Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Endergonic Addition of *N*-Methylamines to Aromatic Ketones Driven by Photochemical Offset of the Entropic Cost

† *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.*

‡*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan.*

E-mail: iwamoto@scl.kyoto-u.ac.jp

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1. General.

All reactions dealing with air- or moisture-sensitive compounds were carried out in well-dried reaction vessels under a positive pressure of dry argon. Photoreactions were carried out using an LED lamp (CCS, HLUV–126UV365, 365 nm). Flash column chromatography was performed on Flash column chromatography on Wakogel 60N, 38–100 μm or on a Biotage SP1 Flash Purification System with prepacked silica cartridges. Preparative recycling gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent.

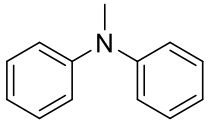
^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400NR NMR spectrometer (391.8 and 98.5 MHz, respectively). The ^{1}H chemical shift values are reported in parts per million (ppm, δ scale) and referenced to the ^{1}H resonance of tetramethylsilane (δ 0.00). The ^{13}C chemical shift values are reported in parts per million, and referenced to the ^{13}C resonance of $CDCl_3$ (δ 77.16). Data are

presented as: chemical shift, multiplicity, coupling constant in Hertz (Hz) and signal area integration in natural numbers. NMR yield was determined by using 1,1,2,2–tetrachloroethane as an internal standard.

Unless otherwise noted, commercially available materials were used without purification. Water content of the solvents was determined with a Karl Fischer Moisture Titrator (MKC-610, Kyoto Electronics Company) to be less than 15 ppm.

2. Preparation of Starting Materials

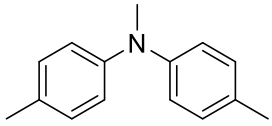
N,*N*–methylpheneylaniline (2a)



To a suspension of sodium hydride (868 mg, 36 mmol) in THF (40 ml) was added diphenylamine (5.07 g, 30 mmol) at room temperature, and then the mixture was stirred for 2 h. After that, methyl iodide (3.0 ml, 45 mmol) was added, and stirred for 24 h at 50 ºC. The reaction mixture was quenched with distilled water (30 ml) and the aqueous layer was extracted with CH_2Cl_2 (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 95/5) and distillation to give the title product as a colorless liquid (3.21 g, 59%).

^{1}H NMR ($CDCl_3$) δ 3.31 (s, 3H), 6.95 (t, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 4H), 7.27 (t, *J* = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 40.4, 120.6, 121.4, 129.0, 149.2. All analytical data are in good accordance with those reported in the literature.[1]

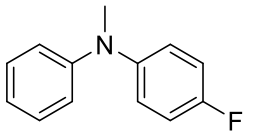
N–methyl–di–*p*–tolylamine (2b)



To a suspension of sodium hydride (291 mg, 12 mmol) in THF (25 ml) was added 4,4'-dimethyldiphenylamine (1.95 mg, 10 mmol) at room temperature, and then the mixture was stirred for 2 h. After that, methyl iodide (1.0 ml, 15 mmol) was added, and stirred for 17 h at room temperature. The reaction mixture was quenched with distilled water (10 ml) and the aqueous layer was extracted with EtOAc (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 100/0 to 80/20) and distillation to give the title product as a colorless liquid (1.58 g, 76%).

^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6H), 3.25 (s, 3H), 6.90 (d, *J* = 8.0 Hz, 4H), 7.06 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 20.8, 40.6, 120.5, 129.8, 130.6, 147.2. All analytical data are in good accordance with those reported in the literature.[2]

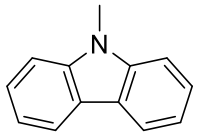
N–methyl–*N*–phenyl–4–fluorolaniline (2c)



To a suspension of sodium hydride (288 mg, 12 mmol) in THF (24 ml) was added 4–fluorophenyl(phenyl)amine (1.88 g, 10 mmol) at 0 ºC, and then the mixture was stirred for 3 h at room temperature. After that, methyl iodide (1.0 ml, 15 mmol) was added, and stirred for 12 h. The reaction mixture was quenched with distilled water (10 ml) and the aqueous layer was extracted with EtOAc (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 100/0 to 80/20) and distillation to give the title product as a colorless liquid (1.06 g, 52%).

^{1}H NMR ($CDCl_3$) δ 3.27 (s, 3H), 6.86–6.91 (m, 3H), 6.97–7.07 (m, 4H), 7.21–7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.7, 116.1 (d, J = 91.6 Hz), 118.2, 120.2, 124.4 (d, J = 34.3 Hz), 129.3, 145.4, 149.5, 158.9 (d, J = 980.5 Hz). All analytical data are in good accordance with those reported in the literature.[1]

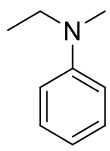
_N_–methylcarbazole (2g)



To a suspension of sodium hydride (144 mg, 6 mmol) in THF (20 ml) was added carbazole (835 mg, 5 mmol) at 0 ºC, and then the mixture was stirred for 2 h at room temperature. After that, methyl iodide (0.5 ml, 8 mmol) was added, and stirred for 20 h. The reaction mixture was quenched with distilled water (10 ml) and the aqueous layer was extracted with CH_2Cl_2 (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by recrystllization with hexane to give the title product as a slightly green solid (603 mg, 67%).

^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H), 7.23 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.47 (t, J = 8.2 Hz, 2H), 8.10 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 29.2, 108.5, 119.0, 120.4, 122.9, 125.8, 141.1. All analytical data are in good accordance with those reported in the literature.[3]

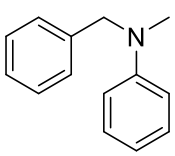
_N_,_N_–ethylmethylaniline



The mixture of _N_–methylaniline (1.1 ml, 10 mmol), potassium carbonate (3.04 g, 22 mmol), bromoethane (0.9 ml, 12 mmol) and acetonitrile (15 ml) was stirred for 15 h at 85 ºC. The reaction mixture was quenched with distilled water (10 ml) and the aqueous layer was extracted with EtOAc (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The product was purified by silica gel column chromatography (hexane/EtOAc = 98/2) and distillation to give the title product as an orange liquid (704 mg, 52%).

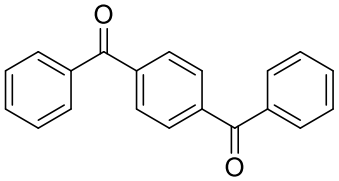
^{1}H NMR ($C_2D_2Cl_4$) δ 1.12 (t, J = 7.3 Hz, 3H), 2.90 (s, 3H), 3.40 (q, J = 7.2 Hz, 2H), 6.66–6.73 (m, 3H), 7.22 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.3, 37.6, 46.9, 112.5, 116.2, 129.3, 149.3. All analytical data are in good accordance with those reported in the literature.[4]

_N_,_N_–benzylmethylaniline



The mixture of *N*–methylaniline (1.1 ml, 10 mmol), potassium carbonate (3.04 g, 22 mmol), benzylbromide (1.2 ml, 12 mmol) and acetonitrile (15 ml) was stirred for 15 h at 85 ºC. The reaction mixture was quenched with distilled water (10 ml) and the aqueous layer was extracted with EtOAc (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 98/2) and distillation to give the title product as a colorless liquid (1.28 g, 65%).
^{1}H NMR ($CDCl_3$) δ 3.00 (s, 3H), 4.52 (s, 2H), 6.69–6.76 (m, 3H), 7.18–7.24 (m, 5H), 7.31 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 38.6, 56.8, 112.5, 116.7, 126.9, 127.0, 128.7, 129.3, 139.2, 149.9. All analytical data are in good accordance with those reported in the literature.[5]

1,4–dibenzoylbenzene



To a solution of terephthaloyl chloride (2.03 g, 10 mmol) in benzene (10 ml) was added $AlCl_3$ (6.76 g, 50 mmol) slowly at 0 ºC, and then the mixture was stirred for 24 h at 50 ºC. The reaction mixture was quenched with distilled water (10 ml) slowly, neutralized with 2 M NaOH aq, and then aqueous layer was extracted with CH_2Cl_2 (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by recrystllization with hexane/CH_2Cl_2 to give the title product as a white solid (603 mg, 67%).
^{1}H NMR ($CDCl_3$) δ 7.52 (t, J = 7.8 Hz, 4H), 7.64 (t, J = 7.6 Hz, 2H), 7.84 (d, J = 7.6 Hz, 4H), 7.90 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 128.6, 129.8, 130.2, 133.1, 137.0, 140.7, 196.0. All analytical data are in good accordance with those reported in the literature.[6]

3. Photoreaction

General Procedure A

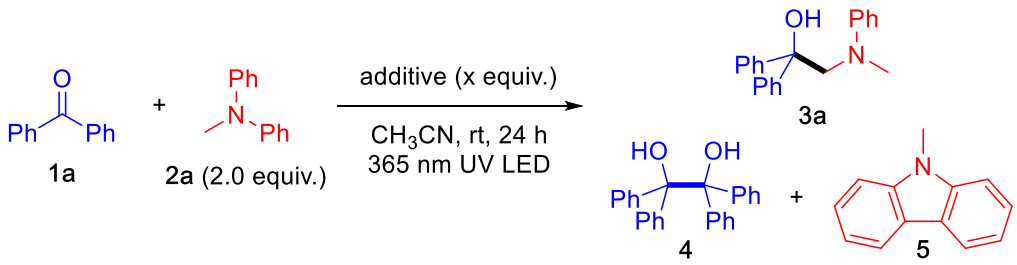
To a dried schlenk filled up with argon gas, aromatic ketone, aniline derivatives (2.0 eq), and base (0.2 eq), CH_3CN (1.0 ml) were added in a glove box. The mixture was stirred for 24 h under irradiation of 365 nm UV LED with a cooling fan. After quenching with 2 M HCl aq followed by extraction with CH_2Cl_2 (10 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The product was purified by silica gel column chromatography (hexane/EtOAc = 100/0 to 80/20).

General Procedure B

To a dried schlenk filled up with argon gas, aromatic ketone, aniline derivatives (4.0 eq), and base (0.4 eq), CH_3CN (5.0 ml) were added in a glove box. The mixture was stirred for 24 h under irradiation of 365 nm UV LED with a cooling fan. After quenching with 2 M HCl aq followed by

extraction with CH_2Cl_2 (10 ml × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The product was purified by GPC.

Table S1. Optimization of base



entry	additive (x)	yield (%)[a]			conversion (%)[a]
		3a	4	5	
1	none	10	81	4	100
2	2,6-lutidine (0.2)	12	25	16	100
3	Li_2CO_3 (0.2)	5	4	20	100
4	LiOH (0.2)	7	N.D.	19	100
5	NaOH (0.2)	69	N.D.	trace	100
6	KOH (0.2)	74	N.D.	trace	100
7	LiOMe	7	N.D.	18	100
8	LiO*t*Bu (0.2)	73	N.D.	trace	100
9	KO*t*Bu (0.2)	48	N.D.	trace	100
10	NaO*t*Bu (0.2)	80	N.D.	trace	98
11	NaO*t*Bu (0.5)	57	N.D.	trace	97
12	NaO*t*Bu (1.0)	53	N.D.	trace	94
13[b]	NaO*t*Bu (0.2)	N.D.	N.D.	trace	11

[a]Determined by ^{1}H NMR. [b]Without light irradiation.
N.D.: not detected. trace: < 1%

Large Scale Synthesis

To a dried schlenk filled up with argon gas, benzophenone (8.7 g, 48 mmol), dimethylaniline (12 ml, 95 mmol), and base (922 mg, 9.6 mmol), CH_3CN (44 ml) were added in a glove box. The mixture was stirred for 24 h under irradiation of 365 nm UV LED with a cooling fan. After quenching with 2 M HCl aq followed by extraction with CH_2Cl_2 (20 ml × 3). The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The product was purified by silica gel column chromatography (hexane/EtOAc = 100/0 to 80/20) and subsequent recrystllization to give the product in 76% yield (11.0 g) as a pale yellow solid.

Reaction under intermittent light-irradiation

The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline **2a** (190.2 mg, 1.04 mmol), benzophenone **1a** (94.8 mg, 0.52 mmol), and sodium

t-butoxide (9.99 mg, 0.10 mmol). Conversion of **1a** and the product yield were monitored by GC analysis.

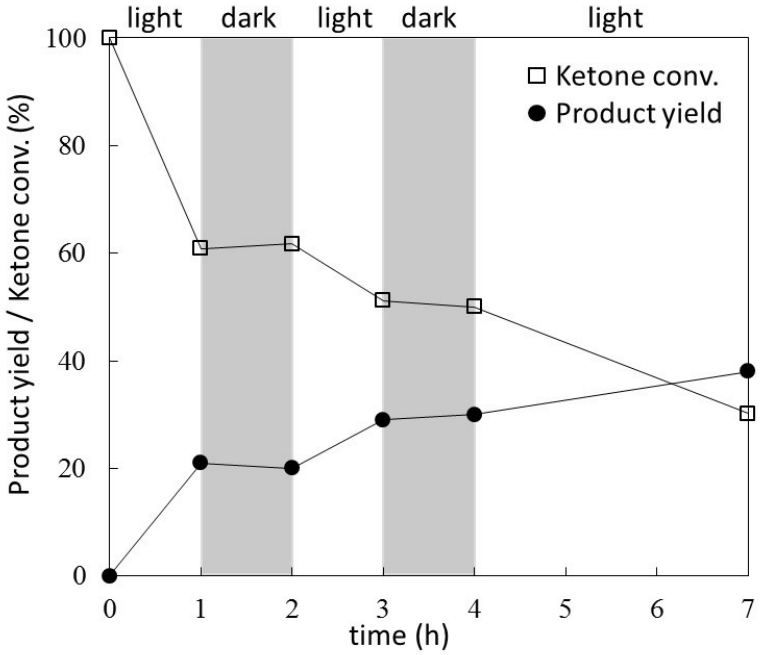
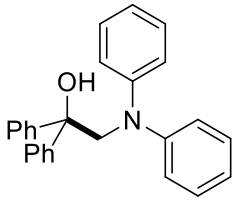


Figure S1. Time profile of reaction between **1a** and **2a** under intermittent light-irradiation.

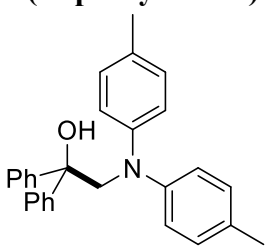
2-(Diphenylamino)-1,1-diphenylethanol (3a)



The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (366.1 mg, 2.00 mmol), benzophenone (181.9 mg, 1.00 mmol), and sodium *t*-butoxide (19.2 mg, 0.20 mmol). The product was obtained in 80% NMR yield. After the purification, the title compound was obtained in 64% yield (234.3 mg).

^{1}H NMR ($CDCl_3$) δ 3.28 (s, $NCH_2C(OH)Ph_2$, 1H), 4.65 (s, $NCH_2C(OH)Ph_2$, 2H), 6.79 (d, J = 7.8 Hz, $N(2,6\text{-}C_6H_5)_2$, 4H), 6.92 (t, J = 7.3 Hz, $N(4\text{-}C_6H_5)_2$, 2H), 7.11–7.22 (m, $N(3,5\text{-}C_6H_5)_2$ & $C(3,4,5\text{-}C_6H_5)_2$, 10H), 7.39 (d, J = 8.2 Hz, $C(2,6\text{-}C_6H_5)_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 64.1, 78.6, 122.2, 122.3, 126.2, 127.0, 128.1, 129.3, 145.1, 149.7; HRMS (EI^+): *m*/*z* $[M]^+$ calcd for $C_{26}H_{23}NO$ 365.1780, found 365.1782. The NMR spectrum is in good accordance with previous literature data.[7]

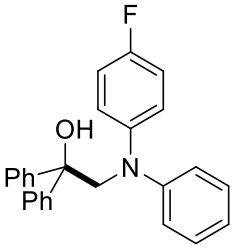
2-(di-p-tolylamino)-1,1-diphenylethanol (3b)



The reaction was performed according to the general procedure A using *N*–methyl–di–*p*–tolylamine (426.9 mg, 2.02 mmol), benzophenone (182.4 mg, 1.00 mmol), and lithium *t*-butoxide (16.3 mg, 0.20 mmol). The product was obtained in 73% NMR yield. The semi-purified product was further purified by recrystallization (Hexane/CH_2Cl_2) to give the title compound in 67% yield (270.3 mg).

^{1}H NMR ($CDCl_3$) δ 2.24 (s, CH_3Ph, 6H), 3.33 (s, NCH$_2$C(OH)Ph$_2$, 1H), 4.57 (s, NCH_2C(OH)Ph$_2$, 2H), 6.66 (d, J = 8.2 Hz, N(2,6-C$_6H_4$CH$_3$)$_2$, 4H), 6.93 (d, J = 8.2 Hz, N(3,5-C$_6H_4$CH$_3$)$_2$, 4H), 7.12–7.22 (m, C(3,4,5-C$_6H_5$)$_2$, 6H), 7.39 (d, J = 7.3 Hz, C(2,6-C$_6H_5$)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 20.7, 64.3, 78.6, 122.2, 126.3, 126.9, 128.1, 129.9, 131.7, 145.4, 147.6; HRMS (FAB$^+$): m/z [M+Na]$^+$ calcd for $C_{28}H_{27}NONa$ 416.1990, found 416.1991.

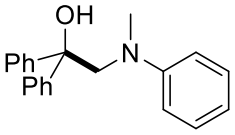
2-(p-fluorophenyl(phenyl)amino)-1,1-diphenylethanol (**3c**)



The reaction was performed according to the general procedure A using *N*,*N*-methyl-(*p*-fluorophenyl)aniline (400.9 mg, 1.99 mmol), benzophenone (182.5 mg, 1.00 mmol), and sodium *t*-butoxide (19.0 mg, 0.20 mmol). The product was obtained in 65% NMR yield. After the purification, the title compound was obtained in 43% yield (164.4 mg).

^{1}H NMR ($CDCl_3$) δ 3.25 (s, NCH$_2$C(OH)Ph$_2$, 1H), 4.61 (s, NCH_2C(OH)Ph$_2$, 2H), 6.70–6.87 (m, 7H), 7.11–7.23 (m, 8H), 7.38 (d, J = 8.4 Hz, C(2,6-C$_6H_5$)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 64.6, 78.6, 116.1 (d, J = 91.2 Hz), 118.9, 120.9, 126.3, 127.0, 127.1, 128.2, 129.3, 145.0, 150.8, 158.2, 159.5 (d, J = 988.0 Hz) ; HRMS (FAB$^+$): m/z [M+Na]$^+$ calcd for $C_{26}H_{22}FNONa$ 406.1583, found 406.1586.

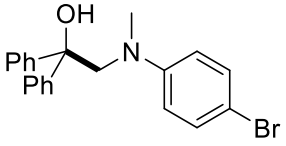
2-(methyl(phenyl)amino)-1,1-diphenylethanol (**3d**)



The reaction was performed according to the general procedure A using *N*,*N*-dimethylaniline (246.0 mg, 2.03 mmol), benzophenone (181.9 mg, 1.00 mmol), and lithium *t*-butoxide (16.3 mg, 0.20 mmol). The product was obtained in 74% NMR yield. After the purification, the title compound was obtained in 67% yield (202.3 mg).

^{1}H NMR ($CDCl_3$) δ 2.45 (s, CH_3NPh, 3H), 3.64 (s, NCH$_2$C(OH)Ph$_2$, 1H), 4.16 (s, NCH_2C(OH)Ph$_2$, 2H), 6.81 (t, J = 7.6 Hz, NCH$_3$(4-C$_6H_5$), 1H), 6.93 (d, J = 8.3 Hz, NCH$_3$(2,6-C$_6H_5$), 2H), 7.20–7.27 (m, NCH$_3$(3,5-C$_6H_5$) & C(4-C$_6H_5$)$_2$, 4H), 7.35 (t, J = 7.8 Hz, C(3,5-C$_6H_5$)$_2$, 4H), 7.55 (d, J = 7.4 Hz, C(2,6-C$_6H_5$)$_2$, 4H); ^{13}C NMR ($C_2D_2Cl_4$) δ 39.7, 66.1, 76.8, 114.6, 118.8, 126.1, 127.3, 128.6, 129.3, 146.1, 152.1; HRMS (FAB$^+$): m/z [M+Na]$^+$ calcd for $C_{21}H_{21}NONa$ 326.1521, found 326.1524. The NMR spectrum is in good accordance with previous literature data.[7]

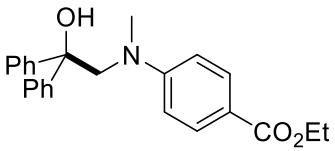
2-(methyl(p-bromophenyl)amino)-1,1-diphenylethanol (**3e**)



The reaction was performed according to the general procedure A using 4-bromo-*N*,*N*-dimethylaniline (400.5 mg, 2.00 mmol), benzophenone (182.0 mg, 1.00 mmol), and sodium *t*-butoxide (19.2 mg, 0.20 mmol). The product was obtained in 55% NMR yield. The semi–purified product was purified by GPC to give the title compound in 55% yield (208.9 mg).

^{1}H NMR ($C_2D_2Cl_4$) δ 2.44 (s, CH_3NAr, 3H), 4.13 (s, NCH_2C(OH)Ph$_2$, 2H), 6.77 (d, J = 9.2 Hz, NCH$_3$(2,6-C$_6H_4$Br), 2H), 7.28–7.31 (m, NCH$_3$(3,5-C$_6H_4$Br) & C(4-C$_6H_5$)$_2$, 4H), 7.38 (t, J = 7.8 Hz, C(3,5-C$_6H_5$)$_2$, 4H), 7.52 (d, J = 8.0 Hz, C(2,6-C$_6H_5$)$_2$, 4H); ^{13}C NMR ($C_2D_2Cl_4$) δ 39.9, 65.6, 77.3, 110.4, 115.9, 126.1, 127.4, 128.6, 131.8, 145.7, 151.0; HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_{21}H_{20}BrNO$ 381.0728, found 381.0725. IR: ν(cm^{-1}) 3056, 1591, 1493, 1449, 1361, 1264, 1179, 1126, 1059, 809, 732, 699, 657, 608.

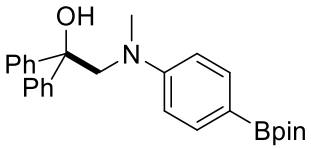
2-(4-ethoxycarbonylphenyl(methyl)amino)-1,1-diphenylethanol (3f)



The reaction was performed according to the general procedure A using 4-ethoxycarbonyl-*N,N*-dimethylaniline (386.6 mg, 2.00 mmol), benzophenone (182.3 mg, 1.00 mmol), and sodium *t*-butoxide (19.1 mg, 0.20 mmol). The product was obtained in 51% NMR yield. After the purification, the title compound was obtained in 40% yield (150.4 mg).

^{1}H NMR ($CDCl_3$) δ 1.36 (t, J = 7.3 Hz, C(=O)OCH$_2$CH_3, 3H), 2.59 (s, CH_3NAr, 3H), 2.91 (s, NCH$_2$C(OH)Ph$_2$, 1H), 4.26 (s, NCH_2C(OH)Ph$_2$, 2H), 4.31 (q, J = 7.2 Hz, C(=O)OCH_2CH$_3$, 2H), 6.79 (d, J = 9.6 Hz, NCH$_3$(2,6-C$_6H_4$C=O), 2H), 7.27 (t, J = 7.3 Hz, C(4-C$_6H_5$)$_2$, 2H), 7.35 (t, J = 7.6 Hz, C(3,5-C$_6H_5$)$_2$, 4H), 7.50 (d, J = 8.2 Hz, C(2,6-C$_6H_5$)$_2$, 4H), 7.85 (d, J = 9.2 Hz, NCH$_3$(3,5-C$_6H_4$C=O), 2H); ^{13}C NMR ($CDCl_3$) δ 14.6, 39.9, 60.4, 64.0, 78.1, 112.2, 119.2, 126.2, 127.5, 128.6, 131.2, 145.5, 154.6, 166.9; HRMS (FAB$^+$): m/z [M+H]$^+$ calcd for $C_{24}H_{26}NO_3$ 376.1913, found 376.1914. IR: ν(cm^{-1}) 1684, 1603, 1523, 1284, 1185, 1127, 770, 698.

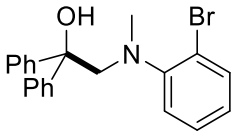
2-(methyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl))amino)-1,1-diphenylethanol (3g)



The reaction was performed according to the general procedure A using *N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine (494.8 mg, 2.00 mmol), benzophenone (182.0 mg, 1.00 mmol), and sodium *t*-butoxide (19.2 mg, 0.20 mmol). The product was obtained in 71% NMR yield. After the purification, the title compound was obtained in 70% yield (301.3 mg).

^{1}H NMR ($CDCl_3$) δ 1.31 (s, B(OC(CH$_3$)$_2$)$_2$, 12H), 2.48 (s, CH_3NAr, 3H), 3.24 (s, NCH$_2$C(OH)Ph$_2$, 1H), 4.21 (s, NCH_2C(OH)Ph$_2$, 2H), 6.84 (d, J = 8.7 Hz, NCH$_3$(2,6-C$_6H_4$B), 2H), 7.25 (t, J = 7.6 Hz, C(4-C$_6H_5$)$_2$, 2H), 7.33 (t, J = 8.0 Hz, C(3,5-C$_6H_5$)$_2$, 4H), 7.51 (d, J = 7.3 Hz, C(2,6-C$_6H_5$)$_2$, 4H), 7.64 (d, J = 8.7 Hz, NCH$_3$(3,5-C$_6H_4$B), 2H); ^{13}C NMR ($C_2D_2Cl_4$) δ 25.1, 39.7, 64.7, 77.6, 83.5, 112.9, 126.2, 127.4, 128.6, 136.3, 145.8, 153.9; HRMS (FAB$^+$): m/z [M+Na]$^+$ calcd for $C_{27}H_{32}NO_3BNa$ 452.2378, found 452.2380. IR: ν(cm^{-1}) 2962, 1604, 1362, 1260, 1091, 1017, 798, 735, 702.

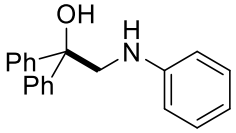
2-(methyl(o-bromophenyl)amino)-1,1-diphenylethanol (3h)



The reaction was performed according to the general procedure A using 2-bromo-*N*,*N*-dimethylaniline (394.0 mg, 1.97 mmol), benzophenone (182.4 mg, 1.00 mmol), and sodium *t*-butoxide (20.2 mg, 0.21 mmol). The product was obtained in 45% NMR yield. The semi–purified product was further purified by GPC to give the title product in 41% yield (157.1 mg).

^{1}H NMR ($CDCl_3$) δ2.40 (s, C*H*$_3$NAr, 3H), 3.92 (s, NC*H*$_2$C(OH)Ph$_2$, 2H), 5.13 (s, NCH$_2$C(O*H*)Ph$_2$, 1H), 6.91–6.95 (m, 1H), 7.13–7.21 (m, 4H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.48–7.54 (m, 5H); ^{13}C NMR ($C_2D_2Cl_4$) δ 45.4, 66.3, 75.1, 122.5, 125.4, 125.6, 126.3, 126.6, 128.0, 128.6, 133.1, 146.1, 151.6; HRMS (FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{21}H_{20}BrNONa$ 406.0608, found 406.0609. IR: ν(cm^{-1}) 3416, 3021, 1602, 1503, 1449, 1317, 1265, 1181, 1063, 1026, 944, 910, 733, 692, 653, 603, 511.

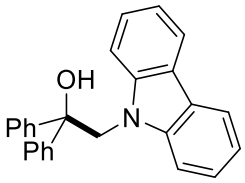
2-(phenylamino)-1,1-diphenylethanol (**3i**)



The reaction was performed according to the general procedure A using *N*-methylaniline (214.2 mg, 1.99 mmol), benzophenone (181.3 mg, 0.99 mmol), and lithium *t*-butoxide (16.8 mg, 0.21 mmol). The product was obtained in 23% NMR yield. After the purification, the title product was obtained in 23% yield (67.4 mg).

^{1}H NMR ($CDCl_3$) δ 3.38 (s, NCH$_2$C(O74*H*)Ph$_2$, 1H), 3.66 (s, N*H*Ph, 1H), 3.89 (d, *J* = 4.4 Hz, NC*H*$_2$C(OH)Ph$_2$, 2H), 6.70 (dd, *J* = 8.8, 1.0 Hz, NH(2,6-C$_6$*H*$_5$), 2H), 6.77 (t, *J* = 8.0 Hz, NH(4-C$_6$*H*$_5$), 1H), 7.18 (t, *J* = 8.0 Hz, NH(3,5-C$_6$*H*$_5$), 2H), 7.28 (t, *J* = 7.2 Hz, C(4-C$_6$*H*$_5$)$_2$, 2H), 7.36 (t, *J* = 8.0 Hz, C(3,5-C$_6$*H*$_5$)$_2$, 4H), 7.50 (d, *J* = 8.0 Hz, C(2,6-C$_6$*H*$_5$)$_2$, 4H); ^{13}C NMR ($C_2D_2Cl_4$) δ 53.9, 77.3, 114.0, 118.7, 126.0, 127.4, 128.5, 129.3, 144.5, 147.7; HRMS (FAB$^-$): *m*/*z* [M–H]$^-$ calcd for $C_{20}H_{18}NO$ 288.1388, found 288.1387. IR: ν(cm^{-1}) 3056, 3021, 1602, 1503, 1449, 1317, 1265, 1181, 1063, 1026, 944, 910, 733, 692, 653, 603, 511.

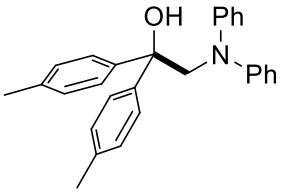
2-(9H-carbazole)-1,1-diphenylethanol (**3j**)



The reaction was performed according to the general procedure A using *N*-methylcarbazole (108.7 mg, 0.60 mmol), benzophenone (54.8 mg, 0.30 mmol), and sodium *t*-butoxide (5.8 mg, 0.06 mmol). The product was obtained in 55% NMR yield. After the purification, the title compound was obtained in 21% yield (22.5 mg).

^{1}H NMR ($CDCl_3$) δ 2.76 (s, NCH$_2$C(O*H*)Ph$_2$, 1H), 5.09 (s, NC*H*$_2$C(OH)Ph$_2$, 2H), 6.97 (d, *J* = 8.2 Hz, N(6-C$_6$*H*$_4$)$_2$, 2H), 7.14–7.23 (m, N(4-C$_6$*H*$_4$)$_2$ & N(5-C$_6$*H*$_4$)$_2$, 4H), 7.25–7.32 (m, C(3,4,5-C$_6$*H*$_5$)$_2$, 6H), 7.40 (dd, *J* = 8.0, 2.0 Hz, C(2,6-C$_6$*H*$_5$)$_2$, 4H), 8.01 (d, *J* = 6.9 Hz, N(3-C$_6$*H*$_4$)$_2$, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 79.0, 110.0, 119.4, 120.0, 123.3, 125.7, 126.5, 127.8, 128.6, 142.1, 145.1; HRMS (FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{26}H_{21}NONa$ 386.1521, found 386.1522. IR: ν(cm^{-1}) 3055, 1596, 1483, 1453, 1326, 1264, 895, 732, 700, 598.

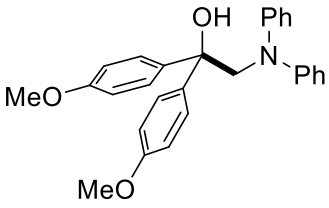
2-(diphenylamino)-1,1-(di-p-tolyl)ethanol (3k)



The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (366.7 mg, 2.00 mmol), 4,4'-(dimethyl)benzophenone (210.1 mg, 1.00 mmol), and lithium *t*-butoxide (18.3 mg, 0.22 mmol). The product was obtained in 86% NMR yield. The semi–purified product was further purified by GPC to give the title compound in 66% yield (258.9 mg).

^{1}H NMR ($CDCl_3$) δ 2.26 (s, C($C_6H_4CH_3$)$_2$ 6H), 3.14 (s, $NCH_2C(OH)Ar_2$, 1H), 4.60 (s, $NCH_2C(OH)Ar_2$, 2H), 6.78 (d, J = 7.8 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.91 (t, J = 7.3 Hz, N(4-C_6H_5)$_2$, 2H), 6.99 (d, J = 8.3 Hz, C(3,5-$C_6H_4CH_3$)$_2$, 4H), 7.13 (t, J = 8.0 Hz, N(3,5-C_6H_5)$_2$, 4H), 7.25 (d, J = 7.4 Hz, C(2,6-$C_6H_4CH_3$)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 21.1, 64.2, 78.6, 122.2 (2C), 126.2, 128.8, 129.3, 136.5, 142.4, 149.8; HRMS (FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{28}H_{27}NONa$ 416.1990, found 416.1989. IR: ν(cm^{-1}) 3006, 2992, 1590, 1497, 1276, 1267, 1261, 764, 750, 694, 576.

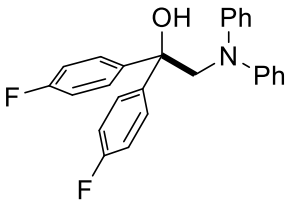
2-(diphenylamino)-1,1-(di-p-anisyl)ethanol (3l)



The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (365.8 mg, 2.00 mmol), 4,4'-(dimethoxy)benzophenone (242.8 mg, 1.00 mmol), and sodium *t*-butoxide (19.3 mg, 0.20 mmol). The product was obtained in 73% NMR yield. The semi–purified product was further purified by GPC to give the title compound in 51% yield (219.4 mg).

^{1}H NMR ($CDCl_3$) δ 3.13 (s, $NCH_2C(OH)Ar_2$, 1H), 3.75 (s, C($C_6H_4OCH_3$)$_2$, 6H), 4.57 (s, $NCH_2C(OH)Ar_2$, 2H), 6.72 (d, J = 9.2 Hz, C(3,5-$C_6H_4OCH_3$)$_2$, 4H), 6.79 (d, J = 7.8 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.92 (t, J = 7.4 Hz, N(4-C_6H_5)$_2$, 2H), 7.14 (t, J = 8.2 Hz, N(3,5-C_6H_5)$_2$, 4H), 7.27 (d, J = 6.0 Hz, C(3,5-$C_6H_4OCH_3$)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 64.3, 78.4, 113.5, 122.2, 127.6, 129.3, 137.6, 149.8, 158.5; HRMS (FAB$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{28}H_{28}NO_3$ 426.2069, found 426.2071. IR: ν(cm^{-1}) 3017, 2971, 2943, 1739, 1589, 1509, 1497, 1442, 1365, 1264, 1230, 1217, 1033, 896, 833, 731, 700, 583, 527.

2-(diphenylamino)-1,1-(di-p-fluorophenyl)ethanol (3m)

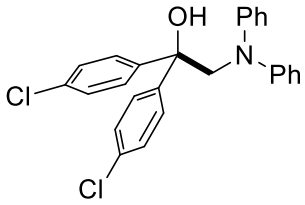


The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (364.7 mg, 1.99 mmol), 4,4'-(difluoro)benzophenone (218.5 mg, 1.00 mmol), and sodium *t*-butoxide (19.0 mg, 0.20 mmol). The product was obtained in 63% yield NMR yield. After the purification, the title product was obtained in 60% yield (261.1 mg).

^{1}H NMR ($CDCl_3$) δ 3.35 (s, $NCH_2C(OH)Ar_2$, 1H), 4.59 (s, $NCH_2C(OH)Ar_2$, 2H), 6.79 (d, J = 9.2 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.87 (m, C(2,6-C_6H_4F)$_2$, 4H), 6.95 (t, J = 7.6 Hz, N(4-C_6H_5)$_2$, 2H), 7.16 (t, J = 7.8 Hz, N(3,5-C_6H_5)$_2$, 4H), 7.32 (dd, J = 6.0, 5.5 Hz, C(3,5-C_6H_4F)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ, 64.3, 78.0, 114.9 (d, J = 88.0 Hz), 122.2, 122.6, 128.1, 129.5, 140.8, 149.5, 161.9 (d, J = 999.6 Hz); HRMS

(FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{26}H_{21}F_2NONa$ 424.1489, found 424.1489. IR: ν(cm^{-1}) 3006, 2990, 1589, 1493, 1275, 1261, 1224, 1159, 1077, 834, 764, 750, 697, 576.

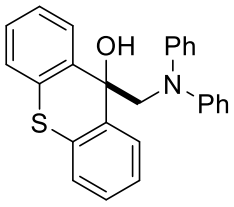
2-(diphenylamino)-1,1-(di-p-chlorophenyl)ethanol (**3n**)



The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (360.7 mg, 1.97 mmol), 4,4'-(dichloro)benzophenone (251.4 mg, 1.00 mmol), and lithium *t*-butoxide (16.1 mg, 0.20 mmol). The product was obtained in 68% NMR yield. The semi–purified product was further purified by GPC to give the title compound in 40% yield (171.88 mg).

^{1}H NMR ($CDCl_3$) δ 3.37 (s, $NCH_2C(OH)Ar_2$, 1H), 4.57 (s, $NCH_2C(OH)Ar_2$, 2H), 6.78 (d, *J* = 7.8 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.95 (t, *J* = 7.6 Hz, N(4-C_6H_5)$_2$, 2H), 7.13–7.17 (m, 8H), 7.28 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 64.0, 77.9, 122.2, 122.7, 127.7, 128.3, 129.5, 133.2, 143.3, 149.4; HRMS (FAB$^-$): *m*/*z* [M–H]$^-$ calcd for $C_{26}H_{20}Cl_2NO$ 432.0922, found 432.0920. IR: ν(cm^{-1}) 2987, 1590, 1491, 1264, 1093, 1012, 896, 833, 764, 731, 701, 599, 527.

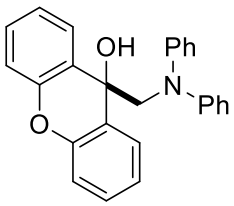
2-(diphenylamino)-1,1-(9H-thioxanthene)ethanol (**3o**)



The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (365.2 mg, 1.99 mmol), thioxanthone (212.6 mg, 1.00 mmol), and sodium *t*-butoxide (19.2 mg, 0.20 mmol). The product was obtained in 46% NMR yield. The semi–purified product was further purified by GPC to give the title product in 9% yield (33.7 mg).

^{1}H NMR ($CDCl_3$) δ 3.18 (s, $NCH_2C(OH)Ar_2$, 1H), 4.13 (s, $NCH_2C(OH)Ar_2$, 2H), 6.80 (d, *J* = 7.8 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.85 (t, *J* = 7.6 Hz, N(4-C_6H_5)$_2$, 2H), 7.10 (t, *J* = 8.2 Hz, N(3,5-C_6H_5)$_2$, 4H), 7.16–7.26 (m, C(3,4-C_6H_4)$_2$, 4H), 7.33 (dd, 7.6, 1.4 Hz, 2H), 7.84 (dd, 7.8, 1.4 Hz, 2H); ^{13}C NMR ($C_2D_2Cl_4$) δ 57.5, 76.8, 121.3, 121.5, 125.8, 126.1, 126.6, 127.5, 128.9, 130.0, 138.1, 148.8; HRMS (FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{26}H_{21}NOSNa$ 418.1242, found 418.1239. IR: ν(cm^{-1}) 3060, 1588, 1492, 1458, 1441, 1348, 1274, 1263, 1182, 1058, 841, 763, 750, 694, 646, 594, 510.

2-(diphenylamino)-1,1-(9H-xanthene)ethanol (**3p**)

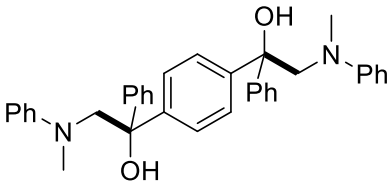


The reaction was performed according to the general procedure A using *N*,*N*-methyl(phenyl)aniline (367.7 mg, 2.01 mmol), xanthone (196.3 mg, 1.00 mmol), and sodium *t*-butoxide (19.0 mg, 0.20 mmol). The product was obtained in 26% NMR yield. The semi–purified product was further purified by GPC and recrystllization (Hexane/CH_2Cl_2) to give the title product in 2% yield (9.1 mg).

^{1}H NMR ($CDCl_3$) δ 2.54 (s, $NCH_2C(OH)Ar_2$, 1H), 4.09 (s, $NCH_2C(OH)Ar_2$, 2H), 6.68 (d, *J* = 8.0 Hz, N(2,6-C_6H_5)$_2$, 4H), 6.83 (t, *J* = 7.4 Hz, N(4-C_6H_5)$_2$, 2H), 7.05–7.11 (m, 8H), 7.27 (td, *J* = 7.6, 2.0 Hz, 2H), 7.71 (dd, 8.0, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 65.4, 71.1, 116.2, 121.6 (2C), 123.6, 126.4, 127.0,

129.0, 129.2, 149.4, 150.7; HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{26}H_{23}NO$ 380.1645, found 380.1643. IR: ν(cm^{-1}) 3023, 3014, 2978, 1603, 1591, 1496, 1475, 1450, 1420, 1270, 1264, 1191, 1034, 900, 764, 752.

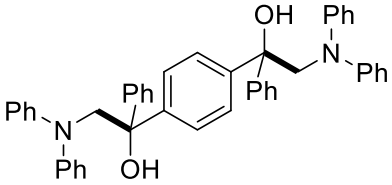
Double coupling product (**3q**)



The reaction was performed according to the general procedure B using *N*,*N*-dimethylaniline (148.2 mg, 1.23 mmol), 1,4–dibenzoylbenzene (85.7 mg, 0.30 mmol), and lithium *t*-butoxide (10.4 mg, 0.13 mmol). The product was obtained as a white solid (94.2 mg, 60%).

^{1}H NMR ($CDCl_3$) δ 2.45 (s, 2NPhC*H*$_3$CH$_2$, 6H), 3.62 (s, NCH$_2$CPhAr(O*H*), 2H), 4.08–4.13 (m, 2NPhCH$_3$C*H*$_2$, 4H), 6.80 (t, *J* = 7.3 Hz, 2NCH$_3$(4-C$_6$*H*$_5$), 2H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 2NCH$_3$(2,6-C$_6$*H*$_5$), 4H), 7.19–7.26 (m, 2NCH$_3$(2,6-C$_6$*H*$_5$) & 2C(4-C$_6$*H*$_5$), 6H), 7.34 (td, *J* = 7.8, 1.8 Hz, 2C(3,5-C$_6$*H*$_5$), 4H), 7.51–7.53 (m, 2C(2,6-C$_6$*H*$_5$) & C(C$_6$*H*$_4$), 8H); ^{13}C NMR ($CDCl_3$) δ 40.1, 66.3, 76.6, 114.8, 119.1, 126.0, 127.1, 128.4, 129.0, 129.2, 144.8, 146.0, 151.7; HRMS (FAB$^+$): *m*/*z* [M+Na]$^+$ calcd for $C_{36}H_{37}N_2O_2Na$ 551.2674, found 551.2674. IR: ν(cm^{-1}) 3029, 3005, 1599, 1504, 1361, 1298, 1186, 1120, 1060, 1033, 764, 759.

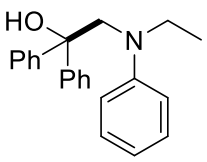
Double coupling product (**3r**)



The reaction was performed according to the general procedure B using *N*,*N*-methy(phenyl)aniline (212.7 mg, 1.16 mmol), 1,4-dibenzoylbenzene (85.7 mg, 0.30 mmol), and lithium *t*-butoxide (10.0 mg, 0.13 mmol). The product was obtained as a white solid (95.6 mg, 49%).

^{1}H NMR ($CDCl_3$) δ 3.24 (s, NCH$_2$CPhAr(O*H*), 2H), 4.57–4.59 (m, 2NPh$_2$C*H*$_2$, 4H), 6.74 (d, *J* = 7.8 Hz, 2N(2,6-C$_6$*H*$_5$)$_2$, 8H), 6.85 (t, *J* = 7.6 Hz, 2N(4-C$_6$*H*$_5$)$_2$, 4H), 7.03–7.08 (m, 2N(3,5-C$_6$*H*$_5$)$_2$, 8H), 7.14–7.25 (m, 2C(3,4,5-C$_6$*H*$_5$) & C(C$_6$*H*$_4$), 10H), 7.36 (d, *J* = 7.8 Hz, 2C(2,6-C$_6$*H*$_5$) 4H); ^{13}C NMR ($CDCl_3$) δ 64.2, 78.2, 78.3, 122.2, 122.3, 125.8, 126.3, 127.0, 128.1, 129.3, 143.7, 143.8, 145.1, 145.2, 149.6; HRMS (FAB$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{46}H_{41}N_2O_2$ 653.3168, found 653.3169. IR: ν(cm^{-1}) 3061, 3040, 1738, 1731, 1588, 1494, 1446, 1355, 1231, 1068, 751, 696, 593.

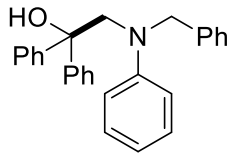
2-(ethyl(phenyl)amino)-1,1-diphenylethanol (**3s**)



The reaction was performed according to the general procedure A using *N*,*N*-ethyl(methyl)aniline (270.8 mg, 2.00 mmol), benzophenone (182.6 mg, 1.00 mmol), and sodium *t*-butoxide (19.3 mg, 0.20 mmol). The product was obtained in 78% NMR yield. The semi–purified product was further purified by GPC to give the title compound in 63% yield (200.7 mg).

^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.1 Hz, NPhMeCH$_2$C*H*$_3$, 3H), 2.91 (q, *J* = 7.0 Hz, NPhMeC*H*$_2$CH$_3$, 2H), 3.65 (s, NCH$_2$C(O*H*)Ph$_2$, 1H), 4.16 (s, NC*H*$_2$C(OH)Ph$_2$, 2H), 6.78 (t, *J* = 7.3 Hz, NEtCH$_2$(4-C$_6$*H*$_5$), 1H), 6.92 (d, *J* = 8.2 Hz, NCH$_3$(2,6-C$_6$*H*$_5$), 2H), 7.18–7.26 (m, NCH$_3$(3,5-C$_6$*H*$_5$) & C(4-C$_6$*H*$_5$)$_2$, 4H), 7.33 (t, *J* = 7.8 Hz, C(3,5-C$_6$*H*$_5$)$_2$, 4H), 7.55 (d, *J* = 8.2 Hz, C(2,6-C$_6$*H*$_5$)$_2$, 4H); ^{13}C NMR ($C_2D_2Cl_4$) δ 10.7, 45.4, 62.8, 76.5, 114.9, 118.3, 125.7, 126.9, 128.2, 129.1, 145.9, 149.8; HRMS (FAB$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{22}H_{24}NO$ 318.1858, found 318.1859. IR: ν(cm^{-1}) 3061, 2984, 1597, 1495, 1448, 1361, 1265, 1198, 1168, 1125, 1061, 994, 948, 733, 696, 651, 601.

2-(benzyl(phenyl)amino)-1,1-diphenylethanol (3t)



The reaction was performed according to the general procedure A using *N*,*N*-benzyl(methyl)aniline (395.9 mg, 2.00 mmol), benzophenone (182.1 mg, 1.00 mmol), and sodium *t*-butoxide (19.0 mg, 0.20 mmol). The product was obtained in 88% NMR yield. After the purification, the title compound was obtained in 78% yield (297.0 mg).

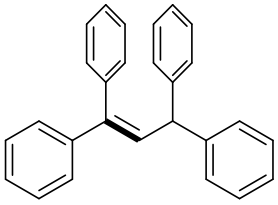
^{1}H NMR ($CDCl_3$) δ 3.42 (s, NCH$_2$C(O*H*)Ph$_2$, 1H), 4.11 (s, 2H), 4.32 (s, 2H), 6.76 (t, *J* = 7.3 Hz, NCH$_3$(4-C$_6$*H*$_5$), 1H), 6.93 (d, *J* = 8.2 Hz, 4H), 7.13–7.26 (m, 7H), 7.31 (t, *J* = 7.8 Hz, C(3,5-C$_6$*H*$_5$)$_2$, 4H), 7.51 (d, *J* = 7.3 Hz, C(2,6-C$_6$*H*$_5$)$_2$, 4H); ^{13}C NMR ($CDCl_3$) δ 53.8, 62.3, 77.6, 114.6, 118.5, 126.0, 126.8, 127.1, 127.2, 128.5, 128.6, 129.3, 137.6, 146.0, 150.7; HRMS (FAB$^+$): *m*/*z* [M+H]$^+$ calcd for $C_{27}H_{26}NO$ 380.2014, found 380.2016. The NMR spectrum is in good accordance with previous literature data.[7]

4. Synthesis of enamine:

General Procedure C.

To a dried schlenk filled up with argon gas, aminoalcohol, molecular sieve, and CCl_4 (1.0 ml) were added in a glove box. It was stirred at 80 °C for 20 h. After the reaction, the mixture was diluted with CH_2Cl_2, followed by filtration, and the solvent was removed under reduced pressure to afford the crude product.

***N*-(2,2-Diphenylvinyl)-*N*,*N*-diphenylmine (4a)**

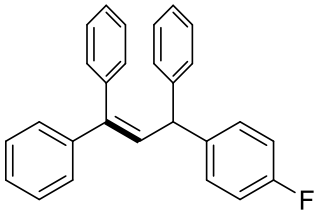


The reaction was performed according to the general procedure C using aminoalcohol **3a** (36.5 mg, 0.10 mmol) and molecular sieve 4Å (70.4 mg). The product was obtained in 71% NMR yield.

^{1}H NMR ($CDCl_3$) δ 6.73 (s, Ph$_2$(C=)*H*, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.92–6.99 (m, 9H), 7.09 (t, *J* = 8.0 Hz, 4H), 7.22–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 122.6, 122.8, 126.4, 126.8, 127.6, 127.7, 128.3, 128.9, 130.2, 130.5, 131.4, 139.1, 142.2, 145.9;

HRMS (EI$^+$): *m*/*z* [M]$^+$ calcd for $C_{26}H_{21}N$ 347.1674, found 347.1682. The NMR spectrum is in good accordance with previous literature data.[8]

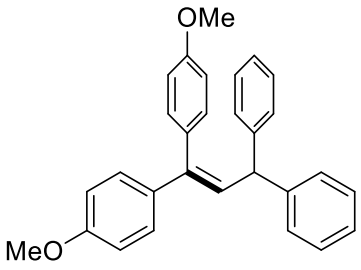
***N*-(2,2-Diphenylvinyl)-*N*-phenyl-*N*-*p*-fluorophenylmine (4b)**



The reaction was performed according to the general procedure C using aminoalcohol **3l** (41.6 mg, 0.10 mmol) and molecular sieve 4Å (70.0 mg). The product was obtained in 78% NMR yield. The crude product was further purified by recrystllization to give the title compound in 53% yield (20.9 mg) as a white solid.

^{1}H NMR ($C_2D_2Cl_4$) δ 6.72–6.76 (m, 3H), 6.88–7.01 (m, 10H), 7.14 (t, *J* = 8.4 Hz, 2H), 7.22–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 115.5 (d, *J* = 91.6 Hz), 120.9, 122.4, 125.4 (d, *J* = 34.4 Hz), 126.6, 126.8, 127.5, 127.8, 128.3, 129.0, 130.2 (2C), 131.4, 139.0, 141.5, 142.0, 146.6, 159.0 (d, *J* = 984.4 Hz); HRMS (EI$^+$): *m*/*z* [M]$^+$ calcd for $C_{26}H_{20}FN$ 365.1580, found 365.1581. IR: ν(cm^{-1}) 3022, 1590, 1503, 1493, 1275, 1261, 1221, 838, 814, 764, 750, 694.

***N*-(2,2-Di-*p*-tolylvinyl)-*N*-phenyl-*N*-*p*-fluorophenylmine (4c)**



The reaction was performed according to the general procedure C using aminoalcohol **3c** (44.6 mg, 0.10 mmol) and molecular sieve 4 Å (70.7 mg). The product was obtained in 93% NMR yield. The crude product was further purified by silica gel column chromatography (hexane/EtOAc = 100/0 to 80/20) to give the title compound in 60% yield (25.7 mg) as a white solid.

^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3H), 3.81 (s, 3H), 6.52 (d, *J* = 8.8 Hz, 2H), 6.57 (s, $Ar_2(C=)H$, 1H), 6.82–6.87 (m, 6H), 6.98 (d, *J* = 8.8 Hz, 4H), 7.09 (t, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.3, 55.5, 113.2, 113.7, 122.3, 122.5, 128.7, 128.8, 129.5, 130.7, 131.1, 131.8, 134.9, 146.0, 158.3, 158.9; HRMS (EI$^+$): *m*/*z* [M]$^+$ calcd for $C_{28}H_{25}NO_2$ 407.1885, found 407.1885. IR: ν(cm^{-1}) 3035, 2957, 1603, 1588, 1570, 1510, 1491, 1464, 1293, 1242, 1172, 1107, 1034, 914, 831, 694, 571, 541.

5. DFT calculation

All calculations were carried out by using the Gaussian 09 program packages.[S9] Geometry optimizations were performed at B3LYP/6-311++G** with GD3BJ empirical dispersion[S10] and PCM solvent model (solvent=acetonitrile). Vibrational frequencies were calculated at the same level. Translational entropy was corrected by the method of Whiteside.[S11]

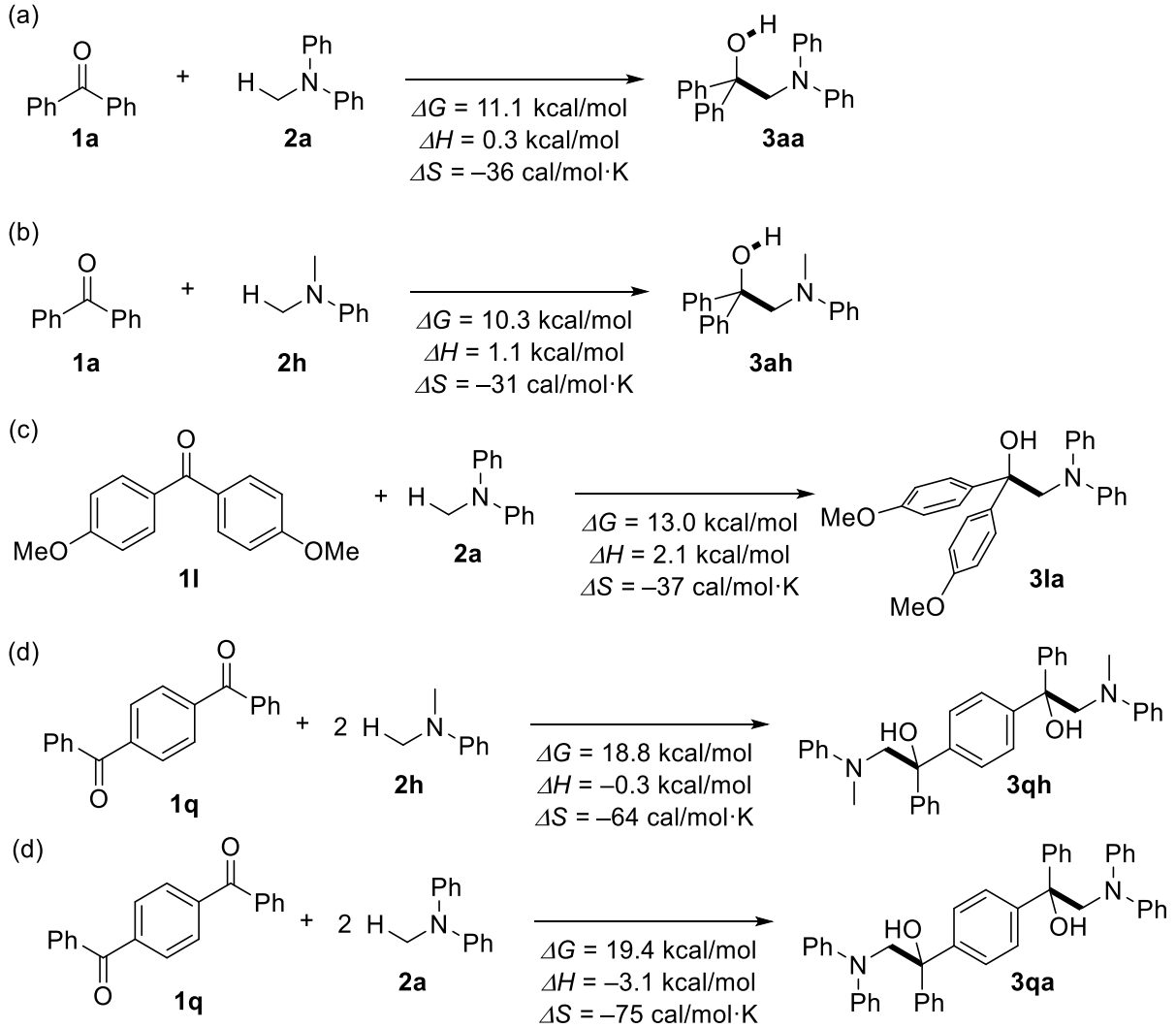
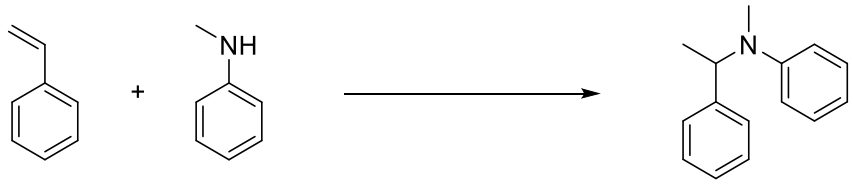


Figure S1. Thermodynamics estimated by DFT calculation at 298.150 K and 1.0000 atm.

To check the validity of the present calculation, thermodynamics for hydroamination between styrene and *N*–methylaniline was estimated, because its experimental thermodynamic parameters were already reported by Hartwig (Table S1). The calculated energy values for hydroamination (entry 2) are close to the experimental values (entry 3).[S12] Notably, the calculation without correction of translational entropy obviously overestimate the entropic penalty (entry 1). Based on these results, we concluded that the thermodynamic parameters obtained by the above calculation is certainly valid.



entry	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol·K)	method
1[a]	5.2	–10.9	–43	calc.
2[a,b]	1.3	–10.9	–32	calc.
3[c]	–0.28 ± 0.05	–10.0 ± 0.8	–27 ± 4	exp.

[a]DFT calculation were performed by B3LYP-GD3(BJ)/6-311++G(d,p) with PCM solvent model (solvent=toluene). Energies were calculated at 378.150 K and 1 atm. [b]Translational entropy was corrected by the method of Whiteside. [c]These values were experimentally measured by Hartwig.[S12]

Table S2. Thermodynamics of hydroamination of styrene with *N*–methylaniline.

Cartesian coordinates for optimized compounds.

Benzophenone **1a**

C	-1.288193	0.36845	0.031285	O	-0.000005	2.348607	0.00001
C	-1.406813	-0.863582	0.687307	H	-0.543027	-1.307941	1.164695
C	-2.640597	-1.506034	0.752796	H	-2.728641	-2.450789	1.275649
C	-3.758163	-0.934957	0.145918	H	-4.715198	-1.441644	0.187496
C	-3.645876	0.291048	-0.513334	H	-4.513851	0.734037	-0.98701
C	-2.42079	0.945623	-0.558731	H	-2.324353	1.90212	-1.057061
C	2.640637	-1.506012	-0.752805	H	2.72871	-2.450759	-1.275667
C	3.75817	-0.934938	-0.145864	H	4.715209	-1.44162	-0.187403
C	3.645845	0.291057	0.513399	H	4.513795	0.734045	0.987123
C	2.420753	0.945625	0.558747	H	2.324288	1.902115	1.057085
C	1.288188	0.368455	-0.031333	H	0.543085	-1.307923	-1.164803
C	1.406846	-0.863567	-0.687365	N–diphenylmethylamine **2a**			
C	-0.000005	1.122084	-0.000051	C	1.226216	0.331709	-0.091091
C	-0.000005	1.122084	-0.000051	C	1.307517	-0.969952	-0.627839

C	2.512843	-1.657386	-0.644784	Aminoalchol **3aa**			
C	3.679546	-1.074767	-0.141074	C	2.27338	-1.066784	-0.596911
C	3.610311	0.21386	0.380376	C	3.526148	-0.571777	-1.005648
C	2.403774	0.913004	0.412684	C	4.685454	-1.306471	-0.788023
C	-2.634296	-1.34198	0.994803	C	4.634872	-2.559598	-0.174203
C	-3.697613	-0.962539	0.175164	C	3.395971	-3.060894	0.219616
C	-3.520147	0.074418	-0.740517	C	2.22753	-2.328139	0.021674
C	-2.289527	0.718359	-0.844835	C	0.424325	3.123998	-2.065264
C	-1.222383	0.343677	-0.021001	C	1.132997	3.88893	-1.142086
C	-1.407845	-0.689153	0.905766	C	1.855316	3.242685	-0.137021
N	0.018535	1.03432	-0.118338	C	1.85472	1.857214	-0.046196
C	0.011932	2.451314	0.235258	C	1.137613	1.081587	-0.9668
H	0.419349	-1.43379	-1.036502	C	0.43223	1.732555	-1.986298
H	2.543682	-2.656094	-1.0662	N	1.102411	-0.332423	-0.838486
H	4.618561	-1.6144	-0.159758	C	-0.180176	-0.997639	-0.999849
H	4.501367	0.687772	0.777141	C	-1.13664	-1.030566	0.247872
H	2.385162	1.907518	0.835774	O	-0.87593	-2.306209	0.861795
H	-2.7626	-2.140841	1.716268	C	-2.592766	-0.970877	-0.23194
H	-4.652598	-1.46892	0.249292	C	-0.807961	0.079066	1.257127
H	-4.336605	0.374704	-1.387133	C	0.257227	-0.120001	2.144648
H	-2.147666	1.509661	-1.571488	C	0.617355	0.862135	3.0625
H	-0.587675	-0.979884	1.550516	C	-0.076016	2.06994	3.105759
H	0.765348	2.989754	-0.3425	C	-3.013548	-0.00473	-1.155539
H	-0.964135	2.869665	0.000986	C	-4.342622	0.066375	-1.565892
H	0.206085	2.611218	1.304509	C	-5.281184	-0.832888	-1.062596

C	-4.874542	-1.800281	-0.146893	H	-1.688261	3.210983	2.252705
C	-3.542875	-1.867882	0.261955	H	-2.336192	1.473662	0.654389
C	-1.136739	2.278183	2.228493	N,N–dimethylaniline **2h**			
C	-1.501991	1.289811	1.315873	C	1.939572	1.197633	0.018662
H	3.586672	0.388476	-1.499984	C	2.653785	0.00001	0.042906
H	5.6359	-0.899841	-1.11562	C	1.939588	-1.197625	0.018569
H	5.540625	-3.130496	-0.009215	C	0.549463	-1.207328	-0.035418
H	3.33148	-4.030622	0.701006	C	-0.184756	-0.000006	-0.079611
H	1.280907	-2.723809	0.362044	C	0.549444	1.20732	-0.035325
H	-0.13191	3.606735	-2.860698	N	-1.568029	-0.000013	-0.177056
H	1.124501	4.970609	-1.203429	C	-2.291022	-1.24001	0.06838
H	2.405156	3.822415	0.595598	H	2.467741	2.144563	0.048154
H	2.391576	1.366331	0.753159	H	3.735991	0.000013	0.08802
H	-0.106241	1.159532	-2.729865	H	2.467775	-2.144547	0.04798
H	-0.707081	-0.530669	-1.824434	H	0.036954	-2.158521	-0.044555
H	-0.012305	-2.034341	-1.28918	H	0.036922	2.158507	-0.04438
H	-1.202663	-2.287913	1.769042	H	-3.355063	-1.061604	-0.075993
H	0.818242	-1.043811	2.109353	H	-1.987484	-2.015356	-0.638157
H	1.448326	0.685901	3.735998	H	-2.137216	-1.623127	1.087448
H	0.207105	2.839033	3.81496	C	-2.291019	1.240011	0.06821
H	-2.309405	0.715023	-1.554245	H	-3.355047	1.061634	-0.076303
H	-4.641955	0.824861	-2.279888	H	-2.137349	1.623204	1.087275
H	-6.315031	-0.781519	-1.383345	H	-1.987355	2.015299	-0.638337
H	-5.591678	-2.510093	0.249224	Aminoalchol **3ah**			
H	-3.245671	-2.637526	0.961302	C	-2.647451	-0.461363	0.436582

C	-3.881701	0.061322	0.882127	H	-1.768716	-1.905055	-0.910887
C	-5.08836	-0.453592	0.414002	H	0.295407	-0.598515	1.788832
C	-5.1174	-1.504041	-0.500527	H	-0.416064	-1.755639	0.686824
C	-3.902165	-2.024521	-0.949996	H	0.551728	-0.272798	-2.255914
C	-2.688748	-1.516259	-0.502071	H	-0.982171	1.437877	-1.388253
N	-1.446542	0.059392	0.897768	H	-0.91245	3.896403	-1.525181
C	-0.209354	-0.693849	0.828975	H	1.026715	5.143399	-0.594273
C	0.785893	-0.272865	-0.298718	H	2.308307	-0.402775	2.023731
O	0.185394	-0.760244	-1.508968	H	4.447593	-1.525374	2.381099
C	2.126351	-0.976512	-0.054319	H	5.552564	-2.752488	0.522529
C	0.914216	1.252364	-0.391097	H	4.449702	-2.843089	-1.70305
C	-0.130693	1.971745	-0.989673	H	2.281903	-1.740624	-2.057006
C	-0.091339	3.360903	-1.062441	H	2.90171	3.886661	0.443094
C	0.995479	4.061386	-0.539784	H	2.836271	1.439154	0.565073
C	2.757267	-0.938086	1.196815	C	-1.469335	1.158486	1.852536
C	3.980821	-1.571457	1.403995	H	-2.046881	1.999487	1.463843
C	4.601177	-2.258847	0.362487	H	-1.891961	0.858894	2.821616
C	3.9825	-2.307742	-0.884369	H	-0.451625	1.508919	2.010266
C	2.756111	-1.675676	-1.087337	Ketone **1l**			
C	2.044421	3.356374	0.04458	C	-1.28258	0.697705	0.049738
C	2.004906	1.963496	0.115666	C	-1.401486	-0.554212	0.676861
H	-3.906386	0.866906	1.601651	C	-2.626534	-1.192993	0.758766
H	-6.015659	-0.026753	0.780841	C	-3.766566	-0.603332	0.194478
H	-6.058649	-1.902582	-0.85921	C	-3.665591	0.644693	-0.43494
H	-3.894263	-2.833398	-1.672862	C	-2.433638	1.284573	-0.487707

C	2.626591	-1.192852	-0.758995	H	6.366672	0.192793	-0.237012
C	3.766618	-0.603203	-0.194679	Aminoalchol **3la**			
C	3.665602	0.644762	0.434852	C	-2.389227	-2.040624	0.234277
C	2.433626	1.284598	0.4877	C	-3.627757	-2.09148	0.900614
C	1.282587	0.697746	-0.049791	C	-4.652756	-2.904266	0.43164
C	1.401529	-0.554124	-0.677015	C	-4.472954	-3.701977	-0.700238
C	-0.000008	1.447694	0.000003	C	-3.243761	-3.666436	-1.355463
O	-0.000025	2.679373	0.00005	C	-2.213419	-2.843379	-0.905324
H	-0.534167	-1.018273	1.128085	C	-1.113505	1.464578	3.286971
H	-2.725142	-2.149424	1.257025	C	-2.104169	2.342755	2.854828
H	-4.530589	1.117409	-0.877874	C	-2.861513	2.008158	1.730715
H	-2.353891	2.25391	-0.963828	C	-2.621247	0.826706	1.042405
H	2.725221	-2.149263	-1.257296	C	-1.618112	-0.057637	1.464407
H	4.530596	1.117486	0.877784	C	-0.875732	0.272128	2.605862
H	2.35387	2.253899	0.963889	N	-1.346724	-1.236695	0.723878
H	0.53422	-1.018189	-1.128253	C	0.043211	-1.614417	0.51591
O	-4.917939	-1.309957	0.307554	C	0.820742	-0.88735	-0.640846
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C	-6.117863	-0.756562	-0.242604	C	2.29639	-0.760871	-0.247673
H	-6.022573	-0.613079	-1.32193	C	0.184924	0.460496	-0.995883
H	-6.898676	-1.485119	-0.037925	C	-0.953737	0.476411	-1.816268
H	-6.365967	0.193217	0.237871	C	-1.611934	1.657877	-2.114913
C	6.117702	-0.756831	0.243331	C	-1.156467	2.869468	-1.584843
H	6.021475	-0.613192	1.322554	C	2.681699	-0.232298	0.994457
H	6.898377	-1.485753	0.039428	C	4.016876	-0.084523	1.337565

C	5.020314	-0.469358	0.441238	H	1.520959	1.719739	0.124863
C	4.660301	-1.003747	-0.796237	O	-1.884818	3.978058	-1.903637
C	3.309554	-1.143455	-1.123235	O	6.30503	-0.289255	0.862846
C	-0.01621	2.878119	-0.782002	C	7.361845	-0.659512	-0.023716
C	0.640789	1.679548	-0.500659	H	7.315094	-0.0846	-0.953018
H	-3.780733	-1.495493	1.790403	H	8.285719	-0.427852	0.501749
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H	-3.08218	-4.274489	-2.238842	H	-2.192587	5.964047	-1.717553
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H	-0.114611	-0.400598	2.978346	C	-5.086394	-1.611793	0.546852
H	0.585087	-1.460068	1.442895	C	-6.23734	-1.037153	0.009977
H	0.093822	-2.682098	0.306079	C	-6.200987	0.266573	-0.489889
H	0.887144	-1.273376	-2.574402	C	-5.018041	0.993744	-0.447296
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H	1.934307	0.088004	1.709587	C	1.055585	0.564183	0.717437
H	4.299736	0.327365	2.298738	C	-0.211025	1.127575	0.79113
H	5.409262	-1.319112	-1.509161	C	-1.277265	0.567868	0.07848
H	3.057923	-1.573731	-2.083111	C	-1.055537	-0.564368	-0.716314
H	0.369497	3.797982	-0.365692	C	-2.612425	1.241656	0.136958

O	-2.675498	2.461335	0.23545	C	4.655285	-2.708251	0.148781
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H	-7.161962	-1.601655	-0.017547	C	6.101639	-1.477815	-1.876373
H	-7.095392	0.712334	-0.908451	C	5.211866	-0.728499	-1.116079
H	-4.979644	2.008683	-0.82244	N	3.582676	-0.596236	0.704151
H	0.386475	-2.000973	-1.405275	C	3.619252	0.851094	0.771724
H	1.867117	0.99217	1.291306	C	2.551433	1.604129	-0.087422
H	-0.386436	2.00077	1.406407	O	3.042144	1.51052	-1.434739
H	-1.867057	-0.992304	-1.290234	C	2.505184	3.070797	0.35652
C	2.612508	-1.241813	-0.135858	C	1.19101	0.906495	-0.007748
C	3.851307	-0.416027	-0.072562	C	1.00942	-0.281101	-0.732222
C	3.893472	0.893204	-0.569997	C	-0.175324	-0.997402	-0.642336
C	5.018537	-0.993513	0.446481	C	-1.224067	-0.548942	0.164702
C	5.085786	1.61188	-0.548101	C	2.379896	3.424421	1.707082
H	3.00502	1.34161	-0.995239	C	2.330259	4.760721	2.097967
C	6.201435	-0.266195	0.488031	C	2.404395	5.774586	1.144641
H	4.980559	-2.008394	0.821826	C	2.529807	5.436204	-0.200616
C	6.237232	1.037461	-0.012047	C	2.582998	4.09772	-0.587959
H	5.115248	2.618257	-0.947914	C	-1.056793	0.638376	0.87147
H	7.096221	-0.711793	0.90595	C	0.136202	1.35668	0.78528
H	7.161801	1.602087	0.01467	H	4.113295	-3.21351	0.935084
O	2.675573	-2.461551	-0.233545	H	5.660082	-4.50472	-0.428813
Aminoalchol **3qh**				H	6.973673	-3.420822	-2.248339
C	4.470081	-1.324978	-0.071977	H	6.652674	-0.985118	-2.670457

H	5.057107	0.311935	-1.356907	O	-3.296923	-0.785416	1.295354
H	3.490948	1.1394	1.813357	H	-4.101966	-1.306825	1.38752
H	4.595916	1.225027	0.460886	C	-3.308152	-1.104852	-1.129461
H	2.305915	1.64455	-2.042854	H	-4.22595	-1.694115	-1.106808
H	1.810725	-0.654042	-1.354583	H	-2.70895	-1.498683	-1.950471
H	-0.277901	-1.920598	-1.201074	N	-3.608899	0.280694	-1.429298
H	2.307322	2.660788	2.471019	C	-4.729909	0.922802	-0.928647
H	2.233116	5.006742	3.149058	C	-4.842568	2.329173	-1.004758
H	2.367199	6.814462	1.447534	C	-5.816455	0.221024	-0.357973
H	2.59209	6.213488	-0.953666	C	-5.978153	2.986776	-0.538331
H	2.698793	3.854229	-1.635159	H	-4.035408	2.916872	-1.417662
H	-1.863927	1.010654	1.486427	C	-6.941862	0.89198	0.102624
H	0.227517	2.27702	1.344631	H	-5.79584	-0.856227	-0.27728
C	-2.251698	-2.807793	0.475228	C	-7.04141	2.282491	0.021377
C	-1.728329	-3.15281	1.728546	H	-6.021502	4.068197	-0.611202
C	-2.463359	-3.820389	-0.46218	H	-7.753956	0.314535	0.531072
C	-1.429724	-4.474264	2.038627	H	-7.920709	2.798619	0.38679
H	-1.554408	-2.372428	2.459305	C	2.828865	-1.272172	1.750653
C	-2.162794	-5.149612	-0.153103	H	2.108865	-0.575088	2.173596
H	-2.859735	-3.596868	-1.443295	H	2.265054	-2.114948	1.345243
C	-1.646735	-5.48134	1.095303	H	3.477946	-1.638935	2.557419
H	-1.024984	-4.720769	3.013564	C	-2.624203	1.046393	-2.181579
H	-2.334548	-5.921704	-0.894144	H	-3.112847	1.618754	-2.975792
H	-1.413046	-6.512408	1.333677	H	-2.052464	1.738503	-1.554155
C	-2.535254	-1.325662	0.205444	H	-1.919135	0.357144	-2.641685

Aminoalchol **3qa**

C	-3.420767	-1.257096	1.800362
C	-3.695217	-2.637331	1.74144
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C	-3.411171	-2.846605	4.139432
C	-3.153268	-1.478994	4.206398
C	-3.148996	-0.689885	3.058163
C	-3.837507	-1.218428	-2.993604
C	-2.772229	-2.089038	-3.211342
C	-1.957596	-2.44971	-2.137055
C	-2.191003	-1.932812	-0.869783
C	-3.25252	-1.04738	-0.645034
C	-4.083211	-0.708389	-1.720009
N	-3.457421	-0.472693	0.640024
C	-3.684746	0.962446	0.705581
C	-2.417828	1.89575	0.674728
O	-2.176964	2.217423	2.057214
C	-2.742643	3.17345	-0.109464
C	-1.19057	1.167919	0.113045
C	-0.466363	0.322208	0.960099
C	0.62609	-0.397084	0.493635
C	1.031416	-0.302128	-0.837445
C	-3.352506	3.116827	-1.369766
C	-3.608065	4.277148	-2.096669
C	-3.262326	5.522537	-1.574974
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C	-2.405727	4.428227	0.403777
C	0.311582	0.537556	-1.685071
C	-0.777663	1.266042	-1.216003
H	-3.925698	-3.096971	0.789991
H	-3.898262	-4.474516	2.814536
H	-3.403128	-3.456355	5.0348
H	-2.936741	-1.013857	5.16196
H	-2.912232	0.361913	3.133561
H	-4.490416	-0.938225	-3.812444
H	-2.578064	-2.482264	-4.202273
H	-1.120364	-3.117132	-2.290033
H	-1.531831	-2.19162	-0.053593
H	-4.931554	-0.05338	-1.568141
H	-4.333331	1.239756	-0.117377
H	-4.226753	1.200785	1.619979
H	-1.27185	2.537835	2.148263
H	-0.759718	0.21302	1.994902
H	1.158751	-1.023329	1.19502
H	-3.622106	2.162663	-1.80577
H	-4.078742	4.205251	-3.070345
H	-3.463281	6.426572	-2.137745
H	-2.390992	6.553824	0.100821
H	-1.952534	4.506569	1.382718
H	0.614644	0.637861	-2.71759

H	-1.2991	1.914527	-1.905211	H	5.889047	0.393843	-0.946282
C	1.738979	-2.516141	-1.756228	C	4.626926	3.446259	-1.754648
C	1.691068	-2.908687	-3.094863	H	2.731141	4.209033	-1.073306
C	1.312095	-3.423997	-0.779512	H	6.451038	2.420771	-2.262197
C	1.242579	-4.18172	-3.450255	H	4.870779	4.333607	-2.327073
H	1.991434	-2.212856	-3.866354	C	3.750028	-0.032517	1.830803
C	0.864319	-4.693741	-1.130556	C	3.39089	-1.146198	2.619291
H	1.304679	-3.142856	0.265773	C	4.219235	1.112662	2.511396
C	0.830785	-5.080911	-2.470648	C	3.477411	-1.099688	4.008214
H	1.211856	-4.464667	-4.496163	H	3.042665	-2.065173	2.170844
H	0.534726	-5.37782	-0.357307	C	4.298404	1.143734	3.898384
H	0.479288	-6.068345	-2.745485	H	4.522549	1.9825	1.946768
C	2.215549	-1.102639	-1.368106	C	3.925741	0.041805	4.668358
O	2.687385	-0.402792	-2.523513	H	3.186515	-1.977059	4.575351
H	3.510542	-0.812653	-2.812434	H	4.662734	2.044757	4.379759
C	3.374385	-1.226333	-0.334582	H	3.987698	0.070846	5.749193
H	4.263726	-1.541442	-0.896148				
H	3.157074	-2.039293	0.345412				
N	3.651038	-0.026824	0.439172				
C	3.992381	1.15659	-0.290453				
C	3.105834	2.233577	-0.321579				
C	5.200469	1.230106	-0.982611				
C	3.425138	3.376802	-1.048482				
H	2.168839	2.161225	0.215212				
C	5.513496	2.370465	-1.720643				

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7. ^{1}H and ^{13}C NMR spectra

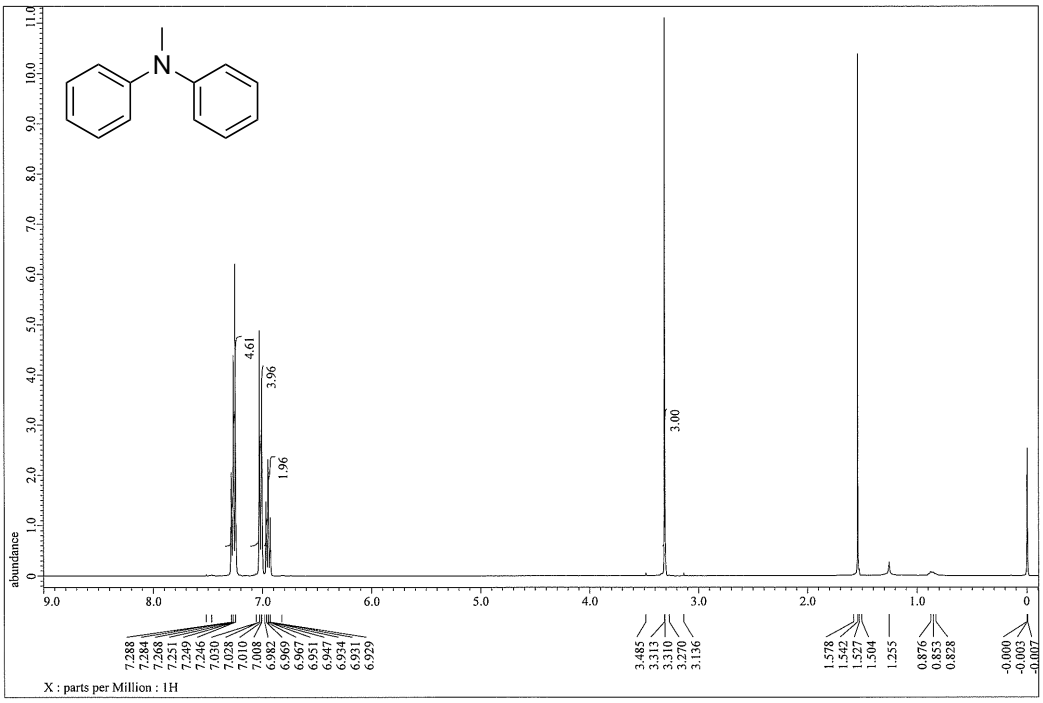

Figure S2. ^{1}H NMR Spectrum of ***N,N*–methylpheneylaniline**.

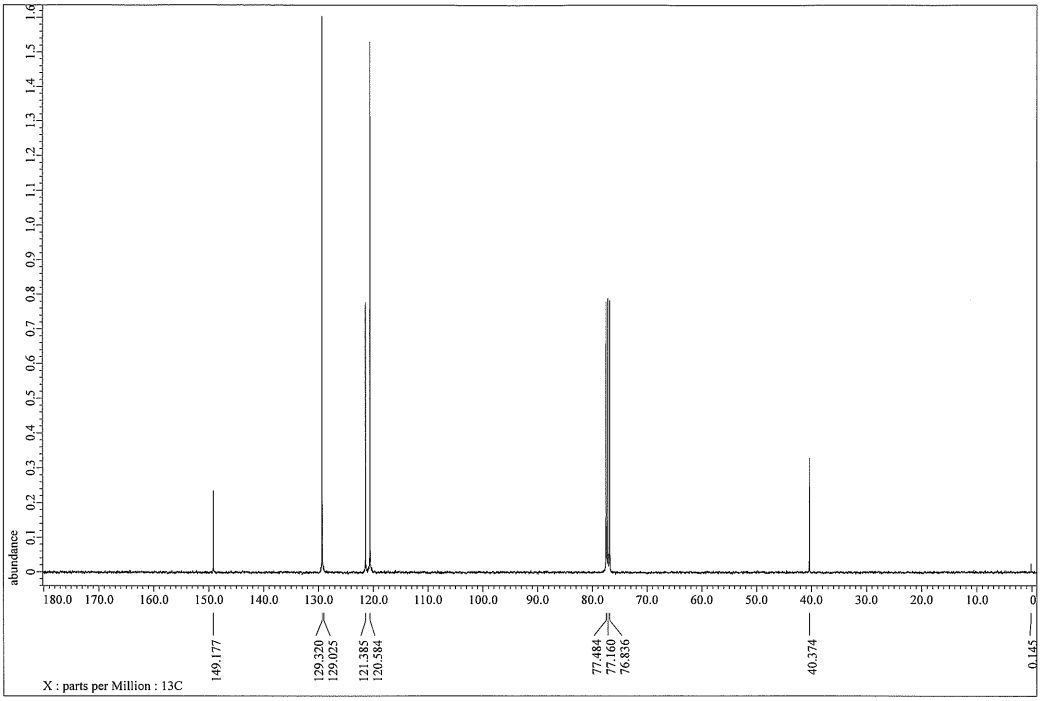

Figure S3. ^{13}C NMR Spectrum of ***N,N*–methylpheneylaniline**.

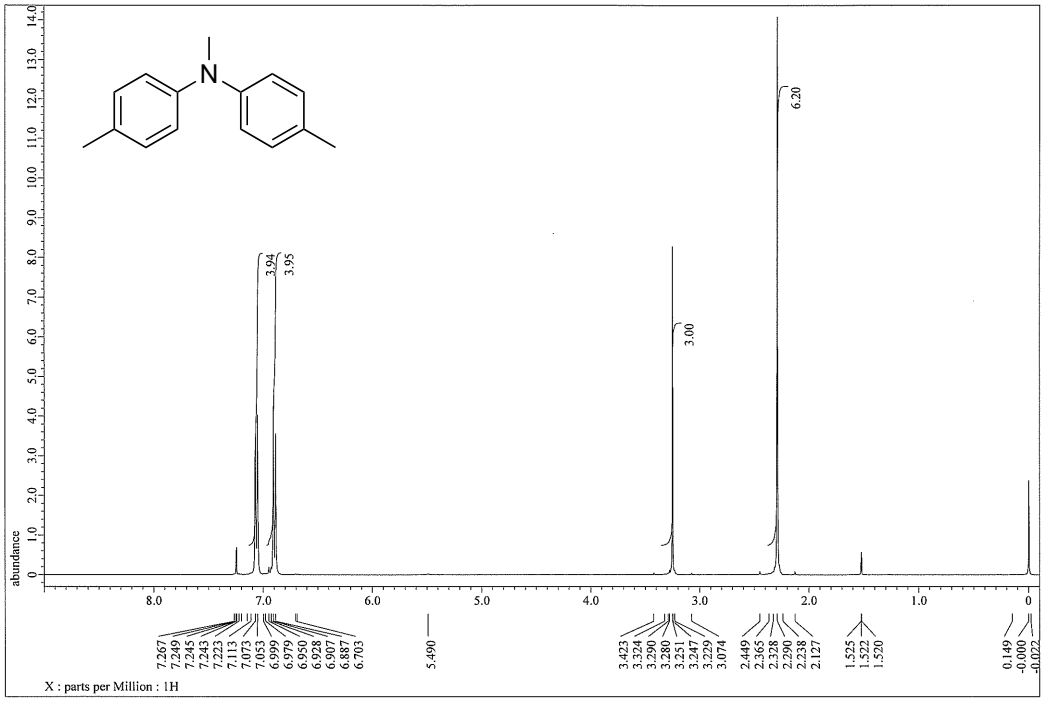

Figure S4. ^{1}H NMR Spectrum of ***N*–methyl–di–p–tolylamine**.

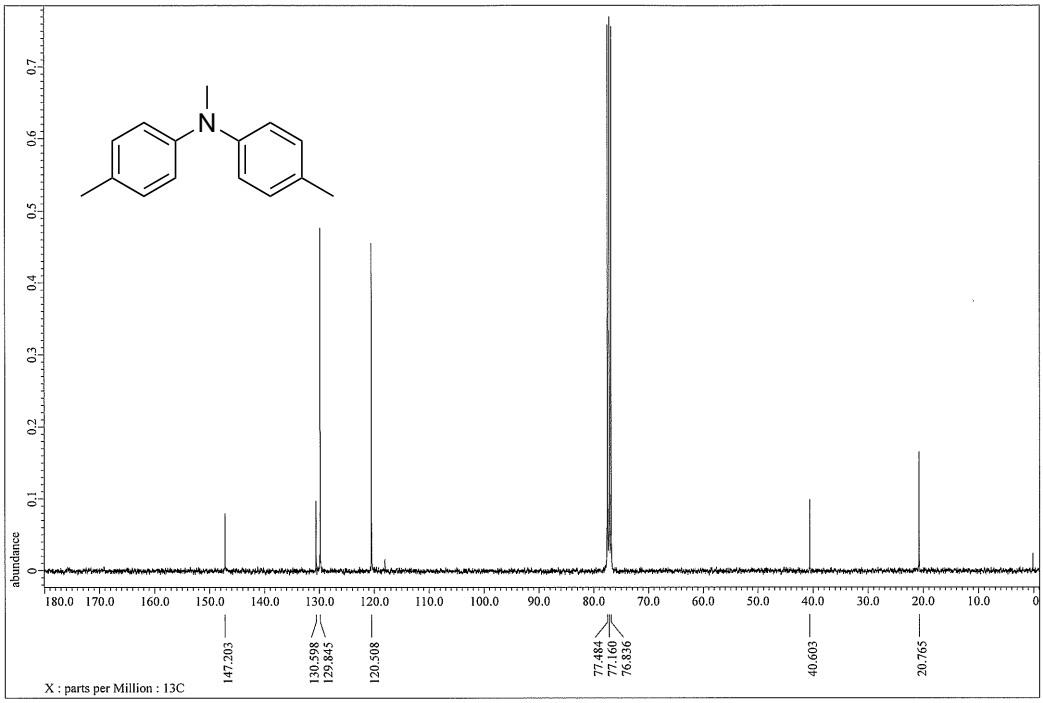

Figure S5. ^{13}C NMR Spectrum of ***N*–methyl–di–p–tolylamine**.

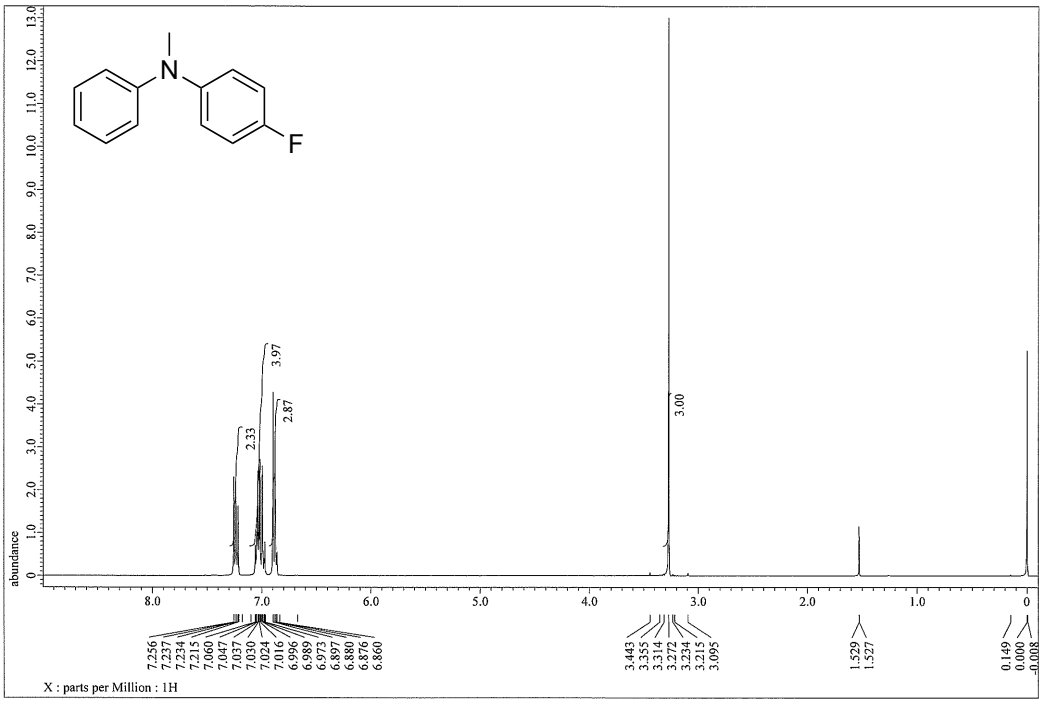

Figure S6. ^{1}H NMR Spectrum of ***N*–methyl–*N*–phenyl–4–fluorolaniline**.

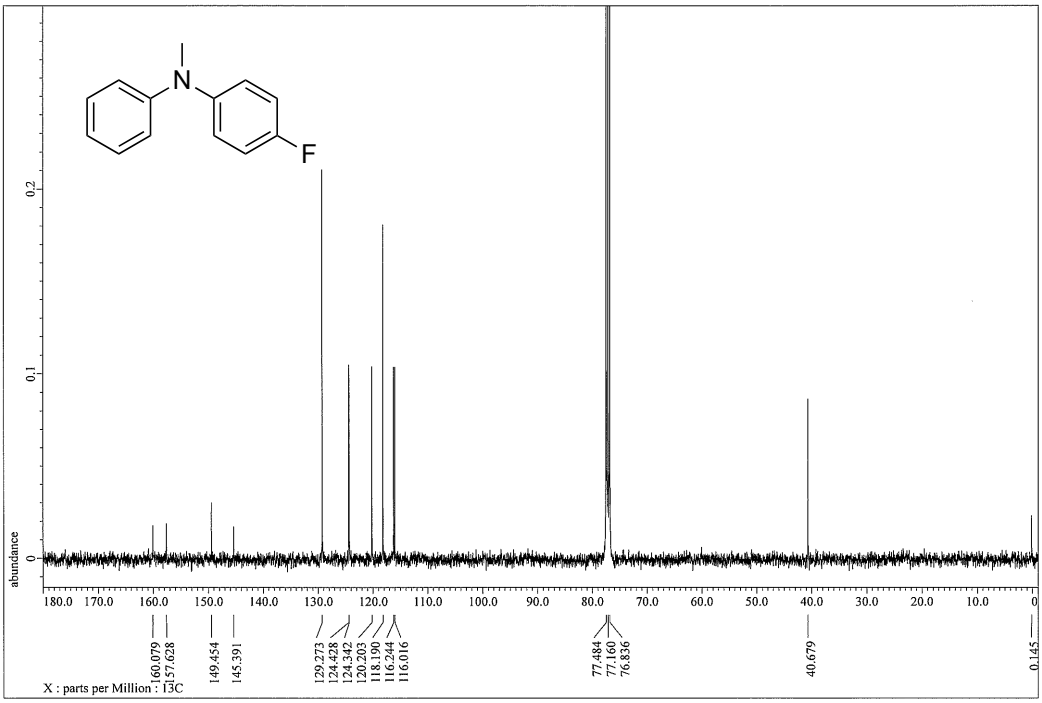

Figure S7. ^{13}C NMR Spectrum of ***N*–methyl–*N*–phenyl–4–fluorolaniline**.

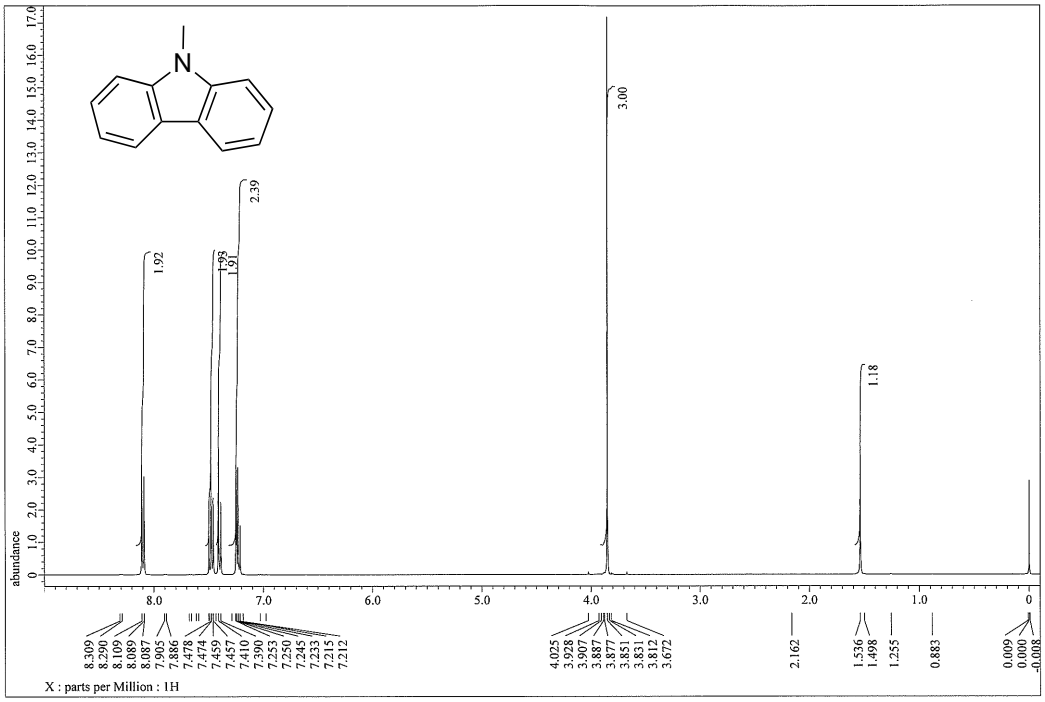

Figure S8. ^{1}H NMR Spectrum of ***N*–methylcarbazole**.

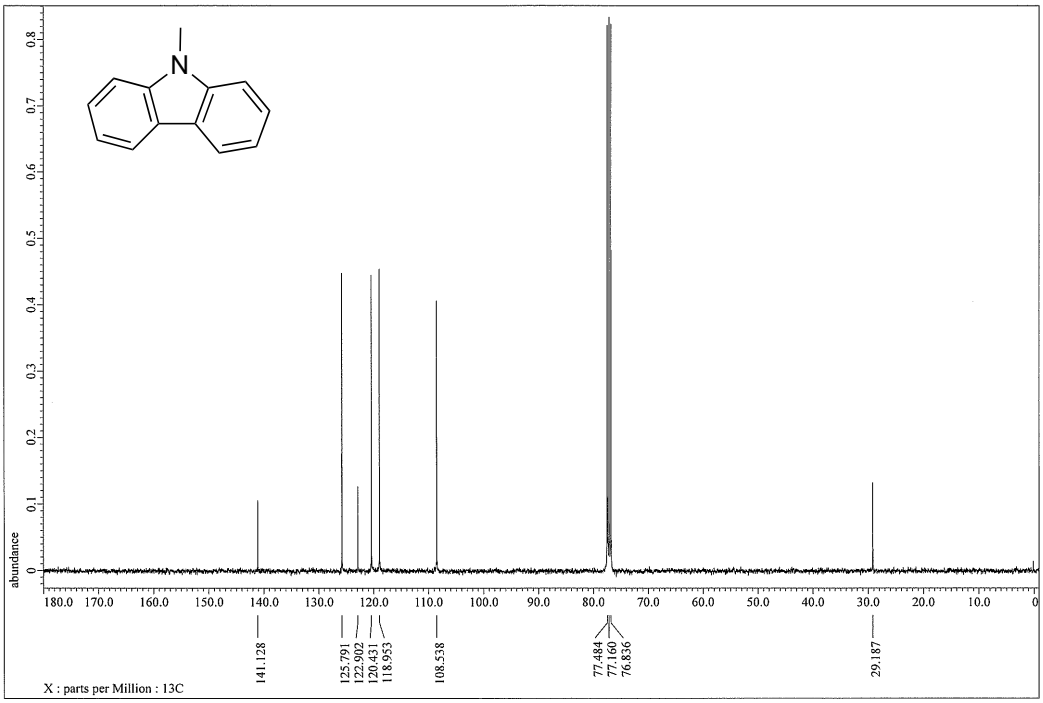

Figure S9. ^{1}H NMR Spectrum of ***N*–methylcarbazole**.

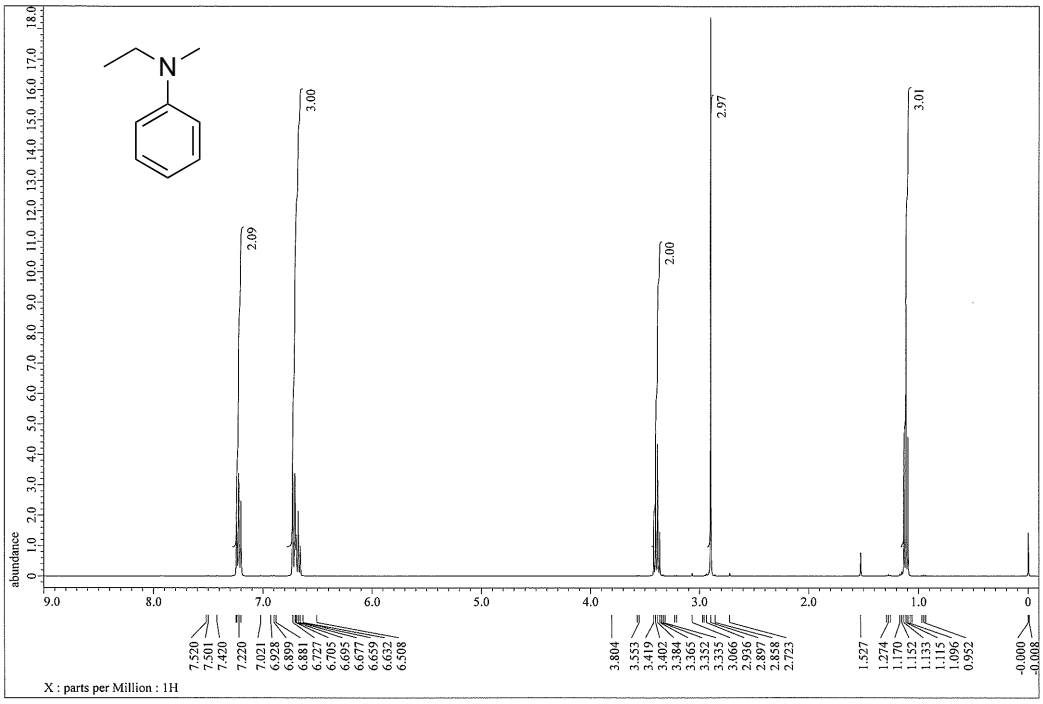

Figure S10. ^{1}H NMR Spectrum of ***N,N*–ethylmethylaniline.**

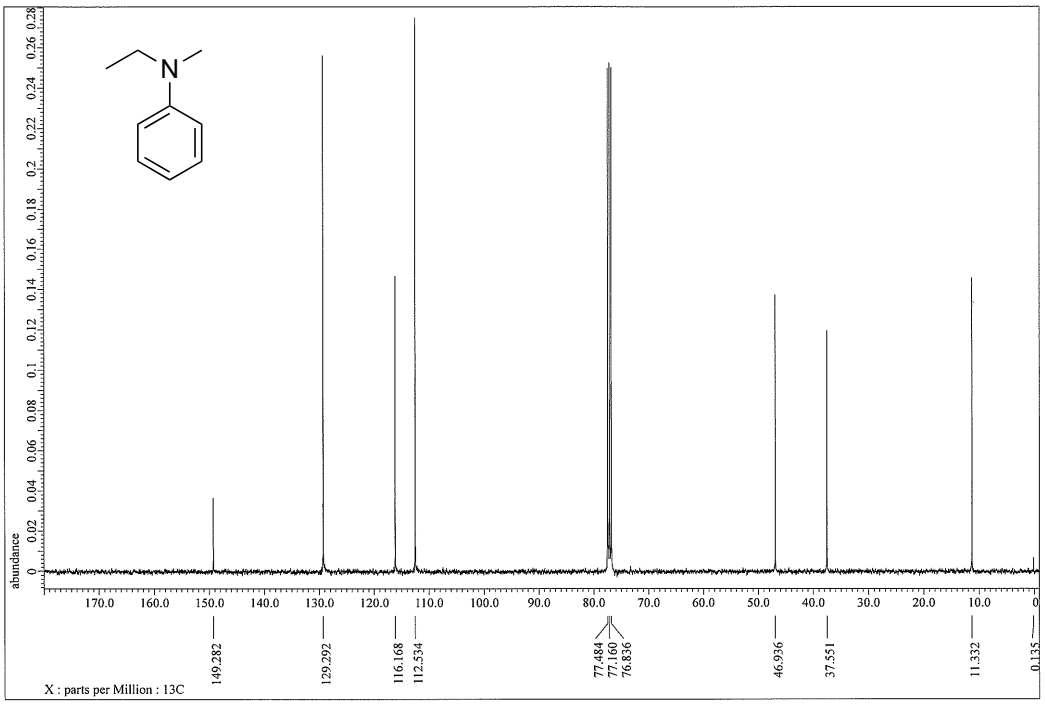

Figure S11. ^{13}C NMR Spectrum of ***N,N*–ethylmethylaniline.**

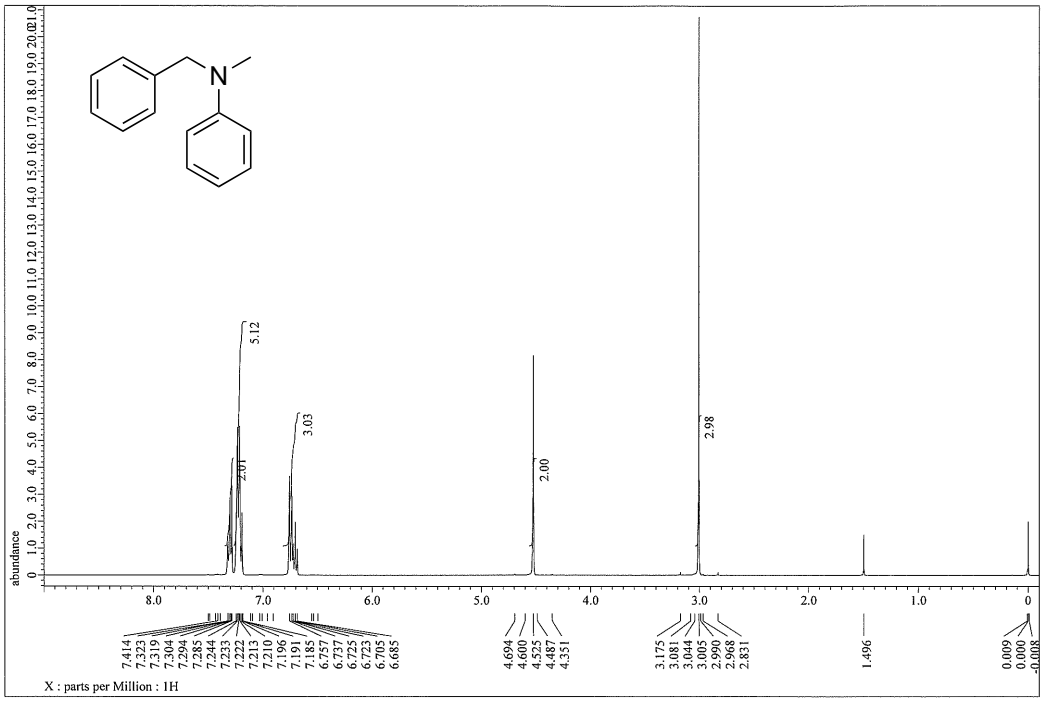

Figure S12. ^{1}H NMR Spectrum of ***N,N*–benzylmethylaniline.**

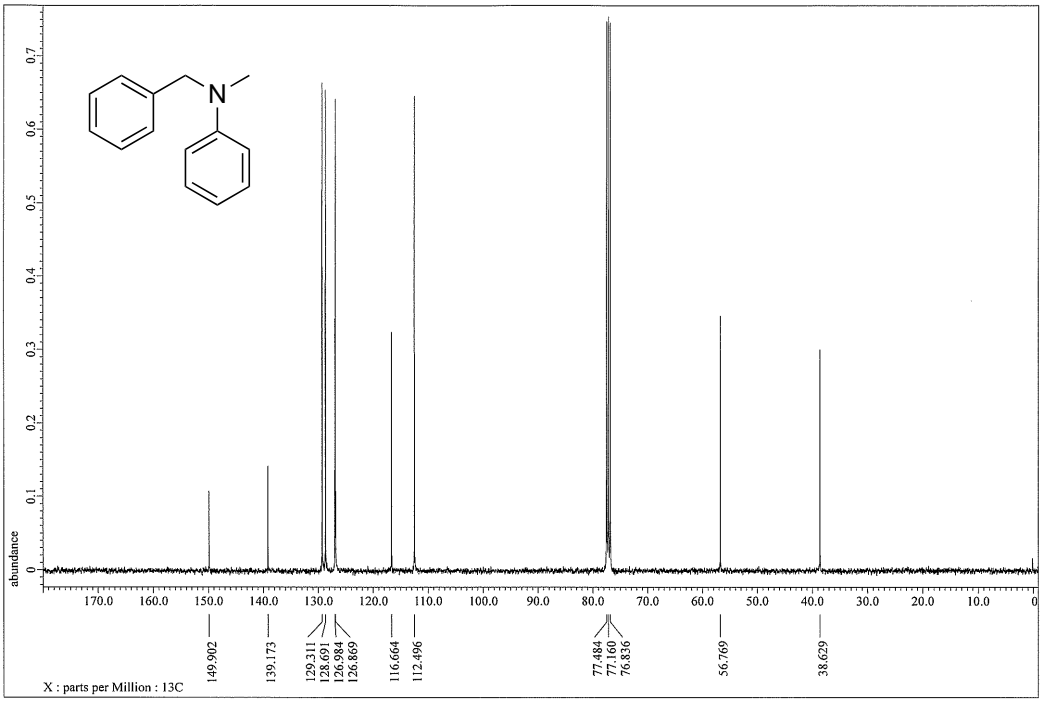

Figure S13. ^{13}C NMR Spectrum of ***N,N*–benzylmethylaniline.**

Figure S14. ^{1}H NMR Spectrum of **1,4–benzoylbenzene.**

Figure S15. ^{13}C NMR Spectrum of **1,4–benzoylbenzene.**

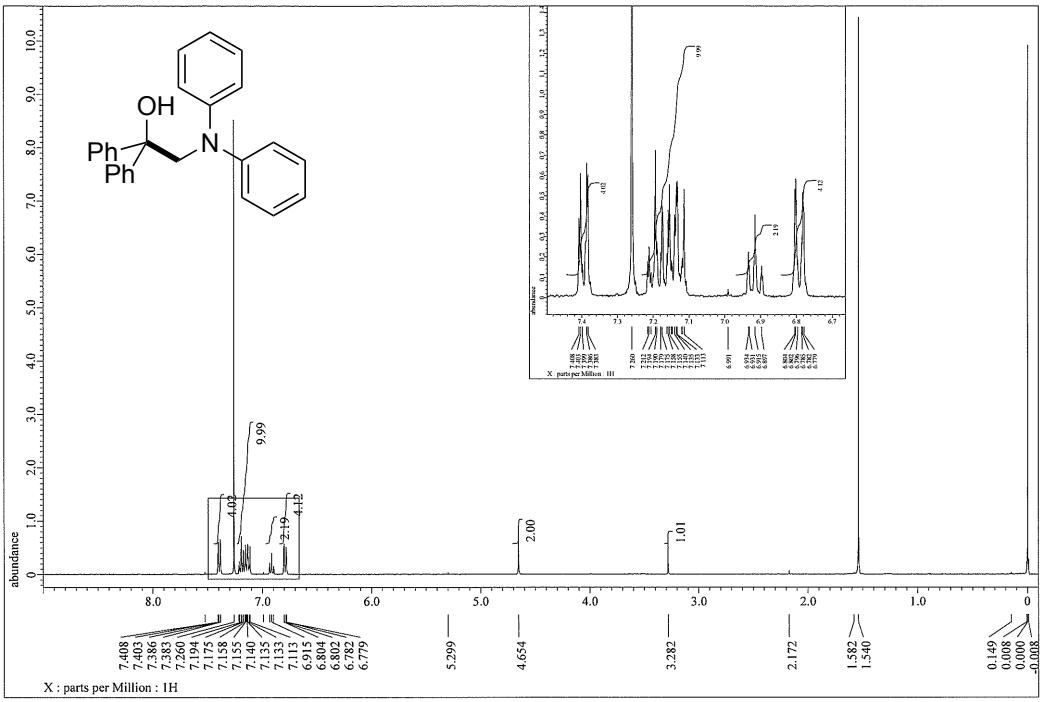

Figure S16. ^{1}H NMR Spectrum of **3a.**

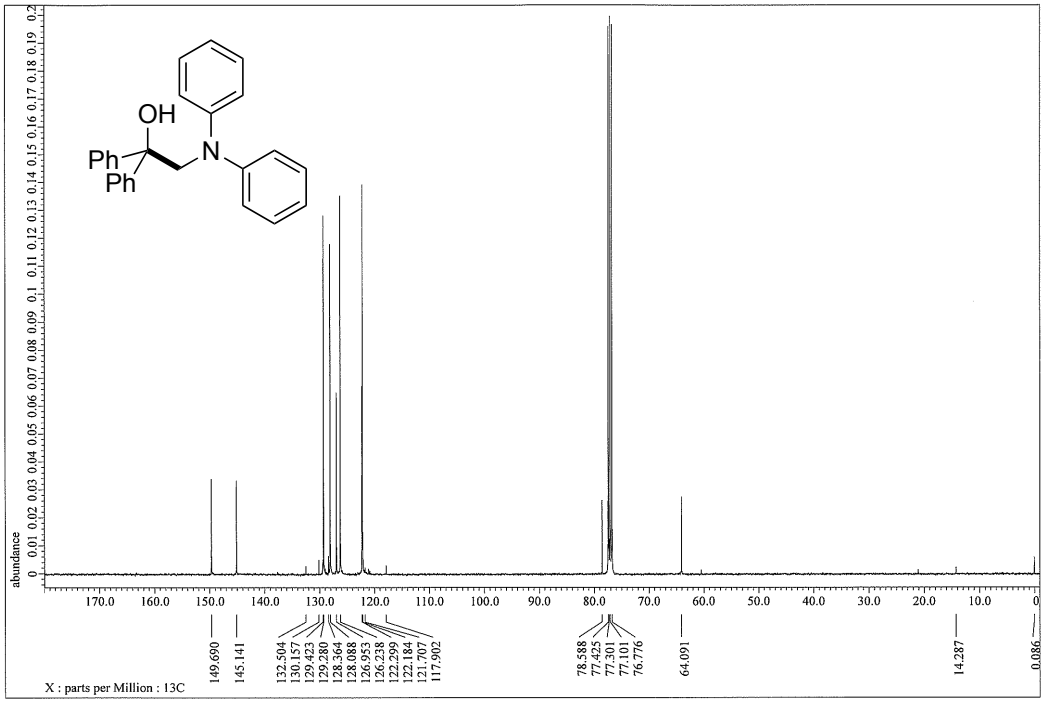

Figure S17. ^{13}C NMR Spectrum of **3a.**

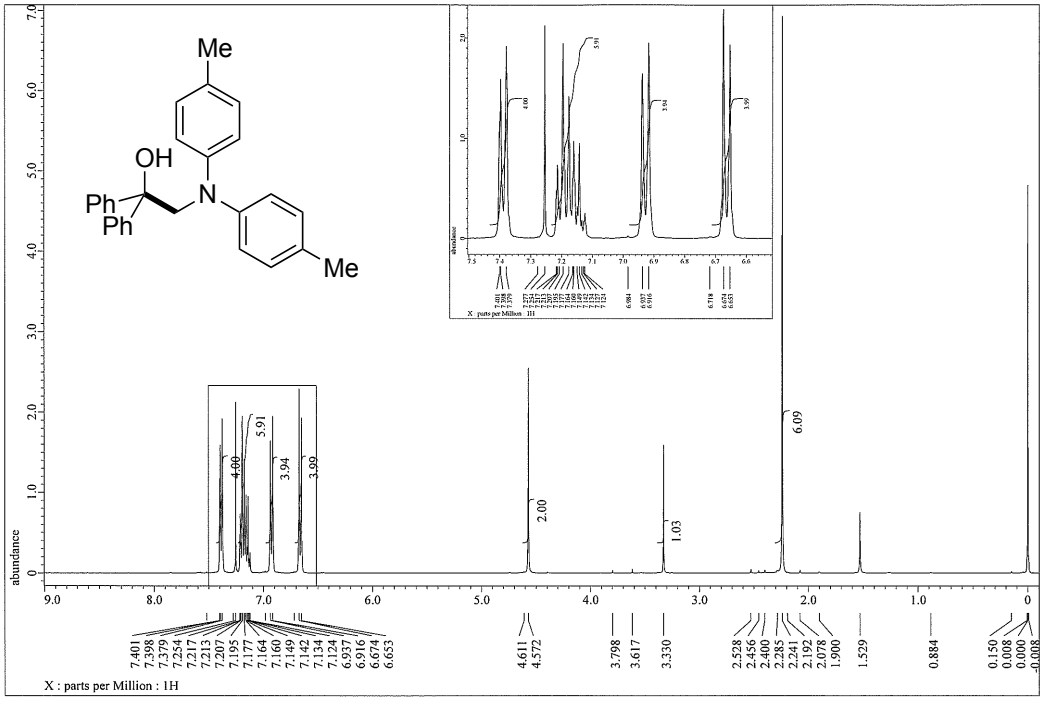

Figure S18. ^{1}H NMR Spectrum of **3b.**

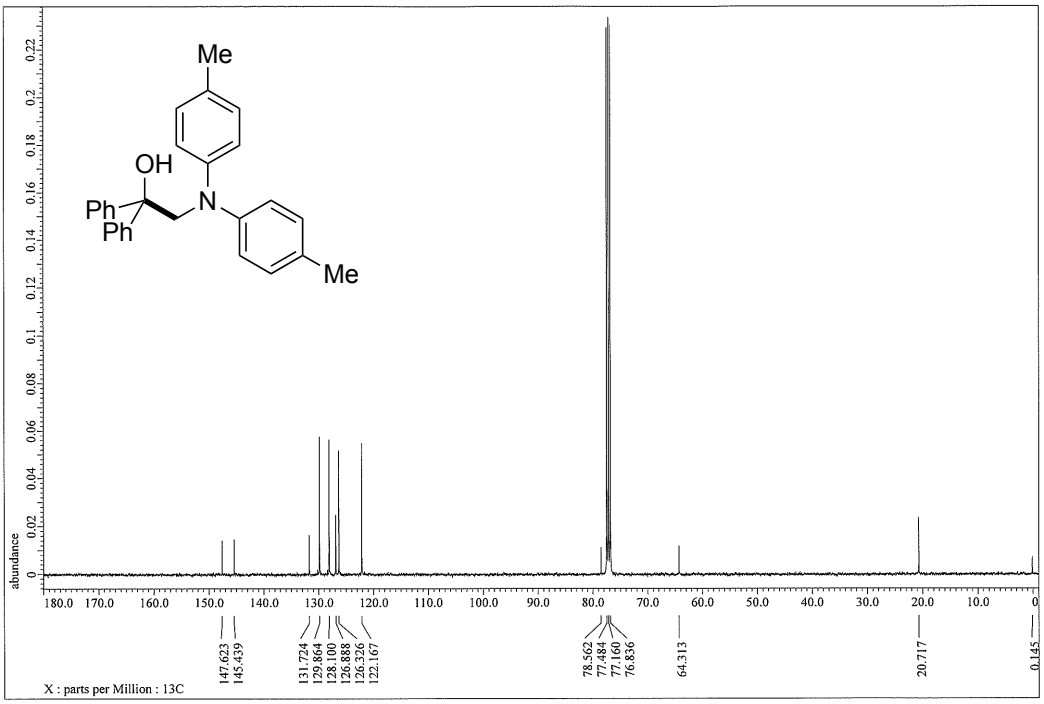

Figure S19. ^{13}C NMR Spectrum of **3b.**

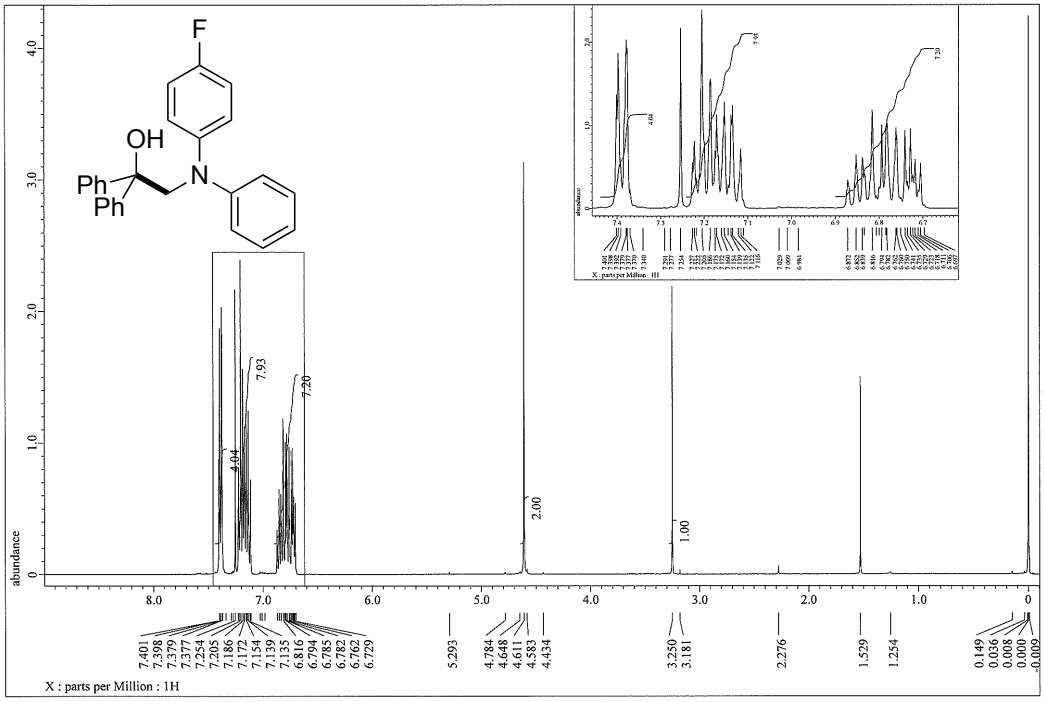

Figure S20. ^{1}H NMR Spectrum of **3c.**

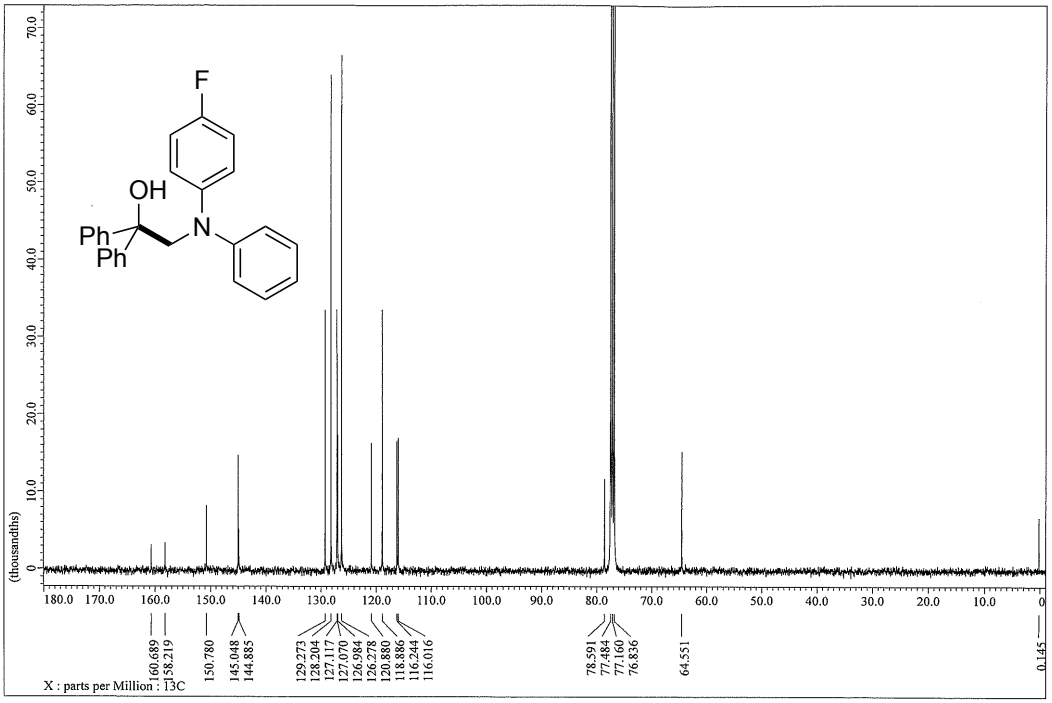

Figure S21. ^{13}C NMR Spectrum of **3c.**

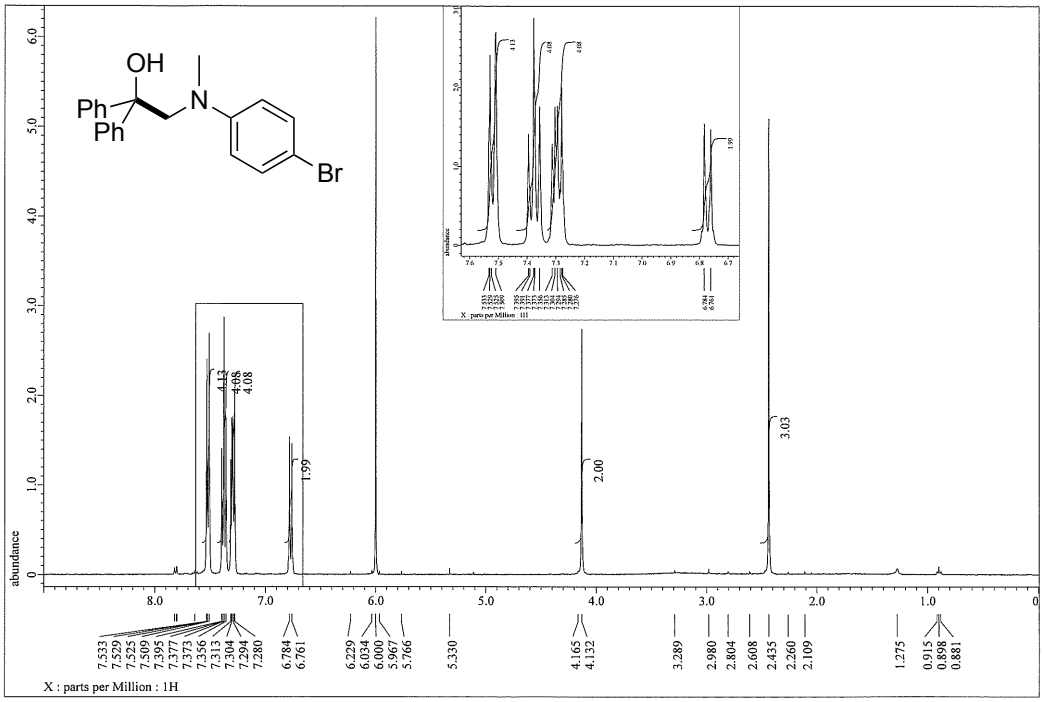

Figure S22. ^{1}H NMR Spectrum of **3d.**

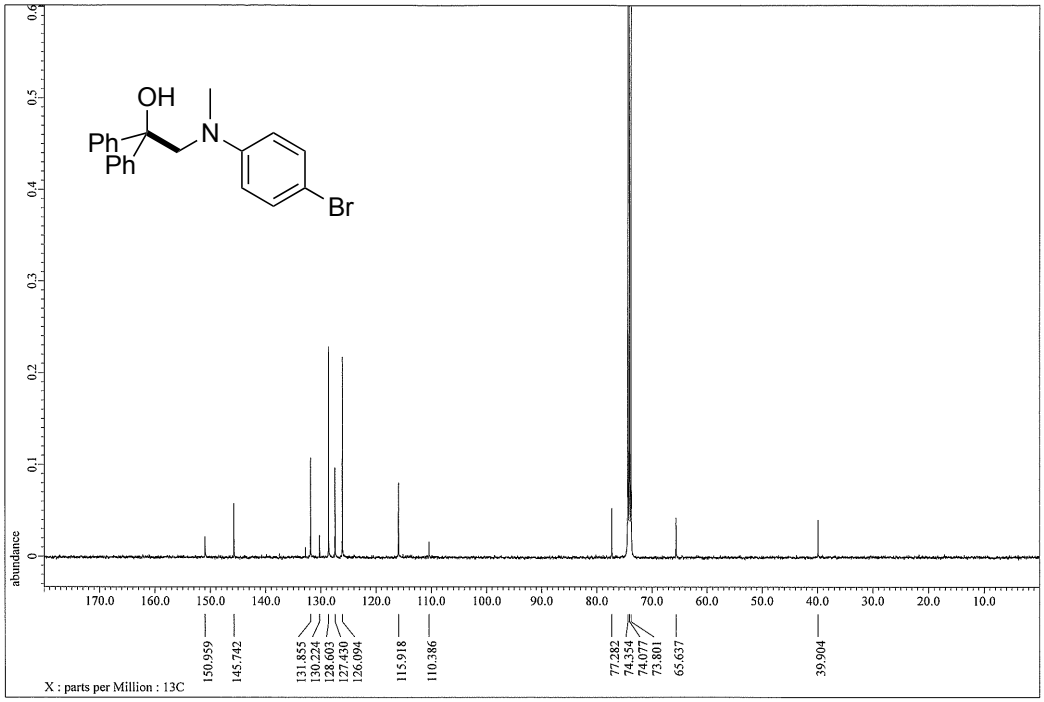

Figure S23. ^{13}C NMR Spectrum of **3d.**

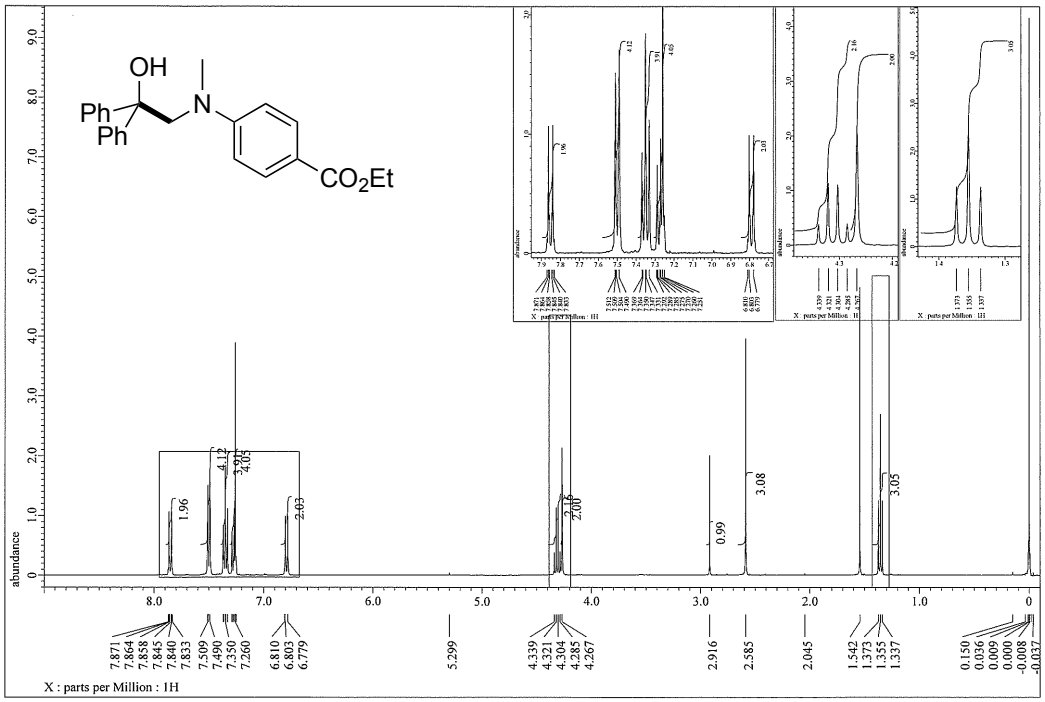

Figure S24. ^{1}H NMR Spectrum of **3e.**

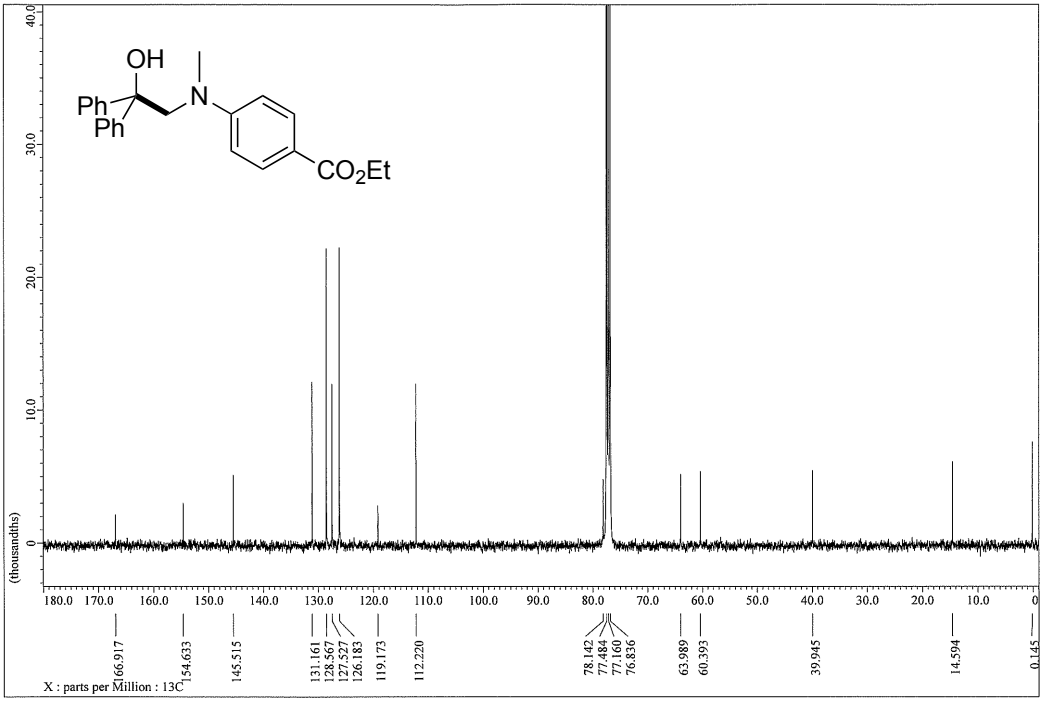

Figure S25. ^{13}C NMR Spectrum of **3e.**

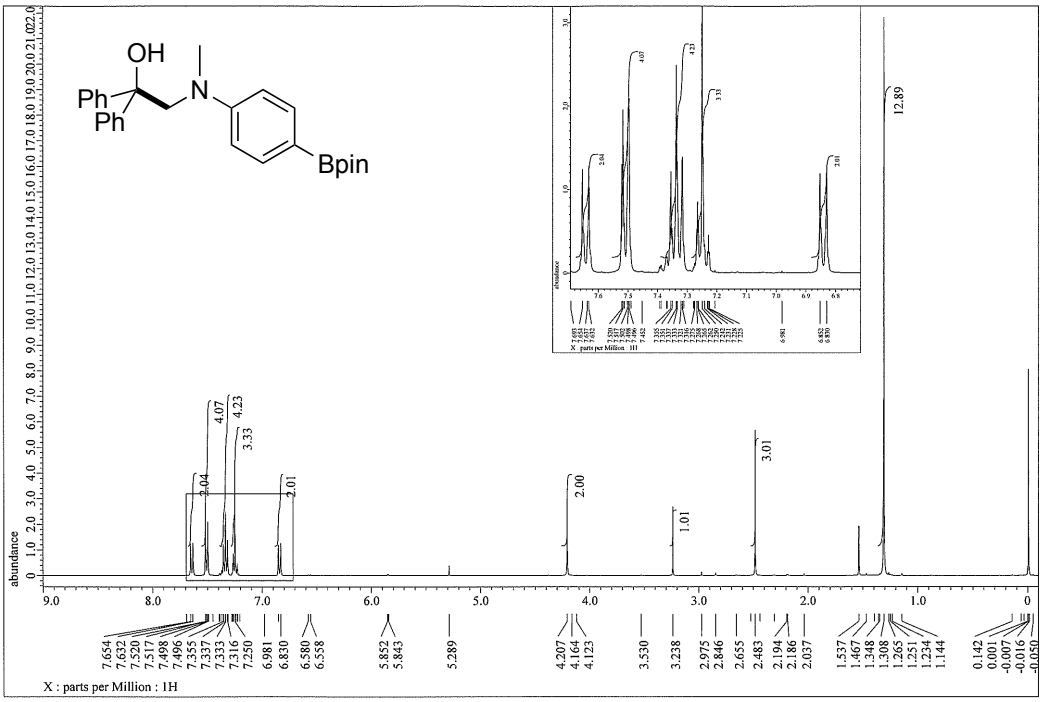

Figure S26. ^{1}H NMR Spectrum of **3f.**

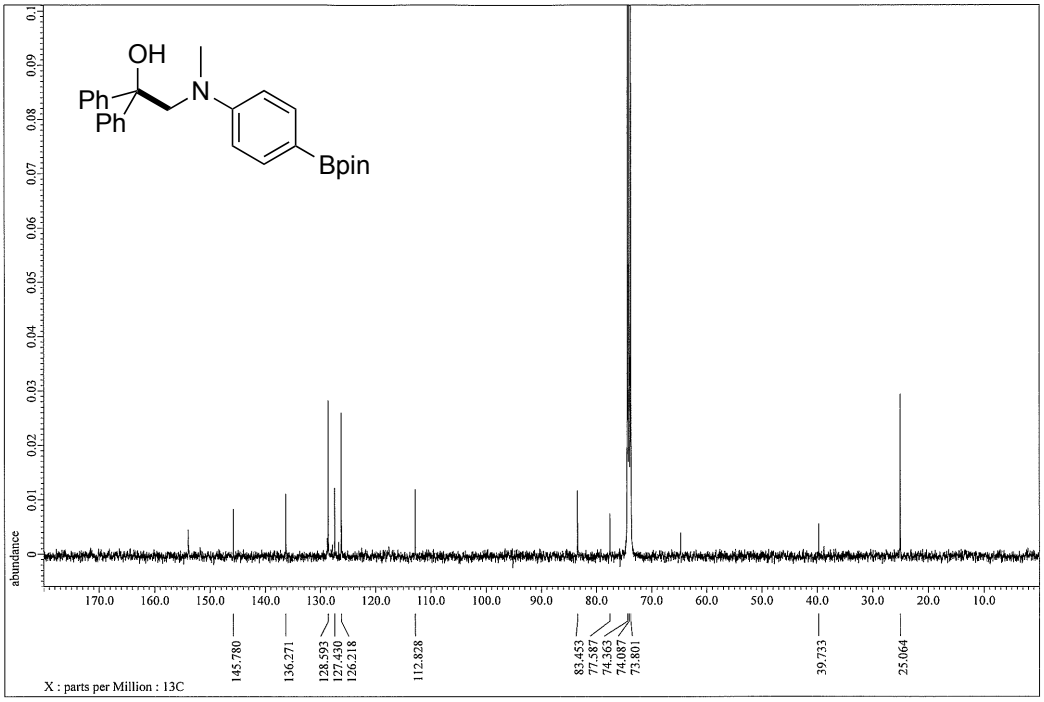

Figure S27. ^{13}C NMR Spectrum of **3f.**

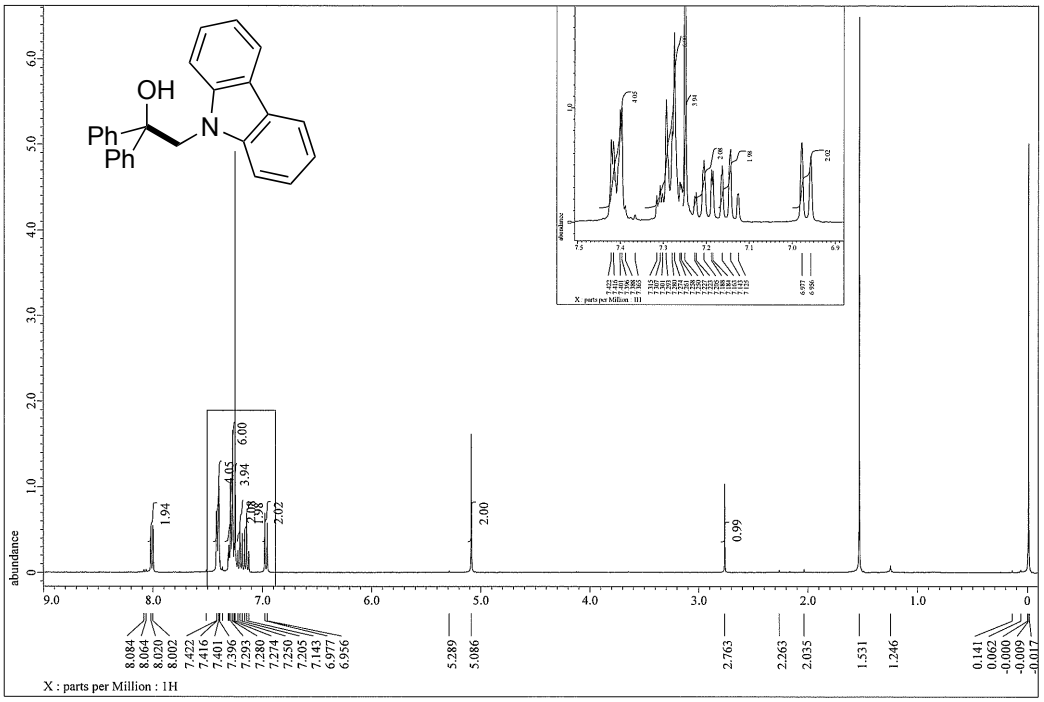

Figure S28. ^{1}H NMR Spectrum of **3g.**

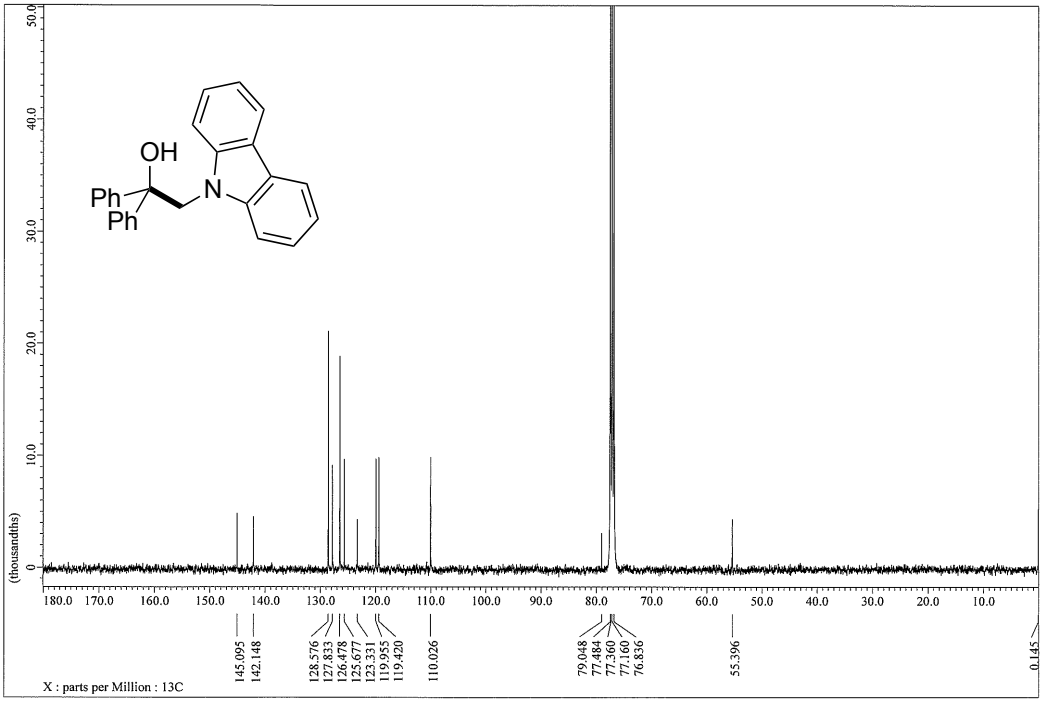

Figure S29. ^{13}C NMR Spectrum of **3g.**

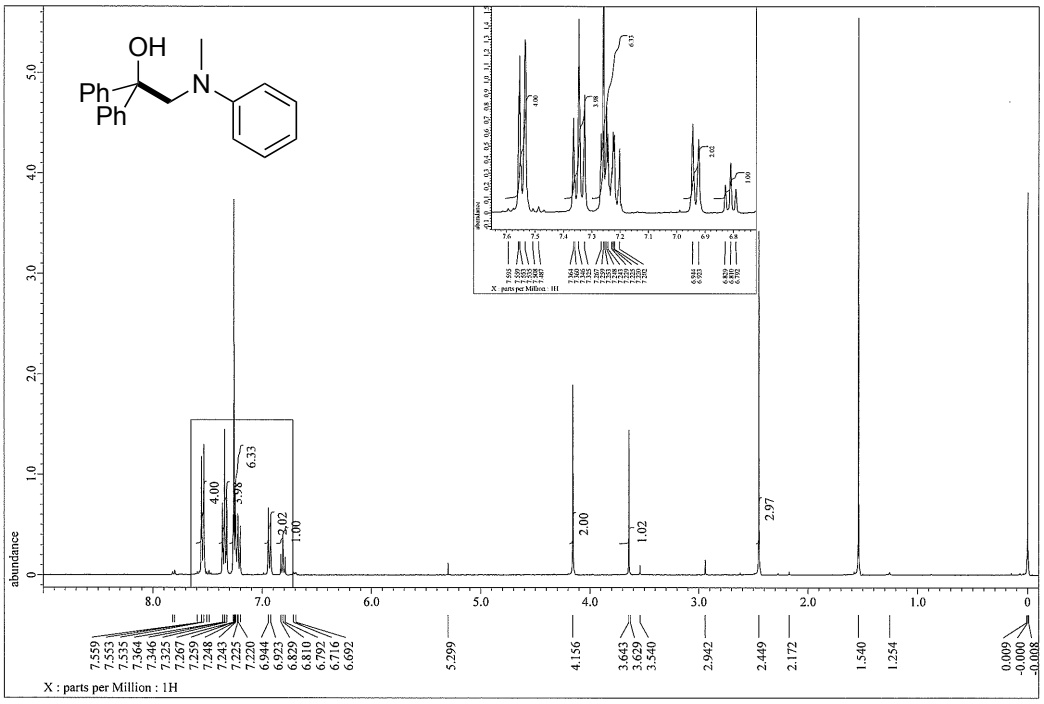

Figure S30. ^{1}H NMR Spectrum of **3h.**

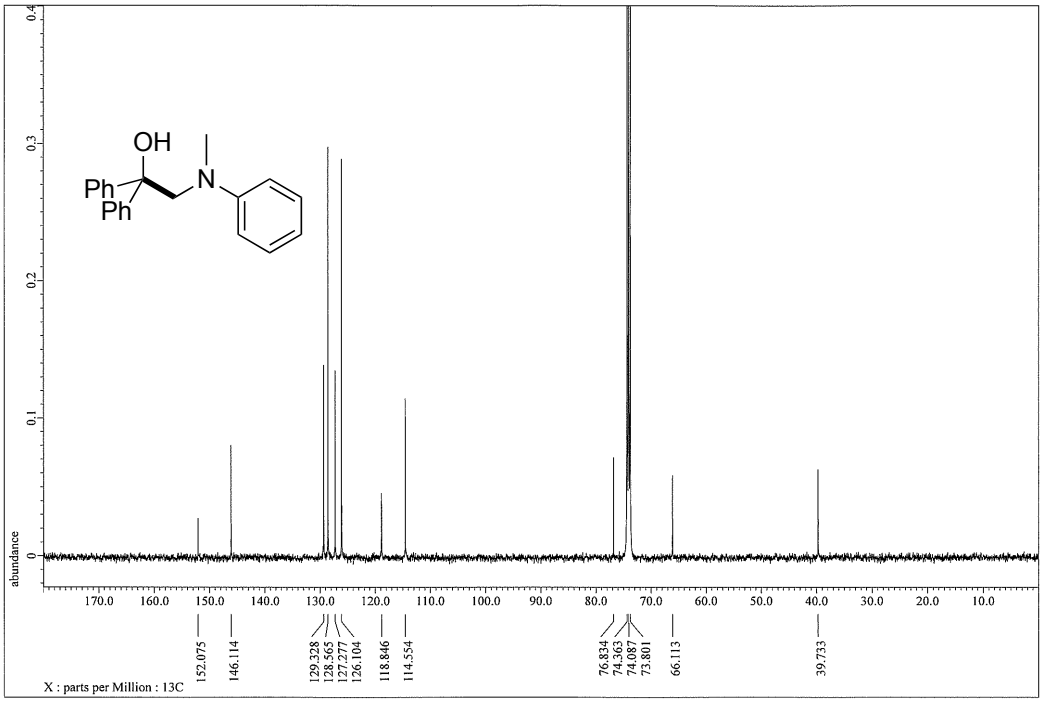

Figure S31. ^{13}C NMR Spectrum of **3h.**

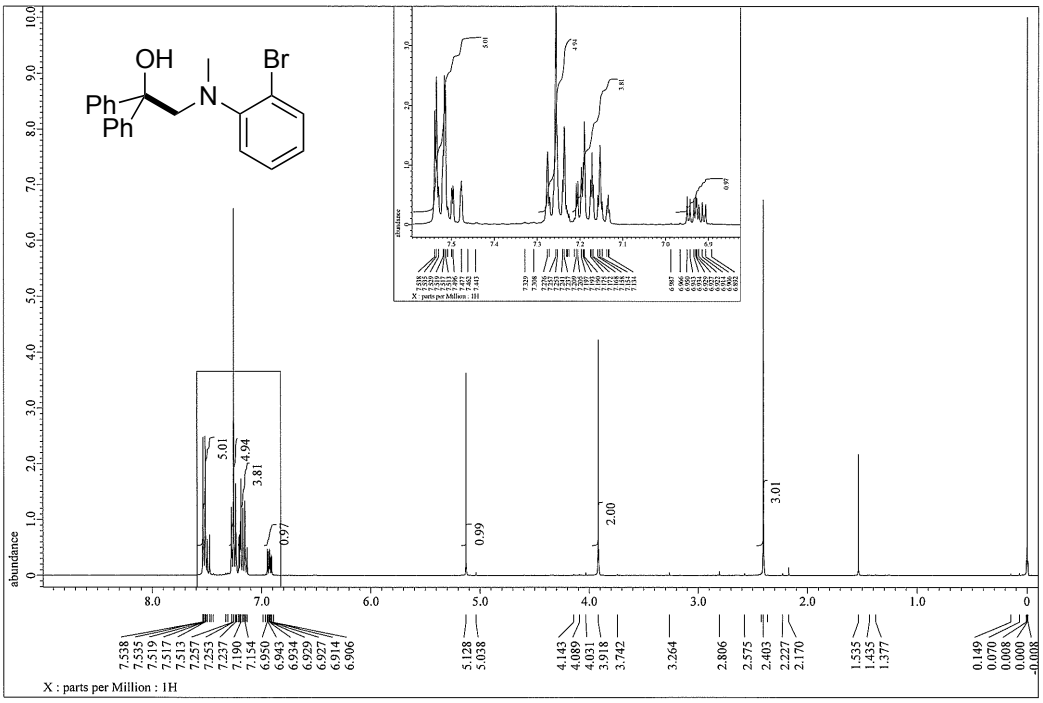

Figure S32. ^{1}H NMR Spectrum of **3i.**

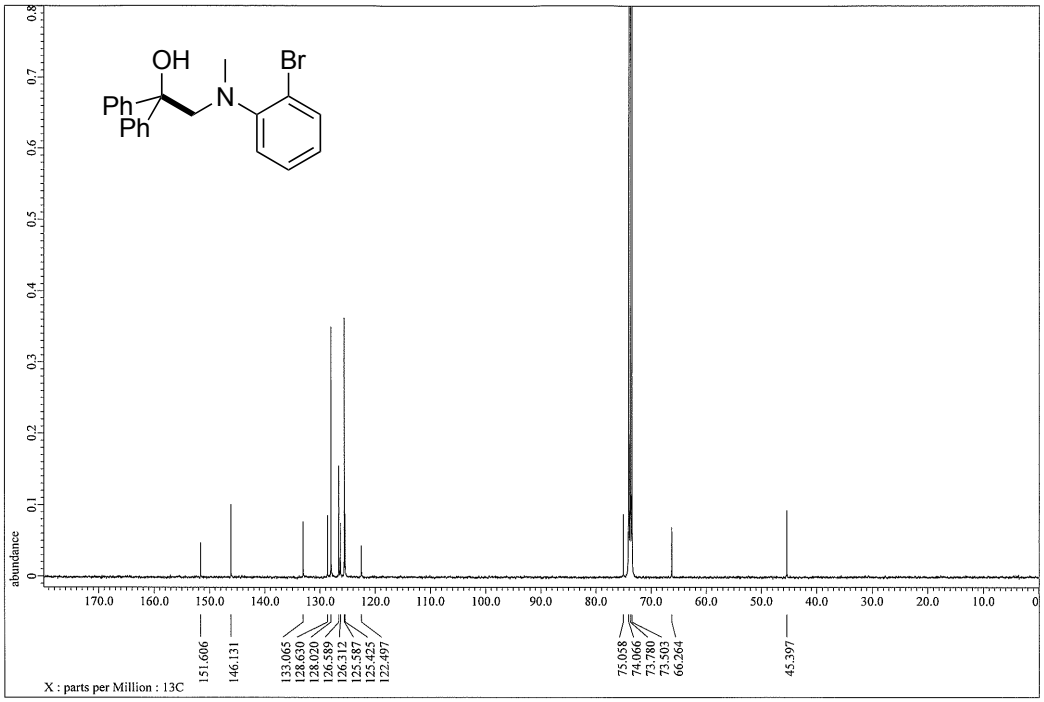

Figure S33. ^{13}C NMR Spectrum of **3i.**

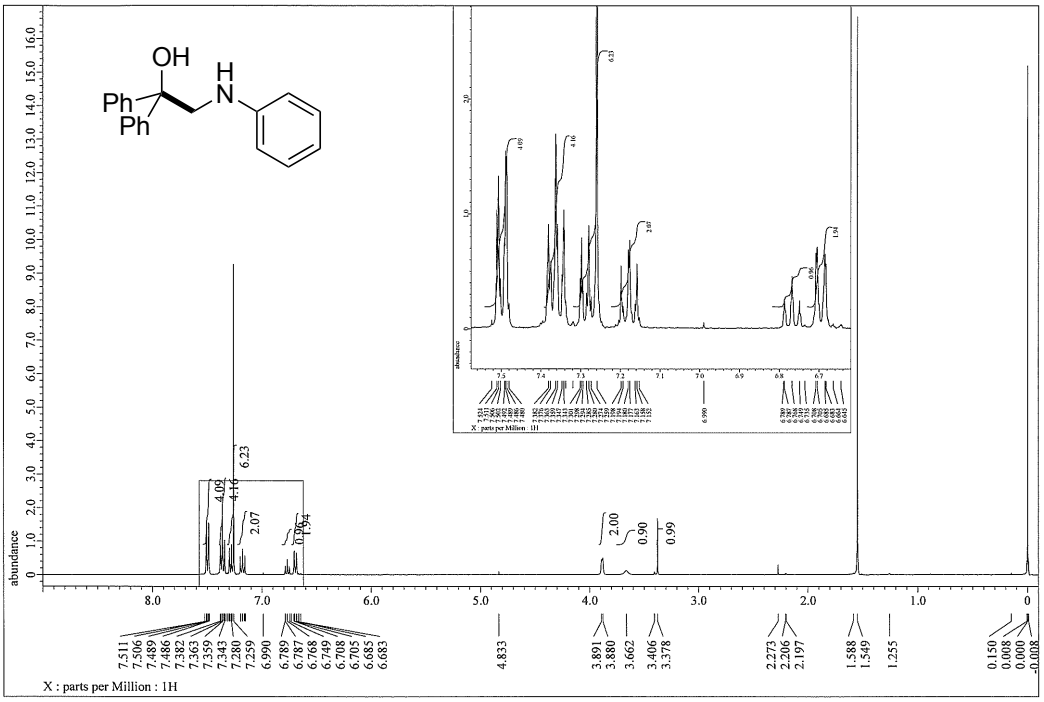

Figure S34. ^{1}H NMR Spectrum of **3j.**

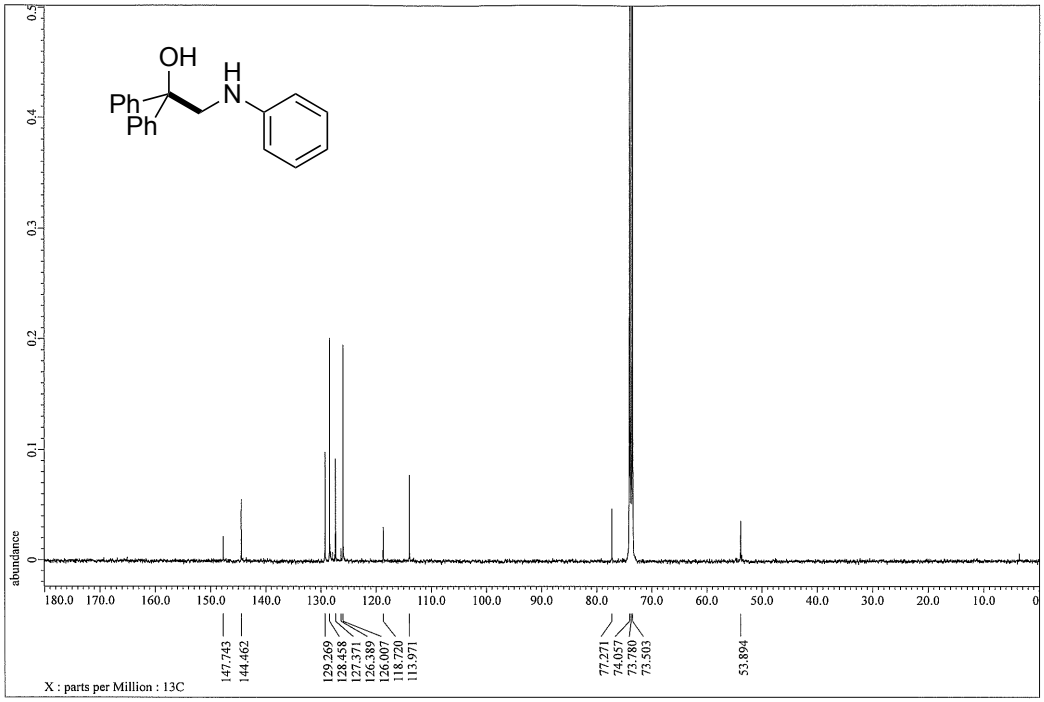

Figure S35. ^{13}C NMR Spectrum of **3j.**

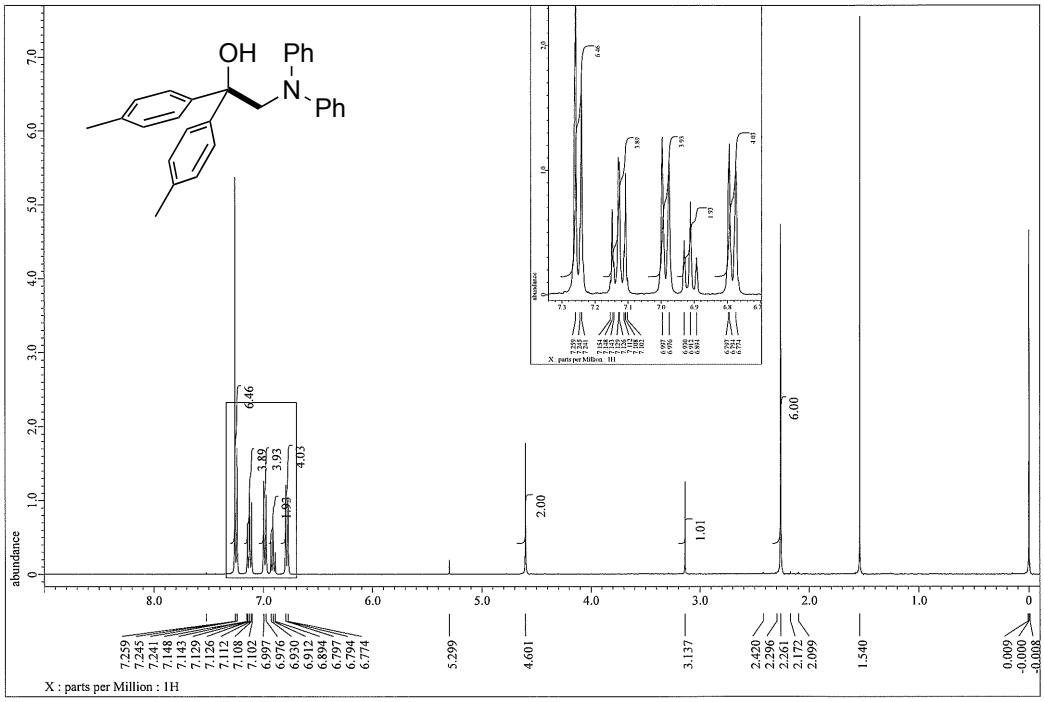

Figure S36. ^{1}H NMR Spectrum of **3k.**

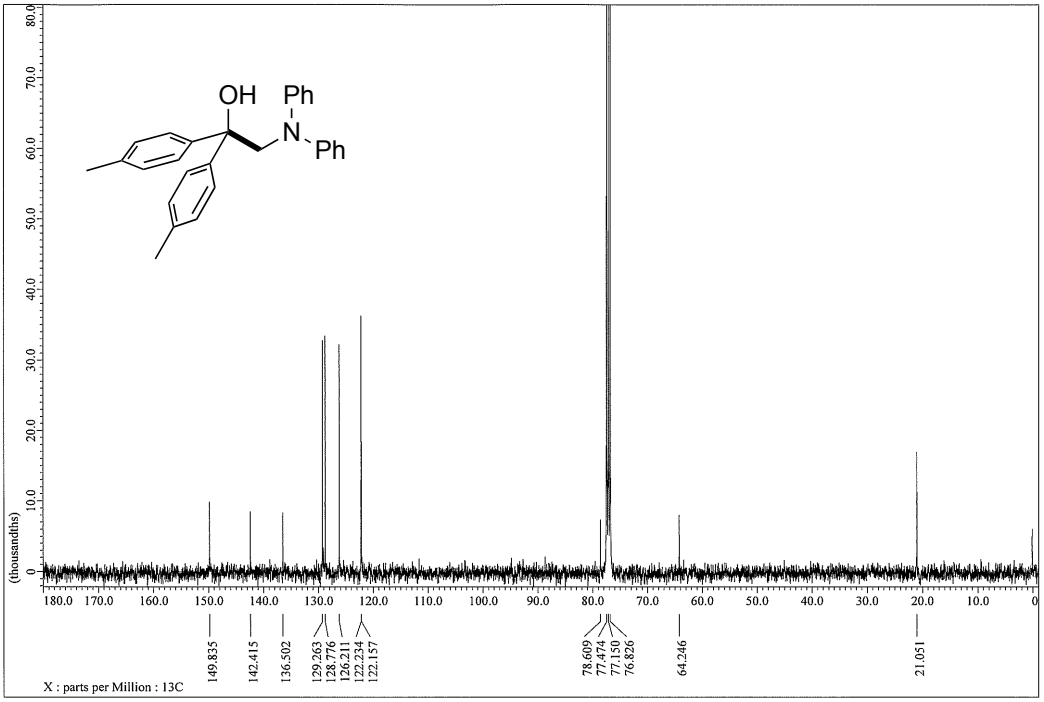

Figure S37. ^{13}C NMR Spectrum of **3k.**

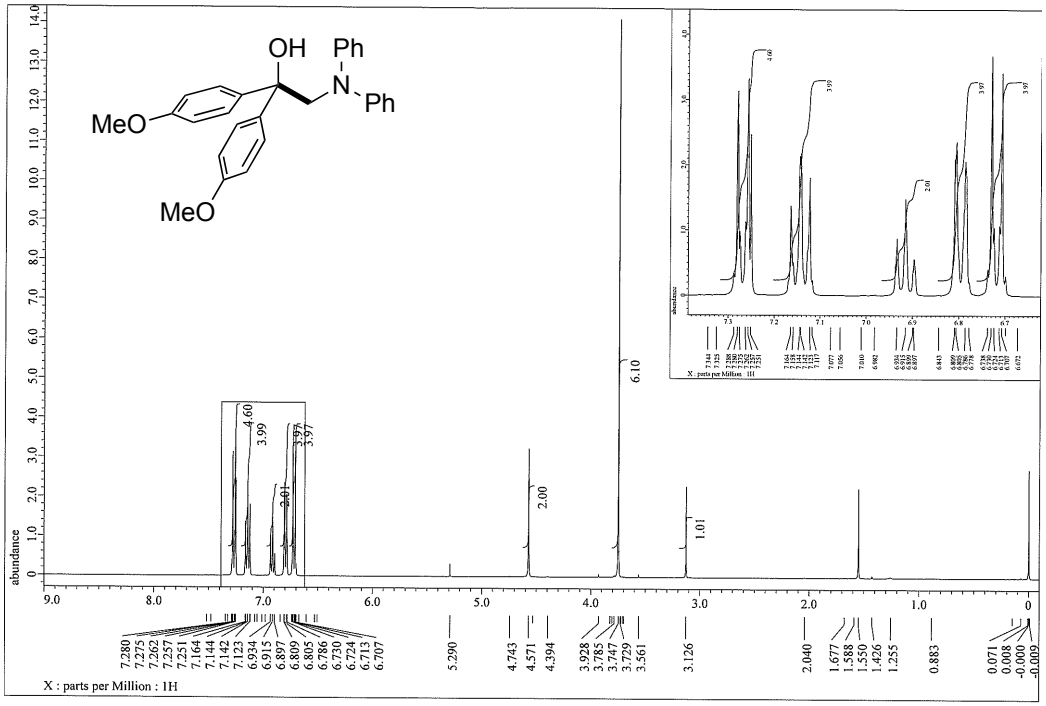

Figure S38. ^{1}H NMR Spectrum of **3l.**

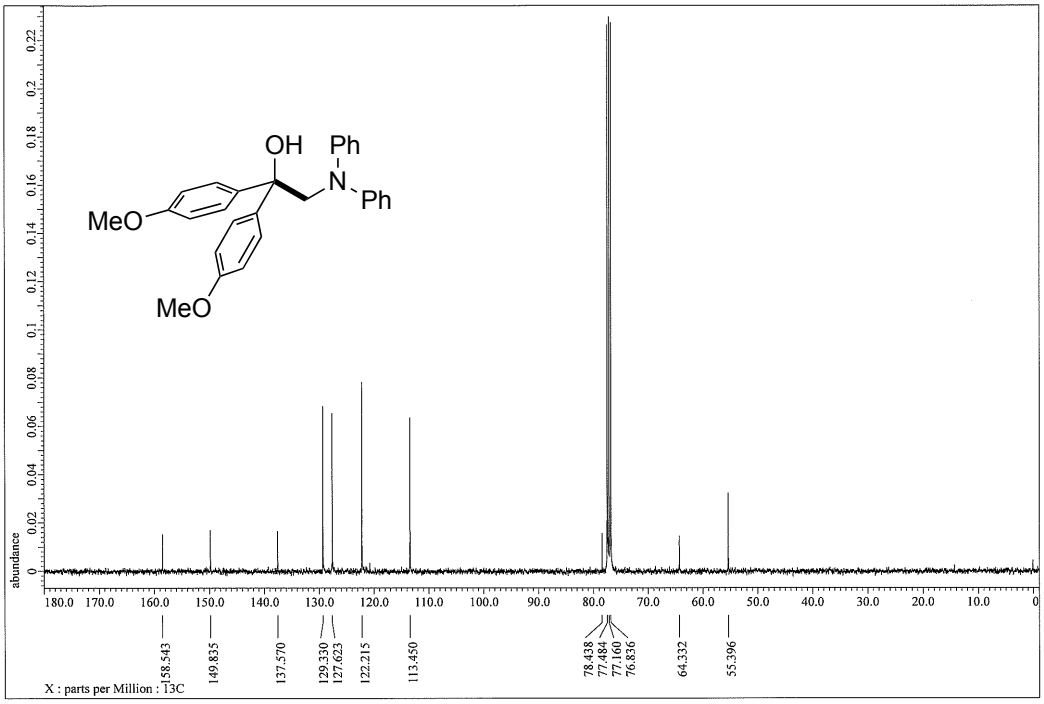

Figure S39. ^{13}C NMR Spectrum of **3l.**

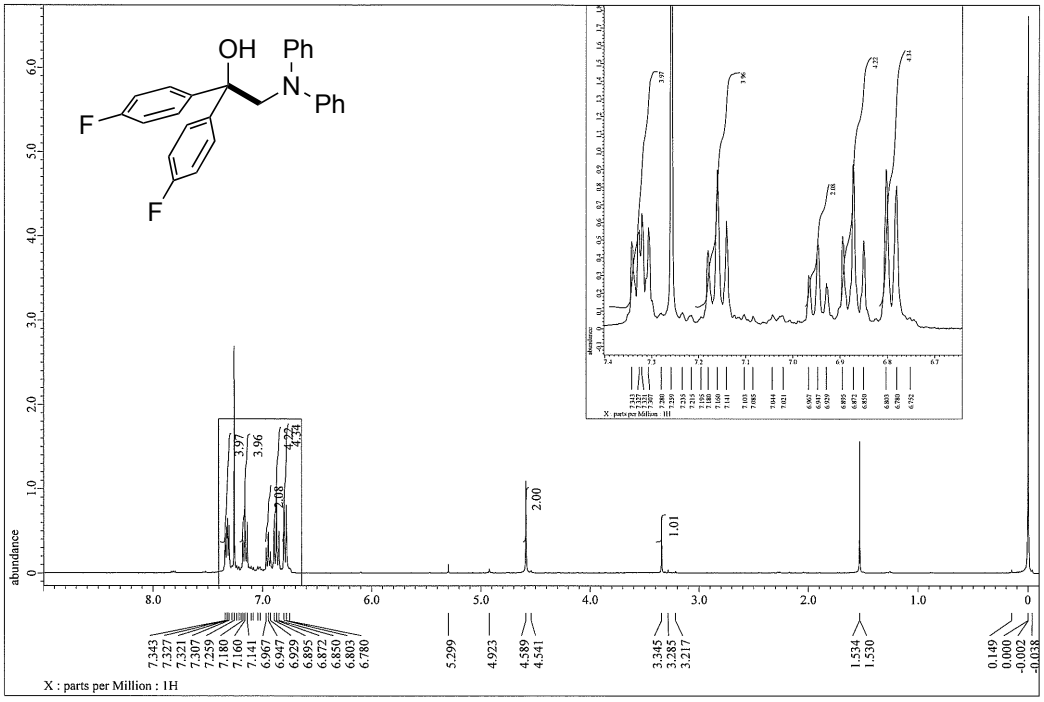

Figure S40. ^{1}H NMR Spectrum of **3m.**

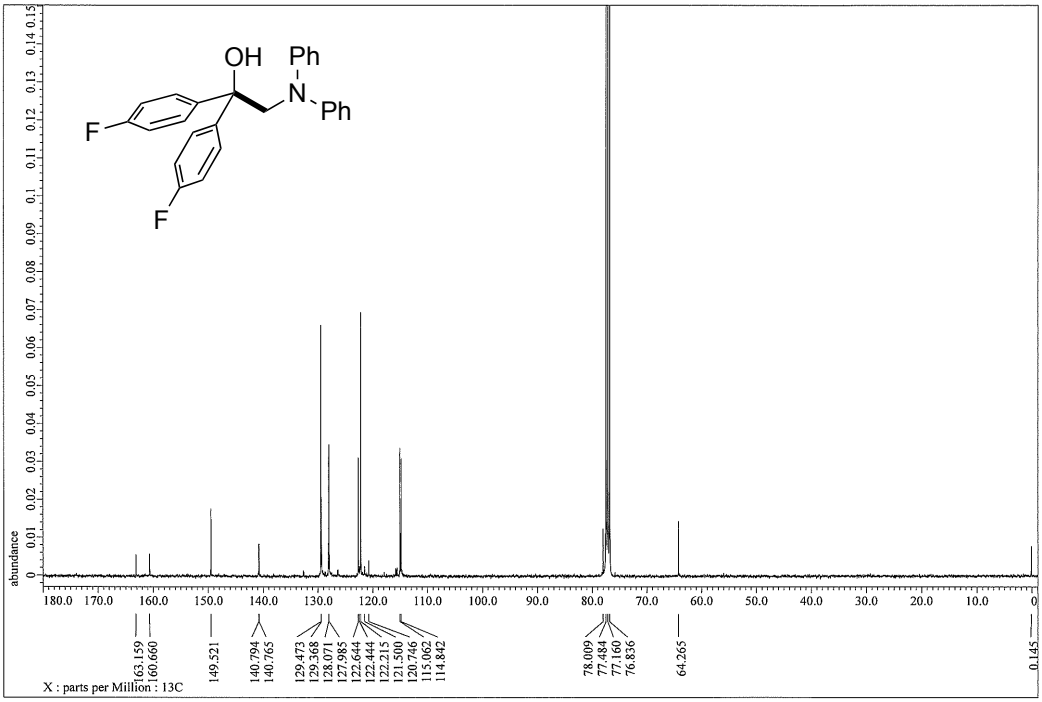

Figure S41. ^{13}C NMR Spectrum of **3m.**

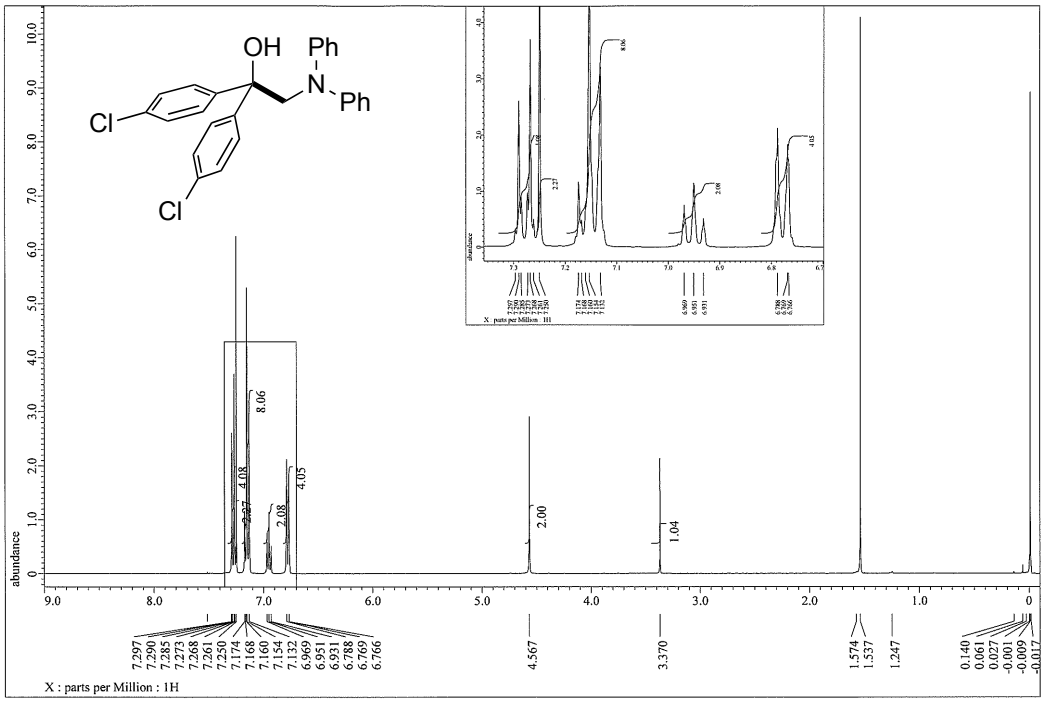

Figure S42. ^{1}H NMR Spectrum of **3n.**

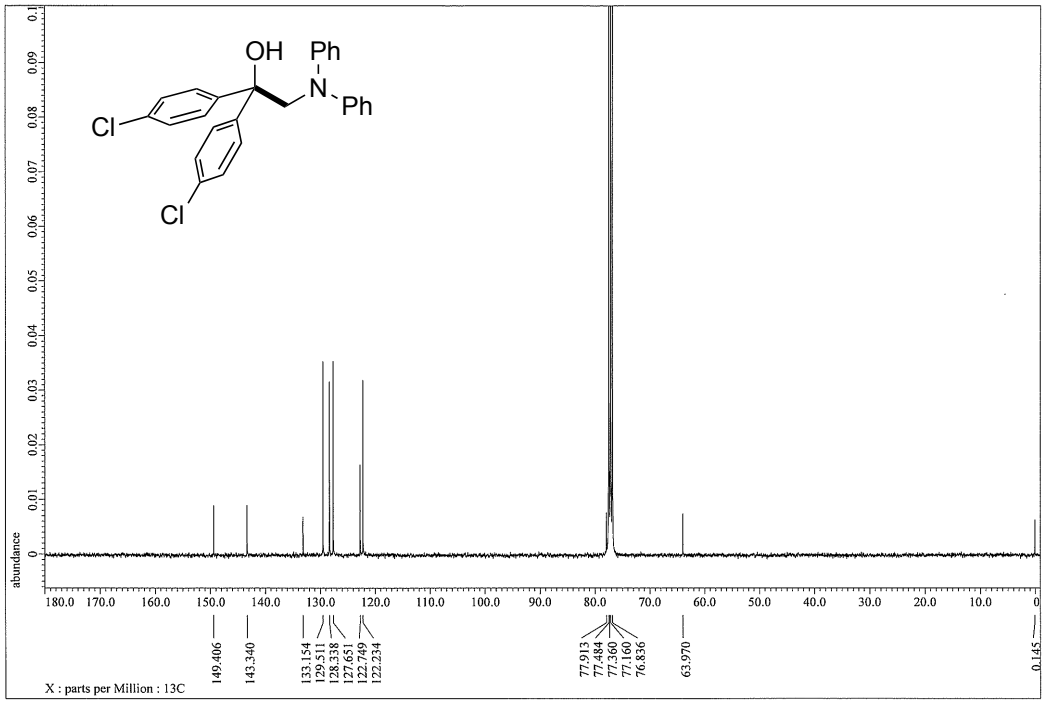

Figure S43. ^{13}C NMR Spectrum of **3n.**

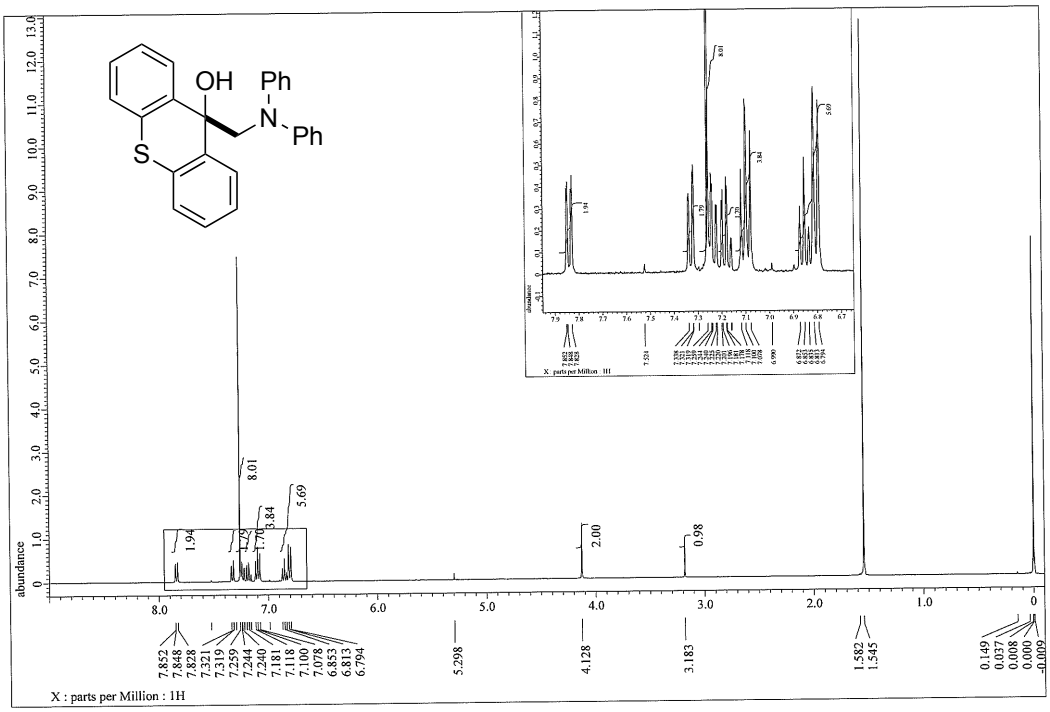

Figure S44. ^{1}H NMR Spectrum of **3o.**

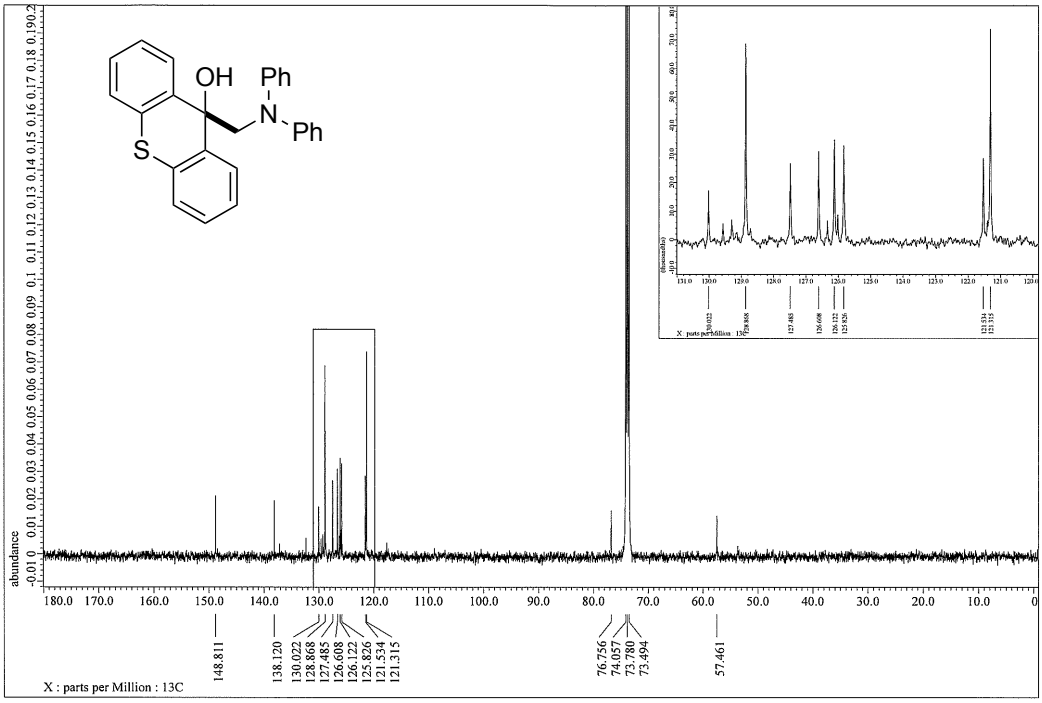

Figure S45. ^{13}C NMR Spectrum of **3o.**

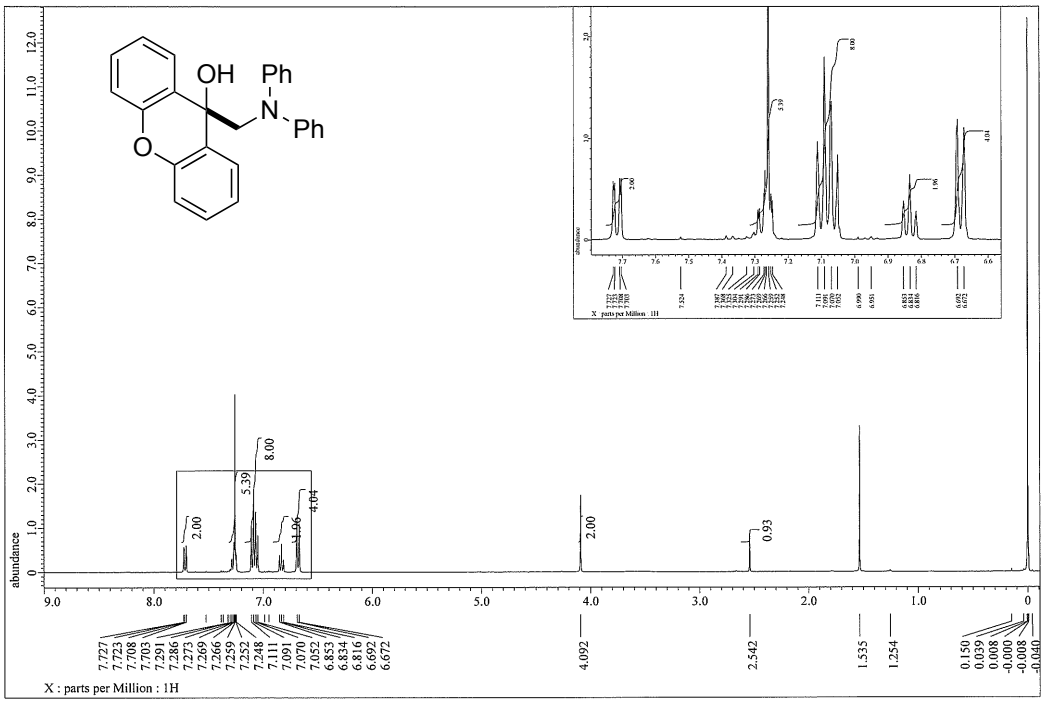

Figure S46. ^{1}H NMR Spectrum of **3p.**

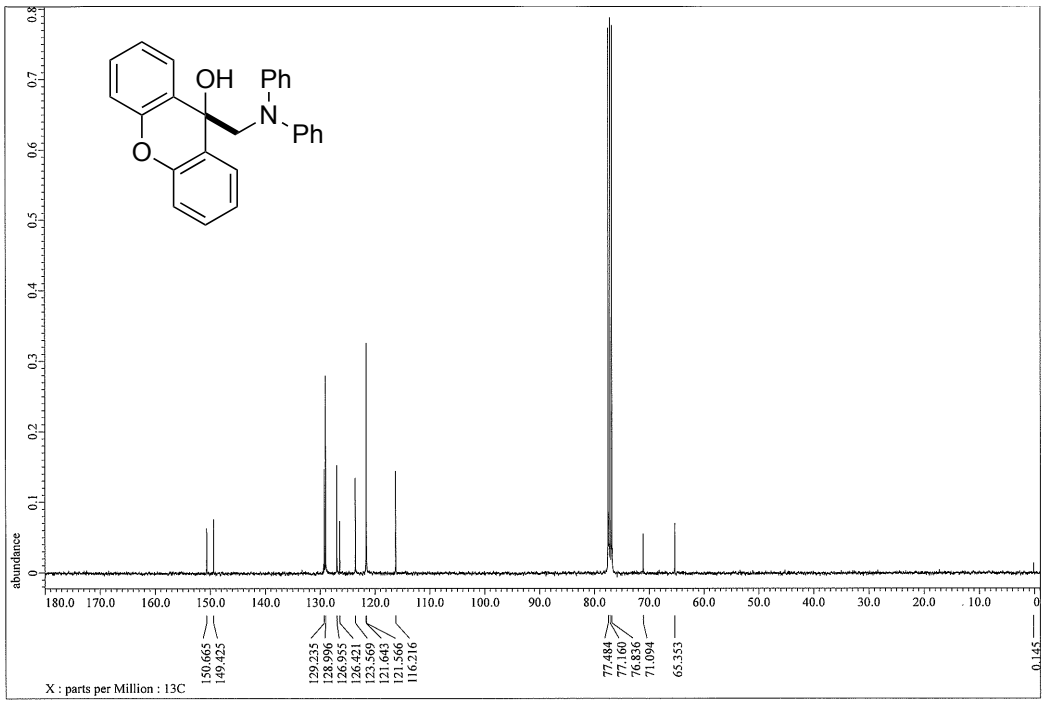

Figure S47. ^{13}C NMR Spectrum of **3p.**

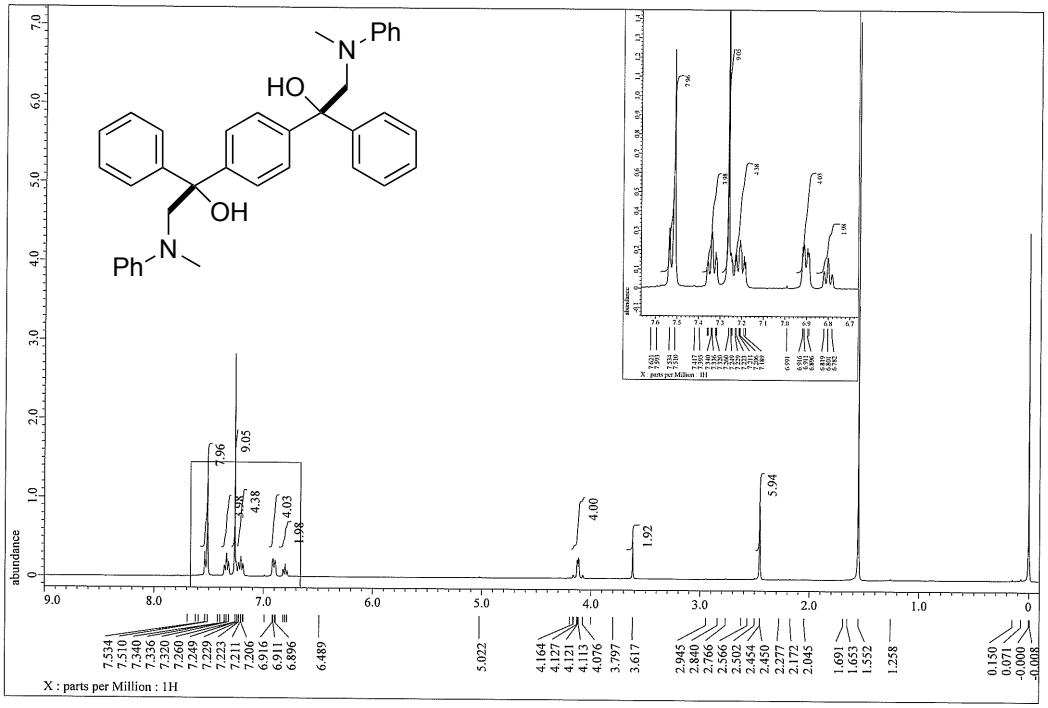

Figure S48. ^{1}H NMR Spectrum of **3q.**

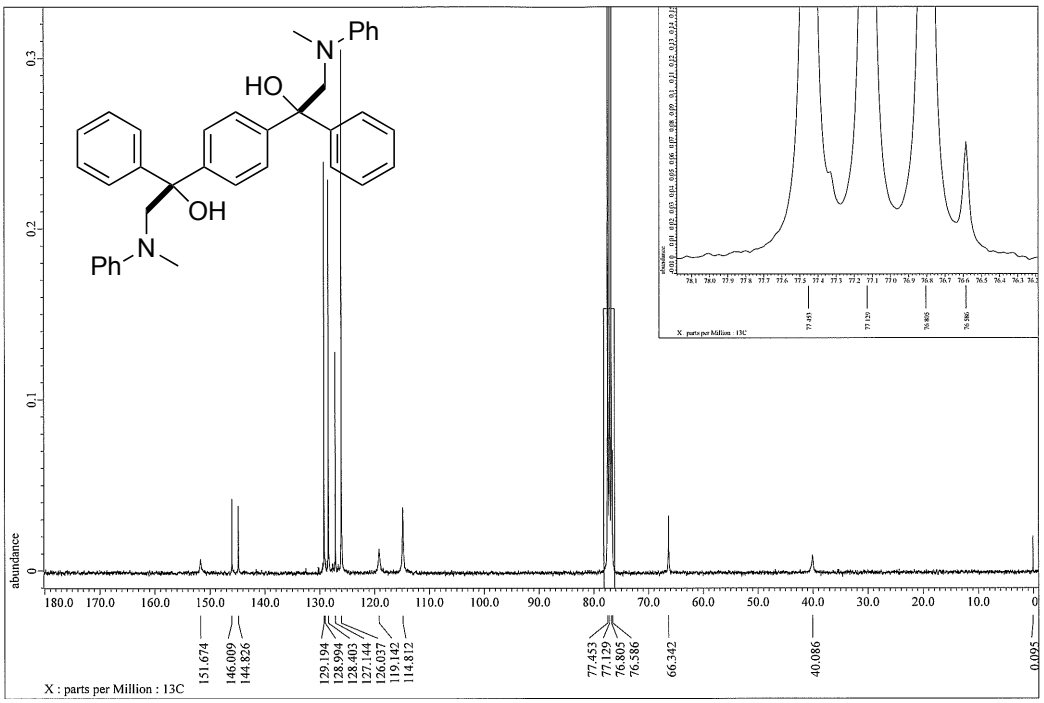

Figure S49. ^{13}C NMR Spectrum of **3q.**

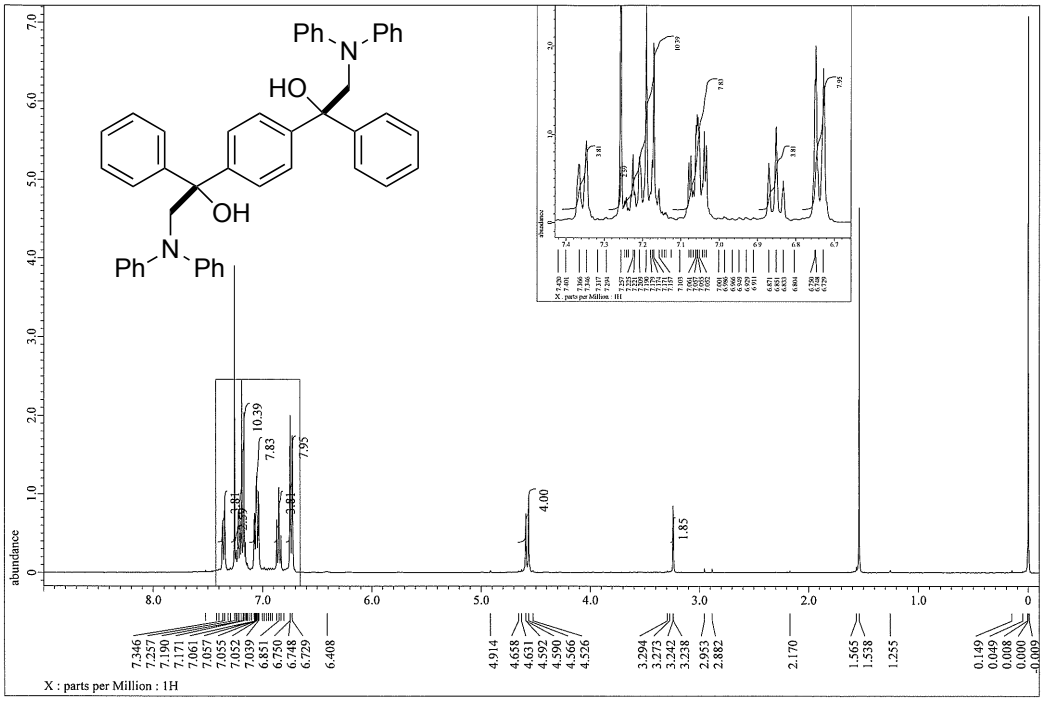

Figure S50. ^{1}H NMR Spectrum of **3r.**

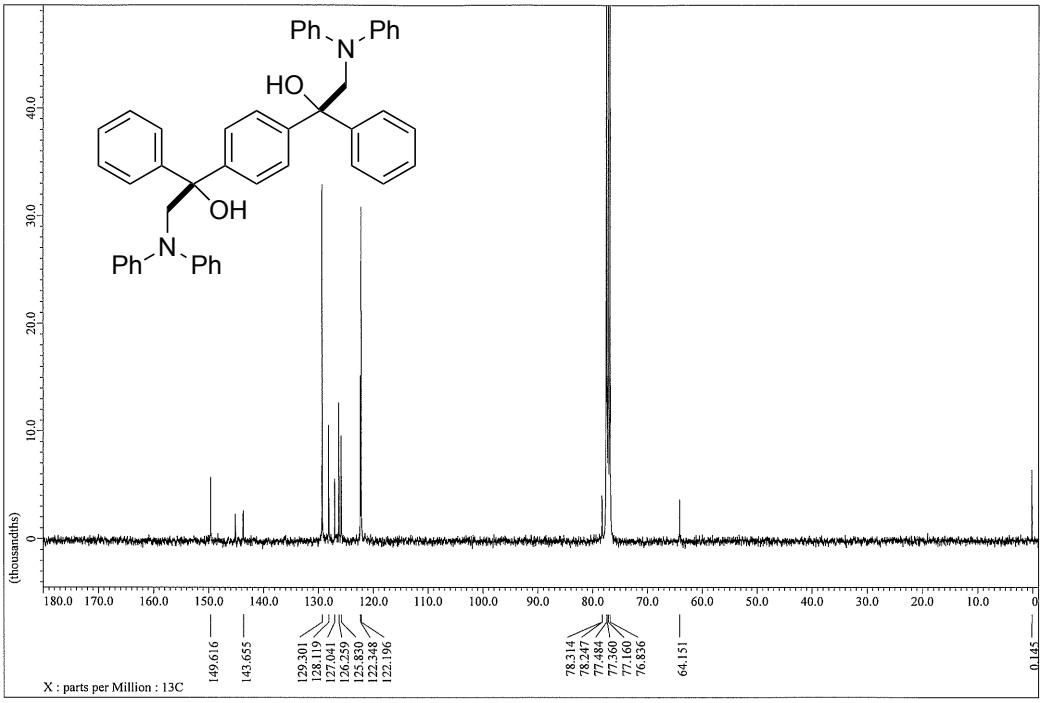

Figure S51. ^{13}C NMR Spectrum of **3r.**

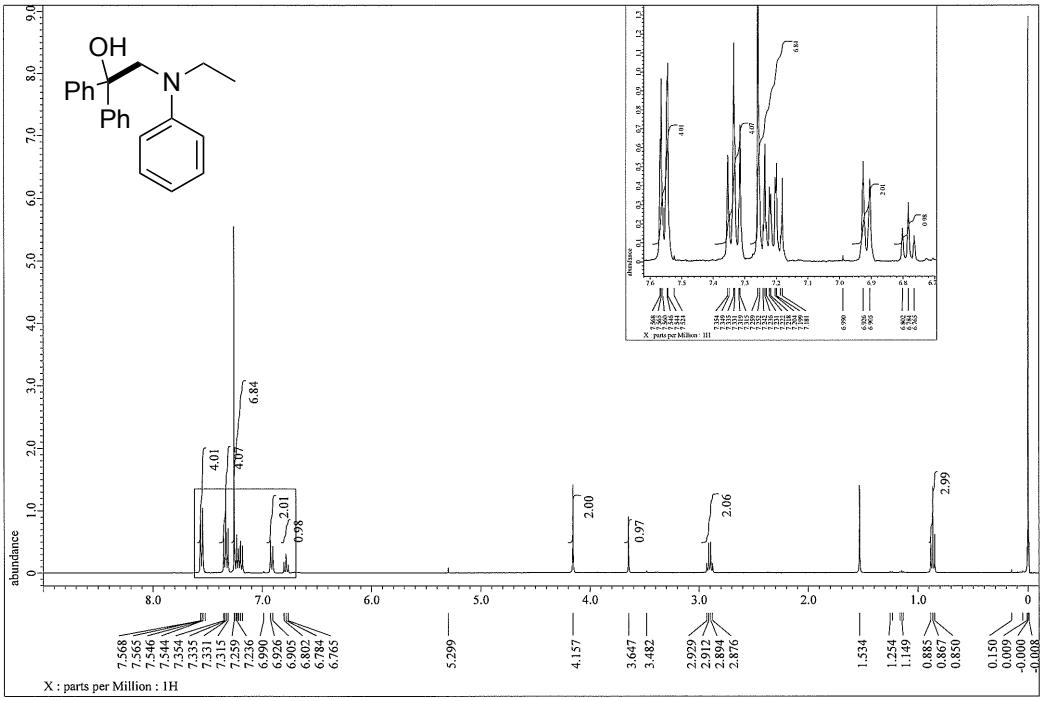

Figure S52. ^{1}H NMR Spectrum of **3s.**

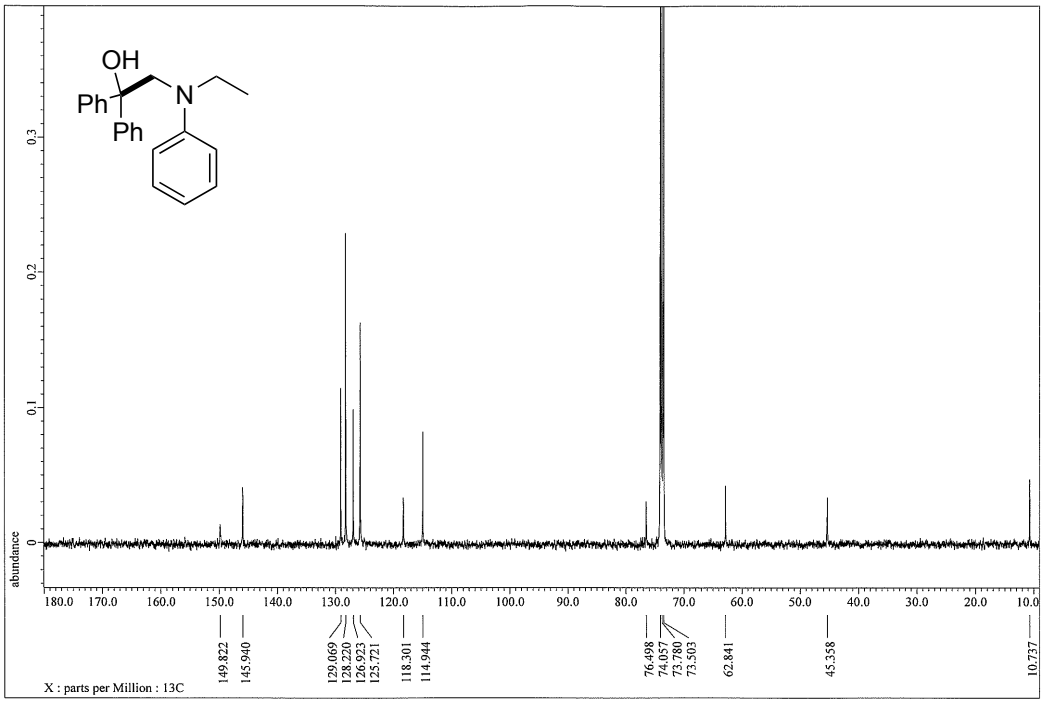

Figure S53. ^{13}C NMR Spectrum of **3s.**

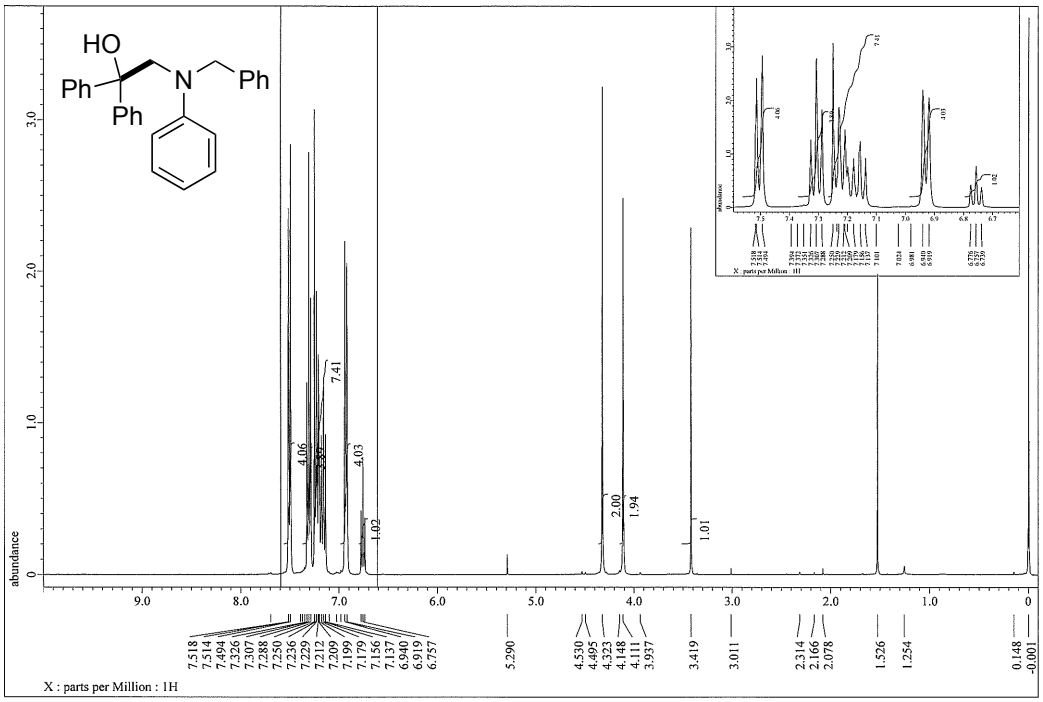

Figure S54. ^{1}H NMR Spectrum of **3t.**

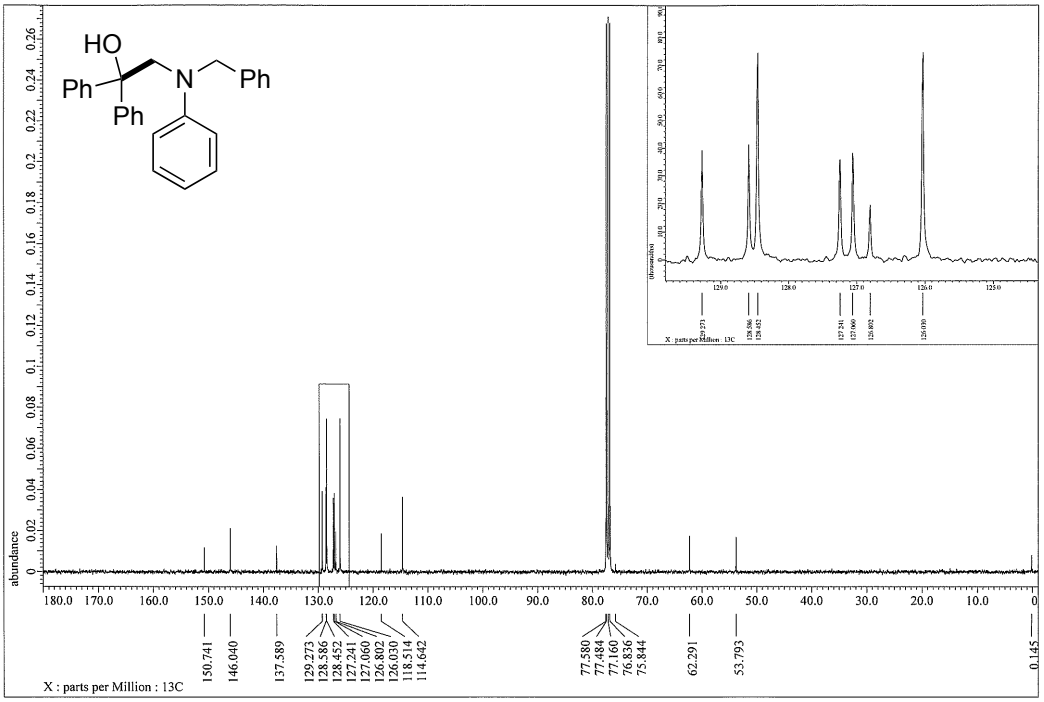

Figure S55. ^{13}C NMR Spectrum of **3t.**

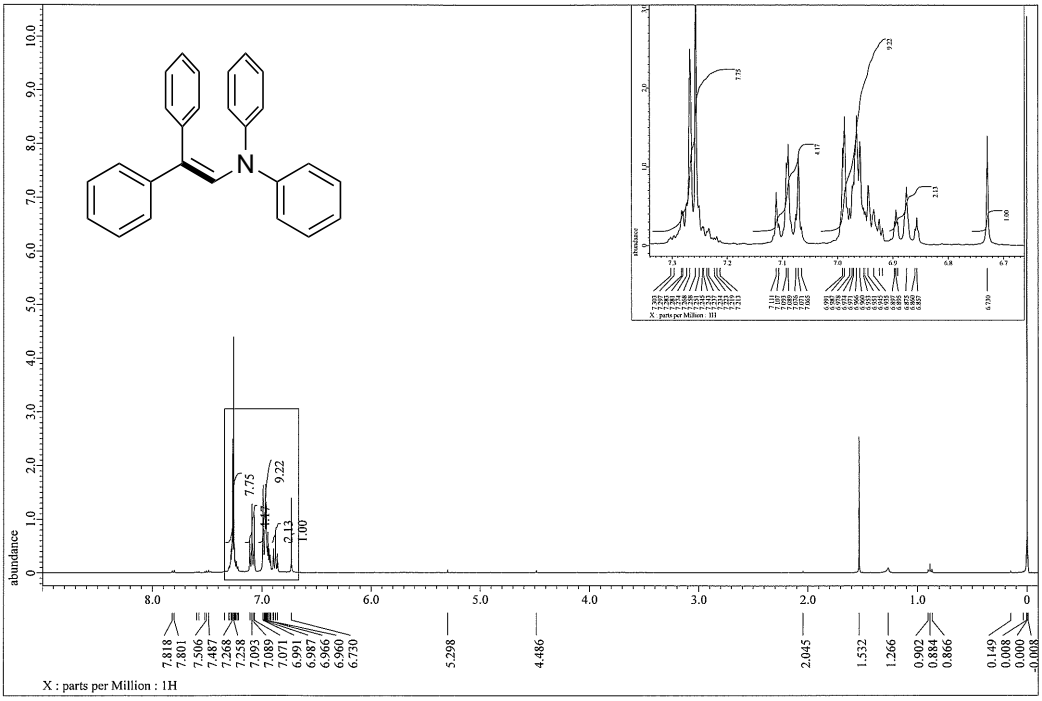

Figure S56. ^{1}H NMR Spectrum of **4a.**

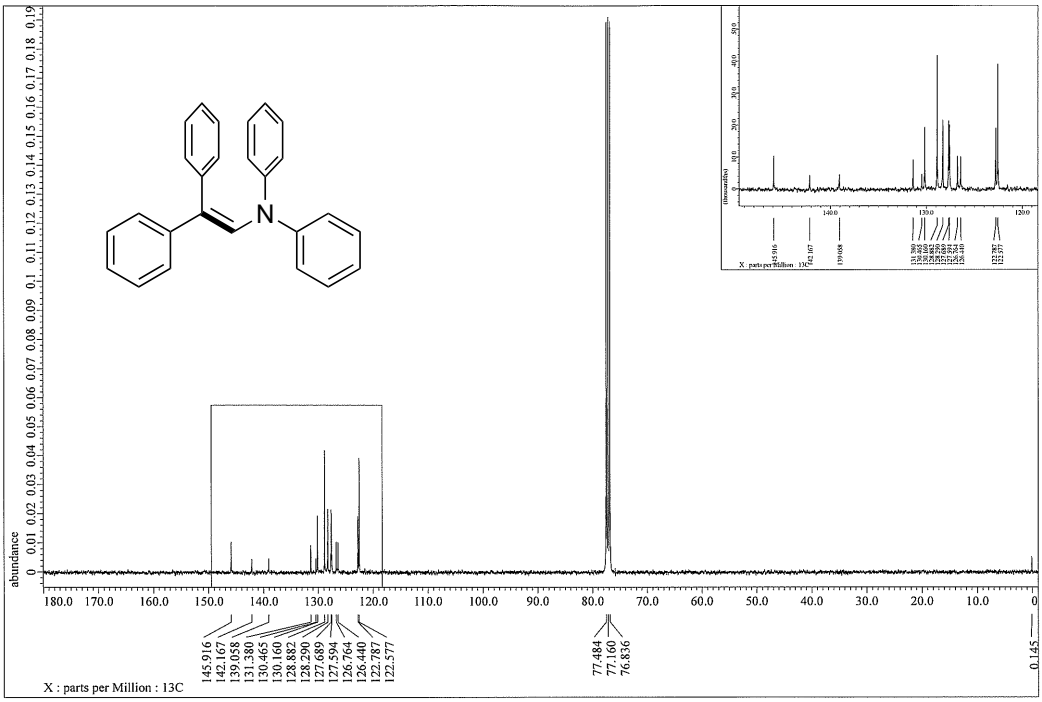

Figure S57. ^{13}C NMR Spectrum of **4a.**

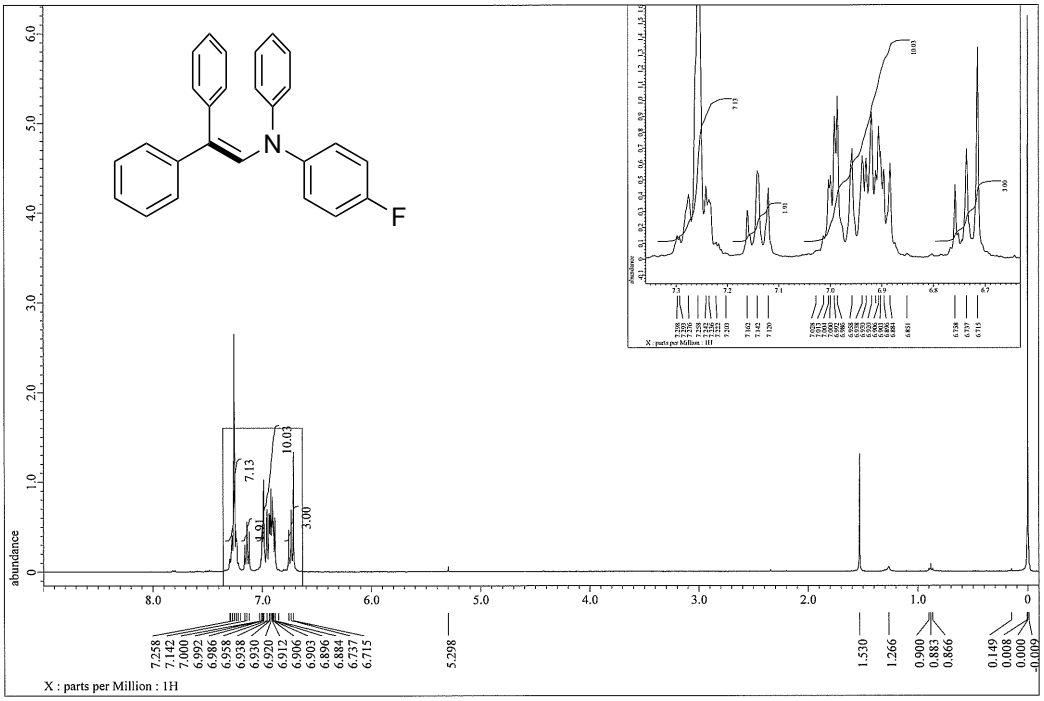

Figure S58. ^{1}H NMR Spectrum of **4b.**

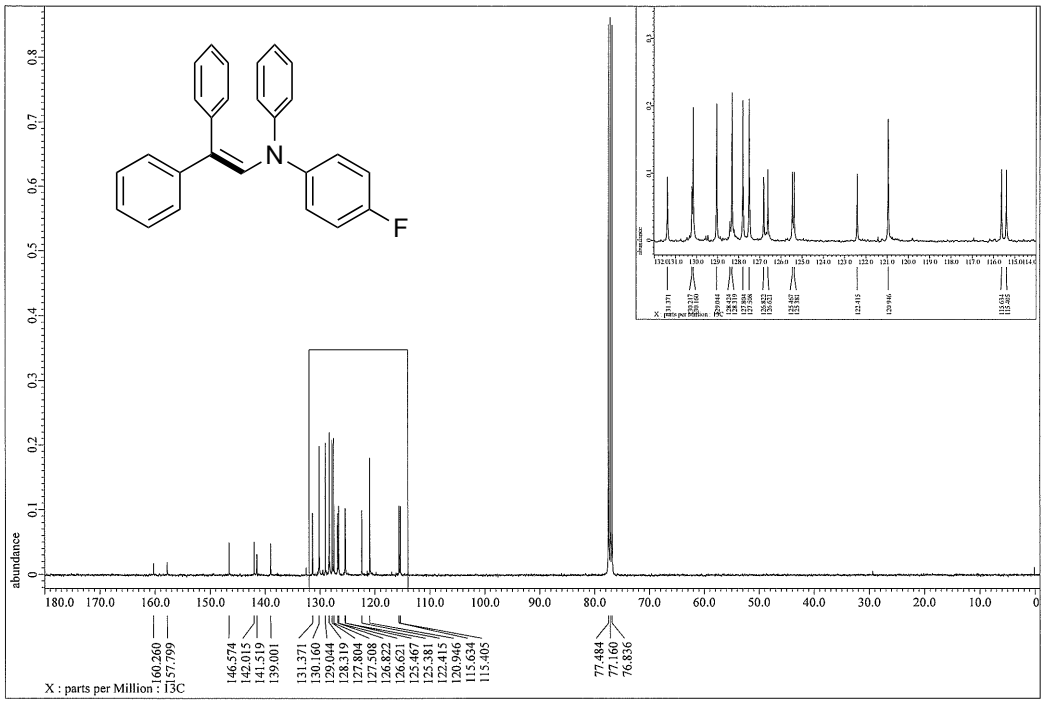

Figure S59. ^{13}C NMR Spectrum of **4b.**

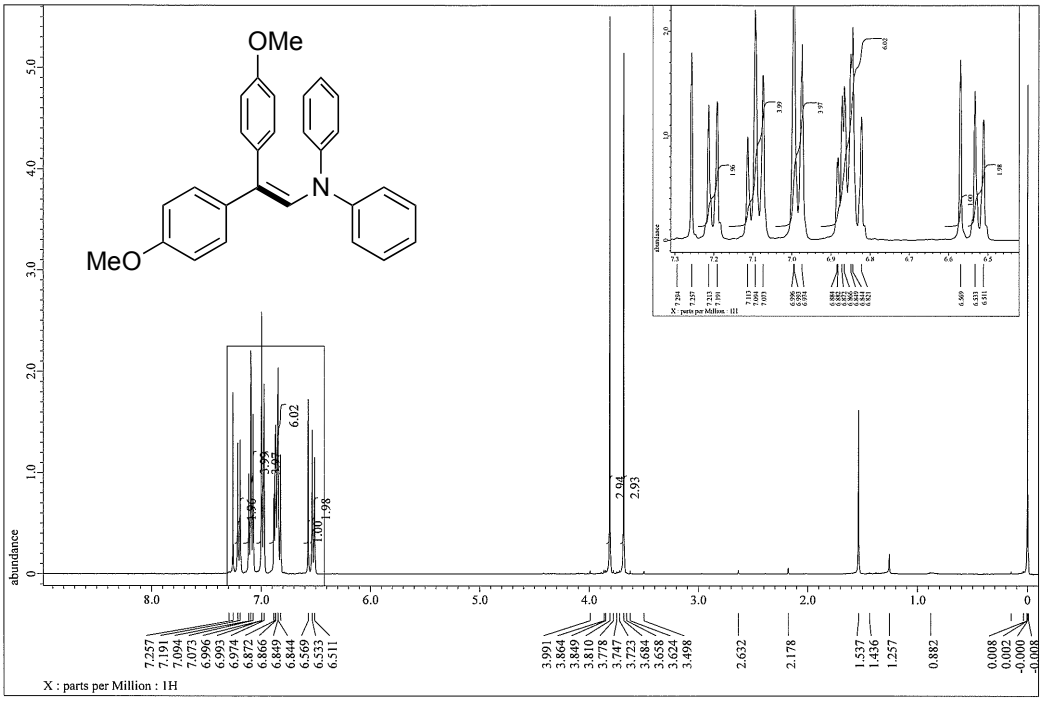

Figure S60. ^{1}H NMR Spectrum of **4c.**

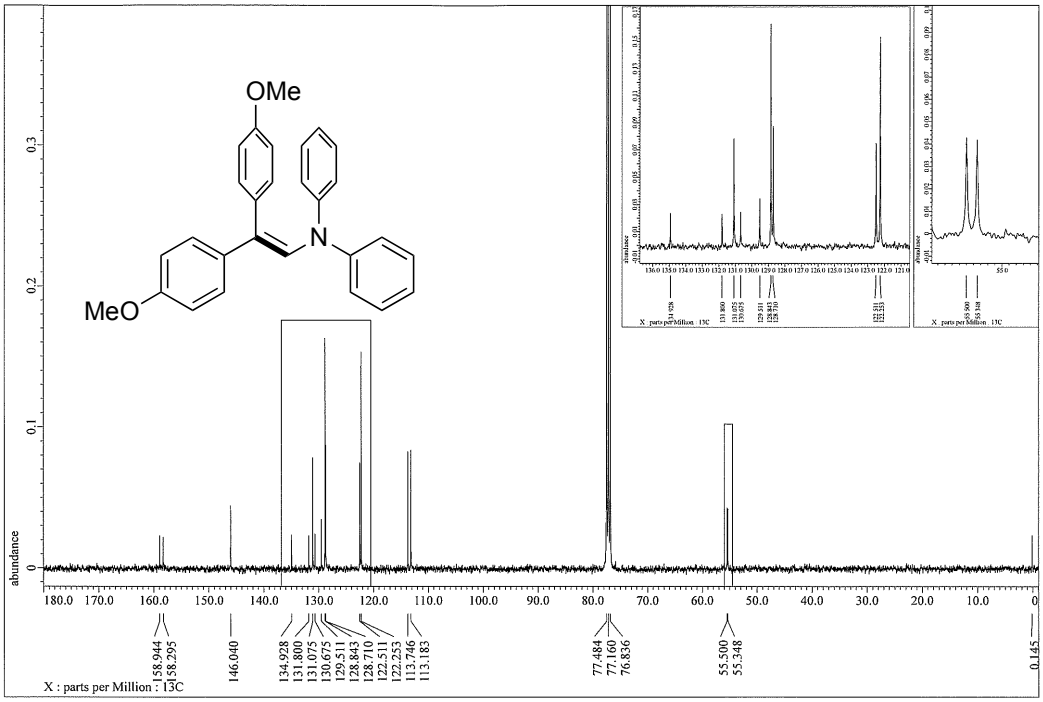

Figure S61. ^{13}C NMR Spectrum of **4c.**