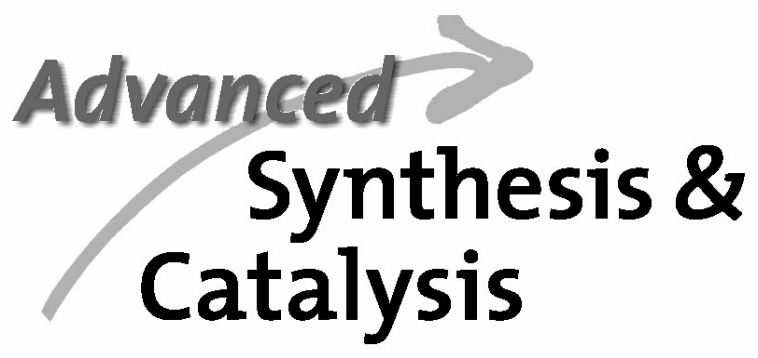

Supporting Information

Supporting Information for:

Nickel-Catalyzed Highly Selective Hydrovinylation of α-Ketal Vinylarenes

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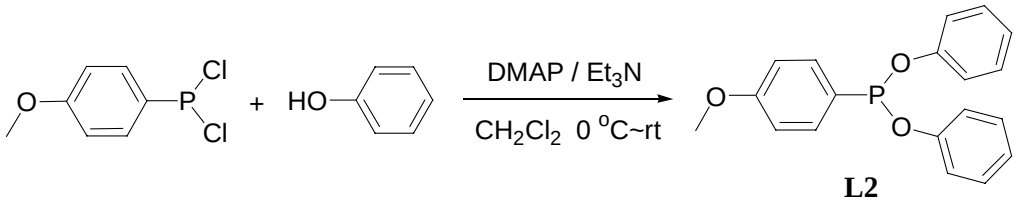
CONTENTS

General:

The reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Commercially available reagents were used as received without further purification unless otherwise noted. Ethylene (99.9%) was purchased from BAPB Gases Company, Ltd., Beijing, China. Anhydrous dichloromethane was distilled from calcium hydride under nitrogen before use. Anhydrous toluene and ether was distilled from sodium benzophenone ketyl under nitrogen before use. $P(OPh)_3$ was distilled under vacuum before use. $[Ni(allyl)Br]_2$,[1] NaBArF,[2] $PPh_2(OPh)$[3] and $PPh(OPh)_2$[4] were prepared according to the literature procedures. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer at 400 MHz (^1H NMR), 100 MHz (^{13}C NMR) and 162 MHz (^{31}P NMR) or a Bruker AV 300 spectrometer at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR) in $CDCl_3$. Chemical shifts were reported in ppm down field from internal Me_4Si and external 85% H_3PO_4, respectively. HRMS were recorded on a VG ZAB-HS mass spectrometer with EI resource or an IonSpec FT-ICR mass spectrometer with ESI and APCI resource. GC analyses were performed using a Hewlett Packard Model HP 6890 Series equipped with HP-5 column.

(1) Preparation and Analytic Data of Ligands

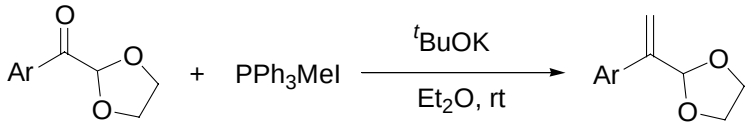
Diphenyl 4-methoxyphenylphosphonite (L2)



L2

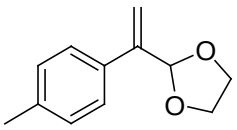
Under a nitrogen atmosphere, phenol (1.9 g, 20 mmol), DMAP (0.6 g, 0.5 mmol), Et_3N (3.5 mL) and CH_2Cl_2 (50 mL) were added into a 100 mL Schlenk tube equipped with a stirring bar. The mixture was cooled to 0 °C and dichloro(4-methoxyphenyl)phosphine (2.0 g, 10 mmol) was injected by syringe. The mixture was warmed to room temperature and stirred for 20 h. After the solvent was evaporated under vacuum, the residue was re-dissolved with 40 mL dry ether and filtrated. The filtrate was concentrated in vacuum and purified by chromatography on silica gel column with ether/petroleum ether (1:3, v/v) to afford **L2** (2.4 g, 74%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.69 (m, 2H), 7.24–6.93 (m, 12H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0, 131.7, 129.7, 123.6, 120.3, 120.2, 114.2, 114.1, 55.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 160.4; HRMS (ESI) Calcd for [M+H, $C_{19}H_{18}O_3P$]$^+$: 325.0988; Found: 325.0986.

(2) Preparation and Analytic Data of New Substrates



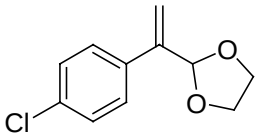
General procedure: Under a nitrogen atmosphere, the mixture of PPh_3MeI (4.5 g, 11.0 mmol) and ^{t}BuOK (1.3 g, 11.5 mmol) in ether was stirred for 2 h to give a yellow cloudy mixture. Then (1,3-dioxolan-2-yl)arylmethanone (10.0 mmol) was slowly added. After stirring for 1 h, the mixture was filtrated through a silica pad. The filtrate was concentrated under vacuum and the residue was purified by chromatography (ethyl acetate/petroleum ether = 1:10, v/v) to give α-ketal vinylarenes. The analysis data of α-ketal vinylarenes were illustrated below.

2-(1-*p*-Tolylvinyl)-1,3-dioxolane (1b)



Yield: 84%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 5.77 (s, 1H), 5.68 (s, 1H), 5.62 (s, 1H), 4.13–3.99 (m, 4H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 137.5, 135.3, 129.0, 127.1, 115.5, 104.1, 65.1, 21.2; HRMS (EI) Calcd for $C_{12}H_{14}O_2$: 190.0994; Found: 190.0995.

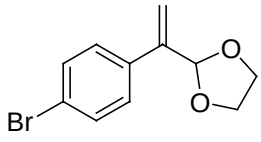
2-(1-(4-Chlorophenyl)vinyl)-1,3-dioxolane (1d)



Yield: 54%; pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.60 (s, 1H), 5.59 (s, 1H), 5.50 (s, 1H), 4.01–3.92 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 136.4, 133.7, 128.6, 128.4, 117.1, 104.0, 65.1; HRMS (EI) Calcd for

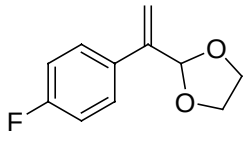
$C_{11}H_{11}ClO_2$: 210.0448; Found: 210.0449.

2-(1-(4-Bromophenyl)vinyl)-1,3-dioxolane (1e)



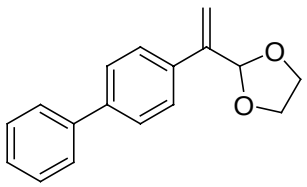
Yield: 58%; pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 5.60 (s, 1H), 5.59 (s, 1H), 5.52 (s, 1H), 4.03–3.96 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 136.9, 131.3, 129.0, 122.0, 117.1, 103.9, 65.1; HRMS (EI) Calcd for $C_{11}H_{11}BrO_2$: 253.9942; Found: 253.9929.

2-(1-(4-Fluorophenyl)vinyl)-1,3-dioxolane (1f)



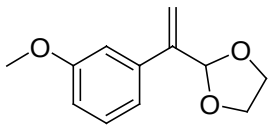
Yield: 55%; Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.7 and 5.4 Hz, 2H), 6.90 (t, *J* = 8.7 Hz, 2H), 5.49 (s, 1H), 5.46 (s, 1H), 5.36 (s, 1H), 3.89–3.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 160.9, 144.1, 129.1, 116.6, 115.2, 104.2, 65.1; HRMS (EI) Calcd for $C_{11}H_{11}FO_2$: 194.0743; Found: 194.0736.

2-(1-(4-Biphenyl)vinyl)-1,3-dioxolane (1g)



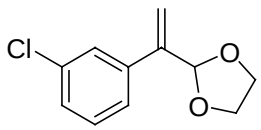
Yield: 55%; offwhite solid; mp: 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.25 (m, 9H), 5.66 (s, 1H), 5.59 (s, 1H), 5.55 (s, 1H), 3.97–3.87 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 140.9, 140.7, 137.0, 128.9, 127.7, 127.5, 127.1, 127.0, 116.3, 104.1, 65.2; HRMS (EI) Calcd for $C_{17}H_{16}O_2$: 252.1150; Found: 252.1152.

2-(1-(3-Methoxyphenyl)vinyl)-1,3-dioxolane (1h)



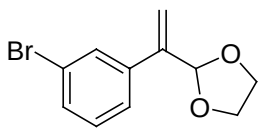
Yield: 80%; colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.1 Hz 1H), 7.07–7.04 (m, 2H), 6.82–6.79 (m, 1H), 5.60 (s, 1H), 5.56 (s, 1H), 5.50 (s, 1H), 3.98–3.84 (m, 4H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.0, 139.5, 129.2, 119.7, 116.5, 113.3, 113.1, 104.0, 65.1, 55.2; HRMS (EI) Calcd for $C_{12}H_{14}O_3$: 206.0943; Found: 206.0940.

2-(1-(3-Chlorophenyl)vinyl)-1,3-dioxolane (1i)



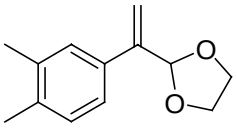
Yield: 56%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.25 (m, 4H), 5.61 (s, 2H), 5.53 (s, 1H), 4.06–3.94 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 139.8, 134.1, 129.4, 127.8, 127.5, 125.5, 117.7, 103.9, 65.1; HRMS (EI) Calcd for $C_{11}H_{11}ClO_2$: 210.0448; Found: 210.0447.

2-(1-(3-Bromophenyl)vinyl)-1,3-dioxolane (1j)



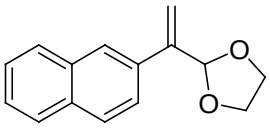
Yield: 78%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.63 (m, 1H), 7.43–7.37 (m, 2H), 7.17–7.11 (m, 1H), 5.58 (s, 1H), 5.56 (s, 1H), 5.48 (s, 1H), 3.98–3.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 140.1, 130.8, 130.3, 129.8, 126.0, 122.4, 117.7, 103.9, 65.1; HRMS (EI) Calcd for $C_{11}H_{11}BrO_2$: 253.9942; Found: 253.9939.

2-(1-(3,4-Dimethylphenyl)vinyl)-1,3-dioxolane (1k)



Yield: 79%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.19 (m, 2H), 7.05–7.03 (m, 1H), 5.61 (s, 1H), 5.50 (d, J = 1.2 Hz, 1H), 5.44 (d, J = 1.5 Hz, 1H), 3.94–3.84 (m, 4H), 2.22 (s, 3H), 2.20(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 136.3, 136.2, 135.8, 129.7, 128.5, 124.7, 115.3, 104.1, 65.1, 20.0, 19.5; HRMS (EI) Calcd for $C_{13}H_{16}O_2$: 204.1150; Found: 204.1150.

2-(1-(Naphthalen-2-yl)vinyl)-1,3-dioxolane (1l)



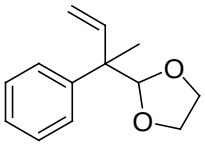
Yield: 78%; viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.03–7.61 (m, 7H), 5.96–5.86 (m, 3H), 4.09–3.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 135.7, 133.6, 133.2, 128.6, 128.0, 127.8, 126.3, 126.2, 125.6, 116.8, 104.1, 65.2; HRMS (EI) Calcd for $C_{15}H_{14}O_2$: 226.0994; Found: 226.0991.

(3) General Procedure for Catalytic Hydrovinylation of α-ketal vinylarene

Under an nitrogen atmosphere, $[Ni(allyl)Br]_2$ (20 μmol), phosphorous ligand (40 μmol) and fresh distilled CH_2Cl_2 (3.0 mL) were introduced into a Schlenk tube equipped with a stirring bar. The mixture was stirred at room temperature for 1 min and transferred to another Schlenk tube contained NaBArF (48 μmol) and CH_2Cl_2 (2.0 mL). After stirring for 5 min. The inert atmosphere in the Schlenk tube was replaced by ethylene three times and the α-ketal vinylarene was introduced. The reaction mixture was stirred at room temperature for a proper time (monitored by GC). After the reaction completed, the selectivity of product was determined by GC (HP-5 column). The reaction mixture was concentrated under reduced pressure, and the residue was chromatographied on silica gel column to give pure product. The analysis data of the products were illustrated below.

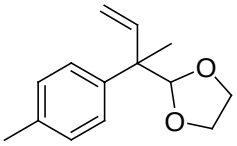
(4) Analytic Data for Hydrovinylation Products

2-(2-Phenylbut-3-en-2-yl)-1,3-dioxolane (2a)



Yield: 94%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.21 (m, 5H), 6.23 (dd, J = 17.6 and 10.8 Hz, 1H), 5.29–5.16 (m, 3H), 3.85 (s, 4H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.3, 128.0, 127.8, 126.5, 114.8, 108.4, 65.5, 48.9, 20.2; HRMS (EI) Calcd for $C_{13}H_{16}O_2$: 204.1150; Found: 204.1141. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 ^{o}C; initial temperature, 120 ^{o}C; rate, 10 ^{o}C/min; final temperature, 250 ^{o}C; t_R of substrate **1a**, 4.24 min; t_R of product **2a**, 5.27 min; t_R of oligomers, 6.80–7.25 min.

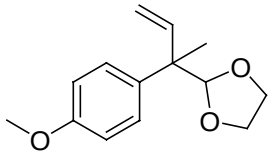
2-(2-*p*-Tolylbut-3-en-2-yl)-1,3-dioxolane (2b) [7]



Yield: 92%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.12 (dd, J = 17.7 and 11.1 Hz, 1H), 5.15(d, J = 11.1 Hz, 1H), 5.07 (d J = 17.7 Hz, 1H), 5.03 (s, 1H), 3.73 (s, 4H), 2.22 (s, 3H), 1.36 (s, 3H). GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 ^{o}C; initial temperature, 120 ^{o}C; rate, 10

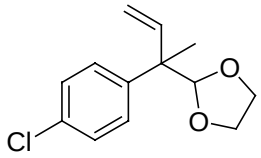
°C/min; final temperature, 250 °C; t_R of substrate **1b**, 5.24 min; t_R of product **2b**, 6.17 min; t_R of oligomers, 7.70–8.20 min.

2-(2-(4-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane (2c)



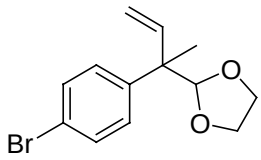
Yield: 83%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 6.12 (dd, J = 17.7 and 10.8 Hz, 1H), 5.14 (dd, J = 10.8 and 1.2 Hz, 1H), 5.07 (dd, J = 17.7 and 1.2 Hz, 1H), 5.00 (s, 1H), 3.73 (s, 4H), 3.68 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 142.5, 135.5, 128.8, 114.4, 113.3, 108.5, 65.4, 55.2, 48.2, 20.3; HRMS (EI) Calcd for $C_{14}H_{18}O_3$: 234.1256; Found: 234.1251. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1c**, 6.89 min; t_R of product **2c**, 7.70 min; t_R of oligomers, 9.20–9.70 min.

2-(2-(4-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane (2d)



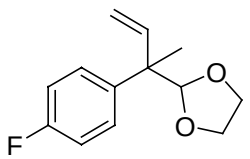
Yield: 89%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 6.09 (dd, J = 17.7 and 11.1 Hz, 1H), 5.17 (dd, J = 11.1 and 1.2 Hz, 1H), 5.07 (dd, J = 17.7 and 1.2 Hz, 1H), 4.98 (s, 1H), 3.74–3.69 (m, 4H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 141.8, 132.3, 129.4, 128.0, 115.1, 108.1, 65.4, 48.6, 20.3; HRMS (APCI) Calcd for [M+H, $C_{13}H_{16}ClO_2$]$^+$: 239.0833; Found: 239.0828. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1d**, 6.00 min; t_R of product **2d**, 7.06 min; t_R of oligomers, 8.60–9.10 min.

2-(2-(4-Bromophenyl)but-3-en-2-yl)-1,3-dioxolane (2e)



Yield: 82%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.09 (dd, J = 17.4 and 10.8 Hz, 1H), 5.18 (dd, J = 10.8 and 0.9 Hz, 1H), 5.08 (dd J = 17.7 and 1.2 Hz, 1H), 4.99 (s, 1H), 3.74 (s, 4H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 141.7, 130.9, 129.8, 120.6, 115.1, 108.0, 65.4, 48.6, 20.3; HRMS (APCI) Calcd for [M+H, $C_{13}H_{16}BrO_2$]$^+$: 283.0328; Found: 283.0323. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 150 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1e**, 4.54 min; t_R of product **2e**, 5.48 min; t_R of oligomers, 6.70–7.25 min.

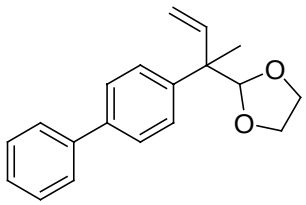
2-(2-(4-Fluorophenyl)but-3-en-2-yl)-1,3-dioxolane (2f)



Yield: 91%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, J = 9.0 and 5.7 Hz, 2H), 6.91 (t, J = 8.7 Hz, 2H), 6.11 (dd, J = 17.7 and 11.1 Hz, 1H), 5.17 (d, J = 11.1 Hz, 1H), 5.08 (d, J = 17.7 Hz, 1H), 5.00 (s, 1H), 3.74 (s, 4H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 159.9, 142.1, 139.0, 129.5, 114.7, 108.2, 65.4, 48.4, 20.4; HRMS (APCI) Calcd for [M+H, $C_{13}H_{16}FO_2$]$^+$: 223.1129; Found: 223.1126. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C;

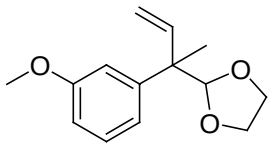
t_R of substrate **1f**, 4.56 min; t_R of product **2f**, 5.61 min; t_R of oligomers, 7.10–7.60 min.

2-(2-(4-Biphenyl)but-3-en-2-yl)-1,3-dioxolane (2g)



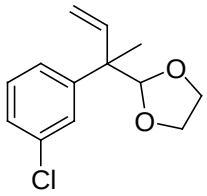
Yield: 88%; viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.36 (m, 9H), 6.33 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.6 Hz, 1H), 5.25 (s, 1H), 3.91 (s, 4H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.2, 141.0, 139.2, 128.8, 128.2, 127.2, 127.1, 126.7, 114.9, 108.4, 65.5, 48.7, 20.2; HRMS (EI) Calcd for $C_{19}H_{20}O_2$: 280.1463; Found: 280.1472. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1g**, 12.06 min; t_R of product **2g**, 12.88 min; t_R of oligomers, 14.05–14.55 min.

2-(2-(3-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane (2h)



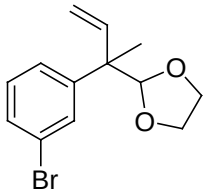
Yield: 87 %; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.1 Hz, 1H), 6.96–6.93 (m, 2H), 6.71–6.67 (m, 1H), 6.12 (dd *J* = 17.7 and 11.1 Hz, 1H), 5.18 (dd, *J* = 11.1 and 1.2 Hz, 1H), 5.10 (dd, *J* = 17.7 and 1.2 Hz, 1H), 5.06 (s, 1H), 3.78 (s, 4H), 3.71 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 145.3, 142.0, 128.8, 120.1, 114.7, 114.4, 111.2, 108.3, 65.4, 55.1, 48.9, 20.0; HRMS (EI) Calcd for $C_{14}H_{18}O_3$: 234.1256; Found: 234.1259. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1h**, 6.58 min; t_R of product **2h**, 7.41 min; t_R of oligomers, 8.75–9.35 min.

2-(2-(3-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane (2i)



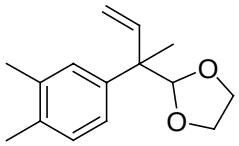
Yield: 88%; pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.20 (m, 4H), 6.18 (dd, *J* = 17.6 and 11.2 Hz, 1H), 5.30 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.6 Hz, 1H), 5.11 (s, 1H), 3.85 (s, 4H), 1.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 141.5, 133.9, 129.1, 128.2, 126.6, 126.1, 115.2, 108.0, 65.4, 48.9, 20.2; HRMS (APCI) Calcd for [M+H, $C_{13}H_{16}ClO_2$]$^+$: 239.0833; Found: 239.0830. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1i**, 6.50 min; t_R of product **2i**, 7.40 min; t_R of oligomers, 8.80–9.35 min.

2-(2-(3-Bromophenyl)but-3-en-2-yl)-1,3-dioxolane (2j)



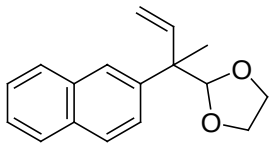
Yield: 91%; pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 1.8 Hz, 1H), 7.30–7.24 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.08 (dd, *J* = 17.7 and 11.1 Hz, 1H), 5.19 (dd, *J* = 11.1 and 1.2 Hz, 1H), 5.09 (dd, *J* = 17.7 and 1.2 Hz, 1H), 4.99 (s, 1H), 3.74 (s, 4H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 141.5, 131.1, 129.5, 129.4, 126.6, 122.2, 115.3, 108.0, 65.4, 48.9, 20.3; HRMS (APCI) Calcd for [M+H, $C_{13}H_{16}BrO_2$]$^+$: 283.0328; Found: 283.0324. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1j**, 7.25 min; t_R of product **2j**, 8.25 min; t_R of oligomers, 9.70–9.80 min.

2-(2-(3,4-Dimethylphenyl)but-3-en-2-yl)-1,3-dioxolane (2k)



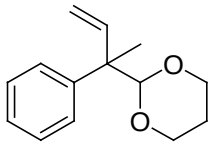
Yield: 83 %; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09–6.97 (m, 3H), 6.12 (dd, *J* = 17.7 and 11.1 Hz, 1H), 5.17–5.04 (m, 3H), 3.74 (s, 4H), 2.16 (s, 3H), 2.13 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.1, 134.8, 133.5, 128.3, 127.8, 124.0, 113.3, 107.4, 64.3, 47.3, 19.0, 18.9, 18.2; HRMS (EI) Calcd for $C_{15}H_{20}O_2$: 232.1463; Found: 232.1465. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1k**, 6.51 min; t_R of product **2k**, 7.23 min; t_R of oligomers, 8.45–9.10 min.

2-(2-(Naphthalen-2-yl)but-3-en-2-yl)-1,3-dioxolane (2l)



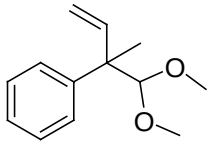
Yield: 87%; pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.29 (m, 7H), 6.20 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.22–5.07(m, 3H), 3.68 (s, 4H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.3, 133.5, 132.5, 128.5, 127.7, 127.6, 126.7, 126.1, 126.0, 115.4, 108.6, 108.5, 65.7, 49.3, 20.6; HRMS (EI) Calcd for $C_{17}H_{18}O_2$: 254.1307; Found: 254.1304. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 150 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1l**, 6.98 min; t_R of product **2l**, 7.76 min; t_R of oligomers, 8.98–9.45 min.

2-(2-Phenylbut-3-en-2-yl)-1,3-dioxane (2m)



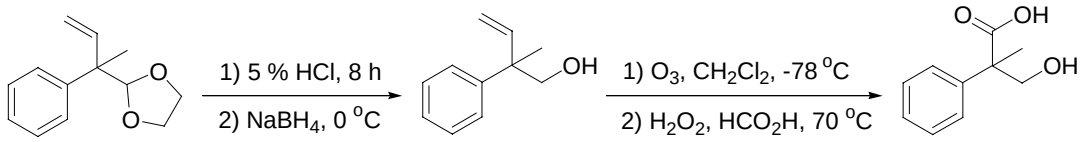
Yield: 50%; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.19 (m, 5H), 6.31 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.11 (d, *J* = 18.0 Hz, 1H), 4.76 (s, 1H), 4.16–4.12 (m, 2H), 3.76 (t, *J* = 12.0 Hz, 2H), 2.13–2.01(m, 1H), 1.46 (s, 3H), 1.33–1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.8, 128.1, 127.7, 126.3, 114.3, 106.5, 67.5, 49.3, 26.0, 21.1; HRMS (EI) Calcd for $C_{14}H_{18}O_2$: 218.1307; Found: 218.1304. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 150 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1m**, 4.01 min; t_R of product **2m**, 4.73 min; t_R of oligomers, 6.56–7.11 min.

1-(2-(Dimethoxymethyl)but-3-en-2-yl)benzene (2n)



Yield: 70%; colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.16 (m, 5H), 6.30 (dd, *J* = 17.4 and 10.8 Hz, 1H), 5.23 (dd, *J* = 11.1 and 1.5 Hz, 1H), 5.08 (dd, *J* = 17.7 and 1.2 Hz, 1H), 4.34 (s,1H), 3.38 (s, 3H), 3.33 (s, 3H), 1.45 (s 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 142.7, 127.9, 127.6, 126.2, 114.3, 112.6, 58.4, 50.5, 20.4; HRMS (APCI) Calcd for $[M+H, C_{13}H_{19}O_2]^+$: 207.1380; Found: 207.1386. GC analysis conditions: HP–5 column, carrier gas, N_2 (2.0 mL/min); inject temperature, 250 °C; initial temperature, 120 °C; rate, 10 °C/min; final temperature, 250 °C; t_R of substrate **1n**, 3.87 min; t_R of product **2n**, 4.75 min; t_R of oligomers, 6.10–6.55 min.

(5) Preparation of 2-Methyltropic Acid [8]



2a **3** **4**

HC1 (5%, 20 mL) was added slowly to a solution of **2a** (470 mg, 2.30 mmol) in THF (20 mL) at 0 °C. After stirring for 8 h at rt, the reaction was completed (detected by GC). The resulting mixture was extracted with ether (2 × 50 mL). The combined organic phase was washed with water (50 mL) and concentrated. The residue was dissolved in ethanol (5 mL), $NaBH_4$ (400 mg 10.5 mmol) was added at 0 °C. The resulting suspension was stirred for 1 h and diluted with ether (100 mL) and several drops of acetic acid. The mixture was washed with brine, and dried with anhydrous Na_2SO_4. After filtration and evaporation of solvents, the residue was purified on a silica gel pad (EA/PE, v/v 1:4) to afford **3** [9] (340 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 6.07 (dd, *J* = 17.7 and 11.1 Hz, 1H), 5.26 (dd, *J* = 10.8 and 1.2 Hz, 1H), 5.15 (dd, *J* = 17.7 and 1.2 Hz, 1H), 3.77 (d, *J* = 3.6 Hz, 2H), 1.46 (s, 1H), 1.42 (s, 3H).

Ozone was bubbled into a solution of **3** (81 mg, 0.5 mmol) in CH_2Cl_2 (25 mL) at –78 °C until the solution turned to a persistent blue color.[10] After consumption of compound **3** the mixture was stirred at this temperature for additional 20 min. Nitrogen gas was bubbled into the solution to replace ozone until the solution become colorless. The reaction mixture was warmed to room temperature and concentrated under vacuum. The residue was dissolved in formic acid (0.6 mL) and 30% H_2O_2 (0.3 mL) and heated at 70 °C for 10 h. The reaction mixture was added Et_2O (50 mL) and extracted with 10% NaOH (3 × 10 mL). The combined basic aqueous phase was washed with Et_2O (60 mL). After acidifying with 3 N HCl to pH 1, the mixture was extracted with Et_2O (3 × 40 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated to afford acid **4** (60 mg, 62%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 5H), 4.10 (d, *J* = 11.6 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.1, 139.5, 128.7, 127.6, 127.6, 126.2, 69.1, 52.4, 20.0.

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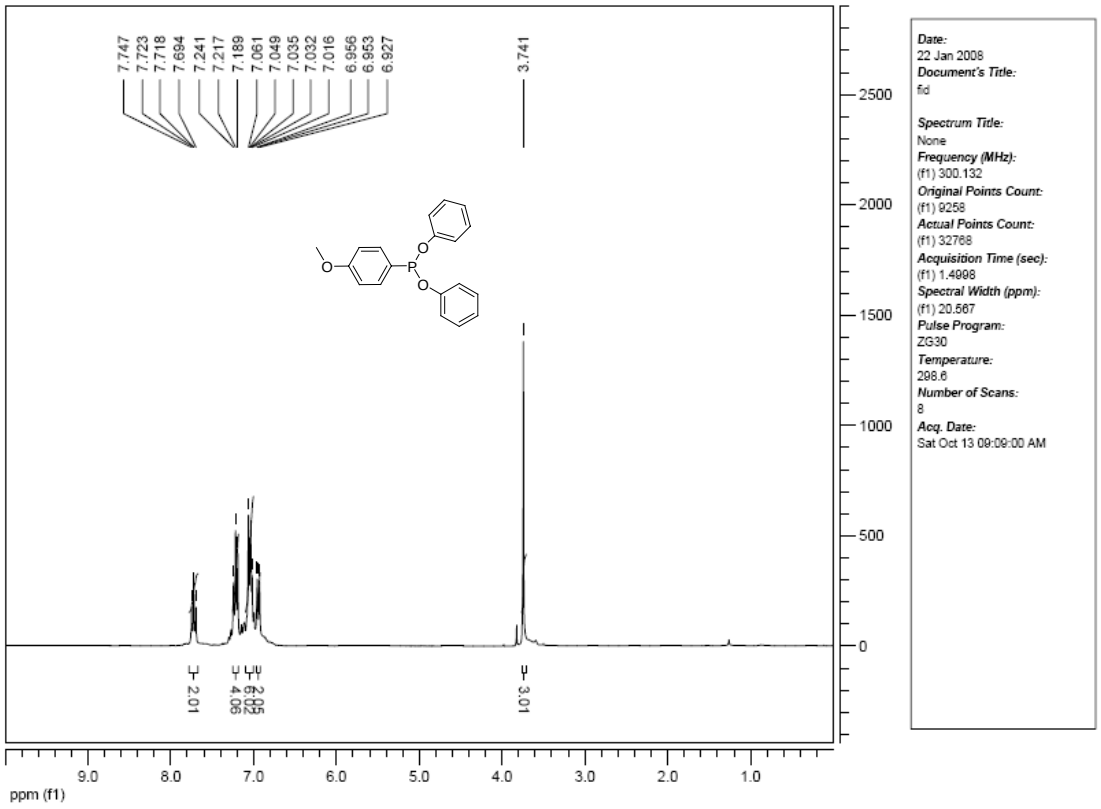
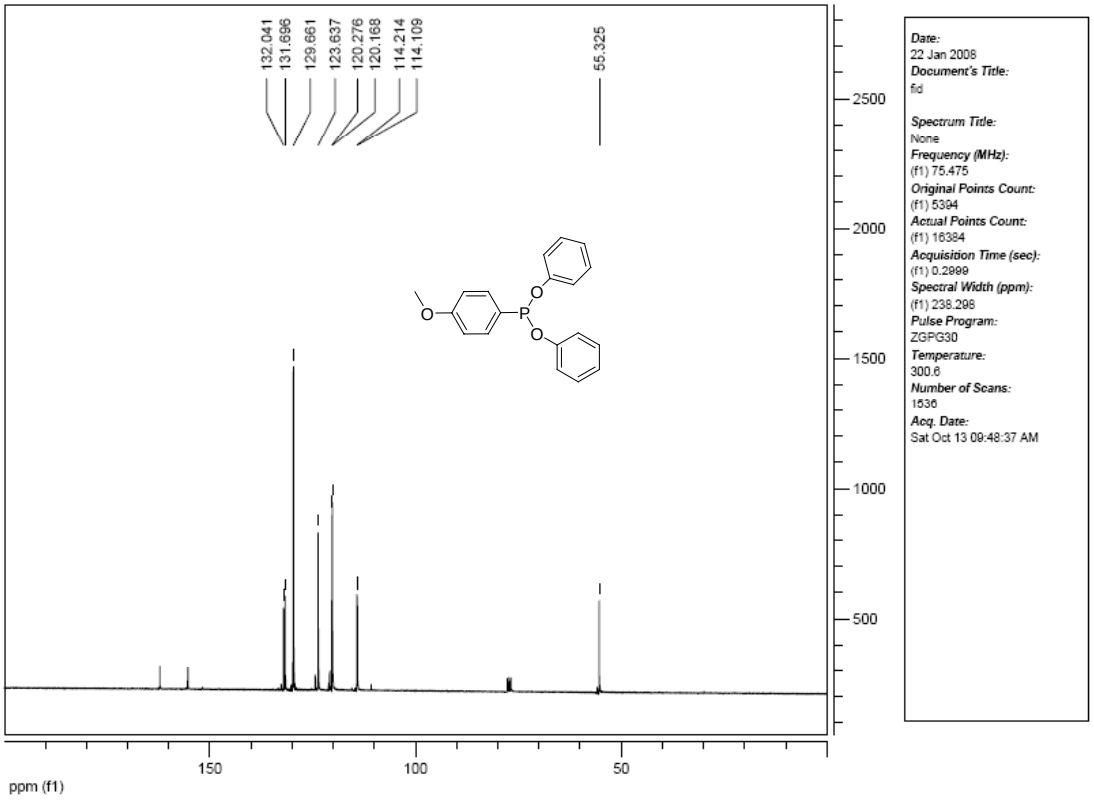
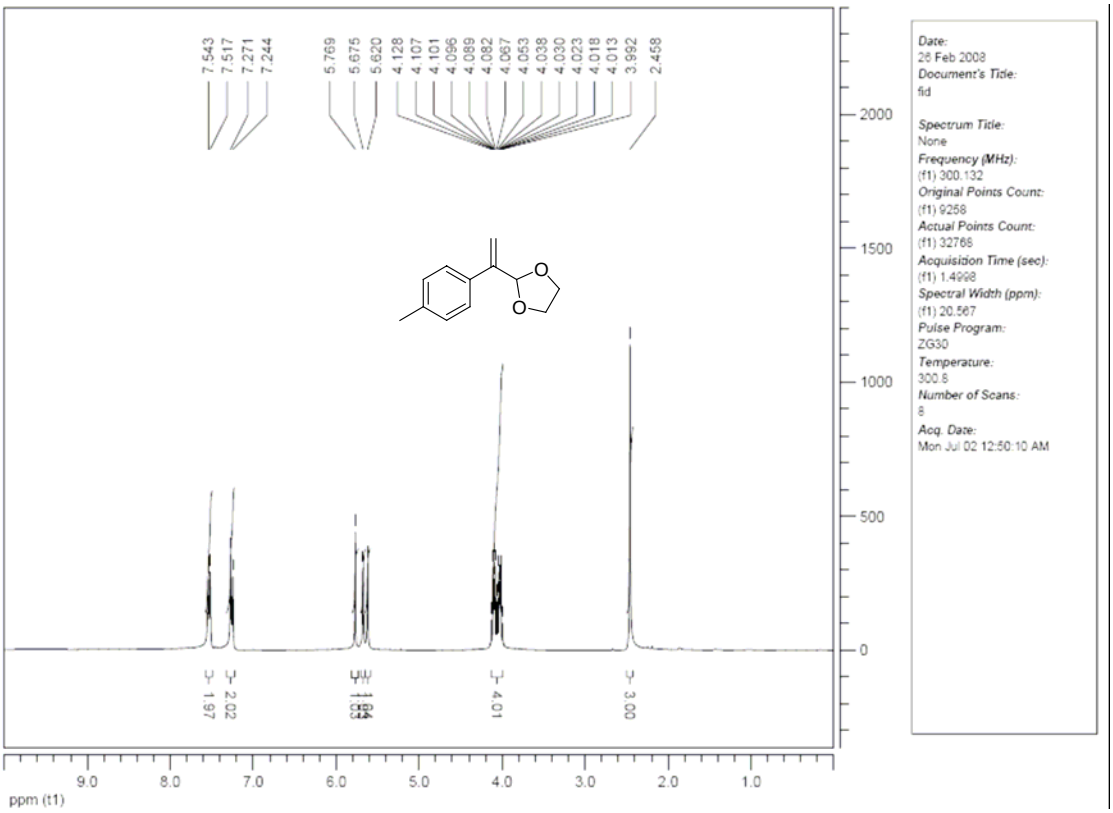
(6) NMR Spectra for New Compounds

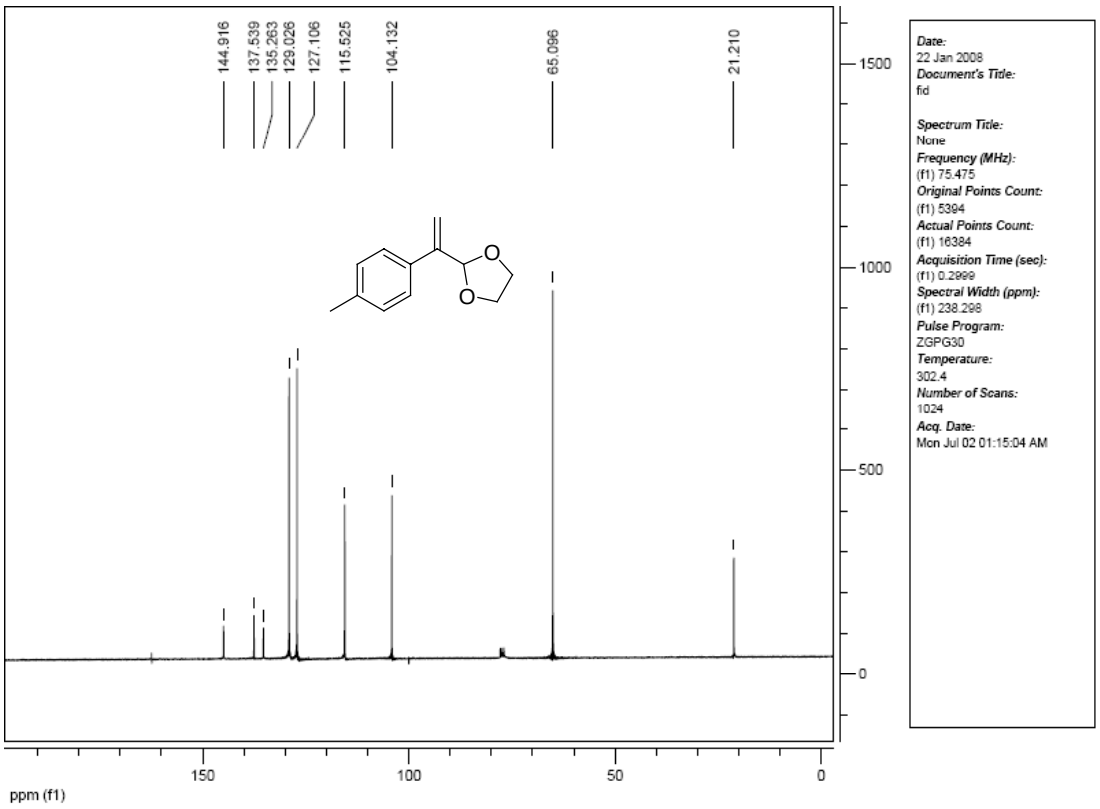
Diphenyl 4-methoxyphenylphosphonite



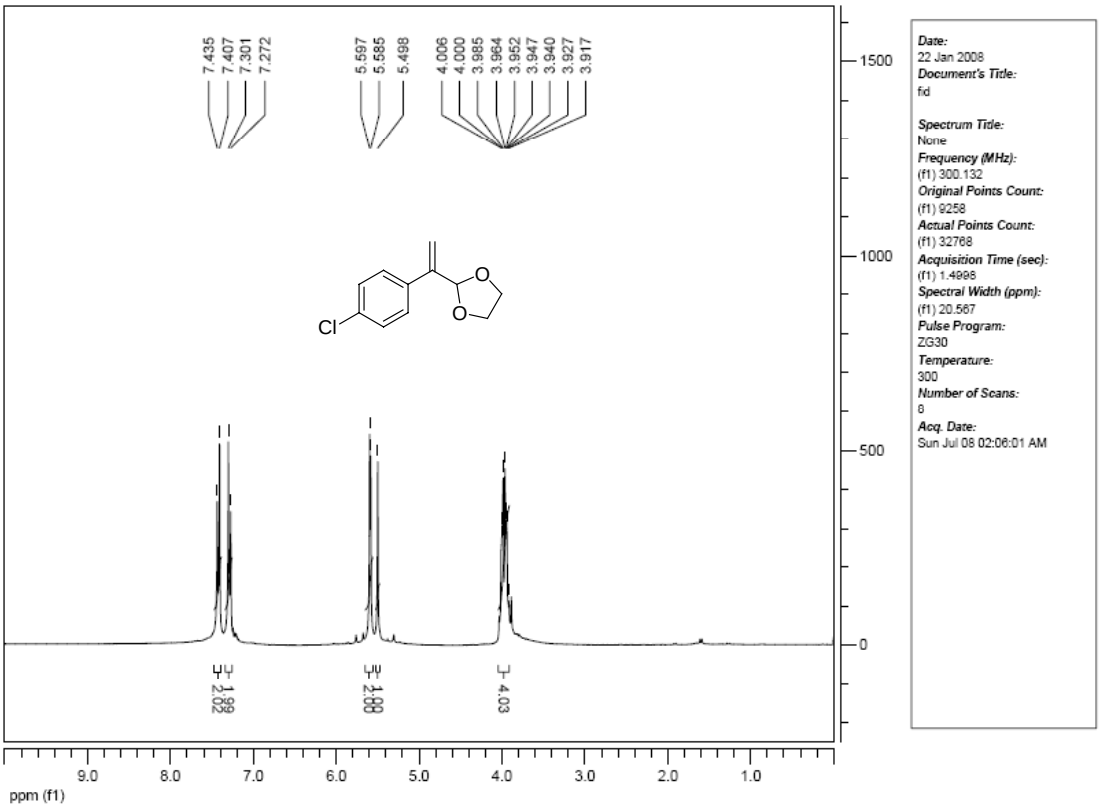


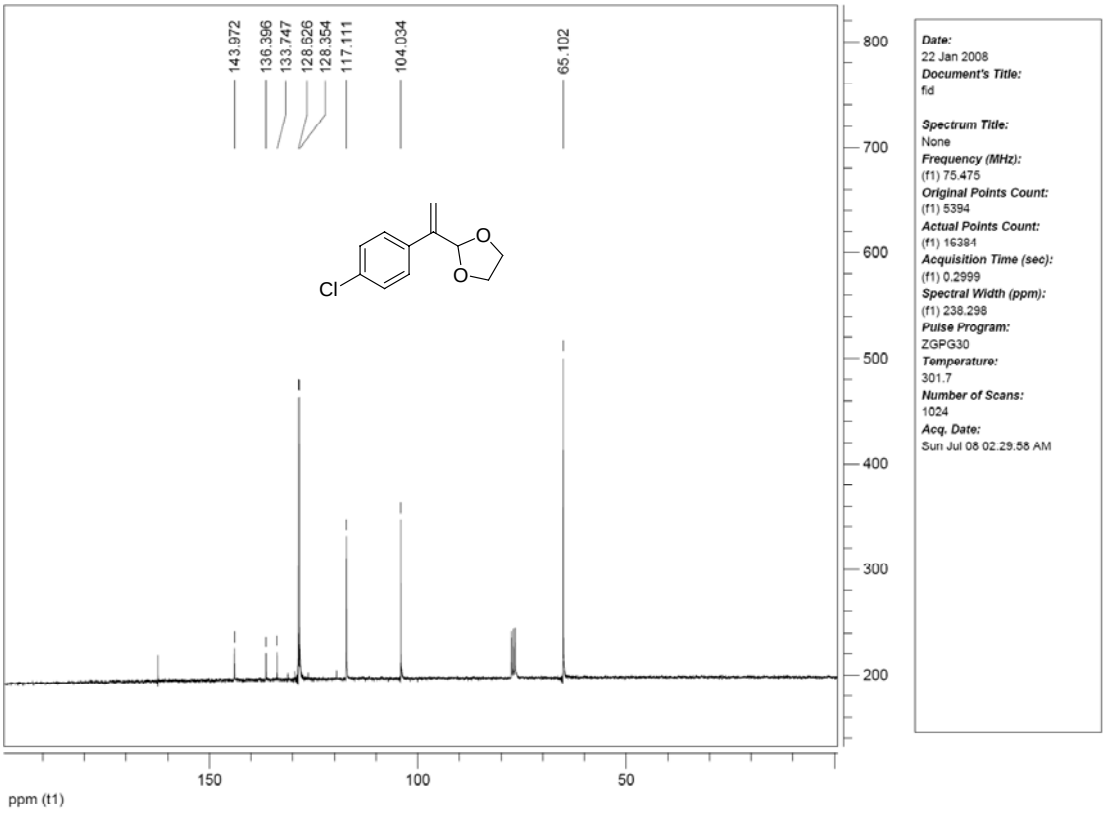
2-(1-*p*-Tolylvinyl)-1,3-dioxolane



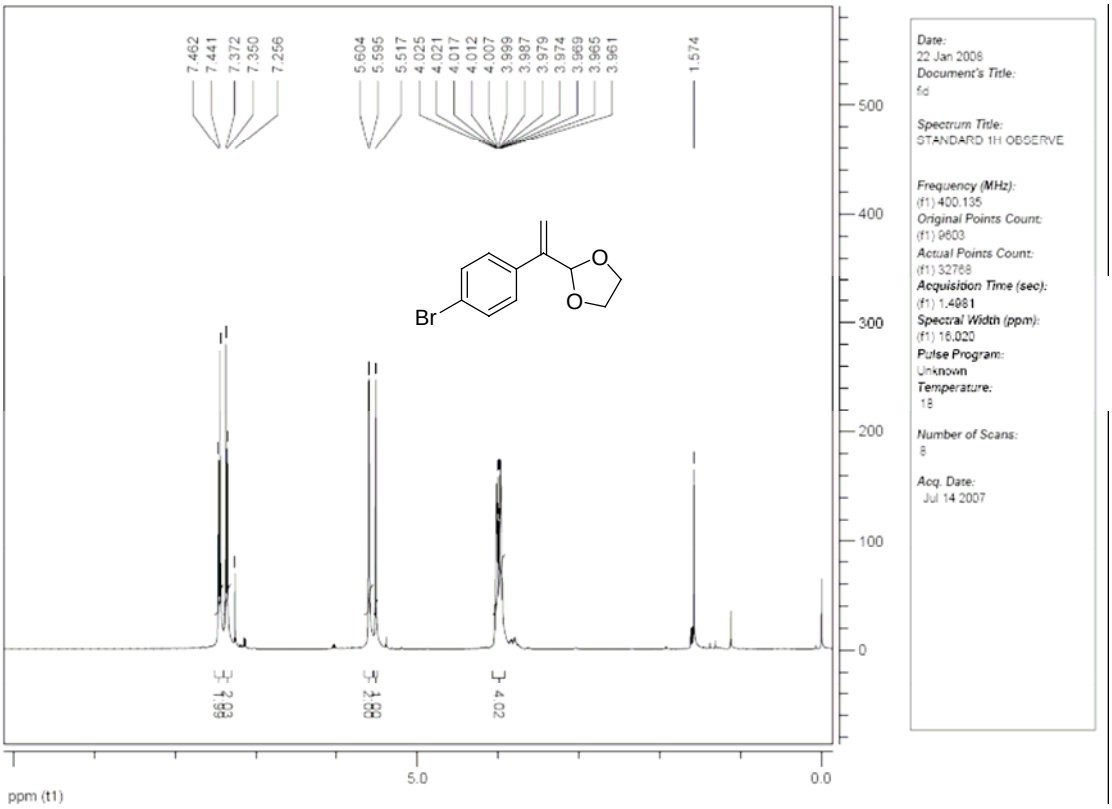


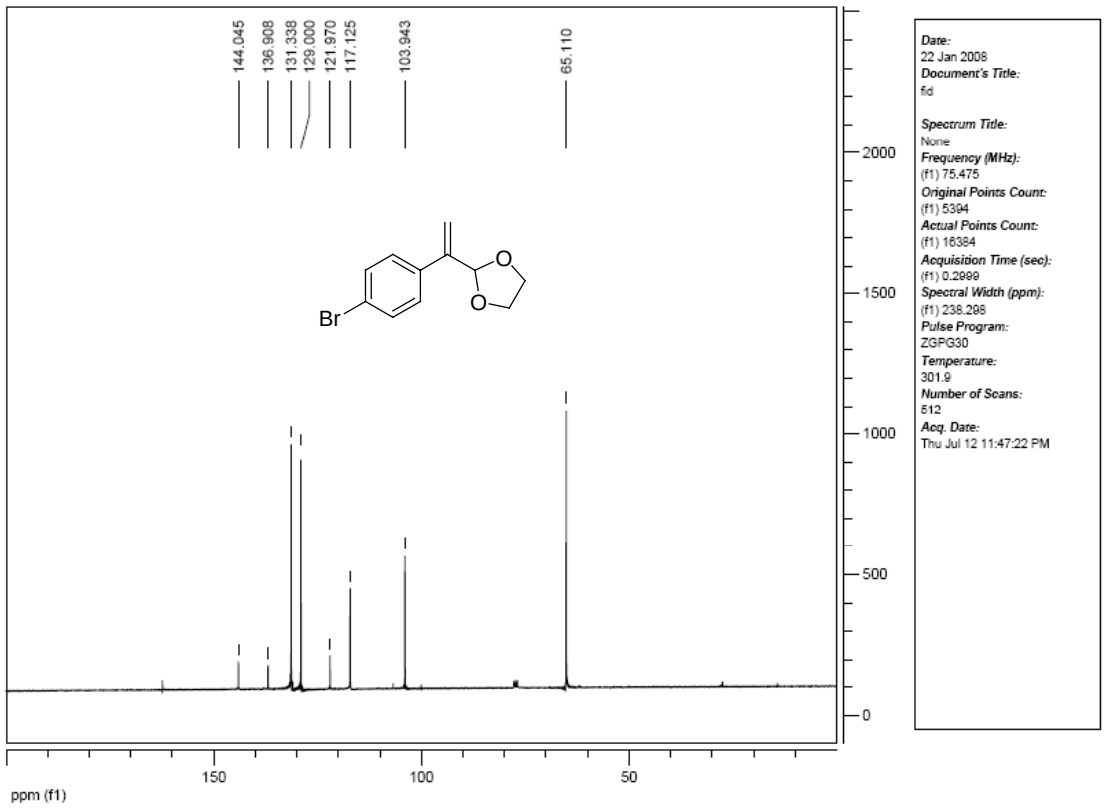
2-(1-(4-Chlorophenyl)vinyl)-1,3-dioxolane



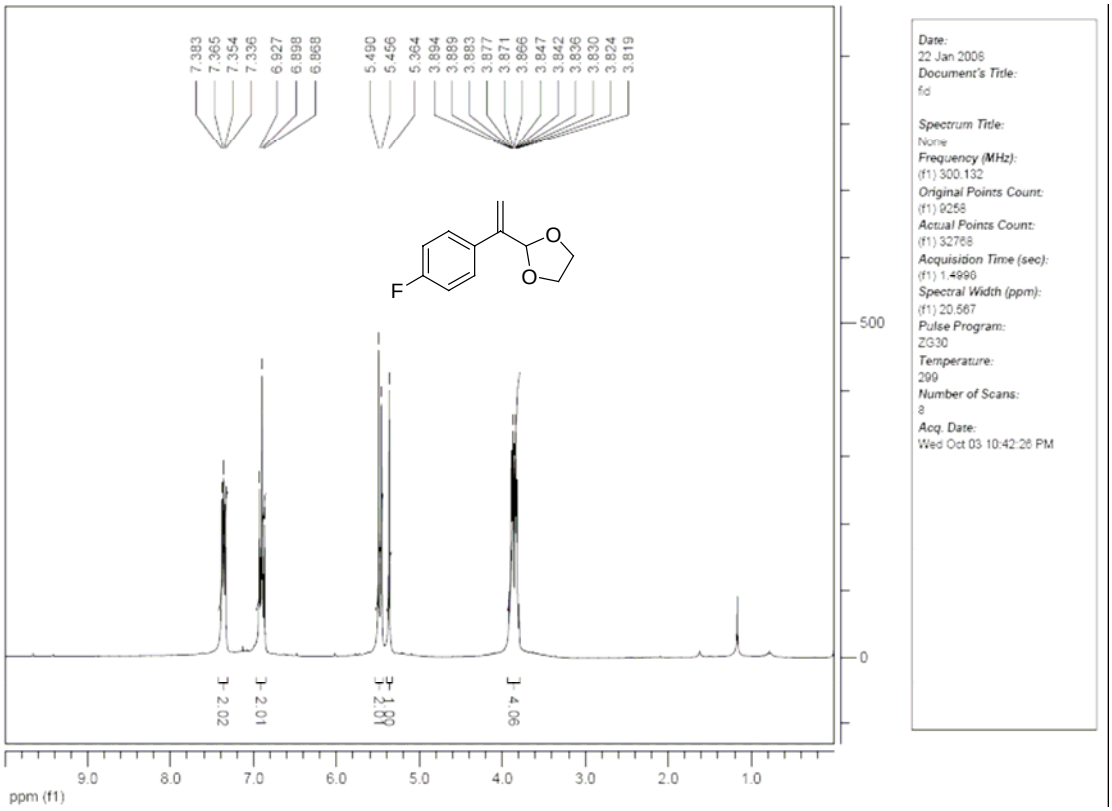


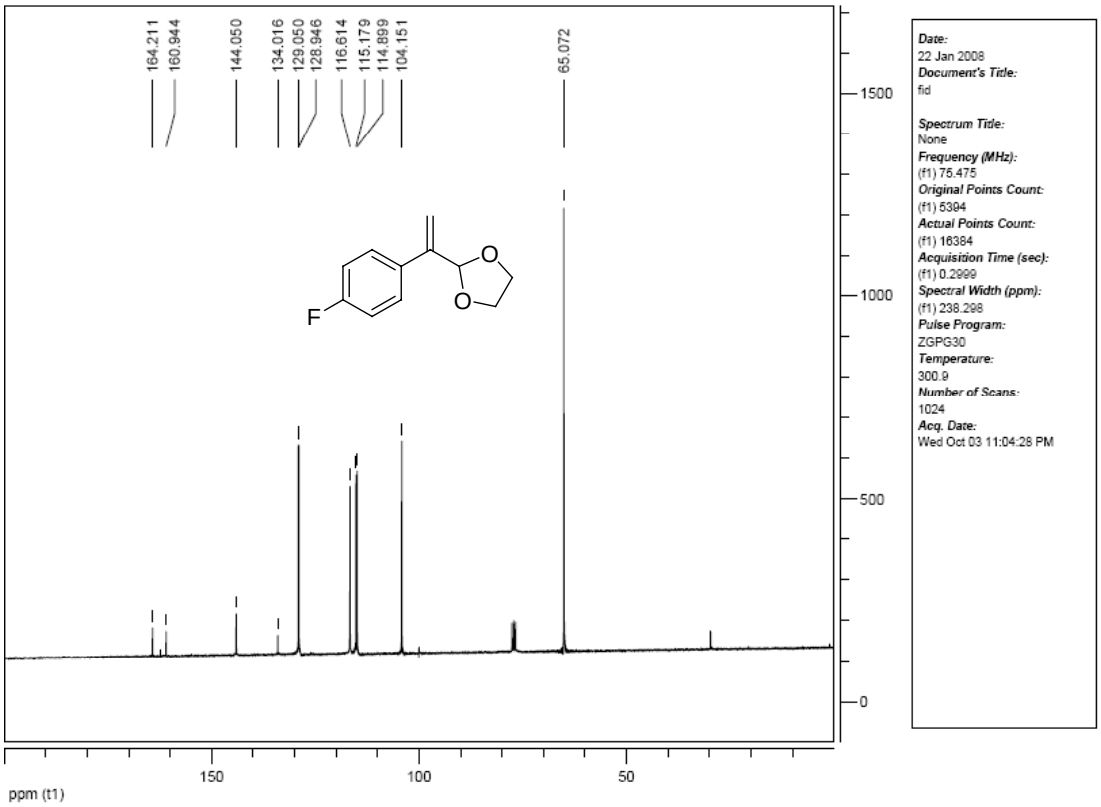
2-(1-(4-Bromophenyl)vinyl)-1,3-dioxolane



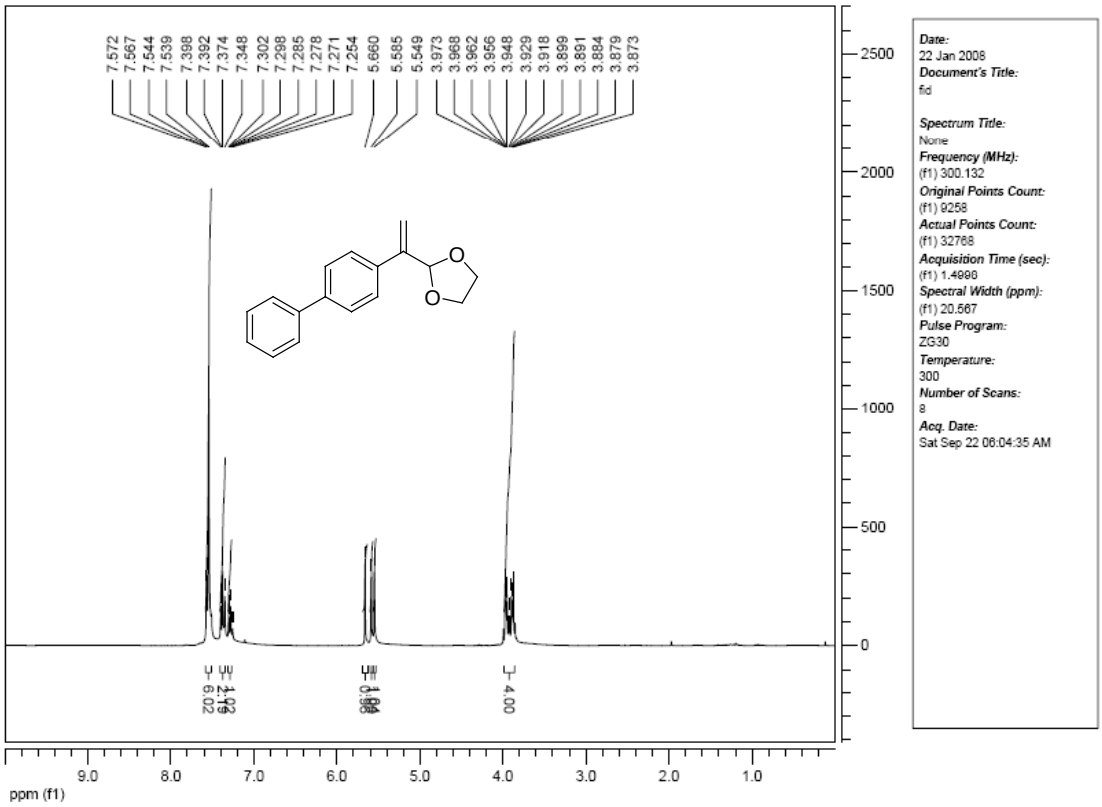


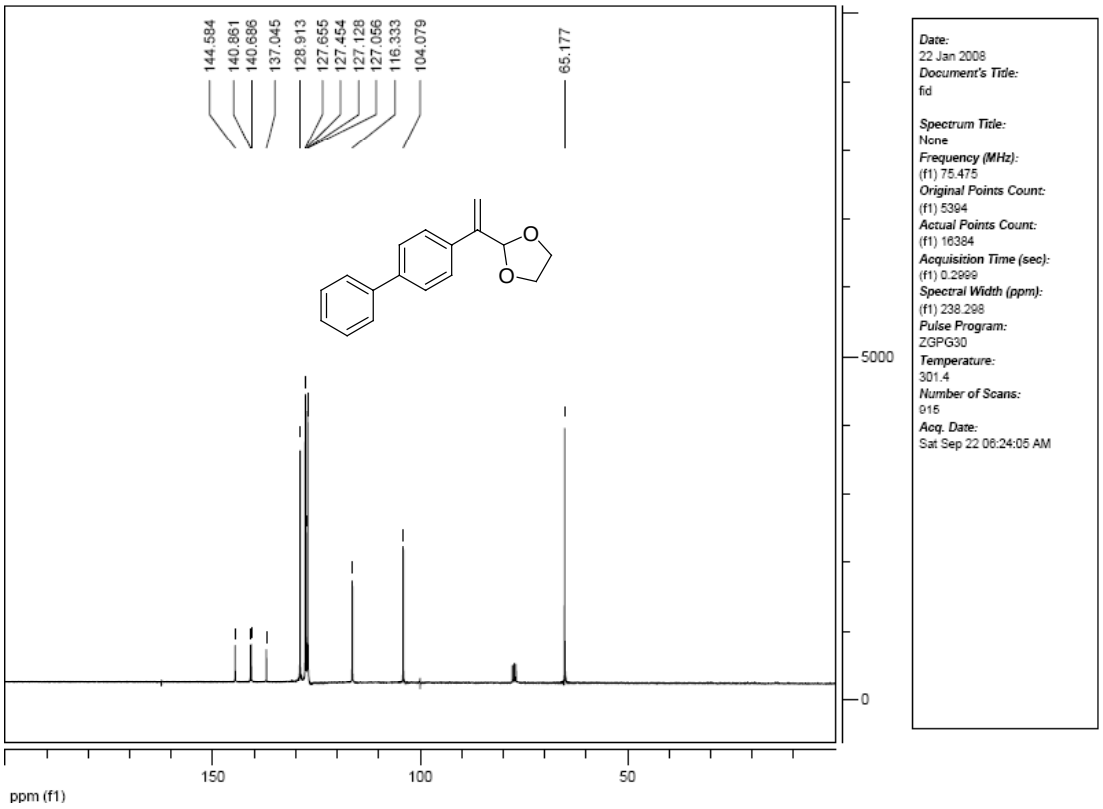
2-(1-(4-Fluorophenyl)vinyl)-1,3-dioxolane



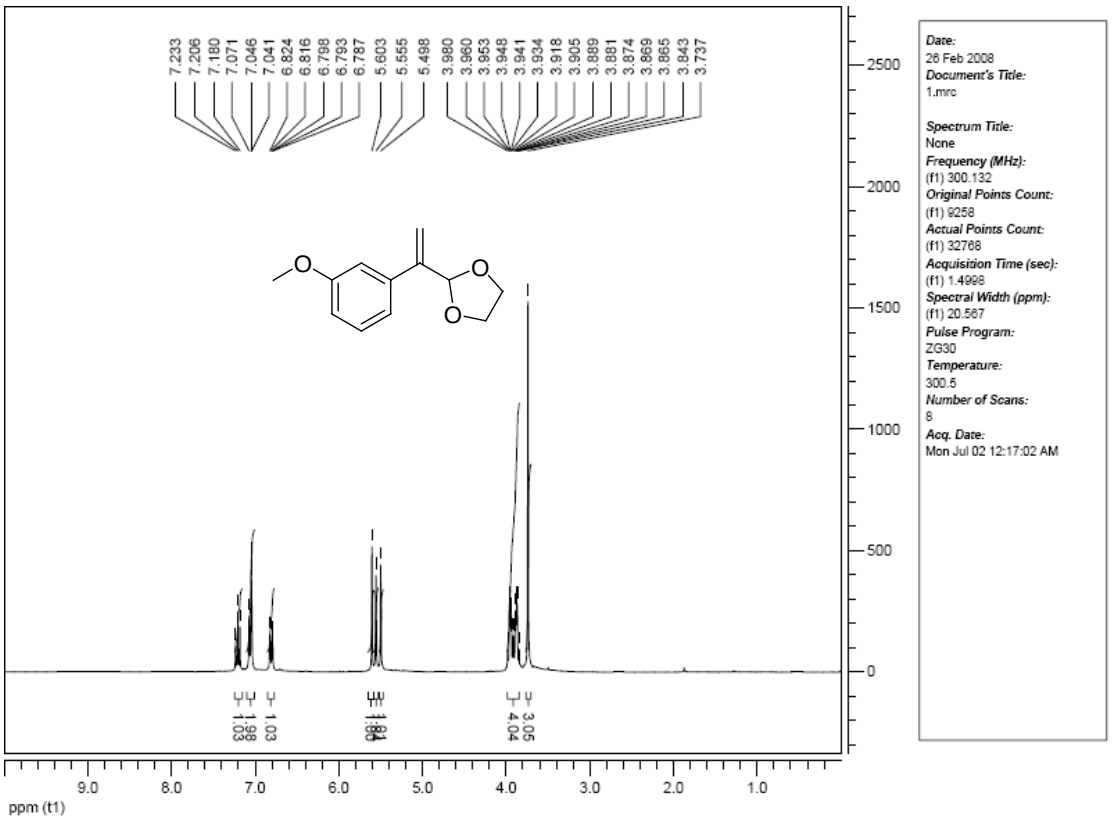


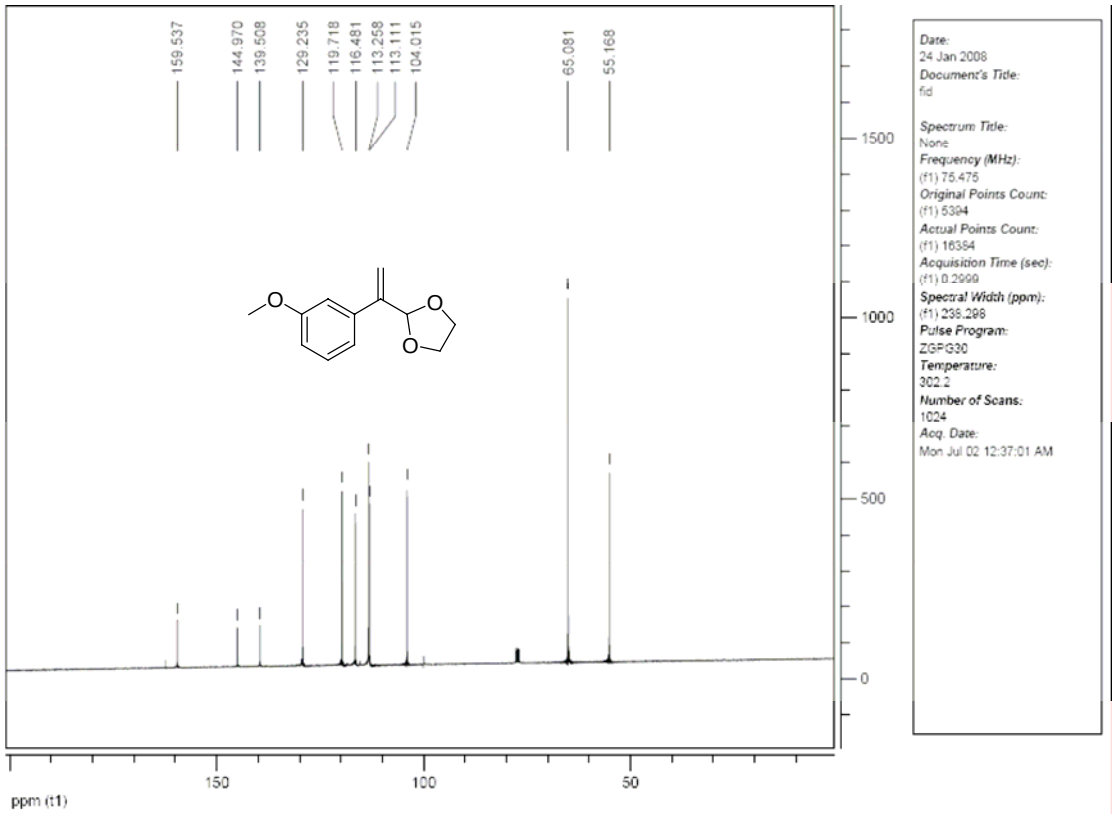
2-(1-(4-Biphenyl)vinyl)-1,3-dioxolane



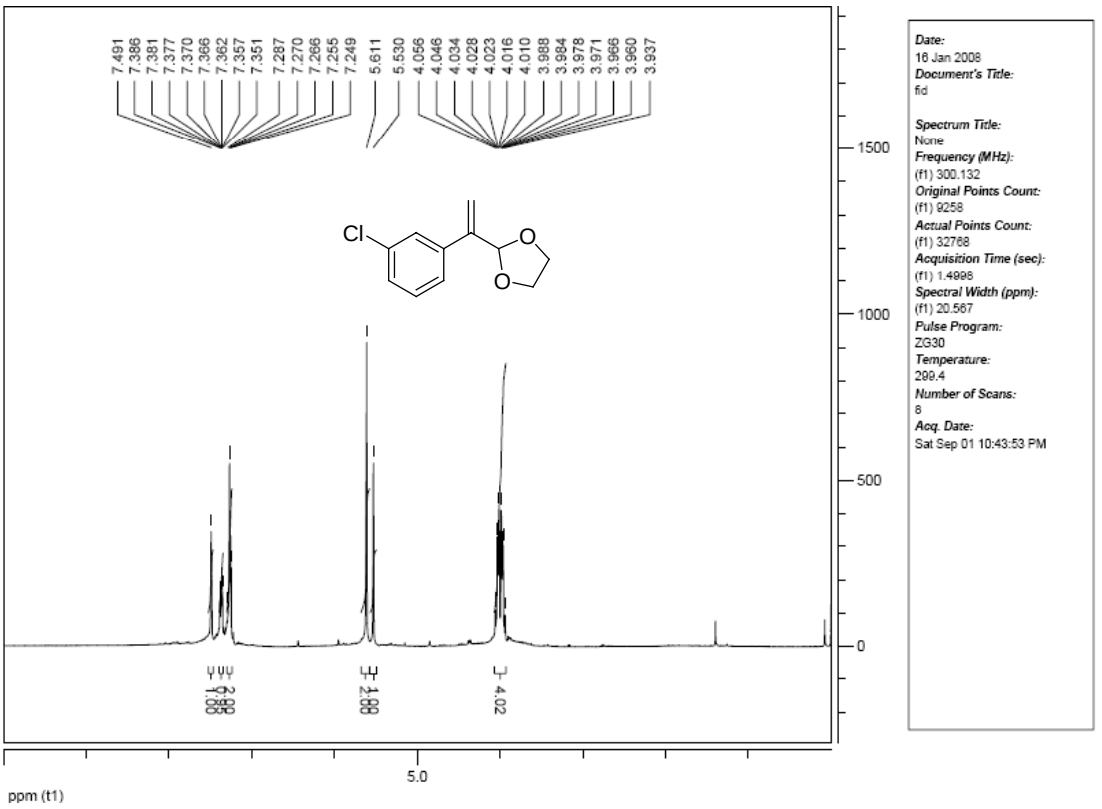


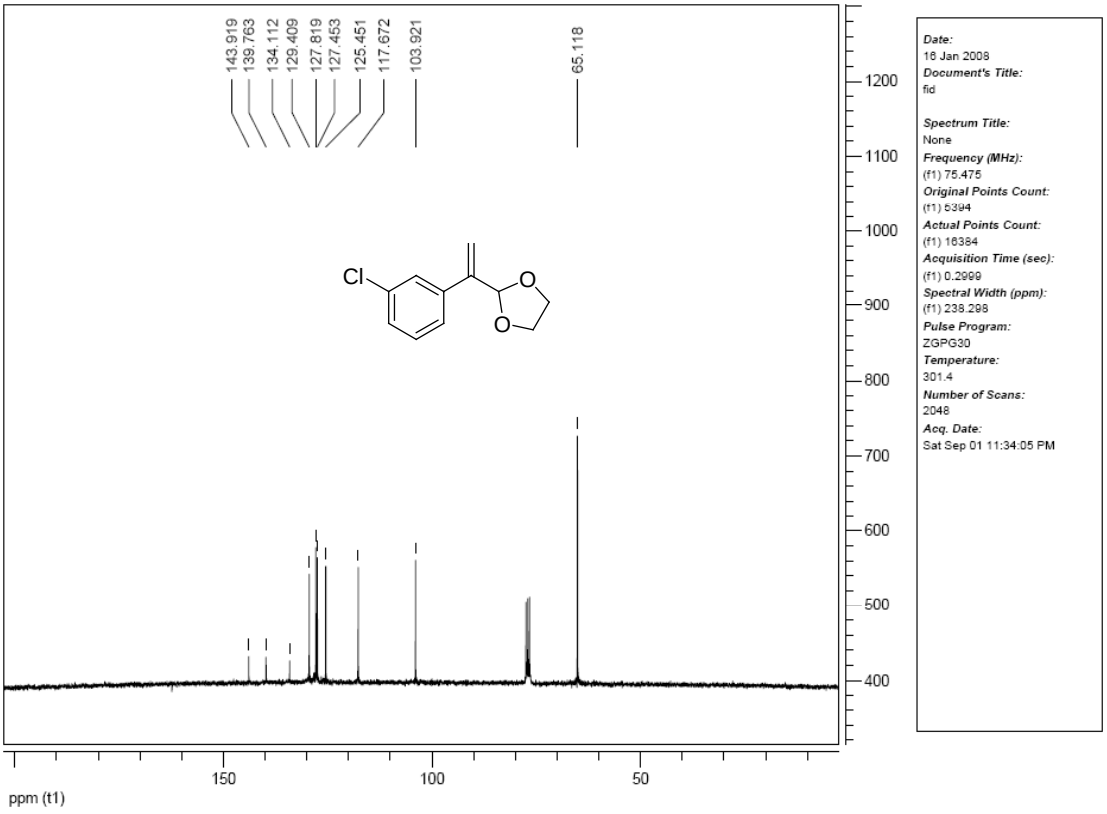
2-(1-(3-Methoxyphenyl)vinyl)-1,3-dioxolane



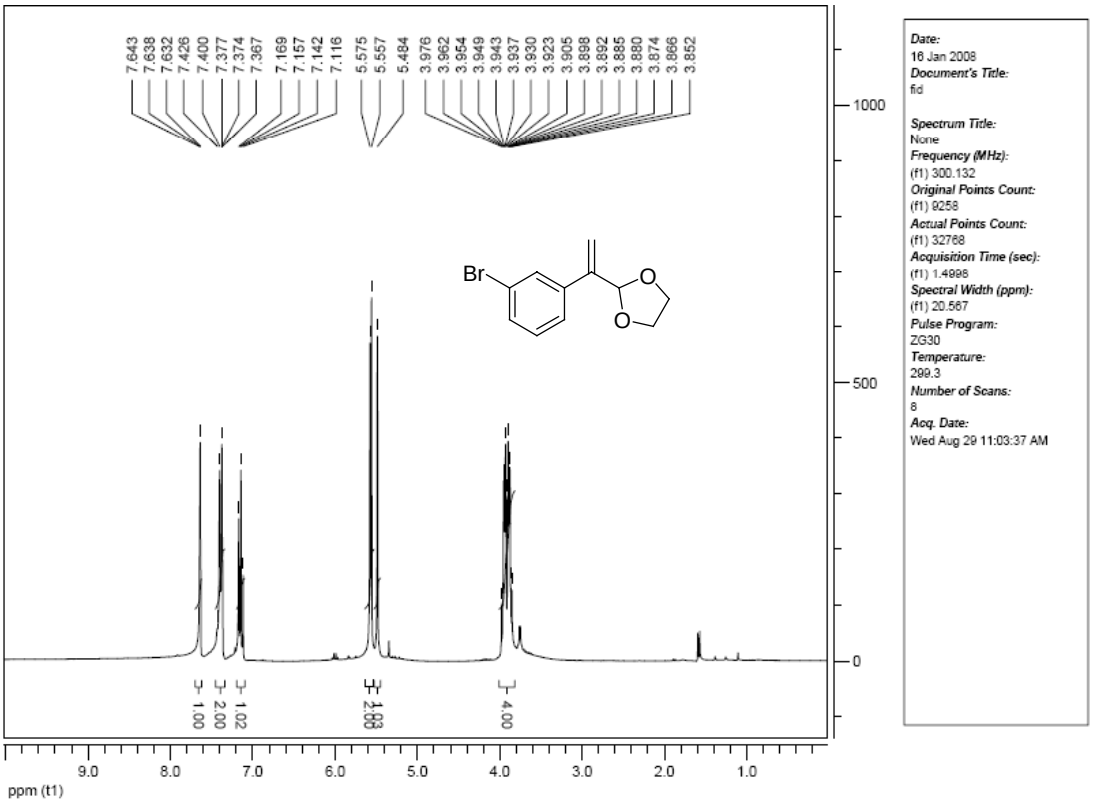


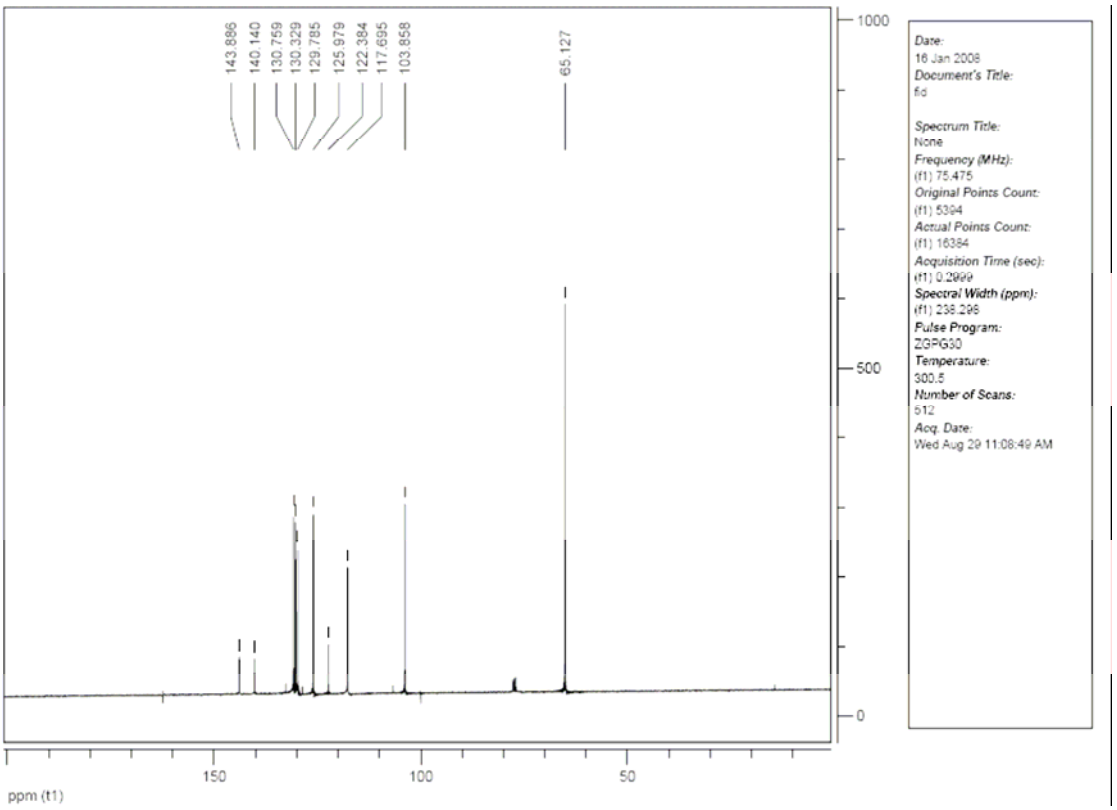
2-(1-(3-Chlorophenyl)vinyl)-1,3-dioxolane



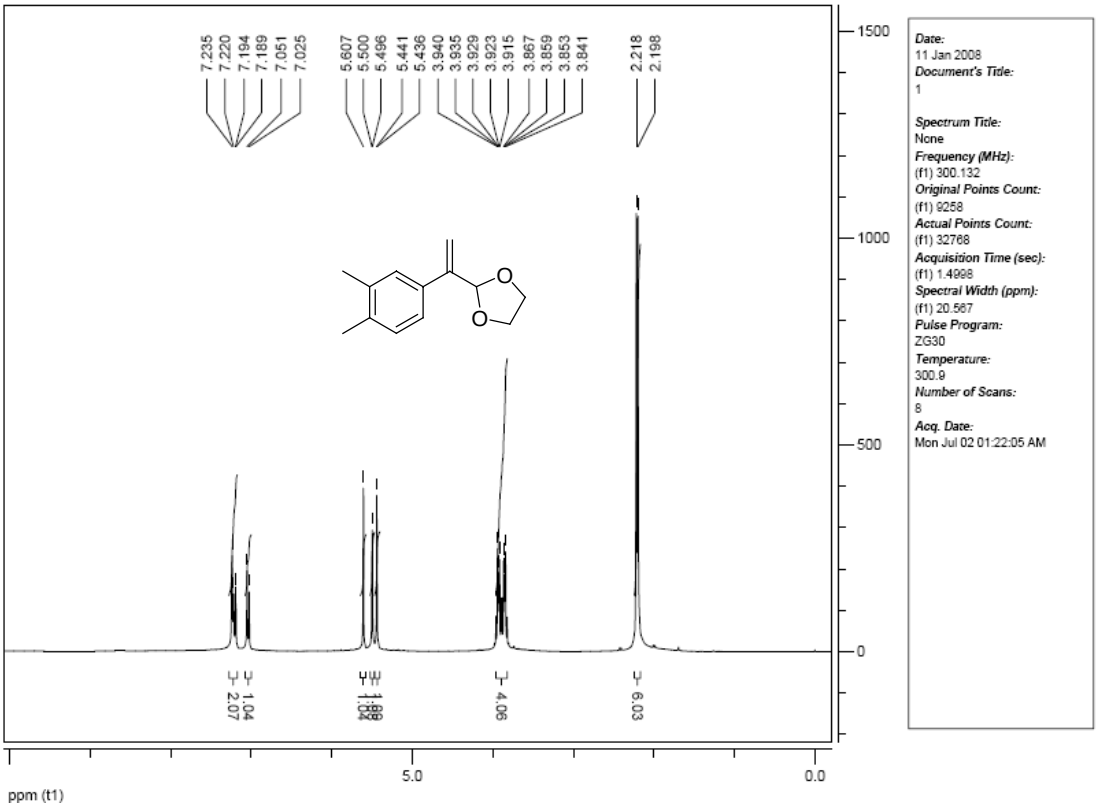


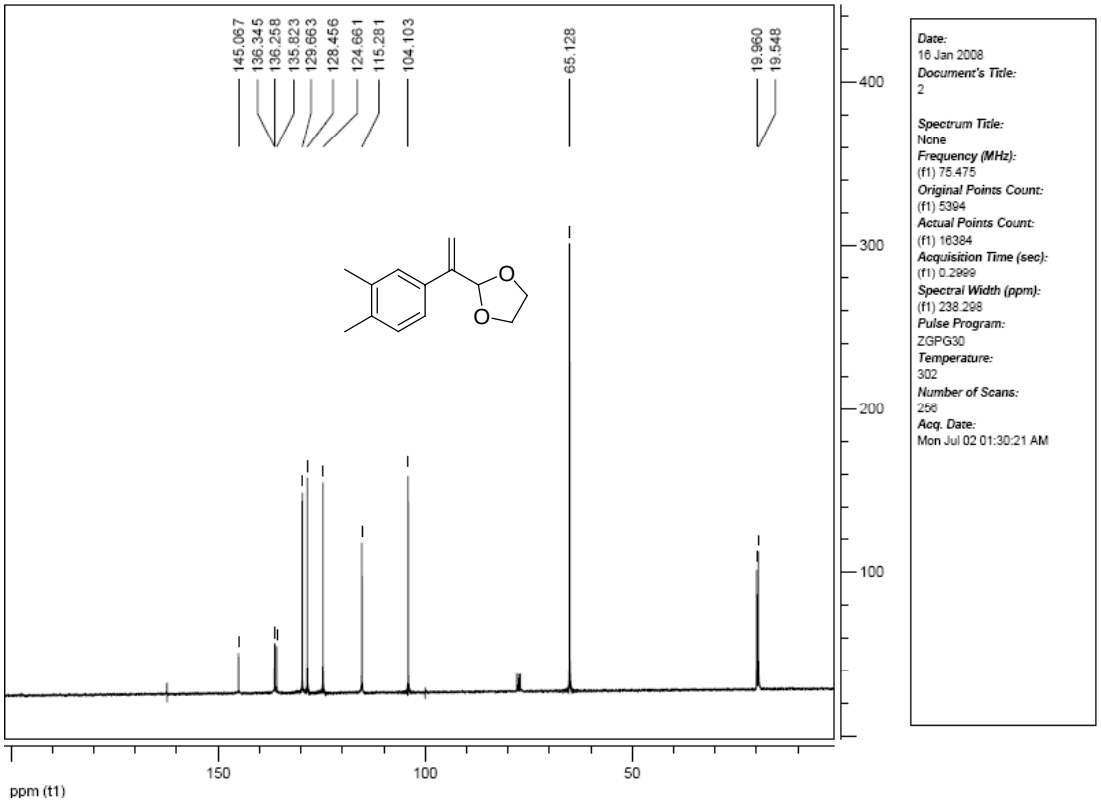
2-(1-(3-Bromophenyl)vinyl)-1,3-dioxolane



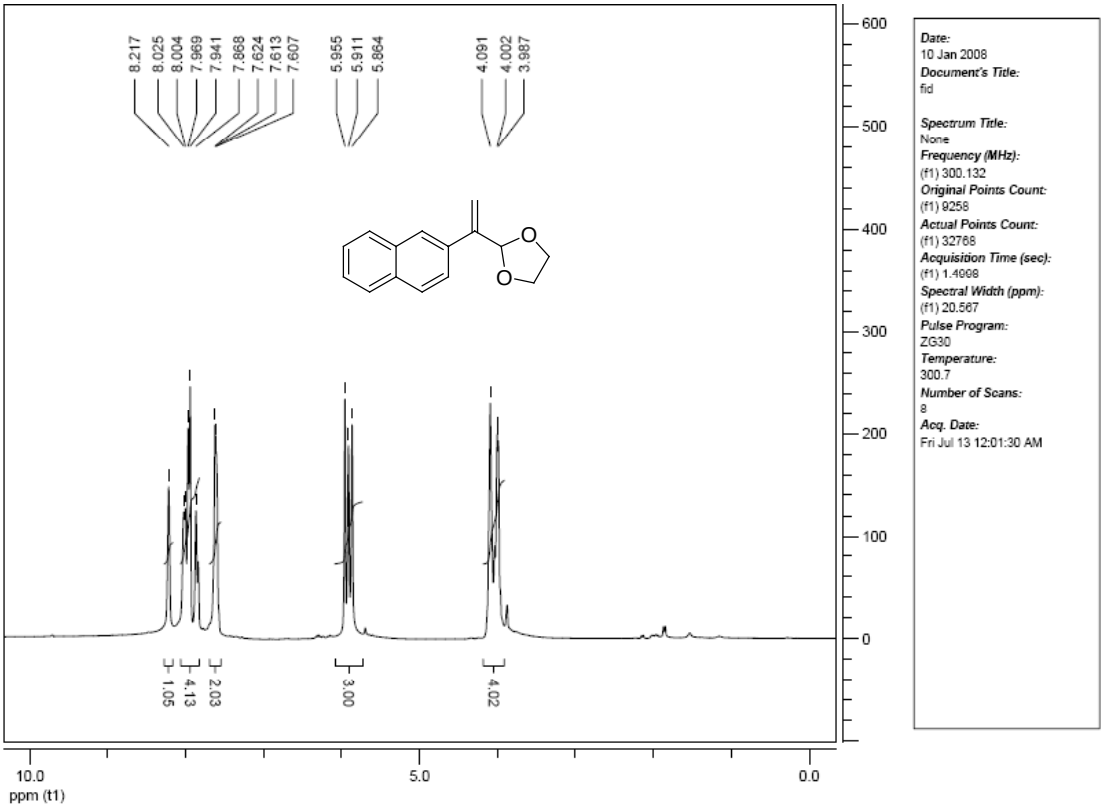


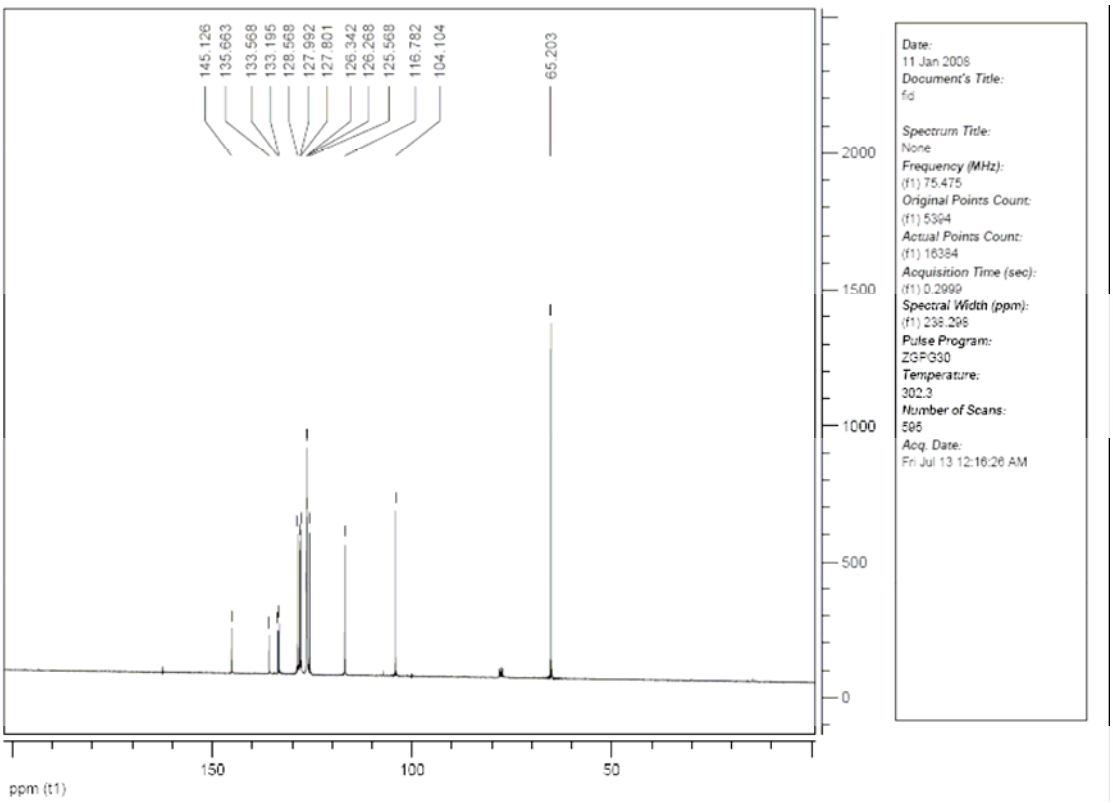
2-(1-(3,4-Dimethylphenyl)vinyl)-1,3-dioxolane



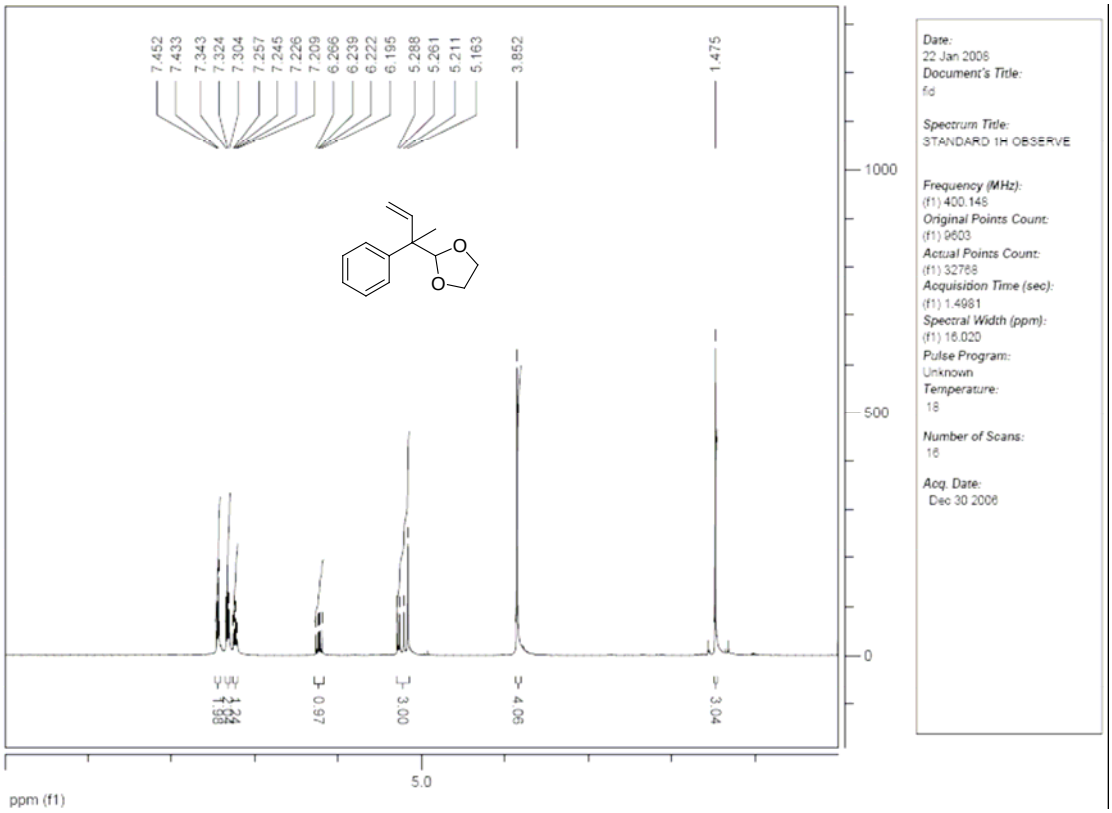


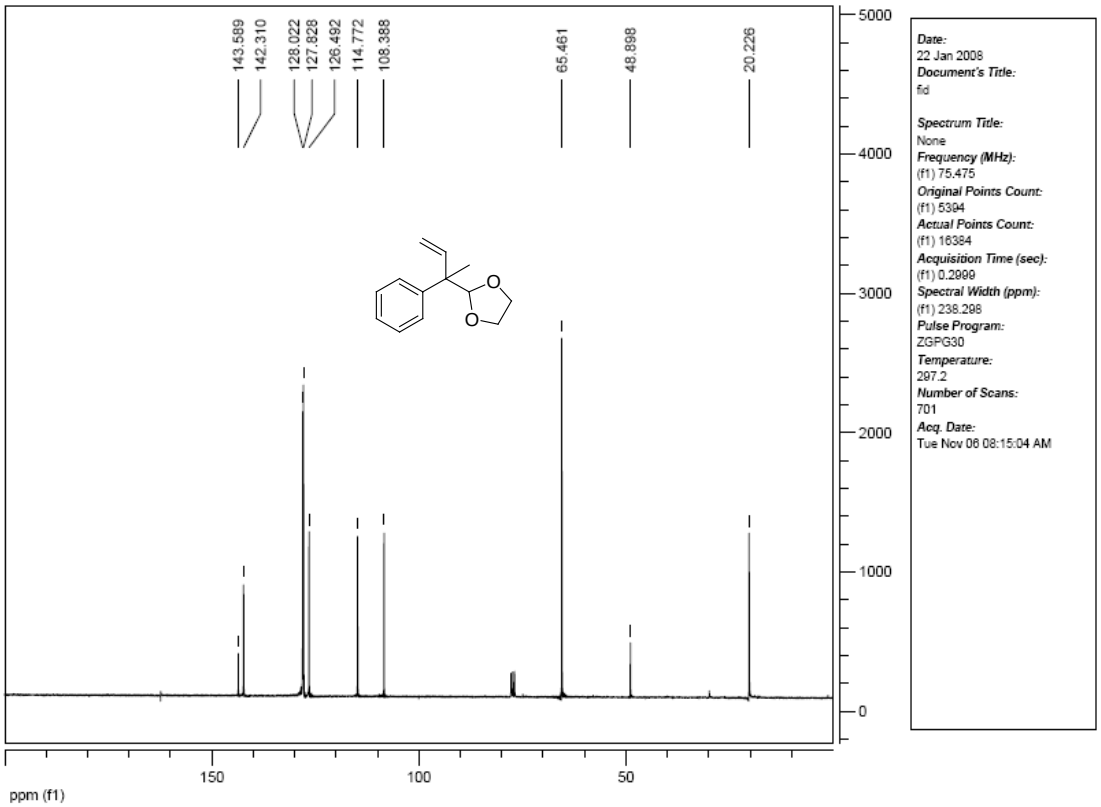
2-(1-(Naphthalen-2-yl)vinyl)-1,3-dioxolane



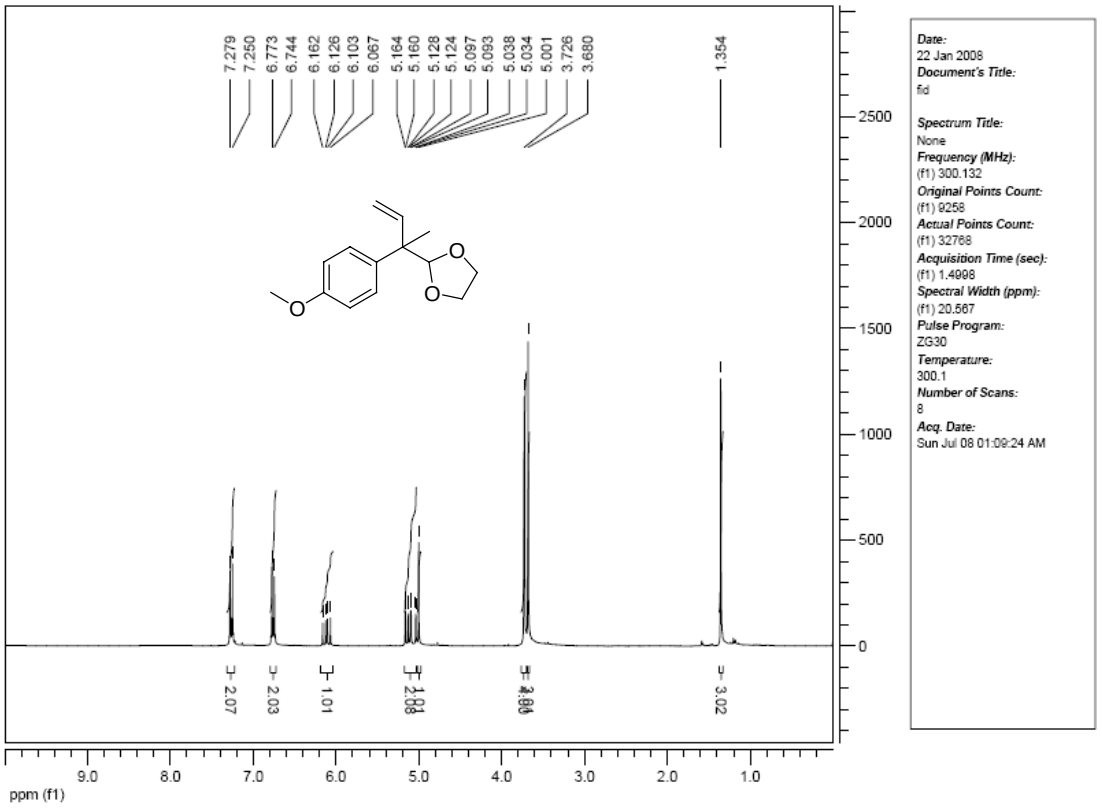


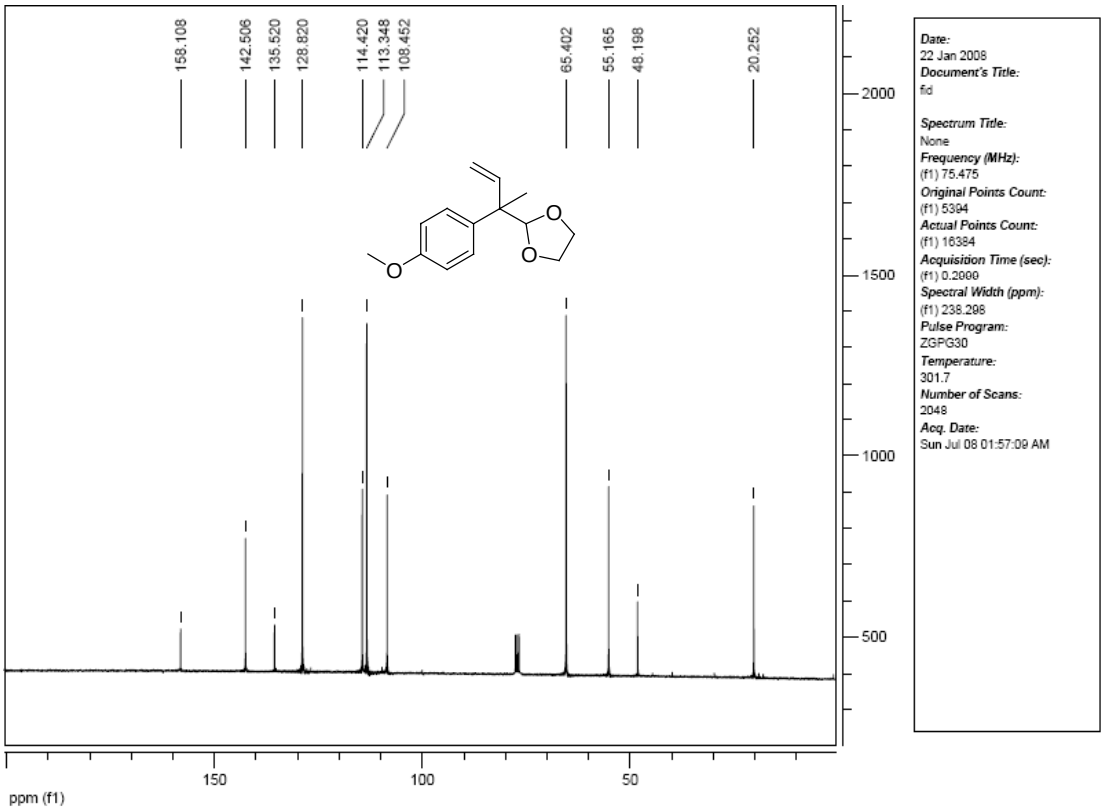
2-(2-Phenylbut-3-en-2-yl)-1,3-dioxolane



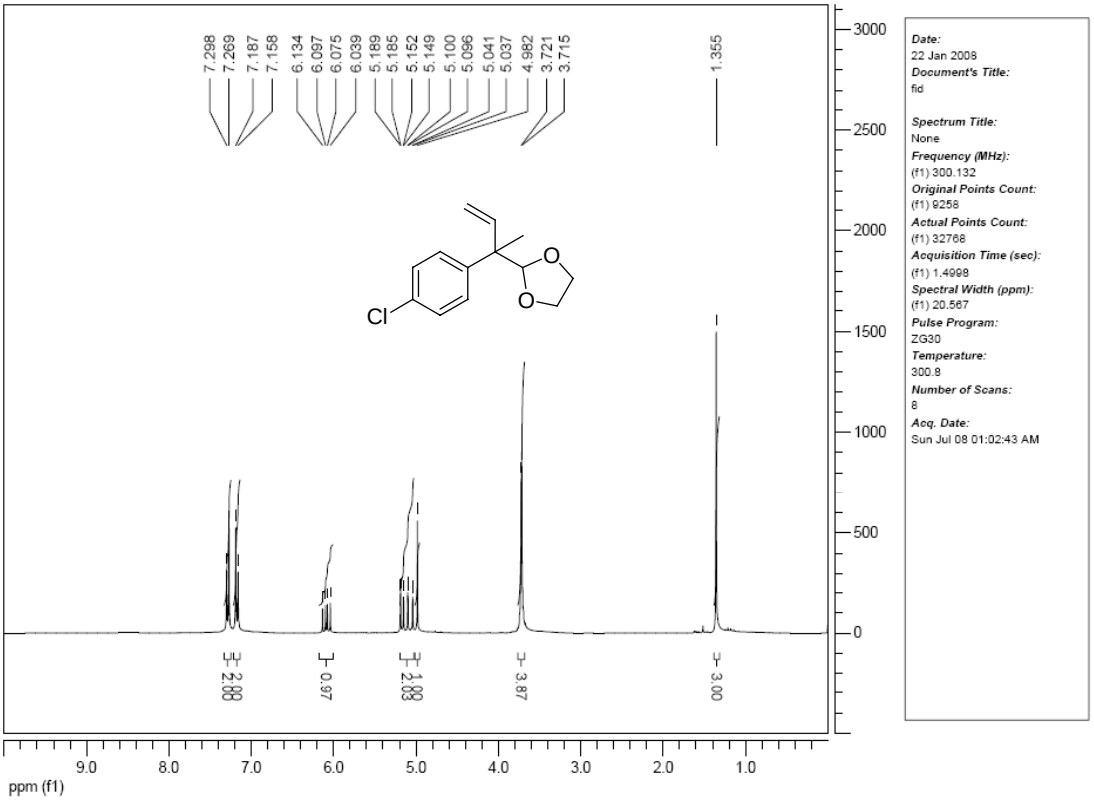


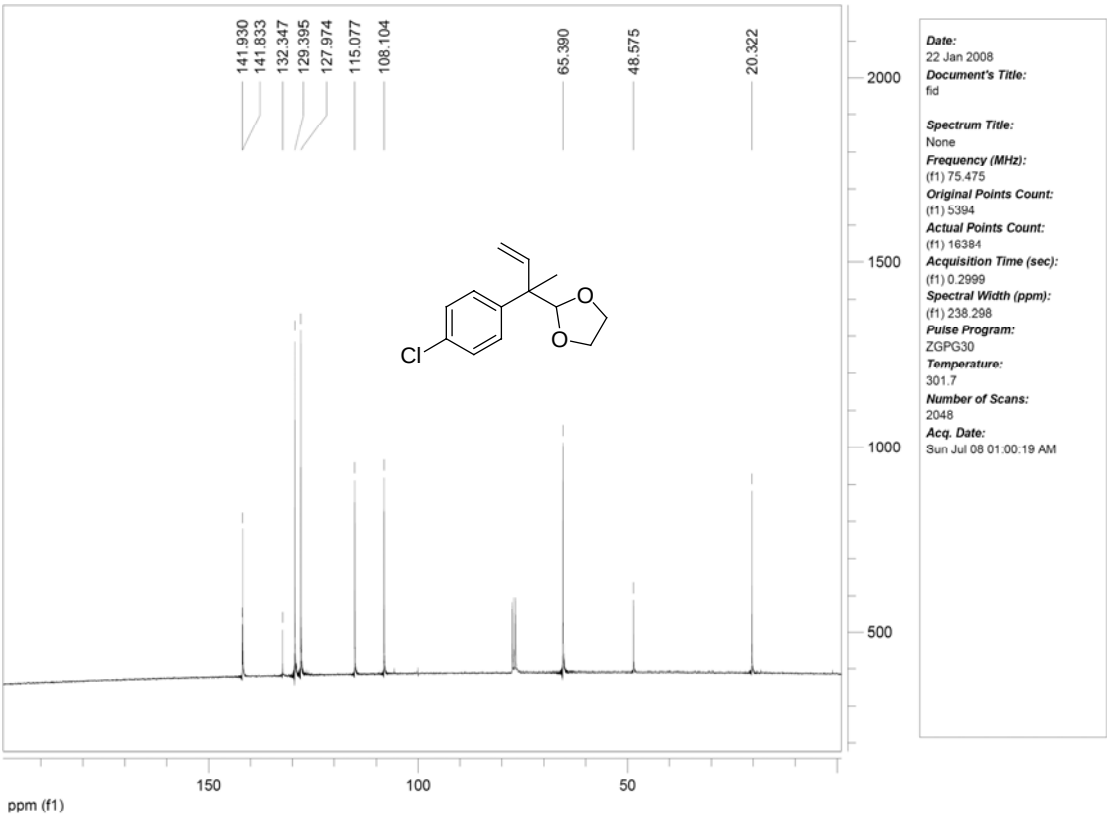
2-(2-(4-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane





2-(2-(4-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane





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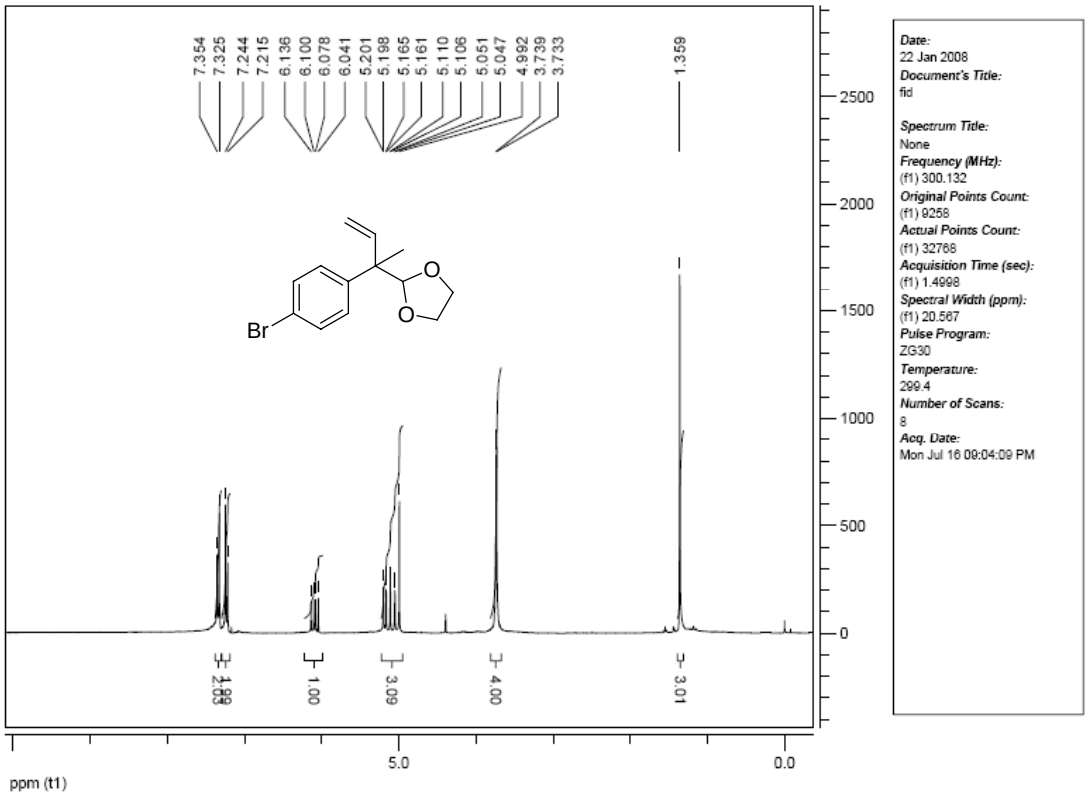
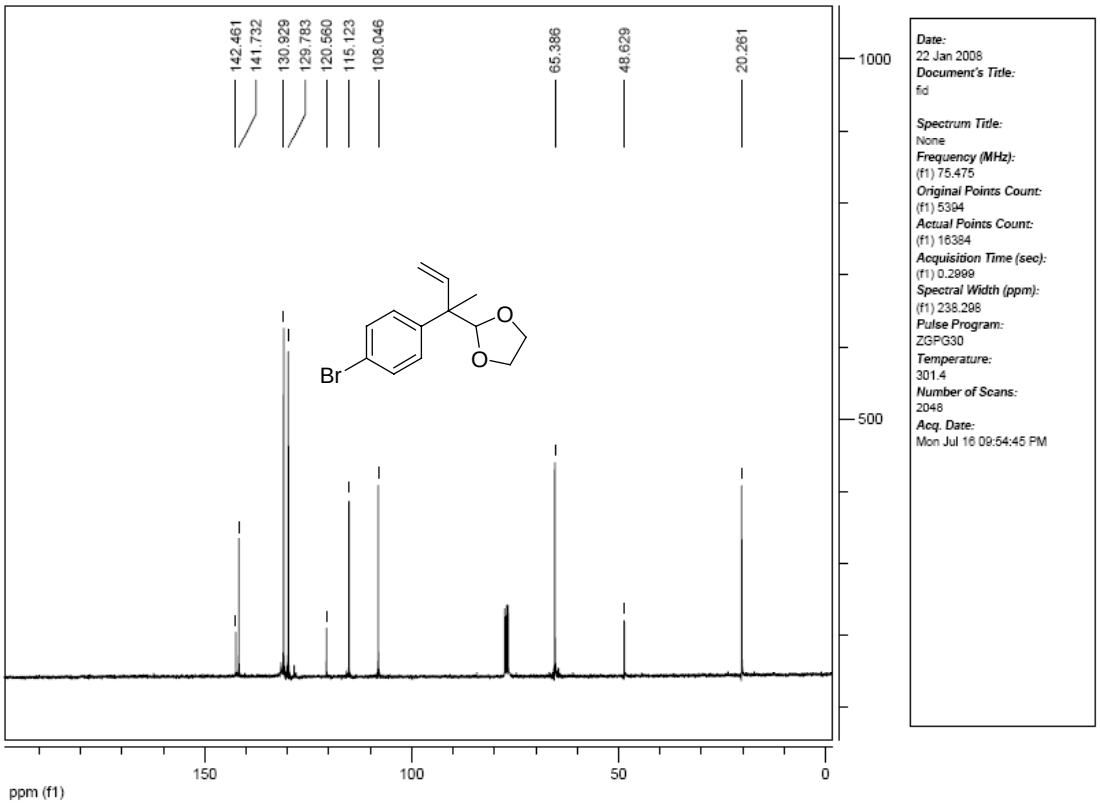
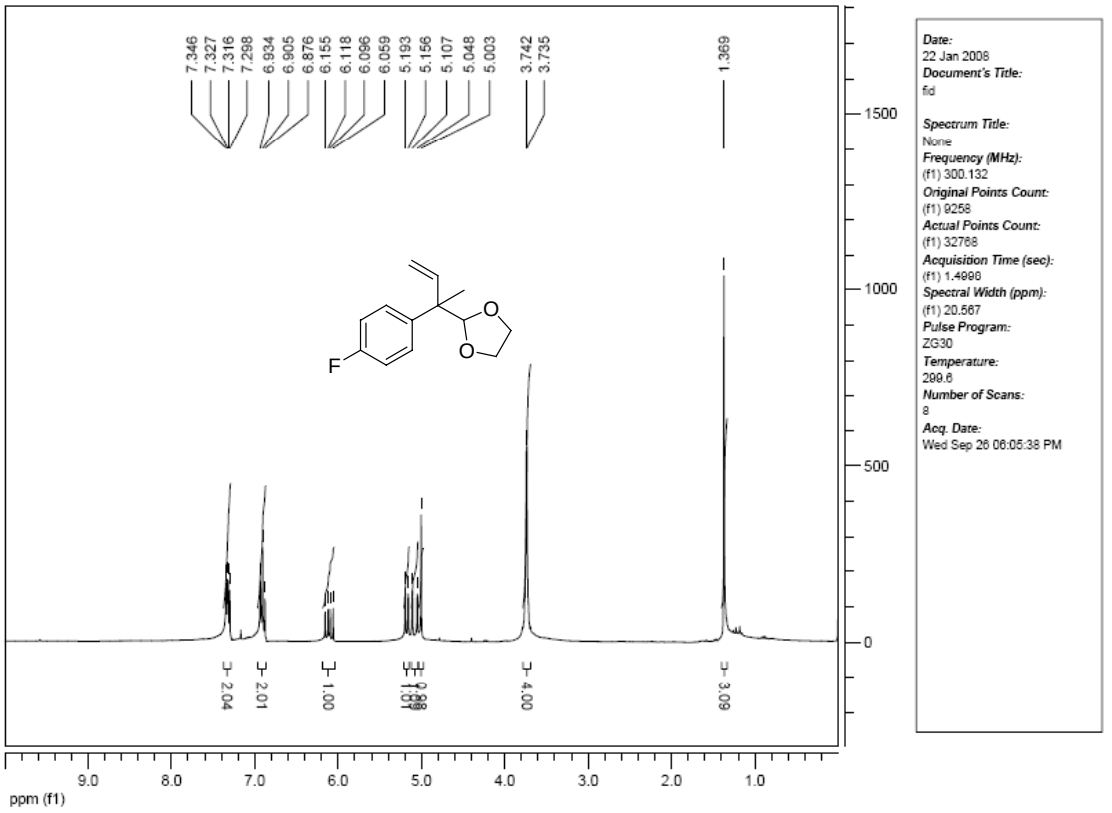
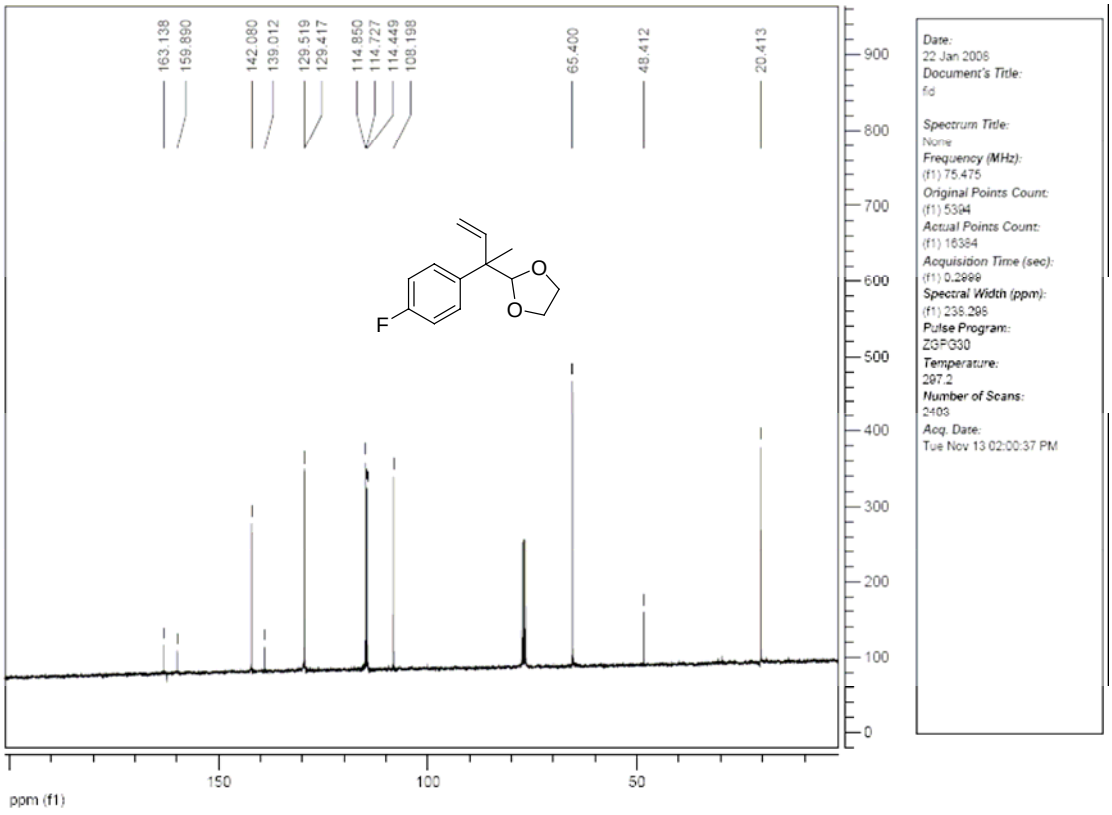




2-(2-(4-Fluorophenyl)but-3-en-2-yl)-1,3-dioxolane





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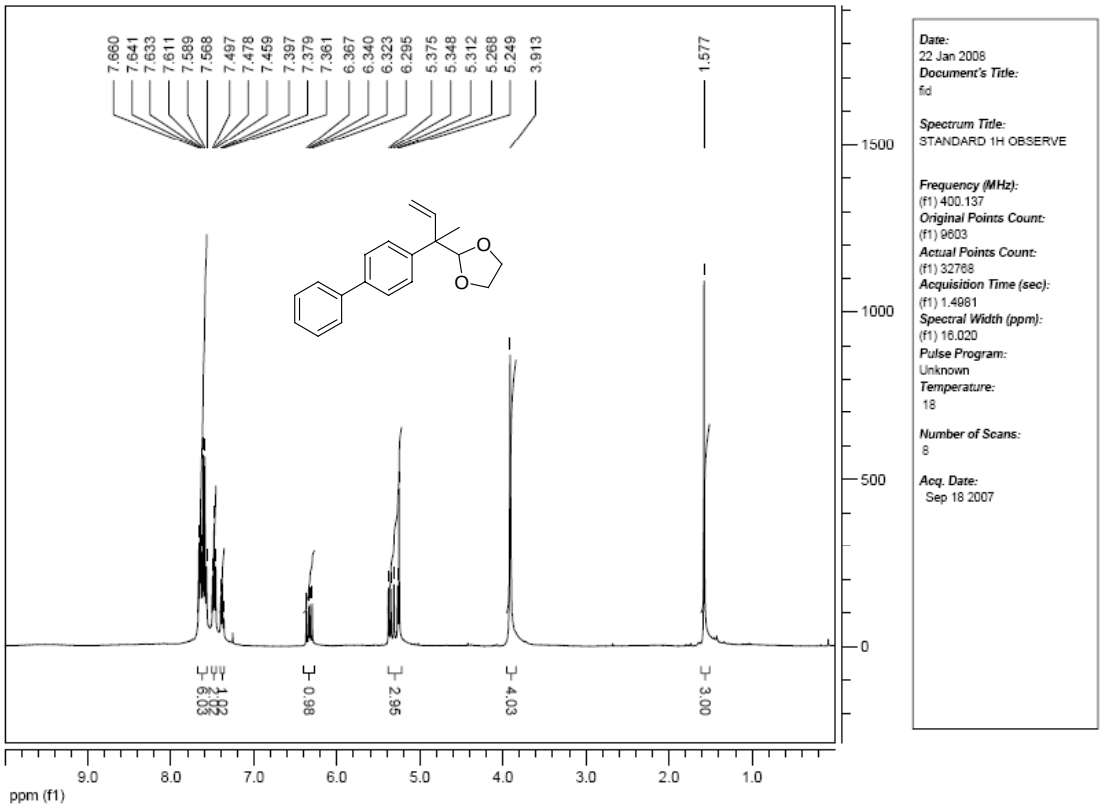
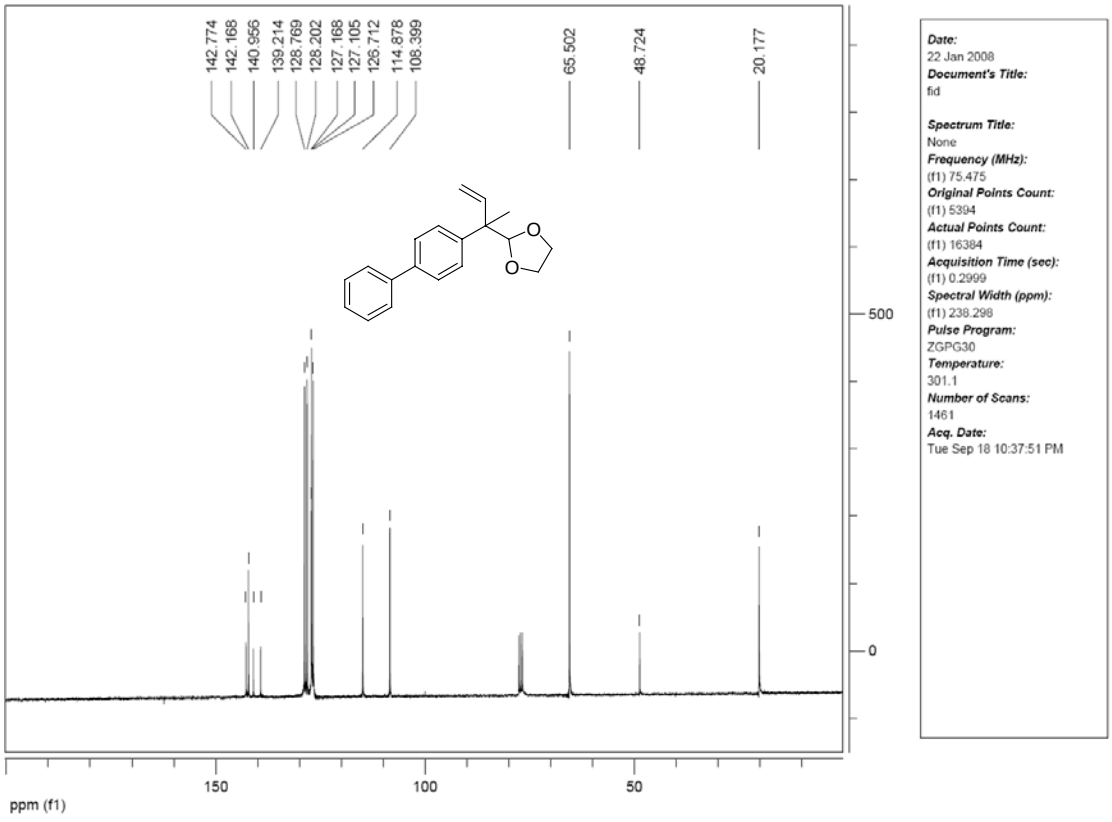
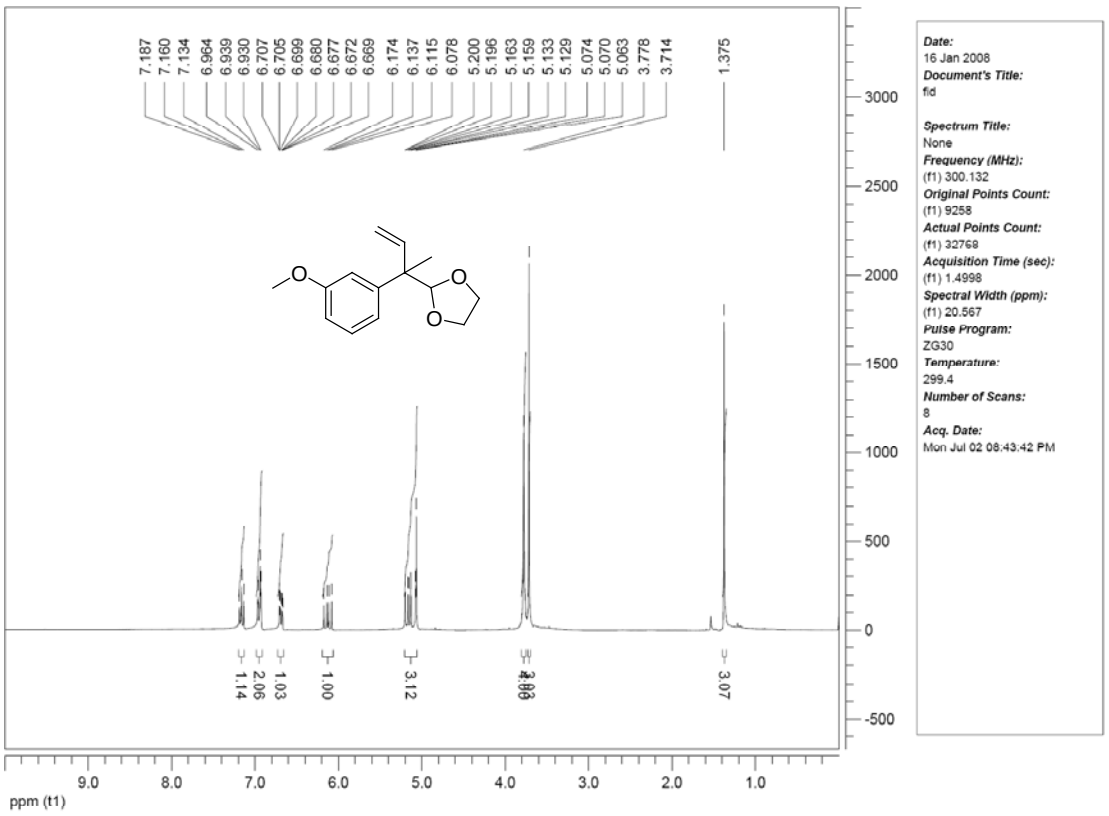
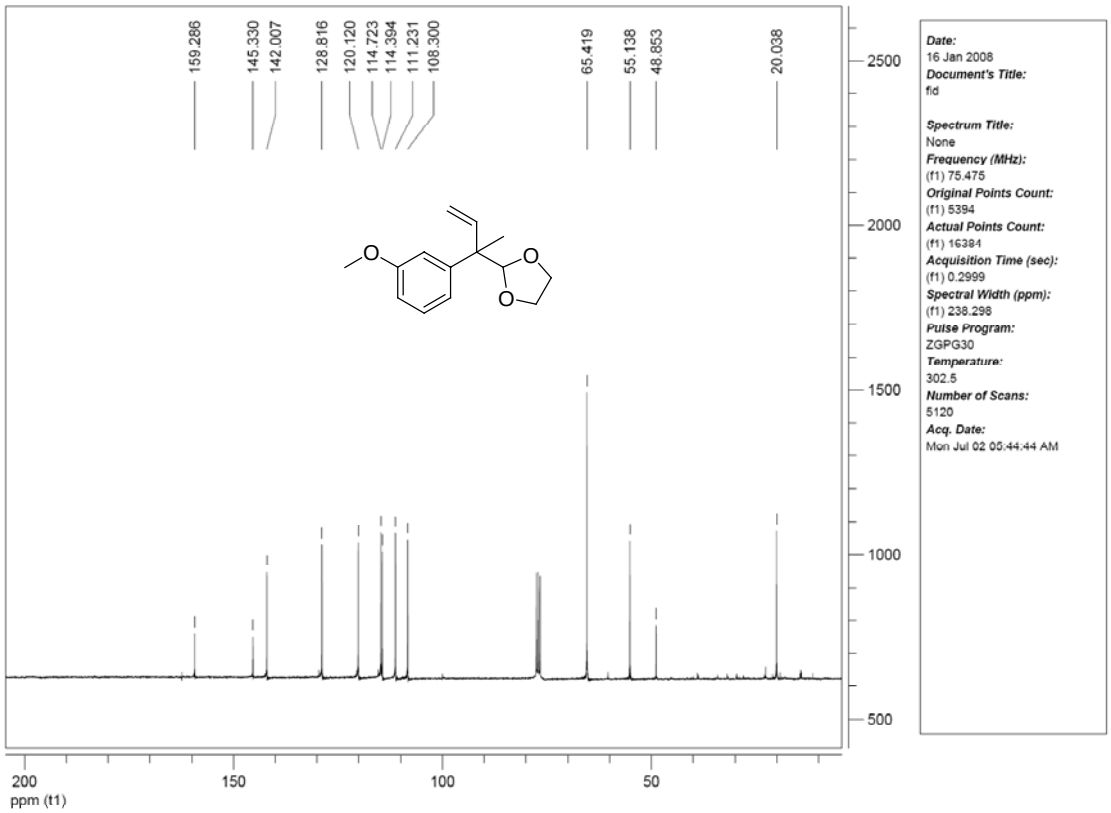


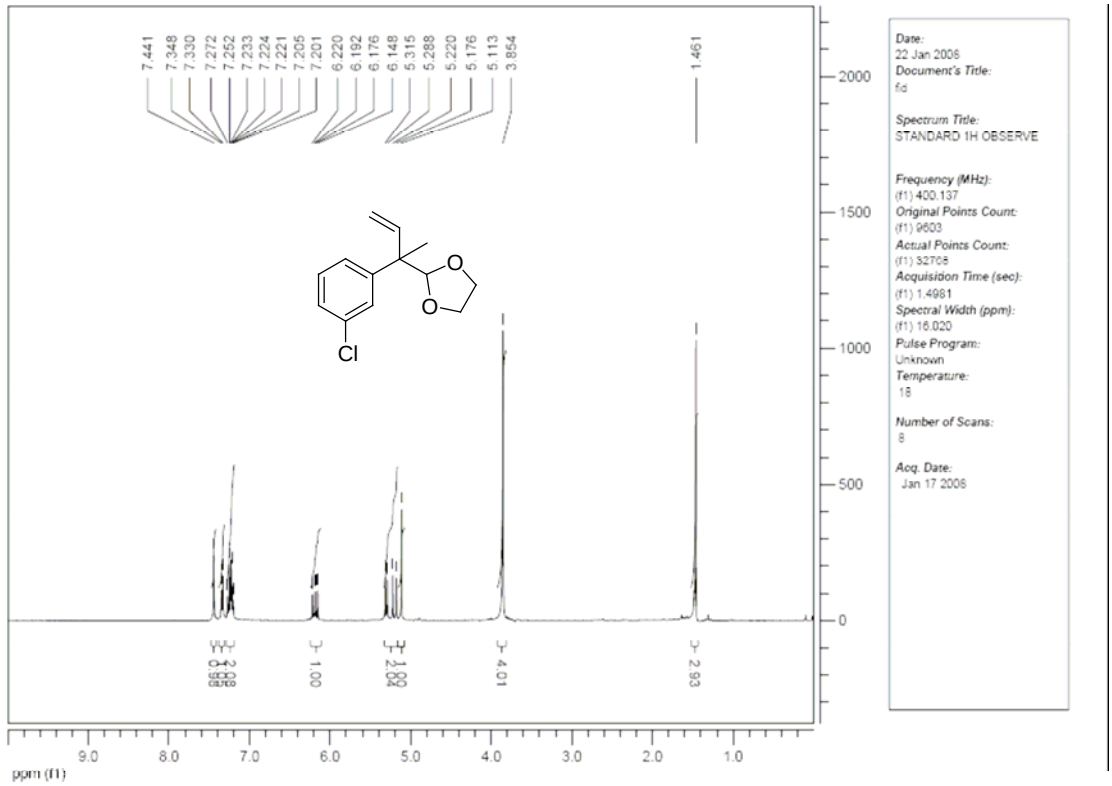


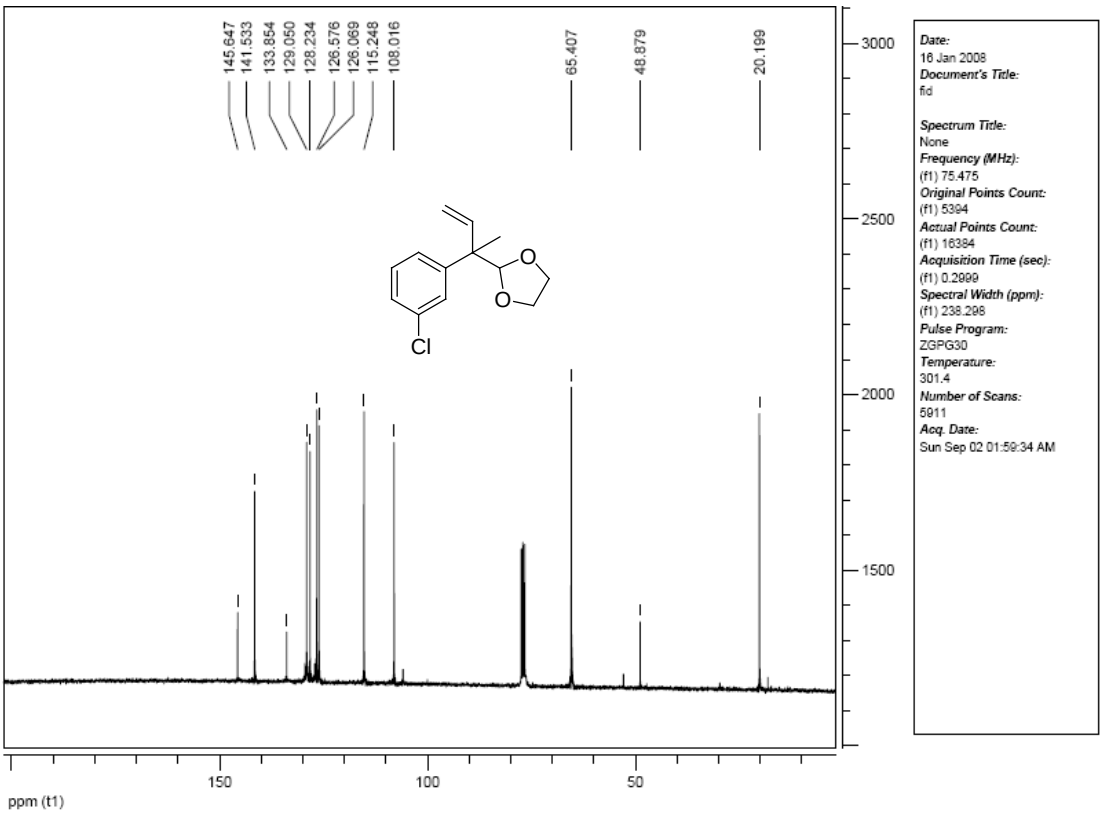
2-(2-(3-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane



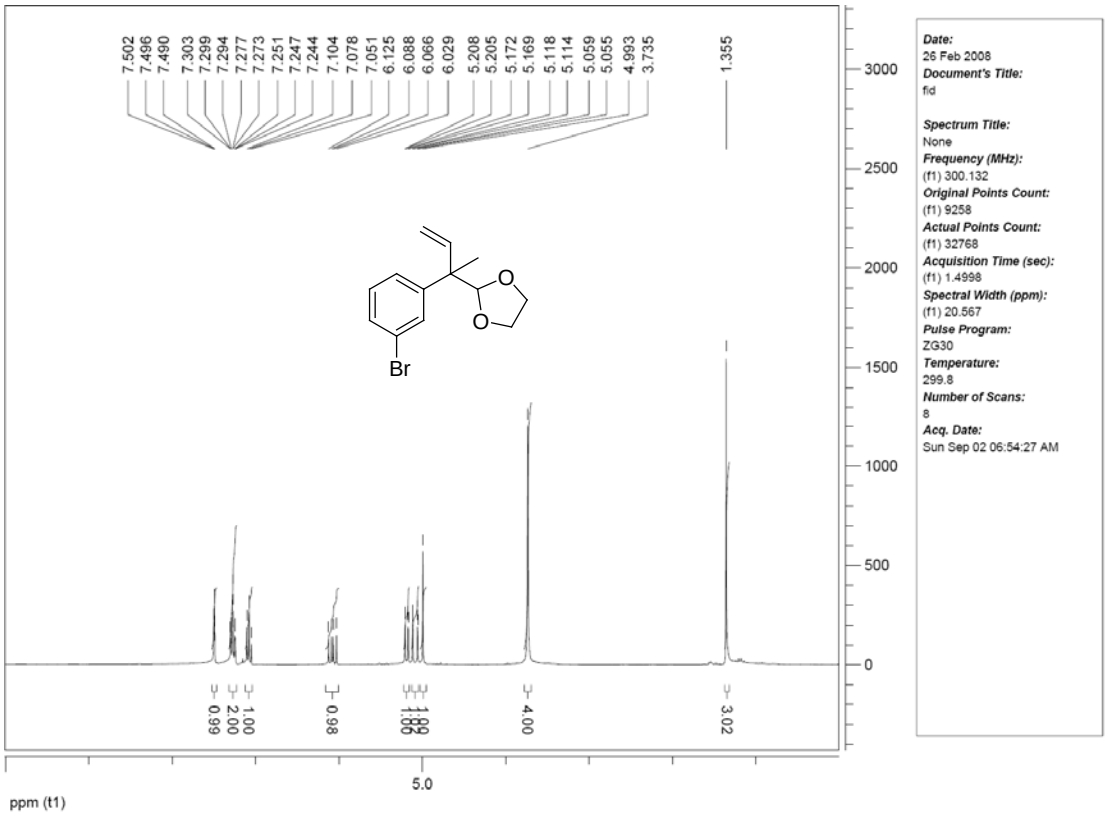


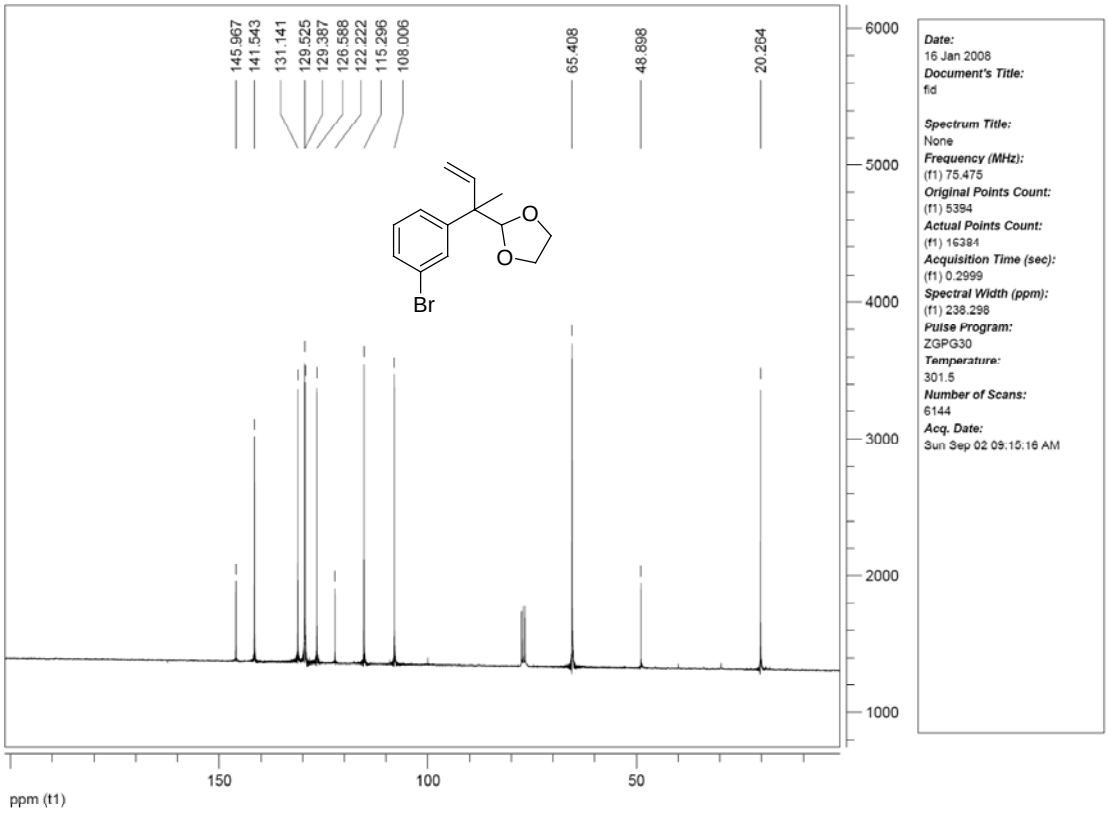
2-(2-(3-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane



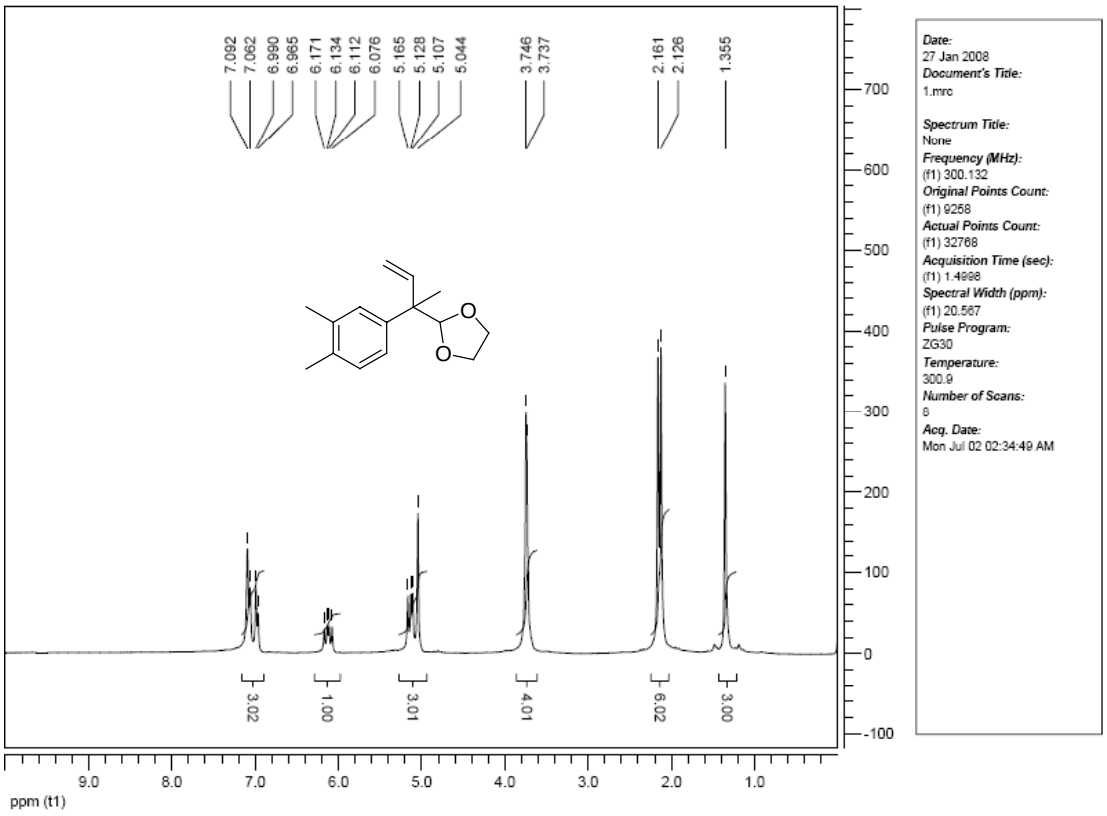


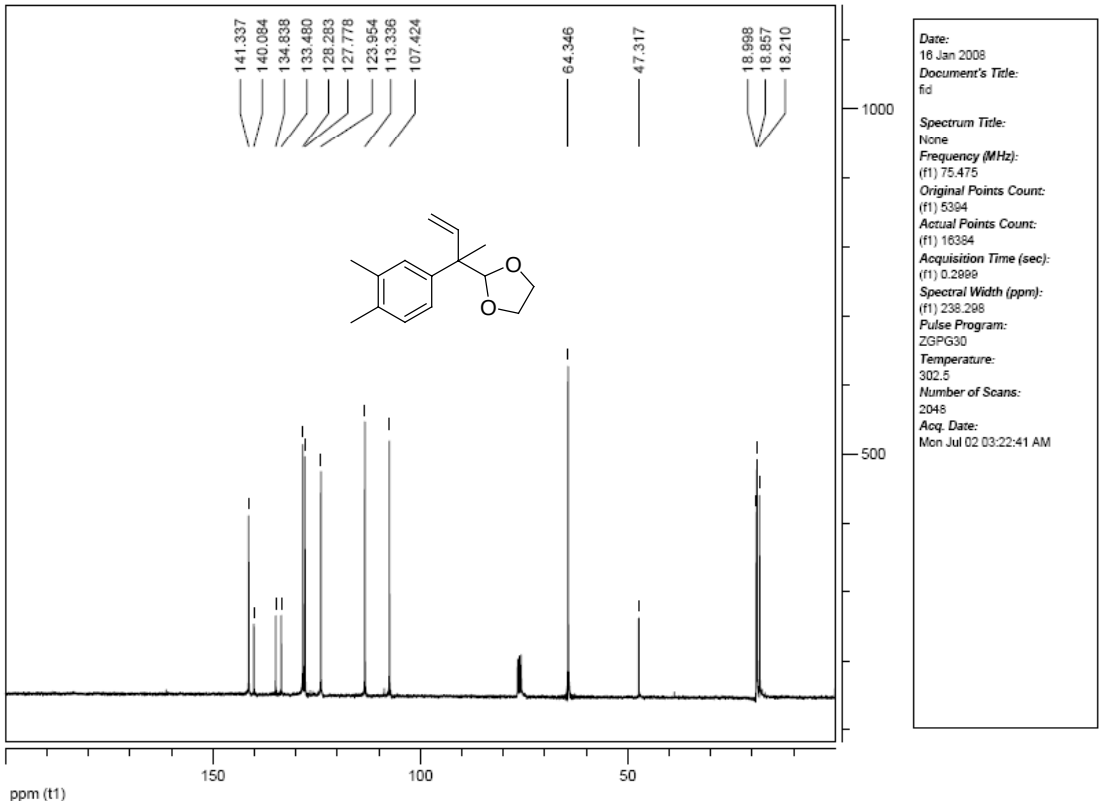
2-(2-(3-Bromophenyl)but-3-en-2-yl)-1,3-dioxolane



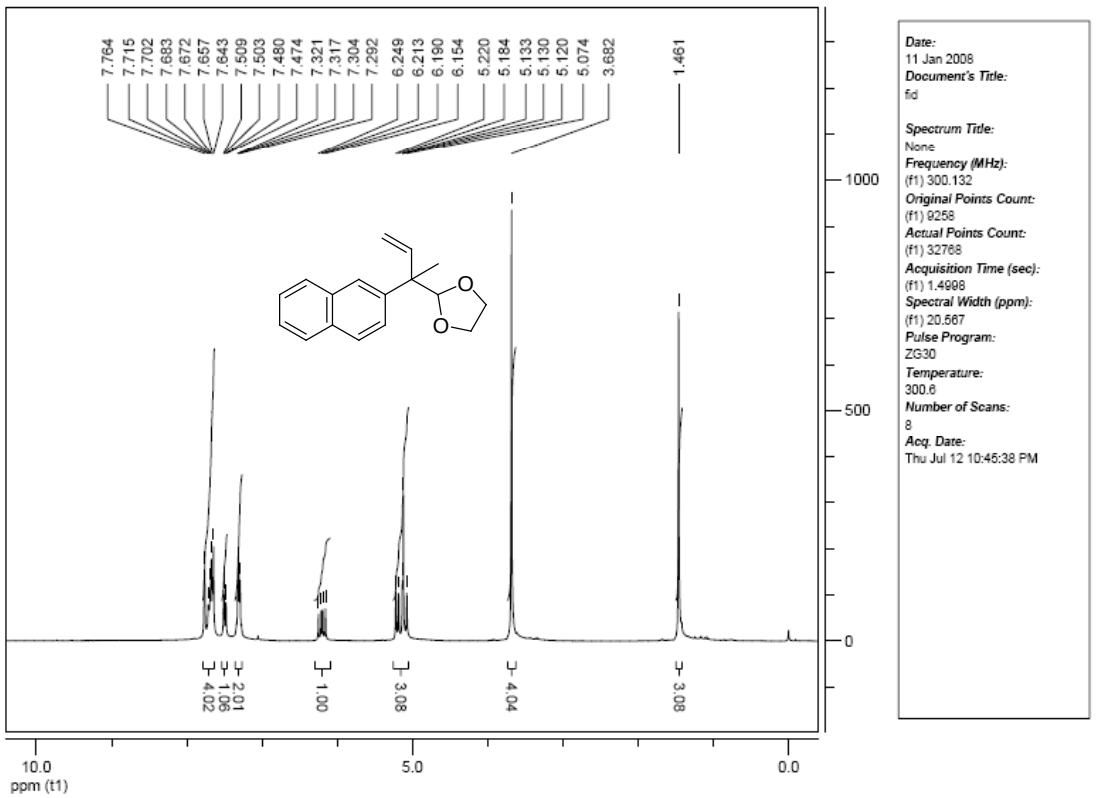


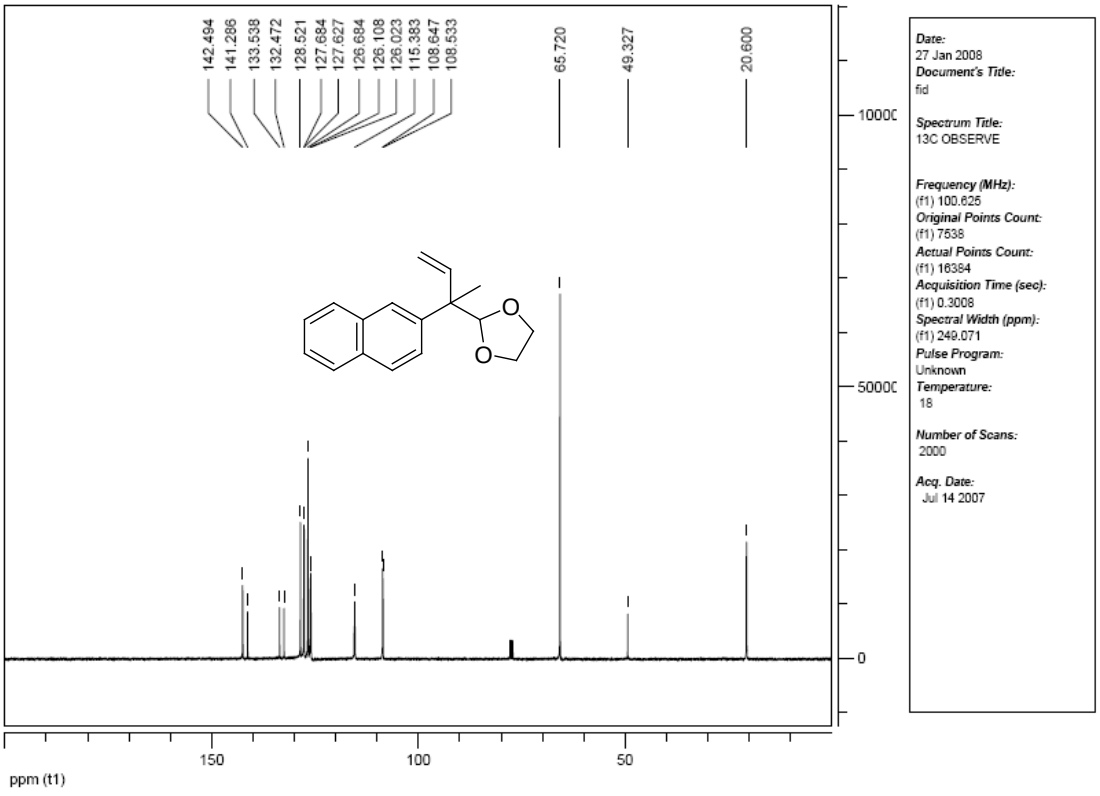
2-(2-(3,4-Dimethylphenyl)but-3-en-2-yl)-1,3-dioxolane



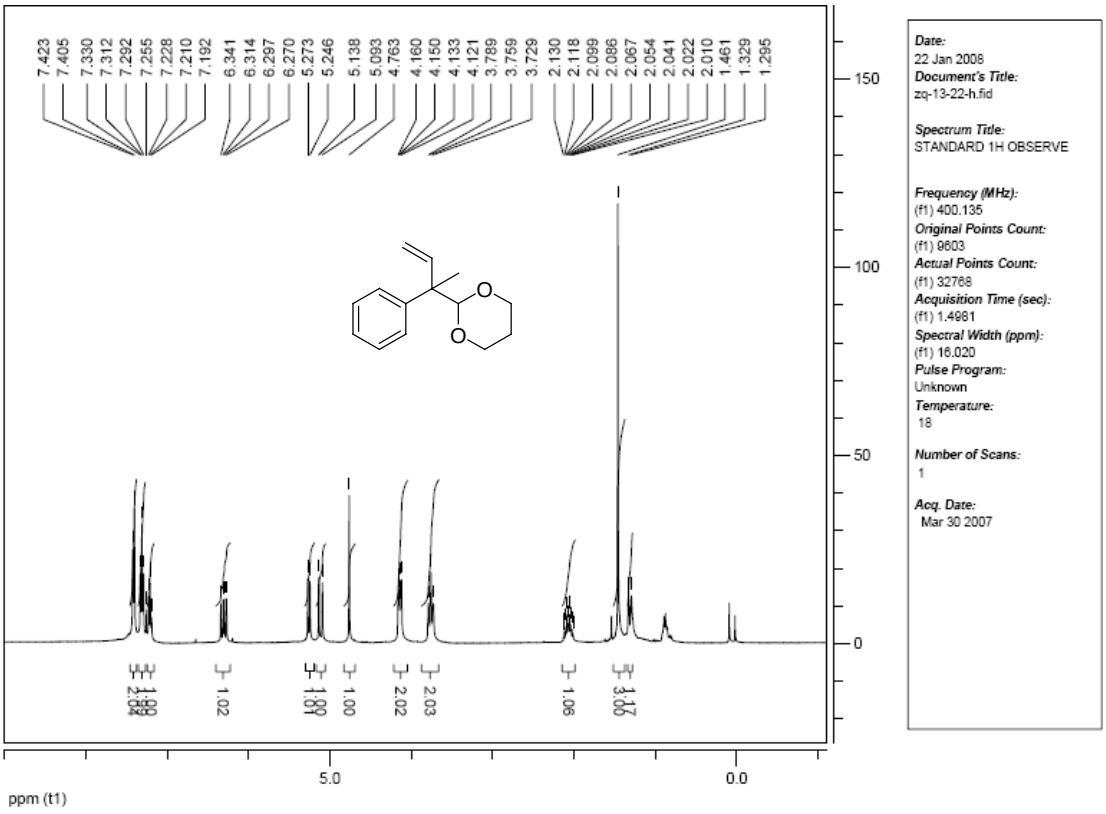


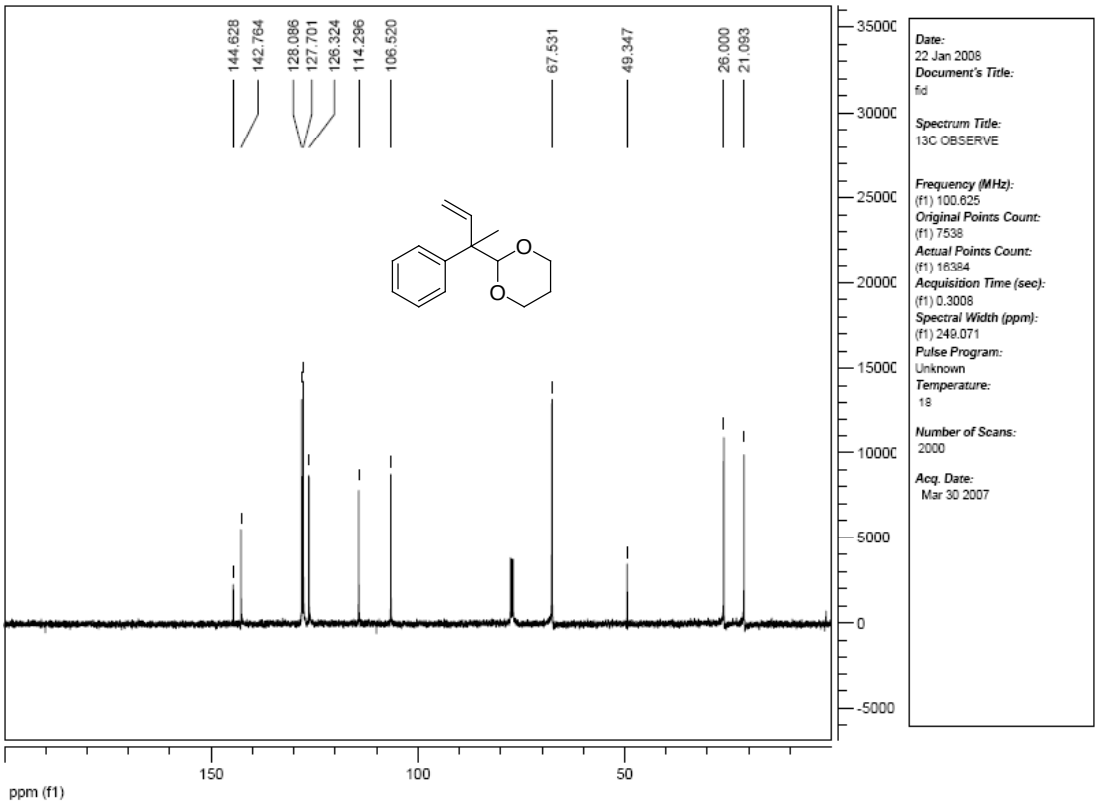
2-(2-(Naphthalen-2-yl)but-3-en-2-yl)-1,3-dioxolane



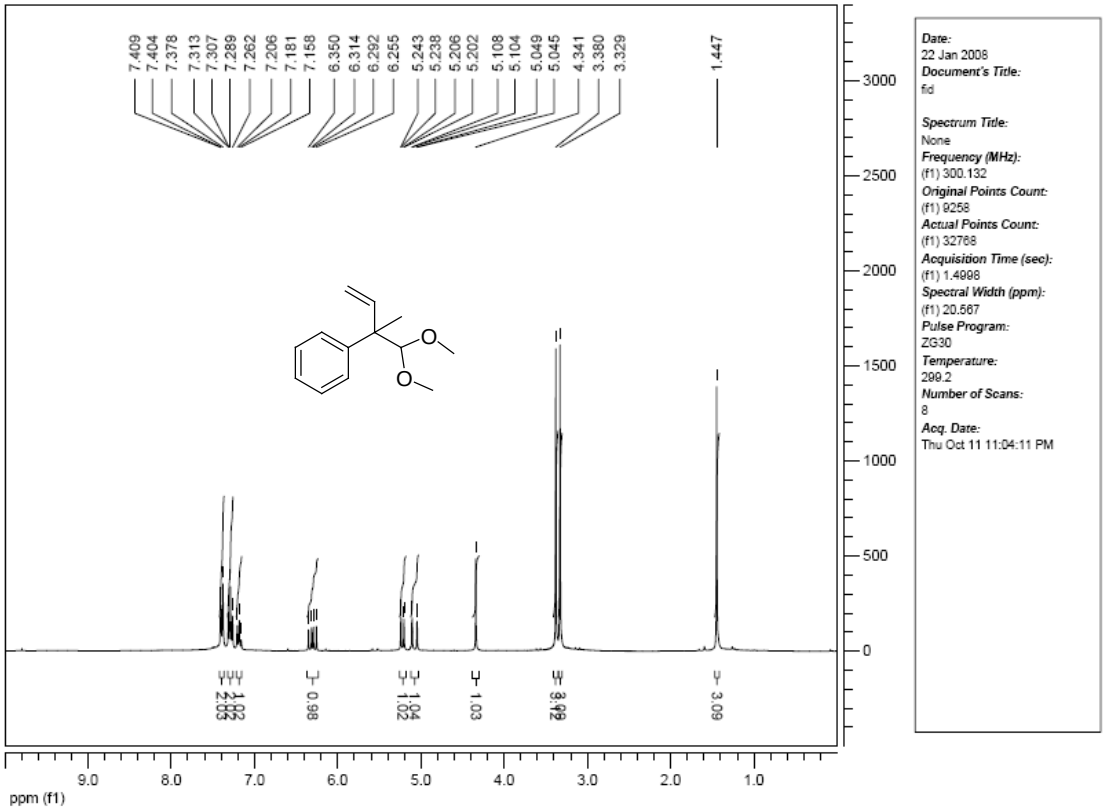


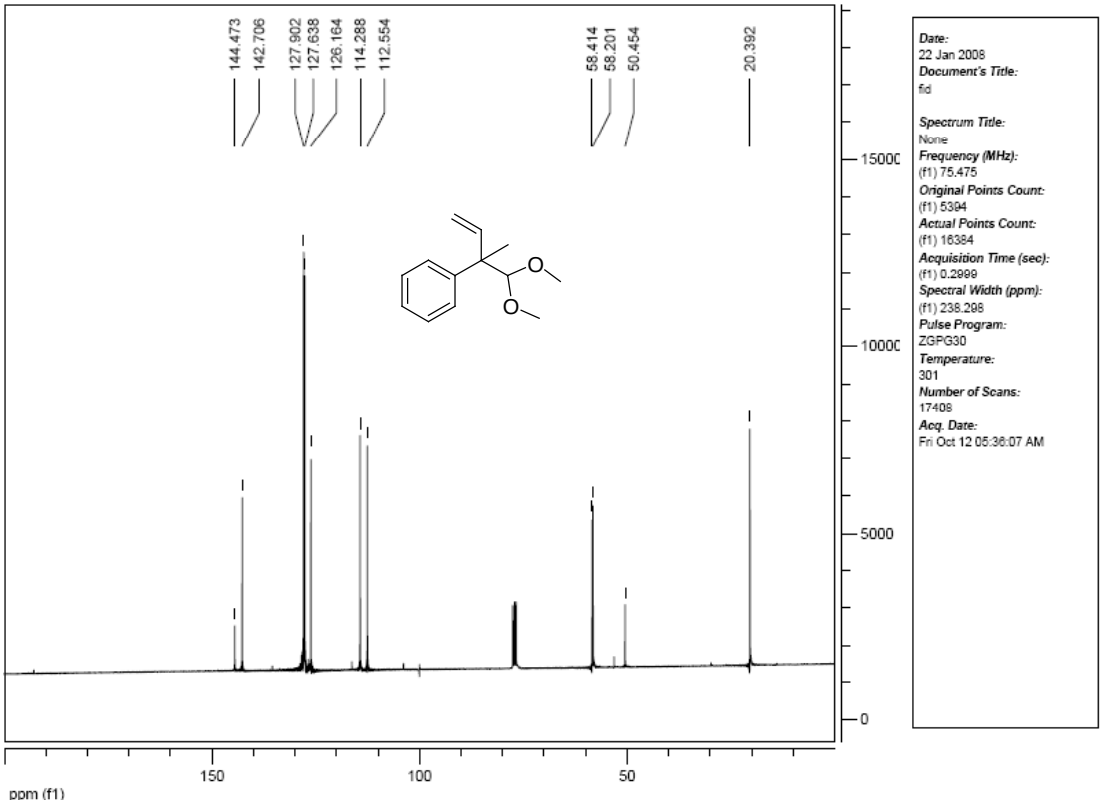
2-(2-Phenylbut-3-en-2-yl)-1,3-dioxane





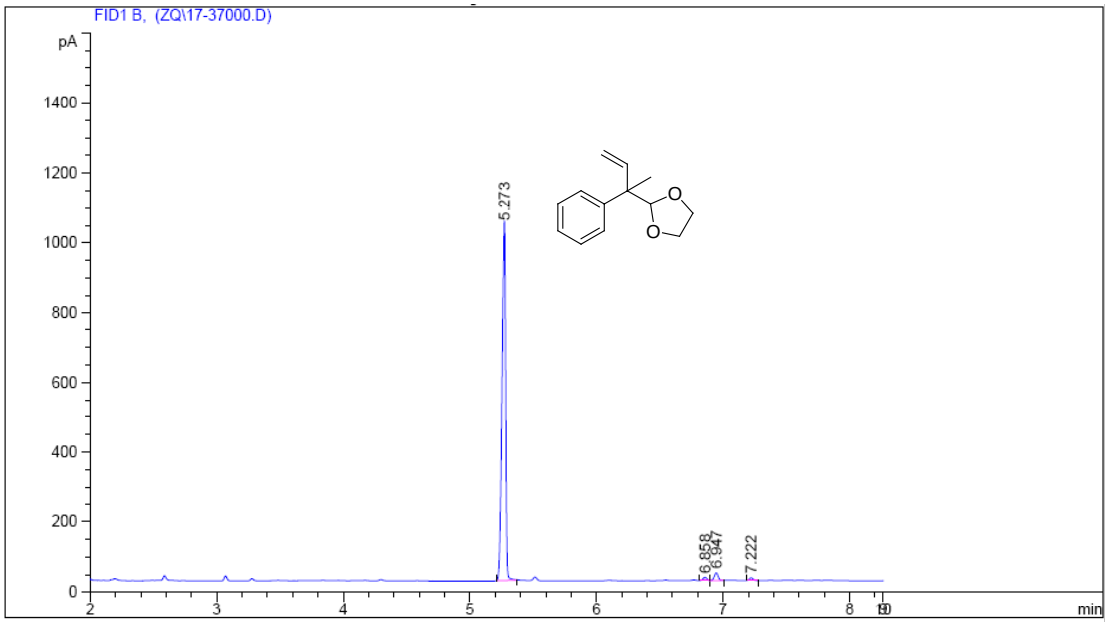
1-(2-(Dimethoxymethyl)but-3-en-2-yl)benzene



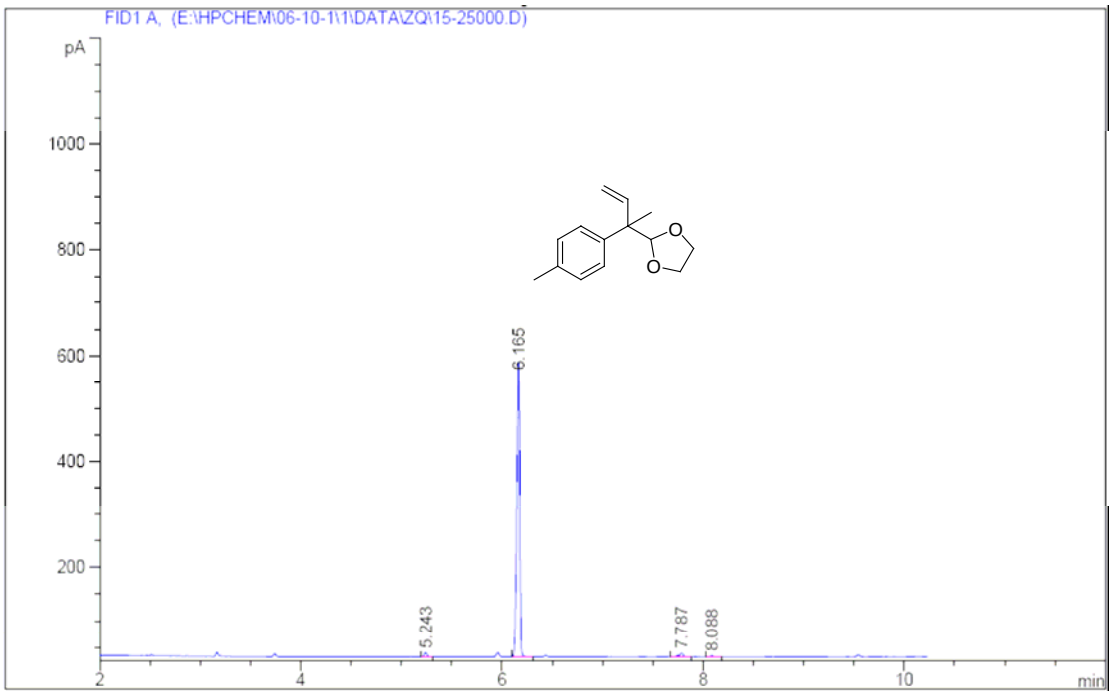


(7) GC Charts for Hydrovinylation Products

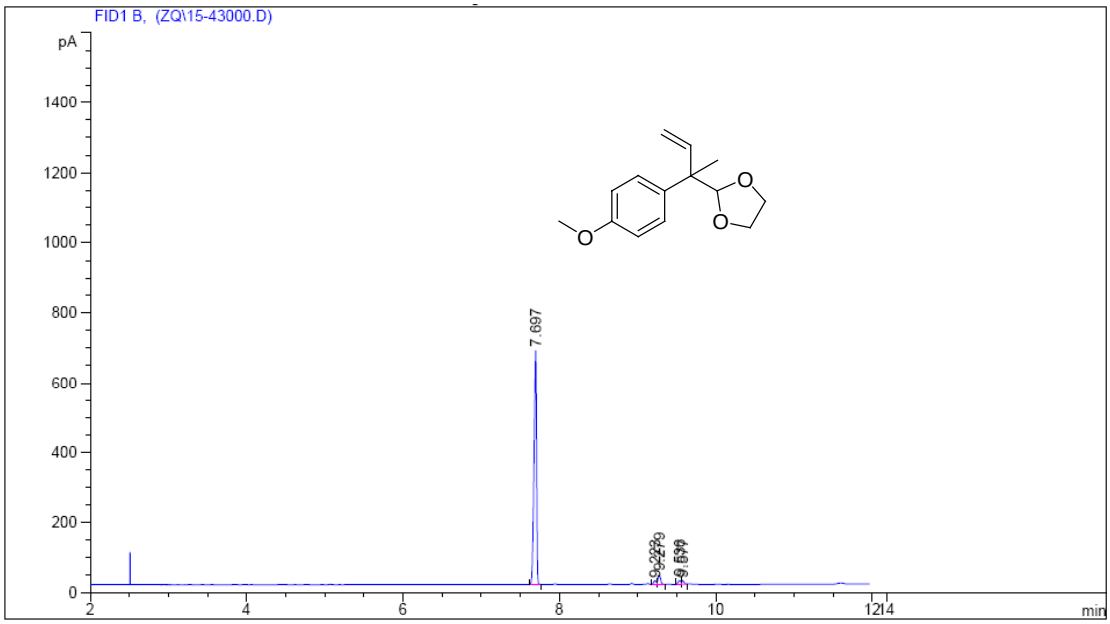
2-(2-Phenylbut-3-en-2-yl)-1,3-dioxolane



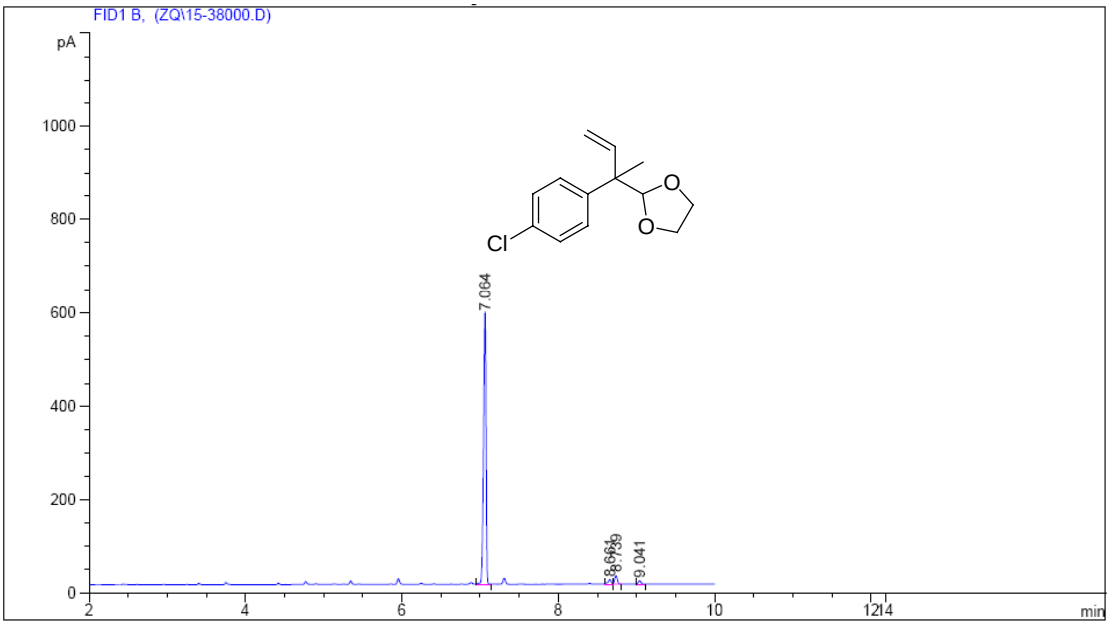
2-(2-(4-Methylphenyl)but-3-en-2-yl)-1,3-dioxolane



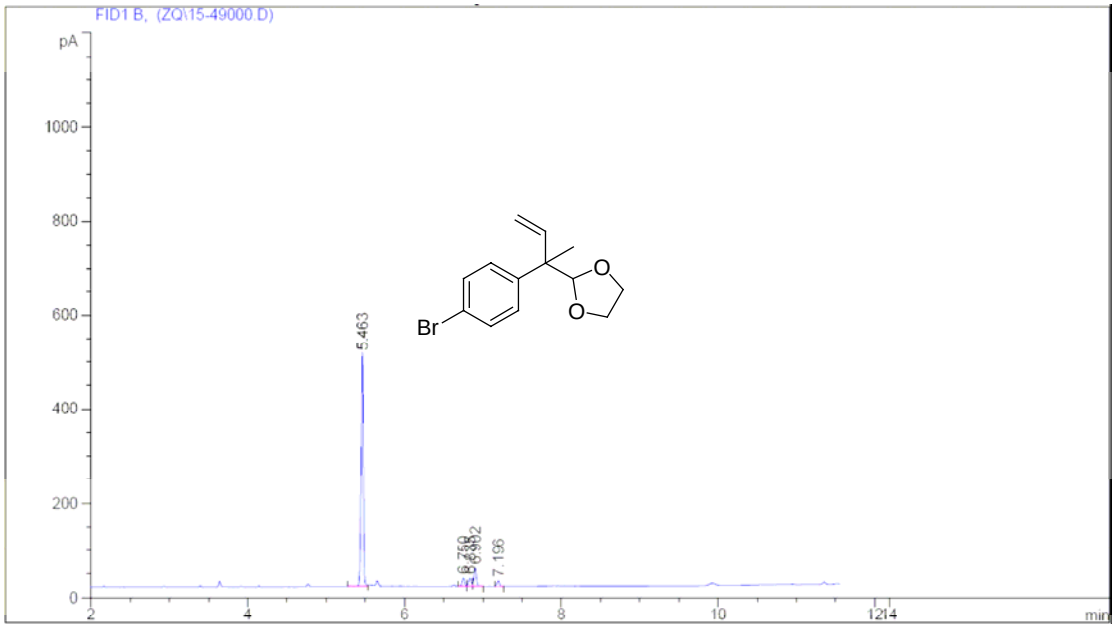
2-(2-(4-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane



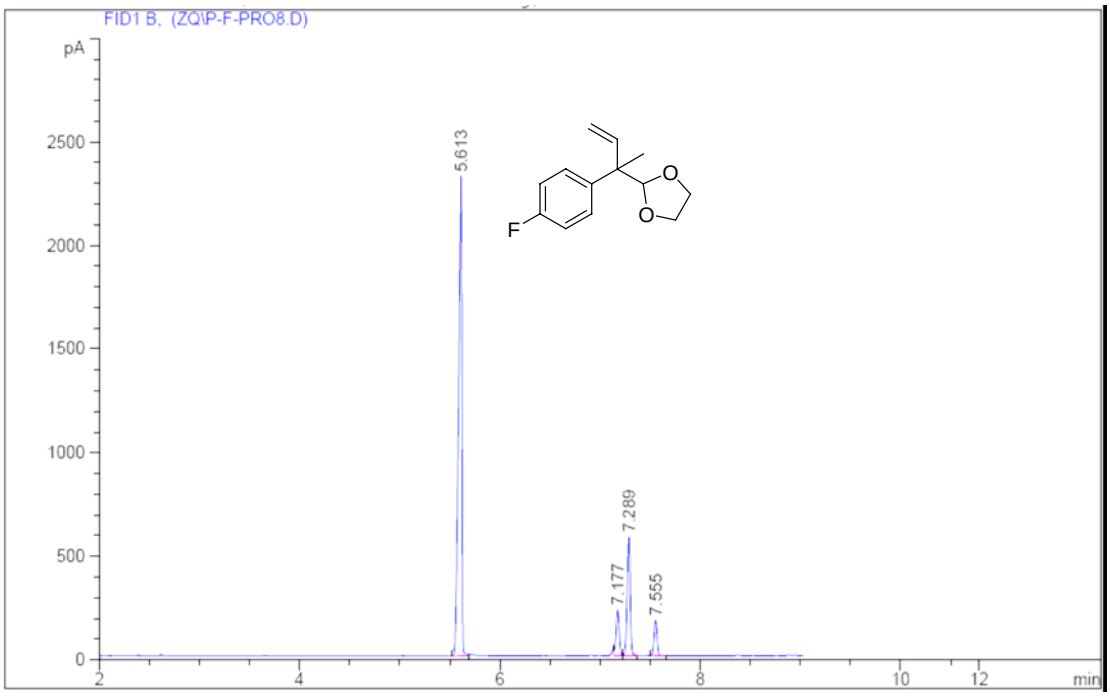
2-(2-(4-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane



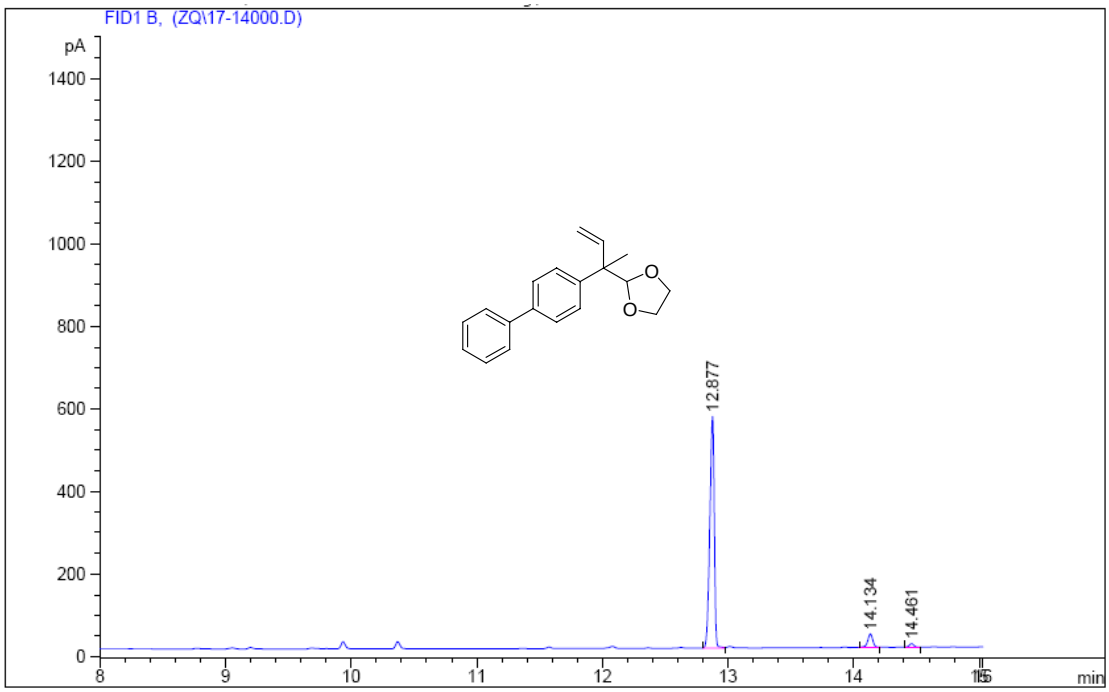
2-(2-(4-Bromophenyl)but-3-en-2-yl)-1,3-dioxolane



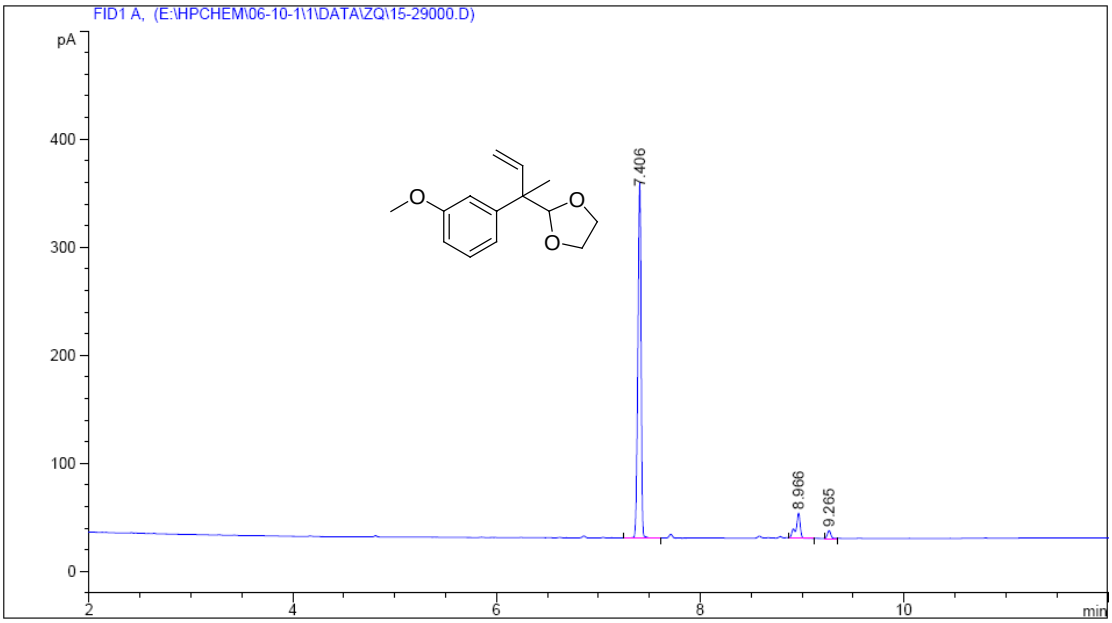
2-(2-(4-Fluorophenyl)but-3-en-2-yl)-1,3-dioxolane



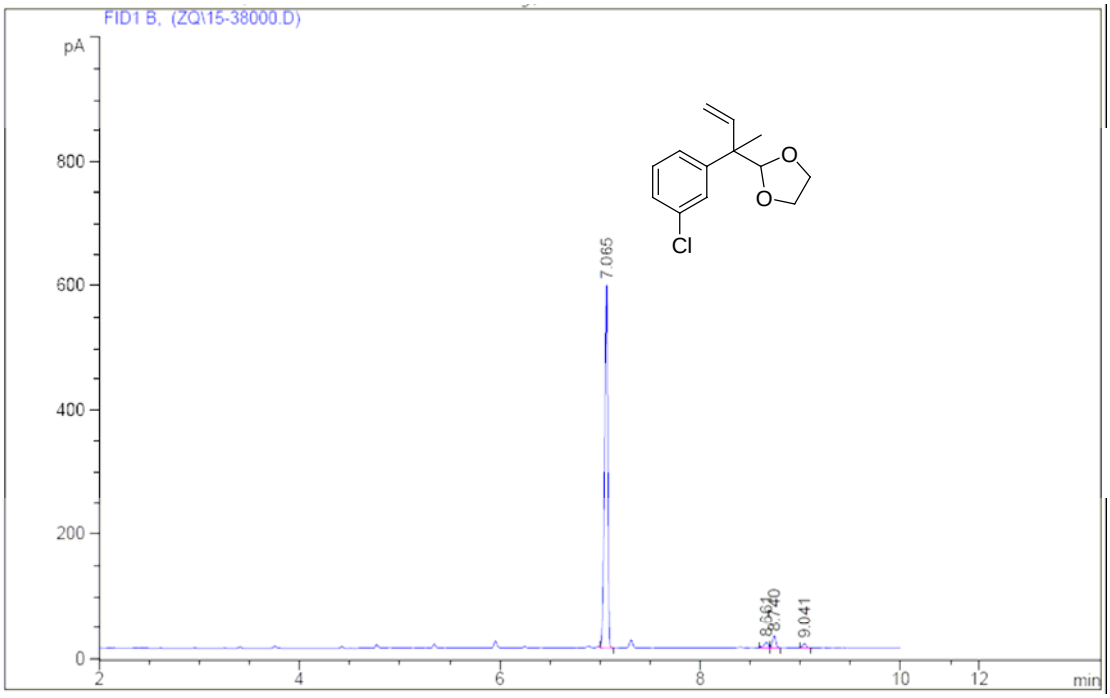
2-(2-(4-Biphenyl)but-3-en-2-yl)-1,3-dioxolane



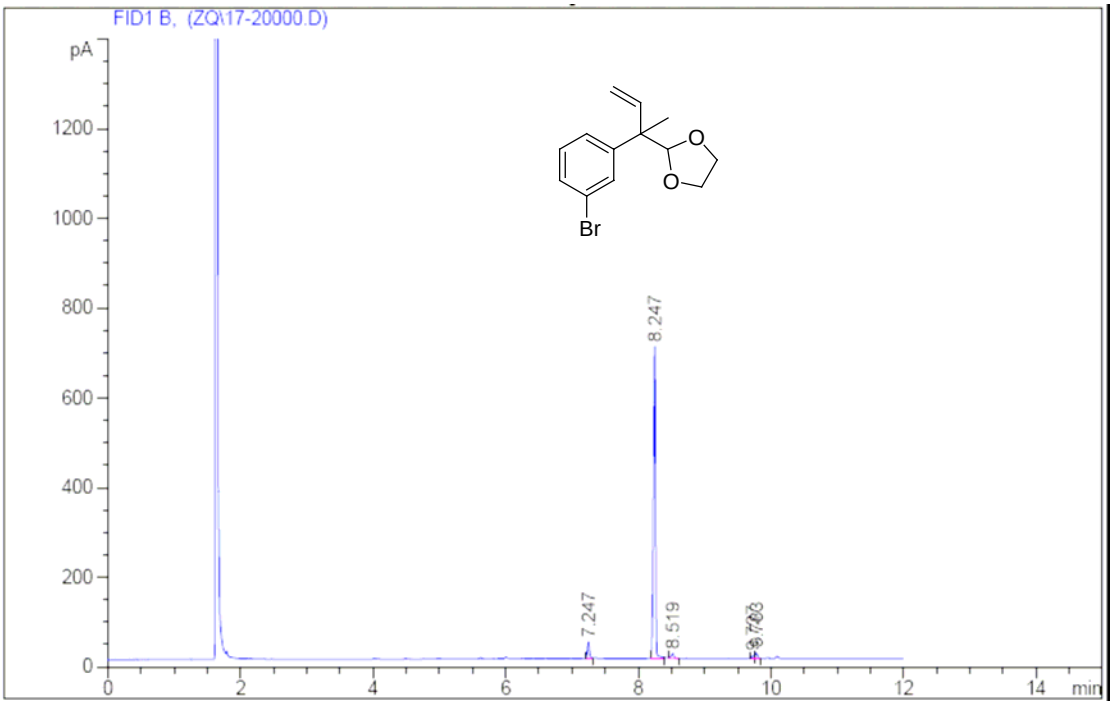
2-(2-(3-Methoxyphenyl)but-3-en-2-yl)-1,3-dioxolane



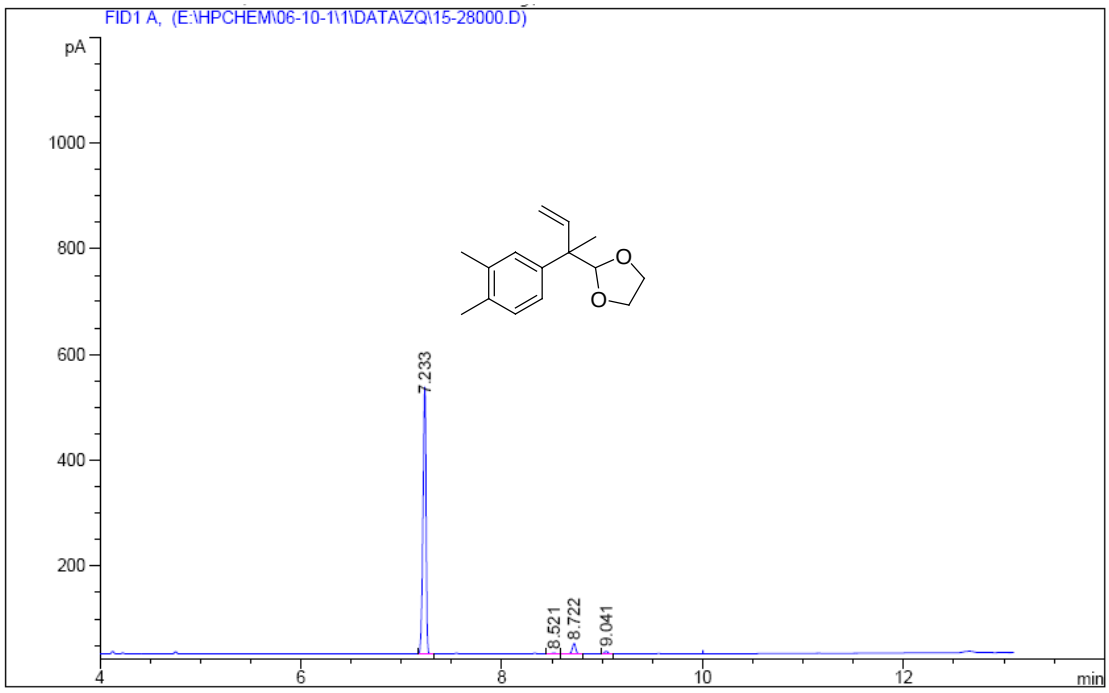
2-(2-(3-Chlorophenyl)but-3-en-2-yl)-1,3-dioxolane



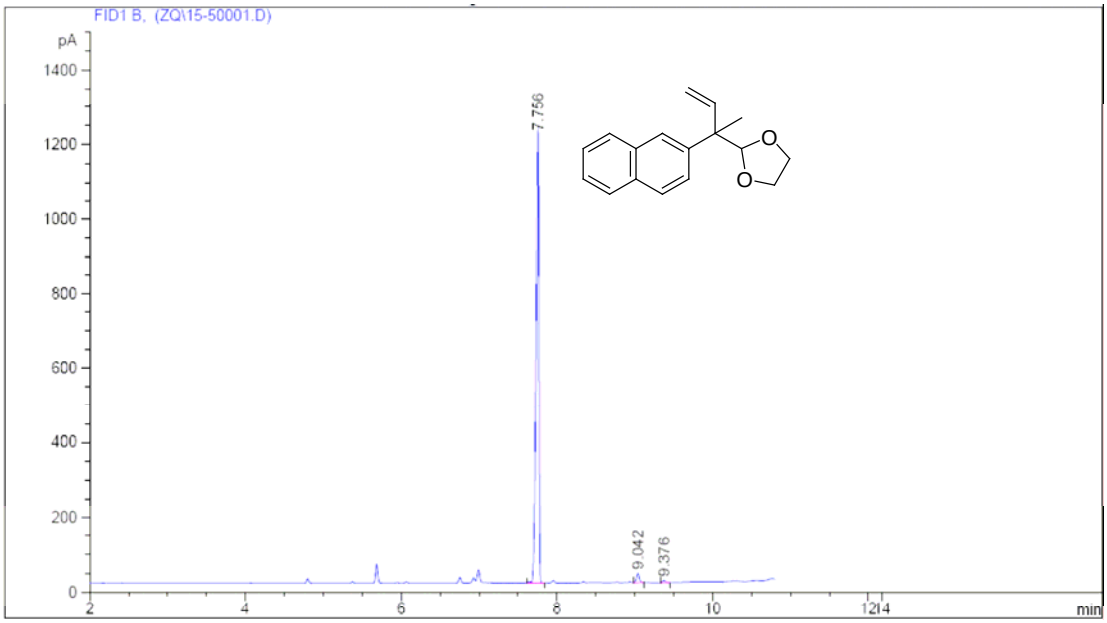
2-(2-(3-Bromophenyl)but-3-en-2-yl)-1,3-dioxolane



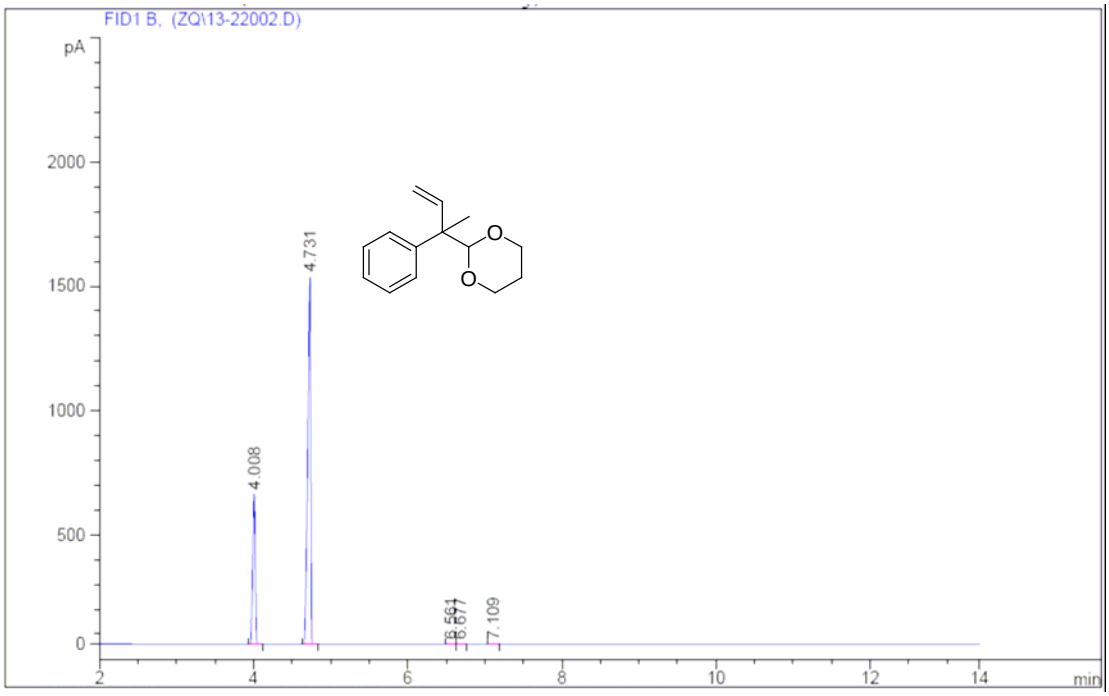
2-(2-(3,4-Dimethylphenyl)but-3-en-2-yl)-1,3-dioxolane



2-(2-(Naphthalen-2-yl)but-3-en-2-yl)-1,3-dioxolane



2-(2-Phenylbut-3-en-2-yl)-1,3-dioxane



1-(2-(Dimethoxymethyl)but-3-en-2-yl)benzene