"On water" sp^3-sp^2 cross-couplings between benzylic and alkenyl halides

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Instrumentation and Chemicals

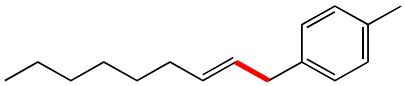
General. Reactions were performed in 5 mL microwave vials under an argon atmosphere containing a Teflon coated stir bar and septum. All commercially available reagents were used without further purification. Zinc dust 98.0% was purchased from Strem Chemicals (catalog #93-3060) or from Across and was stored in the glove box, as was $PdCl_2(Amphos)_2$ (CAS #887919-35-9) obtained from Johnson Matthey ($PdCl_2(Amphos)_2$ = dichloro-bis(*p*-dimethylaminophenyl-di-*t*-butyllphosphine)palladium(II); .Pd-132, catalog #C4138). Alkenyl halides were prepared following literature procedures.

Column chromatography was preformed using Silicycle Silia-P 60 Å flash silica gel. GC analyses were recorded on a Hewlett-Packard HP 6890 chromatograph equipped with a capillary column HP-1 (30 m × 0.25 mm × 0.25 μm). ^1H and ^{13}C NMR spectra were measured on a Varian Inova-400 (400 and 100 MHz, respectively) spectrometer at ambient temperature. Proton NMR data were recorded as follows: chemical shift in ppm referenced from residual solvent peak ($CDCl_3$, 7.26 ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet, h = heptet, m = multiplet), coupling constant (Hz), and integration. ^{13}C Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$, 77.00 ppm). Mass spectral data were acquired on either a VF Autospec or an analytical VG-70-250 HF instrument.

Experimental Procedures and Characterization Data

General Procedure (Table 2). In a 5 mL microwave vial under argon containing zinc dust (3.0 or 4.0 mmol) and $PdCl_2(Amphos)_2$ (14 mg, 0.02 mmol, 2 mol %) was added degassed water (3 mL). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, 116 mg, 1 mmol) was added at rt followed by the addition of the benzylic halide (2 or 3 mmol) and the alkenyl halide (1 mmol). The vial was stirred vigorously at rt for 6 h. The product was extracted with EtOAc. Silica gel (1 g) was added to the combined organic phase and solvents were removed under vacuum. The resulting dry, crude silica was introduced on top of a silica gel chromatography column to purify the product. NMR experiments in support of GC/GCMS data were performed on crude, unpurified product. In all cases the results obtained by both methods were within 5%.

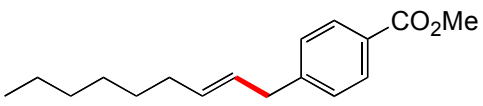
(*E*)-1-Methyl-4-(non-2-en-1-yl)benzene (2)



From (*E*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *E/Z* – 99/1), 1-(chloromethyl)-4-methylbenzene (281 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 82% isolated yield (*E/Z* – 99/1) using hexane as eluent.

^1H NMR (400 MHz): δ 7.12-7.07 (m, 4H), 5.59-5.47 (m, 2H), 3.30 (d, *J* = 5.5 Hz, 2H), 2.33 (s, 3H), 2.03 (q, *J* = 7.0 Hz, 2H), 1.37-1.28 (m, 8H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 137.9, 135.1, 131.7, 128.8, 128.7, 128.1, 38.4, 32.3, 31.5, 29.3, 28.7, 22.4, 20.8, 13.9. HRMS ($C_{16}H_{24}$); calcd. 216.1878, found 216.1874.

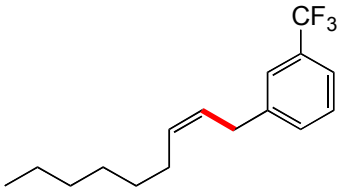
(*E*)-Methyl 4-(non-2-en-1-yl)benzoate (3)



From (*E*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *E/Z* – 99/1), methyl 4-(chloromethyl)benzoate (554 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 91% isolated yield (*E/Z* – 99/1) using (hexane/EtOAc 10/1) as eluent.

^{1}H NMR (400 MHz): δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.55-5.52 (m, 2H), 3.91 (s, 3H), 3.38 (d, *J* = 3.9 Hz, 2H), 2.05-2.00 (m, 2H), 1.37-1.26 (m, 8H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 167.0, 146.4, 132.8, 129.5, 128.3, 127.6, 127.4, 51.8, 38.8, 32.3, 31.5, 29.1, 28.6, 22.4, 13.9. HRMS ($C_{17}H_{24}O_2$); calcd. 260.1776, found 260.1778.

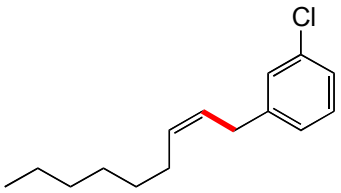
(*Z*)-1-(Non-2-en-1-yl)-3-(trifluoromethyl)benzene (4)



From (*Z*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *Z/E* – 99/1), methyl 1-(chloromethyl)-3-(trifluoromethyl)benzene (584 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 84% isolated yield (*Z/E* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.46-7.38 (m, 4H), 5.61-5.52 (m, 2H), 3.46 (d, *J* = 6.4 Hz, 2H), 2.15 (q, *J* = 6.8 Hz, 2H), 1.42-1.28 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 141.9, 131.9, 131.5, 130.9, 130.6, 130.3, 129.9, 128.5, 128.4, 126.5, 125.4, 122.7, 122.5, 122.5, 122.5, 122.4, 120.0, 33.0, 31.5, 29.3, 28.8, 27.1, 22.4, 13.9. HRMS ($C_{16}H_{21}F_3$); calcd. 270.1595, found 270.1606.

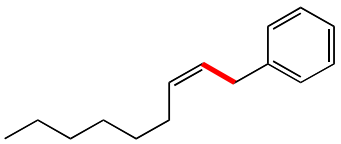
(*Z*)-1-Chloro-3-(non-2-en-1-yl)benzene (5)



From (*Z*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *Z/E* – 99/1), 1-chloro-3-(chloromethyl)benzene (322 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 89% isolated yield (*Z/E* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.23-7.16 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 5.59-5.48 (m, 2H), 3.38 (d, *J* = 6.3 Hz, 2H), 2.15 (q, *J* = 7.1 Hz, 2H), 1.42-1.30 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 143.1, 133.9, 131.6, 129.4, 128.3, 126.8, 126.3, 125.8, 32.9, 31.6, 29.4, 28.8, 27.1, 22.5, 13.9. HRMS ($C_{15}H_{21}Cl$); calcd. 236.1332, found 236.1330.

(*Z*)-Non-2-en-1-ylbenzene (6)

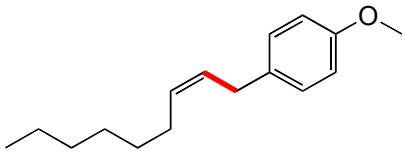


From (*Z*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *Z/E* – 99/1), (chloromethyl)benzene (253 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 95% isolated yield (*Z/E* – 98/2) using hexane as eluent. Isomerization took place during purification, while GC/GCMS on crude material showed *Z/E* – 99/1.

^{1}H NMR (400 MHz): δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.29-7.21 (m, 3H), 5.60-5.52 (m, 2H), 3.42 (d, *J* = 6.4 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.43-1.30 (m, 8H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 141.2, 131.0,

128.3, 128.3, 127.9, 125.7, 33.4, 31.7, 29.6, 29.0, 27.2, 22.6, 14.0. HRMS ($C_{15}H_{22}$); calcd. 202.1722, found 202.1718.

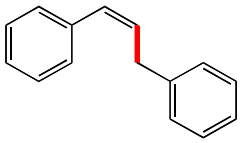
(*Z*)-1-Methoxy-4-(non-2-en-1-yl)benzene (7)



From (*Z*)-1-iodooct-1-ene (238 mg, 1.0 mmol, *Z/E* – 99/1), 1-(chloromethyl)-4-methoxybenzene (470 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 81% isolated yield (*Z/E* – 97/3) using (hexane/EtOAc 10/1) as eluent. Isomerization took place during purification, while GC/GCMS on crude material showed *Z/E* – 99/1.

^{1}H NMR (400 MHz): δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.55-5.47 (m, 2H), 3.79 (s, 3H), 3.34 (d, *J* = 6.2 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.41-1.26 (m, 8H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 157.7, 133.3, 130.6, 129.1, 128.3, 113.7, 55.2, 32.5, 31.7, 29.6, 28.9, 27.1, 22.6, 14.0. HRMS ($C_{16}H_{24}O$); calcd. 232.1827, found 232.1826.

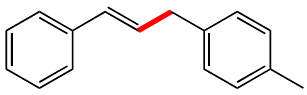
(*Z*)-Prop-1-ene-1,3-diyldibenzene (8)



From (*Z*)-(2-bromovinyl)benzene (183 mg, 1.0 mmol, *Z/E* – 99/1), (chloromethyl)benzene (253 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 90% isolated yield (*Z/E* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.37-7.34 (m, 6H), 7.29-7.24 (m, 4H), 6.62 (d, *J* = 11.5 Hz, 1H), 5.93-5.80 (m, 1H), 3.71 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz): δ 140.8, 137.2, 130.7, 130.0, 128.7, 128.5, 128.4, 128.3, 126.8, 126.1, 34.7. HRMS ($C_{15}H_{14}$); calcd. 194.1096, found 194.1090.

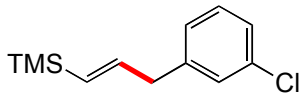
1-Methyl-4-(3-phenylallyl)benzene (9) (*E/Z* – 83/17)



From (2-bromovinyl)benzene (183 mg, 1.0 mmol, *E/Z* – 83/17), 1-(chloromethyl)-4-methylbenzene (281 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 85% isolated yield (*E/Z* – 83/17). (*E*)-1-Methyl-4-(3-phenylallyl)benzene was separated from (*Z*)-isomer on preparative TLC using hexane as eluent.

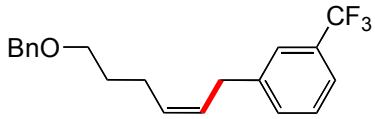
(*E*)-^{1}H NMR (400 MHz): δ 7.37-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 7.16-7.12 (m, 4H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.8 Hz, *J* = 6.6 Hz, 1H), 3.52 (d, *J* = 6.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz): δ 137.3, 136.8, 135.5, 130.6, 129.3, 129.0, 128.3, 128.3, 126.8, 125.9, 38.7, 20.8. HRMS ($C_{16}H_{16}$); calcd. 208.1252, found 208.1256.

(*E*)-(3-(3-Chlorophenyl)prop-1-en-1-yl)trimethylsilane (10) (*E*/*Z* – 93/7)



From (*E*)-(2-bromovinyl)trimethylsilane (179 mg, 1.0 mmol, *E*/*Z* – 93/7), 1-chloro-3-(chloromethyl)benzene (322 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 77% isolated yield (*E*/*Z* – 92/8) using hexane as eluent.
^{1}H NMR (400 MHz): δ 7.27-7.17 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.11 (dd, *J* = 18.4 Hz, *J* = 6.2 Hz, 1H), 5.71 (d, *J* = 18.4 Hz, 1H), 3.43 (d, *J* = 6.3 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (100 MHz): δ 143.9, 141.8, 133.9, 132.1, 129.4, 128.6, 126.7, 126.3, 126.0, 125.9, 42.6, -1.4. HRMS ($C_{12}H_{17}ClSi$); calcd. 224.0788, found 224.0784.

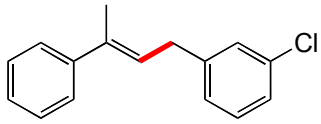
(*Z*)-1-(6-(Benzyloxy)hex-2-en-1-yl)-3-(trifluoromethyl)benzene (11)



From (*Z*)-(((5-iodopent-4-en-1-yl)oxy)methyl)benzene (302 mg, 1.0 mmol, *E*/*Z* – 1/99), methyl 1-(chloromethyl)-3-(trifluoromethyl)benzene (584 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 95% isolated yield (*E*/*Z* – 1/99) using (hexane/EtOAc 10/1) as eluent.

^{1}H NMR (400 MHz): δ 7.47-7.26 (m, 9H), 5.59-5.57 (m, 2H), 4.51 (s, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 3.46 (d, *J* = 5.2 Hz, 2H), 2.28 (q, *J* = 6.0 Hz, 2H), 1.75 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz): δ 141.8, 138.3, 131.5, 130.9, 130.6, 130.3, 129.9, 128.6, 128.4, 128.2, 128.0, 127.4, 127.3, 127.3, 125.4, 124.8, 124.8, 124.8, 124.7, 122.7, 122.6, 122.6, 122.5, 122.5, 72.7, 69.4, 32.9, 29.4, 23.7. HRMS ($C_{20}H_{21}F_3O$); calcd. 334.1544, found 344.1551.

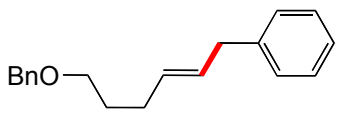
(*E*)-1-Chloro-3-(3-phenylbut-2-en-1-yl)benzene (12)



From (*E*)-(1-bromoprop-1-en-2-yl)benzene (197 mg, 1.0 mmol, *E*/*Z* – 99/1), 1-chloro-3-(chloromethyl)benzene (322 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 92% isolated yield (*E*/*Z* – 99/1) using (hexane/EtOAc 10/1) as eluent. The product was contaminated with 2-3% of inseparable 1,2-bis(3-chlorophenyl)ethane.

^{1}H NMR (400 MHz): δ 7.43-7.41 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.18 (m, 4H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.93 (tdd, *J* = 7.4 Hz, *J* = 2.7 Hz, *J* = 1.3 Hz, 2H), 3.55 (d, *J* = 7.4 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz): δ 143.1, 142.8, 136.2, 134.0, 129.5, 128.3, 128.0, 126.7, 126.4, 125.9, 125.5, 125.5, 34.7, 15.8. HRMS ($C_{16}H_{15}Cl$); calcd. 242.0862, found 242.0857.

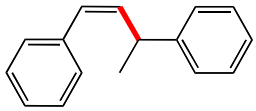
(*E*)-(6-(Benzyloxy)hex-2-en-1-yl)benzene (13)



From (*E*)-(((5-iodopent-4-en-1-yl)oxy)methyl)benzene (302 mg, 1.0 mmol, *E/Z* – 99/11), (chloromethyl)benzene (253 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 96% isolated yield (*E/Z* – 99/1) using (hexane/EtOAc 10/1) as eluent.

^{1}H NMR (400 MHz): δ 7.36-7.32 (m, 4H), 7.30-7.27 (m, 3H), 7.20-7.17 (m, 3H), 5.62-5.48 (m, 2H), 4.49 (s, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 3.33 (d, *J* = 6.5 Hz, 2H), 2.14 (q, *J* = 7.5 Hz, 2H), 1.71 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz): δ 140.9, 138.5, 131.1, 129.3, 128.4, 128.3, 128.3, 127.5, 127.4, 125.8, 72.8, 69.7, 38.9, 29.4, 29.0. HRMS ($C_{19}H_{22}O$); calcd. 266.1671, found 266.1669.

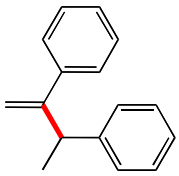
(*Z*)-But-1-ene-1,3-diyldibenzene (14)



From (*Z*)-(2-bromovinyl)benzene (183 mg, 1.0 mmol, *Z/E* – 99/1), (1-chloroethyl)benzene (281 mg, 2.0 mmol), and zinc dust (195 mg, 3.0 mmol), the product was obtained in 83% isolated yield (*Z/E* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.36-7.19 (m, 10H), 6.50 (d, *J* = 11.5 Hz, 1H), 5.84 (dd, *J* = 11.5 Hz, *J* = 10.6 Hz, 1H), 4.05-4.00 (m, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 145.9, 137.2, 136.8, 128.4, 128.3, 128.0, 127.6, 126.7, 126.5, 125.9, 37.5, 22.7. HRMS ($C_{16}H_{16}$); calcd. 208.1252, found 208.1248.

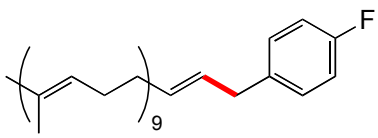
But-1-ene-2,3-diyldibenzene (15)



From (1-bromovinyl)benzene (183 mg, 1.0 mmol, *technical grade 90%*), (1-chloroethyl)benzene (421 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 79% isolated yield (*Z/E* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.32-7.16 (m, 10H), 5.42 (s, 1H), 5.17 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 152.7, 145.2, 142.3, 128.5, 128.2, 127.8, 127.2, 126.8, 126.2, 113.1, 44.2, 21.8. HRMS ($C_{16}H_{16}$); calcd. 208.1252, found 208.1243.

1-Fluoro-4-((2*E*,6*E*,10*E*,14*E*,18*E*,22*E*,26*E*,30*E*,34*E*)-7,11,15,19,23,27,31,35,39-nonamethyltetraconta-2,6,10,14,18,22,26,30,34,38-decaen-1-yl)benzene (16)



From (1*E*,5*E*,9*E*,13*E*,17*E*,21*E*,25*E*,29*E*,33*E*)-1-iodo-6,10,14,18,22,26,30,34,38-nonamethylnonatriaconta-1,5,9,13,17,21,25,29,33,37-decaene (781 mg, 1.0 mmol, *Z/E* – 1/99), 1-(chloromethyl)-4-fluorobenzene (434 mg, 3.0 mmol), and zinc dust (260 mg, 4.0 mmol), the product was obtained in 82% isolated yield (*Z/E* – 1/99) using hexane as eluent.

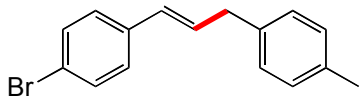
^{1}H NMR (400 MHz): δ 7.13 (dd, *J* = 8.4 Hz, *J* = 5.5 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.59-5.52 (m, 2H), 5.14-5.11 (m, 9H), 3.29 (d, *J* = 6.2 Hz, 2H), 2.11-1.97 (m, 36H), 1.69 (s, 3H), 1.61 (s, 27H). ^{13}C NMR (100 MHz): δ

162.3, 159.9, 136.4, 136.3, 135.2, 134.8, 134.8, 134.7, 134.7, 131.7, 131.0, 129.6, 129.5, 129.5, 128.6, 124.2, 124.0, 124.0, 123.6, 114.9, 114.7, 39.5, 38.0, 32.5, 27.7, 26.6, 26.5, 26.5, 26.4, 25.5, 17.5, 15.9, 15.8. LRMS ($C_{55}H_{83}F$); calcd. 762.6479, found 762.7.

Competition experiments

In a 5 mL microwave vial under argon containing zinc dust (130 mg, 2.0 mmol) and $PdCl_2(Amphos)_2$ (14 mg, 0.02 mmol, 2 mol %) was added degassed water (2 mL). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, 116 mg, 1 mmol) was added at rt followed by the addition of 1-(chloromethyl)-4-methylbenzene (154 mg, 1.1 mmol), the (2-bromovinyl)benzene (1 mmol), and the bromobenzene (1 mmol) for equations 1 and 2 (with *Z*-(2-bromovinyl)benzene (1 mmol) and the *E*-(2-bromovinyl)benzene (1 mmol) with equation 3). The flask was stirred vigorously at rt for 6 h. The product was extracted with EtOAc. The ratio of coupling products was determined from GC data on the crude, unpurified product.

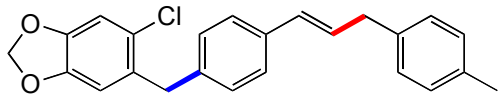
(*E*)-1-Bromo-4-(3-(*p*-tolyl)prop-1-en-1-yl)benzene (18)



From (*E*)-1-bromo-4-(2-bromovinyl)benzene (262 mg, 1.0 mmol, *E/Z* – 99/1), 1-(chloromethyl)-4-methyl-benzene (154 mg, 1.1 mmol), and zinc dust (130 mg, 2.0 mmol), the product was obtained in 84% isolated yield (*E/Z* – 99/1) using hexane as eluent.

^{1}H NMR (400 MHz): δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 4H), 6.36-6.34 (m, 2H), 3.50 (d, *J* = 6.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz): δ 136.8, 136.6, 135.9, 131.7, 130.6, 129.7, 129.3, 128.7, 127.8, 120.8, 39.0, 21.2. HRMS ($C_{16}H_{15}Br$); calcd. 286.0357, found 286.0353.

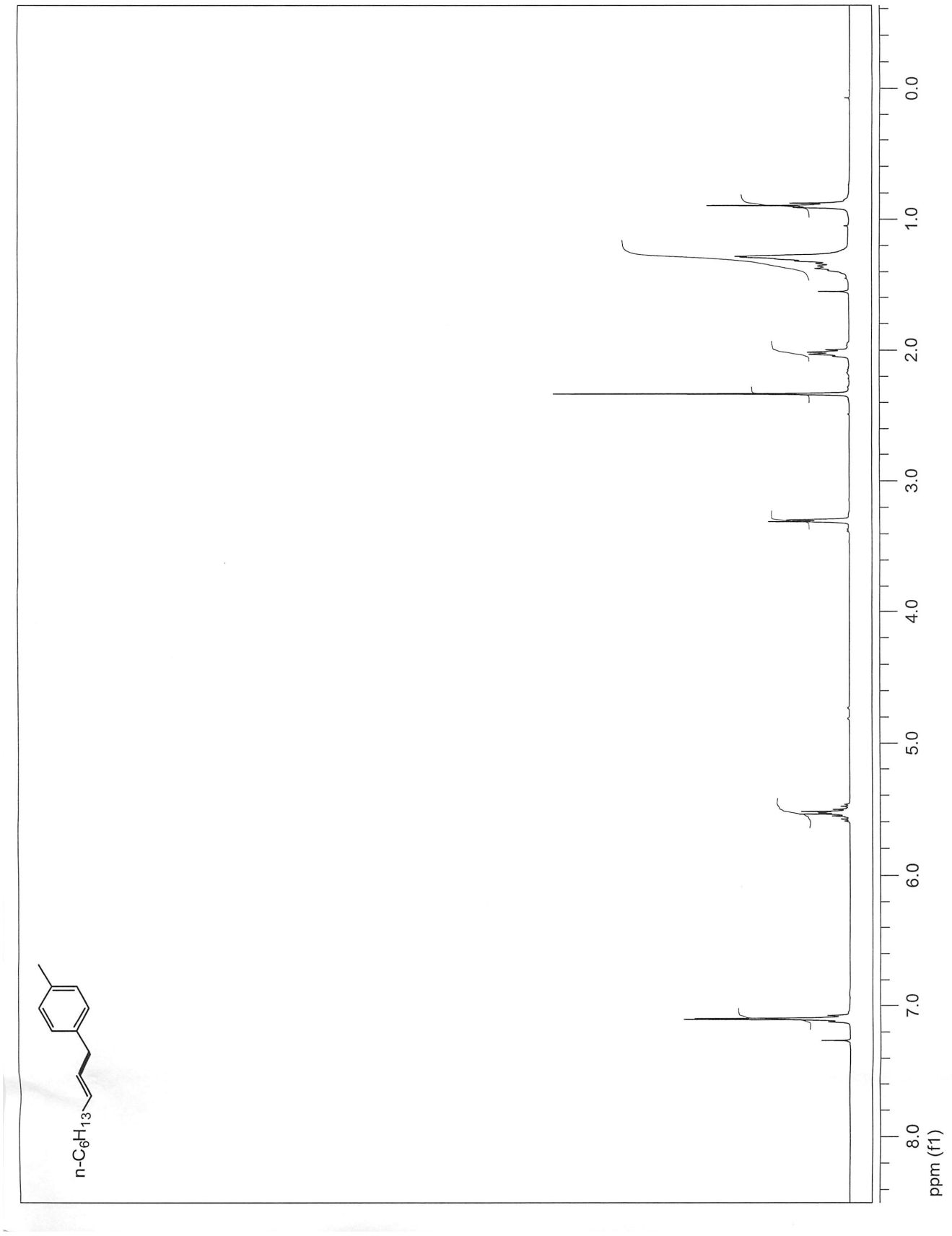
(*E*)-5-Chloro-6-(4-(3-(*p*-tolyl)prop-1-en-1-yl)benzyl)benzo[*d*][1,3]dioxole (19)

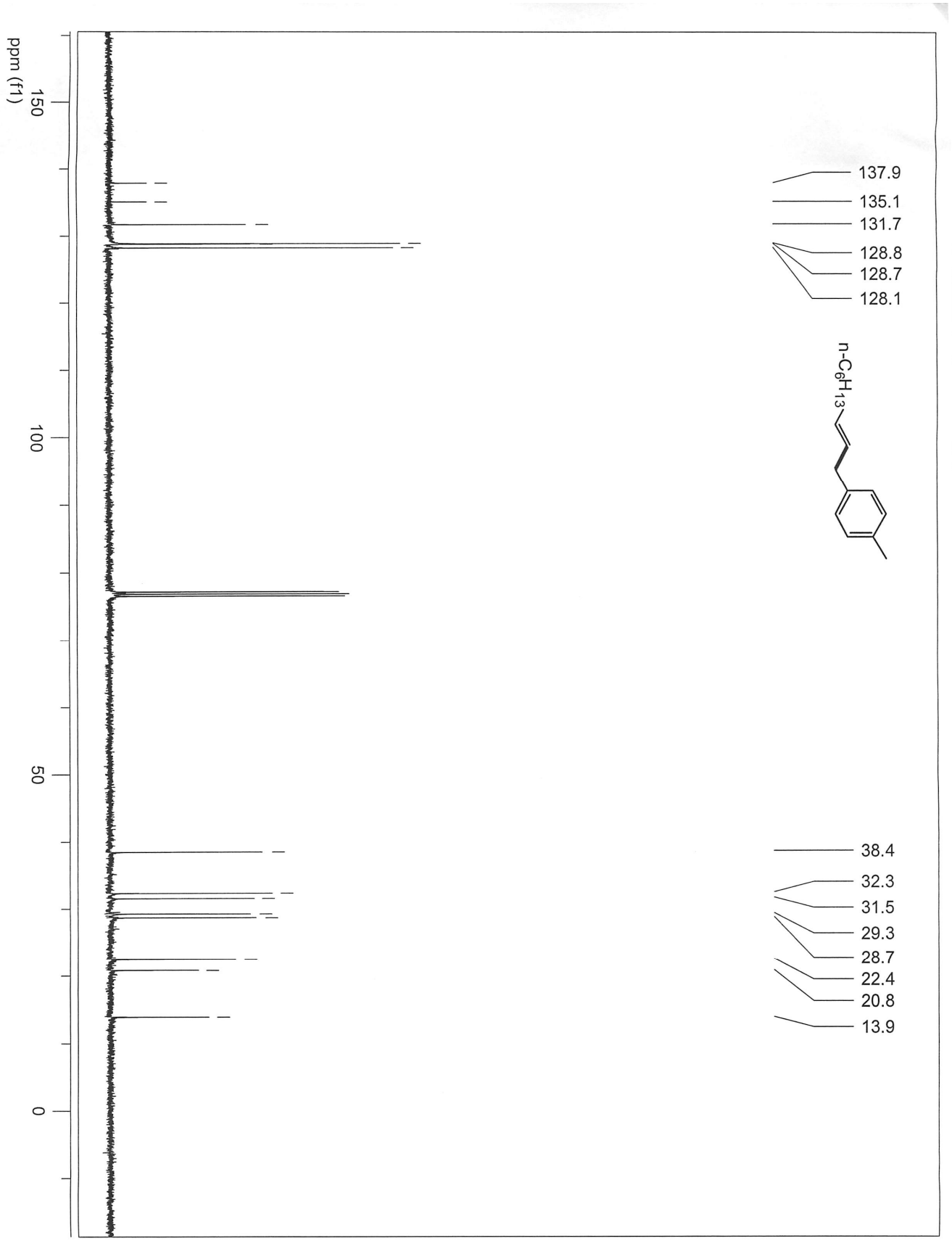


In a 5 mL microwave vial under argon containing zinc dust (130 mg, 2.0 mmol) and $PdCl_2(Amphos)_2$ (14 mg, 0.02 mmol, 2 mol %) was added degassed water (2 mL). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, 116 mg, 1 mmol) was added at rt followed by the addition of (*E*)-1-bromo-4-(2-bromovinyl)benzene (262 mg, 1.0 mmol, *E/Z* – 99/1), and 1-(chloromethyl)-4-methylbenzene (154 mg, 1.1 mmol). The flask was stirred vigorously at rt for 6 h. Zinc dust (260 mg, 4.0 mmol), 5-chloro-6-(chloromethyl)benzo[*d*][1,3]dioxole (615 mg, 3.0 mmol), and degassed water (2 mL) were added to the reaction mixture and the flask was stirred vigorously at rt for an additional 18 h. The product was extracted with EtOAc. Silica gel (1 g) was added to the combined organic phase and solvents were removed under vacuum. The resulting dry, crude silica was introduced on top of a silica gel chromatography column to purify the product. The product was obtained in 81% isolated yield (*E/Z* – 99/1) using (hexane/EtOAc 10/1) as eluent.

^{1}H NMR (400 MHz): δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.12 (brs, 4H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.84 (s, 1H), 6.59 (s, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8 Hz, *J* = 6.7 Hz, 1H), 5.93 (s, 2H), 3.96 (s, 2H), 3.49 (d, *J* = 6.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz): δ 146.8, 146.7, 138.7, 137.2, 135.8, 131.8, 130.6, 130.1, 129.3, 129.2, 129.1, 128.7, 126.4, 110.5, 109.9, 101.7, 39.0, 38.8, 21.1. HRMS ($C_{24}H_{21}ClO_2$); calcd. 376.1230, found 376.1244.

2

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50
0
137.9
135.1
131.7
128.8
128.7
128.1
n-C6H13
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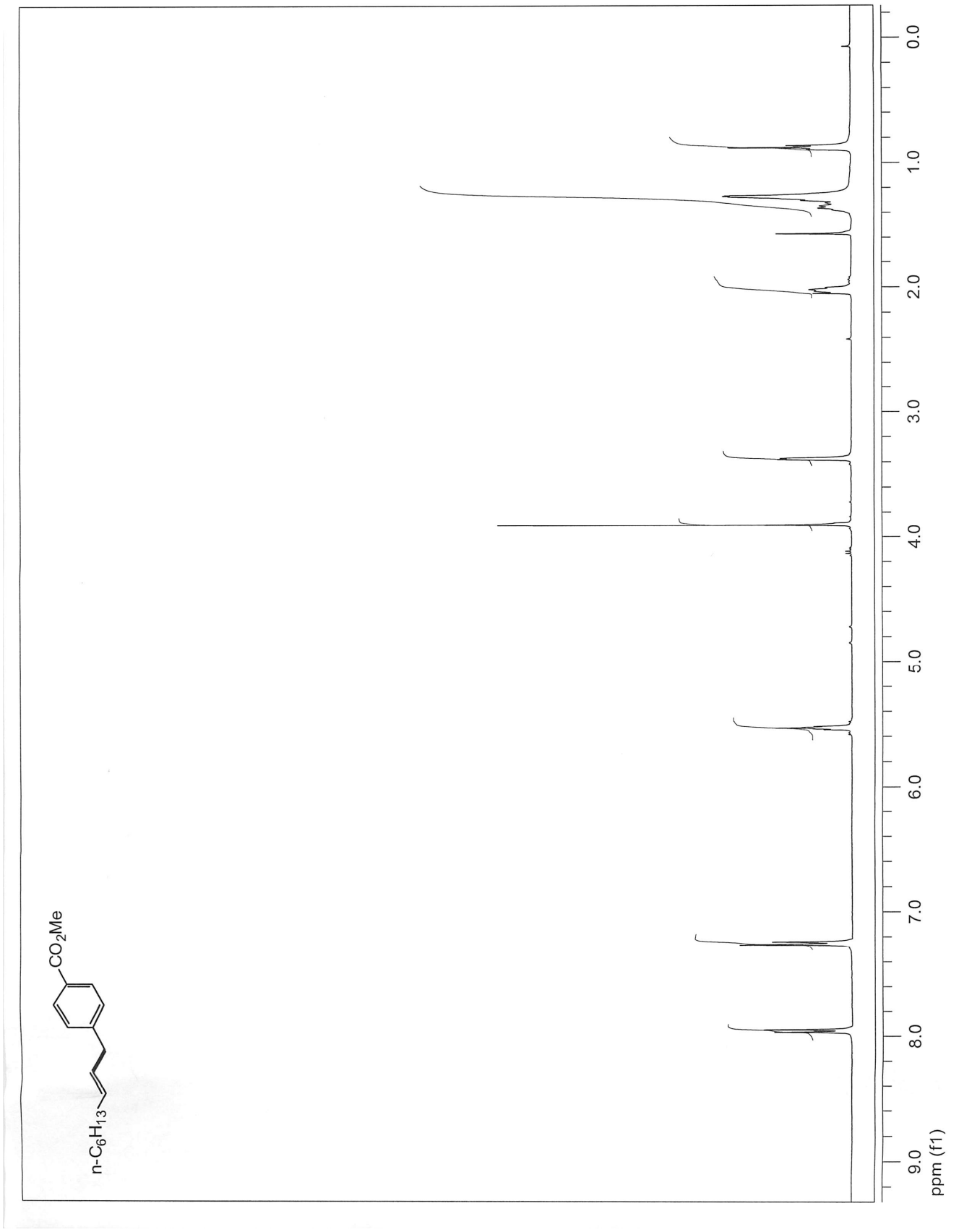
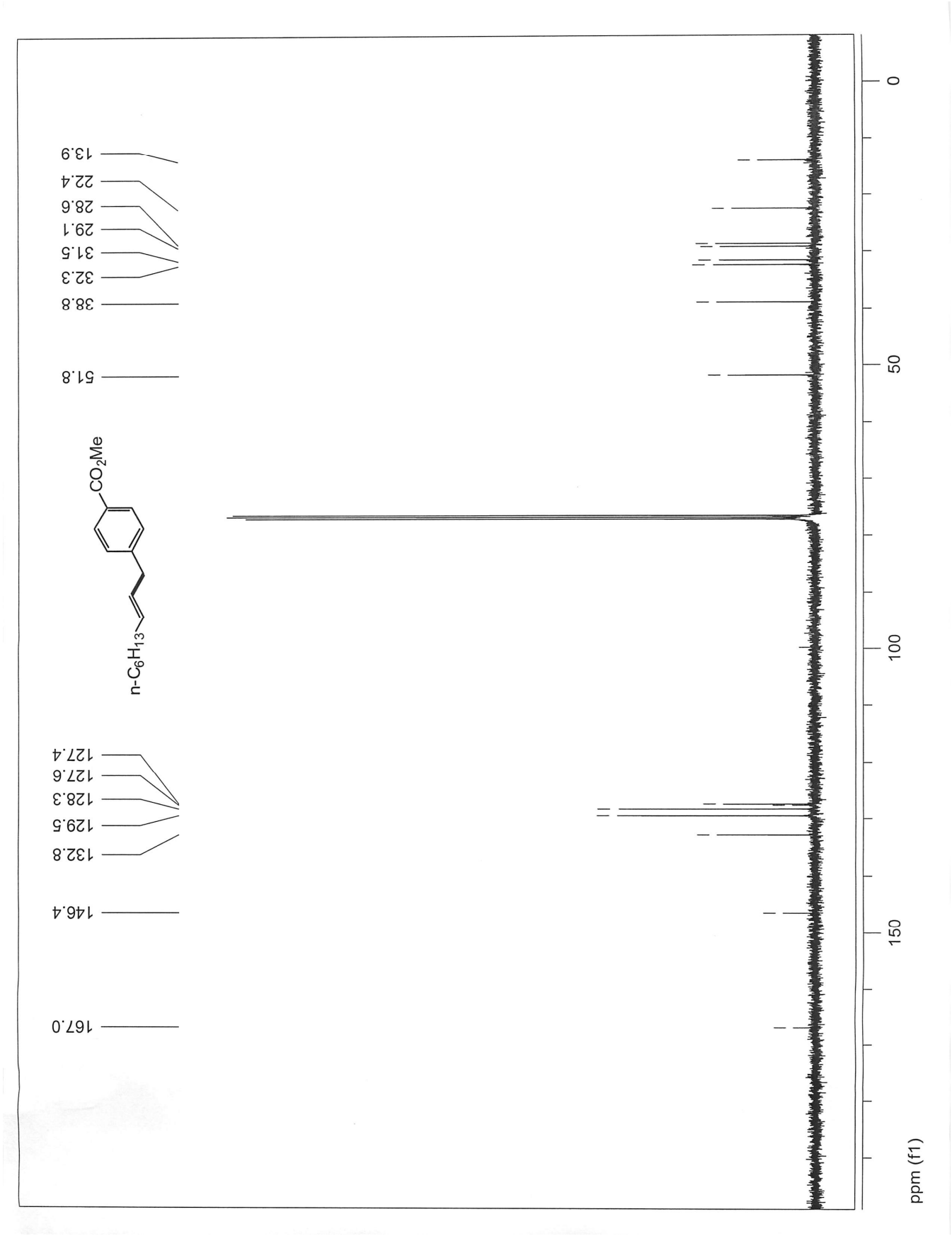
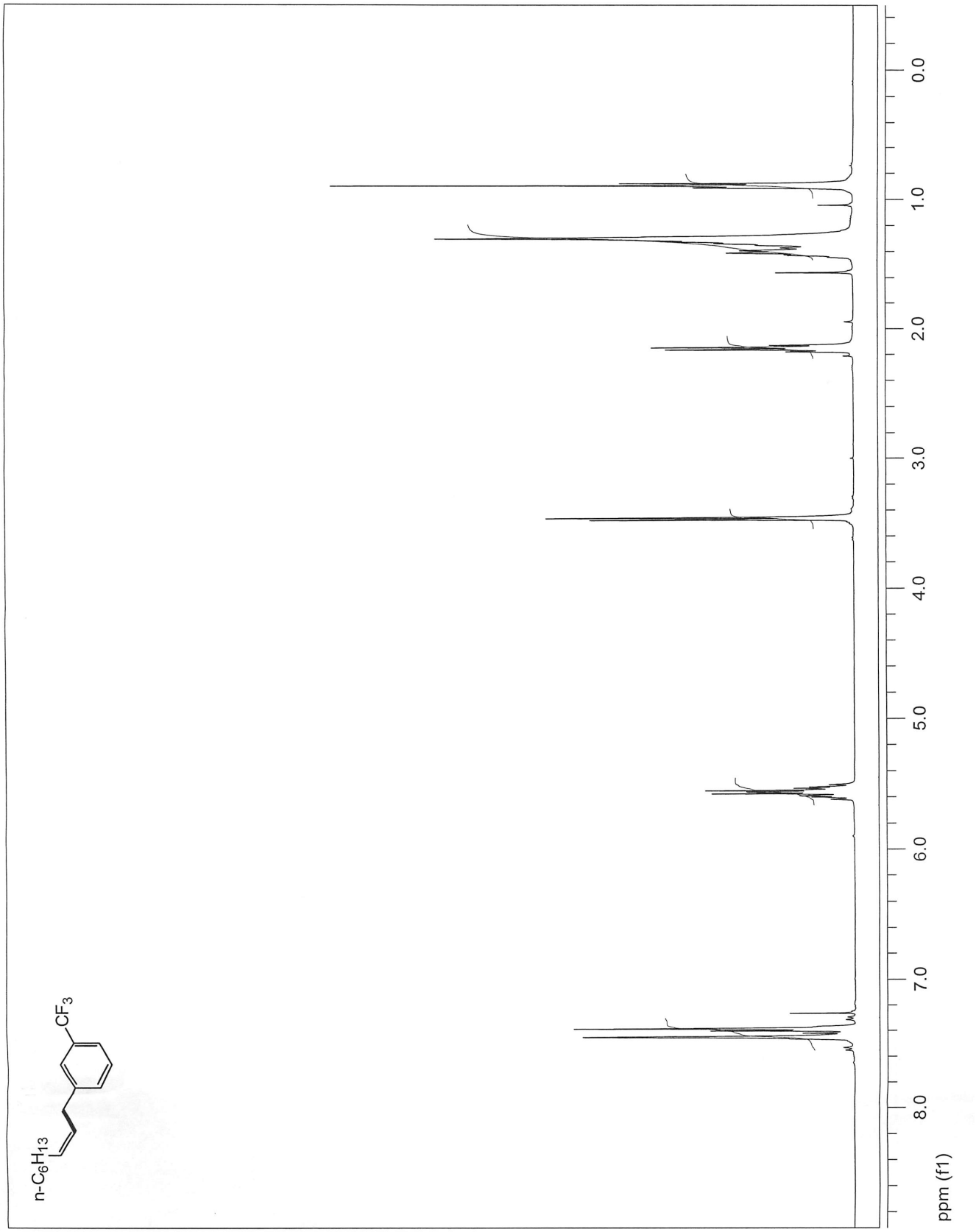
29.3
28.7
22.4
20.8
13.9

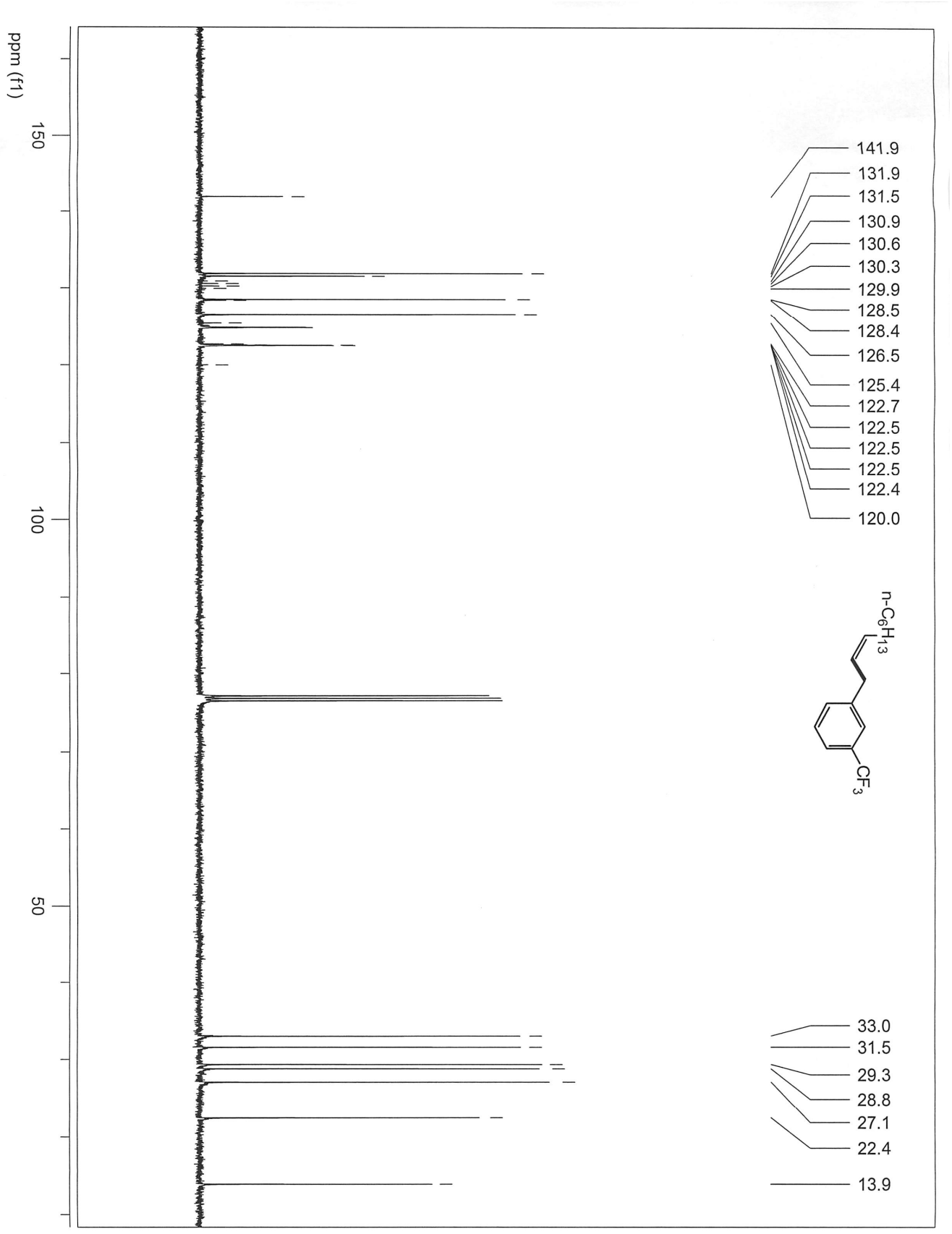
3




13.9
22.4
28.6
29.1
31.5
32.3
38.8
51.8
CO2Me
n-C6H13
127.4
127.6
128.3
129.5
132.8
146.4
167.0
0
50
100
150
ppm (f1)

4




ppm (f1)
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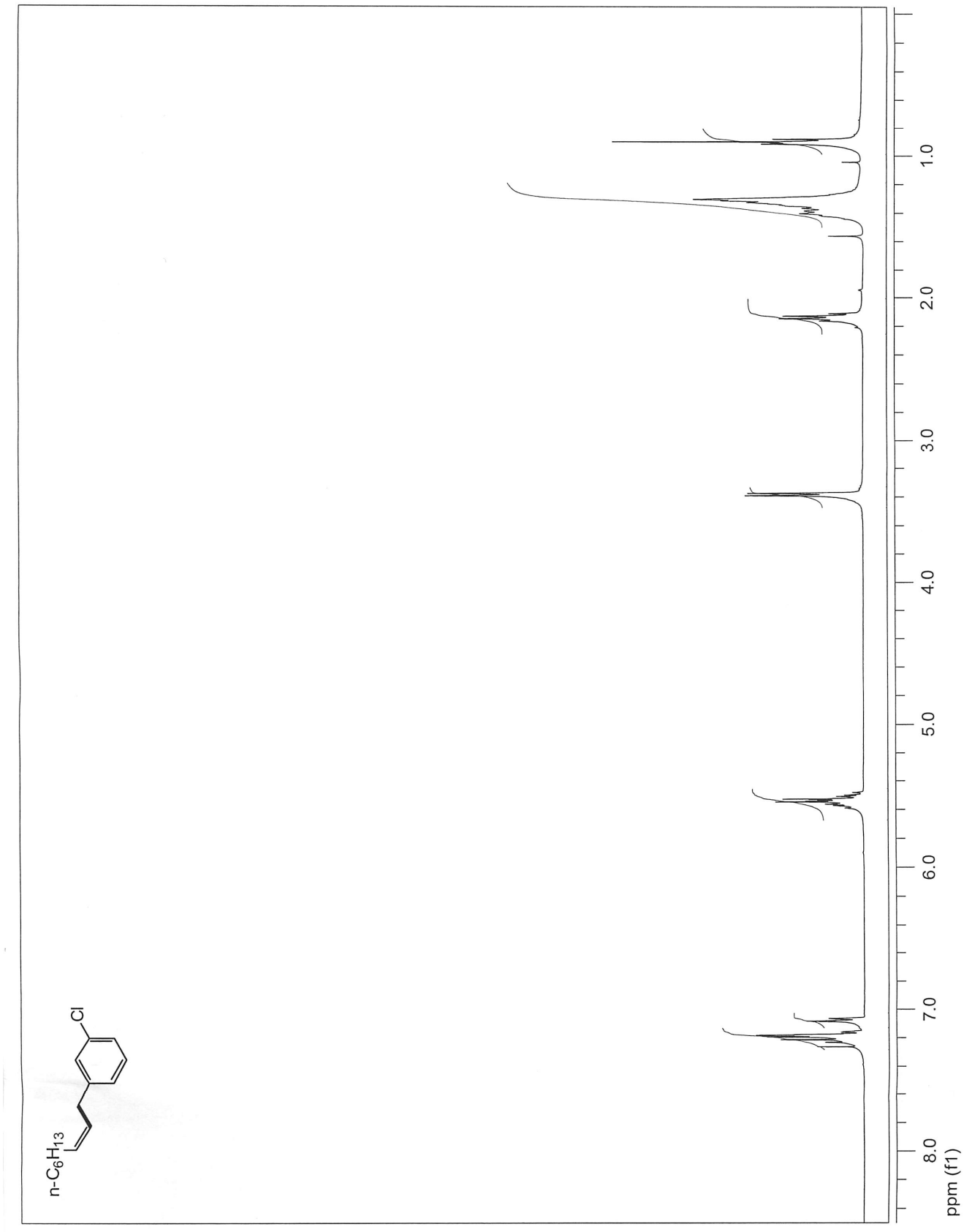
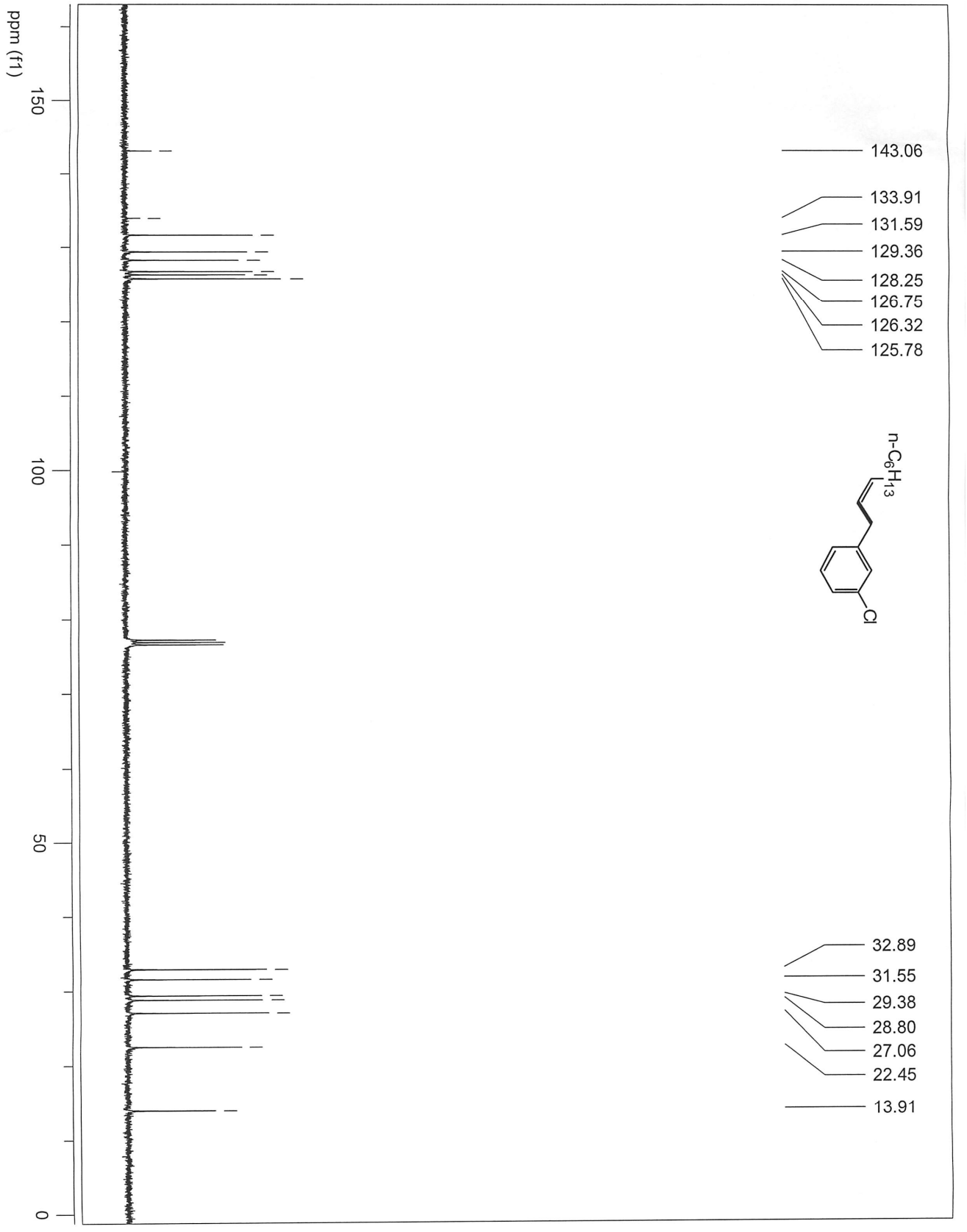
100
50
141.9
131.9
131.5
130.9
130.6
130.3
129.9
128.5
128.4
126.5
125.4
122.7
122.5
122.5
122.5
122.4
120.0
n-C6H13
CF3
33.0
31.5
29.3
28.8
27.1
22.4
13.9

5

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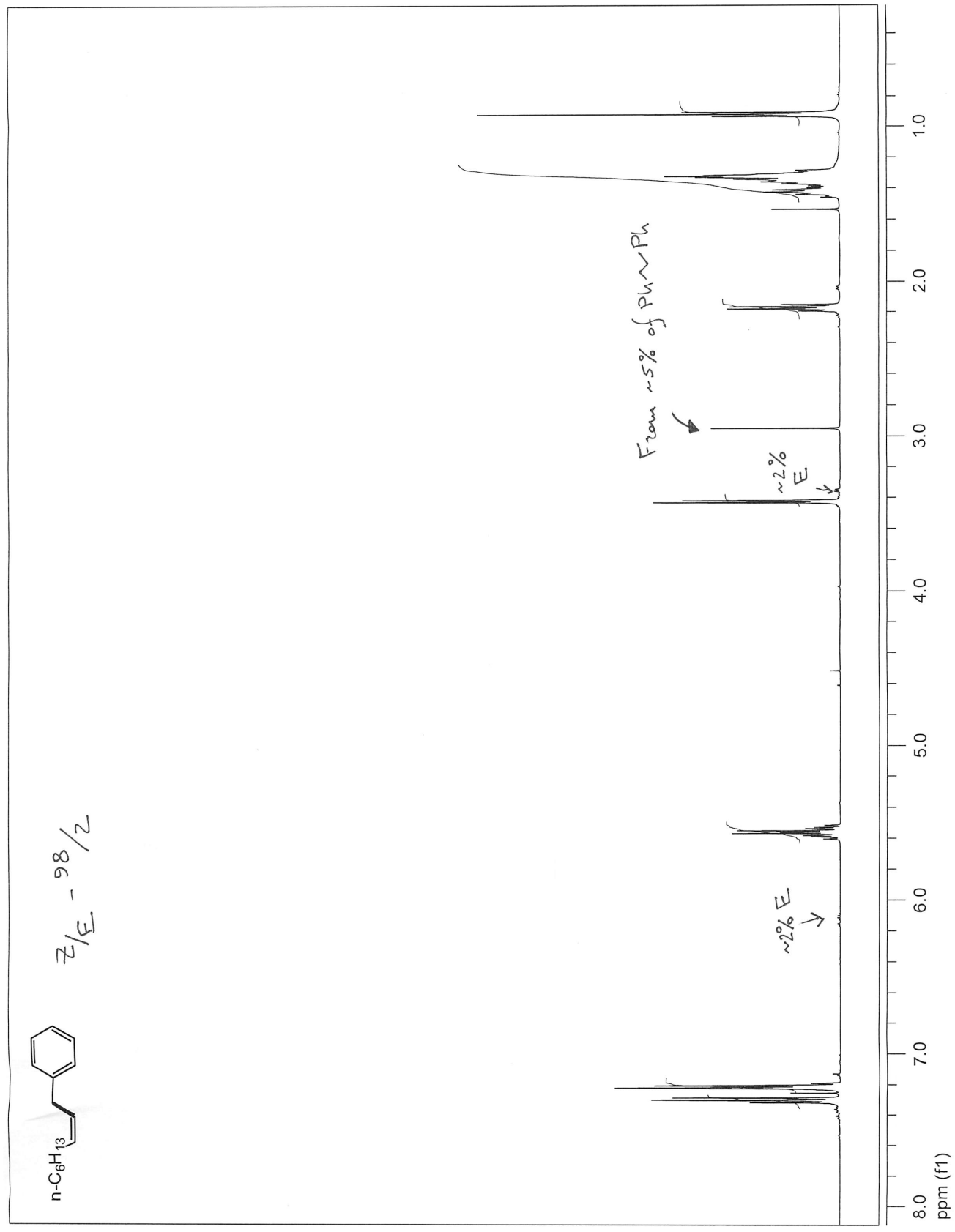
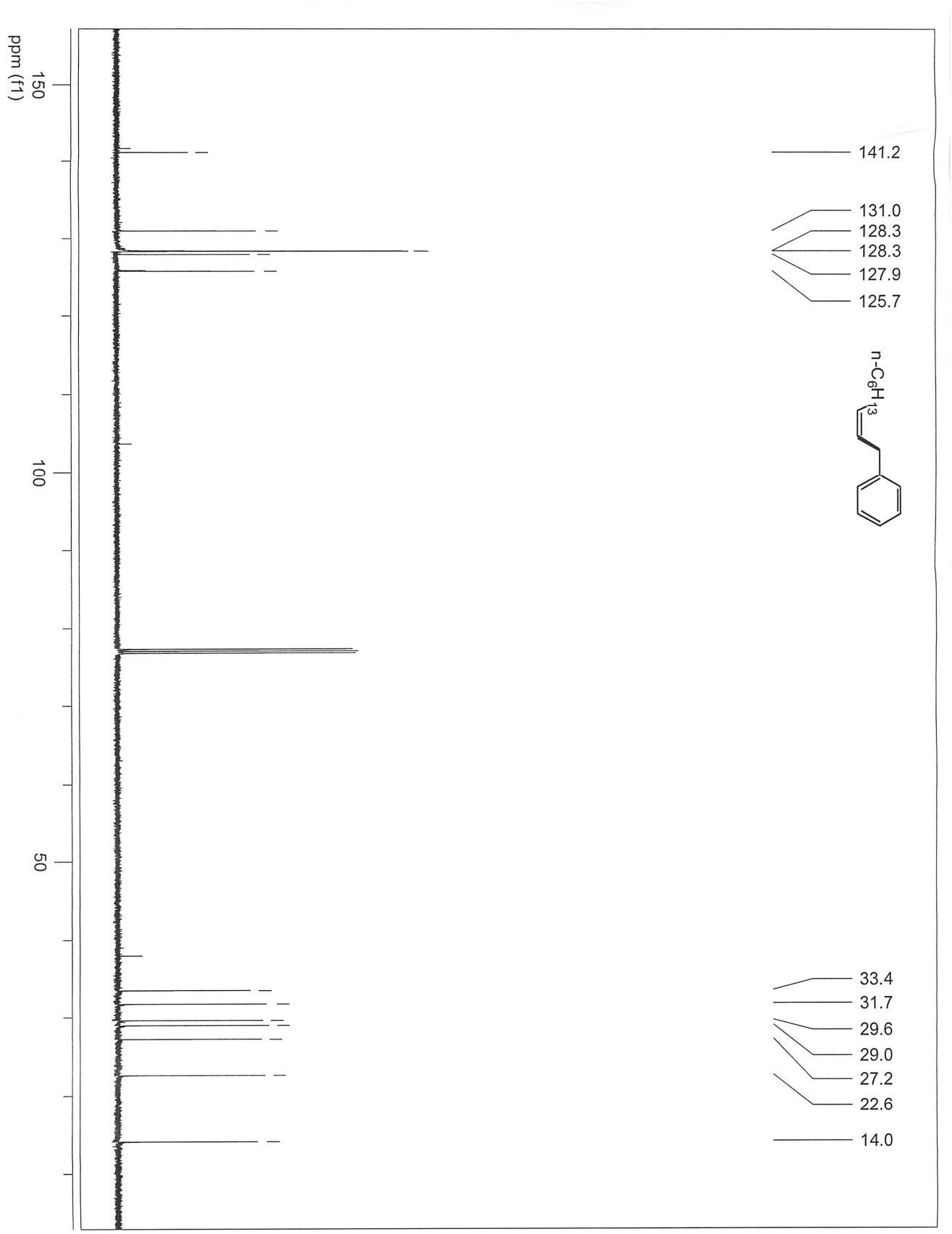
100
50
0
143.06
133.91
131.59
129.36
128.25
126.75
126.32
125.78
n-C6H13
Cl
32.89
31.55
29.38
28.80
27.06
22.45
13.91

6




ppm (f1)
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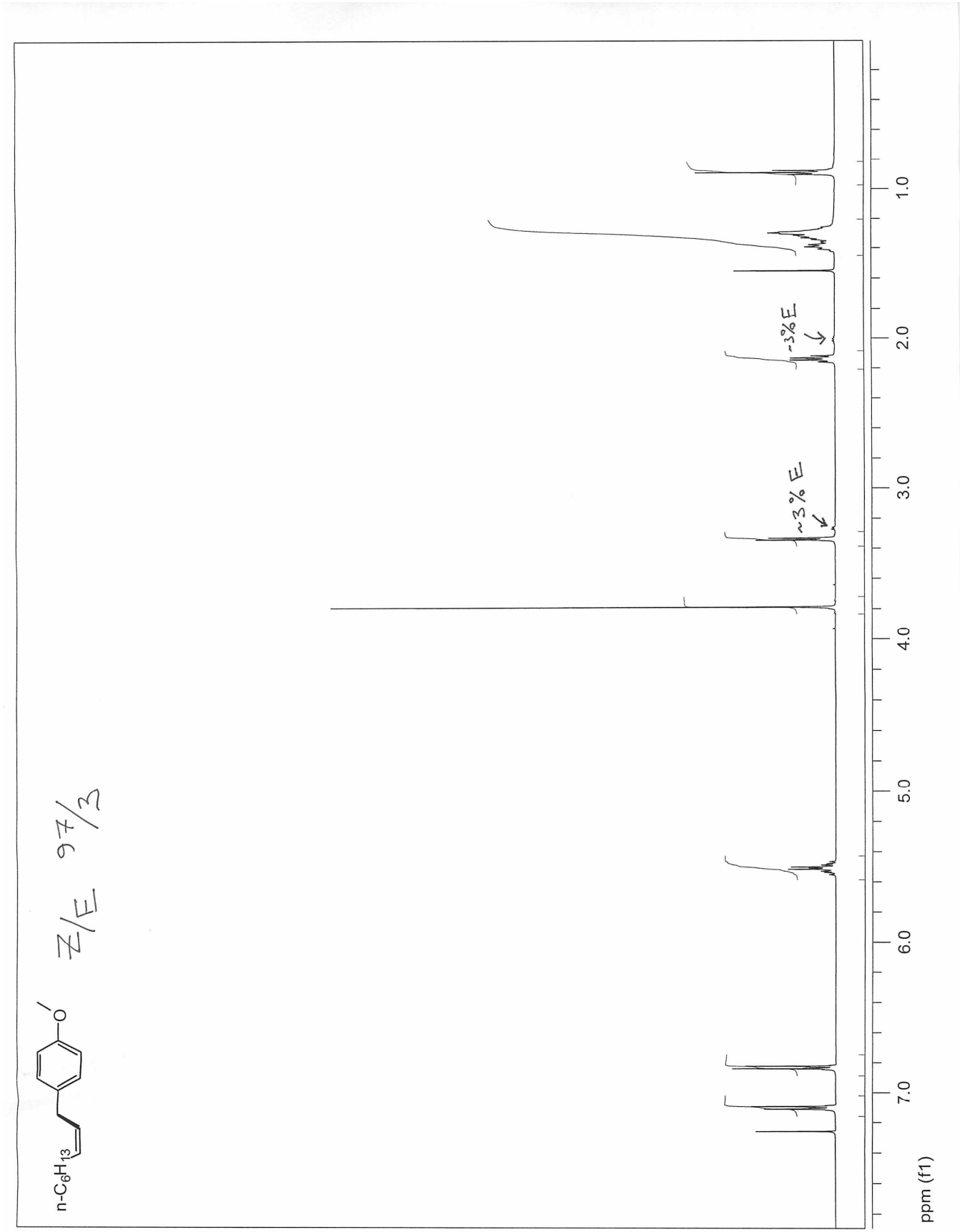
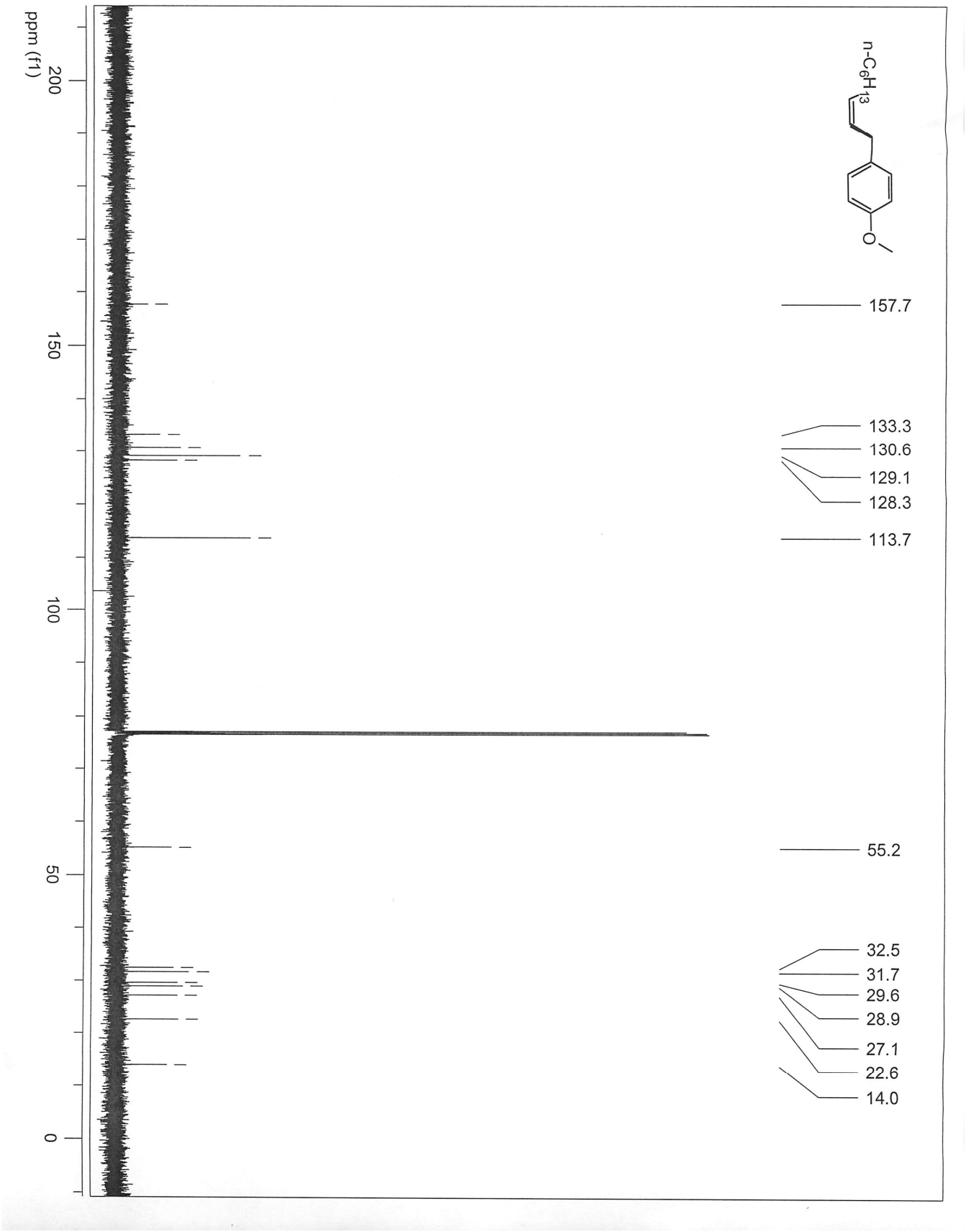
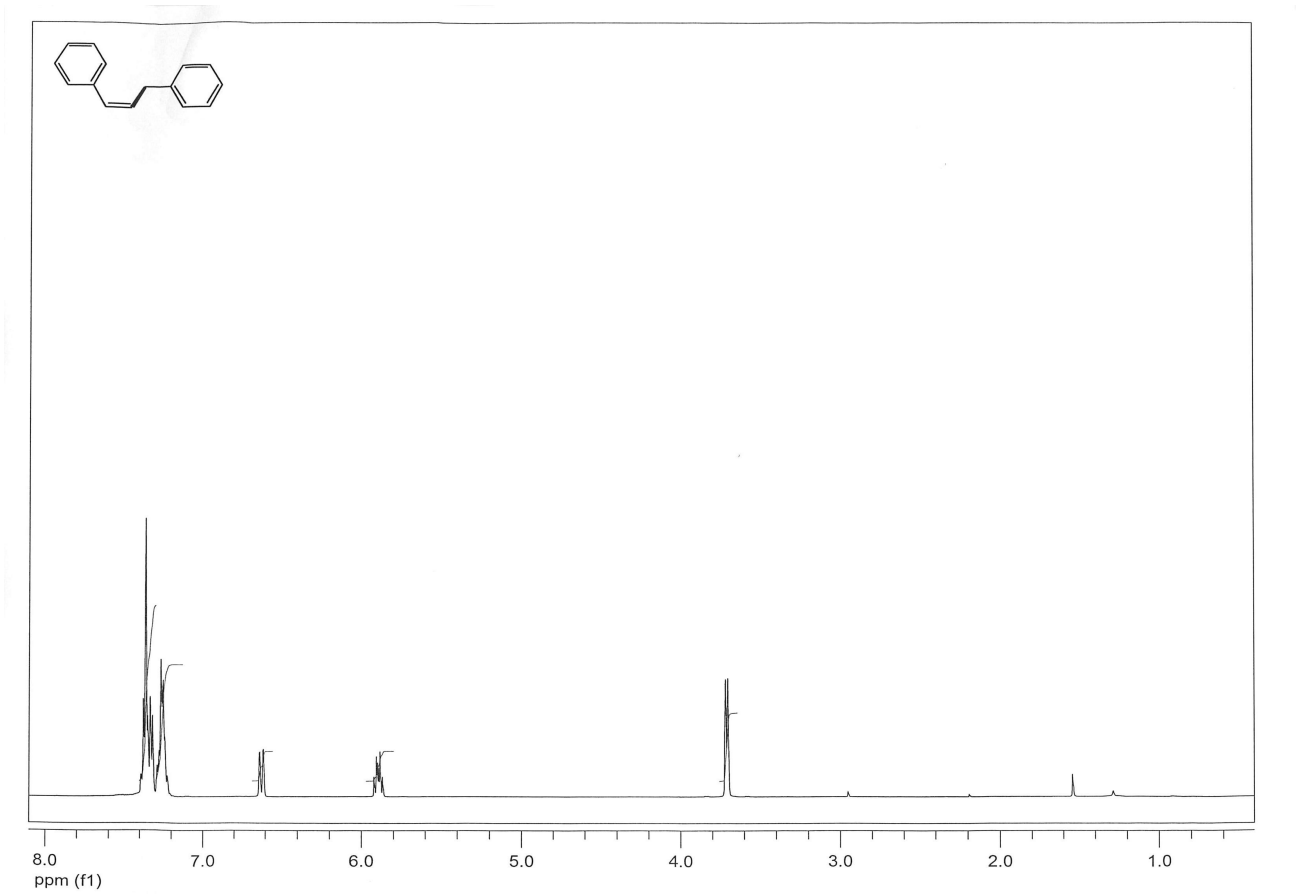
100
50
141.2
131.0
128.3
128.3
127.9
125.7
n-C6H13
33.4
31.7
29.6
29.0
27.2
22.6
14.0

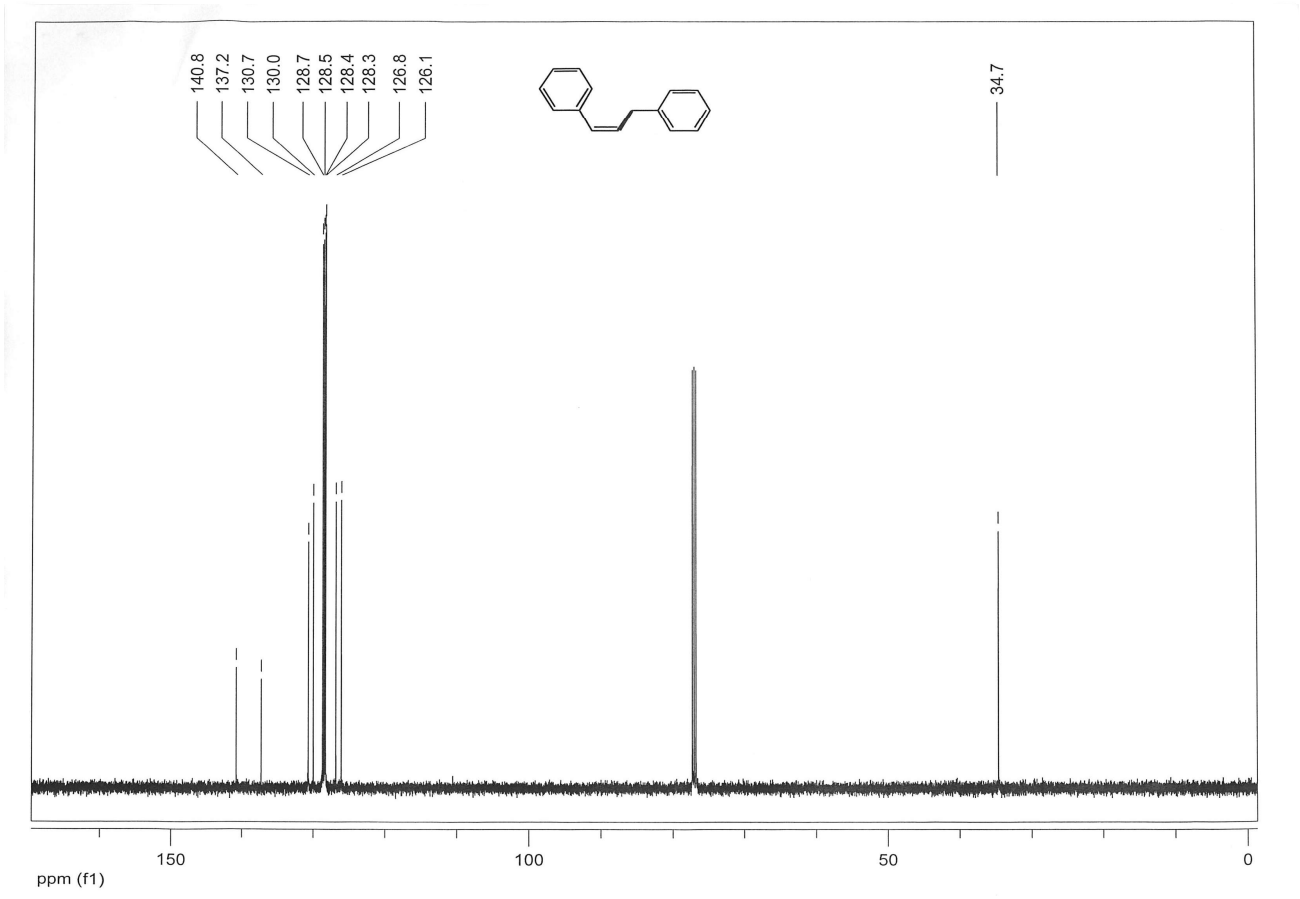
7



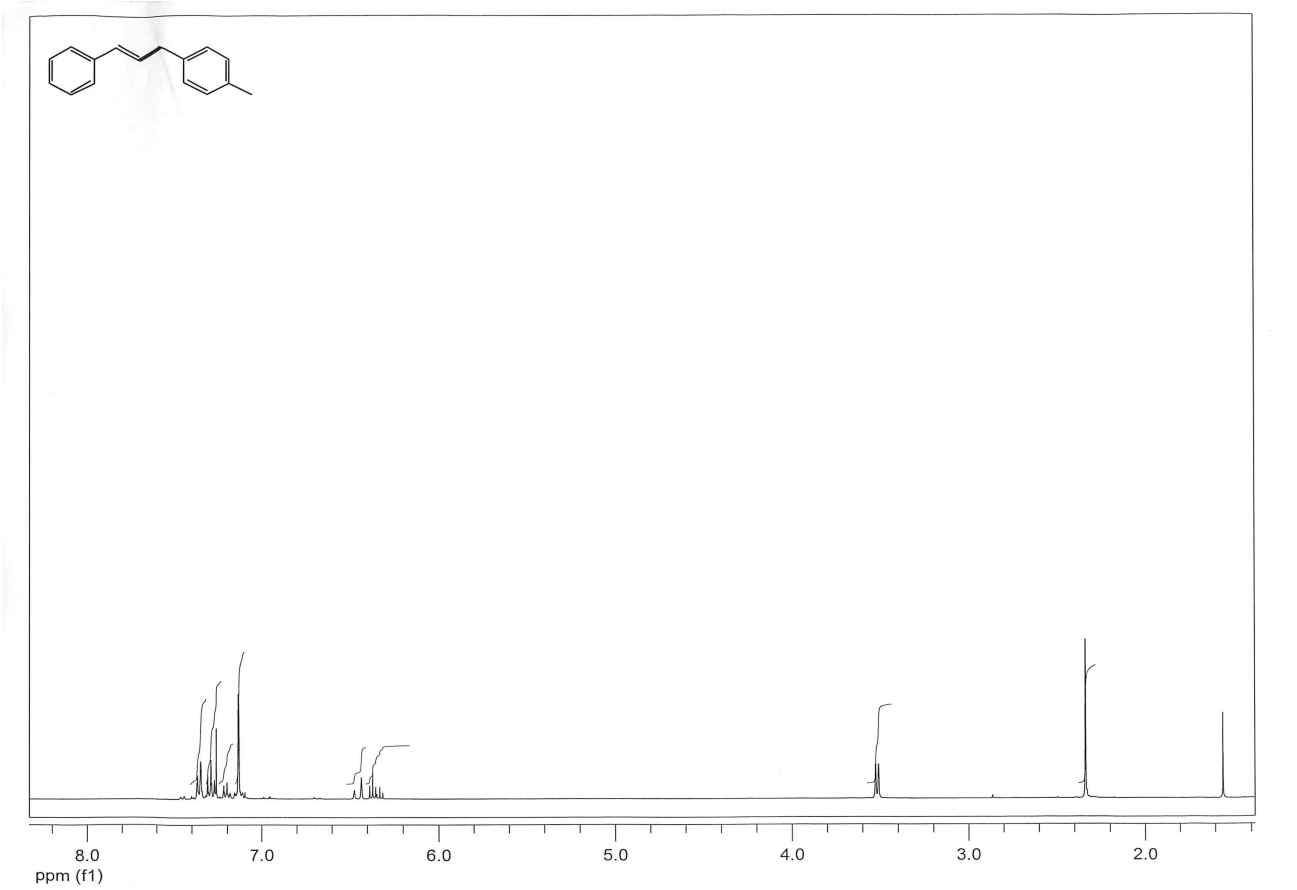

ppm (f1)
200
150
100
50
0
n-C6H13
O
157.7
133.3
130.6
129.1
128.3
113.7
55.2
32.5
31.7
29.6
28.9
27.1
22.6
14.0

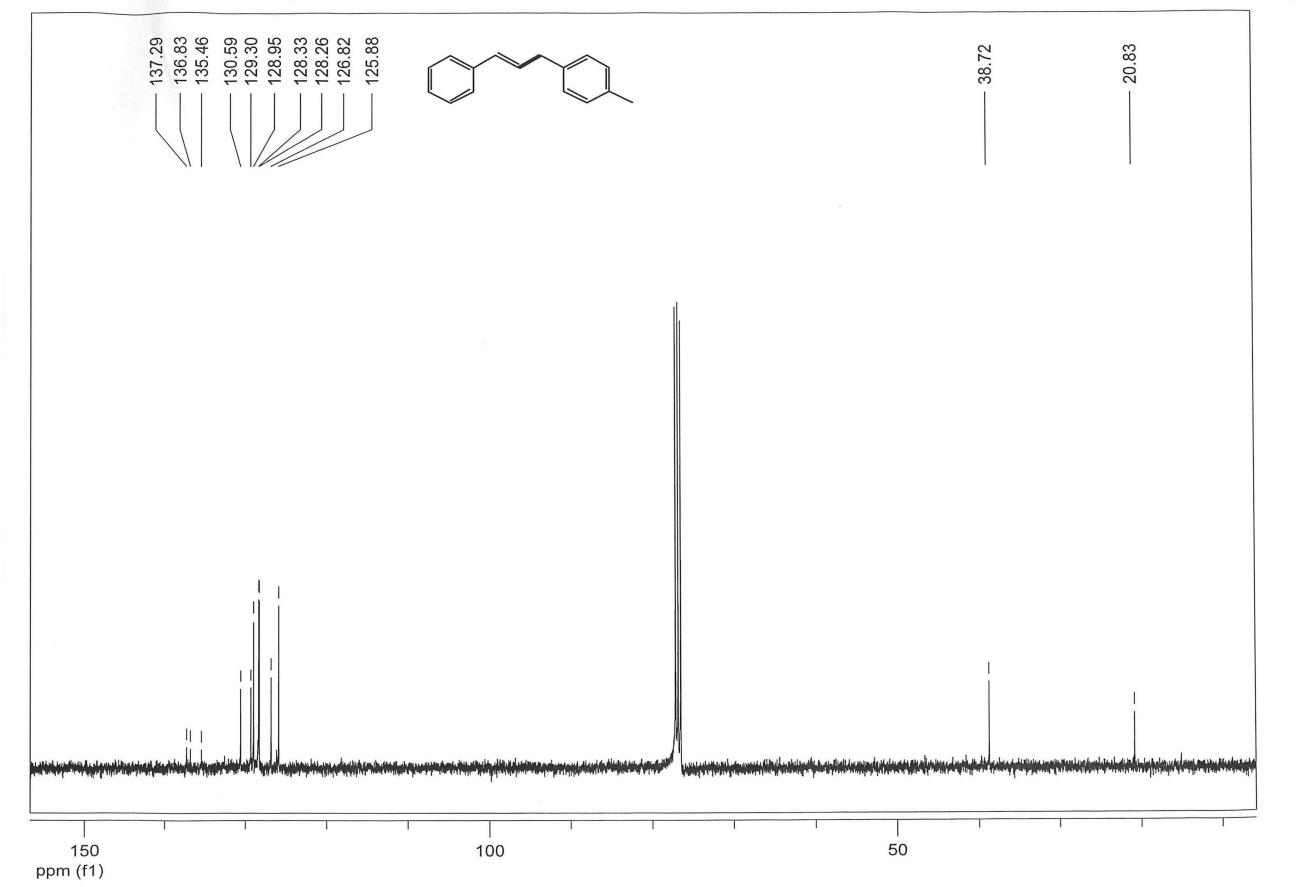
8


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

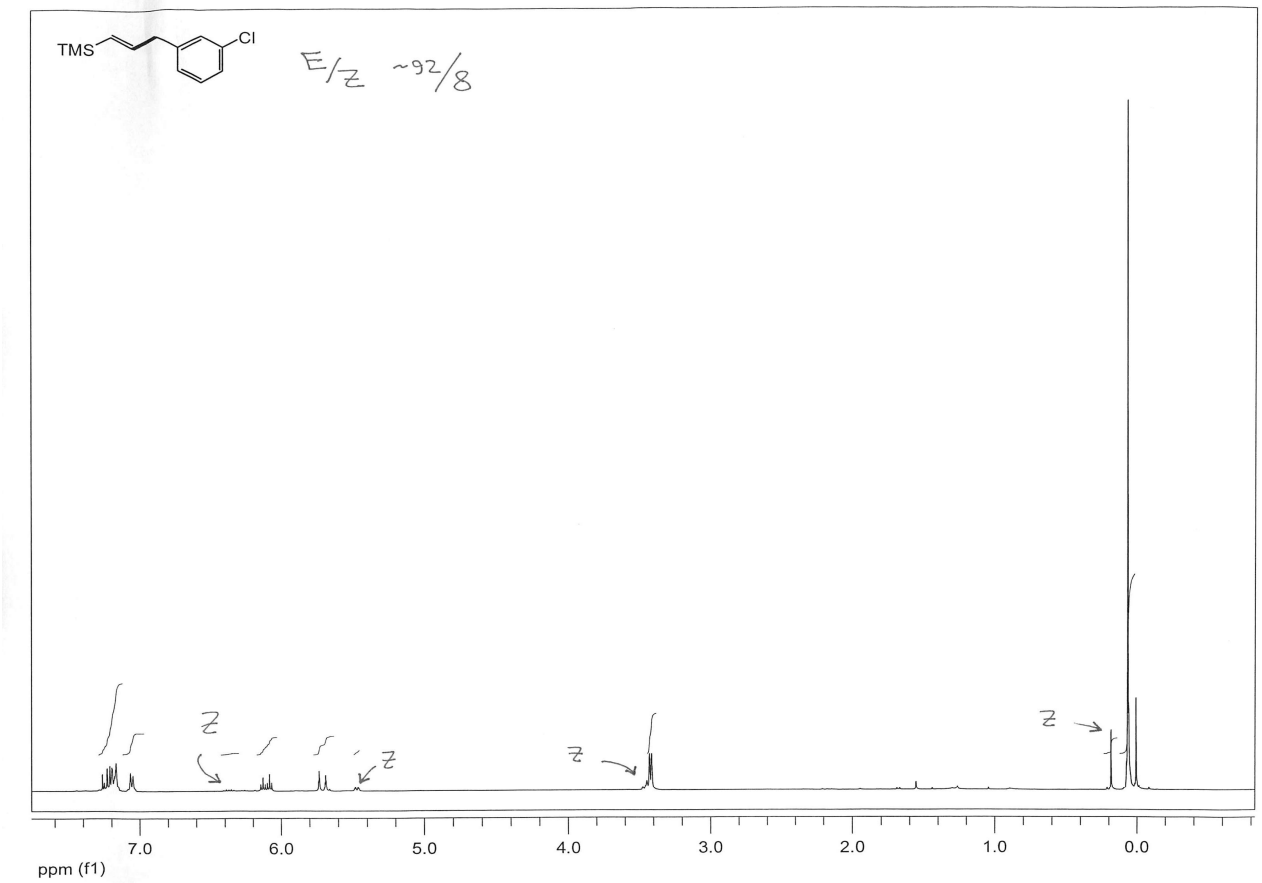

140.8
137.2
130.7
130.0
128.7
128.5
128.4
128.3
126.8
126.1
34.7
150
100
50
0
ppm (f1)

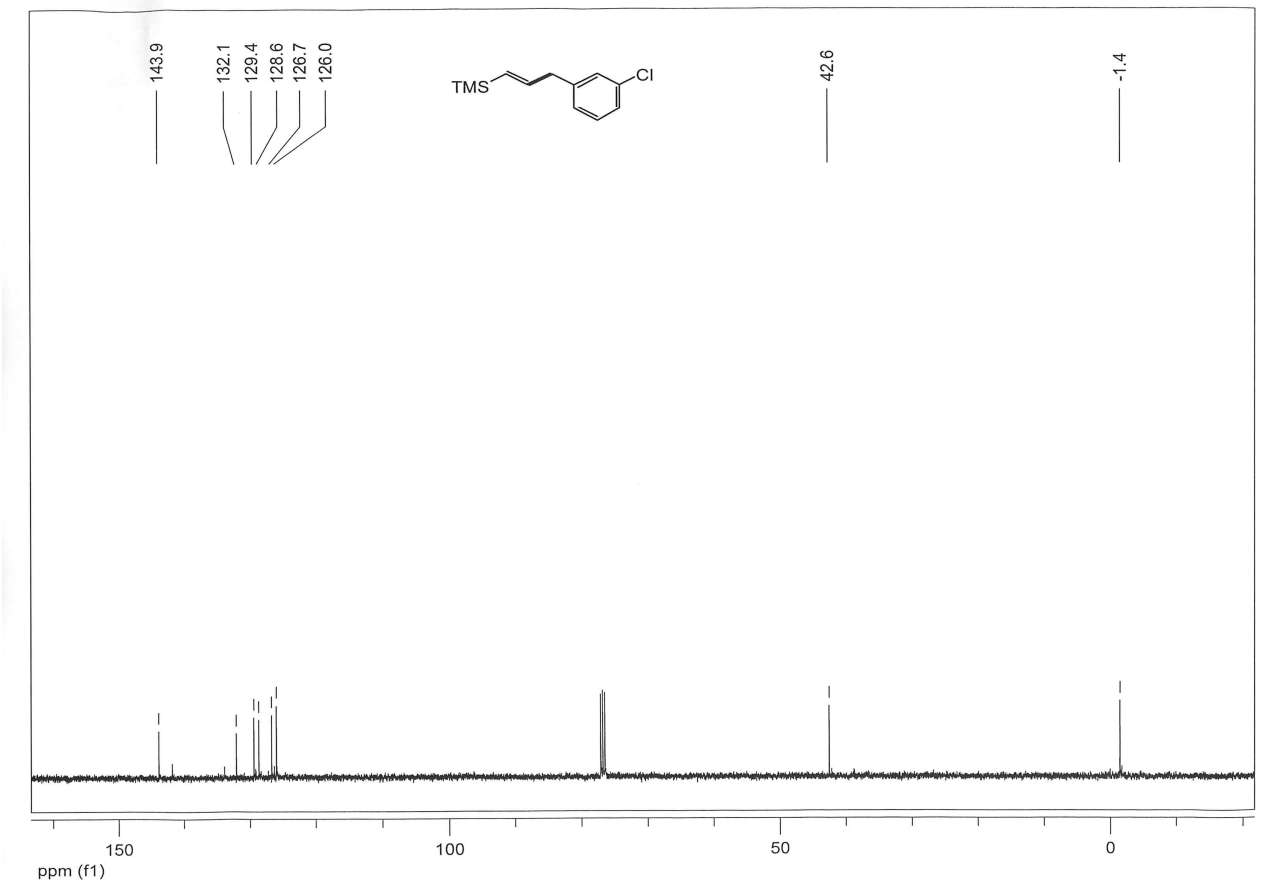
9


8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

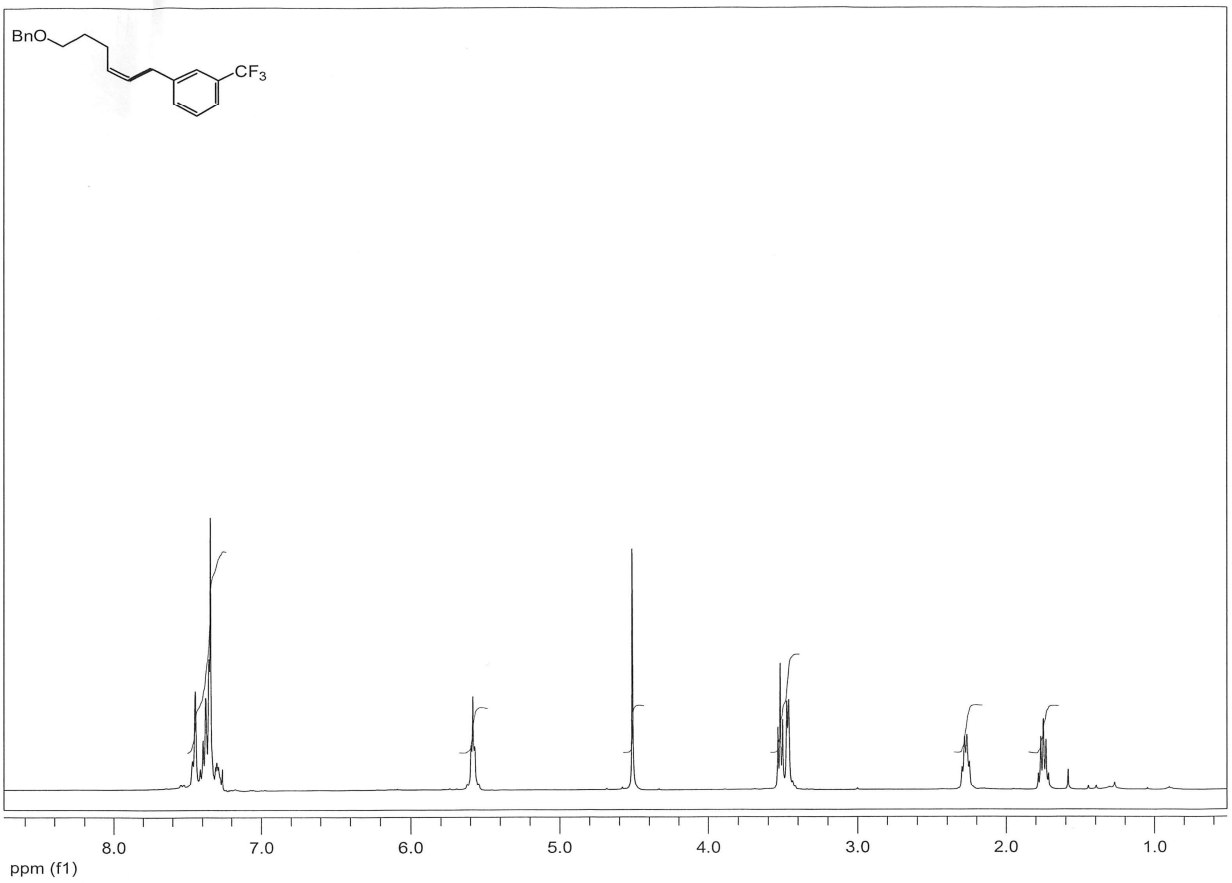

137.29
136.83
135.46
130.59
129.30
128.95
128.33
128.26
126.82
125.88
38.72
20.83
150
100
50
ppm (f1)

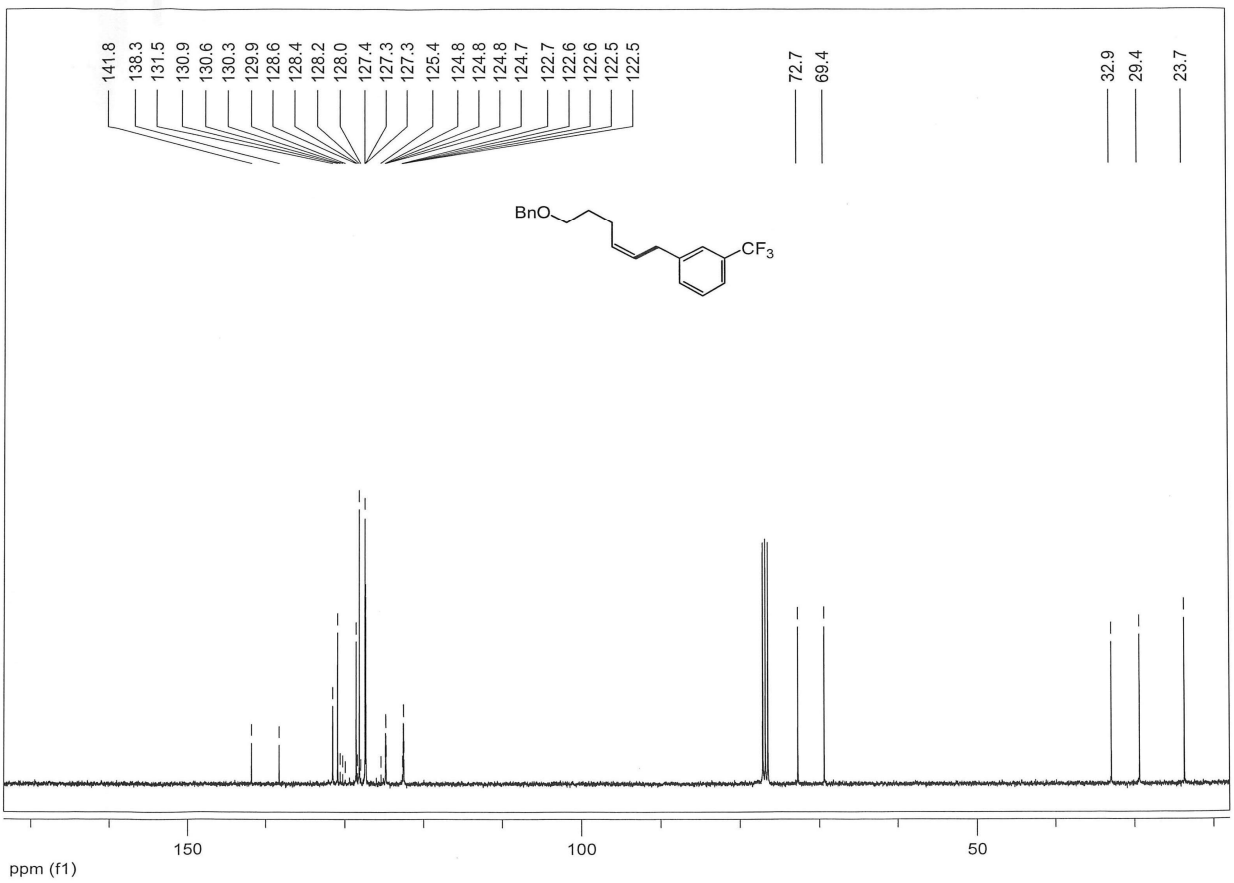
10


TMS
Cl
E/Z ~92/8
Z
Z
Z
Z
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

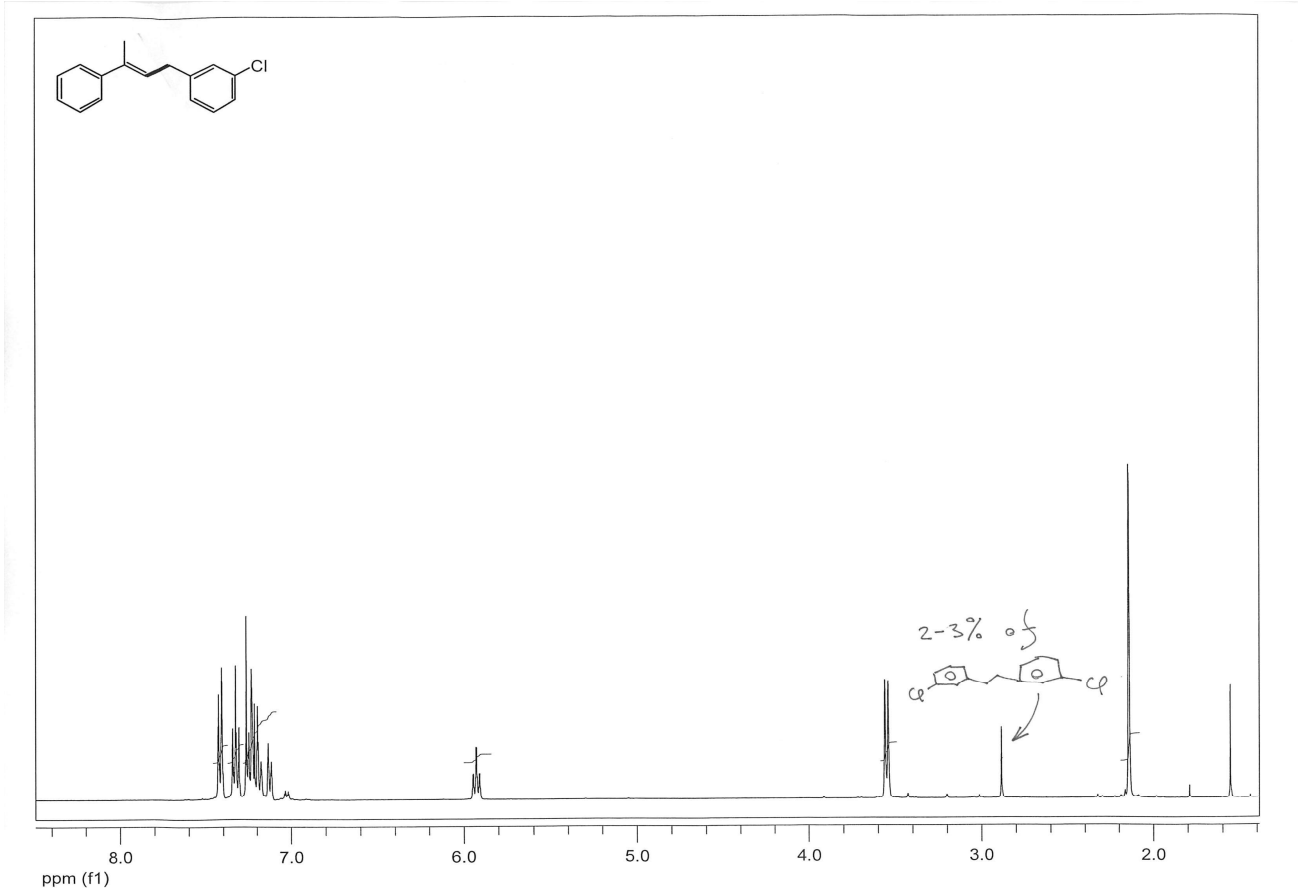

143.9
132.1
129.4
128.6
126.7
126.0
TMS
Cl
42.6
-1.4
150
100
50
0
ppm (f1)

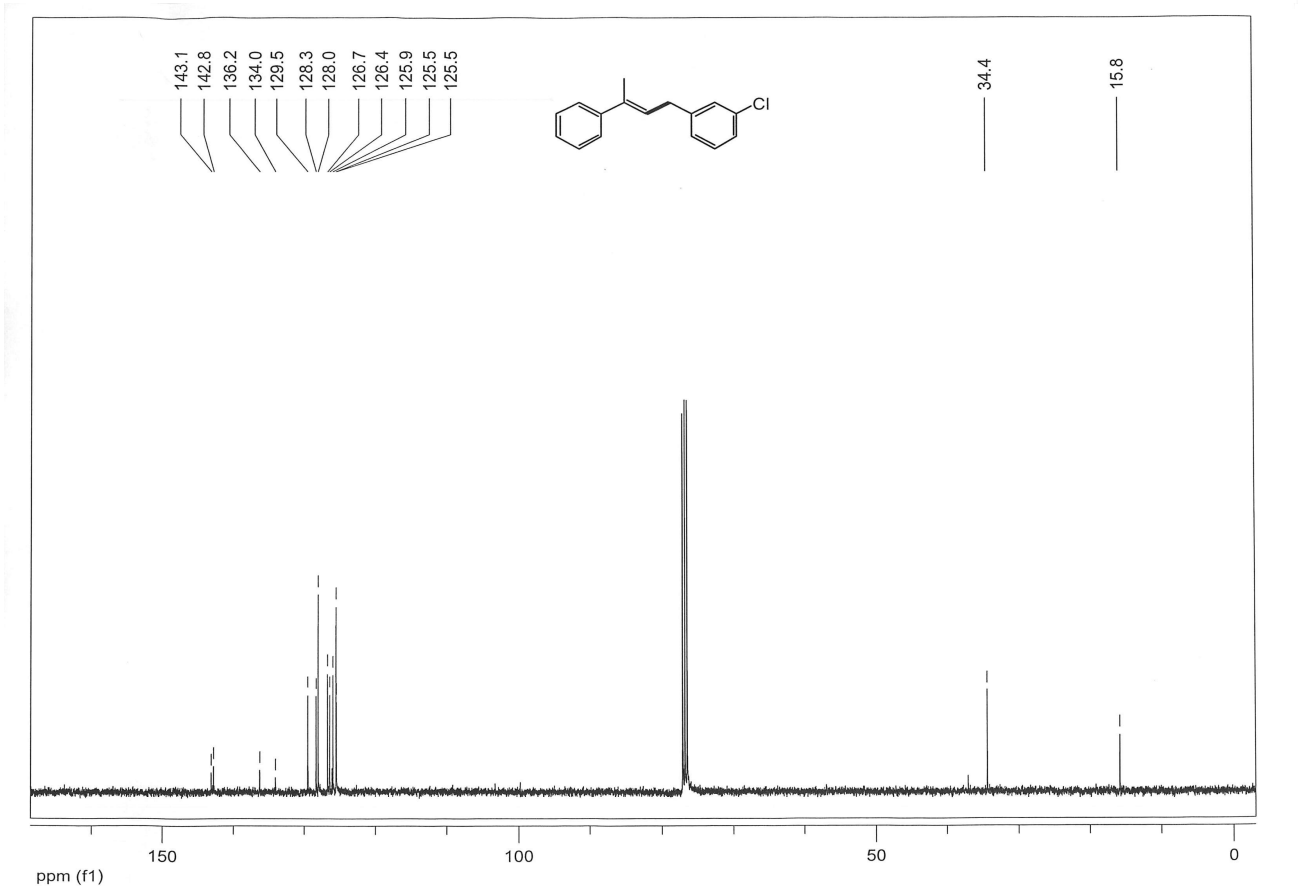
11


BnO
CF3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

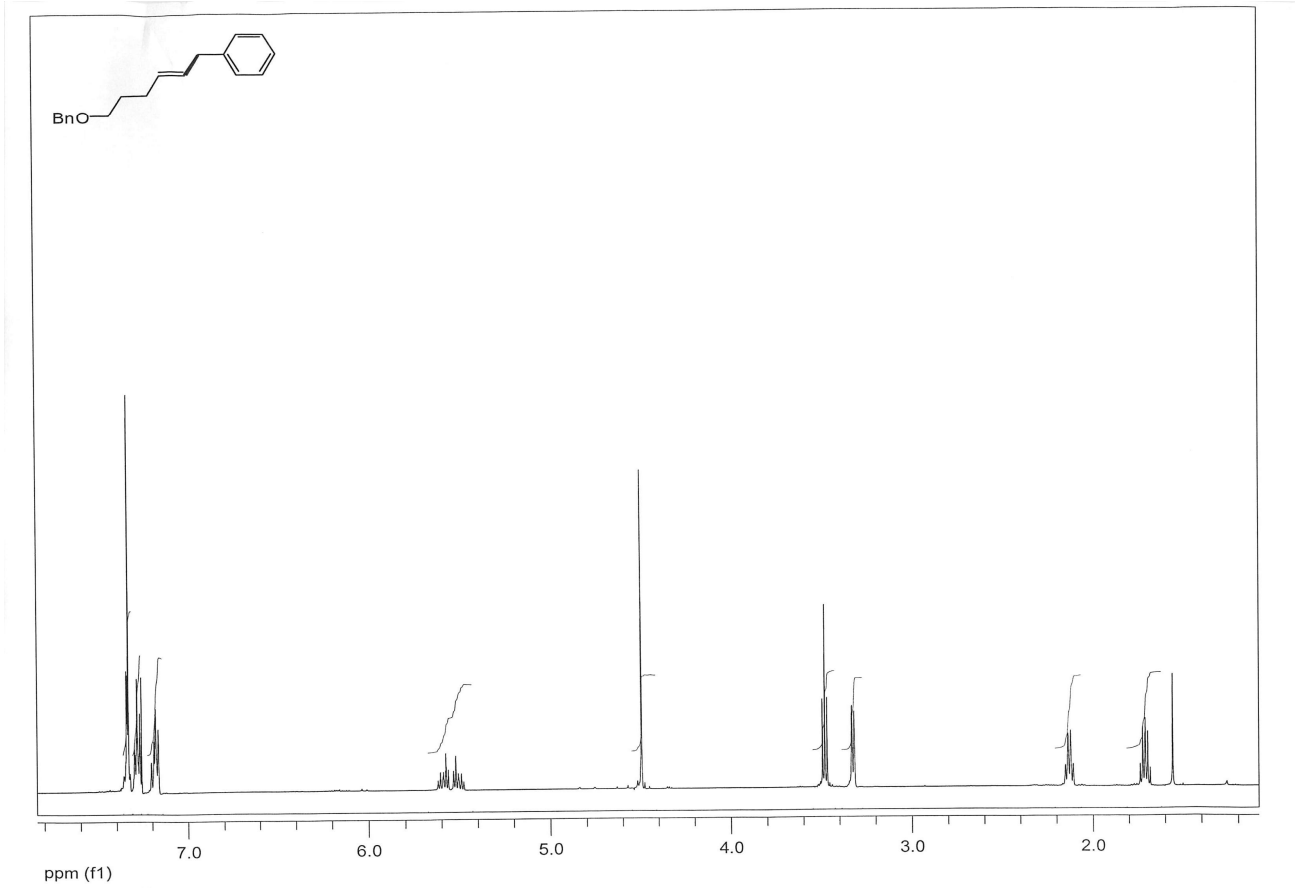

141.8
138.3
131.5
130.9
130.6
130.3
129.9
128.6
128.4
128.2
128.0
127.4
127.3
127.3
125.4
124.8
124.8
124.8
124.7
122.7
122.6
122.6
122.5
122.5
72.7
69.4
32.9
29.4
23.7
BnO
CF3
150
100
50
ppm (f1)

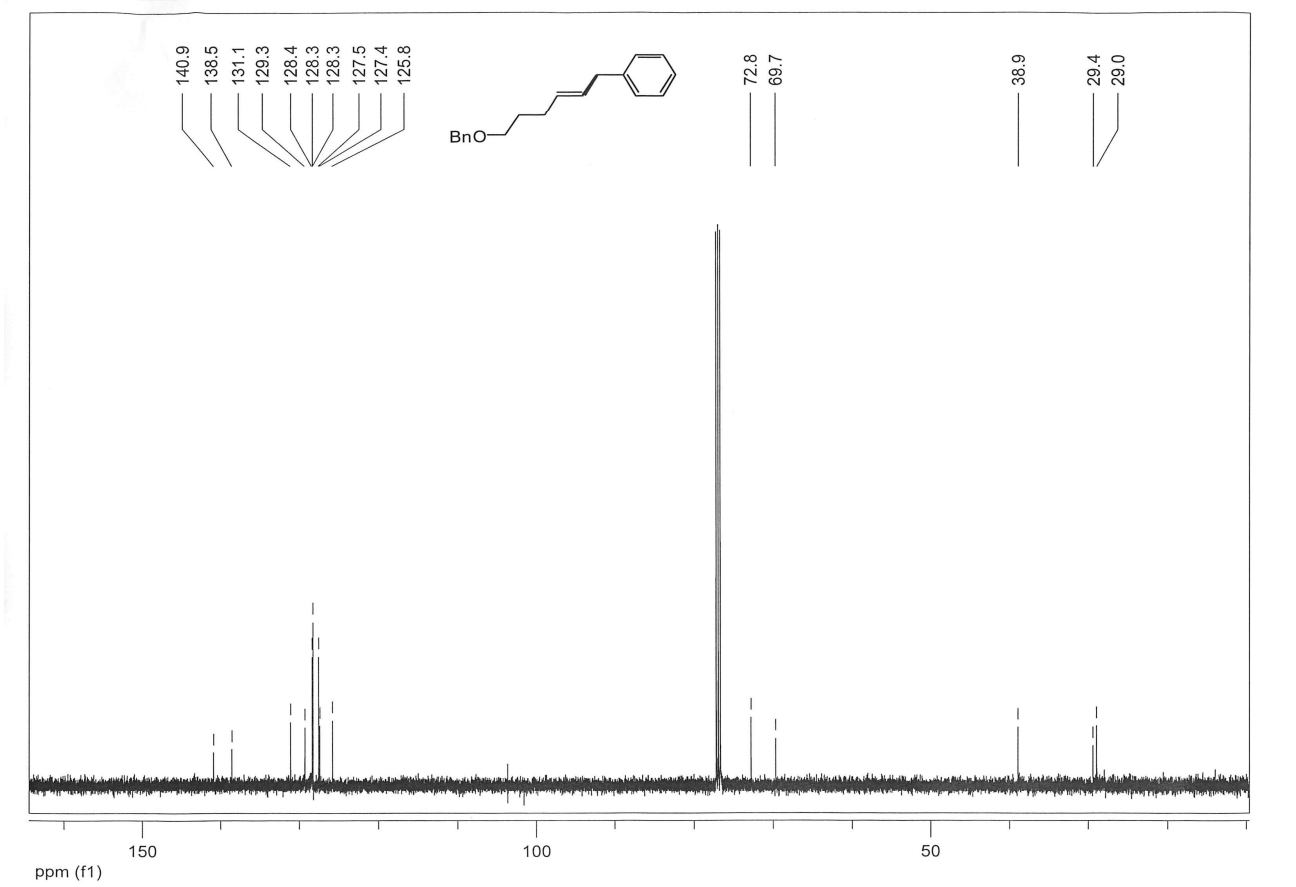
12


Cl
2-3% of
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

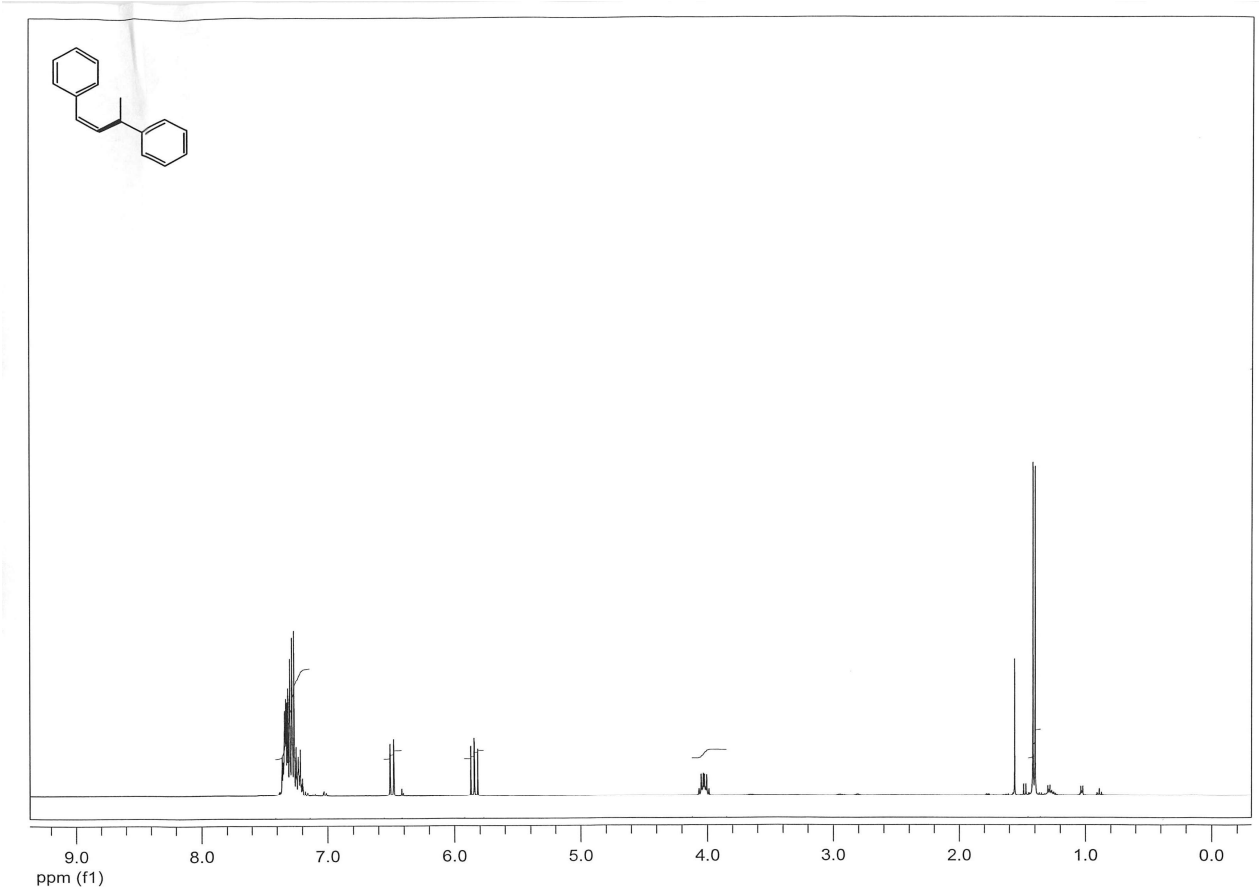

143.1
142.8
136.2
134.0
129.5
128.3
128.0
126.7
126.4
125.9
125.5
125.5
Cl
34.4
15.8
150
100
50
0
ppm (f1)

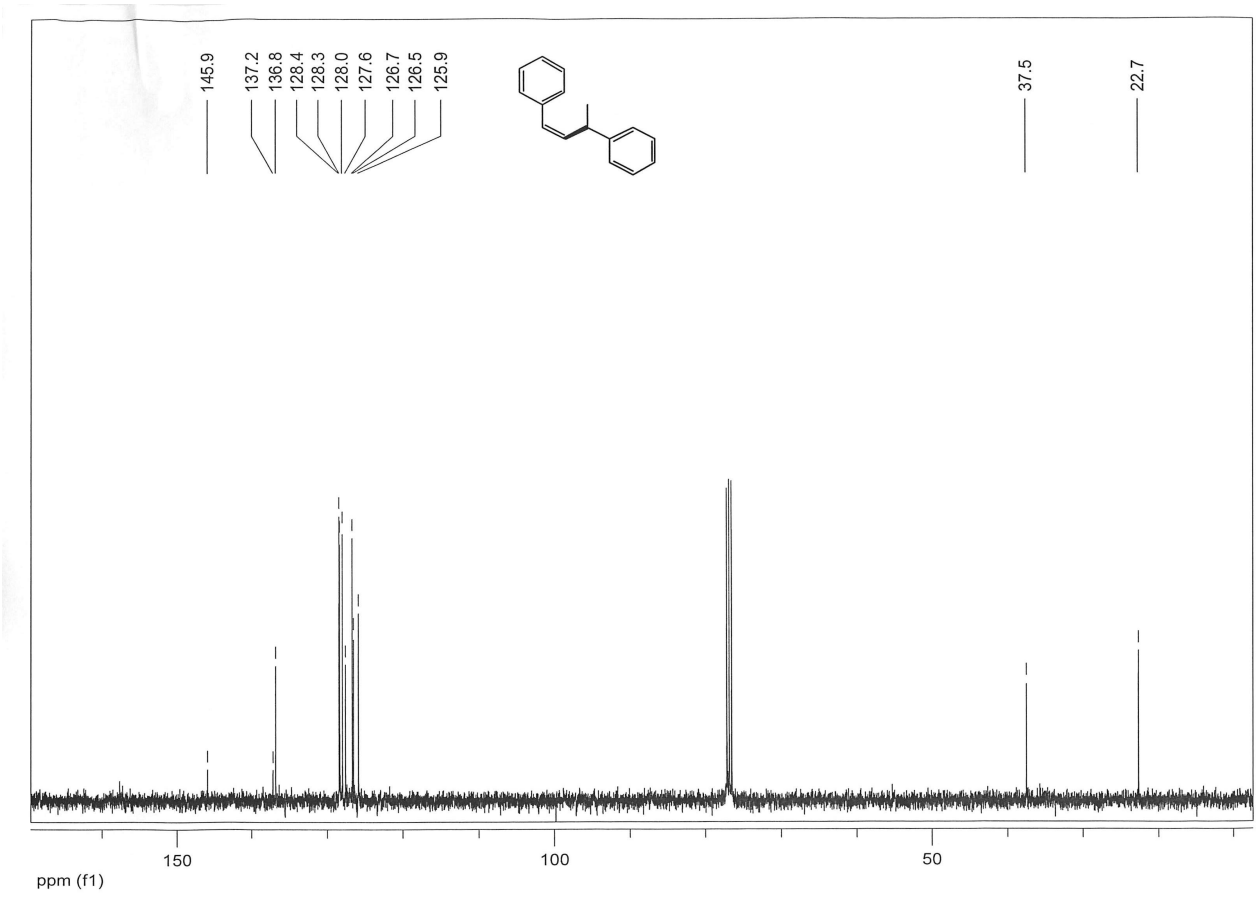
13


BnO
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

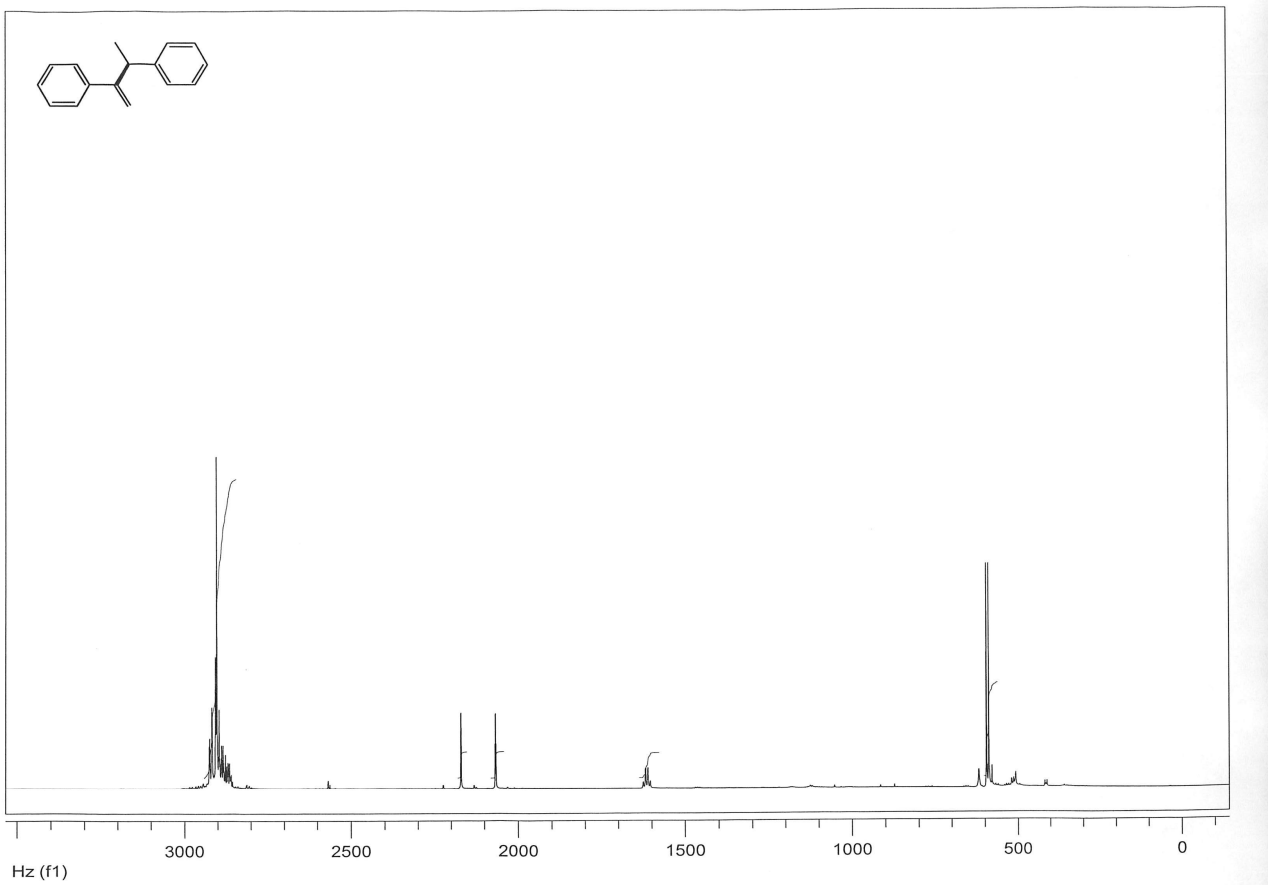

140.9
138.5
131.1
129.3
128.4
128.3
128.3
127.5
127.4
125.8
BnO
72.8
69.7
38.9
29.4
29.0
150
100
50
ppm (f1)

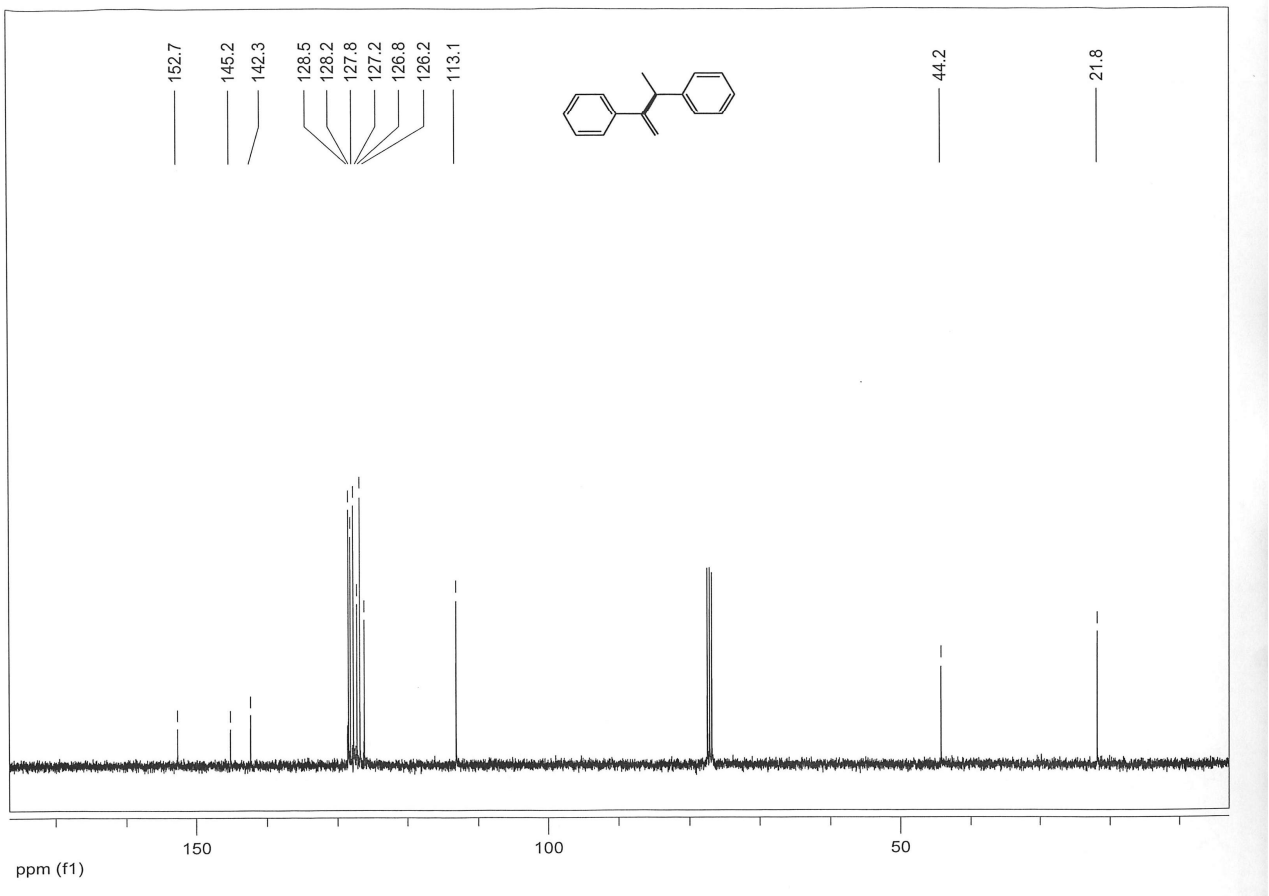
14


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

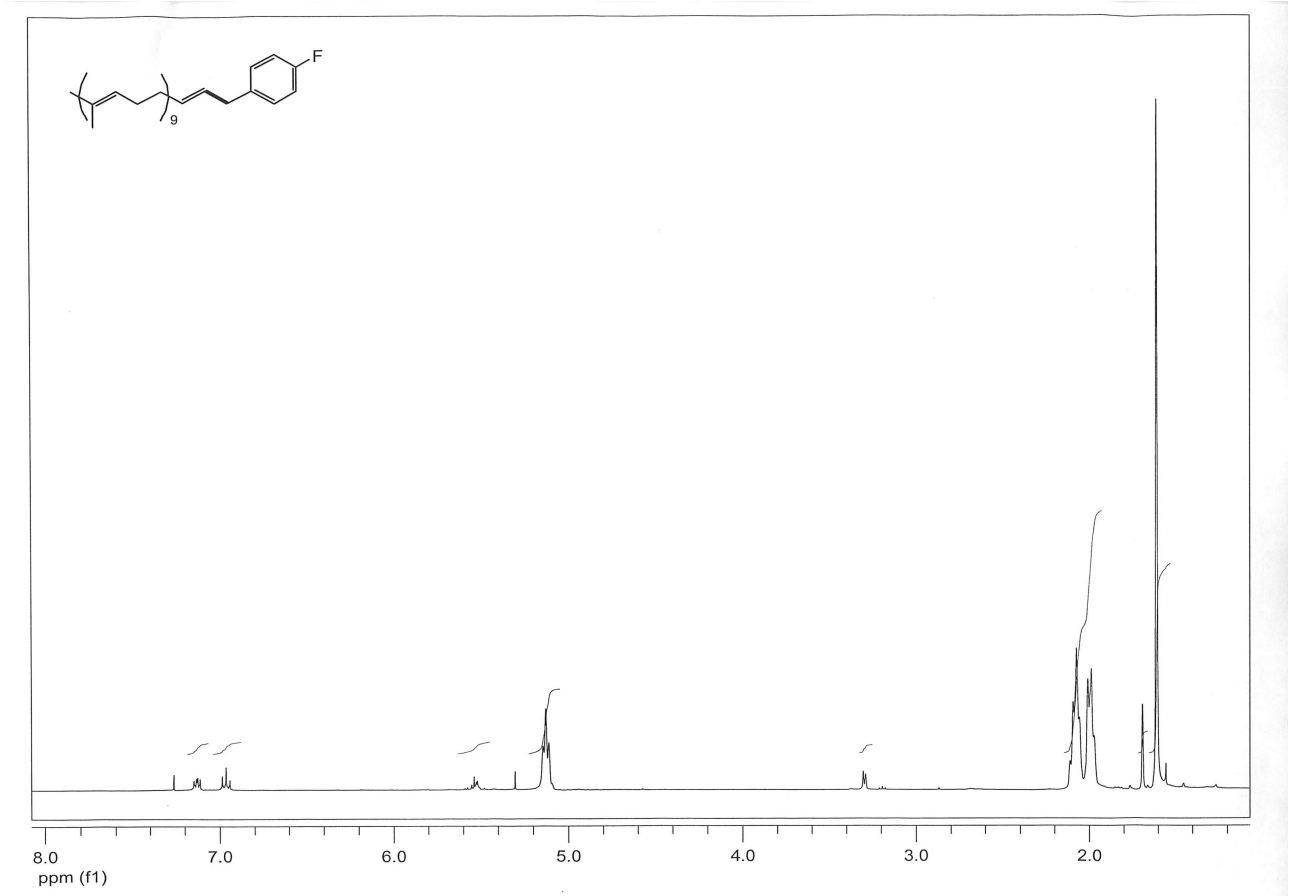

145.9
137.2
136.8
128.4
128.3
128.0
127.6
126.7
126.5
125.9
37.5
22.7
150
100
50
ppm (f1)

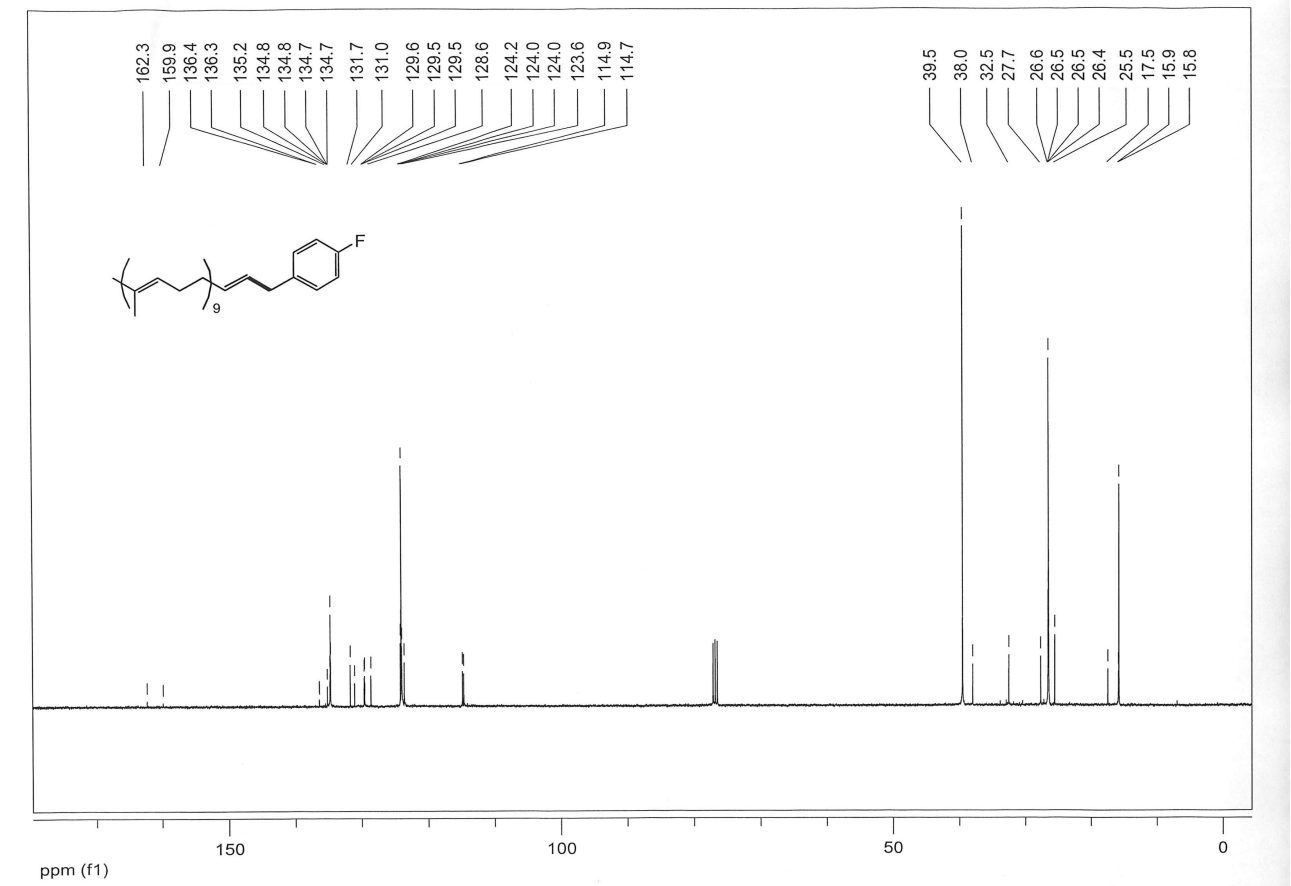
15


3000
2500
2000
1500
1000
500
0
Hz (f1)

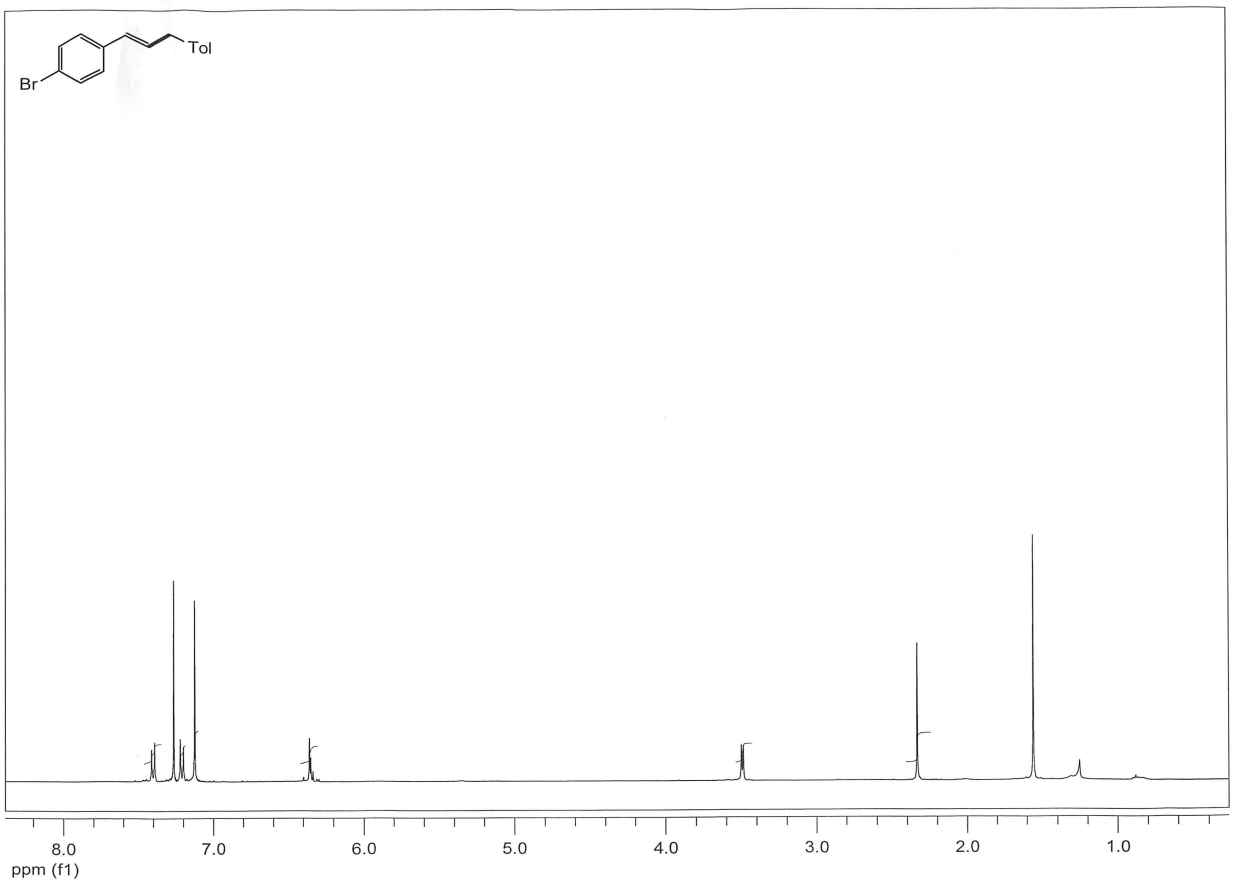

152.7
145.2
142.3
128.5
128.2
127.8
127.2
126.8
126.2
113.1
44.2
21.8
150
100
50
ppm (f1)

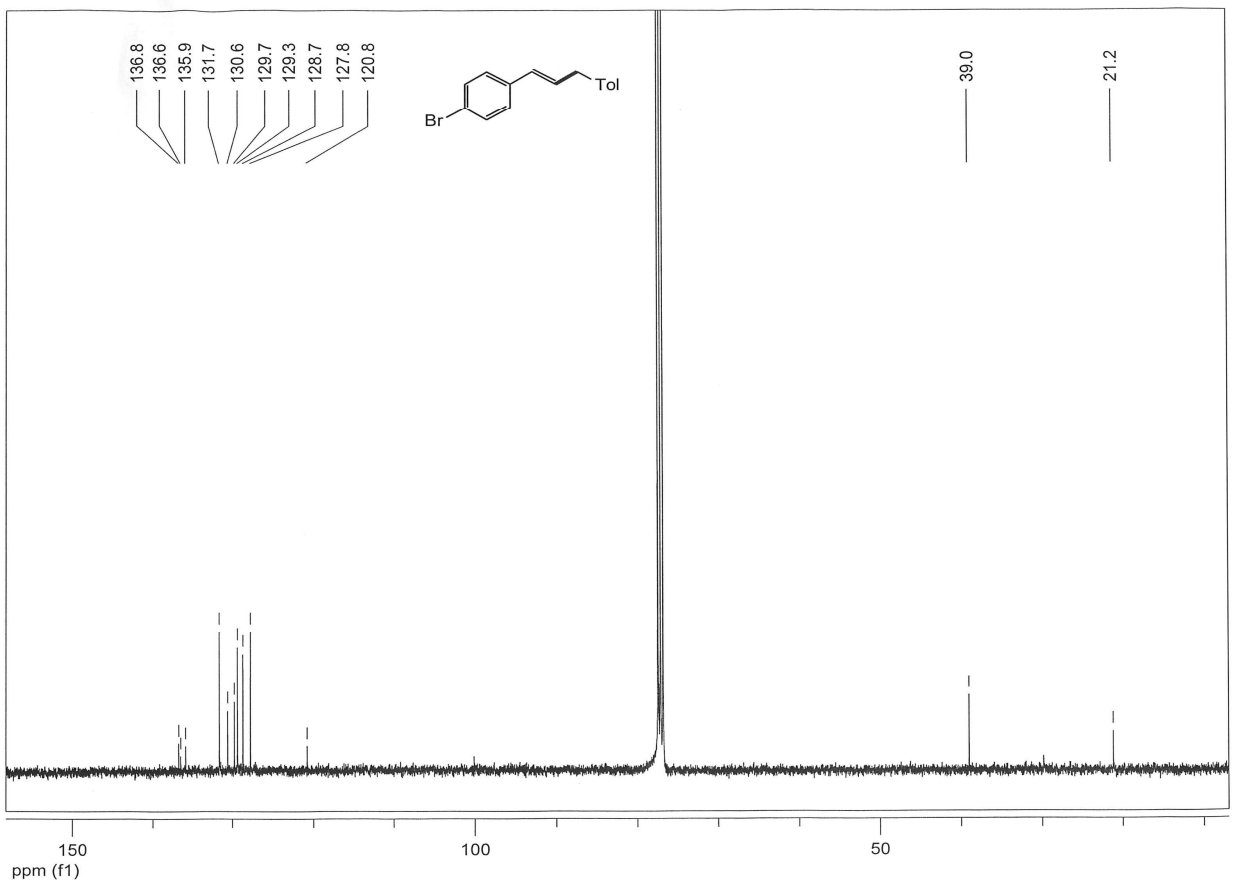
16


F
9
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

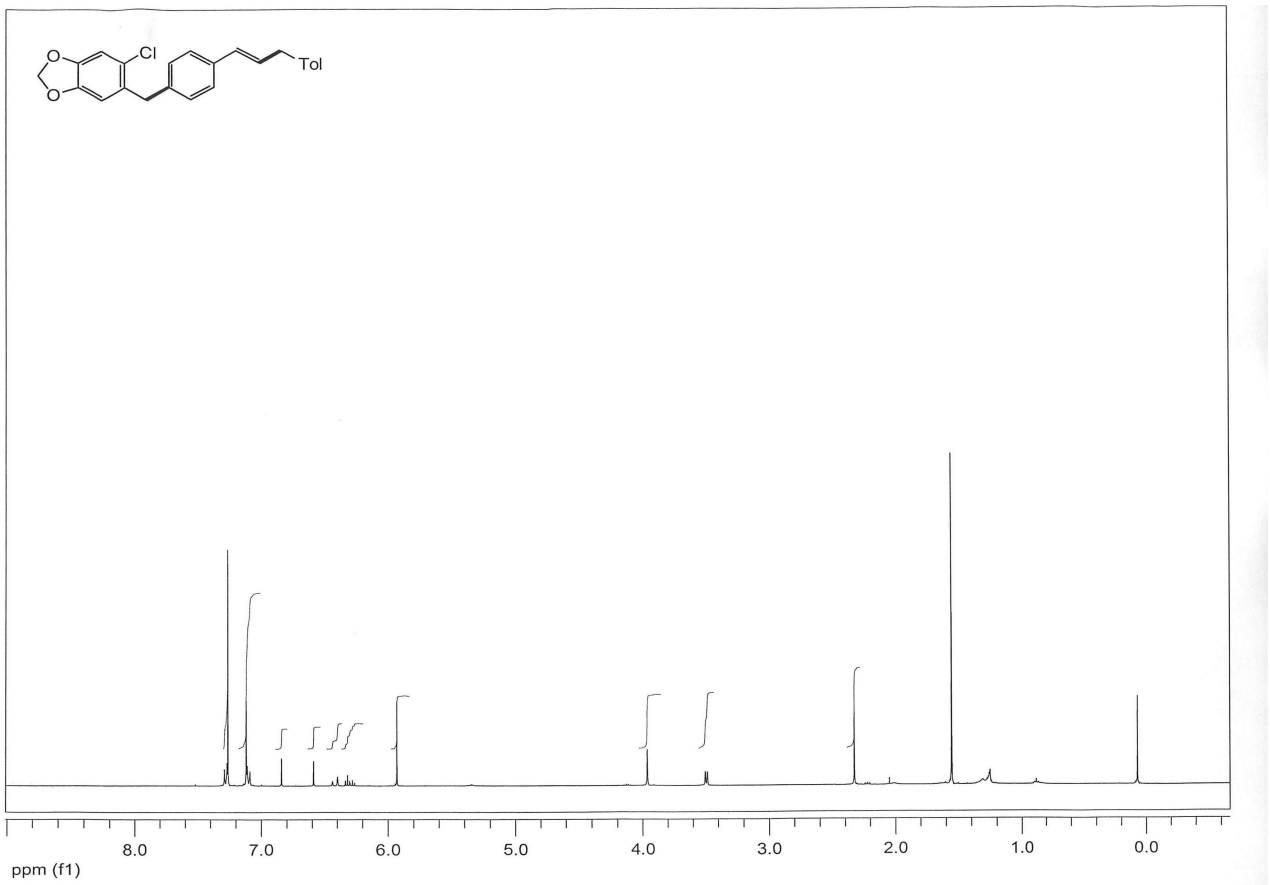

162.3
159.9
136.4
136.3
135.2
134.8
134.8
134.7
134.7
131.7
131.0
129.6
129.5
129.5
128.6
124.2
124.0
124.0
123.6
114.9
114.7
39.5
38.0
32.5
27.7
26.6
26.5
26.5
26.4
25.5
17.5
15.9
15.8
F
9
150
100
50
0
ppm (f1)

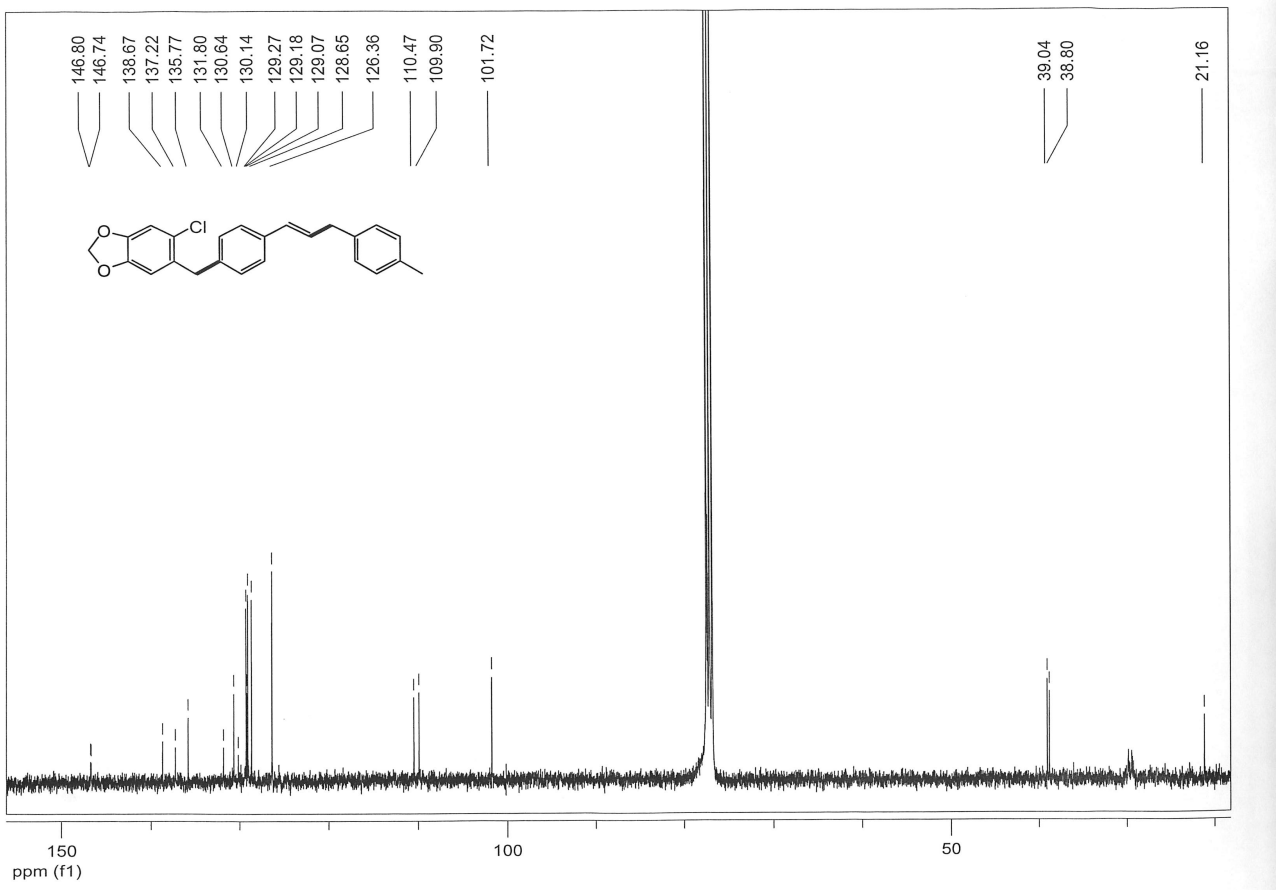
18


Tol
Br
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


136.8
136.6
135.9
131.7
130.6
129.7
129.3
128.7
127.8
120.8
Tol
Br
39.0
21.2
150
100
50
ppm (f1)

19


Cl
Tol
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


146.80
146.74
138.67
137.22
135.77
131.80
130.64
130.14
129.27
129.18
129.07
128.65
126.36
110.47
109.90
101.72
39.04
38.80
21.16
Cl
150
100
50
ppm (f1)