

Intramolecular [1 + 4 + 1] Cycloaddition: Establishment of the Method

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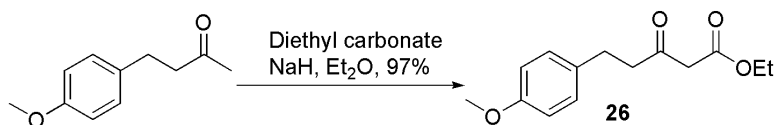
Supporting Information

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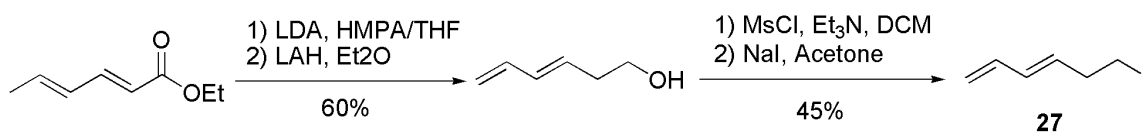
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General:

^1H NMR and ^{13}C NMR spectra were recorded, as solutions in deuteriochloroform (CDCl_3) at 400 MHz and 100 MHz, respectively. ^{13}C multiplicities were determined with the aid of a JVERT pulse sequence, differentiating the signals for methyl and methine carbons as "d" from methylene and quaternary carbons as "u". The infrared (IR) spectra were determined as neat oils. R_f values indicated refer to thin layer chromatography (TLC) on 2.5 x 10 cm, 250 μm analytical plates coated with silica gel GF, unless otherwise noted, and developed in the solvent system indicated. All glassware was oven dried and rinsed with dry solvent before use. THF and diethyl ether were distilled from sodium metal/benzophenone ketyl under dry nitrogen. MTBE is methyl tert-butyl ether and PE is petroleum ether. All reactions were conducted under N_2 and stirred magnetically. Complete ref 8 includes the complete listing for ref 8 of the manuscript with all authors..



To a suspension of NaH (60%, 4.93 g, 123.2 mmol) in dry Et₂O (80 mL) was added diethyl carbonate (9.75 g, 82.6 mmol).¹ The reaction mixture was heated under reflux while methyl ketone (7.13 g, 40.0 mmol) was added over a period of 5 h. Further portions of dry Et₂O were added when the mixture thickened. After stirring for 12 h under reflux, the reaction mixture was quenched with ice water (80 mL) containing glacial acetic acid (20 mL), neutralized with saturated aqueous NaHCO₃ and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield β -ketoester **26** (9.80 g, 97% yield) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.31; ¹H NMR δ 7.05 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.15 (m, 2H), 3.75 (s, 3H), 3.40 (s, 2H), 2.80 (m, 4H), 1.25 (t, 3H); ¹³C NMR δ u 202.1, 167.1, 158.0, 132.6, 61.4, 49.5, 44.8, 28.6; d 129.2, 113.9, 55.2, 14.1.



Following the procedure of Batey,² to a solution of diisopropylamine (20.5 g, 203.0 mmol) in dry THF (180 mL) was added n-BuLi (200 mmol, 83 mL, 2.41 M in hexane) at -10 °C. After stirring at -10 °C for 30 min, the reaction mixture was cooled to -78 °C. HMPA (40 mL) was added and the reaction mixture was stirred at -78 °C for 30 mins. Then ethyl sorbate (14.3 g, 102.1 mmol) was added over a period of 15 min. After

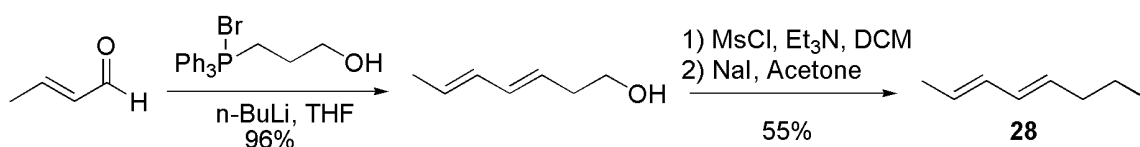
stirring at $-78\text{ }^{\circ}\text{C}$ for 1 h, the reaction mixture was quenched with ice water (200 mL) containing glacial acetic acid (36 mL) and then partitioned between hexane and, sequentially, saturated aqueous NaHCO_3 and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give crude ester.

To a well-stirred suspension of LAH (8.0 g, 210.5 mmol) in dry Et_2O (180 mL) was added a solution of the above crude ester in Et_2O at $0\text{ }^{\circ}\text{C}$ over a period of 10 min. After stirring at rt overnight, the reaction mixture was quenched with saturated aqueous potassium sodium tartrate (50 mL) and then, after filtration, partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alcohol (6.0 g, 60% yield from ethyl sorbate) as a colorless oil: TLC $R_f(\text{CH}_2\text{Cl}_2) = 0.31$;

To a stirred solution of alcohol (6.0 g, 61.2 mmol) in dry CH_2Cl_2 (100 mL) were sequentially added Et_3N (12.4 g, 123 mmol) and mesyl chloride (14.1 g, 123 mmol) at $0\text{ }^{\circ}\text{C}$. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the crude mesylate.

To a stirred solution of the above crude mesylate in acetone (150 mL) was added NaI (27.5 g, 183 mmol) and copper powder (120 mg, 1.89 mmol) at rt. The reaction mixture was stirred at reflux for 2 h. After cooling to rt, the reaction mixture was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) and then partitioned between CH_2Cl_2 and,

sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was filtered through a pad of silica gel to yield iodide **27** (5.75 g, 27% yield from ethyl sorbate) as a pale yellow oil: TLC $R_f(\text{CH}_2\text{Cl}_2) = 0.85$; $^1\text{H NMR } \delta$ 6.25 (m, 1H), 6.05 (m, 1H), 5.55 (m, 1H), 5.10 (d, $J = 16$ Hz, 1H), 4.95 (d, $J = 12$ Hz, 1H), 3.05 (t, $J = 8$ Hz, 2H), 2.60 (m, 2H); $^{13}\text{C NMR } \delta$ u 116.6, 36.6, 4.7; d 136.6, 133.2, 132.6.

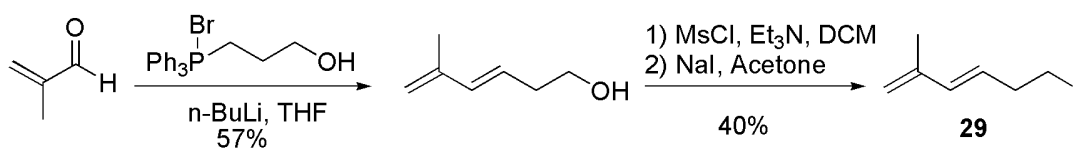


To a suspension of (3-hydroxy propyl) triphenylphosphonium bromide (22.5 g, 56.2 mmol) in dry THF (100 mL) was added $n\text{-BuLi}$ (106 mmol, 43 mL, 2.47 M in hexane) at $0\text{ }^\circ\text{C}$.³ After stirring at $0\text{ }^\circ\text{C}$ for 30 min, a solution of crotonaldehyde (3.30 g, 47.1 mmol) in dry THF (5 ml) was added and the reaction mixture was stirred for another 1 h at $0\text{ }^\circ\text{C}$. The reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alcohol (5.10 g, 96% yield) as a colorless oil : TLC $R_f(\text{CH}_2\text{Cl}_2) = 0.28$;

To a stirred solution of the above alcohol (5.10 g, 45.5 mmol) in dry CH_2Cl_2 (50 mL) were sequentially added Et_3N (9.20 g, 91.1 mmol) and mesyl chloride (10.4 g, 90.4 mmol) at $0\text{ }^\circ\text{C}$. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the

crude mesylate.

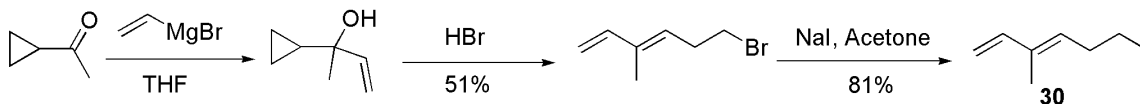
To a stirred solution of the above crude mesylate in acetone (150 mL) was added NaI (23.8 g, 159 mmol) and copper powder (110 mg, 1.73 mmol) at rt. The reaction mixture was stirred at reflux for 2 h. After cooling to rt, the reaction mixture was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (80 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was filtered through a pad of silica gel to yield iodide **28** (5.60 g, 53% yield from crotonaldehyde) as a pale yellow oil: TLC R_f (20% MTBE/PE) = 0.83; ^1H NMR δ 5.90-6.10 (m, 2H), 5.65 (m, 1H), 5.45 (m, 1H), 3.15 (t, J = 8 Hz, 2H), 2.60 (m, 2H), 1.70 (d, J = 8 Hz, 3H); ^{13}C NMR (major isomer) δ u 36.7, 5.4; d 132.7, 131.1, 129.2, 128.9, 18.2.



To a suspension of (3-hydroxy propyl) triphenylphosphonium bromide (24.5 g, 61.1 mmol) in dry THF (100 mL) was added $n\text{-BuLi}$ (115 mmol, 49 mL, 2.35 M in hexane) at $0\text{ }^\circ\text{C}$.³ After stirring at $0\text{ }^\circ\text{C}$ for 30 min, a solution of methacrolein (85%, 4.15 g, 50.4 mmol) in dry THF (5 ml) was added and the reaction mixture was stirred for another 1 h at $0\text{ }^\circ\text{C}$. The reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alcohol (3.20 g, 57% yield) as a colorless oil: TLC R_f (CH_2Cl_2) = 0.27;

To a stirred solution of above alcohol (3.20 g, 28.6 mmol) in dry CH₂Cl₂ (50 mL) were sequentially added Et₃N (5.84 g, 57.8 mmol) and mesyl chloride (6.66 g, 58.1 mmol) at 0 °C. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (50 mL) and then partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated to give the crude mesylate.

To a stirred solution of the above crude mesylate in acetone (150 mL) was added NaI (12.0 g, 80 mmol) and copper powder (55 mg, 0.87 mmol) at rt. The reaction mixture was stirred at reflux for 2 h. After cooling to rt, the reaction mixture was quenched with saturated aqueous Na₂S₂O₃ (80 mL) and then partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was filtered through a pad of silica gel to yield iodide **29** (2.55 g, 23% yield from methacrolein) as a pale yellow oil: TLC *R_f* (CH₂Cl₂) = 0.86; ¹H NMR δ 6.20 (d, *J* = 16 Hz, 1H), 5.55 (m, 1H), 4.95 (d, *J* = 8 Hz, 2H), 3.15 (t, *J* = 8 Hz, 2H), 2.65 (m, 2H), 1.85 (s, 3H); ¹³C NMR δ u 141.6, 115.9, 36.8, 5.1; d 135.2, 128.4, 18.6.

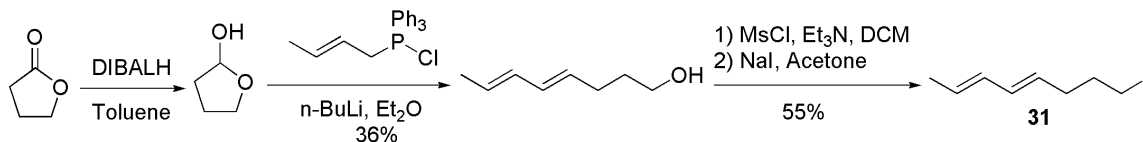


To a stirred solution of cyclopropyl methyl ketone (4.23 g, 50.4 mmol) in dry THF (50 mL) was added vinyl magnesium bromide (55 mmol, 55 mL, 1 M in THF) at -10 °C.⁴ Then the reaction mixture was allowed to warm to rt. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (10 mL) and then

partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated to give the crude allylic alcohol.

To a stirred solution of the above crude allylic alcohol in PE/H₂O (5 mL / 15 mL) was added aqueous HBr (48%, 30 mL) at 0 °C over a period of 5 min. After stirring at 0 °C for 1 h, the reaction mixture was partitioned between PE and, sequentially, water, saturated aqueous NaHCO₃ and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was subject to bulb-to-bulb distillation to yield the bromide (4.50 g, 51% yield from cyclopropyl methyl ketone) as a pale yellow oil (bp = 70 ~ 75 °C, 1 Torr) : TLC R_f (5% MTBE/PE) = 0.81;

To a stirred solution of the above bromide (4.20 g, 24 mmol) in acetone (100 mL) was added NaI (10.9 g, 72.3 mmol) and copper powder (50 mg, 0.78 mmol) at rt. The reaction mixture was stirred at reflux for 45 min. After cooling to rt, the reaction mixture was quenched with saturated aqueous Na₂S₂O₃ (80 mL) and then partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was filtered through a pad of silica gel to yield iodide **30** (4.31 g, 41% yield from cyclopropyl methyl ketone, a ~ 3 : 1 mixture) as a pale yellow oil: TLC R_f (CH₂Cl₂) = 0.86; ¹H NMR δ 6.35 (dd, J = 12 Hz, 1H), 5.40 (t, J = 8 Hz, 1H), 5.15 (d, J = 16 Hz, 1H), 5.00 (d, J = 12 Hz, 1H), 3.10 (t, J = 8 Hz, 2H), 2.70 (m, 2H), 1.70 (s, 3H); ¹³C NMR (major isomer) δ u 136.1, 112.1, 32.5, 4.8; d 140.9, 130.6, 12.0.



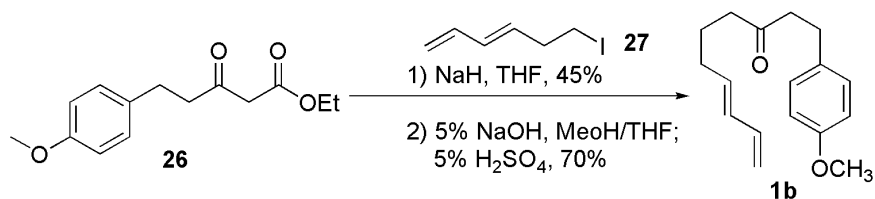
To a stirred solution of gamma-butyrolactone (4.40 g, 51.2 mmol) in toluene (45 mL) was added DIBALH (54.0 mmol, 45 mL, 1.2 M in toluene) at $-78\text{ }^{\circ}\text{C}$.⁵ The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$ for 2 h. Then the reaction mixture was quenched with saturated aqueous NH_4Cl (30 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the crude lactol.

To a suspension of (2-butenyl) triphenylphosphonium chloride (23.0 g, 65.2 mmol) in dry Et_2O (150 mL) was added n-BuLi (61.1 mmol, 26 mL, 2.35 M in hexane) at $0\text{ }^{\circ}\text{C}$. After stirring at $0\text{ }^{\circ}\text{C}$ for 15 min, a solution of the above lactol in dry Et_2O (5 mL) was added over a period of 5 min. Then after stirring for another 30 min at $0\text{ }^{\circ}\text{C}$, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alcohol (2.31 g, 36% yield from gamma-butyrolactone) as a colorless oil : TLC $R_f(\text{CH}_2\text{Cl}_2) = 0.23$;

To a stirred solution of above alcohol (2.30 g, 18.3 mmol) in dry CH_2Cl_2 (50 mL) were sequentially added Et_3N (3.65 g, 36.1 mmol) and mesyl chloride (4.14 g, 36.2 mmol) at $0\text{ }^{\circ}\text{C}$. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the

crude mesylate.

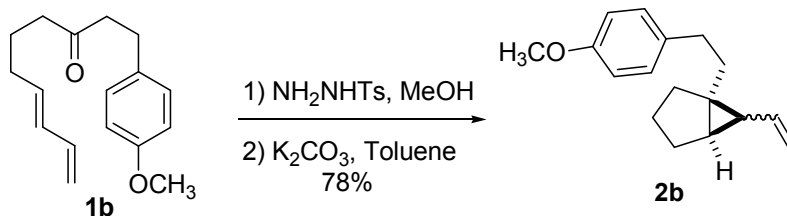
To a stirred solution of the above crude mesylate in acetone (100 mL) was added NaI (7.30 g, 48.7 mmol) and copper powder (40 mg, 0.63 mmol) at rt. The reaction mixture was stirred at reflux for 2 h. After cooling to rt, the reaction mixture was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (80 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was filtered through a pad of silica gel to yield iodide **31** (2.39 g, 20% yield from gamma-butyrolactone, a ~ 5 : 1 mixture) as a pale yellow oil: TLC R_f (CH_2Cl_2) = 0.87; ^1H NMR δ 5.90-6.10 (m, 2H), 5.60 (m, 1H), 5.45 (m, 1H), 3.15 (t, J = 8 Hz, 2H), 2.15 (m, 2H), 1.90 (m, 2H), 1.75 (d, J = 8 Hz, 3H); ^{13}C NMR (major isomer) δ u 33.1, 32.9, 6.4; d 131.8, 131.3, 129.1, 127.7, 18.0.



To a suspension of NaH (60%, 243 mg, 6.07 mmol) in dry THF (10 mL) was added a solution of β -ketoester **26** (1.26 g, 5.03 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **27** (2.12 g, 10.2 mmol) in dry THF (3 mL) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed

to yield alkylated β -ketoester (749 mg, 45% yield) as a colorless oil : TLC R_f (20% MTBE/PE) = 0.67;

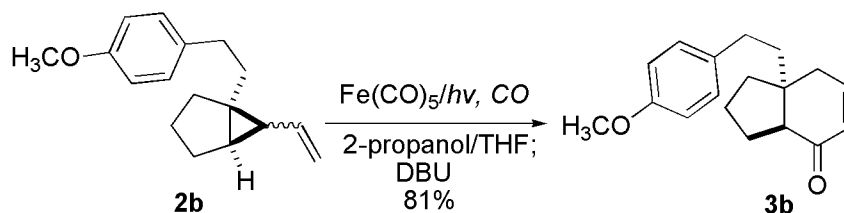
A suspension of the above alkylated β -ketoester (749 mg, 2.27 mmol) and 5% aqueous NaOH (10 mL) in MeOH/THF (10 mL/10 mL) was stirred at 70 °C for 40 min. After cooling to rt, the reaction mixture was diluted with H₂O (10 mL) and the organic solvent was removed at reduced pressure. Then the aqueous residue was neutralized with 5% H₂SO₄ and partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield **1b** (412 mg, 32% yield from β -ketoester) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.71; IR (cm⁻¹) 2828, 1707, 1609, 1240; ¹H NMR δ 7.00 (d, J = 8 Hz, 2H), 6.75 (d, J = 8 Hz, 2H), 6.20 (m, 1H), 5.95 (m, 1H), 5.50 (m, 1H), 5.00 (d, J = 16 Hz, 1H), 4.90 (d, J = 8 Hz, 1H), 3.70 (s, 3H), 2.75 (t, J = 8 Hz, 2H), 2.60 (t, J = 8 Hz, 2H), 2.30 (t, J = 8 Hz, 2H), 1.95 (m, 2H), 1.55 (m, 2H); ¹³C NMR δ u 210.1, 158.0, 133.2, 115.2, 44.6, 42.2, 31.8, 28.9, 23.0; d 137.1, 134.1, 131.8, 129.2, 113.9, 55.3; HRMS calcd for C₁₇H₂₂O₂Na (MNa⁺) 281.1517, obsd 281.1510.



Ketone **1b** (291 mg, 1.13 mmol) and tosylhydrazine (435 mg, 2.34 mmol) were stirred in MeOH (5 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the

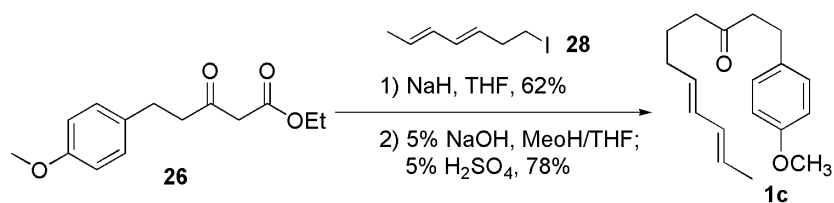
hydrazone : TLC R_f (40% MTBE/PE) = 0.67;

The hydrazone was redissolved in toluene (5 mL), K_2CO_3 (970 mg, 7.03 mmol) was added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 14 h. After cooling to rt, the reaction mixture was partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2b** (213 mg, 78% yield, a ~ 3 : 2 mixture) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.67; IR (cm^{-1}) 3429, 2828, 1614, 1506; 1H NMR δ 7.05 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 5.50-5.70 (m, 1H), 5.05 (d, J = 16 Hz, 1H), 4.90 (d, J = 12 Hz, 1H), 3.75 (s, 3H), 2.60 (m, 2H), 1.60-1.95 (m, 5H), 1.60 (m, 2H), 1.05-1.40 (m, 3H); ^{13}C NMR (major isomer) δ u 157.7, 135.2, 113.0, 40.1, 34.3, 33.3, 32.7, 27.7, 21.6; d 138.2, 129.2, 113.7, 55.3, 31.9, 27.5; HRMS calcd for $C_{17}H_{22}O$ (M^+) 242.1671, obsd 242.1682.



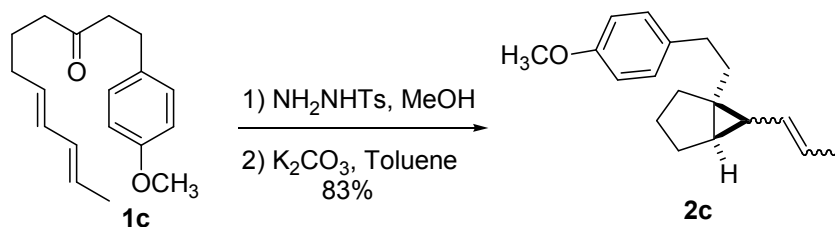
To a solution of alkenyl cyclopropane **2b** (65 mg, 0.27 mmol) in 2-propanol/THF (4 mL/4 mL) was added $Fe(CO)_5$ (107 mg, 0.546 mmol) and K_2CO_3 (2.0 g).⁶ The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 14 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, DBU (82 mg, 0.54 mmol) was added, and the

mixture was stirred at rt for 1 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2b** (27 mg) and cyclohexenone **3b** (34 mg, 81% yield based on starting material not recovered) as a colorless oil: TLC R_f (20% MTBE/ PE) = 0.47; IR (cm^{-1}) 3405, 2936, 1664, 1508, 1240; ^1H NMR δ 7.05 (d, J = 8 Hz, 2H), 6.80 (m, 3H), 6.00 (d, J = 12 Hz, 1H), 3.75 (s, 3H), 2.50 (m, 2H), 2.30-2.40 (m, 3H), 2.05 (m, 1H), 1.90 (m, 1H), 1.70-1.85 (m, 3H), 1.50-1.70 (m, 3H); ^{13}C NMR δ 201.8, 157.8, 134.3, 48.1, 41.3, 37.2, 31.8, 30.8, 28.7, 22.2; d 147.5, 129.0, 127.8, 113.9, 56.1, 55.3; HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2$ (MH^+) 271.1698, obsd 271.1707.



To a suspension of NaH (60%, 197 mg, 4.92 mmol) in dry THF (10 mL) was added a solution of β -ketoester **26** (1.02 g, 4.08 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **28** (1.82 g, 8.20 mmol) in dry THF (3 mL) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkylated β -ketoester (870 mg, 62% yield) as a colorless oil : TLC R_f (20% MTBE/PE) = 0.69;

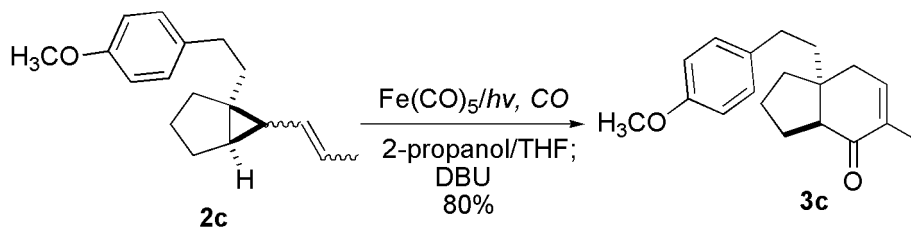
A suspension of the above alkylated β -ketoester (870 mg, 2.53 mmol) and 5% aqueous NaOH (10 mL) in MeOH/THF (10 mL/10 mL) was stirred at 70 °C for 40 min. After cooling to rt, the reaction mixture was diluted with H₂O (10 mL) and the organic solvent was removed at reduced pressure. Then the aqueous residue was neutralized with 5% H₂SO₄ and partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield **1c** (538 mg, 48% yield from β -ketoester) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.78; IR (cm⁻¹) 3489, 2926, 1707, 1246; ¹H NMR δ 7.05 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 5.90-6.05 (m, 2H), 5.55 (m, 1H), 5.45 (m, 1H), 3.75 (s, 3H), 2.80 (t, J = 8 Hz, 2H), 2.65 (t, J = 8 Hz, 2H), 2.35 (t, J = 8 Hz, 2H), 2.00 (m, 2H), 1.70 (d, J = 8 Hz, 3H), 1.60 (m, 2H); ¹³C NMR (major isomer) δ u 210.2, 158.0, 133.2, 44.6, 42.2, 31.9, 28.9, 23.3; d 131.5, 131.2, 130.7, 129.2, 127.3, 113.8, 55.3, 13.3; HRMS calcd for C₁₈H₂₅O₂ (MH⁺) 273.1855, obsd 273.1856.



Ketone **1c** (208 mg, 0.76 mmol) and tosylhydrazine (292 mg, 1.57 mmol) were stirred in MeOH (5 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC R_f (40% MTBE/PE) = 0.65;

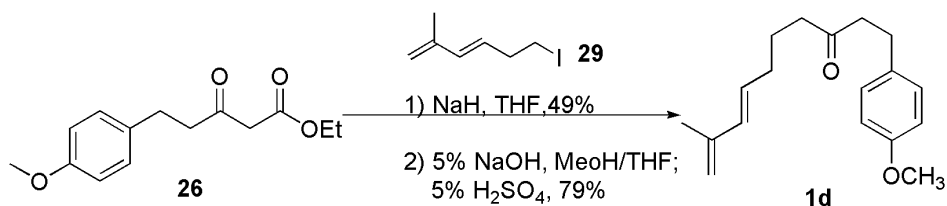
The hydrazone was redissolved in toluene (5 mL), K₂CO₃ (632 mg, 4.58 mmol) was

added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 13 h. After cooling to rt, the reaction mixture was partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2c** (162 mg, 83% yield) as a colorless oil: TLC *R_f* (5% MTBE/ PE) = 0.69; IR (cm⁻¹) 3429, 1638, 1245; ¹H NMR δ 7.05 (d, *J* = 8 Hz, 2H), 6.80 (d, *J* = 8 Hz, 2H), 5.50 (m, 1H), 5.20 (m, 1H), 3.80 (s, 3H), 2.60 (m, 2H), 1.50-1.90 (m, 10H), 1.00-1.30 (m, 3H); ¹³C NMR (major isomer) δ u 157.6, 135.3, 40.2, 34.3, 33.3, 32.6, 27.8, 21.7; d 130.4, 129.2, 123.9, 113.6, 55.3, 31.3, 26.1, 18.1; HRMS calcd for C₁₈H₂₄O (M⁺) 256.1827, obsd 256.1835.



To a solution of alkenyl cyclopropane **2c** (40 mg, 0.16 mmol) in 2-propanol/THF (4 mL/4 mL) was added Fe(CO)₅ (65 mg, 0.33 mmol) and K₂CO₃ (2.0 g). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 13 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, DBU (49 mg, 0.32 mmol) was added, and the mixture was stirred at rt for 2 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2c** (19 mg) and cyclohexenone **3c** (19 mg, 80% yield

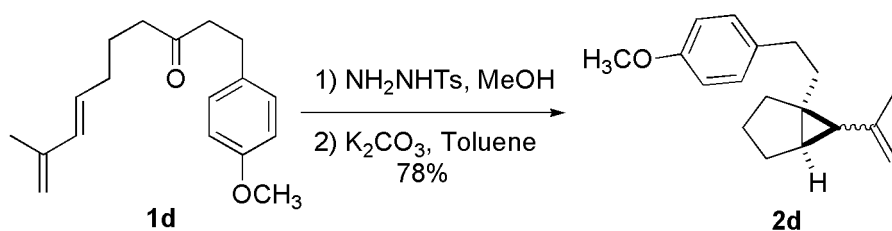
based on starting material not recovered) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.28; IR (cm^{-1}) 3439, 1643; ^1H NMR δ 7.05 (d, $J = 8$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 6.50 (m, 1H), 3.75 (s, 3H), 2.50 (t, $J = 8$ Hz, 2H), 2.40 (t, $J = 8$ Hz, 1H), 2.30 (m, 2H), 2.05 (m, 1H), 1.90 (m, 1H), 1.80 (s, 3H), 1.50-1.80 (m, 4H), 1.20 (t, $J = 8$ Hz, 2H); ^{13}C NMR δ u 201.8, 157.8, 134.5, 133.4, 48.5, 41.3, 37.3, 31.7, 30.8, 29.0, 22.3; d 142.4, 129.1, 113.8, 56.3, 55.3, 15.9; HRMS calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$ (MH^+) 285.1855, obsd 285.1858.



To a suspension of NaH (60%, 249 mg, 6.23 mmol) in dry THF (10 mL) was added a solution of β -ketoester **26** (1.24 g, 4.96 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **29** (2.35 g, 10.6 mmol) in dry THF (3 mL) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkylated β -ketoester (835 mg, 49% yield) as a colorless oil : TLC R_f (20% MTBE/PE) = 0.67;

A suspension of the above alkylated β -ketoester (835 mg, 2.43 mmol) and 5% aqueous NaOH (10 mL) in MeOH/THF (10 mL/10 mL) was stirred at 70 $^\circ\text{C}$ for 40 min. After

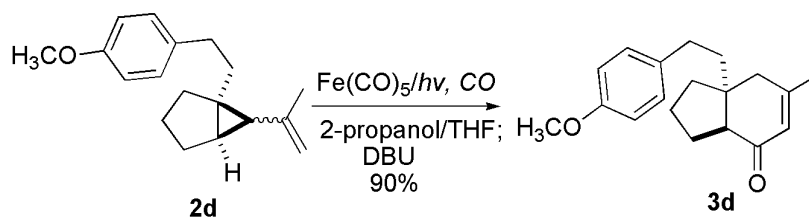
cooling to rt, the reaction mixture was diluted with H₂O (10 mL) and the organic solvent was removed at reduced pressure. Then the aqueous residue was neutralized with 5% H₂SO₄ and partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield **1d** (548 mg, 39% yield from β -ketoester) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.74; IR (cm⁻¹) 2928, 1707, 1510, 1245; ¹H NMR δ 7.00 (d, J = 8 Hz, 2H), 6.75 (d, J = 8 Hz, 2H), 6.05 (d, J = 16 Hz, 1H), 5.50 (m, 1H), 4.80 (s, 2H), 3.70 (s, 3H), 2.75 (t, J = 8 Hz, 2H), 2.60 (t, J = 8 Hz, 2H), 2.30 (t, J = 8 Hz, 2H), 2.00 (m, 2H), 1.70 (s, 3H), 1.60 (m, 2H); ¹³C NMR δ u 210.1, 158.0, 142.0, 133.2, 114.7, 44.7, 42.2, 32.1, 28.9, 23.3; d 133.7, 129.7, 129.2, 113.9, 55.3, 18.7; HRMS calcd for C₁₈H₂₄O₂ (M⁺) 272.1776, obsd 272.1766.



Ketone **1d** (209 mg, 0.77 mmol) and tosylhydrazine (293 mg, 1.57 mmol) were stirred in MeOH (5 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC R_f (40% MTBE/PE) = 0.71;

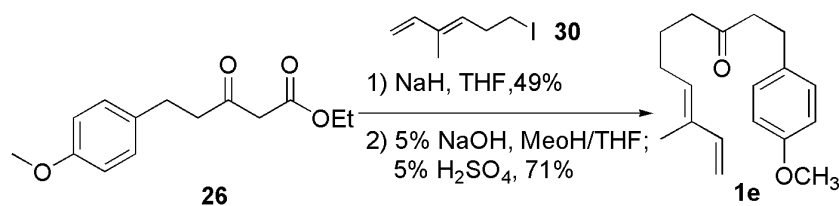
The hydrazone was redissolved in toluene (5 mL), K₂CO₃ (635 mg, 4.60 mmol) was added and the reaction mixture was heated in a sealed tube at 140 °C (oil bath) for 13 h. After cooling to rt, the reaction mixture was partitioned between CH₂Cl₂ and,

sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2d** (154 mg, 78% yield) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.80; IR (cm^{-1}) 2928, 1638, 1510, 1240; ^1H NMR δ 7.05 (d, $J = 8$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 4.80 (s, 1H), 4.50 (s, 1H), 3.75 (s, 3H), 2.55 (m, 2H), 1.80 (s, 3H), 1.65-1.80 (m, 5H), 1.55 (m, 2H), 1.15-1.30 (m, 3H); ^{13}C NMR δ u 157.6, 143.5, 135.3, 109.6, 36.0, 33.5, 32.3, 31.8, 28.0, 21.8; d 129.2, 113.7, 55.3, 30.0, 27.7, 25.1; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}$ (M^+) 256.1827, obsd 256.1826.



To a solution of alkenyl cyclopropane **2d** (56 mg, 0.22 mmol) in 2-propanol/THF (4 mL/4 mL) was added $\text{Fe}(\text{CO})_5$ (88 mg, 0.45 mmol) and K_2CO_3 (2.0 g). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 20 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, DBU (68 mg, 0.45 mmol) was added, and the mixture was stirred at rt for 2 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2d** (8.0 mg) and cyclohexenone **3c** (46.0 mg, 90% yield based on starting material not recovered) as a colorless oil: TLC R_f

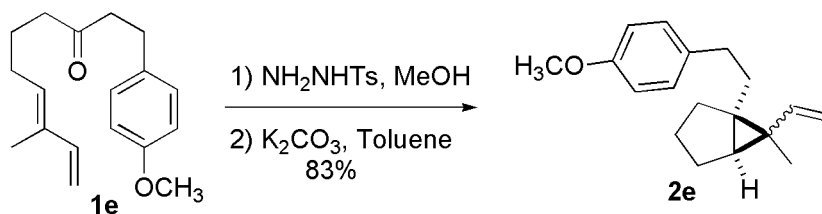
(20% MTBE/ PE) = 0.31; IR (cm⁻¹) 3439, 2938, 1648, 1511; ¹H NMR δ 7.05 (d, *J* = 8 Hz, 2H), 6.80 (d, *J* = 8 Hz, 2H), 5.75 (s, 1H), 3.75 (s, 3H), 2.50 (m, 2H), 2.30 (m, 2H), 2.05 (m, 1H), 1.90 (s, 3H), 1.70-1.85 (m, 4H), 1.50-1.65 (m, 4H); ¹³C NMR δ u 201.9, 159.2, 157.8, 134.4, 48.0, 41.3, 37.2, 37.1, 30.8, 28.8, 22.2; d 129.1, 124.5, 113.9, 55.3, 54.8, 24.6; HRMS calcd for C₁₉H₂₅O₂ (MH⁺) 285.1855, obsd 285.1865.



To a suspension of NaH (60%, 243 mg, 6.07 mmol) in dry THF (10 mL) was added a solution of β -ketoester **26** (1.27 g, 5.08 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **30** (2.26 g, 10.2 mmol) in dry THF (3 mL) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH₄Cl (25 mL) and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extracts were dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield alkylated β -ketoester (851 mg, 49% yield) as a colorless oil : TLC *R_f*(20% MTBE/PE) = 0.66;

A suspension of the above alkylated β -ketoester (851 mg, 2.47 mmol) and 5% aqueous NaOH (10 mL) in MeOH/THF (10 mL/10 mL) was stirred at 70 °C for 40 min. After cooling to rt, the reaction mixture was diluted with H₂O (10 mL) and the organic solvent was removed at reduced pressure. Then the aqueous residue was neutralized with 5%

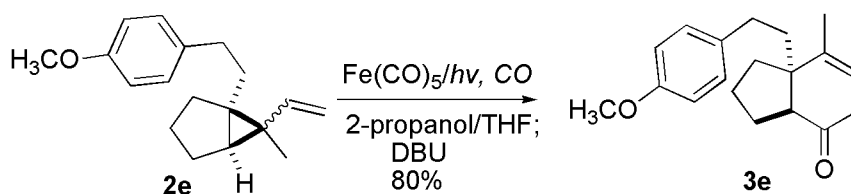
H₂SO₄ and partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield **1e** (478 mg, 35% yield from β -ketoester, a ~ 3 : 1 mixture) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.78; IR (cm⁻¹) 2928, 1707, 1510; ¹H NMR δ 7.05 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 6.30 (m, 1H), 5.40 (t, J = 8 Hz, 1H), 5.05 (d, J = 16 Hz, 1H), 4.95 (d, J = 12 Hz, 1H), 3.75 (s, 3H), 2.80 (t, J = 8 Hz, 2H), 2.65 (t, J = 8 Hz, 2H), 2.35 (t, J = 8 Hz, 2H), 2.10 (m, 2H), 1.65 (s, 3H), 1.60 (m, 2H); ¹³C NMR (major isomer) δ u 210.2, 157.9, 134.8, 133.2, 110.9, 44.6, 42.3, 28.9, 27.5, 23.4; d 141.4, 133.1, 129.2, 113.9, 55.3, 11.7; HRMS calcd for C₁₈H₂₄O₂ (M⁺) 272.1776, obsd 272.1766.



Ketone **1e** (195 mg, 0.72 mmol) and tosylhydrazine (275 mg, 1.48 mmol) were stirred in MeOH (5 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC R_f (40% MTBE/PE) = 0.65;

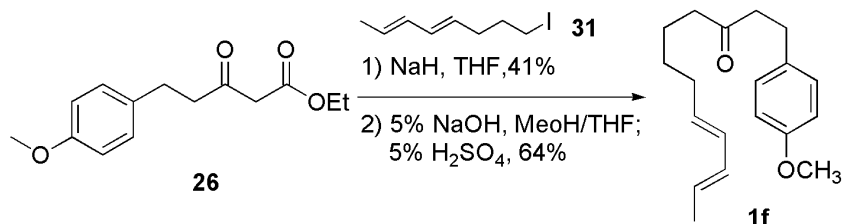
The hydrazone was redissolved in toluene (5 mL), K₂CO₃ (595 mg, 4.31 mmol) was added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 14 h. After cooling to rt, the reaction mixture was partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2e** (153

mg, 83% yield, a ~ 7 : 3 mixture) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.60; IR (cm^{-1}) 3420, 2928, 1634, 1240; ^1H NMR δ 7.05 (m, 2H), 6.80 (m, 2H), 5.65 (m, 1H), 4.95 (m, 2H), 3.75 (s, 3H), 2.50 (m, 2H), 1.40-2.00 (m, 8H), 1.20 (m, 1H), 1.05 (s, 3H); ^{13}C NMR (major isomer) δ u 157.7, 135.2, 110.7, 41.2, 37.1, 33.6, 31.9, 30.2, 27.6, 25.8; d 144.3, 129.2, 113.7, 55.3, 37.1, 12.1; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}$ (M^+) 256.1827, obsd 256.1837.



To a solution of alkenyl cyclopropane **2e** (75 mg, 0.29 mmol) in 2-propanol/THF (4 mL/4 mL) was added $\text{Fe}(\text{CO})_5$ (130 mg, 0.66 mmol) and K_2CO_3 (2.0 g). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 15 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, DBU (96 mg, 0.63 mmol) was added, and the mixture was stirred at rt for 1 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2e** (35 mg) and cyclohexenone **3c** (36 mg, 80% yield based on starting material not recovered) as a colorless oil: TLC R_f (20% MTBE/ PE) = 0.58; IR (cm^{-1}) 3429, 2928, 1697, 1643, 1510; ^1H NMR δ 6.95 (d, $J = 8$ Hz, 2H), 6.70 (d, $J = 8$ Hz, 2H), 5.45 (m, 1H), 3.70 (s, 3H), 2.95 (m, 1H), 2.70 (m, 1H), 2.50 (t, $J = 8$ Hz,

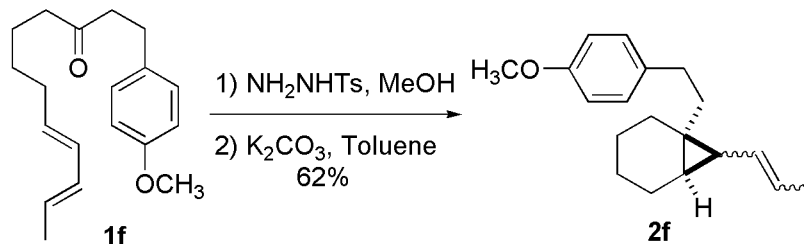
1H), 2.25 (m, 2H), 1.70-1.95 (m, 4H), 1.65 (s, 3H), 1.55 (m, 2H), 1.40 (m, 2H); ¹³C NMR δ u 213.1, 157.7, 134.4, 111.5, 56.2, 41.9, 38.8, 37.6, 30.8, 29.3, 23.3; d 129.1, 119.6, 113.8, 57.7, 55.3, 18.5; HRMS calcd for C₁₉H₂₅O₂ (MH⁺) 285.1855, obsd 285.1861.



To a suspension of NaH (60%, 247 mg, 6.17 mmol) in dry THF (10 mL) was added a solution of β -ketoester **26** (1.24 g, 4.96 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **31** (2.20 g, 9.32 mmol) in dry THF (3 mL) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH₄Cl (25 mL) and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield alkylated β -ketoester (733 mg, 41% yield) as a colorless oil : TLC *R_f* (20% MTBE/PE) = 0.71;

A suspension of the above alkylated β -ketoester (733 mg, 2.05 mmol) and 5% aqueous NaOH (10 mL) in MeOH/THF (10 mL/10 mL) was stirred at 70 °C for 40 min. After cooling to rt, the reaction mixture was diluted with H₂O (10 mL) and the organic solvent was removed at reduced pressure. Then the aqueous residue was neutralized with 5% H₂SO₄ and partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed

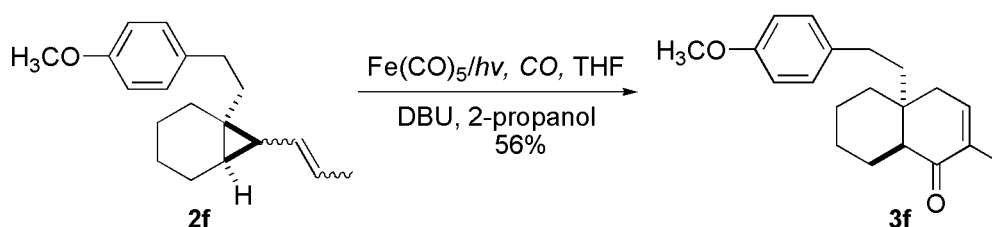
to yield **1f** (377 mg, 26% yield from β -ketoester, a ~ 5 : 1 mixture) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.81; IR (cm^{-1}) 2928, 1708, 1609, 1510; ^1H NMR δ 7.10 (d, $J = 8$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 5.90-6.0 (m, 2H), 5.45-5.55 (m, 2H), 3.75 (s, 3H), 2.85 (t, $J = 8$ Hz, 2H), 2.65 (t, $J = 8$ Hz, 2H), 2.35 (t, $J = 8$ Hz, 2H), 2.05 (m, 2H), 1.75 (d, $J = 8$ Hz, 3H), 1.55 (m, 2H), 1.30 (m, 2H); ^{13}C NMR (major isomer) δ u 210.3, 158.0, 133.2, 44.5, 42.9, 32.3, 29.0, 28.9, 23.3; d 131.6, 131.3, 130.7, 129.2, 127.0, 113.9, 55.3, 18.0; HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$ (M^+) 286.1933, obsd 286.1930.



Ketone **1f** (155 mg, 0.54 mmol) and tosylhydrazine (210 mg, 1.13 mmol) were stirred in MeOH (5 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC R_f (40% MTBE/PE) = 0.76;

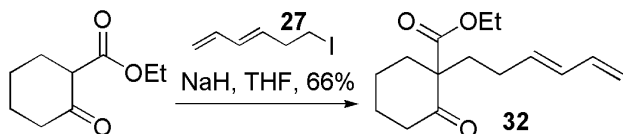
The hydrazone was redissolved in toluene (5 mL), K_2CO_3 (450 mg, 3.26 mmol) was added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 14 h. After cooling to rt, the reaction mixture was partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2f** (90 mg, 62% yield) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.73; IR (cm^{-1}) 2818, 1609,

1452, 1246; ^1H NMR δ 7.10 (d, $J = 8$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 5.50 (m, 1H), 5.25 (m, 1H), 3.75 (s, 3H), 2.60 (m, 2H), 1.40-1.85 (m, 9H), 1.10-1.35 (m, 5H), 0.85 (m, 1H); ^{13}C NMR (major isomer) δ u 157.6, 135.4, 46.3, 39.5, 32.1, 29.7, 26.0, 23.5, 21.5; d 131.7, 129.3, 123.9, 113.7, 55.3, 31.4, 25.9, 18.1; HRMS calcd for $\text{C}_{19}\text{H}_{26}\text{O}$ (M^+) 270.1984, obsd 270.1992.

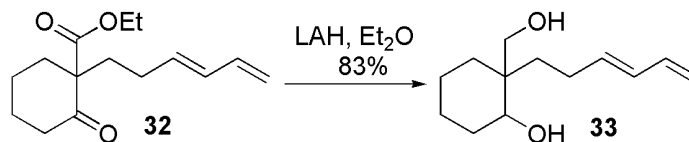


To a solution of alkenyl cyclopropane **2f** (25 mg, 0.09 mmol) in THF (4 mL) was added $\text{Fe}(\text{CO})_5$ (35 mg, 0.18 mmol). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 12 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, THF was removed under reduced pressure and the residue was redissolved in 2-propanol (1 mL). Then DBU (82 mg, 0.54 mmol) was added, and the mixture was stirred at rt for 2 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2f** (12 mg) and cyclohexenone **3f** (8 mg, 56% yield based on starting material not recovered) as a colorless oil: TLC R_f (20% MTBE/ PE) = 0.43; IR (cm^{-1}) 2927, 2855, 1511, 1264; ^1H NMR δ 7.00 (d, $J = 8$ Hz, 2H), 6.80 (d, $J = 8$ Hz, 2H), 6.55 (m, 1H), 3.75 (s, 3H), 2.60 (m, 1H), 2.45 (m, 2H), 2.15 (m, 1H), 2.00 (m, 1H), 1.75

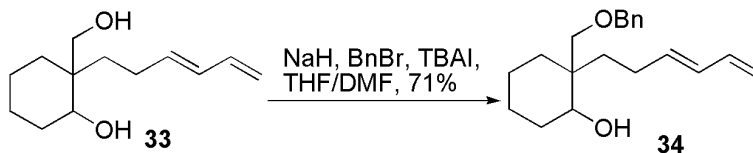
(s, 3H), 1.30-1.55 (m, 10H); ^{13}C NMR δ u 203.0, 157.4, 134.6, 133.5, 42.2, 38.3, 33.8, 29.7, 28.8, 26.3, 24.4, 21.7; d 142.1, 129.1, 113.8, 55.3, 54.3, 15.9; HRMS calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2$ (MH^+) 299.2011, obsd 299.2099.



To a suspension of NaH (60%, 235 mg, 5.87 mmol) in dry THF (5 mL) was added a solution of β -ketoester (760 mg, 4.47 mmol) in dry THF (2 mL) over a period of 3 min at rt. After stirring at rt for 30 min, a solution of iodide **27** (1.87 g, 9.0 mmol) in dry THF (3 ml) was added and then the reaction mixture was stirred at reflux overnight. After cooling to rt, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield unreacted β -ketoester (140 mg) and alkylated β -ketoester **32** (736 mg, 81% yield based on starting material not recovered) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.31; IR (cm^{-1}) 2838, 1712, 1442; ^1H NMR δ 6.35 (m, 1H), 6.05 (m, 1H), 5.65 (m, 1H), 5.10 (d, J = 16 Hz, 1H), 4.95 (d, J = 12 Hz, 1H), 4.20 (m, 2H), 2.35-2.55 (m, 3H), 1.90-2.10 (m, 4H), 1.40-1.70 (m, 5H), 1.25 (t, J = 8 Hz, 3H); ^{13}C NMR δ u 207.8, 171.9, 115.2, 61.2, 60.5, 41.1, 36.2, 34.3, 27.6, 27.4, 22.4; d 137.1, 134.2, 131.3; HRMS calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3$ (MH^+) 251.1647, obsd 251.1656.

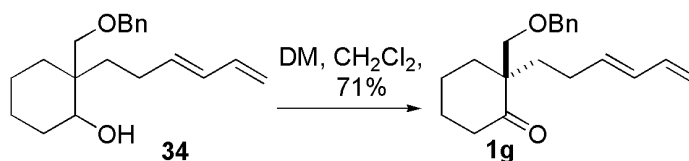


To a suspension of LAH (450 mg, 11.8 mmol) in dry Et₂O (10 mL) was added a solution of alkylated β -ketoester **32** (736 mg, 2.94 mmol) in dry Et₂O (2 mL) over a period of 3 min at rt. Then the reaction mixture was stirred at reflux for 3 h. After cooling to rt, the reaction mixture was quenched with saturated aqueous potassium sodium tartrate (15 mL) and then partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield diol **33** (510 mg, 83% yield) as a colorless oil: TLC R_f (40% MTBE/ PE) = 0.30; IR (cm⁻¹) 3361, 2928, 1452; ¹H NMR δ 6.40 (m, 1H), 6.10 (m, 1H), 5.75 (m, 1H), 5.10 (d, J = 16 Hz, 1H), 4.95 (d, J = 12 Hz, 1H), 3.65 (m, 1H), 3.60 (d, J = 12 Hz, 1H), 3.40 (d, J = 12 Hz, 1H), 2.70 (bs, 2H), 2.05 (m, 2H), 1.60-1.85 (m, 3H), 1.40-1.55 (m, 4H), 1.10-1.35 (m, 3H); ¹³C NMR δ u 114.9, 71.8, 41.2, 30.7, 28.9, 26.0, 24.3, 23.1, 20.0; d 137.2, 135.7, 130.9, 79.3; HRMS calcd for C₁₃H₂₂O₂Na(MNa⁺) 233.1512, obsd 233.1515.



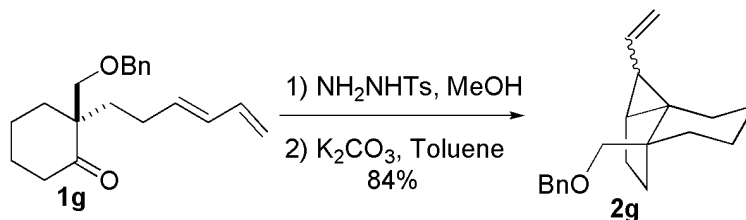
To a well-stirred suspension of NaH (60%, 153 mg, 3.82 mmol) in dry THF (5 mL) was added a solution of diol **33** (510 mg, 2.44 mmol) and tetrabutylammonium iodide (189 mg, 0.51 mmol) in dry THF/DMF (5 mL/2 mL) over a period of 2 min at -20 °C. After

stirring at -20 °C for 5 min, benzyl bromide (433 mg, 2.53 mmol) was added and the reaction mixture was stirred at -20 °C to rt for 2 h. Then the reaction mixture was quenched with saturated aqueous NH₄Cl (10 mL) and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield protected alcohol **34** (521 mg, 71% yield as a colorless oil: TLC *R_f* (20% MTBE/ PE) = 0.53; IR (cm⁻¹) 3459, 2928, 1732, 1451; ¹H NMR δ 7.20-7.40 (m, 5H), 6.30 (m, 1H), 6.05 (m, 1H), 5.75 (m, 1H), 5.10 (d, *J* = 16 Hz, 1H), 4.95 (d, *J* = 12 Hz, 1H), 4.50 (m, 2H), 3.60 (m, 2H), 3.40 (m, 2H), 3.20 (m, 1H), 1.80-2.00 (m, 3H), 1.00-1.70 (m, 9H); ¹³C NMR δ u 137.4, 114.7, 79.0, 73.6, 41.1, 29.1, 28.9, 25.9, 24.2, 23.7, 20.1; d 137.4, 135.8, 130.7, 128.5, 127.8, 127.7, 78.9; HRMS calcd for C₂₀H₂₈O₂Na (MNa⁺) 323.1987, obsd 323.1976.



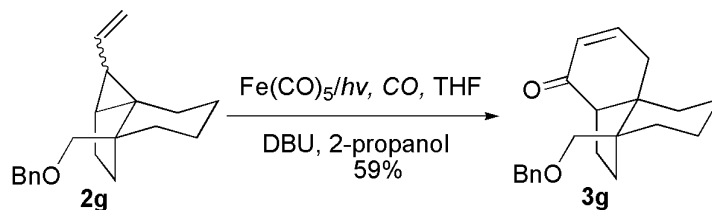
To a stirred solution of the alcohol **34** (521 mg, 1.74 mmol) in dry CH₂Cl₂ (5 mL), was added Dess-Martin periodinane reagent (1.5 g, 3.40 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then concentrated. The residue was chromatographed to yield ketone **1g** (370 mg, 71% yield) as a colorless oil: TLC *R_f* (5% MTBE/ PE) = 0.31; IR (cm⁻¹) 3400, 2928, 1702, 1447; ¹H NMR δ 7.20-7.40 (m, 5H), 6.30 (m, 1H), 6.00 (m, 1H), 5.65 (m, 1H), 5.10 (d, *J* = 16 Hz, 1H), 4.95 (d, *J* = 12 Hz, 1H), 4.50 (m, 2H), 3.60 (d, *J* = 8 Hz, 1H), 3.45 (d, *J* = 8 Hz, 1H), 2.20-2.40 (m, 2H), 1.60-2.00 (m, 10 H); ¹³C NMR δ u 214.1, 138.5, 115.1, 73.4, 72.8, 52.6, 39.5, 35.2, 32.6, 27.0, 26.8, 20.8; d

137.1, 134.6, 131.2, 128.3, 127.5; HRMS calcd for C₂₀H₂₆O₂Na (MNa⁺) 321.1830, obsd 321.1817.

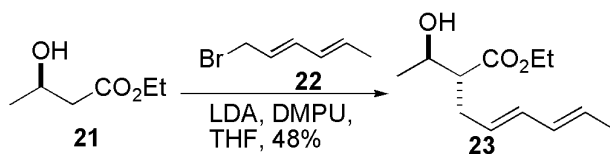


Ketone **1g** (46 mg, 0.18 mmol) and tosylhydrazine (75 mg, 0.4 mmol) were stirred in MeOH (3 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC *R_f*(40% MTBE/PE) = 0.69;

The hydrazone was redissolved in toluene (3 mL), K₂CO₃ (153 mg, 1.1 mmol) was added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 13 h. After cooling to rt, the reaction mixture was partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2g** (36 mg, 84% yield) as a colorless oil: TLC *R_f* (5% MTBE/ PE) = 0.55; IR (cm⁻¹) 3420, 2850, 1629, 1447; ¹H NMR δ 7.20-7.40 (m, 5H), 5.50 (m, 1H), 4.95 (m, 2H), 4.50 (m, 2H), 3.65 (m, 1H), 3.25 (m, 1H), 1.80-2.00 (m, 2H), 1.00-1.60 (m, 11H), 0.85 (m, 1H); ¹³C NMR (major isomer) δ u 139.2, 113.2, 73.8, 73.2, 45.6, 36.7, 33.4, 32.3, 25.8, 25.2, 25.1, 22.3; d 138.0, 128.2, 127.2, 30.5, 26.6; HRMS calcd for C₂₀H₂₆O (M⁺) 282.1984, obsd 282.1993.



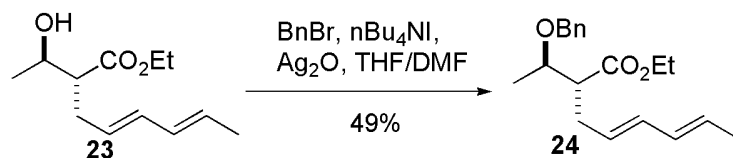
To a solution of alkenyl cyclopropane **2g** (38 mg, 0.13 mmol) in THF (4 mL) was added $\text{Fe}(\text{CO})_5$ (58 mg, 0.29 mmol). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 14 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, THF was removed under reduced pressure and the residue was redissolved in 2-propanol (1 mL). Then DBU (43 mg, 0.28 mmol) was added, and the mixture was stirred at rt for 2 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2g** (18 mg) and cyclohexenone **3g** (13 mg, 59% yield based on starting material not recovered) as a colorless oil: TLC R_f (20% MTBE/ PE) = 0.43; IR (cm^{-1}) 3428, 2928, 1653; ^1H NMR δ 7.20-7.40 (m, 5H), 6.80 (m, 1H), 5.95 (m, 1H), 4.45 (m, 2H), 3.50 (d, $J = 8$ Hz, 1H), 3.25 (d, $J = 8$ Hz, 1H), 3.05 (m, 1H), 2.55 (m, 1H), 2.15 (m, 1H), 1.25-1.85 (m, 12H); ^{13}C NMR δ u 201.7, 138.7, 73.9, 73.4, 48.6, 47.9, 34.6, 32.6, 31.5, 30.3, 25.1, 22.2, 20.9; d 148.4, 128.3, 127.4, 127.3, 127.0, 51.4; HRMS calcd for $\text{C}_{21}\text{H}_{27}\text{O}_2$ (MH^+) 311.2011, obsd 311.2025.



To a well-stirred solution of sorbyl alcohol (14 g, 142.8 mmol) in CH_2Cl_2 (20 mL) at $-10\text{ }^\circ\text{C}$ was added a solution of PBr_3 (15.3 g, 56.4 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min.⁷ After stirring for another 2 h at $-10\text{ }^\circ\text{C}$, the reaction mixture was quenched with saturated aqueous NaHCO_3 (10 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the crude dienyl bromide **22** (20 g).

To a solution of diisopropylamine (1.75 g, 17.3 mmol) in dry THF (10 mL) was added *n*-BuLi (16.5 mmol, 7.0 mL, 2.36 M in hexane) at $-10\text{ }^\circ\text{C}$.⁸ After stirring at $-10\text{ }^\circ\text{C}$ for 30 min, the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ and a solution of ethyl (R)-(-)-3-hydroxybutyrate **21** (960 mg, 7.3 mmol) in THF (2 mL) was added over a period of 3 min, followed by sequentially dienyl bromide **22** (1.4 g, 8.9 mmol) and DMPU (2 mL). Then after stirring at $0\text{ }^\circ\text{C}$ for 24 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkylated **23** (792 mg, 51% yield) as a pale yellow oil: TLC R_f (20% MTBE/PE) = 0.37; $[\alpha]_D -16.2$ (c 1.14, CHCl_3); IR (cm^{-1}) 3429, 2968, 1722, 1643; ^1H NMR δ 5.90-6.10 (m, 2H), 5.40-5.60 (m, 2H), 4.15 (m, 2H), 3.90 (m, 1H), 2.70 (bs, 1H), 2.30-2.45 (m, 3H), 1.70 (d, $J = 8\text{ Hz}$, 3H), 1.15-1.30 (m, 6H); ^{13}C NMR (major isomer) δ u 174.8, 60.5, 32.1; d 132.8, 131.2, 128.2, 126.9, 67.8, 52.3, 21.4, 18.0, 14.2;

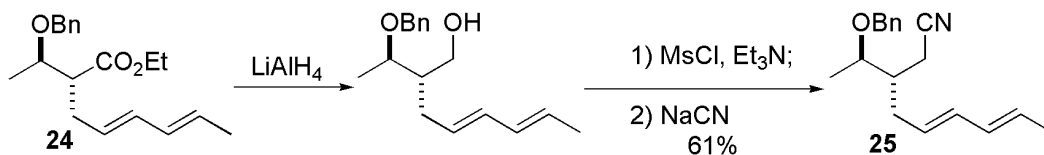
HRMS calcd for C₁₂H₂₀O₃Na (MNa⁺) 235.1310, obsd 235.1302.



To the solution of alcohol **23** (910 mg, 4.3 mmol) and benzyl bromide (4.6 g, 26.9 mmol) in THF/DMF (5 mL/5 mL) was added tetrabutylammonium iodide (162 mg, 0.44 mmol) at rt.⁹ After stirring for 30 min at rt, Ag₂O (3.98 g, 17.2 mmol) was added in one portion.

After stirring at rt overnight, the mixture was filtered through a small pad of packed celite and then concentrated. The residue was chromatographed to yield protected benzyl ether

24 (637 mg, 49% yield) as a colorless oil: TLC *R_f*(5% MTBE/PE) = 0.41; [α]_D -24.3 (c 1.88, CHCl₃); IR (cm⁻¹) 3429, 1727, 1643; ¹H NMR δ 7.20-7.40 (m, 5H), 5.90-6.10 (m, 2H), 5.40-5.60 (m, 2H), 4.40-4.60 (m, 2H), 4.10 (m, 2H), 3.75 (m, 1H), 2.20-2.60 (m, 3H), 1.70 (d, *J* = 8 Hz, 3H), 1.15-1.30 (m, 6H); ¹³C NMR (major isomer) δ u 173.7, 138.6, 71.1, 60.3, 31.1; d 132.5, 131.3, 128.3, 127.9, 127.7, 127.6, 127.5, 76.0, 52.3, 18.0, 17.0, 14.3; HRMS calcd for C₁₉H₂₆O₃Na (MNa⁺) 325.1780, obsd 325.1768.

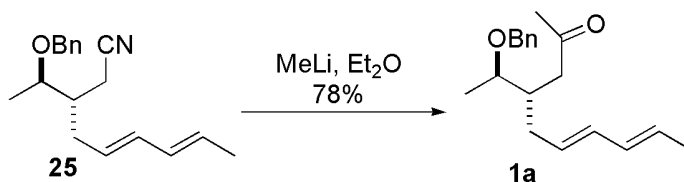


To a suspension of LAH (135 mg, 3.55 mmol) in dry Et₂O (8 mL) was added a solution of ester **24** (351 mg, 1.16 mmol) in dry Et₂O (2 mL) over a period of 3 min at 0 °C. After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous potassium sodium tartrate (5 mL) and then partitioned between CH₂Cl₂ and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated to afford

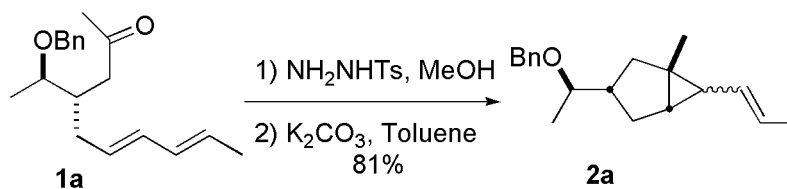
crude alcohol.

To a stirred solution of above alcohol in CH_2Cl_2 (5 mL) were sequentially added Et_3N (237 mg, 2.35 mmol) and mesyl chloride (222 mg, 1.95 mmol) at 0°C . After stirring at rt for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) and then partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated to give the crude mesylate.

To a stirred solution of the above crude mesylate in DMSO (5 mL) was added NaCN (350 mg, 7.14 mmol) at rt. The reaction mixture was stirred at 60°C for 2 h. After cooling to rt, the reaction mixture was diluted with Et_2O (80 mL) and then partitioned between Et_2O and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield the nitrile **25** (190 mg, 61% yield from **24**) as a colorless oil: TLC R_f (20% MTBE/PE) = 0.71; $[\alpha]_D -62.8$ (c 0.94, CHCl_3); IR (cm^{-1}) 3429, 2918, 2240, 1643; ^1H NMR δ 7.20-7.40 (m, 5H), 5.90-6.10 (m, 2H), 5.30-5.60 (m, 2H), 4.55 (d, $J = 12$ Hz, 1H), 4.35 (d, $J = 12$ Hz, 1H), 3.45 (m, 1H), 2.35-2.50 (m, 2H), 2.25 (m, 1H), 2.05 (m, 1H), 1.75 (m, 1H), 1.65 (d, $J = 8$ Hz, 3H), 1.15 (d, $J = 8$ Hz, 3H); ^{13}C NMR (major isomer) δ u 138.3, 119.2, 71.1, 33.3, 17.8; d 133.8, 131.0, 128.7, 128.5, 127.8, 127.7, 126.9, 75.3, 41.9, 18.3, 17.6; HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{ONNa}$ (MNa^+) 292.1677, obsd 292.1664.

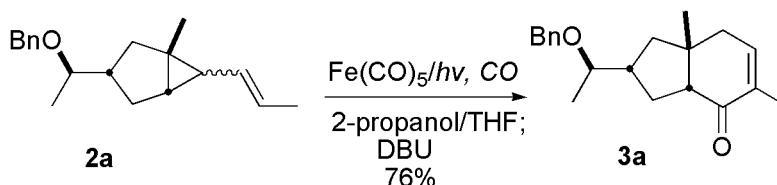


To a stirred solution of nitrile **8** (137 mg, 0.51 mmol) in dry Et₂O (4 mL) was added methyl lithium (1.6 mmol, 1 mL, 1.6 M in Et₂O) at -78 °C over a period of 2 min.¹⁰ Then the reaction mixture was allowed to warm to 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (10 mL) for 10 min and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was chromatographed to yield unreacted nitrile **25** (26 mg) and methyl ketone **1a** (92 mg, 78% yield based on starting material not recovered) as a colorless oil: TLC *R_f*(CH₂Cl₂) = 0.30; [α]_D -47.8 (c 0.54, CHCl₃); IR (cm⁻¹) 3429, 2928, 1707, 1639; ¹H NMR δ 7.20-7.40 (m, 5H), 5.80-6.00 (m, 2H), 5.30-5.50 (m, 2H), 4.50 (d, *J* = 12 Hz, 1H), 4.30 (d, *J* = 12 Hz, 1H), 3.40 (m, 1H), 2.35-2.50 (m, 2H), 2.15 (m, 2H), 2.00 (s, 3H), 1.85 (m, 1H), 1.60 (d, *J* = 8 Hz, 3H), 1.05 (d, *J* = 8 Hz, 3H); ¹³C NMR (major isomer) δ u 208.7, 138.9, 70.7, 44.0, 34.3; d 132.5, 131.4, 129.4, 128.3, 127.7, 127.5, 127.4, 76.3, 40.0, 30.5, 18.0, 16.9; HRMS calcd for C₁₉H₂₆O₂Na (MNa⁺) 309.1830, obsd 309.1822.



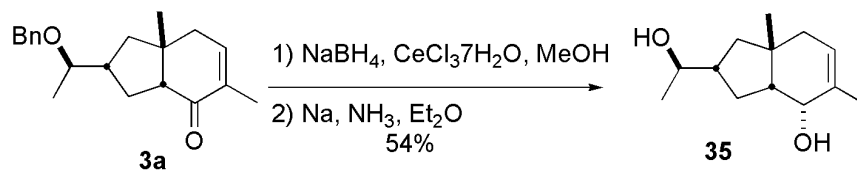
Ketone **1a** (80 mg, 0.28 mmol) and tosylhydrazine (107 mg, 0.57 mmol) were stirred in MeOH (3 mL) at rt overnight. The MeOH was removed under reduced pressure and the residue was passed through a short silica gel pad with 40% MTBE/PE to give the hydrazone : TLC *R_f*(40% MTBE/PE) = 0.62;

The hydrazone was redissolved in toluene (3 mL), K_2CO_3 (235 mg, 1.7 mmol) was added and the reaction mixture was heated in a sealed tube at 130 °C (oil bath) for 14 h. After cooling to rt, the reaction mixture was partitioned between CH_2Cl_2 and, sequentially, water and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to yield alkenyl cyclopropane **2a** (61 mg, 81% yield) as a colorless oil: TLC R_f (5% MTBE/ PE) = 0.53; $[\alpha]_D -78.8$ (c 0.68, $CHCl_3$); IR (cm^{-1}) 3439, 2918, 2859, 1643, 1447; 1H NMR δ 7.10-7.30 (m, 5H), 5.30-5.55 (m, 1H), 4.90-5.15 (m, 1H), 4.30-4.50 (m, 2H), 3.05-3.25 (m, 1H), 2.30-2.50 (m, 1H), 1.50-2.05 (m, 6H), 0.85-1.25 (m, 9H); ^{13}C NMR (major isomer) δ u 139.1, 70.5, 40.9, 33.6, 28.7; d 130.8, 128.3, 127.7, 127.4, 123.7, 79.1, 50.2, 37.8, 33.6, 18.2, 18.0, 17.8; HRMS calcd for $C_{19}H_{26}ONa$ (MNa^+) 293.1881, obsd 293.1871.



To a solution of alkenyl cyclopropane **2a** (54 mg, 0.2 mmol) in 2-propanol/THF (4 mL/4 mL) was added $Fe(CO)_5$ (83 mg, 0.42 mmol) and K_2CO_3 (2.0 g). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 15 h at rt in a Rayonet apparatus (300 nm) set for autocooling. The reaction was halted every 2 h to agitate the tube inside the larger tube, after which photolysis was restarted. At the end of the irradiation, DBU (85 mg, 0.56 mmol) was added, and the mixture was stirred at rt for 1 h. The mixture was diluted with EtOAc (20 mL), filtered through a small pad of packed

silica gel, and then subsequently concentrated. The residue was chromatographed to yield unreacted cyclopropane **2a** (24 mg) and cyclohexenone **3a** (25 mg, 76% yield based on starting material not recovered, a ~ 6 : 1 mixture) as a colorless oil: TLC R_f (5% MTBE/PE) = 0.23; $[\alpha]_D$ -102.7 (c 0.26, CHCl₃); IR (cm⁻¹) 3439, 2103, 1640; ¹H NMR δ 7.20-7.40 (m, 5H), 6.50 (m, 1H), 4.60 (d, J = 12 Hz, 1H), 4.35 (d, J = 12 Hz, 1H), 3.30 (m, 1H), 2.00-2.50 (m, 5H), 1.75 (m, 1H), 1.70 (s, 3H), 1.60 (d, J = 8 Hz, 2H), 1.15 (d, J = 8 Hz, 3H), 1.05 (s, 3H); ¹³C NMR (major isomer) δ u 201.6, 138.9, 133.1, 70.6, 43.8, 41.5, 35.9, 32.7; d 142.7, 128.3, 127.7, 127.4, 78.6, 56.9, 43.7, 27.1, 18.2, 16.0; HRMS calcd for C₂₀H₂₇O₂ (MH⁺) 299.2011, obsd 299.2011.



To a stirred solution of racemic enone (201 mg, 0.67 mmol) in MeOH (1.5 mL) was added a solution of cerium(III) chloride heptahydrate (379 mg, 1.02 mmol) in MeOH (0.5 mL) at -10 °C. Then NaBH₄ (60 mg, 1.58 mmol) was added in one portion. After stirring at -10 °C for 0.5 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (10 mL) and then partitioned between Et₂O and, sequentially, water and brine. The combined organic extract was dried (Na₂SO₄) and concentrated to give the crude alcohol.

To a stirred solution of the above crude alcohol in Et₂O (5 mL) was added MeOH (10 drops) and NH₃ (3 mL) at -78 °C. Then a piece of Na (336 mg, 14.6 mmol) was added and the reaction mixture was stirred at -78 °C until a dark blue color persisted. The

reaction mixture was quenched with solid NH₄Cl until the blue color disappeared. The mixture was diluted with Et₂O (30 mL) and NH₃ was allowed to evaporate at rt. Then the mixture was filtered through a small pad of celite and concentrated. The residue was chromatographed to yield diol **35** (76 mg, 54% yield from racemic enone) as a white solid: mp 116 °C; TLC R_f(20% MTBE/ DCM) = 0.29; IR (cm⁻¹) 3362, 2948, 2884, 1453; ¹H NMR δ 5.35 (m, 1H), 4.20 (d, *J* = 8 Hz, 1H), 3.60 (m, 1H), 1.90-2.10 (m, 3H), 1.85 (m, 1H), 1.75 (s, 3H), 1.60-1.70 (m, 3H), 1.35-1.50 (m, 3H), 1.15 (d, *J* = 8 Hz, 3H), 1.00 (s, 3H); ¹³C NMR δ u 134.4, 43.6, 41.4, 35.6, 30.6; d 121.5, 73.0, 70.6, 51.1, 44.8, 27.3, 22.5, 19.1.

X-ray analysis (following page) confirmed the structure of **35**.

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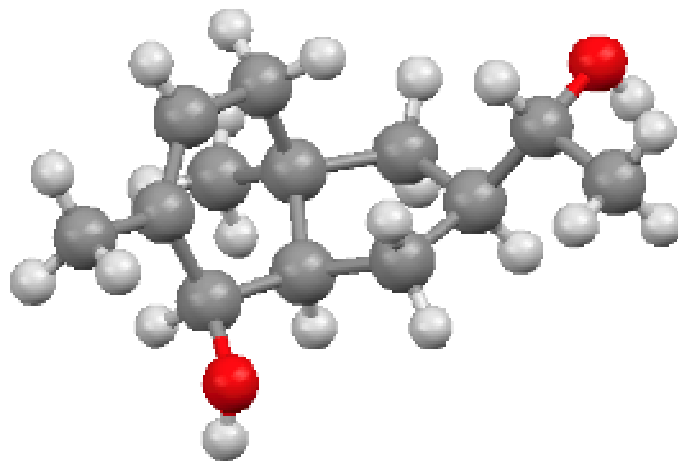
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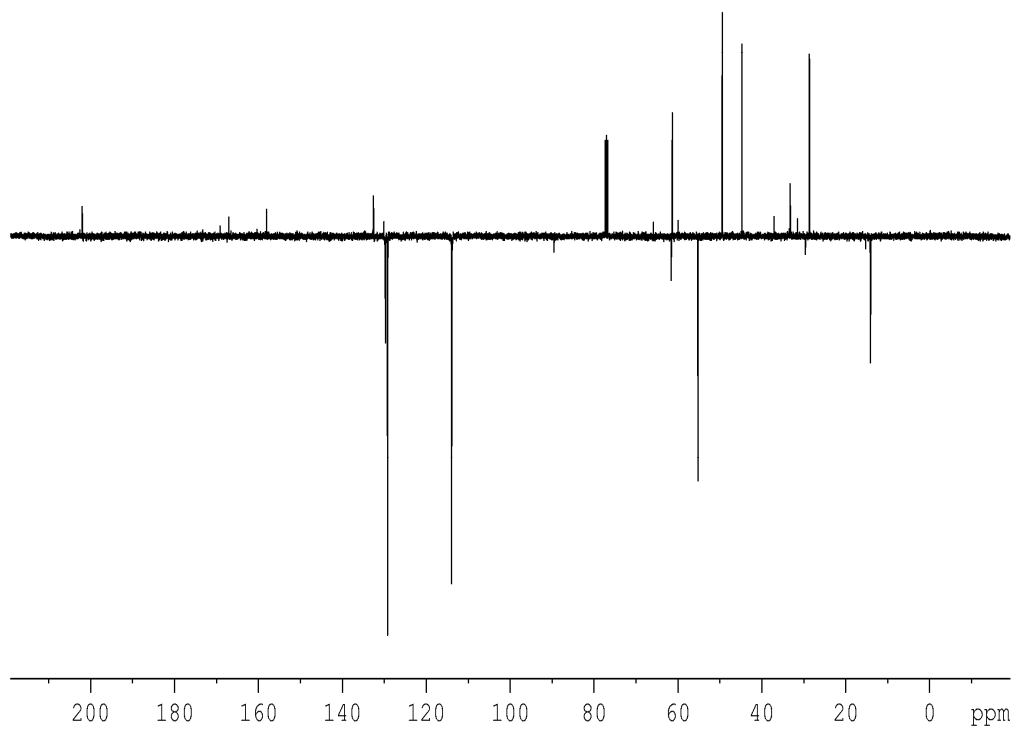
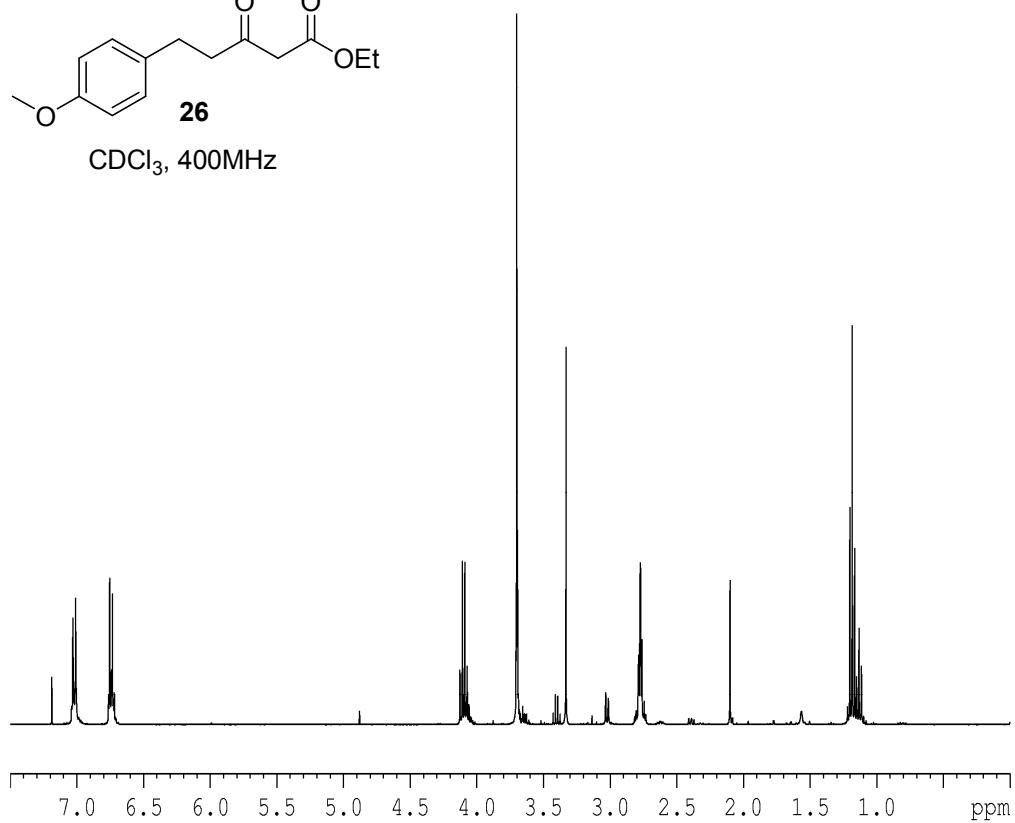
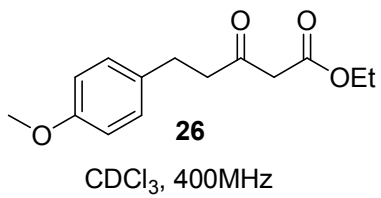
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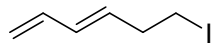
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10. Fuwa, H.; Goto, T.; Sasaki, M. *Org. Lett.* **2008**, 2211-2214

X-ray of Diol **35**

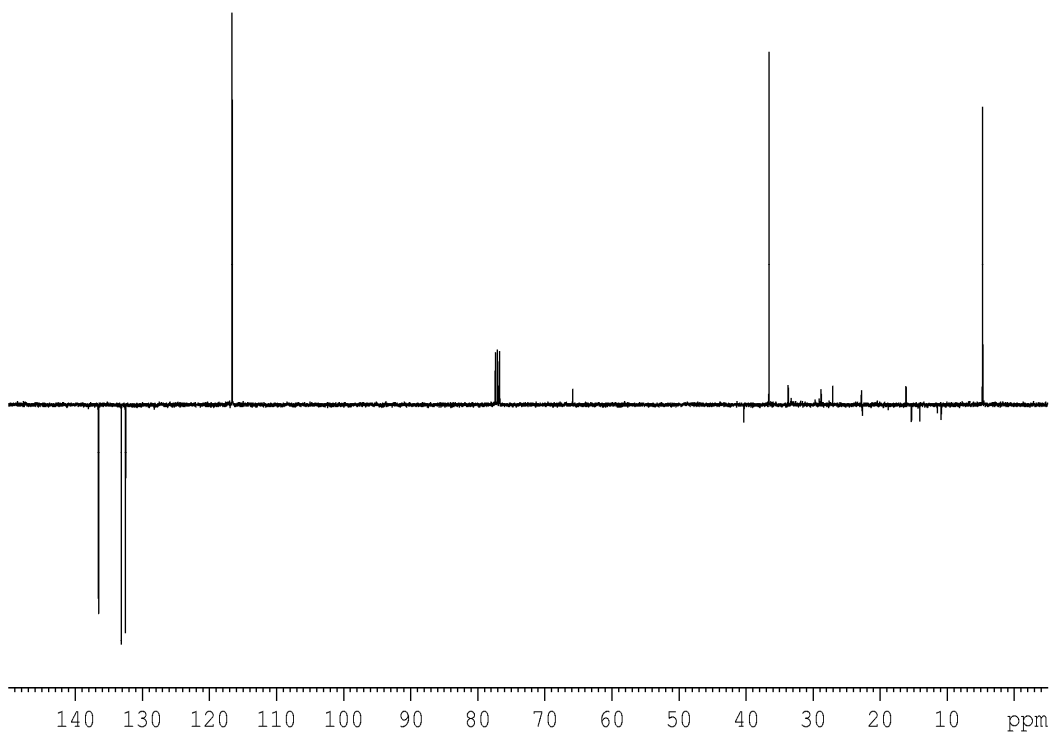
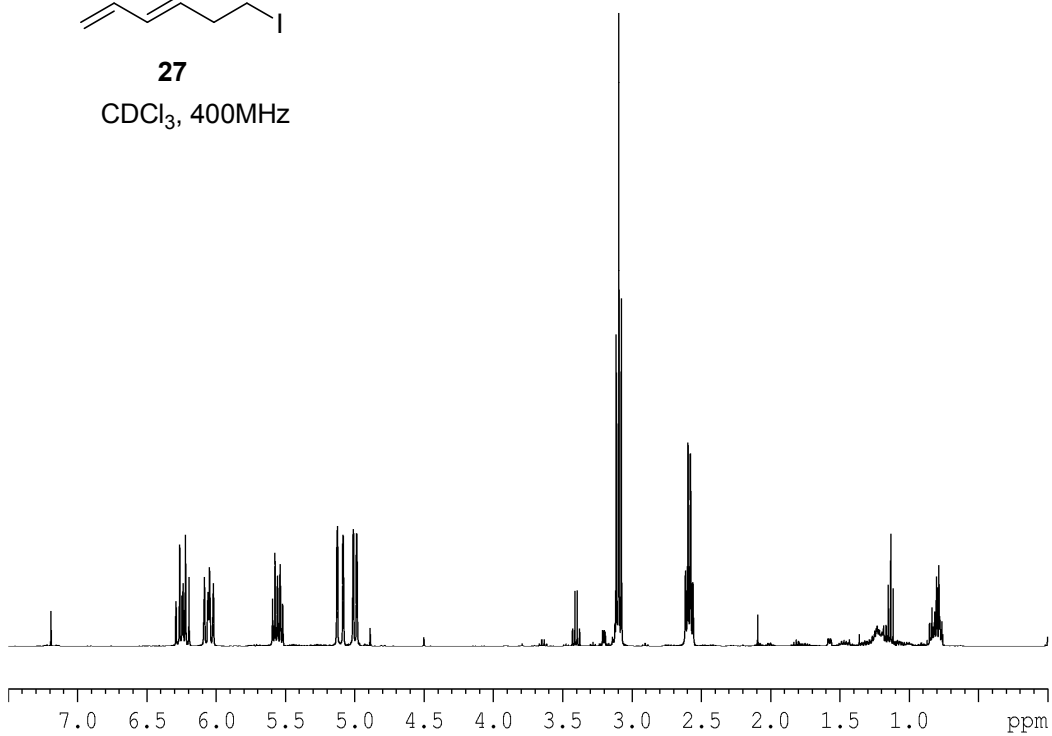


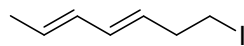




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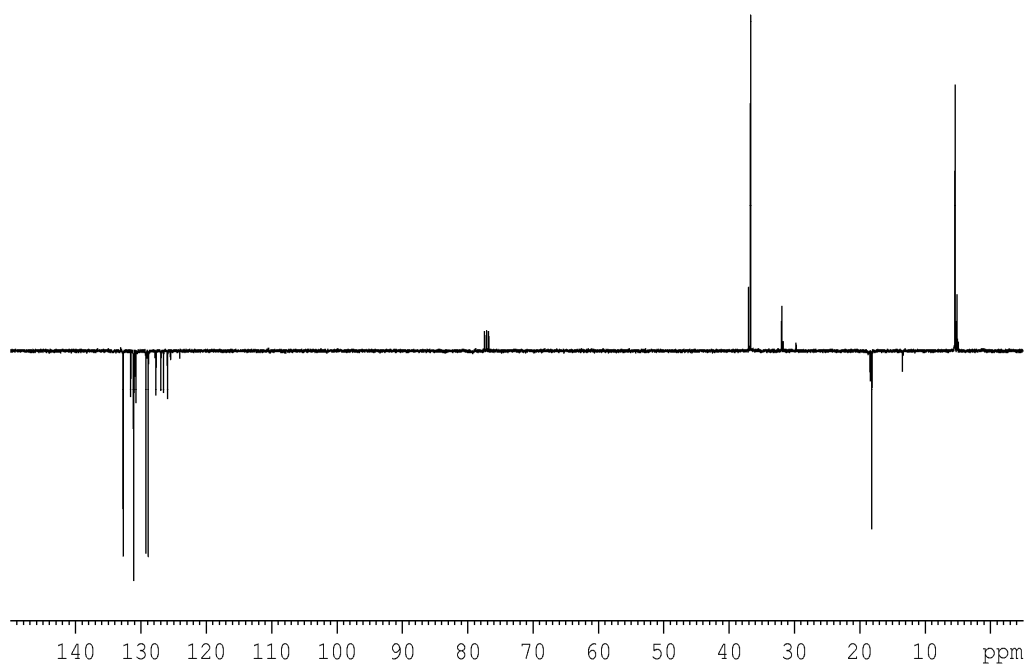
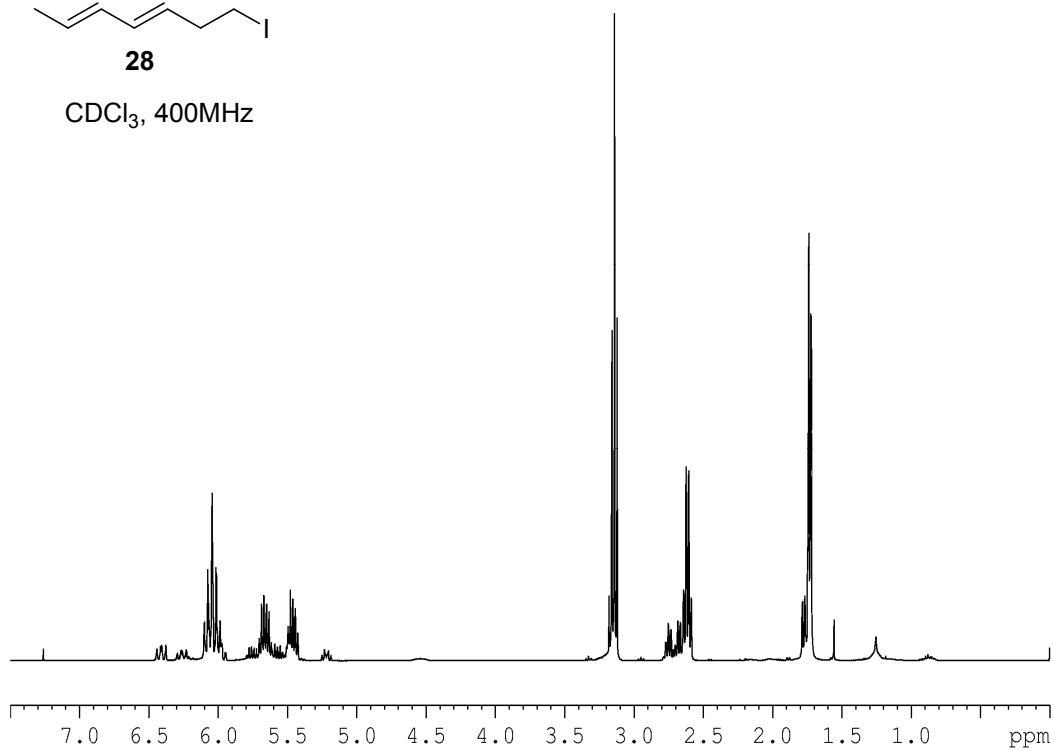
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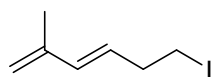




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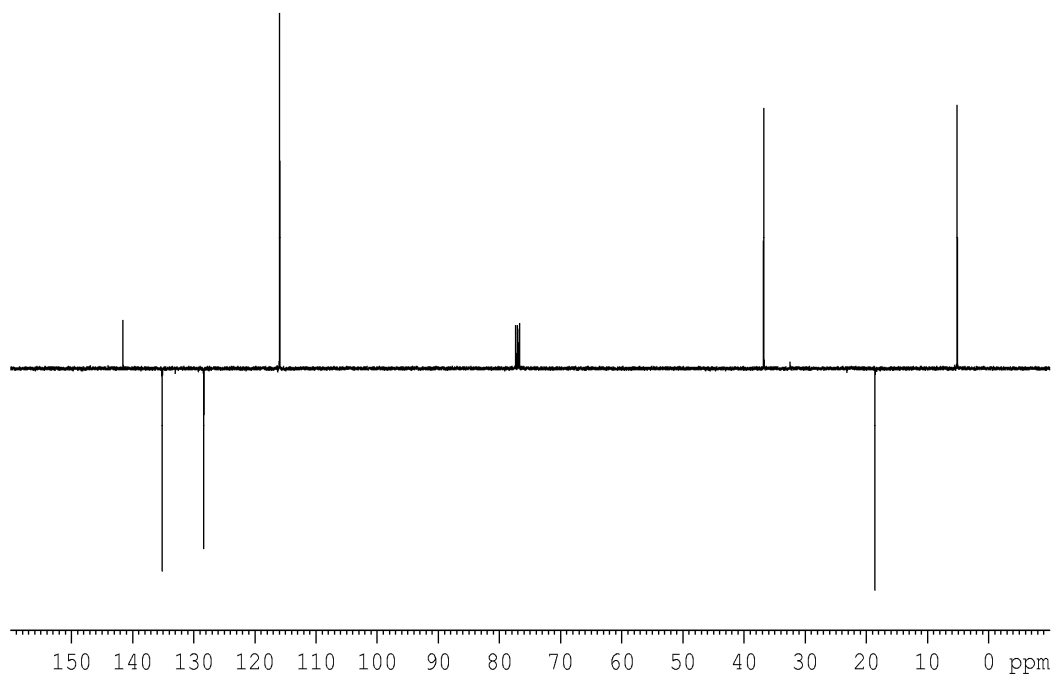
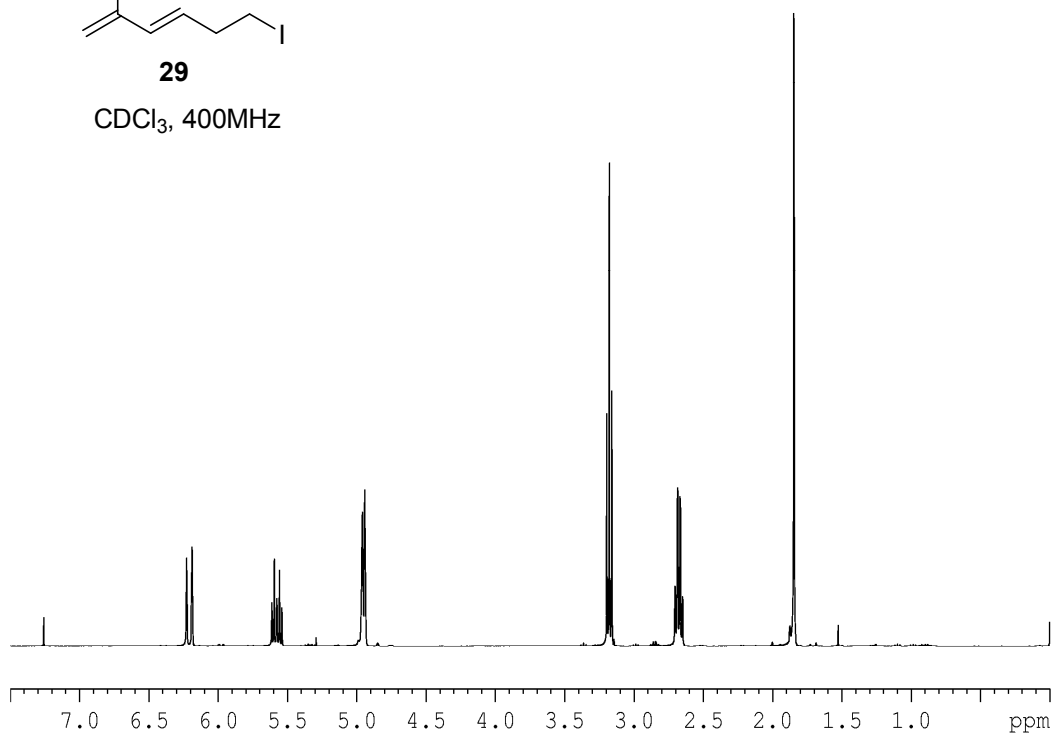
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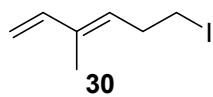




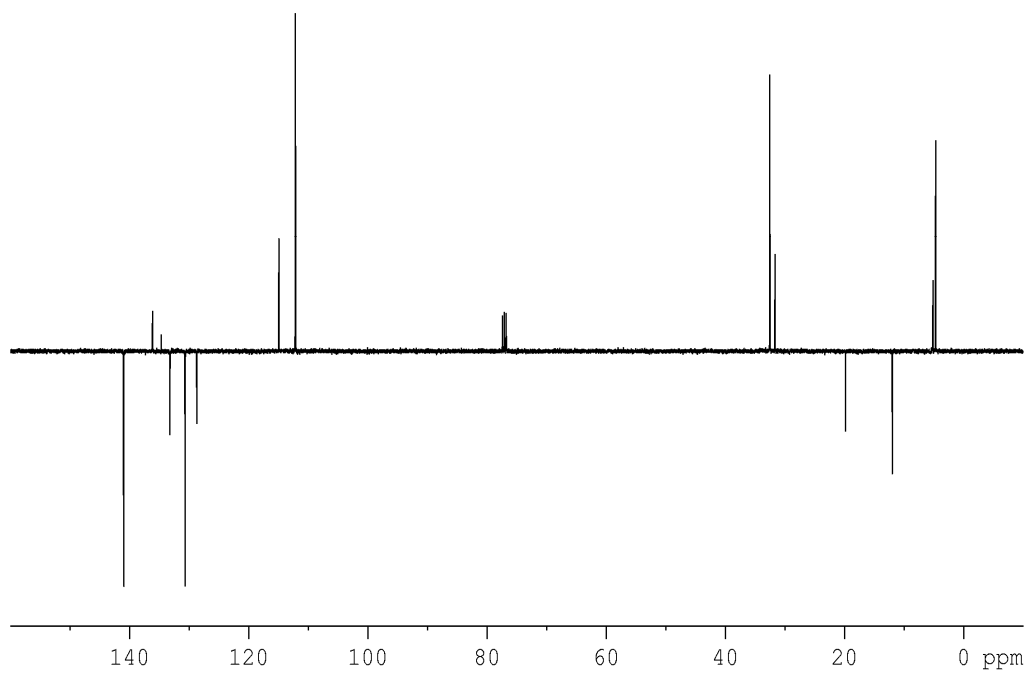
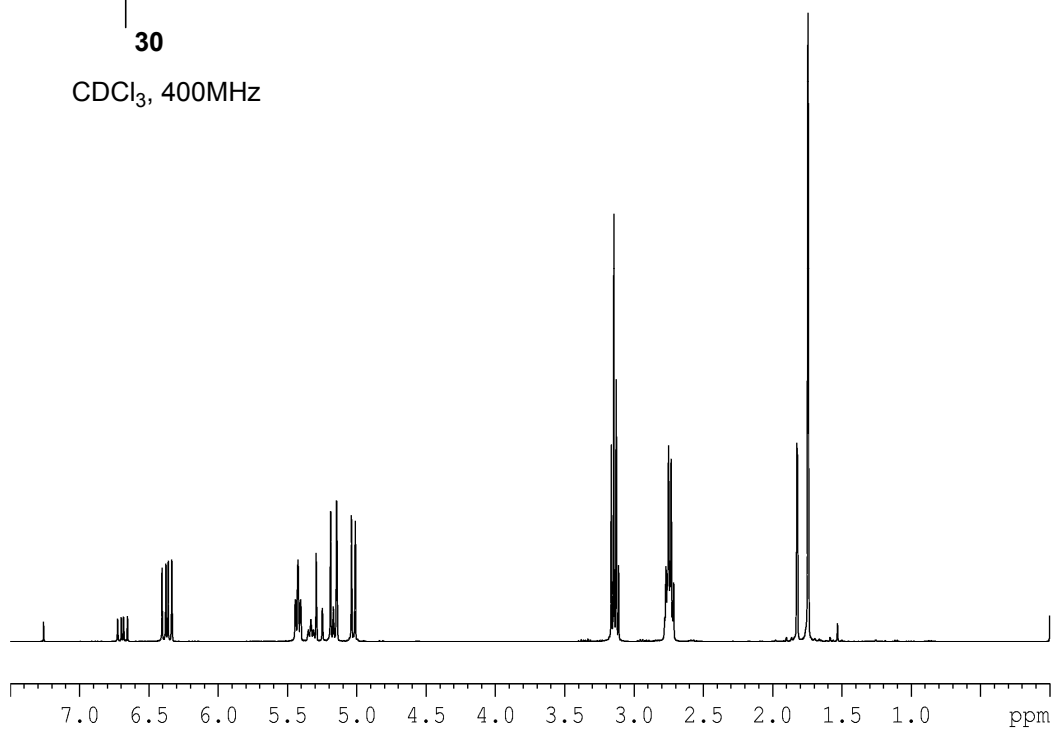
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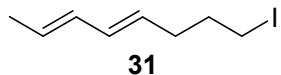
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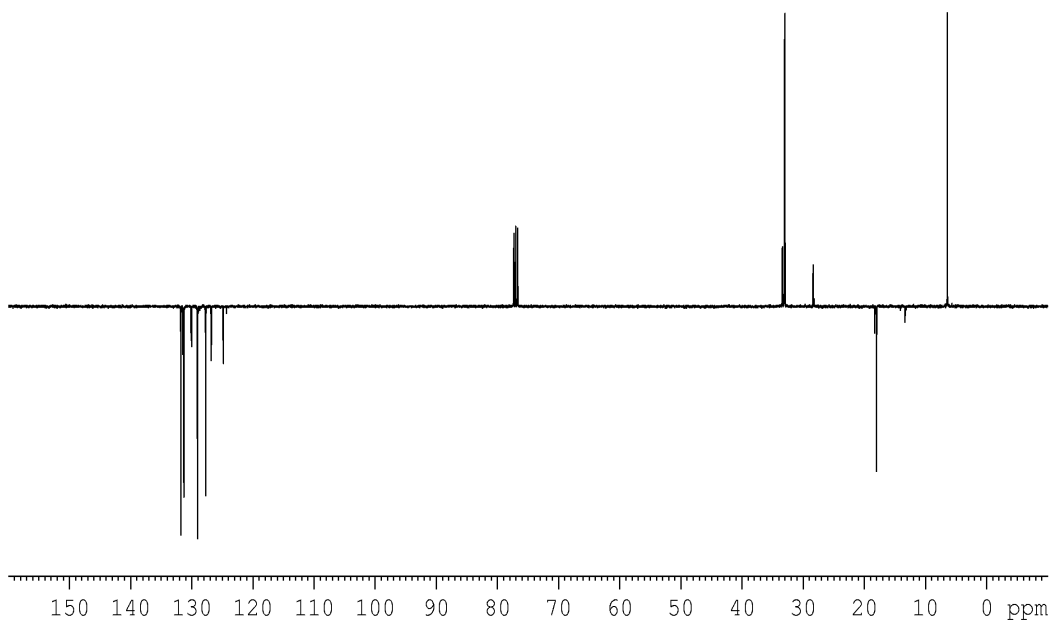
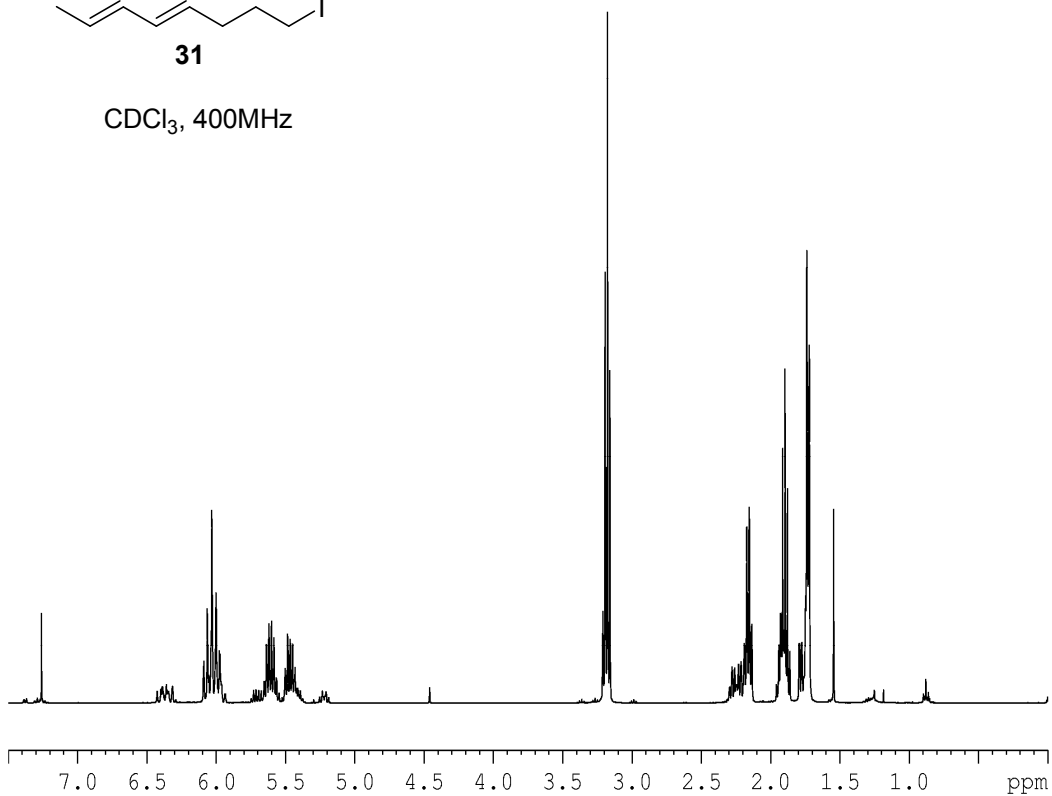
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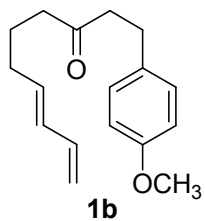




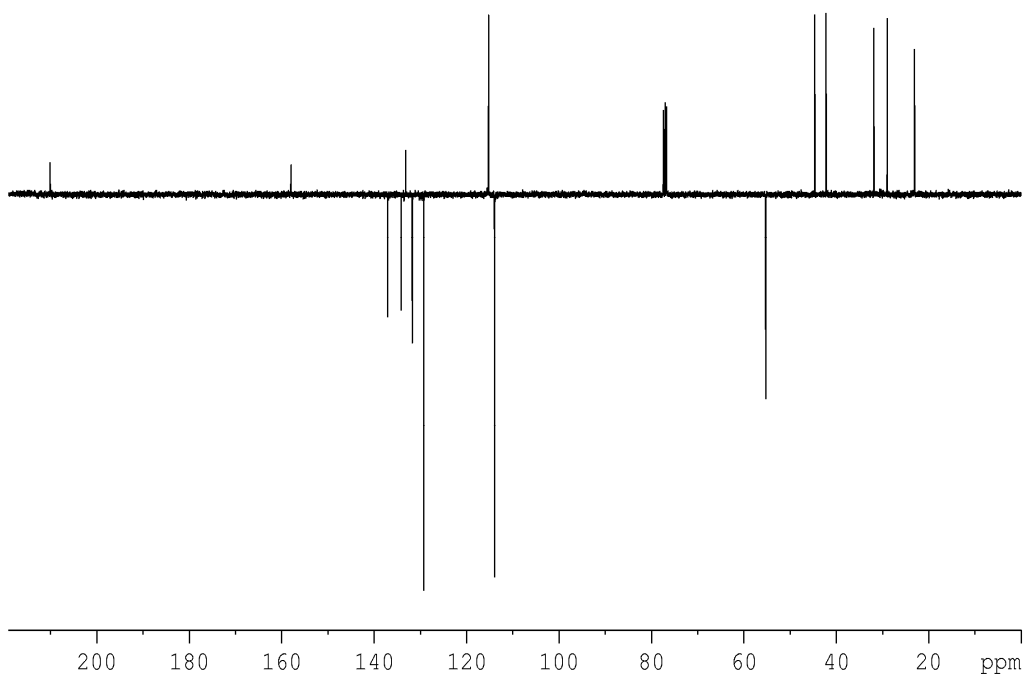
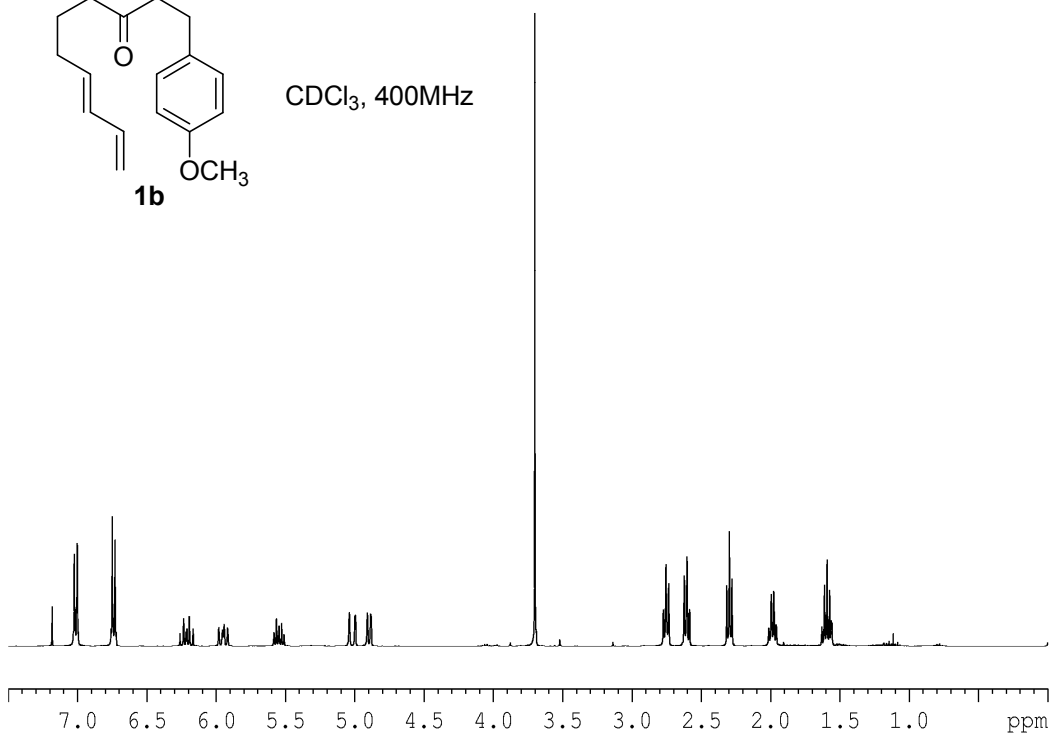
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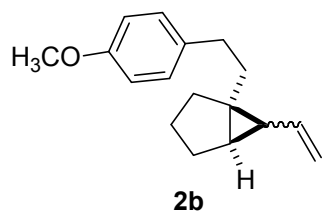
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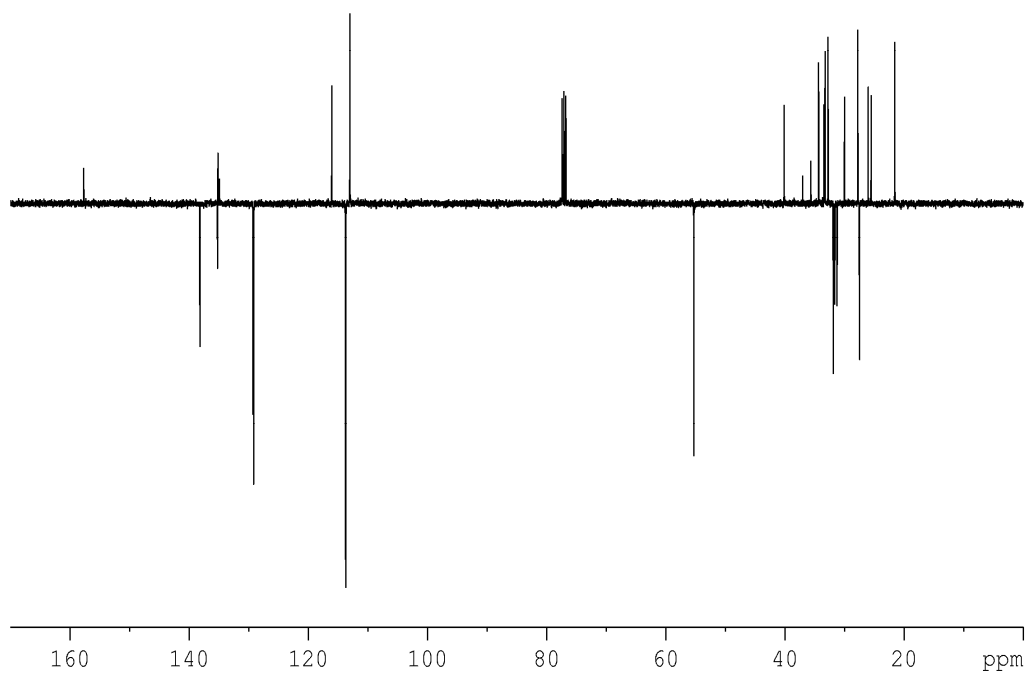
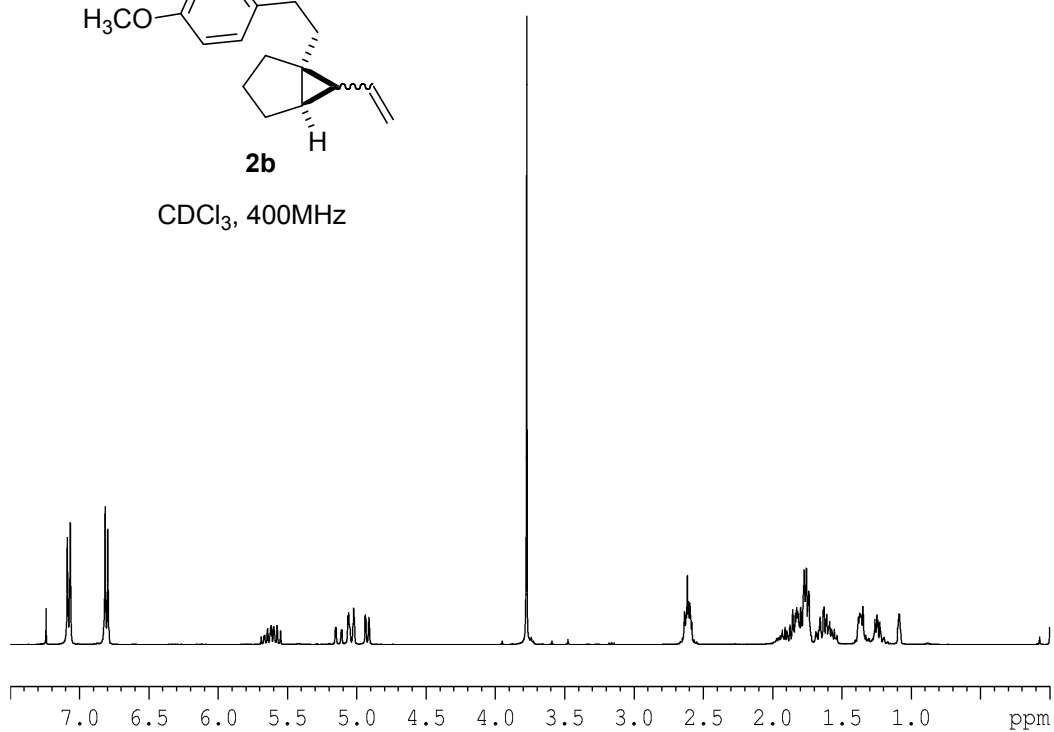


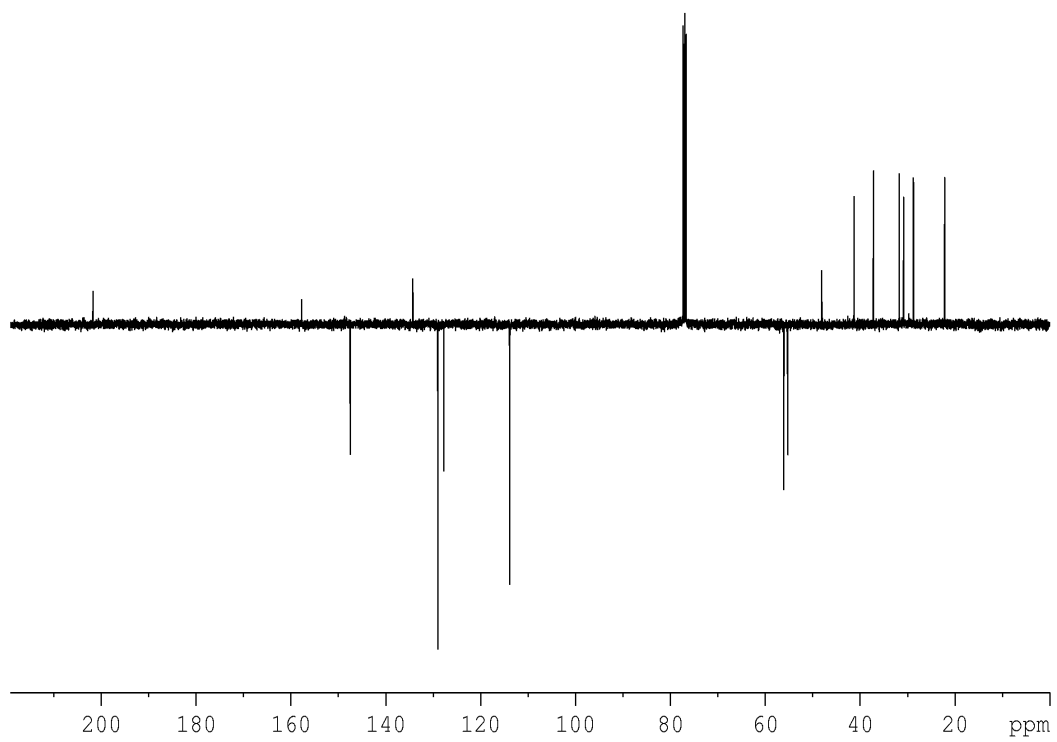
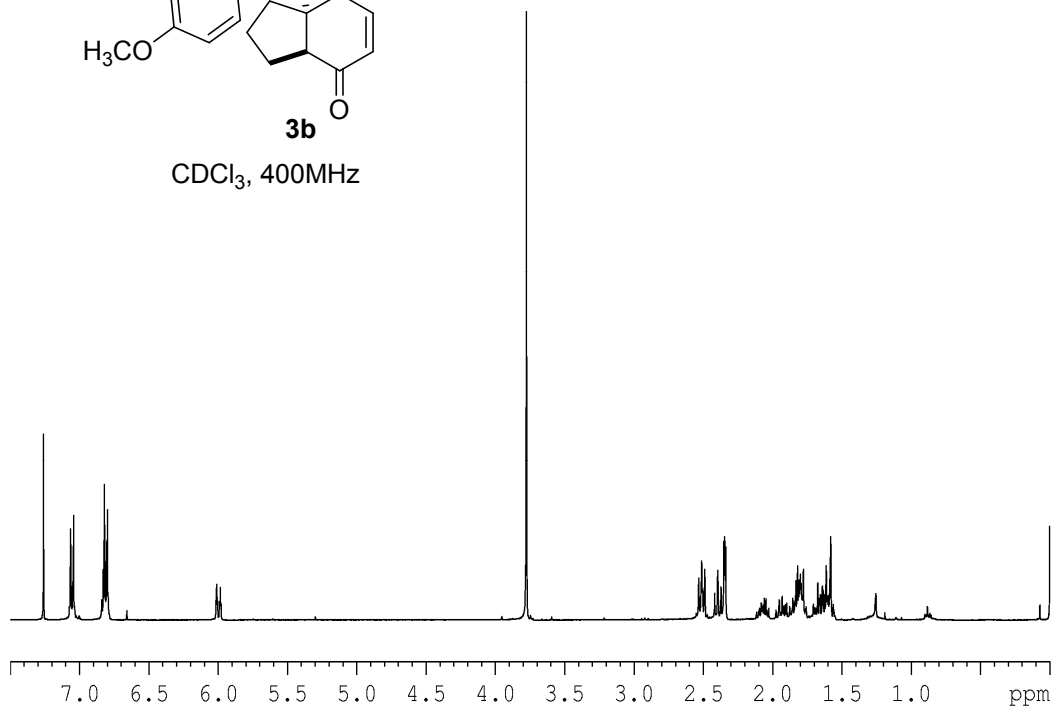
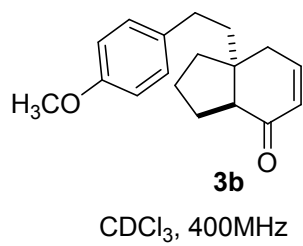
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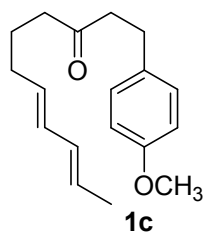




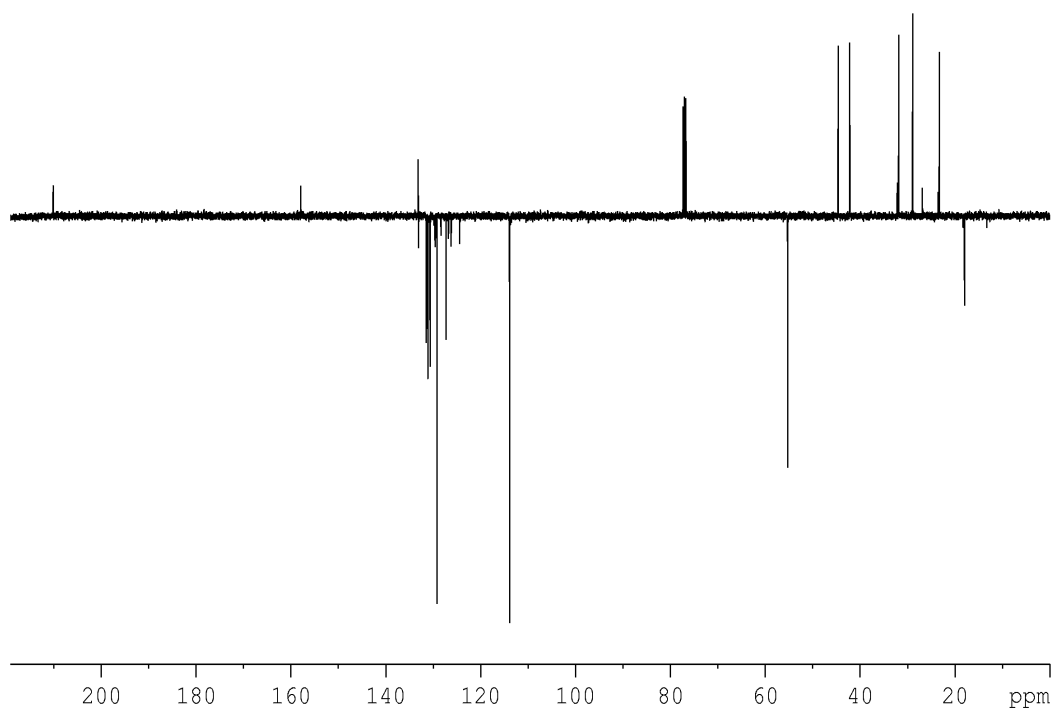
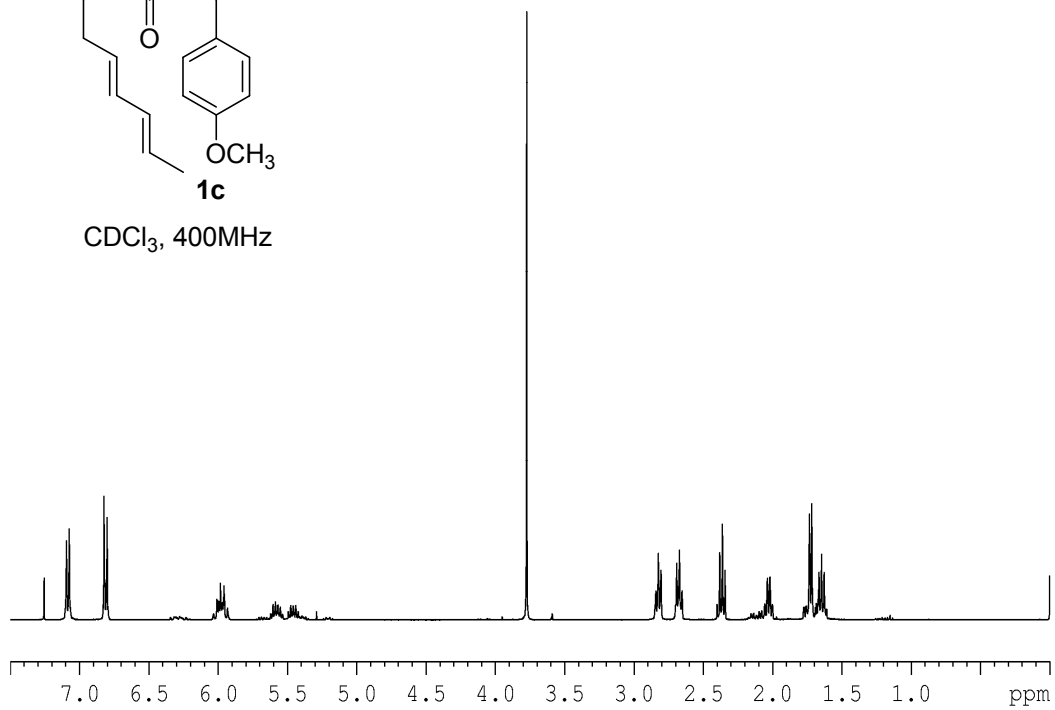
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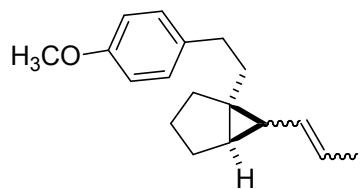




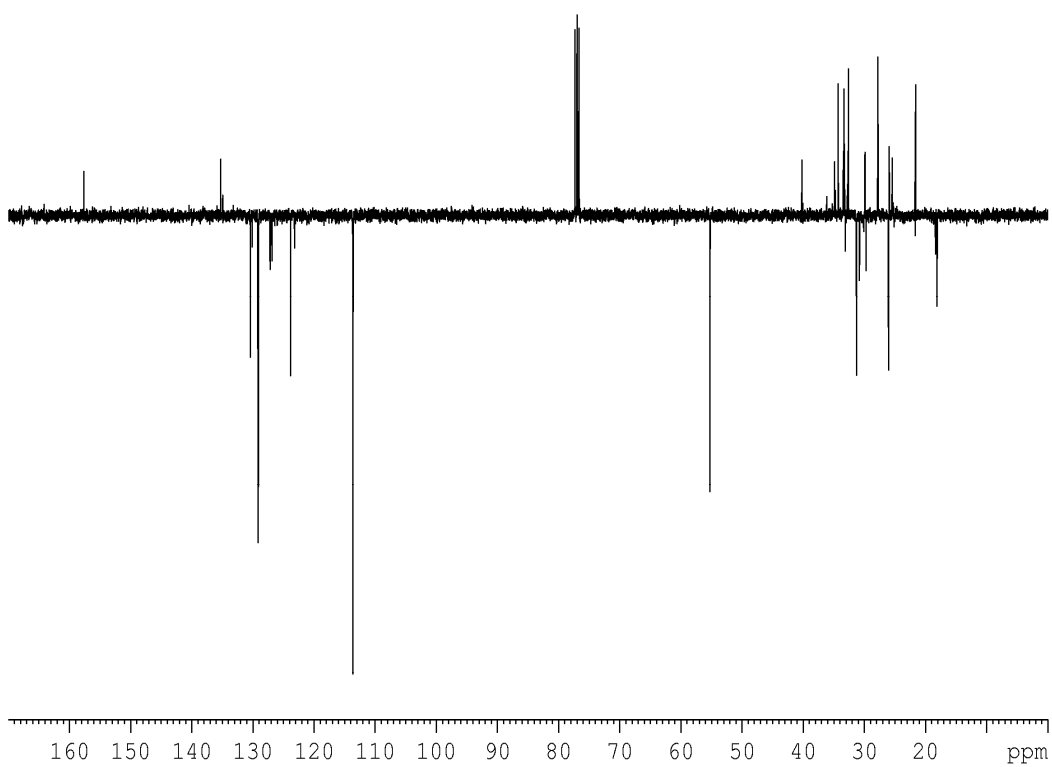
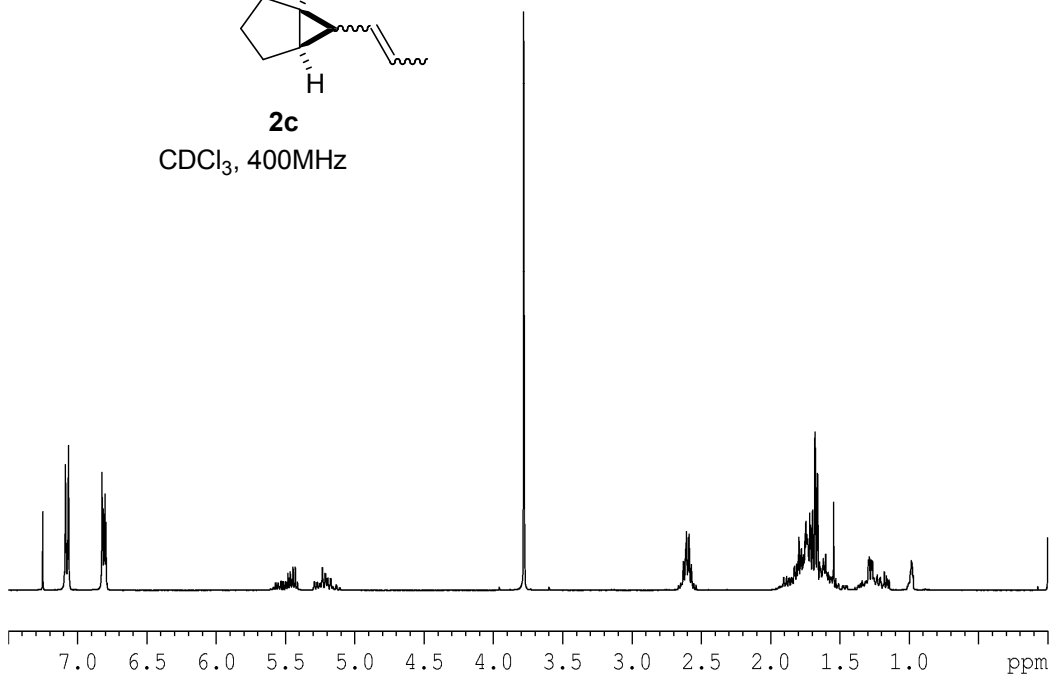


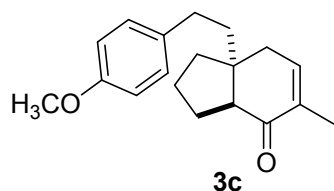
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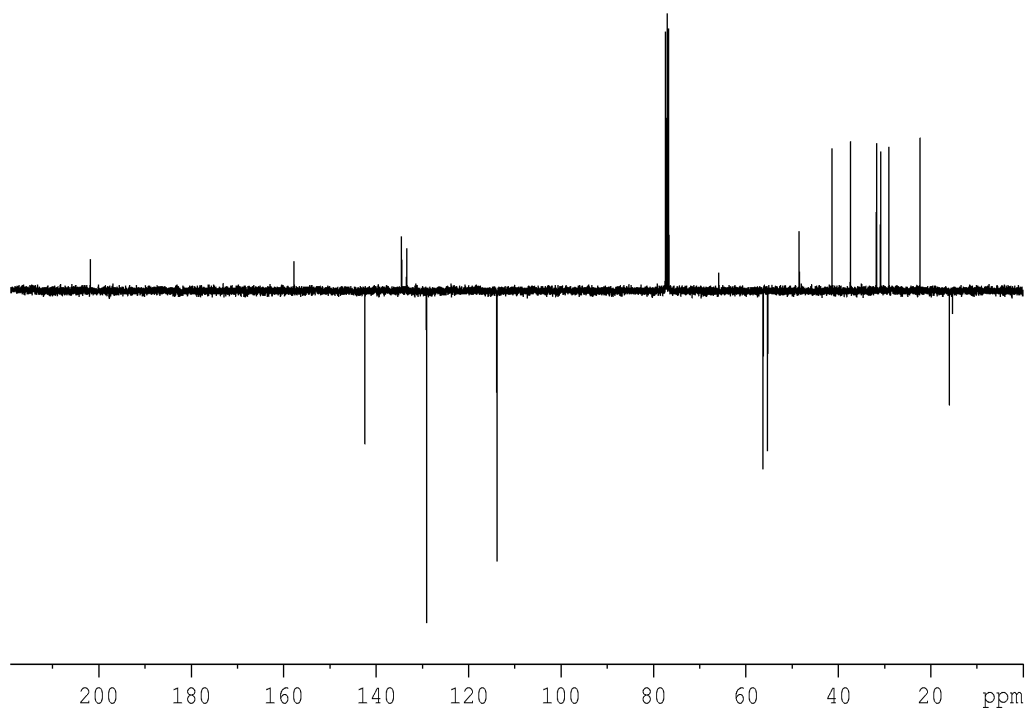
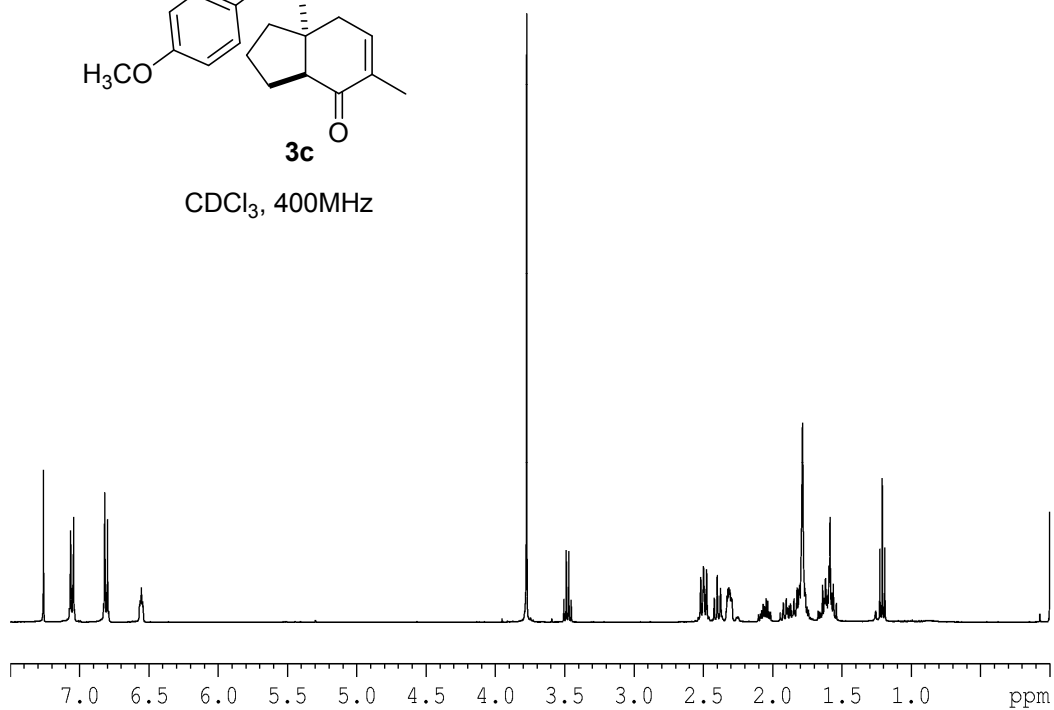


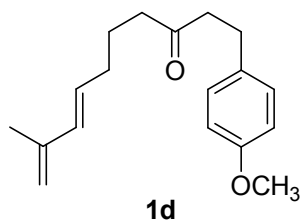
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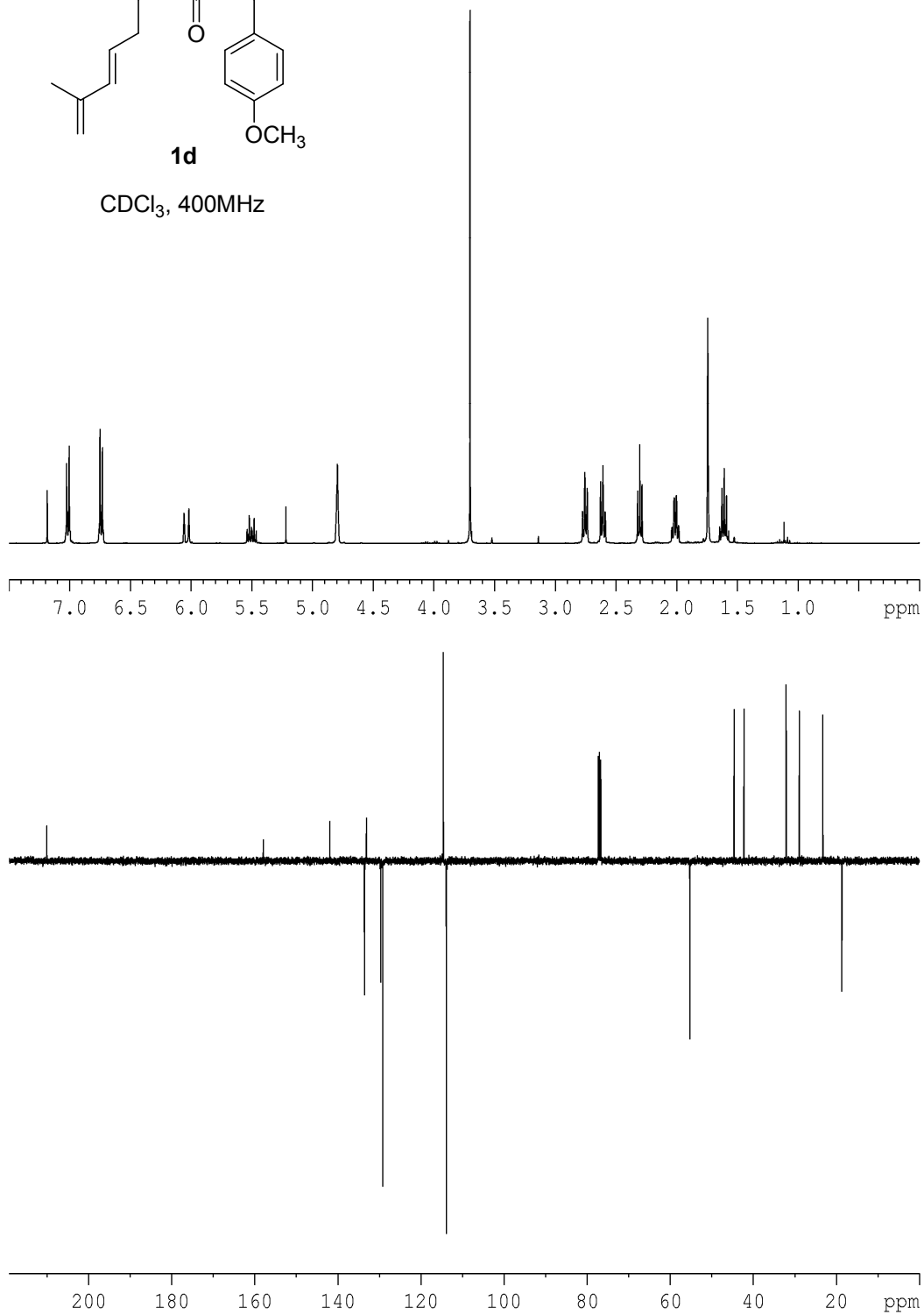


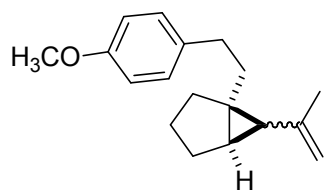
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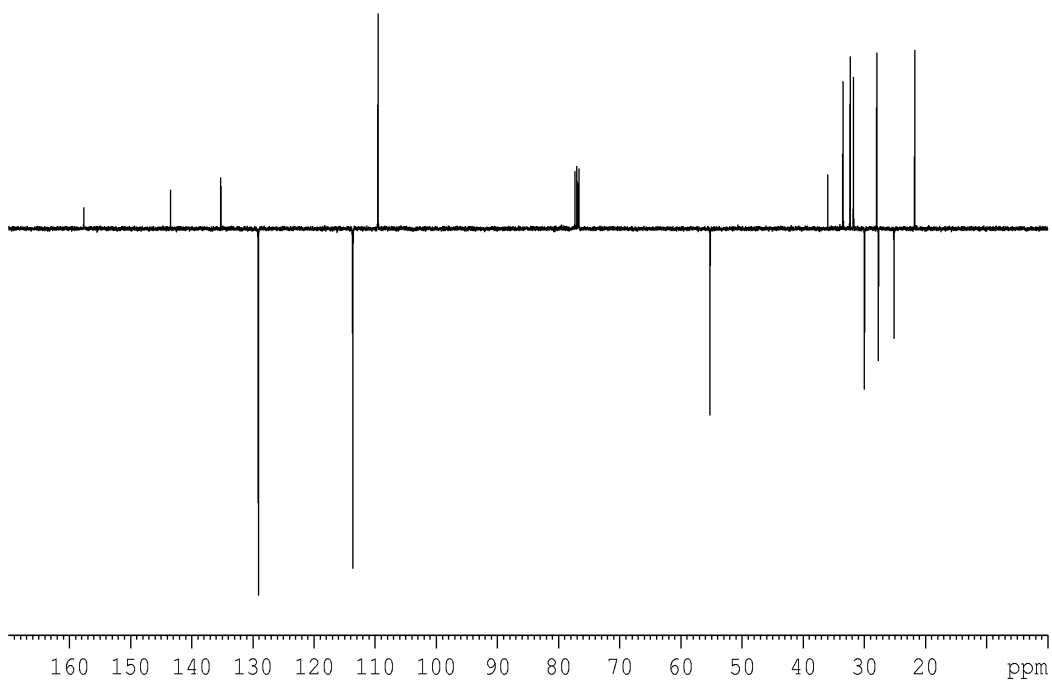
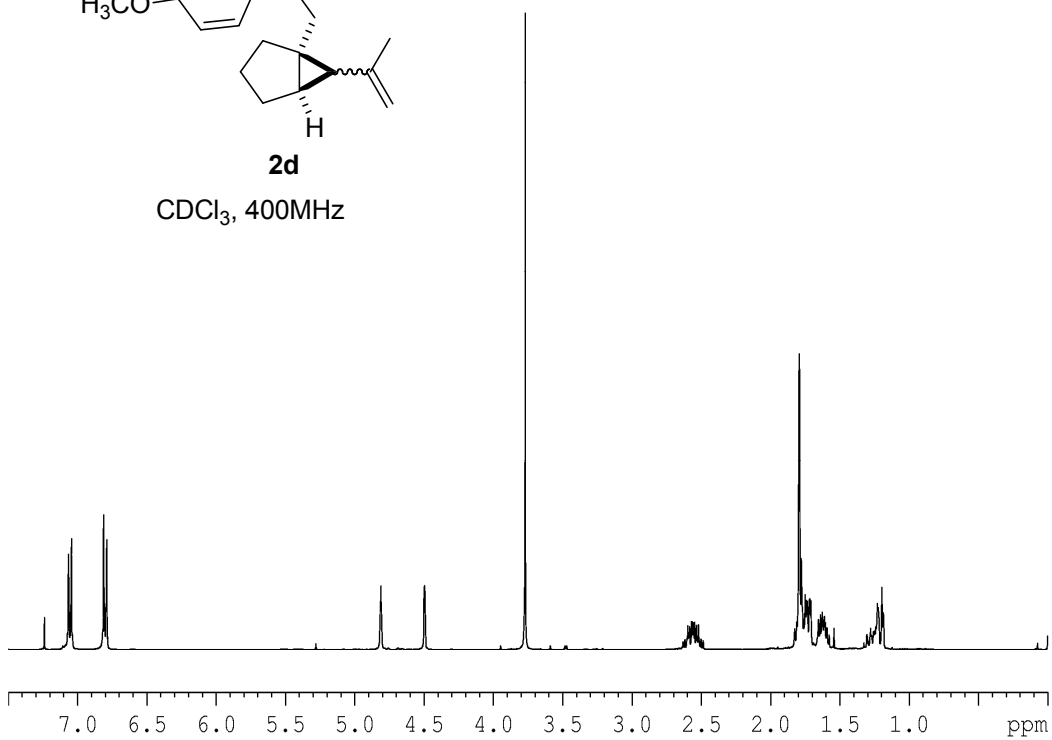
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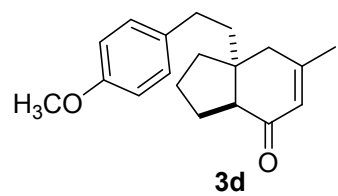




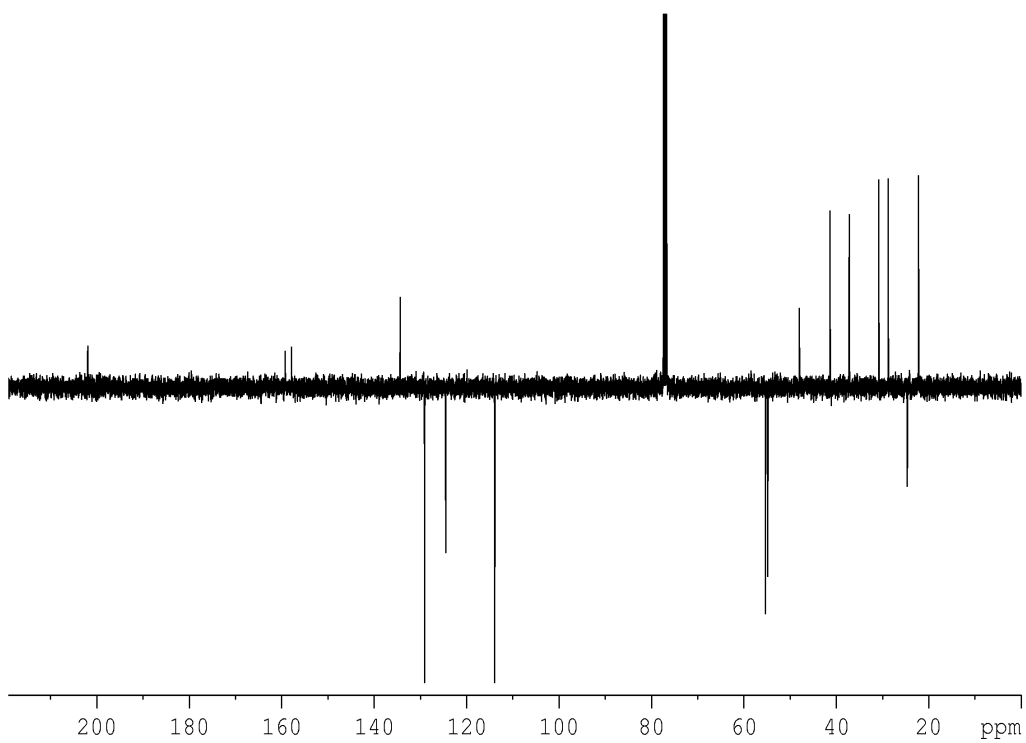
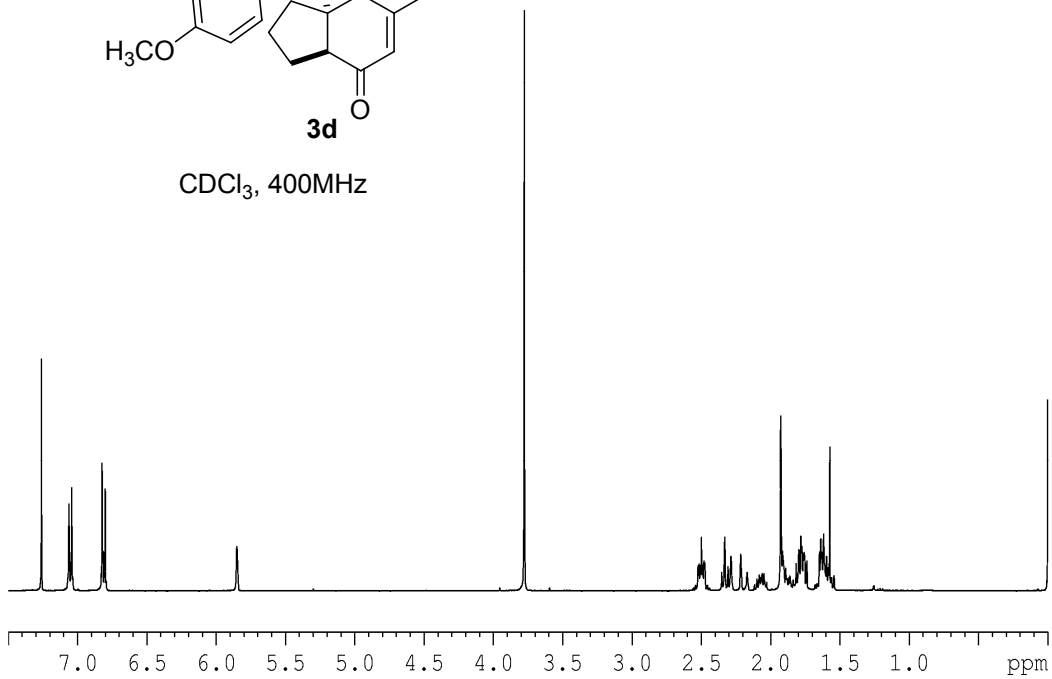
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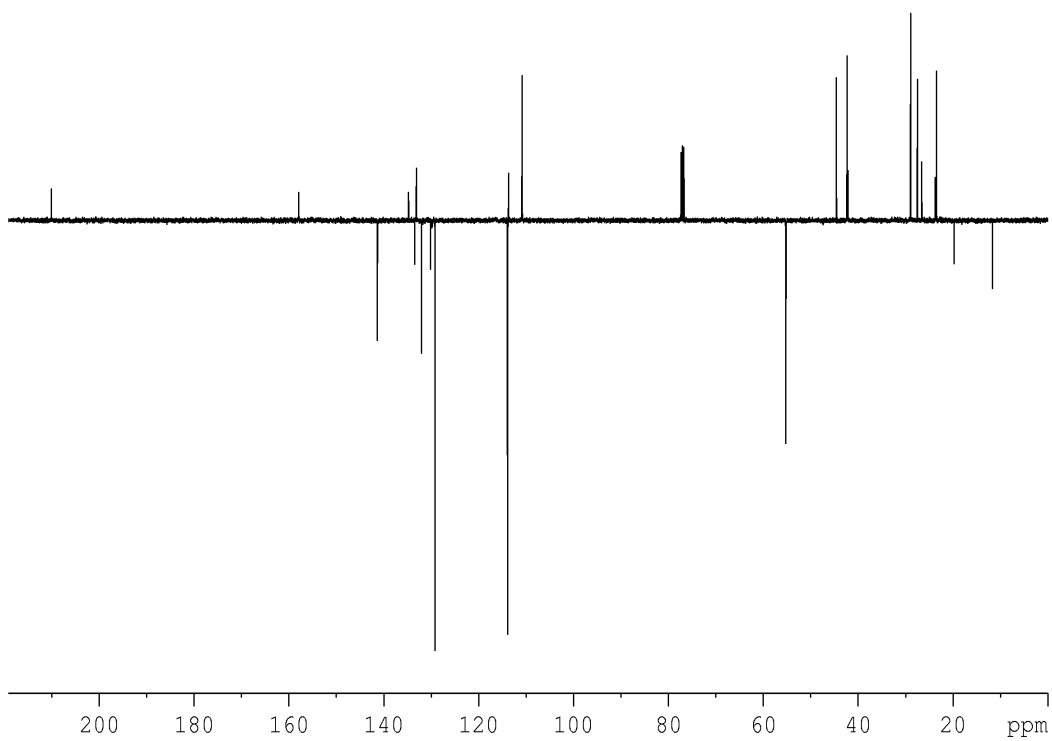
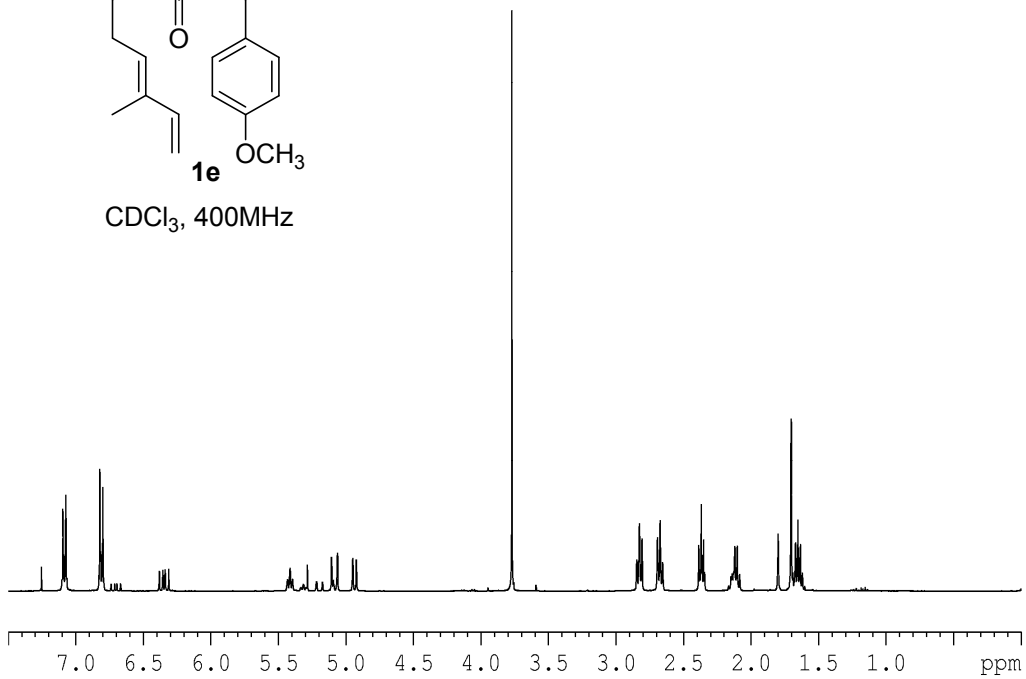
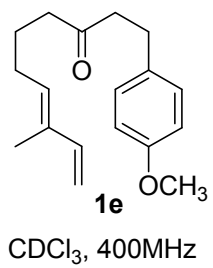
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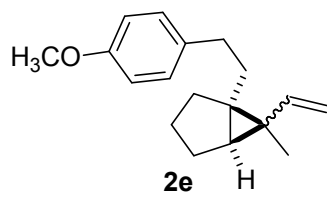




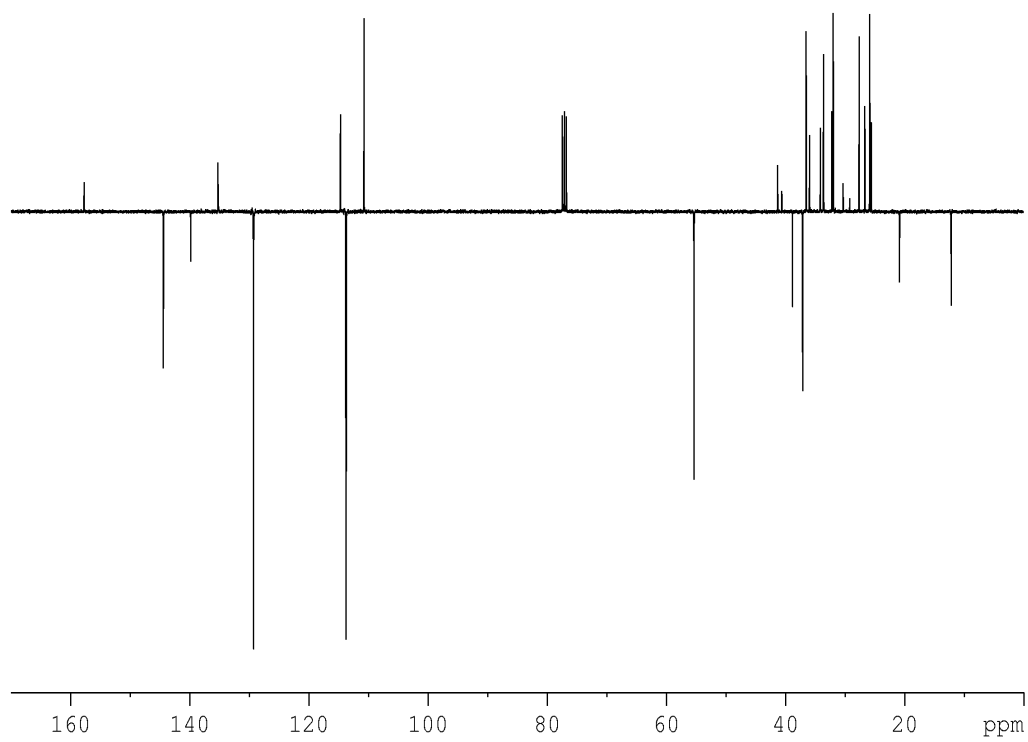
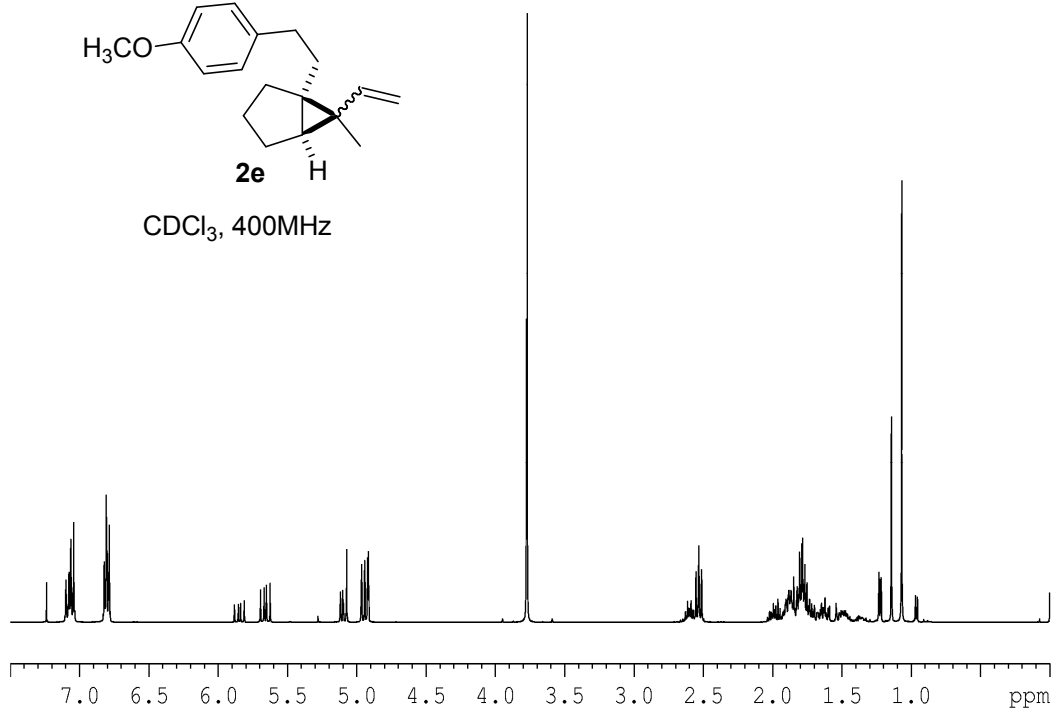
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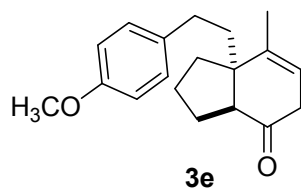




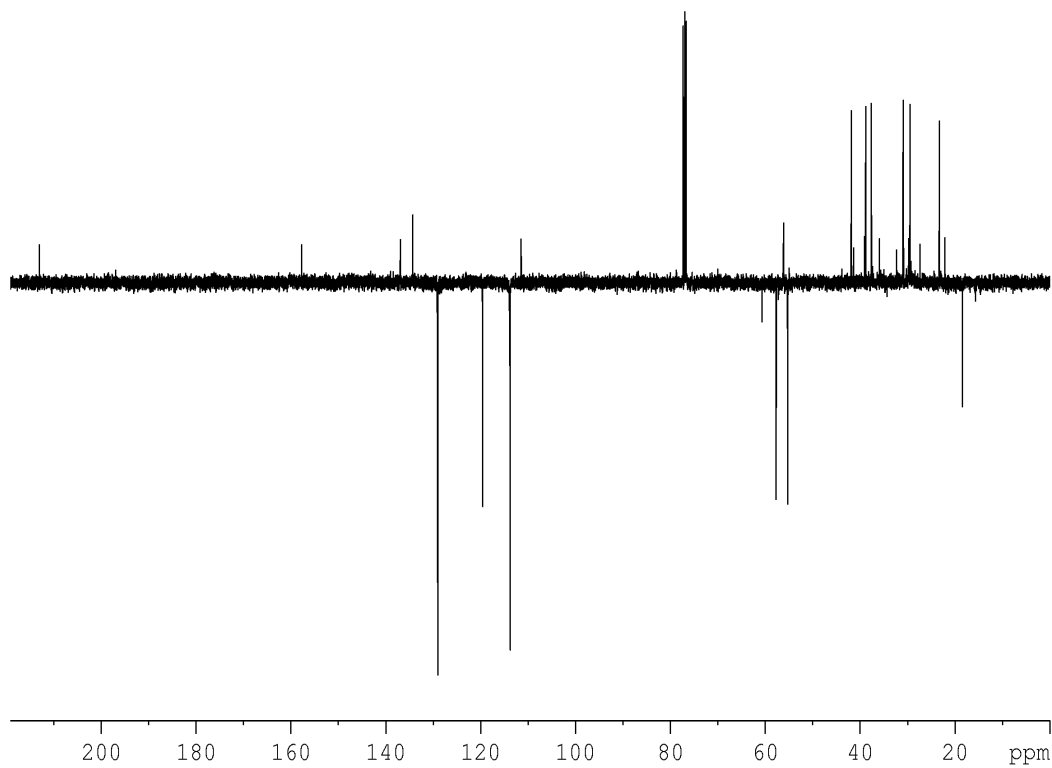
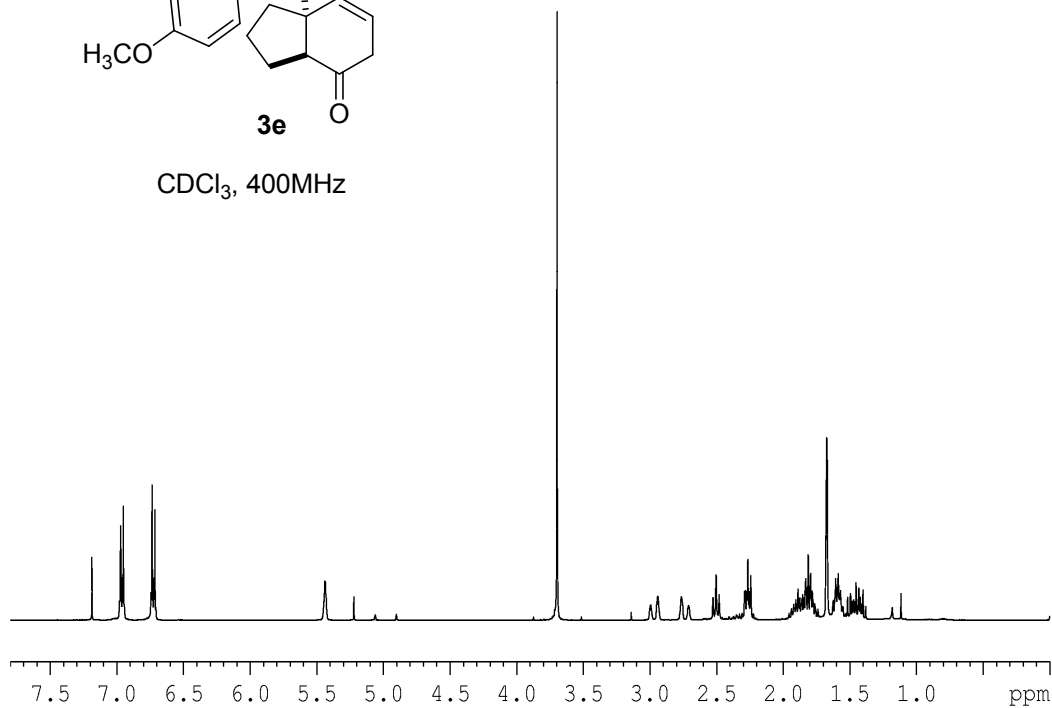


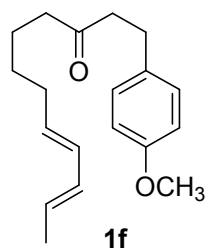
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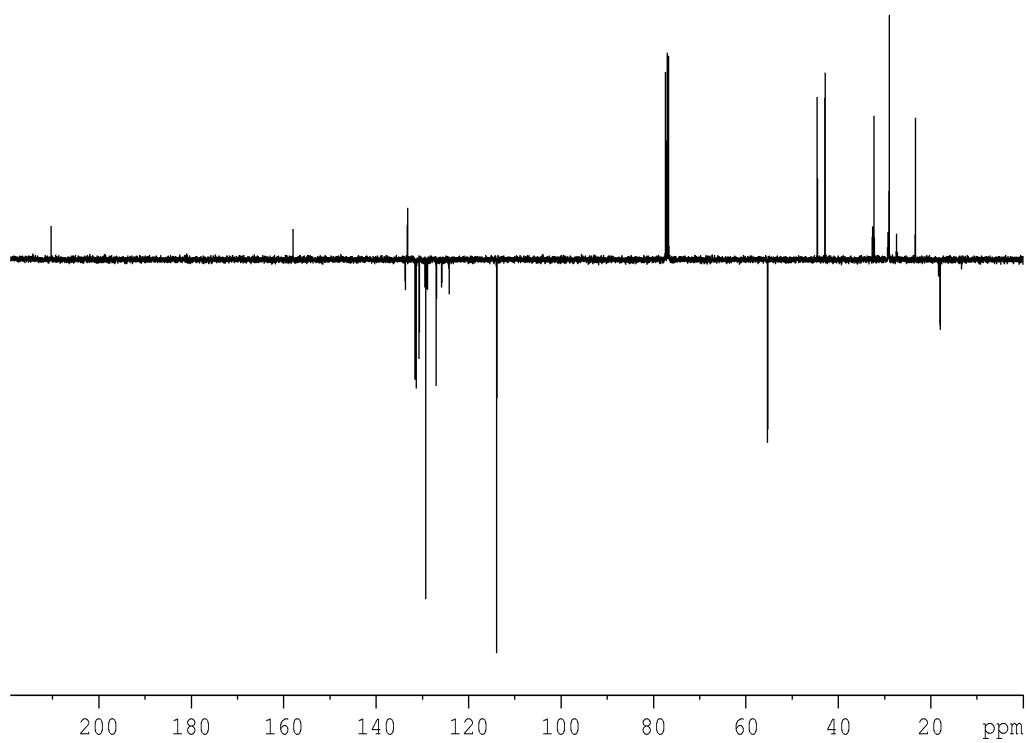
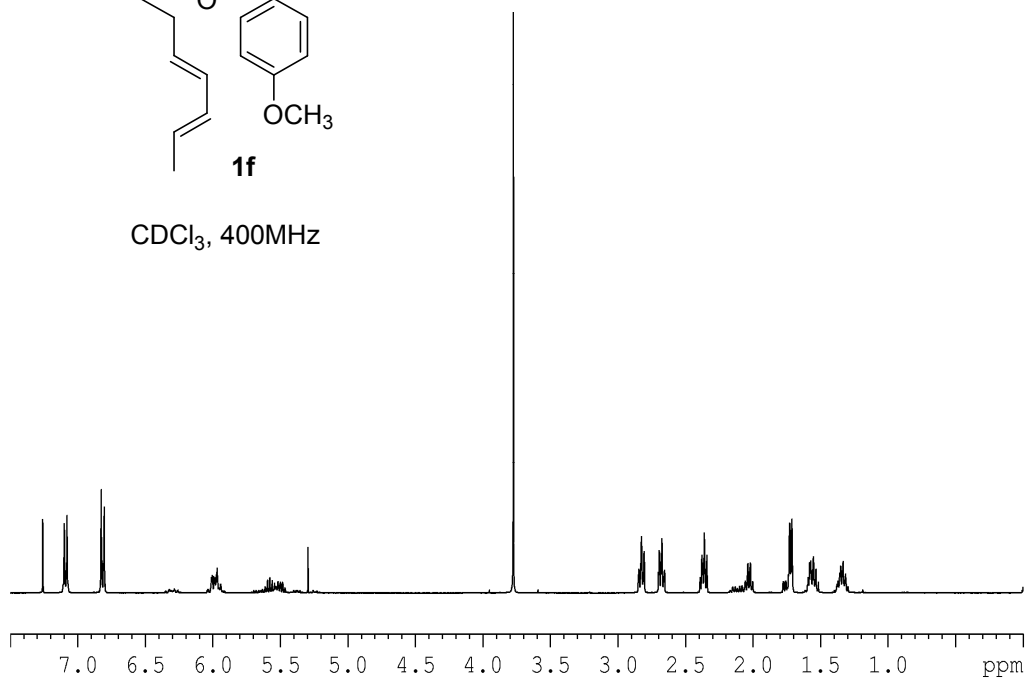


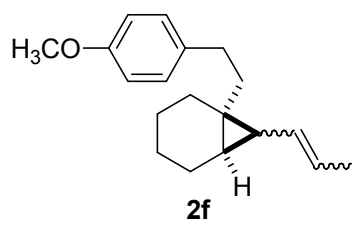
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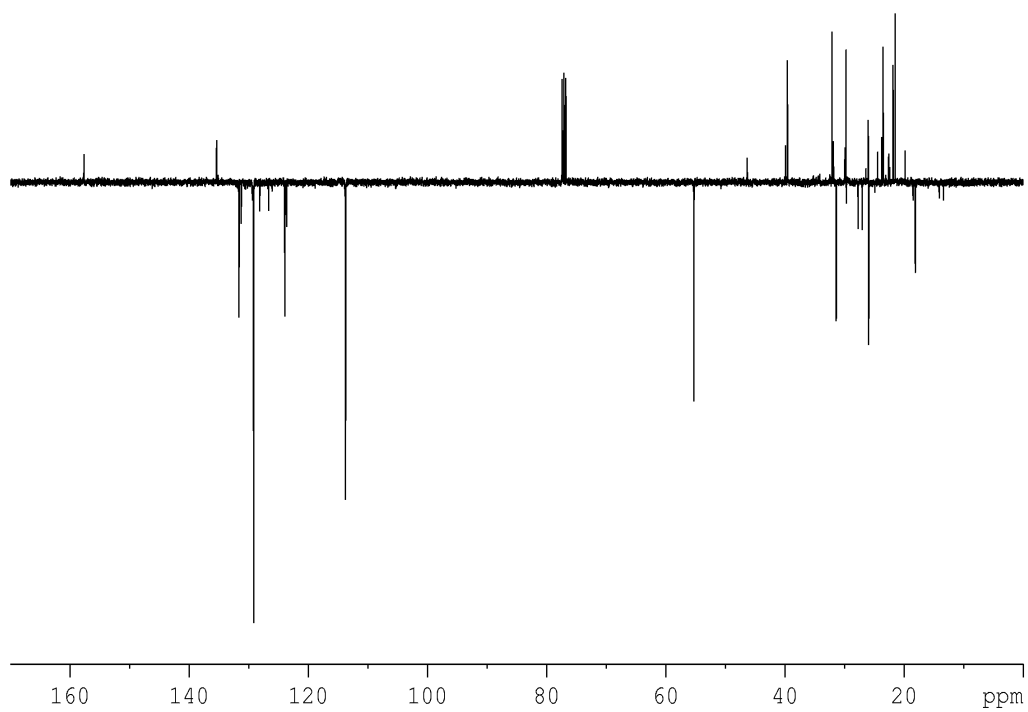
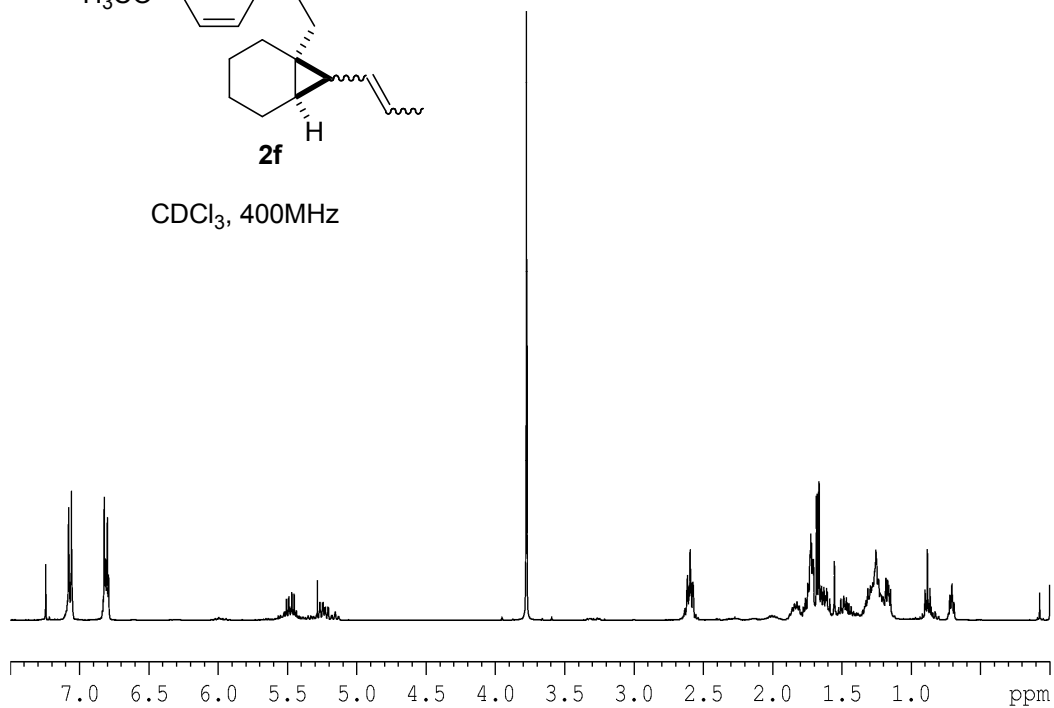


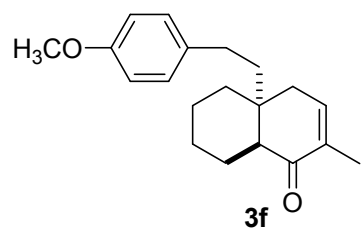
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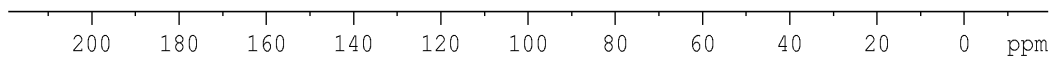
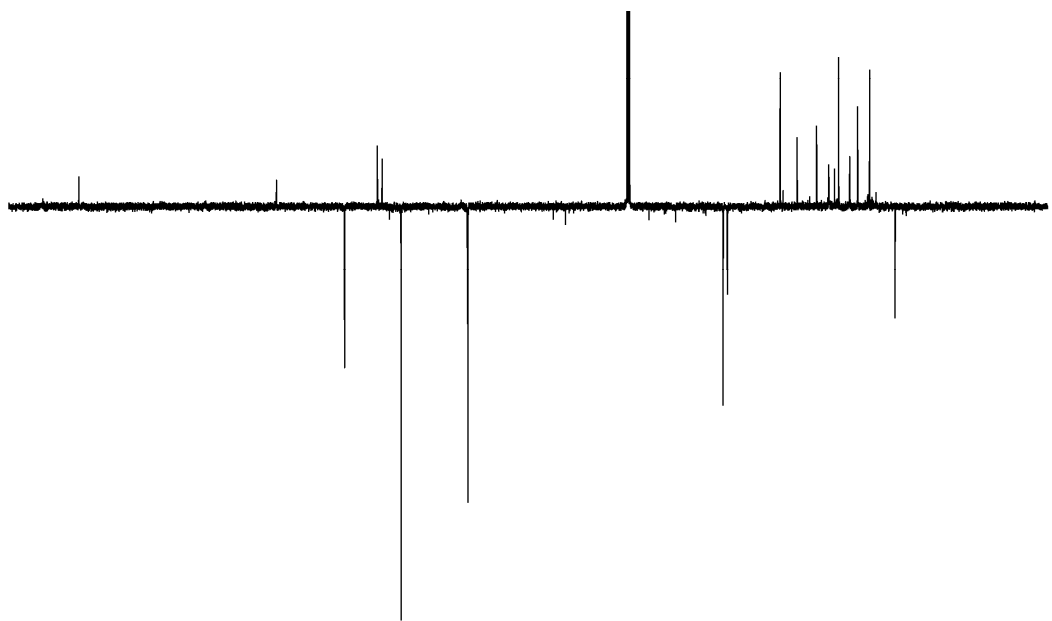
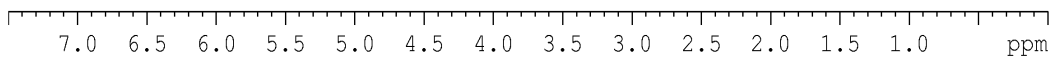
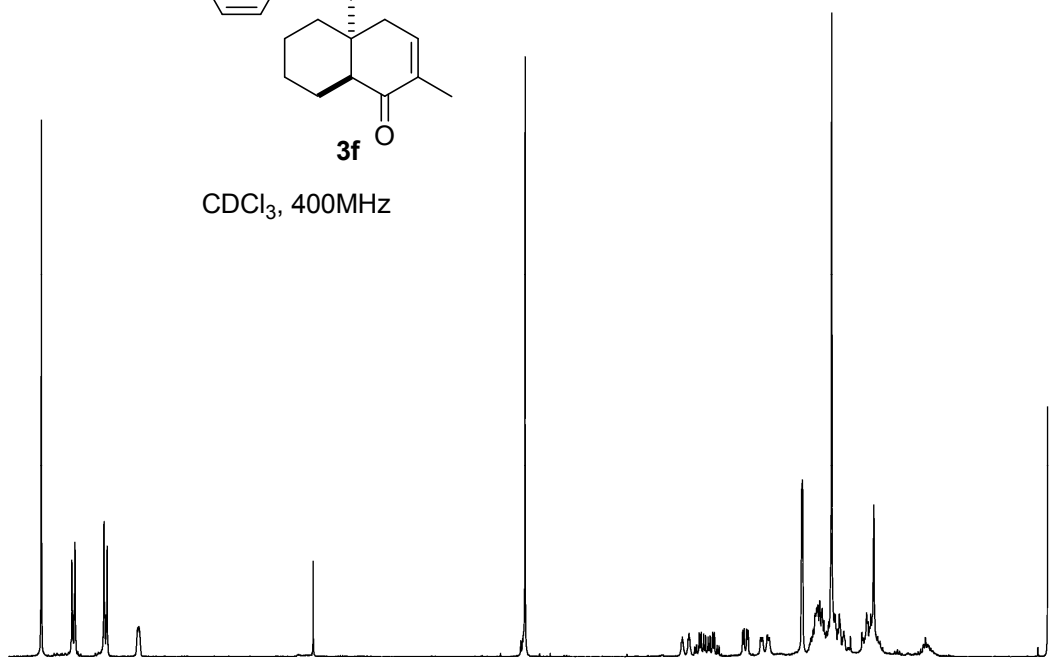


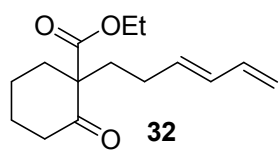
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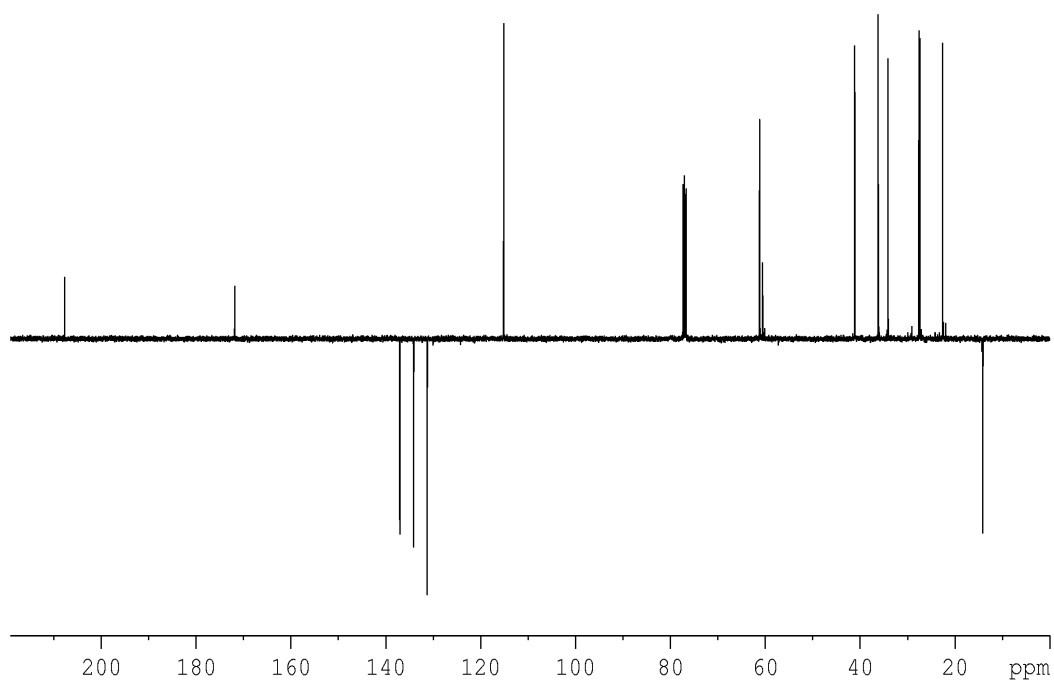
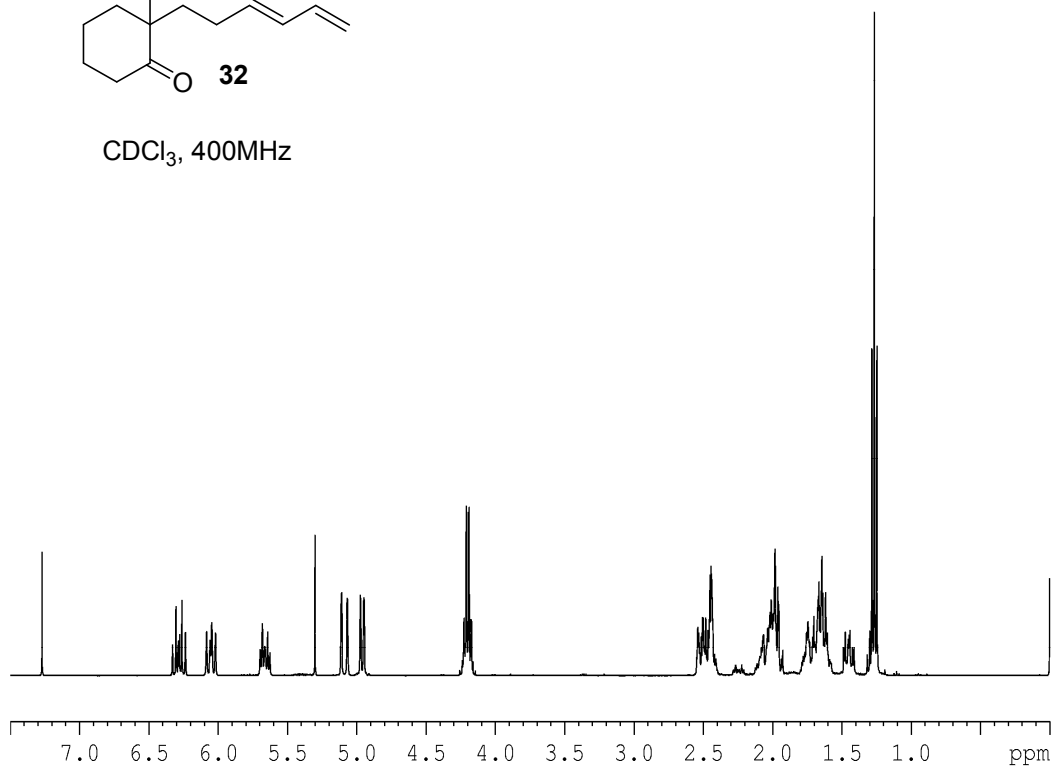


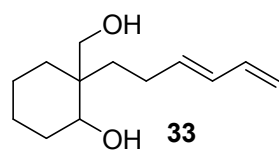
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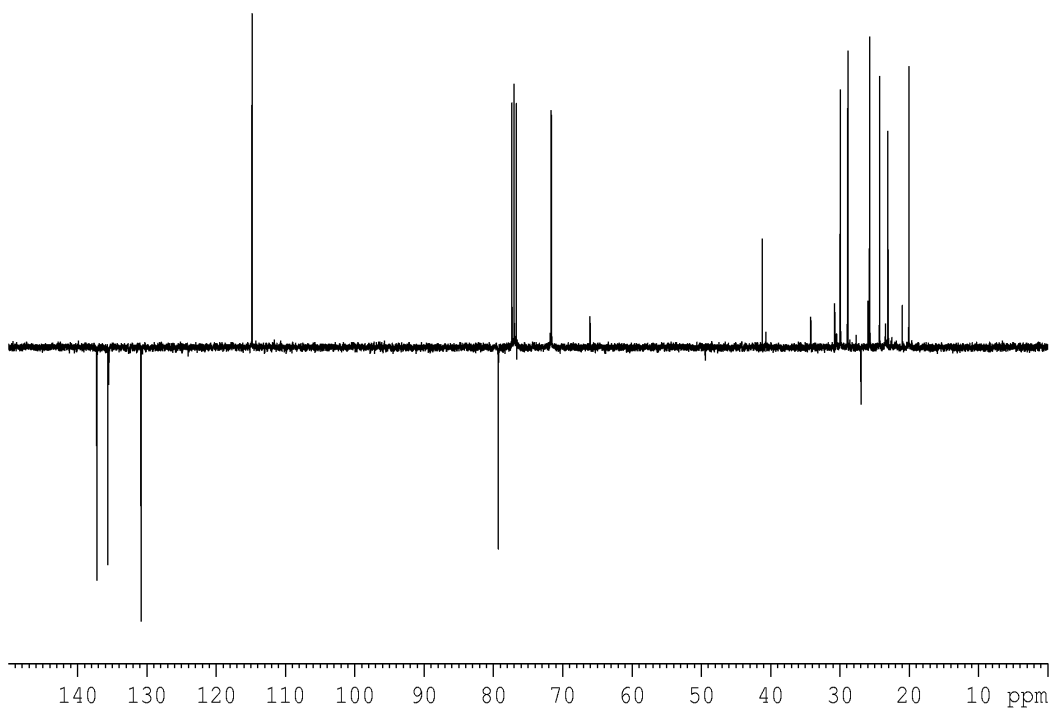
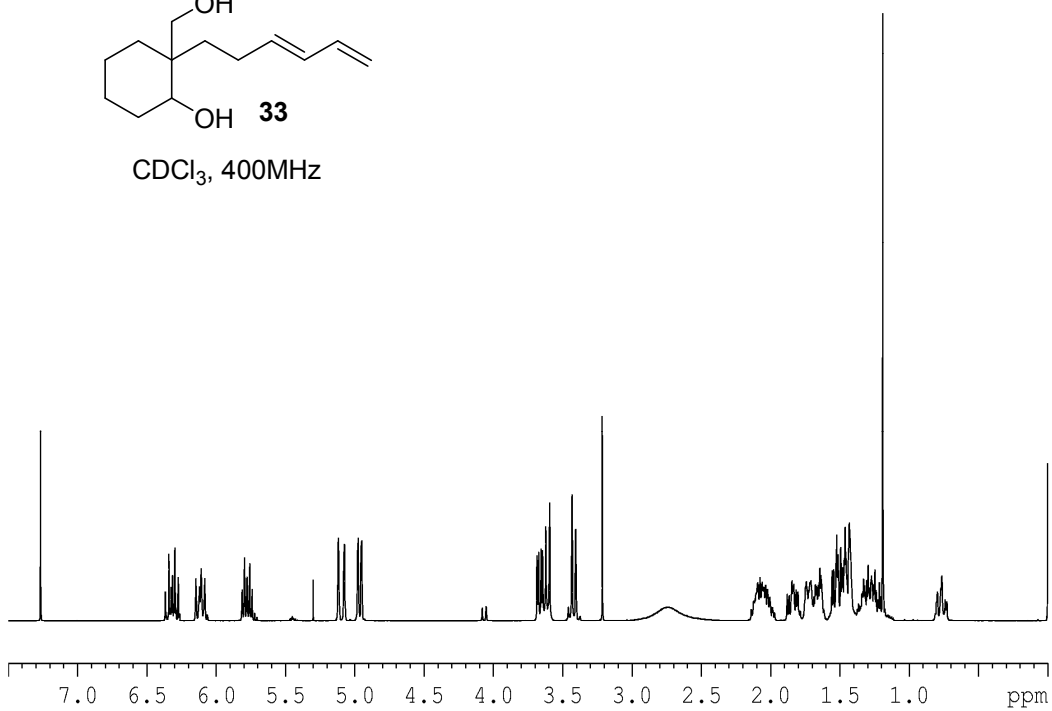


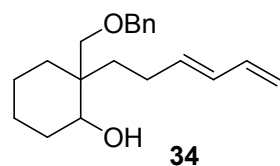
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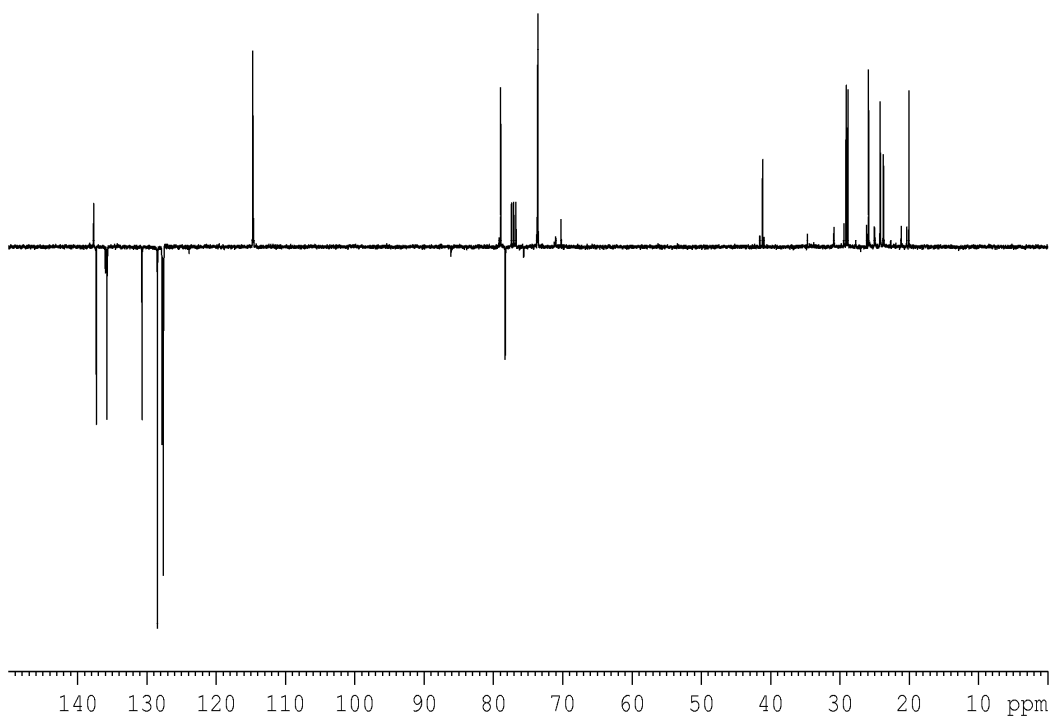
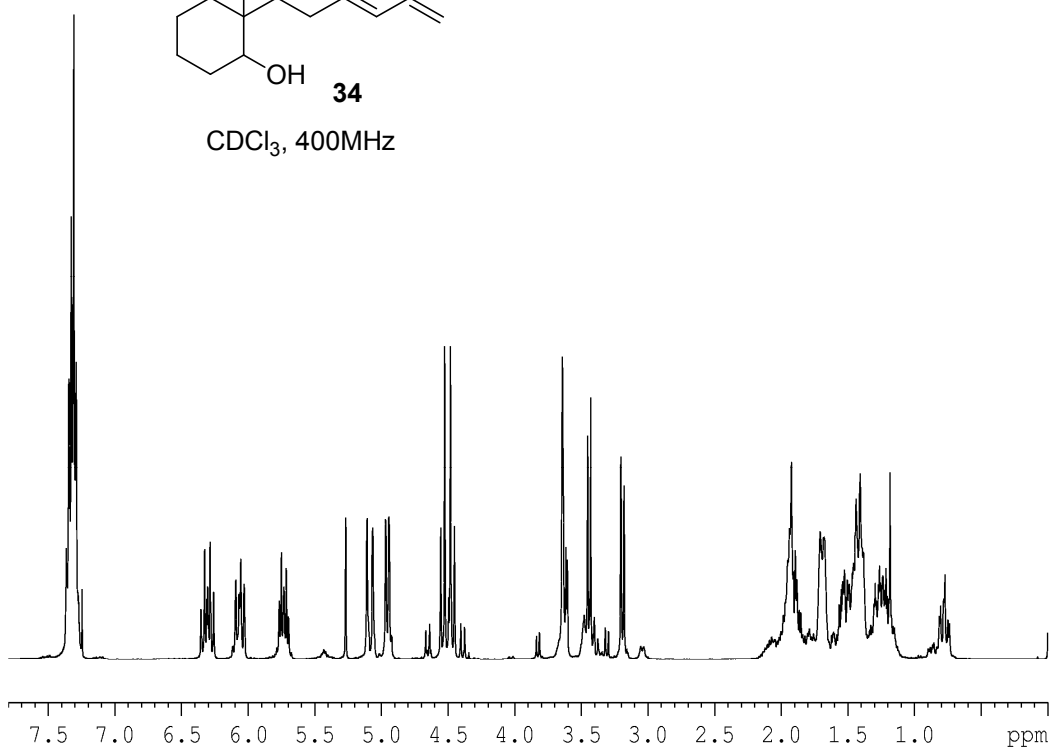


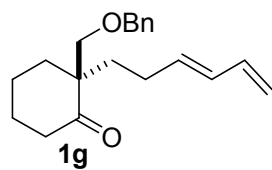
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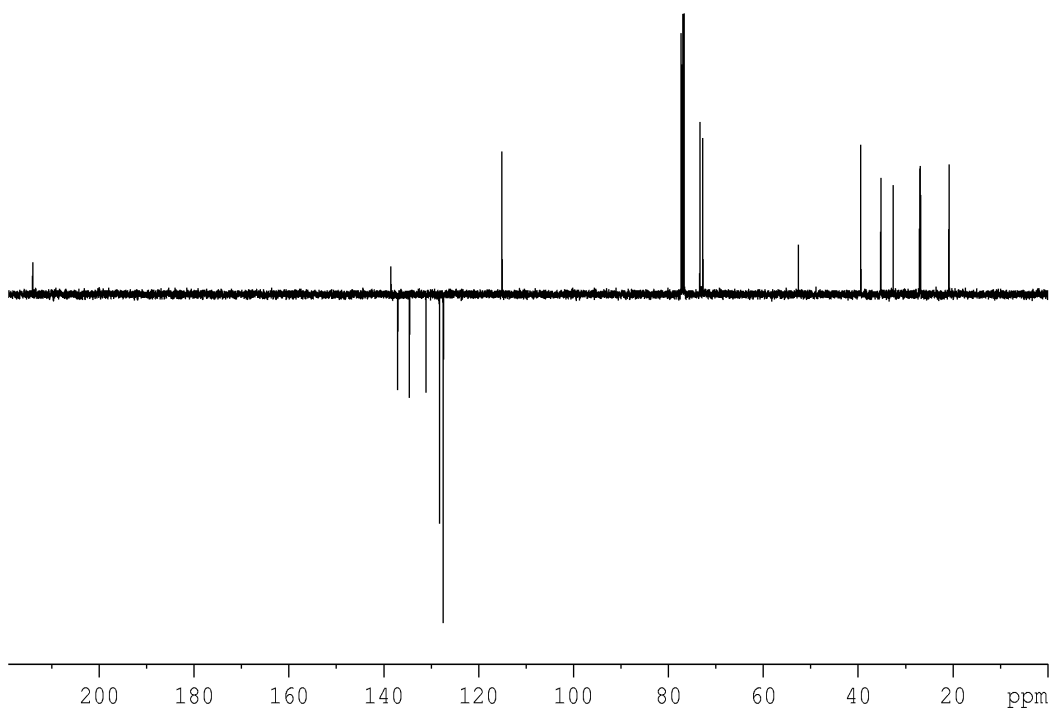
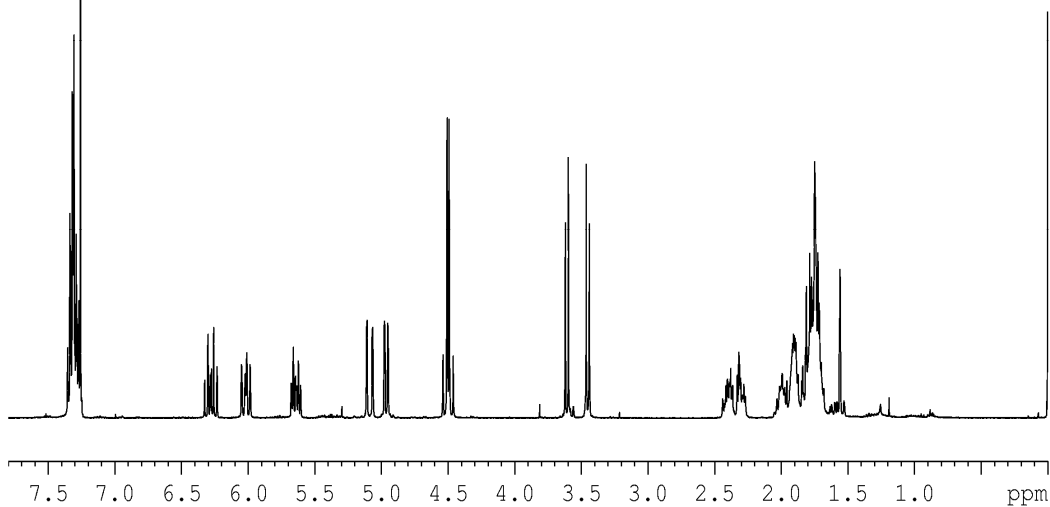


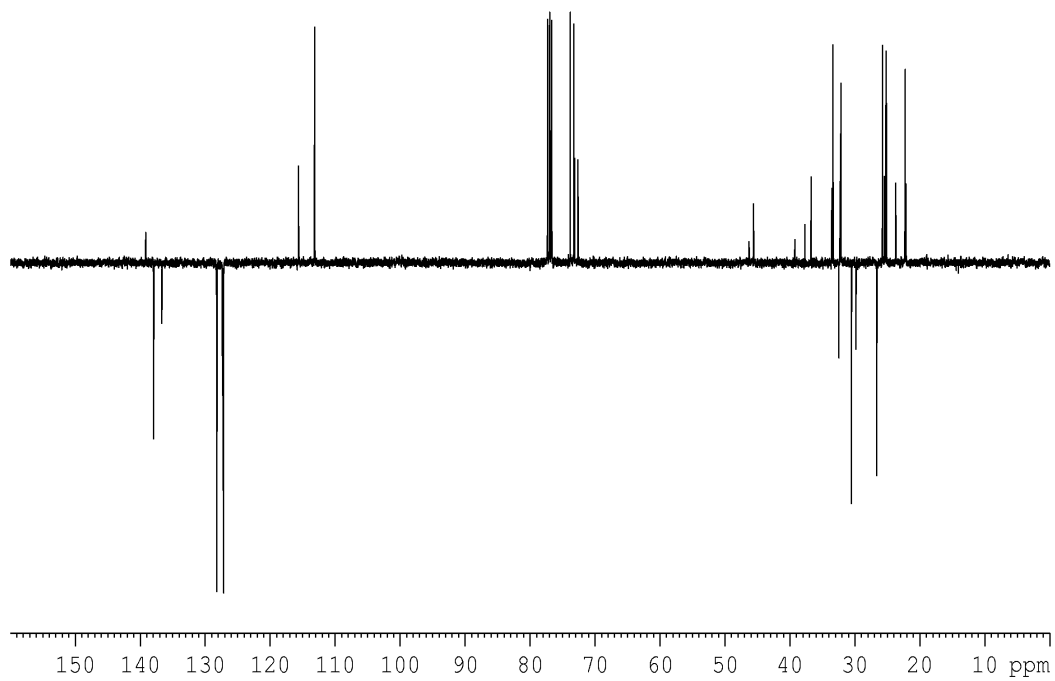
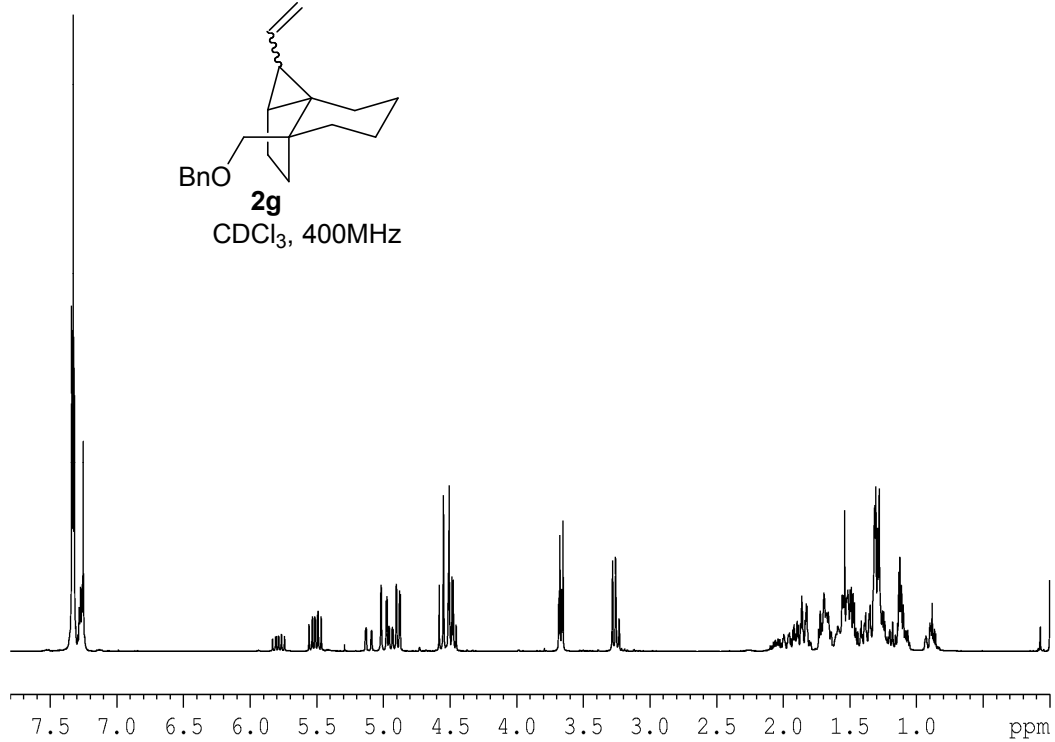
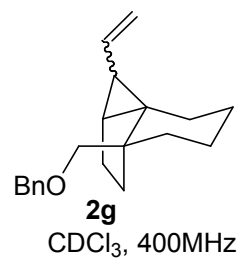
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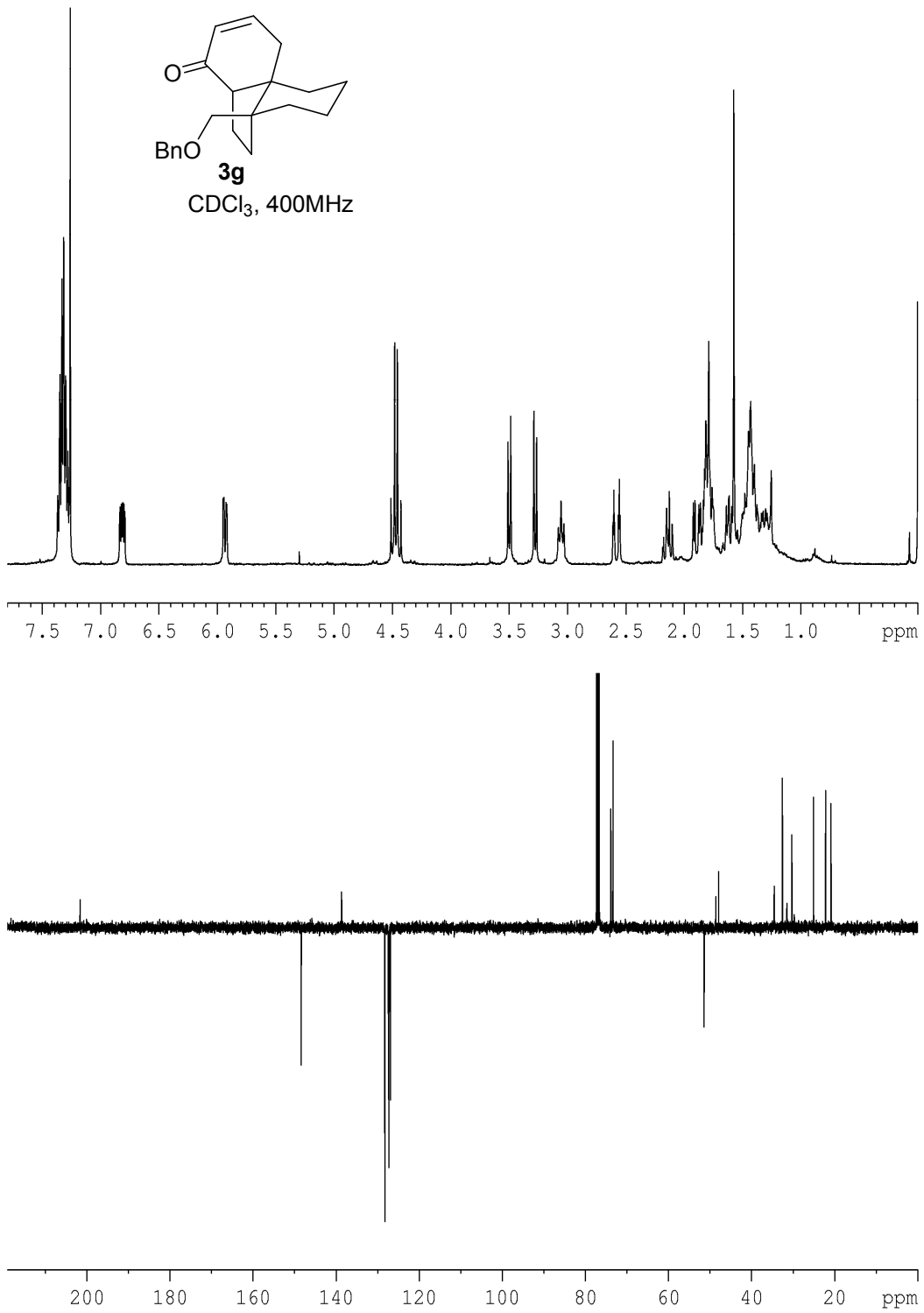


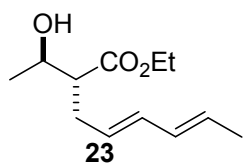


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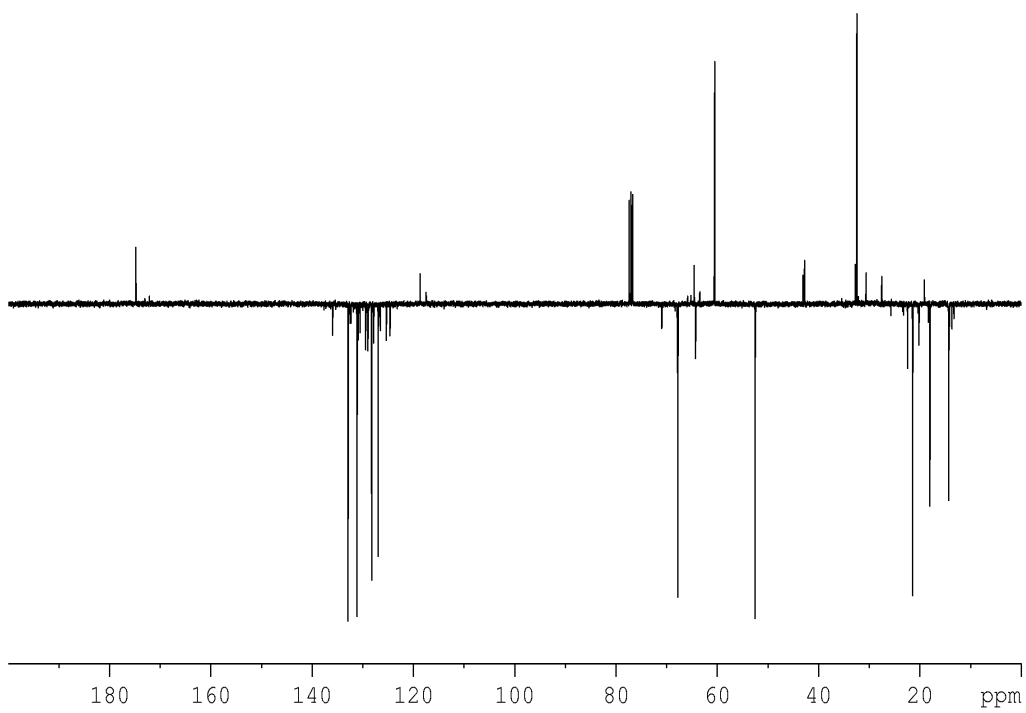
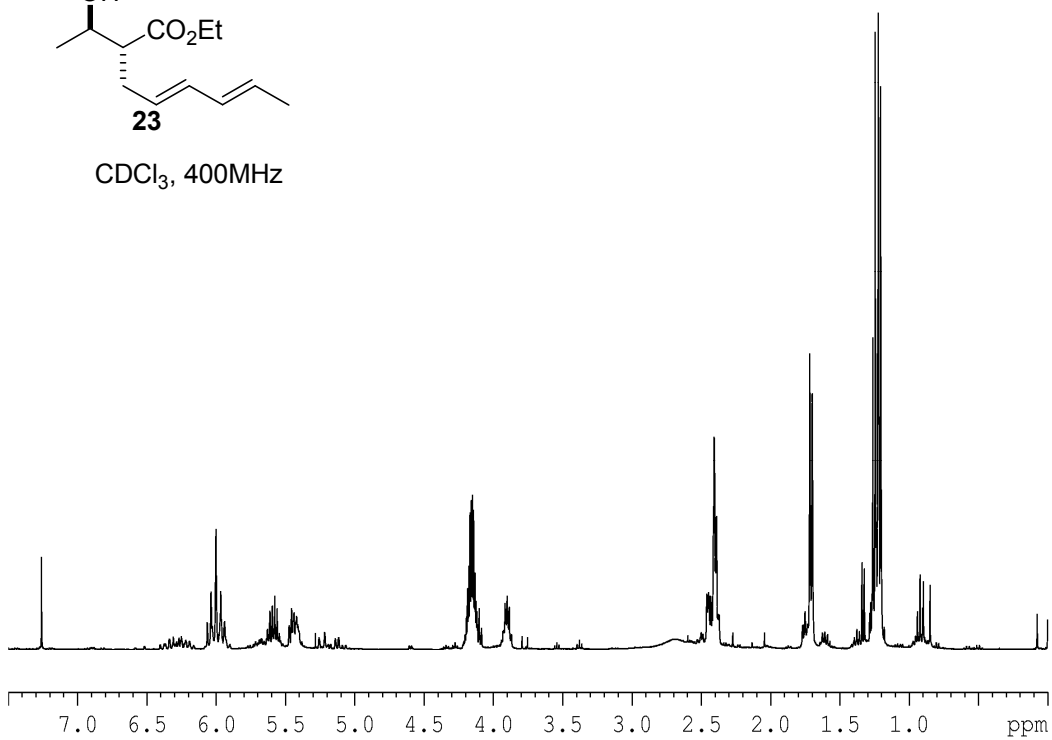


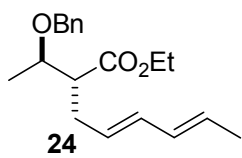




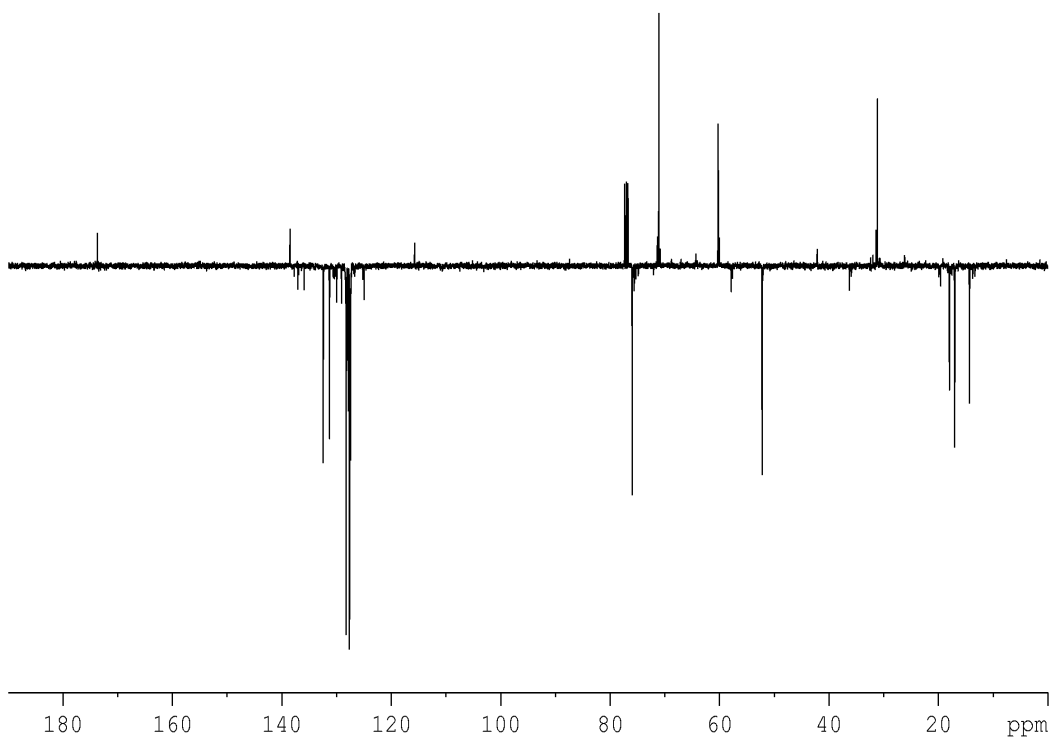
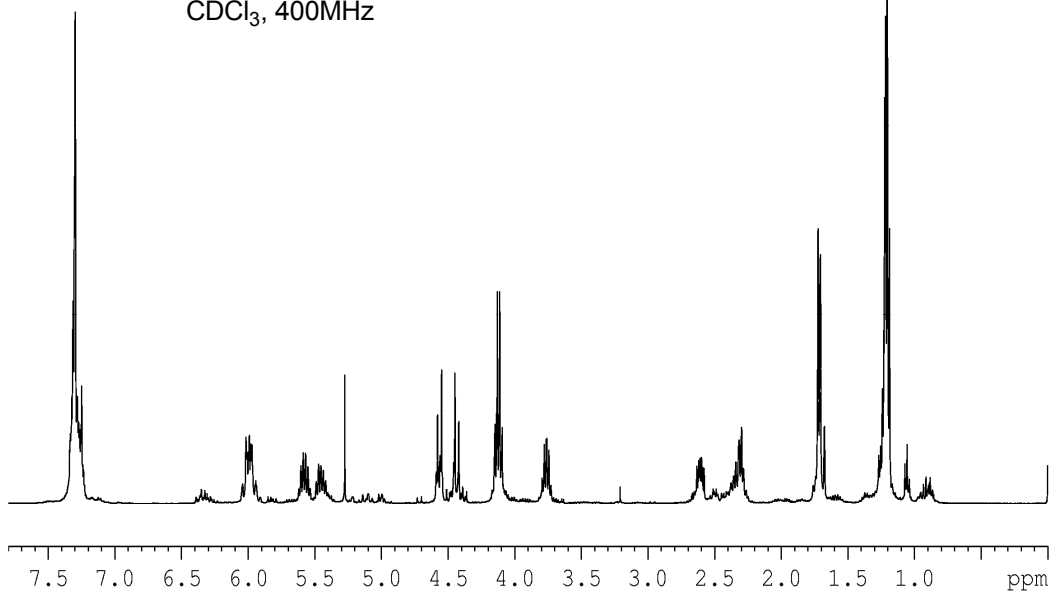


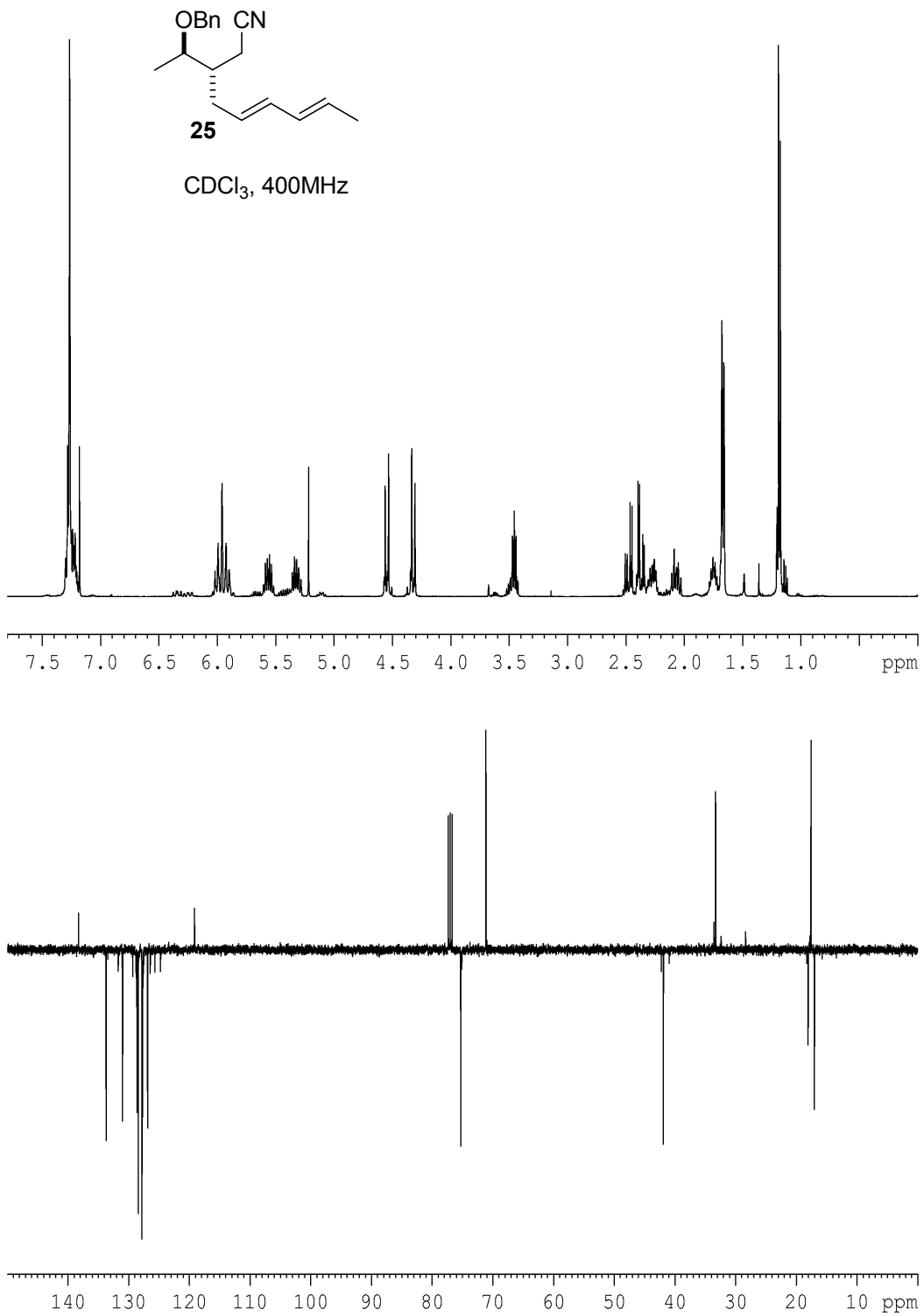
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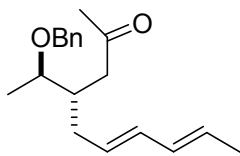




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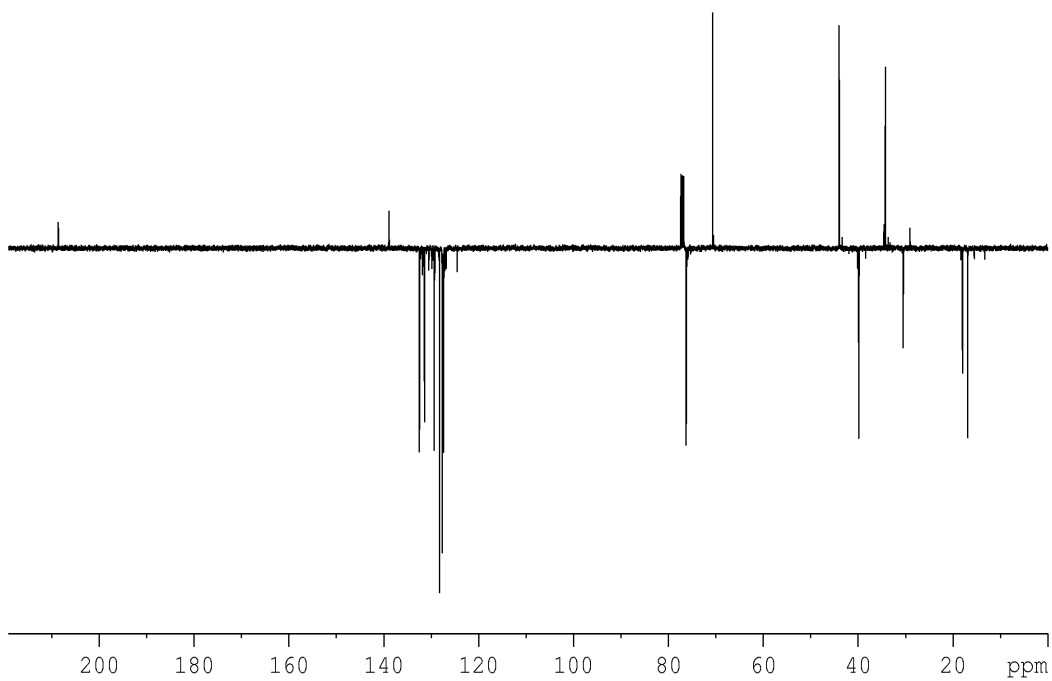
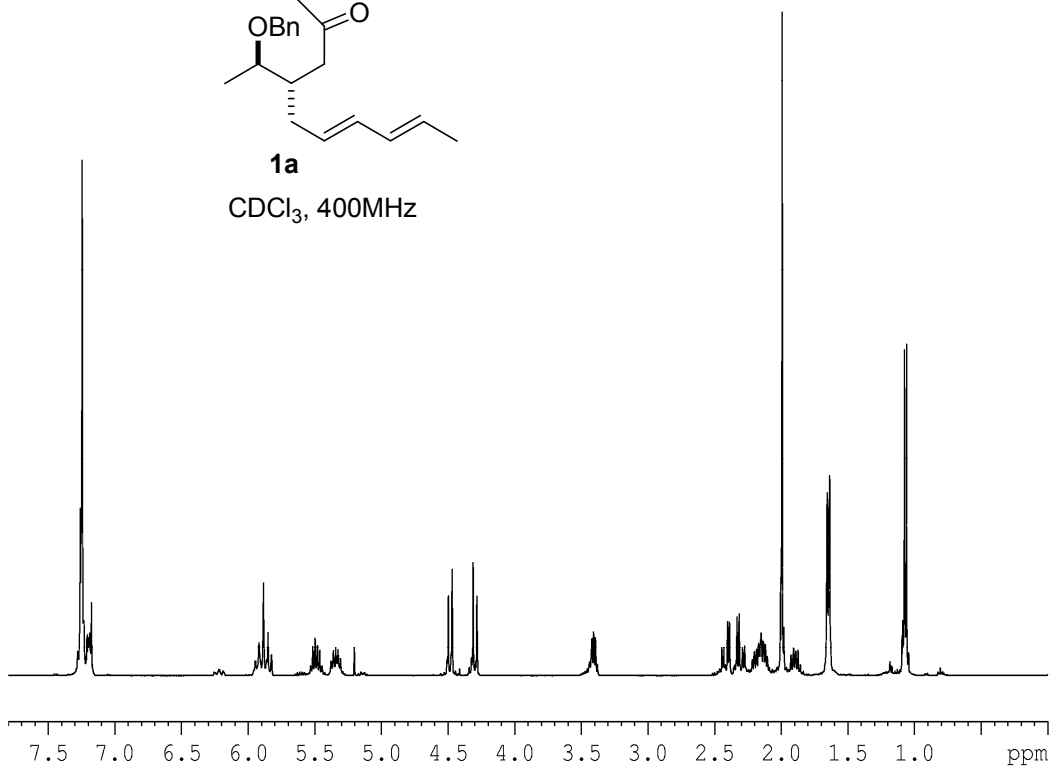


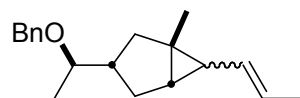




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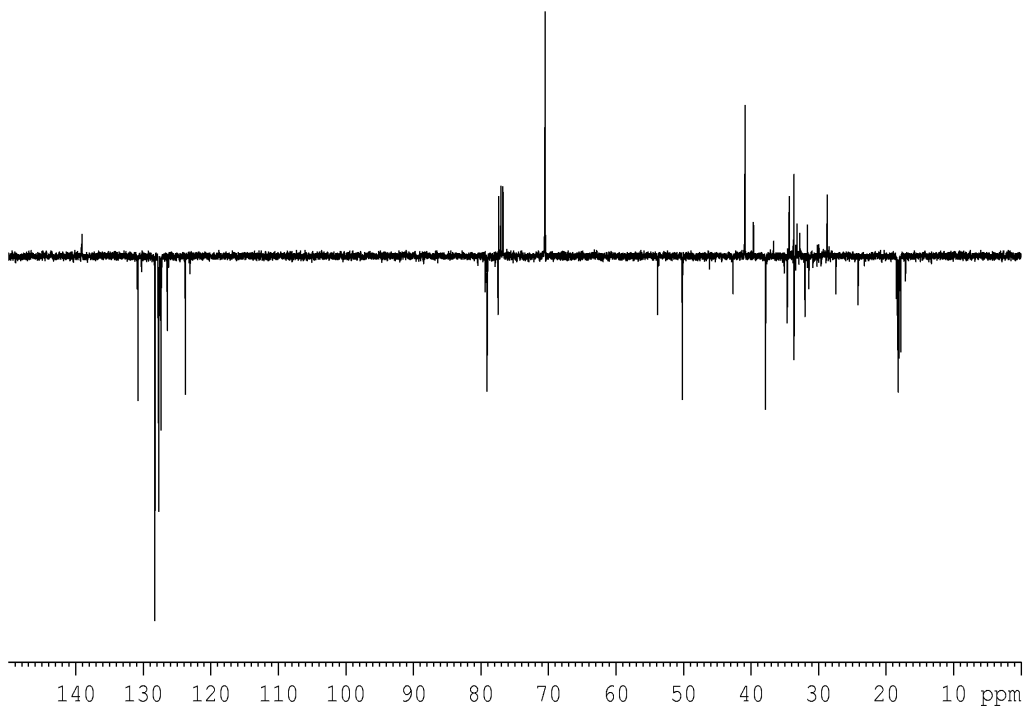
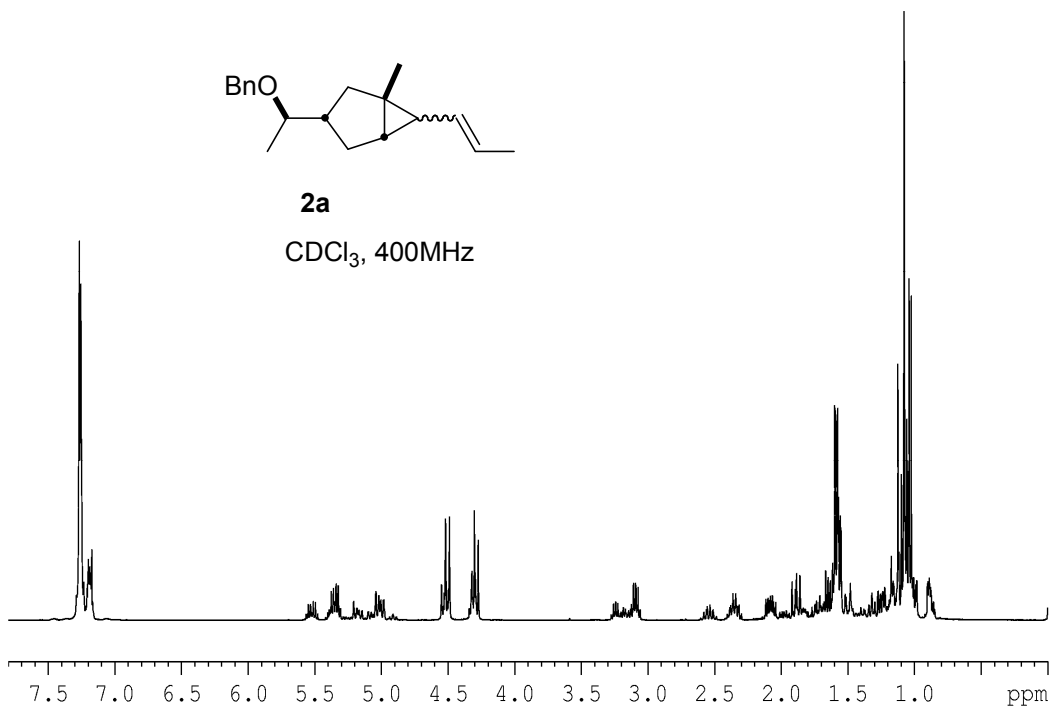
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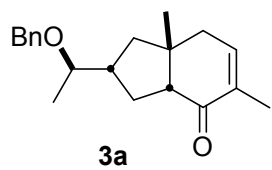




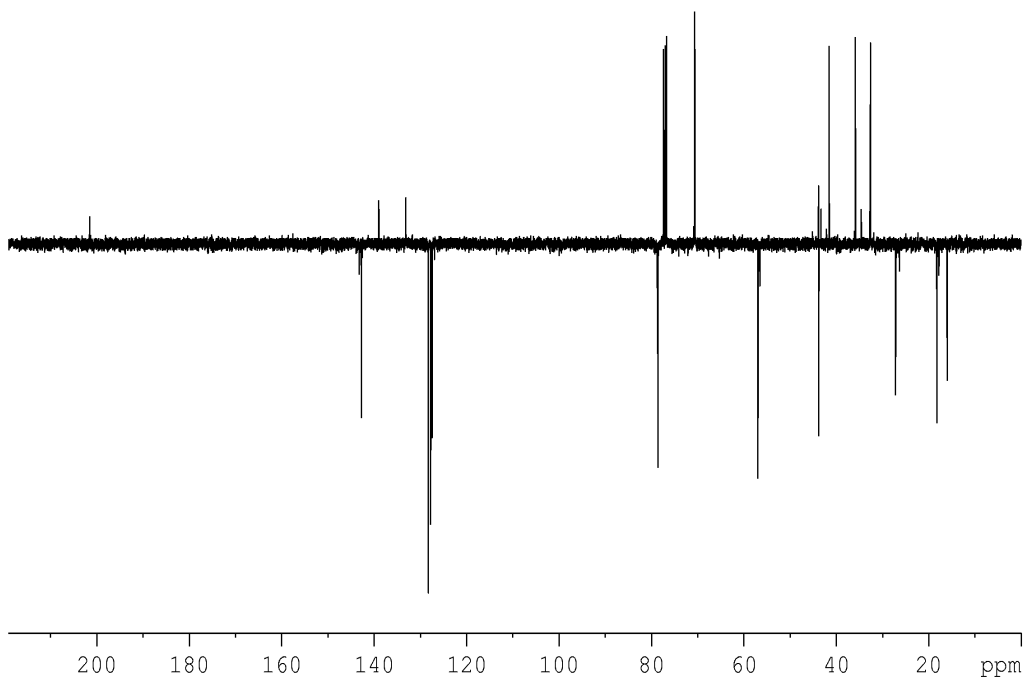
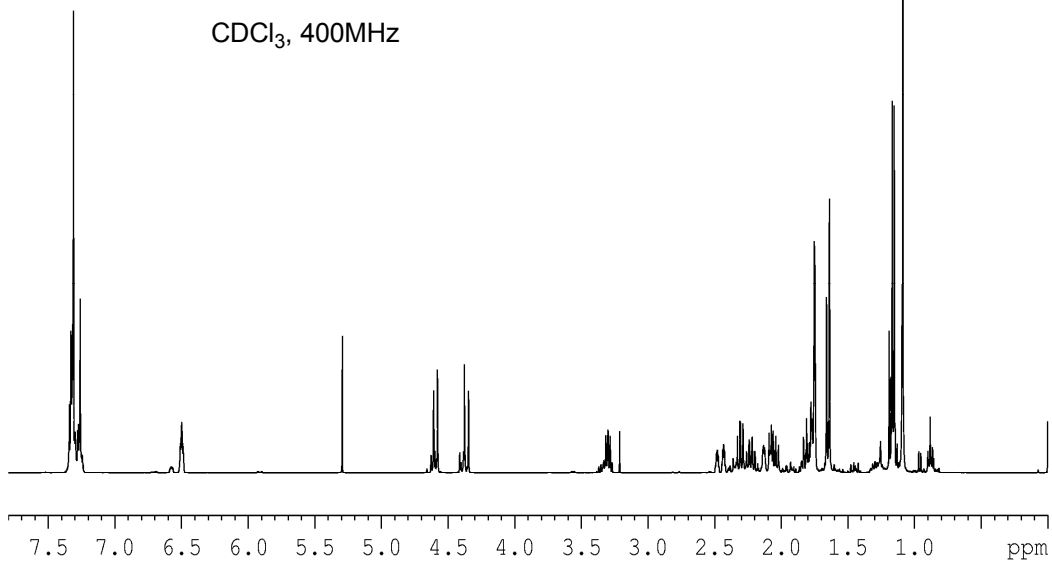
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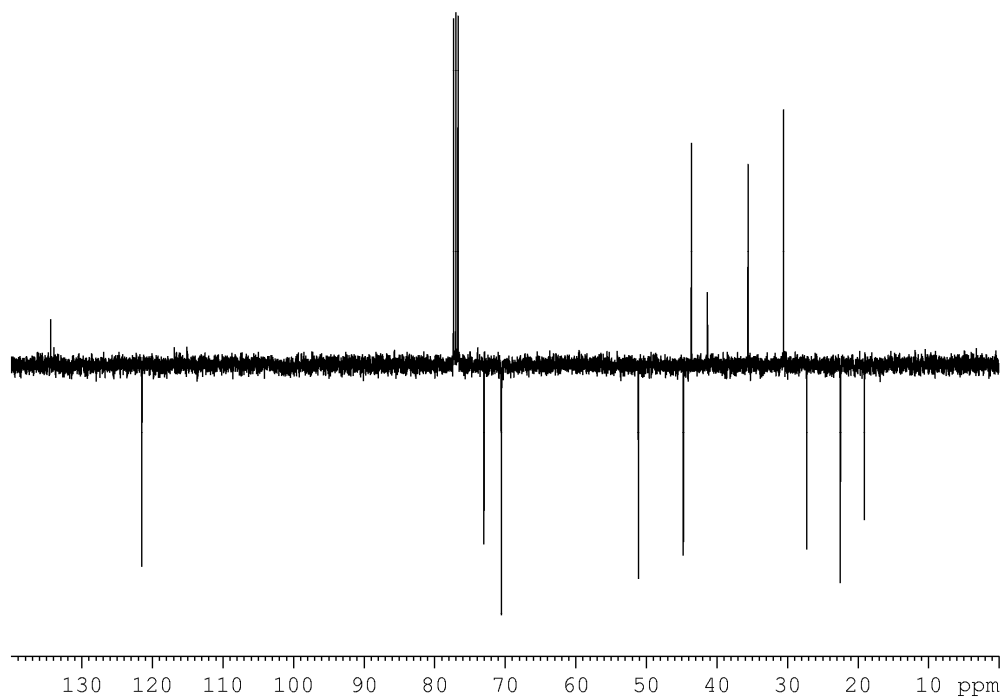
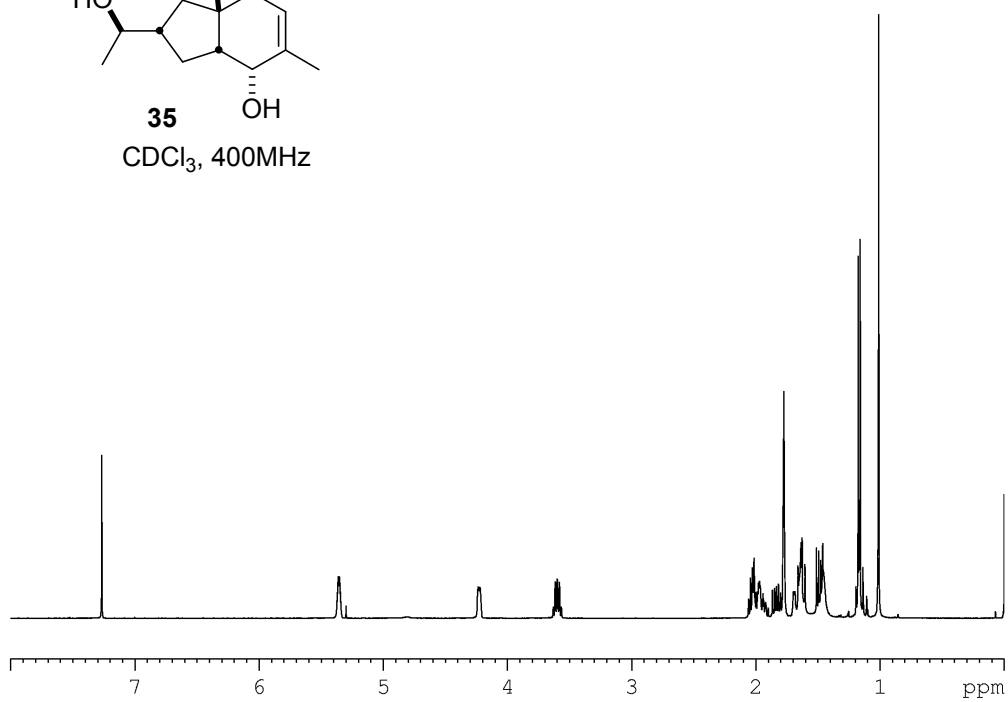
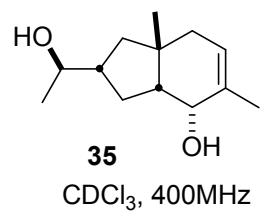
CDCl₃, 400MHz





CDCl₃, 400MHz

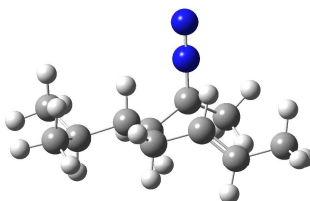




Computational data: All calculations are performed with Gaussian 03 suite of programs.

The optimized geometries and energies for reactants, transition states and products are obtained by quantum calculations at B3LYP/6-31+(d,p) level.

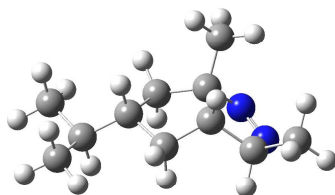
19 (0 kcal/mol)



| | | | |
|-----|-------------|-------------|-------------|
| 0 1 | | | |
| C | -0.23355400 | -1.54971300 | 0.10676700 |
| C | 0.77173000 | 1.58952400 | -0.38831100 |
| C | -0.36570600 | 0.76227600 | -0.95573200 |
| C | -1.04960200 | -0.23321800 | 0.01525500 |
| H | -0.30634700 | -2.08533200 | -0.85049100 |
| H | -0.70215200 | -2.19315100 | 0.86169800 |
| H | -1.11343400 | 1.43467500 | -1.39905400 |
| H | 0.05538200 | 0.19546600 | -1.79690800 |
| H | -1.07320900 | 0.21147300 | 1.02168900 |
| N | 0.71413300 | 2.00437300 | 0.83316400 |
| N | 0.66999800 | 2.34128100 | 1.93859000 |
| C | 1.21676300 | -1.38439200 | 0.47735500 |
| H | 1.41661200 | -0.85725600 | 1.41262400 |
| C | 2.25156200 | -1.86926700 | -0.22041900 |
| H | 2.05055300 | -2.40466300 | -1.15088600 |
| C | -2.53235000 | -0.47171100 | -0.39960800 |
| H | -2.54091100 | -0.66986300 | -1.48328600 |
| C | -3.39608000 | 0.77596700 | -0.13356600 |
| H | -3.00272700 | 1.67848700 | -0.61073400 |
| H | -4.41558500 | 0.62744300 | -0.50595100 |
| H | -3.46197700 | 0.97335200 | 0.94377600 |
| C | -3.18326800 | -1.68023100 | 0.29633600 |
| H | -2.71686500 | -2.62938700 | 0.01879600 |

| | | | |
|---|-------------|-------------|-------------|
| H | -3.13058700 | -1.58300200 | 1.38839700 |
| H | -4.24260800 | -1.74547800 | 0.02446600 |
| C | 3.69692800 | -1.75331200 | 0.17808000 |
| H | 4.15195000 | -2.74310300 | 0.31372700 |
| H | 4.28566100 | -1.24160800 | -0.59448000 |
| H | 3.81083000 | -1.19770300 | 1.11442700 |
| C | 1.92123800 | 2.03986000 | -1.25293700 |
| H | 1.57184600 | 2.65015600 | -2.09739300 |
| H | 2.64088000 | 2.63468200 | -0.68425700 |
| H | 2.44780100 | 1.17053800 | -1.66775500 |

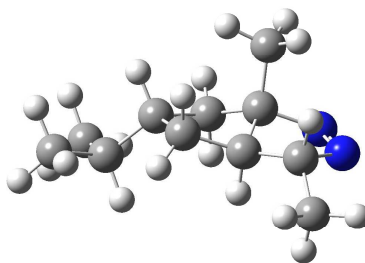
20A (-30.9 kcal/mol)



| | | | |
|-----|-------------|-------------|-------------|
| 0 1 | | | |
| C | -0.35518300 | -1.18699300 | 0.17806800 |
| C | 1.01316300 | -0.55626400 | 0.51421400 |
| C | 0.88129700 | 0.94863900 | 0.13509900 |
| C | -0.59133300 | 1.15976200 | -0.30249700 |
| C | -1.37227200 | -0.03147100 | 0.29594800 |
| H | -0.35376900 | -1.55799100 | -0.85745700 |
| H | -0.58882300 | -2.03846100 | 0.82439800 |
| H | 1.23335700 | -0.67043000 | 1.58093500 |
| H | -0.97496800 | 2.13347000 | 0.01518000 |
| H | -0.65391900 | 1.12949400 | -1.39846600 |
| H | -1.54124800 | 0.16809600 | 1.36711100 |
| N | 1.79593100 | 1.12019400 | -1.04327400 |
| N | 2.46754100 | 0.10962900 | -1.29441800 |
| C | 2.20289900 | -1.02339900 | -0.34345700 |
| H | 1.94290300 | -1.88332900 | -0.97412300 |
| C | 3.49699500 | -1.34452700 | 0.41072800 |
| H | 3.35903200 | -2.22918400 | 1.04090300 |

| | | | |
|---|-------------|-------------|-------------|
| H | 4.31208600 | -1.54336700 | -0.29134400 |
| H | 3.79696800 | -0.50949800 | 1.05278300 |
| C | 1.32695900 | 1.94109800 | 1.21398400 |
| H | 1.33045700 | 2.96052400 | 0.81551500 |
| H | 0.64176100 | 1.90572600 | 2.06804100 |
| H | 2.33551500 | 1.71255600 | 1.57460600 |
| C | -2.74591100 | -0.29492700 | -0.35432000 |
| H | -2.56514000 | -0.49930200 | -1.42160200 |
| C | -3.66856400 | 0.93204000 | -0.25998000 |
| H | -3.24502300 | 1.80534600 | -0.76555400 |
| H | -4.64102800 | 0.72344500 | -0.71961000 |
| H | -3.84992100 | 1.20511600 | 0.78767100 |
| C | -3.43943700 | -1.52690600 | 0.25155200 |
| H | -3.61212700 | -1.38851300 | 1.32678500 |
| H | -4.41403700 | -1.69604100 | -0.21979100 |
| H | -2.84805500 | -2.43873700 | 0.12183400 |

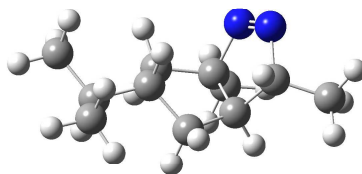
20B (-11.8 kcal/mol)



| | | | |
|-----|-------------|-------------|-------------|
| 0 1 | | | |
| C | 0.32993300 | 0.91801700 | 0.84990700 |
| C | -0.89267200 | 0.51860800 | 0.03070900 |
| C | -0.84556700 | -1.00881900 | 0.04739600 |
| C | 0.58948100 | -1.25584800 | -0.42552500 |
| C | 1.39711100 | -0.16668000 | 0.38706100 |
| H | 0.66287200 | 1.93697200 | 0.63475200 |
| H | 0.15043900 | 0.85725100 | 1.92878600 |
| H | 0.95590600 | -2.26820300 | -0.23204000 |
| H | 0.66364900 | -1.07210100 | -1.50384200 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.81010100 | -0.64756900 | 1.28393100 |
| N | -2.05139700 | -1.34039600 | -0.78087300 |
| N | -2.89630000 | -0.42857300 | -0.68839400 |
| C | -2.38568900 | 0.76816700 | 0.13991400 |
| C | -1.09010400 | -1.69743700 | 1.40808500 |
| H | -1.16566600 | -2.77707100 | 1.24460800 |
| H | -0.26488400 | -1.51895300 | 2.10227700 |
| H | -2.01781500 | -1.36805800 | 1.88365400 |
| C | 2.59661200 | 0.42290100 | -0.38924800 |
| H | 2.19377200 | 0.98582500 | -1.24652000 |
| C | 3.52061100 | -0.67841100 | -0.93732100 |
| H | 3.00337000 | -1.35218900 | -1.62671700 |
| H | 4.36737100 | -0.24006800 | -1.47706700 |
| H | 3.92908800 | -1.28486500 | -0.11867600 |
| C | 3.41579200 | 1.39341200 | 0.47928800 |
| H | 3.85302600 | 0.86783200 | 1.33796200 |
| H | 4.24028300 | 1.82812800 | -0.09652200 |
| H | 2.81310500 | 2.22010800 | 0.86745500 |
| H | -0.65023200 | 0.79413800 | -1.00934700 |
| C | -2.94689800 | 2.05953000 | -0.43822300 |
| H | -2.63823500 | 2.91937900 | 0.16597000 |
| H | -2.59177200 | 2.21474600 | -1.46284200 |
| H | -4.04045400 | 2.02917600 | -0.46069000 |
| H | -2.77171100 | 0.61766100 | 1.15747500 |

20C (-32.1 kcal/mol)

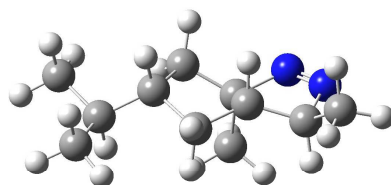


01

| | | | |
|---|-------------|-------------|-------------|
| C | -0.35695800 | -0.91126400 | -0.94465700 |
| C | 1.09124300 | -0.41055300 | -0.75266400 |

| | | | |
|---|-------------|-------------|-------------|
| C | 0.96170500 | 1.04318500 | -0.20594600 |
| C | -0.55348600 | 1.30327600 | -0.03798000 |
| C | -1.20814000 | -0.09115000 | 0.05178900 |
| H | -0.69382000 | -0.69175700 | -1.96757100 |
| H | -0.44471300 | -1.99383500 | -0.80407600 |
| H | -0.74533600 | 1.94134300 | 0.82941900 |
| H | -0.93030600 | 1.82895700 | -0.92662200 |
| H | -1.03959800 | -0.48852400 | 1.06568500 |
| N | 1.58862700 | 0.99677100 | 1.16123500 |
| N | 2.05673000 | -0.11178900 | 1.45281200 |
| C | 1.87765800 | -1.12721800 | 0.36794900 |
| C | 1.67995800 | 2.13550900 | -1.00029400 |
| H | 1.55833000 | 3.10829100 | -0.51317300 |
| H | 2.75244000 | 1.92832200 | -1.07962300 |
| H | 1.26572300 | 2.20124400 | -2.01216900 |
| C | -2.72718200 | -0.11360300 | -0.21289400 |
| H | -2.88620400 | 0.29129000 | -1.22534900 |
| C | -3.49296200 | 0.77951900 | 0.77791500 |
| H | -3.17189000 | 1.82434200 | 0.72321200 |
| H | -4.56932800 | 0.75234000 | 0.57444200 |
| H | -3.34191400 | 0.43652200 | 1.80939900 |
| C | -3.29363900 | -1.54322600 | -0.18413700 |
| H | -3.12934100 | -2.00922400 | 0.79602800 |
| H | -4.37355800 | -1.53689900 | -0.36936500 |
| H | -2.83255300 | -2.18472300 | -0.94170200 |
| H | 1.65610200 | -0.44484300 | -1.68971600 |
| C | 3.24640100 | -1.68713900 | -0.02695300 |
| H | 3.13104400 | -2.49623300 | -0.75568800 |
| H | 3.87277700 | -0.90844500 | -0.47587100 |
| H | 3.76887500 | -2.08206500 | 0.84925300 |
| H | 1.28817400 | -1.93499600 | 0.82237700 |

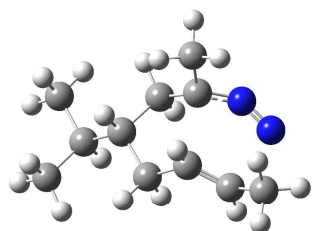
20D (-11.5 kcal/mol)



| | | | |
|-----|-------------|-------------|-------------|
| 0 1 | | | |
| C | -0.29674100 | 1.17821800 | 0.24461400 |
| C | 1.01716000 | 0.53674400 | -0.18330100 |
| C | 0.75008300 | -0.95181200 | 0.03789500 |
| C | -0.57108700 | -1.15055800 | -0.71655000 |
| C | -1.32562700 | 0.23077600 | -0.48950700 |
| H | -0.43319800 | 1.15194800 | 1.33225800 |
| H | -0.40775800 | 2.21795800 | -0.07581200 |
| H | 1.05875500 | 0.65840500 | -1.27934100 |
| H | -0.38997700 | -1.32596700 | -1.78181200 |
| H | -1.14533900 | -2.00049800 | -0.33689700 |
| H | -1.51517500 | 0.67191900 | -1.47813600 |
| N | 2.05240000 | -1.54425400 | -0.41607400 |
| N | 2.97546400 | -0.72386500 | -0.24833600 |
| C | 2.46674200 | 0.64363600 | 0.25412400 |
| H | 2.58896200 | 0.62793800 | 1.34572100 |
| C | 3.32199000 | 1.75129100 | -0.34412000 |
| H | 3.01009800 | 2.72922100 | 0.03795100 |
| H | 4.37627500 | 1.60285300 | -0.09162000 |
| H | 3.23482100 | 1.76542300 | -1.43604400 |
| C | 0.59300400 | -1.41528500 | 1.50322200 |
| H | 0.57066400 | -2.50968500 | 1.52006000 |
| H | 1.41853600 | -1.08858200 | 2.14166400 |
| H | -0.34353700 | -1.05632400 | 1.93703600 |
| C | -2.69742500 | 0.10681800 | 0.20965900 |
| H | -2.54183600 | -0.41060200 | 1.16930300 |
| C | -3.68510300 | -0.72712500 | -0.62448300 |
| H | -3.30997300 | -1.73421700 | -0.83122700 |
| H | -4.64354000 | -0.83131500 | -0.10382500 |

| | | | |
|---|-------------|-------------|-------------|
| H | -3.88272900 | -0.24057000 | -1.58825100 |
| C | -3.30921700 | 1.48564100 | 0.51118700 |
| H | -3.45997100 | 2.05526200 | -0.41498000 |
| H | -4.28627500 | 1.37872700 | 0.99524400 |
| H | -2.67652400 | 2.08487500 | 1.17313300 |

TS-A (14.0 kcal/mol)



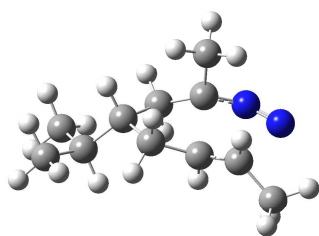
C-C : 2.2Å C-N: 2.3 Å CNN: 142.4°

0 1

| | | | |
|---|-------------|-------------|-------------|
| C | -0.34216600 | -1.27258600 | 0.01880000 |
| C | 0.81429500 | 1.23353100 | 0.11972100 |
| C | -0.60446900 | 1.15447600 | -0.41368000 |
| C | -1.30679300 | -0.08195400 | 0.20300800 |
| H | -0.32123400 | -1.55701700 | -1.04345400 |
| H | -0.71478600 | -2.14585200 | 0.56758900 |
| H | -1.15382000 | 2.07731300 | -0.19298200 |
| H | -0.58332000 | 1.04137300 | -1.50442500 |
| H | -1.42158700 | 0.09689000 | 1.28498400 |
| N | 1.79573700 | 1.31554600 | -0.81131900 |
| N | 2.60163400 | 0.67661000 | -1.36447200 |
| C | 1.06946200 | -0.95891400 | 0.47974300 |
| H | 1.18774400 | -0.80825600 | 1.55480000 |
| C | 2.19245600 | -1.33643000 | -0.23213000 |
| H | 2.05344900 | -1.80139300 | -1.20694900 |
| C | -2.72315100 | -0.32110400 | -0.37656500 |
| H | -2.60714400 | -0.49478800 | -1.45827300 |
| C | -3.64757700 | 0.89611500 | -0.19260800 |
| H | -3.28339200 | 1.78398300 | -0.71763700 |
| H | -4.64987800 | 0.67819200 | -0.57753500 |
| H | -3.75136600 | 1.15181700 | 0.86993600 |

| | | | |
|---|-------------|-------------|-------------|
| C | -3.39189300 | -1.56846300 | 0.22904800 |
| H | -2.84090400 | -2.48658300 | 0.00724400 |
| H | -3.47138100 | -1.47873700 | 1.32025500 |
| H | -4.40635700 | -1.69064200 | -0.16638200 |
| C | 3.55951500 | -1.48966700 | 0.38674000 |
| H | 3.76035400 | -2.53725700 | 0.65414300 |
| H | 4.35421700 | -1.17237800 | -0.29703700 |
| H | 3.64994900 | -0.89717300 | 1.30455400 |
| C | 1.06038700 | 2.02023700 | 1.38812300 |
| H | 0.83321000 | 3.08841600 | 1.26890500 |
| H | 0.40769100 | 1.63346400 | 2.17681600 |
| H | 2.09655900 | 1.92209600 | 1.72477600 |

TS-B (31.1 kcal/mol)

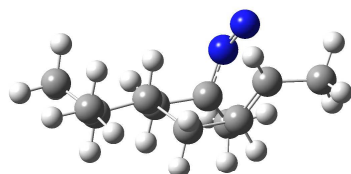


C-C : 2.0Å C-N: 2.7 Å CNN: 137.5°

| | | | |
|-----|-------------|-------------|-------------|
| 0 1 | | | |
| C | 0.35659600 | 1.00947200 | 0.77576000 |
| C | -0.81906800 | -1.16748300 | 0.15867400 |
| C | 0.59013500 | -1.23250800 | -0.37443900 |
| C | 1.38002400 | -0.11071400 | 0.37792500 |
| H | 0.77572800 | 2.00031500 | 0.56777200 |
| H | 0.14850000 | 0.99197400 | 1.85202400 |
| H | 1.06222400 | -2.21026400 | -0.22098700 |
| H | 0.57836200 | -1.04006800 | -1.45350300 |
| H | 1.78956000 | -0.55107000 | 1.29801500 |
| N | -1.89988100 | -1.48273800 | -0.62778100 |
| N | -2.94454800 | -1.02525100 | -0.88008600 |
| C | -0.93853500 | 0.86074800 | -0.01253800 |
| H | -0.75589700 | 0.91007700 | -1.09169200 |
| C | -2.20828500 | 1.29311000 | 0.34181700 |

| | | | |
|---|-------------|-------------|-------------|
| H | -2.44570000 | 1.35537200 | 1.40659100 |
| C | 2.59382300 | 0.41155600 | -0.43166900 |
| H | 2.19898800 | 0.97392600 | -1.29269200 |
| C | 3.47050900 | -0.73118400 | -0.97302900 |
| H | 2.92961800 | -1.38391700 | -1.66460900 |
| H | 4.33689700 | -0.33001500 | -1.51027500 |
| H | 3.85050000 | -1.35276300 | -0.15190000 |
| C | 3.46249900 | 1.36558900 | 0.40660800 |
| H | 2.89650700 | 2.21701000 | 0.79589300 |
| H | 3.90017700 | 0.83639800 | 1.26289300 |
| H | 4.28839000 | 1.76465000 | -0.19247400 |
| C | -3.17807300 | 1.97910700 | -0.58520100 |
| H | -4.20972300 | 1.64443700 | -0.43331300 |
| H | -3.16792600 | 3.06914700 | -0.42233500 |
| H | -2.92299800 | 1.80021500 | -1.63469700 |
| C | -1.04847400 | -1.64922700 | 1.58335500 |
| H | -1.03486200 | -2.74374100 | 1.64549700 |
| H | -0.25893600 | -1.27383600 | 2.23735600 |
| H | -2.01530000 | -1.29272200 | 1.95392000 |

TS-C (15.5 kcal/mol)



C-C : 2.3 Å C-N: 2.3 Å CNN: 142.7°

0 1

| | | | |
|---|-------------|-------------|-------------|
| C | -0.37527100 | -1.05762100 | -0.90304800 |
| C | 0.92328100 | 1.29794100 | -0.15384900 |
| C | -0.59385700 | 1.31940800 | -0.22702200 |
| C | -1.17633500 | -0.08887600 | 0.00333800 |
| H | -0.70081400 | -0.90594100 | -1.94196200 |
| H | -0.62303600 | -2.09312300 | -0.64911500 |
| H | -1.01152600 | 2.05345300 | 0.47105000 |

| | | | |
|---|-------------|-------------|-------------|
| H | -0.86011800 | 1.66214300 | -1.23592900 |
| H | -0.98466200 | -0.36986800 | 1.05106500 |
| N | 1.44240500 | 1.06821200 | 1.07763200 |
| N | 1.90644000 | 0.23238500 | 1.74902600 |
| C | 1.13396500 | -0.85659700 | -0.81344800 |
| H | 1.64052200 | -0.54178300 | -1.72558700 |
| C | 1.90007500 | -1.46900900 | 0.15943600 |
| H | 1.39734800 | -2.09278200 | 0.89725500 |
| C | -2.70783800 | -0.15392300 | -0.21898500 |
| H | -2.89840900 | 0.13767500 | -1.26450800 |
| C | -3.47447800 | 0.82464600 | 0.68966100 |
| H | -3.21664200 | 1.86985900 | 0.49439600 |
| H | -4.55497000 | 0.72214900 | 0.53954100 |
| H | -3.26731000 | 0.61953200 | 1.74779400 |
| C | -3.26228000 | -1.57644100 | -0.02138400 |
| H | -2.84465400 | -2.29037700 | -0.73669600 |
| H | -3.04165500 | -1.94419900 | 0.98899300 |
| H | -4.35082500 | -1.58480900 | -0.14550600 |
| C | 3.39384600 | -1.64752400 | 0.05289000 |
| H | 3.64819000 | -2.64795500 | -0.32585700 |
| H | 3.83410800 | -0.91695700 | -0.63556200 |
| H | 3.88857400 | -1.53455000 | 1.02379600 |
| C | 1.70531300 | 2.27389900 | -1.00496800 |
| H | 1.43508000 | 3.32020400 | -0.80531700 |
| H | 2.78251500 | 2.16305800 | -0.85076400 |
| H | 1.48784100 | 2.07466300 | -2.05942500 |

TS-D



C-C : 2.1 Å C-N: 2.7 Å CNN: 137.2°

0 1

| | | | |
|---|-------------|-------------|-------------|
| C | -0.32257700 | 1.19731200 | 0.20214200 |
| C | 0.70216500 | -1.11361000 | 0.13790800 |
| C | -0.57656100 | -1.17667300 | -0.66323000 |
| C | -1.30497700 | 0.21443300 | -0.49694100 |
| H | -0.41213700 | 1.15474000 | 1.29499400 |
| H | -0.56199800 | 2.22809700 | -0.08380400 |

| | | | |
|---|-------------|-------------|-------------|
| H | -0.34637300 | -1.36879900 | -1.71512000 |
| H | -1.22012200 | -1.99654400 | -0.32236000 |
| H | -1.48005400 | 0.60699800 | -1.50896200 |
| N | 1.88377500 | -1.62263700 | -0.34493800 |
| N | 3.00212100 | -1.28945200 | -0.40035300 |
| C | 1.09510800 | 0.86389200 | -0.23805400 |
| H | 1.15999000 | 0.79352300 | -1.33035600 |
| C | 2.29978300 | 1.21095200 | 0.35458400 |
| H | 2.31115900 | 1.37150000 | 1.43522700 |
| C | -2.69285700 | 0.10850300 | 0.18017300 |
| H | -2.55752700 | -0.40598300 | 1.14492400 |
| C | -3.67597900 | -0.72018400 | -0.66546100 |
| H | -3.30671700 | -1.72972600 | -0.87181900 |
| H | -4.63997500 | -0.82061200 | -0.15466300 |
| H | -3.86143800 | -0.23009100 | -1.62982600 |
| C | -3.30421700 | 1.49073000 | 0.46754900 |
| H | -2.69148100 | 2.08326500 | 1.15308200 |
| H | -3.42234200 | 2.06580300 | -0.45991100 |
| H | -4.29724700 | 1.38565300 | 0.91840100 |
| C | 3.51919000 | 1.68949700 | -0.39030700 |
| H | 3.60073300 | 2.78746100 | -0.34111000 |
| H | 4.44795700 | 1.28234000 | 0.02317900 |
| H | 3.47648000 | 1.40936500 | -1.44783200 |
| C | 0.58583000 | -1.40011700 | 1.62815900 |
| H | 0.47884300 | -2.47429200 | 1.82005800 |
| H | 1.47188500 | -1.03844000 | 2.16031900 |
| H | -0.30035600 | -0.90804400 | 2.03347900 |

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