Aliphatic Imines in Titanium-Mediated Reductive Cross-Coupling: Unique Reactivity of Ti(O*i*-Pr)$_4$ / *n*-BuLi

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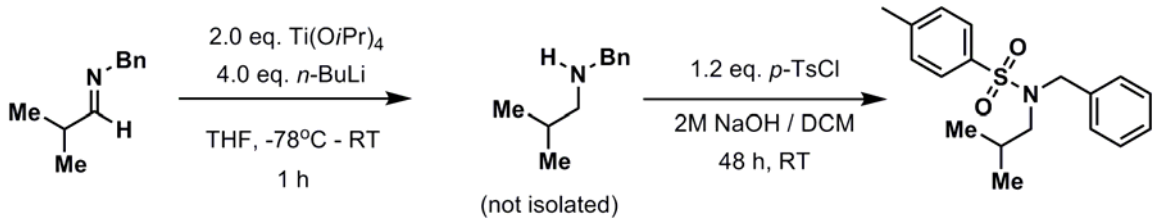
Supporting Information

General Information: All reactions were conducted in flame-dried glass flasks under an argon atmosphere unless otherwise specified. Diethyl ether, tetrahydrofuran, and toluene were dried over activated alumina columns and sparged with argon prior to use. Ti(O*i*-Pr)$_4$ (Aldrich, 97%) was distilled prior to use (69-70 ^{o}C, <1 Torr). Butyllithium was titrated by the method of Love et al.[1] Imines **8**, **14**, **16**, and **22** were prepared according to Jacobsen.[2] In most cases, the imine could be used without further purification for titanium couplings. Vinylcyclohexanol **18** was prepared by addition of vinylmagnesium bromide to cyclohexanone, followed by distillation (40-43 ^{o}C / <1 Torr). 2-phenyl-propen-1-ol **20** was prepared according to Carpenter.[3] Allenes **24**[4], **26**, and **28**[5] were prepared according to Naota.[6] Allene **30** was prepared according to Crabbé.[7]

^{1}H NMR data were recorded in $CDCl_3$ at 400 MHz on a Bruker AM-400 with calibration of spectra to residual $CHCl_3$ (7.26 ppm). ^{13}C data were recorded at 100 MHz on a Bruker AM-400 with calibration to the central line of $CDCl_3$ (77.00 ppm). Infrared spectra were recorded on a PerkinElmer SpectrumOne FT-IR instrument. HRMS data (DART-TOF ionization) were obtained by the University of Florida Mass Spectrometry lab, usually as $(M + H^+)$ or $(M + Na^+)$ ions.

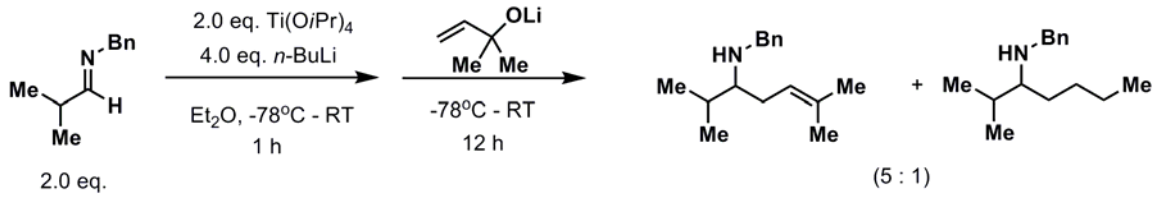
Flash column chromatography was performed using Silicycle SiliaFlash P60 silica gel, 40-63 μm particle size. Compounds purified in this manner were sufficiently pure (NMR) to be used in subsequent transformations.

Experimental Data



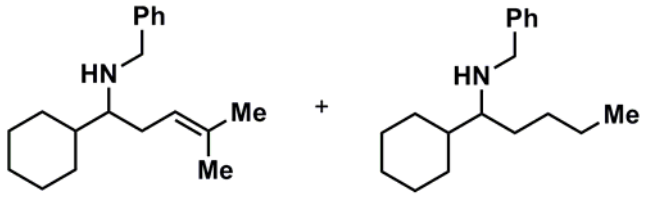
***N*-tosyl-*N*-benzyl-isobutyl amine (11)**: To a solution of freshly distilled Ti(O*i*-Pr)$_4$ (0.59 mL, 2.0 mmol, 2 eq.) in THF (8 mL) at -78 ^{o}C is added *n*-BuLi (1.7 mL of 2.5M solution in hexanes, 4.0 mmol, 4 eq.), resulting in a bright orange solution. After stirring 5 minutes, imine **8** (163 mg, 1.0 mmol) is added in 0.5 mL THF dropwise by syringe, forming a bright yellow-orange solution. This solution is allowed to warm to rt over 1 h, during which it turns light brown, then deep brown-red. After 1 h, to the reaction is added saturated $NH_4Cl_{(aq)}$ (1.2 mL), and the resultant blue suspension left to stir 10 minutes at rt to break up metal salts. The reaction is filtered, and the residue rinsed 3x with 2 mL EtOAc. The crude oil after evaporation is subjected immediately to the next step.

To the clear oil (~200 mg) is added 1.5 mL of 2M NaOH (3 mmol, 3 eq.) and *p*-toluenesulfonyl chloride (240 mg, 1.25 mmol, 1.25 eq.) in 2 mL CH_2Cl_2. The resulting biphasic suspension is stirred vigorously over 2 d, then extracted with dichloromethane (5 mL, 3x), washed with water and brine, and dried over anhyd. $MgSO_4$. Column chromatography (1:10 Et_2O / Hex) yields 160 mg **11** as a clear oil, which solidifies over a few days. 50% yield, 2 steps. ^{1}H (400 MHz, $CDCl_3$): 7.71 (d, *J* = 8 Hz, 2H), 7.30-7.19 (m, 7H), 4.29 (s, 2H), 2.88 (d, *J* = 8Hz, 2H), 2.43 (s, 3H), 1.63 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 6H). ^{13}C (100MHz, $CDCl_3$): 143.1, 137.0, 136.6, 129.7, 128.5, 128.4, 127.6, 127.3, 56.4, 53.0, 26.9, 21.5, 20.0. IR (thin film, NaCl disk, cm^{-1}): 2961, 2926, 2871, 1455, 1337, 1158, 1025, 815, 775, 736, 699, 656, 549. HRMS: Calculated for $C_{18}H_{23}NO_2S$ + Na 340.1342, observed 340.1331.



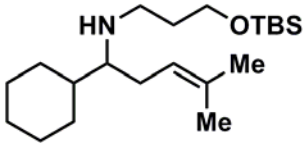
***N*-benzyl-2,6-dimethylhept-5-en-3-amine** (**13**) General Procedure for Allylic Alcohol - Aliphatic Imine Coupling: To 6 mL of Et_2O under Ar and cooled to -78^{o}C is added successively Ti(O*i*-Pr)$_4$ (0.3 mL, 1.0 mmol), and *n*-BuLi (0.8 mL, 2.4 M sol'n in hexanes, 2.0 mmol). The resulting orange solution is stirred for 10 minutes, and then imine **8** (161 mg, 1.0 mmol in 1 mL THF) is added in one portion. The bright orange solution is allowed to warm to rt over 1 h, during which it becomes deep red-brown.

In a separate flask at -30°C the lithium alkoxide of 2-methyl-3-buten-2-ol **12** (52 µL, 0.5 mmol) is generated in 0.5 mL of THF with an equimolar amount of *n*-BuLi, and allowed to warm slowly to 0°C over 15 mins. The orange solution in the first flask is recooled to -78°C, and alkoxide is transferred by syringe dropwise over 5 minutes. The resulting dark red solution is slowly warmed to rt over 12 h, and then 0.8 mL sat'd $NH_4Cl_{(aq)}$ is added dropwise. The resulting blue suspension is stirred 30 minutes, filtered, the flask washed 2x with 5 mL ethyl acetate, and concentrated. The material is loaded directly onto a flash column with 1:8 EtOAc : Hex, yielding 112 mg of an inseparable mixture of **13** (80%) + **13a** (15%), clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.30-7.11 (m, 5H), 5.09 (t, J_1 = 7.6 Hz, 1H), 3.76 (s, 2H), 2.36 (m, 1H), 2.08 (m, 2H), 1.82 (s, 1H), 1.70 (d, J= 1.2 Hz, 3H), 1.62 (s, 3H), 0.91 (d, J_1 = 1.2 Hz, 3H), 0.89 (d, J_1 = 1.2 Hz, 3H). ^{13}C NMR: 141.4, 132.3, 128.3, 128.2, 126.7, 122.2, 62.7, 52.2, 30.1, 29.1, 25.9, 18.7, 18.4, 18.0. IR (thin film, NaCl plate, cm^{-1}): 3027, 2958, 2928, 2871, 1494, 1453, 1382, 1104, 1028, 733, 697. HRMS: Calculated for $C_{16}H_{25}N$ + H, 232.2060, observed 232.2065.

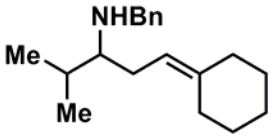


(6 : 1)

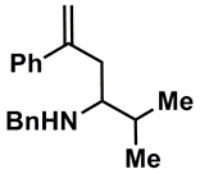
5-cyclohexyl-5-(*N*-benzylamino)-2-methylpent-2-ene (15): Prepared from imine **14** and alcohol **12** following general procedure outlined above. Product was isolated (1:8 EA / Hex) as an inseparable mixture of **15** (62%) and **15a** (10%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.32-7.23 (m, 5H), 5.11 (t, J = 7.24 Hz, 1H), 3.76 (dd, J_1 = 15.2 Hz, J_2 = 13.2 Hz, 2H), 2.37 (m, 1H), 2.13 (m, 2H), 1.75-1.66 (m, 6H), 1.73 (s, 3H), 1.64 (s, 3H), 1.42 (m, 1H), 1.23 (m, 6H). ^{13}C (100 MHz, $CDCl_3$): 141.3, 133.3, 128.3, 128.21, 128.18, 126.7, 122.2, 62.3, 52.2, 40.9, 29.5, 29.4, 29.2, 26.93, 26.85, 26.79, 25.9, 18.0. IR (thin film, NaCl plate, cm^{-1}): 3026, 2923, 2851, 1494, 1450, 1375, 1117, 1028, 984, 731, 697. HRMS: Calculated for $C_{19}H_{29}N$ 272.2373, observed 272.2392.



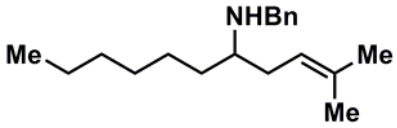
5-(*N*-(3-*tert*-butoxypropyl))-5-cyclohexyl-2-methylpent-2-ene (17): Prepared from imine **16** and alcohol **12** following general procedure outlined above. 81% isolated yield (1:20 EtOAc / Hex). ^{1}H (400 MHz, $CDCl_3$): 5.11 (t, J = 7.6 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 2.64 (m, 2H), 2.26 (m, 1H), 2.04 (m, 2H), 1.71 (d, J_1 = 1Hz, 3H), 1.65 (m, 6H), 1.62 (s, 3H), 1.42-1.08 (m, 6H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C (100 MHz, $CDCl_3$): 133.0, 122.4, 63.2, 61.6, 45.1, 40.9, 35.6, 29.7, 29.4, 29.2, 26.9, 26.83, 26.76, 25.98, 25.94, 18.4, 17.9, -5.3. IR (thin film, NaCl plate, cm^{-1}): 2926, 2854, 1471, 1449, 1377, 1254, 1099, 835, 774. HRMS: Calculated for $C_{21}H_{43}NOSi$ + H 354.3147, observed 354.3194.



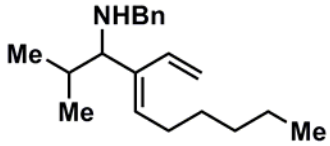
3-(*N*-benzylamino)-4-methylpentenylcyclohexane (19): Prepared from imine **8** and vinylcyclohexanol **18** following general procedure outlined above. 56% isolated yield. ^{1}H (400 MHz, $CDCl_3$): 7.35-7.20 (m, 5H), 5.05 (t, J = 7.6 Hz, 1H), 3.77 (s, 2H), 2.35 (m, 1H), 2.20-2.04 (m, 5H), 1.83 (s, 1H), 1.55-1.20 (m, 6H), 0.98 (d, J_1 = 2.4 Hz, 3H), 0.96 (d, J = 2.4 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 141.6, 141.3, 128.28, 128.26, 128,18, 126.7, 118.8, 62.8, 52.2, 37.4, 30.1, 28.9, 28.7, 28.1, 27.9, 26.9, 18.7, 18.3. HRMS: Calculated for $C_{19}H_{29}N$ + H 272.2373, observed 272.2378.



4-(*N*-benzylamino)-5-methyl-2-phenylhex-1-ene (21): Prepared from imine **8** and alcohol **20** following general procedure outlined above. 52% isolated yield. ^{1}H (400 MHz, $CDCl_3$): 7.31-7.20 (m, 10H), 5.31 (d, J = 1.6 Hz), 5.12 (s, 1H), 3.76 (s, 1H), 3.69 (d, J =12.8 Hz, 1H), 3.56 (d, J = 13.2 Hz, 1H), 2.74 (d, J = 11.6 Hz,1H), 2.44-2.39 (m, 2H), 1.89 (m, 1H), 0.93 (d, J = 3.2 Hz, 3H), 0.92 (d, J = 3.2 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 147.0, 141.0, 140.9, 128.3, 128.2, 128.1, 127.5, 126.7, 126.4, 114.9, 59.8, 52.1, 36.7, 29.6, 18.5, 17.5. IR (thin film, NaCl plate, cm^{-1}): HRMS: Calculated for $C_{20}H_{25}N$ +H 280.2021, observed 280.2069.

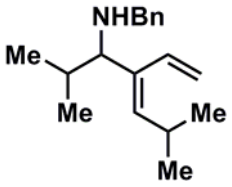


5-(*N*-benzylamino)-2-methylundec-2-ene (23): Prepared from imine **22** and alcohol **12** by general procedure outlined above. (N.B. This reaction works best when imine is freshly prepared before coupling. Lower yields are observed with older batches). 92% isolated yield. ^{1}H (400 MHz, $CDCl_3$): 7.32-7.16 (m, 5H), 5.11 (triplet of septets, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 3.77 (s, 2H), 2.55 (m, 1H), 2.13 (t, J = 7.2 Hz, 2H), 1.72 (s, 3H), 1.63 (s, 3H), 1.45-1.26 (m, 15H), 0.89 (t, J = 7.2 Hz, 4H). ^{13}C (100 MHz, $CDCl_3$): 141.1, 133.6, 128.3, 128.1, 126.7, 121.4, 57.3, 51.4, 34.2, 32.7, 31.9, 29.6, 25.94, 25.87, 22.7, 18.1, 14.1. IR (thin film, NaCl plate, cm^{-1}): 3027, 2956, 2926, 2855, 1494, 1454, 1376, 1103, 1028, 729, 697. HRMS: Calculated for $C_{19}H_{31}N$ + H 274.2529, observed 274.2554.



(3*E*) 3-(1-*N*-benzylamino-2-methylpropyl)-4-methylpenta-1,3-diene (25): To a solution of Ti(O*i*-Pr)$_4$ (0.15 mL, 0.5 mmol, 1.0 eq.) in 3 mL THF at -78^{o}C is added dropwise *n*-BuLi (0.48 mL of 2.3M sol'n in hexanes, 1.0 mmol, 2.0 eq.). The resulting orange solution is stirred for 5 minutes, then imine **8** (81 mg, 1 mmol, 1.0 eq.) is added in 0.5 mL THF dropwise. The bright orange solution is warmed to rt over 1.25 h, resulting in a red-brown suspension.

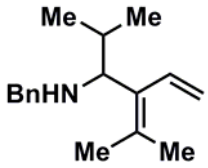
The solution is recooled to -78^{o}C, and the lithium alkoxide of allene **24** (pregenerated in 0.5 mL THF at -30^{o}C with equimolar *n*-BuLi, 56 mg, 0.5 mmol, 1.0 eq.) is added dropwise by syringe over 2 minutes. The solution is stirred for 20 minutes at -78^{o}C, and then placed in an oil bath at 60^{o}C for 12 h. The reaction is cooled to rt, and 0.8 mL $NH_4Cl_{(aq)}$ is added dropwise, resulting in a bluish-white slurry. The reaction is allowed to stir 20 minutes to break up salts, then filtered, washing precipitate 3x with 5 mL EtOAc. After concentration, the residue is loaded directly to a silica flash column (1:20 EtOAc / Hex → 1:10) to yield 56 mg (78%) of diene **25** as a clear oil. ^{1}H (400 MHz, $CDCl_3$): 7.35-7.20 (m, 5H), 6.53 (dd, J_1 = 18 Hz, J_2 = 11.6 Hz, 1H), 5.50 (t, J = 7.2 Hz, 1H), 5.31 (dd, J_1 = 17.6 Hz, J_2 = 1.6 Hz, 1H), 5.13 (dt, J_1 = 11.2 Hz, J_2 = 1.2 Hz, 1H), 3.74 (d, J =13.2 Hz, 1H), 3.49 (d, J =13.2 Hz, 1H), 2.93 (d, J = 7.6 Hz, 1H), 2.23 (q, J = 7.2 Hz, 2H), 1.76 (sept, 1H), 1.50-1.30 (m, 10H), 0.93 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 6.8 Hz, 2H), 0.83 (d, J = 6.8 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 141.4, 136.7, 133.1, 131.6, 128.22, 128.26, 126.6, 114.7, 67.6, 51.5, 31.9, 31.6, 29.7, 27.7, 25.6, 20.4, 19.4, 14.1. IR (thin film, NaCl plate, cm^{-1}): 2956, 2925, 2857, 1454, 900, 697. HRMS: Calculated for $C_{20}H_{31}N$ + H 286.2529, observed 286.2551.



(3*E*) 3-(*N*-benzylamino-2-methylpropyl)-5-methylhexa-1,3-diene (27): To a solution of Ti(O*i*-Pr)$_4$ (0.3 mL, 1.0 mmol, 2.0 eq.) in 4 mL THF at -78^{o}C is added dropwise *n*-BuLi (0.9 mL of 2.3M sol'n in hexanes, 2.0 mmol, 4.0 eq.). The resulting orange solution is stirred for 5 minutes, then imine **8** (161 mg, 1 mmol, 2.0 eq.) is added in 0.5 mL THF dropwise. The bright orange solution is warmed to rt over 1.25 h, resulting in a red-brown suspension.

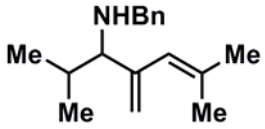
The solution is recooled to -78^{o}C, and the lithium alkoxide of allene **26** (pregenerated in 0.5 mL THF at -30^{o}C with equimolar *n*-BuLi, 56 mg, 0.5 mmol, 1.0 eq.) is added dropwise by syringe over 2 minutes. The solution is stirred for 20 minutes at -78^{o}C, and then warmed to rt overnight. The reaction at rt with 0.8 mL $NH_4Cl_{(aq)}$, allowed to stir 20 minutes to break up salts, and filtered, washing precipitate 3x with 5 mL

EtOAc. After concentration, the residue is loaded directly to a silica flash column (1:15 EtOAc / Hex) to yield 97 mg (75%) of diene **27** as a clear oil. ^{1}H (400 MHz, $CDCl_3$): 7.31 (m, 5H), 6.55 (dd, J_1 = 17.2 Hz, J_2 = 11.6 Hz, 1H), 5.33 (m, 1H), 5.31 (dt, J_1 = 9.6 Hz, J_2 = 1.6 Hz, 1H), 5.12 (dt, J_1 = 11.6 Hz, J_2 = 1.6 Hz, 1H), 3.75 (d, 13.2 Hz, 1H), 3.50 (d, 13.2 Hz, 1H), 2.91 (d, J = 7.2 Hz, 1H), 2.83 (m, 1H), 1.77 (apparent septet, J = 7.2 Hz, 1H), 1.38 (bm, 1H), 1.02 (dd, J_1 = 7.2 Hz, J_2 = 6.8 Hz, 6H), 0.94 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 141.4, 138.9, 134.3, 133.2, 128.3, 128.2, 126.7, 114.6, 67.2, 51.4, 31.9, 26.9, 23.5, 23.4, 20.4, 19.3. IR (thin film, NaCl plate, cm^{-1}): 2958, 2930, 2068, 1729, 1464, 1383, 1361, 1272, 1122, 1100, 1073, 901, 737, 698. HRMS: Calculated for $C_{16}H_{25}N$ + H 258.2177, observed 258.2219



3-(1-*N*-benzylamino-2-methylpropyl)-4-methylpenta-1,3-diene (29): To a solution of Ti(O*i*-Pr)$_4$ (0.3 mL, 1.0 mmol, 2.0 eq.) in 4 mL THF at -78^{o}C is added dropwise *n*-BuLi (0.8 mL of 2.5M sol'n in hexanes, 2.0 mmol, 4.0 eq.). The resulting orange solution is stirred for 5 minutes, then imine **8** (161 mg, 1 mmol, 2.0 eq.) is added in 0.5 mL THF dropwise. The bright orange solution is warmed to rt over 1.25 h, resulting in a red-brown suspension.

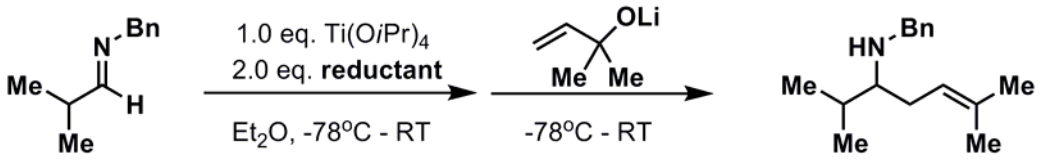
The solution is recooled to -78^{o}C, and the lithium alkoxide of allene **28** (pregenerated in 0.5 mL THF at -30^{o}C with equimolar *n*-BuLi, 49 mg, 0.5 mmol, 1.0 eq.) is added dropwise by syringe over 2 minutes. The solution is stirred for 20 minutes at -78^{o}C, and then warmed to rt overnight. 0.8 mL $NH_4Cl_{(aq)}$ is then added and the reaction is stirred 20 minutes to break up salts, filtered, and the precipitate washed 3x with 5 mL EtOAc. After concentration, the residue is loaded directly to a silica flash column (1:15 EtOAc / Hex) to yield 63 mg (52%) of diene **29** as a clear oil. ^{1}H (400 MHz, $CDCl_3$): 7.35-7.18 (m, 5H), 6.26 (dd, J_1 = 17.6 Hz, J_2 = 11.6 Hz, 1H), 5.19 (dd, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 1H), 5.15 (m, 1H), 3.68 (d, J = 13.2 Hz, 1H), 3.43 (d, J = 13.6 Hz, 1H), 3.15 (d, J = 9.6 Hz, 1H), 1.81 (s, 3H), 1.67 (m, 1H), 1.62 (s, 3H), 1.01 (d, J = 6.8 Hz, 3H), 0.95, (m, 1H), 0.72 (d, J = 6.8 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 141.5, 134.4, 132.9, 132.1, 128.21, 128.19, 125.6, 117.3, 64.1, 51.3, 31.9, 22.5, 20.9, 20.8, 19.9. IR (thin film, NaCl plate, cm^{-1}):3027, 2955, 2924, 2869, 1644, 1621, 1603, 1494, 1454, 1381, 1363, 1156, 1094, 918, 820, 736, 698. HRMS: Calculated for $C_{17}H_{25}N$ + H 244.2021, observed 244.2072.

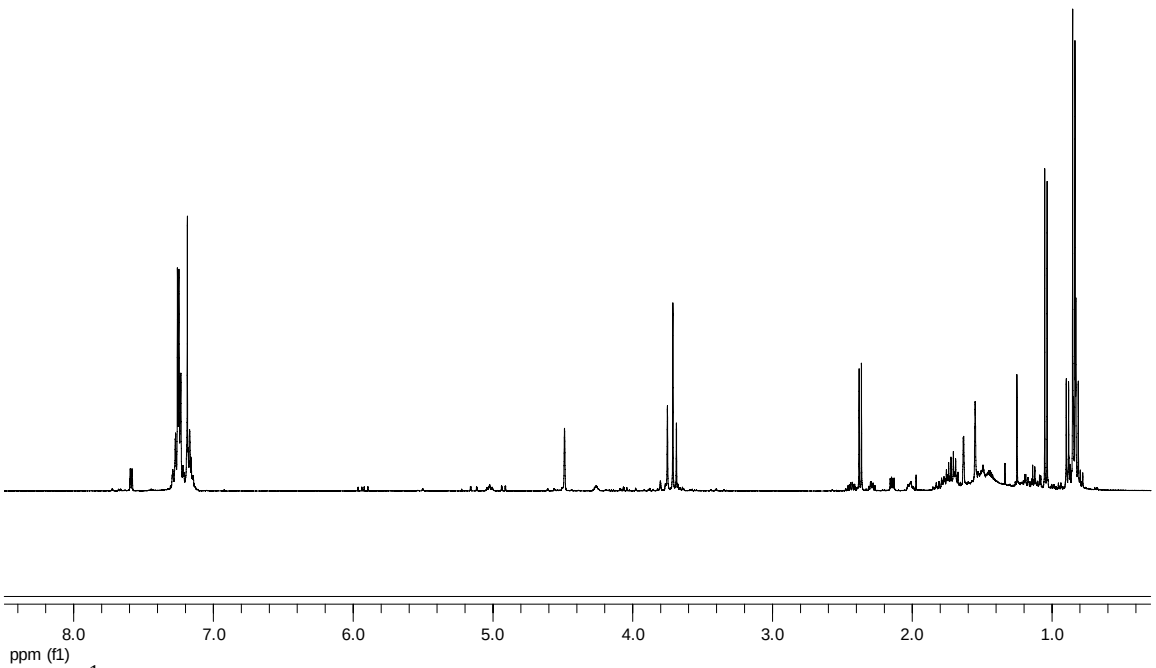


2-(1-*N*-benzylamino-2-methylpropyl)-4-methylpenta-1,3-diene (31): To a solution of Ti(O*i*-Pr)$_4$ (0.3 mL, 1.0 mmol, 2.0 eq.) in 4 mL THF at -78^{o}C is added dropwise *n*-BuLi (0.8 mL of 2.5M sol'n in hexanes, 2.0 mmol, 4.0 eq.). The resulting orange solution is stirred for 5 minutes, then imine **8** (161 mg, 1 mmol, 2.0 eq.) is added in 0.5 mL THF dropwise. The bright orange solution is warmed to rt over 1.25 h, resulting in a red-brown suspension.

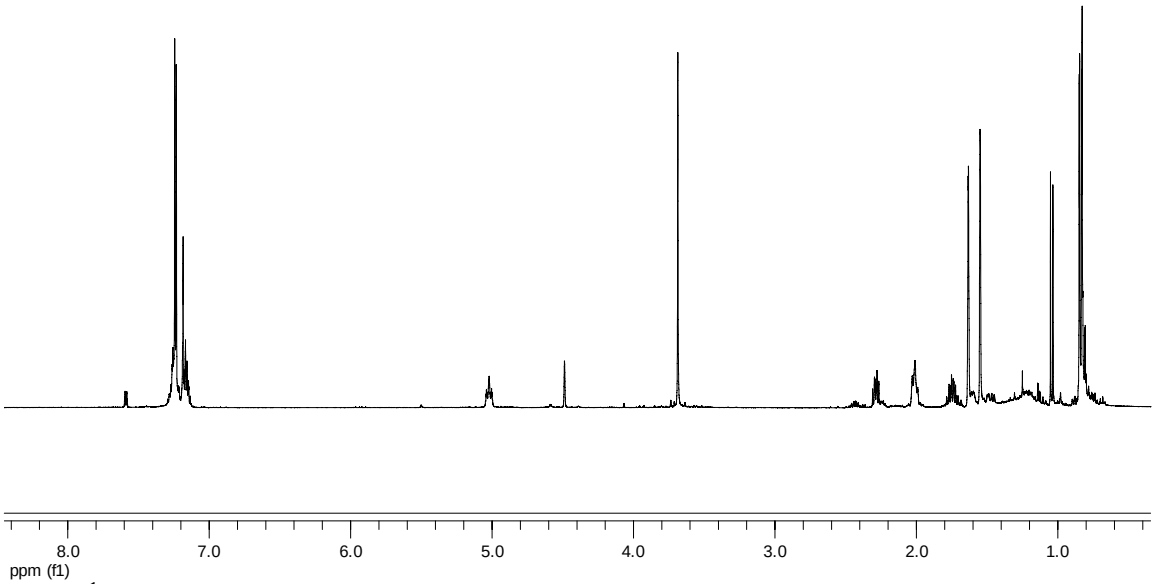
The solution is recooled to -78^{o}C, and the lithium alkoxide of allene **30** (pregenerated in 0.5 mL THF at -30^{o}C with equimolar *n*-BuLi, 49 mg, 0.5 mmol, 1.0 eq.) is added dropwise by syringe over 2 minutes. The solution is stirred for 20 minutes at -78^{o}C, and then warmed to rt overnight. 0.8 mL $NH_4Cl_{(aq)}$ is added at rt, allowed to stir 20 minutes to break up salts, filtered, and the precipitate washed 3x with 5 mL EtOAc. After concentration, the residue is loaded directly to a silica flash column (1:15 EtOAc / Hex) to yield 70 mg (58%) of diene **31** as a lt. yellow oil. ^{1}H (400 MHz, $CDCl_3$): 7.35-7.20 (m, 5H), 5.59 (m, 1H), 4.98 (d, *J* = 2.4 Hz, 1H), 4.92 (m, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 13.2 Hz, 1H), 2.55 (d, *J* = 8.8 Hz, 1H), 1.79 (d, *J* = 1.6 Hz, 3H), 1.76 (d, *J* = 1.2 Hz, 3H), 1.58 (m, 1H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H). ^{13}C (100 MHz, $CDCl_3$): 144.7, 140.1, 135.6, 127.2, 125.6, 121.4, 114.4, 70.0, 66.9, 50.4, 30.1, 25.8, 24.6, 19.3, 18.79, 18.75. IR (thin film, NaCl plate, cm^{-1}): 3028, 2960, 2929, 2871, 1677, 1646, 1624, 1604, 1495, 1453, 1382, 1157, 1101, 1071, 1028, 984, 901, 734, 698. HRMS: Calculated for $C_{17}H_{25}N$ + H 244.2021, observed 244.2071.

^{1}H and ^{13}C Spectra



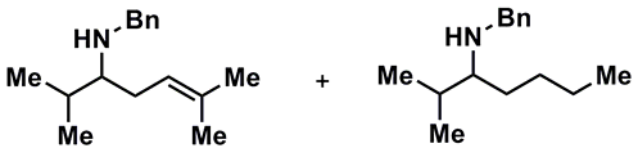


Crude ^{1}H NMR(400MHz, $CDCl_3$); formation of **13** with C_5H_9MgCl / Ti(O*i*-Pr)$_4$ / alcohol **12**, 2 h at rt



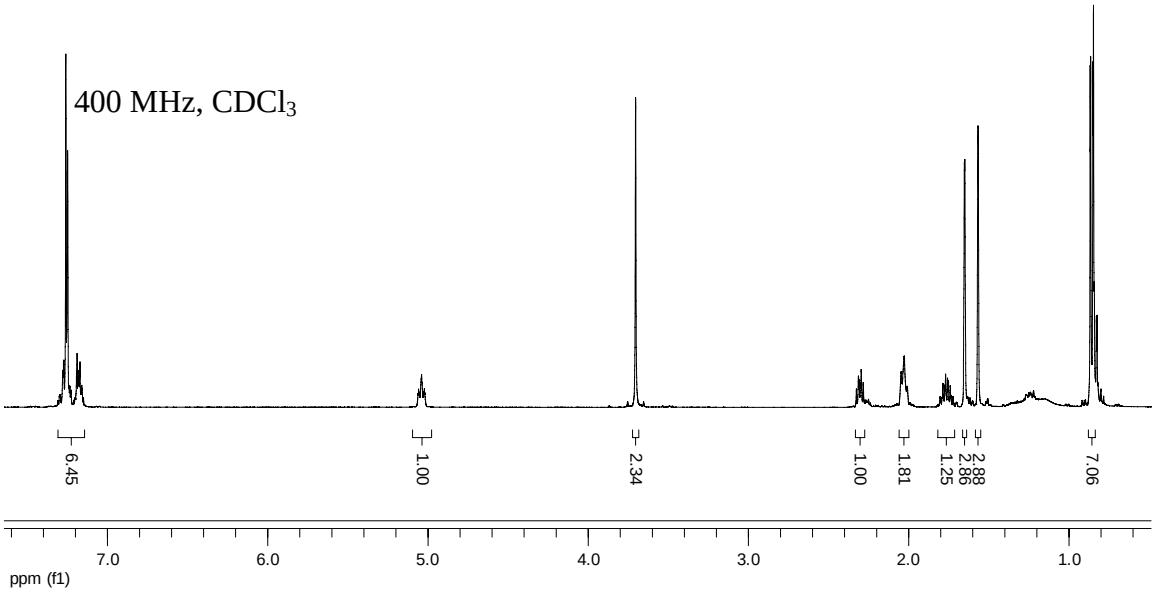
Crude ^{1}H NMR(400 MHz, $CDCl_3$); formation of **13** with *n*-BuLi / Ti(O*i*-Pr)$_4$ / alcohol **12**, 2 h at rt

Compound **13 + 13a**

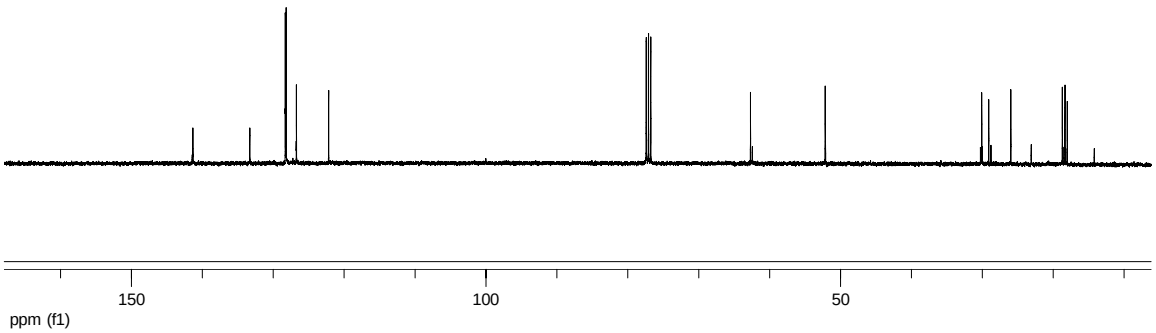


(5 : 1)

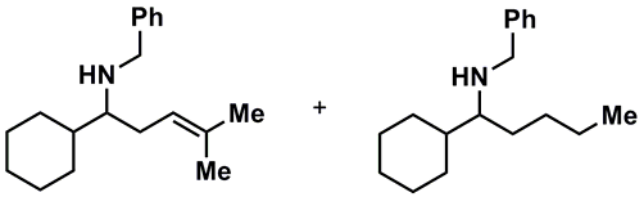
400 MHz, $CDCl_3$



100 MHz, $CDCl_3$

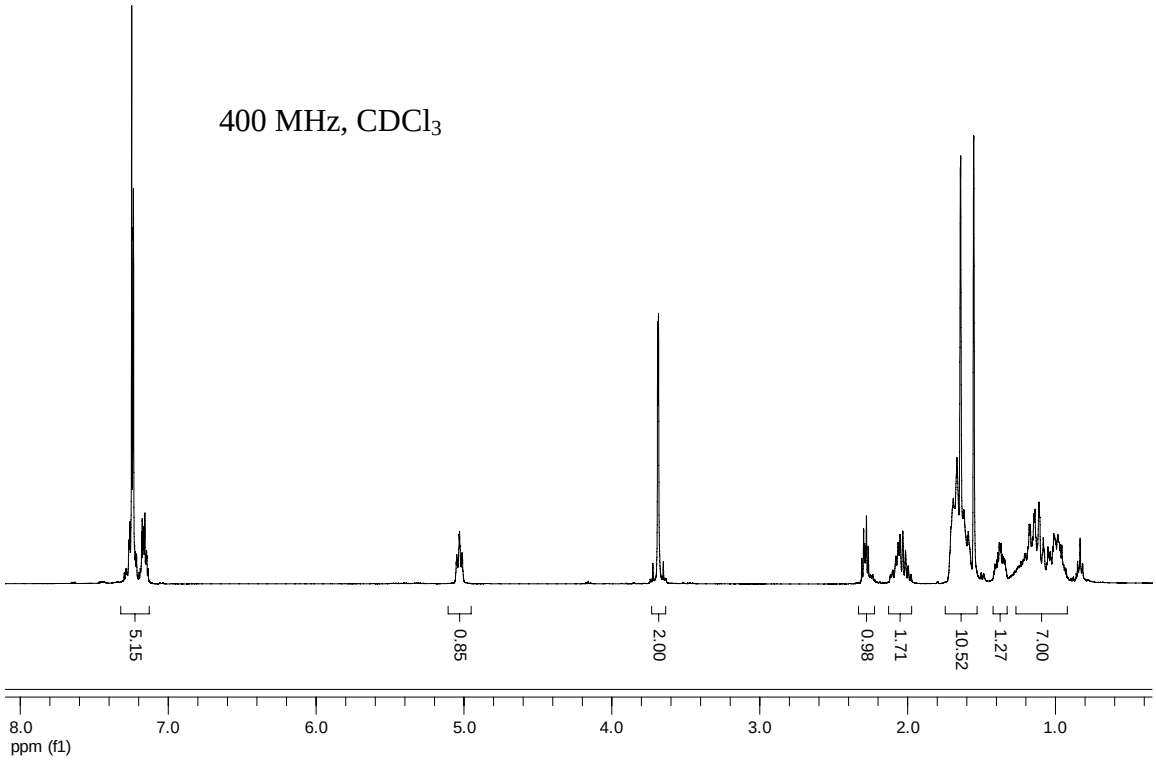


Compound **15** + **15a**

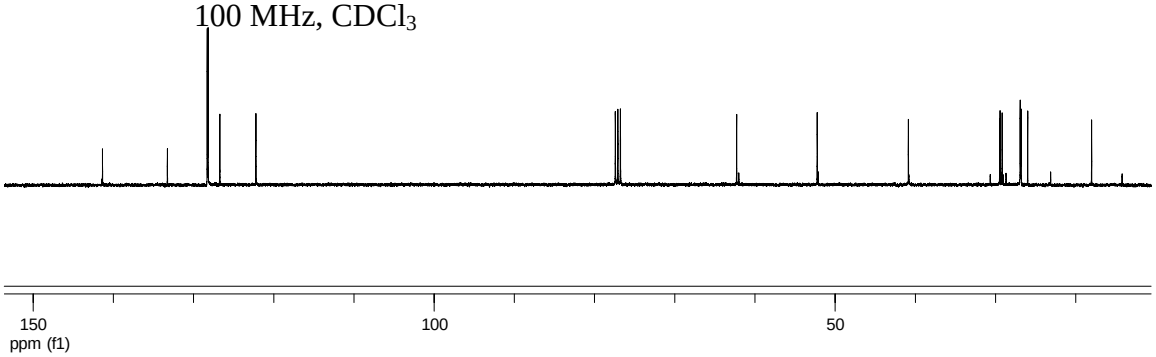


(6 : 1)

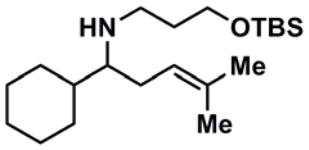
400 MHz, $CDCl_3$



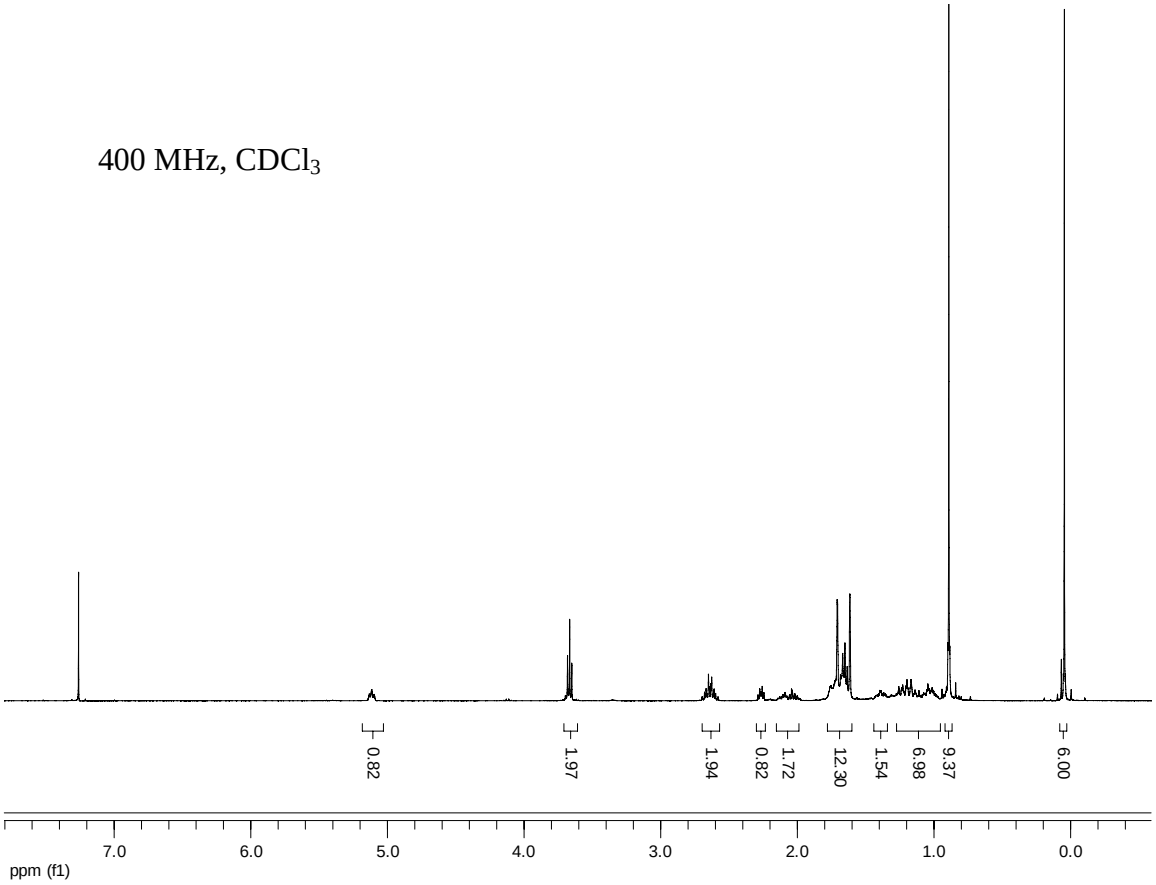
100 MHz, $CDCl_3$



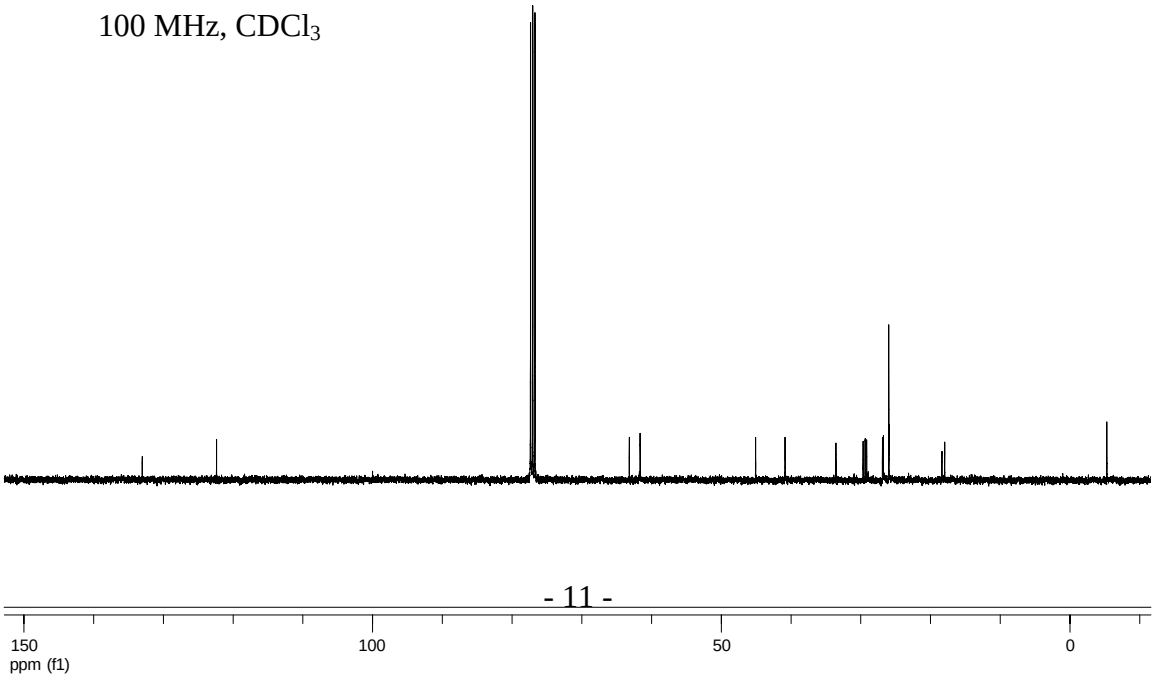
Compound **17**



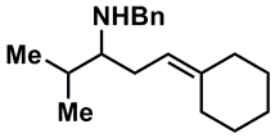
400 MHz, $CDCl_3$



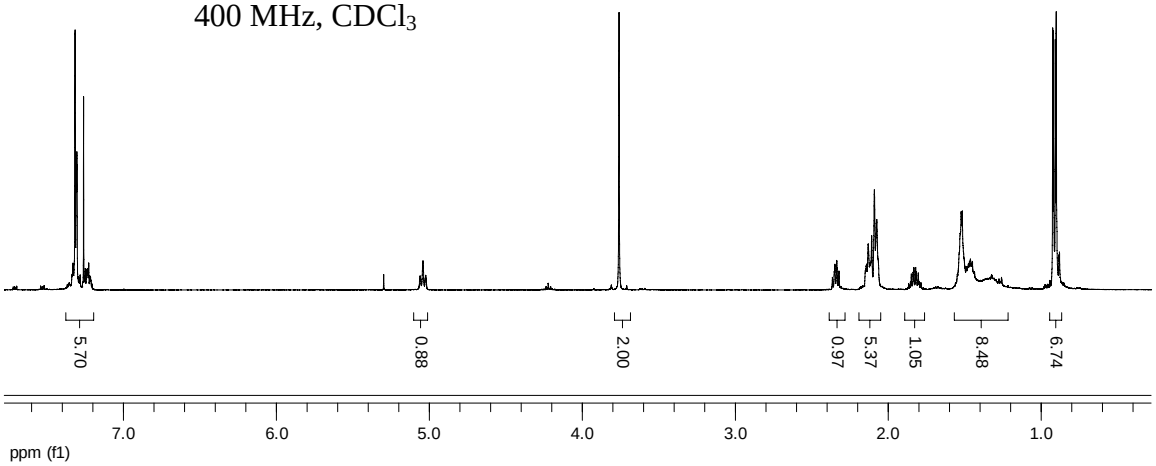
100 MHz, $CDCl_3$



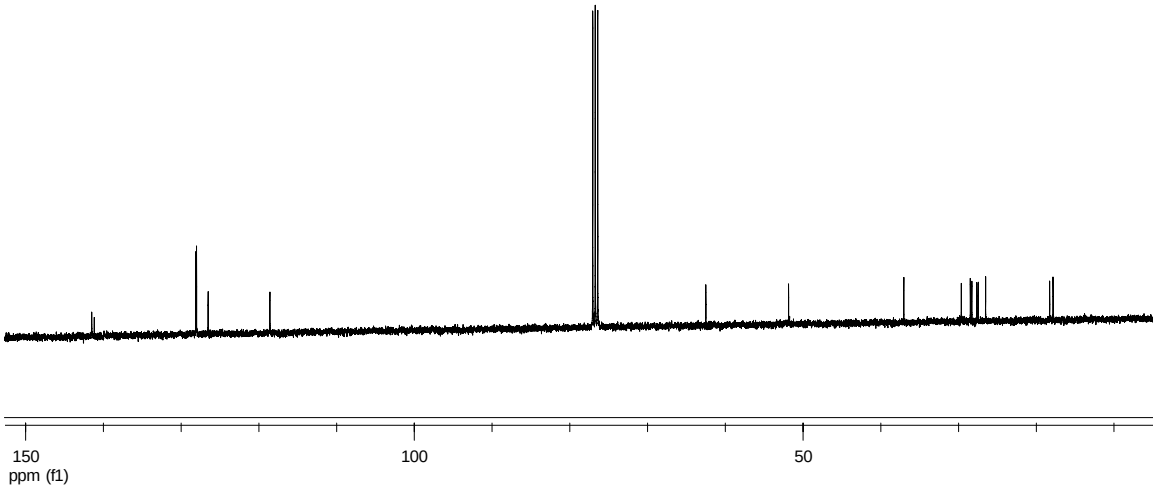
Compound **19**



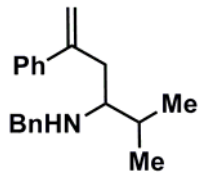
400 MHz, $CDCl_3$



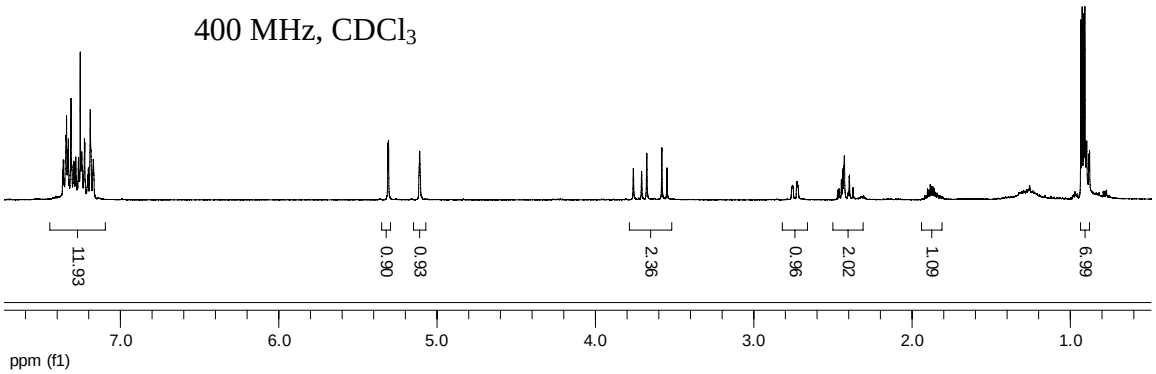
100 MHz, $CDCl_3$



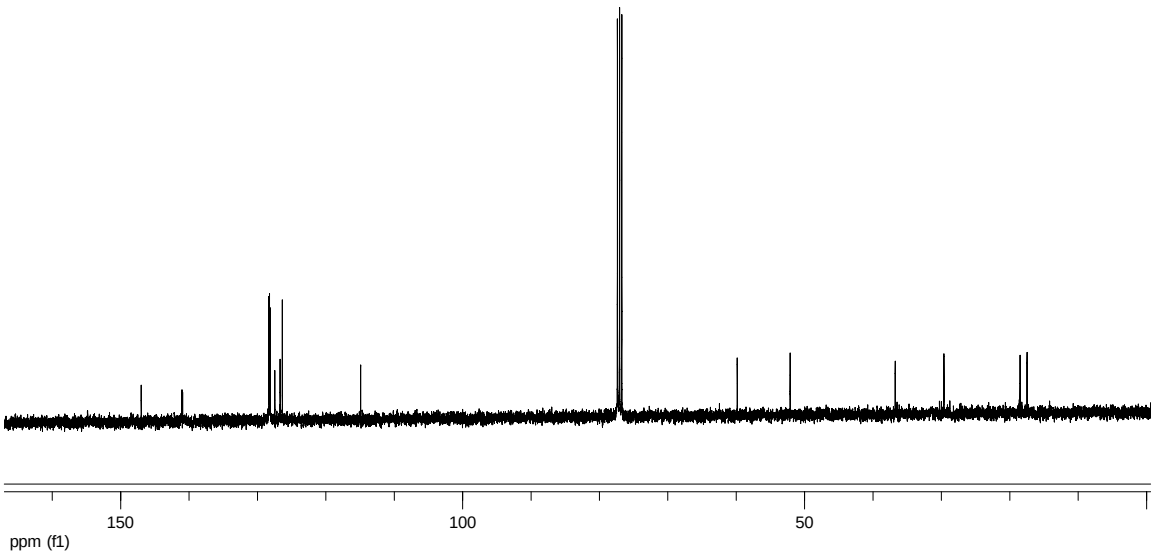
Compound **21**



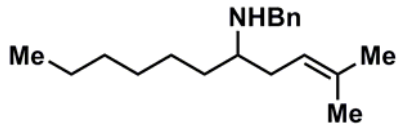
400 MHz, $CDCl_3$



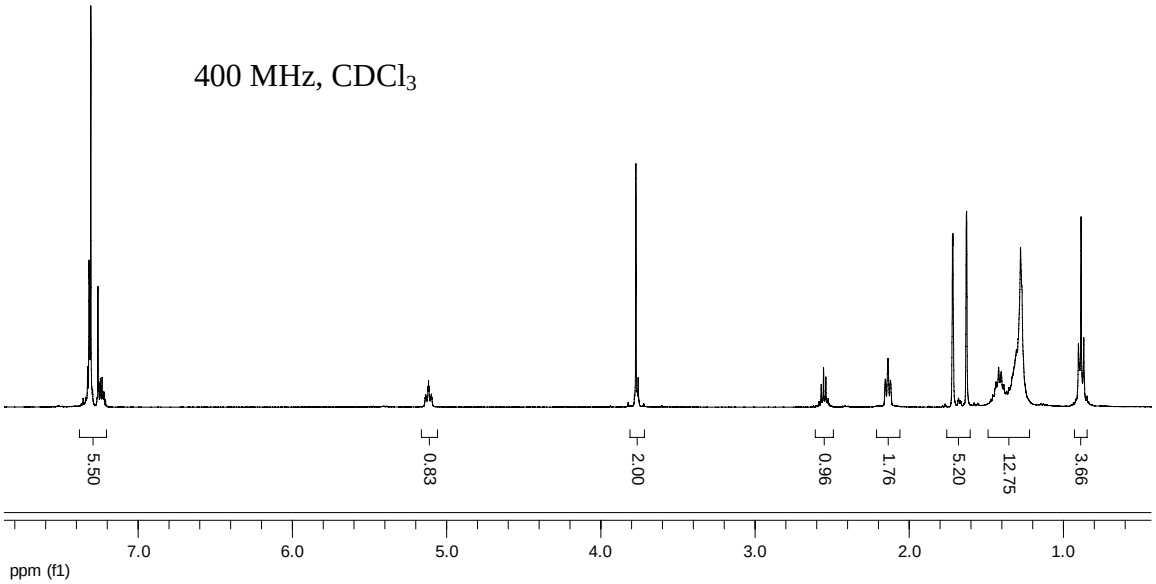
100 MHz, $CDCl_3$



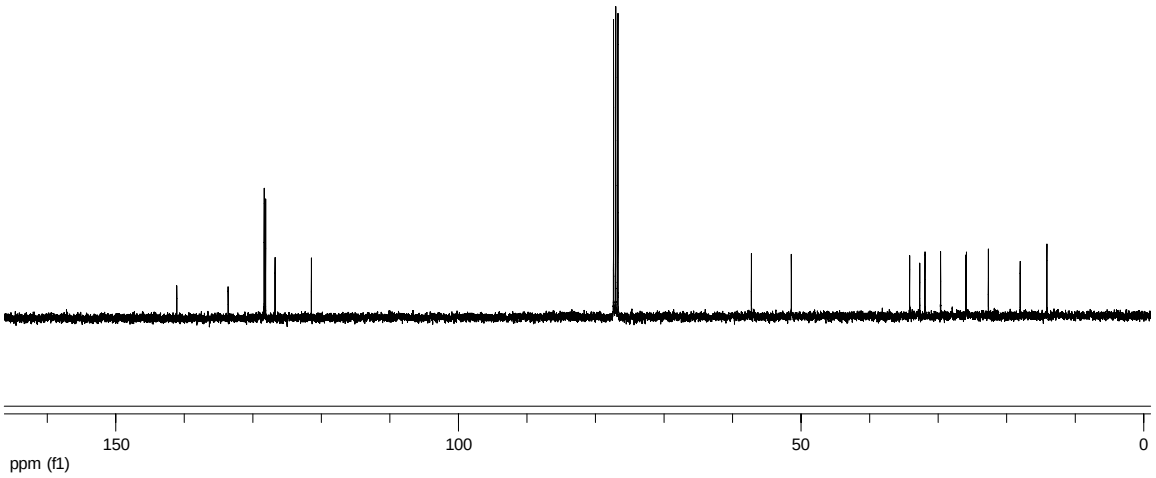
Compound **23**



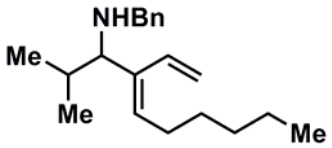
400 MHz, $CDCl_3$



100 MHz, $CDCl_3$

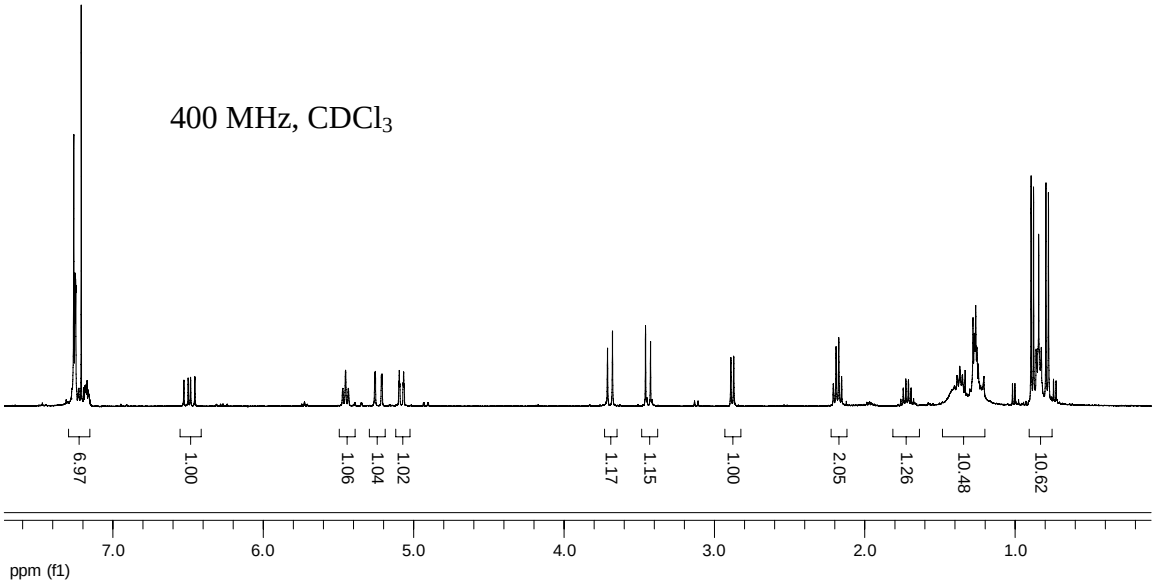


Compound **25**

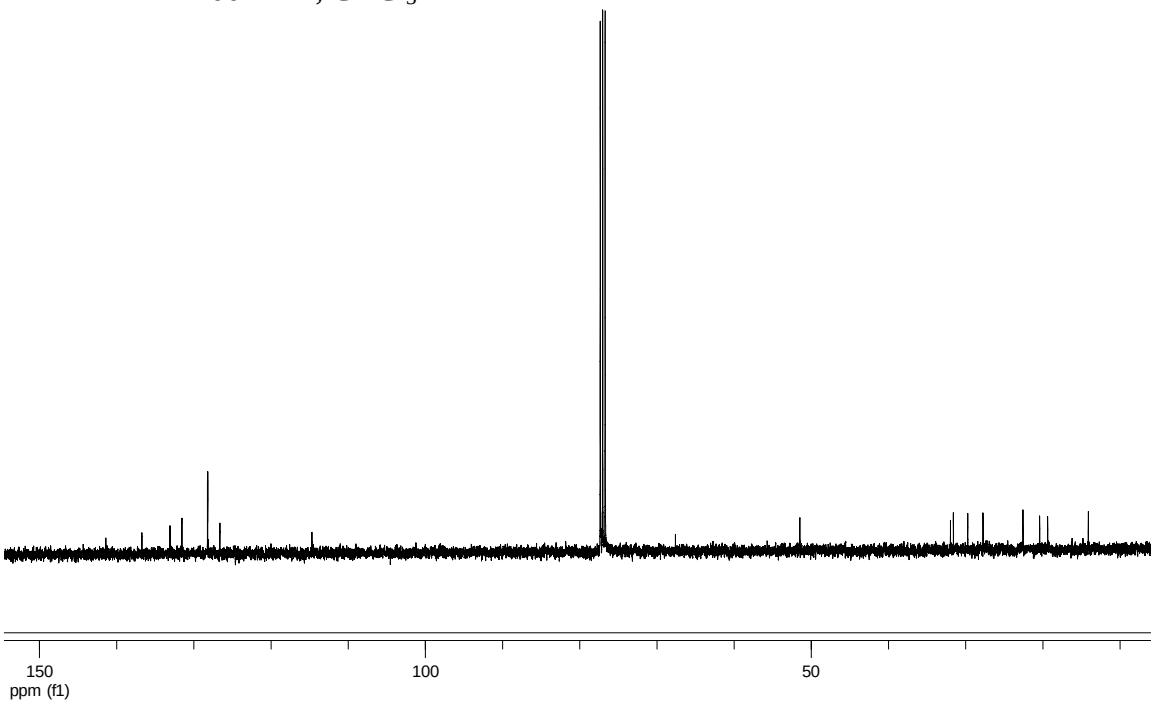


E : Z >10 : 1 (minor peaks are *Z* isomer; crude ratio 4 : 1)

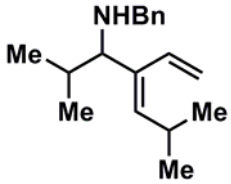
400 MHz, $CDCl_3$



100 MHz, $CDCl_3$

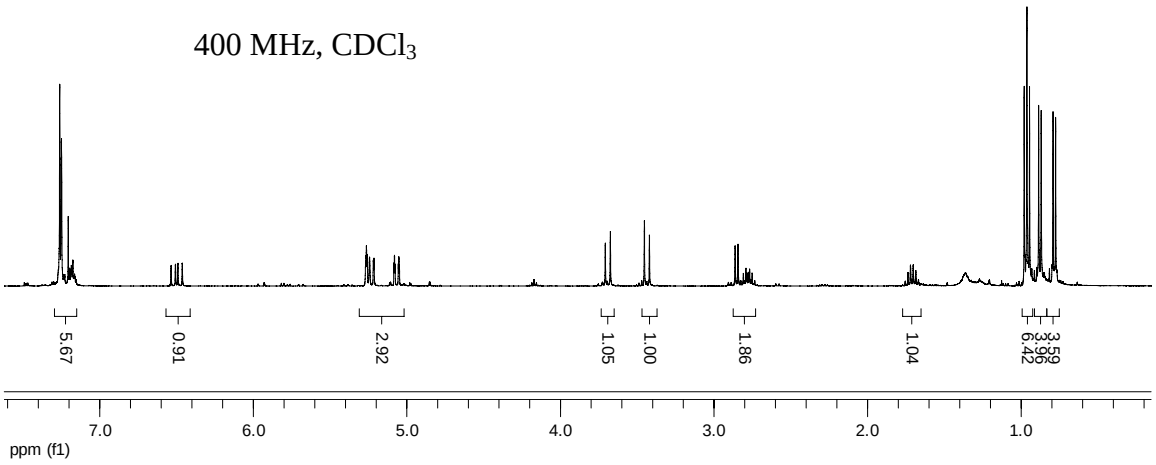


Compound **27**

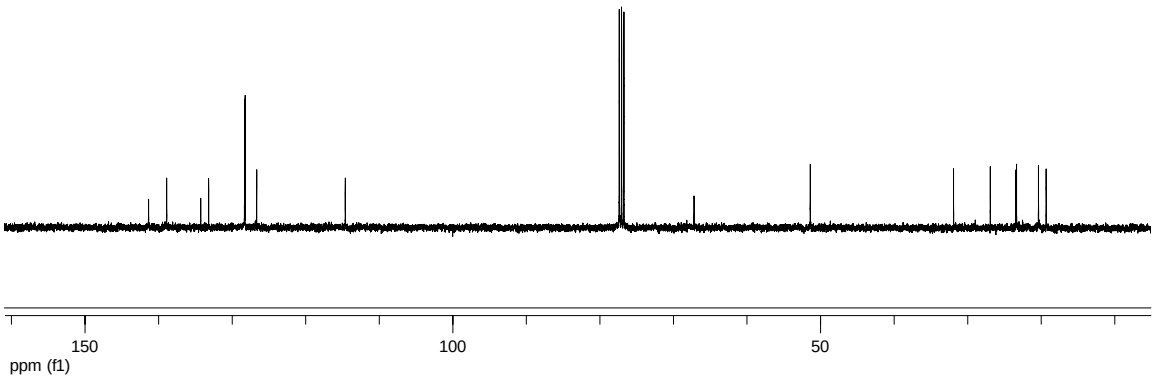


E : Z >10 : 1 (minor peaks are *Z* isomer)

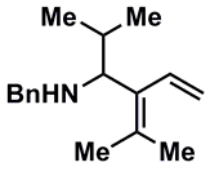
400 MHz, $CDCl_3$



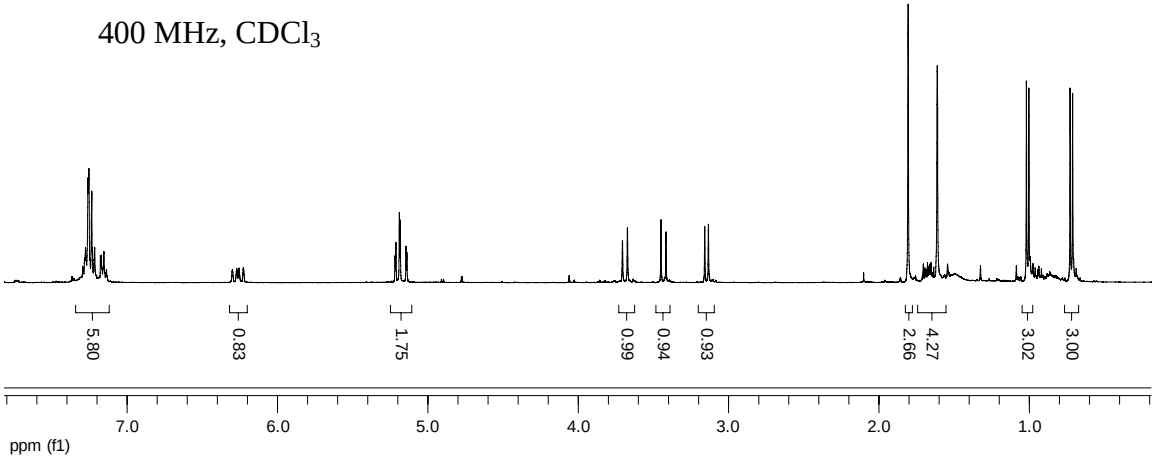
100 MHz, $CDCl_3$



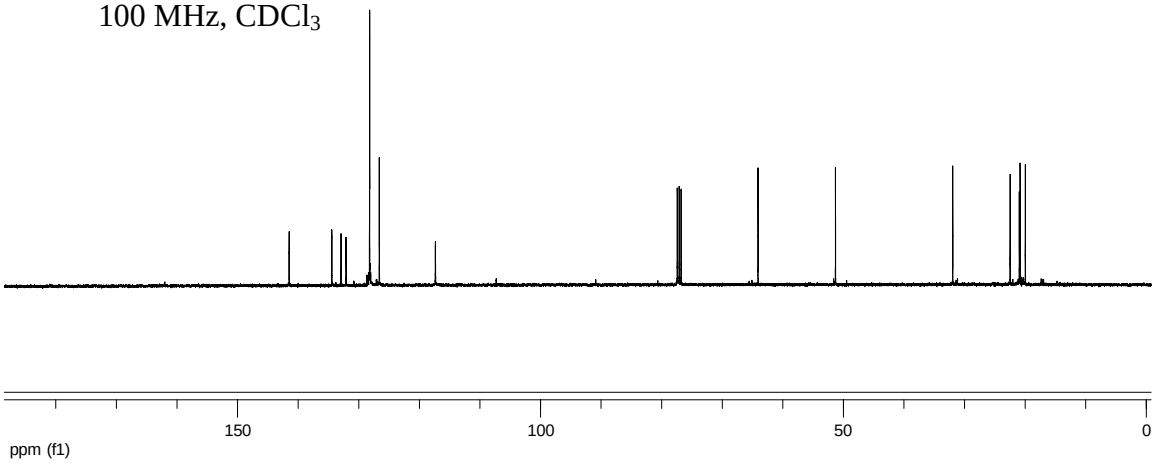
Compound **29**



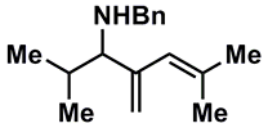
400 MHz, $CDCl_3$

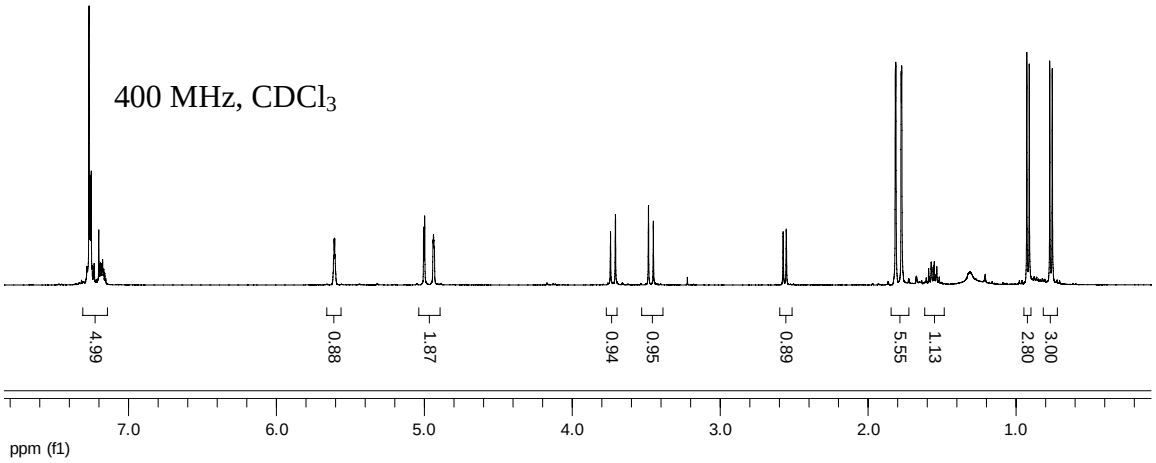


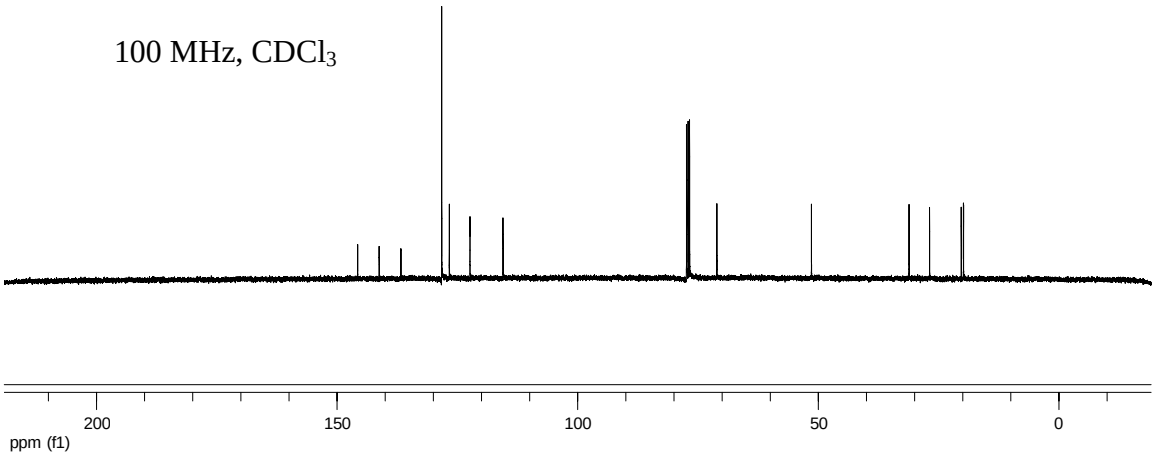
100 MHz, $CDCl_3$



Compound **31**







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