Supporting Information

Nickel-Catalyzed Reductive 1,3-Diene Formation from the Cross-Coupling of Vinyl Bromides

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I. General Information

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glovebox techniques. Anhydrous THF was distilled by sodium/benzophenone ketyl prior to use. DMA (*N*,*N*-dimethylacetamide, 99.5%, extra dry, Acros), was purchased and used directly. Deuterated solvents were used as received. $NiBr_2$ (Alfa Aesar), Zn (Sinopharm, 4N), Anhydrous $MgCl_2$ (Alfa Aesar), *n*-Bu_4NI (Alfa Aesar) were used as received. $NiBr_2$•Bphen (Bphen = 4,7-diphenyl-1,10-phenanthroline) were synthesized according to literature procdures.[1] β-Alkenyl bromides were synthesized according to literature procdures.[2] α-Alkenyl bromides were synthesized according to literature procdures.[3] Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 600 MHz or JEOL 400 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

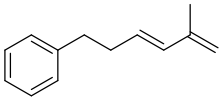
II. Reductive arylation and alkenylation of alkenes

1. <u>General procedure</u>

To a flame-dried Schlenk tube was charged with alkenyl bromide **1** (0.15 mmol, 100 mol%, if it is a solid), alkenyl bromide **2** (0.45 mmol, 300 mol%, if it is a solid), Zn (20 mg, 0.30 mmol, 200 mol%), $NiBr_2$•Bphen (8.3 mg, 0.015 mmol, 10 mol%), $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol%), *n*-Bu_4NI (55.3 mg, 0.15 mmol, 100 mol%). The tube was capped with a rubber septum. After evacuated and backfilled nitrogen three times, alkenyl bromide **1** (0.15 mmol, 100 mol%, if it is liquid) and alkenyl bromide **2** (0.45 mmol, 300 mol%, if it is liquid) were added via a syringe

followed by addition of DMA (1 mL) via a syringe. The reaction mixture was allowed to stir for 12 h under a N_2 atmosphere at 25 °C, and was directly loaded onto a silica column without work-up. The residue was rinsed with small amount of DCM or the eluent prior to column chromatography, with which the product was isolated. The yields reported are the average of at least two experiments, unless otherwise indicated.

2. Details of the characterization data for new compounds



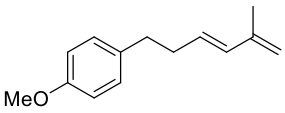
(*E*)-(5-Methylhexa-3,5-dien-1-yl)benzene (3a).

This compound was prepared according to the General Procedure using (*E*)-(4-bromobut-3-en-1-yl)benzene (31.7 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 81% yield as a colorless oil (20.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.35 – 7.30 (m, 2H), 7.24 – 7.20 (m, 3H), 6.23 (d, *J* = 15.7 Hz, 1H), 5.77 – 5.71 (m, 1H), 4.92 (s, 2H), 2.79 – 2.74 (m, 2H), 2.47 (dd, *J* = 15.3, 7.3 Hz, 2H), 1.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.19, 142.01, 133.45, 129.98, 128.55, 128.45, 125.97, 114.75, 36.08, 34.79, 18.82.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



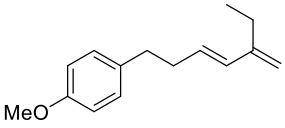
(*E*)-1-Methoxy-4-(5-methylhexa-3,5-dien-1-yl)benzene (3b).

This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 82% yield as a colorless oil (24.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.13 – 7.10 (m, 2H), 6.85 – 6.82 (m, 2H), 6.18 (d, *J* = 15.6 Hz, 1H), 5.73 – 5.66 (m, 1H), 4.88 (s, 2H), 3.79 (s, 3H), 2.70 – 2.64 (m, 2H), 2.40 (dd, *J* = 14.9, 7.0 Hz, 2H), 1.83 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.92, 142.24, 134.14, 133.39, 130.12, 129.43, 114.69, 113.88, 55.39, 35.16, 35.05, 18.83.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



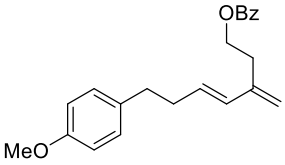
(*E*)-1-Methoxy-4-(5-methylenehept-3-en-1-yl)benzene (3c).

This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), 2-bromobut-1-ene (60.7 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield as a colorless oil (25.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.14 – 7.11 (m, 2H), 6.87 – 6.84 (m, 2H), 6.13 (d, J = 15.8 Hz, 1H), 5.76 (dt, J = 15.7, 6.9 Hz, 1H), 4.91 – 4.89 (m, 2H), 3.81 (s, 3H), 2.70 – 2.67 (m, 2H), 2.41 (dd, *J* = 15.0, 7.1 Hz, 2H), 2.22 (q, *J* = 7.4 Hz, 2H), 1.11 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.90, 147.91, 134.12, 132.74, 129.43, 129.10, 113.85, 112.50, 55.35, 35.19, 35.17, 24.96, 12.82.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



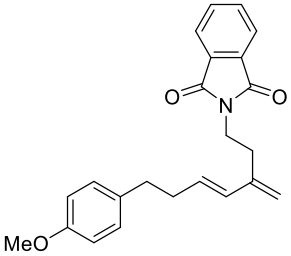
(*E*)-7-(4-Methoxyphenyl)-3-methylenehept-4-en-1-yl benzoate (3d).

This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), 3-bromobut-3-en-1-yl benzoate (114.7 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield as a colorless oil (41.3 mg). Note: 14% of **1b** and 26% of **2d** underwent homo-coupling, and 16% of **2d** underwent hydro-debromination.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 15.8 Hz, 1H), 5.89 – 5.79 (m, 1H), 5.03 (d, *J* = 14.7 Hz, 2H), 4.45 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 2.68 (t, *J* = 7.3 Hz, 4H), 2.41 (dd, *J* = 14.8, 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.67, 157.92, 142.11, 133.92, 132.99, 132.16, 130.50, 130.02, 129.70, 129.42, 128.45, 115.76, 113.88, 63.84, 55.34, 35.12, 35.04, 31.68.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



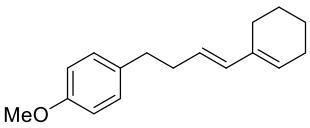
(*E*)-2-(7-(4-Methoxyphenyl)-3-methylenehept-4-en-1-yl)isoindoline -1,3-dione (3e).

This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), 2-(3-bromobut-3-en-1-yl)isoindoline-1,3-dione (126.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 44% yield as a colorless oil (23.8 mg). Note: 54% of **1b** and 6% of **2e** underwent homo-coupling. No hydro-dehalogentaion of **2e** was detected. We reasoned that the homocouplng product of **2e** may have poor solubility due to two phathimide groups, which caused error for analysis.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.81 (m, 2H), 7.74 – 7.66 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.08 (d, *J* = 15.9 Hz, 1H), 5.94 – 5.87 (m, 1H), 4.94 (d, *J* = 12.1 Hz, 2H), 3.85 – 3.80 (m, 2H), 3.78 (s, 3H), 2.69 – 2.63 (m, 2H), 2.59 – 2.54 (m, 2H), 2.39 (dd, *J* = 15.1, 7.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.41, 157.90, 142.74, 134.10, 134.03, 132.32, 131.73, 130.37, 129.46, 123.33, 115.85, 113.88, 55.38, 37.54, 35.24, 35.04, 31.35.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{23}H_{23}NNaO_3^+$): m/z 384.1570; found: 384.1579.



(*E*)-1-(4-(Cyclohex-1-en-1-yl)but-3-en-1-yl)-4-methoxybenzene (3f).

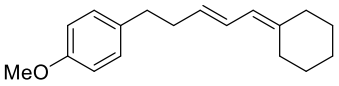
This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), 1-bromocyclohex-1-ene (72.4 mg, 0.45 mmol, 3.0 equiv). After purification by column

chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 46% yield as a colorless oil (16.7 mg). Note: 35% of **1b** and 21% of **2e** underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.11 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 6.07 (d, J = 15.7 Hz, 1H), 5.65 (s, 1H), 5.61 – 5.54 (m, 1H), 3.79 (s, 3H), 2.67 – 2.62 (m, 2H), 2.37 (dd, J = 15.1, 7.3 Hz, 2H), 2.14 – 2.09 (m, 4H), 1.69 – 1.65 (m, 2H), 1.63 – 1.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.86, 135.74, 134.35, 134.01, 129.42, 127.65, 125.88, 113.85, 55.39, 35.47, 35.18, 25.91, 24.75, 22.78, 22.70.

HRMS (ESI) exact mass calculated for [M+Na^+] ($C_{17}H_{22}NaO^+$): m/z 265.1563; found: 265.1568.



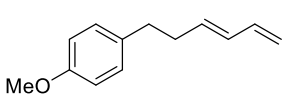
(*E*)-1-(5-Cyclohexylidenepent-3-en-1-yl)-4-methoxybenzene (3g).

This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv), (bromomethylene)cyclohexane (78.7 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield as a colorless oil (23.0 mg). Note: the product contains an inseparable impurity (ratio of the product to the impurity ~7:1, which is attribute a possible *Z*-isomer of the product. Note: 53% of **1b**, 30% of **2g** underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.11 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.2 Hz, 2H), 6.32 (dd, J = 14.7, 11.2 Hz, 1H), 5.74 (d, J = 10.9 Hz, 1H), 5.65 – 5.55 (m, 1H), 3.79 (s, 3H), 2.68 – 2.62 (m, 2H), 2.37 (dd, J = 15.1, 7.3 Hz, 2H), 2.28 – 2.24 (m, 2H), 2.13 – 2.10 (m, 2H), 1.60 – 1.50 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.88, 141.70, 134.30, 131.31, 129.44, 126.54, 121.93, 113.85, 55.40, 37.35, 35.32, 35.23, 29.32, 28.66, 27.86, 26.97.

HRMS (ESI) exact mass calculated for [M+H^+] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



(*E*)-1-(Hexa-3,5-dien-1-yl)-4-methoxybenzene (3h).

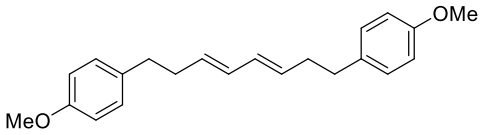
This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (36.2 mg, 0.15 mmol, 1.0 equiv),

bromoethane (THF solution, 1M) (450 μL, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 64% yield as a colorless oil (18.0 mg). Note: 37% of **1b**, 39% of **2h** underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 3.98 (t, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 2.08 – 2.02 (m, 2H), 1.34 – 1.25 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 150.9, 144.5, 129.9, 128.6, 128.0, 127.9, 126.4, 52.1, 51.2, 37.7, 21.2, 14.1.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



(3*E*,5*E*)-1,8-Bis(4-methoxyphenyl)octa-3,5-diene (3i).

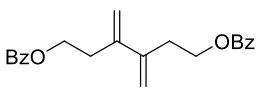
This compound was prepared according to the General Procedure using (*E*)-1-(4-bromobut-3-en-1-yl)-4-methoxybenzene (72.4 mg, 0.3 mmol, 2.0 equiv). After purification by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield as a white solid (39.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.11 – 6.00 (m, 1H), 5.69 – 5.59 (m, 1H), 3.81 (s, 3H), 2.71 – 2.63 (m, 2H), 2.37 (dd, J = 15.1, 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.88, 134.10, 131.83, 130.86, 129.40, 113.83, 55.35, 35.06, 34.84.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_2^+$): m/z 345.1825; found: 345.1826.

M.p. 99-100 °C



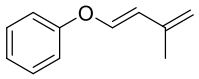
(3*E*,5*E*)-4,5-Dimethylocta-3,5-diene-1,8-diyl dibenzoate (3j).

This compound was prepared according to the General Procedure using 3-bromobut-3-en-1-yl benzoate (76.5 mg, 0.3 mmol, 2.0 equiv). After purification by column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 71% yield as a colorless oil (37.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.05 – 8.02 (m, 5H), 7.58 – 7.52 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 5H), 5.33 (s, 2H), 5.18 (s, 2H), 4.45 (t, *J* = 7.0 Hz, 4H), 2.77 (t, *J* = 7.0 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.65, 142.78, 133.03, 130.44, 129.69, 128.48, 114.86, 63.89, 33.53.

HRMS (ESI) exact mass calculated for [M+Na^+] ($C_{22}H_{22}NaO_4^+$): m/z 373.1410; found: 373.1410.



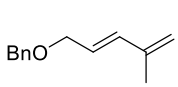
(*E*)-((3-Methylbuta-1,3-dien-1-yl)oxy)benzene (4a).

This compound was prepared according to the General Procedure using (*E*)-((2-bromovinyl)oxy)benzene (29.9 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 84% yield as a colorless oil (20.1 mg). Note: 15% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 – 7.32 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 6.8 Hz, 1H), 5.29 (d, *J* = 6.9 Hz, 1H), 5.08 (s, 1H), 4.89 (s, 1H), 2.09 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.45, 140.71, 139.97, 129.79, 123.13, 116.70, 115.43, 113.31, 23.01.

HRMS (ESI) exact mass calculated for [M+H^+] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



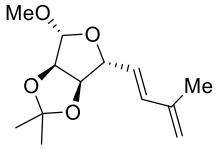
(*E*)-((3-Methylbuta-1,3-dien-1-yl)oxy)benzene (4b).

This compound was prepared according to the General Procedure using (*E*)-(((4-methylpenta-2,4-dien-1-yl)oxy)methyl)benzene (34.1 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield as a colorless oil (22.5 mg). Note: 10% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.38 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.84 – 5.72 (m, 1H), 5.00 (s, 2H), 4.54 (s, 2H), 4.11 (d, *J* = 6.1 Hz, 2H), 1.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.57, 138.44, 135.62, 128.53, 127.93, 127.74, 126.09, 116.96, 72.33, 70.86, 18.66.

HRMS (ESI) exact mass calculated for [M+H^+] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



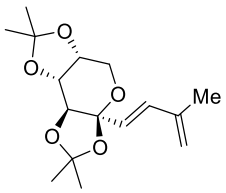
(3a*R*,4*R*,6*R*,6a*R*)-4-Methoxy-2,2-dimethyl-6-((*E*)-3-methylbuta-1,3-dien-1-yl)tetrahydrofuro[3,4-*d*][1,3]dioxole (4c).

This compound was prepared according to the General Procedure using (3a*R*,4*R*,6*R*,6a*R*)-4-((*E*)-2-bromovinyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (41.9 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield as a colorless oil (25.2 mg). Note: 18% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.31 (d, *J* = 15.7 Hz, 1H), 5.65 (dd, *J* = 15.7, 8.7 Hz, 1H), 5.03 – 4.98 (m, 3H), 4.69 (d, *J* = 8.7 Hz, 1H), 4.64 (s, 2H), 3.34 (s, 3H), 1.82 (s, 3H), 1.50 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.26, 135.72, 128.78, 117.74, 112.51, 109.30, 88.26, 85.77, 84.95, 54.63, 31.76, 29.79, 26.62, 25.13, 18.63.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



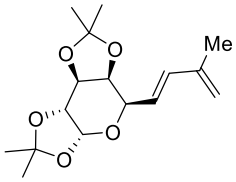
(3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyl-3a-((*E*)-3-methylbuta-1,3-dien-1-yl)tetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (4d).

This compound was prepared according to the General Procedure using (3a*S*,5a*R*,8a*R*,8b*S*)-3a-((*E*)-2-bromovinyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (50.3 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 68% yield as a colorless oil (30.2 mg). Note: 27% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.65 (d, *J* = 15.7 Hz, 1H), 5.71 (d, *J* = 15.7 Hz, 1H), 5.04 (d, *J* = 6.1 Hz, 2H), 4.62 – 4.58 (m, 1H), 4.24 (d, *J* = 7.9 Hz, 1H), 4.20 (d, *J* = 1.8 Hz, 1H), 3.92 (d, *J* = 12.9 Hz, 1H), 3.79 (d, *J* = 13.0 Hz, 1H), 1.85 (s, 3H), 1.56 (s, 3H), 1.50 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.11, 134.09, 129.11, 118.44, 109.19, 108.28, 102.55, 74.27, 70.72, 70.58, 61.28, 26.38, 25.98, 25.01, 24.34, 18.56.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{24}NaO_5^+$): m/z 319.1515; found: 319.1511.



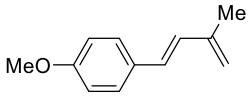
(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyl-5-((*E*)-3-methylbuta-1,3-dien-1-yl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran (4e).

This compound was prepared according to the General Procedure using (3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-5-((*E*)-2-bromovinyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (50.2 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 74% yield as a colorless oil (32.8 mg). Note: 20% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.39 (d, *J* = 15.9 Hz, 1H), 5.75 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.57 (d, *J* = 4.8 Hz, 1H), 4.99 (s, 2H), 4.61 (d, *J* = 7.8 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.20 (d, *J* = 7.8 Hz, 1H), 1.87 (s, 3H), 1.55 (s, 3H), 1.47 (s, 3H), 1.34 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.65, 136.07, 125.17, 117.38, 109.33, 108.58, 96.63, 73.67, 71.00, 70.60, 69.17, 26.31, 26.12, 25.06, 24.43, 18.62.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{24}NaO_5^+$): m/z 319.1515; found: 319.1512.



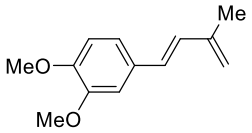
(*E*)-1-Methoxy-4-(3-methylbuta-1,3-dien-1-yl)benzene (4f).

This compound was prepared according to the General Procedure using (*E*)-1-(2-bromovinyl)-4-methoxybenzene (30.2 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield as a colorless oil (20.4 mg). Note: trace amount of homocoupling of the β-vinyl bromide was detected likely due to the styrene-associated oligomerization.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39 – 7.35 (m, 2H), 6.90 – 6.85 (m, 2H), 6.77 (d, *J* = 16.1 Hz, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 5.07 (s, 1H), 5.03 (s, 1H), 3.82 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.28, 142.31, 130.32, 129.85, 128.32, 127.77, 116.42, 114.20, 55.42, 18.77.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



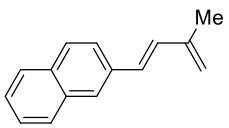
(*E*)-1,2-Dimethoxy-4-(3-methylbuta-1,3-dien-1-yl)benzene (4g).

This compound was prepared according to the General Procedure using (*E*)-4-(2-bromovinyl)-1,2-dimethoxybenzene (36.5 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield as a colorless oil (21.4 mg). Note: trace amount of homocoupling of the β-vinyl bromide was detected likely due to the styrene-associated oligomerization.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.01 – 6.95 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 6.48 (d, *J* = 16.1 Hz, 1H), 5.06 (d, *J* = 32.7 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.18, 148.87, 142.21, 130.62, 130.03, 128.57, 119.87, 116.60, 111.31, 108.87, 56.03, 55.94, 18.77.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



(*E*)-2-(3-methylbuta-1,3-dien-1-yl)naphthalene (4h).

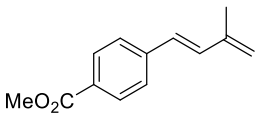
This compound was prepared according to the General Procedure using (*E*)-2-(2-bromovinyl)naphthalene (40.0 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 71% yield as a yellow solid (20.7 mg). Note: trace amount of homocoupling of the β-vinyl bromide was detected likely due to the styrene-associated oligomerization.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 – 7.76 (m, 4H), 7.66 (d, J = 8.7 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.02 (d, J = 16.1 Hz, 1H), 6.72 (d, J = 16.1 Hz, 1H), 5.18 (s, 1H), 5.12 (s, 1H), 2.04 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.25, 135.04, 133.85, 133.10, 132.19, 128.94, 128.35, 128.08, 127.81, 126.61, 126.40, 125.93, 123.74, 117.67, 18.78.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

M.p. 59-60 °C



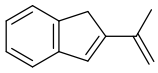
Methyl (*E*)-4-(3-methylbuta-1,3-dien-1-yl)benzoate (4i).

This compound was prepared according to the General Procedure using methyl (*E*)-4-(2-bromovinyl)benzoate (36.1 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: ethyl acetate in petroleum ether), the title compound was isolated in 71% yield as a colorless oil (9.7 mg). Note: trace amount of homocoupling of the β-vinyl bromide was detected likely due to the styrene-associated oligomerization.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 5.17 (d, *J* = 20.4 Hz, 1H), 3.91 (s, 1H), 1.98 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.85, 141.89, 141.72, 134.09, 129.90, 128.69, 127.59, 126.23, 118.93, 51.98, 18.42.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.



2-(Prop-1-en-2-yl)-1*H*-indene (4j).

This compound was prepared according to the General Procedure using 2-bromo-1H-indene (29.0 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 72% yield as a white solid (16.8 mg). Note: 21% of the β-vinyl bromide underwent homo-coupling.

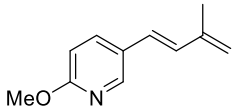
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 5.25 (s, 1H), 5.01 (s, 1H), 3.59 (s, 2H), 2.07 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.48, 145.41, 143.19, 139.75, 127.97, 126.59, 125.06, 123.70, 121.10, 113.05, 38.44, 20.59.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

M.p. 61-62 °C

(*E*)-2-Methoxy-5-(3-methylbuta-1,3-dien-1-yl)pyridine (4k).



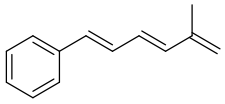
This compound was prepared according to the General Procedure using (*E*)-5-(2-bromovinyl)-2-methoxypyridine (32.1 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield as a colorless oil (18.1 mg). Note: 30% of the β-vinyl bromide underwent homo-coupling.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.14 (d, J = 2.4 Hz, 1H), 7.71 (dd, J = 8.6, 2.4 Hz, 1H), 6.76 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 6.45 (d, J = 16.2 Hz, 1H), 5.08 (d, J = 18.7 Hz, 2H), 3.94 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.67, 145.91, 141.99, 135.48, 131.17, 126.78, 124.88, 117.36, 111.13, 53.67, 18.67.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

((1*E*,3*E*)-5-methylhexa-1,3,5-trien-1-yl)benzene (4l).



This compound was prepared according to the General Procedure using ((1*E*,3*E*)-4-bromobuta-1,3-dien-1-yl)benzene (31.4 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (54.0 mg, 0.45 mmol, 3.0 equiv), LiCl (6.3 mg, 0.15 mmol, 1 equiv), w/o *n*-Bu_4NI. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield as a white solid (20.6 mg). Note: the byproducts for the β-vinyl bromide was not detected by ^{1}H NMR likely due to oligomerization.

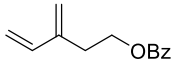
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.86 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.4 Hz, 1H), 6.40 (dd, *J* = 15.4, 10.2 Hz, 1H), 5.05 (s, 1H), 5.03 (s, 1H), 1.93 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.28, 137.58, 136.12, 132.72, 129.57, 129.40, 128.77, 127.60, 126.45, 117.28, 18.69.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

M.p. 36-37 ^oC

3-Methylenepent-4-en-1-yl benzoate (4m).



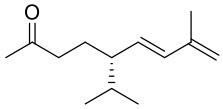
This compound was prepared according to the General Procedure using bromoethane (1M in THF) (157 uL, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (114.7 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated as a white solid that is contaminated with but-3-en-1-yl benzoate. The yield of **4m** (40% yield) was determined by analysis of the mixture using 2,5-dimethyl furan as the internal standard. Note: the α-alkenyl bromide majorly underwent hydro-dehalogenation.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *d* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.41 (dd, *J* = 17.6, 5.0 Hz, 1H), 5.09-5.2 (m, 4H), 4.46 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.2, 138.3, 119.1, 117.8, 113.8, 63.5, 40.6 (partial charateristic peaks)

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

(*S*,*E*)-5-Isopropyl-8-methylnona-6,8-dien-2-one (4n).



This compound was prepared according to the General Procedure using (*S*,*E*)-7-bromo-5-isopropylhept-6-en-2-one **9** (34.9 mg, 0.15 mmol, 1.0 equiv), 2-bromoprop-1-ene (114.7 mg, 0.45 mmol, 3.0 equiv). After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 66% yield as a colorless oil (19.2 mg). The NMR spectra data is identical to the reported.[7] Note: 26% of **9** underwent homo-coupling.

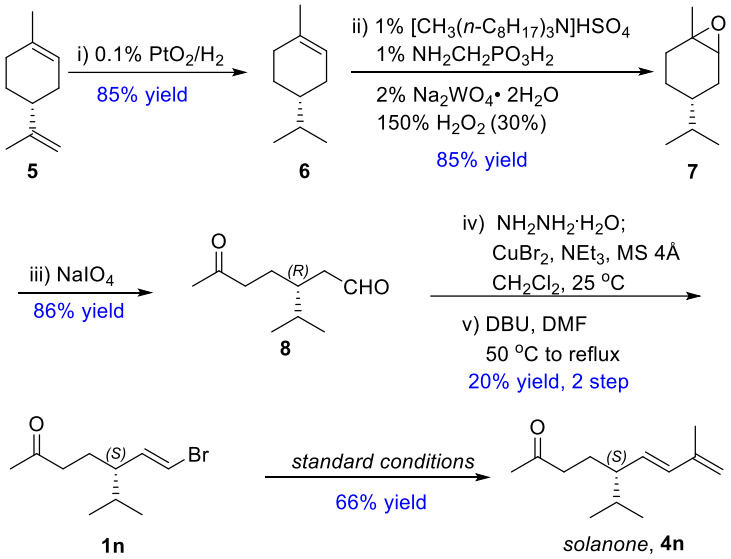
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.03 (d, *J* = 15.6 Hz, 1H), 5.31 (dd, *J* = 15.6, 9.3 Hz, 1H), 4.85 (s, 2H), 2.44 – 2.24 (m, 2H), 2.07 (s, 3H), 1.79 (s, 3H), 1.78 – 1.68 (m, 1H), 1.57 (m, 1H), 1.53 – 1.40 (m, 1H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 209.37, 141.98, 134.48, 132.25, 114.71, 49.45, 42.13, 32.42, 30.19, 26.33, 20.77, 19.29, 18.82.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{21}O_2^+$): m/z 269.1536; found: 269.1539.

$[\alpha]_D^{20}$ = +24.5°

III. Total Synthesis of Solanone (4n)



(*R*)-4-Isopropyl-1-methylcyclohex-1-ene (6)[4] PtO_2 (50 mg, 0.0025 wt/wt) was added to (*R*)-limonene (5) (20.0 g, 0.147 mol) and the reaction vessel was charged with H_2 gas. The solution was stirred vigorously at room temperature under 1 atm of H_2 gas, and the reaction was monitored by GC-MS. After filtration through a cotton plug followed loading silica (200-300 mesh) to give a mixture (16.0 g) of (*R*)-4-isopropyl-1-methylcyclohex-1-ene and 1-isopropyl-4-methylcyclohexane.

(4*R*)-4-Isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (7)[5] A 20 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1.3 g (0.40 mmol) of Na_2WO_4•$2H_2O$, 22.2 mg (0.20 mmol) of $NH_2CH_2PO_3H_2$, 3.4 g (30 mmol) of aqueous of 30% H_2O_2, and 93.2 mg (0.2 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was stirred at room temperature for 15 min, (*R*)-4-isopropyl-1-methylcyclohex-1-ene was added. This mixture was heated to reflux and stirred at 1000 rpm. After 4 h, the mixture was cooled to room temperature, and the organic phase was sperated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$. The organic phase was purified by flash column chromatography (SiO_2: ethyl acetate in petroleum ether = 2%),

and obtained **7** as colorless oil (3.9 g, 85% yield).

(*R*)-3-Isopropyl-6-oxoheptanal (8)[6] To a 100 mL round-bottom flask were added sodium metaperiodaten($NaIO_4$, 4.278 g, 20 mmol) and DI water (13 mL) followed by vigorous mixing for 10 min. After the brief period of stirring, THF (27 mL) was added, subsequent dropwise addition of **7** (1.54 g, 10 mmol) occurred, and the reaction was allowed to stir for 24 h, at which point the iodine salts were filtered off. Ether (Et_2O, 15 mL) was added to the filtrate and transferred to a separatory funnel, and the aqueous phase was washed with Et_2O (3 × 15 mL). The organic layers were combined and washed with DI water (1 × 10 mL) and brine (1 × 10 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to yield **8** (1.46 g, 86% yield) as a clear oil.

(*R*)-7,7-Dibromo-5-isopropylheptan-2-one en route to 9.[7] To a solution of NH_2NH_2 H_2O (0.80 mL, 17 mmol) in CH_2Cl_2 (230 mL) was added (*R*)-3-isopropyl-6-oxoheptanal (**8**) (2.00 g, 11.8 mmol) dissolved in CH_2Cl_2 (8 mL + 2 mL) over 8 min under argon atmosphere at room temperature. After 10 min, Et_3N (4.9 mL, 35 mmol) and MS-4Å (4.0 g) were added to the mixture at the same temperature. Being stirred for 5 min, the suspension was cooled at 0 ℃, and dry $CuBr_2$ (15.8 g, 70.9 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for further 20 min. The mixture was cooled at 0 ℃ and then the reaction was quenched with 3% aqueous NH_3 (100 mL). The resulting solution was extracted with Et_2O (200 mL × 1, 100 mL × 2). The combined organic layer was washed with H_2O (× 1) and brine (× 1), dried over anhydrous Na_2SO_4, and evaporated to dryness *in vacuo*. The residue was purified by flash column chromatography (silica gel 60: 80 g, Et_2O/pentane 1/6) to give (*R*)-7,7-dibromo-5-isopropylheptan-2-one (1.27 g, 34%) as a pale yellow oil.

(*S*,*E*)-7-Bromo-5-isopropylhept-6-en-2-one (9) [7]**.** Under argon atmosphere, a solution of (*R*)-7,7-dibromo-5-isopropylheptan-2-one (1.03 g, 3.18 mmol) and DBU (0.95 mL, 6.3 mmol) in dry DMF (32 mL) was stirred at 50 ℃ for 90 min and then refluxed for 5 h. Being cooled at 0 ℃, the reaction was quenched with saturated aqueous NH_4Cl (20 mL). After separation of the organic

layer, the aqueous layer was extracted with EtOAc (40 mL × 3). The combined organic layer was washed with H_2O (× 2) and brine (× 1), and dried over anhydrous Na_2SO_4, and evaporated to dryness *in vacuo*. The residue was purified by flash column chromatography (silica gel 60: 40 g, CH_2Cl_2/hexane 2/1) to give (*S*,*E*)-7- bromo-5-isopropylhept-6-en-2-one (**9**) (258 mg, 34%, as a colorless oil) and a mixture of **9** and alkyne (318 mg). Further purification of the latter mixture by flash column chromatography (silica gel 60: 40 g, CH_2Cl_2/hexane 4/3) gave (*S*)-**9** (250 mg, 33%) and alkyne (5.8 mg, 1%). The total yield of (*S*,*E*)-7-bromo-5-isopropylhept-6-en-2-one (**9**) was 67% (508 mg).

III. References

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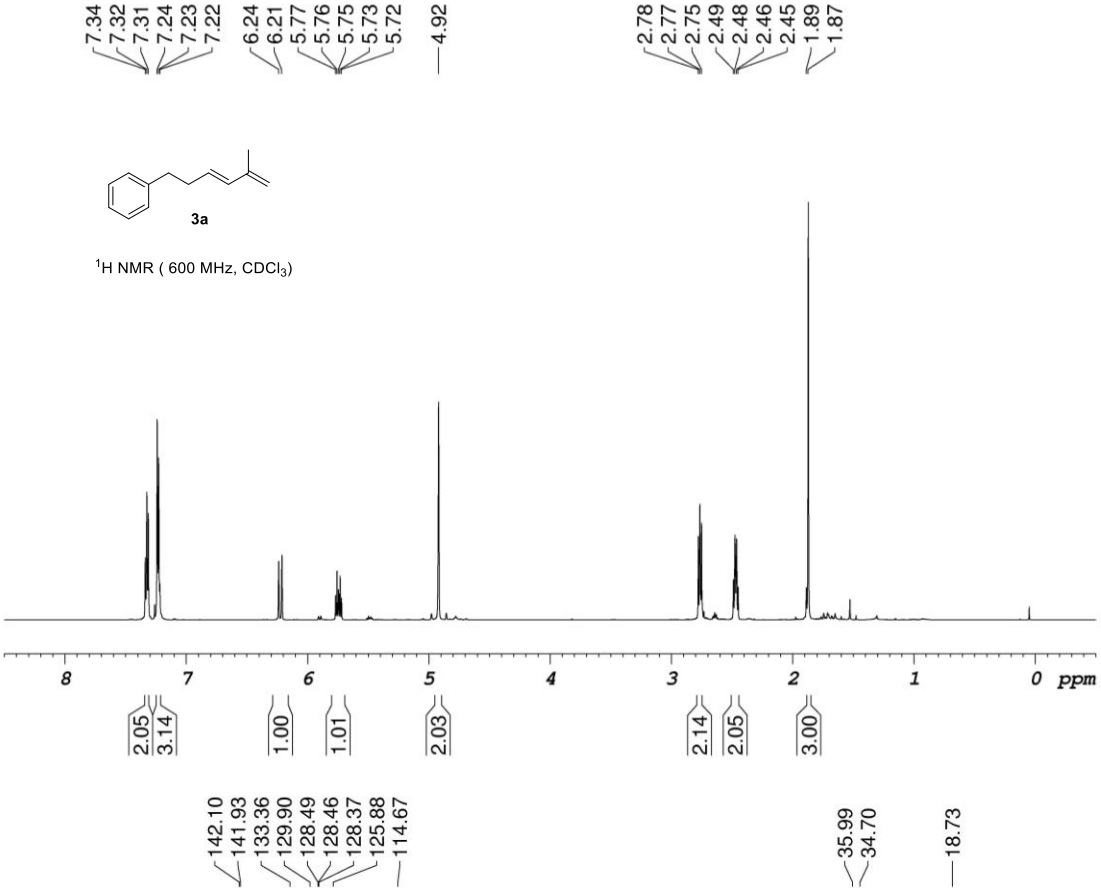
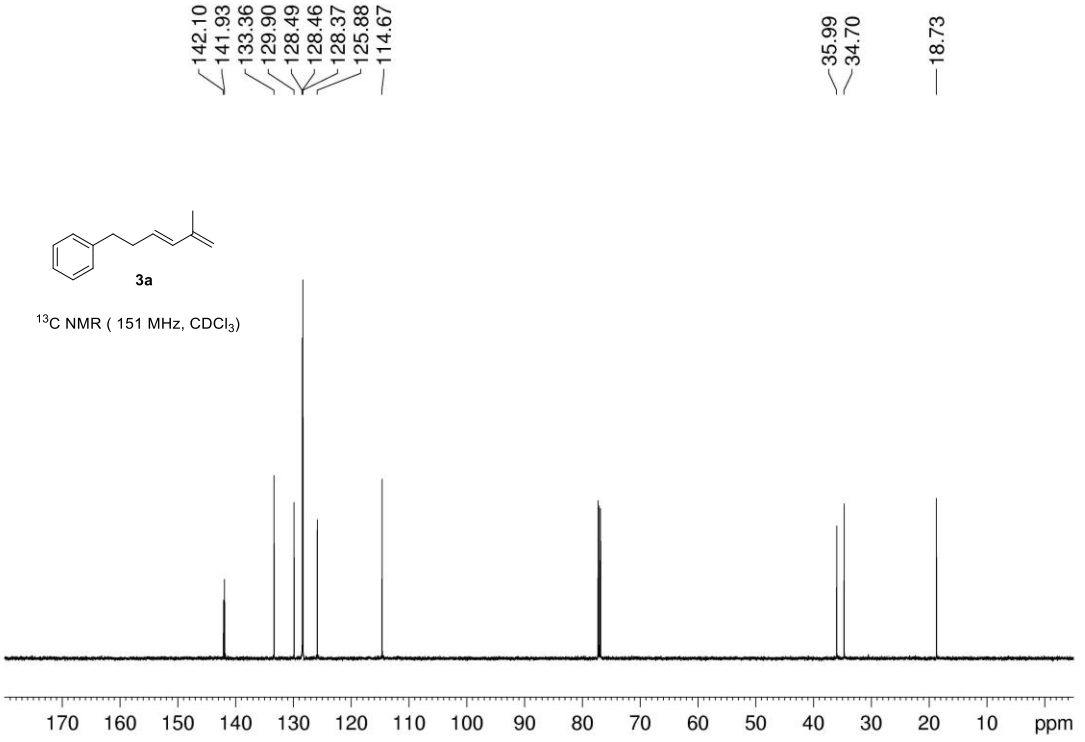
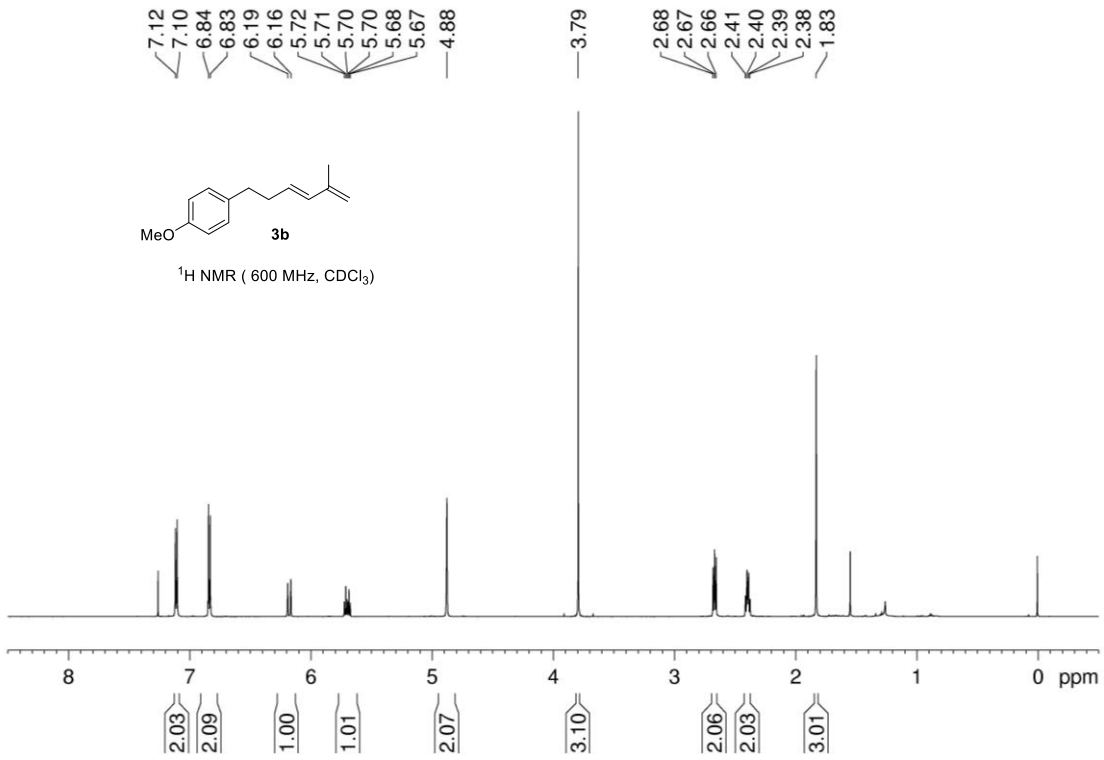
V. Spectroscopic Data (NMR Spectrum)







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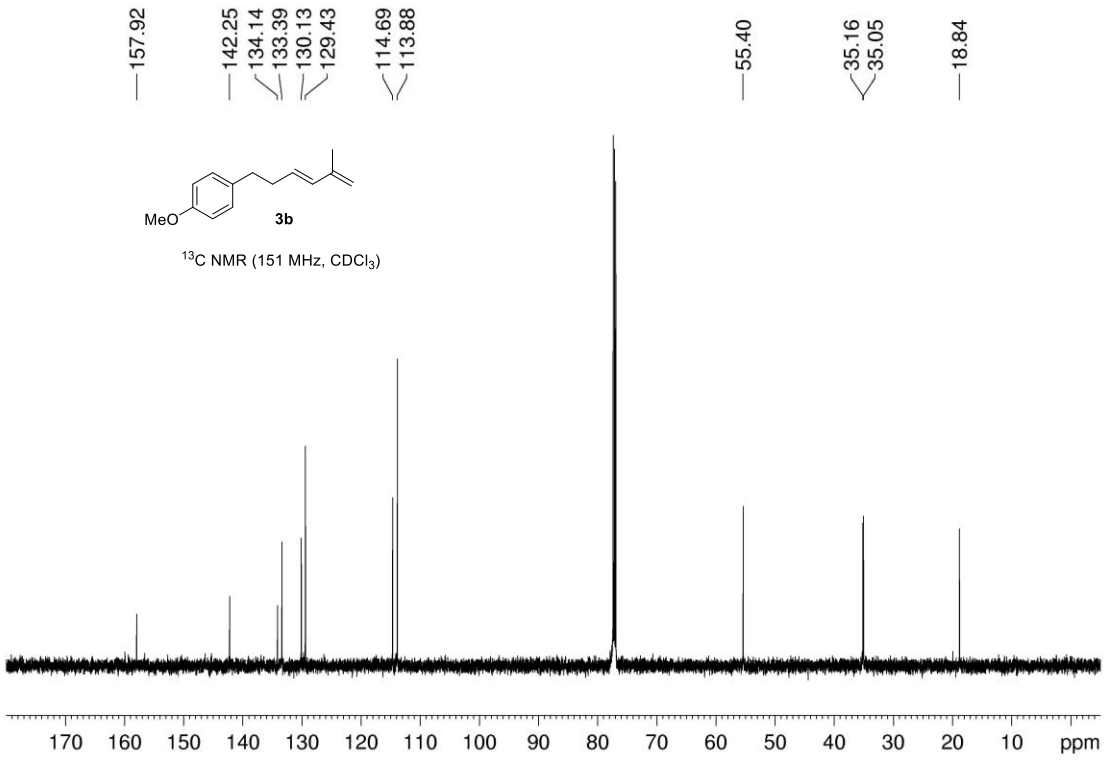
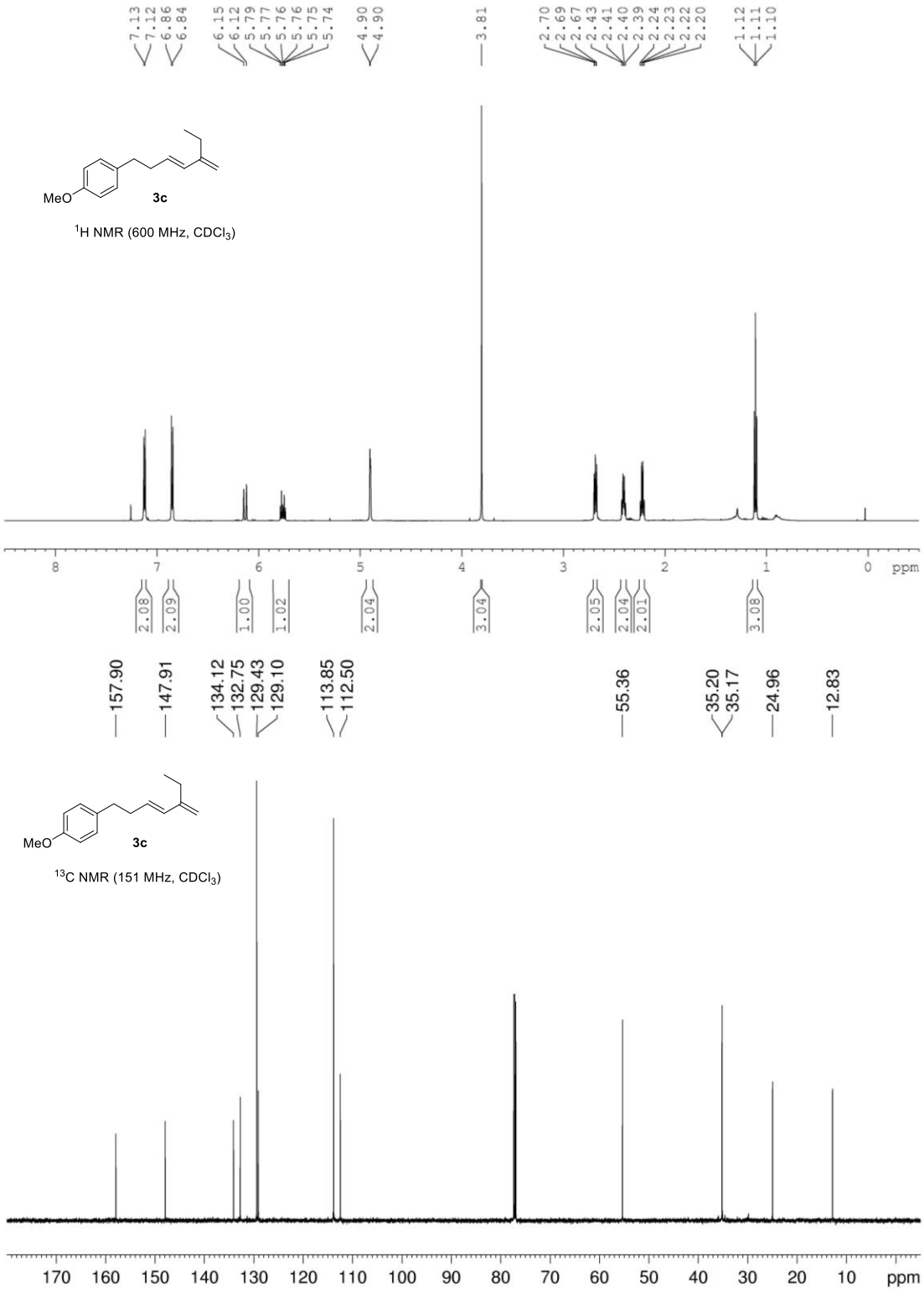


^{13}C NMR (151 MHz, $CDCl_3$)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6.12
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5.77
5.76
5.76
5.75
5.74
4.90
4.90
3.81
2.70
2.69
2.67
2.43
2.41
2.40
2.39
2.24
2.23
2.22
2.20
1.12
1.11
1.10
MeO
3c
1H NMR (600 MHz, CDCl3)
8
7
6
5
4
3
2
1
0
ppm
2.08
2.09
1.00
1.02
2.04
3.04
2.05
2.04
2.01
3.08
157.90
147.91
134.12
132.75
129.43
129.10
113.85
112.50
55.36
35.20
35.17
24.96
12.83
MeO
3c
13C NMR (151 MHz, CDCl3)
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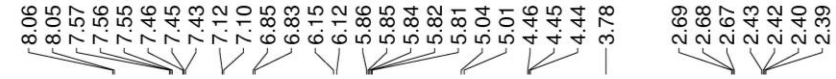
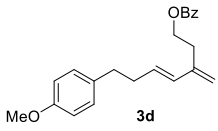
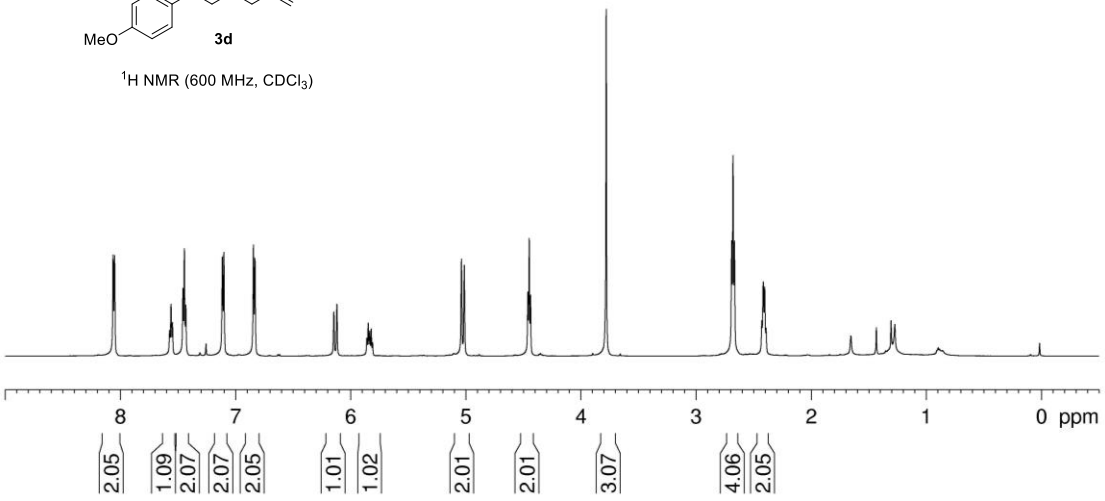
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

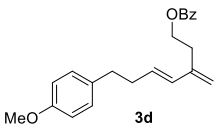




3d

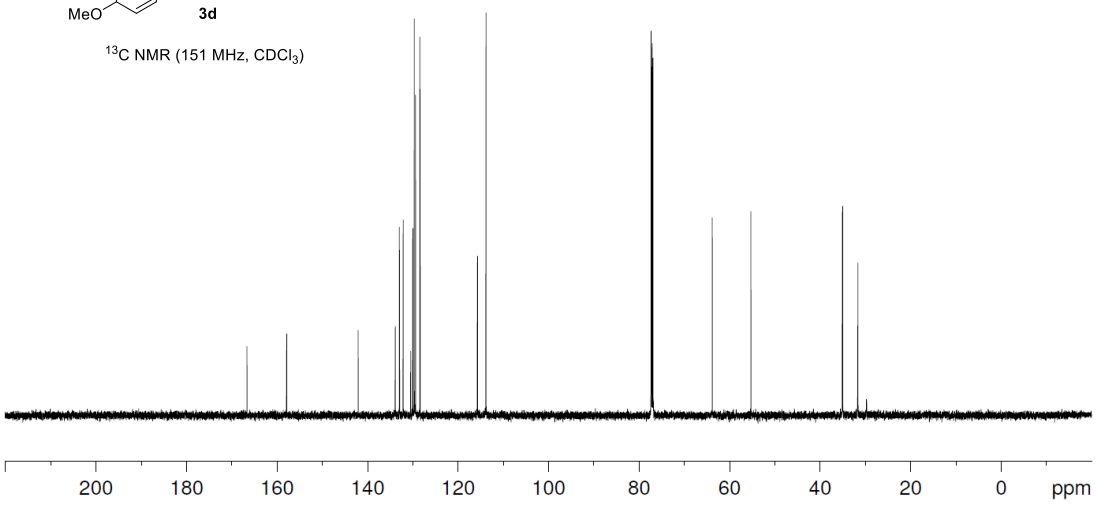
^{1}H NMR (600 MHz, $CDCl_3$)

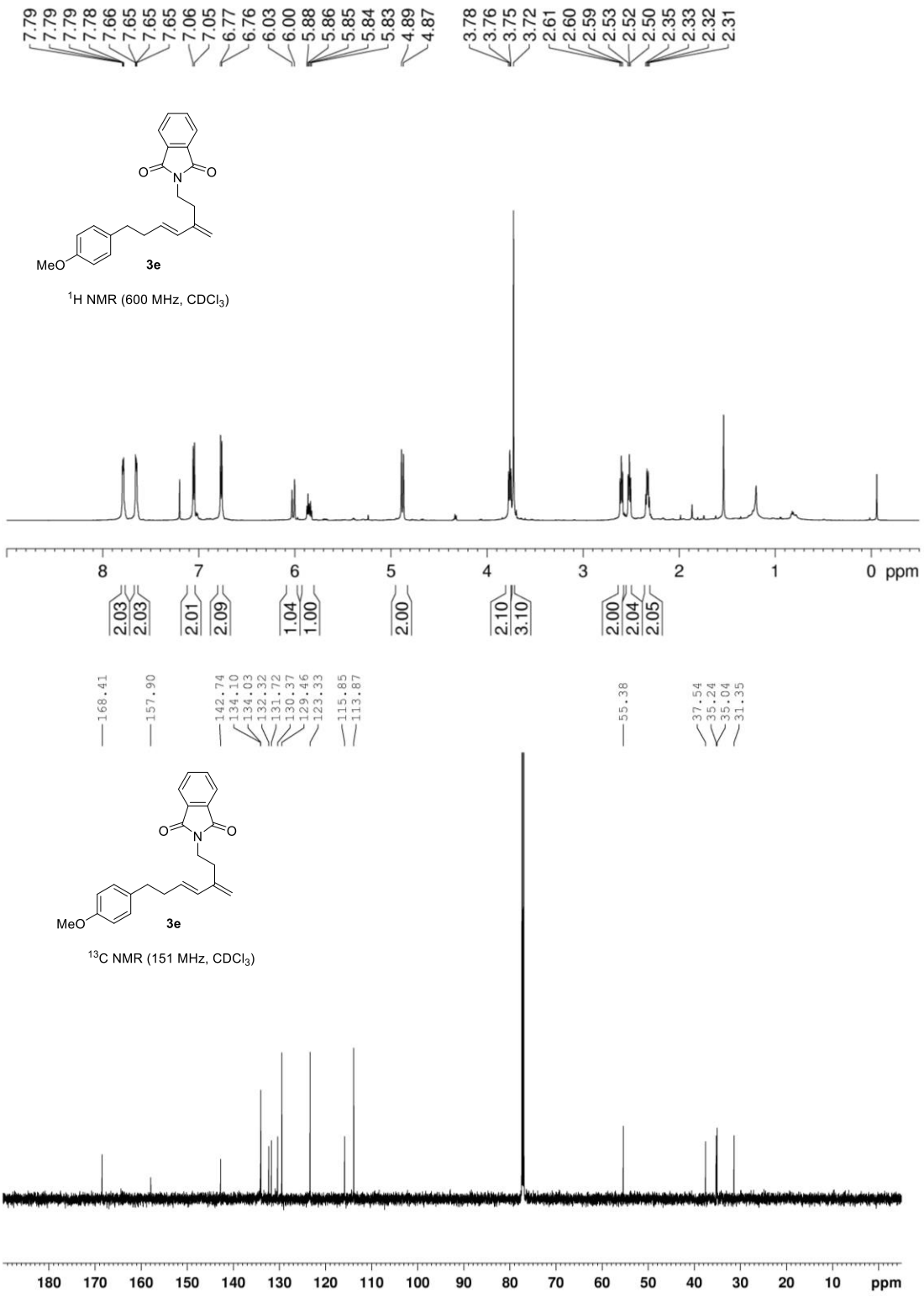




3d

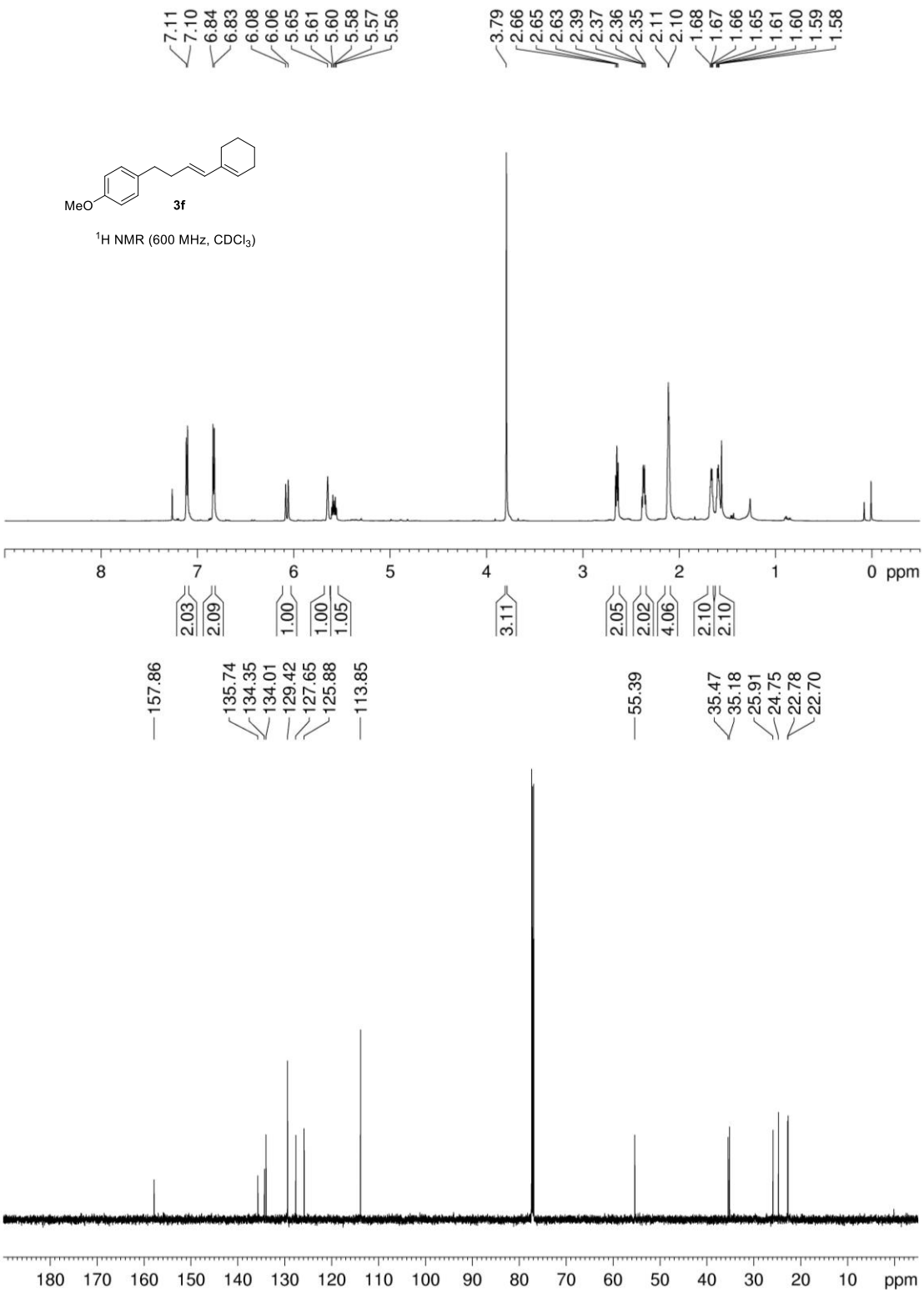
^{13}C NMR (151 MHz, $CDCl_3$)





^{1}H NMR (600 MHz, $CDCl_3$)

^{13}C NMR (151 MHz, $CDCl_3$)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6.84
6.83
6.08
6.06
5.65
5.61
5.60
5.58
5.57
5.56
3.79
2.66
2.65
2.63
2.39
2.37
2.36
2.35
2.11
2.10
1.68
1.67
1.66
1.65
1.61
1.60
1.59
1.58
MeO
3f
^{1}H NMR (600 MHz, $CDCl_3$)
8
7
6
5
4
3
2
1
0 ppm
2.03
2.09
1.00
1.00
1.05
3.11
2.05
2.02
4.06
2.10
2.10
157.86
135.74
134.35
134.01
129.42
127.65
125.88
113.85
55.39
35.47
35.18
25.91
24.75
22.78
22.70
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150
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100
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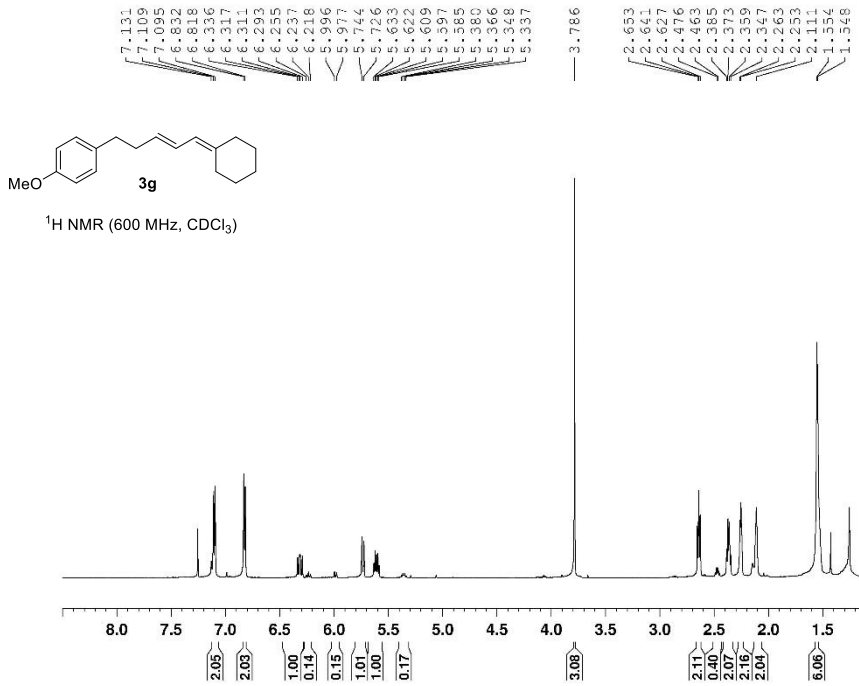
70
60
50
40
30
20
10
ppm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7.095
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6.311
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6.255
6.237
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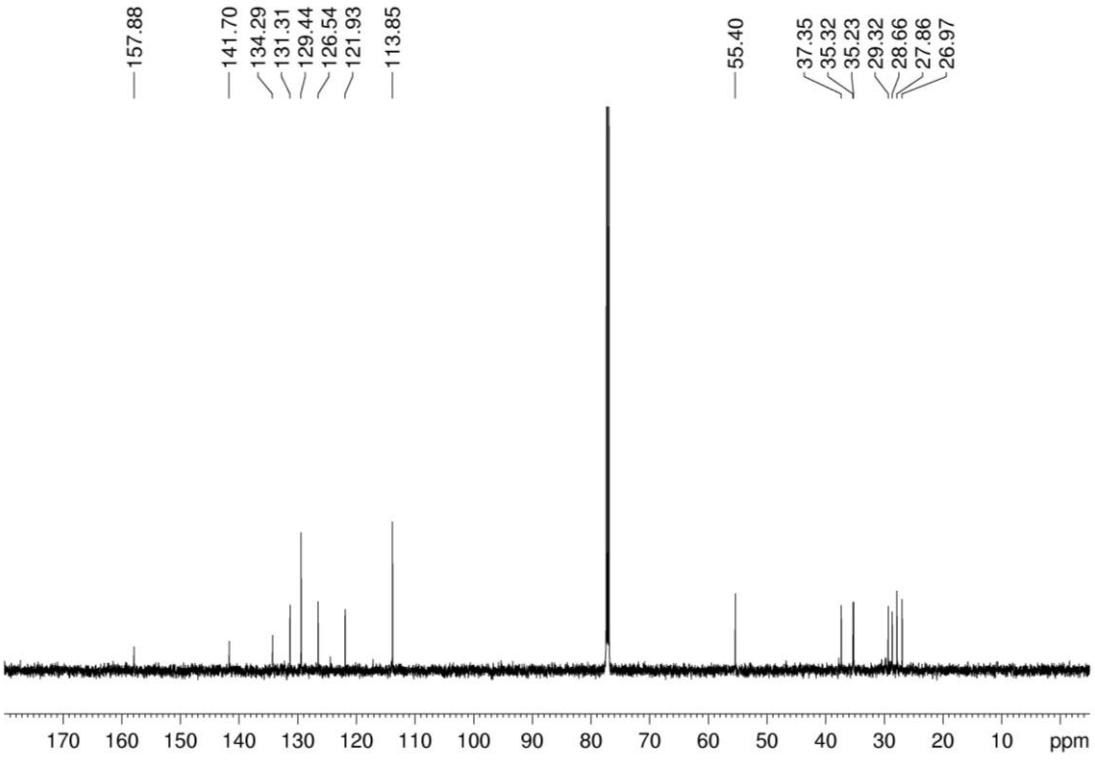
5.996
5.977
5.744
5.726
5.633
5.622
5.609
5.597
5.585
5.380
5.366
5.348
5.337
3.786
2.653
2.641
2.627
2.476
2.463
2.385
2.373
2.359
2.347
2.263
2.253
2.111
1.554
1.548
MeO
3g
^{1}H NMR (600 MHz, CDCl$_3$)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05 2.03 1.00 0.14 0.15 1.01 1.00 0.17 3.08 2.11 0.40 2.07 2.16 2.04 6.06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121.93
113.85
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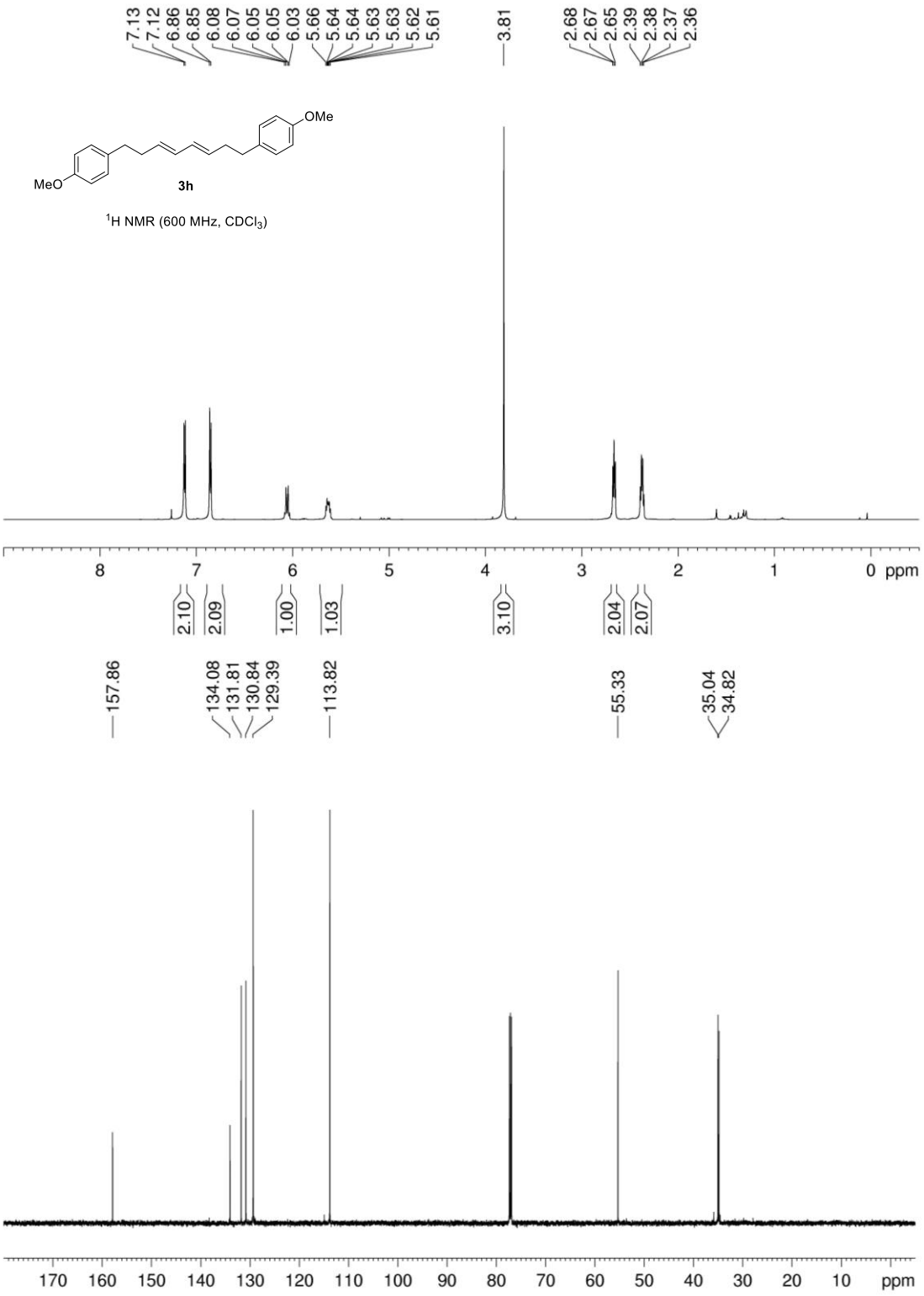
35.23
29.32
28.66
27.86
26.97
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.12
6.86
6.85
6.08
6.07
6.05
6.05
6.03
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5.64
5.63
5.63
5.62
5.61
3.81
2.68
2.67
2.65
2.39
2.38
2.37
2.36
OMe
MeO
3h
1H NMR (600 MHz, CDCl3)
8
7
6
5
4
3
2
1
0 ppm
2.10
2.09
1.00
1.03
3.10
2.04
2.07
157.86
134.08
131.81
130.84
129.39
113.82
55.33
35.04
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40
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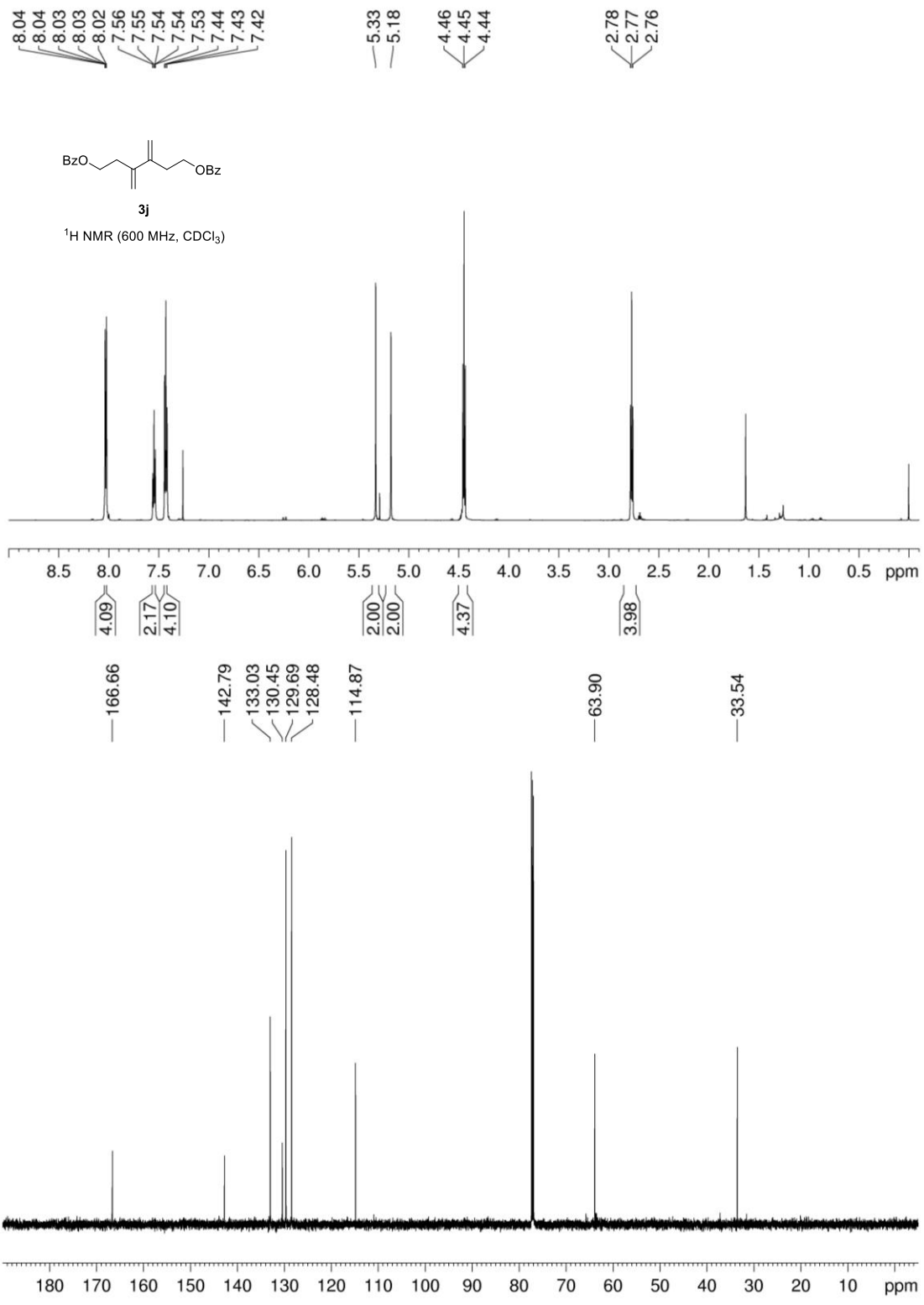
10
ppm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8.04
8.03
8.03
8.02
7.56
7.55
7.54
7.54
7.53
7.44
7.43
7.42
5.33
5.18
4.46
4.45
4.44
2.78
2.77
2.76
BzO
OBz
3j
1H NMR (600 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.09
2.17
4.10
2.00
2.00
4.37
3.98
166.66
142.79
133.03
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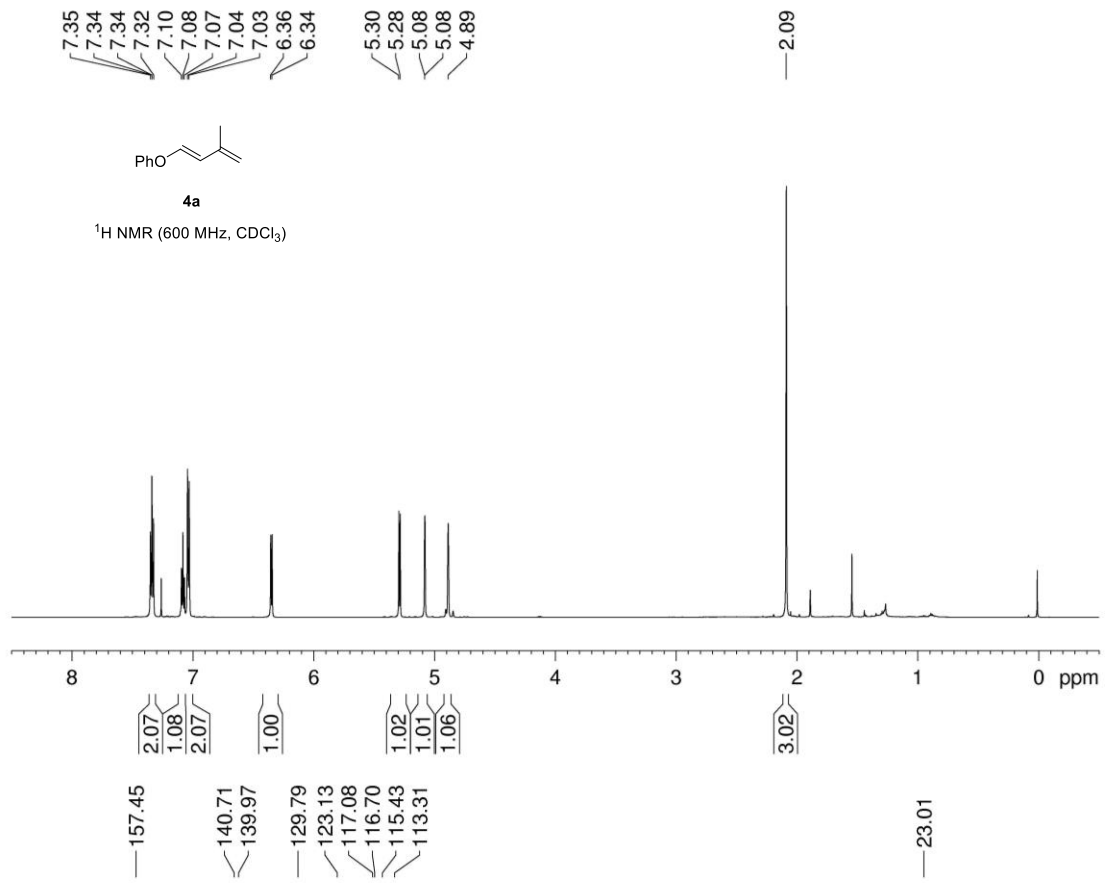
129.69
128.48
114.87
63.90
33.54
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



4a

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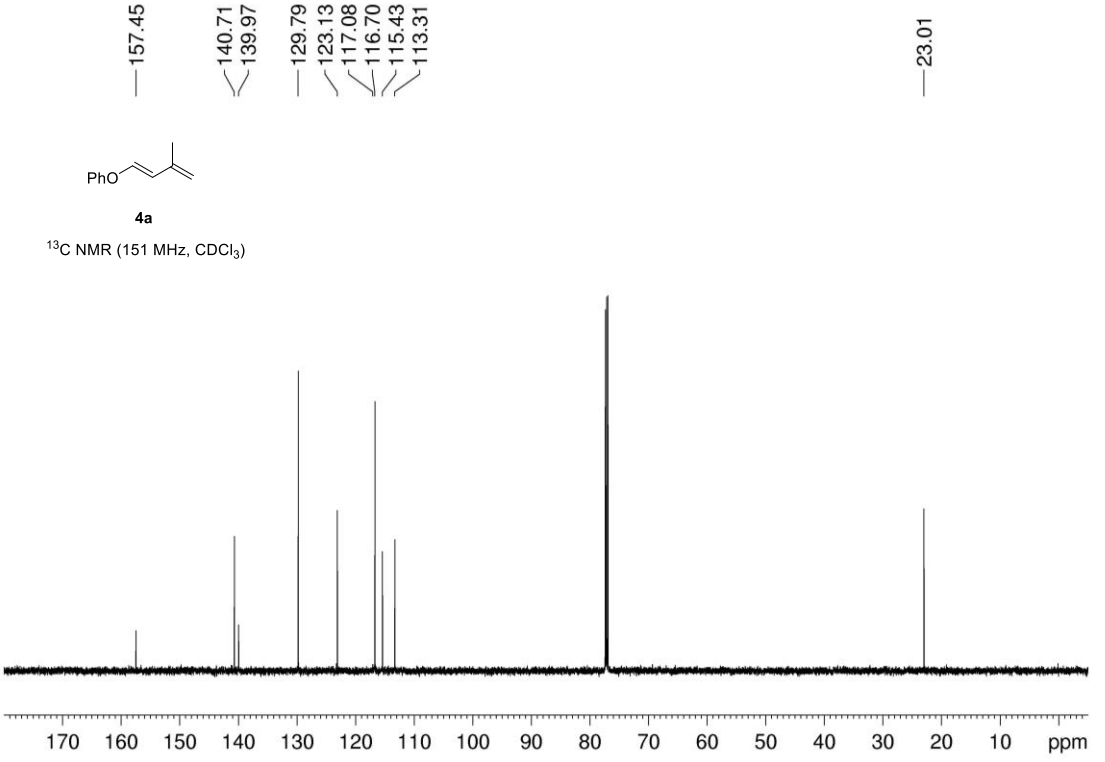
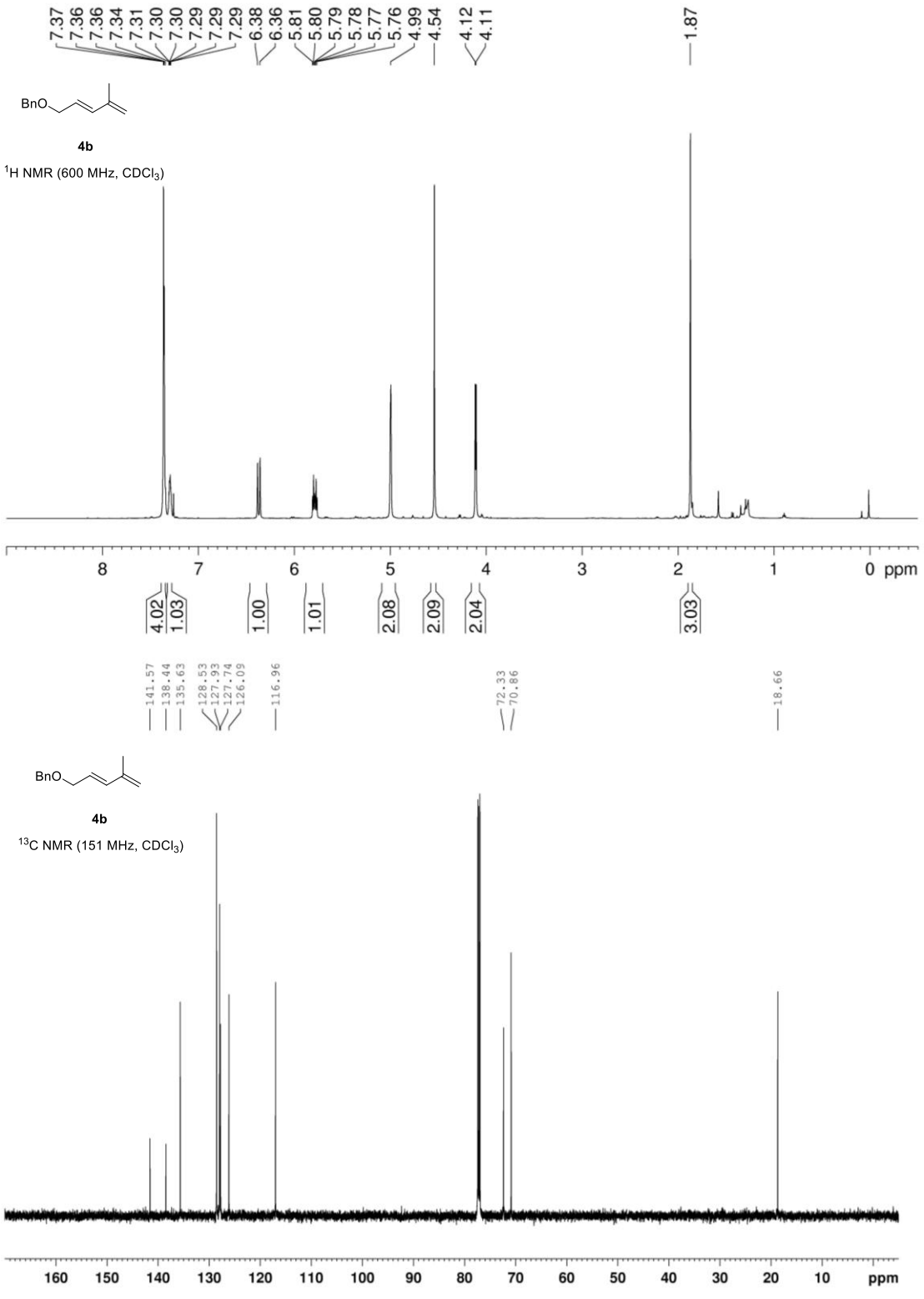


4a

^{13}C NMR (151 MHz, $CDCl_3$)


7.37
7.36
7.36
7.34
7.31
7.30
7.30
7.29
7.29
7.29
6.38
6.36
5.81
5.80
5.79
5.78
5.77
5.76
4.99
4.54
4.12
4.11
1.87
BnO
4b
1H NMR (600 MHz, CDCl3)
8
7
6
5
4
3
2
1
0 ppm
4.02
1.03
1.00
1.01
2.08
2.09
2.04
3.03
141.57
138.44
135.63
128.53
127.93
127.74
126.09
116.96
72.33
70.86
18.66
BnO
4b
13C NMR (151 MHz, CDCl3)
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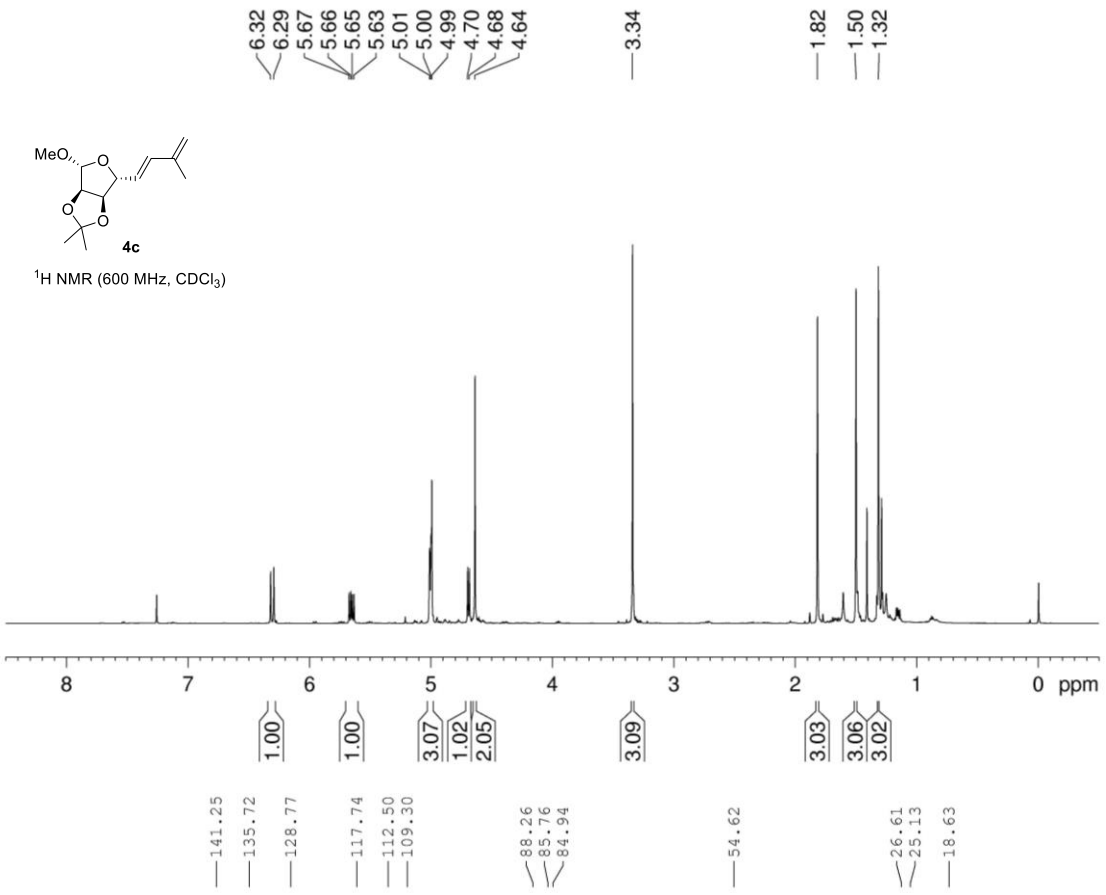
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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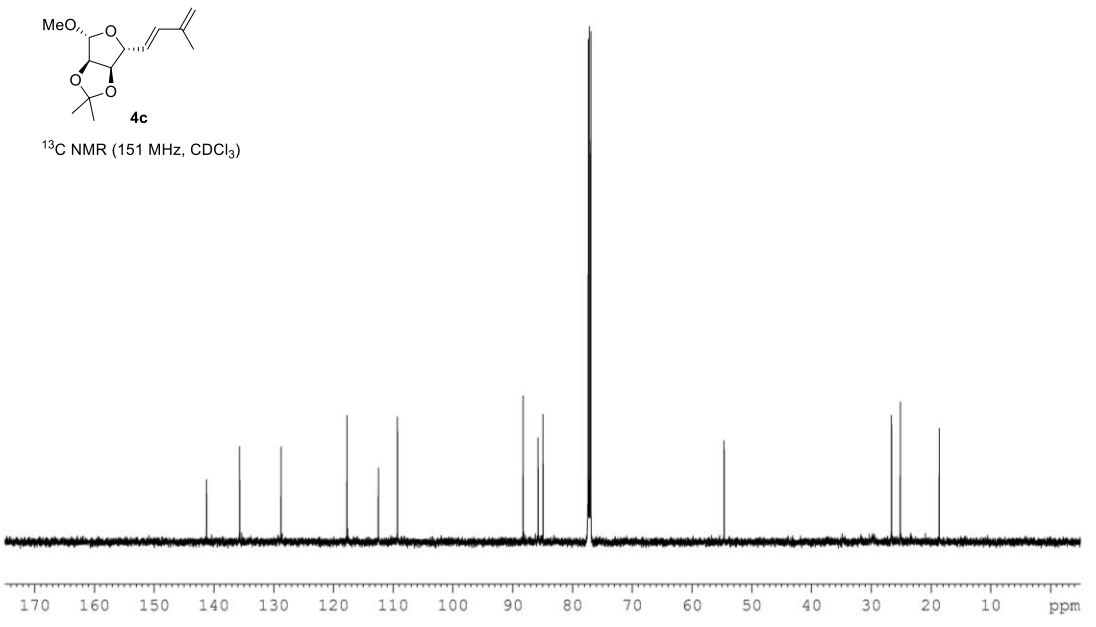

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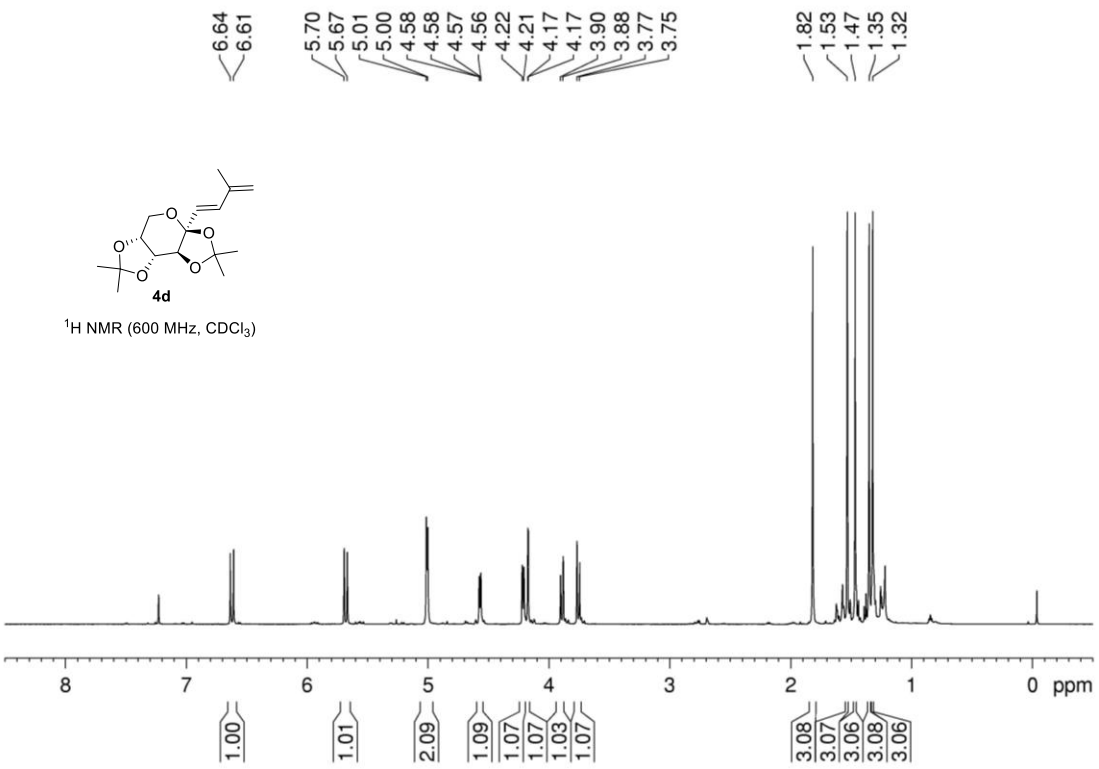
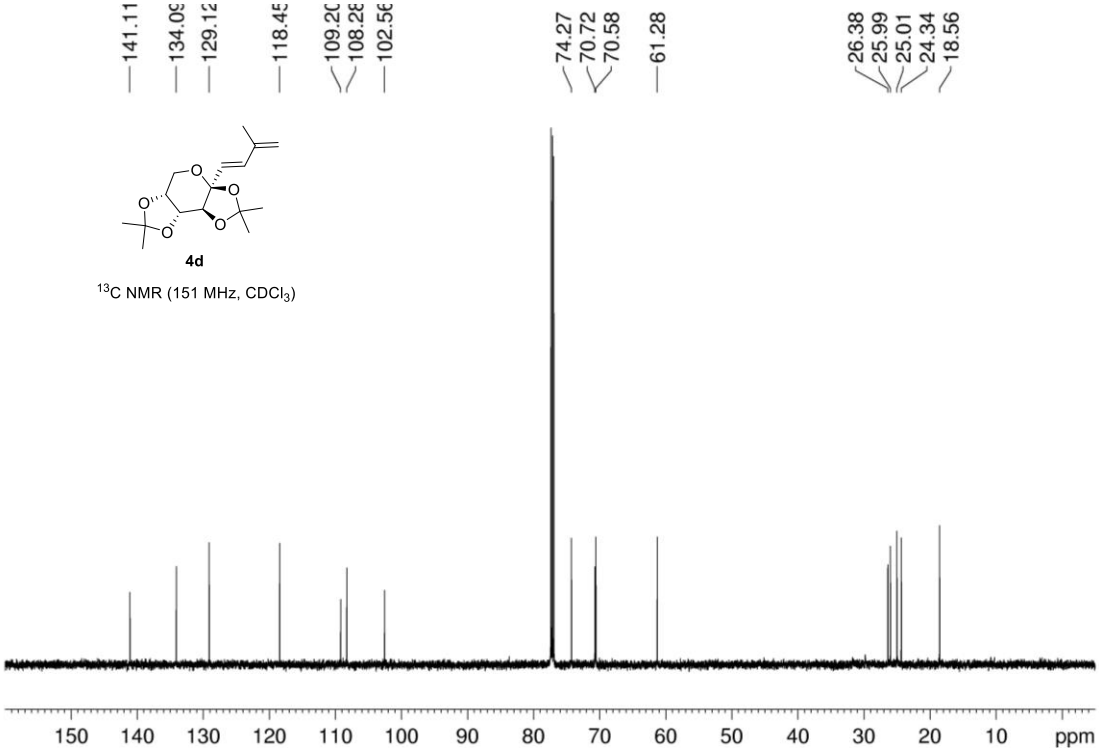


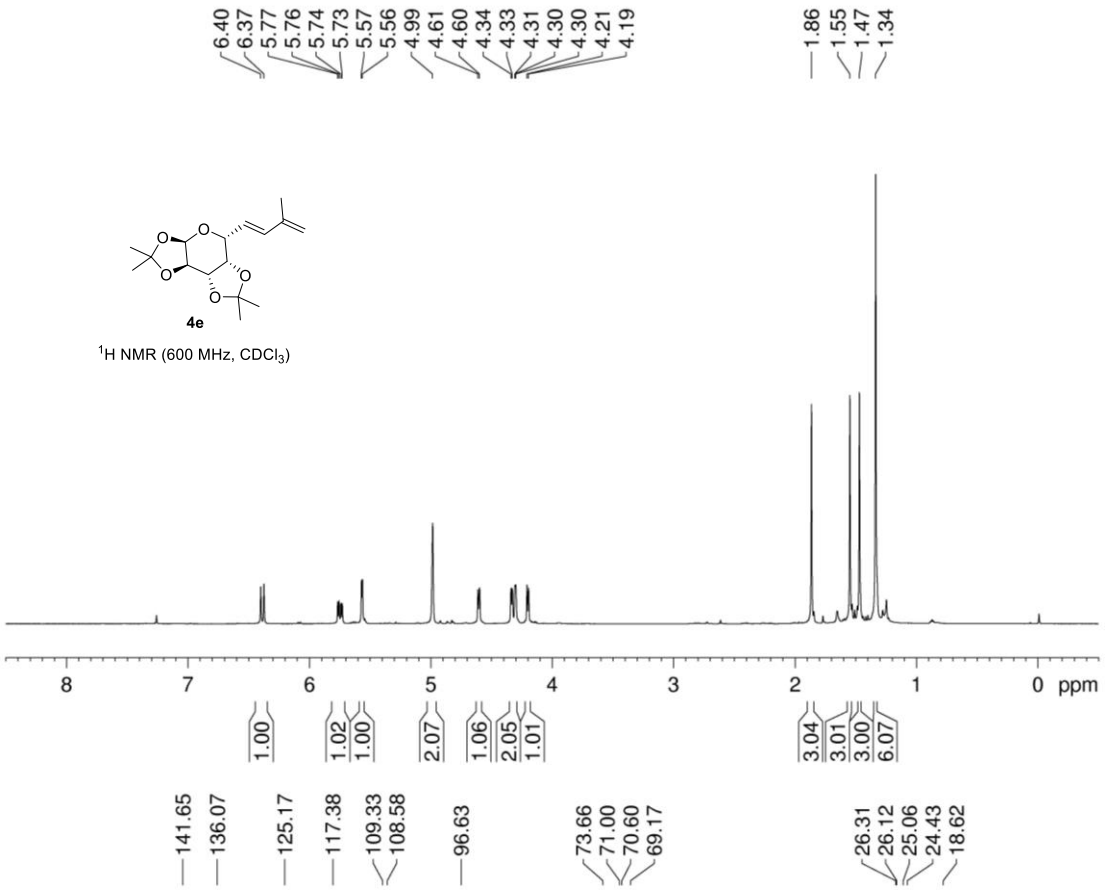
4d

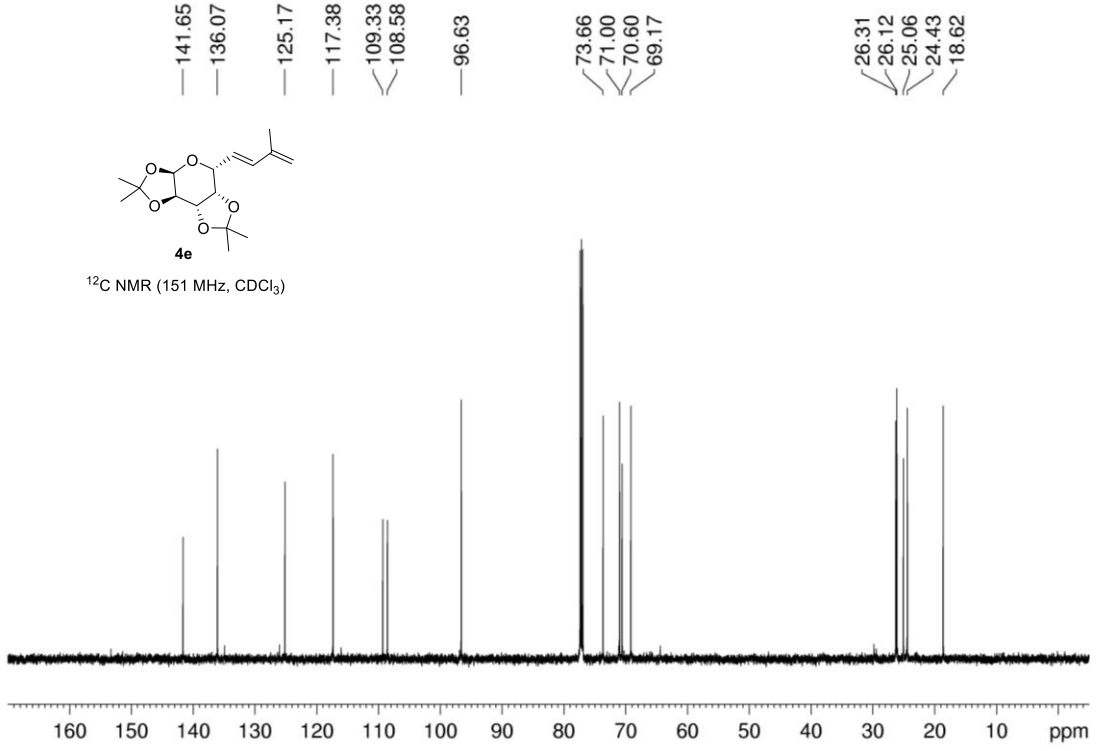
^{1}H NMR (600 MHz, $CDCl_3$)



4d

^{13}C NMR (151 MHz, $CDCl_3$)


6.40
6.37
5.77
5.76
5.74
5.73
5.57
5.56
4.99
4.61
4.60
4.34
4.33
4.31
4.30
4.30
4.21
4.19
1.86
1.55
1.47
1.34
4e
1H NMR (600 MHz, CDCl3)
8
7
6
5
4
3
2
1
0 ppm
1.00
1.02
1.00
2.07
1.06
2.05
1.01
3.04
3.01
3.00
6.07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136.07
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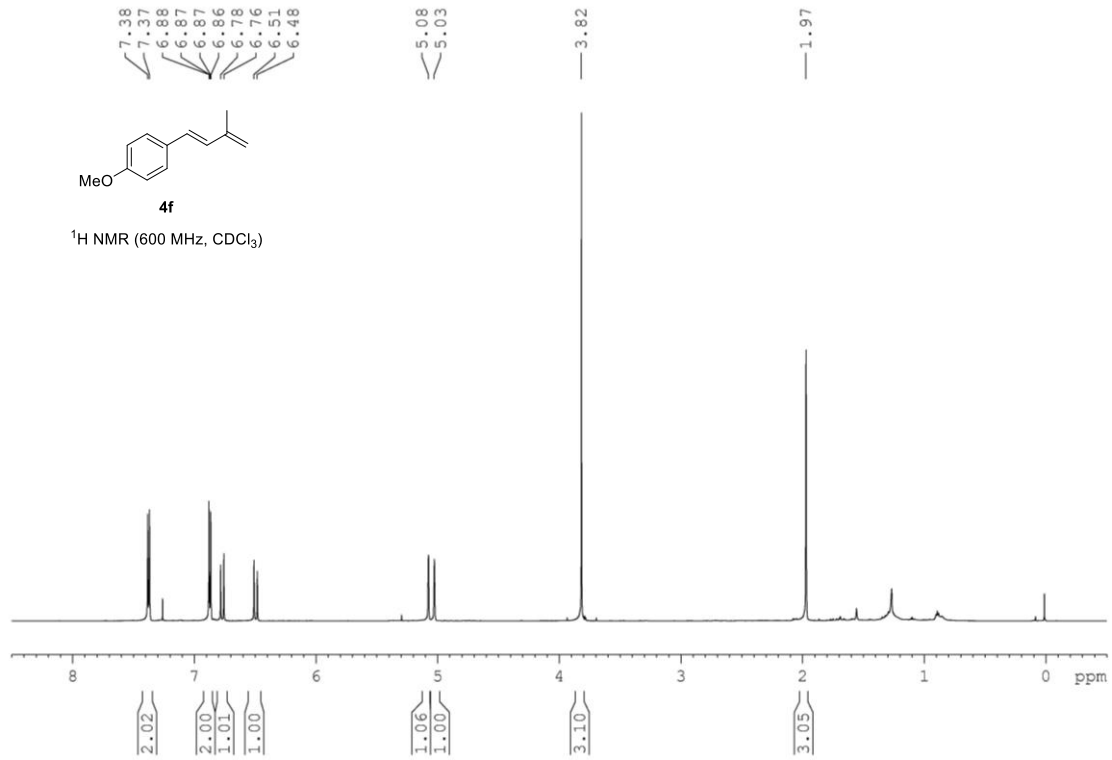
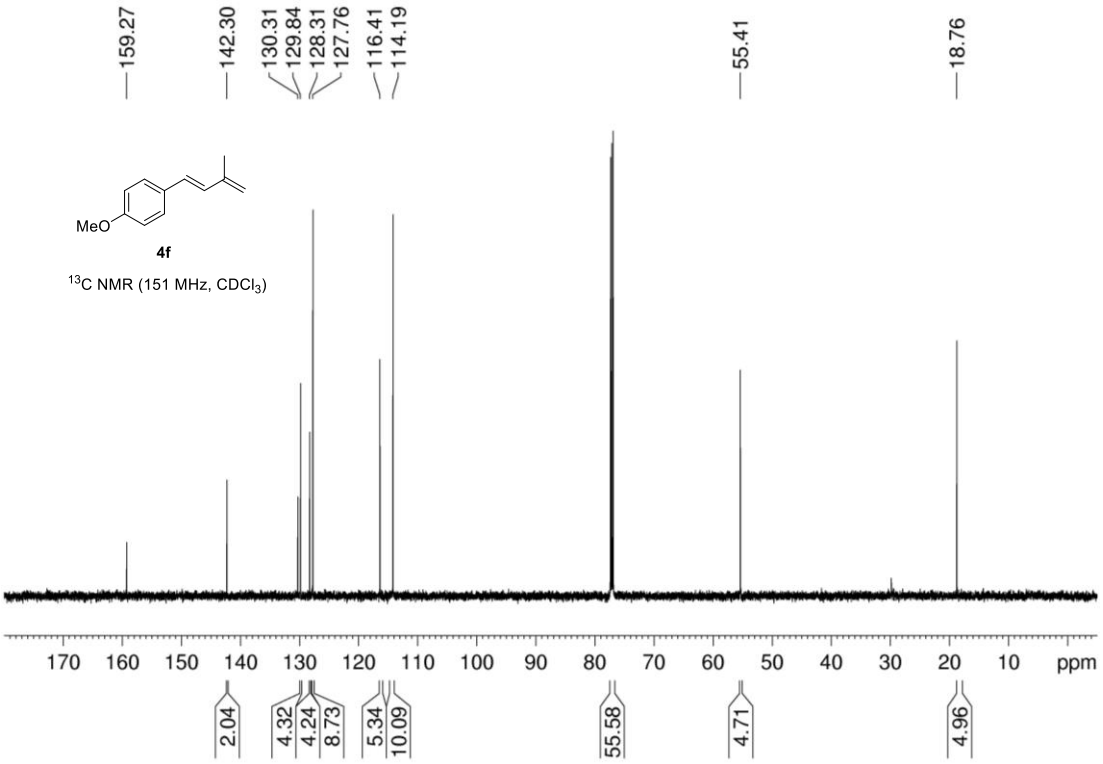
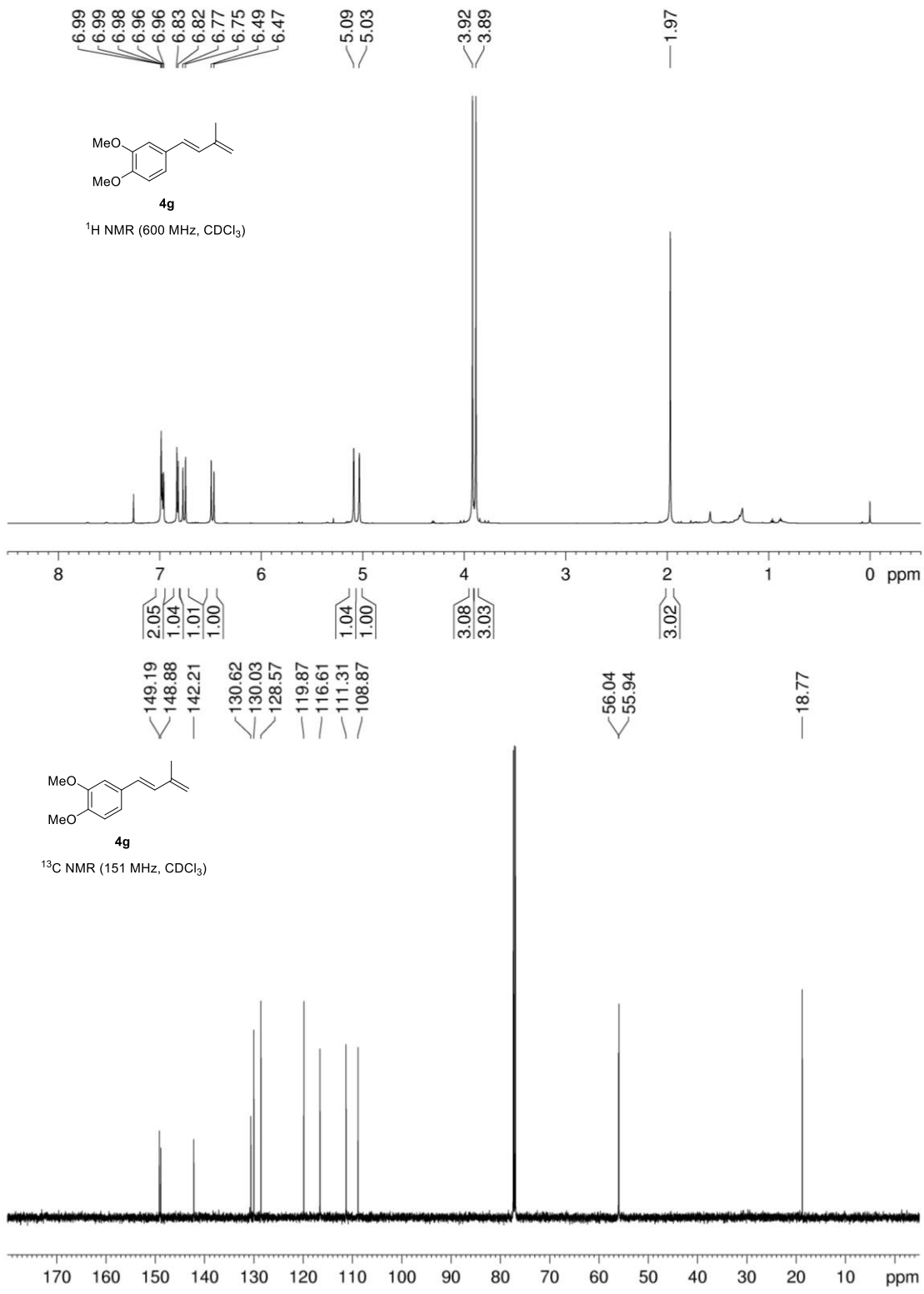
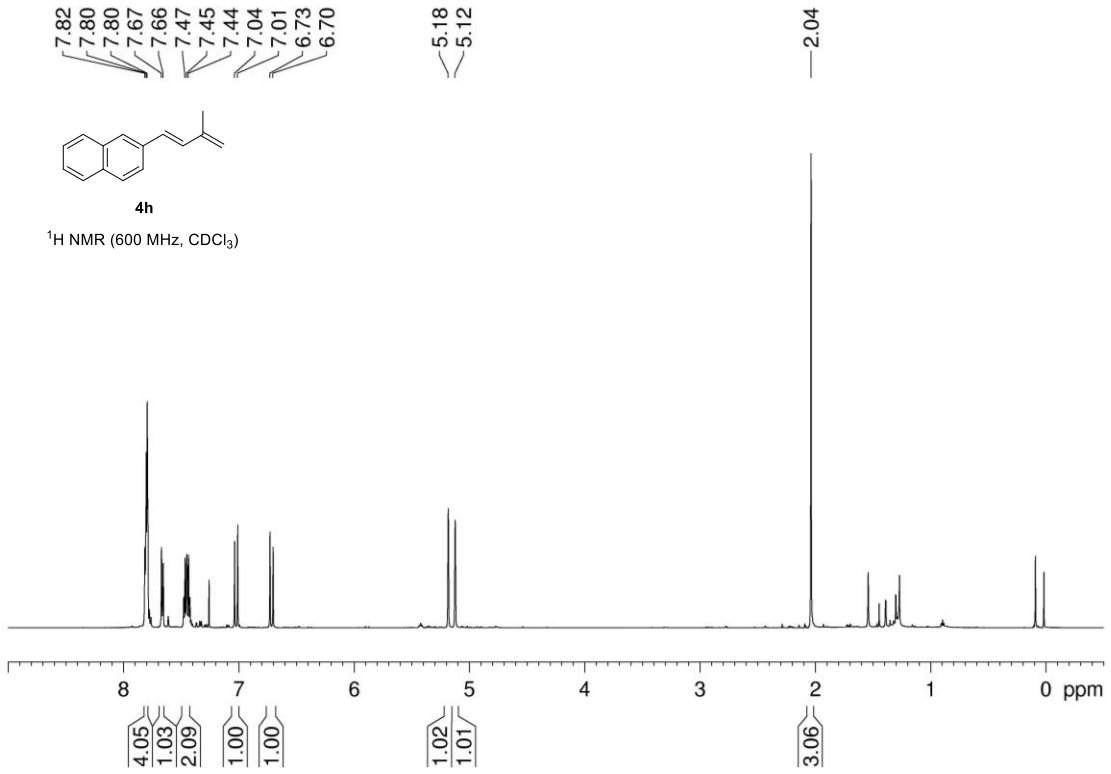
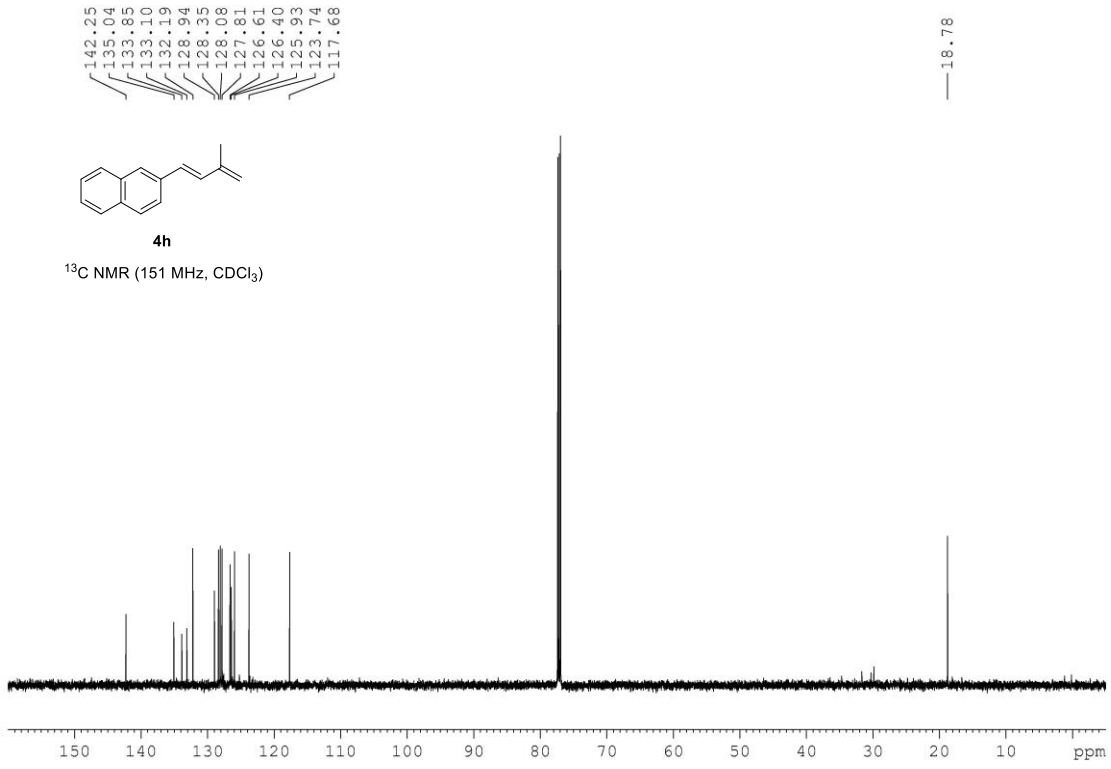
109.33
108.58
96.63
73.66
71.00
70.60
69.17
26.31
26.12
25.06
24.43
18.62
4e
12C NMR (151 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

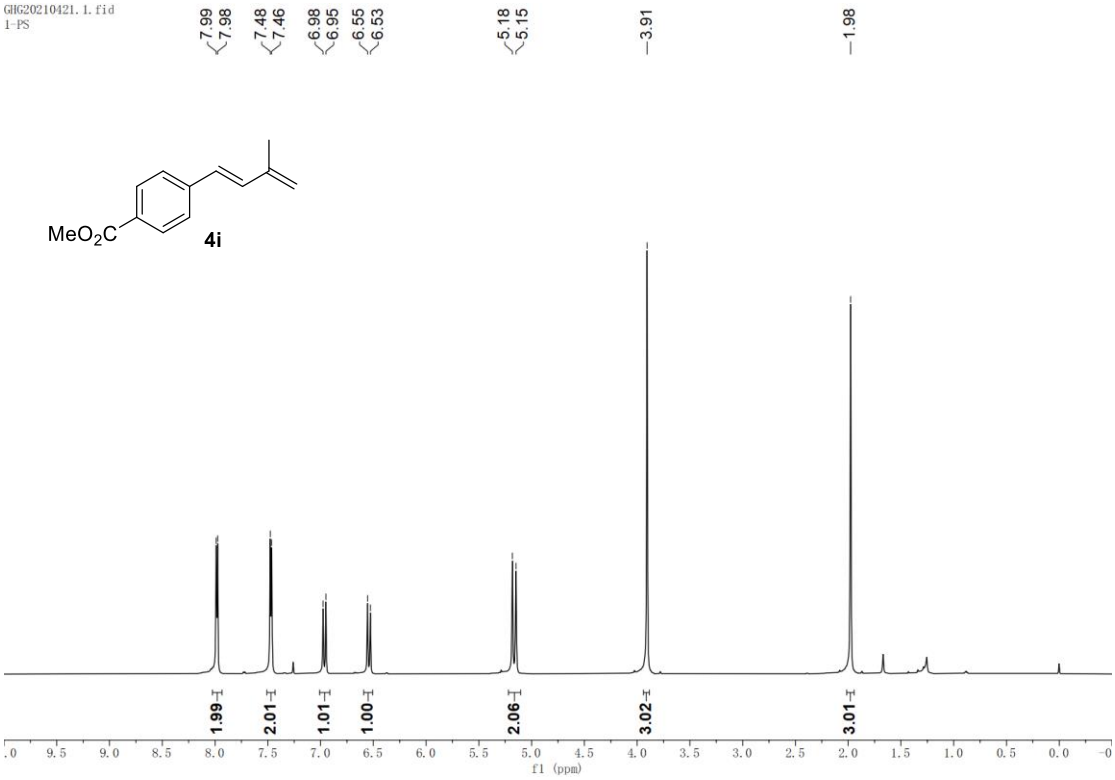

7.38
7.37
6.88
6.87
6.87
6.86
6.78
6.76
6.51
6.48
5.08
5.03
3.82
1.97
MeO
4f
^{1}H NMR (600 MHz, $CDCl_3$)
8
7
6
5
4
3
2
1
0
ppm
2.02
2.00
1.01
1.00
1.06
1.00
3.10
3.05

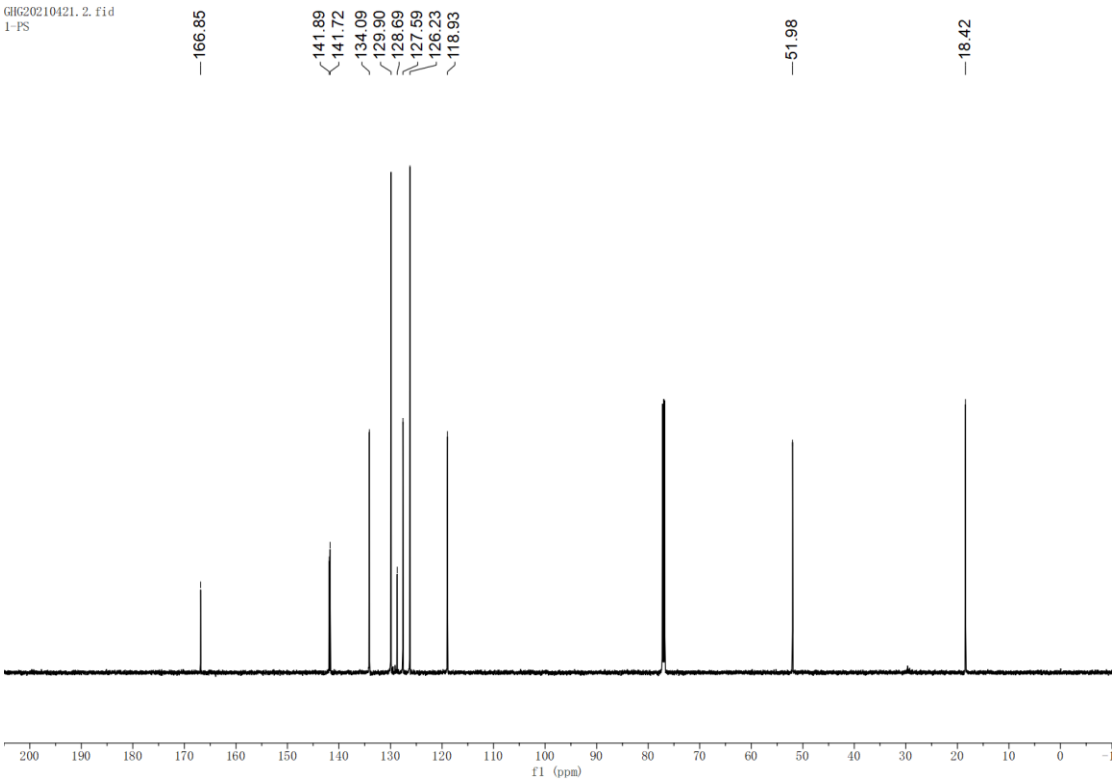

159.27
142.30
130.31
129.84
128.31
127.76
116.41
114.19
55.41
18.76
MeO
4f
^{13}C NMR (151 MHz, $CDCl_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
2.04
4.32
4.24
8.73
5.34
10.09
55.58
4.71
4.96

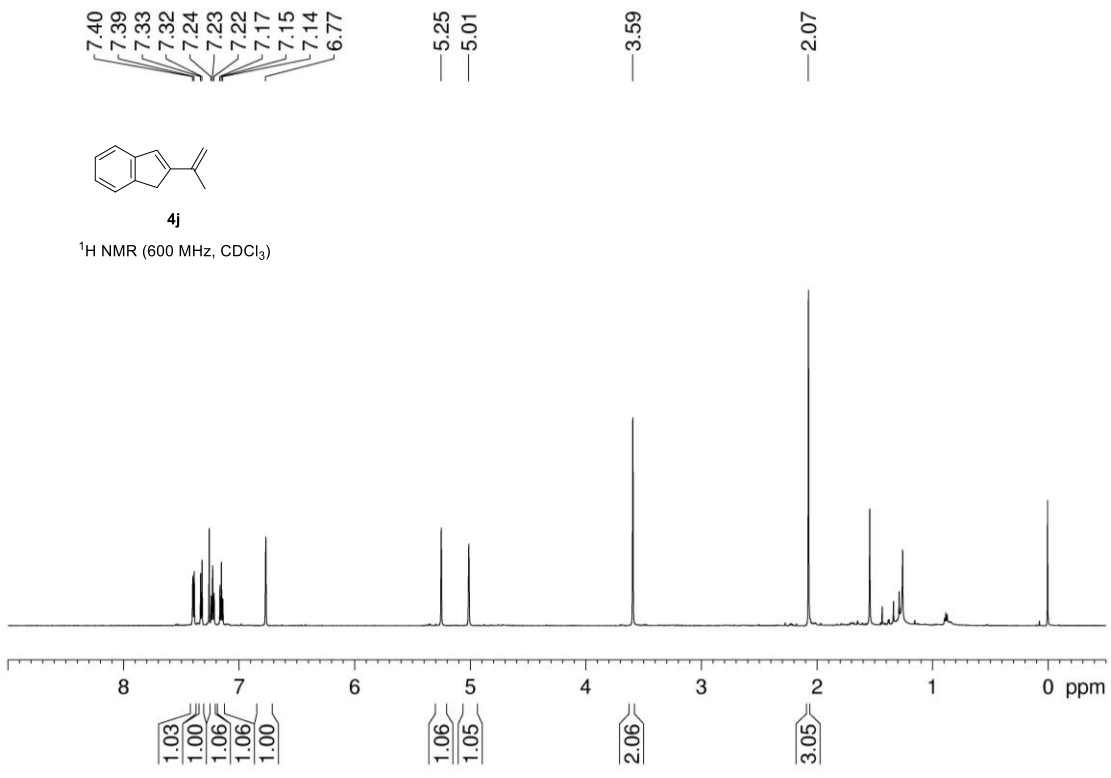

6.99
6.99
6.98
6.96
6.96
6.83
6.82
6.77
6.75
6.49
6.47
5.09
5.03
3.92
3.89
1.97
MeO
MeO
4g
1H NMR (600 MHz, CDCl3)
8
7
6
5
4
3
2
1
0 ppm
2.05
1.04
1.01
1.00
1.04
1.00
3.08
3.03
3.02
149.19
148.88
142.21
130.62
130.03
128.57
119.87
116.61
111.31
108.87
56.04
55.94
18.77
MeO
MeO
4g
13C NMR (151 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.82
7.80
7.80
7.67
7.66
7.47
7.45
7.44
7.04
7.01
6.73
6.70
5.18
5.12
2.04
4h
^{1}H NMR (600 MHz, $CDCl_3$)
8
7
6
5
4
3
2
1
0 ppm
4.05
1.03
2.09
1.00
1.00
1.02
1.01
3.06


142.25
135.04
133.85
133.10
132.19
128.94
128.35
128.08
127.81
126.61
126.40
125.93
123.74
117.68
18.78
4h
^{13}C NMR (151 MHz, $CDCl_3$)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

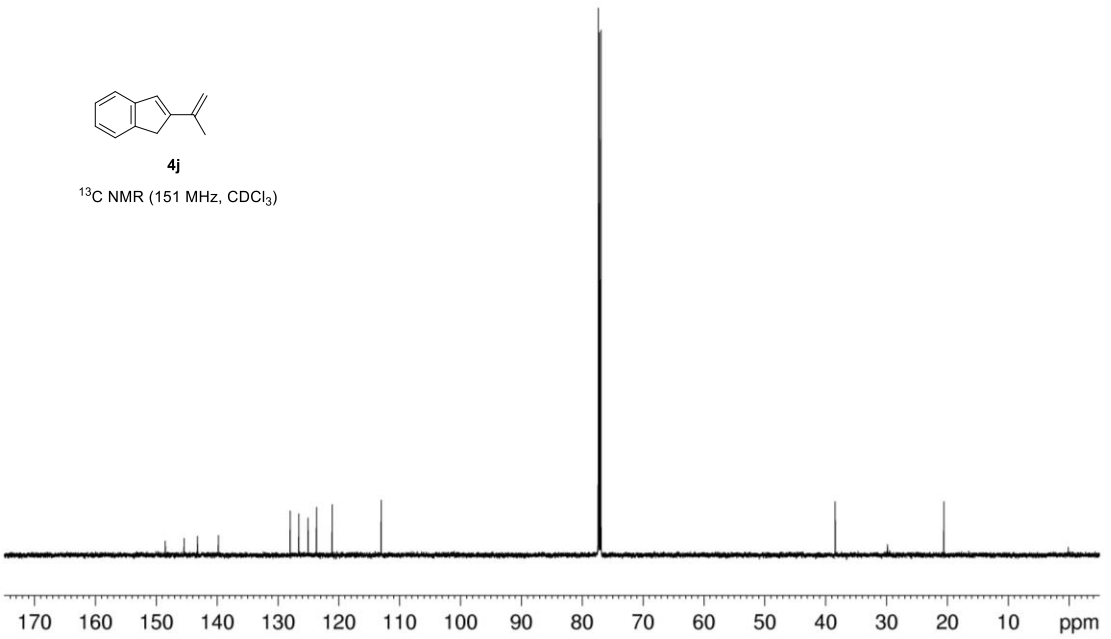

GHG20210421.1.fid
1-PS
7.99
7.98
7.48
7.46
6.98
6.95
6.55
6.53
5.18
5.15
3.91
1.98
MeO2C
4i
1.99
2.01
1.01
1.00
2.06
3.02
3.01
f1 (ppm)


GHG20210421.2.fid
1-PS
166.85
141.89
141.72
134.09
129.90
128.69
127.59
126.23
118.93
51.98
18.42
f1 (ppm)



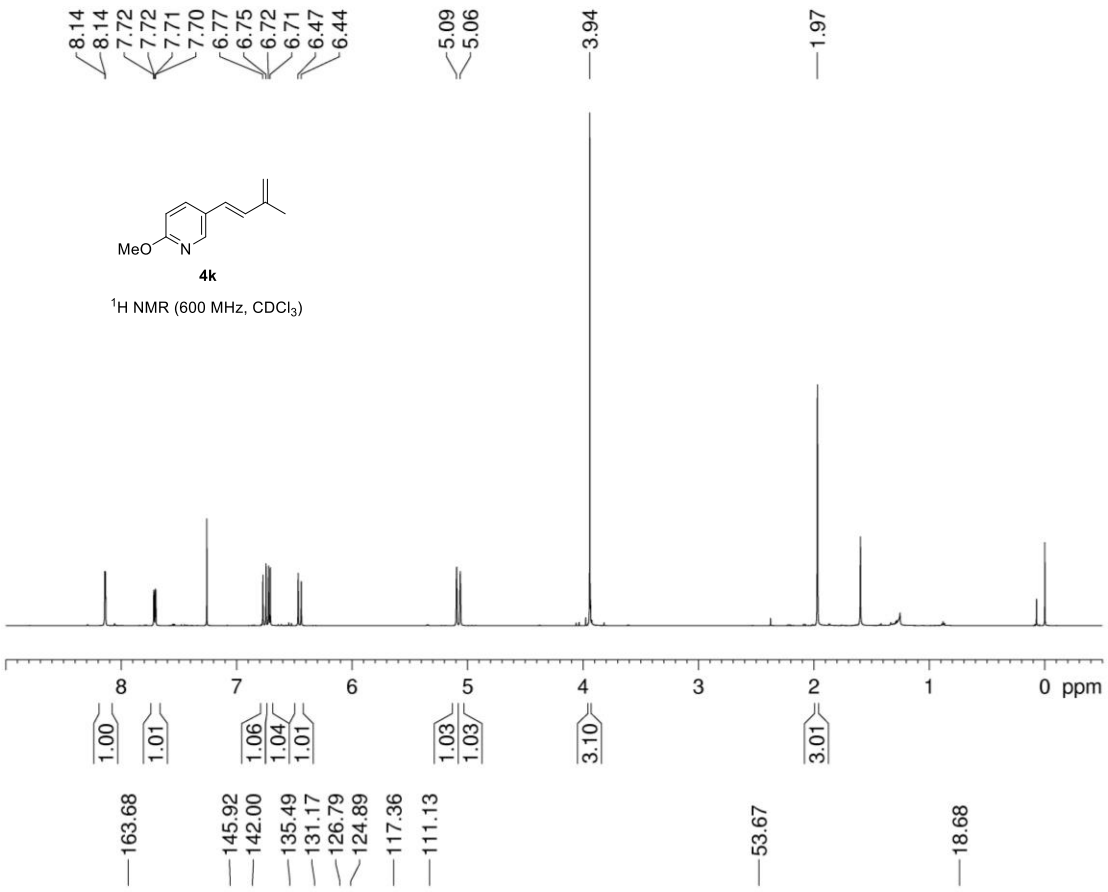
4j

^{1}H NMR (600 MHz, $CDCl_3$)



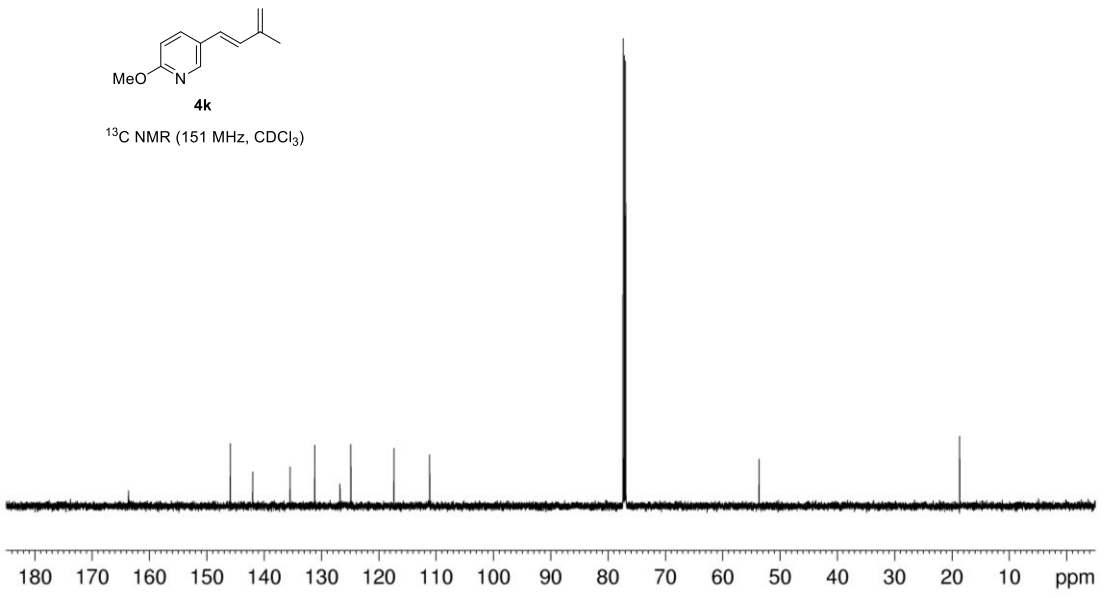
4j

^{13}C NMR (151 MHz, $CDCl_3$)



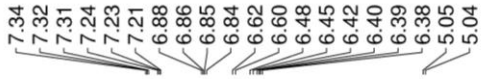
4k

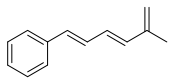
^{1}H NMR (600 MHz, $CDCl_3$)



4k

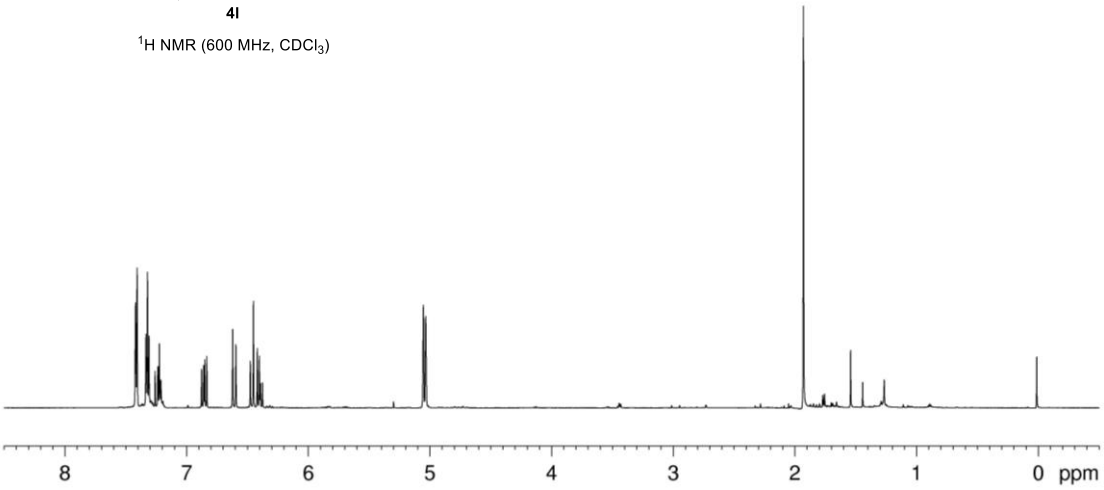
^{13}C NMR (151 MHz, $CDCl_3$)

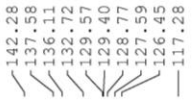


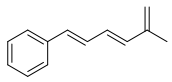


4l

^{1}H NMR (600 MHz, $CDCl_3$)

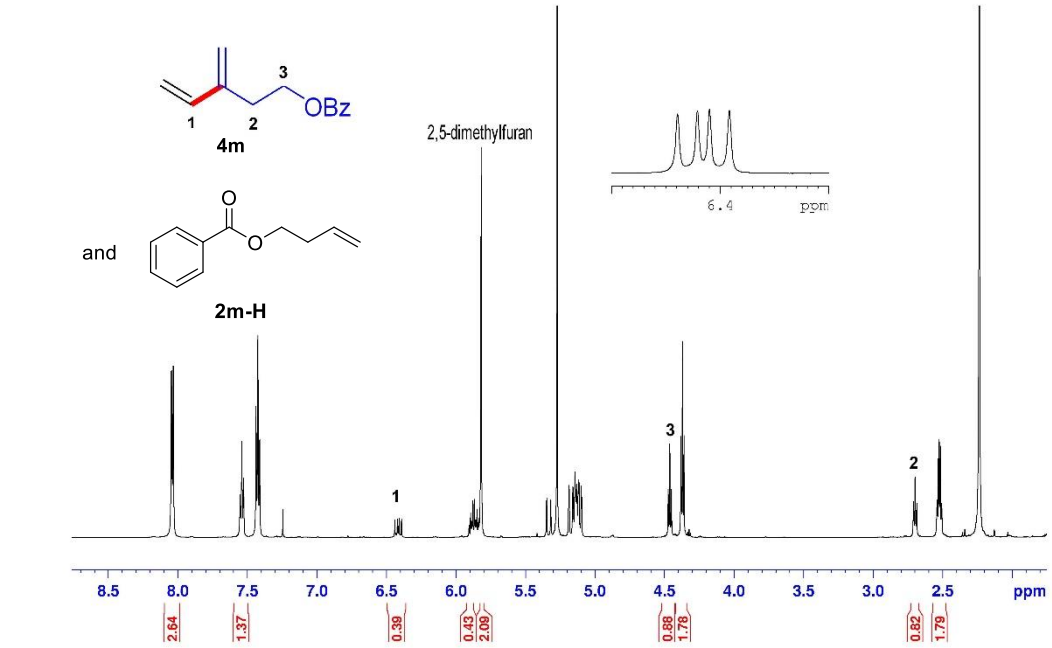


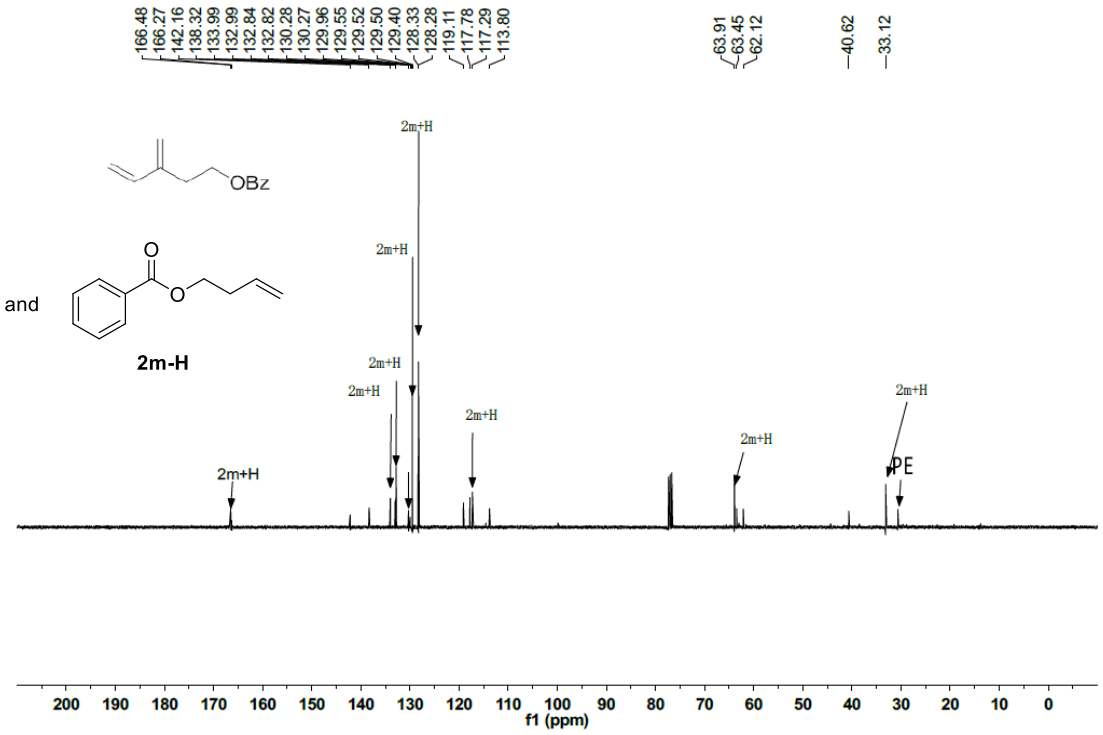




4l

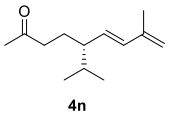
^{13}C NMR (151 MHz, $CDCl_3$)


3
OBz
1
2
4m
and
2m-H
2,5-dimethylfuran
6.4
ppm
1
3
2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
2.64
1.37
0.39
0.43
2.09
0.88
1.78
0.82
1.79


166.48
166.27
142.16
138.32
133.99
132.99
132.84
132.82
130.28
130.27
129.96
129.55
129.52
129.50
129.40
128.33
128.28
119.11
117.78
117.29
113.80
63.91
63.45
62.12
40.62
33.12
OBz
and
2m-H
2m+H
PE

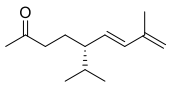
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

LAST 1
single_pulse



4n

^{1}H NMR (400 MHz, $CDCl_3$)



4n

^{13}C NMR (101 MHz, $CDCl_3$)