Supplementary Material (ESI) for Chemical Communications

Tunable stereoselective alkene synthesis by treatment of activated imines with nonstabilized phosphonium ylides

De-Jun Dong, Yuan Li, Jie-Qi Wang and Shi-Kai Tian*

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

Supporting information

Table of contents

General information……...S-2
Preparation of *N*-sulfonyl imines……S-2
General procedure for the olefination reaction of *N*-sulfonyl imines with nonstabilized phosphonium ylides (Table 2)……S-4
Analytical data for the products shown in Table 2…….....S-4
Gram-scale synthesis of alkene **Z3a**……....S-13
General procedure for the synthesis of phosphonium salt **4a** (Table 3)…….S-14
Analytical data for the phosphonium salts shown in Table 3…….....S-14
General procedure for the conversion of phosphonium salt **4a** to alkene **3a** (Table 3).....S-15
Work-up with $H_2{}^{18}O$ (Note 10).....S-15
References.....S-16
Copies of ^{1}H and ^{13}C NMR spectra…….....S-18

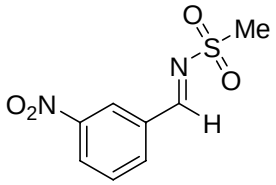
General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 300 MHz and 75 MHz, respectively, using tetramethylsilane as an internal reference. ^{31}P NMR spectra were recorded on a Bruker AC-400 FT spectrometer (162 MHz) using 85% phosphoric acid as an external reference. Chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. Low resolution mass spectra (LRMS) were recorded on a Finnigan LCQ Advantage Max spectrometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Elemental analyses were carried out on a Vario EL III elemental analyzer. Melting points are uncorrected.

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. Phosphonium salts were prepared from triphenylphosphine and alkyl halides according to the literature procedures.[1] Chemicals and solvents were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and AstaTech Pharmaceutical Co., and used as received.

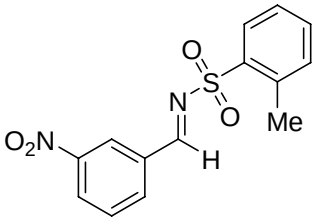
Preparation of *N*-sulfonyl imines

The *N*-sulfonyl imines were prepared according to the literature procedures.[2] Shown below are the analytic data for the new *N*-sulfonyl imines listed in Table 2.



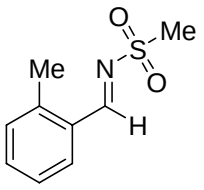
1ea

1ea, white solid. m.p. 122-124 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.73-8.71 (m, 1H), 8.53-8.47 (m, 1H), 8.27-8.21 (m, 1H), 7.80-7.75 (m, 1H), 3.12 (s, 3H).



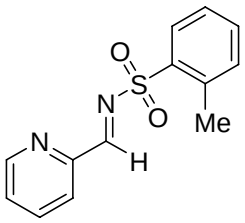
1eg

1eg, white solid. m.p. 133-134 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.51 (s, 1H), 8.73-8.70 (m, 1H), 8.52-8.47 (m, 2H), 8.25-8.21 (m, 1H), 8.03-8.00 (m, 1H), 7.80-7.74 (m, 2H), 7.34-7.29 (m, 1H), 2.70 (s, 3H).



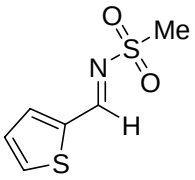
1fa

1fa, white solid. m.p. 104-105 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.81-7.77 (m, 1H), 7.50-7.44 (m, 1H), 7.39-7.33 (m, 1H), 7.27-7.24 (m, 1H), 3.11 (s, 3H), 2.67 (s, 3H).



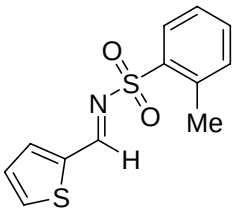
1ig

1ig, white solid. m.p. 123-124 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.82-8.79 (m, 2H), 8.00-7.95 (m, 2H), 7.92-7.85 (m, 2H), 7.56-7.52 (m, 2H), 2.70 (s, 3H).



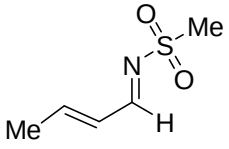
1ka

1ka, white solid. m.p. 91-92 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.80-7.75 (m, 2H), 7.24-7.20 (m, 1H), 3.11 (s, 3H).



1kg

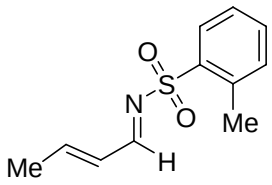
1kg, white solid. m.p. 105-106 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.02-7.99 (m, 1H), 7.80-7.76 (m, 2H), 7.47-7.43 (m, 2H), 7.23-7.20 (m, 2H), 2.69 (s, 3H).



1ma

1ma, white solid. m.p. 77-78 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, J = 3.0 Hz, 1H), 6.93-6.82

(m, 1H), 6.18-6.10 (m, 1H), 3.11 (s, 3H), 2.05-2.03 (m, 3H).



1mg

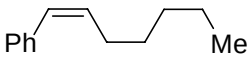
1mg, white solid. m.p. 92-93 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (d, J = 6.0 Hz, 1H), 8.02-8.00 (m, 1H), 7.47-7.43 (m, 2H), 7.34-7.27 (m, 1H), 6.91-6.82 (m, 1H), 6.18-6.10 (m, 1H), 2.69 (s, 3H), 2.04-2.03 (m, 3H).

General procedure for the olefination reaction of *N*-sulfonyl imines with nonstabilized phosphonium ylides (Table 2)

To a stirred suspension of phosphonium salt **2** (0.60 mmol) in tetrahydrofuran (1.0 mL) under nitrogen at -78 ^{o}C was added a solution of *n*-BuLi in hexane (2.50 M, 0.26 mL, 0.65 mmol). The resulting mixture was stirred at -78 ^{o}C for 1 h, and were added *N*-sulfonyl imine **1** (0.50 mmol) and tetrahydrofuran (1.0 mL). The resulting mixture was stirred at -78 ^{o}C for 3 h, warmed naturally to room temperature (in ca. 5 h), and stirred at room temperature for 4 h. Saturated brine (2.0 mL) was added to the mixture, and the organic phase was extracted with petroleum ether (2 x 20 mL), dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by flash column chromatography on silica gel or by preparative thin layer chromatography (TLC), eluting or developing with petroleum ether [For entries 19–23 of Table 2, petroleum ether/ethyl acetate (10:1)] to give alkene **3** (**Z3** or **E3**).

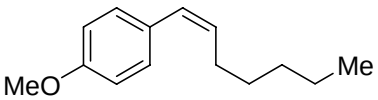
The *Z/E* ratios of alkene products were determined by ^{1}H NMR analysis within four days owing to the isomerization of (*Z*)-alkenes under the influence of light and air at room temperature.

Analytical data for the products shown in Table 2



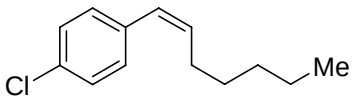
Z3a

Z3a,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.24 (m, 5H), 6.39 (d, J = 12.0 Hz, 1H), 5.65 (dt, J = 12.0, 7.2 Hz, 1H), 2.36-2.26 (m, 2H), 1.35-1.24 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.4, 128.8, 128.5, 128.2, 126.8, 126.5, 31.7, 29.8, 28.7, 22.6, 14.1.



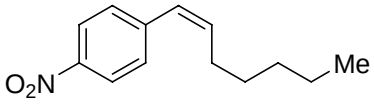
Z3b

Z3b,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.18 (m, 2H), 6.88-6.80 (m, 2H), 6.33 (d, J = 12.0 Hz, 1H), 5.56 (dt, J = 12.0, 7.2 Hz, 1H), 3.80 (s, 3H), 2.35-2.25 (m, 2H), 1.36-1.24 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 131.8, 130.6, 129.9, 128.1, 113.6, 55.2, 31.7, 29.8, 28.7, 22.6, 14.1.



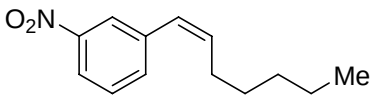
Z3c

Z3c, yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.16 (m, 4H), 6.33 (d, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.32-2.23 (m, 2H), 1.35-1.25 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.1, 130.1, 128.3, 127.6, 127.2, 31.6, 29.8, 29.0, 22.6, 14.1; HRMS (EI): Calcd for $C_{13}H_{17}Cl$ (M): 208.1019. Found: 208.1018.



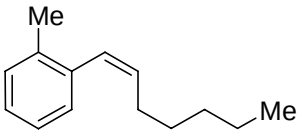
Z3d

Z3d,[4] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20-8.13 (m, 2H), 7.47-7.38 (m, 2H), 6.44 (d, *J* = 11.7 Hz, 1H), 5.87 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.37-2.28 (m, 2H), 1.37-1.25 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 137.3, 129.4, 127.1, 123.6, 31.6, 29.8, 29.4, 22.6, 14.1.



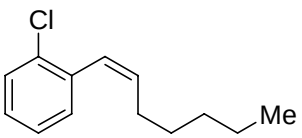
Z3e

Z3e, yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20-8.01 (m, 2H), 7.64-7.40 (m, 2H), 6.43 (d, *J* = 12.0 Hz, 1H), 5.85 (dt, *J* = 12.0, 7.2 Hz, 1H), 2.36-2.27 (m, 2H), 1.37-1.22 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 134.8, 131.9, 129.4, 127.7, 126.7, 123.5, 31.5, 29.8, 29.4, 22.6, 14.1; HRMS (EI): Calcd for $C_{13}H_{17}NO_2$ (M): 219.1259. Found: 219.1262.



Z3f

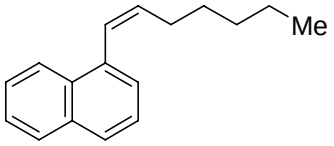
Z3f,[5] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.25 (m, 4H), 6.39 (d, *J* = 11.7 Hz, 1H), 5.65 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.51 (s, 3H), 2.36-2.27 (m, 2H), 1.35-1.24 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4, 129.8, 128.9, 128.6, 128.2, 126.8, 126.0, 31.9, 29.5, 29.1, 22.7, 20.0, 14.2.



Z3g

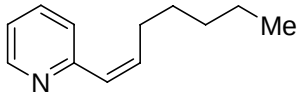
Z3g, yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.09 (m, 4H), 6.49 (d, *J* = 12.0 Hz, 1H),

5.79 (dt, *J* = 12.0, 7.2 Hz, 1H), 2.26-2.13 (m, 2H), 1.48-1.20 (m, 6H), 0.95-0.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 133.4, 128.8, 128.5, 128.2, 126.8, 126.5, 126.0, 31.7, 29.8, 28.7, 22.6, 14.1; HRMS (EI): Calcd for $C_{13}H_{17}Cl$ (M): 208.1019. Found: 208.1024.



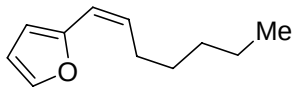
Z3h

Z3h,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.93 (m, 1H), 7.87-7.78 (m, 2H), 7.65-7.48 (m, 4H), 6.85 (d, *J* = 13.2 Hz, 1H), 5.95 (dt, *J* = 13.2, 7.2 Hz, 1H), 2.24-2.13 (m, 2H), 1.35-1.25 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.4, 132.0, 130.5, 129.9, 129.5, 128.6, 127.1, 126.2, 124.6, 123.4, 123.2, 31.8, 29.3, 28.9, 22.7, 14.1.



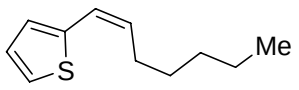
Z3i

Z3i,[6] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60-8.58 (m, 1H), 7.65-7.58 (m, 1H), 7.28-7.22 (m, 1H), 7.11-7.06 (m, 1H), 6.45 (d, *J* = 12.0 Hz, 1H), 5.88 (dt, *J* = 12.0, 7.2 Hz, 1H), 2.60-2.52 (m, 2H), 1.37-1.25 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 137.4, 135.9, 129.8, 128.5, 123.7, 121.0, 31.5, 29.7, 28.7, 22.6, 14.0.



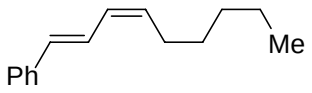
Z3j

Z3j, yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (s, 1H), 6.32-6.24 (m, 1H), 6.17-6.10 (m, 2H), 5.48 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.13-2.05 (m, 2H), 1.43-1.17 (m, 6H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 141.2, 130.4, 117.3, 111.1, 108.7, 32.1, 31.7, 29.3, 22.6, 14.1; HRMS (EI): Calcd for $C_{11}H_{16}O$ (M): 164.1201. Found: 164.1133.



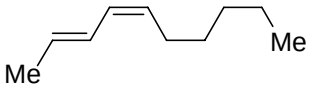
Z3k

Z3k,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (d, *J* = 4.8 Hz, 1H), 7.01-6.94 (m, 2H), 6.51 (d, *J* = 11.7 Hz, 1H), 5.57 (dt, *J* = 11.7, 7.2 Hz, 1H), 2.45-2.35 (m, 2H), 1.43-1.24 (m, 6H), 0.92 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.0, 131.4, 127.2, 127.1, 124.9, 121.7, 31.7, 29.4, 29.2, 22.6, 14.1.



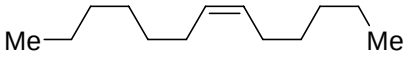
Z3l

Z3l,[7] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.34 (m, 5H), 7.16-7.05 (m, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.29-6.22 (m, 1H), 5.60-5.54 (m, 1H), 2.37-2.30 (m, 2H), 1.35-1.30 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.4, 132.0, 130.5, 129.9, 129.6, 128.6, 127.1, 124.6, 29.0, 28.9, 28.1, 22.7, 14.1.



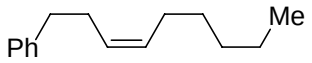
Z3m

Z3m,[8] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.33-6.28 (m, 1H), 6.01-5.95 (m, 1H), 5.70-5.62 (m, 1H), 5.31-5.26 (m, 1H), 2.18-2.11 (m, 2H), 1.79-1.75 (m, 3H), 1.40-1.23 (m, 6H), 0.90 (t, *J* = 6.6 Hz 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.8, 130.0, 128.5, 126.7, 32.6, 31.6, 29.5, 22.6, 18.3, 14.1.



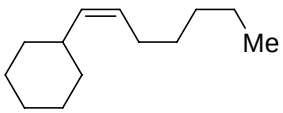
Z3n

Z3n,[9] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.15-5.01 (m, 2H), 2.04-1.96 (m, 4H), 1.65-1.28 (m, 14H), 0.97-0.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.4, 129.9, 34.0, 32.7, 32.6, 31.5, 31.4, 28.2, 25.0, 22.7, 19.2, 14.1, 14.0.



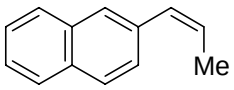
Z3o

Z3o,[10] yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 5H), 5.34-5.21 (m, 2H), 2.80-2.70 (m, 2H), 2.56-2.42 (m, 4H), 1.40-1.20 (m, 6H), 0.97-0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 130.9, 128.7, 128.5, 128.3, 127.3, 36.1, 32.6, 31.6, 29.4, 29.3, 22.7, 14.2.



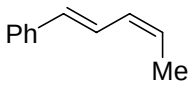
Z3p

Z3p,[11] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.28-5.17 (m, 2H), 2.27-2.22 (m, 1H), 2.06-1.98 (m, 2H), 1.39-1.13 (m, 16H), 0.93-0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 128.2, 33.5, 32.7, 31.6, 29.8, 29.6, 26.2, 26.1, 22.7, 14.1.



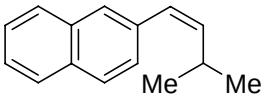
Z3q

Z3q,[12] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.69 (m, 4H), 7.45-7.34 (m, 3H), 6.56 (d, *J* = 12.0 Hz, 1H), 5.85 (dq, *J* = 12.0, 5.4 Hz, 1H), 1.97-1.94 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.3, 130.0, 128.1, 128.0, 127.9, 126.2, 126.1, 126.0, 125.7, 125.5, 125.2, 123.6, 14.8.



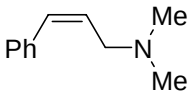
Z3r

Z3r,[13] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.16 (m, 5H), 7.11-7.04 (m, 1H), 6.52 (d, *J* = 14.7 Hz, 1H), 6.22-6.13 (m, 1H), 5.62-5.56 (m, 1H), 1.87-1.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.4, 129.1, 128.7, 128.4, 127.7, 127.6, 127.1, 126.6, 126.4, 125.3, 13.4.



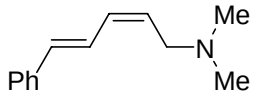
Z3s

Z3s,[14] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.67 (m, 4H), 7.48-7.38 (m, 3H), 6.45 (d, *J* = 11.7 Hz, 1H), 5.60-5.50 (m, 1H), 3.04-2.94 (m, 1H), 1.08 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.0, 133.5, 131.0, 130.9, 128.0, 127.6, 127.3, 127.2, 126.5, 126.1, 126.0, 125.7, 27.3, 23.3.



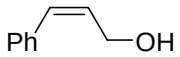
Z3t

Z3t,[15] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.24 (m, 5H), 6.56 (d, *J* = 12.0 Hz, 1H), 5.75 (dt, *J* = 12.0, 7.2 Hz, 1H), 3.21 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.6, 128.8, 128.5, 128.2, 127.2, 126.8, 126.2, 126.1, 67.0, 46.0.



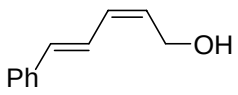
Z3u

Z3u,[16] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.26 (m, 5H), 7.08 (dd, *J* = 11.7, 8.4 Hz, 1H), 6.51 (d, *J* = 11.7 Hz, 1H), 6.22-6.14 (m, 1H), 5.62-5.55 (m, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.2, 128.8, 128.5, 128.2, 127.2, 126.8, 126.2, 125.8, 124.4, 68.2, 47.2.



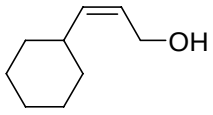
Z3v

Z3v,[17] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.20 (m, 5H), 6.60 (d, *J* = 12.0 Hz, 1H), 5.99-5.86 (m, 1H), 4.47 (d, *J* = 5.7 Hz, 2H), 1.98 (s, br., 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.0, 130.5, 129.9, 129.5, 128.6, 127.1, 126.3, 124.6, 60.1.



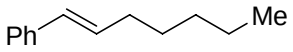
Z3w

Z3w,[18] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.20 (m, 5H), 7.09 (dd, *J* = 11.7, 8.4 Hz, 1H), 6.72 (d, *J* = 11.7 Hz, 1H), 6.21-6.14 (m, 1H), 5.62-5.58 (m, 1H), 4.46 (d, *J* = 6.0 Hz, 2H), 1.58 (s, br., 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.5, 129.3, 129.1, 128.7, 128.4, 127.7, 127.6, 127.1, 126.6, 126.4, 61.2.



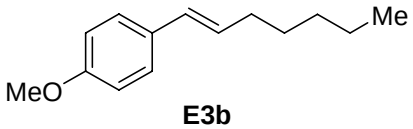
Z3x

Z3x,[19] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.64-5.52 (m, 1H), 5.49-5.31 (m, 1H), 4.24 (d, *J* = 6.6 Hz, 2H), 2.87 (s, br., 1H), 2.30-2.14 (m, 1H), 1.75-1.55 (m, 5H), 1.39-1.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.0, 127.5, 62.5, 27.1, 26.6, 26.1, 26.0, 25.8, 25.4.



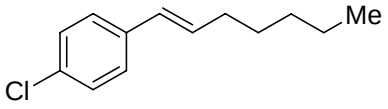
E3a

E3a,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.14 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.9, 6.9 Hz, 1H), 2.24-2.15 (m, 2H), 1.48-1.38 (m, 6H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 131.3, 129.8, 128.8, 128.2, 126.5, 126.0, 33.1, 31.7, 28.7, 22.6, 14.1.



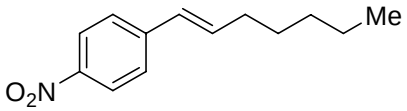
E3b

E3b,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.19 (m, 2H), 6.88-6.81 (m, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.07 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.79 (s, 3H), 2.21-2.13 (m, 2H), 1.48-1.39 (m, 6H), 0.95-0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 130.0, 129.2, 128.1, 127.0, 114.0, 55.3, 33.1, 31.5, 29.3, 22.6, 14.1.



E3c

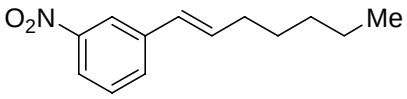
E3c,[20] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.16 (m, 4H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 7.2 Hz, 1H), 2.23-2.15 (m, 2H), 1.49-1.38 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0, 130.1, 128.6, 128.3, 127.6, 33.1, 29.6, 28.6, 22.6, 14.1.



E3d

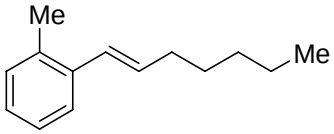
E3d,[4] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 6.47-6.42 (m, 2H), 2.29-2.22 (m, 2H), 1.59-1.40 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR

(75 MHz, $CDCl_3$): δ 147.9, 144.9, 136.3, 129.4, 126.4, 124.1, 33.3, 31.6, 28.9, 22.6, 14.1.



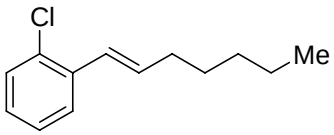
E3e

E3e,[21] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20-8.05 (m, 2H), 7.59-7.41 (m, 2H), 6.46-6.38 (m, 2H), 2.31-2.21 (m, 2H), 1.61-1.43 (m, 6H), 0.94-0.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2, 136.2, 131.9, 129.1, 127.7, 121.4, 120.5, 33.0, 31.5, 29.8, 22.6, 14.1.



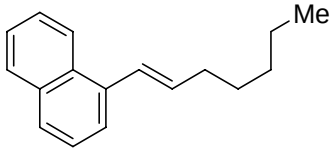
E3f

E3f,[5] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.14 (m, 4H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.9, 6.9 Hz, 1H), 2.39 (s, 3H), 2.24-2.15 (m, 2H), 1.48-1.38 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 131.3, 129.8, 128.8, 128.2, 126.5, 126.0, 33.1, 31.7, 28.7, 22.6, 20.1, 14.1.



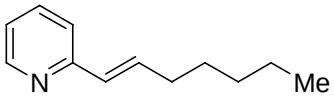
E3g

E3g,[22] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.46 (m, 1H), 7.38-7.33 (m, 1H), 7.25-7.13 (m, 2H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.9, 6.9 Hz, 1H), 2.23-2.13 (m, 2H), 1.37-1.20 (m, 6H), 0.94-0.84 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 133.3, 131.3, 128.8, 128.1, 126.8, 126.4, 126.0, 33.1, 31.5, 29.7, 22.6, 14.1.



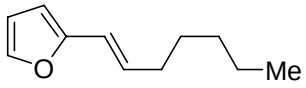
E3h

E3h,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14-8.13 (m, 1H), 7.72-7.59 (m, 3H), 7.42-7.15 (m, 3H), 7.07 (d, *J* = 15.9 Hz, 1H), 6.17 (dt, *J* = 15.9, 6.9 Hz, 1H), 2.37-2.27 (m, 2H), 1.37-1.25 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.3, 130.0, 128.1, 128.0, 127.9, 126.2, 126.1, 126.0, 125.7, 125.5, 125.2, 123.6, 32.1, 29.6, 28.6, 21.7, 14.1.



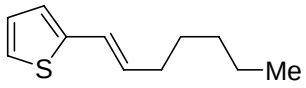
E3i

E3i,[23] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52-8.50 (m, 1H), 7.66-7.58 (m, 1H), 7.28-7.21 (m, 1H), 7.12-7.06 (m, 1H), 6.79-6.71 (m, 1H), 6.51-6.43 (m, 1H), 2.29-2.25 (m, 2H), 1.55-1.26 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 136.4, 136.2, 135.9, 128.5, 123.7, 121.5, 32.8, 29.4, 28.7, 22.6, 14.0.



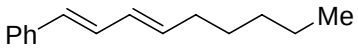
E3j

E3j, yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.26 (m, 1H), 6.32-6.28 (m, 1H), 6.17-6.08 (m, 3H), 2.40-2.31 (m, 2H), 1.43-1.17 (m, 6H), 0.89-0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 141.2, 131.6, 118.6, 111.1, 105.9, 32.8, 31.7, 29.8, 22.6, 14.1; HRMS (EI): Calcd for $C_{11}H_{16}O$ (M): 164.1201. Found: 164.1156.



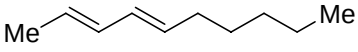
E3k

E3k,[3] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, *J* = 5.1 Hz, 1H), 7.06-7.00 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.12 (dt, *J* = 15.9, 6.9 Hz, 1H), 2.25-2.16 (m, 2H), 1.60-1.33 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.4, 127.2, 127.1, 124.1, 123.0, 121.7, 32.9, 31.5, 29.0, 22.6, 14.1.



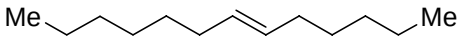
E3l

E3l,[21] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.16 (m, 5H), 6.75 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.24-6.11 (m, 1H), 5.88-5.76 (m, 1H), 2.18-2.10 (m, 2H), 1.42-1.24 (m, 6H), 0.95-0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.4, 132.0, 130.5, 129.9, 129.6, 128.6, 127.1, 126.4, 124.6, 32.9, 31.8, 29.4, 22.7, 14.1.



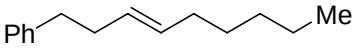
E3m

E3m,[8] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03-5.95 (m, 2H), 5.33-5.26 (m, 2H), 2.06-2.01 (m, 2H), 1.74-1.70 (m, 3H), 1.43-1.30 (m, 6H), 0.92-0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.3, 130.3, 129.0, 127.2, 32.8, 29.2, 27.7, 22.6, 18.1, 14.1.



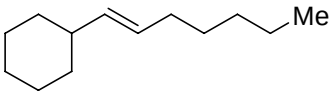
E3n

E3n,[24] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40-5.33 (m, 2H), 2.03-1.97 (m, 4H), 1.30-1.20 (m, 14H), 0.94-0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.4, 130.1, 34.8, 32.2, 32.1, 31.9, 31.8, 29.8, 28.2, 25.8, 23.9, 19.2, 14.1.



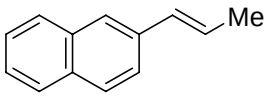
E3o

E3o,[10] yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.22 (m, 5H), 5.42-5.36 (m, 2H), 2.98-2.92 (m, 2H), 2.73-2.57 (m, 4H), 1.64-1.52 (m, 6H), 0.94-0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 129.7, 128.8, 128.5, 128.1, 126.7, 38.9, 33.1, 31.8, 29.4, 28.9, 22.6, 14.1.



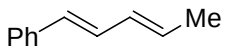
E3p

E3p,[25] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40-5.36 (m, 2H), 2.33-2.20 (m, 1H), 1.76-1.58 (m, 2H), 1.37-1.24 (m, 16H), 0.92-0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 128.2, 36.4, 31.6,. 29.8, 29.6, 27.3, 26.2, 22.7, 14.1.



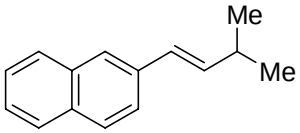
E3q

E3q,[12] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81-7.76 (m, 4H), 7.45-7.39 (m, 3H), 6.53 (d, J = 15.9 Hz, 1H), 6.38-6.27 (m, 1H), 1.95-1.94 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.2, 130.0, 128.1, 127.9, 127.8, 127.5, 127.3, 126.2, 125.7, 125.2, 123.6, 18.6.



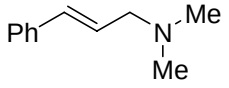
E3r

E3r,[13] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.25 (m, 5H), 6.75 (dd, J = 15.6, 10.5 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.20-6.14 (m, 1H), 5.87-5.77 (m, 1H), 1.31-1.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.4, 132.0, 130.5, 129.9, 129.5, 128.6, 127.1, 126.2, 124.6, 19.1.



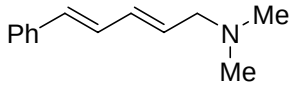
E3s

E3s,[14] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.34 (m, 7H), 6.49 (d, J = 16.9 Hz, 1H), 6.35-6.26 (m, 1H), 2.56-2.45 (m, 1H), 1.12 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 133.5, 132.6, 132.2, 129.0, 128.9, 128.0, 127.6, 127.3, 126.5, 126.1, 125.7, 29.0, 23.8.



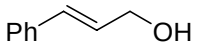
E3t

E3t,[26] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.16 (m, 5H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.0 Hz, 1H), 3.11 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.2, 128.8, 128.6, 128.5, 128.2, 127.2, 126.8, 124.4, 67.0, 49.2.



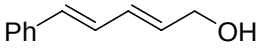
E3u

E3u,[27] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.20 (m, 5H), 6.80 (dd, *J* = 15.9, 10.2 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.30-6.16 (m, 1H), 5.83-5.73 (m, 1H), 3.20 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.4, 132.0, 130.5, 129.9, 129.5, 128.6, 127.1, 126.2, 124.6, 67.7, 51.0.



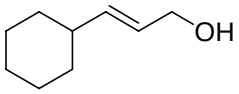
E3v

E3v,[28] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.20 (m, 5H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.39-6.28 (m, 1H), 4.29 (d, *J* = 5.7 Hz, 2H), 1.97 (s, br., 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 131.1, 128.6, 128.5, 127.7, 126.5, 63.6.



E3w

E3w,[29] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.14 (m, 5H), 6.75 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 6.39-6.28 (m, 1H), 5.87-5.77 (m, 1H), 4.09 (d, *J* = 5.7 Hz, 2H), 1.84 (s, br., 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.8, 131.8, 131.1, 129.0, 128.7, 128.6, 128.5, 127.3, 126.3, 63.4.



E3x

E3x,[30] yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70-5.55 (m, 2H), 4.06 (d, *J* = 6.6 Hz, 2H), 2.24 (s, br., 1H), 2.06-1.96 (m, 1H), 1.75-1.55 (m, 5H), 1.38-1.15 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.3, 126.6, 66.2, 28.9, 26.6, 26.1, 26.0, 25.2, 25.1.

Gram-scale synthesis of alkene Z3a

To a stirred suspension of phosphonium salt **2a** (5.13 g, 12.0 mmol) in tetrahydrofuran (20.0 mL) under nitrogen at -78 ^{o}C was added a solution of *n*-BuLi in hexane (2.50 M, 5.2 mL, 13.0 mmol). The resulting mixture was stirred for 1 h, and were added *N*-sulfonyl imine **1aa** (1.83 g, 10.0 mmol) and tetrahydrofuran (3.0 mL). The resulting mixture was stirred at -78 ^{o}C for 3 h, warmed naturally to room temperature (in 5 h), and stirred at room temperature for 4 h. Saturated brine (10.0 mL) was added to the mixture, and the organic phase was extracted with petroleum ether (2 x 50 mL), dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (100:1), to afford

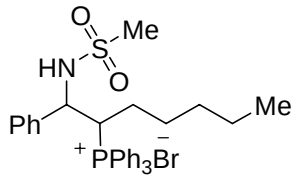
alkene **Z3a** (1.34 g, 77%, >99:1 *Z/E*) as a yellowish oil.

General procedure for the synthesis of phosphonium salt 4a (Table 3)

To a stirred suspension of phosphonium salt **2a** (0.60 mmol) in tetrahydrofuran (1.0 mL) under nitrogen at -78 ^{o}C was added a solution of *n*-BuLi in hexane (2.50 M, 0.26 mL, 0.65 mmol). The resulting mixture was stirred for 1 h, and were added *N*-sulfonyl imine **1a** (0.50 mmol) and tetrahydrofuran (1.0 mL). The resulting mixture was stirred at -78 ^{o}C for 1 h, added 40% aqueous HBr (0.14 mL, 1.0 mmol), and stirred at -78 ^{o}C for 2 h. The mixture was concentrated and purified by preparative TLC, developing with dichloromethane/methanol (20:1), to give phosphonium salt **4a**.

The relative configuration for phosphonium salt **4a** was tentatively assigned based on its conversion to alkene **3a** (*vide infra*).

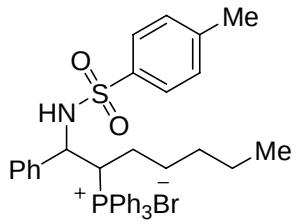
Analytical data for the phosphonium salts shown in Table 3



4aa

Table 3, entry 1: Phosphonium salt **4aa** was obtained in 63% yield as a single *anti* isomer (>99:1 *anti/syn*). White solid; m.p. 144-145 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.70 (m, 20H), 3.70-3.60 (m, 1H), 3.22-3.15 (m, 1H), 2.05-1.99 (m, 7H), 1.68-1.58 (m, 2H), 1.29-1.18 (m, 2H), 0.84-0.79 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.0, 133.5, 131.9, 130.5, 129.8 (d, J = 15.8 Hz), 127.3, 127.1, 126.2, 124.6, 123.3, 123.1, 59.4, 46.2, 35.1, 31.8, 29.1 (d, J = 30.3 Hz), 22.7, 14.2; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 25.0; Anal. calcd. for $C_{32}H_{37}BrNO_2PS$ (%): C, 62.95; H, 6.11; N, 2.29. Found: C, 62.72; H, 6.12; N, 2.30.

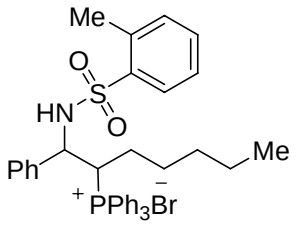
Table 3, entry 2: Phosphonium salt **4aa** was obtained in 73% yield as a 90:10 mixture of *anti/syn* isomers. White solid; Partial ^{1}H NMR (300 MHz, $CDCl_3$) for the *syn* isomer: δ 3.85-3.79 (m, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) for the *syn* isomer: δ 24.4.



4ac

Table 3, entry 3: Phosphonium salt **4ac** was obtained in 66% yield as an 84:16 mixture of *anti/syn* isomers. White solid; ^{1}H NMR (300 MHz, $CDCl_3$) for the *anti* isomer: δ 7.88-7.65 (m, 24H), 3.50-3.45 (m, 1H), 3.16-3.08 (m, 1H), 2.57 (s, 3H), 2.06-1.99 (m, 4H), 1.70-1.56 (m, 2H), 1.31-1.17 (m, 2H), 0.86-0.80 (m, 3H); Partial ^{1}H NMR (300 MHz, $CDCl_3$) for the *syn* isomer: 3.90-3.84 (m,

1H); ^{31}P NMR ($CDCl_3$, 162 MHz) for the *anti* isomer: δ 24.0; ^{31}P NMR ($CDCl_3$, 162 MHz) for the *syn* isomer: 24.6; Anal. calcd. for $C_{38}H_{41}BrNO_2PS$ (%): C, 66.47; H, 6.02; N, 2.04. Found: C, 66.23; H, 6.04; N, 2.05.



4ag

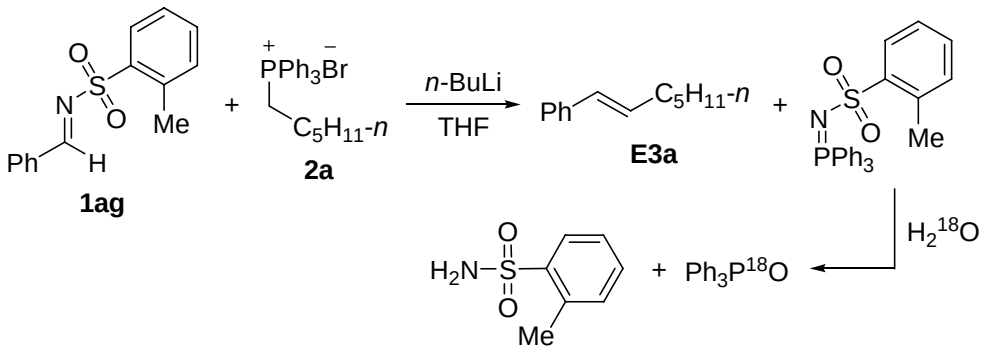
Table 3, entry 4: Phosphonium salt **4ag** was obtained in 69% yield as a single *syn* isomer (<1:99 *anti/syn*). White solid; m.p. 150-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-7.68 (m, 24H), 3.63-3.56 (m, 1H), 3.20-3.14 (m, 1H), 2.68 (s, 3H), 2.05-1.99 (m, 4H), 1.69-1.58 (m, 2H), 1.30-1.19 (m, 2H), 0.85-0.79 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.2, 135.0, 133.9, 133.7, 131.4, 130.6, 130.4, 129.8 (d, J = 15.5 Hz), 129.2, 128.2, 126.6, 51.1, 34.4, 30.1 (d, J = 23.2 Hz), 22.7, 22.3, 21.7, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ (ppm): 25.1; Anal. calcd. for $C_{38}H_{41}BrNO_2PS$ (%): C, 66.47; H, 6.02; N, 2.04. Found: C, 66.60; H, 6.03; N, 2.05.

Table 3, entry 5: Phosphonium salt **4ag** was obtained in 64% yield as a 41:59 mixture of *anti/syn* isomers. White solid; Partial ^{1}H NMR (300 MHz, $CDCl_3$) for the *anti* isomer: δ 4.01-3.96 (m, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.1.

General procedure for the conversion of phosphonium salt 4a to alkene 3a (Table 3)

To a stirred suspension of phosphonium salt **4a** (0.25 mmol) in tetrahydrofuran (1.0 mL) under nitrogen at -78 °C was added a solution of *n*-BuLi in hexane (2.50 M, 0.12 mL, 0.30 mmol). The resulting mixture was stirred at -78 °C for 3 h, warmed naturally to room temperature (in ca. 5 h), and stirred at room temperature for 4 h. Saturated brine (2.0 mL) was added to the mixture, and the organic phase was extracted with petroleum ether (2 x 20 mL), dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by preparative TLC, developing with petroleum ether, to give alkene **3a**. The yields are 73% (entry 1), 51% (entry 2), 86% (entry 3), 89% (entry 4), and 55% (entry 5).

Work-up with $H_2{}^{18}O$ (Note 10)

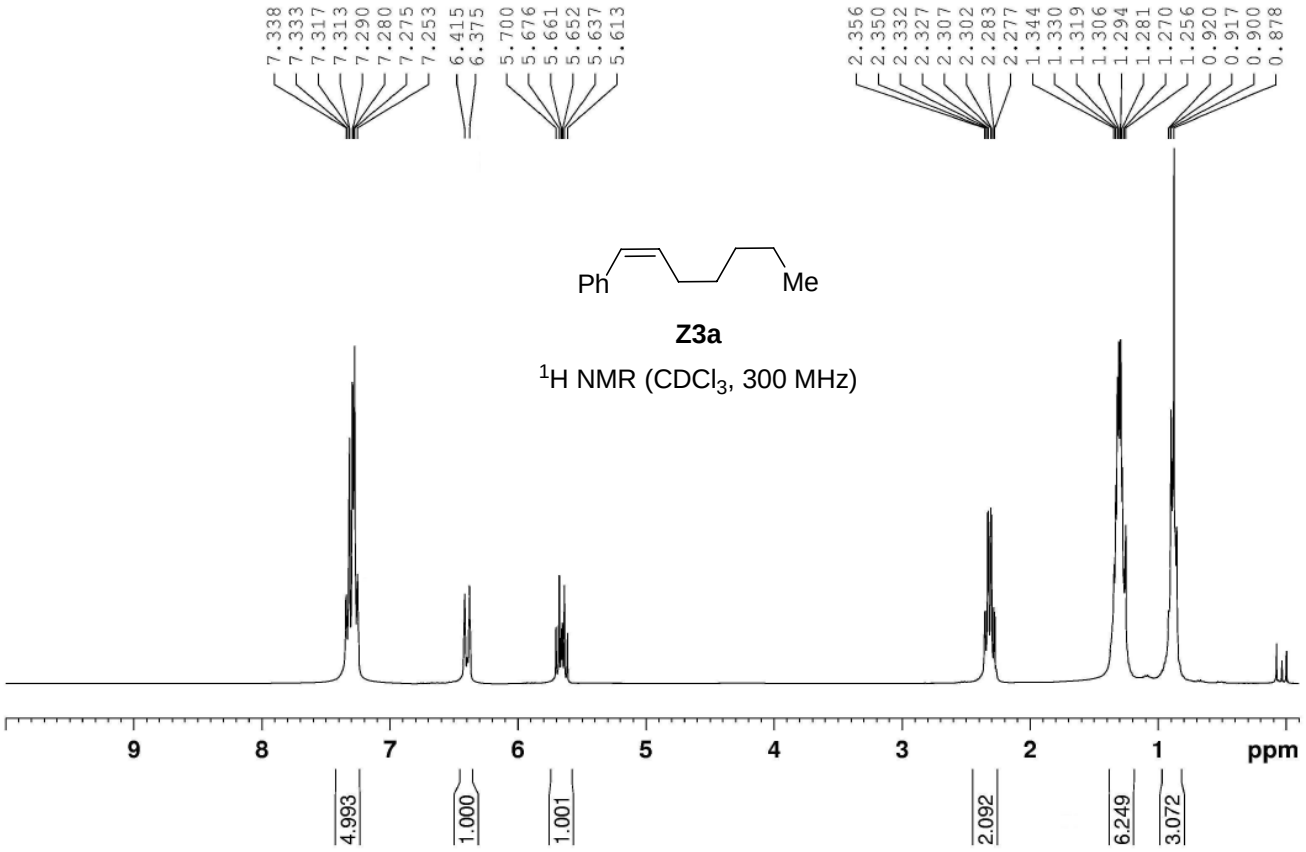


To a stirred suspension of phosphonium salt **2a** (256 mg, 0.60 mmol) in tetrahydrofuran (1.0 mL) under nitrogen at -78 ^{o}C was added a solution of *n*-BuLi in hexane (2.50 M, 0.26 mL, 0.65 mmol). The resulting mixture was stirred for 1 h, and were added *N*-sulfonyl imine **1ag** (130 mg, 0.50 mmol) and tetrahydrofuran (1.0 mL). The resulting mixture was stirred at -78 ^{o}C for 3 h, warmed naturally to room temperature (in 5 h), and stirred at room temperature for 4 h. Heavy oxygen water (98%, 91 μL, 5.0 mmol) was added to the mixture and stirred at room temperature for 4 h. Saturated brine (2.0 mL) was added to the mixture, and the organic phase was extracted with petroleum ether (2 x 20 mL), dried over anhydrous magnesium sulfate, and concentrated. The residue was purified directly by preparative TLC, developing with petroleum ether/ethyl acetate (3:1) to give $PPh_3{}^{18}O$ (115 mg, 82%) and *o*-toluenesulfonamide (62.0 mg, 72%). MS (ESI) found for $C_{18}H_{16}{}^{18}OP$ (MH): 281.3; MS (ESI) found for $C_7H_8NO_2S$ (M-H): 170.3.

References

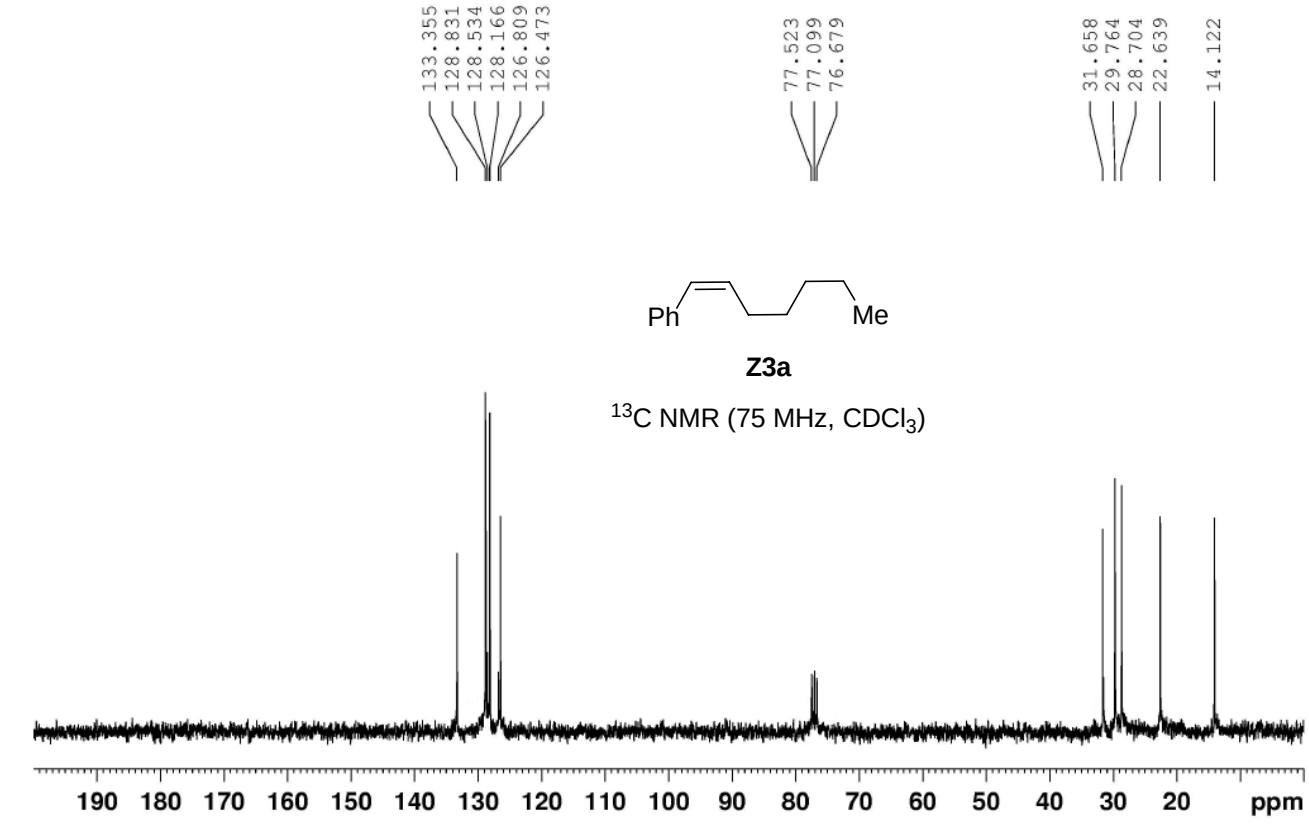
(1) M. Shi and B. Xu, *J. Org. Chem.*, 2002, **67**, 294.
(2) (*a*) M. Yamanaka, A. Nishida and M. Nakagawa, *J. Org. Chem.*, 2003, **68**, 3112; (*b*) D.-J. Dong, H.-H. Li and S.-K. Tian, *J. Am. Chem. Soc*., 2010, **132**, 5018.
(3) S. E. Denmark and D. Wehrli, *Org. Lett.*, 2000, **2**, 565.
(4) S. E. Denmark and R. F. Sweis, *J. Am. Chem. Soc.*, 2001, **123**, 6439.
(5) S. E. Denmark and R. F. Sweis, *Org. Lett.*, 2002, **4**, 3771.
(6) Y.-G. Lim, J.-B. Kang and Y. H. Kim, *J. Chem. Soc., Perkin Trans. 1*, 1998, 699.
(7) S. E. Denmark and J. Y. Choi, *J. Am. Chem. Soc.,* 1999, **121**, 5821.
(8) T. L. Underiner and H. L. Goering, *J. Org. Chem.*, 1991, **56**, 2563.
(9) M. Huhtasaari, H. J. Schäfer and H. Luftmann, *Acta Chem. Scand. B*, 1983, **37**, 537.
(10) A. G. M. Barrett and G. A. Flygare, *J. Org. Chem.* 1991, **56**, 638.
(11) M. Periasamy, A. S. B. Prasad and Y. Suseela, *Tetrahedron*, 1995, **51**, 2743.
(12) L.-F. Huang, C.-H. Huang, B. Stulgies, A. de Meijere and T.-Y. Luh, *Org. Lett.*, 2003, **5**, 4489.
(13) W. Kirmse and S. Kopannia, *J. Org. Chem.*, 1998, **63**, 1178.
(14) M. R. Pitts, J. R. Harrison and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 2001, 955.
(15) R. W. Jemison, T. Laird, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1436.
(16) T. Laird, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2033.
(17) I. S. Kim, G. R. Dong and Y. H. Jung, *J. Org. Chem.*, 2007, **72**, 5424.
(18) K. S. Feldman and D. A. Mareska, *J. Org. Chem.*, 1999, **64**, 5650.
(19) S. A. Reed and S. C. White, *J. Am. Chem. Soc.,* 2008, **130**, 3316.
(20) D. Mirk, J.-M. Grassot and J. Zhu, *Synlett*, 2006, 1255.
(21) S. E. Denmark and Z. Wang, *Org. Lett.,* 2001, **3**, 1073.
(22) G. W. Kabalka, N.-S. Li, D. Tejedor, R. R. Malladi and S. Trotman, *J. Org. Chem.,* 1999, **64**, 3157.
(23) S. E. Denmark and J. M. Kallemeyn, *J. Am. Chem. Soc.,* 2006, **128**, 15958.
(24) W. Hoebold and R. Keck, *J. Prakt. Chem*., 1975, **317**, 1054.
(25) B. Breit and D. Breuninger, *Synthesis*, 2005, 147.
(26) M. Gómez-Gallego, M. J. Mancheño, P. Ramírez, C. Piñar and M. A. Sierra, *Tetrahedron,* 2000,

56, 4893.
(27) M. Nikaido, R. Aslanian, F. Scavo, P. Helquist, B. Åakermark and J.-E. Bäeckvall, *J. Org. Chem.,* 1984, **49**, 4738.
(28) M. Mahesh, J. A. Murphy and H. P. Wessel, *J. Org. Chem.,* 2005, **70**, 4118.
(29) D. D. Kim, S. J. Lee and P. Beak, *J. Org. Chem.,* 2005, **70**, 5376.
(30) D. J. Pippel, G. A. Weisenburger, N. C. Faibish and P. Beak, *J. Am. Chem. Soc.,* 2001, **123**, 4919.



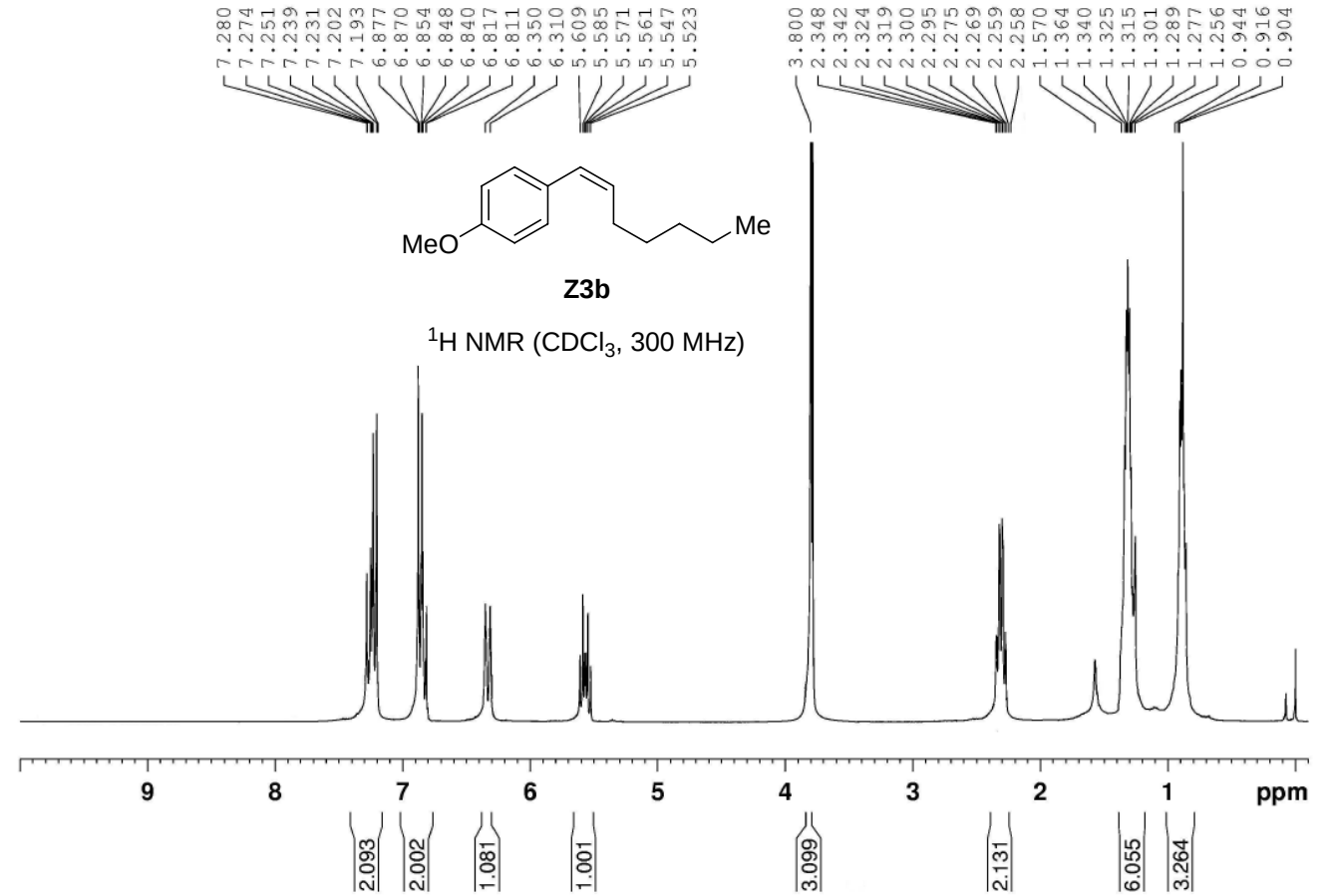
Z3a

^{1}H NMR ($CDCl_3$, 300 MHz)



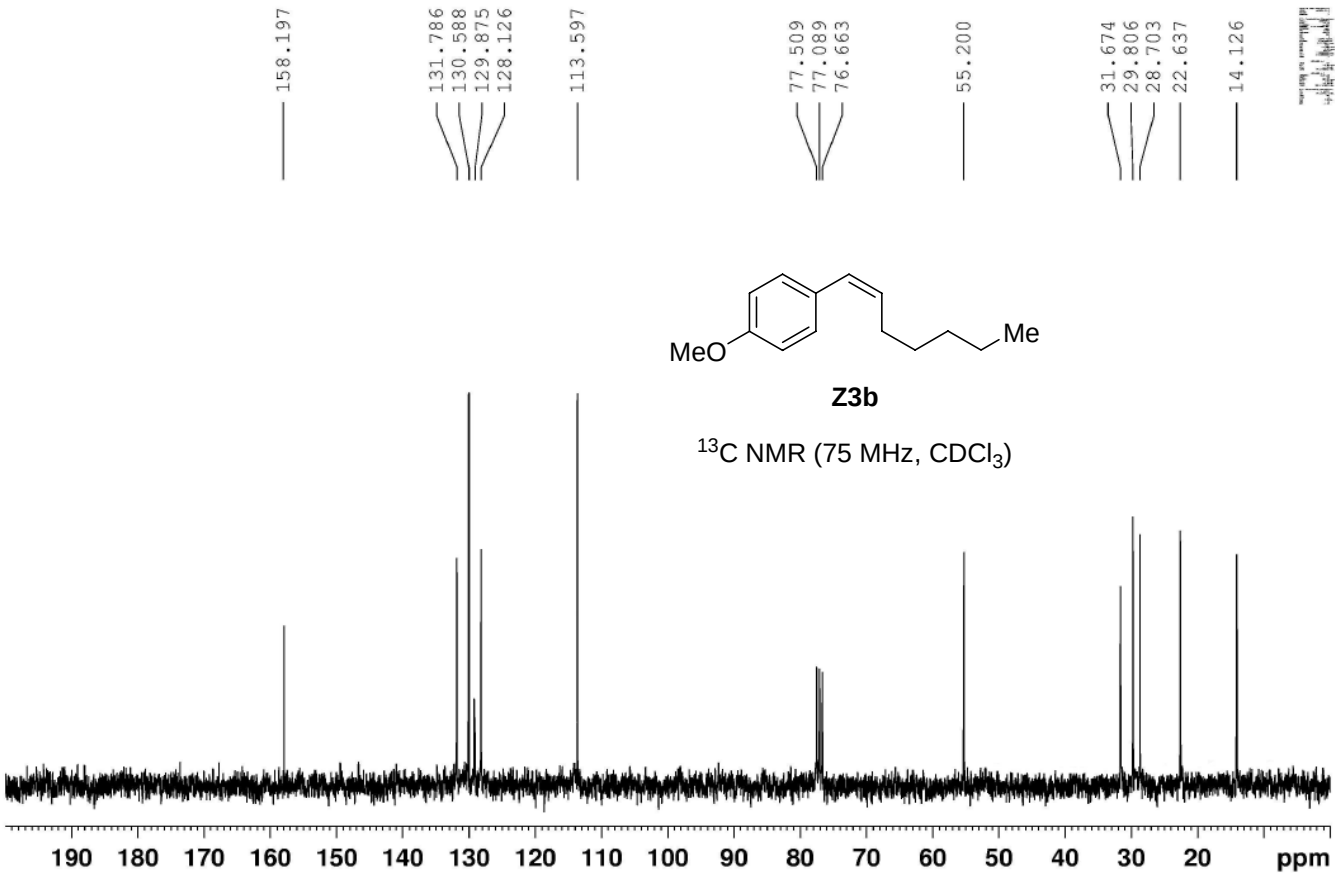
Z3a

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



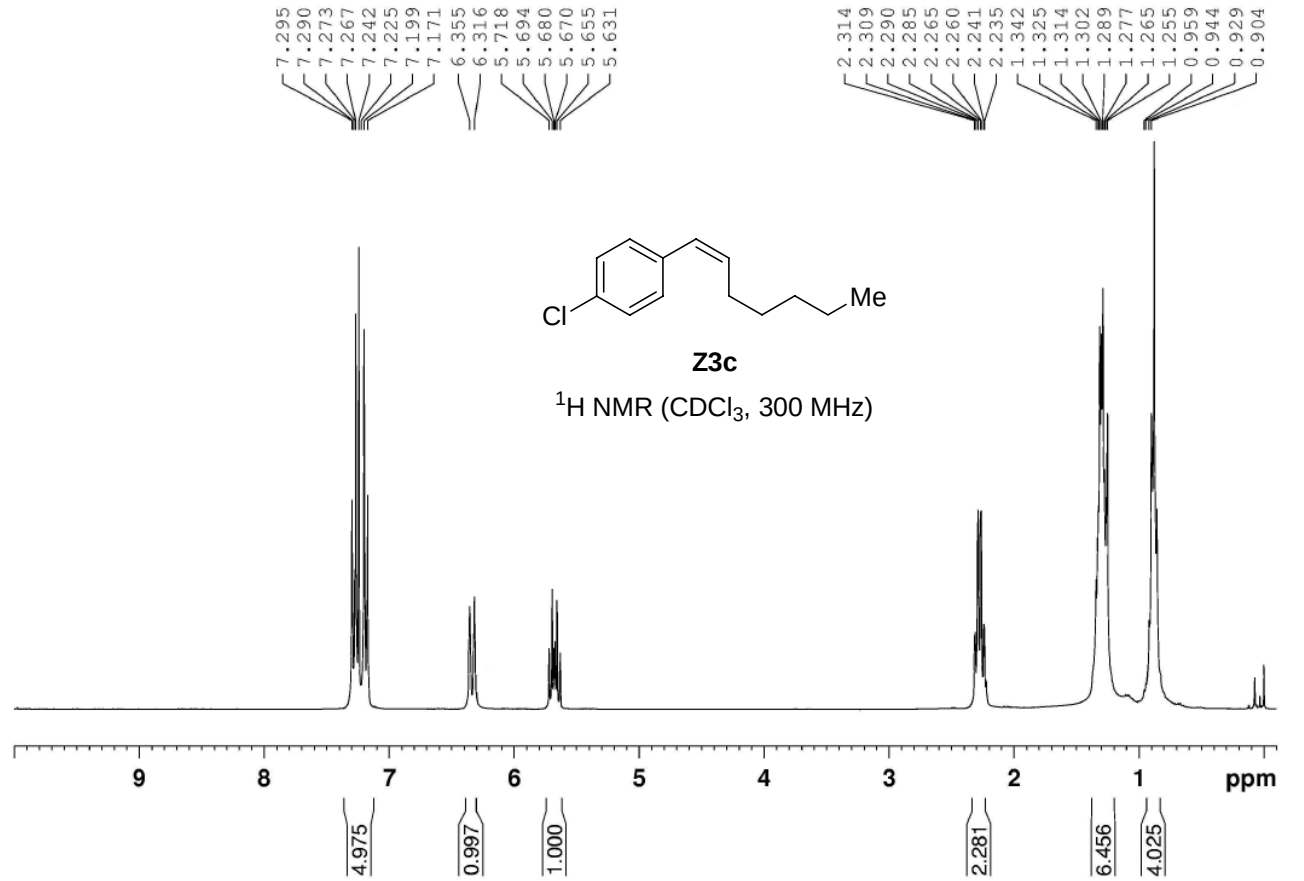
Z3b

^{1}H NMR ($CDCl_3$, 300 MHz)



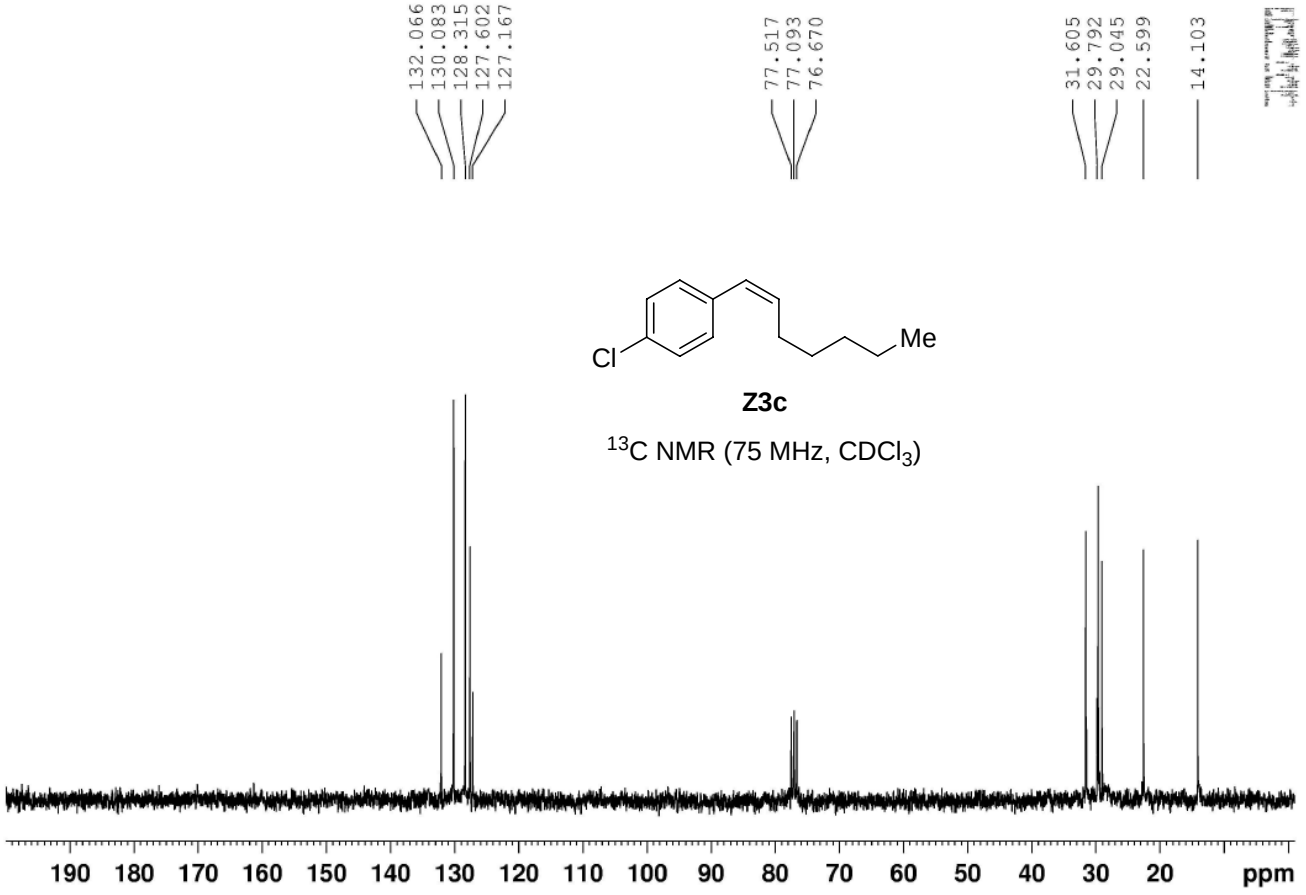
Z3b

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



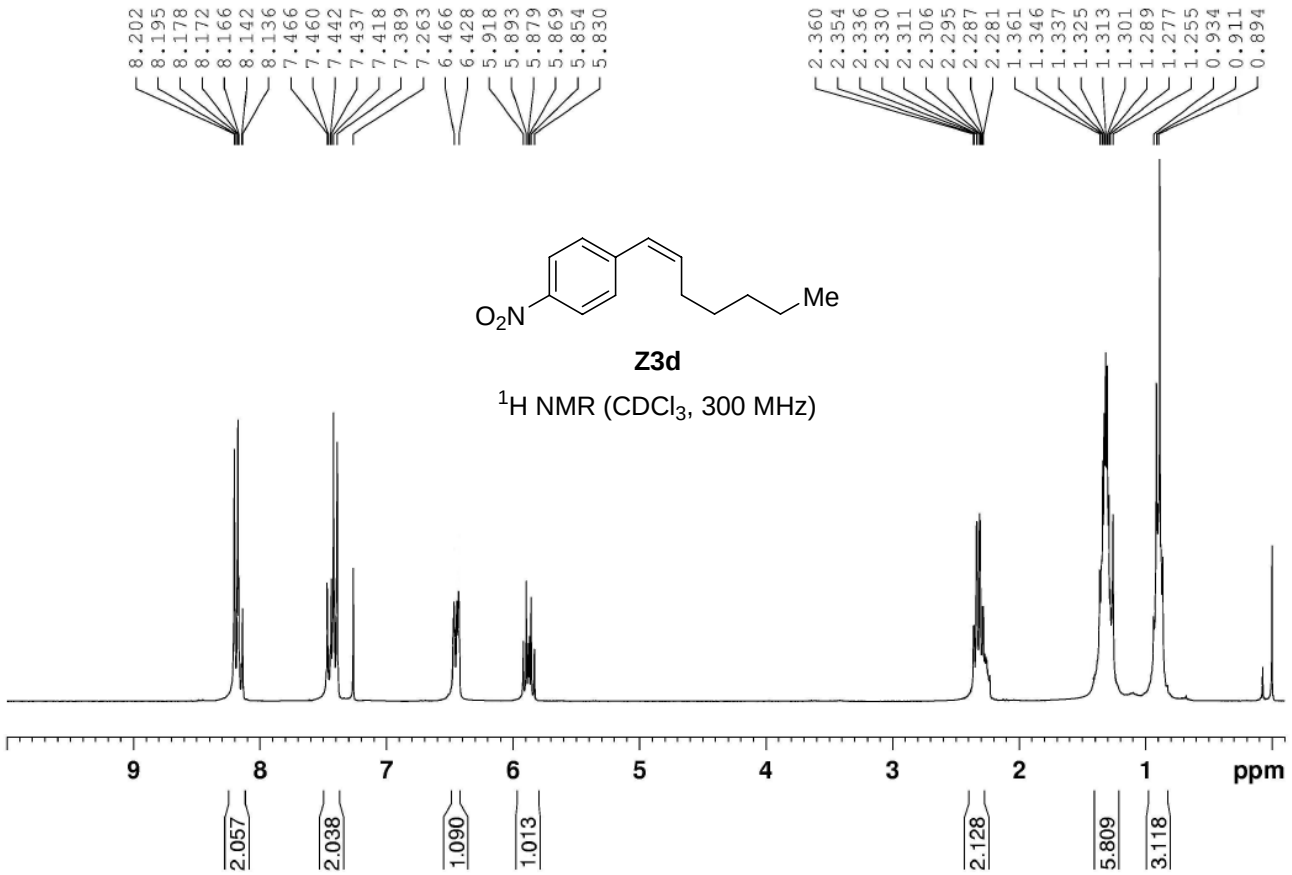
Z3c

^{1}H NMR ($CDCl_3$, 300 MHz)



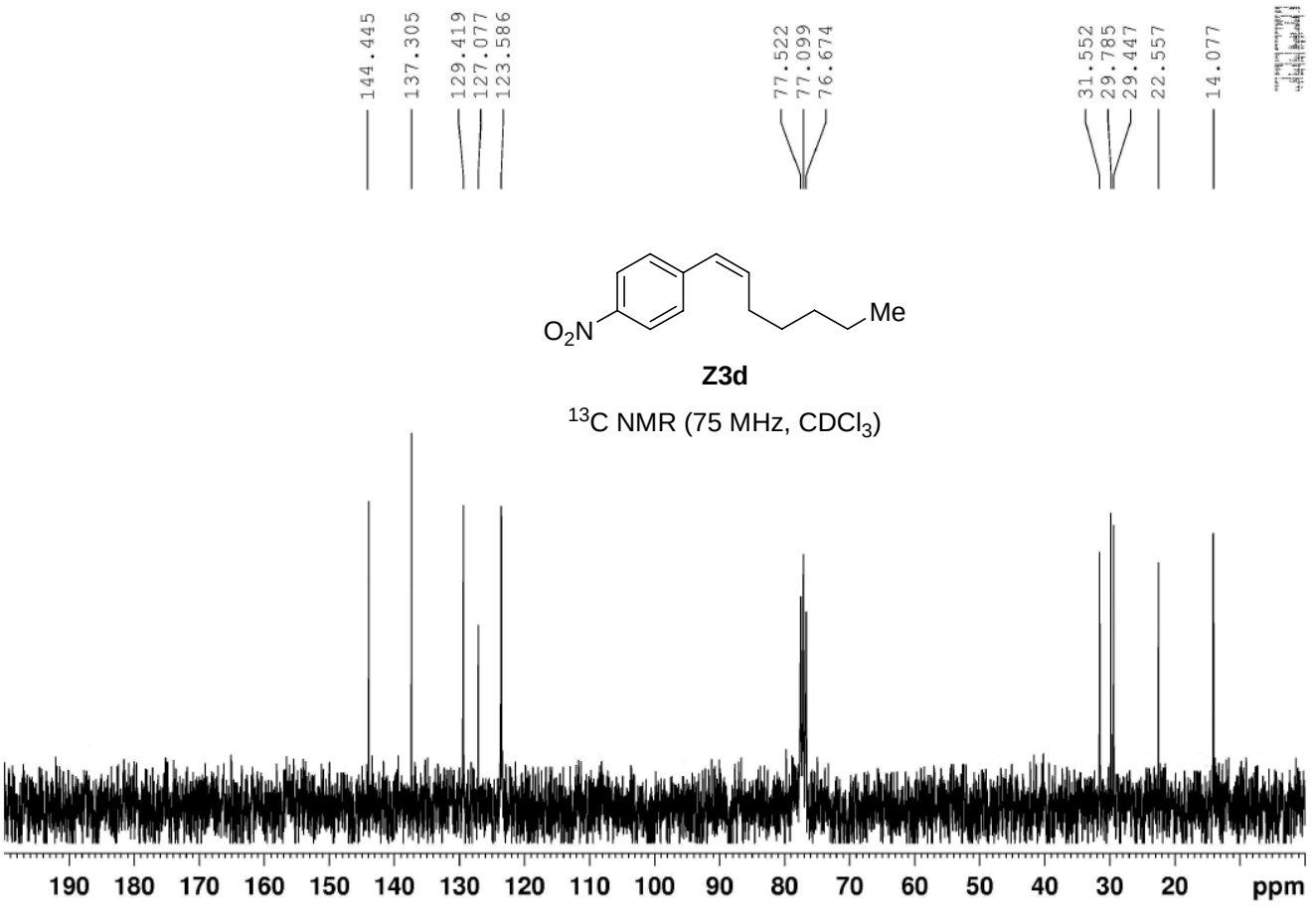
Z3c

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



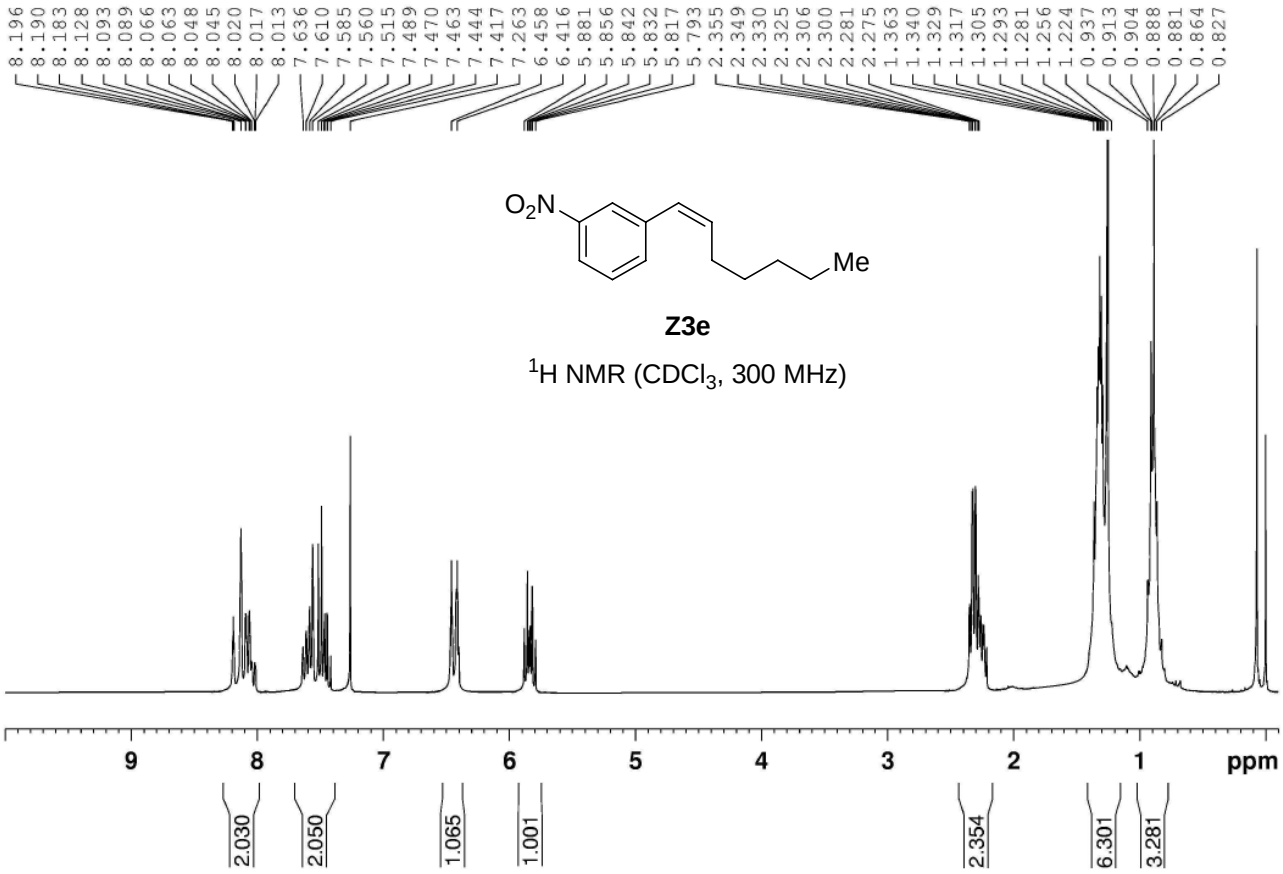
Z3d

^{1}H NMR ($CDCl_3$, 300 MHz)



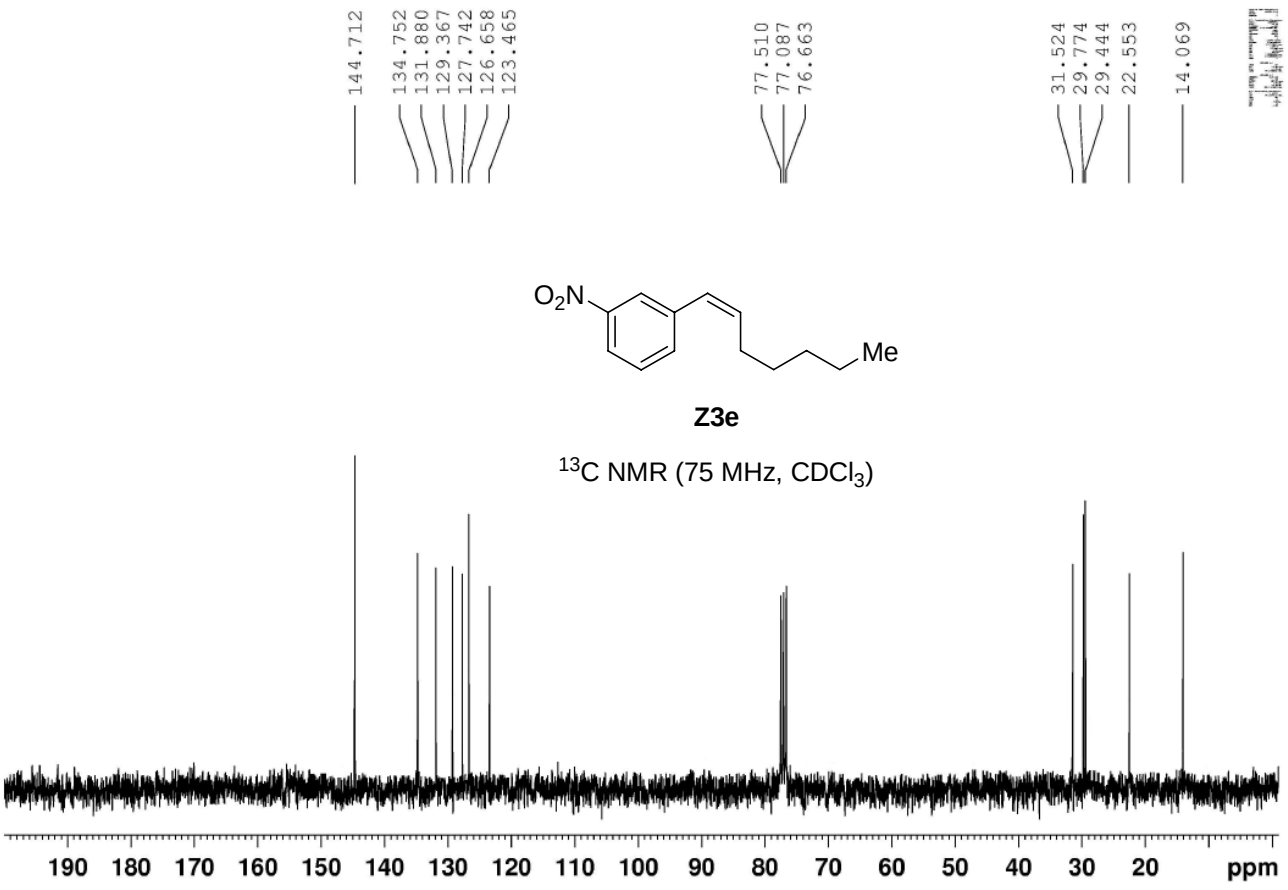
Z3d

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



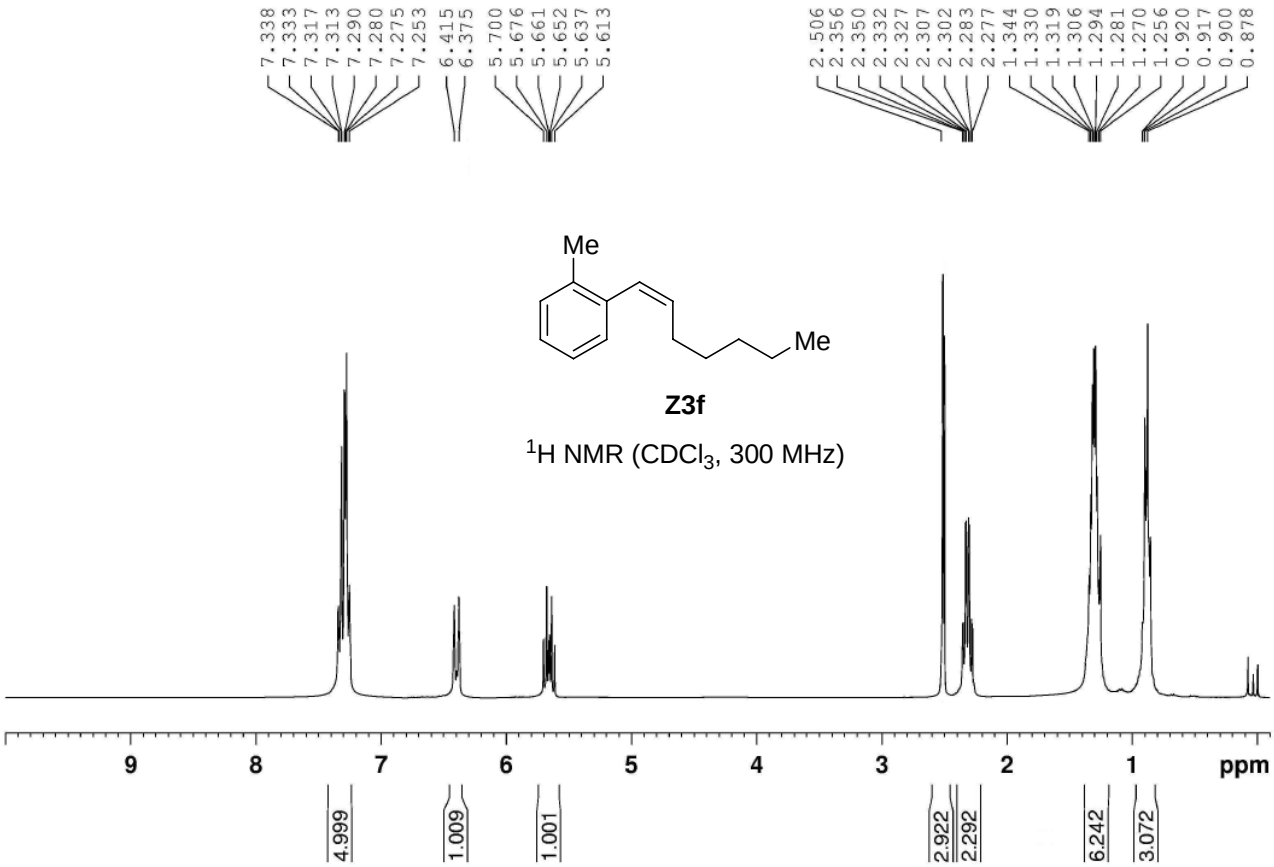
Z3e

^{1}H NMR ($CDCl_3$, 300 MHz)



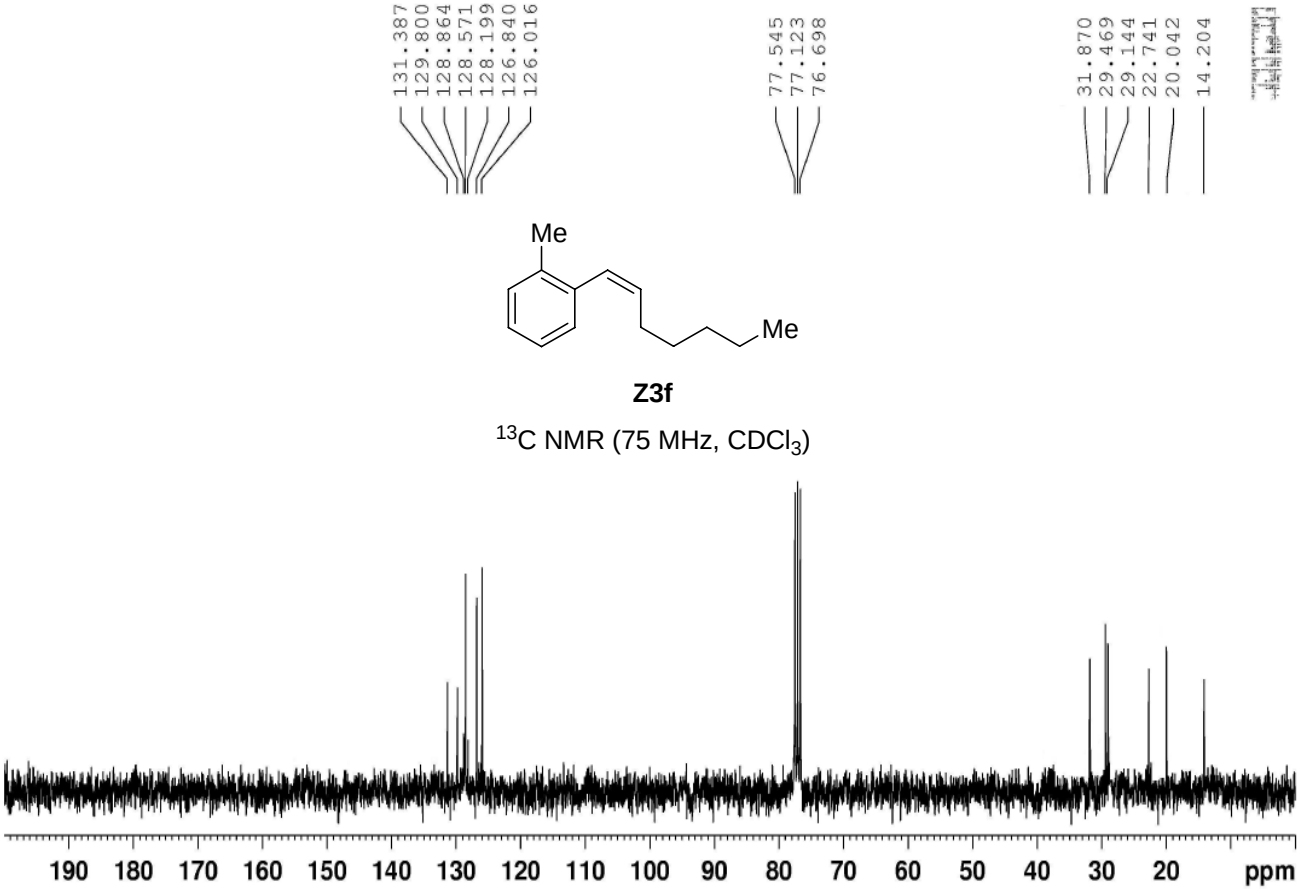
Z3e

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



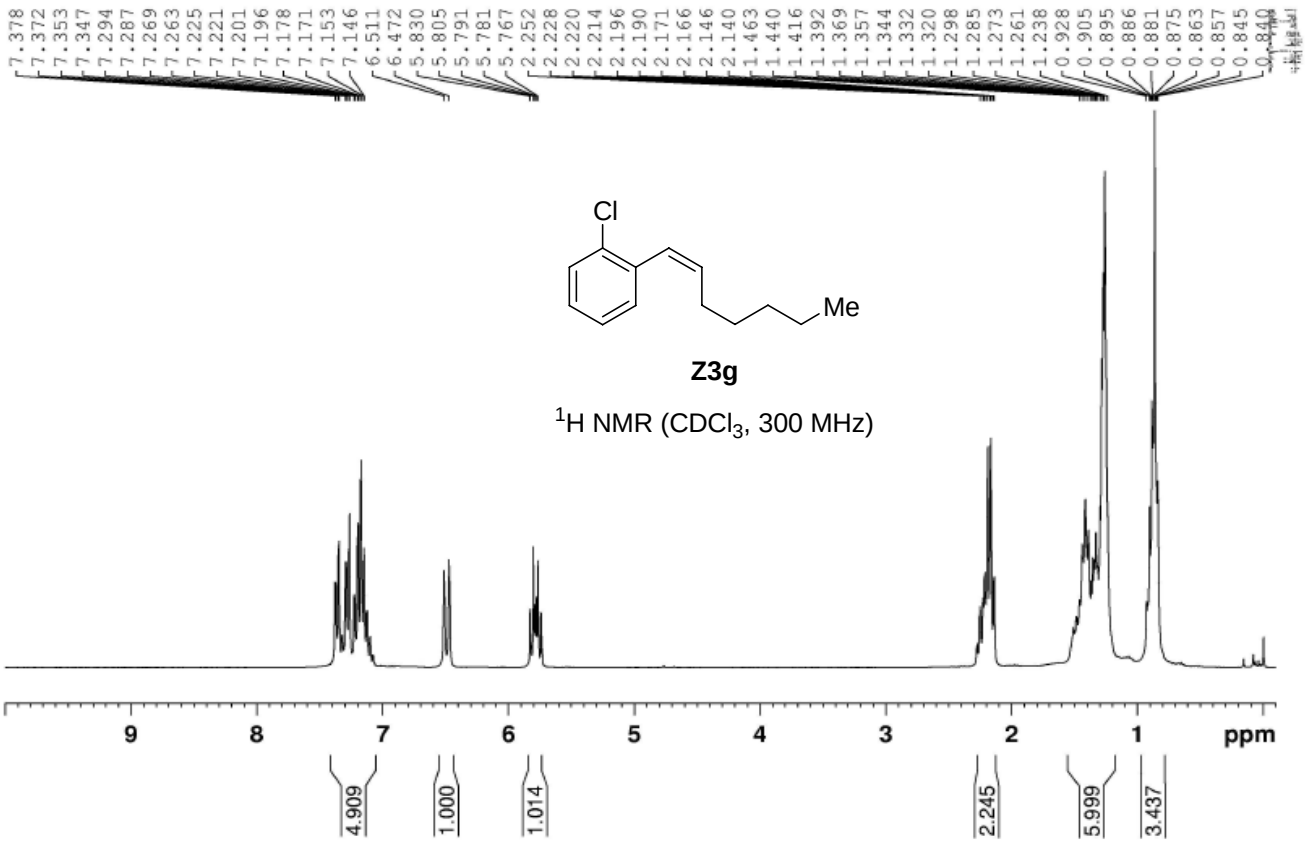
Z3f

^{1}H NMR ($CDCl_3$, 300 MHz)



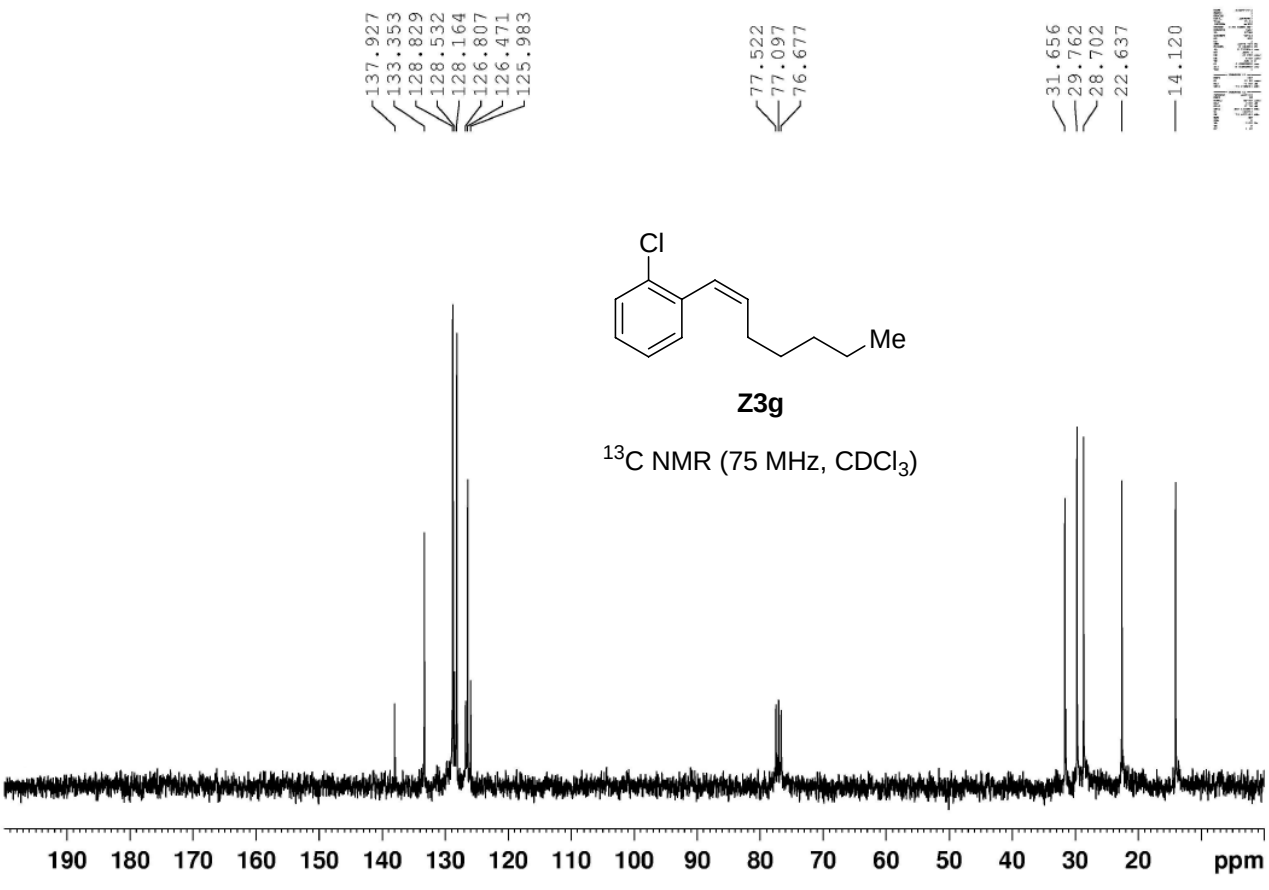
Z3f

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



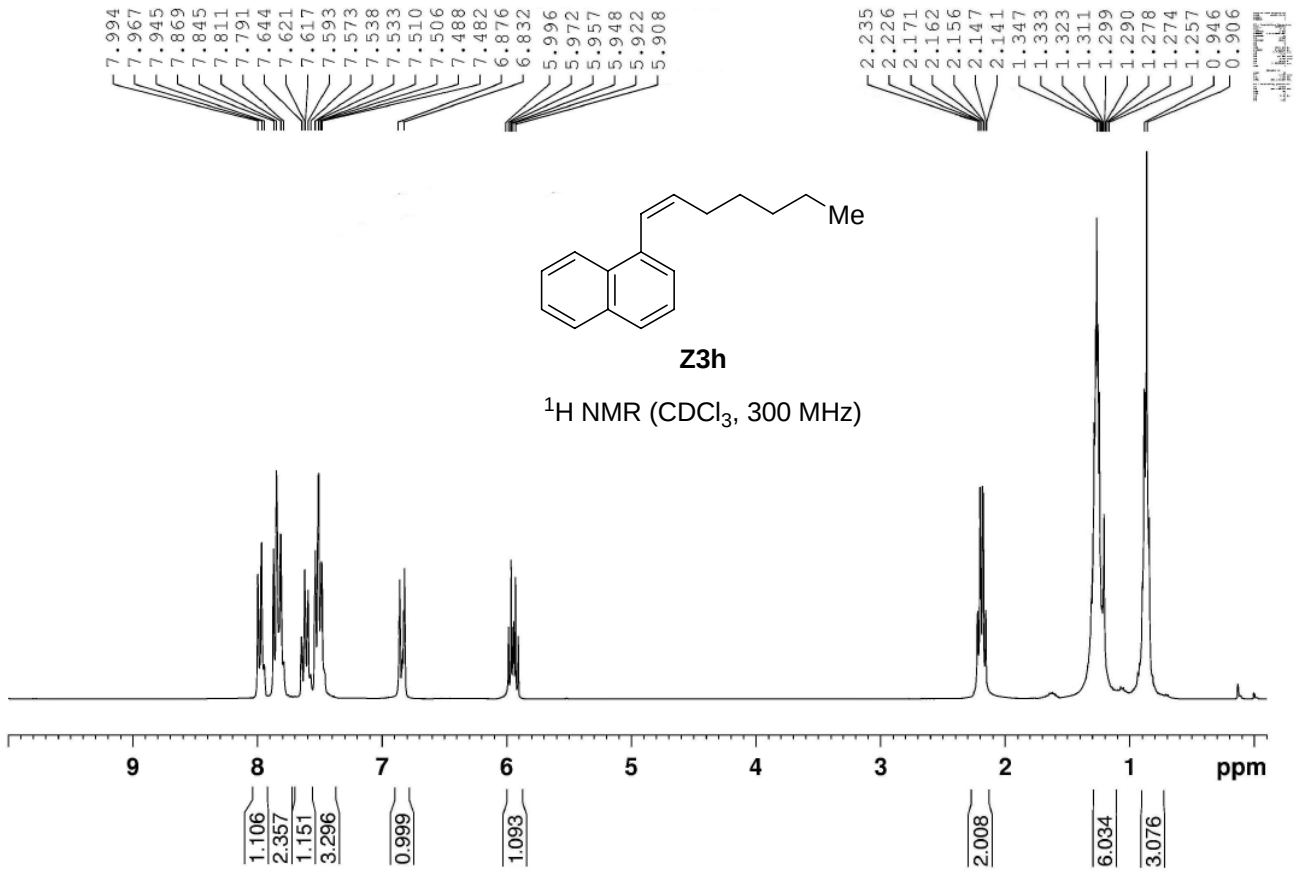
Z3g

^{1}H NMR ($CDCl_3$, 300 MHz)



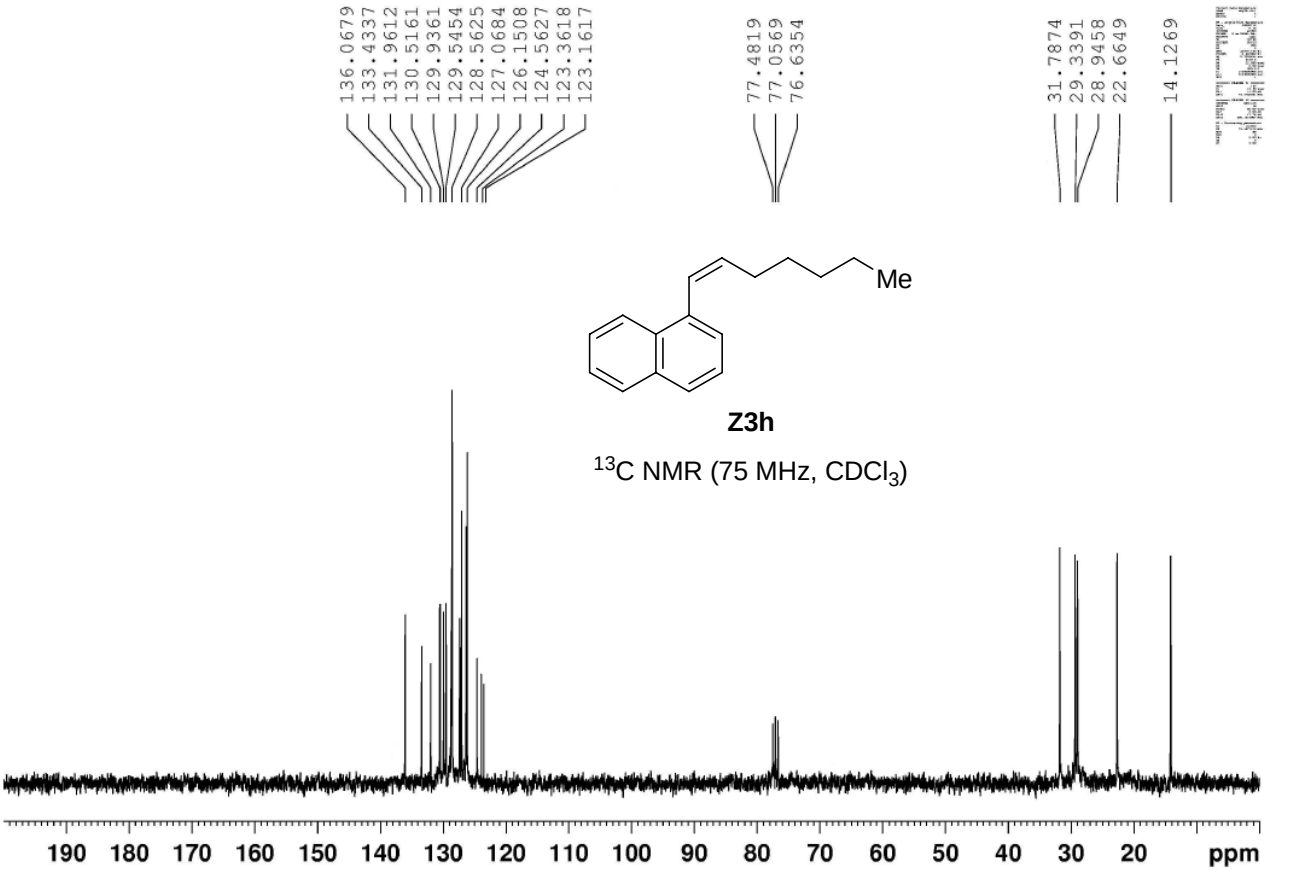
Z3g

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



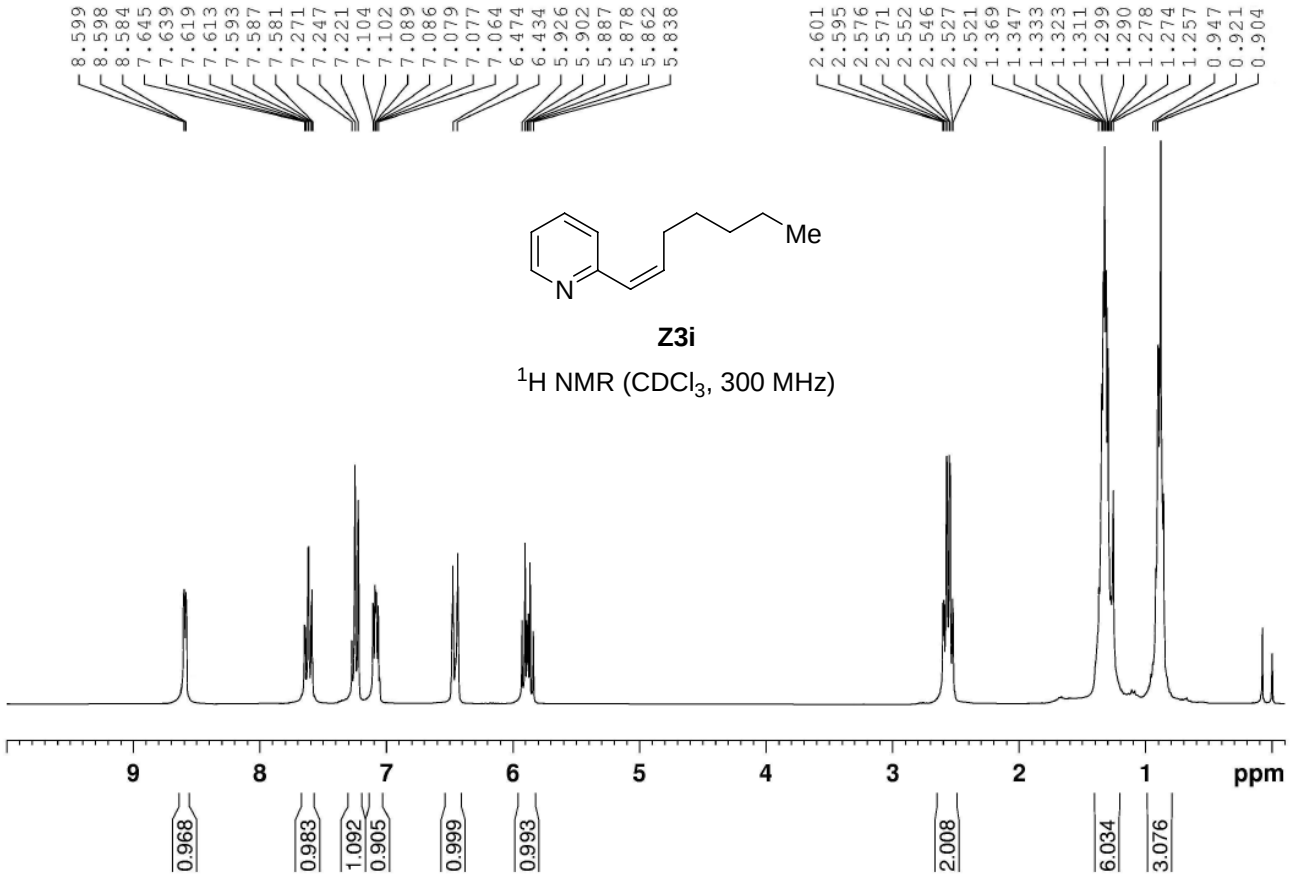
Z3h

^{1}H NMR ($CDCl_3$, 300 MHz)



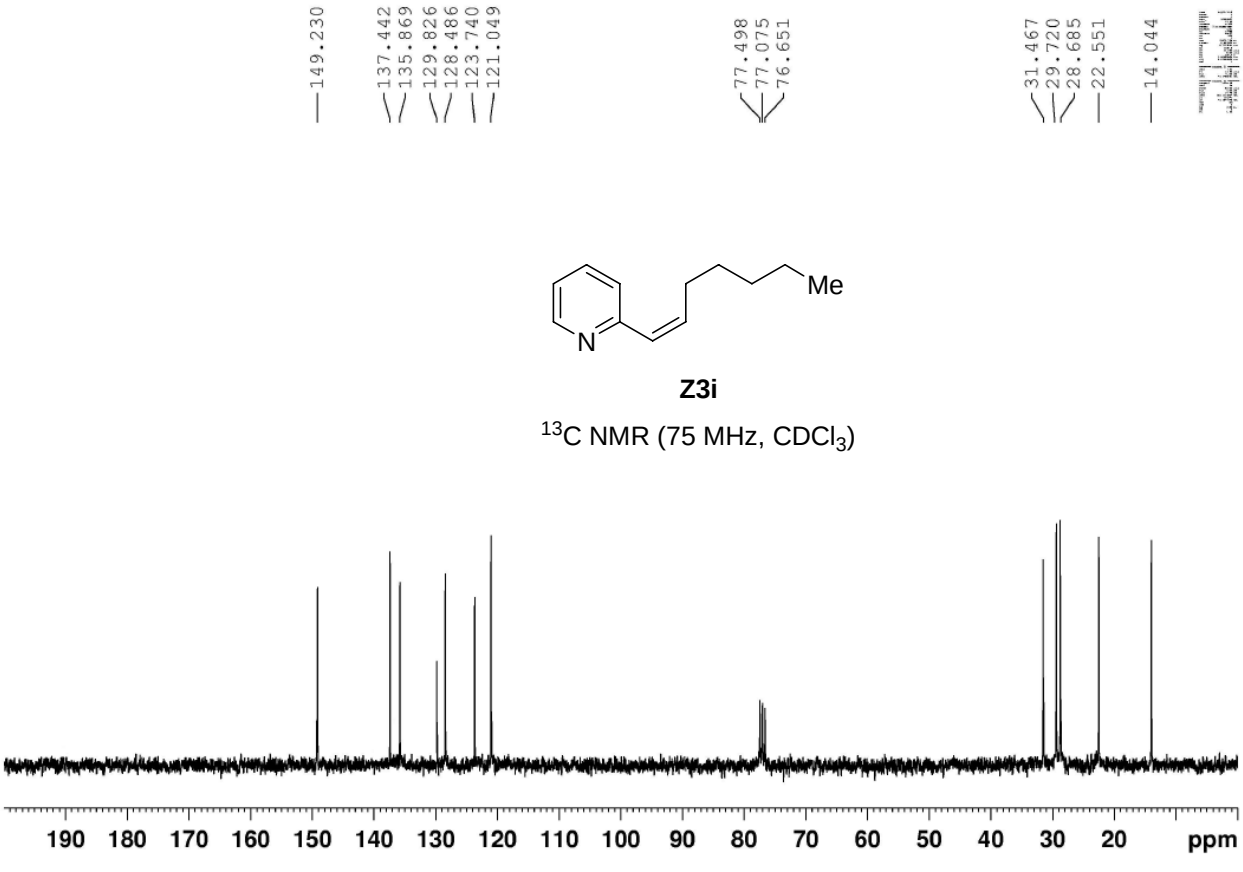
Z3h

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



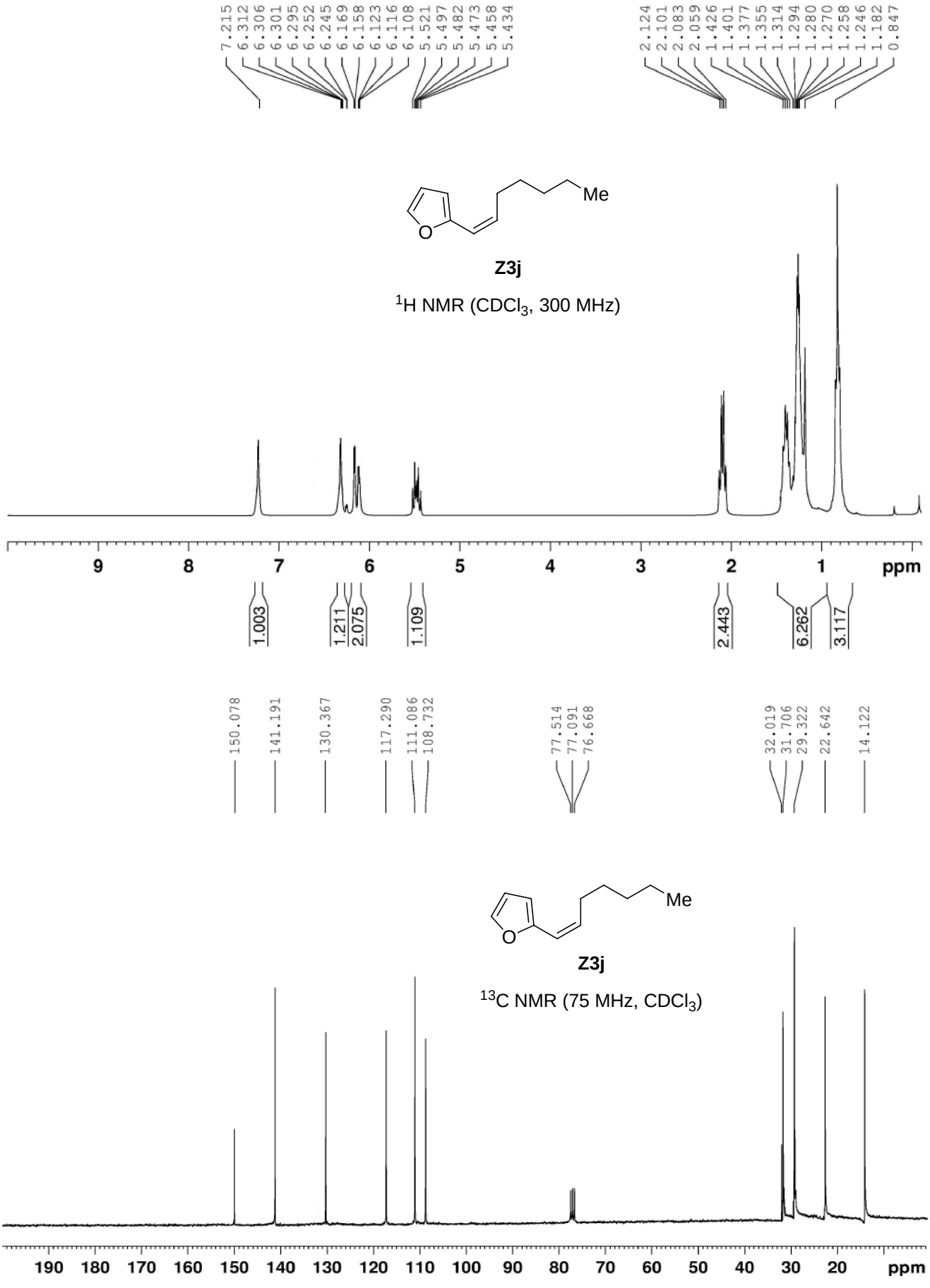
Z3i

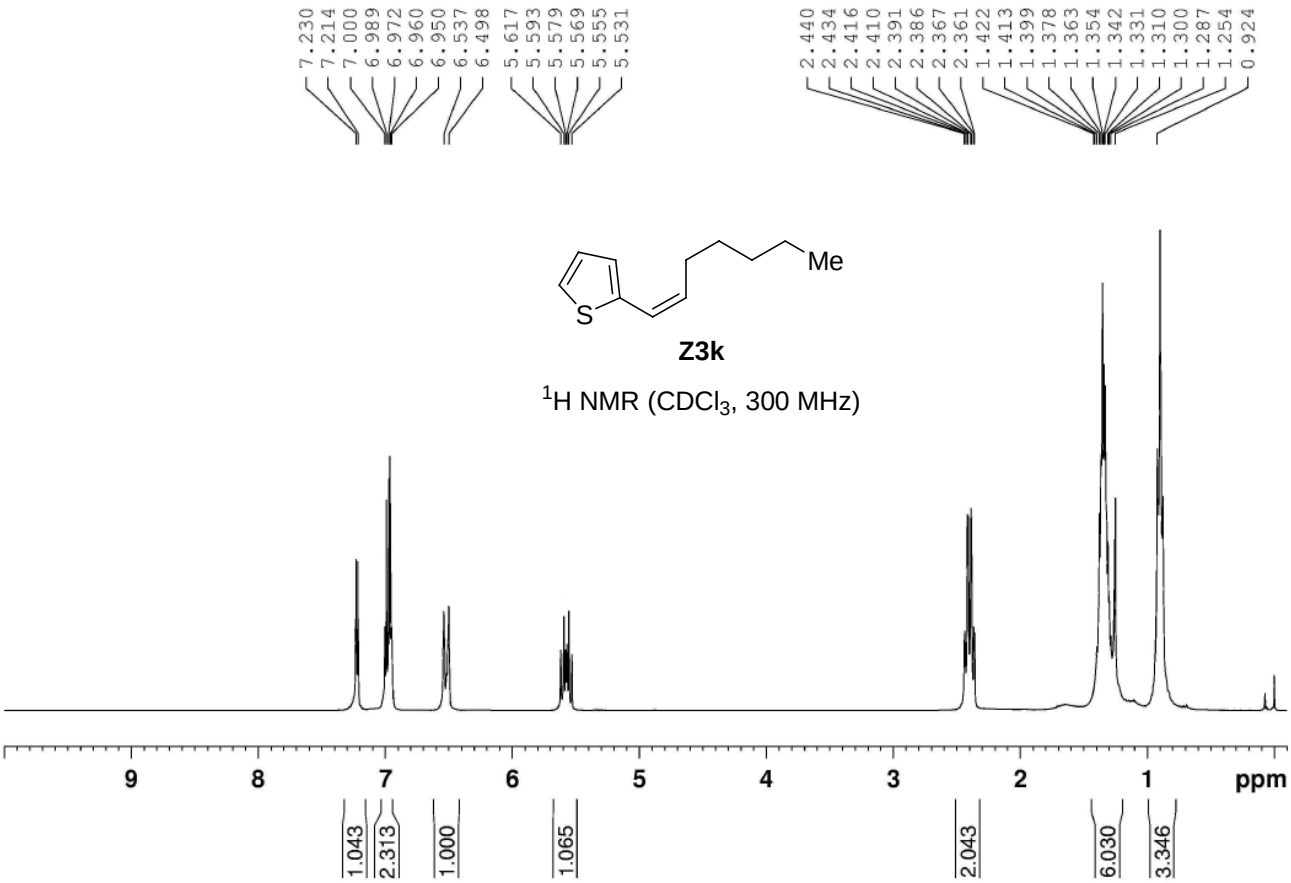
^{1}H NMR ($CDCl_3$, 300 MHz)



Z3i

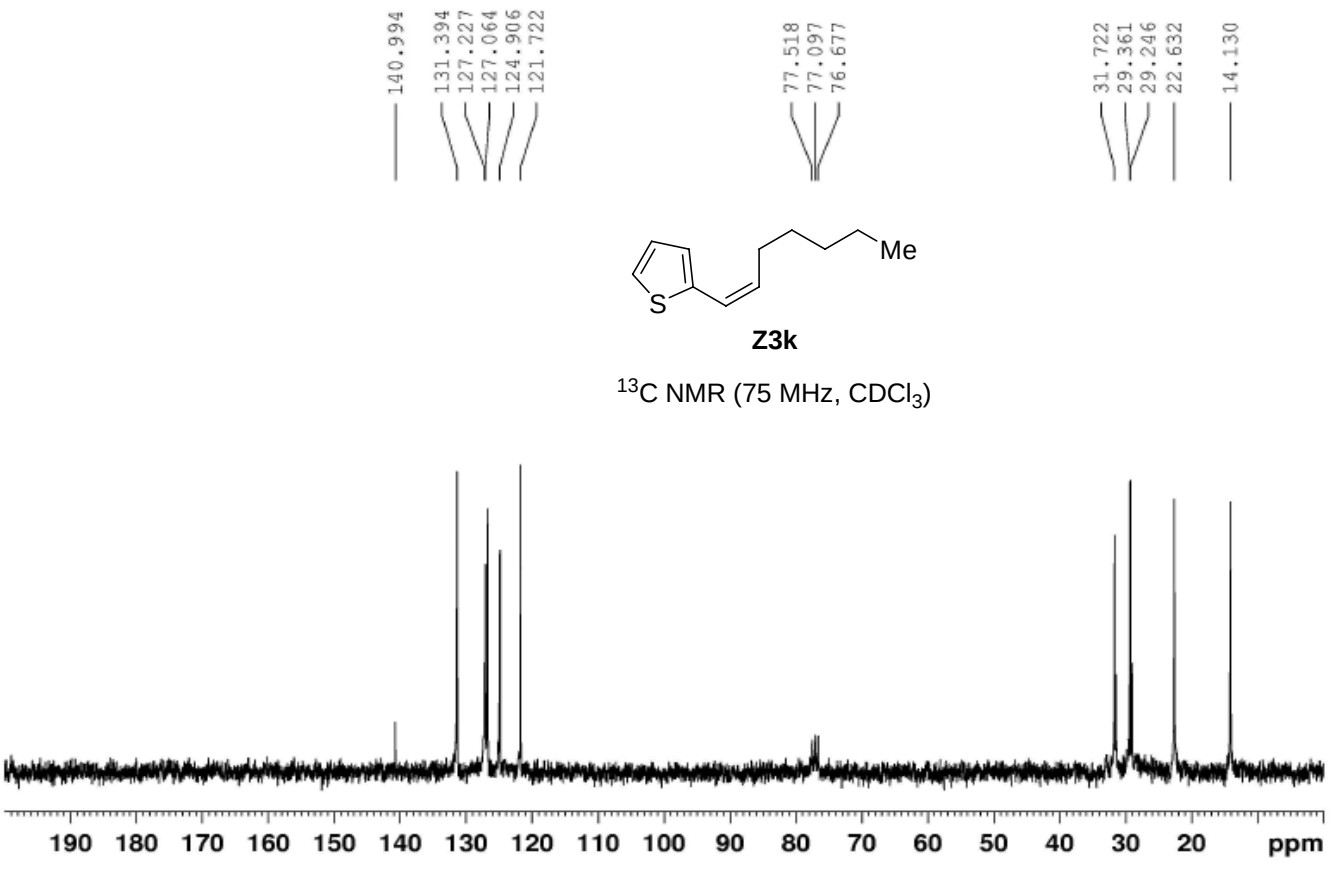
^{13}C NMR (75 MHz, $CDCl_3$)


7.215
6.312
6.306
6.301
6.295
6.252
6.245
6.169
6.158
6.123
6.116
6.108
5.521
5.497
5.482
5.473
5.458
5.434
2.124
2.101
2.083
2.059
1.426
1.401
1.377
1.355
1.314
1.294
1.280
1.270
1.258
1.246
1.182
0.847
Me
O
Z3j
1H NMR (CDCl3, 300 MHz)
9
8
7
6
5
4
3
2
1
ppm
1.003
1.211
2.075
1.109
2.443
6.262
3.117
150.078
141.191
130.367
117.290
111.086
108.732
77.514
77.091
76.668
32.019
31.706
29.322
22.642
14.122
Me
O
Z3j
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



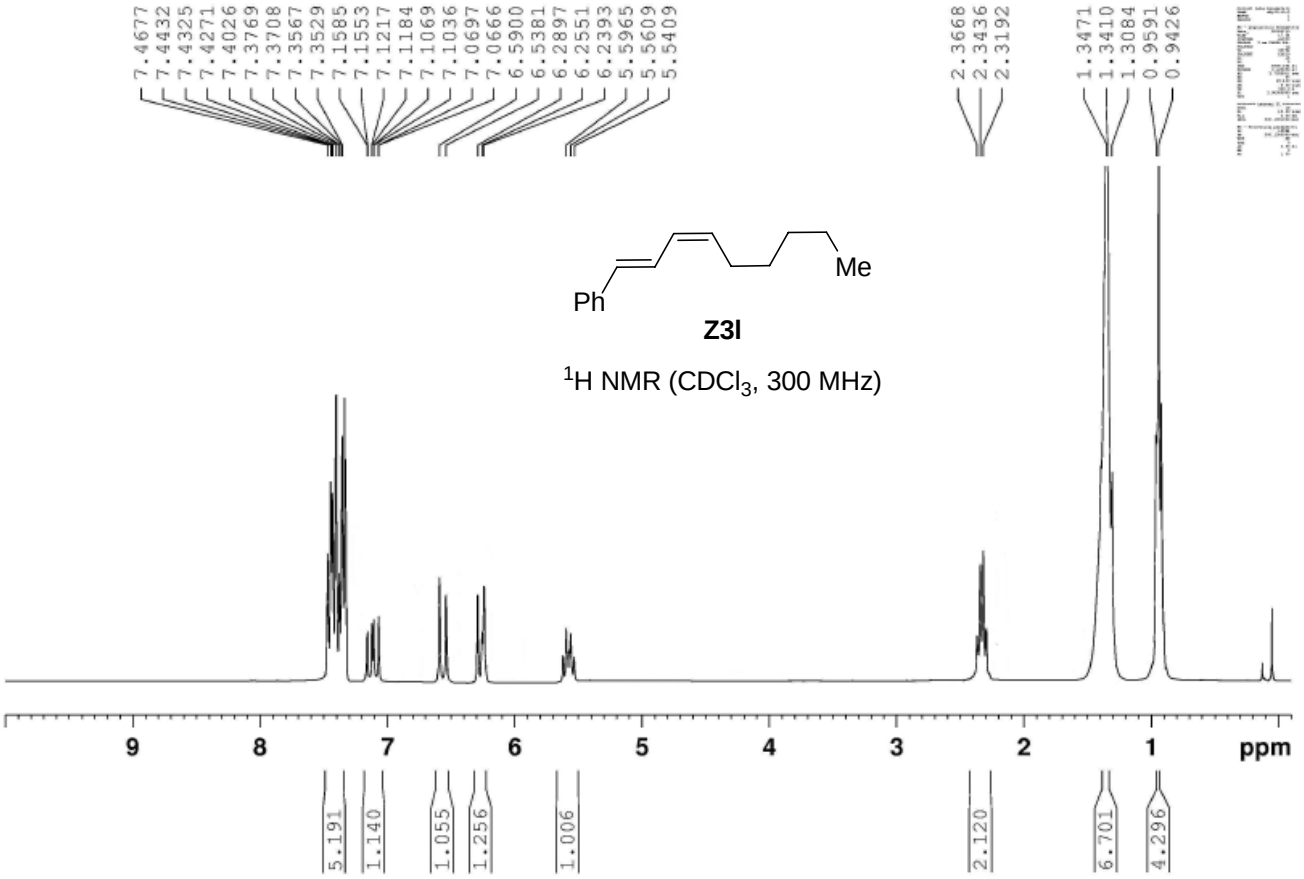
Z3k

^{1}H NMR ($CDCl_3$, 300 MHz)



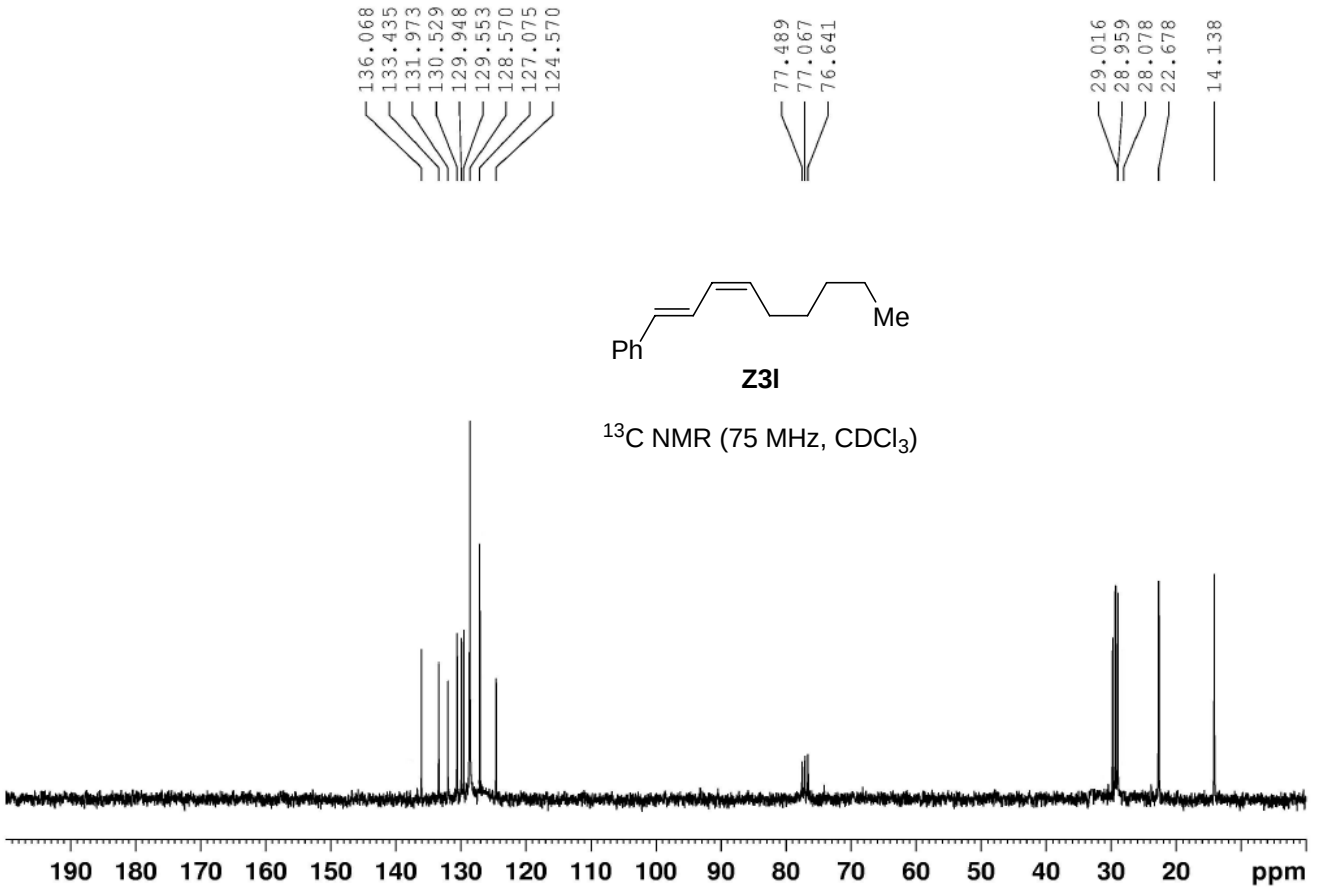
Z3k

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



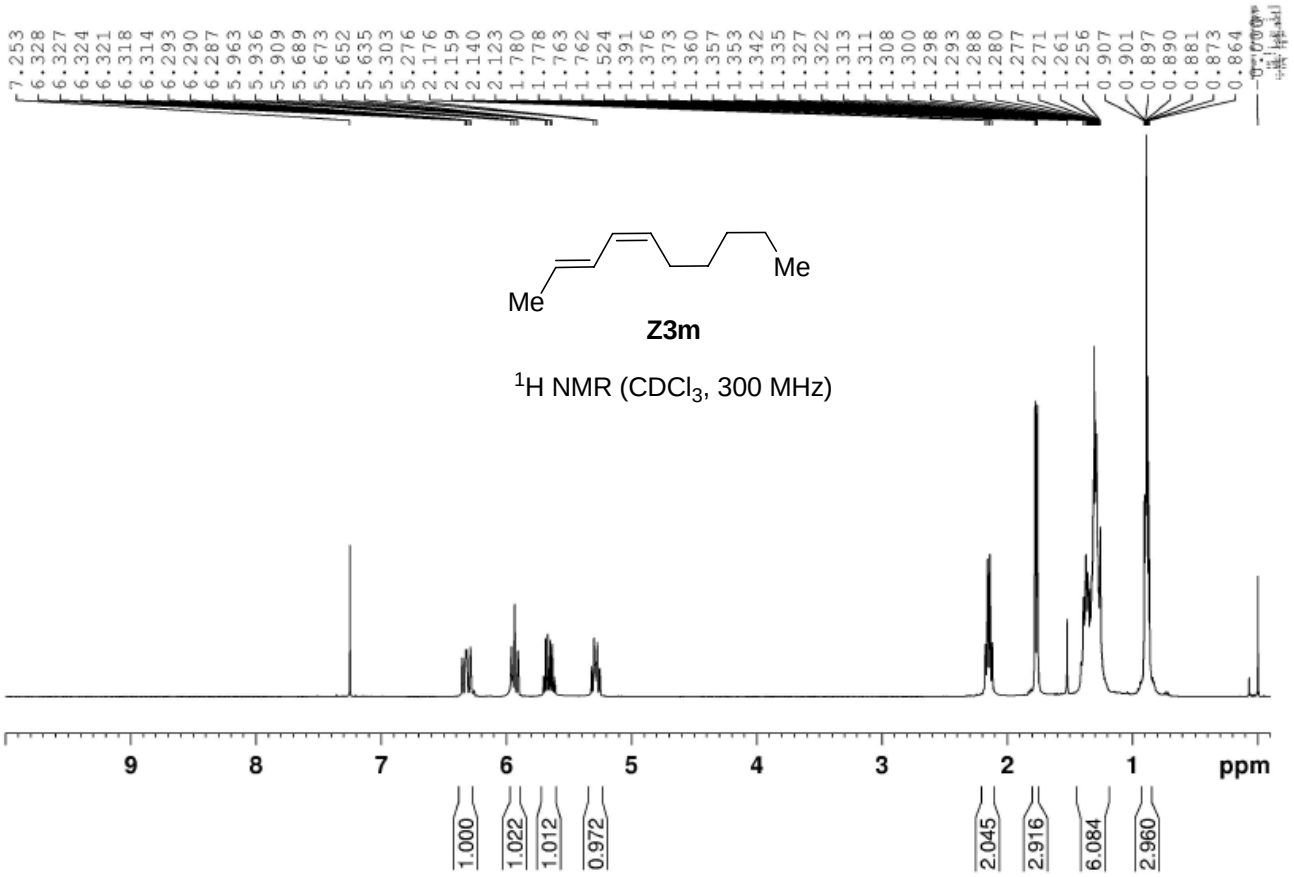
Z3l

^{1}H NMR ($CDCl_3$, 300 MHz)



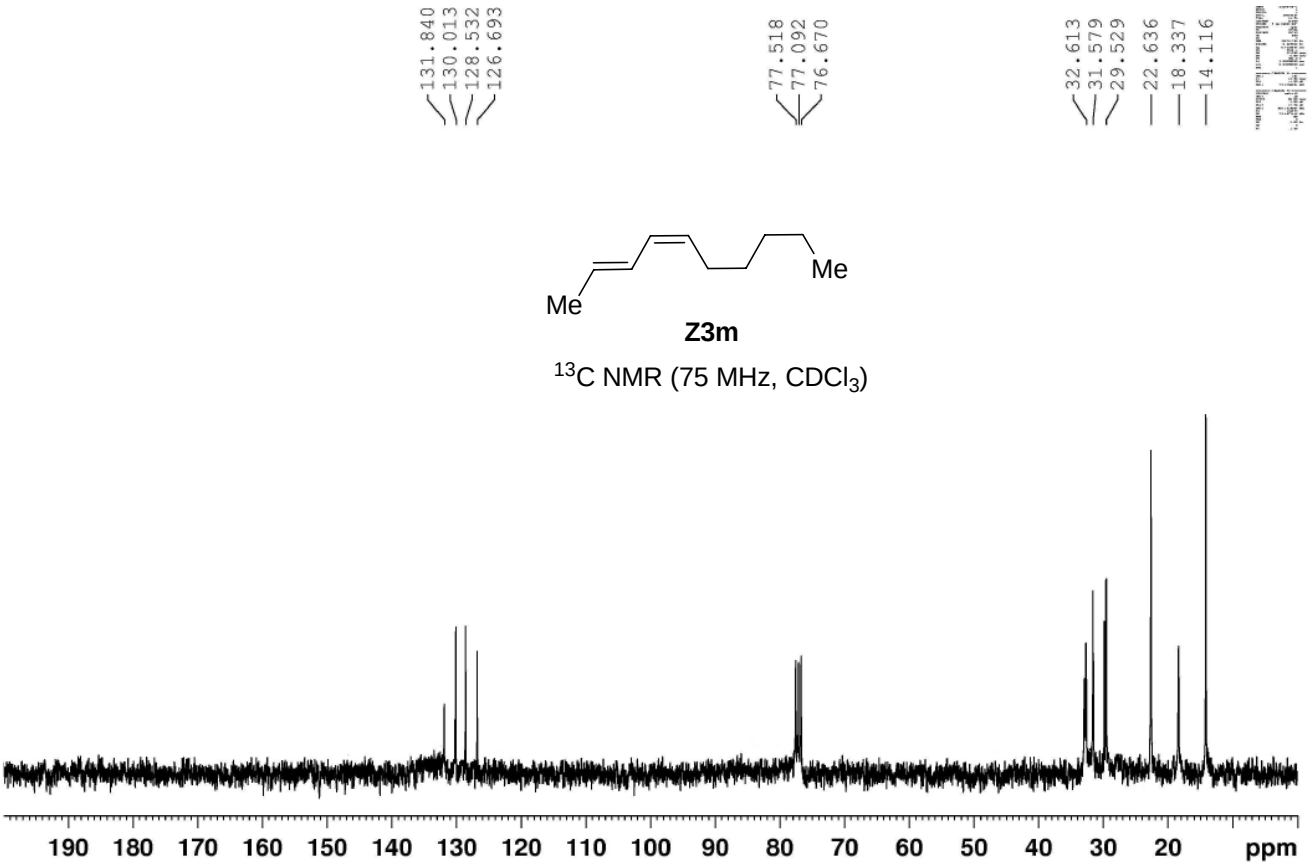
Z3l

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



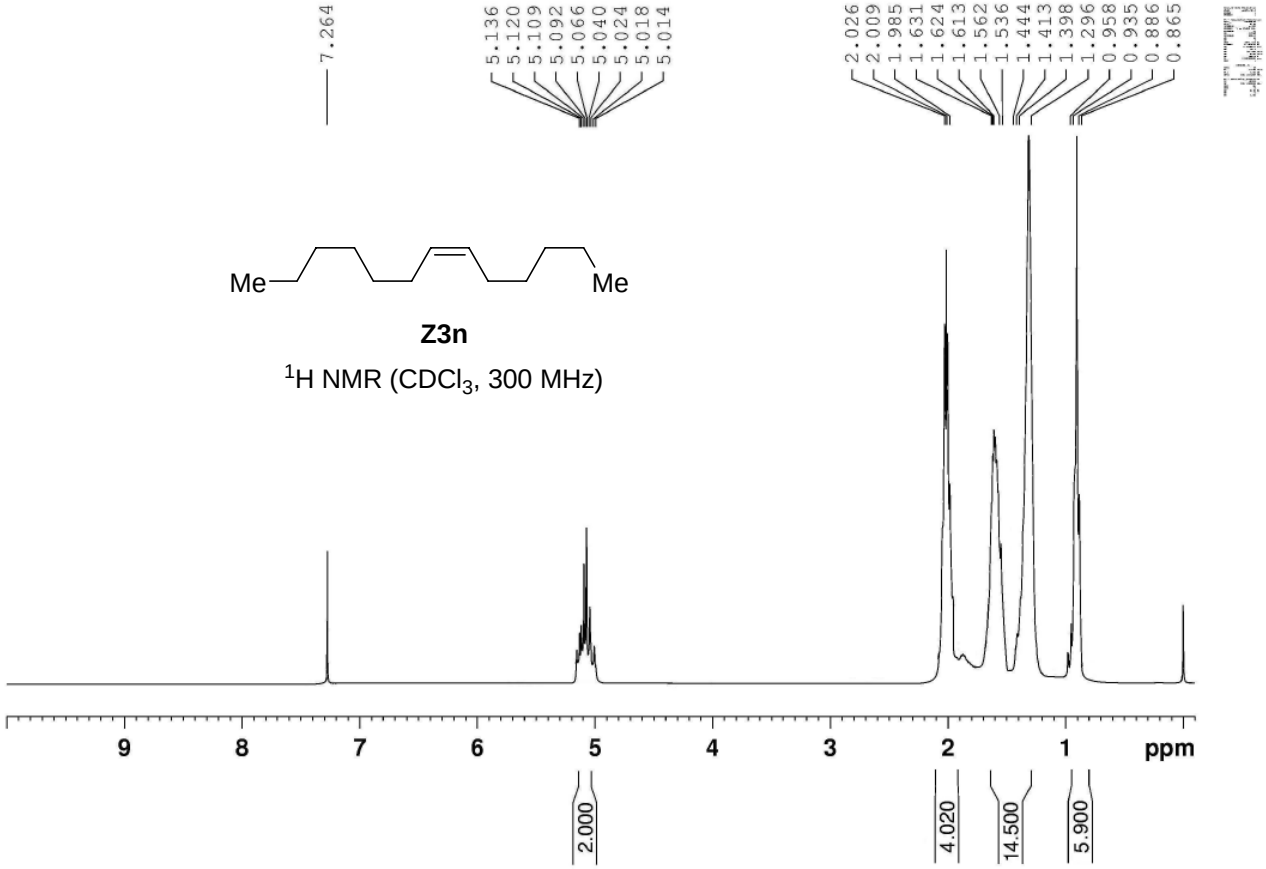
Z3m

^{1}H NMR ($CDCl_3$, 300 MHz)



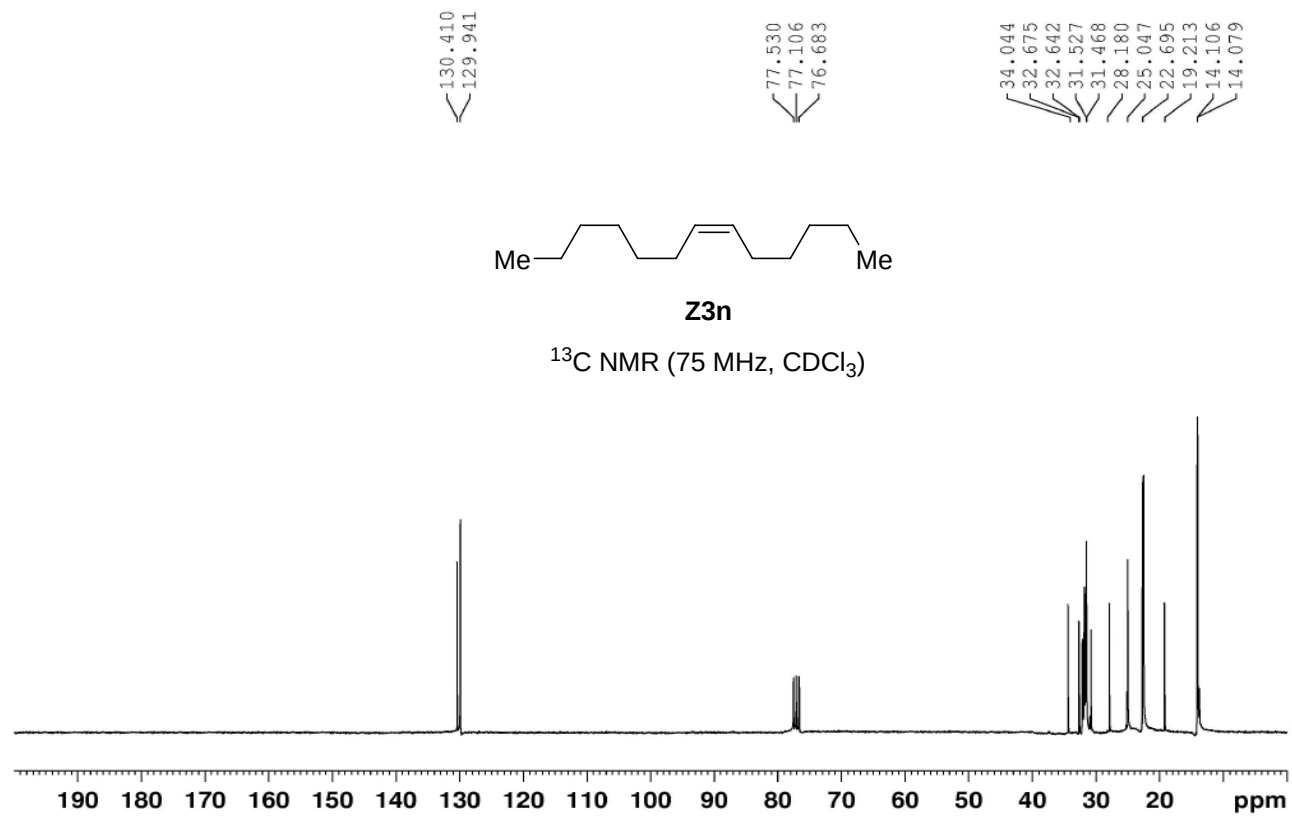
Z3m

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



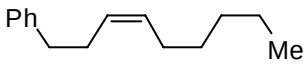
Z3n

^{1}H NMR ($CDCl_3$, 300 MHz)



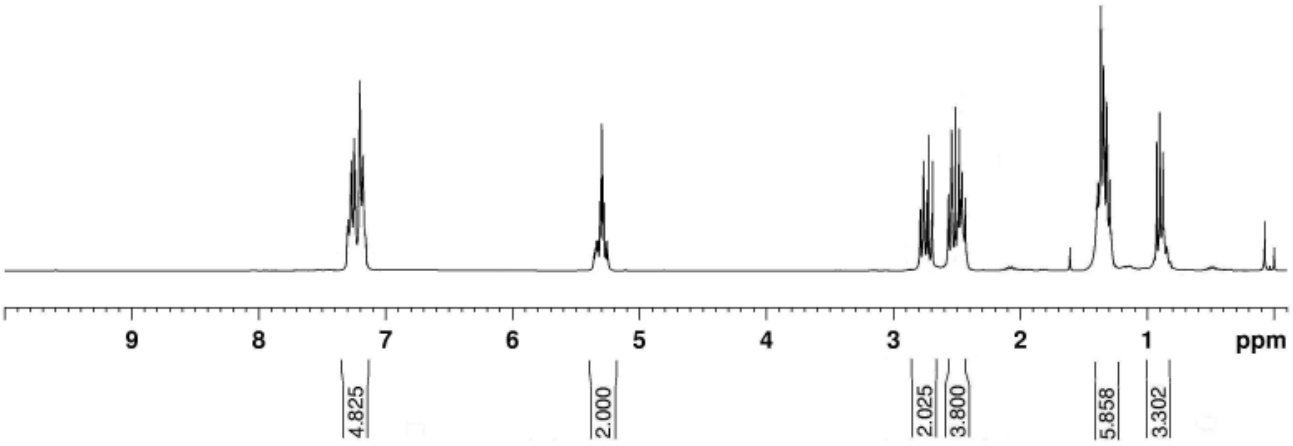
Z3n

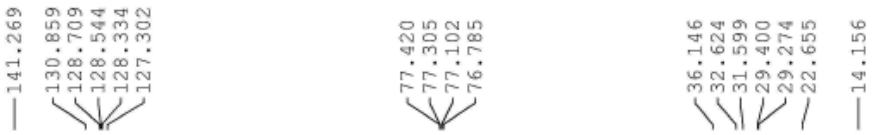
^{13}C NMR (75 MHz, $CDCl_3$)

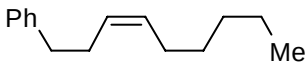


Z3o

^{1}H NMR ($CDCl_3$, 300 MHz)

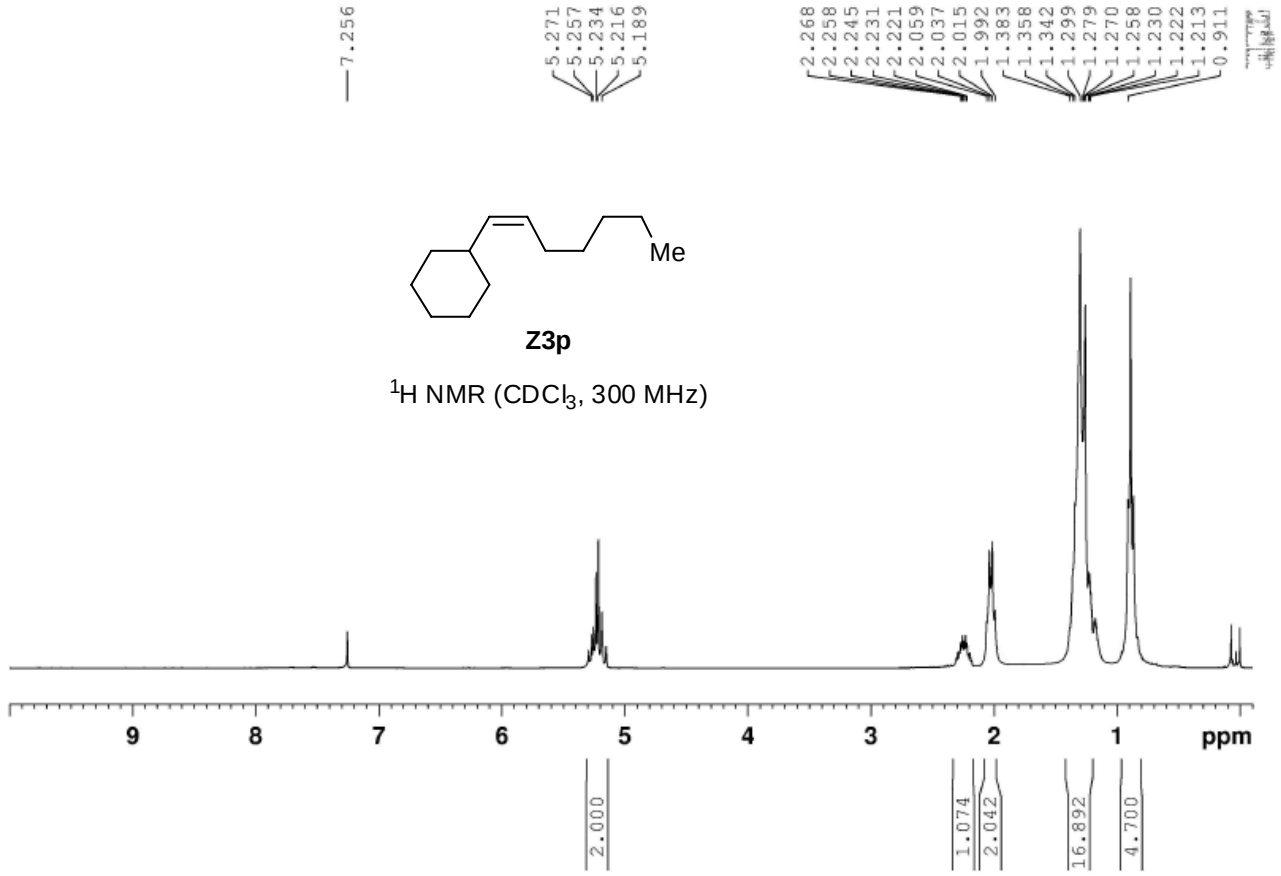






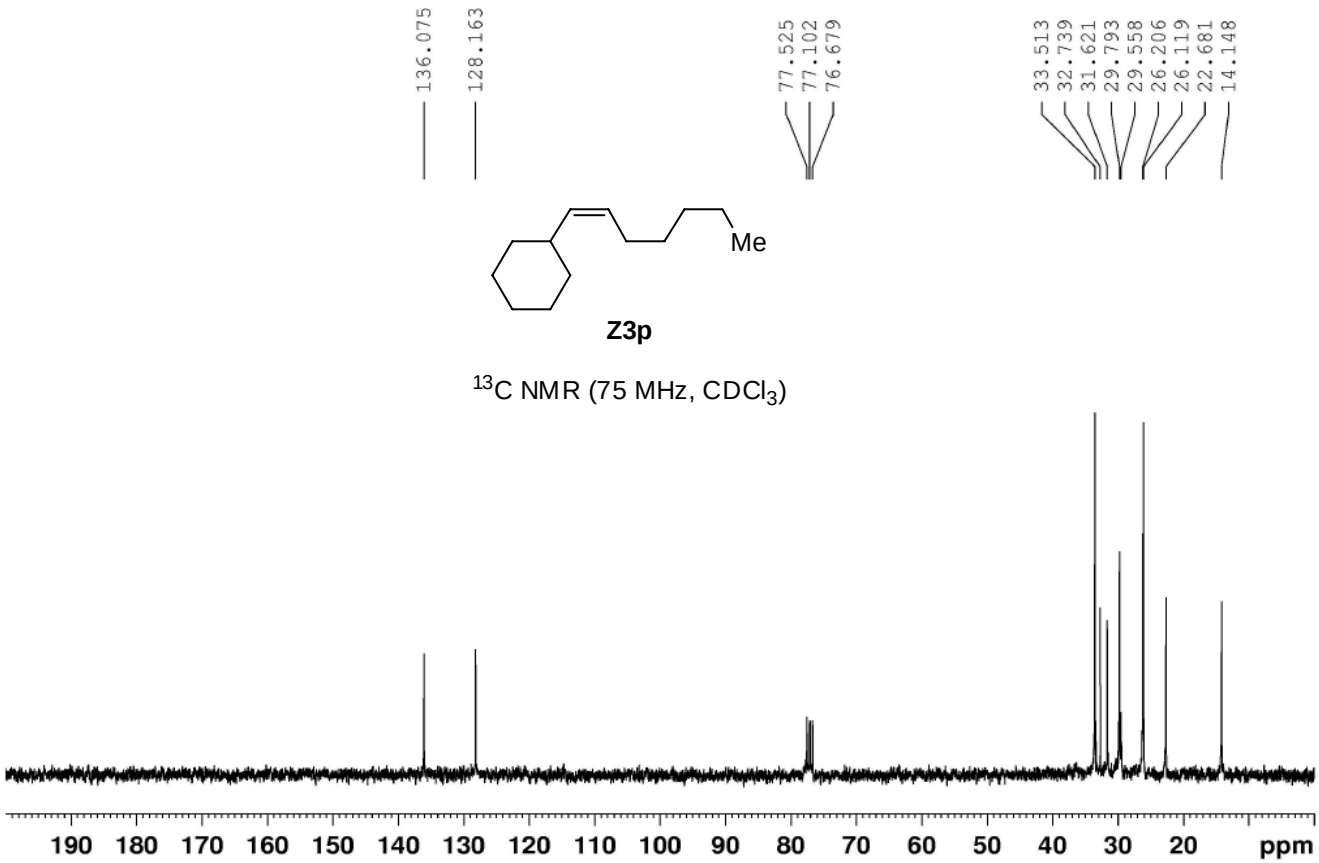
Z3o

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



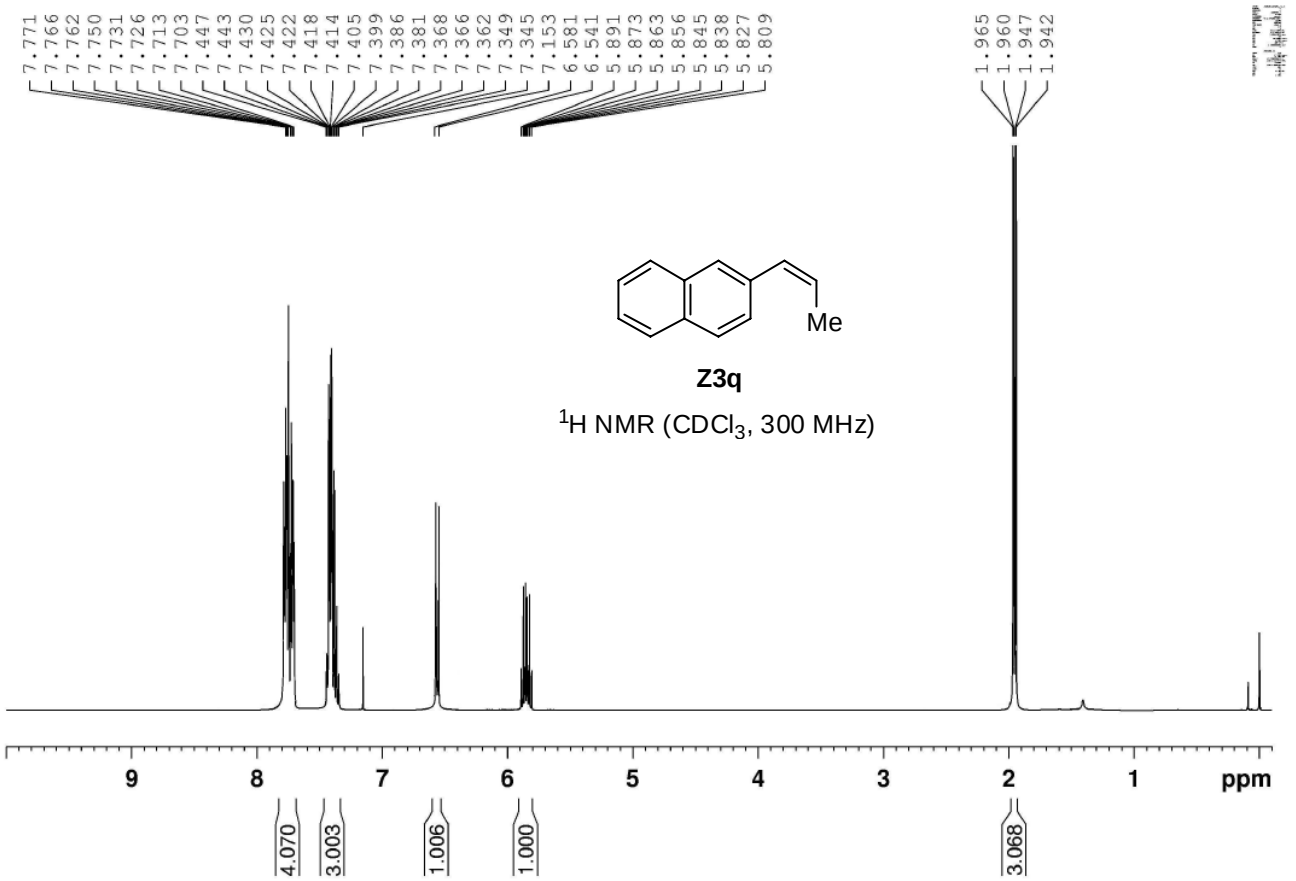
Z3p

^{1}H NMR ($CDCl_3$, 300 MHz)



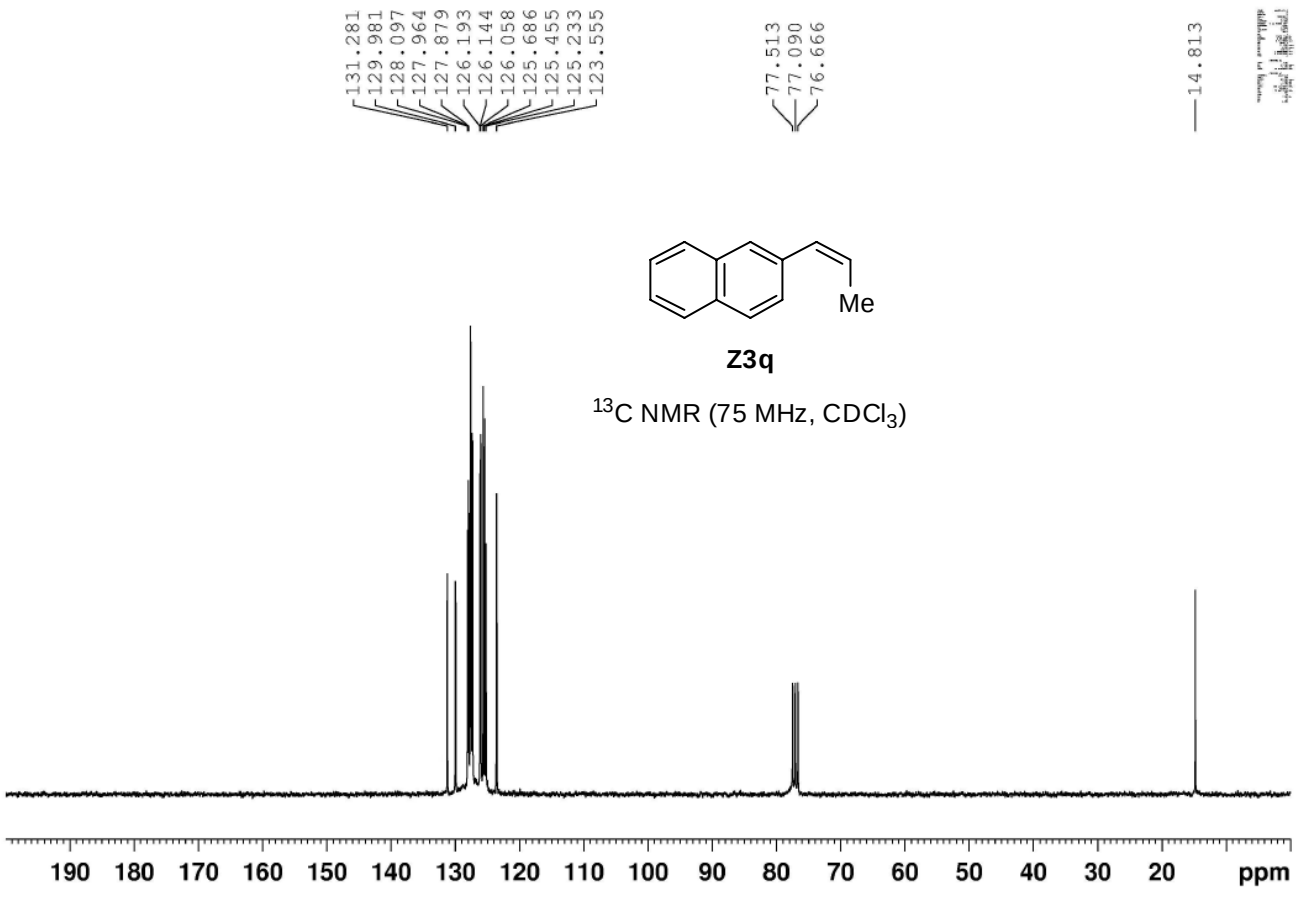
Z3p

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



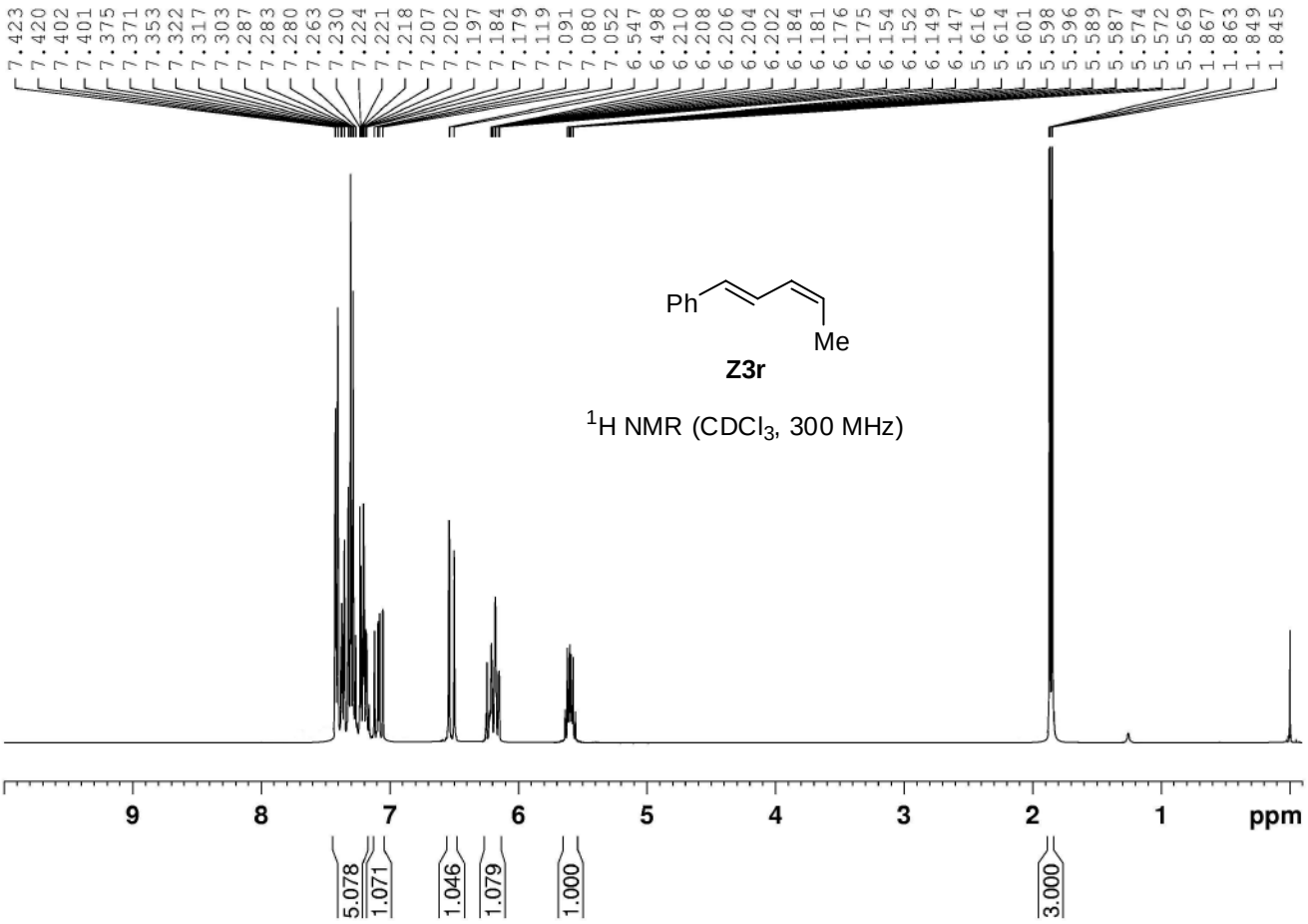
Z3q

^{1}H NMR ($CDCl_3$, 300 MHz)



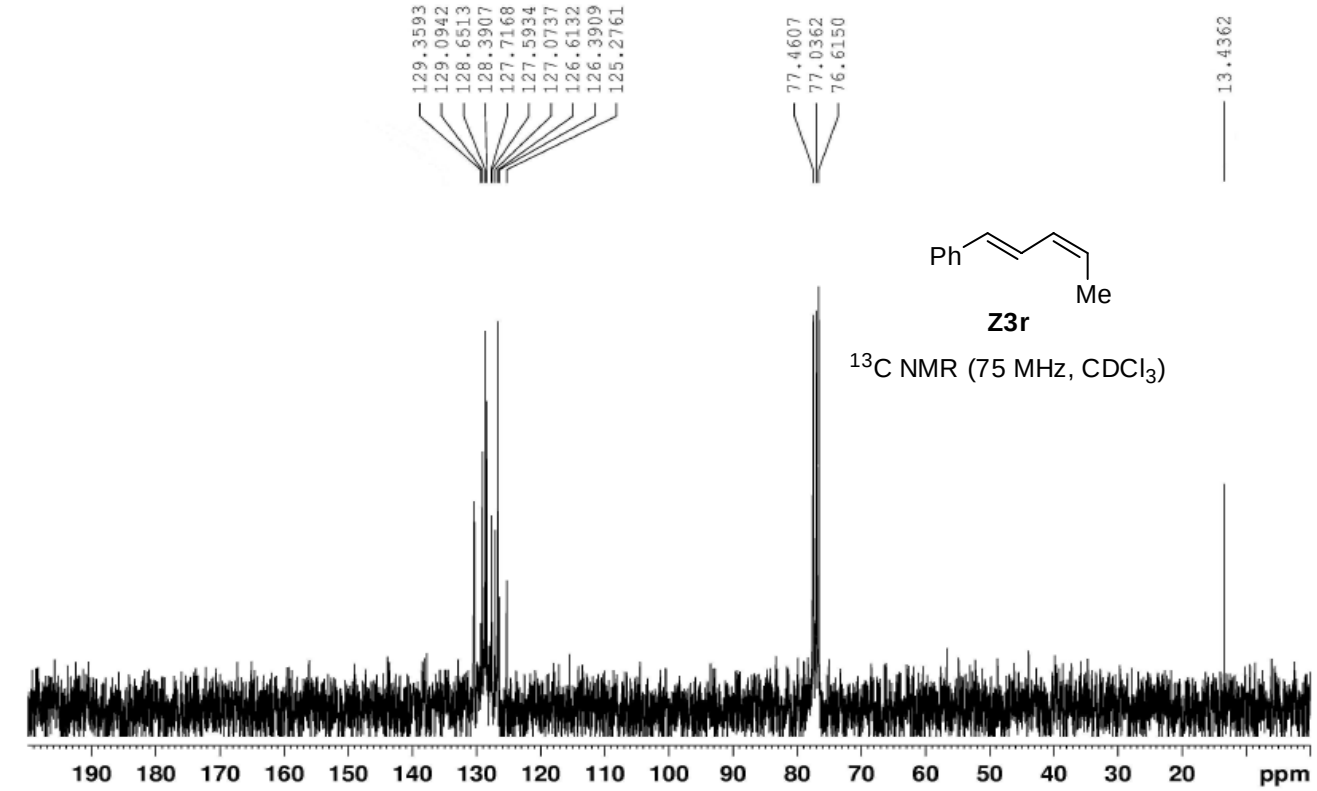
Z3q

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



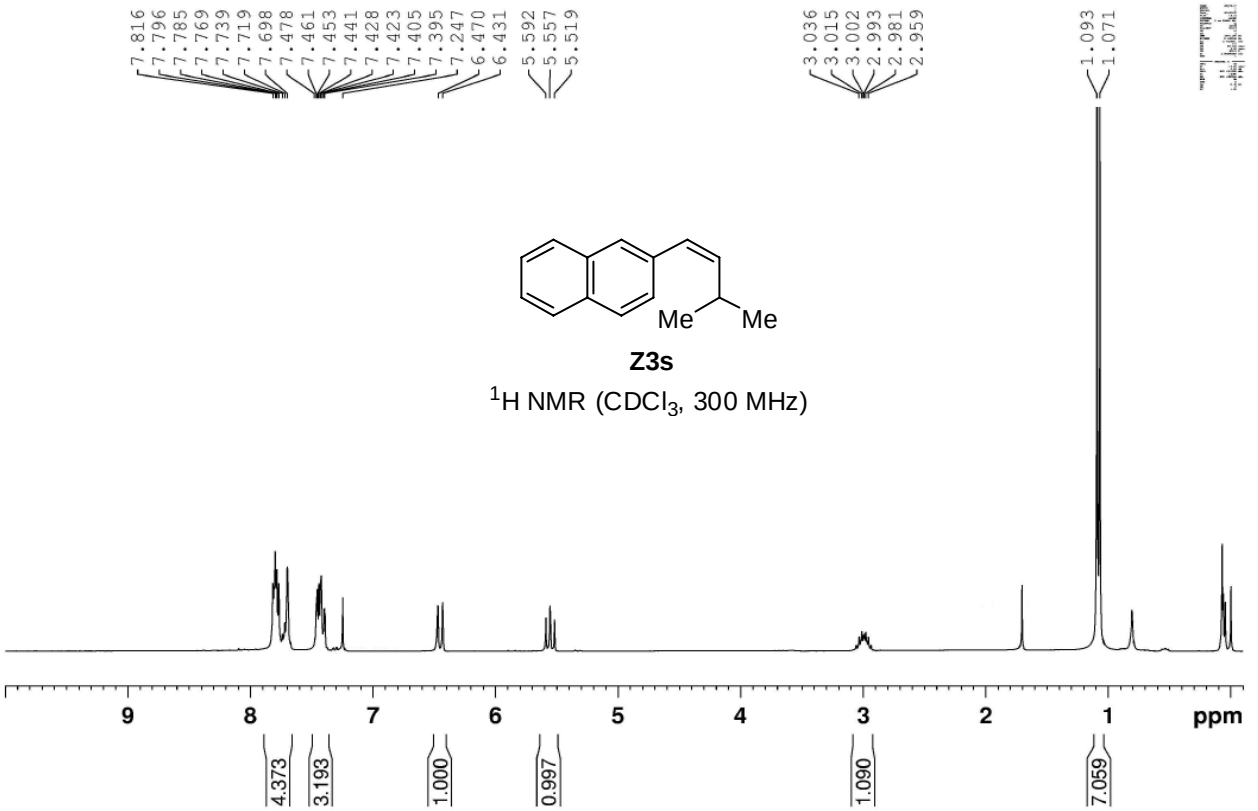
Z3r

^{1}H NMR ($CDCl_3$, 300 MHz)



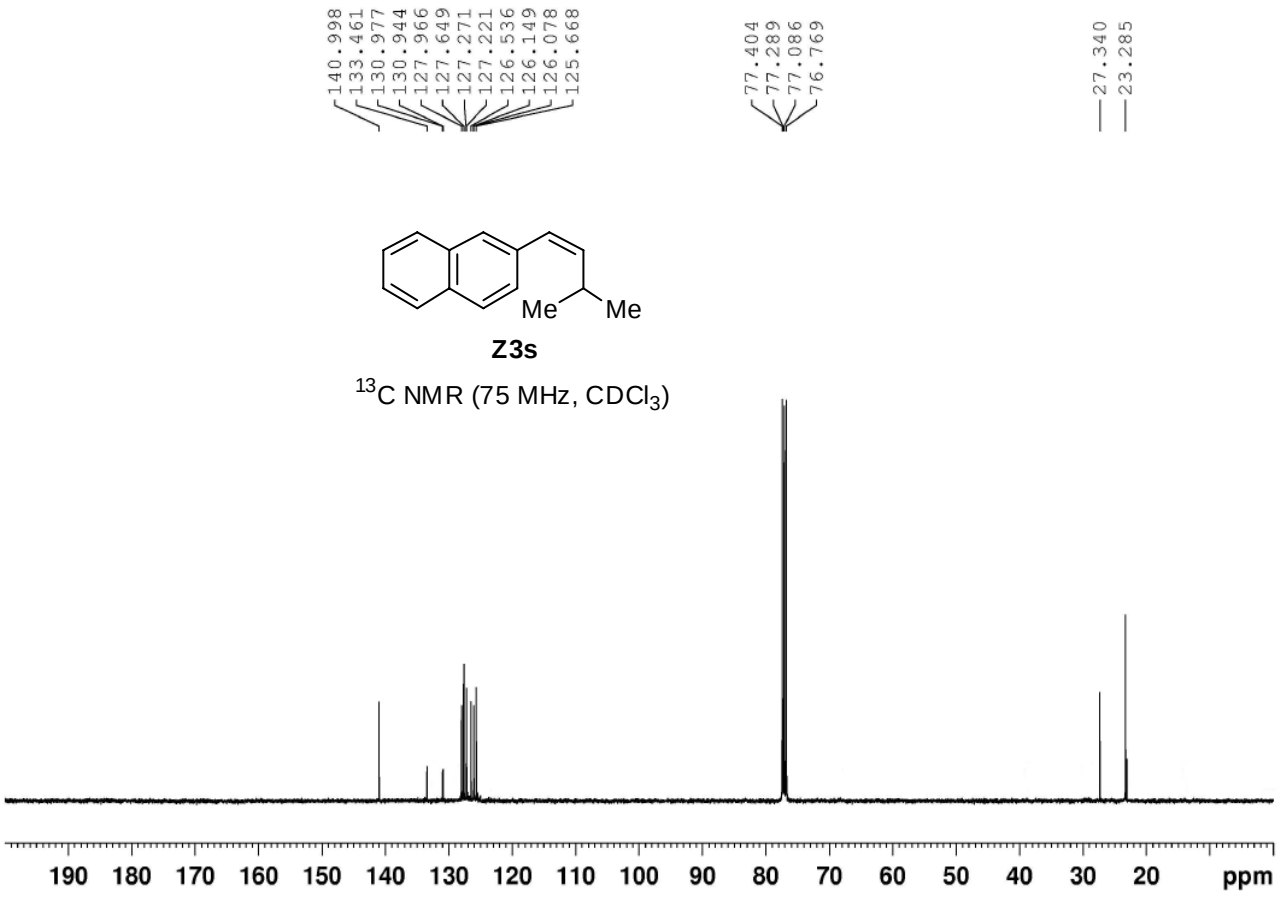
Z3r

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



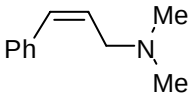
Z3s

^{1}H NMR ($CDCl_3$, 300 MHz)



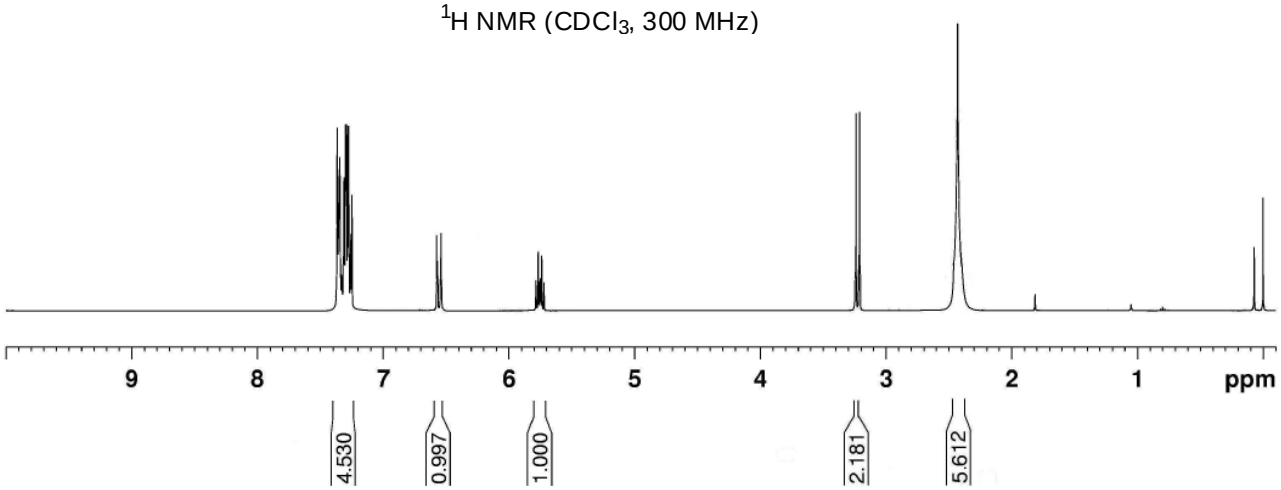
Z3s

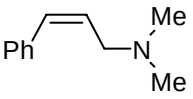
^{13}C NMR (75 MHz, $CDCl_3$)



Z3t

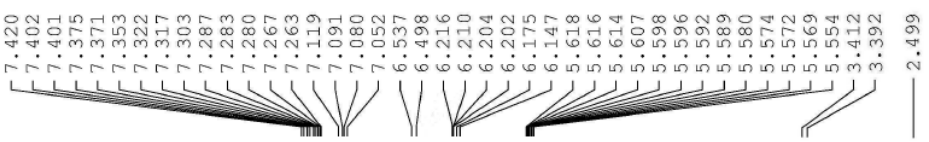
^{1}H NMR ($CDCl_3$, 300 MHz)

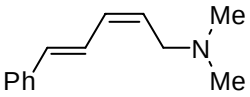




Z3t

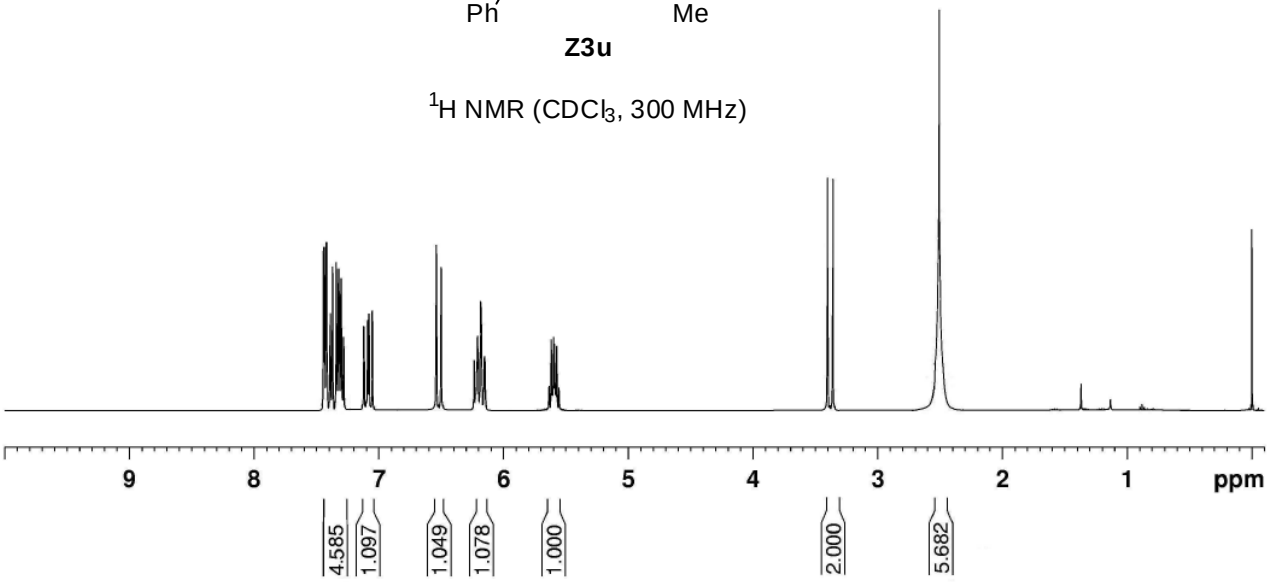
^{13}C NMR (75 MHz, $CDCl_3$)

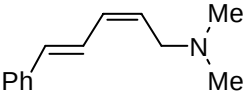




Z3u

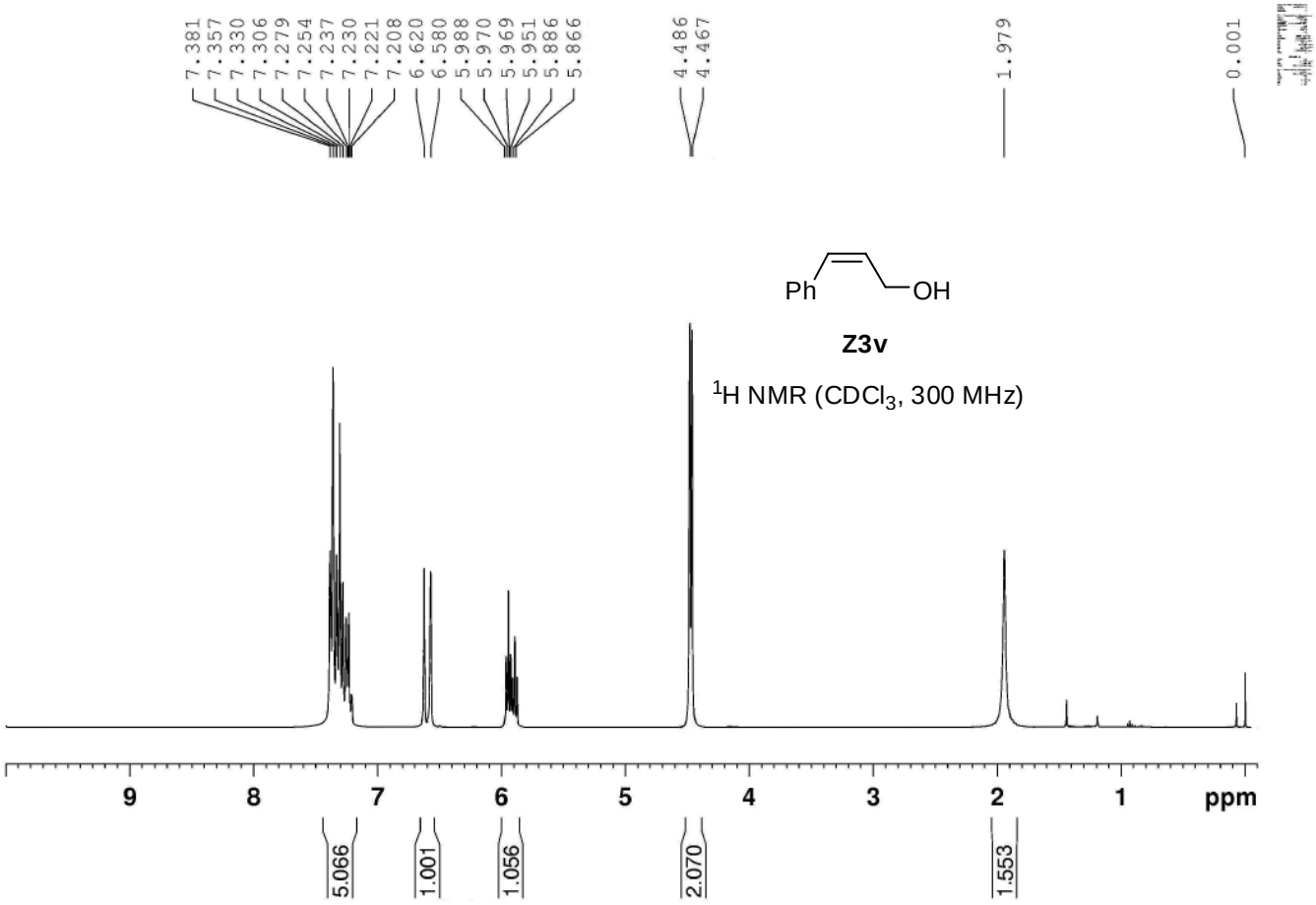
^{1}H NMR ($CDCl_3$, 300 MHz)





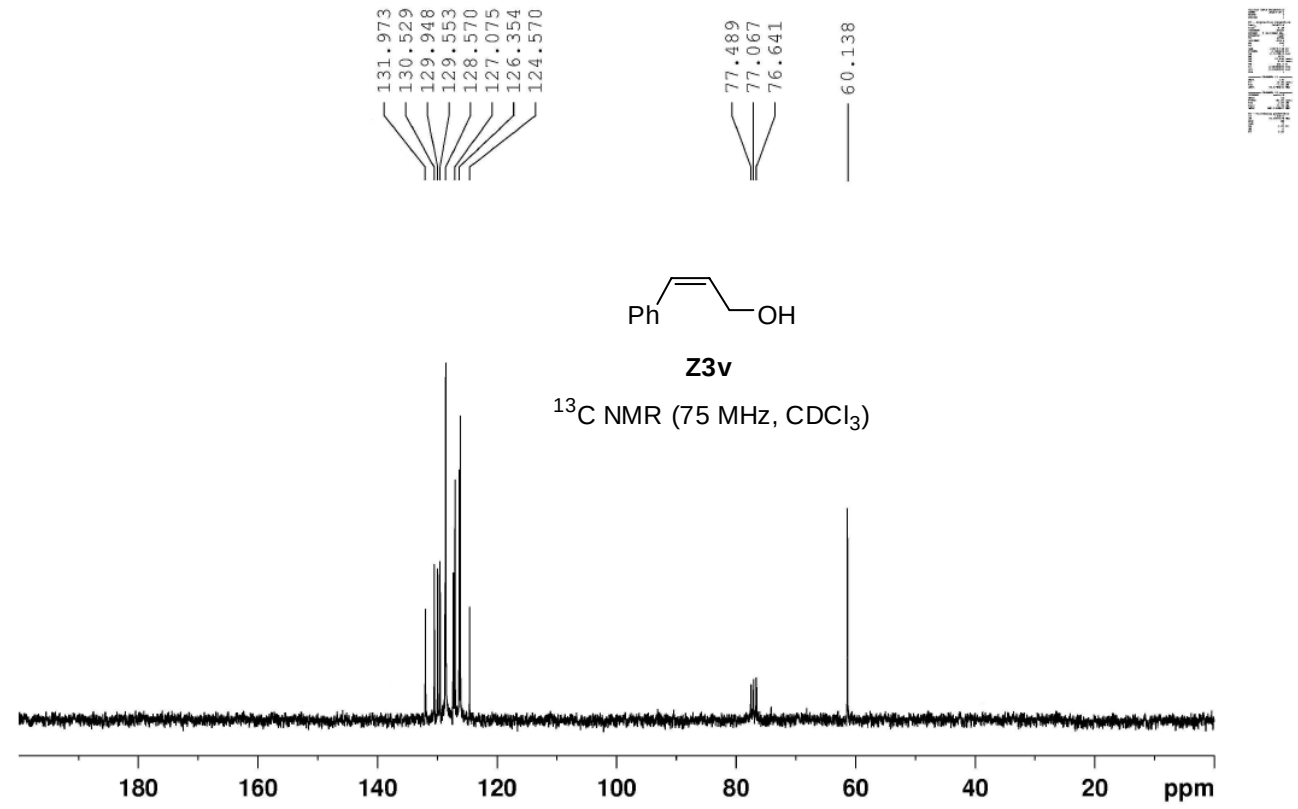
Z3u

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



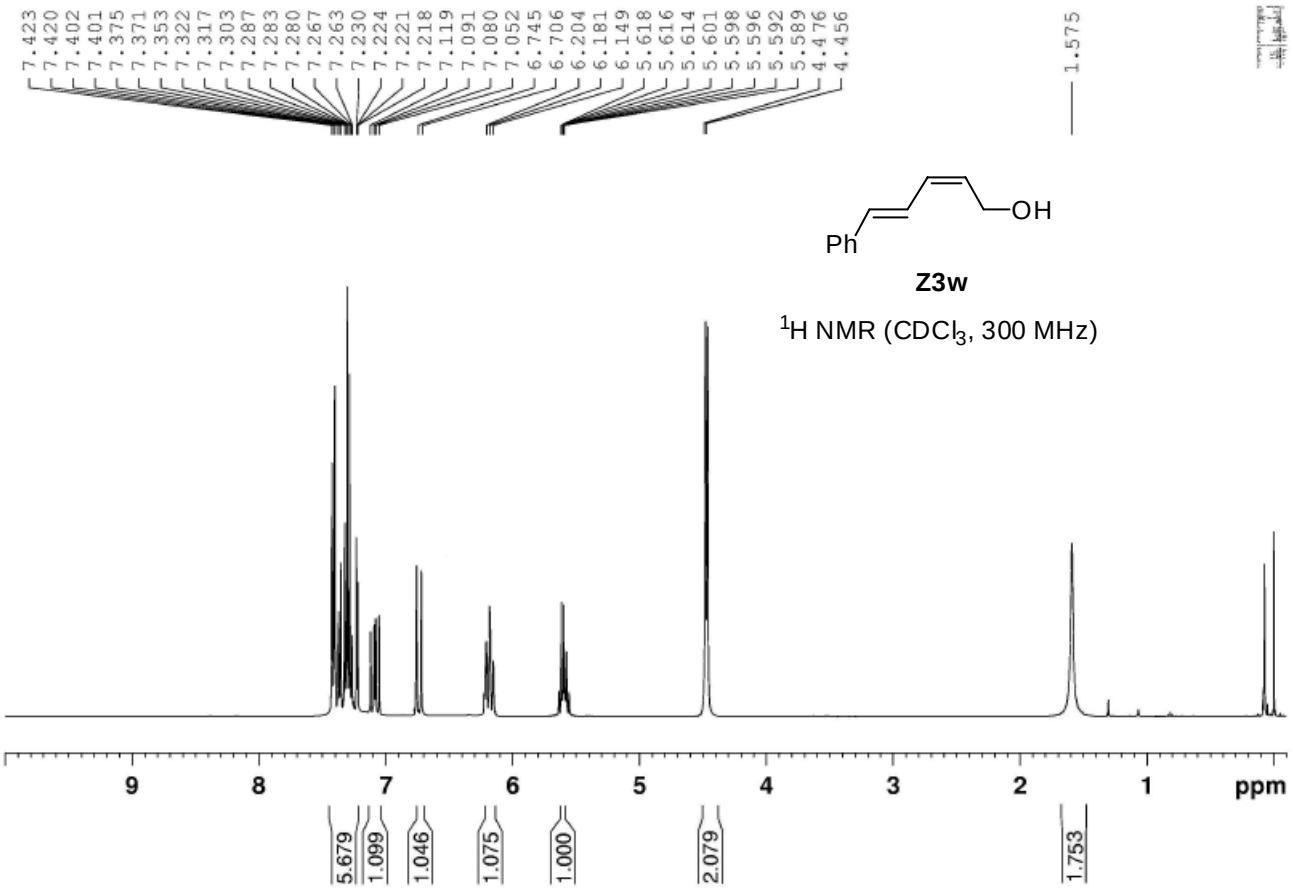
Z3v

^{1}H NMR ($CDCl_3$, 300 MHz)



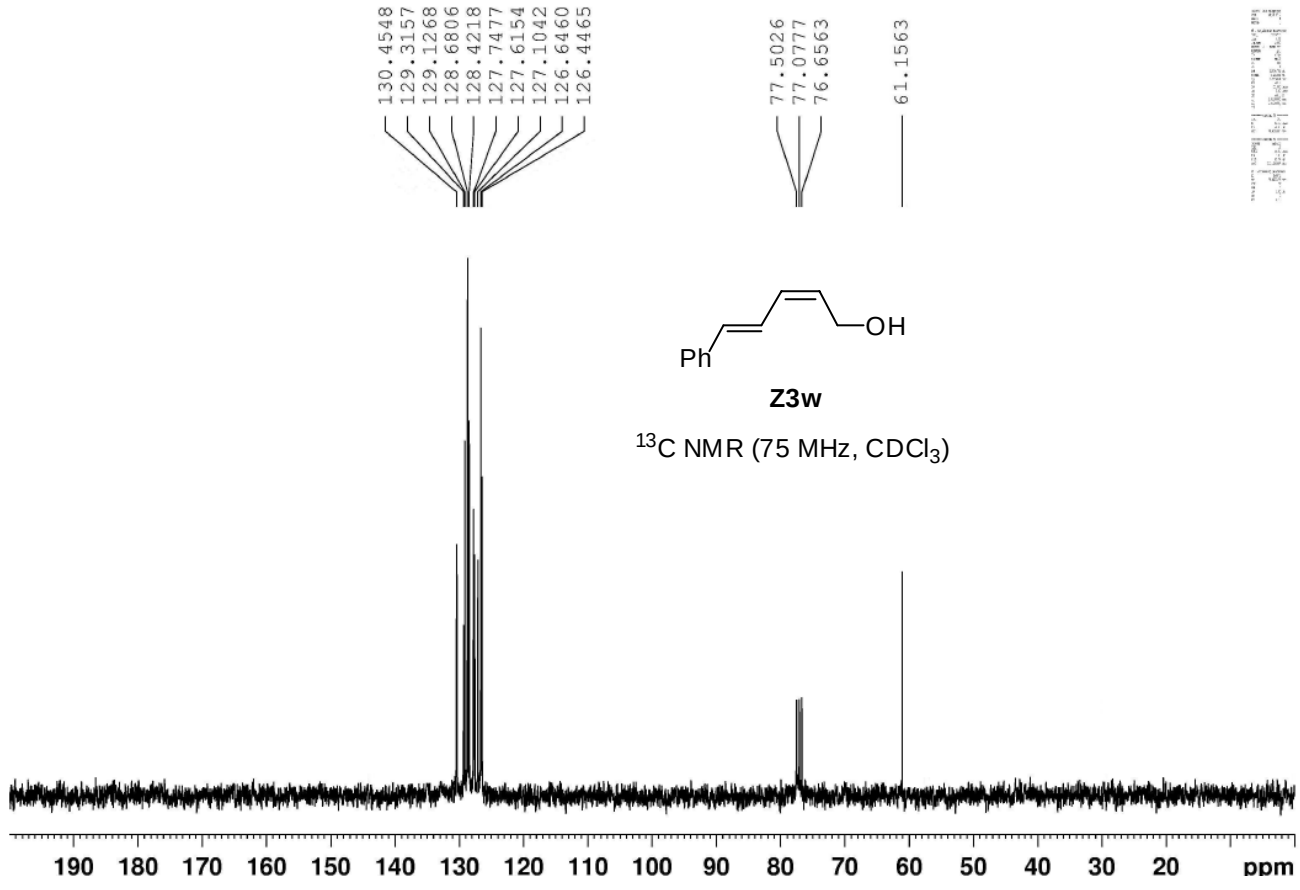
Z3v

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



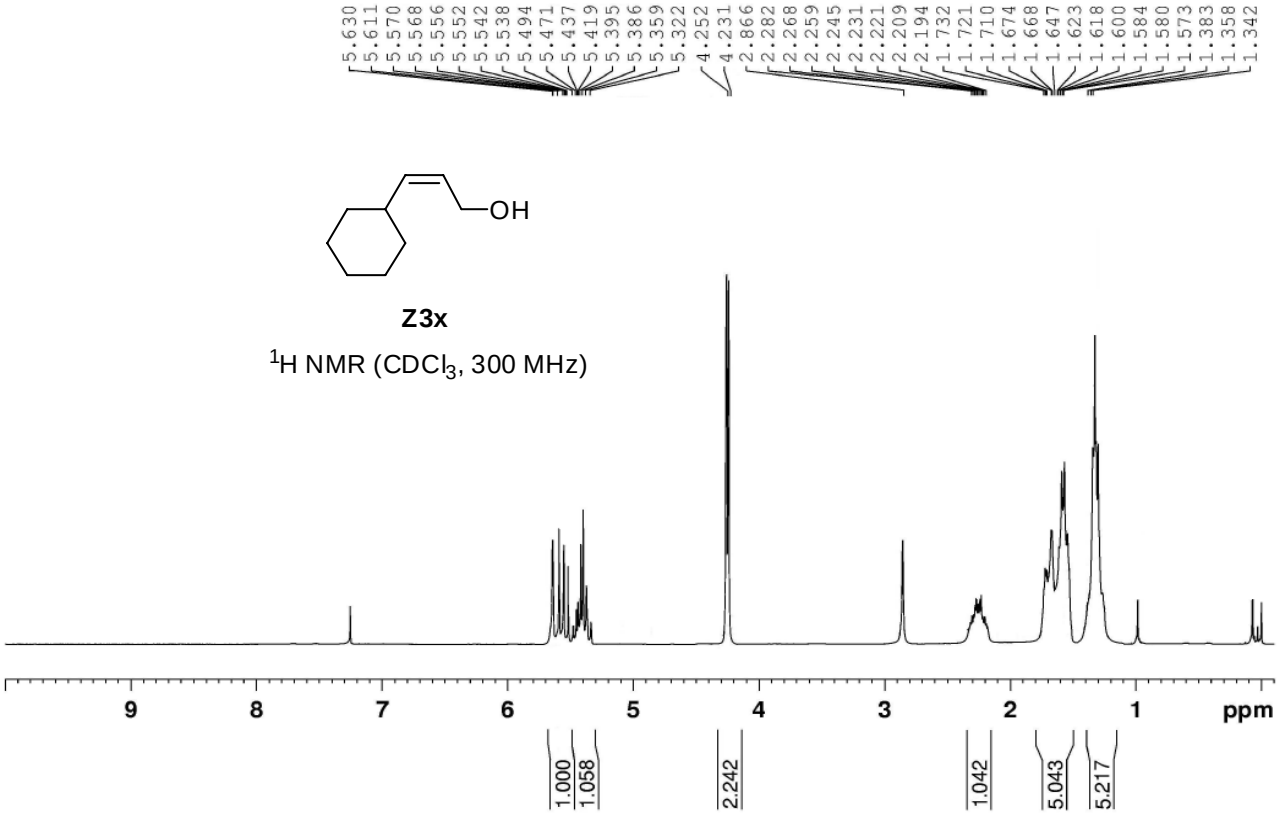
Z3w

^{1}H NMR ($CDCl_3$, 300 MHz)



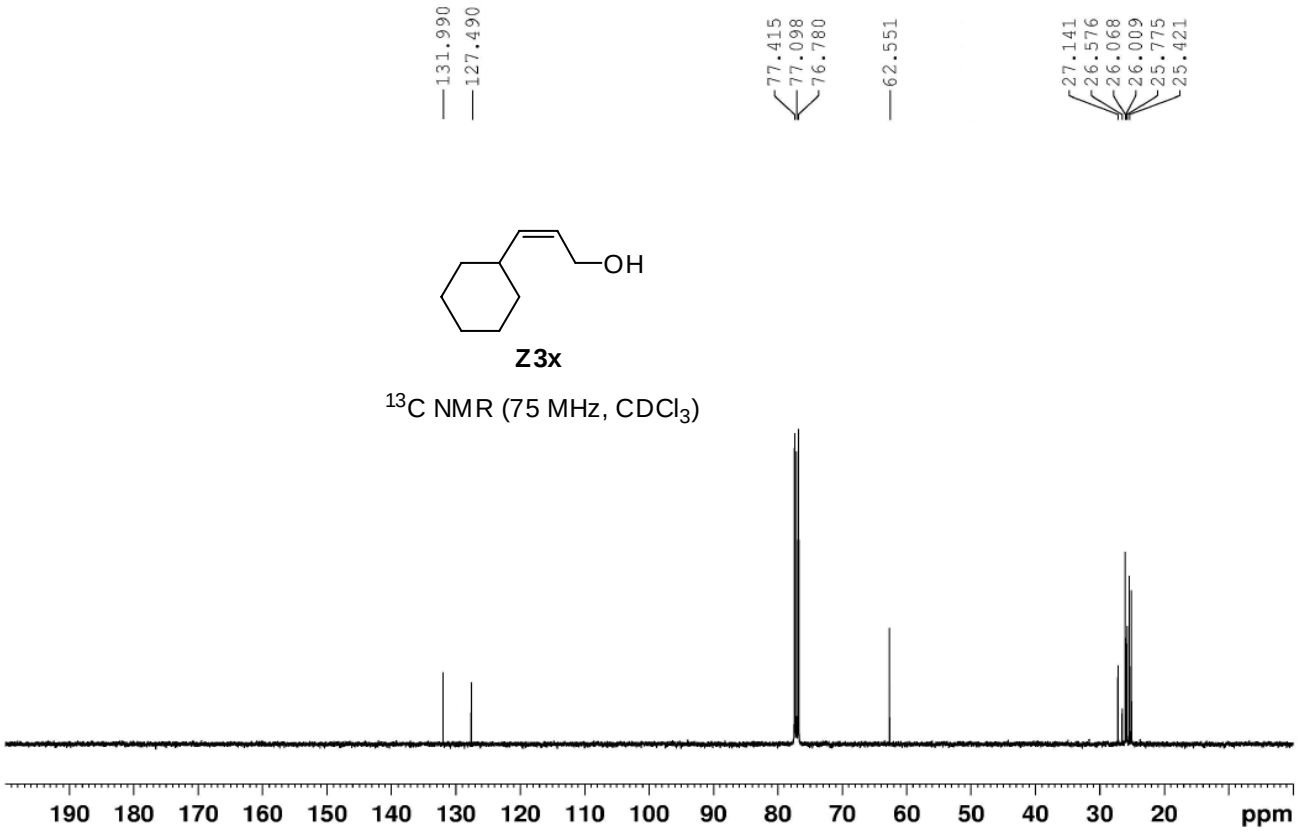
Z3w

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



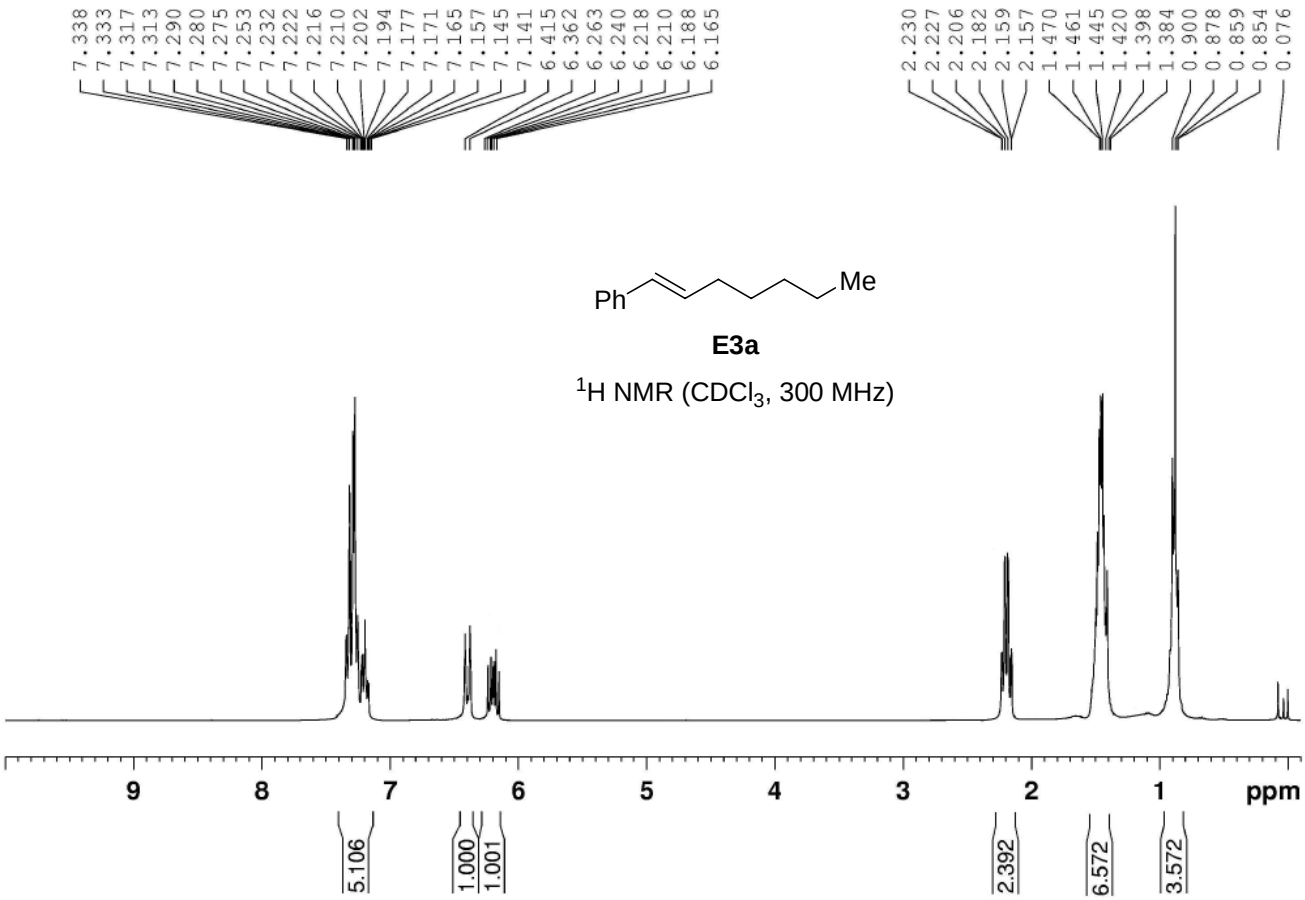
Z3x

^{1}H NMR ($CDCl_3$, 300 MHz)



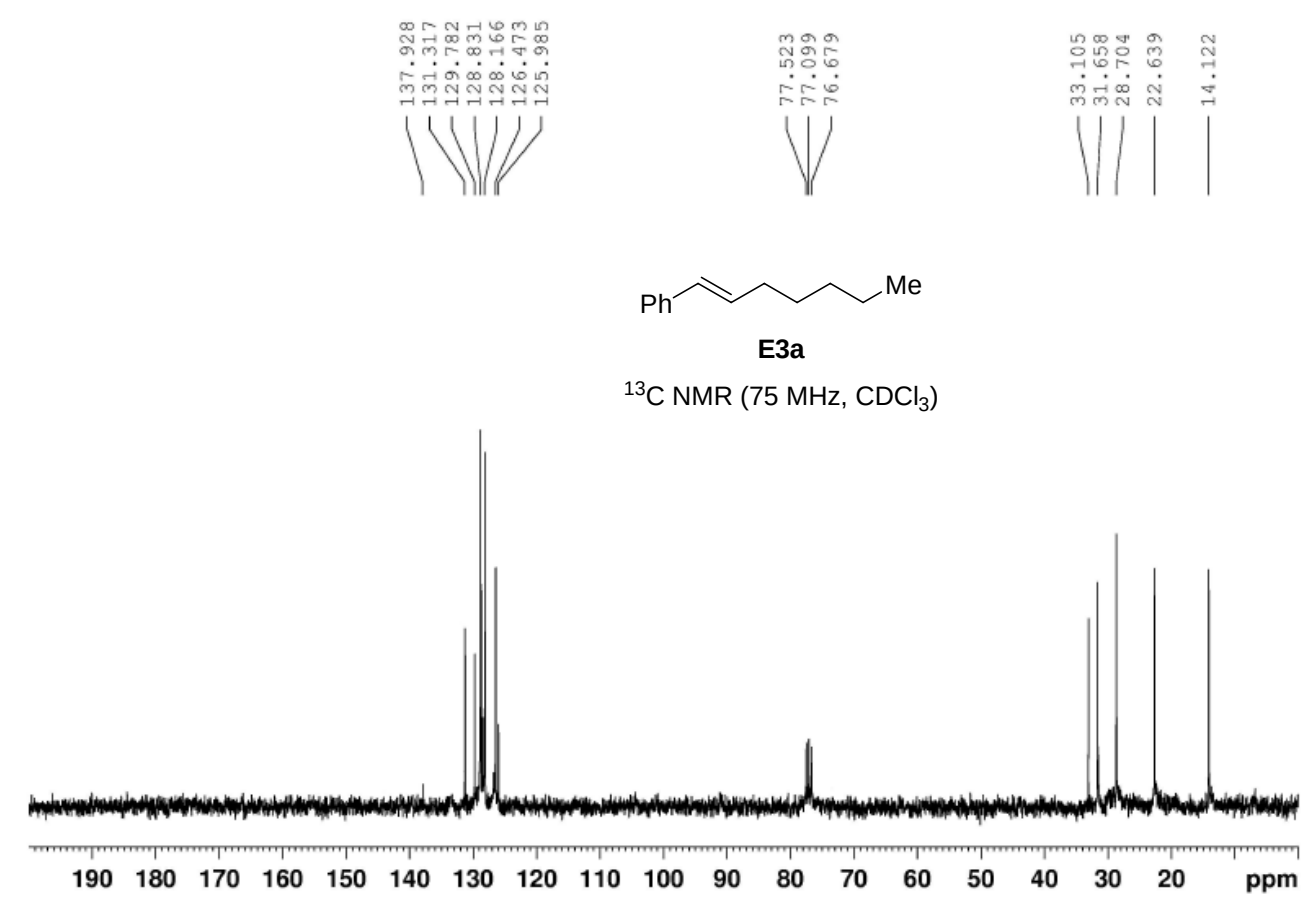
Z3x

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



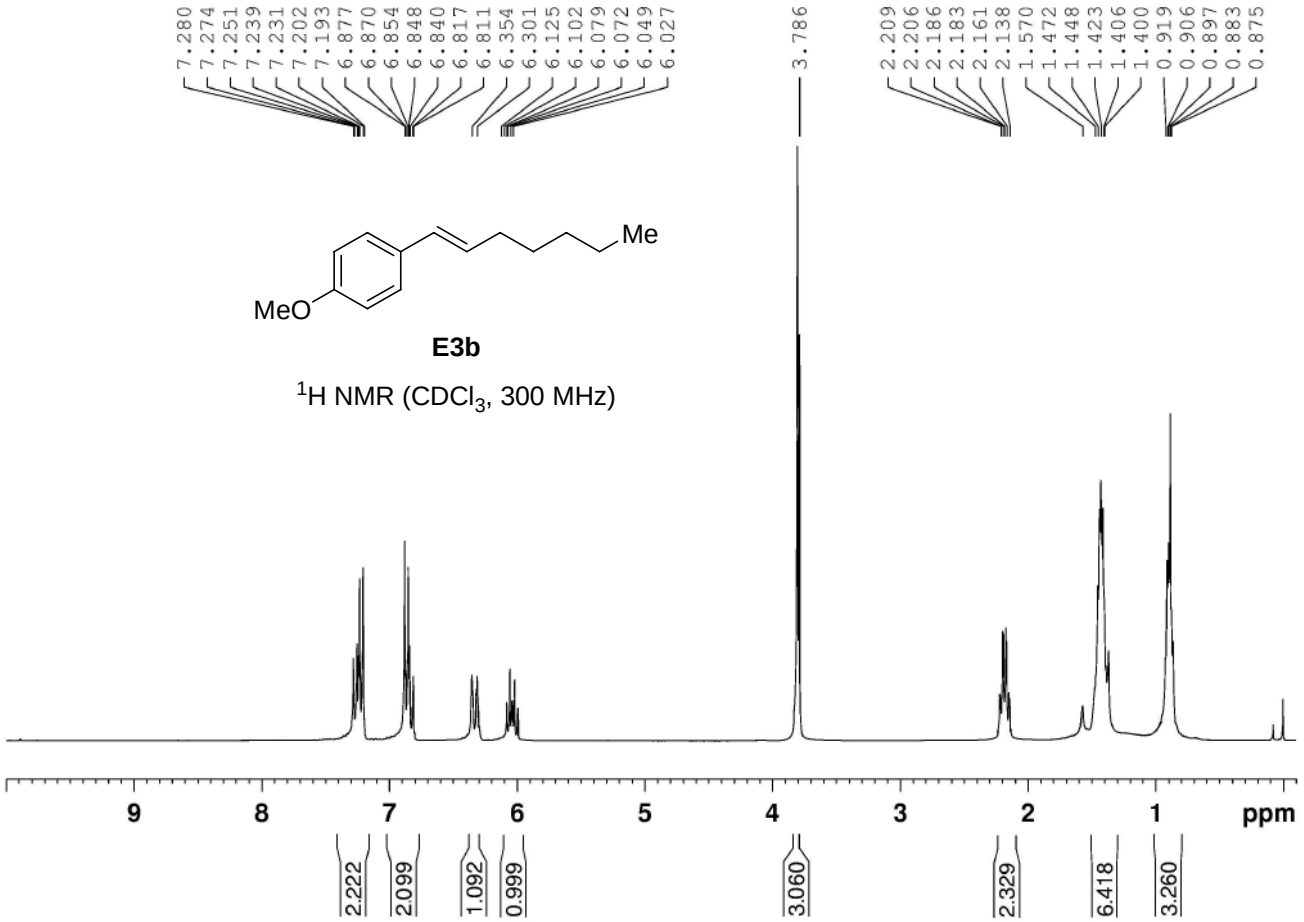
E3a

^{1}H NMR ($CDCl_3$, 300 MHz)



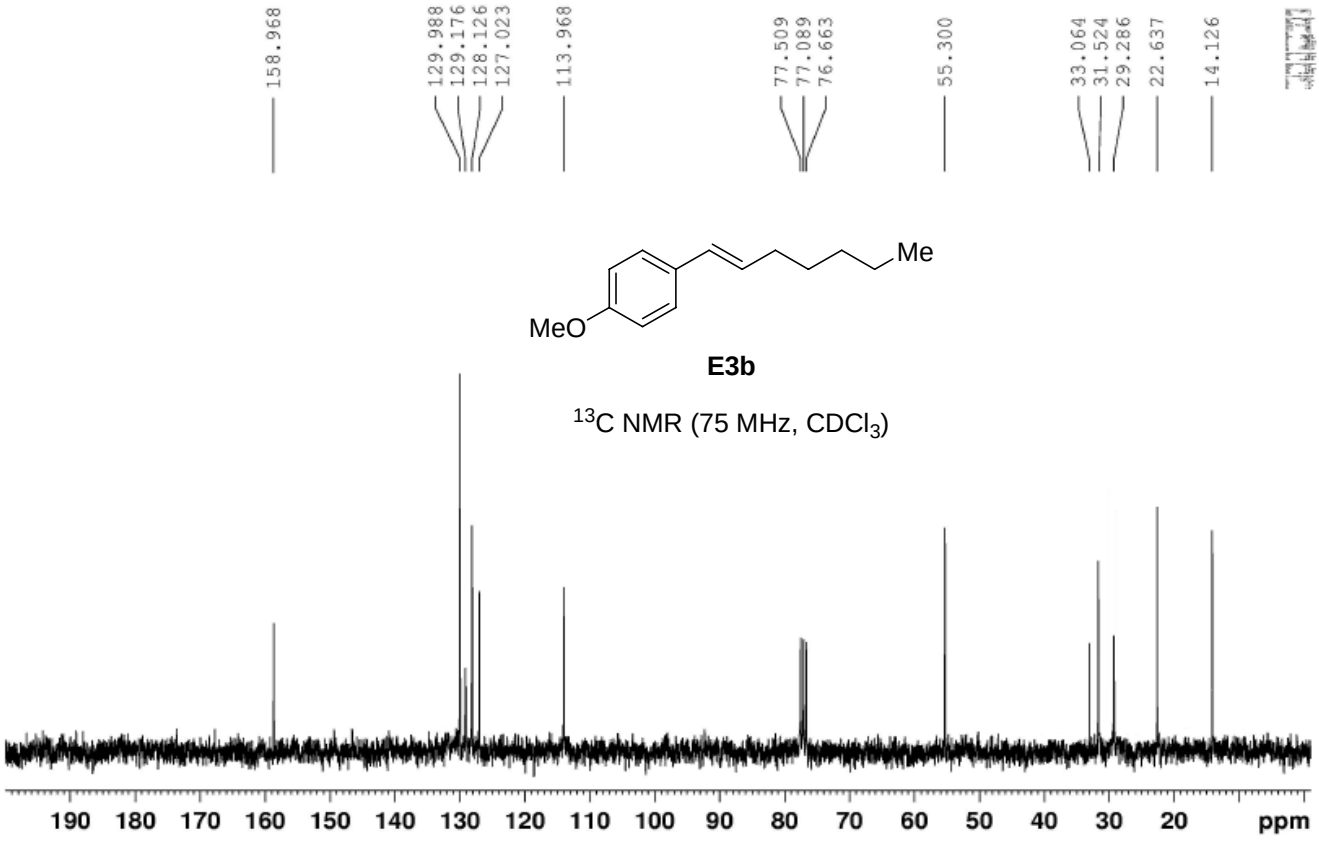
E3a

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



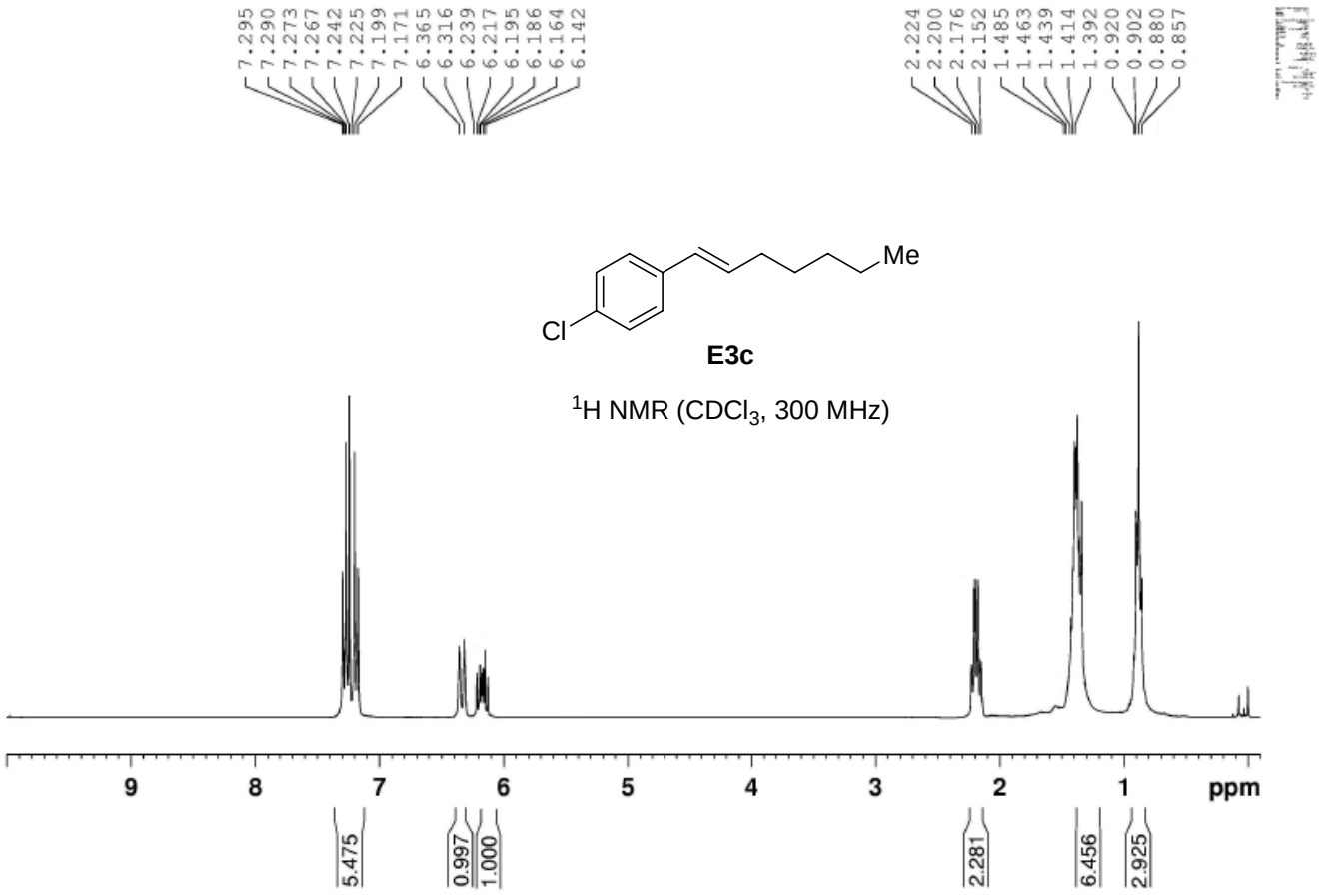
E3b

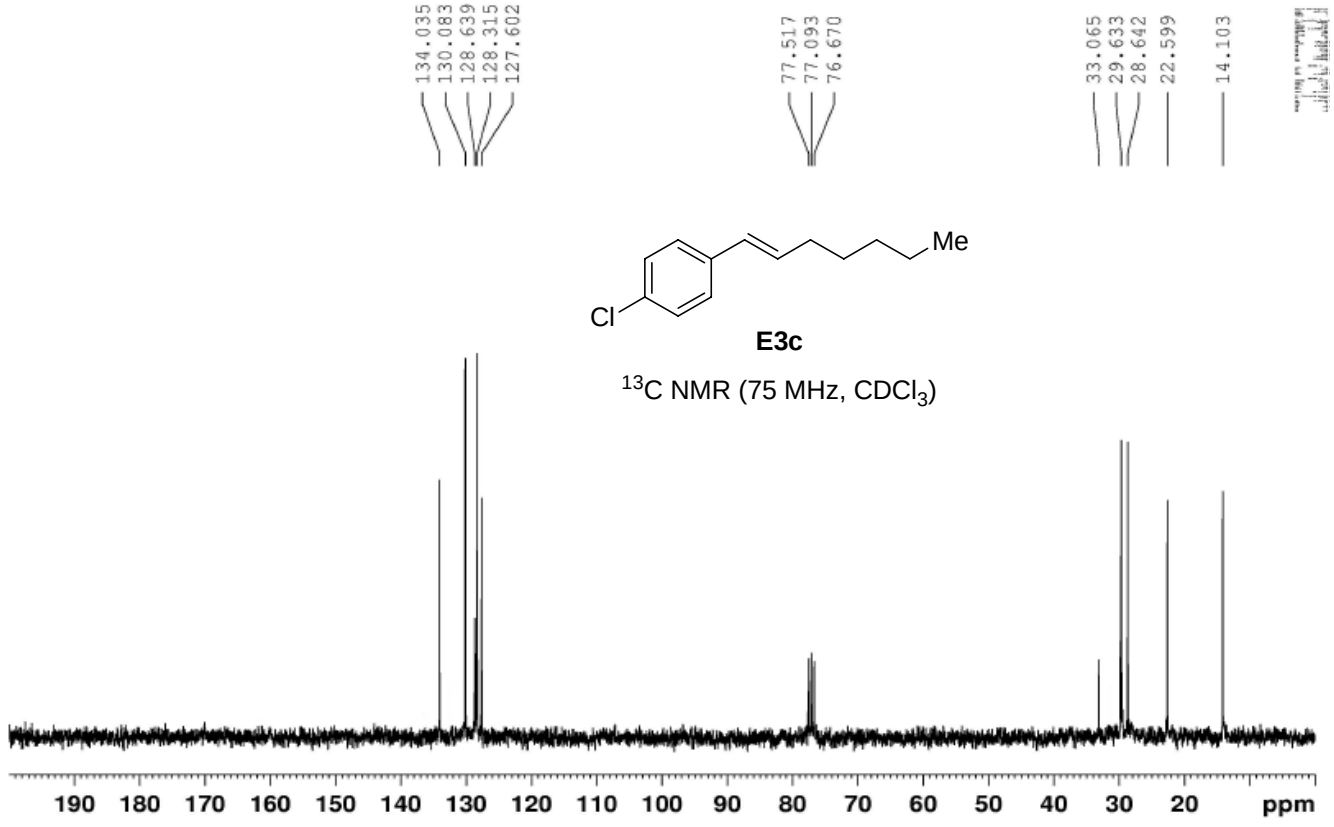
^{1}H NMR ($CDCl_3$, 300 MHz)

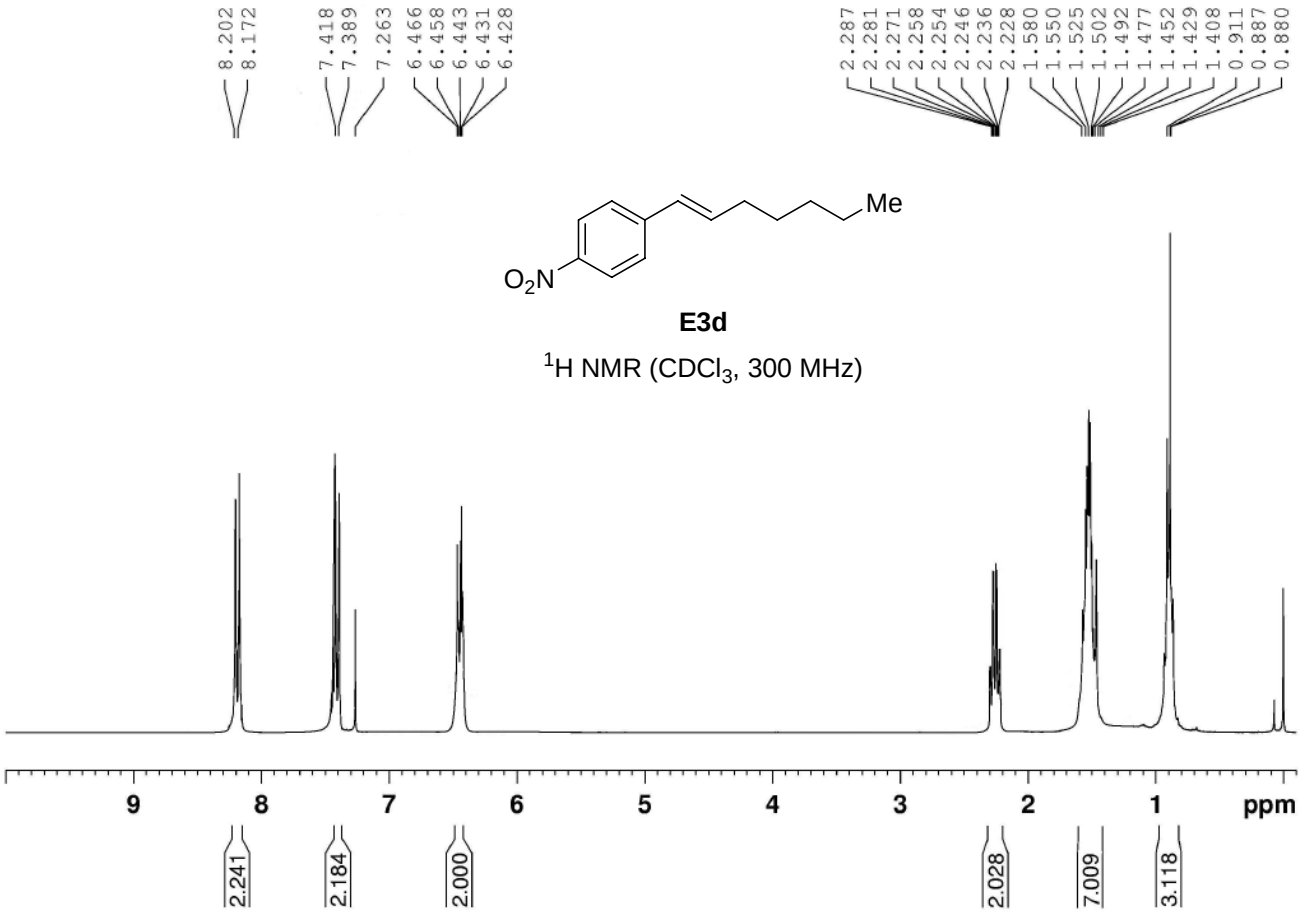


E3b

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

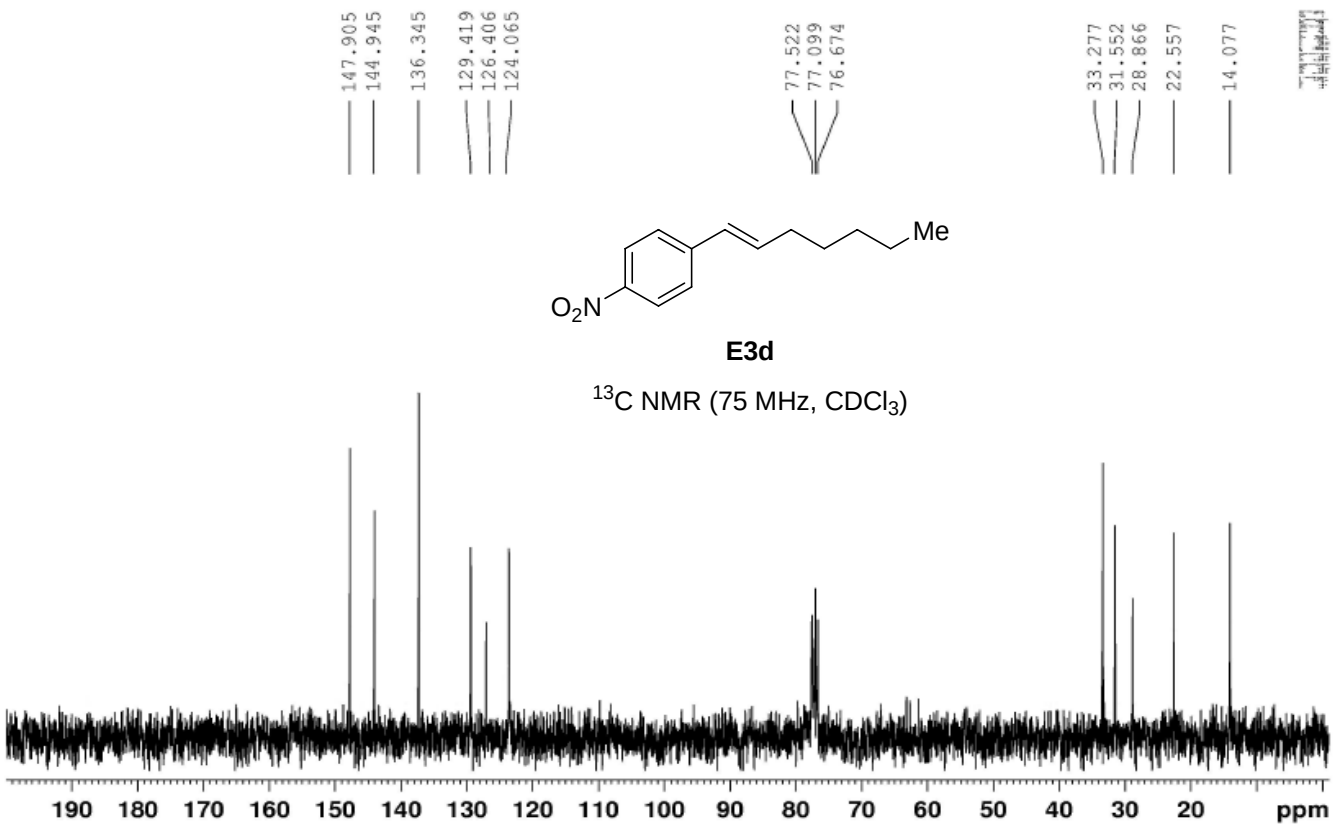

7.295
7.290
7.273
7.267
7.242
7.225
7.199
7.171
6.365
6.316
6.239
6.217
6.195
6.186
6.164
6.142
2.224
2.200
2.176
2.152
1.485
1.463
1.439
1.414
1.392
0.920
0.902
0.880
0.857
Me
Cl
E3c
^{1}H NMR ($CDCl_3$, 300 MHz)
9
8
7
6
5
4
3
2
1
ppm
5.475
0.997
1.000
2.281
6.456
2.925


134.035
130.083
128.639
128.315
127.602
77.517
77.093
76.670
33.065
29.633
28.642
22.599
14.103
Me
Cl
E3c
^{13}C NMR (75 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



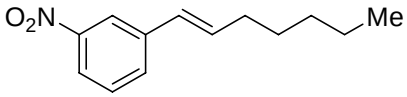
E3d

^{1}H NMR ($CDCl_3$, 300 MHz)



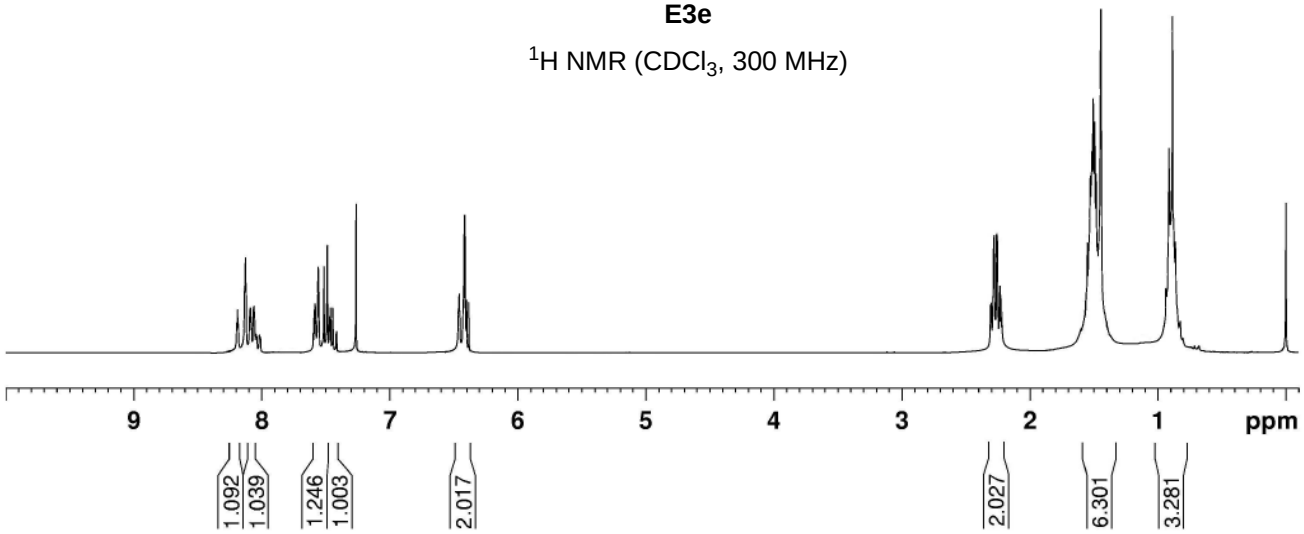
E3d

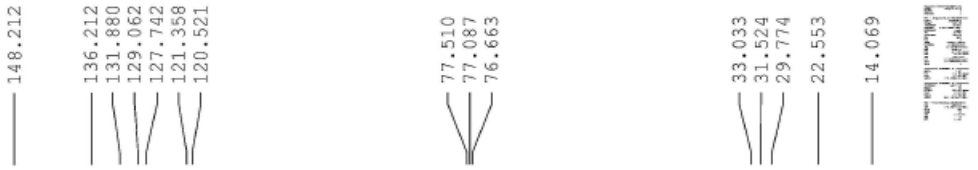
^{13}C NMR (75 MHz, $CDCl_3$)

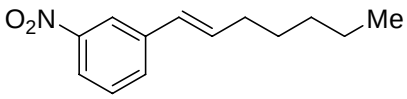


E3e

^{1}H NMR ($CDCl_3$, 300 MHz)

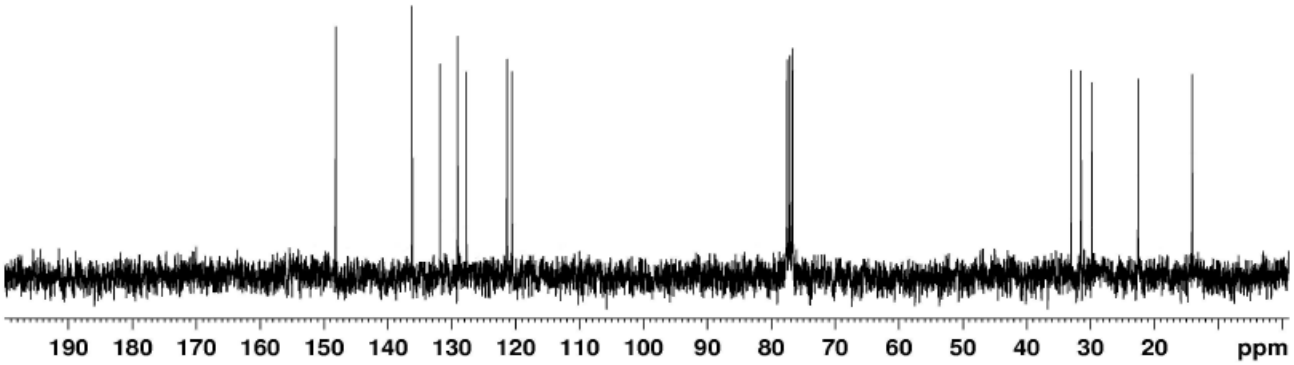


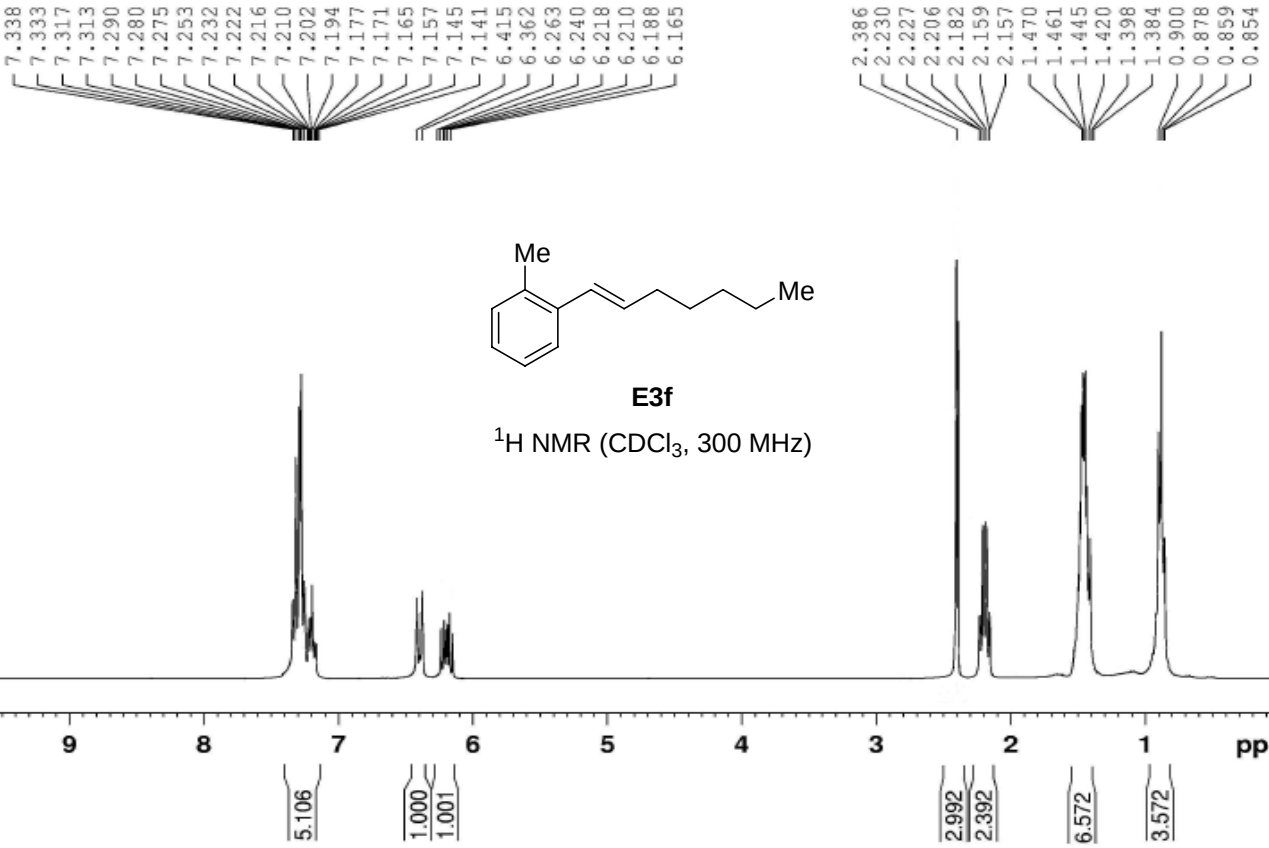




E3e

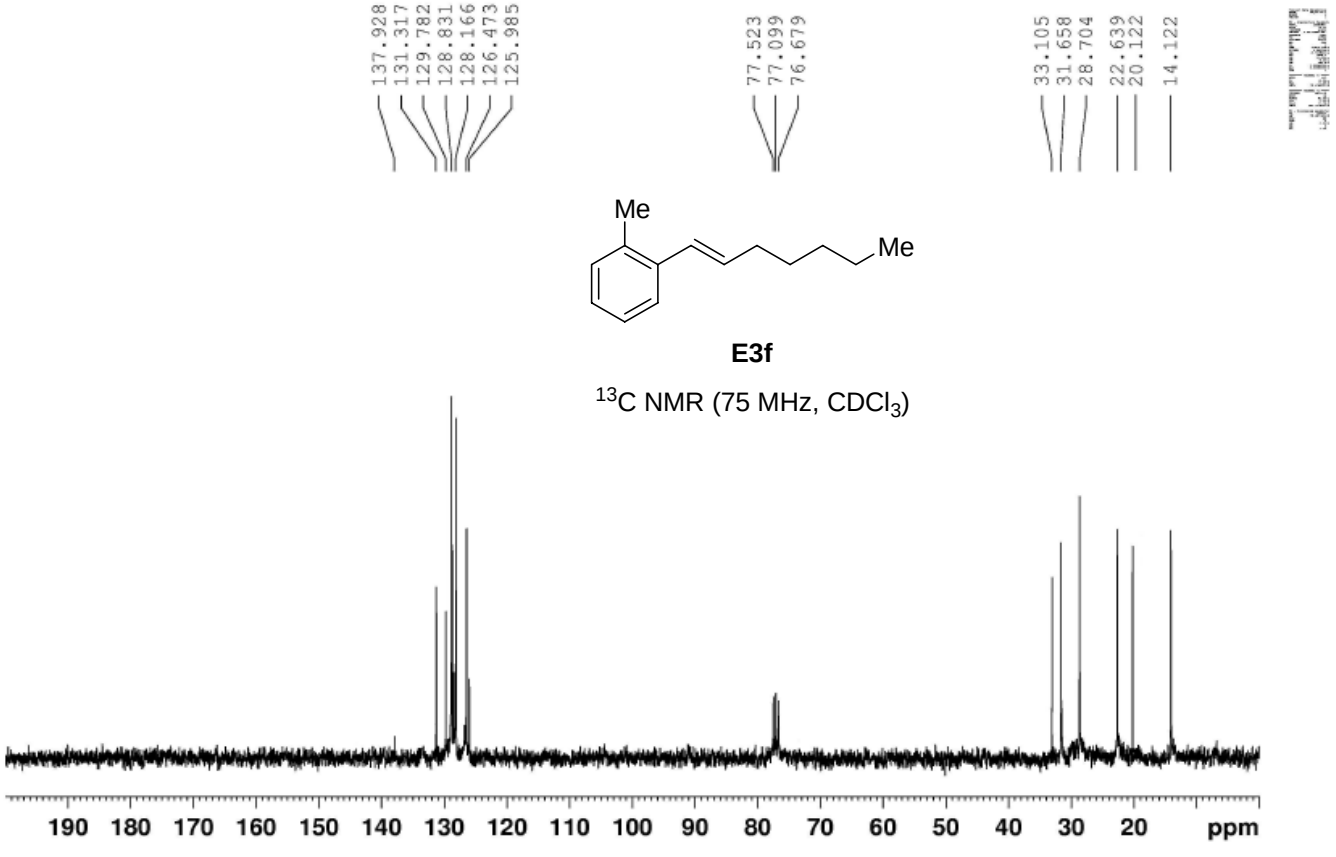
^{13}C NMR (75 MHz, $CDCl_3$)





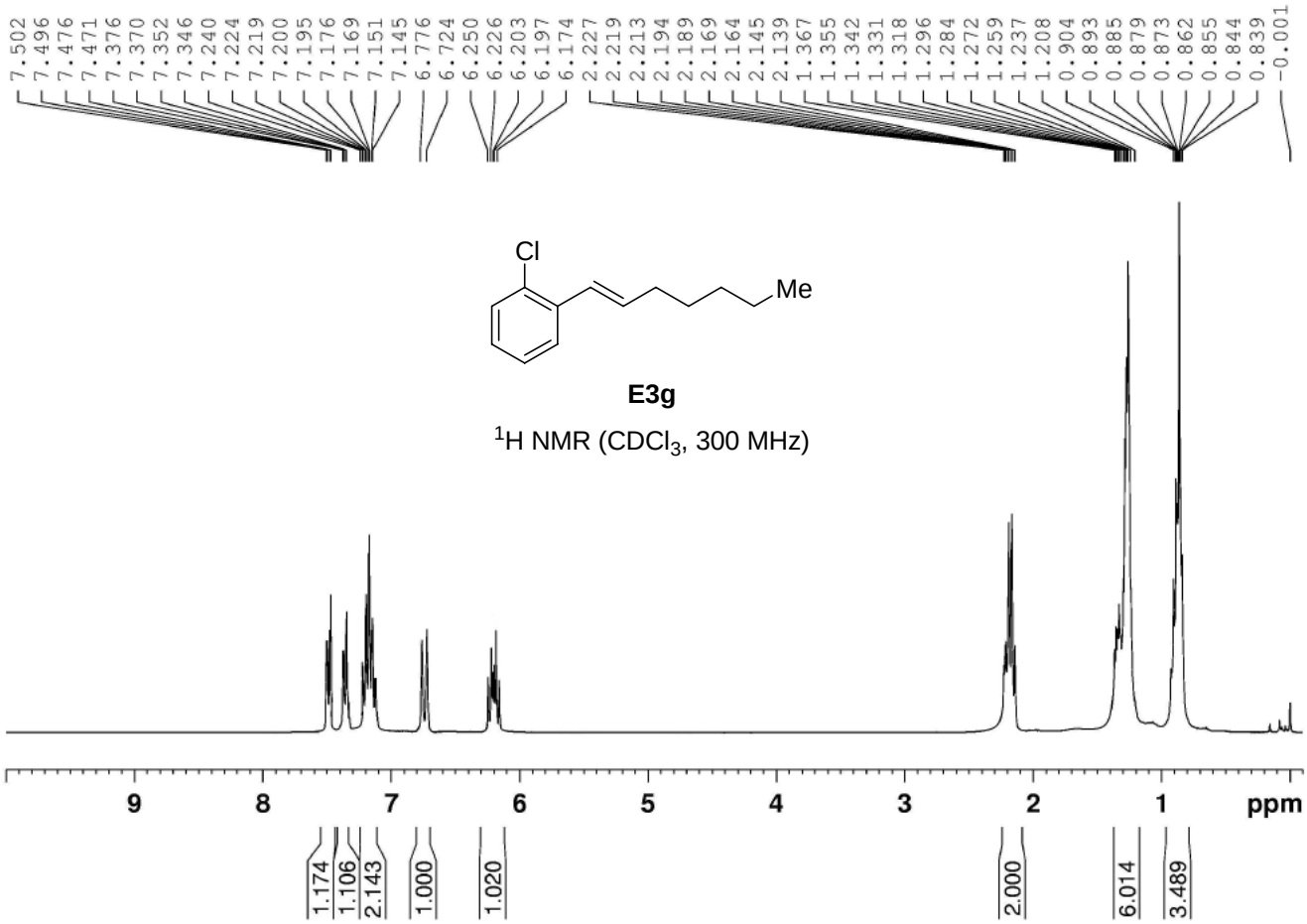
E3f

^{1}H NMR ($CDCl_3$, 300 MHz)



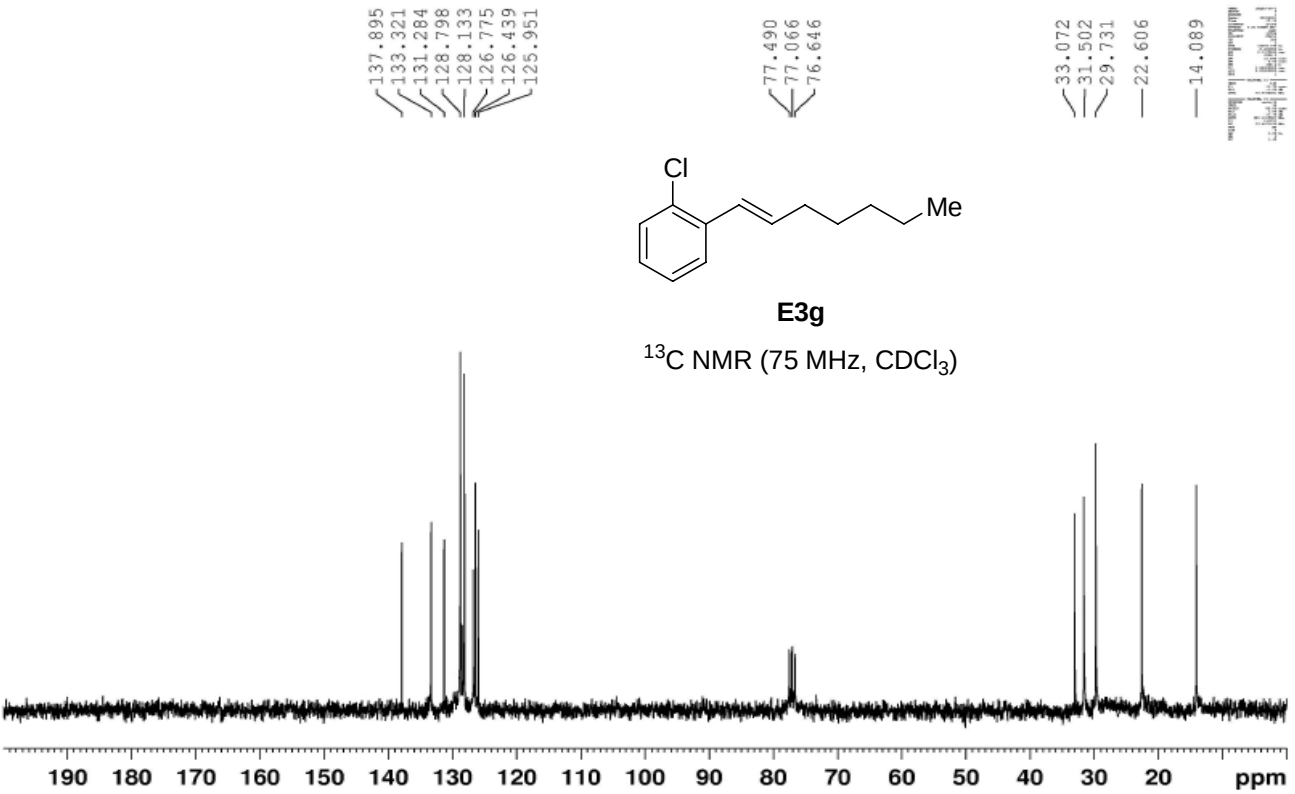
E3f

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



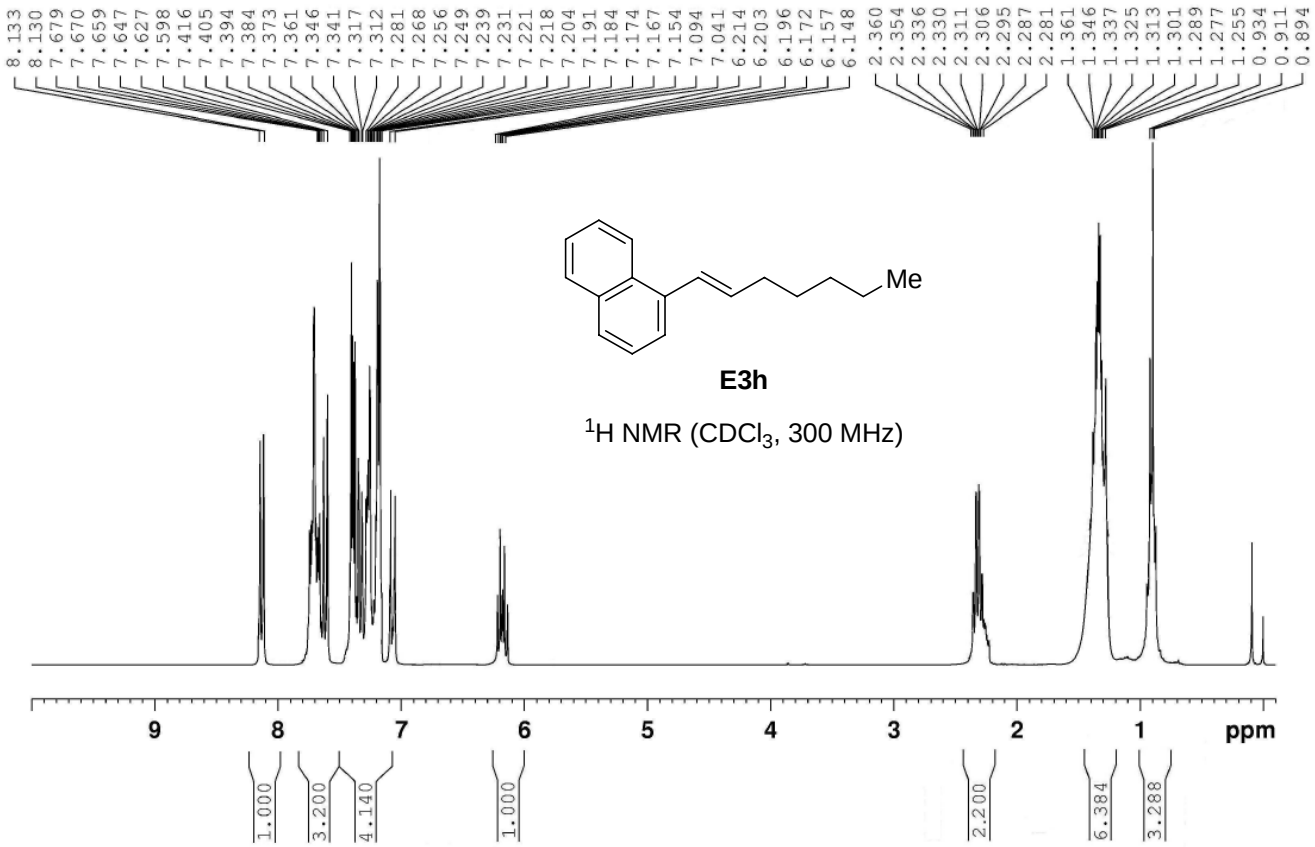
E3g

^{1}H NMR ($CDCl_3$, 300 MHz)



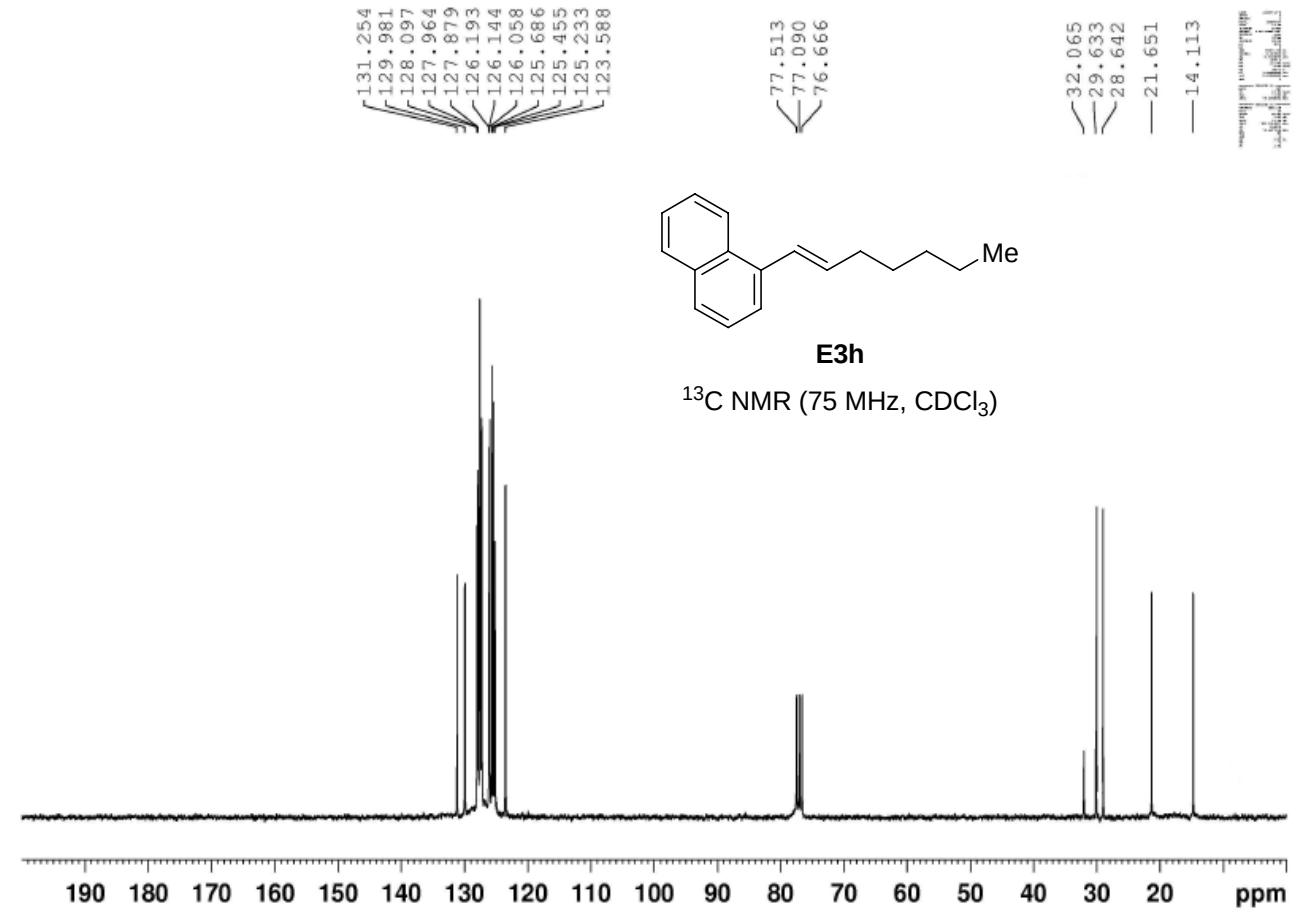
E3g

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



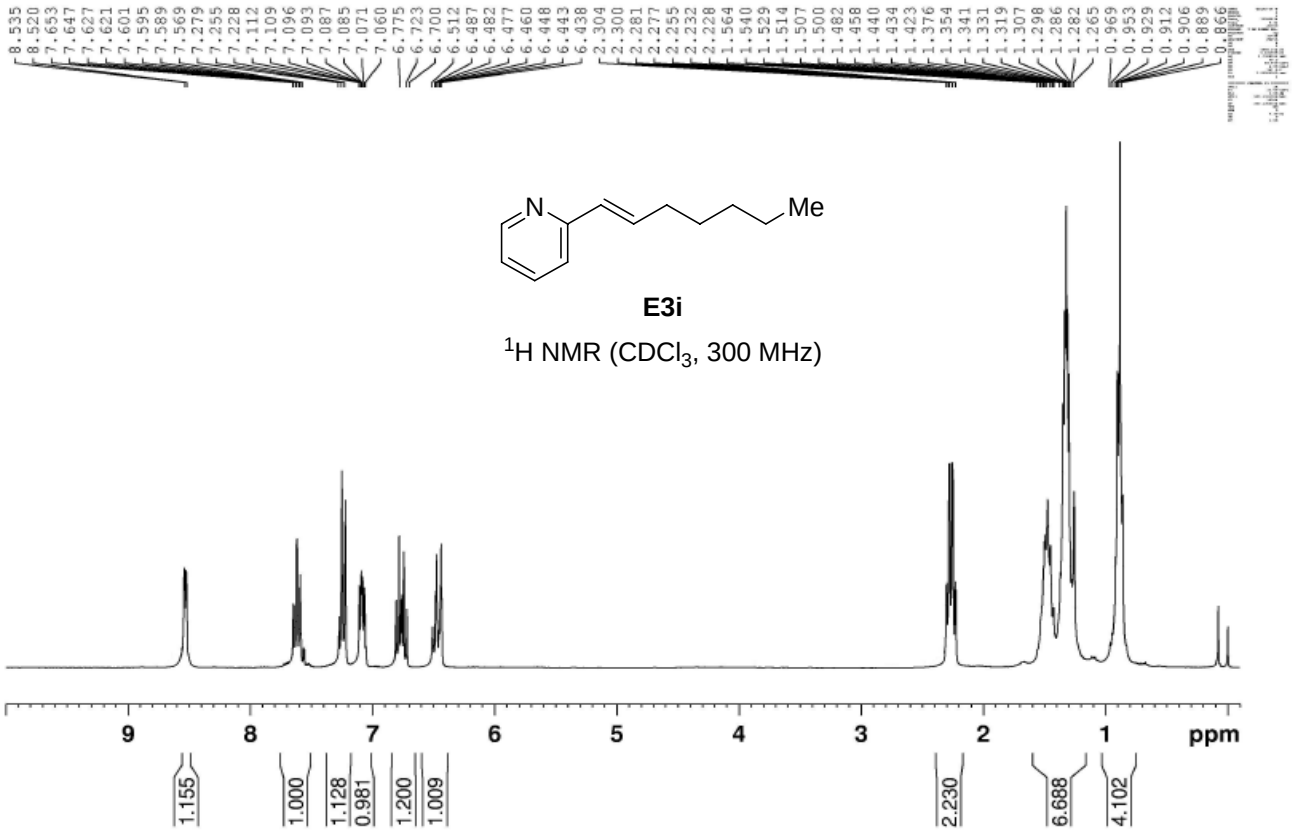
E3h

^{1}H NMR ($CDCl_3$, 300 MHz)



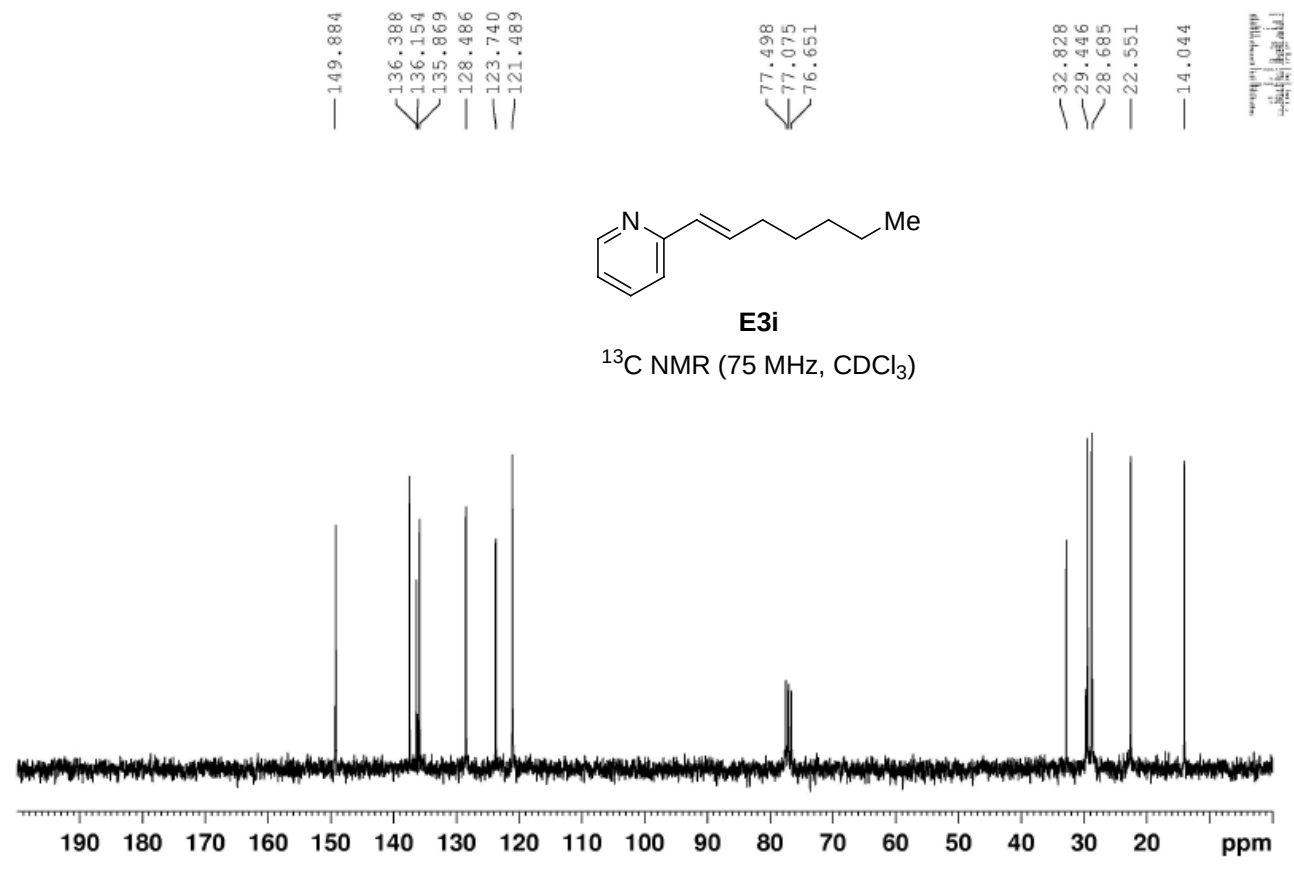
E3h

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



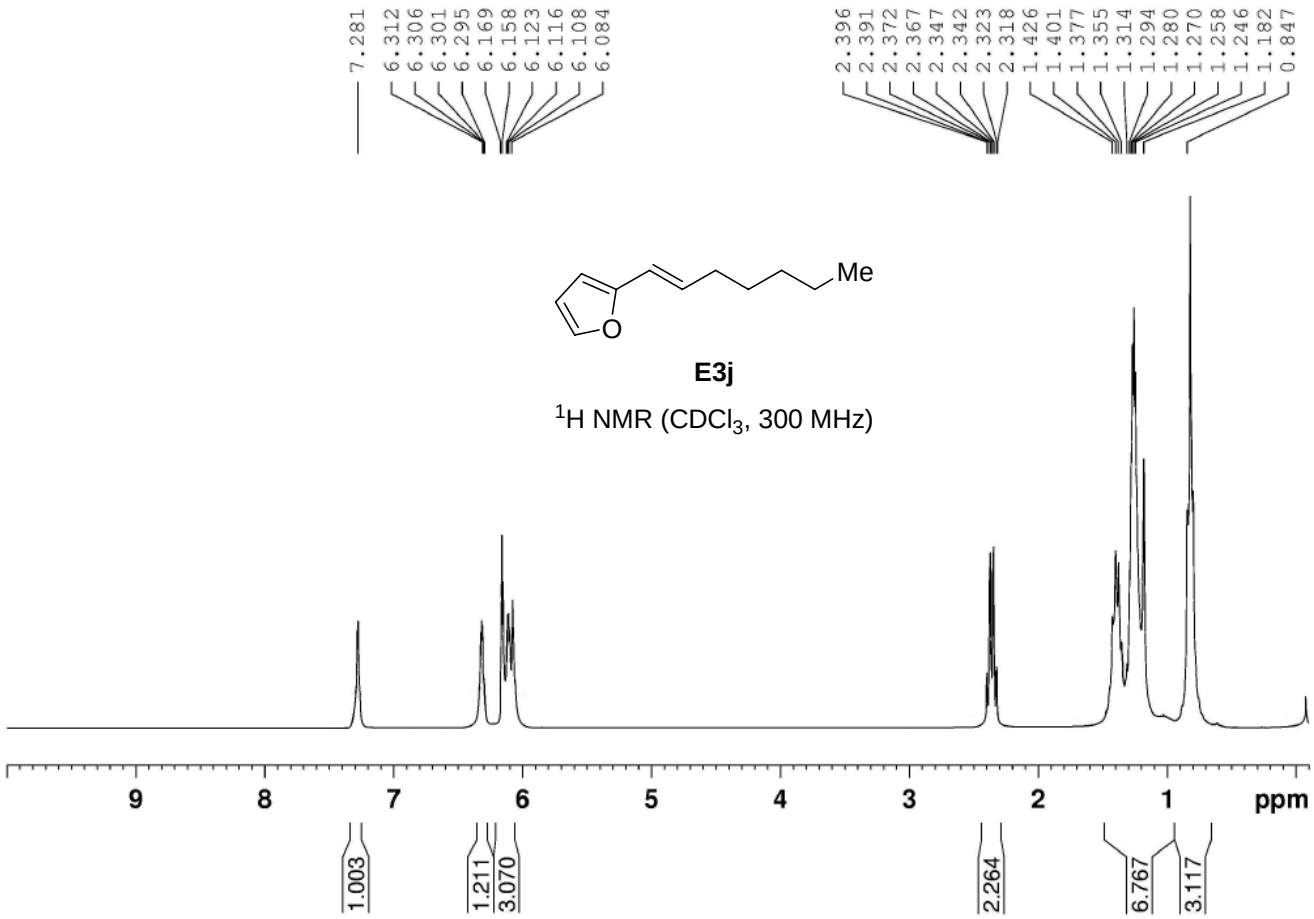
E3i

^{1}H NMR ($CDCl_3$, 300 MHz)



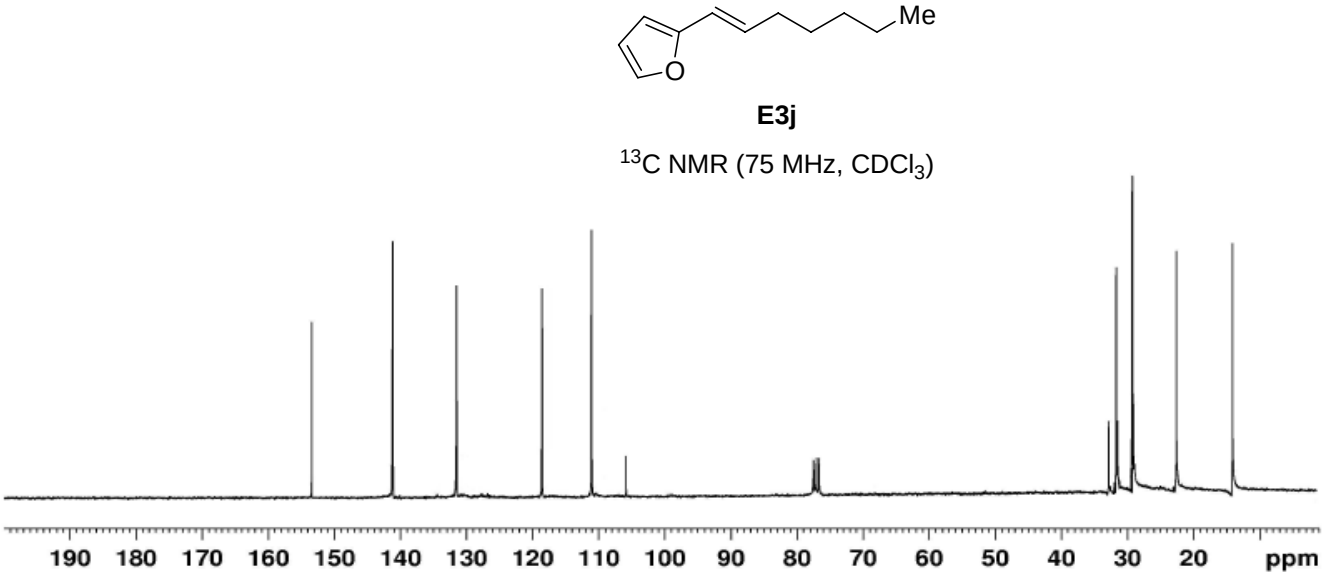
E3i

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



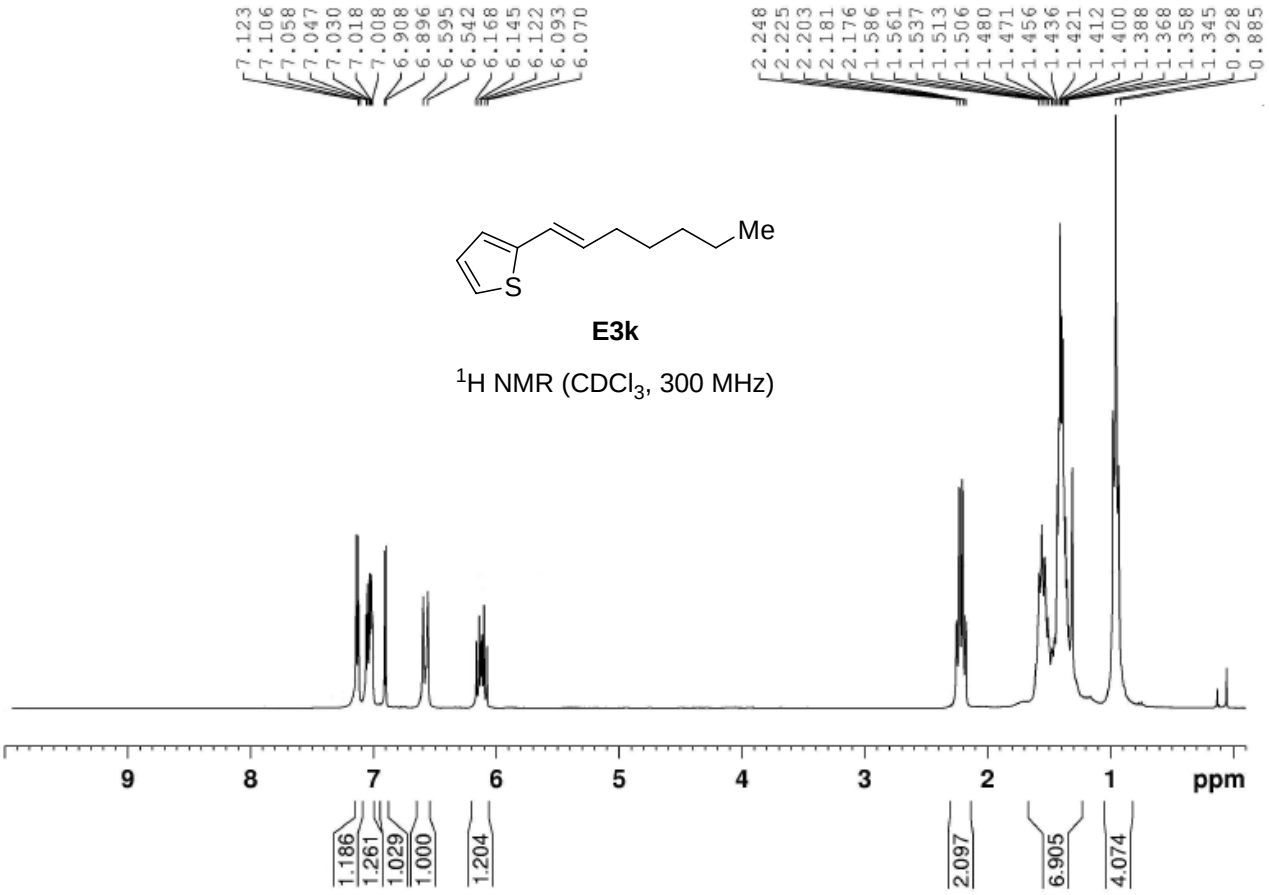
E3j

^{1}H NMR ($CDCl_3$, 300 MHz)



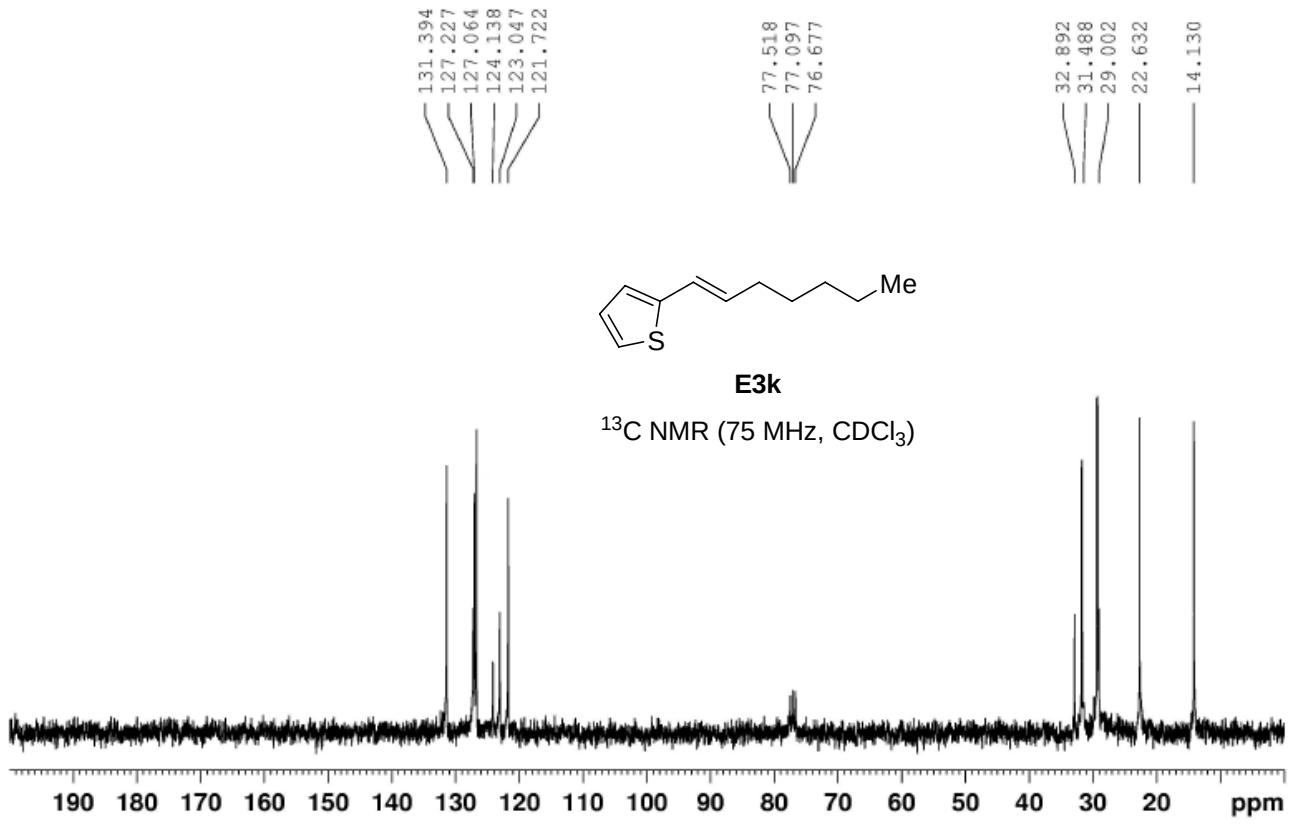
E3j

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



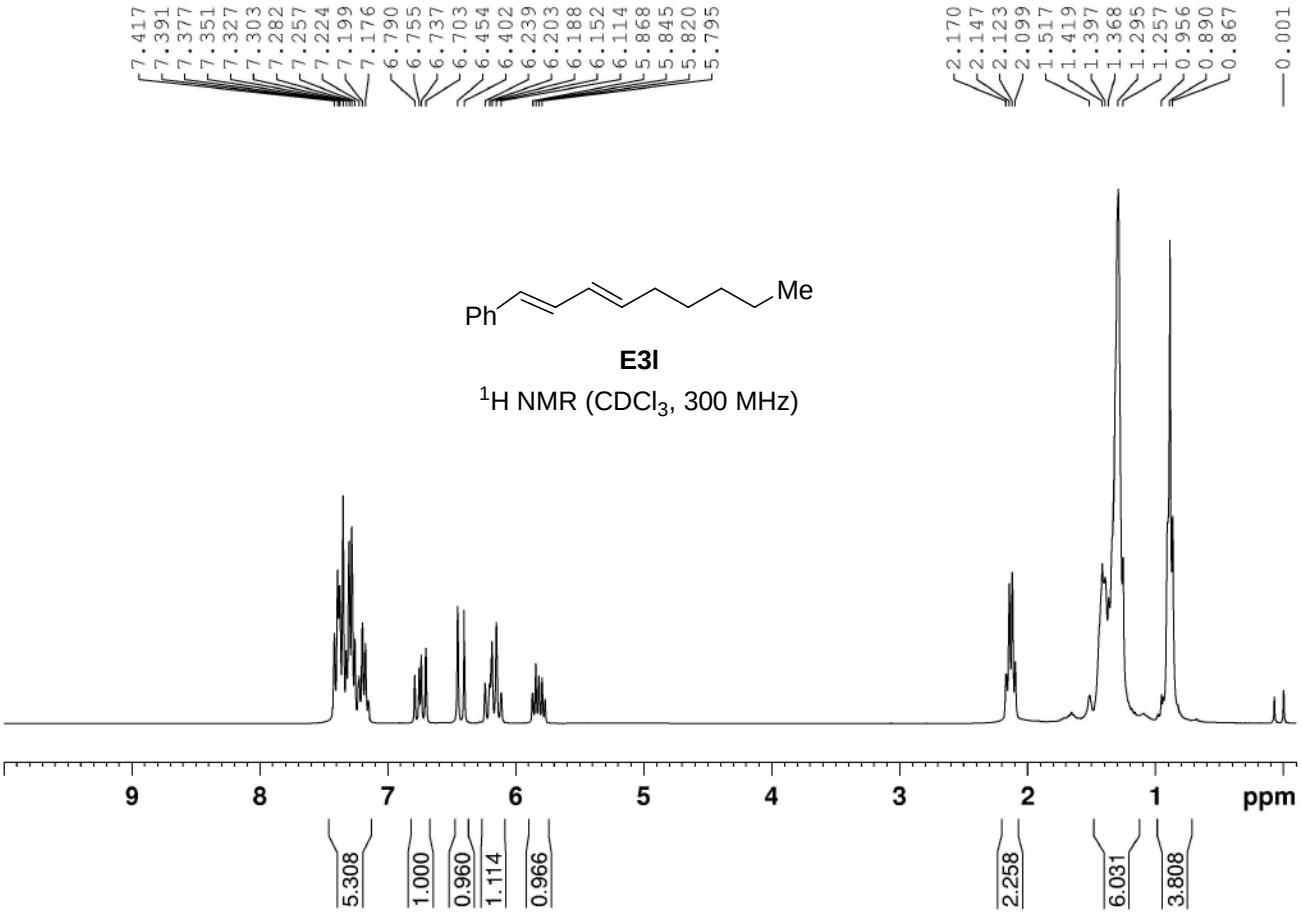
E3k

^{1}H NMR ($CDCl_3$, 300 MHz)



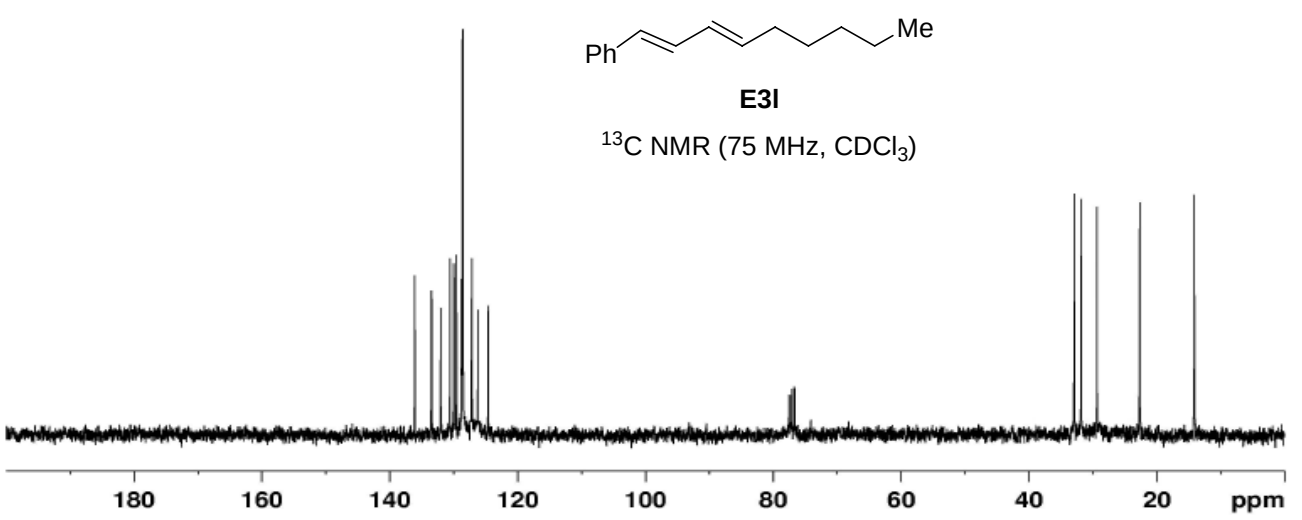
E3k

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



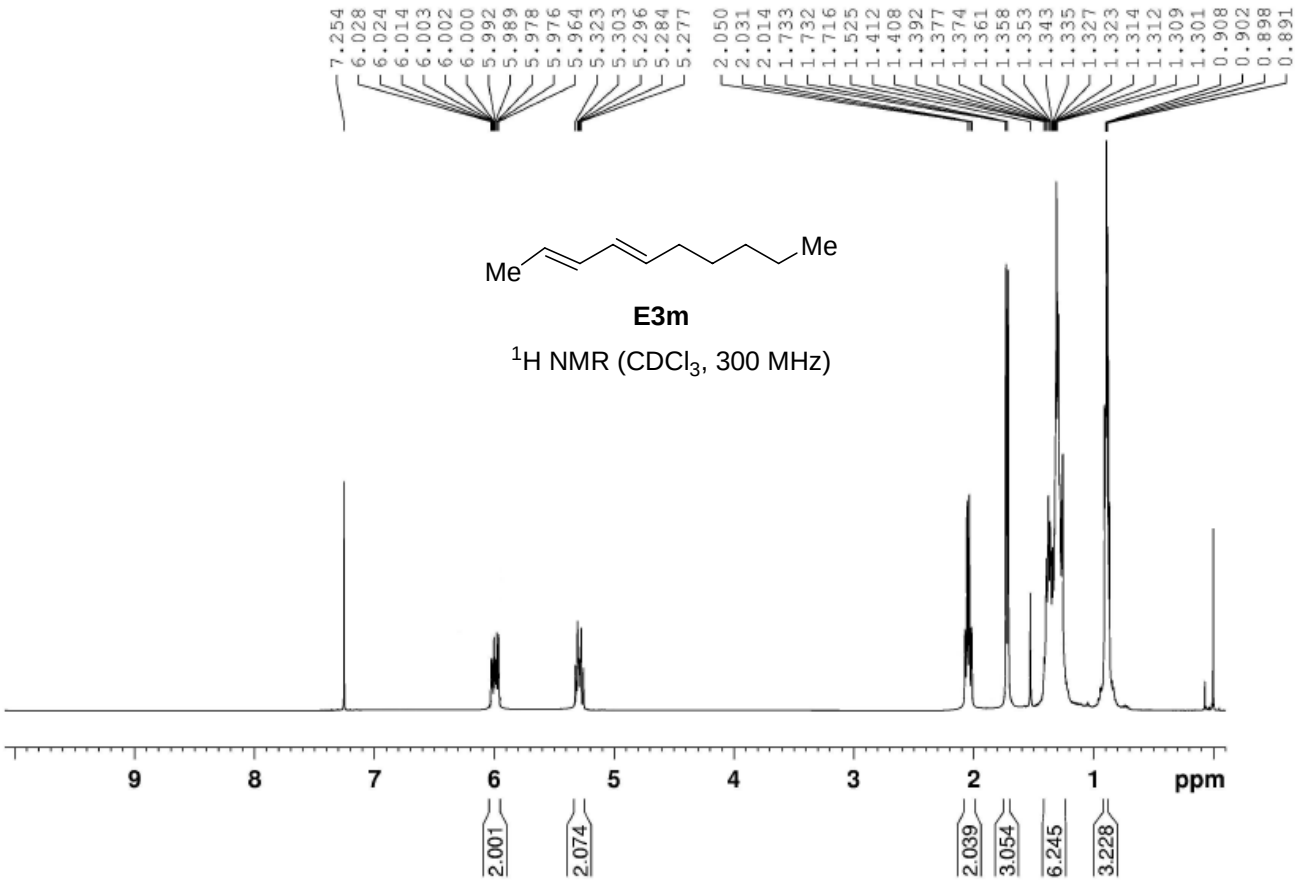
E3l

^{1}H NMR ($CDCl_3$, 300 MHz)



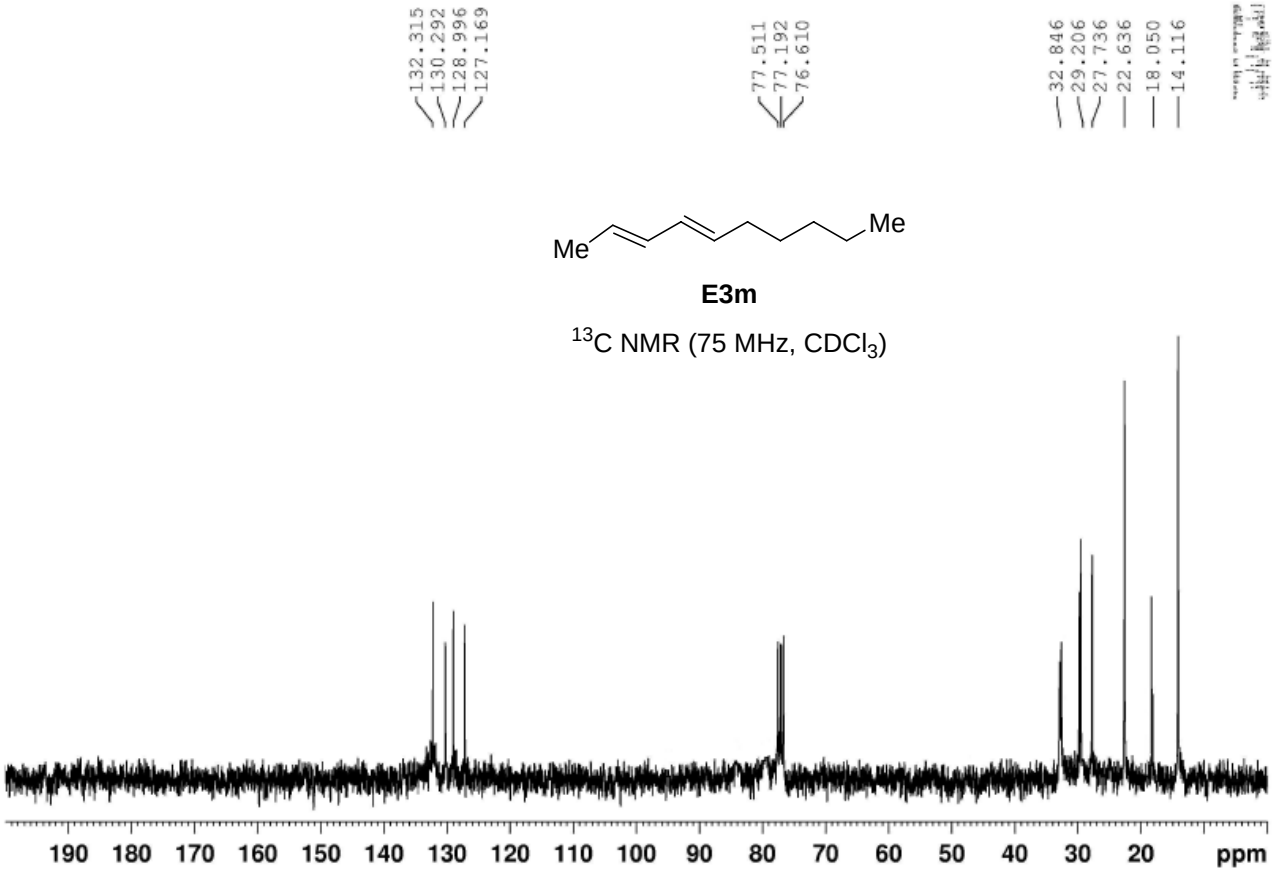
E3l

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



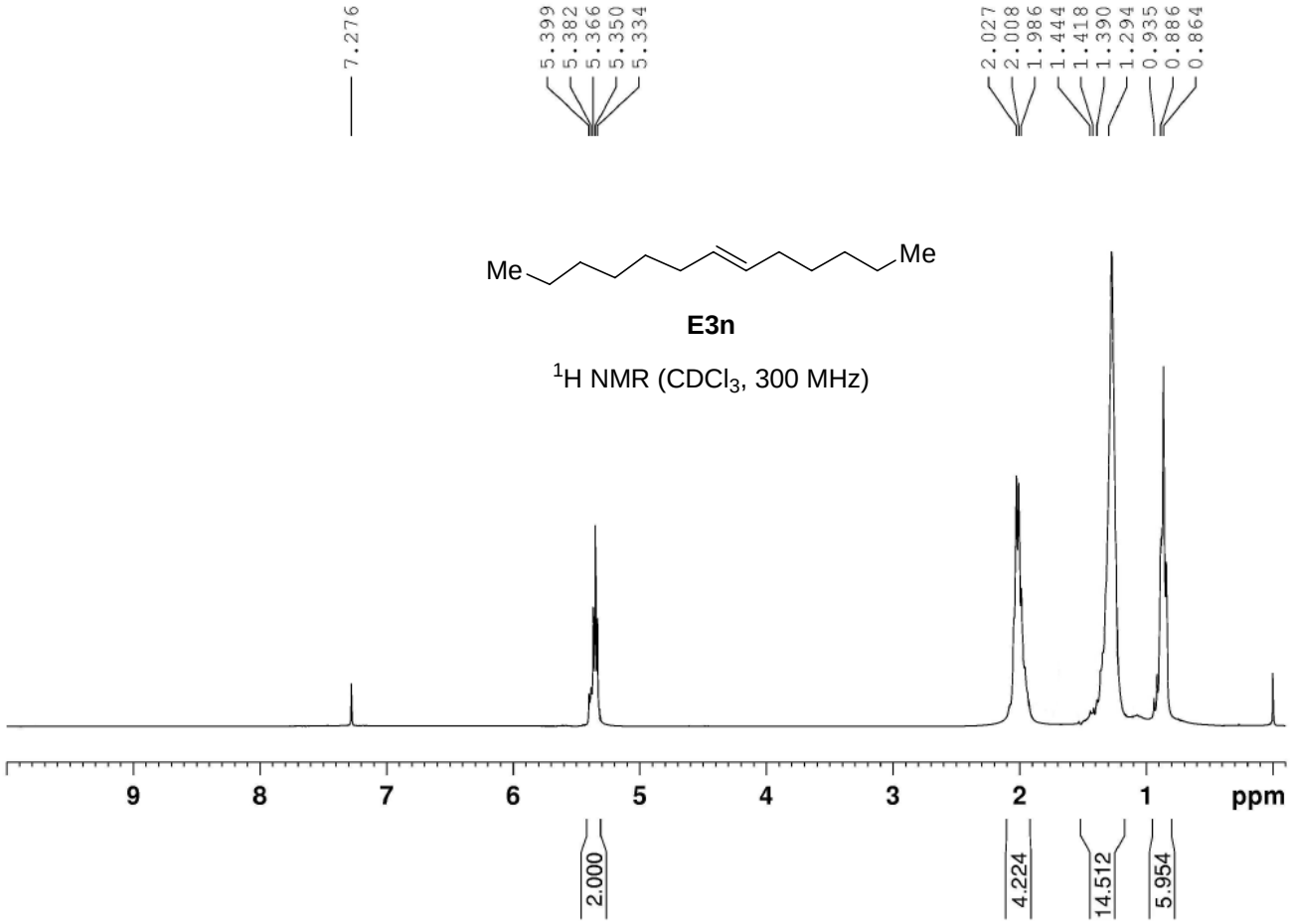
E3m

^{1}H NMR ($CDCl_3$, 300 MHz)



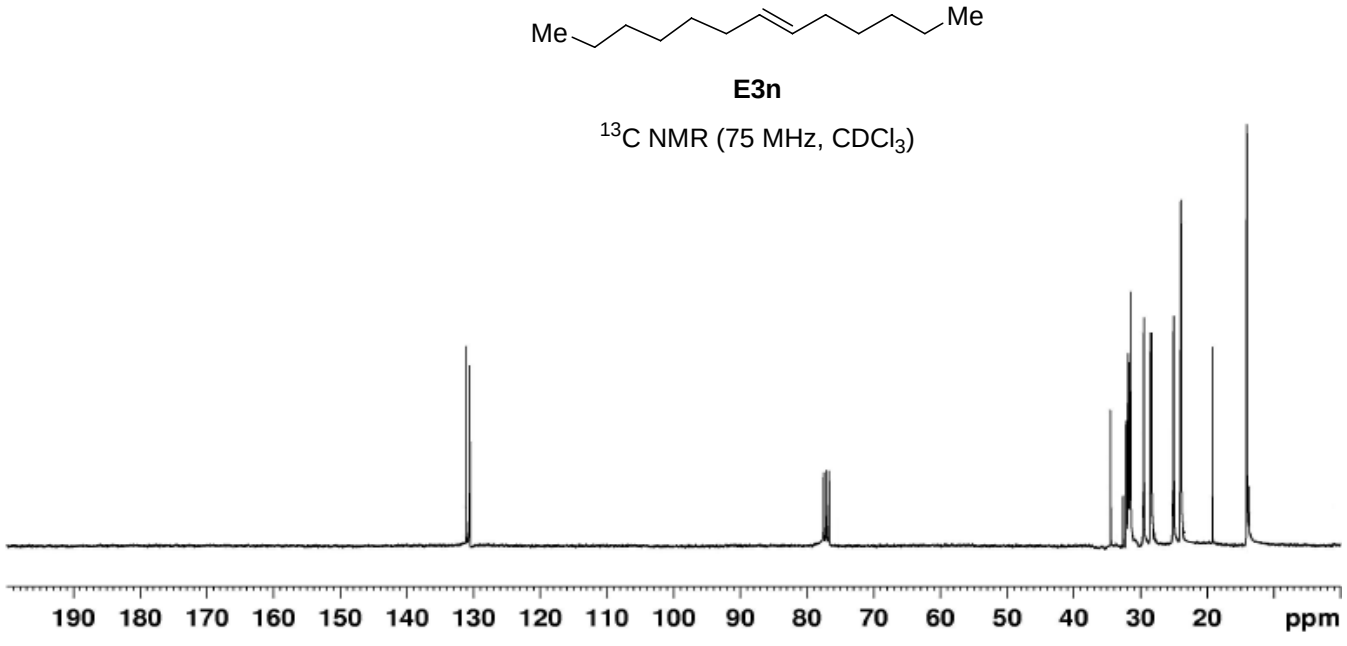
E3m

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



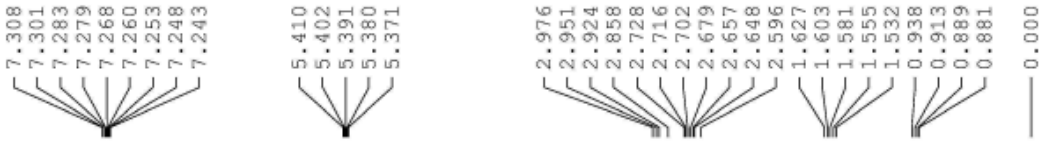
E3n

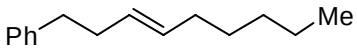
^{1}H NMR ($CDCl_3$, 300 MHz)



E3n

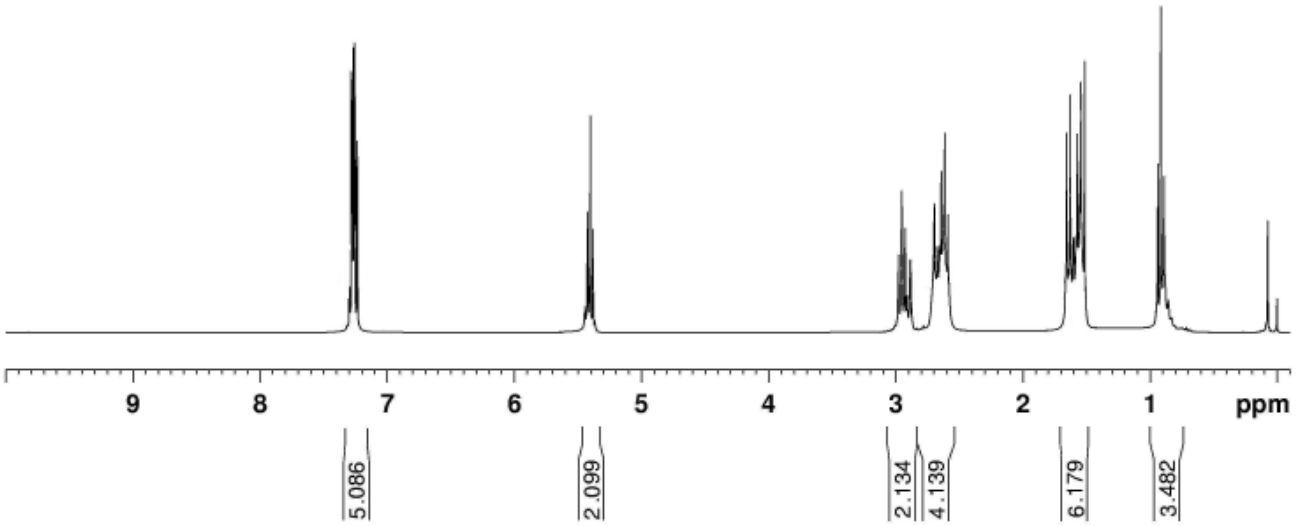
^{13}C NMR (75 MHz, $CDCl_3$)

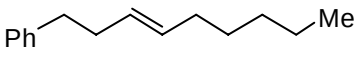




E3o

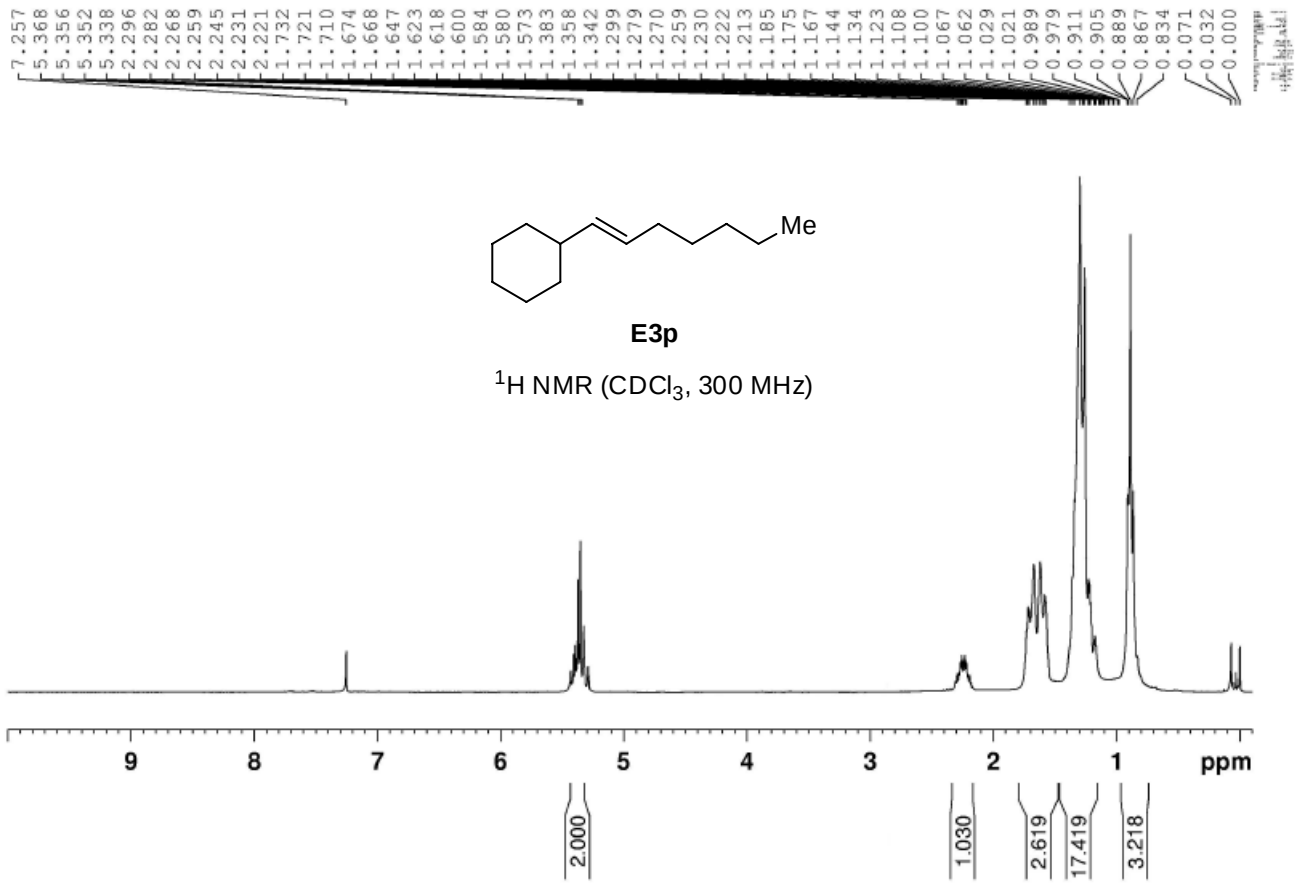
^{1}H NMR ($CDCl_3$, 300 MHz)





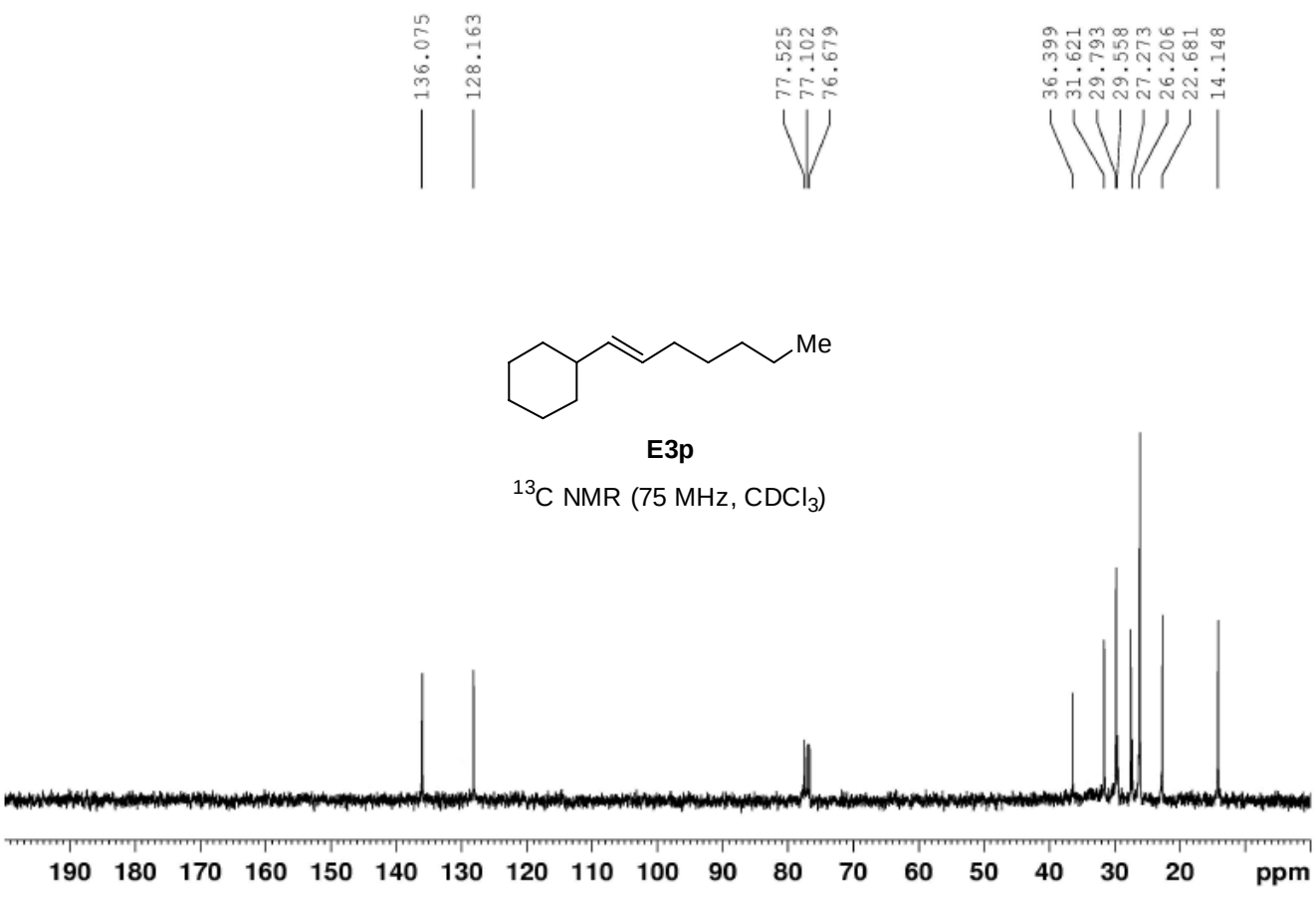
E3o

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



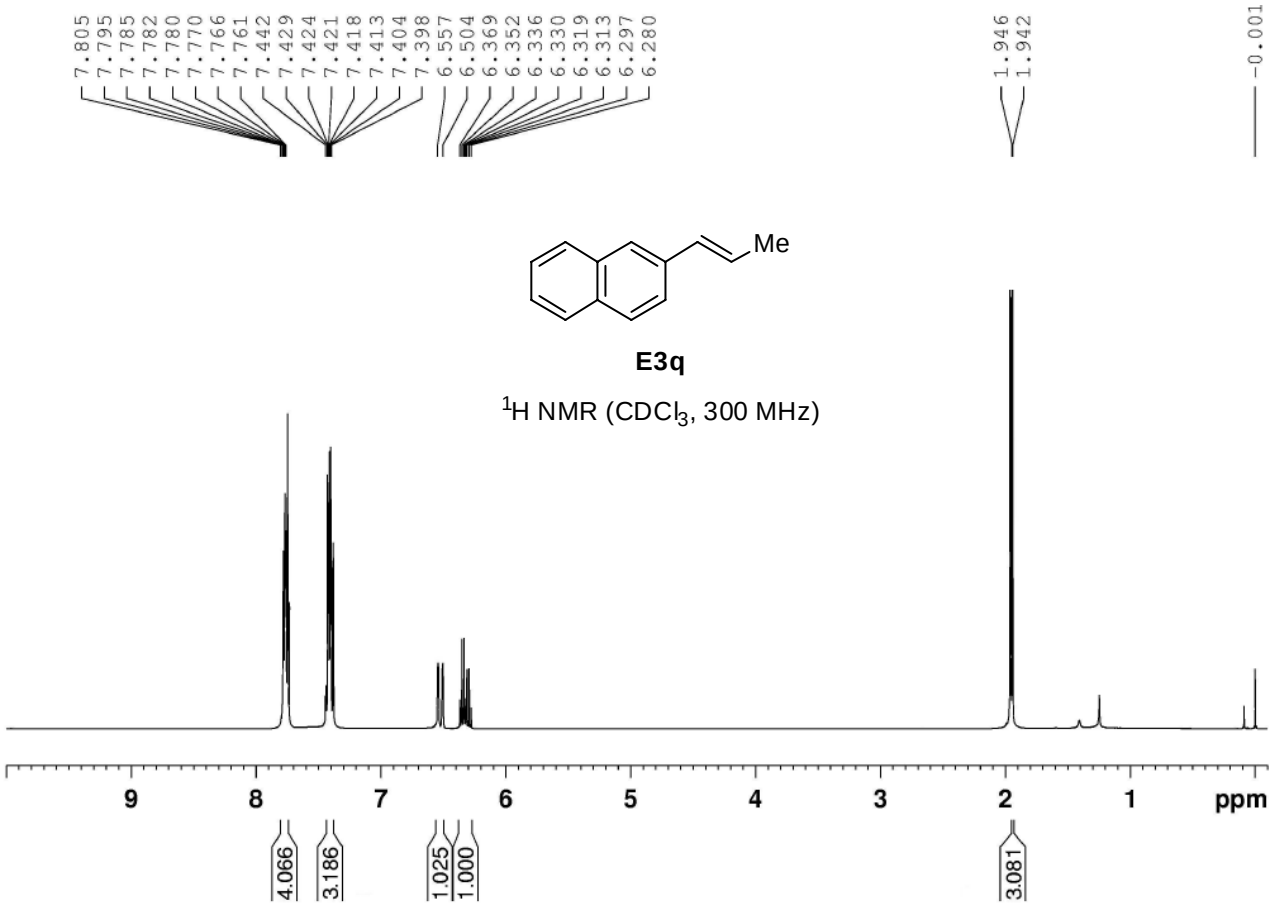
E3p

^{1}H NMR ($CDCl_3$, 300 MHz)



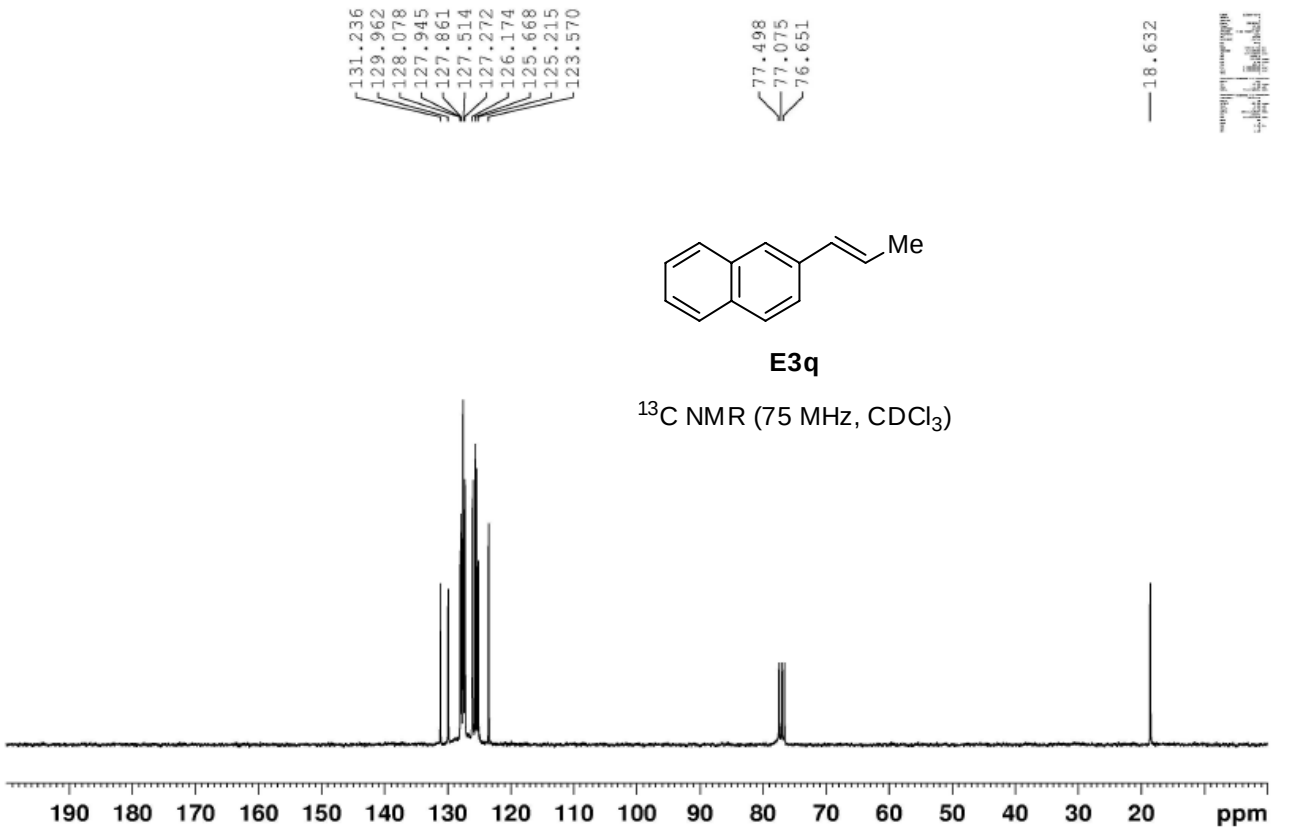
E3p

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



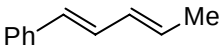
E3q

^{1}H NMR ($CDCl_3$, 300 MHz)



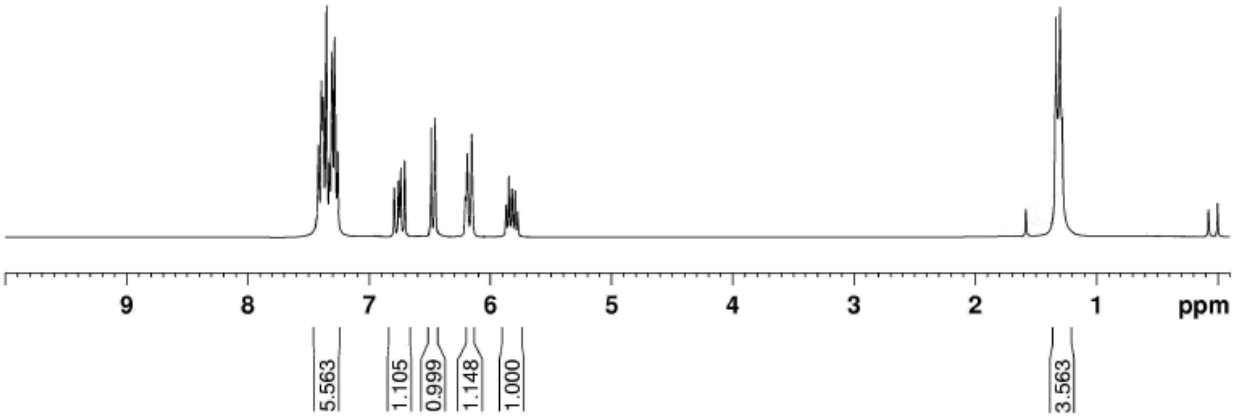
E3q

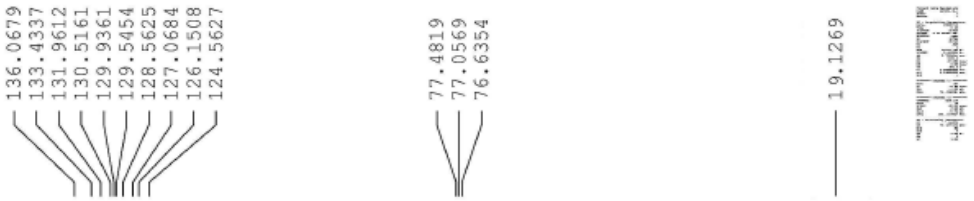
^{13}C NMR (75 MHz, $CDCl_3$)

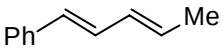


E3r

^{1}H NMR ($CDCl_3$, 300 MHz)

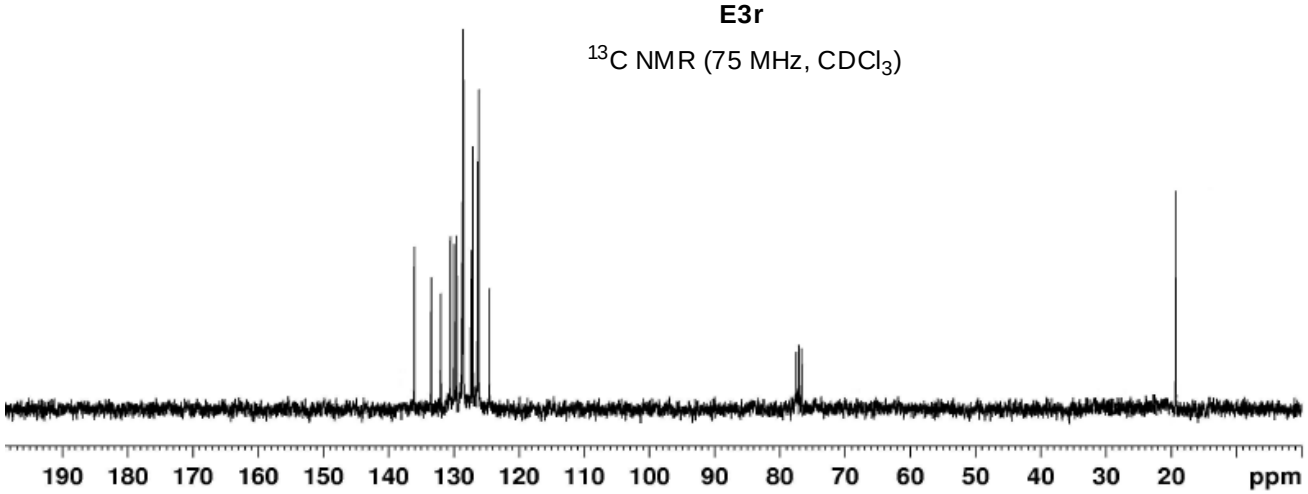


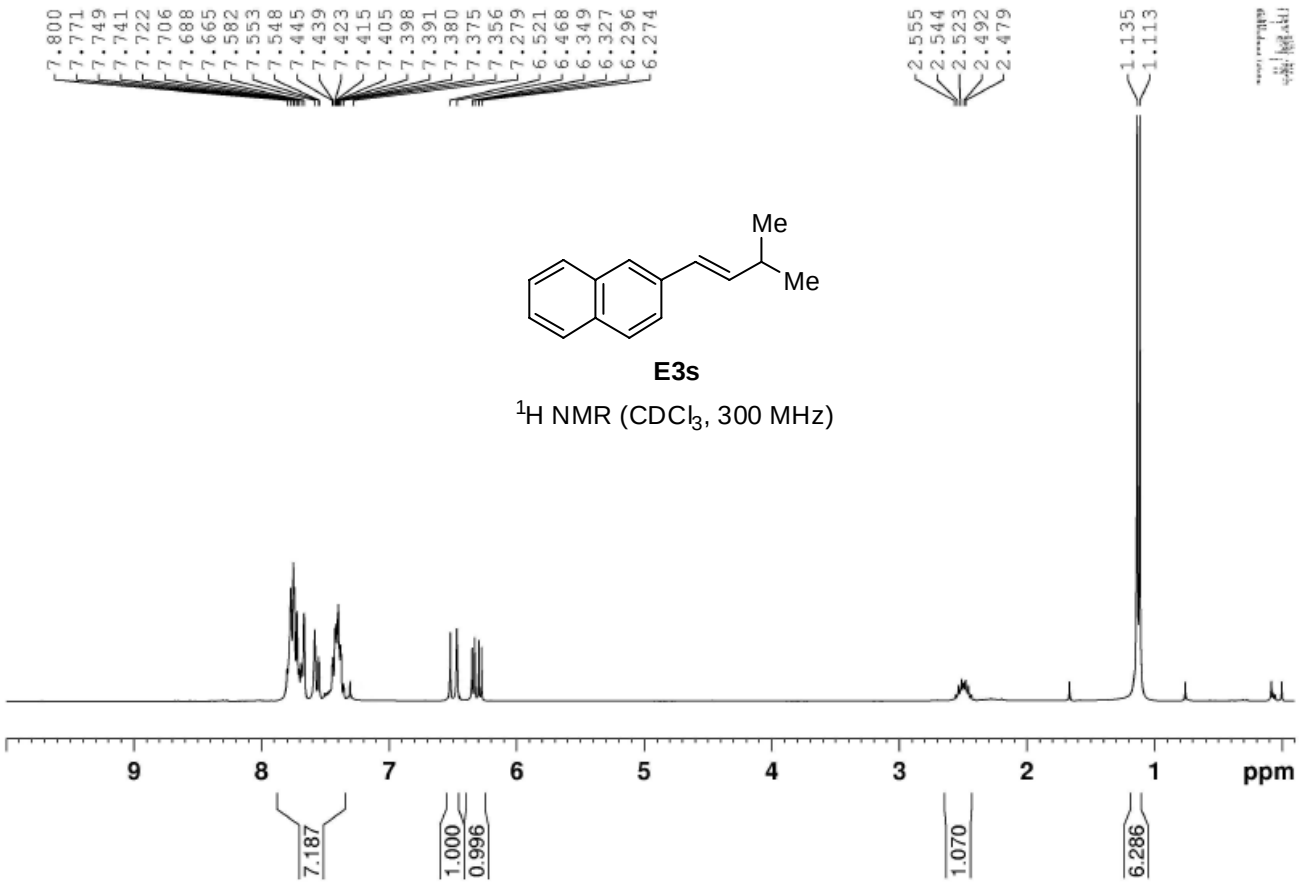




E3r

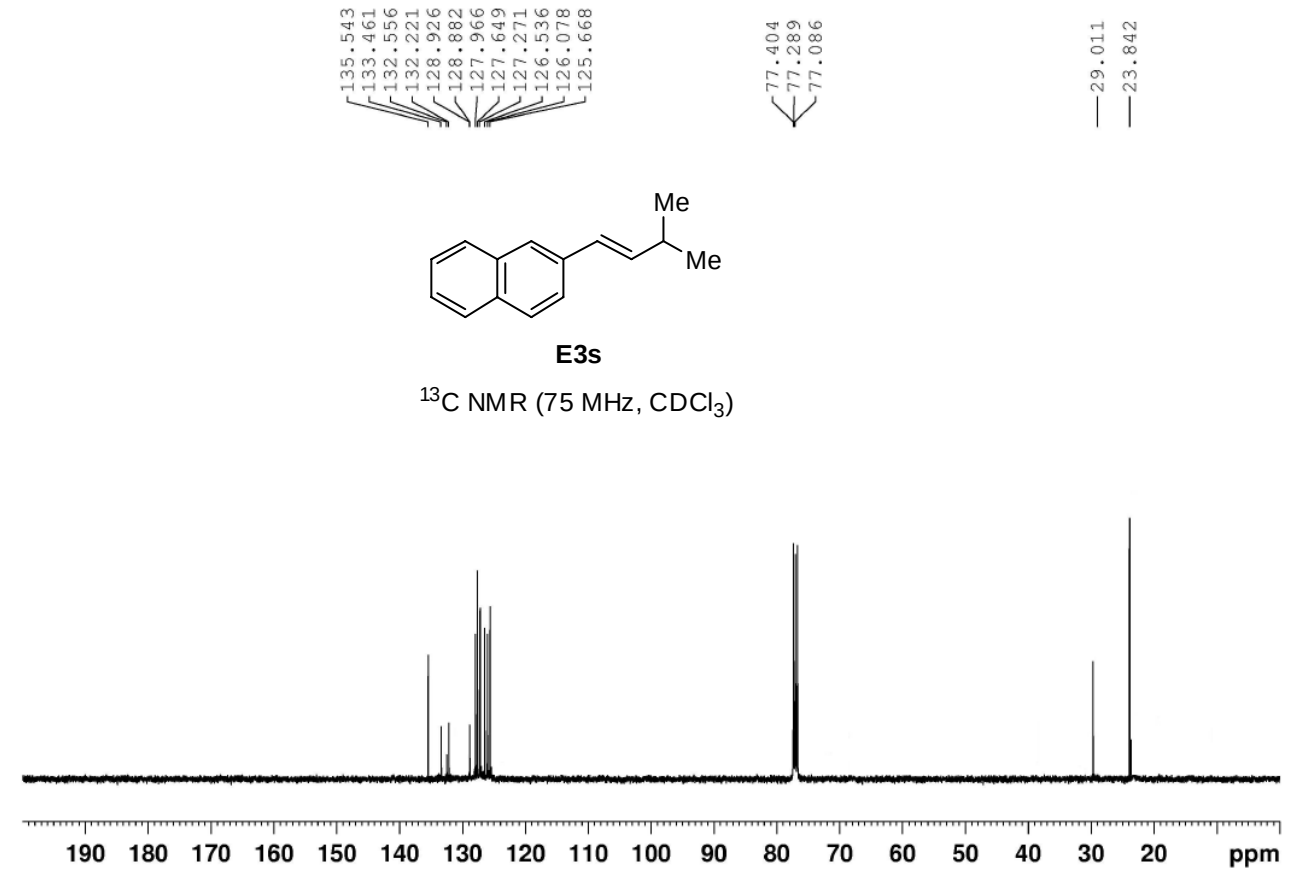
^{13}C NMR (75 MHz, $CDCl_3$)





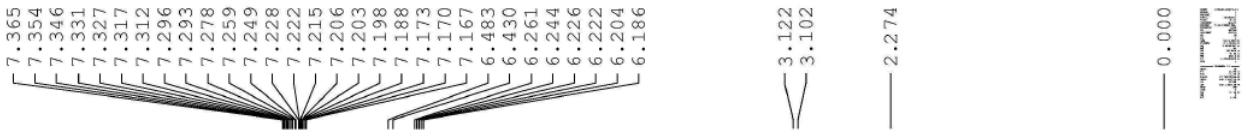
E3s

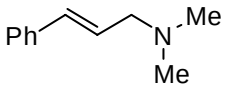
^{1}H NMR ($CDCl_3$, 300 MHz)



E3s

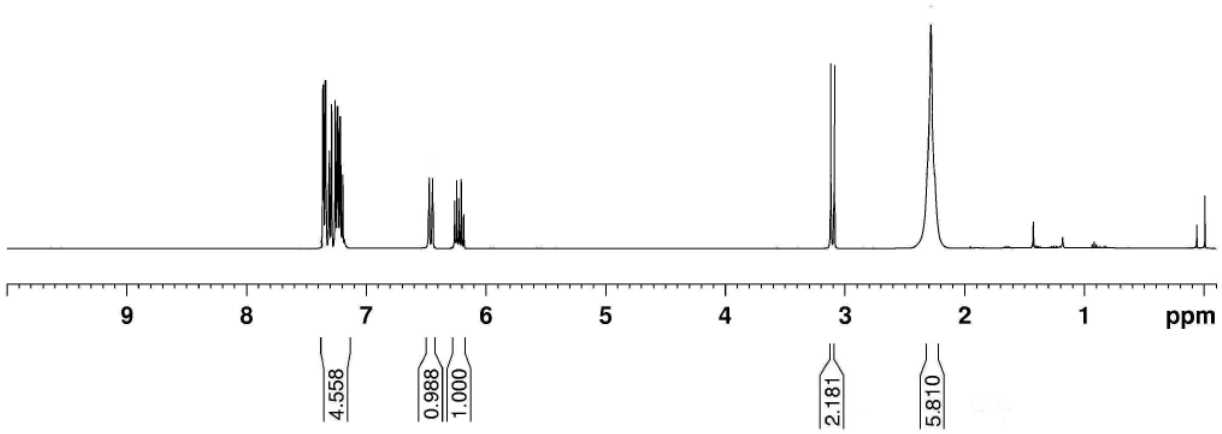
^{13}C NMR (75 MHz, $CDCl_3$)

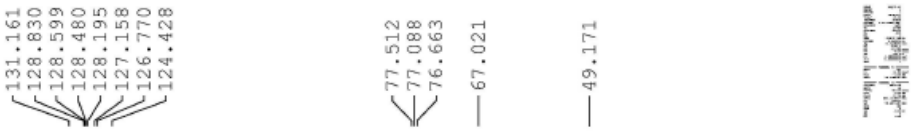


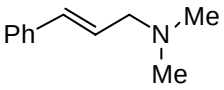


E3t

^{1}H NMR ($CDCl_3$, 300 MHz)

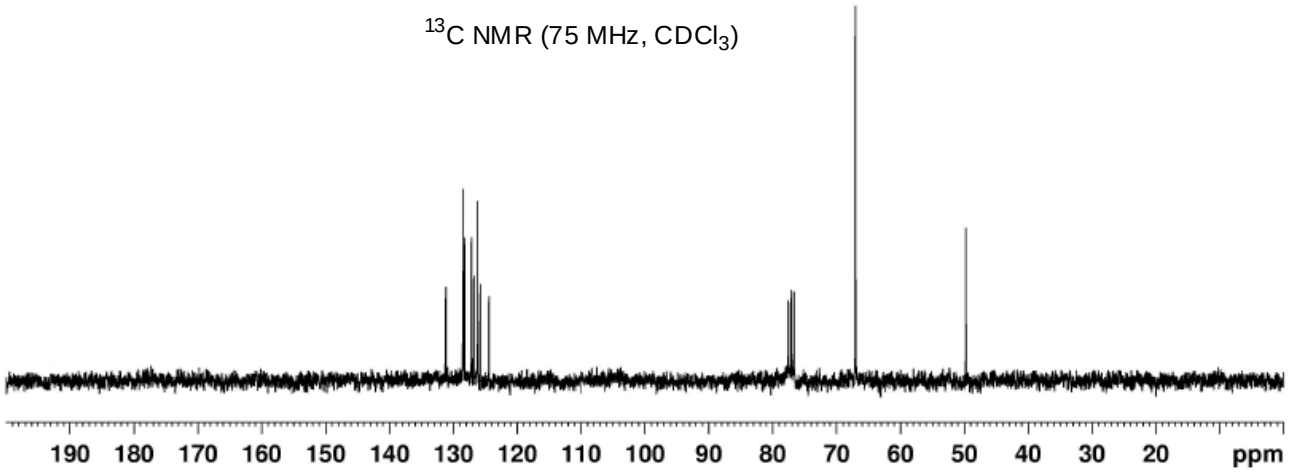


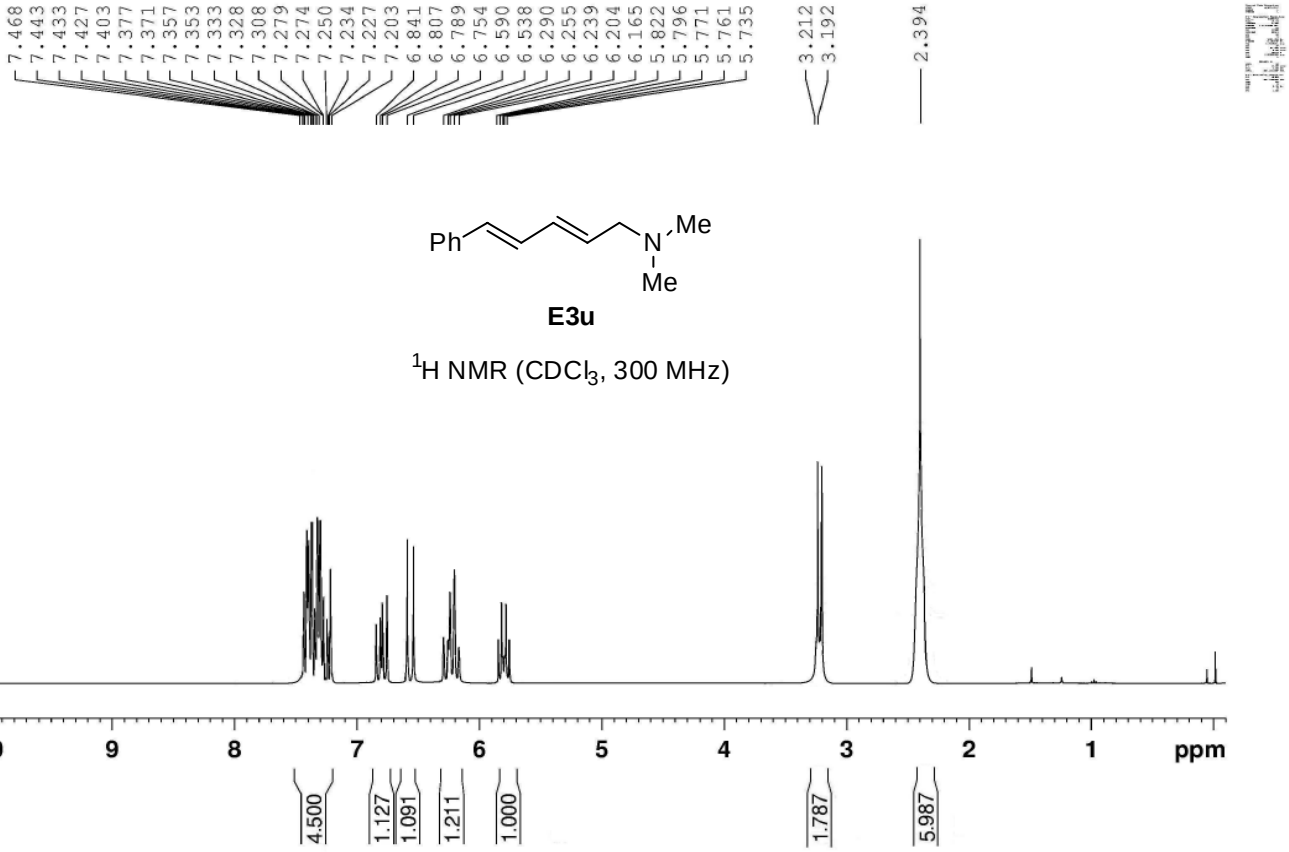




E3t

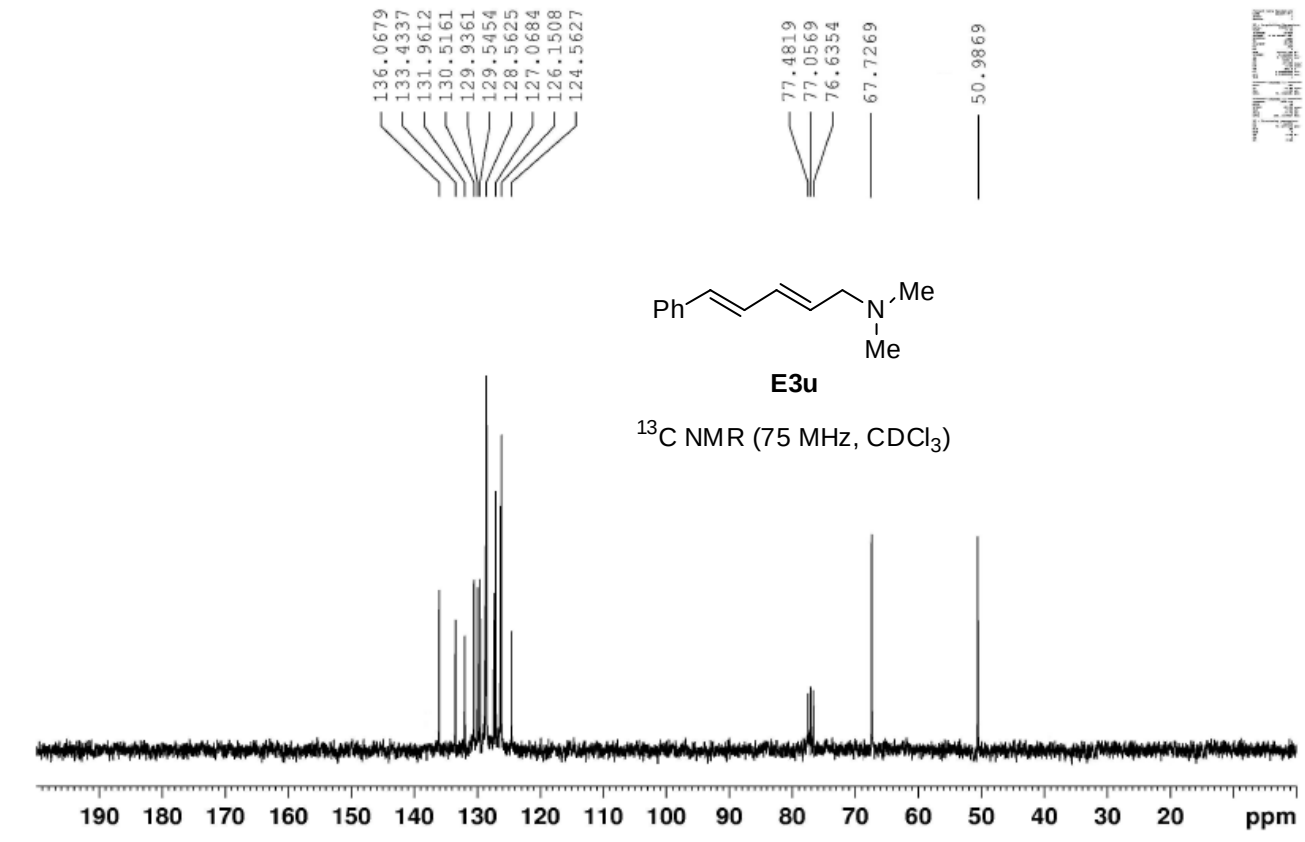
^{13}C NMR (75 MHz, $CDCl_3$)





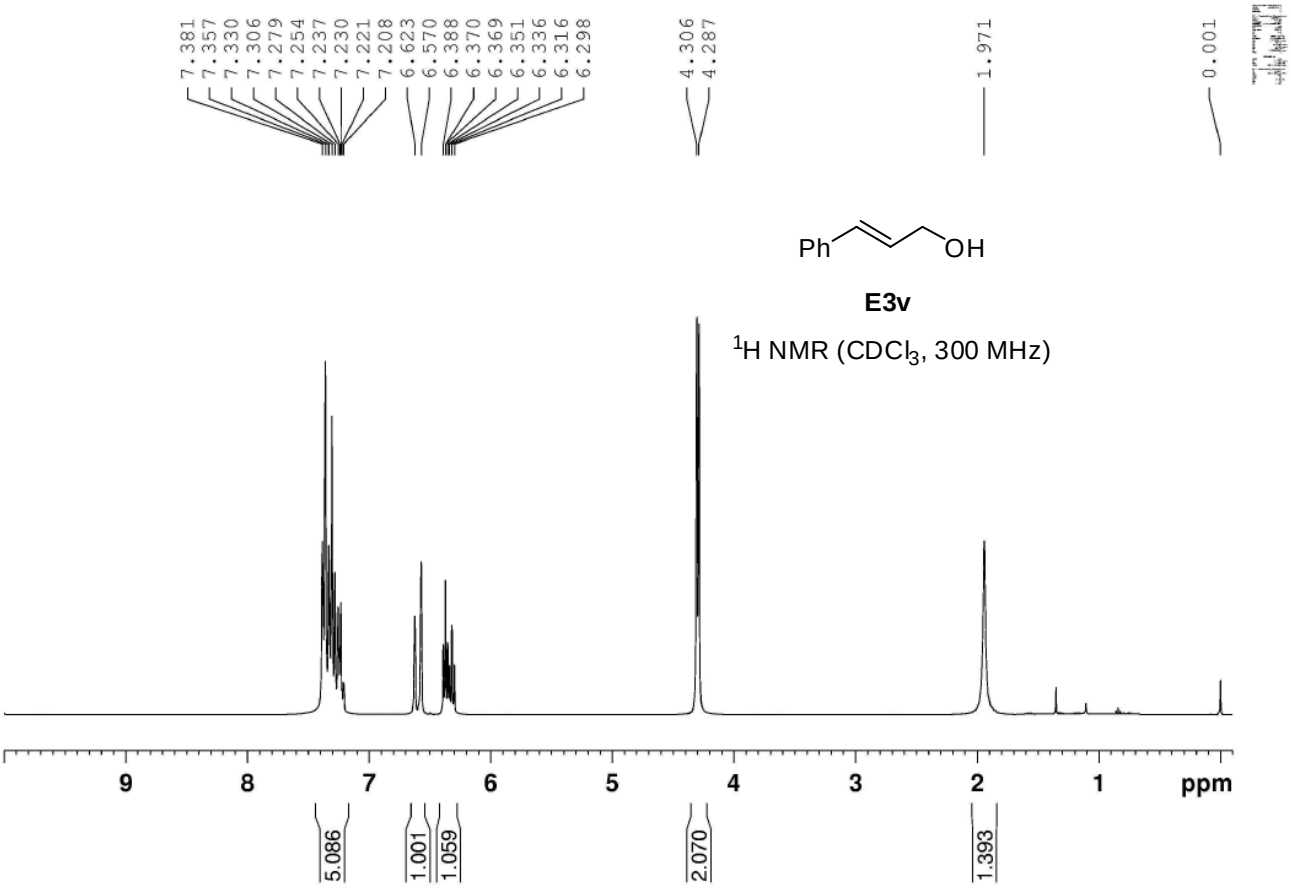
E3u

^{1}H NMR ($CDCl_3$, 300 MHz)



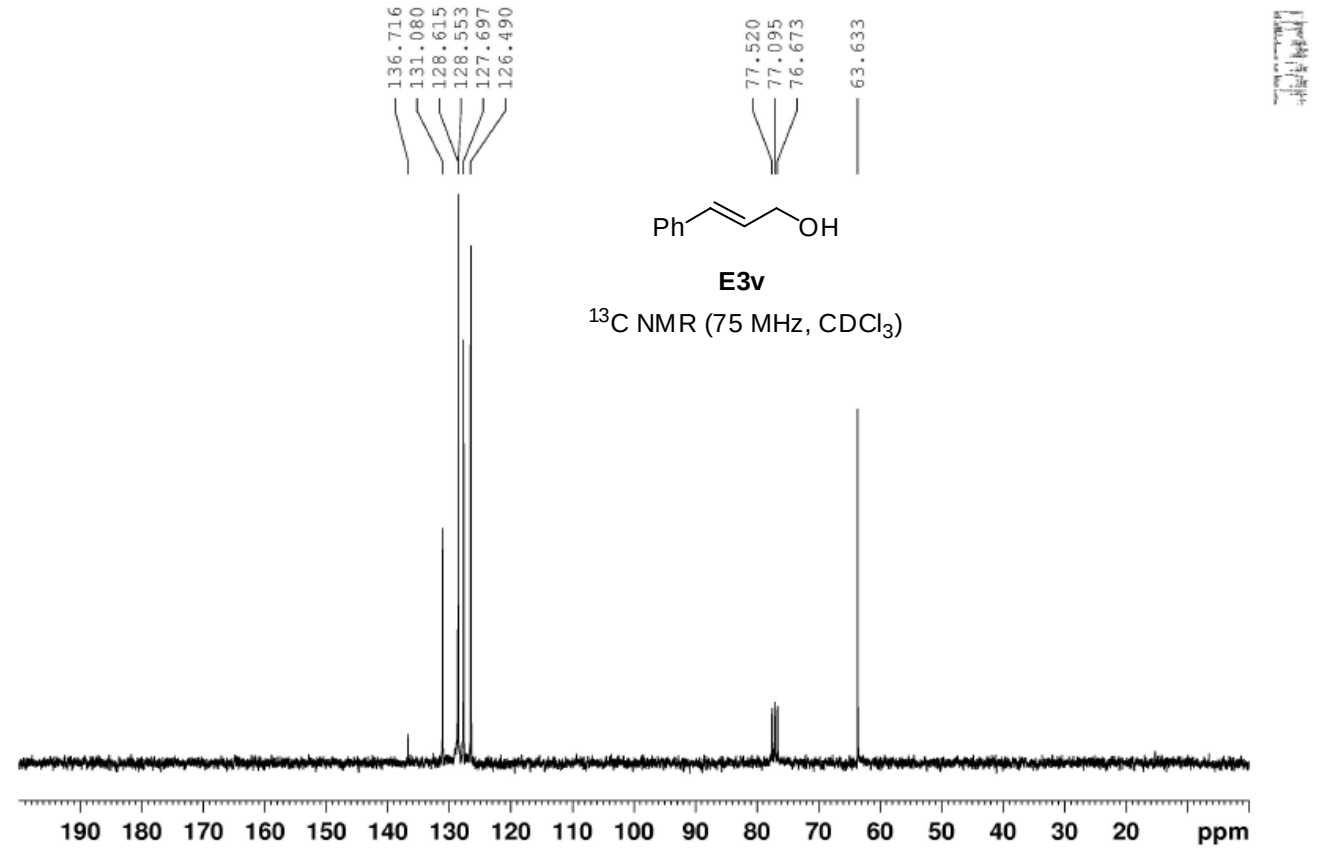
E3u

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



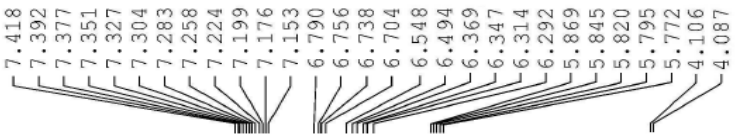
E3v

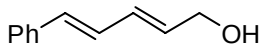
^{1}H NMR ($CDCl_3$, 300 MHz)



E3v

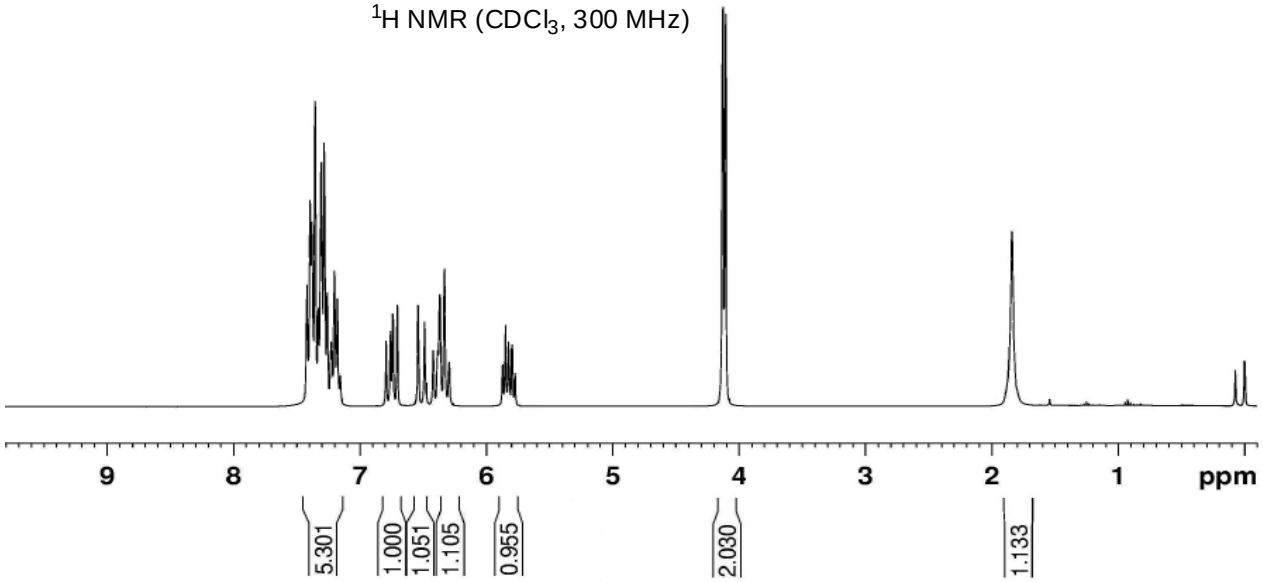
^{13}C NMR (75 MHz, $CDCl_3$)

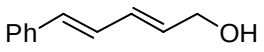




E3w

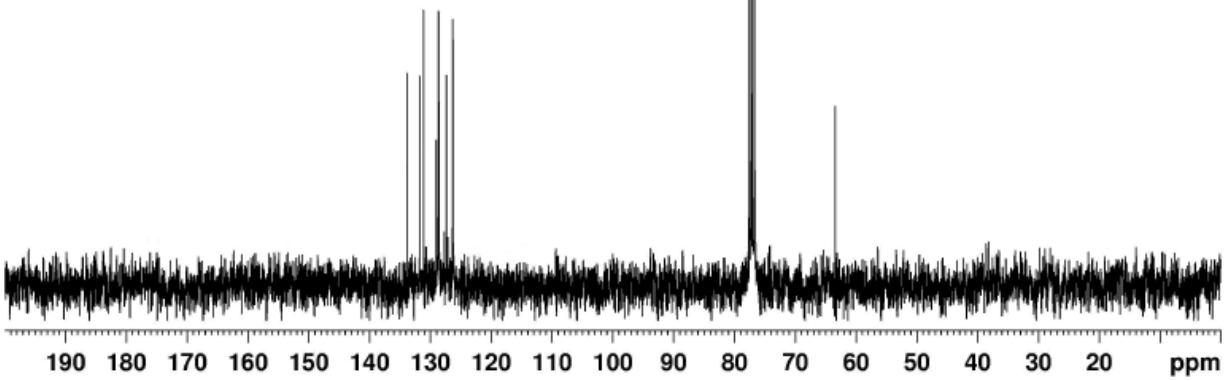
^{1}H NMR ($CDCl_3$, 300 MHz)

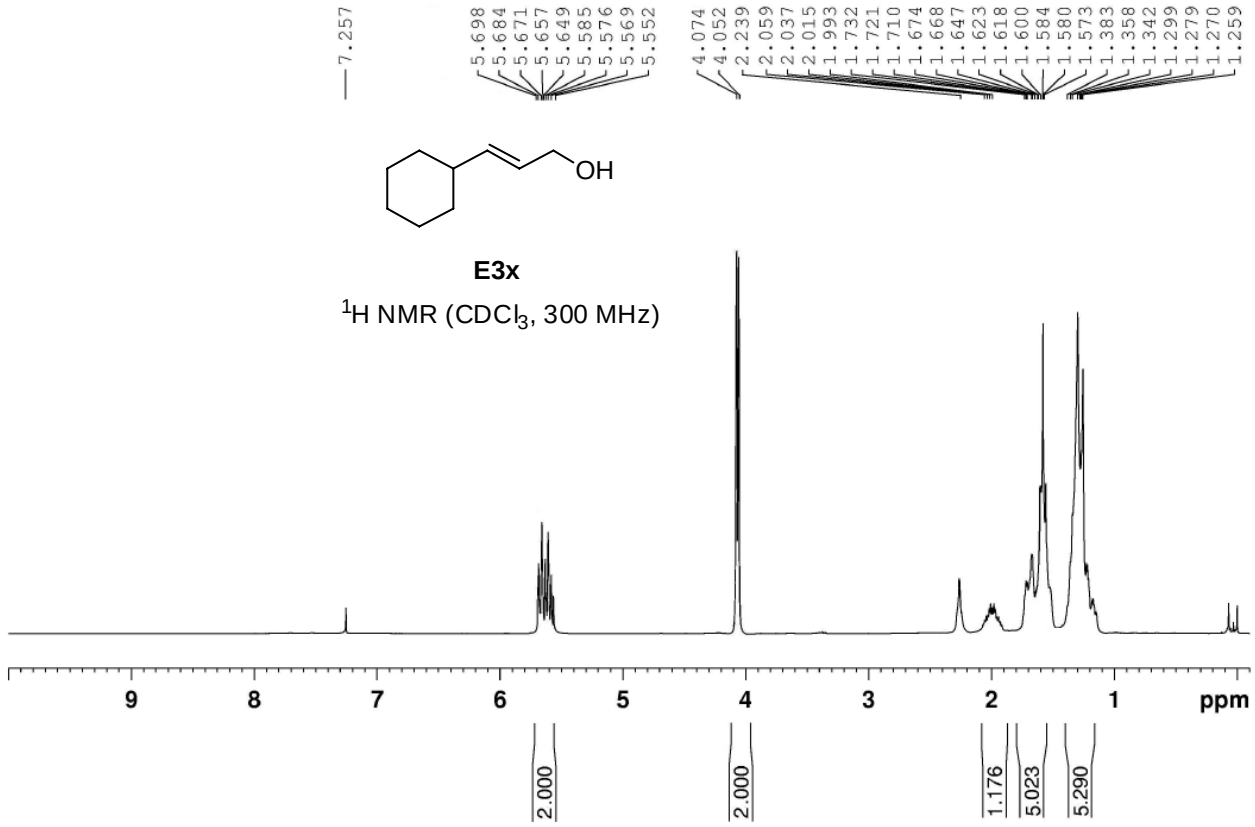




E3w

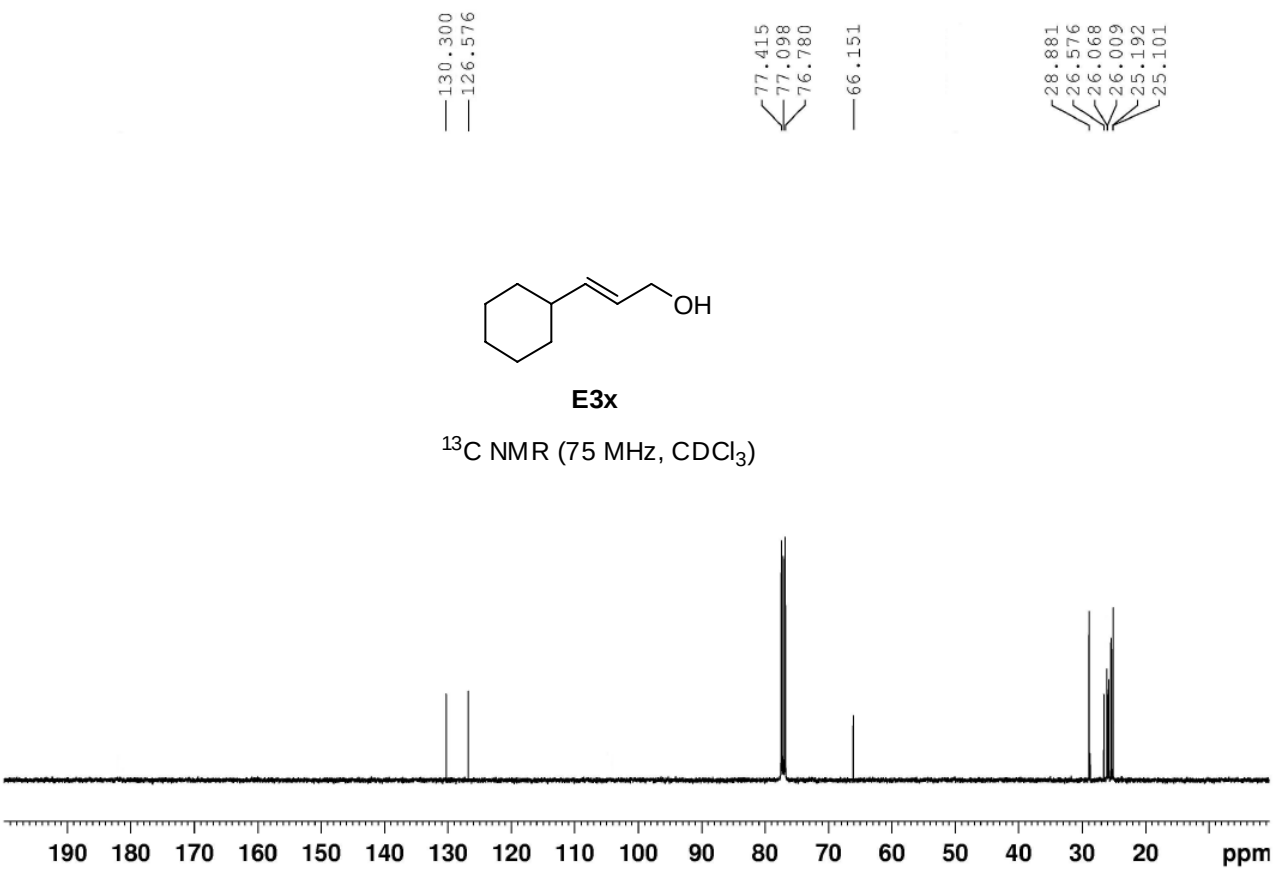
^{13}C NMR (75 MHz, $CDCl_3$)





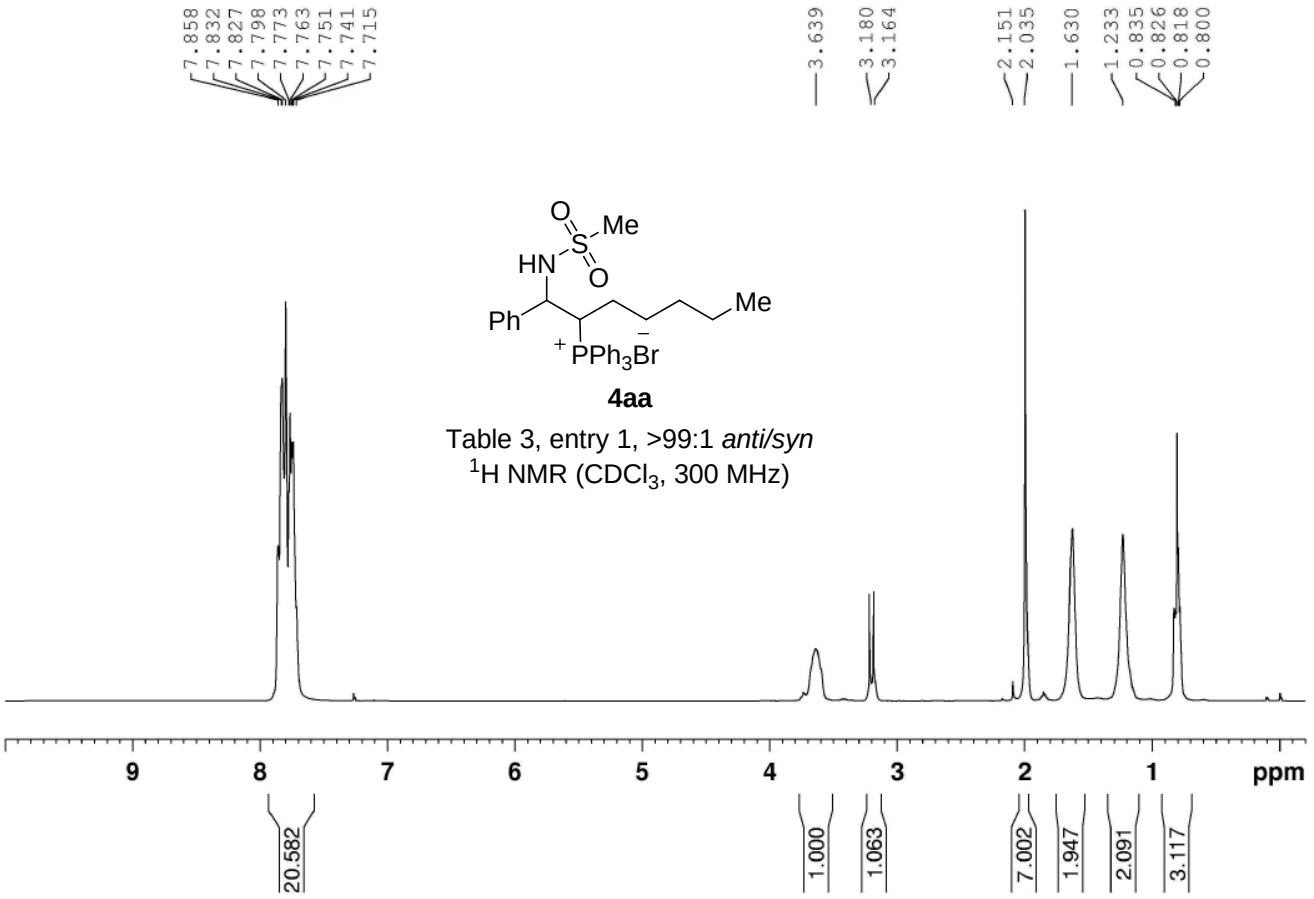
E3x

^{1}H NMR ($CDCl_3$, 300 MHz)



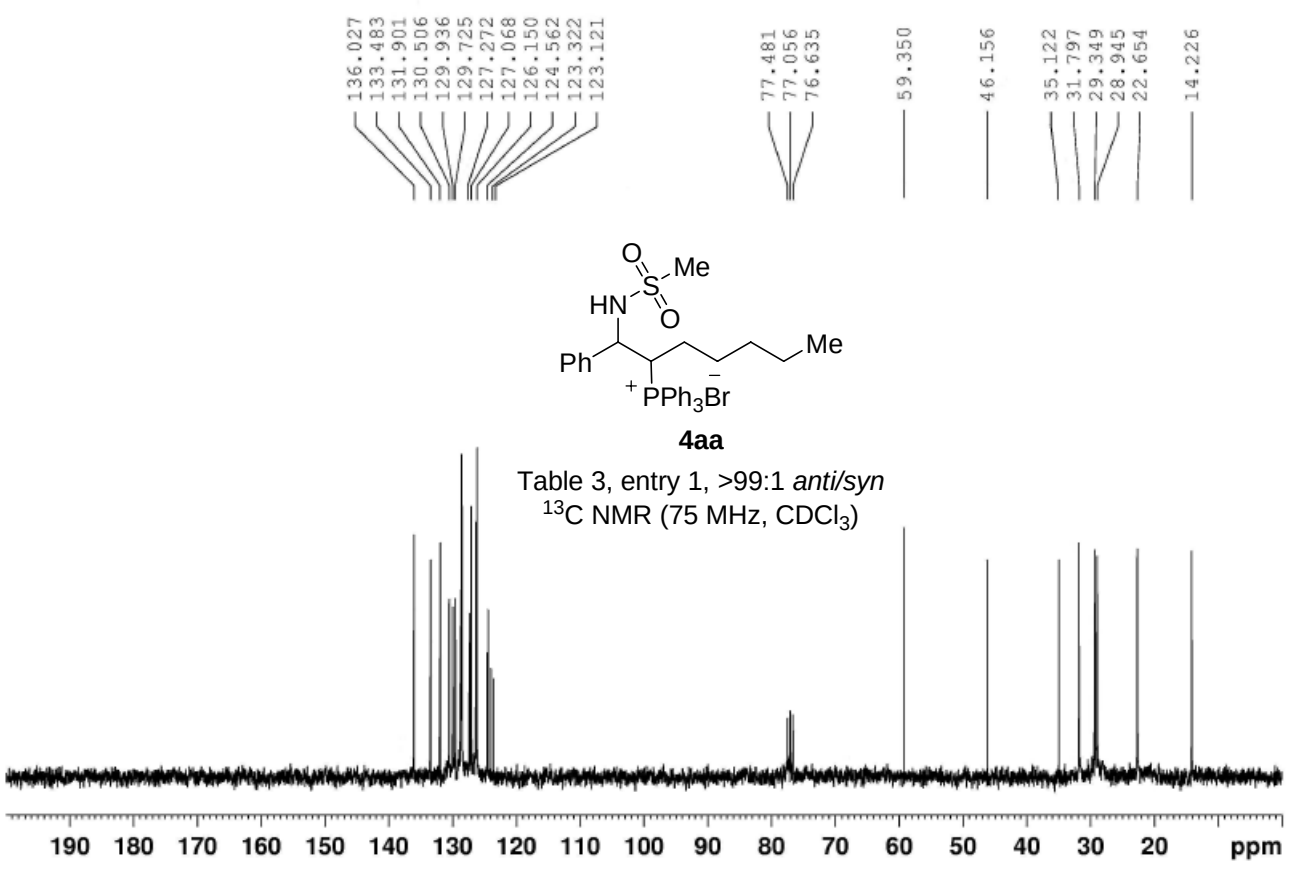
E3x

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



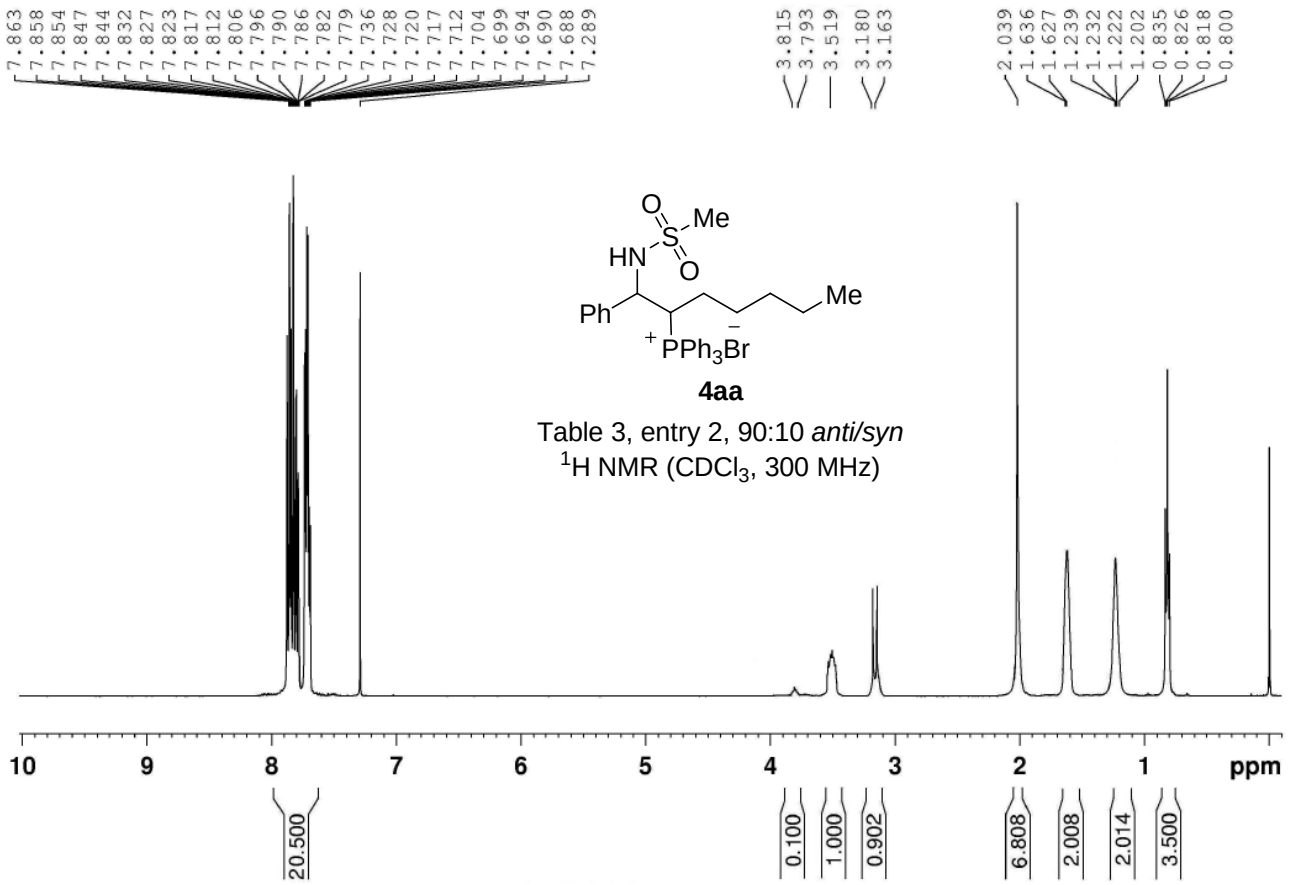
4aa

Table 3, entry 1, >99:1 *anti/syn*
^{1}H NMR ($CDCl_3$, 300 MHz)



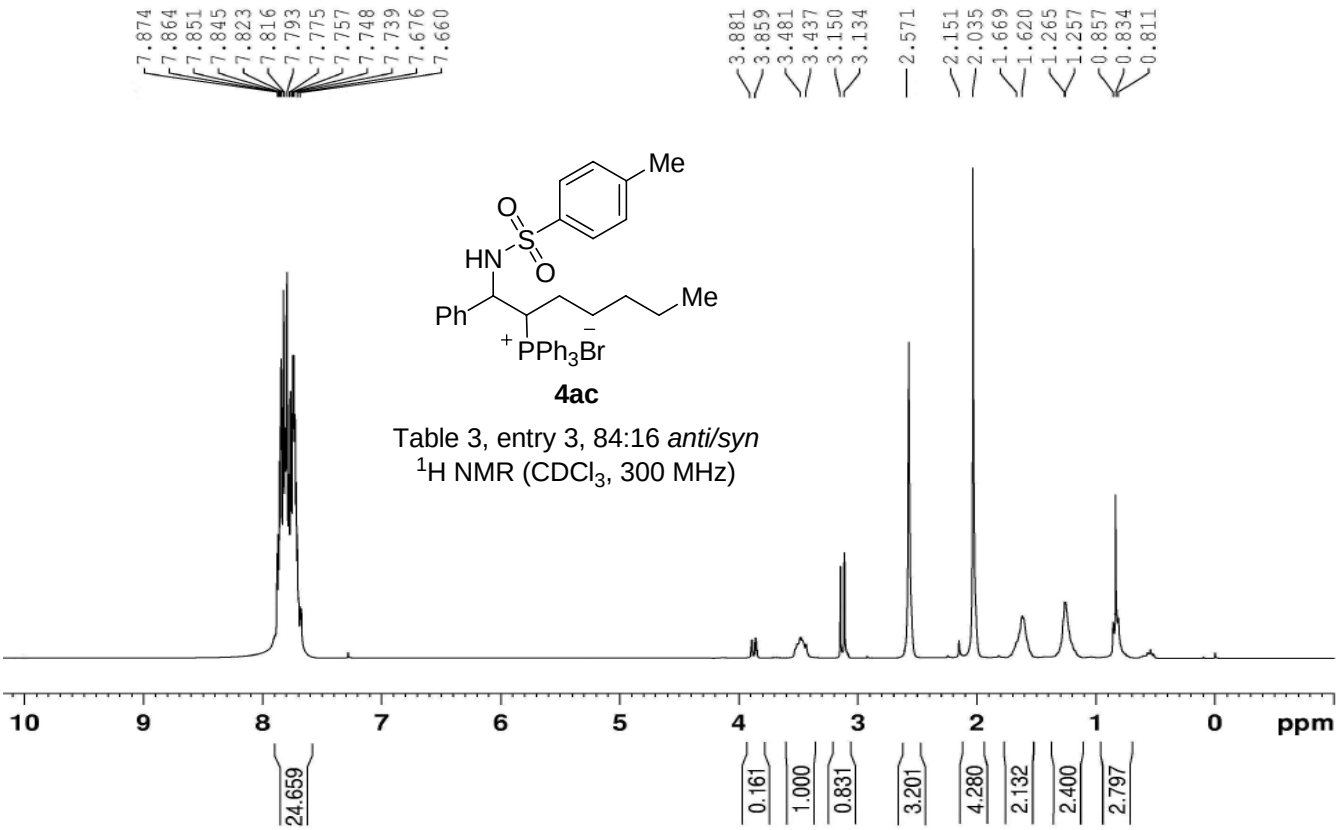
4aa

Table 3, entry 1, >99:1 *anti/syn*
^{13}C NMR (75 MHz, $CDCl_3$)



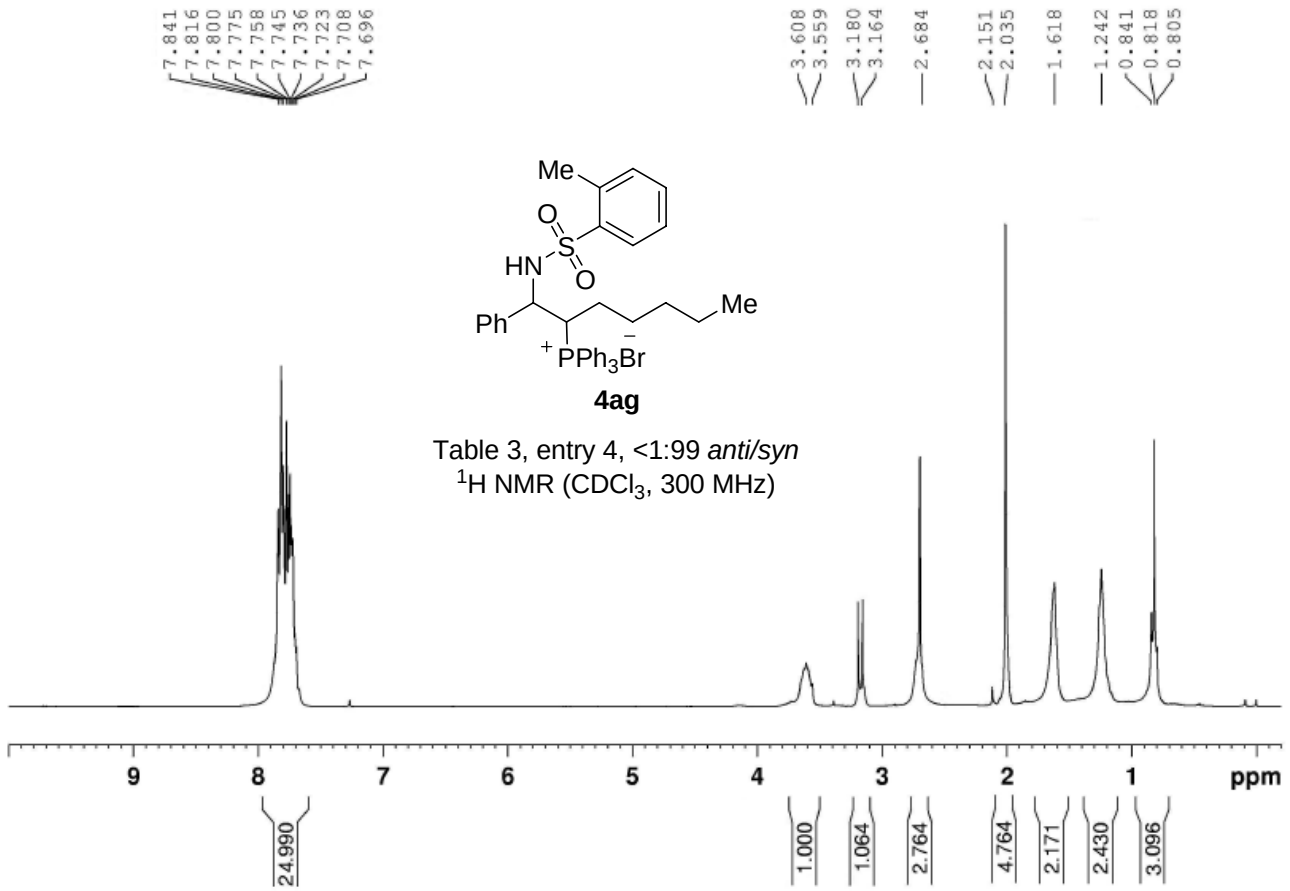
4aa

Table 3, entry 2, 90:10 *anti/syn*
^{1}H NMR ($CDCl_3$, 300 MHz)



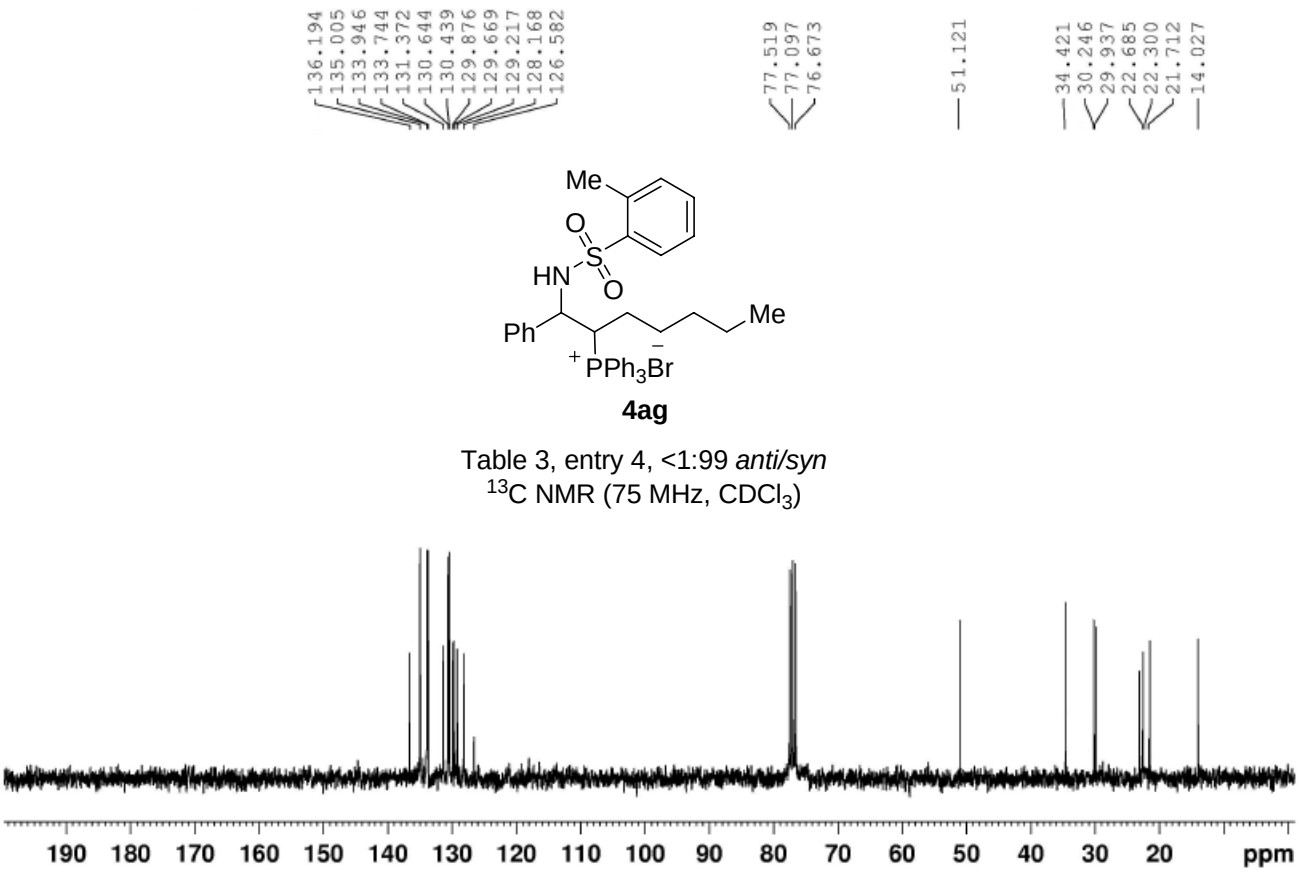
4ac

Table 3, entry 3, 84:16 *anti/syn*
^{1}H NMR ($CDCl_3$, 300 MHz)



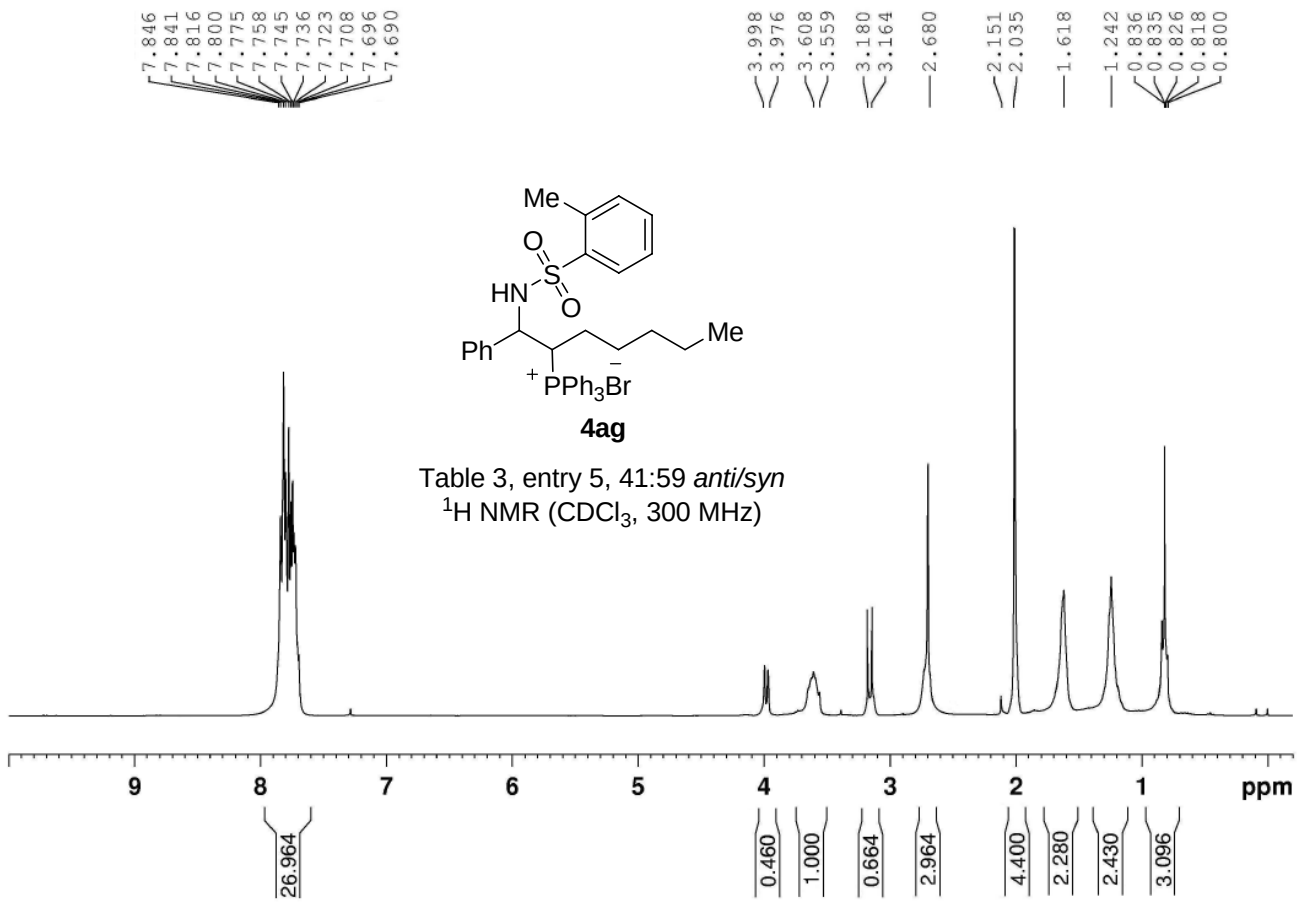
4ag

Table 3, entry 4, <1:99 *anti/syn*
^{1}H NMR ($CDCl_3$, 300 MHz)



4ag

Table 3, entry 4, <1:99 *anti/syn*
^{13}C NMR (75 MHz, $CDCl_3$)


7.846
7.841
7.816
7.800
7.775
7.758
7.745
7.736
7.723
7.708
7.696
7.690
3.998
3.976
3.608
3.559
3.180
3.164
2.680
2.151
2.035
1.618
1.242
0.836
0.835
0.826
0.818
0.800
Me
O
S
HN
O
Ph
Me
+
PPh3Br
−
4ag
Table 3, entry 5, 41:59 anti/syn
1H NMR (CDCl3, 300 MHz)
9
8
7
6
5
4
3
2
1
ppm
26.964
0.460
1.000
0.664
2.964
4.400
2.280
2.430
3.096