Catalytic Enantioselective Conjugate Allylation of Unsaturated Methylidene Ketones

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Supporting Information

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General Information

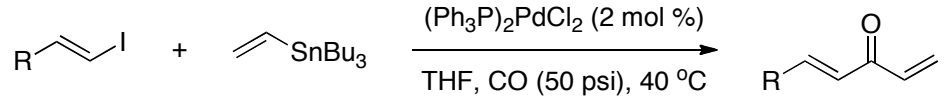
^{1}H NMR spectra were recorded on either a Varian Gemini-400 (400 MHz), a Varian Gemini-500 (500 MHz), a Varian Inova-500 (500 MHz), or a Varian Gemini-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-400 (100 MHz), a Varian Gemini-500 (125 MHz), or a Varian Gemini-600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), potassium permanganate ($KMnO_4$) in water, or phosphomolybdic acid (PMA) in ethanol. Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supelco β-Dex 120 column or a Supelco Chiraldex G-TA with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Berger Instruments Supercritical Chromatograph equipped with an Alcott auto sampler and a Knauer UV detector with methanol as the modifier. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 1120 compact chromatograph equipped with gradient pump and variable wavelength detector. Carbonylation was performed in an Argonaut Technologies Endeavor® Catalyst Screening System using CO supplied by Airgas, Inc.

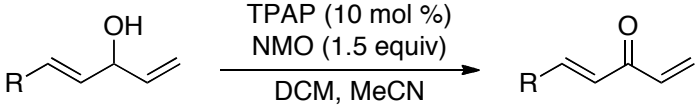
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene (PhMe) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine was distilled from calcium hydride. Neutral alumina (Al_2O_3, 32-63 μm) was purchased from Sorbent Technologies. Tris(dibenzylideneacetone) dipalladium(0) ($Pd_2(dba)_3$), *trans*-dichlorobis(triphenylphosphine) palladium(II) ($(Ph_3P)_2PdCl_2$), and tetrapropylammonium perruthenate (TPAP) were purchased from Strem Chemicals, Inc. Tributylvinylstannane was purchased from Alfa Aesar. Allylboronic acid pinacol ester [allylB(pin)] was generously donated by Frontier Scientific, Inc. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

Experimental Procedures

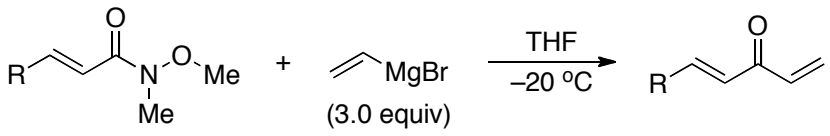
Preparation of Unsaturated Methylidene Ketones



Representative Procedure A:[1] An oven-dried glass reaction vial was placed into a well of the Argonaut Technologies Endeavor® and charged with *trans*-dichlorobis(triphenylphosphine) palladium(II) (61 mg, 0.09 mmol) and THF (4.3 mL). To the resulting solution was added (*E*)-(2-iodovinyl)cyclohexane (1.020 g, 4.33 mmol), and tributylvinylstannane (1.5 mL, 5.20 mmol). The Endeavor was sealed and purged with CO. Stirring was started at 400 rpm and the Endeavor was heated to 40 °C and charged with 50 psi CO for 4 hours. The Endeavor was vented and cooled to ambient temperature. The vial was removed. The reaction mixture was diluted with 9:1 pentane:diethyl ether and filtered through neutral alumina. The solution was concentrated *in vacuo*, then diluted with diethyl ether (40 mL) and saturated aqueous KF solution (20 mL). The mixture was allowed to stir for 3 hours, then the organics were collected, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford 518 mg (73%) of a light yellow oil. R_f = 0.24 (30:1 hexanes:ethyl acetate, stain in $KMnO_4$).



Representative Procedure B: Under N_2 atmosphere, a flame-dried round-bottomed flask with stir bar was charged with 4Å molecular sieves. A separate flame-dried flask was charged with (*E*)-1-phenylpenta-1,4-dien-3-ol (250 mg, 1.56 mmol), DCM (10 mL), and acetonitrile (1 mL). This solution was transferred to the first flask containing sieves by cannula. *N*-methylmorpholine-*N*-oxide (274 mg, 2.34 mmol) was added under N_2, and the resulting solution stirred 5 minutes. Tetrapropylammonium perruthenate (55 mg, 0.16 mmol) was then added and solution was allowed to stir overnight. The solution was filtered on silica and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford 145 mg (59%) of a yellow oil. R_f = 0.20 (30:1 hexanes:ethyl acetate, stain in $KMnO_4$).

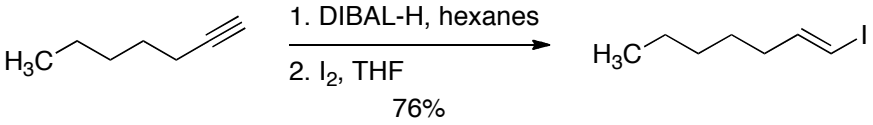


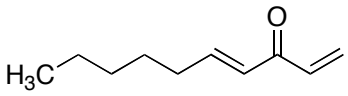
Representative Procedure C: To a flame-dried round-bottomed flask with stir bar was added (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-*N*-methoxy-*N*-methylacrylamide (200 mg, 0.85 mmol). The flask was flushed with N_2 and THF (8 mL) was added. The resulting solution was cooled to –20 °C

[1] Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417.

(ethylene glycol/dry ice) and vinylmagnesium bromide (2.55 mL, 1 M in THF) was added dropwise. The reaction was monitored by TLC and upon consumption of starting material at 1.5 hours, the reaction mixture was poured onto a pad of silica that had been slurry-packed in 1:1 hexane:ethyl acetate and flushed through the plug with 1:1 hexane:ethyl acetate in order to avoid the 1,4-addition of methoxymethylamine into the resulting vinyl ketone product. The solution was then concentrated *in vacuo*, and the crude reaction mixture was purified on silica gel (10:3:1 toluene:hexanes:ethyl acetate) to afford 58 mg (34%) of a yellow solid. R_f = 0.35 (10:3:1 toluene:hexanes:ethyl acetate, stain in $KMnO_4$).

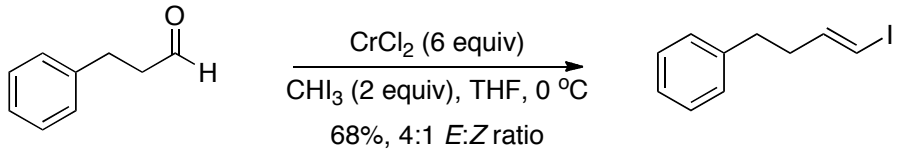
Preparation of (E)-deca-1,4-dien-3-one. From (*E*)-1-iodohept-1-ene, synthesized as shown below,[2] procedure A was followed.

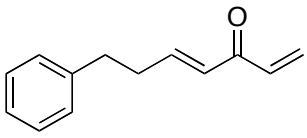




(E)-deca-1,4-dien-3-one **(Table 2, entry 1; Compound SI-1).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, *J* = 6.8 Hz), 1.29-1.33 (4H, m), 1.47-1.51 (2H, m), 2.25 (2H, app qd, *J* = 6.8 Hz, 1.6 Hz), 5.81 (1H, dd, *J* = 10.4 Hz, 1.6 Hz), 6.28 (1H, dd, *J* = 17.6 Hz, 1.6 Hz), 6.36 (1H, app dt, *J* = 15.6 Hz, 1.6 Hz), 6.61 (1H, dd, *J* = 17.6 Hz, 10.4 Hz), 6.95 (1H, app dt, *J* = 15.6 Hz, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.4, 27.7, 31.3, 32.6, 128.0, 128.0, 134.8, 148.9, 189.5; IR (neat): 2962 (s), 2932 (s), 2865 (m), 1662 (s), 1632 (s), 1611 (s), 1468 (w), 1396 (s), 1223 (s), 1105 (m), 978 (s) cm^{-1}. HRMS-(ESI+) for $C_{10}H_{17}O$ [M+H]: calculated: 153.1279, found: 153.1284. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a light yellow oil (285 mg, 57% yield). R_f = 0.20 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Preparation of (E)-7-phenylhepta-1,4-dien-3-one. From (*E*)-(4-iodobut-3-en-1-yl)benzene, synthesized as shown below,[3] procedure A was followed.





(E)-7-phenylhepta-1,4-dien-3-one **(Table 2, entry 2; Compound SI-2).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56-2.61 (2H, m), 2.81 (2H, t, *J* = 7.5 Hz), 5.81 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.26 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.38 (1H, app dt, *J* = 15.5 Hz, 1.5 Hz), 6.58 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 6.97 (1H, app dt, *J* = 15.5 Hz, 7.5 Hz), 7.18-7.23 (3H, m), 7.28-7.31 (2H, m); ^{13}C

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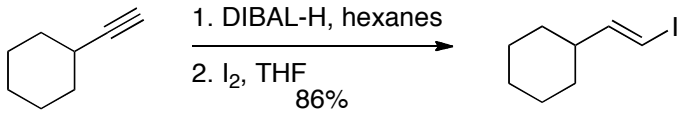
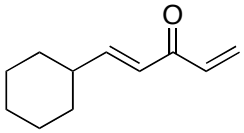
[2] Simpson, J. H.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

[3] Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.

NMR (125 MHz, $CDCl_3$): δ 34.4, 34.4, 126.2, 128.3, 128.5, 128.5, 128.6, 134.9, 140.7, 147.6, 189.7; IR (neat): 2927 (br, w), 1665 (s), 1631 (s), 1610 (s), 1454 (w), 1403 (s), 1216 (m), 984 (s), 746 (w), 699 (s) cm^{-1}. HRMS-(ESI+) for $C_{13}H_{15}O_2$ [M+H]: calculated: 187.1123, found: 187.1118. The crude reaction mixture was purified on silica gel (25:1 hexanes: ethyl acetate) to afford a clear, colorless oil (251 mg, 72% yield, *E* isomer only). R_f = 0.13 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

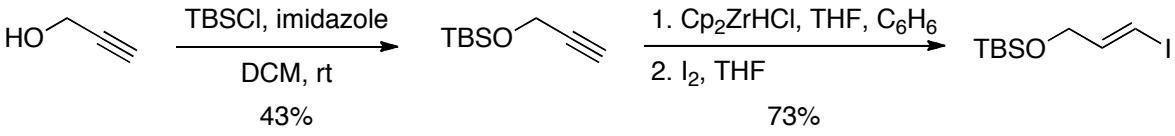
Preparation of (E)-1-cyclohexylpenta-1,4-dien-3-one. From (*E*)-(2-iodovinyl)cyclohexane, synthesized as shown below,[2] procedure A was followed.

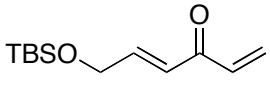




(*E*)-1-cyclohexylpenta-1,4-dien-3-one (Table 2, entry 3; Compound SI-3). ^1H NMR (400 MHz, $CDCl_3$): δ 1.12-1.37 (5H, m), 1.66-1.71 (1H, m), 1.73-1.80 (4H, m), 2.13-2.22 (1H, m), 5.80 (1H, dd, *J* = 10.8 Hz, 1.6 Hz), 6.25-6.33 (2H, m), 6.62 (1H, dd, *J* = 17.2 Hz, 10.8 Hz), 6.88 (1H, dd, *J* = 16.0 Hz, 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 25.9, 31.7, 40.9, 125.7, 128.2, 134.9, 153.9, 190.2; IR (neat): 2925 (s), 2852 (m), 1665 (s), 1630 (m), 1612 (m), 1449 (w), 1403 (m), 1213 (m), 985 (m), 963 (m) cm^{-1}. HRMS-(ESI+) for $C_{11}H_{17}O$ [M+H]: calculated: 165.1279, found: 165.1281. The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford a light yellow oil (518 mg, 73% yield). R_f = 0.24 (30:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Preparation of (E)-6-((tert-butyldimethylsilyl)oxy)hexa-1,4-dien-3-one. From (*E*)-*tert*-butyl((3-iodoallyl)oxy)dimethylsilane, synthesized as shown below,[4] procedure A was followed.





(*E*)-6-((*tert*-butyldimethylsilyl)oxy)hexa-1,4-dien-3-one (Table 2, entry 4; Compound SI-4). ^1H NMR (500 MHz, $CDCl_3$): δ 0.09 (6H, s), 0.93 (9H, s), 4.39 (2H, dd, *J* = 3.5 Hz, 2.5 Hz), 5.84 (1H, dd, *J* = 11.0 Hz, 1.5 Hz), 6.29 (1H, dd, *J* = 17.5 Hz, 1.5 Hz), 6.59 (1H, dd, *J* = 17.5 Hz, 11.0 Hz), 6.68 (1H, app dt, *J* = 15.5 Hz, 2.5 Hz), 6.97 (1H, app dt, *J* = 15.5 Hz, 3.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –5.4, 18.3, 25.8, 62.4, 125.3, 128.6, 135.4, 146.8, 189.6; IR (neat): 2930 (w), 2857 (w), 1669 (m), 1637 (w), 1255 (m), 1135 (s), 963 (m), 835 (s), 778 (m) cm^{-1}. HRMS-(ESI+) for $C_{12}H_{23}O_2Si$ [M+H]: calculated: 227.1467, found: 227.1465. The crude reaction mixture was purified on silica gel (35:1-25:1 hexanes:ethyl acetate) to afford a clear, colorless oil (265 mg, 73% yield). R_f = 0.10 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

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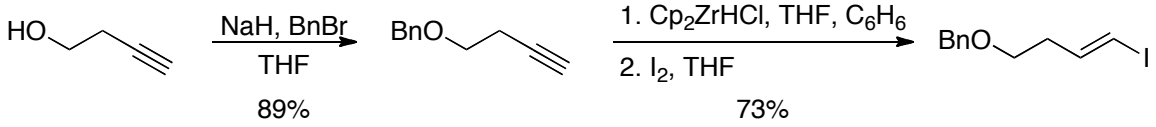
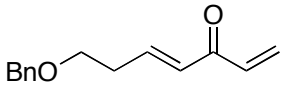
[4] Labinger, J. A.; Schwartz, J. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 333.

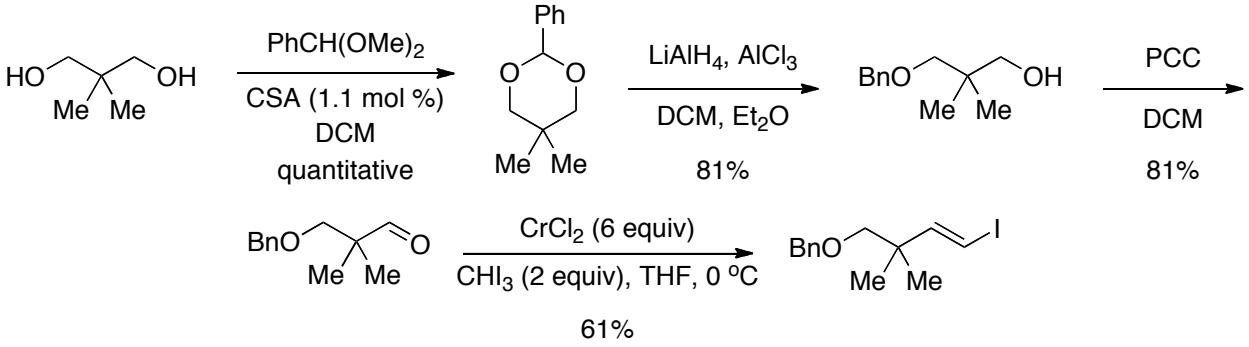
Preparation of (E)-7-(benzyloxy)hepta-1,4-dien-3-one. From (*E*)-(((4-iodobut-3-en-1-yl)oxy)methyl)benzene, synthesized as shown below,[4] procedure A was followed.

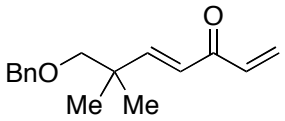




(*E*)-7-(benzyloxy)hepta-1,4-dien-3-one (Table 2, entry 5; Compound SI-5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.57 (2H, app qd, J = 6.5 Hz, 1.5 Hz), 3.62 (2H, t, J = 6.5 Hz), 4.53 (2H, s), 5.82 (1H, dd, J = 10.5 Hz, 1.5 Hz), 6.28 (1H, dd, J = 17.0 Hz, 1.5 Hz), 6.44 (1H, app dt, J = 16.0 Hz, 1.5 Hz), 6.60 (1H, dd, J = 17.0 Hz, 10.5 Hz), 6.96 (1H, app dt, J = 16.0 Hz, 6.5 Hz), 7.28-7.37 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.1, 68.3, 73.1, 127.7, 127.7, 128.4, 128.6, 129.5, 134.8, 138.0, 145.2, 189.6; IR (neat): 2858 (br, w), 1666 (s), 1632 (m), 1610 (m), 1403 (w), 1097 (s), 985 (m), 742 (m), 699 (m), 407 (m) cm^{-1}. HRMS-(ESI+) for $C_{14}H_{17}O_2$ [M+H]: calculated: 217.1229, found: 217.1224. The crude reaction mixture was purified on silica gel (25:1-15:1 hexanes:ethyl acetate) to afford a light yellow oil (216 mg, 56% yield). R_f = 0.12 (15:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Preparation of (E)-7-(benzyloxy)-6,6-dimethylhepta-1,4-dien-3-one. From (*E*)-(((4-iodo-2,2-dimethylbut-3-en-1-yl)oxy)methyl)benzene, synthesized as shown below,[5] procedure A was followed.





(*E*)-7-(benzyloxy)-6,6-dimethylhepta-1,4-dien-3-one (Table 2, entry 6; Compound SI-6). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (6H, s), 3.29 (2H, s), 4.52 (2H, s), 5.81 (1H, dd, J = 10.5 Hz, 1.5 Hz), 6.28 (1H, dd, J = 17.5 Hz, 1.5 Hz), 6.33 (1H, d, J = 16.0 Hz), 6.63 (1H, dd, J = 17.5 Hz, 10.5 Hz), 6.97 (1H, d, J = 16.0 Hz), 7.28-7.36 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9, 38.5, 73.3, 78.2, 125.4, 127.4, 127.5, 128.3, 128.4, 134.9, 138.4, 155.3, 190.2; IR (neat): 2963 (w), 2867 (br, w), 1665 (s), 1630 (m), 1612 (m), 1404 (m), 1212 (w), 1104 (s), 987 (m), 738 (m), 698 (m) cm^{-1}. HRMS-(ESI+) for $C_{16}H_{21}O_2$ [M+H]: calculated: 245.1542, found: 245.1534. The crude reaction mixture was purified on silica gel (35:1-30:1 hexanes:ethyl acetate) to afford a clear, colorless oil (203 mg, 71% yield). R_f = 0.14 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

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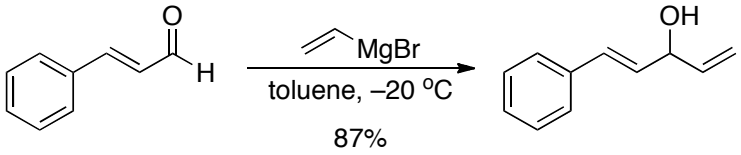
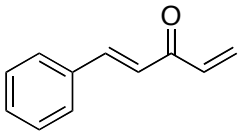
[5] Burks, H. E.; Kliman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.

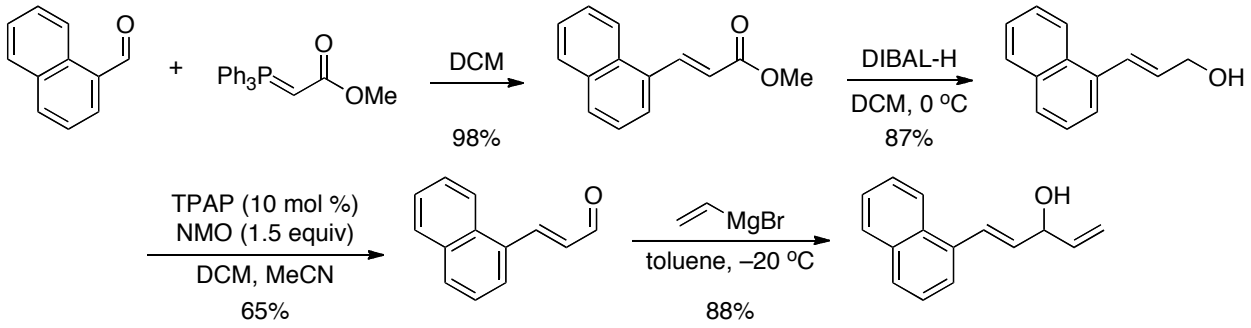
Preparation of (E)-1-phenylpenta-1,4-dien-3-one. From (*E*)-1-phenylpenta-1,4-dien-3-ol, synthesized as shown below, procedure B was followed.

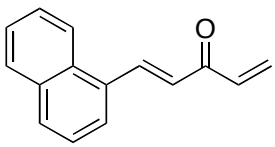




(*E*)-1-phenylpenta-1,4-dien-3-one (Table 2, entry 7; Compound SI-7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.39 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.72 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 7.02 (1H, d, *J* = 16.0 Hz), 7.40-7.42 (3H, m), 7.58-7.60 (2H, m), 7.68 (1H, d, *J* = 16.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.1, 128.4, 128.6, 128.9, 130.6, 134.6, 135.4, 143.9, 189.5; IR (neat): 1656 (s), 1622 (s), 1594 (s), 1450 (w), 1402 (m), 1200 (m), 1104 (m), 988 (m), 688 (w) cm^{-1}. HRMS-(ESI+) for $C_{11}H_{11}O$ [M+H]: calculated: 159.0810, found: 159.0813. The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford a yellow oil (145 mg, 59% yield). R_f = 0.20 (30:1 hexanes:ethyl acetate, stain in $KMnO_4$).

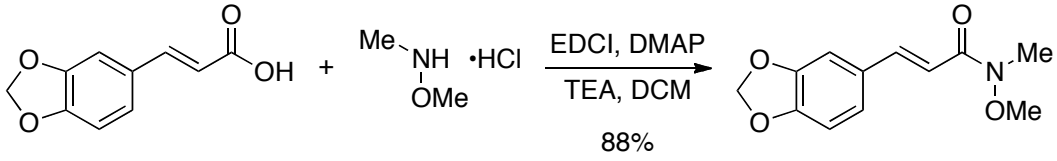
Preparation of (E)-1-(naphthalen-1-yl)penta-1,4-dien-3-one. From (*E*)-1-(naphthalen-1-yl)penta-1,4-dien-3-ol, synthesized as shown below, procedure B was followed.

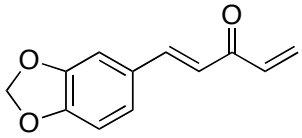




(*E*)-1-(naphthalen-1-yl)penta-1,4-dien-3-one (Table 2, entry 8; Compound SI-8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (1H, dd, *J* = 10.8 Hz, 1.2 Hz), 6.44 (1H, dd, *J* = 17.6 Hz, 1.2 Hz), 6.77 (1H, dd, *J* = 17.6 Hz, 10.8 Hz), 7.12 (1H, d, *J* = 16.0 Hz), 7.49-7.62 (3H, m), 7.84 (1H, d, *J* = 7.2 Hz), 7.88-7.93 (2H, m), 8.23 (1H, d, *J* = 8.0 Hz), 8.55 (1H, dd, *J* = 16.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.6, 125.3, 125.7, 126.5, 126.7, 127.2, 129.02, 129.03, 131.1, 131.9, 132.3, 133.9, 136.0, 141.1, 189.6; IR (neat): 3049 (w), 1655 (m), 1617 (m), 1592 (s), 1509 (w), 1402 (m), 1347 (m), 1202 (m), 1112 (m), 982 (m), 799 (m), 777 (s) cm^{-1}. HRMS-(ESI+) for $C_{15}H_{13}O$ [M+H]: calculated: 209.0966, found: 209.0970. The crude reaction mixture was purified on silica gel (20:1 hexanes:ethyl acetate) to afford a yellow oil (164 mg, 50% yield). R_f = 0.27 (20:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Preparation of (E)-1-(benzo[d][1,3]dioxol-5-yl)penta-1,4-dien-3-one. From (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-*N*-methoxy-*N*-methylacrylamide, synthesized as shown below, procedure C was followed.





(*E*)-1-(benzo[*d*][1,3]dioxol-5-yl)penta-1,4-dien-3-one (Table 2, entry 9; Compound SI-9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.86 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.02 (2H, s), 6.36 (1H, dd, *J* = 17.5 Hz, 1.5 Hz), 6.69 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 6.84 (1H, s), 6.84 (1H, d, *J* = 16.0 Hz), 7.06-7.10 (2H, m), 7.60 (1H, d, *J* = 16.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.6, 106.6, 108.7, 122.3, 125.1, 128.2, 129.1, 135.6, 143.8, 148.4, 150.0, 189.3; IR (neat): 1651 (m), 1585 (s), 1490 (s), 1448 (s), 1404 (m), 1359 (w), 1249 (s), 1206 (s), 1095 (m), 1037 (s), 985 (m), 930 (m), 854 (w), 813 (m) cm^{-1}. HRMS-(ESI+) for $C_{12}H_{11}O_3$ [M+H]: calculated: 203.0708, found: 203.0710. The crude reaction mixture was purified on silica gel (10:3:1 toluene:hexanes:ethyl acetate) to afford 58 mg (34%) of a yellow solid. R_f = 0.35 (10:3:1 toluene:hexanes:ethyl acetate, stain in $KMnO_4$).

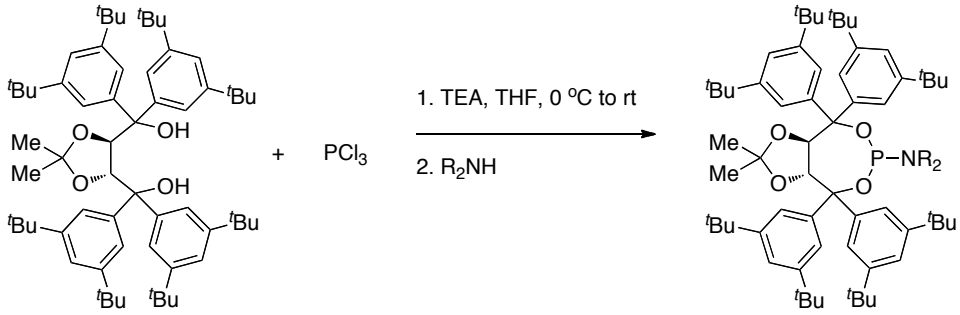
Preparation of Phosphonite Ligands

Phosphonite ligand **L1** was prepared according to literature procedure.[6]

Preparation of Phosphoramidite Ligands

Phosphoramidite ligand **L2** was prepared according to literature procedure.[7]

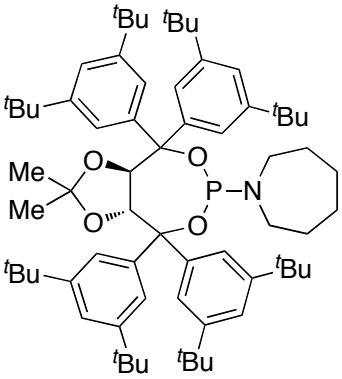
Phosphoramidite ligands **L3**, **L4,** (***R,R,S***)**-L6**, and (***S,S,S***)**-L6** were prepared according to representative procedure A for phosphoramidite synthesis, as follows. Characterization of **L3** is in accordance with the literature.[6]



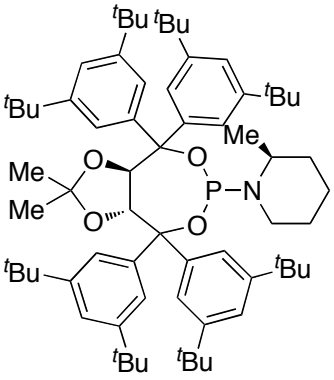
[6] Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.

[7] Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. *Org. Lett.*, **2005**, *7*, 5505.

Representative Procedure A: To a flame-dried 25 mL round-bottomed flask equipped with magnetic stir bar was added 3,5-di-*tert*-butylphenylTADDOL (400 mg, 0.44 mmol). The flask was flushed with N_2, then THF (6 mL) was added. The solution was cooled to 0 °C, then triethylamine (0.2 mL, 1.49 mmol), and phosphorus trichloride (0.05 mL, 0.52 mmol) were added, dropwise. The solution was warmed to rt for 45 min, then was cooled to 0 °C again, and (*S*)-(+)-2-methylpiperidine (0.1 mL, 0.87 mmol) was added. The solution was allowed to warm to rt and stir overnight. Diethyl ether (10 mL) was then added to the solution, and the triethylamine hydrochloride salts precipitated out of solution. The reaction mixture was filtered over celite and washed with diethyl ether (3 x 10 mL), then the filtrate was concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (35:1 hexane:ethyl acetate) to afford a white solid (414 mg, 91% yield). R_f = 0.30 (30:1 hexanes: ethyl acetate, stain in PMA).

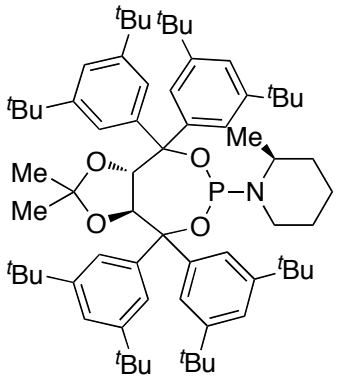


[3,5-(*tert*-Butyl)$_2$-TADDOL]PNC$_6$H$_{12}$ (Table 1, entry 7, L4; Compound SI-10). Representative procedure A was followed, employing azepane as amine nucleophile. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.05 (3H, s), 1.24 (18H, s), 1.26 (18H, s), 1.28 (18H, s), 1.29 (18H, s), 1.49 (3H, s), 1.64-1.71 (4H, m), 1.72-1.84 (4H, m), 3.38-3.51 (4H, m), 4.66 (1H, d, J = 9.0 Hz), 5.30 (1H, dd, J = 9.0 Hz, 2.5 Hz), 7.12 (2H, d, J = 1.5 Hz), 7.20 (1H, t, J = 2.0 Hz), 7.21-7.23 (2H, m), 7.24 (1H, t, J = 2.0 Hz), 7.39 (2H, br s), 7.63 (2H, d, J = 1.5 Hz), 7.65 (2H, d, J = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 27.1, 28.0, 31.4, 31.6, 31.6 (d, $^3J_{CP}$ = 4.0 Hz), 34.8, 34.9, 35.0, 46.8 (d, $^2J_{CP}$ = 21.0 Hz), 80.7, 80.8, 82.4, 82.5, 83.6, 83.8, 83.89, 83.92, 109.6, 119.9, 120.0, 120.1, 120.6, 121.5, 122.0, 123.7, 141.2, 142.2, 146.3, 146.6, 148.6, 148.7, 149.1, 149.5. ^{31}P NMR (202 MHz, $CDCl_3$): δ 141.5. IR (neat): 3084 (w), 2958 (s), 2907 (s), 2860 (m), 1599 (m), 1480 (m), 1451 (m), 1396 (m), 1362 (m), 1244 (m), 1198 (m) cm^{-1}. LRMS-(ESI+) for $C_{69}H_{104}NO_4P$ [M+H]: calculated: 1042.8, found: 1043.3. $[\alpha]^{20}_D$ = -37 (c = 2.0, $CHCl_3$). The crude reaction mixture was purified on silica gel (55:1 hexanes:ethyl acetate) to afford 179 mg (88%) of a white solid. R_f = 0.38 (55:1 hexanes:ethyl acetate, stain in PMA).



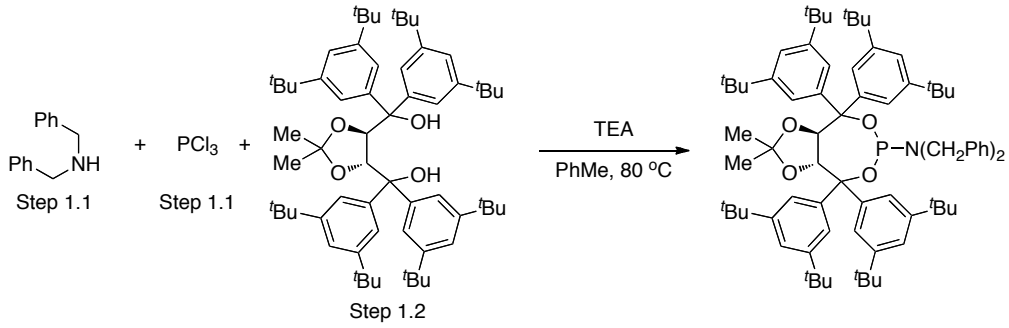
[3,5-(*tert*-Bu)$_2$-TADDOL]PNC$_6$H$_{12}$ (Scheme 2, (*R*,*R*,*S*)-L6; Compound SI-11). Representative procedure A was followed, employing (*S*)-(+)-2-methylpiperidine as amine nucleophile. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.06 (3H, s), 1.25 (18H, s), 1.27 (18H, s), 1.30 (18H, s), 1.31 (18H, s), 1.51 (4H, br s), 1.58-1.74 (3H, m), 1.74-1.87 (2H, m), 3.34-3.46 (1H, m), 3.47-3.59 (1H, m), 4.03-4.17 (1H, m), 4.65 (1H, d, J = 8.5 Hz), 5.28 (1H, dd, J = 8.5 Hz, 2.5 Hz), 7.15 (2H, d, J = 2.0 Hz), 7.19-7.24 (3H, m), 7.26 (1H, t, J = 1.5 Hz), 7.36-7.48 (2H, m), 7.65 (2H, d, J = 1.5 Hz), 7.67 (2H, d, J = 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.7 (d, $^2J_{CP}$ = 9.6 Hz), 20.8, 23.8, 27.6, 28.0, 31.4, 31.48, 31.49, 31.5, 32.7, 34.75, 34.76, 34.9, 35.0, 39.9 (d, $^2J_{CP}$ = 19.0 Hz), 47.6 (d, $^2J_{CP}$ = 20.0 Hz), 80.65, 80.59, 82.4, 82.5, 83.6, 83.7, 83.87, 83.90, 109.4, 119.8, 119.9, 120.1, 120.5, 121.6, 122.0, 123.7, 141.4, 142.3, 146.3, 146.6, 148.6,

148.7, 149.1, 149.5; ^{31}P NMR (202 MHz, $CDCl_3$): δ 137.6. IR (neat): 3076 (w), 2962 (s), 2907 (s), 2861 (m), 1599 (m), 1472 (m), 1388 (m), 1362 (m), 1248 (m), 1206 (m), 1160 (m) cm^{-1}. LRMS-(ESI+) for $C_{69}H_{104}NO_4P$ [M+H]: calculated: 1042.8, found: 1043.3. $[\alpha]^{20}_D$ = -23 (*c* = 2.3, $CHCl_3$). The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford 414 mg (91%) of a white solid. R_f = 0.30 (30:1 hexanes:ethyl acetate, stain in PMA).



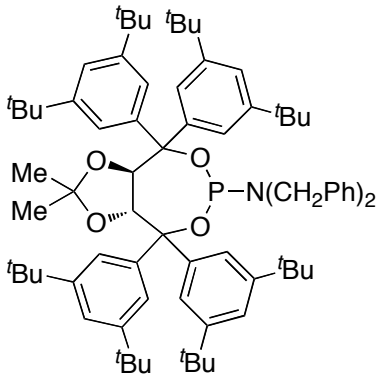
[3,5-(*tert*-Bu)$_2$-TADDOL]PNC$_6$H$_{12}$ (Scheme 2, (*S,S,S*)-L6; Compound SI-12). Representative procedure A was followed, employing (*S*)-(+)-2-methylpiperidine as amine nucleophile and di-*tert*-butylphenylTADDOL derived from D-tartaric acid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.10 (3H, s), 1.30 (18H, s), 1.32 (18H, s), 1.34 (18H, s), 1.34 (18H, s), 1.52-1.65 (5H, m), 1.65-1.74 (2H, m), 1.74-1.87 (1H, m), 1.93-2.03 (1H, m), 3.33 (1H, app q, *J* = 12.0 Hz), 3.51-3.62 (1H, m), 4.30-4.40 (1H, m), 4.65 (1H, d, *J* = 8.5 Hz), 5.28 (1H, dd, *J* = 8.5 Hz, 2.5 Hz), 7.20 (2H, d, *J* = 2.0 Hz), 7.24-7.30 (4H, m), 7.50 (2H, br s), 7.69 (2H, d, *J* = 1.5 Hz), 7.73 (2H, d, *J* = 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.1 (d, $^2J_{CP}$ = 5.1 Hz), 20.4, 23.8, 27.7, 28.1, 31.4, 31.5, 32.2, 34.77, 34.79, 34.9, 35.0, 40.0, (d, $^2J_{CP}$ = 27.0 Hz) 46.6 (d, $^2J_{CP}$ = 15.0 Hz), 80.46, 80.49, 82.1, 82.2, 83.9, 84.04, 84.09, 84.1, 109.5, 119.9, 120.1, 120.5, 121.5, 122.0, 123.7, 141.1, 142.3, 146.5, 146.6, 146.7, 148.7, 149.1, 149.4; ^{31}P NMR (202 MHz, $CDCl_3$): δ 138.0. IR (neat): 3075 (w), 2962 (s), 2911 (s), 2865 (m), 1599 (m), 1480 (m), 1396 (m), 1379 (m), 1362 (s), 1252 (s), 1201 (m) cm^{-1}. LRMS-(ESI+) for $C_{69}H_{104}NO_4P$ [M+H]: calculated: 1042.8, found: 1043.4. $[\alpha]^{20}_D$ = +29 (*c* = 3.4, $CHCl_3$). The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford 181 mg (80%) of a white solid. R_f = 0.47 (30:1 hexanes:ethyl acetate, stain in PMA).

Preparation of [3,5-(*tert*-Bu)$_2$-TADDOL]PN(CH$_2$Ph)$_2$ (L5)



To an oven-dried scintillation vial equipped with a magnetic stir bar in the dry-box was added triethylamine (35 mg, 0.25 mmol) and PhMe (2.5 mL). To this solution was added freshly distilled dibenzylamine (40 mg, 0.20 mmol), followed by phosphorus trichloride (28 mg, 0.20 mmol). The vial was capped with a teflon cone-lined cap and sealed with electrical tape. The vial was removed from the dry-box and heated to 80 °C with stirring 12 h. The reaction was cooled to ambient temperature, then a solution of 3,5-di-*tert*-butylphenylTADDOL (183 mg, 0.20

mmol) in PhMe (0.5 mL) was added in the dry-box. The vial that had contained the solution of the diol was rinsed with THF (0.5 mL), and this was added to the reaction vessel. The scintillation vial was capped and sealed and removed from the dry-box and allowed to stir at 80 °C for 7 h. The reaction was cooled to ambient temperature and diethyl ether (5 mL) was added to the reaction mixture. Triethylamine hydrochloride salts precipitated out of the solution, and the reaction mixture was filtered over celite and washed with diethyl ether (3 x 10 mL), then the filtrate was concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (55:1 hexanes:ethyl acetate) to afford 37 mg (16%) of a white solid. R_f = 0.38 (55:1 hexanes:ethyl acetate, stain in PMA).

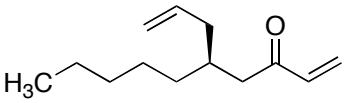


[3,5-(*tert*-Bu)$_2$-TADDOL]PN(CH$_2$Ph)$_2$ (Table 1, entry 8, L5; Compound SI-13). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.10 (3H, s), 1.12 (18H, s), 1.21 (18H, s), 1.23 (18H, s), 1.28 (18H, s), 1.47 (3H, s), 3.97 (2H, dd, *J* = 15.6 Hz, 10.8 Hz), 4.73 (1H, d, *J* = 9.0 Hz), 4.82 (2H, dd, *J* = 15.6 Hz, 7.8 Hz), 5.42 (1H, dd, *J* = 9.0 Hz, 2.4 Hz), 7.15 (1H, t, *J* = 1.8 Hz), 7.16-7.21 (3H, m), 7.21-7.22 (2H, m), 7.22-7.23 (3H, m), 7.23-7.25 (3H, m), 7.35-7.39 (6H, br m), 7.71 (2H, d, *J* = 1.8 Hz), 7.72 (2H, d, *J* = 1.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.0, 28.0, 29.7, 30.3, 31.3, 31.4, 31.48, 31.50, 34.6, 34.8, 34.9, 35.0, 47.8, 47.9 , 81.9, 83.0, 83.1, 83.5, 83.6, 110.1, 119.9, 120.1, 120.2, 120.5, 121.6, 121.9, 123.7, 126.6, 128.2, 128.4, 138.71, 138.72, 140.6, 142.1, 146.2, 146.7, 148.5, 148.7, 148.9, 149.3, 149.8; ^{31}P NMR (161 MHz, $CDCl_3$): δ 138.5. IR (neat): 2961 (s), 2904 (m), 2865 (m), 1598 (m), 1477 (w), 1455 (w), 1393 (w), 1249 (m), 1201 (m), 1059 (m), 946 (w), 880 (m), 864 (m), 787 (w), 710 (w) cm^{-1}. HRMS-(TOF MS ES+) for $C_{77}H_{107}NO_4P$ [M+H]: calculated: 1140.7938, found: 1140.7972. $[\alpha]^{20}_D$ = -42.7 (*c* = 0.22, $CHCl_3$). The crude reaction mixture was purified on silica gel (55:1 hexanes: ethyl acetate) to afford 37 mg (16%) of a white solid. R_f = 0.38 (55:1 hexanes:ethyl acetate, stain in PMA).

Representative Procedure for Conjugate Allylation

An oven-dried 2-dram vial equipped with a magnetic stir bar was charged with tris(dibenzylideneacetone) dipalladium(0) (3 mg, 0.003 mmol), (*R*,*R*,*S*)-**L6** (8 mg, 0.008 mmol), and toluene (0.26 mL) in a dry-box under argon atmosphere. The vial was capped and stirred for five minutes, then (*E*)-6-((*tert*-butyldimethylsilyl)oxy)hexa-1,4-dien-3-one (30 mg, 0.132 mmol) was added, followed by allylboronic acid pinacol ester (27 mg, 0.159 mmol). The vial was sealed, removed from the dry-box, and allowed to stir at rt for 14 h. The reaction was quenched with saturated aqueous NH_4Cl solution (0.5 mL) and extracted into dichloromethane (3 x 3 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a clear, colorless oil (32.3 mg, 91% yield). R_f = 0.31 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

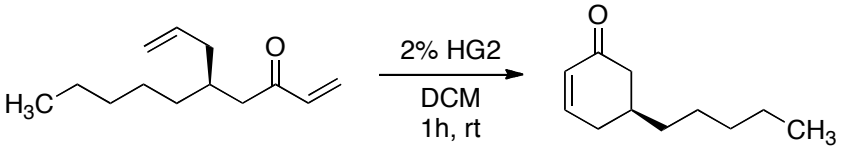
Characterization and Analysis of Stereochemistry



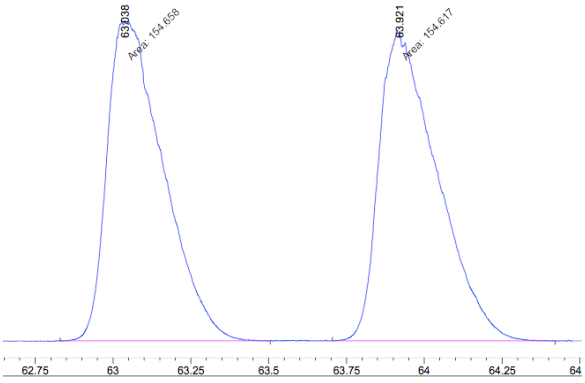
(*S*)-5-allyldec-1-en-3-one (Table 2, entry 1; Compound SI-14). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 7.2 Hz), 1.20-1.31 (8H, m), 1.98-2.15 (3H, m), 2.45 (1H, dd, *J* = 16.4 Hz, 6.4 Hz), 2.54 (1H, dd, *J* = 16.4 Hz, 6.4 Hz), 4.98-5.02 (2H, m), 5.69-5.79 (1H, m), 5.79 (1H, dd, *J* = 10.4 Hz, 0.8 Hz), 6.20 (1H, dd, *J* = 17.6 Hz, 1.2 Hz), 6.35 (1H, ddd, *J* = 17.6 Hz, 10.4 Hz, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 26.4, 32.0, 33.8, 33.8, 38.3, 44.0, 116.5, 127.6, 136.5, 136.9, 200.6; IR (neat): 3076 (w), 2958 (s), 2924 (s), 2848 (s), 1700 (s), 1683 (s), 1641 (m), 1611 (m), 1459 (m), 1396 (m), 1379 (m), 1299 (w), 1202 (w) cm^{-1}. HRMS-(ESI+) for $C_{13}H_{23}O$ [M+H]: calculated: 195.1749, found: 195.1836. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a clear, colorless oil (31.0 mg, 59% yield). R_f = 0.33 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

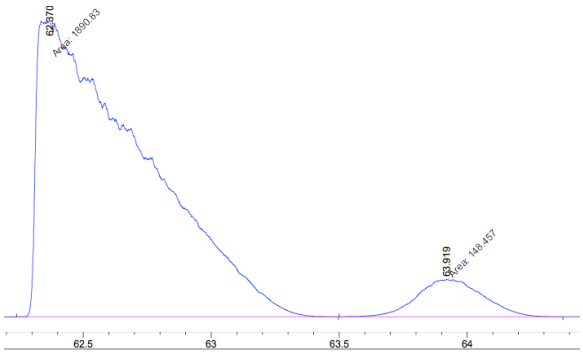
The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for GC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. The absolute stereochemistry was assigned by analogy (see page S-14).



Chiral GLC (CD-GTA, Supelco, 80 °C for 30 min, ramp 2 °C/min up to 120 °C, 20 psi) - analysis of metathesis product.

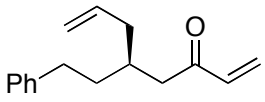


Racemic



Derived From Reaction Product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	62.370	MM	0.4794	1890.82520	65.73421	92.72012
2	63.919	MM	0.2994	148.45734	8.26445	7.27988

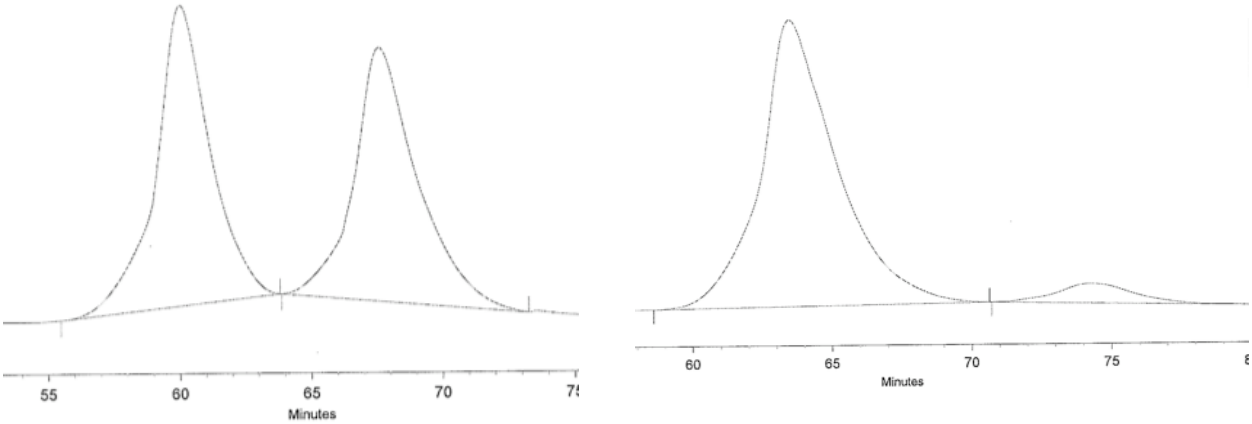


(*S*)-5-phenethylocta-1,7-dien-3-one (Table 2, entry 2; Compound SI-15). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60-1.68 (2H, m), 2.07-2.12 (1H, m), 2.15-2.21 (2H, m), 2.52 (1H, dd, *J* = 16.5 Hz, 6.5 Hz), 2.56-2.68 (3H, m), 5.02-5.06 (2H, m), 5.72-5.80 (1H, m), 5.79 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.20 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.34 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 7.16-7.19 (3H, m), 7.25-7.29 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.2, 33.4, 35.7, 38.1, 43.8, 117.0, 125.7, 128.0, 128.3, 128.3, 136.1, 136.8, 142.3, 200.5; IR (neat): 2923 (br, m), 1680 (s), 1614 (w), 1454 (w), 1401 (m), 1076 (w), 992 (m), 914 (m), 747 (m), 699 (s) cm^{-1}. HRMS-(ESI+) for $C_{16}H_{21}O$ [M+H]: calculated: 229.1592, found: 229.1597. The crude reaction mixture was purified on silica gel (33:1 hexanes:ethyl acetate) to afford a clear, colorless oil (38.9 mg, 79% yield). R_f = 0.23 (31:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for HPLC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. The absolute stereochemistry was assigned by analogy.

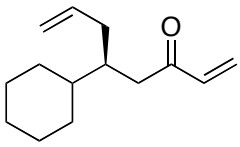
Chiral HPLC (OD, Chiralcel, 1 mL/min, 0.8% isopropanol, 220 nm) - analysis of metathesis product.



Racemic

Derived From Reaction Product

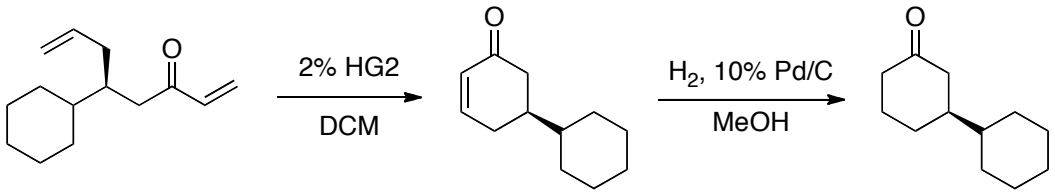
Time	Area	Area %	Height	Height %
63.467	66011756	93.55	344336	93.60
74.233	4553520	6.45	23543	6.40



(*S*)-5-cyclohexylocta-1,7-dien-3-one (Table 2, entry 3; Compound SI-16). The title compound was prepared *via* the representative procedure for conjugate allylation, with the following modification: the reaction was quenched with 5 drops glacial acetic acid, then allowed to stir for 15 minutes at room temperature. After this time, saturated aqueous NH_4Cl solution (0.5 mL) was added and the extraction protocol described in the general procedure was followed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94-1.05 (2H, m), 1.07-1.25 (3H, m), 1.29-1.37 (1H, m), 1.58-1.74 (5H, m), 1.90-2.02 (2H, m), 2.11-2.18 (1H, m), 2.45 (1H, dd, J = 16.4 Hz, 6.8 Hz), 2.54 (1H, dd, J = 16.4 Hz, 6.0 Hz), 4.96-5.01 (2H, m), 5.66-5.75 (1H, m), 5.78 (1H, dd, J = 10.4 Hz, 1.2 Hz), 6.20 (1H, dd, J = 17.6 Hz, 1.2 Hz), 6.35 (1H, dd, J = 17.6 Hz, 10.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 29.6, 30.0, 35.8, 38.8, 40.3, 41.2, 116.3, 127.6, 136.8, 137.4, 201.1; IR (neat): 2924 (s), 2582 (m), 2358 (w), 1699 (m), 1682 (m), 1615 (w), 1448 (m), 1401 (m), 1082 (w), 993 (m), 960 (w), 912 (m) cm^{-1}. HRMS-(ESI+) for $C_{14}H_{23}O$ [M+H]: calculated: 207.1749, found: 207.1744. The crude reaction mixture was purified on silica gel (34:1 hexanes:ethyl acetate) to afford a clear, colorless oil (35.7 mg, 57% yield). R_f = 0.39 (34:1 hexanes:ethyl acetate, stain in $KMnO_4$).

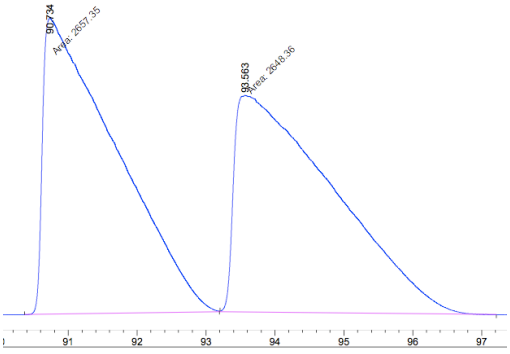
Proof of Stereochemistry:

The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for GC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. Absolute stereochemistry was determined first by hydrogenation of the metathesis product (below), then comparison of its optical rotation ($[\alpha]^{20}_D$ = -14.566 (*c* = 0.81, $CHCl_3$)) with the rotation of authentic (*R*)-3-cyclohexylcyclohexanone ($[\alpha]^{22}_D$ = +11.9 (*c* = 1.05, $CHCl_3$)) as previously reported in the literature,[8] and the stereochemistry was assigned to be the opposite configuration.

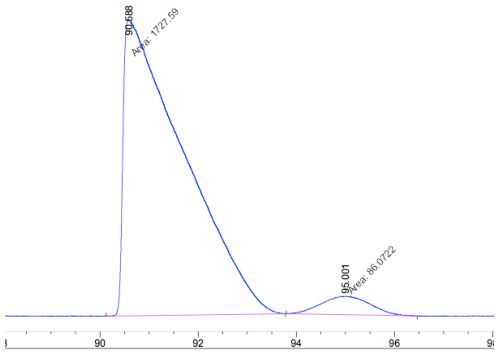


[8] Tuttle, J. B.; Ouellet, S. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 12662.

Chiral GLC (β-dex, Supelco, 130 °C, 20 psi) - analysis of the metathesis product.

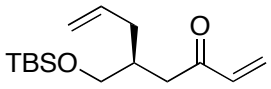


Racemic



Derived from Reaction Product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	90.588	MM	1.4299	1727.58643	20.13632	95.25422
2	95.001	MM	1.1440	86.07224	1.25395	4.74578

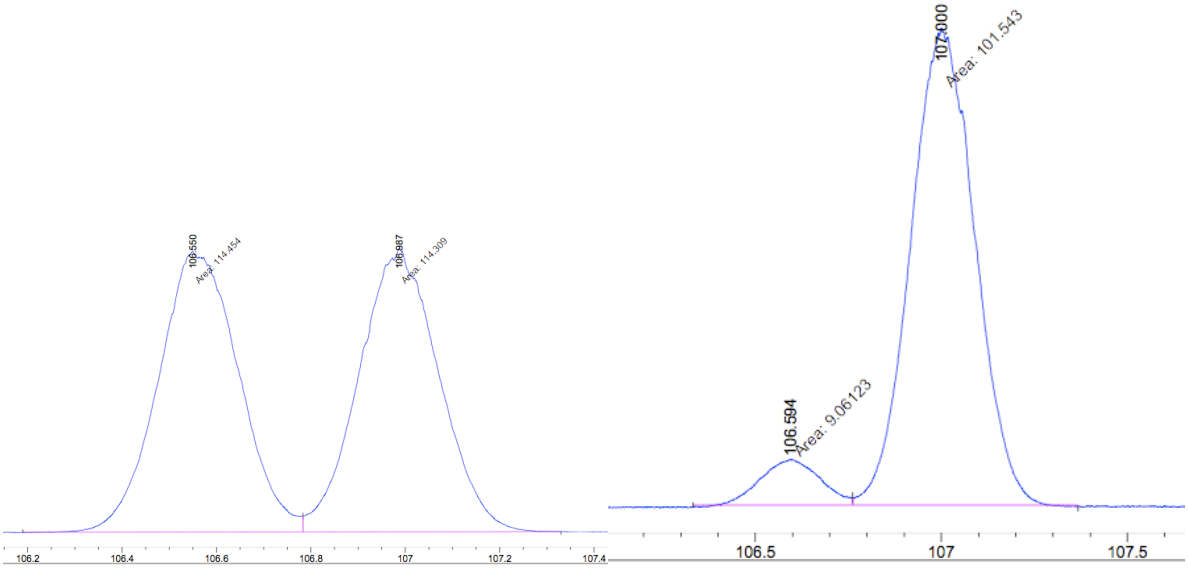


(*S*)-5-((*tert*-butyldimethylsilyloxy)methyl)octa-1,7-dien-3-one (Table 2, entry 4; Compound SI-17). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.01 (3H, s), 0.02 (3H, s), 0.88 (9H, s), 1.99-2.07 (1H, m), 2.13-2.24 (2H, m), 2.46 (1H, dd, *J* = 16.4 Hz, 6.4 Hz), 2.71 (1H, dd, *J* = 16.4 Hz, 6.4 Hz), 3.48 (1H, dd, *J* = 10.0 Hz, 5.2 Hz), 3.54 (1H, dd, *J* = 10.0 Hz, 5.2 Hz), 4.95-5.04 (2H, m), 5.70-5.80 (1H, m), 5.80 (1H, dd, *J* = 10.4 Hz, 1.2 Hz), 6.21 (1H, dd, *J* = 17.6 Hz, 1.2 Hz), 6.35 (1H, dd, *J* = 17.6 Hz, 10.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –5.5, 18.2, 25.9, 35.6, 36.6, 40.6, 64.6, 116.6, 127.8, 136.5, 137.0, 200.6; IR (neat): 2955 (m), 2929 (m), 2857 (m), 1684 (w), 1401 (w), 1254 (m), 1097 (m), 836 (s), 777 (m) cm^{-1}. HRMS-(ESI+) for $C_{15}H_{29}O_2Si$ [M+H]: calculated: 269.1937, found: 269.1929. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a clear, colorless oil (32.2 mg, 91% yield). R_f = 0.31 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

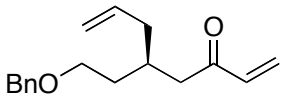
Enantioselectivity was determined by GC analysis of the title compound as compared to racemic material, prepared using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. Absolute stereochemistry was assigned by analogy.

Chiral GLC (CD-GTA, Supelco, 65 °C for 40 min, ramp 0.8 °C/min up to 120 °C, 20 psi) - analysis of the title compound.



Racemic Reaction Product

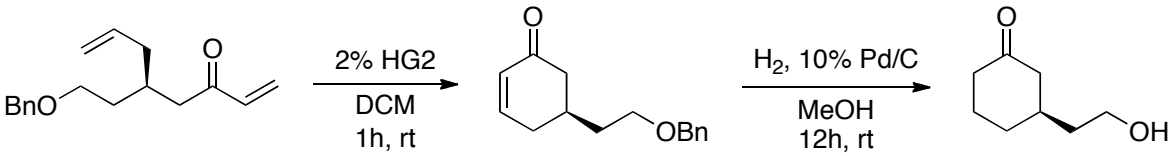
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	106.594	MF	0.1866	9.06123	8.09493e-1	8.19251
2	107.000	FM	0.1994	101.54268	8.48935	91.80749



(*R*)-5-(2-(benzyloxy)ethyl)octa-1,7-dien-3-one (Table 2, entry 5; Compound SI-18). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56-1.72 (2H, m), 2.02-2.15 (2H, m), 2.26 (1H, app p, J = 1.6 Hz), 2.55 (2H, d, J = 6.8 Hz), 3.51 (2H, app dt, J = 6.4 Hz, 2.4 Hz), 4.47 (2H, s), 4.98-5.04 (2H, m), 5.68-5.76 (1H, m), 5.77 (1H, dd, J = 10.4 Hz, 1.2 Hz), 6.17 (1H, dd, J = 17.6 Hz, 1.2 Hz), 6.32 (1H, dd, J = 17.6 Hz, 10.4 Hz), 7.27-7.34 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.1, 33.6, 38.5, 43.8, 68.3, 72.8, 117.0, 127.5, 127.6, 127.9, 128.3, 136.2, 136.8, 138.4, 200.5; IR (neat): 2923 (s), 2855 (s), 1698 (s), 1680 (s), 1614 (m), 1454 (m), 1401 (m), 1365 (m), 1206 (w), 1100 (s), 1028 (w), 993 (m), 962 (m), 914 (m), 736 (s), 698 (s) cm^{-1}. HRMS-(ESI+) for $C_{17}H_{23}O_2$ [M+H]: calculated: 259.1698, found: 259.1702. The crude reaction mixture was purified on silica gel (24:1 toluene:diethyl ether) to afford a clear, colorless oil (26.0 mg, 53% yield). R_f = 0.28 (21:1 toluene:diethyl ether, stain in PMA).

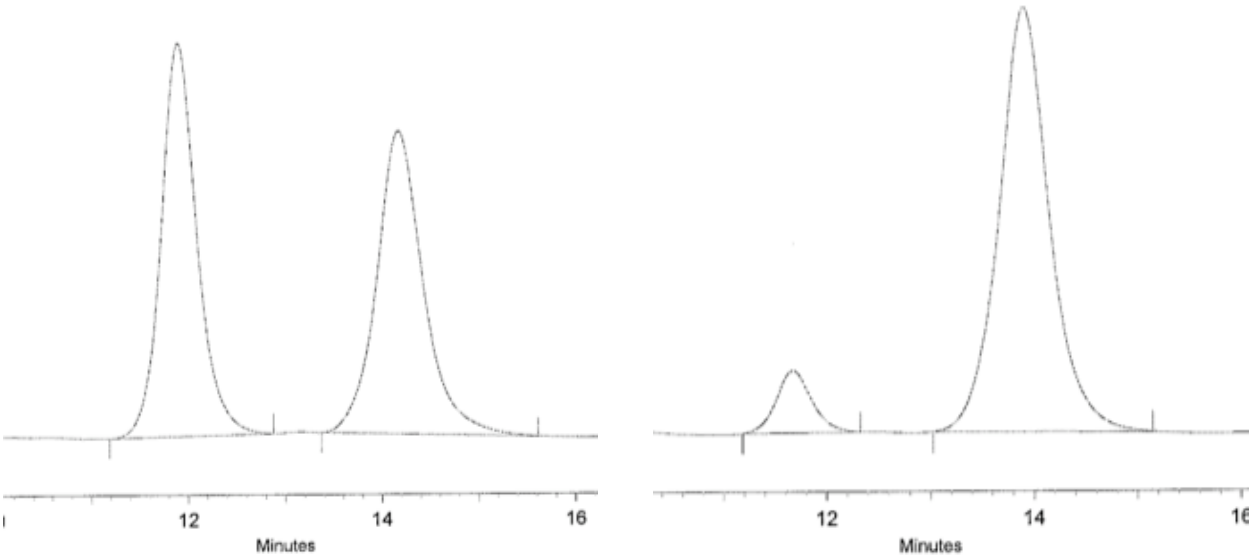
Proof of Stereochemistry:

Enantioselectivity was determined by HPLC analysis of the title compound as compared to racemic material, prepared using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. In order to determine the absolute stereochemistry, the reaction product was treated with Hoveyda-Grubbs second generation catalyst followed by catalytic hydrogenation, as shown below. The optical rotation of the compound derived from the allylation reaction product ($[\alpha]^{20}_D$ = -9.914 (c = 0.355, $CHCl_3$)) was compared to the rotation of authentic (*S*)-3-(2-hydroxyethyl)cyclohexanone ($[\alpha]^{20}_D$ = +14.0 (c = 0.08, $CHCl_3$) as previously reported in the literature,[9] and the stereochemistry was assigned to be the opposite configuration.



[9] Jiricek, J.; Blechert, S. *J. Am. Chem. Soc.* **2004**, *126*, 3534.

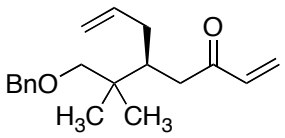
Chiral HPLC (OD, Chiralcel, 1 mL/min, 1.0% isopropanol, 220 nm) - analysis of title compound.



Racemic

Reaction Product

Time	Area	Area %	Height	Height %
11.667	3124720	9.41	130298	12.82
13.883	30081289	90.59	885967	87.18

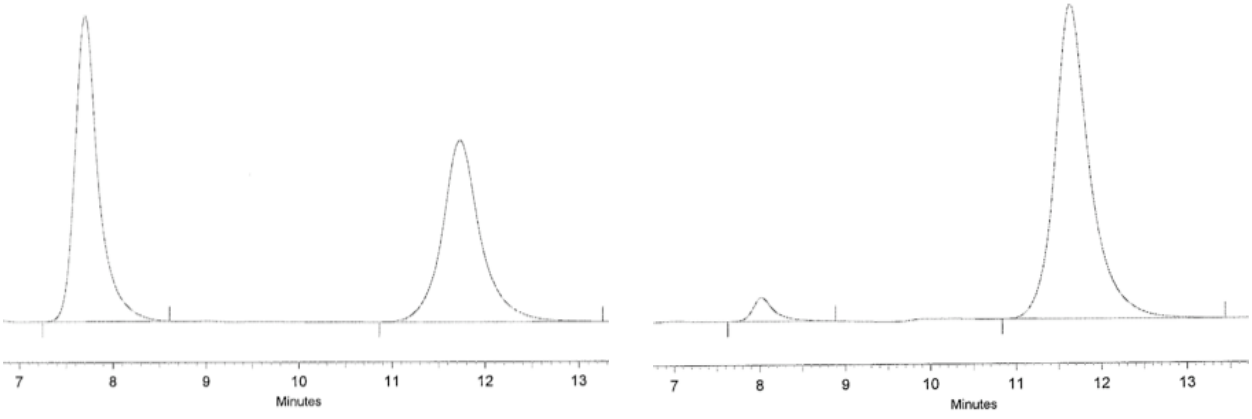


(*S*)-5-(1-benzyloxy)-2-methylpropan-2-yl)octa-1,7-dien-3-one (Table 2, entry 6; Compound SI-19). The title compound was prepared *via* the representative procedure for conjugate allylation, with the following modifications: The conjugated allylation was allowed to stir at room temperature for 48 h, rather than 14 h. Additionally, for reaction work-up, the reaction was diluted with $CHCl_3$ (0.5 mL), then quenched with glacial acetic acid (0.2 mL) and allowed to stir at 45 °C for 3 h. After this time, saturated aqueous NH_4Cl solution (0.5 mL) was added and the extraction protocol described in the general procedure was followed. ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, s), 0.92 (3H, s), 1.75-1.82 (1H, m), 2.30-2.36 (2H, m), 2.39 (1H, dd, J = 17.0 Hz, 6.0 Hz), 2.71 (1H, dd, J = 17.0 Hz, 5.0 Hz), 3.18 (2H, dd, J = 14.5 Hz, 9.0 Hz), 4.43 (2H, s), 4.91-4.98 (2H, m), 5.65-5.73 (1H, m), 5.69 (1H, dd, J = 10.5 Hz, 1.0 Hz), 6.15 (1H, dd, J = 17.5 Hz, 1.0 Hz), 6.32 (1H, dd, J = 17.5 Hz, 10.5 Hz), 7.26-7.35 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.6, 23.3, 35.4, 37.4, 39.1, 40.8, 73.0, 78.1, 116.1, 127.1, 127.3, 127.4, 128.2, 136.6, 138.3, 138.7, 200.6; IR (neat): 2959 (m), 2926 (m), 2855 (m), 1683 (s), 1616 (w), 1454 (m), 1399 (m), 1365 (m), 1098 (s), 993 (m), 911 (m), 736 (m), 698 (m) cm^{-1}. HRMS-(ESI+) for $C_{19}H_{27}O_2$ [M+H]: calculated: 287.2011, found: 287.2007. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a clear, colorless oil (28.2 mg, 81% yield). R_f = 0.21 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

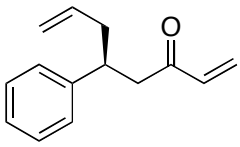
Enantioselectivity was determined by HPLC analysis of the title compound as compared to racemic material, prepared using $Pd_2(dba)_3$ and a 1:1 mixture of **(*R,R,S*)-L6** and **(*R,R,R*)-L6** as the racemic catalyst system in the conjugate allylation reaction. Absolute stereochemistry was determined by analogy.

Chiral HPLC (OD, Chiralcel, 1 mL/min, 1% isopropanol, 220nm) - analysis of title compound.



Racemic Reaction Product

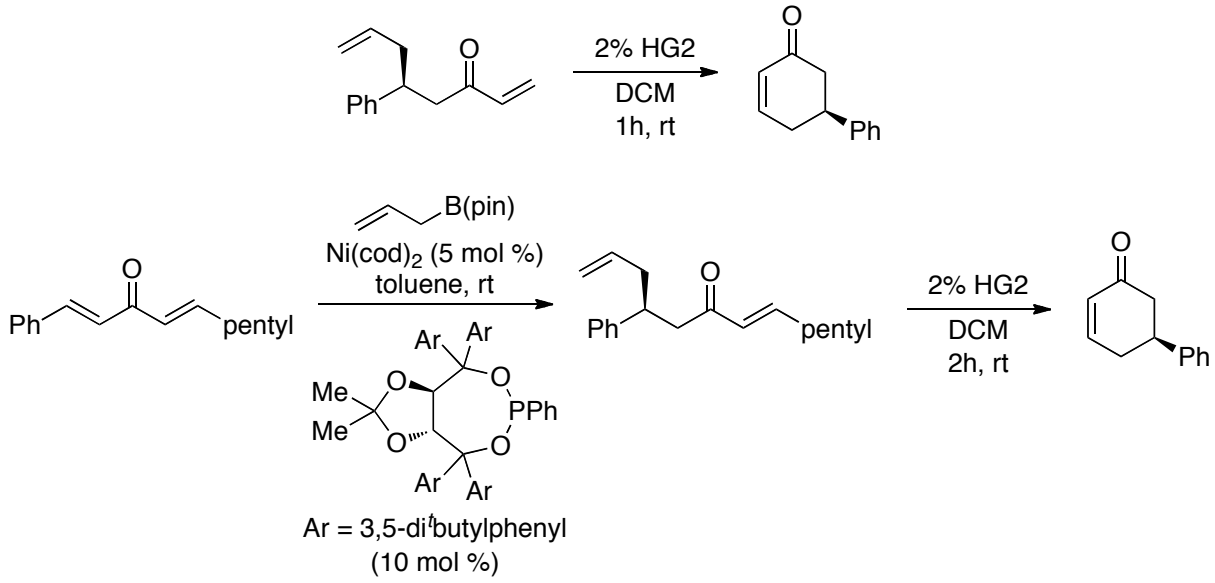
Time	Area	Area %	Height	Height %
8.017	269914	4.50	15175	7.08
11.650	5725910	95.50	199241	92.92



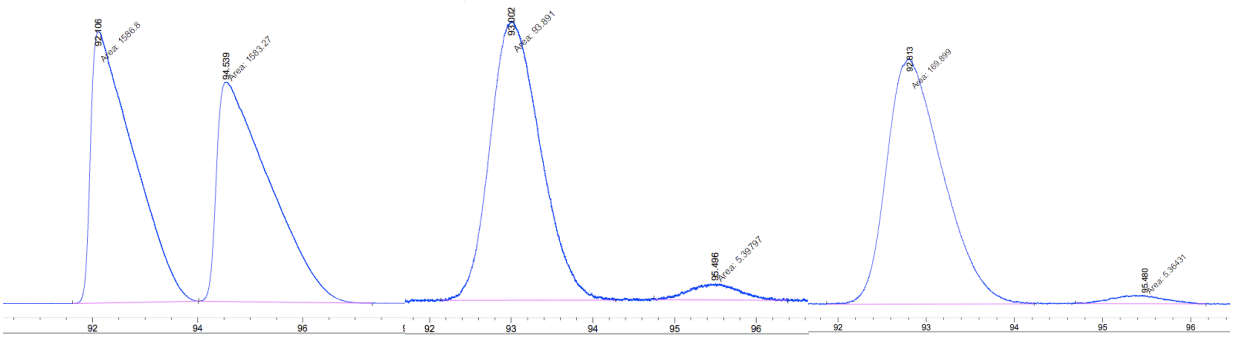
(*S*)-5-phenylocta-1,7-dien-3-one (Table 2, entry 7; Compound SI-20). The title compound was prepared *via* the representative procedure for conjugate allylation ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.40 (2H, app t, *J* = 7.0 Hz), 2.90 (2H, app dq, *J* = 16.0 Hz, 6.5 Hz), 3.33 (1H, p, *J* = 7.0 Hz), 4.95-5.01 (2H, m), 5.65 (1H, app ddt, *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz), 5.76 (1H, dt, *J* = 10.5 Hz, 0.5 Hz), 6.15 (1H, dt, *J* = 17.5 Hz, 0.5 Hz), 6.28 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 0.5 Hz), 7.17-7.20 (3H, m), 7.27-7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.6, 40.7, 45.6, 116.8, 126.4, 127.5, 128.1, 128.4, 136.1, 136.7, 144.1, 199.4; IR (neat): 2923 (br, w), 1680 (s), 1614 (w), 1401 (m), 1076 (w), 1032 (m), 915 (m), 761 (m), 700 (s) cm^{-1}. HRMS-(ESI+) for $C_{14}H_{17}O$ [M+H]: calculated: 201.1279, found: 201.1277. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a light yellow oil (35.7 mg, 80% yield). R_f = 0.21 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Proof of Stereochemistry:

The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for GC analysis, as depicted below. The analogous racemic material was prepared *via* the same route, using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. Absolute stereochemistry was determined by comparison of the GC trace of the metathesis product to authentic (*S*)-5-phenylcyclohex-2-enone, prepared as shown below.[6]

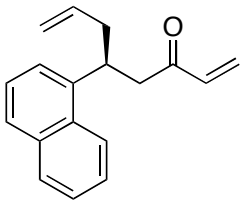


Chiral GLC (β-dex, Supelco, 130 °C, 25 psi) - analysis of the metathesis product.



Racemic Derived from Reaction Product From Authentic Product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	93.002	MM	0.7148	93.89096	2.18914	94.56337
2	95.496	MM	0.6915	5.39797	1.30109e-1	5.43663

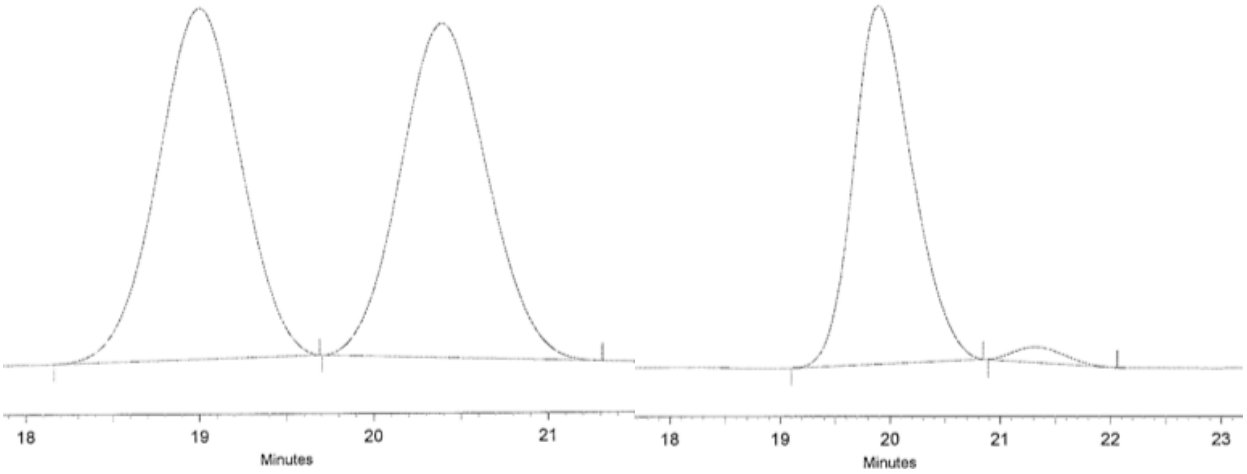


(*S*)-5-(naphthalen-1-yl)octa-1,7-dien-3-one (Table 2, entry 8; Compound SI-21). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.50-2.61 (2H, m), 3.00 (1H, dd, *J* = 17.0 Hz, 5.5 Hz), 3.09 (1H, dd, *J* = 17.0 Hz, 8.0 Hz), 4.32 (1H, app p, *J* = 7.0 Hz), 4.93-4.96 (1H, m), 5.03 (1H, app dq, *J* = 17.0 Hz, 1.5 Hz), 5.68 (1H, app ddt, *J* = 17.0 Hz, 10.5 Hz, 7.0 Hz), 5.77 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.18 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.32 (1H, dd, *J* = 17.5 Hz, 10.5 Hz), 7.36 (1H, dd, *J* = 7.0 Hz, 1.0 Hz), 7.43 (1H, app t, *J* = 7.5), 7.48 (1H, app td, *J* = 6.5 Hz, 1.0 Hz), 7.54 (1H, app td, *J* = 7.0 Hz, 1.5 Hz), 7.72 (1H, d, *J* = 8.0 Hz), 7.85 (1H, dd, *J* = 8.0 Hz), 8.20 (1H, d, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.9, 45.3, 116.9, 123.2, 125.3, 125.5, 126.0, 126.9, 128.0, 128.9, 131.6, 134.0, 136.1, 136.7, 140.2, 199.3; IR (neat): 2957 (m), 2921 (s), 2851 (m), 1681 (m), 1614 (w), 1464 (w), 1398 (m), 992 (w), 965 (w), 915 (w), 797 (m), 778 (s) cm^{-1}. HRMS-(ESI+) for $C_{18}H_{19}O$ [M+H]: calculated: 251.1436, found: 251.1424. The crude reaction mixture was purified on silica gel (30:1 hexanes:ethyl acetate) to afford a light yellow oil (22.2 mg, 37% yield). R_f = 0.23 (30:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

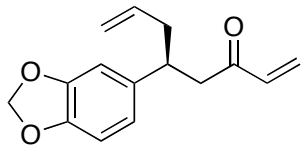
Enantioselectivity was determined by HPLC analysis of the title compound as compared to racemic material, prepared using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. Absolute stereochemistry was assigned by analogy.

Chiral HPLC (OD-R, Chiralcel, 1.5 mL/min, 0.6% isopropanol, 220nm) - analysis of title compound.



Racemic Reaction Product

Time	Area	Area %	Height	Height %
19.883	14745341	96.41	398643	95.89
21.317	549196	3.59	17102	4.11

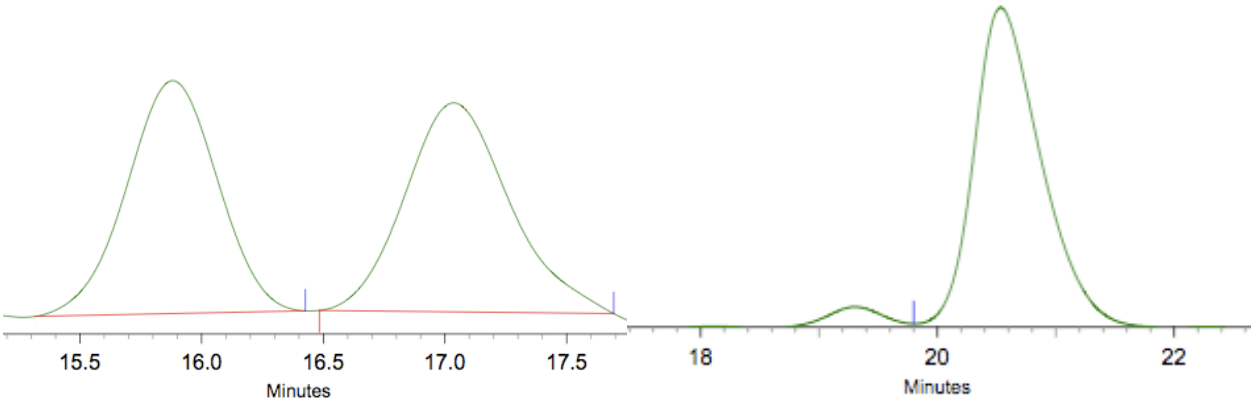


(*S*)-5-(benzo[*d*][1,3]dioxol-5-yl)octa-1,7-dien-3-one (Table 2, entry 9; Compound SI-22). The title compound was prepared *via* the representative procedure for conjugate allylation. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (2H, app dt, *J* = 7.0 Hz, 1.5 Hz), 2.84 (2H, app dq, *J* = 16.5 Hz, 6.5 Hz), 3.25 (1H, app p, *J* = 7.0 Hz), 4.95-5.01 (2H, m), 5.65 (1H, app ddt, *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz), 5.76 (1H, dd, *J* = 10.5 Hz, 1.5 Hz), 5.92 (2H, s), 6.15 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.28 (1H, dd, *J* = 18.0 Hz, 10.5 Hz), 6.64 (1H, dd, *J* = 8.0 Hz, 1.5 Hz), 6.69 (1H, d, *J* = 1.5), 6.71 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.6, 40.8, 45.8, 100.8, 107.7, 108.1, 116.8, 120.6, 128.1, 136.1, 136.7, 138.0, 145.9, 147.6, 199.4; IR (neat): 2919 (m), 2851 (w), 1711 (m), 1611 (w), 1503 (m), 1489 (s), 1441 (m), 1245 (s), 1098 (w), 1039 (m), 935 (w), 811 (w) cm^{-1}. HRMS-(ESI+) for $C_{15}H_{17}O_3$ [M+H]: calculated: 245.1178, found: 245.1174. The crude reaction mixture was purified on silica gel (24:1 hexanes:ethyl acetate) to afford a light yellow oil (34.9 mg, 76% yield) that could not be separated from dibenzylideneacetone (38.2 mg, mass of product mixture). R_f = 0.24 (24:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Analysis of Stereochemistry:

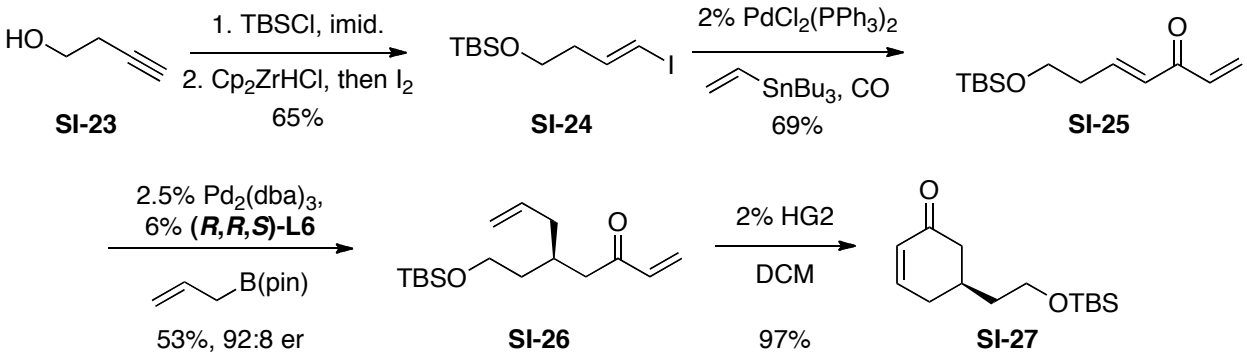
Enantioselectivity was determined by HPLC analysis of the title compound as compared to racemic material, prepared using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. Absolute stereochemistry was assigned by analogy.

Chiral HPLC (OD-R, Chiralcel, 1.0 mL/min, 0.5% isopropanol, 220nm) - analysis of title compound.



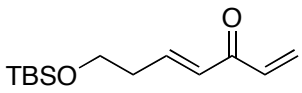
Retention Time	Area	Area %	Height	Height %
19.303	25462821	5.20	758410	6.05
20.533	463864021	94.80	11771477	93.95

Synthesis and Characterization of Cyclohexenone 11 (Scheme 3).



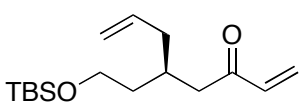
Compound **SI-24** was synthesized from commercially available homopropargyl alcohol **SI-23** following literature procedure, and spectral data for **SI-24** is an accordance with the literature.[10]

Compound **SI-25** was synthesized from **SI-24** *via* Stille carbonylative cross coupling as described in Representative Procedure A for the synthesis of unsaturated methylidene ketones.



(*E*)-7-(*tert*-butyldimethylsilyloxy)hepta-1,4-diene-3-one (Scheme 3, compound 9; Compound SI-25). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (6H, s), 0.89 (9H, s), 2.47 (2H, qd, *J* = 6.4 Hz, 1.6 Hz), 3.75 (2H, t, *J* = 6.4 Hz), 5.82 (1H, dd, *J* = 10.4 Hz, 1.6 Hz), 6.28 (1H, dd, *J* = 17.6 Hz, 1.6 Hz), 6.41 (1H, dt, *J* = 16.0 Hz, 1.2 Hz), 6.61 (1H, dd, *J* = 17.6 Hz, 10.4 Hz), 6.94 (1H, dt, *J* = 16.0 Hz, 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.3, 25.9, 36.2, 61.5, 101.3, 128.4, 129.7, 134.7, 145.6, 189.7; IR (neat): 2955 (w), 2930 (w), 2857 (w), 1669 (m), 1634 (w), 1613 (w), 1403 (w), 1255 (m), 1097 (s), 984 (m), 836 (s), 777 (s) cm^{-1}. HRMS-(ESI+) for $C_{13}H_{25}O_2Si$ [M +H]: calculated: 241.1624, found: 241.1617. The crude reaction mixture was purified on silica gel (35:1 hexanes:ethyl acetate) to afford a light yellow oil (317 mg, 69% yield). R_f = 0.15 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

Compound **SI-26** was synthesized *via* the representative procedure for conjugate allylation from **SI-25**.



(*R*)-5-(2-(*tert*-butyldimethylsilyloxy)ethyl)octa-1,7-dien-3-one (Scheme 3, compound 10; Compound SI-26). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.03 (6H, s), 0.88 (9H, s), 1.46-1.52 (1H, m), 1.54-1.60 (1H, m), 2.03-2.07 (1H, m), 2.12-2.15 (1H, m), 2.22 (1H, p, *J* = 6.5 Hz), 2.56 (2H, d, *J* = 7.0 Hz), 3.65 (2H, dd, *J* = 6.5 Hz, 3.5 Hz), 4.99-5.03 (2H, m), 5.70-5.78 (1H, m), 5.79 (1H, dd, *J* = 10.5 Hz, 1.0 Hz), 6.20 (1H, dd, *J* = 17.5 Hz, 1.0 Hz), 6.34 (1H, dd, *J* = 17.5 Hz, 10.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –5.3, 18.3, 25.9, 30.9, 36.6, 38.4, 43.9, 61.2, 116.9, 127.9,

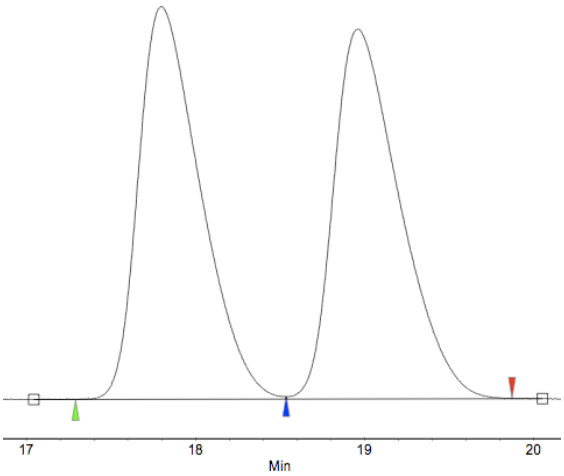
[10] Germain, J.; Deslongchamps, P. *J. Org. Chem.* **2002**, *67*, 5269.

136.3, 136.8, 200.6; IR (neat): 2928.5 (w), 2856.8 (w), 1682.4 (w), 1400.0 (w), 1253.5 (m), 1095.1 (s), 993.4 (w), 959.0 (w), 912.9 (w), 834.3 (s), 774.6 (s) cm^{-1}. HRMS-(ESI+) for $C_{16}H_{31}O_2Si$ [M+H]: calculated: 283.2093, found: 283.2087. The crude reaction mixture was purified on silica gel (40:1 hexanes:ethyl acetate) to afford a clear, colorless oil (25.7 mg, 53% yield). R_f = 0.35 (35:1 hexanes:ethyl acetate, stain in $KMnO_4$).

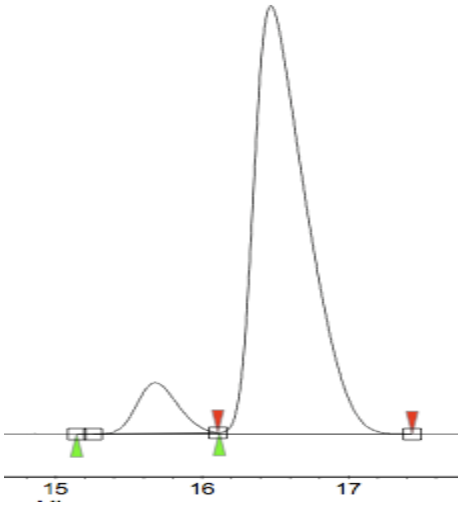
Proof of Stereochemistry:

The title compound was treated with Hoveyda-Grubbs second generation catalyst to afford the ring closing metathesis product for SFC analysis, as depicted in the above Scheme (**SI-26** to **SI-27**). The analogous racemic material was prepared *via* the same route, using $Ni(cod)_2$ and triphenylphosphine as the achiral catalyst system in the conjugate allylation reaction. In order to determine absolute stereochemistry, the metathesis product was subjected to deprotection of the silyl ether, followed by 1,4-hydrogenation of the enone to afford **SI-28**, as shown below. The optical rotation of **SI-28**, derived from the conjugate allylation product ($[\alpha]^{20}_D$ = -9.349 (*c* = 0.385, $CHCl_3$)) was compared to the rotation of authentic (*S*)-3-(2-hydroxyethyl)cyclohexanone ($[\alpha]^{20}_D$ = +14.0 (*c* = 0.08, $CHCl_3$) as previously reported in the literature,[9] and the stereochemistry was assigned to be the opposite configuration.

*Chiral SFC (OD-H, Chiralpak, 220nm, 1.0 mL/min, 0.4% MeOH, 150 bar, 50 °C) - analysis of metathesis product **SI-27**.*

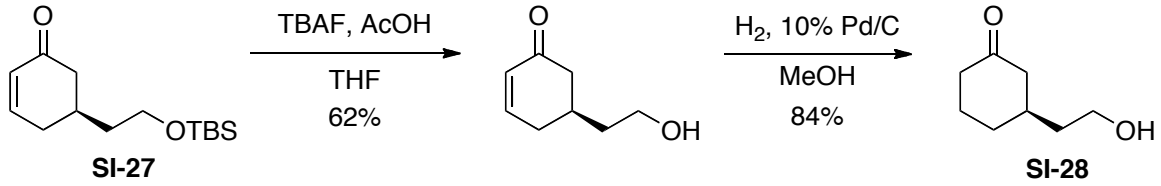


Racemic



Derived from Reaction Product

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	15.14	15.68	16.11	0.00	8.49	590.1	191.7	8.492
1	UNKNOWN	16.12	16.47	17.44	0.00	91.51	4992.3	2065.5	91.508

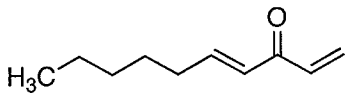


SI-27 **SI-28**

Compound **SI-27** was synthesized from **SI-26** as described by literature procedure.[11] Spectral data is in accordance with the literature.[12]

[11] Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

[12] Zhu, L.; Lauchli, R.; Loo, M. Shea, K. J. *Org. Lett.* **2007**, *9*, 2269.



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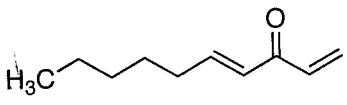
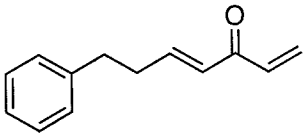
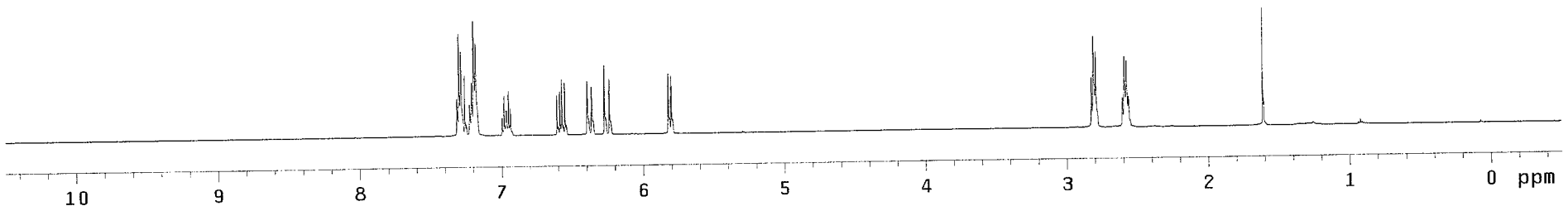
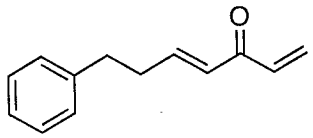


SI-1

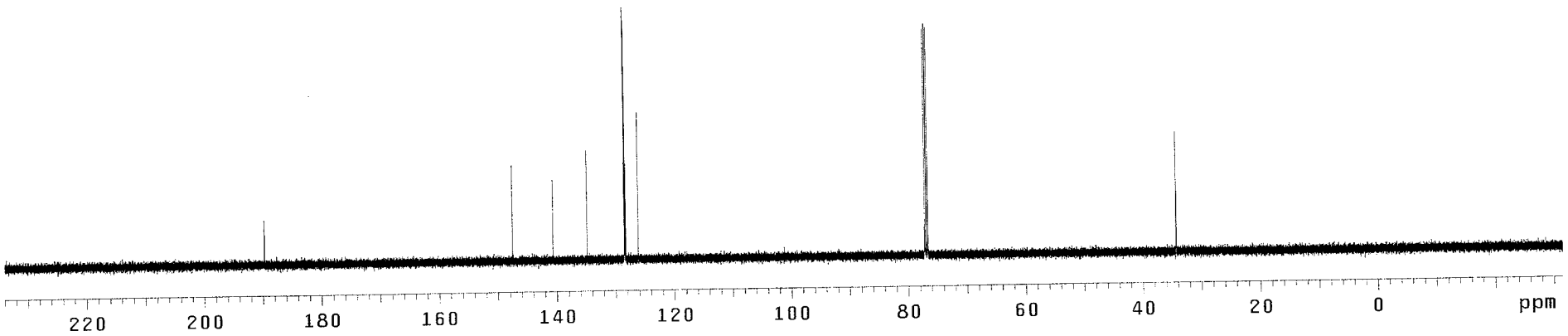


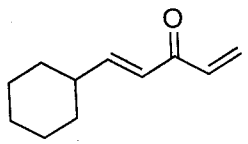
SI-2



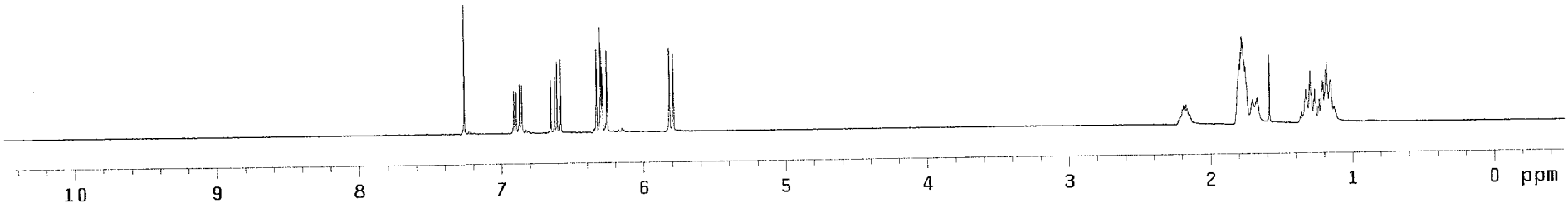


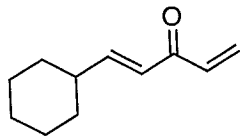
SI-2



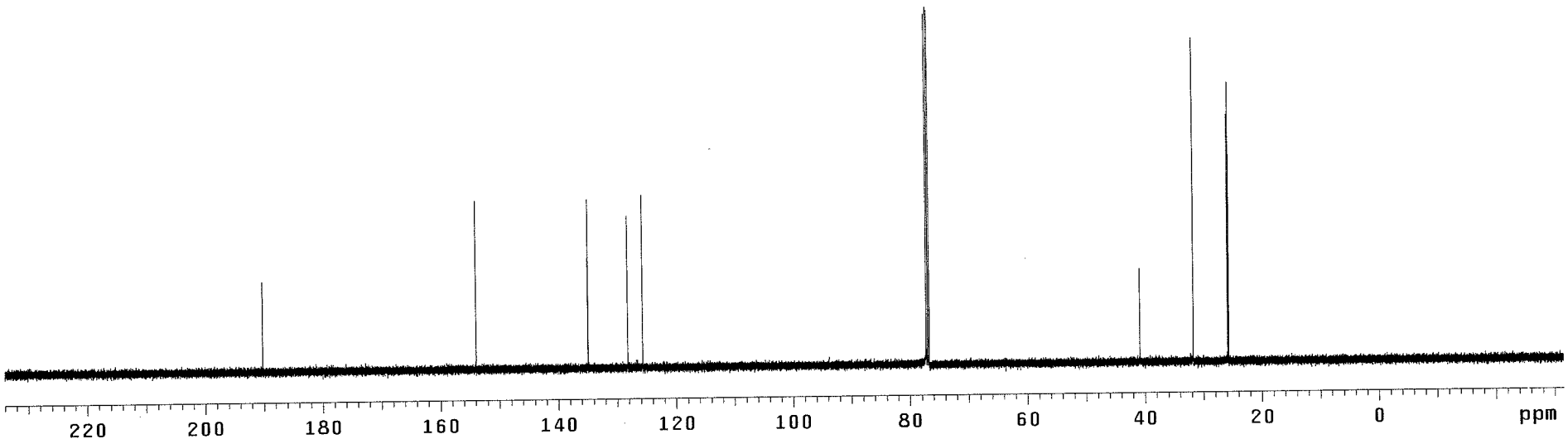


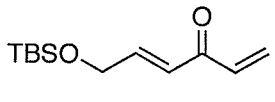
SI-3





SI-3





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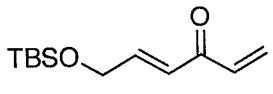
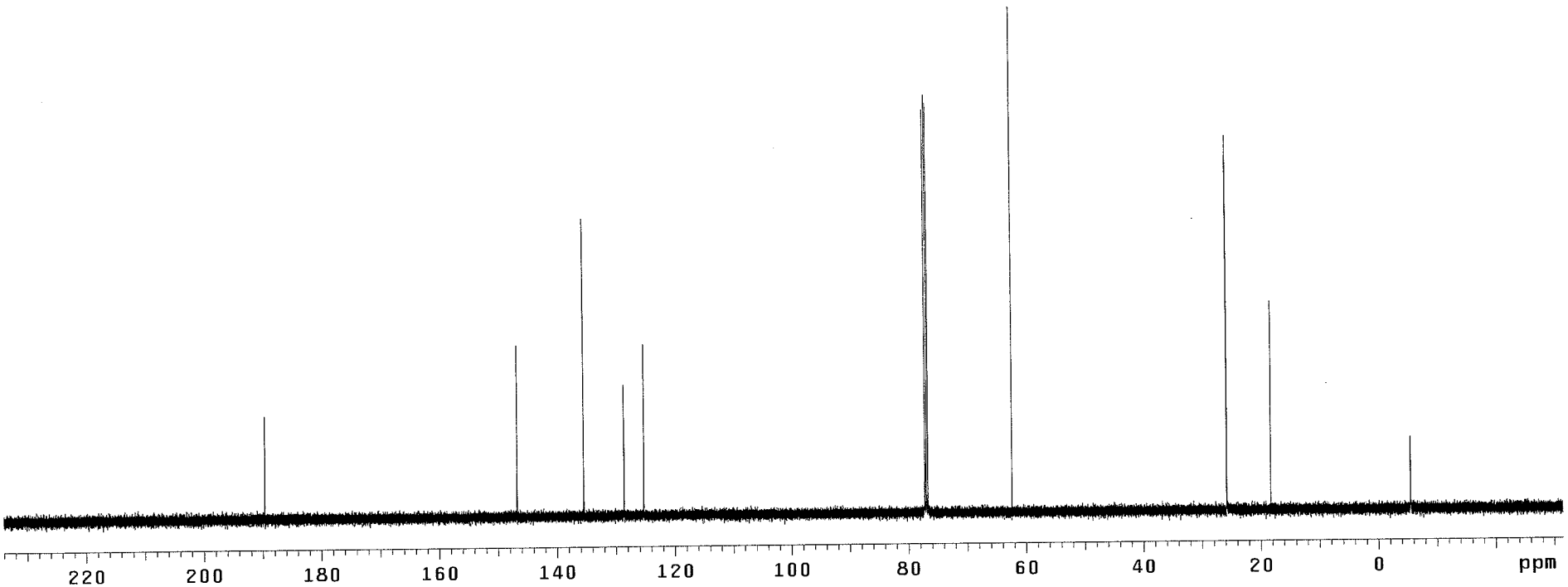
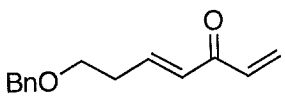
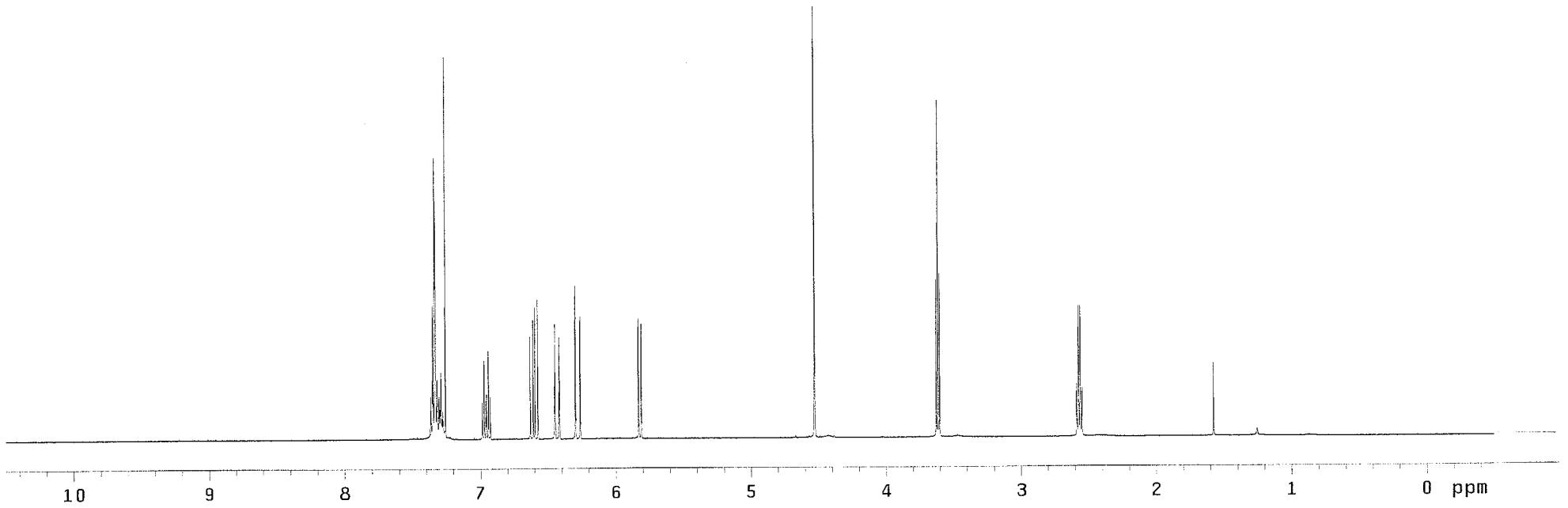


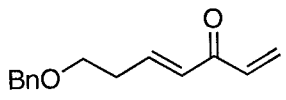
SI-4



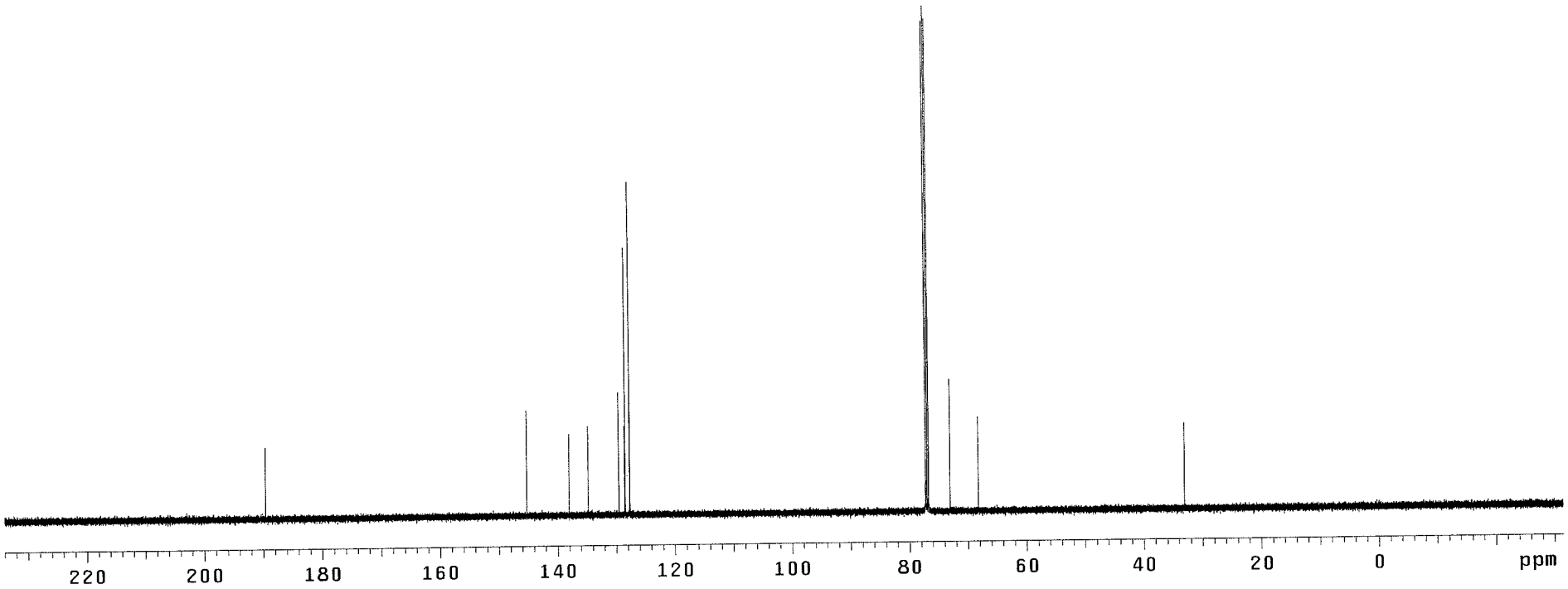


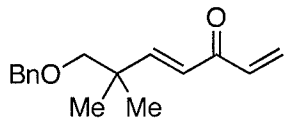
SI-5



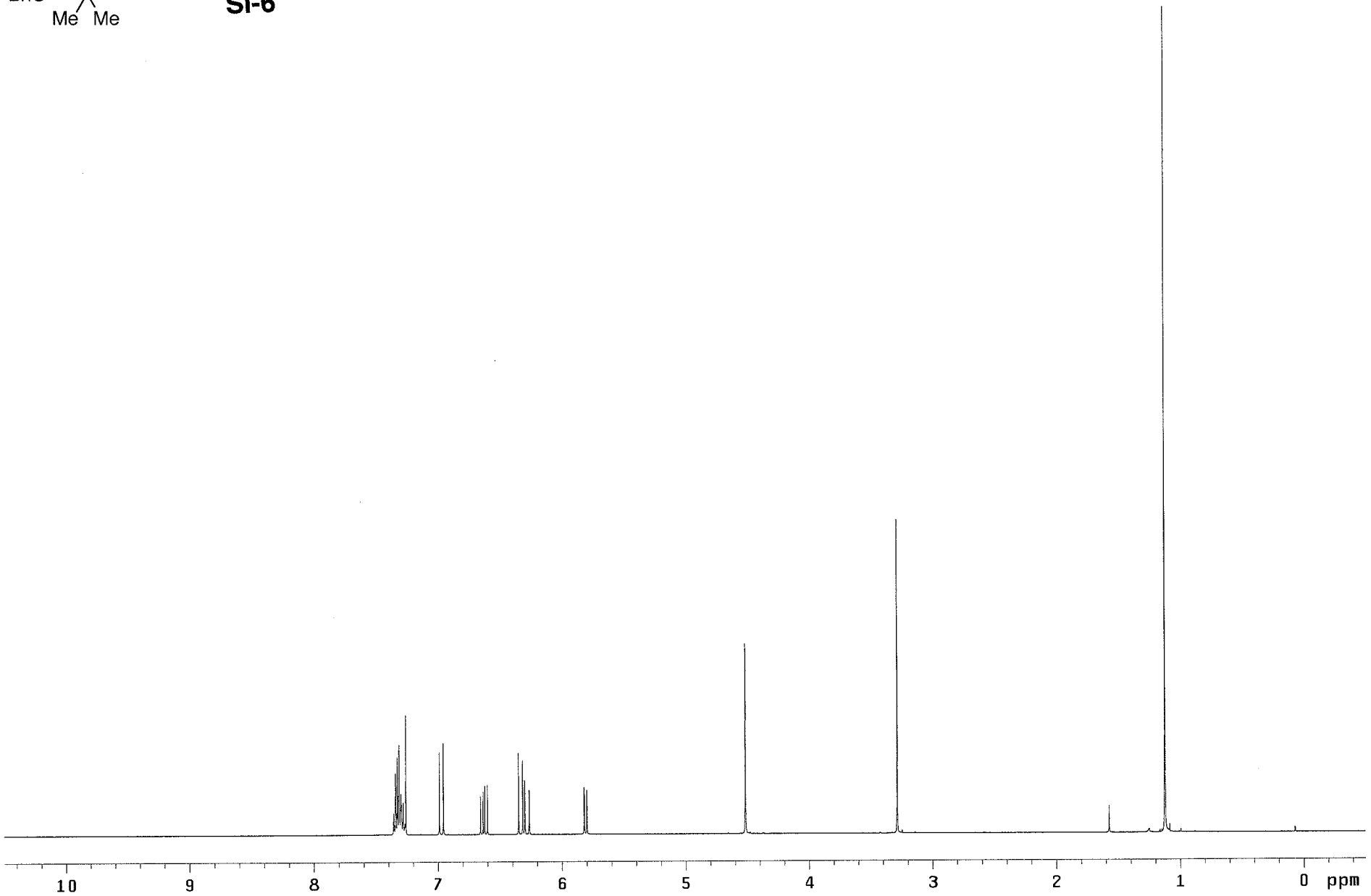


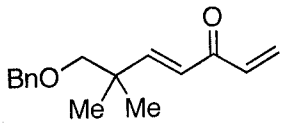
SI-5





SI-6





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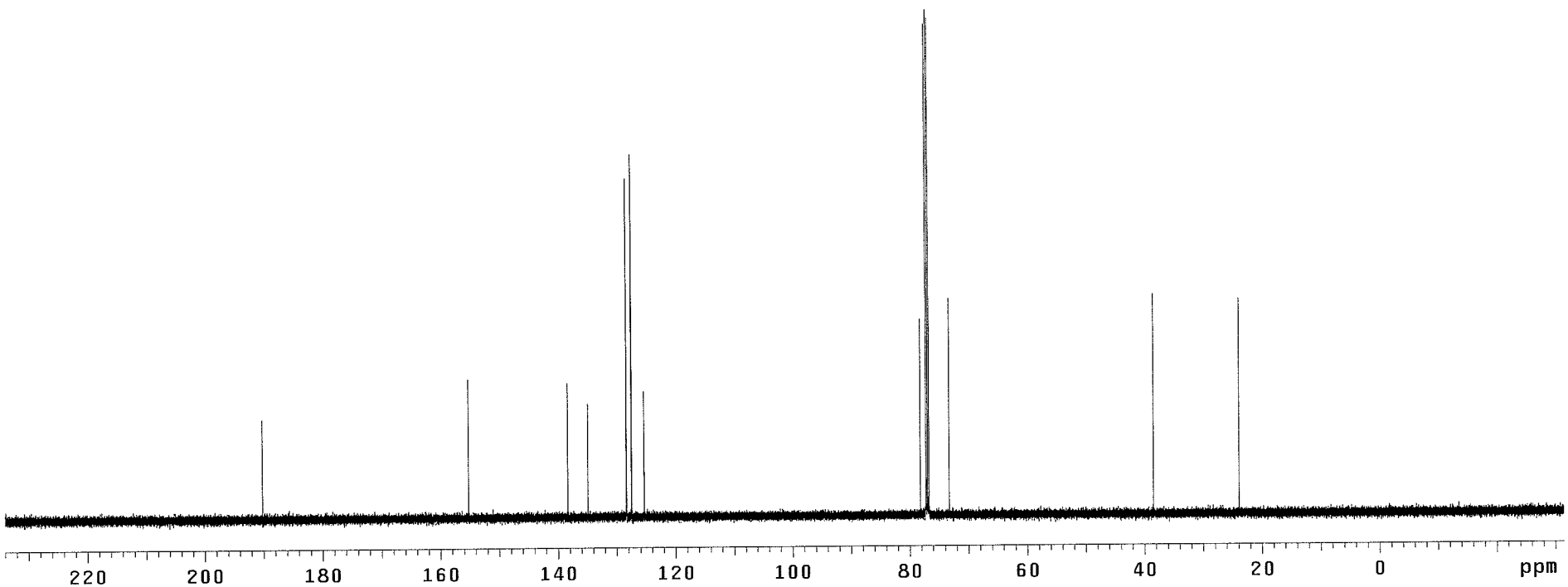

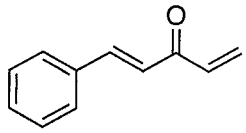

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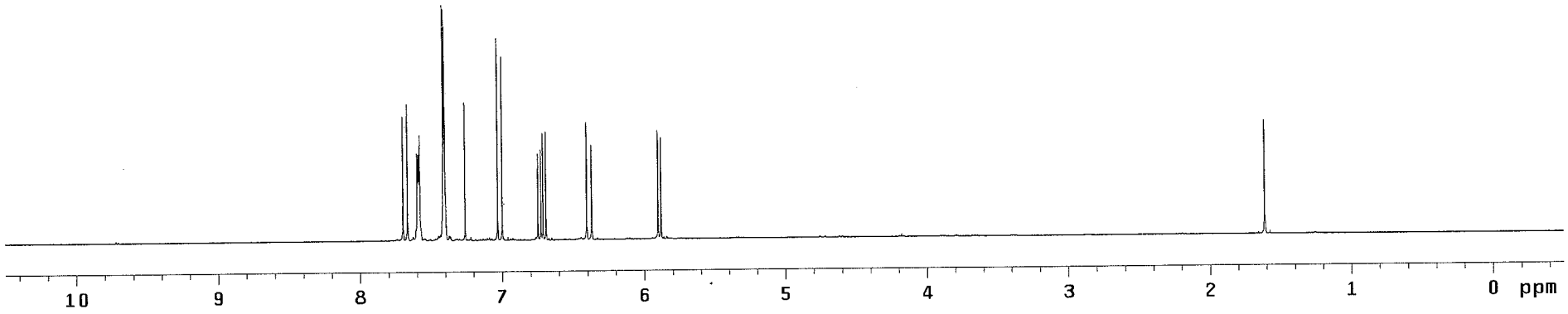

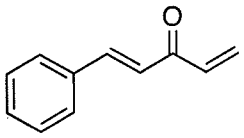

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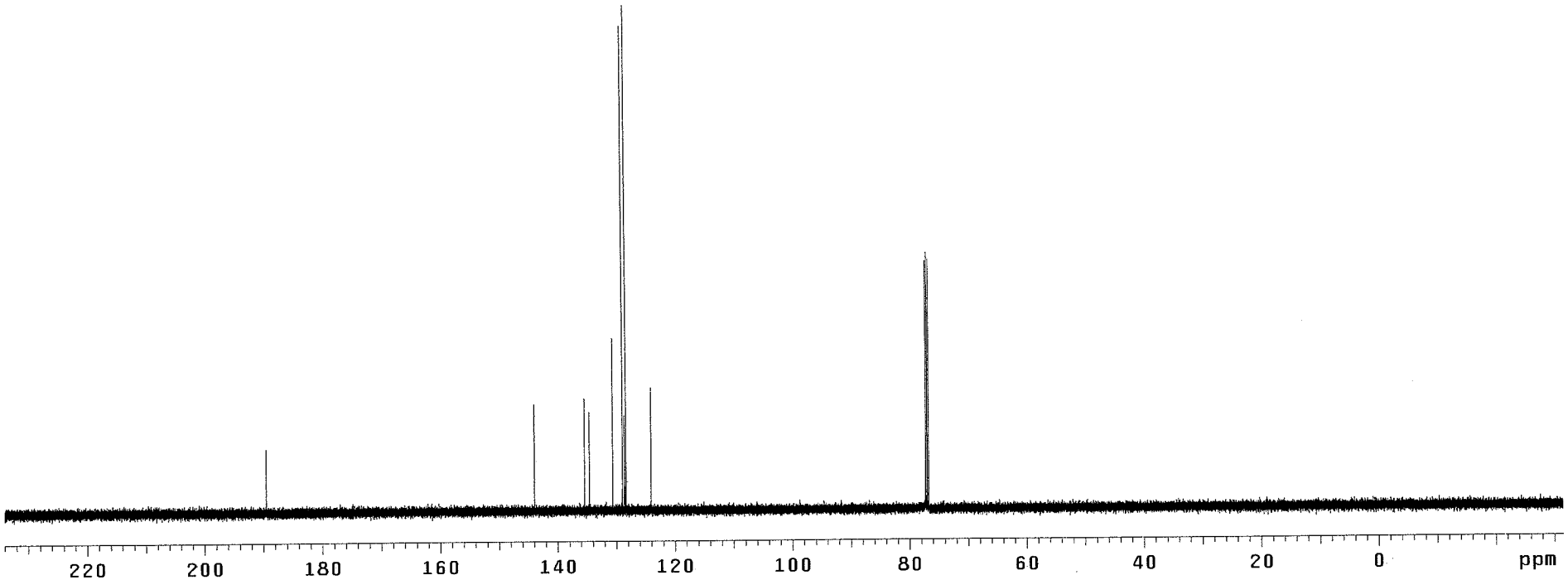
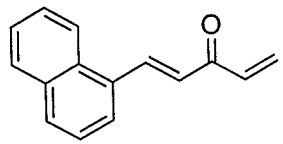
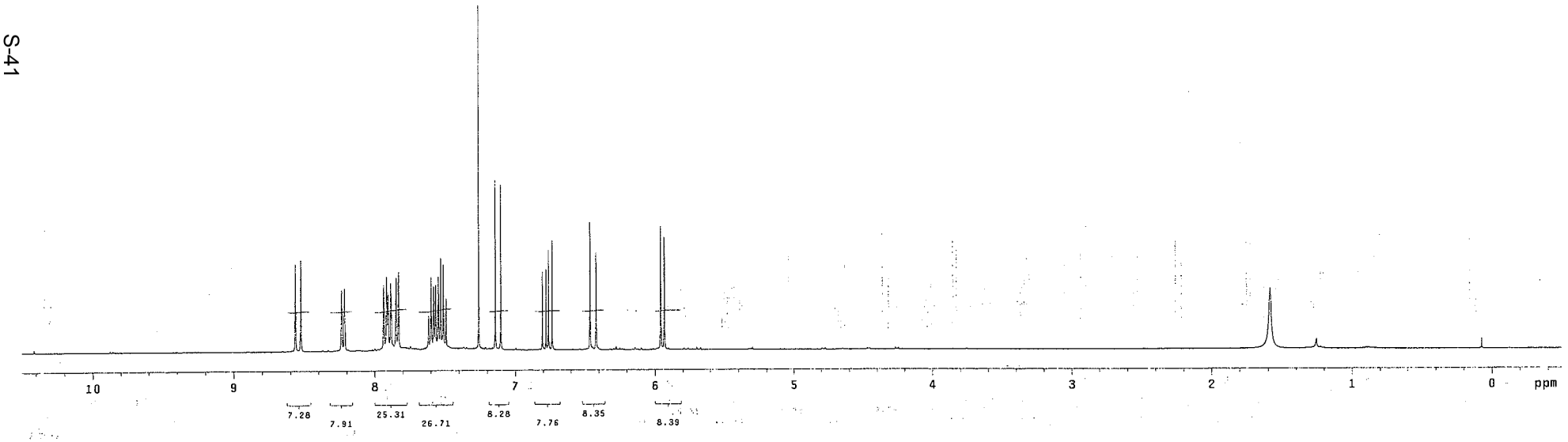
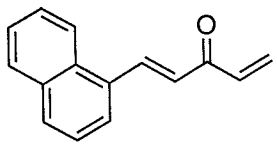


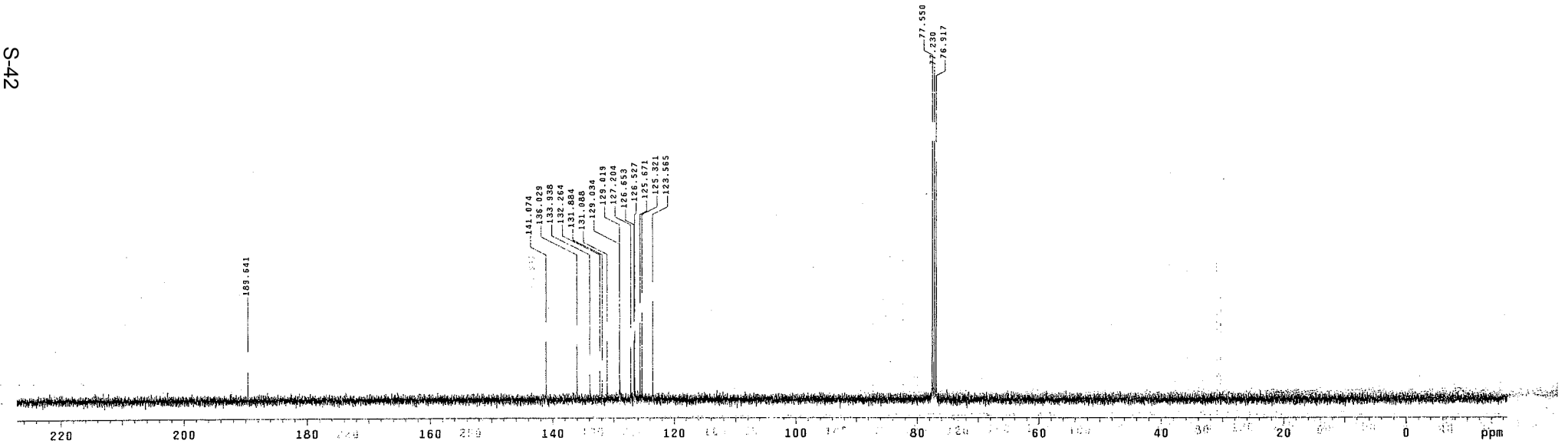


SI-8





SI-8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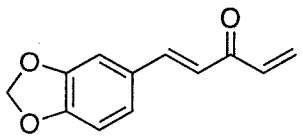

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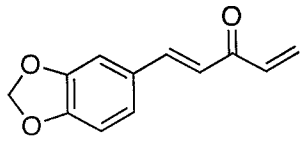

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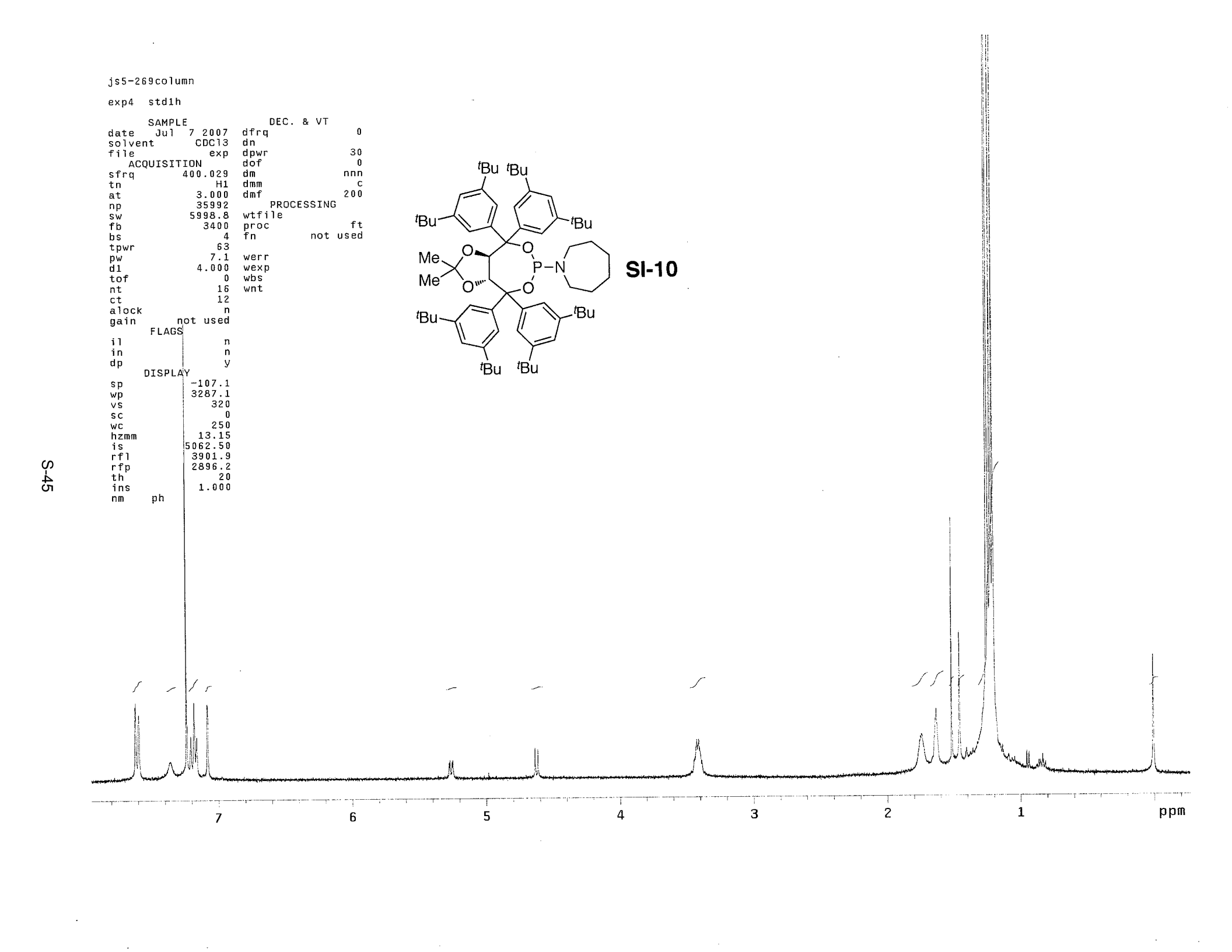
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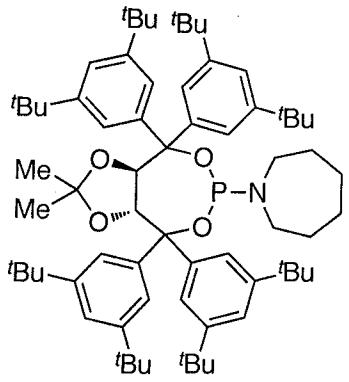
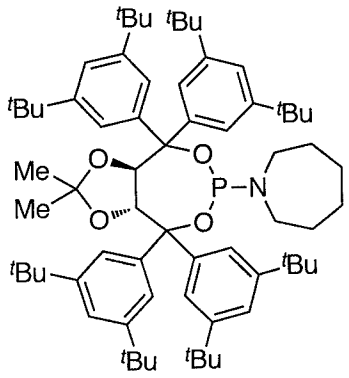
tpwr 63
pw 7.1
d1 4.000
tof 0
nt 16
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -107.1
wp 3287.1
vs 320
sc 0
wc 250
hzmm 13.15
is 5062.50
rfl 3901.9
rfp 2896.2
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 0
dn
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
tBu
Me
O
P
N
SI-10
7
6
5
4
3
2
1
ppm

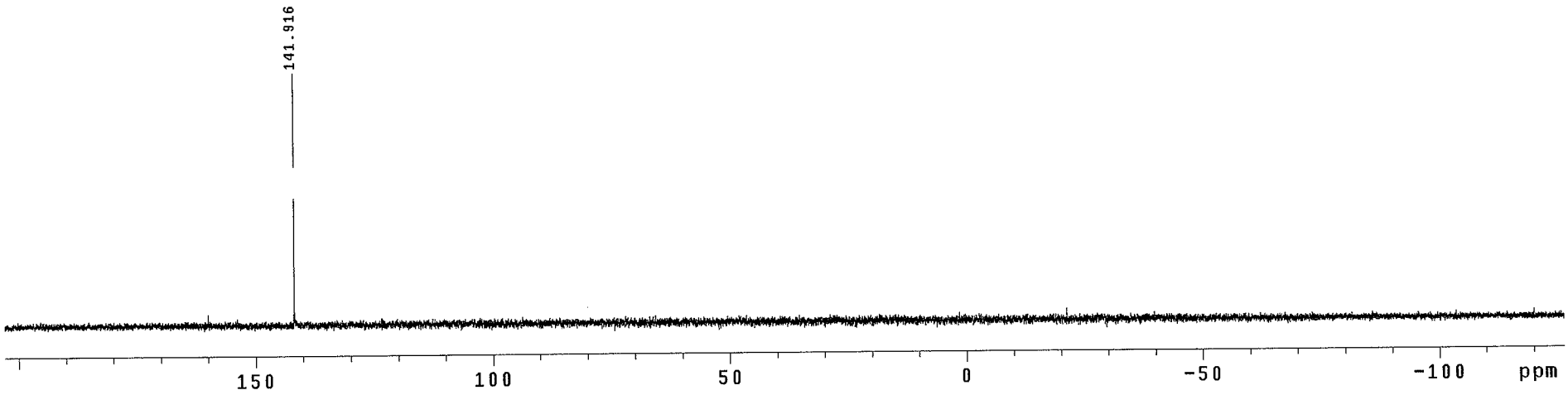

tBu
tBu
tBu
tBu
Me
Me
O
O
O
P
N
O
tBu
tBu
tBu
tBu

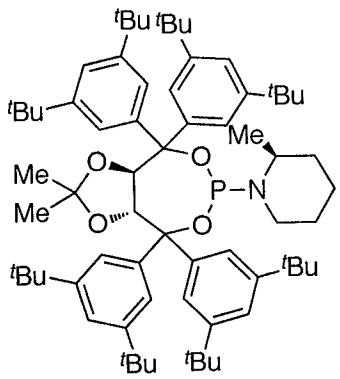
SI-10

220
200
180
160
140
120
100
80
60
40
20
0
ppm


tBu
tBu
tBu
tBu
Me
Me
O
O
O
O
P
N
tBu
tBu
tBu
tBu

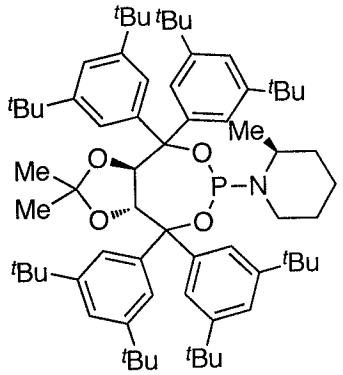
SI-10


141.916
150
100
50
0
-50
-100
ppm

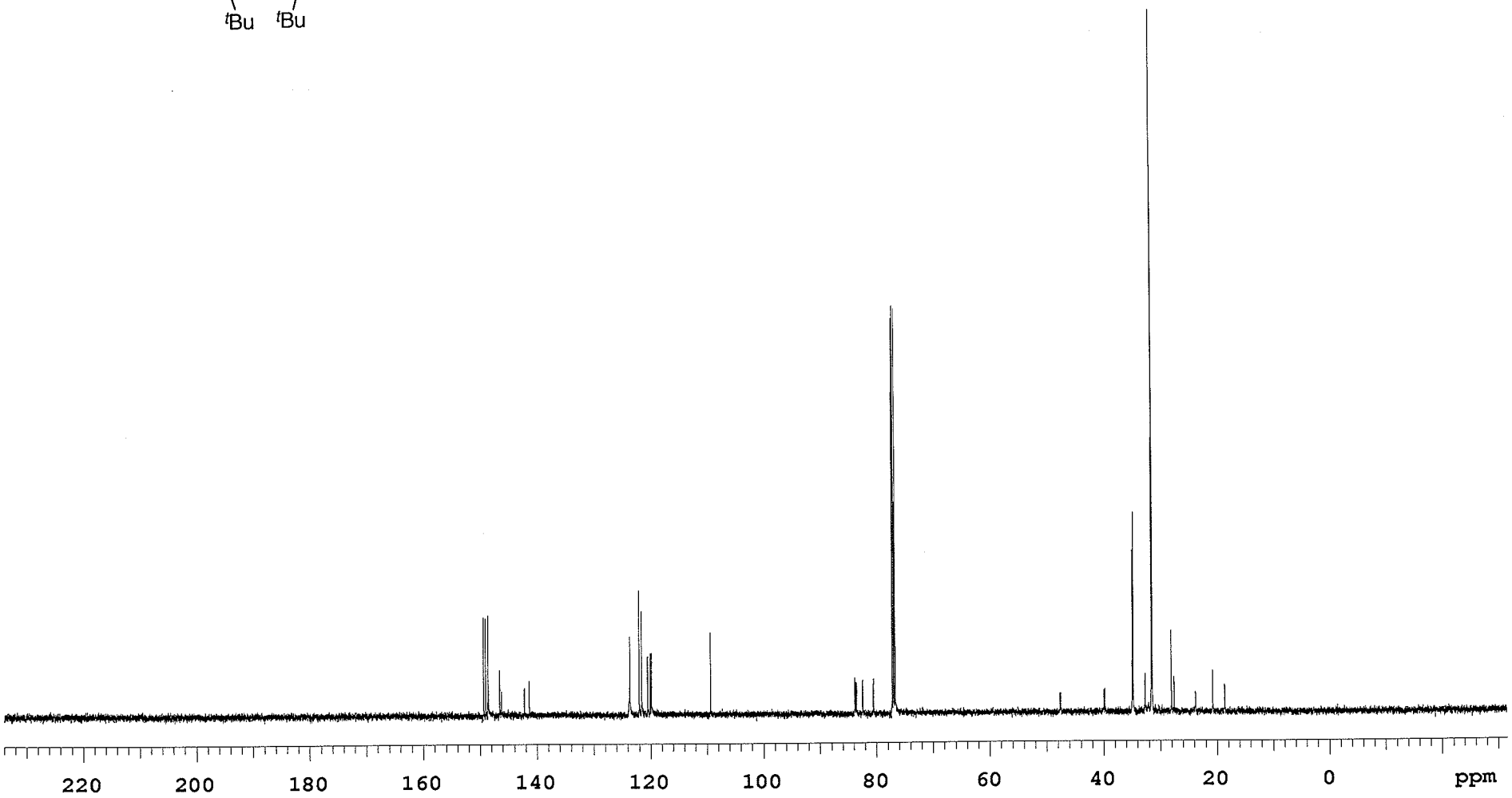

tBu
tBu
tBu
tBu
Me
O
O
Me
P
N
Me
O
O
tBu
tBu
tBu
tBu

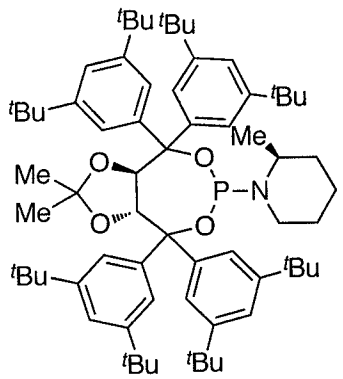
SI-11

10
9
8
7
6
5
4
3
2
1
0
ppm


tBu tBu
tBu
tBu
Me
O
O
P–N
Me
Me
O
O
tBu
tBu
tBu
tBu

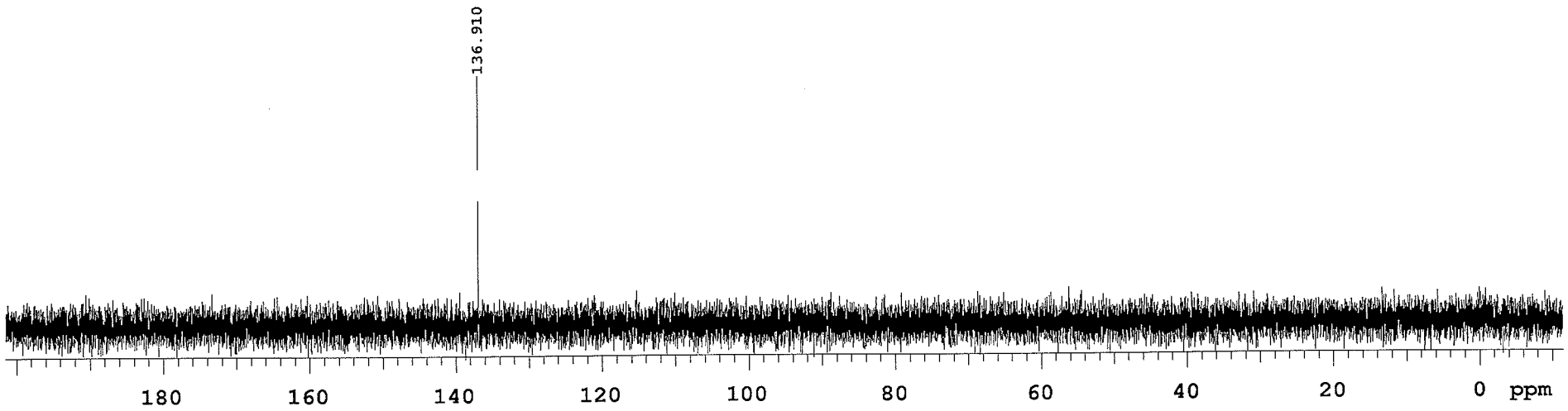
SI-11

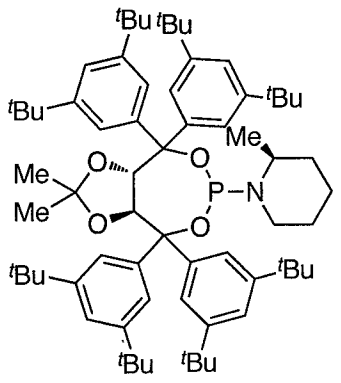

220
200
180
160
140
120
100
80
60
40
20
0
ppm


tBu
tBu
tBu
tBu
Me
Me
Me
O
O
P
N
O
O
tBu
tBu
tBu
tBu

SI-11

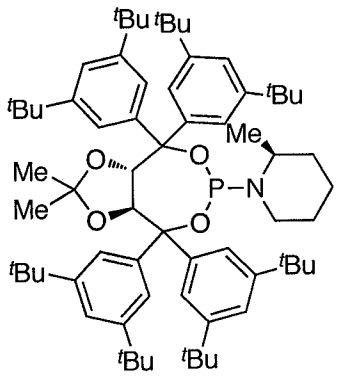
VARIAN


136.910
180
160
140
120
100
80
60
40
20
0
ppm


tBu tBu
tBu
tBu
Me
Me
Me
O
O
P–N
O
O
tBu
tBu
tBu
tBu

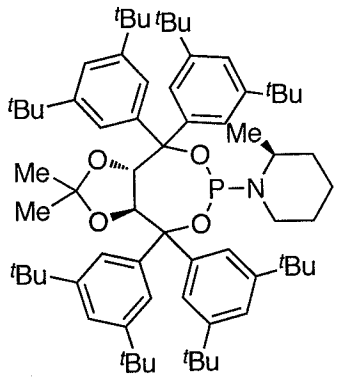
SI-12

10
9
8
7
6
5
4
3
2
1
ppm

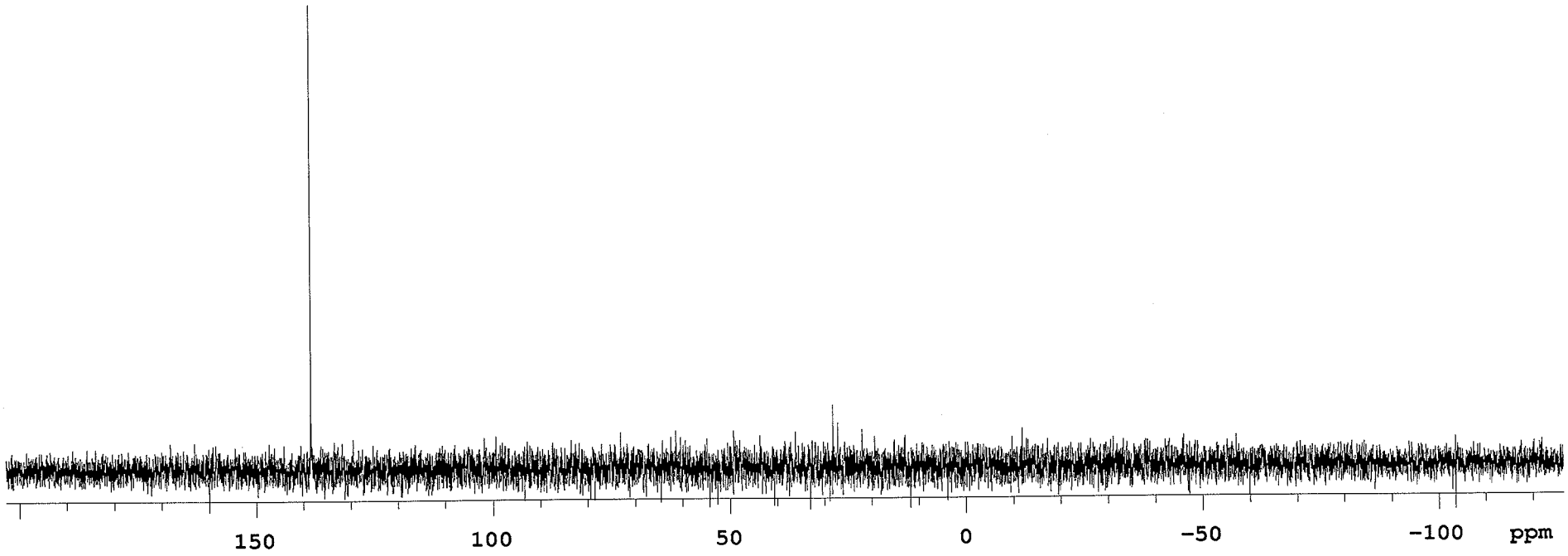

tBu
tBu
tBu
tBu
Me
Me
Me
O
O
O
O
P
N
tBu
tBu
tBu
tBu

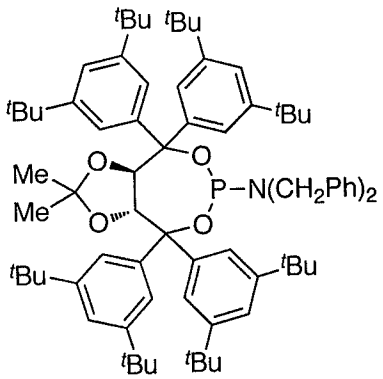
SI-12

220
200
180
160
140
120
100
80
60
40
20
0
ppm


tBu
tBu
tBu
tBu
Me
O
O
P–N
Me
Me
O
O
tBu
tBu
tBu
tBu

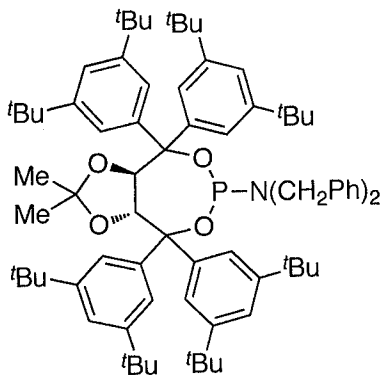
SI-12


150
100
50
0
−50
−100
ppm


tBu
tBu
tBu
tBu
Me
Me
O
O
O
O
P–N(CH2Ph)2
tBu
tBu
tBu
tBu

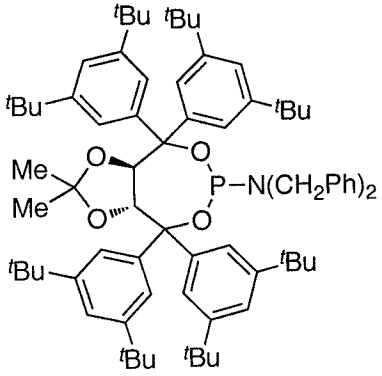
SI-13

10
9
8
7
6
5
4
3
2
1
ppm

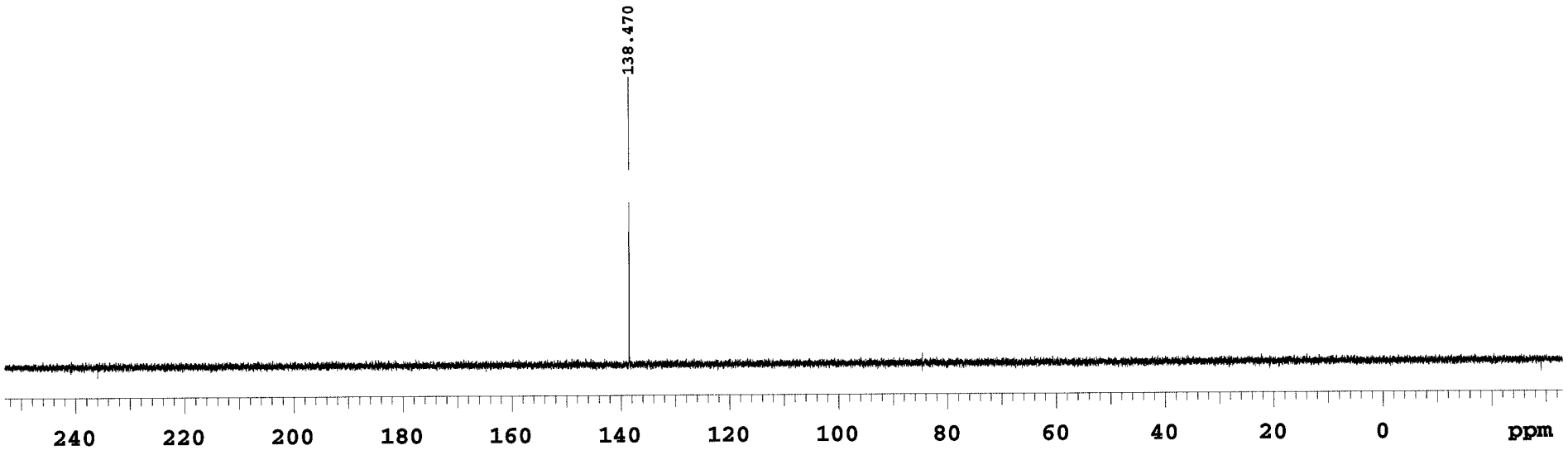

tBu
tBu
tBu
tBu
Me
Me
O
O
O
O
P–N(CH2Ph)2
tBu
tBu
tBu
tBu

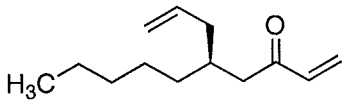
SI-13

220
200
180
160
140
120
100
80
60
40
20
0
ppm

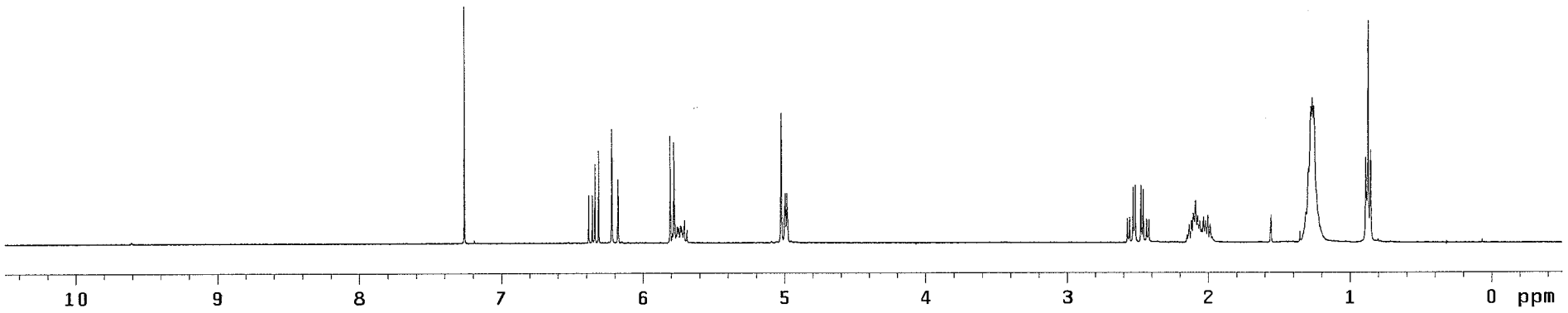

tBu
tBu
tBu
tBu
Me
Me
O
O
O
O
P–N(CH2Ph)2
tBu
tBu
tBu
tBu

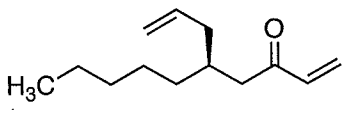
SI-13


138.470
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

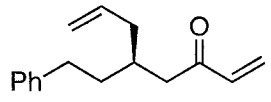


SI-14

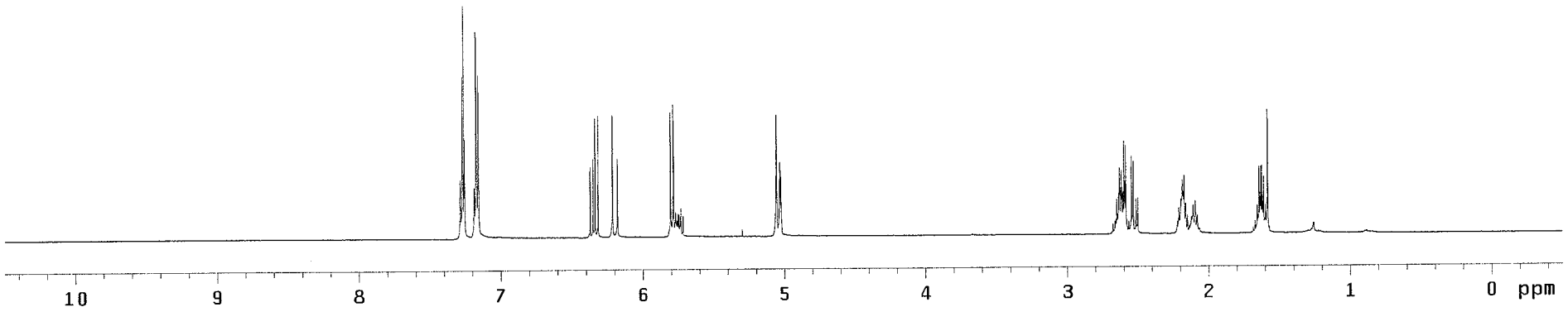


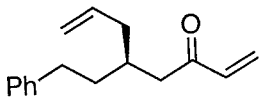


SI-14

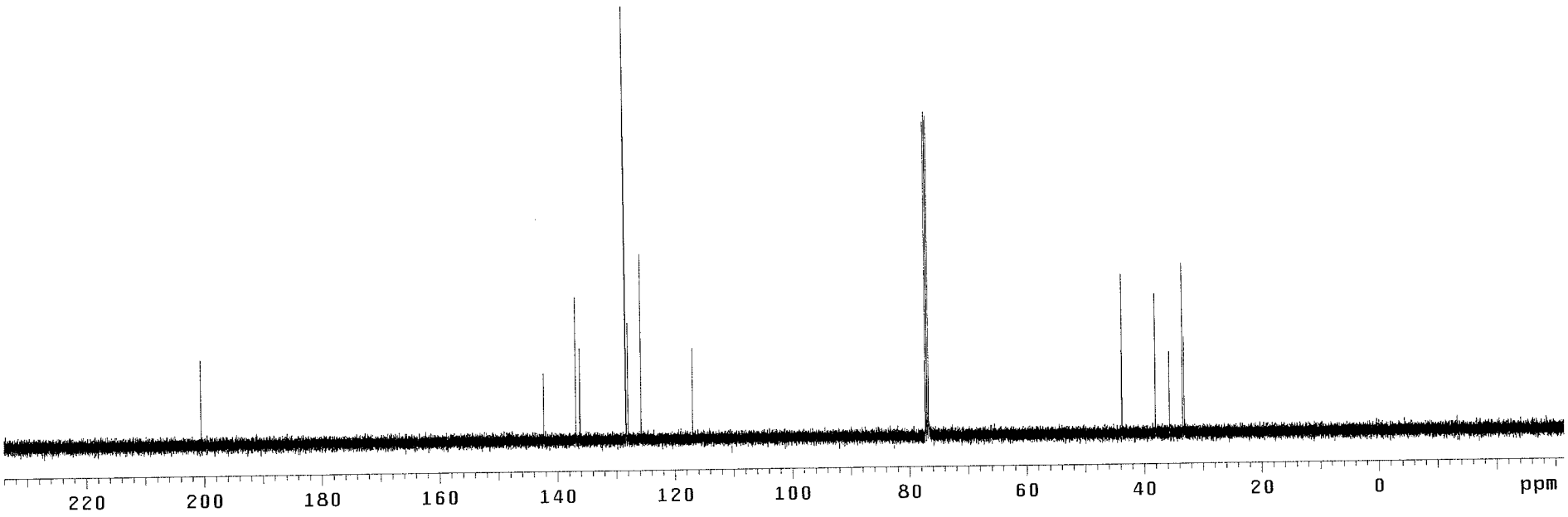


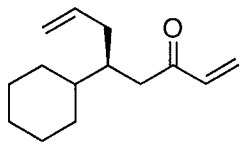
SI-15



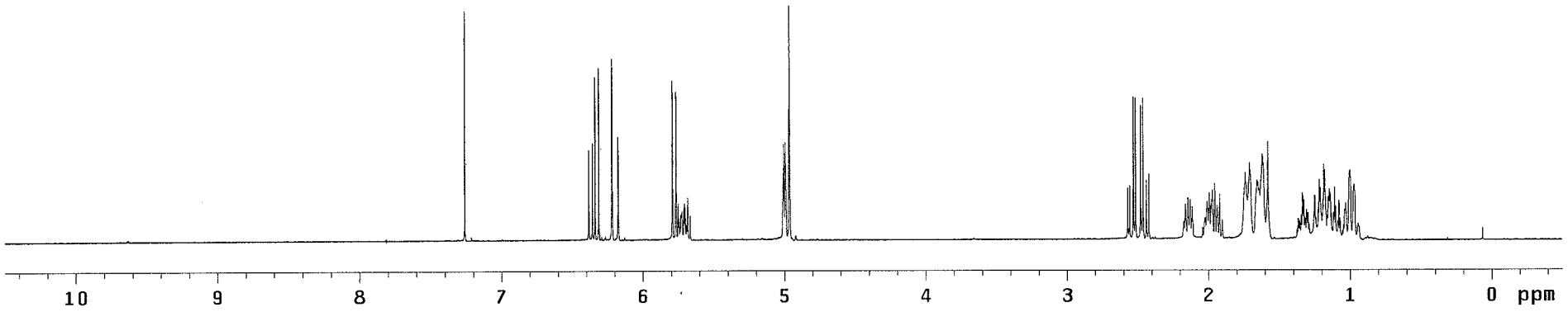


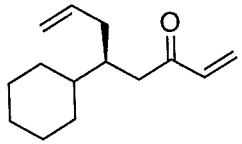
SI-15



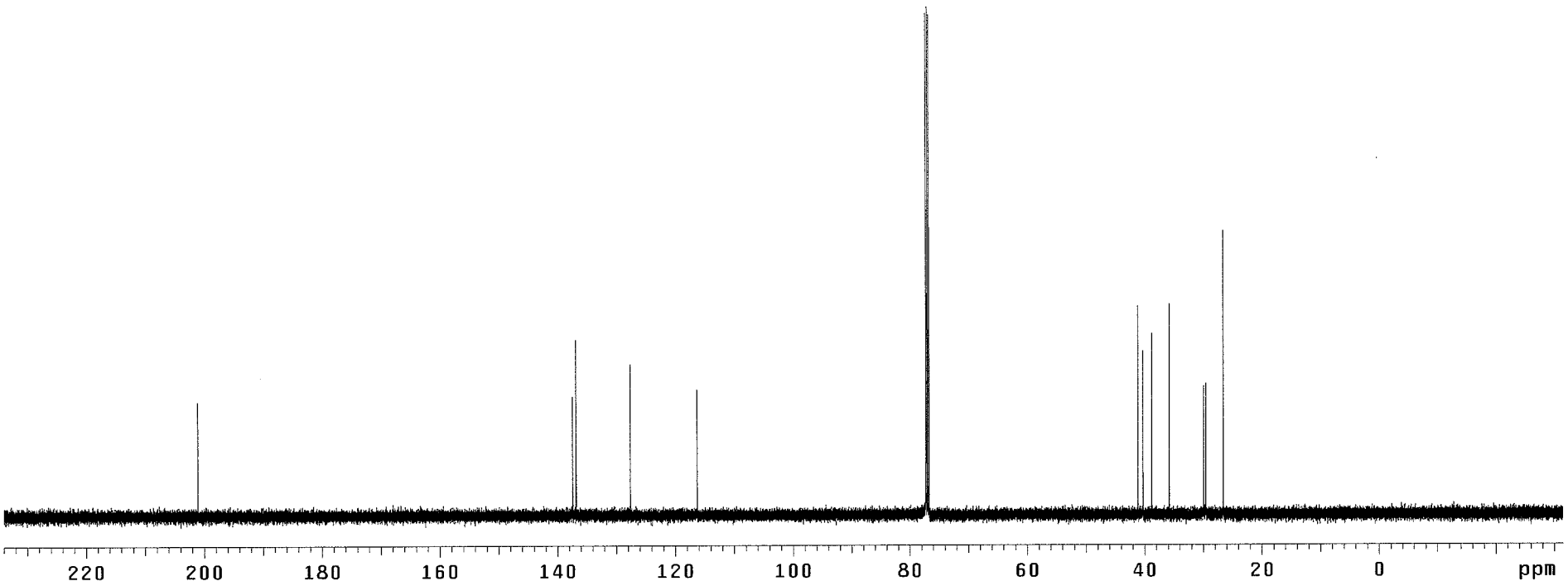


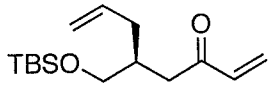
SI-16



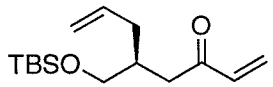


SI-16

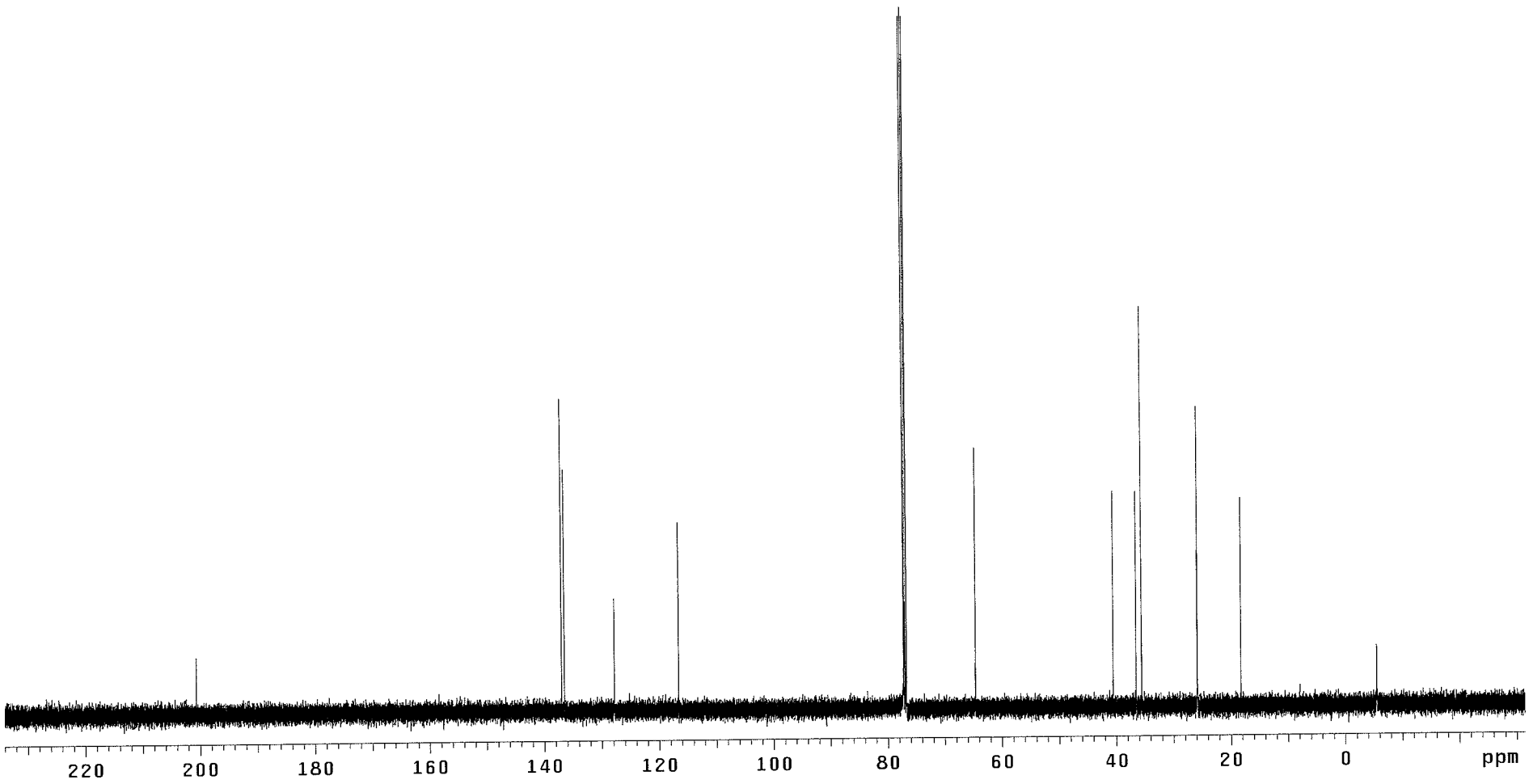


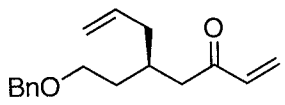


SI-17

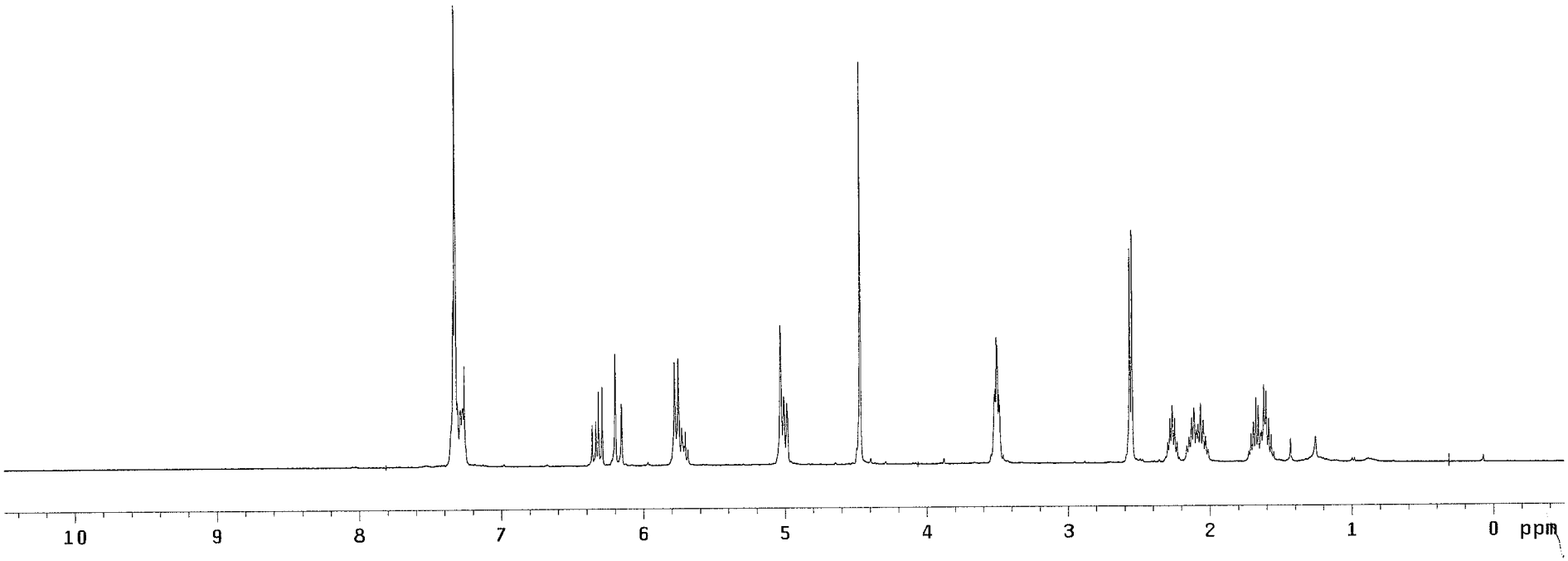


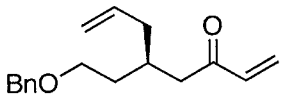
SI-17



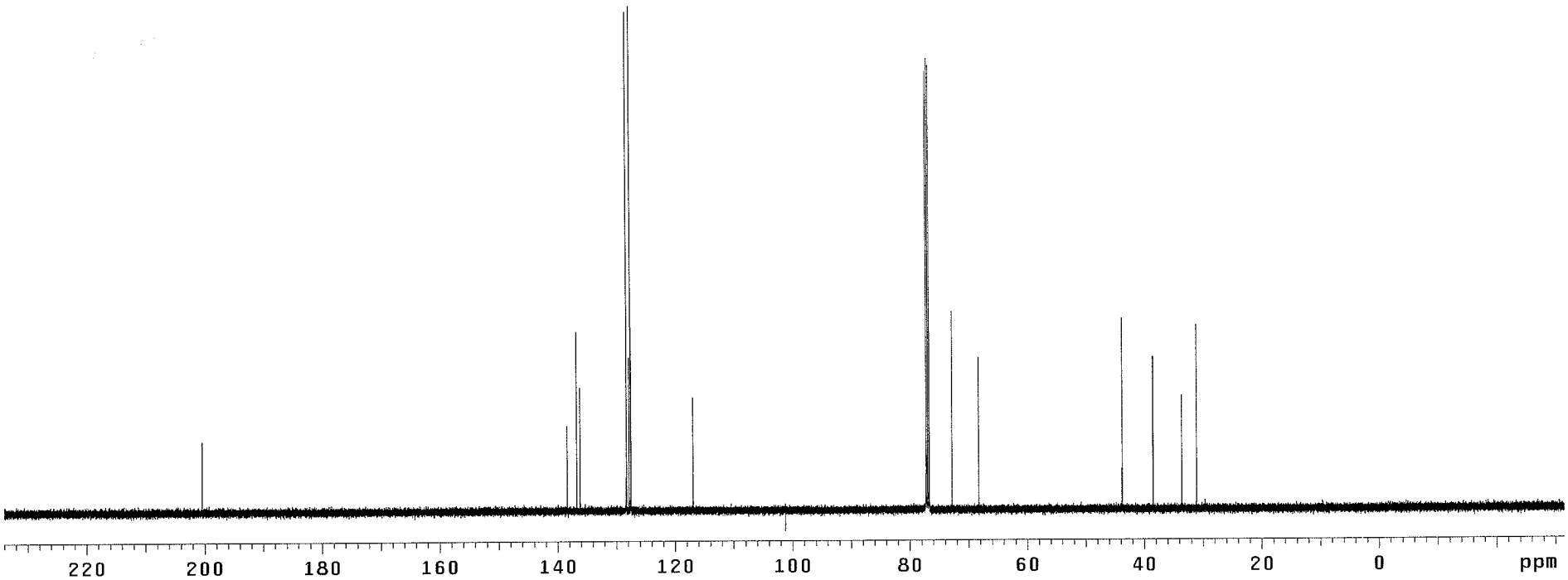


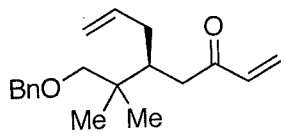
SI-18



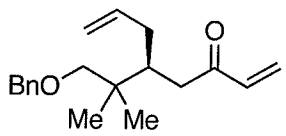


SI-18

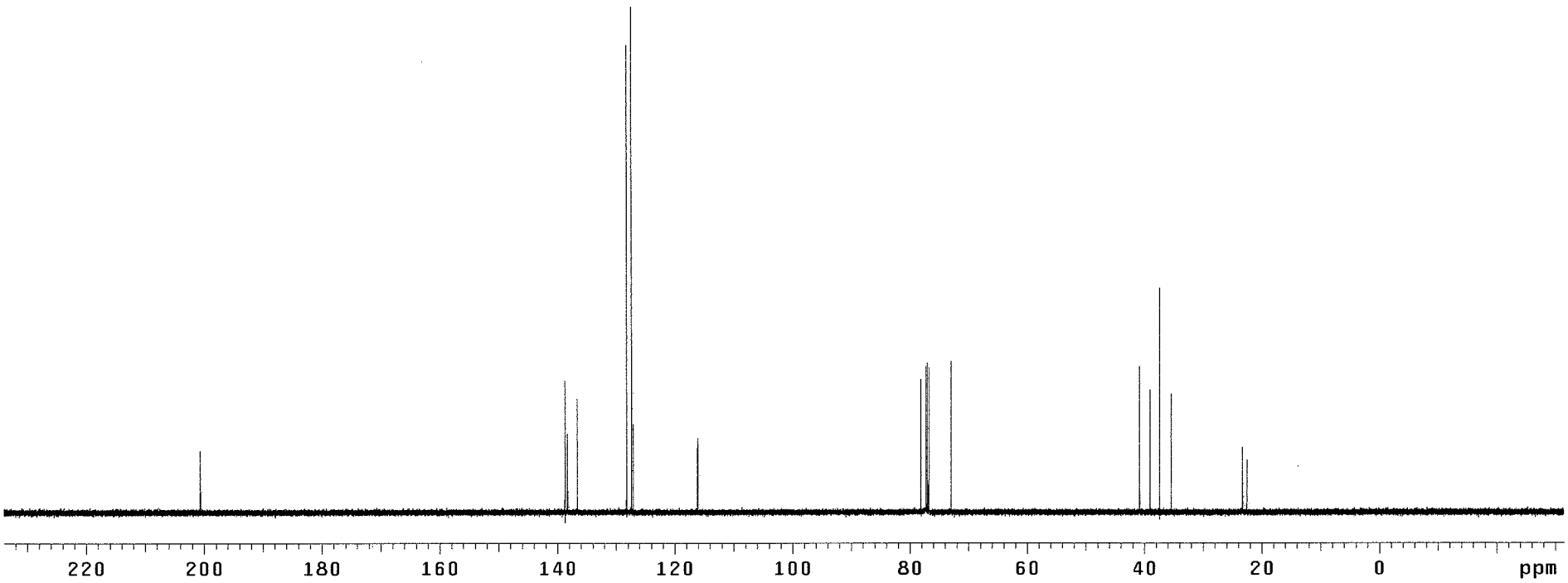


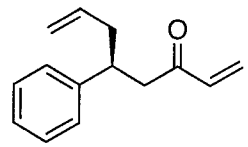


SI-19

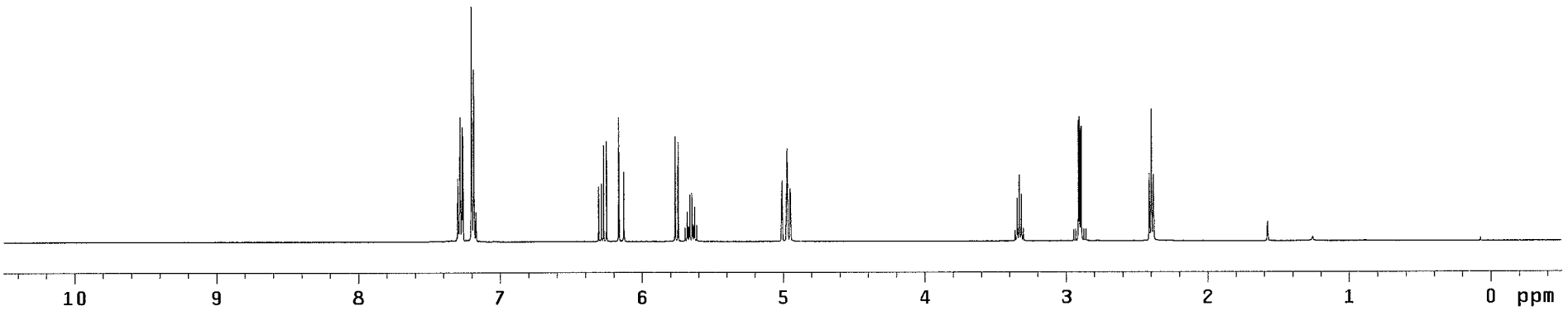


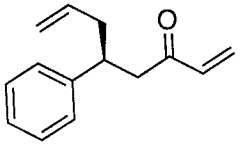
SI-19



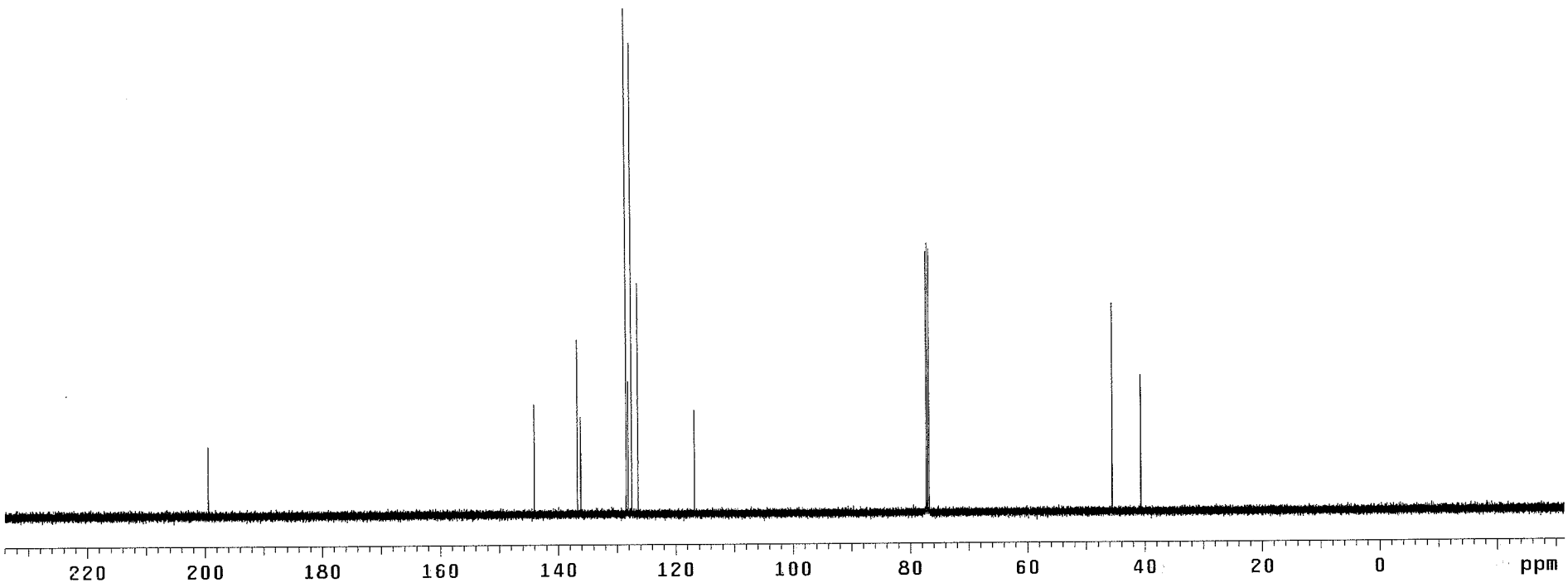


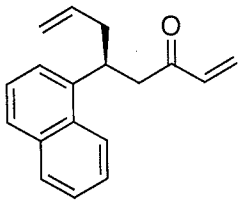
SI-20



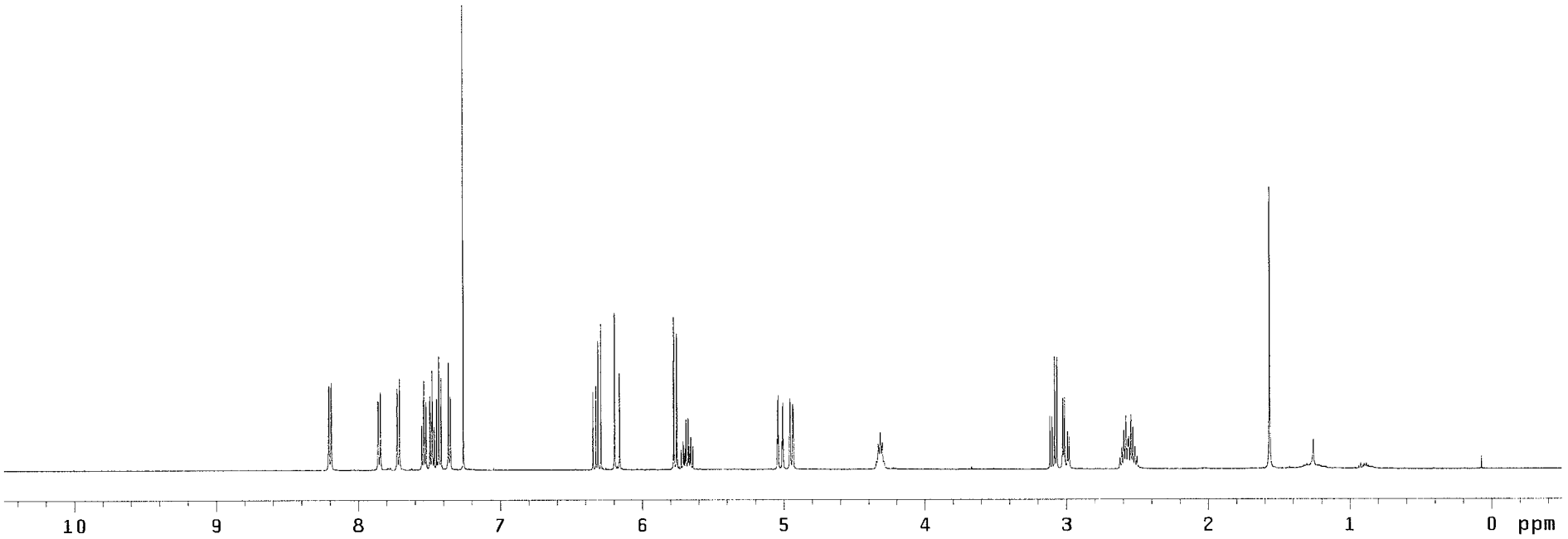


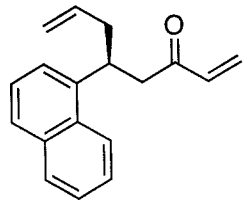
SI-20



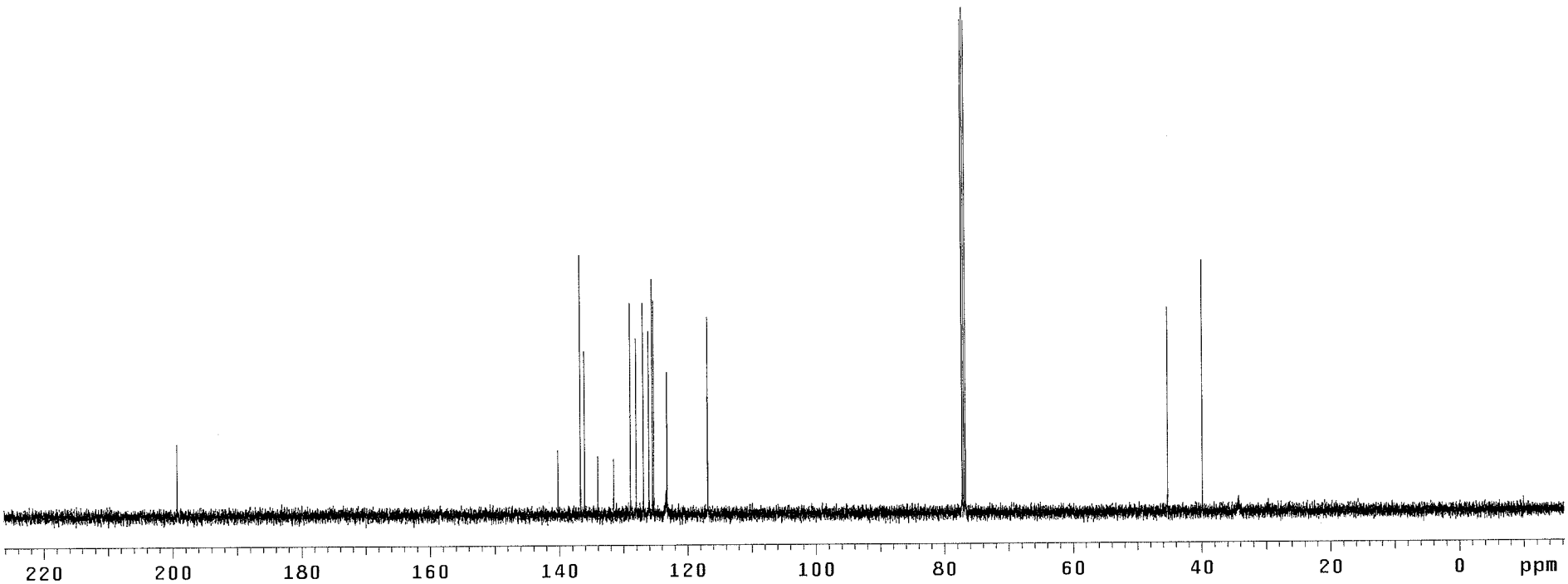


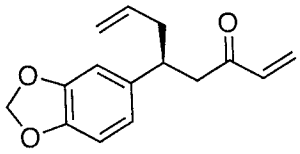
SI-21



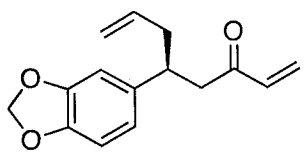


SI-21

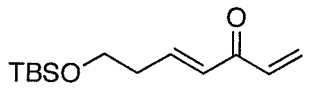




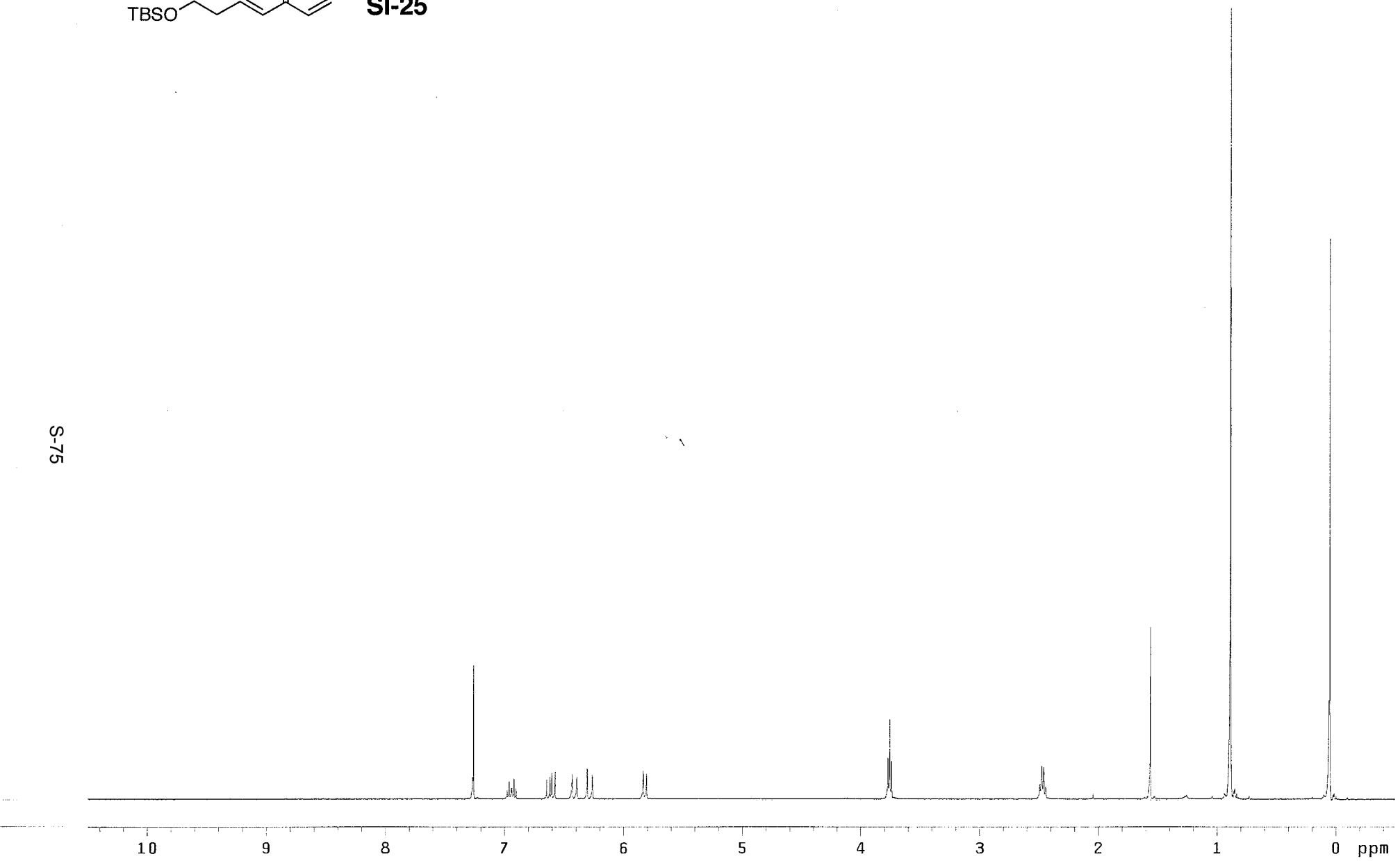
SI-22

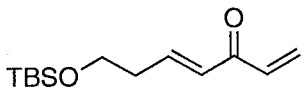


SI-22

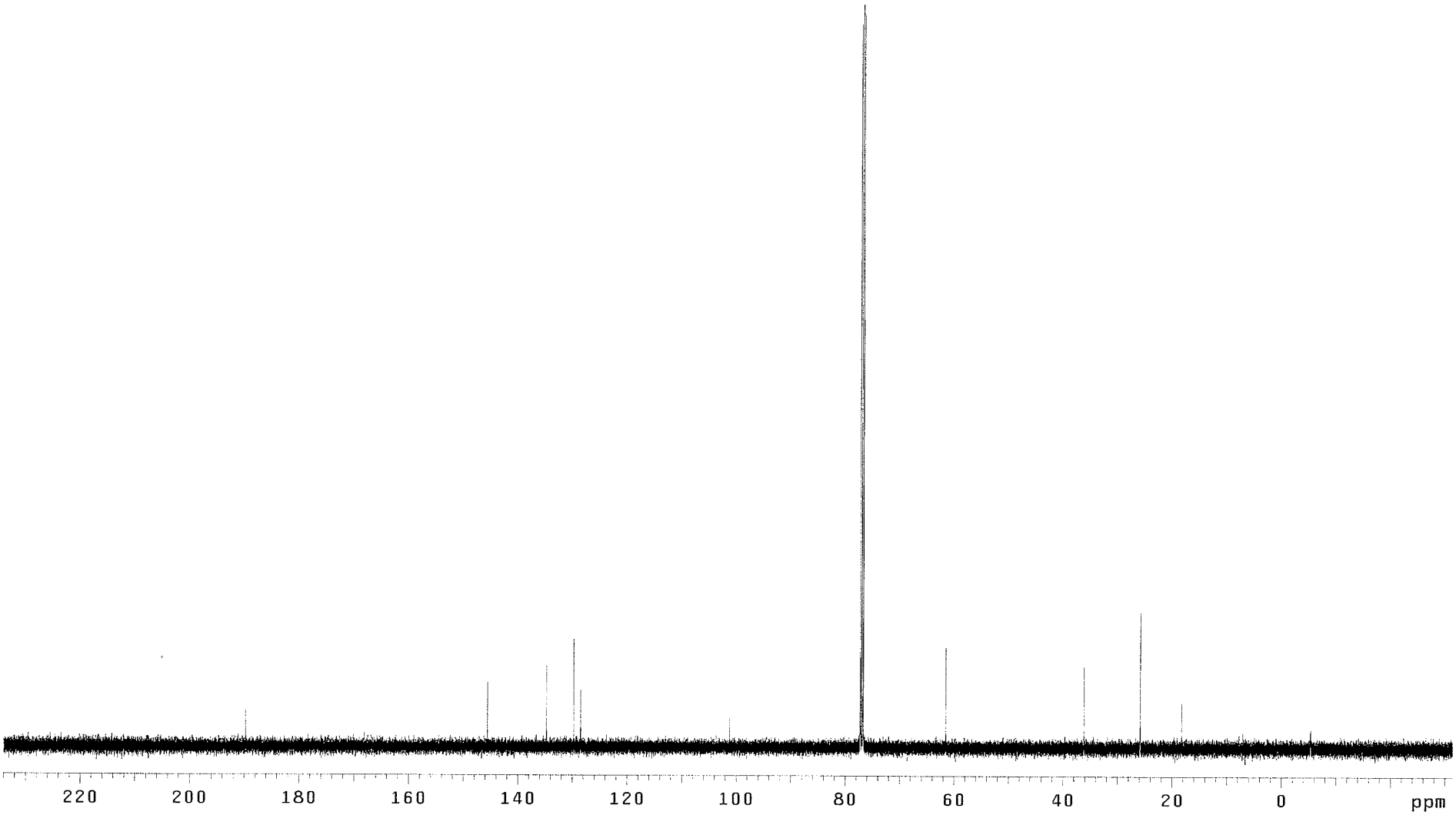


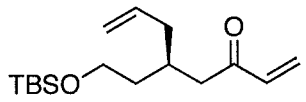
SI-25



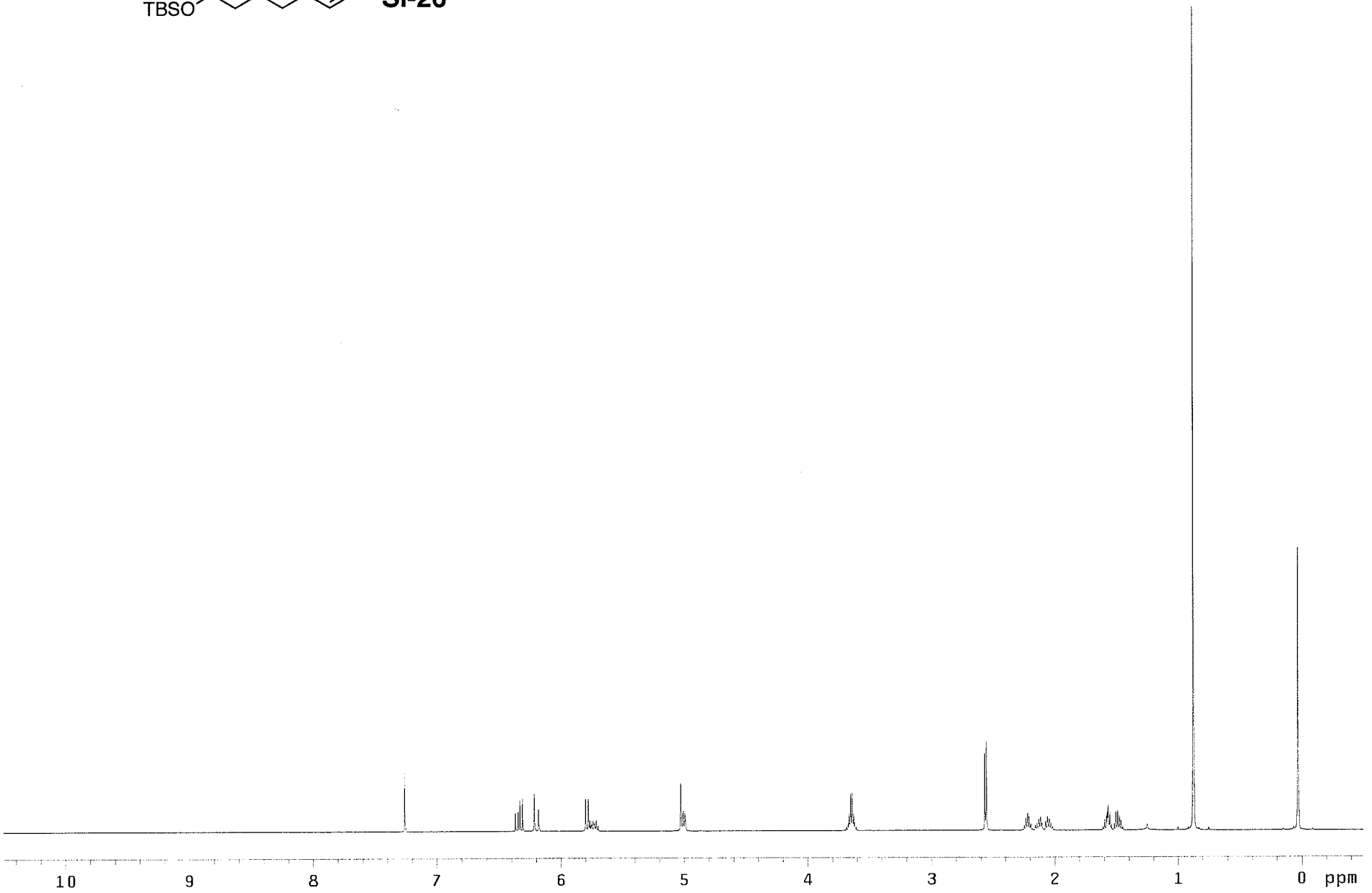


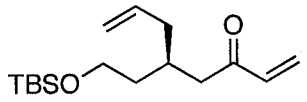
SI-25





SI-26





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