Supporting Information

Rh(I)-Catalyzed [5 + 1] Cycloaddition of Vinylcyclopropanes and CO for the Synthesis of α,β- and β,γ-Cyclohexenones

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Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and dichloroethane were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for 13C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on Mettler-Toledo ReactIR iC10 system with a SiComp probe and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

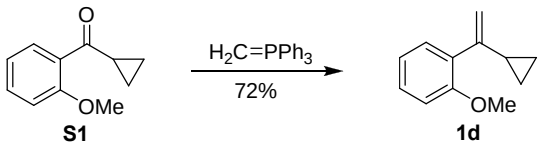
Abbreviations:
Bn = benzyl
DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
DCE = 1,2-dichloroethane
DIBAL-H = diisobutylaluminum hydride
DMP = Dess-Martin periodinane
dppp = 1,3-bis(diphenylphosphino)propane
EA = ethyl acetate
PE = petroleum ether
TBS = *t*-butyldimethylsilyl
THF = tetrahydrofuran
TLC = thin layer chromatography

2. Experimental Procedures and Characterization Data

2.1 Synthesis of VCP Substrates

Substrates **1a**,[1] **1b**,[2] **1c**,[3] **1e**,[3] **1g**,[4] **1h**,[4] **1k**,[5] **1l**,[6] **1m**,[7] **1n**,[8] **1o**,[8] **1o'**,[9] **1p**,[10] **1r**,[11] and **1t**[4] were synthesized according to the reported literature.

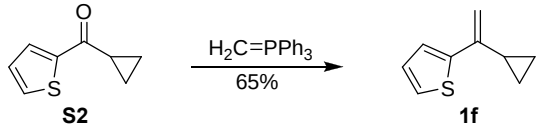
VCP (1d)



To a suspension of methyltriphenylphosphonium bromide (1.60 g, 4.48 mmol) in THF (20 mL) at 0 °C was added *n*-BuLi (1.6 M solution in hexane, 2.80 mL, 4.48 mmol), and the resulting solution was stirred for 30 min at 0 °C. Then a solution of ketone **S1**[12] (438 mg, 2.49 mmol) in THF (10 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford VCP **1d** (314 mg, 72%).

1d: Pale yellow oil, TLC R_f = 0.31 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (ddd, *J* = 8.2, 7.4, and 1.8 Hz, 1H), 7.13 (dd, *J* = 7.4 and 1.8 Hz, 1H), 6.90 (ddd, *J* = 8.2, 6.9, and 3.2 Hz, 2H), 5.11 (dd, *J* = 1.7 and 1.0 Hz, 1H), 4.96 (d, *J* = 1.8 Hz, 1H), 3.83 (s, 3H), 1.79-1.71 (m, 1H), 0.73-0.63 (m, 2H), 0.50-0.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 149.4, 131.4, 130.2, 128.3, 120.3, 111.3, 110.8, 55.5, 16.7, 6.6. IR (neat): υ 2961, 1605, 1497, 1244, 1028 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{15}O$ $(M+H)^+$: 175.1117. Found: 175.1117.

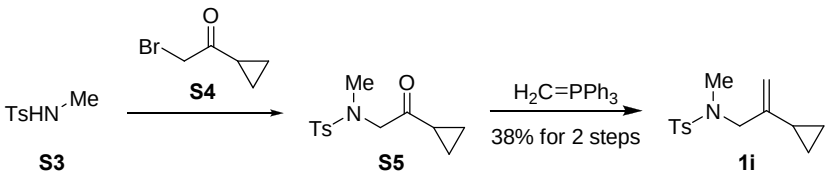
VCP (1f)



To a suspension of methyltriphenylphosphonium bromide (2.11 g, 5.90 mmol) in THF (20 mL) at 0 °C was added *n*-BuLi (1.6 M solution in hexane, 3.69 mL, 5.90 mmol), and the resulting solution was stirred for 30 min at 0 °C. Then a solution of ketone **S2** (commercially available, 500 mg, 3.28 mmol) in THF (10 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford VCP **1f** (320 mg, 65%).

1f: Pale yellow oil, TLC R_f = 0.69 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.22 (m, 1H), 7.20-7.15 (m, 1H), 7.04-6.96 (m, 1H), 5.33 (s, 1H), 4.86 (s, 1H), 1.79-1.67 (m, 1H), 0.86-0.76 (m, 2H), 0.66-0.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 143.0, 127.2, 124.1, 123.5, 108.3, 15.8, 6.1. IR (neat): υ 2924, 1620, 1419, 1229, 1024 cm^{-1}. MS (EI) for $C_9H_{10}S$: 150 $(M)^+$.

VCP (1i)

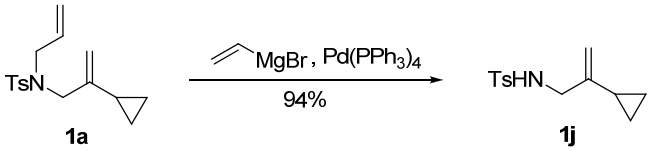


To a flask charged with tosylamide **S3**[13] (400 mg, 2.26 mmol) and acetone (30 ml) was added K_2CO_3 (414 mg, 3.00 mmol), followed by α-bromoketone **S4**[14] (478 mg, 3.00 mmol). The reaction mixture was stirred at room temperature overnight. The resulting solution was filtered and the filtrate was concentrated. The crude product **S5** was directly subjected to the next Wittig reaction.

To a suspension of methyltriphenylphosphonium bromide (1.45 g, 4.07 mmol) in THF (20 mL) at 0 °C was added *n*-BuLi (1.6 M solution in hexane, 2.54 mL, 4.07 mmol), and the resulting solution was stirred for 30 min at 0 °C. Then a solution of the crude ketone **S5** in THF (10 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE:EA = 10:1) to afford VCP **1i** (222 mg, 38% for 2 steps).

1i: Pale yellow oil, TLC R_f = 0.51 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.75 (d, J = 11.2 Hz, 2H), 3.59 (s, 2H), 2.63 (s, 3H), 2.44 (s, 3H), 1.45-1.34 (m, 1H), 0.77-0.67 (m, 2H), 0.53-0.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 143.3, 134.5, 129.6, 127.5, 110.0, 55.9, 34.1, 21.5, 13.6, 6.8. IR (neat): υ 2931, 1602, 1456, 1341, 1162 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{20}NO_2S$ $(M+H)^+$: 266.1209. Found: 266.1208.

VCP (1j)

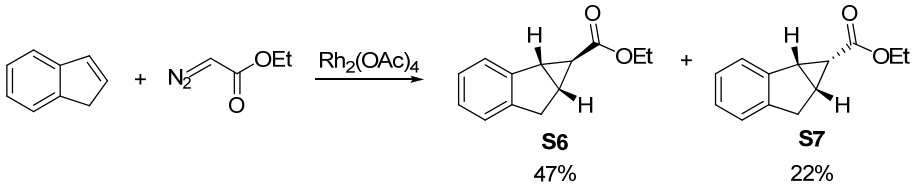


To a suspension of $Pd(PPh_3)_4$ (74 mg, 0.064 mmol) in THF (20 mL) at 0 °C was added vinylmagnesium bromide (0.7 M solution in THF, 7.31 mL, 5.12 mmol), followed by VCP **1a** (500 mg, 1.28 mmol). The reaction mixture was warmed to 30 °C and stirred overnight. Saturated aqueous $NaHCO_3$ was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE:EA = 5:1) to afford VCP **1j** (302 mg, 94%).

1j: Pale yellow oil, TLC R_f = 0.25 (PE:EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.74 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.79 (d, J = 0.8 Hz, 1H), 4.68 (s, 1H), 4.65 (t, J = 6.2 Hz, 1H), 3.57 (d, J = 6.3 Hz, 2H), 2.43 (s, 3H), 1.29-1.17 (m, 1H), 0.66-0.60 (m, 2H), 0.43-0.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 143.4, 136.9, 129.7, 127.12, 109.0, 48.1, 21.5, 14.0, 6.3. IR (neat): υ 3301, 3062, 1616, 1266 cm^{-1}. HRMS (ESI) calcd

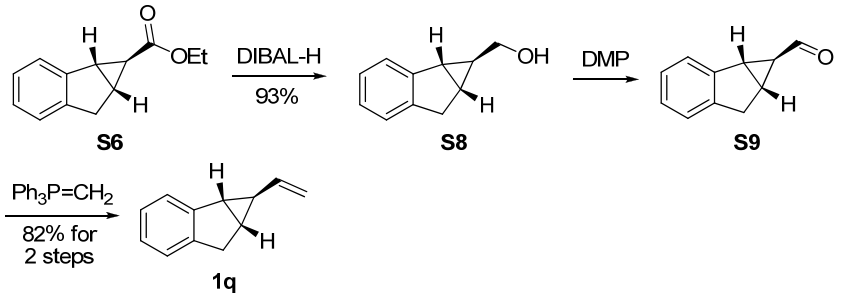
for $C_{13}H_{18}NO_2S$ $(M+H)^+$: 252.1053. Found: 252.1051.

VCP (1q)



To an ether solution (5 mL) of 1H-indene (1.59 g, 13.69 mmol) and $Rh_2(OAc)_4$ (16.9 mg, 0.038 mmol), N_2CHCO_2Et (2.61 g, 22.9 mmol) dissolved in ether (15 mL) was added at room temperature during a period of 100 min. The reaction mixture was diluted with 20 mL petrol ether and filtered over a short silica gel (eluted with diethyl ether). The crude product was purified by column chromatography (eluted with PE:EA = 150:1) to afford the *trans* isomer **S6** (1.28 g, 47%) and the *cis* isomer **S7**[15] (0.60 g, 22%).

S6: Colorless oil, TLC R_f = 0.50 (PE:EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 1H), 7.18-7.09 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.17 (dd, *J* = 17.5 and 6.3 Hz, 1H), 3.04 (d, *J* = 17.5 Hz, 1H), 2.95 (d, *J* = 6.3 Hz, 1H), 2.47-2.40 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 143.6, 141.7, 126.34, 126.30, 125.2, 123.9, 60.5, 35.3, 34.3, 30.7, 26.3, 14.2. IR (neat): υ 2916, 1721, 1404, 1177 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1067. Found: 203.1063.



To a cold solution (0 °C) of the *trans* ester substrate **S6** (1.09 g, 5.40 mmol) in Et_2O (25 ml) was added dropwise DIBAL-H (1M solution in hexane, 13.5 mL, 13.5 mmol) over a period of 5 min, and the mixture was stirred at 0 °C for 5 min before saturated aqueous sodium potassium tartrate was added to quench the reaction. The mixture was stirred at rt until a clear mixture was obtained. The aqueous layer was extracted with diethyl ether, and the combined extract was washed with water and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (eluted with PE:EA = 10:1 to 6:1) to afford the *trans* alcohol **S8** (806 mg, 93%).

S8: Colorless oil, TLC R_f = 0.35 (PE:EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.3, 1H), 7.15-7.05 (m, 3H), 3.57 (d, *J* = 7.0 Hz, 2H), 3.19 (dd, *J* = 17.2 and 7.0, 1H), 2.97 (d, *J* = 17.2 Hz, 1H), 2.33 (d, *J* = 6.2 Hz, 1H), 1.82-1.74 (m, 1H), 1.65-1.56 (m, 1H), 0.80-0.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 142.3, 125.9, 125.5, 125.2 123.3, 64.9, 35.1, 32.0, 29.3, 21.2. IR (neat): υ 3319, 2916, 1479, 1028 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{12}NaO$ $(M+Na)^+$: 183.0780. Found: 183.0776.

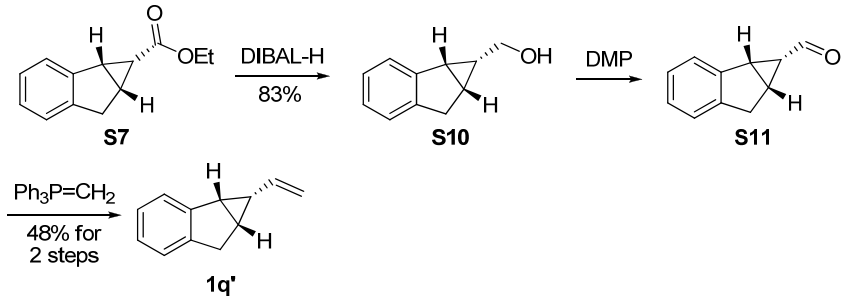
To a cold solution (0 °C) of the *trans* alcohol **S8** (758 mg, 4.73 mmol) in DCM (20 ml) was added a mixture

of DMP (3.09 g, 7.28 mmol) and $NaHCO_3$ (1.16 g, 13.81 mmol) in one portion. The reaction mixture was stirred at rt for 2 h before 20 mL of petrol ether was added. The mixture was purified by flash column chromatography (eluted with PE:EA = 10:1) to afford a crude product of the *trans* aldehyde **S9**, which is directly subjected to the next Wittig reaction.

To a suspension of methyltriphenylphosphonium bromide (2.96 g, 8.29 mmol) in THF (25 mL) at 0 °C was added *n*-BuLi (1.6 M solution in hexane, 5.0 mL, 8.0 mmol), and the resulting solution was stirred for 15 min at 0 °C. Then a solution of the *trans* aldehyde **S9** in THF (15 mL) was added dropwise at 0 °C, and the resulting mixture was stirred for 5 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford *trans* VCP **1q** (603 mg, 82% for 2 steps).

1q: Colorless oil, TLC R_f = 0.80 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.4 Hz, 1H), 7.17-7.04 (m, 3H), 5.51 (dt, *J* = 17.0 and 10.1 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.90 (d, *J* = 10.1 Hz, 1H), 3.22 (dd, *J* = 17.2 and 6.7 Hz, 1H), 3.01 (d, *J* = 17.2 Hz, 1H), 2.47-2.41 (m, 1H), 1.95-1.87 (m, 1H), 1.09-1.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 142.1, 139.3, 126.0, 125.6, 125.2, 123.4, 112.1, 35.5, 33.8, 33.3, 25.0. IR (neat): υ 3039, 1635, 1475, 1438 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{12}$ $(M)^+$: 156.0939. Found: 156.0941.

VCP (1q')



The *cis* ester substrate **S7** (734 mg, 3.63 mmol) was converted to the *cis* alcohol **S10** (484 mg, 83%) following the procedure for converting **S6** to **S8**.

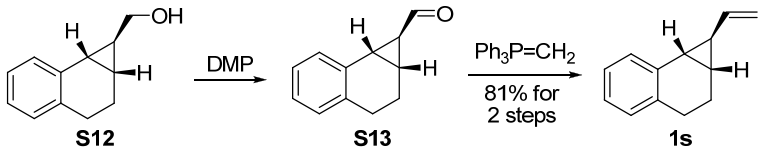
S10: Colorless oil, TLC R_f = 0.30 (PE:EA = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1H), 7.15-7.07 (m, 3H), 3.30 (dd, *J* = 11.5 and 7.1 Hz, 1H), 3.20-3.10 (m, 2H), 2.84 (d, *J* =17.4 Hz, 1H), 2.65 (t, *J* = 7.1 Hz, 1H), 2.00 (q, *J* = 7.2, 1H), 1.52-1.42 (m, 1H), 1.30-1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 141.4, 126.3, 125.9, 124.3, 123.9, 57.7, 31.6, 28.3, 24.0, 20.5. IR (neat): υ 3322, 2916, 1479, 1255, 1024 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{12}NaO$ $(M+Na)^+$: 183.0780. Found: 183.0777.

The *cis* acohol **S10** (420 mg, 2.62 mmol) was converted to *cis* VCP **1q'** (196 mg, 48% for 2 steps) following the procedures for converting **S8** to **1q**.

1q': Colorless oil, TLC R_f = 0.80 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 1H), 7.15-7.06 (m, 3H), 5.26-5.17 (m, 1H), 4.96-4.84 (m, 2H), 3.18 (dd, *J* = 17.5 and 7.0 Hz, 1H), 2.87 (d, *J* = 17.5 Hz, 1H), 2.74 (t, *J* = 7.1 Hz, 1H), 2.11 (q, *J* = 7.1 Hz, 1H), 1.86 (q, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.4,

133.4, 126.3, 125.8, 124.5, 124.0, 116.4, 32.0, 31.3, 26.1, 23.5. IR (neat): υ 3028, 2920, 1635, 1479, 1438 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{12}$ $(M)^+$: 156.0939. Found: 156.0941.

VCP (1s)



S12 **S13** **1s**

The *trans* acohol **S12**[16] (705 mg, 4.04 mmol) was converted to *trans* VCP **1s** (560 mg, 81% for 2 steps) following the procedures for converting **S8** to **1q**.

1s: Colorless oil, TLC R_f = 0.80 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 1H), 7.13-6.99 (m, 3H), 5.57-5.48 (m, 1H), 5.03 (d, *J* = 16.9 Hz, 1H), 4.89 (d, *J* = 10.2 Hz, 1H), 2.62 (dd, *J* = 16.0 and 5.5 Hz, 1H), 2.50 (dd, *J* = 16.0 and 6.2 Hz, 1H), 2.18 (dd, *J* = 13.1 and 6.1 Hz, 1H), 1.95 (dd, *J* = 8.1 and 2.5 Hz, 1H), 1.89-1.82 (m, 1H), 1.78-1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 137.1, 133.6, 128.6, 128.4, 126.0, 125.0, 112.0, 25.9, 25.6, 25.3, 23.1, 18.8. IR (neat): υ 3024, 2928, 1639, 1494, 1445 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{15}$ $(M+H)^+$: 171.1168. Found: 171.1168.

2.2 General Procedures for Rh(I)-Catalyzed [5 + 1] Cycloadditions

General Procedures:

Preparation of the Cationic Rh(I) Catalyst Solution: Anhydrous DCE (6.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (11.7 mg, 30.0 μmol) and $AgSbF_6$ (24.7 mg, 72.0 μmol, 1.2 equiv to Rh) or AgOTf (18.5 mg, 72.0 μmol, 1.2 equiv to Rh) under argon. The mixture was stirred at room temperature for 10 min. The resulting yellow suspension was left until the formed AgCl precipitated. The supernatant was suitable for use in the [5 + 1] cycloaddition reactions as the catalyst precursor ($[Rh(I)^+]$ = 10.0 μmol/mL).

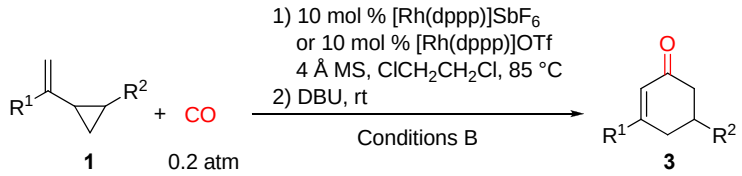
General Procedure A for the [5 + 1] Cycloaddition Reaction (Conditions A): Under argon, the above $Rh(I)^+$ solution (1.5 mL, 15.0 μmol) was added to flame-dried reaction tube containing 1,3-bis(diphenylphosphino)-propane [7.4 mg, 18.0 μmol, 1.2 equiv to $Rh(I)^+$] and the newly activated 4 Å molecular sieves (100 mg). The resulting orange suspension was stirred at room temperature for 10 min, and then a solution of the VCP substrate (0.15 mmol) in DCE (1.5 mL) was added. Then the reaction mixture was bubbled with a mixed gas of CO/N_2 (balloon pressured mixed gas of 20% CO and 80% N_2) for 5 min. The reaction tube was immersed into an oil bath (75 ºC or 85 ºC as indicated) and reacted under the atmosphere pressure of the mixed gas of CO and N_2 (v/v = 1/4). When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and filtered through a thin pad of silica gel. The filter cake was washed with PE/EA, and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding [5 + 1] cycloadduct (all reported yields were isolated yields).

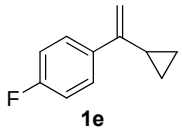
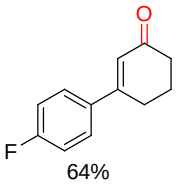
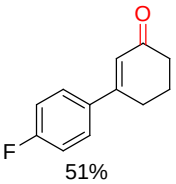
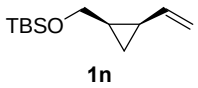
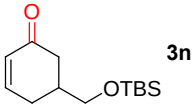
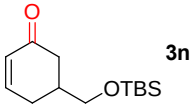
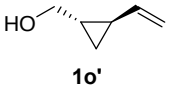
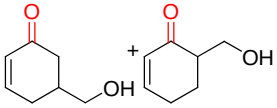
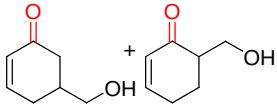
General Procedure B for the [5 + 1] Cycloaddition Reaction (Conditions B): Under argon, the above $Rh(I)^+$ solution (1.5 mL, 15.0 μmol) (with either SbF_6^- or OTf^- as the counterion) was added to flame-dried reaction tube containing 1,3-bis(diphenylphosphino)propane [7.4 mg, 18.0 μmol, 1.2 equiv to $Rh(I)^+$] and the newly activated 4 Å molecular sieves (100 mg). The resulting orange suspension was stirred at room temperature for 10 min, and then a solution of the VCP substrate (0.15 mmol) in DCE (1.5 mL) was added. Then the reaction mixture was bubbled with a mixed gas of CO/N_2 (balloon pressured mixed gas of 20% CO and 80% N_2) for 5 min. The reaction tube was immersed into an oil bath (75 ºC or 85 ºC as indicated) and reacted under the atmosphere pressure of the mixed gas of CO and N_2 (v/v = 1/4). When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and DBU (22.0 μL, 0.15 mmol) or $TsOH•H_2O$ (142.6 mg, 0.75 mmol) was added. The reaction system was stirred at the indicated temperature (rt or 50 ºC). When TLC indicated a complete transformation from β,γ-cyclohexenone to α,β-cyclohexenone, the mixture was filtered through a thin pad of silica gel. The filter cake was washed with PE/EA, and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding [5 + 1] cycloadduct (all reported yields were isolated yields).

We point out here that either counterion SbF_6^- or OTf^- can be used for the [5 + 1] reaction under conditions B. Using $[Rh(dppp)]SbF_6$ as the catalyst helps to generate the conjugated cyclohexenone (see Table 1). Therefore, for substrates in Table 2, we chose $[Rh(dppp)]SbF_6$ as the catalyst to catalyze the [5 + 1] reactions under conditions B. This is supported by the [5 + 1] reaction of **1e** using $[Rh(dppp)]SbF_6$ as the catalyst, which gave higher yield than that using [Rh(dppp)]OTf as the catalyst (entry 1, Table S1). This suggests that for vinylcyclopropanes without substituents on the cyclopropyl rings, using $[Rh(dppp)]SbF_6$ as the catalyst under conditions B is the better choice. However, for the [5 + 1] reactions of vinylcyclopropanes with substituents on

the cyclopropyl rings, we preferred to use [Rh(dppp)]OTf as the catalyst, which gave higher yields than [Rh(dppp)]SbF_6 did. For example, the [5 + 1] reactions of **1n** and **1o'** gave higher yields using [Rh(dppp)]OTf than those using [Rh(dppp)]SbF_6 (entries 2 and 3). To obtain the highest yields of new substrates in the future study, we suggest that both [Rh(dppp)]SbF_6 and [Rh(dppp)]OTf catalysts under conditions B should be tested.

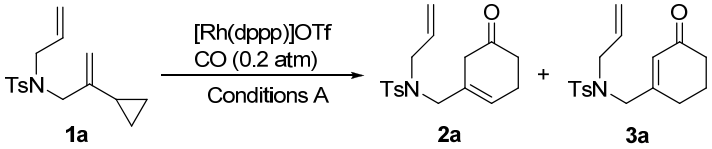
Table S1. Comparison of the [5 + 1] Cycloaddition Yields Using Different Counter Ions Under Conditions B.



entry	substrate	yield [Rh(dppp)]SbF_6	yield [Rh(dppp)]OTf
1	 **1e**	 **3e** 64%	 **3e** 51%
2	 **1n**	 **3n** 60%	 **3n** 65%
3	 **1o'**	 **3o** 34% **3o'** 12%	 **3o** 54% **3o'** 8%

Experimental Data for the Rh(I)-Catalyzed [5 + 1] Cycloaddition

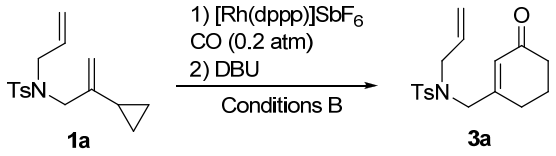
Cycloadducts (2a & 3a)



Following the general procedure A, VCP **1a** (45.4 mg, 0.156 mmol) was converted to cycloadducts **2a** (30.4 mg, 61%) and **3a** (7.8 mg, 16%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

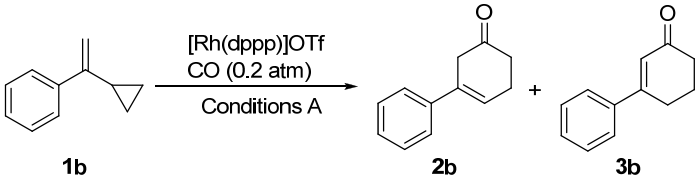
2a: Colorless oil, TLC R_f = 0.58 (PE:EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.84-5.78 (m, 1H), 5.63-5.51 (m, 1H), 5.14-5.05 (m, 2H), 3.76 (d, J = 6.5 Hz, 2H), 3.71 (s, 2H), 2.79 (s, 2H), 2.47-2.41 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 143.5, 137.1, 132.6, 131.4, 129.7, 127.2, 125.6, 119.2, 52.1, 50.0, 40.9, 38.1, 24.8, 21.5. IR (neat): υ 2946, 1717, 1605, 1512, 1341 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{22}NO_3S$ $(M+H)^+$: 320.1315. Found: 320.1318.

3a: Colorless oil, TLC R_f = 0.49 (PE:EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.91 (s, 1H), 5.60-5.46 (m, 1H), 5.15-5.05 (m, 2H), 3.85 (s, 2H), 3.75 (d, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 2.41-2.31 (m, 4H), 2.05-1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 159.7, 143.7, 136.5, 131.9, 129.8, 127.2, 120.0, 52.1, 51.0, 37.5, 26.9, 22.3, 21.5. IR (neat): υ 2954, 1672, 1605, 1427, 1162 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{21}NNaO_3S$ $(M+Na)^+$: 342.1134. Found: 342.1129.



Following the general procedure B, VCP **1a** (43.5 mg, 0.149 mmol) was converted to cycloadduct **3a** (38.2 mg, 80%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

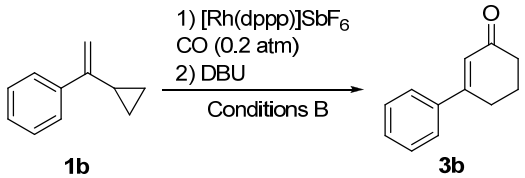
Cycloadducts (2b & 3b)



Following the general procedure A, VCP **1b** (22.2 mg, 0.154 mmol) was converted to cycloadducts **2b** (17.6 mg, 66%) and **3b**[17] (3.2 mg, 12%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

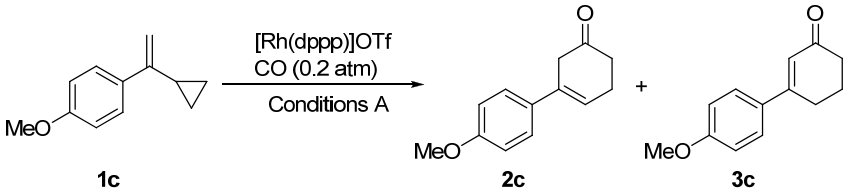
2b: Colorless oil, TLC R_f = 0.46 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.26 (m, 5H), 6.36-6.30 (m, 1H), 3.28 (d, *J* = 1.8 Hz, 2H), 2.70-2.61 (m, 2H), 2.59-2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 139.8, 135.0, 128.5, 127.6, 125.1, 123.6, 42.0, 38.0, 25.3. IR (neat): υ 2931, 1717, 1609, 1449, 1199 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{13}O$ $(M+H)^+$: 173.0961. Found: 173.0960.

3b: Colorless oil, TLC R_f = 0.35 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.50 (m, 2H), 7.46-7.38 (m, 3H), 6.42 (s, 1H), 2.78 (t, *J* = 5.6 Hz, 2H), 2.49 (t, *J* = 8.0 Hz, 2H), 2.22-2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 159.7, 138.8, 129.9, 128.7, 126.1, 125.4, 37.2, 28.1, 22.8.



Following the general procedure B, VCP **1b** (23.2 mg, 0.160 mmol) was converted to cycloadduct **3b** (20.2 mg, 73%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

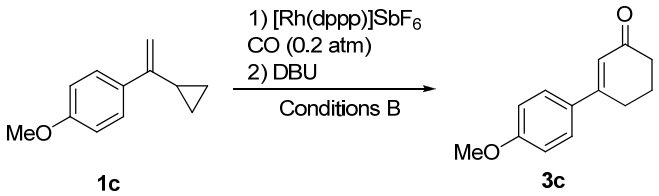
Cycloadducts (2c & 3c)



Following the general procedure A, VCP **1c** (28.1 mg, 0.161 mmol) was converted to cycloadducts **2c** (17.1 mg, 53%) and **3c**[3] (7.3 mg, 22%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

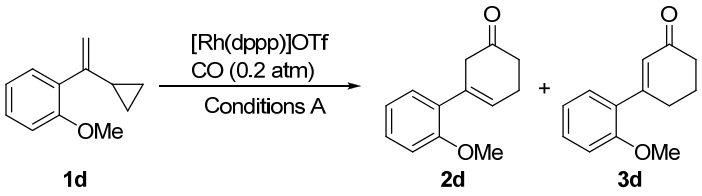
2c: Colorless oil, TLC R_f = 0.38 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.27 (m, 2H), 6.91-6.84 (m, 2H), 6.26-6.21 (m, 1H), 3.81 (s, 3H), 3.24 (d, *J* = 1.8 Hz, 2H), 2.67-2.59 (m, 2H), 2.57-2.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 159.2, 134.3, 132.3, 126.1, 121.8, 113.9, 55.3, 42.1, 38.1, 25.2. IR (neat): υ 2942, 1713, 1602, 1516, 1255 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1067. Found: 203.1065.

3c: Colorless oil, TLC R_f = 0.27 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 3.85 (s, 3H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.20-2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 161.2, 159.1, 130.8, 127.6, 123.7, 114.1, 55.4, 37.2, 27.8, 22.7.



Following the general procedure B, VCP **1c** (25.6 mg, 0.147 mmol) was converted to cycloadduct **3c** (22.7 mg, 76%). Catalyst: 10 mol % $[Rh(dppp)]SbF_6$, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

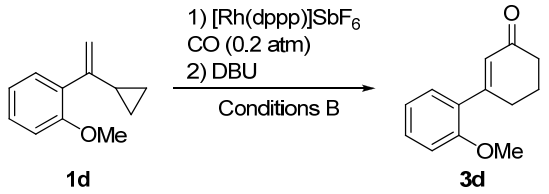
Cycloadducts (2d & 3d)



Following the general procedure A, VCP **1d** (24.3 mg, 0.139 mmol) was converted to cycloadducts **2d** (15.0 mg, 53%) and **3d**[17] (2.8 mg, 10%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2d: Colorless oil, TLC R_f = 0.36 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.23 (m, 1H), 7.16 (dd, *J* = 7.5 and 1.7 Hz, 1H), 6.97-6.84 (m, 2H), 6.01-5.95 (m, 1H), 3.81 (s, 3H), 3.30 (d, *J* = 1.8 Hz, 2H), 2.65-2.58 (m, 2H), 2.58-2.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 156.7, 135.8, 130.6, 129.6, 128.7, 125.4, 120.7, 110.8, 55.3, 43.4, 38.0, 25.1. IR (neat): υ 2954, 1710, 1605, 1494, 1251, 1024 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$: 203.1067. Found: 203.1063.

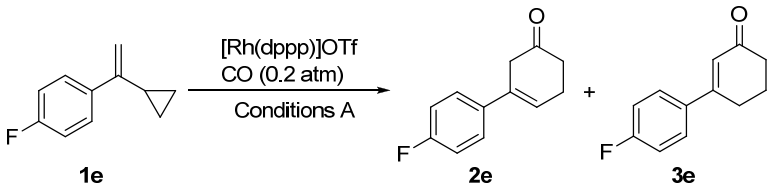
3d: Colorless oil, TLC R_f = 0.26 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (td, J = 8.3 and 1.5 Hz, 1H), 7.20 (dd, J = 7.5 and 1.4 Hz, 1H), 7.01-6.90 (m, 2H), 6.20 (s, 1H), 3.84 (s, 3H), 2.74 (t, J = 5.4 Hz, 2H), 2.48 (t, J = 6.0 Hz, 2H), 2.17-2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 161.6, 156.6, 130.3, 129.7, 128.7, 128.2, 120.7, 111.2, 55.4, 37.5, 30.1, 23.3.



1d **3d**

Following the general procedure B, VCP **1d** (26.9 mg, 0.154 mmol) was converted to cycloadduct **3d** (19.7 mg, 63%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

Cycloadducts (2e & 3e)

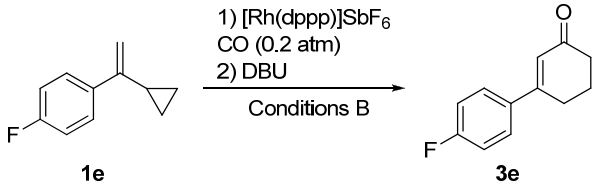


1e **2e** **3e**

Following the general procedure A, VCP **1e** (25.3 mg, 0.156 mmol) was converted to cycloadducts **2e** (17.1 mg, 58%) and **3e**[17] (2.0 mg, 7%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2e: Colorless oil, TLC R_f = 0.64 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 2H), 7.08-6.99 (m, 2H), 6.31-6.24 (m, 1H), 3.24 (d, J = 1.8 Hz, 2H), 2.69-2.61 (m, 2H), 2.59-2.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 135.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.0, 126.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 123.5 (d, $J_{C\text{-}F}$ = 1.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22 Hz), 42.1, 37.9, 25.2. IR (neat): υ 2931, 1717, 1605, 1512, 1229 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{12}FO$ $(M+H)^+$: 191.0867. Found: 191.0871.

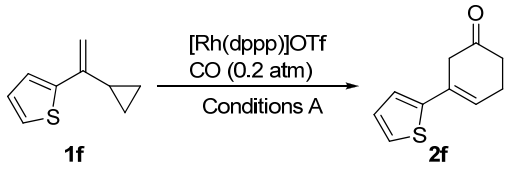
3e: Colorless oil, TLC R_f = 0.52 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.47 (m, 2H), 7.10 (t, J = 8.6 Hz, 2H), 6.37 (s, 1H), 2.75 (t, J = 5.6 Hz, 2H), 2.48 (t, J = 6.0 Hz, 2H), 2.23-2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 163.8 (d, $J_{C\text{-}F}$ = 249 Hz), 158.4, 134.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.0 (d, $J_{C\text{-}F}$ = 8.4 Hz), 125.3 (d, $J_{C\text{-}F}$ = 1.1 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22 Hz), 37.1, 28.1, 22.72.



1e **3e**

Following the general procedure B, VCP **1e** (21.7 mg, 0.133 mmol) was converted to cycloadduct **3e** (16.3 mg, 64%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

Cycloadduct (2f)

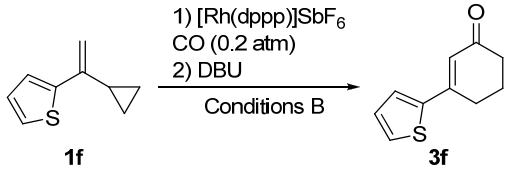


1f **2f**

Following the general procedure A, VCP **1f** (21.5 mg, 0.143 mmol) was converted to cycloadduct **2f** (11.6 mg, 46%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2f: Colorless oil, TLC R_f = 0.45 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 4.7 Hz, 1H), 6.98 (dd, *J* = 5.0 and 3.7 Hz, 1H), 6.92 (d, *J* = 2.9 Hz, 1H), 6.3-6.33 (m, 1H), 3.28 (d, *J* = 0.9 Hz, 2H), 2.68-2.60 (m, 2H), 2.59-2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 143.9, 129.5, 127.4, 124.0, 122.4, 122.3, 41.9, 38.1, 25.1. IR (neat): υ 2931, 1717, 1594, 1423, 1248 cm^{-1}. HRMS (ESI) calcd for $C_{10}H_{10}NaOS$ $(M+Na)^+$: 201.0345. Found: 201.0341.

Cycloadduct (3f)

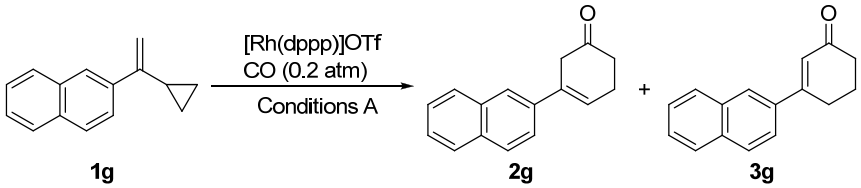


1f **3f**

Following the general procedure B, VCP **1f** (22.5 mg, 0.150 mmol) was converted to cycloadduct **3f**[18] (11.5 mg, 43%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

3f: Colorless oil, TLC R_f = 0.34 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 5.0 and 0.7 Hz, 1H), 7.41-7.37 (m, 1H), 7.10 (dd, *J* = 4.9 and 3.9 Hz, 1H), 6.43 (s, 1H), 2.79 (t, *J* = 5.7 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.20-2.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 152.4, 142.8, 128.7, 128.2, 127.3, 122.8, 37.2, 28.0, 22.4.

Cycloadducts (2g & 3g)

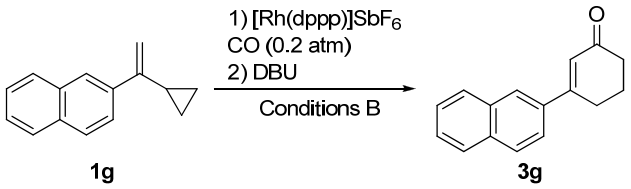


1g **2g** **3g**

Following the general procedure A, VCP **1g** (30.0 mg, 0.154 mmol) was converted to cycloadducts **2g** (25.2 mg, 74%) and **3g**[19] (4.6 mg, 13%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2g: White solid, TLC R_f = 0.34 (PE:EA = 10:1), m.p. 88-90 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.77 (m, 3H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.58 (dd, *J* = 8.7 and 1.9 Hz, 1H), 7.52-7.40 (m, 2H), 6.53-6.46 (m, 1H), 3.40 (d, *J* = 1.8 Hz, 2H), 2.76-2.65 (m, 2H), 2.63-2.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 136.8, 134.8, 133.4, 132.8, 128.1, 128.1, 127.5, 126.3, 126.0, 124.1, 123.6, 123.4, 42.0, 38.0, 25.4. IR (neat): υ 3062, 1713, 1605, 1359, 1192 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O$ $(M+H)^+$: 223.1117. Found: 223.1115.

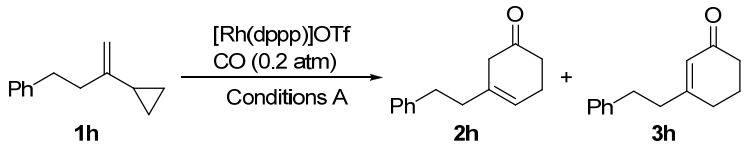
3g: White solid, TLC R_f = 0.26 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 1.3 Hz, 1H), 7.91-7.82 (m, 3H), 7.65 (dd, *J* = 8.7 and 1.9 Hz, 1H), 7.57-7.48 (m, 2H), 6.57 (s, 1H), 2.95-2.87 (m, 2H), 2.58-2.48 (m, 2H), 2.26-2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 159.4, 135.9, 134.0, 133.1, 128.7, 128.5, 127.6, 127.2, 126.7, 126.1, 125.7, 123.3, 37.3, 28.1, 22.8.



1g **3g**

Following the general procedure B, VCP **1g** (29.6 mg, 0.152 mmol) was converted to cycloadduct **3g** (28.7 mg, 85%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

Cycloadducts (2h & 3h)

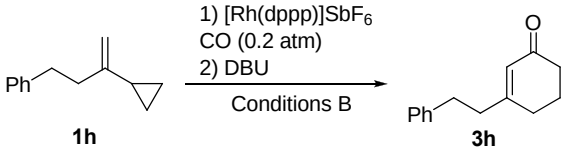


1h **2h** **3h**

Following the general procedure A, VCP **1h** (26.7 mg, 0.155 mmol) was converted to cycloadducts **2h** (12.8 mg, 41%) and **3h**[20] (13.3 mg, 43%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

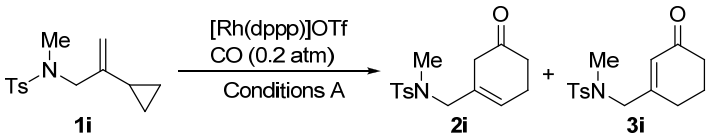
2h: Colorless oil, TLC R_f = 0.51 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 2H), 7.23-7.14 (m, 3H), 5.66-5.61 (m, 1H), 2.84 (s, 2H), 2.79-2.70 (m, 2H), 2.48-2.39 (m, 4H), 2.37-2.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 141.6, 135.5, 128.4, 128.3, 126.0, 121.3, 43.1, 38.4, 34.0, 24.9. IR (neat): υ 3028, 2935, 1717, 1605, 1199 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{17}O$ $(M+H)^+$: 201.1274. Found: 201.1279.

3h: Colorless oil, TLC R_f = 0.36 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 2H), 7.24-7.15 (m, 3H), 5.90 (s, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.9 Hz, 2H), 2.35 (t, *J* = 6.5 Hz, 2H), 2.29 (t, *J* = 5.8 Hz, 2H), 2.04-1.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.7, 165.2, 140.7, 128.5, 128.2, 126.3, 126.0, 39.6, 37.3, 33.4, 29.9, 22.7.



Following the general procedure B, VCP **1h** (26.6 mg, 0.154 mmol) was converted to cycloadducts **3h** (26.3 mg, 85%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

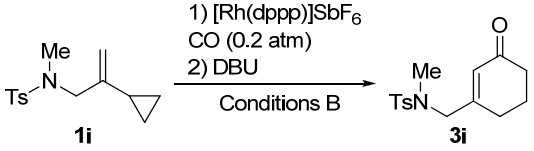
Cycloadducts (2i & 3i)



Following the general procedure A, VCP **1i** (39.8 mg, 0.150 mmol) was converted to cycloadducts **2i** (28.6 mg, 65%) and **3i** (6.5 mg, 15%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

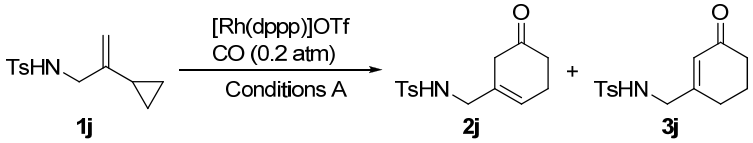
2i: Colorless oil, TLC R_f = 0.48 (PE:EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.85-5.79 (m, 1H), 3.53 (s, 2H), 2.89 (s, 2H), 2.63 (s, 3H), 2.50-2.45 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 143.5, 134.3, 131.3, 129.7, 127.4, 125.7, 55.4, 40.7, 38.1, 34.2, 24.8, 21.5. IR (neat): υ 2983, 1717, 1602, 1456, 1345 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}NO_3S$ $(M+H)^+$: 294.1158. Found: 294.1159.

3i: Colorless oil, TLC R_f = 0.40 (PE:EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.94 (s, 1H), 3.70 (s, 2H), 2.65 (s, 3H), 2.45 (s, 3H), 2.43-2.36 (m, 4H), 2.08-1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 159.0, 143.8, 134.0, 129.8, 127.4, 55.6, 37.5, 35.0, 26.8, 22.4, 21.5. IR (neat): υ 2957, 1672, 1602, 1456, 1166 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}NO_3S$ $(M+H)^+$: 294.1158. Found: 294.1159.



Following the general procedure B, VCP **1i** (37.7 mg, 0.142 mmol) was converted to cycloadduct **3i** (32.4 mg, 78%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

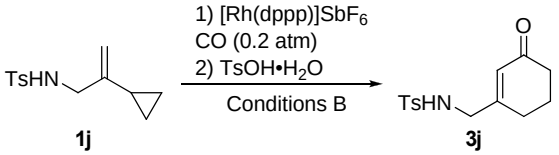
Cycloadducts (2j & 3j)



Following the general procedure A, VCP **1j** (39.2 mg, 0.156 mmol) was converted to cycloadducts **2j** (29.8 mg, 68%) and **3j** (5.9 mg, 14%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

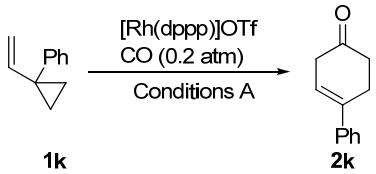
2j: Pale yellow oil, TLC R_f = 0.46 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.83-5.77 (m, 1H), 5.10 (t, *J* = 6.2 Hz, 1H), 3.52 (d, *J* = 6.2 Hz, 2H), 2.74 (s, 2H), 2.43 (s, 3H), 2.41-2.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 143.6, 137.1, 131.6, 129.7, 127.1, 124.7, 48.2, 40.7, 37.9, 24.7, 21.5. IR (neat): υ 3289, 1713, 1605, 1449, 1330 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{18}NO_3S$ $(M+H)^+$: 280.1002. Found: 280.1001.

3j: Pale yellow oil, TLC R_f = 0.35 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.92 (s, 1H), 4.81 (t, *J* = 6.4 Hz, 1H), 3.70 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.33 (t, *J* = 5.6 Hz, 2H), 2.26 (t, *J* = 5.9 Hz, 2H), 2.00-1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 159.3, 143.9, 136.7, 129.9, 127.1, 126.0, 48.0, 37.4, 27.1, 22.3, 21.5. IR (neat): υ 3281, 2928, 1657, 1602, 1430, 1155 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{18}NO_3S$ $(M+H)^+$: 280.1002. Found: 280.1005.



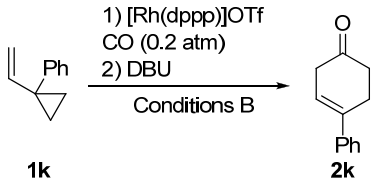
Following the general procedure B, VCP **1j** (35.0 mg, 0.139 mmol) was converted to cycloadduct **3j** (19.8 mg, 51%). Catalyst: 10 mol % [Rh(dppp)]SbF_6, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 5 equiv $TsOH·H_2O$, rt, 2 h.

Cycloadduct (2k)



Following the general procedure A, VCP **1k** (22.2 mg, 0.154 mmol) was converted to cycloadduct **2k**[21] (21.1 mg, 80%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

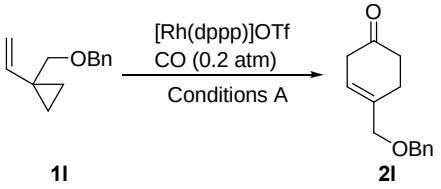
2k: Colorless oil, TLC R_f = 0.65 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.32 (m, 4H), 7.31-7.26 (m, 1H), 6.09 (t, *J* = 3.9 Hz, 1H), 3.10-3.04 (m, 2H), 2.91 (td, *J* = 6.9 and 1.1 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 140.7, 137.8, 128.5, 127.4, 125.2, 121.0, 39.9, 38.7, 27.9.



1k **2k**

Following the general procedure B, VCP **1k** (23.8 mg, 0.165 mmol) was converted to cycloadduct **2k** (22.7 mg, 80%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

Cycloadduct (2l)

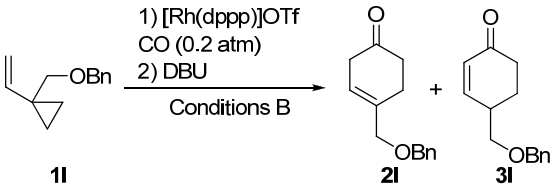


1l **2l**

Following the general procedure A, VCP **1l** (28.4 mg, 0.151 mmol) was converted to cycloadduct **2l** (13.7 mg, 42%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 36 h.

2l: Colorless oil, TLC R_f = 0.42 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 7.32-7.27 (m, 1H), 5.80-5.75 (m, 1H), 4.51 (s, 2H), 3.99 (s, 2H), 2.93-2.88 (m, 2H), 2.56-2.44 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 138.1, 135.8, 128.4, 127.7, 121.3, 73.2, 72.2, 39.4, 38.3, 26.1. IR (neat): υ 2868, 1717, 1460, 1207, 1076 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ $(M+Na)^+$: 239.1042. Found: 239.1041.

Cycloadduct (3l)

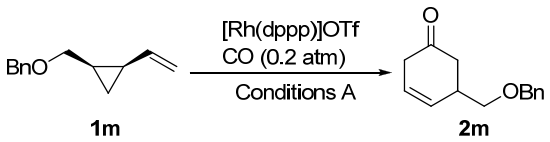


1l **2l** **3l**

Following the general procedure B, VCP **1l** (29.3 mg, 0.155 mmol) was converted to cycloadducts **2l** (1.0 mg, 3%) and **3l**[22] (13.0 mg, 39%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 36 h; then 1 equiv DBU, rt, 1 h.

3l: Colorless oil, TLC R_f = 0.38 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (m, 5H), 6.95 (ddd, J = 10.2, 2.5, and 1.3 Hz, 1H), 6.04 (dd, J = 10.2 and 2.5 Hz, 1H), 4.55 (s, 2H), 3.49 (qd, J = 9.0 and 6.7 Hz, 2H), 2.81-2.68 (m, 1H), 2.57-2.48 (m, 1H), 2.44-2.31 (m, 1H), 2.17-2.08 (m, 1H), 1.89-1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 151.6, 138.0, 130.1, 128.5, 127.8, 127.6, 73.3, 72.4, 37.0, 36.7, 25.9.

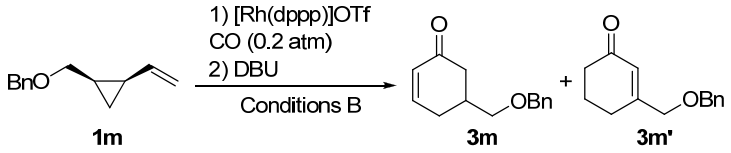
Cycloadduct (2m)



Following the general procedure A, VCP **1m** (30.0 mg, 0.159 mmol) was converted to cycloadduct **2m** (21.6 mg, 63%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 75 ºC, reaction time: 48 h.

2m: Colorless oil, TLC R_f = 0.52 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 5.91-5.79 (m, 2H), 4.51 (s, 2H), 3.50-3.38 (m, 2H), 2.97-2.79 (m, 3H), 2.58 (dd, *J* = 14.5 and 6.4 Hz, 1H), 2.49 (dd, *J* = 14.5 and 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.4, 138.1, 128.7, 128.4, 127.7, 127.6, 125.3, 73.2, 73.0, 42.4, 39.8, 38.0. IR (neat): υ 2872, 1717, 1497, 1456, 1102 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ $(M+Na)^+$: 239.1043. Found: 239.1040.

Cycloadducts (3m & 3m')

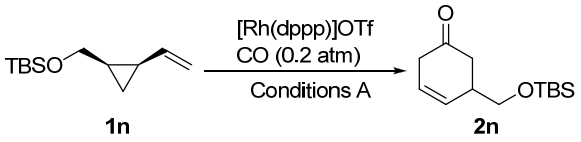


Following the general procedure B, VCP **1m** (30.3 mg, 0.161 mmol) was converted to cycloadducts **3m**[23] (19.4 mg, 56%) and **3m'**[24] (3.5 mg, 10%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 75 ºC, reaction time: 48 h; then 1 equiv DBU, rt, 1 h.

3m: Colorless oil, TLC R_f = 0.43 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.26 (m, 5H), 6.97 (ddd, *J* = 10.1, 5.3, and 2.7 Hz, 1H), 6.02 (dd, *J* = 10.1 and 2.7 Hz, 1H), 4.51 (s, 2H), 3.43 (qd, J = 9.4 and 5.3 Hz, 2H), 2.58-2.37 (m, 3H), 2.36-2.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 149.4, 138.1, 129.7, 128.4, 127.7, 127.5, 73.2, 73.1, 41.1, 35.6, 29.0.

3m': Colorless oil, TLC R_f = 0.38 (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.28 (m, 5H), 6.18-6.15 (m, 1H), 4.56 (s, 2H), 4.10 (s, 2H), 2.46-2.38 (m, 2H), 2.28 (t, *J* = 5.9 Hz, 2H), 2.08-1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 161.3, 137.6, 128.5, 127.9, 127.7, 124.9, 72.8, 72.0, 37.8, 26.4, 22.5.

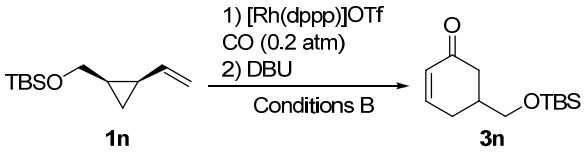
Cycloadduct (2n)



Following the general procedure A, VCP **1n** (30.3 mg, 0.142 mmol) was converted to cycloadduct **2n** (21.8 mg, 64%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2n: Colorless oil, TLC R_f = 0.53 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85-5.80 (m, 2H), 3.67-3.50 (m, 2H), 2.94-2.78 (m, 2H), 2.78-2.70 (m, 1H), 2.54 (dd, *J* = 14.7 and 6.1 Hz, 1H), 2.43 (dd, *J* = 14.7 and 7.0 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5, 128.7, 125.2, 66.2, 42.2, 40.1, 39.8, 25.8, 18.3, -5.5. IR (neat): υ 2935, 1717, 1471, 1259 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{25}O_2Si$ $(M+H)^+$: 241.1618. Found: 241.1616.

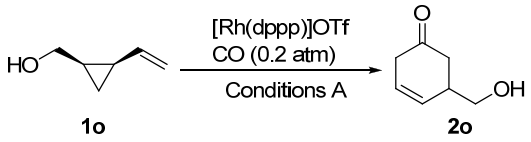
Cycloadduct (3n)



Following the general procedure B, VCP **1n** (33.4 mg, 0.157 mmol) was converted to cycloadduct **3n**[25] (24.6 mg, 65%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

3n: Colorless oil, TLC R_f = 0.43 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (ddd, *J* = 10.2, 5.5, and 2.3 Hz, 1H), 6.06-5.99 (m, 1H), 3.57 (qd, *J* = 10.2 and 4.4 Hz, 2H), 2.54-2.19 (m, 5H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 149.7, 129.7, 66.1, 40.9, 37.7, 28.6, 25.9, 18.3, -5.5.

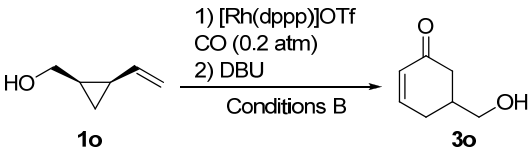
Cycloadduct (2o)



Following the general procedure A, VCP **1o** (15.9 mg, 0.162 mmol) was converted to cycloadduct **2o** (8.4 mg, 41%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 75 ºC, reaction time: 48 h.

2o: Colorless oil, TLC R_f = 0.38 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97-5.83 (m, 2H), 3.70-3.61 (m, 2H), 2.98-2.84 (m, 2H), 2.87-2.79 (m, 1H), 2.60 (dd, *J* = 14.4 and 6.3 Hz, 1H), 2.51 (dd, *J* = 14.4 and 6.9 Hz, 1H), 1.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 126.3, 124.0, 62.0, 49.4, 40.6, 28.7. IR (neat): υ 3412, 2928, 1710, 1400, 1043 cm^{-1}. HRMS (ESI) calcd for $C_7H_{10}NaO_2$ $(M+Na)^+$: 149.0573. Found: 149.0575.

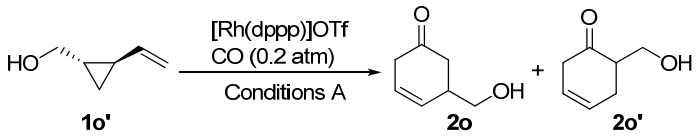
Cycloadduct (3o)



Following the general procedure B, VCP **1o** (14.9 mg, 0.152 mmol) was converted to cycloadduct **3o**[25] (6.7 mg, 35%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 75 ºC, reaction time: 48 h; then 1 equiv DBU, rt, 1 h.

3o: Colorless oil, TLC R_f = 0.30 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (ddd, *J* = 9.9, 5.4, and 2.5 Hz, 1H), 6.08-6.01 (m, 1H), 3.64 (qd, J = 10.6 and 5.2 Hz, 2H), 2.61-2.44 (m, 2H), 2.43-2.18 (m, 3H), 1.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 149.4, 129.8, 66.0, 40.6, 37.5, 28.5.

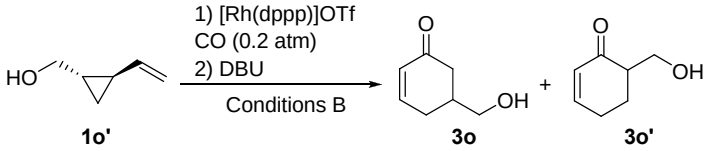
Cycloadduct (2o')



Following the general procedure A, VCP **1o'** (14.3 mg, 0.146 mmol) was converted to cycloadducts **2o** (12.5 mg, 68%) and **2o'** (2.0 mg, 11%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2o': Colorless oil, TLC R_f = 0.44 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.77-5.69 (m, 1H), 3.84-3.69 (m, 2H), 3.10-3.00 (m, 1H), 2.91-2.73 (m, 2H), 2.58-2.48 (m, 2H), 2.38-2.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 126.3, 124.0, 62.0, 49.4, 40.6, 28.7. IR (neat): υ 3415, 2928, 1710, 1404, 1043 cm^{-1}. HRMS (ESI) calcd for $C_7H_{10}NaO_2$ $(M+Na)^+$: 149.0573. Found: 149.0576.

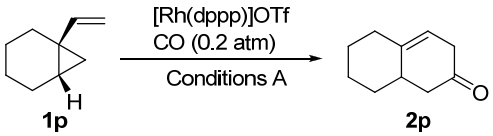
Cycloadduct (3o')



Following the general procedure B, VCP **1o'** (16.0 mg, 0.163 mmol) was converted to cycloadducts **3o** (11.1 mg, 54%) and **3o'** (1.6 mg, 8%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

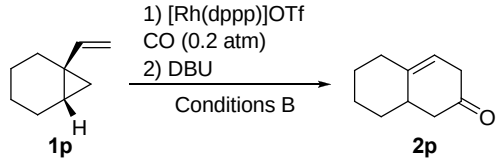
3o': Colorless oil, TLC R_f = 0.37 (PE:EA = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-6.99 (m, 1H), 6.03 (dt, *J* = 10.0 and 1.9 Hz, 1H), 3.81 (ddd, *J* = 11.6, 7.4, and 4.3 Hz, 1H), 3.71 (ddd, *J* = 11.4, 8.9, and 4.2 Hz, 1H), 2.97 (dd, *J* = 8.9 and 4.3 Hz, 1H), 2.60-2.50 (m, 1H), 2.49 – 2.42 (m, 2H), 2.05-1.94 (m, 1H), 1.89-1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.1, 151.2, 129.6, 63.6, 48.3, 25.7, 25.4. IR (neat): υ 3389, 2928, 1669, 1393, 1035 cm^{-1}. HRMS (ESI) calcd for $C_7H_{10}NaO_2$ $(M+Na)^+$: 149.0573. Found: 149.0575.

Cycloadduct (2p)



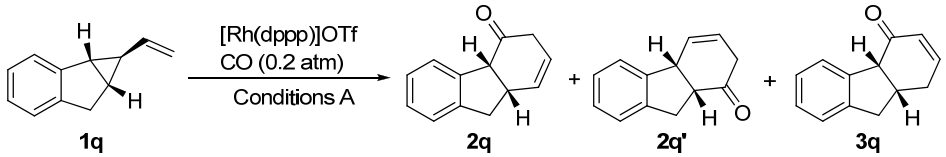
Following the general procedure A, VCP **1p** (20.7 mg, 0.169 mmol) was converted to cycloadduct **2p**[26] (14.1 mg, 56%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h.

2p: Colorless oil, TLC R_f = 0.58 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37-5.31 (m, 1H), 2.98-2.89 (dm, *J* = 20.5, 1H), 2.81-2.71 (dm, *J* = 20.5, 1H), 2.59 (ddd, *J* = 13.5, 6.6, and 1.7 Hz, 1H), 2.54-2.42 (m, 1H), 2.36-2.21 (m, 2H), 2.06-1.94 (m, 1H), 1.93-1.85 (m, 1H), 1.85-1.74 (m, 2H), 1.46-1.10 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 140.9, 115.4, 46.1, 40.1, 40.0, 35.9, 34.5, 27.3, 25.6.



Following the general procedure B, VCP **1p** (20.4 mg, 0.167 mmol) was converted to cycloadduct **2p** (14.0 mg, 56%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 24 h; then 1 equiv DBU, rt, 1 h.

Cycloadducts (2q & 2q' & 3q)

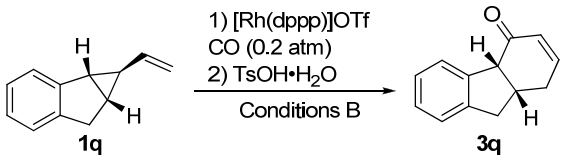


Following the general procedure A, VCP **1q** (22.6 mg, 0.144 mmol) was converted to cycloadducts **2q**[27] (10.0 mg, 38%), **2q'** (3.3 mg, 12%), and **3q**[27] (1.7 mg, 6%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 48 h.

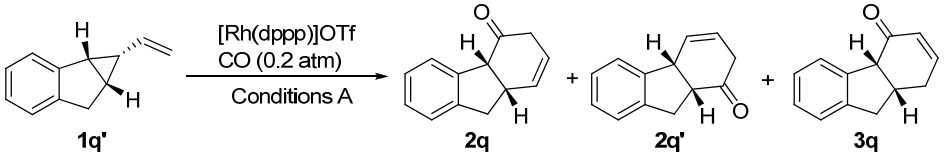
2q: Pale yellow solid, TLC R_f = 0.61 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.12 (m, 4H), 5.74-5.68 (m, 1H), 5.67-5.59 (m, 1H), 4.01 (d, *J* = 7.5 Hz, 1H), 3.65-3.51 (m, 1H), 3.28 (dd, *J* = 15.7 and 8.1 Hz, 1H), 3.01-2.77 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 142.8, 140.3, 130.3, 127.7, 126.7, 125.2, 124.4, 122.8, 57.7, 43.7, 39.5, 37.4.

2q': Yellow solid, TLC R_f = 0.55 (PE:EA = 10:1) , m.p. 40-42 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.14 (m, 4H), 6.05-5.98 (m, 1H), 5.78-5.72 (m, 1H), 4.33-4.23 (m, 1H), 3.44 (dd, *J* = 15.6 and 6.2 Hz, 1H), 3.36-3.28 (m, 1H), 3.05 (dd, *J* = 15.6 and 8.4 Hz, 1H), 2.99-2.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 144.0, 141.1, 128.1, 127.1, 126.9, 124.9, 123.5, 122.6, 51.1, 49.1, 37.9, 33.6. IR (neat): υ 3032, 2928, 1713, 1479 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{13}O$ $(M+H)^+$: 185.0961. Found: 185.0965.

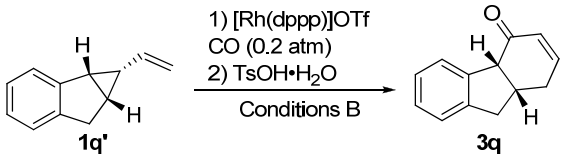
3q: Yellow oil, TLC R_f = 0.43 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.32 (dm, 1H), 7.29-7.17 (m, 3H), 6.93 (ddd, *J* = 10.1, 5.0, and 3.5 Hz, 1H), 6.18-6.13 (m, 1H), 3.87 (d, *J* = 6.9 Hz, 1H), 3.21-3.01 (m, 2H), 2.76 (dd, *J* = 15.1 and 3.6 Hz, 1H), 2.57-2.45 (m, 1H), 2.22-2.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 149.9, 142.5, 139.1, 130.2, 127.4, 127.0, 124.9, 124.8, 54.4, 38.5, 27.8.



Following the general procedure B, VCP **1q** (22.5 mg, 0.144 mmol) was converted to cycloadduct **3q** (6.6 mg, 25%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 48 h; then 5 equiv $TsOH \cdot H_2O$, 50 ºC, 4 h.



Following the general procedure A, VCP **1q'** (23.2 mg, 0.148 mmol) was converted to cycloadducts **2q** (9.8 mg, 36%), **2q'** (2.7 mg, 10%), and **3q** (1.5 mg, 6%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 48 h.



Following the general procedure B, VCP **1q'** (23.4 mg, 0.150 mmol) was converted to cycloadduct **3q** (7.2 mg, 26%). Catalyst: 10 mol % [Rh(dppp)]OTf, substrate concentration: 0.05 M, temperature: 85 ºC, reaction time: 48 h; then 5 equiv $TsOH \cdot H_2O$, 50 ºC, 4 h.

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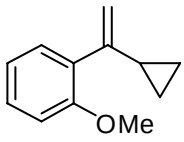
3. ^{1}H and ^{13}C-NMR Spectra for New Compounds



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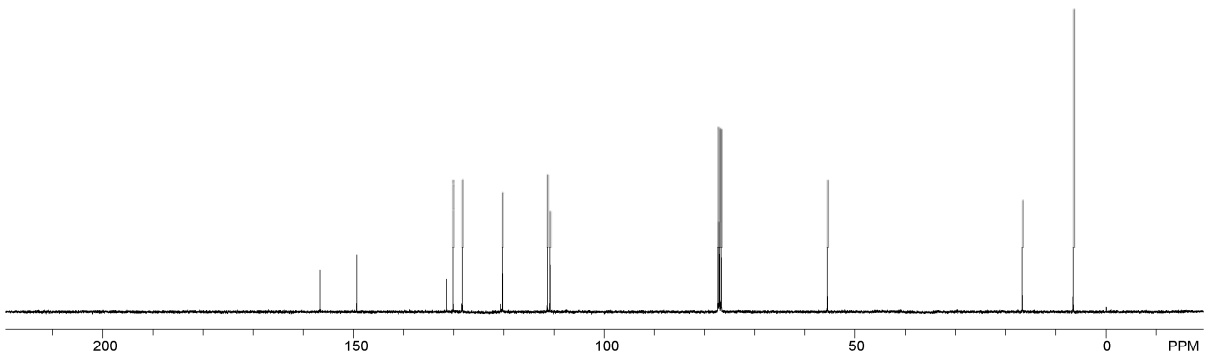

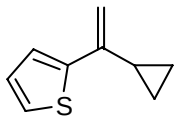

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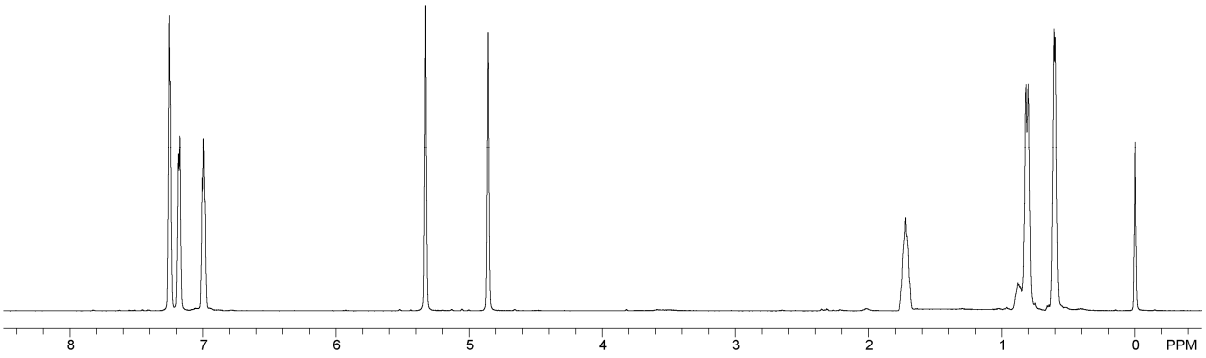

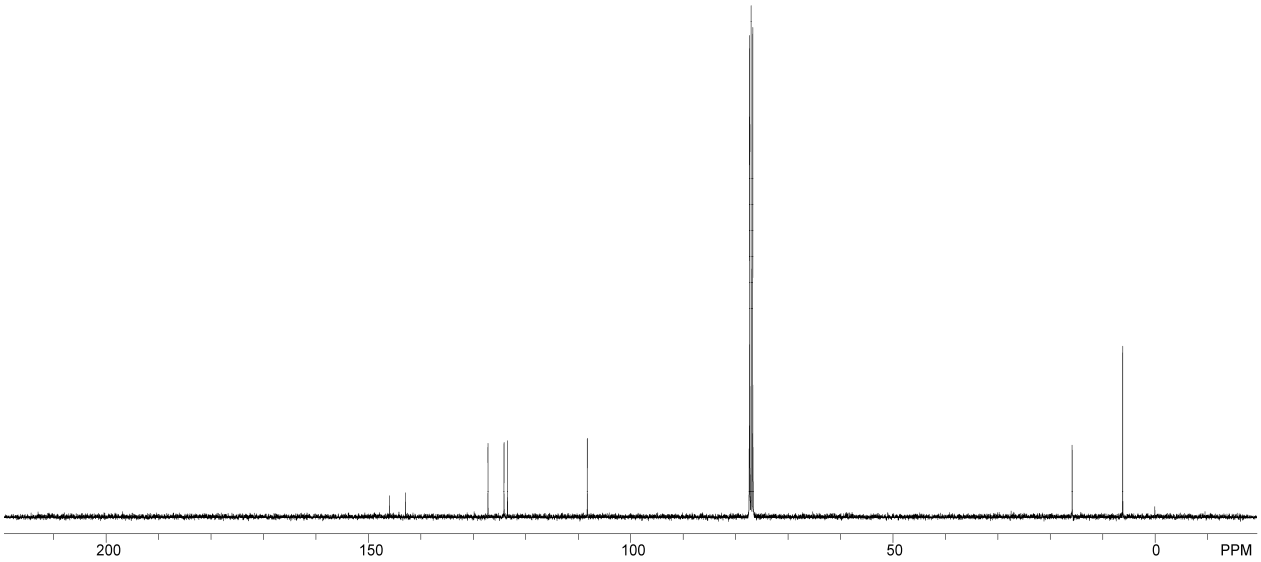

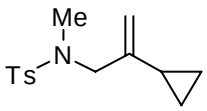

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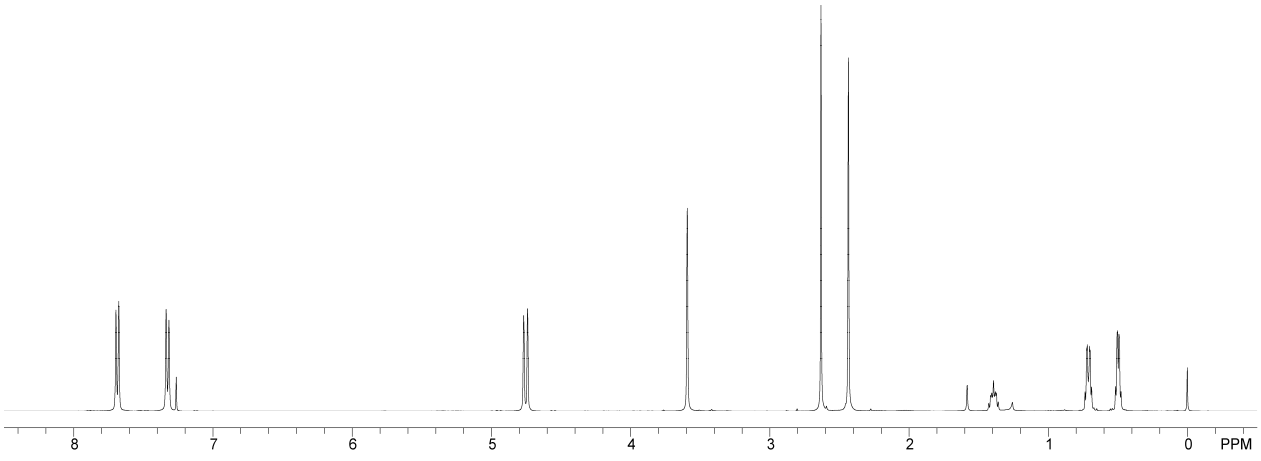

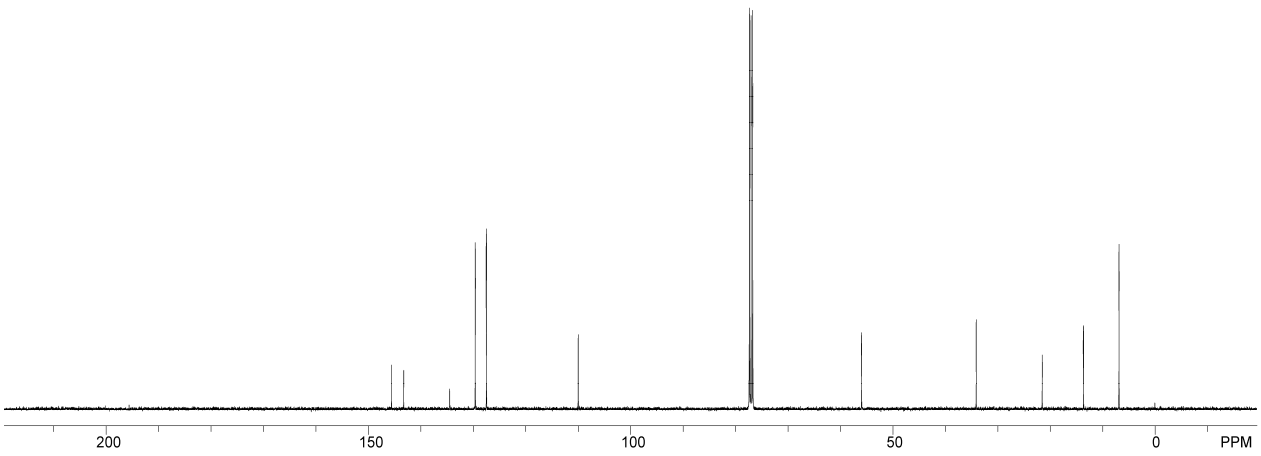

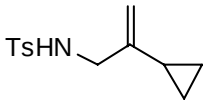

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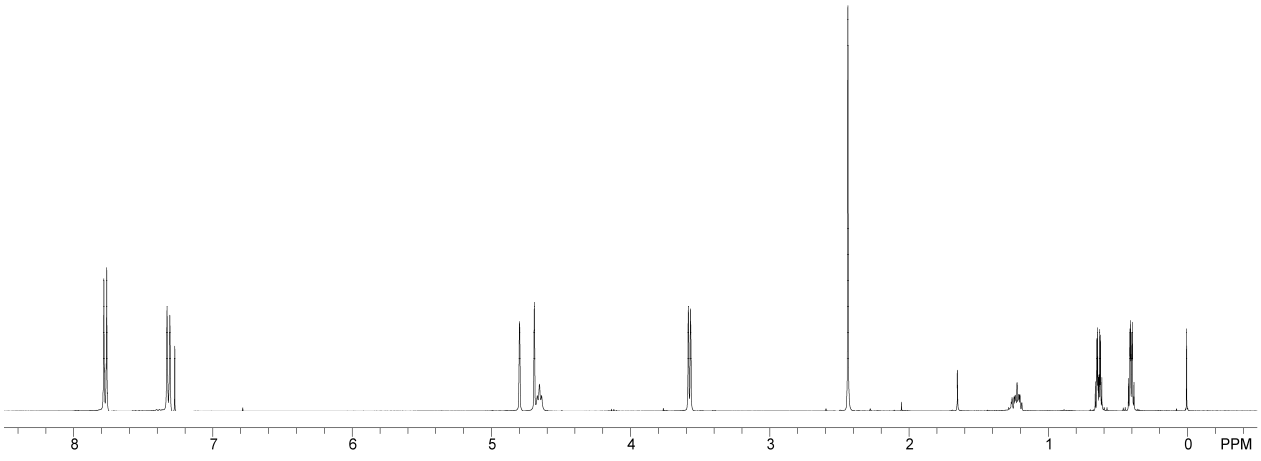

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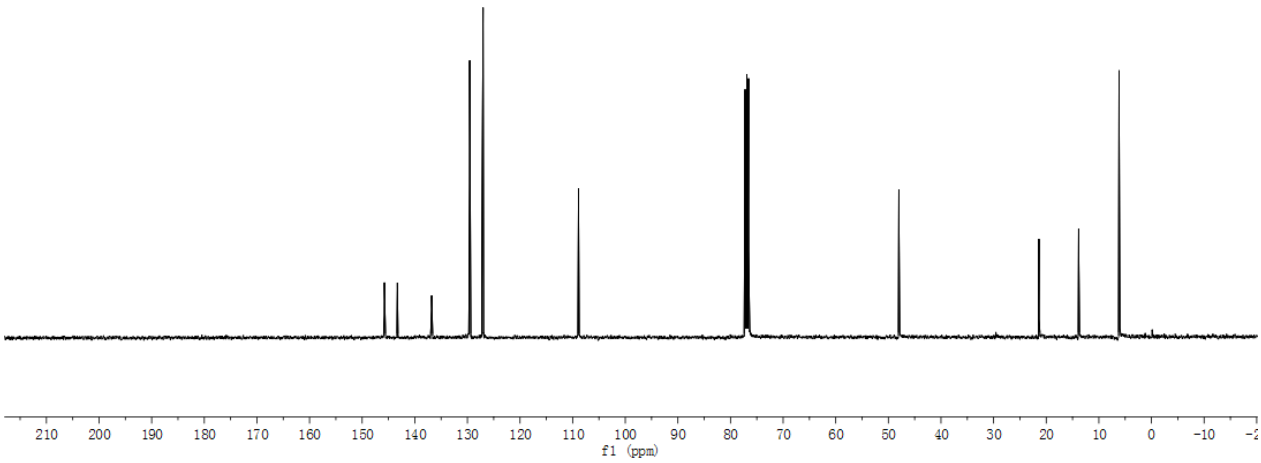
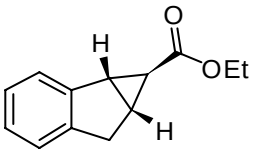
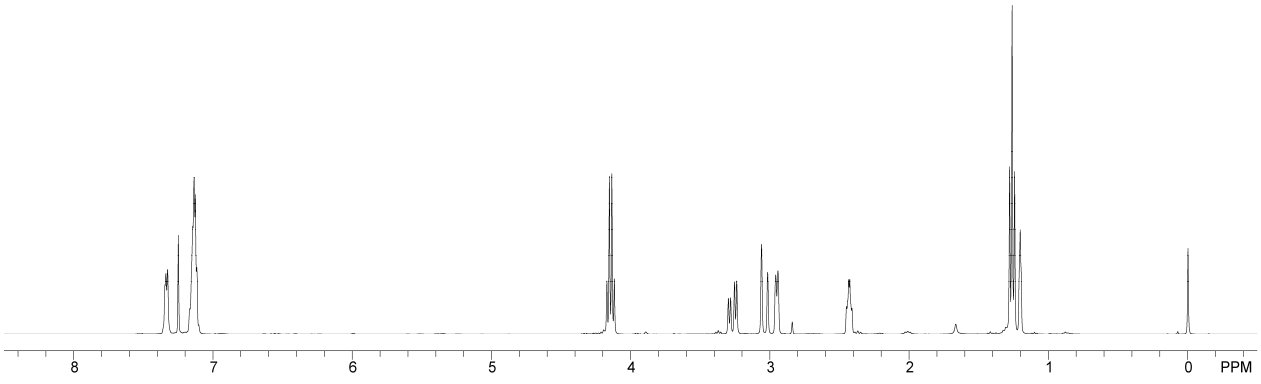
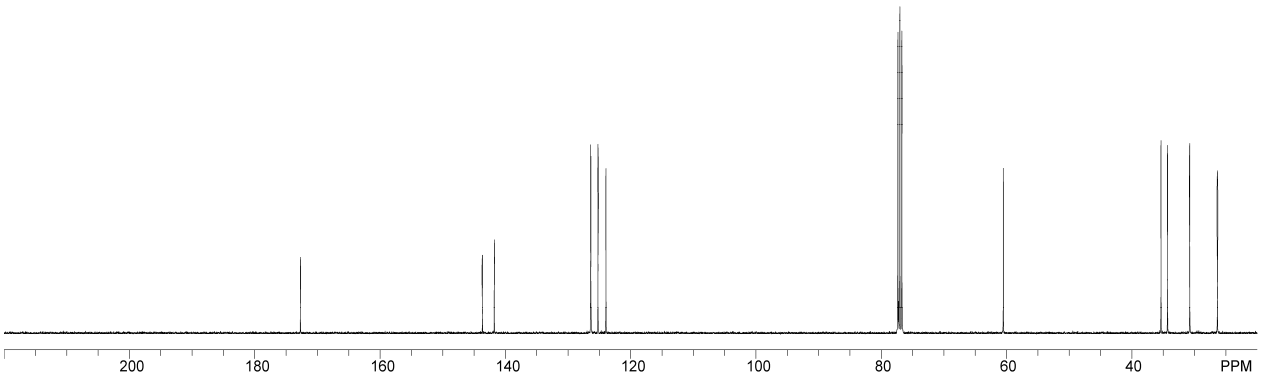
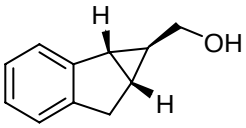




S6







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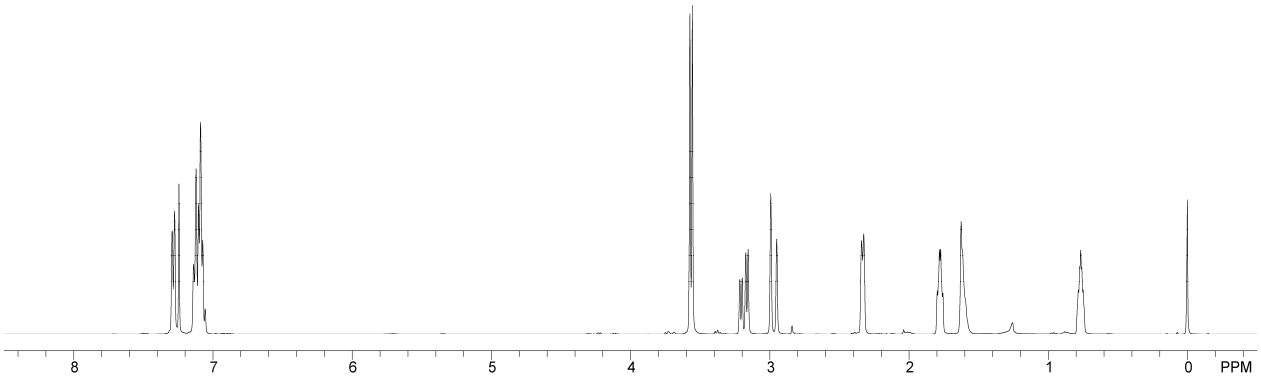

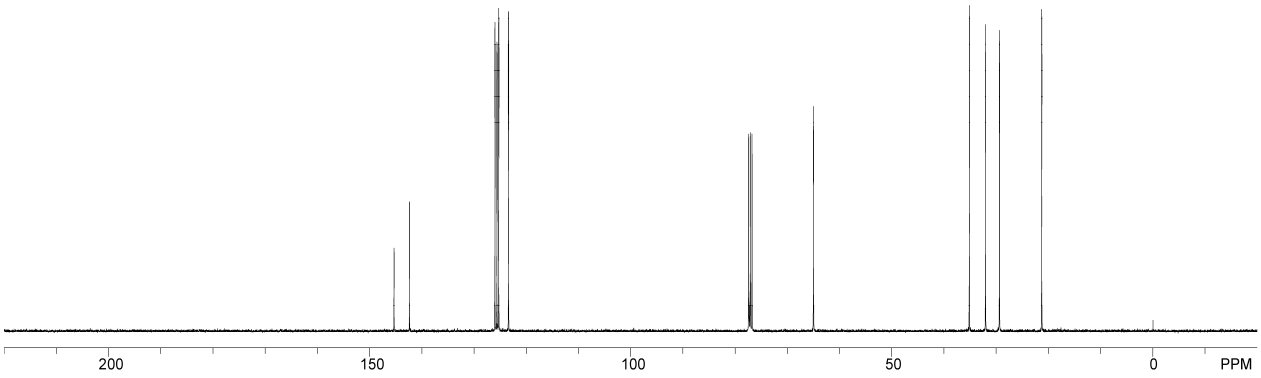

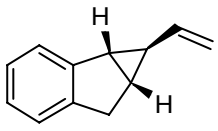

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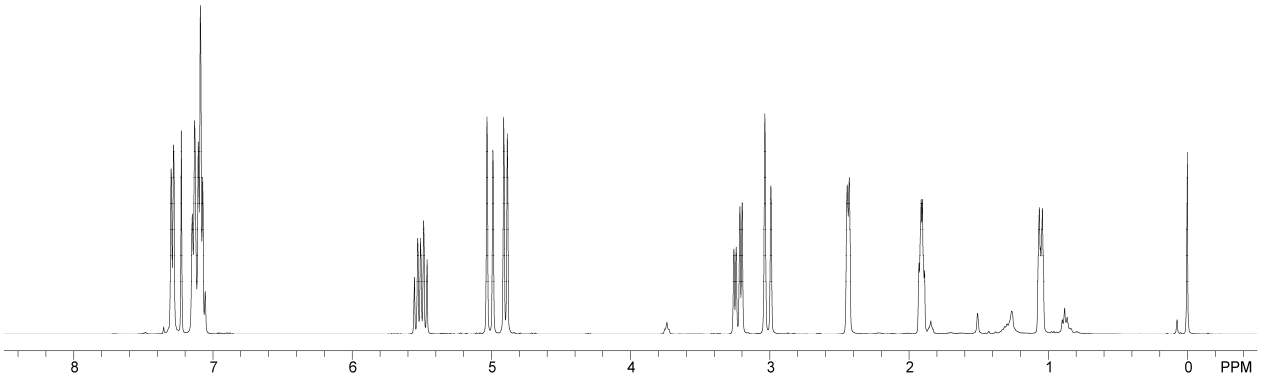

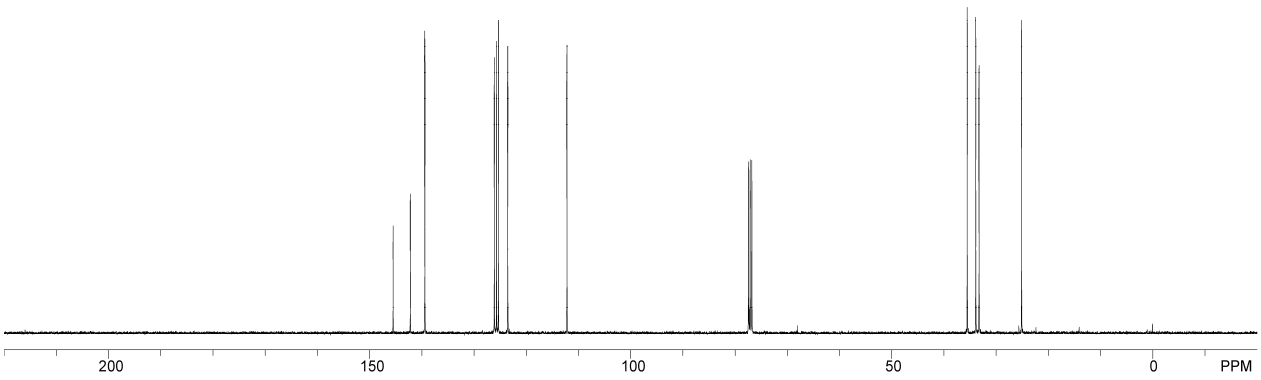

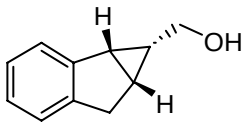

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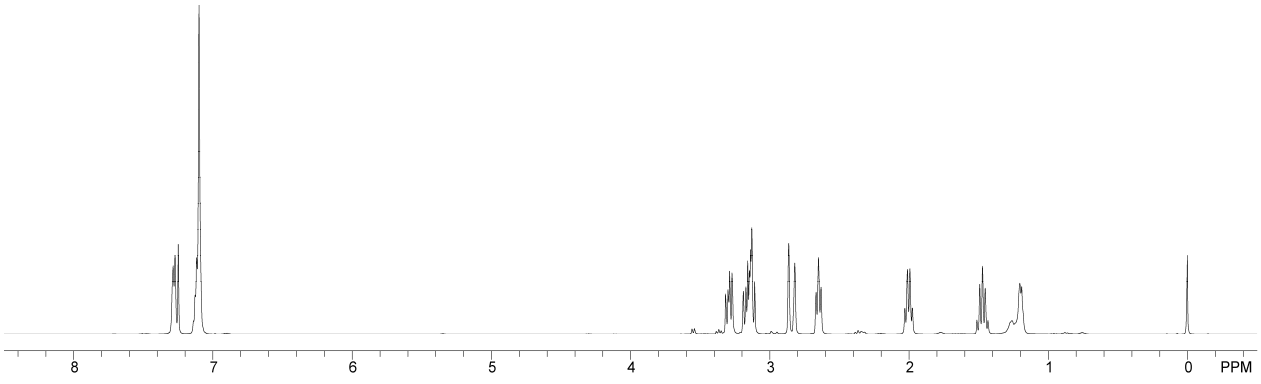

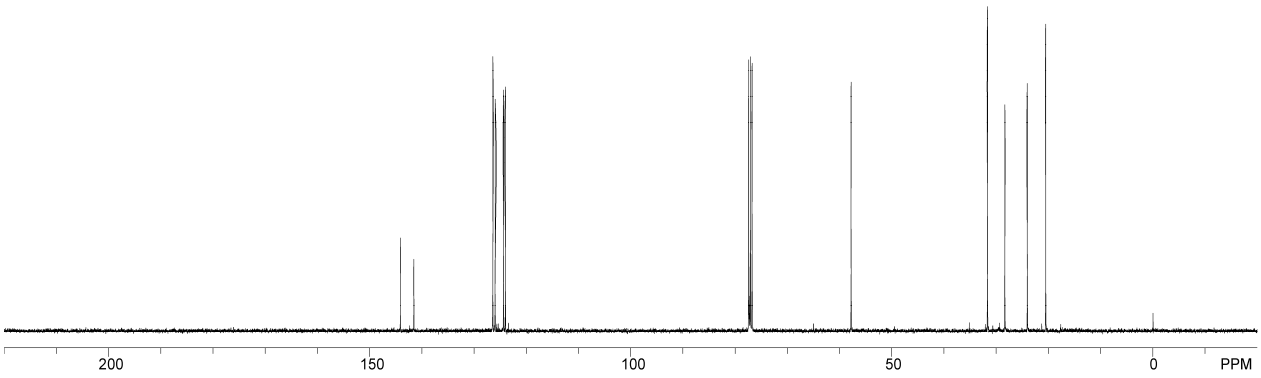

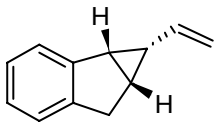

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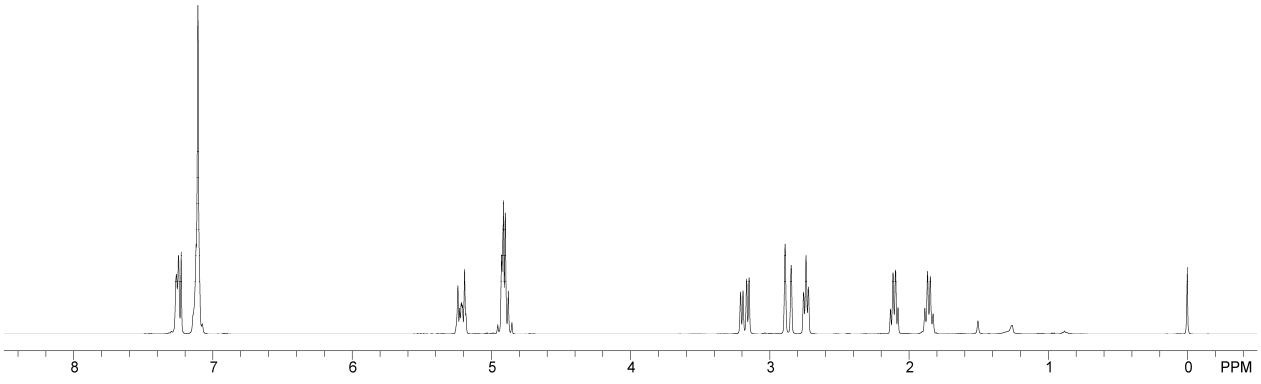

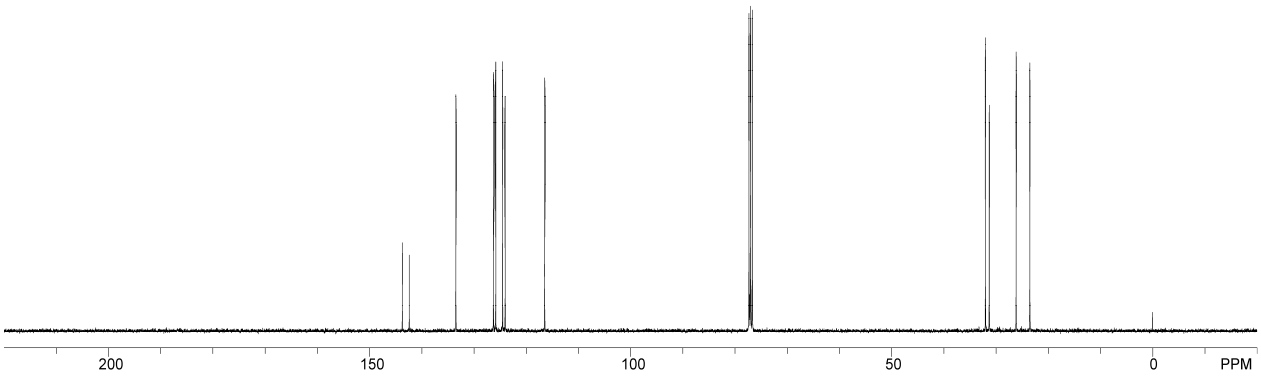

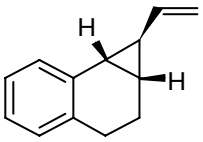

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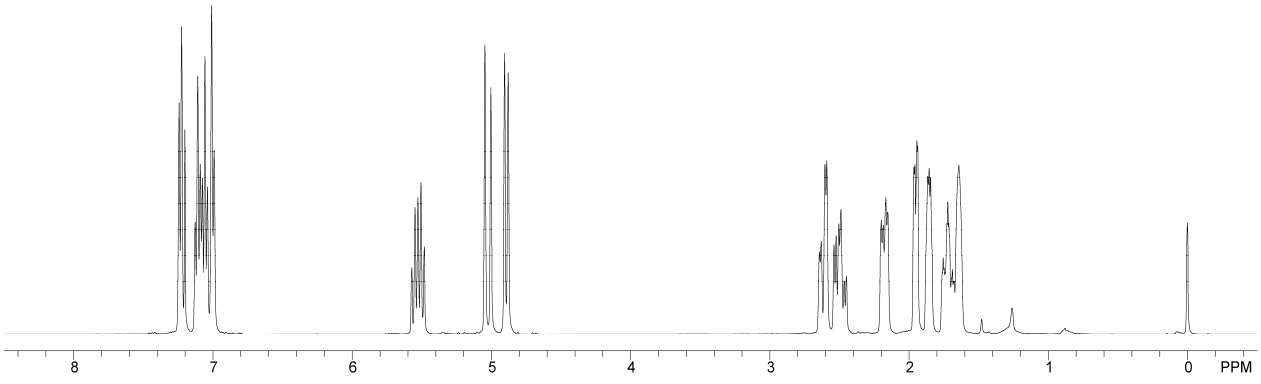

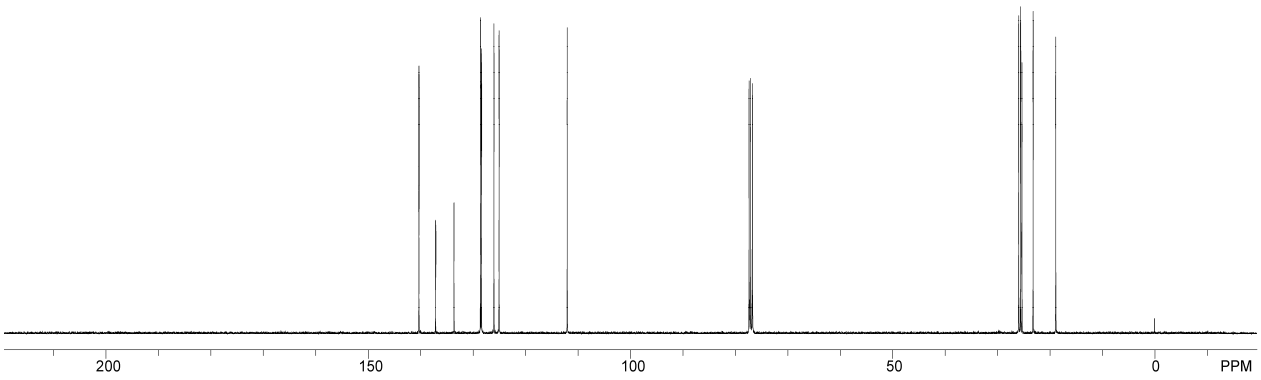

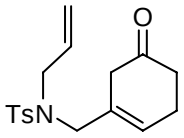

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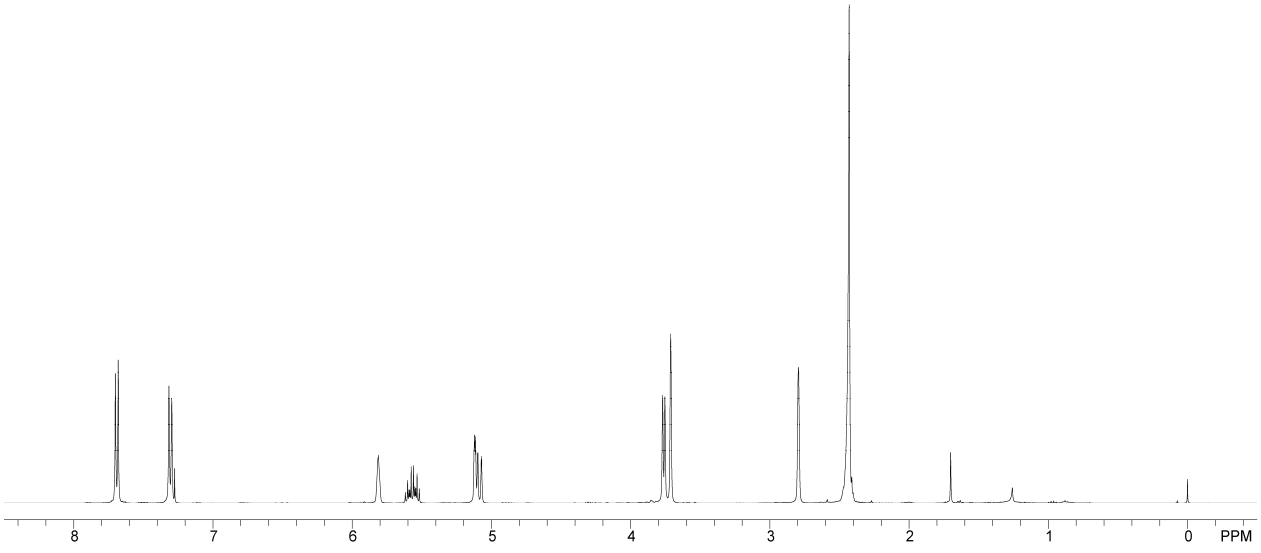

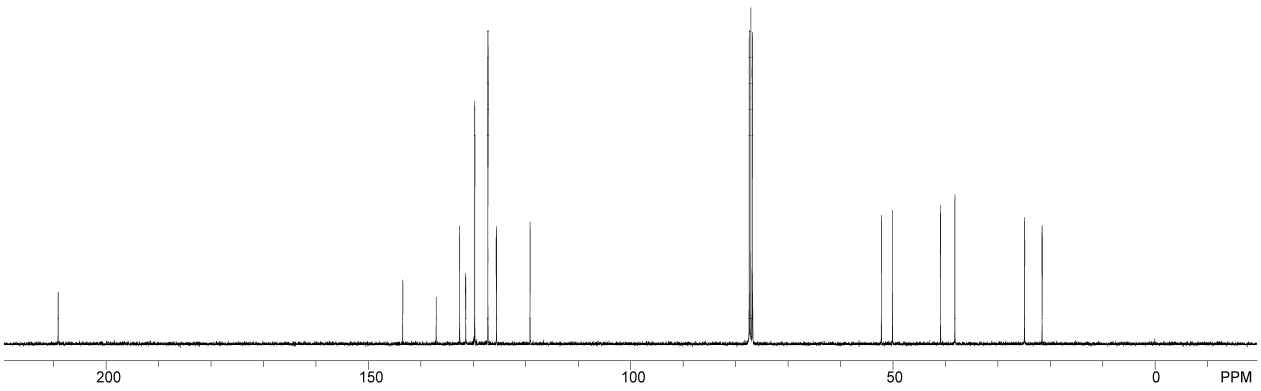

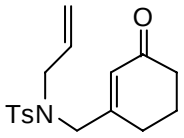

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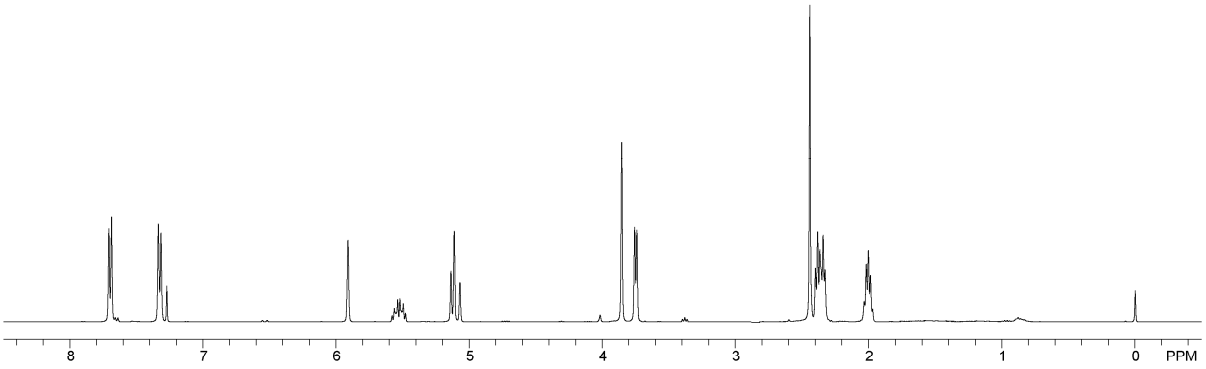

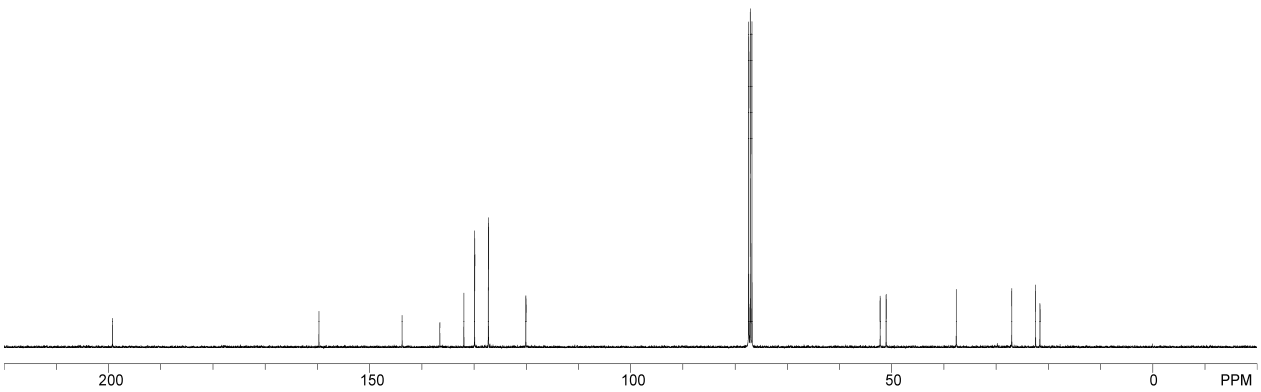

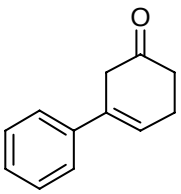

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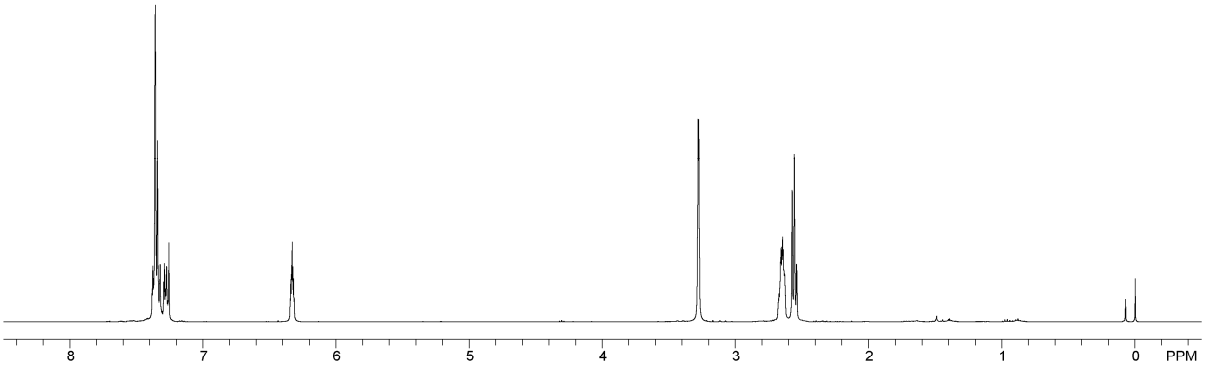

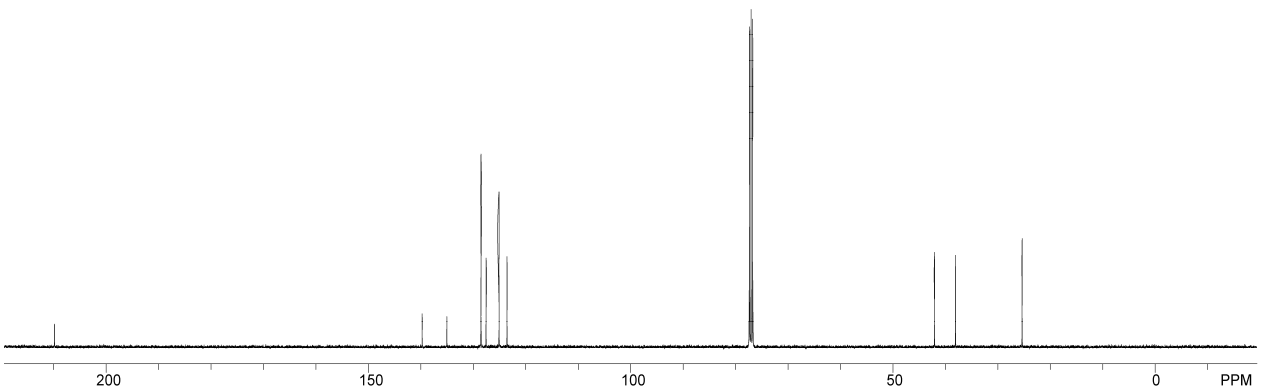

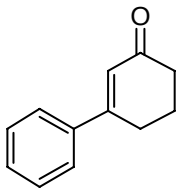

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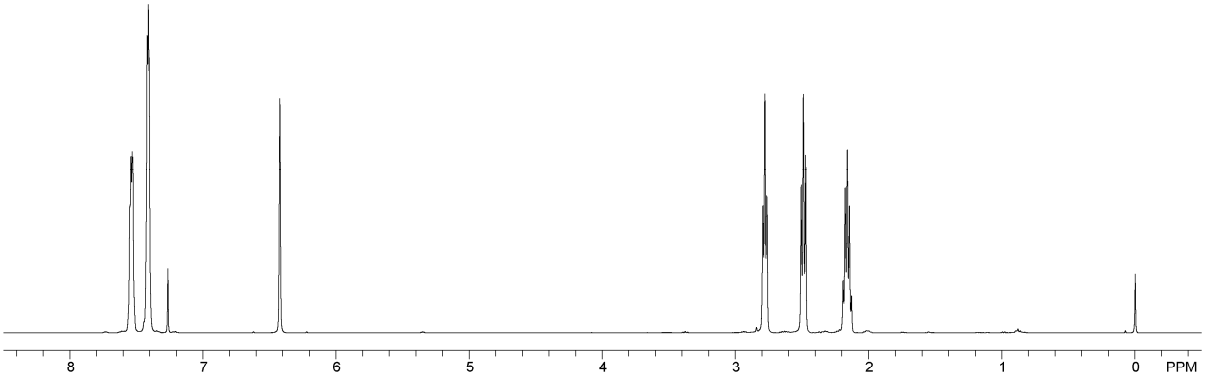

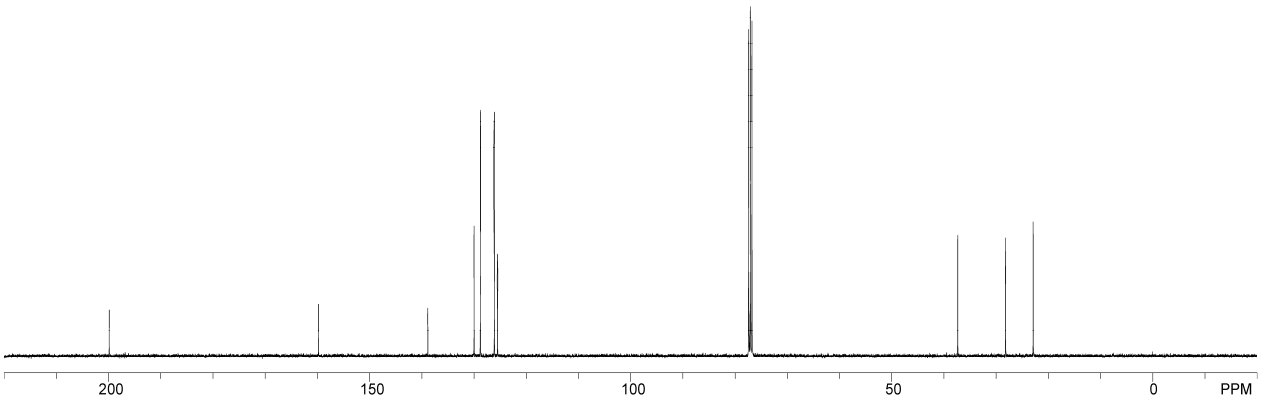

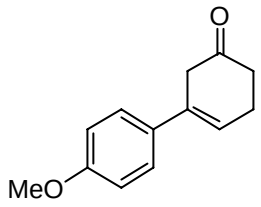

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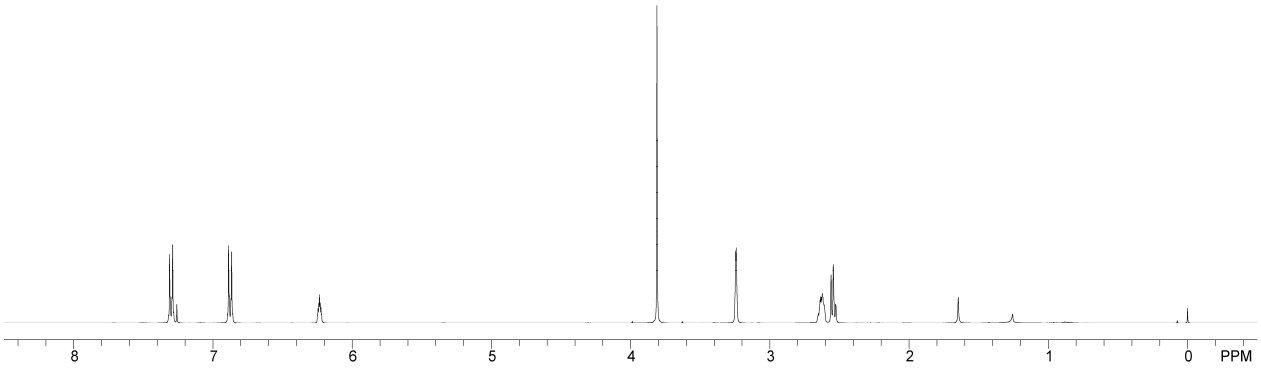

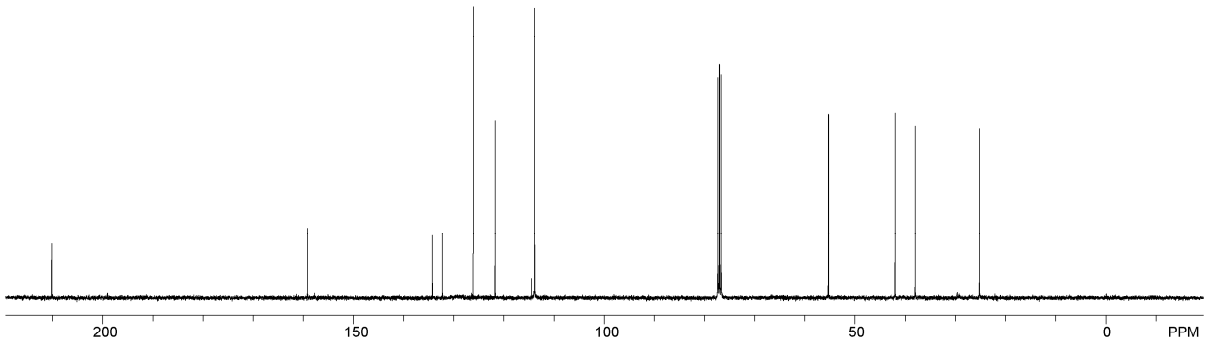

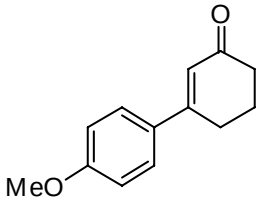

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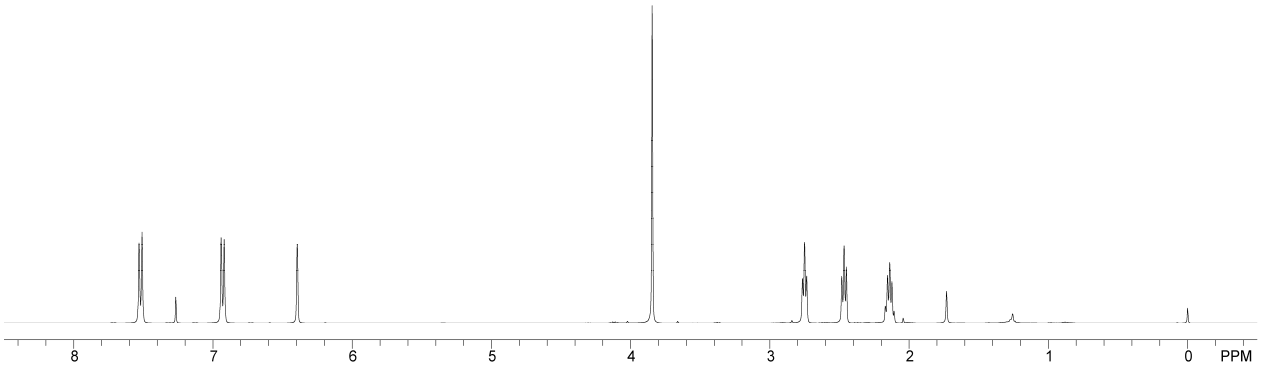

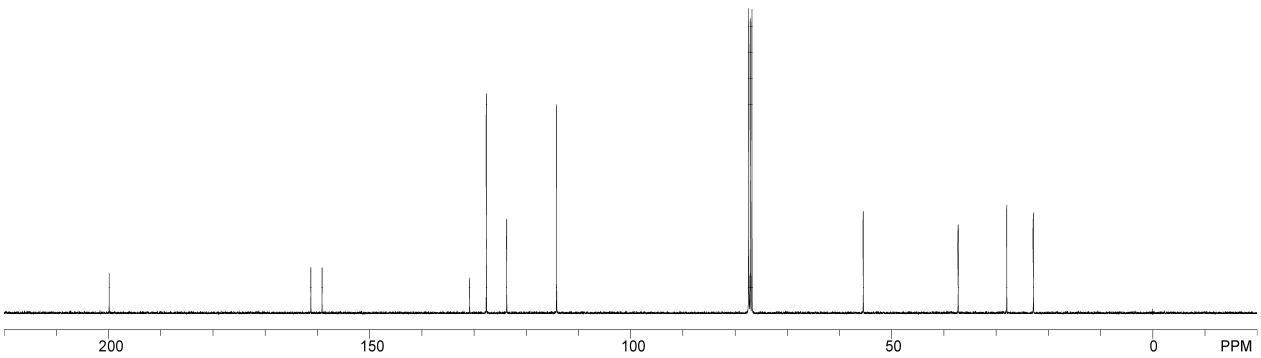

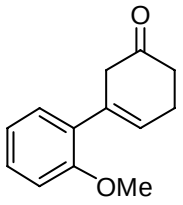

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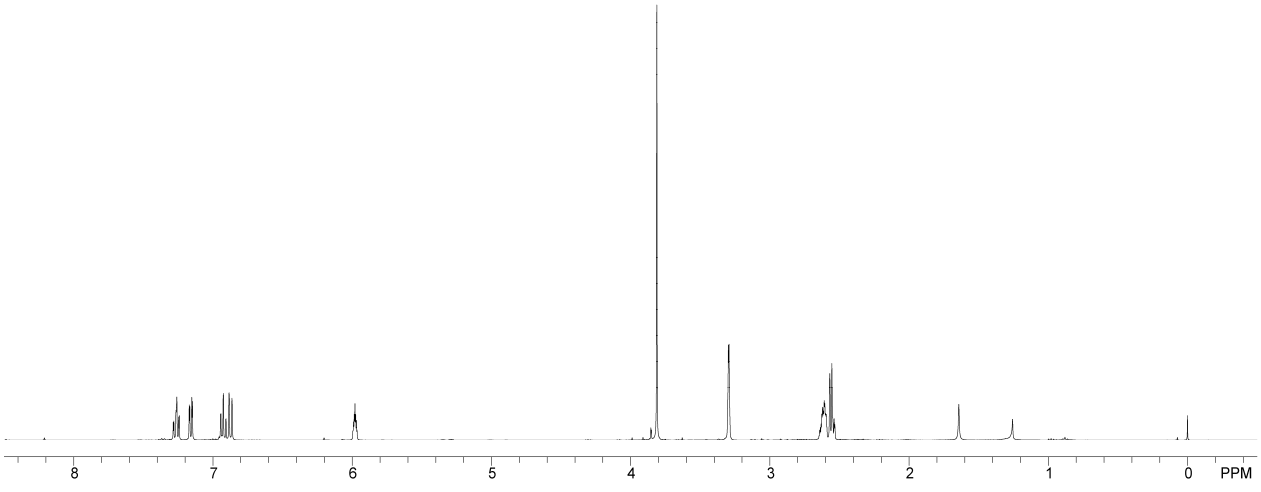

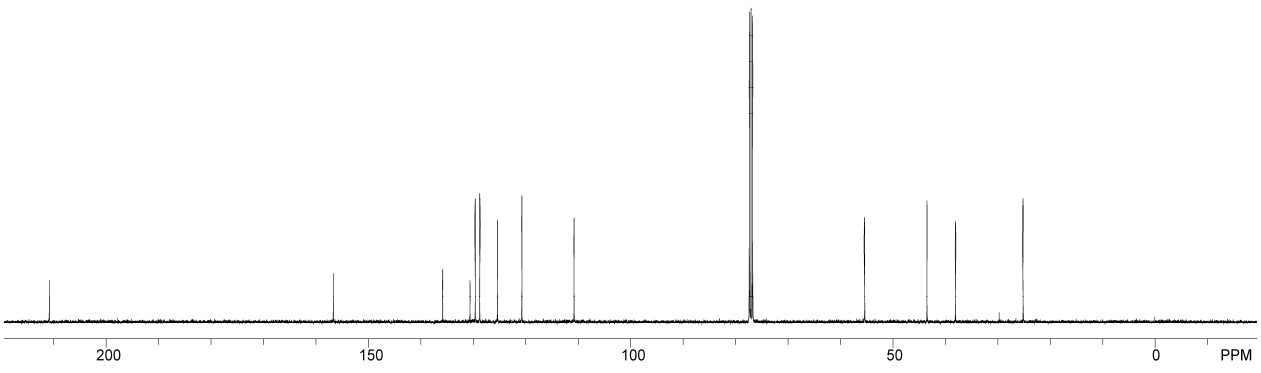

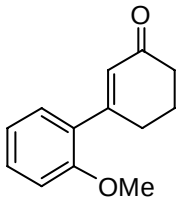

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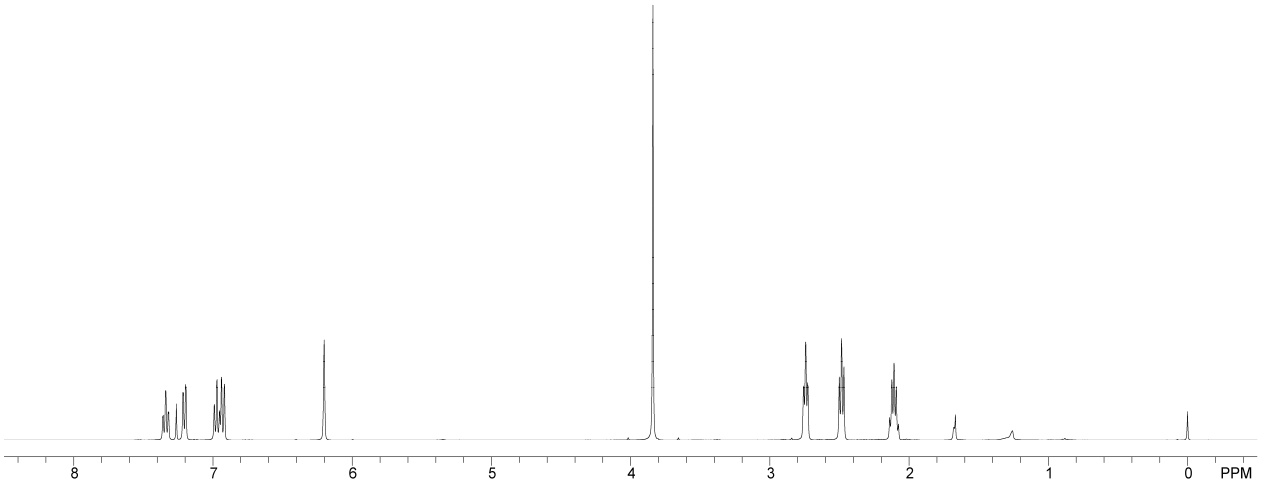

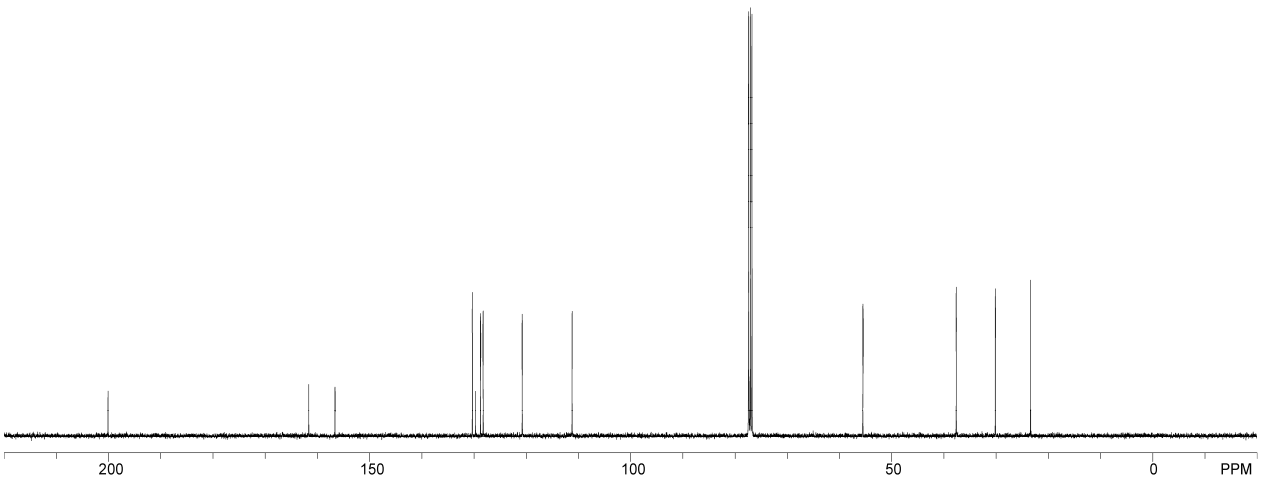

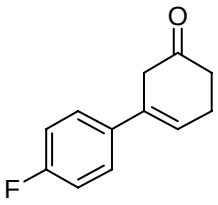

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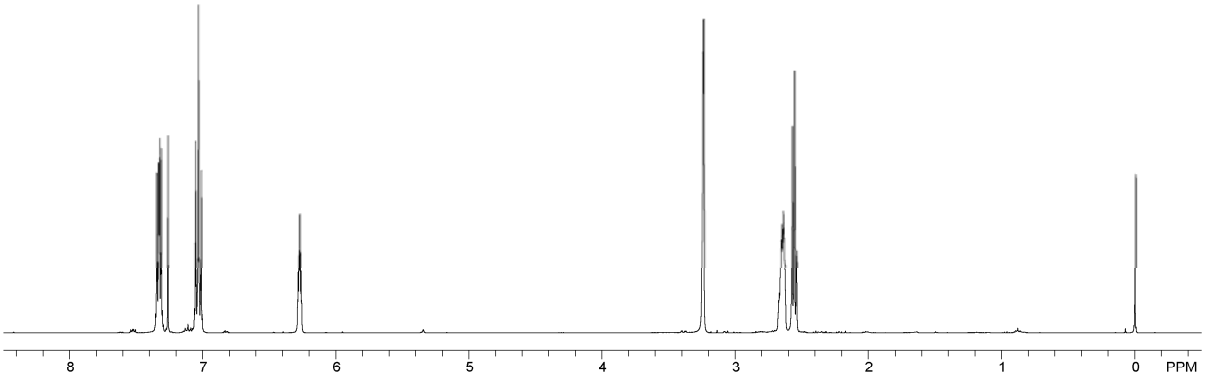

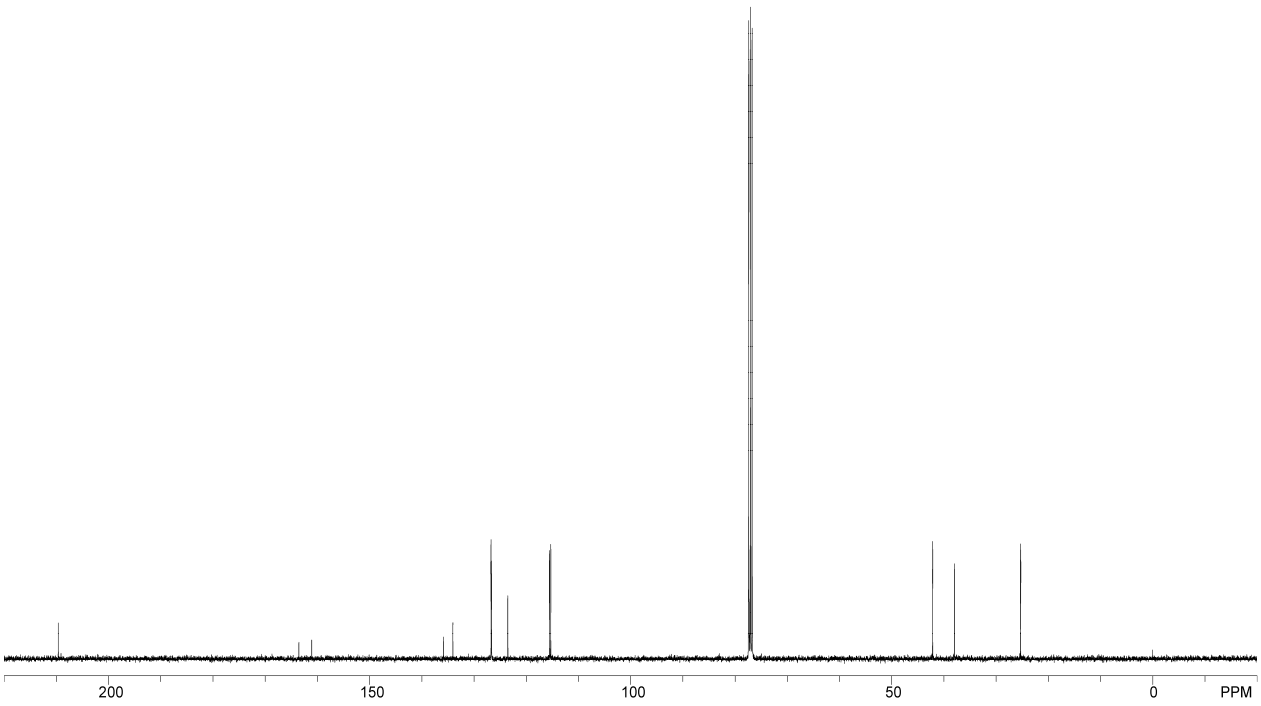

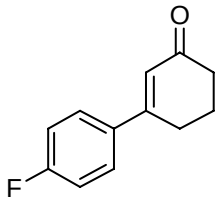

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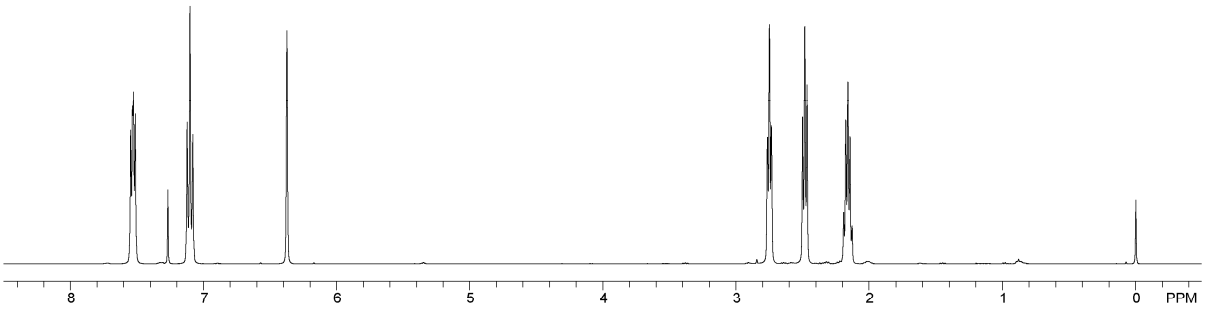

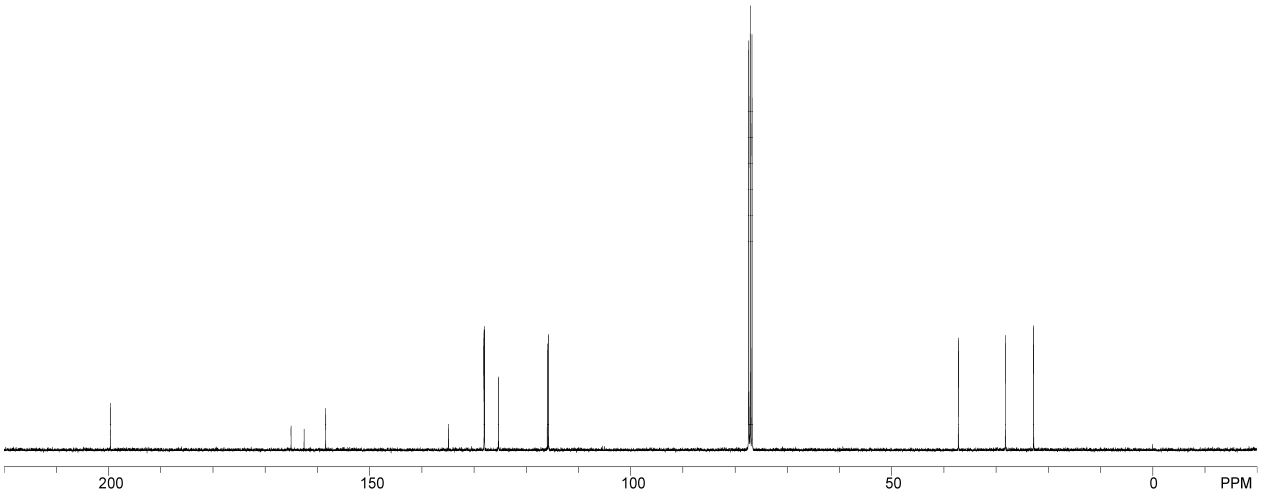

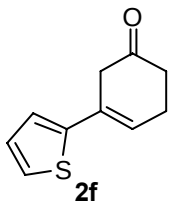

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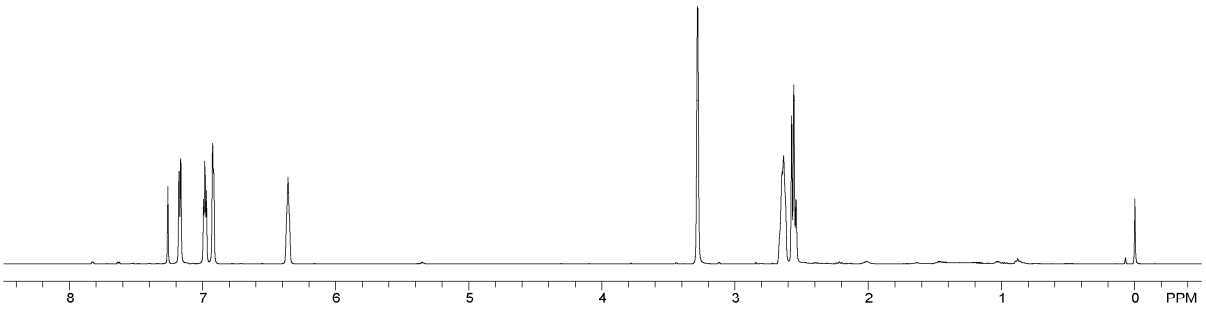

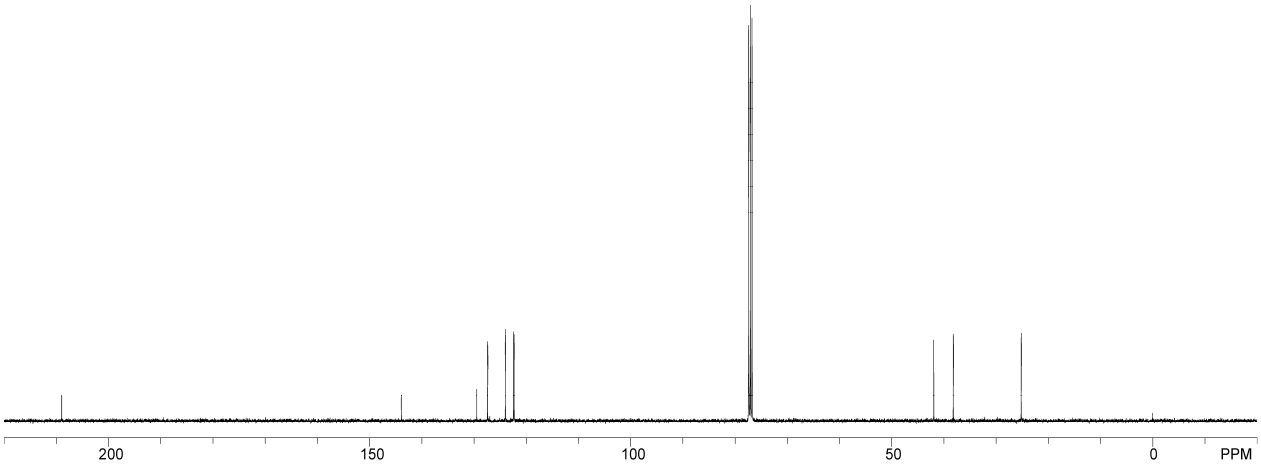

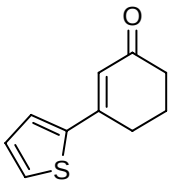

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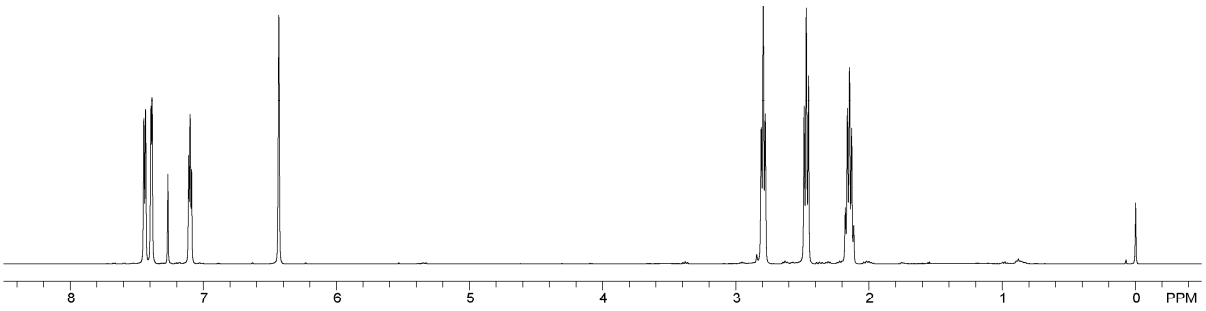

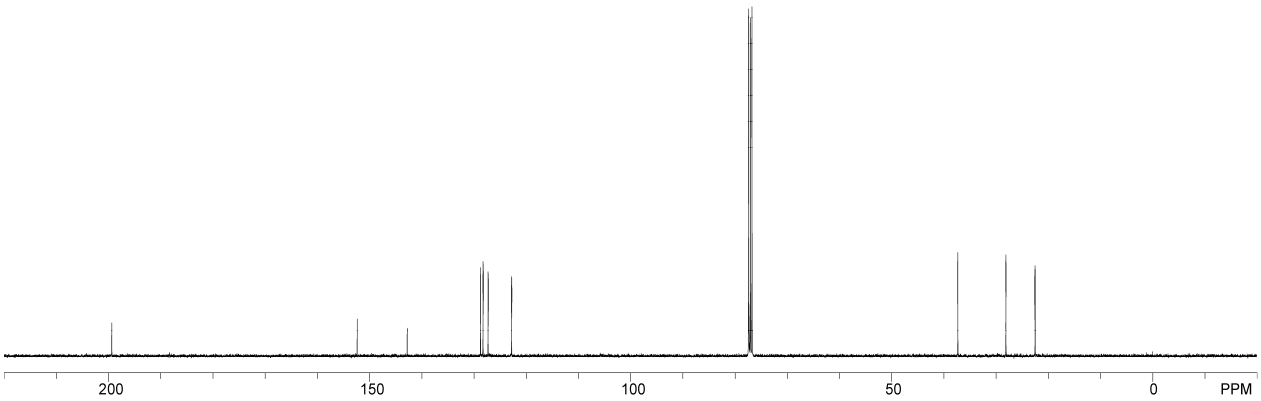

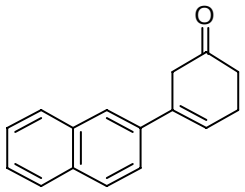

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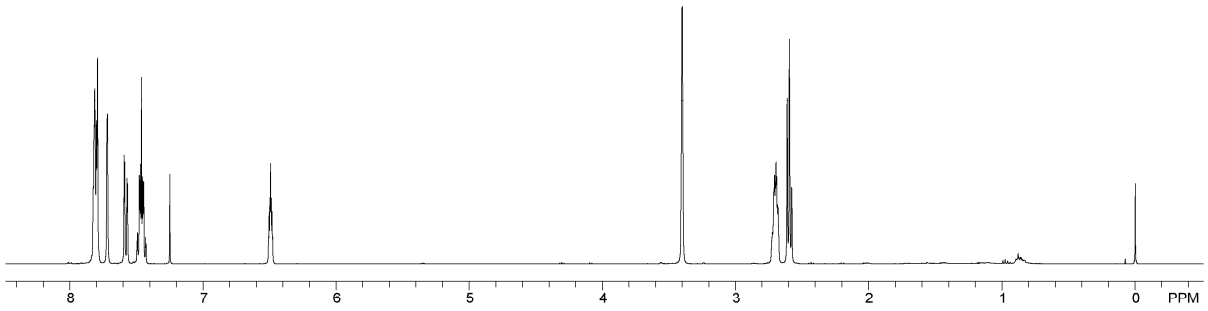

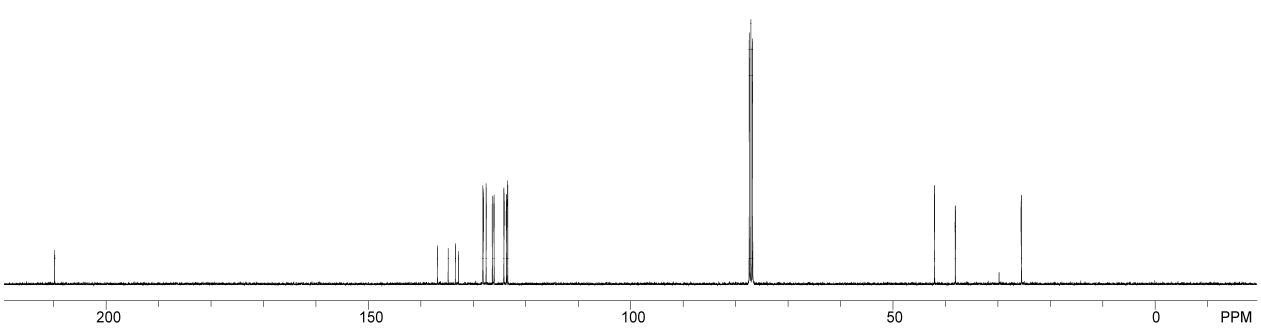

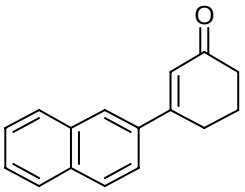

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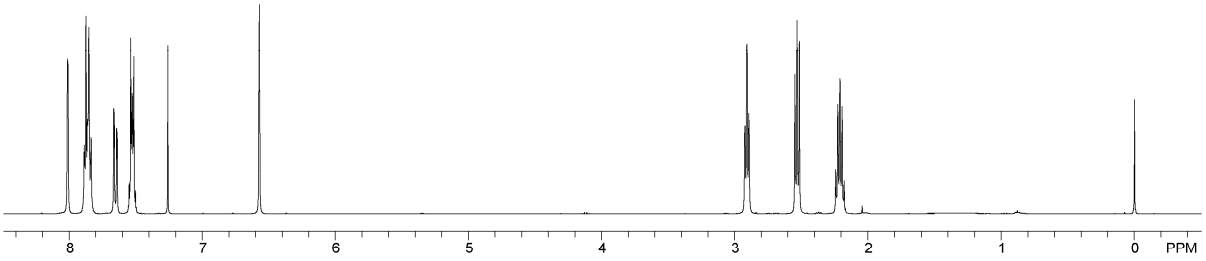

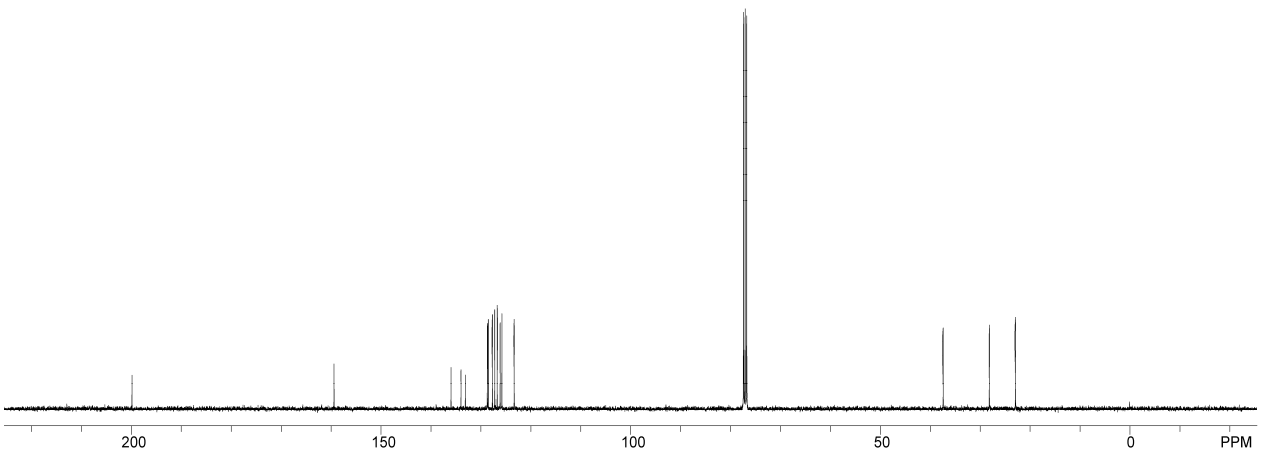

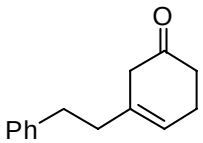

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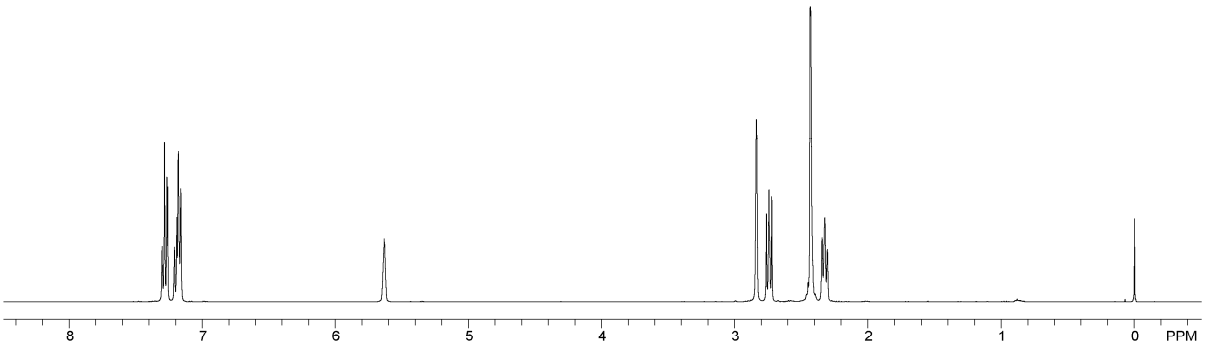

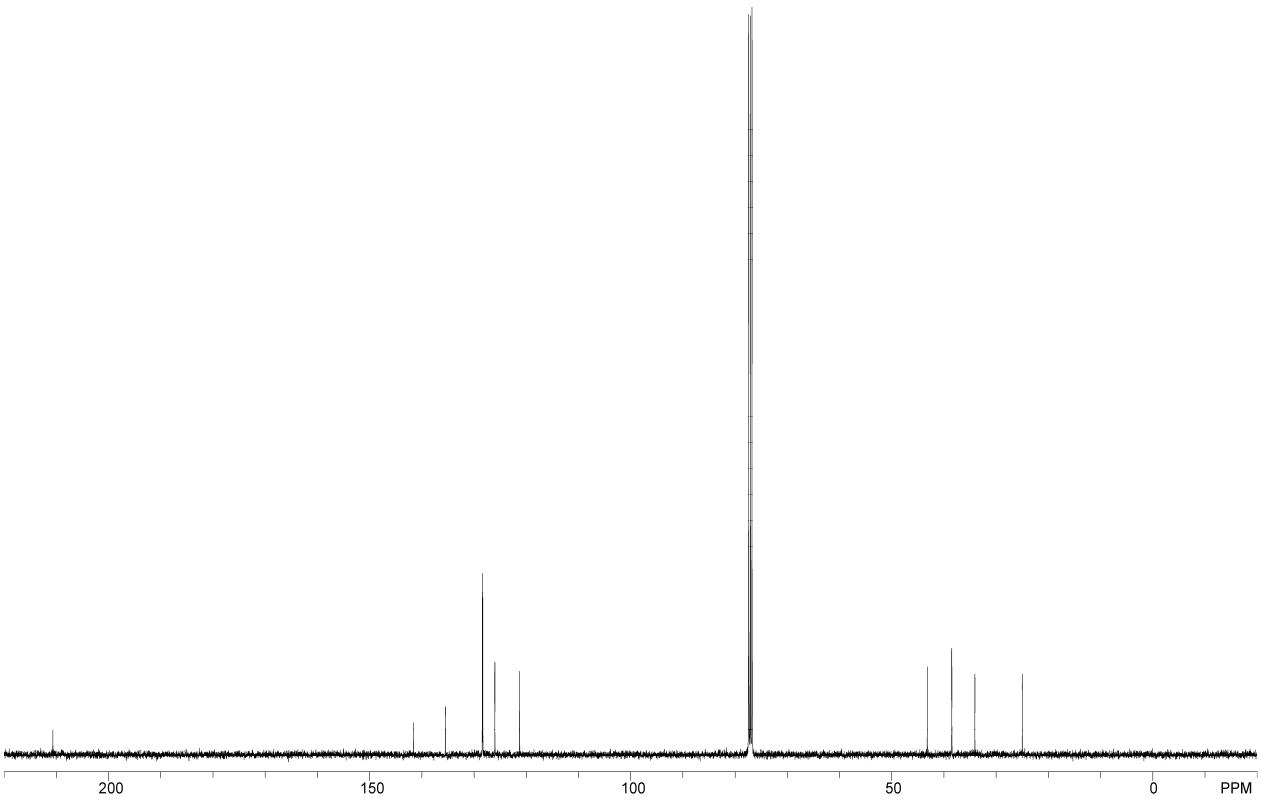

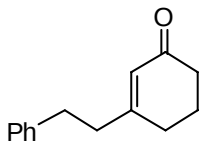

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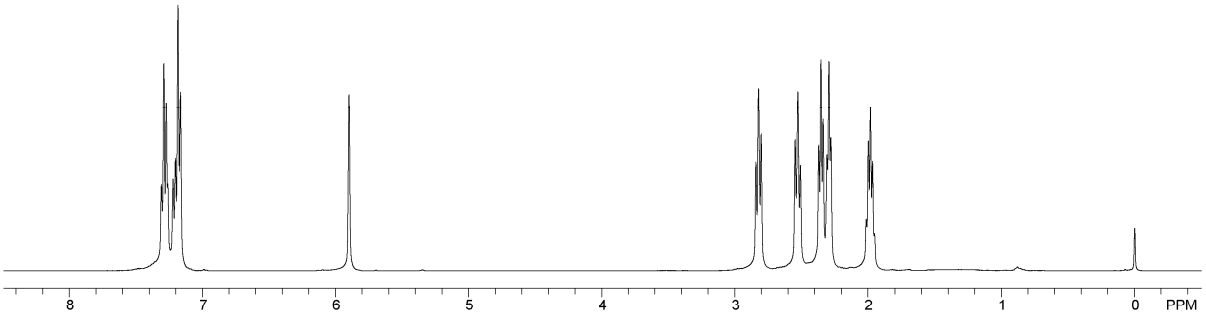

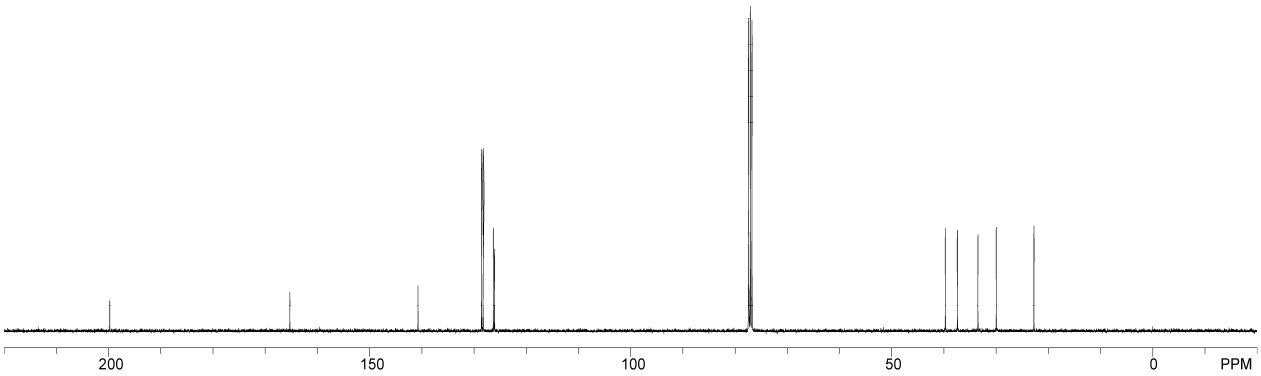

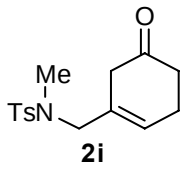

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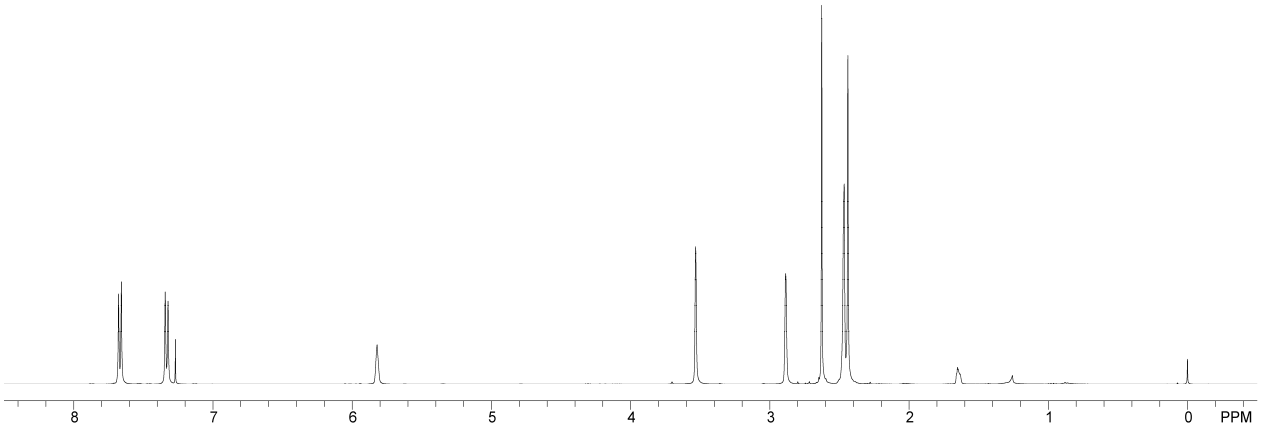

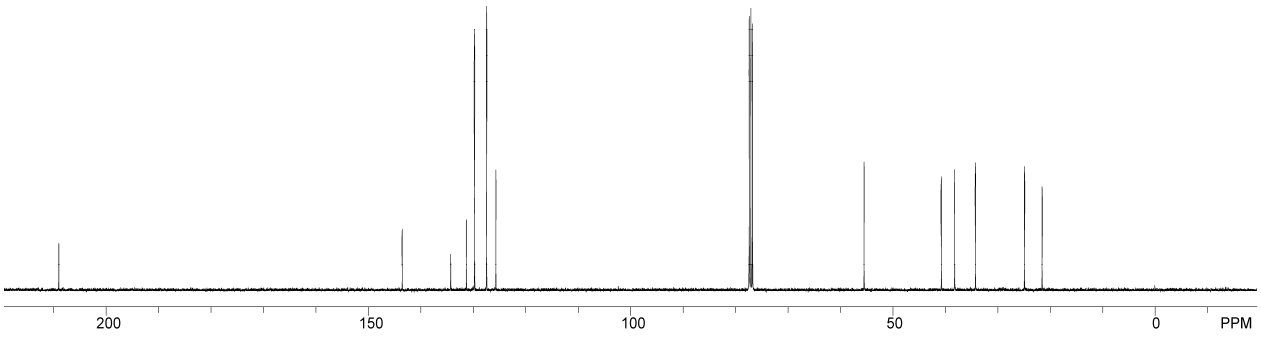

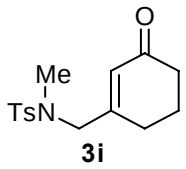

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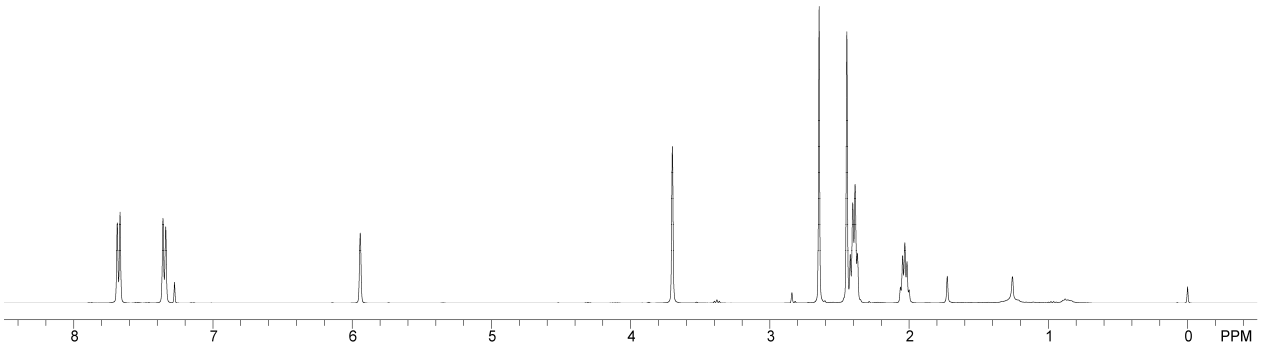

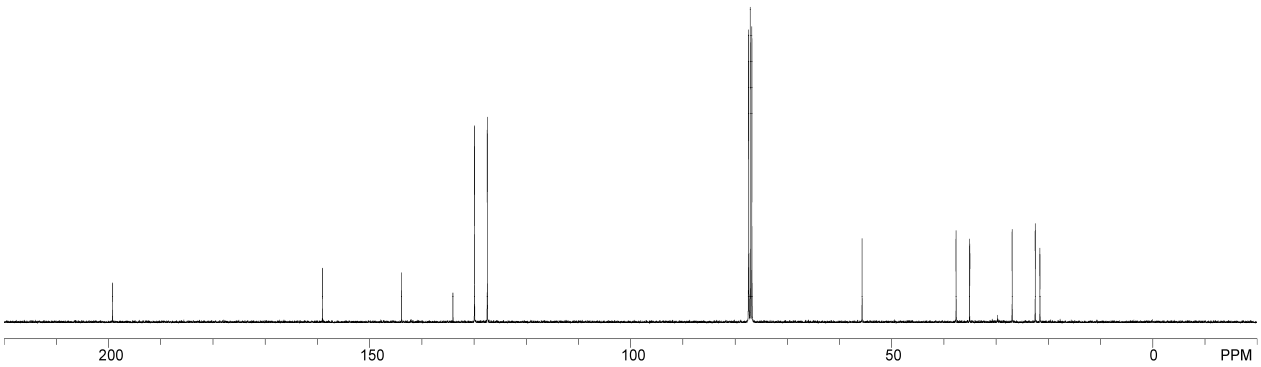

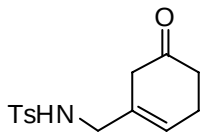

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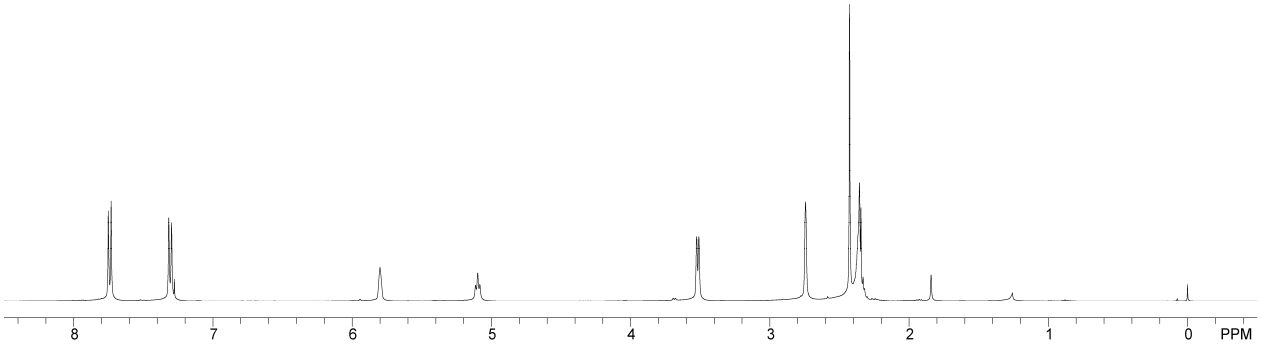

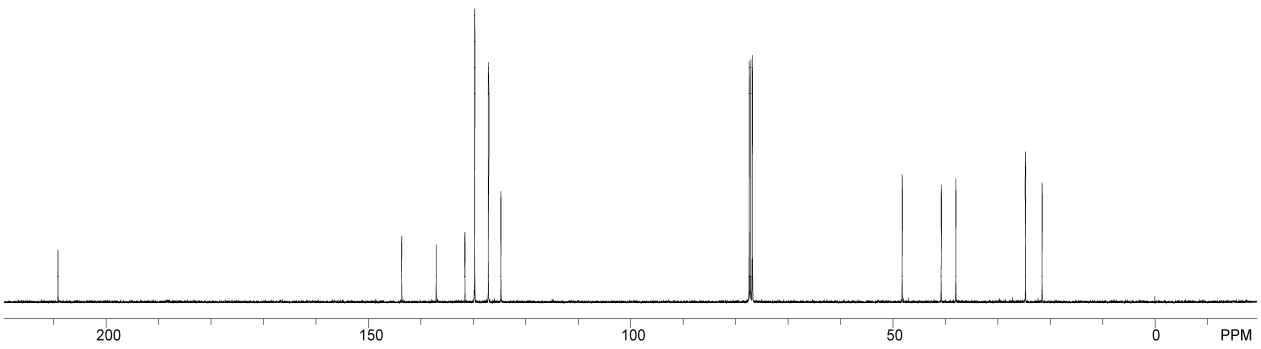

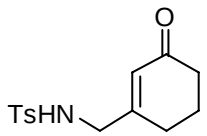

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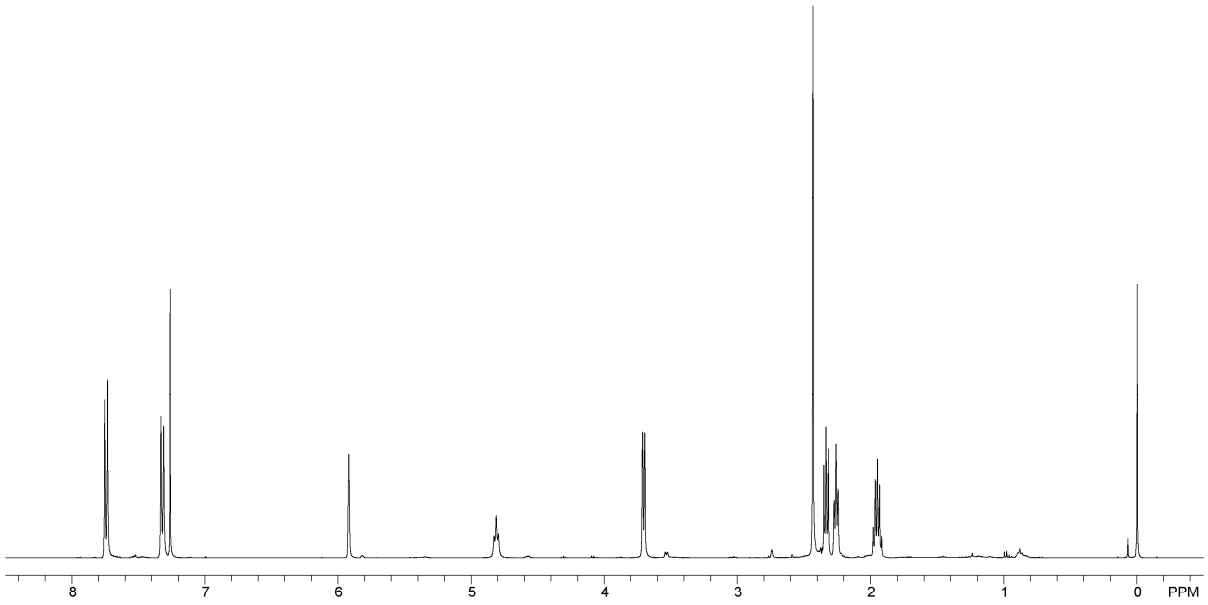

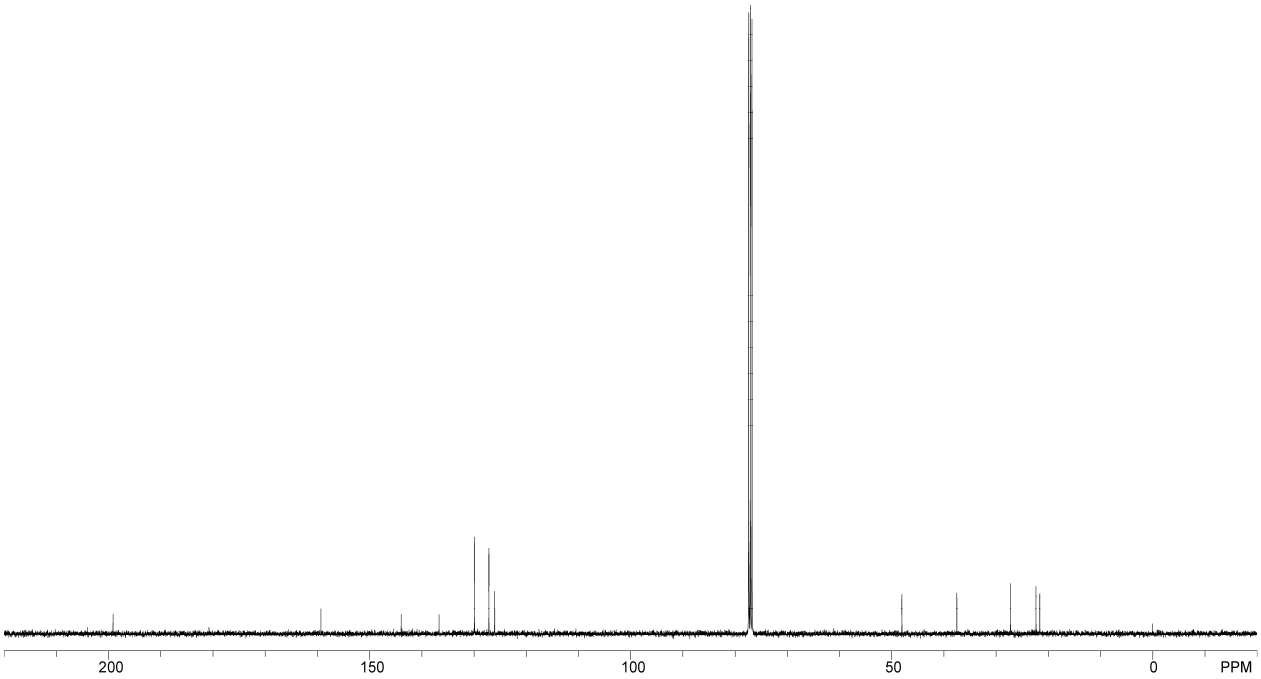

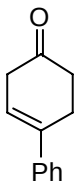

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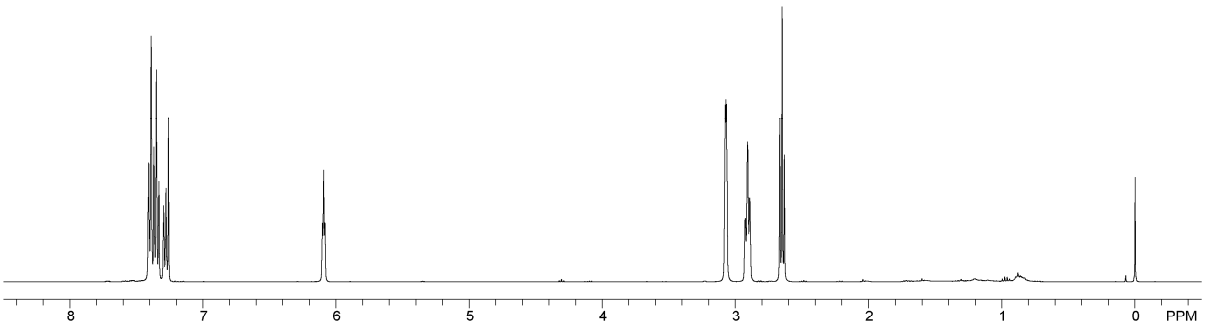

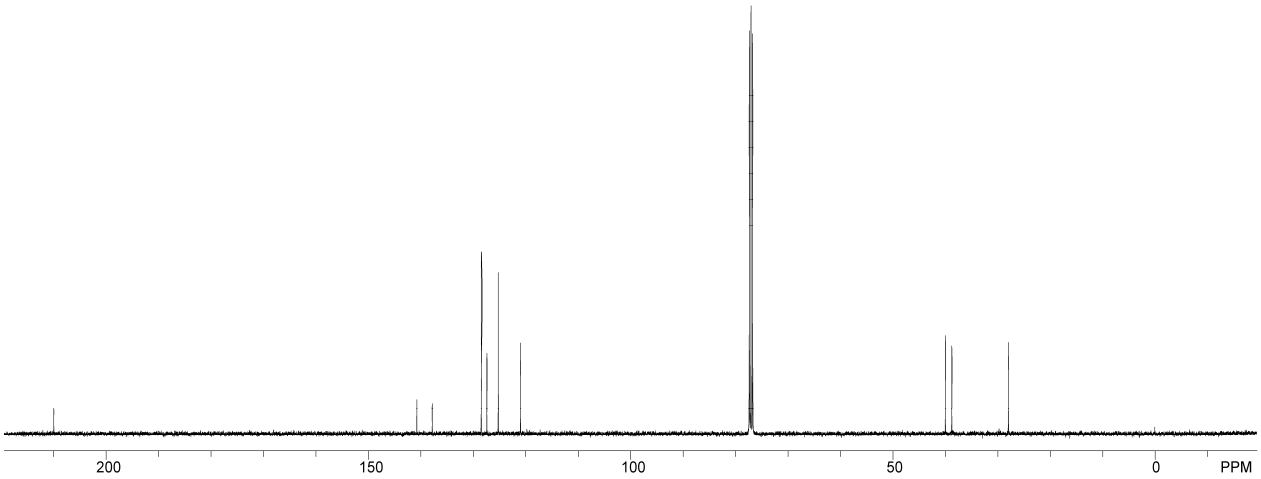

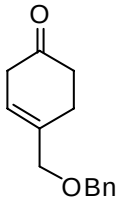

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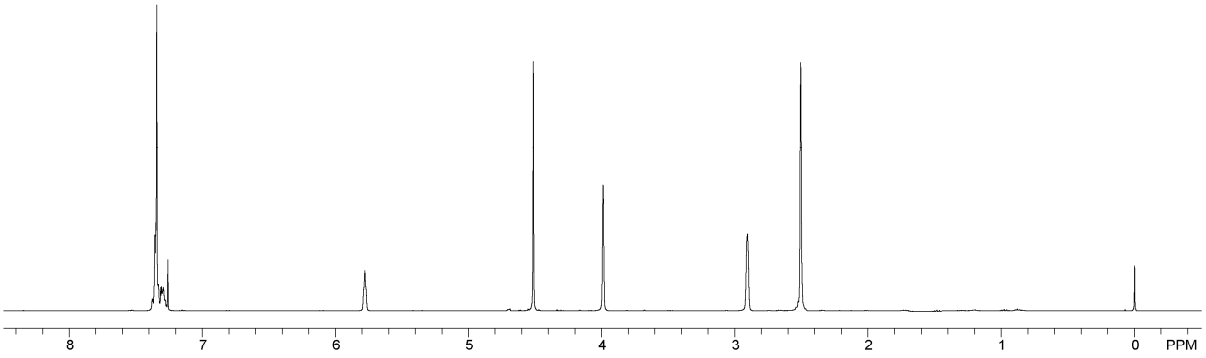

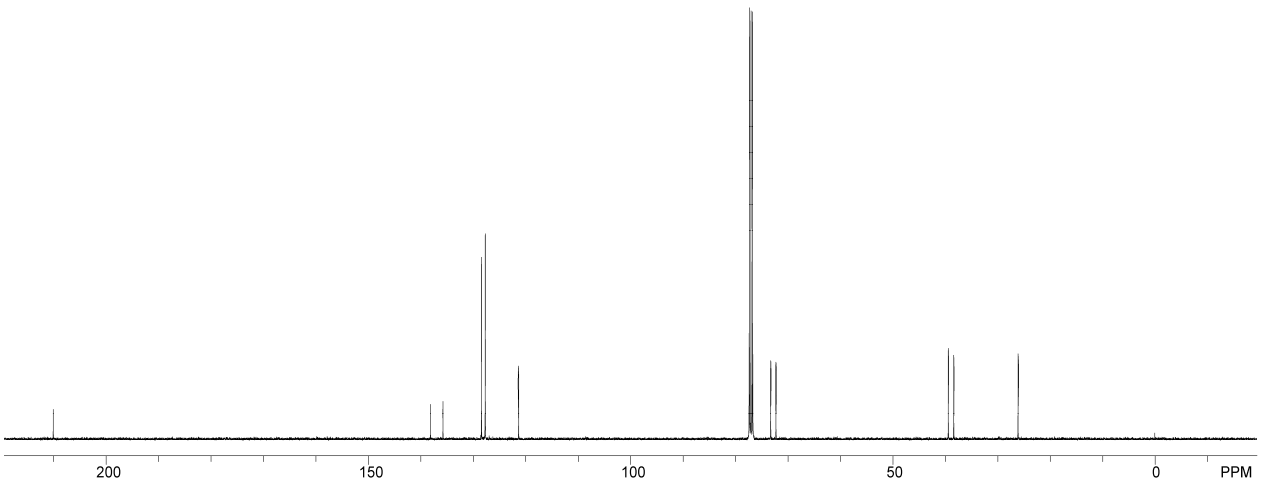

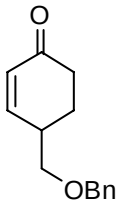

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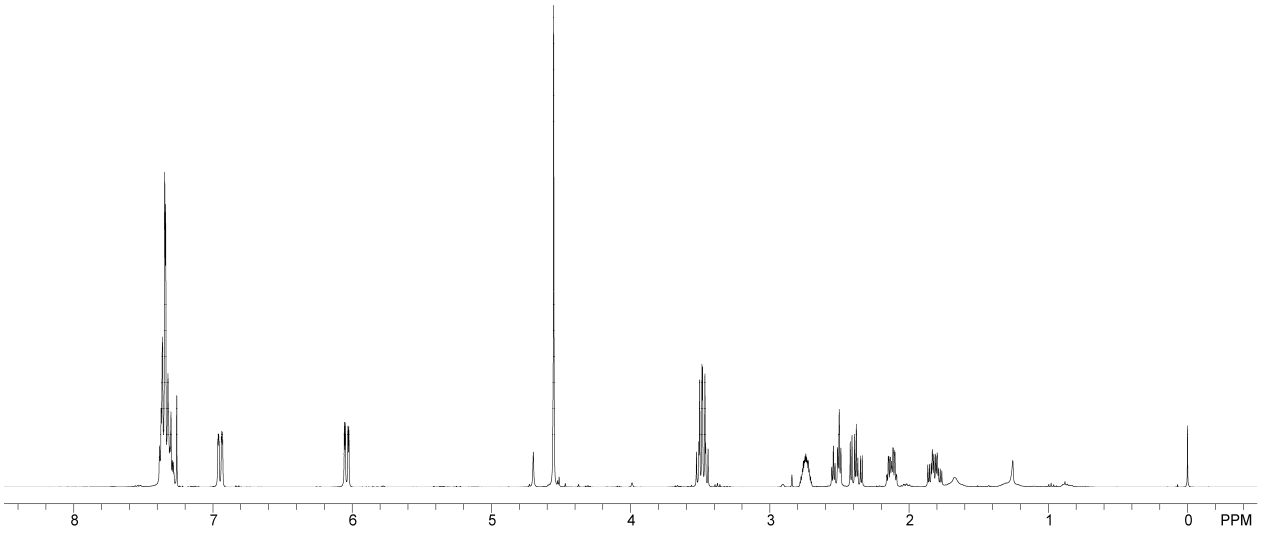

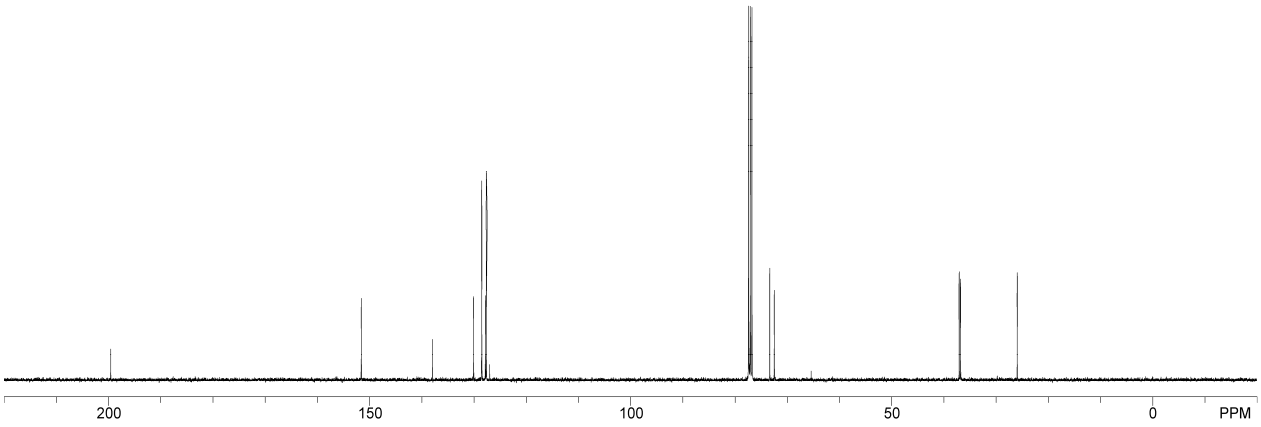

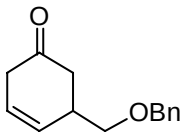

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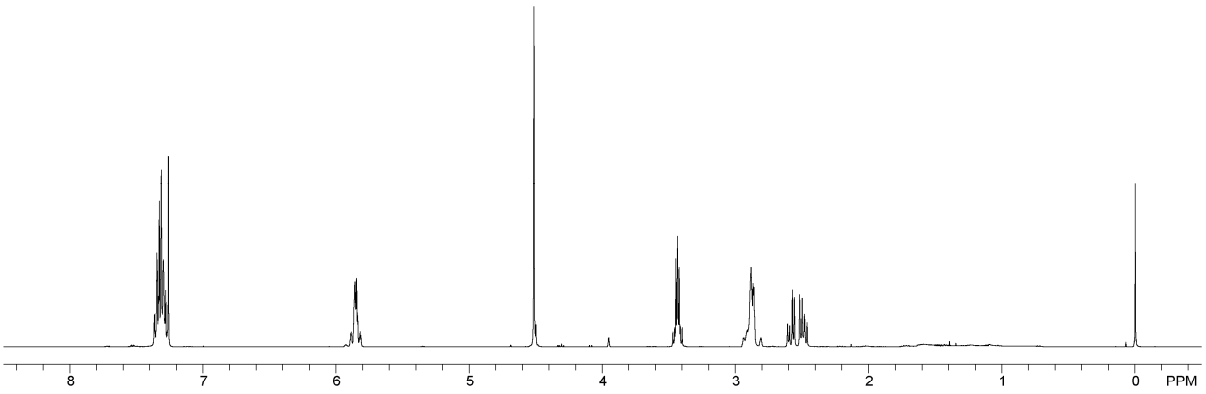

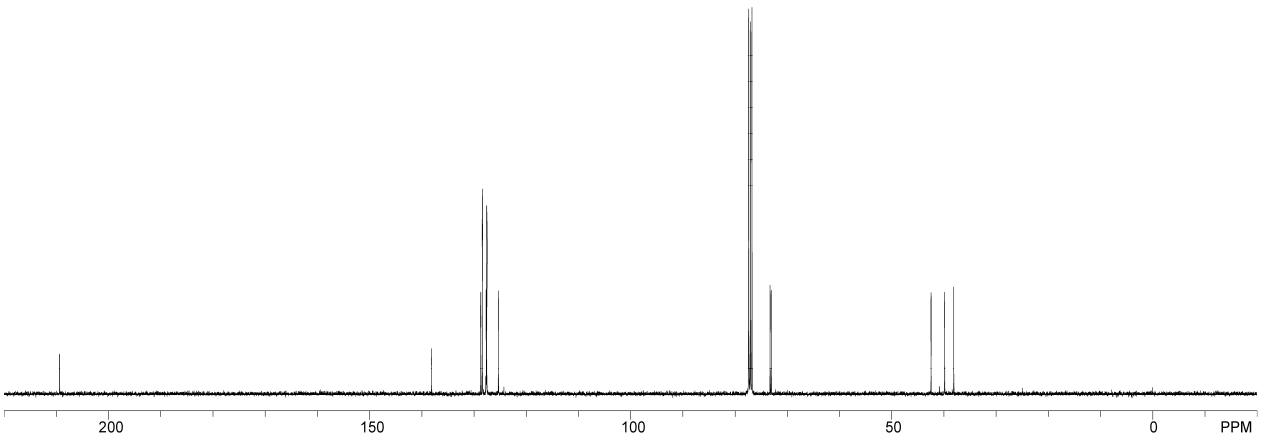

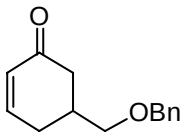

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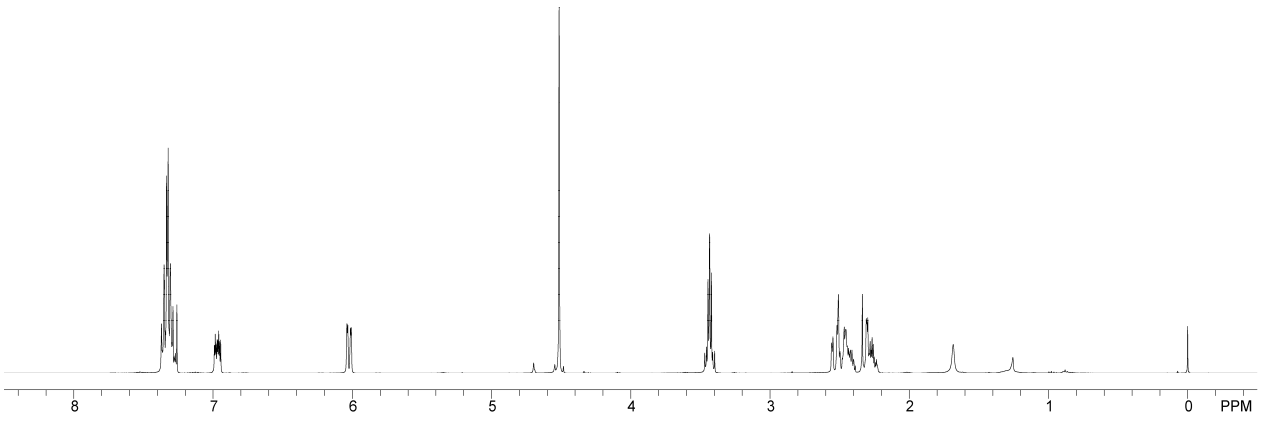

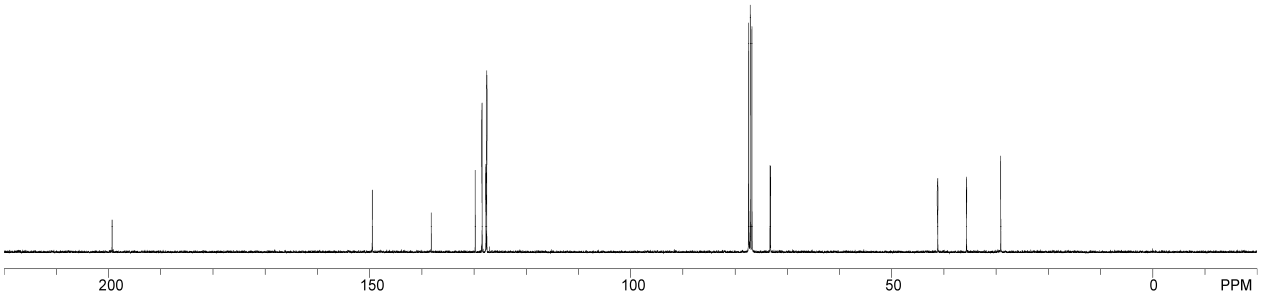

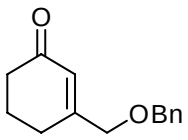

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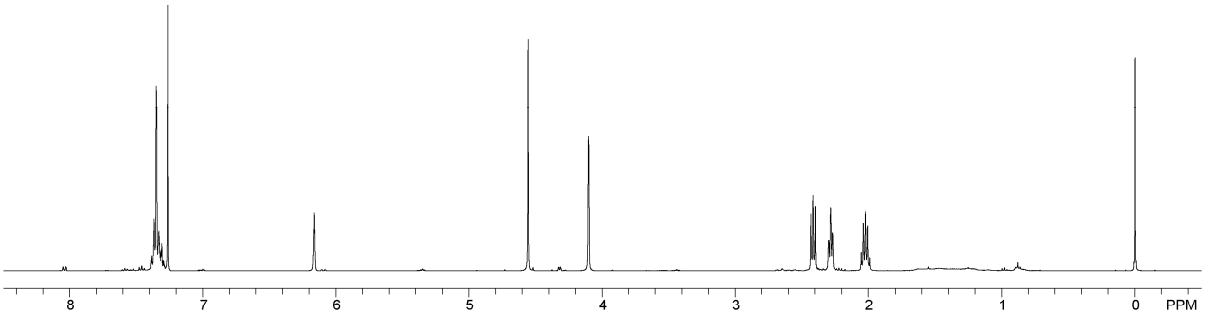

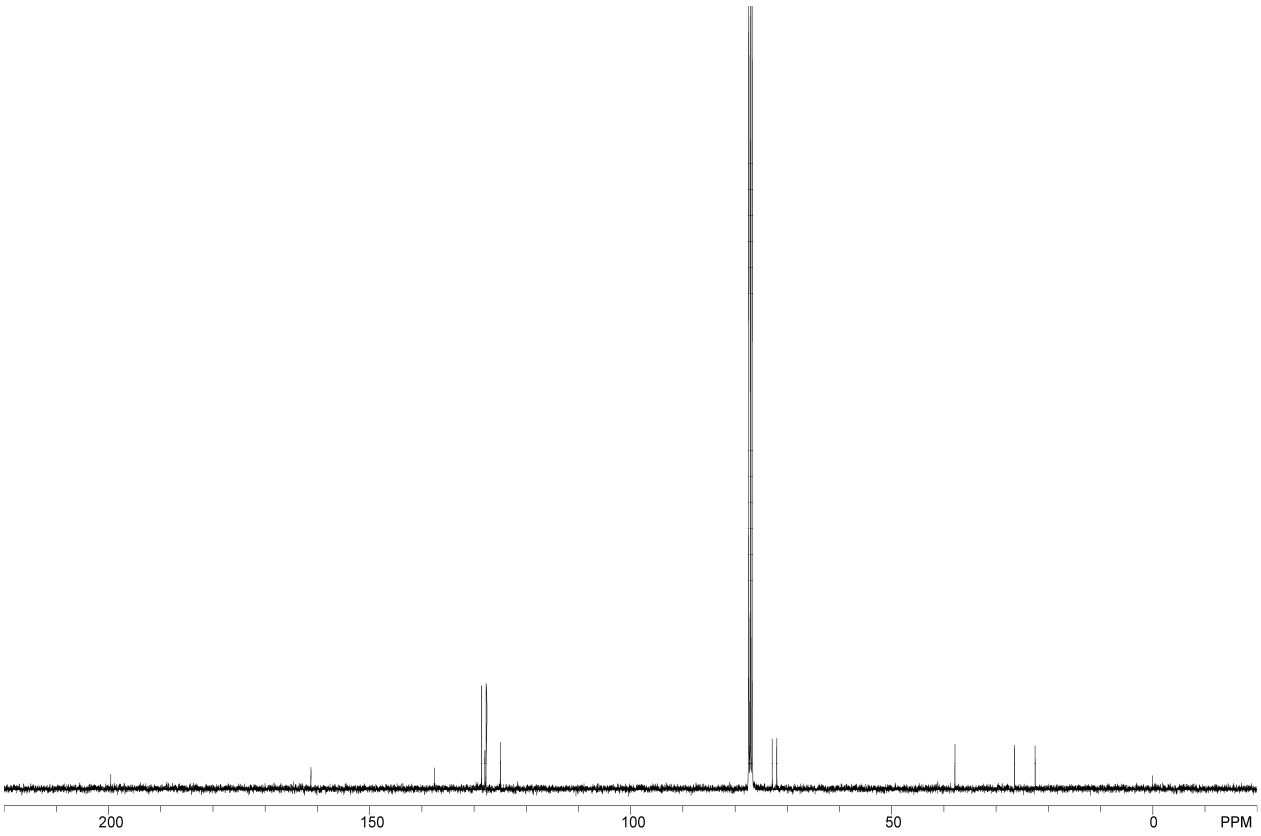

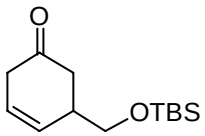

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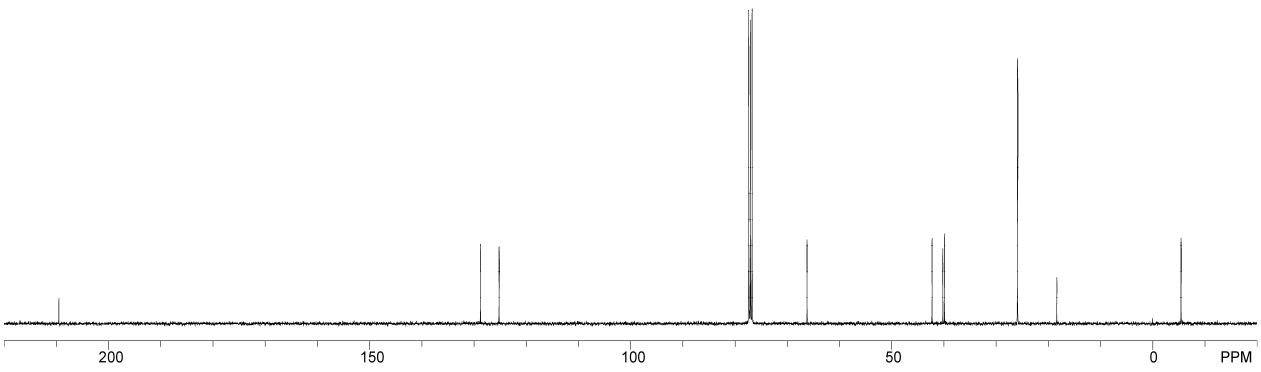

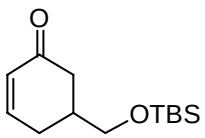

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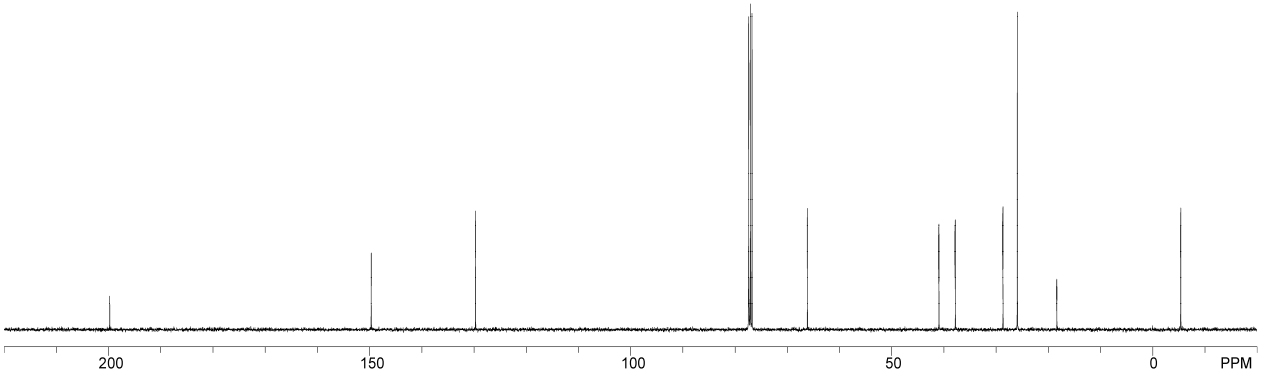

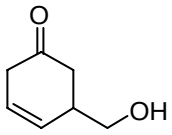

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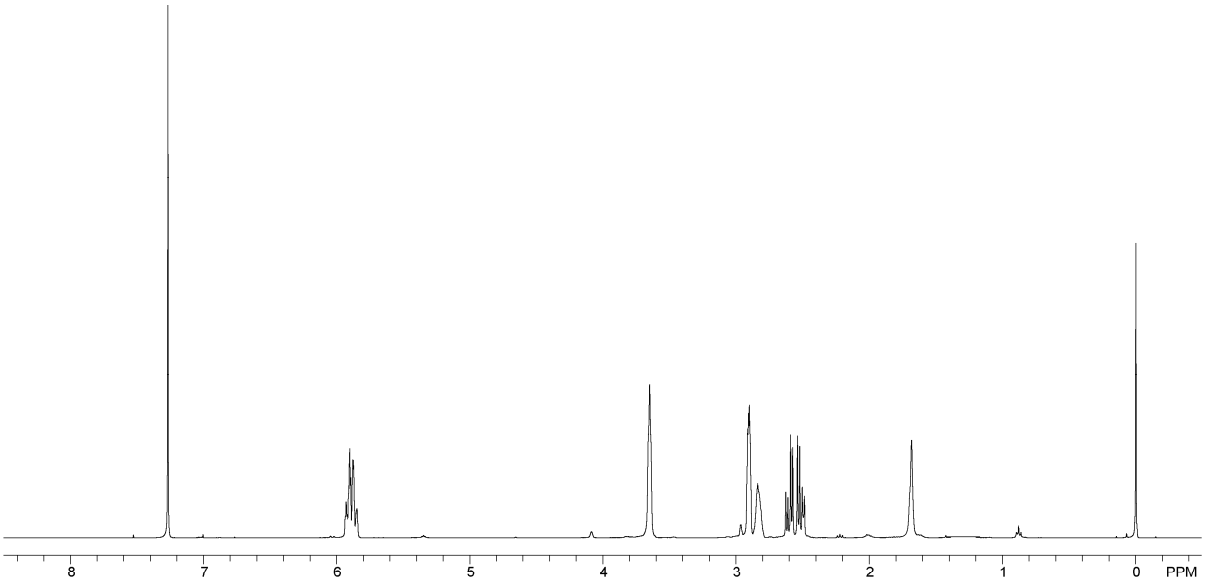

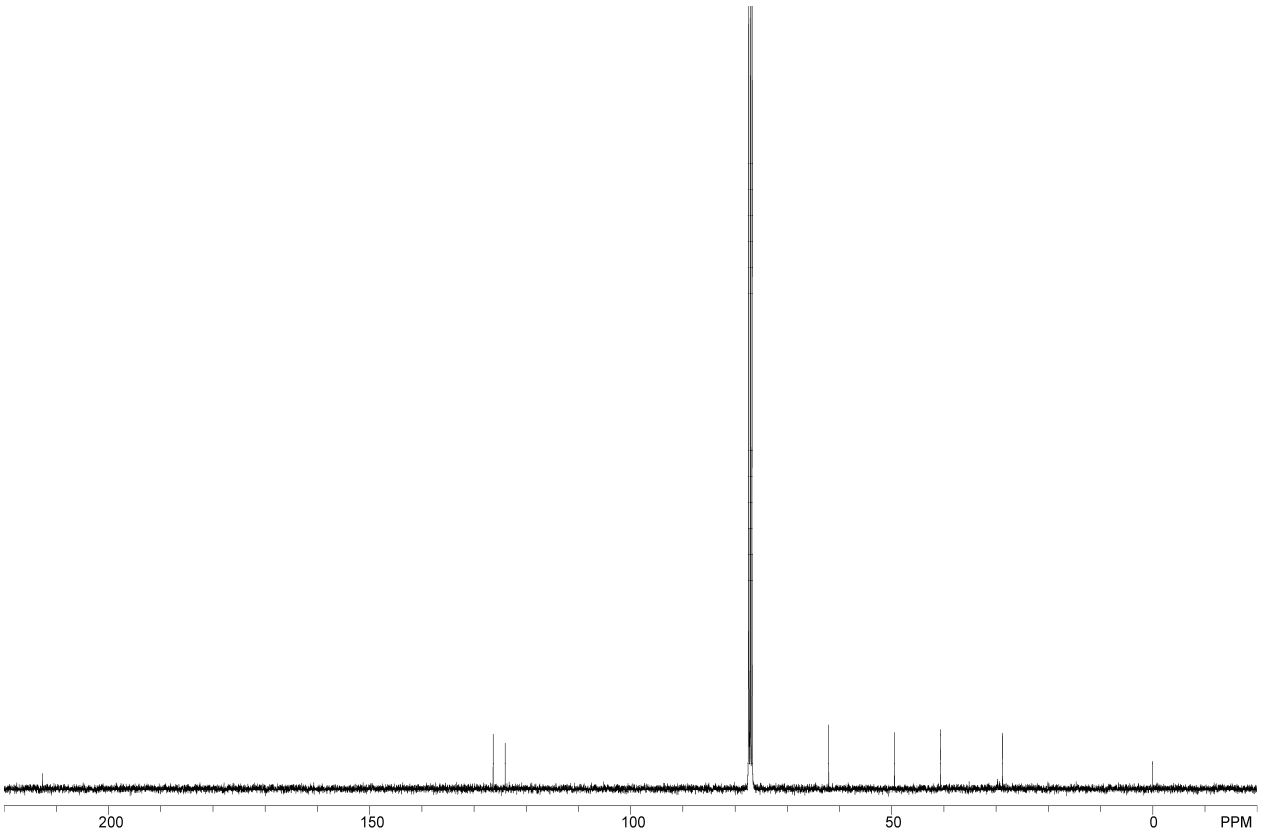

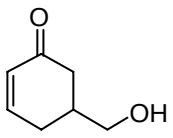

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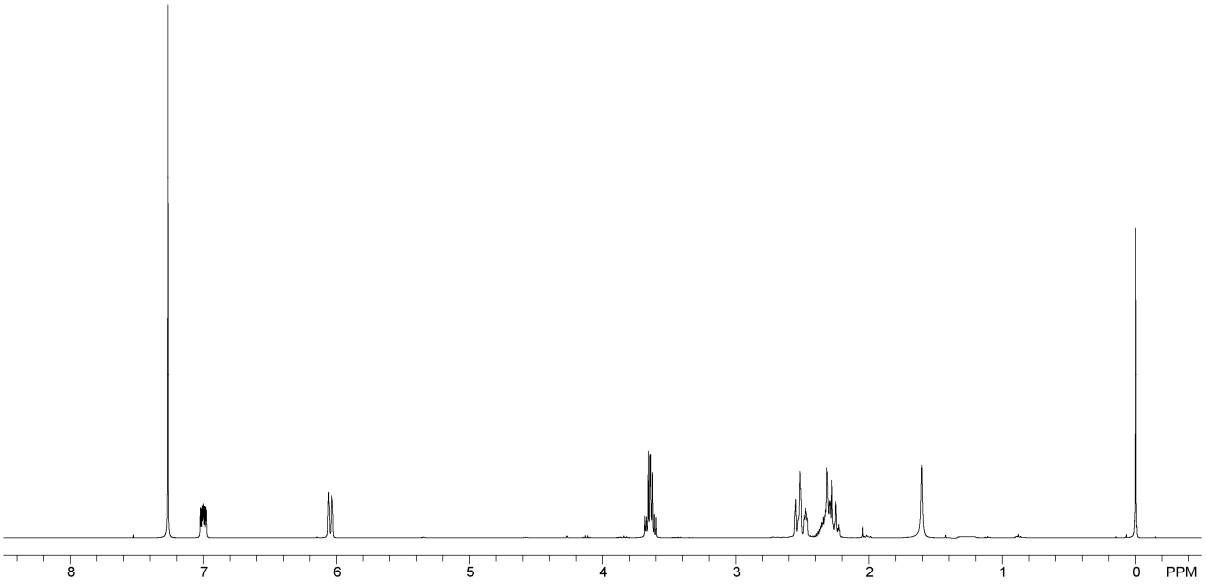

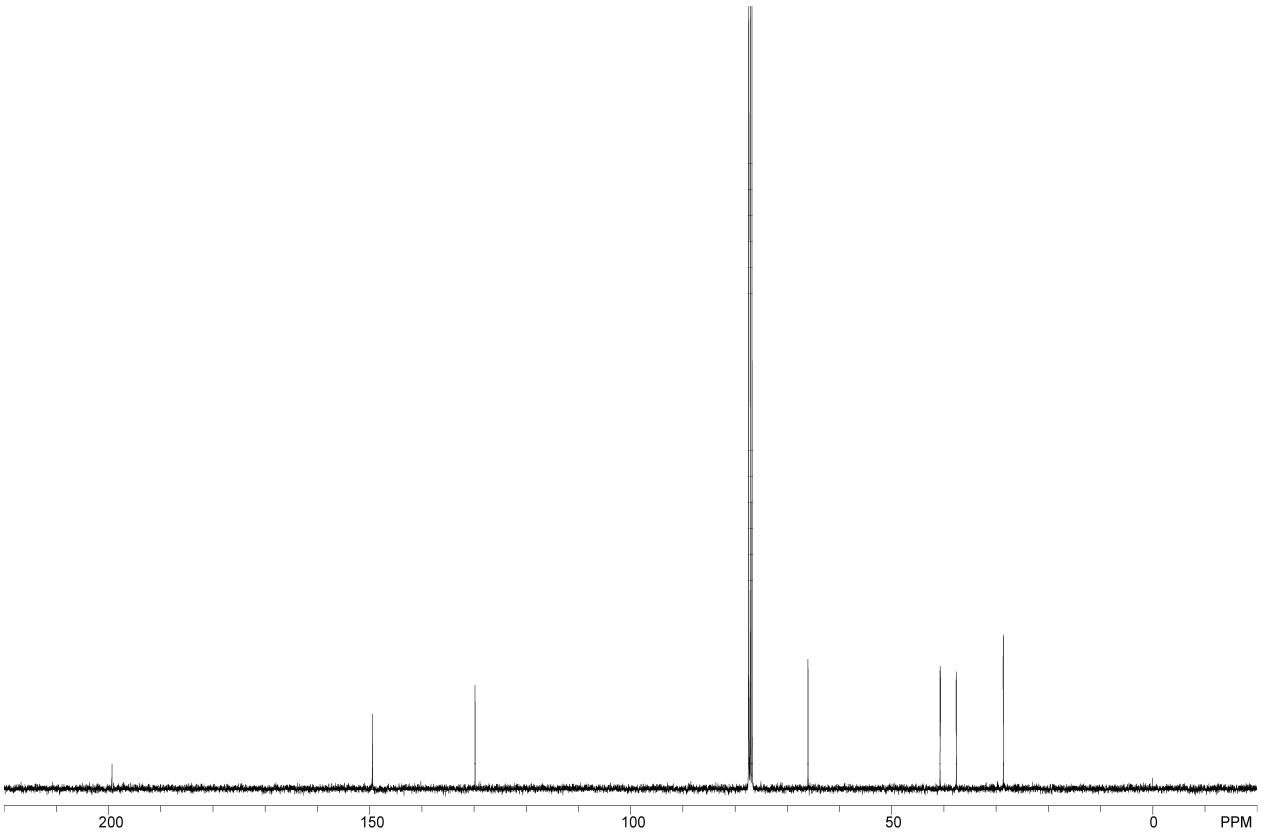

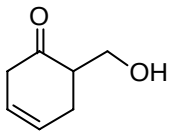

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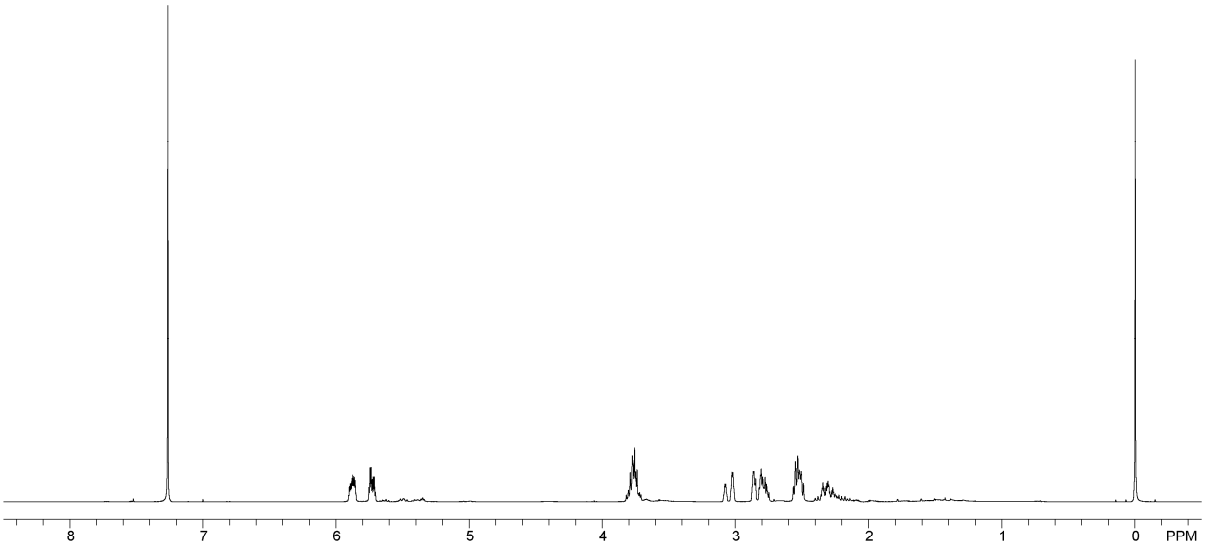

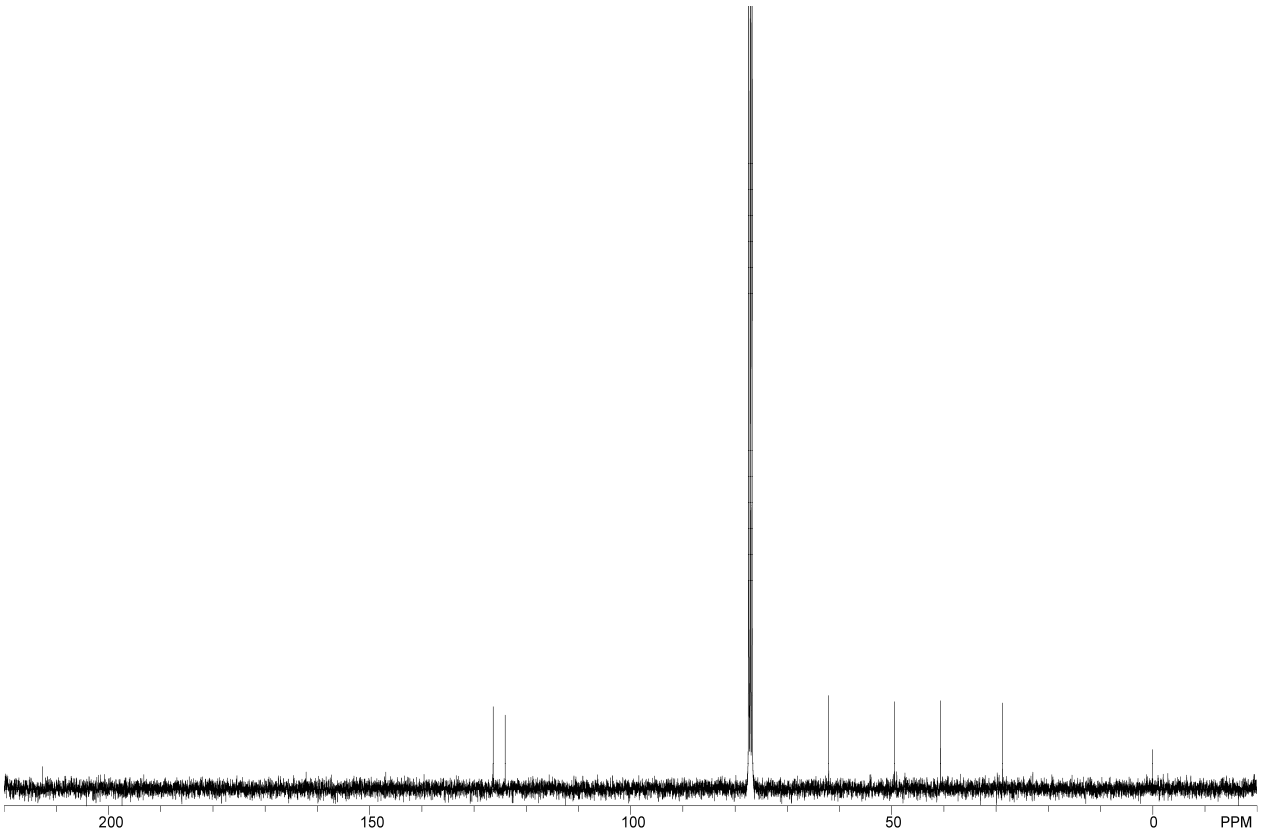

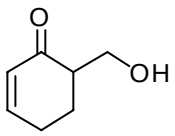

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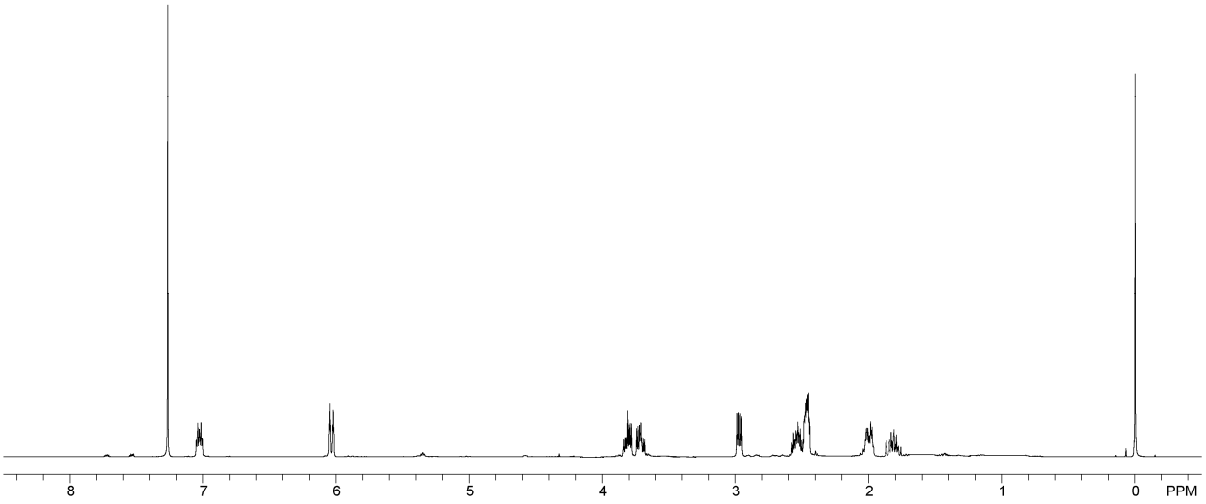

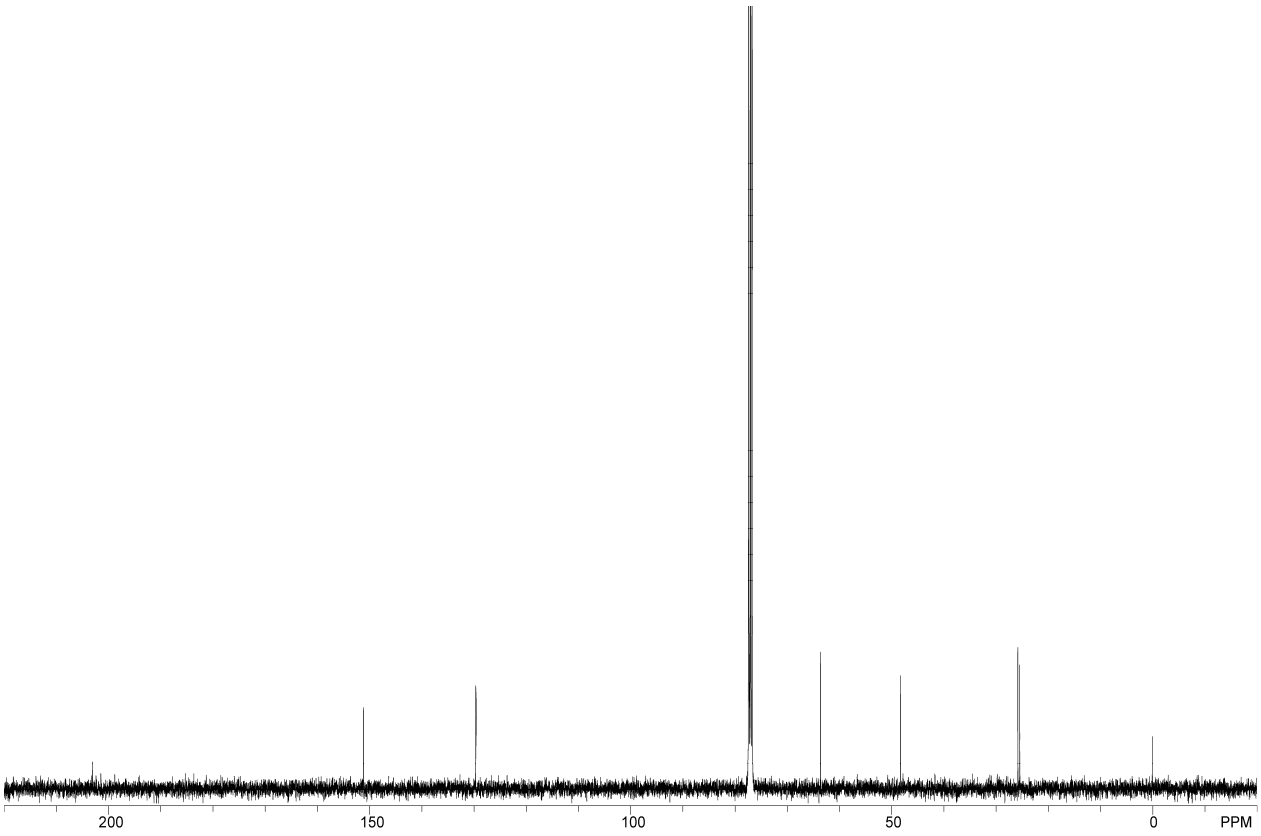

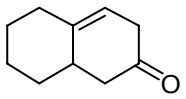

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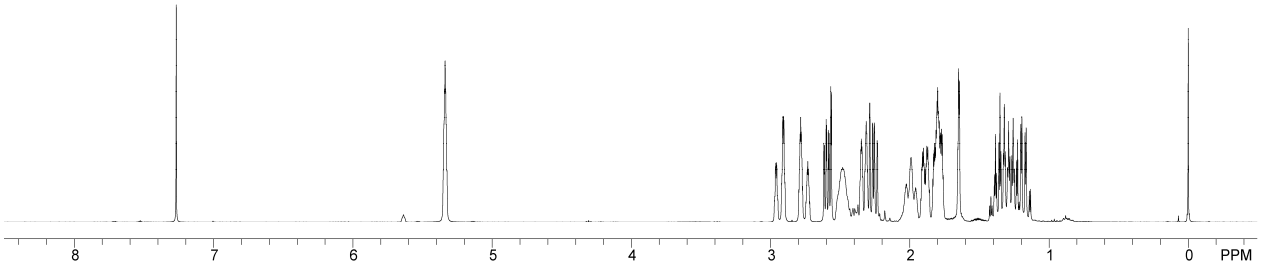

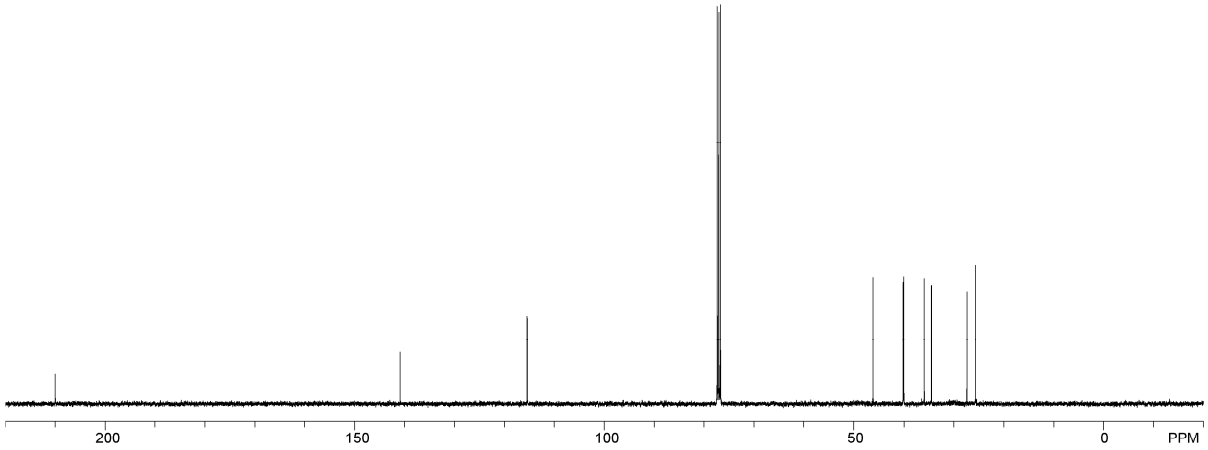

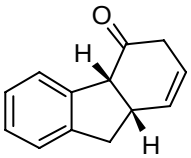

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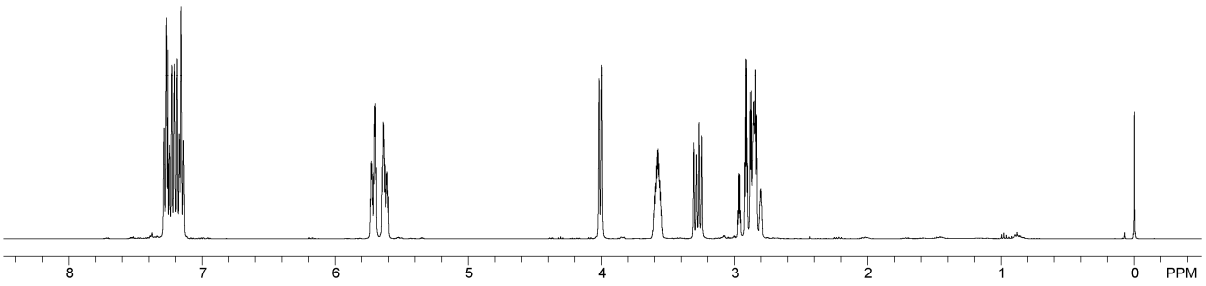

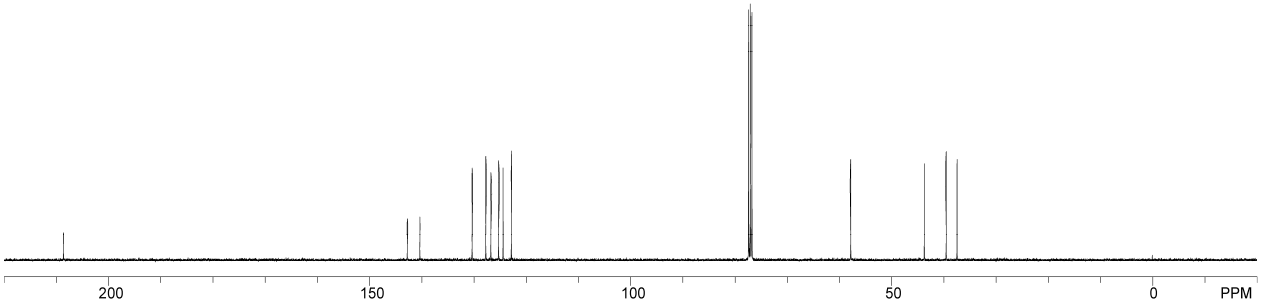

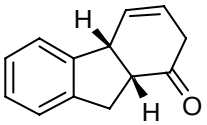

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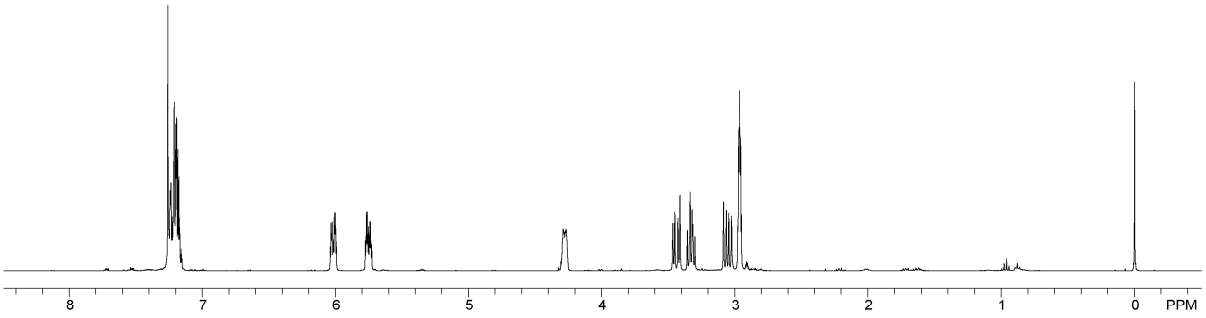

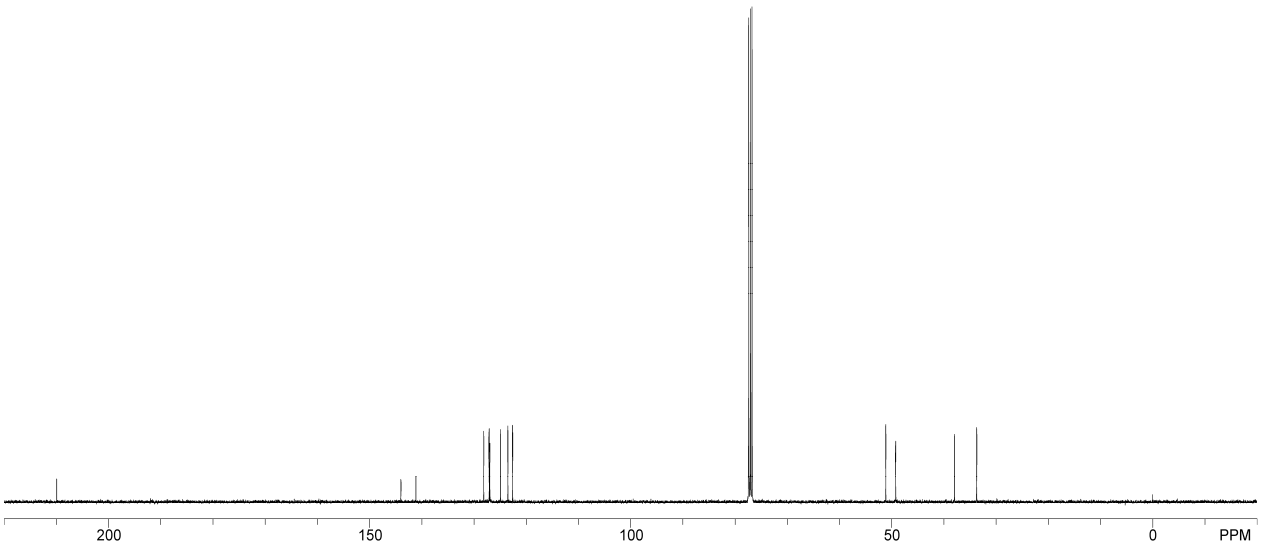

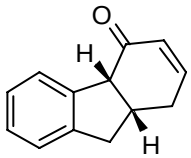

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