Supporting Information for

Highly efficient synthesis of aldenamines from carboxamides by iridium-catalyzed silane-reduction/dehydration under mild conditions

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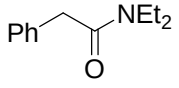
Contents

1. General Methods: All reactions were carried out under a nitrogen or argon atmosphere. Dehydrated benzene, toluene, ether, dichloromethane, tetrahydrofuran (THF) and diethylzinc in 1.0 M hexane solution were purchased from Kanto Chemical Co., Ltd., and used as received. xylene was distilled under an inert atmosphere from sodium/benzophenone prior to use. Polymethylhydrosiloxane (PMHS) and tetramethyldisiloxane (TMDS) were purchased from Gelest Inc., and used as received. Pentamethyldisiloxane was purchased from FluoroChem. Dimethylphenylsilane, triethylsilane, allyl bromide and diiodomethane were purchased from Tokyo Chemical Industry Co., Ltd. Karstedt's catalyst in 0.1 M xylene solution were purchased from Aldrich Chemical Co. Diphenylsilane was purchased from Chisso Co. ^{1}H and ^{13}C NMR spectra were measured on JEOL GSX-270 (270 MHz), ECA 400 (395 MHz) and ECA 600 (600 MHz) spectrometers. Chemical shifts for ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.1), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-550 spectrometer. ICP-MS and HRMS analyses were performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide (Merck, aluminum oxide 150 F_{254}, neutral) and glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. (μ_3;η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ [(ACE)$Ru_3(CO)_7$][1a,b] and citronellic acid *N*-benzyl-*N*-methylamide (**1h**)[1c] were prepared by the method reported previously. $IrCl(CO)(PPh_3)_2$,[2a] $RhCl(PPh_3)_3$,[2b] $[RhCl(cod)]_2$,[2c] $Pt(dba)_2$,[2d] $PtCl_2(cod)$,[2e] and 1,2-bis(dimethylsilyl)ethane[2f,g] were prepared by the literature method.

2. Preparation and Spectral Data of Carboxamides.

***N,N*-Diethylphenylacetamide (1a):**[3] This compound was prepared from phenylacetyl chloride and diethylamine. IR (neat) ν 2973, 2933, 1639, 1455, 1428, 1280, 1132, 1074, 794, 727 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.09 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 3.30 (q, *J* = 7.2 Hz, 2H), 3.39 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 2H), 7.20-7.36 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 12.4, 13.6, 39.5, 40.2, 41.8, 126.0, 127.9, 128.1, 135.0, 169.4; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 11.7 min.



***N*-Methyl-*N*-phenylphenylacetamide (1b):**[4] This compound was prepared from phenylacetyl chloride and *N*-methylaniline. mp 60-63 °C; IR (KBr) ν 3061, 3029, 1655, 1594, 1495, 1376, 1269, 1119, 773, 728 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 3.28 (s, 3H), 3.46 (s, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.17-7.26 (m, 3H), 7.32-7.43 (m, 3H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 33.5, 40.8, 126.4, 127.5, 127.8, 128.2, 128.9, 129.6, 135.3, 143.8, 170.9.

4-(Phenylacethyl)morpholine (1c):[5] This compound was prepared from phenylacetyl chloride and morpholine. IR (KBr) ν 2981, 2860, 1643, 1434, 1274, 1115, 965, 762 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 3.40-3.51 (m, 4H), 3.64 (bs, 4H), 3.73 (s, 2H), 7.21-7.28 (m, 3H), 7.33 (dd, *J* = 7.7, 6.8 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 40.9, 42.2, 46.6, 66.5, 66.9, 127.0, 128.6, 128.9, 134.9, 169.7; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 18.4 min.

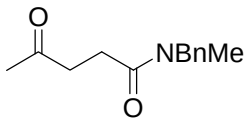
4-(*n*-Hexanoyl)morpholine (1d):[6] This compound was prepared from hexanoyl chloride and morpholine. IR (neat) ν 2957, 2857, 1644, 1430, 1271, 1245, 1115, 1030, 965, 848 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.26-1.40 (m, 4H), 1.55-1.70 (m, 2H), 2.30 (t, *J* = 7.7 Hz, 2H), 3.42-3.50 (m, 2H), 3.58-3.71 (m, 6H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 14.0, 22.5, 25.0, 31.7, 33.2, 41.9, 46.1, 66.8, 67.1, 172.0; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 9.3 min.

6-Bromo-1-(morpholine-4-yl)-hexan-1-one (1e):[7] This compound was prepared from 6-bromohexanoyl chloride and morpholine. IR (neat) ν 2929, 2856, 1646, 1431, 1272, 1228, 1115, 1031, 848 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.42- 1.58 (m, 2H), 1.59-1.75 (m, 2H), 1.82-1.96 (m, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 3.36-3.71 (m, 10H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 24.3, 28.0, 32.6, 32.8, 33.7, 42.0, 46.0, 66.7, 67.0, 171.4.

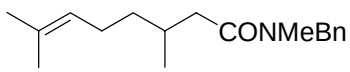
N*-Benzyl-*N*-methyl-7-carbomethoxyheptanamide (1f):**[8] This compound was prepared from suberic acid monomethyl ester and pivaloyl chloride followed by the reaction with benzylmethylamine. IR (KBr) ν 2937, 2863, 1734, 1651, 1452, 1205, 1171, 1080, 733 cm^{-1}. Spectroscopic data of this amide were obtained as a mixture of two rotational isomers. ***major isomer: ^1H NMR (395 MHz, $CDCl_3$) δ 1.23-1.50 (m, 4H), 1.53-1.81 (m, 4H), 2.21-2.47 (m, 4H), 2.90 (s, 3H), 3.66 (s, 3H), 4.59 (s, 2H), 7.11-7.41 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.8, 25.0, 29.0, 29.1, 33.5, 34.02, 34.04, 50.8, 51.5, 126.3, 128.0, 128.6, 137.6, 173.1, 174.3. ***minor isomer:*** ^1H NMR (395 MHz, $CDCl_3$) δ 1.23-1.50 (m, 4H), 1.53-1.81 (m, 4H), 2.21-2.47 (m, 4H), 2.94 (s, 3H), 3.65 (s, 3H), 4.53 (s, 2H), 7.11-7.41 (m, 5H); ^{13}C NMR (67.8

MHz, $CDCl_3$) δ 24.8, 25.2, 28.9, 29.1, 33.0, 33.9, 34.9, 51.5, 53.4, 127.3, 127.6, 128.9, 136.8, 173.5, 174.2.

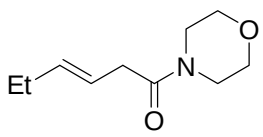
N*-Benzyl-*N*-methyl-4-oxo-pentanamide (1g):** This compound was prepared from levulinic acid and pivaloyl chloride followed by the reaction with benzylmethylamine. IR (neat) ν 2919, 1715, 1646, 1450, 1402, 1369, 1164, 731, 700 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1260. Spectroscopic data of this amide were obtained as a mixture of two rotational isomers. ***major isomer: ^{1}H NMR (395 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.65 (t, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.95 (s, 3H), 4.58 (s, 2H), 7.19-7.41 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 27.0, 29.8, 34.3, 37.72, 50.5, 126.1, 127.5, 128.2, 137.0, 171.3, 207.4. ***minor isomer:*** ^{1}H NMR (395 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.66 (t, *J* = 6.3 Hz, 2H), 2.80 (t, *J* = 6.3 Hz, 2H), 2.93 (s, 3H), 4.57 (s, 2H), 7.19-7.41 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 26.7, 29.7, 33.5, 37.70, 52.7, 126.9, 127.2, 128.5, 136.2, 171.5, 207.3.



Citronellic acid *N*-benzyl-*N*-methylamide (1h):[1c] This compound was prepared from citronellic acid and pivaloyl chloride followed by the reaction with *N*-methylbenzylamine. IR (neat) ν 2962, 2923, 1649, 1452, 1401, 1262, 1118, 1077, 733 cm^{-1}; Spectroscopic data of this amide were obtained as a mixture of two rotational isomers. ***major isomer*:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.98 (d, *J* = 6.6 Hz, 3H), 1.21 (m, 1H), 1.40 (m, 1H), 1.60 (s, 3H), 1.67 (s, 3H), 1.90-2.11 (m, 3H), 2.19 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.37 (dd, *J* = 14.8, 5.5 Hz, 1H), 2.91 (s, 3H), 4.60 (s, 2H), 5.10 (t, *J* = 7.1 Hz, 1H), 7.14-7.37 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8, 25.5, 25.7, 27.1, 30.0, 34.9, 37.1, 40.7, 50.7, 124.4, 127.2, 128.0, 128.5, 131.3, 137.6, 172.7. ***minor isomer*:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.6 Hz, 3H), 1.21 (m, 1H), 1.40 (m, 1H), 1.57 (s, 3H), 1.65 (s, 3H), 1.90-2.11 (m, 3H), 2.20 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.36 (dd, *J* = 14.8, 5.5 Hz, 1H), 2.93 (s, 3H), 4.52 (d, *J* = 16.5 Hz, 1H), 4.54 (d, *J* = 16.5 Hz, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 7.14-7.37 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 17.6, 25.5, 25.6, 28.4, 30.0, 33.8, 37.0, 40.4, 53.4, 124.5, 126.2, 127.5, 128.8, 131.3, 136.7, 173.1.



(*E*)-1-(morpholine-4-yl)-3-hexen-1-one (1i): This compound was prepared from (*E*)-3-hexenoyl chloride and morpholine. IR (neat) ν 2967, 2849, 1644, 1434, 1277, 1229, 1115, 1034, 974, 745 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.3 Hz, 3H), 2.00-2.11 (m, 2H), 3.08 (d, *J* = 5.8 Hz, 2H), 3.42-3.50 (m, 2H), 3.57-3.71 (m, 6H), 5.47-5.64 (m, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 13.2, 25.1, 37.0, 41.5, 45.8, 66.2, 66.4, 121.1, 135.2, 169.6; HRMS (EI) calcd for $C_{10}H_{17}NO_2$ 183.1259, found 183.1254.



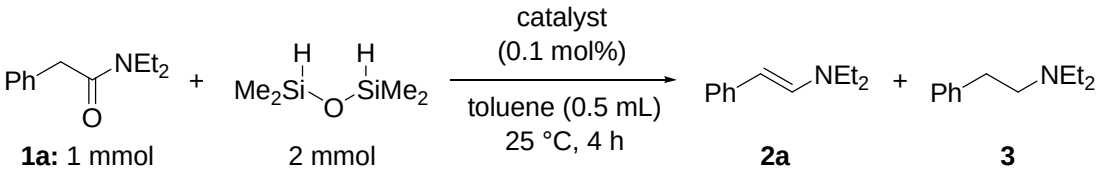
3. General Procedure for the Reduction/Dehydration of Carboxamides.

$IrCl(CO)(PPh_3)_2$/TMDS (Table 2): To a 0.1 *M* solution of $IrCl(CO)(PPh_3)_2$ in toluene (0.5 mL; 0.05 mmol of [Ir]) was added the substrate (1 mmol) and TMDS (268 mg, 2.0 mmol) at 25 °C. After it was stirred at 25 °C for 30 min, the solvent was removed under reduced pressure. The conversion of the substrate and the chemical yields of both enamine and amine were determined by capillary GLC (hexamethylbenzeene as an internal standard) or ^1H NMR (ferrocene or tetrachloroethane as an internal standard) analysis. ***Isoration of Enamines (2a-c and 2i):*** After the reaction was completed, a solution of KOH in MeOH (3.8 *M*, 5 mL) was added to the reaction mixture and resultant solution was stirred at 25 °C for 30 min. After the solvent was removed under reduced pressure, the resultant residue was washed five times with ether (totally 30 mL). The combined organic solution was filtered through a pad of Celite and the filtrate was evaporated under reduced pressure to give the enamines (**2a-c** and **2i**). **2a:** 149 mg (85%); **2b:** 180 mg (86%); **2c:** 155 mg (82%); **2i:** 144 mg (86%). ***Isolation of Enamine 2d*:** After the reaction was completed, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography [ether-hexane (containing 1% of Et_3N)] gave phenylacetaldehyde (70%) and **2d** (23%).

$IrCl(CO)(PPh_3)_2$/PMHS (Table 3): To a 0.2 *M* solution of $IrCl(CO)(PPh_3)_2$ in toluene (0.5 mL; 0.01 mmol of [Ir]) was added the substrate (1 mmol) and PMHS (266 mg, Si–H = 4.0 mmol) at 25 °C. The homogeneous solution turns to gel after 15 min. After it was allowed to stand for 15 min, the resultant residue was washed ten times with ether (totally 30 mL), and the combined organic solution was filtered through a pad of Celite and the filtrate was evaporated under reduced pressure. **2b:** 199 mg (95%); **2c:** 180 mg (95%); **2d:** 152 mg (90%); **2f:** 237 mg (86%); **2h:** 247 mg (96%); **2i:** 164 mg (98%).

ICP-MS Analysis of the Product: The iridium content in enamines was determined by ICP-MS analysis: enamine **2c** obtained by the above procedure was dissolved in an aqueous solution of HCl, and the concentration of HCl was adjusted to 5×10^{-3} wt%. The content of **2** in this solution was 6.2×10^{-3} mol/L. The measurement was performed using this solution. The iridium content was calibrated with a commercially available standard reagent (ACROS: iridium atomic absorption standard solution, 1 mg/mL Ir in 5% HCl); five standard solutions, of which Ir concentration is in a range from 5ppb to 200ppb, were used for calibration. In both cases, the Ir content was bellow identification limit.

Various Transition Metal Catalysts/TMDS: To a solution of catalyst (0.001 mmol, 0.1 mol%) in toluene (0.5 mL) was added TMDS (268 mg, 2.0 mmol) through a microsyringe and the mixture was stirred at 25 °C for 30 min followed by addition of *N*,*N*-diethylphenylacetamide **1a** (191 mg, 1 mmol). After it was stirred at 25 °C for 4 h, the solvent was removed under reduced pressure. The conversion of **1a** and the chemical yields of both enamine **2a** and amine **3** were determined by capillary GLC analysis with hexamethylbenzeene as an internal standard. GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 6.6 min (**3**), 10.3 min (**2a**), 11.7 min (**1a**).



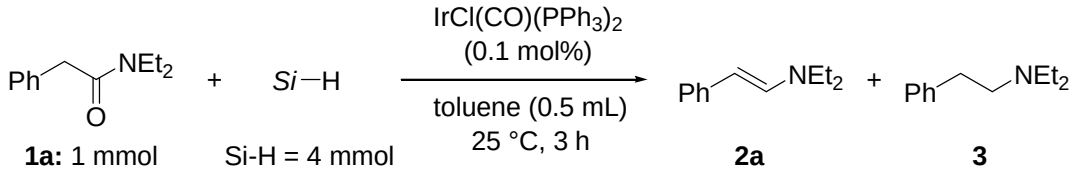
1a: 1 mmol 2 mmol **2a** **3**

Table S-1. Reaction of **1a** with TMDS catalyzed by various transition metal catalysts.

catalyst	yield (%)[a]		catalyst	yield (%)[a]	
	enamine **2a**	amine **3**		enamine **2a**	amine **3**
$Ru_3(CO)_{12}$	<1	<1	$RhCl(PPh_3)_3$	3	<1
$(ACE)Ru_3(CO)_7$	13	4	$[RhCl(cod)_2]_2$	11	<2
$(ACE)Ru_3(CO)_7$[b]	54	46			
$PtCl_2(cod)$	43	8	$IrCl_3 \cdot H_2O$	<1	<1
$Pt(dba)_2$	38	6	$[IrCl(cod)_2]_2$	3	<1
Karstedt's cat.	41	7	$IrCl(CO)(PPh_3)_2$[c]	96	<1

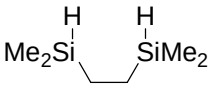
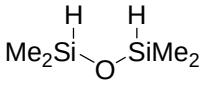
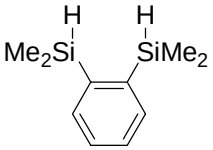
[a] Determined by GLC analysis. [b] 1 mol% of catalyst was used. [c] For 30 min.

$IrCl(CO)(PPh_3)_2$/Various Hydrosilanes: To a 0.2 *M* solution of $IrCl(CO)(PPh_3)_2$ in toluene (0.5 mL, 0.01 mmol of [Ir]) was added hydrosilane (Si–H = 4.0 mmol) through a microsyringe and the mixture was stirred at 25 °C for 30 min followed by addition of *N*,*N*-diethylphenylacetamide **1a** (191 mg, 1 mmol). After it was stirred at 25 °C for 4 h, the solvent was removed under reduced pressure. The conversion of **1a** and the chemical yields of both enamine **2a** and amine **3** were determined by capillary GLC analysis with hexamethylbenzeene as an internal standard.

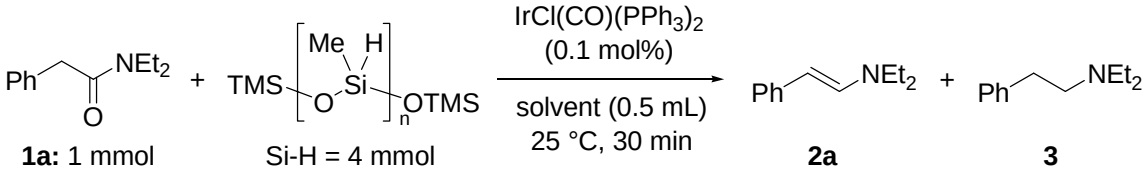


1a: 1 mmol Si-H = 4 mmol **2a** **3**

Table S-2. Reaction of **1a** with various hydrosilanes catalyzed by $IrCl(CO)(PPh_3)_2$.

hydrosilane	yield (%)		hydrosilanev	yield (%)[a]	
	2a	**3**		**2a**	**3**
Et_3SiH	<1	<1	Ph_2SiH_2	<1	<1
$PhMe_2SiH$	3	<1		<1	<1
$TMSOSiMe_2H$	5	<1			
 (30 min) (0.1 mol%)	>99	<1		<1	<1
(0.05 mol%)	96	<1			
(0.01 mol%)	82	<1			

IrCl(CO)(PPh$_3$)$_2$/PMHS; Solvent Effects: To a 0.02 *M* solution of $IrCl(CO)(PPh_3)_2$ in solvent (0.5 mL, 0.1 mmol of [Ir]) was added PMHS (266 mg, Si–H = 4.0 mmol) through a microsyringe and the mixture was stirred at 25 °C for 30 min followed by addition of *N*,*N*-diethylphenylacetamide **1a** (1 mmol). The homogeneous solution turns to gel after 15 min. After it was allowed to stand for 15 min, the resultant residue was washed ten times with ether (totally 30 mL), and the combined organic solution was evaporated under reduced pressure. The conversion of **1a** and the chemical yields of both enamine **2a** and amine **3** were determined by capillary GLC analysis with hexamethylbenzeene as an internal standard.



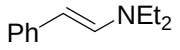
1a: 1 mmol Si-H = 4 mmol **2a** **3**

Table S-3. The reaction of **1a** with PMHS catalyzed by $IrCl(CO)(PPh_3)_2$.

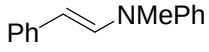
solvent	conversion (%)	yield (%)		selectivity (% enamine)
		enamine **2a**	amine **3**	
toluene	>99	93	7	93.0
benzene	>99	91	7	92.8
xylene	>99	85	15	85.0
Et_2O	>99	91	9	91.0
THF	>99	88	11	88.9
CH_2Cl_2	>99	82	18	82.0

4. Spectral Data of Enamines.

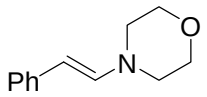
(*E*)-*N*,*N*-Diethylstyrylamine (2a):[9] IR (neat) ν 2961, 2931, 1635, 1594, 1403, 1260, 1110, 937, 788 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.3 Hz, 6H), 3.16 (q, *J* = 7.3 Hz, 4H), 5.16 (d, *J* = 14.1 Hz, 1H), 6.75 (d, *J* = 14.1 Hz, 1H), 6.93 (tt, *J* = 6.6, 2.3 Hz, 1H), 7.10-7.23 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.3, 45.3, 96.1, 122.7, 123.1, 128.4, 137.6, 140.2; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 10.3 min.



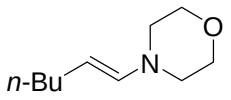
(*E*)-*N*-Methyl-*N*-phenylstyrylamine (2b):[10a] IR (neat) ν 3057, 3024, 2896, 1638, 1592, 1497, 1343, 1257, 1127, 936, 753 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 3.29 (s, 3H), 5.66 (d, *J* = 14.0 Hz, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 7.03-7.10 (m, 3H), 7.13-7.39 (m, 7H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 35.6, 103.6, 117.9, 121.4, 124.3, 124.4, 128.7, 129.4, 134.1, 139.0, 147.7.



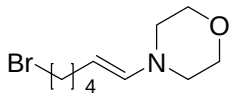
(*E*)-4-Styrylmorpholine (2c):[10] IR (KBr) ν 2964, 2828, 1637, 1594, 1439, 1379, 1227, 1115, 1018, 937, 811 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.04 (t, *J* = 4.9 Hz, 4H), 3.77 (t, *J* = 4.9 Hz, 4H), 5.44 (d, *J* = 14.2 Hz, 1H), 6.62 (d, *J* = 14.2 Hz, 1H), 7.04 (t, *J* = 6.3 hz, 1H), 7.16-7.28 (m, 4H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 49.1, 66.5, 101.6, 124.3, 124.5, 128.6, 138.7, 139.7; HRMS (EI) calcd for $C_{12}H_{15}NO$ 189.1154, found 189.1153; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 15.5 min.



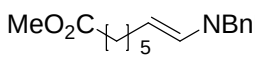
(*E*)-4-(1-Hexenyl)morpholine (2d):[11] IR (neat) ν 2957, 2923, 2854, 1655, 1450, 1379, 1260, 1160, 1121, 1014, 939, 865 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.20-1.37 (m, 4H), 1.95 (td, *J* = 7.3, 6.9 Hz, 2H), 2.75 (t, *J* = 4.9 Hz, 4H), 3.70 (t, *J* = 4.9 Hz, 4H), 4.45 (dt, *J* = 13.9, 6.9 Hz, 1H), 5.78 (d, *J* = 13.9 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 22.1, 30.1, 33.4, 49.6, 66.6, 103.1, 139.5; GLC (TC-1, 30 m, detection FID, column temp. 170 °C), t_R = 6.0 min.



(*E*)-4-(6-Bromo-1-hexenyl)morpholine (2e): ^1H NMR (270 MHz, $CDCl_3$) δ 1.37-1.56 (m, 2H), 1.78-1.93 (m, 2H), 2.00 (td, *J* = 7.3, 6.9 Hz, 2H), 2.77 (t, *J* = 4.9 Hz, 4H), 3.41 (t, *J* = 6.9 Hz, 2H), 3.72 (t, *J* = 4.9 Hz, 4H), 4.41 (dt, *J* = 13.9, 6.9 Hz, 1H), 5.81 (d, *J* = 13.9 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.5, 29.6, 32.2, 34.0, 49.5, 66.6, 101.8, 140.0; HRMS (EI) calcd for $C_{10}H_{18}BrNO$ 247.0572, found 247.0571.



(*E*)-*N*-Benzyl-*N*-methyl-7-carbomethoxy-1-heptenylamine (2f): IR (neat) ν 2931, 2853, 1728, 1653, 1453, 1373, 1259, 1119, 1073, 738, 699 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.23-1.35 (m, 4H), 1.52-1.63 (m, 2H), 1.94 (dt, *J* = 7.2, 6.3 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 3.62 (s, 3H), 3.96 (s, 2H), 4.16 (dt, *J* = 13.5, 7.2 Hz, 1H),



6.04 (d, *J* = 13.5 Hz, 1H), 7.15-7.29 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.9, 28.6, 30.3, 31.2, 34.2, 36.6, 51.4, 59.2, 99.0, 127.0, 127.9, 128.3, 138.8, 139.4, 174.3; HRMS (EI) calcd for $C_{17}H_{25}NO_2$ 275.1885, found 275.1888.

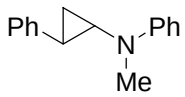
***N*-Benzyl-*N*-methyl-4-oxo-1-pentenylamine (2g):** ^{1}H NMR (396 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.56 (s, 3H), 3.03 (d, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 4.20 (dt, *J* = 13.5, 7.2 Hz, 1H), 6.17 (d, *J* = 13.5 Hz, 1H), 7.18-7.35 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 36.6, 45.8, 59.0, 67.9, 89.1, 127.2, 127.7, 128.5, 138.5, 142.2, 209.2; HRMS (EI) calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1304.

***N*-Benzyl-*N*-methyl-3,7-dimethyl-oct-1,6-dienylamine (2h):** IR (neat) ν 2961, 2918, 2860, 1651, 1453, 1375, 1260, 1198, 1059, 935, 735, 698 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 3H), 1.19-1.40 (m, 2H), 1.61 (bs, 3H), 1.69 (bs, 3H), 1.88-2.13 (m, 3H), 2.48 (s, 3H), 4.02 (s, 2H), 4.10 (dd, *J* = 14.0, 8.2 Hz, 1H), 5.12 (tm, *J* = 7.2 Hz, 1H), 6.05 (d, *J* = 14.0 Hz, 1H), 7.21-7.35 (m, 5H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 17.8, 22.8, 25.8, 26.1, 34.8, 36.7, 28.9, 59.3, 106.1, 125.3, 127.0, 128.0, 128.4, 130.9, 138.2, 138.9; HRMS (EI) calcd for $C_{18}H_{27}N$ 257.2143, found 257.2147.

(*E*,*E*)-4-(1,3-Hexadienyl)morpholine (2i): IR (neat) ν 2961, 2853, 1648, 1454, 1433, 1270, 1117, 970, 907 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 3H), 2.06 (qd, *J* = 7.5, 6.8 Hz, 2H), 2.88 (t, *J* = 4.8 Hz, 4H), 3.71 (t, *J* = 4.8 Hz, 4H), 5.21 (dd, *J* = 13.5, 10.1 Hz, 1H), 5.41 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.94 (dd, *J* = 15.5, 10.1 Hz, 1H), 6.03 (d, *J* = 13.5 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 14.3, 25.9, 49.1, 66.5, 103.1, 128.06, 128.11, 141.1. ^{13}C NMR (99.5 MHz, C_6D_6) δ 14.6, 26.4, 49.1, 66.3, 103.5, 127.2, 129.3, 141.4. HRMS (EI) calcd for $C_{10}H_{17}NO$ 167.1310, found 167.1317.

5. Cyclopropanation of 2b. To a solution of **2b** (Table 3. entry 3; 201 mg) in benzene (2 mL) was added 1.2 mL of Et_2Zn in hexane (1.0 *N*; 1.2 mmol of Et_2Zn) at 0 °C. To the mixture was added CH_2I_2 (97 μL, 1.2 mmol) dropwise at that temperature. The resultant yellow suspension was gradually warmed to ambient temperature and then was allowed to further stir for 2 h. The reaction mixture was diluted with ether (4 mL) and then quenched by addition of 10% aqueous NH_4OH solution (4 mL). The organic layer was separated and dried over $MgSO_4$. Purification by silica gel chromatography (hexane/ether = 9:1) gave *trans*-*N*-(2-phenylcyclopropyl)-*N*-methylaniline (**4**) in 61% yield (136 mg).

***trans*-*N*-(2-Phenylcyclopropyl)-*N*-methylaniline (4):** IR (neat) ν 3026, 2930, 2871, 1600, 1502, 1340, 1115, 910, 753, 695 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.30-1.38 (m, 2H), 2.08 (ddd, *J* = 9.6, 6.6, 3.3 Hz, 1H), 2.59 (m, 1H), 3.04 (s, 3H), 6.77 (t, *J* = 7.1 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.20-7.25 (m, 3H), 7.33 (dd, *J* = 7.7, 7.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.8, 27.5, 38.7, 44.1, 113.9, 117.7, 125.9, 126.0, 128.5, 129.0, 141.2, 150.4; HRMS (EI) calcd for $C_{16}H_{17}N$ 223.1361, found 223.1360.



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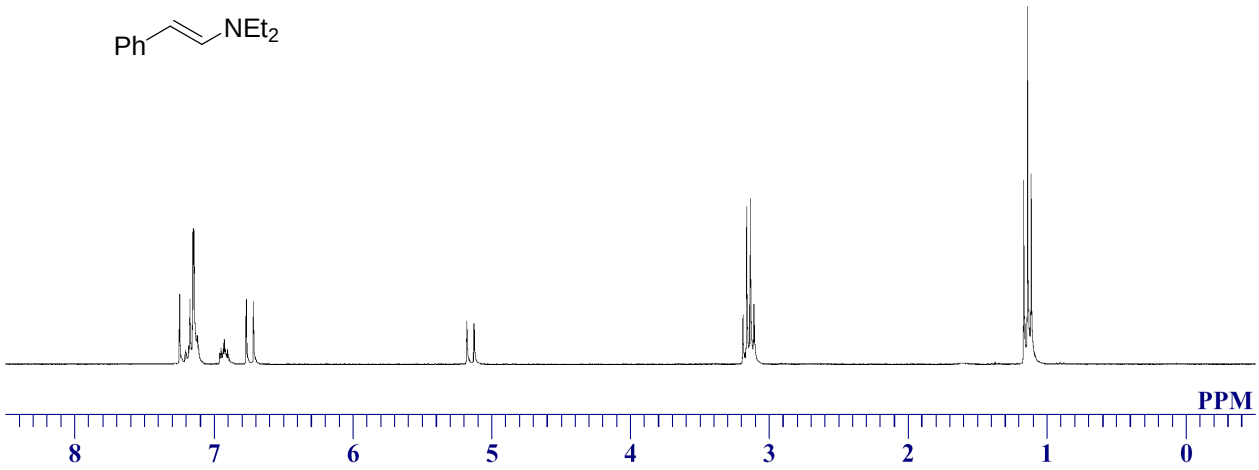
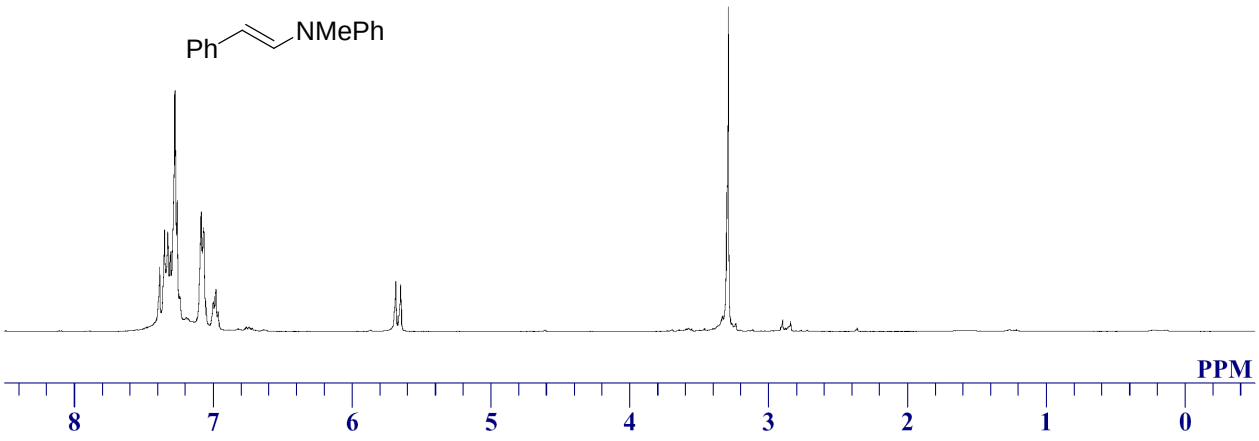
7. NMR Spectra of Enamines and Cyclopropanation Product 4

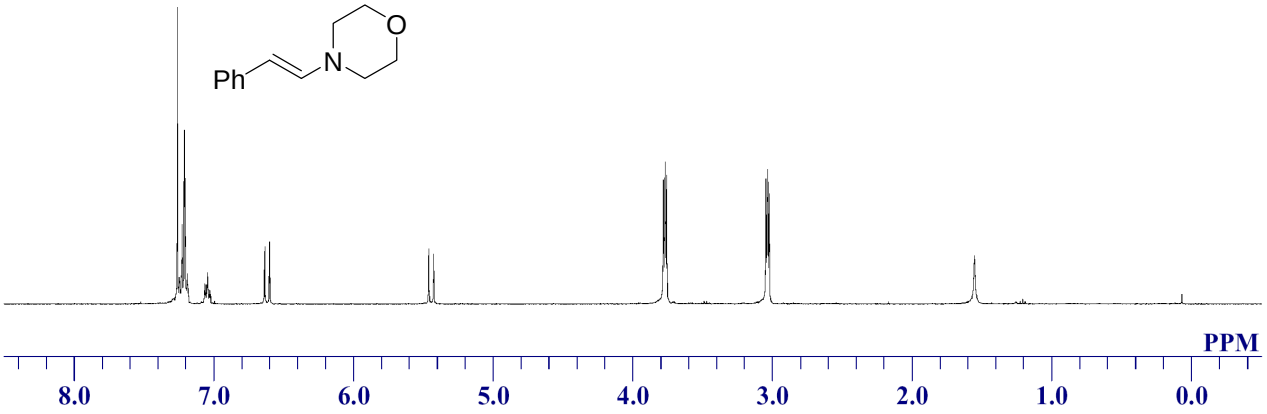
(*E*)-*N*,*N*-Diethyl-styrylamine (2a) : Table 2, Entry 1



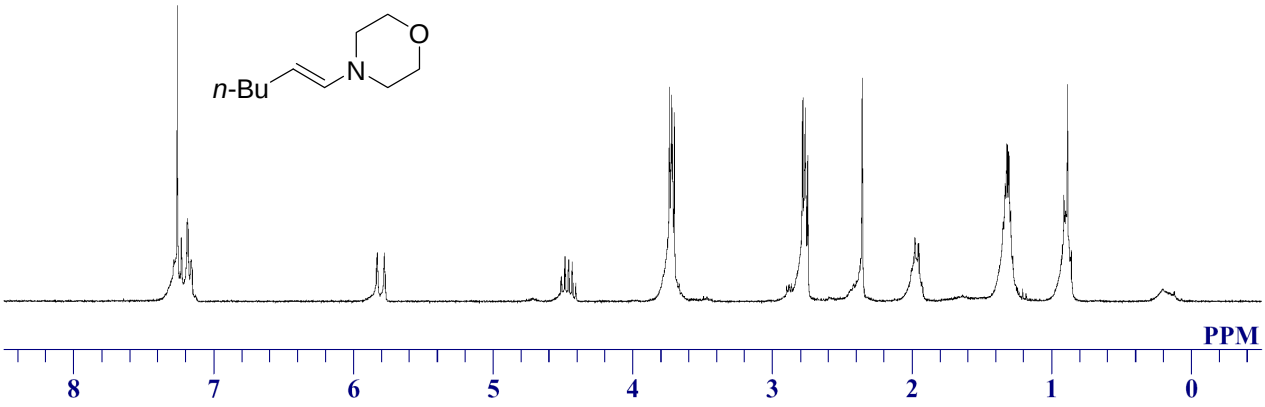
(*E*)-*N*-Methyl-*N*-phenylstyrylamine (2b) : Table 3, Entry 2



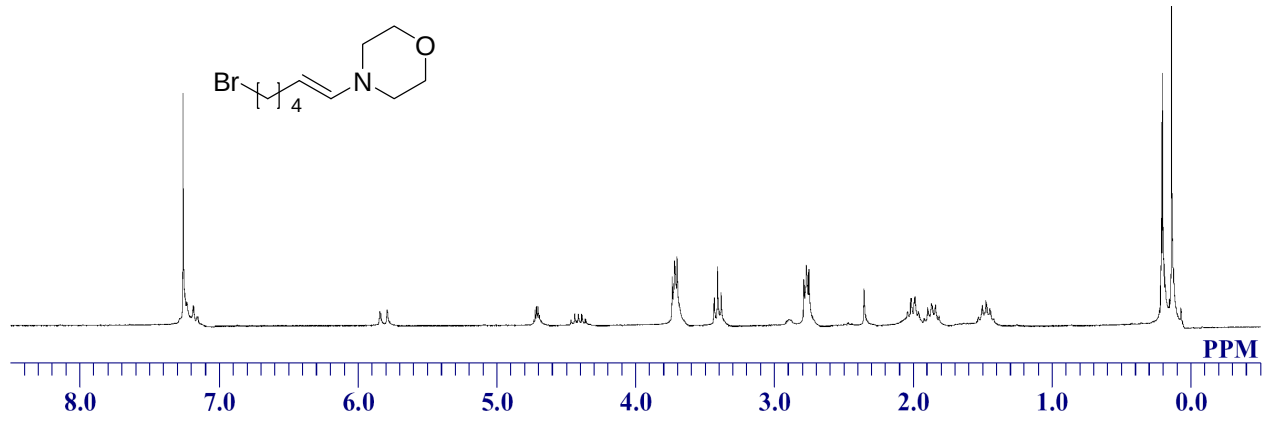
(*E*)-4-Styrylmorpholine (2c) : Table 3, Entry 3



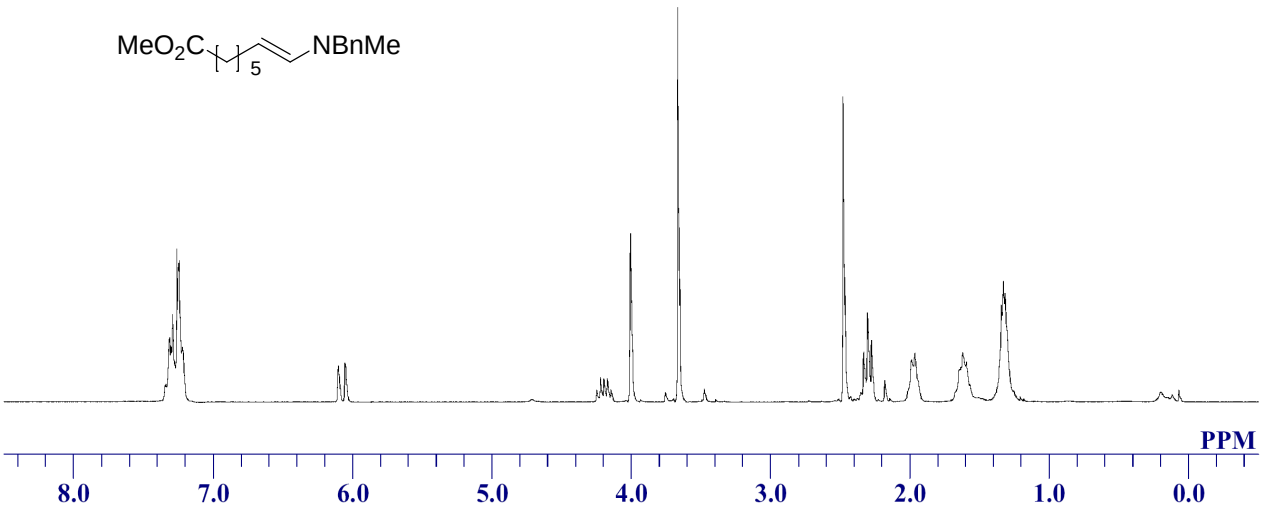
(*E*)-4-(1-Hexenyl)morpholine (2d) : Table 3, Entry 4



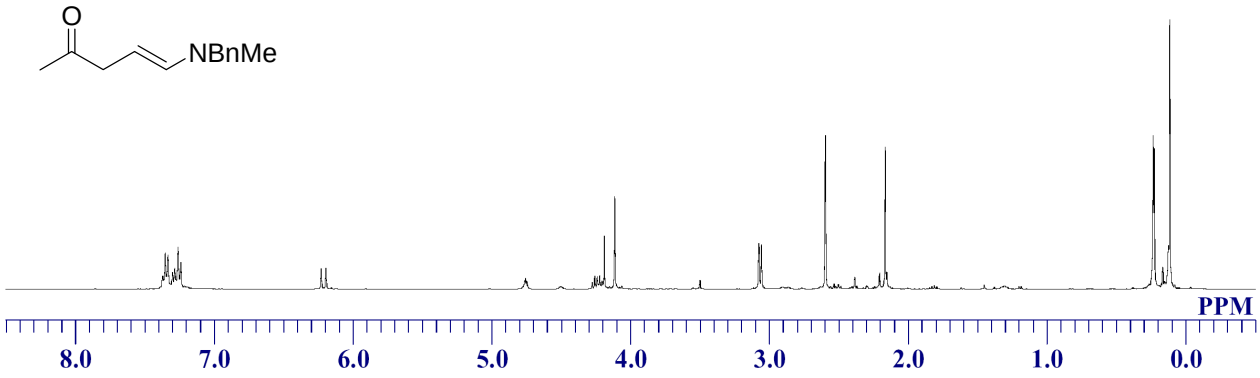
(*E*)-4-(6-Bromo-1-hexenyl)morpholine (2e) : Table 2, Entry 5



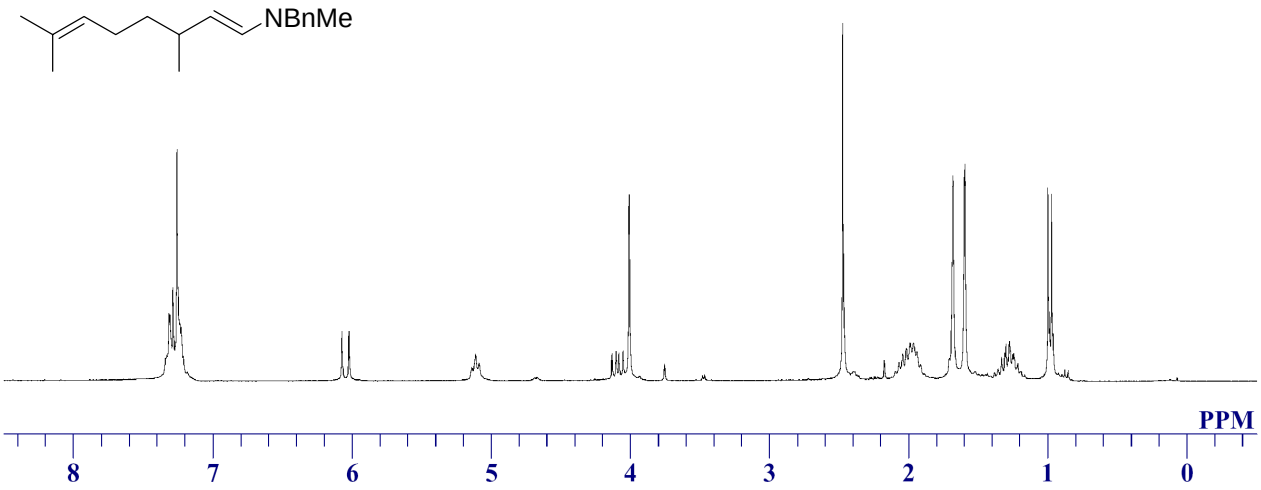
(*E*)-*N*-Benzyl-*N*-methyl-7-carbomethoxy-1-heptenylamine (2f): Table 3, Entry 6



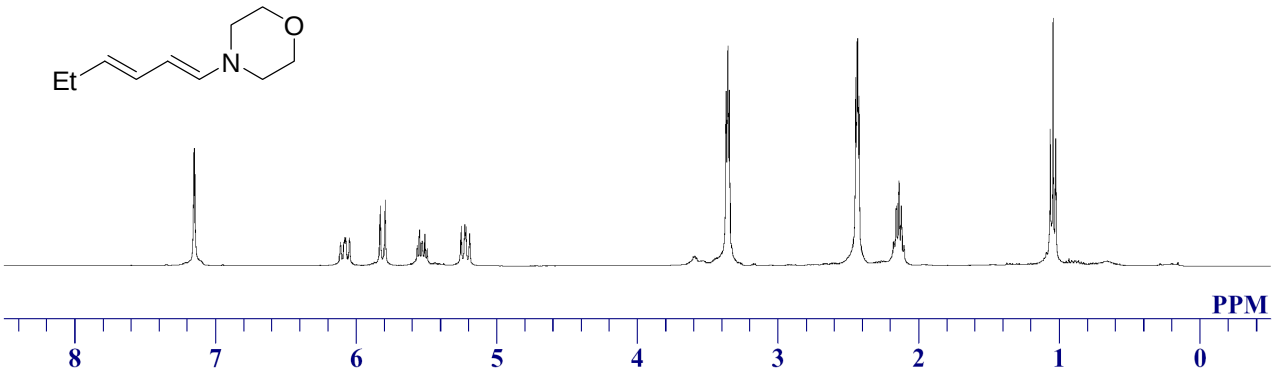
_N_-Benzyl-_N_-methyl-4-oxo-1-pentenylamine (2g) : Table 2, Entry 7



_N_-Benzyl-_N_-methyl-3,7-dimethyl-oct-1,6-dienylamine (2h) : Table 3, Entry 7



(_E_,_E_)-4-(1,3-Hexadienyl)morpholine (2i) : Table 3, Entry 10



trans-*N*-(2-Phenylcyclopropyl)-*N*-methylaniline (4)