Supporting Information

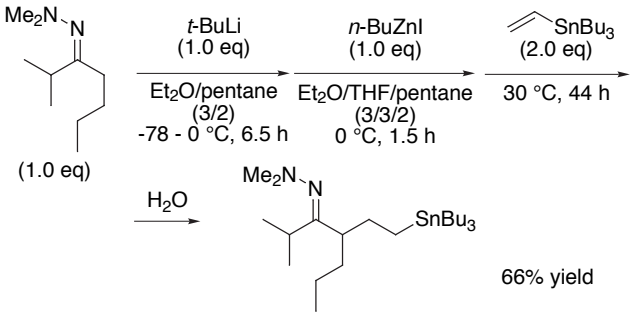
General. All ^{1}H NMR spectra taken at 400 MHz and ^{13}C NMR spectra taken at 100 MHz using JEOL AL-400 are reported in ppm (δ). IR spectra recorded on a React IR 1000 Reaction Analysis System equipped with DuraSamplIR (ASI Applied System) are reported in cm^{-1}. Mass spectra are taken at Simadzu LCMS-QP8000.

Solvent. Anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. and dried over molecular sieves in a storage flask. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 10 ppm.

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co, Aldrich Inc., and other commercial suppliers and were used either distilled or recrystallized before use. $ZnCl_2$ was purchased from Aldrich Inc., and activated by $SOCl_2$ and dried over P_2O_5 under reduced pressure. $ZnBr_2$ was purchased from Kanto Chemical Co., and dried over P_2O_5 under reduced pressure. Phosphate standard buffer solution (pH 6.9 at 20 °C) was purchased from Yoneyama Reagent and used for hydrolysis of *gem*-Zn/Sn dimetallic species.

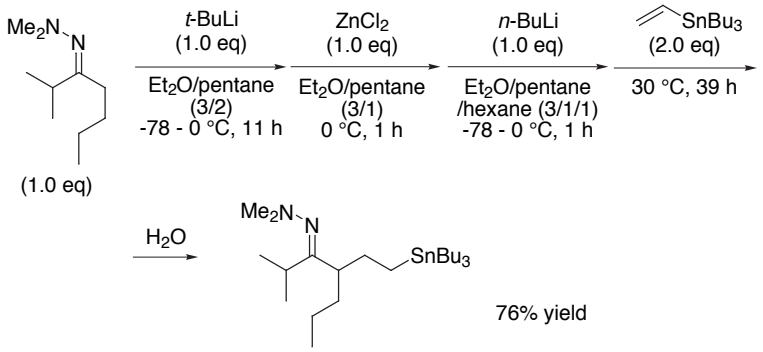
2-Methyl-4-(2-(tributylstannyl)ethyl)heptan-3-one *N,N*-dimethyl-hydrazone (5b):

Carbozincation Procedure Using Butylzinc Iodide (Method A):



To a solution of 2-methylheptan-3-one *N,N*-dimethylhydrazone (210 μL, 1.0 mmol) in Et_2O (1.0 mL) was added *t*-BuLi (1.52 M in pentane, 658 μL, 1.0 mmol) at -78 °C, and the mixture was warmed to 0 °C. After 6.5 h, a solution of *n*-butylzinc iodide (1.04 M in THF, 962 μL, 1.0 mmol) was added to a suspension of lithiated hydrazone at 0 °C. After 1.5 h, tributylvinylstannane (584 μL, 2.0 mmol) was added at 0 °C, and the mixture was warmed to 30 °C. After 44 h, a buffer solution was added. A 30% potassium sodium tartrate was added to wash the mixture. The aqueous layer was extracted three times with Et_2O. The combined organic extracts were washed with saturated sodium chloride solution, dried over sodium sulfate, and evaporated in vacuo. The residual colorless oil (871 mg) was purified on silica gel (44 g, hexane and then 3% EtOAc in hexane) to obtain **5b** (323 mg, 66%, R_f = 0.61, 20% EtOAc in hexane).

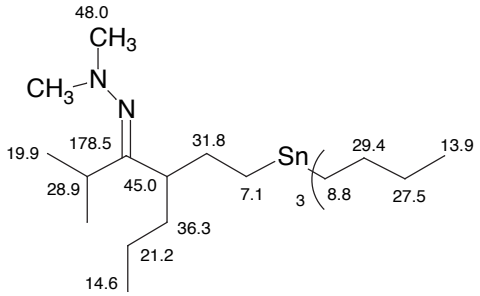
Carbozincation Procedure Reported Previously[1] (Method B):



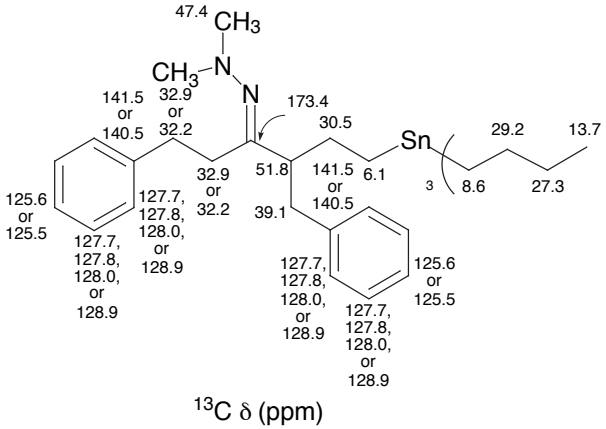
To a solution of 2-methylheptan-3-one *N,N*-dimethylhydrazone (84.1 μL, 0.40 mmol) in Et_2O (0.40 mL) was added *t*-BuLi (1.52 M in pentane, 263 μL, 0.40 mmol) at -78 °C, and the mixture was warmed to 0 °C. After 11 h, $ZnCl_2$ (1.0 M in Et_2O, 0.40 mL, 0.40 mmol) was added to a white suspension of lithiated hydrazone at 0 °C. After 1 h, BuLi (1.60 M in hexane, 250 μL, 0.40 mmol) was added to the white suspension of zincated hydrazone at -78 °C, and the mixture was warmed to 0 °C.

After 1 h, tributylvinylstannane (234 μL, 0.80 mmol) was added to the white suspension at 0 °C, and the mixture was warmed to 30 °C. After 39 h, the standard buffer solution was added to the reaction mixture. The same work up procedure as described for Method A led to obtain **5b** (148 mg, 76%).

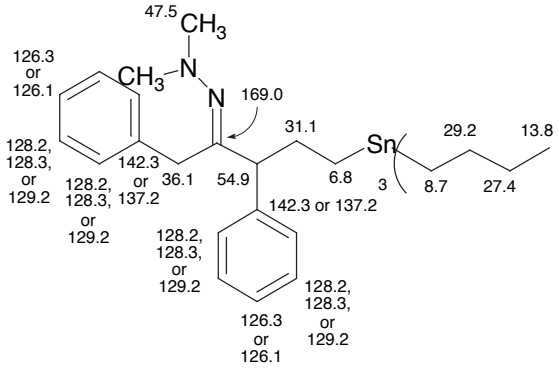
5b: IR (neat): 2956 (s), 2926 (s), 2872, 2852 (s), 1623, 1465 (s), 1418, 1377, 1362, 1340, 1293, 1195, 1154, 1071, 1021, 975, 834, 669 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) **δ**.65-0.94 (m, 20H, $CHCH_2CH_2Sn$, $CH_3CH_2CH_2CH_2Sn$, $CH_3CH_2CH_2CH_2Sn$, $CH_3CH_2CH_2CH$), 1.04 (d, J = 7.0 Hz, 3H, $CH(CH_3)$ (CH'_3)), 1.05 (d, J = 7.0 Hz, 3H, $CH(CH_3)$ (CH'_3)), 1.21-1.34 (m, 8H, $CH_3CH_2CH_2CH$, $CH_3CH_2CH_2CH_2Sn$), 1.34-1.78 (m, 10H, $CH_3CH_2CH_2CH_2Sn$, $CH_3CH_2CH_2CH$, $CHCH_2CH_2Sn$), 2.13 (quint, J = 6.6 Hz, 1H, $CHCH_2CH_2Sn$), 2.38 (s, 6H, $N(CH_3)_2$), 3.52 (septet, J = 7.0 Hz, 1H, $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.1, 8.8 (3C), 13.9 (3C), 14.6, 19.9 (2C), 21.2, 27.5 (3C), 28.9, 29.4 (3C), 31.8, 36.3, 45.0, 48.0 (2C), 178.5; Anal. Calcd for $C_{24}H_{52}N_2Sn$: C, 59.15; H, 10.75; N, 5.75; Found: C, 59.17; H, 10.68; N, 5.63.



4-Benzyl-1-phenyl-6-(tributylstannyl)hexan-3-one *N*,*N*-dimethylhydrazone (5a): R_f = 0.85, 20% EtOAc in hexane; IR (neat): 2954 (s), 2924 (s), 2871, 2852 (s), 1631 (br), 1604, 1496 (s), 1465, 1454 (s), 1419, 1376, 1340, 1292, 1156, 1072, 1030, 1021, 833 (br), 745 (s), 697 cm-1 (s); ^{1}H NMR (400 MHz, CDCl3) δ 0.6-0.85 (m, 2H, $CHCH_2CH_2Sn$), 0.79 (m, 6H, $CH_3CH_2CH_2CH_2Sn$), 0.87 (m, 9H, $CH_3CH_2CH_2CH_2Sn$), 0.87 (m, 6H, $CH_3CH_2CH_2CH_2Sn$), 1.44 (m, 6H, $CH_3CH_2CH_2CH_2Sn$), 1.6-1.85 (m, 2H, $CHCH_2CH_2Sn$), 2.31-2.63 (m, 11H, CH_2CH_2Ph, $N(CH_3)_2$, CH_2CH_2Ph, $CHCH_2Ph$), 2.76-2.88 (m, 2H, $CHCH_2Ph$), 7.1-7.3 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.1, 8.6 (3C), 13.7 (3C), 27.3 (3C), 29.2 (3C), 30.5, 32.2, 32.9, 39.1, 47.4 (2C), 51.8, 125.5, 125.6, 127.7 (2C), 127.8 (2C), 128.0 (2C), 128.9 (2C), 140.5, 141.5, 173.4; Anal. Calcd for $C_{33}H_{54}N_2Sn$: C, 66.34; H, 9.11; N, 4.69; Found: C, 66.57; H, 9.12; N, 4.55.



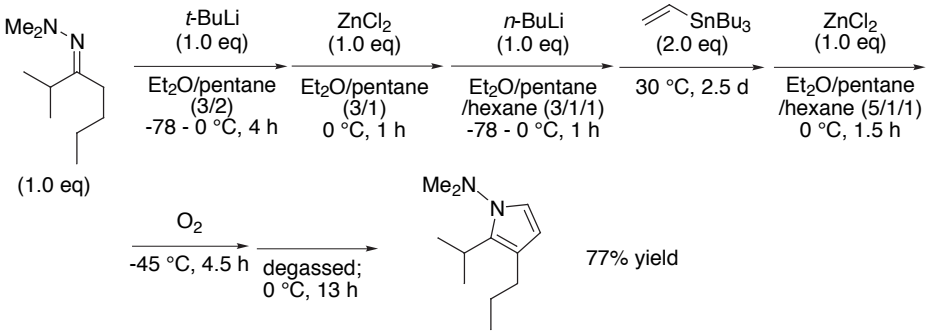
1,3-diphenyl-5-(tributylstannyl)pentan-2-one *N*,*N*-dimethylhydrazone (5c): R_f = 0.73, 20% EtOAc in hexane; IR (neat) 3083, 3064, 3028, 2954 (s), 2925(s), 2871, 2854(s), 2816, 2770 (br), 1601, 1508, 1495, 1453, 1340, 907, 757, 734, 701 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.3-1.1 (m, 17H, $CHCH_2CH_2Sn$, $CH_3CH_2CH_2CH_2Sn$, $CH_3CH_2CH_2CH_2Sn$), 1.1-1.6 (m, 12H, $CH_3CH_2CH_2CH_2Sn$, $CH_3CH_2CH_2CH_2Sn$), 1.6-2.3 (m, 2H, $CHCH_2CH_2Sn$), 2.51 (s, 6H, $N(CH_3)_2$), 2.98 (d, J = 14.2 Hz, 1H, CHH'Ph), 3.19 (t, J = 7.0 Hz, 1H, $C(=NNMe_2)CHPh$), 4.29 (d, J = 14.2 Hz, 1H, CHH'Ph), 7.0-7.3 (m, 10H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8 ($CHCH_2CH_2Sn$), 8.7 (3C), 13.8 (3C), 27.4 (3C), 29.2 (3C), 31.1, 36.1, 47.5 (2C), 54.9, 126.1, 126.3 (2C), 128.2 (2C), 128.3 (2C), 128.3 (2C), 129.2, 137.2, 142.3, 169.0; ESI-MS (MeOH): *m*/*z* 571 $[M+H]^+$.



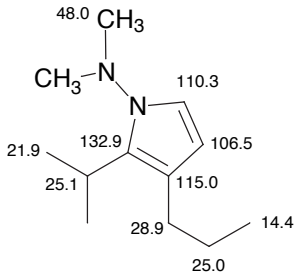
^{13}C δ (ppm)

1-(Dimethylamino)-2-(1-methylethyl)-3-propyl-1*H*-pyrrole (4b):

(Representative Procedure for Synthesis of 1-(dimethylamino)-1*H*-pyrrole)



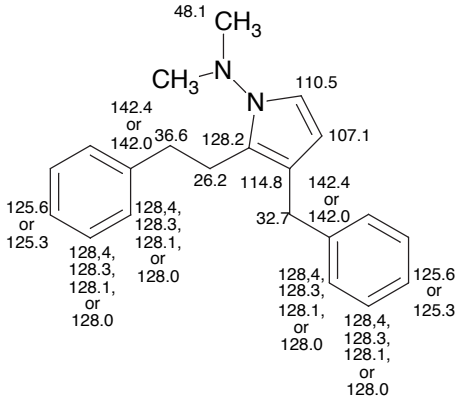
To *gem*-Zn/Sn dimetallic prepared from hydrazone **1b** by the carbozincation Method A or B was added a solution of $ZnCl_2$ (1.0 M in Et_2O, 0.40 mL, 0.40 mmol) at 0 °C. After 1 h, the reaction mixture was stirred under O_2 atmosphere at -45 °C for 4.5 h. The suspension thus obtained was degassed and stirred under N_2 atmosphere at 0 °C for 13 h. After the addition of triethylamine (112 μL, 0.80 mmol) at 0 °C, the reaction mixture was directly passed through a column filled with silica gel (20.0 g, hexane and then 3%-10% EtOAc in hexane). The crude product thus obtained (214 mg) was further purified on silica gel (11 g, hexane and then 3%-10% EtOAc in hexane) to obtain **4b** (60 mg, 77%, colorless oil, R_f = 0.64, 20% EtOAc in hexane): IR (neat): 2955 (s), 2928 (s), 2896 (s), 1454 (s), 1376, 1354, 1261, 1200, 1106, 1093, 1019, 982 (s), 911 (s), 820, 801, 733, 672 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.29 (d, *J* = 7.2 Hz, 2H, $CH(CH_3)_2$), 1.52 (tq, *J* = 7.8, 7.4 Hz, 2H, $CH_2CH_2CH_3$), 2.37 (t, *J* = 7.8 Hz, 2H, $CH_2CH_2CH_3$), 2.76 (s, 6H, $N(CH_3)_2$), 3.19 (septet, *J* = 7.2 Hz, 1H, $CH(CH_3)_2$), 5.93 (d, *J* = 3.3 Hz, 1H, CHCHN), 6.75 (d, *J* = 3.3 Hz, 1H, CHCHN); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.9 (2C), 25.0, 25.1, 28.9, 48.0 (2C), 106.5, 110.3, 115.0, 132.9; ESI-MS (MeOH): *m*/*z* 195 $[M+H]^+$.



^{13}C δ (ppm)

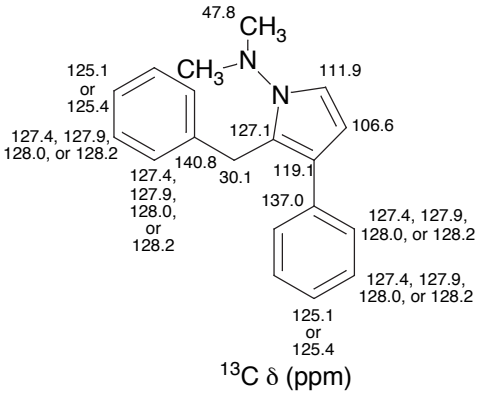
3-Benzyl-1-(dimethylamino)-2-(2-phenylethyl)-1*H*-pyrrole (4a): IR (neat): 2858 (s), 2825 (s), 1061, 1491 (s), 1251 (s), 1319, 1213, 1185, 1162, 1071, 1047, 1036, 1029, 1019, 951, 846, 804, 754, 723 (s), 705, 697 (s), 688, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.67-2.74 (m, 2H, CH_2CH_2Ph), 2.75 (s, 6H, $N(CH_3)_2$), 2.82-2.89 (m, 2H, CH_2CH_2Ph), 3.66 (s, 2H, $PhCH_2C(Ar)$), 5.89 (d, *J* = 3.0 Hz, 1H, CHCHN),. 6.81 (d, *J* = 3.0 Hz, 1H, CHCHN), 7.09-7.29 (m, 10H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 32.7, 36.6, 48.1 (2C), 107.1, 110.5, 114.8, 125.3, 125.6, 128.0 (2C), 128.1 (2C), 128.2,

128.3 (2C), 128.4 (2C), 142.0, 142.4; APCI-MS (positive mode): *m/z*: 305 $[M+H]^+$; Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.79; H, 8.14; N, 9.14.



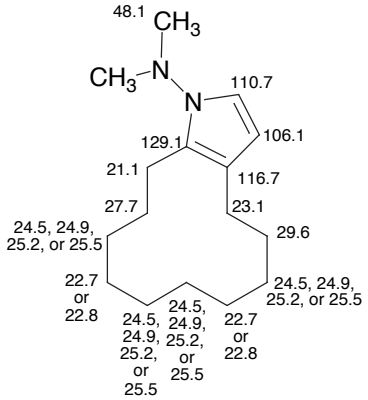
^{13}C δ (ppm)

1-(Dimethylamino)-2-benzyl-3-phenyl-1*H*-pyrrole (4c): ^1H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 6H, $N(CH_3)_2$), 4.17 (s, 2H, CH_2), 6.38 (d, *J* = 3.2 Hz, 1H, C*H*CHN), 6.98 (d, *J* = 3.2 Hz, 1H, CHC*H*N), 7.03-7.44 (m, 10H, aromatic C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 47.8 (2C), 106.6, 111.9, 119.1, 125.1, 125.4, 127.1, 127.4 (2C), 127.9 (2C), 128.0 (2C), 128.2 (2C), 137.0. 140.8.



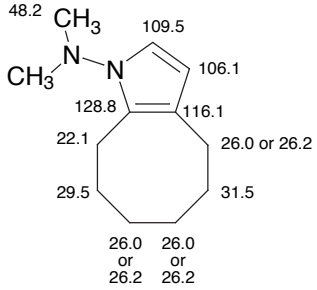
^{13}C δ (ppm)

1-(Dimethylamino)-1,4,5,6,7,8,9,10,11,12,13-undecahydrocyclododeca[b]pyrrole (4d): IR (neat): 2987, 2926 (s), 2853 (s), 2825, 2782, 1711, 1467 (s), 1454 (s), 1444, 1348, 1310, 1260, 1017, 965, 906, 766, 754, 708, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24-1.33 (m, 4H, $CH_2CH_2CH_2C(Ar)$), 1.33-1.39 (m, 4H, $CH_2CH_2CH_2CH_2CH_2C(Ar)$), 1.39-1.50 (m, 4H, $CH_2CH_2CH_2CH_2C(Ar)$), 1.56-1.65 (m, 2H, CH_2CH_2CCN), 1.65-1.74 (m, 2H, CH_2CH_2CN), 2.37 (t, *J* = 7.2 Hz, 2H, CH_2CCN), 2.55 (t, *J* = 7.0 Hz, 2H, CH_2CN), 2.76 (s, 6H, $N(CH_3)_2$), 5.96 (d, *J* = 3.2 Hz, 1H, C*H*CHN), 6.83 (d, *J* = 3.2 Hz, 1H, CHC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 22.7, 22.8, 23.1, 24.5, 24.9, 25.2, 25.5, 27.7, 29.6, 48.1 (2C), 106.1, 110.7, 116.7, 129.1; APCI-MS (positive mode): *m/z*: 249 $[M+H]^+$.



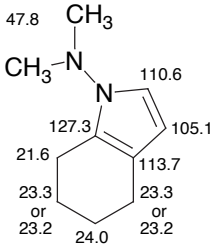
^{13}C δ (ppm)

1-(Dimethylamino)-1,4,5,6,7,8,9-heptahydrocycloocta[b]pyrrole (4e): IR (neat): 3090, 2988, 2952, 2922 (s), 2851 (s), 2825, 2783, 1453 (s), 1260 (s), 1159, 1016, 937, 908, 797, 783, 749, 711, 670 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) _ 1.34-1.44 (m, 4H, CH_2CH$_2$CH$_2$C(Ar)), 1.52-1.65 (m, 4H, CH_2CH$_2$C(Ar)), 2.54 (t, *J* = 6.2 Hz, 2H, CH_2CCN), 2.74 (t, *J* = 6.2 Hz, 2H, CH_2CN), 2.77 (s, 6H, N(CH_3)$_2$), 5.89 (d, *J* = 3.0 Hz, 1H, C*H*CHN), 6.79 (d, *J* = 3.0 Hz, 1H, CHC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 26.0 (2C), 26.2, 29.5, 31.5, 48.2 (2C), 106.1, 109.5, 116.1, 128.8; APCI-MS (positive mode): *m*/*z*: 193 $[M+H]^+$.



^{13}C δ (ppm)

1-(Dimethylamino)-4,5,6,7-tetrahydro-1*H*-indole (4f): IR (neat) 2954, 2925 (s), 2853 (s), 1741 (s), 1466, 1453 (s), 1445, 1373, 1291, 1260 (s), 1241, 11633, 1126, 1093, 1037, 1019, 912 (s), 802 (s), 732 (s). 702, 678 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 1.66-2.86 (m, 4H, CH$_2$CH_2CH_2CH$_2$), 2.48 (t, *J* = 6.0 Hz, 2H, CH_2CCN), 2.56 (t, *J* = 6.2 Hz, 2H, CH_2CN), 2.77 (s, 6H, N(CH_3)$_2$), 5.92 (d, *J* = 3.0 Hz, 1H, C*H*CHN), 6.78 (d, *J* = 3.0 Hz, 1H, CHC*H*N); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.2, 23.3, 24.0. 47.8 (2C), 105.1, 110.6, 113.7, 127.3; APCI-MS (positive mode): *m*/*z*: 165 $[M+H]^+$.

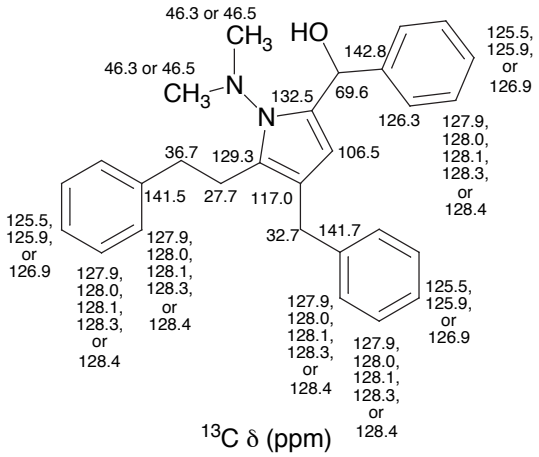


^{13}C δ (ppm)

(4-Benzyl-1-(dimethylamino)-5-(2-phenylethyl)-1*H*-pyrrol-2-yl) phenylmethanol:

(Procedure for Directed Litiation of 1-(dimethylamino)-1*H*-pyrrole)

To a mixture of 3-benzyl-1-(dimethylamino)-2-(2-phenylethyl)-1*H*-pyrrole (**4a**) (48 mg, 0.16 mmol) and *N,N,N',N'*-tetramethylethylenediamine (26 μL, 0.17 mmol) was added BuLi (1.60 M in hexane, 108 μL, 0.17 mmol) at room temperature, and the dark brown solution thus obtained was warmed up to 50 °C. After 1.5 h, benzaldehyde was added dropwise at 0 °C. The resulting orange solution was stirred at 0 °C for 3.5 h, and the standard buffer solution was added. The standard aqueous work up procedure and purification on silica gel afforded the title compound (45 mg, 70%, R_f = 0.26, 20% EtOAc in hexane): ^1H NMR (400 MHz, $CDCl_3$) δ 2.70-2.78 (m, 2H, CH$_2$CH_2Ph), 2.82-2.92 (m, 2H, CH_2CH$_2$Ph), 2.88 (s, 3H, N(CH_3) (CH$_3$)), 2.96 (s, 3H, N(CH$_3$) (CH_3)), 3.27 (d, *J* = 6.2 Hz, 1H, O*H*), 3.69 (s, 2H, PhCH_2C(Ar)), 5.52 (s, 1H, C*H*CRN),. 5.87 (d, *J* = 6.2 Hz, 1H, C*H*OH), 7.0-7.5 (m, 15H, aromatic C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 32.7, 36.7, 46.3, 46.5, 69.6, 106.5, 117.0, 125.5, 125.9, 126.3 (2C), 126.9, 127.9 (2C), 128.0 (2C), 128.1 (2C), 128.3 (2C), 128.4 (2C), 129.3, 132.5, 141.5, 141.7, 142.8; ESI-MS (MeOH): *m*/*z*: 433 $[M+23 (Na)]^+$.



Removal of *N,N*-Dimethylamino Group

Reductive removal of *N,N*-dimethylamino group under Birch condition was carried out using the same procedure reported in literature.[2]

(1) Kubota, K.; Nakamura, E. *Angew. Chem. Int. Ed. Engl.* **1997,** *36*, 2491-2493; Nakamura, E.; Kubota, K. *Tetrahedron Lett.* **1997**, *38*, 7099-7102.
(2) Enders, D.; Maaßen, R.; Han, S.-H. *Liebigs Ann.* **1996**, 1565-1574.