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A Novel C-H Insertion via Deoxygenation of Amides by a Sm/SmI_2 Mixed System

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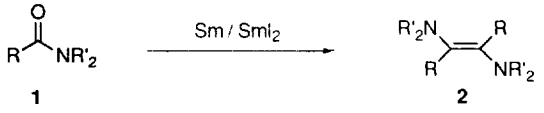
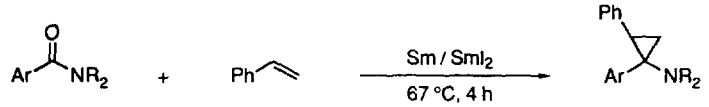
Abstract: *A samarium/samarium diiodide mixed system successfully effects novel aminocyclopropanation and C-H insertion via the deoxygenation of amides. Styrenes undergo aminocyclopropanation by the reaction with aromatic amides, samarium metal, and samarium diiodide. Furthermore, the reaction of aliphatic amides with Sm/SmI_2 in the presence of alkylbenzenes like toluene causes benzylic C-H insertion giving the corresponding phenylethylamine derivatives in good yields.* © 1997 Elsevier Science Ltd.

Recently it has been reported that the use of low-valent samarium species (Sm, Sm(Hg), and SmI_2) in conjunction with dihalomethanes leads to the efficient cyclopropanation of allylic alcohols[1] and metal enolates.[2] In these reactions, samarium-based carbenoids are proposed to act as key species. We have recently revealed that a samarium/samarium diiodide mixed system successfully effects the deoxygenative coupling of amides to provide *vic*-diaminoalkenes (**2**) in high yields (eq 1).[3,4] The coupling reaction is suggested to involve an α-aminocarbene species[5-7] which undergoes dimerization giving **2**. In this article, we wish to report novel aminocyclopropanation and C-H insertion reaction based on the Sm/SmI_2-induced deoxygenation of amides.



1 **2** (1)

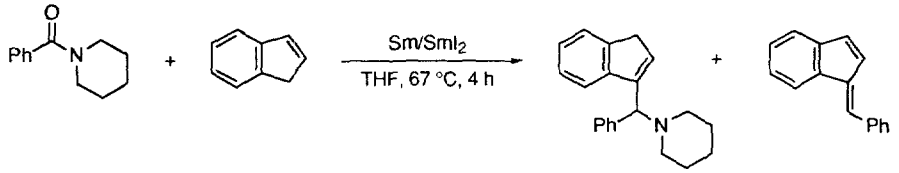
To capture the α-aminocarbene species with olefins, we examined the reaction of *N,N*-disubstituted aromatic amides with Sm/SmI_2 in the presence of several olefinic compounds such as ethyl acrylate, styrene, and butyl vinyl ether. In the case of electron-deficient olefins like ethyl acrylate, the reduction of the olefins with Sm/SmI_2 took place in preference to the desired reduction of amides,[8] whereas electron-rich olefins like butyl vinyl ether could not capture the α-aminocarbene species (the deoxygenative coupling of amides proceeded exclusively). As the result, the desired aminocyclopropanation was found to occur successfully in the presence of excess styrene (eq 2).[9,10]



(2)

	Ar =	R_2N =	
3a	Ph	1-piperidino	45%
3b	*p*-Me-C_6H_4	1-piperidino	56%
3c	β-naphthyl	1-piperidino	58%
3d	Ph	diethylamino	42%

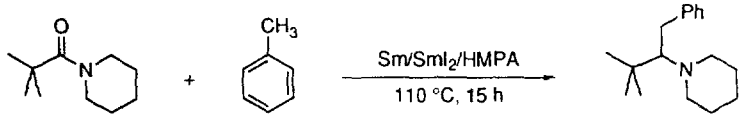
In the case of indene, the desired aminocyclopropanation did not proceed at all, and more interestingly, novel insertion reaction of aminocarbene species to the benzylic C-H bond of indene took place affording **4a** and **4b** in 42% and 38% yields, respectively (eq 3).



4a, 42% **4b**, 38%

(3)

This result prompted us to examine the C-H insertion reaction[11] with several benzylic compounds. In the reaction of aromatic amides with toluene by using Sm/SmI_2, the deoxygenative coupling to give *vic*-diaminoalkenes proceeded in preference to the desired C-H insertion reaction. Contrary to this, the Sm/SmI_2-induced reduction of aliphatic amides like pivaloylpiperidine in the presence of toluene successfully provided the corresponding benzylic insertion product (**5b**) in good yields (eq 4). Compared with the case of aromatic amides, relatively slow generation of aliphatic α-aminocarbene species might contribute to suppression of the dimerization of α-aminocarbene species.

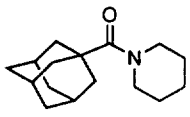
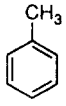
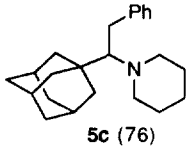
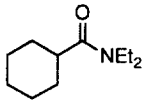
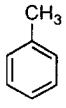
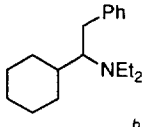
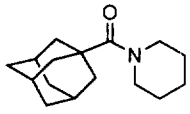
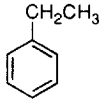
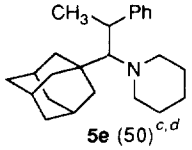
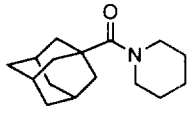
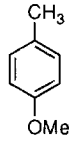
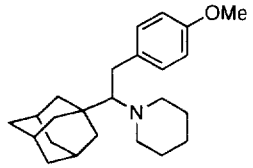
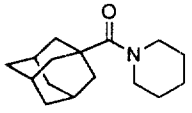
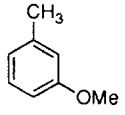
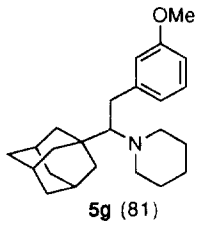


5b, 62%

(4)

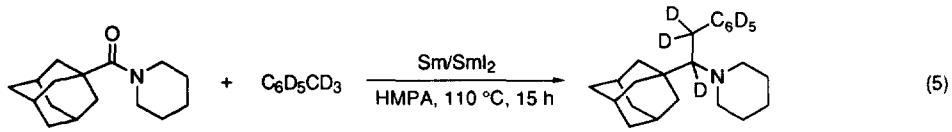
With aliphatic amides bearing a bulky substituent like 1-adamantyl groups, the benzylic C-H insertion proceeded efficiently: the reduction of 1-adamantanecarbonylpiperidine with Sm/SmI_2 in the presence of HMPA[12] in toluene at 110 °C for 15 h selectively afforded the insertion product **5c** in 76% yield (entry 1 in Table 1). Similarly, the benzylic C-H insertion reaction with ethylbenzene (entry 3) and methoxytoluenes (entries 4 and 5) occurred efficiently. In contrast, the use of secondary alkyl amides like *N,N*-diethylcyclohexylamide resulted in the low yield of the desired benzylic insertion product (**5d**), due to the competitive intramolecular insertion to give enamines like *N,N*-(diethylamino)methylenylcyclohexane and also to the formation of **2d** (entry 2).

Table 1. Sm/SmI_2-Induced C-H Insertion Reaction[a]

entry	amide	benzylic compound	product (yield,%)
1			 **5c** (76)
2			 **5d** (25)[b]
3			 **5e** (50)[c,d]
4			 **5f** (53)
5			 **5g** (81)

[a]Amide (1 mmol), benzylic compound (5 mL), Sm (0.5 mmol), SmI_2 (2.2 mmol), HMPA (0.5 mL), 110 °C, 15 h. [b]Bis(*N*,*N*-diethylamino)-1,2-dicyclohexylethene (**2d**, 12%) was also obtained. [c]Obtained as a diastereoisomeric mixture [67/33]. [d]136 °C.

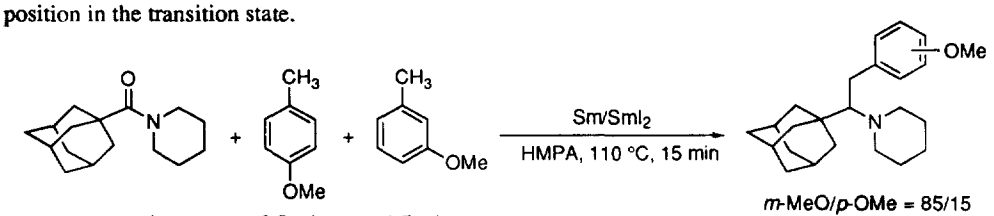
To get insight into the reaction pathway, we examined the C-H insertion reaction by using toluene labeled with deuteriums: Sm/SmI_2-induced reaction of 1-adamantanecarbonylpiperidine with toluene-d_8 afforded the benzylic C-D insertion product (**5c**-d_8) mainly, as indicated in eq 5.



(5)

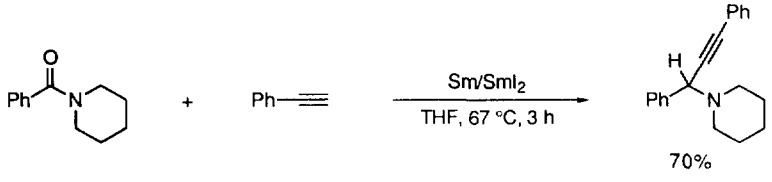
5c-d_8, 96%; **5c-d_7**, 4%

Interestingly, the competitive reaction using *m*- and *p*-methoxytoluenes provided the corresponding *m*- and *p*-methoxyl substituted insertion products with the ratio of 85/15 (eq 6). Although the mechanistic details of this insertion reaction have not been clarified yet, this result suggests the anionic character at the benzylic position in the transition state.



(6)

The present C-H insertion reaction is applicable to terminal acetylenes. For example, the Sm/SmI_2-induced reaction of benzoylpiperidine with phenylacetylene afforded the corresponding propargylic piperidine in good yield (eq 7).



(7)

In summary, this work describes a novel example of C-H insertion into alkylbenzenes *via* the deoxygenation of amides by Sm/SmI_2. Further studies on the scope and precise mechanism are underway.

EXPERIMENTAL

General Comments.

^{1}H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on a JEOL JNM-GSX-270 using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to $\delta(Me_4Si)$ value by using $\delta(CDCl_3) = 76.9$ ppm. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-DX303 in the analytical section of our department. Elemental analyses were also performed there.

Samarium powder in oil (99.9%) was purchased from High Purity Chemicals, and was used after washing with dry pentane, followed by drying for 4 h under reduced pressure.

The C-H insertion reaction was performed as follows. In a 20 mL two-necked flask equipped with a condenser were placed under argon atmosphere samarium powder (2 mmol), freshly distilled (sodium / benzophenone ketyl) THF (5 mL), and 1,2-diiodoethane (1 mmol). Heating of the mixture at 67 °C for 1 h with magnetic stirring provided samarium metal / samarium diiodide mixed reagent (Sm/SmI_2). Then the solvent (THF) was removed under reduced pressure. To the resulting dark-black solid were added toluene (5 mL), HMPA (0.5 mL), and amide (1 mmol). The mixture was stirred under reflux for 16 h. After the reaction was complete, saturated $NaHCO_3$ (40 mL) was added to the reaction mixture, and the products were extracted with diethyl ether (20 mL x 3). The combined extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Purification by column chromatography on silica gel using hexane/Et_2O/Et_3N = 90/9/1 as an eluent provided the desired insertion products. Alternatively, Sm/SmI_2/HMPA in toluene can be prepared conveniently by the reaction of samarium metal (2.1 mmol) with diiodoethane (1.1 mmol) in a mixed solvents of toluene (5 mL) and HMPA (0.5 mL) at the refluxing temperature for 8 h.

The aminocyclopropanation of olefins was performed as follows. The Sm/SmI_2 reagent was prepared as described above. To the THF solution of Sm/SmI_2 were added an amide (1 mmol) and styrene (5 mL), and the resulting solution was stirred at 67 °C for 4 h. After similar workup as described in the C-H insertion reaction, the desired aminocyclopropanation product was purified by column chromatography on silica gel (φ 2 cm x length 10 cm, Fuji silisia, BW-820MH) using hexane/Et_2O = 10/1 as an eluent.

The following spectroscopic and elemental analyses were performed on these samples.

1-Piperidino-1,2-diphenylcyclopropane (3a). A pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.16 (m, 2 H), 1.26 (m, 4 H), 1.38 (dd, 2 H, J = 8.3, 1.0 Hz), 2.11 (m, 2 H), 2.33 (t like, 3 H), 7.14-7.32 (m, 8 H), 7.45 (d, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 24.4, 26.1, 32.0, 50.8, 55.8, 125.4, 126.9, 127.1, 127.5, 128.3, 130.5, 138.8, 138.8; IR (neat) 3056, 3023, 2932, 2801, 1601, 1497, 1443, 1319, 1247, 1118, 1032, 767, 748, 696 cm^{-1}; MS (EI), m/z = 277 (M^+, 27). Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.25; H, 8.43; N, 4.92.

1-Piperidino-1-(*p*-tolyl)-2-phenylcyclopropane (3b). A pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.16 (m, 2 H), 1.26 (m, 4 H), 1.35 (d, 2 H, J = 8.3 Hz), 2.10 (m, 2 H), 2.35 (m, 6 H), 7.11-7.28 (m, 7 H), 7.42-7.45 (m, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.1, 21.6, 24.4, 26.1, 32.1, 50.8, 55.5, 125.3, 127.1, 128.2, 128.3, 130.4, 135.9, 136.4, 138.9; IR (neat) 3020, 2932, 2802, 1603, 1498, 1456, 1246, 1117, 910, 748, 733, 695 cm^{-1}; MS (EI), m/z = 291 (M^+, 39); HRMS calcd for $C_{21}H_{25}N$ 291.1987, found 291.1970.

1-Piperidino-1-(2'-naphthyl)-2-phenylcyclopropane (3c). An orange solid: mp 51-52 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.08 (brs, 2 H), 1.29 (brs, 4 H), 1.52 (brs, 2 H), 2.22 (brs, 2H), 2.45 (brs, 3 H), 7.27-7.54 (m, 9 H), 7.77-7.87 (dd, 2 H, J = 7.4, 18.4 Hz), 8.48, (brs, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.7, 24.1, 26.3, 33.7, 51.2, 53.4, 124.8, 125.1, 125.3, 125.6, 126.0, 127.4, 127.8, 128.3, 128.6, 130.1, 133.4, 133.9, 135.1, 138.7; IR (KBr) 3037, 2931, 2802, 1603, 1496, 1441, 1237, 801, 775, 695 cm^{-1}; MS (EI), m/z = 327 (M^+, 61); HRMS calcd for $C_{24}H_{25}N$ 327.1987, found 327.2003.

1-Diethylamino-1,2-diphenylcyclopropane (3d). A yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (t,

6 H, J = 7.3 Hz), 1.54, (dd, 1 H, J = 4.9, 9.2 Hz), 1.64, (dd, 1 H, J = 4.9, 7.0 Hz), 2.32-2.50 (m, 5 H), 7.21-7.49 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 22.6, 30.8, 46.4, 55.1, 125.4, 126.8, 127.2, 127.7, 128.5, 128.6, 130.0, 138.9; IR (neat) 3024, 2968, 2818, 1601, 1498, 1444, 1257, 1030, 910, 767, 696 cm^{-1}; MS (EI), m/z = 265 (M^+, 57); HRMS calcd for $C_{19}H_{23}N$ 265.1830, found 265.1830. Anal. Calcd for $C_{19}H_{23}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.11; H, 7.88; N, 5.99.

3-(α-Piperidinobenzyl)indene (4a). A yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43 (m, 2 H), 1.57 (m, 4 H), 2.42 (brs, 4 H), 3.31 (s, 2 H), 4.46 (s, 1 H), 6.48 (brs, 1 H) 7.10-7.28 (m, 5 H), 7.38 (d, 1 H, J = 7.3 Hz), 7.46 (d, 2 H, J = 6.0 Hz), 7.69 (d, 1 H, J = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.7, 26.3, 37.7, 53.0, 71.1, 121.2, 123.5, 124.4, 125.8, 126.8, 128.1, 128.6, 130.3, 141.1, 144.2, 144.7, 145.7; IR (neat) 3061, 3024, 2932, 2795, 1600, 1452, 1117, 909, 771, 726, 699 cm^{-1}. MS (EI), m/z = 289 (M^+, 10); HRMS calcd for $C_{21}H_{23}N$ 289.1830, found 289.1834.

1-(Phenylmethylenyl)indene (4b). A yellow solid: mp 82-83 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.02 (s, 1 H), 7.18-7.48 (m, 9 H), 7.60 (dd, 1 H, J = 7.3 Hz), 7.69 (dd, 1 H, J = 6.2 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 119.1, 121.0, 125.1, 126.1, 127.6, 128.3, 128.7, 128.7, 130.2, 134.5, 136.9, 137.5, 140.1, 142.1; IR (KBr) 3110, 1495, 1444, 1336, 795, 750, 697 cm^{-1}; MS (EI), m/z = 204 (M^+, 92); HRMS calcd for $C_{16}H_{12}$ 204.0939, found 204.0949.

2-Piperidino-3,3-dimethylbutylbenzene (5b). A pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (s, 9 H), 1.29-1.39 (m, 6 H), 2.51-2.58 (m, 5 H), 2.77-2.81 (m, 2 H), 7.17-7.26 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.1, 27.2, 28.1, 32.5, 37.6, 53.1, 75.5, 125.3, 127.9, 129.3, 143.1; IR (neat) 3026, 2931, 1604, 1495, 1452, 1440, 1100, 1032, 1008, 729, 698 cm^{-1}; MS (EI), m/z = 245 (M^+, 0.3); HRMS (M^+) calcd for $C_{17}H_{27}N$ 245.2143, found 245.2165.

1-(α-Piperidinophenethyl)adamantane (5c). A white solid: mp 59.5-60.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29-1.41 (m, 6 H), 1.51-1.73 (m, 12 H), 1.96 (brs, 3 H), 2.35 (t like, 1 H, J = 7.08 Hz), 2.51 (brs, 4 H), 2.77 (m, 2 H), 7.14-7.25 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.1, 27.2, 28.9, 31.0, 37.5, 39.6, 40.2, 53.5, 76.4, 125.3, 127.9, 129.4, 143.4; IR (KBr) 3024, 2904, 2846, 1603, 1494, 1452, 1099, 1031, 723, 697 cm^{-1}; MS (EI), m/z = 323 (M^+, 0.4). Anal. Calcd for $C_{23}H_{33}N$: C, 85.39; H, 10.28; N, 4.33. Found: C, 85.15; H, 10.19; N, 4.60.

[α-(Diethylamino)phenethyl]cyclohexane (5d). A pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, 6 H, J = 7.1 Hz), 1.07-1.38 (m, 5 H), 1.65 (m, 5 H), 1.99 (d, 1 H, J = 12.7 Hz), 2.36-2.77 (m, 7 H), 7.14-7.27 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.0, 26.7, 30.9, 31.6, 34.4, 41.3, 44.7, 67.0, 125.2, 128.0, 129.2, 142.8; IR (neat) 3025, 2924, 2852, 1602, 1494, 1449, 1379, 1200, 1068, 724, 698 cm^{-1}; MS (CI), m/z = 260 (M^++1, 27); HRMS (M^++1) calcd for $C_{18}H_{29}N$ 260.2379, found 260.2371.

(*E*)-1,2-Bis(diethylamino)-1,2-di(cyclohexyl)ethene (2d). A colorless solid: mp 79-80 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, 12 H, J = 7.1 Hz), 1.03-1.75 (m, 20 H), 2.26 (m, 2 H), 2.59-2.90 (m, 8 H); ^{13}C

NMR (68 MHz, $CDCl_3$) δ 16.0, 26.5, 27.2, 31.6, 42.5, 49.8, 151.6; IR (KBr) 2965, 2923, 2848, 1450, 1189, 1046, 892, 806, 745, 627 cm^{-1}; MS (EI), *m/z* = 334 (M^+, 79); HRMS (M^+) calcd for $C_{22}H_{42}N_2$ 334.3348, found 334.3339.

1-(α-Piperidino-β-methylphenethyl)adamantane (5e). Isolated as a diastereoisomeric mixture (67:33). Thus, the following spectral and analytical data were obtained by using this sample: ^1H NMR (270 MHz, $CDCl_3$) δ 1.15-1.45 (m, 9 H), 1.55-1.75 (m, 12 H), 1.89-1.94 (brs, 3 H), 2.21-2.29 (d, 1 H, *J* = 6.1, 4.9 Hz), 2.56-2.61 (m, 2 H), 2.77 (m, 1 H), 2.93 (m, 1 H), 3.08-3.19 (m, 1 H), 7.13-7.30 (m, 5 H); ^{13}C NMR (68 MHz, $CDCl_3$) major isomer: δ 23.6, 24.9, 26.8, 29.0, 37.3, 39.9, 41.3, 41.8, 53.7, 80.4, 125.1, 127.4, 128.6, 148.6; minor isomer: δ 20.5, 25.2, 27.4, 29.0, 37.2, 40.1, 41.4, 42.1, 54.1, 80.1, 125.3, 127.5, 127.9, 149.9; IR (neat) 3060, 3024, 2904, 2847, 1601, 1451, 1171, 1101, 759, 699 cm^{-1}; MS (EI), *m/z* = 335 (M^+-2, 0.6), 232 (M^+-$PhCHCH_3$, 100), 202 (M^+-adamantyl, 72); HRMS (M^+-2) calcd for $C_{24}H_{35}N$-2 335.2613, found 335.2609.

1-(α-Piperidino-*p*-methoxylphenethyl)adamantane (5f). A white solid: mp 122.5-123.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.29-1.47 (m, 6 H), 1.53-1.72 (m, 12 H), 1.95 (brs, 3 H), 2.28 (t like, 1 H, *J* = 7.1 Hz), 2.50 (brs, 4 H), 2.70 (d like, 2 H, *J* = 7.8 Hz), 3.77 (s, 3 H), 6.79 (d, 2 H, *J* = 8.5 Hz), 7.15 (d, 2 H, *J* = 8.5 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.1, 27.2, 28.9, 29.9, 37.4, 39.4, 40.2, 53.5, 55.2, 76.4, 113.3, 130.1, 135.2, 157.4; IR (KBr) 2904, 2846, 1612, 1512, 1246, 1177, 1100, 1040, 1004, 819 cm^{-1}; MS (CI), *m/z* = 354 (M^++1, 21). Anal. Calcd for $C_{24}H_{35}NO$: C, 81.54; H, 9.98; N, 3.96. Found: C, 81.72; H, 10.18; N, 3.92.

1-(α-Piperidino-*m*-methoxylphenethyl)adamantane (5g). An colorless oil: ^1H NMR (270 MHz, $CDCl_3$) δ 1.30-1.44 (m, 6 H), 1.47-1.80 (m, 12 H), 1.94 (brs, 3 H), 2.34 (t, 1 H, *J* = 6.8 Hz), 2.53 (brs, 4 H), 2.75 (d, 2 H, *J* = 6.8 Hz), 3.79 (s, 3 H), 6.70 (d, 1 H, *J* = 7.8 Hz), 6.79 (d, 2 H, *J* = 12.2 Hz), 7.18 (t, 1 H, *J* = 7.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.1, 27.2, 28.8, 31.0, 37.4, 39.5, 40.2, 53.4, 55.1, 76.14 110.3, 115.3, 121.9, 128.7, 145.0, 159.3; IR (neat) 2906, 2846, 1601, 1491, 1453, 1263, 1151, 1100, 1054, 1006, 908, 777, 756, 734, 694 cm^{-1}; MS (CI), *m/z* = 354 (M^++1, 16); HRMS (M^++1) calcd for $C_{24}H_{35}NO$ 354.2797, found 354.2785.

1,3-Diphenyl-3-piperidino-propyne. A yellow oil: ^1H NMR (270 MHz, $CDCl_3$) δ 1.35 (m, 2 H), 1.51 (m, 4 H), 2.46 (t, 4 H, *J* = 5.4 Hz), 4.71 (s, 1 H), 7.19-7.35 (m, 6 H), 7.43 (m, 2 H), 7.55 (d, 2 H, *J* = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.3, 25.9, 50.5, 62.2, 85.8, 87.8, 127.4, 127.8, 127.9, 128.1, 128.4, 129.6, 131.6, 138.3; IR (neat) 3060, 3030, 2933, 1599, 1490, 1450, 1262, 1096, 1027, 803, 756, 692 cm^{-1}; MS (EI), *m/z* = 275 (M^+, 11).

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