

## A Stereoselective Synthesis of Dienes from *N*-Allylhydrazones

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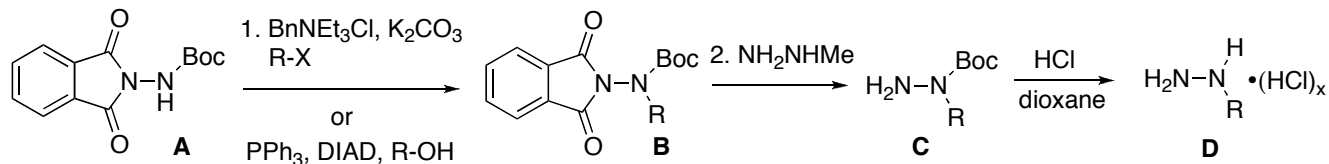
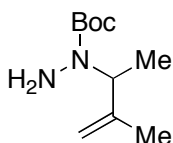
### Supporting Information

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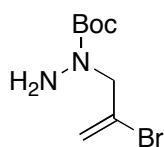
**General Information.** All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. Acetonitrile, THF and CH<sub>2</sub>Cl<sub>2</sub> were purified by passage through a bed of activated alumina.<sup>1</sup> 1,2-Dichloroethane was used as supplied by Aldrich. Reagents were purified prior to use unless otherwise stated following the guidelines of Armarego and Chai.<sup>2</sup> Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh) or silver nitrate-impregnated silica gel, prepared according to Li and coworkers.<sup>3</sup> Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde, ceric ammonium nitrate stain or potassium permanganate followed by heating. Film infrared spectra were recorded using a BioRad Excalibur and a BioRad FTS-60. Diamond infrared spectra were recorded using a Thermo Mattson ATR. <sup>1</sup>H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) or Inova 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 7.26 ppm) or tetramethylsilane (0.00 ppm). Two-dimensional NMR experiments were run on a Bruker Avance III 500 (500 MHz). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; integration; coupling constant(s) in Hz. Proton-decoupled <sup>13</sup>C-NMR spectra were recorded on a Varian Inova 500 (125 MHz) or Inova 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 77.00 ppm). Mass spectra data were obtained on a Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.

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1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.
  2. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; 5th Ed., Butterworth-Heinemann, 2003.
  3. Li, T. S.; Li, J. T.; Li, H. Z. *Journal of Chromatography A*, **1995**, 715, 372–375

## A. Synthesis of Hydrazine Derivatives

Scheme S1: Outline of *N*-Allylhydrazine Preparation**tert-Butyl****1-((3-methylbut-3-en-2-yl)hydrazinecarboxylate:**

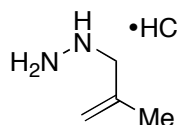
Diisopropylazodicarboxylate (5.50 mL, 28.6 mmol) was added dropwise to a stirred solution of 3-methylbut-3-en-2-ol (2.46 g, 28.6 mmol), *tert*-butyl 1,3-dioxoisindolin-2-ylcarbamate (**A**, 5.00 g, 19.1 mmol) and triphenylphosphine (7.50 g, 28.6 mmol) in THF (286 mL) at 0 °C. When the reaction was complete as determined by TLC (5 h), the solvent was removed under vacuum to afford an oily residue. Purification by flash chromatography on silica gel using 10% EtOAc in hexanes afforded the alkylated derivative **B** (4.44 g, 70%). The alkylated derivative **B** (4.70 g, 14.2 mmol) was dissolved in THF (71 mL) and treated with methylhydrazine hydrate (0.88 mL, 28.5 mmol) at 0 °C. The reaction was then allowed to warm to room temperature and stirred for 2 days, at which point all of the starting material was consumed and a white precipitate had formed. The reaction mixture was filtered over a pad of celite and the collected filtrate concentrated under reduced pressure to yield an oil that was further purified by flash chromatography on silica gel in 20% EtOAc/Hexanes. The isolated alkylated hydrazine derivative required additional purification. It was dissolved in EtOAc (250 mL) and extracted with 1.0 M HCl (3 x 150 mL). The acidic aqueous layers were adjusted to pH 10 by addition of 5.0 M NaOH. The basic solution was then extracted with EtOAc (3 x 100 mL). The combined organic extracts were diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded title compound **C** as a yellow oil (1.33 g, 47%): IR (film) 2976, 1690, 1388, 1123 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 4.92 (s, 1H); 4.84 (s, 1H); 4.55 (s, 1H); 3.55 (bs, 1H); 1.70 (s, 3H); 1.48 (s, 9H); 1.29 (d, 3H, *J* = 6.7 Hz); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) δ 145.5, 111.8, 80.8, 28.7, 21.0, 15.9; HRMS (EI): Exact mass calcd for C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> [M-C<sub>4</sub>H<sub>8</sub>]<sup>+</sup>, 144.0893. Found 144.0887.

**tert-Butyl 1-(2-bromoallyl)hydrazinecarboxylate:**

2,3-Dibromopropene (3.70 mL, 38.1 mmol) was added to a stirred suspension of *tert*-butyl 1,3-dioxoisindolin-2-ylcarbamate (**A**, 5.00 g, 19.1 mmol), K<sub>2</sub>CO<sub>3</sub> (10.5 g, 76.3 mmol) and benzyltriethylammonium chloride (87 mg, 3.8 mmol) in MeCN (80 mL) at room temperature. When the reaction was complete as determined by TLC (36 h), the mixture was diluted with water (75 mL) and brine solution (75 mL) and extracted with Et<sub>2</sub>O (3 x 75 mL). The organic layers were combined, diluted with hexanes (20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration under reduced pressure afforded alkylated derivative **B**, which did not require further purification. Alkylated derivative **B** (7.20 g, 19.1 mmol) was diluted in THF (125 mL) and treated with methylhydrazine hydrate (2.00 mL, 38.1 mmol) at 0 °C. After 36 h at room temperature, all starting material had been consumed and a white precipitate had formed. The mixture was filtered over a pad of celite and the collected filtrate concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel with 10% EtOAc in hexanes, which afforded title compound **C** (4.1 g, 85% over two steps): IR (diamond) 2976, 1693, 1387, 893 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 5.71 (s, 1H); 5.57 (s, 1H); 4.22 (s, 2H); 4.04 (bs, 2H); 1.47 (s, 9H); <sup>13</sup>C NMR (100 MHz,

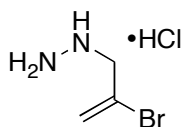
$\text{CDCl}_3$ )  $\delta$  130.0, 118.1, 81.5, 58.8, 28.5; HRMS (EI): Exact mass calcd for  $\text{C}_4\text{H}_7\text{N}_2\text{O}_2\text{Br}$   $[\text{M}-\text{C}_4\text{H}_8]^+$ , 193.9685. Found 193.9682.

## B. Synthesis of *N*-Allylhydrazine Hydrochloride Salts



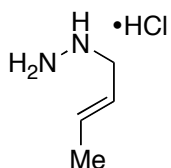
### (2-Methylallyl)hydrazine hydrochloride (**12a**):

A 4 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(2-methylallyl)hydrazinecarboxylate (279 mg, 1.50 mmol) and allowed to stir for 4 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12a** which did not require purification: IR (diamond) 2946, 1411, 1201, 868  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ) 6.01 (h, 1H,  $J$  = 6.6 Hz); 5.58 (m, 2H); 3.67 (d, 2H,  $J$  = 7.3 Hz); 1.74 (d, 3H,  $J$  = 5.5 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  136.9, 119.9, 52.9, 17.1; HRMS (ESI): Exact mass calcd for  $\text{C}_4\text{H}_{11}\text{N}_2$   $[\text{M}]^+$ , 86.0844. Found 86.0829.



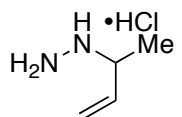
### (2-Bromoallyl)hydrazine hydrochloride (**12b**):

A 4 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(2-bromoallyl)hydrazinecarboxylate (377 mg, 1.50 mmol) and allowed to stir for 4 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12b** which did not require purification: mp (decomp.) 124–127  $^\circ\text{C}$ ; IR (film) 3054, 2985, 1420, 1265, 895, 736, 705  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ) 6.06 (s, 1H); 5.74 (s, 1H); 4.96 (b s, 4H); 3.80 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  126.6, 121.5, 57.5; HRMS (ESI): Exact mass calcd for  $\text{C}_3\text{H}_8\text{BrN}_2$   $[\text{M}]^+$ , 149.9793. Found 149.9794.



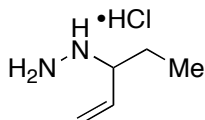
### (*E*)-But-2-enylhydrazine hydrochloride (**12c**):

A 4 M solution of HCl in dioxane (2.0 mL) was added to (*E*)-*tert*-butyl 1-(but-2-enyl)hydrazinecarboxylate (279 mg, 1.50 mmol) and allowed to stir for 4 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12c** which did not require purification: IR (film) 3252, 968, 851  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) 6.03 (m, 1H); 5.67 (m, 1H); 3.64 (d, 2H,  $J$  = 6.8 Hz); 1.76 (d, 3H,  $J$  = 6.8 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  136.3, 120.4, 53.2, 17.0; HRMS (ESI): Exact mass calcd for  $\text{C}_4\text{H}_{11}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 87.0922. Found 87.0812.



### But-3-en-2-ylhydrazine hydrochloride (**12d**):

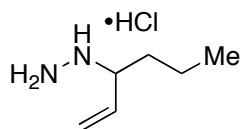
A 4 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(but-3-en-2-yl)hydrazinecarboxylate (279 mg, 1.50 mmol) and allowed to stir 4 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12d** which did not require purification: IR (film) 3260, 3165, 2979, 1383  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.51–7.48 (b s, 4H); 6.06 (ddd, 1H,  $J$  = 18.1, 10.3, 8.2 Hz); 5.66 (d, 1H,  $J$  = 17.0 Hz); 5.55 (d, 1H,  $J$  = 10.2 Hz); 4.30 (t, 1H,  $J$  = 7.1 Hz); 1.61 (d, 3H,  $J$  = 6.6 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.6, 123.7, 60.2, 16.7; HRMS (ESI): Exact mass calcd for  $\text{C}_4\text{H}_{11}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 87.0922. Found 87.0901.



### Pent-1-en-3-ylhydrazine hydrochloride (**12e**):

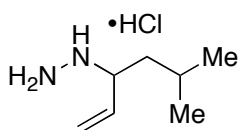
A 4 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(pent-1-en-3-yl)hydrazinecarboxylate (300 mg, 1.50 mmol) and allowed to stir for 12 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12e** which did not require purification: mp (decomp.) 45–47  $^\circ\text{C}$ ; IR (diamond) 3221, 2716, 1583, 1532  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

(500 MHz,  $\text{CDCl}_3$ ) 7.96 (b s, 4H), 5.85 (dt, 1H,  $J = 17.4, 9.3$  Hz); 5.60 (d, 1H,  $J = 18.3$  Hz); 5.56 (d, 1H,  $J = 12.1$  Hz); 3.81 (t, 1H,  $J = 9.3$  Hz); 2.05 (m, 1H); 1.78 (p, 1H,  $J = 8.2$  Hz); 0.96 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.1, 125.6, 66.5, 23.8, 10.1; HRMS (ESI): Exact mass calcd for  $\text{C}_5\text{H}_{13}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 101.1079. Found 101.1072.



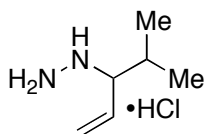
**Hex-1-en-3-ylhydrazine hydrochloride (12f):** A 4 M solution of HCl in dioxane solution (2.0 mL) was added to *tert*-butyl 1-(hex-1-en-3-yl)hydrazinecarboxylate: (322 mg, 1.50 mmol) and allowed to stir for 10 h at room temperature.

Concentration in vacuo afforded *N*-allylhydrazine salt **12f** which did not require purification: IR (diamond) 2960, 1462, 916, 729  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.84 (bs, 4H); 5.87 (dt, 1H,  $J = 17.6, 9.3$  Hz); 5.58 (d, 1H,  $J = 17.8$  Hz); 5.55 (d, 1H,  $J = 11.2$  Hz); 3.83 (td, 1H,  $J = 9.7, 4.0$  Hz); 1.96 (obs m, 1H); 1.74 (dddd, 1H,  $J = 14.6, 10.1, 4.9$  Hz); 1.46–1.30 (obs m, 2H); 0.95 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.7, 125.1, 65.1, 32.4, 19.0, 13.8; HRMS (ESI): Exact mass calcd for  $\text{C}_6\text{H}_{15}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 114.1157. Found 114.1154.



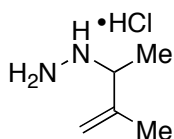
**(5-Methylhex-1-en-3-yl)hydrazine hydrochloride (12g):** A solution of 4 M HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(5-methylhex-1-en-3-yl)hydrazinecarboxylate (344 mg, 1.50 mmol) and allowed to stir for 10 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12g**

which did not require purification: IR (diamond) 2956, 1723, 1369, 932  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) 5.67 (ddd, 1H,  $J = 16.8, 10.2, 9.3$  Hz); 5.52 (d, 1H,  $J = 3.5$  Hz); 5.49 (d, 1H,  $J = 11.2$  Hz); 3.59 (ddd, 1H,  $J = 9.3, 5.5, 5.5$  Hz); 3.32 (obs s, 3H); 1.67 (h, 1H,  $J = 6.4$  Hz); 1.52–1.47 (obs m, 2H); 0.98 (d, 3H,  $J = 6.6$  Hz); 0.93 (d, 3H,  $J = 6.4$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  133.8, 122.7, 63.1, 39.8, 24.5, 22.5, 20.6; HRMS (ESI): Exact mass calcd for  $\text{C}_7\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 129.2233. Found 129.1390.



**(4-Methylpent-1-en-3-yl)hydrazine hydrochloride (12h):**

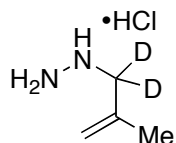
A 4 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(4-methylpent-1-en-3-yl)hydrazinecarboxylate (322 mg, 1.50 mmol) and allowed to stir for 5 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12h** which did not require purification: mp (decomp.) 126–128  $^{\circ}\text{C}$ ; IR (film) 3204, 2959, 1590, 1506, 928  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.20 (bs, 3H); 5.83 (dt, 1H,  $J = 9.8, 1.8$  Hz); 5.54 (d, 1H,  $J = 10.4$  Hz); 5.50 (d, 1H,  $J = 18.2$  Hz); 3.48 (dd, 1H,  $J = 5.9, 3.1$  Hz); 2.24 (h, 1H,  $J = 6.6$  Hz); 1.04 (d, 3H,  $J = 6.8$  Hz); 1.02 (d, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  130.0, 125.1, 71.1, 29.2, 19.9, 17.9; HRMS (ESI): Exact mass calcd for  $\text{C}_6\text{H}_{15}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 115.1235. Found 115.0871.



**(3-Methylbut-3-en-2-yl)hydrazine hydrochloride (12i):**

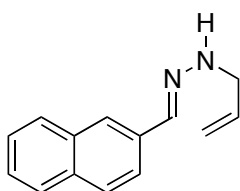
A 4 M solution of HCl in dioxane solution (2.0 mL) was added to *tert*-butyl 1-((3-methylbut-3-en-2-yl)hydrazinecarboxylate (377 mg, 1.50 mmol) and allowed to stir for 5 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12i** which did not require purification: mp (decomp.) 103–104  $^{\circ}\text{C}$ ; IR (diamond) 3215, 2728, 1584, 1520, 1090  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6.55 (bs, 4H); 5.25 (s, 1H); 5.19 (s, 1H); 3.83 (q, 1H,  $J = 6.8$  Hz); 1.90 (s, 3H); 1.51 (dd, 3H,  $J = 6.8, 2.0$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 118.5, 62.7, 18.9, 16.0; HRMS (ESI): Exact mass calcd for  $\text{C}_5\text{H}_{13}\text{N}_2$   $[\text{M}]^+$ , 100.1001. Found: 100.1005.



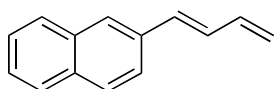


**(1,1-*d*<sub>2</sub>-2-Methylallyl)hydrazine hydrochloride (12l):** A 4.0 M solution of HCl in dioxane (2.0 mL) was added to *tert*-butyl 1-(1,1-*d*<sub>2</sub>-methylallyl)hydrazinecarboxylate (282 mg, 1.50 mmol) and allowed to stir for 10 h at room temperature. Concentration in vacuo afforded *N*-allylhydrazine salt **12l** which did not require purification: IR (diamond) 2852, 2347, 1447, 912 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.72 (bs, 5H); 5.27 (s, 1H); 5.18 (s, 1H); 1.92 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.8, 120.3, 67.3, 28.3, 21.6; HRMS (ESI): Exact mass calcd for C<sub>4</sub>H<sub>9</sub>D<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup>, 89.1048. Found 89.1050.

### C. Synthesis of Mono-Substituted Dienes<sup>4</sup>

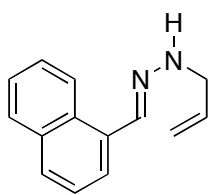


**1-Allyl-2-(naphthalen-2-ylmethylene)hydrazine (9a):** A 70% solution of allylhydrazine in H<sub>2</sub>O (792 μL, 7.90 mmol) was added to a stirred solution of 2-naphthaldehyde (1.00 g, 6.55 mmol) in EtOH (15 mL) under N<sub>2</sub> atmosphere. After stirring 12 h at room temperature a white precipitate had formed. H<sub>2</sub>O (50 mL) was added to the reaction mixture, further precipitating the white solid. The solid was collected by vacuum filtration and quickly placed under high vacuum. Drying for 24 h under vacuum afforded the title compound as an off-white powder (1.3 g, 94%): mp (decomp.) 49–55 °C; IR (film) 3249, 3048, 2841, 1595, 1482, 1109 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.95 (d, 1H, *J* = 8.2 Hz); 7.84–7.79 (m, 4H); 7.72 (s, 1H); 7.49 (m, 2H); 6.03 (ddt, 1H, *J* = 16.3, 10.8, 5.9 Hz); 5.60 (bs, 1H); 5.35 (d, 1H, *J* = 17.2 Hz); 5.25 (d, 1H, *J* = 10.2 Hz); 3.95 (d, 2H, *J* = 5.7 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.3, 134.5, 133.5, 133.4, 133.2, 128.2, 127.9, 127.7, 126.2, 125.9, 125.8, 122.9, 117.3, 51.6; HRMS (ESI): Exact mass calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>, 211.1235. Found 211.1227.



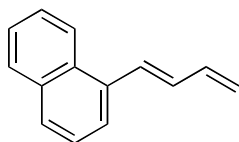
**(*E*)-2-(Buta-1,3-dienyl)naphthalene (10a):** A solution of *N*-allylhydrazone **9a** (210 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was allowed to stir at 0 °C for 2 h, then warmed to room temperature and stirred for 30 min. DBU (598 μL, 4.00 mmol) was then added to the reaction mixture, which was stirred for 1.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure to afford an off-white solid (20:1 *E*:*Z* by <sup>1</sup>H NMR). Purification by column chromatography on AgNO<sub>3</sub> impregnated silica gel in hexanes → 5% EtOAc/hexanes afforded the title compound as a crystalline white solid (141 mg, 78% yield): mp (decomp.) 90–92 °C; IR (film) 3046, 1682, 1627, 1307, 1003 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.82 (m, 3H); 7.78 (s, 1H); 7.66 (dd, 1H, *J* = 8.8, 1.5 Hz); 7.48 (app pd, 2H, *J* = 6.8, 1.5 Hz); 6.96 (dd, 1H, *J* = 15.6, 10.7 Hz); 6.76 (d, 1H, *J* = 15.6 Hz); 6.60 (ddd, 1H, *J* = 17.1, 10.3, 10.3 Hz); 5.42 (d, 1H, *J* = 17.1 Hz); 5.25 (d, 1H, *J* = 9.8 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.2, 134.6, 133.6, 133.0, 132.9, 130.0, 128.2, 128.0, 127.6, 126.5, 126.3, 125.9, 123.4, 117.8; HRMS (EI): Exact mass calcd for C<sub>14</sub>H<sub>12</sub> [M]<sup>+</sup>, 180.0934. Found 180.0933.

4. In some instances a brominated byproduct (~5%) was observed in the unpurified reaction mixture. Purification using silver-impregnated silica gel removed this byproduct effectively.



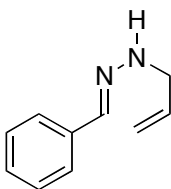
**1-Allyl-2-(naphthalene-1-ylmethylene)hydrazine (9b):** A 70% solution of allylhydrazine in H<sub>2</sub>O (103  $\mu$ L, 1.00 mmol) was added to a stirred solution of 1-naphthaldehyde (136  $\mu$ L, 1.00 mmol) in EtOH (2 mL) under N<sub>2</sub> atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 4 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis:

IR (film) 3388, 3056, 2912, 1507, 1419, 1176 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.55 (d, 1H, *J* = 8.4 Hz); 8.26 (s, 1H); 7.84 (d, 1H, *J* = 8.2 Hz); 7.77 (d, 2H, *J* = 7.7 Hz); 7.48 (m, 3H); 6.02 (m, 1H); 5.61 (bs, 1H); 5.33 (dd, 1H, *J* = 17.2, 1.3 Hz); 5.22 (d, 1H, *J* = 10.3 Hz); 3.97 (d, 2H, *J* = 5.9 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.5, 134.6, 133.8, 131.2, 130.4, 128.6, 128.5, 126.3, 125.7, 125.4, 125.1, 124.0, 117.3, 51.9; HRMS (ESI): Exact mass calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>[M+H]<sup>+</sup>, 211.1235. Found 211.1225.



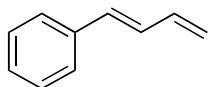
**(E)-1-(Buta-1,3-dienyl)naphthalene (10b):** A solution of *N*-allylhydrazone **9b** (210 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was allowed to

stir at 0 °C for 2 h, then warmed to room temperature and stirred for 30 min. DBU (598  $\mu$ L, 4.00 mmol) was then added to the reaction mixture, which was stirred 3 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by <sup>1</sup>H NMR). Purification by column chromatography on AgNO<sub>3</sub> impregnated silica gel in hexanes  $\rightarrow$  1% EtOAc/hexanes afforded the title compound as a clear oil (135 mg, 75% yield): IR (film) 3040, 1684, 1593, 1508, 999 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.19 (d, 1H, *J* = 8.2 Hz); 7.89 (app d, 1H, *J* = 7.7 Hz); 7.81 (d, 1H, *J* = 8.2 Hz); 7.71 (d, 1H, *J* = 7.1 Hz); 7.58–7.48 (m, 3H); 7.40 (d, 1H, *J* = 15.4 Hz); 6.91 (dd, 1H, *J* = 15.4, 10.4 Hz); 6.71 (ddd, 1H, *J* = 16.8, 10.4, 10.2 Hz); 5.45 (d, 1H, *J* = 16.8 Hz); 5.29 (d, 1H, *J* = 10.1 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.4, 134.5, 133.7, 132.4, 131.1, 129.6, 128.6, 128.0, 126.0, 125.7, 125.6, 123.6, 123.4, 118.0; HRMS (EI): Exact mass calcd for C<sub>14</sub>H<sub>12</sub>[M]<sup>+</sup>, 180.0934. Found 180.0937.



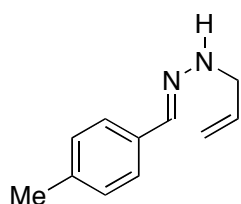
**1-Allyl-2-benzylidenehydrazine (9c):** A 70% solution of allylhydrazine in H<sub>2</sub>O (103  $\mu$ L, 1.00 mmol) was added to a stirred solution of benzaldehyde (101  $\mu$ L, 1.00 mmol) in EtOH (2 mL) under N<sub>2</sub> atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil or solid dried under high vacuum for 2 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3390,

3078, 2914, 1642, 1596 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.59 (s, 1H); 7.54 (d, 2H, *J* = 7.5 Hz); 7.32 (t, 2H, *J* = 7.5 Hz); 7.25 (m, 1H); 5.96 (m, 1H); 5.71 (bs, 1H); 5.27 (dd, 1H, *J* = 17.2, 1.3 Hz); 5.18 (d, 1H, *J* = 10.2 Hz); 3.87 (d, 2H, *J* = 5.9 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.3, 135.8 (two coincident signals), 134.4, 128.4 (two coincident signals), 127.9, 125.8, 117.3, 51.6; HRMS (ESI): Exact mass calcd for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>[M+H]<sup>+</sup>, 161.1079. Found 161.1070.

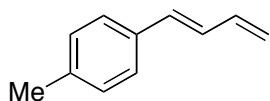


**(E)-Buta-1,3-dienylbenzene (10c):** A solution of *N*-allylhydrazone **9c** (160 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C,

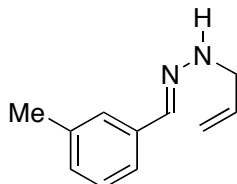
under N<sub>2</sub> atmosphere. The reaction was allowed to warm to room temperature and stirred for 2 h. DBU (598  $\mu$ L, 4.00 mmol) was then added to the reaction mixture, which was stirred for 18 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by <sup>1</sup>H NMR). Purification by column chromatography on AgNO<sub>3</sub> impregnated silica gel in hexanes  $\rightarrow$  5% EtOAc/hexanes afforded the title compound as a clear oil (61 mg, 47% yield): IR (film) 3082, 3027, 1779, 1603, 1000 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.45 (d, 2H, *J* = 7.3 Hz); 7.36 (t, 2H, *J* = 7.3 Hz); 7.27 (m, 1H); 6.84 (dd, 1H, *J* = 15.1, 10.3 Hz); 6.61 (d, 1H, *J* = 16.1 Hz); 6.56 (ddd, 1H, *J* = 17.3, 10.3, 10.3 Hz); 5.38 (d, 1H, *J* = 17.1 Hz); 5.22 (d, 1H, *J* = 9.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.2, 137.1, 132.8, 129.6, 128.6 (two coincident signals), 127.6, 126.4 (two coincident signals), 117.6; HRMS (EI): Exact mass calcd for C<sub>10</sub>H<sub>10</sub> [M]<sup>+</sup>, 130.0777. Found 130.0774.



**1-Allyl-2-(4-methylbenzylidene)hydrazine (9d):** A 70% solution of allylhydrazine in H<sub>2</sub>O (103  $\mu$ L, 1.00 mmol) was added to a stirred solution of 4-methylbenzaldehyde (118  $\mu$ L, 1.00 mmol) in EtOH (2 mL) under N<sub>2</sub> atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 2 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3344, 3077, 2919, 1599, 1511, 1103 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.59 (s, 1H); 7.43 (d, 2H, *J* = 8.1 Hz); 7.14 (d, 2H, *J* = 7.9 Hz); 5.97 (m, 1H); 5.53 (bs, 1H); 5.27 (dd, 1H, *J* = 17.2, 1.5 Hz); 5.18 (dd, 1H, *J* = 10.2, 1.3 Hz); 3.87 (d, 2H, *J* = 5.9 Hz); 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.0 (two coincident signals), 134.6, 133.0, 129.2 (two coincident signals); 125.8 (two coincident signals), 117.3, 51.8, 21.3; HRMS (ESI): Exact mass calcd for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>, 175.1235. Found 175.1229.

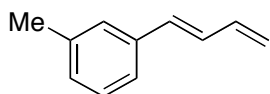


**(E)-1-(Buta-1,3-dienyl)-4-methylbenzene (10d):** A solution of *N*-allylhydrazone **9d** (174 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was stirred 2 h at 0 °C. DBU (598  $\mu$ L, 4.00 mmol) was then added to the reaction mixture, which was stirred for 2 h at 0 °C, then allowed to warm to room temperature and stirred 1h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by <sup>1</sup>H NMR). Purification by column chromatography on AgNO<sub>3</sub> impregnated silica gel in hexanes  $\rightarrow$  5% EtOAc/hexanes afforded the title compound as a clear oil (101 mg, 70% yield): IR (film) 3024, 2921, 1679, 1608, 1005 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.28 (d, 2H, *J* = 7.9 Hz); 7.12 (d, 2H, *J* = 7.9 Hz); 6.73 (dd, 1H, *J* = 15.7, 10.6 Hz); 6.51 (d, 1H, *J* = 15.9 Hz); 6.47 (m, 1H); 5.29 (d, 1H, *J* = 16.8 Hz); 5.12 (d, 1H, *J* = 10.1 Hz); 2.31 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.4, 137.3, 134.3, 132.8, 129.3 (two coincident signals), 128.6, 126.3 (two coincident signals), 117.0, 21.2; HRMS (EI): Exact mass calcd for C<sub>11</sub>H<sub>12</sub> [M]<sup>+</sup>, 144.0934. Found 144.0928.

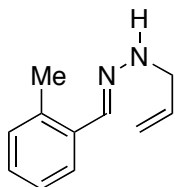


**1-Allyl-2-(3-methylbenzylidene)hydrazine (9e):** A 70% solution of allylhydrazine in H<sub>2</sub>O (103  $\mu$ L, 1.00 mmol) was added to a stirred solution of 3-methylbenzaldehyde (118  $\mu$ L, 1.00 mmol) in EtOH (2 mL) under N<sub>2</sub> atmosphere.

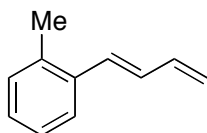
The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 2 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3341, 3012, 2918, 1594, 1573, 916  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.58 (s, 1H); 7.39 (s, 1H); 7.31 (d, 1H,  $J = 7.5$  Hz); 7.22 (t, 1H,  $J = 7.5$  Hz); 7.07 (d, 1H,  $J = 7.5$  Hz); 5.97 (m, 1H); 5.46 (bs, 1H); 5.29 (d, 1H,  $J = 17.2$  Hz); 5.18 (d, 1H,  $J = 10.2$  Hz); 3.88 (d, 2H,  $J = 5.7$  Hz); 2.34 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 137.8, 135.7, 134.6, 128.9, 128.4, 126.3, 123.3, 117.3, 51.7, 21.3; HRMS (ESI): Exact mass calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 175.1235. Found 175.1226.



**(*E*)-1-(Buta-1,3-dienyl)-3-methylbenzene (10e):** A solution of *N*-allylhydrazone **9e** (210 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0  $^\circ\text{C}$  for 2 h, then warmed to room temperature and stirred for 30 min. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 3 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  1% EtOAc/hexanes afforded the title compound as a clear oil (94 mg, 65% yield): IR (film) 3014, 2920, 1633, 1601, 1000  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.20 (m, 3H); 7.03 (m, 1H); 6.77 (dd, 1H,  $J = 15.6, 10.6$  Hz); 6.52 (d, 1H,  $J = 15.2$  Hz); 6.48 (m, 1H); 5.31 (d, 1H,  $J = 16.7$  Hz); 5.20 (d, 1H,  $J = 9.7$  Hz); 2.33 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 137.2, 137.0, 132.9, 129.4, 128.5, 128.4, 127.1, 123.6, 117.4, 21.4 ; HRMS (EI): Exact mass calcd for  $\text{C}_{11}\text{H}_{12}$   $[\text{M}]^+$ , 144.0934. Found 144.0928.

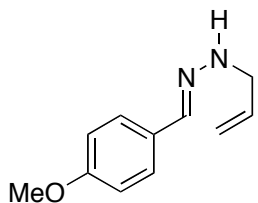


**1-Allyl-2-(2-methylbenzylidene)hydrazine (9f):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 2-methylbenzaldehyde (116  $\mu\text{L}$ , 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 2 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3337, 3063, 2920, 1586, 1457, 1094  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.84 (s, 1H); 7.73 (m, 1H); 7.19-7.11 (m, 3H); 5.97 (m, 1H); 5.61 (bs, 1H); 5.28 (dd, 1H,  $J = 17.4, 1.5$  Hz); 5.19 (dd, 1H,  $J = 10.2, 1.5$  Hz); 3.89 (d, 2H,  $J = 5.9$  Hz); 2.39 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 135.0, 134.6, 133.7, 130.5, 127.8, 126.0, 125.4, 117.3, 51.9, 19.5; HRMS (ESI): Exact mass calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 175.1235. Found 175.1228.



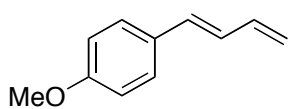
**(*E*)-1-(Buta-1,3-dienyl)-2-methylbenzene (10f):** A solution of *N*-allylhydrazone **9f** (174 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0  $^\circ\text{C}$  for 10 min, then warmed to room temperature and stirred for 2 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 1.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The

collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  1% EtOAc/hexanes afforded the title compound as a clear oil (95 mg, 66% yield): IR (film) 3016, 2971, 1702, 1598, 1000  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.49 (d, 1H,  $J = 6.8$  Hz); 7.15 (m, 3H); 6.78 (d, 1H,  $J = 15.6$  Hz); 6.69 (dd, 1H,  $J = 15.4, 10.1$  Hz); 6.4 (ddd, 1H,  $J = 16.7, 10.1, 10.1$  Hz); 5.33 (d, 1H,  $J = 16.8$  Hz); 5.16 (d, 1H,  $J = 10.1$  Hz); 2.35 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 135.9, 135.6, 130.7, 130.5, 130.4, 127.5, 126.1, 125.1, 117.5, 19.8; HRMS (EI): Exact mass calcd for  $\text{C}_{11}\text{H}_{12}[\text{M}]^+$ , 144.0934. Found 144.0936.



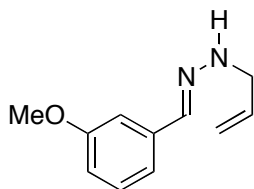
**1-Allyl-2-(4-methoxybenzylidene)hydrazine (9g):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 4-methoxybenzaldehyde (122  $\mu\text{L}$ , 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 48 h to afford a crystalline solid. The unpurified *N*-allylhydrazone

was used directly in the subsequent diene synthesis: mp (decomp.) 34-35  $^\circ\text{C}$ ; IR (film) 3214, 3078, 2958, 2836, 1609, 1251  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.55 (s, 1H); 7.44 (d, 2H,  $J = 8.5$  Hz); 6.83 (d, 2H,  $J = 8.8$  Hz); 5.93 (ddt, 1H,  $J = 16.4, 10.5, 5.9$  Hz); 5.32 (bs, 1H); 5.23 (d, 1H,  $J = 17.3$  Hz); 5.13 (d, 1H,  $J = 10.3$  Hz); 3.81 (d, 2H,  $J = 5.6$  Hz); 3.76 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 138.0, 134.7, 128.5, 127.2 (two coincident signals), 117.2, 113.9 (two coincident signals), 55.2, 51.9; HRMS (ESI): Exact mass calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O} [\text{M}+\text{H}]^+$ , 191.1186. Found 191.1180.



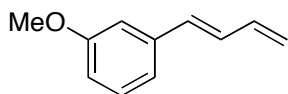
**(E)-1-(Buta-1,3-dienyl)-4-methoxybenzene (10g):** A solution of *N*-allylhydrazone **9g** (190 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$

(10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was allowed to warm to room temperature and stirred for 30 min. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 40 min. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow residue (20:1 E:Z by  $^1\text{H}$  NMR) which required no further purification (112 mg, 70% yield): IR (film) 3034, 2959, 1677, 1597, 1005  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.36 (d, 2H,  $J = 8.6$  Hz); 6.88 (d, 2H,  $J = 8.6$  Hz); 6.70 (dd, 1H,  $J = 15.6, 10.6$  Hz); 6.53 (m, 2H); 5.31 (d, 1H,  $J = 16.8$  Hz); 5.15 (d, 1H,  $J = 9.7$  Hz); 3.82 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 137.3, 132.3, 129.8, 127.59 (two coincident signals), 127.56, 116.4, 114.0 (two coincident signals); 55.2; HRMS (EI): Exact mass calcd for  $\text{C}_{11}\text{H}_{12}\text{O} [\text{M}]^+$ , 160.0883. Found 160.0881.



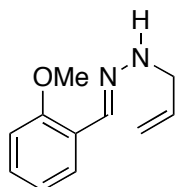
**1-Allyl-2-(3-methoxybenzylidene)hydrazine (9h):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 3-methoxybenzaldehyde (122  $\mu\text{L}$ , 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 22 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 4 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3380, 3074, 2935, 2832, 1662, 1569  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.56 (s, 1H); 7.23 (t, 1H,  $J = 7.9$  Hz); 7.15

(s, 1H); 7.07 (d, 1H,  $J = 7.5$  Hz); 6.81 (dd, 1H,  $J = 8.2, 2.4$  Hz); 5.96 (m, 1H); 5.51 (bs, 1H); 5.28 (dd, 1H,  $J = 17.2, 1.3$  Hz); 5.19 (dd, 1H,  $J = 10.2, 0.9$  Hz); 3.88 (d, 2H,  $J = 5.9$  Hz); 3.82 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 137.2, 137.0, 134.4, 129.4, 118.9, 117.3, 114.4, 109.8, 55.1, 51.5; HRMS (ESI): Exact mass calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O} [\text{M}+\text{H}]^+$ , 191.1184. Found 191.1180.



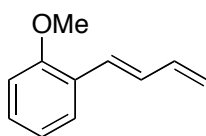
**(E)-1-(Buta-1,3-dienyl)-3-methoxybenzene (10h):** A solution of *N*-allylhydrazone **9h** (190 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$

(10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0 °C for 2 h, then warmed to room temperature and stirred for 30 min. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 1.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  5 % EtOAc/hexanes afforded the title compound as a clear oil (110 mg, 69% yield): IR (film) 3083, 2999, 2832, 1602, 1576, 1271  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.22 (t, 1H,  $J = 7.9$  Hz); 6.99 (d, 1H,  $J = 7.7$  Hz); 6.93 (s, 1H); 6.77 (m, 2H); 6.52 (d, 1H,  $J = 15.9$  Hz); 6.48 (m, 1H); 5.33 (d, 1H,  $J = 16.8$  Hz); 5.17 (d, 1H,  $J = 10.1$  Hz); 3.79 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 138.5, 137.0, 132.7, 129.9, 129.5, 119.1, 117.8, 113.3, 111.5, 55.1; HRMS (EI): Exact mass calcd for  $\text{C}_{11}\text{H}_{12}\text{O} [\text{M}]^+$ , 160.0883. Found 160.0879.



**1-Allyl-2-(2-methoxybenzylidene)hydrazine (9i):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 2-methoxybenzaldehyde (121  $\mu\text{L}$ , 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 4 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3383, 3071, 2833, 1600, 1488

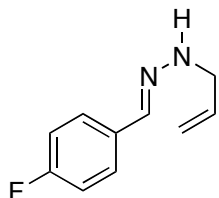
$1245 \text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 8.01 (s, 1H); 7.81 (dd, 1H,  $J = 7.7, 1.5$  Hz); 7.24 (td, 1H,  $J = 8.4, 1.5$  Hz); 6.94 (t, 1H,  $J = 7.3$  Hz); 6.86 (d, 1H,  $J = 8.2$  Hz); 5.98 (m, 1H); 5.50 (bs, 1H); 5.27 (dd, 1H,  $J = 17.2, 1.5$  Hz); 5.18 (dd, 1H,  $J = 10.3, 1.1$  Hz); 3.88 (d, 2H,  $J = 6.0$  Hz); 3.83 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 134.7, 133.6, 129.0, 125.3, 124.3, 120.7, 117.1, 110.7, 55.4, 51.8; HRMS (ESI): Exact mass calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O} [\text{M}+\text{H}]^+$ , 191.1184. Found 191.1172.



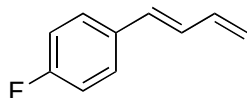
**(E)-1-(Buta-1,3-dienyl)-2-methoxybenzene (10i):** A solution of *N*-allylhydrazone **9i** (190 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round

bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was allowed to warm to room temperature and stirred for 2 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 2.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  1 % EtOAc/hexanes afforded the title compound as a clear oil (110 mg, 69% yield): IR (film) 3040, 3001, 2939, 1594, 1241, 1002  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.54 (dd, 1H,  $J = 7.3, 1.5$  Hz); 7.27 (td, 1H,  $J = 8.8, 1.5$  Hz); 7.86-

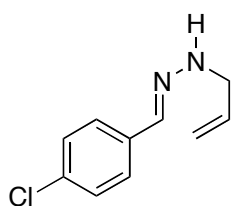
7.01 (m, 4H); 6.61 (ddd, 1H,  $J = 17.1, 10.3, 10.3$  Hz); 5.38 (d, 1H,  $J = 17.6$  Hz); 5.21 (d, 1H,  $J = 10.3$  Hz); 3.90 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 137.9, 130.2, 128.6, 127.6, 127.4, 126.0, 120.6, 116.9, 110.8, 55.4; HRMS (APPI): Exact mass calcd for  $\text{C}_{11}\text{H}_{13}\text{O}$   $[\text{M}+\text{H}]^+$ , 161.0968. Found 161.0962.



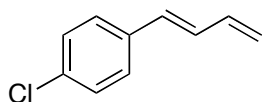
**1-Allyl-2-(4-fluorobenzylidene)hydrazine (9j):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 4-fluorobenzaldehyde (106  $\mu\text{L}$ , 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 2 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3333, 3076, 2914, 1604, 1507, 1229  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.56 (s, 1H); 7.51 (m, 2H); 7.01 (app t, 2H,  $J = 5.8$  Hz); 5.96 (m, 1H); 5.58 (bs, 1H); 5.27 (dd, 1H,  $J = 17.2, 1.5$  Hz); 5.19 (dd, 1H,  $J = 10.3, 1.3$  Hz); 3.86 (d, 2H,  $J = 5.9$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6 (d,  $J = 247.5$  Hz), 136.2, 134.4, 132.0, 127.4, 127.3(5), 117.4, 115.5, 115.4, 51.6; HRMS (ESI): Exact mass calcd for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{F}$   $[\text{M}+\text{H}]^+$ , 179.0985. Found 179.0984.



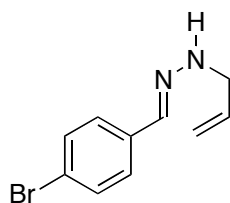
**(E)-1-(Buta-1,3-dienyl)-4-fluorobenzene (10j):** A solution of *N*-allylhydrazone **9j** (178 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was stirred for 2 h at 0  $^\circ\text{C}$ , then warmed to room temperature and stirred 30 min. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 1.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  1 % EtOAc/hexanes afforded the title compound as a clear oil (75 mg, 51% yield): IR (film) 3087, 3038, 3012, 2969, 1598, 1506, 1230  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.38 (dd, 2H,  $J = 8.4, 5.5$  Hz); 7.02 (t, 2H,  $J = 8.6$  Hz); 6.72 (dd, 1H,  $J = 15.4, 10.6$  Hz); 6.54 (d, 1H,  $J = 15.2$  Hz); 6.50 (m, 1H); 5.35 (d, 1H,  $J = 16.7$  Hz); 5.19 (d, 1H,  $J = 9.9$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $J = 247.0$  Hz), 137.0, 133.2, 131.5, 129.3, 127.9, 127.8, 117.7, 115.6, 115.4; HRMS (APPI): Exact mass calcd for  $\text{C}_{10}\text{H}_{10}\text{F}$   $[\text{M}+\text{H}]^+$ , 149.0767. Found 149.0767.



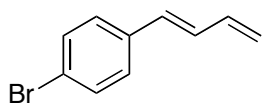
**1-Allyl-2-(4-chlorobenzylidene)hydrazine (9k):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 4-chlorobenzaldehyde (195 mg, 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 3 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3335, 3080, 2980, 2842, 1597, 1489  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.53 (s, 1H); 7.46 (d, 2H,  $J = 8.5$  Hz); 7.29 (d, 2H,  $J = 8.4$  Hz); 5.96 (m, 1H); 5.61 (bs, 1H); 5.28 (d, 1H,  $J = 17.2$  Hz); 5.20 (d, 1H,  $J = 10.2$  Hz); 3.88 (d, 2H,  $J = 5.7$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 135.7, 134.4, 134.3, 133.5, 128.7 (two coincident signals), 127.0 (two coincident signals), 117.5, 51.5; HRMS (ESI): Exact mass calcd for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Cl}$   $[\text{M}+\text{H}]^+$ , 195.0689. Found 195.0681.



**(E)-1-(Buta-1,3-dienyl)-4-chlorobenzene (10k):** A solution of *N*-allylhydrazone **9k** (195 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was stirred for 2 h at 0 °C, then warmed to room temperature and stirred 30 min. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 1.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  1 % EtOAc/hexanes afforded the title compound as a clear oil (96 mg, 58% yield): IR (film) 3086, 3038, 3013, 2969, 1601, 1488  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.29 (d, 2H,  $J$  = 8.6 Hz); 7.25 (d, 2H,  $J$  = 8.4 Hz); 6.73 (dd, 1H,  $J$  = 15.7, 10.4 Hz); 6.51-6.43 (m, 2H); 5.33 (d, 1H,  $J$  = 17.0 Hz); 5.19 (d, 1H,  $J$  = 10.1 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 135.6, 133.1, 131.4, 130.1, 128.7 (two coincident signals), 127.5 (two coincident signals), 118.2; HRMS (APPI): Exact mass calcd for  $\text{C}_{10}\text{H}_{10}\text{Cl} [\text{M}+\text{H}]^+$ , 165.0471. Found 165.0461.



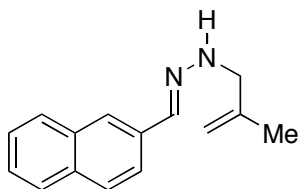
**1-Allyl-2-(4-bromobenzylidene)hydrazine (9l):** A 70% solution of allylhydrazine in  $\text{H}_2\text{O}$  (103  $\mu\text{L}$ , 1.00 mmol) was added to a stirred solution of 4-bromobenzaldehyde (185 mg, 1.00 mmol) in EtOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction was allowed to stir 16 h at room temperature. The solvent was then removed under vacuum and the resulting oil dried under high vacuum for 1.5 h. The unpurified *N*-allylhydrazone was used directly in the subsequent diene synthesis: IR (film) 3391, 3080, 2980, 1597, 1487, 1122  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.49 (s, 1H); 7.44 (d, 2H,  $J$  = 8.4 Hz); 7.39 (d, 2H,  $J$  = 8.6 Hz); 5.95 (m, 1H); 5.56 (bs, 1H); 5.27 (dd, 1H,  $J$  = 17.2, 1.1 Hz); 5.19 (d, 1H, 10.4 Hz); 3.87 (d, 2H,  $J$  = 5.7 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 135.3, 134.8, 134.1, 131.5 (two coincident signals), 127.1 (two coincident signals), 121.5, 117.4, 51.3; HRMS (ESI): Exact mass calcd for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Br} [\text{M}+\text{H}]^+$ , 239.0184. Found 239.0169.



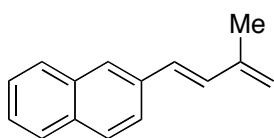
**(E)-1-Bromo-4-(buta-1,3-dienyl)benzene (10l):** A solution of *N*-allylhydrazone **9l** (239 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was allowed to warm to room temperature and stirred for 3 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 2.5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (20:1 E:Z by  $^1\text{H}$  NMR). Purification by column chromatography on  $\text{AgNO}_3$  impregnated silica gel in hexanes  $\rightarrow$  5 % EtOAc/hexanes afforded the title compound as a clear oil (129 mg, 62% yield): IR (film) 3085, 1777, 1601, 1485, 1000  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.41 (d, 2H,  $J$  = 8.4 Hz); 7.23 (d, 2H,  $J$  = 8.4 Hz); 6.75 (dd, 1H,  $J$  = 15.7, 10.4 Hz); 6.51-6.43 (m, 2H); 5.34 (d, 1H,  $J$  = 16.8 Hz); 5.20 (d, 1H,  $J$  = 10.4 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 136.0, 131.7 (two coincident signals), 131.5, 130.2, 127.8 (two coincident signals), 121.3, 118.3; HRMS (EI): Exact mass calcd for  $\text{C}_{10}\text{H}_9\text{Br} [\text{M}]^+$ , 209.9862. Found 209.9861.



## D. Synthesis of Substituted Dienes

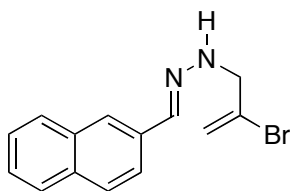
**1-(2-Methylallyl)-2-(naphthalen-2-ylmethylene)hydrazine (13a):**

A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (2-methylallyl)hydrazine hydrochloride **12a** (184 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was then removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a white solid that was used directly in the subsequent diene synthesis: mp (decomp.) 54–56 °C; IR (film) 3054, 2985, 1265, 895, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.95 (dd, 1H,  $J$  = 8.3, 1.5 Hz); 7.83–7.76 (m, 4H); 7.71 (s, 1H); 7.48 (ddd, 2H,  $J$  = 13.7, 6.8, 5.4 Hz); 5.72 (s, 1H); 5.04 (s, 1H); 4.99 (s, 1H); 3.89 (s, 2H); 1.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 136.8, 133.9, 133.6, 133.4, 128.4, 128.1, 127.9, 126.4, 126.0, 125.9, 123.1, 112.3, 55.1, 20.9; HRMS (ESI): Exact mass calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2$  [ $\text{M}+\text{H}$ ] $^+$ , 224.1314. Found 224.1314.



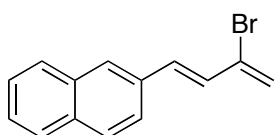
**(E)-2-(3-Methylbuta-1,3-dienyl)naphthalene (14a):** A solution of *N*-allylhydrazone **13a** (199 mg, 0.89 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (183 mg, 0.98 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere.

The reaction was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for 1 h. DBU (538  $\mu\text{L}$ , 3.60 mmol) was then added to the reaction mixture, which was stirred 10 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (>20:1 E:Z by  $^1\text{H}$  NMR spectroscopy) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (131 mg, 68% yield from 2-naphthaldehyde): mp (decomp.) 79–81 °C; IR (diamond) 3053, 2977, 1622, 1587, 1366, 961, 884  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.82 (app t, 4H,  $J$  = 3.7 Hz); 7.69 (d, 1H,  $J$  = 8.8 Hz); 7.48 (app p, 2H,  $J$  = 7.3 Hz); 7.06 (d, 1H,  $J$  = 16.1 Hz); 6.75 (d, 1H,  $J$  = 16.1 Hz); 5.22 (s, 1H); 5.16 (s, 1H); 2.07 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 135.1, 133.9, 133.1, 132.2, 129.0, 128.4, 128.1, 127.9, 126.7, 126.4, 126.0, 123.8, 117.8, 18.8; HRMS (APPI): Exact mass calcd for  $\text{C}_{15}\text{H}_{15}$  [ $\text{M}+\text{H}$ ] $^+$ , 195.1175. Found 195.1178.

**1-(2-Bromoallyl)-2-(naphthalen-2-ylmethylene)hydrazine (13b):**

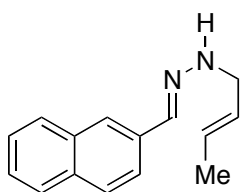
A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (2-bromoallyl)hydrazine hydrochloride **12b** (281 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 64–68 °C; IR (film) 3050,

2882, 1678, 1635, 1224  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.89 (dd, 1H,  $J = 8.5, 1.2$  Hz); 7.82–7.76 (m, 5H); 7.47 (t, 2H,  $J = 3.8$  Hz); 5.88 (s, 2H); 5.61 (s, 1H); 4.12 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 139.5, 133.8, 133.6, 133.3, 131.5, 128.6, 128.3, 126.8, 126.6, 126.4, 123.2, 118.4, 57.5; HRMS (ESI): Exact mass calcd for  $\text{C}_{14}\text{H}_{14}\text{BrN}_2[\text{M}+\text{H}]^+$ , 288.0262. Found 288.0262.



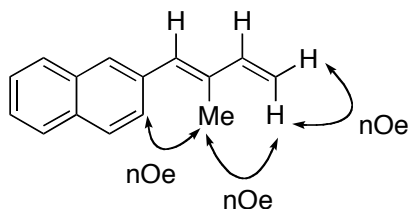
**(E)-2-(3-Bromobuta-1,3-dienyl)naphthalene (14b):** A solution of *N*-allylhydrazone **13b** (285 mg, 0.98 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (193 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere.

The reaction was allowed to stir at 0  $^\circ\text{C}$  for 1 h, then warmed to room temperature and stirred for 1 h. DBU (590  $\mu\text{L}$ , 3.90 mmol) was then added to the reaction mixture, which was stirred 8 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (>20:1 E:Z by  $^1\text{H}$  NMR spectroscopy) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (152 mg, 59% yield from 2-naphthaldehyde): mp (decomp.) 83–87  $^\circ\text{C}$ ; IR (diamond) 3058, 1688, 1594, 1174, 953  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.85 (s, 1H); 7.84 (d, 1H,  $J = 2.4$  Hz); 7.821 (s, 1H); 7.81 (d, 1H,  $J = 4.4$  Hz); 7.64 (dd, 1H,  $J = 8.8, 1.0$  Hz); 7.49 (app, 2H,  $J = 2.9$  Hz); 7.13 (d, 1H,  $J = 15.1$  Hz); 6.86 (d, 1H,  $J = 15.1$  Hz); 5.98 (s, 1H); 5.75 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 133.7, 133.6, 133.5, 130.2, 128.6, 128.4, 128.0, 127.9, 127.1, 126.7, 126.6, 123.9, 120.5; HRMS (EI): Exact mass calcd for  $\text{C}_{14}\text{H}_{11}\text{Br}[\text{M}]^+$ , 258.0044. Found 258.0046.



**1-((E)-But-2-enyl)-2-(naphthalen-2-ylmethylene)hydrazine (13c):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (*E*)-but-2-enylhydrazine hydrochloride **12c** (184 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under

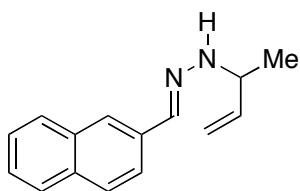
reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 54–55  $^\circ\text{C}$ ; IR (diamond) 3051, 2967, 1600, 1361, 1338, 997  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.87 (dd, 1H,  $J = 8.8, 1.5$  Hz); 7.80 (m, 4H); 7.75 (s, 1H); 7.45 (m, 2H); 5.74 (dt, 1H,  $J = 15.2, 6.1$  Hz); 5.66 (m, 1H); 5.51 (bs, 1H); 3.86 (t, 2H,  $J = 5.4$  Hz); 1.74 (d, 3H,  $J = 6.0$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.3, 133.9, 1336., 133.5, 129.5, 128.5, 128.1, 127.0, 126.4, 126.1, 123.1, 51.3, 18.1; HRMS (ESI): Exact mass calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2[\text{M}+\text{H}]^+$ , 224.1314. Found 224.1316.



**(E)-2-(2-Methylbuta-1,3-dienyl)naphthalene (14c):** A solution of *N*-allylhydrazone **13c** (213 mg, 0.95 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (186 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0

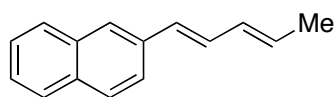
$^\circ\text{C}$  for 1 h, then warmed to room temperature and stirred for 1 h. DBU (568  $\mu\text{L}$ , 3.80 mmol) was then

added to the reaction mixture, which was stirred 10 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (3:1 E:Z, determined by nOe experiments) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (116 mg, 60% yield from 2-naphthaldehyde): mp (decomp.) 54–56°C; IR (diamond) 3082, 3051, 2967, 1601, 1016, 1196, 1179 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.89–7.82 (m, 4H); 7.53–7.50 (m, 3H); 6.76 (s, 1H); 6.70 (m, 1H); 5.43 (d, 1H, *J* = 17.1 Hz); 5.26 (d, 1H, *J* = 10.7 Hz); 2.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.2, 135.4, 132.0, 130.2, 128.4, 128.3, 128.0, 127.9, 126.4, 126.1, 126.0, 116.0, 113.4, 20.8, 13.6; HRMS (APPI): Exact mass calcd for C<sub>15</sub>H<sub>15</sub> [M+H]<sup>+</sup>, 195.1175. Found 195.1174.

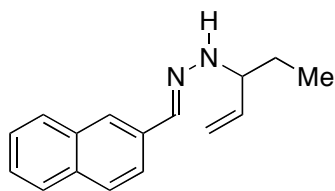


**1-(But-3-en-2-yl)-2-(naphthalen-2-ylmethylene)hydrazine (13d):**

A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of but-3-en-2-ylhydrazine hydrochloride **12d** (184 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by <sup>1</sup>H-NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in Et<sub>2</sub>O (20 mL), and washed with sat. NaHCO<sub>3</sub> (3 x 20 mL). The organics were then diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 56–58 °C; IR (diamond) 3053, 2973, 1116, 855 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.88 (d, 1H, *J* = 8.8 Hz); 7.79 (m, 3H); 7.77 (m, 2H); 7.45 (m, 2H); 5.94 (m, 1H); 5.38 (d, 1H, *J* = 5.8 Hz); 5.25 (d, 1H, *J* = 17.1 Hz); 5.14 (d, 1H, *J* = 10.2 Hz); 4.07 (app h, 1H, *J* = 6.3 Hz); 1.36 (d, 3H, *J* = 6.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.9, 138.7, 133.9, 133.7, 133.6, 128.5, 128.3, 128.1, 126.5, 126.3, 126.2, 123.3, 115.3, 56.8, 20.1; HRMS (ESI): Exact mass calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup>, 224.1314. Found 224.1316.

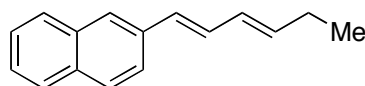


**2-((1E,3E)-Penta-1,3-dienyl)naphthalene (14d):** A solution of *N*-allylhydrazone **13d** (211 mg, 0.94 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (184 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for 1 h. DBU (560 μL, 3.80 mmol) was then added to the reaction mixture, which was stirred 10 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (a 10:1 mixture of the major isomer to others by <sup>1</sup>H NMR spectroscopy) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (122 mg, 63% yield from 2-naphthaldehyde): mp (decomp.) 94–97°C IR (film) 3016, 2905, 1589, 985 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.81 (m, 3H); 7.75 (s, 1H); 7.65 (dd, 1H, *J* = 8.8, 1.5 Hz); 7.47 (m, 2H); 6.93 (dd, 1H, *J* = 15.6, 10.7 Hz); 6.67 (d, 1H, *J* = 15.6 Hz); 6.32 (dd, 1H, *J* = 15.6, 10.7 Hz); 5.93 (dq, 1H, *J* = 13.7, 6.8 Hz); 1.90 (d, 3H, *J* = 6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.5, 134.1, 133.1, 132.3, 130.9, 130.2, 130.1, 128.5, 128.2, 128.0, 126.5, 126.3, 125.9, 123.8, 18.8; HRMS (APPI): Exact mass calcd for C<sub>15</sub>H<sub>15</sub> [M+H]<sup>+</sup>, 195.1174. Found 195.1172.



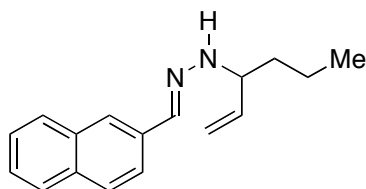
**1-(Naphthalen-2-ylmethylene)-2-(pent-1-en-3-yl)hydrazine (13e):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of pent-1-en-3-ylhydrazine hydrochloride **12e** (205 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature.

The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in Et<sub>2</sub>O (20 mL), and washed with sat. NaHCO<sub>3</sub> (3 x 20 mL). The organics were then diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 50–52 °C; IR (diamond) 2965, 1459, 1124, 919 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>) 7.95 (d, 1H,  $J$  = 8.3 Hz); 7.84 (m, 3H); 7.78 (d, 2H,  $J$  = 8.8 Hz); 7.49 (p, 2H,  $J$  = 6.8 Hz); 5.88 (ddd, 1H,  $J$  = 17.1, 10.2, 6.8 Hz); 5.40 (obs bs, 1H); 5.30 (d, 1H,  $J$  = 17.1 Hz); 5.25 (d, 1H,  $J$  = 10.7 Hz); 3.89 (q, 1H,  $J$  = 6.8 Hz); 1.85 (s, 1H,  $J$  = 7.3 Hz); 1.70 (s, 1H,  $J$  = 7.3 Hz); 1.05 (t, 3H,  $J$  = 7.3 Hz);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.6, 138.4, 134.0, 133.8, 133.6, 128.5, 128.3, 128.1, 126.5, 126.2, 123.4, 116.4, 63.2, 27.1, 10.6, 10.5; HRMS (ESI): Exact mass calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>[M]<sup>+</sup>, 238.147. Found 238.1473.



**2-((1E,3E)-Hexa-1,3-dienyl)naphthalene (14e):** A solution of *N*-allylhydrazone **13e** (238 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over

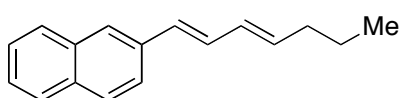
30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for 1 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 8 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (a 10:1 mixture of the major isomer to others by  $^1\text{H}$  NMR spectroscopy) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (147 mg, 71% yield from 2-naphthaldehyde): mp (decomp) 74–76 °C; IR (diamond) 2961, 2870, 1453, 986, 737 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>) 7.84 (d, 2H,  $J$  = 7.8 Hz); 7.83 (s, 1H); 7.76 (s, 1H); 7.67 (d, 1H,  $J$  = 8.8 Hz); 7.49 (app p, 2H,  $J$  = 7.3 Hz); 6.96 (dd, 1H,  $J$  = 15.6, 10.7 Hz); 6.67 (d, 1H,  $J$  = 15.6 Hz); 6.33 (dd, 1H,  $J$  = 15.1, 11.2 Hz); 5.99 (dt, 1H,  $J$  = 15.1, 6.3 Hz); 2.27 (p, 2H,  $J$  = 7.3 Hz); 1.15 (td, 3H,  $J$  = 7.3, 2.0 Hz);  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.9, 135.5, 134.1, 133.1, 130.4, 130.2, 130.0, 128.5, 128.2, 128.0, 126.5, 126.3, 125.9, 123.8, 26.3, 13.9; HRMS (APPI): Exact mass calcd for C<sub>16</sub>H<sub>17</sub> [M+H]<sup>+</sup>, 209.1330. Found 209.1328.



**1-(Hex-1-en-3-yl)-2-(naphthalen-2-ylmethylene)hydrazine (13f):**

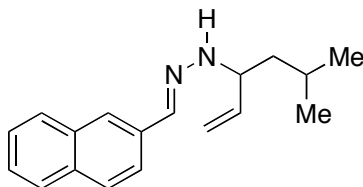
A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of hex-1-en-3-ylhydrazine hydrochloride **12f** (226 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in Et<sub>2</sub>O (20 mL), and washed with sat. NaHCO<sub>3</sub> (3 x 20 mL). The organics were then diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 38–40 °C; IR (diamond) 2955, 1460, 1094, 914 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>) 7.94 (dd, 1H,  $J$  = 8.8, 1.3 Hz); 7.82 (m, 3H); 7.76 (d, 2H,

$J = 12.6$  Hz); 7.47 (dt, 2H,  $J = 5.7, 1.3$  Hz); 5.87 (ddd, 1H,  $J = 17.4, 10.4, 7.0$ ); 5.40 (obs bs, 1H), 5.28 (d, 1H,  $J = 17.4$  Hz); 5.22 (d, 1H,  $J = 10.4$  Hz); 1.76 (p, 2H,  $J = 6.4$  Hz); 1.61 (h, 1H,  $J = 7.8$  Hz); 1.49 (h, 2H,  $J = 7.8$  Hz); 1.02 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.0, 138.3, 134.0, 133.8, 133.6, 128.5, 128.3, 128.1, 126.5, 126.2, 123.4, 116.1, 61.5, 53.0, 36.5, 19.4, 14.4; HRMS (ESI): Exact mass calcd for  $\text{C}_{17}\text{H}_{20}\text{N}_2$   $[\text{M}]^+$ , 252.1627. Found 252.1625.



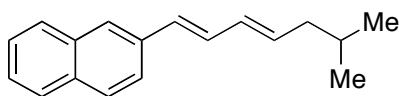
**2-((1E,3E)-Hepta-1,3-dienyl)naphthalene (14f):** A solution of *N*-allylhydrazone **13f** (252 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over

30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was stirred for 3 h at 0 °C, then warmed to room temperature and stirred 1 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (an 11:1 mixture of the major isomer to others by  $^1\text{H}$  NMR spectroscopy). Purification by column chromatography on silica gel in hexanes afforded the title compound as an off-white solid (167 mg, 75% yield): mp (decomp.) 75–78 °C; IR (film) 3046, 2954, 2867, 1677, 1618, 989  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.85–7.80 (m, 3H), 7.80 (s, 1H); 7.76 (s, 1H); 7.60 (dd, 1H,  $J = 8.8, 1.5$  Hz); 7.51–7.45 (m, 2H); 6.95 (dd, 1H,  $J = 15.6, 10.7$  Hz); 6.65 (d, 1H,  $J = 15.6$  Hz); 6.32 (dd, 1H,  $J = 15.1, 10.3$  Hz); 5.93 (dt, 1H,  $J = 14.7, 7.3$  Hz); 2.21 (app q, 2H, 6.8 Hz); 1.54 (h, 2H,  $J = 7.3$  Hz); 1.02 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 136.0, 135.2, 133.7, 132.8, 130.7, 130.1, 129.8, 128.1, 127.8, 127.6, 126.2, 125.9, 125.6, 123.4, 35.0, 22.5, 13.8; HRMS (APPI): Exact mass calcd for  $\text{C}_{17}\text{H}_{18}$   $[\text{M}]^+$ , 222.14085. Found 222.14016.

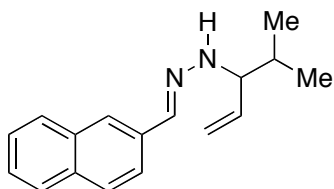


**1-(5-Methylhex-1-en-3-yl)-2-(naphthalen-2-ylmethylene)hydrazine (13g):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (5-methylhex-1-en-3-yl)hydrazine hydrochloride **12g** (247 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (12 h). The MeOH was

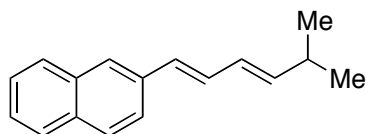
removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 49–51 °C; IR (diamond) 2954, 1338, 1168, 1051  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.95 (dd, 1H,  $J = 8.6, 1.6$  Hz); 7.86–7.82 (m, 3H); 7.79 (s, 1H); 7.76 (s, 1H); 7.49 (m, 2H); 5.87 (ddd, 1H,  $J = 17.2, 10.2, 7.0$  Hz); 5.30 (dt, 1H,  $J = 17.2, 1.3$  Hz); 5.28 (obs bs, 1H); 5.22 (dt, 1H,  $J = 10.2, 1.2$ ); 1.85 (sep, 1H,  $J = 6.8$  Hz); 1.66 (h, 1H,  $J = 7.0$  Hz); 1.50 (h, 1H,  $J = 7.0$  Hz); 1.04 (t, 6H,  $J = 6.1$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 138.2, 134.0, 133.8, 133.6, 128.5, 128.3, 126.5, 126.2 (two coincident signals), 123.4, 116.0, 59.9, 43.5, 25.0, 23.2, 22.9; HRMS (ESI): Exact mass calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_2$   $[\text{M}]^+$ , 266.1783. Found 266.1779.



**2-((1E,3E)-6-Methylhepta-1,3-dienyl)naphthalene (14g):** A solution of *N*-allylhydrazone **13g** (266 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was stirred for 3 h at 0 °C, then warmed to room temperature and stirred 1 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (a 10:1 mixture of the major isomer to others by  $^1\text{H}$  NMR spectroscopy). Purification by column chromatography on silica gel in hexanes afforded the title compound as an off-white solid (190 mg, 80% yield): mp (decomp.) 70–75 °C; IR (film) 3040, 2952, 2867, 1678, 1619, 991  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.84 (m, 3H); 7.77 (s, 1H); 7.68 (dd, 1H,  $J = 8.3, 1.0$  Hz); 7.50 (m, 2H); 6.97 (dd, 1H,  $J = 15.6, 4.9$  Hz); 6.67 (d, 1H,  $J = 16.1$  Hz); 6.32 (dd, 1H,  $J = 15.1, 10.7$  Hz); 5.94 (dt, 1H,  $J = 15.1, 7.3$  Hz); 2.15 (t, 2H,  $J = 7.3$  Hz); 1.79 (m, 1H), 1.03 (d, 6H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 134.9, 133.7, 132.8, 131.7, 130.1, 129.8, 128.1, 127.8, 127.6, 126.2, 125.9, 125.6, 123.4, 42.3, 28.6, 22.4, 22.3; HRMS (APPI): Exact mass calcd for  $\text{C}_{18}\text{H}_{20} [\text{M}]^+$ , 236.15650. Found 236.15602.

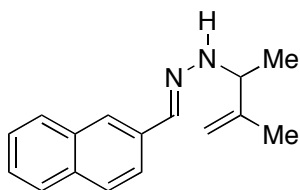


**1-(4-Methylpent-1-en-3-yl)-2-(naphthalen-2-ylmethylene)hydrazine (13h):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (4-methylpent-1-en-3-yl)hydrazine hydrochloride **12h** (226 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 43–45 °C; IR (diamond) 2954, 1644, 1092, 913, 689  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.88 (d, 1H,  $J = 8.8$  Hz); 7.85–7.76 (m, 5H); 7.45 (m, 2H); 5.60 (bs, 1H); 5.25 (d, 1H,  $J = 5.9$  Hz); 5.22 (s, 1H); 3.74 (t, 1H,  $J = 6.4$  Hz); 2.05 (o, 1H,  $J = 6.8$  Hz); 1.03 (d, 3H,  $J = 6.8$  Hz); 0.98 (d, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9, 137.5, 134.0, 133.7, 133.5, 128.2, 128.0, 126.5, 126.1, 126.0, 123.3, 117.2, 67.2, 31.4, 19.5, 18.5, 18.4; HRMS (ESI): Exact mass calcd for  $\text{C}_{17}\text{H}_{21}\text{N}_2 [\text{M}+\text{H}]^+$ , 252.1627. Found 252.1628.



**2-((1E,3E)-5-Methylhexa-1,3-dienyl)naphthalene (14h):** A solution of *N*-allylhydrazone **13h** (205 mg, 0.81 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (157 mg, 0.89 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0 °C for 1 h, then warmed to room temperature and stirred for 1 h. DBU (480  $\mu\text{L}$ , 3.20 mmol) was then added to the reaction mixture, which was stirred 10 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (a 13:1 mixture of the major isomer to others by  $^1\text{H}$  NMR

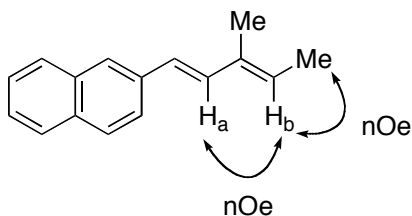
spectroscopy) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (115 mg, 52% yield from 2-naphthaldehyde): mp (decomp.) 64–66°C; IR (diamond) 3053, 2958, 2865, 1460, 1167, 989  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.79 (m, 3H); 7.72 (s, 1H); 7.62 (d, 1H,  $J = 8.3$  Hz); 7.44 (m, 2H); 6.90 (dd, 1H,  $J = 15.6, 10.3$  Hz); 6.64 (d, 1H,  $J = 15.6$  Hz); 6.25 (dd, 1H,  $J = 15.1, 10.2$  Hz); 5.88 (dd, 1H,  $J = 15.1, 6.8$  Hz); 2.45 (h, 1H,  $J = 6.8$  Hz); 1.10 (d, 6H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.6, 143.4, 130.5, 130.3, 128.4, 128.1, 128.0, 127.9, 126.7, 126.5, 126.2, 125.9, 123.7, 31.6, 30.0, 23.0, 22.7; HRMS (EI): Exact mass calcd for  $\text{C}_{17}\text{H}_{18}$   $[\text{M}]^+$ , 222.1403. Found 222.1401.



**(E)-1-(3-Methylbut-3-en-2-yl)-2-(naphthalen-2-ylmethylene)hydrazine**

**(13i):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (3-methylbut-3-en-2-yl)hydrazine hydrochloride **12i** (205 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and

stirred until completion (8 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as an oil that was used directly in the subsequent diene synthesis: IR (diamond) 2967, 2361, 1629, 1130, 742  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.88 (d, 1H,  $J = 8.3$  Hz); 7.79 (m, 4H); 7.72 (s, 1H); 7.45 (p, 2H,  $J = 6.8$  Hz); 5.55 (bs, 1H); 5.01 (s, 1H); 4.91 (s, 1H); 4.03 (q, 1H,  $J = 6.3$  Hz); 1.80 (s, 3H); 1.37 (d, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2, 137.7, 134.0, 133.7, 133.5, 128.4, 128.1, 128.0, 126.4, 126.1, 123.2, 111.5, 111.4, 59.4, 19.4, 19.0; HRMS (ESI): Exact mass calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 238.147. Found 238.1473.

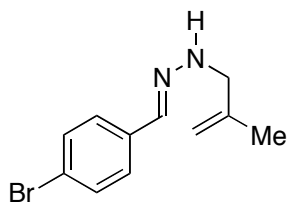


**2-((1E,3E)-3-Methylpenta-1,3-dienyl)naphthalene**

**(14i):**

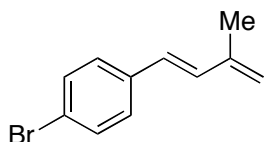
A solution of *N*-allylhydrazone **13i** (229 mg, 0.96 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (188 mg, 1.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0 °C for 1 h, then warmed to room

temperature and stirred for 1 h. DBU (575  $\mu\text{L}$ , 3.80 mmol) was then added to the reaction mixture, which was stirred 9 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure and the resulting residue (6:1 E:Z, determined by nOe experiments) purified by column chromatography on silica gel in hexanes to afford a white crystalline solid (133 mg, 64% yield from 2-naphthaldehyde): mp (decomp.) 74–76°C; IR (diamond) 3052, 2911, 1590, 1364, 956  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.79 (d, 2H,  $J = 6.3$  Hz); 7.76 (d, 1H,  $J = 4.9$  Hz); 7.64 (d, 1H,  $J = 8.8$  Hz); 7.45 (m, 3H); 6.95 (d, 1H,  $J = 16.1$  Hz); 6.62 (d, 1H,  $J = 16.1$  Hz); 5.78 (q, 1H,  $J = 6.8$  Hz); 1.91 (s, 3H); 1.83 (d, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 135.1, 134.6, 134.0, 132.9, 128.7, 128.4, 128.1, 127.9, 126.4, 126.1, 125.7, 125.6, 123.8, 14.5, 12.4; HRMS (EI): Exact mass calcd for  $\text{C}_{16}\text{H}_{16}$   $[\text{M}]^+$ , 208.1247. Found 208.1247.



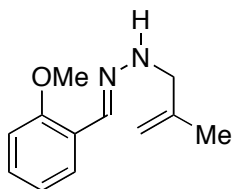
**1-(4-Bromobenzylidene)-2-(2-methylallyl)hydrazine (13j):** A solution of 4-bromobenzaldehyde (185 mg, 1.00 mmol), (2-methylallyl)hydrazine hydrochloride **12j** (1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (10.0 mL) was stirred under N<sub>2</sub> atmosphere at room temperature for 12 h. The MeOH was removed under reduced pressure and the resulting residue dissolved in Et<sub>2</sub>O (20 mL), and washed with sat. NaHCO<sub>3</sub> (20 mL).

The aqueous phase was extracted with Et<sub>2</sub>O (2 x 10 mL). The organics were then diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded the title compound as a crystalline solid that was dried under high vacuum for 12 h and then used directly in the subsequent diene synthesis: mp (decomp.) 62 °C; IR (thin film) 3078, 2970, 2915, 1651, 1594, 1485 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.48 (s, 1H); 7.45–7.38 (m, 4H); 5.68 (bs, 1H); 4.93 (s, 1H); 4.91 (s, 1H); 3.79 (s, 2H); 1.79 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 142.1, 135.0, 134.8, 131.6 (two coincident signals), 127.2 (two coincident signals), 121.5, 112.3, 54.7, 20.7; HRMS (ESI): Exact mass calcd for C<sub>11</sub>H<sub>14</sub>BrN<sub>2</sub> [M+H]<sup>+</sup>, 253.0340. Found 253.0340.



**(E)-1-Bromo-4-(3-methylbuta-1,3-dienyl)benzene (14j):** A solution of *N*-allylhydrazone **13j** (253 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a

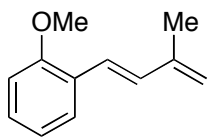
foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was stirred for 2 h at 0 °C, then warmed to room temperature and stirred 30 min. DBU (598 μL, 4.00 mmol) was then added to the reaction mixture at 0 °C, which was stirred 5 h at 0 °C. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow solid (>20:1 E:Z by <sup>1</sup>H NMR spectroscopy). Purification by column chromatography on silica gel in hexanes afforded the title compound as a yellow crystalline solid (148 mg, 66% yield): mp (decomp.) 50–55 °C; IR (film) 3083, 1796, 1674, 1309, 1004 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.42 (dd, 2H, *J* = 8.4, 1.6 Hz); 7.27 (d, 2H, *J* = 8.4 Hz); 6.84 (d, 1H, *J* = 16.3 Hz); 6.44 (d, 1H, *J* = 16.1 Hz); 5.12 (s, 1H), 5.10 (s, 1H); 1.95 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.7, 136.3, 132.3, 131.6 (two coincident signals), 127.9 (two coincident signals), 127.4, 121.1, 118.0, 18.5; HRMS (APPI): Exact mass calcd for C<sub>11</sub>H<sub>12</sub>Br [M+H]<sup>+</sup>, 223.01235 Found 223.01073.



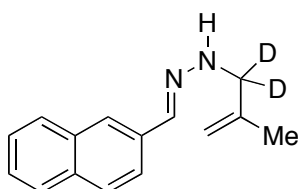
**1-(2-Methoxybenzylidene)-2-(2-methylallyl)hydrazine (13k):** A solution of 2-methoxybenzaldehyde (121 μL, 1.00 mmol), (2-methylallyl)hydrazine hydrochloride **12k** (1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (10.0 mL) was stirred under N<sub>2</sub> atmosphere at room temperature for 12 h. The MeOH was removed under reduced pressure and the resulting residue dissolved in Et<sub>2</sub>O (20 mL), and washed with sat. NaHCO<sub>3</sub> (20 mL). The aqueous

phase was extracted with Et<sub>2</sub>O (2 x 10 mL). The organics were then diluted with hexanes and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure afforded the title compound as a yellow oil that was dried under high vacuum for 12 h and then used directly in the subsequent diene synthesis: IR (thin film) 3075, 2837, 1652, 1601, 1462 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.99 (s, 1H); 7.81 (dd, 1H, *J* = 7.9, 1.5 Hz); 7.22 (td, 1H, *J* = 8.8, 1.8 Hz); 6.93 (t, 1H, *J* = 7.6 Hz); 6.85 (d, 1H, *J* = 8.2 Hz); 5.59 (bs, 1H); 4.94 (s, 1H); 4.89 (s, 1H); 3.82 (s, 3H); 3.80 (s, 2H); 1.78 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.6, 142.6, 132.9, 128.9, 125.3, 124.4, 120.8, 112.0, 110.8, 55.4, 55.1, 20.8; HRMS (ESI): Exact mass calcd for C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup>, 205.1341. Found 205.1345.

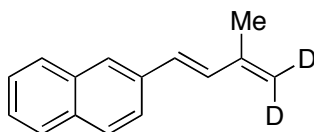




**(E)-1-Methoxy-2-(3-methylbuta-1,3-dienyl)benzene (14k):** A solution of *N*-allylhydrazone **13k** (204 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was stirred for 3 h at 0 °C, then warmed to room temperature and stirred 1 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (>20:1 E:Z by  $^1\text{H}$  NMR spectroscopy). Purification by column chromatography on silica gel in hexanes afforded the title compound as a clear oil (102 mg, 59% yield): IR (film) 3077, 3001, 2943, 2835, 1595, 1488  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.50 (dd, 1H,  $J = 7.8, 1.5$  Hz); 7.19 (td, 1H,  $J = 8.8, 1.5$  Hz); 6.90 (m, 3H); 6.84 (d, 1H,  $J = 8.3$  Hz); 5.09 (s, 1H); 5.04 (s, 1H); 3.83 (s, 3H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 156.7, 142.6, 132.0, 128.4, 126.4, 126.2, 123.2, 120.6, 116.8, 110.8, 55.4, 18.6; HRMS (EI): Exact mass calcd for  $\text{C}_{12}\text{H}_{14}\text{O}[\text{M}]^+$ , 174.1039. Found 174.1033.



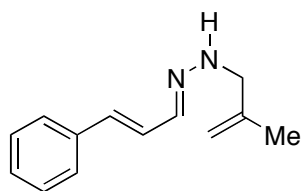
**1-(1,1- $d_2$ -2-Methylallyl)-2-(naphthalen-2-ylmethylene)hydrazine (13l):** A solution of 2-naphthaldehyde (256 mg, 1.00 mmol) in MeOH (5.0 mL) was cannulated (1 mL MeOH rinse) into a stirred solution of (1,1- $d_2$ -2-methylallyl)hydrazine hydrochloride **12l** (187 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.5 mmol) in MeOH (5.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (12 h). The MeOH was removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (20 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 20 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a crystalline solid that was used directly in the subsequent diene synthesis: mp (decomp.) 48–50°C; IR (diamond) 2716, 1577, 1447, 912  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.93 (dd, 1H,  $J = 15.4, 6.8$  Hz); 7.84 (m, 3H); 7.80 (s, 1H); 7.73 (s, 1H); 7.51–7.47 (m, 2H); 5.7 (b s, 1H); 5.03 (s, 1H); 4.99 (s, 1H); 1.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 134.1, 133.8, 133.6, 128.5, 128.4, 128.2, 126.5, 126.2, 126.1, 123.3, 112.6, 54.6 (p, 1C,  $J = 21.3$  Hz); 28.6, 21.1; HRMS (ESI): Exact mass calcd for  $\text{C}_{15}\text{H}_{15}\text{D}_2\text{N}_2[\text{M}+\text{H}]^+$ , 226.1439. Found 226.1440.



**1-(1,1- $d_2$ -2-Methylallyl)-2-(naphthalen-2-ylmethylene)hydrazine (14l):** A solution of *N*-allylhydrazone **13l** (226 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0 °C, under  $\text{N}_2$  atmosphere. The reaction was stirred for 3 h at 0 °C, then warmed to room temperature and stirred 1 h. DBU (598  $\mu\text{L}$ , 4.00 mmol) was then added to the reaction mixture, which was stirred 5 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). The collected filtrate was concentrated under reduced pressure to afford a yellow oil (>20:1 E:Z by  $^1\text{H}$  NMR spectroscopy, a single regioisomer). Purification by column chromatography on silica gel in hexanes afforded the title compound as an off-white solid (145 mg, 74% yield): mp (decomp.) 85 °C ;IR (film) 3050, 3019, 2952, 2867, 1677, 1619, 992  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.85 (m, 4H); 7.72 (d, 1H,  $J = 8.8$  Hz); 7.51 (m, 2H); 7.10 (d, 1H,  $J = 16.1$  Hz);

6.78 (d, 1 H,  $J = 16.1$  Hz); 2.10 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 134.8, 133.6, 132.9, 131.9, 128.7, 128.2, 127.9, 127.6, 126.5, 126.2, 125.7, 123.5, 116.9 (p, 1C,  $J = 24.0$  Hz), 18.5; HRMS (APPI): Exact mass calcd for  $\text{C}_{15}\text{H}_{13}\text{D}_2$   $[\text{M}+\text{H}]^+$ , 197.13004. Found 197.12916.

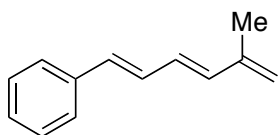
### E. Triene Synthesis



#### 1-(2-Methylallyl)-2-((*E*)-3-phenylallylidene)hydrazine:

*Trans*-

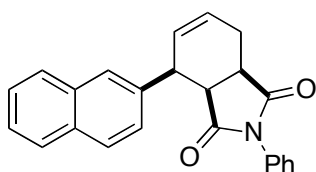
cinnamaldehyde (130  $\mu\text{L}$ , 1.00 mmol) was slowly added to a stirred solution of (2-methylallyl)hydrazine hydrochloride **12a** (184 mg, 1.50 mmol) and potassium carbonate (207 mg, 1.50 mmol) in MeOH (10.0 mL) at room temperature. The reaction was monitored by  $^1\text{H}$ -NMR spectroscopy and stirred until completion (12 h). The MeOH was then removed under reduced pressure and the resulting residue dissolved in  $\text{Et}_2\text{O}$  (15 mL), and washed with sat.  $\text{NaHCO}_3$  (3 x 15 mL). The organics were then diluted with hexanes and dried over  $\text{Na}_2\text{SO}_4$ . Concentration under reduced pressure afforded the title compound as a yellow oil that was used directly in the subsequent diene synthesis: IR (film) 3045, 1670, 1580, 945  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.47–7.43 (m, 3H); 7.35 (t, 2H,  $J = 7.3$  Hz); 7.26 (t, 1H,  $J = 7.3$  Hz); 6.94 (dd, 1H,  $J = 16.1$ , 9.3 Hz); 6.63 (d, 1H,  $J = 16.1$  Hz); 5.60 (bs, 1H); 4.96 (d, 2H,  $J = 5.4$  Hz); 3.80 (s, 2H); 1.82 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 139.7, 137.2, 133.2, 129.1, 128.9, 128.0, 127.3, 126.9, 126.7, 112.3, 55.3, 21.0; HRMS (ESI): Exact mass calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$ , 201.1392. Found 201.1382.



**((1*E*,3*E*)-5-Methylhexa-1,3,5-trienyl)benzene (16):** A solution of 1-(2-methylallyl)-2-((*E*)-3-phenylallylidene)hydrazine (200 mg, 1.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (2 mL  $\text{CH}_2\text{Cl}_2$  rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196

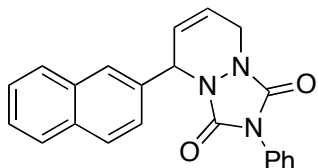
mg, 1.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) in a foil-covered round bottom flask at 0  $^\circ\text{C}$ , under  $\text{N}_2$  atmosphere. The reaction was allowed to stir at 0  $^\circ\text{C}$  for 1 h, then warmed to room temperature and stirred for 2 h. DBU (900  $\mu\text{L}$ , 6.00 mmol) was then added to the reaction mixture, which was stirred 2 h. The reaction mixture was passed under vacuum through a pad of silica gel (3.5 cm diameter, 4 cm height) and which was then rinsed with  $\text{CH}_2\text{Cl}_2$  (100 mL). Care was taken to perform all purification procedures in the dark. The collected filtrate was concentrated under reduced pressure and the resulting residue (a 9:1 mixture of major isomer to the minor isomers by  $^1\text{H}$  NMR spectroscopy) purified by column chromatography on silica gel in hexanes to afford a yellow crystalline solid (91.2 mg, 54% yield from 2-naphthaldehyde): mp (decomp.) 54–56  $^\circ\text{C}$ ; IR (film) 3016, 1446, 990  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.46 (d, 2H,  $J = 7.8$  Hz); 7.37 (t, 2H,  $J = 7.3$  Hz); 7.27 (t, 1H,  $J = 7.3$  Hz); 6.90 (dd, 1H,  $J = 15.6$ , 10.0 Hz); 6.65 (d, 1H,  $J = 15.6$  Hz); 6.51 (d, 1H,  $J = 15.4$  Hz); 6.44 (dd, 1H,  $J = 15.1$ , 10.0 Hz); 5.10 (s, 1H); 5.08 (s, 1H); 1.98 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 137.7, 136.3, 132.9, 129.7, 129.5, 129.0, 128.9, 127.7, 126.8, 126.7, 117.5, 18.8; HRMS (APPI): Exact mass calcd for  $\text{C}_{13}\text{H}_{15}$   $[\text{M}+\text{H}]^+$ , 171.1174. Found 171.1175.

### E. Merged Diene Synthesis and Diels–Alder Sequence



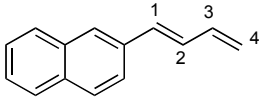
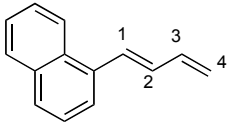
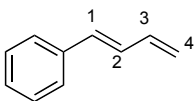
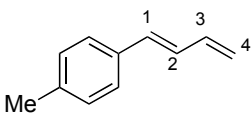
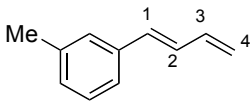
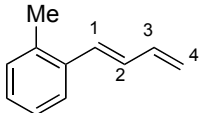
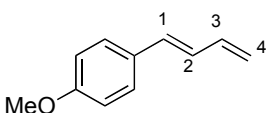
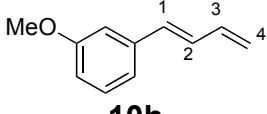
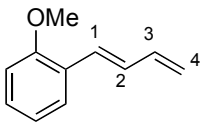
**4-(Naphthalen-2-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isindole-1,3(2*H*)-dione (18):** A solution of *N*-allylhydrazone **9a** (105 mg, 0.50 mmol) in 1,2-dichloroethane (5 mL) under  $\text{N}_2$  atmosphere was added dropwise by cannula (1 mL 1,2-dichloroethane rinse) over 30 min to a

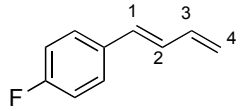
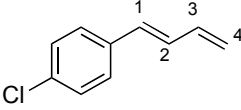
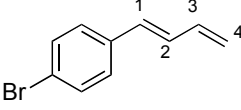
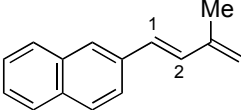
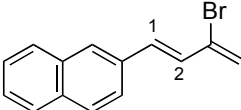
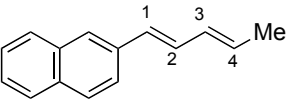
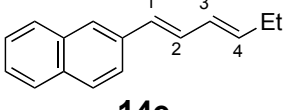
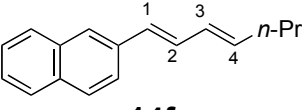
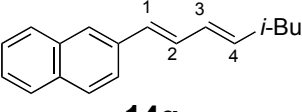
stirred solution of *N*-bromosuccinimide (98 mg, 0.55 mmol) in 1,2-dichloroethane (5 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was stirred for 1 h at 0 °C, then warmed to room temperature. DBU (299 µL, 2.00 mmol) was then added to the reaction mixture, which was heated to reflux. After 15 minutes at reflux the reaction was allowed to cool until reflux had subsided and *N*-phenylmaleimide (433 mg, 2.50 mmol) was added in one portion. Reflux was resumed and the reaction stirred for 22 h. At this point, more *N*-phenylmaleimide (87 mg, 0.50 mmol) was added to reaction, which was heated at reflux for an additional 8 h. The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure. Only one diastereomer was clearly identifiable by <sup>1</sup>H NMR analysis of the crude material. Purification by column chromatography on silica gel in 10% EtOAc/Hexanes → 30% EtOAc/Hexanes (~200 mL of 10% EtOAc/Hexanes was run through the column before increasing the polarity and beginning to collect fractions) afforded the title compound as crystalline solid (98 mg, 56% yield, endo diastereomer determined by NOESY): mp (decomp.) 55 °C; IR (film) 3055, 2959, 2924, 1710, 1597, 1498 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.80–7.75 (m, 3H); 7.69 (s, 1H); 7.46 (m, 2H); 7.31 (dd, 1H, *J* = 8.5, 1.8 Hz); 7.19–7.09 (m, 3H); 6.43 (d, 2H, *J* = 7.3 Hz); 6.28 (m, 1H); 6.21 (m, 1H); 4.13 (app t, 1H, *J* = 6.4 Hz); 3.55 (app t, 1H, *J* = 7.6 Hz); 3.93 (td, 1H, *J* = 10.0, 2.6 Hz); 3.09 (app d, 1H, *J* = 18.2 Hz); 2.62 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 178.5, 176.5, 135.6, 133.2, 132.7, 131.3, 129.0, 128.7 (two coincident signals); 128.2, 128.1, 128.0, 127.9, 127.4, 127.2, 127.1, 126.2, 126.0 (two coincident signals); 125.9(8), 44.8, 40.9, 38.1, 21.9; HRMS (ESI): Exact mass calcd for C<sub>24</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup>, 354.1494 Found 354.1491.

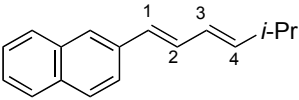
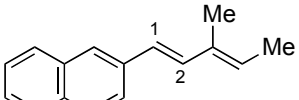
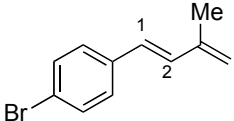
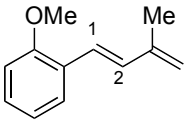
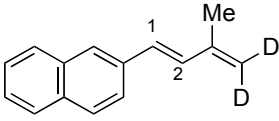
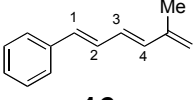


**5-(Naphthalen-2-yl)-2-phenyl-5,8-dihydro-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H)-dione (20):** A solution of *N*-allylhydrazone **9a** (210 mg, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under N<sub>2</sub> atmosphere was added dropwise by cannula (2 mL CH<sub>2</sub>Cl<sub>2</sub> rinse) over 30 min to a stirred solution of *N*-bromosuccinimide (196 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) in a foil-covered round bottom flask at 0 °C, under N<sub>2</sub> atmosphere. The reaction was stirred for 2 h at 0 °C, then warmed to room temperature and stirred 40 min. DBU (598 µL, 4.00 mmol) was then added to the reaction mixture, which was stirred 2 h at room temperature. A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (175 mg, 1.00 mmol) in DCM (5 mL) was added by cannula. After 3 h stirring, more 4-phenyl-1,2,4-triazoline-3,5-dione (175 mg, 1.00 mmol) was added in one portion and the reaction heated at reflux for 18 h. At this point the reaction was allowed to cool to room temperature and more 4-phenyl-1,2,4-triazoline-3,5-dione (350 mg, 2.00 mmol) was added in one portion. Stirring continued for 8 h. The solvent was removed under reduced pressure and the resulting residue purified by column chromatography on silica gel in 30% EtOAc/Hexanes → 50% EtOAc/Hexanes to afford the title compound as a white crystalline solid (273 mg, 77% yield): mp (decomp.) 209 °C; IR (film) 3056, 2924, 2852, 1773, 1717, 1599, 1417 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.88 (s, 1H); 7.82 (m, 3H); 7.54 (dd, 1H, *J* = 8.5, 1.5 Hz); 7.48 (app dd, 2H, *J* = 6.2, 3.2 Hz); 7.36 (m, 4H); 7.27 (m, 1H); 6.17 (m, 1H); 6.07 (m, 1H); 5.71 (app s, 1H); 4.57 (app dt, 1H, *J* = 16.7, 2.1 Hz); 4.18 (dd, 1H, *J* = 16.7, 2.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 153.1, 151.2, 133.4, 133.3, 133.0, 131.0, 128.9 (two coincident signals), 128.6, 128.2, 128.0 (two coincident signals), 127.6, 126.5, 126.3, 125.5, 125.3, 125.2, (two coincident signals), 120.5, 57.5, 43.9; HRMS (ESI): Exact mass calcd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>, 356.1399 Found 356.1403.

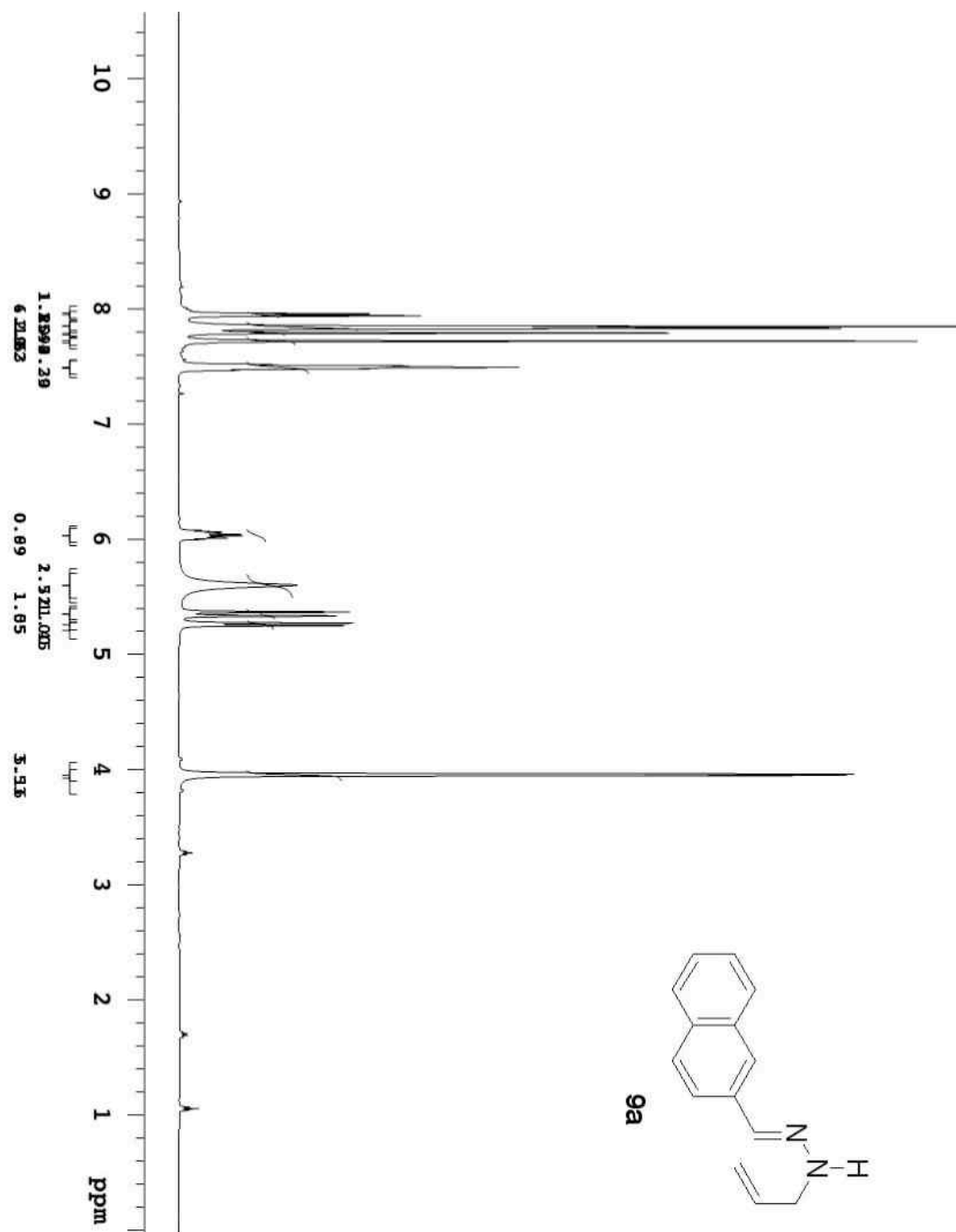
**Table 1.** Summary of NMR spectroscopic data: diene selectivity and stereochemistry

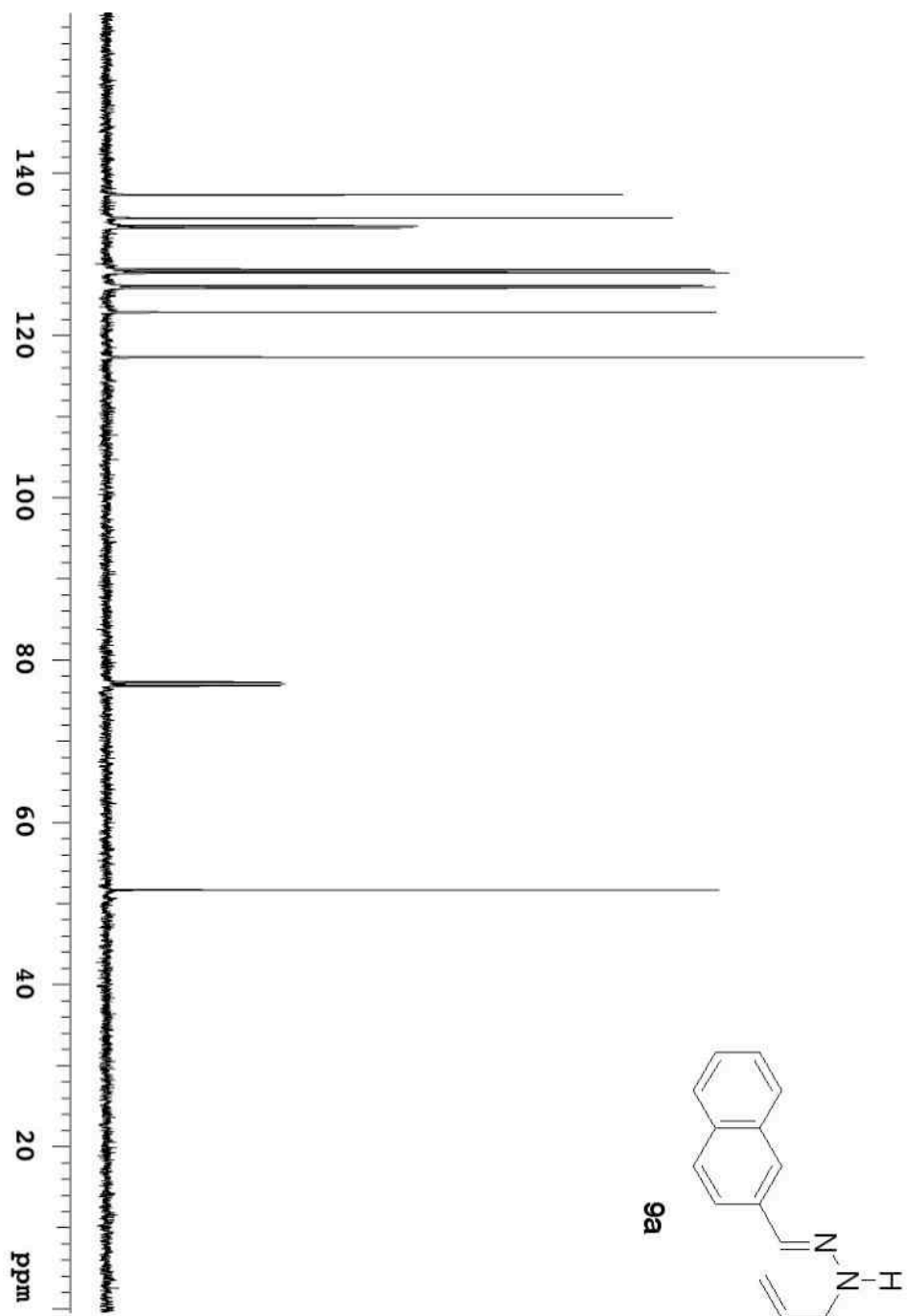
Entry	Compound	<i>E:Z</i>	$J_{1,2}$ (Hz)	$J_{3,4}$ (Hz)
1	 <b>10a</b>	20:1	15.6	
2	 <b>10b</b>	20:1	15.4	
3	 <b>10c</b>	20:1	16.1	
4	 <b>10d</b>	20:1	15.9	
5	 <b>10e</b>	20:1	15.2	
6	 <b>10f</b>	20:1	15.6	
7	 <b>10g</b>	20:1	15.4	
8	 <b>10h</b>	20:1	15.9	
9	 <b>10i</b>	20:1	16.1	

Entry	Compound	<i>E:Z</i>	$J_{1,2}$ (Hz)	$J_{3,4}$ (Hz)
10	 <b>10j</b>	20:1	15.2	
11	 <b>10k</b>	20:1	15.4	
12	 <b>10l</b>	20:1	15.7	
13	 <b>14a</b>	20:1	16.1	
14	 <b>14b</b>	20:1	15.1	
16	 <b>14d</b>	10:1 <sup>*</sup>	15.6	13.7
17	 <b>14e</b>	10:1 <sup>*</sup>	15.6	15.1
18	 <b>14f</b>	11:1 <sup>*</sup>	15.6	14.7
19	 <b>14g</b>	10:1 <sup>*</sup>	16.1	15.1

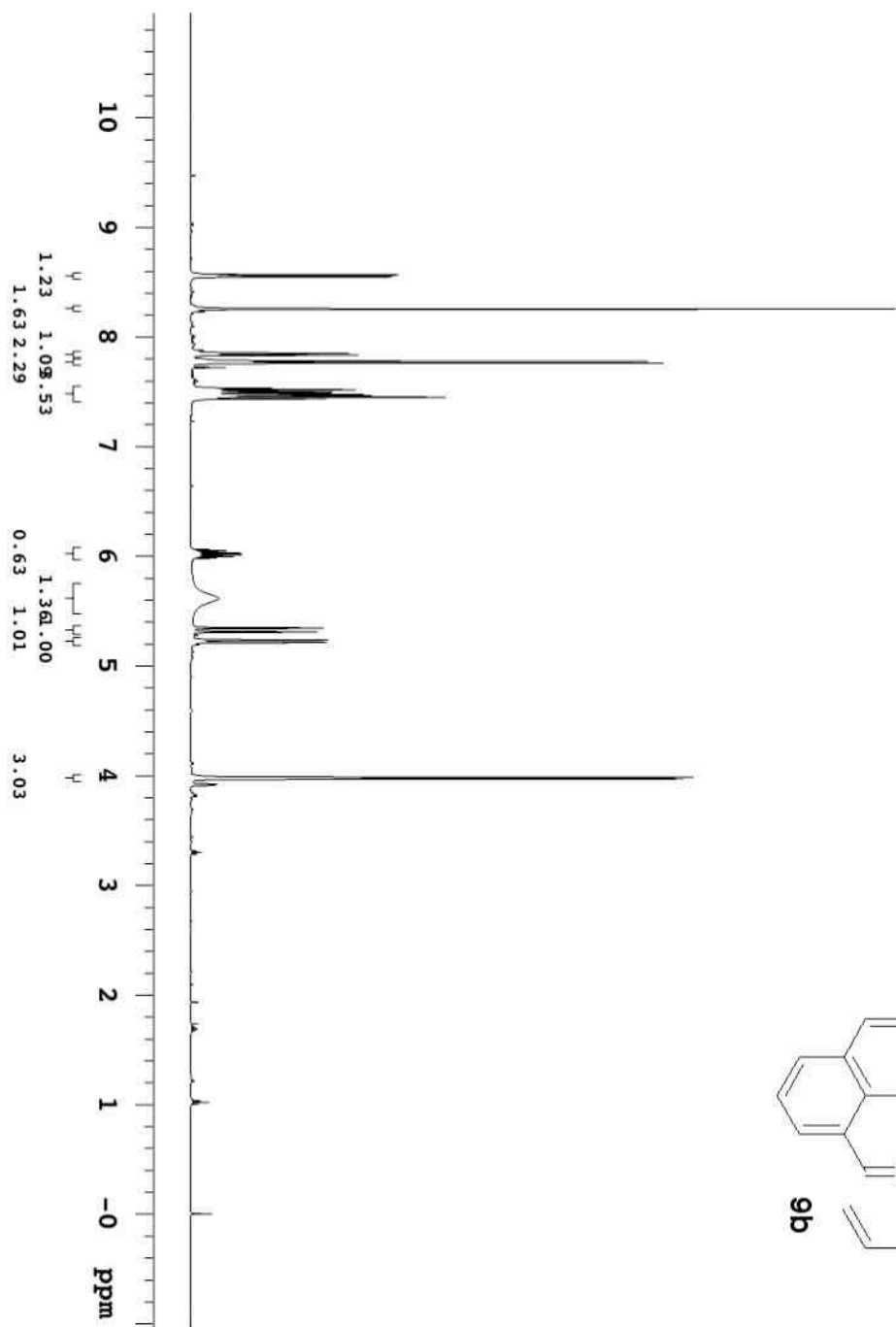
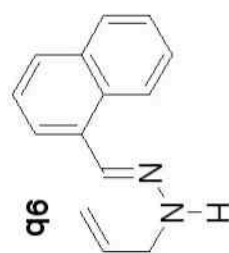
Entry	Compound	<i>E:Z</i>	$J_{1,2}$ (Hz)	$J_{3,4}$ (Hz)
20	 <b>14h</b>	13:1 <sup>*</sup>	15.6	15.1
21	 <b>14i</b>	6:1 <sup>*</sup>	16.1	
22	 <b>14j</b>	20:1	16.3	
23	 <b>14k</b>	20:1	16.1 (in d <sub>6</sub> -benzene)	
24	 <b>14l</b>	20:1	16.1	
25	 <b>16</b>	9:1 <sup>*</sup>	15.6	15.1

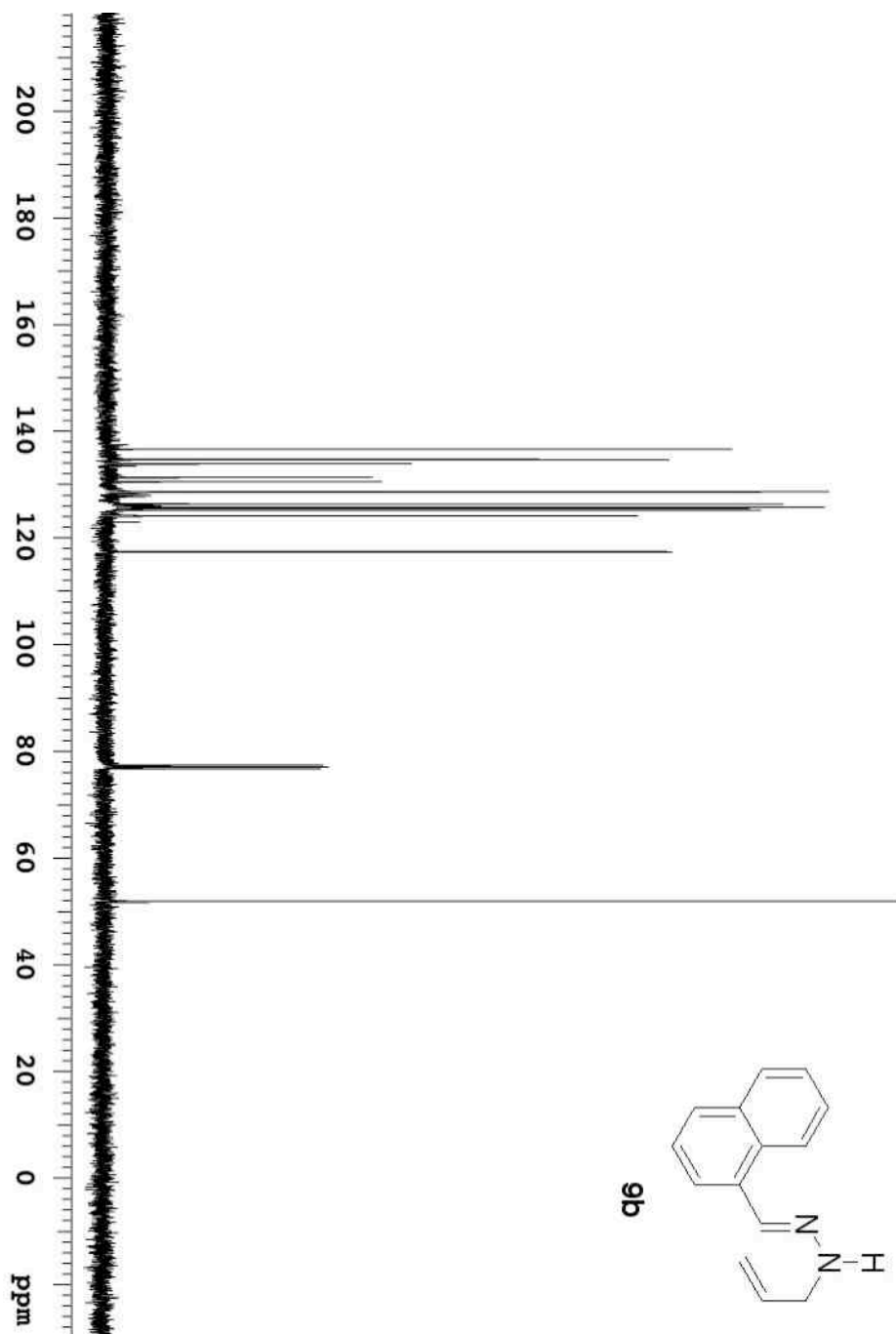
<sup>\*</sup> Refers to the ratio of the major (*E,E*)-isomer to the sum of the other isomers.

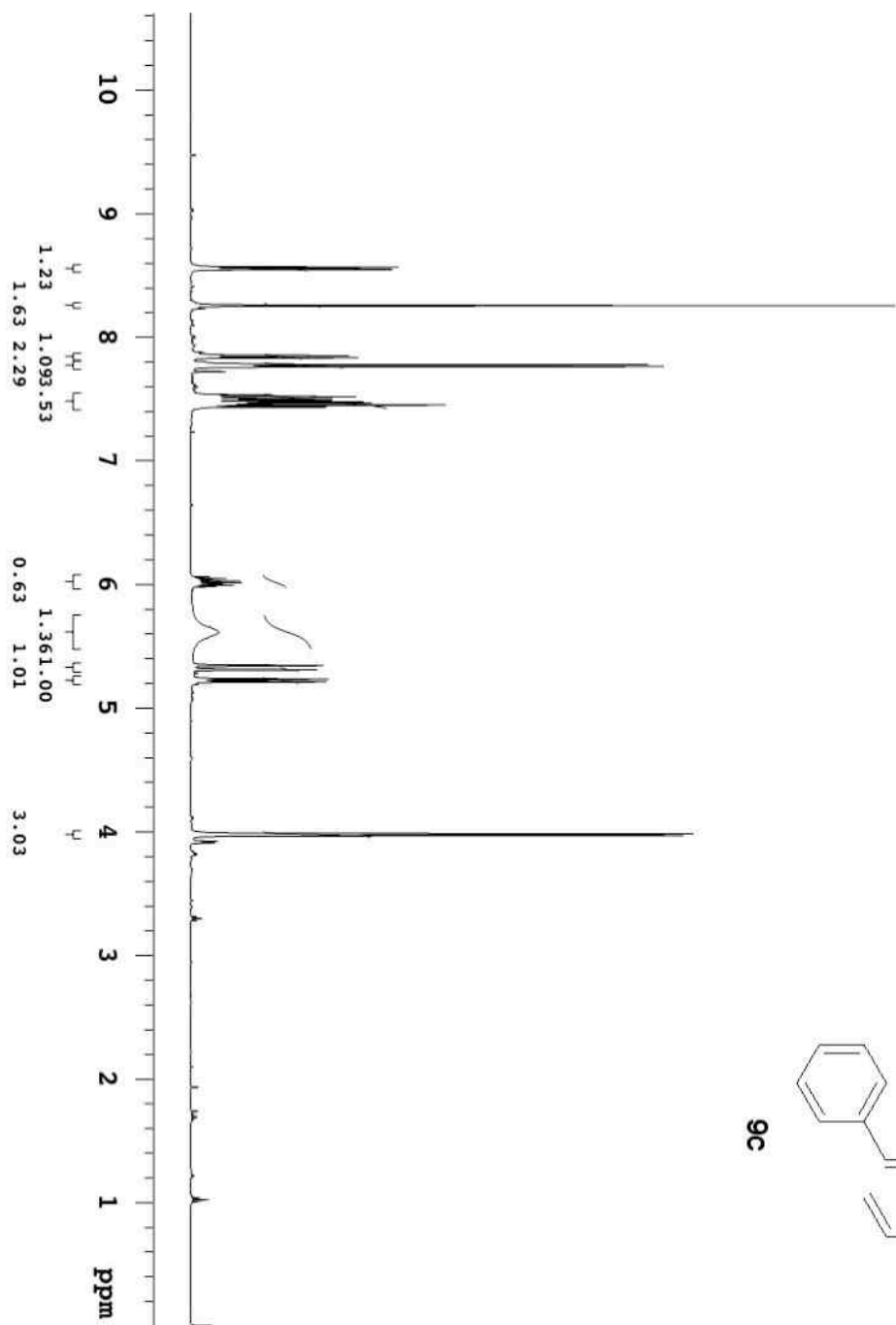
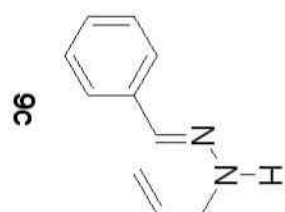
**$^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra:**

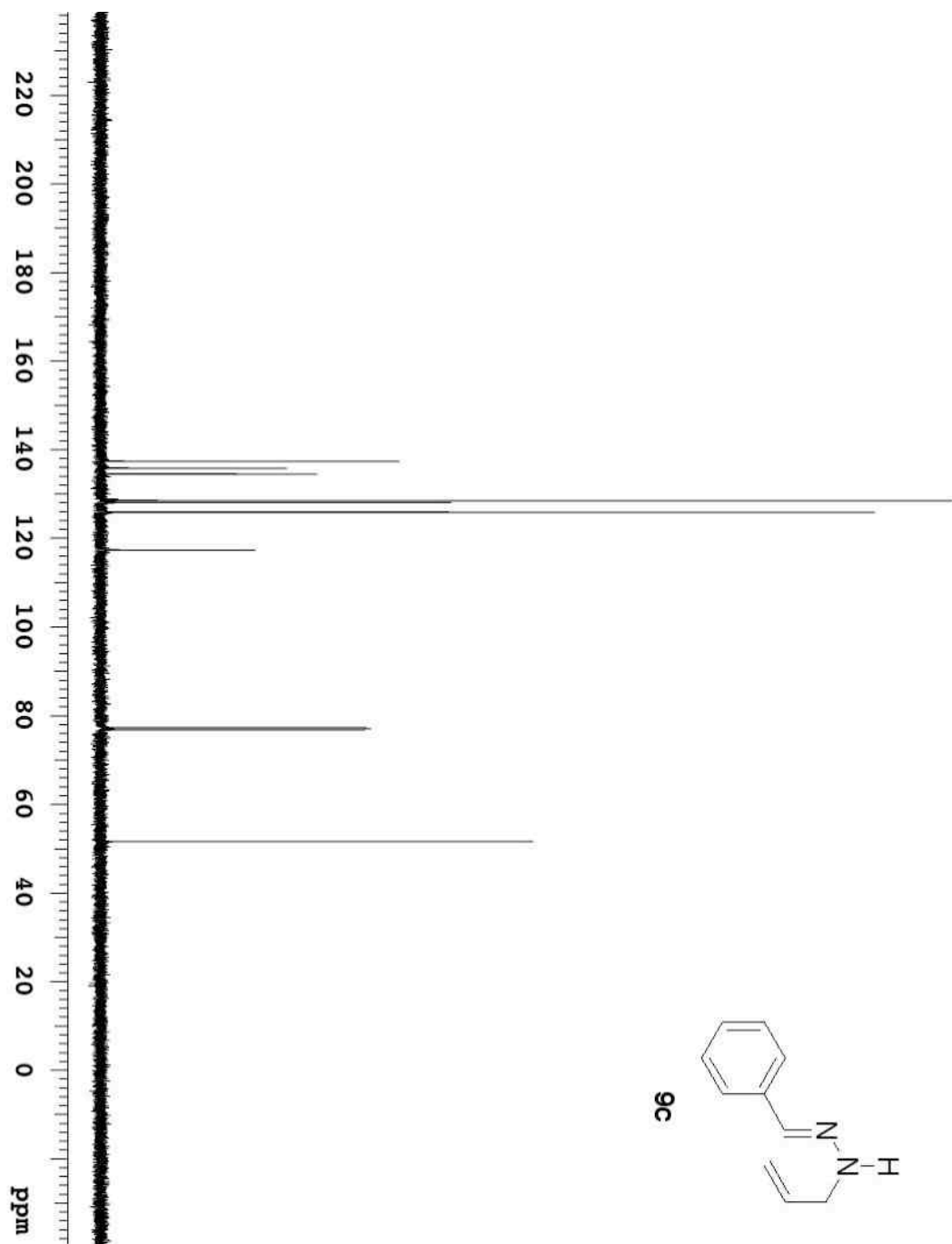


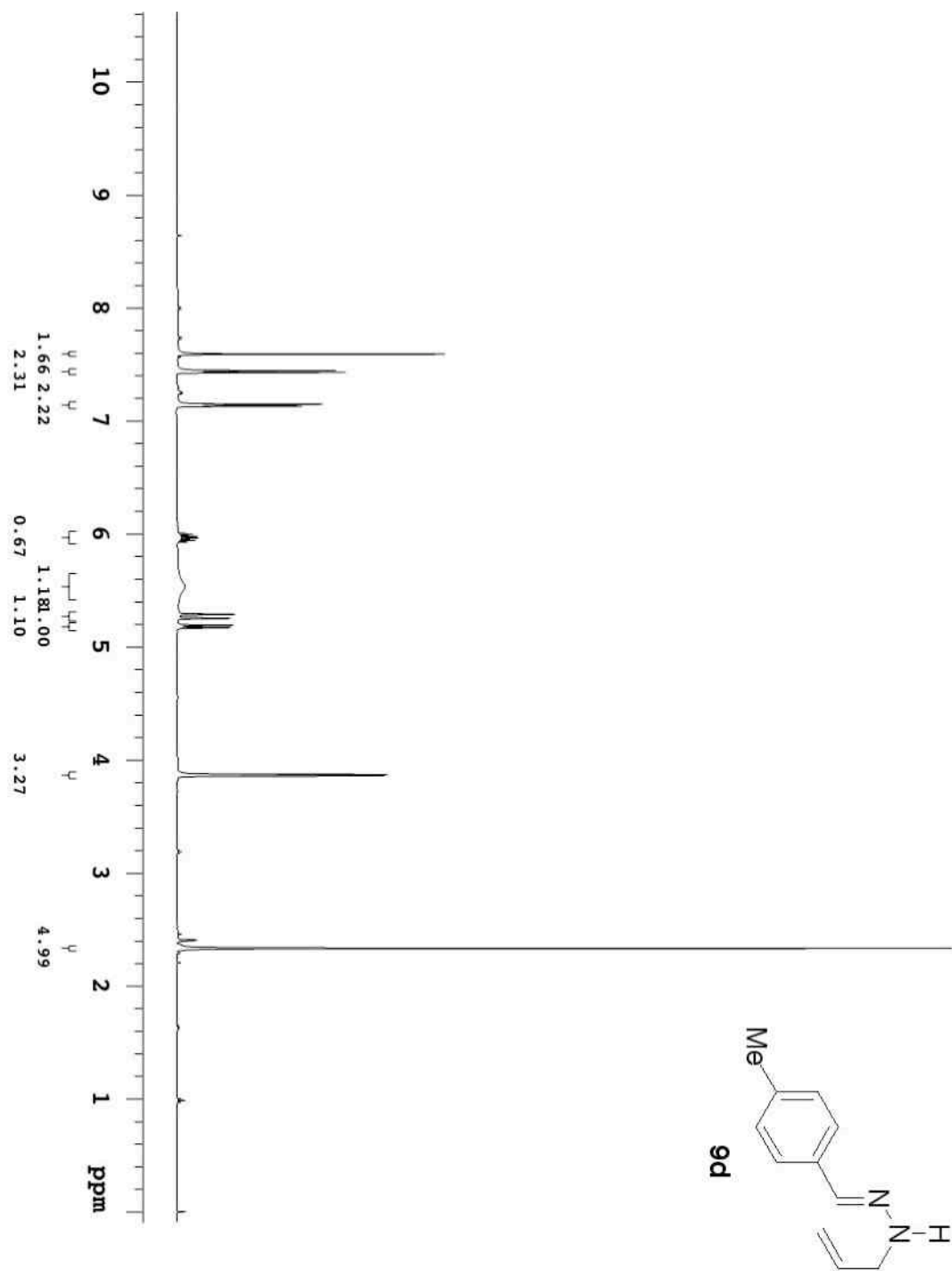


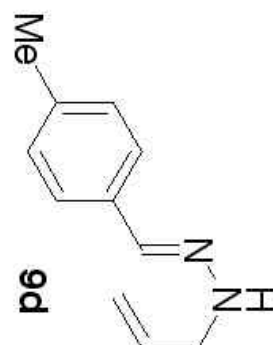






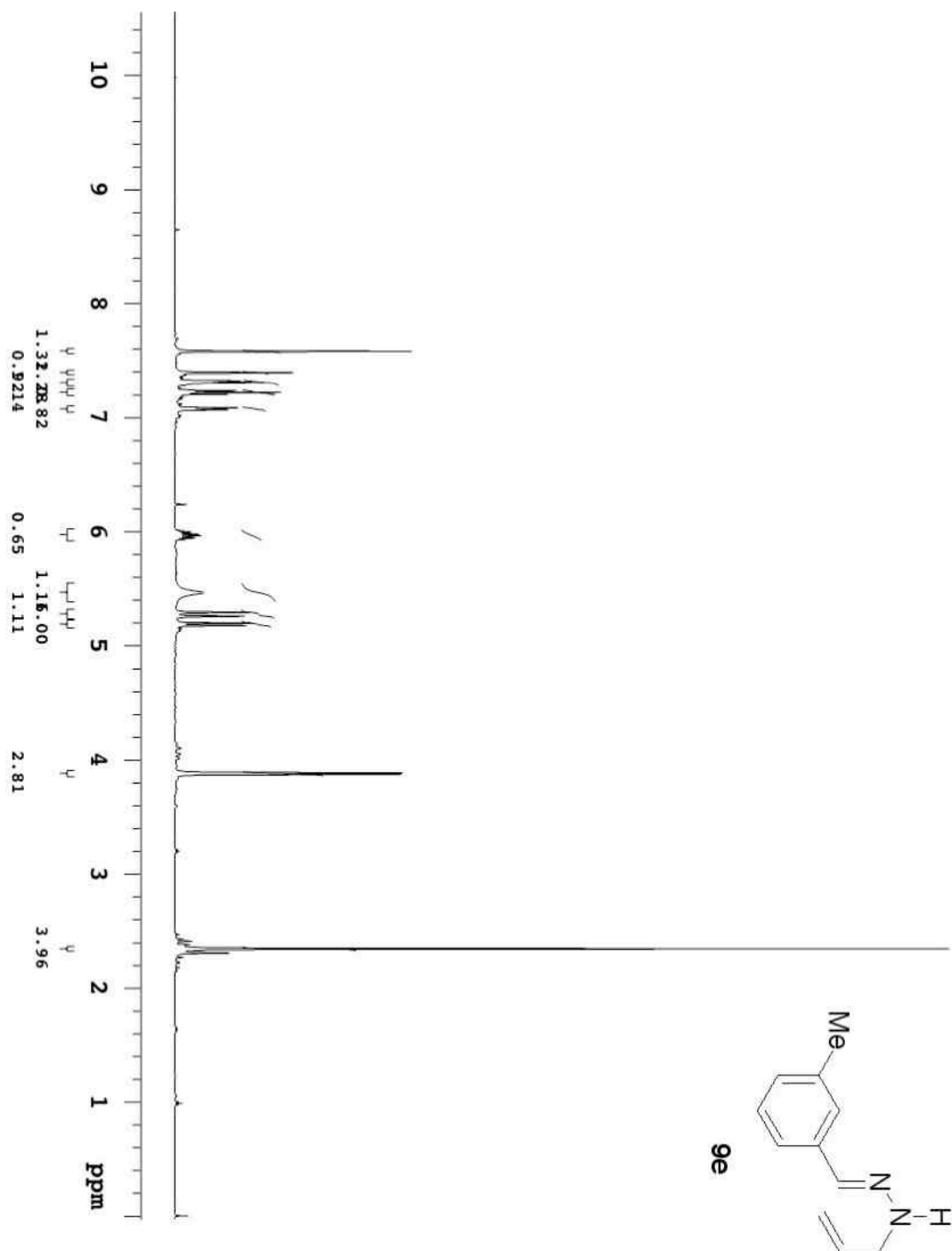


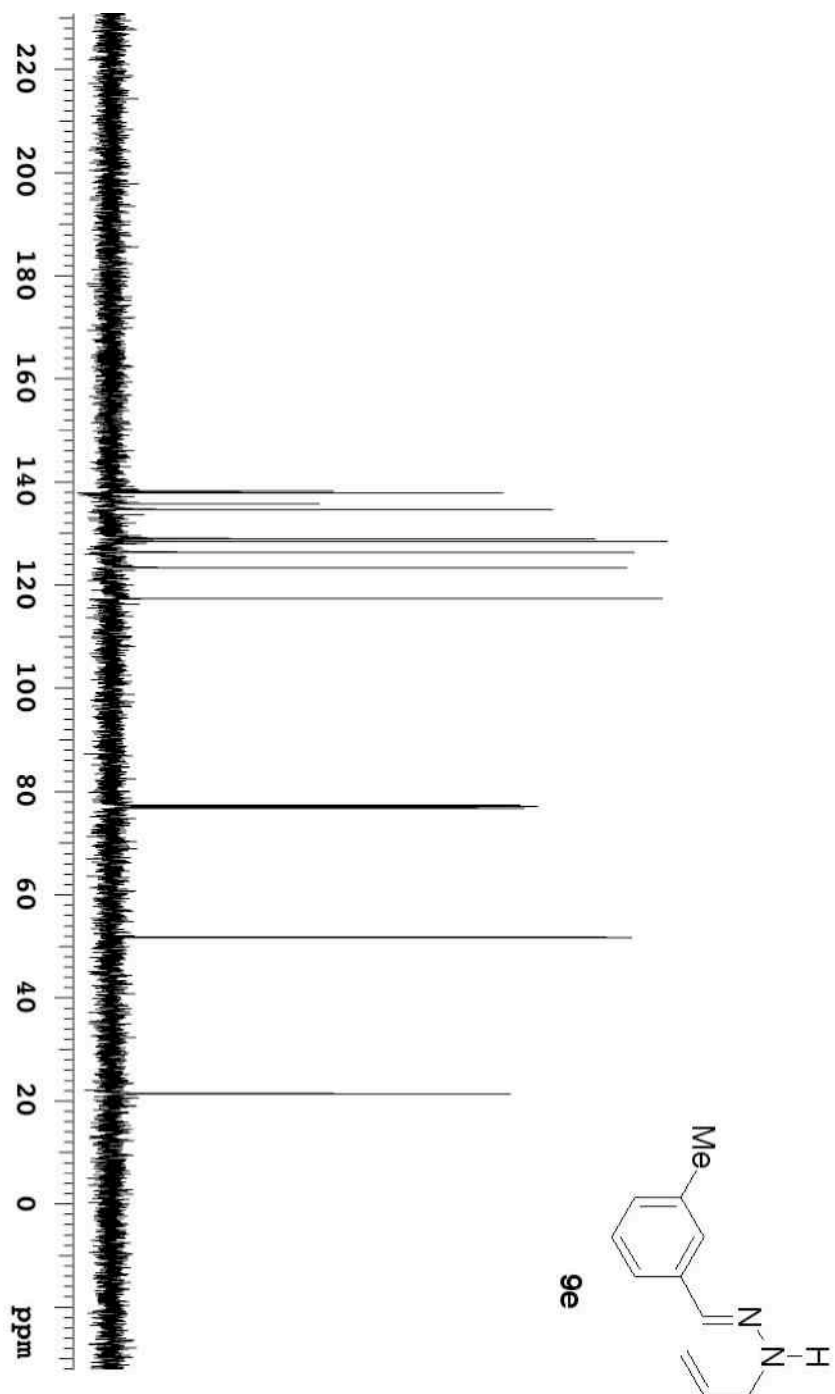




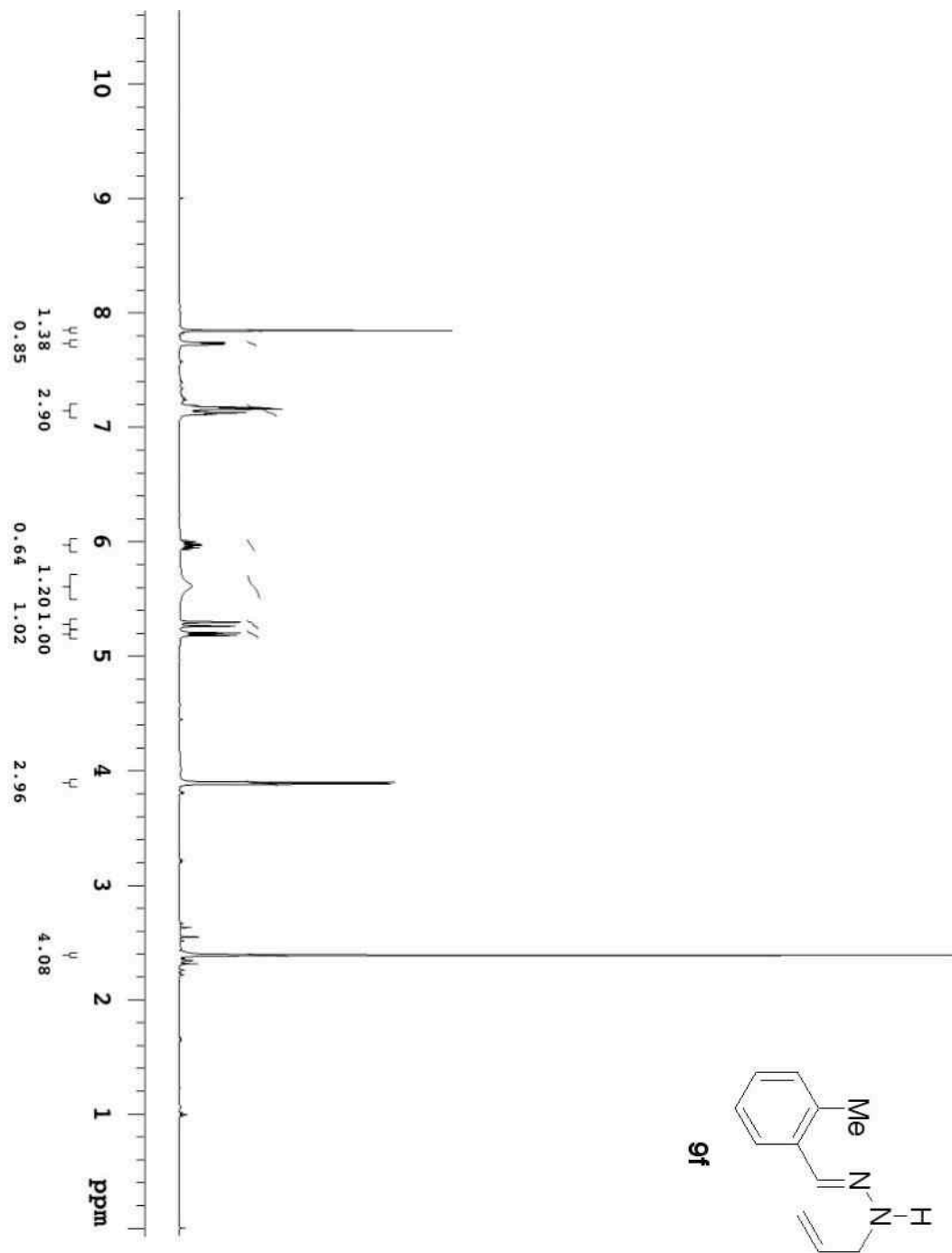
INDEX	FREQUENCY	PPM	HEIGHT
1	1736.814	137.986	65.8
2	16906.970	134.643	50.3
3	16700.828	133.001	24.7
4	16223.023	129.146	125.0
5	15882.676	125.848	122.5
6	14723.028	117.251	70.2
7	9700.578	77.253	32.1
8	9668.322	76.496	33.0
9	8636.569	76.743	32.2
10	6948.083	51.757	65.6
11	2671.097	21.272	50.3

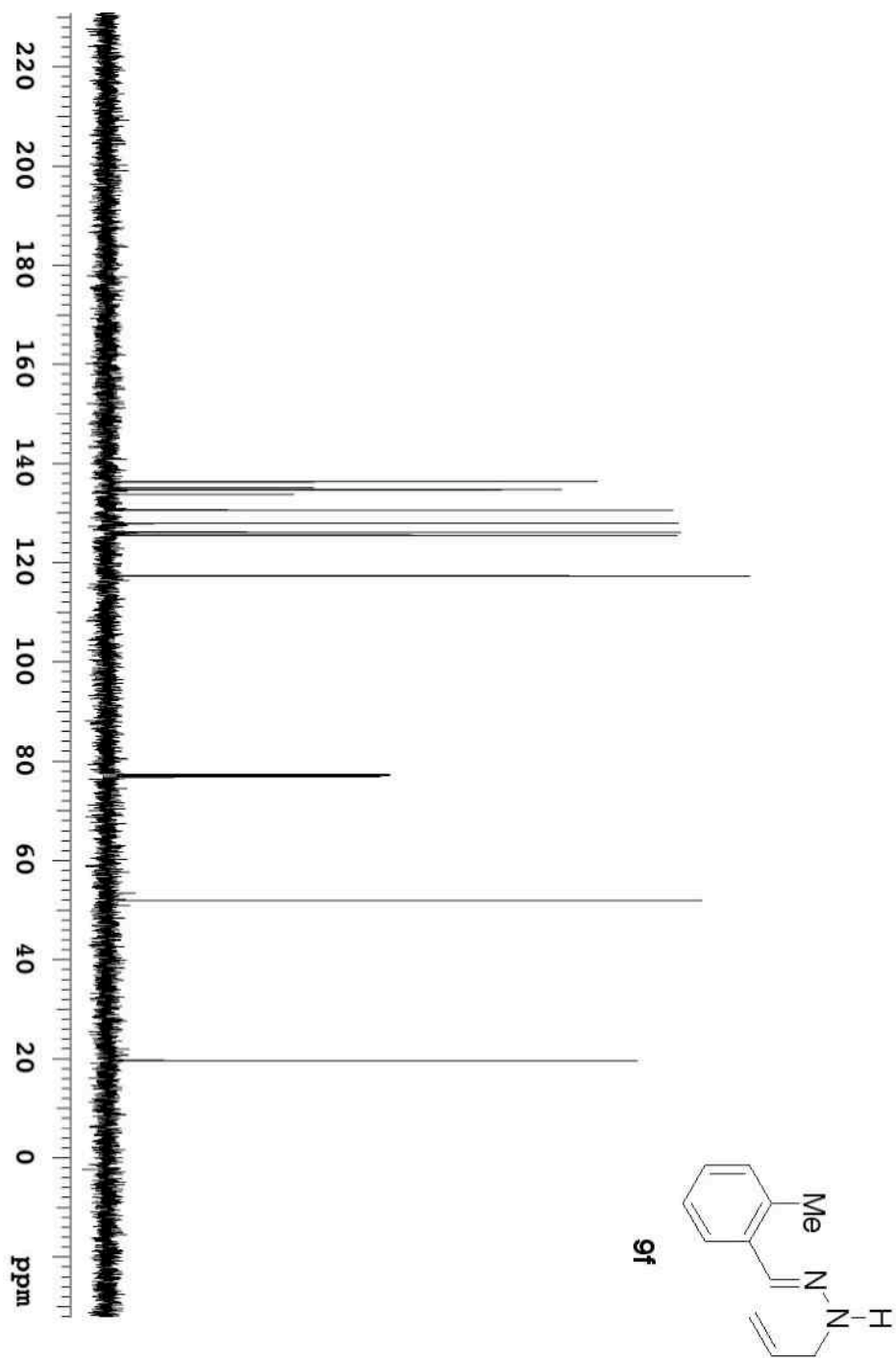


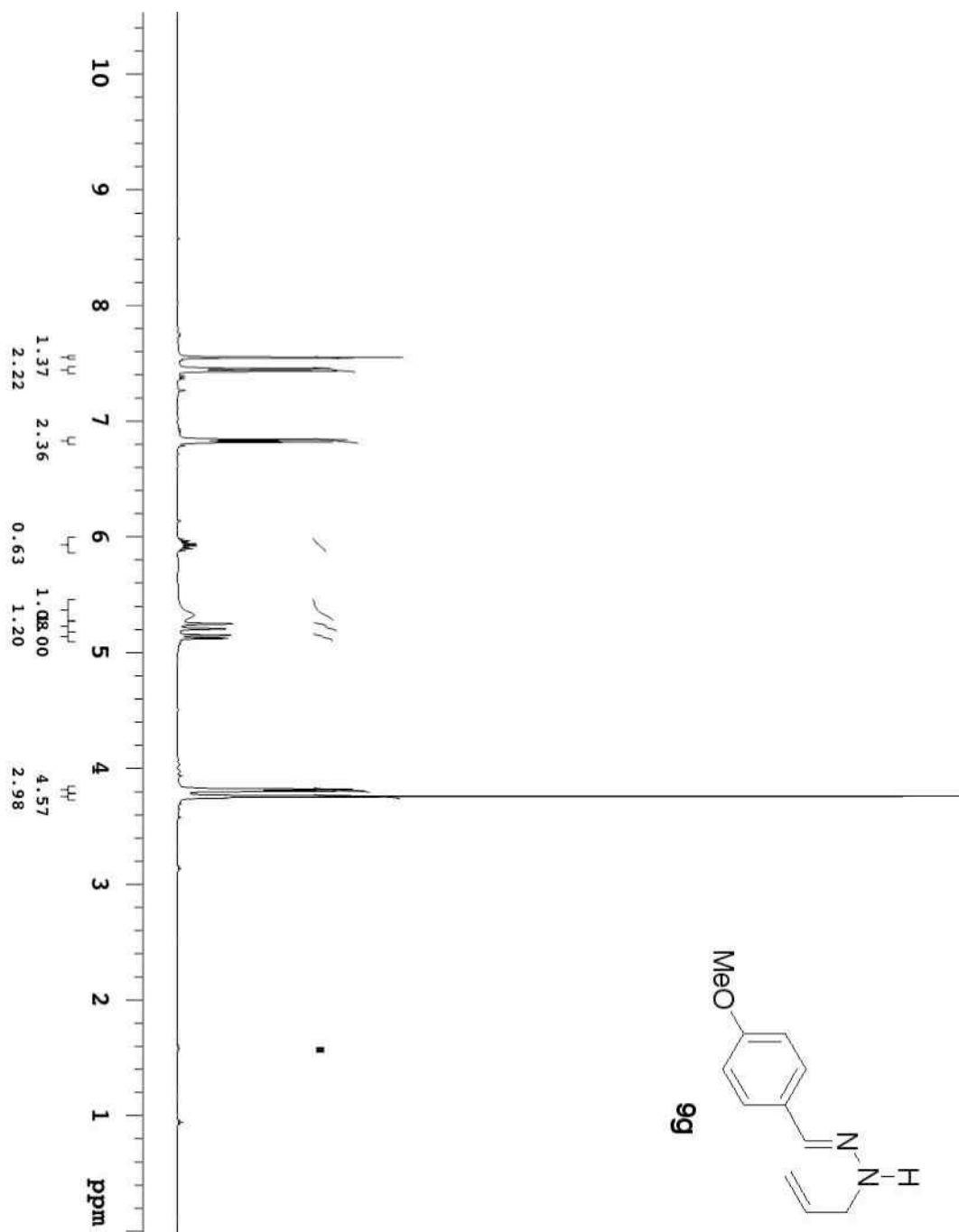


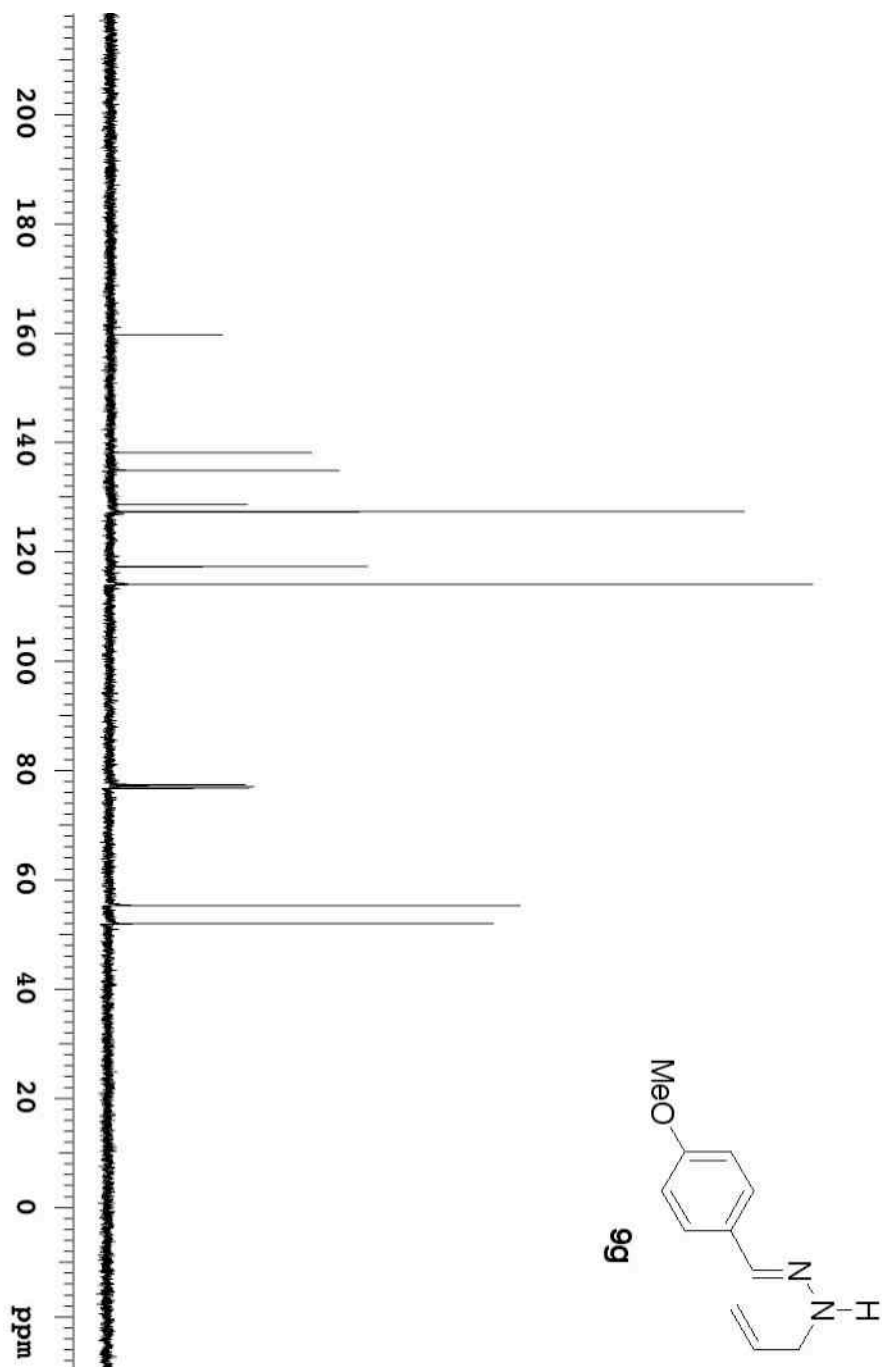


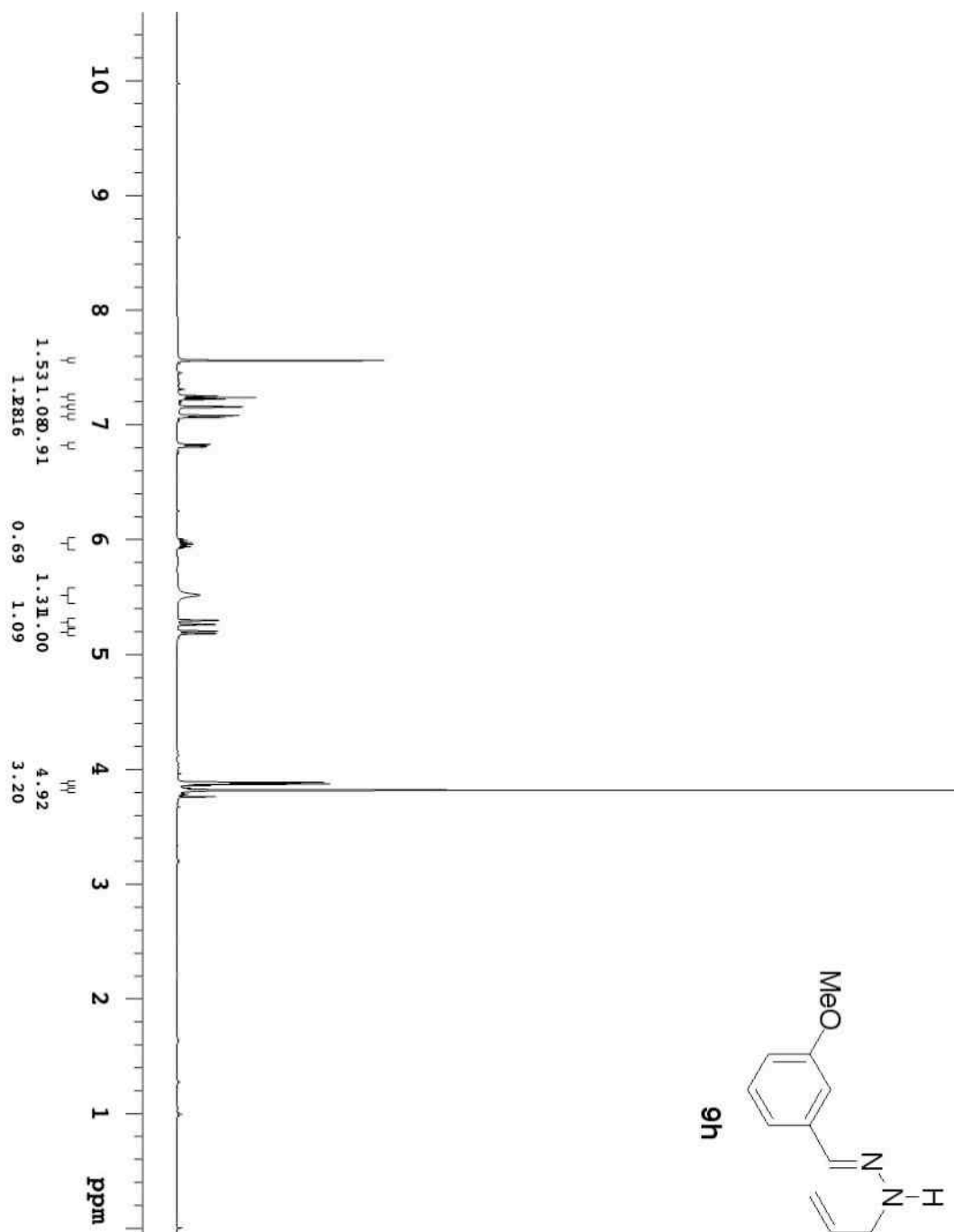


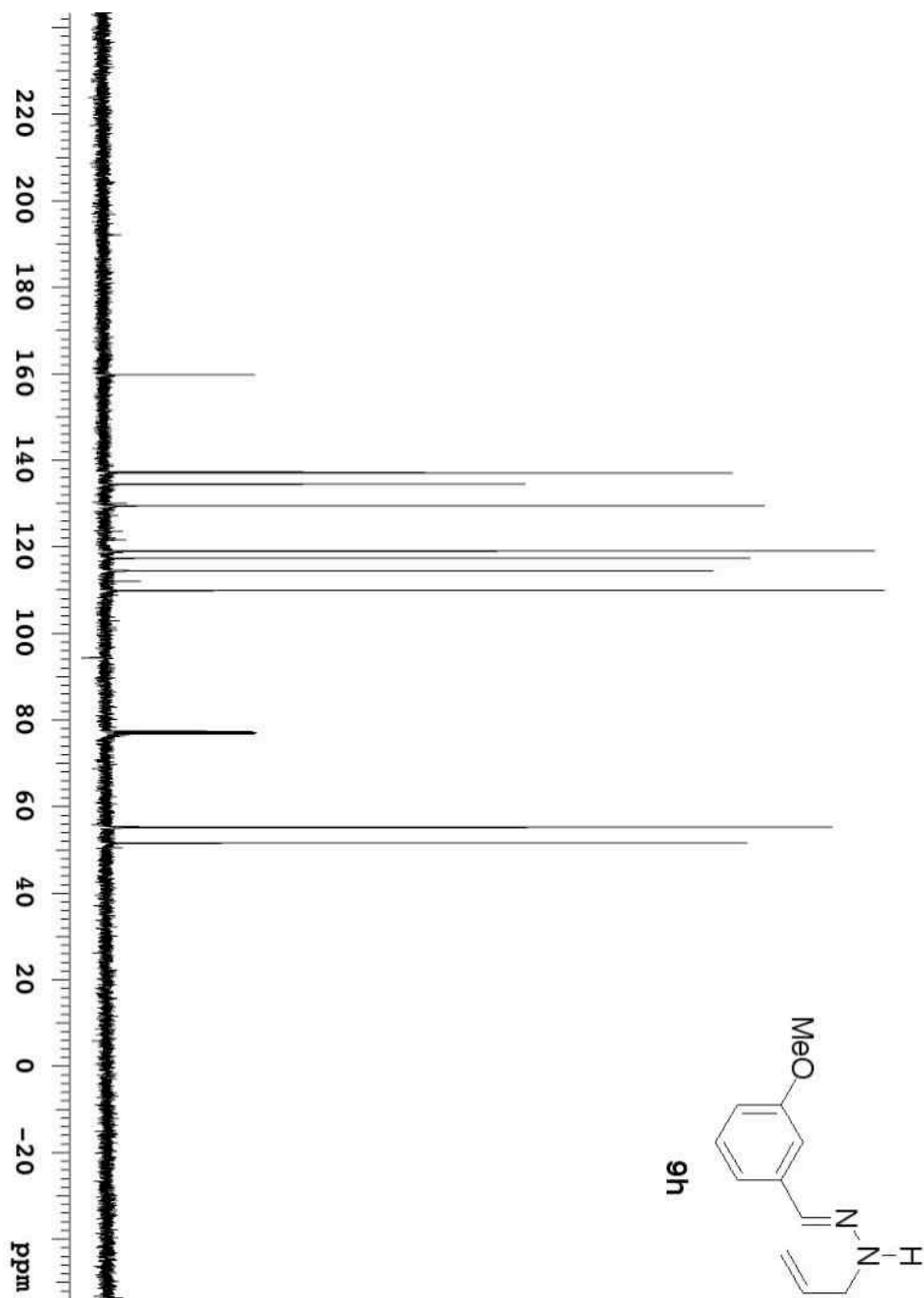


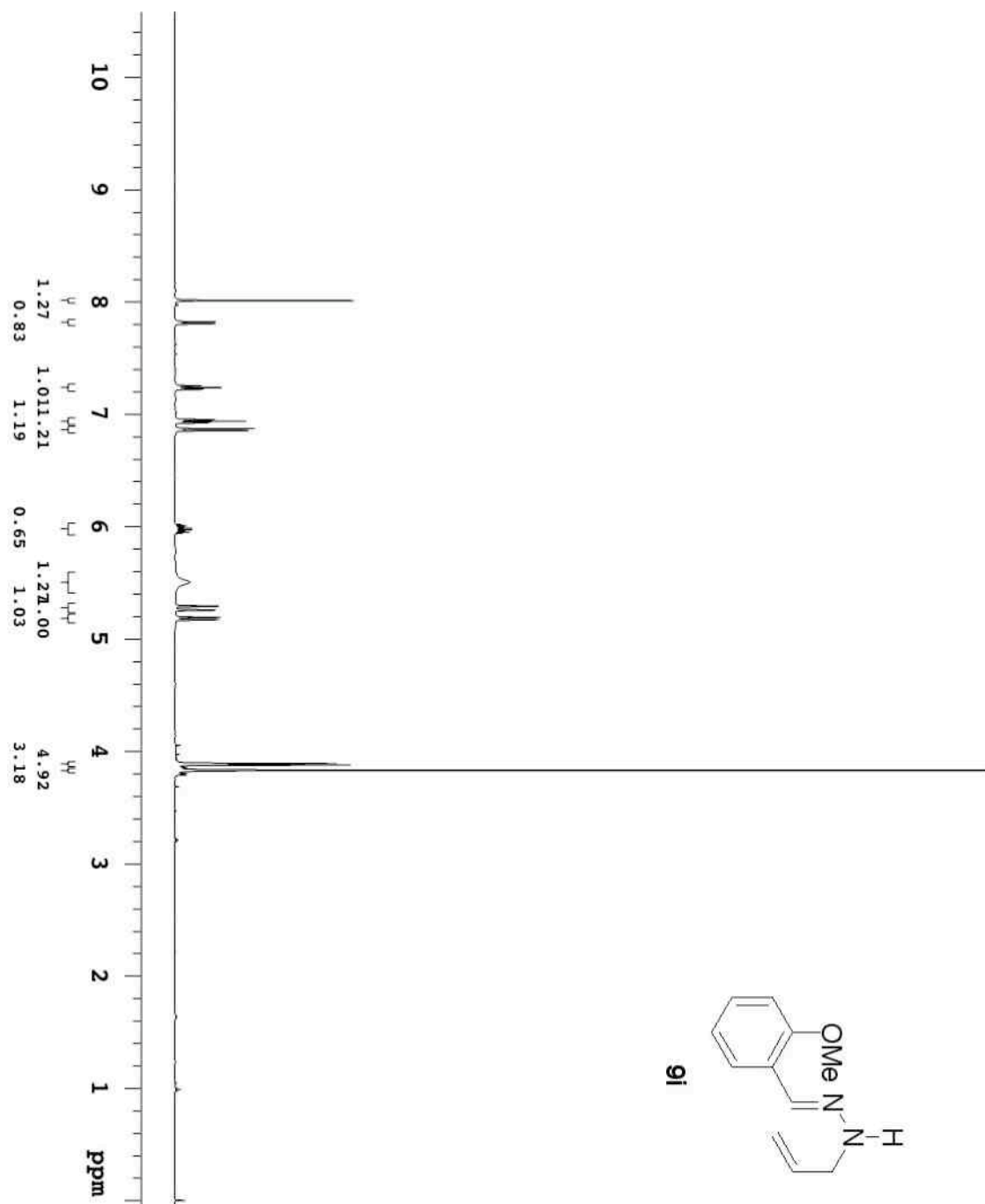


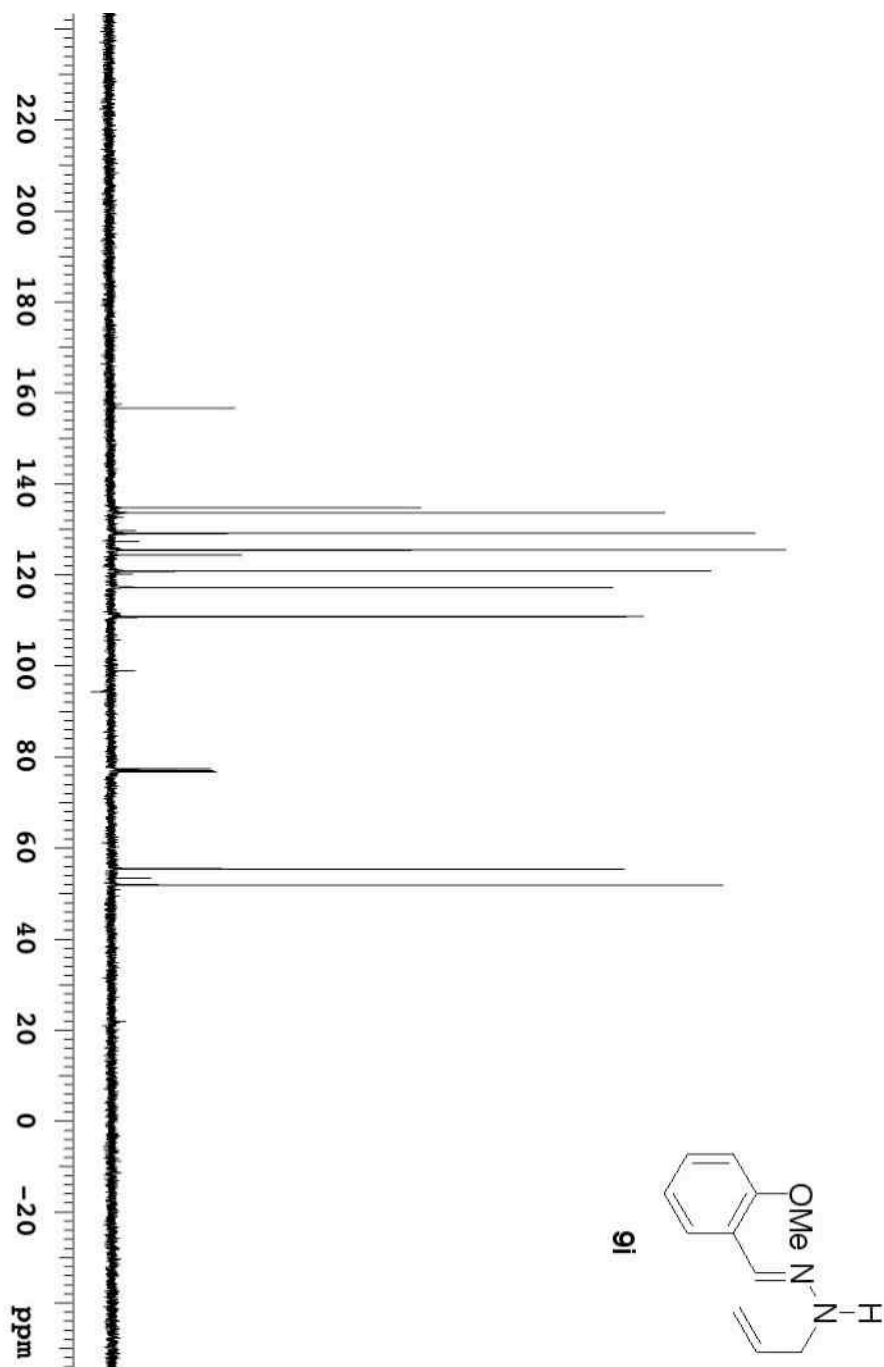




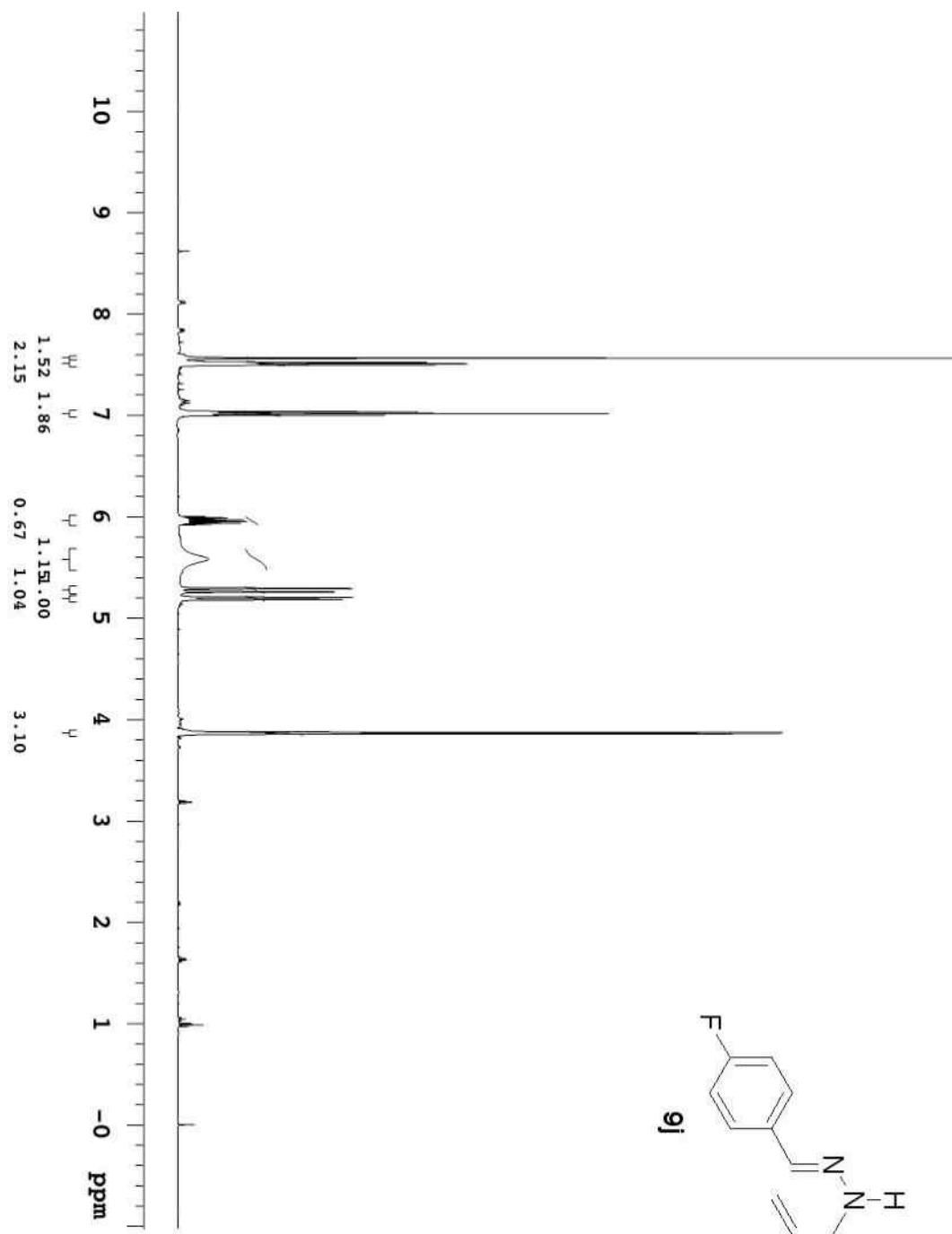


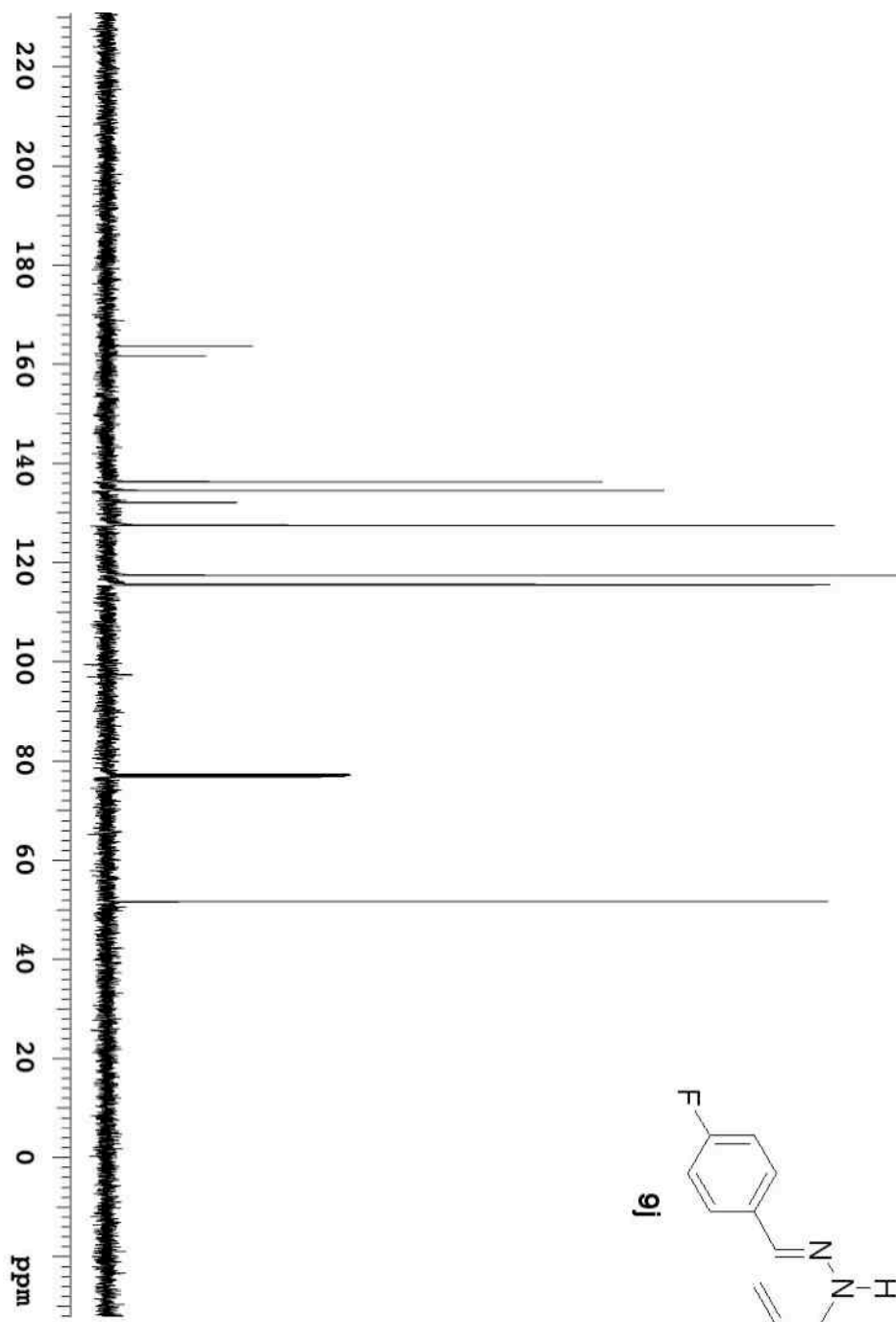


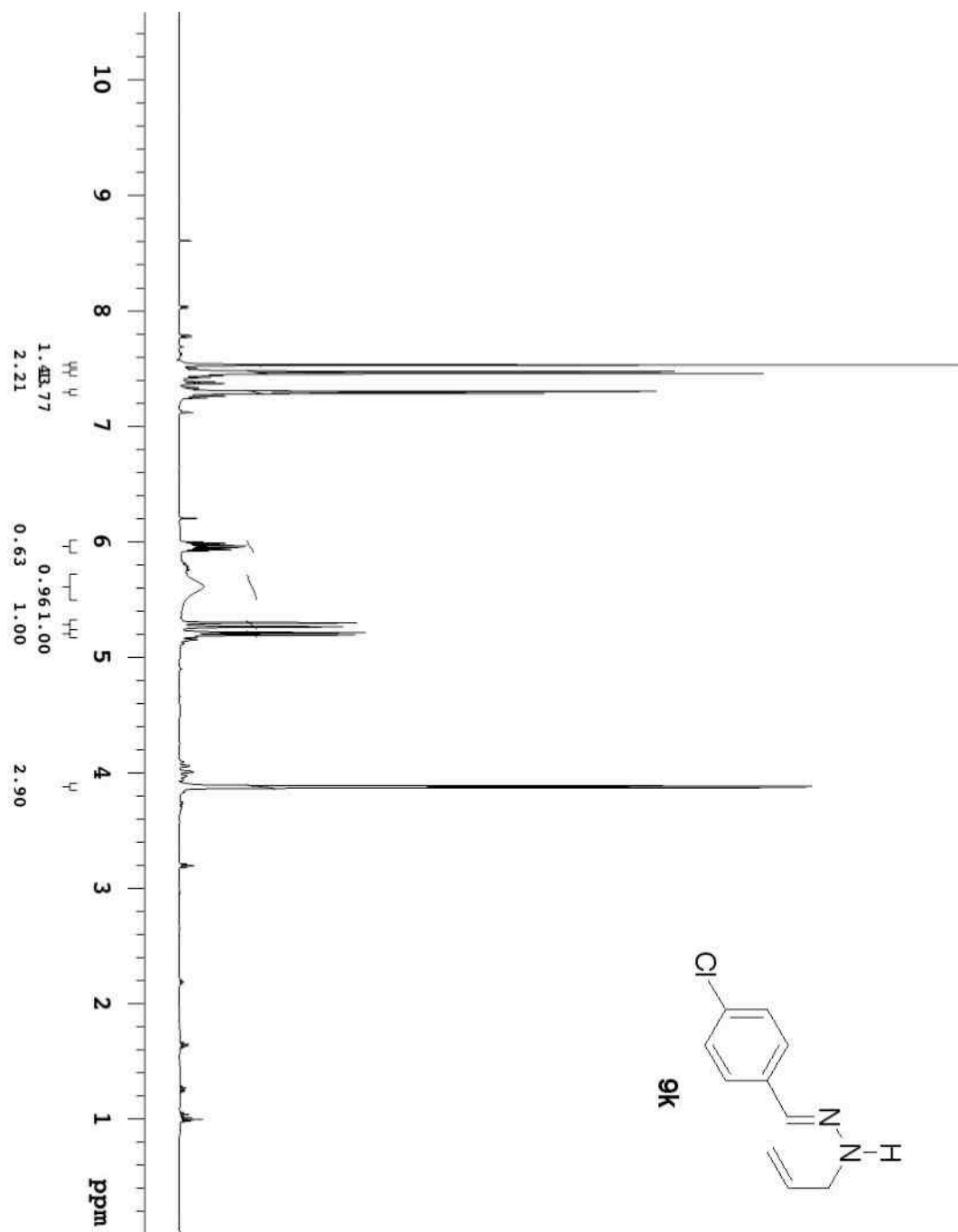


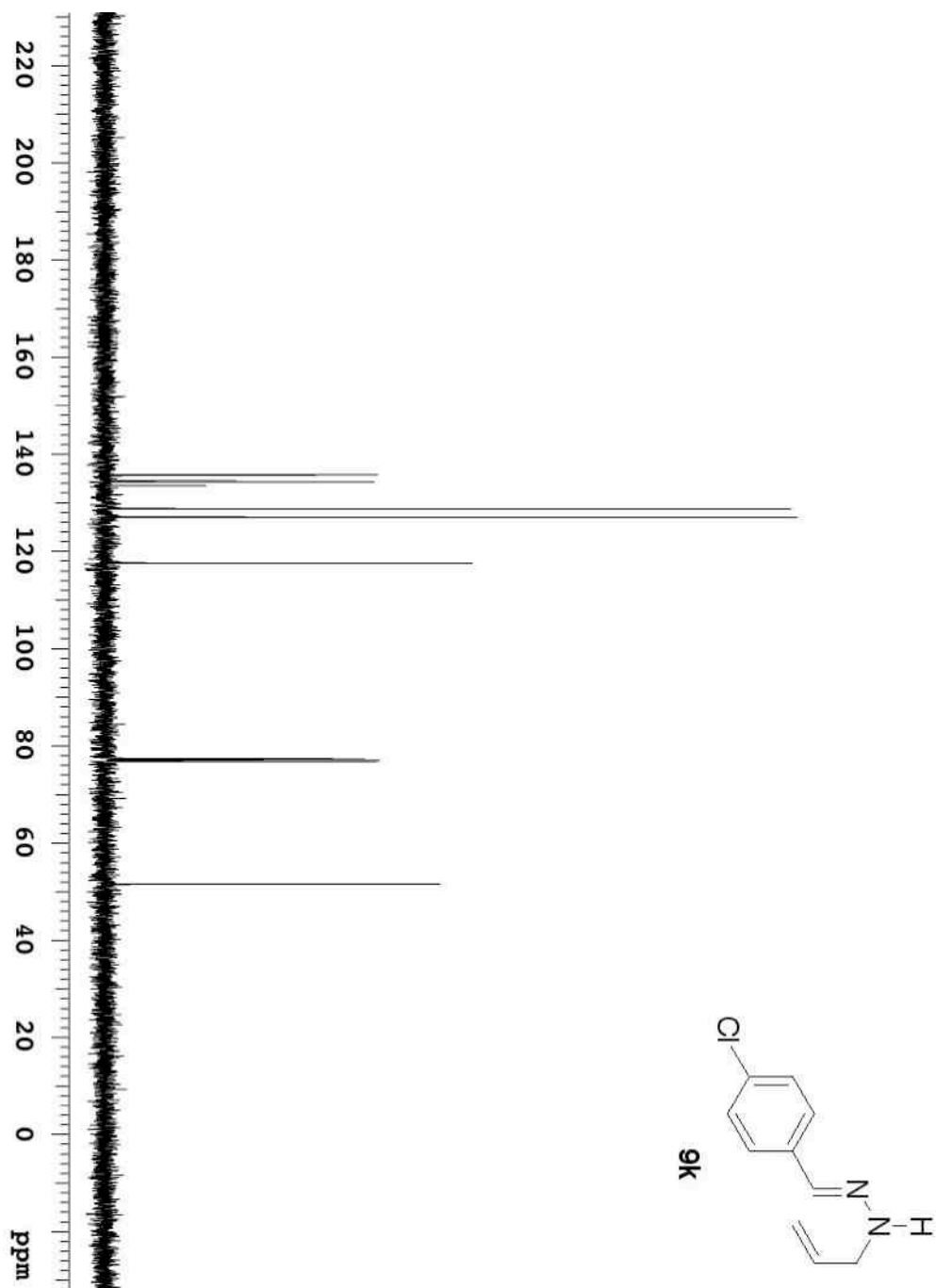


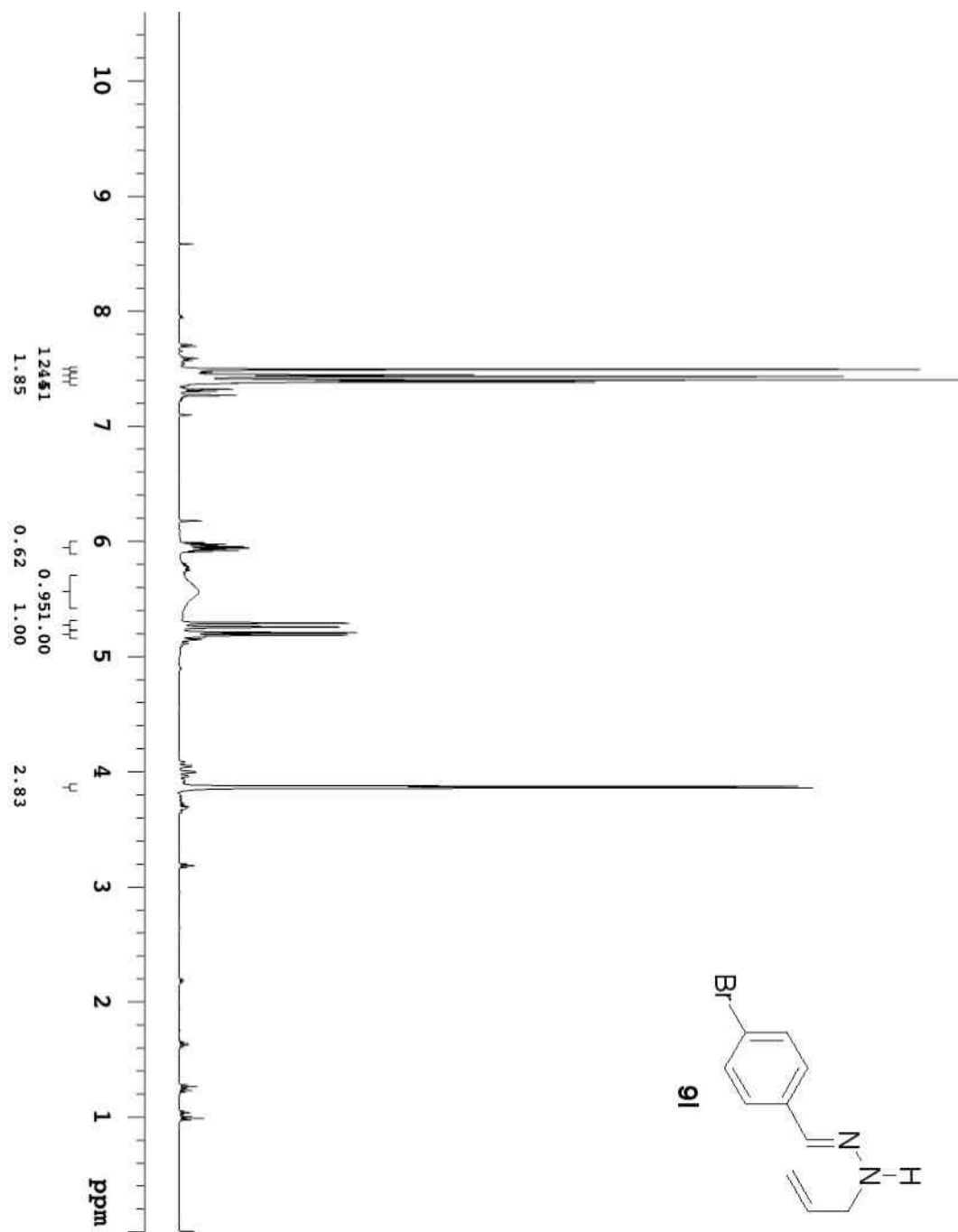


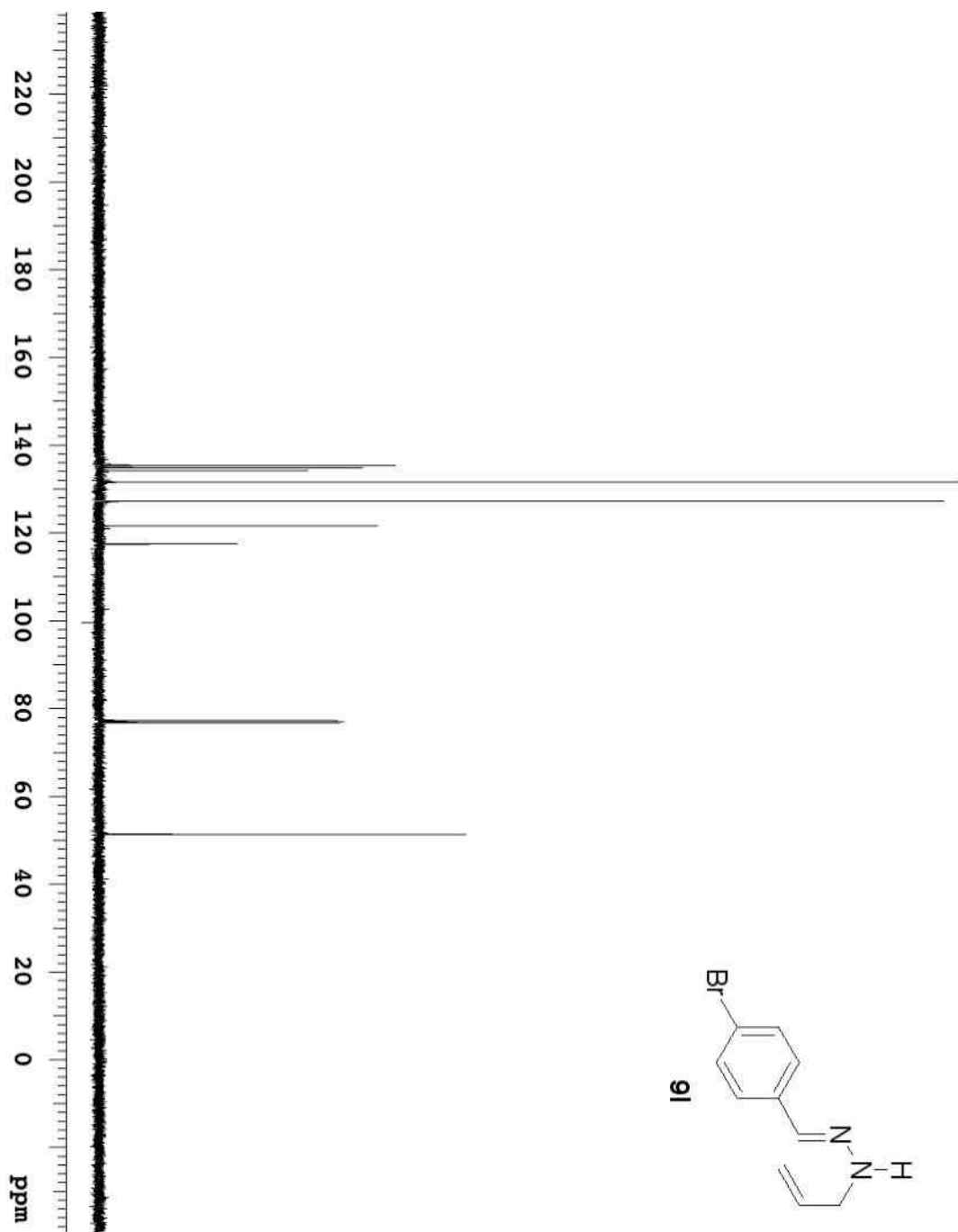


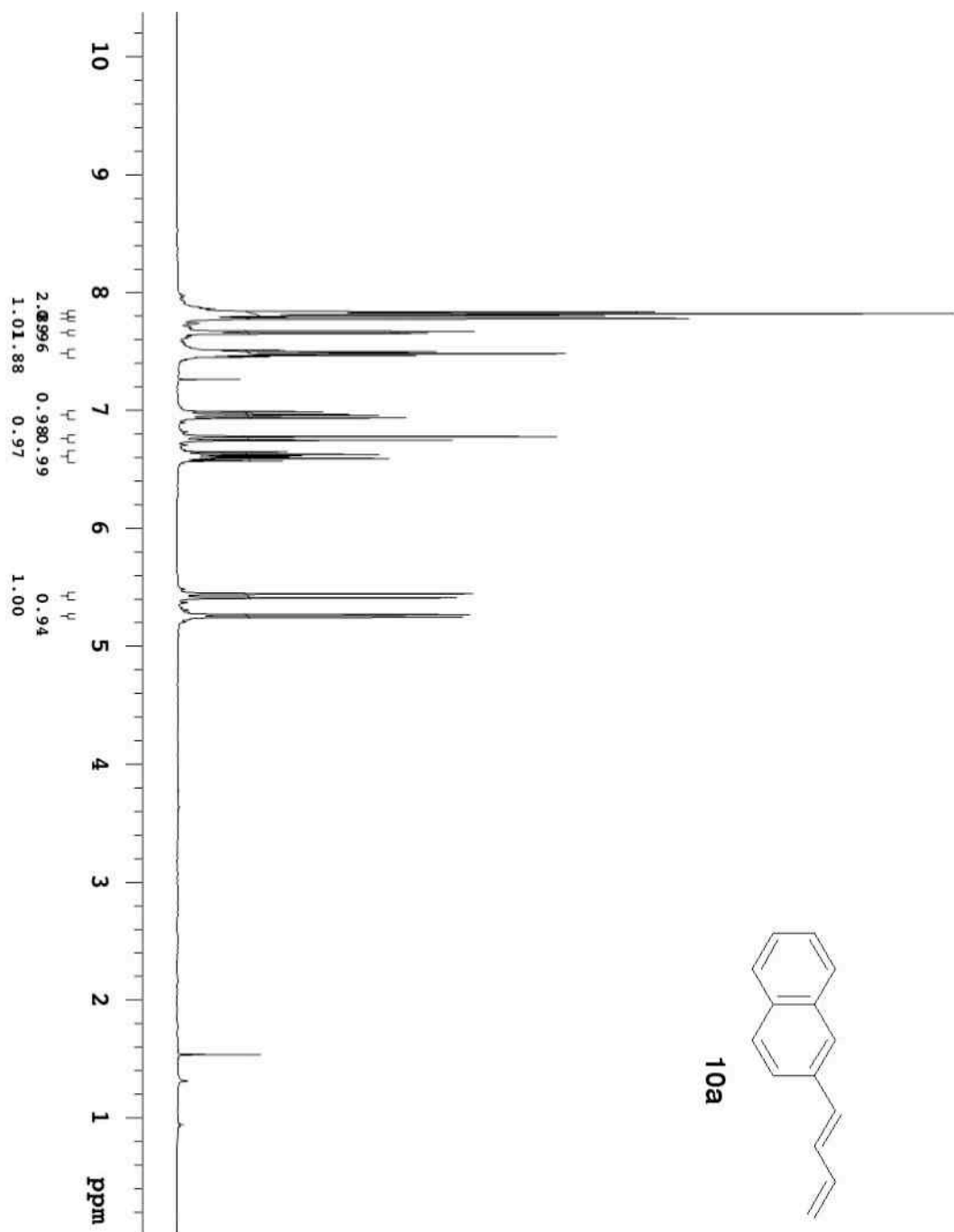


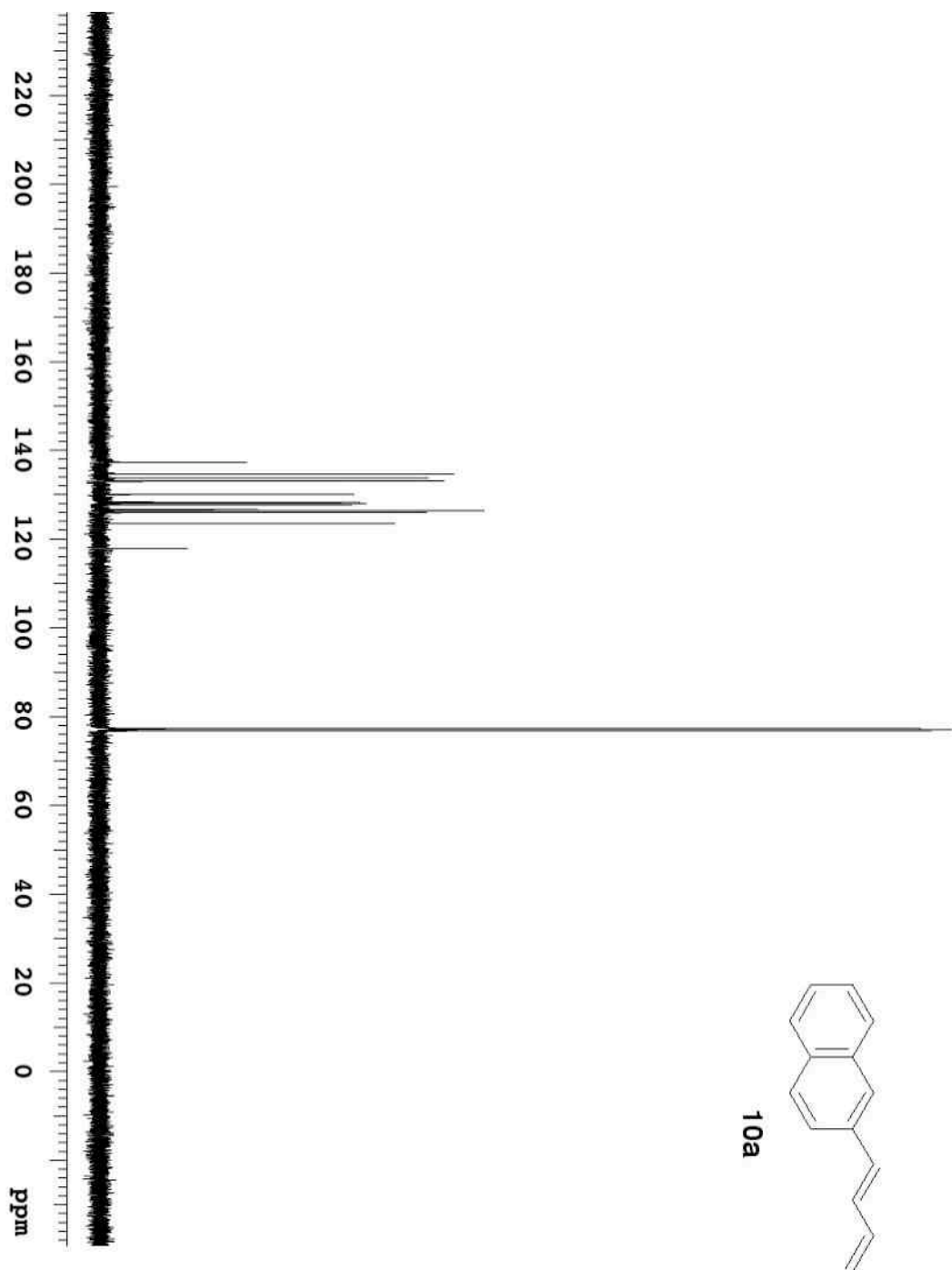




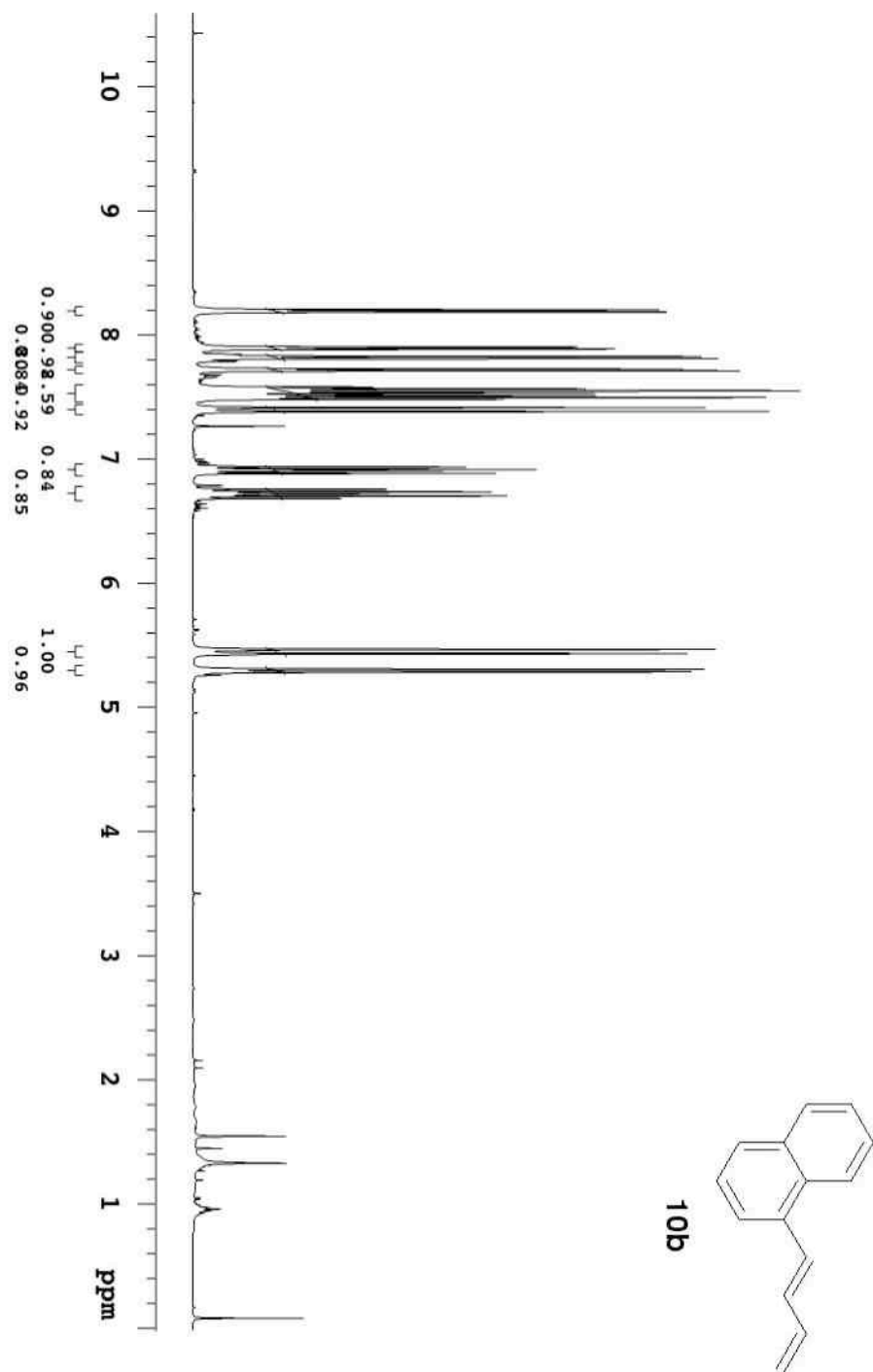


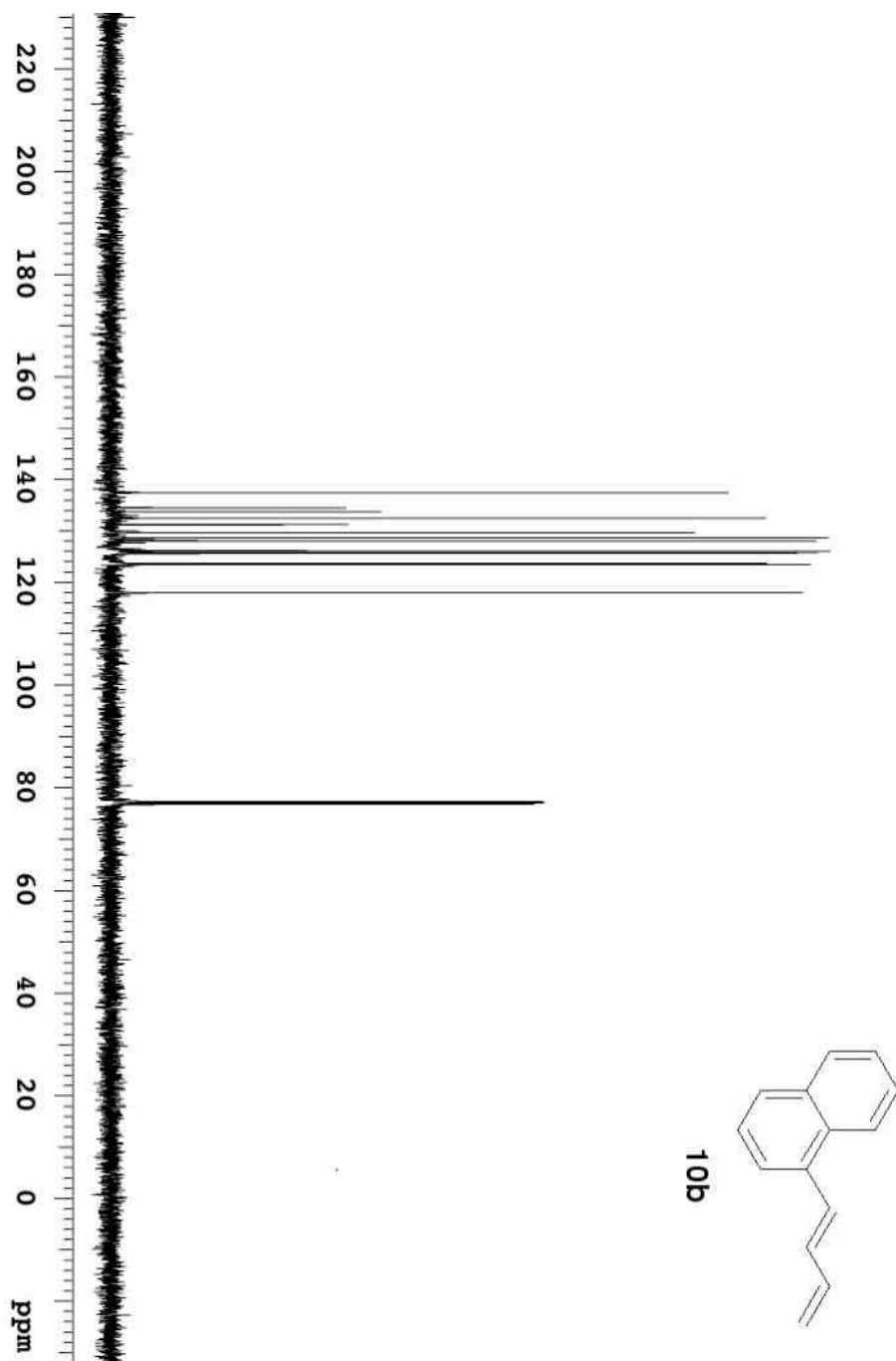


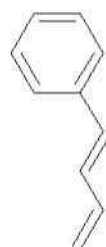










**10c**