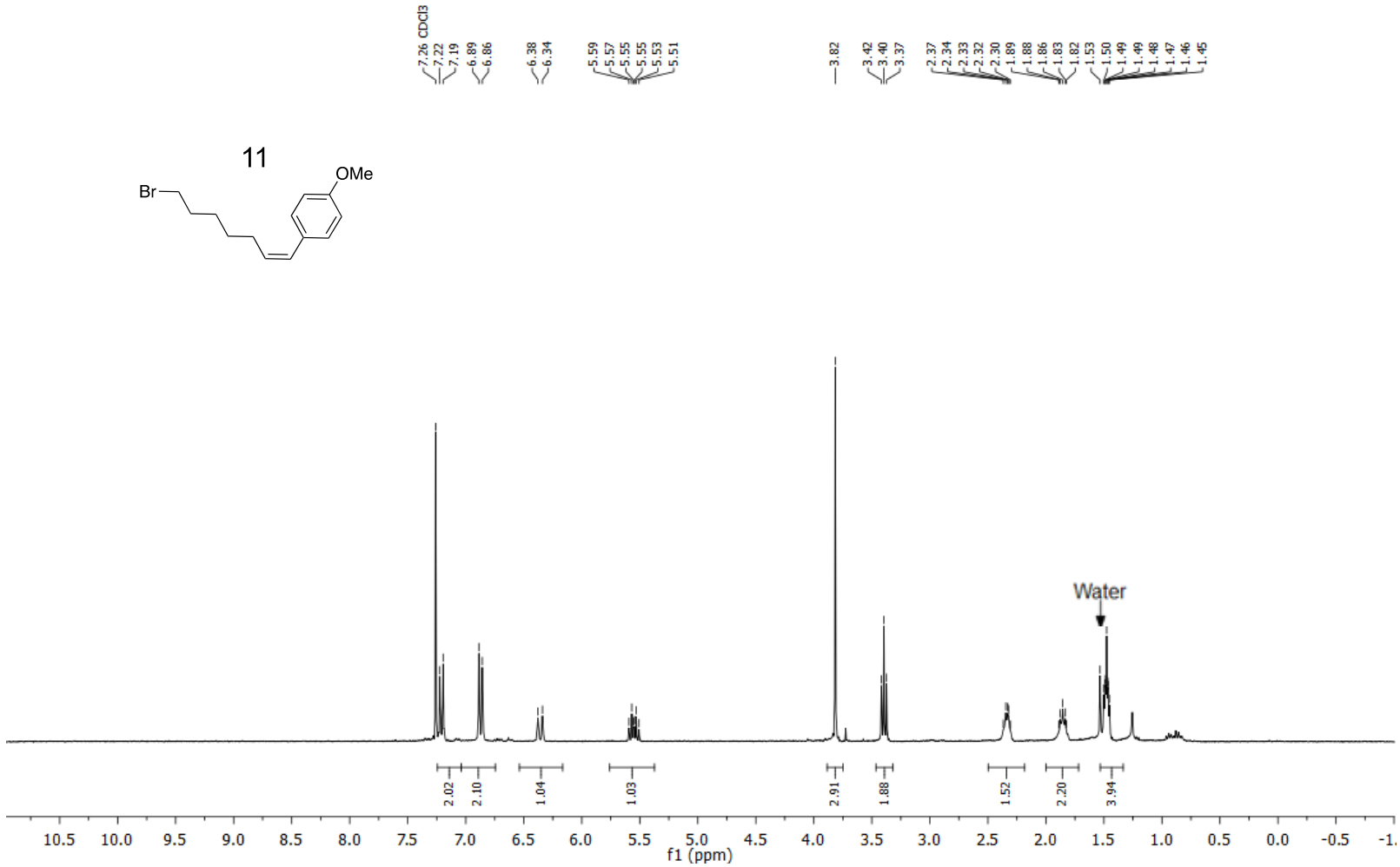


GC Trace of Crude Reaction Mixture

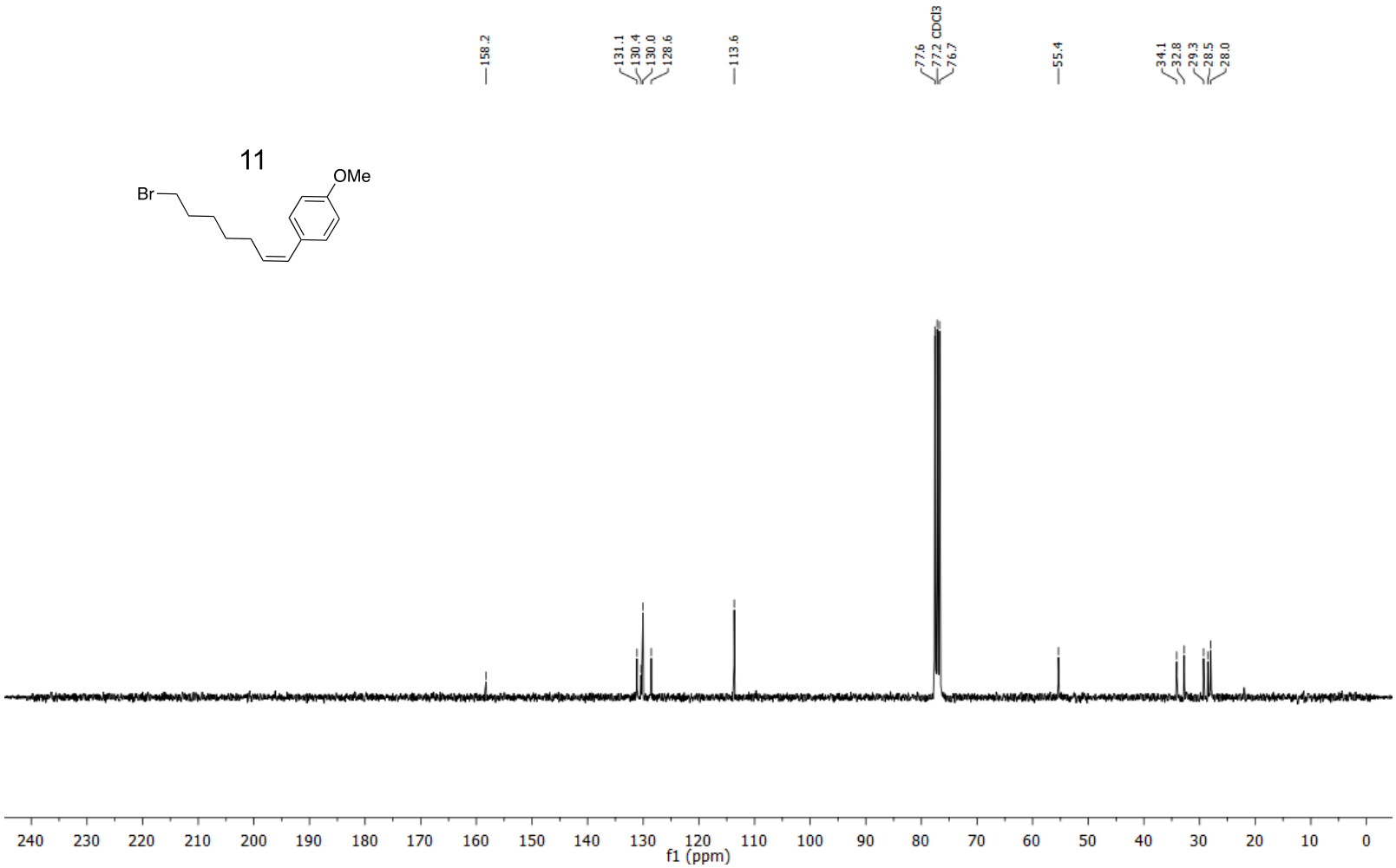


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.558	18785	12699	100.000		V		
Total		18785	12699					

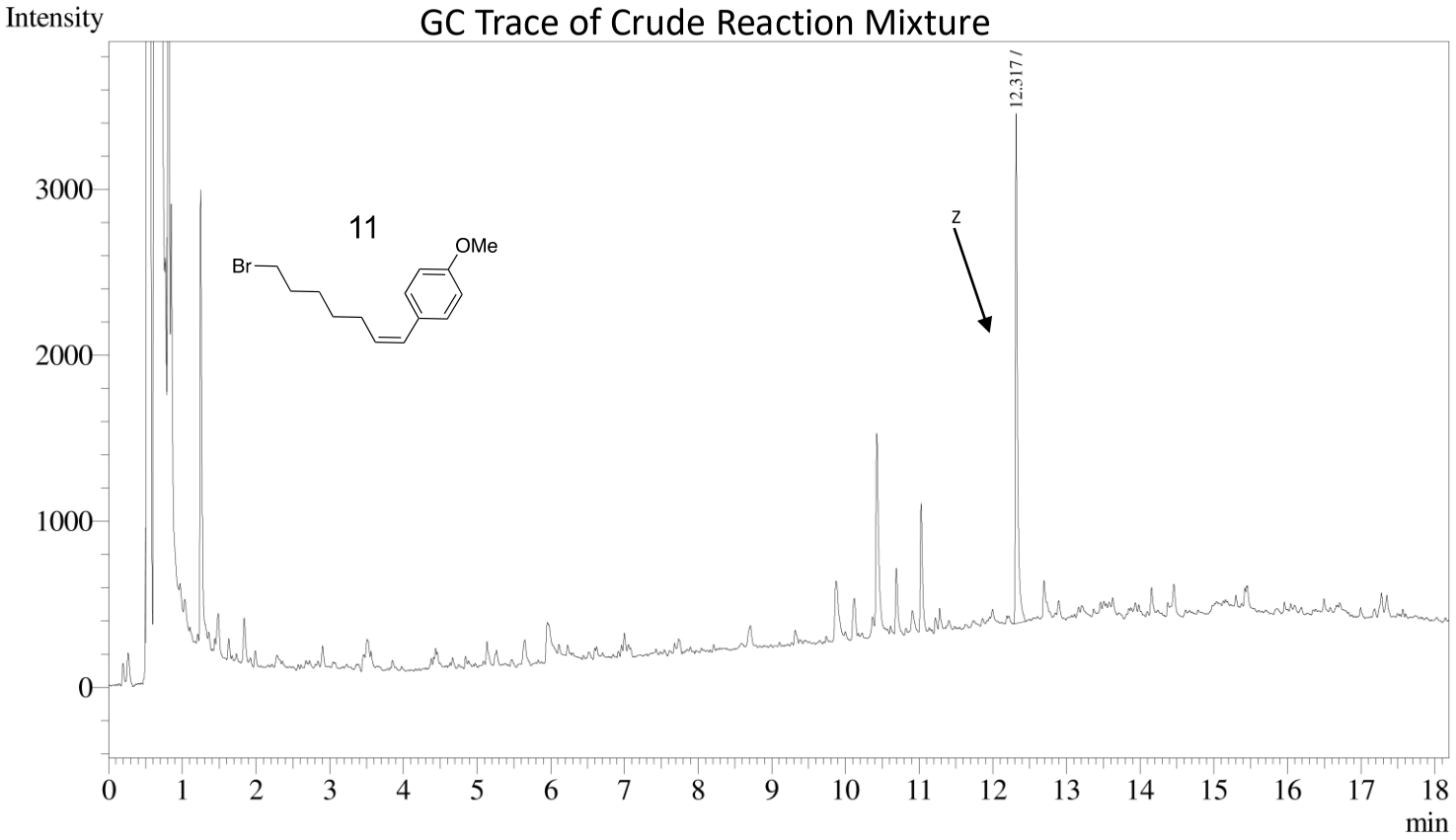
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 (**d**, *J* = 8.7 Hz, 2H), 6.87 (**d**, *J* = 8.7 Hz, 2H), 6.36 (**d**, *J* = 11.6 Hz, 1H), 5.55 (**dt**, *J* = 11.6, 7.2 Hz, 1H), 3.82 (**s**, 3H), 3.40 (**t**, *J* = 6.8 Hz, 2H), 2.50 – 2.18 (m, 2H), 2.00 – 1.72 (m, 2H), 1.53 – 1.33 (m, 4H).



^{13}C NMR (75 MHz, $CDCl_3$) 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.

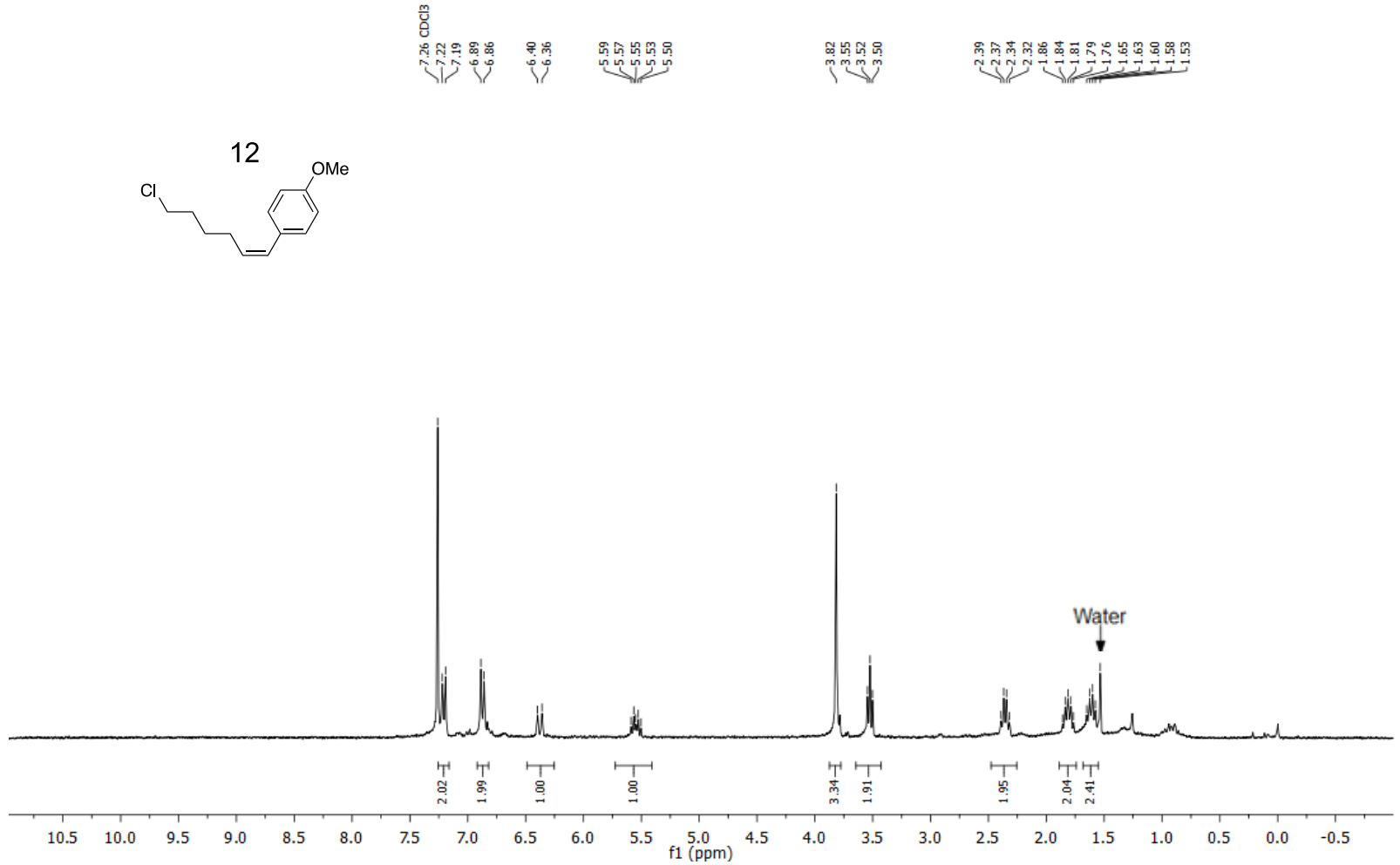


GC Trace of Crude Reaction Mixture

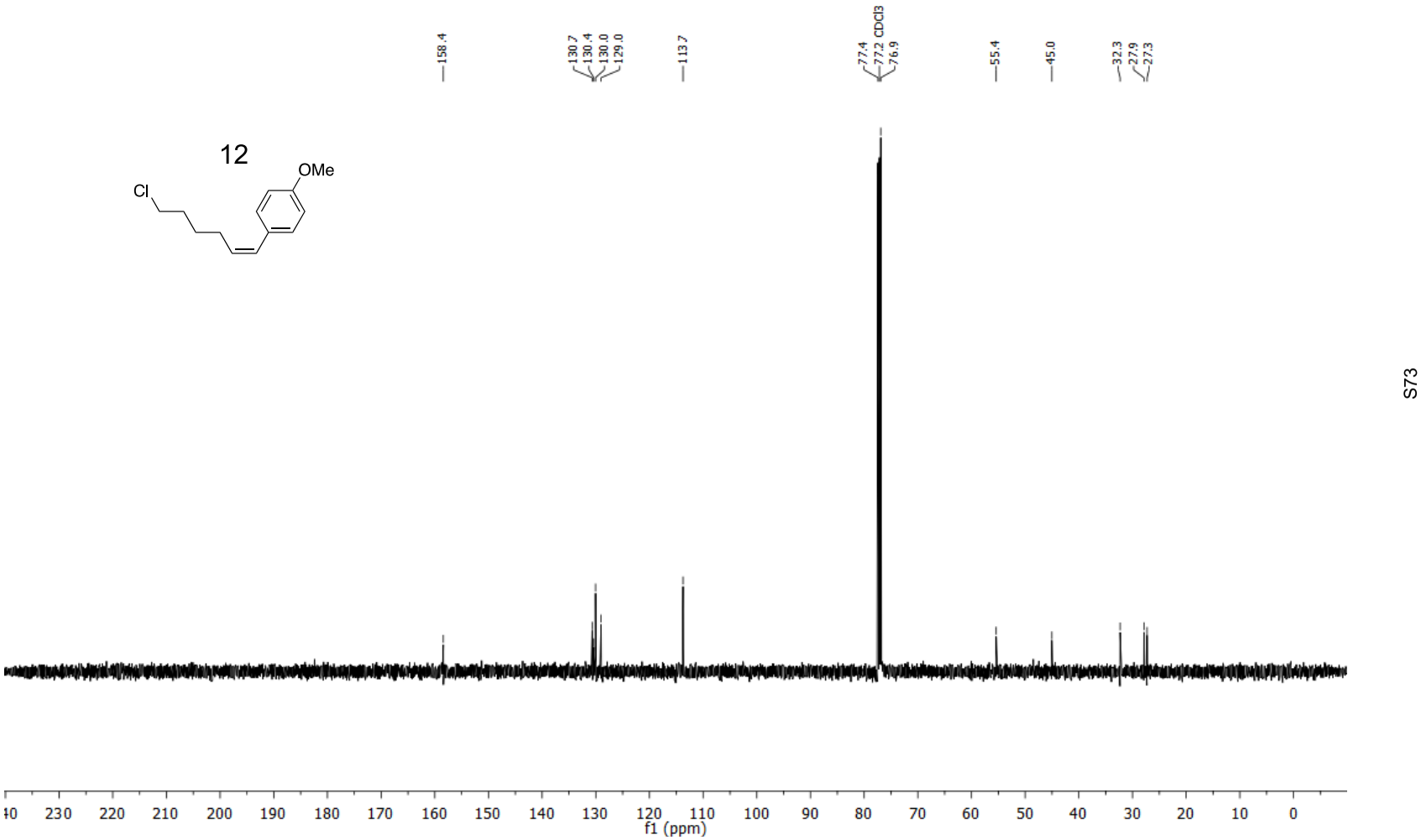


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.317	6027	3021	100.000				
Total		6027	3021					

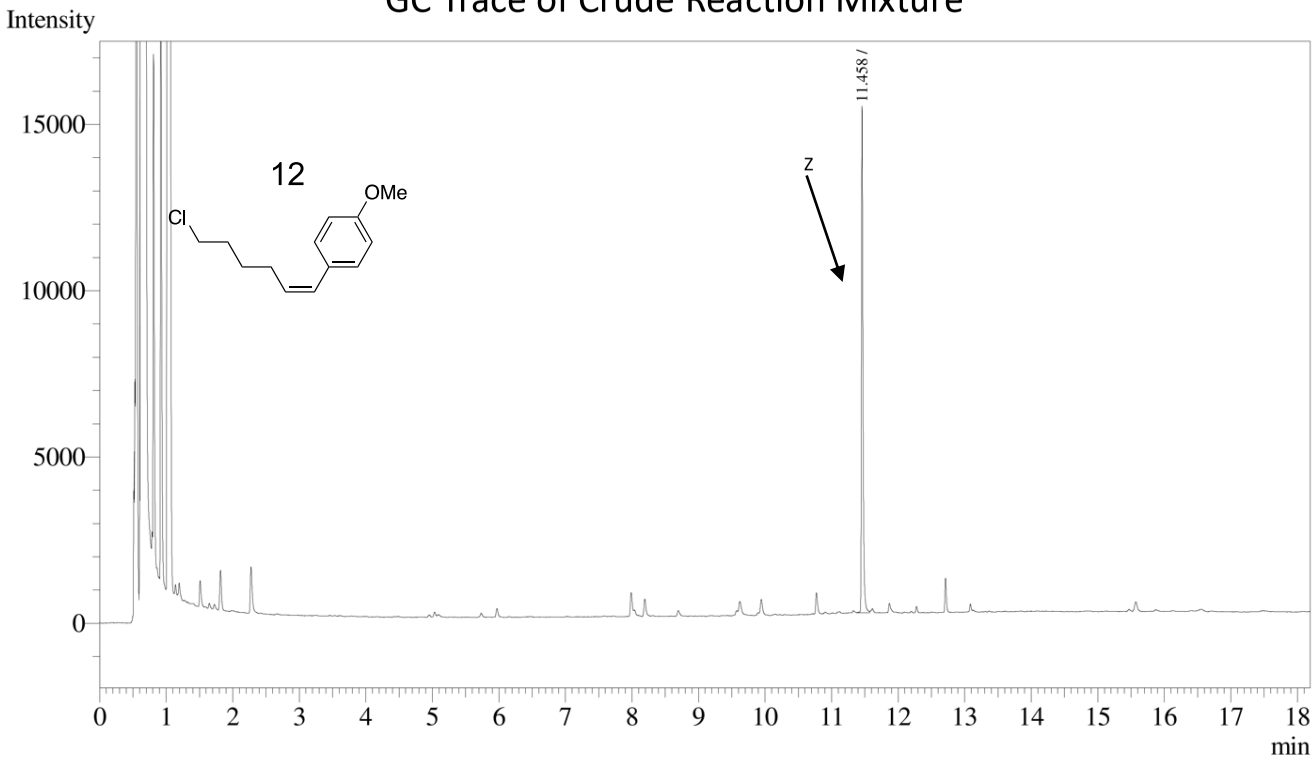
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 11.5 Hz, 1H), 5.72 – 5.41 (m, 1H), 3.82 (s, 3H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.48 – 2.26 (m, 2H), 1.89 –-1.74 (m, 2H), 1.68 – 1.55 (m, 2H).



^{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.

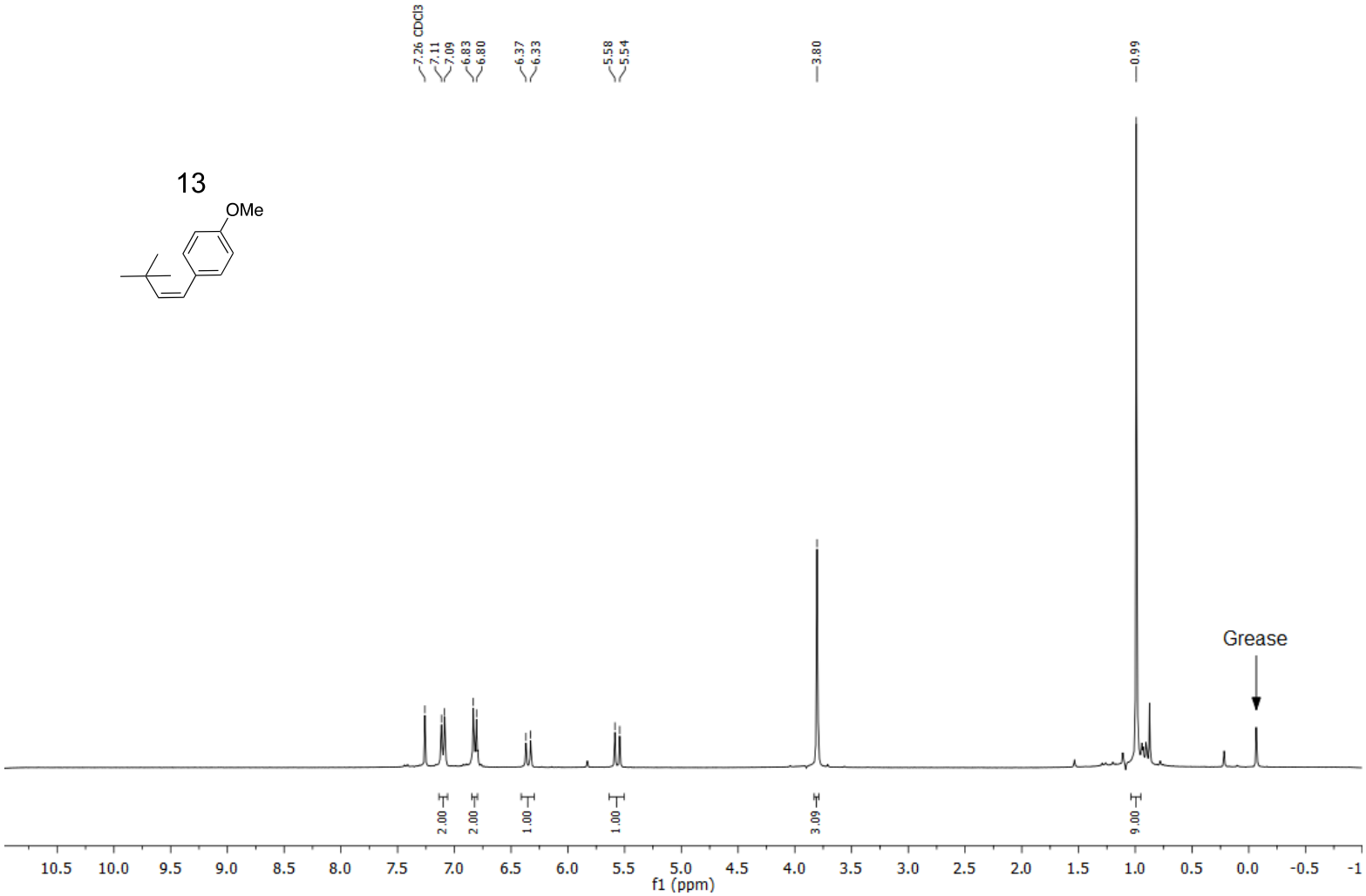


GC Trace of Crude Reaction Mixture

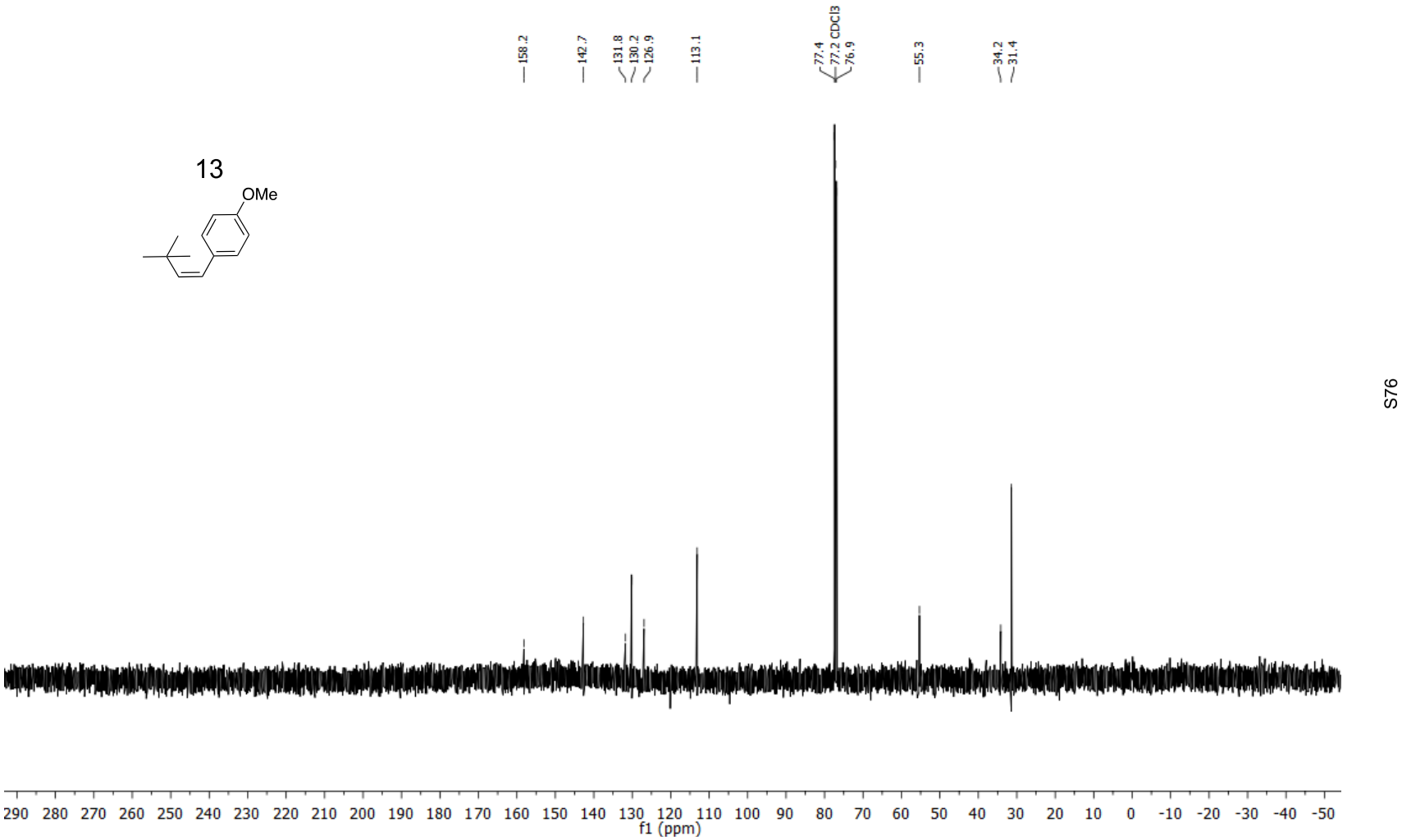


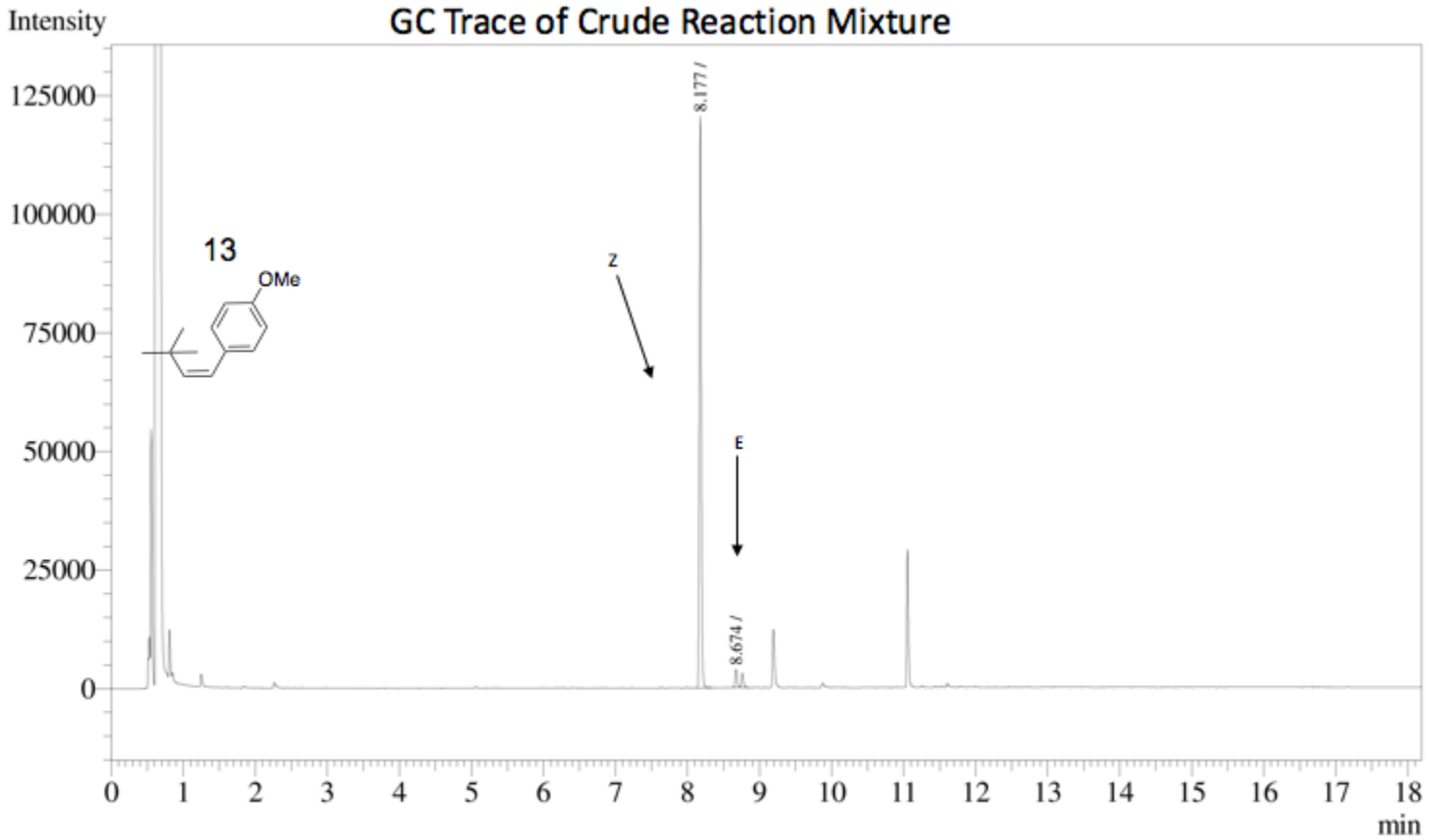
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.458	24227	14800	100.000		V		
Total		24227	14800					

^{1}H 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).



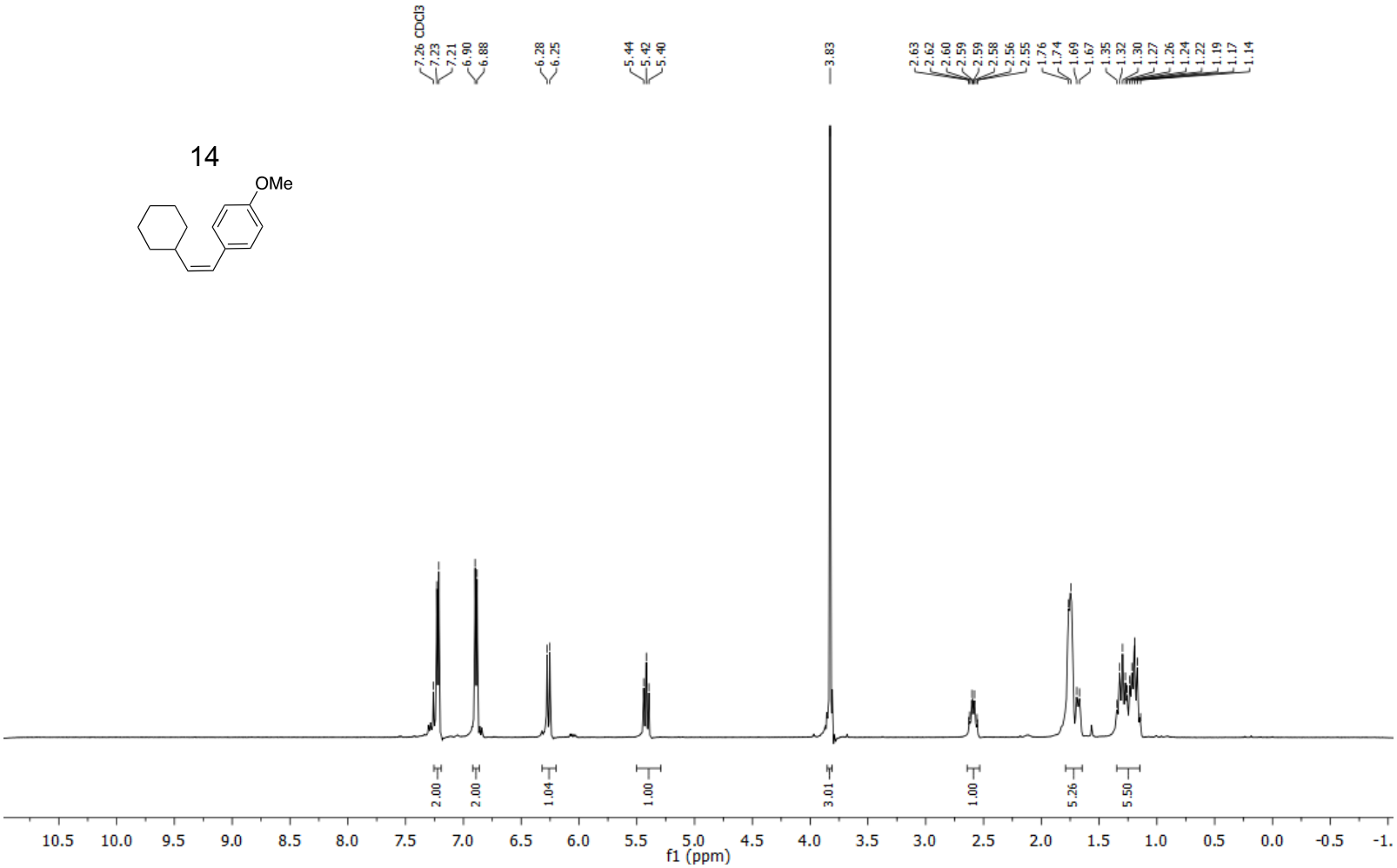
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.2 , 142.7 , 131.8, 130.2 , 126.9 , 113.1 , 55.3 , 34.2 , 31.4 .



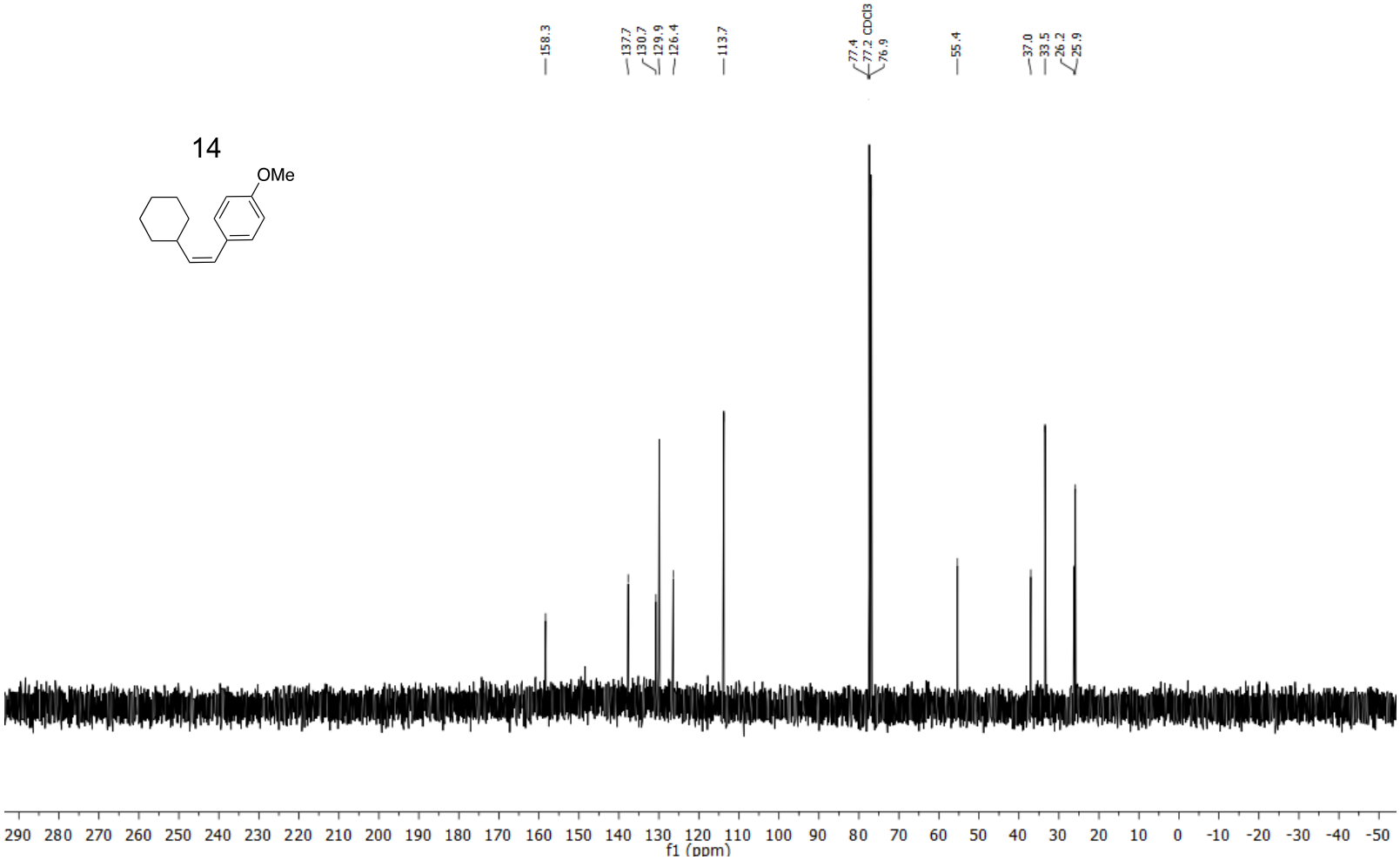


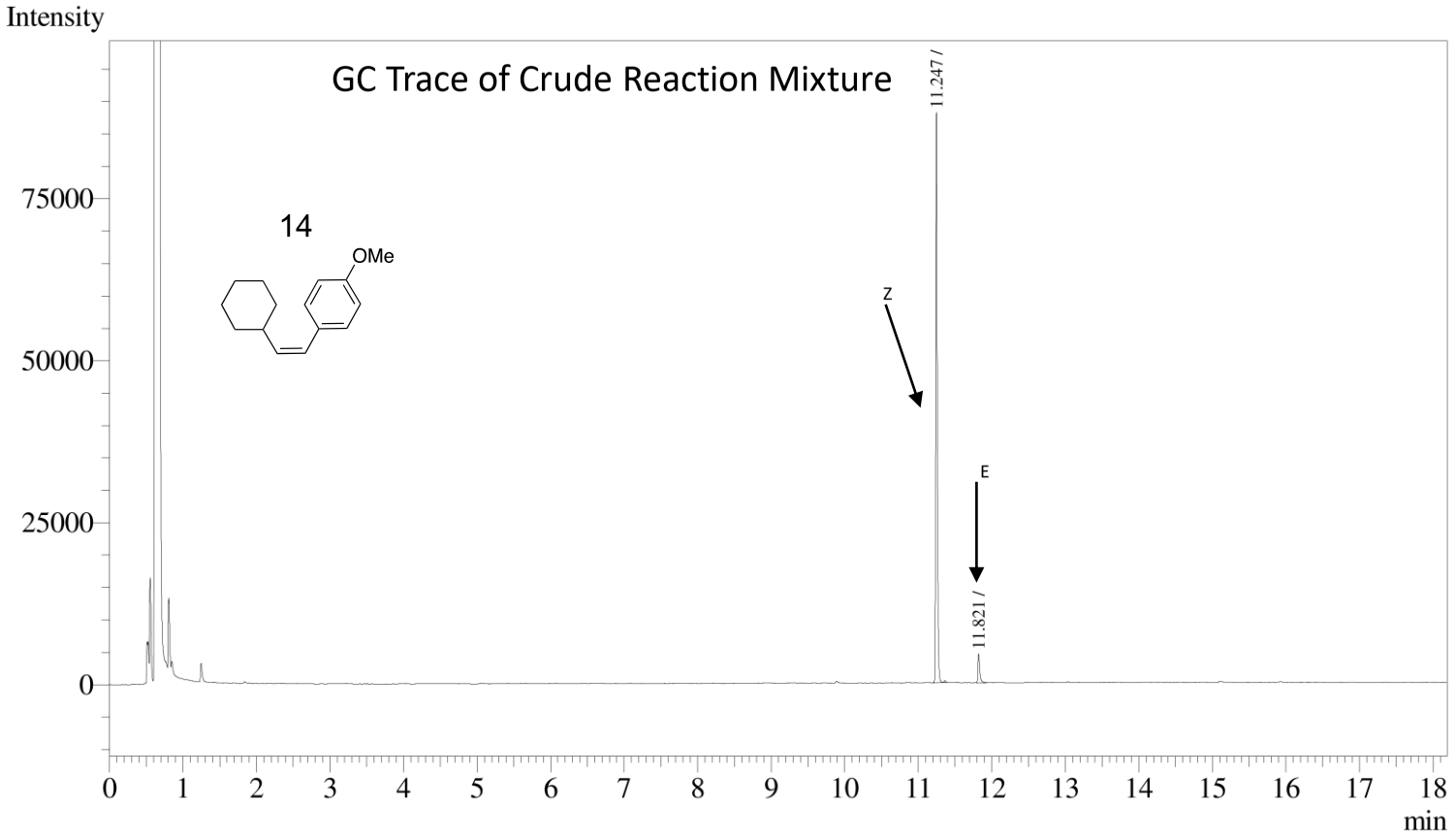
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	8.177	216002	118486	94.188		S		
2	8.674	13328	3772	5.812				
Total		229330	122258					

^{1}H 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).



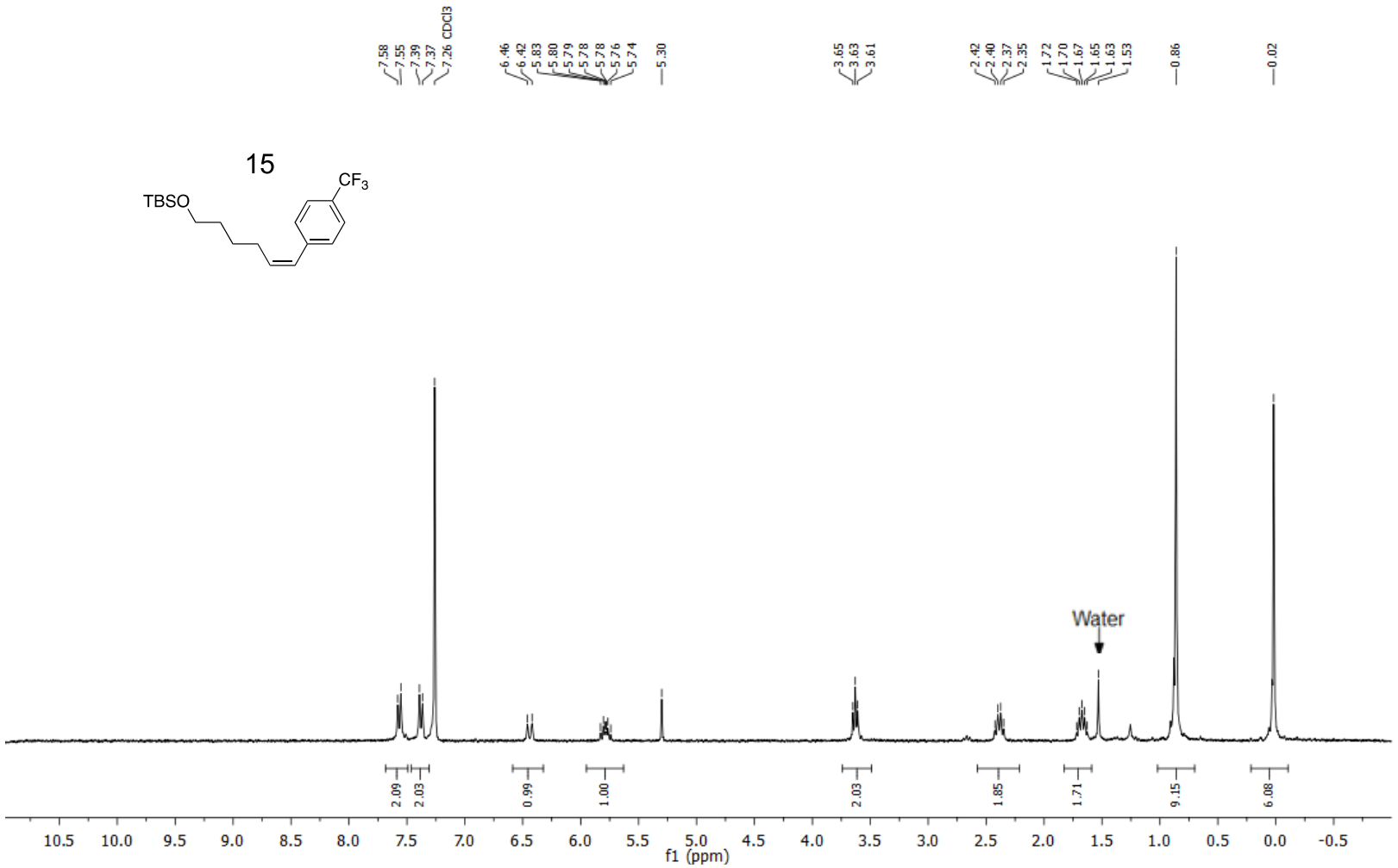
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.3 , 137.7 , 130.7 , 129.9 , 126.4 , 113.7 , 55.4 , 37.0 , 33.5 , 26.2 , 25.9 .



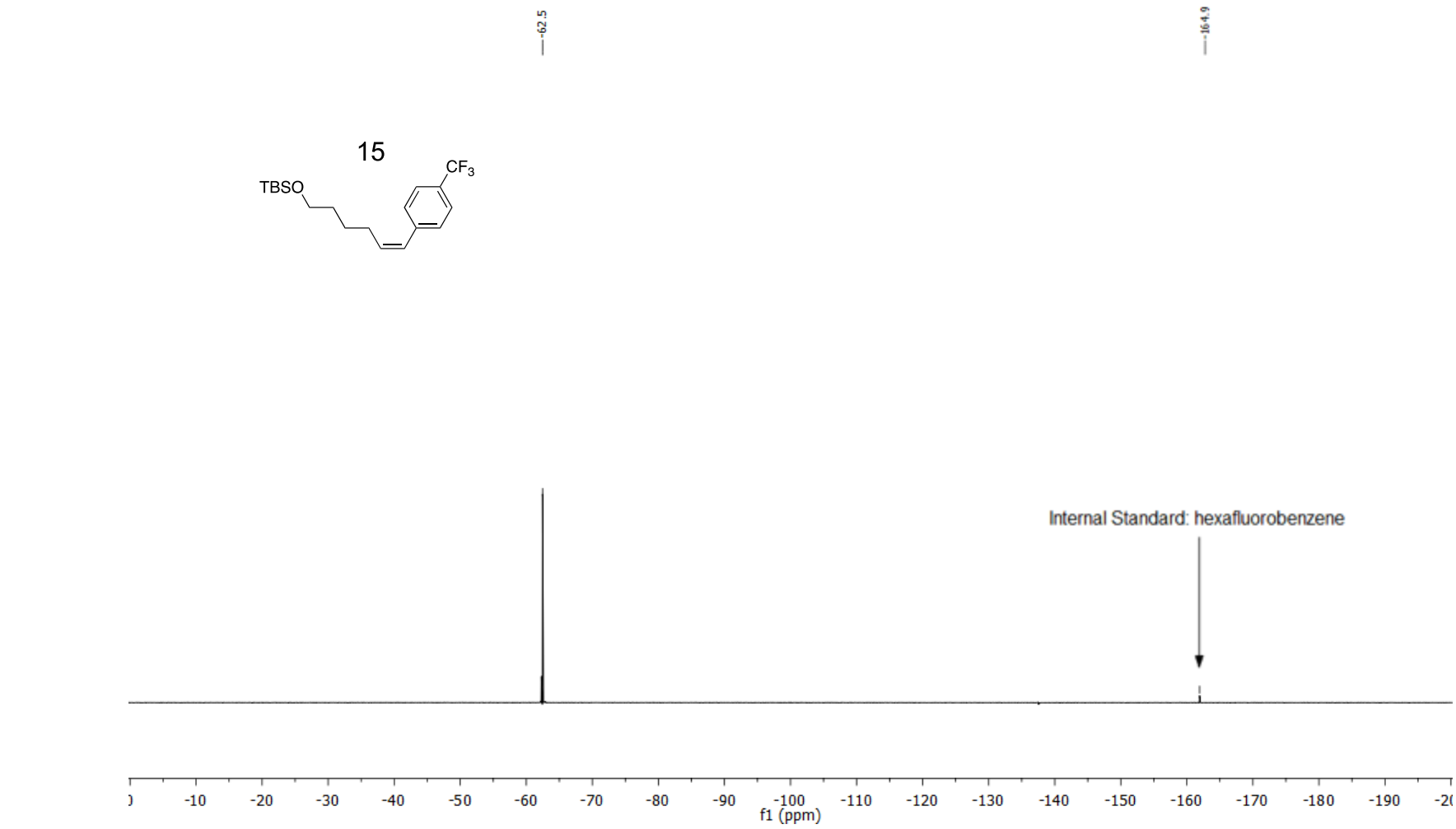


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.247	127283	84442	94.320		S		
2	11.821	7666	4321	5.680				
Total		134949	88763					

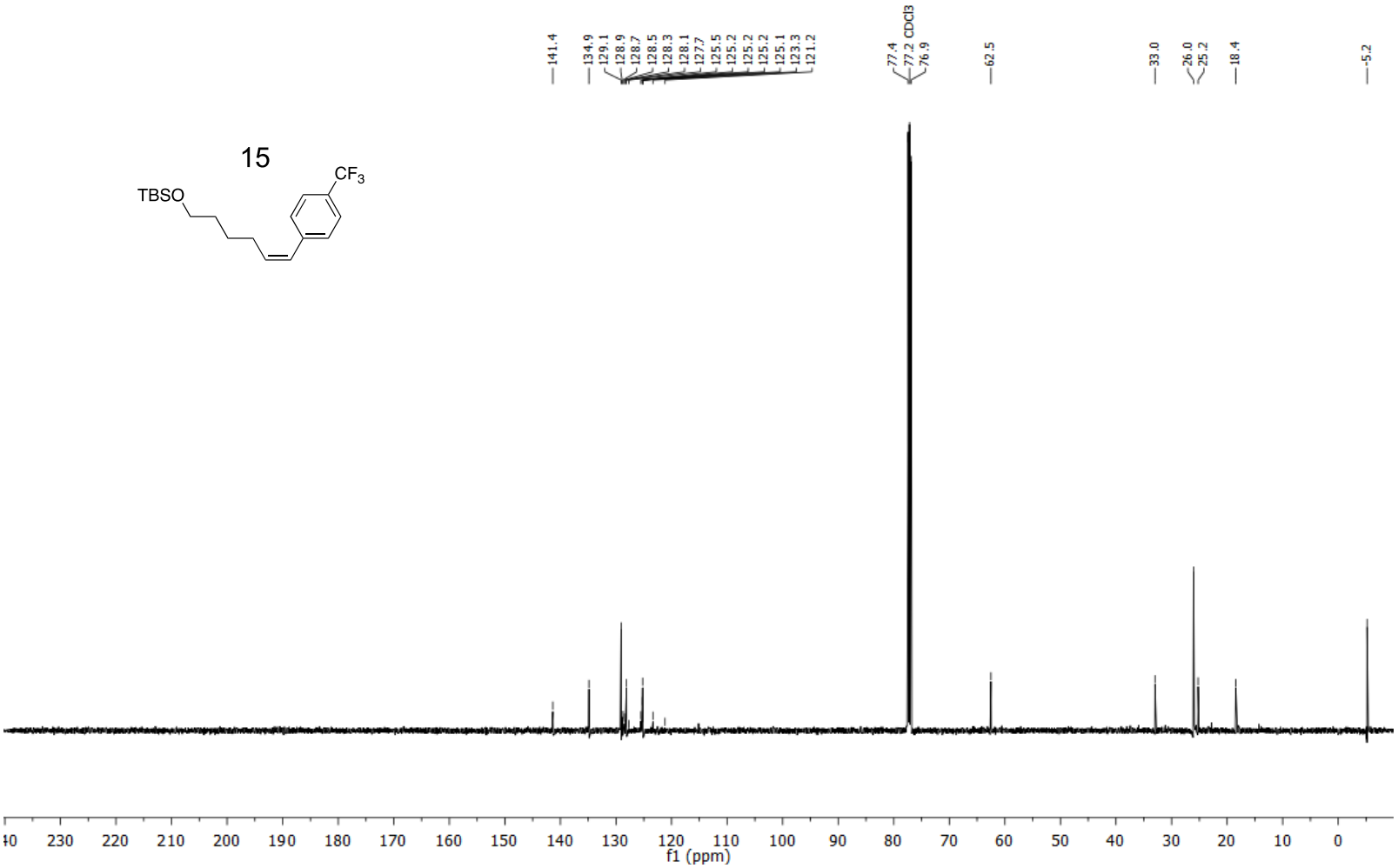
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 11.8 Hz, 1H), 5.95 – 5.63 (m, 1H), 3.63 (t, *J* = 6.2 Hz, 2H), 2.58 – 2.21 (m, 2H), 1.83 – 1.58 (m, 2H), 0.02 (s, 6H).



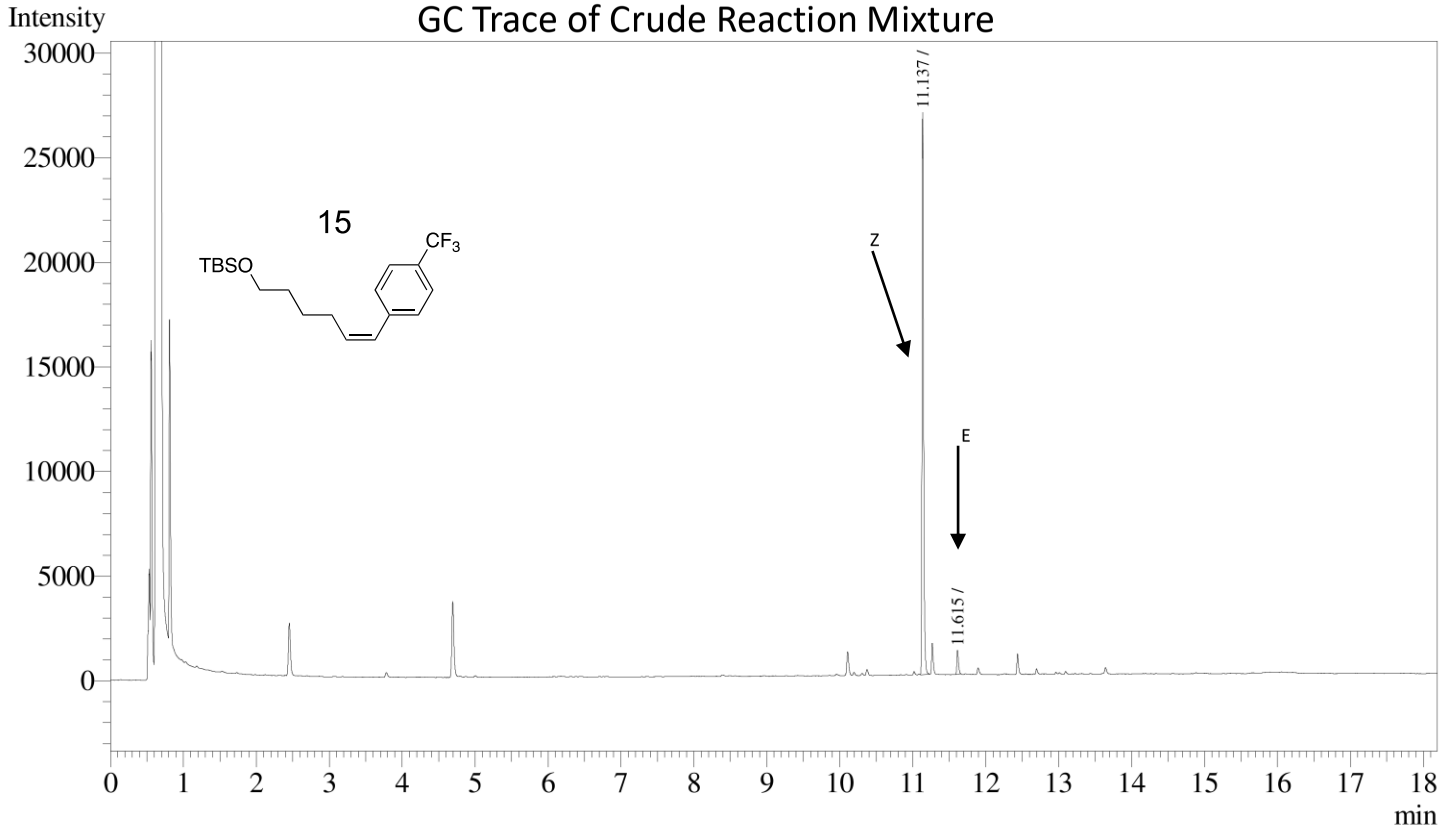
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5.



^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.4, 134.9, 129.1, 128.6 (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.

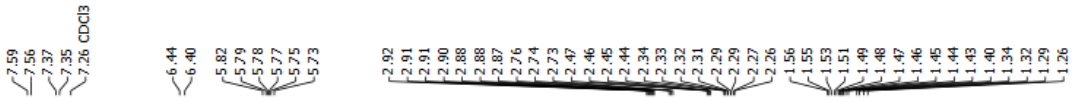


GC Trace of Crude Reaction Mixture



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					

^{1}H 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).



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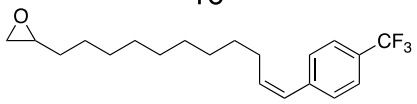
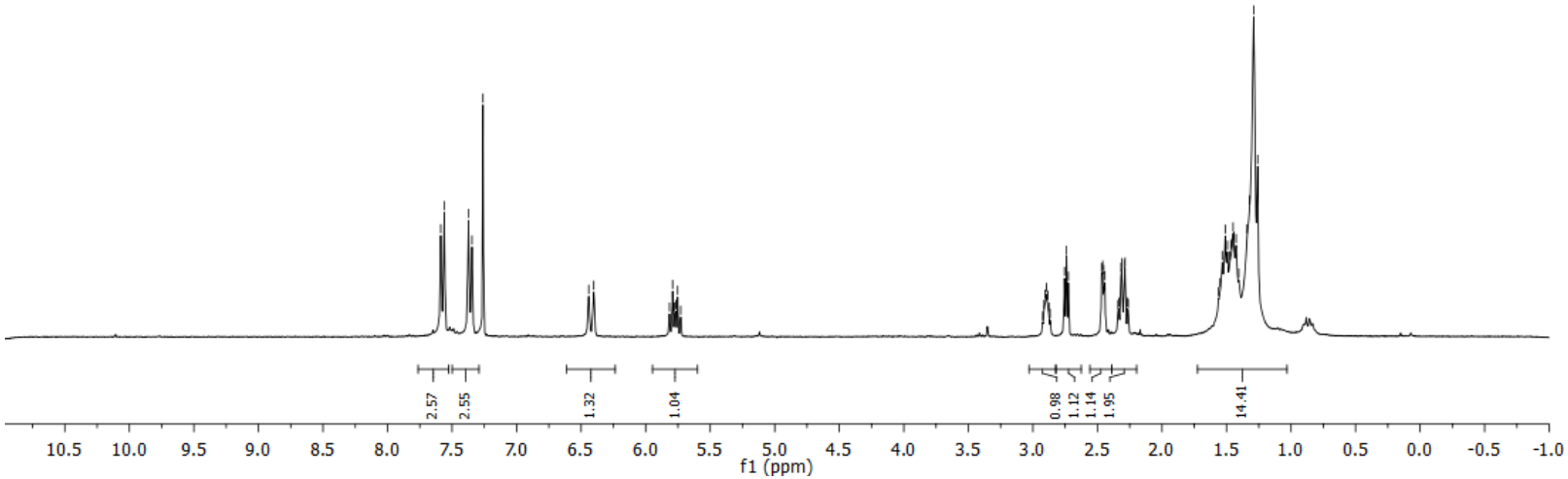
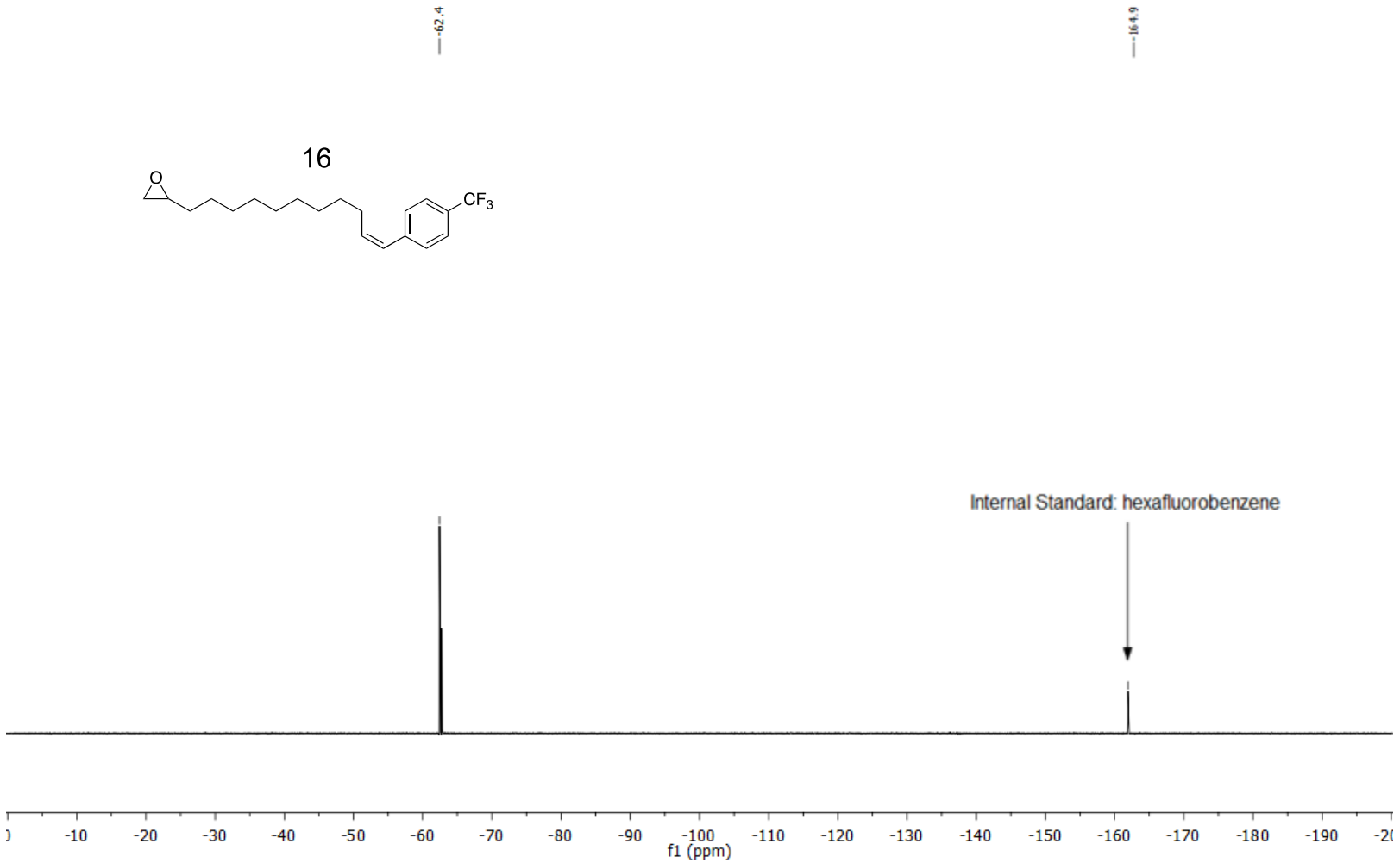
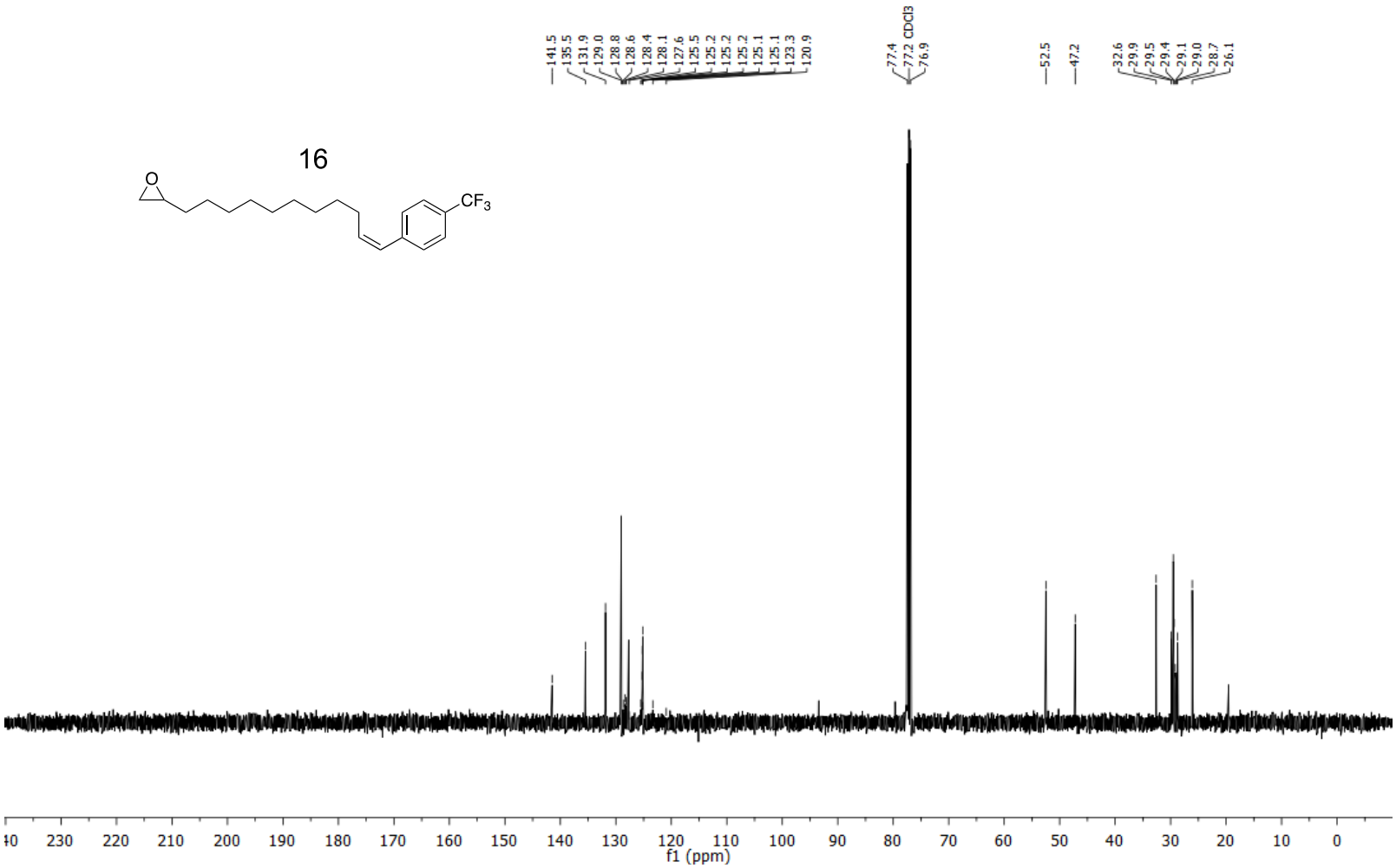




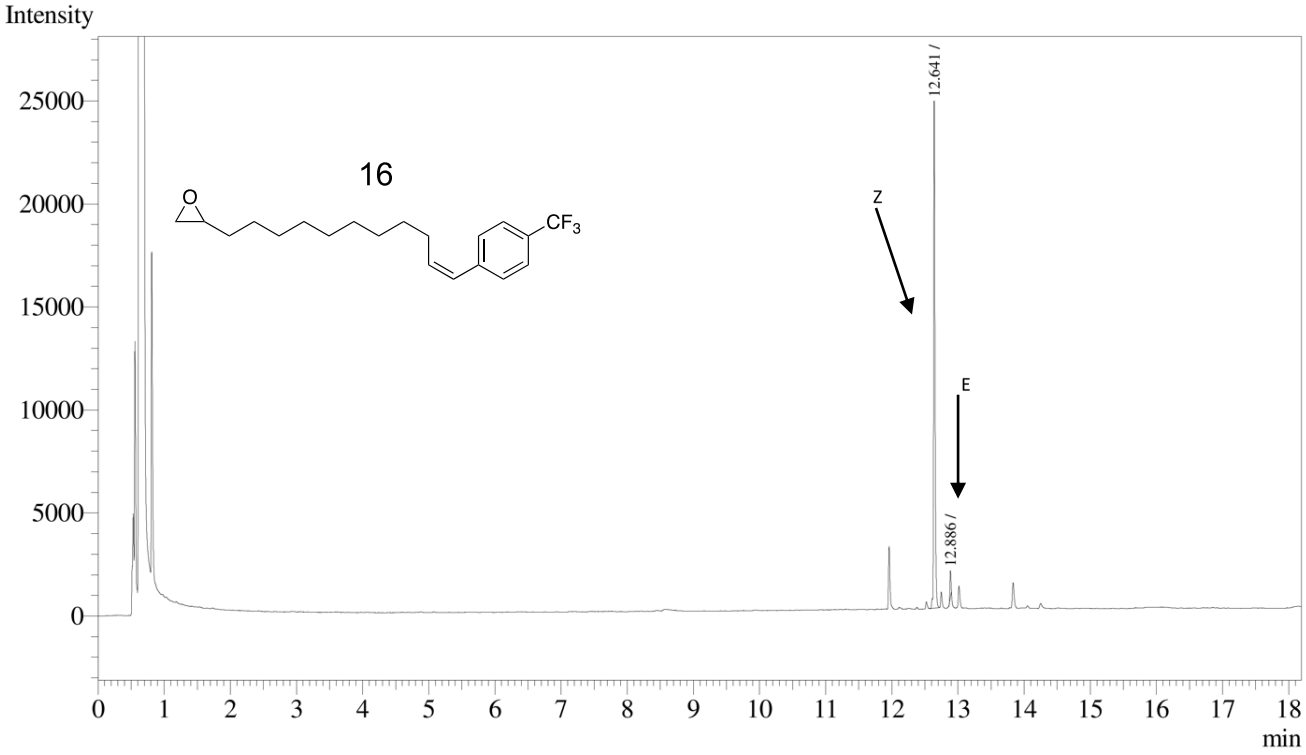
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.



^{13}C 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.

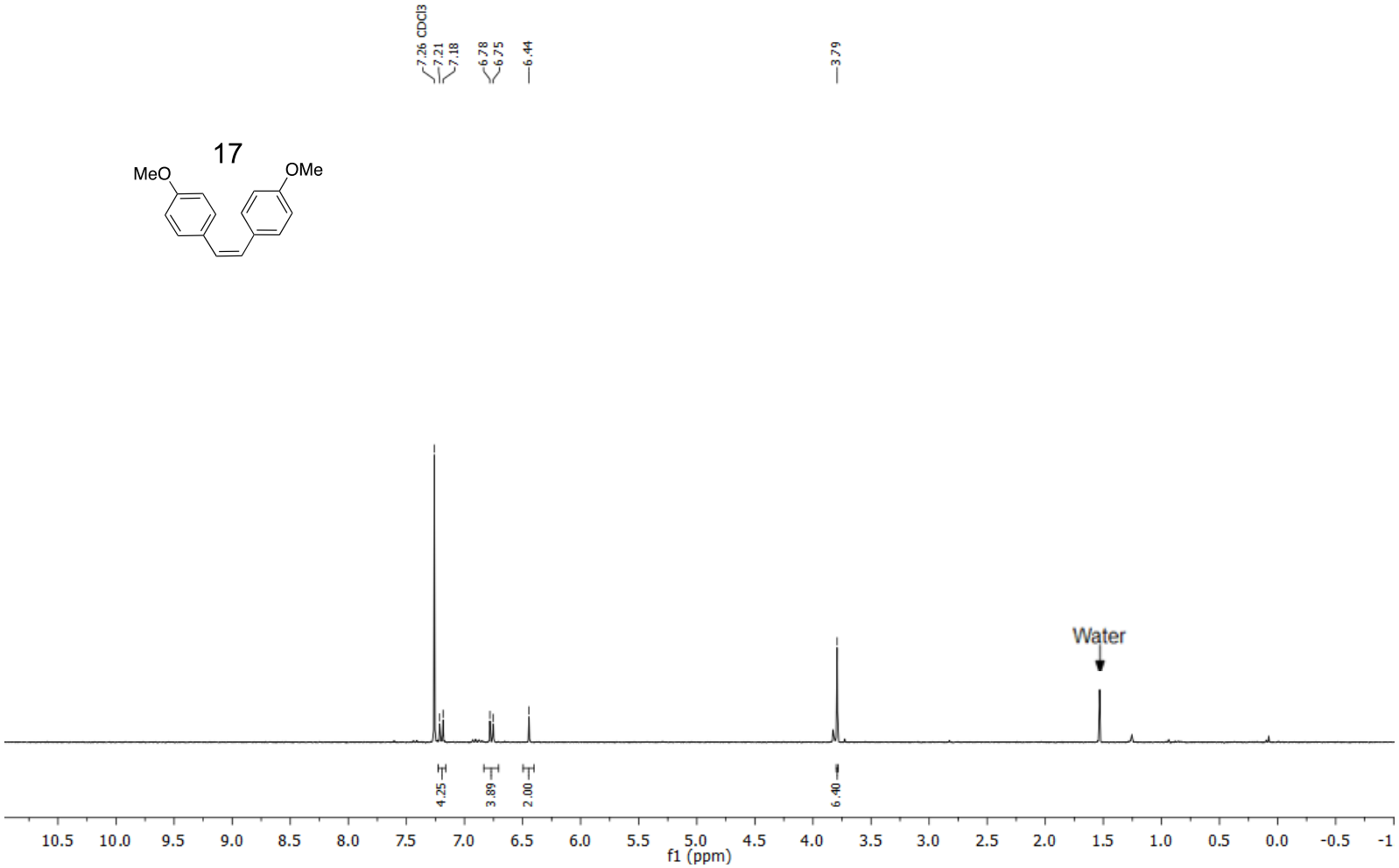


GC Trace of Crude Reaction Mixture

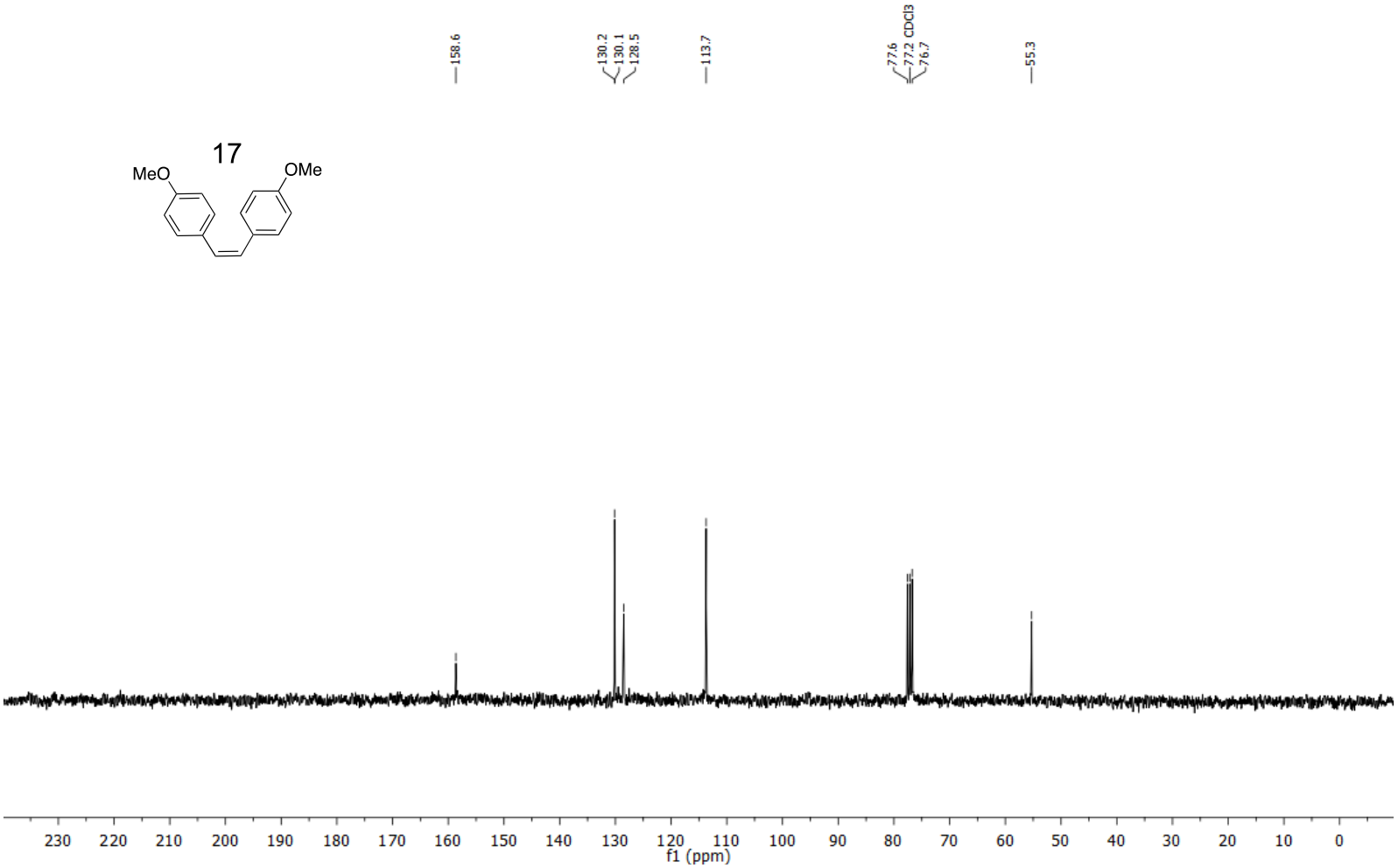


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.641	35406	24309	96.105		V		
2	12.886	1435	1289	3.895				
Total		36841	25598					

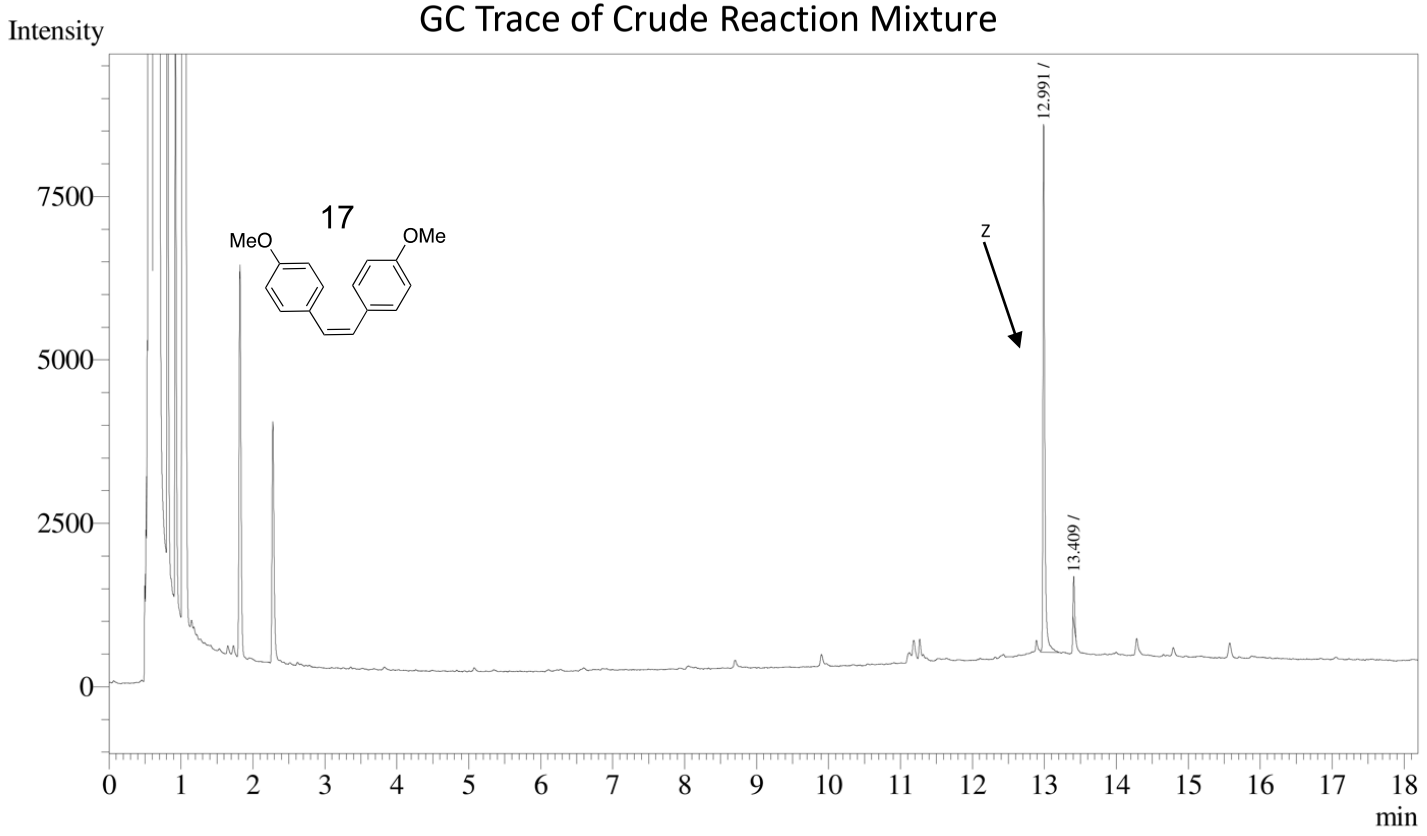
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.20 (**d**, *J* = 8.7 Hz, 4H), 6.77 (**d**, *J* = 8.7 Hz, 4H), 6.44 (**s**, 2H), 3.79 (**s**, 6H).



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

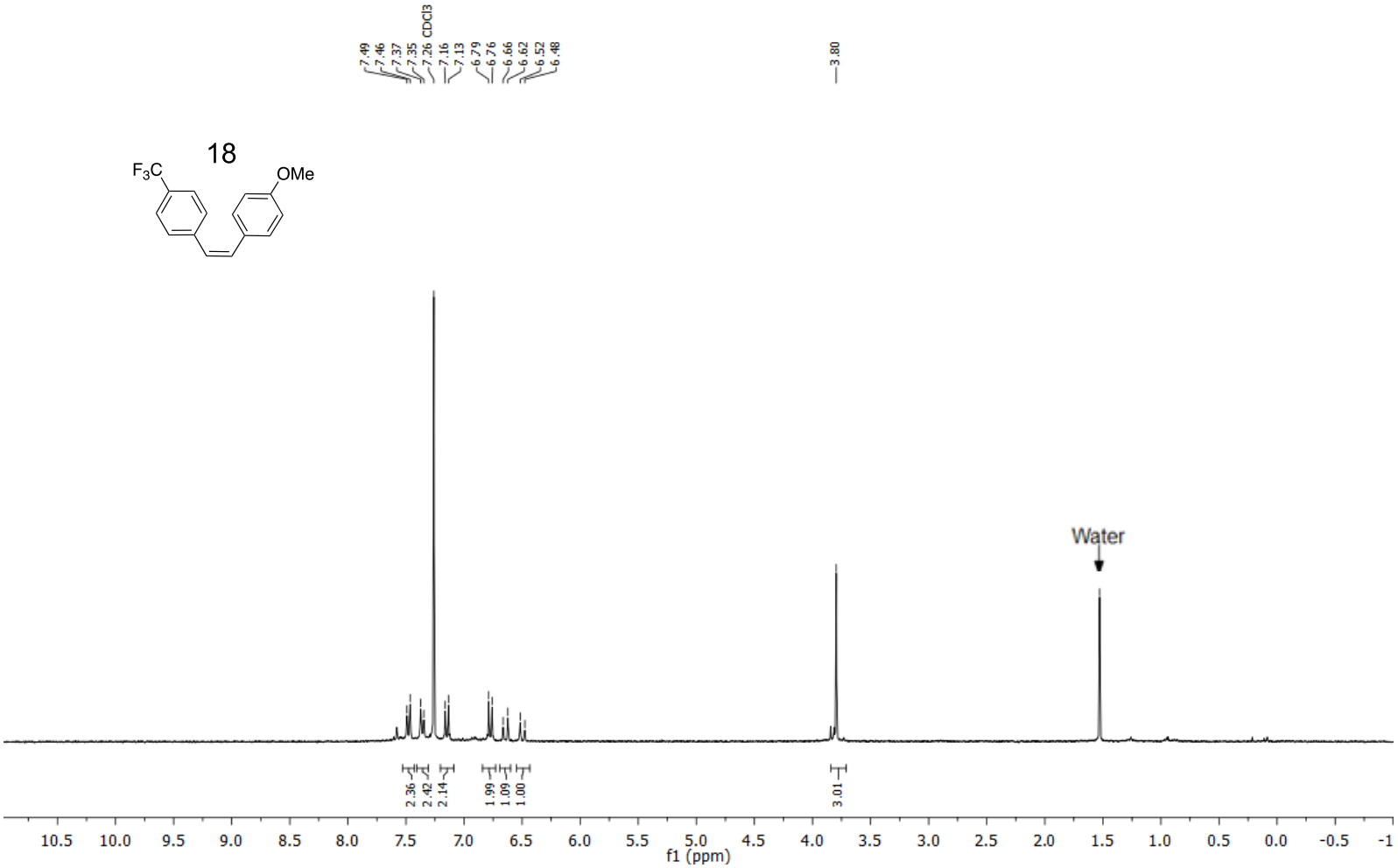


GC Trace of Crude Reaction Mixture

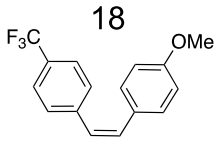


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.991	13966	7999	94.324		V		
2	13.409	840	660	5.676				
Total		14806	8659					

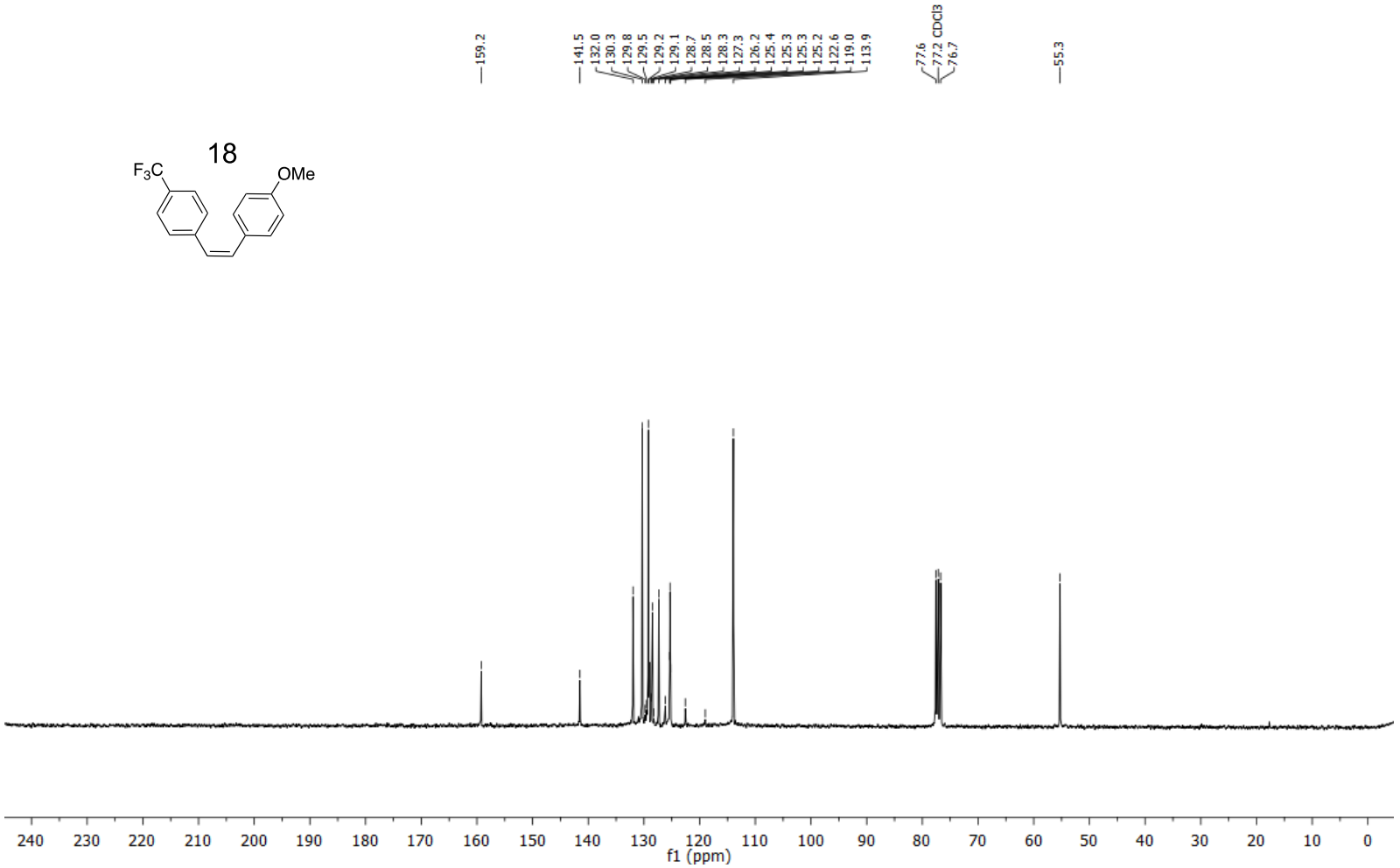
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.48 (**d**, *J* = 8.2 Hz, 2H), 7.36 (**d**, *J* = 8.2 Hz, 2H), 7.15 (**d**, *J* = 8.8 Hz, 2H), 6.77 (**d**, *J* = 8.8 Hz, 2H), 6.64 (**d**, *J* = 12.2 Hz, 1H), 6.50 (**d**, *J* = 12.2 Hz, 1H), 3.80 (**s**, 3H).



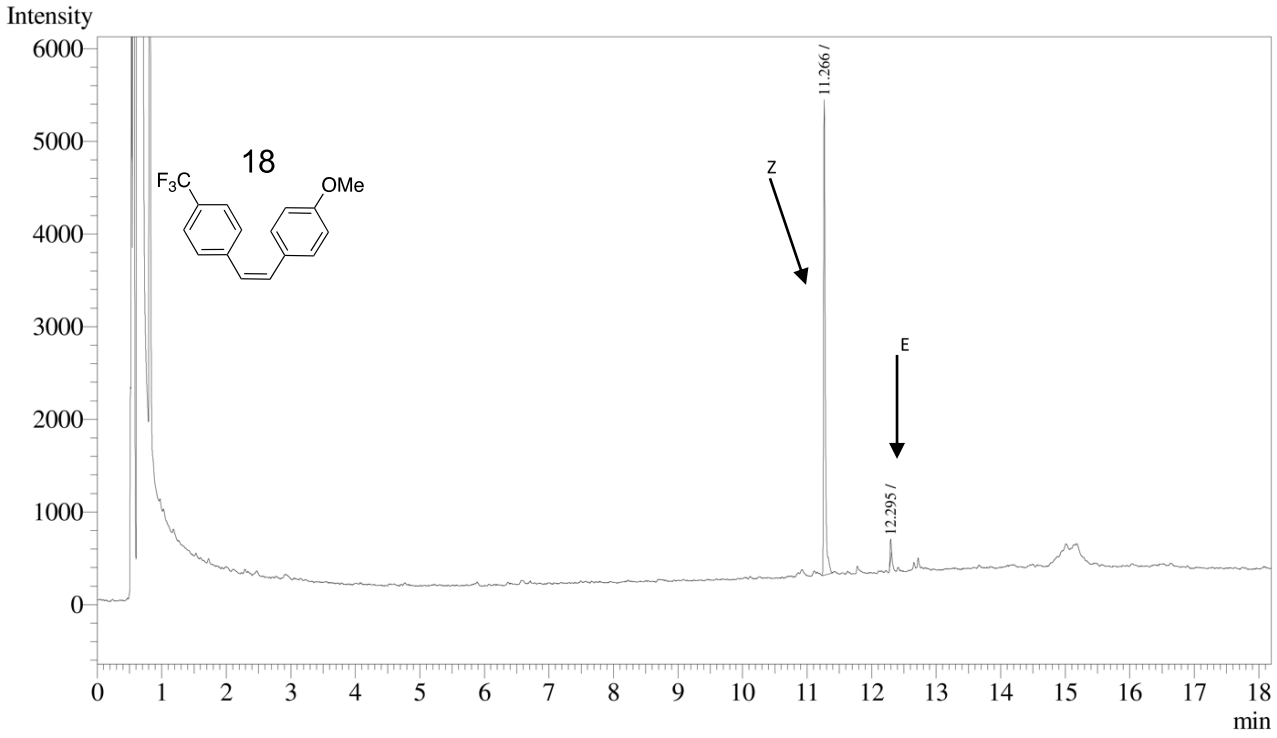
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5.



^{13}C NMR (75 MHz, Chloroform-*d*) 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.

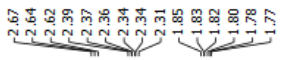


GC Trace of Crude Reaction Mixture



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.266	8974	4972	97.006				
2	12.295	277	222	2.994				
Total		9251	5194					

^{1}H 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).



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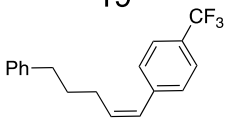
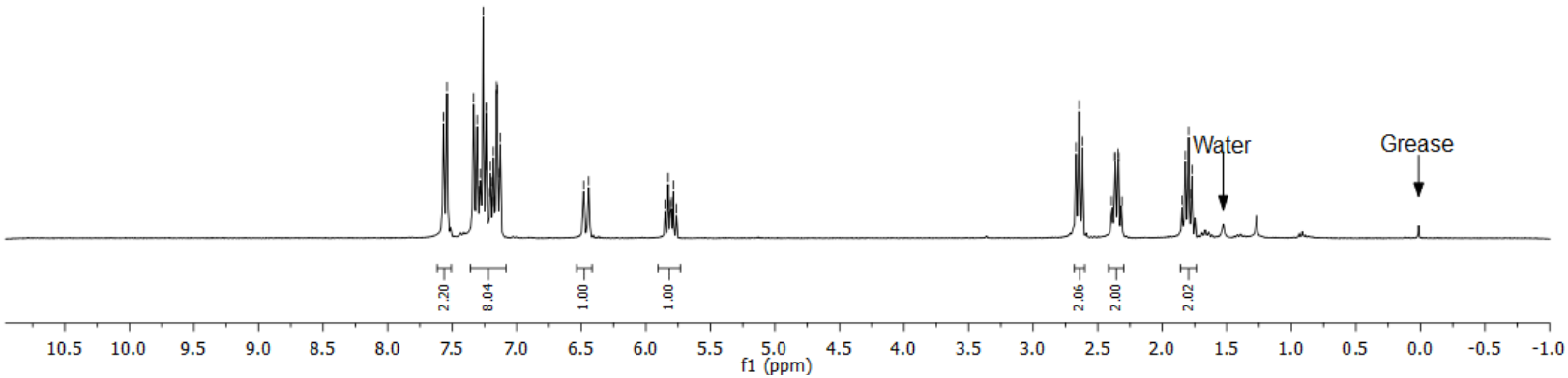
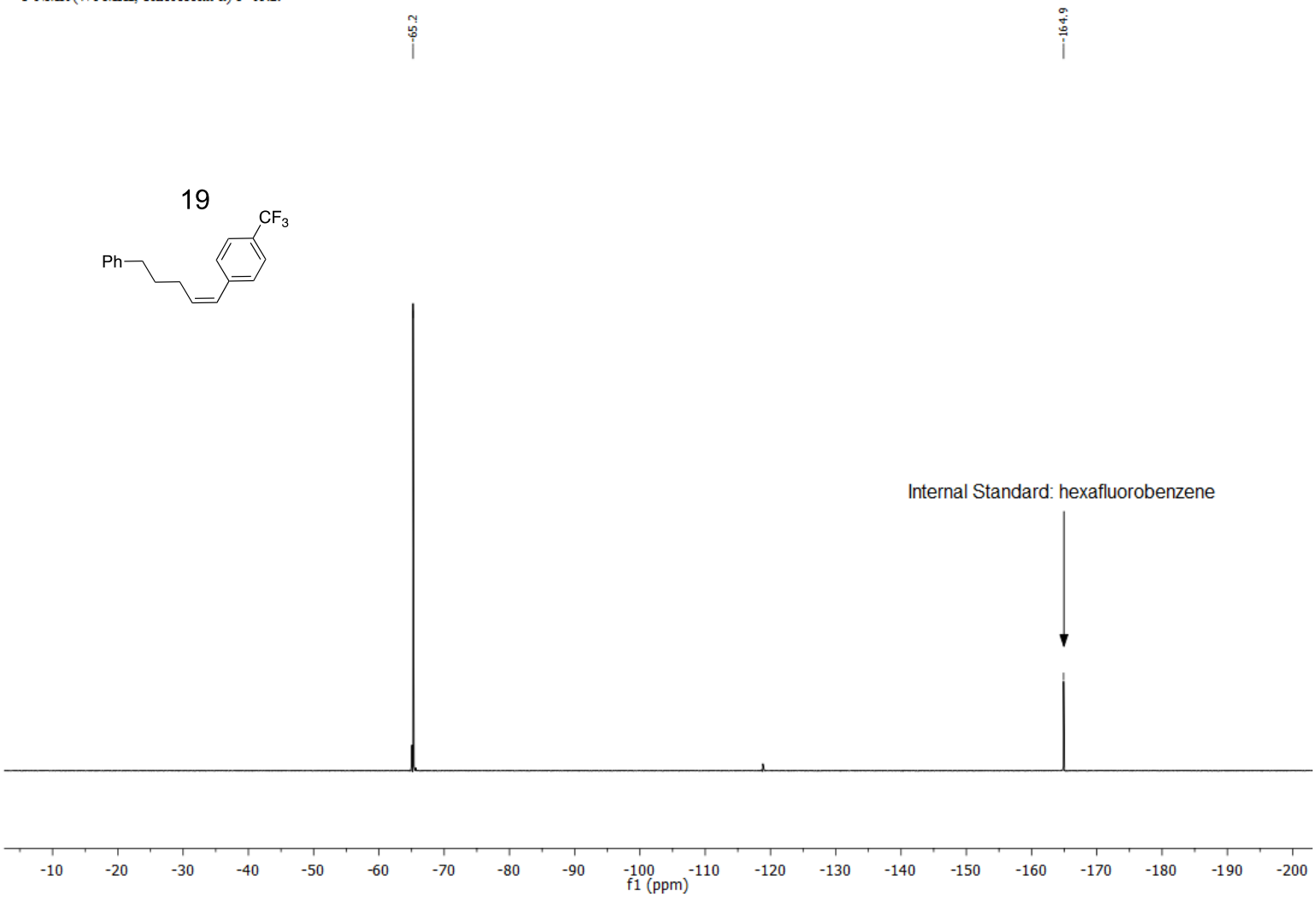
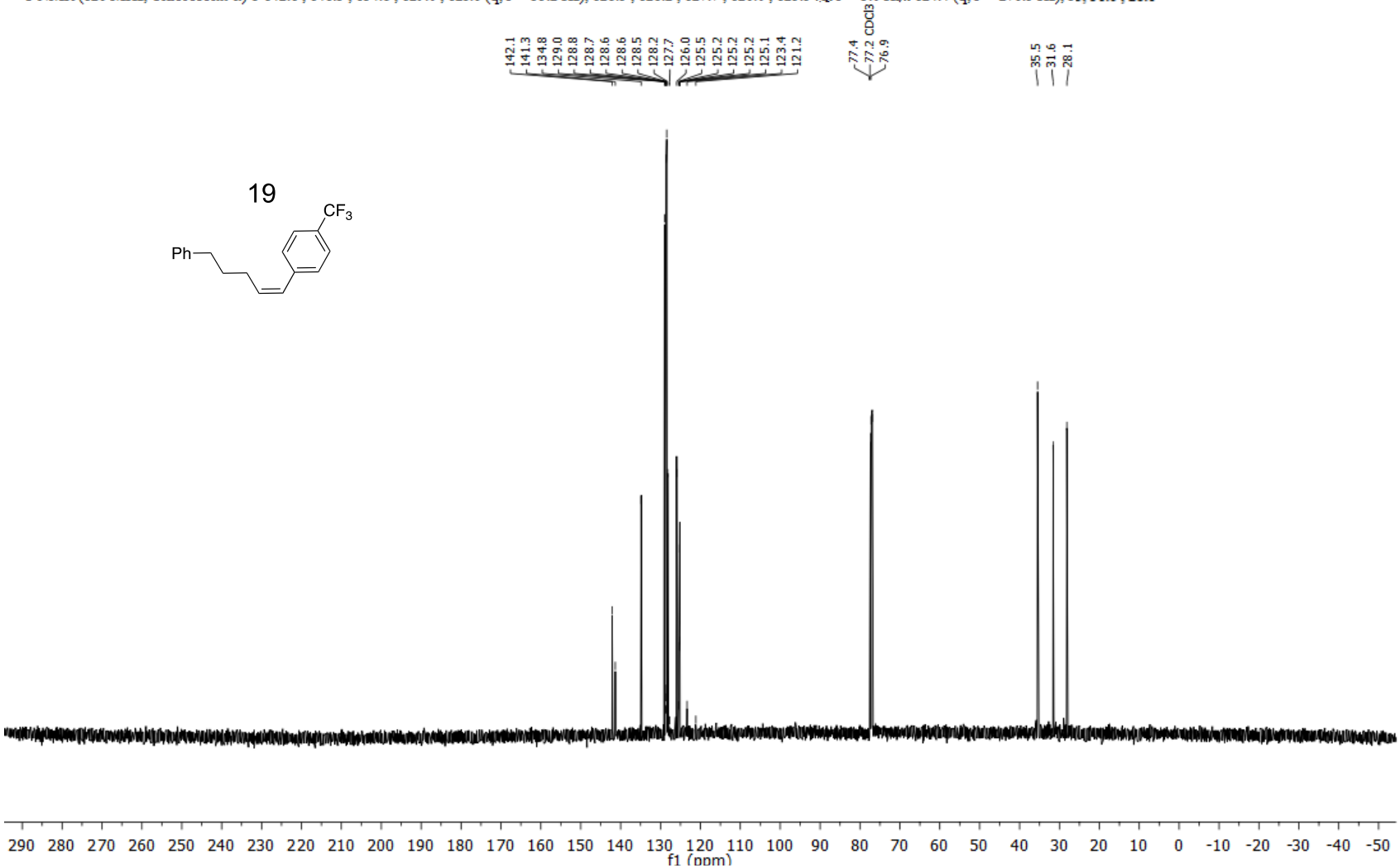


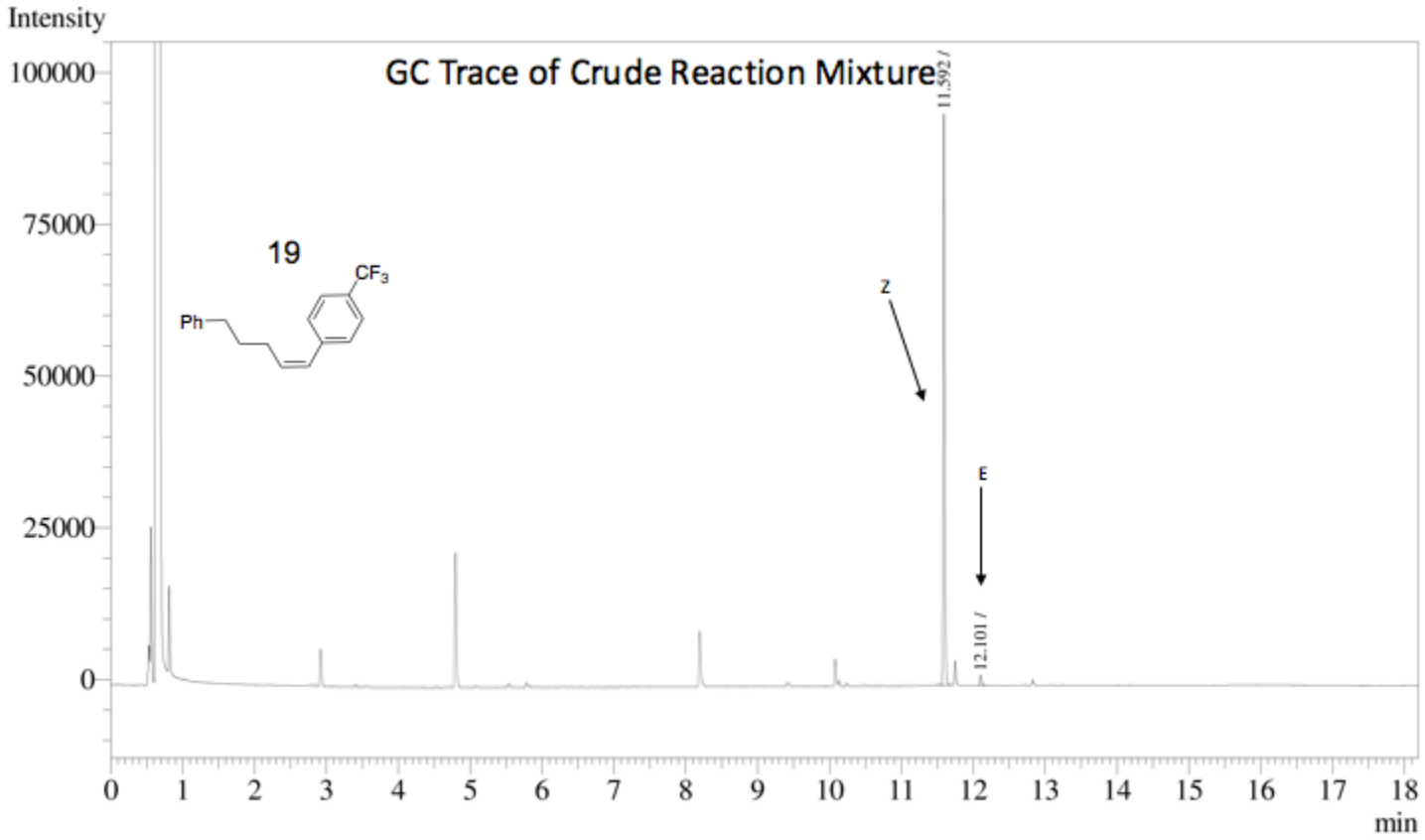


^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.2.



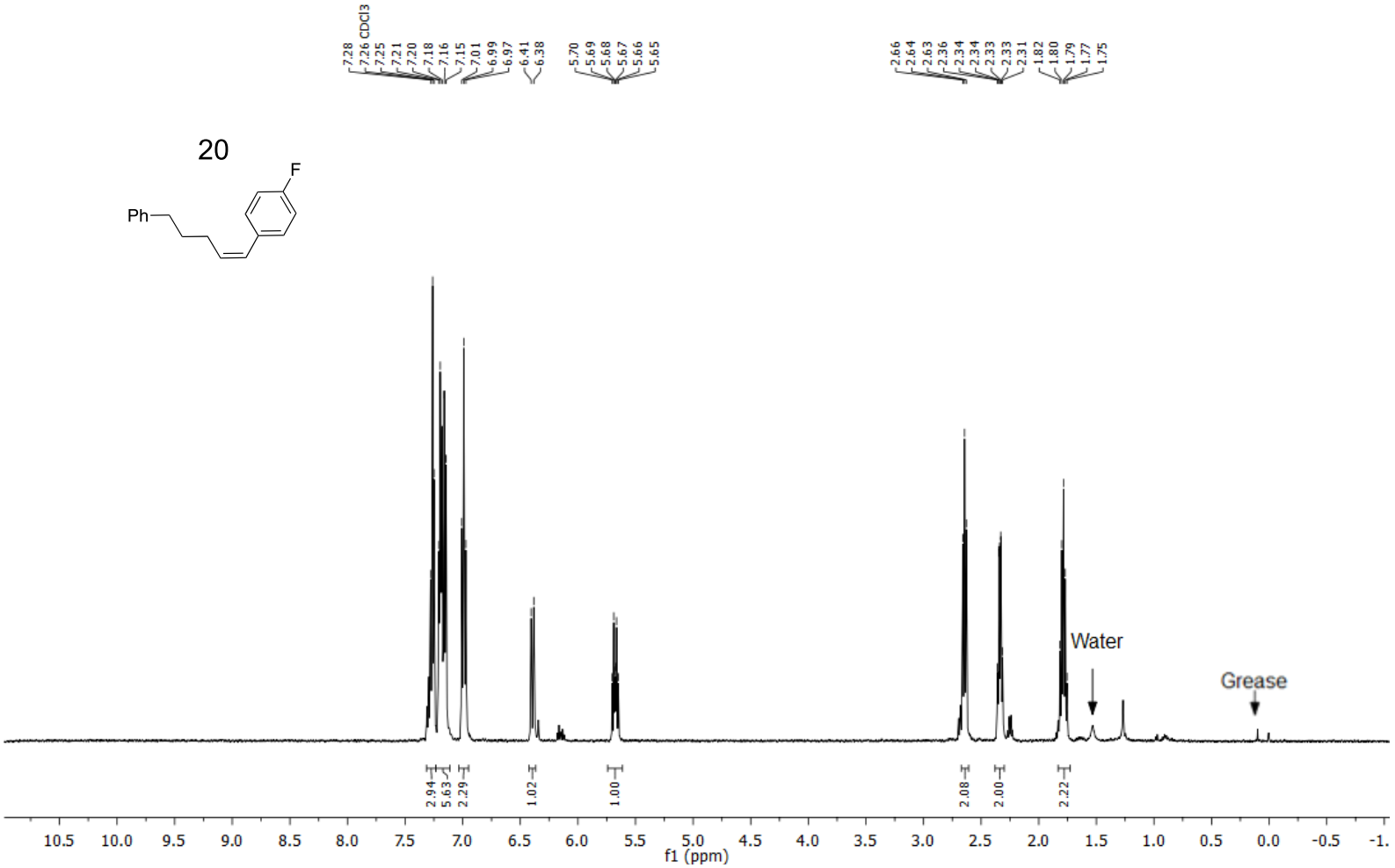
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.1 , 141.3 , 134.8 , 129.0 , 128.6 (q, *J* = 35.2 Hz), 128.5 , 128.2 , 127.7 , 126.0 , 125.5 (q, *J* = 3.0 Hz), 124.4 (q, *J* = 276.5 Hz), 35, 31.6 , 28.1



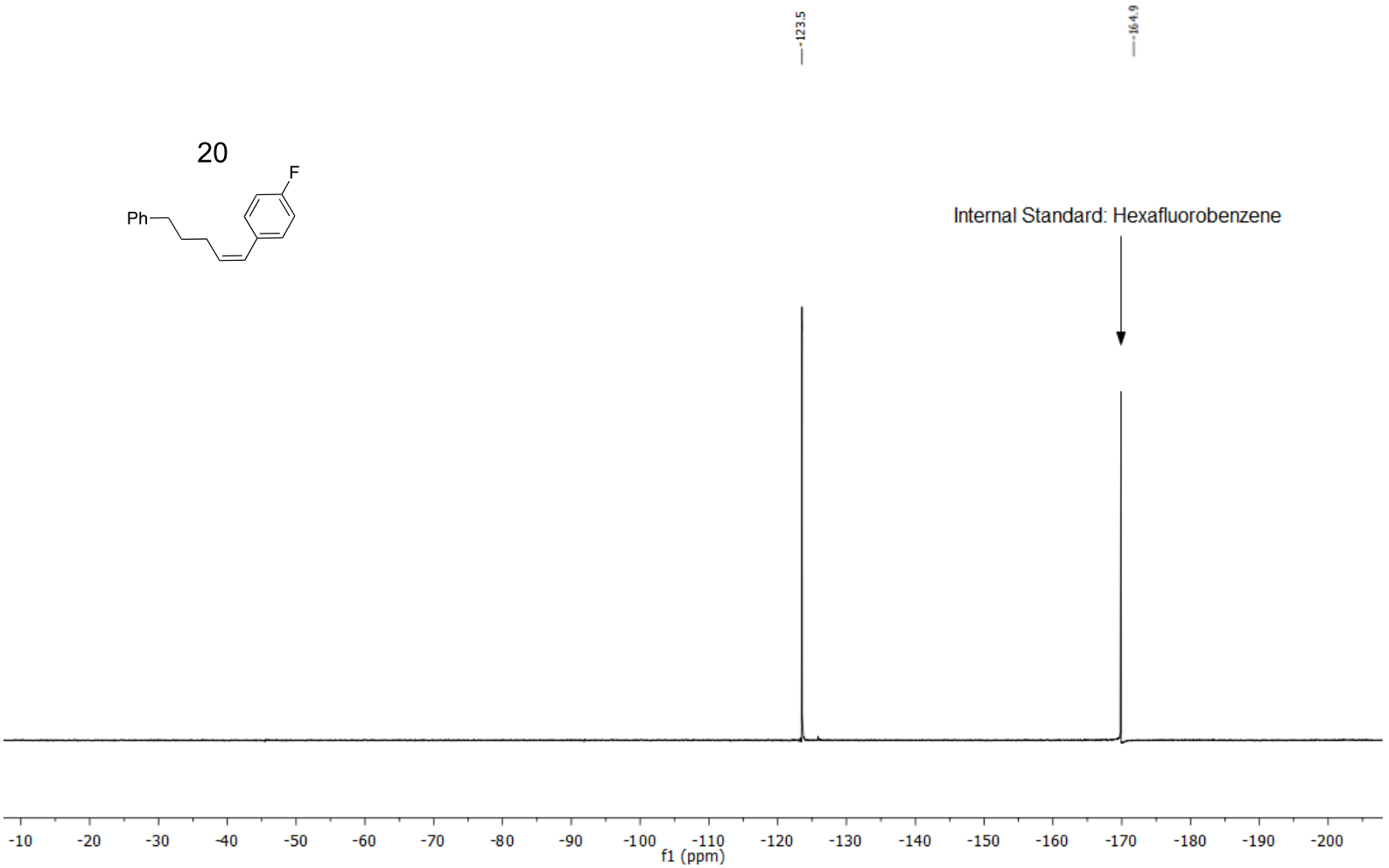


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.592	134060	91508	97.797		V		
2	12.101	6095	1680	4.445				
Total		137080	93188					

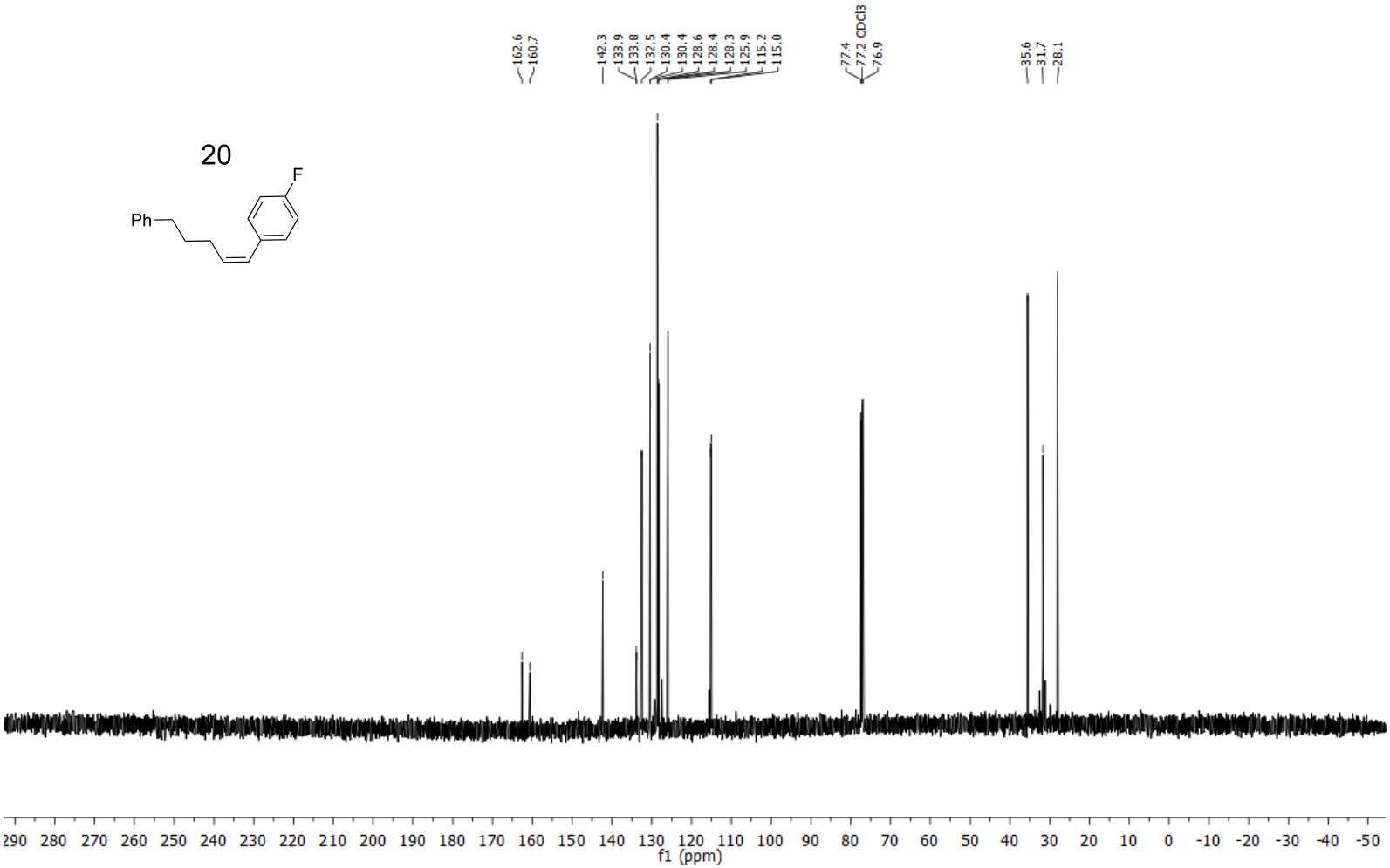
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.23 (m, 3H), 7.23 – 7.13 (m, 4H), 7.04 – 6.95 (m ,2H), 6.39 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.33 (dt, *J* = 7.6, 7.3Hz, 2H), 1.79 (p, *J* = 7.6 Hz, 2H).

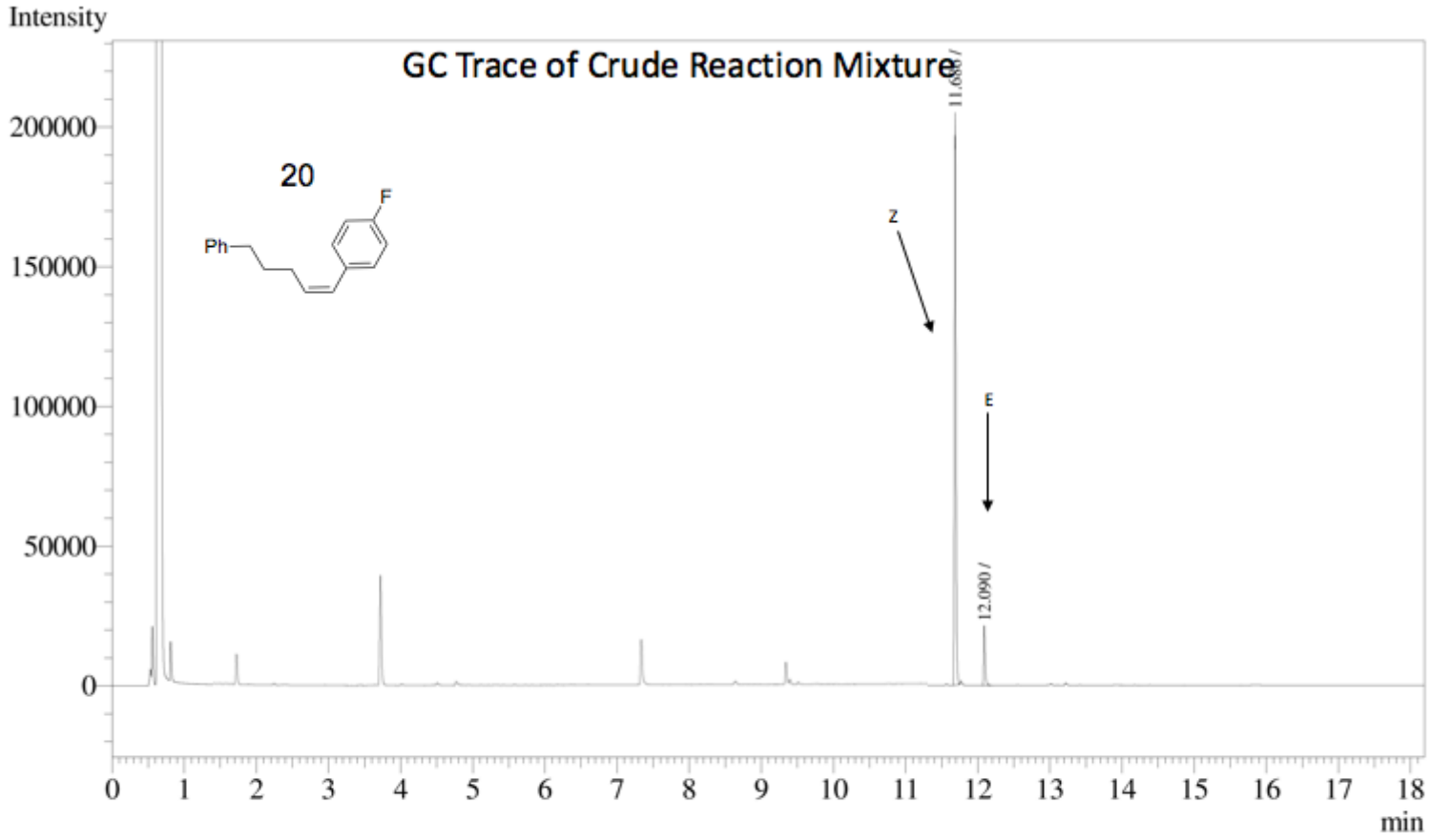


^{19}F NMR (471 MHz, Chloroform-*d*) δ -123.5 .



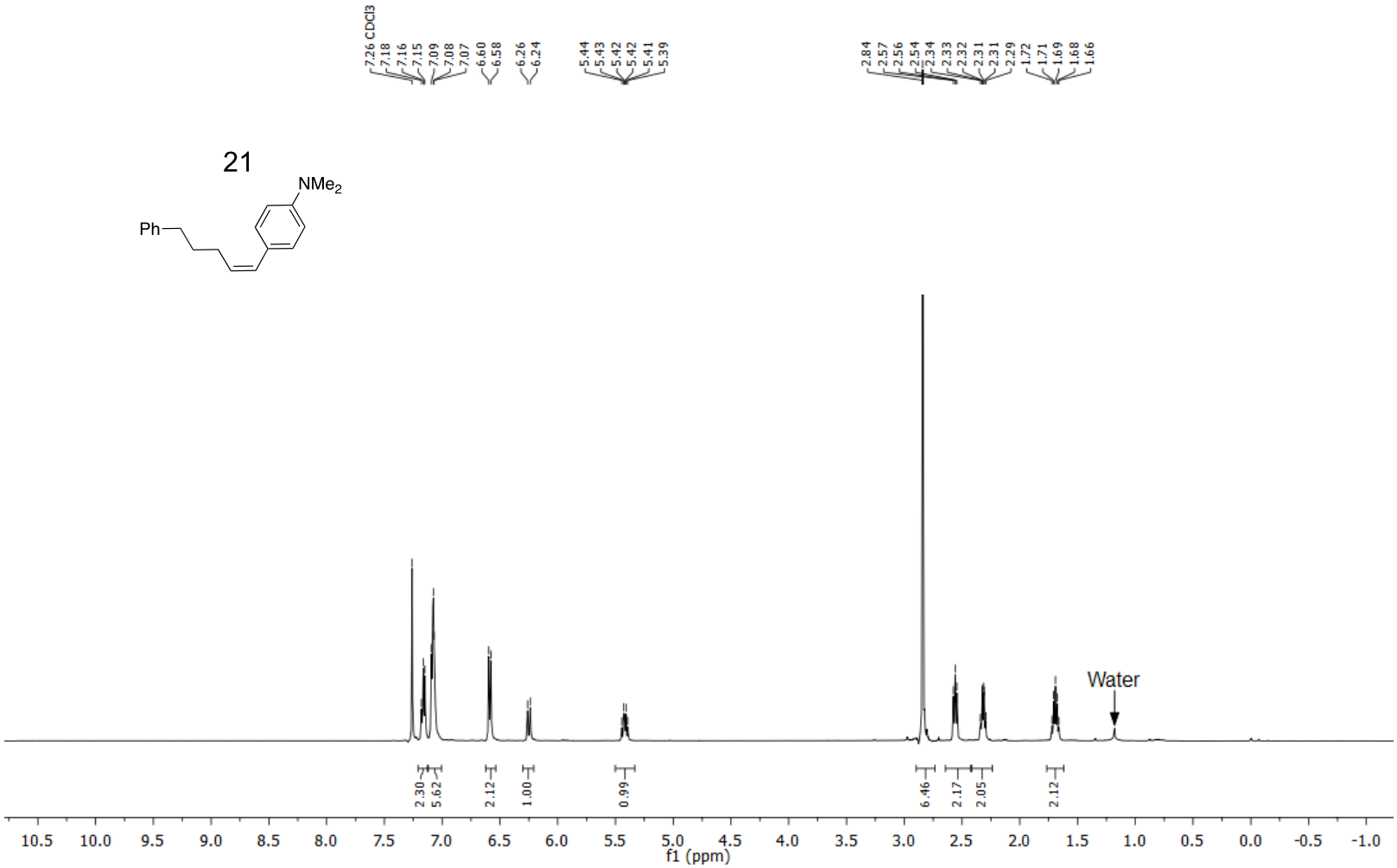
^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 246.1 Hz), 142.3 , 133.8 (d, *J* = 3.1 Hz), 132.5 , 130.4 (d, *J* = 7.9 Hz), 128.6 , 128.4 , 128.3 , 125.9 , 115.1 (d, *J* = 21.3 Hz), 35.6 , 31.7 , 27.1 .



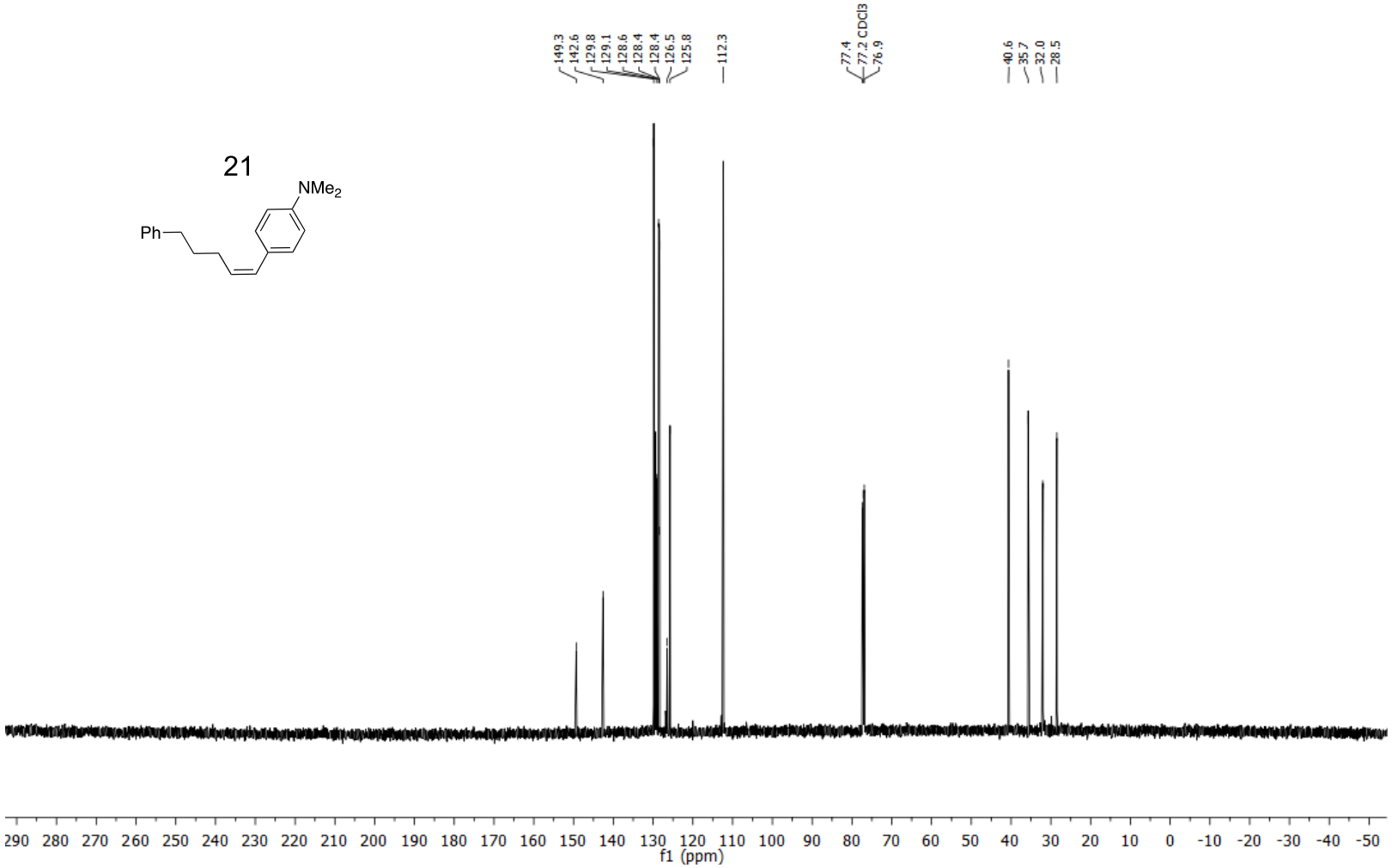


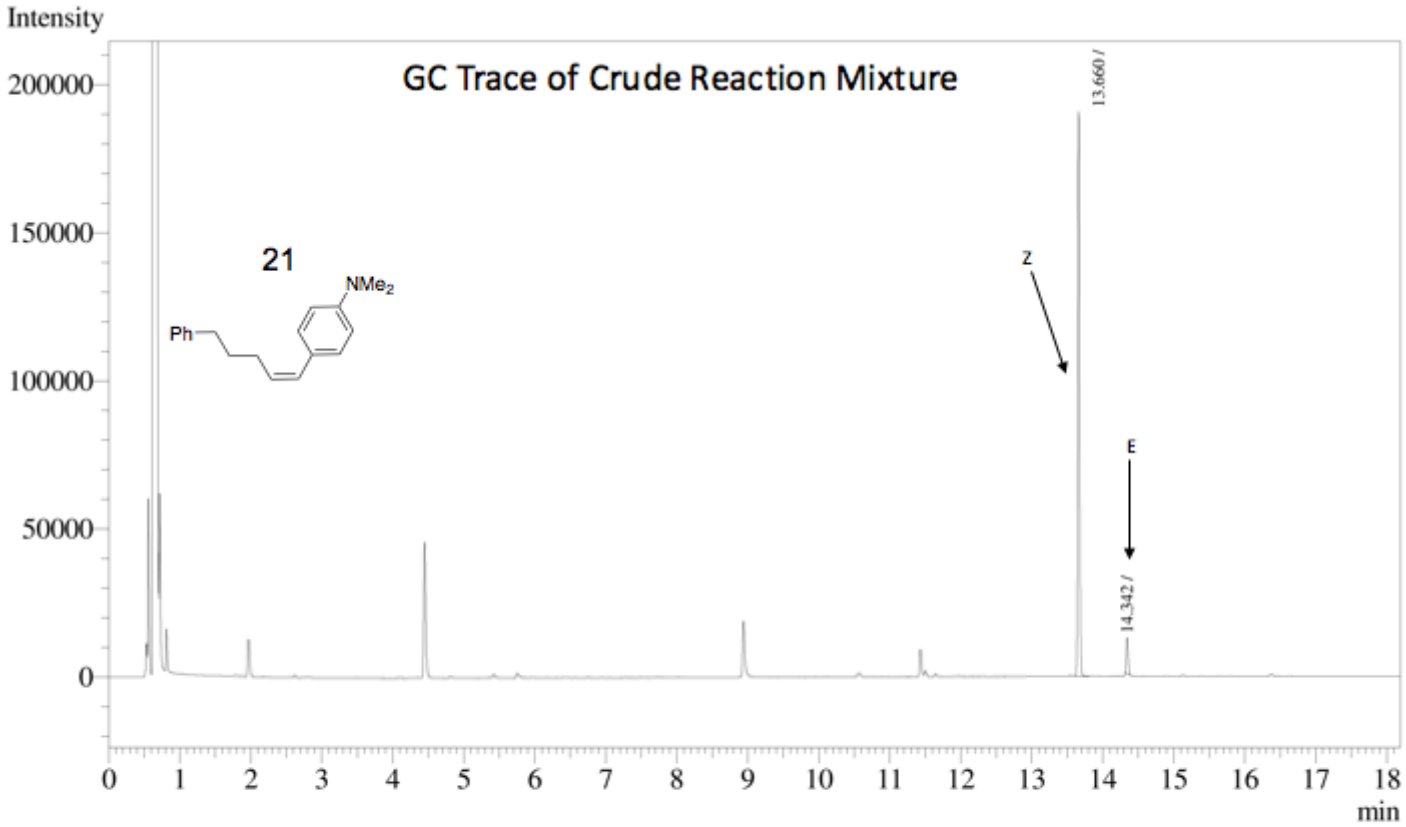
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.686	280659	193958	90.090				
2	12.090	27972	21013	8.979				
Total		311531	214971					

^{1}H 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* = 7.2Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H).



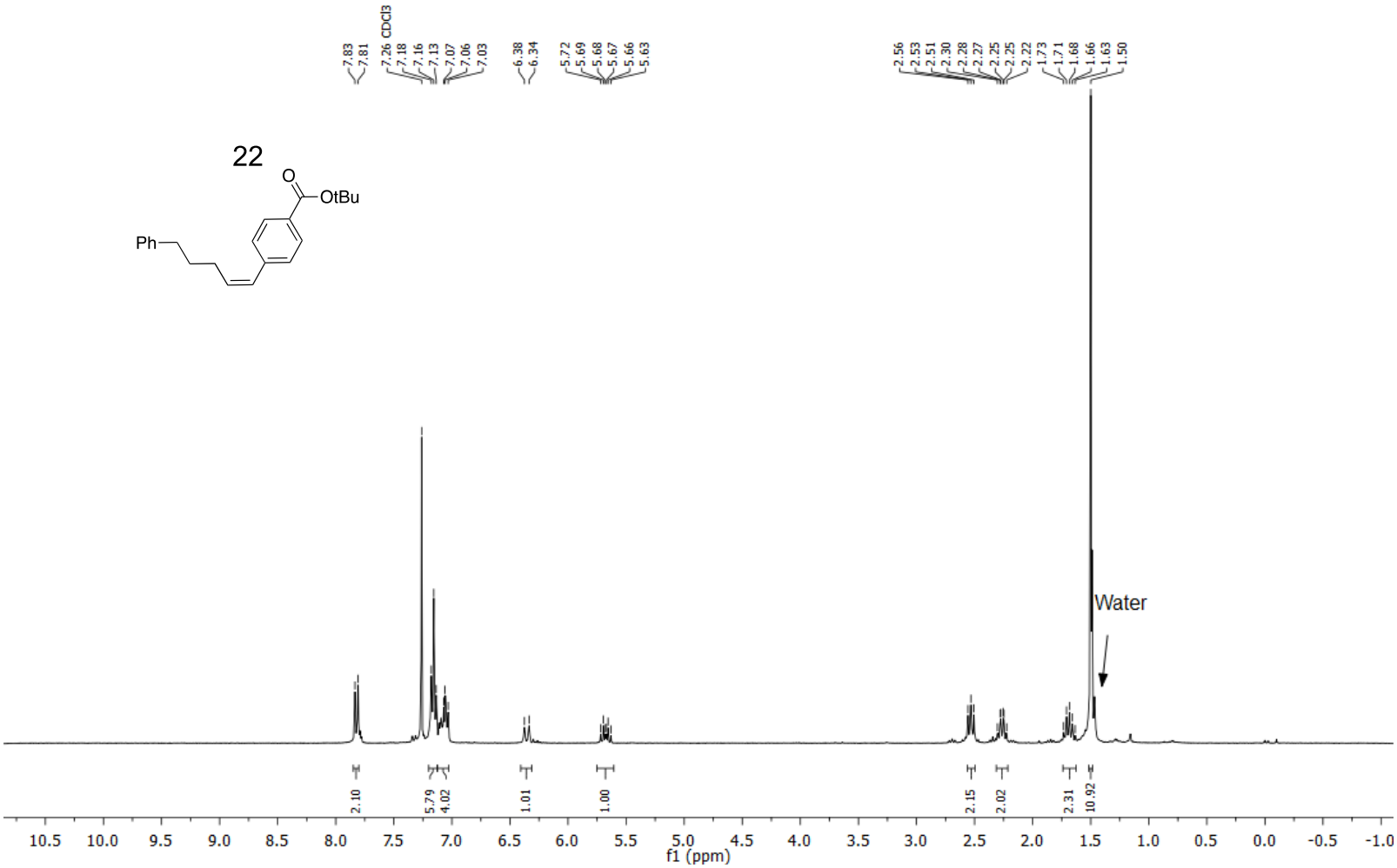
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.3 , 142.6 , 129.8 , 129.1 , 128.6 , 128.4 , 126.5 , 125.8 , 112.3 , 40.6 , 35.7 , 32.0 , 28.5 .



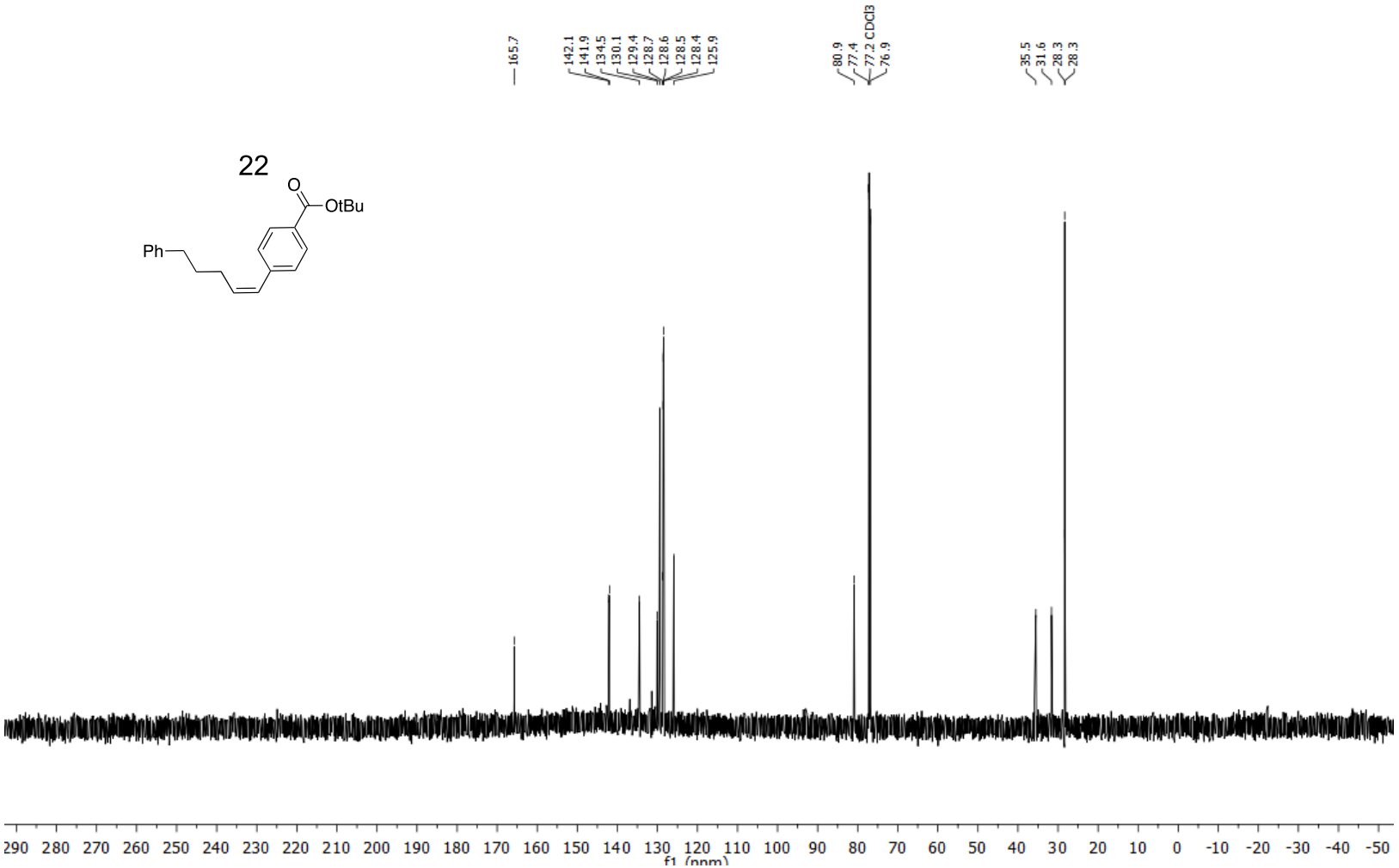


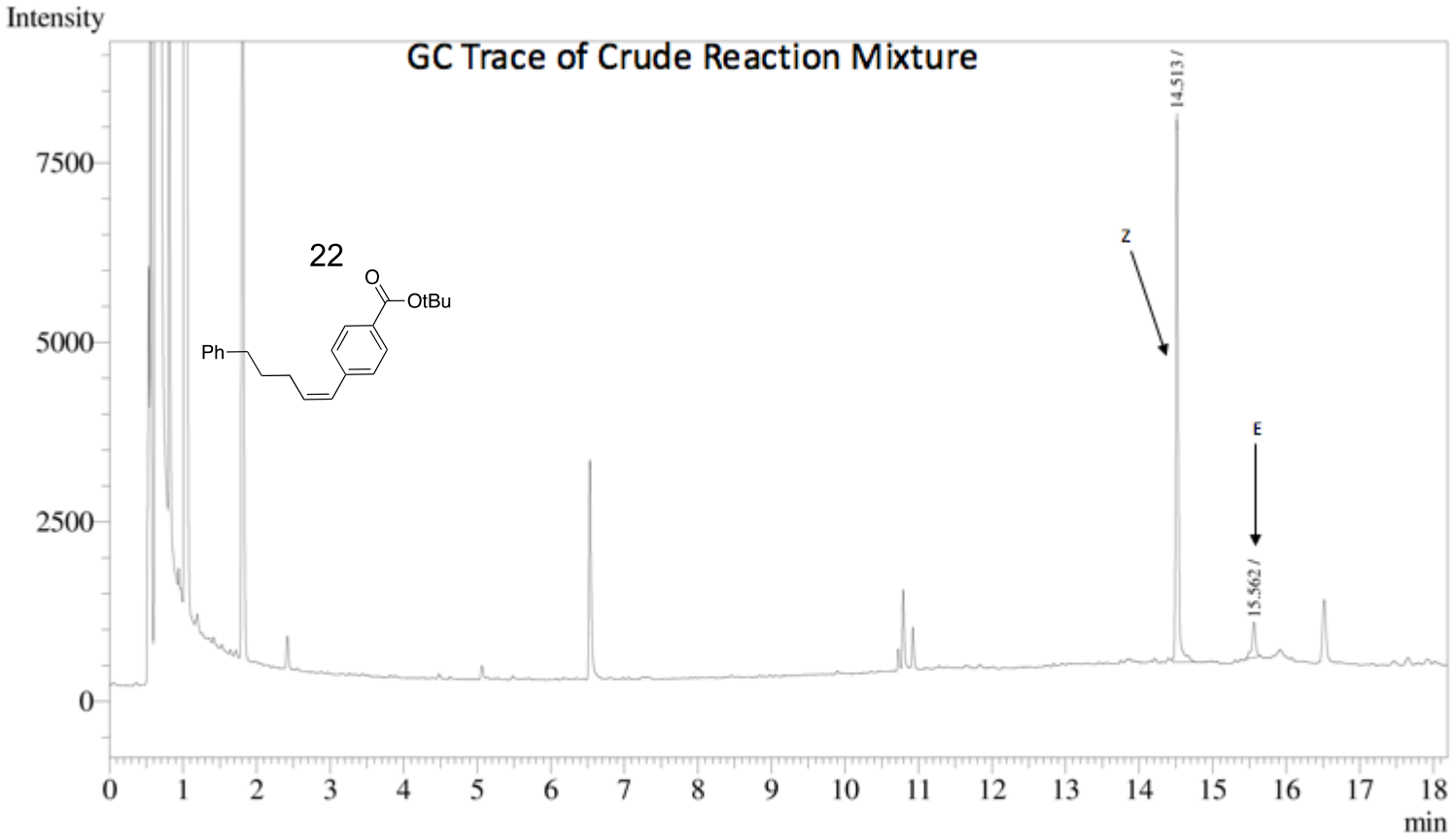
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.660	317118	184436	93.291		V		
2	14.342	26519	12067	7.774				
Total		339923	196503					

^{1}H 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).



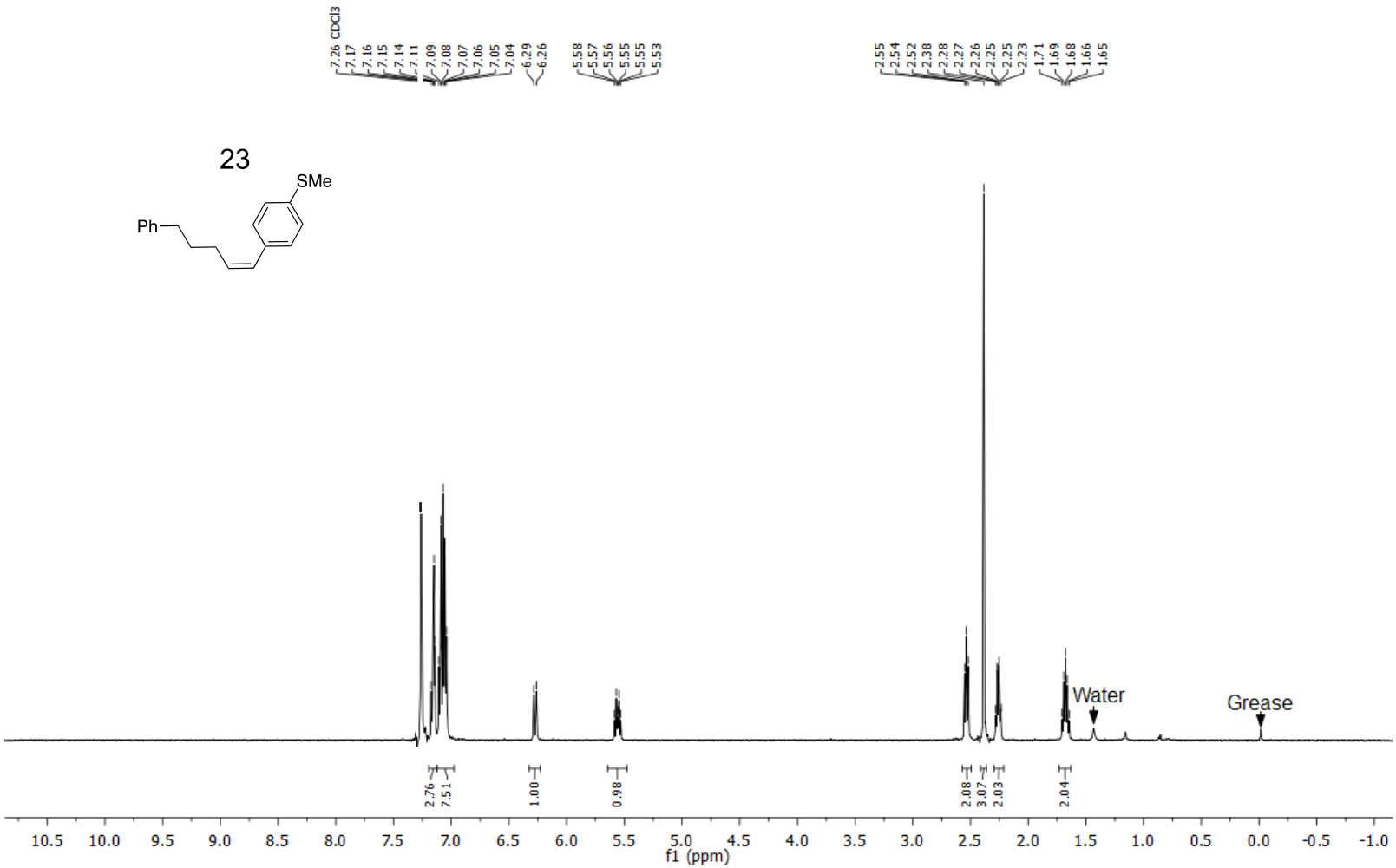
^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.7 , 142.2 , 141.9 , 134.5 , 130.1 , 129.4 , 128.7 , 128.6 , 128.5 , 128.4 , 125.9 , 80.9 , 35.5 , 31.6 , 28.3 , 28.3 .



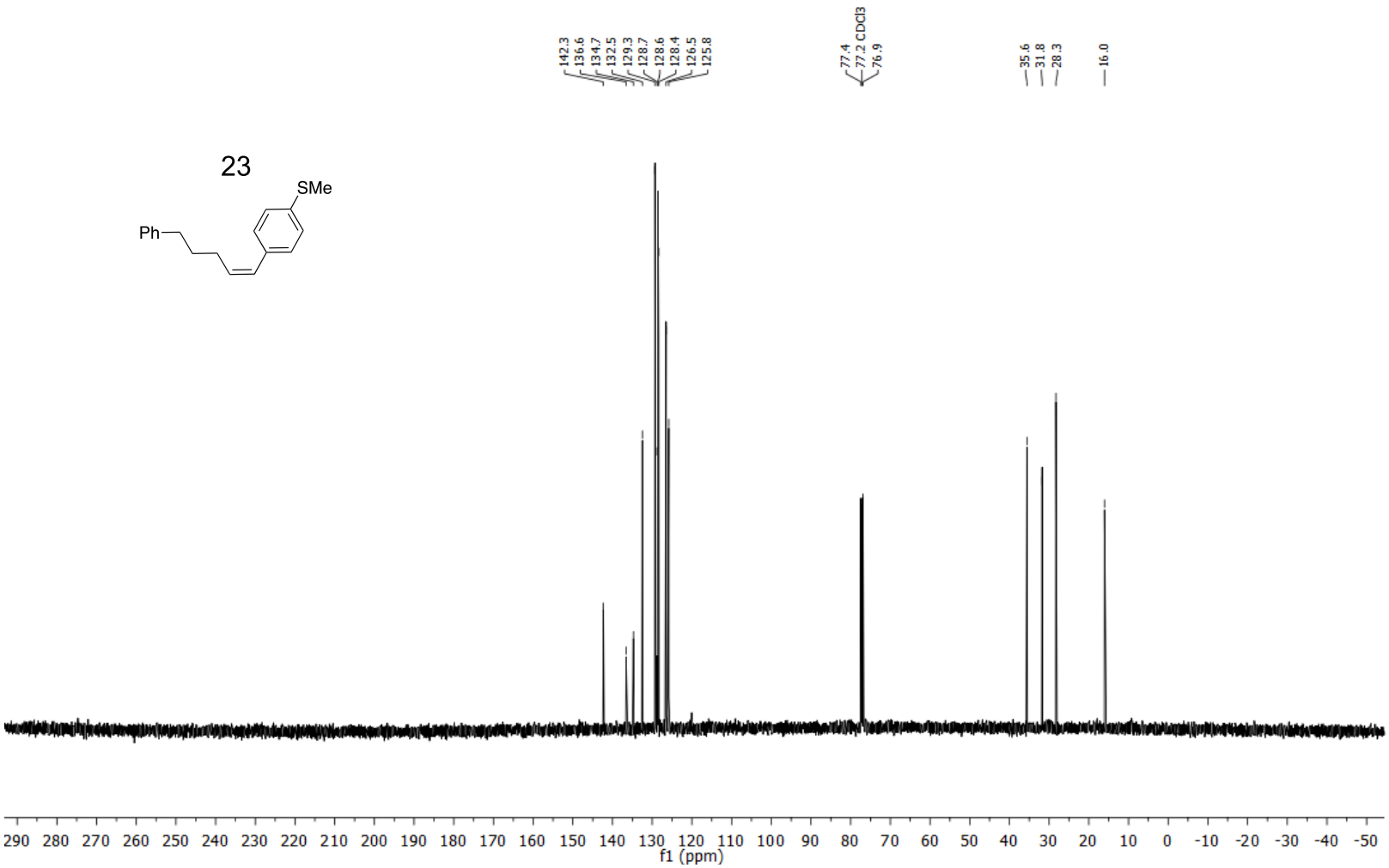


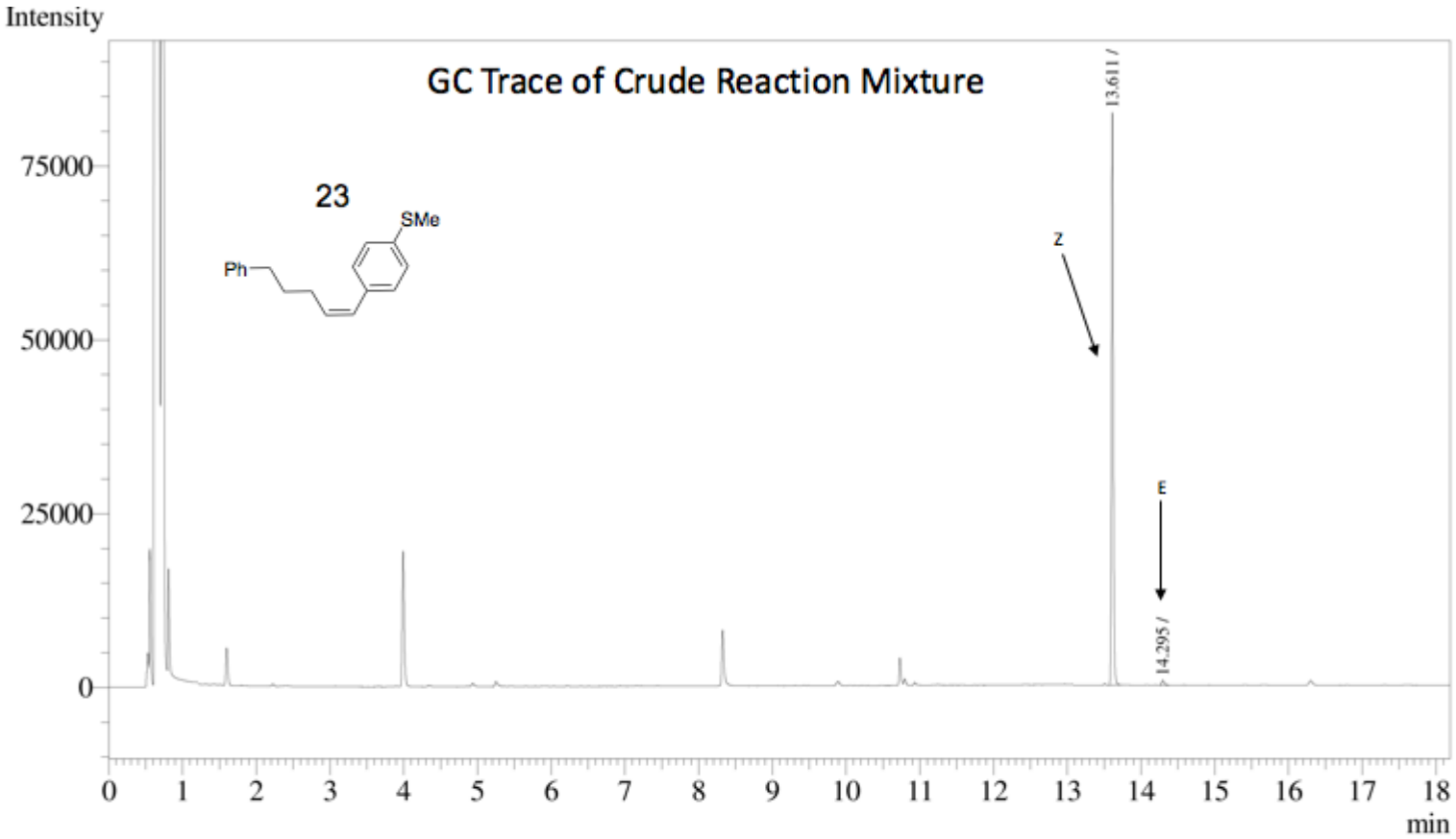
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.513	17273	7559	91.108		SV		
2	15.562	1686	491	8.892				
Total		18959	8050					

^{1}H 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).



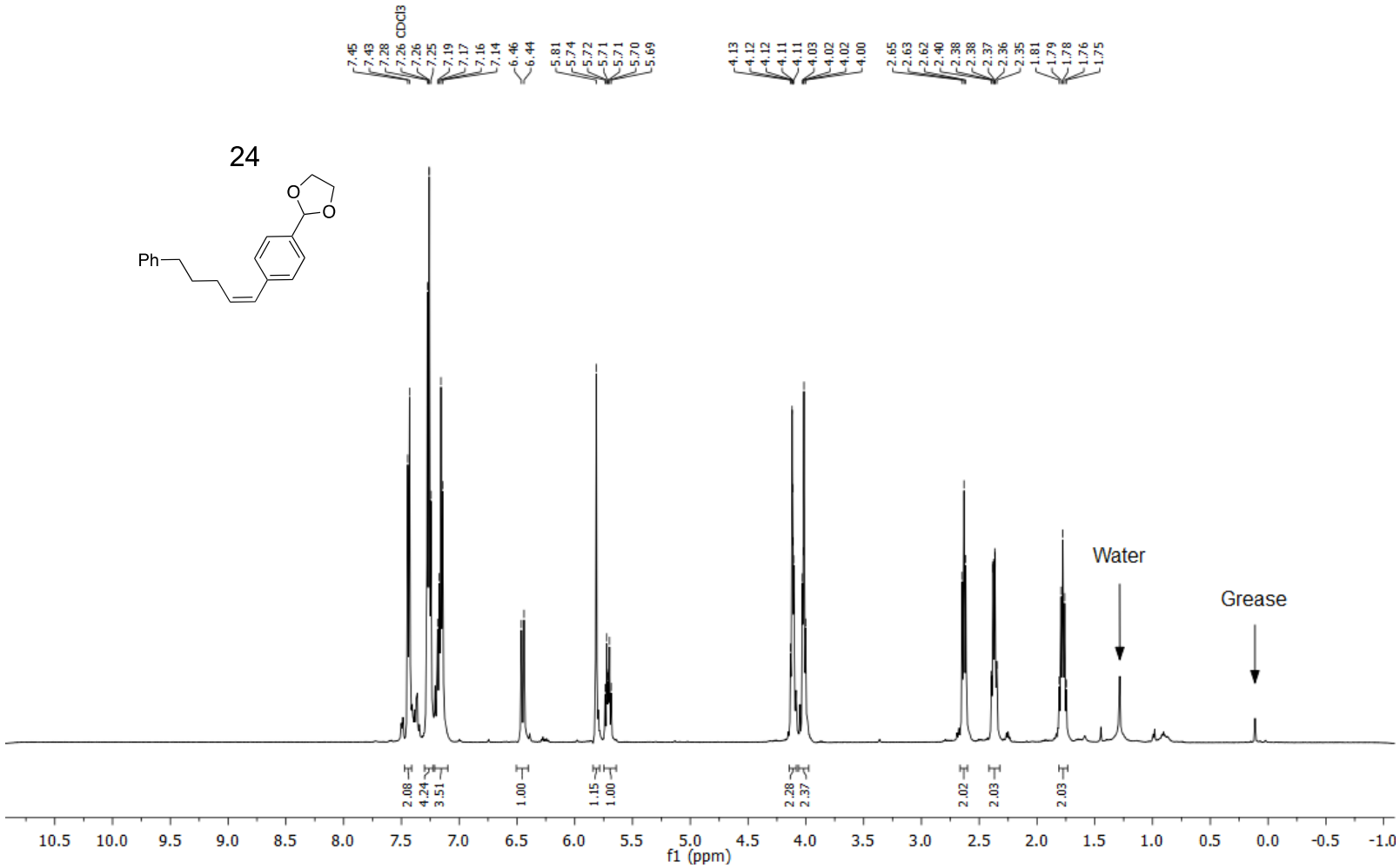
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.3 , 136.6 , 134.7 , 132.5 , 129.3 , 128.7 , 128.6 , 128.4 , 126.5 , 125.8 , 35.6 , 31.8 , 28.3 , 16.0 .



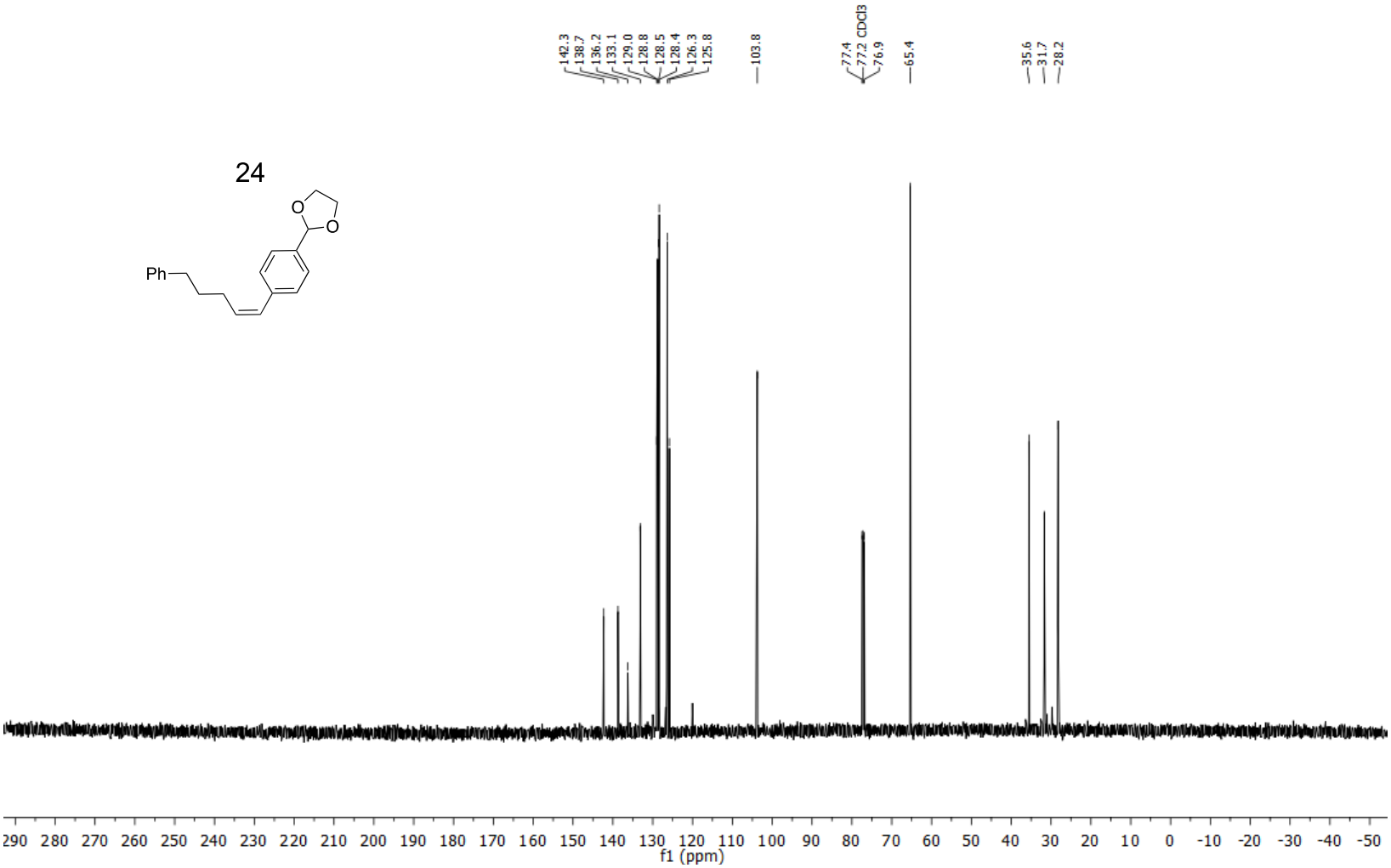


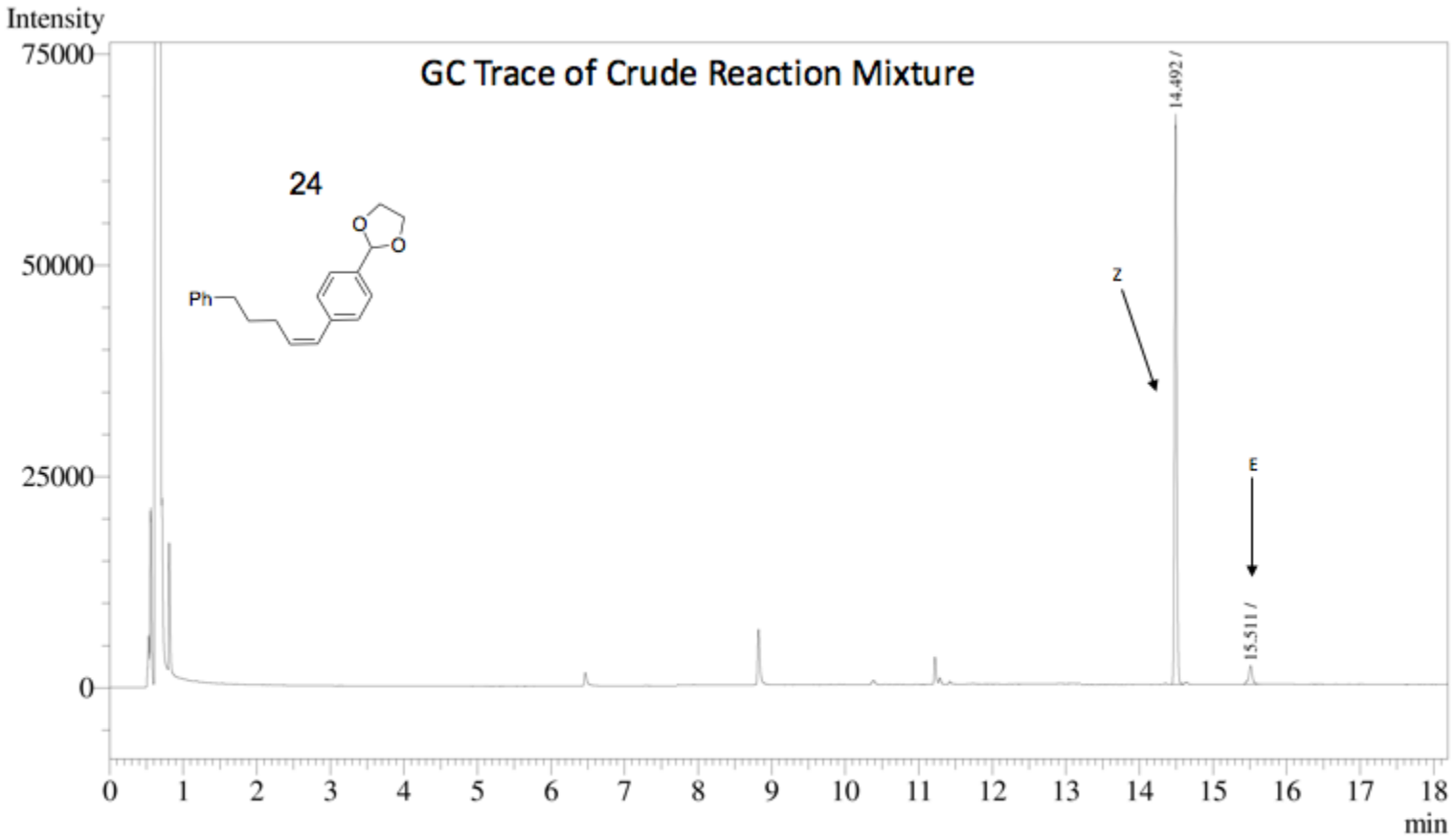
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.611	137239	81404	98.767		V		
2	14.295	1713	683	1.233				
Total		138952	82087					

^{1}H 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* = 7.3 Hz, 2H), 1.78 (p, *J* = 7.6 Hz, 2H).



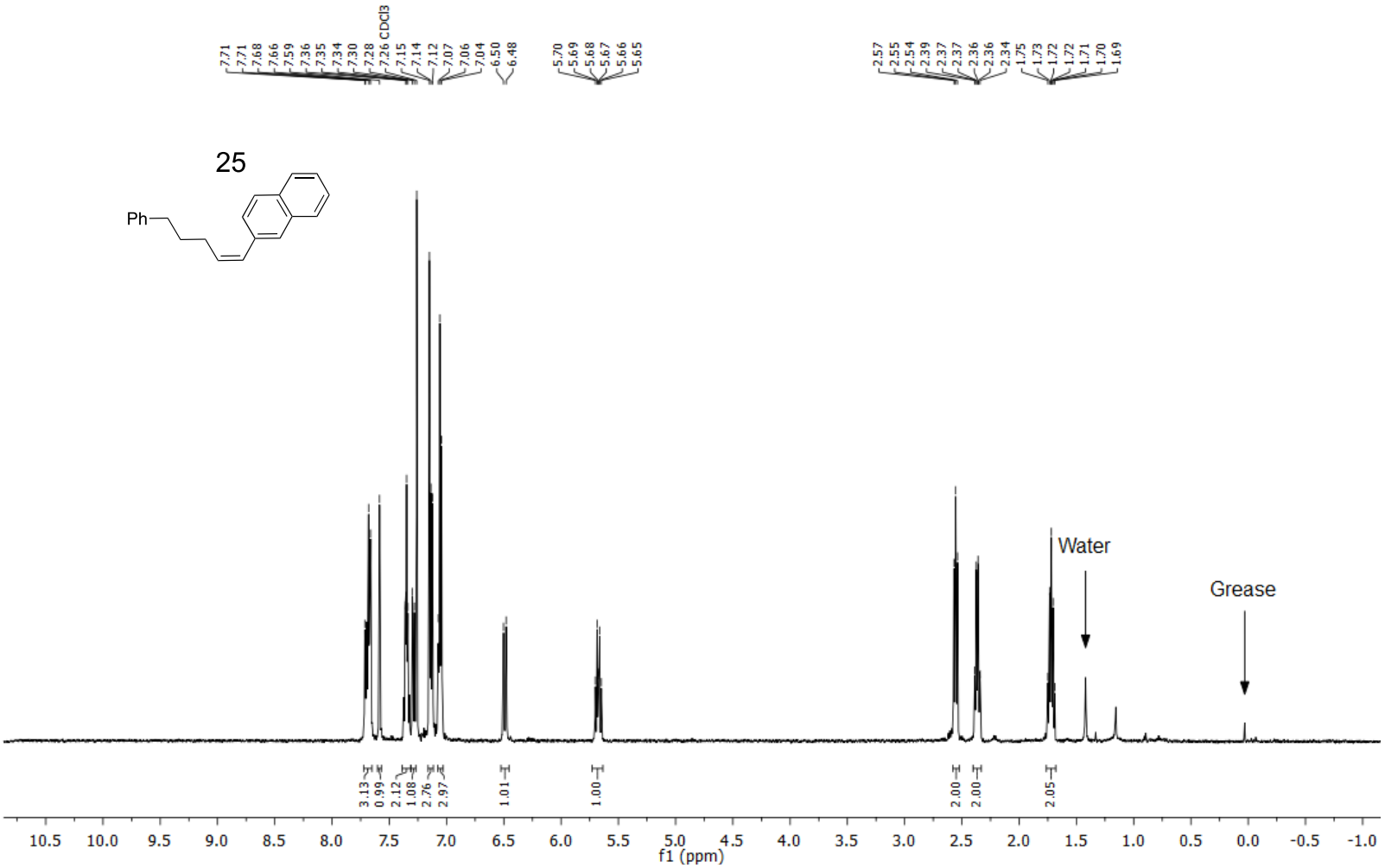
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.3 , 138.7 , 136.2 , 133.1 , 129.0 , 128.8 , 128.5 , 128.4 , 126.3 , 125.8 , 103.8 , 65.4 , 35.6 , 31.7 , 28.2 .



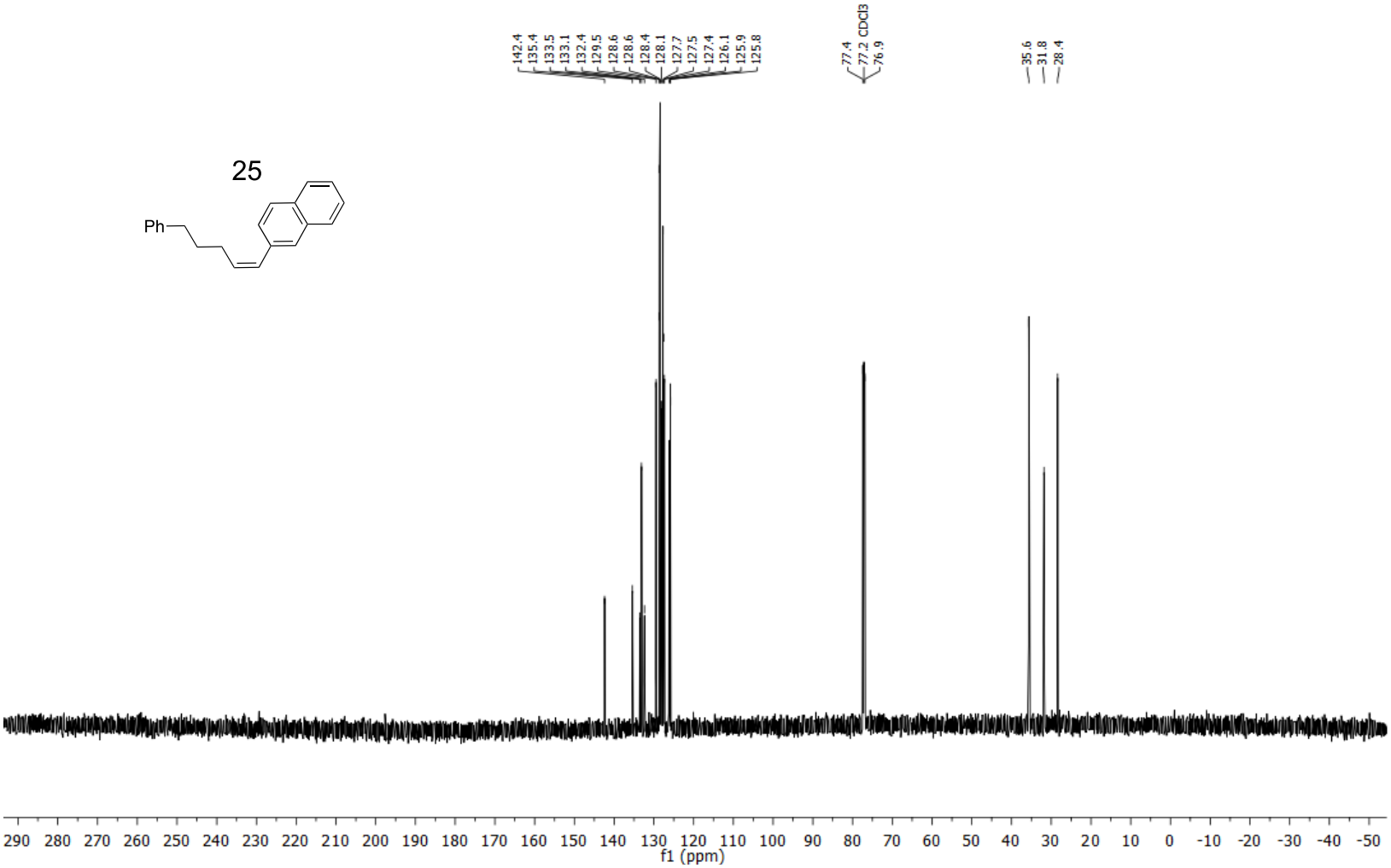


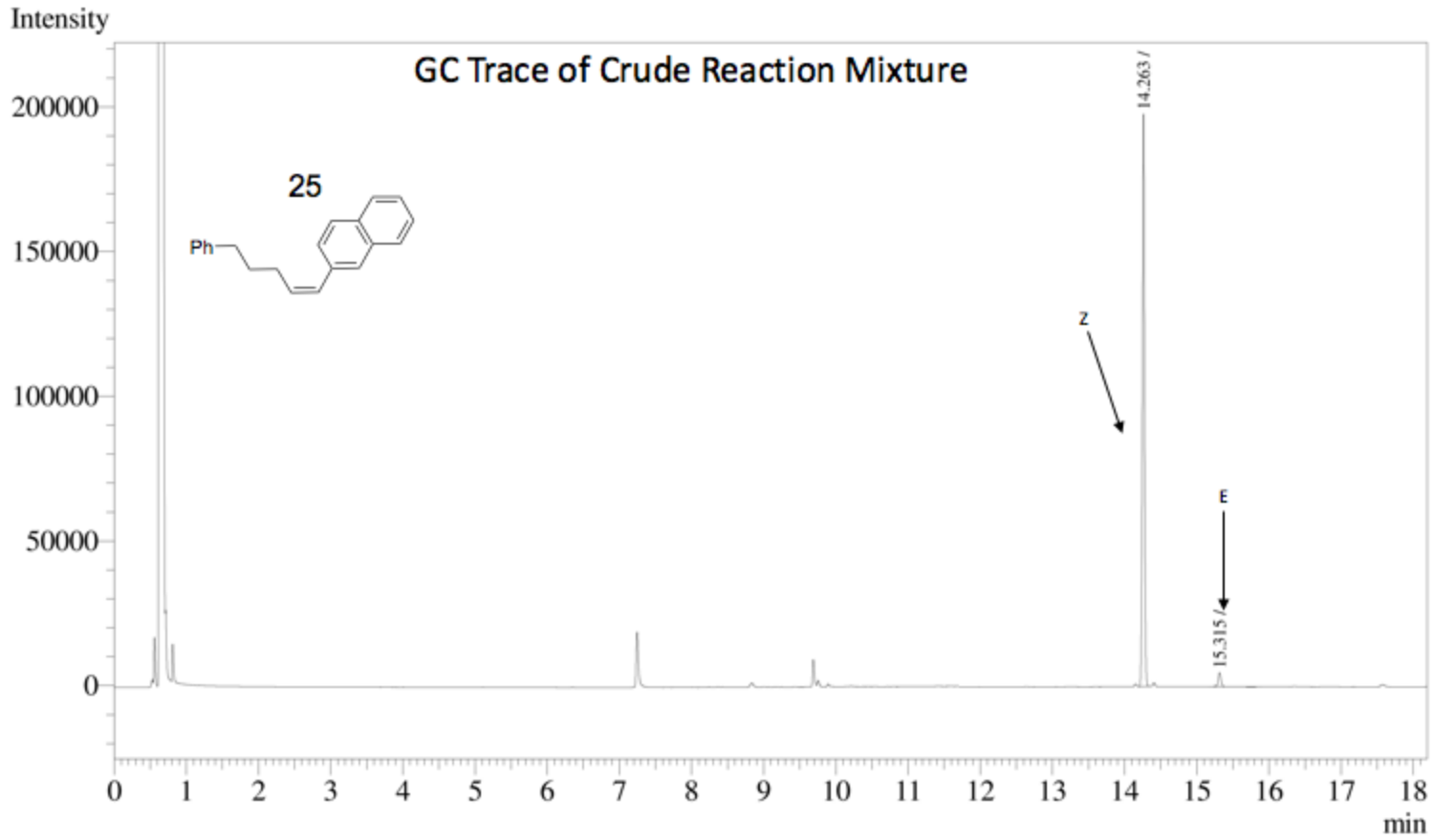
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.492	135555	67026	94.745				
2	15.511	7519	2215	5.255				
Total		143074	69241					

^{1}H 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* = 7.5 Hz, 2H).



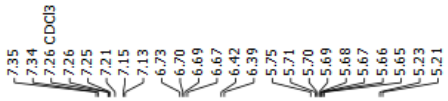
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4, 135.4 , 133.5 , 133.1 , 132.4 , 129.5 , 128.6 , 128.6 , 128.4 , 127.7 , 127.7 , 127.5 , 127.4 , 126.1 , 125.9 , 125.8 , 35.6 , 31.8 , 28.4 .

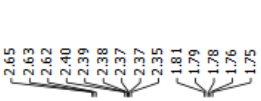




Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.263	392696	194775	96.816				
2	15.315	13540	4892	3.338				
Total		405611	199667					

^{1}H 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 (p, *J* = 7.6 Hz, 2H).





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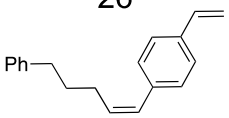
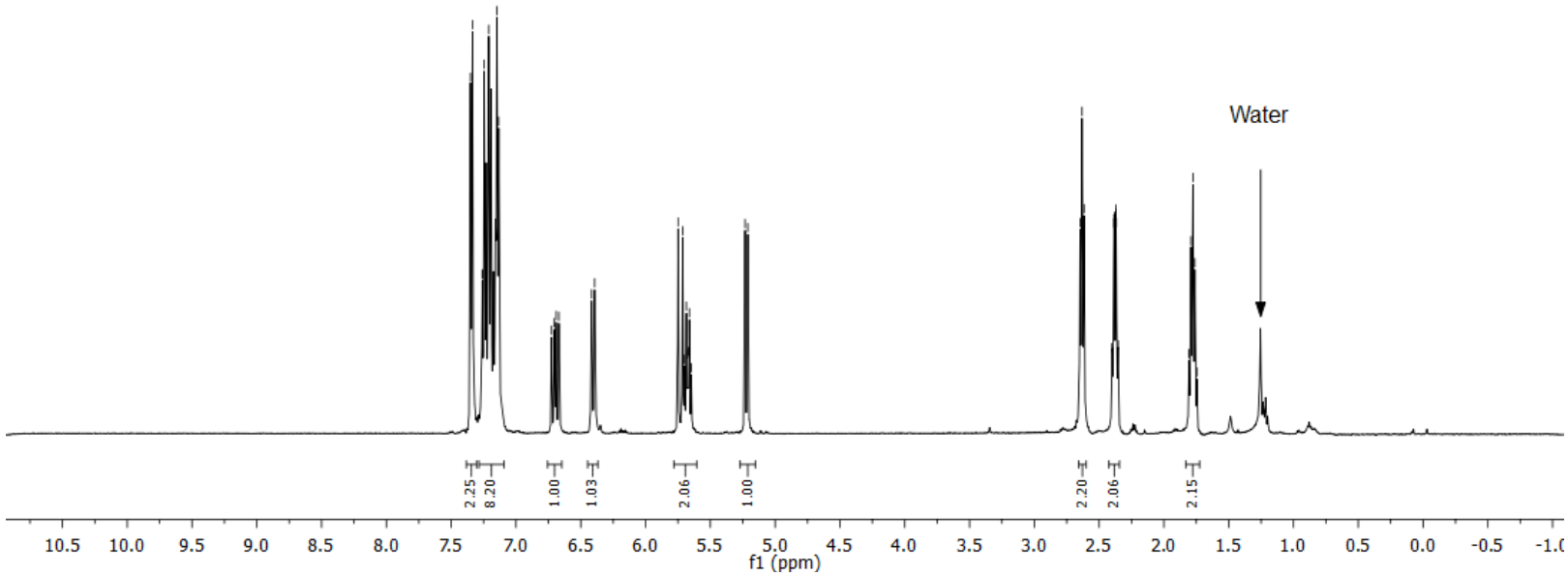
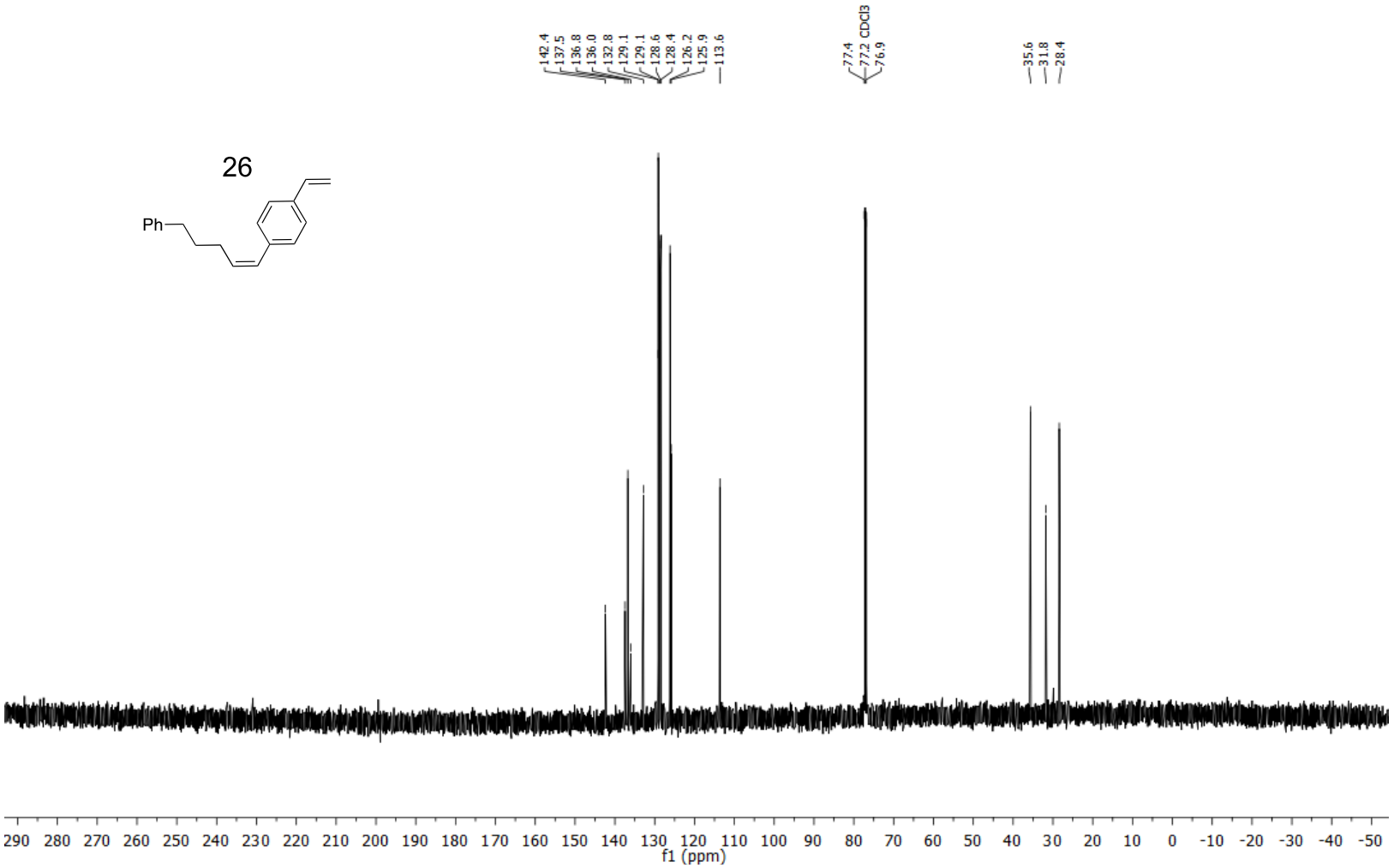
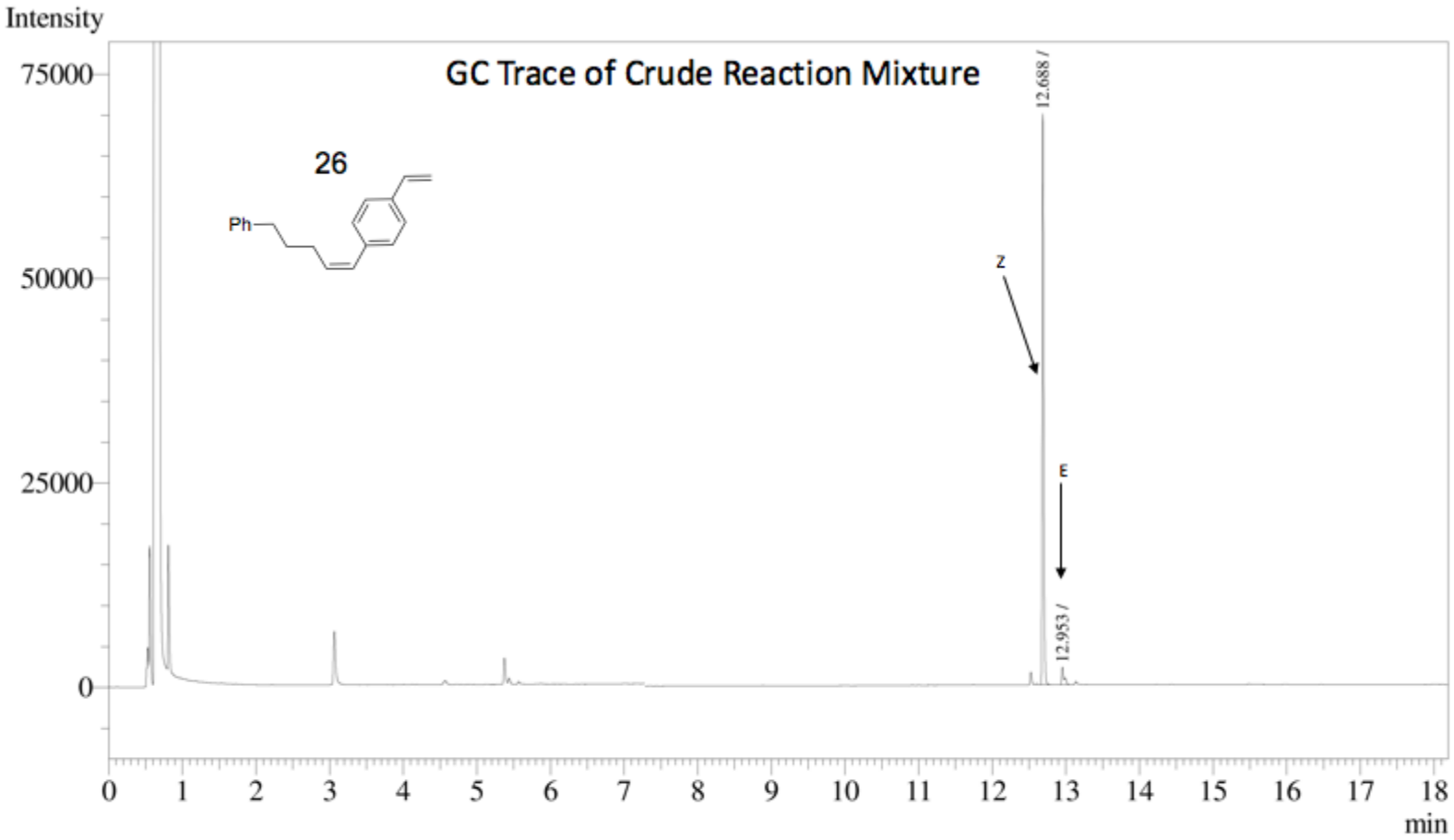




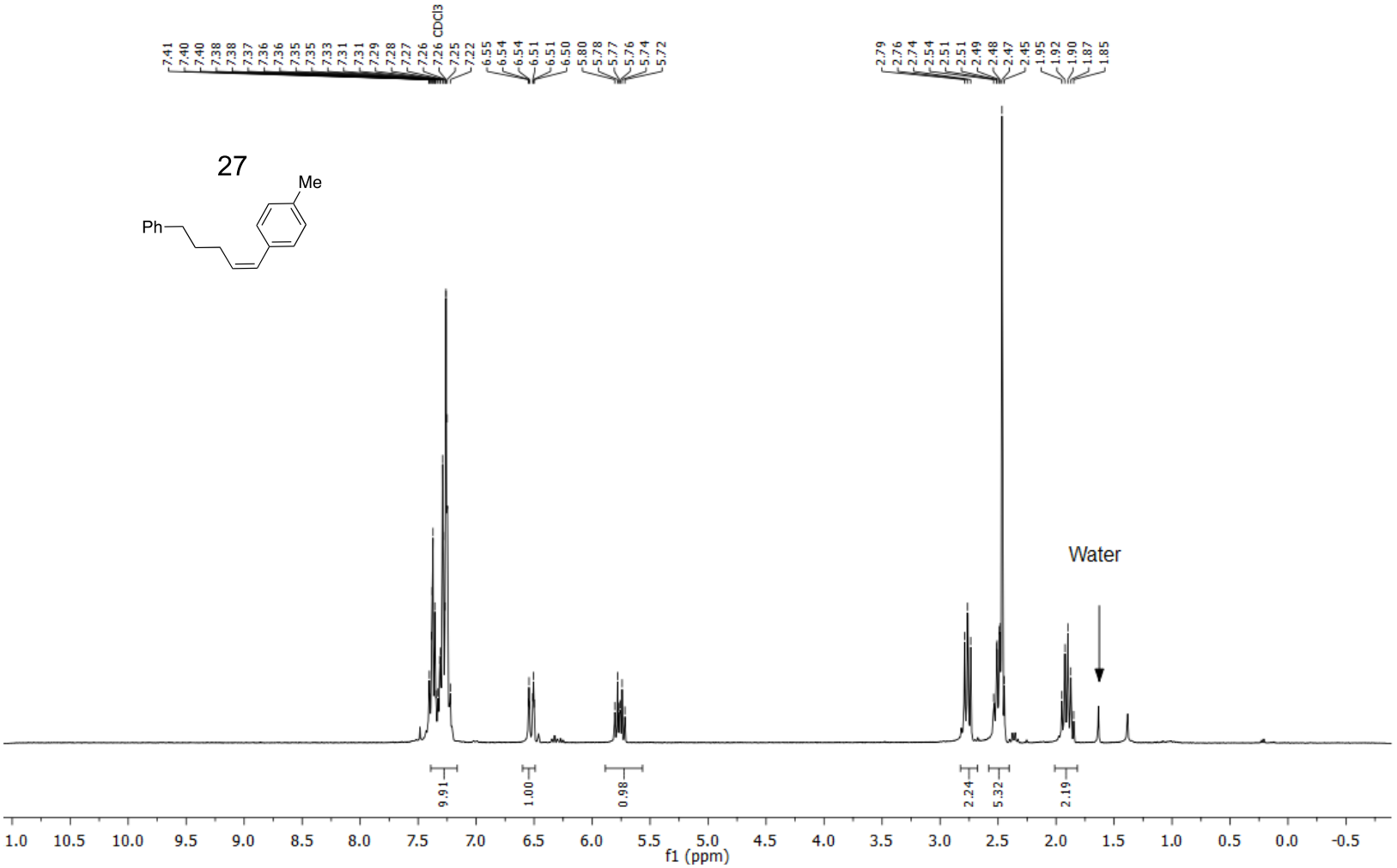
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4 , 137.5 , 136.8 , 136. , 132.8 , 129.1 , 129.1 , 128.6 , 128.4 , 126.2 , 125.9 , 113.6 , 35.6 , 31.8 , 28.4 .



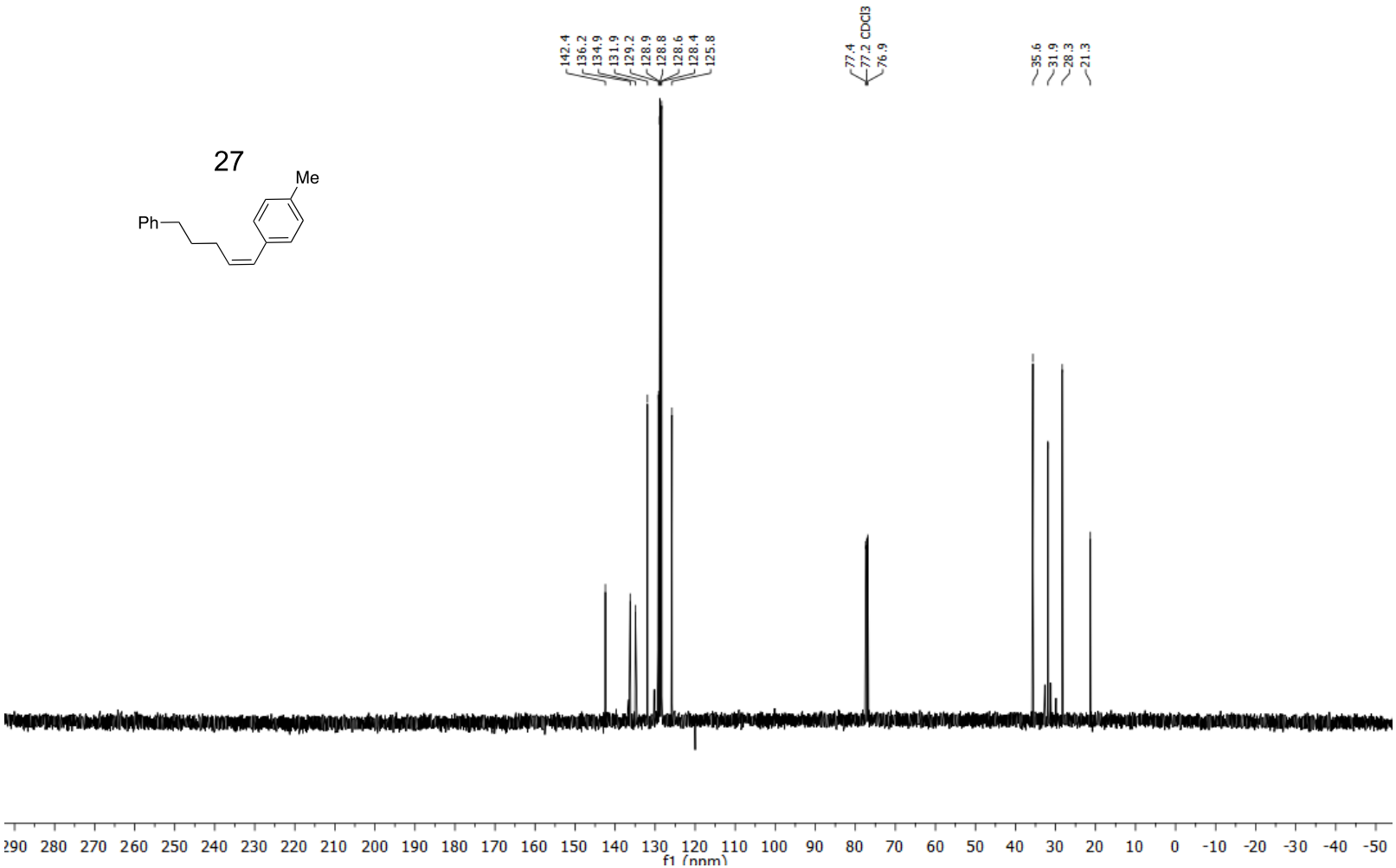


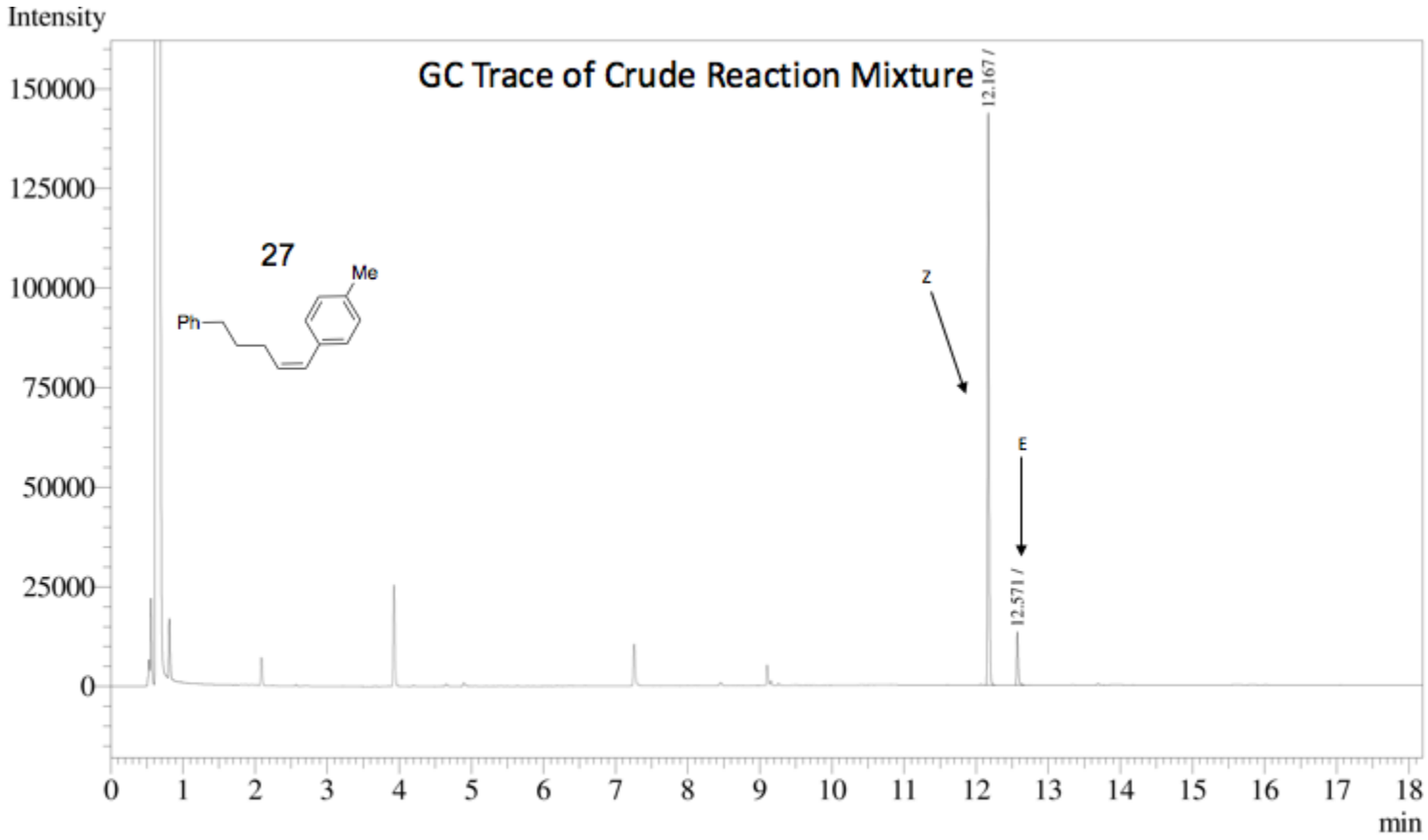
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.688	94745	68679	95.338				
2	12.953	4633	2130	4.662				
Total		99378	70809					

^{1}H 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, 5H), 1.90 (p, *J* = 7.7 Hz, 2H).



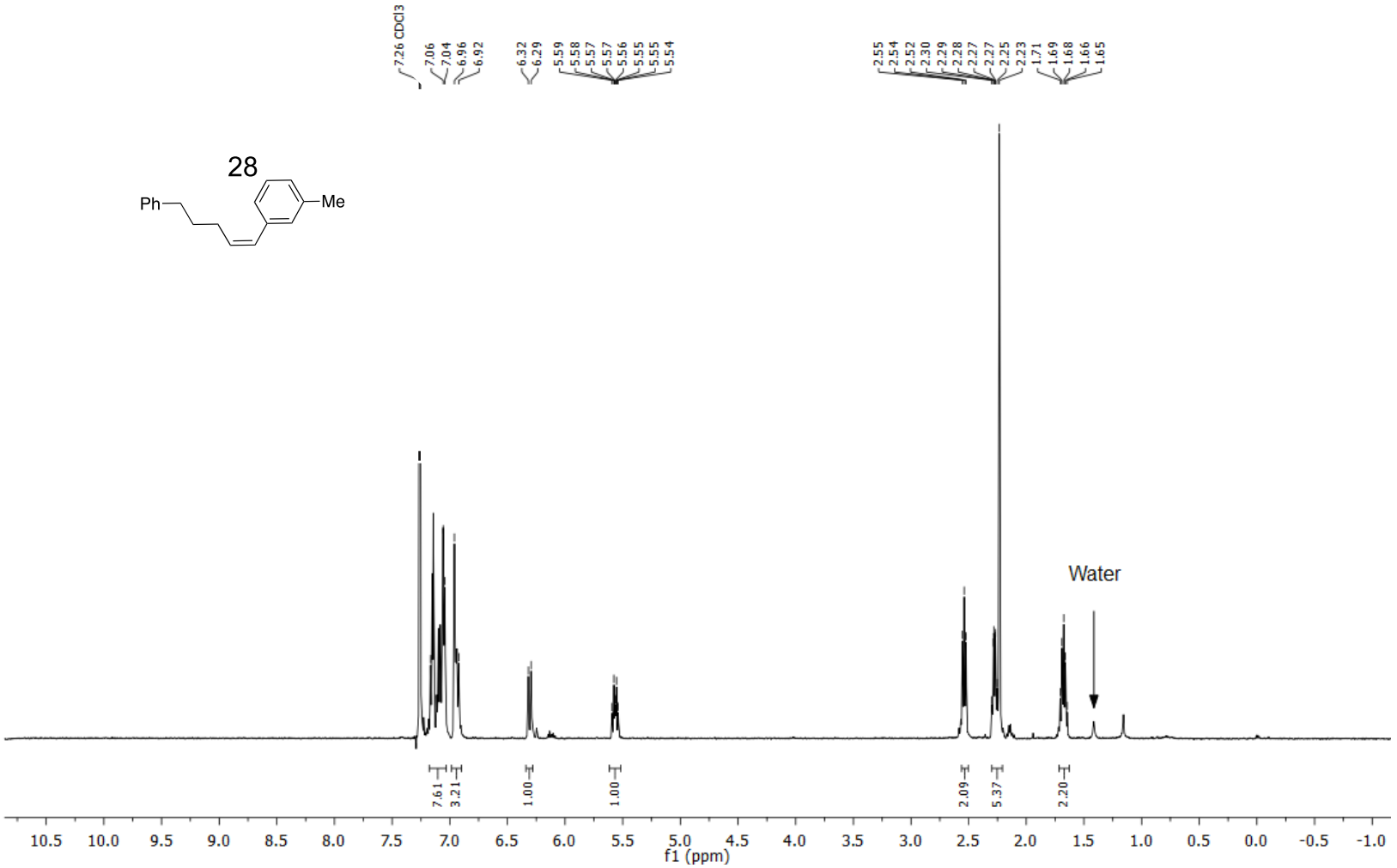
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4 , 136.2 , 134.9 , 131.9 , 129.2 , 128.8 , 128.6 , 128.4 , 128.4 , 125.8 , 35.6 , 31.9 , 28.3 , 21.3 .



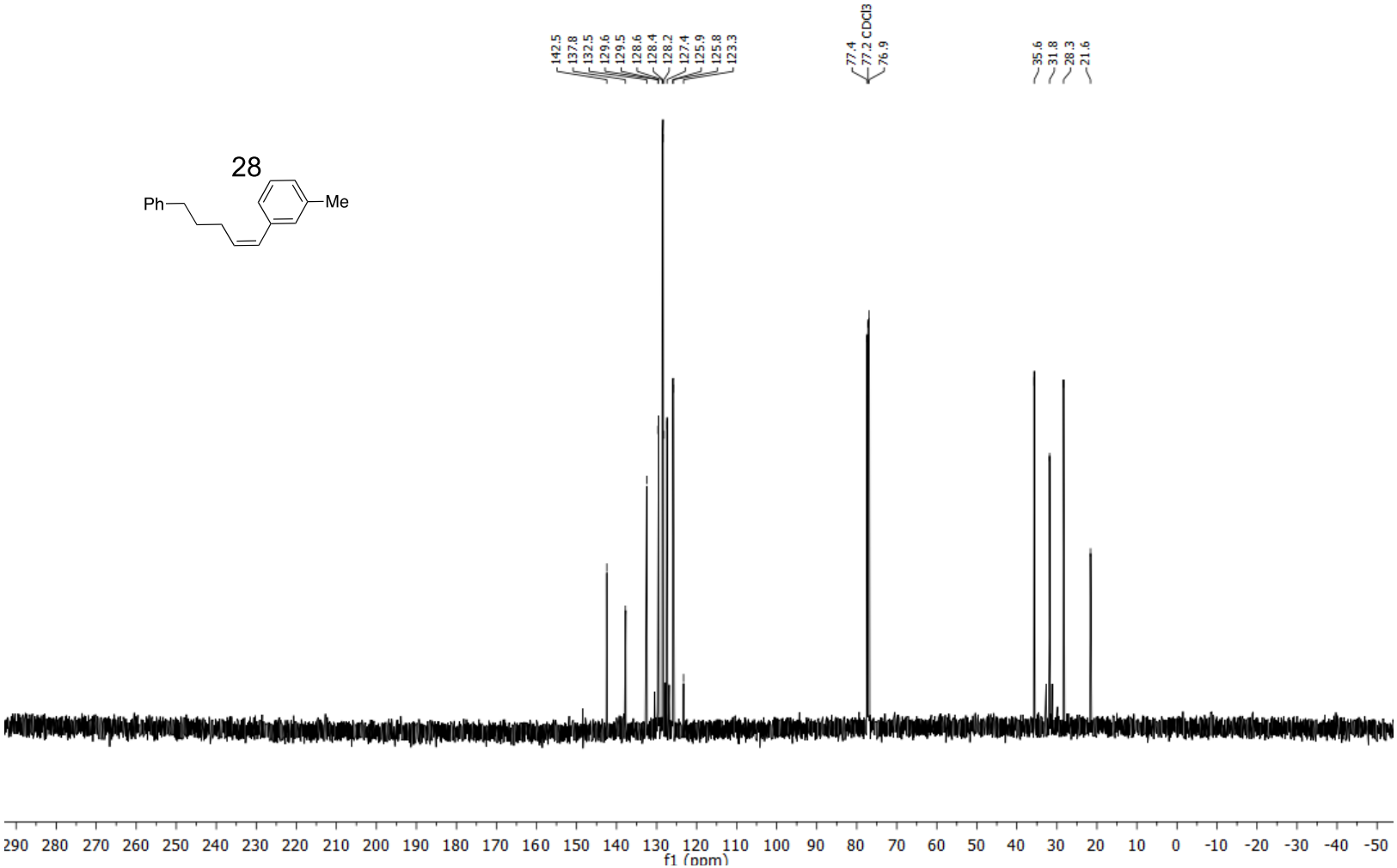


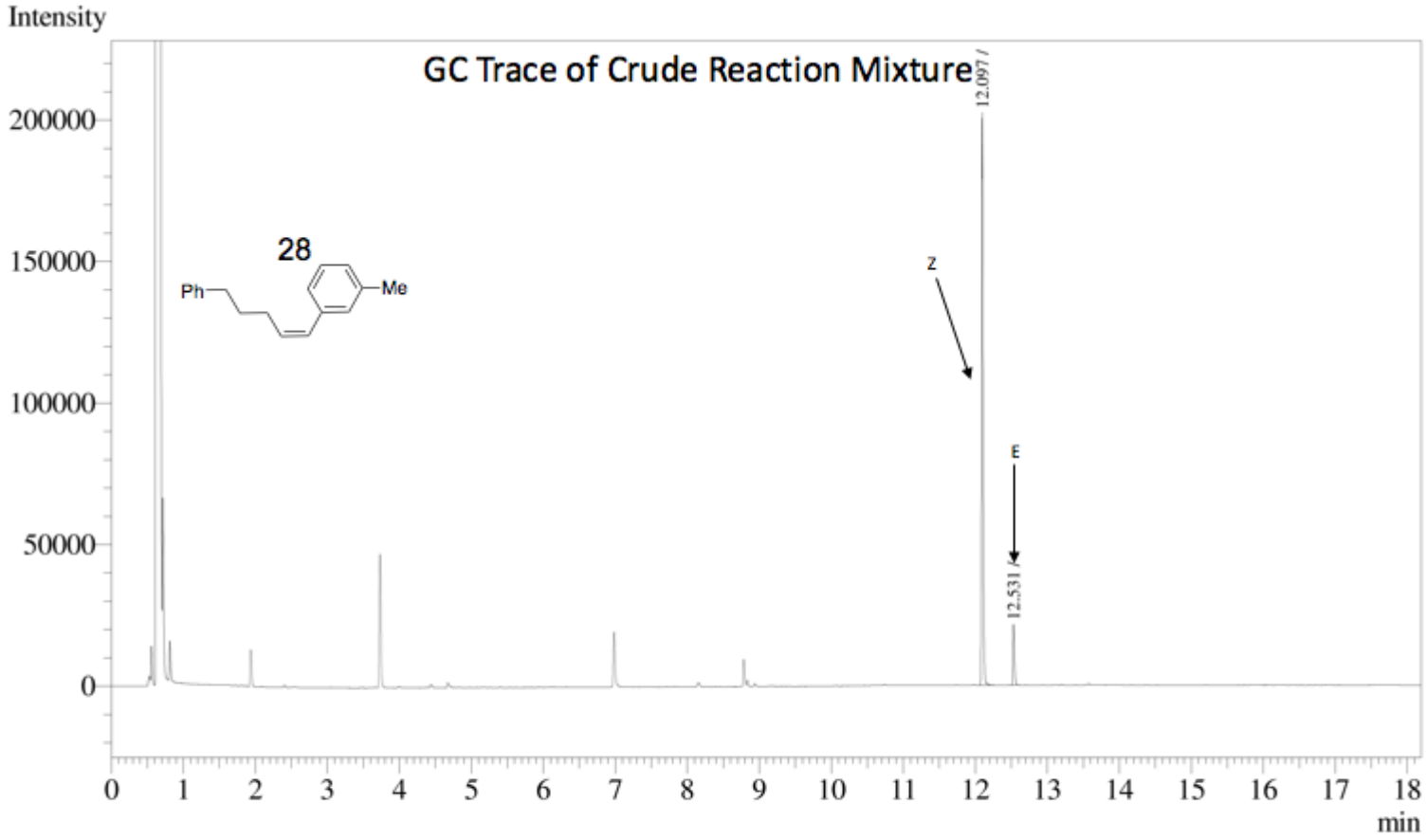
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.167	197658	137034	90.852				
2	12.571	19903	13258	9.148				
Total		217561	150292					

^{1}H 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).



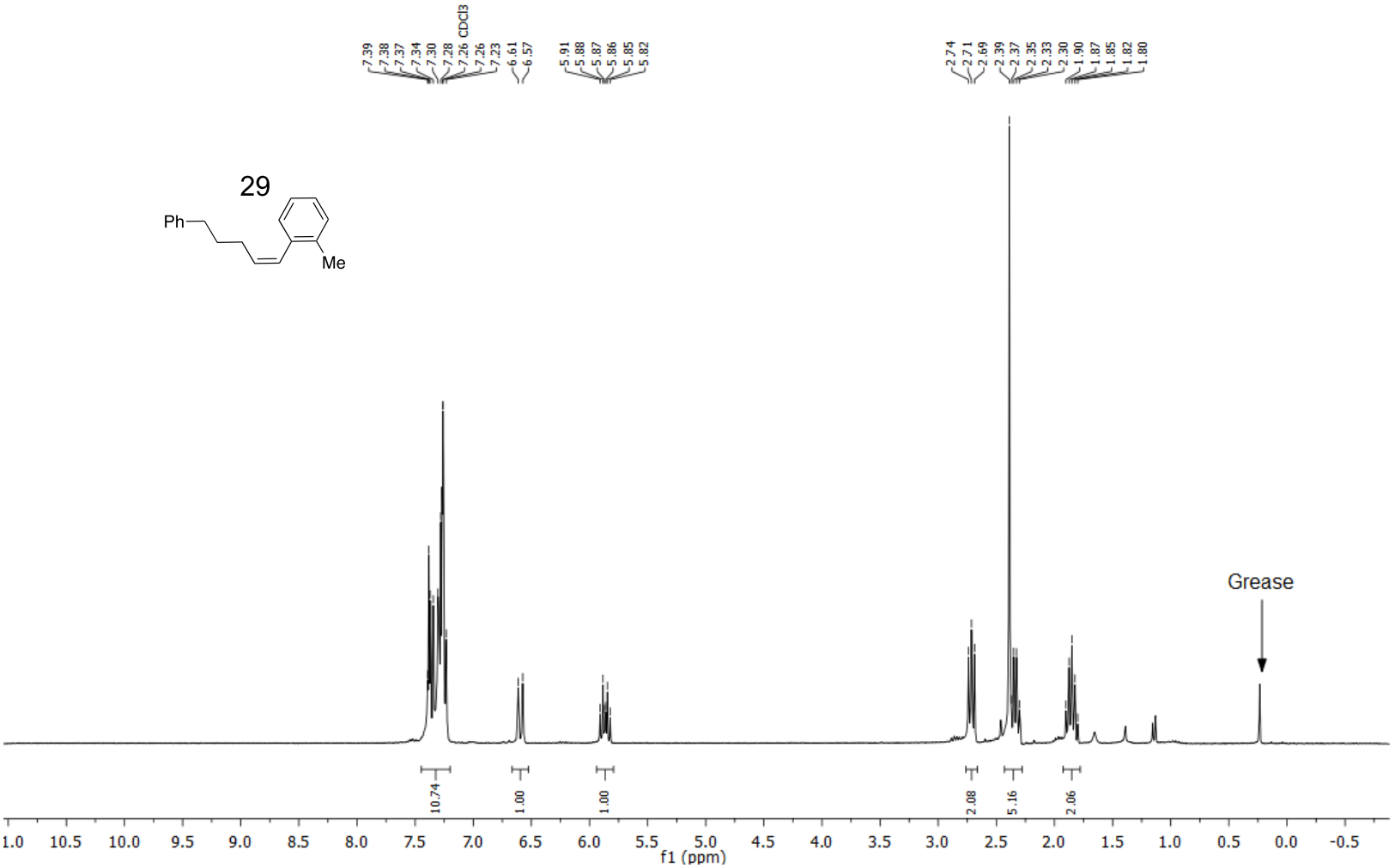
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.5 , 137.8 132.5 , 129.6 , 129.5 , 128.6 , 128.4 , 128.2 , 127.4 , 125.9 , 125.8 , 123.3 , 35.6 , 31.8 , 28.3 , 21.6 .



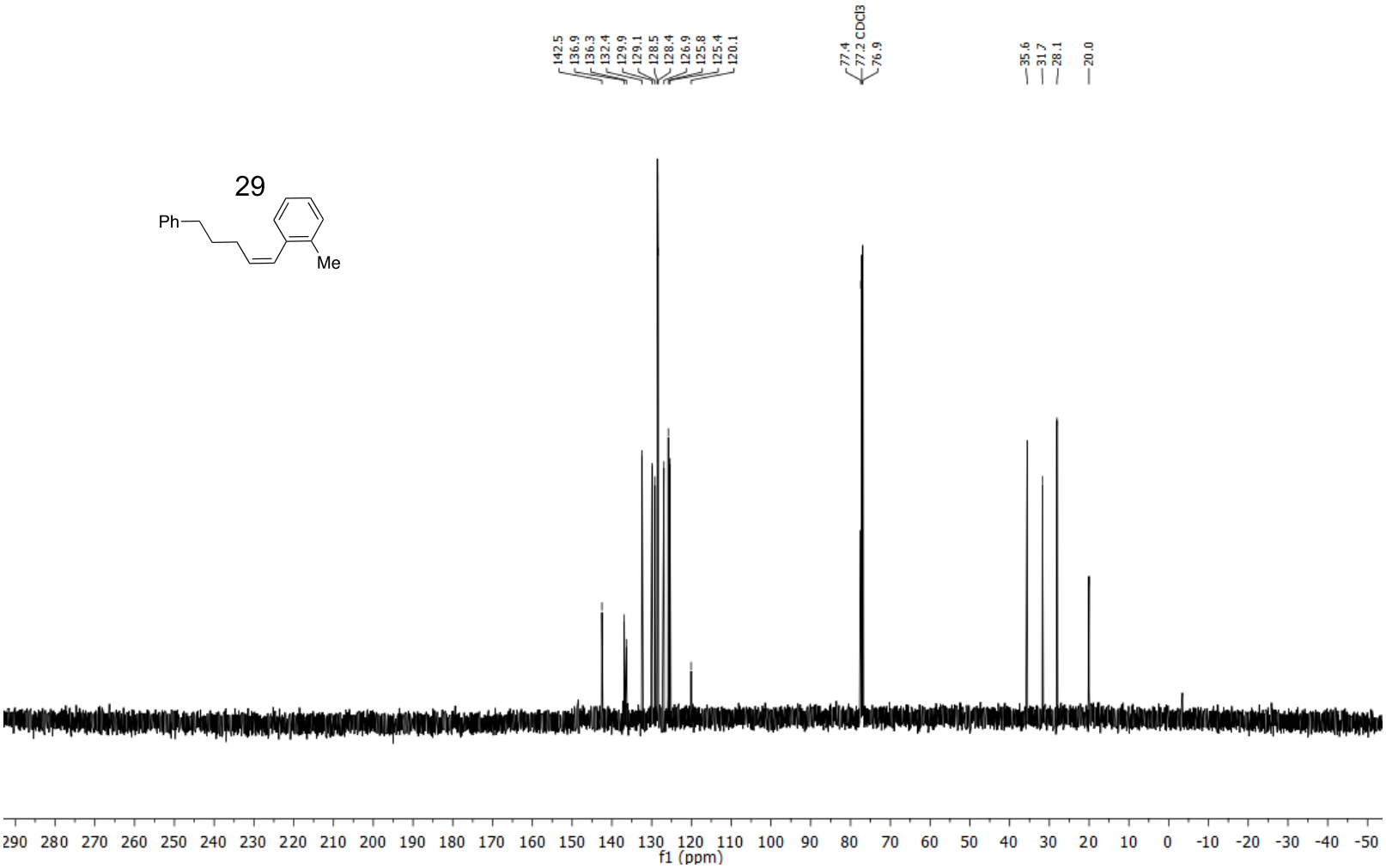


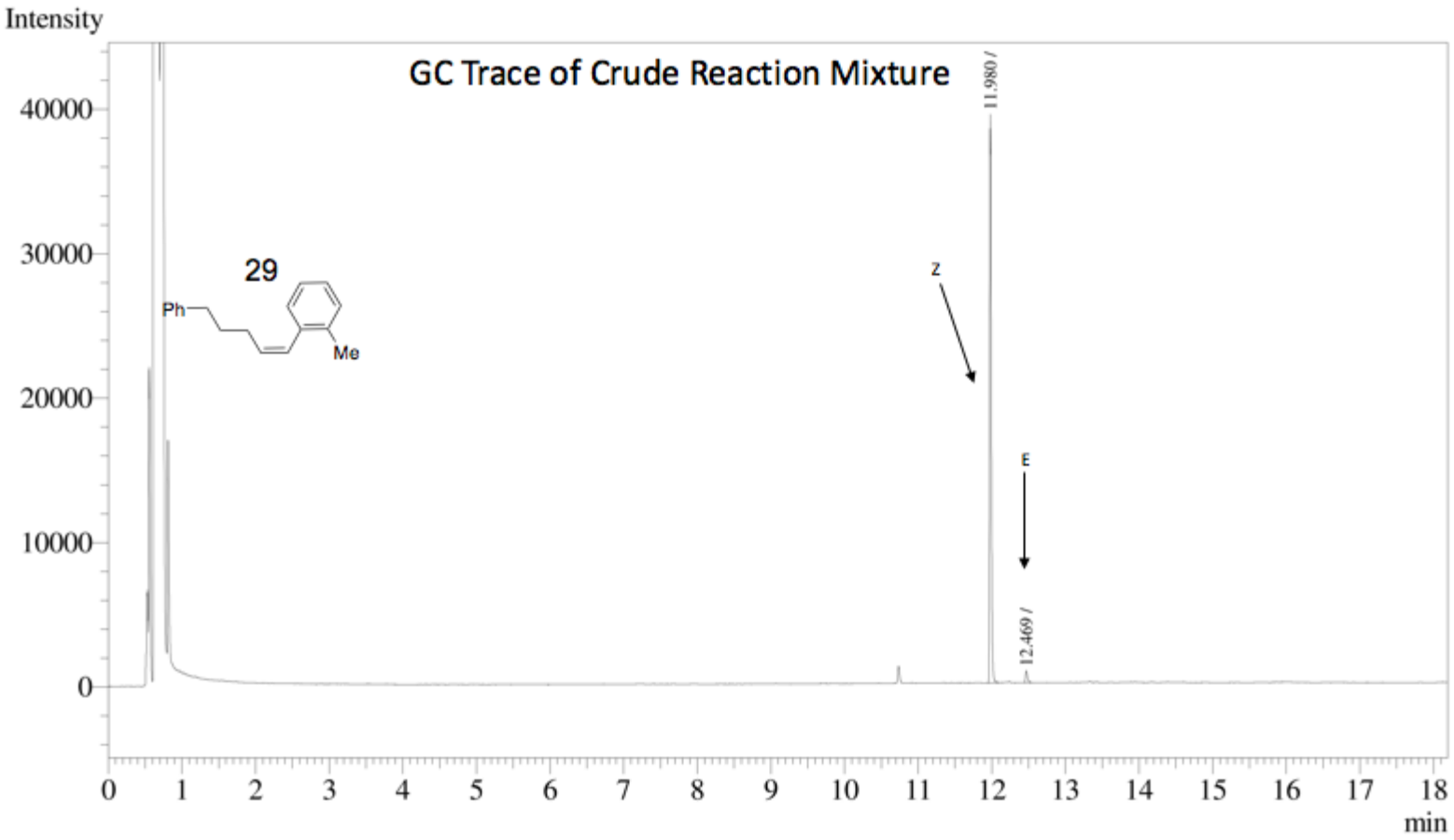
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.097	272632	193192	90.014				
2	12.531	27423	20515	9.054				
Total		302877	213707					

^{1}H 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).



^{13}C 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 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.980	56467	37859	97.237				
2	12.469	1605	829	2.763				
Total		58072	38688					

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 (m, 4H), 7.21 – 6.90 (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* = 7.6Hz, 2H), 2.27 – 2.15 (m, 2H), 1.69 (p, *J* = 7.6 Hz, 2H).

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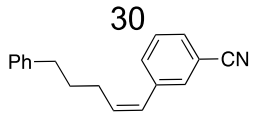
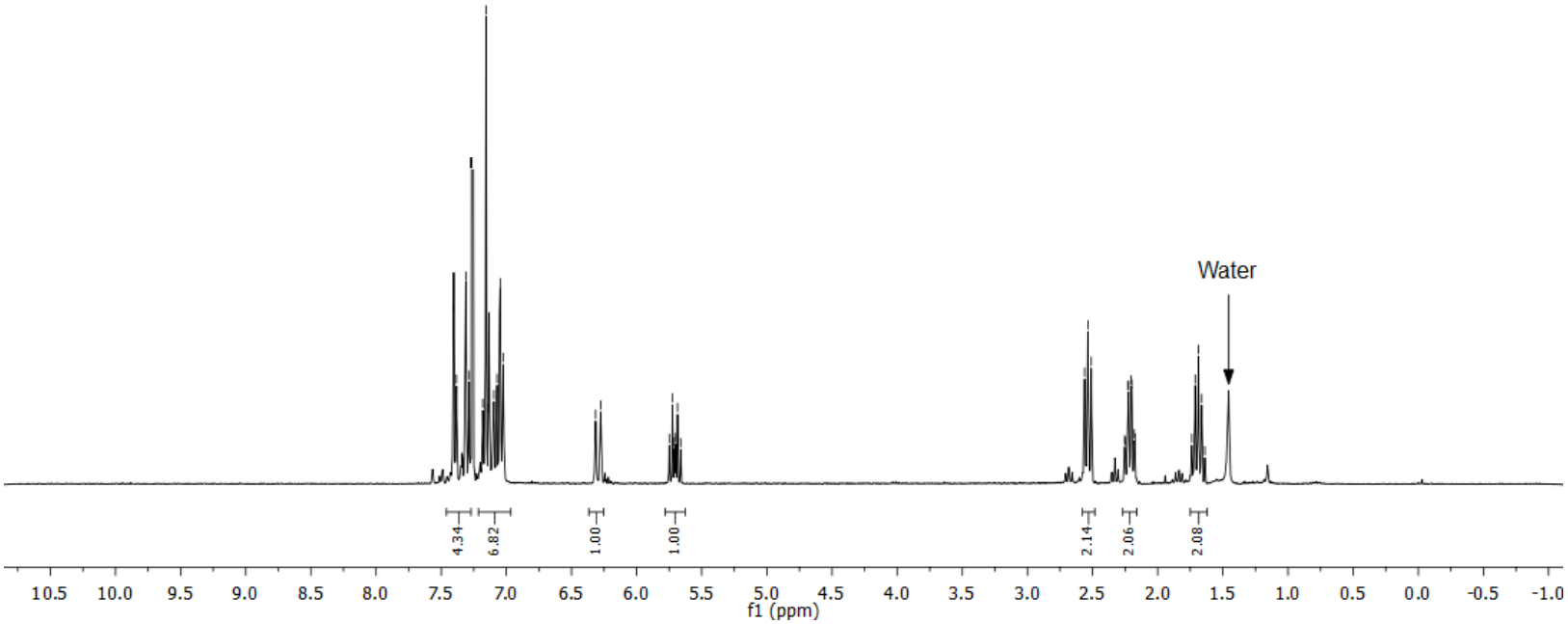
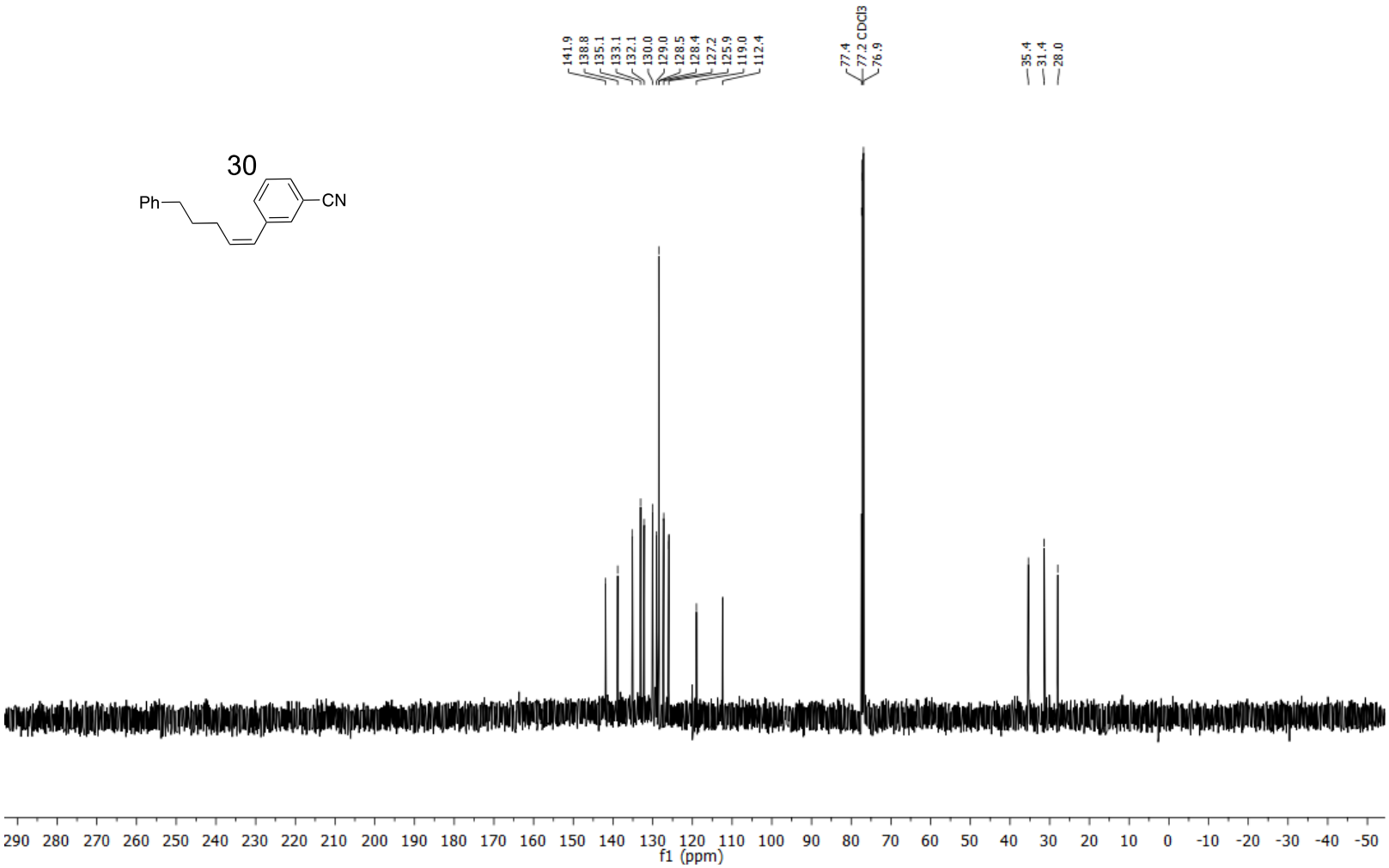
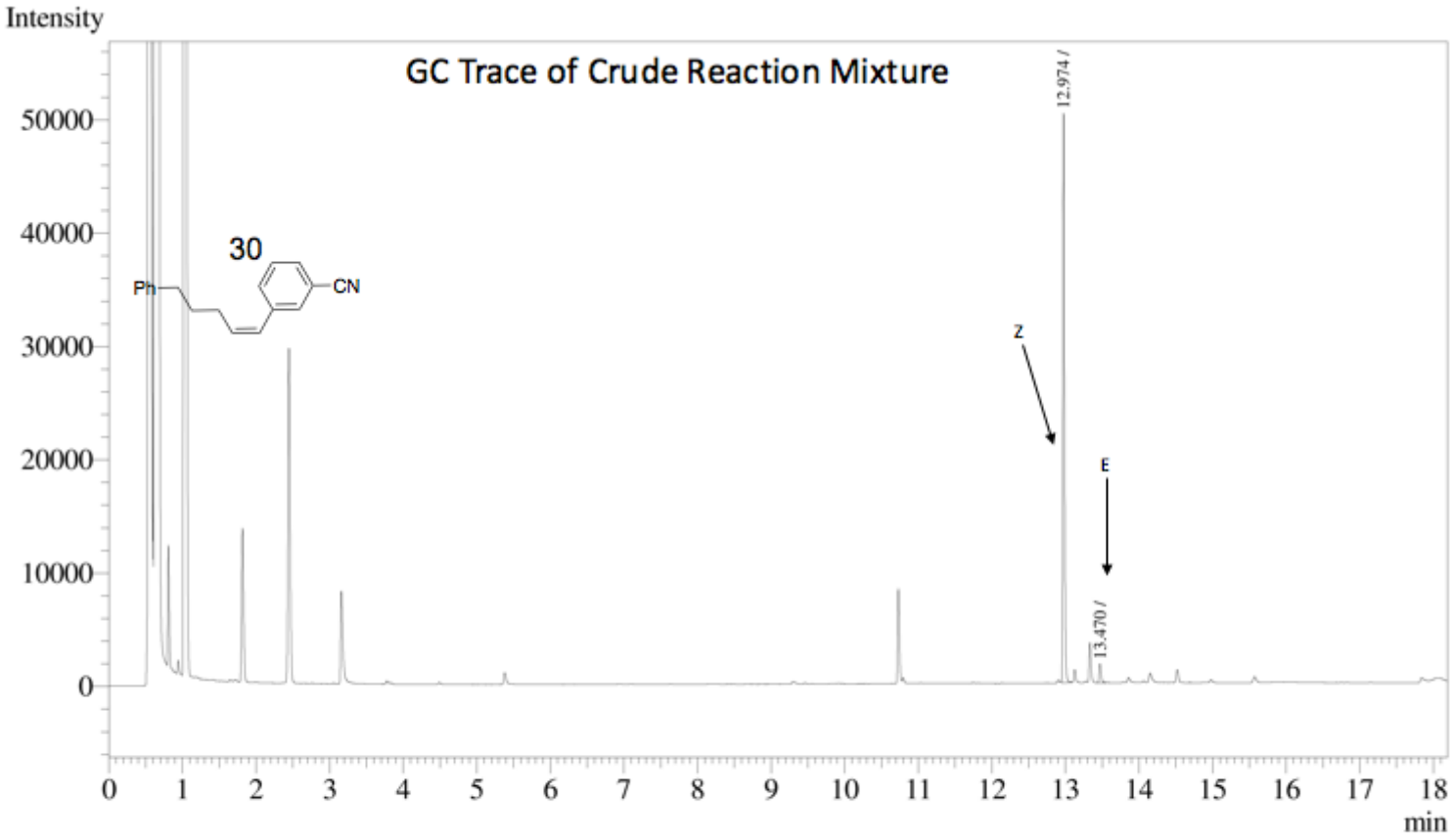




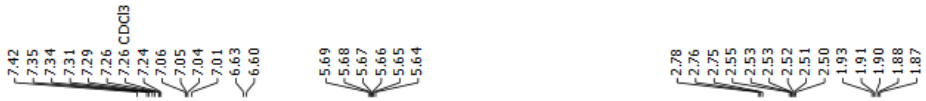
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.9 , 139.8 , 135.1 , 133.1 , 132.1 , 130.0 , 129.0 , 128.8 , 128.4 , 127.2 , 125.9 , 119.0 ,112.4 , 35.4 , 31.4 , 28.0 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.974	74317	47876	95.977		V		
2	13.470	3115	1660	4.023				
Total		77432	49536					

^{1}H 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).



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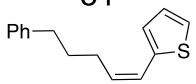
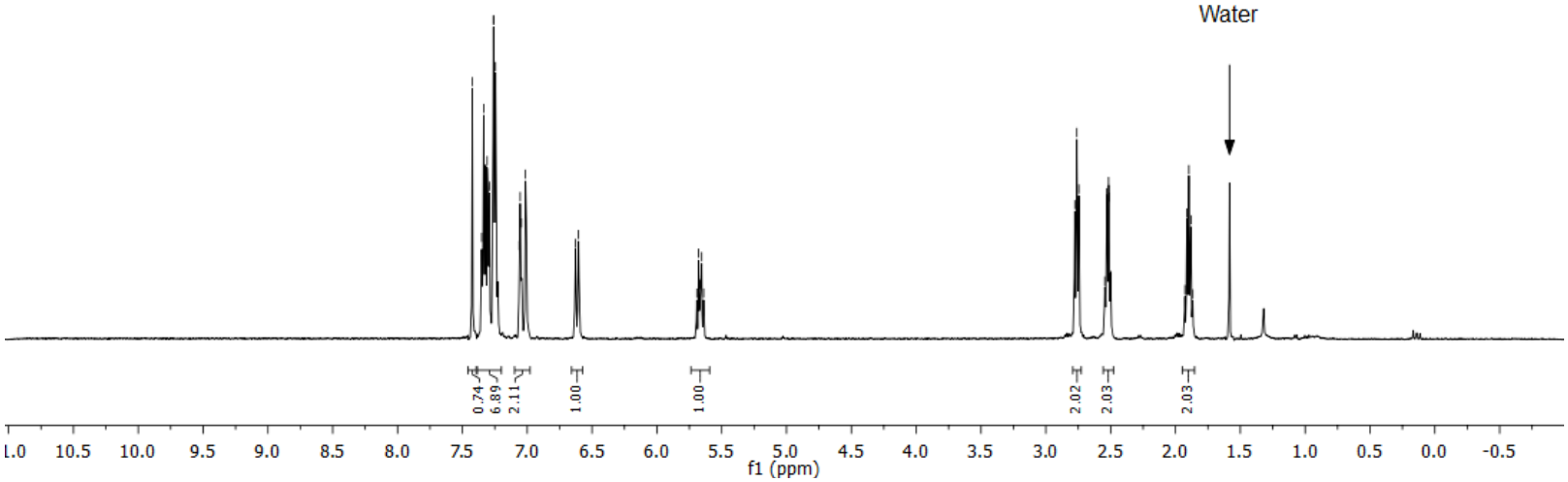
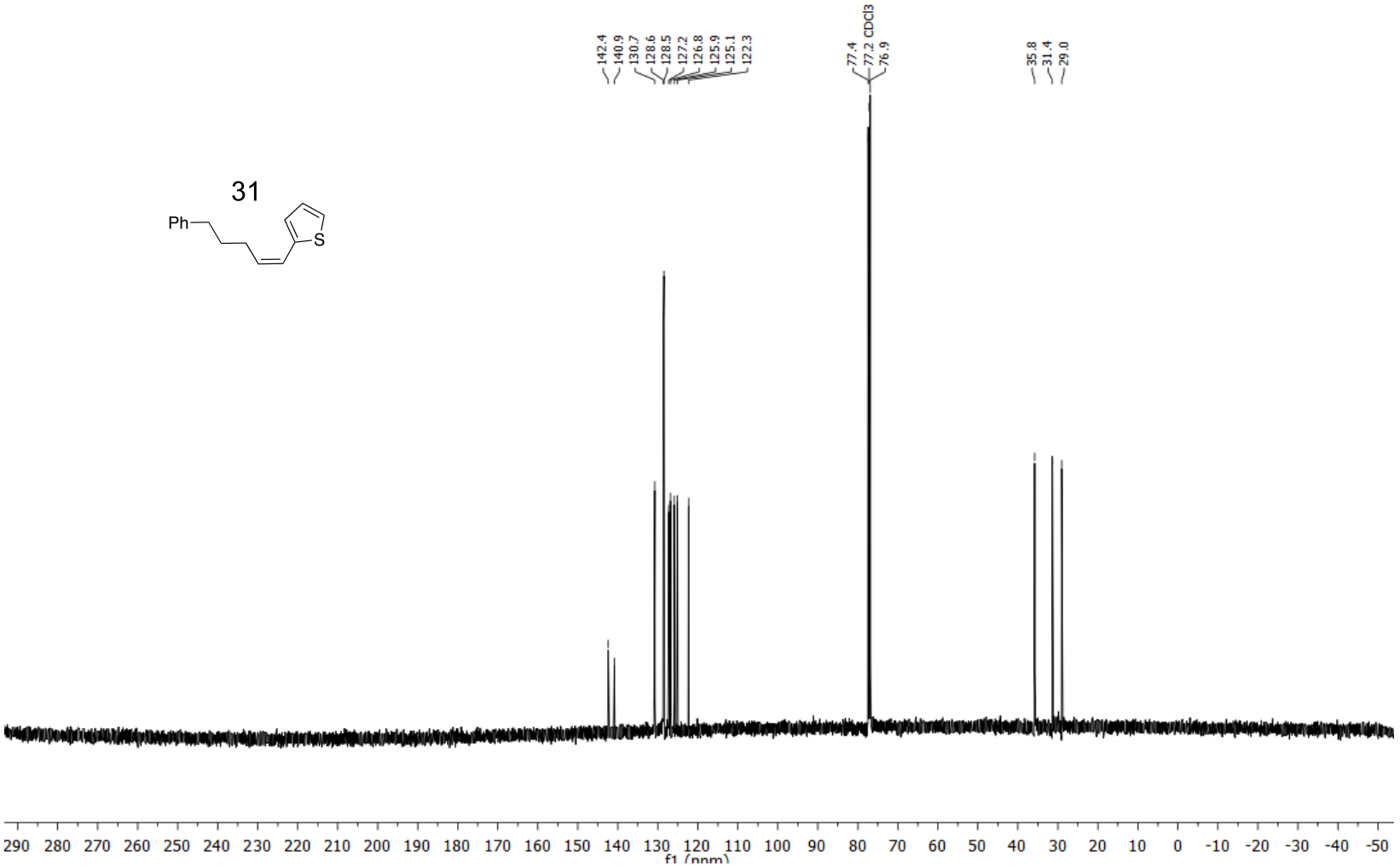
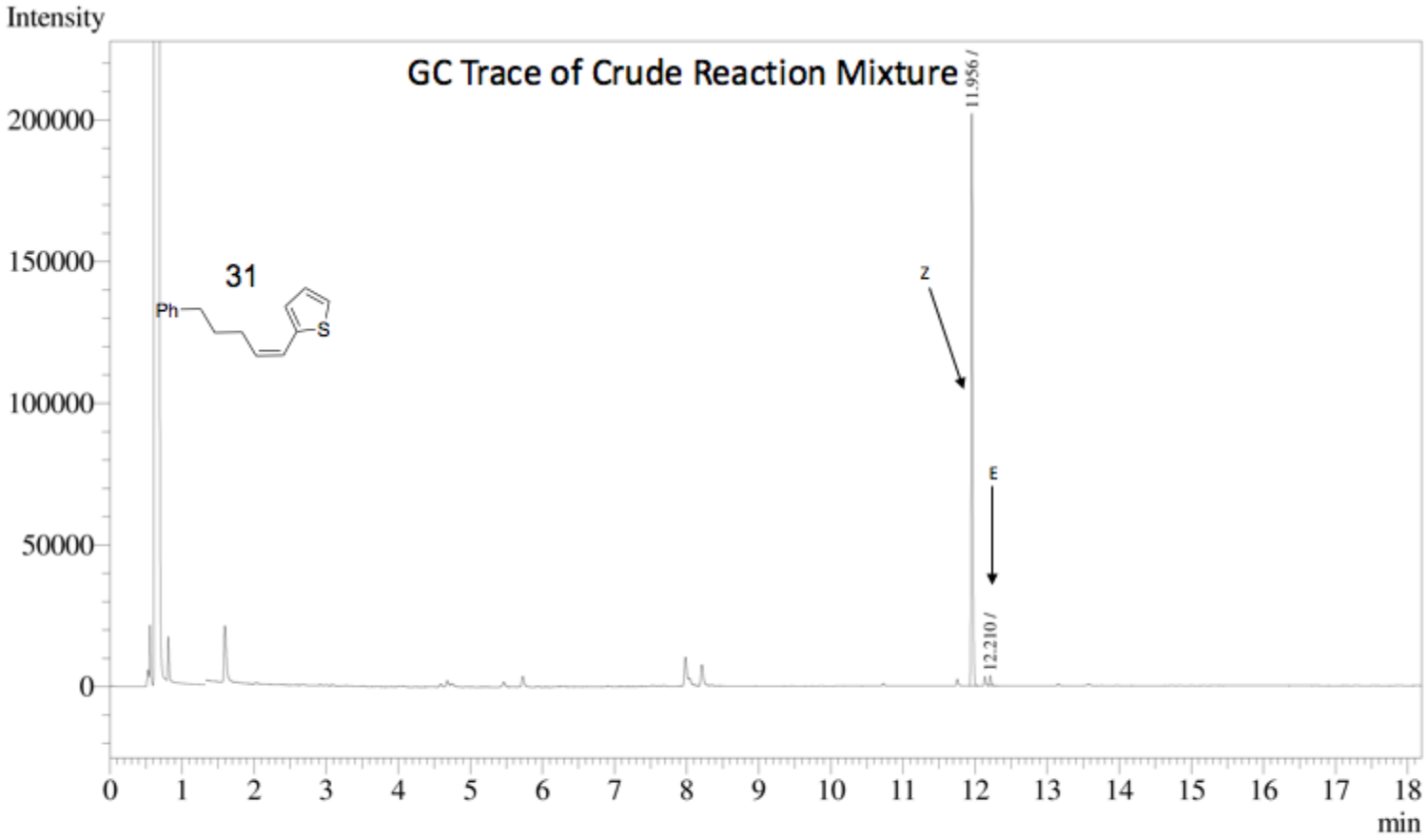




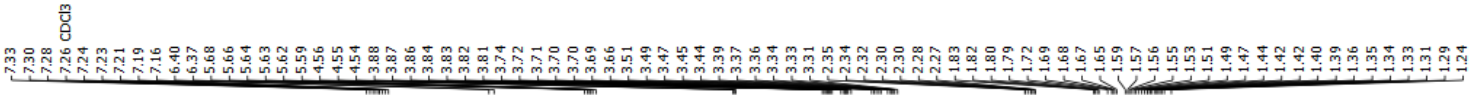
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4 , 140.9 , 130.7 , 128.6 , 128.5 , 127.2 , 126.8 , 125.9 , 125.1 , 122.3 , 35.8 , 31.4 , 29.0 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.956	277470	195899	98.197		V		
2	12.210	5331	3456	1.887				
Total		282564	199355					

^{1}H 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).



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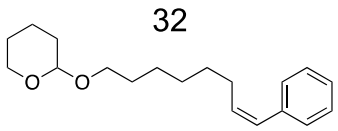
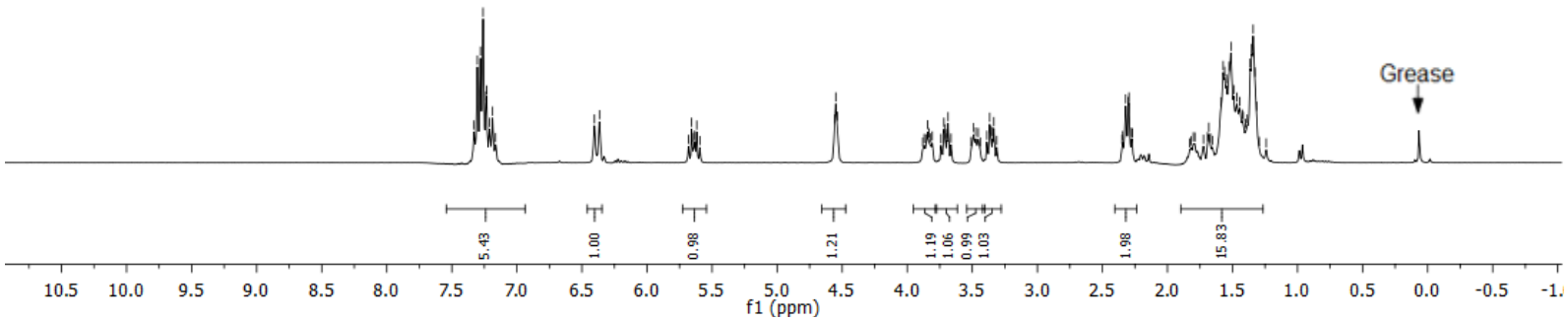
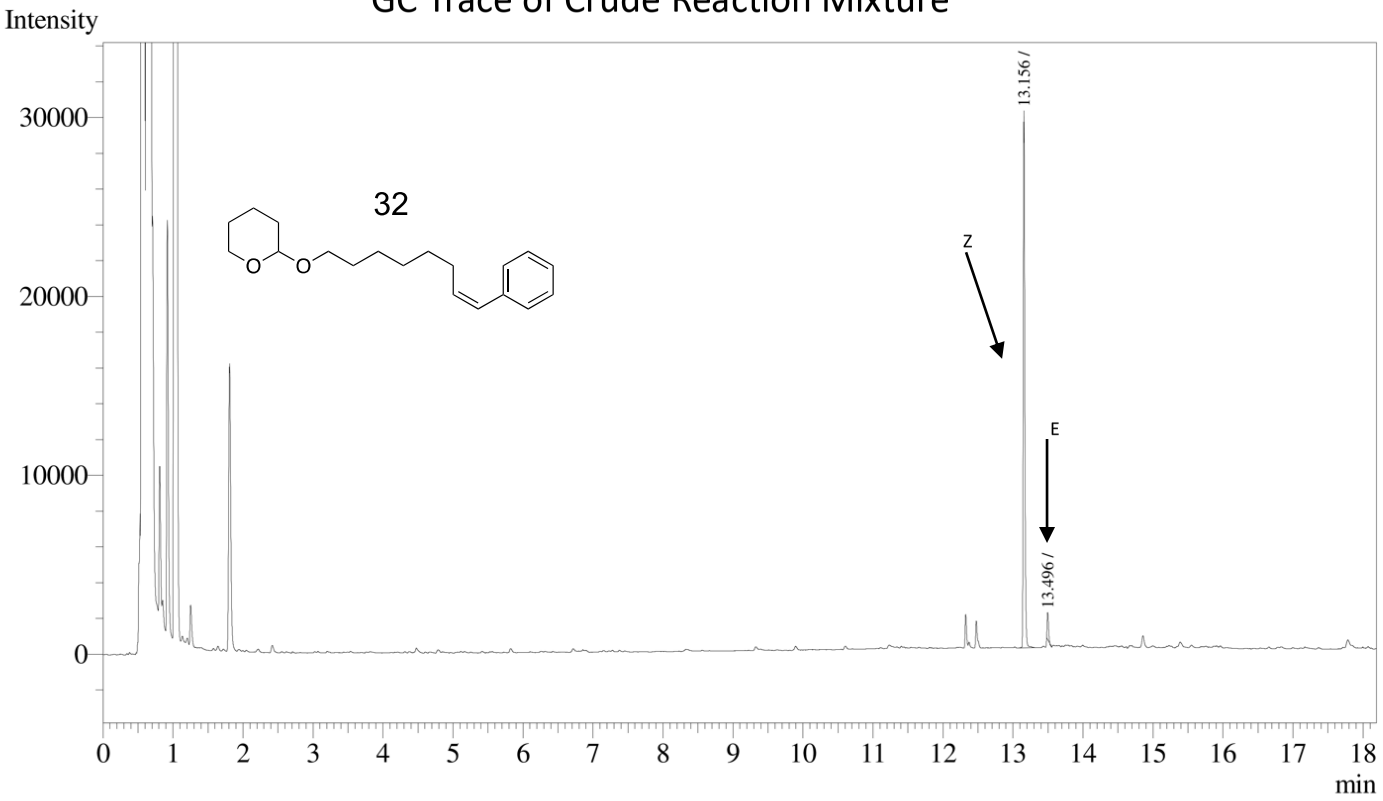


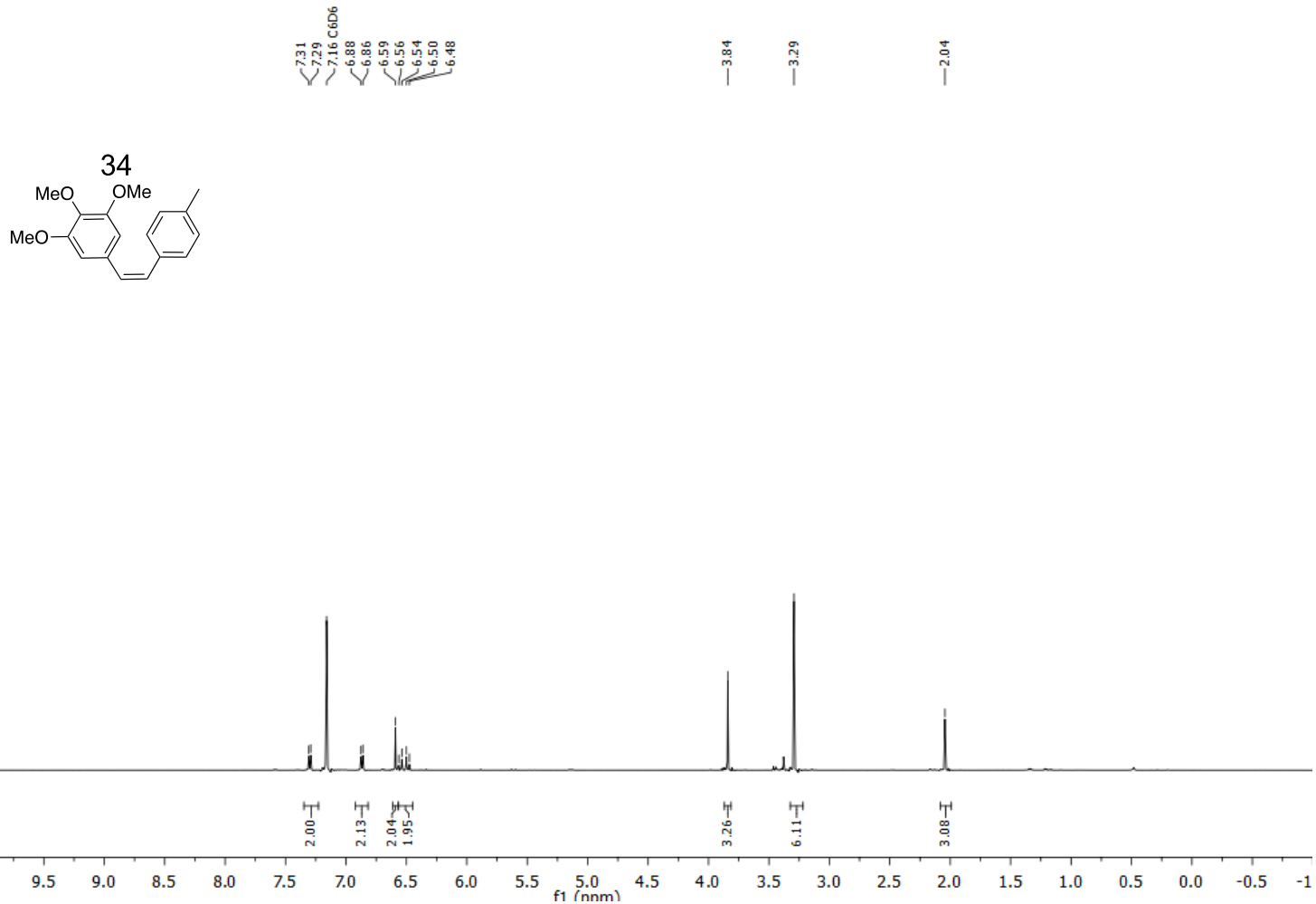


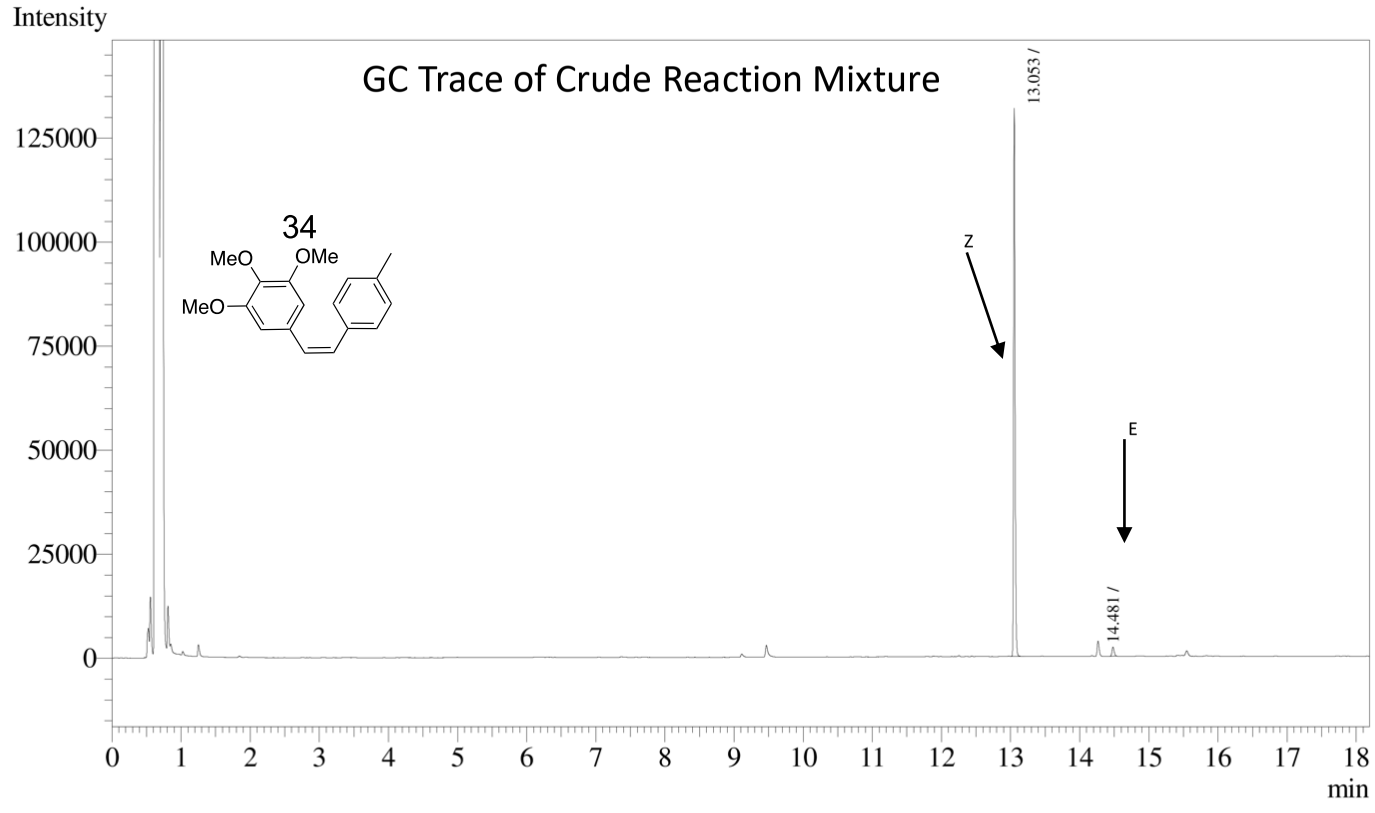
GC Trace of Crude Reaction Mixture



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

^{1}H NMR (500 MHz, Benzene-d_6) 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).

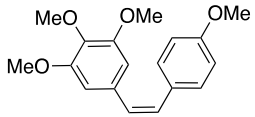


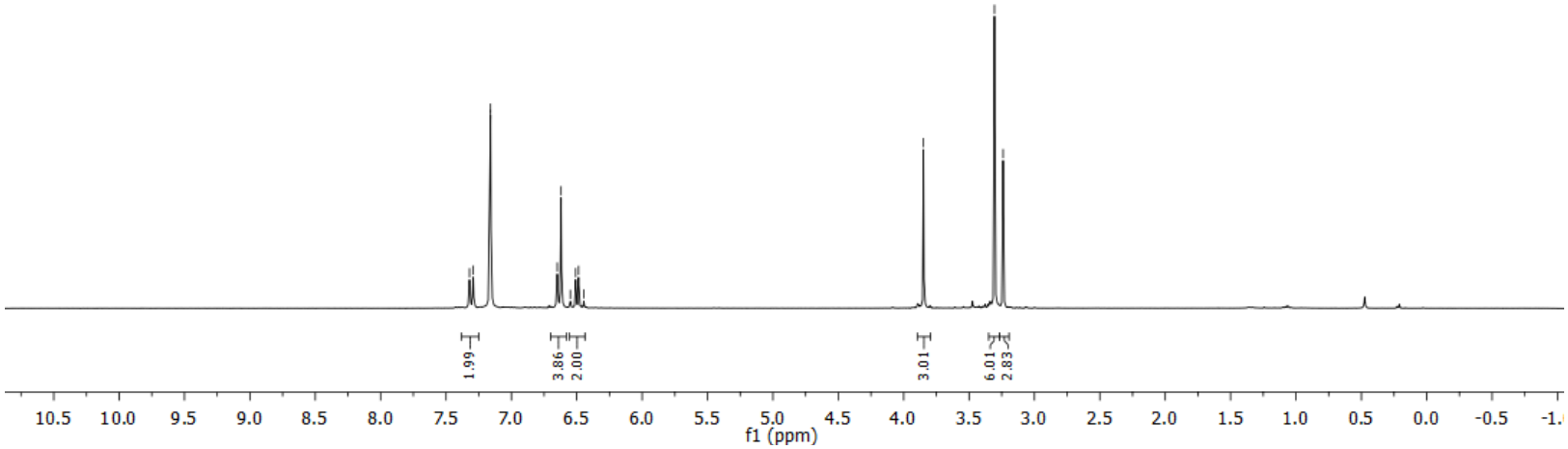


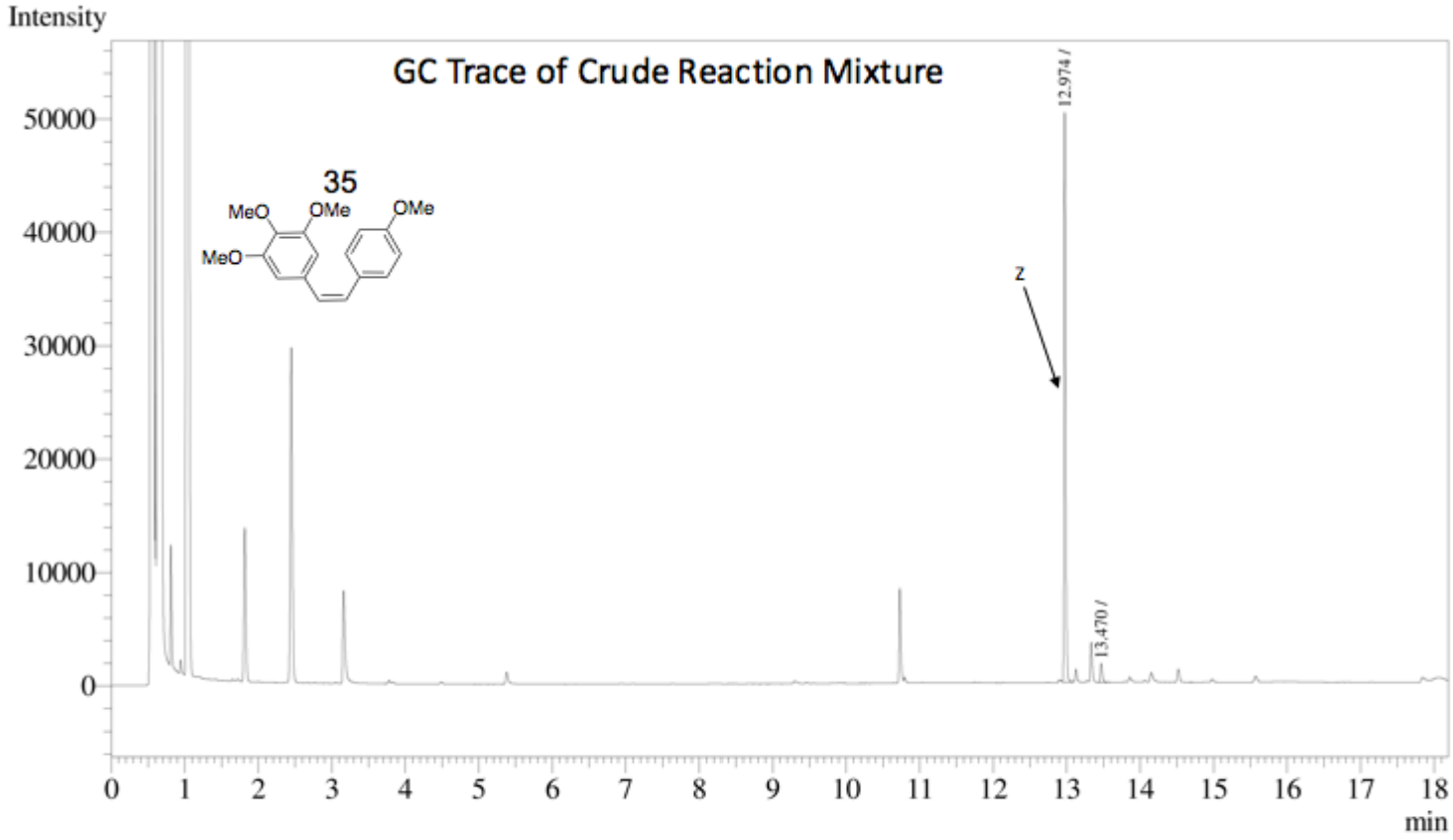
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.053	190816	127146	97.566		V		
2	14.481	4761	2183	2.434				
Total		195577	129329					

^{1}H 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).

35

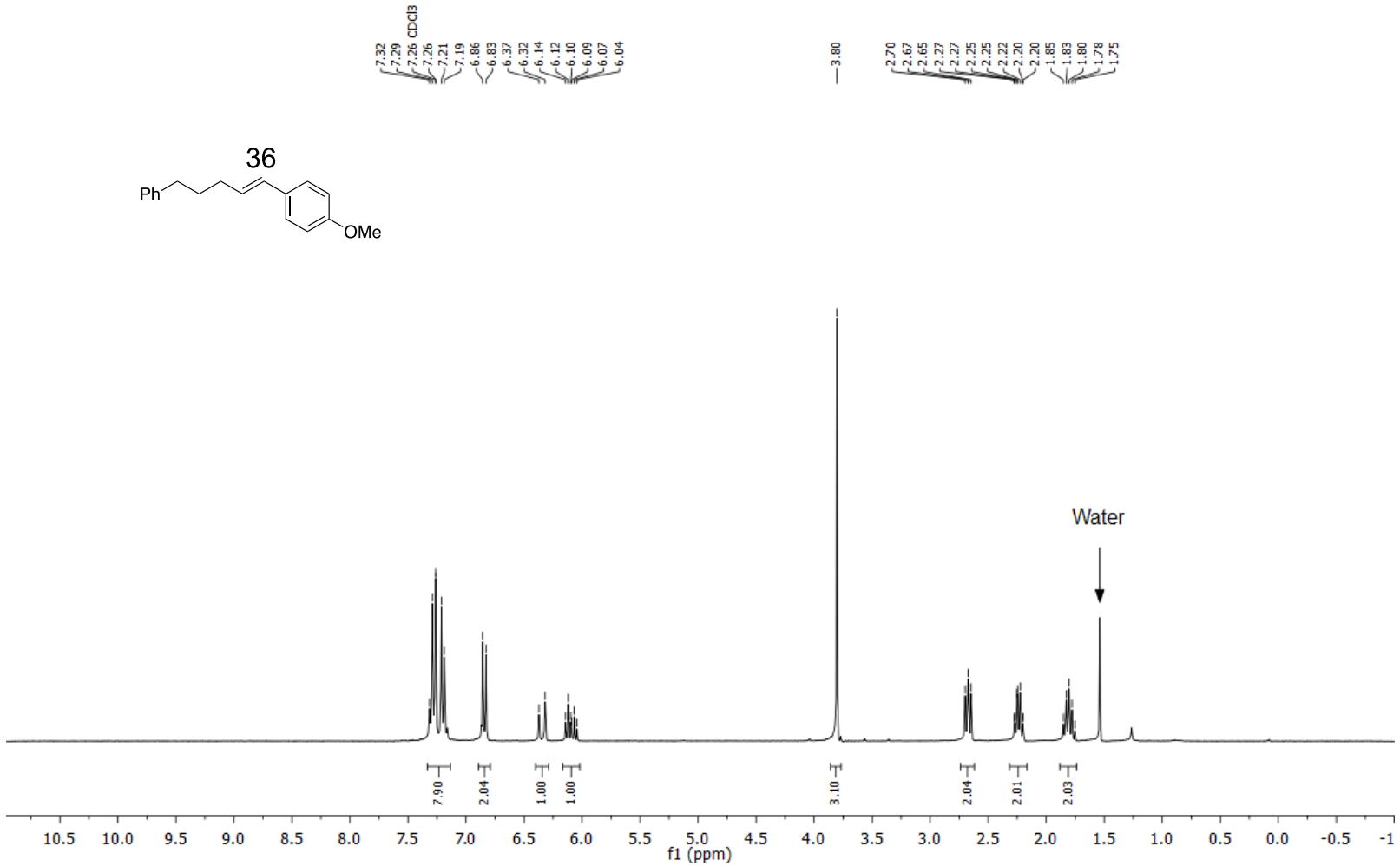




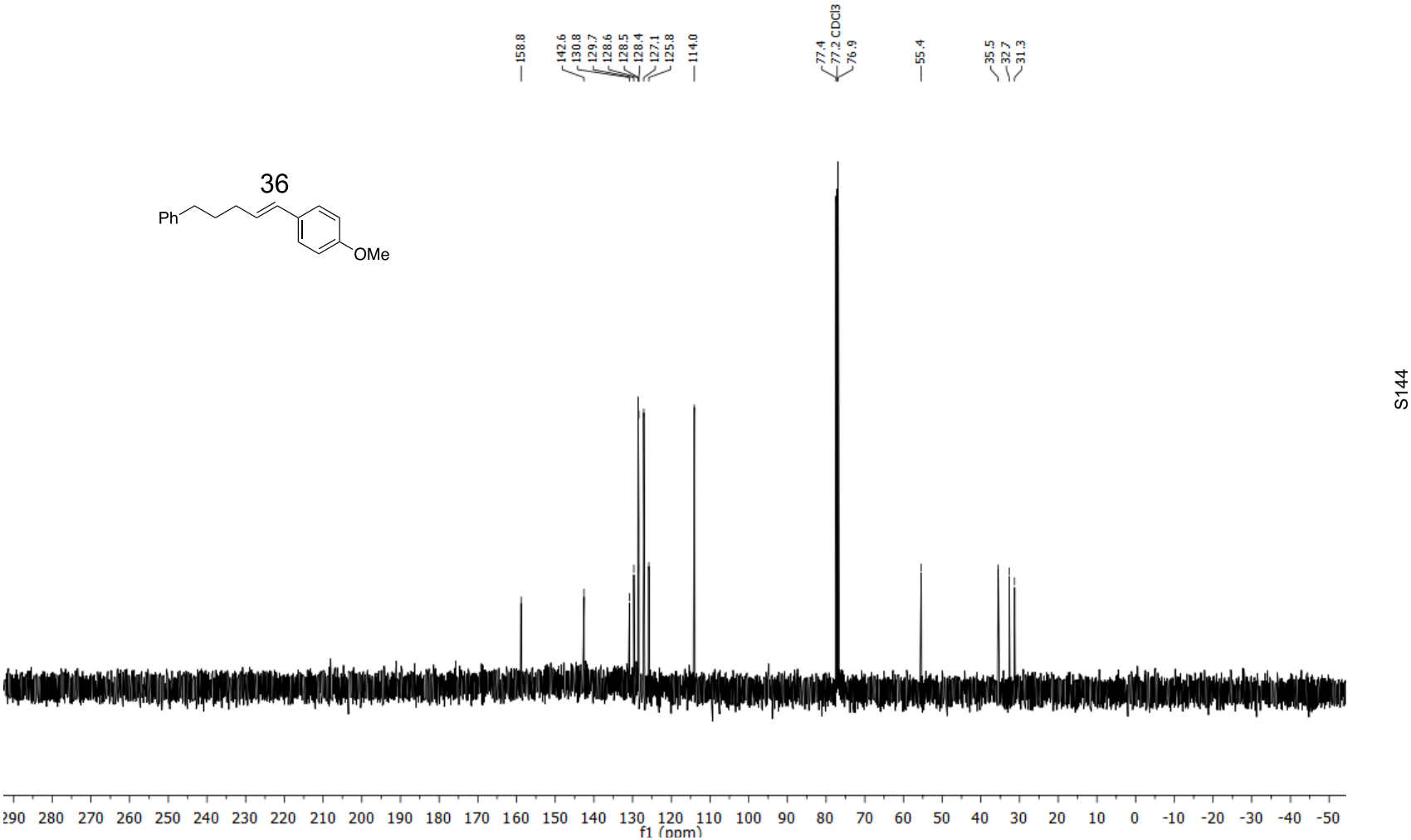


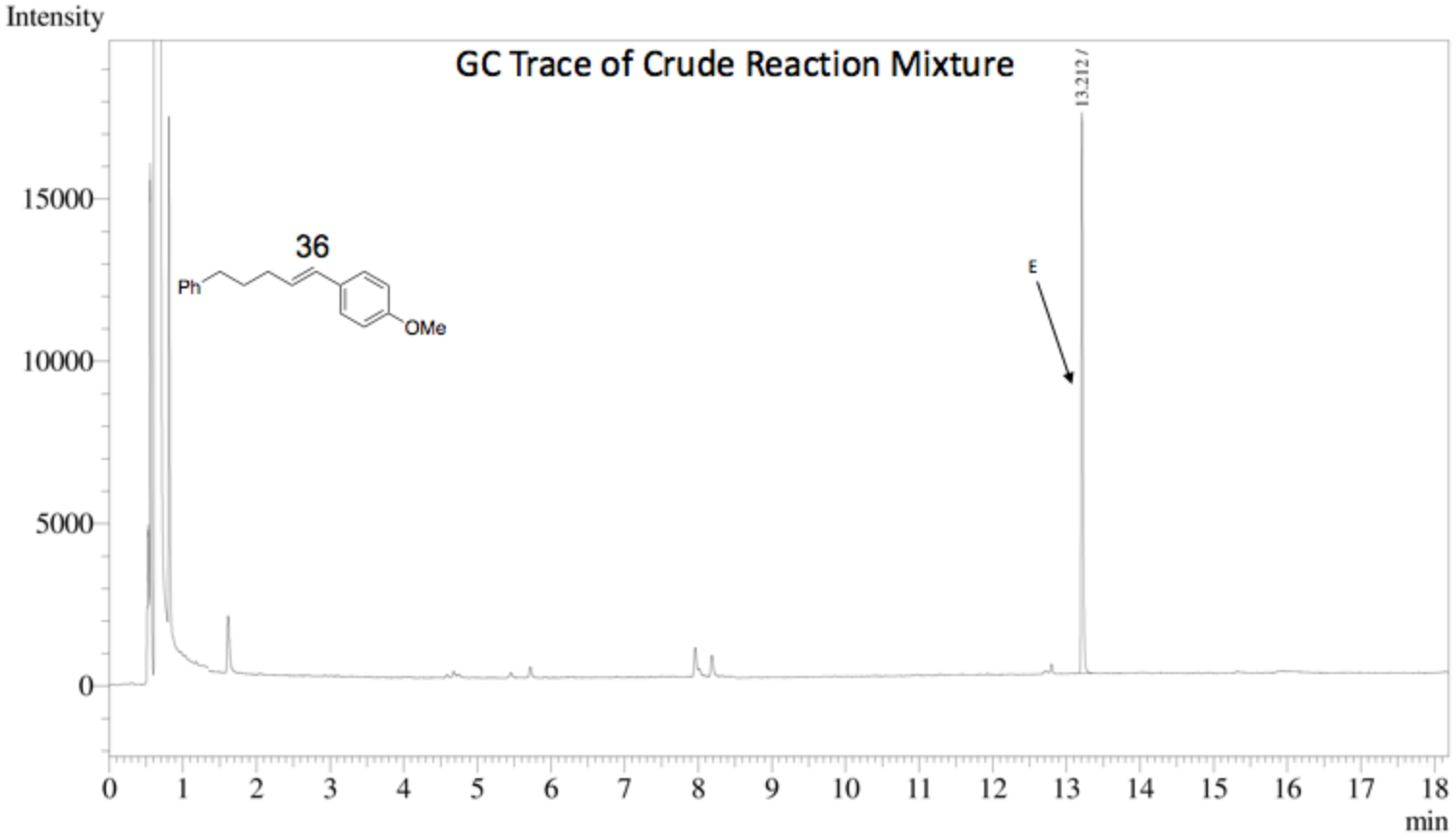
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.974	74317	47876	95.977		V		
2	13.470	3115	1660	4.023				
Total		77432	49536					

^{1}H 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).



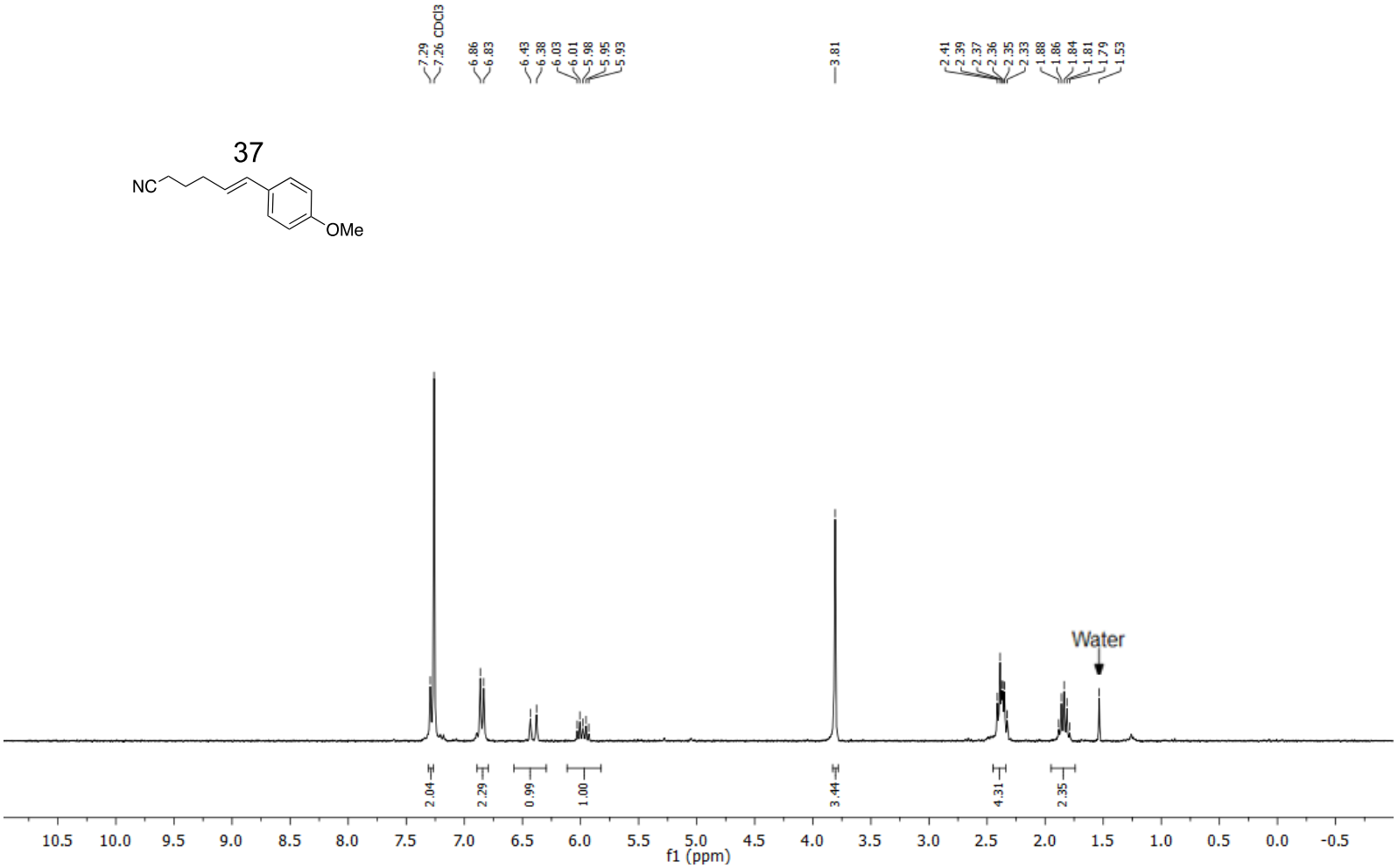
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.8 , 142.6 , 130.8 , 129.7 , 128.6 , 128.5 , 128.4 , 127.1 , 125.8 , 114.0 , 55.4 , 35.5 , 32.7 , 31.3 .



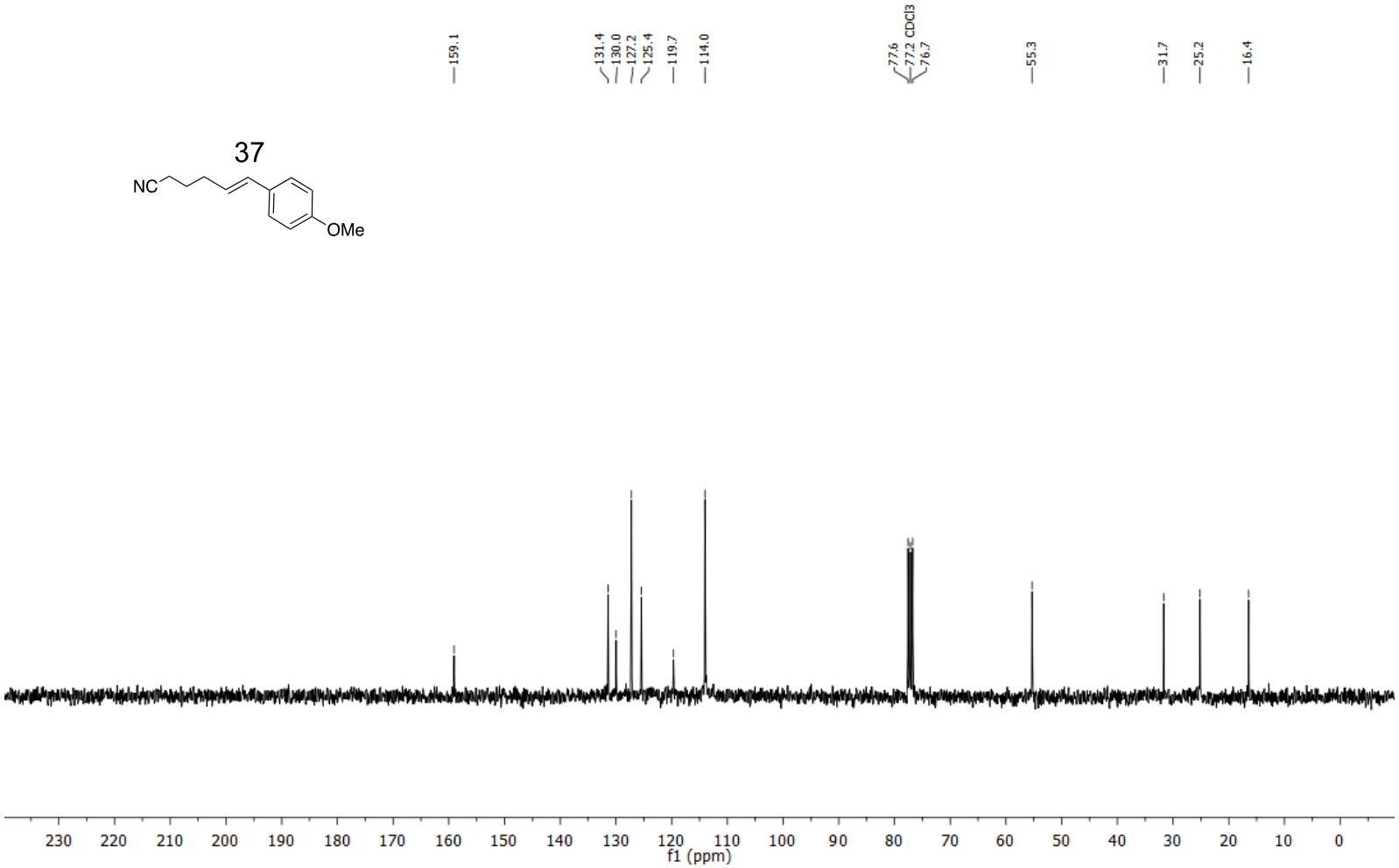


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.212	27412	16678	100.000				
Total		27412	16678					

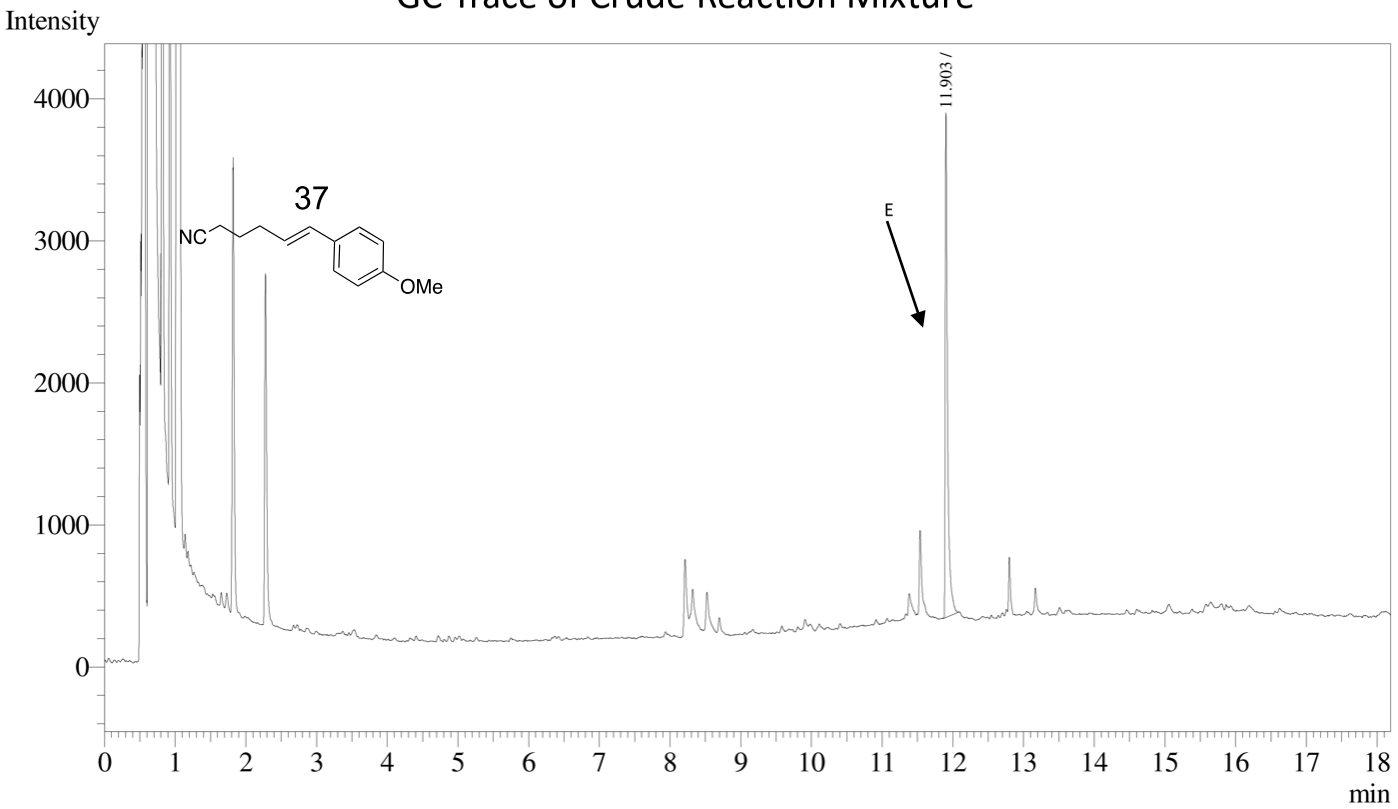
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.98 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.34 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H).



^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.4, 130.0, 127.2, 125.4, 119.7, 114.0, 55.3, 31.7, 25.2, 16.4.

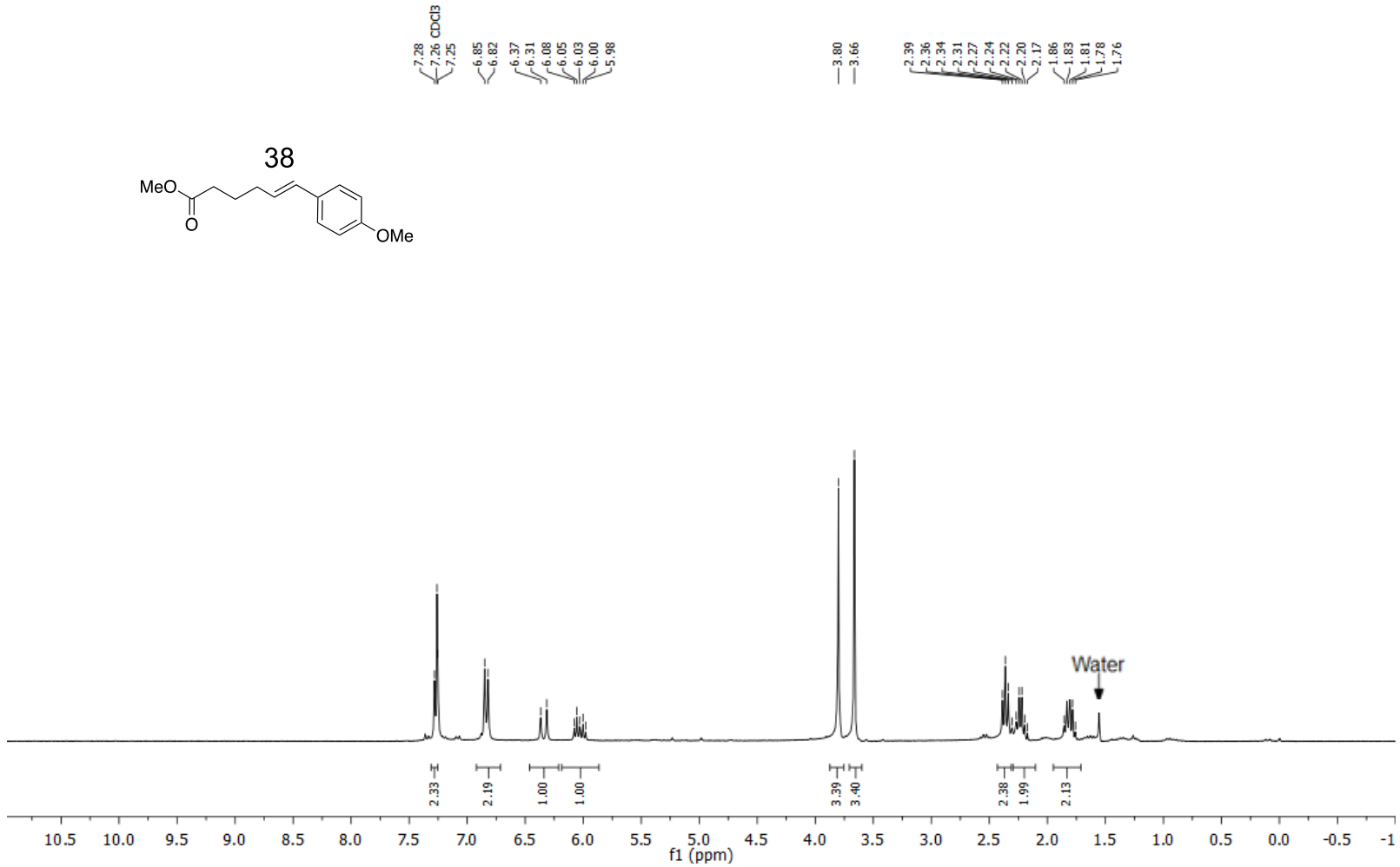


GC Trace of Crude Reaction Mixture

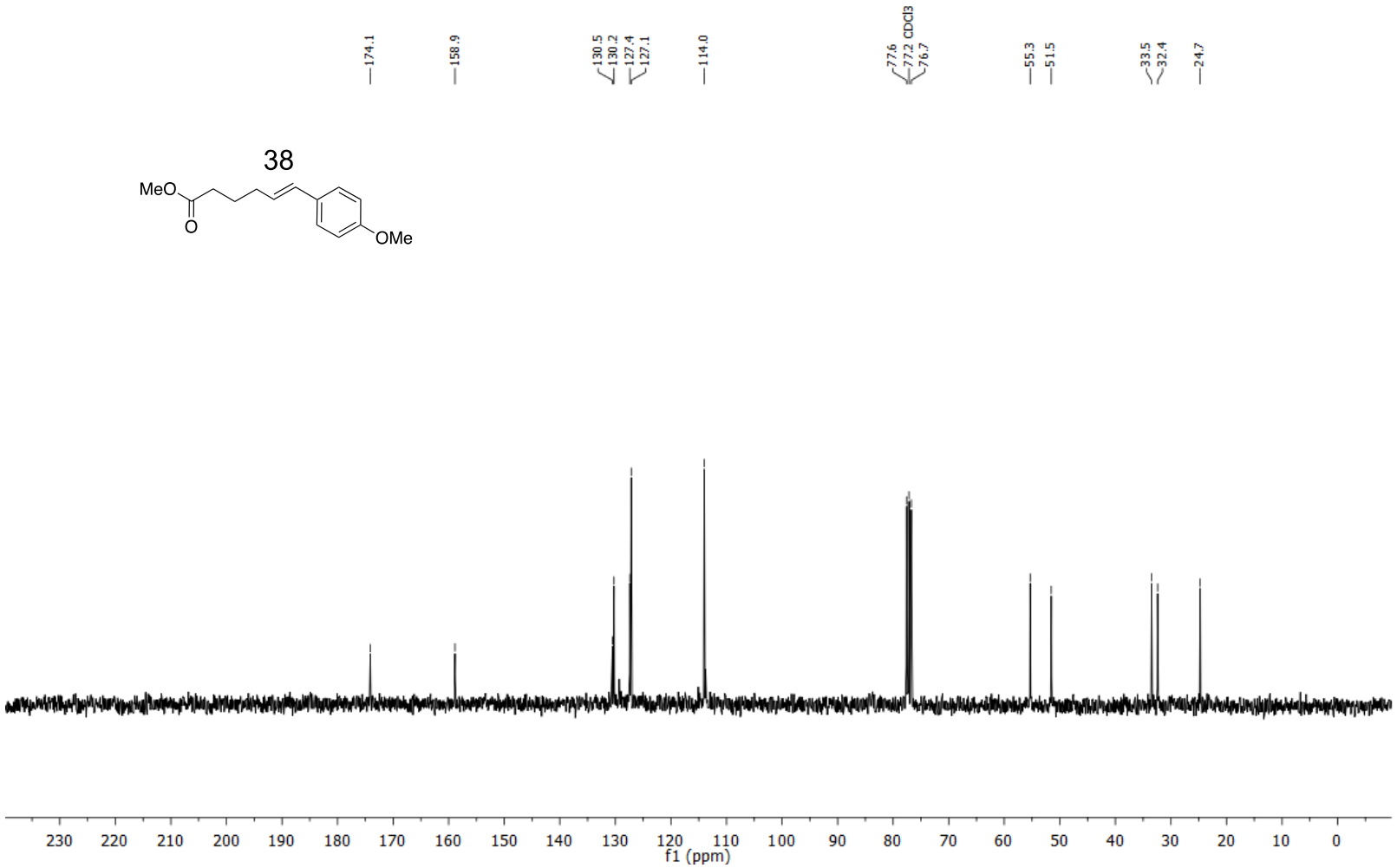


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.903	8189	3531	100.000				
Total		8189	3531					

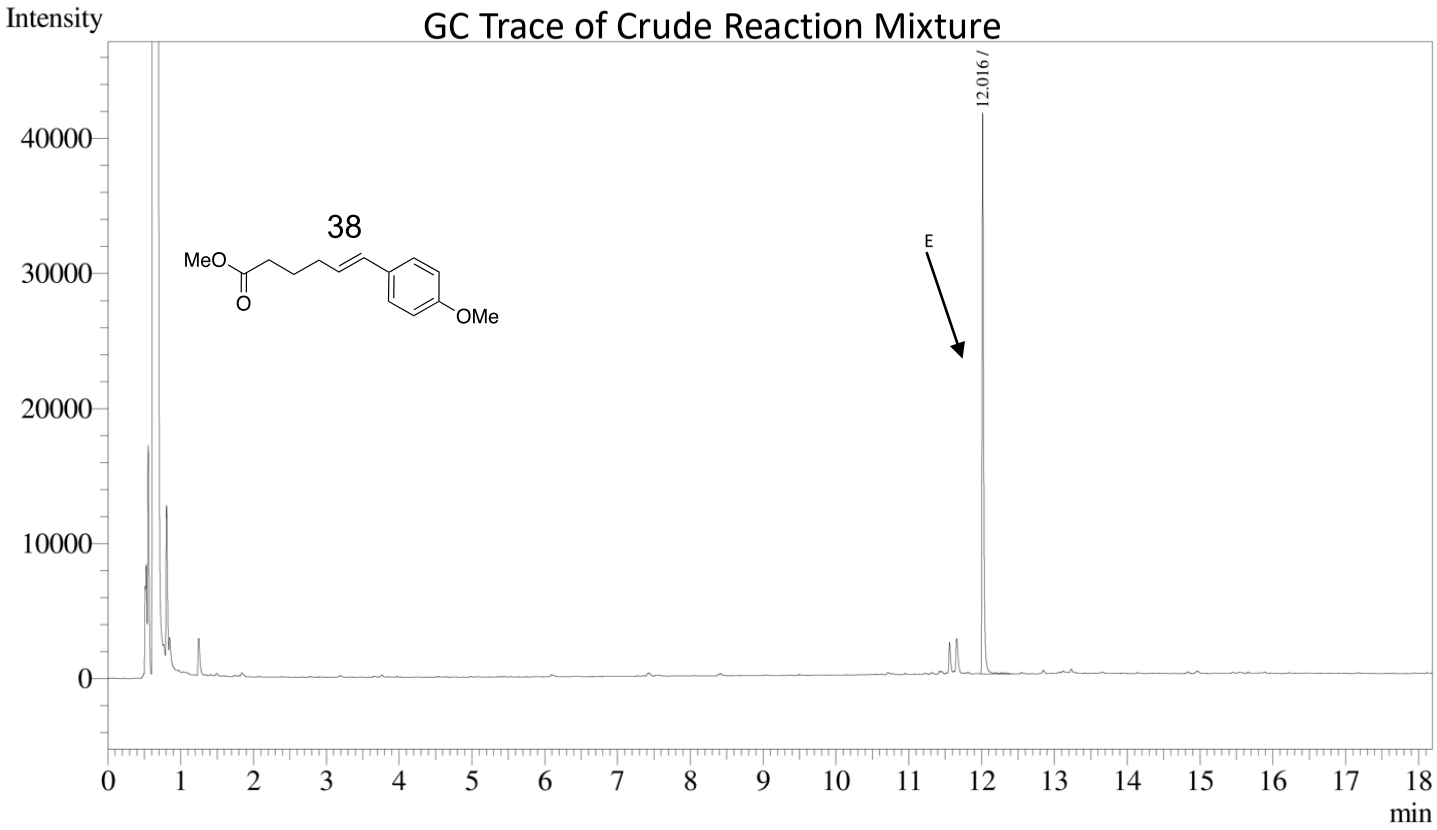
^{1}H NMR (300 MHz, Chloroform-d) δ 7.27 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.11 – 5.95 (m, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.45 – 2.30 (m, 2H), 2.34 – 2.14 (m, 2H), 1.81 (p, J = 7.3 Hz, 2H).



^{13}C NMR (75 MHz, $CDCl_3$) 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.

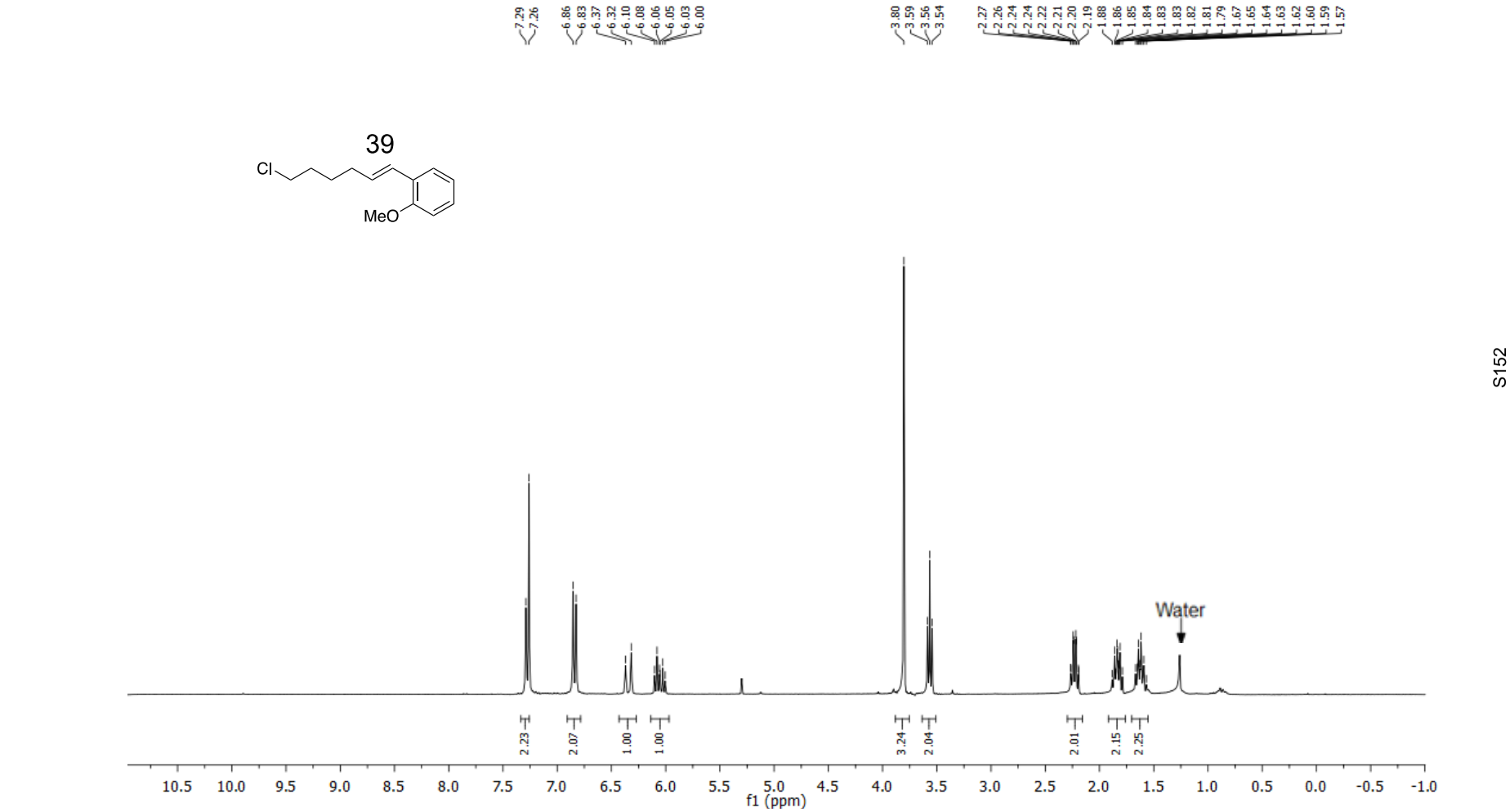


GC Trace of Crude Reaction Mixture

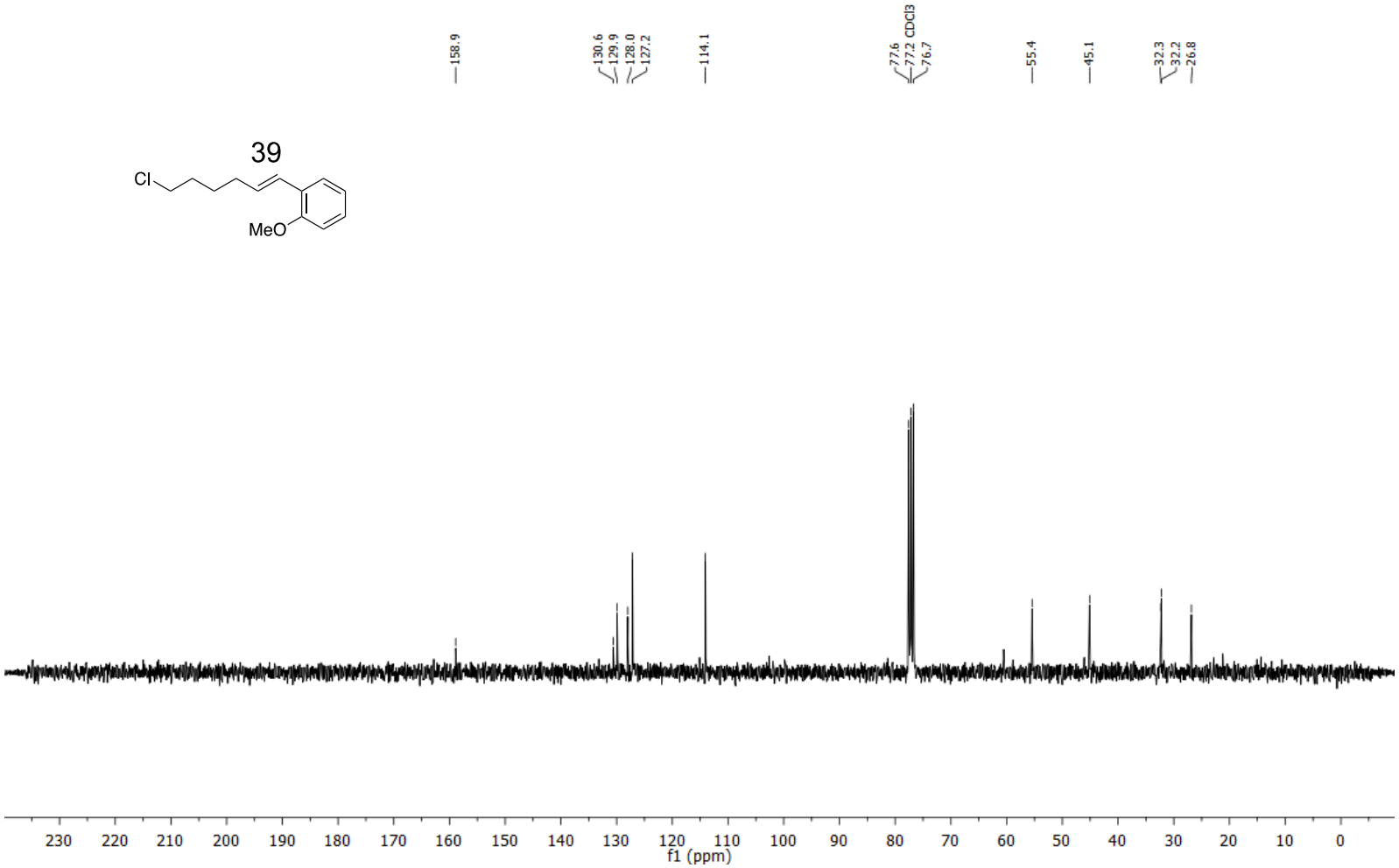


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.016	62340	41073	100.000		S		
Total		62340	41073					

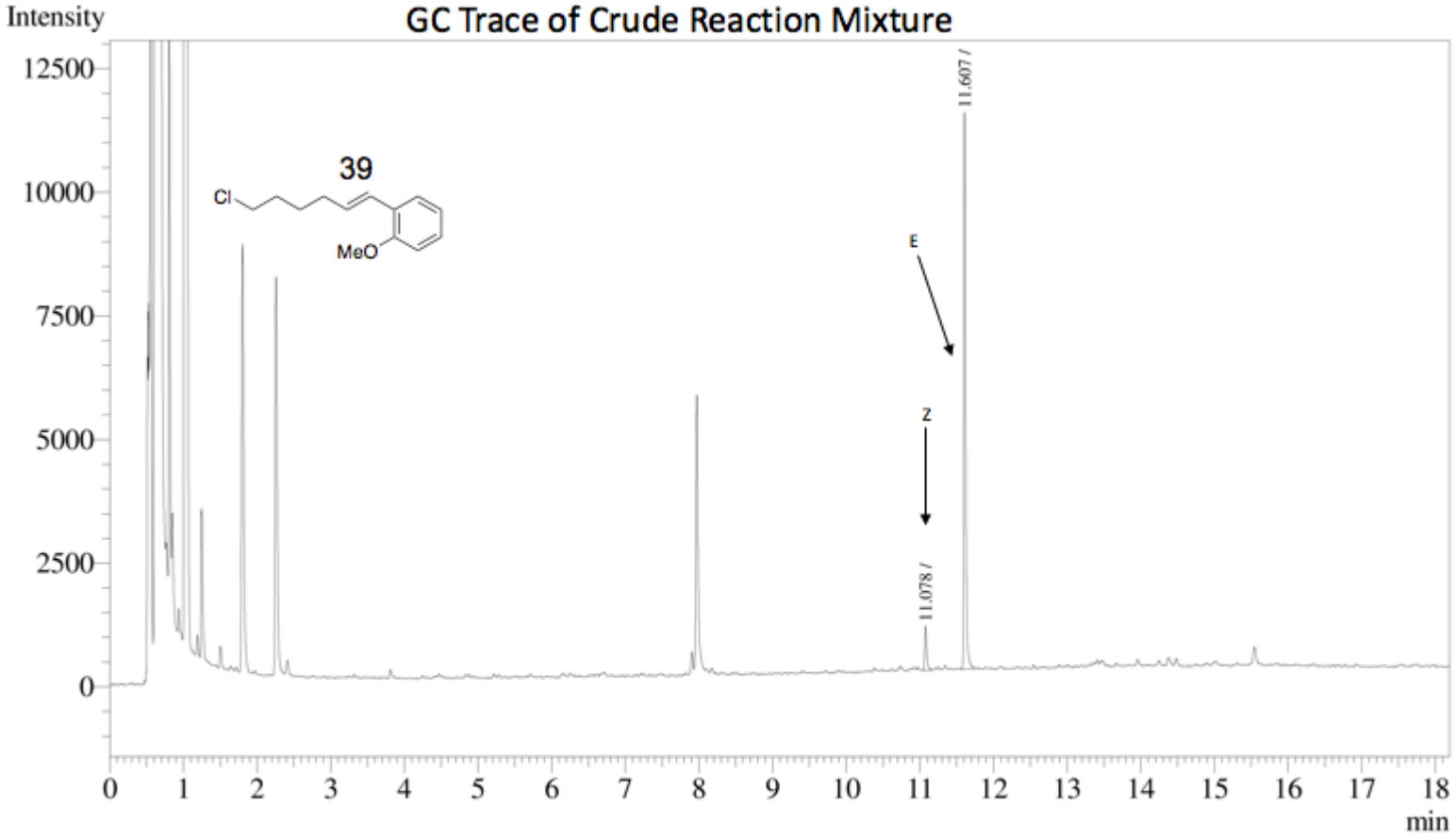
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.80 (s, 3H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 1.92 – 1.76 (m, 2H), 1.70 – 1.55 (m, 2H).



^{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.

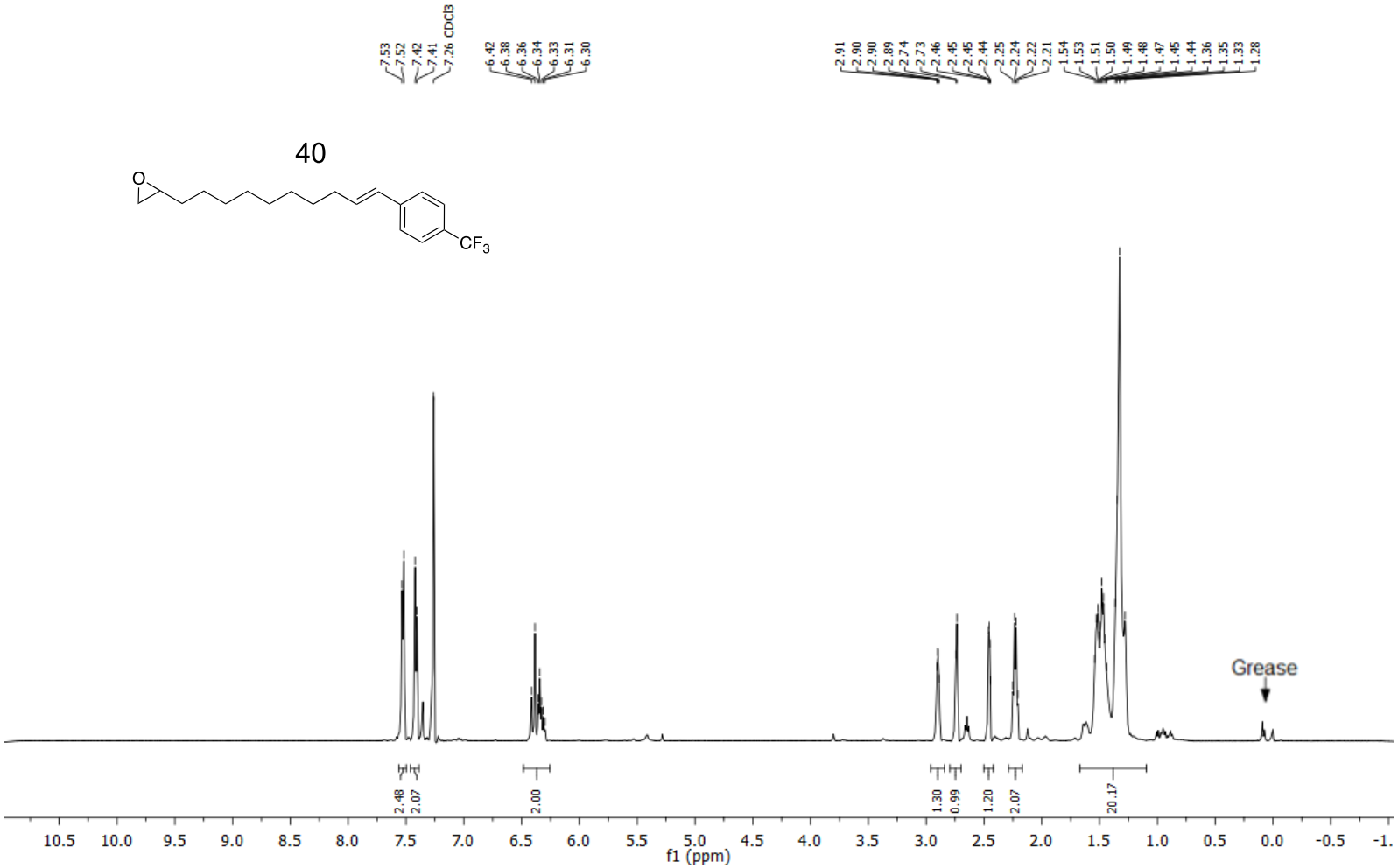


GC Trace of Crude Reaction Mixture

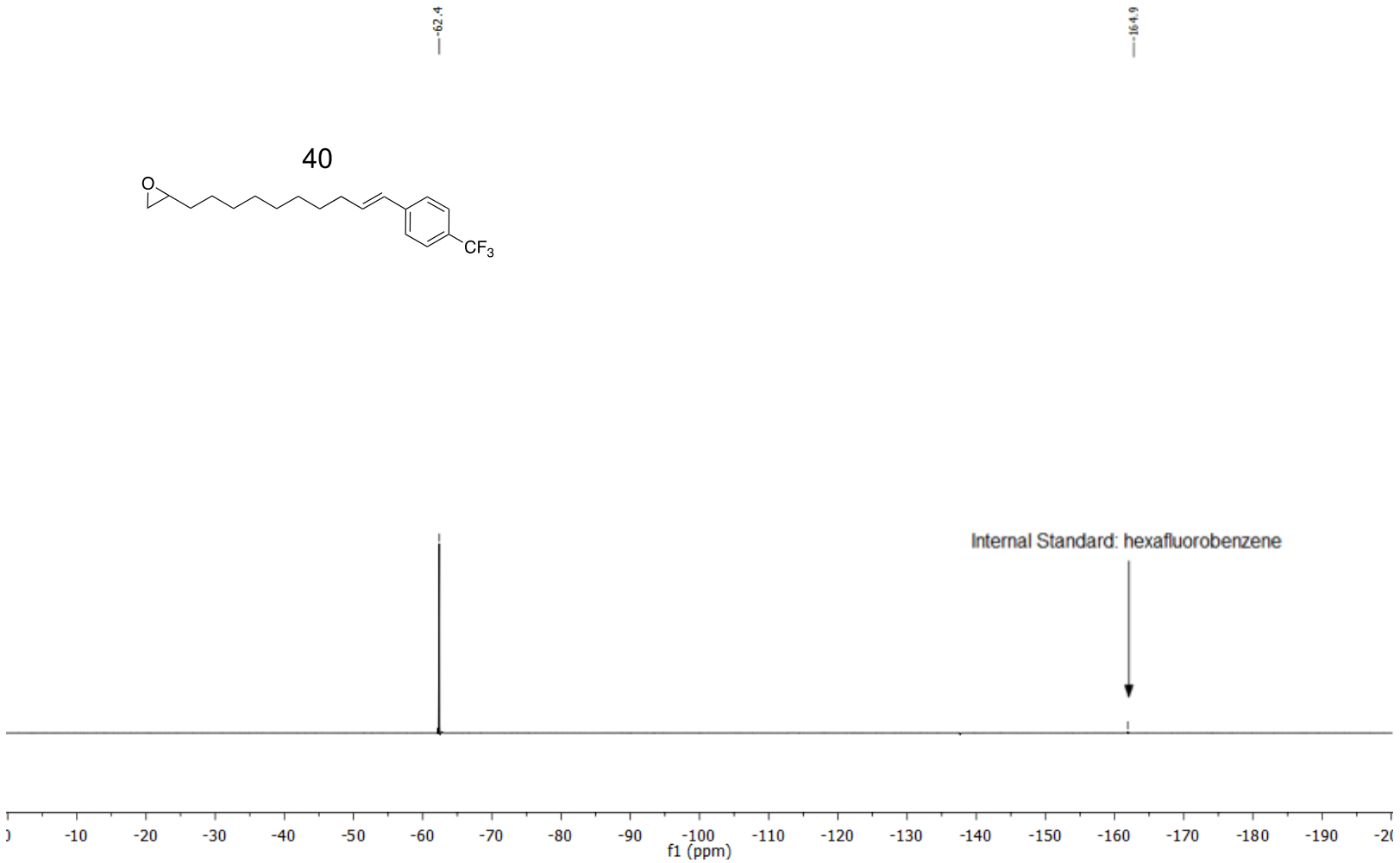


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.078	1789	885	8.336				
2	11.607	18345	10929	91.664				
Total		20013	11814					

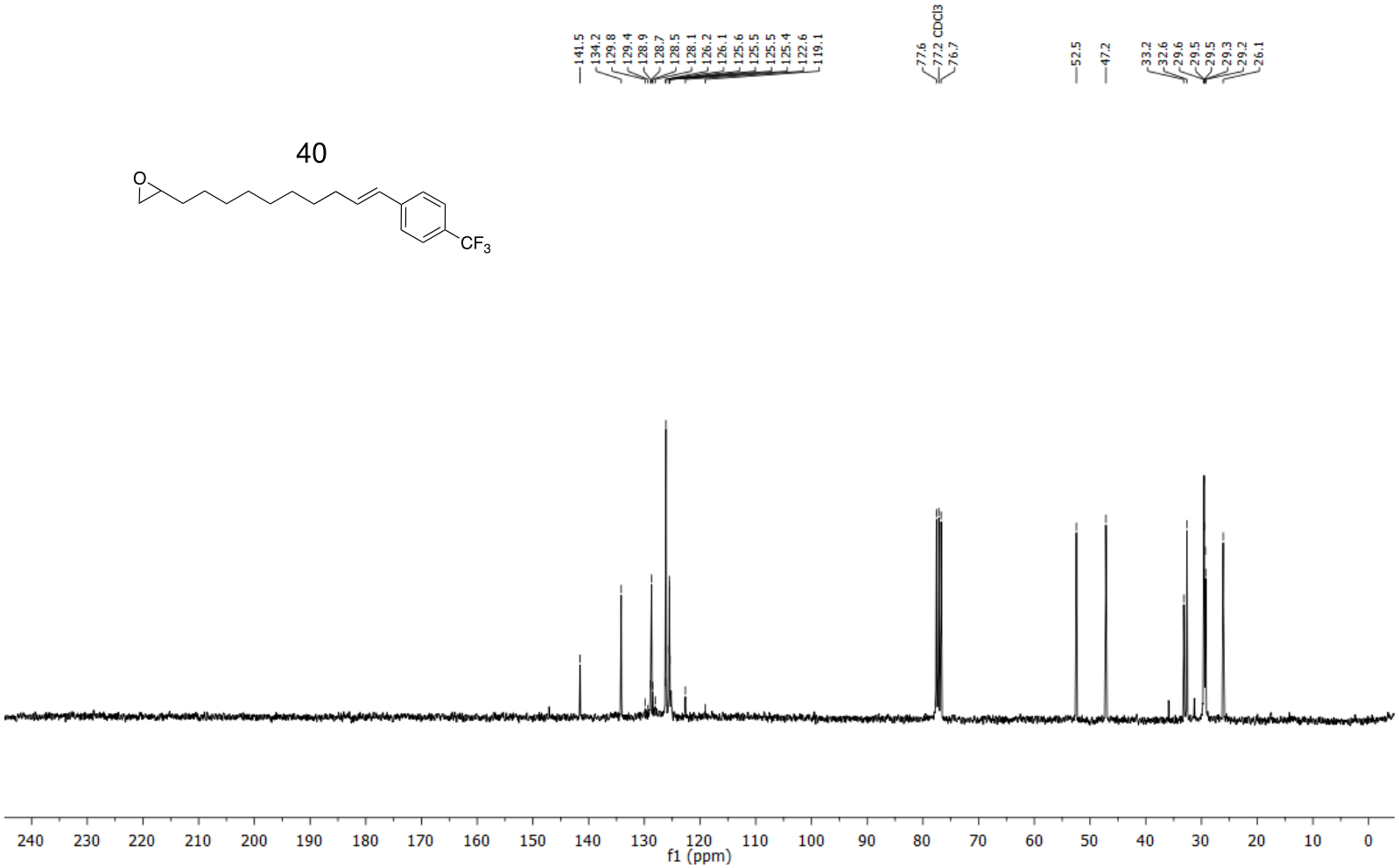
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 6.48 – 6.26 (m, 2H), 2.96 – 2.84 (m, 1H), 2.79 – 2.70 (m, 1H), 2.50 – 2.42 (m, 1H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.67 – 1.10 (m, 20H).



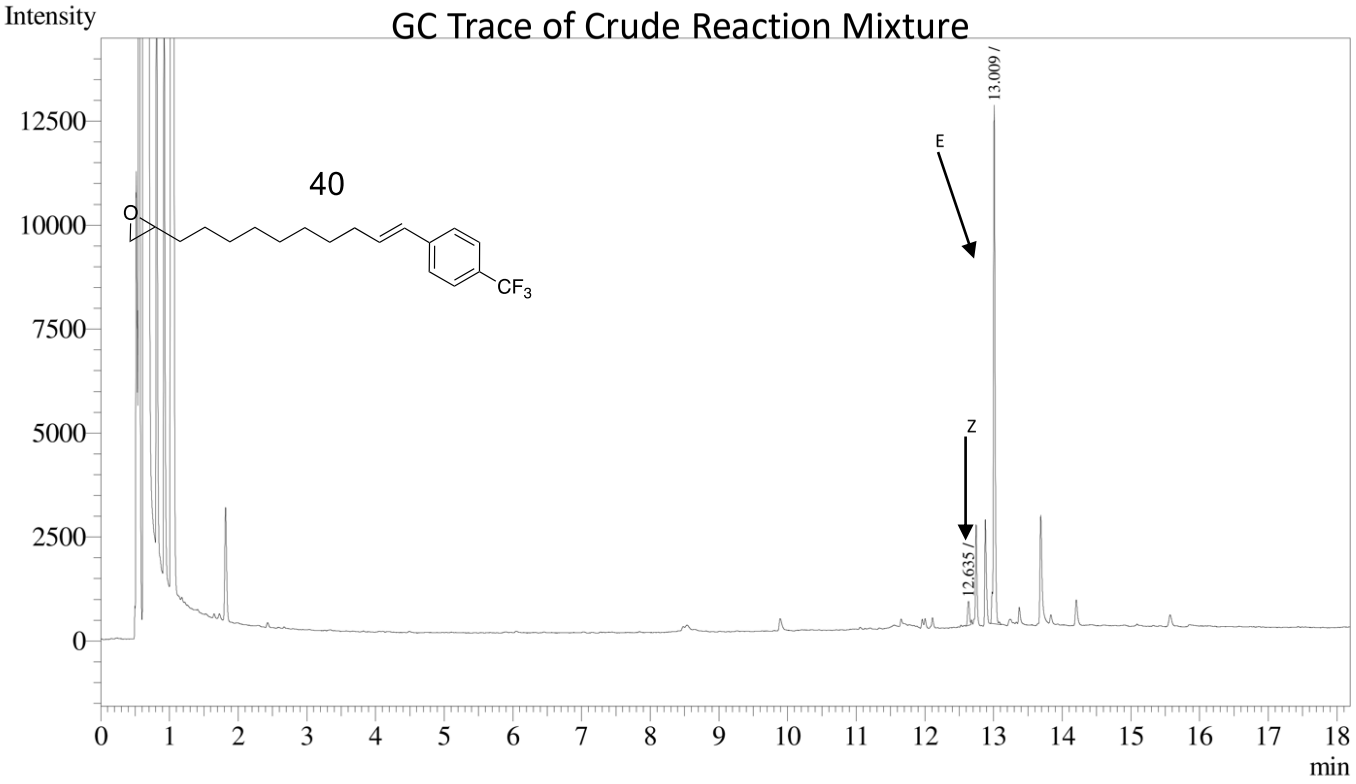
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.



^{13}C 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 .

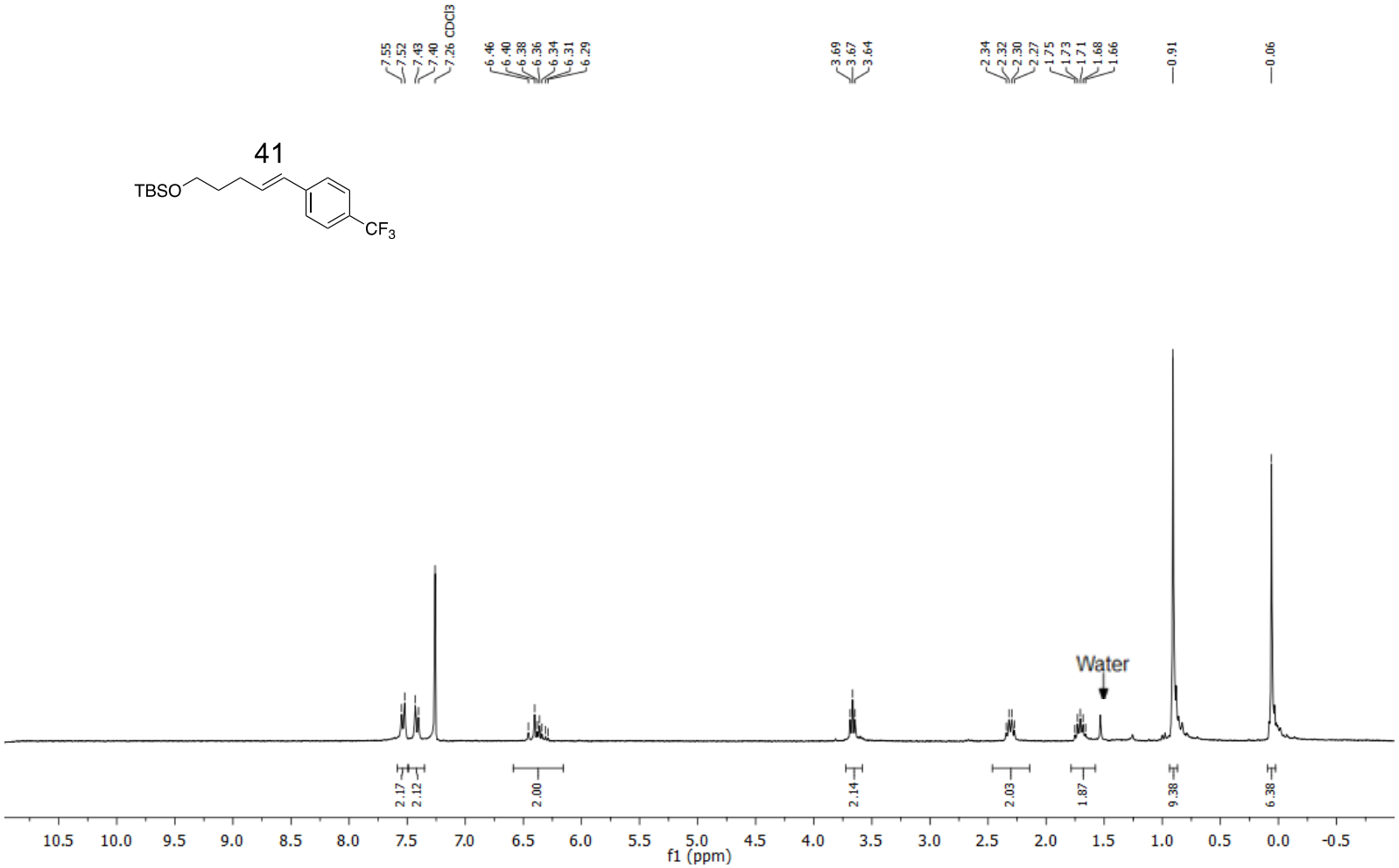


GC Trace of Crude Reaction Mixture

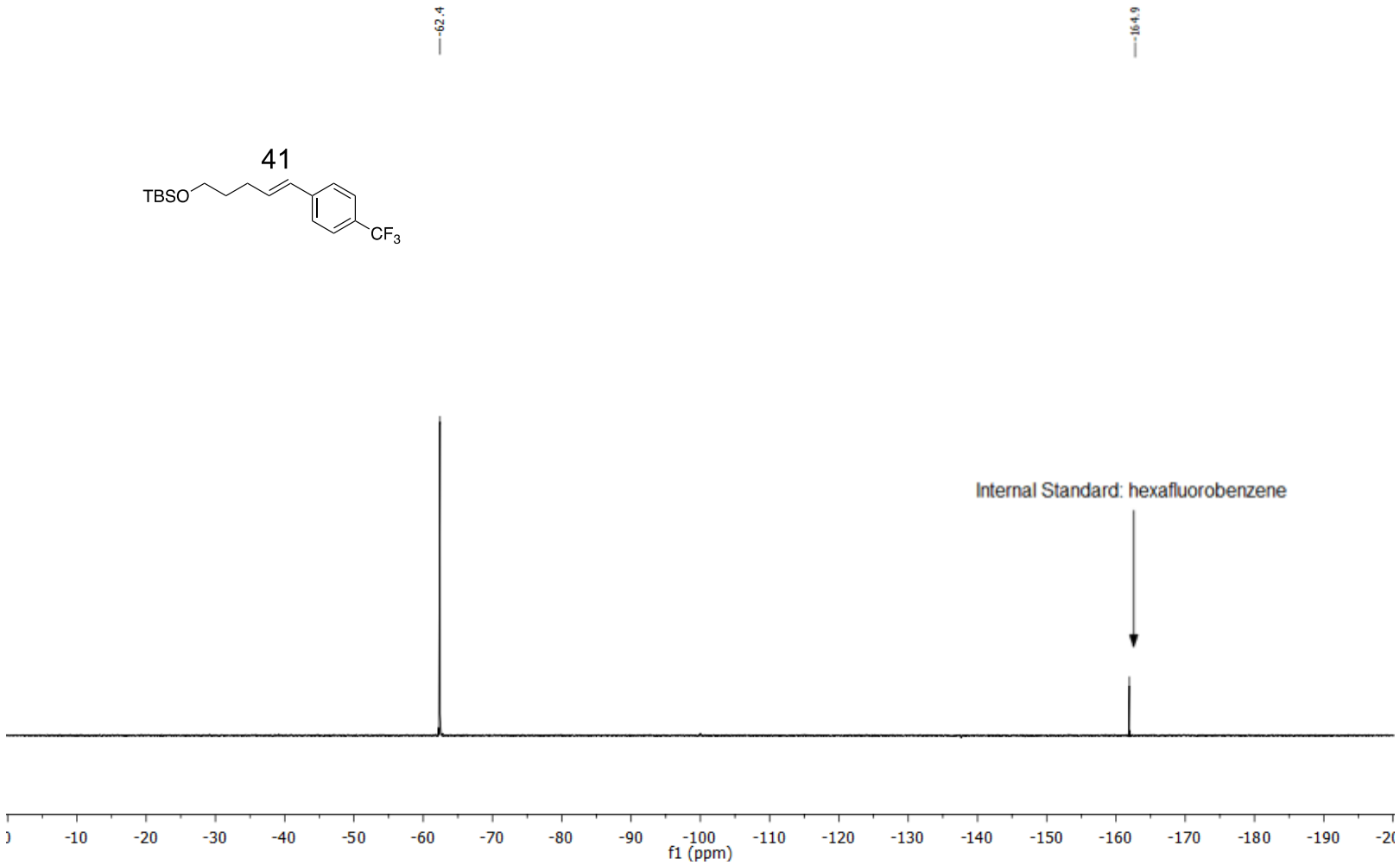


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.635	1112	571	5.343				
2	13.009	19701	12346	94.657		S		
Total		20813	12917					

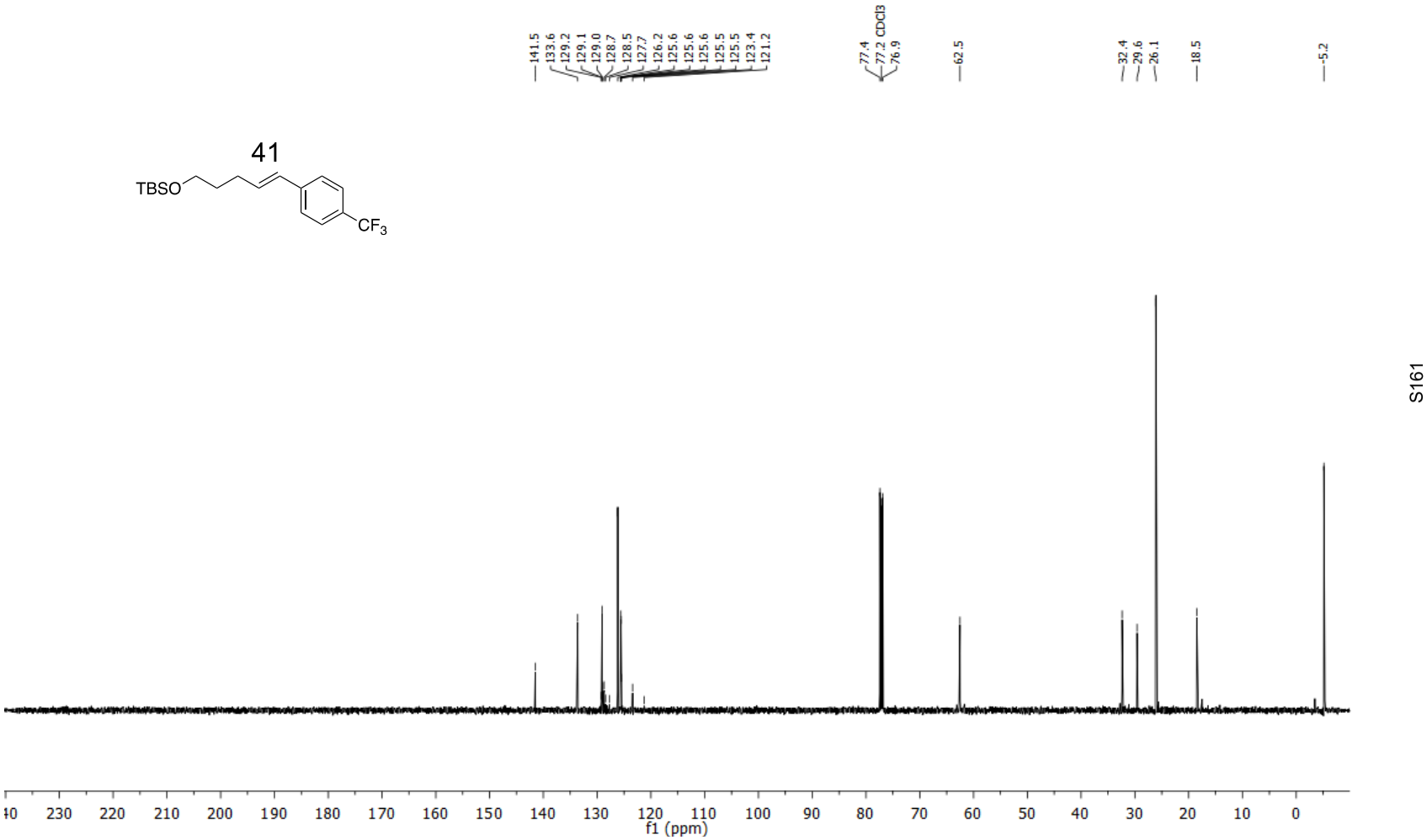
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.59 – 6.16 (m, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.31 (q, *J* = 6.9 Hz, 2H), 1.79 – 1.58 (m, 2H), 0.91 (s, 9H), 0.06 (s, 6H).



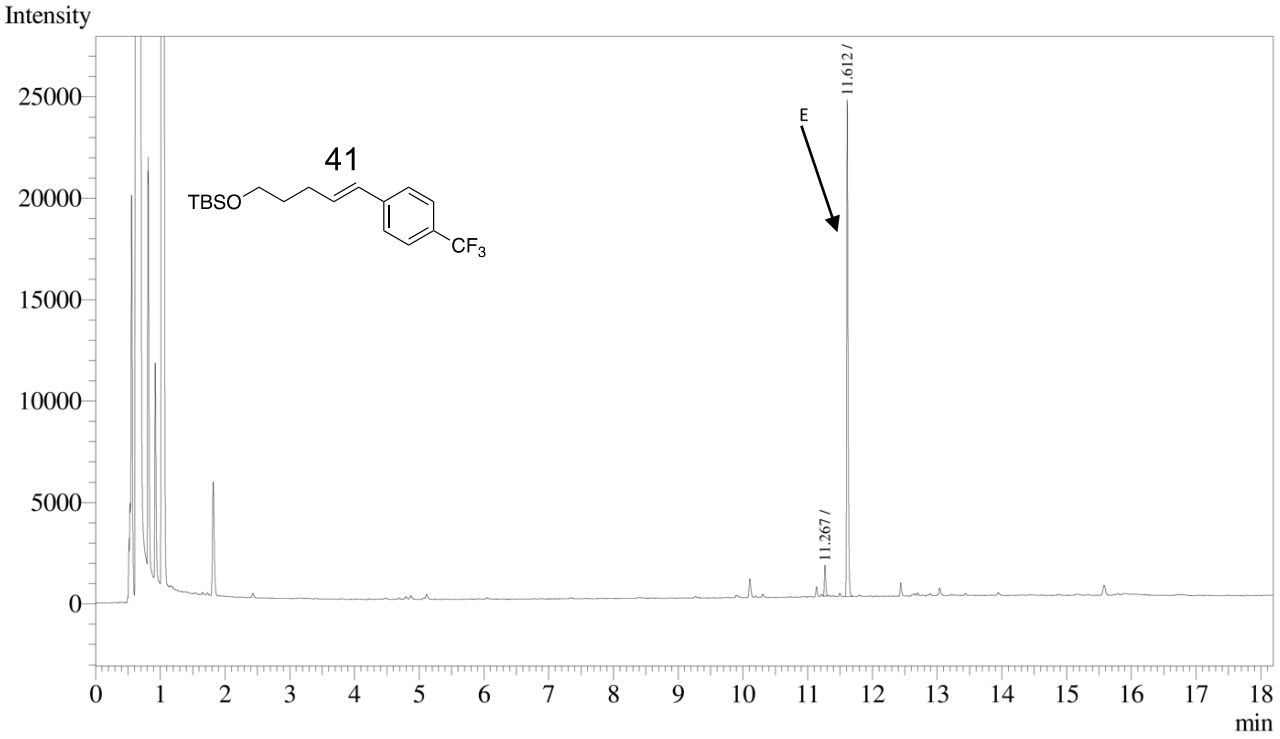
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.



^{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 .

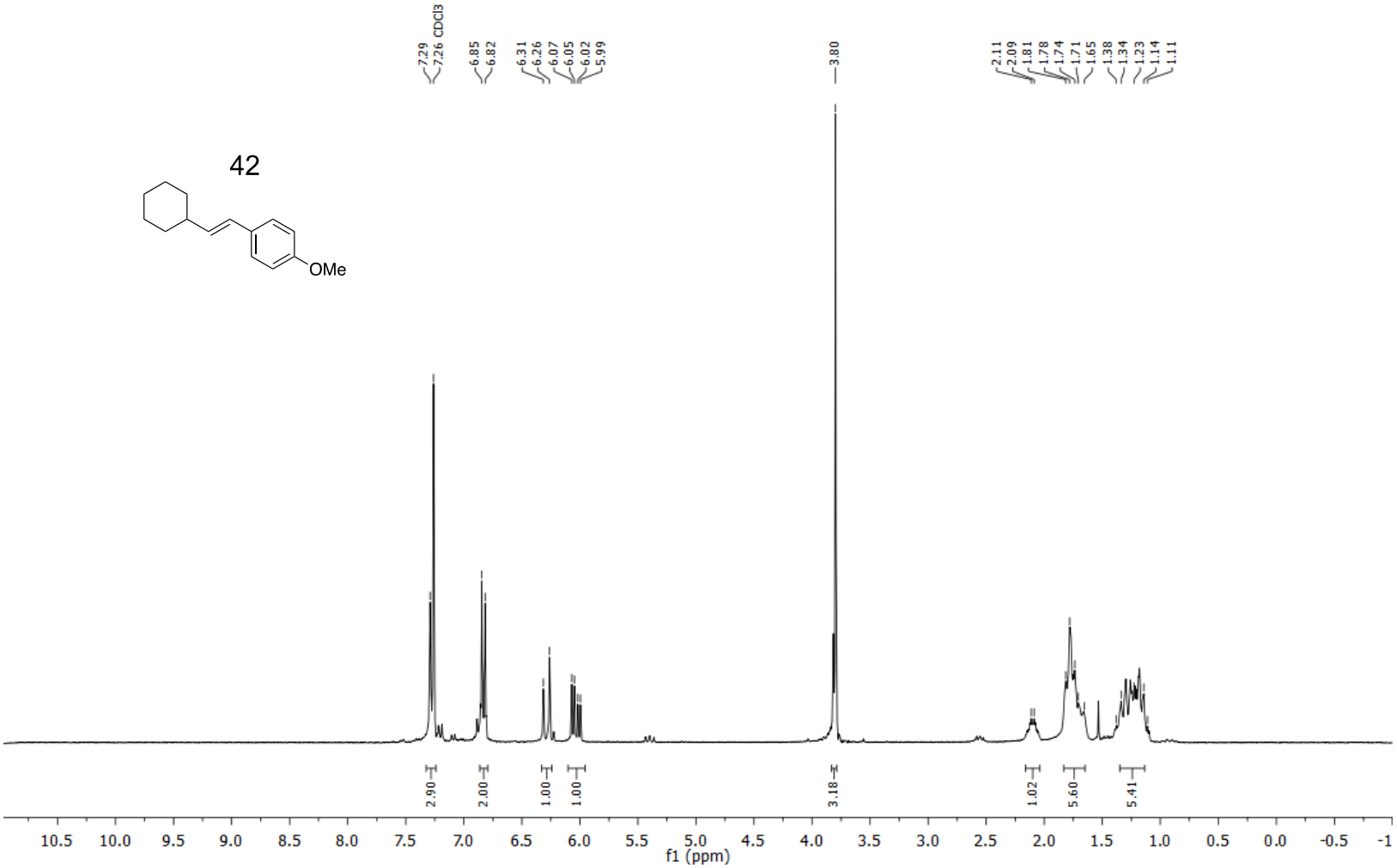


GC Trace of Crude Reaction Mixture

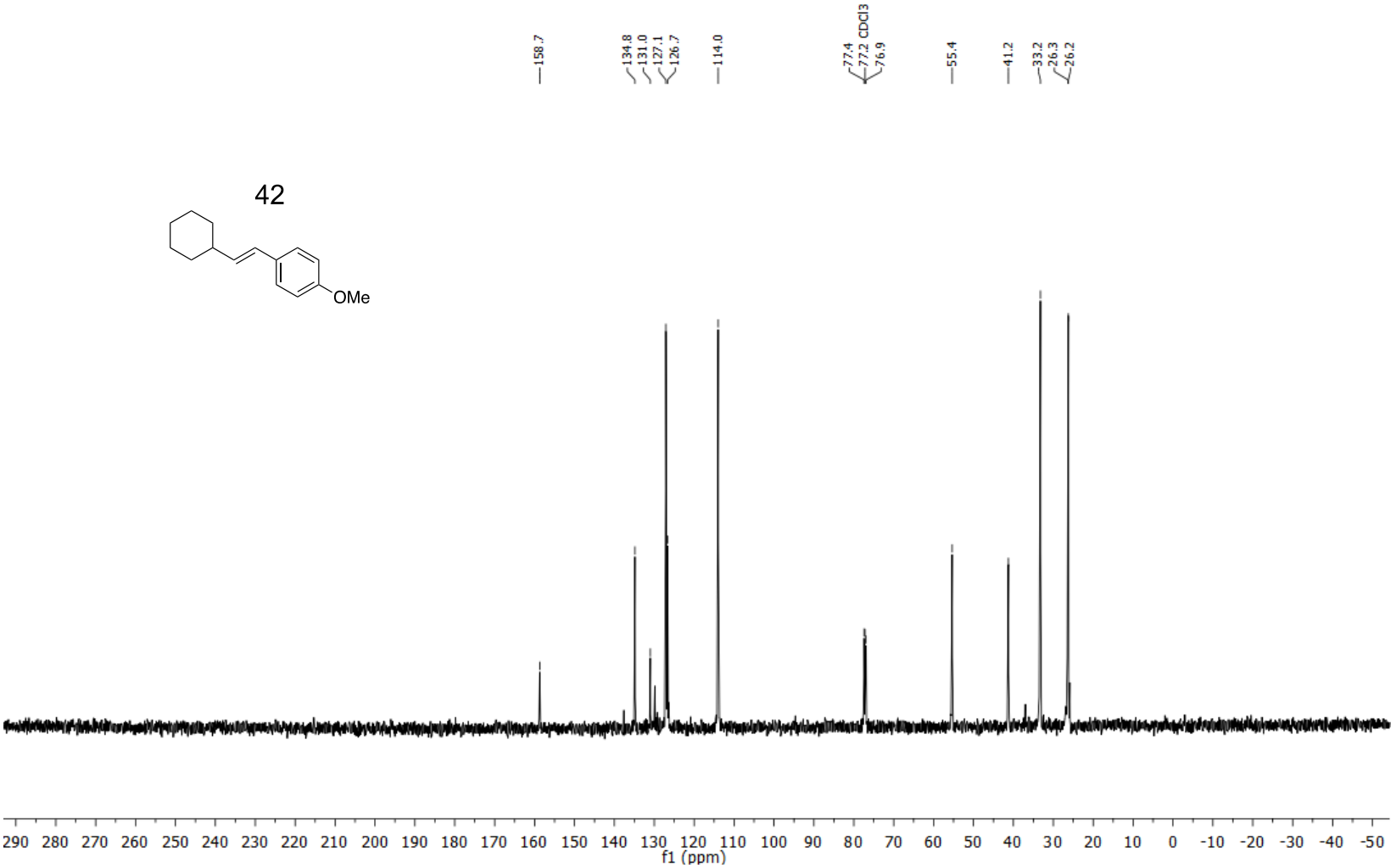


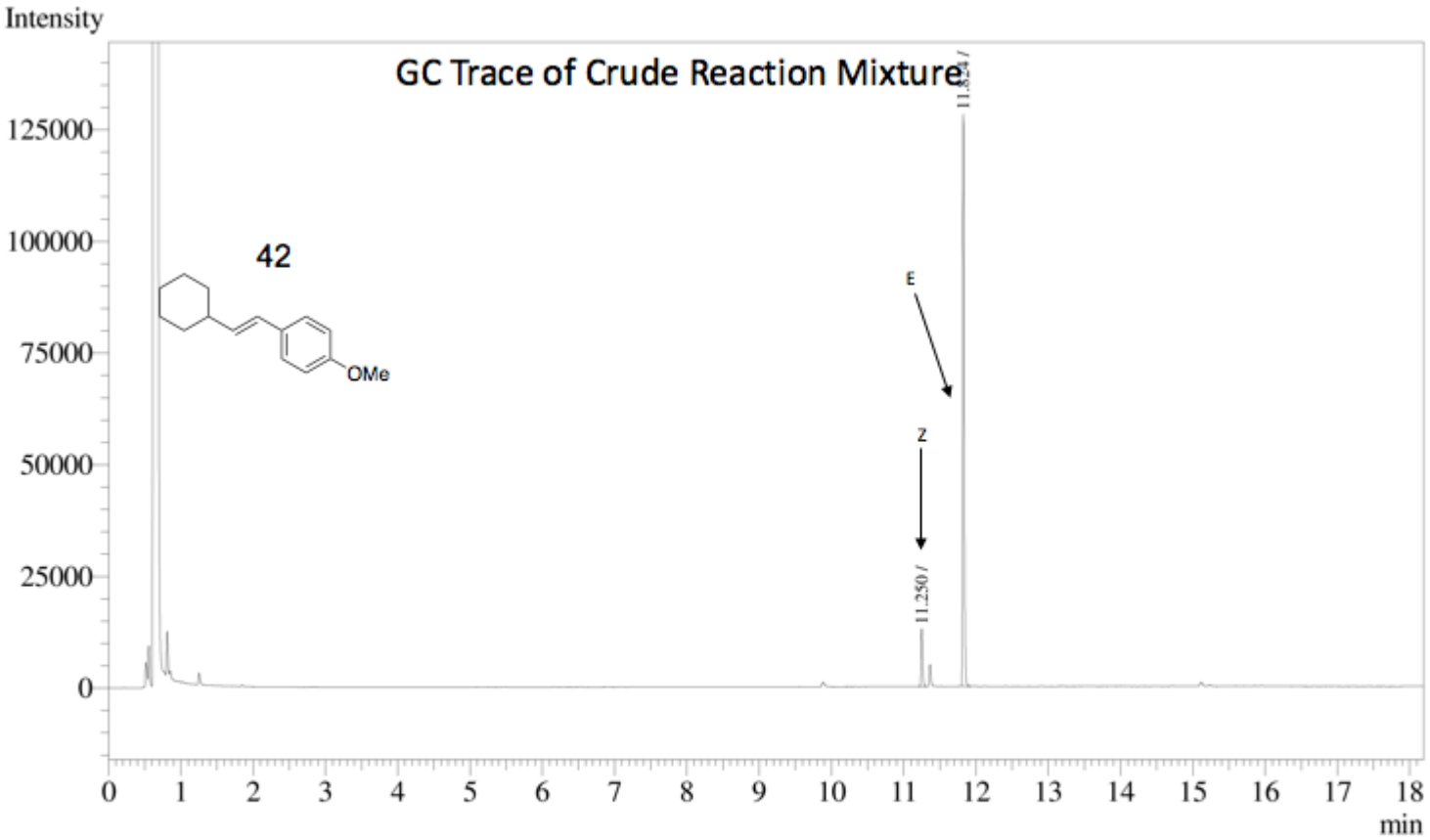
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.267	2245	1511	5.889		V		
2	11.612	35877	23649	94.111				
Total		38122	25160					

^{1}H 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).



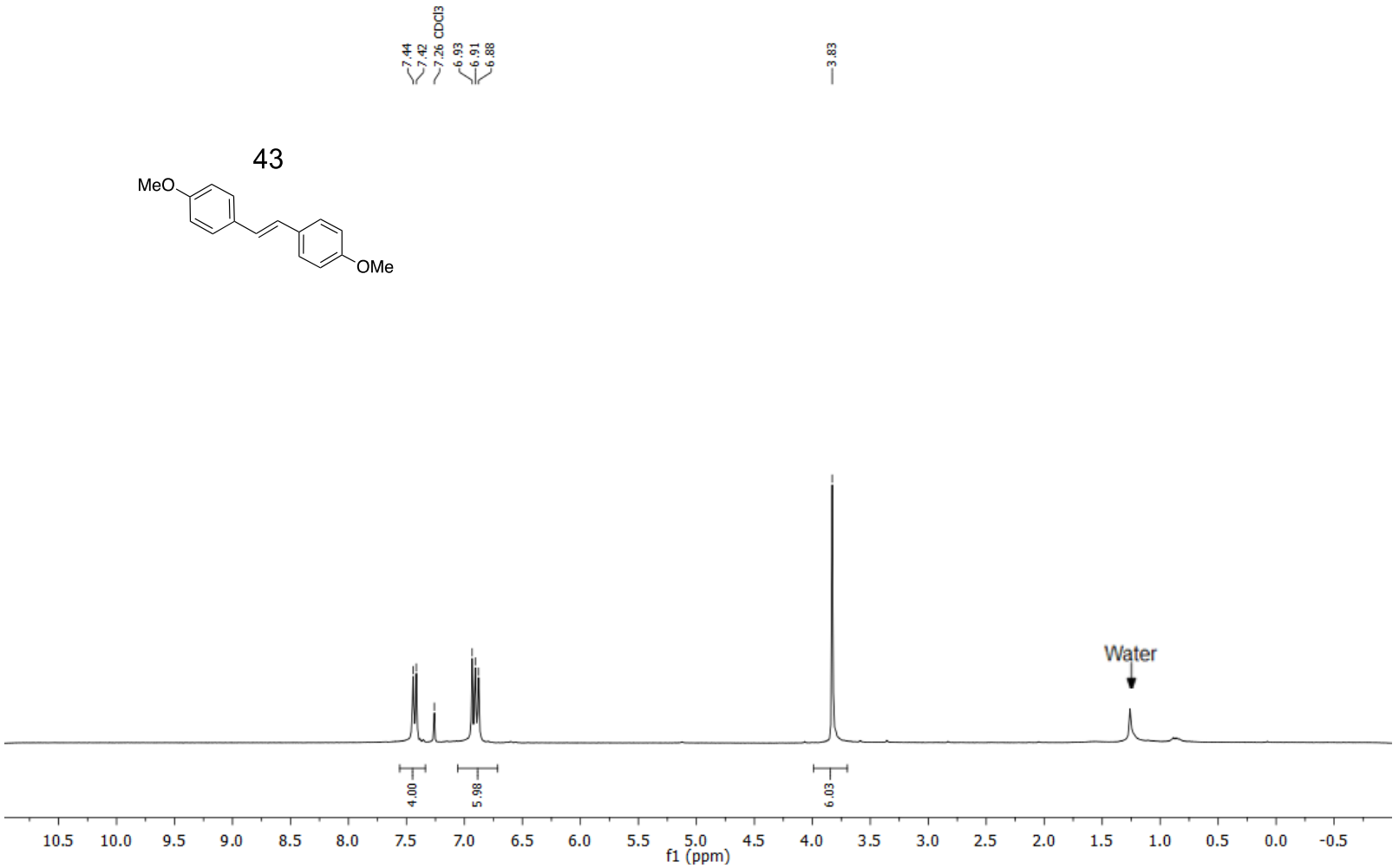
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.7 , 134.8 , 131.0 , 127.1 , 126.7 , 114.0 , 55.4 , 41.2 , 33.2 , 26.2 , 26.2.



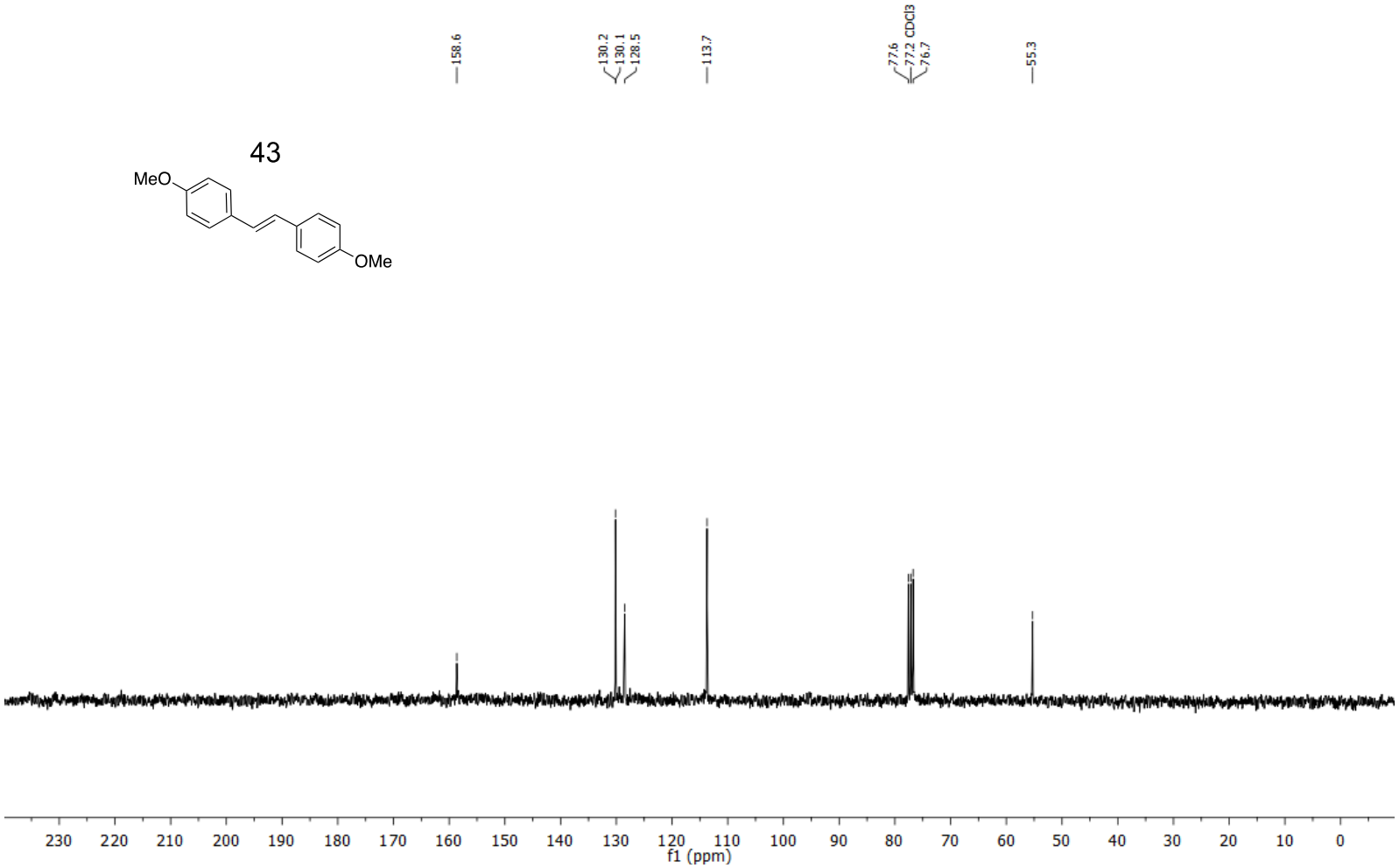


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.250	17832	12852	9.100				
2	11.824	176760	126399	90.202				
Total		195961	139251					

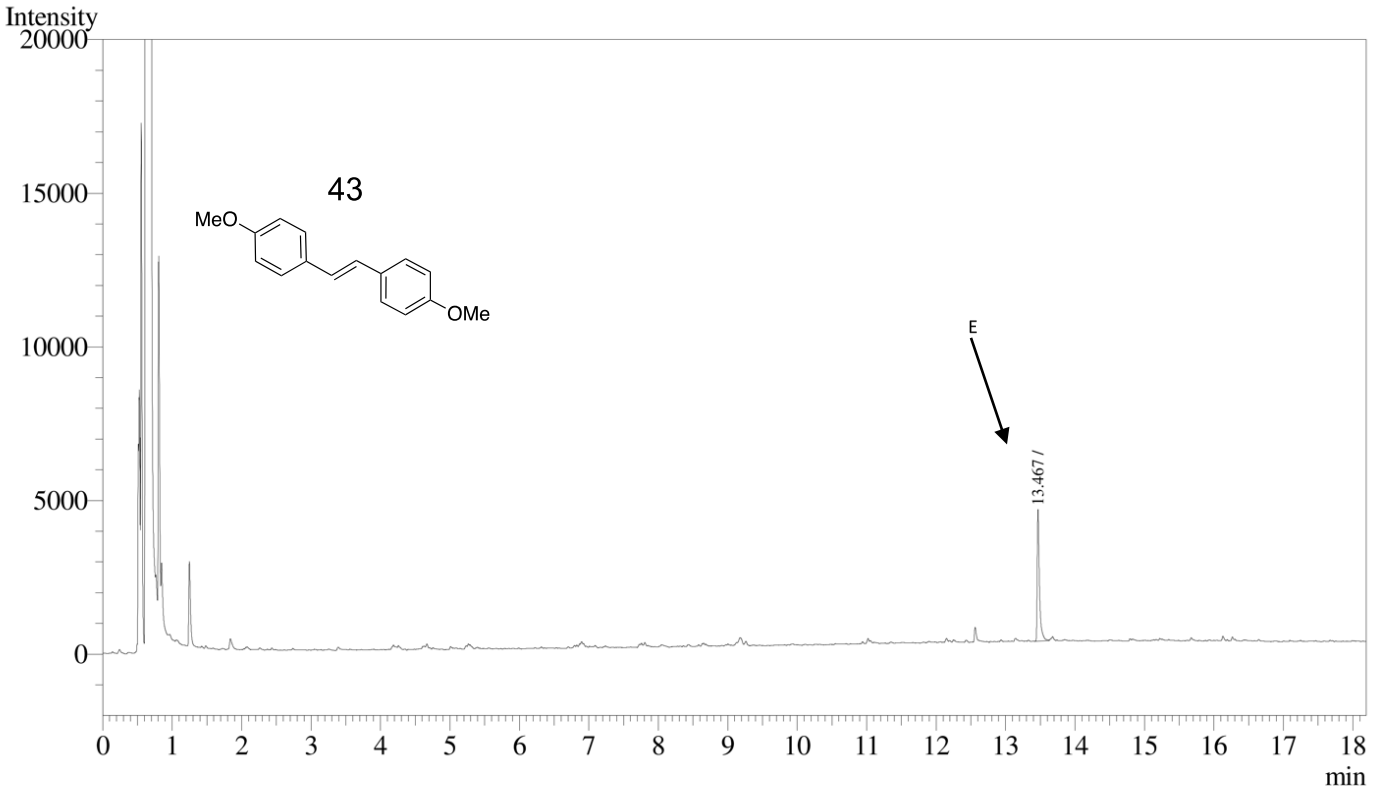
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.4 Hz, 4H), 7.06 – 6.71 (m, 6H), 3.83 (s, 6H).



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

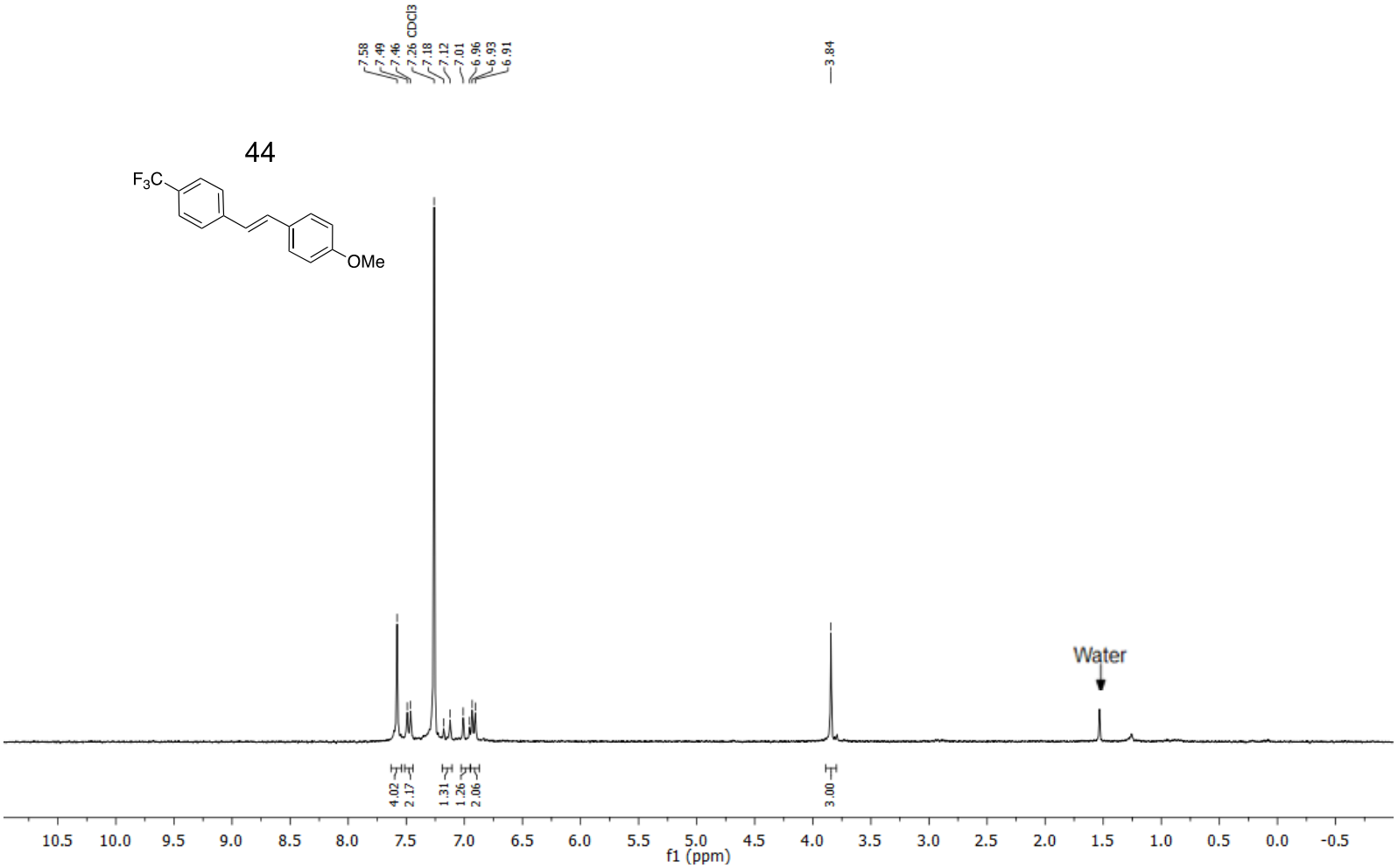


GC Trace of Crude Reaction Mixture

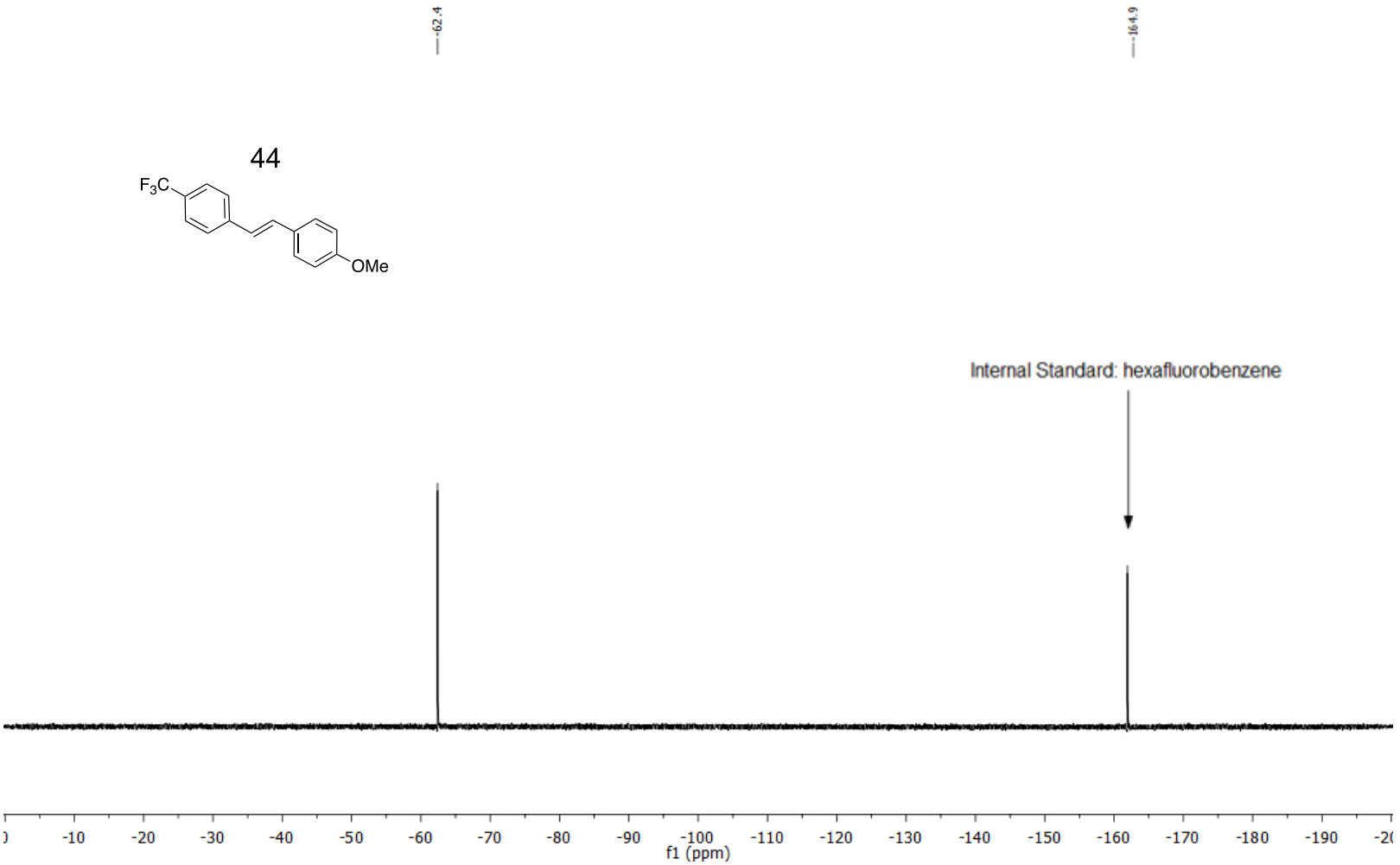


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.467	9758	4256	100.000				
Total		9758	4256					

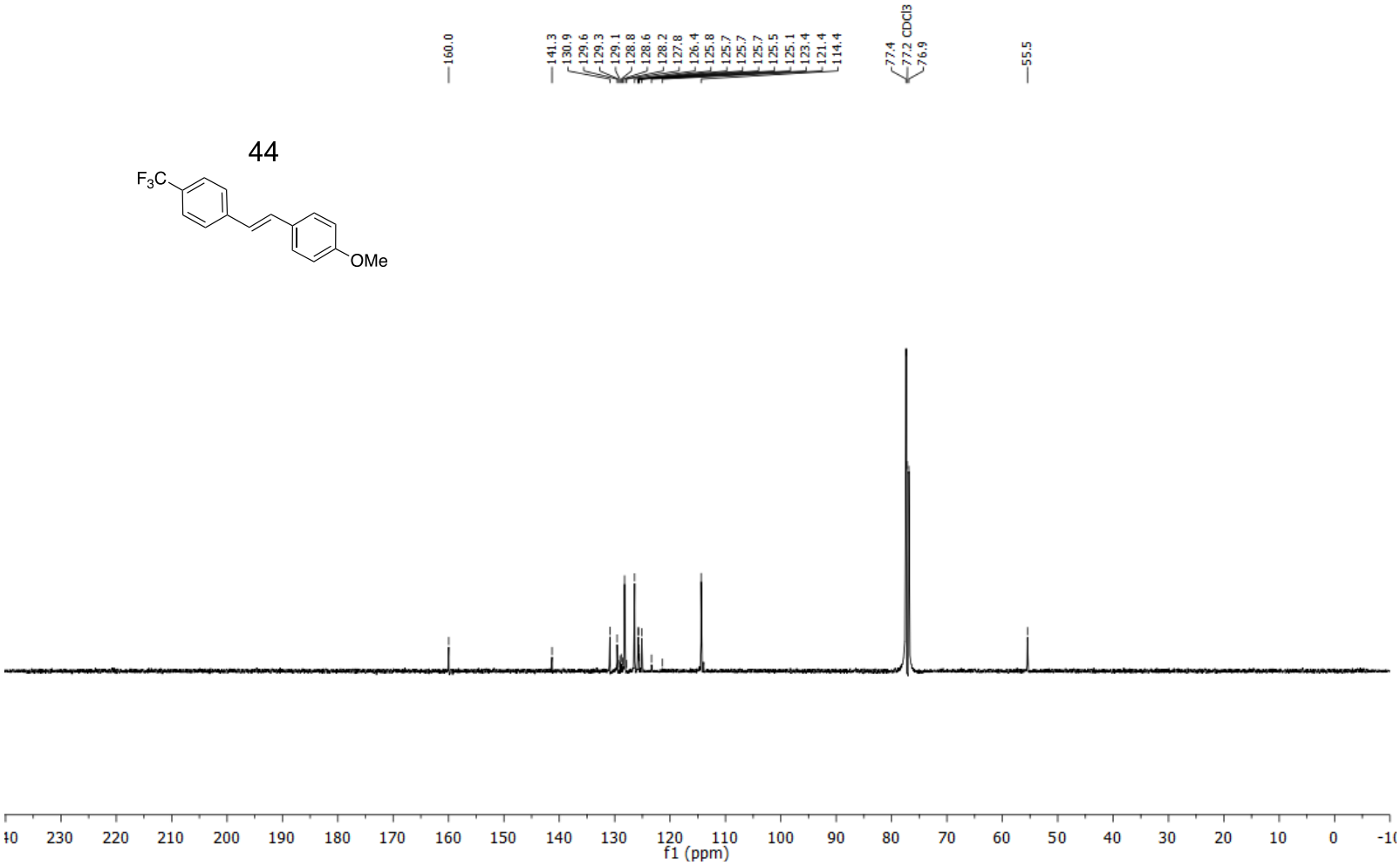
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 16.4 Hz, 1H), 6.98 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H).



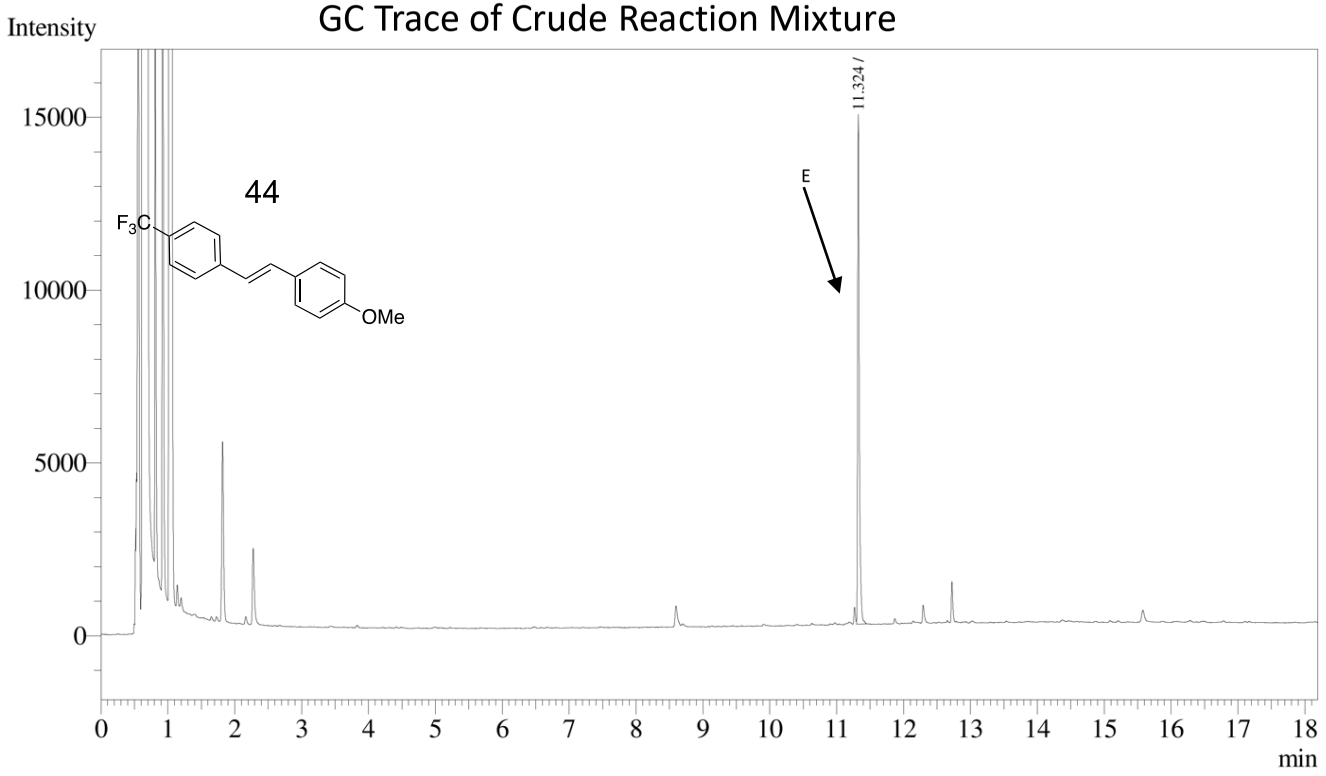
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.



^{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 .

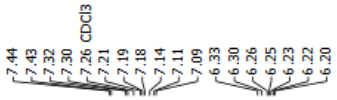


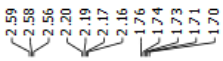
GC Trace of Crude Reaction Mixture

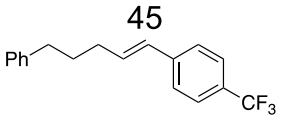


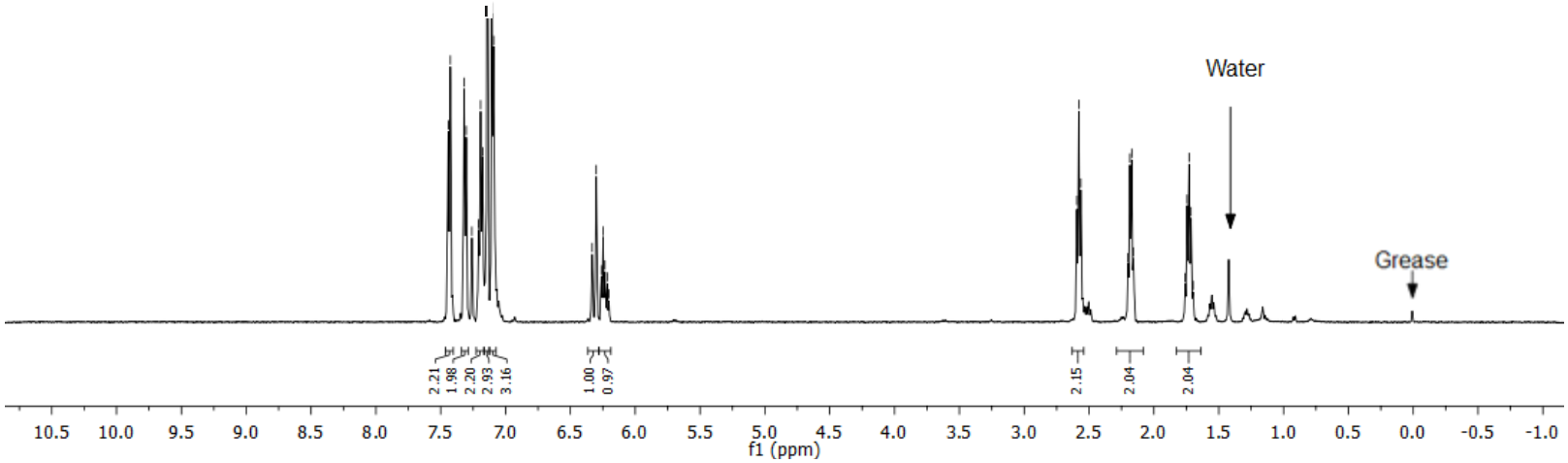
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.324	24744	14558	100.000		V		
Total		24744	14558					

^{1}H 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).

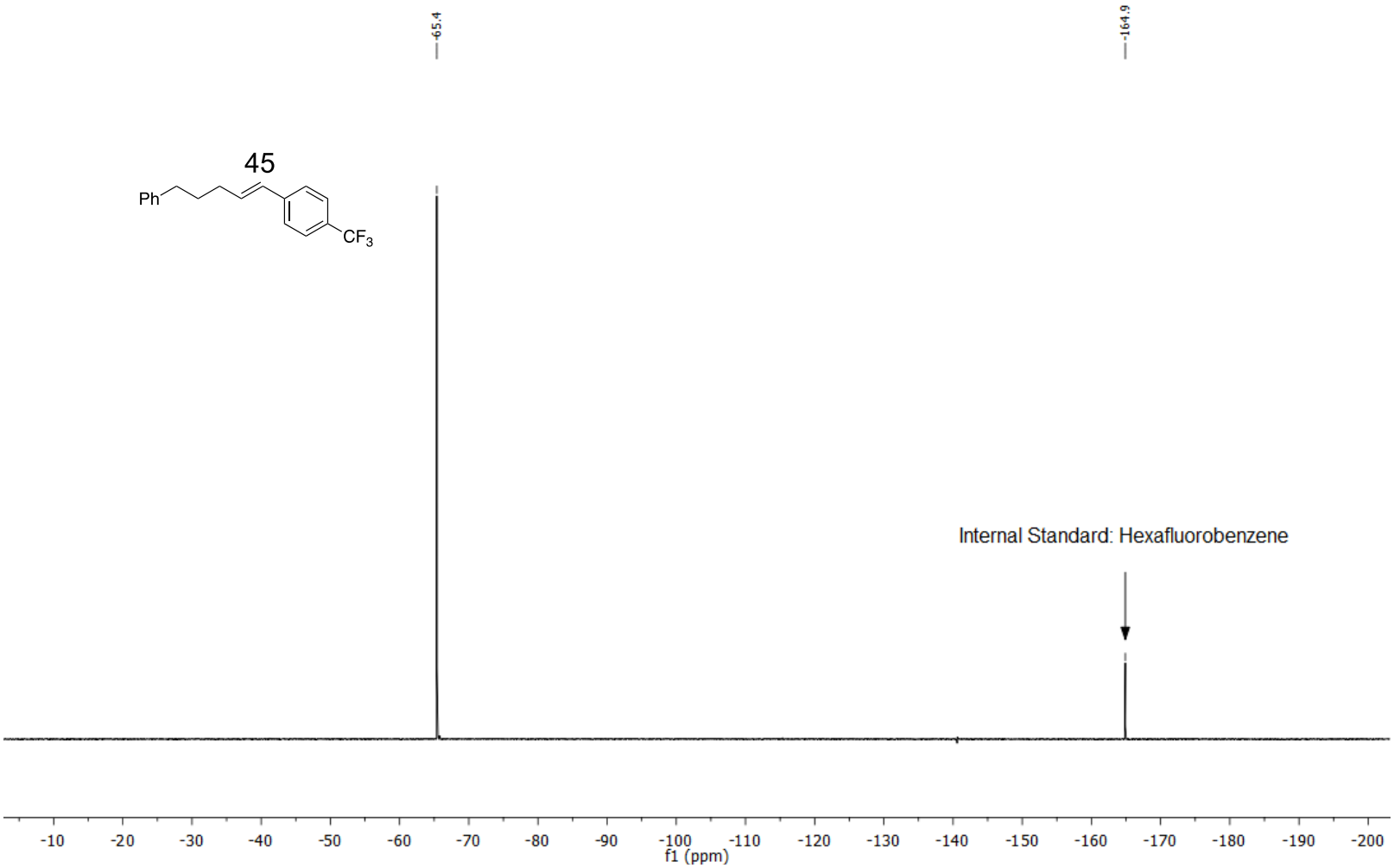




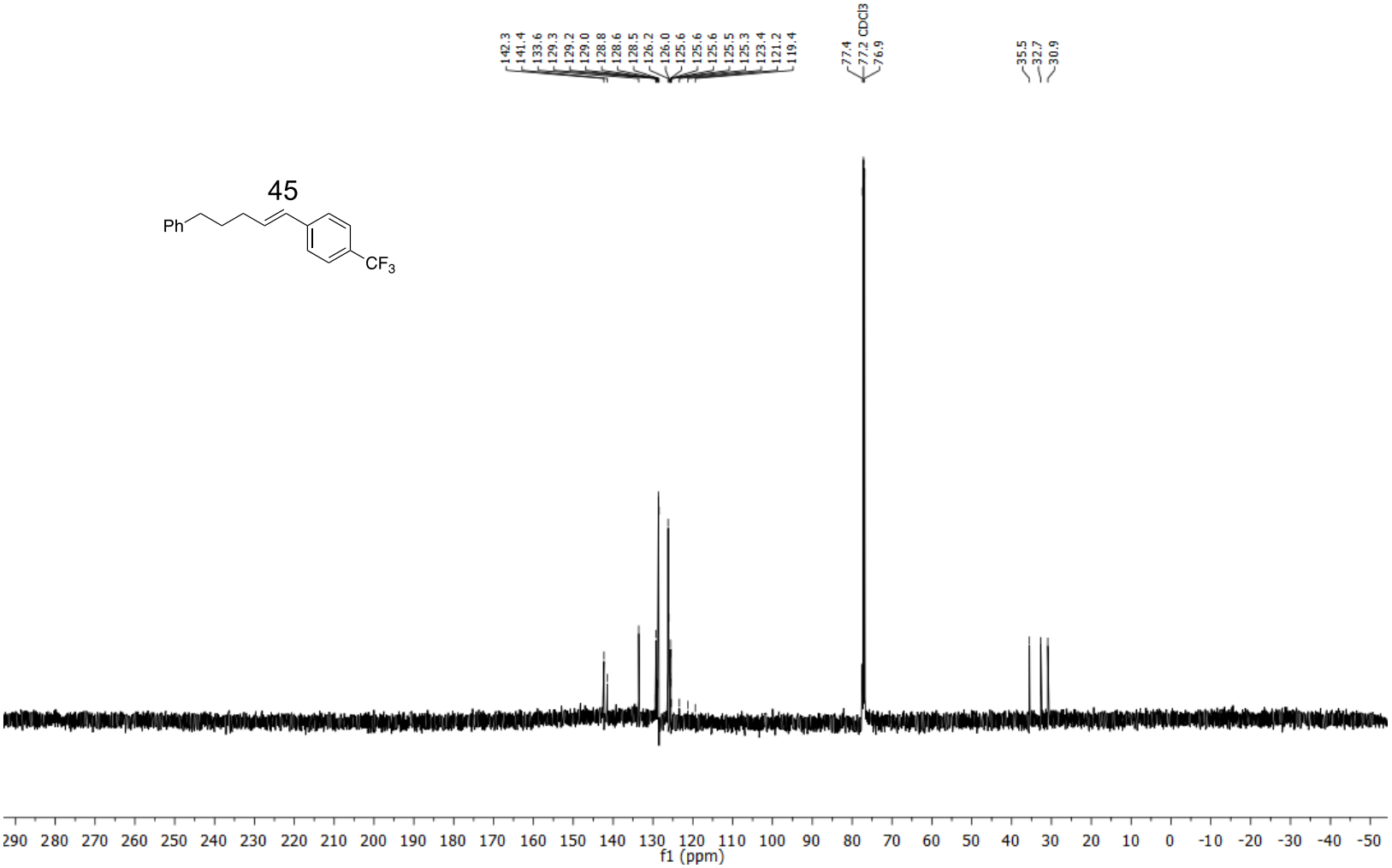


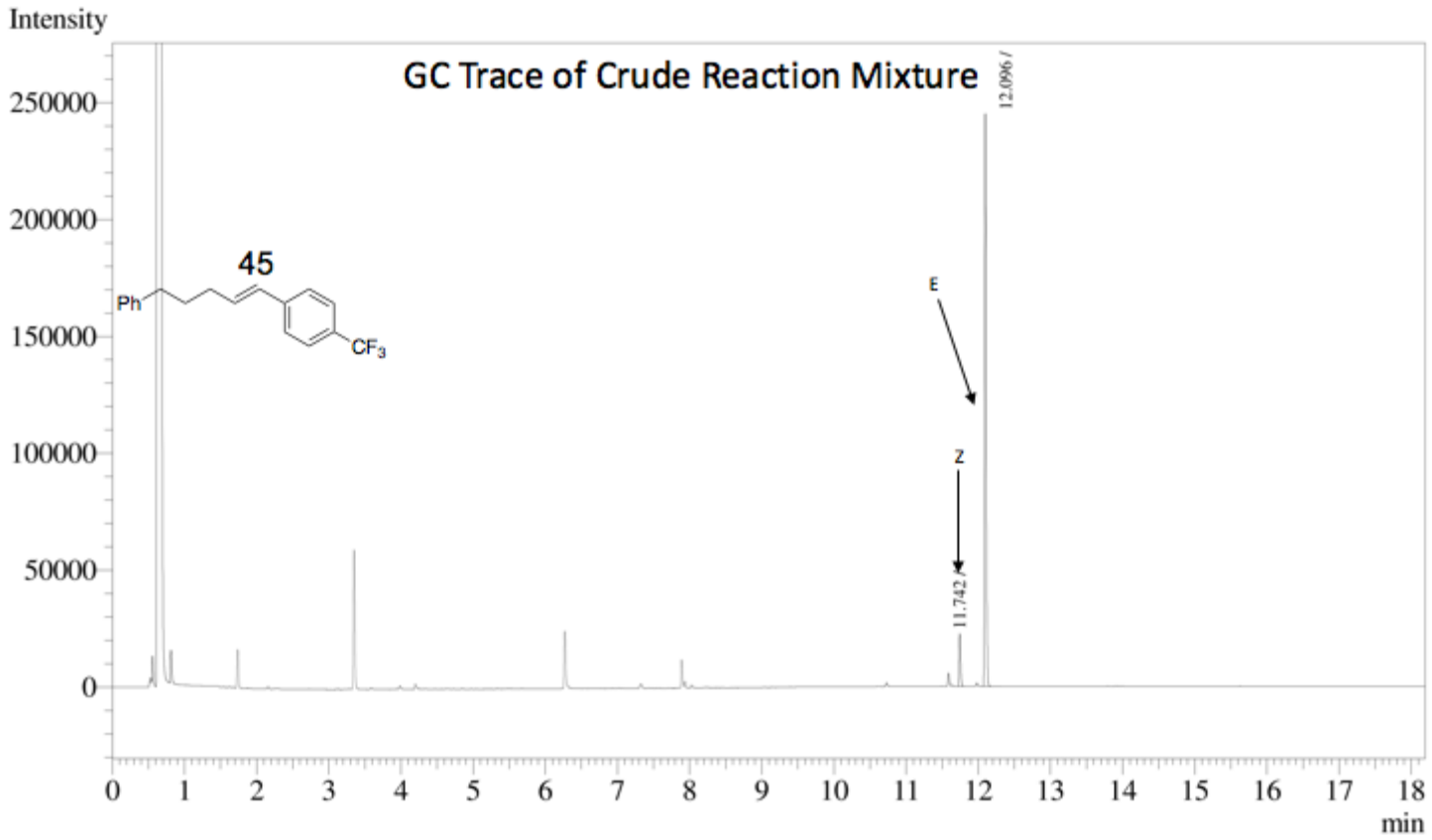


^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.4 .



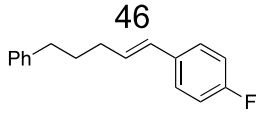
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.3 , 141.4 , 133.6 , 129.3 , 128.7 (q, *J* = 19.5 Hz), 128.6 , 128.5 , 126.0, 125.6 , 125.4 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 271.2 Hz), 35.5 , 32.7 , 30.9 .

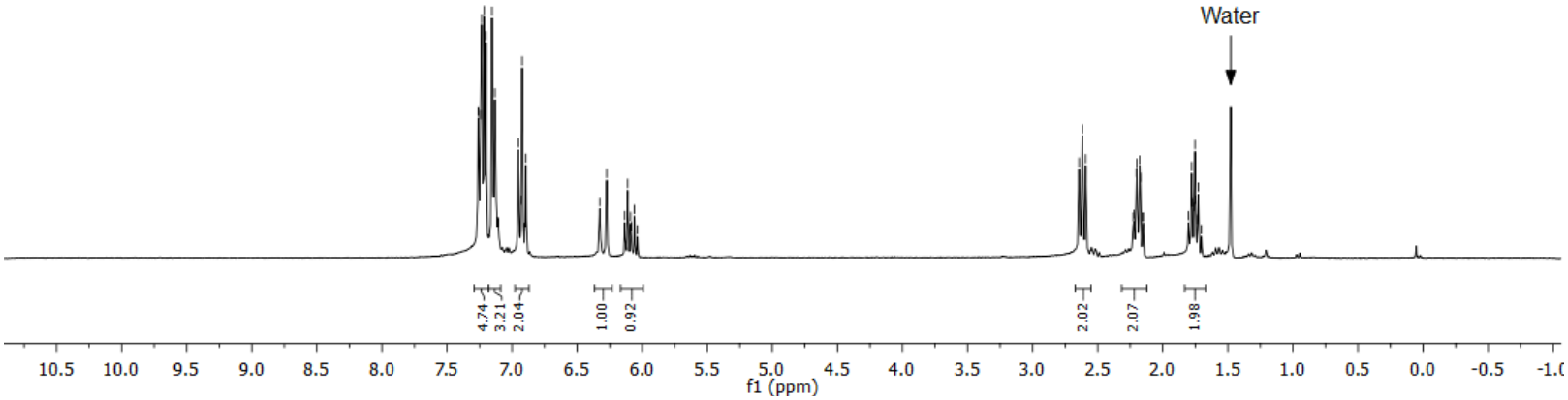




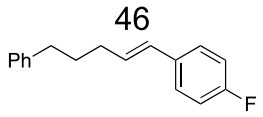
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.742	30972	21600	8.589				
2	12.096	329623	234370	91.411				
Total		360595	255970					

^{1}H 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).

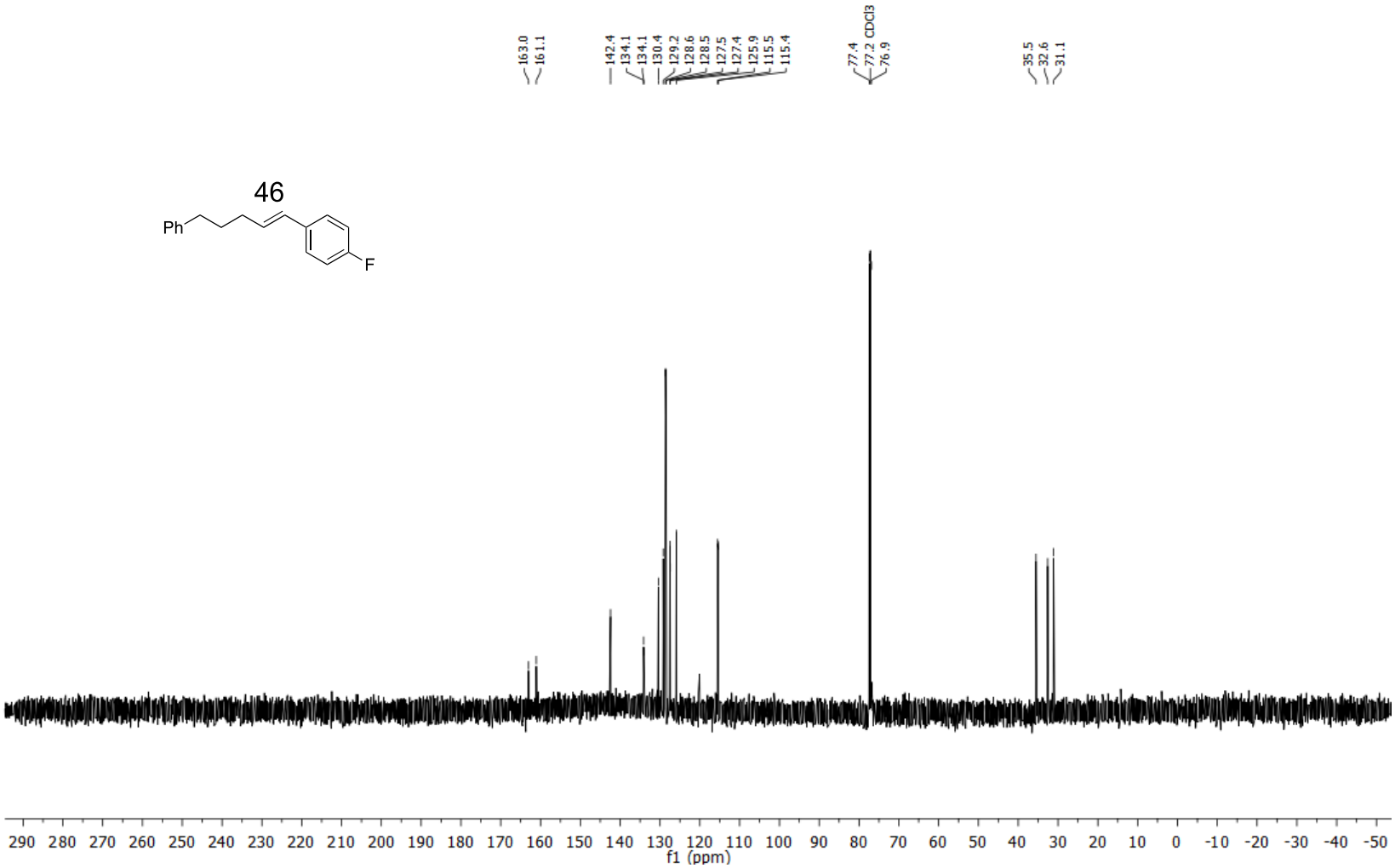


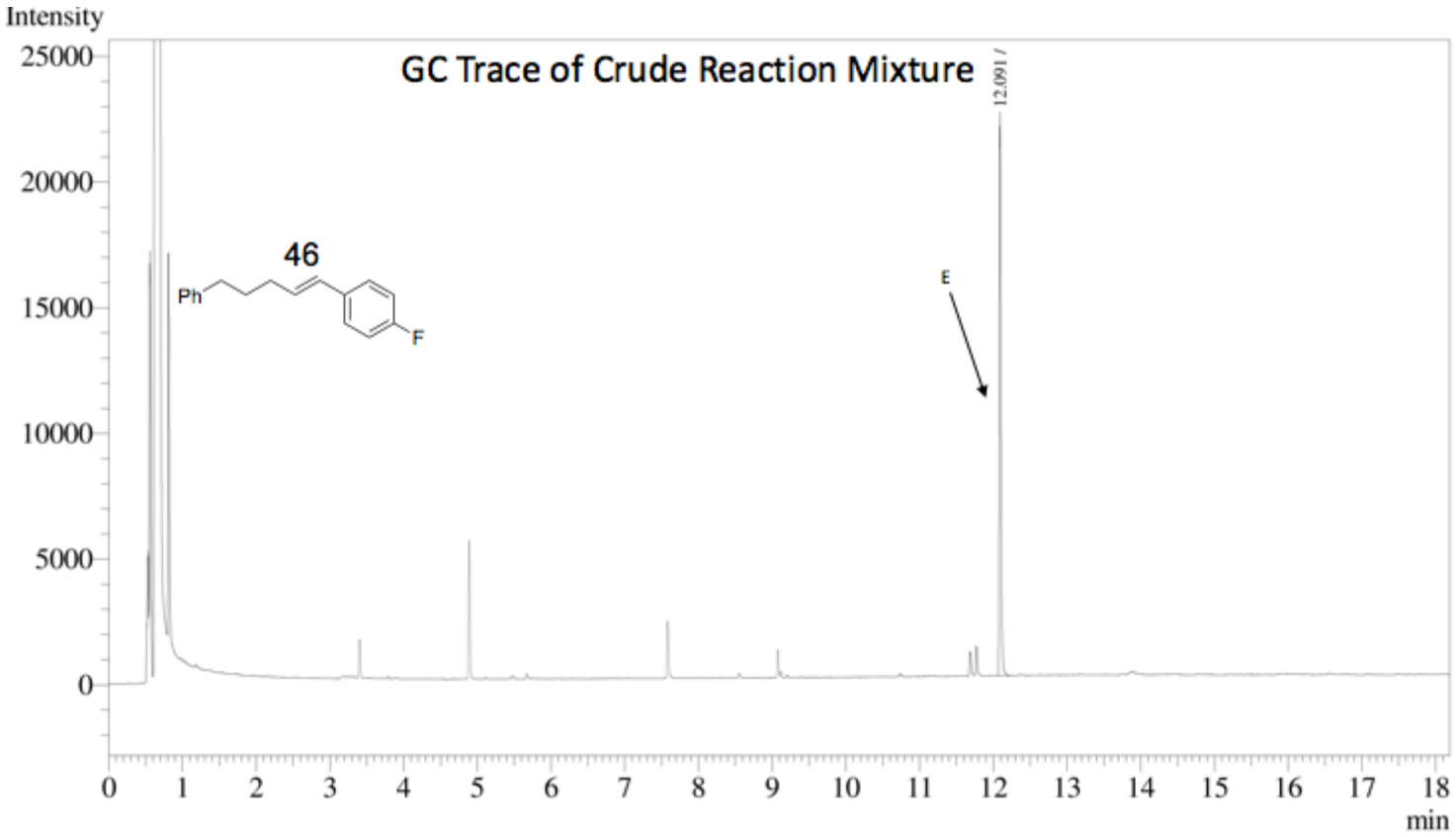


^{19}F NMR (471 MHz, Chloroform-*d*) δ -123.8.



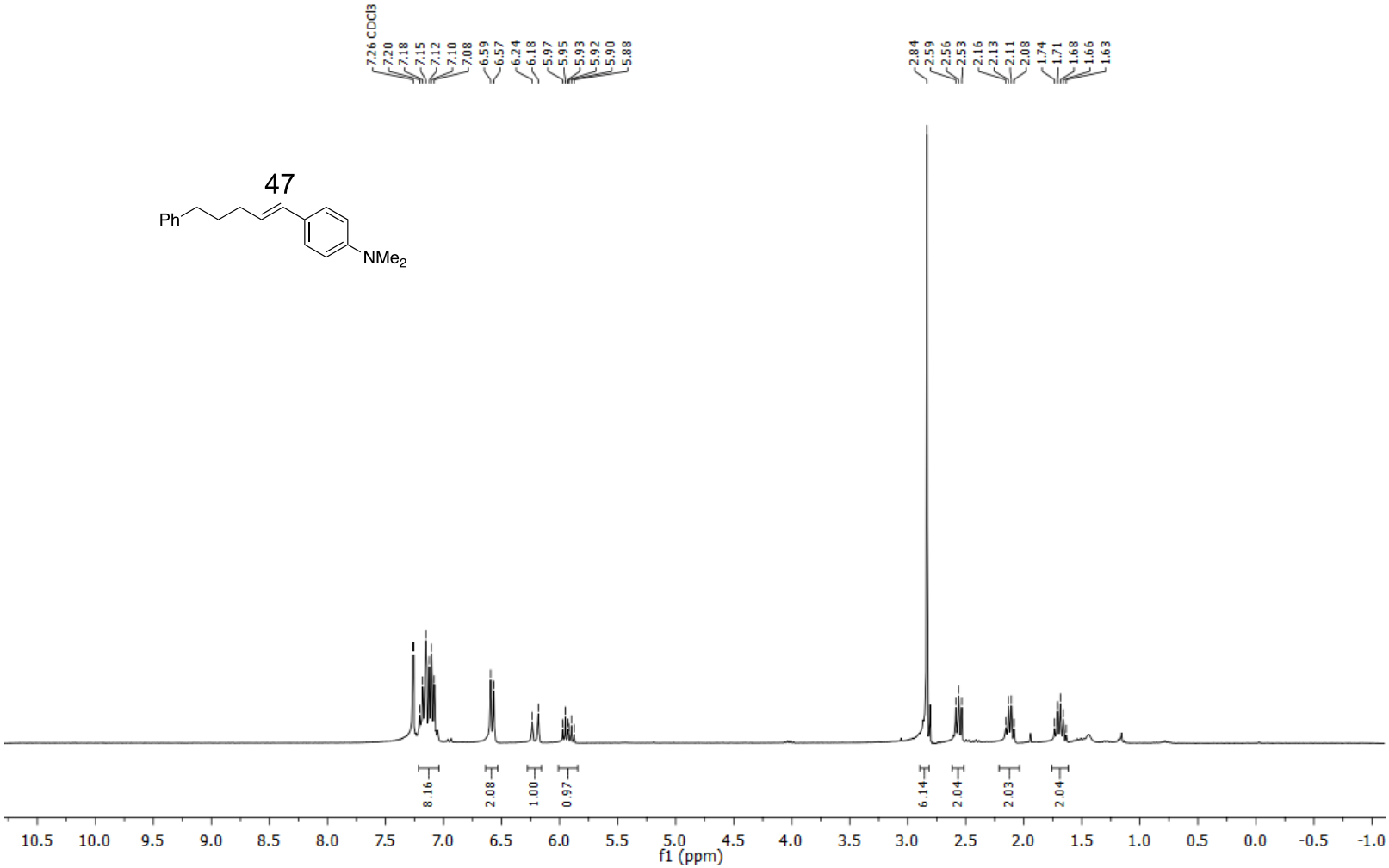
^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.6 Hz), 142.4 , 134.1 (d, *J* = 2.7 Hz), 130.4 , 129.2 , 128.6 (d, *J* = 17.5 Hz), 127.4 (d, *J* = 7.8 Hz), 125.9 , 115.5 , 115.4 , 35.5 , 32.6 , 31.1 .



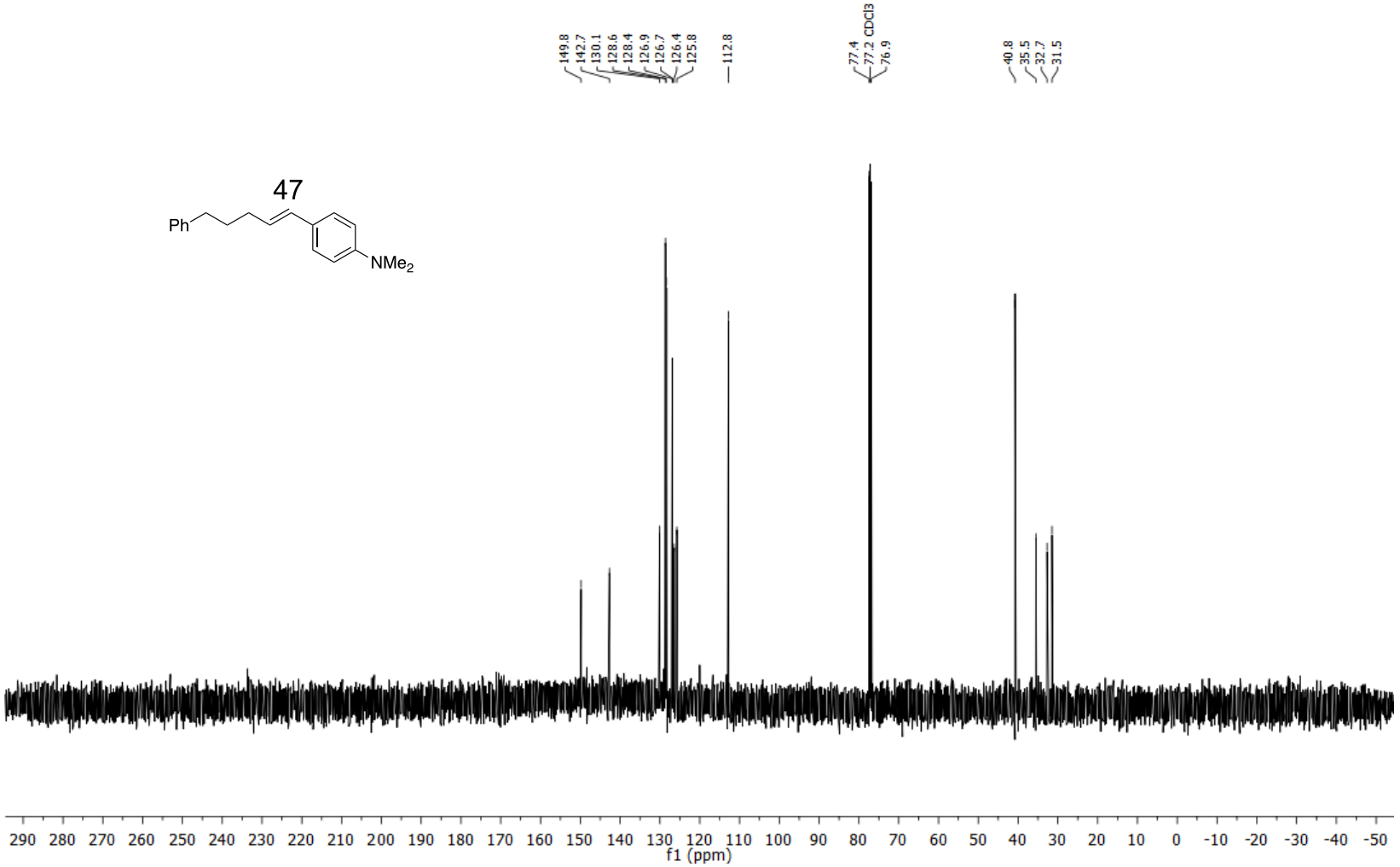


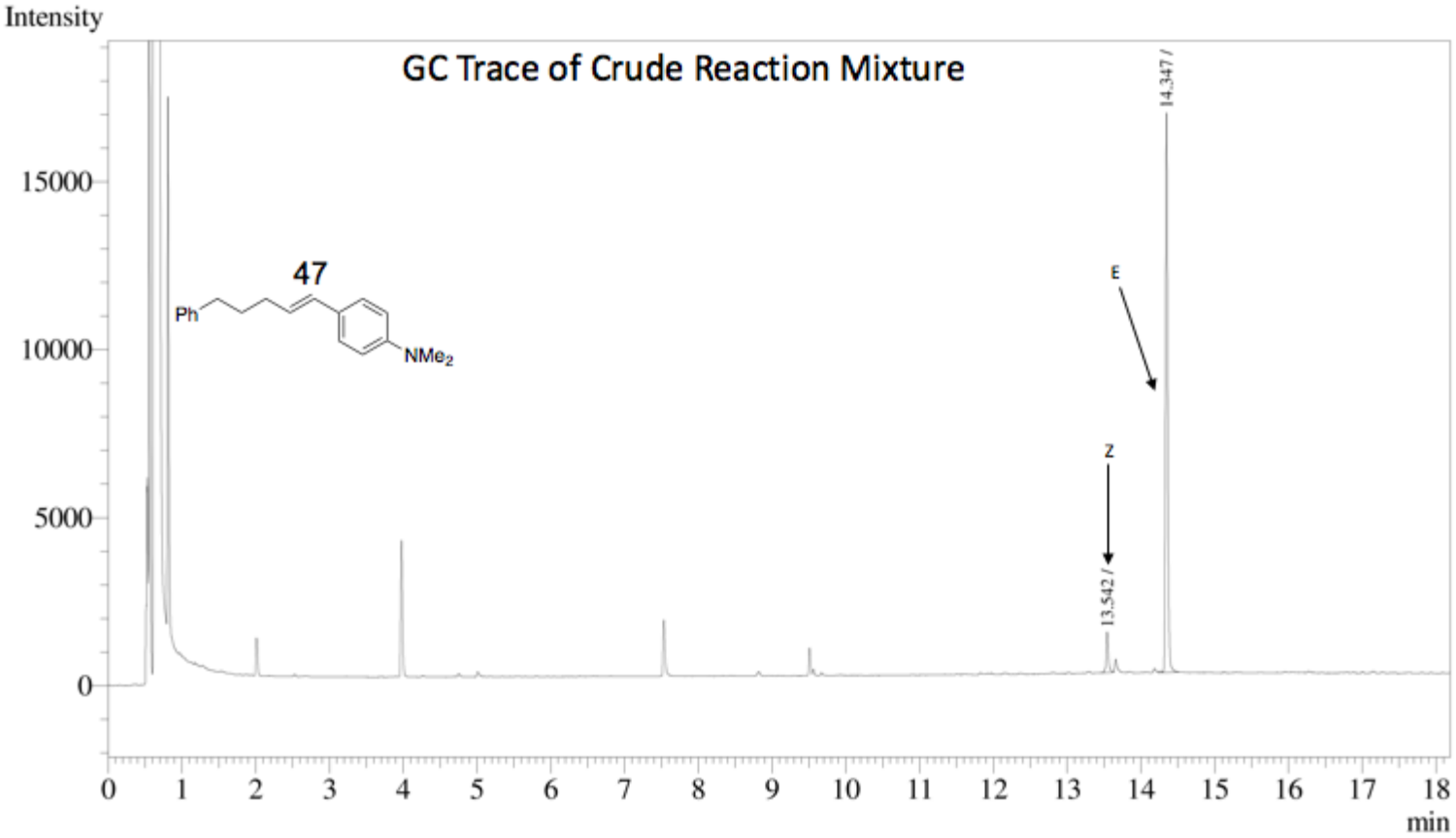
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.091	33249	21902	100.000				
Total		33249	21902					

^{1}H 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).



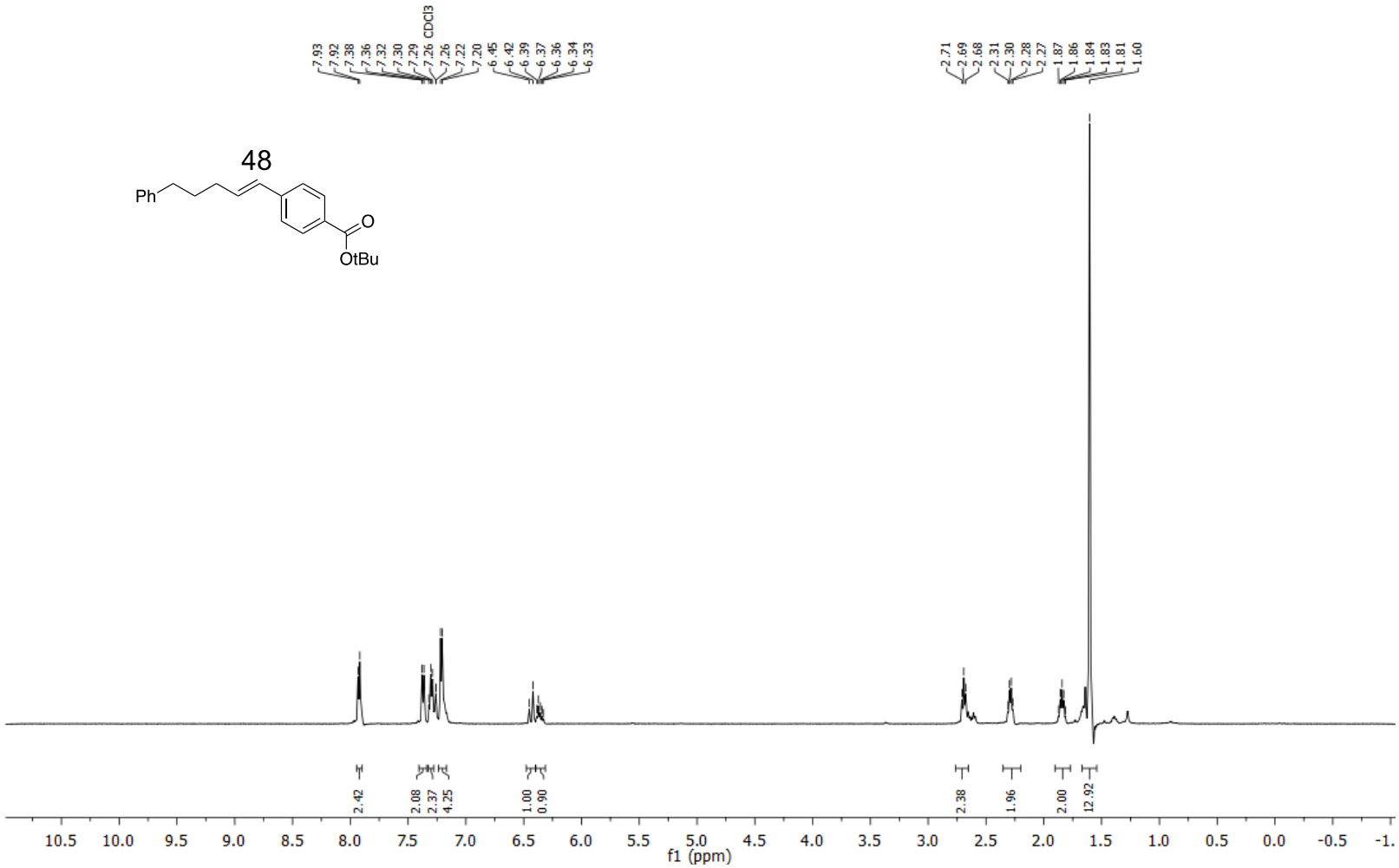
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.8 , 142.7 , 130.1 , 128.6 , 128.4 , 126.9 , 126.7 , 126.4 , 125.7 , 112.7 , 40.7 , 35.5 , 32.7 , 31.5 .



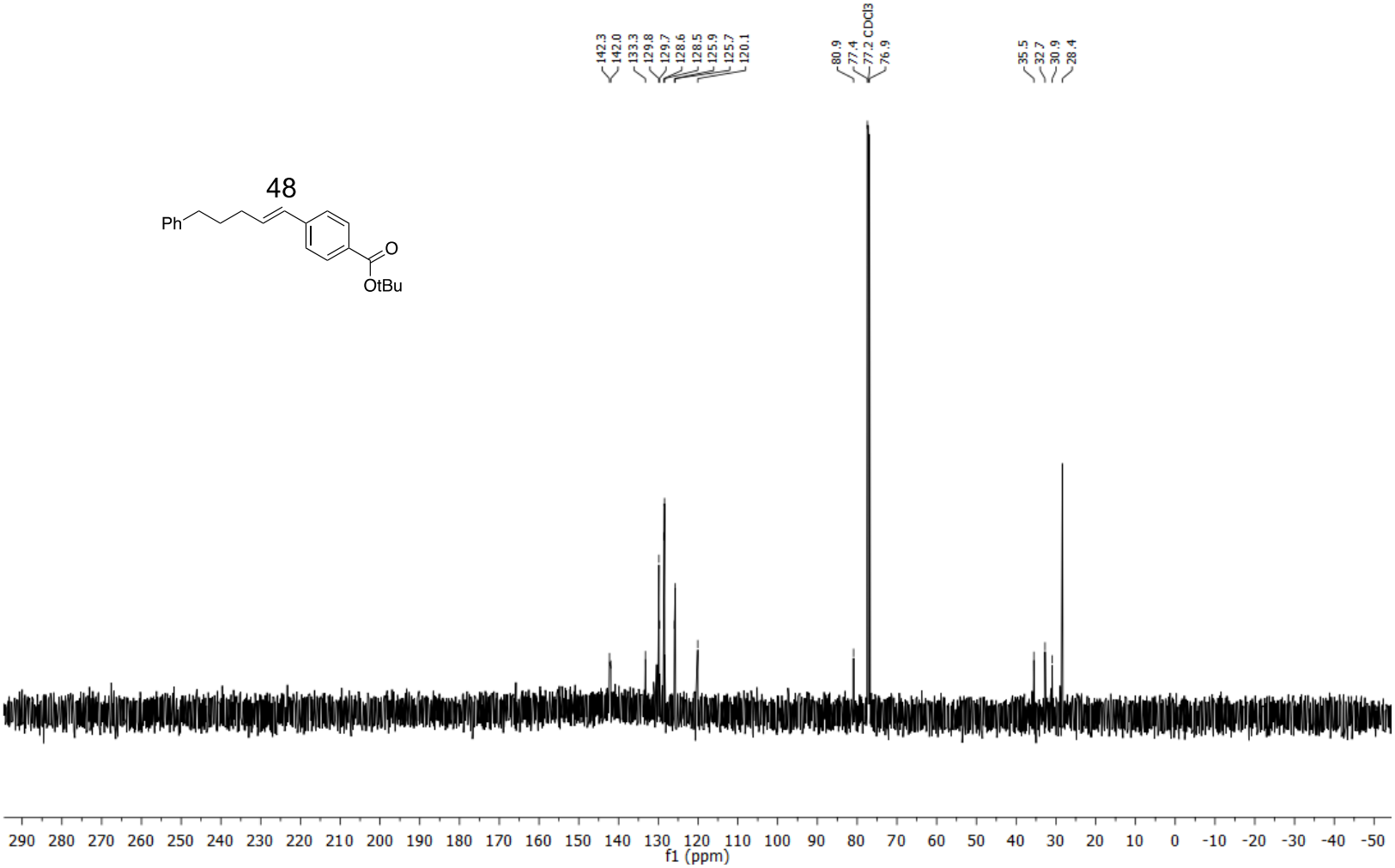


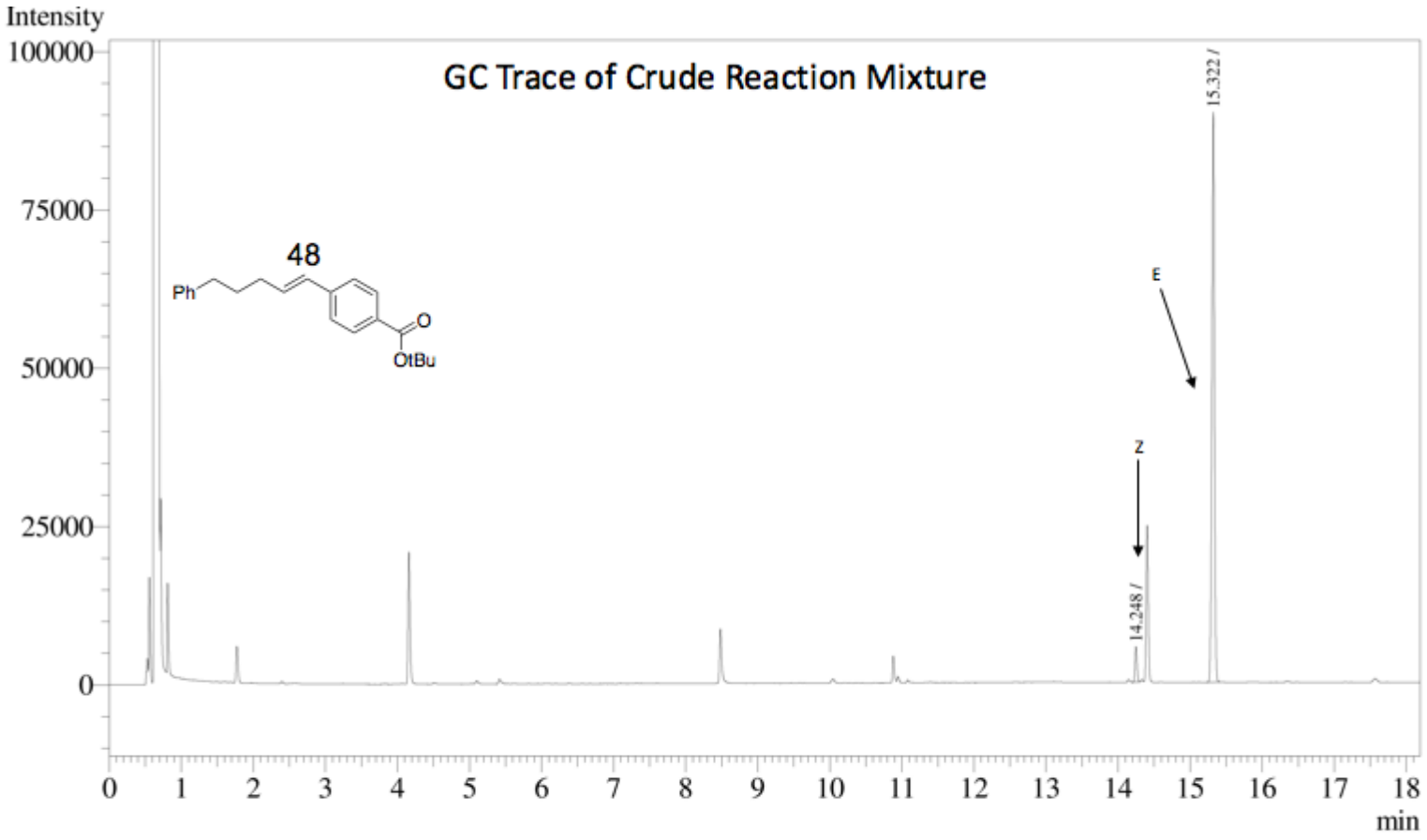
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.542	2486	1195	6.709				
2	14.347	34571	16462	93.291		V		
Total		37057	17657					

^{1}H 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).



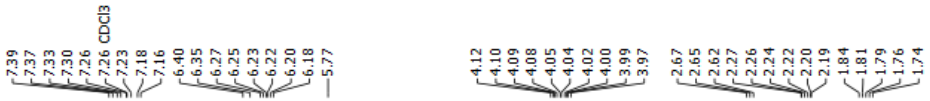
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.3 , 142.0 , 133.3 , 129.8 , 129.7 , 128.6 , 128.5 , 125.9 , 125.7 , 120.1 , 80.9 , 35.5 , 32.7 , 30.9 , 28.4 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.248	10694	5525	4.647				
2	15.322	219419	89235	95.353				
Total		230113	94760					

^{1}H 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)



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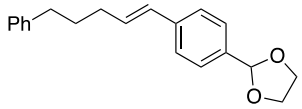
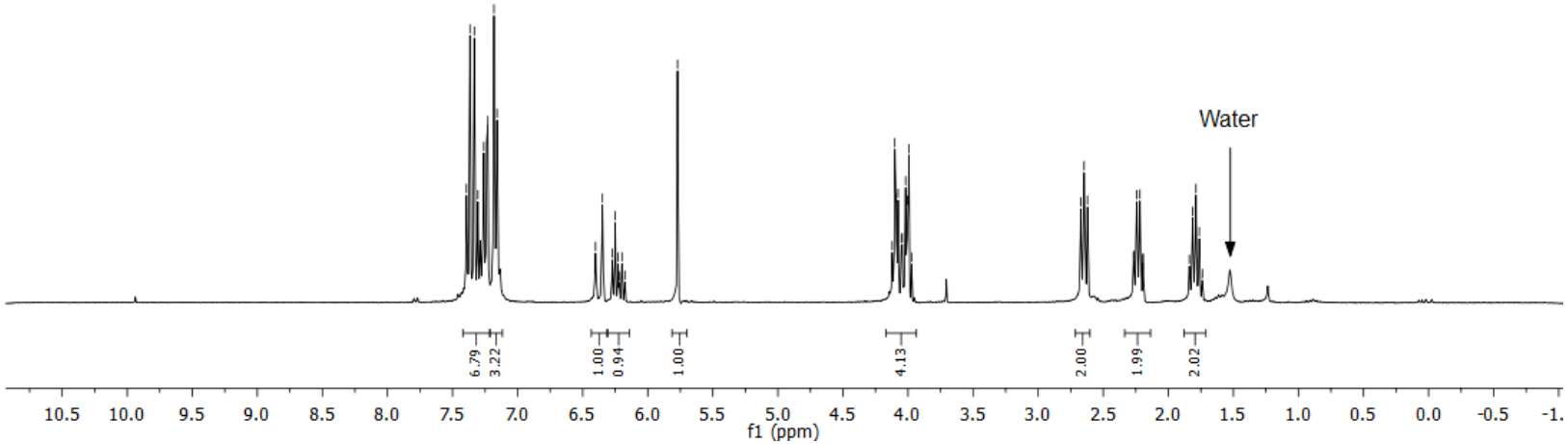
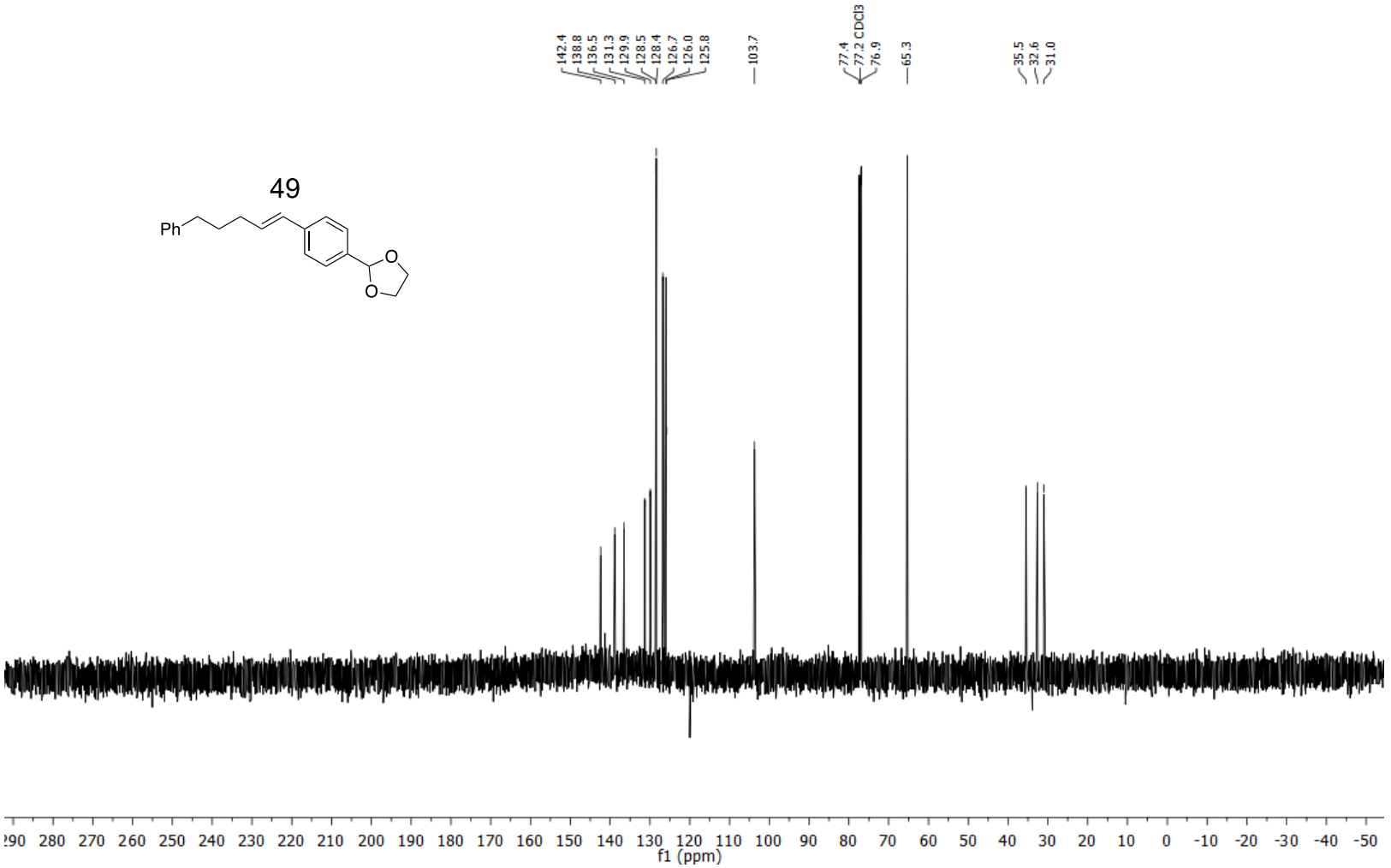
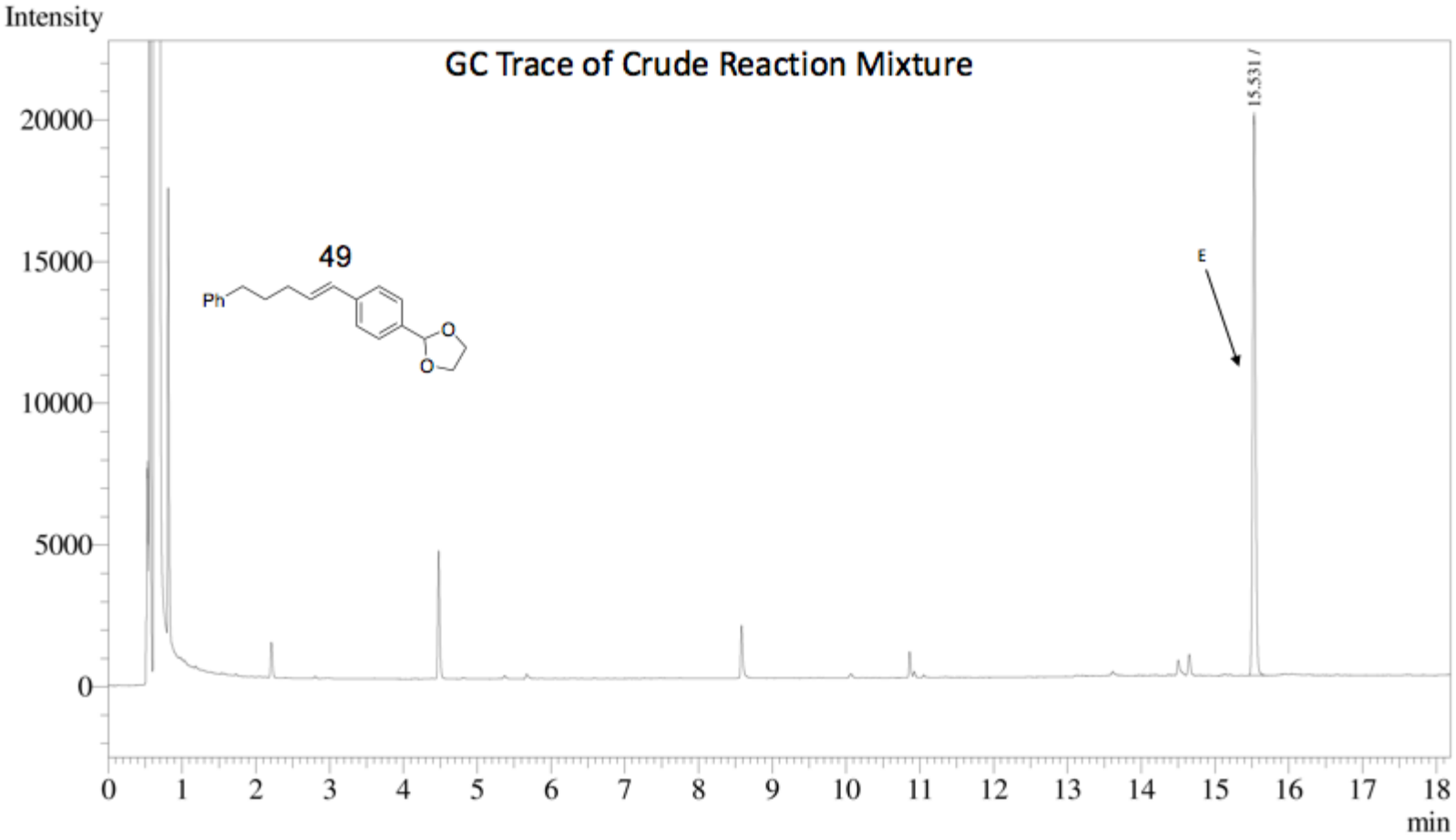




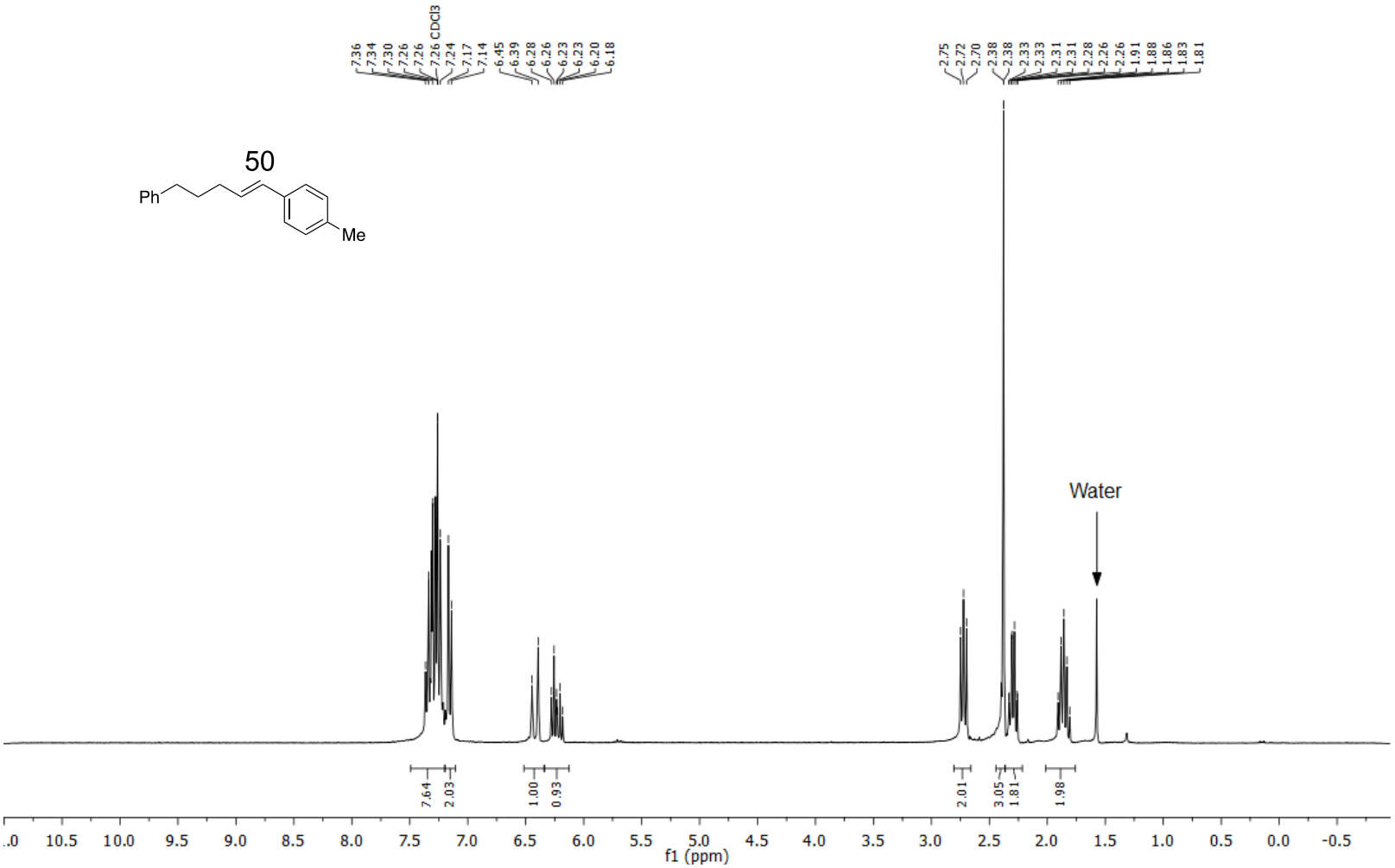
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4 , 138.8 , 136.5 , 131.3 , 129.9 , 128.5 , 128.4 , 126.7 , 126.0 , 125.8 , 103.7 , 65.3 , 35.5 , 32.6 , 31.0 .



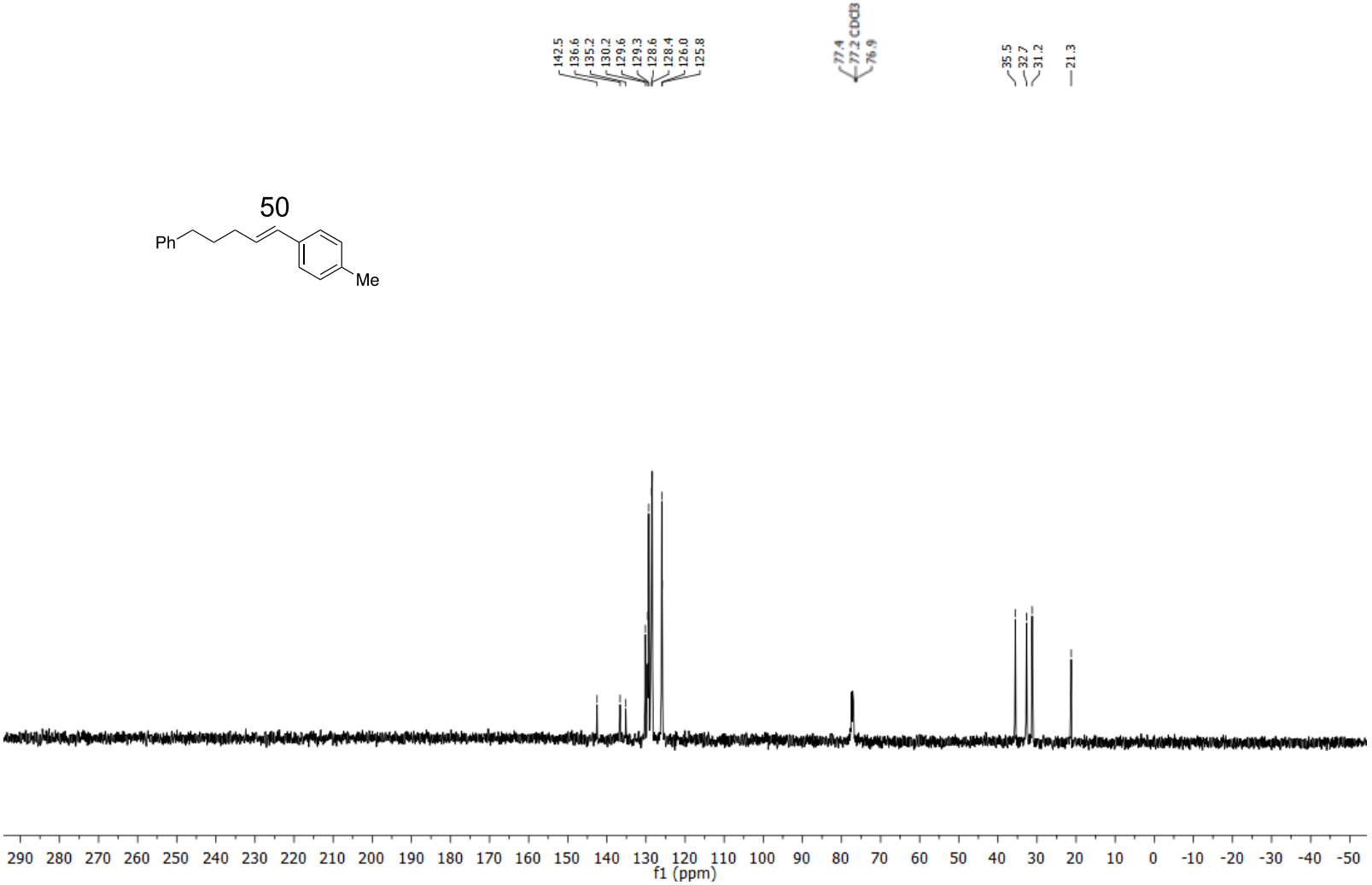


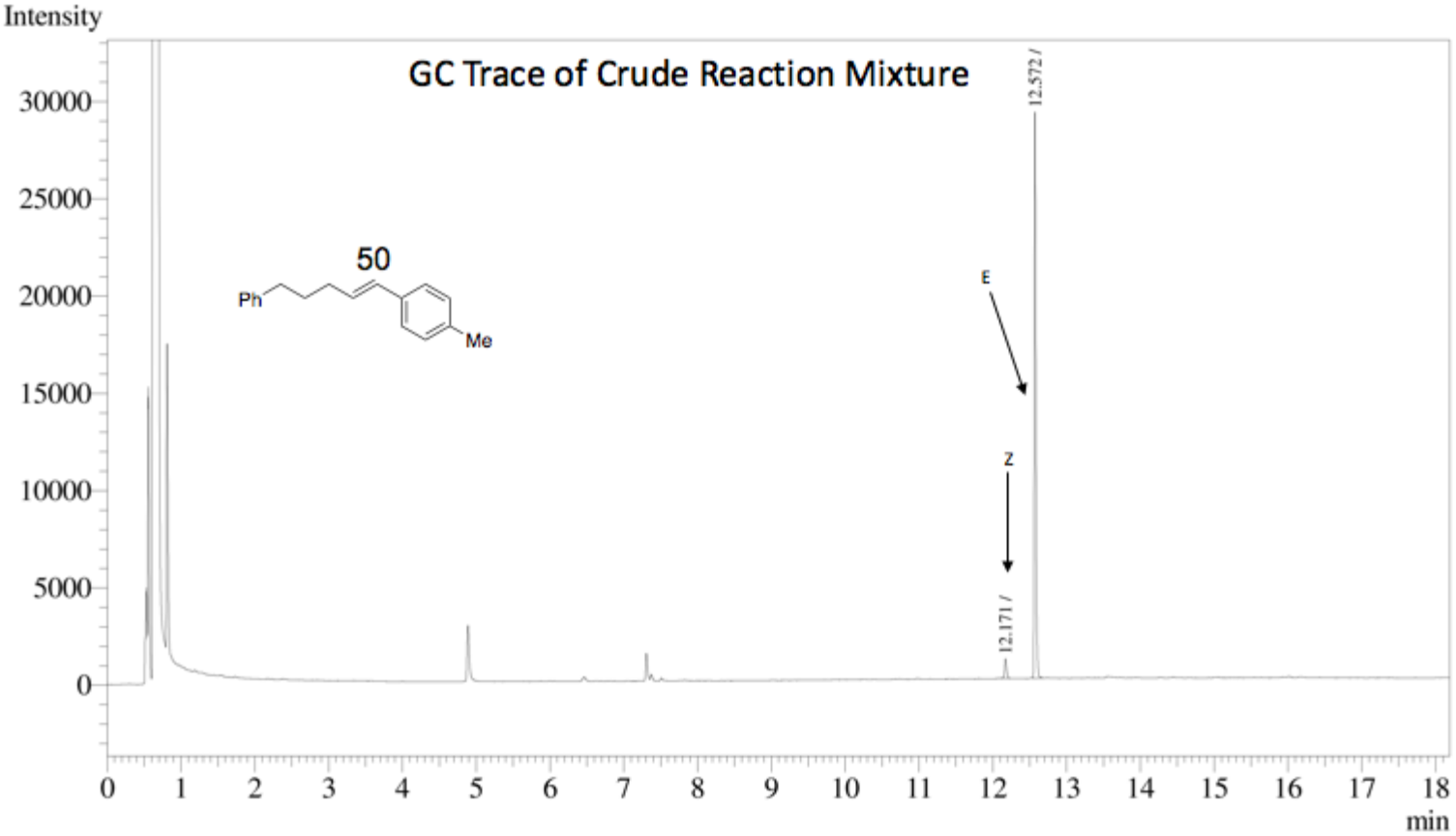
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	15.531	52679	19692	100.000				
Total		52679	19692					

^{1}H 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).



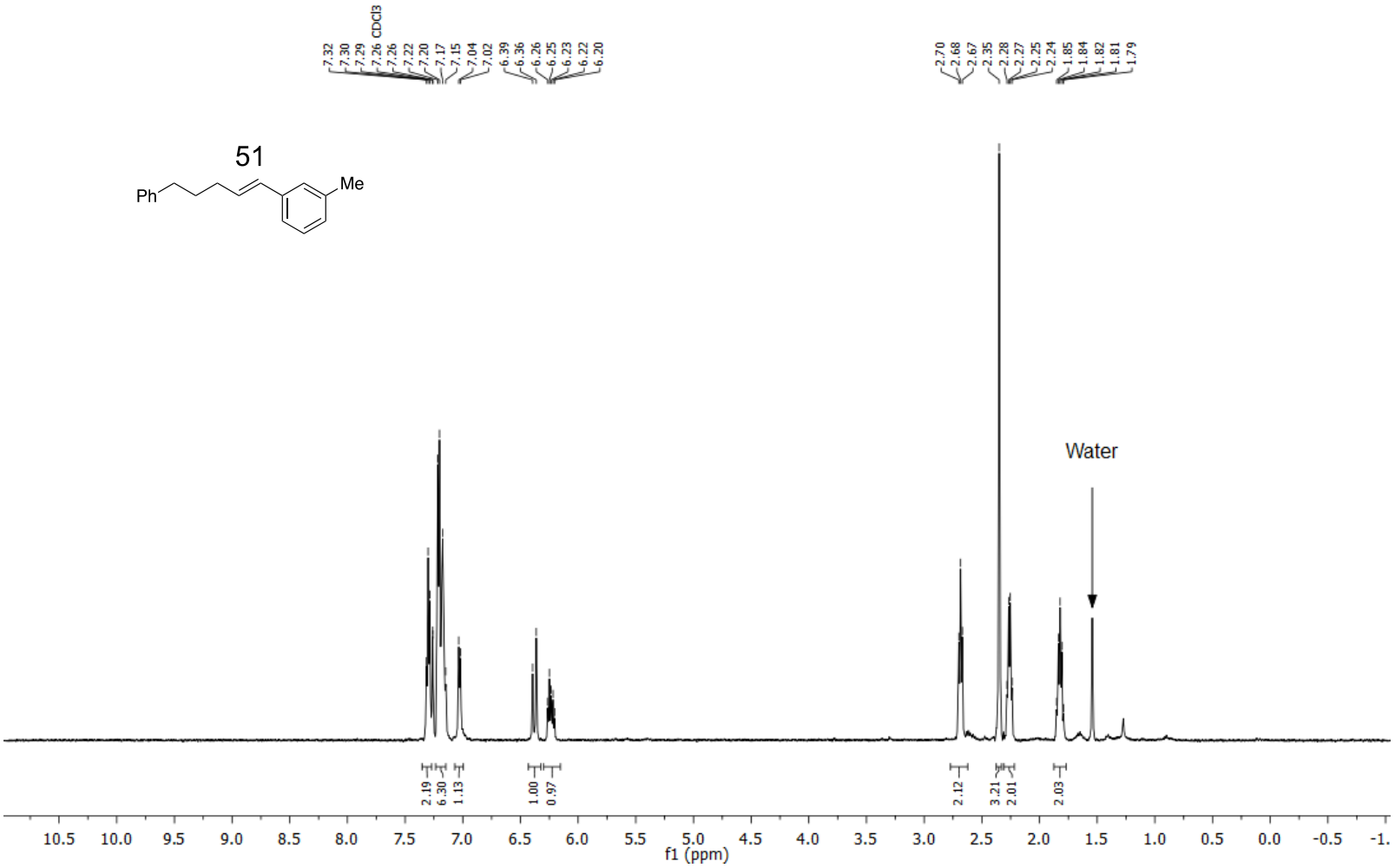
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.5 , 136.6 , 135.2 , 130.2 , 129.6 , 129.3 , 128.6 , 128.4 , 126.0 , 125.8 , 35.5 , 32.7 , 31.2 , 21.3 .



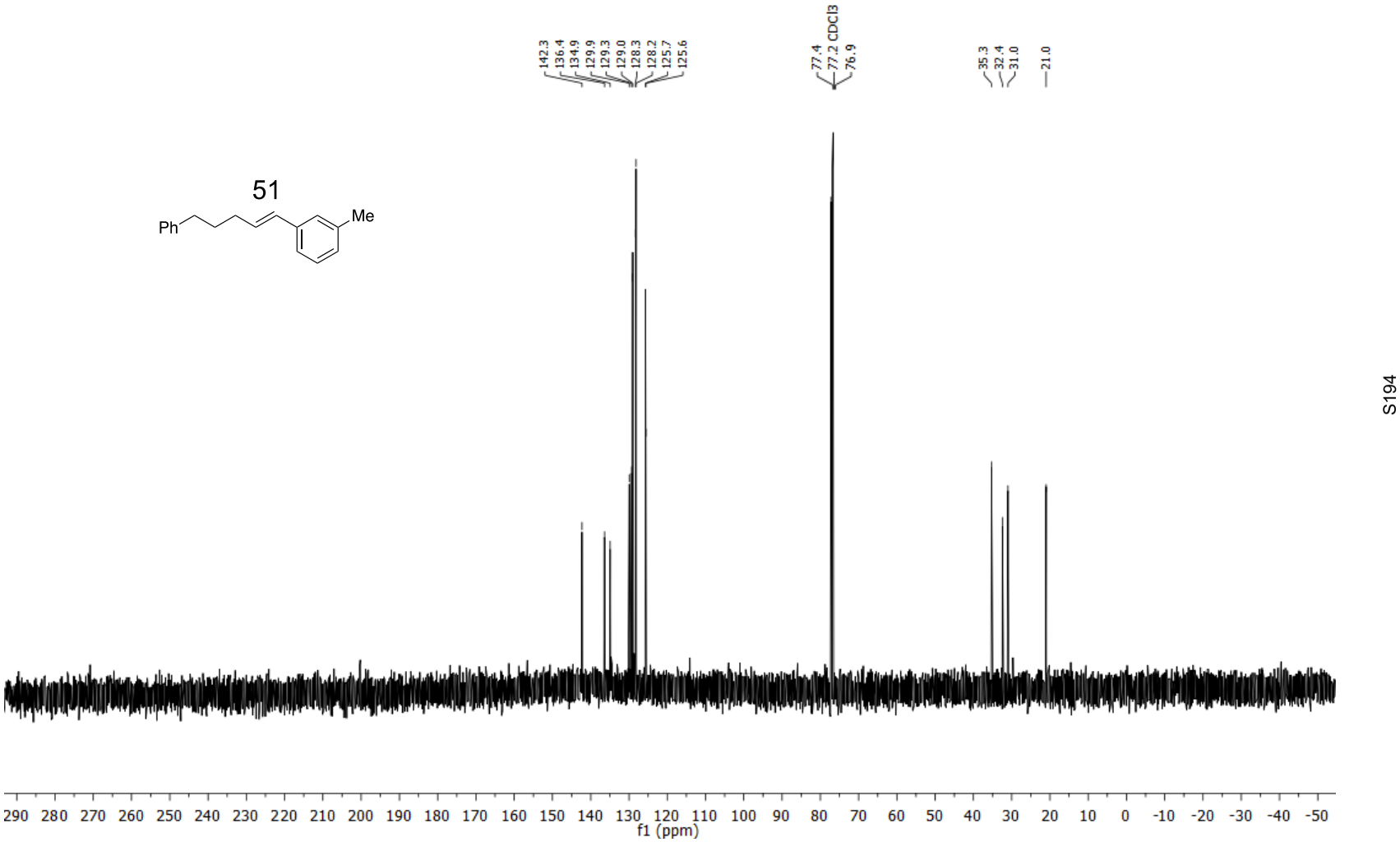


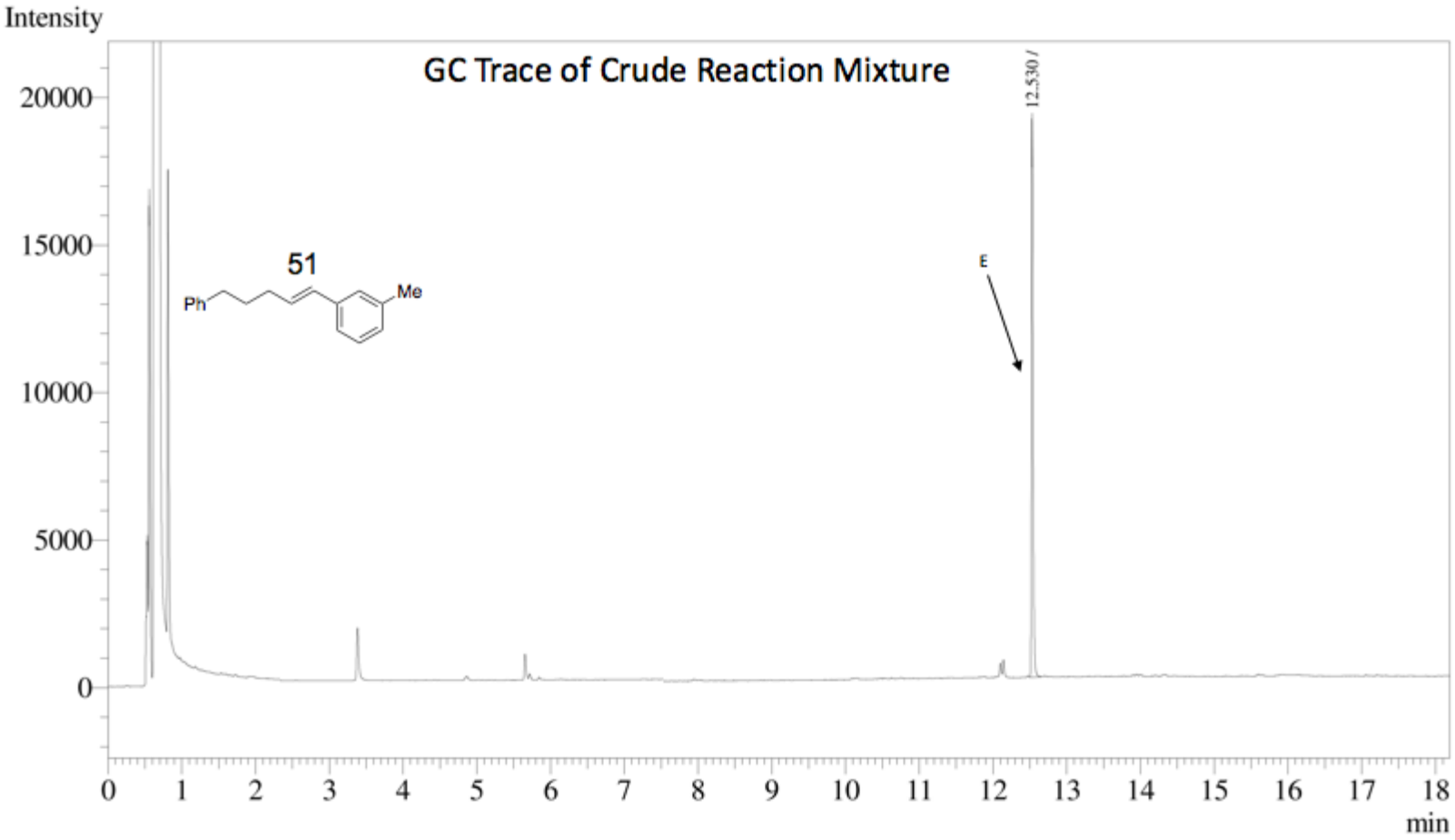
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.171	1868	996	4.359				
2	12.572	40991	27846	95.641		V		
Total		42859	28842					

^{1}H 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).



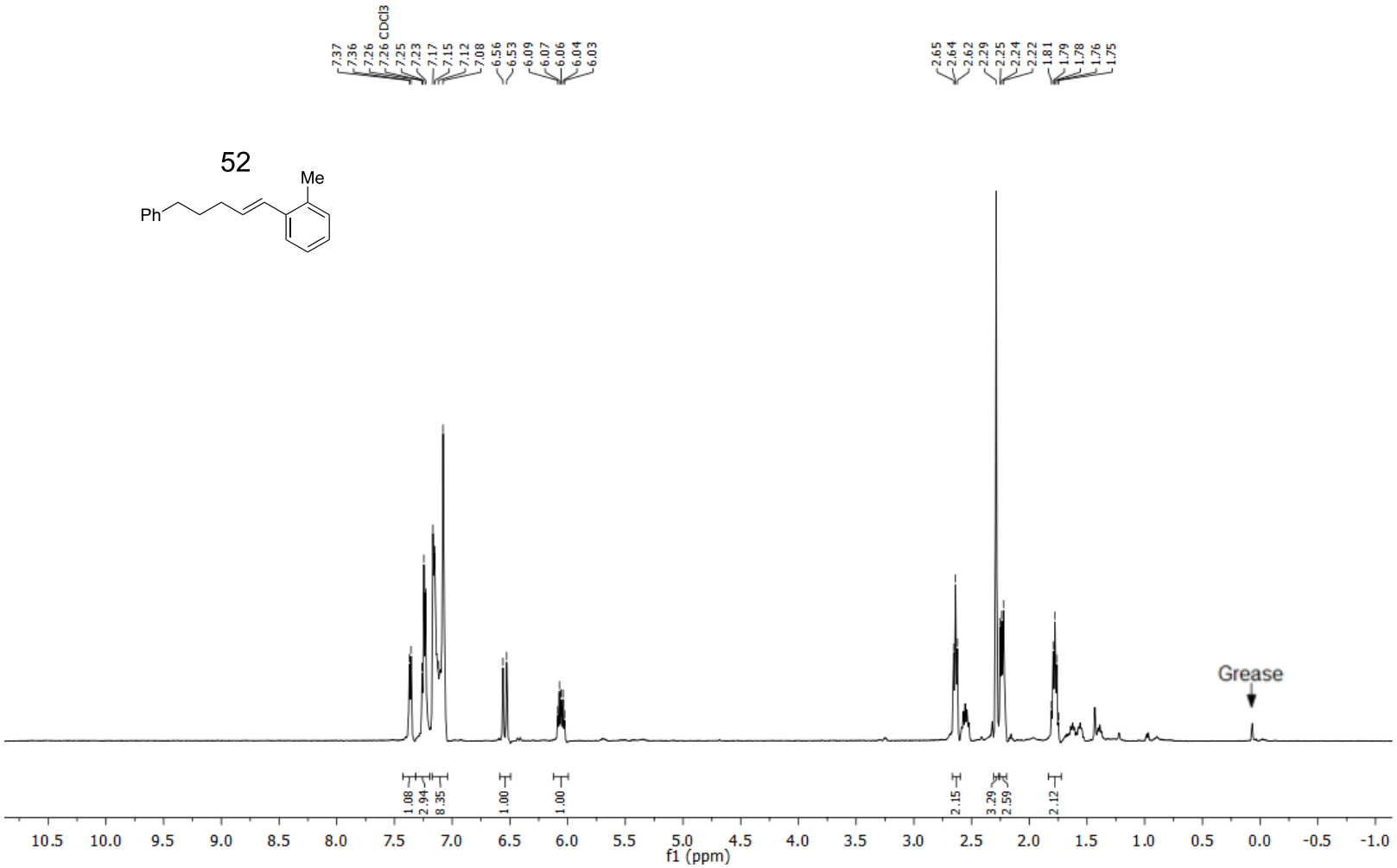
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.3 , 136.4 , 134.9 , 129.9 , 129.3 , 129.0 , 128.3 , 128.2 , 125.7 , 125.6 , 35.3 , 32.4 , 31.0 , 21.0 .



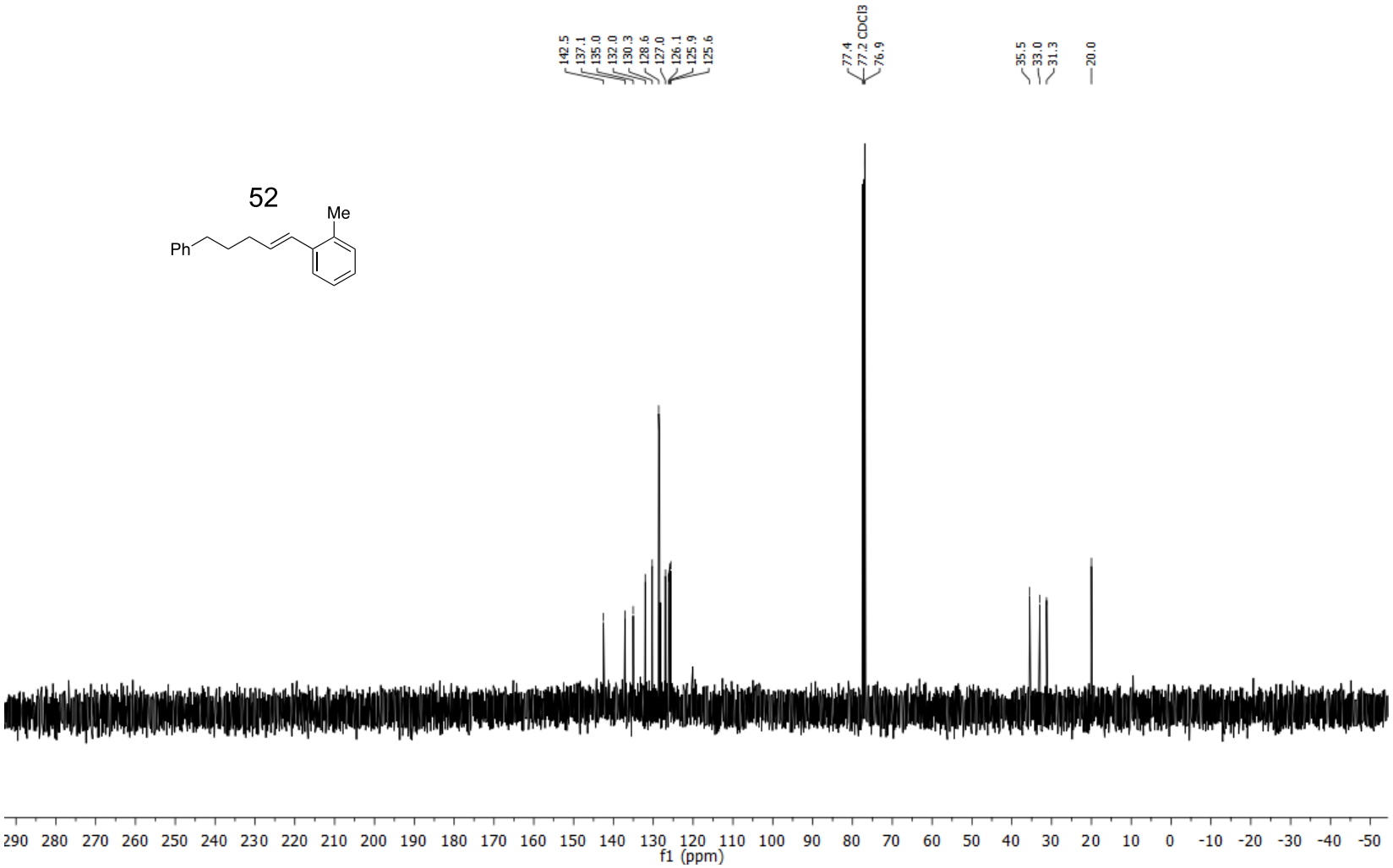


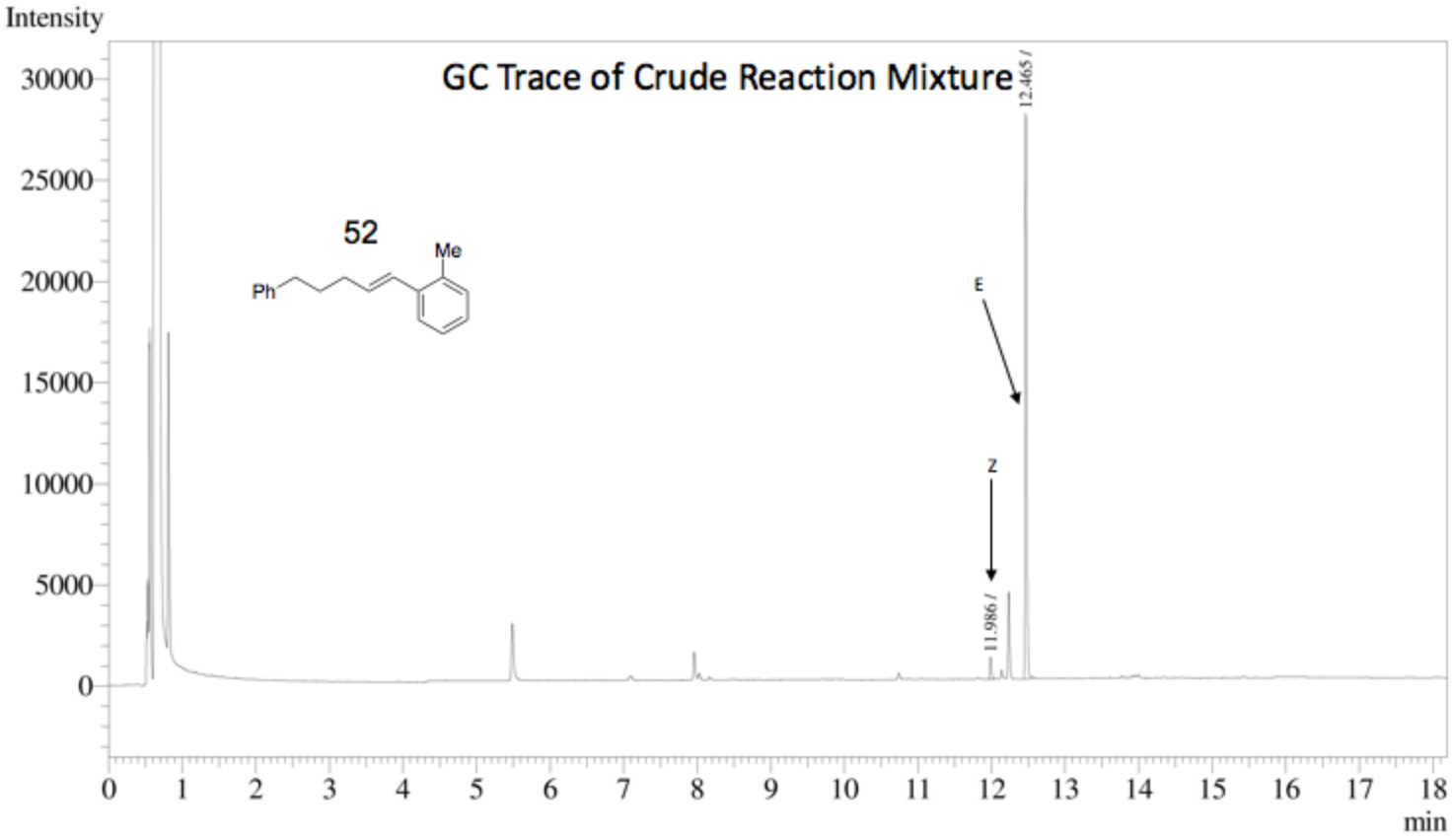
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.530	27853	18411	100.000		V		
Total		27853	18411					

^{1}H 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).



^{13}C 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 .





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.986	1628	1088	3.977				
2	12.465	39301	26666	96.023				
Total		40929	27754					

^{1}H 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).

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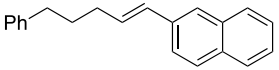
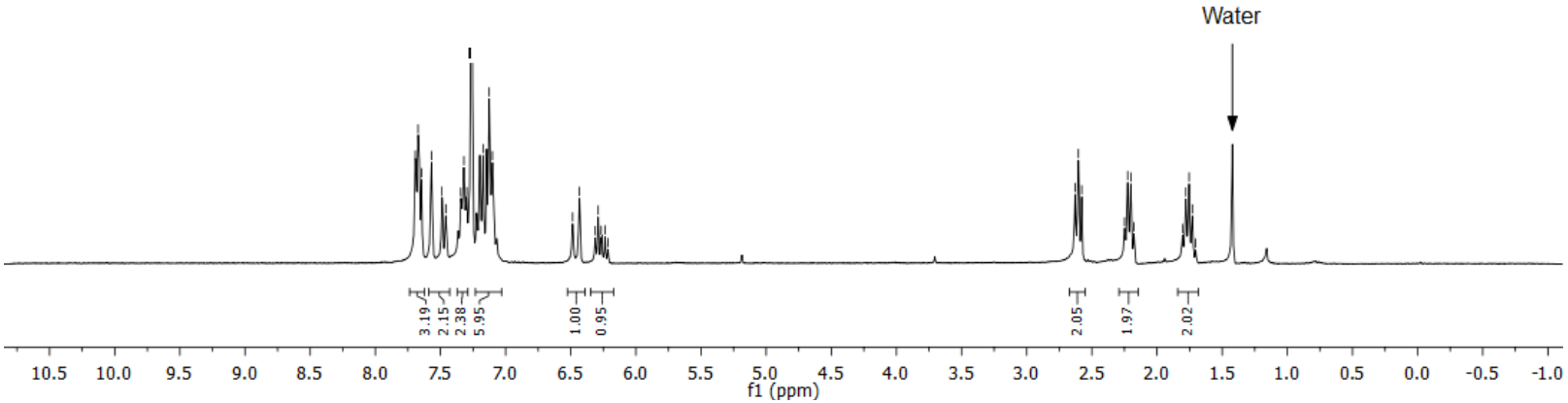
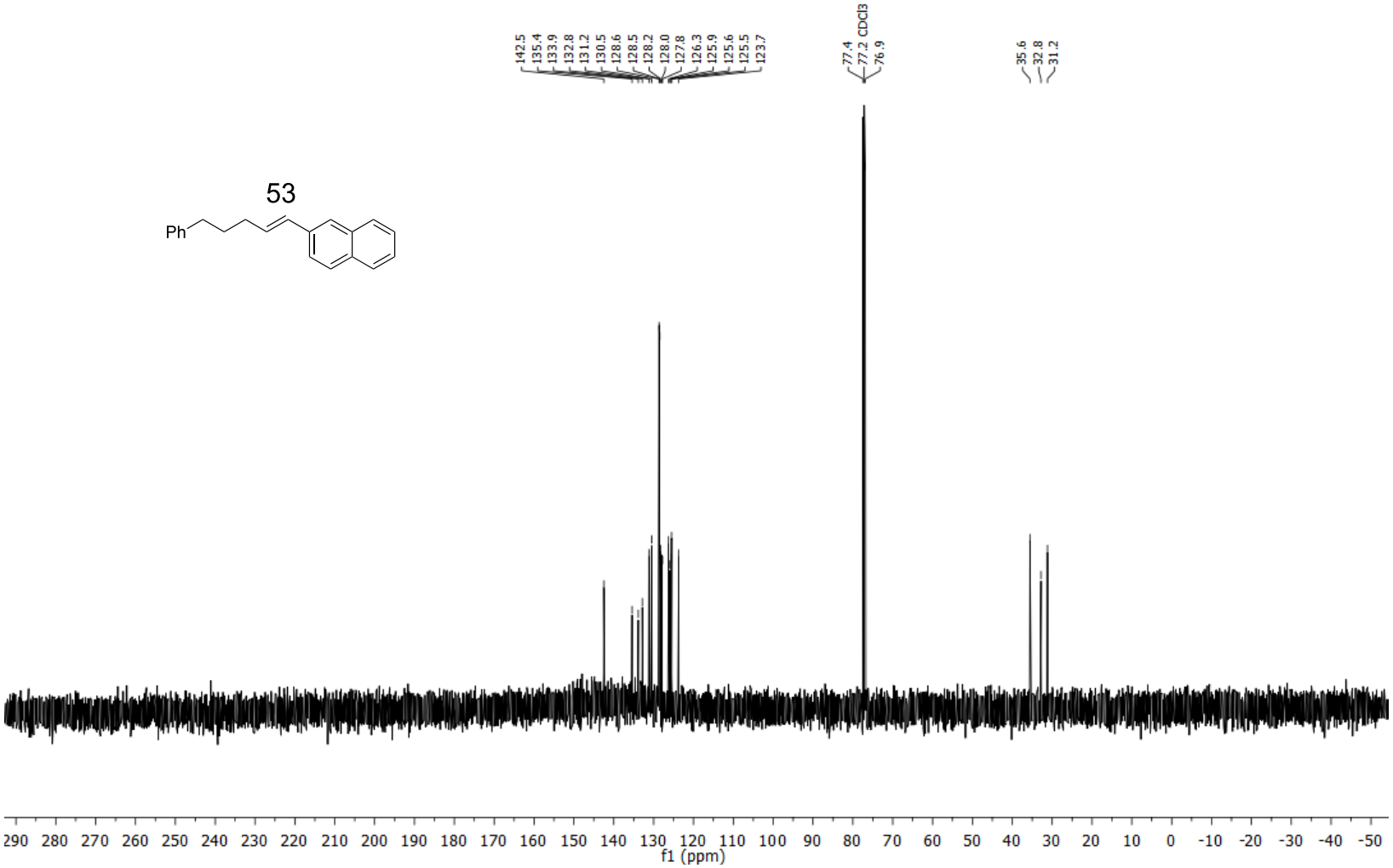
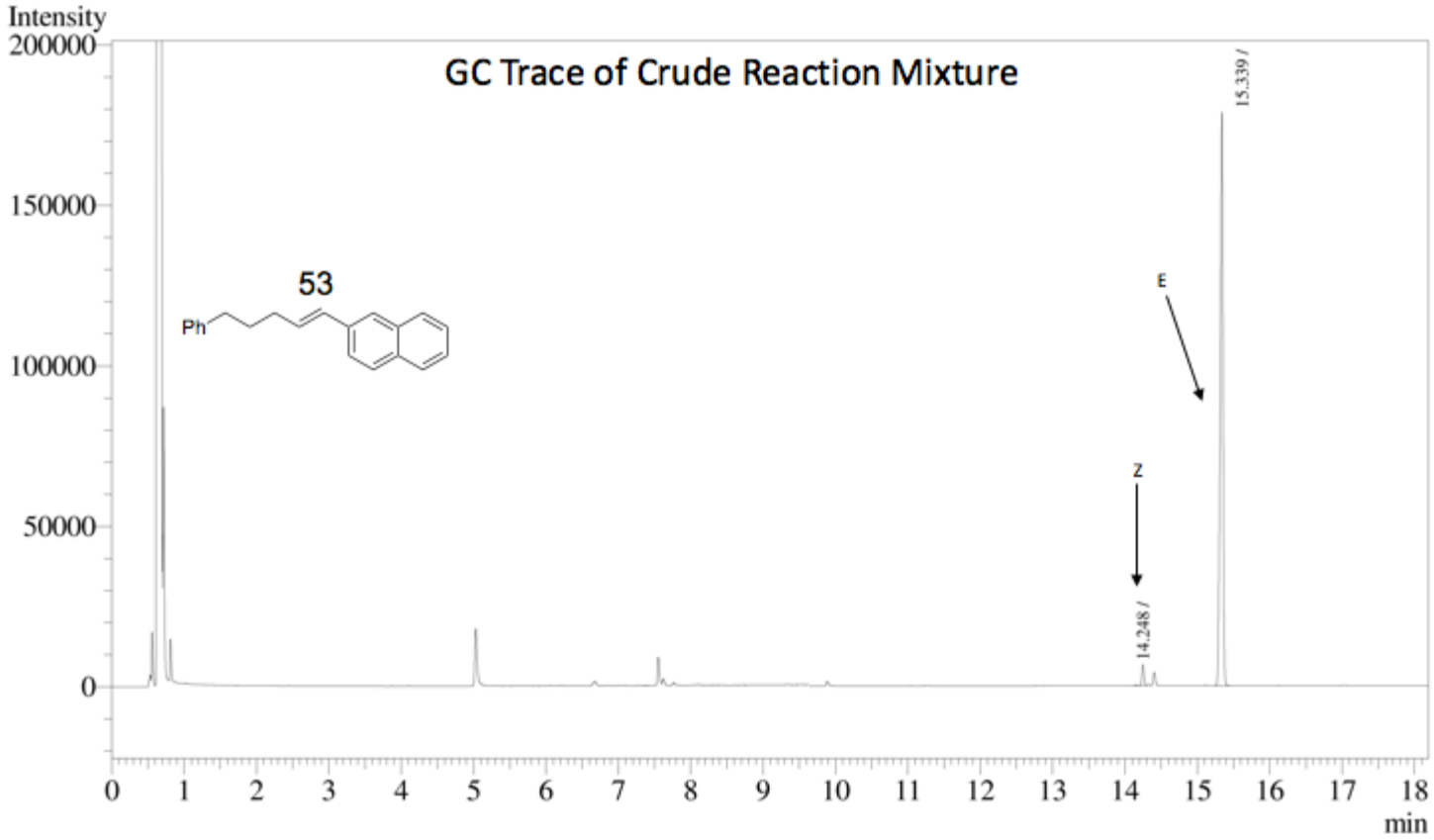




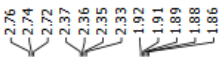
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.5 , 135.4 , 133.9 , 132.8 , 131.2 , 130.5 , 128.6 , 128.5 , 128.2 , 127.9 , 127.8 , 126.3 , 125.9 , 125.6 , 125.5 , 123.7 , 35.6 , 32.8 , 31.2 .



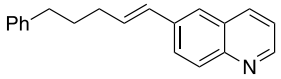


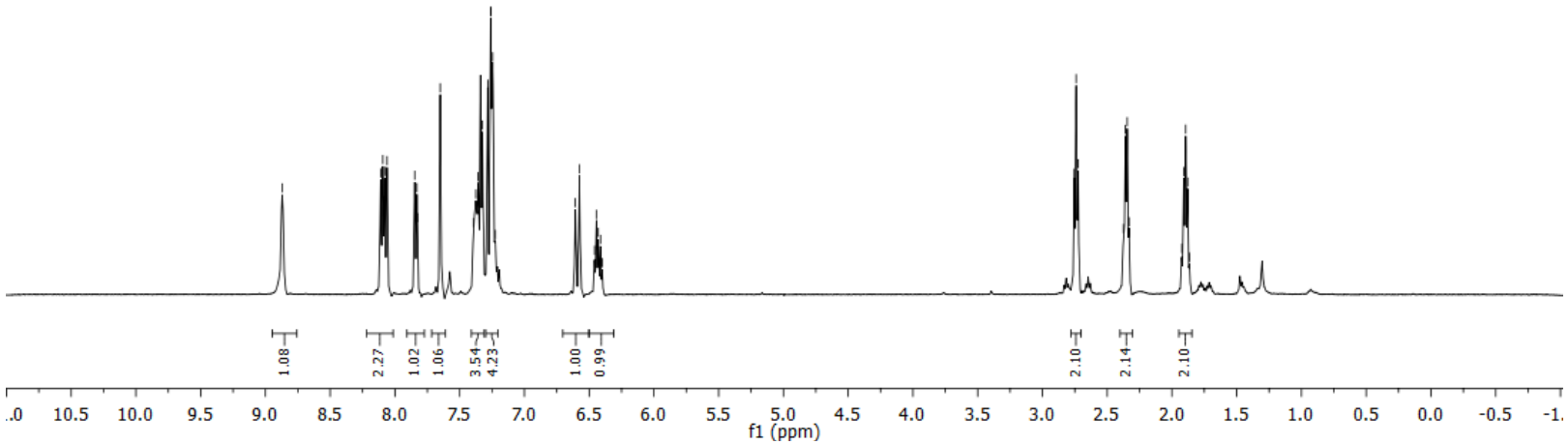
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.248	12591	6361	2.599				
2	15.339	471929	177266	97.401				
Total		484520	183627					

^{1}H 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).

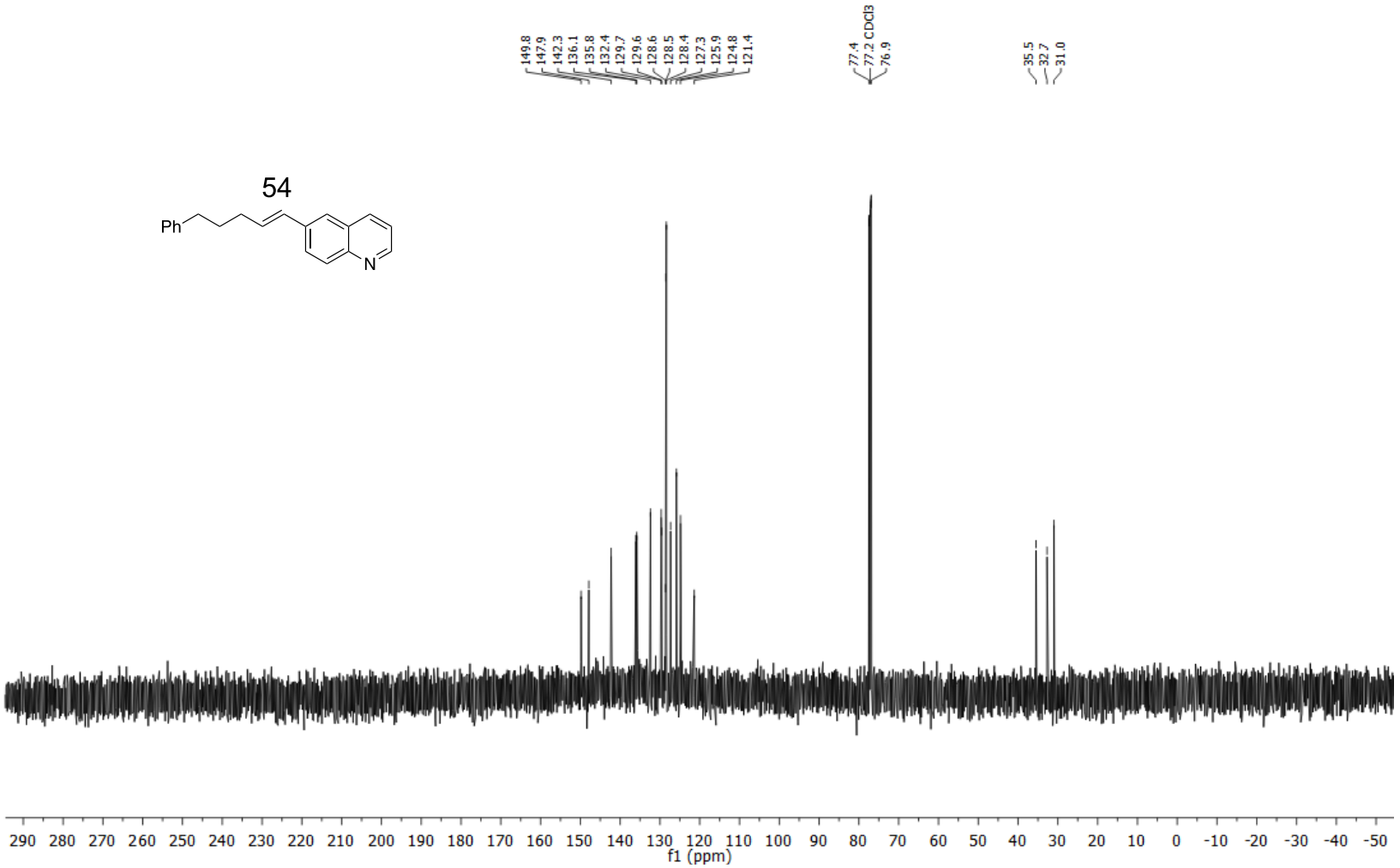


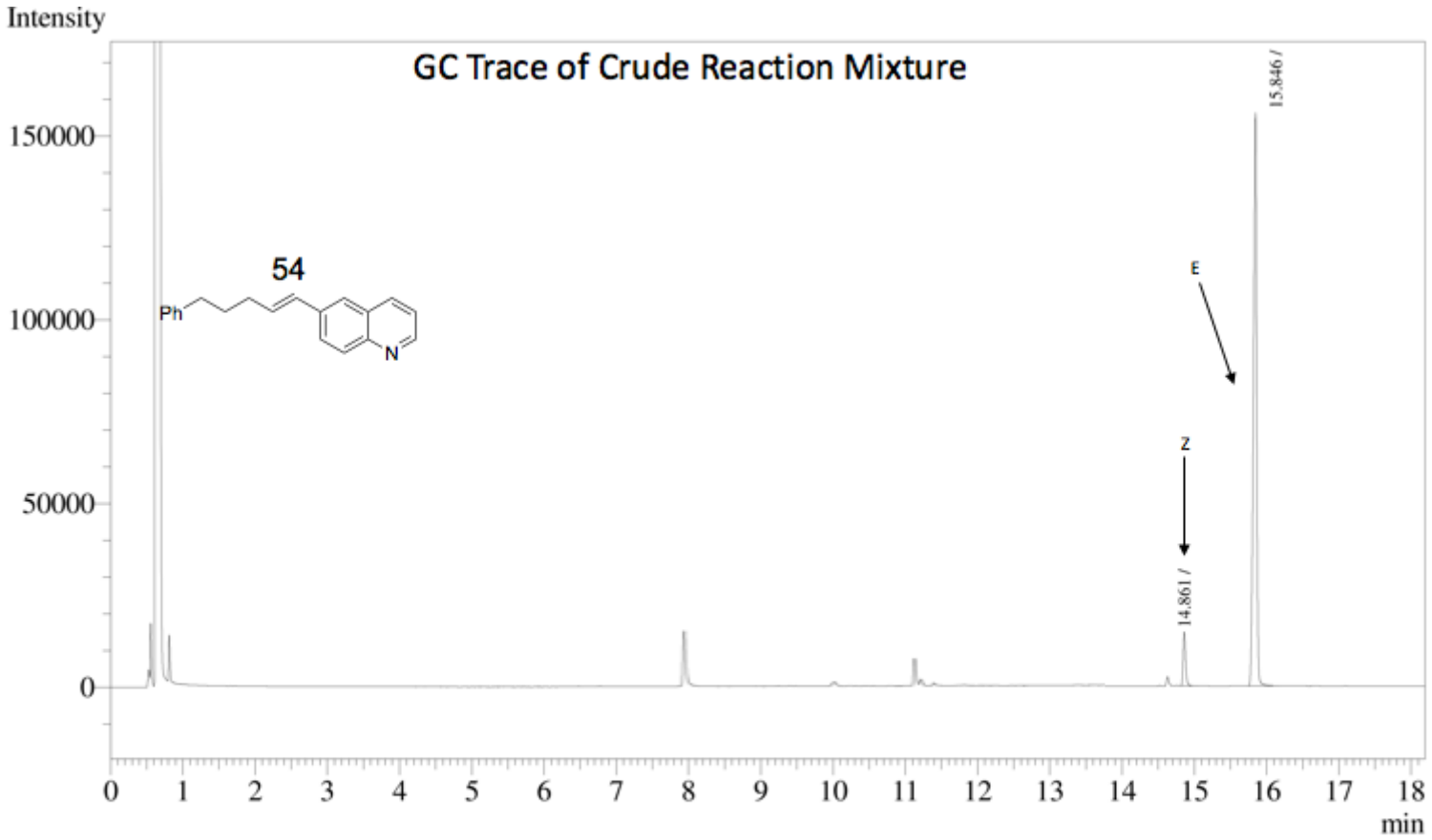
54





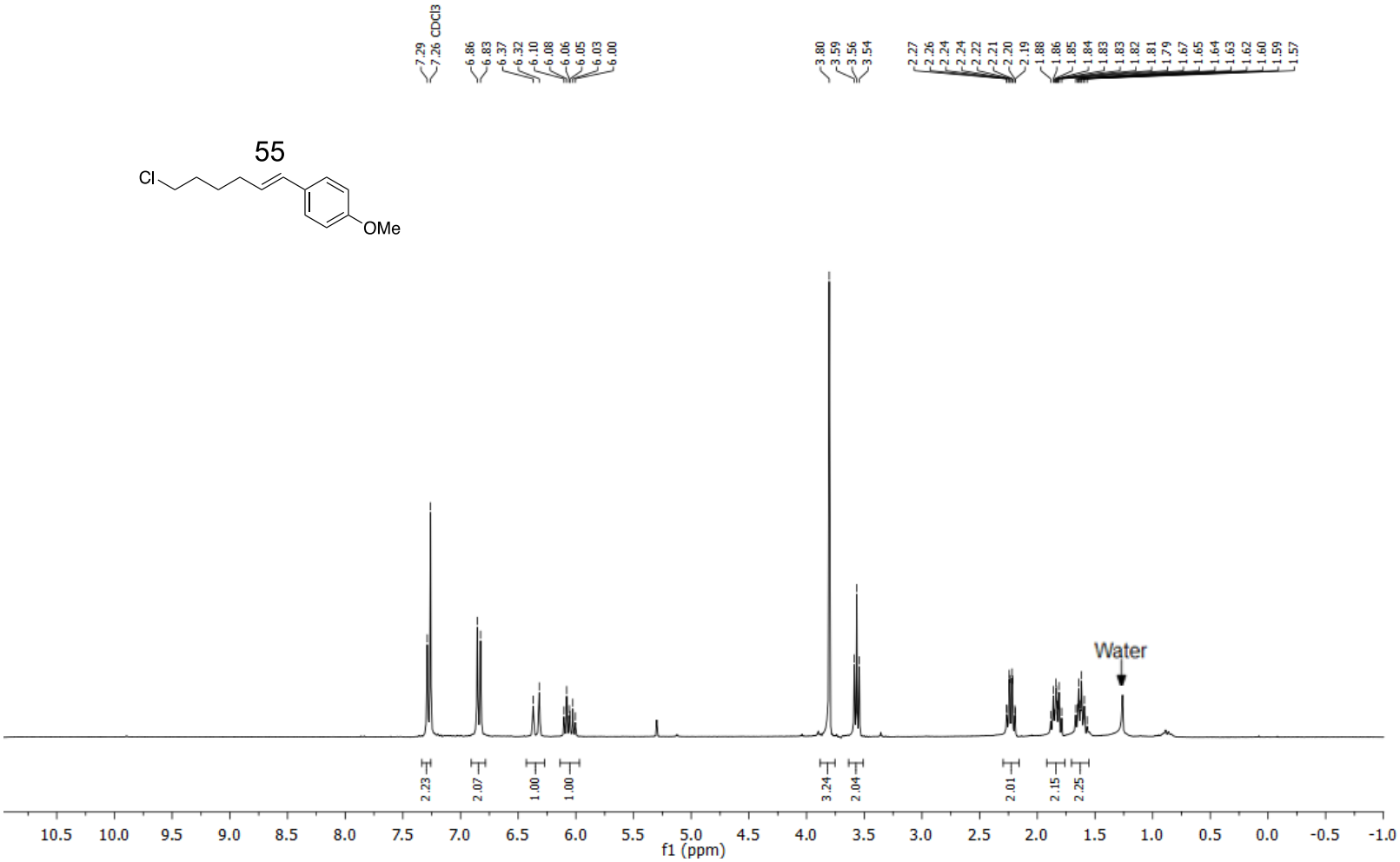
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.8 , 147.9 , 142.3 , 136.1 , 135.8 , 132.4 , 129.7 , 129.6 , 128.6 , 128.5 , 128.4 , 127.3 , 125.9 , 124.8 , 121.4 , 35.5 , 32.7 , 31.0 .



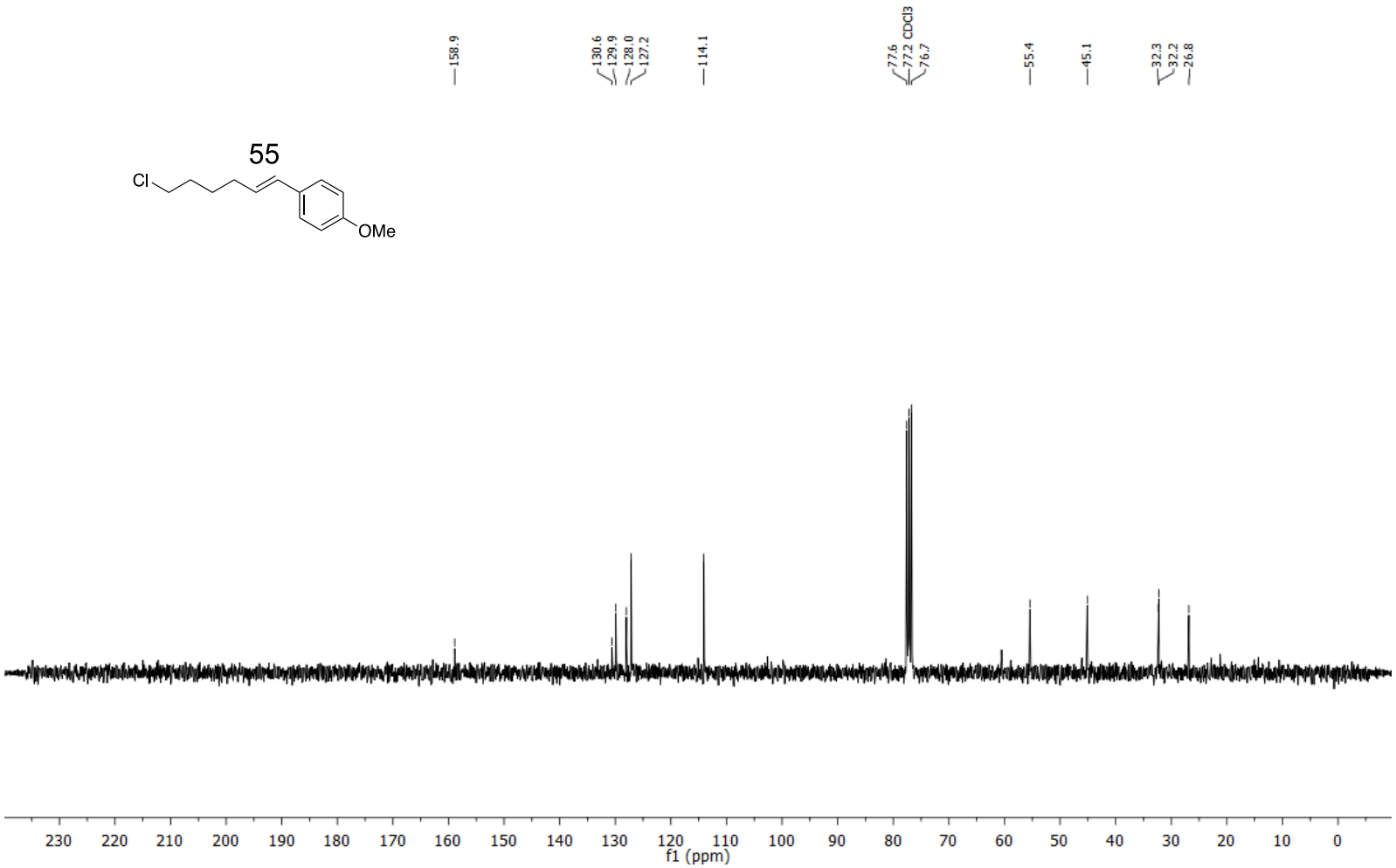


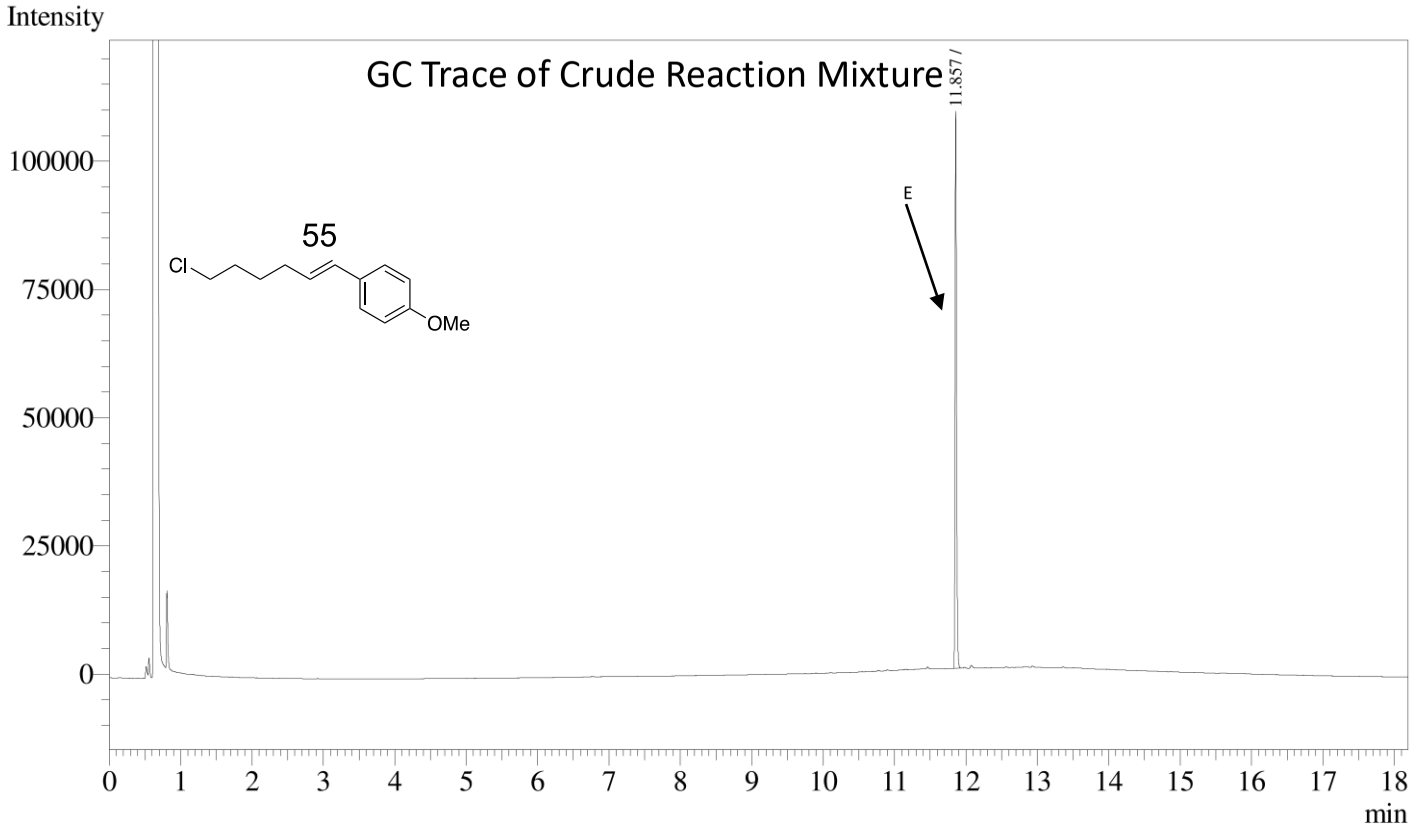
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	14.861	35463	14615	6.850				
2	15.846	482279	155531	93.150				
Total		517742	170146					

^{1}H 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).



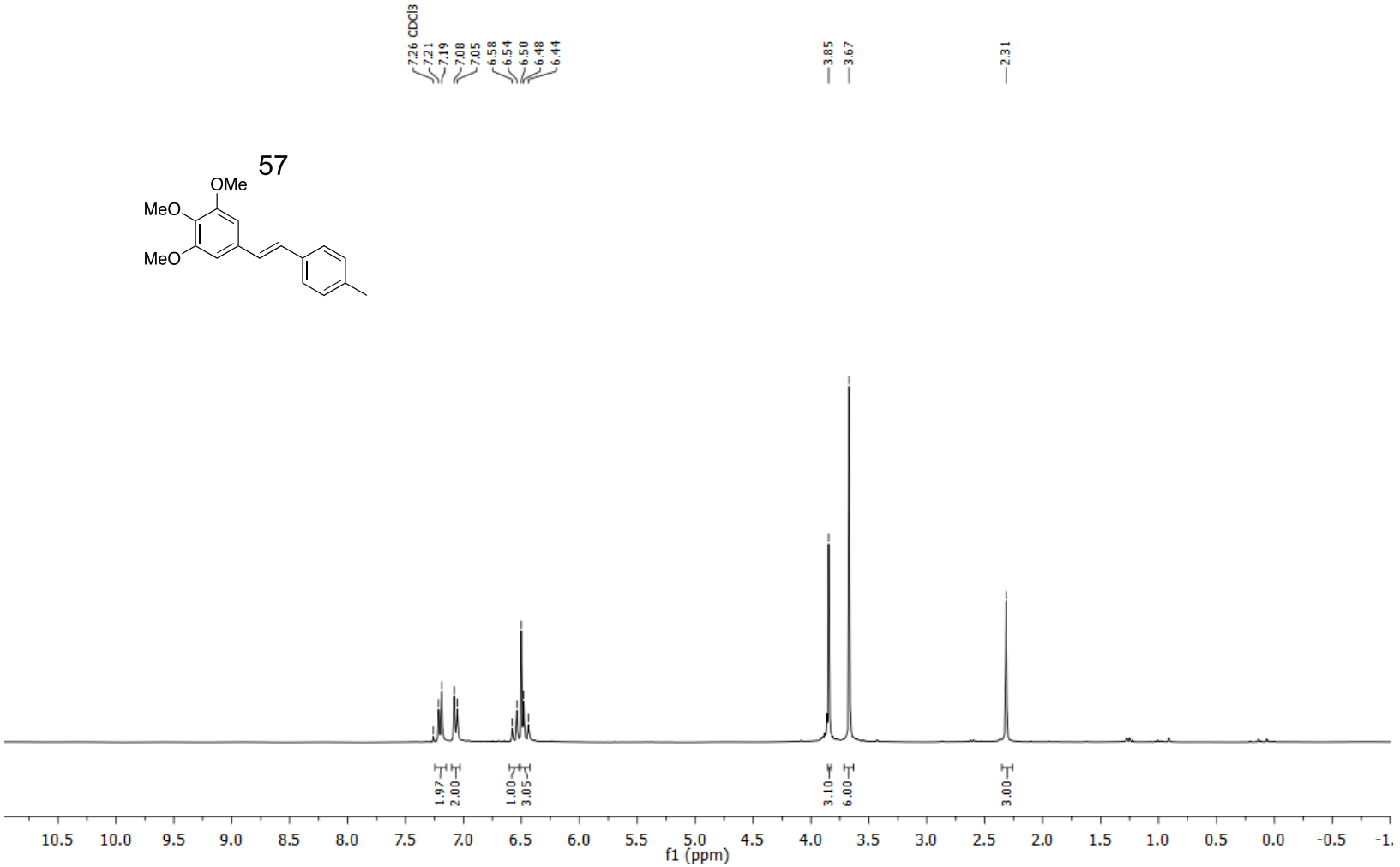
^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 130.6, 129.9, 127.2, 127.2, 114.1, 55.4, 45.1, 32.3, 32.2, 26.8.

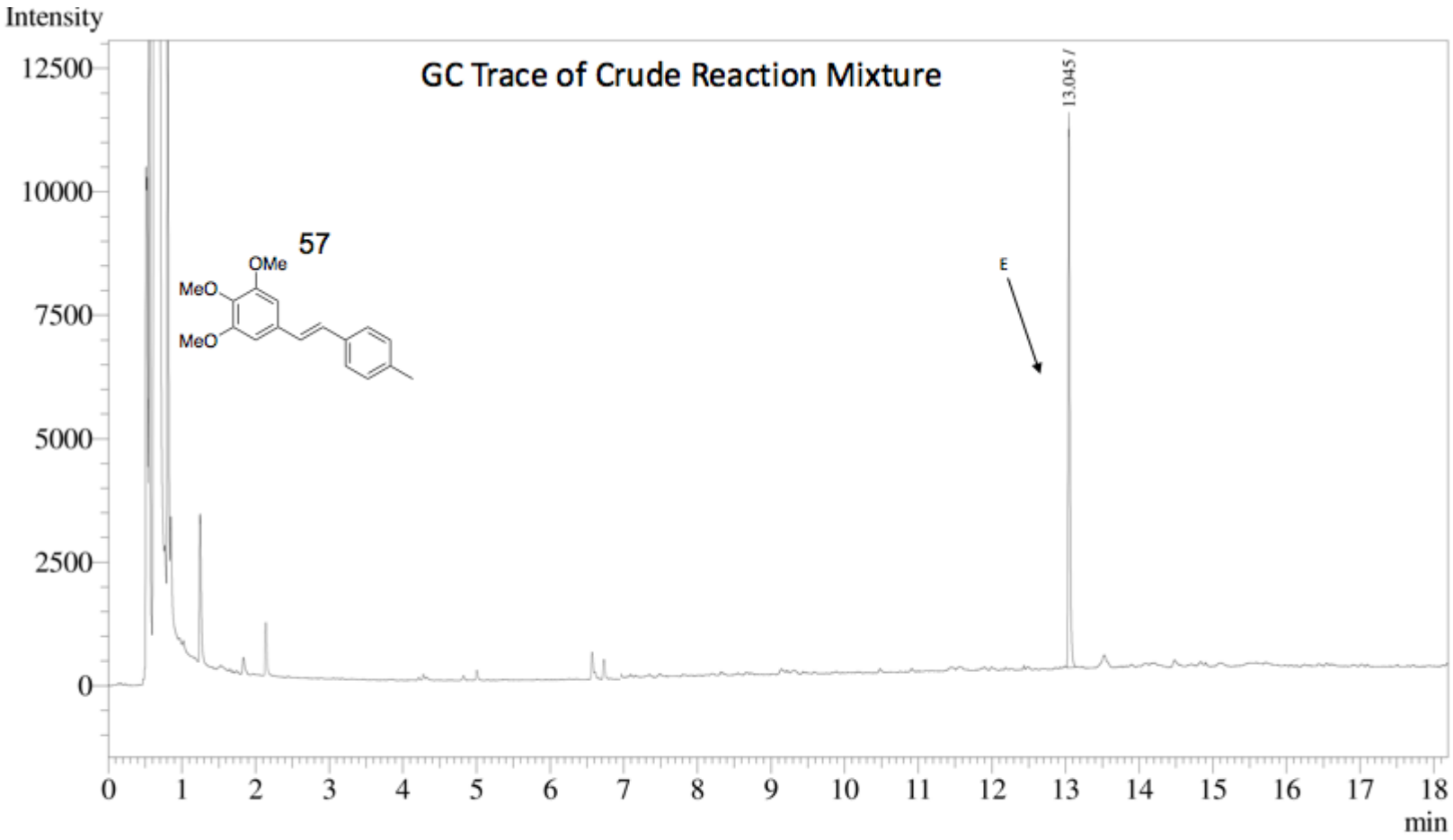




Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.857	149723	107232	100.000				
Total		149723	107232					

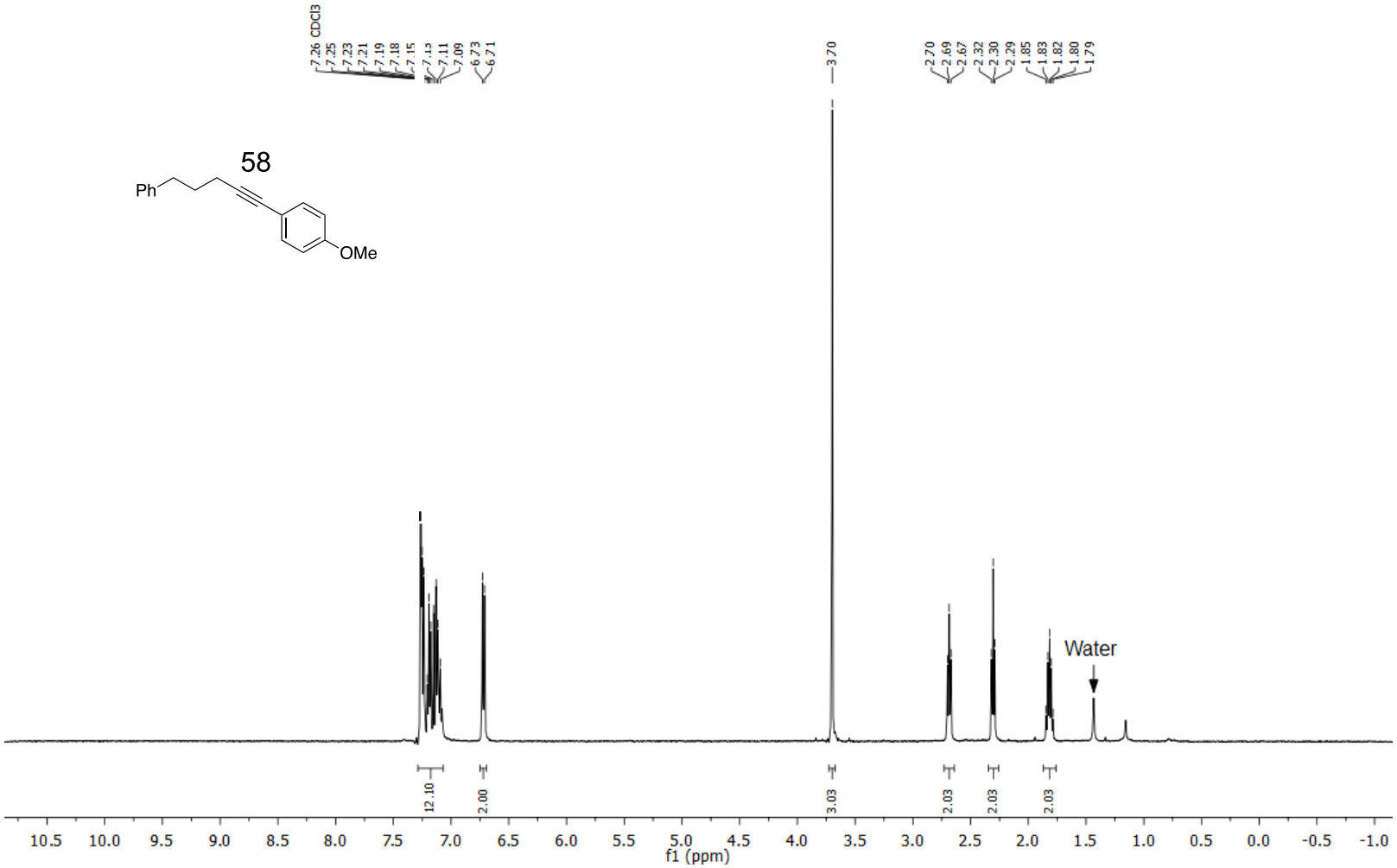
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 12.2 Hz, 1H), 6.52 – 6.43 (m, 3H), 3.85 (s, 3H), 3.67 (s, 6H), 2.31 (s, 3H).





Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	13.045	18087	11095	100.000		V		
Total		18087	11095					

^{1}H 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).



^{1}H NMR (500 MHz, Chloroform-*d*) 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).