Influence of *α*-Coordinating Groups of Aldehyde on *E/Z*-Selectivity and Use of Quaternary Ammonium Counter Ion for Enhanced *E*-Selectivity in Julia-Kocienski Reaction.

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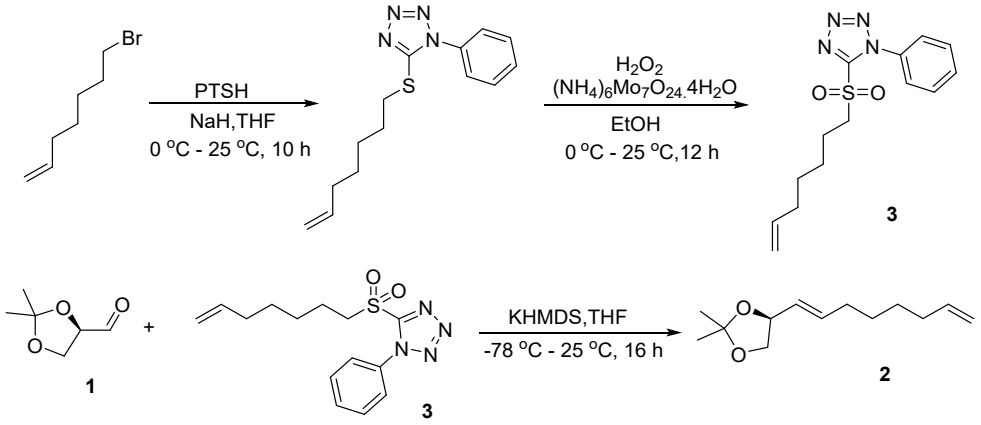
General Information: Until otherwise mentioned all the reactions were performed under an atmosphere of argon and nitrogen in flame dried glassware. Tetrahydrofuran (THF) was double distilled from LAH, Dichloromethane (DCM) was distilled from CaH_2 before use. Commercially available reagents were used as received. Tetrabutylammonium halides were dried under high vacuum for 24 h before prior to use. Silicon oil bath was used for reactions that required heating. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel glass plates (60-F_{254}) that were analyzed by fluorescence upon 254 nm irradiation or by staining with p-anisaldeyde/AcOH/H_2SO_4/EtOH or by staining with $KMnO_4$ solution. The products were purified by column chromatography on silica gel (spherical, neutral, 100−230 μm) with an eluent of Pet-ether/EtOAc. NMR spectra were

recorded with Advance III-500 (Bruker) (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer and referenced to the solvent peak at 7.26 ppm (^{1}H), 77.00 ppm (^{13}C) for $CDCl_3$ and 96.16 ppm (^{13}C) for CCl_4. Infrared spectra were recorded with a Bruker-Alpha (ATR-ZnSe) spectrometer and reported as wavenumber (cm^{-1}). A Q-Exactive benchtop HRMS was used for the high-resolution analysis.

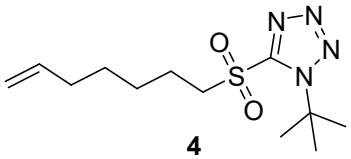
EXPERIMENTAL DETAILS



Preparation of 5-(hept-6-en-1-ylsulfonyl)-1-phenyl-1H-tetrazole (3): General procedure I**:** To a stirred suspension of NaH (1.122 g, 11.22 mmol, 60 % in paraffin oil) in THF (30 mL) was added 1-phenyl-1H-tetrazole-5-thiol (PTSH) (2 g, 11.22 mmol) at 0 °C. After 30 min 7-bromohept-1-ene (2.013 g, 11.22 mmol) was added dropwise to the reaction mixture. The resulting mixture was allowed to warm to room temperature. After 12 h, the completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with saturated aqueous NH_4Cl (20 mL), the organic layer was separated. The aqueous layer was extracted with EtOAc (20 mL x 2), the combined organic layers were washed with water, brine, dried over $NaSO_4$, filtered and the solvents were removed under reduced pressure to get the sulfide.

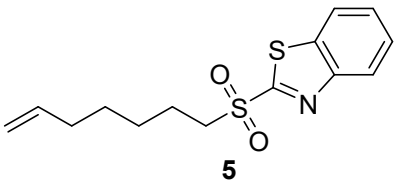
The above residue was then dissolved in ethanol to which, ammonium heptamolybdate (1.3 g, 1.12 mmol) dissolved in H_2O_2, 30% solution (1.2 ml, 11.2 mmol) was added at 0 °C. After 10 h of stirring, the completion of the reaction was confirmed by TLC analysis, ethanol was evaporated and the crude was dissolved in water (30 ml) and ethyl acetate (30 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (20 ml x 2). The combined organic layer was washed with water, followed by brine, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (silica

gel, 10% EtOAc/ Pet ether) to obtain the desired sulfone **3** (2.9 g, 81%) as a yellow liquid (R_f = 0.5 in 10% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.69 (d, *J* = 5Hz, 2H), 7.65-7.60 (m, 3H), 5.82-5.74 (m, 1H), 5.03-4.96 (dd, *J* = 7.6, 17.5 Hz, 2H), 3.75-3.72 (t, *J* = 7.75 Hz, 2H), 2.10-2.06 (q, *J* = 7 Hz, 2H), 2.00-1.94 (m, 2H), 1.58-1.46 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 131.5, 129.7, 125.1, 115.0, 55.9, 33.2, 28.1, 27.5, 21.9; IR (neat) 3159, 2968, 2260, 1807, 1631, 1469, 1269, 1093, 908, 738 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M + H]^+$ Calculated for $C_{14}H_{18}N_4O_2S$ 307.1223, Found 307.1246



4

1-(*tert*-butyl)-5-(hept-6-en-1-ylsulfonyl)-1*H*-tetrazole (4): General procedure I was followed for the synthesis of sulfone **4**, from 7-bromohept-1-ene and 1-(tert-butyl)-1H-tetrazole-5-thiol. The product **7** (0.9 g, 92%) obtained as a yellow liquid. (R_f= 0.5 in 20 % EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83-5.75 (m, 1H), 1.55-1.47 (m, 4H), 5.03-4.96 (dd, *J* = 15, 25 Hz, 2H), 3.82-3.79 (t, *J* = 5, 15 Hz, 2H), 2.11-2.07 (q, *J* = 10, 15 Hz, 2H), 2.02-1.96 (m, 2H), 1.86 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 114.9, 99.9, 65.4, 56.6, 33.2, 29.7, 28.1, 27.6, 22.0; IR (neat) 2969, 2937, 2867, 1507, 1466, 1389, 1249, 1149, 1093, 916, 763, 669 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{12}H_{23}N_4O_2S$ 287.1536; Found 287.1534.



5

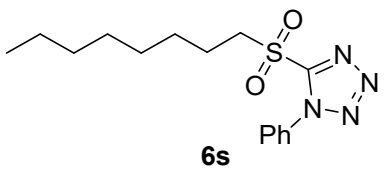
2-(hept-6-en-1-ylsulfonyl)benzothiazole (5): General procedure I was followed for the synthesis of sulfone **5**, from 7-bromohept-1-ene and benzothiazole. The product **8** (1.4 g, 84%) obtained as a yellow liquid. (R_f = 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21-8.19 (d, *J* = 10 Hz, 1H), 8.01-8.00 (d, *J* = 5 Hz, 1H), 1.47-1.42 (m, 4H), 7.64-7.58 (m, 2H) 1.92-1.86 (m, 2H), 5.75-5.65 (m, 1H), 4.97-4.89 (m, 2H), 3.51-3.48 (m, 2H), 2.05-2.01 (q, *J* = 10, 15 Hz, 2H), 1.87-2.01 (m, 2H), 1.44-1.48 (m, 4H) ; ^{13}C NMR (125 MHz, CCl_4+$CDCl_3$): δ 138.3, 125.9, 124.5, 114.9, 109.5, 73.6, 72.5, 69.3, 68.9, 39.4, 34.3, 33.5, 27.9,

26.8, 26.0, 25.8; IR (neat) 2939, 1480, 1338, 1154, 769, 735 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{14}H_{18}NO_2S_2$ 296.0773; Found 296.0770.

Condition A: To a stirred solution of sulfone (0.5 mmol) and (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde[1] (0.6 mmol) in THF (10 mL), was added KHMDS (0.75 mmol, 1.17 M solution in THF) dropwise at -78 °C. After stirring for 30 min, the reaction mixture was wormed to 25 °C and stirred for 16 h. The reaction mixture was then treated with water and the organic layer was extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified with column chromatography (silica gel, 5% EtOAc/ Pet ether) to obtain the olefin.

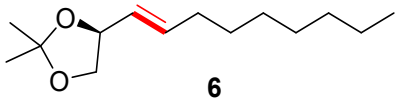
Condition B – Modified Julia-Kocienski reaction: To the stirred suspension of TBAB (2.5 mmol), sulfone (0.5 mmol) and aldehyde (0.6 mmol) in THF (10 mL), was added KHMDS (0.75 mmol, 1.17 M in THF) dropwise over 30 min using syringe pump at -78 °C. After stirring for 30 min, the reaction mixture was brought to 25 °C and stirred for 14 h. The completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with H_2O (15 mL) and the organic layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified with column chromatography (silica gel, 5% EtOAc/ Pet ether) to obtain the olefin.

(*S*,*E*)-2,2-dimethyl-4-(octa-1,7-dien-1-yl)-1,3-dioxolane (2): Olefin **2** was prepared from aldehyde **1**[17] and sulfone **3** using condition B. The product **2** (87 mg, 83%, *E*:*Z* = 7.0:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^1H NMR (500 MHz, $CDCl_3$) δ 5.83-5.75 (m, 2H), 5.45-5.41 (dd, *J* = 7.5, 15.5 Hz, 1H), 5.03-4.93 (m, 2H), 4.48-4.44 (q, *J* = 8 Hz, 1H), 4.07-4.04 (m, 1H), 3.57- 3.54 (t, *J* = 8.5 Hz, 1H), 2.06-2.04 (m, 4H), 1.42 (s, 3H), 1.41-1.38 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 135.9, 127.3, 114.4, 109.0, 69.5, 33.5, 32.1, 28.4, 28.3, 26.7, 25.9; IR (neat) 2949, 2873, 1741, 1509, 1473, 1383, 1260, 1225, 1161, 1107, 1068, 843, 781 cm^{-1}; HRMS (ESI-quadrupole) m/z: [M+H]+ Calculated for $C_{13}H_{23}O_2$ 211.1693; Found 211.1693; $[M+Na]^+$ Calculated for $C_{13}H_{22}O_2Na$ 233.1512; Found 233.1513.



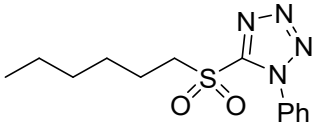
6s

5-(octylsulfonyl)-1-phenyl-1H-tetrazole (6s): General procedure I was followed for the synthesis of sulfone **6s**, from 1-bromooctane and 1-phenyl-1H-tetrazole-5-thiol. The product **6s** (1.48 g, 89 %) obtained as a pale-yellow solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.68 (m, 2H), 7.64-7.58 (m, 3H), 3.74-3.71 (t, *J* = 5 Hz, 2H), 1.98-1.89 (m, 2H), 1.52-1.45 (m, 2H), 1.36-1.24 (m, 8H), 0.89-0.86 (t, *J* = 5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 133.1, 131.4, 129.7, 125.1, 56.0, 31.6, 28.8, 28.1, 22.6, 21.9, 14.0; IR (neat) 2939, 2871, 1505, 1469, 1347, 1156, 767 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{15}H_{23}N_4O_2S$ 323.1541; Found 323.1534; $[M+Na]^+$ Calculated for $C_{15}H_{22}N_4O_2SNa$ 345.1361; Found 345.1353.



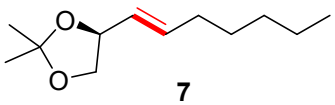
6

(*S*,*E*)-2,2-dimethyl-4-(non-1-en-1-yl)-1,3-dioxolane (6): Olefin **6** was prepared from aldehyde **1** and sulfone **6s** using condition B. The product **6** (68 mg, 60%, *E*:*Z* = 5.3:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76-5.82 (m, 1H), 5.38-5.45 (m, 1H), 4.44-4.49 (m, 1H), 4.05-4.07 (dd, *J* = 5, 10 Hz, 1H), 3.50-3.57 (dd, *J* = 5, 15 Hz, 1H), 2.02-2.07 (m, 2H), 1.43 (s, 3H), 1.39 (s, 3H), 1.26-1.30 (m, 10H), 0.87-0.90 (t, *J* = 5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 136.2, 127.1, 109.0, 77.5, 69.5, 32.3, 31.8, 29.15, 29.13, 28.9, 26.8, 25.9, 22.6, 14.1; IR (neat) 3001, 2972, 2943, 2872, 1469, 1381, 1254, 1225, 1164, 1068, 974, 866 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{26}O_2Na$ 249.1825; Found 249.1835.



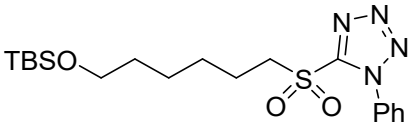
7s

5-(hexylsulfonyl)-1-phenyl-1H-tetrazole (7s): General procedure I was followed for the synthesis of sulfone **7s**, from 1-bromohexane and 1-phenyl-1H-tetrazole-5-thiol. The product **7s** (1.52 g, 92 %) obtained as a white solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.70 (m, 2H), 7.58-7.62 (m, 3H), 3.71-3.74 (t, *J* = 5 Hz, 2H), 1.92-.1.98 (m, 2H), 1.50-1.53 (m, 2H), 1.33-1.34 (m, 4H), 0.89-9.92 (t, *J* = 5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 133.0, 131.4, 129.7, 125.0, 55.9, 30.9, 27.7, 22.2, 21.9, 13.8; IR (neat) 2940, 2872, 1505, 1469, 1348, 1158, 770 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{13}H_{19}N_4O_2S$ 295.1228; Found 295.1223; $[M+Na]^+$ Calculated for $C_{13}H_{18}N_4O_2SNa$ 317.1048; Found 317.1041.



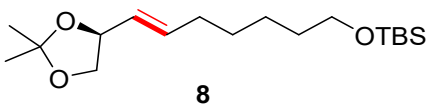
7

(*S*,*E*)-4-(hept-1-en-1-yl)-2,2-dimethyl-1,3-dioxolane (7): Olefin **7** was prepared from aldehyde **1** and sulfone **7s** using condition B. The product **7** (98 mg, 99%, *E*:*Z* = 3.3:1) obtained as a pale-yellow liquid. (R_f = 0.75 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76-5.82 (m, 1H), 5.38-5.45 (m, 1H), 4.44-4.46 (m, 1H), 4.04-4.07 (dd, *J* = 5, 15 Hz, 1H), 3.49-3.57 (dd, *J* = 15, 5 Hz, 1H), 2.02-2.07 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.28-1.38 (m, 6H), 0.87-0.89 (t, *J* = 5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 127.1, 109.0, 77.4, 69.5, 32.2, 31.4, 28.6, 26.8, 25.9, 22.5, 14.0; IR (neat) 3000, 2972, 2942, 2874, 1470, 1381, 1252, 1223, 1162, 1066, 1035, 974, 866 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{12}H_{23}O_2$ 199.1692; Found 199.1691; $[M+Na]^+$ Calculated for $C_{12}H_{22}O_2Na$ 221.1512; Found 221.1510.



8s

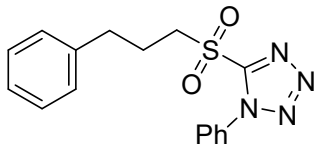
5-((6-((*tert*-butyldimethylsilyl)oxy)hexyl)sulfonyl)-1-phenyl-1*H*-tetrazole (8s): General procedure I was followed for the synthesis of sulfone **8s**, from ((6-bromohexyl)oxy)(tert-butyl)dimethylsilane and 1-phenyl-1H-tetrazole-5-thiol. The product **8s** (1.35g, 94 %) obtained as a yellow liquid. (R_f = 0.5 in 10 % EtOAc in petroleum ether) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.53 (m, 3H), 3.62-3.65 (t, *J* = 5 Hz, 2H), 3.50-3.53 (t, *J* = 5 Hz, 2H), 1.85-1.92 (m, 2H), 1.44-147 (m, 4H), 1.34-1.43 (m, 2H), 0.81 (s, 9H), -0.05 (s, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.2, 129.6, 125.0, 62.7, 55.8, 32.3, 28.0, 26.0, 25.3, 22.6, 18.3, -5.2,; IR (neat) 2944, 2872, 1506, 1471, 1347, 1259, 1157, 1103, 1048, 1017, 839, 765, 733, 692, 630 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{19}H_{33}N_4O_3SSi$ 425.2042; Found 425.2039; $[M+Na]^+$ Calculated for $C_{19}H_{32}N_4O_3SSiNa$ 447.1862; Found 447.1856.



8

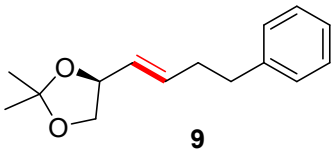
(*S*,*E*)-*tert*-butyl((7-(2,2-dimethyl-1,3-dioxolan-4-yl)hept-6-en-1-yl)oxy)dimethylsilane (8): Olefin **8** was prepared from aldehyde **1** and sulfone **8s** using condition B. The product **8** (82 mg, 50%, *E*:*Z* = 8.5:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum

ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74-5.80 (m, 1H), 5.39-5.43 (dd, *J* = 8, 15 Hz, 1H), 4.42-4.68 (t, *J* = 7.8 Hz, 1H), 4.02-4.07 (t, *J* = 7, 1 H), 3.57-3.60 (t, *J* = 6.5 Hz, 3H), 3.52-3.55 (t, *J* = 8 Hz, 1H), 2.03-2.08 (m, 2H), 1.93 (m, 2H), 1.48-1.53 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H), 1.31-1.36 (m, 2H), 0.89 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$ + CCl_4) δ 135.6, 127.5, 127.4, 108.9, 77.4, 72.0, 69.5, 32.3, 31.4, 29.4, 28.7, 27.8, 26.9, 26.8, 26.1, 22.5,14.1; IR (neat) 3000, 2945, 2911, 2874, 1740, 1513, 1471, 1383, 1259, 1220, 1165, 1106, 1065, 976, 842, 780. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{36}O_3SiNa$ 351.2331; Found 351.2330.



9s

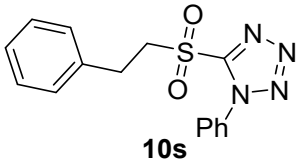
1-phenyl-5-((3-phenylpropyl)sulfonyl)-1H-tetrazole (9s): General procedure I was followed for the synthesis of sulfone **9s**, from (3-bromopropyl)benzene and 1-phenyl-1H-tetrazole-5-thiol. The product **9s** (1.49 g, 91 %) obtained as a white solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.56 (m, 2H), 7.53-7.50 (m, 3H), 7.24-7.21 (t, *J* = 10 Hz, 2H), 7.17-7.13 (m, 1H), 7.10-7.09 (d, *J* = 5 Hz, 2H), 3.63-3.59 (t, *J* = 10 Hz, 2H), 2.76-2.73 (t, *J* = 5 Hz, 2H), 2.23-2.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 139.2, 133.2, 131.5, 129.7, 128.8, 128.5, 126.7, 125.1, 55.2, 33.9, 23.6; IR(neat) 3085, 3043, 2939, 2880, 1606, 1505, 1405, 1348, 1269, 1235, 1166, 1110, 1083, 1052, 1021, 767 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{16}H_{17}N_4O_2S$ 329.1067; Found 329.1067; [M+Na]+ Calculated for $C_{16}H_{16}N_4O_2SNa$ 351.0886; Found 351.0885.



9

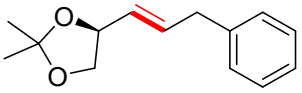
(*S*,*E*)-2,2-dimethyl-4-(4-phenylbut-1-en-1-yl)-1,3-dioxolane 9: Olefin **9** was prepared from aldehyde **1** and sulfone **9s** using condition B. The product **9** (80 mg, 69%, *E*:*Z* = 9.2:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.29 (m, 2H), 7.16-7.2 (m, 3H), 5.80-5.85 (m, 1H), 5.45-5.49 (dd, *J* = 15, 5 Hz, 1H), 4.43 (q, *J* = 15, 10 Hz, 1H),1.38 (s, 3H),), 4.03-4.05 (dd, *J* = 5, 5 Hz 1H), 3.51-3.54 (t, *J* = 15 Hz, 1H), 2.67-2.74 (m, 2H), 2.34-2.4 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 134.7, 128.4, 128.3, 128.0, 125.9, 109.1, 77.2, 69.4, 35.3, 34.0, 26.7, 25.9; IR (neat) 3040, 3000, 2942, 2874, 1460, 1379, 1253, 1220, 1160, 1063, 972, 864, 748 cm^{-1}. HRMS (ESI-

quadrupole) m/z: $[M+H]^+$ Calculated for $C_{15}H_{21}O_2$ 233.1536; Found 233.1536; $[M+Na]^+$ Calculated for $C_{15}H_{20}O_2Na$ 255.1354; Found 255.1354.



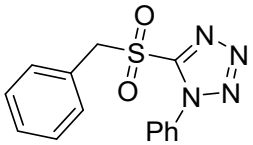
10s

5-(phenethylsulfonyl)-1-phenyl-1H-tetrazole (10s): General procedure I was followed for the synthesis of sulfone **10s**, from (2-bromoethyl)benzene and 1-phenyl-1H-tetrazole-5-thiol. The product **10s** (1.57 g, 93%) obtained as a white solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.68 (m, 2H), 7.64-7.61 (m, 3H), 7.34-7.31 (t, *J* = 5 Hz, 2H), 7.28-7.25 (m, 3H), 4.01-3.98 (m, 2H), 3.28-3.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 136.3, 133.0, 131.5, 129.8, 129.0, 128.5, 127.4, 125.1, 57.3, 28.5; IR (neat) 3107, 3064, 3039, 2988, 1610, 1506, 1464, 1421, 1534, 1163 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{15}H_{15}N_4O_2S$ 315.0910; Found 315.0912; $[M+Na]^+$ Calculated for $C_{15}H_{14}N_4O_2SNa$ 337.0730; Found 337.0731.



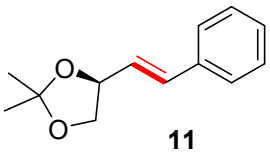
10

(*S*,*E*)-2,2-dimethyl-4-(3-phenylprop-1-en-1-yl)-1,3-dioxolane (10): Olefin **10** was prepared from aldehyde **1** and sulfone **10s** using condition B. The product **10** (72 mg, 66%, *E*:*Z* = 9.8:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.23 (m, 2H), 7.09-7.15 (m, 3H), 5.84-5.90 (dt, *J* = 10, 15 Hz, 1H), 5.42-5.47 (dd, *J* = 5, 15 Hz, 1H), 4.87-4.91 (q, *J* = 5 Hz, 1H), 4.41-4.45 (q, *J* = 5 Hz, 1H), 3.99-4.01 (t, *J* = 5 Hz, 1H), 3.49-3.52 (t, *J* = 10 Hz, 1H), 3.32-3.33 (d, *J* = 5 Hz, 2H), 1.35 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 139.5, 134.1, 128.7, 128.4, 128.4, 126.2, 109.1, 76.7, 69.4, 38.6, 26.7, 25.9; IR (neat) 3004, 2946, 2889, 1382, 1261, 1225, 1163, 1068, 978, 867 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{18}O_2Na$ 241.1199; Found 241.1200.



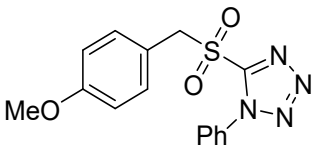
11s

5-(benzylsulfonyl)-1-phenyl-1H-tetrazole (11s): General procedure I was followed for the synthesis of sulfone **11s**, from (bromomethyl)benzene and 1-phenyl-1H-tetrazole-5-thiol. The product **11s** (1.53 g, 90%) obtained as a white solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-5.58 (t, *J* = 5 Hz, 1H), 7.47-7.50 (t, *J*= 5 Hz, 2H), 7.29-7.41 (m, 7H), 4.93 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 132.8, 131.7, 131.4, 129.8, 129.4, 129.1, 125.3, 124.8, 62.4; IR (neat) 2980, 2935, 2896, 2869, 1544, 1505, 1468, 1442, 1357, 1162, 1133, 1108, 916, 887, 792, 769, 696 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{14}H_{13}N_4O_2S$ 301.0759; Found 301.0754; $[M+Na]^+$ Calculated for $C_{14}H_{12}N_4O_2SNa$ 323.0578; Found 323.0573.



11

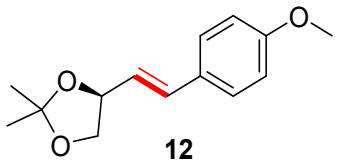
(*S*,*E*)-2,2-dimethyl-4-styryl-1,3-dioxolane (11): Olefin **11** was prepared from aldehyde **1** and sulfone **11s** using condition B. The product **11** (68 mg, 67%, *E*:*Z* = 6.5:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.39 (m, 2H), 7.27-7.33 (m, 2H), 7.23-7.26 (m, 1H), 6.65-6.68 (d, *J* = 15 Hz, 1H), 6.13-6.18 (dd, *J* = 15, 10 Hz, 1H), 4.65-4.70 (ddd, *J* = 15, 10 Hz, 1H), 4.14-4.16 (dd, *J* = 10, 5 Hz, 1H), 3.66-3.69 (dd, *J* = 10, 5 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 133.3, 128.7, 128.6, 128.3, 126.6, 109.4, 77.2, 69.5, 26.7, 25.79; IR (neat) 3043, 3000, 2948, 2886, 1501, 1458, 1379, 1250, 1219, 1160, 1060, 1031, 970, 866, 750 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{13}H_{16}O_2Na$ 227.1043; Found 227.1044.



12s

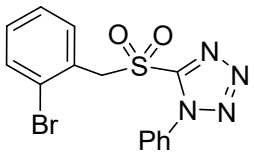
5-((4-methoxybenzyl)sulfonyl)-1-phenyl-1H-tetrazole (12s): General procedure I was followed for the synthesis of sulfone **12s**, from 1-(bromomethyl)-4-methoxybenzene and 1-phenyl-1H-tetrazole-5-thiol. The product **12s** (1.46g, 89%) obtained as a pale-yellow solid. (R_f = 0.5 in 10 % EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.55 (t, *J* = 5 Hz, 1H), 7.51-7.48 (t, *J* = 10 Hz, 2H), 7.36-7.35 (d, *J* = 5 Hz, 2H), 7.25-7.24 (d, *J* = 5 Hz, 2H), 6.87-6.85 (d, *J* = 10 Hz, 2H), 4.87 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz,CCl_4+$CDCl_3$): δ 160.8, 152.9, 132.9, 131.2, 129.3, 125.3, 116.4, 114.5, 64.1, 61.8, 55.2; IR (neat) 2944, 1815, 1779, 1618, 1521, 1471, 1427, 1357, 1263, 1187, 1163, 1143, 1111, 1037, 882, 845, 769 cm^{-1}.

HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{15}H_{15}N_4O_3S$ 331.0859; Found 331.0859; $[M+Na]^+$ Calculated for $C_{15}H_{14}N_4O_3SNa$ 353.0679; Found 353.0679.



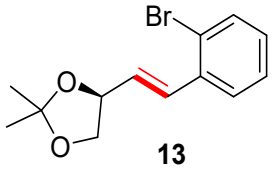
12

(*S,E*)-4-(4-methoxystyryl)-2,2-dimethyl-1,3-dioxolane (12): Olefin **12** was prepared from aldehyde **1** and sulfone **12s** using condition B. The product **12** (94 mg, 80%, *E*:*Z* = 6.6:1) obtained as a pale-yellow liquid (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.34 (m, 2H), 7.20-7.22 (m, 2H), 6.64-6.66 (d, *J* = 10 Hz, 1H), 6.59-6.62 (d, *J* = 15 Hz, 1H), 5.99-6.04 (dd, *J* = 10 Hz, 5 Hz, 1H), 4.63-4.67 (m, 1H), 4.13-4.15 (m, 1H), 3.81 (s, 1 H), 3.80 (s, 3H), 3.65-3.67 (dd, *J* = 5, 10 Hz, 1H), 1.47 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 133.1, 130.0, 127.8, 124.3, 114.0, 109.3, 77.4, 69.5, 55.3, 26.7, 25.9,; IR (neat) 3001, 2947, 2890, 1615, 1518, 1468, 1380, 1305, 1252, 1182, 1160, 1061, 1036.35, 972.35, 846.87, 815.24, 735 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{18}O_3Na$ 257.1148; Found 257.1168.



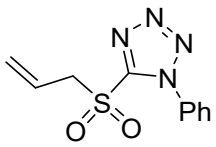
13s

5-((2-bromobenzyl)sulfonyl)-1-phenyl-1H-tetrazole (13s): General procedure I was followed for the synthesis of sulfone **13s**, from 1-bromo-2-(bromomethyl)benzene and 1-phenyl-1H-tetrazole-5-thiol. The product **13s** (1.26g, 83%) obtained as a white solid. (R_f= 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.56 (d, *J* = 10 Hz, 1H), 7.52-7.49 (t, *J* = 10 Hz, 1H), 7.46-7.42 (q, *J* = 5 Hz, 5H), 7.26-7.19 (m, 2 H), 5.19 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 133.7, 133.4, 132.8, 130.4, 131.4, 129.50, 128.00, 126.6, 125.2, 124.1, 61.7; IR (neat) 2932, 2865, 1504, 1480, 1448, 1405, 1361, 1164, 1033, 772 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{14}H_{12}BrN_4O_2S$ 378.9859, 380.9838; Found 378.9855, 380.9834.



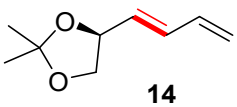
13

(*S,E*)-4-(2-bromostyryl)-2,2-dimethyl-1,3-dioxolane (13): Olefin **13** was prepared from aldehyde **1** and sulfone **13s** using condition B. The product **13** (92 mg, 65%, *E*:*Z* = 9.6:1) obtained as a pale-yellow liquid. (R_f = 0.75 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.48 (m, 2H), 7.18-7.22 (m, 1H), 7.02-7.05 (m, 1H), 6.93 (d, *J* = 15 Hz, 1H), 6.02-6.07 (dd, *J* = 10, 15 Hz 1H), 4.64-4.68 (q, *J* = 5 Hz, 1H), 4.11-4.14 (t, *J* = 5 Hz, 1H), 3.63-3.66 (t, *J* = 5 Hz, 1H),1.42 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 131.9, 130.9, 128.9, 128.2, 126.5, 126.2, 122.7, 108.6, 75.9, 68.4, 25.7, 24.9,; IR (neat) 3001, 2950, 2886, 1475, 1381, 1257, 1222, 1161, 1066, 1031, 972, 867, 757 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{13}H_{15}BrO_2Na$ 305.0148, 307.0127; Found 305.0143, 307.0122.



14s

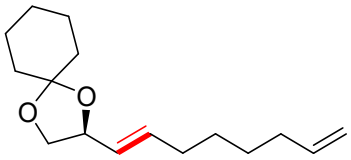
5-(allylsulfonyl)-1-phenyl-1H-tetrazole (14s): General procedure I was followed for the synthesis of sulfone **14s**, from 3-bromoprop-1-ene and 1-phenyl-1H-tetrazole-5-thiol. The product **14s** (1.611 g, 78%) obtained as a pale-yellow liquid. (R_f = 0.5 in 10 % EtOAc in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57-7.66 (m, 5H), 5.58-5.57 (d, *J* = 5 Hz, 1H), 5.54-5.55 (d, *J* = 5 Hz, 1H), 4.42-4.44 (d, *J* = 10 Hz, 2H),; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 132.9, 131.5, 129.7, 127.8, 125.2, 121.8, 60.2; IR (neat) 2932, 1603, 1505, 1469, 1427, 1352, 1255, 1157, 1108, 1084, 1051, 1020, 994, 951, 871, 768, 694, 665 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{10}H_{11}N_4O_2S$ 251.0602; Found 251.0598; $[M+Na]^+$ Calculated for $C_{10}H_{10}N_4O_2SNa$ 273.0422; Found 273.0416.



14

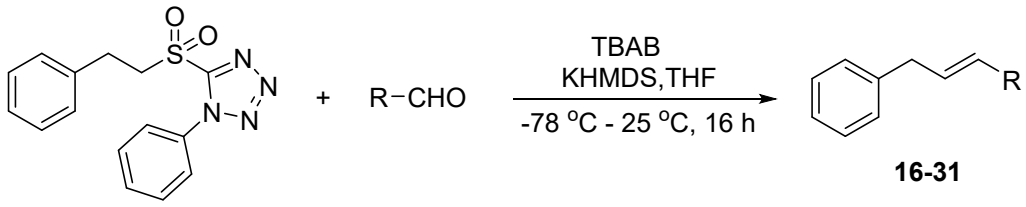
(*S,E*)-4-(buta-1,3-dien-1-yl)-2,2-dimethyl-1,3-dioxolane (14): Olefin **14** was prepared from aldehyde **1** and sulfone **14s** using condition B. The product **14** (42 mg, 55%, *E*:*Z* = 2.8:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24-6.35 (m, 2H), 5.61-5.66 (dd, *J* = 10, 15 Hz, 1H), 5.19-5.21 (m, 1H), 5.11-

5.13 (m, 1H), 4.48-4.53 (q, J = 10 Hz, 1H), 4.05-4.10 (dd, J = 5, 15 Hz, 1H), 3.54-3.58 (dd, J = 5, 15 Hz, 1H), 3.49-3.57 (dd, J = 5, 15 Hz, 1H), 2.02-2.07 (m, 2H), 1.41 (s, 3H), 1.37 (s, 3H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 133.8, 130.8, 118.4, 109.3, 76.6, 69.4, 26.7, 26.0; IR (neat) 3001, 2944, 2875, 1612, 1465, 1381, 1257, 1223, 1160, 1129, 1064, 1009, 913, 866, 798cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_9H_{15}O_2$ 155.1067; Found 155.1065.

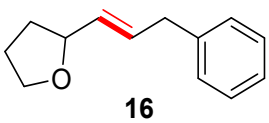


15

(*S*,*E*)-2-(octa-1,7-dien-1-yl)-1,4-dioxaspiro[4.5]decane (15): Olefin **15** was prepared from 1,4-dioxaspiro[4.5]decane-2-carbaldehyde[2] and sulfone **3** using condition B. The product **15** (73 mg, 59%, E:Z = 5.9:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 5.43-5.38 (dd, J = 10, 15 Hz, 1H), 5.81-5.72 (m, 2H), 4.99-4.92 (dd, J = 15, 25 Hz, 2H), 4.45-4.41 (q, J = 10 Hz, 1H), 4.04-4.01 (t, J = 10 Hz, 1H), 3.53-3.50 (t, J = 5 Hz, 1H), 2.05-2.04 (m, 4H), 1.65-1.55 (m, 8H), 1.41-1.39 (m, 6H); ^{13}C NMR (125 MHz,CCl_4+$CDCl_3$) δ 138.6, 135.2, 127.9, 114.6, 109.6, 69.1, 36.4, 35.6, 33.6, 32.1, 28.4, 25.2, 23.9, 23.9; IR (neat) 3099, 3075, 3041, 2942, 2875, 1610, 1502, 1459, 1098, 1073, 1033, 978, 914, 738 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{16}H_{26}O_2Na$ 273.1825; Found 273.1826.



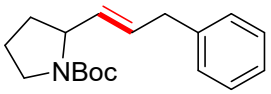
10s **16-31**



16

(*E*)-2-(3-phenylprop-1-en-1-yl)tetrahydrofuran (16): The olefin **16** was prepared from tetrahydrofuran-2-carboxaldehyde and sulfone **10s** using conditions B. The product **10** (28 mg, 30%, E:Z = 15.7:1) obtained as a colourless liquid. (R_f = 0.6 in 5% EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 7.29-7.25 (dd, J = 5, 15 Hz, 2H), 7.20-7.17 (t, J = 5 Hz, 3H),

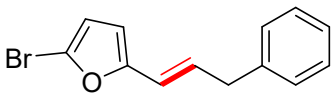
4.29-4.25 (q, J = 5 Hz, 1H), 3.90-3.87 (q, J = 10 Hz, 1H), 3.78-3.74 (q, J = 5 Hz, 1H), 3.38-3.37 (d, J = 5 Hz, 2H), 2.06-2.00 (m, 1H), 1.93-1.88 (m, 2H), 1.64-1.57 (m, 1H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.2, 130.9, 128.6, 128.4, 126.0, 79.7, 67.9, 38.6, 32.2, 25.9; IR (neat) 3097, 3074, 3043, 2981, 2942, 2875, 1503, 1460, 1058, 975, 750 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{13}H_{17}O$ 189.1274; Found 189.1276.



17

(*E*)-*tert*-butyl (*S*)-2-(3-phenylprop-1-en-1-yl)pyrrolidine-1-carboxylate (17): The olefin **17** was prepared from *N*-boc-pyrrolidine-2-carboxaldehyde[3] and sulfone **10s** using conditions B. The product **17** (80 mg, 60%) obtained as a yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). {Note: The NMR of product **17** was complex to analyze the diastereomeric ratio, to analyze *E*/*Z*-ratio the Boc group was deprotected}

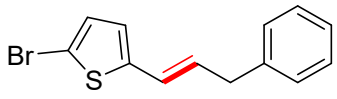
A portion of the compound **17** (25 mg, 0.08 mmol) was treated with TFA (0.5 mL) in dichloromethane (2 mL) at 0 °C for 3 h. The solvents were evaporated and the crude compound was purified using column chromatography (silica gel, 5% MeOH in CH_2Cl_2) to obtain the corresponding olefin "(*E*)-2-(3-phenylprop-1-en-1-yl)pyrrolidine" (13 mg, 80%, *E*:*Z* = 19.2:1) as yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.20 (m, 2H), 7.07-7.10 (m, 3H), 5.65-5.71 (m, 1H), 5.44-5.50 (m, 1H), 3.48-3.52 (q, J = 5 Hz, 1H), 3.26-3.28 (d, J = 10 Hz, 2H), 2.97-3.07 (m, 1H), 2.80-2.88 (m, 1H), 1.67-1.92 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.8, 130.4, 128.5, 128.4, 126.0, 60.7, 46.0, 38.7, 32.1, 25.0; IR (neat) 3376, 2971, 2937, 2740, 1632, 1501, 1458, 1419, 1032, 978, 790, 747, 704cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{13}H_{18}N$ 188.1439; Found 188.1433.



18

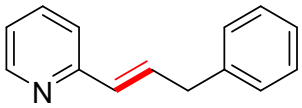
(*E*)-2-bromo-5-(3-phenylprop-1-en-1-yl)furan (18): The olefin **18** was prepared from 5-bromofuran-2-carbaldehyde and sulfone **10s** using conditions B. The product **18** (88 mg, 67%, *E*:*Z* = 9.5:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5 % EtOAc in petroleum ether). ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (t, J = 8 Hz, 2H), 7.25-7.20 (m, 3H), 6.35-6.29 (m, 1H), 6.24-6.23 (d, J = 3 Hz, 1H), 6.13 (s, 1H), 6.10- 6.09 (s, 1H), 3.50-3.49 (d, J = 7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 139.5, 129.0, 128.7, 128.5, 126.3, 120.8, 118.7, 112.8,

108.9, 39.0; IR (neat) 3366, 2974, 1736, 1636, 1492, 1388, 1254.94, 1161, 1040, 880, 764 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M + H]^+$ Calculated for $C_{13}H_{12}BrO$ 263.0066, 265.0046; Found 263.0067, 265.0047.



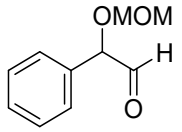
19

(*E*)-2-bromo-5-(3-phenylprop-1-en-1-yl)thiophene (19): The olefin **19** was prepared from 5-bromothiophene-2-carbaldehyde and sulfone **10s** using conditions B. The product **19** (124 mg, 89%, *E*:*Z* = 45.4:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 6.85-6.84 (m, 1H), 6.59-6.58 (d, *J* = 4 Hz, 1H), 6.41-6.38 (d, *J* = 15.5 Hz, 1H), 6.11-6.05 (m, 1H), 3.47-3.46 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, CCl_4+$CDCl_3$) δ 144.3, 139.3, 130.0, 129.7, 128.8, 128.6, 126.4, 124.9, 123.9, 110.3, 39.1; IR (neat) 3063, 2923, 2854, 1724, 1672, 1602 1494, 1416, 1201, 1051, 959, 798 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M + H]^+$ Calculated for $C_{13}H_{12}BrS$ 278.9837, 280.9807; Found 278.9815, 280.9785.



20

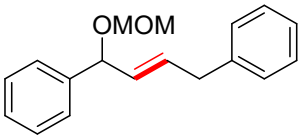
(*E*)-2-(3-phenylprop-1-en-1-yl)pyridine (20): The olefin **20** was prepared from pyridine-2-carbaldehyde and sulfone **10s** using conditions B. The product **20** (92 mg, 94%, *E*:*Z* =11.7:1) obtained as a pale-brown liquid. (R_f = 0.65 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38-8.39 (d, *J* = 4.5 Hz, 1H), 7.42-7.45 (m, 2H), 7.15-7.18 (m, 2H), 7.06-7.12 (m, 4H), 6.93-6.95 (m, 1H), 6.70-6.77 (m, 1H), 6.36-6.39 (d, *J* = 16 Hz, 1H), 3.46-3.47 (d, *J* = 7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$ + CCl_4) δ 155.8, 149.4, 139.4, 136.2, 134.1, 130.1, 128.7, 128.5, 126.2, 121.6, 120.1, 39.1; IR (neat) 3074, 3042, 3018, 1657, 1592, 1436, 1304, 1155, 977, 753 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+H]^+$ Calculated for $C_{14}H_{14}N$ 196.1121; Found 196.1121.



21a

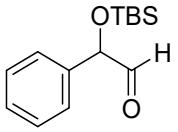
2-(methoxymethoxy)-2-phenylacetaldehyde (21a):[4] To a stirred solution of ethyl 2-hydroxy-2-phenylacetate (1.5 g, 8.3 mmol) and DIPEA (1.73 ml, 9.9 mmol) in DCM (20 mL), MOMCl (0.75 ml, 9.9 mmol) was added at 0 °C. The reaction mixture was allowed to stir at 25 °C for 6 h and the completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with aq. NH_4Cl (15 mL) and organic layer was extracted with DCM (20 mL x 2). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum to obtain the desired product as yellow oil.

General Procedure II: The crude product (1.5 g, 6.6 mmol) was dissolved in DCM (15 mL), and then treated with DIBAL-H (5.72 ml, 8.02 mmol) by adding dropwise (15 min) at -78 °C. After 15 min, the completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with aq. potassium sodium tartrate (10 mL) at -78 °C and allowed to stir at 25 °C for 1 h. The organic layer was extracted with DCM (15 mL x 2), dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography to yield the desired aldehyde **21a** (0.9 g, 76%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (d, J = 5 Hz, 1H), 7.35-7.43 (m, 5H), 5.04 (d, J = 5 Hz, 1H), 4.74-4.79 (dd, J = 10 Hz, 15 Hz, 2H), 3.42 (s, 3H); IR (neat) 2932, 1741, 1709, 1460, 1212, 1109, 1023, 922, 755 cm^{-1}.



21

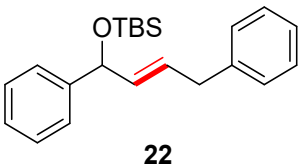
(*E*)-(1-(methoxymethoxy)but-2-ene-1,4-diyl)dibenzene (21): The olefin **21** was prepared from **21a** and sulfone **10s** using conditions B. The product **21** (117 mg, 87%, *E*:*Z* = 5.2:1) obtained as a pale-yellow liquid. (R_f = 0.6 in 5% EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 3H), 7.20-7.16 (m, 4H), 7.11-7.06 (m, 3H), 5.85-5.79 (m, 1H), 5.62-5.55 (m, 1H), 5.01-5.00 (d, J = 7 Hz, 1H), 4.66-4.64 (d, J = 10 Hz, 1H), 4.51-4.50 (d, J = 6.5 Hz, 1H), 3.32-3.31 (d, J = 7 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 139.9, 132.3, 131.5, 128.6, 128.5, 127.6, 126.9, 126.8, 126.1, 93.4, 77.7, 55.4, 38.7; IR (neat) 3077, 2949, 1735, 1610, 1459, 1367, 1282, 1102, 974, 852 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{20}O_2Na$ 291.1355; Found 291.1352.



22a

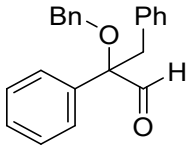
2-((tert-butyldimethylsilyl)oxy)-2-phenylacetaldehyde (22a):[5] To a stirred solution of ethyl 2-hydroxy-2-phenylacetate (4 g, 22.2 mmol) in DMF (50 ml) was added imidazole (1.81g, 26.63 mmol). TBSCl (4.1g, 26.6 mmol) was then added at 0 °C and stirred for 30 min. The reaction mixture was allowed to stir at 25 °C for 12 h and the reaction completion was confirmed by TLC analysis. The reaction mixture was treated with aq. NH_4Cl (20 mL), washed with ice-cold brine water and the organic layer was extracted with ethyl acetate (15 mL x 2). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The product was obtained as a pale-yellow oil (87%) and was used for further steps.

The crude TBS protected alcohol was then converted to aldehyde **22a** following the general procedure II. The aldehyde **22a** (1.2 g, 75%) was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.51-9.52 (d, J = 5 Hz, 1H), 7.38-7.39 (m, 4H), 7.32-7.34 (m, 1H), 5.01 (d, J = 5 Hz, 1H), 0.95 (s, 9H), 0.12 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 143.7, 128.4, 127.6, 125.7, 17.7, 54.0, 25.7, 18.1, -4.62, -5.13; IR (neat) 2968, 2945, 2872, 1744, 1711, 1261, 1208, 1108, 1076, 837, 708 cm^{-1}.



22

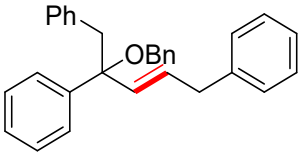
(*E*)-*tert*-butyl((1,4-diphenylbut-2-en-1-yl)oxy)dimethylsilane (22): The olefin **22** was prepared from aldehyde **22a** and sulfone **10s** using conditions B. The product **22** (152 mg, 90%, *E*:*Z* = 25.9:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 7.29-7.20 (m, 6H), 7.17-7.11 (m, 4H), 5.80-5.74 (m, 1H), 5.60-5.55 (dd, J = 5, 15 Hz, 1H), 5.13-5.12 (d, J = 6.5 Hz, 1H), 3.32-3.31 (d, J = 7 Hz, 2H), 0.85 (s, 9H), 0.00 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 140.3, 135.3, 128.7, 128.5, 128.4, 128.1, 126.9, 126.0, 125.9, 75.4, 38.5, 25.9, 18.3, -4.5, -4.8; IR (neat) 3043, 2945, 2870, 1501, 1260, 1070, 975, 782 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{22}H_{30}OSiNa$ 361.1958 Found 361.1955.



23a

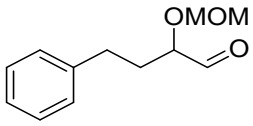
2-(benzyloxy)-2,3-diphenylpropanal (23a): To a stirred suspension of NaH (1.1 g, 27.72 mmol, 60 % in paraffin oil) in DMF (20 mL) was added ethyl 2-hydroxy-2-phenylacetate (2 g, 11.09 mmol) at 0 °C. After stirring for 15 min, benzylbromide (2.9 ml, 25 mmol) was added dropwise. The reaction mixture was allowed to stir for 6 h and the completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with aq. NH_4Cl (20 mL), washed with ice-cold water, brine and extracted with ethyl acetate (20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was passed through a small bed of silica gel using 10% EtOAc/ Pet ether.

The ester obtained above was directly used in next step to convert into aldehyde **23a**, following the general procedure II. The aldehyde **23a** (0.95 g, 68%) obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.33-7.34 (m, 2H), 7.21-7.29 (m, 8H), 7.07-7.08 (m, 3H), 6.95-6.97 (m, 2H), 4.58-4.68 (d, J = 10 Hz, 1H), 4.46-4.48 (d, J = 10 Hz, 1H), 3.53-3.56 (d, J = 15Hz, 1H), 3.38-3.41(d, J = 15Hz, 1H); IR (neat) 2970.58, 2938.25, 2868.73, 1742.72, 1466.53, 1385.39, 1267.06, 1097.83, 1023.59, 808.14 cm^{-1}.



23

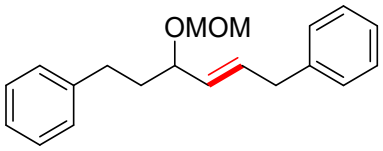
(*E*)-(2-(benzyloxy)pent-3-ene-1,2,5-triyl)tribenzene (23): The olefin **23** was prepared from aldehyde **23a** and sulfone **10s** using conditions B. The product **23** (162 mg, 80%, E:Z = 31.4:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5 % EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 7.29-7.16 (m, 13H), 7.06-7.02 (m, 5H), 6.82-6.80 (d, J = 7 Hz, 2H), 5.93-5.98 (m, 1H), 5.78-5.74 (d, J = 15.5 Hz, 1H), 4.40-4.38 (d, J = 12 Hz, 1H), 4.33-4.31 (d, J = 12 Hz, 1H), 3.39-3.37 (d, J = 6.5 Hz, 2H), 3.25-3.16 (q, J = 13.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 140.0, 139.4, 136.7, 133.4, 131.8, 130.9, 128.6, 128.5, 128.2, 128.0, 127.8, 127.3, 126.9, 126.1, 126.0, 82.1, 64.9, 53.4, 47.2, 39.1; IR (neat) 3078, 3045, 2970, 2941, 2918, 2876, 1503, 1459, 1036, 987, 739 cm^{-1}. HRMS (ESI-quadrupole) m/z: $[M + Na]^+$ Calculated for $C_{30}H_{28}ONa$ 427.2032; Found 427.2029.



24a

2-(methoxymethoxy)-4-phenylbutanal (24a):[6] To a stirred solution of 5-phenylpent-1-en-3-ol[7] (1 g, 6.17 mmol) in DCM (10 ml) was sequentially added DIPEA (3.2 ml, 18.51 mmol) and MOMCl (0.7 ml, 9.25 mmol) at 0 °C. After 10 min, the reaction mixture was warmed to 25 °C and stirred for 10 h. The completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with $NaHCO_3$ and the organic layer extracted with EtOAc (15 ml x 2), washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified using column chromatography (silica gel, pet ether) to obtain the desired product as yellow oil (78%).

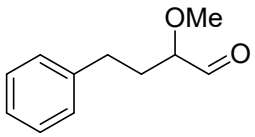
General procedure III**:** The MOM protected allylic alcohol (0.9 g, 4.8 mmol) obtained above was dissolved in DCM (10 ml) cooled to -78 °C, O_3 gas was passed for 5 min and the completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with PPh_3 (1.25 g, 4.8 mmol) and was allowed to warm to 25 °C. The crude product was purified using flash column chromatography (silica gel, 5% EtOAc/ Pet ether) to obtain **27a** (0.949 g, 94 %) as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63-9.62 (d, *J* = 5 Hz, 1H), 7.30-7.26 (m, 2H), 7.21-7.18 (t, *J* = 10 Hz, 3H),), 4.77-4.76 (d, *J* = 5 Hz, 1H), 4.71-4.69 (d, *J* = 10 Hz, 1H), 3.89-3.87 (t, *J* = 5 Hz, 1H), 3.44 (s, 3H), 2.80-2.72 (m, 2H), 2.02-1.98 (q, *J* = 10 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 128.6, 128.5, 126.3, 97.0, 96.1, 81.9, 56.1, 31.8, 30.9; IR (neat) 2959, 1743, 1461, 1117, 1095, 1040 cm^{-1}.



24

(*E*)-(4-(methoxymethoxy)hex-2-ene-1,6-diyl)dibenzene (24): The olefin **24** was prepared from aldehyde **24a** and sulfone **10s** using conditions B. The product **24** (93 mg, 63%, *E*:*Z* = 2.3:1) obtained as a pale-yellow liquid. (R_f = 0.6 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 5H), 7.21-7.17 (m, 6H), 5.84-5.78 (m, 1H), 5.43-5.38 (dd, *J* = 10, 15 Hz, 1H), 4.74-4.73 (d, *J* = 5 Hz, 1H), 4.54-4.53 (d, *J* = 5 Hz, 1H), 4.05-4.01 (q, *J* = 5, 15 Hz, 1H), 3.41-3.39 (m, 1H), 3.37 (s, 3H), 2.77-2.71 (m, 1H), 2.68-2.62 (m, 1H), 1.99-1.92 (m, 1H), 1.85-1.78 (m, 1H),; ^{13}C NMR (125 MHz, CCl_4 + $CDCl_3$) δ 142.0, 139.9, 132.9,

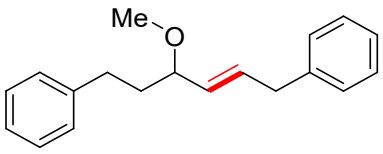
131.4, 128.5, 128.5, 128.4, 126.1, 125.8, 96.2, 93.6, 76.3, 55.4, 38.8, 37.5, 31.9; IR (neat) 3074, 3041, 3007, 2955, 2903, 1610, 1503, 1460, 1218, 1154, 1101, 1041, 979, 923 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{24}O_2Na$ 319.1668, Found 319.1664.



25a

2-methoxy-4-phenylbutanal (25a):[8] To a stirred suspension of NaH (0.5 g, 12.3 mmol, 60% in paraffin oil) in THF (20 mL), 5-phenylpent-1-en-3-ol[23] (1g, 6.17 mmol) in THF (5 mL) was added dropwise at 0 °C. After stirring for 30 minutes, the reaction mixture was warmed to 25 °C and the methyl iodide (6.8 mmol) was added dropwise. After 10 h at room temperature the reaction mixture was treated with sat. NH_4Cl and the organic layer was extracted with EtOAc (10ml x 3). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated over vacuum. The crude product was purified with column chromatography (silica gel, 5% EtOAc/ Pet Ether) to give the desired product.

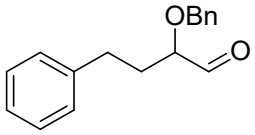
The product was then converted to aldehyde **25a** following the general procedure III. The aldehyde **25a** (0.949 g, 94 %) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.31-7.28 (t, *J* = 10 Hz, 3H), 7.22-7.18 (d, *J* = 5 Hz, 2H), 3.55-3.52 (q, *J* = 5 Hz, 1H), 3.46 (s, 3H), 2.79-2.68 (m, 2H), 1.99-1.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 140.9, 128.6, 128.5, 126.2, 84.7, 58.3, 31.5, 30.8; IR (neat) 3078, 3049, 2953, 2844, 1741, 1501, 1461, 1180, 1122, 1077, 1037, 914 cm^{-1}.



25

(*E*)-(4-(methoxy)hex-2-ene-1,6-diyl)dibenzene (25): The olefin **25** was prepared from aldehyde **25a** and sulfone **10s** using conditions B. The product **25** (81 mg, 61%, *E*:*Z* = 6.6:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.17 (m, 5H), 7.14-7.06 (m, 5H), 5.75-5.67 (m, 1H), 5.35-5.30 (dd, *J* = 10, 15 Hz, 1H), 3.45-3.41 (q, *J* = 5 Hz, 1H), 3.34-3.33 (d, *J* = 5 Hz, 2H), 3.19 (s, 3H), 2.65-2.55 (m, 2H), 1.89-1.82 (m, 1H),1.73-1.66 (m, 1H); ^{13}C NMR (125 MHz, CCl_4+$CDCl_3$) δ 142.1, 140.1, 132.8, 131.9, 128.5, 128.5, 128.4, 128.3, 126.1, 125.7, 81.4, 55.9, 38.8, 37.3,

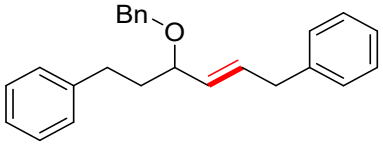
31.7; IR (neat) 3078, 3047, 3013, 2992, 2946, 2919, 2880, 2857, 2831, 1502, 1457, 1108, 1030 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{19}H_{22}ONa$ 289.1562, Found 289.1559.



26a

2-(benzyloxy)-4-phenylbutanal (26a):[9] To a stirred suspension of NaH (0.5 g, 12.3 mmol, 60% in paraffin oil) in THF (20 mL), 5-phenylpent-1-en-3-ol[23] (1g, 6.17 mmol) in THF (5 mL) was added dropwise at 0 °C. After stirring for 30 minutes, the reaction mixture was warmed to 25 °C and the benzyl bromide (6.8 mmol) was added dropwise. After 10 h at room temperature the reaction mixture was treated with sat. NH_4Cl and the organic layer was extracted with EtOAc (10 ml x 3). The combined organic layer was washed with water, brine, dried over Na_2SO_4 and concentrated over vacuum. The crude was purified by short pad of silica gel column to obtain (3-(benzyloxy)hex-5-en-1-yl)benzene (91%) as a yellow oil liquid.

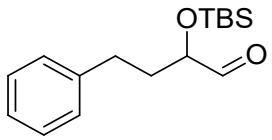
The benzyl ether obtained above was directly converted to aldehyde **26a** following the general procedure III. The product **26a** (0.949 g, 94 %) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.38-7.37 (d, *J* = 5 Hz, 3H), 7.35-7.32 (m, 1H), 7.29-7.25 (m, 3H), 7.22-7.18 (m, 1H), 7.15-7.14 (d, *J* = 5 Hz, 2H), 4.69-4.67 (d, *J* = 10 Hz, 1H), 4.54-4.52 (d, *J* = 10 Hz, 1H), 3.77-3.74 (t, *J* = 5, 15 Hz, 1H), 2.83-2.77 (m, 1H), 2.74-2.68 (m, 1H), 2.02-1.97 (m, 2H); ^{13}C NMR (125 MHz,CCl_4+ $CDCl_3$) δ 203.7, 140.9, 137.3, 128.6, 128.6, 128.5, 128.2, 128.1, 126.2, 30.9, 31.7, 72.7, 82.6; IR (neat) 3074, 2974, 1733, 1611, 1504, 1460, 1419, 1366, 1088, 915 cm^{-1}.



26

(*E*)-(4-(benzyloxy)hex-2-ene-1,6-diyl)dibenzene (26): The olefin **26** was prepared from aldehyde **26a** and sulfone **10s** using conditions B. The product **26** (142 mg, 83%, *E*:*Z* = 14.2:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.00 (m, 15H), 5.69 –5.63 (m, 1H), 5.39-5.34 (dd, *J* = 15, 10 Hz, 1H), 4.48-4.46 (d, *J* = 10 Hz, 1H), 4.22-4.20 (d, *J* = 10 Hz, 1H), 3.64-3.60 (dd, *J* = 15, 5 Hz, 1H), 3.31-3.29 (dd, *J* = 6.4, 3.0 Hz, 2H), 2.63–2.53 (m, 2H), 1.92–1.67 (m, 2H); ^{13}C NMR (125 MHz, CCl_4 + $CDCl_3$) δ 142.1, 140.1, 138.8, 132.8, 132.1, 128.53, 128.5, 128.5, 128.3, 128.3,

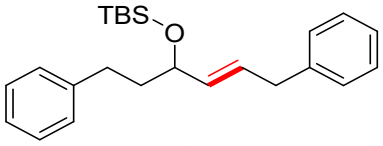
127.8, 127.4, 126.2, 125.7, 79.1, 69.9, 38.8, 37.5, 31.8; IR (neat) 3099, 3075, 3041, 2942, 2875, 1610, 1502, 1459, 1098, 1073, 1033, 978, 914 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{25}H_{26}ONa$ 365.1875, Found 365.1867.



27a

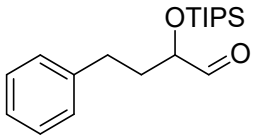
2-((tert-butyldimethylsilyl)oxy)-4-phenylbutanal (27a):[10] To a stirred solution of 5-phenylpent-1-en-3-ol[23] (1 g, 6.17mmol) in CH_2Cl_2 (12 ml), was added TBSCl (1.11 g, 7.4 mmol), imidazole (1.2 g, 18.5 mmol), DMAP (75 mg, 0.61mmol) and stirred for 12 h at 25 °C. The completion of the reaction was confirmed by TLC analysis. The reaction was treated with H_2O (15 mL), and the organic layer was extracted with DCM (20 ml x 2). The combined organic layers were washed with brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, pet ether) to give the desired product as yellow oil (83%).

The above olefin then converted to aldehyde **27a** following the general procedure III. The aldehyde **27a** (0.949 g, 94%) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.19-7.17 (d, *J* = 5 Hz, 2H), 7.11-7.08 (t, *J* = 5 Hz, 3H), 3.94-3.92 (t, *J* = 5 Hz, 1H), 2.65-2.57 (m, 2H), 1.93-1.81 (m, 2H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (125 MHz,CCl_4+ $CDCl_3$) δ 203.9, 141.2, 128.5, 128.4, 126.1, 34.6, 30.8, 25.8, 18.3, -4.5, -4.8; IR (neat) 2969, 2872, 1746, 1469, 1263, 1123, 846 cm^{-1}.



27

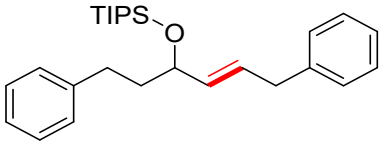
(*E*)-*tert*-butyl((1,6-diphenylhex-4-en-3-yl)oxy)dimethylsilane (27): The olefin **27** was prepared from aldehyde **27a** and sulfone **10s** using conditions B. The product **27** (157 mg, 86%, *E*:*Z* = 14.5:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^1H NMR (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 6H), 7.20-7.15 (m, 5H), 5.65-5.60 (m, 1H), 5.45-5.41 (dd, *J* = 5 Hz, 1H), 4.06-4.03 (q, *J* = 5, 10 Hz, 1H), 3.29-3.27 (d, *J* =10 Hz, 2H), 2.62-2.48 (m, 2 H), 1.77-1.66 (m, 2H), -0.05 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (125 MHz, CCl_4 + $CDCl_3$) δ 142.5, 140.3, 134.9, 129.1, 128.5, 128.4, 128.3, 126.0, 125.6, 73.0, 40.2, 38.7, 31.7, 25.9, 18.3, 0.1, -4.1, -4.7; IR (neat) 3340, 3079, 2974, 2873, 1608, 1508, 1032, 995, 789 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{24}H_{34}OSiNa$ 389.2271, Found 389.2250.



28a

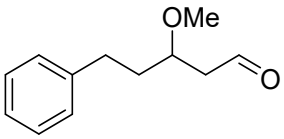
4-phenyl-2-((triisopropylsilyl)oxy)butanal (28a): To a stirred solution of 5-phenylpent-1-en-3-ol (1 g, 6.17 mmol) in CH_2Cl_2 (12 ml), was added TIPSOTf (2.6 ml, 9.22 mmol), Et_3N (1.7 ml, 12.3 mmol), DMAP (75 mg, 0.61 mmol) and stirred for 12 h at 25 ^oC. The completion of the reaction was confirmed by TLC analysis. The reaction mixture was treated with H_2O (15 mL), and the organic layer was extracted with DCM (20ml x 2). The combined organic layers were washed with water, brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure.

The crude product obtained above was converted to aldehyde **28a** following the general procedure III. The aldehyde **28a** (1 g, 94 %) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 9.55-9.54 (d, *J* = 5 Hz, 1H), 7.61-7.57 (m, 2H), 7.10-7.07 (m, 3H),4.06-4.03 (m, 1H) 2.70-2.54 (m, 2H), 1.92-1.92 (m, 2H), 1.00 (m, 21H); IR (neat) 2994, 2735, 1742, 1582, 1275, 1094, 832 cm^{-1}.



28

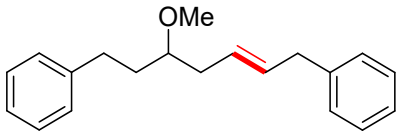
(*E*)-((1,6-diphenylhex-4-en-3-yl)oxy)triisopropylsilane (28): The olefin **28** was prepared from aldehyde **28a** and sulfone **10s** using conditions B. The product **28** (126 mg, 62%, *E*:*Z* = 22.5:1) obtained as a pale-yellow liquid. (R_f = 0.8 in petroleum ether). ^1H NMR (500 MHz, $CDCl_3$) δ 7.20-7.14 (m, 4H), 7.11-7.04 (m, 6H), 5.67-5.61 (m, 1H), 5.47-5.43 (dd, *J* = 15, 5 Hz, 1H), 4.19-4.15 (dd, *J* = 10, 5 Hz, 1H), 3.29-3.31 (d, *J* = 10 Hz, 2H), 2.64-2.50 (m, 2H), 1.84-1.72 (m, 2H), 1.00 (s, 3H), 0.96 (s, 18H). ^{13}C NMR (125 MHz, CCl_4 + $CDCl_3$) δ 142.4, 140.2, 134.9, 129.5, 128.6, 128.4, 128.3, 126.1, 125.7, 73.2, 40.6, 38.8, 31.4, 18.3, 18.2, 12.5. IR (neat) 3295, 2944, 1615, 1469, 1123, 981, 767. HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{27}H_{40}OSiNa$ 431.2740, Found 431.2741.



29a

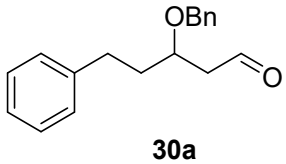
3-methoxy-5-phenylpentanal (29a):[8] Methylation of 1-phenylhex-5-en-3-ol[8] was carried out following a similar procedure used methylation of 5-phenylpent-1-en-3-ol to obtain (3-(methyloxy)hex-5-en-1-yl)benzene (0.98 g, 92%) as a yellow oil liquid.

General procedure III was followed for the synthesis of aldehyde **29a**, from the corresponding methyl protected homoallylic alcohol. The product obtained (0.941 g, 94 %) as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73-9.72 (t, *J* = 5 Hz, 1H), 7.22-7.17 (q, *J* = 10 Hz, 2H), 7.12-7.10 (t, *J* = 5 Hz, 3H), 3.67-3.64 (m, 1H), 3.28 (s, 3H), 2.67-2.55 (m, 3H), 2.50-2.45(m, 1H), 1.89-1.81 (m, 1H), 1.79-1.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 140.8, 128.6, 128.5, 126.1, 84.7, 58.3, 31.4, 30.7; IR (neat) 2942.58, 1734.83, 1122.26, 1091.90, 756.71, 706 cm^{-1}.



29

(*E*)-(5-methoxyhept-2-ene-1,7-diyl)dibenzene (29): The olefin **29** was prepared from aldehyde **29a** and sulfone **10s** using conditions B. The product **29** (83 mg, 59%, *E*:*Z* = 4.2:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 5H), 7.21-7.16 (m, 6H), 5.68-5.62 (m, 1H), 5.46-5.40 (m, 1H), 3.37 (s, 3H), 3.25-3.20 (m, 1H), 2.33-2.24 (m, 2H), 2.64-2.60 (m, 1H), 2.77-2.71 (m, 1H), 1.82-1.73 (q, *J* = 5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 140.8, 131.7, 128.5, 128.4, 128.4, 128.35, 127.39, 125.96, 125.72, 79.89, 56.57, 39.19, 36.23, 35.31, 31.54; IR (neat) 3077, 2941, 2837, 1611, 1502, 1367, 1196, 1035, 977,749 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{24}ONa$ 303.1719, Found 303.1720.

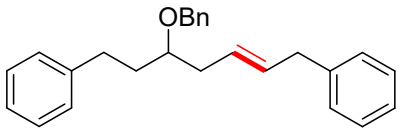


30a

3-(benzyloxy)-5-phenylpentanal (30a): benzylation of 1-phenylhex-5-en-3-ol[8] was carried out following a similar procedure used benzylation of 5-phenylpent-1-en-3-ol to produce (3-(benzyloxy)hex-5-en-1-yl)benzene.

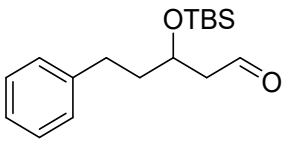
General procedure III was followed for the synthesis of aldehyde **30a**, from the above benzyl protected alkene. The aldehyde **30a** (0.919 g, 92 %) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71-9.70 (t, *J* = 5 Hz, 1H), 7.29-7.17 (m, 7H), 7.12-7.07 (m, 3H), 4.46 (s, 2H), 3.92-3.87 (m, 1H), 2.69-2.57 (m, 3H), 2.55-2.50 (m,

1H), 1.96-1.88 (m, 1H), 1.85-1.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 140.9, 137.2, 128.6, 128.5, 128.4, 128.2, 128.1, 126.2, 82.6, 72.6, 31.7, 30.9; IR (neat) 3080, 2947.91, 2745.72, 1732.98, 1504.77, 1406, 1216, 1034.83, 744 cm^{-1}.



30

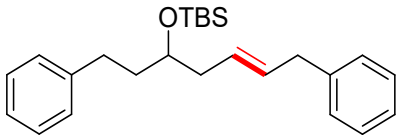
(*E*)-(5-(benzyloxy)hept-2-ene-1,7-diyl)dibenzene (30): The olefin **30** was prepared from aldehyde **30a** and sulfone **10s** using conditions B. The product **30** (172 mg, 97%, *E*:*Z* = 12.4:1) obtained as a pale-yellow liquid. (R_f = 0.7 in 5% EtOAc in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.35 (d, *J* = 5 Hz, 4H), 7.31-7.26 (m, 6H), 7.22-7.15 (m, 6H), 5.70-5.64 (m, 1H), 5.58-5.52 (m, 1H), 4.61-4.59 (d, *J* = 10 Hz, 1H), 4.50-4.48 (d, *J* = 10 Hz, 1H), 3.50-3.45 (m, 1H), 3.37-3.36 (d, *J* = 5 Hz, 2H), 2.81-2.75 (m, 1H), 2.68-2.62 (m, 1H), 2.38-2.35 (q, *J* = 5 Hz, 2H), 1.91-1.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 140.8, 138.9, 131.7, 128.5, 128.44, 128.40, 128.38, 128.35, 128.3, 127.8, 127.5, 125.9, 125.7, 70.9, 78.0, 39.2, 36.9, 35.7, 31.7; IR (neat) 3077, 2938, 2873, 1611, 1459, 1360, 1100, 1034, 977, 743 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{26}H_{28}ONa$ 379.2032, Found 379.2030.



31a

3-((*tert*-butyldimethylsilyl)oxy)-5-phenylpentanal (31a):[11] Silylation of 1-phenylhex-5-en-3-ol[8] was carried out following a similar procedure used for TBDMS protection of 5-phenylpent-1-en-3-ol to provide *tert*-butyldimethyl((1-phenylhex-5-en-3-yl)oxy)silane in (88%).

The above obtained olefin was converted to aldehyde **31a** following the general procedure III. The aldehyde **31a** (0.920 g, 93 %) obtained as a yellow liquid. (R_f = 0.5 in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65-9.64 (t, *J* = 5 Hz, 1H), 7.12-7.09 (t, *J* = 5 Hz, 2H), 7.03-6.99 (dd, *J* = 10, 15 Hz, 3H), 4.11-4.06 (m, 1H), 2.52-2.45 (m, 2H), 2.43-2.40 (m , 2H), 1.72-1.67 (q, *J* = 10 Hz, 9H), 0.73 (s, 9H), -0.11 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 141.2, 128.5, 128.4, 126.1, 34.6, 30.86, 25.8, 12.3, -4.5, -4.8; IR (neat) 2970, 2874, 1737, 1262, 1116, 843 cm^{-1}.



31

(*E*)-*tert*-butyl((1,7-diphenylhept-5-en-3-yl)oxy)dimethylsilane (31): The olefin **31** was prepared from aldehyde **31a** and sulfone **10s** using conditions B. The product **31** (181 mg, 95%, *E*:*Z* = 11.8:1) obtained as a pale-yellow liquid. (R_f = 0.8 in 5% EtOAc in petroleum ether). ^{1}HNMR(500 MHz, $CDCl_3$) δ 7.21-7.17 (m, 5H), 7.12-7.06 (m, 5H), 5.56-5.51 (m, 1H), 5.46 (m, 1H), 3.72-3.64 (m, 1H), 3.27-3.26 (d, *J* = 5 Hz, 2H), 2.64-2.58 (m, 1H), 2.53-2.47 (m, 1H), 2.18-2.15 (t, *J* = 5 Hz, 10 Hz, 2H), 1.74-1.61 (m, 2H), -0.02 (s, 3H), 0.83 (s, 9H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 140.8, 131.4, 128.5, 128.38, 128.36, 128.3, 127.9, 125.9, 125.7, 71.9, 40.5, 39.2, 38.7, 31.7, 25.9, 18.2, -4.3, -4.5; IR (neat) 3077, 2968, 2871, 1502, 1476, 1262, 1099, 980, 781 cm^{-1}; HRMS (ESI-quadrupole) m/z: $[M+Na]^+$ Calculated for $C_{25}H_{36}OSiNa$ 403.2433, Found 403.2428.

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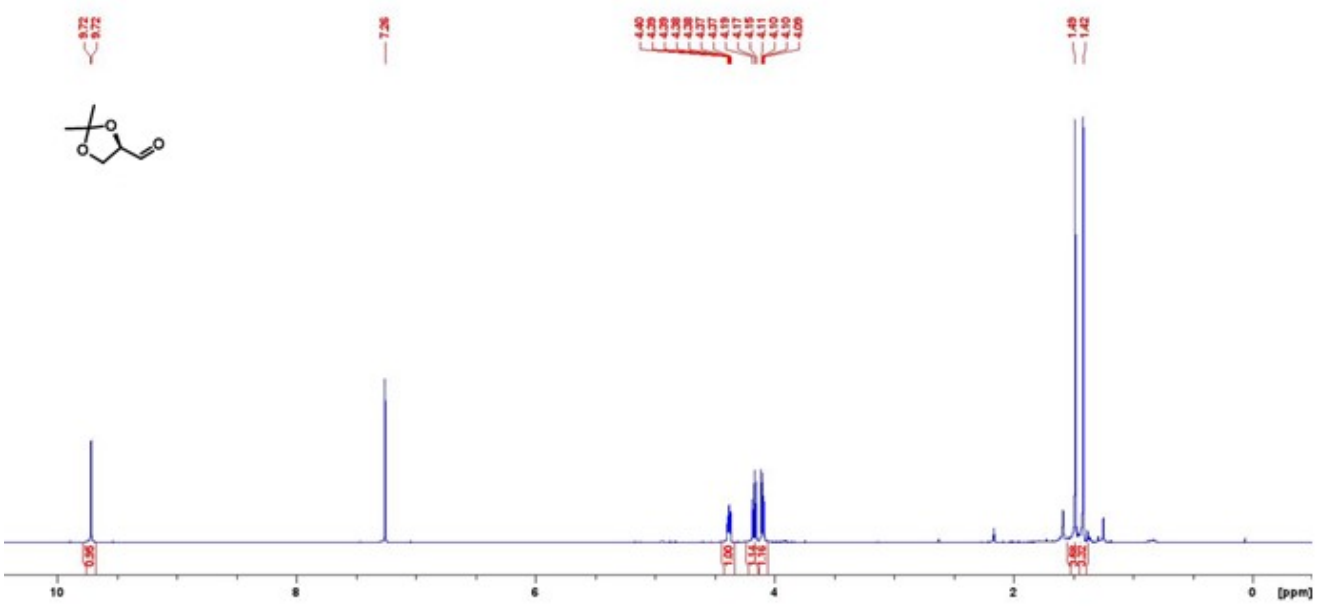
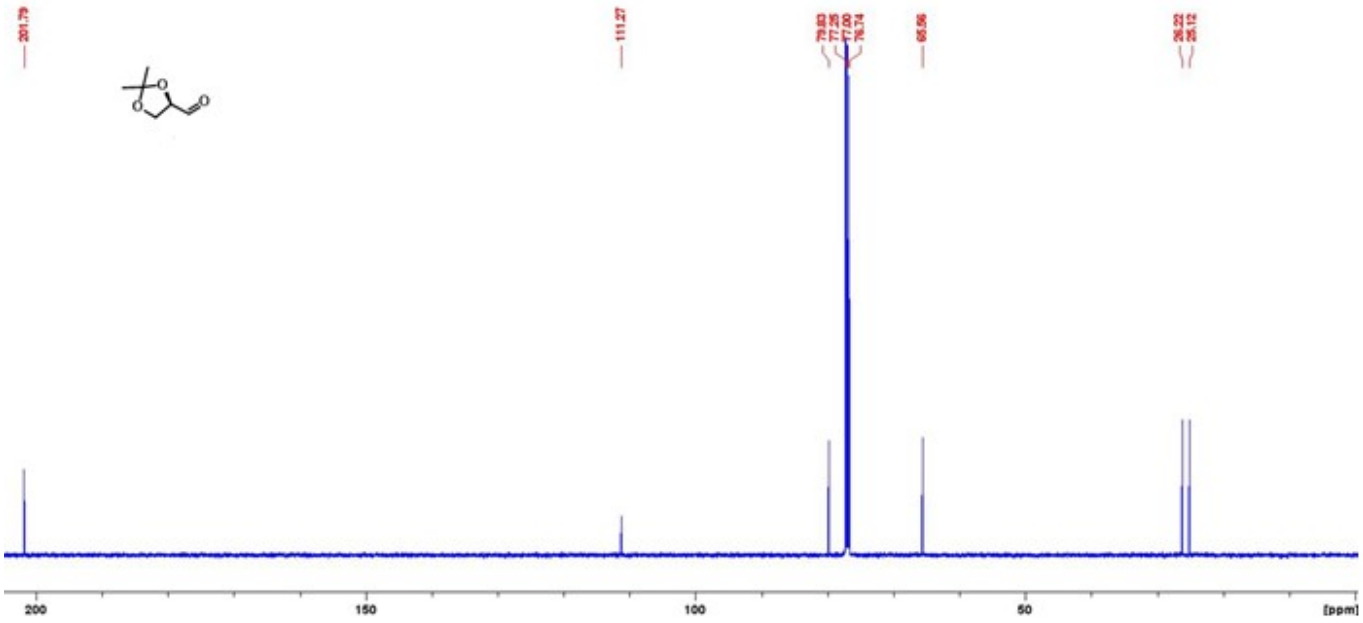
Spectral Data (For olefins, the E/Z ratios were showed by the highlighted regions of crude compounds. The clean ^{1}H- and ^{13}C-NMR spectra were recorded after the column purification.)



^{1}H NMR of compound 1



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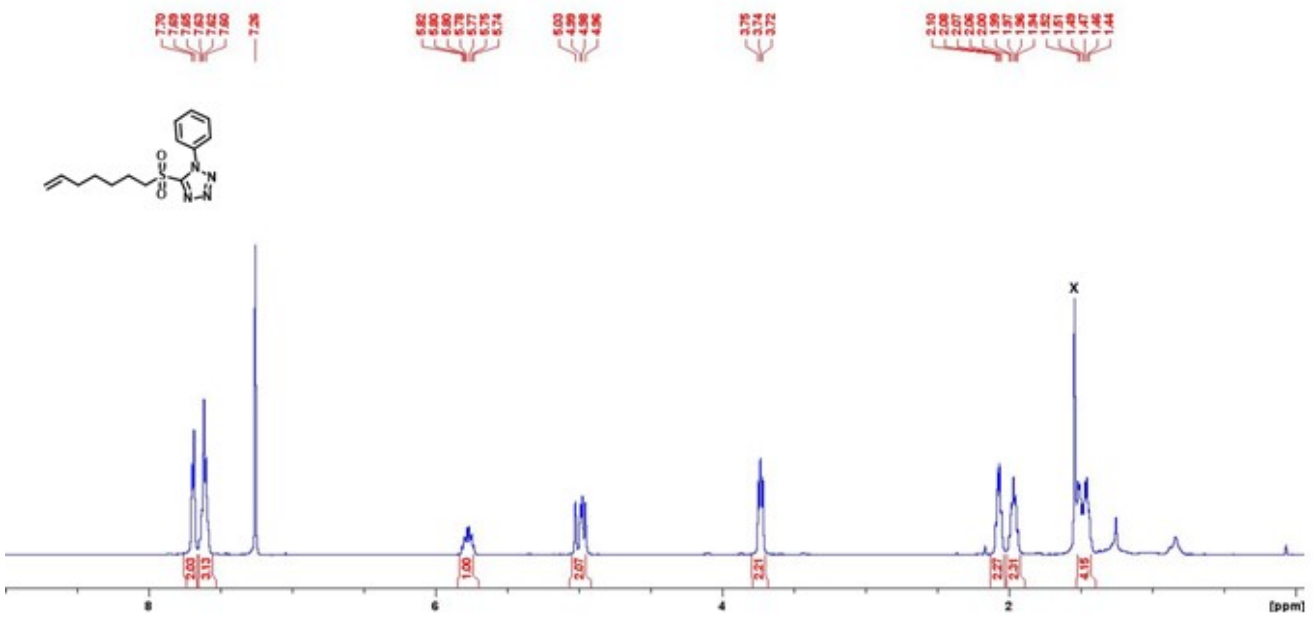
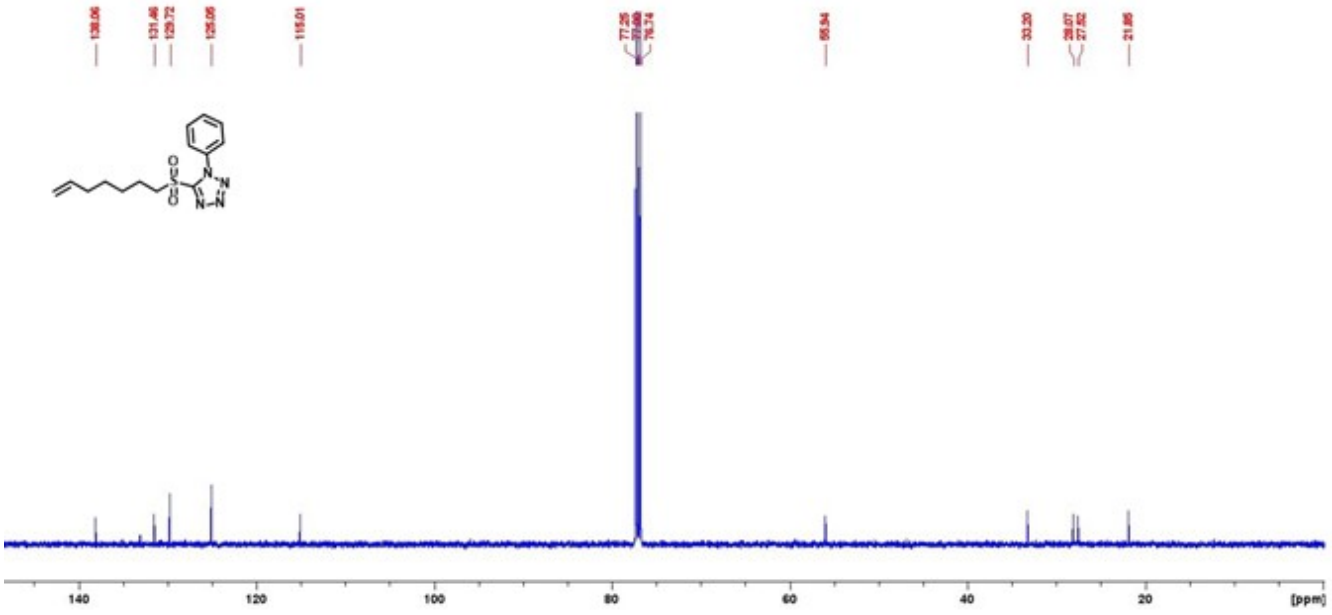


^{1}H NMR of compound 3



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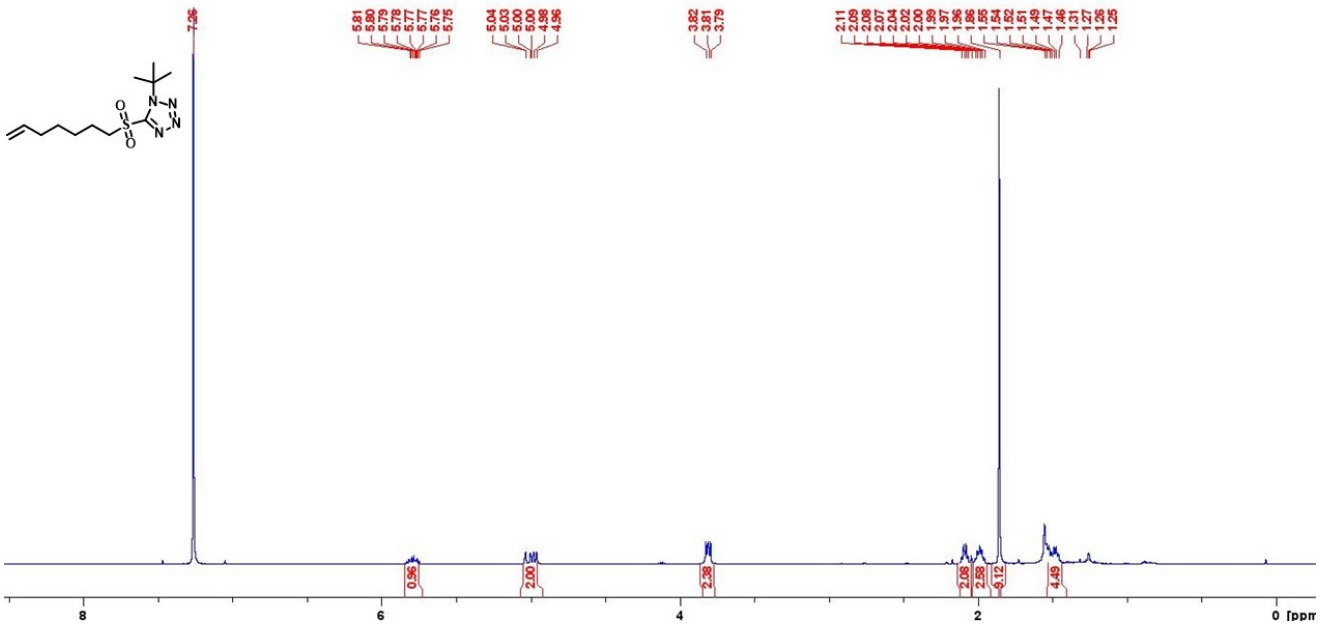
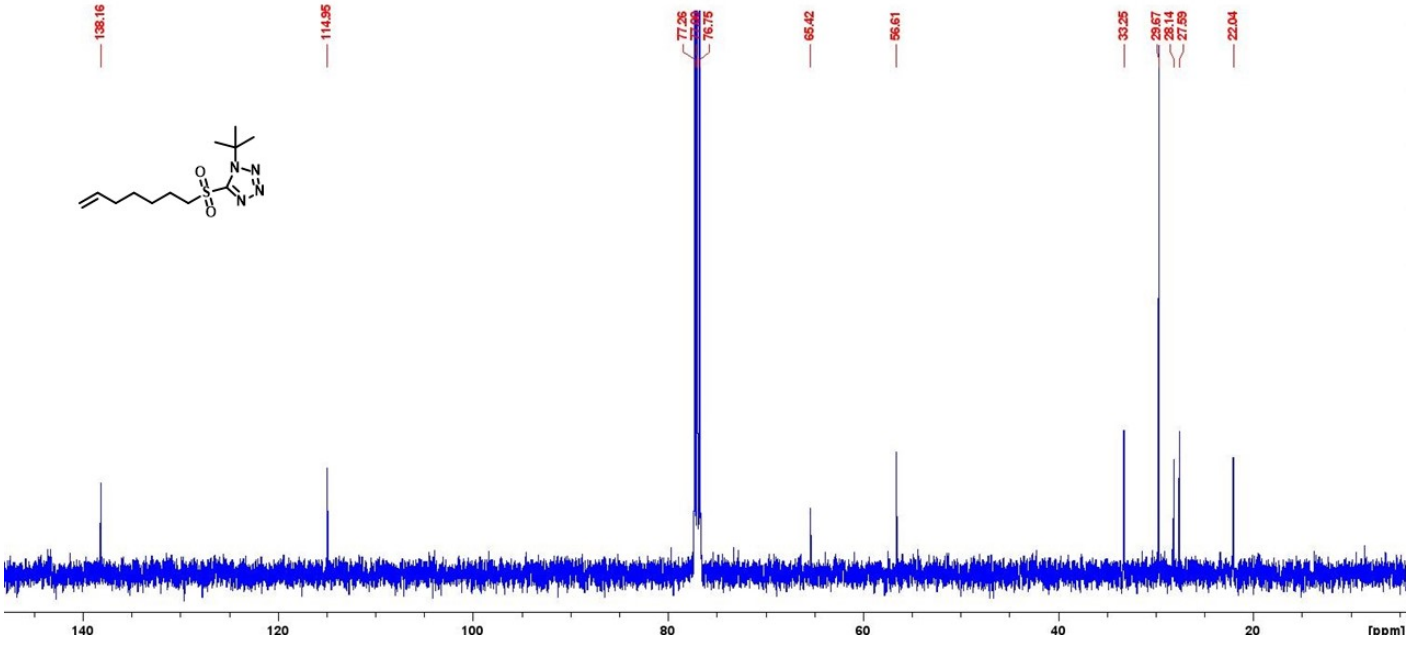


^{1}H NMR of compound 4



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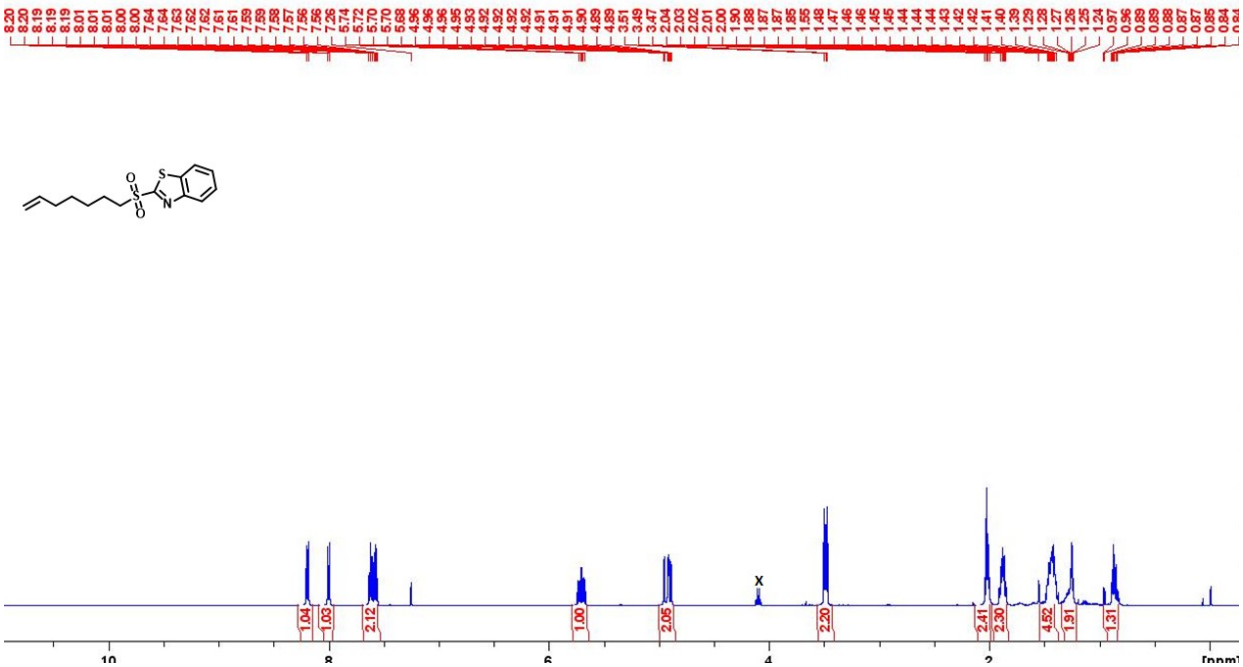
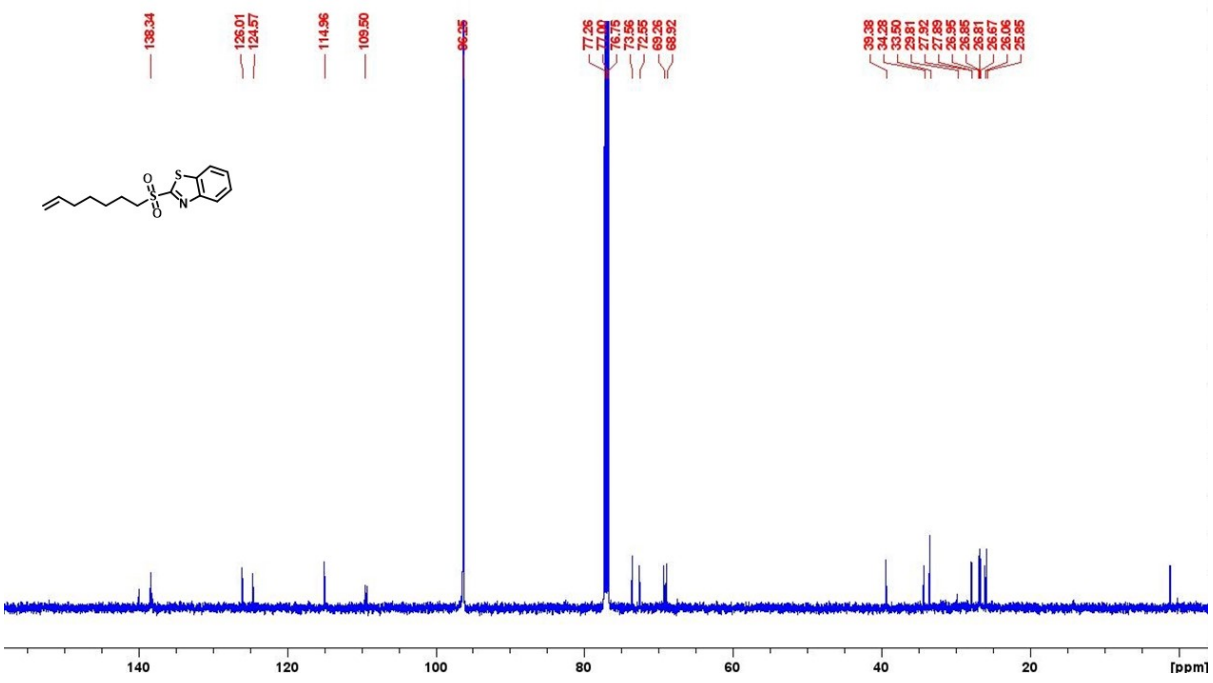
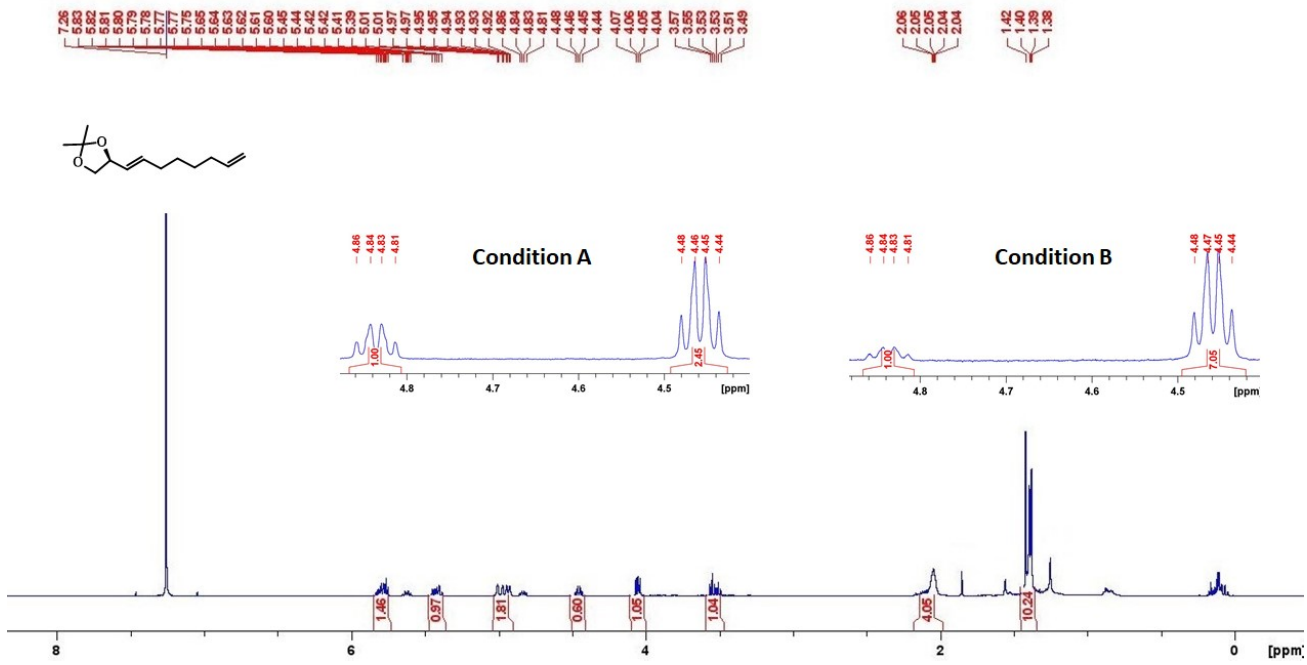


^{1}H NMR of compound 5



^{13}C NMR of compound 5



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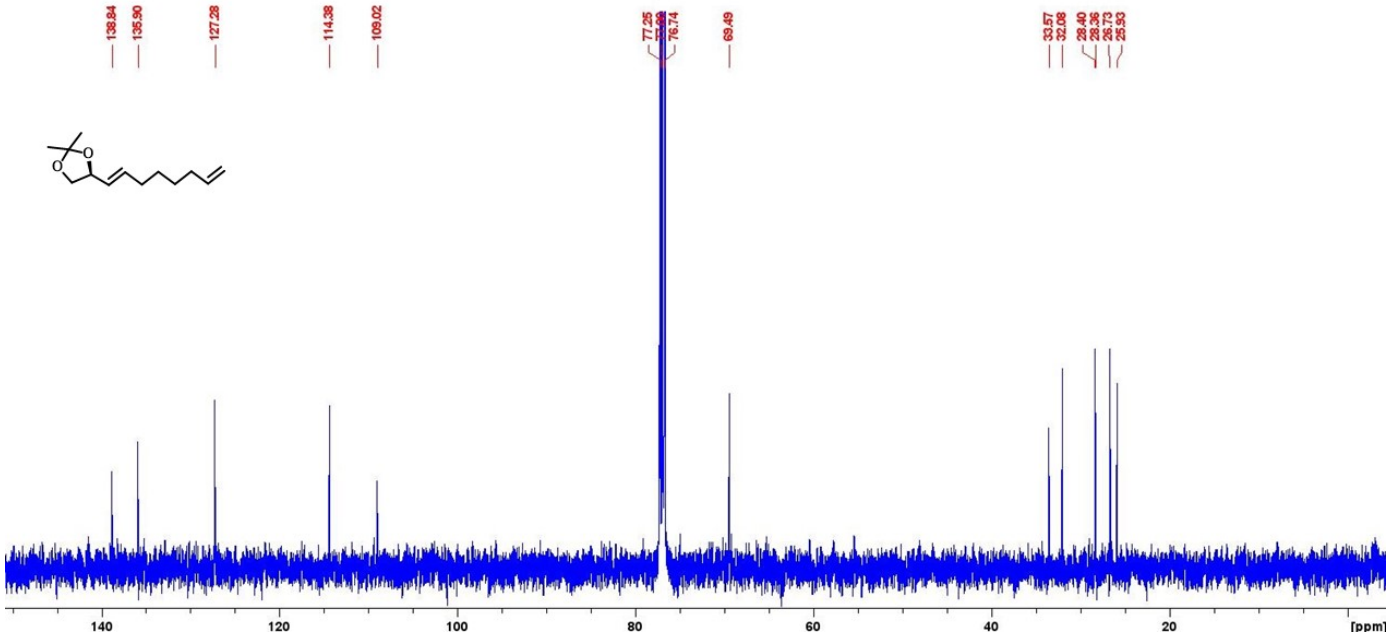

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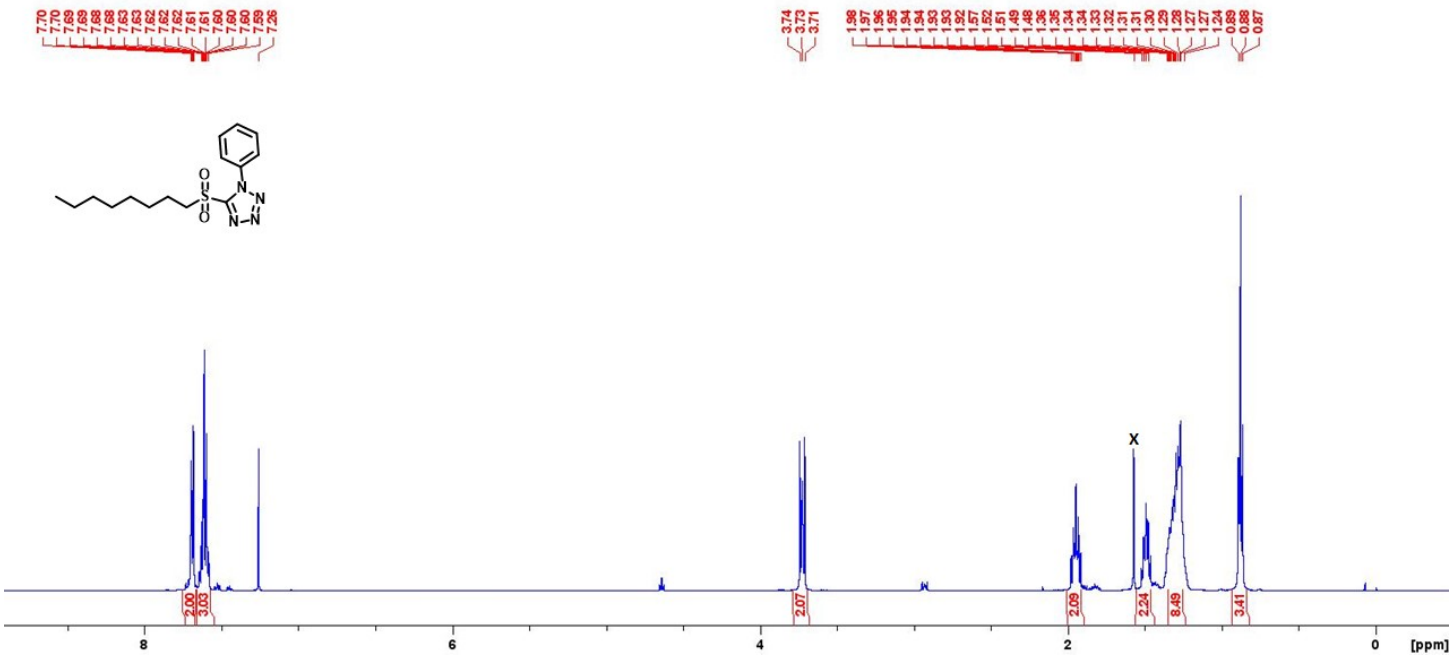
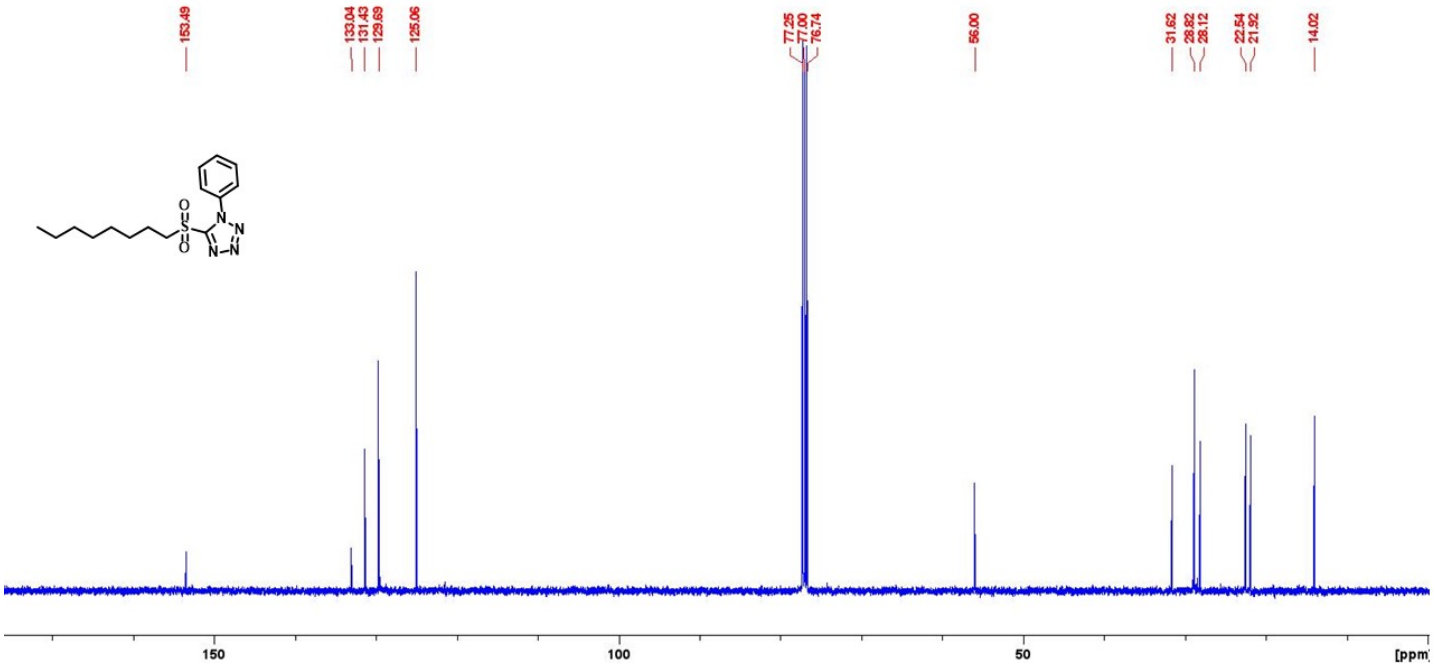


^{1}H NMR of compound 6s



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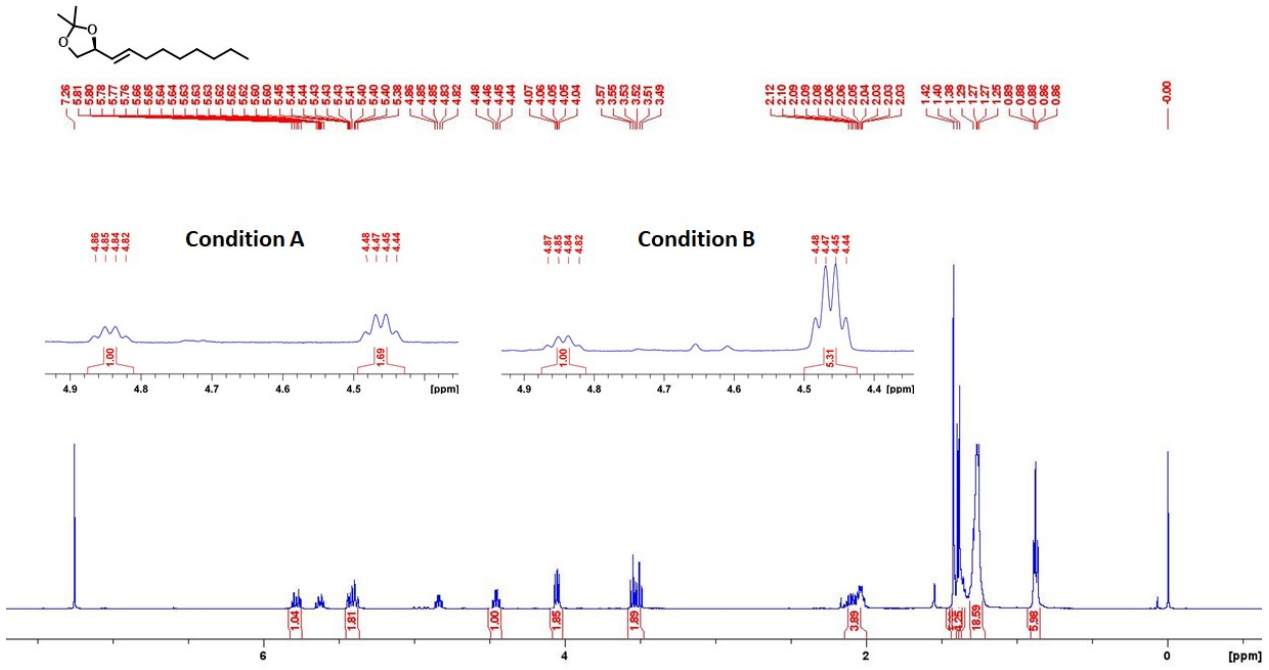

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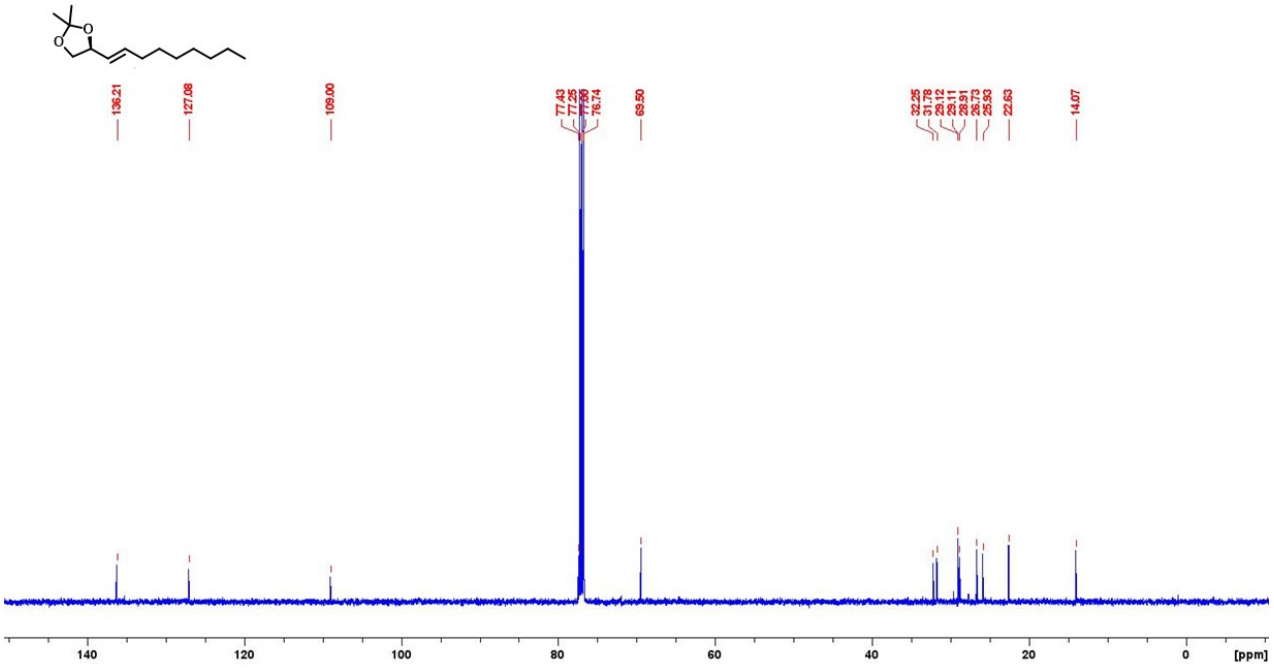

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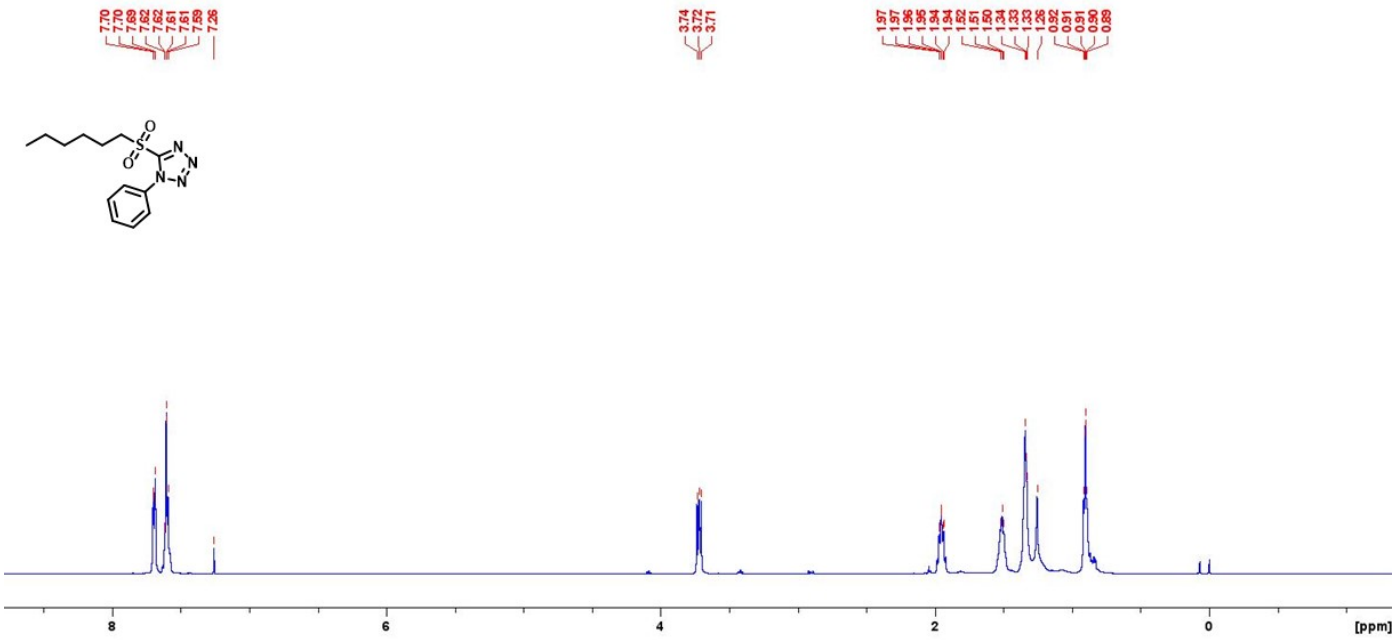

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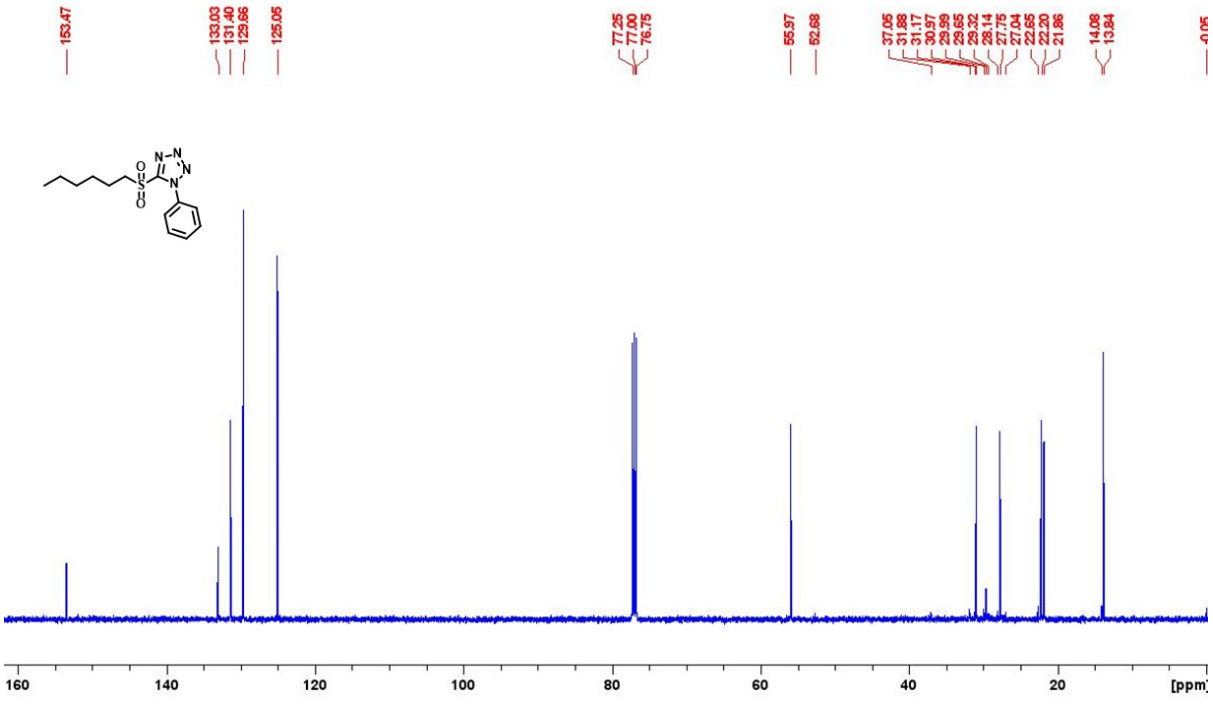

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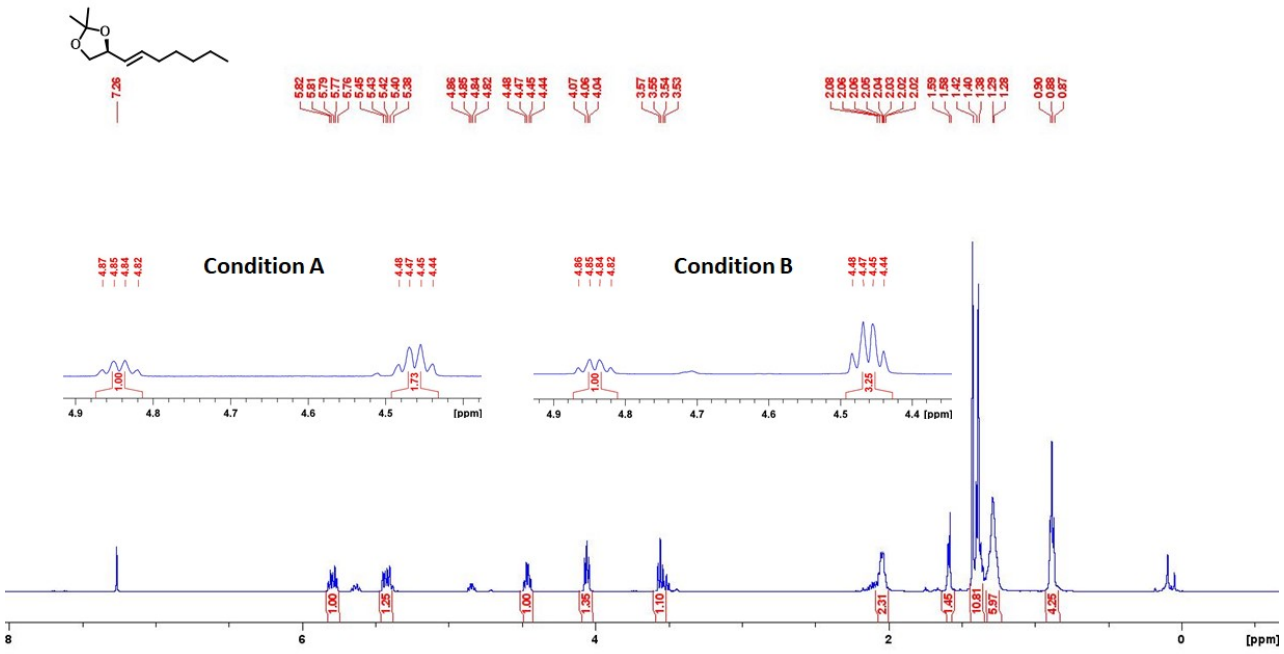

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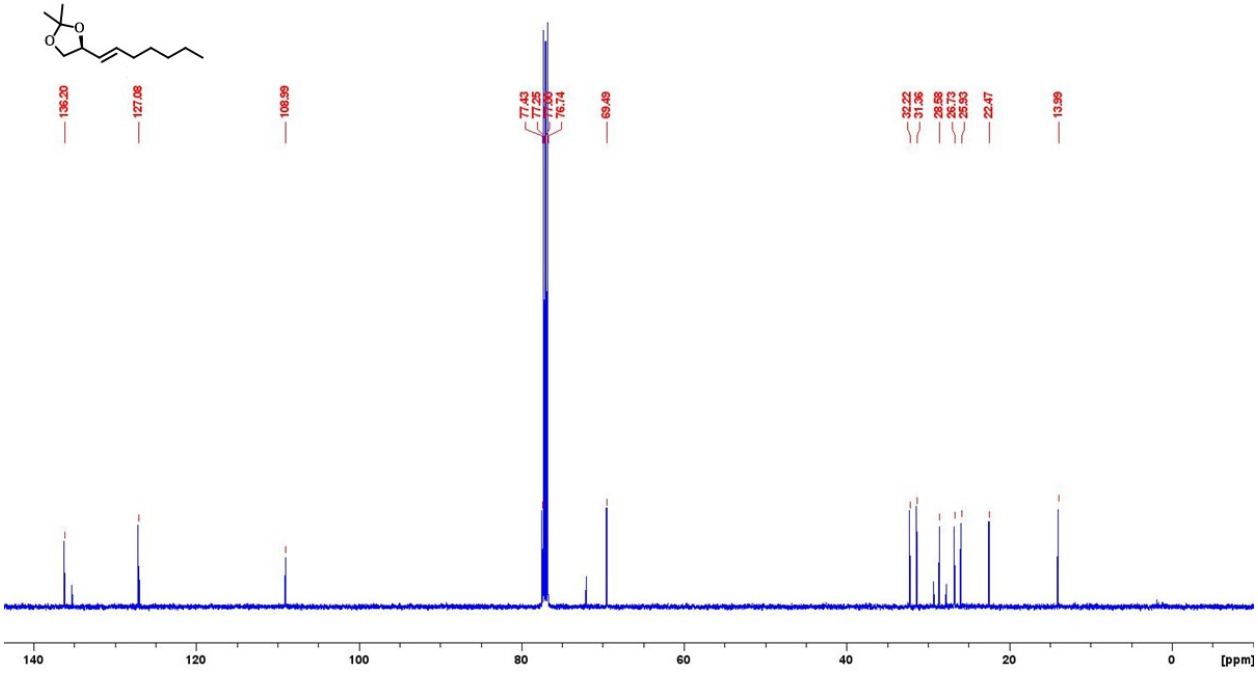

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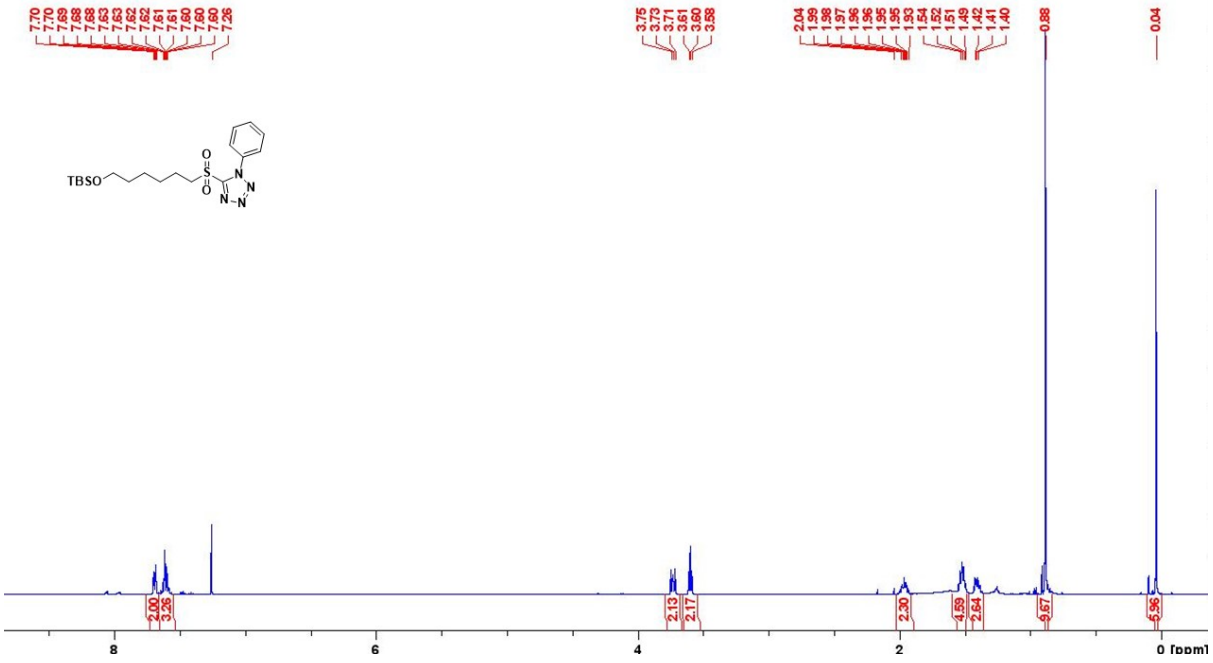

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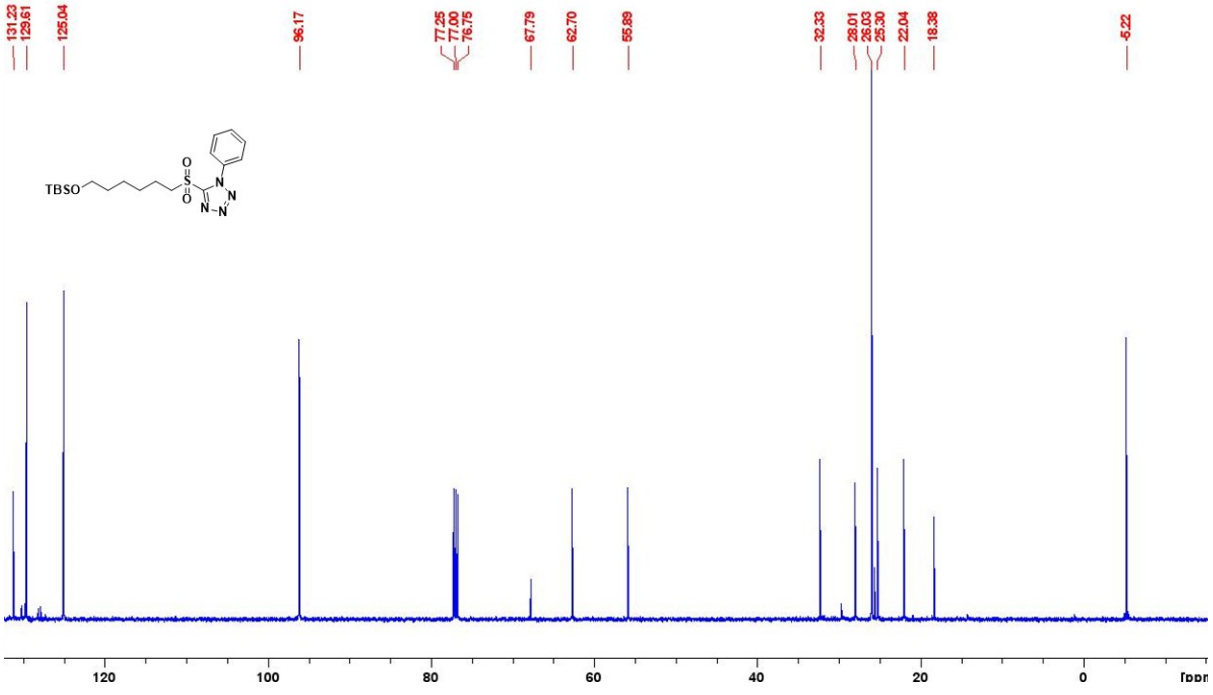

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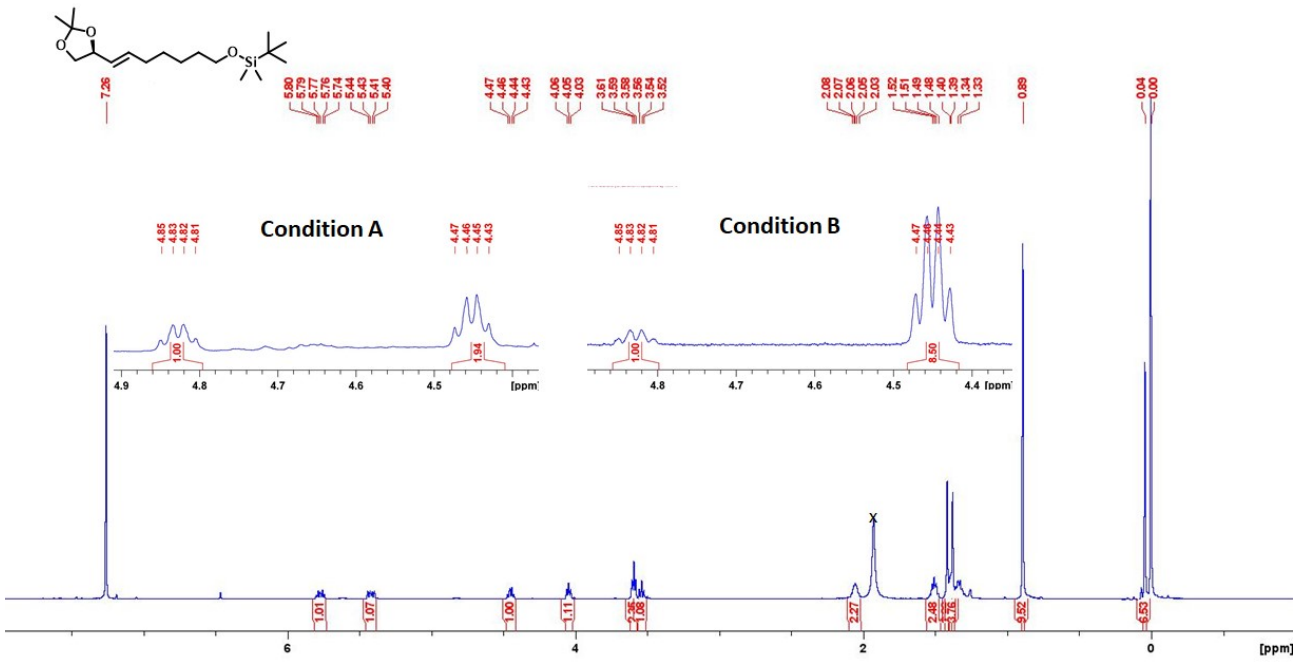

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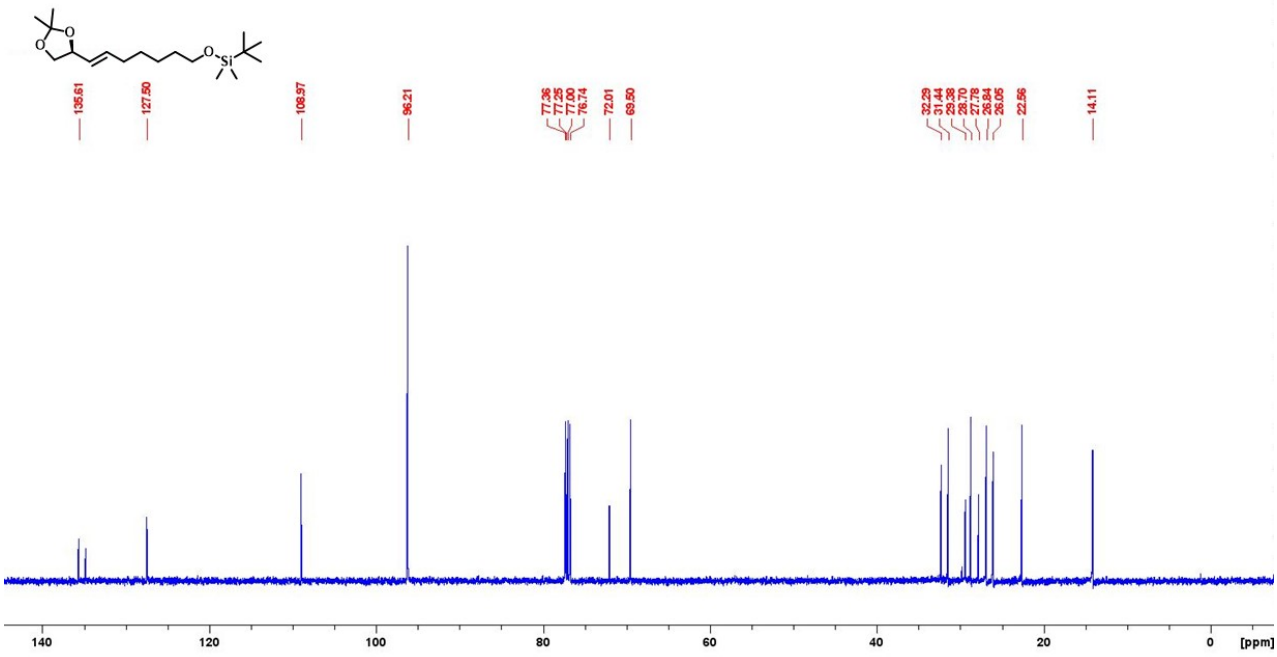

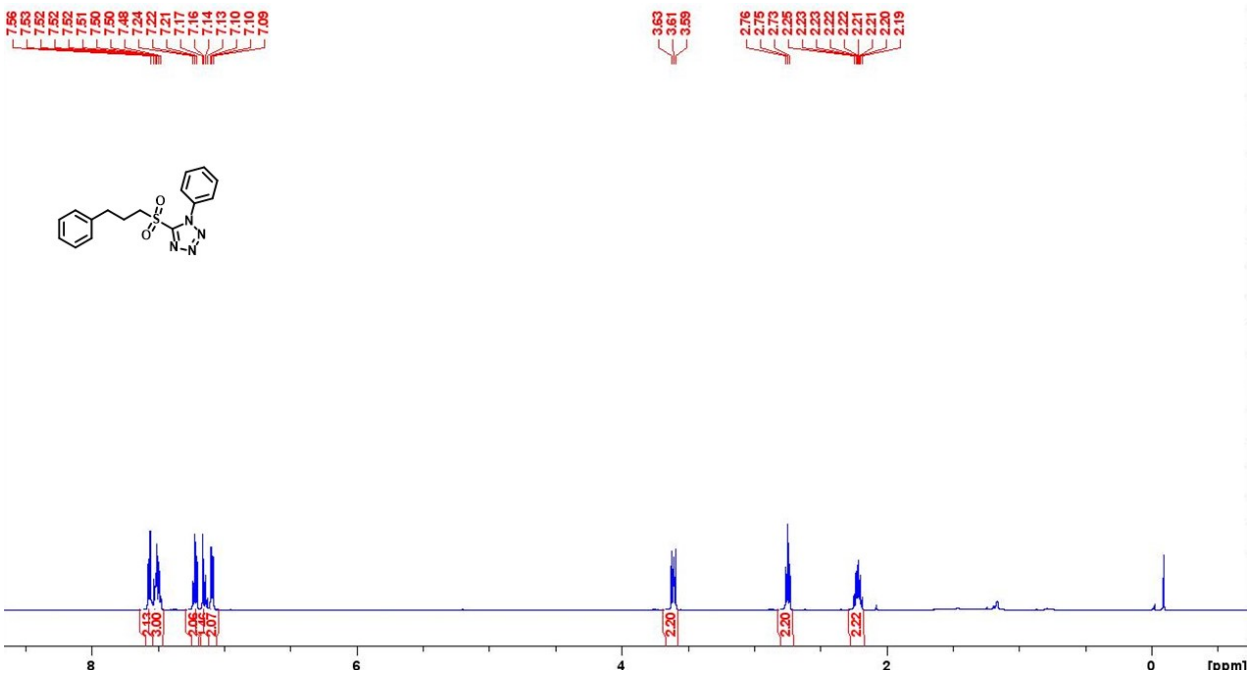

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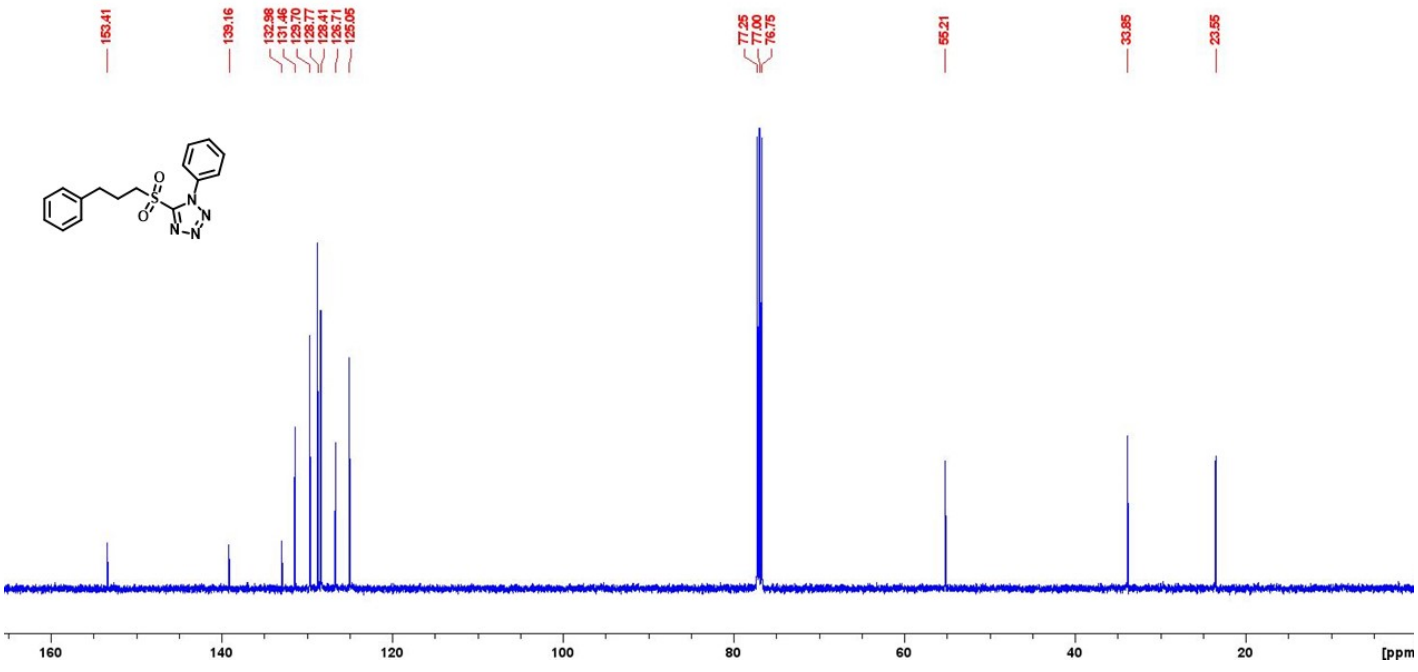

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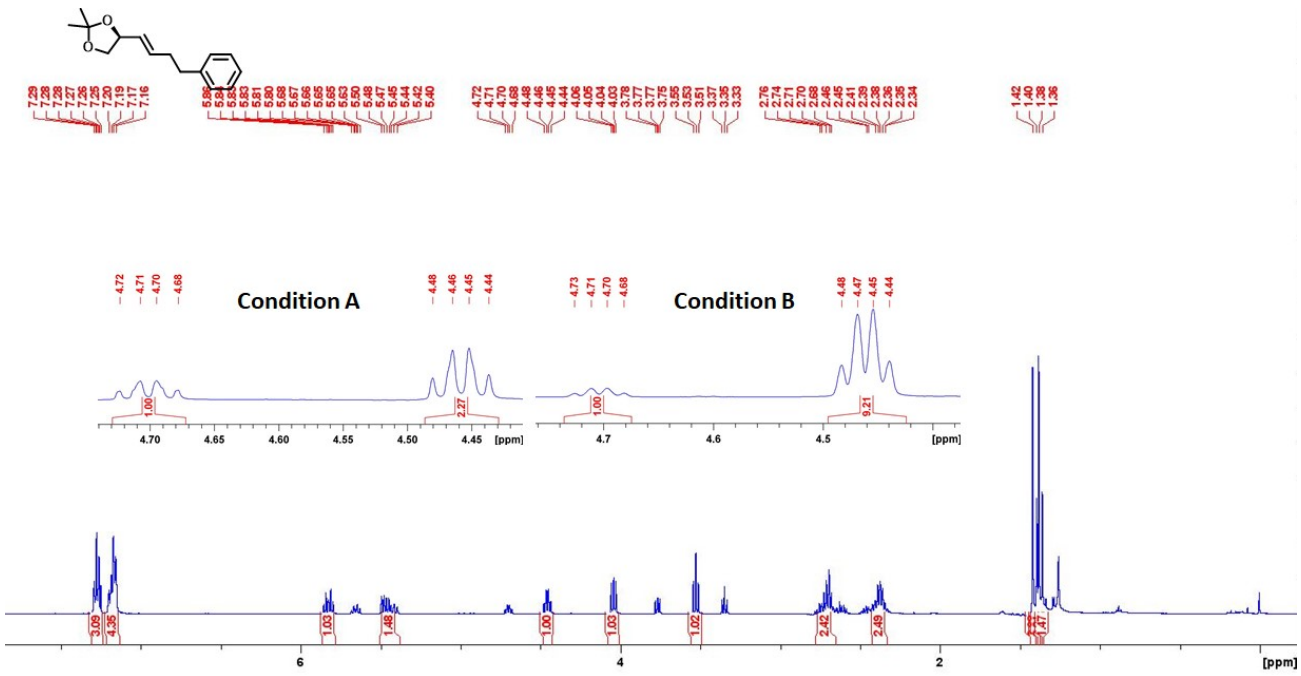

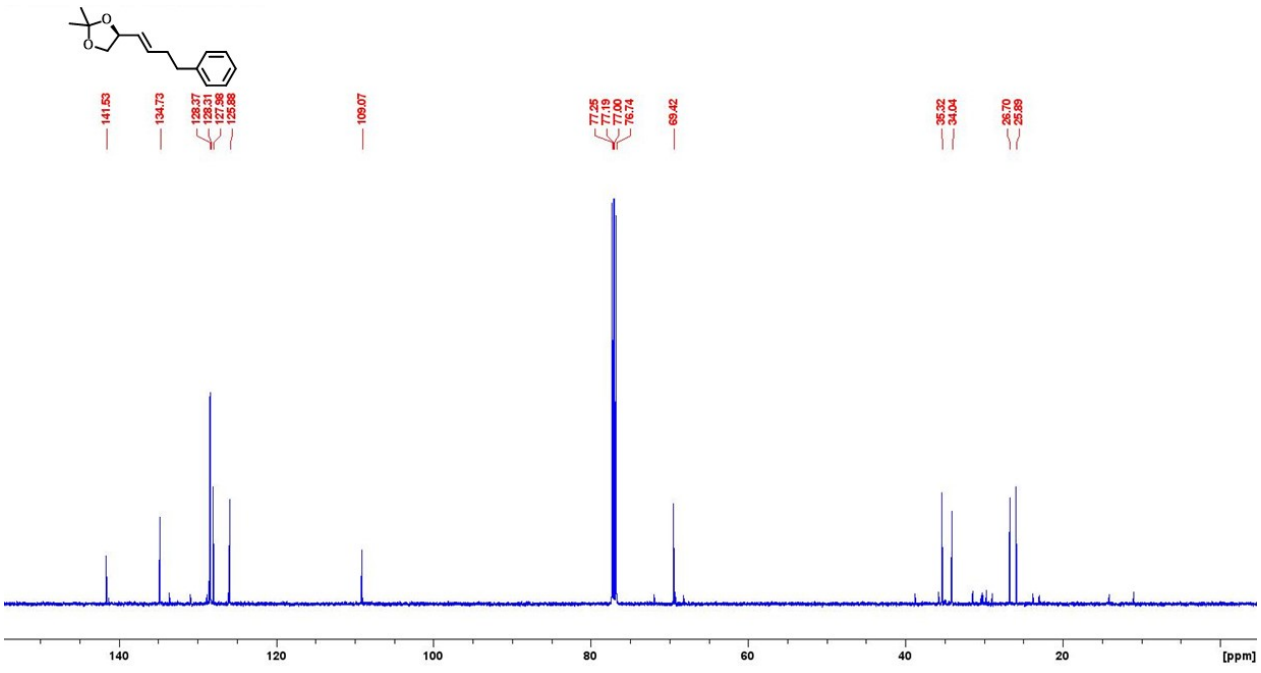

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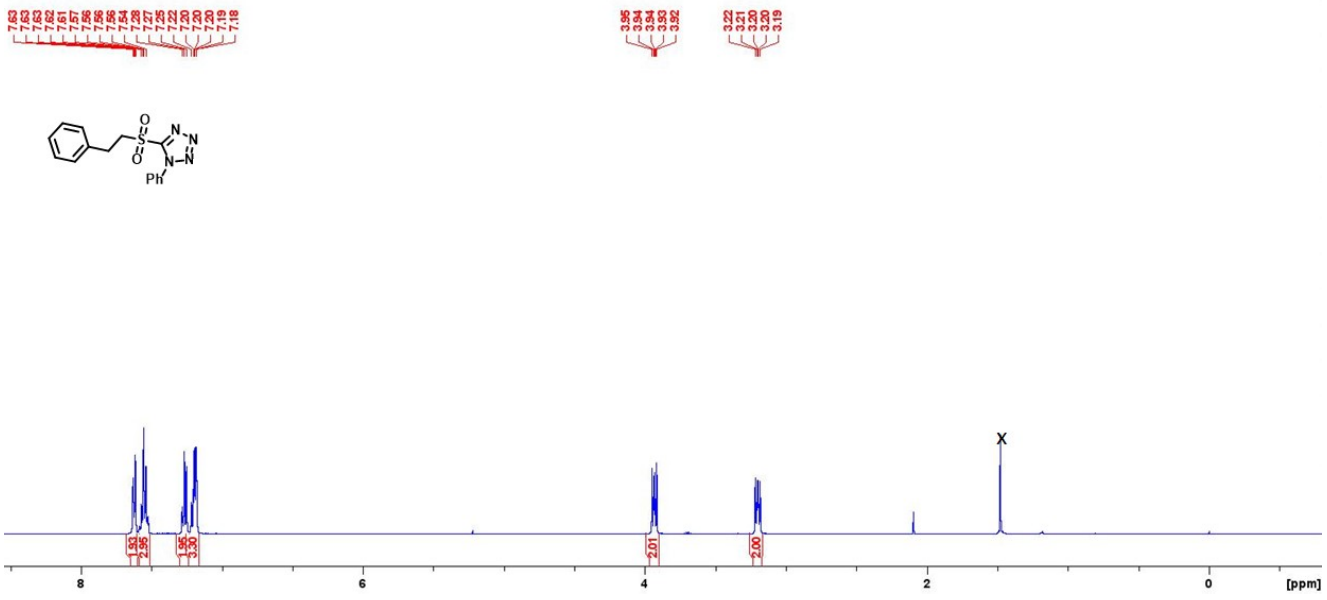
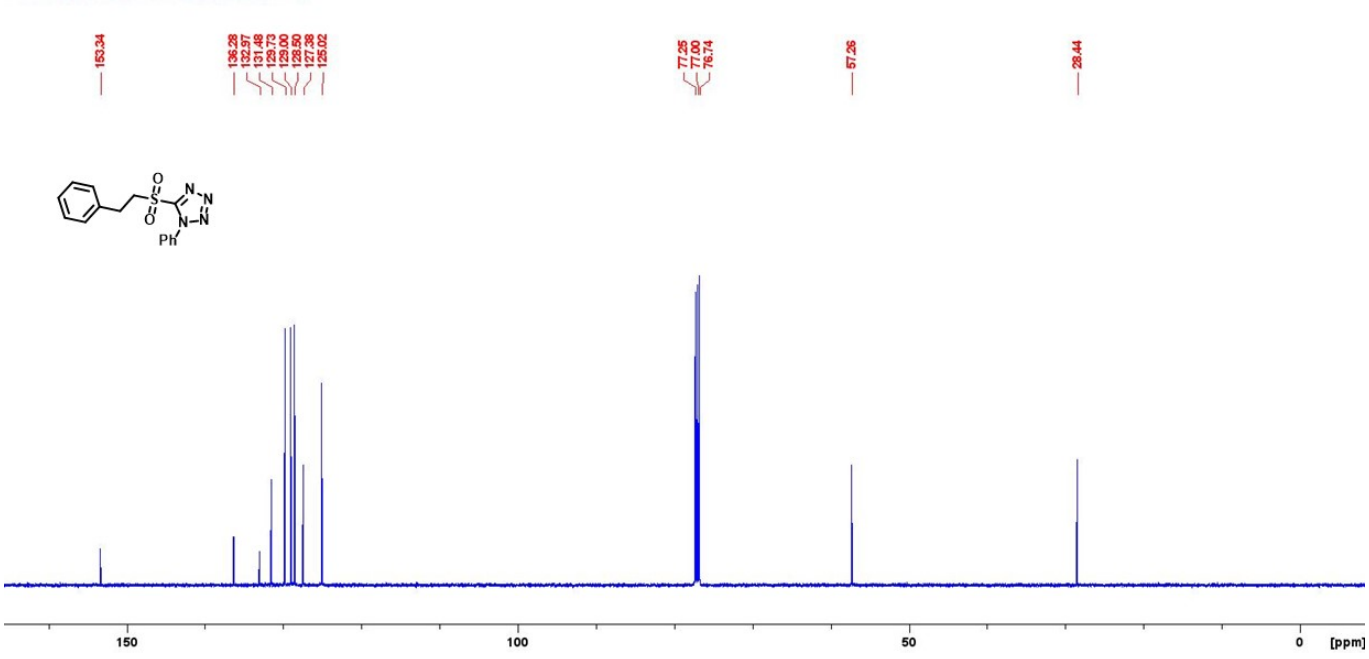


^{1}H NMR of compound 10s

^{1}H NMR of compound 9



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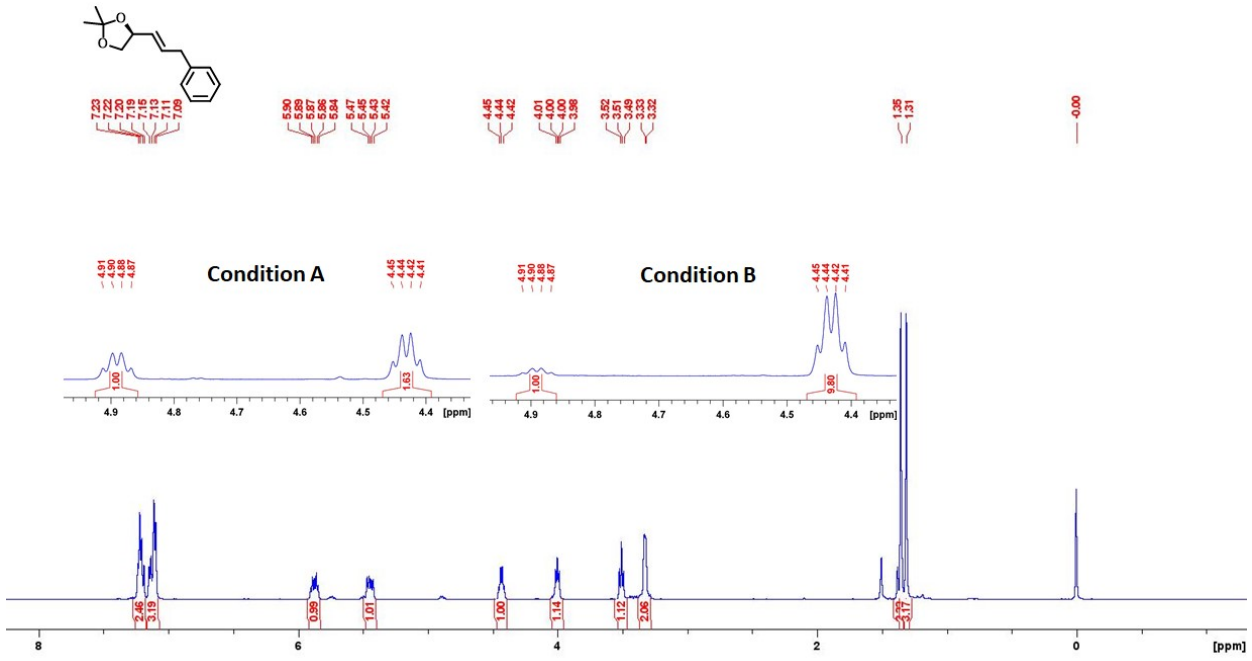

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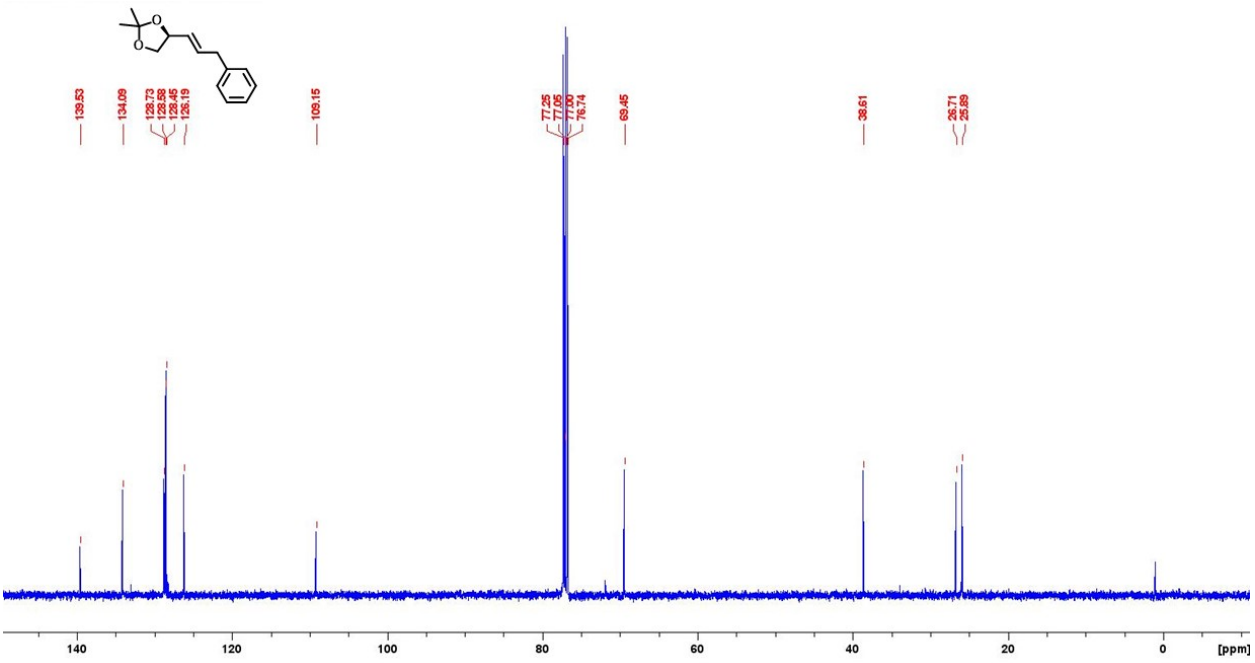

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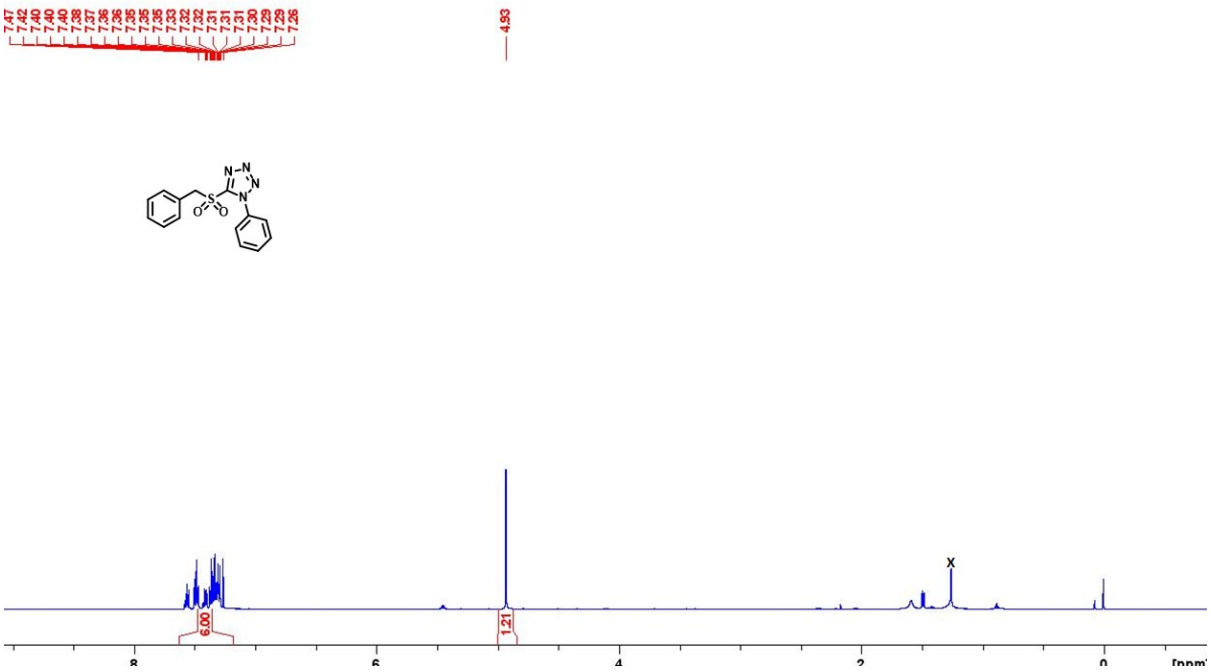

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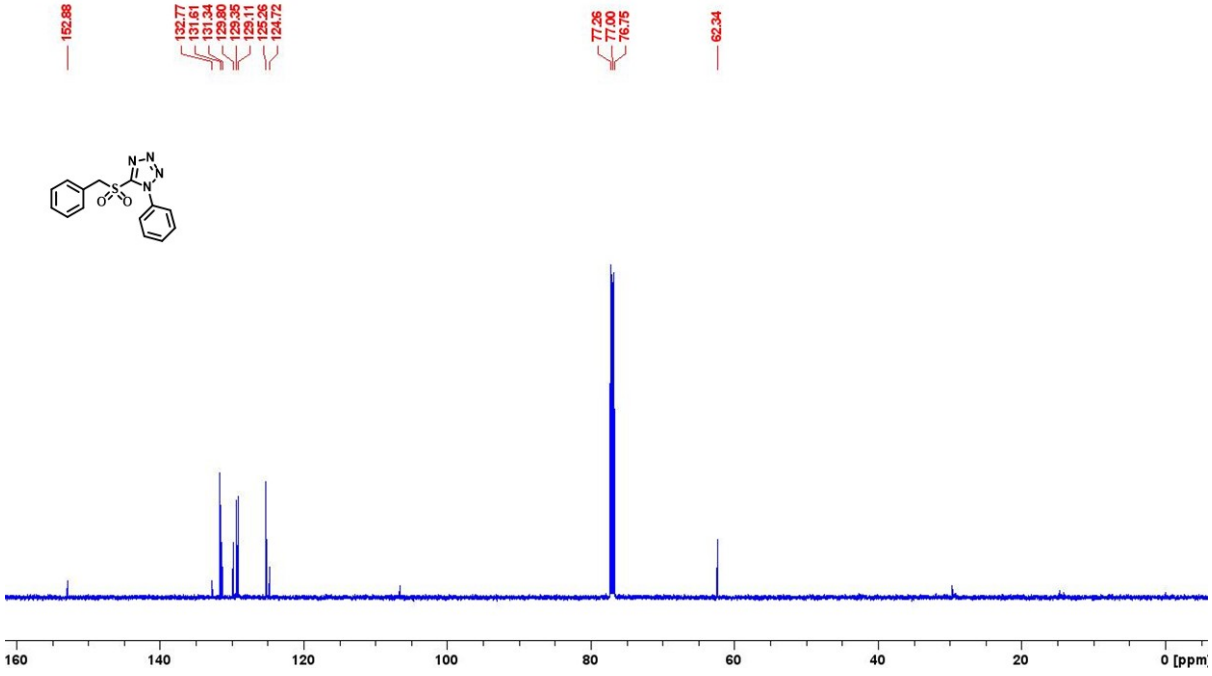

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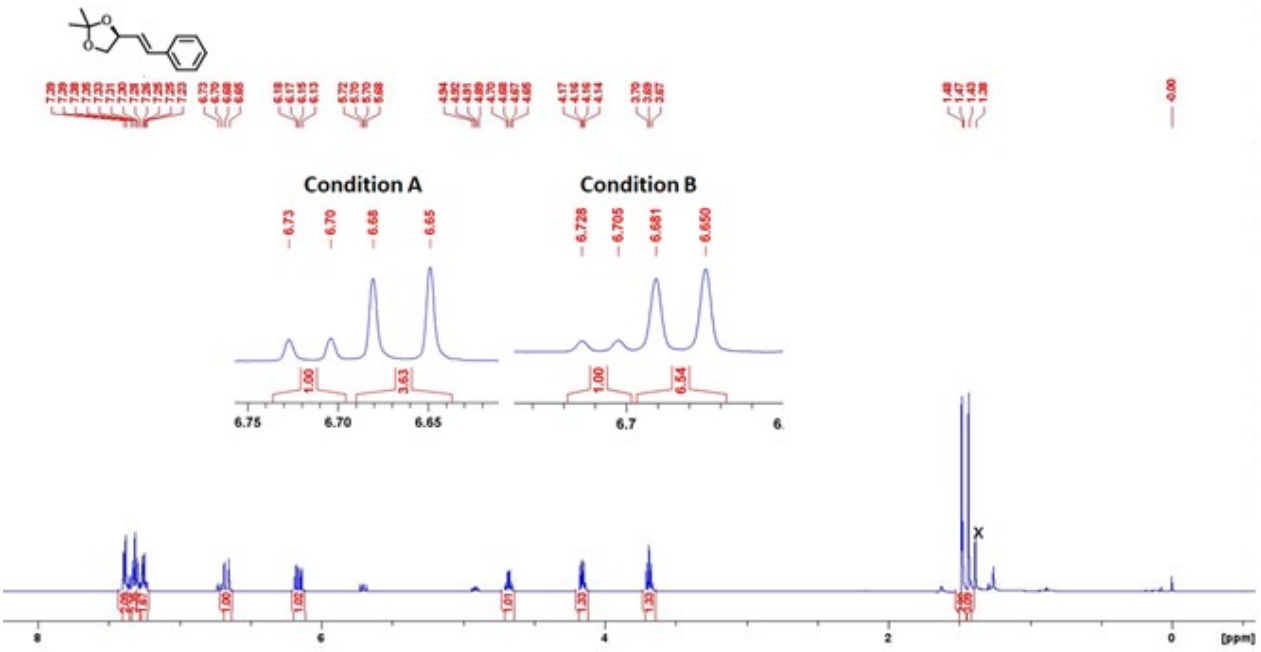

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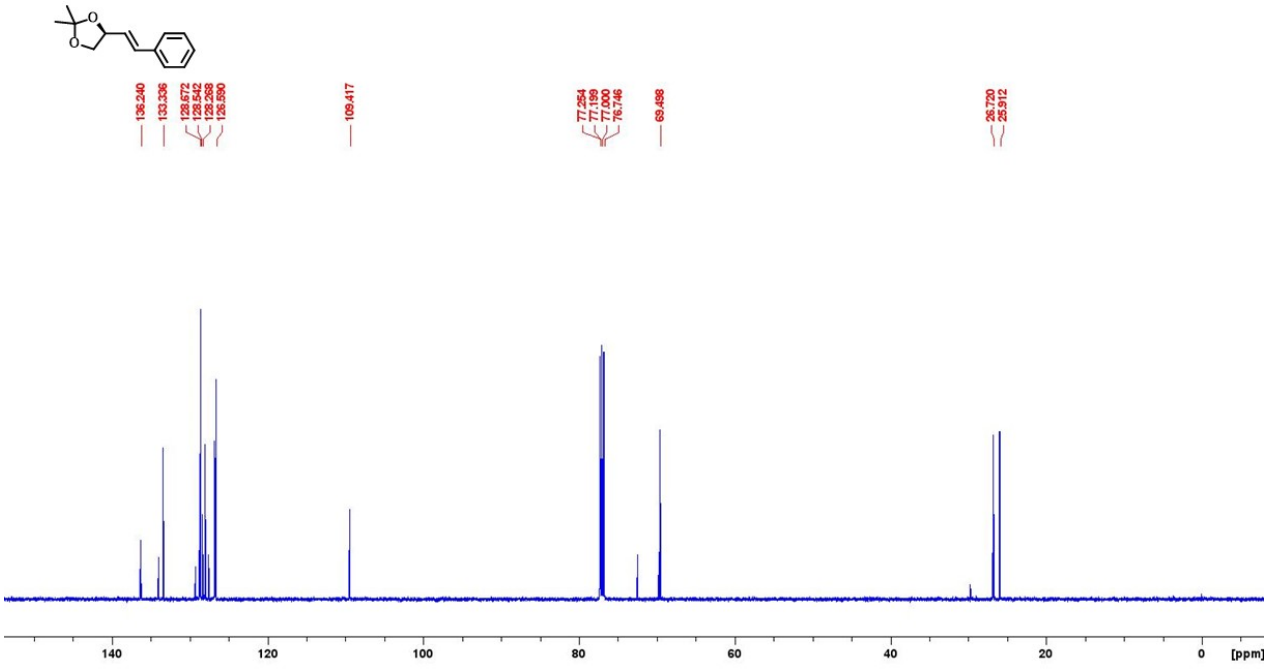

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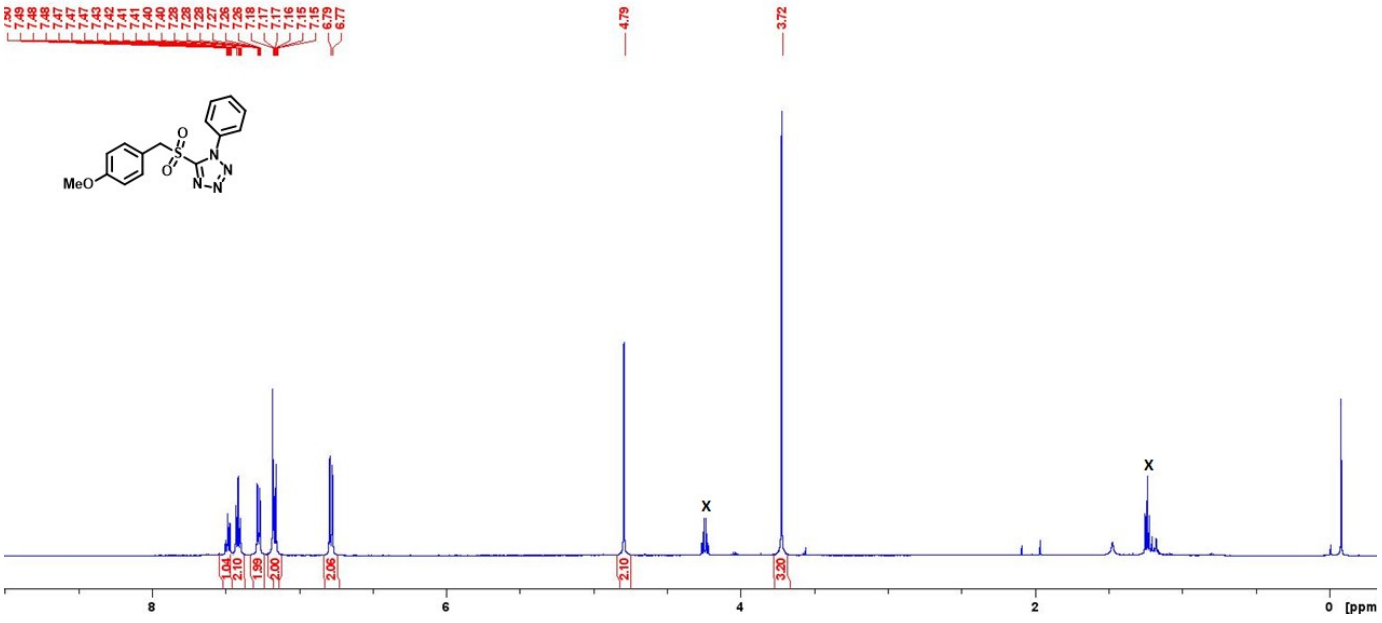

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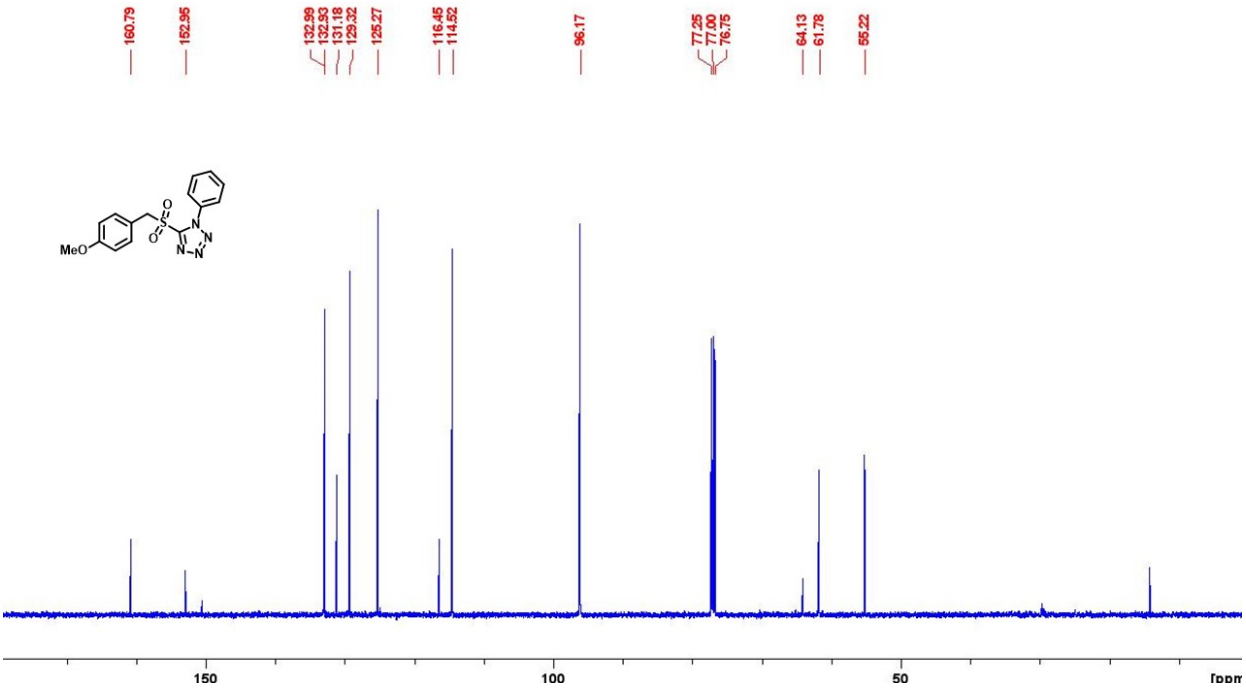

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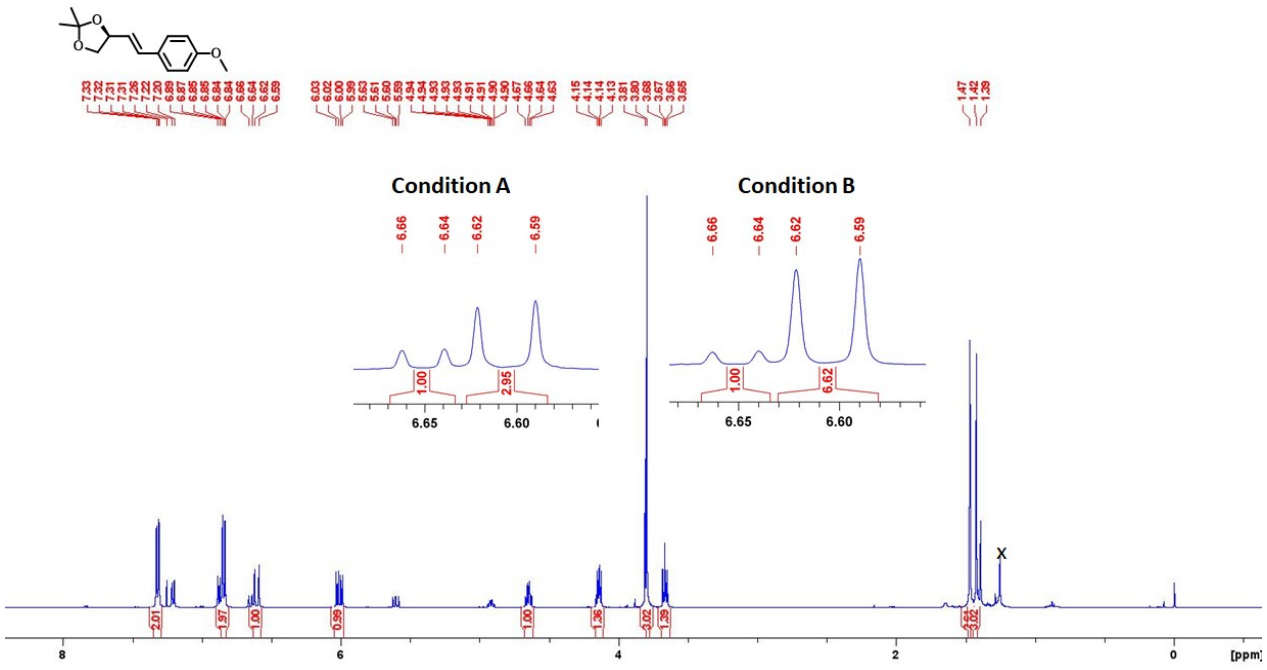

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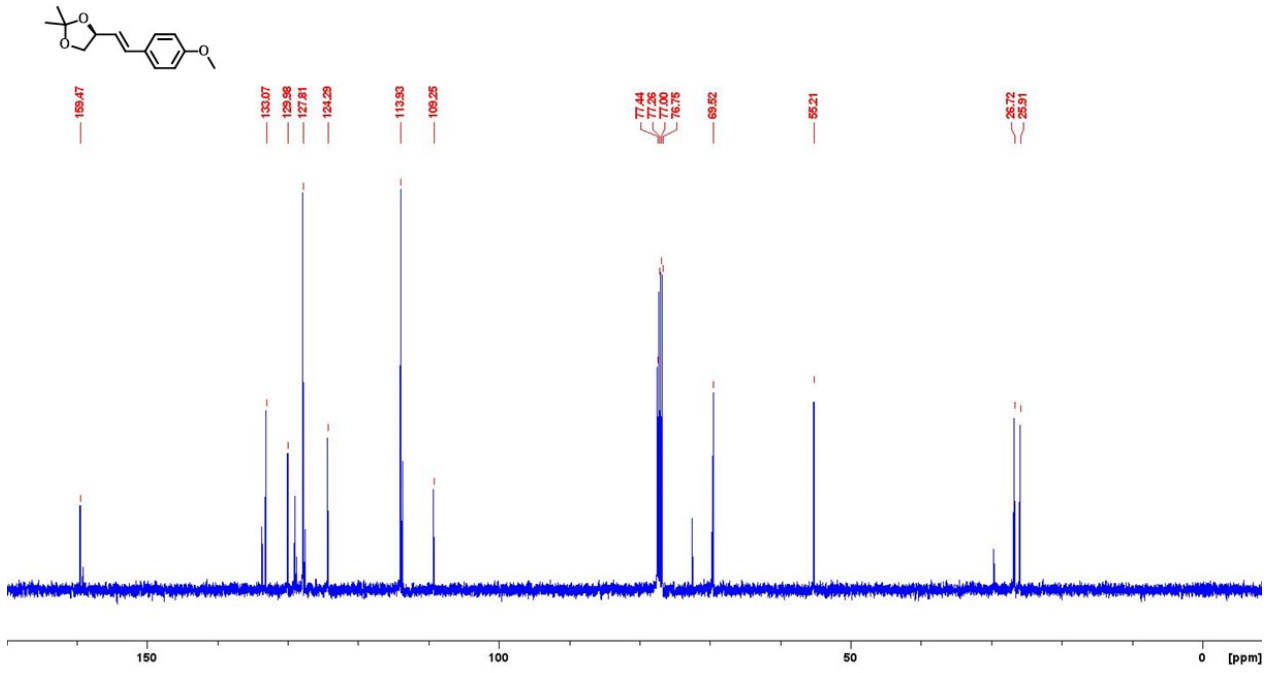

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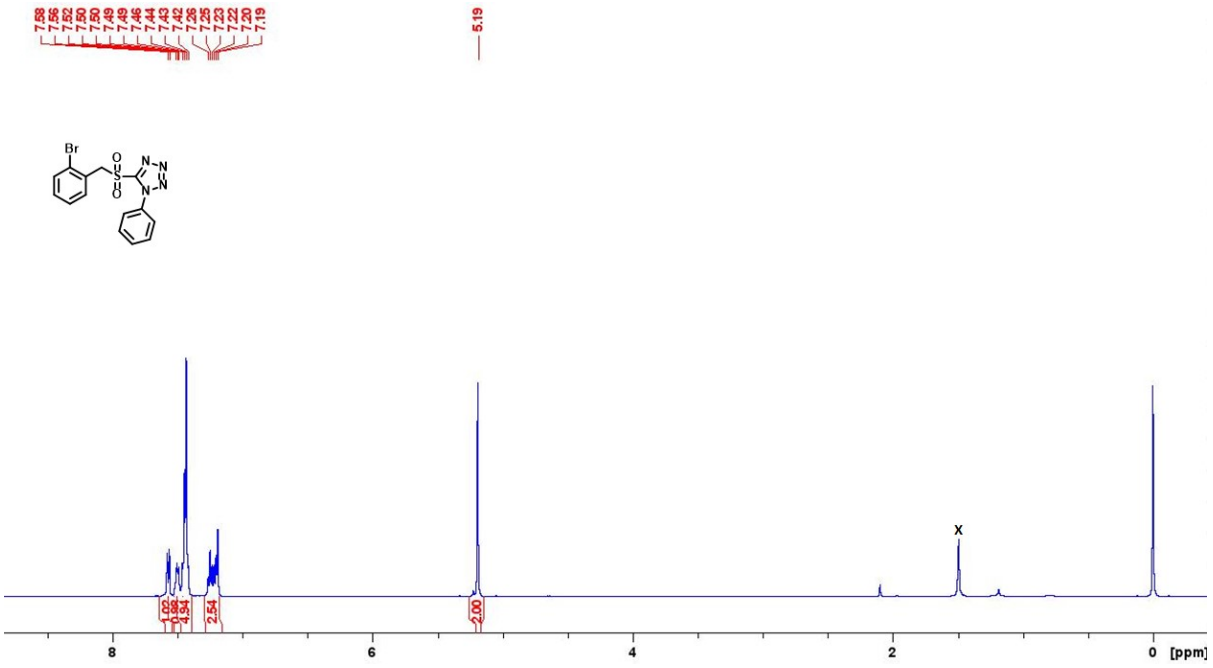

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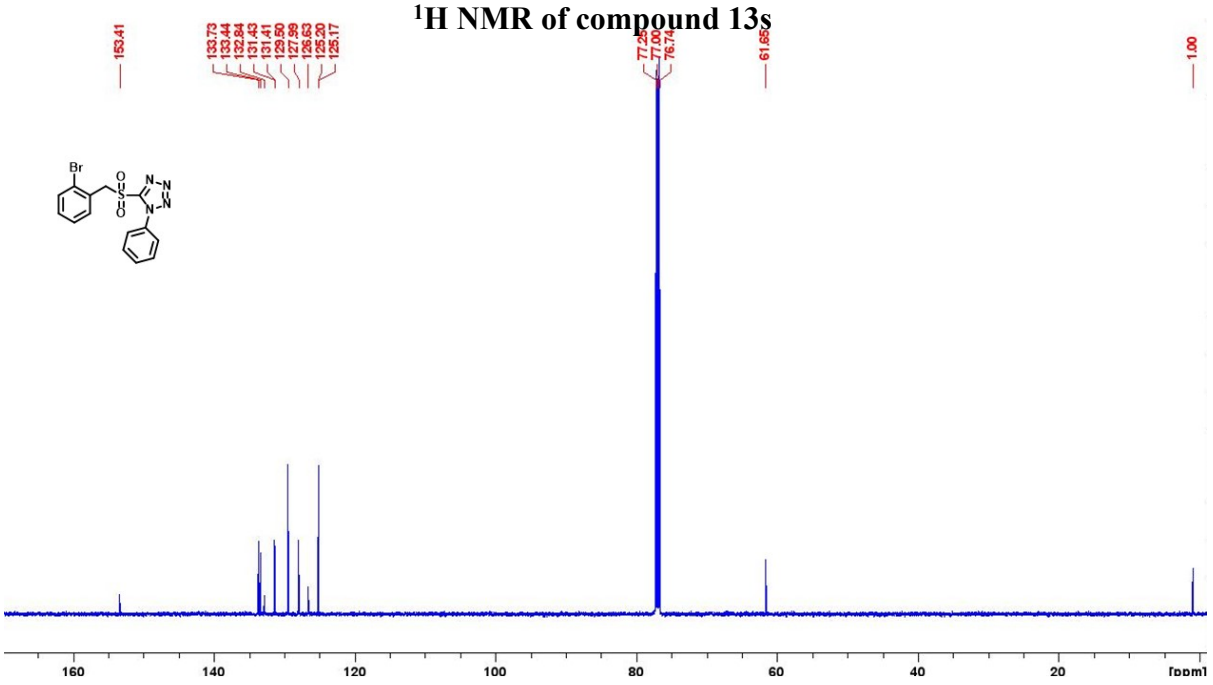

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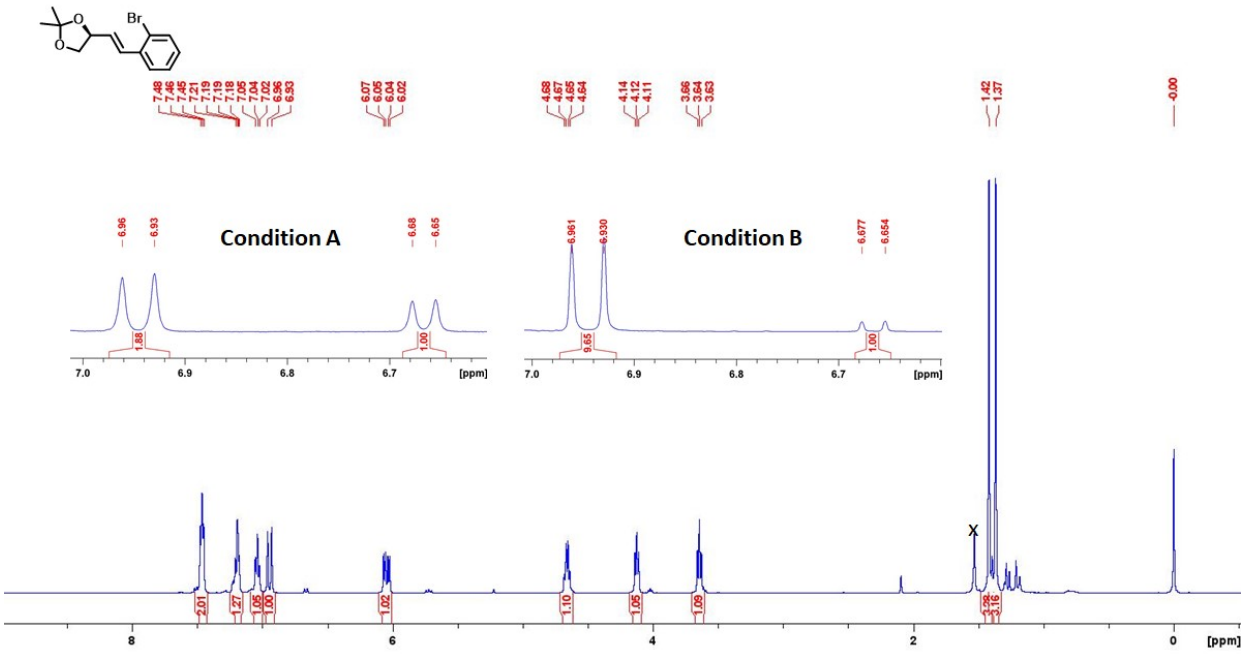

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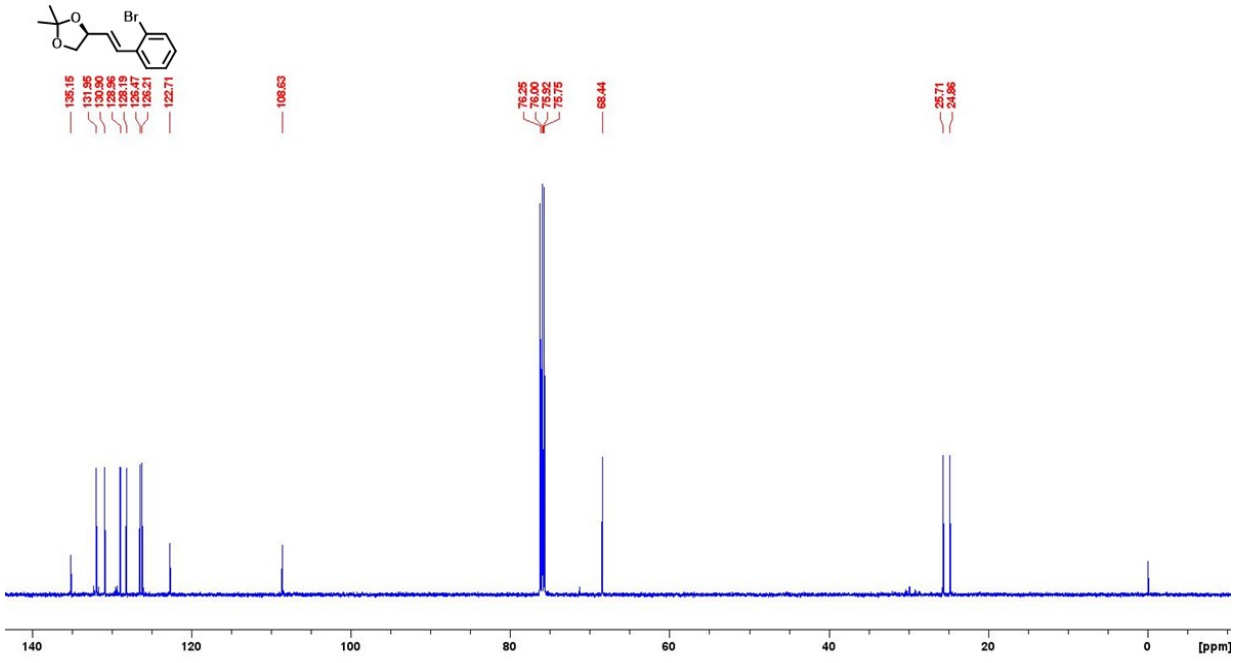

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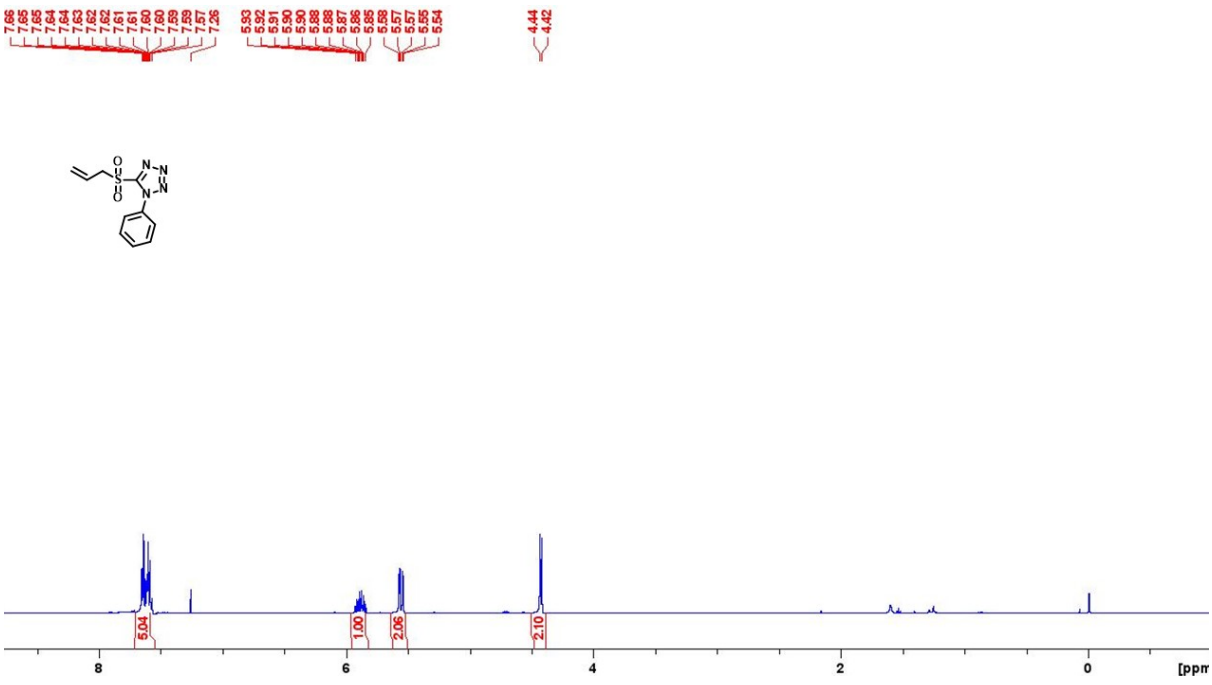

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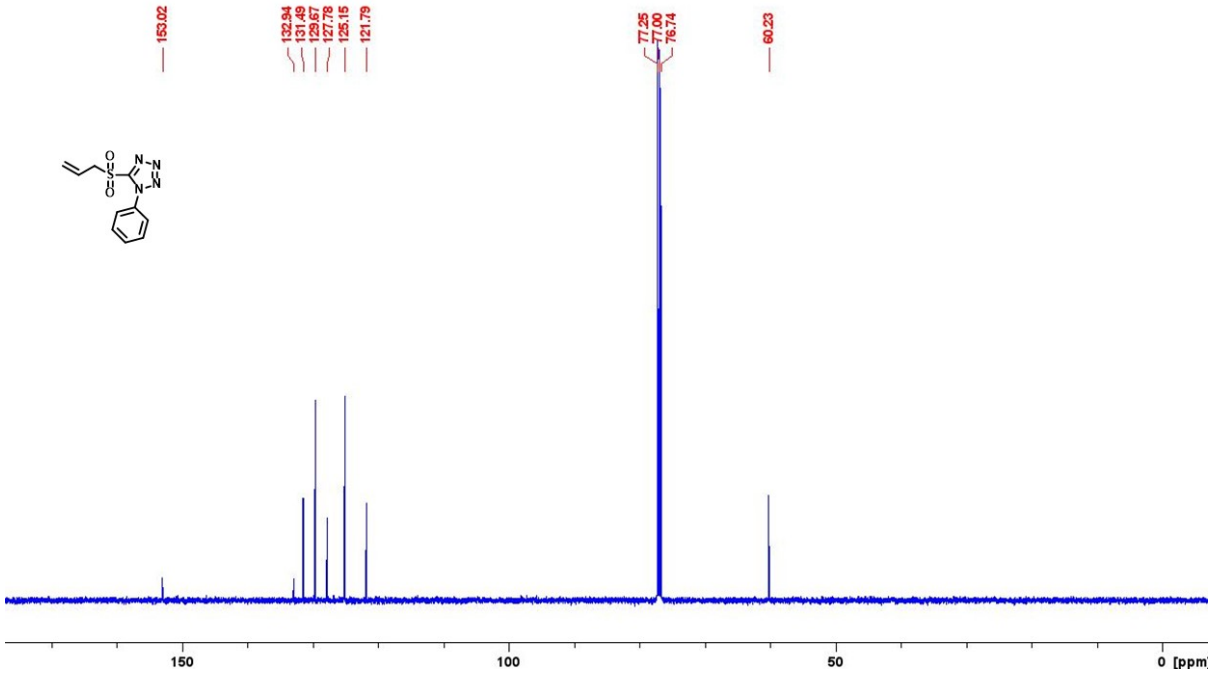

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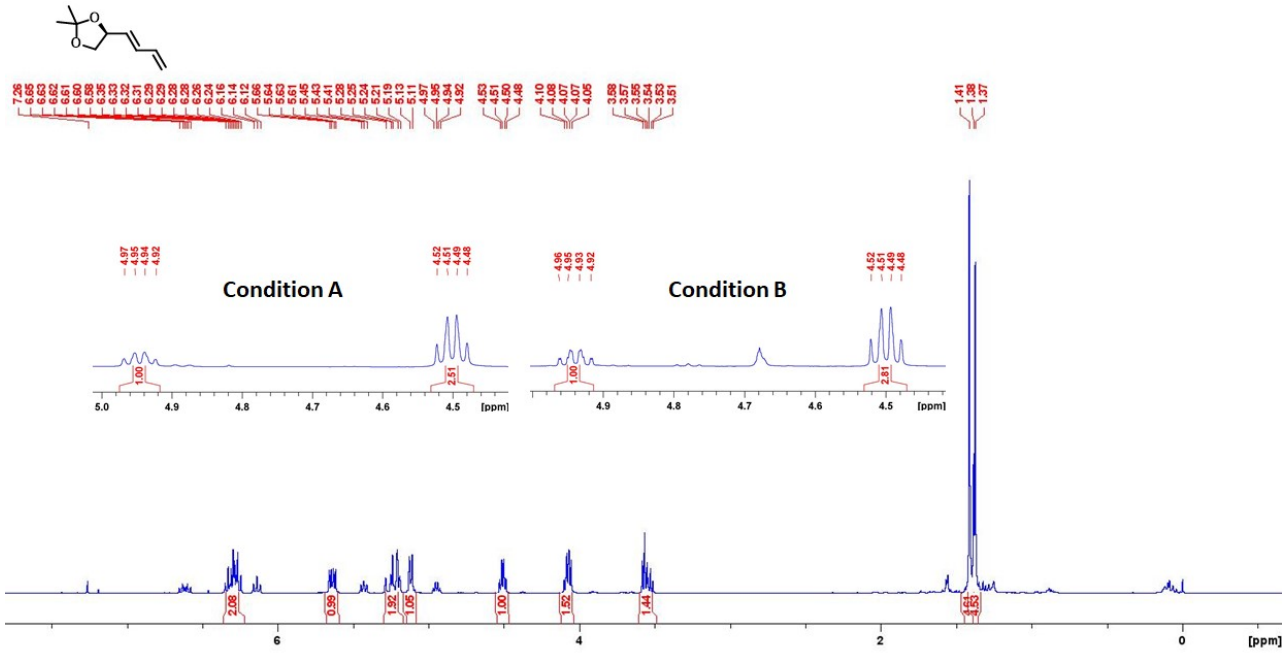

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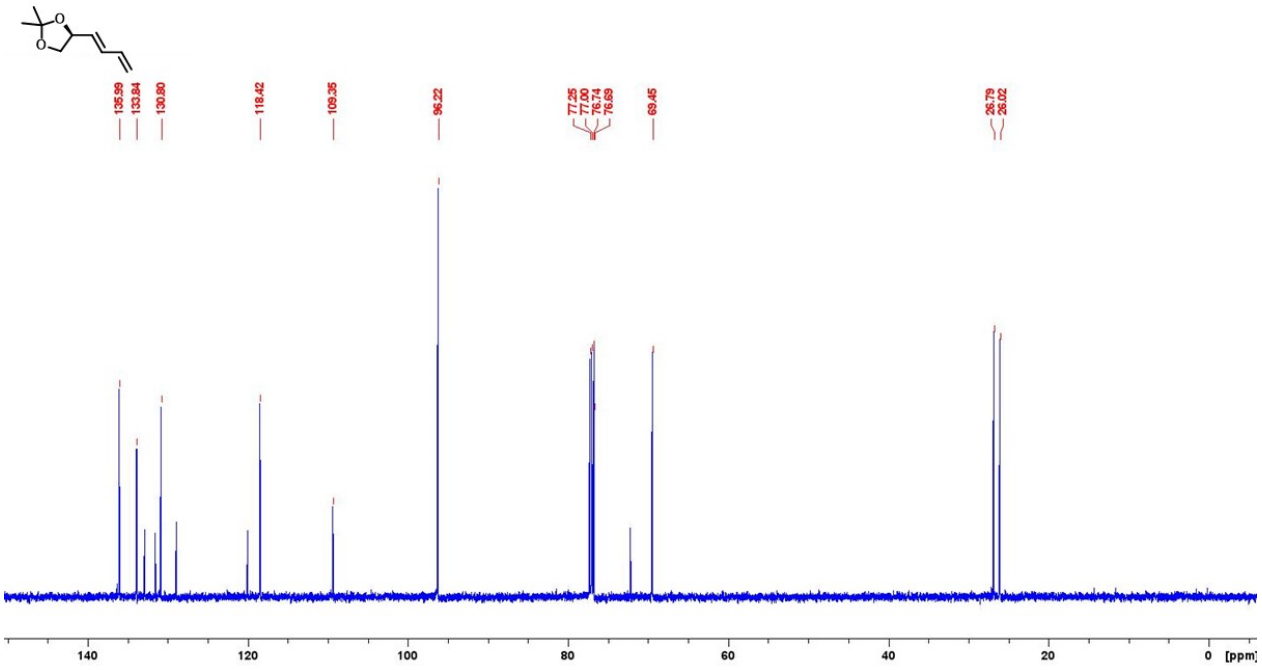

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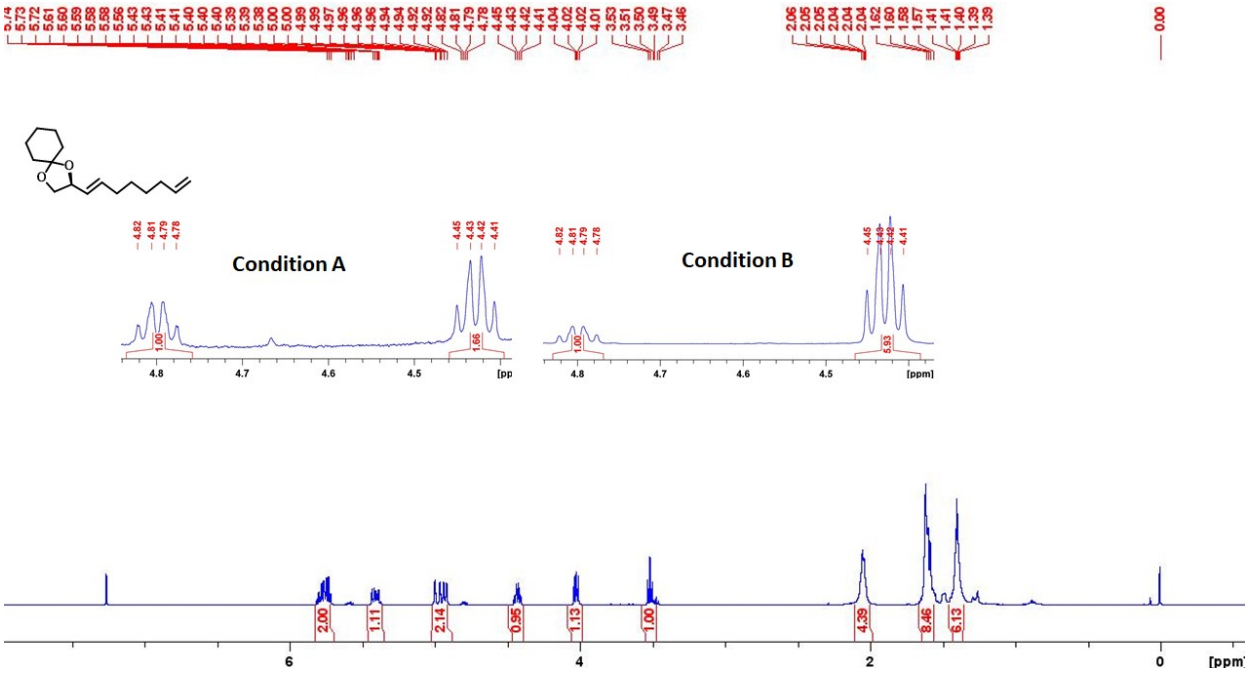

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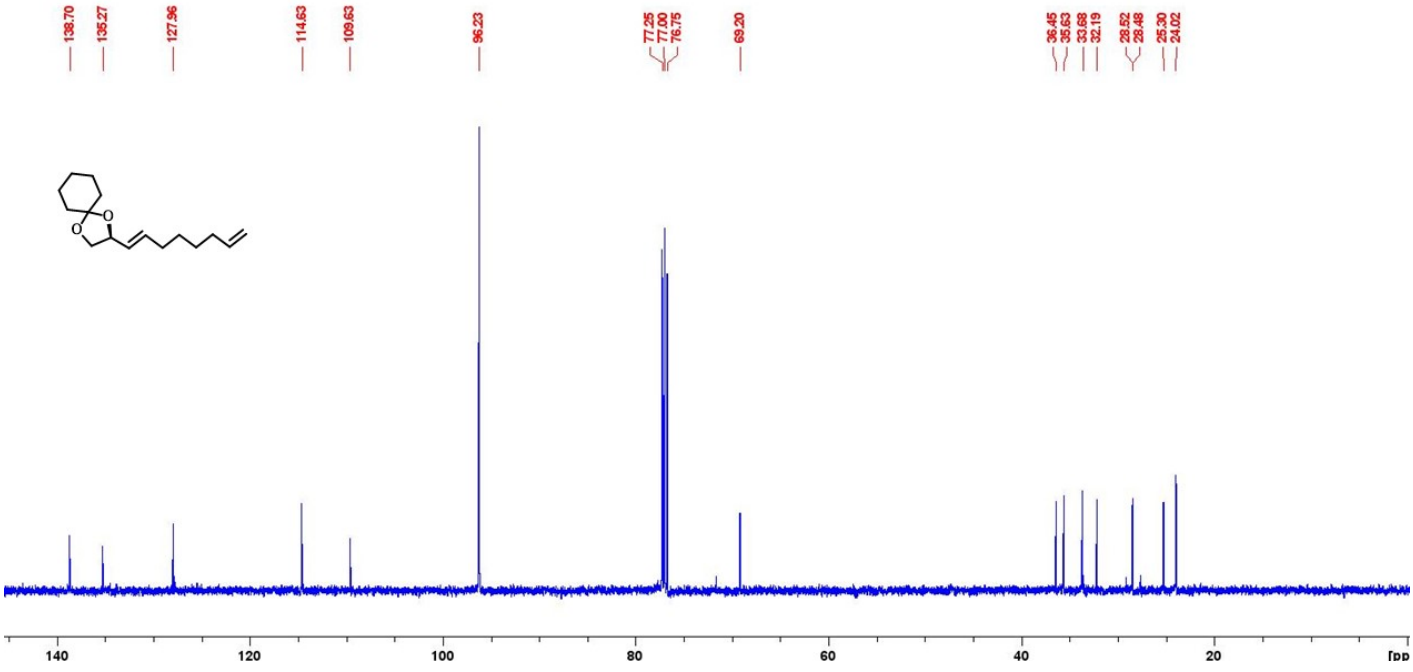

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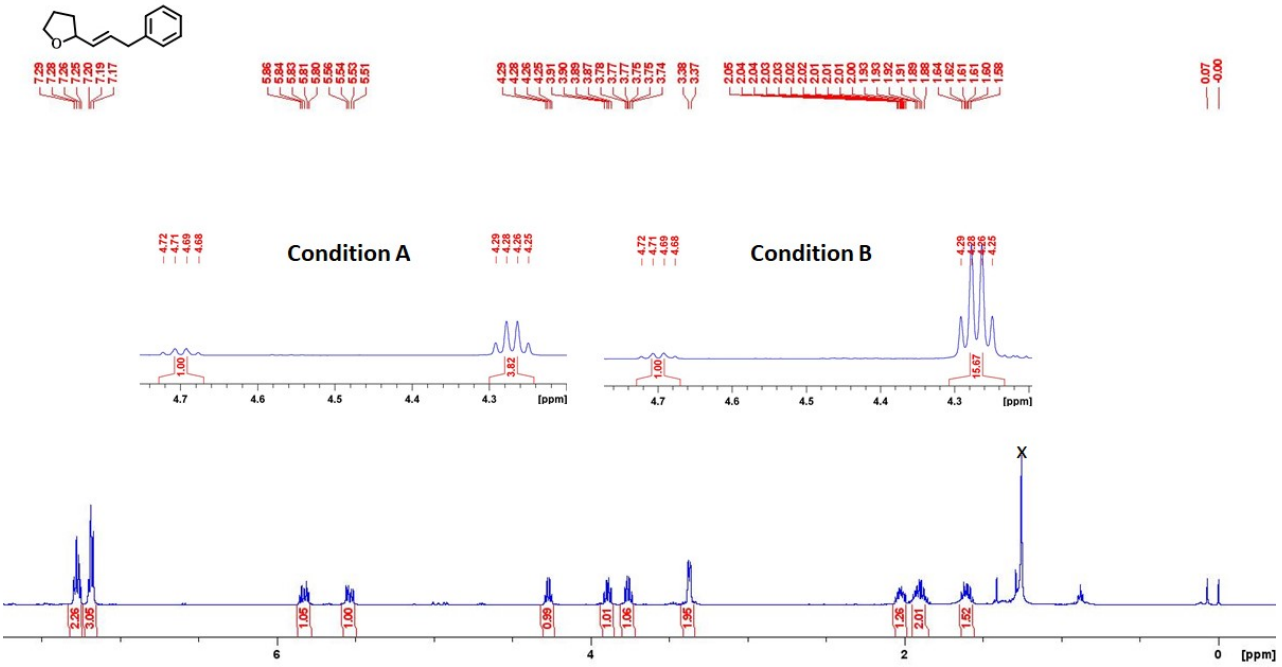
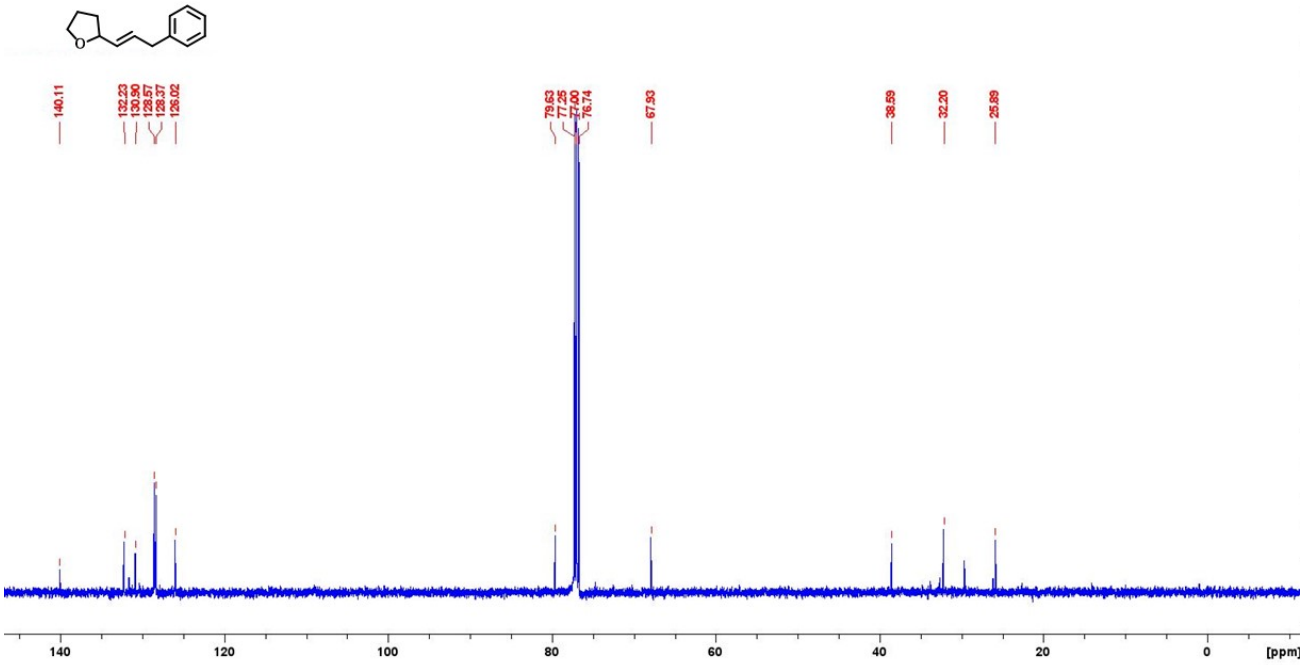


^{1}H NMR of compound 16



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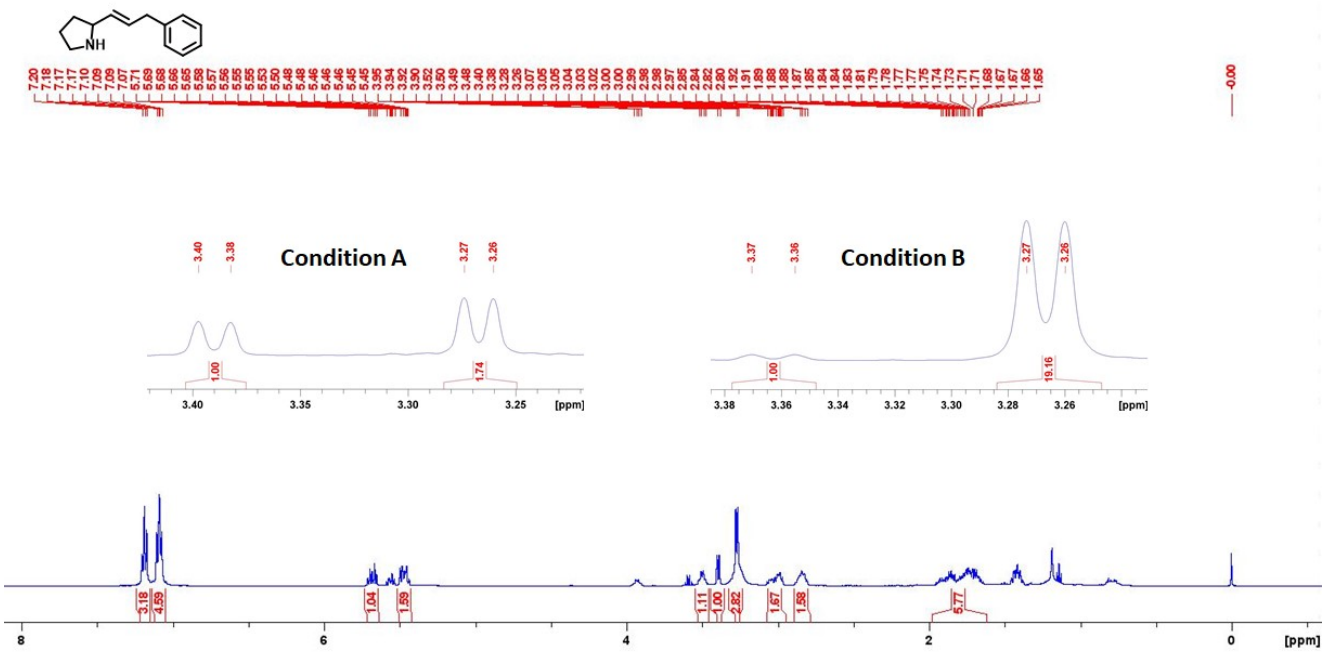
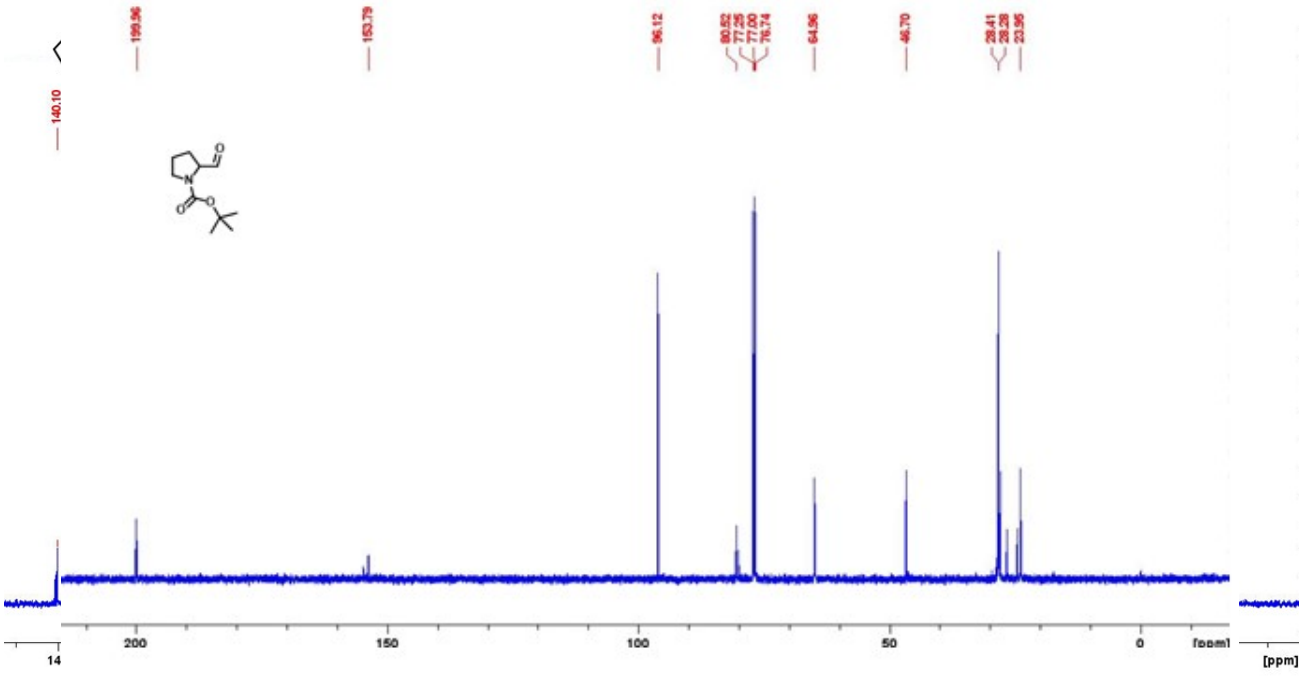
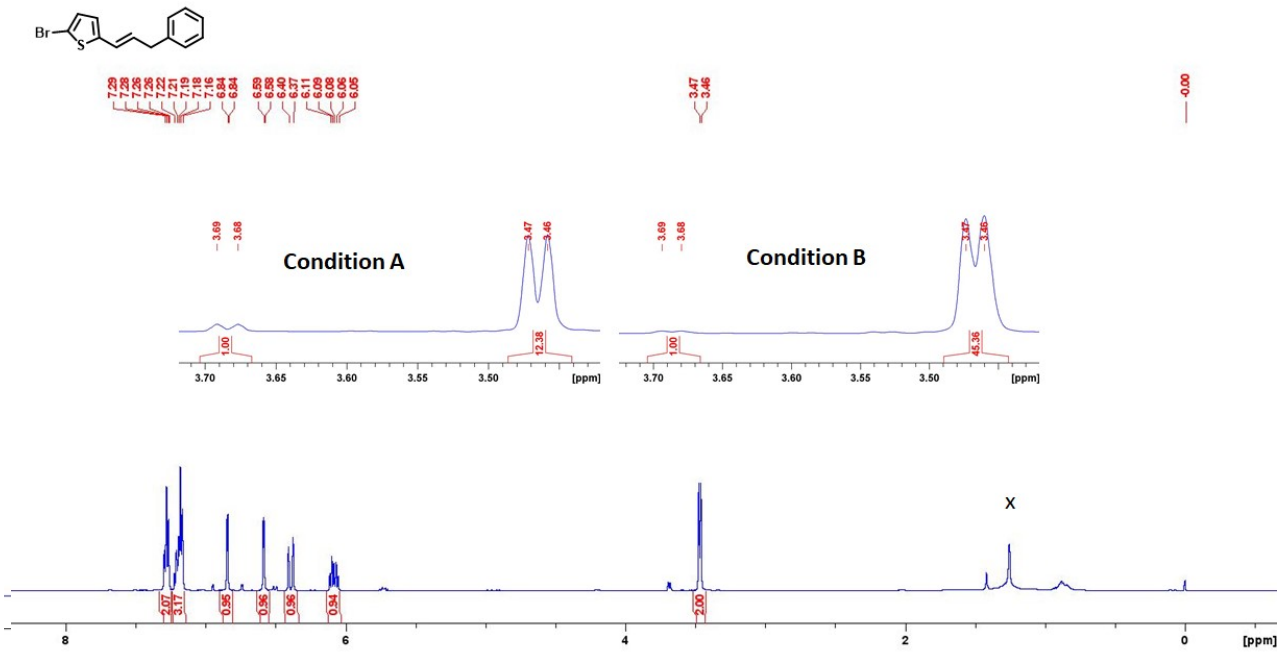


^{1}H NMR of compound 17a

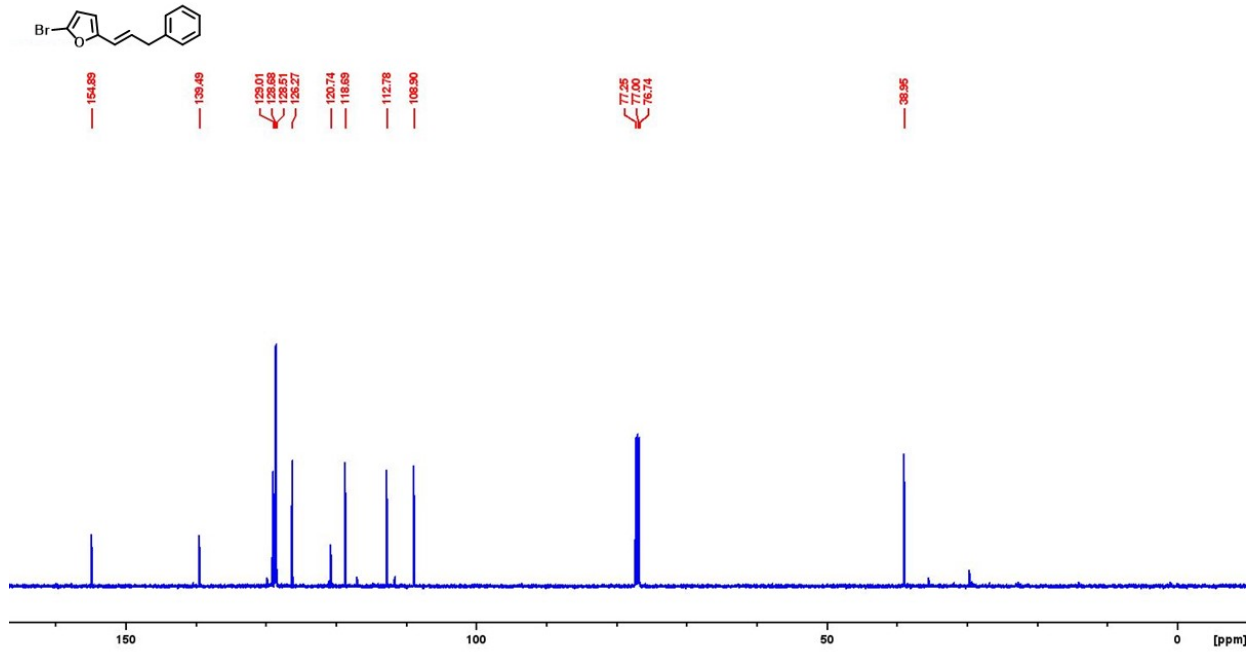


^{13}C NMR of compound 17

^{13}C NMR of compound 17a

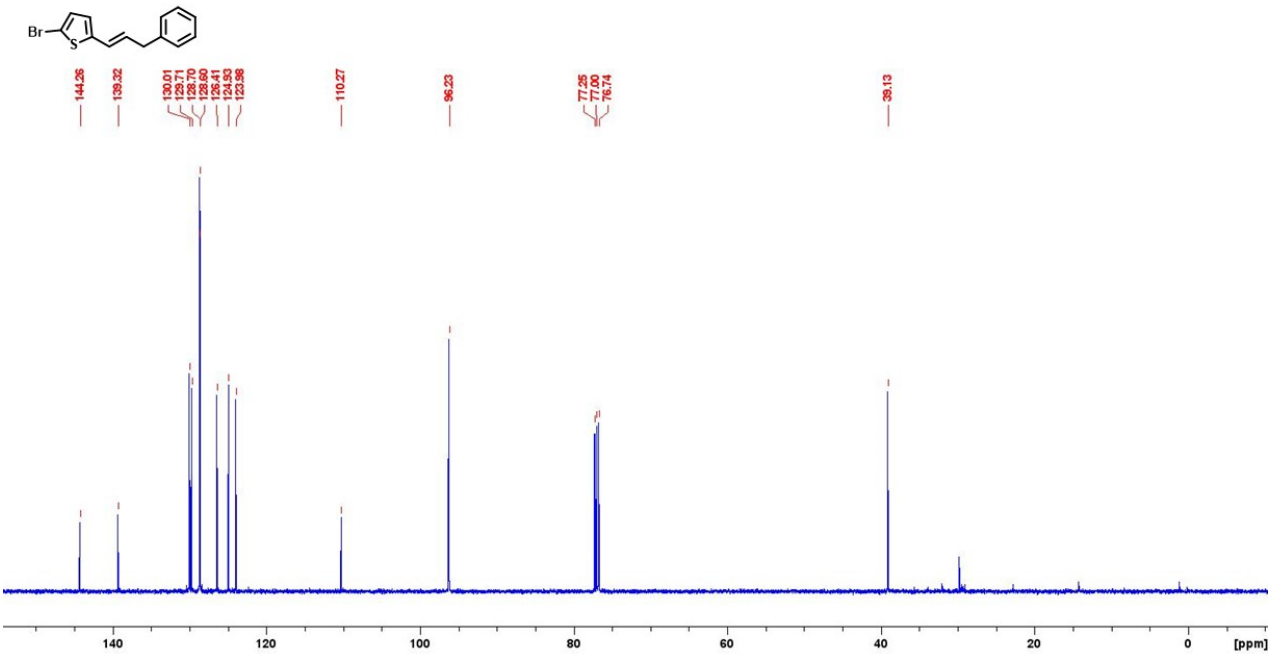


^{1}H NMR of compound 18

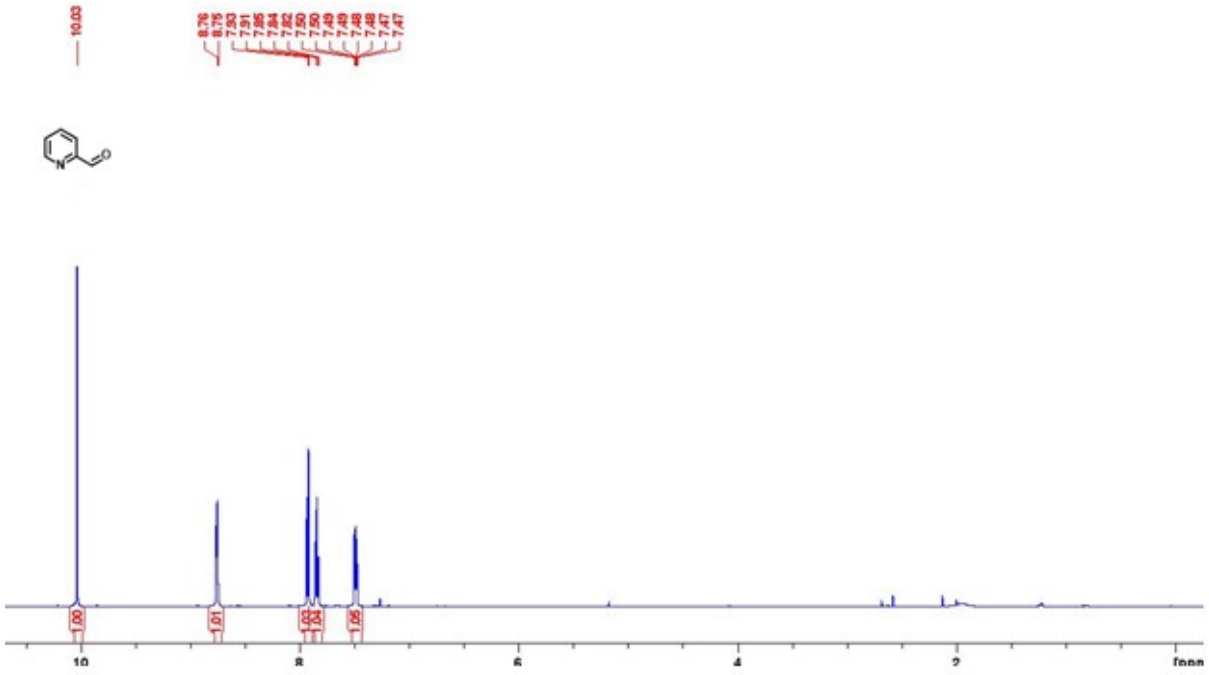


^{13}C NMR of compound 18

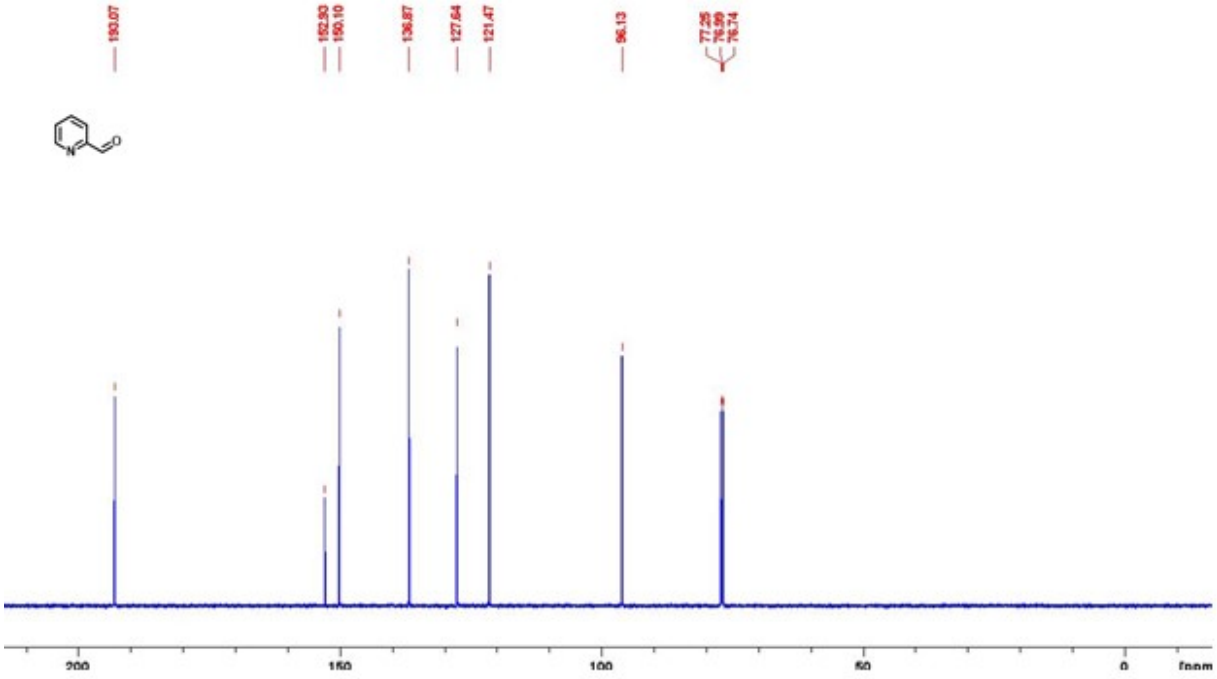
^{1}H NMR of compound 19



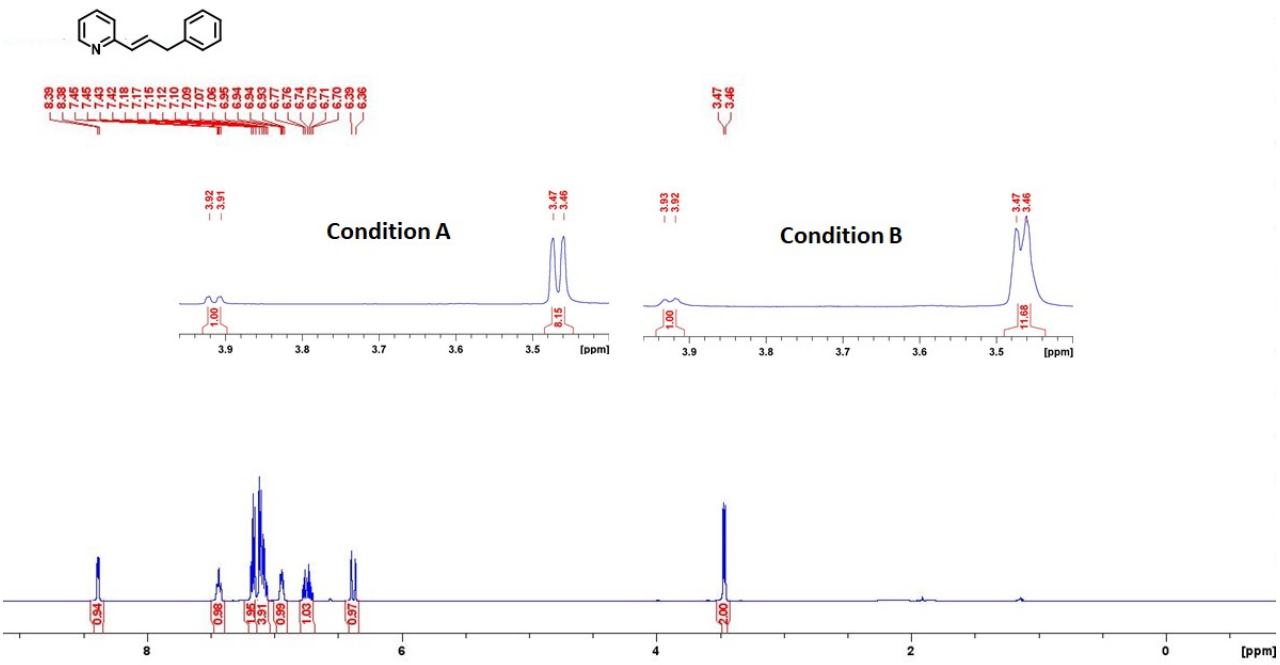
^{13}C NMR of compound 19



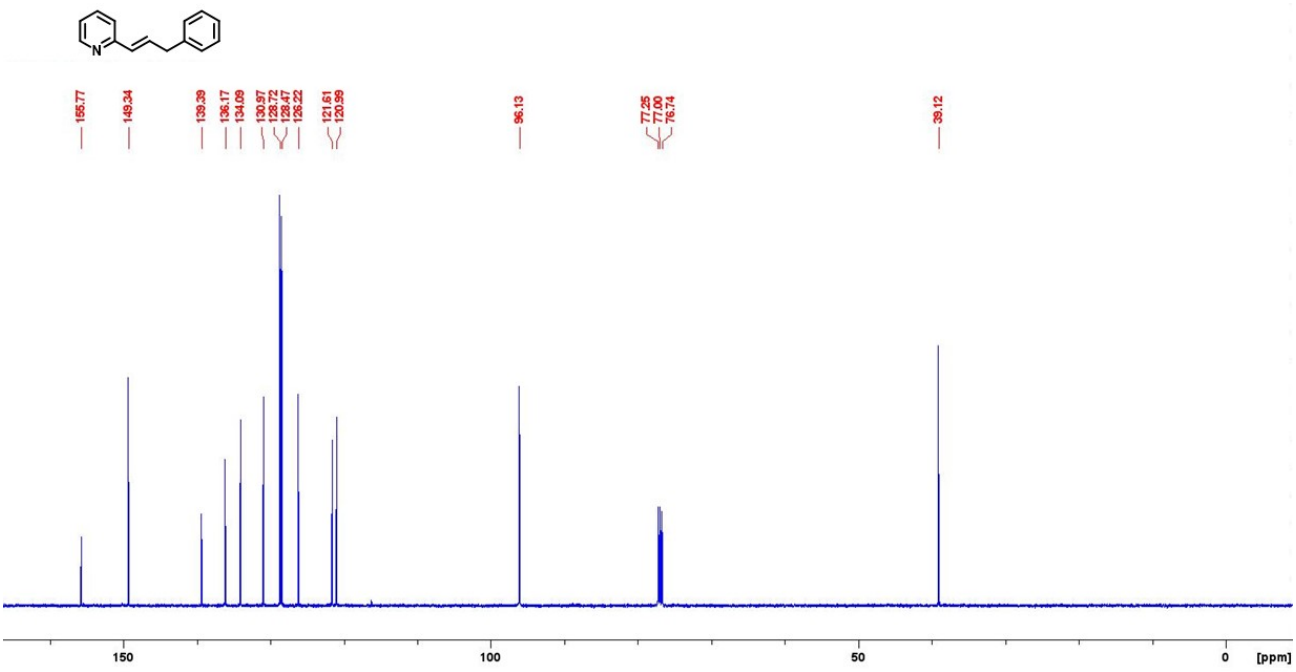
^{1}H NMR of compound 20a



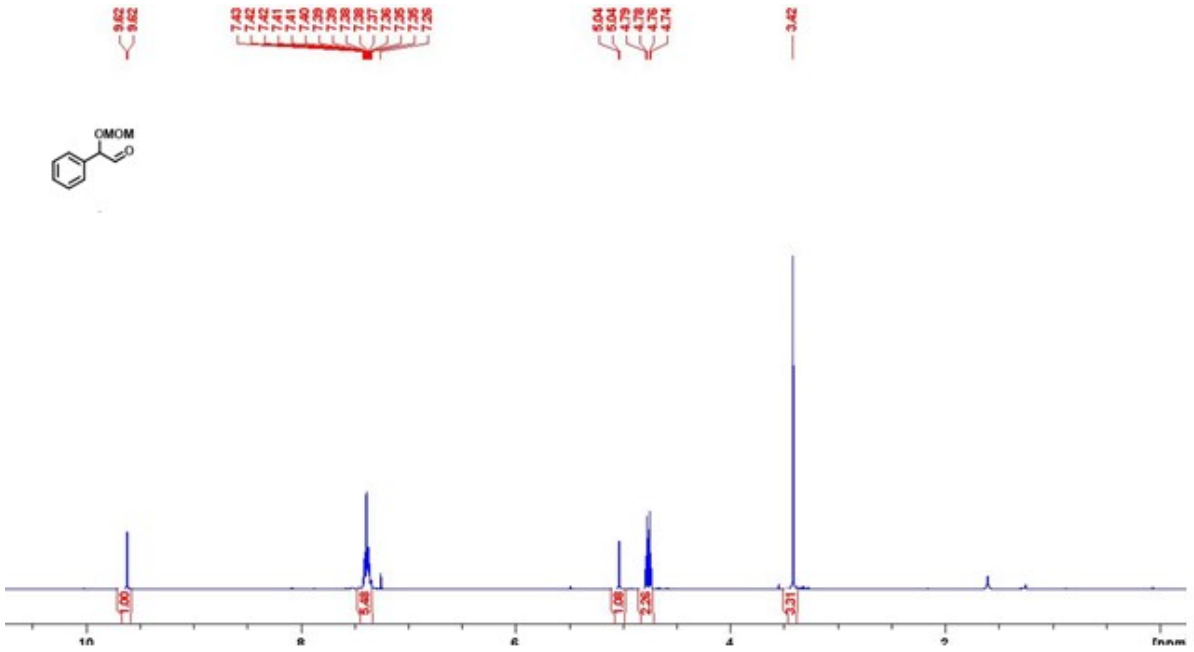
^{13}C NMR of compound 20a



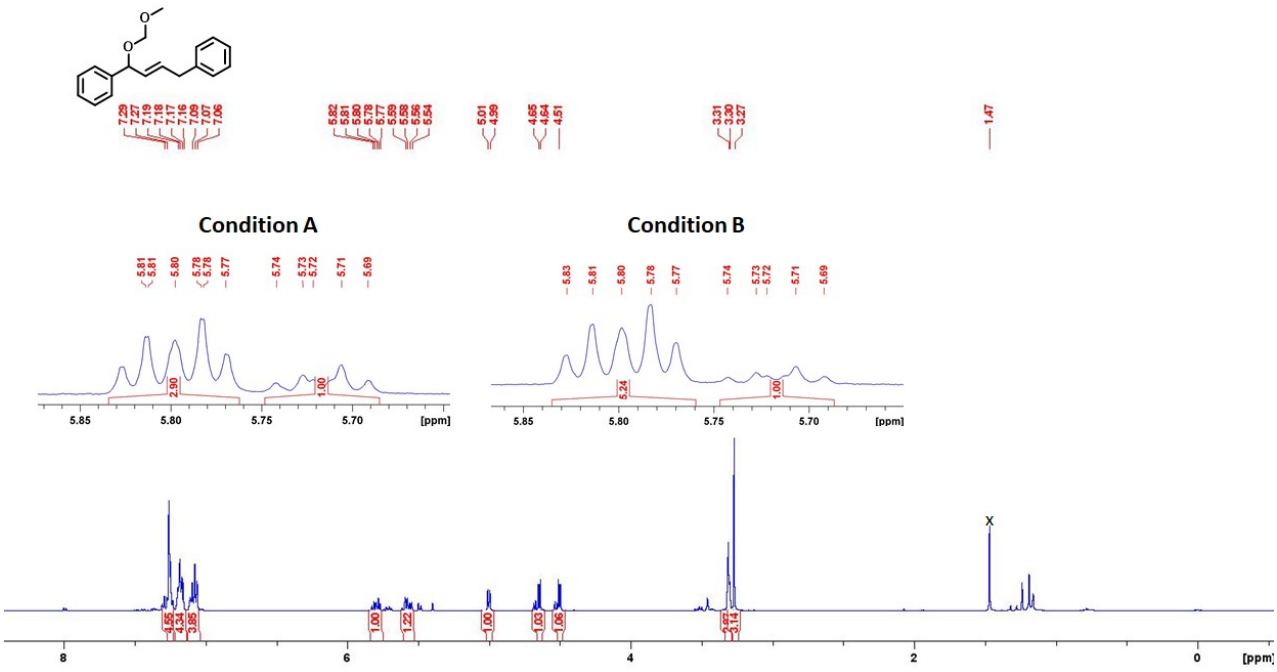
^{1}H NMR of compound 20



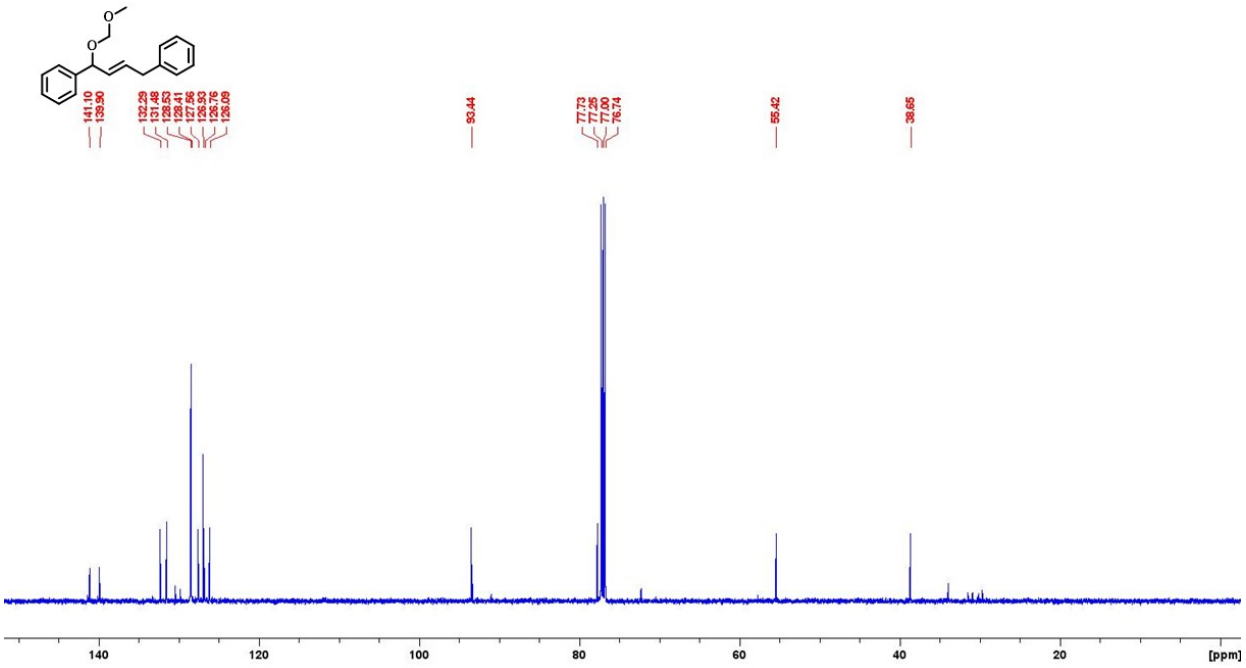
^{13}C NMR of compound 20



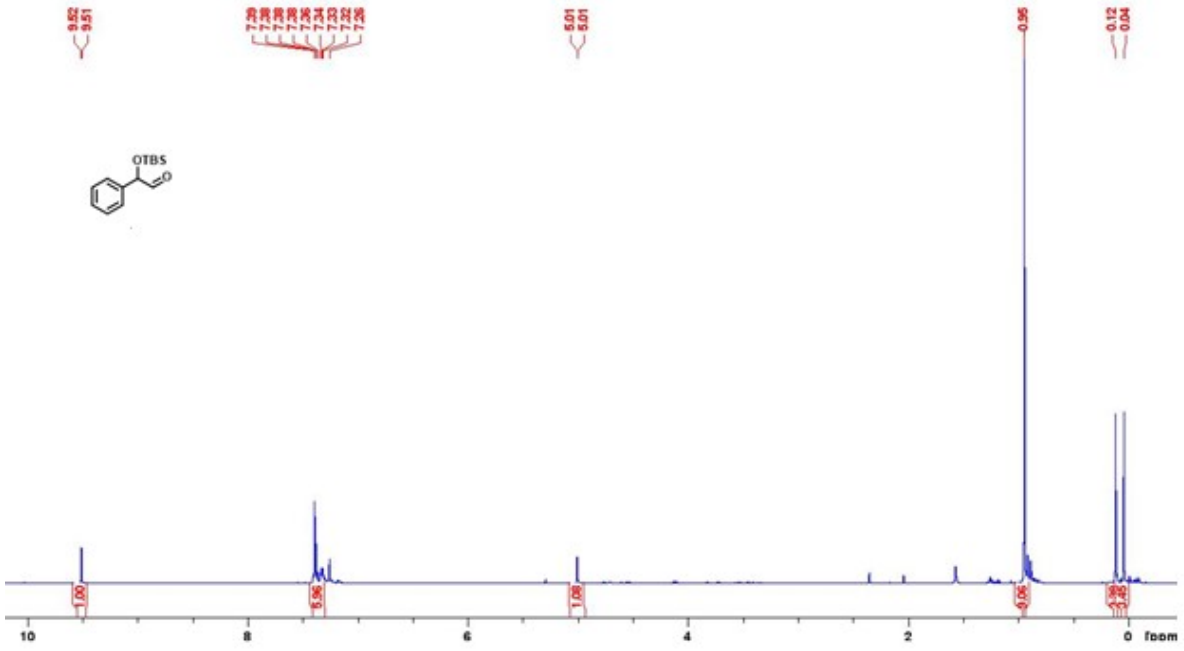
^{1}H NMR of compound 21a



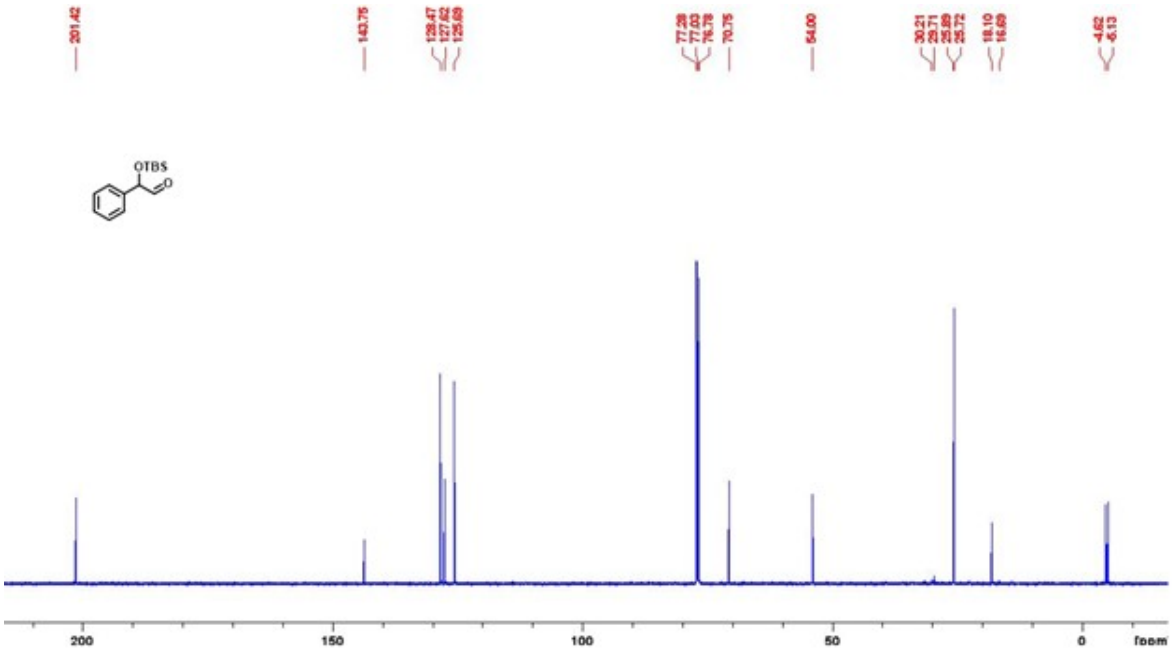
^{1}H NMR of compound 21



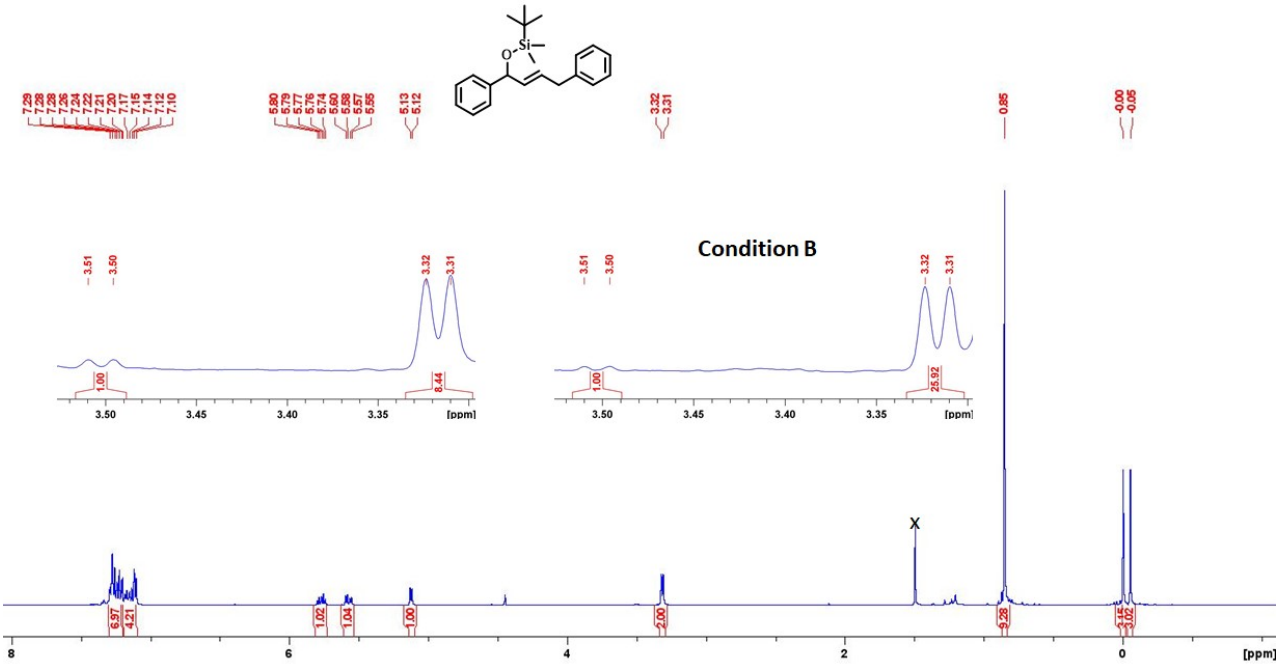
^{13}C NMR of compound 21



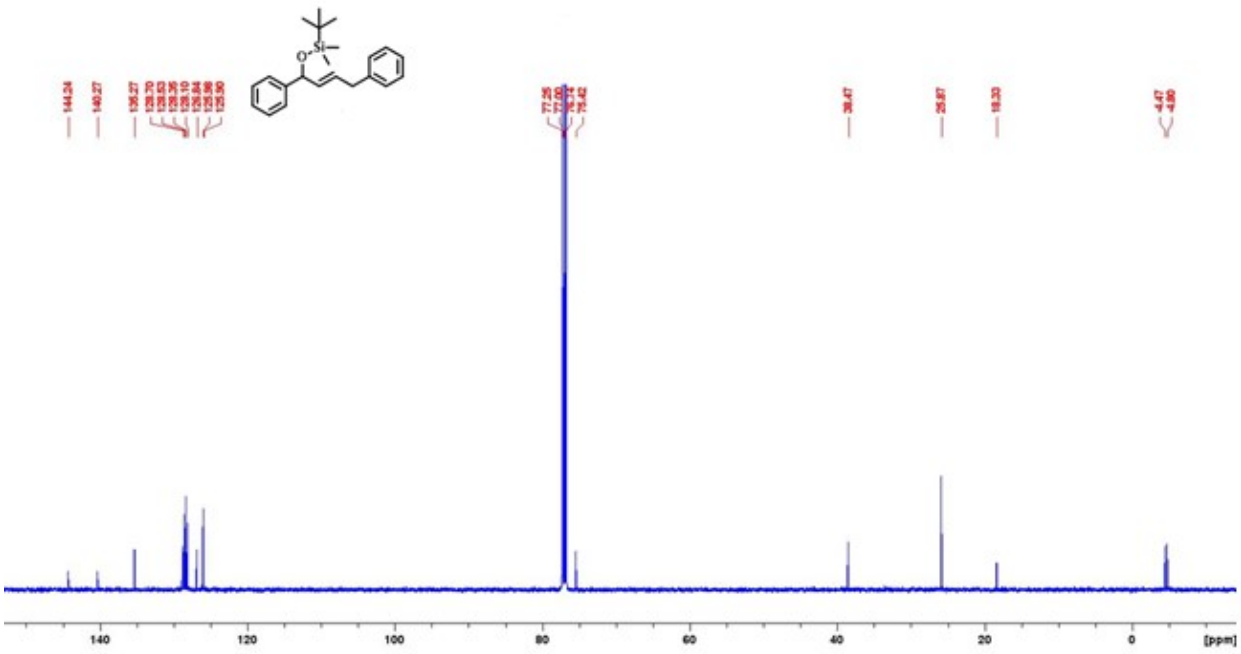
^{1}H NMR of compound 22a



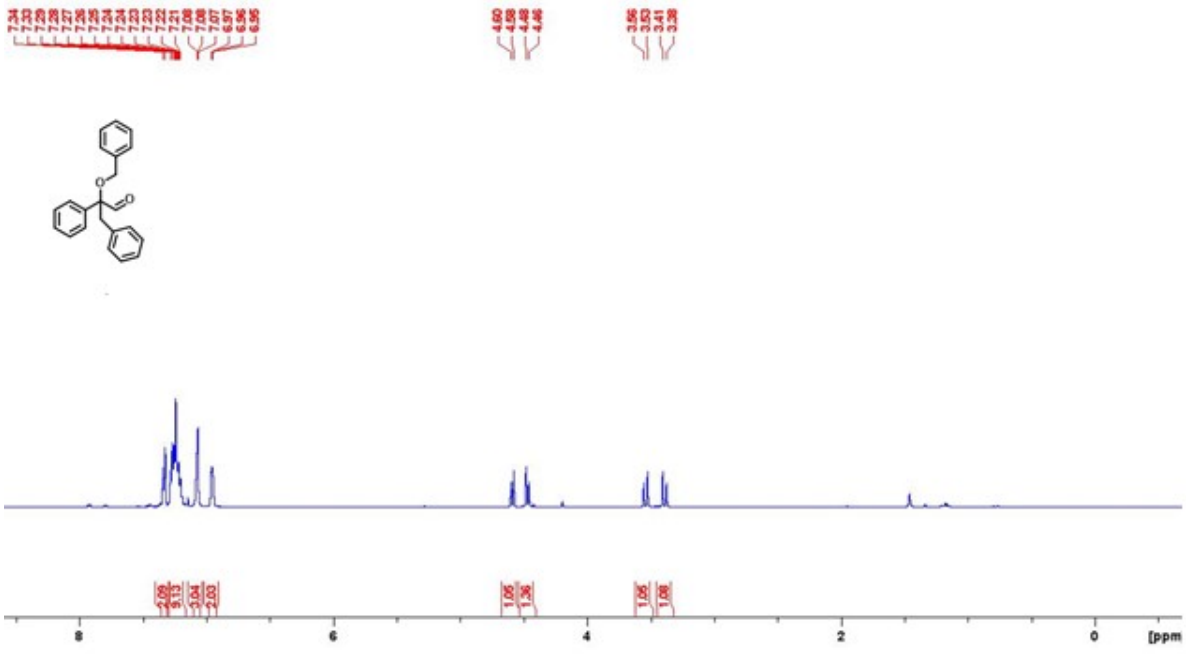
^{13}C NMR of compound 22a



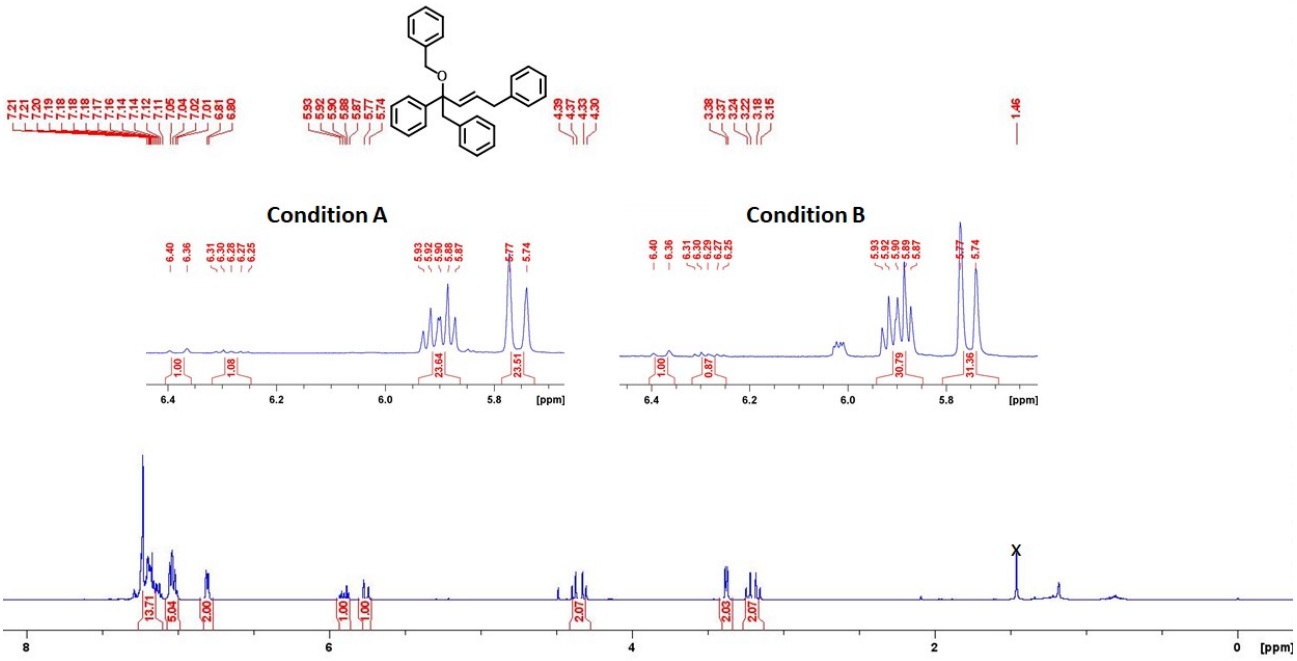
^{1}H NMR of compound 22



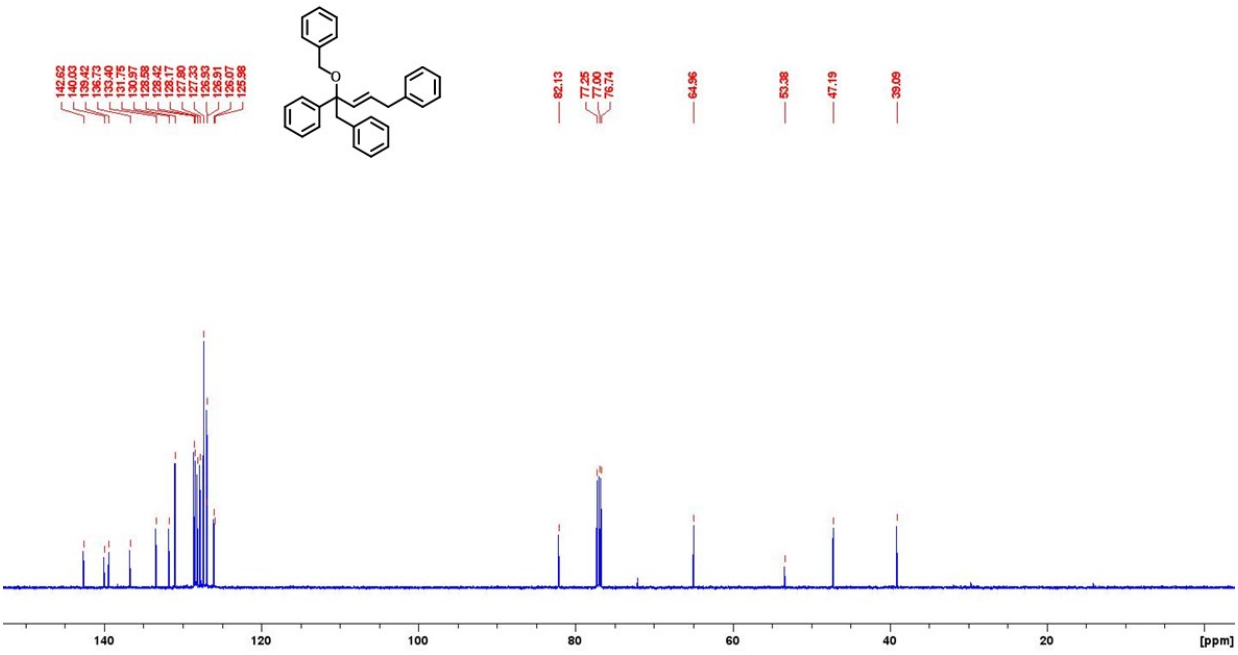
^{13}C NMR of compound 22



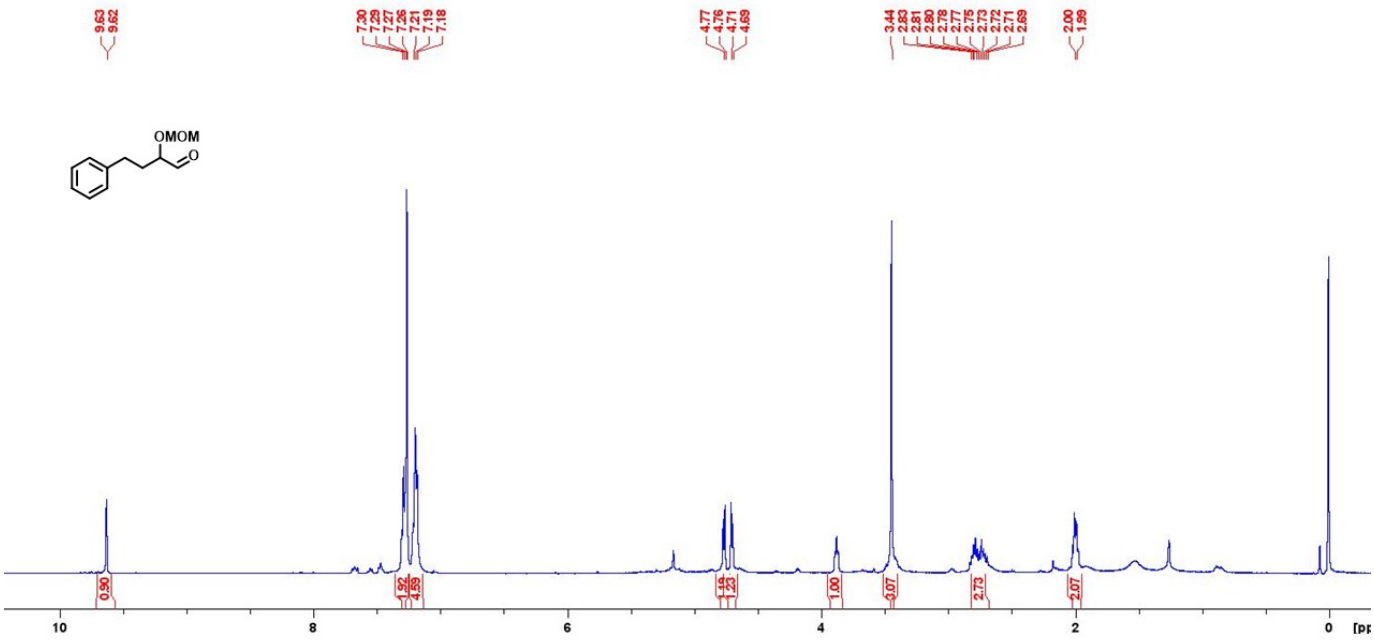
^{1}H NMR of compound 23a



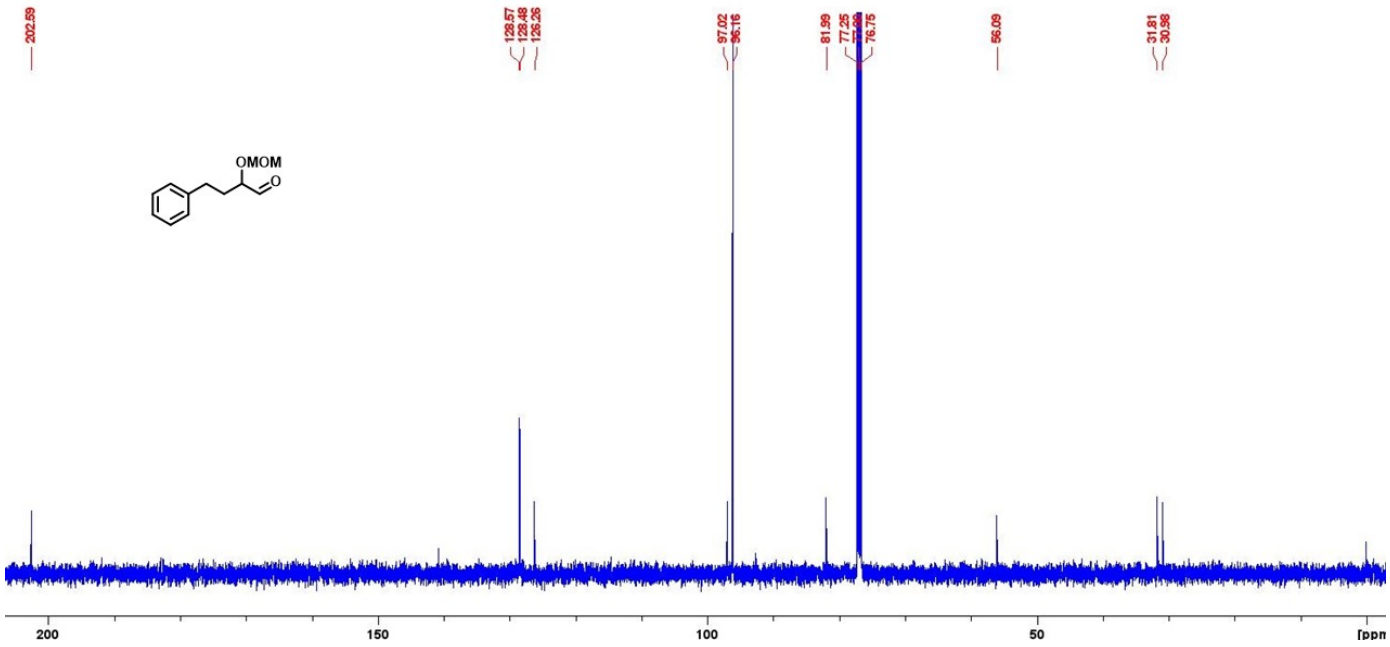
^{1}H NMR of compound 23



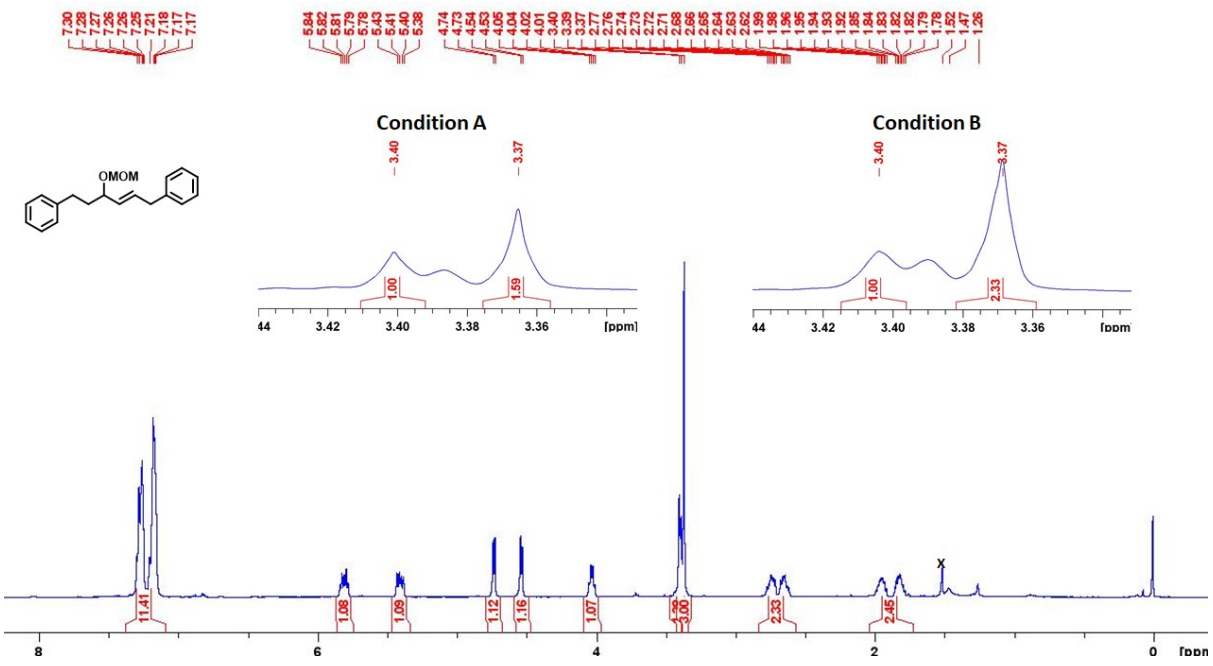
^{13}C NMR of compound 23



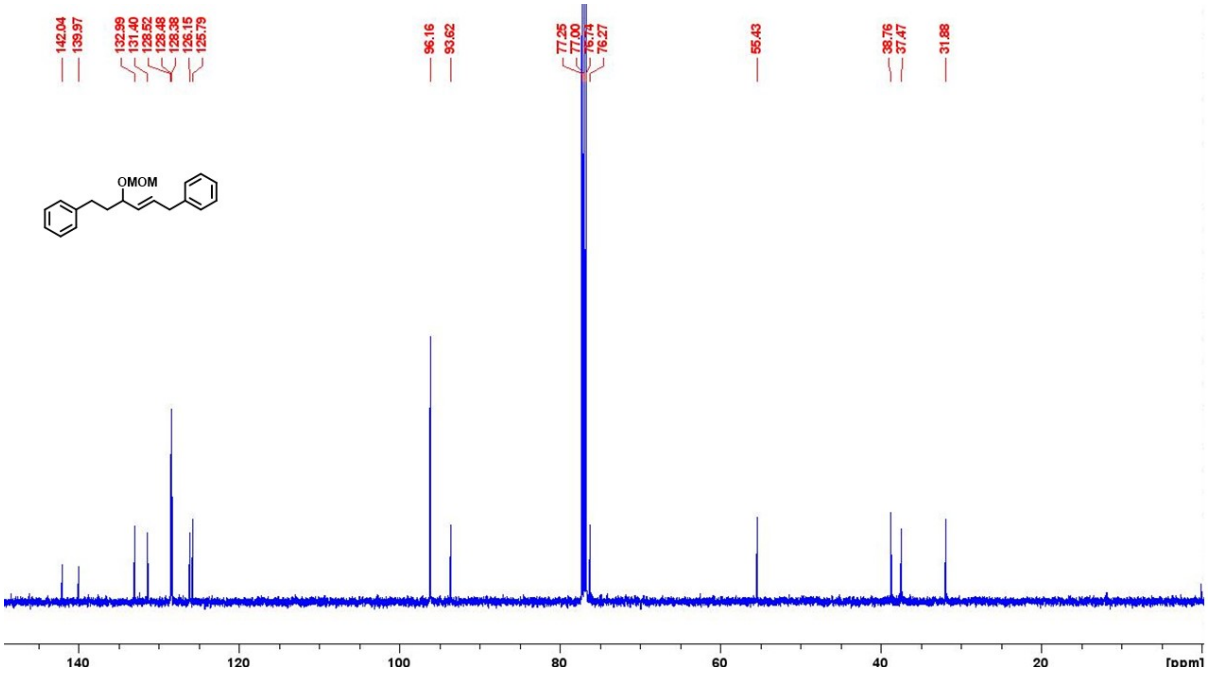
^{1}H NMR of compound 24a



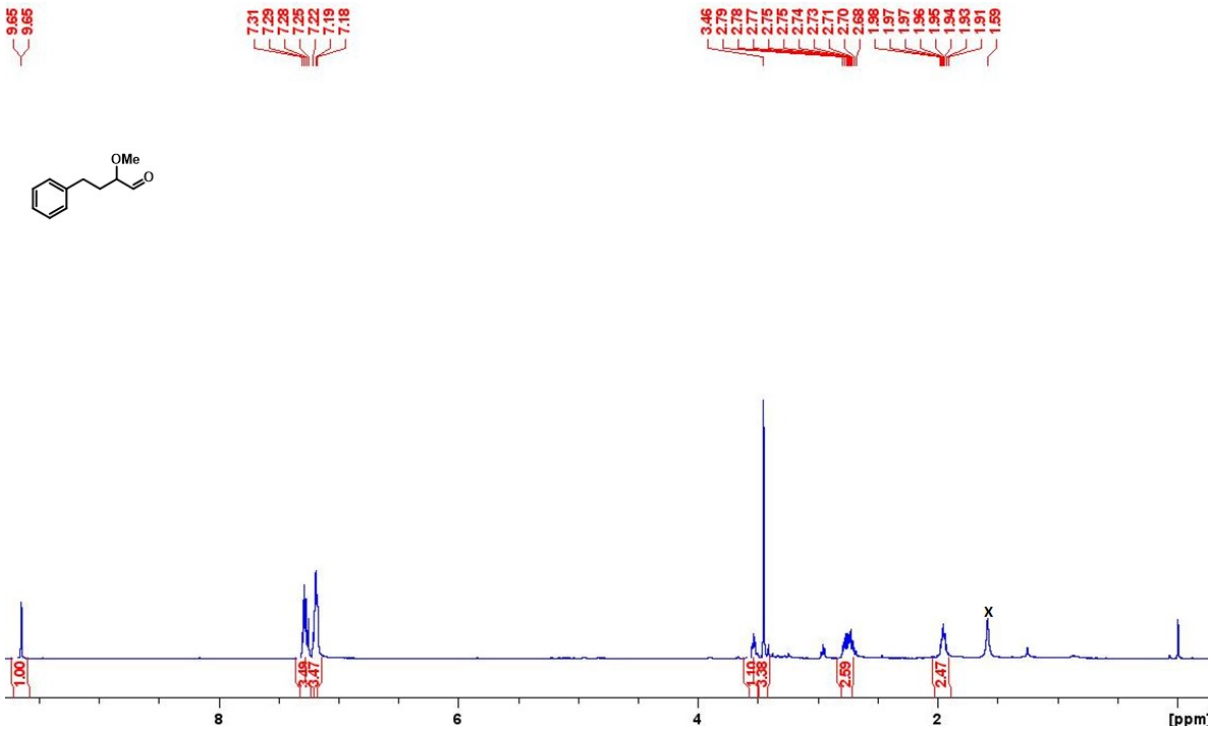
^{13}C NMR of compound 24a



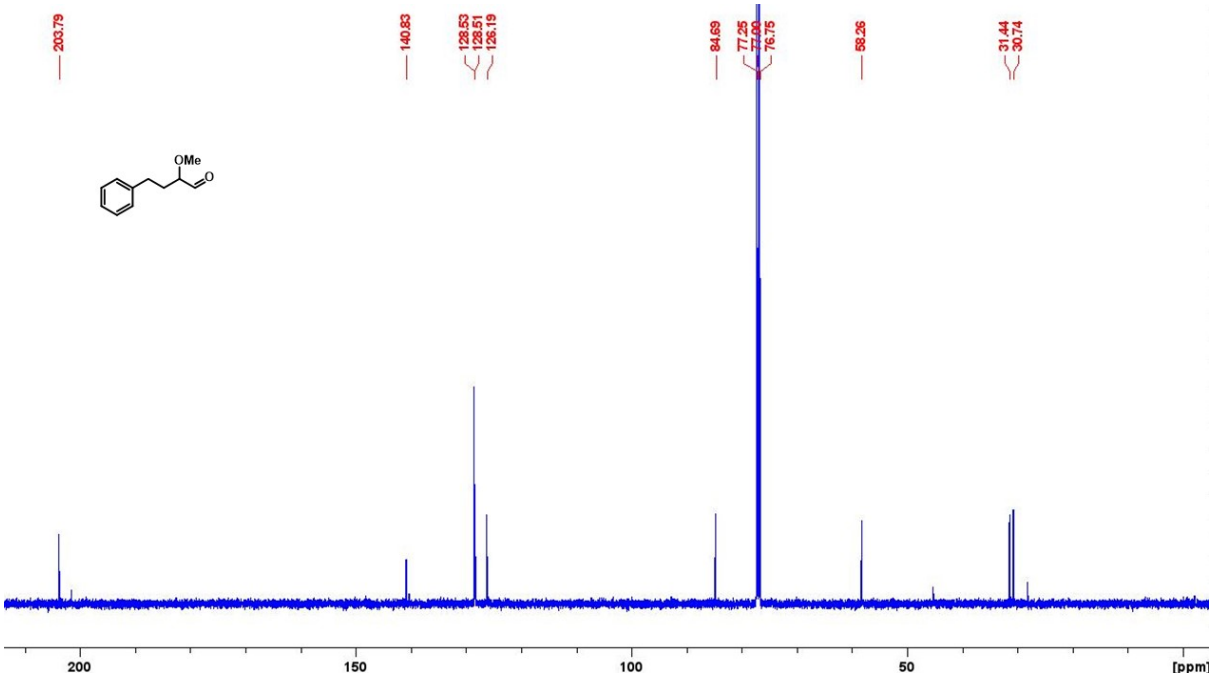
^{1}H NMR of compound 24



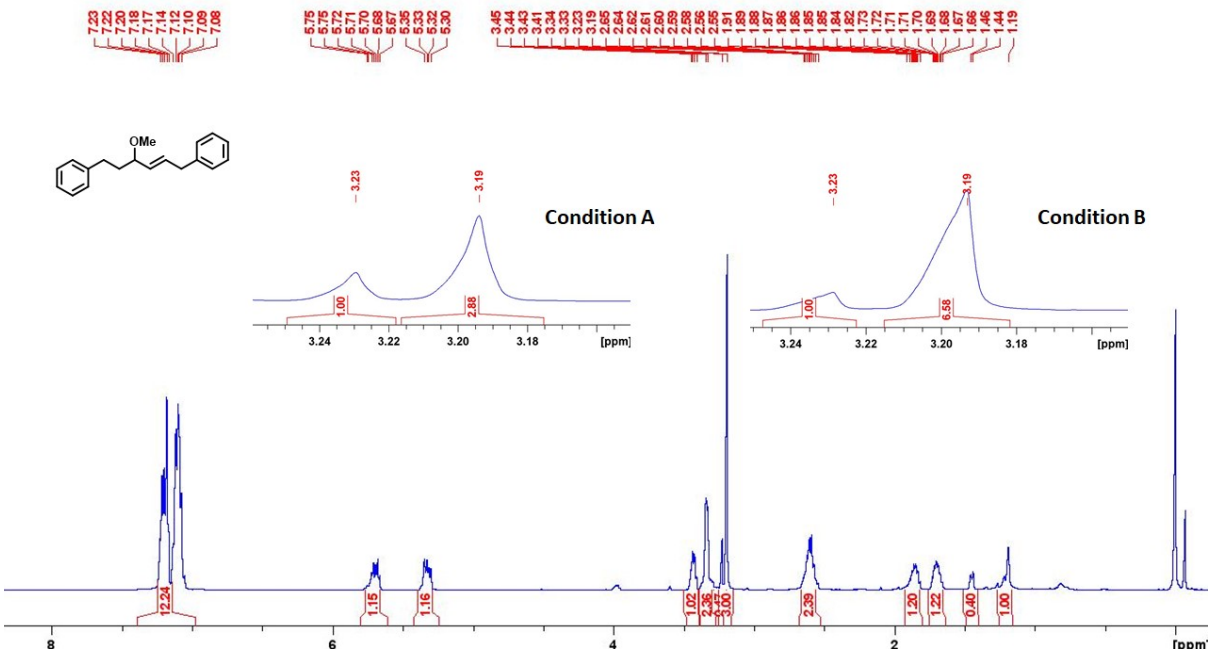
^{13}C NMR of compound 24



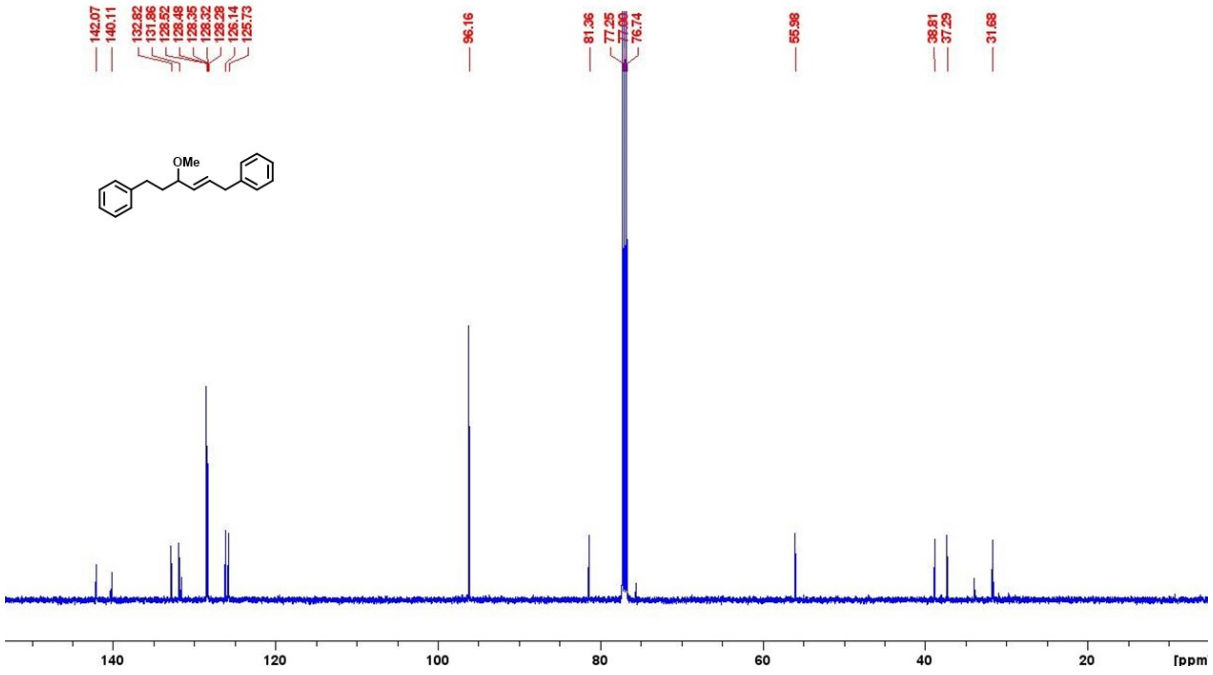
^{1}H NMR of compound 25a



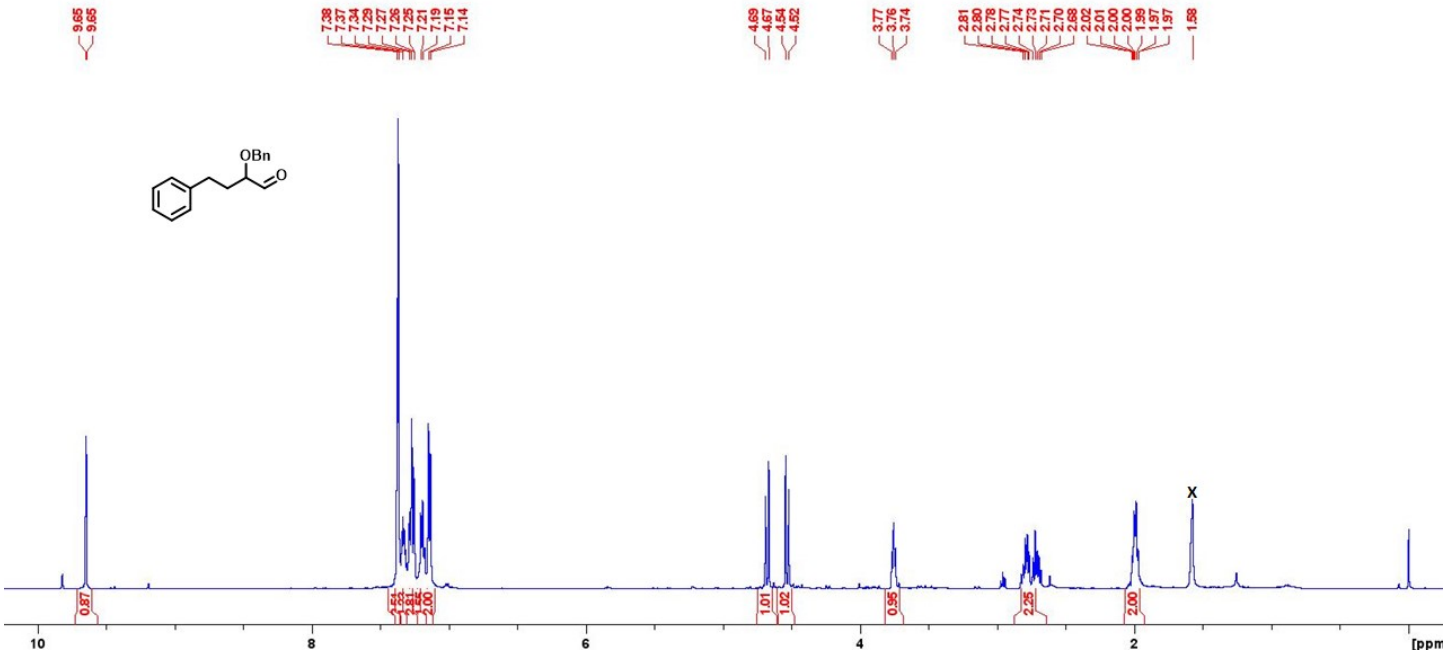
^{13}C NMR of compound 25a



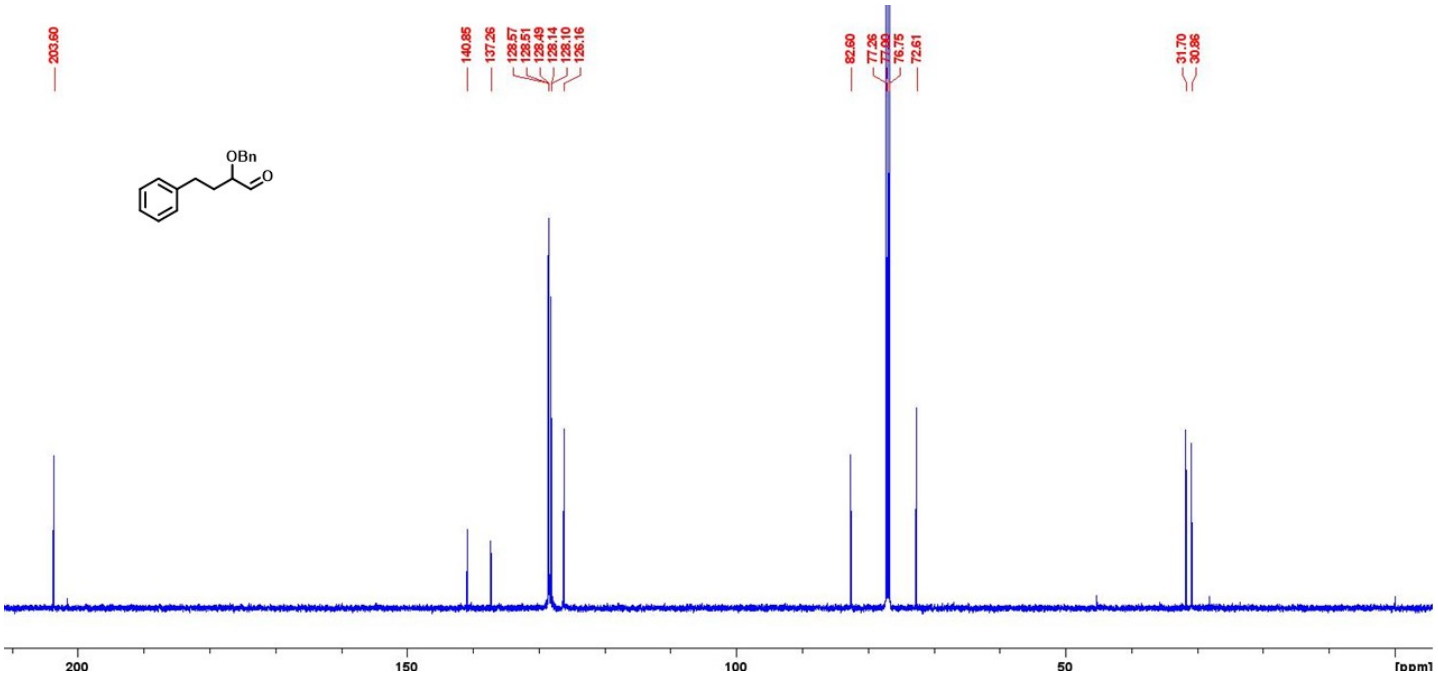
^{1}H NMR of compound 25



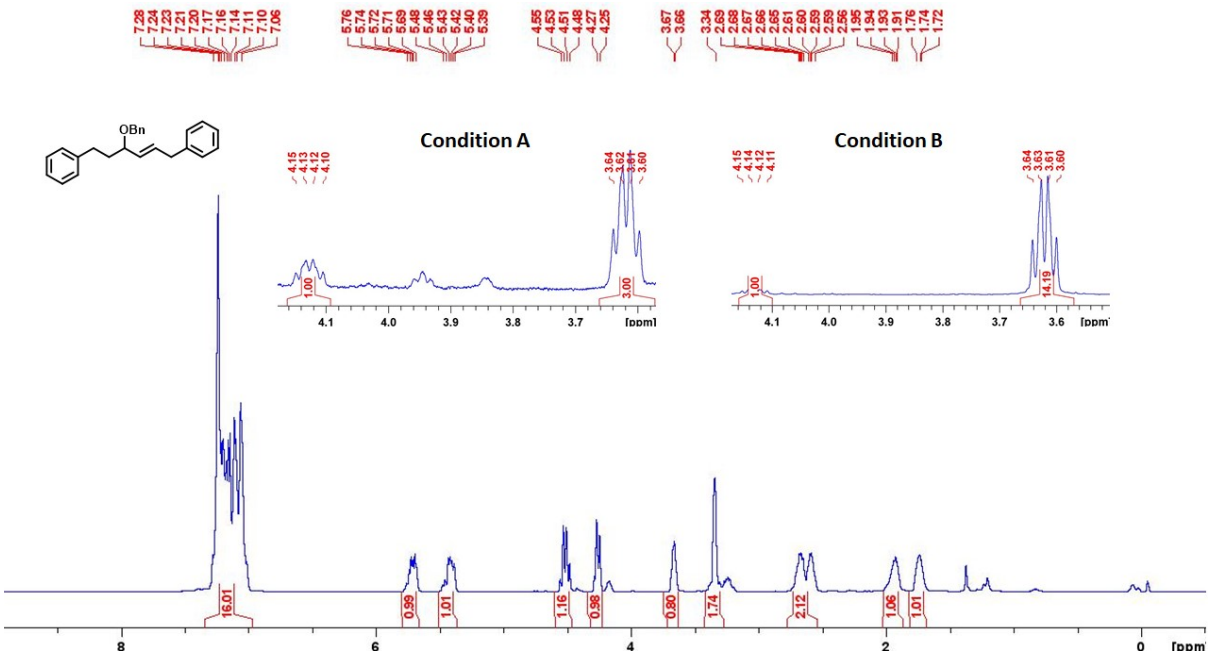
^{13}C NMR of compound 25



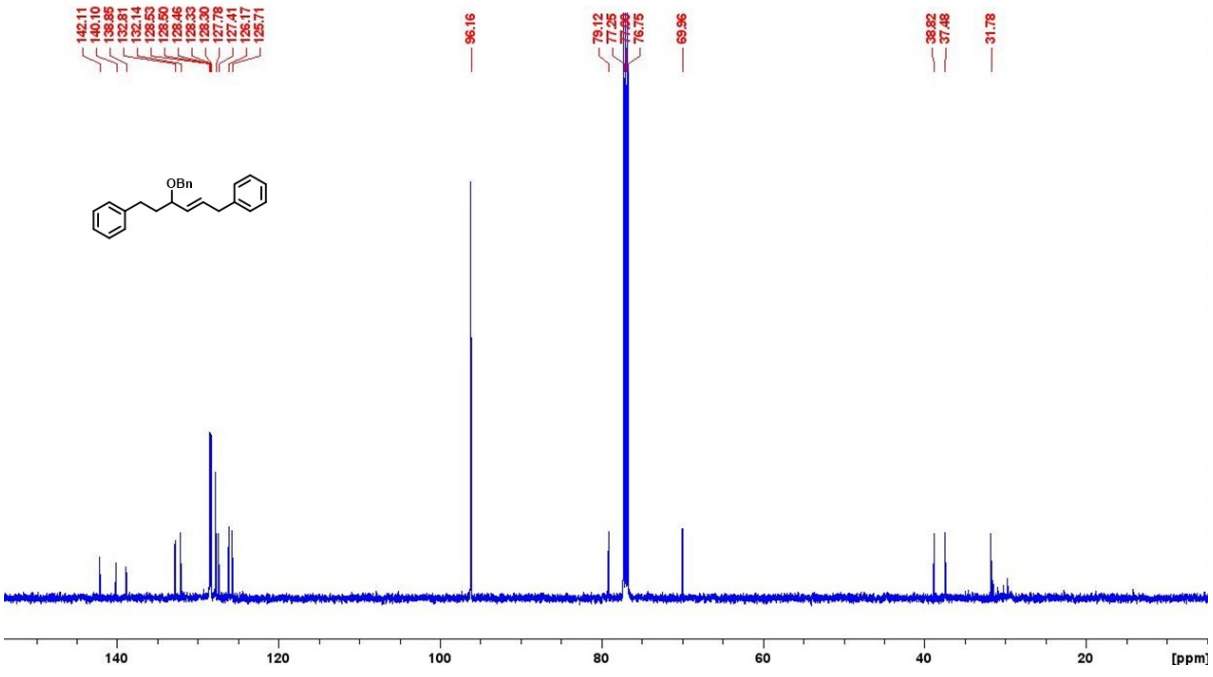
^{1}H NMR of compound 26a



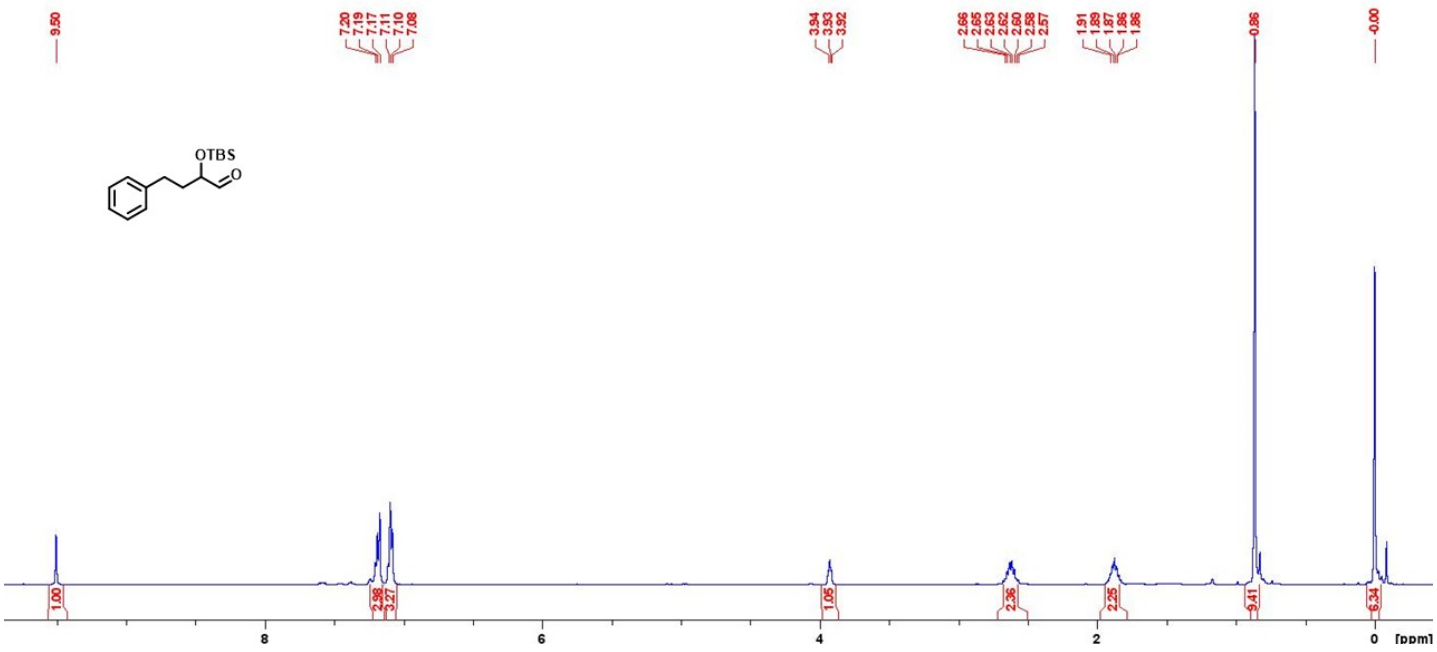
^{13}C NMR of compound 26a



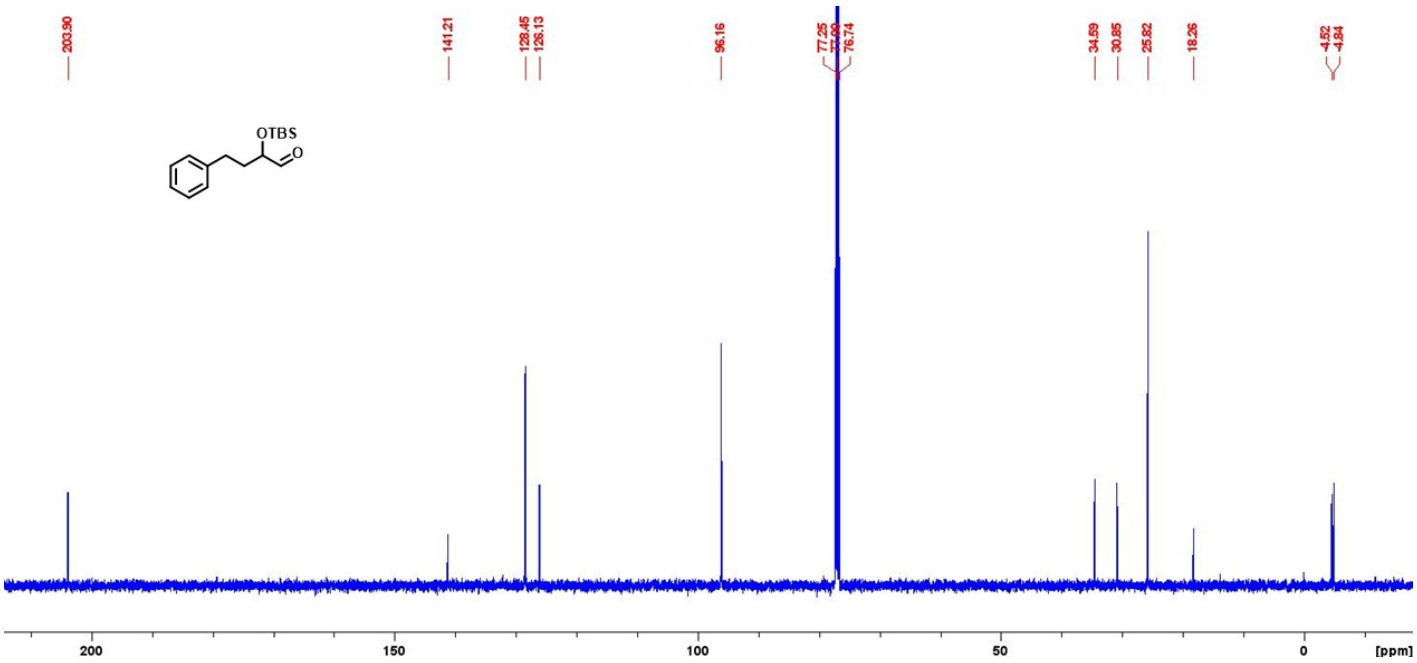
^{1}H NMR of compound 26



^{13}C NMR of compound 26



^{1}H NMR of compound 27a



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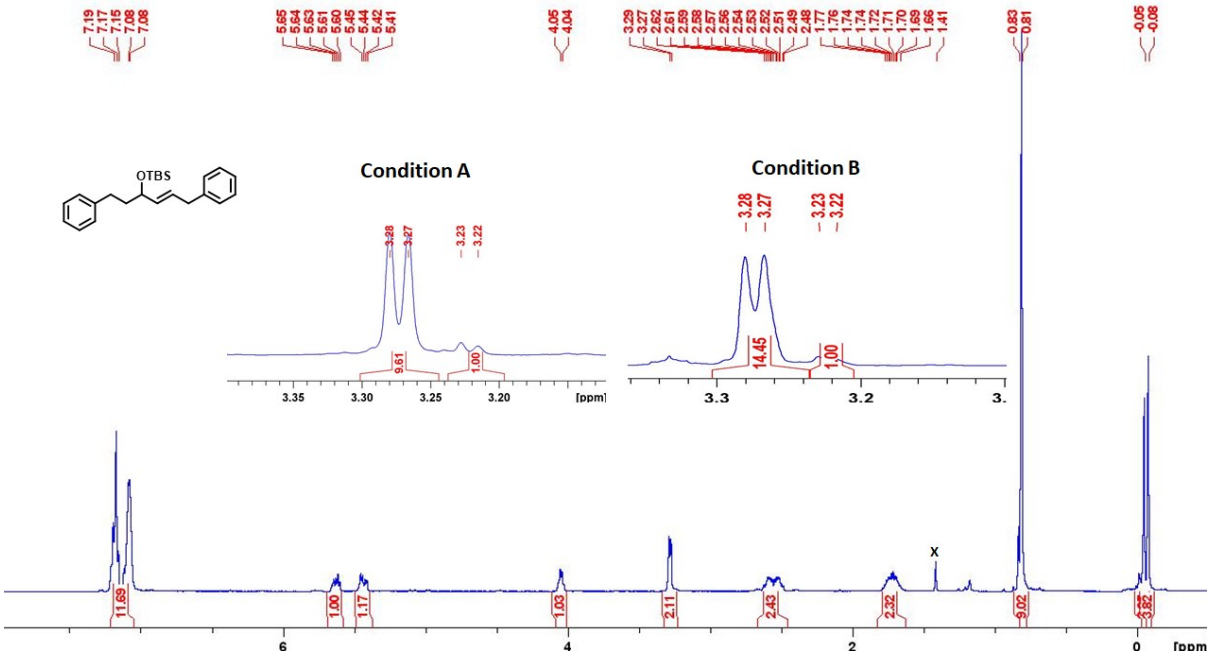
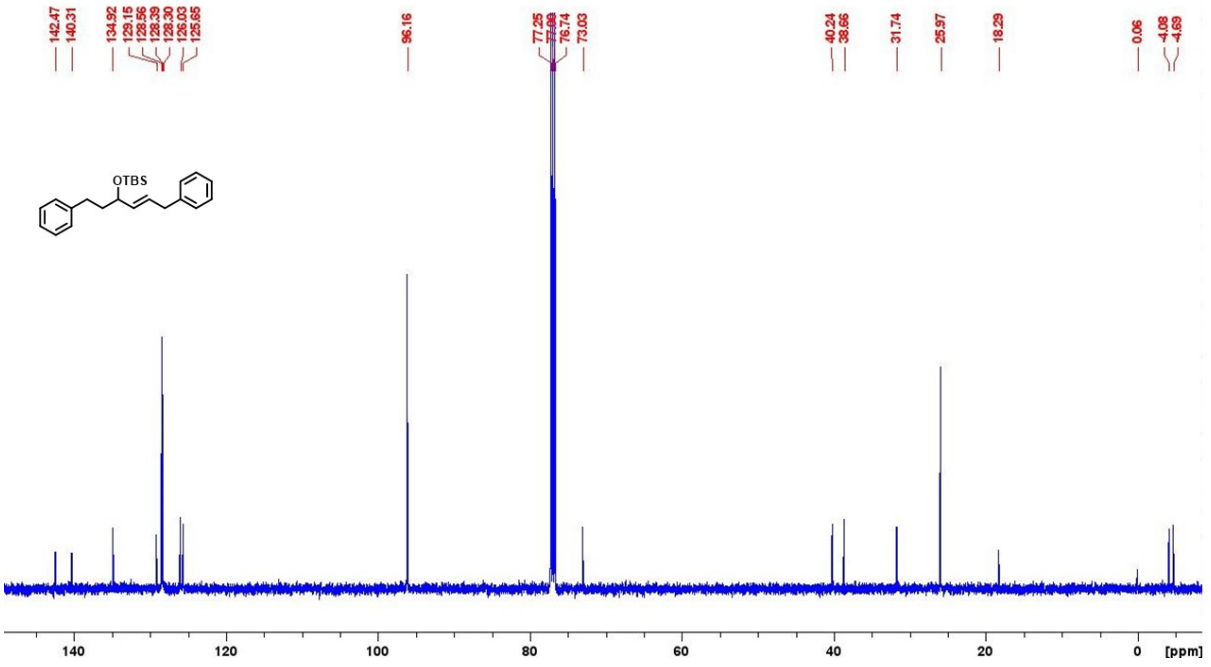
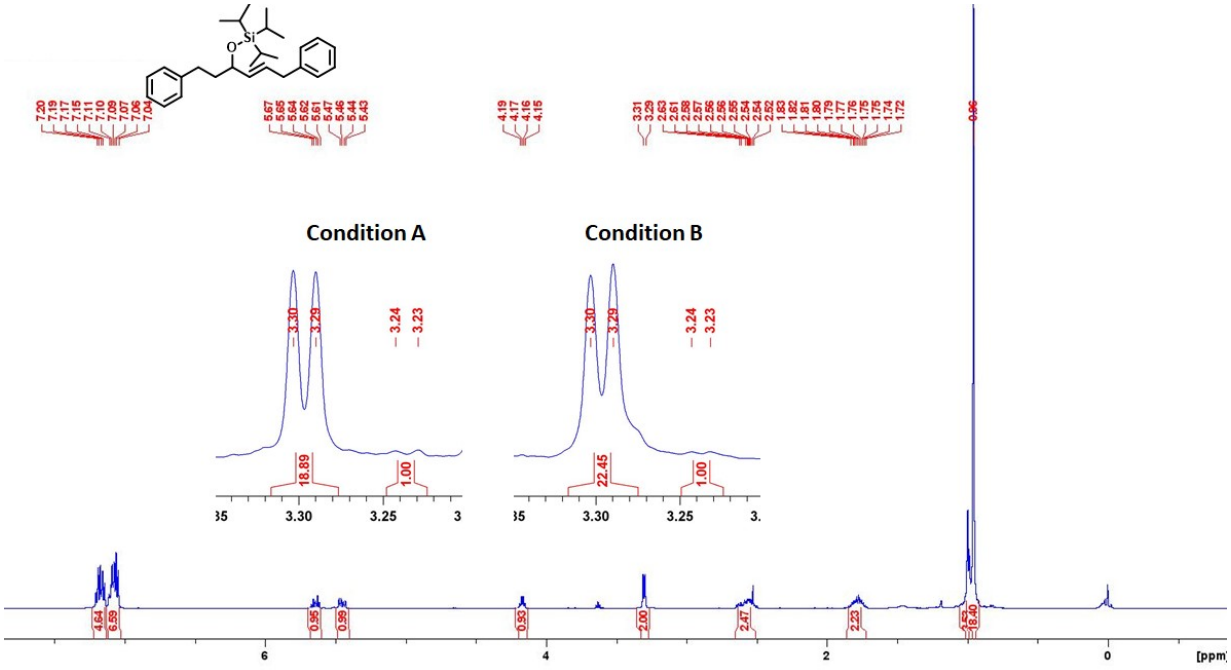


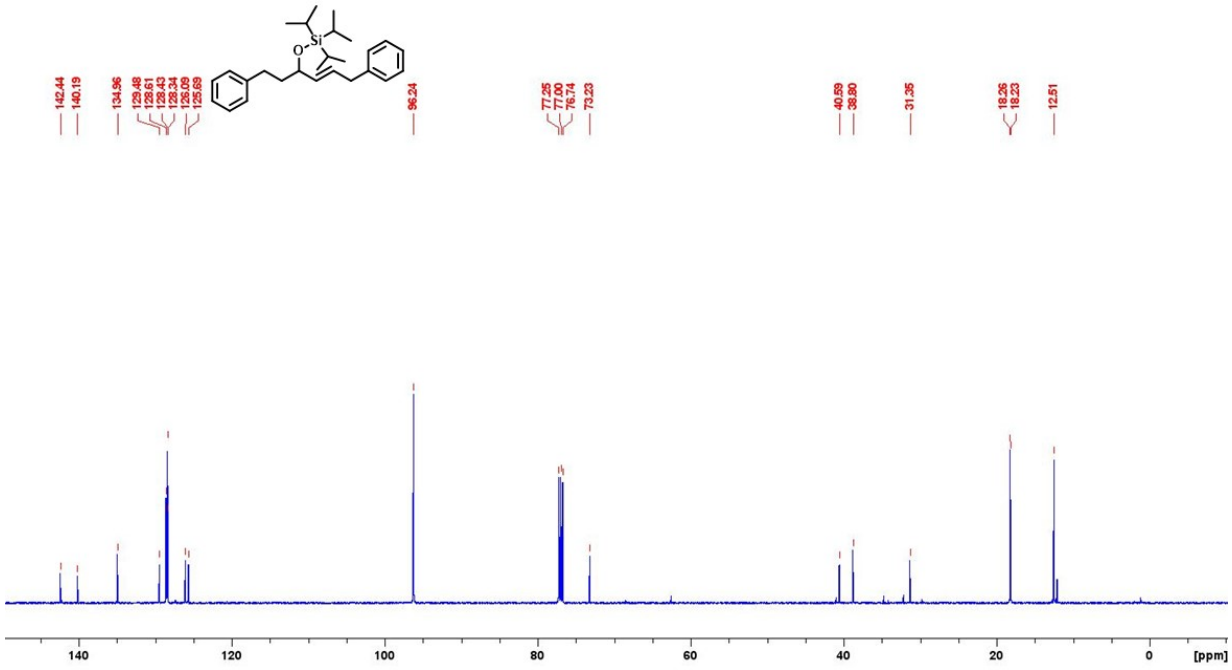
^{1}H NMR of compound 27



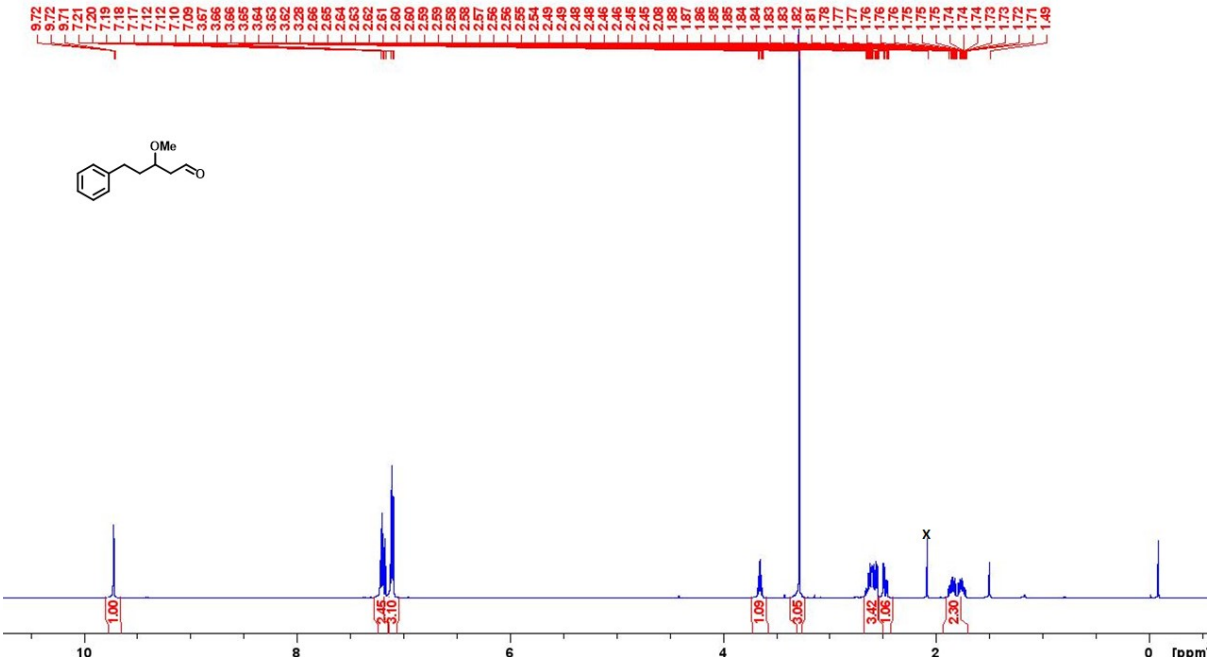
^{13}C NMR of compound 27



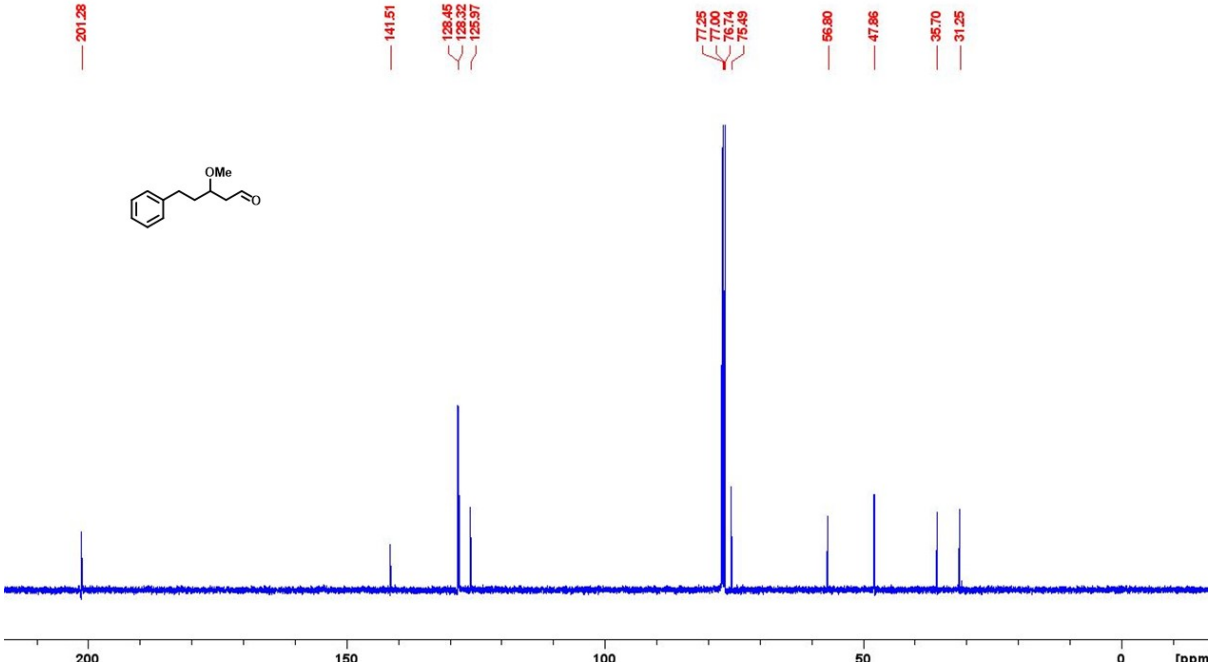
^{1}H NMR of compound 28



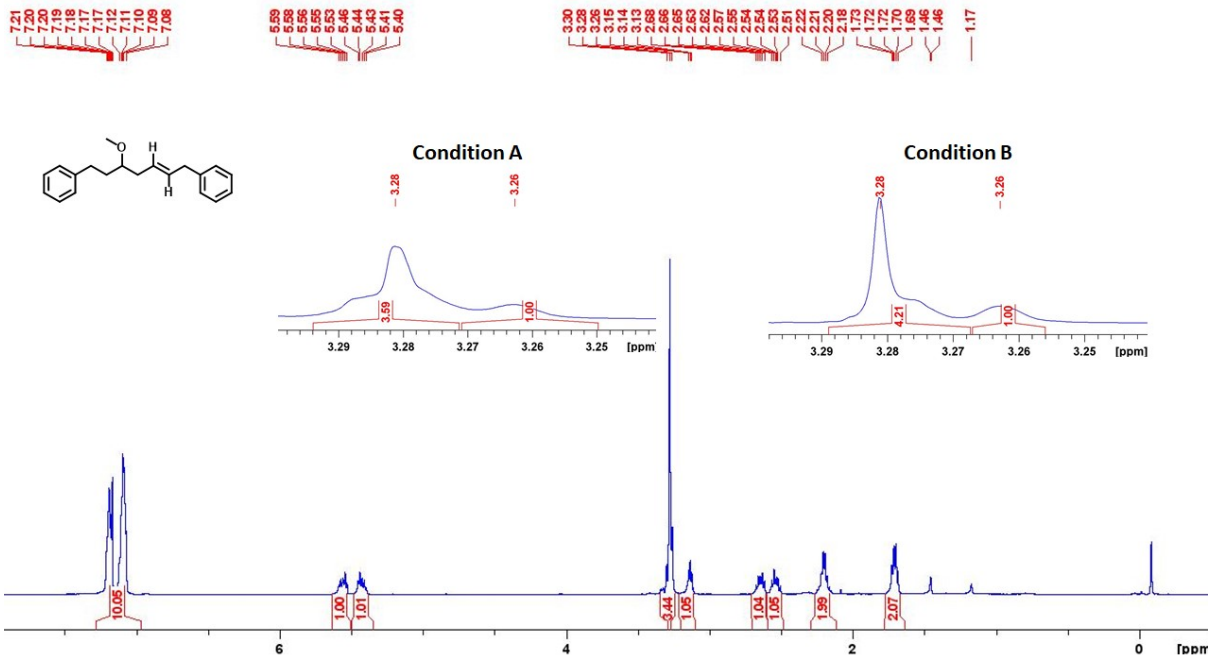
^{13}C NMR of compound 28



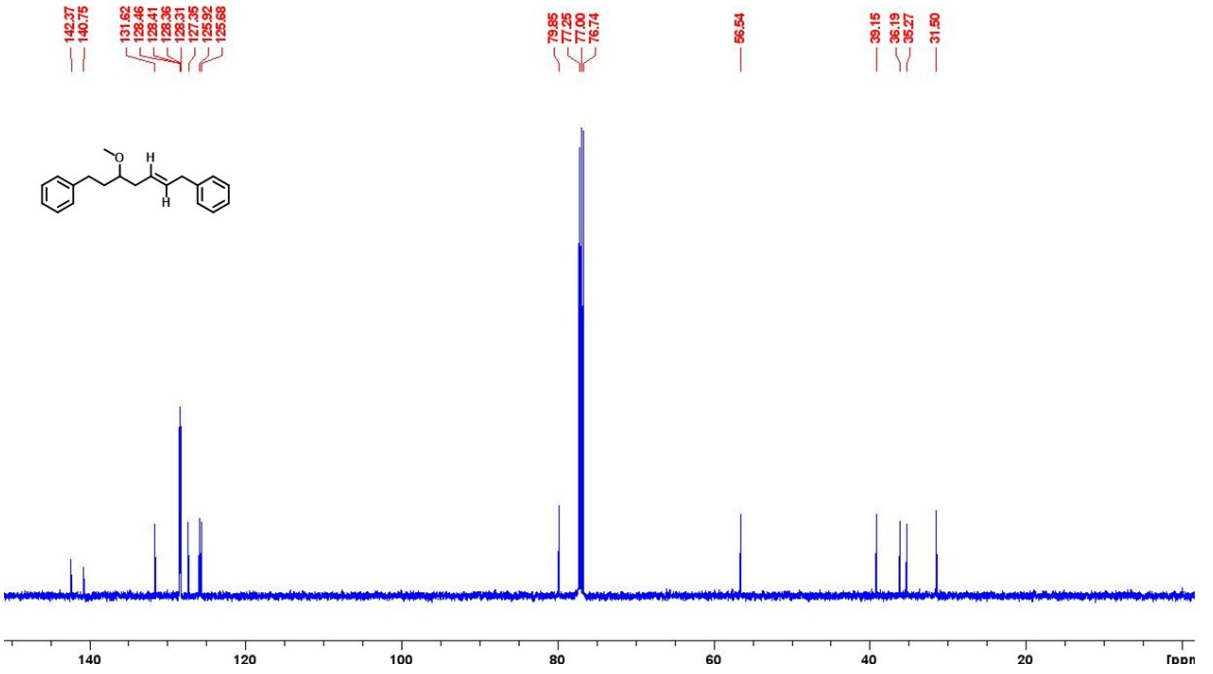
^{1}H NMR of compound 29a



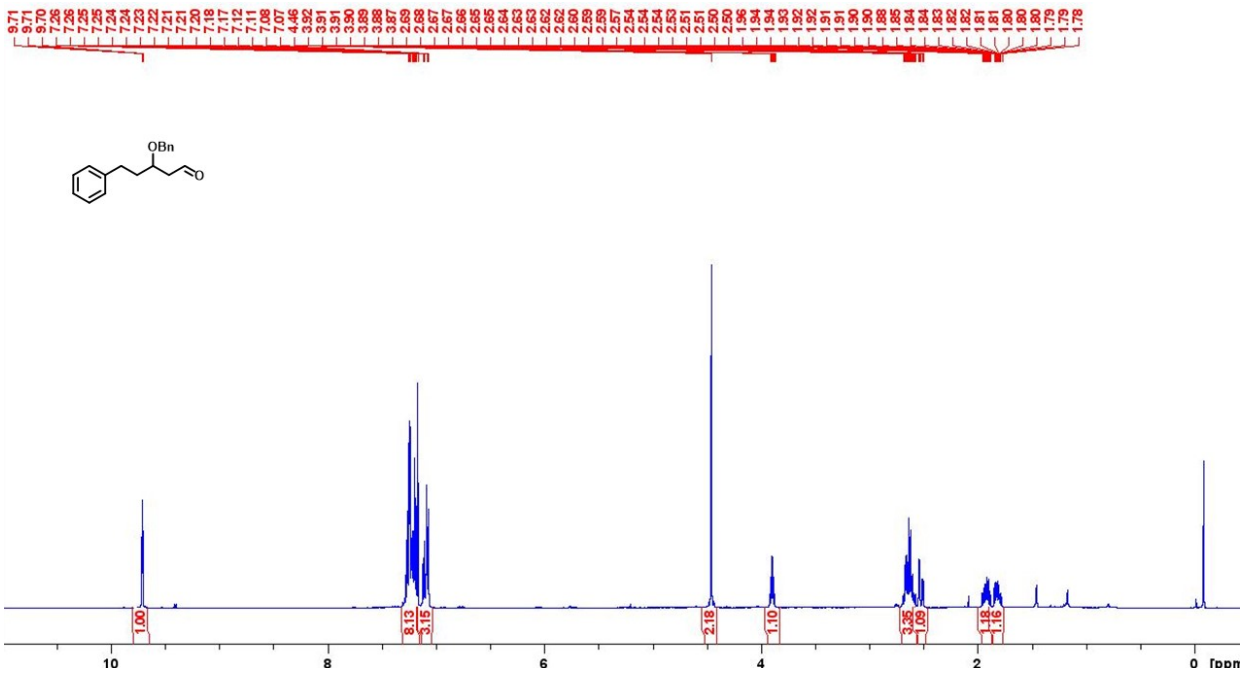
^{13}C NMR of compound 29a



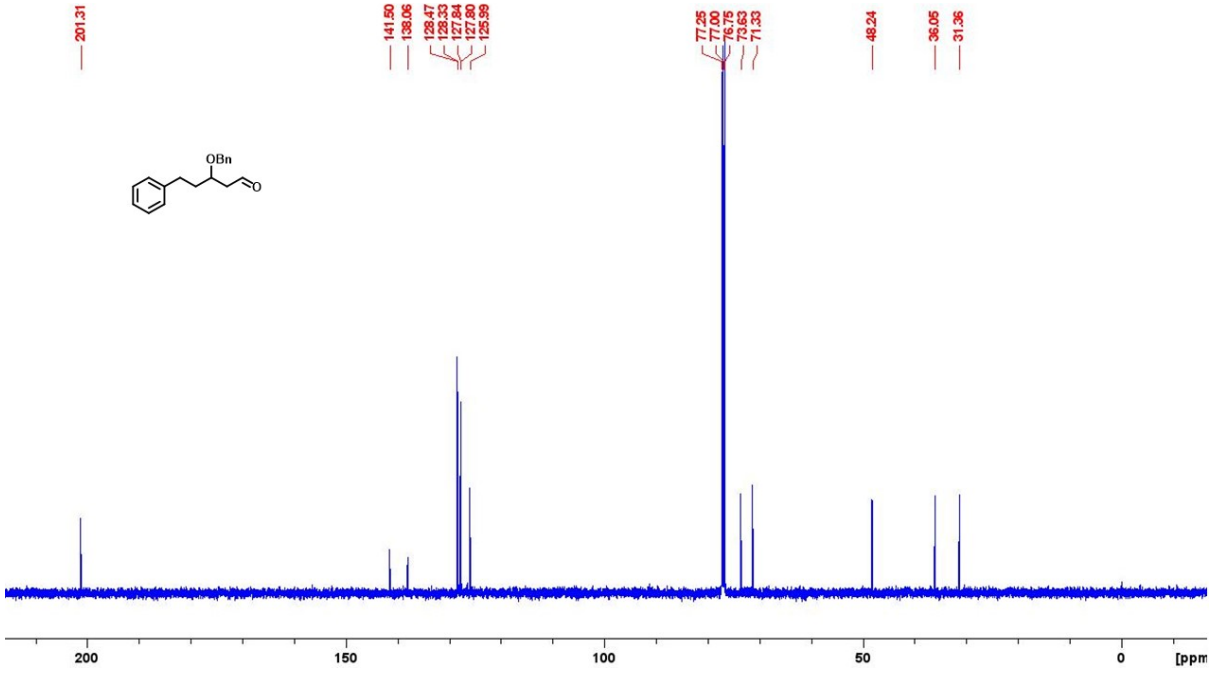
^{1}H NMR of compound 29



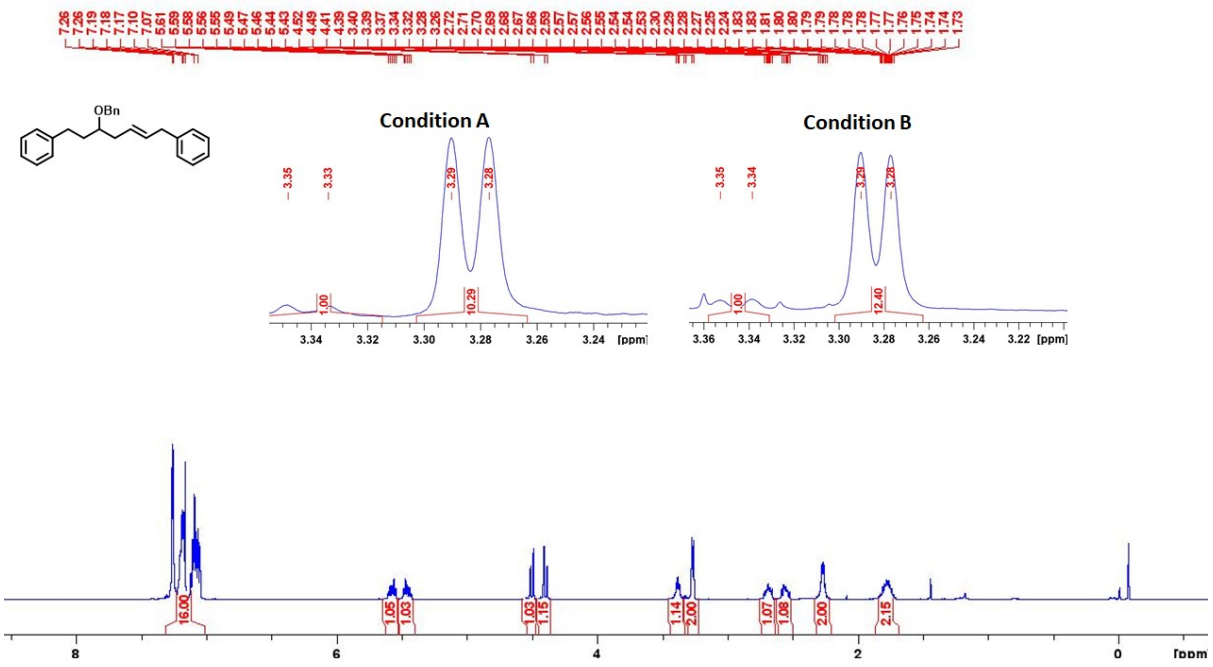
^{13}C NMR of compound 29



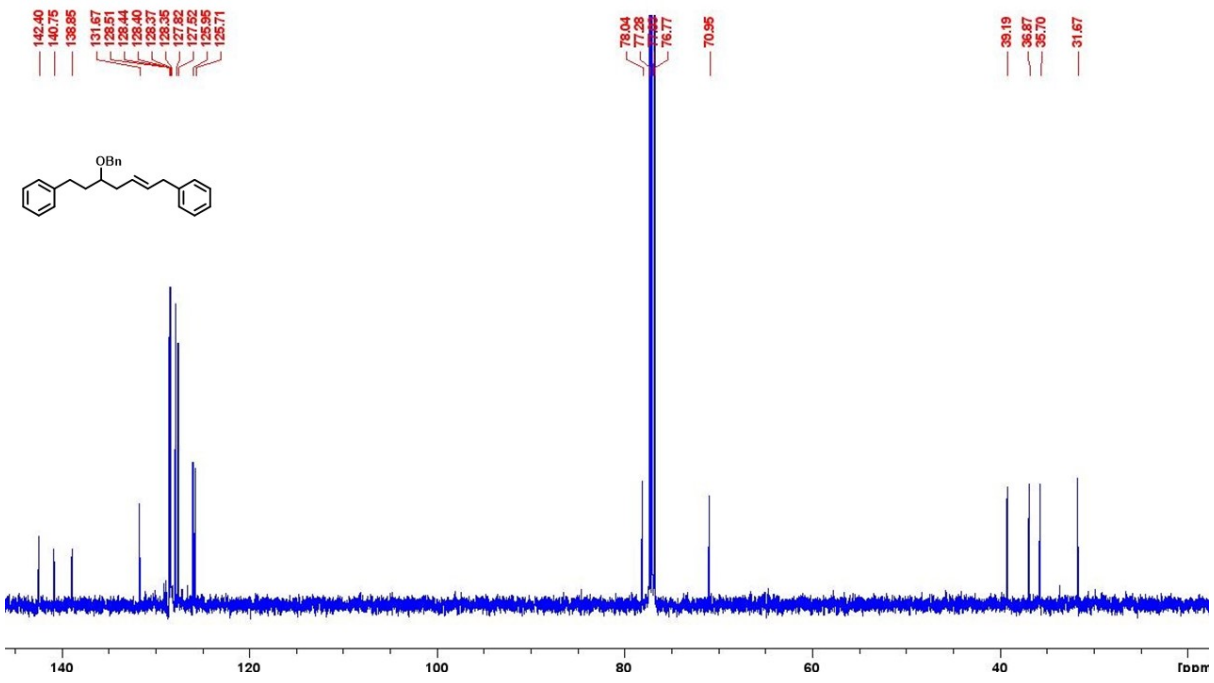
^{1}H NMR of compound 30a



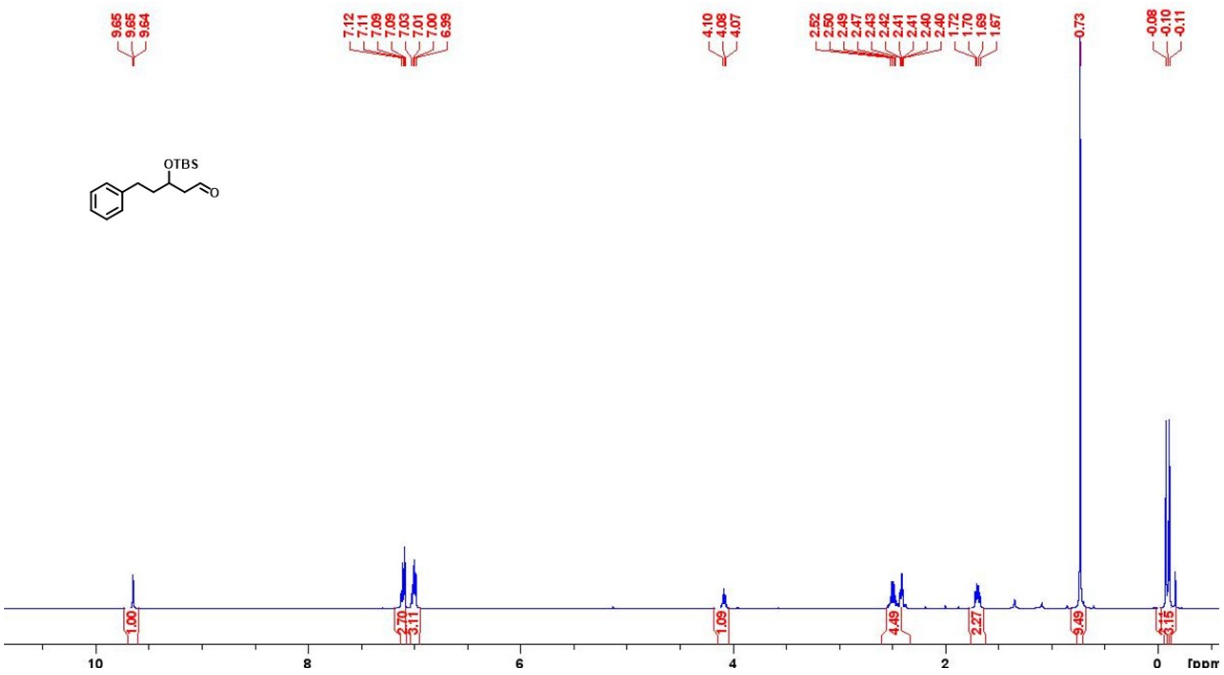
^{13}C NMR of compound 30a



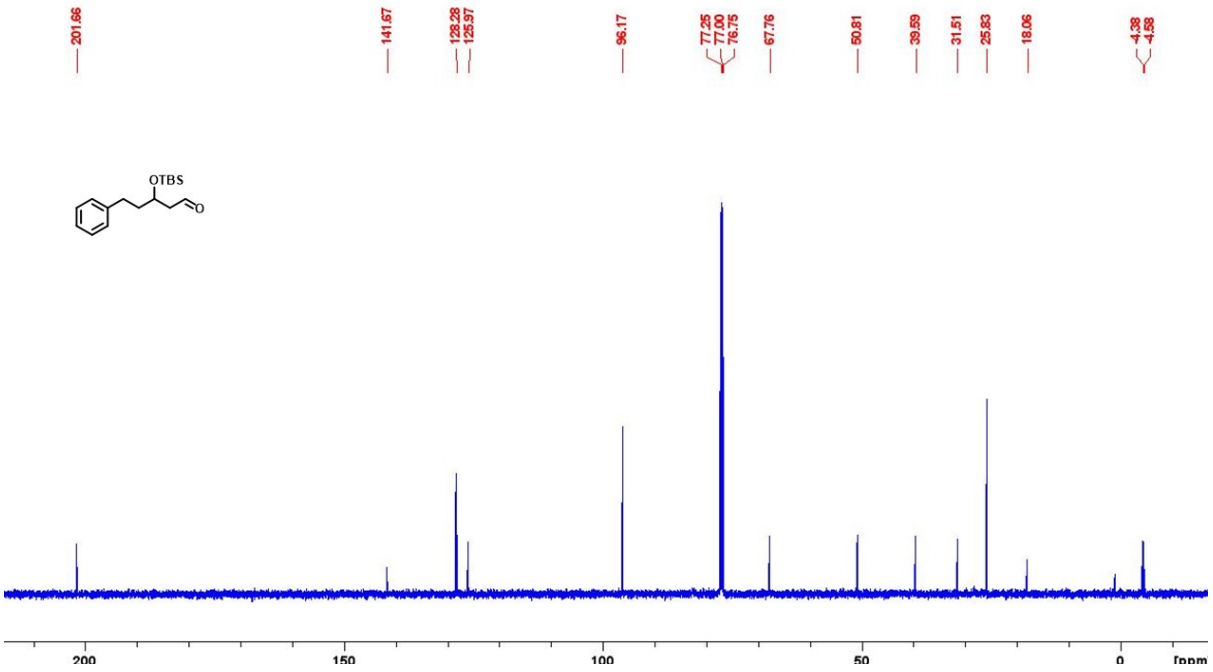
^{1}H NMR of compound 30



^{13}C NMR of compound 30



^{1}H NMR of compound 31a



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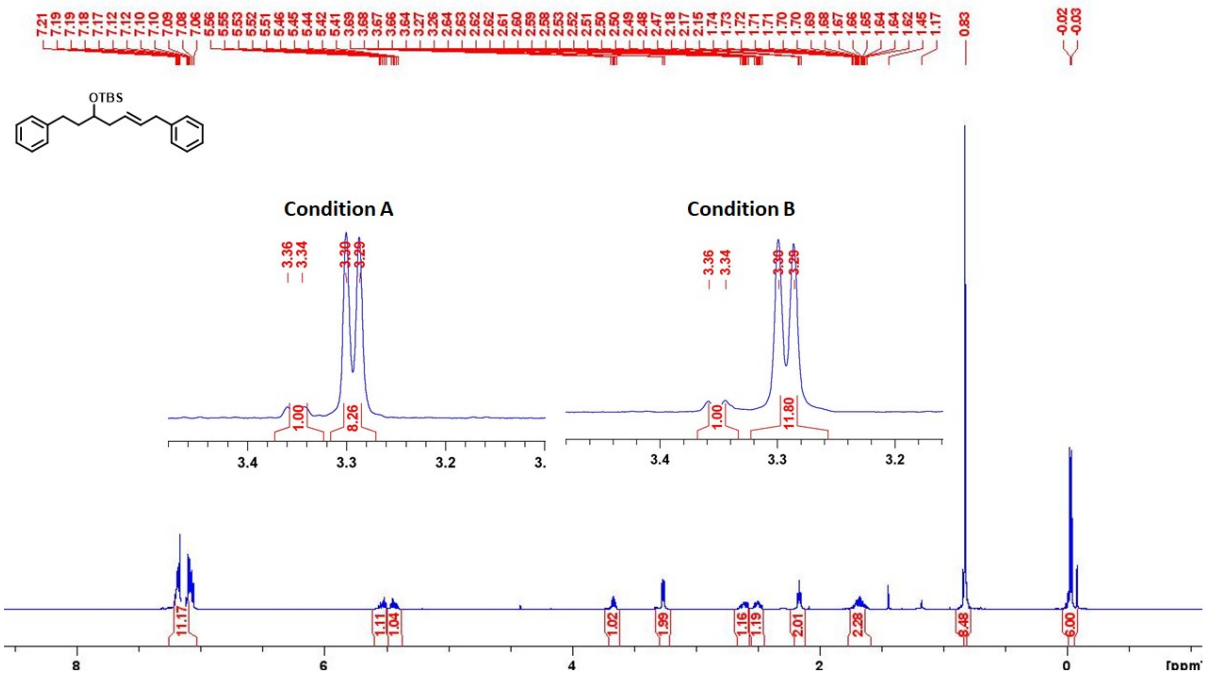
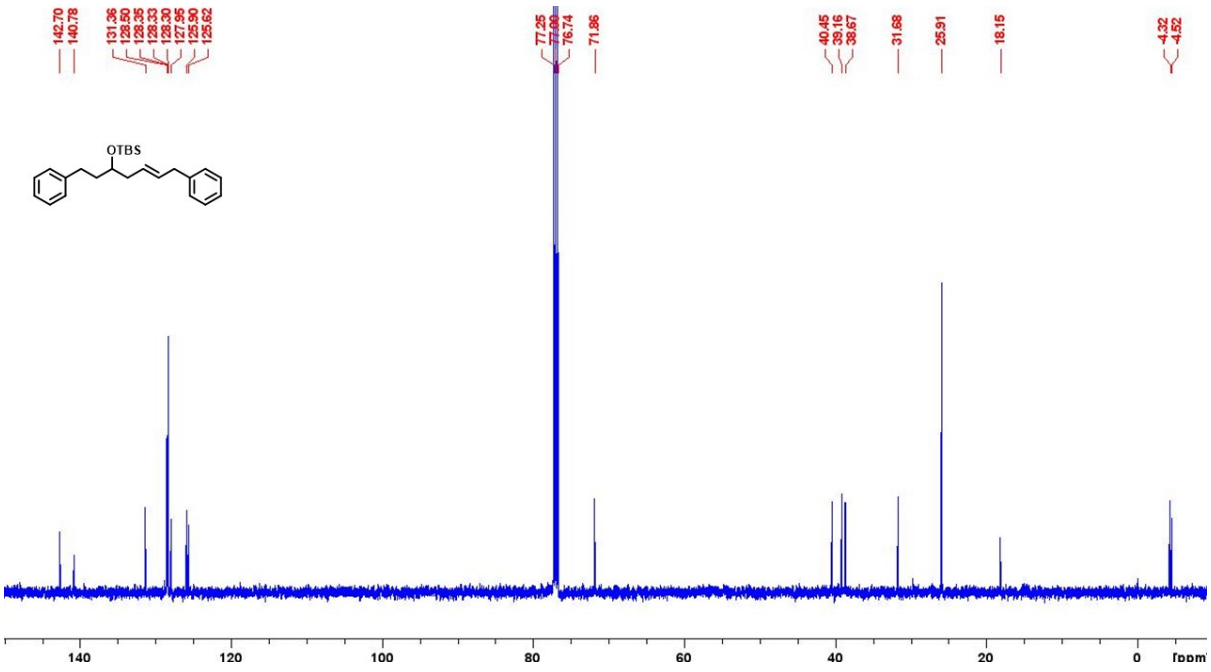


^{1}H NMR of compound 31



^{13}C NMR of compound 31