Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ruthenium(II)-catalysed direct synthesis of ketazines using secondary alcohols

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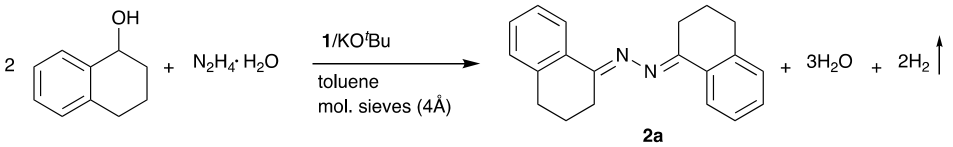
Index

General Experimental: All the catalytic experiments were carried out using standard Schlenk techniques under argon atmosphere. All the stoichiometric experiments were performed in nitrogen atmosphere MBRAUN glove box. Dry solvents were prepared according to standard procedures. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa-aesar, Himedia Chemicals and used without further purification. ^{1}H, ^{13}C spectra were recorded at Bruker AV-700 (^{1}H: 700 MHz, ^{13}C: 175 MHz) and Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz). ^{1}H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS) (δ 0.00 ppm) and ^{13}C {^{1}H} NMR chemical shifts are referenced in parts per million (ppm) with respect to $CDCl_3$ (δ 77.160 ppm). NMR spectroscopy abbreviations corresponds to: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets, br, broad; m, multiplet. Assignment of spectra was done based on 1-D (dept-135) NMR techniques. Perkin-Elmer FT-IR spectrophotometer was used to record IR spectra. Mass spectra were recorded on Bruker microTOF-Q II Spectrometer. Melting points were obtained using U-Tech Mild Steel Melting Point Apparatus.

Optimization Studies for the Catalytic Synthesis of Ketazine 2a Using Tetraline-1-ol

Tetraline-1-ol was selected as a benchmark substrate along with hydrazine hydrate to find the optimal reaction conditions for ketazine synthesis catalyzed by ruthenium pincer complex **1**. To begin, the reaction of tetraline-1-ol (0.5 mmol), hydrazine hydrate (0.75 mmol) and catalyst **1** (1 mol%) and 2 mol% of base (KO^{t}Bu) in toluene with molecular sieves (4 Å) was performed at 135 °C. The reaction progress was analyzed by gas chromatography (GC), which indicated the complete conversion of starting material within 12 h. The desired ketazine product **2a** was isolated in 75% yield and trace amount of hydrazone formation was also observed (entry 1, Table 1). Under similar reaction condition, increasing the base load to 5 mol% provided the product **2a** in 95% isolated yield (entry 2, Table 1). On decreasing the temperature to 125 °C, quantitative conversion was observed and azine product **2a** was isolated in 97% yield (entry 3, Table 1). Further, decreasing the temperature to 110 °C, the yield of azine product diminished to 64% and 34% of hydrazone intermediate was isolated (entry 4, Table 1). Under identical conditions, the reaction of tetraline-1-ol with 0.7 equiv of hydrazine hydrate at 125 °C provided 62% azine product and 35% unreacted ketone was isolated after column chromatography (entry 5, Table 1) indicating the involvement of ketone intermediacy in the reaction and the requirement for excess amount of hydrazine hydrate. When the reaction was performed without base, 30% conversion of alcohol was observed and the ketazine **2a** isolated in 14% yield (entry 6, Table 1), which indicates that hydrazine hydrate can also serve as a base in this catalytic protocol. Surprisingly, when the reaction was performed without molecular sieves, the product formation drastically decreased to 5% (entry 7, Table 1), which revealed that efficient removal of in situ formed water is essential to shift the equilibrium towards product formation and for the success of this catalytic process. Finally, the control experiments were performed using only base and without catalyst and base (entries 8,9, Table 1) no azine product was observed. Further, we have also employed the Milstein Ru-PNP$^{t\mathrm{Bu}}$ pincer catalyst in azine synthesis under reported reaction conditions using tetralin-1-ol in which no azine product (**2a**) was observed.[1] These experiments clearly confirmed that ketazine synthesis is a catalytic process and the catalyst **1** is crucial to success of the reaction.

Table S1. Optimization of Reaction Conditions for the Synthesis of Ketazines 2a Using Tetraline-1-ol [a]



entry	time (h)	temp. (°C)	conv. (%)[b]	yield (%)[c]
1[d]	12	135	>99	75
2	12	135	>99	95

3	**12**	**125**	**>99**	**97**
4[e]	12	110	>99	64
5[f]	12	125	>99	62
6[g]	24	125	30	14
7[h]	12	125	>99	5
8[i]	24	125	-	-
9[j]	24	125	-	-

[a] Catalytic conditions: catalyst **1** (1 mol %), base (5 mol%), tetraline-1-ol (0.5 mmol), hydrazine hydrate (0.75 mmol) and toluene (2 mL) with molecular sieves (4 Å) were heated at 125 °C in a Schlenk flask for 12 h. [b] Conversion of tetraline-1-ol was determined by GC analysis. [c] Isolated yield after column chromatography. [d] Reaction was performed with 2 mol% base. [e] 34% of hydrazone was isolated. [f] 0.7 equiv of hydrazine hydrate was used and 35% of 1-tetralone was also isolated after column chromatography. [g] The reaction was performed without base. [h] The reaction was performed without molecular sieves. [i] Reaction was performed with base and without catalyst **1**. [j] Reaction was performed without catalyst **1** and base.

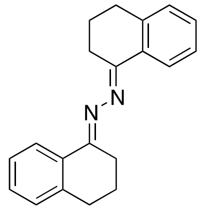
General Optimization Procedure for Synthesis of Azines Using Tetraline-1-ol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.01 mmol), base (0.02-0.05 mmol), tetraline-1-ol (0.5 mmol), toluene (2 mL) and molecular sieves (4 Å, 1g) under nitrogen atmosphere inside a glove box. The flask was taken out of the glove box and hydrazine hydrate (0.75 mmol) was added to the reaction mixture under argon flow. The flask was equipped with a condenser and immersed into a pre-heated oil bath of 125 °C with stirring in an open system under the flow of argon for 12 h. The completion of reaction was monitored using GC analysis. After cooling to room temperature, 0.5 mmol of internal standard (benzene) was added into the reaction mixture and conversion of secondary alcohol (tetraline-1-ol) was calculated using GC analysis. Further, the solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/petroleum ether mixture as an eluent. Yields were calculated for isolated pure products.

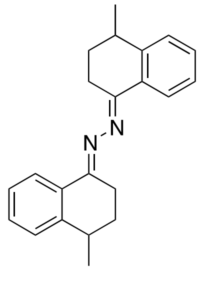
General Procedure for Synthesis of Azines Using Benzylic Secondary Alcohols:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.01 mmol), base (0.05 mmol), secondary alcohol (0.5 mmol), toluene (2 mL) and molecular sieves (4 Å, 1g) under nitrogen atmosphere inside a glove box. The flask was taken out of the glove box and hydrazine hydrate (0.75 mmol) was added to the reaction mixture under argon flow. The flask was equipped with a condenser and immersed into a pre-heated oil bath of 125 °C with stirring in an open system under the flow of argon for 12 h. The completion of reaction was monitored using GC analysis. After cooling to room temperature, 0.5 mmol of internal standard (benzene) was added into the reaction mixture and conversion of secondary alcohols was calculated using GC analysis. Further, the solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/petroleum ether mixture as an eluent. Compounds **2c, 2f, 2g,** and **2h** were crystallized from CH_2Cl_2/Hexane. Yields were calculated for isolated pure products.

Spectral Data of Symmetrical Benzylic Ketazine Products:



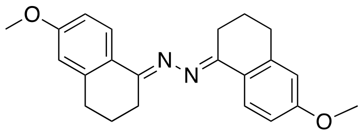
1,2-bis((*E*)-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine (2a): Yellow solid. Yield: 97%. Melting Point: 124-126 °C. IR (DCM): 3061, 3017, 2938, 2835, 1606, 1588, 1479, 1450, 1429, 1347, 1326, 1293, 1118, 1027, 756, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8 Hz, 2H, ArC*H*), 7.17-7.24 (m, 4H, ArC*H*), 7.10 (d, *J* = 8 Hz, 2H, ArC*H*), 2.76 (t, *J* = 6 Hz, 4H, CH_2), 2.69 (t, *J* = 8 Hz, 4H, CH_2,) 1.85 (quint, *J* = 6.4 Hz, 4H, CH_2). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 157.24 (*C*=N), 140.65 (quat-*C*), 133.01 (Ar*C*H), 129.59 (quat-*C*), 128.77 (Ar*C*H), 126.44 (Ar*C*H), 125.63 (Ar*C*H), 30.07 (*C*H_2), 27.48 (*C*H_2), 22.26 (*C*H_2). HRMS (ESI) m/z calcd for $C_{20}H_{20}N_2$ $(M+H)^+$: 289.1686, found: 289.1699.



1,2-bis((*E*)-4-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine (2b): Yellow solid**.** Yield: 94%. Melting Point: 104-106 °C. IR (DCM): 3062, 2960, 2924, 2869, 1606, 1562, 1476, 1457, 1416, 1375, 1350, 1330, 1291, 1012, 760, 744, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8 Hz, 2H, ArC*H*), 7.16-7.27 (m, 6H, ArC*H*), 2.85-2.93 (m, 2H, C*H*), 2.63-2.82 (m, 4H, CH_2), 1.90-1.98 (m, 2H, CH_2), 1.58-1.68

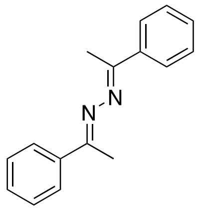
(m, 2H, C*H*$_2$), 1.25 (d, *J* = 8 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6MHz, CDCl$_3$): δ 157.32 (*C*=N), 145.32 (quat-*C*), 132.30 (quat-*C*), 129.80 (Ar*C*H), 127.23 (Ar*C*H), 126.32 (Ar*C*H), 125.68 (Ar*C*H), 33.04 (*C*H), 29.41 (*C*H$_2$), 24.59 (*C*H$_2$), 20.88 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{22}H_{24}N_2$ (M+H)$^+$: 317.2012, found: 317.2017.

1,2-bis((*E*)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine (2c): Yellow solid.



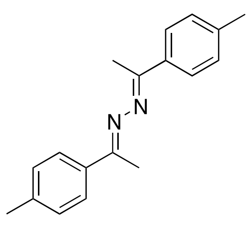
Yield: 82%. Melting Point: 170-172 °C. IR (DCM)**:** 3047, 3002, 2982, 2965, 2962, 2855, 2835, 1613, 1589, 1491, 1462, 1454, 1345, 1324, 1272, 1256, 1182, 1146, 1128, 1054, 1035, 872, 825, 815, 733 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.17 (d, *J* = 8.8 Hz, 2H, ArC*H*), 6.75 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 2H, ArC*H*), 6.60 (d, *J* = 2.4 Hz, 2H, ArC*H*), 3.77 (s, 6H, C*H*$_3$), 2.70-2.74 (m, 8H, C*H*$_2$), 1.81-1.87 (m, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 160.64 (quat-*C*), 157.77 (*C*=N), 142.45 (quat-*C*), 127.34 (Ar*C*H), 126.24 (quat-*C*), 113.04 (Ar*C*H), 112.78 (Ar*C*H), 55.40 (O*C*H$_3$), 30.46 (*C*H$_2$), 27.27 (*C*H$_2$), 22.38 (*C*H$_2$). HRMS (ESI) m/z calcd for $C_{22}H_{24}N_2O_2$ (M+H)$^+$: 349.1911, found: 349.1905.

(1*E*,2*E*)-1,2-Bis(1-phenylethylidene)hydrazine (2d):[2] Yellow solid**.** Yield: 92%. Melting Point:



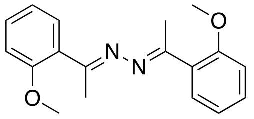
117-119 °C; lit. 122-123 °C.[3] IR (DCM): 3062, 2958, 1603, 1567, 1492, 1444, 1361, 1309, 1285, 1178, 1075, 1023, 760 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82-7.85 (m, 4H, ArC*H*), 7.33-7.35 (m, 6H, ArC*H*), 2.24 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 157.84 (*C*=N), 138.58 (quat-*C*), 129.74 (Ar*C*H), 128.47 (Ar*C*H), 126.75 (Ar*C*H), 15.17 (*C*H$_3$). MS (ESI) m/z calcd for $C_{16}H_{16}N_2$ (M+H)$^+$: 237.13, found: 237.13.

(1*E*,2*E*)-1,2-Bis(1-(p-tolyl)ethylidene)hydrazine (2e):[2] Yellow solid. Yield: 90%. Melting Point:

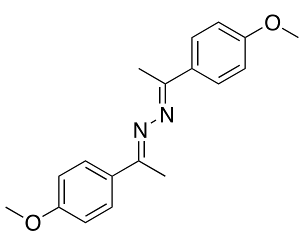


126-128 °C; lit. 134-135 °C.[4] IR (DCM): 3061, 2916, 1601, 1562, 1403, 1359, 1293, 1181, 1113, 1014, 817, 712 cm^{-1}. ^{1}H NMR (700 MHz, CDCl$_3$): δ 7.84 (d, *J* = 7.7 Hz, 4H, ArC*H*), 7.26 (d, *J* = 7.7 Hz, 4H, ArC*H*), 2.43 (s, 6H, ArC*H*$_3$), 2.34 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (175 MHz, CDCl$_3$): δ 157.72 (*C*=N), 139.69

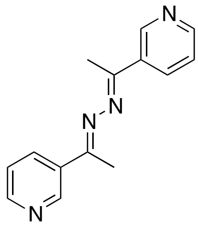
(quat-*C*), 135.82 (quat-*C*), 129.06 (Ar*C*H), 126.57 (Ar*C*H), 21.36 (Ar*C*H$_3$), 14.97 (*C*H$_3$). MS (ESI) m/z calcd for $C_{18}H_{20}N_2$ (M+H)$^+$: 265.17, found: 265.17.



(1*E*,2*E*)-1,2-Bis(1-(2-methoxyphenyl)ethylidene)hydrazine (2f):[2] White solid. Yield: 81%. Melting Point: 80-82 °C; lit. 75-76 °C.[5] IR (DCM): 3000, 2960, 2924, 2836, 1599, 1489, 1463, 1435, 1360, 1302, 1265, 1240, 1180, 1025, 936, 804, 753 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H, ArC*H*), 7.35-7.40 (m, 2H, ArC*H*), 6.96-7.04 (m, 4H, ArC*H*), 3.89 (s, 6H, OC*H*$_3$), 2.24 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6MHz, CDCl$_3$): δ 158.84 (quat-*C*), 157.68 (*C*=N), 130.21 (Ar*C*H), 129.75 (Ar*C*H), 129.70 (Ar*C*H), 120.81 (quat-*C*), 111.28 (Ar*C*H), 55.64 (O*C*H$_3$), 18.89 (*C*H$_3$). MS (ESI) m/z calcd for $C_{18}H_{20}N_2O_2$ (M+H)$^+$: 297.16, found: 297.16.



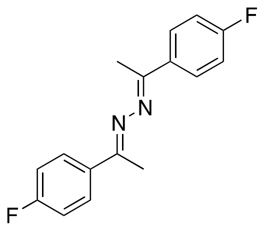
(1*E*,2*E*)-1,2-Bis(1-(4-methoxyphenyl)ethylidene)hydrazine (2g):[2] Yellow solid. Yield: 86%. Melting Point: 190-192 °C; lit. 196-197 °C.[6] IR (DCM): 3011, 2964, 2928, 2836, 1594, 1507, 1454, 1444, 1412, 1365, 1303, 1252, 1173, 1115, 1026, 968, 835, 805 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, *J* = 8.8 Hz, 4H, ArC*H*), 6.87 (d, *J* = 8.8 Hz, 4H, ArC*H*), 3.79 (s, 6H, OC*H*$_3$), 2.25 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 160.96 (quat-*C*), 157.96 (*C*=N), 131.48 (quat-*C*), 128.21 (Ar*C*H), 113.78 (Ar*C*H), 55.48 (O*C*H$_3$), 14.93 (*C*H$_3$). MS (ESI) m/z calcd for $C_{18}H_{20}N_2O_2$ (M+H)$^+$: 297.16, found: 297.16.



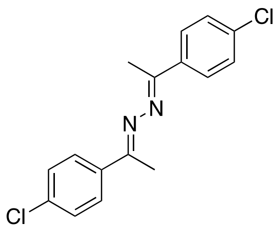
(1*E*,2*E*)-1,2-Bis(1-(pyridin-3-yl)ethylidene)hydrazine (2h): Yellow solid**.** Yield: 82%. Melting Point: 100-102 °C. IR (DCM): 2938, 1606, 1584, 1563, 1482, 1410, 1366, 1293, 1200, 1121, 1021, 813, 704 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.04 (d, *J* = 1.6 Hz, 2H, ArC*H*), 8.58 (dd, J_1 = 4.4 Hz, J_2 = 1.2 Hz, 2H, ArC*H*), 8.15 (dt, J_1 = 8 Hz, J_2 = 2 Hz, 2H, ArC*H*), 7.29 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 2H, ArC*H*), 2.29 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 156.93 (*C*=N), 150.76 (Ar*C*H), 148.29 (Ar*C*H), 134.00

(Ar*C*H), 133.76 (quat-*C*), 123.39 (Ar*C*H), 14.97 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{14}H_{14}N_4$ (M+H)$^+$: 239.1291, found: 239.1292.

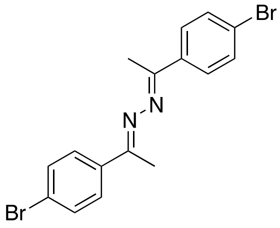
(1*E*,2*E*)-1,2-Bis(1-(4-fluorophenyl)ethylidene)hydrazine (2i):[2] Bright yellow solid. Yield: 91%. Melting Point: 128-130 °C; lit. 130-132 °C.[7] IR (DCM): 3072, 2955, 1604, 1503, 1414, 1294, 1232, 1155, 1099, 1012, 838 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82-7.85 (m, 4H, ArC*H*), 7.03 (t, *J* = 8.8 Hz, 4H, ArC*H*), 2.25 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.18 (quat-*C*), 162.70 (quat-*C*), 157.55 (*C*=N), 134.71 (quat-*C*), 134.68 (quat-*C*), 128.73 (Ar*C*H), 128.65 (Ar*C*H), 115.54 (Ar*C*H), 115.33 (Ar*C*H), 15.12 (*C*H$_3$). MS (ESI) m/z calcd for $C_{16}H_{14}F_2N_2$ (M+H)$^+$: 273.12, found: 273.12.



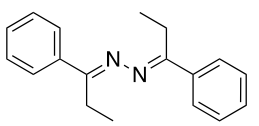
(1*E*,2*E*)-1,2-Bis(1-(4-chlorophenyl)ethylidene)hydrazine (2j):[2] White solid. Yield: 89%. Melting Point: 132-133 °C; lit. 133-134 °C.[8] IR (DCM): 3068, 2960, 1607, 1592, 1487, 1396, 1361, 1301, 1106, 1012, 830, 765, 717 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.77 (d, *J* = 8 Hz, 4H, ArC*H*), 7.31 (d, *J* = 8 Hz, 4H, ArC*H*), 2.22 (s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 157.43 (*C*=N), 136.85 (quat-*C*), 135.92 (quat-*C*), 128.70 (Ar*C*H), 128.07 (Ar*C*H), 15.06 (*C*H$_3$). MS (ESI) m/z calcd for $C_{16}H_{14}Cl_2N_2$ (M+H)$^+$: 305.06, found: 305.06.



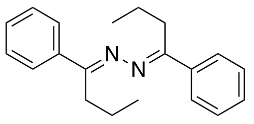
(1*E*,2*E*)-1,2-Bis(1-(4-bromophenyl)ethylidene)hydrazine (2k):[2] White solid. Yield: 91%. Melting Point: 153-155 °C; lit. 164-165 °C.[9] IR (DCM): 3070, 2924, 1606, 1584, 1483, 1394, 1361, 1301, 1077, 1007, 824, 760, 713 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, *J* = 8 Hz, 4H, ArC*H*), 7.47 (d, *J* = 8 Hz, 4H, ArC*H*), 2.21(s, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 157.46 (*C*=N), 137.27 (quat-*C*), 131.67 (Ar*C*H), 128.32 (Ar*C*H), 124.32 (quat-*C*), 15.02 (*C*H$_3$). MS (ESI) m/z calcd for $C_{16}H_{14}Br_2N_2$ (M+H)$^+$: 392.96, found: 392.96.



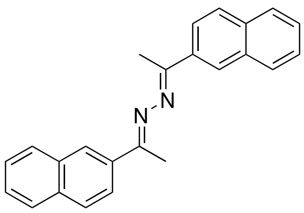
(1*E*,2*E*)-1,2-Bis(1-phenylpropylidene)hydrazine (2l):[2] Yellow solid. Yield: 58%. Melting Point: 66 °C; lit. 66-68 °C.[10] IR (DCM): 2972, 2934, 2874, 1601, 1570, 1494, 1461, 1445, 1373, 1325, 1286, 1063, 770, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.85 (m, 4H, ArC*H*), 7.35-7.39 (m, 6H, ArC*H*), 2.82 (q, *J* = 7.6 Hz, 4H, C*H*$_2$), 1.06 (t, *J* = 7.6 Hz, 6H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 163.03 (*C*=N), 137.52 (quat-*C*), 129.63 (Ar*C*H), 128.55 (Ar*C*H), 127.01 (Ar*C*H), 22.08 (*C*H$_2$), 11.53 (*C*H$_3$). MS (ESI) m/z calcd for $C_{18}H_{20}N_2$ $(M+H)^+$: 265.17, found: 265.17.



(1*E*,2*E*)-1,2-Bis(1-phenylbutylidene)hydrazine (2m): Yellow solid. Yield: 90%. Melting Point: 38-40 °C; lit. 38 °C.[4] IR (DCM): 2960, 2929, 2870, 1599, 1570, 1492, 1444, 1290, 1179, 1028, 761, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J_1 = 8 Hz, J_2 = 2.4 Hz, 4H, ArC*H*), 7.31-7.37 (m, 6H, ArC*H*), 2.81 (t, *J* = 8 Hz, 4H, C*H*$_2$), 1.43-1.54 (m, 4H, C*H*$_2$), 0.89 (t, *J* = 8 Hz, 6H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 162.70 (*C*=N), 137.98 (quat-*C*), 129.59 (Ar*C*H), 128.51 (Ar*C*H), 127.05 (Ar*C*H), 30.73(*C*H$_2$), 20.61 (*C*H$_2$), 14.62 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{20}H_{24}N_2$ $(M+H)^+$: 293.2012, found: 293.2018.



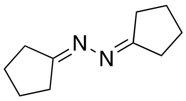
(1*E*,2*E*)-1,2-Bis(1-(naphthalen-2-yl)ethylidene)hydrazine (2n): Orange solid**.** Yield: 89%. Melting Point: 188-190 °C. IR (DCM): 3055, 2922, 1600, 1503, 1433, 1367, 1292, 1271, 1127, 862, 825, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.6 Hz, 4H, ArC*H*), 7.82-7.90 (m, 6H, ArC*H*), 7.47-7.50 (m, 4H, ArC*H*), 2.45 (s, 6H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 157.86 (*C*=N), 135.99 (quat-*C*), 134.20 (quat-*C*), 133.26 (quat-*C*), 128.84 (Ar*C*H), 128.09 (Ar*C*H), 127.83 (Ar*C*H), 126.97 (Ar*C*H), 126.81 (Ar*C*H), 126.47 (Ar*C*H), 124.18 (Ar*C*H), 15.16 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{24}H_{20}N_2$ $(M+H)^+$: 337.1696, found: 337.1708.



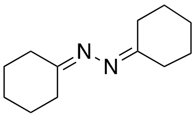
General Procedure for Synthesis of Azines Using Aliphatic Secondary Alcohols:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.02 mmol), base (0.10 mmol), secondary alcohol (0.5 mmol), toluene (2 mL) and molecular sieves (4 Å) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box and hydrazine hydrate (1.5 mmol) was added to the reaction mixture under argon flow. The flask was equipped with a condenser and immersed into a pre-heated oil bath of 125 °C with stirring in an open system under a flow of argon for 12 h. The completion of reaction was monitored using GC analysis. After cooling to room temperature, 0.5 mmol of internal standard (benzene) was added into the reaction mixture and conversion of secondary alcohols was calculated using GC analysis. Further, solvent was evaporated and crude reaction mixture was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/petroleum ether mixture as an eluent. Compound **3m** was crystalized from DCM/hexane. Yields were calculated for isolated pure products.

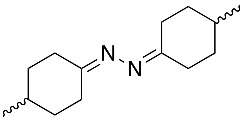
Spectral Data of Aliphatic Ketazine Products:



1,2-Dicyclopentylidenehydrazine (3a): Yellow liquid. Yield: 74%. IR (DCM): 2981, 2839, 1623, 1442, 1338, 1261, 1143, 912, 735 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.37 (t, *J* = 6.4 Hz, 4H, C*H*$_2$), 2.29 (t, *J* = 7.2 Hz, 4H, C*H*$_2$), 1.67-1.72 (m, 8H, C*H*$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 174.74 (*C*=N), 33.29 (*C*H$_2$), 29.45 (*C*H$_2$), 24.90 (*C*H$_2$), 24.75 (*C*H$_2$). HRMS (ESI) m/z calcd for $C_{10}H_{16}N_2$ (M+H)$^+$: 165.1386, found: 165.1398.

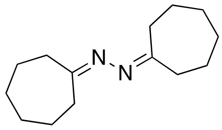


1,2-Dicyclohexylidenehydrazine (3b): Yellow liquid**.** Yield: 84%. IR (DCM): 2930, 2855, 1638, 1447, 1344, 1265, 1133, 904, 735 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.24-2.32 (m, 8H, C*H*$_2$), 1.53-1.66 (m, 12H, C*H*$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.47 (*C*=N), 35.80 (*C*H$_2$), 27.96 (*C*H$_2$), 27.66 (*C*H$_2$), 26.48 (*C*H$_2$), 26.05 (*C*H$_2$). HRMS (ESI) m/z calcd for $C_{12}H_{20}N_2$ (M+H)$^+$: 193.1699, found: 193.1703.

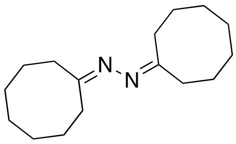


1,2-Bis(4-methylcyclohexylidene)hydrazine (3c): Yellow liquid**.** Yield: 92%. ^{1}H NMR analysis of the crude reaction mixture showed the cis-trans isomer ratio of 90:10 as determined by comparison of the following signals: δ 1.03 (d, *J* = 6.8 Hz, 6H, C*H*$_3$)-minor, 0.96 (d, *J* = 6.8 Hz, 6H, C*H*$_3$)-major. IR (DCM): 2949, 2923, 2852, 1640, 1456, 1376, 1198, 1134, 732 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.94-3.03 (m, 2H, C*H*$_2$) (both isomers), 2.46-

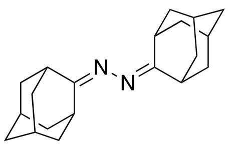
2.50 (m, 2H, $\mathrm{C}\mathit{H}_2$)-major, 2.33-2.38 (m, 2H, $\mathrm{C}\mathit{H}_2$)-minor, 2.19-2.28 (m, 2H, $\mathrm{C}\mathit{H}_2$) (both isomers), 1.98-2.06 (m, 2H, $\mathrm{C}\mathit{H}_2$)-minor, 1.88-1.93 (m, 2H, $\mathrm{C}\mathit{H}_2$)-major, 1.77-1.86 (m, 4H, $\mathrm{C}\mathit{H}_2$) (both isomers), 1.67-1.71 (m, 2H, $\mathrm{C}\mathit{H}_2$) (both isomers), 1.38-1.50 (m, 2H, $\mathrm{C}\mathit{H}_2$)-minor, 1.22-1.30 (m, 2H, $\mathrm{C}\mathit{H}_2$)-major, 1.09-1.15 (m, 2H, C*H*) (both isomers), 1.03 (d, *J* = 6.8 Hz, 6H, $\mathrm{C}\mathit{H}_3$)-minor, 0.96 (d, *J* = 6.8 Hz, 6H, $\mathrm{C}\mathit{H}_3$)-major. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ 165.65 (*C*=N), 165.58 (*C*=N), 35.63 ($\mathit{C}\mathrm{H}_2$), 34.98 ($\mathit{C}\mathrm{H}_2$), 34.52 ($\mathit{C}\mathrm{H}_2$), 34.48 ($\mathit{C}\mathrm{H}_2$), 32.16 (*C*H), 27.15 ($\mathit{C}\mathrm{H}_2$), 27.10 ($\mathit{C}\mathrm{H}_2$), 21.67 ($\mathit{C}\mathrm{H}_3$). HRMS (ESI) m/z calcd for $\mathrm{C_{14}H_{24}N_2}$ $(\mathrm{M+H})^+$: 221.2012, found: 221.2011.



1,2-Dicycloheptylidenehydrazine (3d): Yellow liquid**.** Yield: 89%. IR (DCM): 2923, 2851, 1621, 1453, 1347, 1263, 1178, 955, 860, 734 $\mathrm{cm^{-1}}$. $^1\mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl_3}$): δ 2.41 (t, *J* = 5.6 Hz, 4H, $\mathrm{C}\mathit{H}_2$), 2.28 (t, *J* = 5.2 Hz, 4H, $\mathrm{C}\mathit{H}_2$), 1.47-1.60 (m, 16H, $\mathrm{C}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ 165.78 (*C*=N), 37.06 ($\mathit{C}\mathrm{H}_2$), 31.48 ($\mathit{C}\mathrm{H}_2$), 30.53 ($\mathit{C}\mathrm{H}_2$), 30.30 ($\mathit{C}\mathrm{H}_2$), 27.59 ($\mathit{C}\mathrm{H}_2$), 25.00 ($\mathit{C}\mathrm{H}_2$). HRMS (ESI) m/z calcd for $\mathrm{C_{14}H_{24}N_2}$ $(\mathrm{M+H})^+$: 221.2012, found: 221.2024.

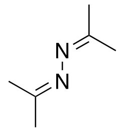


1,2-Dicyclooctylidenehydrazine (3e): Yellow liquid**.** Yield: 87%. IR (DCM): 2928, 2856, 1617, 1464, 1348, 1158, 668 $\mathrm{cm^{-1}}$. $^1\mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl_3}$): δ 2.30-2.36 (m, 8H, $\mathrm{C}\mathit{H}_2$), 1.69-1.75 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.58-1.61 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.40-1.50 (m, 12H, $\mathrm{C}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ 167.98 (*C*=N), 35.70 ($\mathit{C}\mathrm{H}_2$), 29.88 ($\mathit{C}\mathrm{H}_2$), 27.35 ($\mathit{C}\mathrm{H}_2$), 27.20 ($\mathit{C}\mathrm{H}_2$), 26.29 ($\mathit{C}\mathrm{H}_2$), 25.21 ($\mathit{C}\mathrm{H}_2$), 24.56 ($\mathit{C}\mathrm{H}_2$). HRMS (ESI) m/z calcd for $\mathrm{C_{16}H_{28}N_2}$ $(\mathrm{M+H})^+$: 249.2325, found: 249.2338.

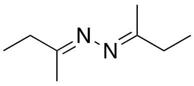


1,2-Di(adamantan-2-ylidene)hydrazine (3f):[11] White solid. Yield: 78%. Melting Point: 316-318 °C; lit. 314-316 °C.[12] IR (DCM): 2916, 2851, 1643, 1450, 1078, 908, 732 $\mathrm{cm^{-1}}$. $^1\mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl_3}$): δ 3.28-3.35 (m, 2H, C*H*), 2.67-2.71 (m, 2H, C*H*), 2.01-2.08 (m, 8H), 1.89-1.95 (m, 10H), 1.70-1.83 (m, 4H), 1.52-1.61 (m, 2H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ 171.25 (*C*=N), 39.66 (*C*H), 39.41 (*C*H), 38.12, 36.69, 31.79, 27.99. MS (ESI) m/z calcd for $\mathrm{C_{20}H_{28}N_2}$ $(\mathrm{M+H})^+$: 297.23, found: 297.23.

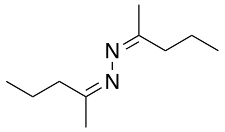
1,2-Di(propan-2-ylidene)hydrazine (3g):[13] Yield: 50%, was calculated by ^{1}H NMR spectroscopy using mesitylene as internal standard. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.56 (s, 6H, CH_3), 2.42 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 160.43 (C=N), 25.39 (CH$_3$), 18.18 (CH$_3$).



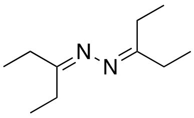
1,2-Di(butan-2-ylidene)hydrazine (3h): Yellow liquid. Yield: 73%, was calculated by ^{1}H NMR spectroscopy using mesitylene as internal standard. ^{1}H NMR analysis of the crude reaction mixture showed the *E*/*Z* isomer ratio of 70:30 as determined by comparison of the following signals: δ 3.01 (s, 6H, CH_3)-minor, 2.70 (s, 6H, CH_3)-major. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.01 (s, 6H, CH_3)-minor, 2.70 (s, 6H, CH_3)-major, 2.51-2.53 (m, 4H, CH_2)-minor, 2.34-2.36 (m, 4H, CH_2)-major, 1.68-1.74 (m, 6H, CH_3)-major, 1.51-1.57 (m, 6H, CH_3)-minor. ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 163.65 (C=N), 162.75 (C=N), 162.52 (C=N), 31.95 (CH$_2$), 31.05 (CH$_2$), 24.75 (CH$_2$), 22.87 (CH$_3$), 22.25 (CH$_3$), 16.31 (CH$_3$), 16.18 (CH$_3$), 10.85 (CH$_3$), 10.47 (CH$_3$).



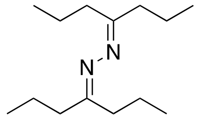
1,2-Di(pentan-2-ylidene)hydrazine (3i): Pale yellow liquid. Yield: 90%, was calculated by ^{1}H NMR spectroscopy using mesitylene as internal standard. ^{1}H NMR analysis of the crude reaction mixture showed the *E*/*Z* isomer ratio of 72:28 as determined by comparison of the following signals: δ 0.88 (t, *J* = 7.6 Hz, 6H, CH_3)-major, 0.82 (t, *J* = 7.6 Hz, 6H, CH_3)-minor. IR (DCM): 3015, 2960, 2872, 1640, 1464, 1361, 1251, 1203, 1095, 1037, 835, 732, 687 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.15-2.17 (m, 4H, CH_2)-both isomer, 1.91 (s, 6H, CH_3)-minor, 1.69 (s, 6H, CH_3)-major, 1.49-1.58 (m, 4H, CH_2)-major, 1.32-1.42 (m, 4H, CH_2)-minor, 0.88 (t, *J* = 7.6 Hz, 6H, CH_3)-major, 0.82 (t, *J* = 7.6 Hz, 6H, CH_3)-minor. ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 162.58 (C=N), 161.94 (C=N), 161.34 (C=N), 40.76 (CH$_2$), 33.72 (CH$_2$), 19.86 (CH$_2$), 19.83 (CH$_3$), 19.55 (CH$_3$), 16.60 (CH$_3$), 16.47 (CH$_3$), 14.19 (CH$_3$), 13.83 (CH$_3$). HRMS (ESI) m/z calcd for $C_{10}H_{20}N_2$ (M+H)$^+$: 169.1699, found: 169.1725.



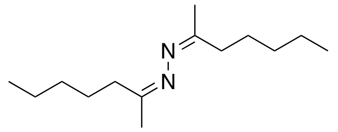
1,2-Di(pentan-3-ylidene)hydrazine (3j): Brown liquid**.** Yield: 83%. IR (DCM): 2960, 2870, 1659, 1452, 1411, 1195, 911, 731 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.36-2.45 (m, 8H,



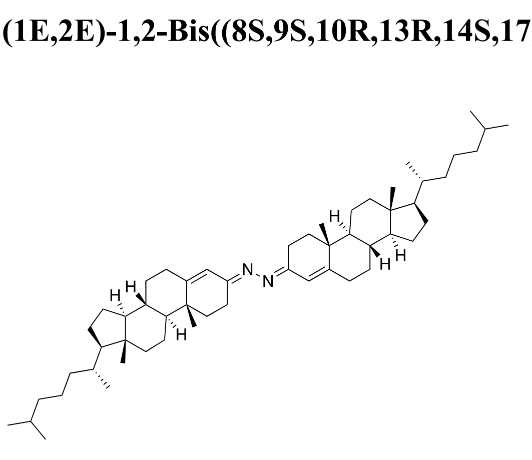
CH_2), 1.78-1.81 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$): δ 174.32 (*C*=N), 33.36 (*C*H$_2$), 29.39 (*C*H$_2$), 24.93 (*C*H$_3$), 24.77 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{10}H_{20}N_2$ $(M+H)^+$: 169.1699, found: 169.1721.



1,2-Di(heptan-4-ylidene)hydrazine (3k): Colorless liquid**.** Yield: 84%. IR (DCM): 2961, 2932, 2872, 1630, 1463, 1378, 1240, 1058, 909, 730 cm^{-1}. ^1H NMR (400 MHz, CDCl$_3$): δ 2.14-2.19 (m, 8H, CH_2), 1.49-1.59 (m, 4H, CH_2), 1.32-1.41 (m, 4H, CH_2), 0.87-0.90 (t, *J* = 7.6 Hz, 6H, CH_3) 0.81-0.85 (t, *J* = 7.6 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$): δ 165.10 (*C*=N), 38.77 (*C*H$_2$), 32.88 (*C*H$_2$), 19.98 (*C*H$_2$), 19.54 (*C*H$_2$), 14.58 (*C*H$_3$), 14.17 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{14}H_{28}N_2$ $(M+H)^+$: 225.2325, found: 225.2332.



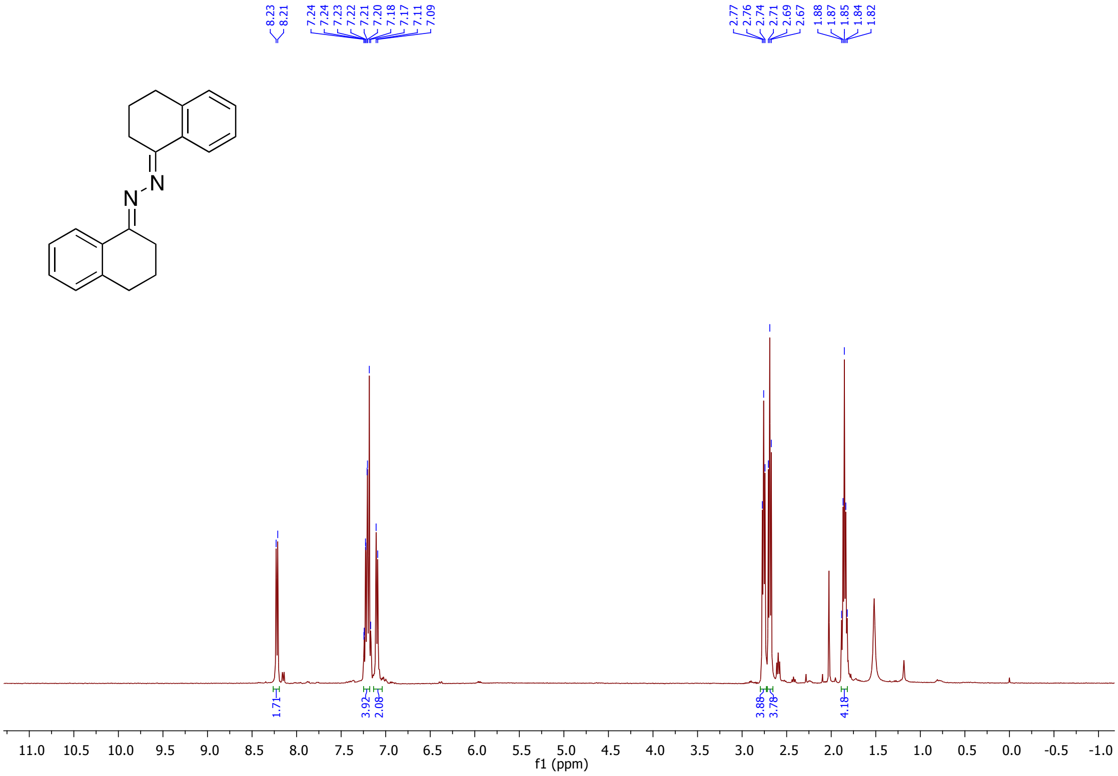
1,2-Di(heptan-2-ylidene)hydrazine (3l): Colorless liquid. Yield: 90%. ^1H NMR analysis of the crude reaction mixture showed the *E*/*Z* isomer ratio of 79:21 as determined by comparison of the following signals: δ 1.47-1.53 (m, 12H, CH_2)-minor, 1.18-1.35 (m, 12H, CH_2)-major. IR (DCM): 2956, 2927, 2859, 1640, 1459, 1361, 1260, 1099, 1019, 805, 730 cm^{-1}. ^1H NMR (400 MHz, CDCl$_3$): δ 2.27-2.35 (m, 4H, CH_2)-minor, 2.18-2.22 (m, 4H, CH_2)-major, 1.92 (s, 6H, CH_3)-minor, 1.70 (s, 6H, CH_3)-major, 1.47-1.53 (m, 12H, CH_2)-minor, 1.18-1.35 (m, 12H, CH_2)-major, 0.79-0.84 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$): δ 162.95 (*C*=N), 162.27 (*C*=N), 161.70 (*C*=N), 38.87 (*C*H$_2$), 32.00 (*C*H$_2$), 31.85 (*C*H$_2$), 31.65 (*C*H$_2$), 29.83 (*C*H$_2$), 26.35 (*C*H$_2$), 26.31 (*C*H$_2$), 25.90 (*C*H$_2$), 23.03 (*C*H$_2$), 22.61 (*C*H$_2$), 22.50 (*C*H$_2$), 16.76 (*C*H$_2$), 16.61 (*C*H$_2$), 14.13 (*C*H_3), 14.05 (*C*H_3). HRMS (ESI) m/z calcd for $C_{14}H_{28}N_2$ $(M+H)^+$: 225.2325, found: 225.2336.



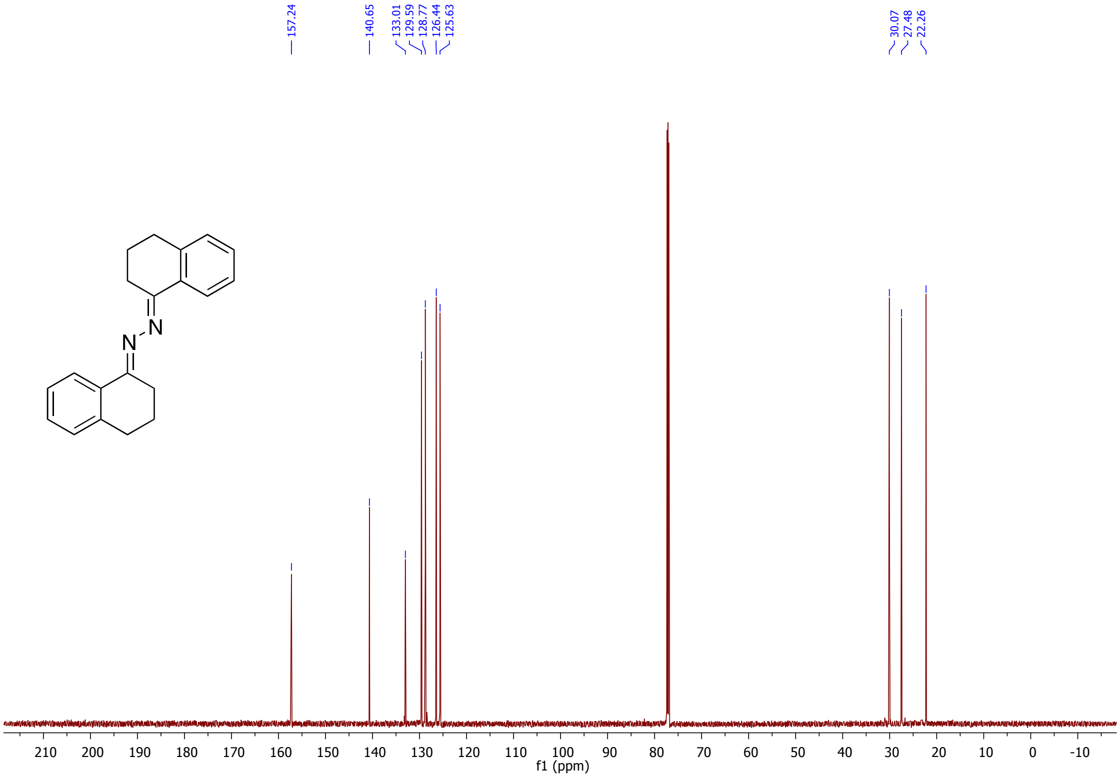
(1E,2E)-1,2-Bis((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl) 1,2,6,7,8,9,10,11,12,13,14,15,16,17tetradecahydro3Hcyclopenta[a]phenanthren-3-ylidene)hydrazine (3m): Yellow solid**.** Yield: 45%. Melting Point: 220-222 °C; lit. 232-234 °C.[14] IR (DCM): 2929, 2867, 1633, 1581, 1465, 1442, 1373, 1332, 1241, 1196, 1130, 1111, 1086, 1029, 955, 734, 677 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (s, 2H, C*H*), 3.04-3.10 (m, 2H), 1.28-2.35 (m, 38H), 0.87-1.15 (m, 40H), 0.67 (s, 6H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 161.67 (*C*=N), 158.65 (olefinic-*C*), 121.95 (olefinic-*C*H), 56.31, 56.20, 53.97, 42.54, 39.96, 39.65, 38.33, 36.28, 35.96, 35.91, 35.53, 32.88, 32.47, 28.34, 28.15, 24.39, 23.96, 22.70, 22.06, 21.48, 18.80, 17.87, 12.10. HRMS (ESI) m/z calcd for $C_{54}H_{88}N_2$ $(M+H)^+$: 765.7020, found: 765.7005.

^{1}H and ^{13}C NMR Spectra of Ketazine Products:

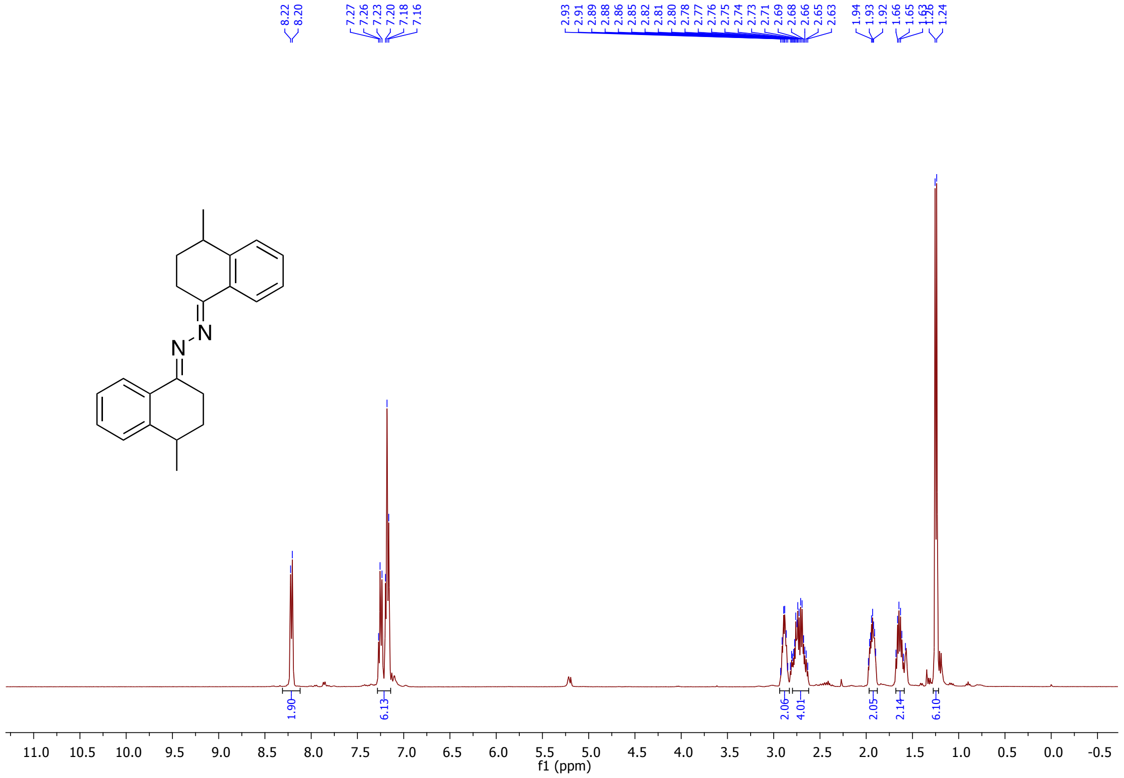
^{1}H NMR spectrum of 1,2-bis((*E*)-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2a):**



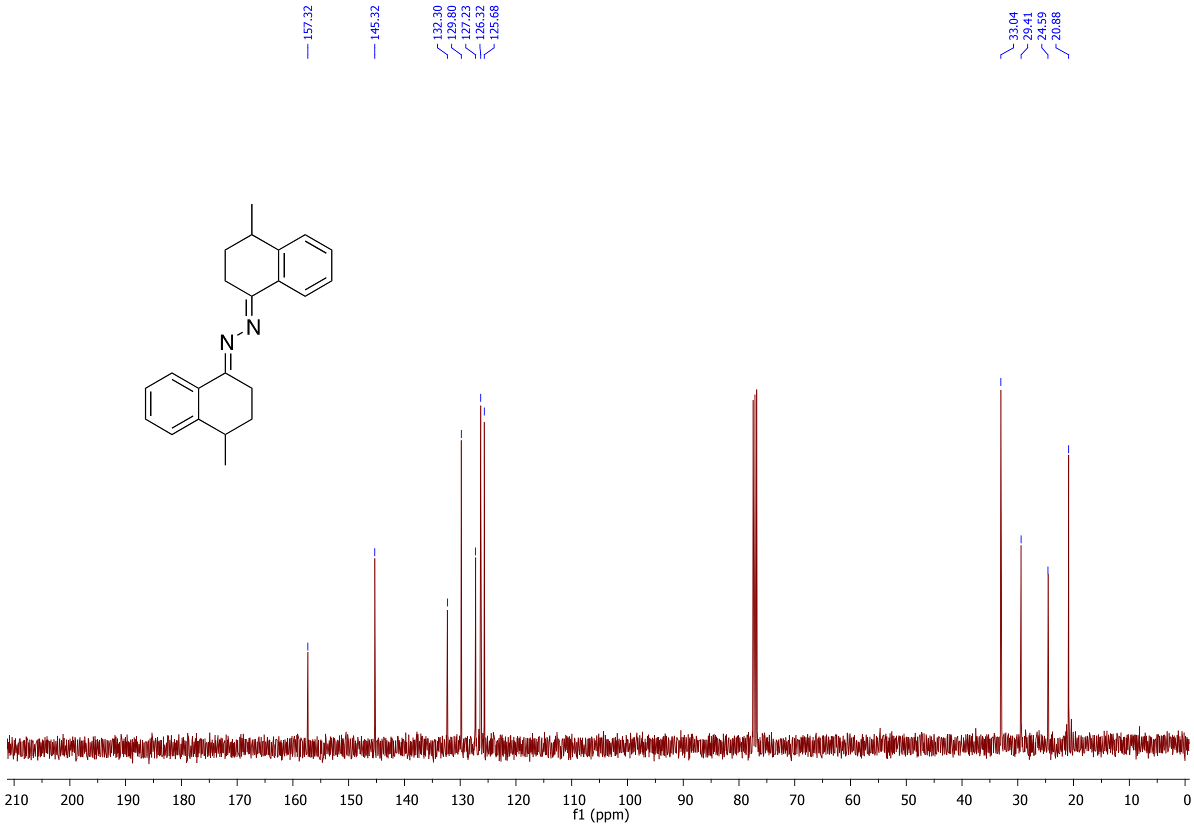
^{13}C NMR spectrum of 1,2-bis((*E*)-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2a):**



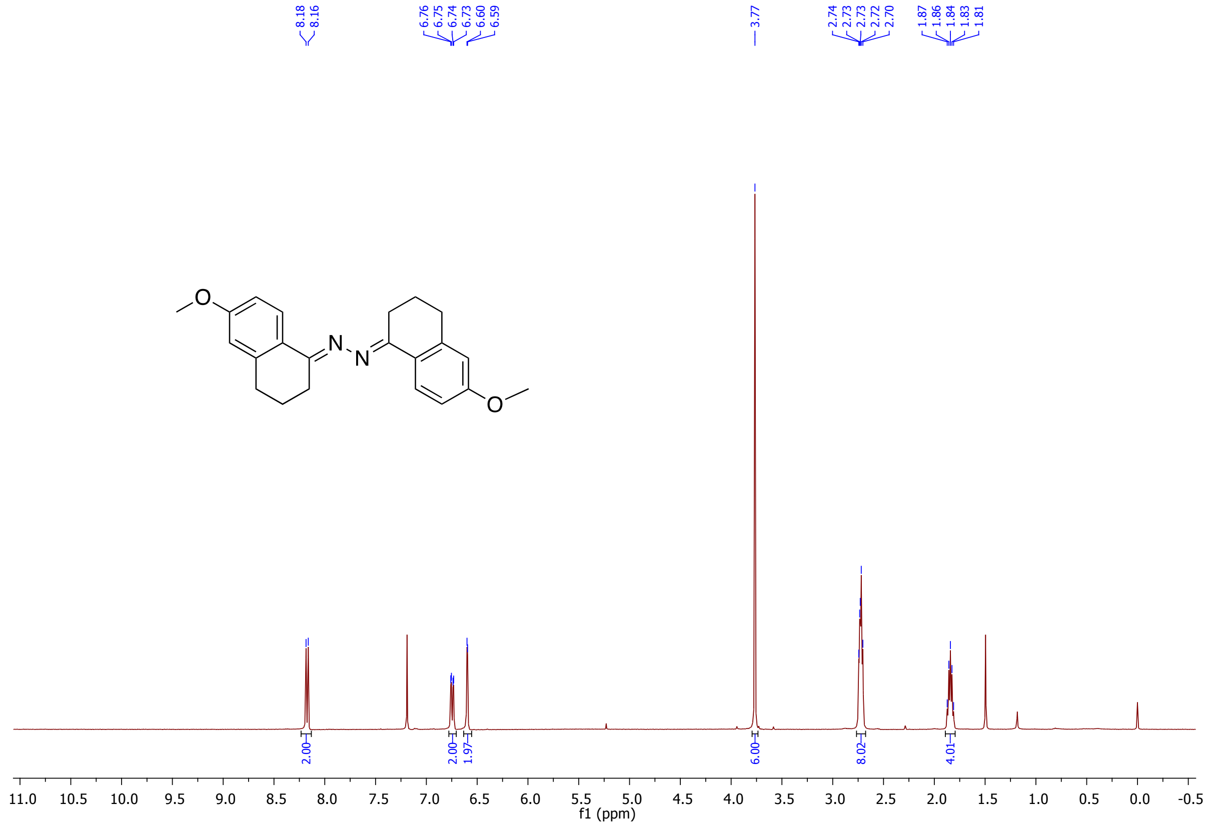
^{1}H NMR spectrum of 1,2-bis((*E*)-4-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2b):**



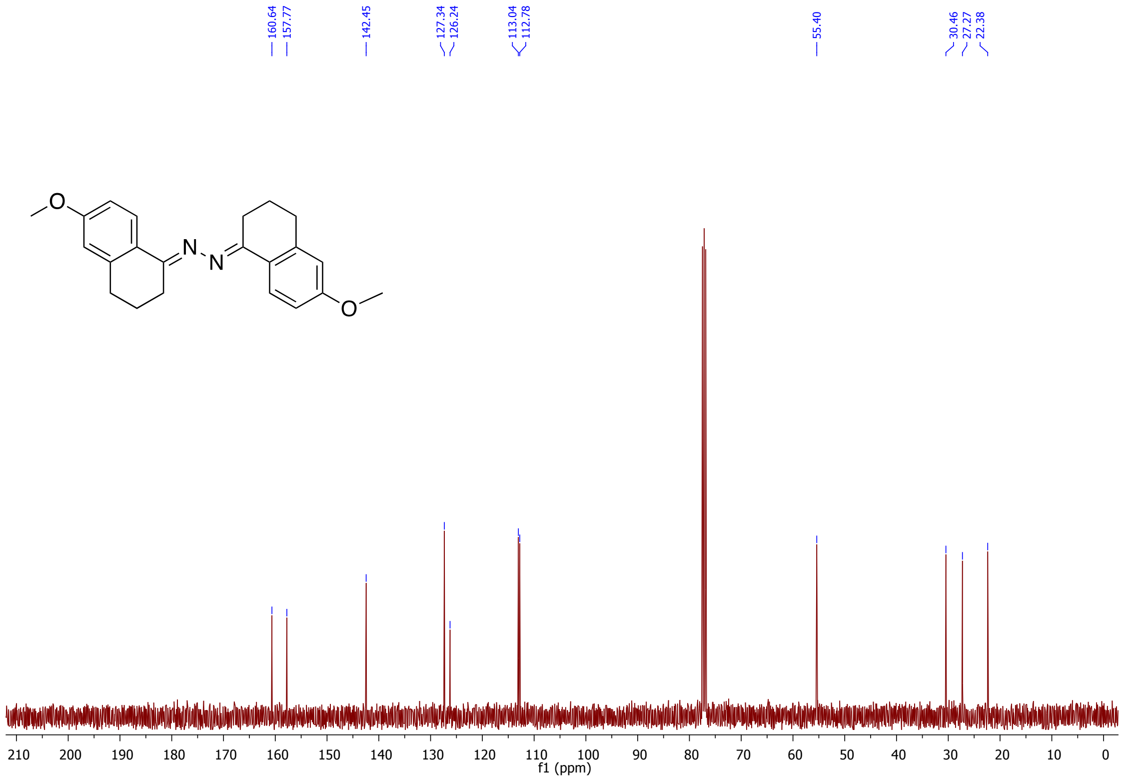
^{13}C NMR spectrum of 1,2-bis((*E*)-4-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2b):**



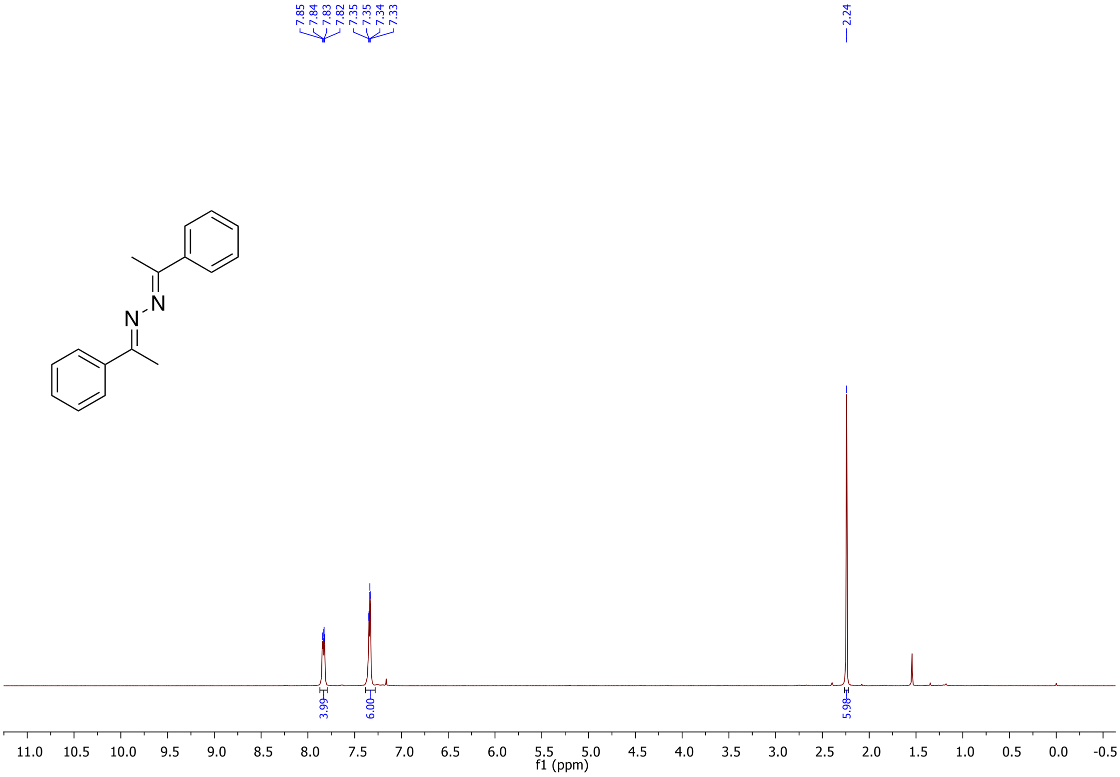
^{1}H NMR spectrum of 1,2-bis((*E*)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2c):**



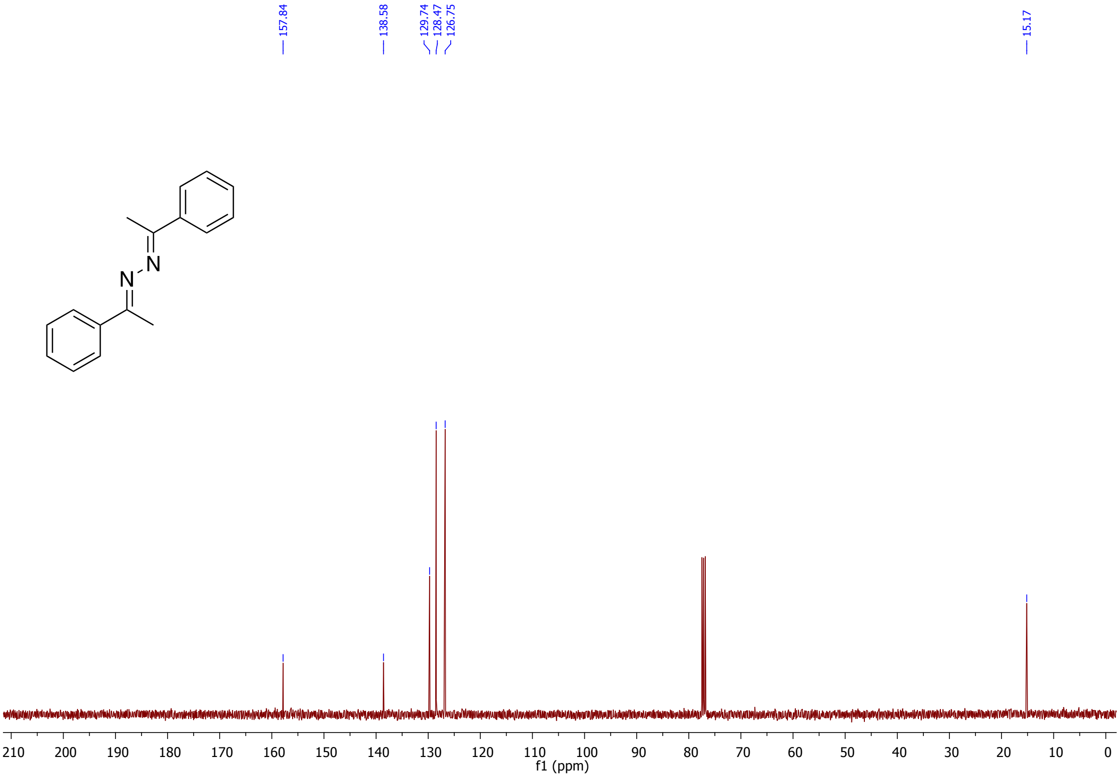
^{13}C NMR spectrum of 1,2-bis((*E*)-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine **(2c):**



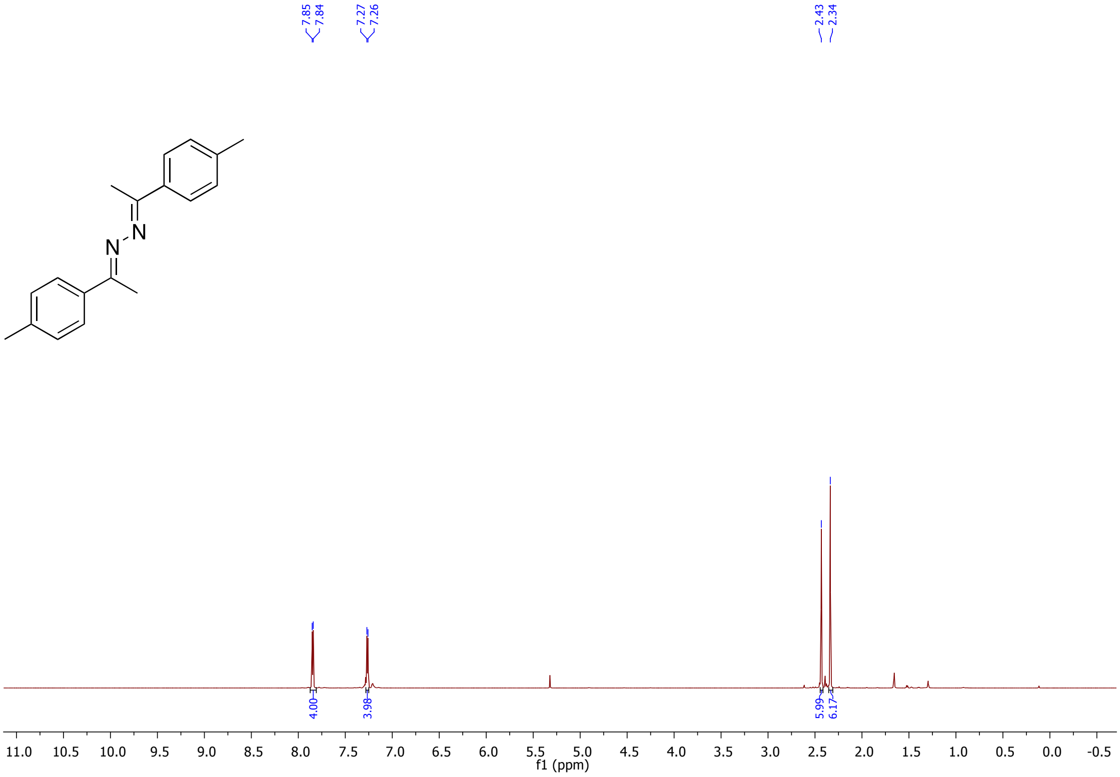
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine **(2d):**



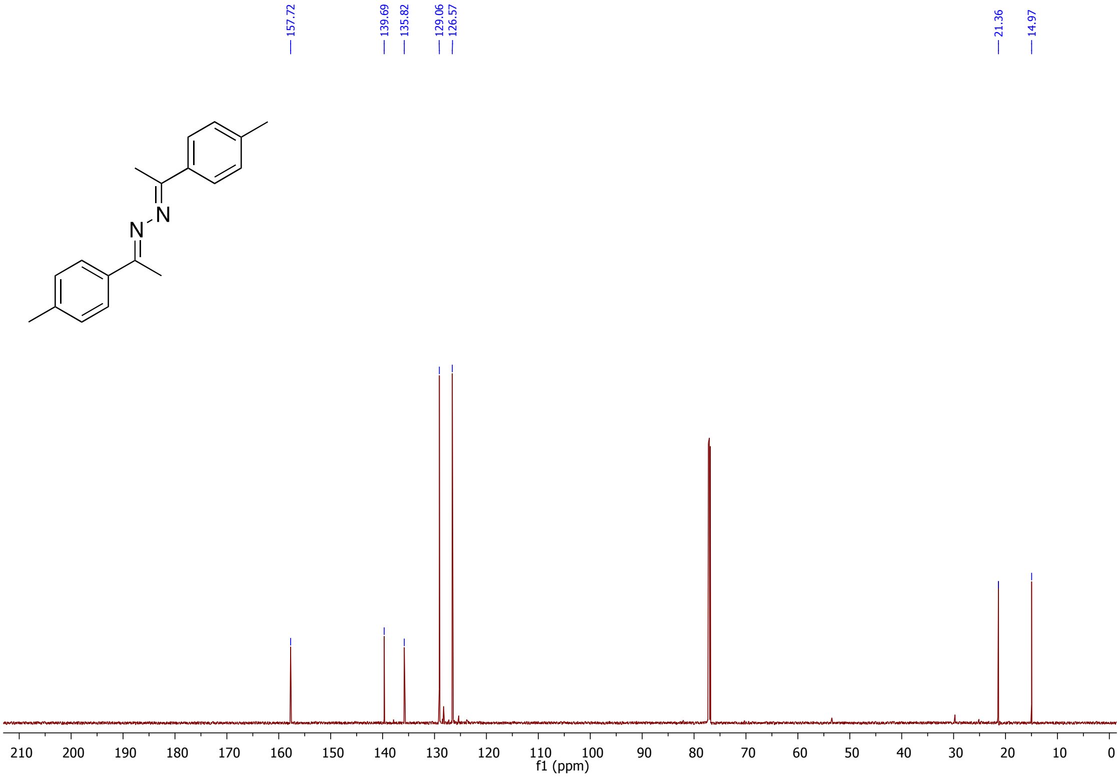
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine **(2d):**



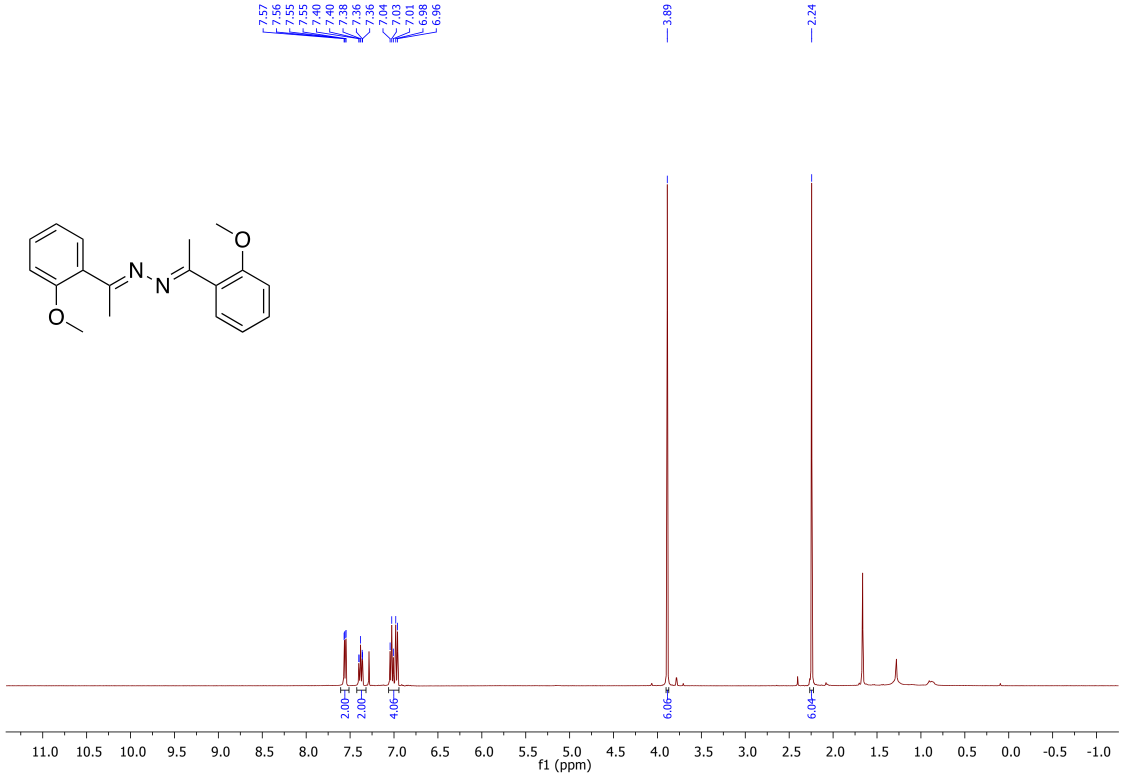
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(p-tolyl)ethylidene)hydrazine **(2e):**



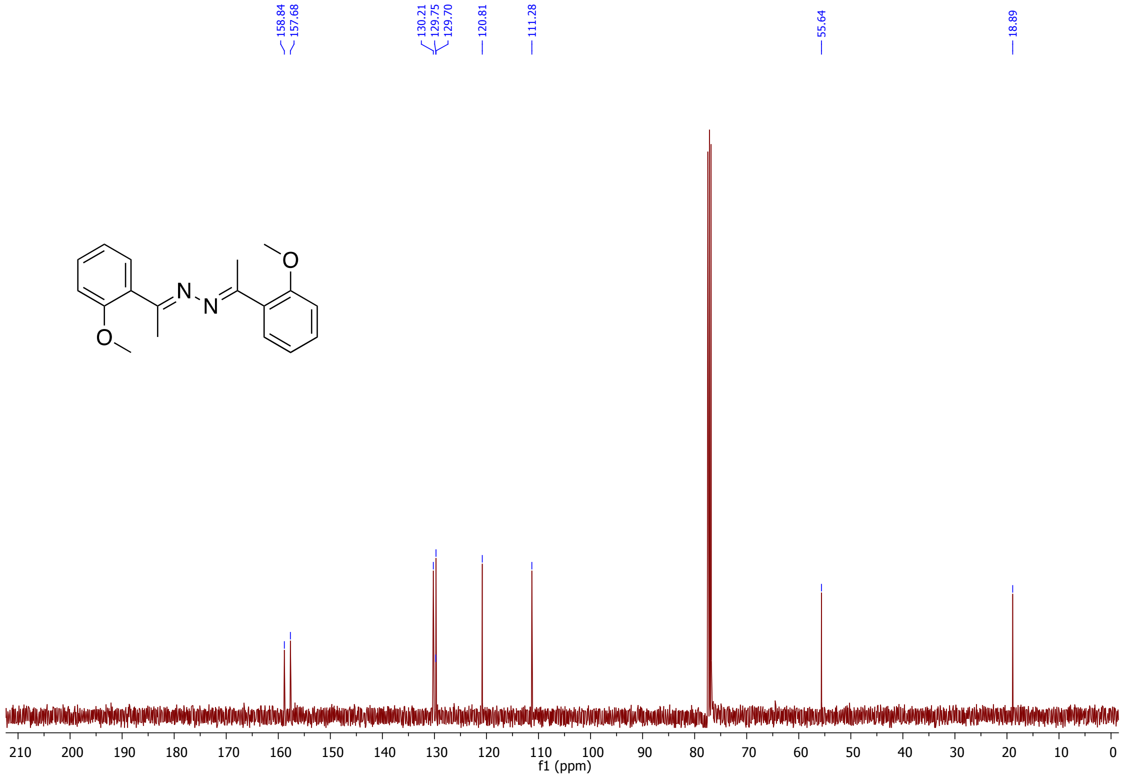
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(p-tolyl)ethylidene)hydrazine **(2e):**



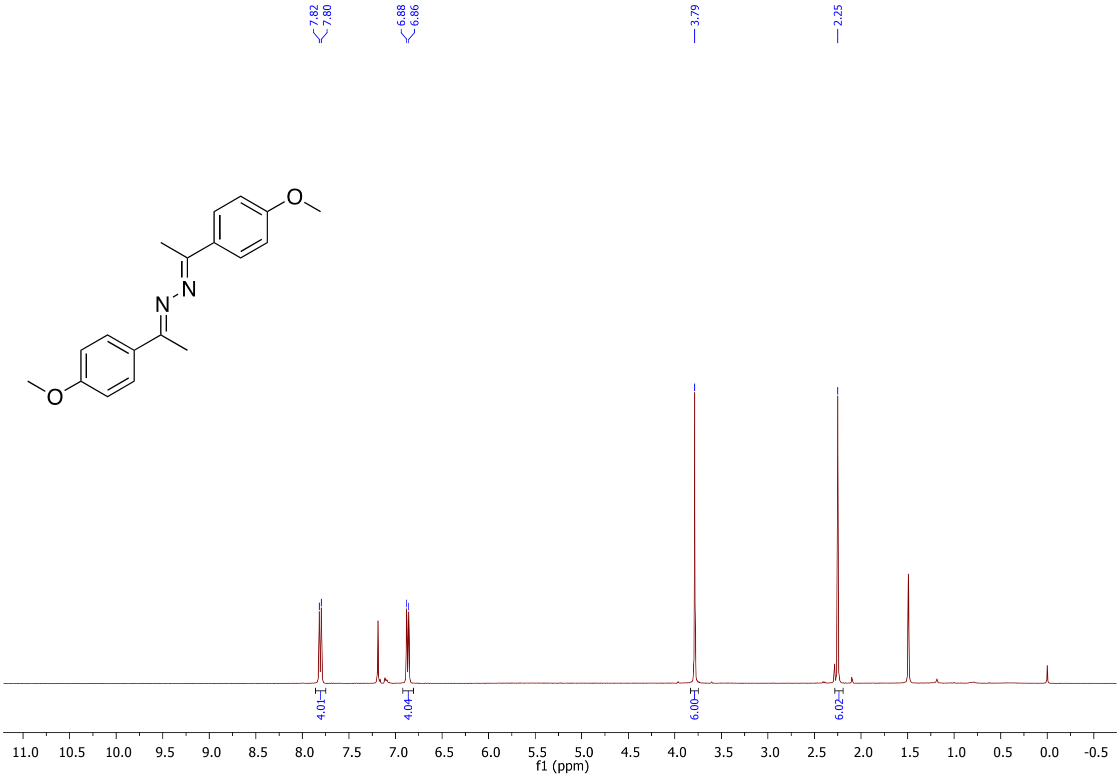
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(2-methoxyphenyl)ethylidene)hydrazine **(2f):**



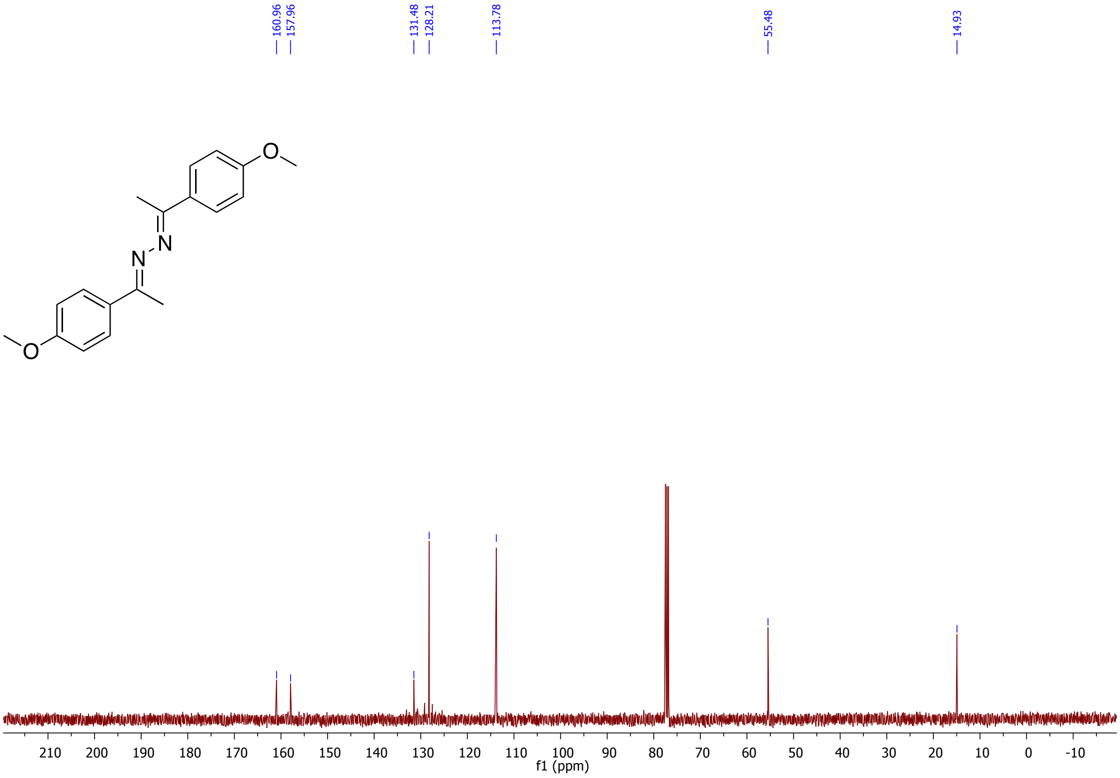
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(2-methoxyphenyl)ethylidene)hydrazine **(2f):**



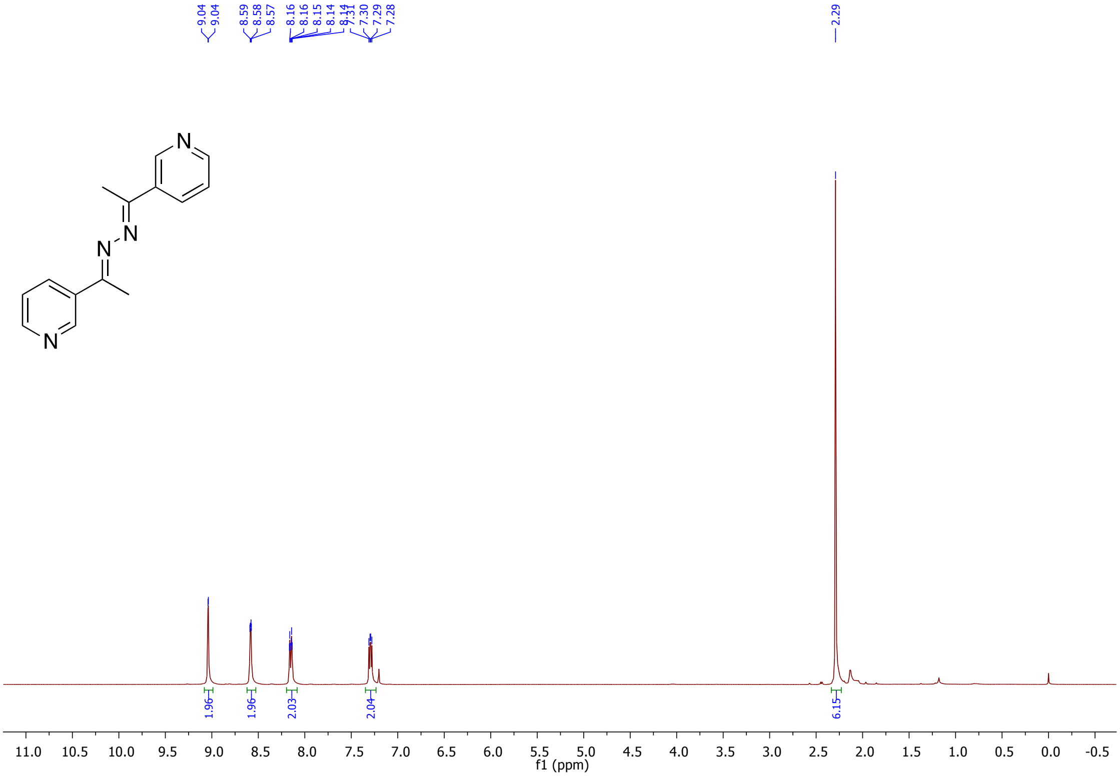
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine **(2g):**



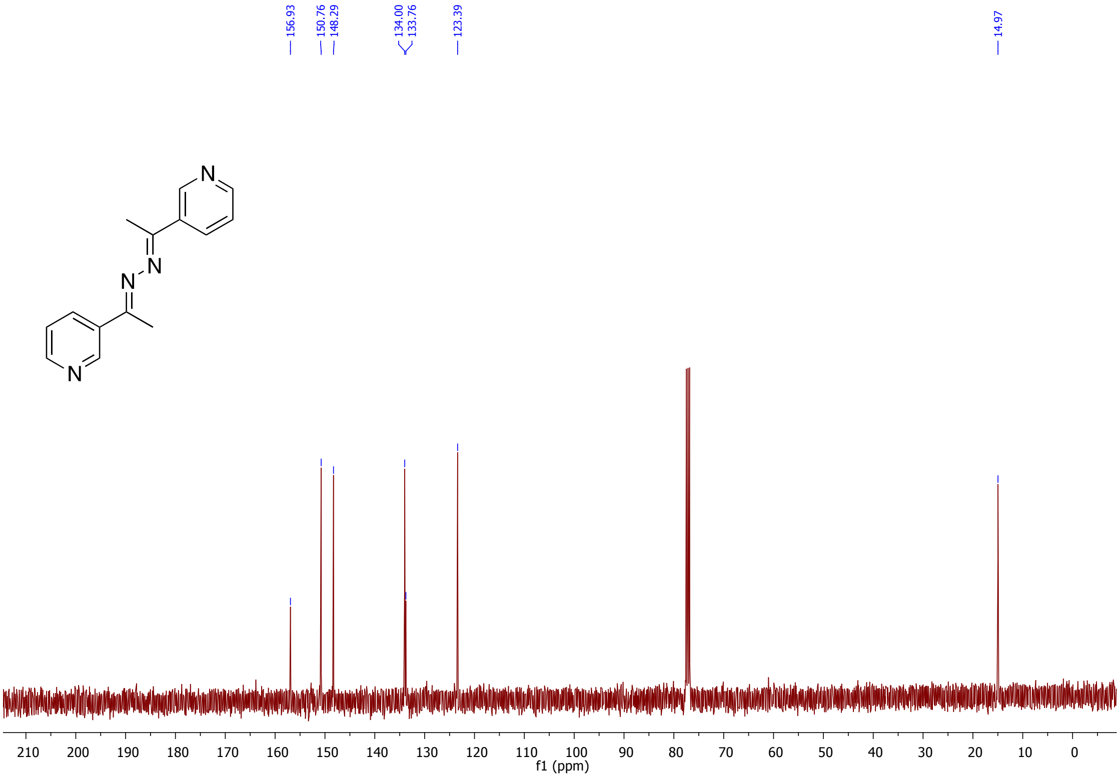
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine **(2g):**



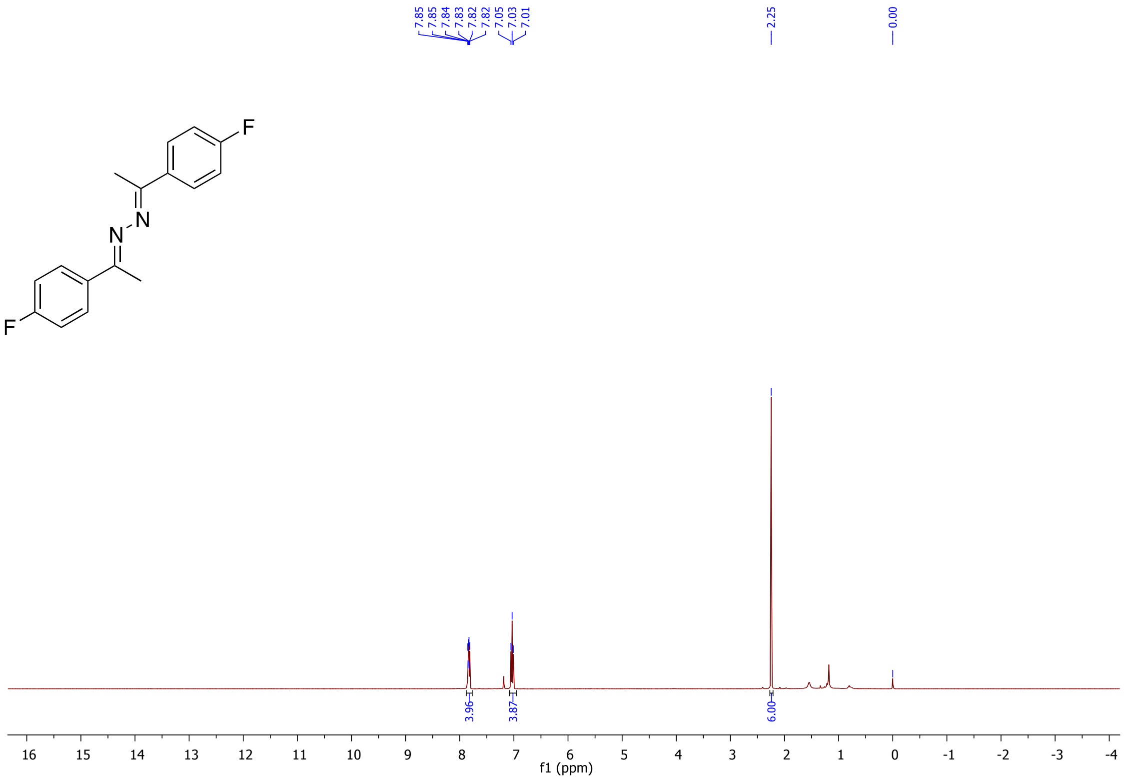
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine **(2h):**



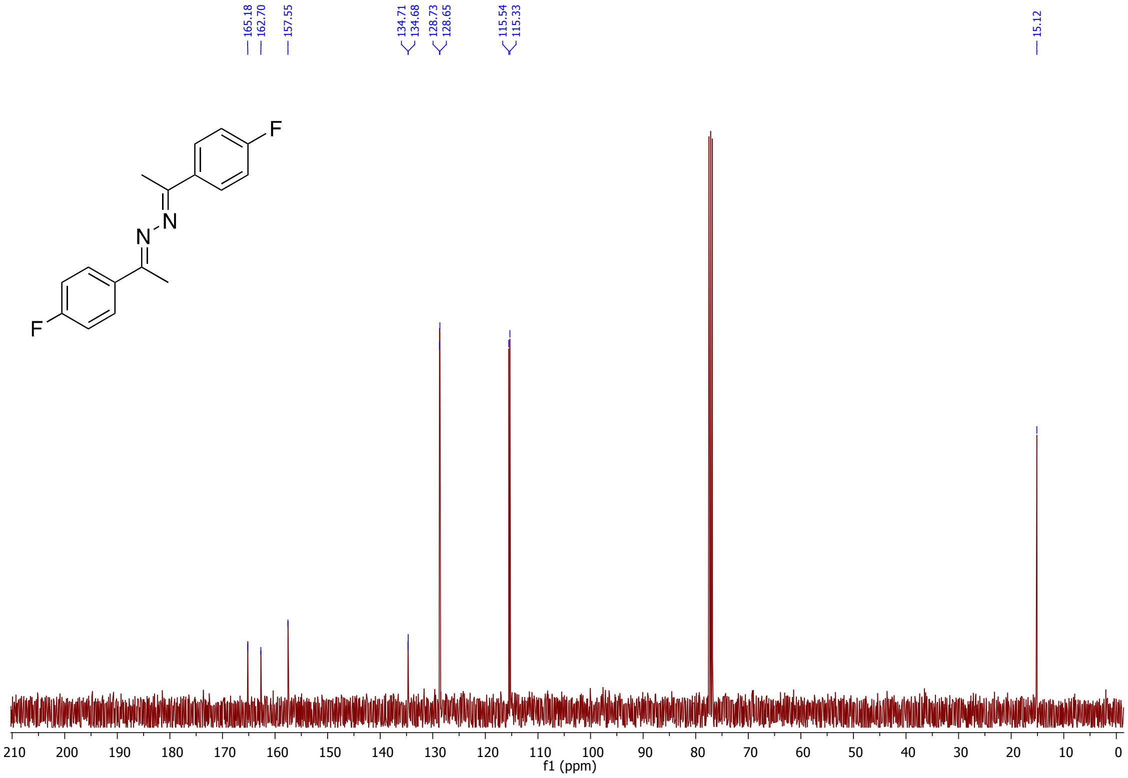
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine **(2h):**



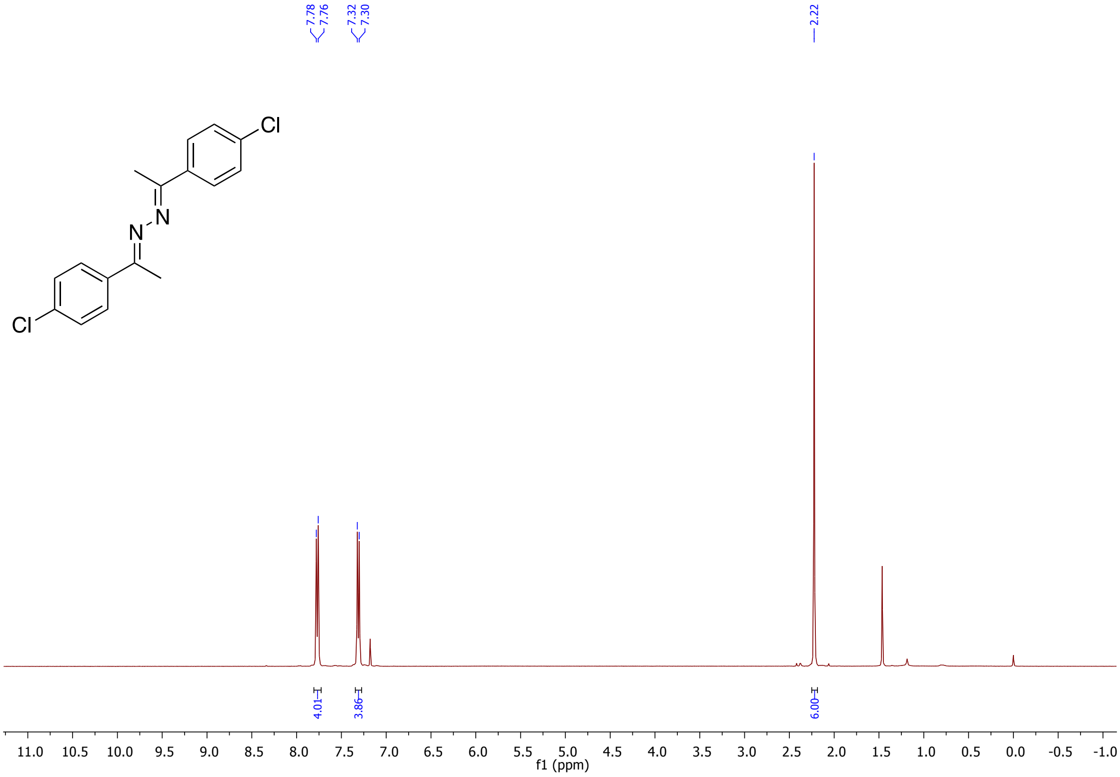
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-fluorophenyl)ethylidene)hydrazine **(2i):**



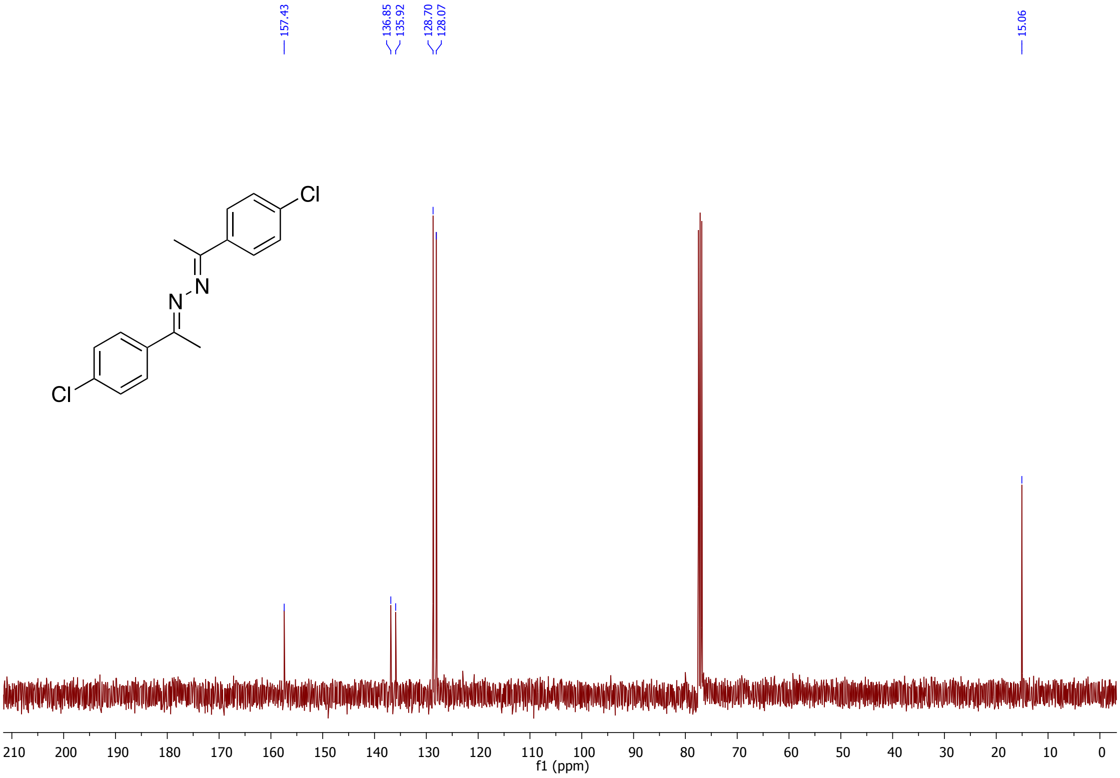
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-fluorophenyl)ethylidene)hydrazine **(2i):**



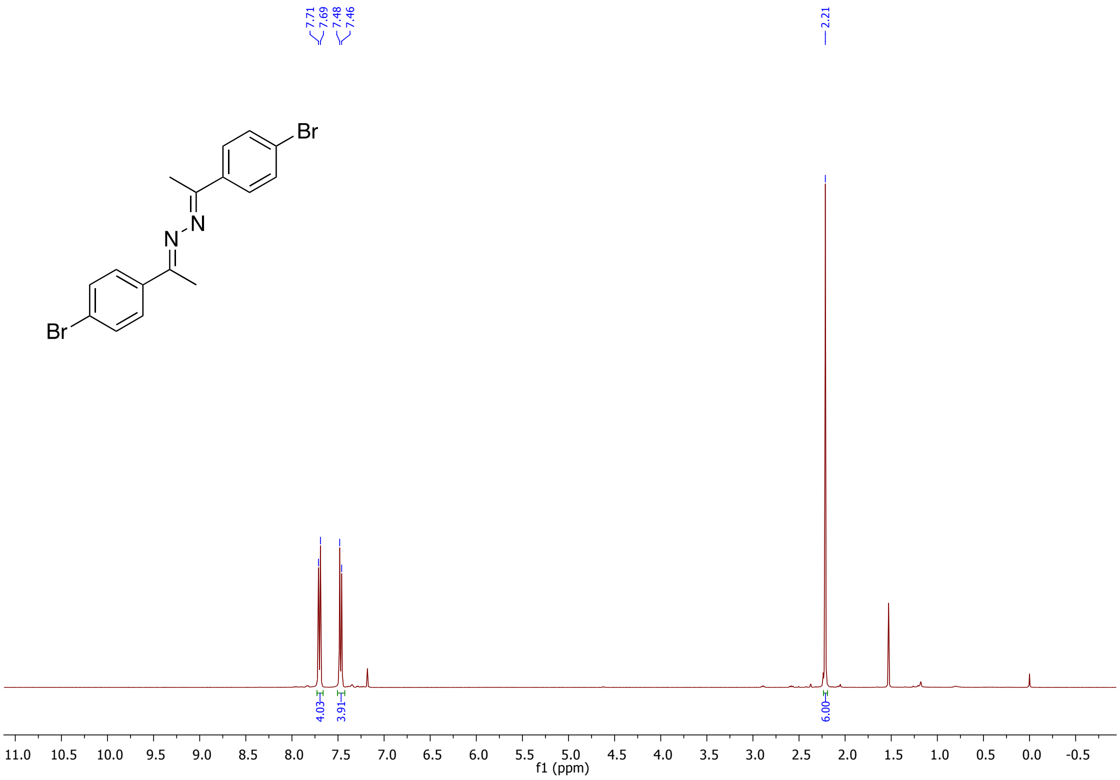
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-chlorophenyl)ethylidene)hydrazine **(2j):**



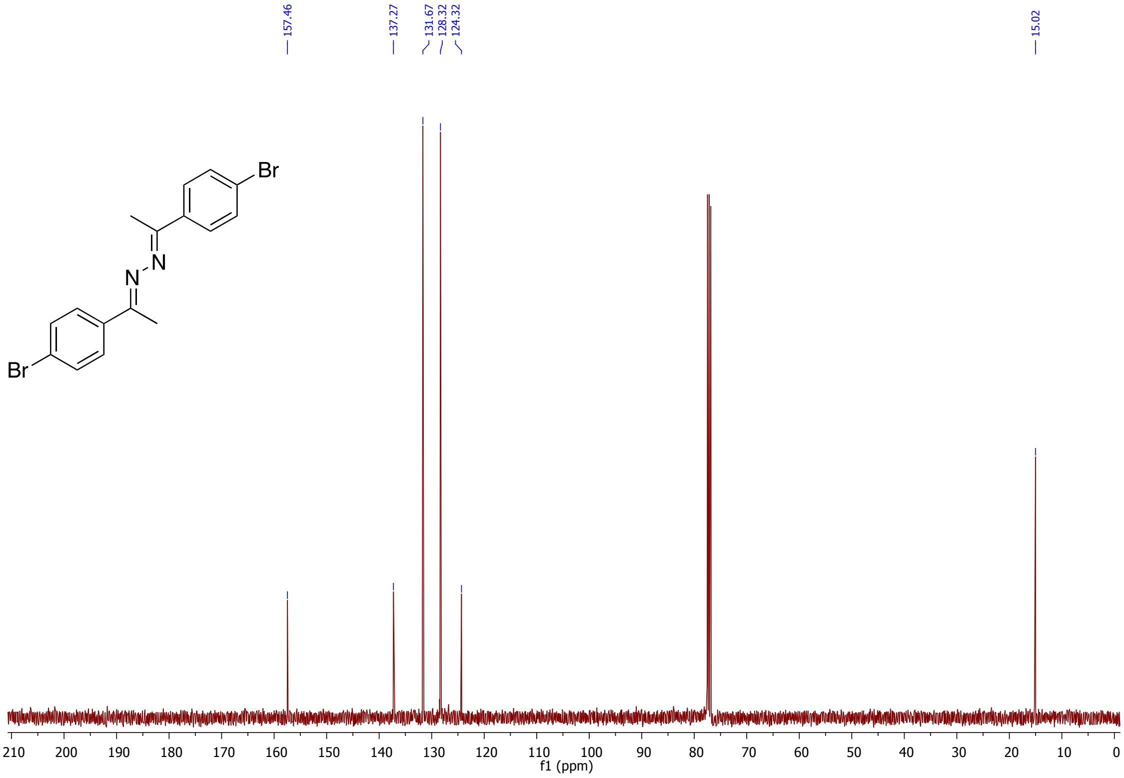
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-chlorophenyl)ethylidene)hydrazine **(2j):**



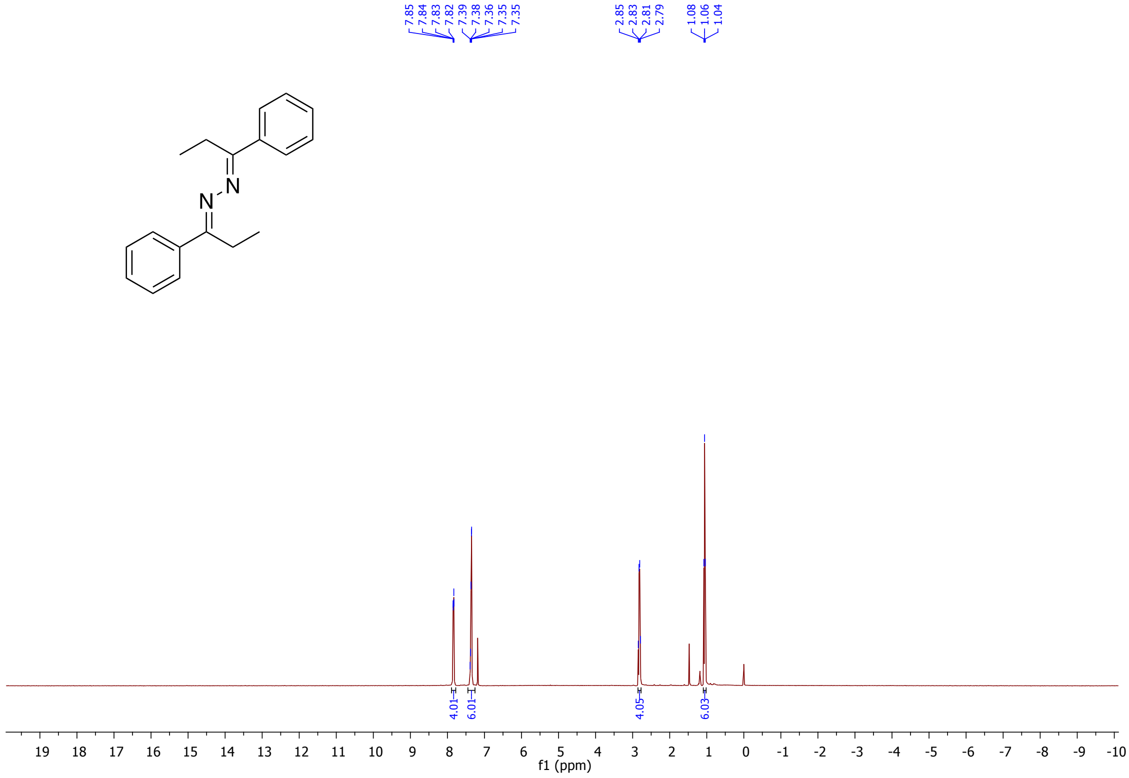
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine **(2k)**:



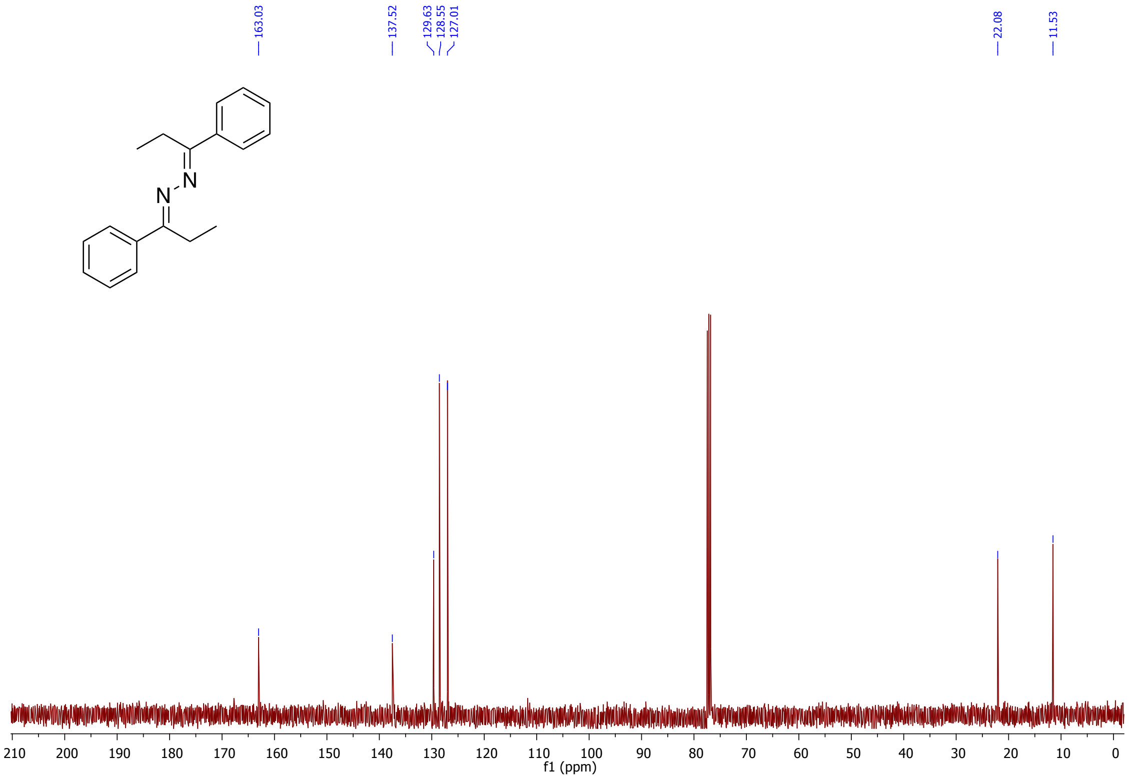
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine **(2k):**



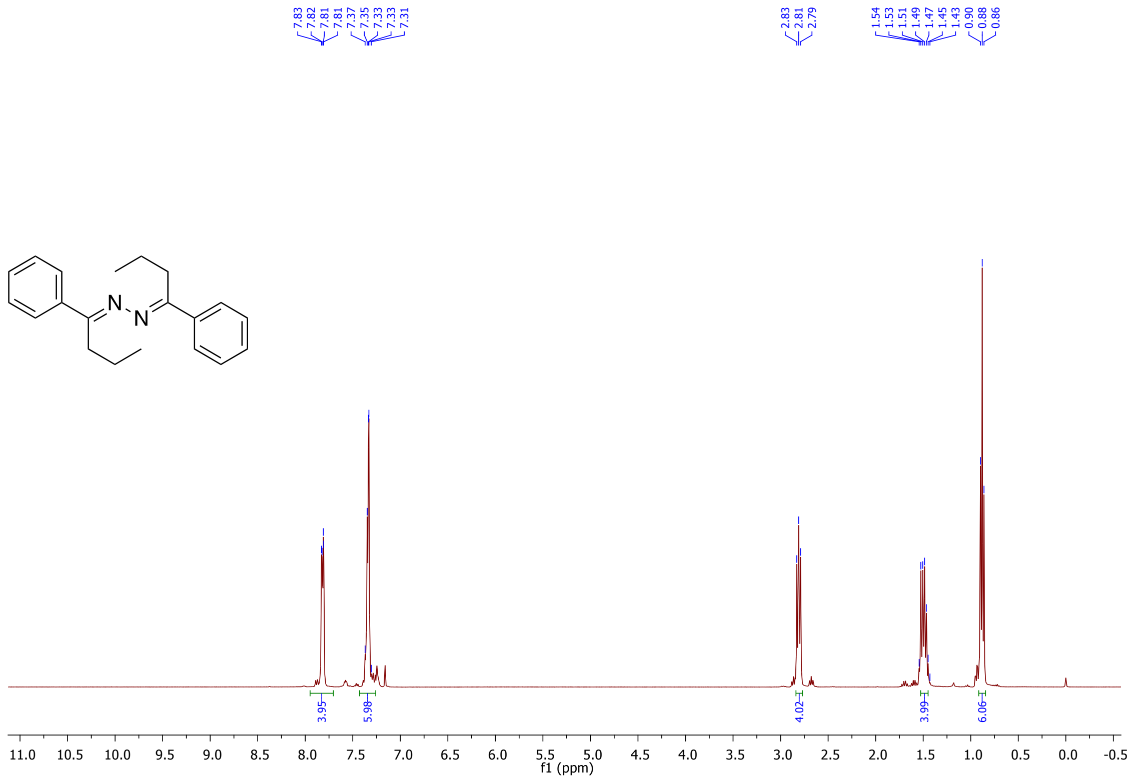
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylpropylidene)hydrazine **(2l):**



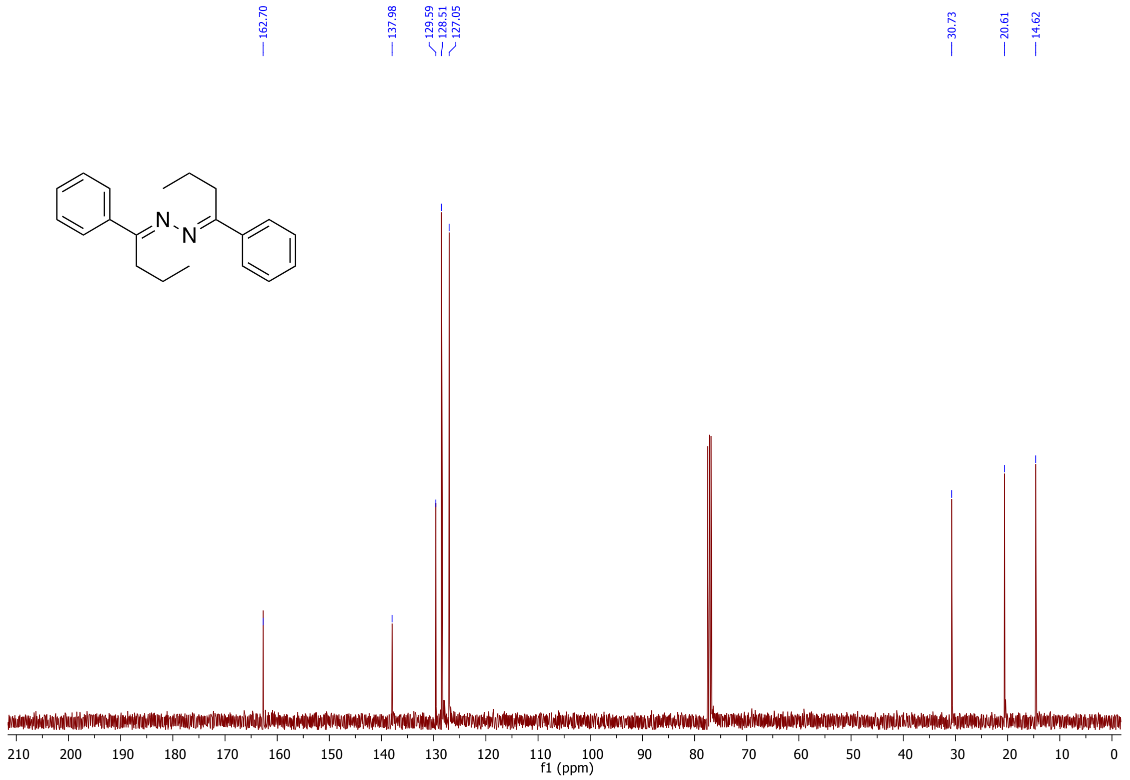
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylpropylidene)hydrazine **(2l):**



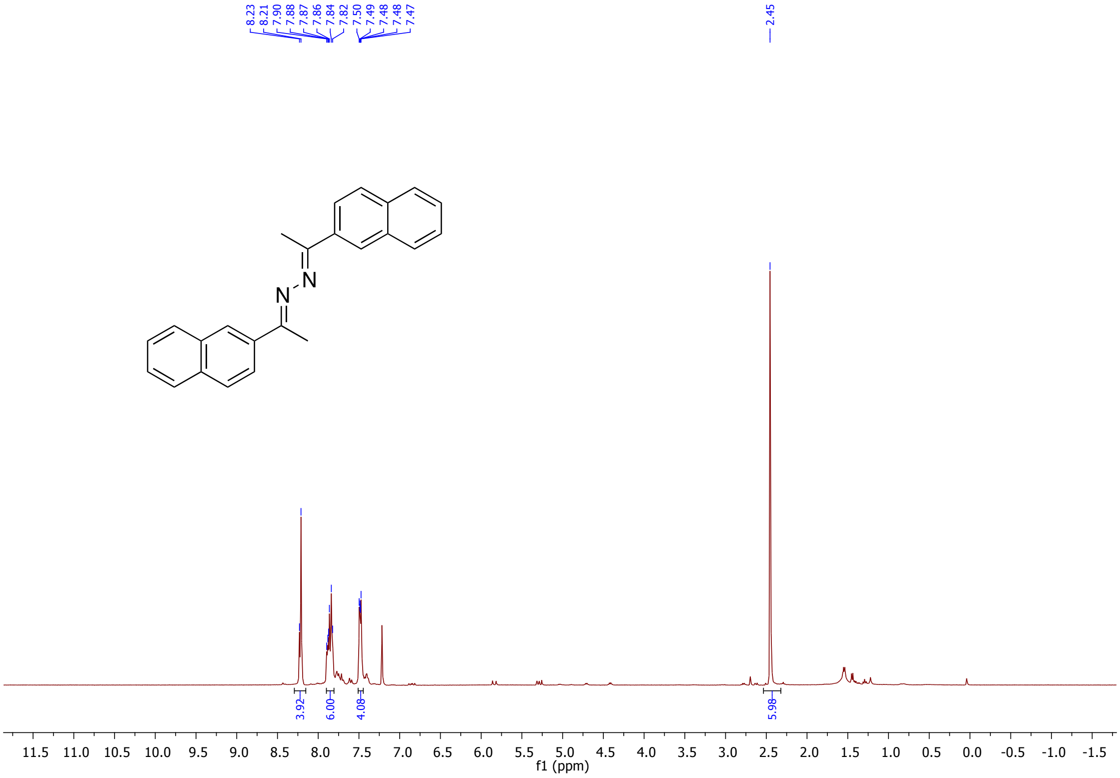
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylbutylidene)hydrazine **(2m):**



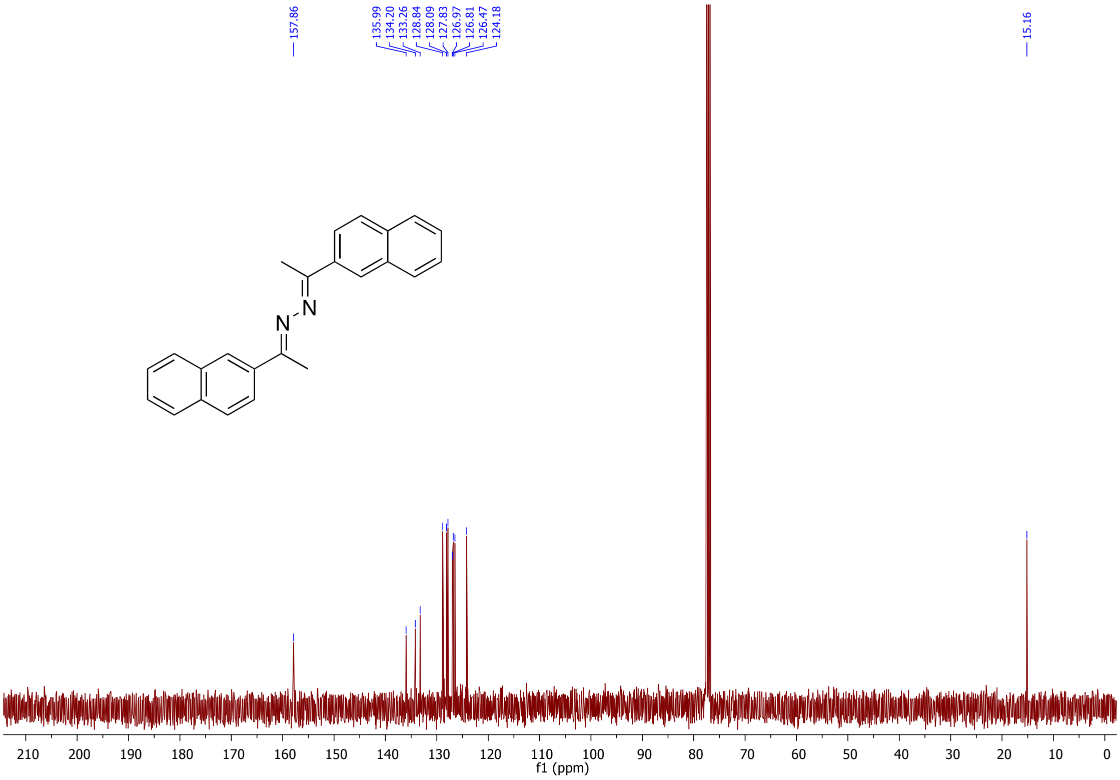
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-phenylbutylidene)hydrazine **(2m):**



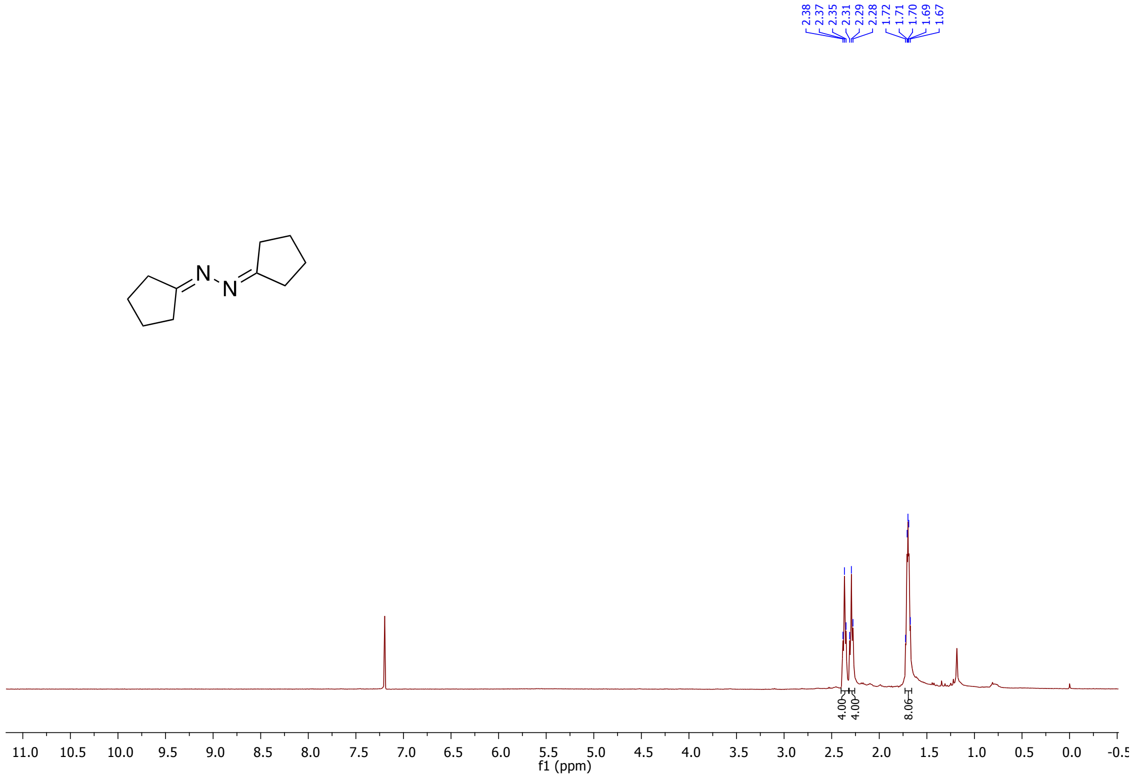
^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(naphthalen-2-yl)ethylidene)hydrazine **(2n):**



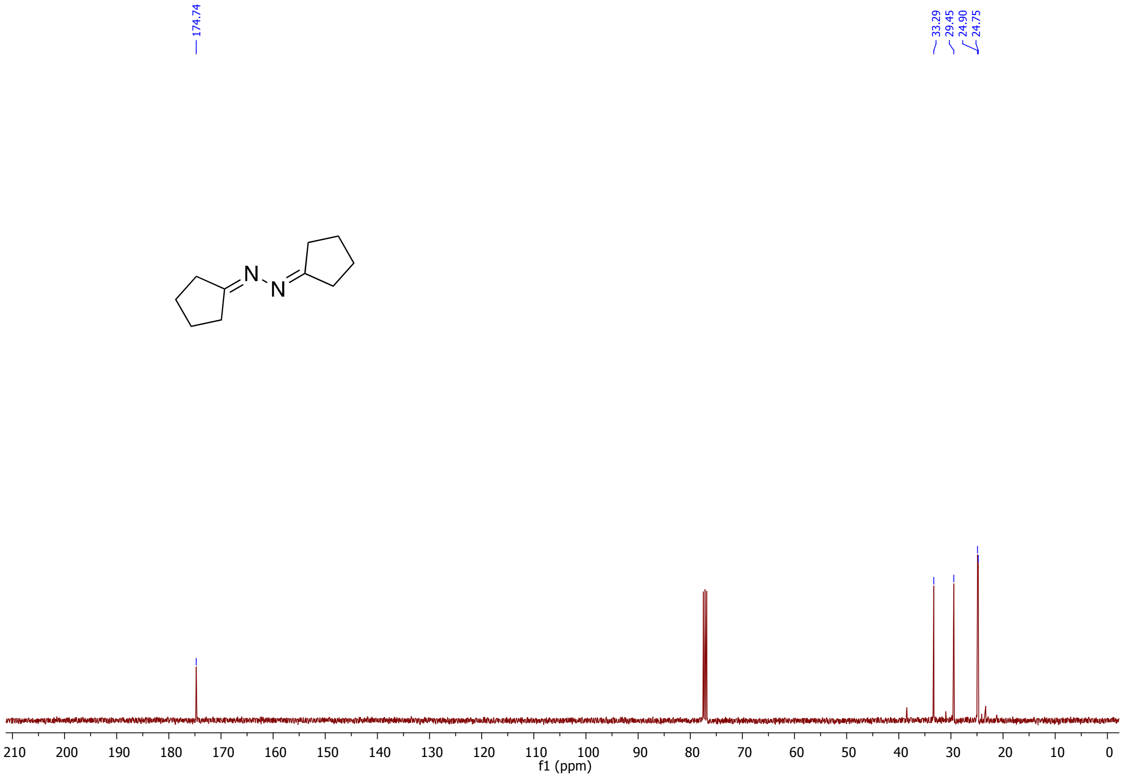
^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis(1-(naphthalen-2-yl)ethylidene)hydrazine **(2n):**



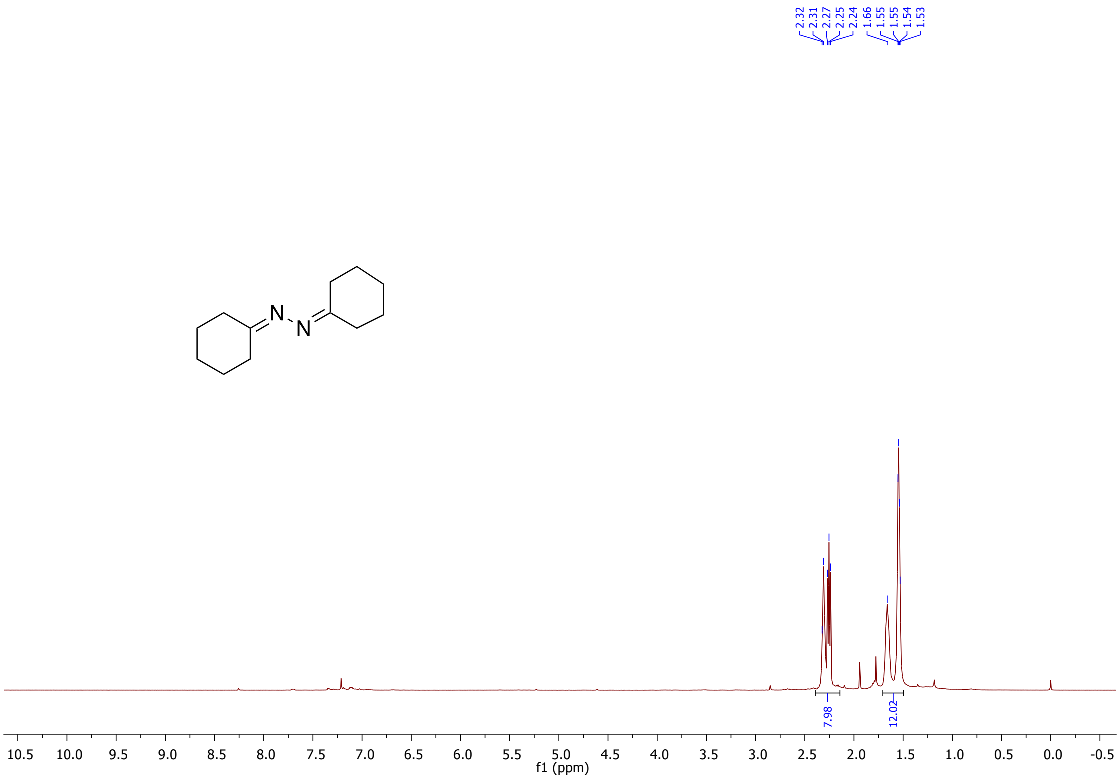
^{1}H NMR spectrum of 1,2-dicyclopentylidenehydrazine **(3a):**



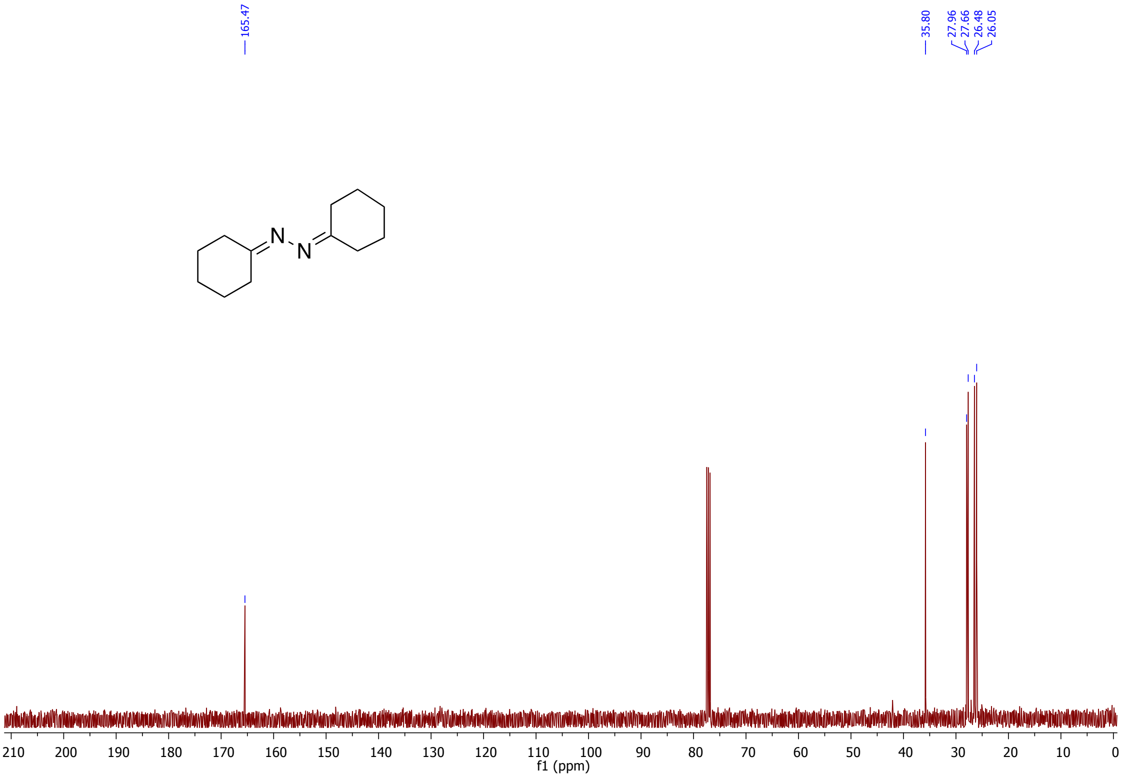
^{13}C NMR spectrum of 1,2-dicyclopentylidenehydrazine **(3a):**



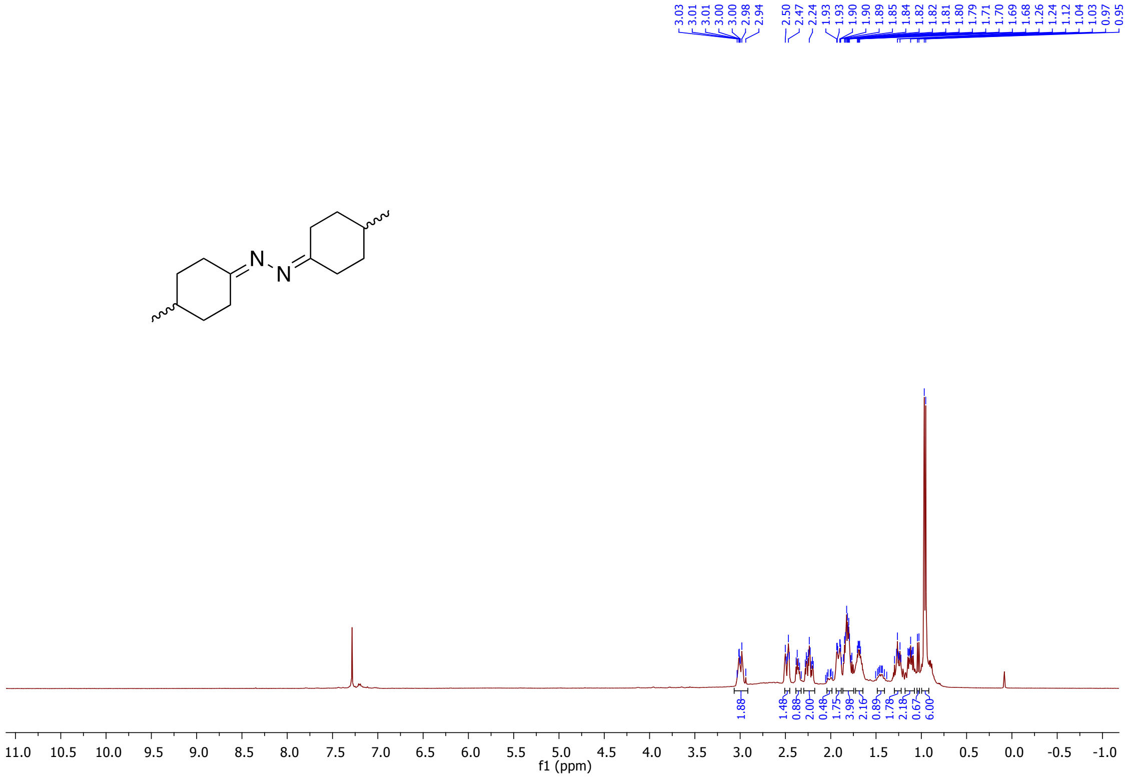
^{1}H NMR spectrum of 1,2-dicyclohexylidenehydrazine **(3b):**



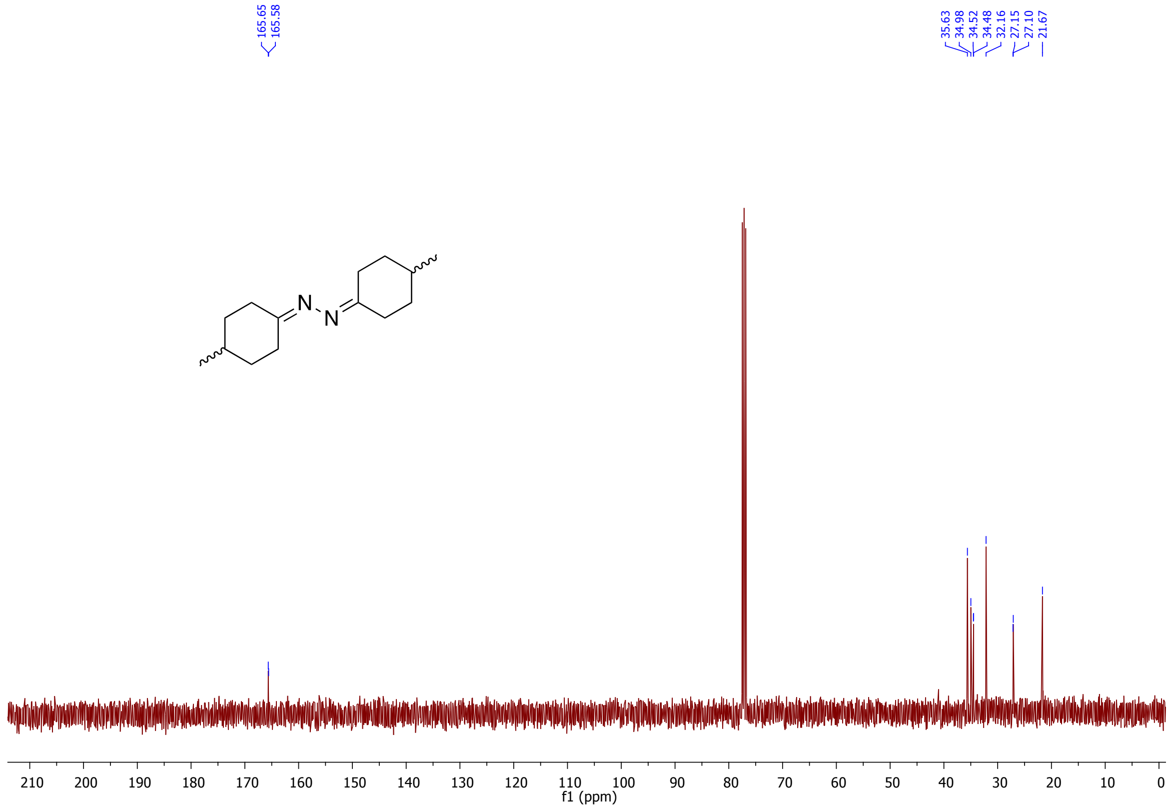
^{13}C NMR spectrum of 1,2-dicyclohexylidenehydrazine **(3b):**



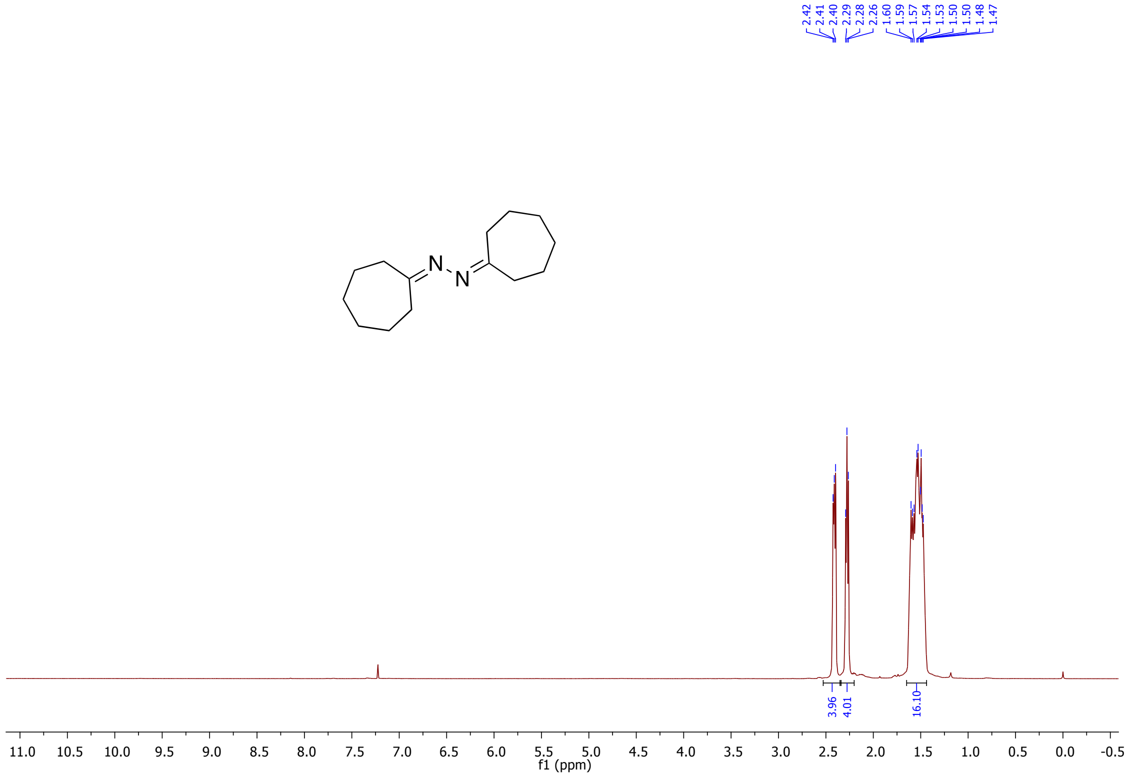
^{1}H NMR spectrum of 1,2-bis(4-methylcyclohexylidene)hydrazine (mixture of cis and trans) **(3c):**



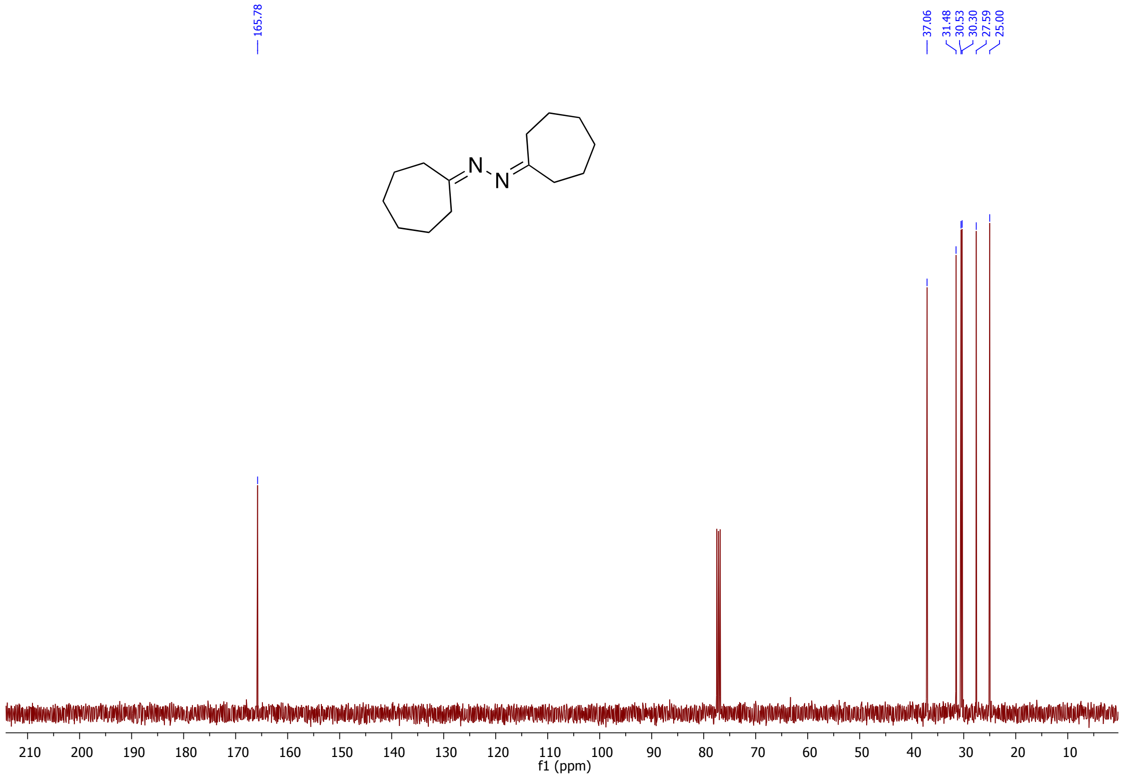
^{13}C NMR spectrum of 1,2-bis(4-methylcyclohexylidene)hydrazine (mixture of cis and trans) **(3c):**



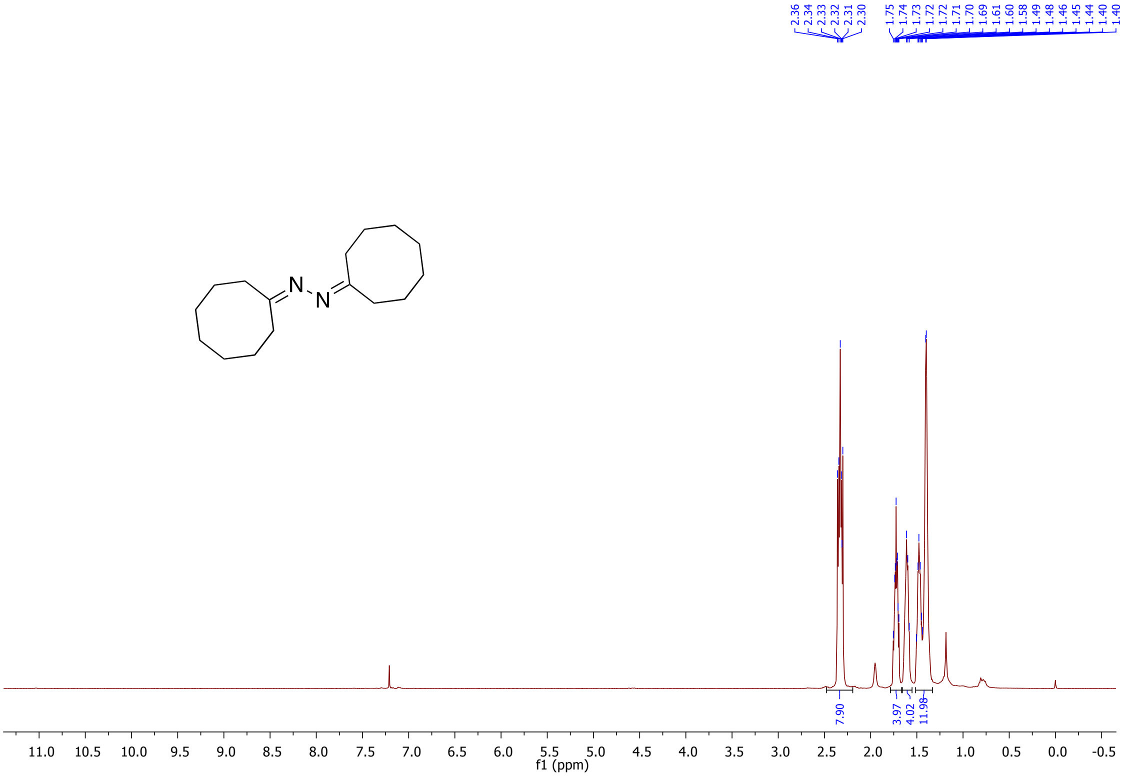
^{1}H NMR spectrum of 1,2-dicycloheptylidenehydrazine **(3d):**



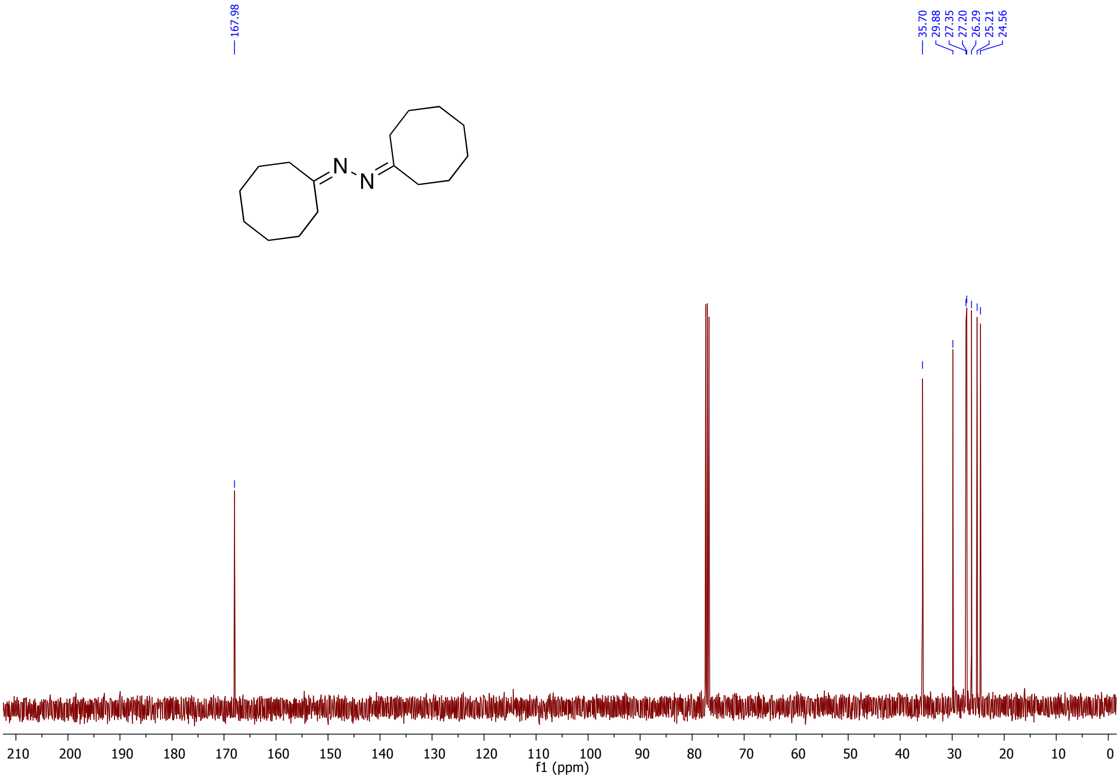
^{13}C NMR spectrum of 1,2-dicycloheptylidenehydrazine **(3d):**



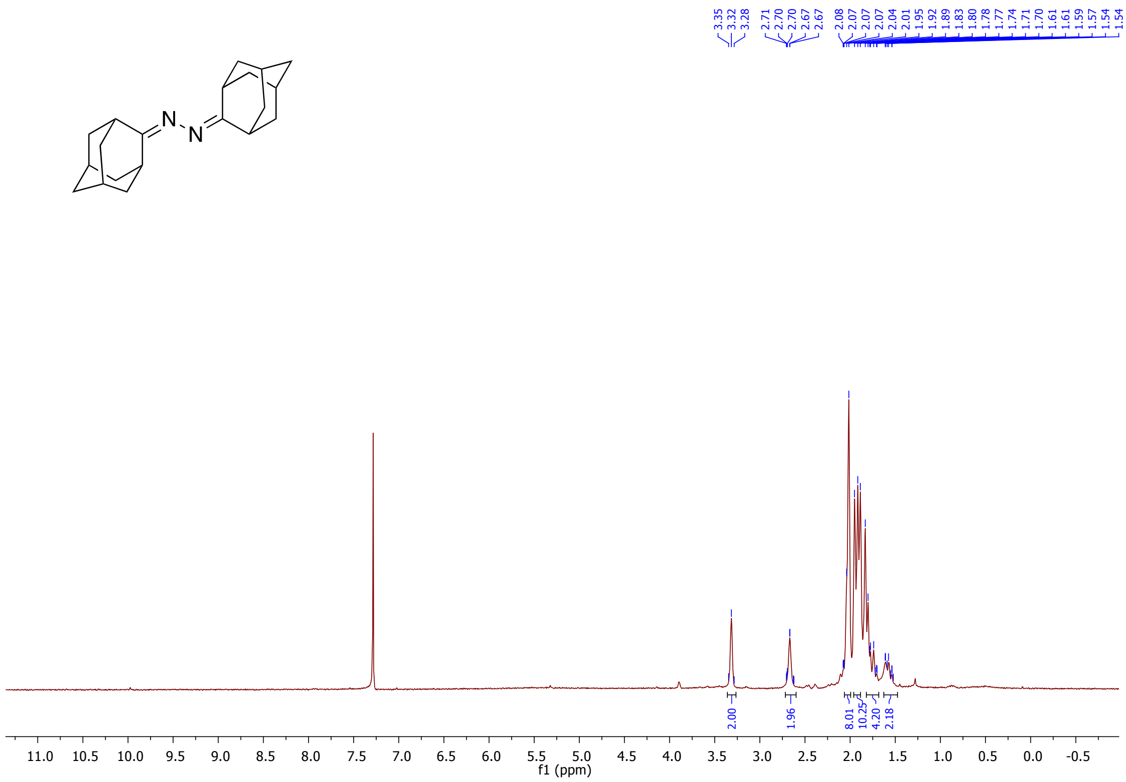
^{1}H NMR spectrum of 1,2-dicyclooctylidenehydrazine **(3e):**



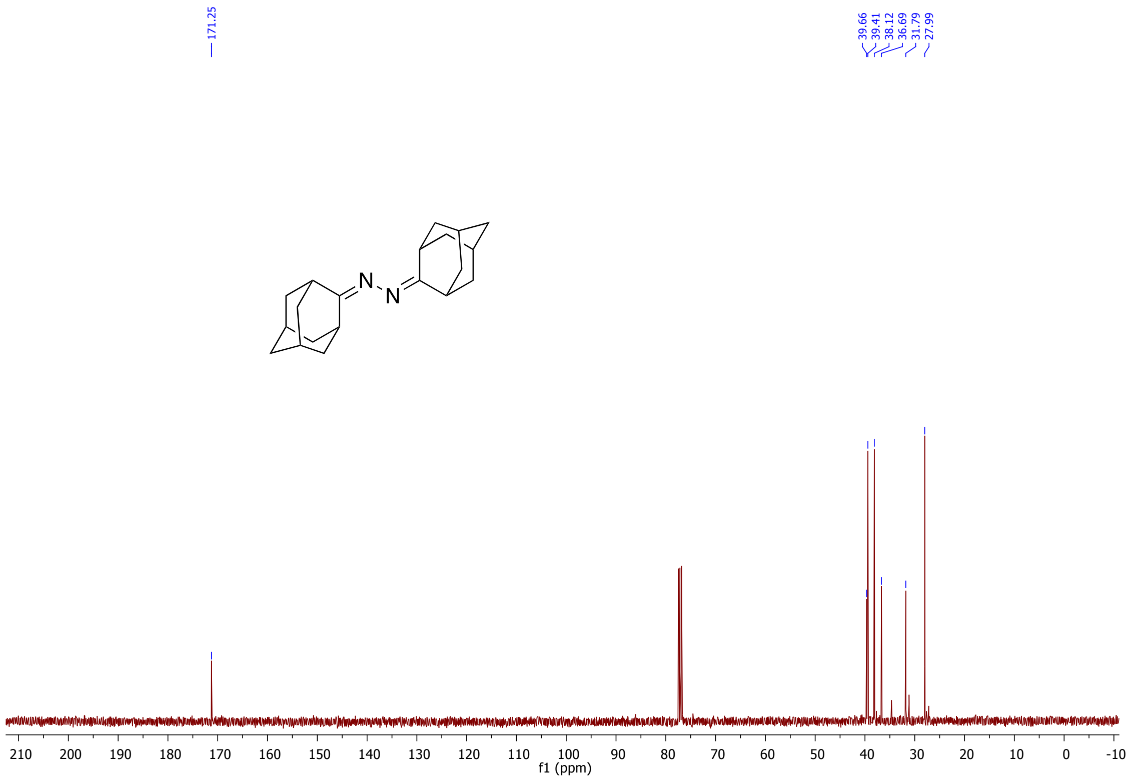
^{13}C NMR spectrum of 1,2-dicyclooctylidenehydrazine **(3e):**



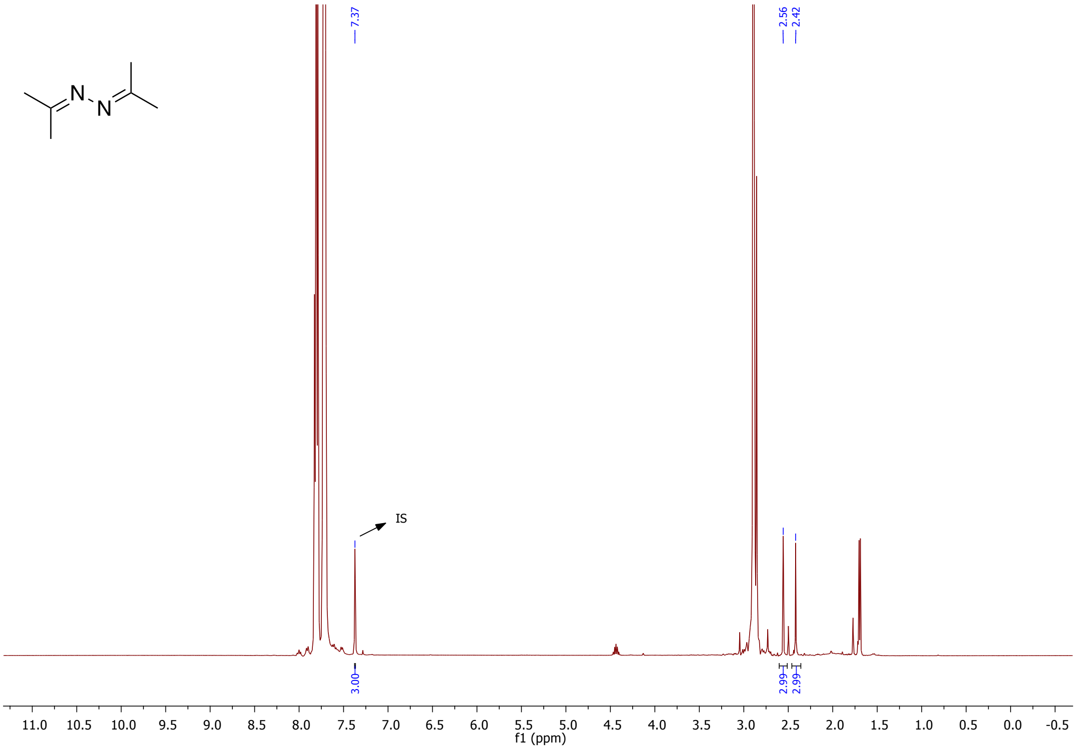
^{1}H NMR spectrum of 1,2-di(adamantan-2-ylidene)hydrazine **(3f):**



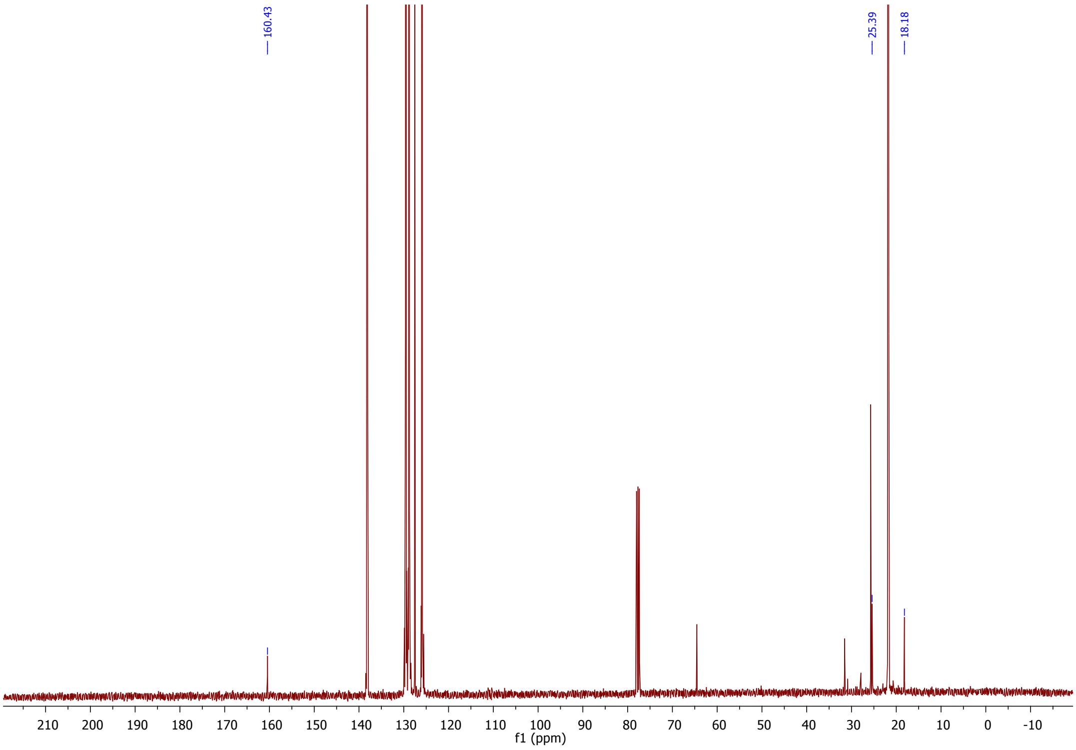
^{13}C NMR spectrum of 1,2-di(adamantan-2-ylidene)hydrazine **(3f):**



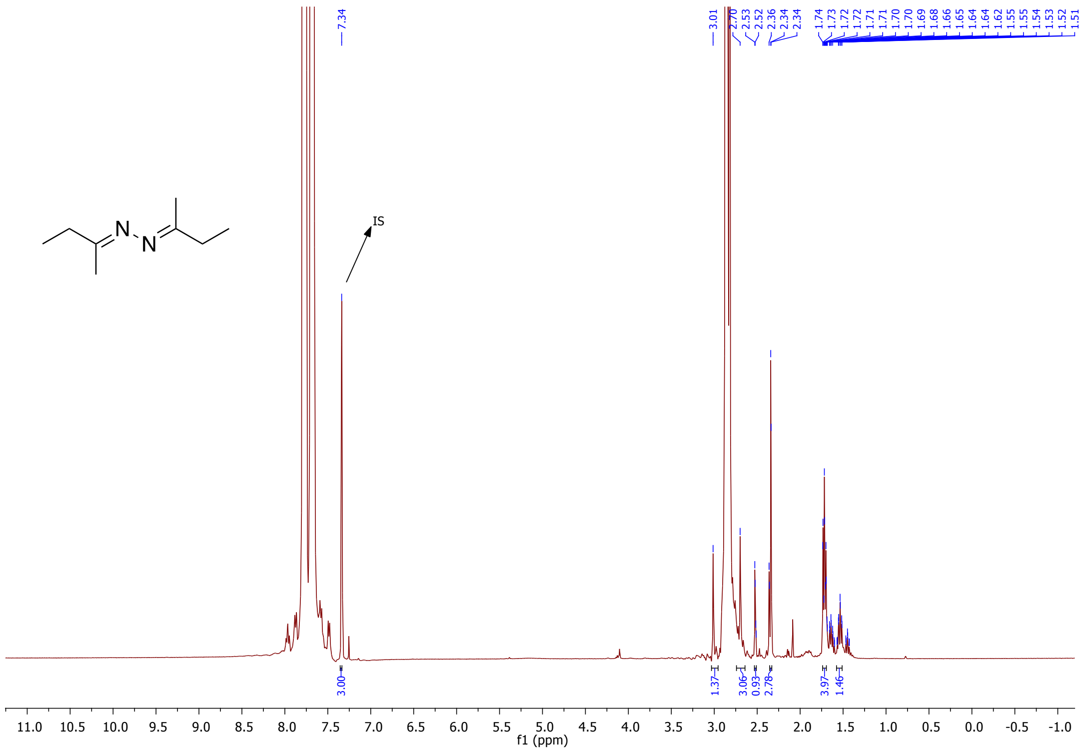
^{1}H NMR spectrum of 1,2-di(propan-2-ylidene)hydrazine **(3g)** using mesitylene as an internal standard:



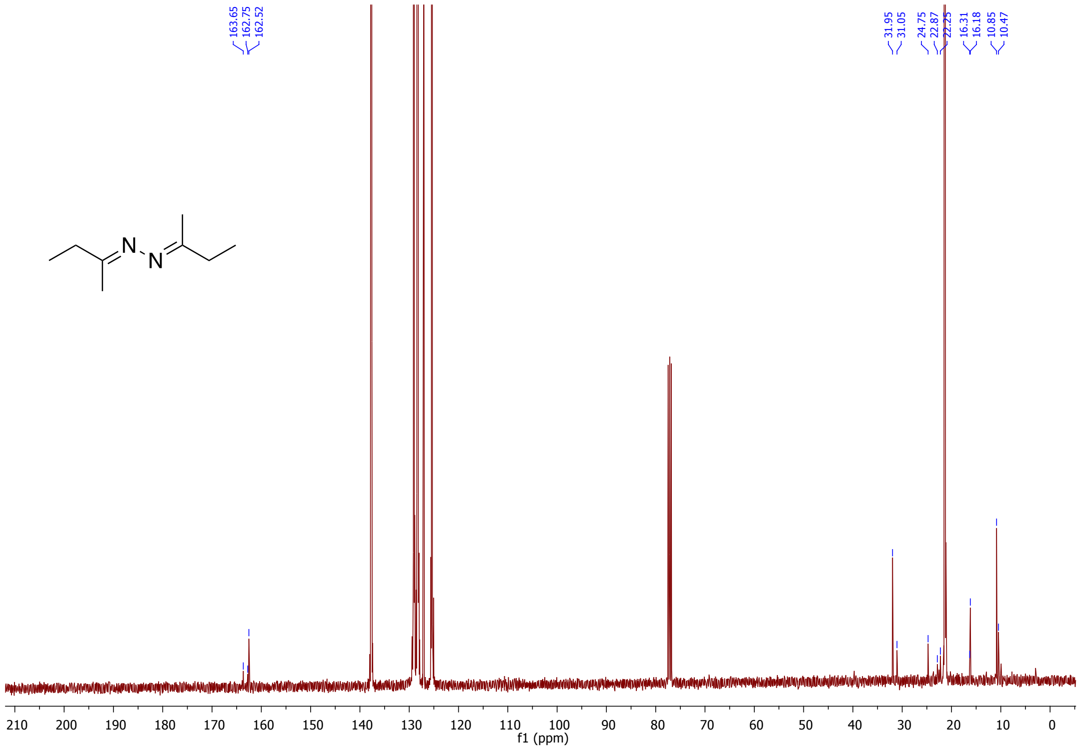
^{13}C NMR spectrum of 1,2-di(propan-2-ylidene)hydrazine **(3g)** using mesitylene as an internal standard:



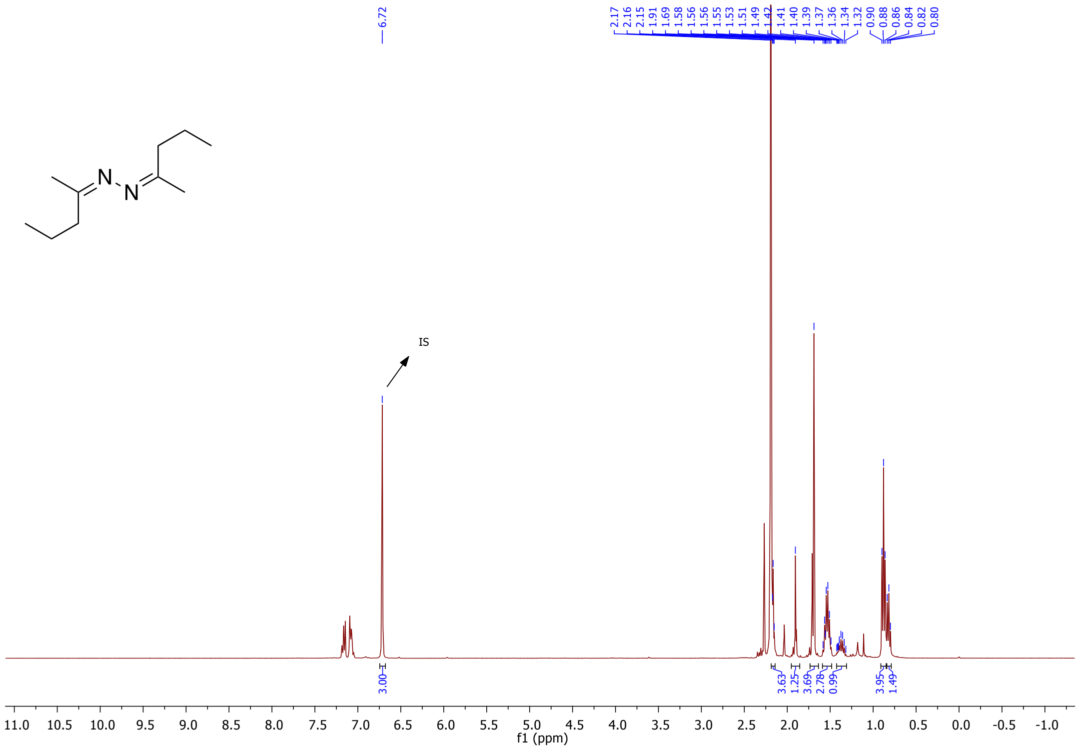
^{1}H NMR spectrum of 1,2-di(butan-2-ylidene)hydrazine **(3h)** (for *E*/*Z* mixture) using mesitylene as an internal standard:



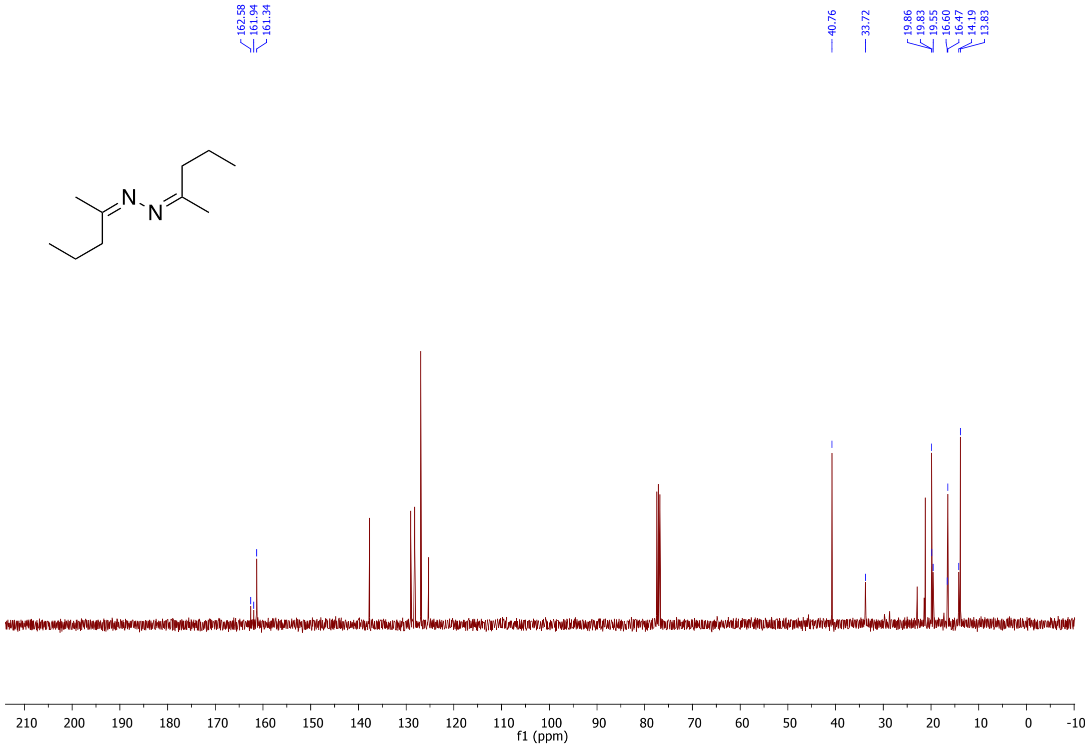
^{13}C NMR spectrum of 1,2-di(butan-2-ylidene)hydrazine **(3h)** (for *E*/*Z* mixture) using mesitylene as an internal standard:



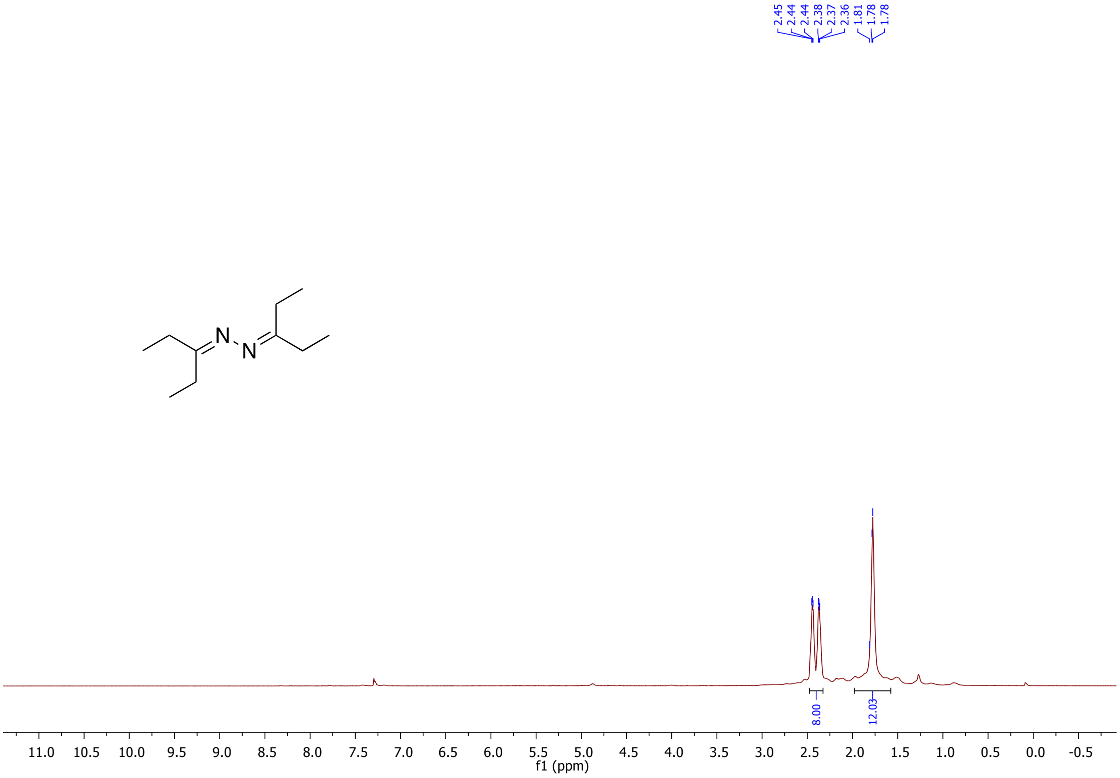
^{1}H NMR spectrum of 1,2-di(pentan-2-ylidene)hydrazine **(3i)** (for *E*/*Z* mixture) using mesitylene as an internal standard:



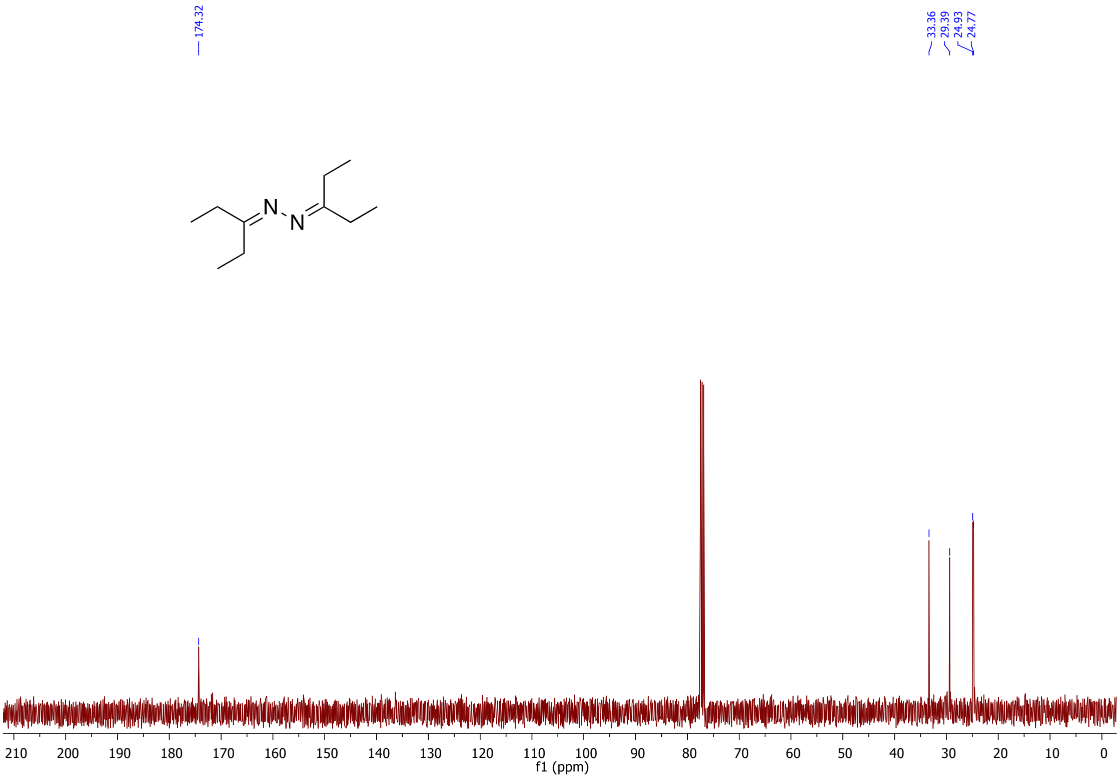
^{13}C NMR spectrum of 1,2-di(pentan-2-ylidene)hydrazine **(3i)** (for *E*/*Z* mixture) using mesitylene as an internal standard:



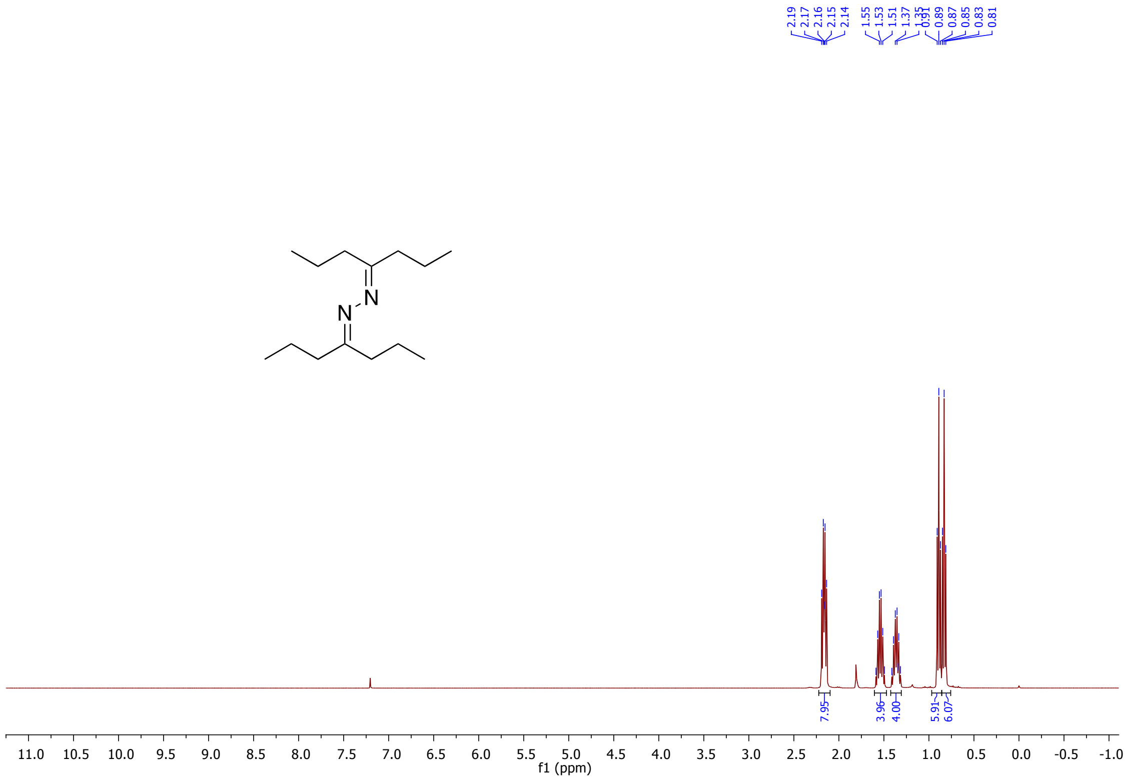
^{1}H NMR spectrum of 1,2-di(pentan-3-ylidene)hydrazine **(3j):**



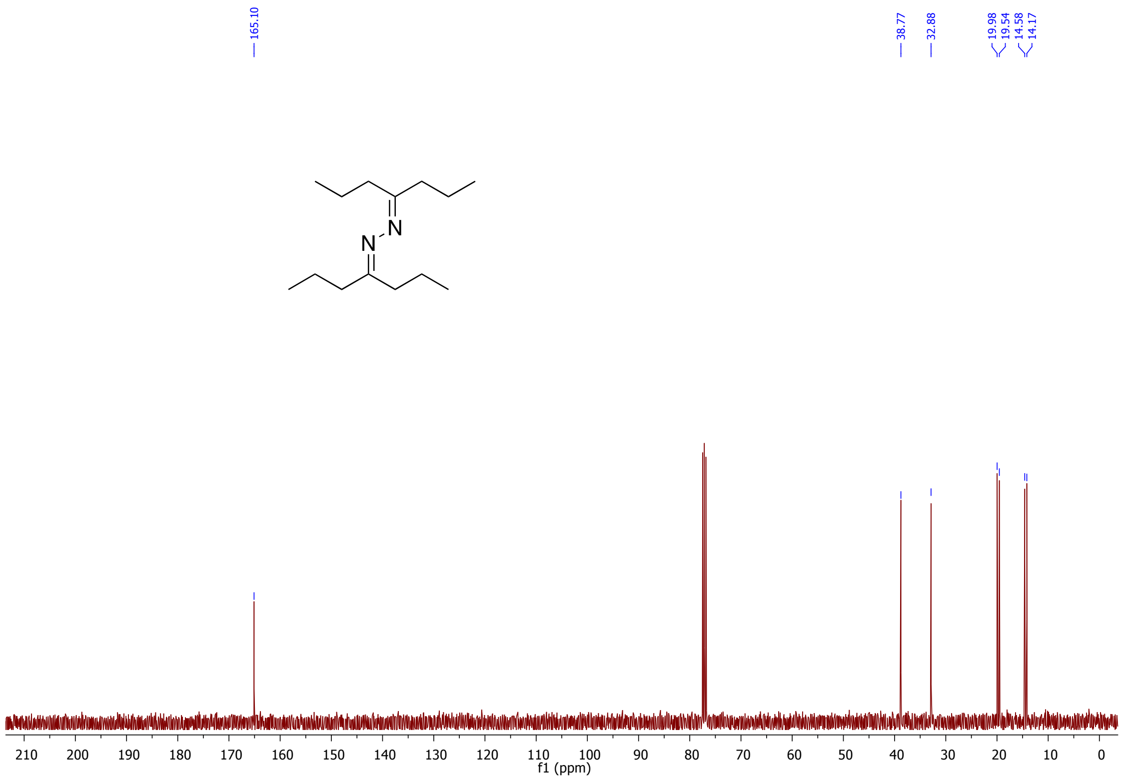
^{13}C NMR spectrum of 1,2-di(pentan-3-ylidene)hydrazine **(3j):**



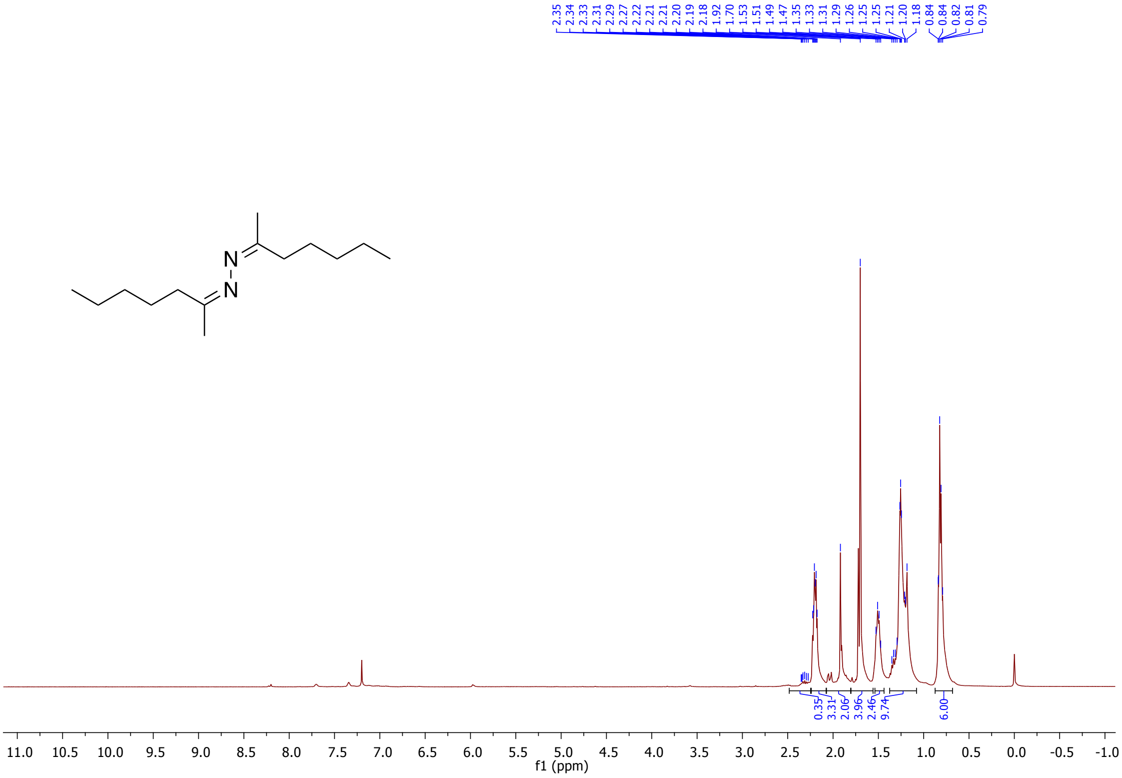
^{1}H NMR spectrum of 1,2-di(heptan-4-ylidene)hydrazine **(3k)**:



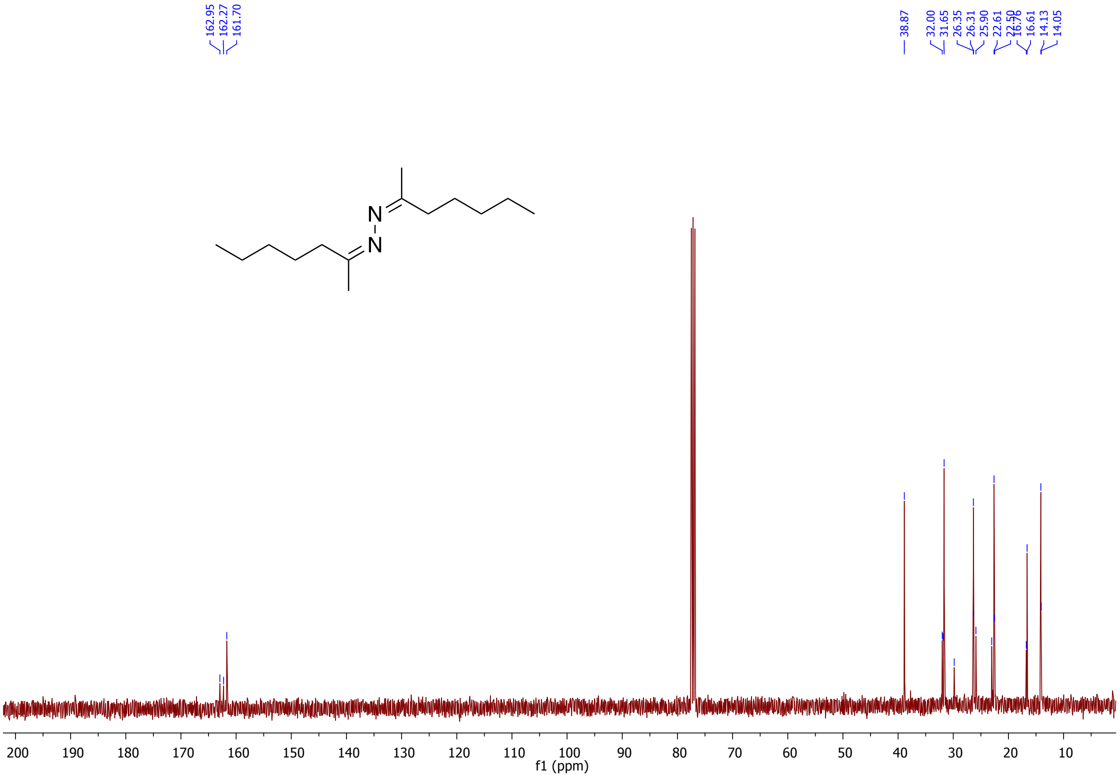
^{13}C NMR spectrum of 1,2-di(heptan-4-ylidene)hydrazine **(3k):**



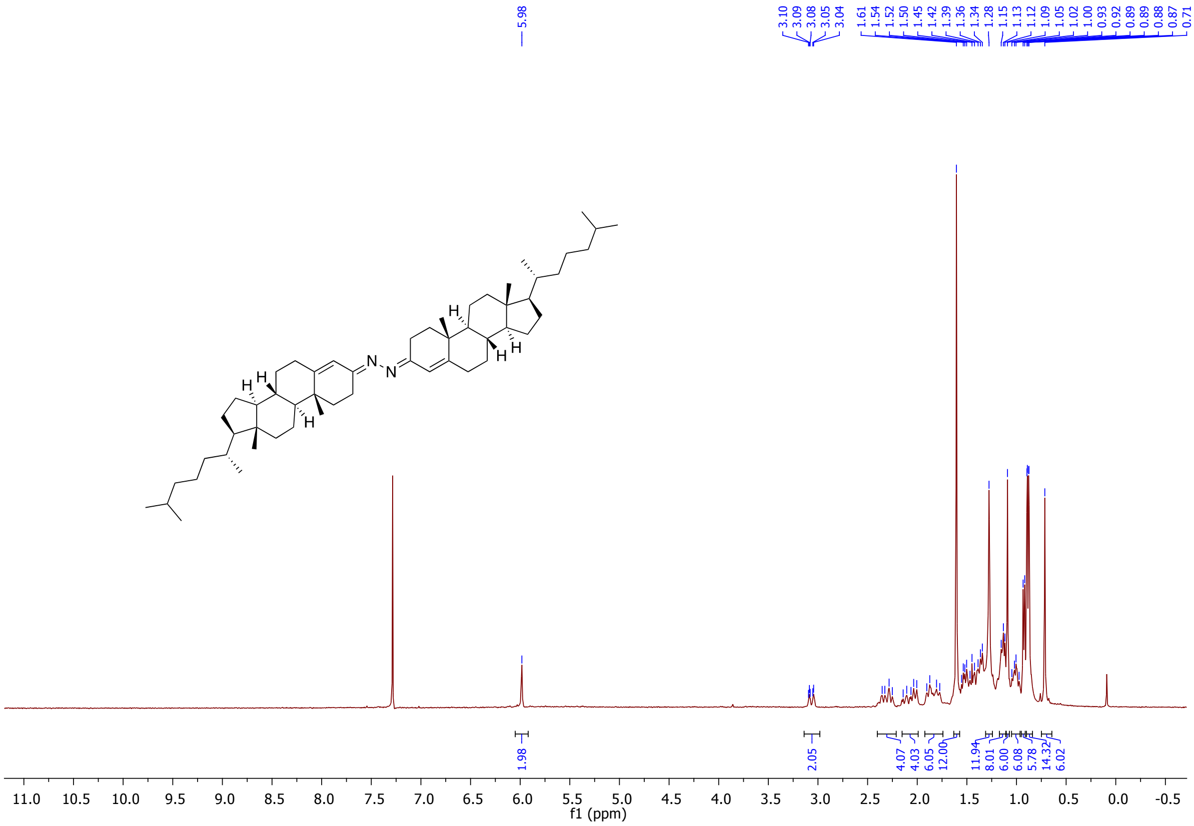
^{1}H NMR spectrum of 1,2-di(heptan-2-ylidene)hydrazine (for *E*/*Z* mixture) **(3l):**



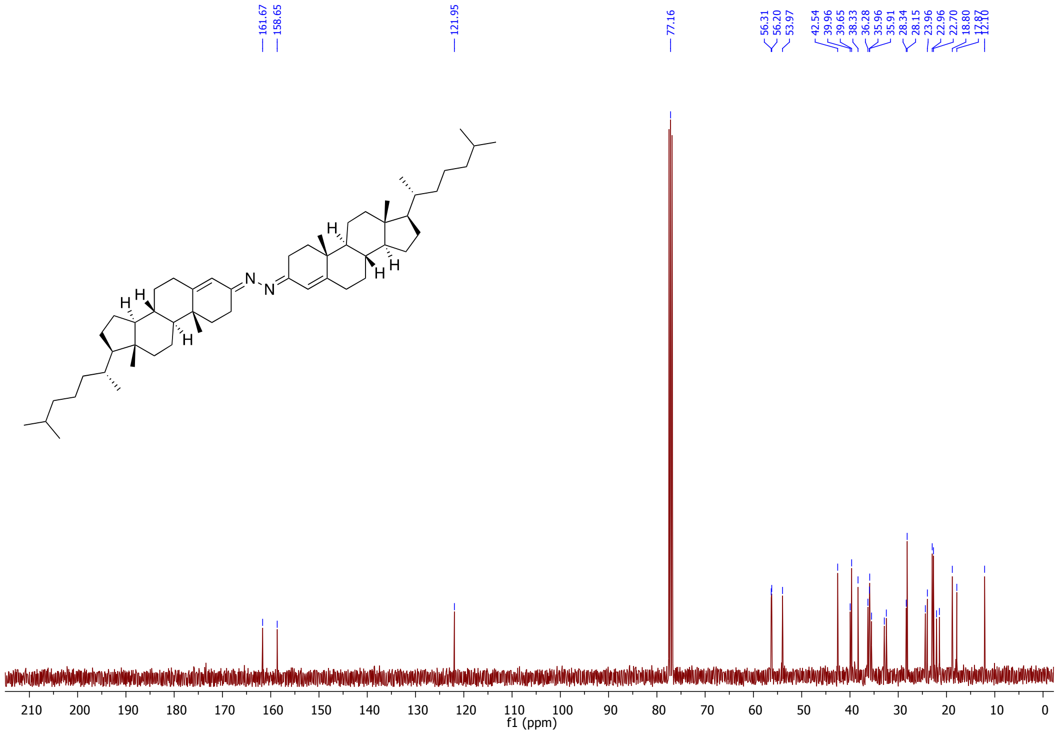
^{13}C NMR spectrum of 1,2-di(heptan-2-ylidene)hydrazine (for *E*/*Z* mixture) **(3l):**



^{1}H NMR spectrum of (1*E*,2*E*)-1,2-bis((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-ylidene)hydrazine **(3m):**

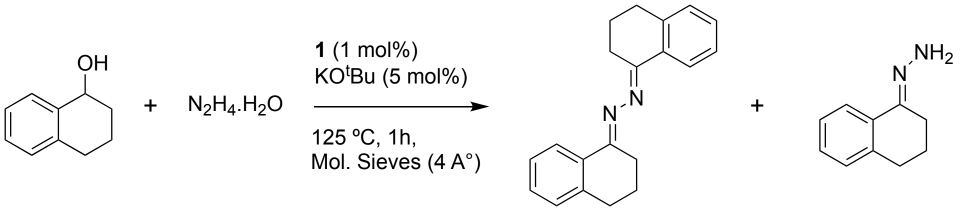


^{13}C NMR spectrum of (1*E*,2*E*)-1,2-bis((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-ylidene)hydrazine **(3m):**



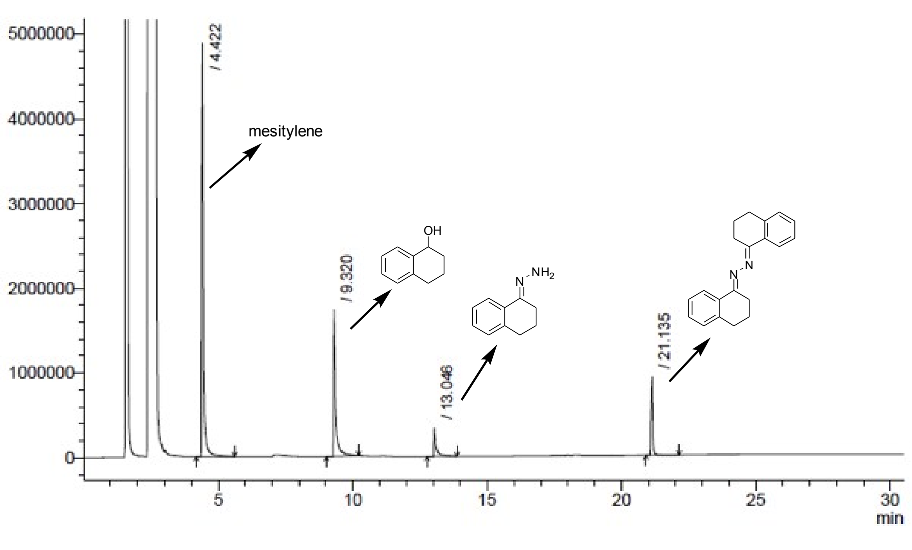
The Observation of Hydrazone Intermediate in Reaction Mixture:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.01 mmol), base (0.05 mmol), tetraline-1-ol (0.5 mmol), toluene (2 mL) and molecular sieves (4 Å) under nitrogen atmosphere inside a glove box. The flask was taken out of the glove box and hydrazine hydrate (0.75 mmol) and mesitylene (0.5 mmol, internal standard) were added to the reaction mixture under argon flow. The flask was equipped with a condenser and immersed into a pre-heated oil bath of 125 °C with stirring in an open system under the flow of argon. After 1 hour, the reaction was stopped and the crude reaction mixture analyzed by GC. The formation of hydrazone intermediate was observed in GC and further isolated and confirmed by NMR analysis. ^{1}H and ^{13}C NMR spectra display a broad singlet at δ 5.203 ppm (N*H*$_2$) and a carbon signal at δ 147.09 ppm (*C*=N), respectively indicating the formation of hydrazone intermediate.

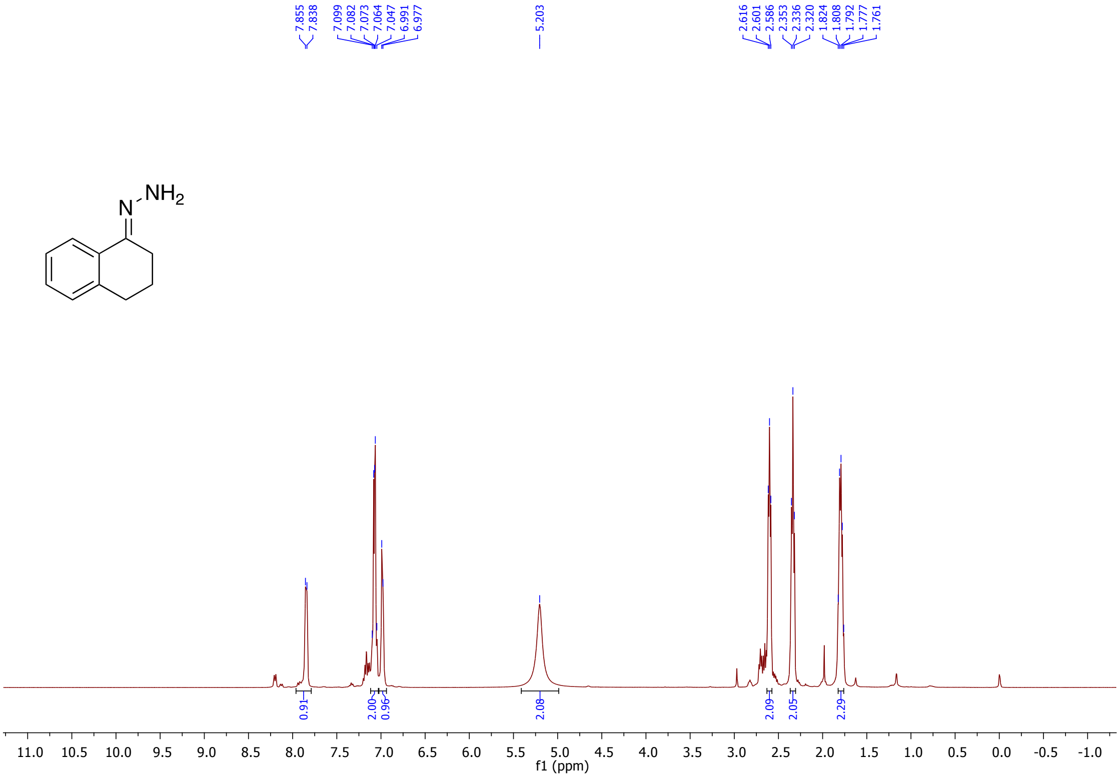


Scheme S1. The Observation of Hydrazone Intermediate in Reaction Mixture.

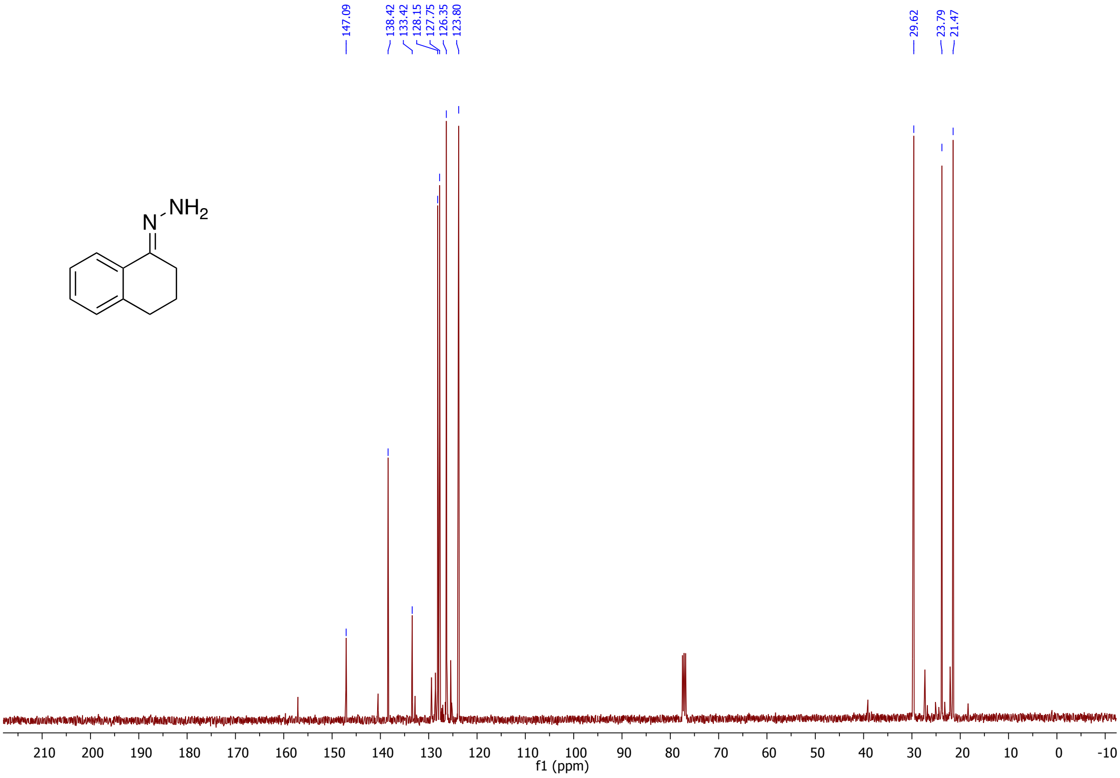
GC Spectrum for the reaction mixture after 1h:



^{1}H NMR spectrum of (3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine:



^{13}C NMR spectrum of (3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine:



X-Ray Analysis of Azine Products 2d and 2n: Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å, multilayer optics). Intensities were integrated with SAINT+[15] and corrected for absorption with SADABS.[16] The structures were solved by direct methods and refined on F^2 with SHELXL-97[17] using Olex-2[18] software.

Crystal Data of Azine product 2d: $C_{16}H_{16}N_2$, yellow block, M = 236.31 gm/mol, monoclinic with space group P121/n 1, a = 11.6991(2) Å, b = 7.55240(18) Å, c = 14.8701(3) Å, α = 90°, β = 97.7197° , γ = 90°, V = 1301.96 (5) Å^3, Z = 1, F(000) = 504, μ-(CuK$_\alpha$) = 0.138 mm^{-1}, 2θ$_{max}$ = 152.442, ρ$_{calcd}$ = 0.301 g/cm^3, T = 294.5(3) K, 9610 Reflections collected, 2656 unique, R_1 = 0.0433, WR_2 = 0.1293 (all data). Residual electron density max/min = 0.190/-0.149e.Å^{-3}. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 1889888**.

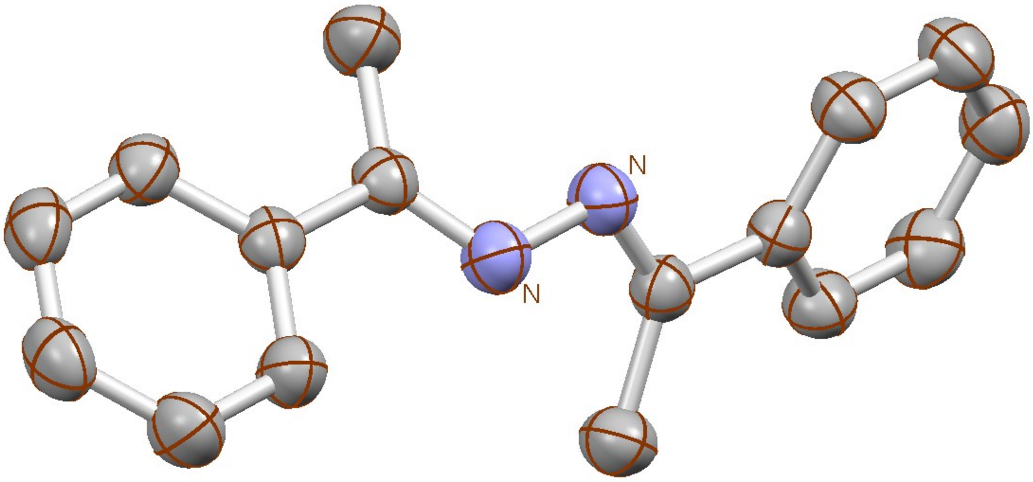


Figure S1: Ortep Structure of (1*E*,2*E*)-1,2-bis(1-phenylethylidene)hydrazine 2d. Ellipsoids are Drawn with 50% Probability.

Crystal Data of Azine Product 2n: $C_{24}H_{20}N_2$, yellow block, *M* = 336.42 gm/mol, monoclinic with space group P121/C1, *a* = 18.8305(5) Å, *b* = 5.31570(13) Å, *c* = 9.2092(2) Å, *α* = 90°, *β* = 100.656° (3), *γ* = 90°, *V* = 905.92 (4) Å^3, *Z* = 1, *F*(000) = 178, μ-(CuK$_\alpha$) = 0.278 mm^{-1}, 2θ$_{max}$ = 152.354, ρ$_{calcd}$ = 0.617 g/cm^3, T = 298.21(10) K, 6917 Reflections collected, 1849 unique, R_1 = 0.0463, WR_2 = 0.1481 (all data). Residual electron density max/min = 0.175/-0.108e.Å^{-3}. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 1889889**.

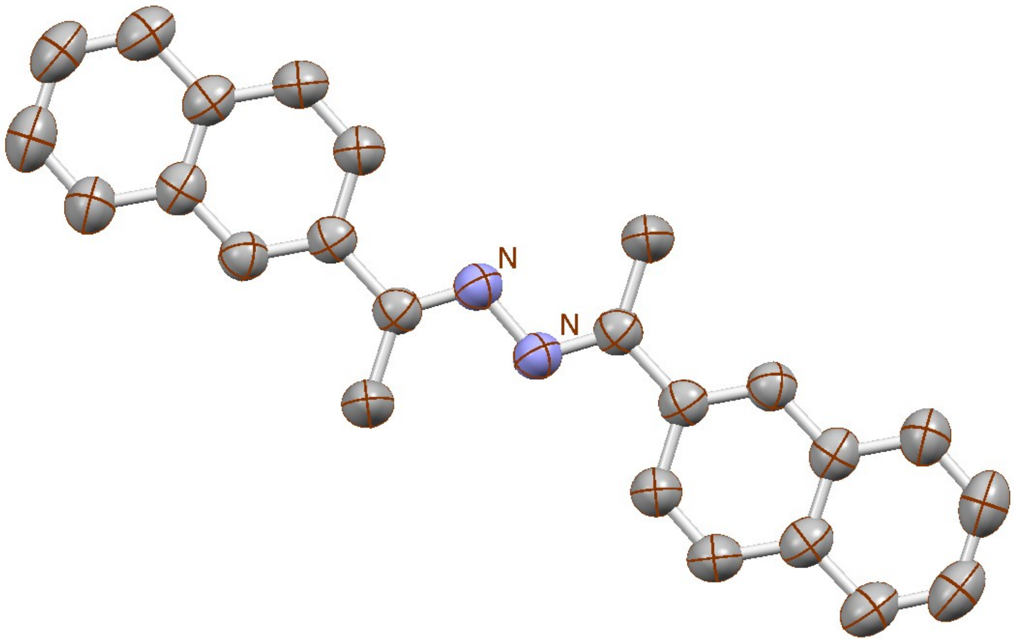


Figure S2: Ortep Structure of (1*E*,2*E*)-1,2-Bis(1-(naphthalen-2-yl)ethylidene)hydrazine (2n). Ellipsoids are Drawn with 50% Probability.

X-ray Analysis of Azine Product 3m: Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART[15] software packages and corrected for absorption with SADABS.[16] The structure was solved by direct methods and refined on F^2 with SHELXL-97[17] using Olex-2[18] software.

Crystal Data of Azine Product 3m: $C_{54}H_{88}N_2$, yellow block, M = 765.26 g/mol, monoclinic with space group P1211 , a = 13.5019(4) Å, b = 10.2073(3) Å, c = 17.0548(5) Å, α = 90º, β = 95.130(3)º, γ = 90º, V = 2340.97(12) Å^3, Z = 2, F(000) = 852 , μ-(MoK$_\alpha$) = 0.061 mm^{-1}, 2θ$_{max}$ = 58.03 , ρ$_{calcd}$ = 1.086 g/cm^3, T = 194.20(10) K, 25355 reflections measured , 8342 unique, R$_1$ = 0.0534, WR_2 = 0.1423 (all data). Residual electron density max/min = 0.406/-0.317e.Å^{-3}. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number **CCDC 1889890**.

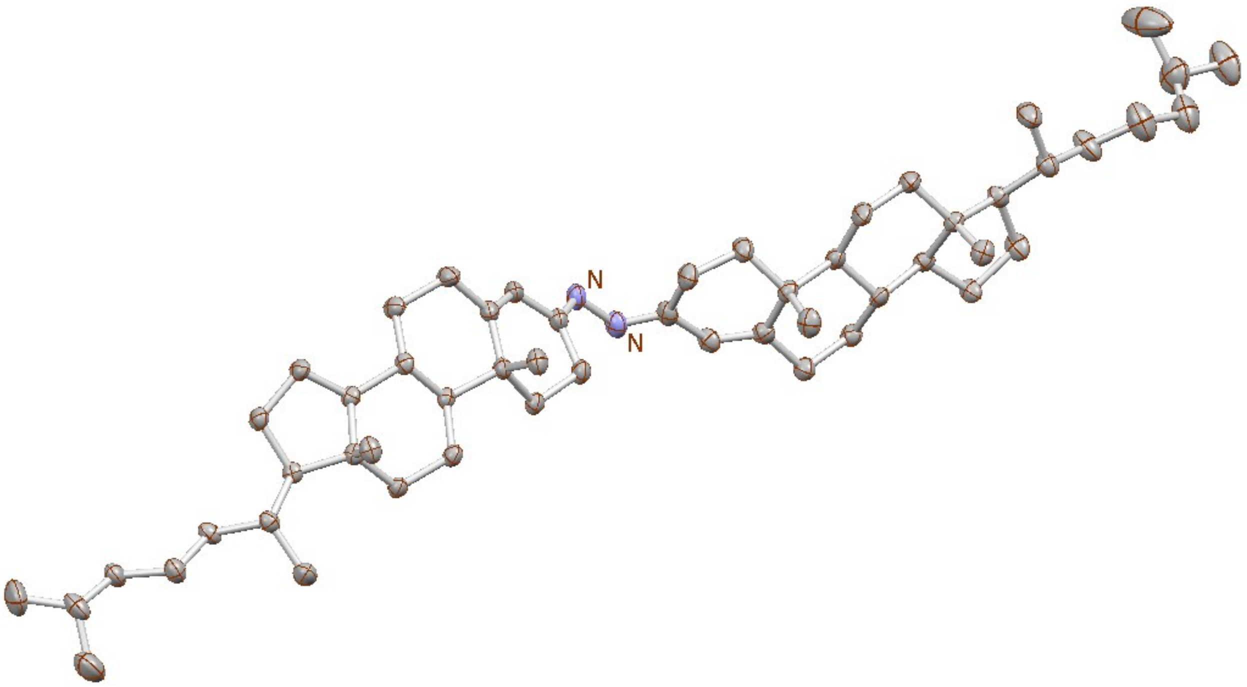


Figure S3: Ortep Structure of (1*E*,2*E*)-1,2-Bis((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)1,2,6,7,8,9,10,11,12,13,14,15,16,17tetradecahydro-3Hcyclopenta[a]phe-nanthren-3-ylidene)hydrazine (3m). Ellipsoids are Drawn with 50% Probability.

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