Supporting Information

Synergistic Combination of Visible-Light Photo-Catalytic Electron and Energy Transfer Facilitating Multicomponent Synthesis of β-Functionalized α,α-Diarylethylamines

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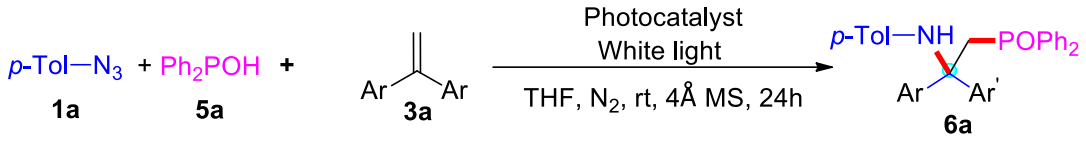
Table of Contents

I. Reaction Optimization

Table S1. Optimization of the Reaction Conditions with Diphenylphosphine Oxide[a]

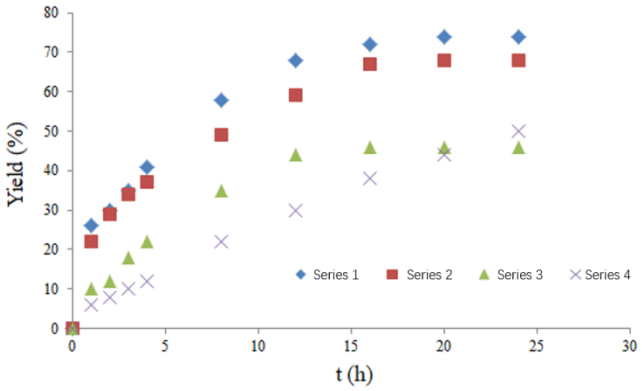


entry	ratio (1a:2a:3a)	PC (mol%)	4 Å MS (mg/mmol)	additive (2.0 eq.)	yield (%)[b]
1	1.2:2:1	$Ir(mppy)_3$ (2.5 mol%)	50	–	34
2	1.2:2:1	$Ir(ppy)_3$ (2.5 mol%)	50	–	50
3	1.2:2:1	$Ir(dF\text{-}ppy)_3$ (2.5 mol%)	50	–	50[c]
4	1.2:2:1	$Ir(dtbby)(ppy)_2PF_6$ (2.5 mol%)	50	–	22
5	1.2:2:1	$Ru(bpy)_3(PF_6)_2$ (2.5 mol%)	50	–	N.D.
6	1.2:2:1	EosinY (2.5 mol%)	50	–	trace
7	2.0:2:1	$Ir(dF\text{-}ppy)_3$ (2.5 mol%)	50	–	66
8	2.5:2:1	$Ir(dF\text{-}ppy)_3$ (2.5 mol%)	50	–	72
9	2.5:2:1	$Ir(dF\text{-}ppy)_3$ (1.0 mol%)	50	–	72
10	2.5:2:1	$Ir(dF\text{-}ppy)_3$ (1.0 mol%)	50	$NaHCO_3$	46
11	2.5:2:1	–	50	–	N.D.
12[d]	2.5:2:1	$Ir(dF\text{-}ppy)_3$ (1.0 mol%)	50	–	N.D.

[a] Conditions: **1a** (0.12-0.30 mmol), **3a** (0.20 mmol), **5a** (0.10 mmol), photocatalyst (1.0-2.5 mol%), white light, THF (1.0 mL), nitrogen, rt, 4Å MS, 24h. [b] All yields were assessed by crude ^1H NMR spectroscopy using dibromomethane as an internal standard. [c] 44% of the raw materials **1a** are left. [d] No light.

II. Experimental Procedures of Mechanistic Studies

1. Triplet Nitrene Trapping



Series 1 = "Ir(mppy)$_3$ and blue light"; Series 2 = "Ir(ppy)$_3$ and blue light"; Series 3 = "Ir(dtbbpy)(ppy)$_2$PF$_6$ and blue light"; Series 4 = "No Ir(III)".

Figure S1-1-1. Decomposition of azide **1a** over time under different conditions

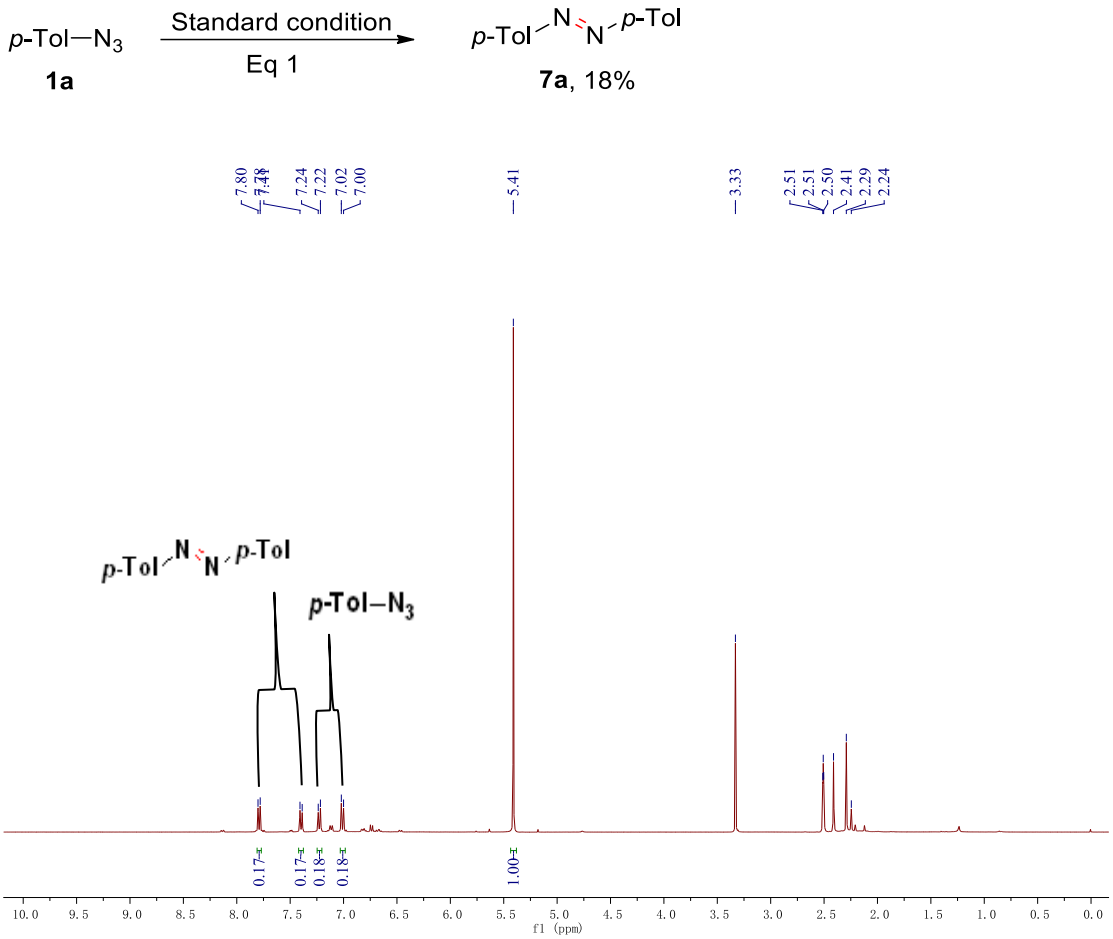
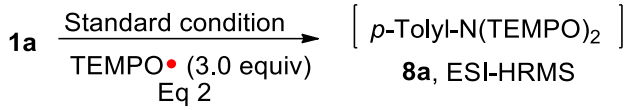
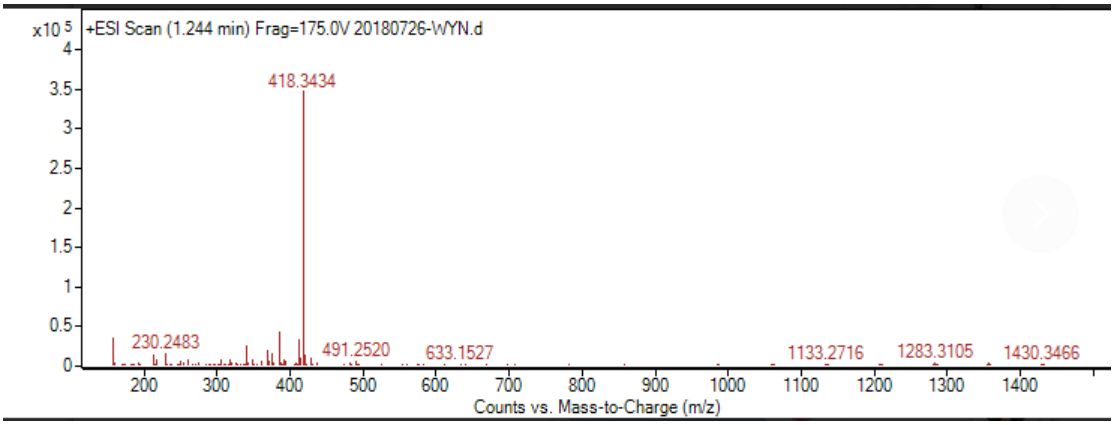


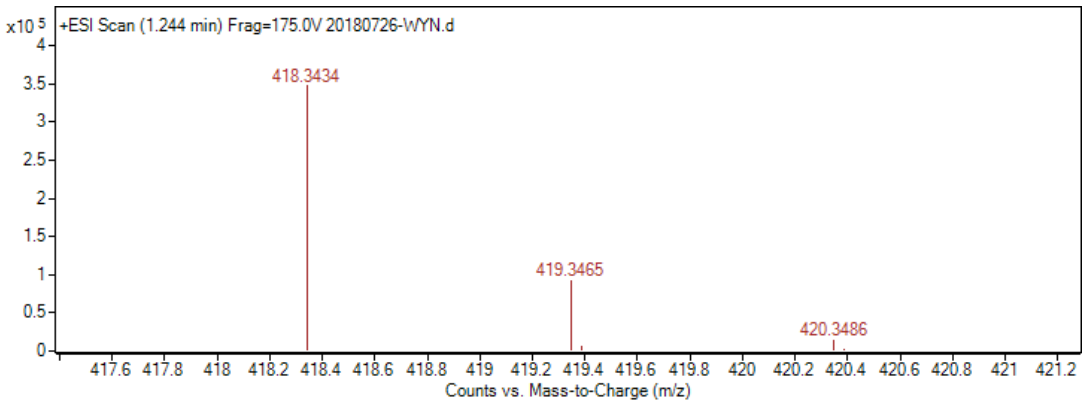
Figure S1-1-2. ^{1}H NMR spectrum of crude reaction mixture and the yield was assessed by crude ^{1}H NMR spectroscopy using dibromomethane as an internal standard.



Compound **8a:** HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{25}H_{44}N_3O_2$: 418.3434, found: 418.3434



Compound **8a:** HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{25}H_{44}N_3O_2$: 418.3434, m/z: 418.3434 (100.0%), 419.3467 (27.0%), 420.3501 (3.5%), 419.3404 (1.1%)



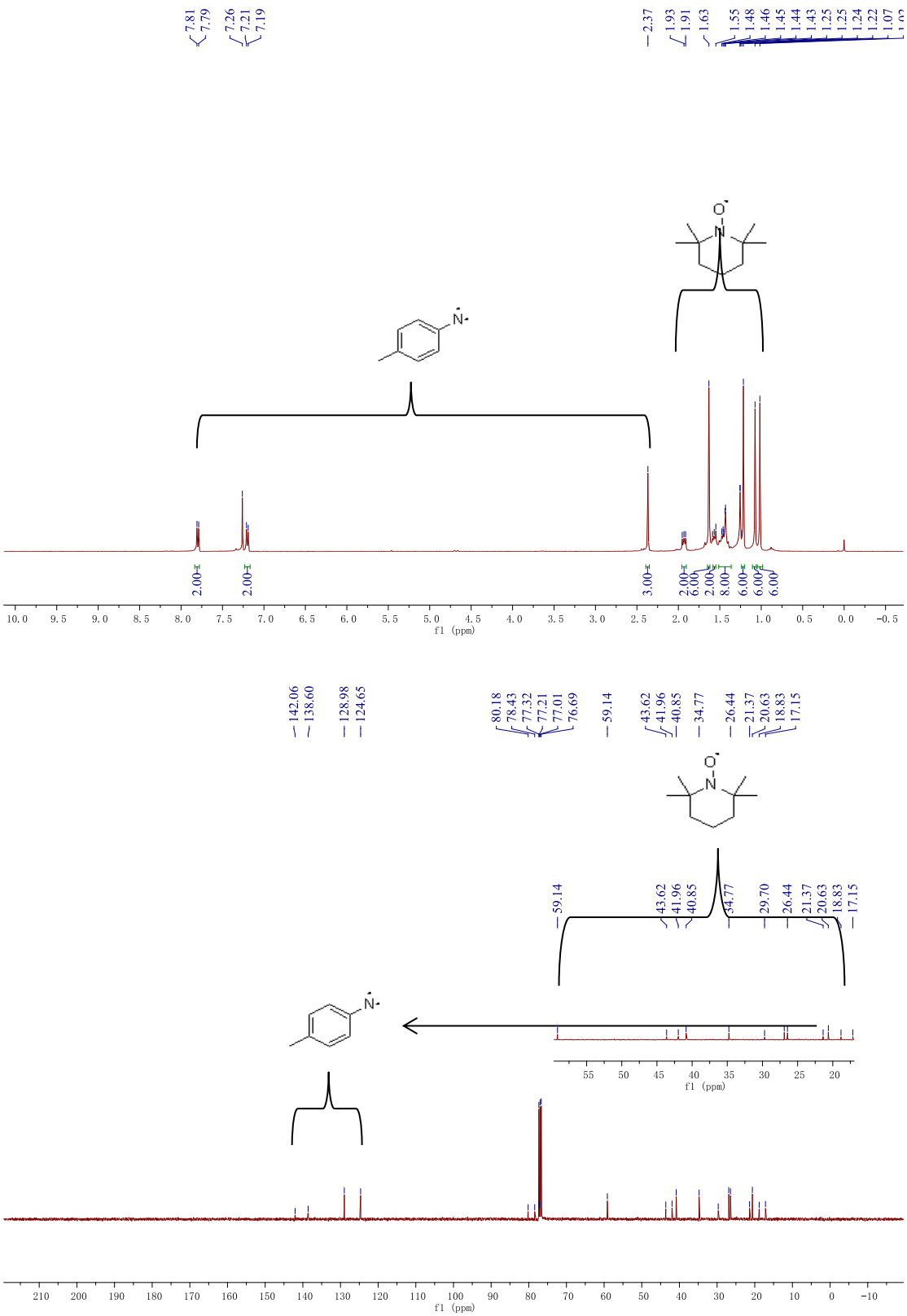
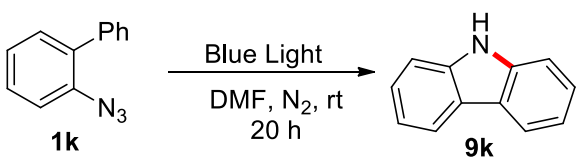
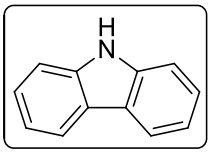


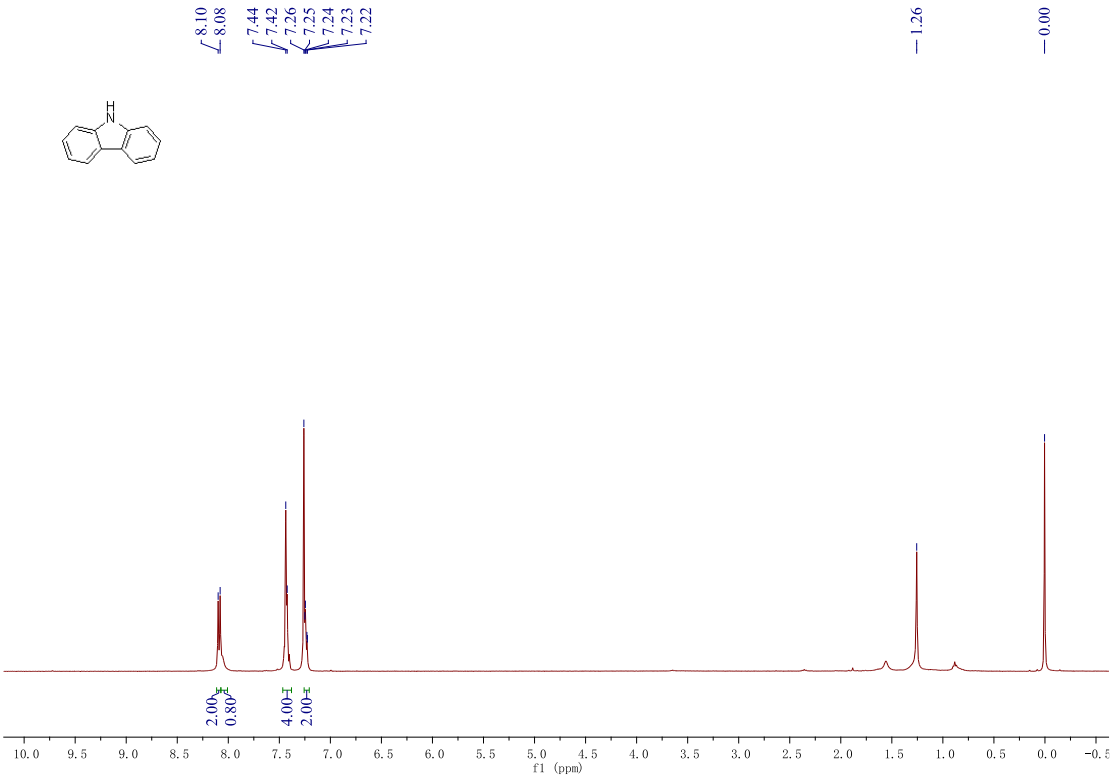
Figure S1-1-3. The ESI-HRMS and NMR of compound **8a**



-	50%	not observed	33%	Eq 3
$Ir(mppy)_3$ (2.5% mol)	13%	14%	34%	Eq 4



9H-carbazole (9k): TLC R_f = 0.5 (EA: PE = 1:10); 16.7 mg/0.2 mmol, 50% yield; white solid, mp 245-246 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09 (d, J = 7.8 Hz, 3H), 7.43 (d, J = 5.6 Hz, 4H), 7.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 139.4, 125.8, 123.3, 120.3, 119.4, 110.5; IR (neat): 3404, 2921, 1459, 1333, 1217, 747, 728 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{12}H_{10}N$: 168.0813, found: 168.0807.



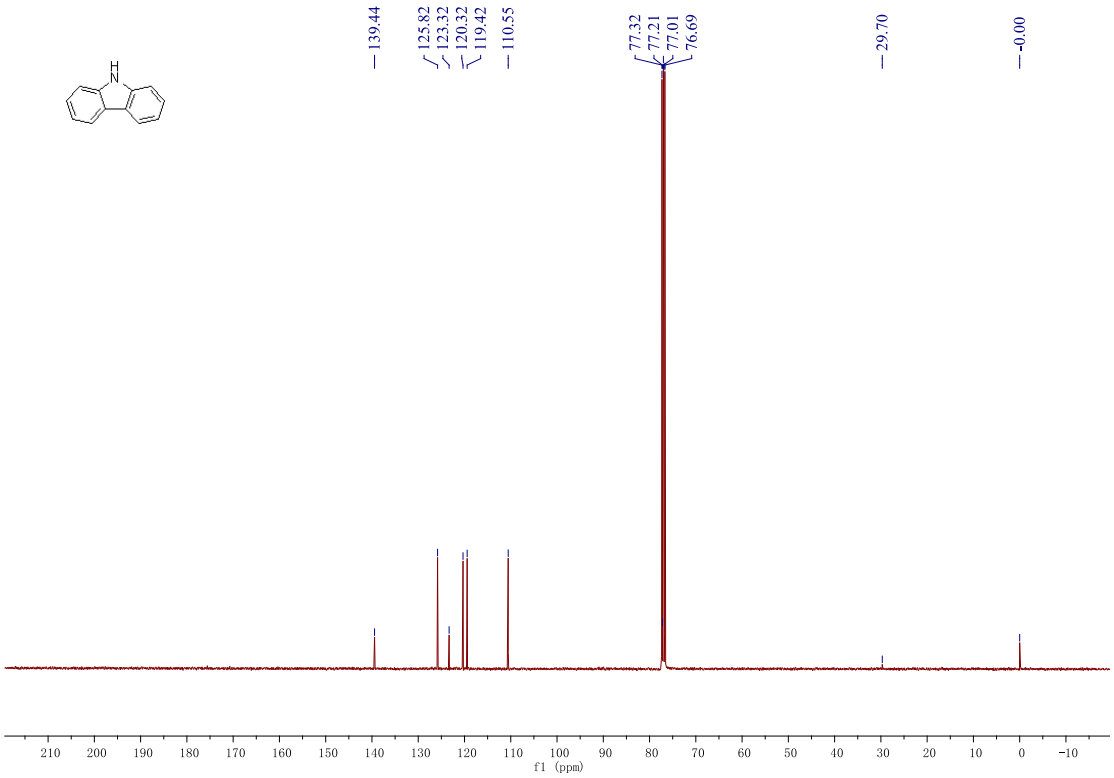
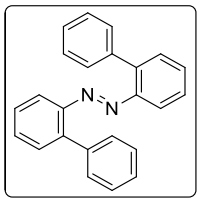
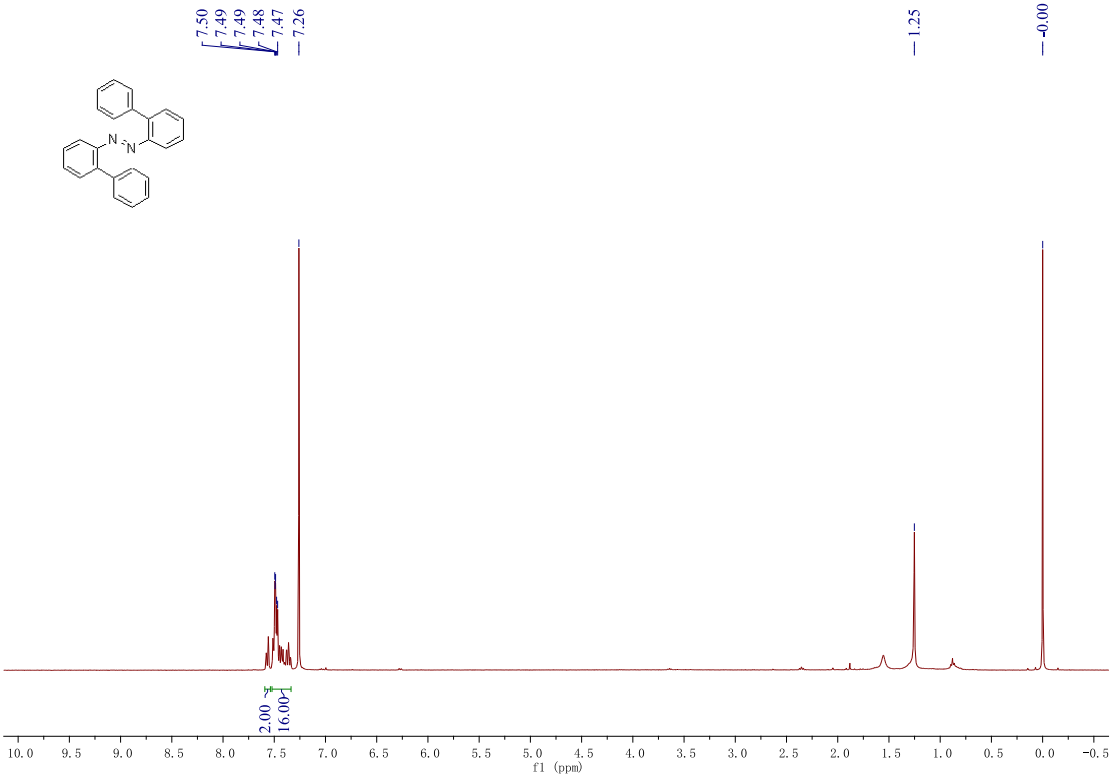


Figure S1-1-4. Spectral Copies of ^{1}H,^{13}C NMR of Compound **9k** Obtained in this Study



1,2-di([1,1'-biphenyl]-2-yl)diazene (10k): TLC R_f = 0.5 (EA: PE = 1:10); 9.3 mg/0.2 mmol, 14% yield; orange solid, mp 133-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.57 (d, J = 8.0 Hz, 2H), 7.52-7.34 (m, 16H); ^{13}C NMR (101 MHz, CDCl3; δ, ppm) 149.8, 141.5, 138.9, 130.9, 130.8, 130.7, 128.0, 127.7, 127.3, 116.3; IR (neat): 3048, 1586, 1470, 768, 732, 723 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{19}N_2$: 335.1548, found: 335.1551.



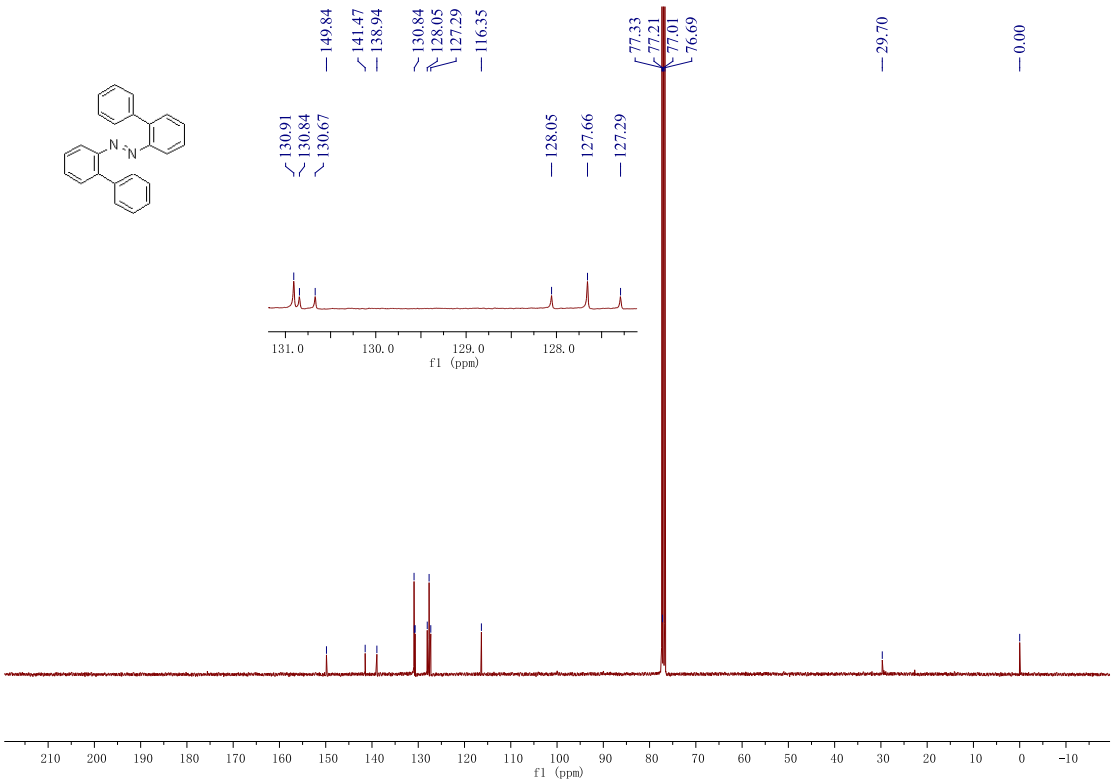
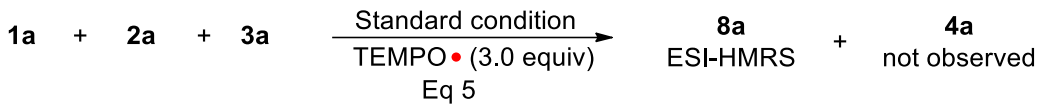
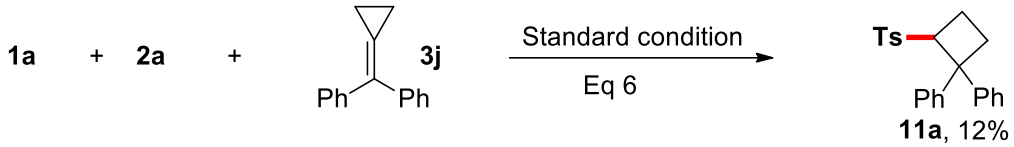


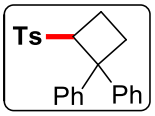
Figure S1-1-5. Spectral Copies of ^{1}H,^{13}C NMR of Compound **10k** Obtained in this Study


1a + 2a + 3a
Standard condition
TEMPO• (3.0 equiv)
8a
ESI-HMRS
+
4a
not observed

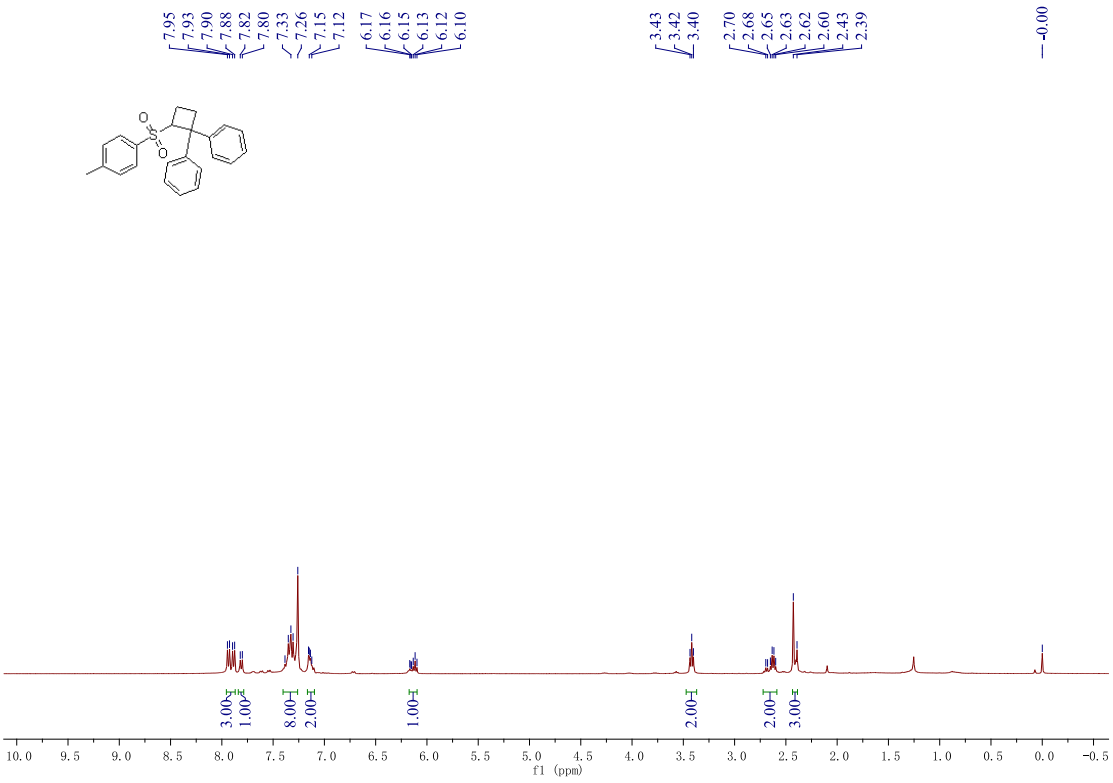
Eq 5

2. Radical Clock





(2-tosylcyclobutane-1,1-diyl)dibenzene (11a): TLC R_f = 0.5 (EA: PE = 1:5); 8.7 mg/0.2 mmol, 12% yield; white solid, mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.91 (m, 3H), 7.81 (d, J = 8.2 Hz, 1H), 7.34 (m, 8H), 7.14 (m, 2H), 6.17-6.10 (m, 1H), 3.42 (t, J = 6.7 Hz, 2H), 2.65 (dt, J = 20.7, 6.9 Hz, 2H), 2.44-2.39 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 144.8, 144.3, 142.7, 141,1, 140.9, 138.5, 130.6, 130.0, 129.9, 129.6, 128.6, 128.4, 127.9, 127.6, 127.5, 127.4, 127.3, 32.6, 32.3, 21.6; IR (neat): 3058, 2923, 2852, 1593, 1318, 1152, 1104, 758, 699 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{23}O_2S$: 363.1419, found: 363.1414.



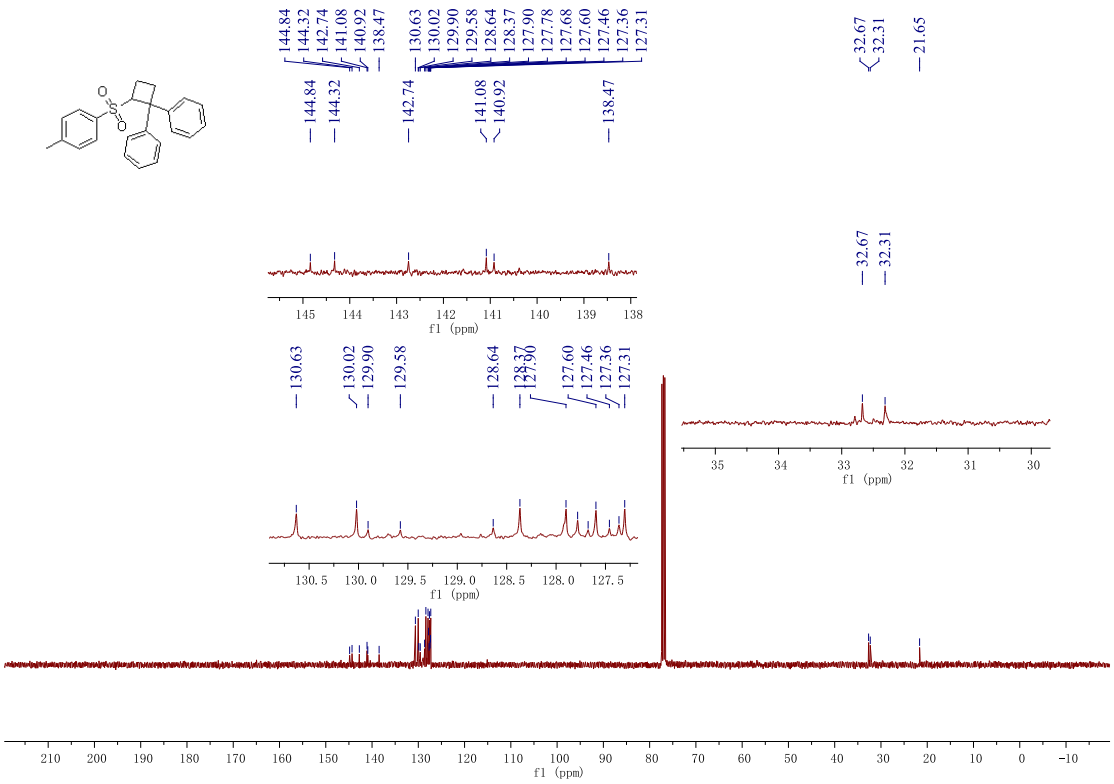
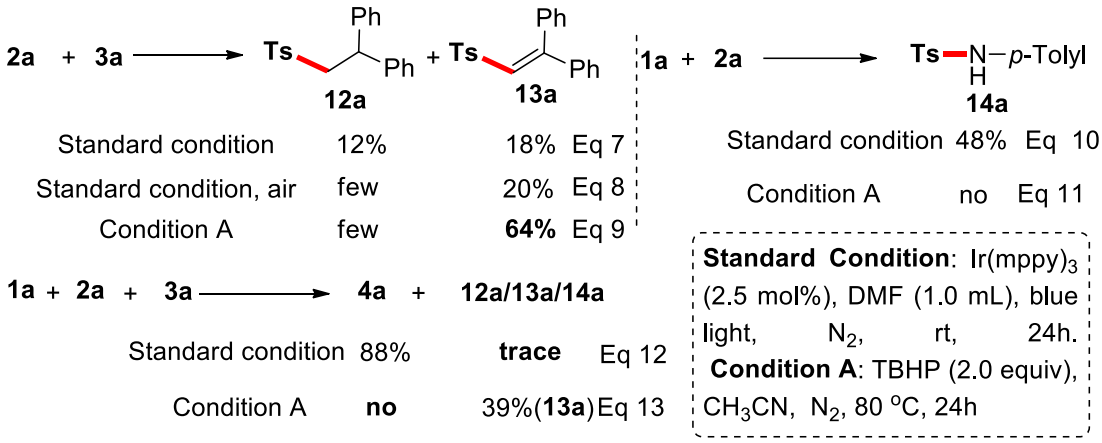
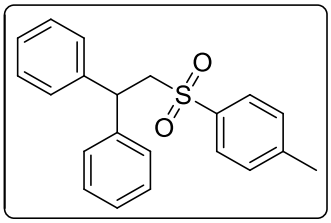


Figure S1-2 Spectral Copies of ^{1}H , ^{13}C NMR of Compound **11a** Obtained in this Study

3. Photocatalyst (Standard Condition) vs TBHP (Condition A) Induced Radical Reactions.





(2-tosylethane-1,1-diyl)dibenzene (12a): TLC R_f = 0.5 (EA: PE = 1:5); Colorless solid, mp 121-123°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.87 (m, 4H), 7.44 (d, J = 8.4 Hz, 2H), 7.35-7.32 (m, 4H), 7.30 (s, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 5.56 (s, 1H), 5.50 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl3; δ, ppm) 148.6, 146.3, 144.1, 140.3, 129.9, 128.9, 128.4, 128.2, 128.1, 127.8, 127.5, 116.6, 21.6; IR (neat): 3048, 1586, 1470, 768, 732, 723 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{21}H_{21}O_2S$: 337.1259, found: 337.1257.

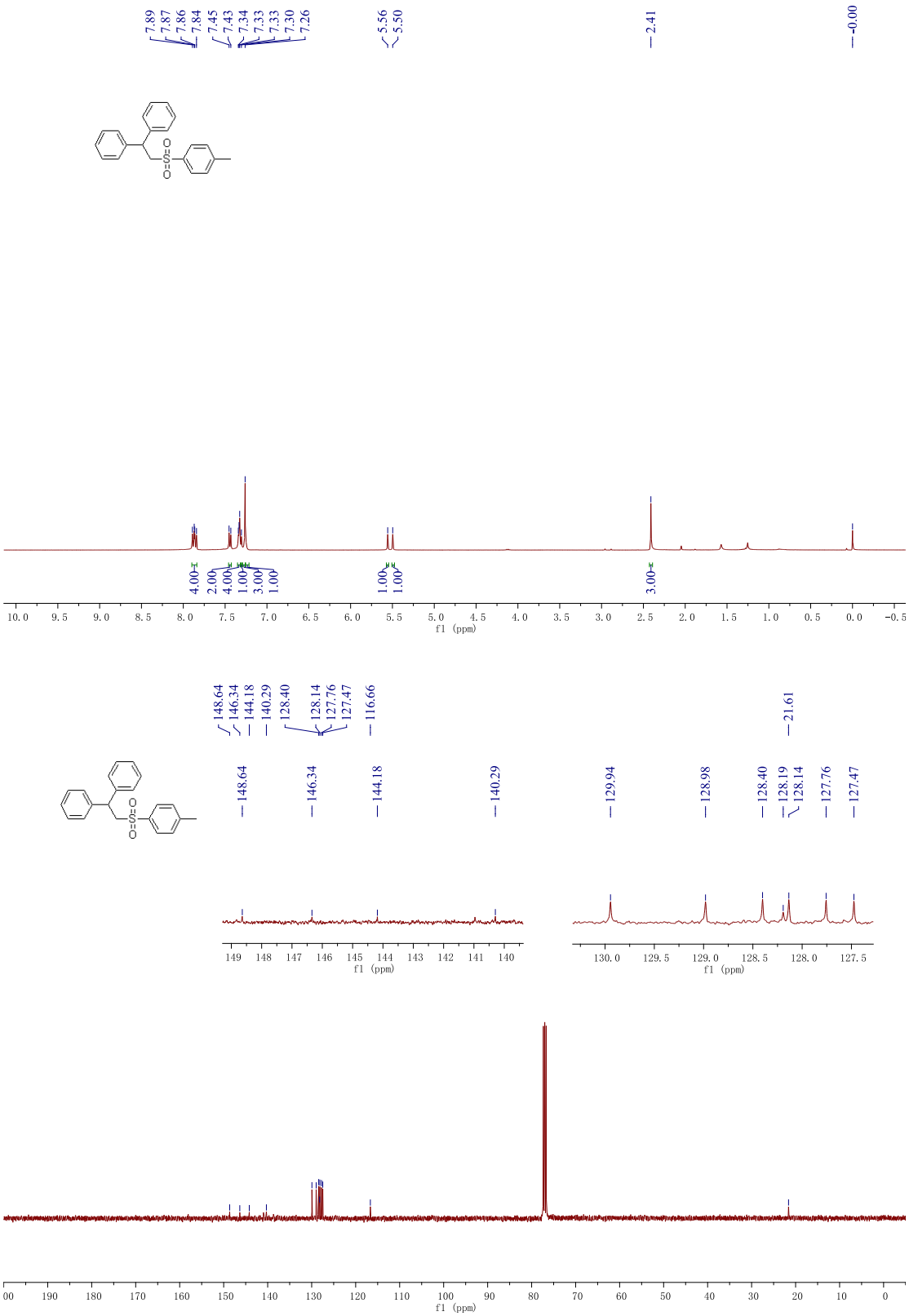
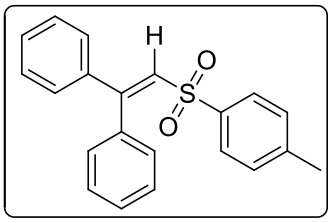
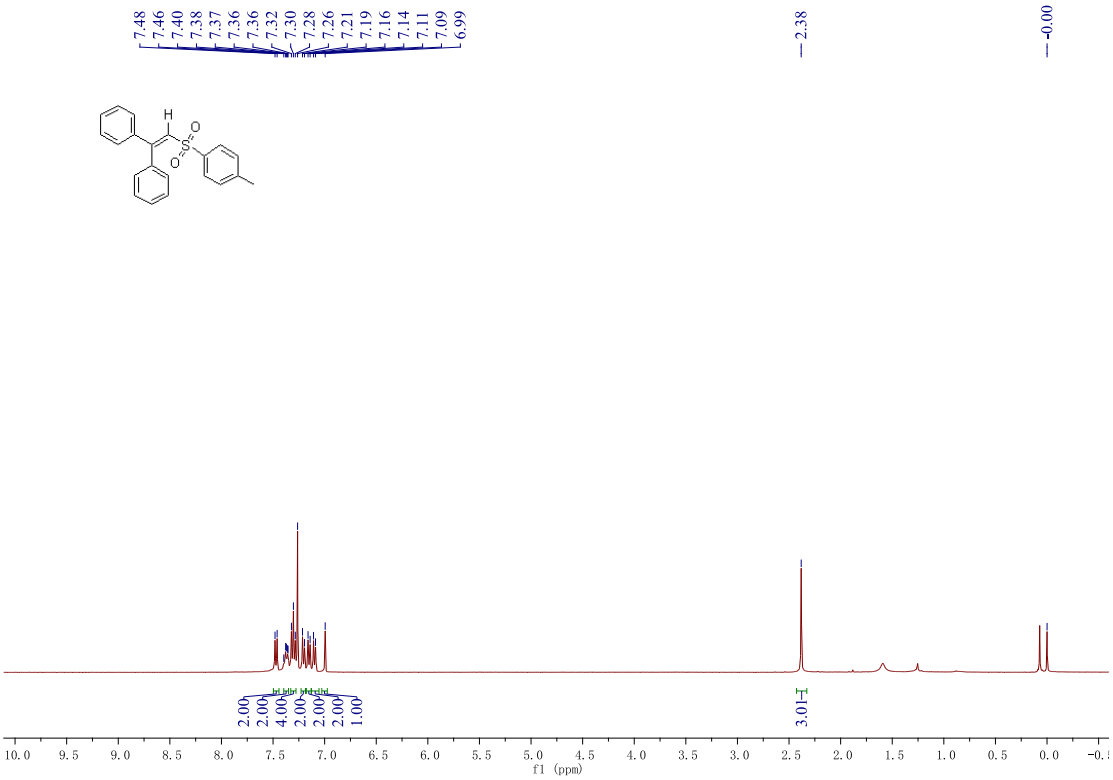


Figure S1-3-1. Spectral Copies of ^{1}H, ^{13}C NMR of Compound **12a** Obtained in this Study



(2-tosylethene-1,1-diyl)dibenzene (13a): TLC R_f = 0.5 (EA: PE = 1:5); white solid, mp 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.47 (d, J = 8.1 Hz, 2H), 7.40-7.35 (m, 2H), 7.30 (m, 4H), 7.20 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.7 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 154.7, 143.7, 139.2, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.6, 128.2, 127.8, 127.7, 21.6; IR (neat): 3056, 2917, 2849, 1594, 1568, 1489, 1444, 1314, 1301, 1149, 1137, 1084, 1030; cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{21}H_{21}O_2S$: 357.0926, found: 357.0930.



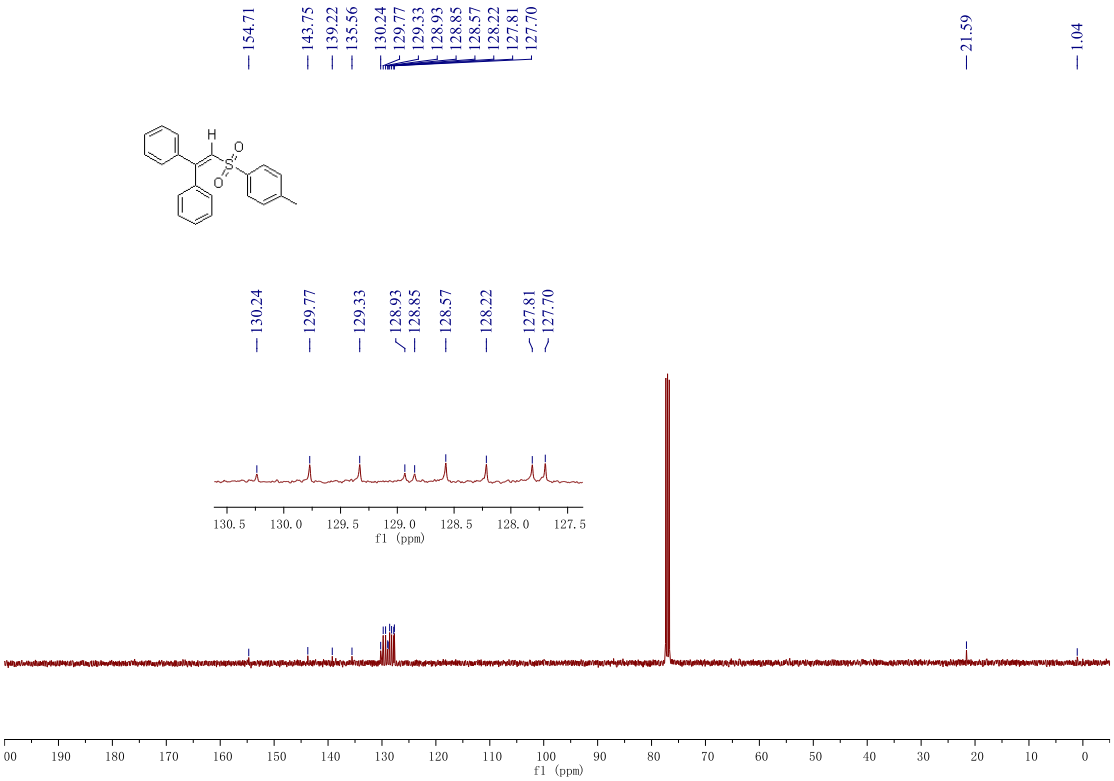
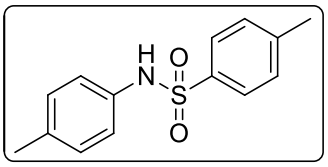
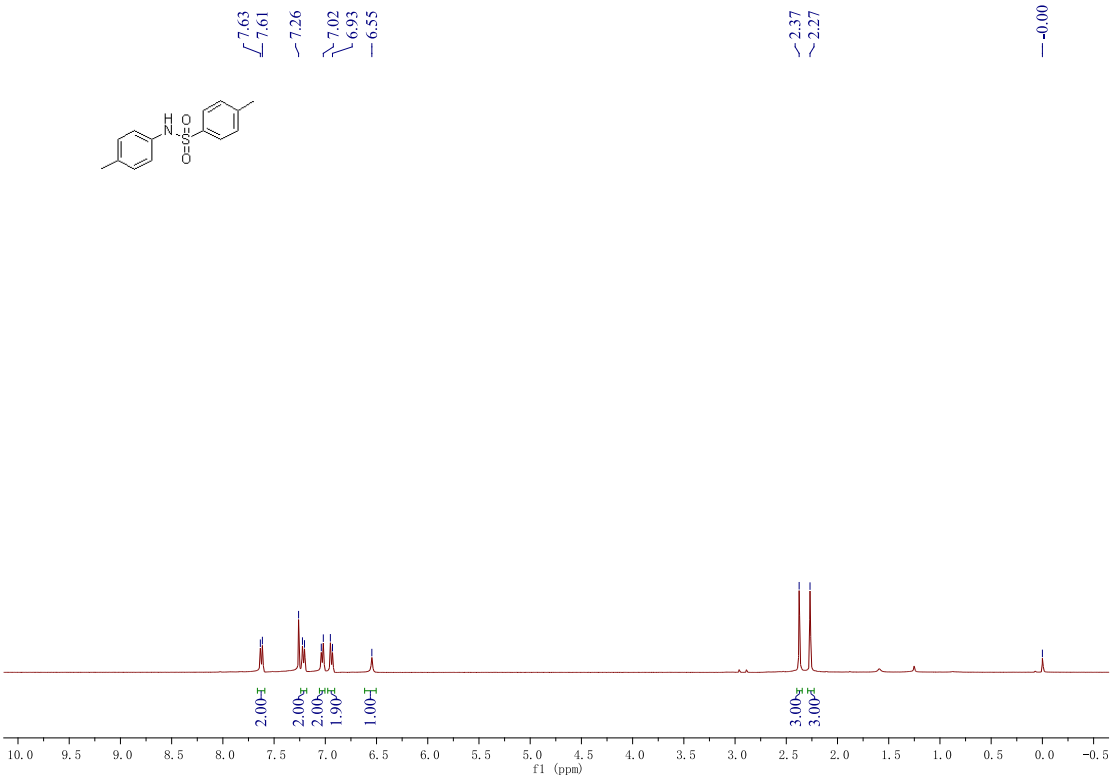


Figure S1-3-2. Spectral Copies of ^{1}H, ^{13}C NMR of Compound **13a** Obtained in this Study



4-methyl-N-(p-tolyl)benzenesulfonamide (14a): TLC R_f = 0.5 (EA: PE = 1:10); 25.0 mg/0.2 mmol, 48% yield; white solid, mp 114-116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.62 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.55 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl3; δ, ppm) 143.7, 136.1, 135.4, 133.7, 129.8, 129.6, 127.3, 122.4, 21.6, 20.9; IR (neat): 3251, 2923, 2853, 1509, 1331, 1159, 1091, 812, 667, 551 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{14}H_{16}NO_2S$: 284.0721, found: 284.0723.



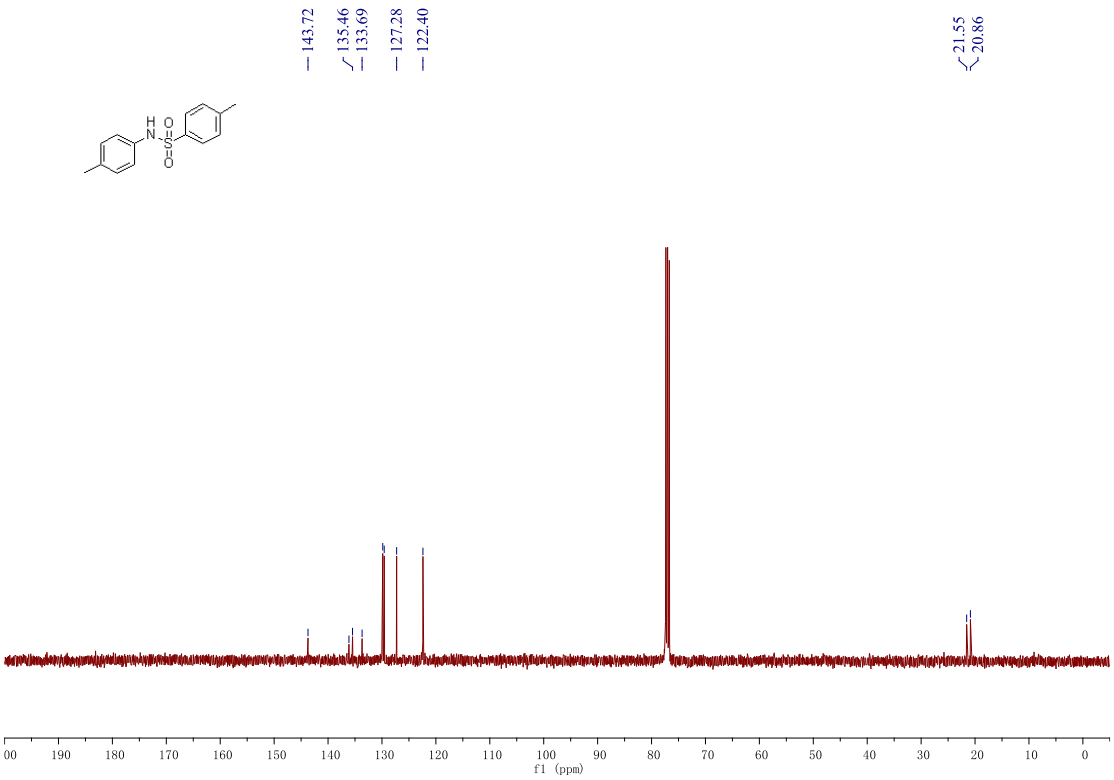


Figure S1-3-3. Spectral Copies of ^{1}H, ^{13}C NMR of Compound **14a** Obtained in this Study

4. Luminescence Quenching Experiment

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The emission intensity was collected at 520 nm. The samples were prepared by mixing by $Ir(mppy)_3$ (2.5×10^{-4} mol/L) and different amount of quenchers (*p*-methylphenyl azide **1a** and 1,1-diphenylethylene **3a**) in DMF (total volume = 1.0 mL) in a light path quartzfluorescence cuvette. The concentration of **1a** and **3a** stock solution both are 1.0 mol/mL in DMF. For each quenching experiment, different volumes of quenchers (**1a** and **3a**) **s**tock solution was titrated to a mixed solution of $Ir(mppy)_3$ (5, 10, 10, 10, 10, 20, 20, 40, $80*10^{-3}$ mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S2-1.

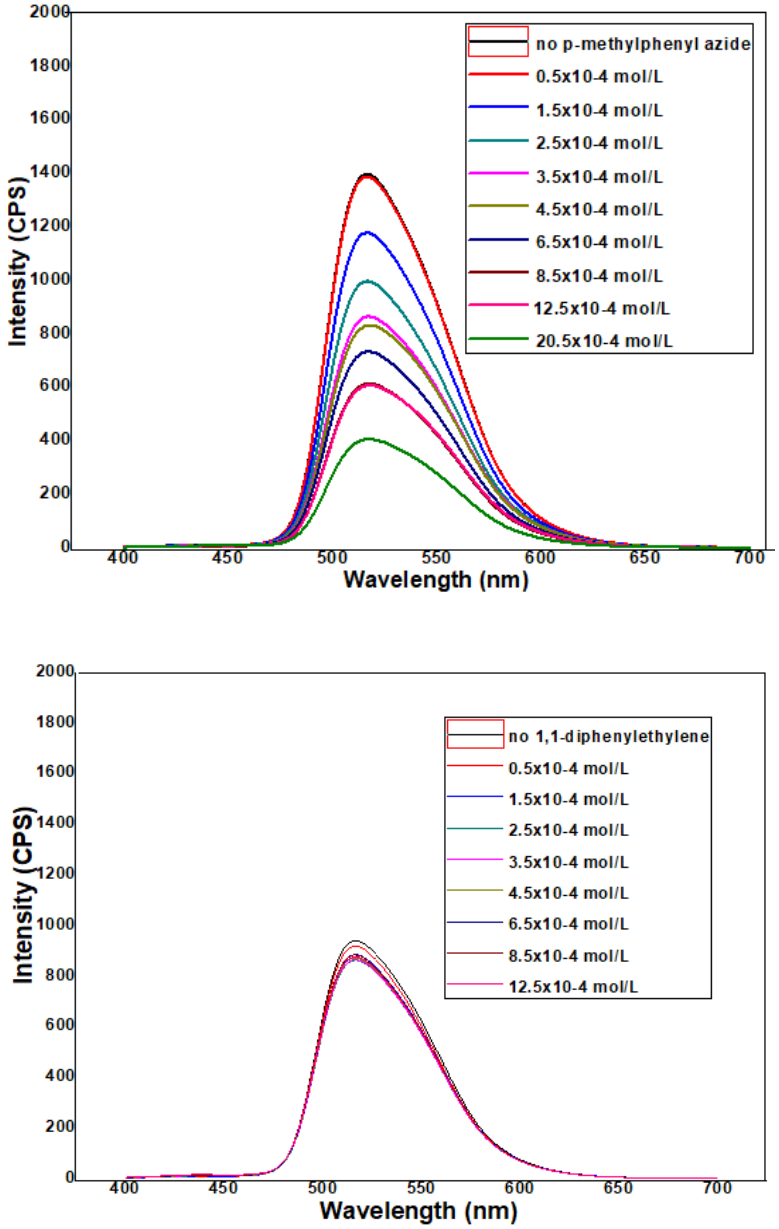


Figure S2-1. Quenching of $Ir(mppy)_3$ fluorescence emission in the presence of quenchers (*p*-methylphenyl azide **1a** and 1,1-diphenylethylene **3a**)

An indeed fluorescence quenching phenomenon of $Ir(mppy)_3$ under various concentrations of quenchers (*p*-methylphenyl azide **1a** and 1,1-diphenylethylene **3a**) was demonstrated in a curve of $[I_0/I]$ vs C , as shown in Figure S2-2 (Stern-Volmer plots).

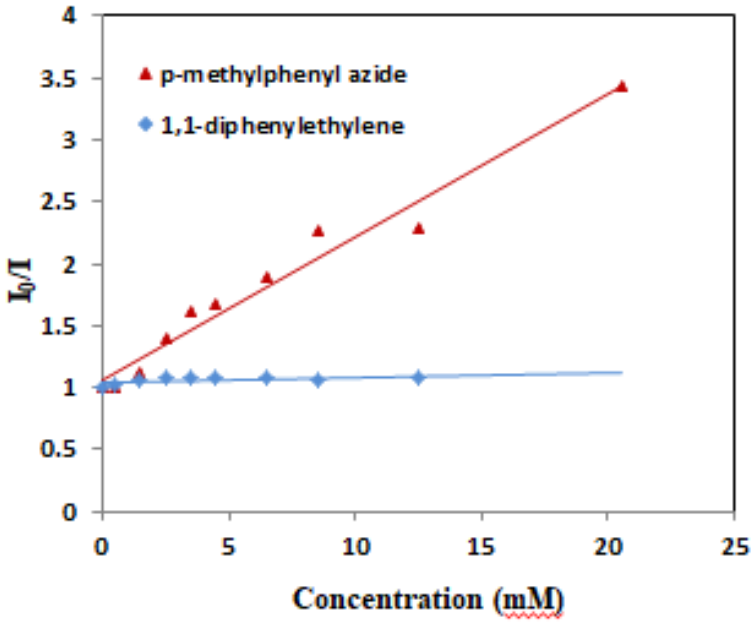


Figure S2-2. Luminescence quenching of $Ir(mppy)_3$ by quenchers (p-methylphenyl azide **1a** and 1,1-diphenylethylene **3a**)

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The emission intensity was collected at 520 nm. The samples were prepared by mixing by $Ir(mppy)_3$ (2.5×10^{-4} mol/L) and different amount of 4-methybenzenesulfinic acid **2a** in DMF (total volume = 1.0 mL) in a light path quartzfluorescence cuvette. The concentration of **2a** stock solution are 7.6×10^{-3} mol/mL in DMF. For each quenching experiment, different volumes of **2a s**tock solution was titrated to a mixed solution of $Ir(mppy)_3$ (5, 5, 5, 5, 5, 5, $5*10^{-3}$ mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S2-3. An fluorescence quenching phenomenon of $Ir(mppy)_3$ under various concentrations of **1a** was shown in Figure S2-4 (Stern-Volmer plots).

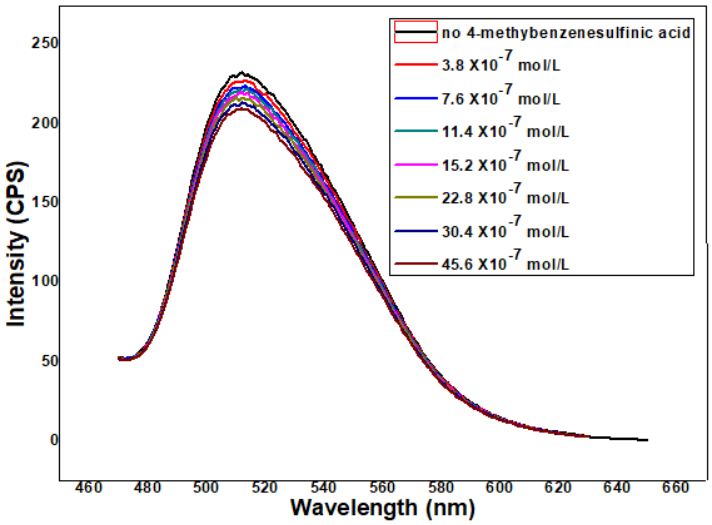


Figure S2-3. Quenching of $Ir(mppy)_3$ fluorescence emission in the presence of 4-methybenzenesulfinic acid **2a**

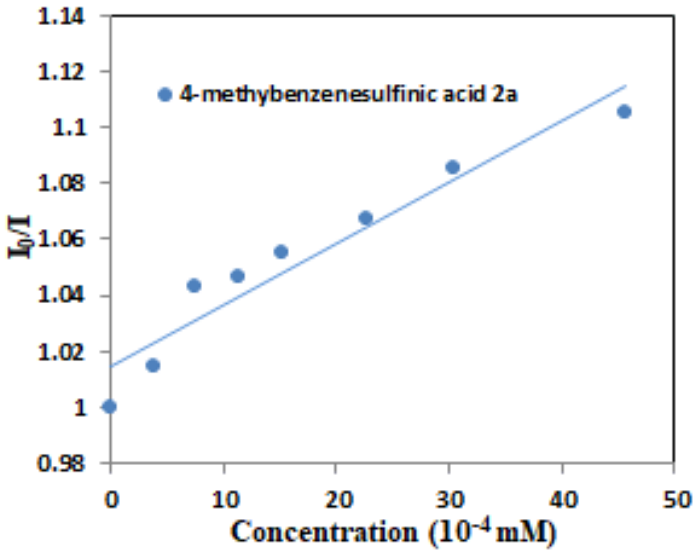


Figure S2-4. Luminescence quenching of $Ir(mppy)_3$ by 4-methybenzenesulfinic acid **2a**

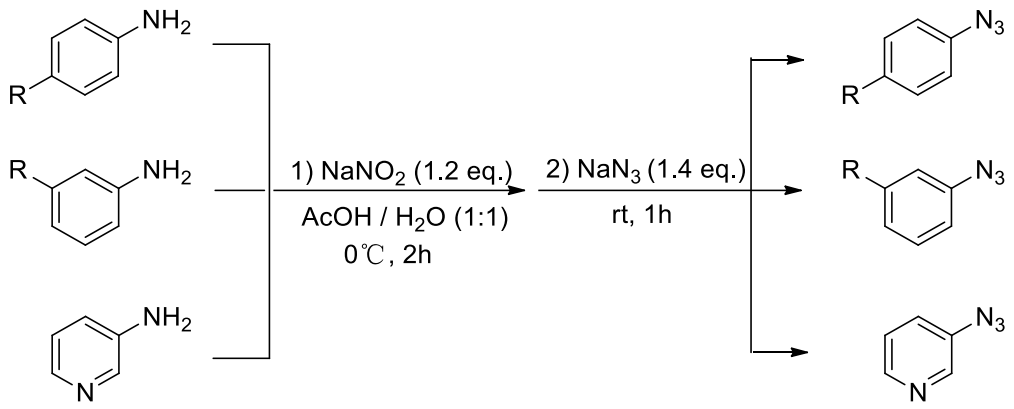
III. General Information

Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates. Visualization of TLC was achieved by the use of UV light (254 nm). Column chromatography was performed on silica gel (300-400 mesh) using a proper eluent. ^{1}H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane or chloroform-d ($CDCl_3$) at 7.26 ppm. The following abbreviations were used to describe peak splitting patterns: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz (Hz). The fully decoupled ^{13}C NMR was recorded on FT AM 400 (100 MHz). Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-d. Infrared (IR) spectra were recorded neat in KBr cell. Frequencies are given in centimeter inverse (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained by using the UHD Accurate-Mass Q-TOF. Melting points (mp) were determined with a digital electrothermal apparatus without further correction. Stern-Volmer fluorescence quenching experiments were taken at ambient temperature using Edinburgh FS5 spectrofluorometer. The LED strips (2 meter, 12W) were directly got from the supermarket. Wavelength of the blue LEDs is at 470 nm. Unless otherwise mentioned, all commercial reagents and solvents were used without further purification. Various azide[1-4], arylsulfinic acid[5] and 1,1-diarylethylene[6] were prepared according to the literature procedures.

IV.General Procedures for the Preparation of Starting Materials

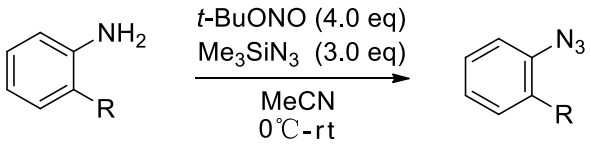
1. Preparation of Various Azides

1.1. Preparation of *p*-aryl azide, *m*-aryl azide and heteroaryl azide (1a-1h, 1i, 1j, 1n and 1o)[1]



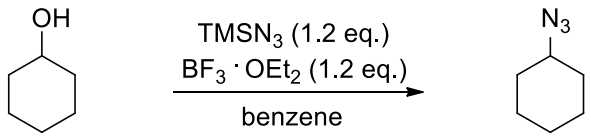
In a two-neck round-bottom flask were charged with AcOH (10.0 mL), H_2O (10.0 mL) and aniline (10.0 mmol), then the mixture was cooled in an ice-bath. $NaNO_2$ (1.2 eq.) was added slowly below 10°C. The orange solution was left to stir for 1 h at 0°C. Then NaN_3 (1.4 eq.) was added (maximum temperature 0° C), the color disappeared and evolution of gases was observed. The reaction was left at 0° C for 10 minutes and then 2h at rt. The solution was diluted with water and CH_2Cl_2. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na_2SO_4, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.

1.2. Preparation of *o*-aryl azide (1k-1m and 1p)[2]



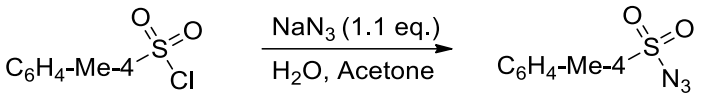
The corresponding aniline derivative (1.0 eq.) was dissolved in MeCN (0.2 M) and cooled to 0 °C. *t*-Butyl nitrite (4.0 eq.) and trimethylsilyl azide (3.0 eq.) were added slowly and the resulting mixture was warmed to room temperature. After 1 h, the solution was diluted with water and CH_2Cl_2. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na_2SO_4, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.

1.3. Preparation of azidocyclohexane (1c')[3]



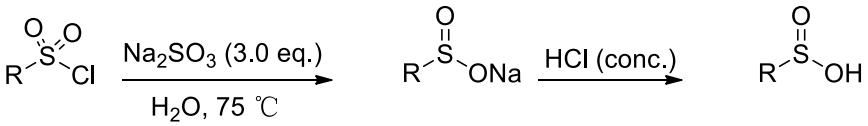
To a 10 mL reaction tube containing the alcohol (2.0 mmol) in benzene (4 mL) was added trimethylsilyl azide (1.2 eq.), followed by $BF_3 \cdot OEt_2$ (1.2 eq.). The mixture allowed to stir for 24 h at 23℃ under nitrogen atmosphere. The reaction system was extracted with Et_2O (3 x 25 mL), washed with water (2 x 25 mL), dried over Na_2SO_4, and the organic phase was concentrated under reduced pressure (bath temperature 35 ºC). The residue was purified by flash chromatography (hexane) to afford the white solid (203.8 mg, 58% yield).

1.4. Preparation of *p*-tosyl azide (1d')[4]



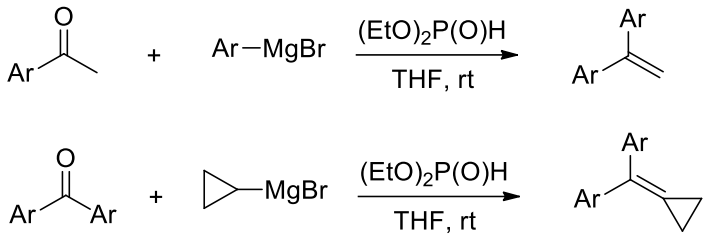
To a 100 mL flask , a solution of sodium azide (2.86 g, 44 mmol) in water (12 mL) and acetone (20 mL) was rapidly added a solution of *p*-toluenesulfonyl chloride (1.0 eq.) in acetone (20 mL). The mixture warmed slightly and two phases were formed. After stirring at room temperature for 4 h, acetone was evaporated under reduced pressure (bath temperature 35 ºC), the residue was extracted with CH_2Cl_2 (3 x 25 mL), washed with water (2 x 25 mL), dried over Na_2SO_4, and the organic phase was concentrated under reduced pressure (bath temperature 35 ºC) to give the compound as a colorless oil (7.78 g, 98% yield).

2. Preparation of sulfinic acids (2a and 2q-2t)[5]



To a 50 mL flask containing Na_2SO_3 (3.0 eq.) was added, and the solid was completely dissolved in pure water. Then substituted sulfonyl chloride (10.0 mmol) was added into reaction system. The mixture was stirred at 75 ℃ for 5 h. Then, this aqueous solution was washed with chloroform twice, acidified with excess concentrated HCl solution, cooled and filtered. The white precipitate was recrystallized from water, affording the substituted sulfinic acids.

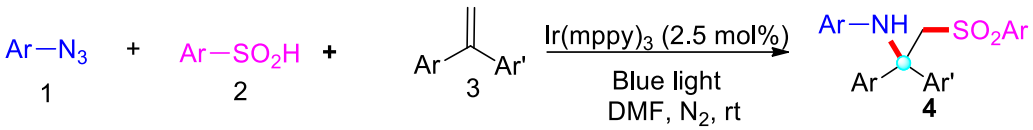
3. Preparation of olefins (3u-3z, 3a', 3b' and 3c')[6]



To a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added Grignard reagents in THF (0.5 M, 2.2 mL, 2.2 eq.) at room temperature, and the mixture was stirred for 30 min, then the diethyl phosphite (1.2 eq.) was added to this mixture at room temperature. After 5 h, the solution was diluted with water and CH_2Cl_2. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na_2SO_4, filtered and the solvents were concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 1:45) afforded the corresponding product.

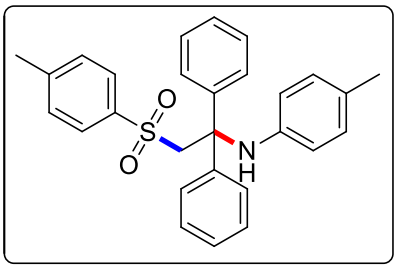
V. Experimental Procedure for Products 4 and 6

1. Synthesis Procedure of Products 4

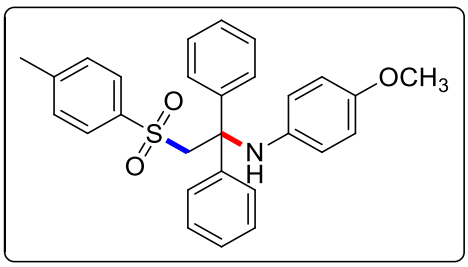


Under the protection of N_2, corresponding sulfinic acid (0.2 mmol), olefins (2.0 eq.), azide (1.2 eq.), Ir(mppy)$_3$ (2.5 mol%) and anhydrous *N,N*-dimethylformamide (degassed) (2.0 mL) were added to a 10 mL glass vial equipped with a stirring bar. The solution was stirred at a distance of 1.5 cm from a 24 W blue LED lamp at room temperature (a fan was equipped to control the temperature to 28~32 ℃) for 24 hours. The reaction system was extracted with ethyl acetate (3 x 10 mL), washed with NaCl aqueous (10 mL), dried over Na_2SO_4, and concentrated the organic layer under reduced pressure. The product was purified by flash chromatography on silicagel using petroleum ether / ethyl acetate (15:1).

2. Spectroscopic Data of Products 4

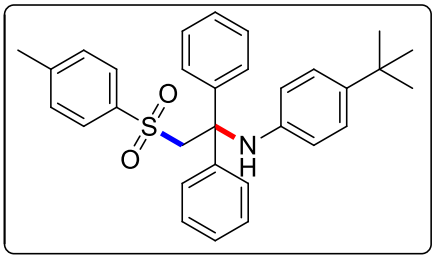


***N*-(1,1-diphenyl-2-tosylethyl)-4-methylaniline (4a):** TLC R_f = 0.5 (EA: PE = 1:5); 77.6 mg, 88% yield; white solid, mp 165-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.38-7.33 (m, 4H), 7.23 (d, J = 9.0 Hz, 3H), 7.16 (d, J = 6.0 Hz, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 6.26 (d, J = 8.3 Hz, 2H), 6.01 (s, 1H), 4.29 (s, 2H), 2.34 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 143.8, 142.8, 142.2, 137.8, 129.5, 129.2, 128.4, 128.0, 127.3, 117.6, 64.7, 63.9, 21.5, 20.4; IR (neat): 3390, 3055, 2922, 2864, 1615, 1515, 1316, 1137, 811, 700 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{28}H_{28}NO_2S$: 442.1840, found: 442.1841.

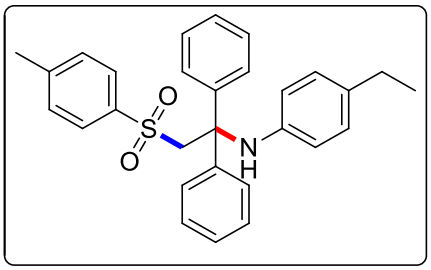


***N*-(1,1-diphenyl-2-tosylethyl)-4-methoxyaniline (4b):** TLC R_f = 0.5 (EA: PE = 1:3); 76.8 mg, 84% yield; white solid, mp 174-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.38-7.33 (m, 4H), 7.23 (d, J = 9.0 Hz, 3H), 7.16 (d, J = 6.0 Hz, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 6.26 (d,

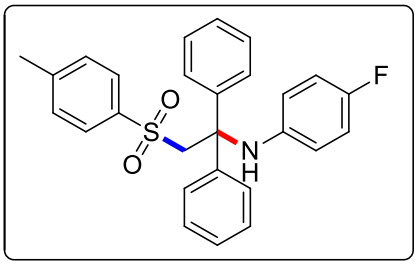
J = 8.3 Hz, 2H), 6.01 (s, 1H), 4.29 (s, 2H), 2.34 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.8, 142.8, 142.2, 137.8, 129.5, 129.2, 128.4, 128.0, 127.3, 117.6, 64.7, 63.9, 21.5, 20.4; IR (neat): 3381, 3059, 2936, 2835, 1600, 1505, 1455, 1317, 743, 701 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{28}H_{27}NNaO_3S$: 480.1610, found: 480.1612.



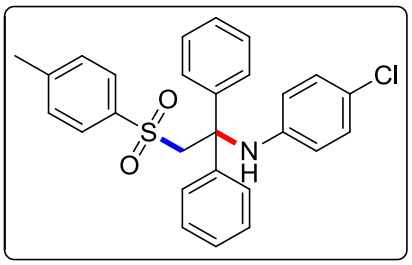
4-(*tert*-butyl)-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4c): TLC R_f = 0.5 (EA: PE = 1:5); 79.2 mg, 82% yield; white solid, mp 168-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.39 (m, 4H), 7.23-7.18 (m, 5H), 7.16 (m, 3H), 7.02-6.96 (m, 4H), 6.30 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H), 4.37 (s, 2H), 2.33 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.8, 142.8, 141.6, 138.1, 129.4, 128.5, 127.3, 127.2, 127.0, 125.5, 117.1, 64.7, 62.5, 33.8, 31.5, 21.5; IR (neat): 3387, 3058, 2961, 2865, 1596, 1516, 1316, 1140, 737, 702 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{31}H_{33}NNaO_2S$: 506.2130, found: 506.2131.



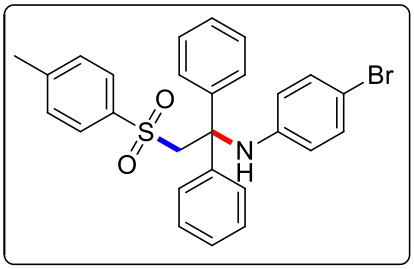
***N*-(1,1-diphenyl-2-tosylethyl)-4-ethylaniline (4d):** TLC R_f = 0.5 (EA: PE = 1:5); 81.9 mg, 90% yield; white solid, mp 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.39-7.35 (m, 4H), 7.21 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 5H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 4.32 (s, 2H), 2.47 (q, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.8, 143.0, 142.5, 129.4, 128.4, 128.0, 127.4, 127.3, 127.2, 117.6, 64.7, 63.4, 27.8, 21.5, 15.7; IR (neat): 3386, 3061, 2918, 2850, 1515, 1447, 1316, 1219, 820, 772 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{29}H_{29}NNaO_2S$: 478.1817, found: 478.1818.



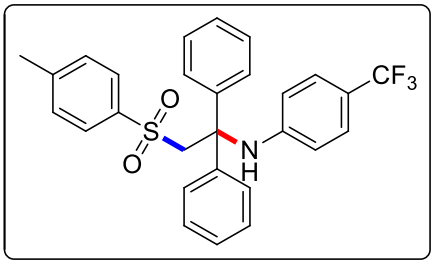
***N*-(1,1-diphenyl-2-tosylethyl)-4-fluoroaniline (4e):** TLC R_f = 0.5 (EA: PE = 1:5); 69.4 mg, 78% yield; white solid, mp 183-184 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.32-7.30 (m, 4H), 7.24-7.22 (m, 3H), 7.18-7.16 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.67 (m, 2H), 6.32-6.29 (m, 2H), 6.04 (s, 1H), 4.26 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 156.8 (d, *J* = 238.4 Hz), 144.0, 142.0, 141.4, 137.7, 129.5, 128.4, 127.4 (t, *J* = 3.0 Hz), 119.1 (d, *J* = 8.1 Hz), 115.1 (d, *J* = 22.2 Hz), 64.9, 63.7, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) -125.63; IR (neat): 3388, 3060, 3029, 2925, 1597, 1507, 1316, 1138, 761, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{27}H_{24}FNNaO_2S$: 468.1410, found: 468.1408.



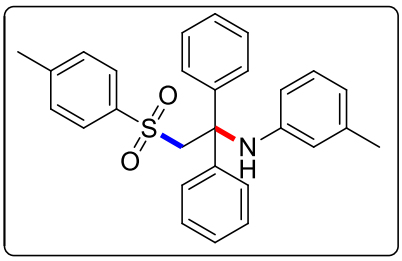
4-chloro-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4f): TLC R_f = 0.5 (EA: PE = 1:5); 66.4 mg, 72% yield; white solid, mp 177-178 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.35-7.30 (m, 4H), 7.24 (s, 2H), 7.18 (d, *J* = 3.9 Hz, 6H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.29 (s, 1H), 6.24 (d, *J* = 8.7 Hz, 2H), 4.24 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 144.1, 144.0, 141.1, 137.4, 129.6, 128.5, 127.5, 127.4, 118.1, 64.82, 64.78, 21.5; IR (neat): 3385, 3059, 3030, 2926, 1597, 1493, 1317, 1138, 817, 703 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{27}H_{24}ClNNaO_2S$: 484.1114, found: 484.1124.



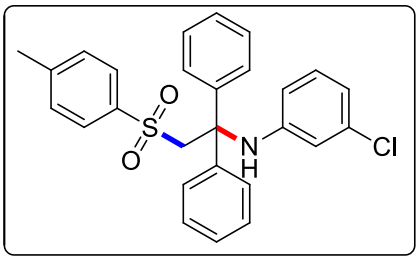
4-bromo-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4g): TLC R_f = 0.5 (EA: PE = 1:5); 77.8 mg, 77% yield; white solid, mp 172-173 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.32 (m, 4H), 7.24 (s, 2H), 7.21-7.16 (m, 6H), 7.03 (m, 4H), 6.33 (s, 1H), 6.19 (d, *J* = 8.8 Hz, 2H), 4.23 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 144.5, 140.9, 131.4, 129.6, 128.5, 127.5, 127.4, 118.4, 100.0, 65.0, 21.6; IR (neat): 3378, 2925, 2851, 1592, 1489, 1317, 1136, 745, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{27}H_{24}BrNNaO_2S$: 528.0609, found: 528.0607.



***N*-(1,1-diphenyl-2-tosylethyl)-4-(trifluoromethyl)aniline (4h):** TLC R_f = 0.5 (EA: PE = 1:5); 80.2 mg, 81% yield; white solid, mp 174-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.33 (m, 4H), 7.26 (m, 3H), 7.21-7.18 (m, 5H), 7.17 (s, 1H), 7.15 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.69 (s, 1H), 6.32 (d, *J* = 8.5 Hz, 2H), 4.25 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 148.3, 144.2, 138.7 (d, *J* = 318.2 Hz), 128.6 (t, *J* = 97.0 Hz), 127.4 (d, *J* = 2.0 Hz), 125.8 (q, *J* = 3.0 Hz), 119.6 (d, *J* = 32.3 Hz), 115.4, 65.6, 64.9, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) -61.22; IR (neat): 3381, 3061, 3033, 2928, 1615, 1526, 1324, 1137, 755, 701 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{28}H_{25}F_3NO_2S$: 496.1558, found: 496.1560.

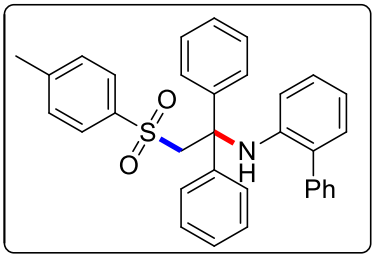


***N*-(1,1-diphenyl-2-tosylethyl)-3-methylaniline (4i):** TLC R_f = 0.5 (EA: PE = 1:5); 64.4 mg, 73% yield; white solid, mp 154-155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.36 (m, 4H), 7.26 (s, 1H), 7.24 (s, 1H), 7.20-7.15 (m, 6H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.79 (m, 1H), 6.48 (d, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), 6.12 (s, 1H), 6.01 (d, *J* = 8.1 Hz, 1H), 4.29 (s, 2H), 2.34 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 145.3, 143.9, 141.9, 138.3, 137.7, 129.5, 128.4, 127.4, 127.3, 119.5, 118.2, 113.9, 64.7, 64.3, 21.5; IR (neat): 3389, 3056, 3033, 2922, 1606, 1490, 1316, 1138, 770, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{27}NNaO_2S$: 464.1660, found: 464.1659.

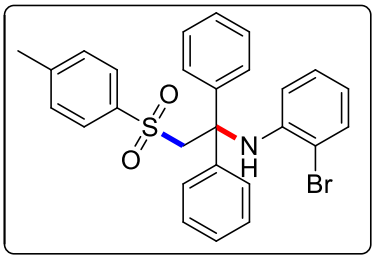


3-chloro-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4j): TLC R_f = 0.5 (EA: PE = 1:5); 46.1 mg, 50% yield; yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.33 (m, 4H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.19 (m, 6H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.82 (m, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 6.37 (s, 1H), 6.29 (s, 1H), 6.16 (m, 1H), 4.25 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 146.7, 144.1, 140.9, 137.3, 134.2, 129.6, 129.5, 128.5, 127.6, 127.5, 118.3, 116.5, 114.7, 65.0, 64.8, 21.5;

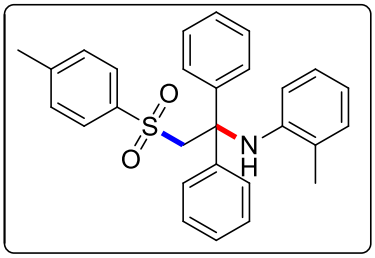
IR (neat): 3384, 3059, 3031, 2926, 1596, 1481, 1317, 1138, 739, 701 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{27}H_{24}ClNNaO_2S$: 484.1114, found: 484.1111.



***N*-(1,1-diphenyl-2-tosylethyl)-[1,1'-biphenyl]-2-amine (4k):** TLC R_f = 0.5 (EA: PE = 1:5); 55.3 mg, 55% yield; white solid, mp 188-189 ℃; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.67 (d, J = 7.3 Hz, 2H), 7.59 (m, 2H), 7.47 (d, J = 7.4 Hz, 1H), 7.32 (d, J = 6.7 Hz, 4H), 7.19-7.11 (m, 9H), 6.98 (d, J = 8.1 Hz, 2H), 6.76-6.64 (m, 2H), 6.17 (s, 1H), 5.87 (d, J = 7.8 Hz, 1H), 4.23 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 143.8, 142.1, 141.4, 139.7, 137.7, 130.3, 130.0, 129.9, 129.4, 128.9, 128.7, 128.5, 127.6, 127.51, 127.47, 127.32, 127.29, 127.26, 117.4, 114.7, 64.9, 64.5, 21.5; IR (neat): 3377, 3058, 2926, 2860, 1596, 1513, 1319, 1144, 740, 702 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{33}H_{29}NNaO_2S$: 526.1817, found: 526.1818.

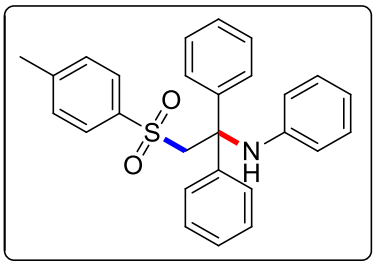


2-bromo-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4l): TLC R_f = 0.5 (EA: PE = 1:5); 56.6 mg, 56% yield; yellow oily liquid; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.44 (d, J = 1.4 Hz, 0.5H), 7.42 (d, J = 1.4 Hz, 0.5H), 7.35 (m, 6H), 7.20 (m, 6H), 7.01 (d, J = 8.1 Hz, 2H), 6.82 (s, 1H), 6.64-6.58 (m, 1H), 6.44 (m, 1H), 5.77 (m, 1H), 4.33 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 143.9, 142.2, 140.5, 137.2, 132.6, 129.5, 128.5, 127.6, 127.5, 118.3, 115.5, 65.7, 21.5; IR (neat): 3358, 3060, 3027, 2926, 1595, 1494, 1321, 1139, 743, 701 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{27}H_{24}BrNNaO_2S$: 528.0609, found: 528.0606.

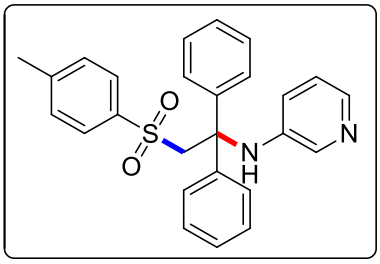


***N*-(1,1-diphenyl-2-tosylethyl)-2-methylaniline (4m):** TLC R_f = 0.5 (EA: PE = 1:5); 58.2 mg, 66% yield; yellow oily liquid; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.39-7.35 (m, 4H), 7.25-7.22 (m, 2H), 7.20-7.14 (m, 6H), 7.11-7.08 (m, 1H), 7.03-6.99 (m, 2H), 6.59-6.52 (m, 2H), 6.29 (s, 1H),

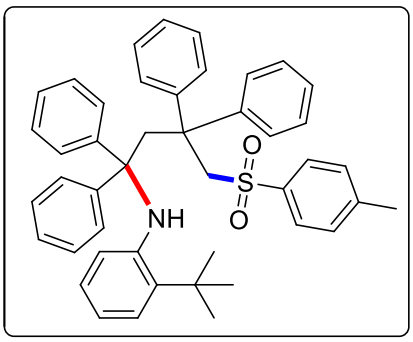
5.75-5.69 (m, 1H), 4.30 (s, 2H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 143.9, 143.4, 140.9, 137.4, 130.2, 129.5, 128.4, 127.7, 127.5, 127.3, 124.1, 117.3, 114.3, 66.1, 64.7, 21.5, 18.5; IR (neat): 3400, 3058, 2926, 2858, 1591, 1484, 1317, 1136, 747, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{27}NNaO_2S$: 464.1660, found: 464.1663.



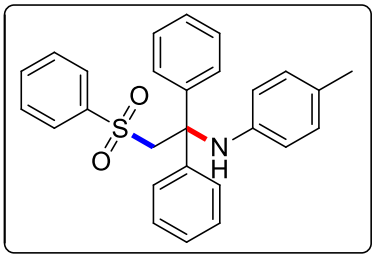
***N*-(1,1-diphenyl-2-tosylethyl)aniline (4n):** TLC R_f = 0.5 (EA: PE = 1:5); 64.9 mg, 76% yield; white solid, mp 168-169 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.40-7.33 (m, 4H), 7.23 (d, J = 6.8 Hz, 3H), 7.17 (d, J = 6.6 Hz, 5H), 7.01 (d, J = 8.1 Hz, 2H), 6.95 (m, 2H), 6.66 (m, 1H), 6.34 (d, J = 7.9 Hz, 2H), 6.18 (s, 1H), 4.29 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 145.4, 143.9, 141.8, 137.7, 129.5, 128.6, 128.4, 127.4, 127.3, 118.6, 117.1, 64.8, 64.2, 21.5; IR (neat): 3389, 3056, 3028, 2925, 1600, 1496, 1317, 1138, 750, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{27}H_{25}NNaO_2S$: 450.1504, found: 450.1508.



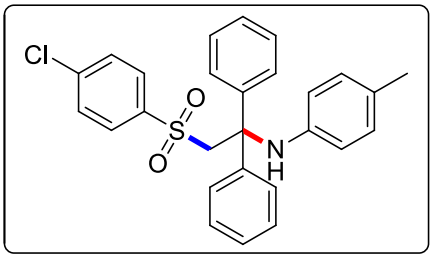
***N*-(1,1-diphenyl-2-tosylethyl)pyridin-3-amine (4o):** TLC R_f = 0.5 (EA: PE = 1:5); 30.0 mg, 35% yield; yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 4.6 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H), 7.34-7.30 (m, 4H), 7.28 (s, 2H), 7.19 (d, J = 3.4 Hz, 6H), 7.04 (d, J = 8.0 Hz, 2H), 6.80 (m, 1H), 6.45 (s, 1H), 6.42 (s, 1H), 4.24 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 142.2, 129.6, 128.7, 127.8, 127.5, 123.7, 65.3, 64.9, 21.5; IR (neat): 3371, 3056, 2923, 2850, 1581, 1478, 1316, 1139, 763, 702 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{26}H_{25}N_2O_2S$: 429.1636, found: 429.1638.



2-(tert-butyl)-*N*-(1,1,3,3-tetraphenyl-4-tosylbutyl)aniline (4p): TLC R_f = 0.5 (EA: PE = 1:5); 62.3 mg, 47% yield; white solid, mp 168-169 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.34 (d, *J* = 3.7 Hz, 4H), 7.27 (s, 1H), 7.14 (m, 8H), 7.11 (s, 9H), 7.07 (s, 1H), 7.06-7.02 (m, 3H), 6.42 (s, 1H), 6.31 (d, *J* = 8.6 Hz, 1H), 5.68 (d, *J* = 8.7 Hz, 1H), 4.56 (s, 2H), 4.22 (s, 2H), 2.35 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 144.8, 143.9, 143.3, 140.9, 140.1, 137.4, 134.3, 132.9, 129.5, 129.3, 128.3, 128.2, 127.50, 127.45, 127.37, 127.2, 126.1, 116.9, 67.6, 66.0, 55.9, 34.7, 30.1, 21.6; IR (neat): 3435, 3058, 2960, 2871, 1597, 1494, 1318, 1134, 737, 701 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{45}H_{45}NNaO_2S$: 686.3069, found: 686.3056.

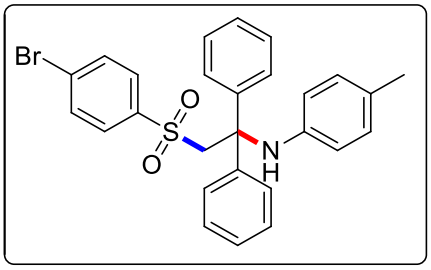


***N*-(1,1-diphenyl-2-(phenylsulfonyl)ethyl)-4-methylaniline (4q):** TLC R_f = 0.5 (EA: PE = 1:5); 66.6 mg, 78% yield; white solid, mp 165-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.42 (m, 1H), 7.34 (d, *J* = 7.3 Hz, 6H), 7.22 (s, 1H), 7.21-7.13 (m, 7H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 8.2 Hz, 2H), 6.00 (s, 1H), 4.32 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 142.8, 142.2, 140.8, 132.9, 129.2, 128.9, 128.4, 128.2, 127.4, 127.3, 117.8, 64.7, 63.7, 20.4; IR (neat): 3389, 3058, 3024, 2920, 1615, 1514, 1447, 1307, 738, 700 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{27}H_{25}NNaO_2S$: 450.1504, found: 450.1505.

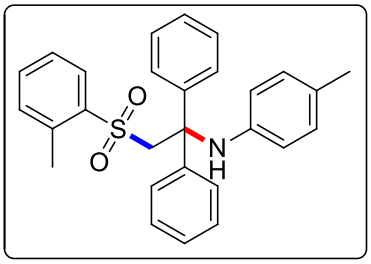


***N*-(2-((4-chlorophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4r):** TLC R_f = 0.5 (EA: PE = 1:5); 63.6 mg, 69% yield; white solid, mp 175-176 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.33 (m, 5H), 7.24 (s, 1H), 7.17 (m, 8H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 8.2 Hz, 2H), 5.92 (s, 1H), 4.33 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 142.6, 142.1, 139.7, 139.0, 129.3,

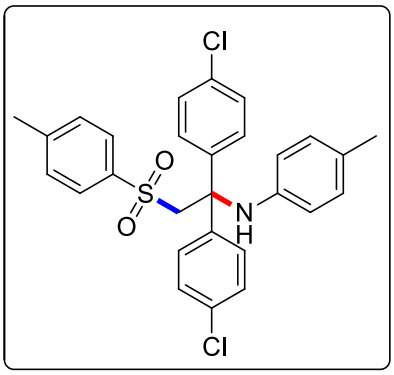
129.1, 128.9, 128.5, 128.3, 127.4, 127.3, 117.7, 64.6, 63.8, 20.4; IR (neat): 3394, 3058, 3024, 2921, 1615, 1582, 1447, 1317, 737, 701 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{27}H_{24}ClNNaO_2S$: 484.1114, found: 484.1113.



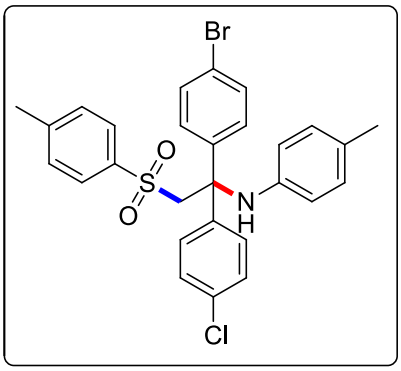
***N*-(2-((4-bromophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4s):** TLC R_f = 0.5 (EA: PE = 1:5); 70.7 mg, 70% yield; white solid, mp 172-173 ℃; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.36-7.30 (m, 6H), 7.26 (s, 2H), 7.20-7.16 (m, 6H), 7.16 (s, 1H), 6.78 (d, J = 8.3 Hz, 2H), 6.25 (d, J = 8.4 Hz, 2H), 4.33 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 142.6, 142.1, 139.5, 132.1, 131.9, 130.6, 129.8, 129.3, 129.1, 128.9, 128.5, 128.2, 127.9, 127.4, 127.3, 117.7, 64.6, 63.8, 20.4; IR (neat): 3391, 3084, 3022, 2919, 1615, 1514, 1317, 1157, 761, 700 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{27}H_{24}BrNNaO_2S$: 528.0609, found: 528.0607.



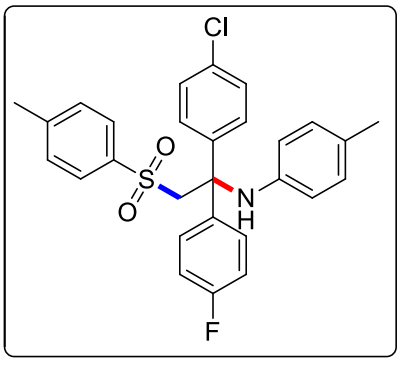
***N*-(1,1-diphenyl-2-(o-tolylsulfonyl)ethyl)-4-methylaniline (4t):** TLC R_f = 0.5 (EA: PE = 1:5); 60.9 mg, 69% yield; yellow oily liquid; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.35 (s, 2H), 7.34-7.32 (m, 2H), 7.30 (s, 1H), 7.28 (m, 1H), 7.18-7.16 (m, 1H), 7.15 (s, 2H), 7.13 (d, J = 5.7 Hz, 3H), 7.09 (d, J = 7.3 Hz, 1H), 6.98 (m, 1H), 6.74 (d, J = 8.2 Hz, 2H), 6.24 (d, J = 8.4 Hz, 2H), 6.08 (s, 1H), 4.29 (s, 2H), 2.51 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 142.8, 141.8, 138.6, 136.9, 133.1, 132.2, 129.7, 129.2, 127.9, 127.4, 126.5, 117.4, 64.7, 63.4, 20.4, 20.3; IR (neat): 3391, 3058, 3023, 2921, 1615, 1515, 1310, 1153, 787, 701 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{28}H_{27}NNaO_2S$: 464.1660, found: 464.1659.



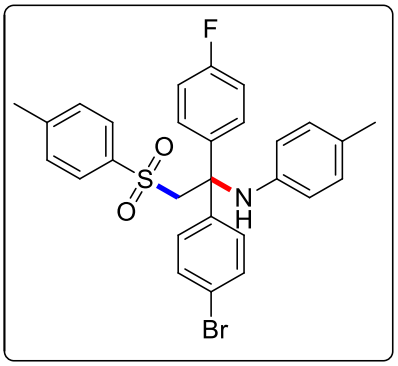
***N*-(1,1-bis(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4u):** TLC R_f = 0.5 (EA: PE = 1:5); 78.4 mg, 77% yield; white solid, mp 168-169 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.22 (m, 6H), 7.08 (m, 6H), 6.79 (d, J = 8.2 Hz, 2H), 6.24 (d, J = 8.3 Hz, 2H), 6.04 (s, 1H), 4.16 (s, 2H), 2.40 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 144.4, 142.2, 139.9, 137.1, 133.6, 129.6, 129.3, 129.0, 128.5, 127.4, 117.8, 64.5, 64.1, 21.6, 20.4; IR (neat): 3390, 3029, 2922, 2865, 1615, 1515, 1317, 1138, 813, 717 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{25}Cl_2NNaO_2S$: 532.0881, found: 532.0878.



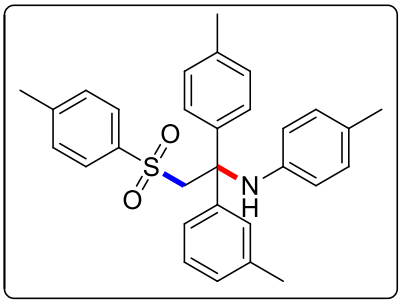
***N*-(1-(4-bromophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4v):** TLC R_f = 0.5 (EA: PE = 1:5); 84.1 mg, 76% yield; white solid, mp 163-164 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.23 (m, 6H), 7.17-7.06 (m, 6H), 6.79 (d, J = 8.2 Hz, 2H), 6.24 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 4.16 (s, 2H), 2.41 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 144.4, 142.1, 140.4, 140.0, 137.1, 133.6, 131.5, 129.6, 129.4, 129.3, 129.0, 128.59, 128.56, 127.4, 121.9, 117.8, 64.4, 64.2, 21.6, 20.4; IR (neat): 3390, 3025, 2921, 2854, 1614, 1514, 1317, 1138, 812, 758 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{25}BrClNNaO_2S$: 576.0376, found: 576.0377.



***N*-(1-(4-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4w):** TLC R_f = 0.5 (EA: PE = 1:5); 84.8 mg, 86% yield; white solid, mp 171-172 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.28 (m, 3H), 7.23-7.19 (m, 3H), 7.08 (m, 4H), 6.86 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.24 (d, *J* = 8.4 Hz, 2H), 6.03 (s, 1H), 4.18 (s, 2H), 2.39 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 161.9 (d, *J* = 248.5 Hz), 144.4, 142.3, 140.0, 137.5 (d, *J* = 3.0 Hz), 137.3, 133.5, 129.3 (d, *J* = 9.1 Hz), 128.5, 128.4, 127.4, 117.8, 115.3 (d, *J* = 21.2 Hz), 64.4 (d, *J* = 47.0 Hz), 21.5, 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) -114.52; IR (neat): 3390, 3027, 2921, 2853, 1598, 1510, 1317, 1137, 813, 712 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{25}ClFNNaO_2S$: 516.1177, found: 516.1179.

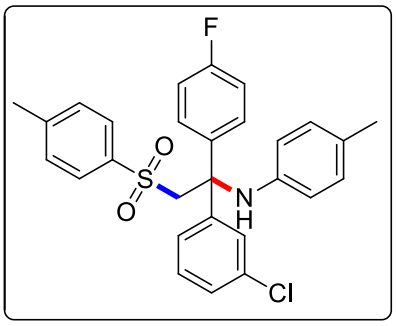


***N*-(1-(4-bromophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4x):** TLC R_f = 0.5 (EA: PE = 1:5); 87.0 mg, 81% yield; white solid, mp 158-159 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.30-7.26 (m, 2H), 7.25-7.20 (m, 4H), 7.16-7.12 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.89-6.83 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.24 (d, *J* = 8.4 Hz, 2H), 6.04 (s, 1H), 4.17 (s, 2H), 2.40 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 161.9 (d, $J_{C\text{-}F}$ = 248.5 Hz), 144.4, 142.2, 140.4, 137.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 137.2, 131.3, 129.4 (d, $J_{C\text{-}F}$ = 9.1 Hz), 128.5, 127.4, 121.8, 117.8, 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 64.3 (d, $J_{C\text{-}F}$ = 41.0 Hz), 21.6, 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) -114.41; IR (neat): 3394, 3022, 2920, 2857, 1599, 1486, 1317, 1137, 814, 757 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{25}BrFNNaO_2S$: 560.0671, found: 560.0674.

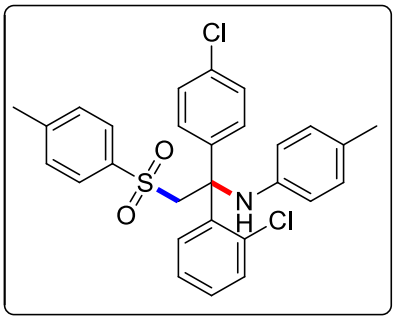


4-methyl-*N*-(1-(m-tolyl)-1-(p-tolyl)-2-tosylethyl)aniline (4y): TLC R_f = 0.5 (EA: PE = 1:5); 42.2 mg, 45% yield; white solid, mp 138-139 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.29 (s, 1H), 7.24 (s, 3H), 7.22 (s, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 4H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.30 (d, *J* = 8.4 Hz, 2H), 6.05 (s, 1H), 4.27 (s, 2H), 2.39 (s, 3H), 2.29 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.6, 143.0, 139.3, 137.8, 136.9, 129.8, 129.3, 129.1, 129.0, 128.4, 128.3, 127.7, 127.5, 127.3, 117.5, 64.5, 64.2, 21.5, 20.9, 20.4; IR (neat): 3390, 3024, 2921, 2853,

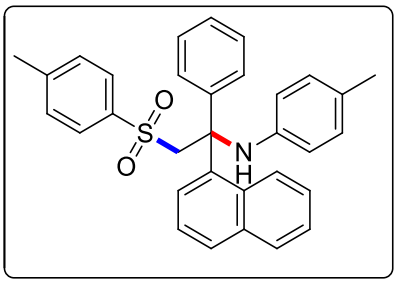
1614, 1515, 1315, 1138, 811, 772 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{31}NNaO_2S$: 492.1973, found: 492.1976.



***N*-(1-(3-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4z):** TLC R_f = 0.5 (EA: PE = 1:5); 69.1 mg, 70% yield; yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.29 (m, 4H), 7.24 (s, 1H), 7.18-7.11 (m, 3H), 7.07 (d, J = 8.1 Hz, 2H), 6.87 (m, 2H), 6.80 (d, J = 8.3 Hz, 2H), 6.25 (d, J = 8.4 Hz, 2H), 5.97 (s, 1H), 4.20 (s, 2H), 2.39 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 161.9 (d, J = 248.5 Hz), 144.4, 144.1, 142.2, 137.4 (d, J = 3.0 Hz), 137.3, 134.4, 129.8, 129.6, 129.3 (d, J = 8.1 Hz), 128.7, 127.8, 127.6, 127.4, 125.6, 118.0, 115.4 (d, J = 21.2 Hz), 64.3 (d, J = 41.0 Hz), 21.5, 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm) -114.52; IR (neat): 3389, 3024, 2923, 2857, 1596, 1510, 1302, 1139, 813, 759 cm^{-1}; HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{28}H_{25}ClFNNaO_2S$: 516.1177, found: 516.1179.



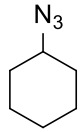
***N*-(1-(2-chlorophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4a'):** TLC R_f = 0.5 (EA: PE = 1:5); 76.4 mg, 75% yield; yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93 (s, 1H), 7.30 (m, 3H), 7.14 (m, 3H), 7.06 (m, 4H), 6.90 (d, J = 7.8 Hz, 1H), 6.78 (m, 2H), 6.26 (m, 2H), 6.00 (s, 1H), 4.99 (m, 1H), 4.14 (m, 1H), 2.36 (d, J = 4.1 Hz, 3H), 2.16 (d, J = 5.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 144.1, 141.5, 137.8, 136.6, 133.6, 133.3, 131.6, 130.9, 130.2, 129.3, 129.1, 128.1, 127.7, 127.0, 120.5, 64.8, 60.0, 21.6, 20.5; IR (neat): 3396, 3005, 2914, 2849, 1513, 1490, 1275, 1141, 765, 750 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{28}H_{25}Cl_2NNaO_2S$: 532.0881, 532.0879, found: 307.1812.



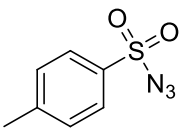
4-methyl-*N*-(1-(naphthalen-1-yl)-1-phenyl-2-tosylethyl)aniline (4b'): TLC R_f = 0.5 (EA: PE = 1:5); 49.1 mg, 50% yield; white solid, mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78 (s, 1H), 7.72-7.67 (m, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.44 (m, 2H), 7.41-7.38 (m, 2H), 7.32 (m, 1H), 7.17 (m, 5H), 6.80-6.75 (m, 4H), 6.33 (d, J = 8.3 Hz, 2H), 6.11 (s, 1H), 4.38 (s, 2H), 2.18 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 143.8, 142.8, 142.4, 139.2, 137.4, 132.8, 132.4, 129.24, 129.20, 128.5, 128.4, 128.1, 127.6, 127.40, 127.35, 127.26, 126.3, 126.1, 125.8, 118.1, 64.8, 63.7, 21.4, 20.4; IR (neat): 3391, 3055, 2922, 2864, 1615, 1515, 1316, 1136, 748, 700 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{32}H_{29}NNaO_2S$: 514.1817, found: 514.1821.

3. Substrates Failing to Undergo Efficient Reaction

Azide:

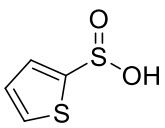


4c' giving 6% yield

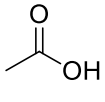


4d' N.D.

Sulfinic acid:

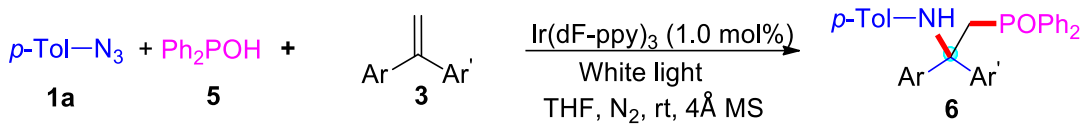


2e' N.D.



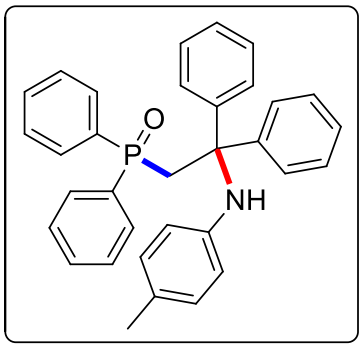
2f' N.D.

4. Synthesis Procedure of Products 6

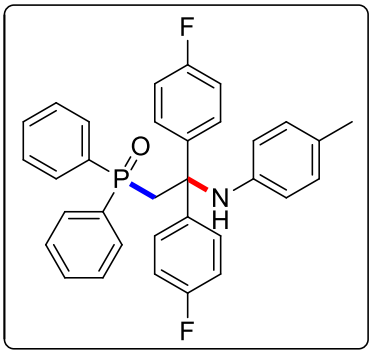


Under the protection of N_2, corresponding diphenylphosphine oxide (0.2 mmol), olefins (2.0 eq.), azide (2.5 eq.), $Ir(dF\text{-}ppy)_3$ (1.0 mol%), 4Å M.S.(100.0 mg) and anhydrous THF (degassed) (2.0 mL) were added to a 10 mL glass vial equipped with a stirring bar. The solution was stirred at a distance of 1.5 cm from a 24 White LED lamp at room temperature (a fan was equipped to control the temperature to 28~32 ℃) for 24h. The reaction system was concentrated under reduced pressure and the product was purified by flash chromatography on silicagel using petroleum ether / ethyl acetate (9:1).

5. Spectroscopic Data of Products 6

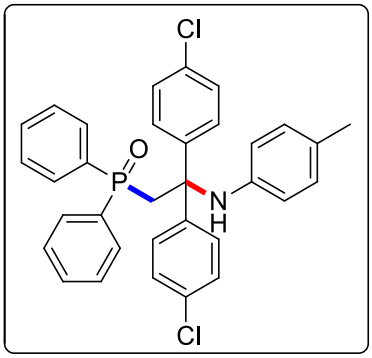


(2,2-diphenyl-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6a): TLC R_f = 0.5 (EA: PE = 1:3); 70.1 mg, 72% yield; white solid, mp 196-197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.44-7.33 (m, 10H), 7.25 (m, 4H), 7.06 (m, 6H), 6.93 (s, 1H), 6.72 (d, J = 7.5 Hz, 2H), 6.29 (d, J = 7.3 Hz, 2H), 3.43 (d, J = 9.8 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, CDCl3; δ, ppm) 143.8 (d, J = 23.2 Hz), 134.1, 131.1, 130.4 (d, J = 9.1 Hz), 128.9, 128. (d, J = 12.1 Hz), 128.0 (d, J = 6.1 Hz), 126.9 (d, J = 20.2 Hz), 117.5, 65.5, 41.8 (d, J = 70.7 Hz), 20.4; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.29; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{33}H_{31}NOP$: 488.2143, found: 488.2124.

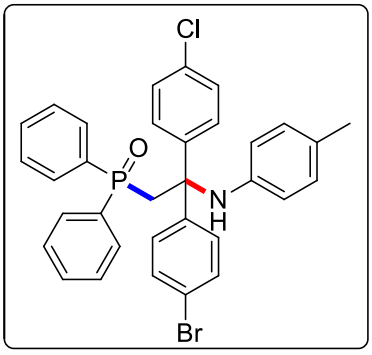


(2,2-bis(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6b): TLC R_f = 0.5 (EA: PE = 1:3); 66.9 mg, 64% yield; white solid, mp 237-238 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.45-7.39 (m, 6H), 7.35-7.27 (m, 9H), 6.78-6.71 (m, 6H), 6.27 (d, J = 8.4 Hz, 2H), 3.35 (d, J = 9.9 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 161.6 (d, J = 247.4 Hz), 143.4,

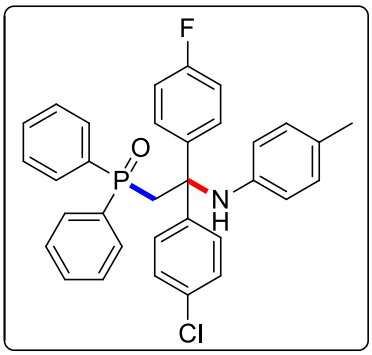
139.1 (d, *J* = 3.0 Hz), 133.2 (d, *J* = 101.0 Hz), 131.3 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 9.1 Hz), 129.8 (d, *J* = 8.1 Hz), 129.0, 128.4 (d, *J* = 11.1 Hz), 127.6, 117.8, 114.7 (d, *J* = 21.1 Hz), 64.8 (d, *J* = 4.0 Hz), 42.6 (d, *J* = 68.0 Hz), 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) 115.88; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.08; IR (neat): 3307, 3055, 2922, 2853, 1602, 1507, 1229, 1160, 747, 715 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{28}F_2NNaOP$: 546.1775, found: 546.1778.



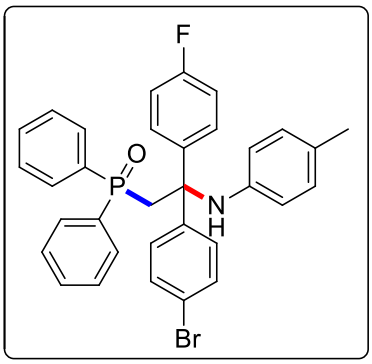
(2,2-bis(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6c): TLC R_f = 0.5 (EA: PE = 1:3); 68.8 mg, 62% yield; white solid, mp 226-227 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.45-7.38 (m, 6H), 7.32-7.26 (m, 8H), 7.01 (d, *J* = 8.6 Hz, 4H), 6.93 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 8.4 Hz, 2H), 3.31 (d, *J* = 9.9 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.2, 141.7 (d, *J* = 8.1 Hz), 141.66, 133.0 (t, *J* = 49.5 Hz), 131.3 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 10.1 Hz), 129.3 (d, *J* = 42.4 Hz), 128.4 (d, *J* = 12.1 Hz), 128.1, 117.8, 64.9, 42.4 (d, *J* = 67.7 Hz), 20.4; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.03; IR (neat): 3320, 3053, 2927, 2859, 1600, 1497, 1275, 1176, 815, 747 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{28}Cl_2NNaOP$: 578.1184, found: 578.1185.



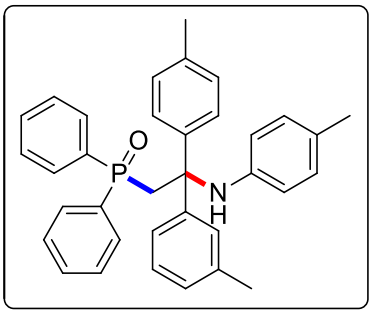
(2-(4-bromophenyl)-2-(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6d): TLC R_f = 0.5 (EA: PE = 1:3); 80.3 mg, 67% yield; white solid, mp 222-223 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.45-7.37 (m, 6H), 7.32-7.27 (m, 6H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 8.4 Hz, 2H), 3.31 (d, *J* = 9.9 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 143.2, 142.1 (d, *J* = 8.1 Hz), 141.7 (d, *J* = 8.1 Hz), 133.5 (d, *J* = 15.1 Hz), 132.5 (d, *J* = Hz), 131.3 (q, *J* = 2.0 Hz), 131.0, 130.3 (d, *J* = Hz), 129.5 (t, *J* = 40.0 Hz), 128.4 (d, *J* = 12.1 Hz), 127.9 (d, *J* = 42.4 Hz), 121.3, 117.7, 65.0, 64.9, 42.5 (d, *J* = 68.7 Hz), 20.4; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.01; IR (neat): 3307, 3055, 2922, 2853, 1614, 1512, 1486, 1178, 747, 694 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{28}BrClNNaOP$: 622.0678, found: 622.0680.



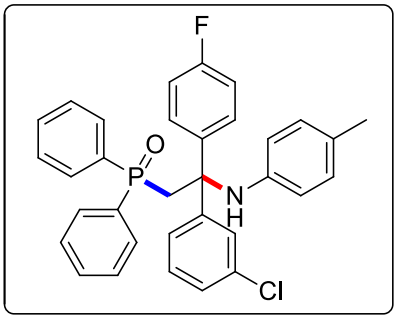
(2-(4-chlorophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6e): TLC R_f = 0.5 (EA: PE = 1:3); 70.1 mg, 65% yield; white solid, mp 231-232 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.42-7.36 (m, 7H), 7.35-7.25 (m, 8H), 7.02-6.97 (m, 2H), 6.92 (s, 1H), 6.78-6.75 (m, 3H), 6.27 (d, *J* = 8.4 Hz, 2H), 3.33 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 161.7 (d, *J* = 247.4 Hz), 143.4, 141.8 (d, *J* = 7.1 Hz), 139.1 (dd, *J* = 6.0, 3.0 Hz), 133.6 (d, *J* = 39.4 Hz), 132.9, 132.6 (d, *J* = 40.4 Hz), 131.4 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 3.0 Hz), 130.3 (dd, *J* = 6.0, 3.0 Hz), 129.8 (d, *J* = 8.1 Hz), 129.6, 129.1, 128.4 (dd, *J* = 7.0, 5.0 Hz), 128.0, 127.7, 117.8, 114.8 (d, *J* = 22.1 Hz), 64.9 (d, *J* = 4.0 Hz), 42.5 (d, *J* = 68.7 Hz), 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) 115.64; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.03; IR (neat): 3310, 3055, 2921, 2855, 1603, 1508, 1437, 1178, 771, 748 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{28}ClFNNaOP$: 562.1479, found: 562.1477.



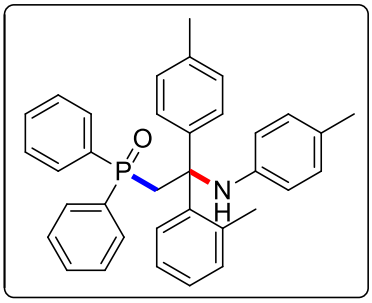
(2-(4-bromophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6f): TLC R_f = 0.5 (EA: PE = 1:3); 82.8 mg, 71% yield; white solid, mp 229-230 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.49-7.37 (m, 6H), 7.33 (m, 5H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.24-7.18 (m, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.92 (s, 1H), 6.83-6.71 (m, 4H), 6.27 (d, *J* = 8.4 Hz, 2H), 3.32 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 161.6 (d, *J* = 247.4 Hz), 143.3, 141.8 (d, *J* = 7.1 Hz), 139.1 (dd, *J* = 6.0, 3.0 Hz), 133.6 (d, *J* = 54.5 Hz), 132.6 (d, *J* = 55.5 Hz), 131.4 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 3.0 Hz), 131.1, 130.3 (dd, *J* = 5.0, 4.0 Hz), 129.9, 129.8 (d, *J* = 8.1 Hz), 129.0, 128.4 (dd, *J* = 8.0, 3.0 Hz), 127.7, 121.2, 117.8, 114.8 (d, *J* = 21.12 Hz), 64.9 (d, *J* = 4.0 Hz), 42.4 (d, *J* = 68.7 Hz), 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) 115.59; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.03; IR (neat): 3312, 3056, 2921, 2855, 1603, 1485, 1437, 1178, 819, 714 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{28}BrFNNaOP$: 606.0974, found: 606.0977.



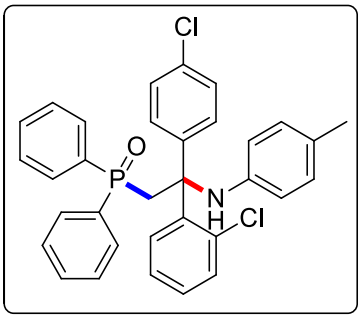
diphenyl(2-(*m*-tolyl)-2-(*p*-tolyl)-2-(*p*-tolylamino)ethyl)phosphine oxide (6g): TLC R_f = 0.5 (EA: PE = 1:3); 64.9 mg, 63% yield; white solid, mp 205-206 ℃; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.69-7.64 (m, 1H), 7.51-7.46 (m, 1H), 7.42-7.39 (m, 2H), 7.38-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.27 (s, 2H), 7.24-7.21 (m, 4H), 7.13-7.08 (m, 0.80H), 6.97-6.95 (d, *J* = 8.0 Hz, 0.55H), 6.85 (m, 4H), 6.71 (d, *J* = 8.3 Hz, 1.52H), 6.66 (d, *J* = 9.3 Hz, 0.20H), 6.60 (d, *J* = 8.2 Hz, 0.48H), 6.30 (d, *J* = 8.4 Hz, 1.45H), 3.38-3.34 (m, 2H), 2.35 (s, 0.5H), 2.23 (d, *J* = 4.7 Hz, 1H), 2.20 (s, 5H), 2.12 (s, 2.5H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 144.1, 140.7 (d, *J* = 7.1 Hz),, 136.2, 133.6 (d, *J* = 100.0 Hz), 131.3 (d, *J* = 3.0 Hz), 130.9, 130.8 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 9.1 Hz), 129.7, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 126.2 (d, *J* = 90.9 Hz), 117.3, 115.3, 65.1 (d, *J* = 4.0 Hz), 42,9 (d, *J* = 70.7 Hz), 20.9, 20.4; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.27; IR (neat): 3307, 3053, 2920, 2851, 1563, 1472, 1397, 1183, 824, 696 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{35}H_{34}NNaOP$: 538.2276, found: 538.2273.



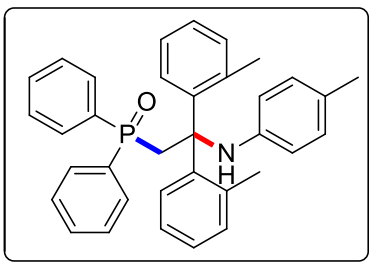
(2-(3-chlorophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6h): TLC R_f = 0.5 (EA: PE = 1:3); 57.1 mg, 53% yield; Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.48-7.37 (m, 7H), 7.32 (m, 7H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 6.75 (m, 4H), 6.29 (d, *J* = 8.4 Hz, 2H), 3.34 (d, *J* = 10.0 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 161.6 (d, *J* = 248.4 Hz), 146.0 (d, *J* = 7.1 Hz), 143.3, 138.8 (dd, *J* = 6.0, 3.0 Hz), 134.0, 133.6 (d, *J* = 54.5 Hz), 132.6 (d, *J* = 55.5 Hz), 131.5 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 3.0 Hz), 130.3 (q, *J* = 5.0 Hz), 129.7 (d, *J* = 8.1 Hz), 129.4, 129.1, 128.4 (d, *J* = 12.1 Hz), 128.2, 127.8, 127.2, 126.1, 117.9, 114.8 (d, *J* = 21.2 Hz), 65.0 (d, *J* = 4.0 Hz), 41.5 (d, *J* = 69.7 Hz), 20.4; ^{19}F NMR (376 MHz, $CDCl_3$; *δ*, ppm) 115.71; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 28.94; IR (neat): 3311, 3051, 2923, 2853, 1507, 1437, 1220, 1178, 825, 747 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{33}H_{29}ClFNOP$: 540.1659, found: 540.1661.



diphenyl(2-(*o*-tolyl)-2-(*p*-tolyl)-2-(*p*-tolylamino)ethyl)phosphine oxide (6i): TLC R_f = 0.5 (EA: PE = 1:3); 69.1 mg, 67% yield; Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.55 (d, *J* = 7.4 Hz, 1H), 7.46-7.26 (m, 9H), 7.21-7.07 (m, 6H), 6.90 (d, *J* = 6.8 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 3.54 (m, 1H), 3.27 (m, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 144.1, 143.4 (d, *J* = 9.1 Hz), 140.1 (d, *J* = 7.1 Hz), 138.4, 135.9, 134.7 (d, *J* = 100.0 Hz), 132.8, 132.5 (d, *J* = 101.0 Hz), 131.2 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.1 Hz), 130.3 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 10.1 Hz), 129.7, 129.0, 128.8, 128.3 *J* = 12.1 Hz), 128.0, 127.9, 127.8, 127.7, 127.6, 127.1, 125.3, 120.3, 115.3, 65.8 (d, *J* = 3.0 Hz), 39.0 (d, *J* = 73.7 Hz), 21.8, 20.8, 20.5; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.32; IR (neat): 3322, 3055, 2922, 2855, 1514, 1437, 1186, 1116, 803, 696 cm^{-1}; HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{35}H_{34}NNaOP$: 538.2276, found: 538.2279.



(2-(2-chlorophenyl)-2-(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6j): TLC R_f = 0.5 (EA: PE = 1:3); 66.6 mg, 60% yield; Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.90 (d, *J* = 7.7 Hz, 1H), 7.71-7.63 (m, 2H), 7.50-7.29 (m, 7H), 7.24-7.12 (m, 7H), 6.93 (m, 1H), 6.72 (m, 3H), 6.29 (d, *J* = 8.4 Hz, 2H), 4.05 (m, 1H), 3.37 (m, 1H), 2.13 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; *δ*, ppm) 142.7, 141.26, 139.23, 133.1 (d, *J* = 18.15 Hz), 131.6 (d, *J* = 30. Hz), 130.9 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 10.1 Hz), 130.1 (d, *J* = 9.1 Hz), 129.0 (d, *J* = 16.1 Hz), 128.7 (d, *J* = 12.1 Hz), 127.9, 127.8 (d, *J* = 4.0 Hz), 126.6, 119.9, 65.8 (d, *J* = 3.0 Hz), 20.4; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 28.80; IR (neat): 3306, 3051, 2923, 2854, 1511, 1436, 1219, 1116, 772, 749 cm^{-1}; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{33}H_{29}Cl_2NOP$: 556.1364, found: 556.1367.



(2,2-di-*o*-tolyl-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6k): TLC R_f = 0.5 (EA: PE = 1:3); 51.5 mg, 50% yield; Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.48 (m, 3H), 7.43-7.39 (m, 4H), 7.22 (d, J = 7.5 Hz, 2H), 7.11-7.03 (m, 8H), 6.95 (m, 2H), 6.68 (d, J = 8.2 Hz, 2H), 6.21 (d, J = 8.4 Hz, 2H), 3.54 (d, J = 10.3 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 144.0, 142.9 (d, J = 7.1 Hz), 141. (d, J = 9.1 Hz), 132.0 (d, J = 36.4 Hz), 131.7 (d, J = 4.1 Hz), 131.4 (d, J = 43.4 Hz), 131.3 (d, J = 3.0 Hz), 128.8, 128.2, 127.9, 126.9, 126.0, 125.4, 125.3, 116.4, 65.8 (d, J = 4.0 Hz), 41.8 (d, J = 67.7 Hz), 21.06, 21.02, 20.3; ^{31}P NMR (121.5 MHz, CDCl3; δ, ppm) 29.39; IR (neat): 3306, 3055, 2923, 2854, 1615, 1515, 1447, 1171, 751, 699 cm^{-1}; HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{35}H_{35}NOP$: 516.2456, found: 516.2457.

VI. References

[1] M. I. Mangione, R. A. Spanevello, M. B. Anzardi, *RSC Adv.* 2017, **7**, 47681-47688.

[2] I. T. Alt, C. Guttroff, B. Plietker, *Angew.Chem.Int. Ed.* 2017, **56**,10582-10586.

[3] M. Dryzhakov, M. Hellal, E. Wolf, F. C. Falk, J. Moran, *J. Am. Chem. Soc*. **2015**, *137*, 9555-9558.

[4] H. Keipour, T. Ollevier, *Org. Lett.* 2017, **19**, 573.

[5] P. Qian, Y. Deng, H. B. Mei, J. L. Han, J. Zhou, Y. Pan, *Org. Lett.* 2017, **19**, 4798-4801.

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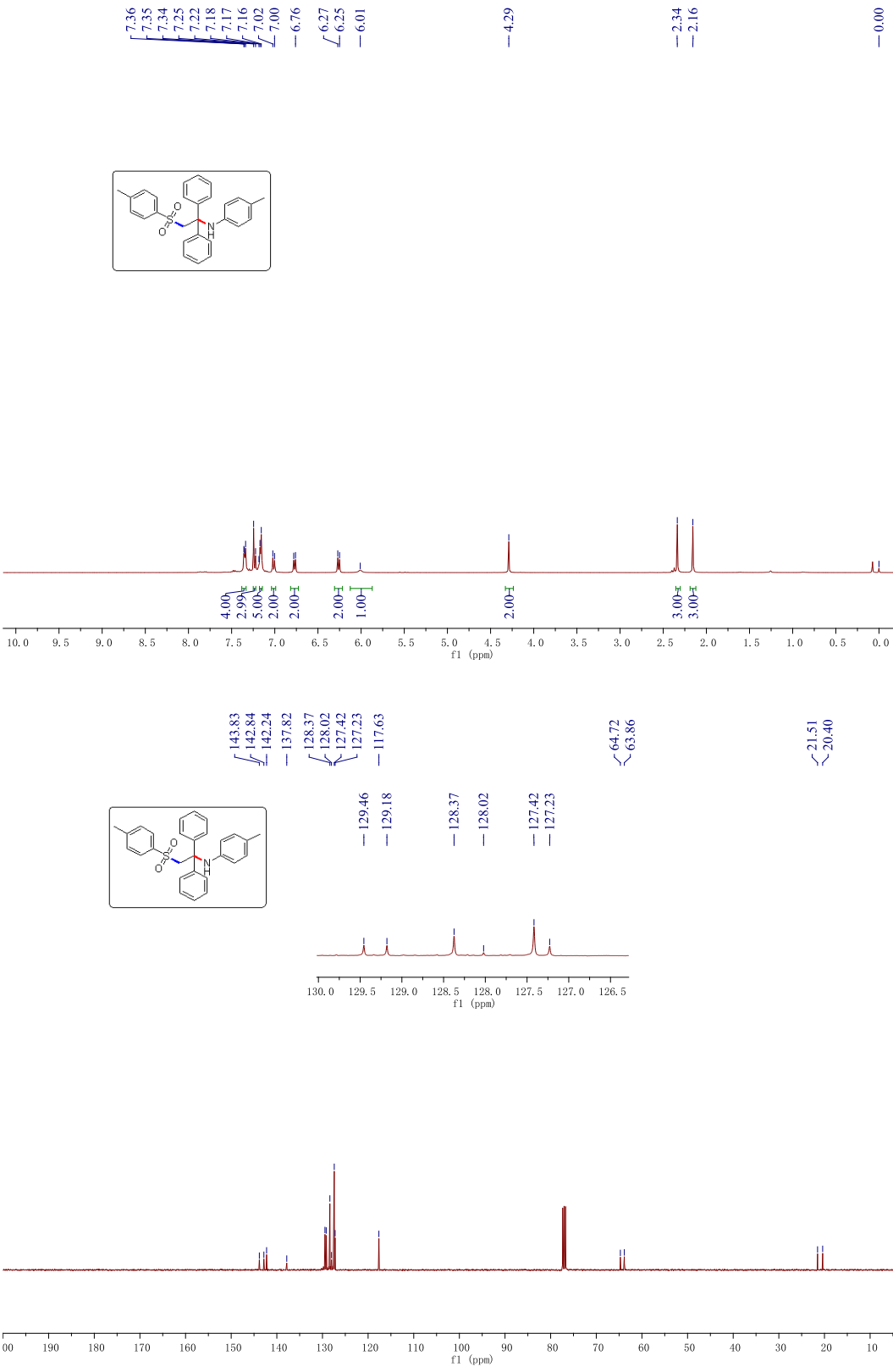
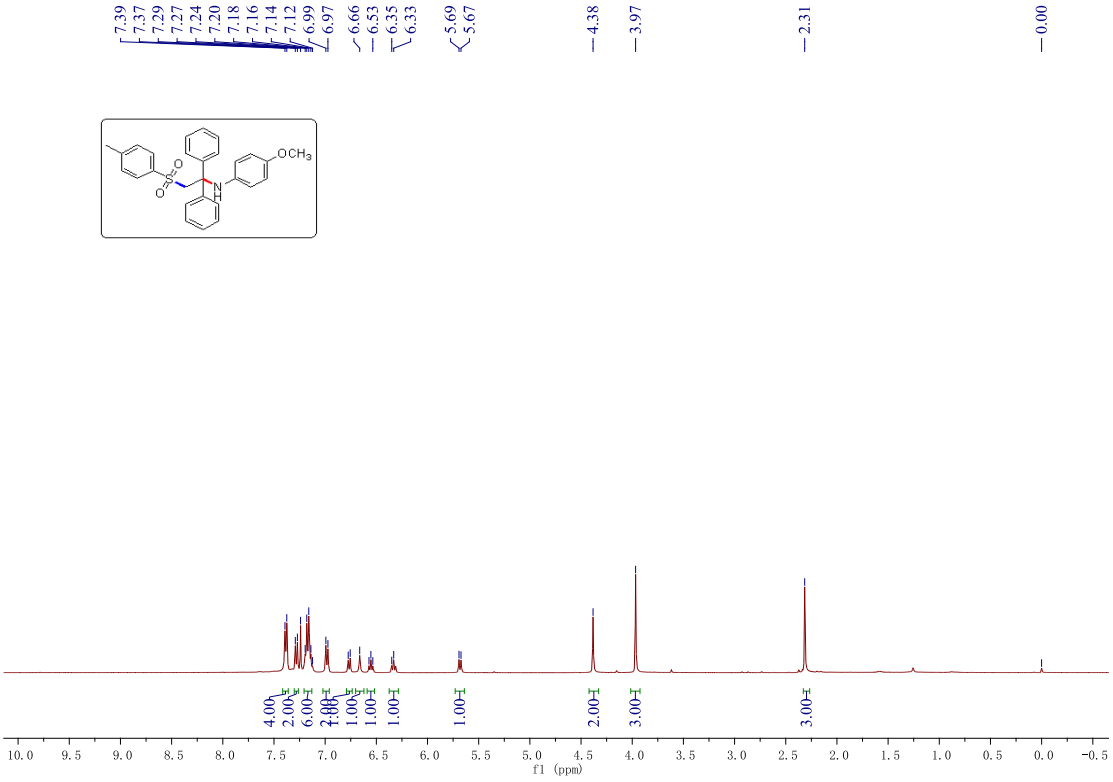
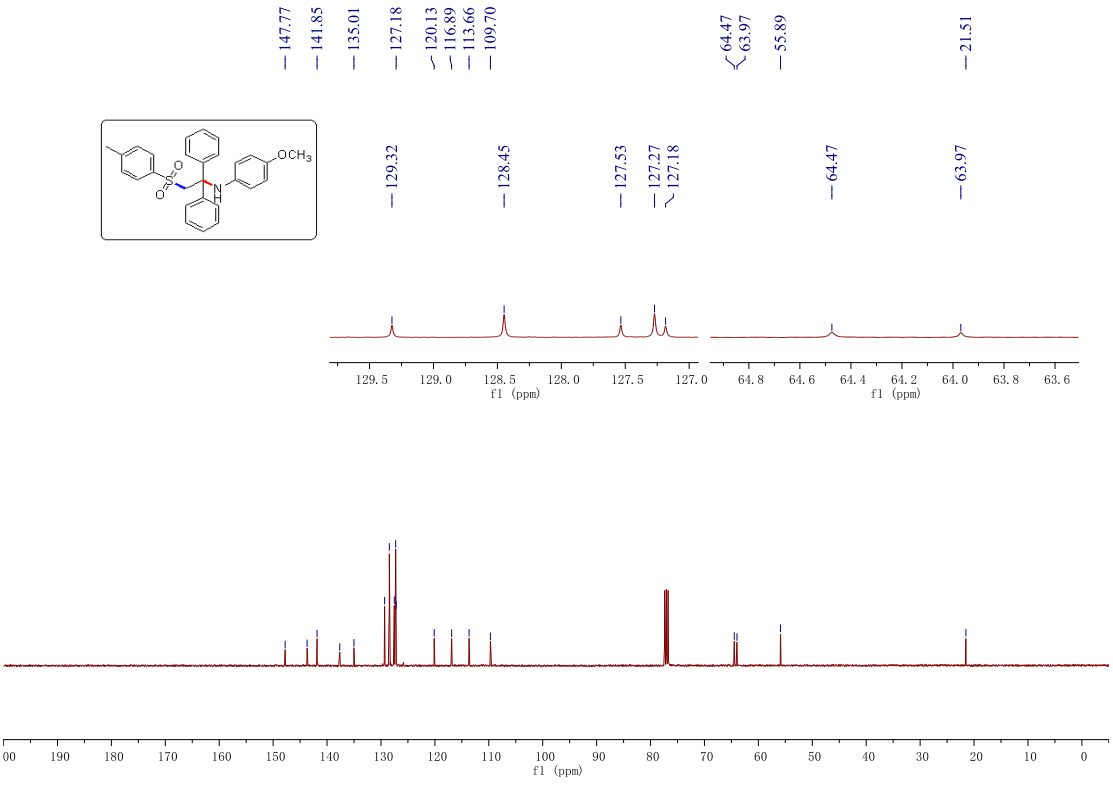
VII. Spectral Copies of ^{1}H , ^{13}C NMR of Products 4 and 6

N-(1,1-diphenyl-2-tosylethyl)-4-methylaniline (4a)

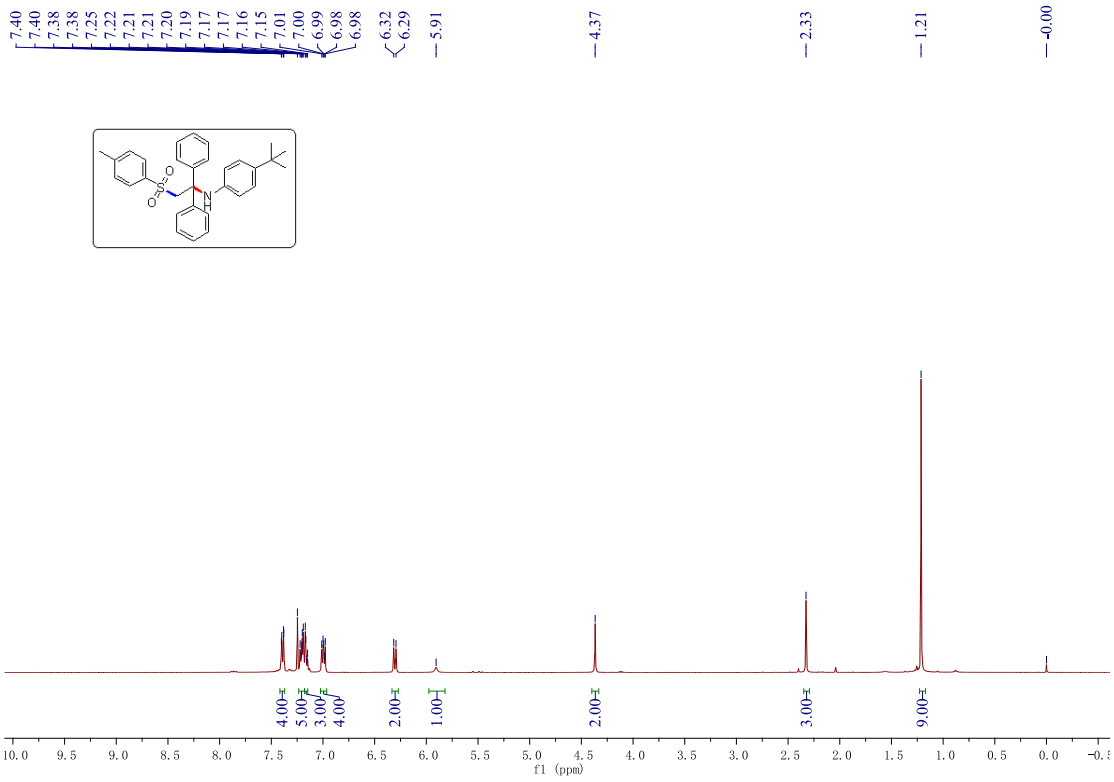


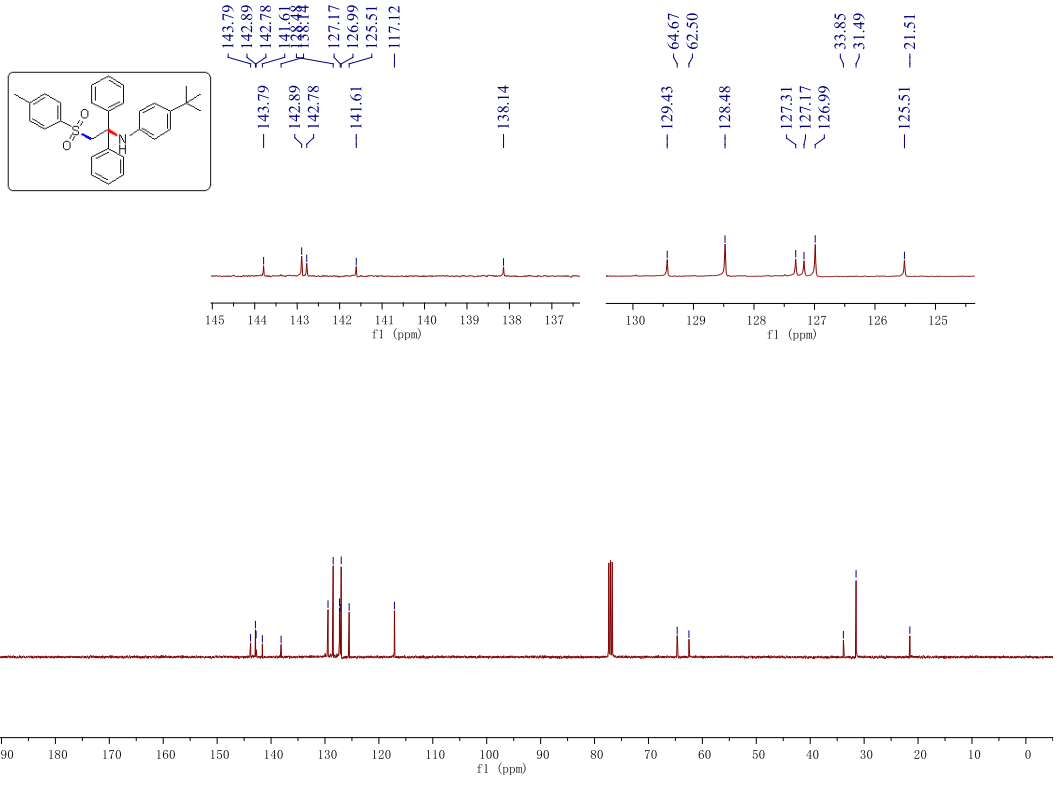
N-(1,1-diphenyl-2-tosylethyl)-4-methoxyaniline (4b)



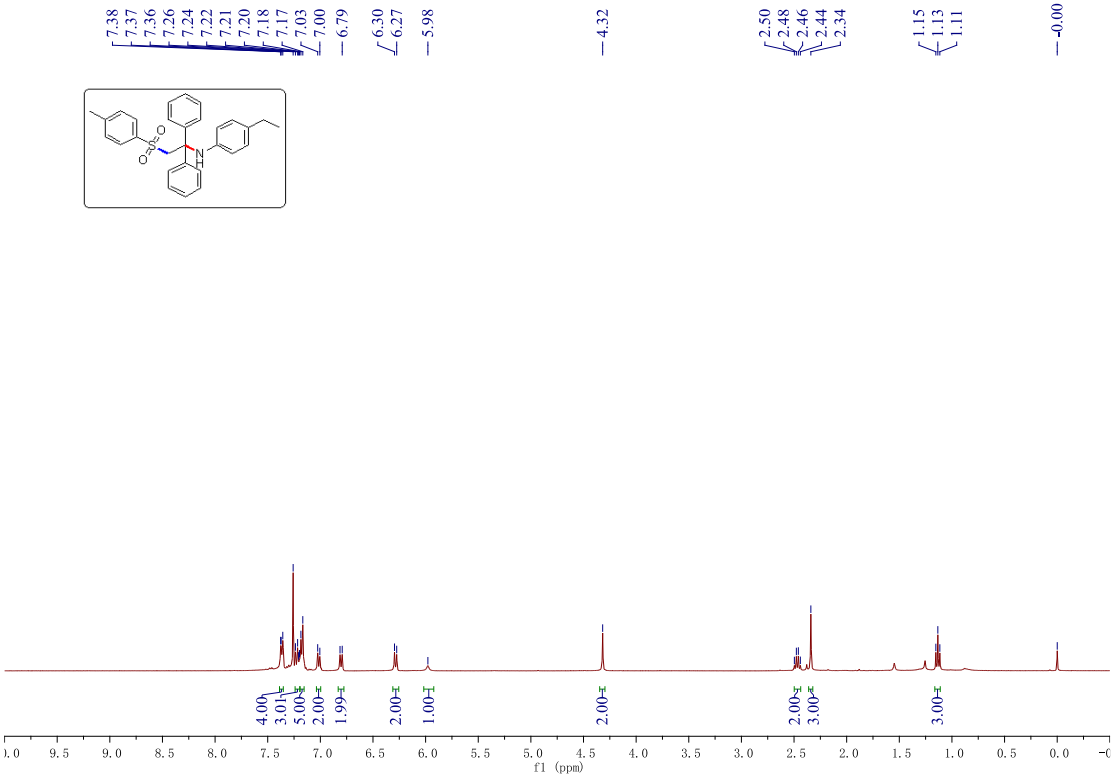


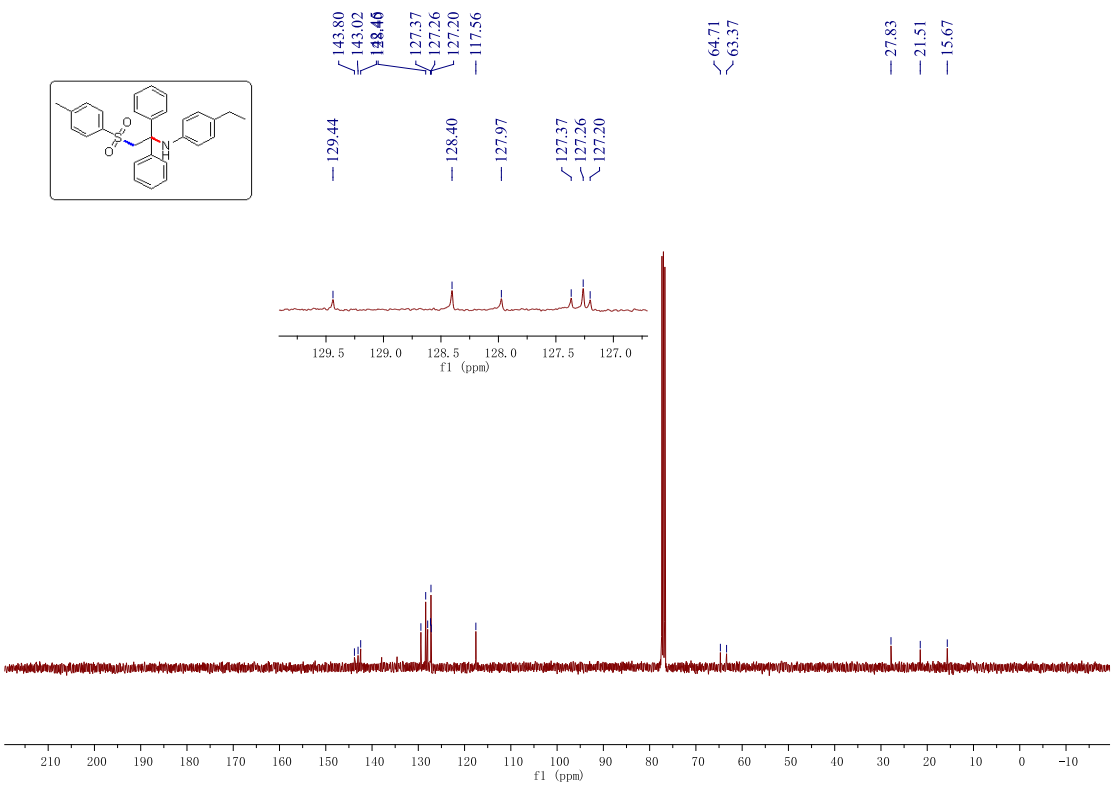
4-(*tert*-butyl)-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4c)



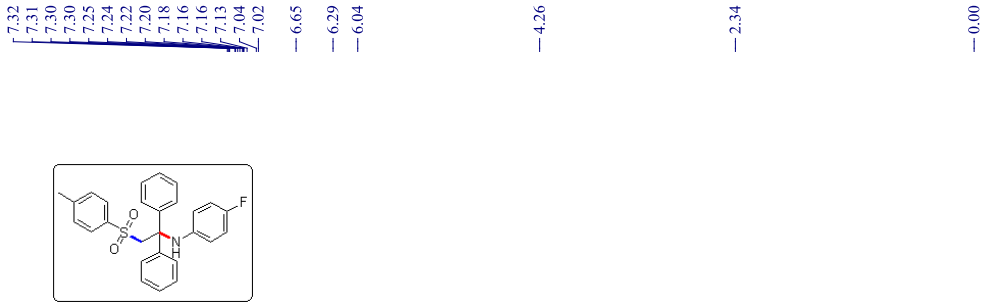


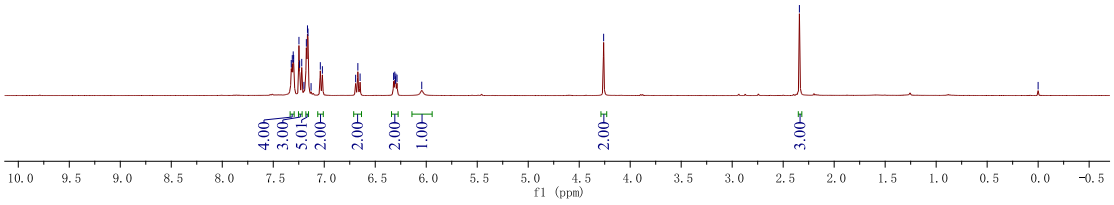
N-(1,1-diphenyl-2-tosylethyl)-4-ethylaniline (4d)

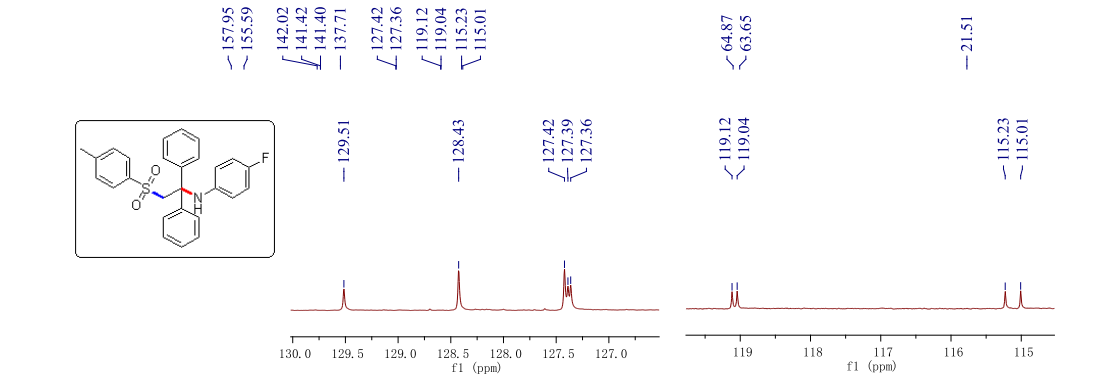


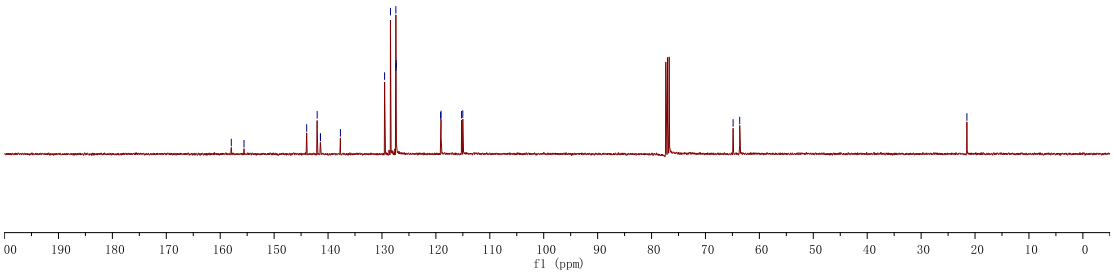


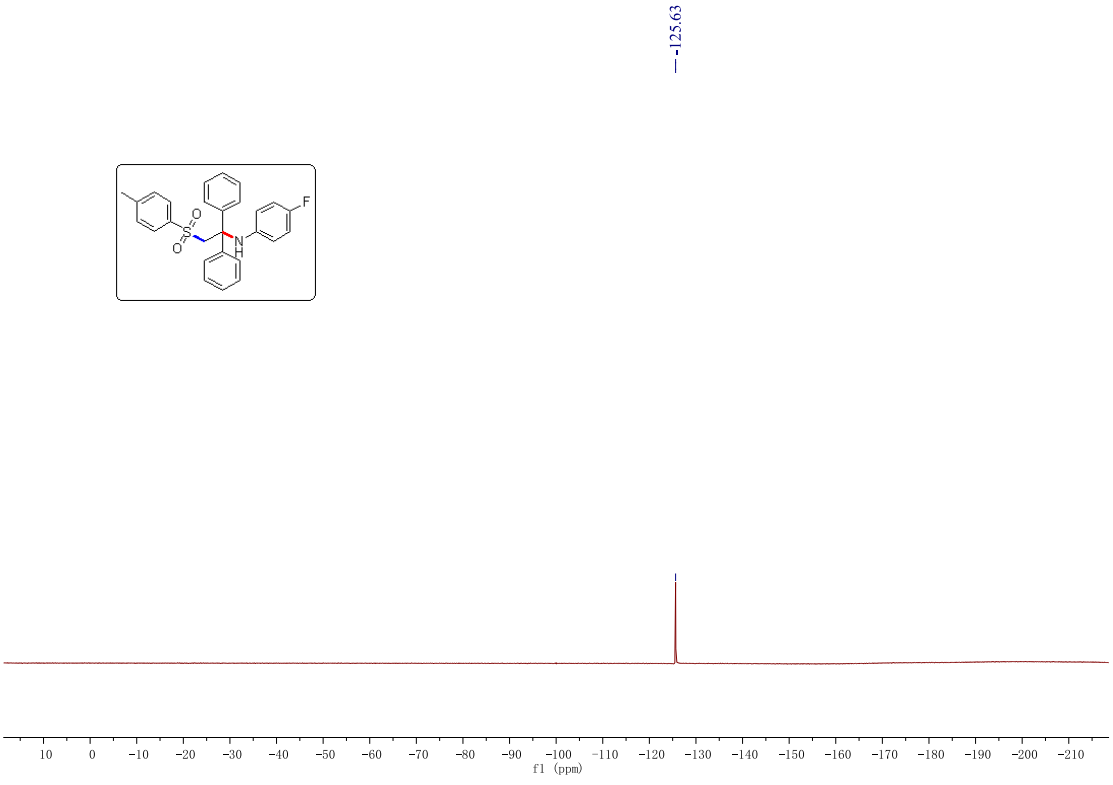
N-(1,1-diphenyl-2-tosylethyl)-4-fluoroaniline (4e)










-125.63
F
O
O
S
N
H
10
0
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-20
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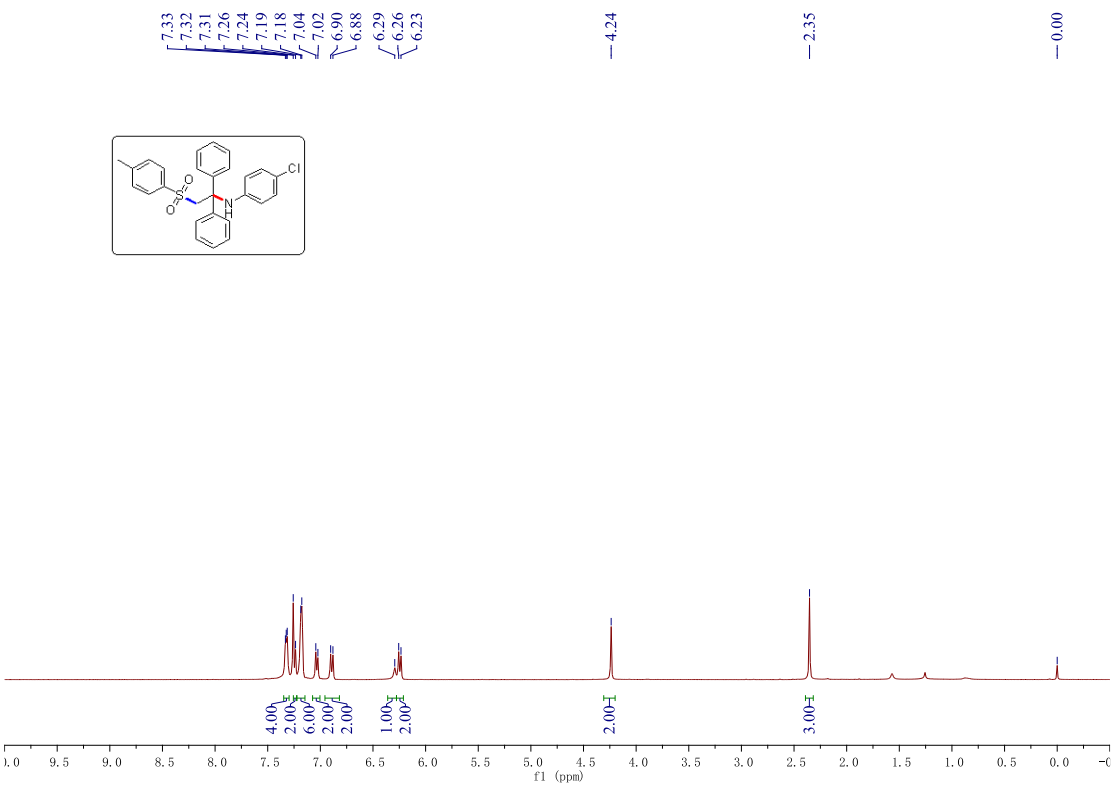
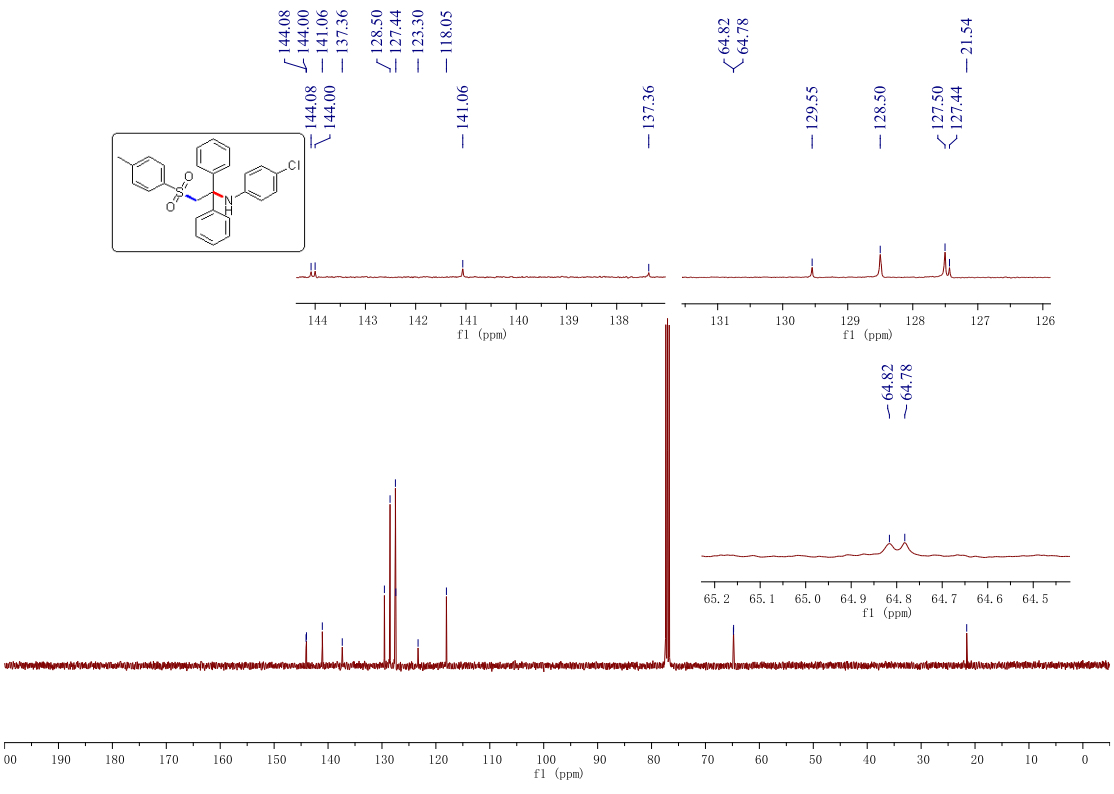
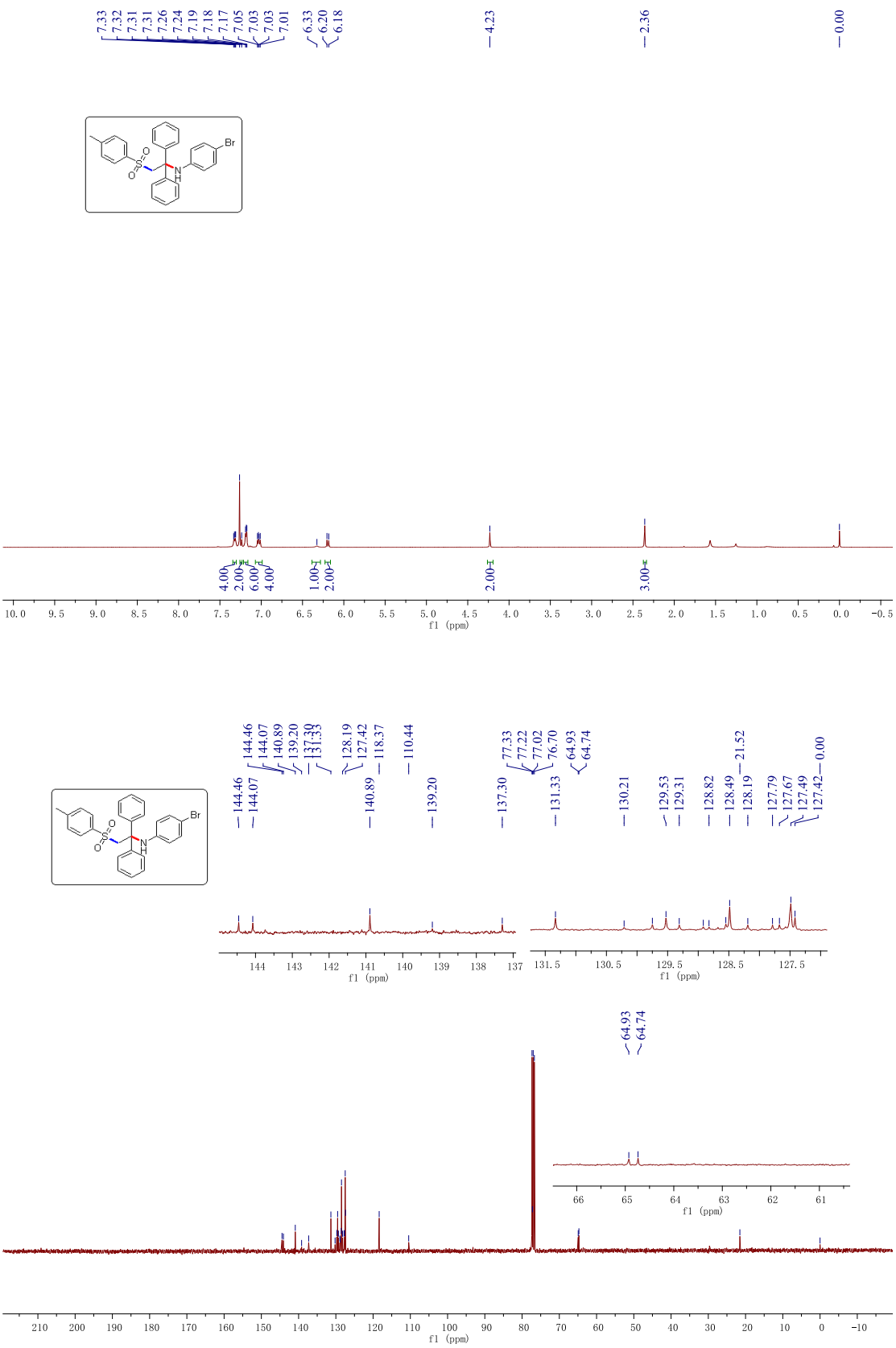
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4-chloro-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4f)

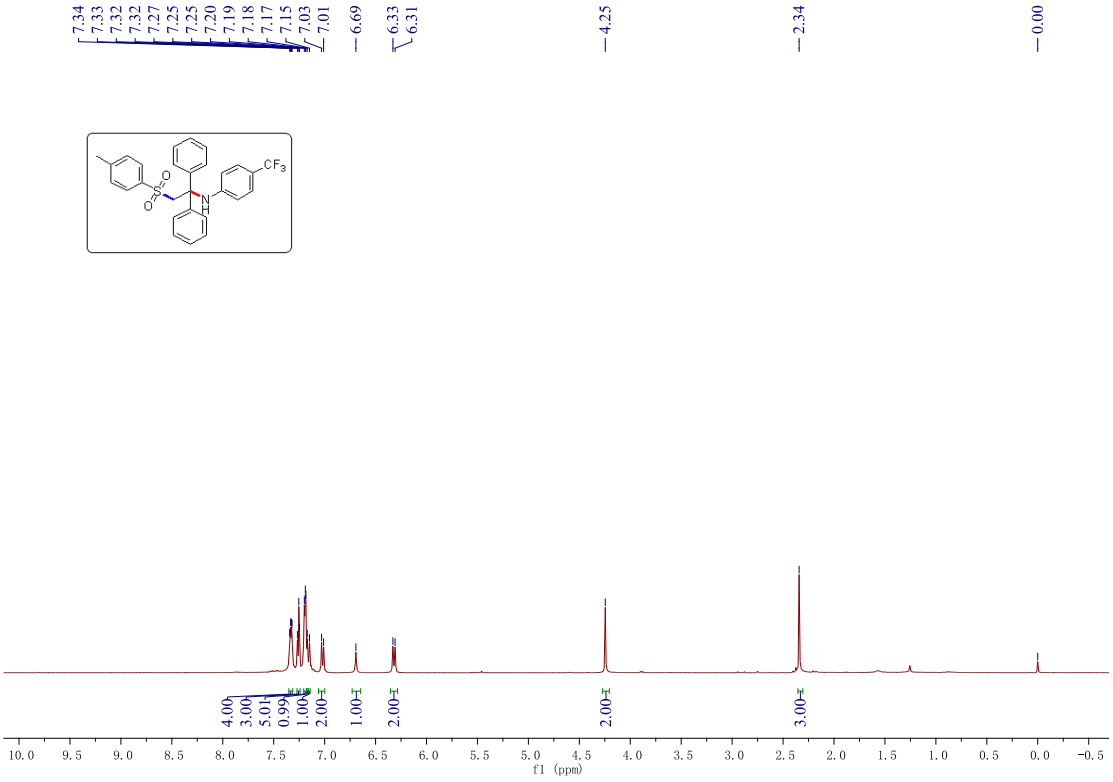


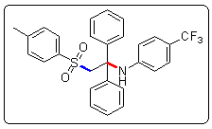


4-bromo-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4g)



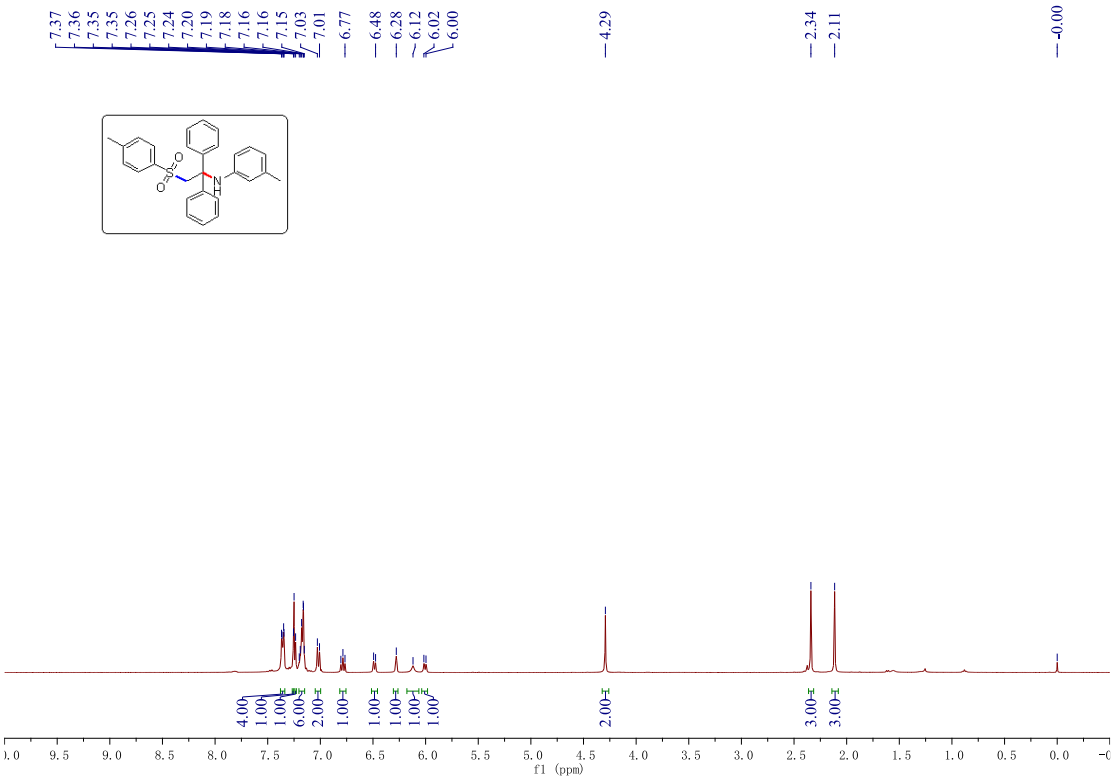
N-(1,1-diphenyl-2-tosylethyl)-4-(trifluoromethyl)aniline (4h)

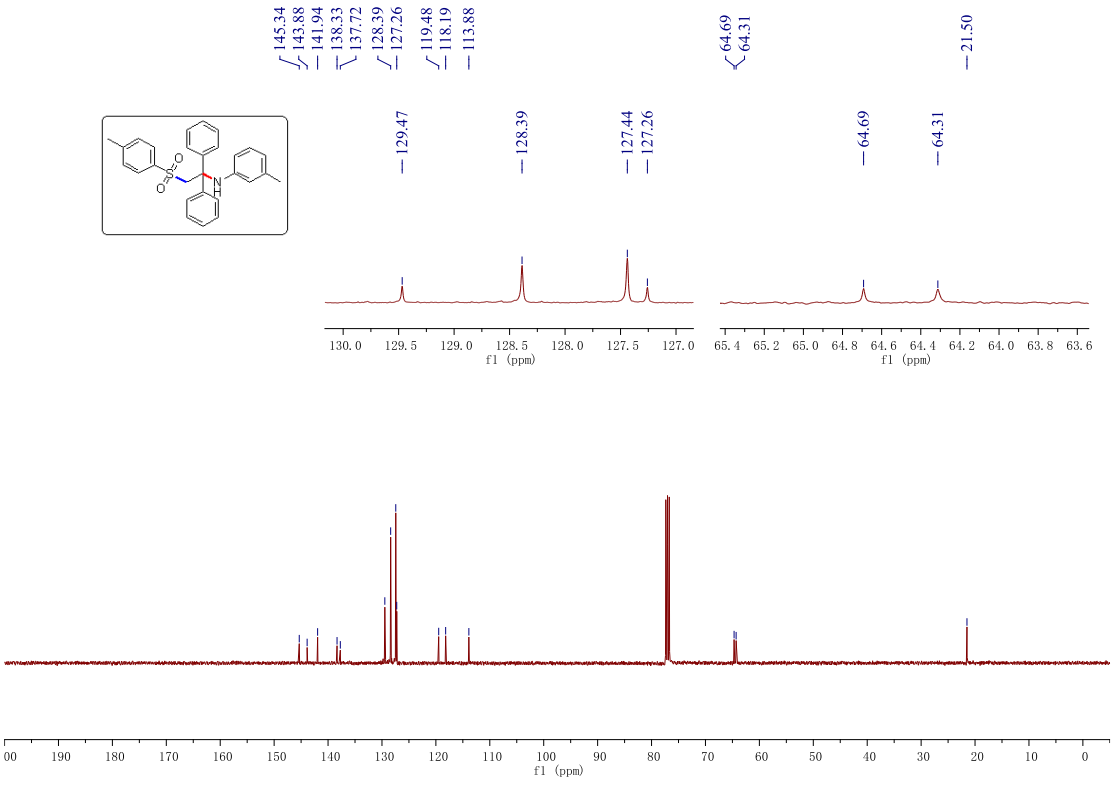



O
S
O
N
H
CF3

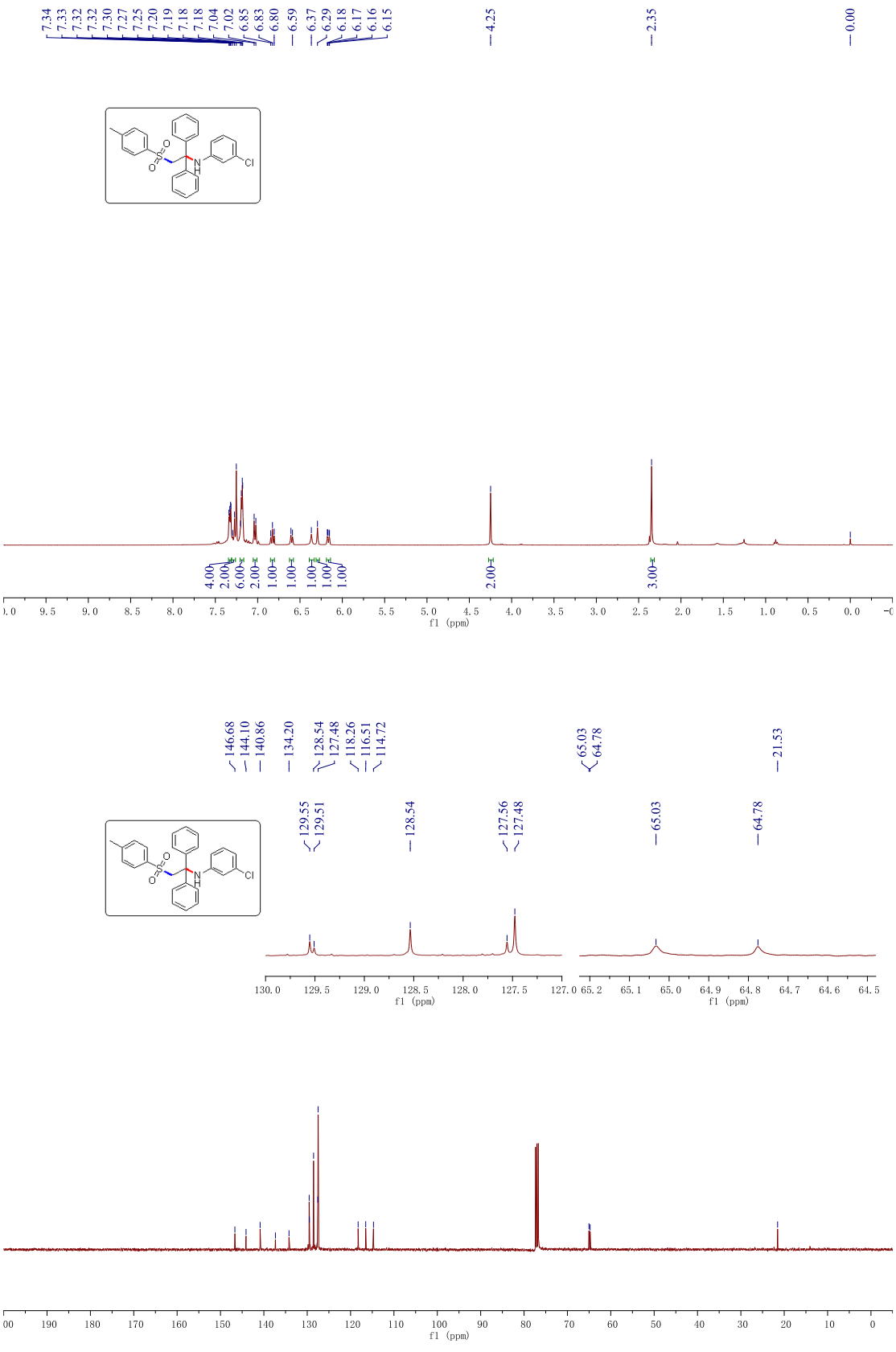
-61.22
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135
f1 (ppm)

N-(1,1-diphenyl-2-tosylethyl)-3-methylaniline (4i)

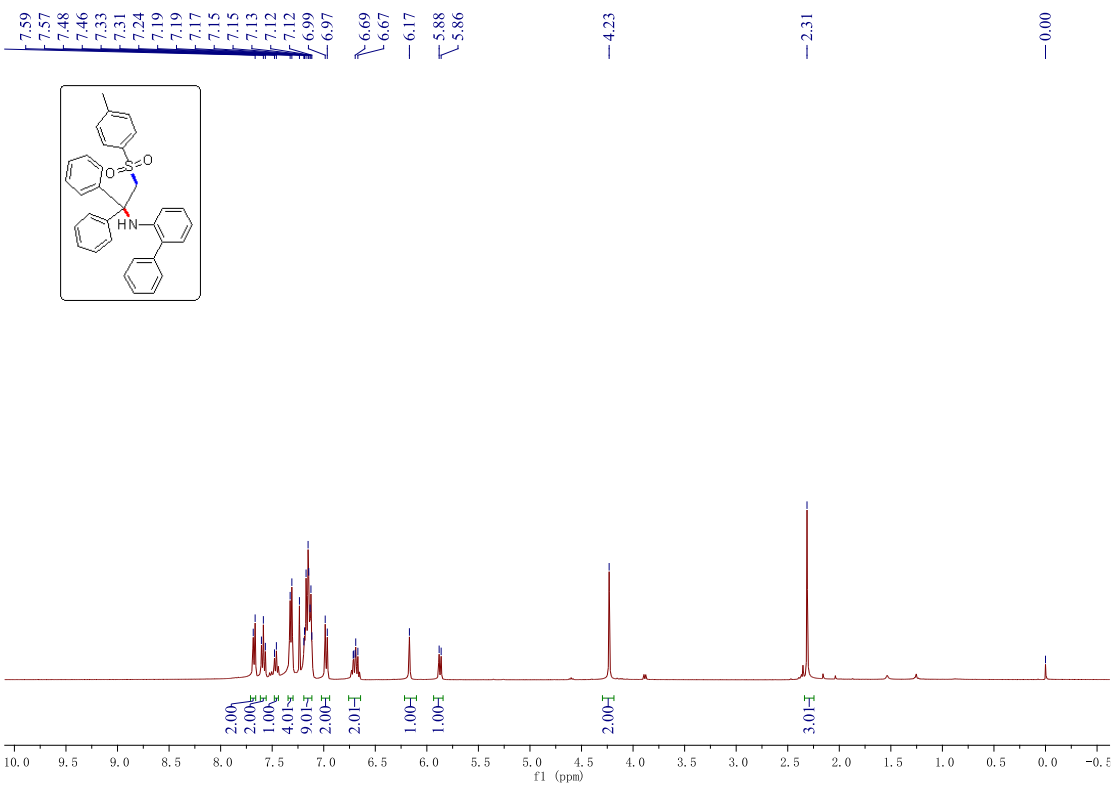


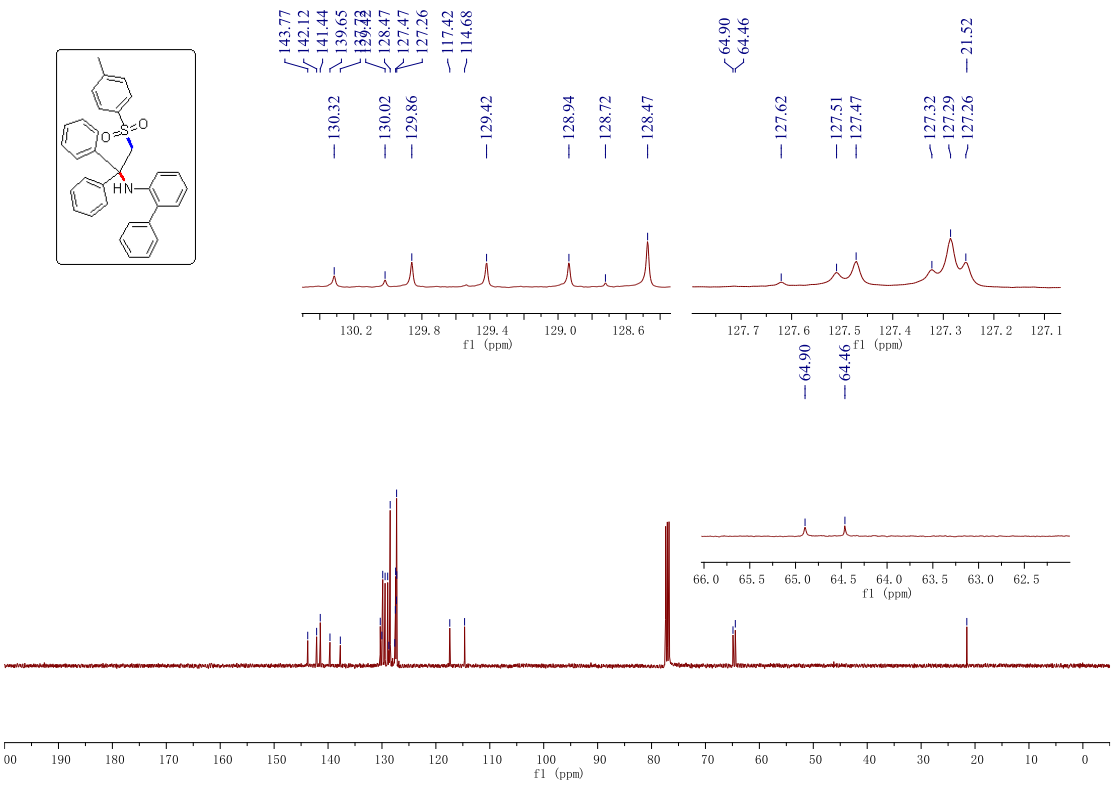


3-chloro-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4j)

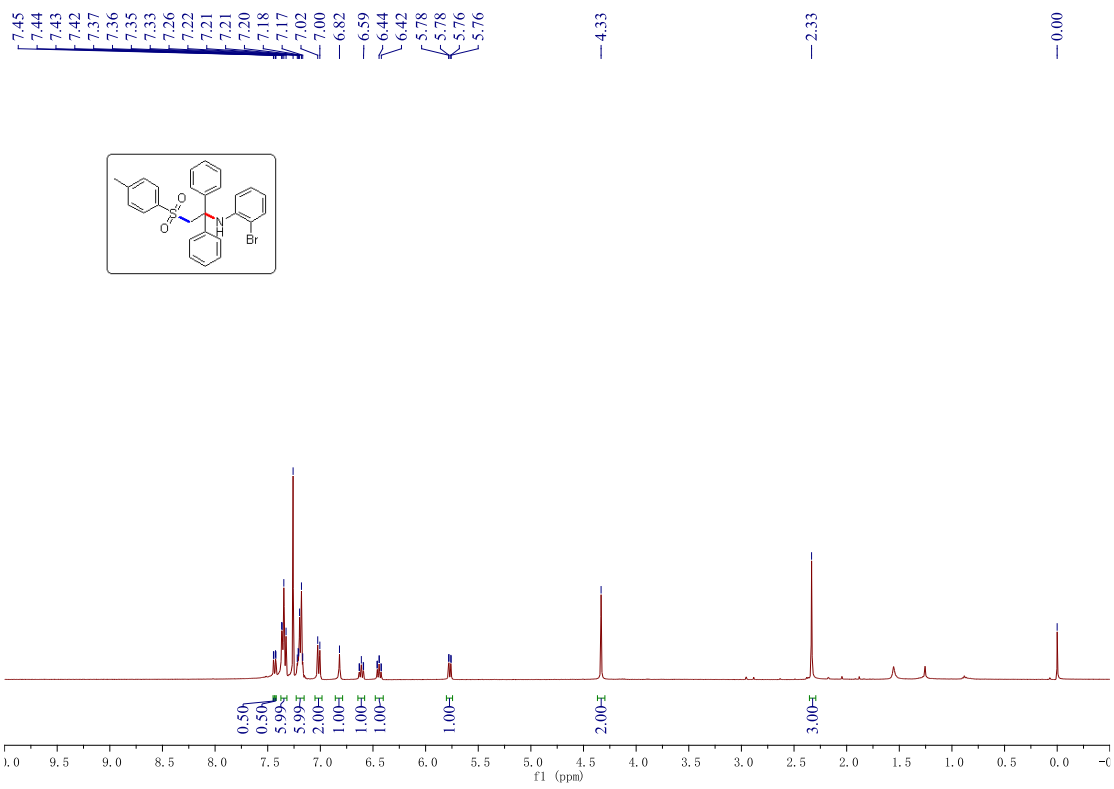


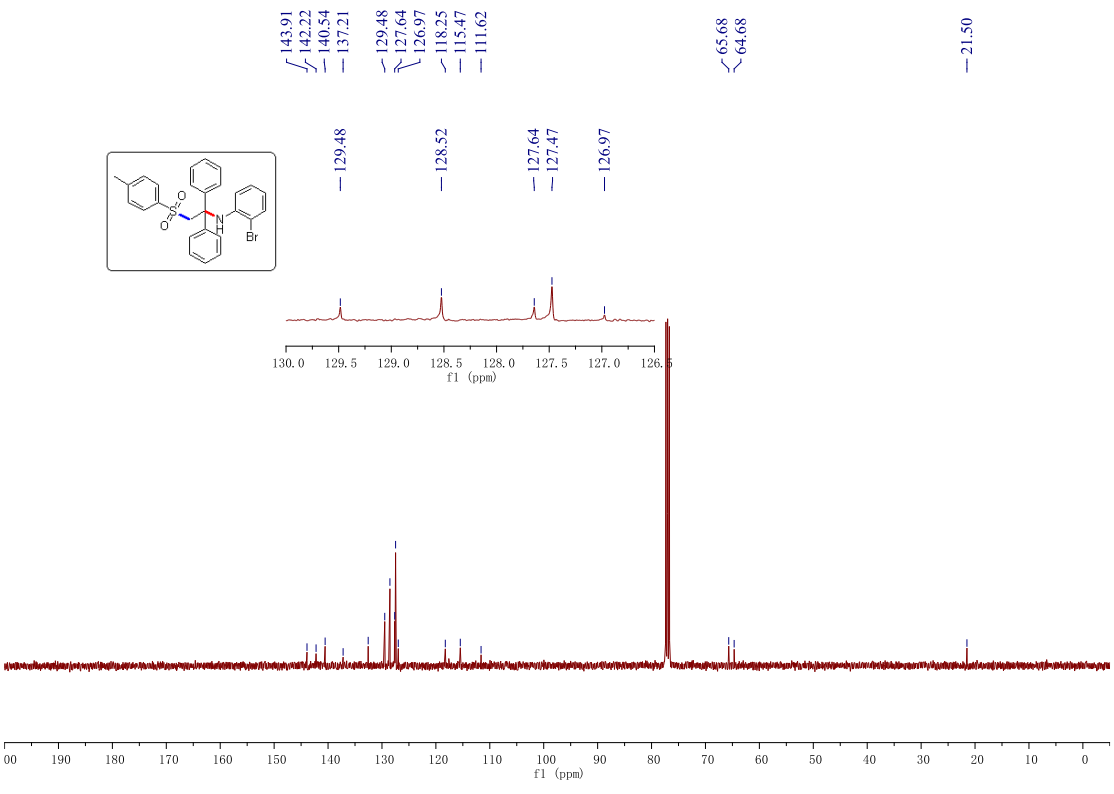
N-(1,1-diphenyl-2-tosylethyl)-[1,1'-biphenyl]-2-amine (4k)



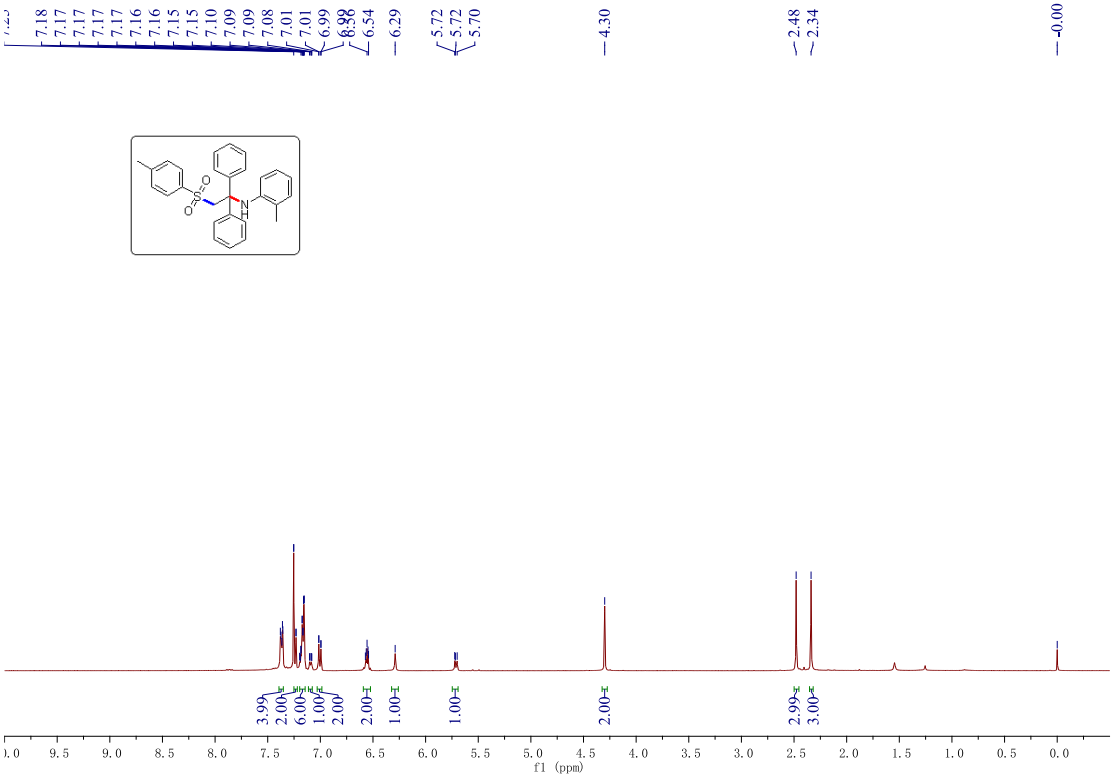


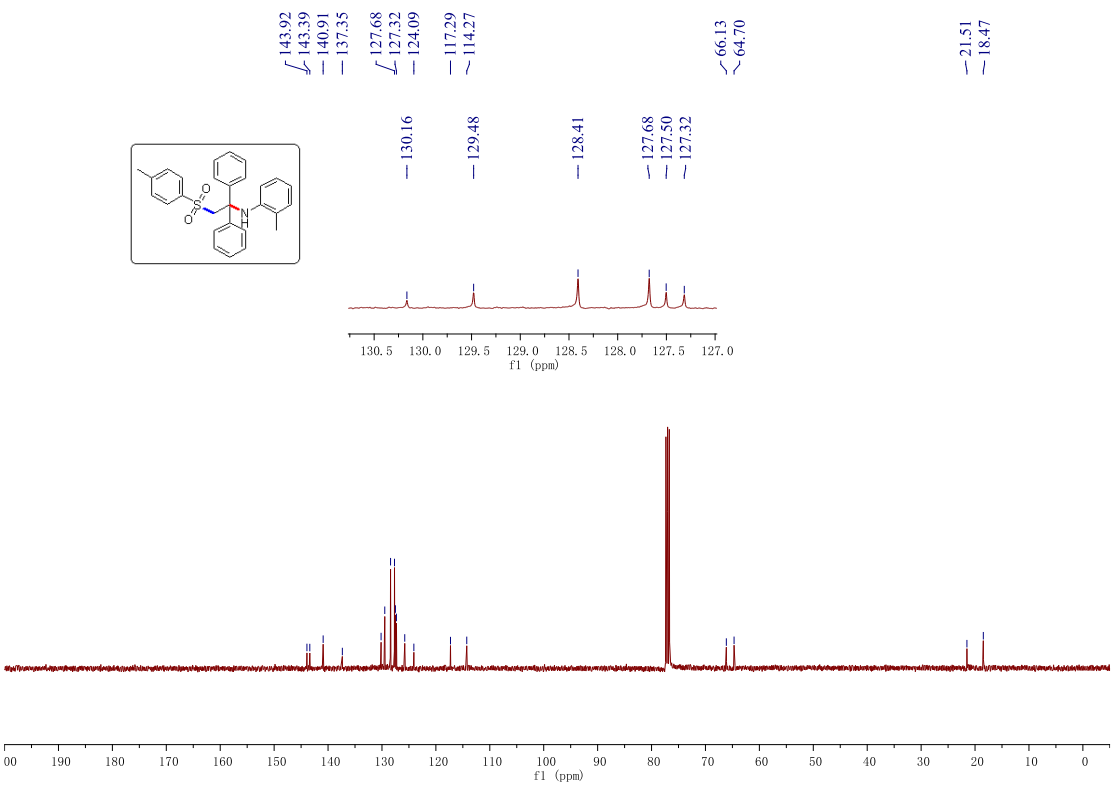
2-bromo-*N*-(1,1-diphenyl-2-tosylethyl)aniline (4l)



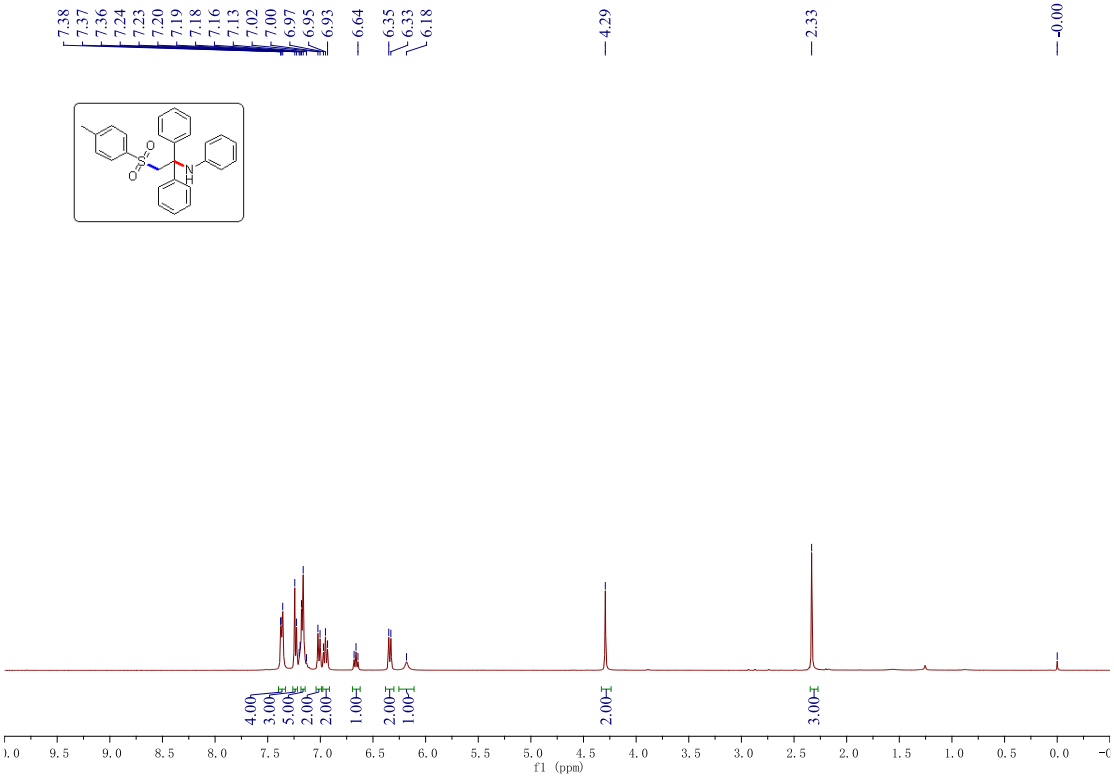


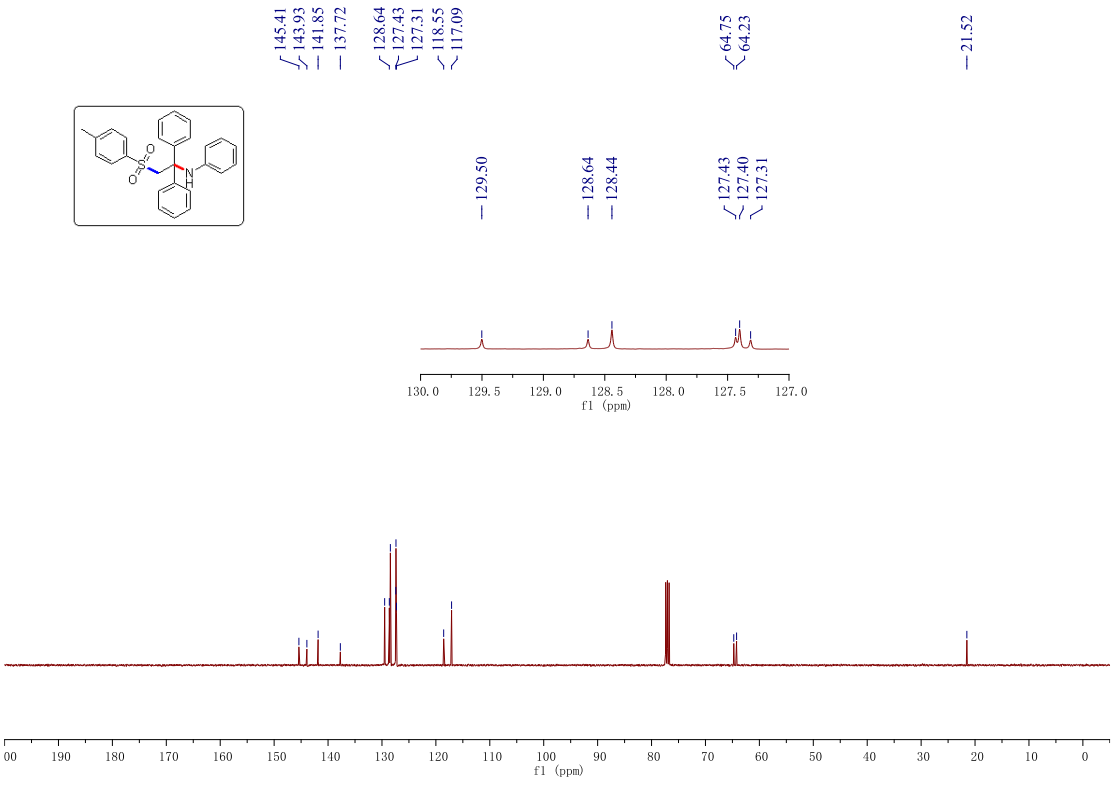
N-(1,1-diphenyl-2-tosylethyl)-2-methylaniline (4m)



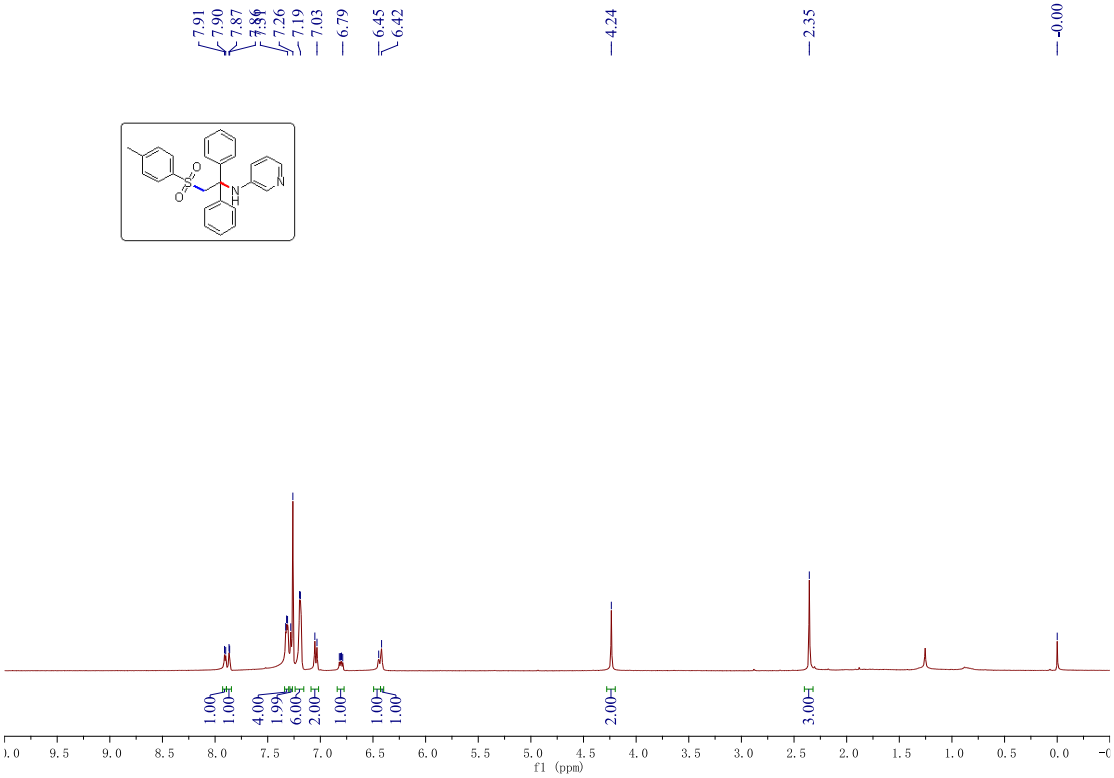


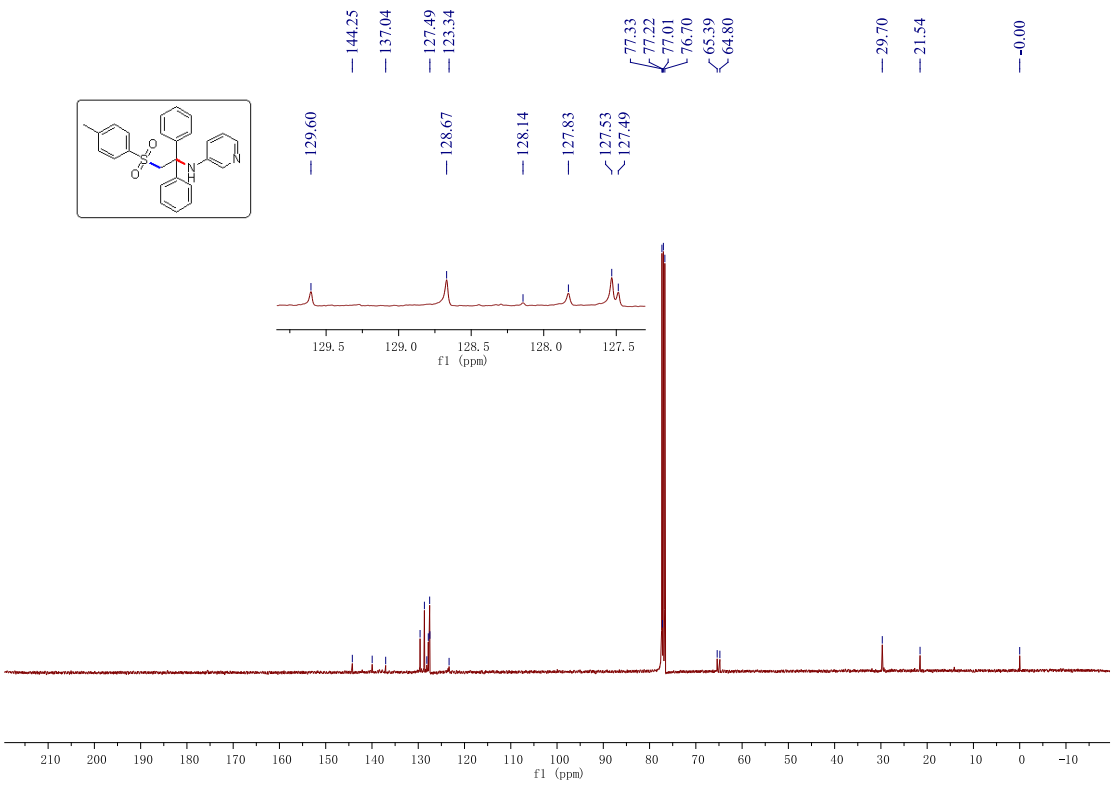
N-(1,1-diphenyl-2-tosylethyl)aniline (4n)



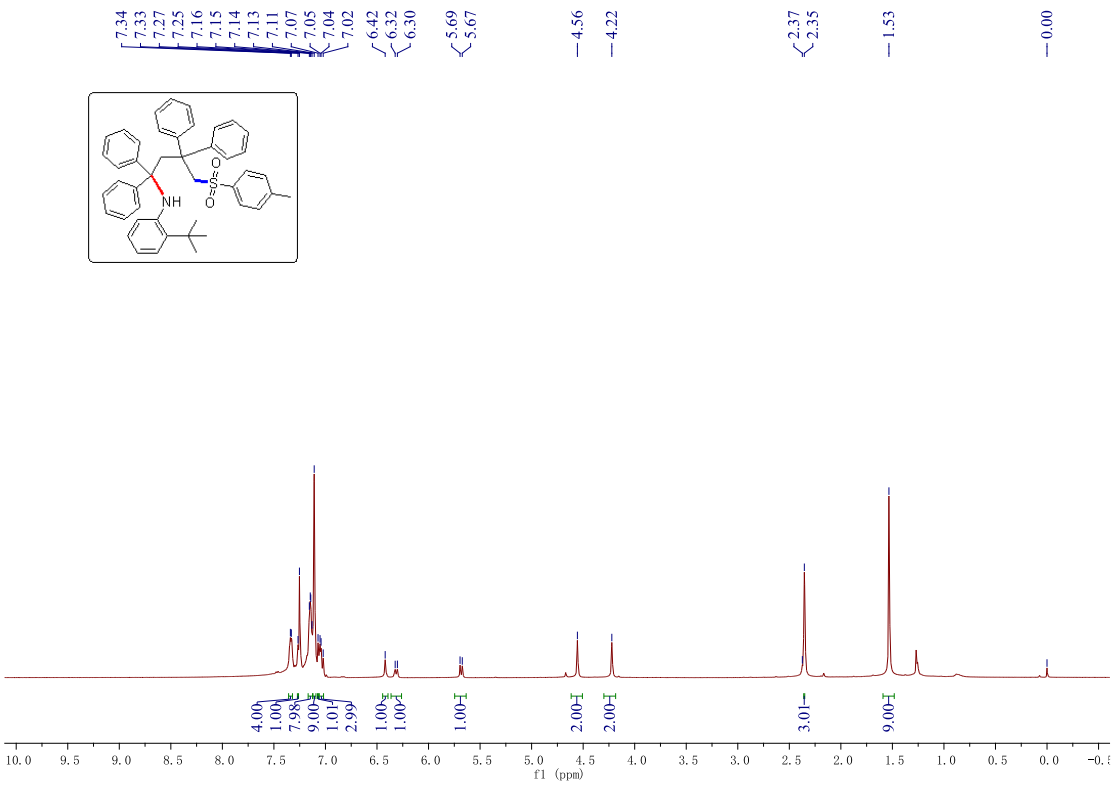


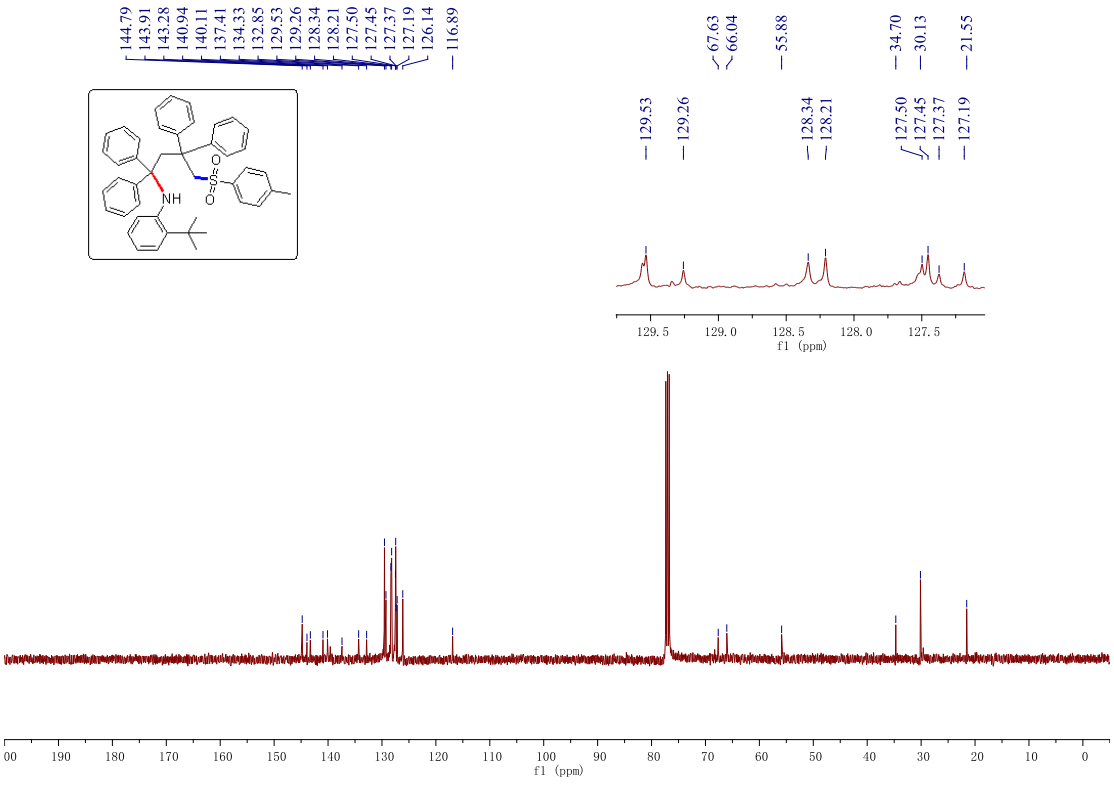
N-(1,1-diphenyl-2-tosylethyl)pyridin-3-amine (4o)



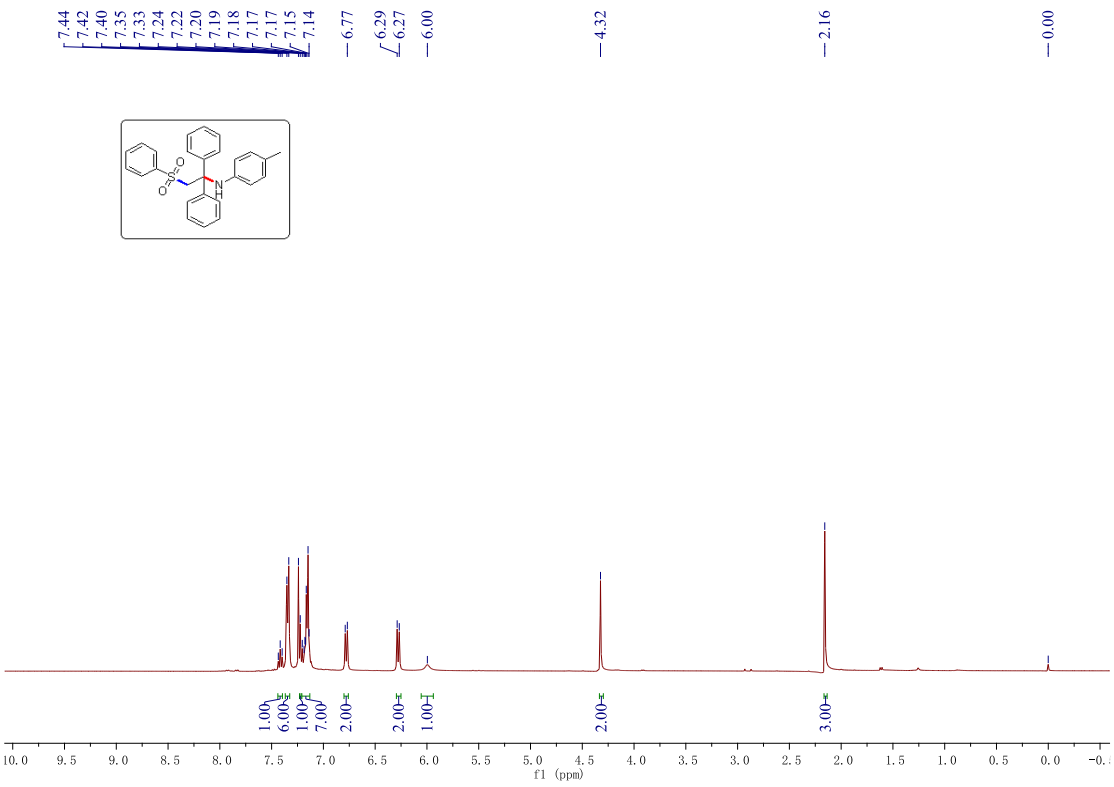


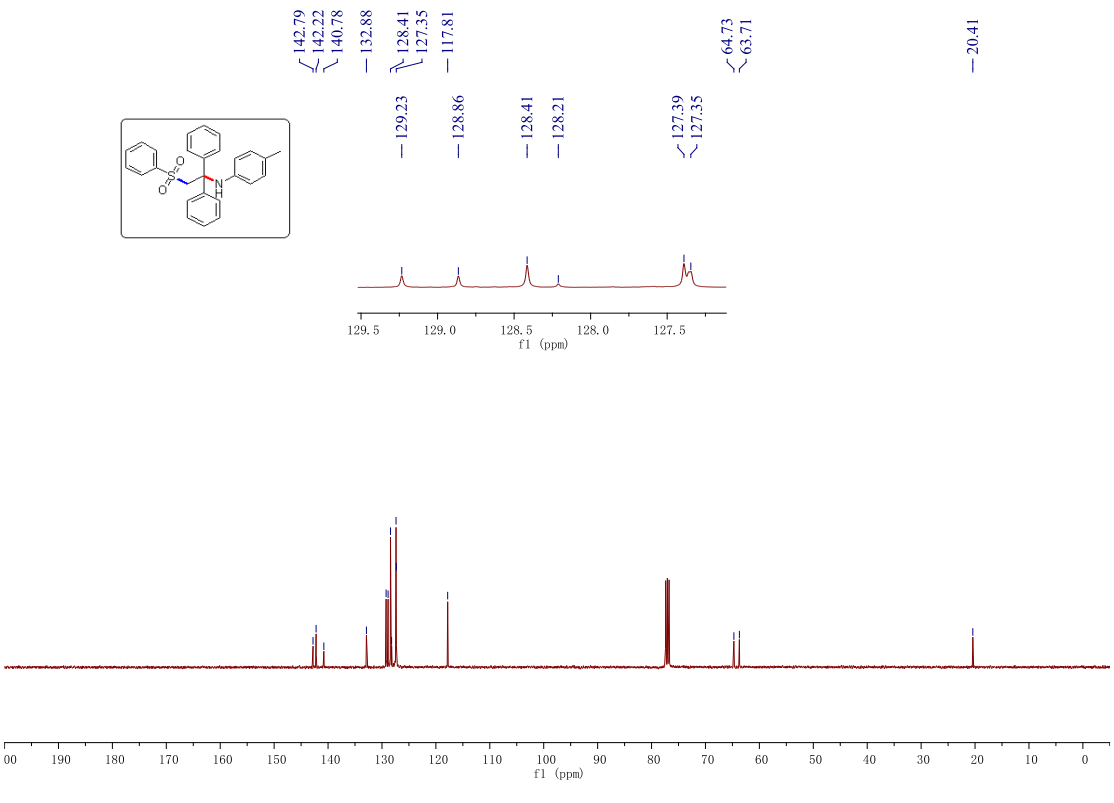
2-(tert-butyl)-*N*-(1,1,3,3-tetraphenyl-4-tosylbutyl)aniline (4p)



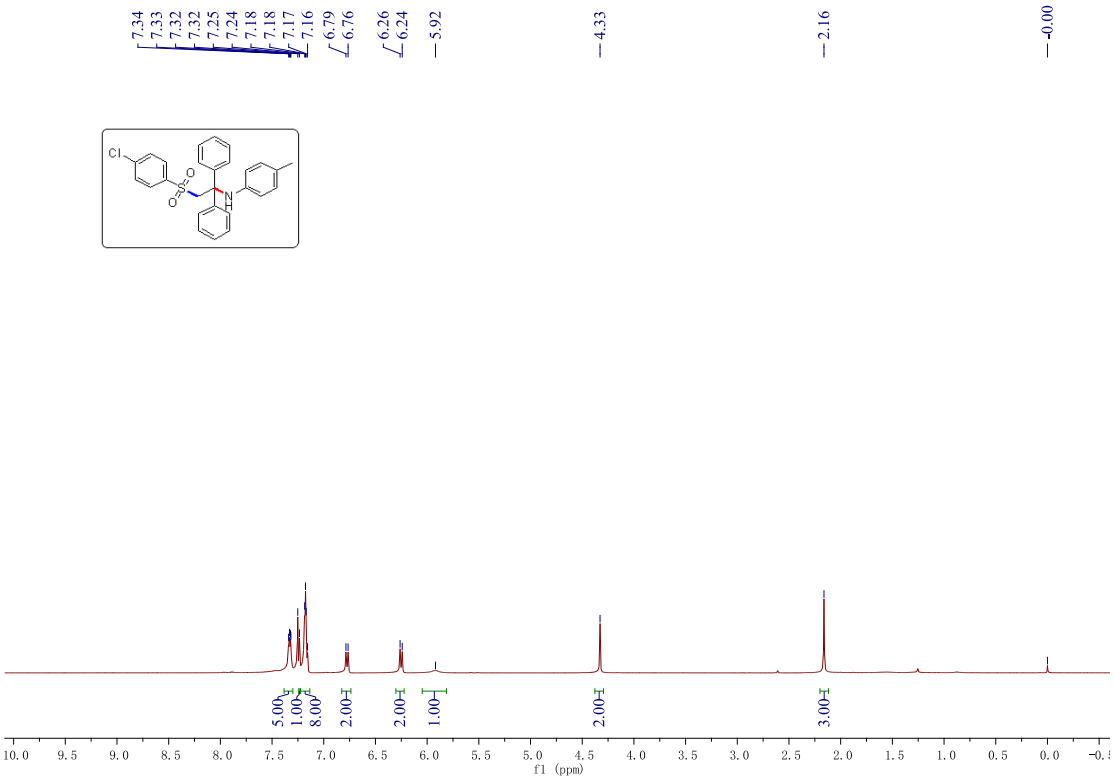


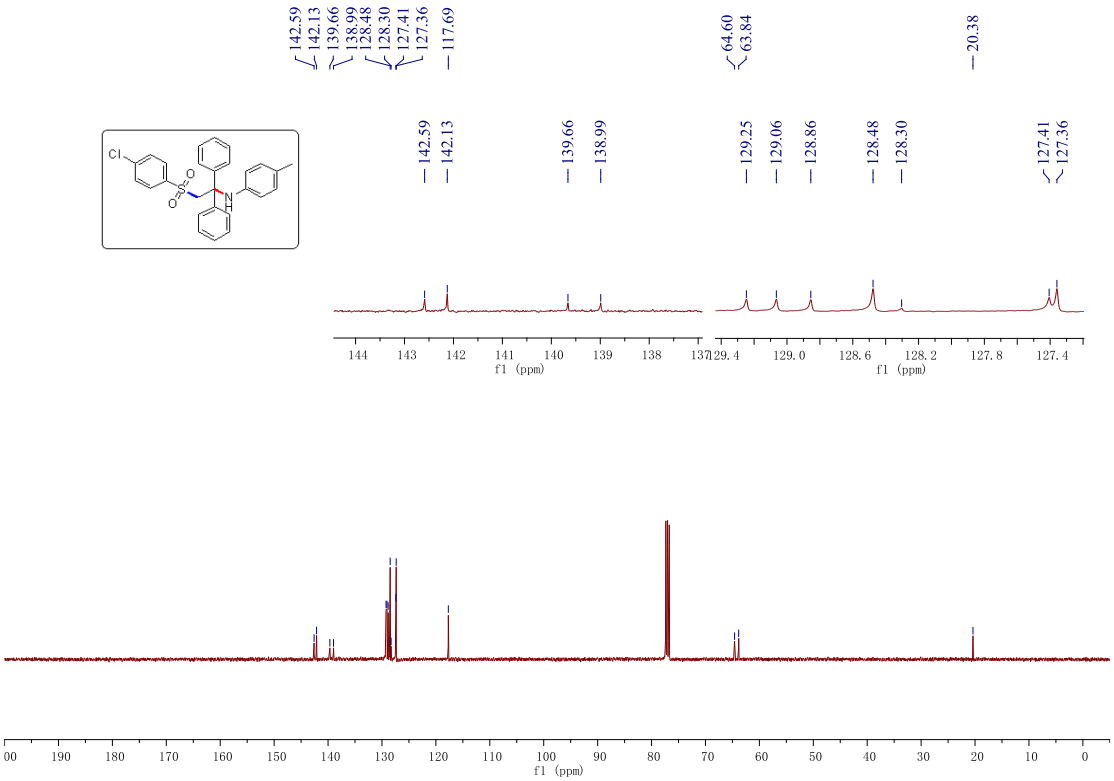
N-(1,1-diphenyl-2-(phenylsulfonyl)ethyl)-4-methylaniline (4q)



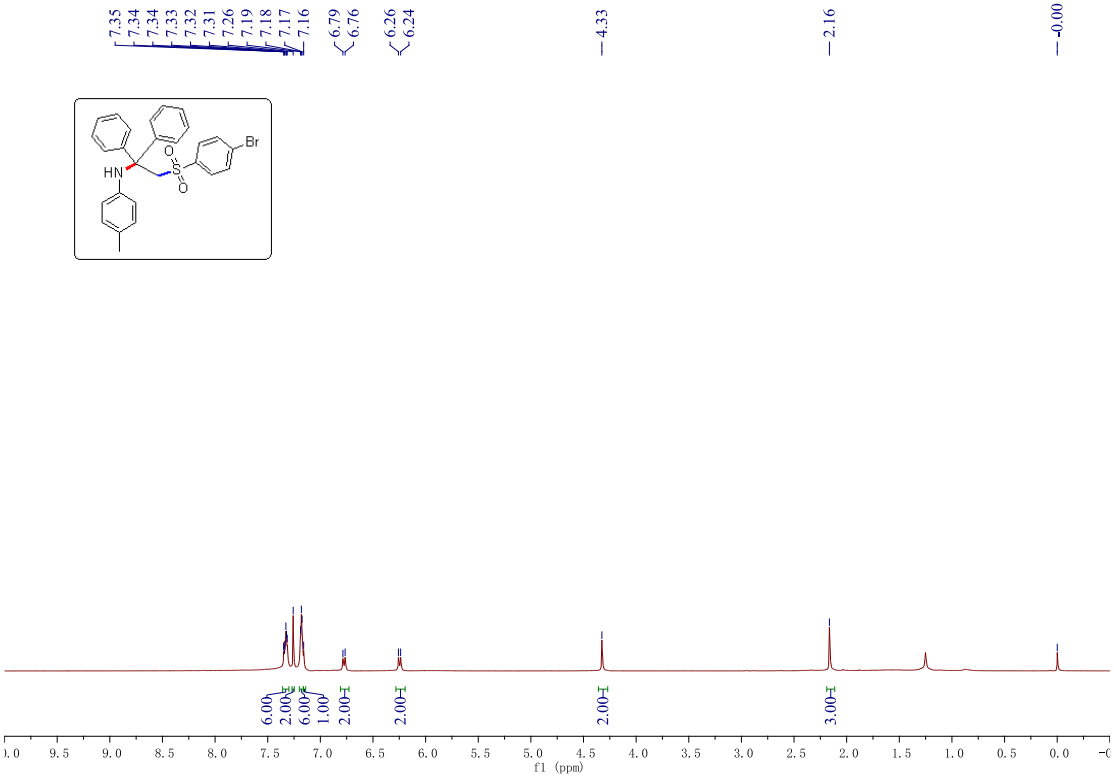


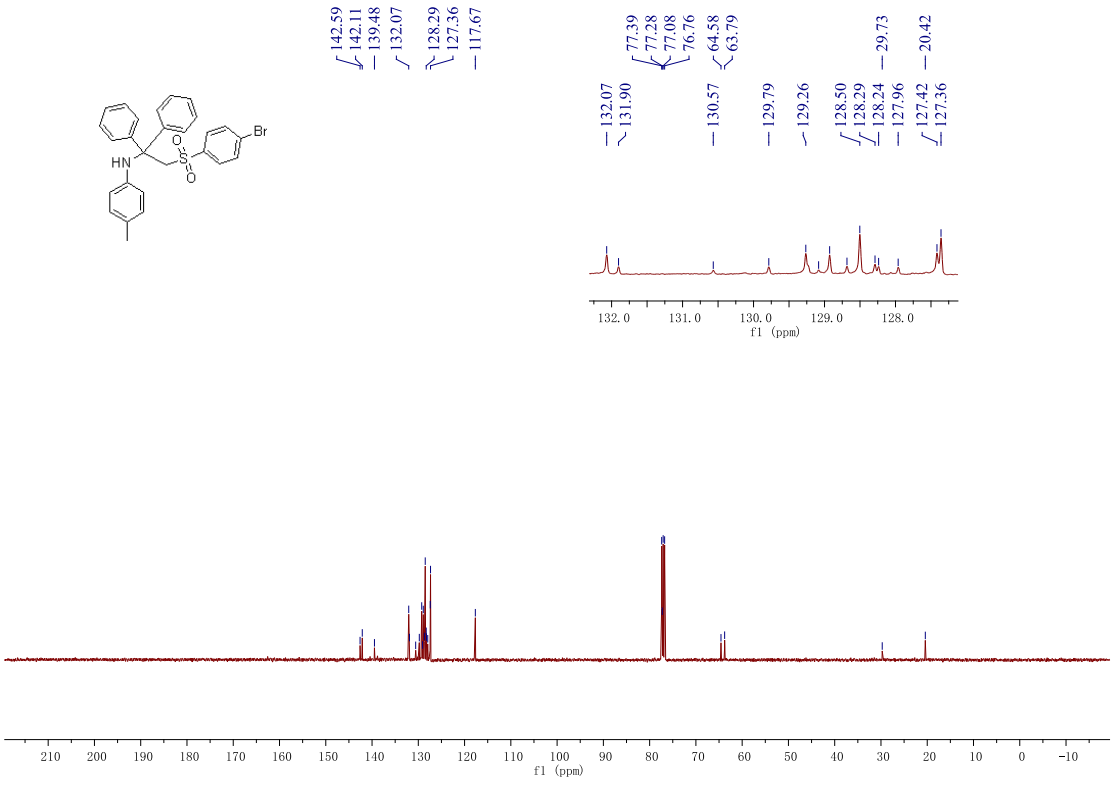
N-(2-((4-chlorophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4r)



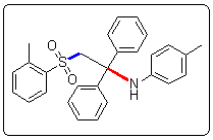


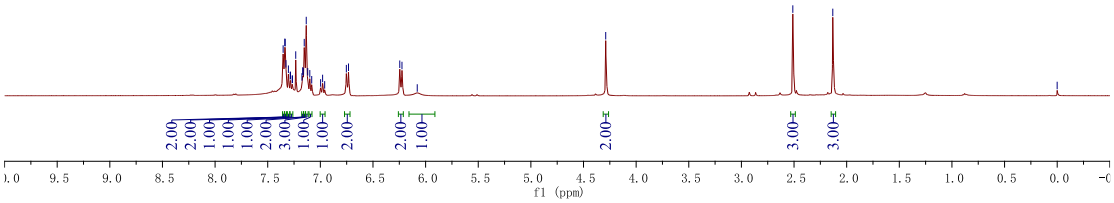
N-(2-((4-bromophenyl)sulfonyl)-1,1-diphenylethyl)-4-methylaniline (4s)

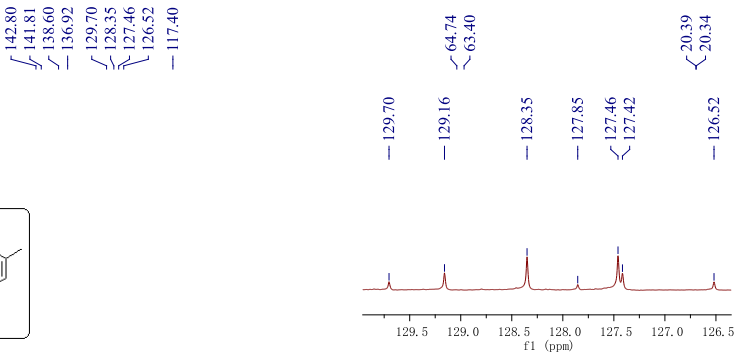


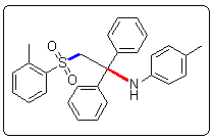


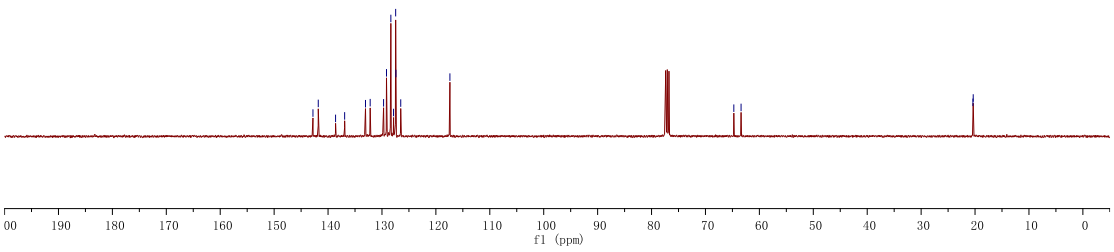
N-(1,1-diphenyl-2-(o-tolylsulfonyl)ethyl)-4-methylaniline (4t)



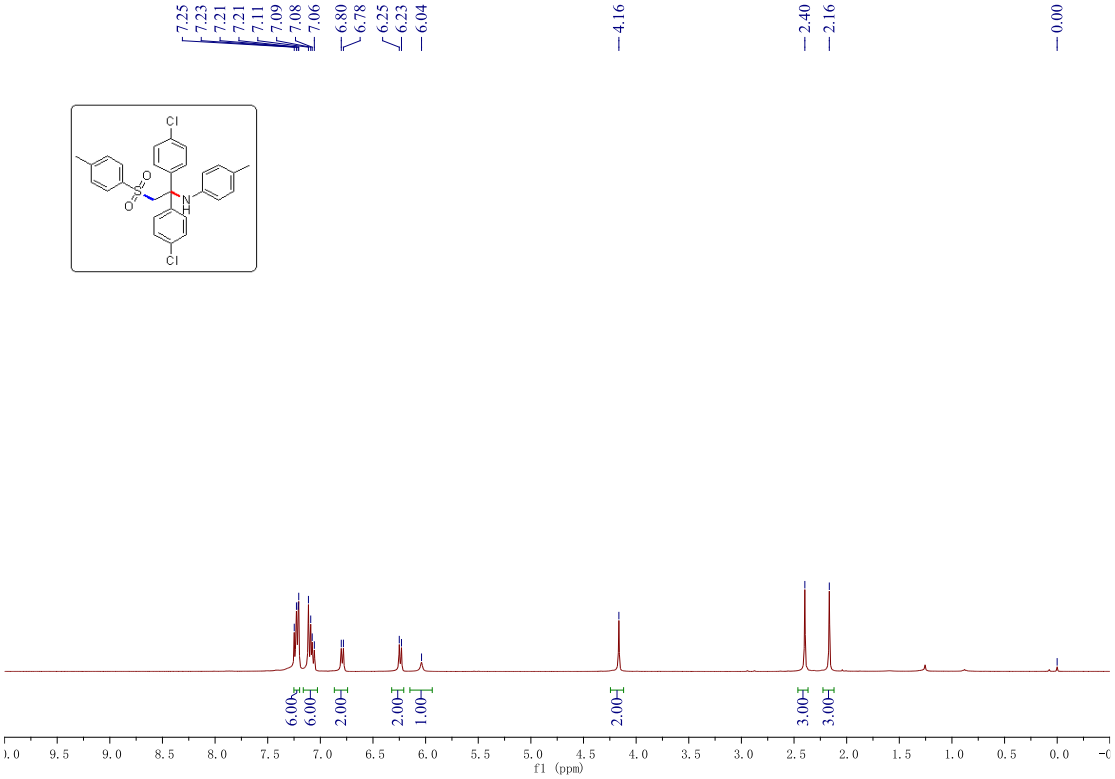


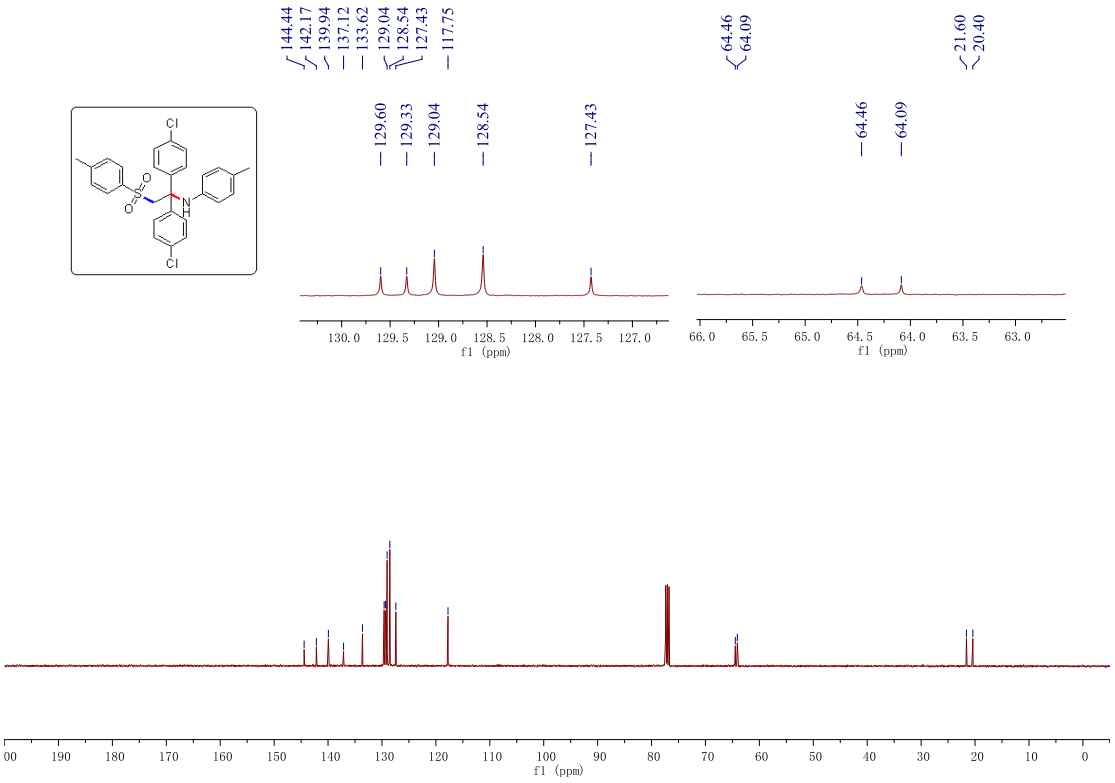




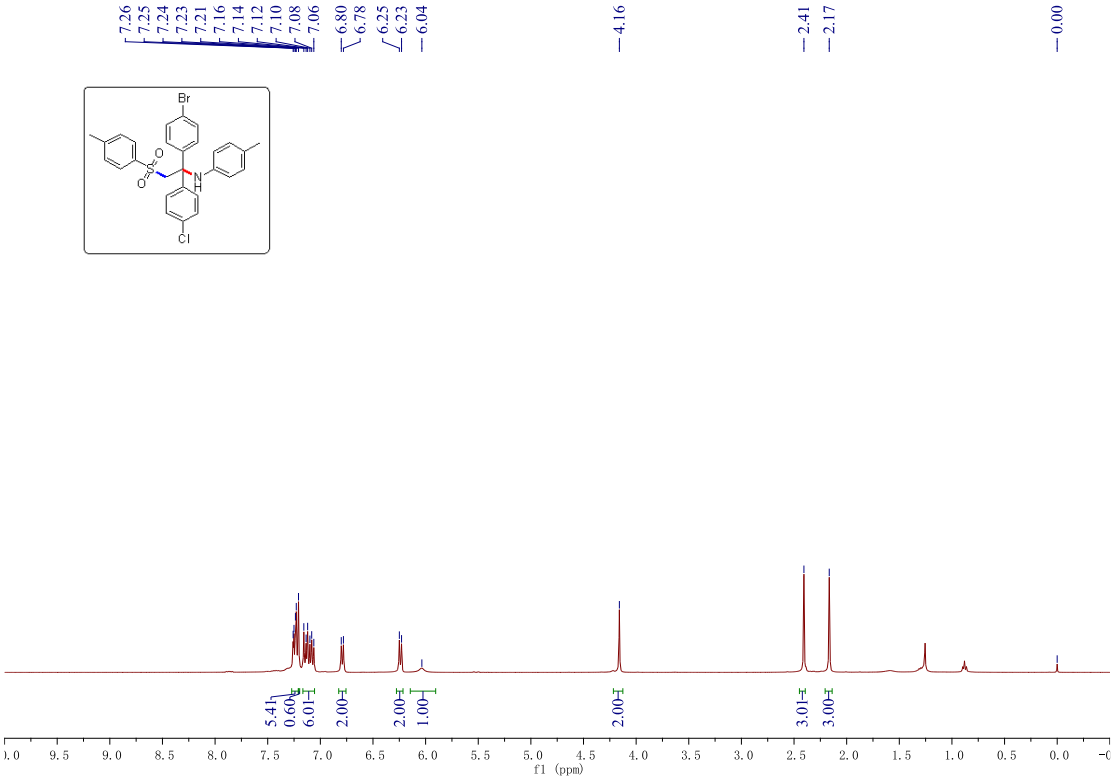


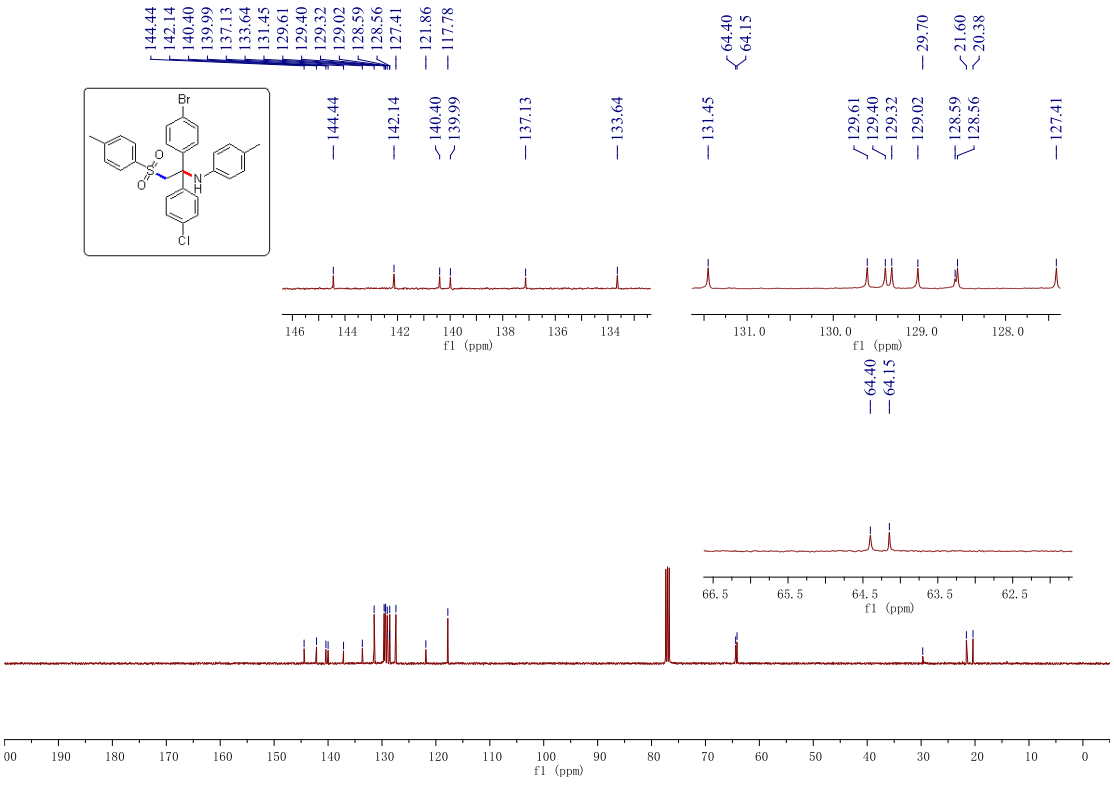
N-(1,1-bis(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4u)



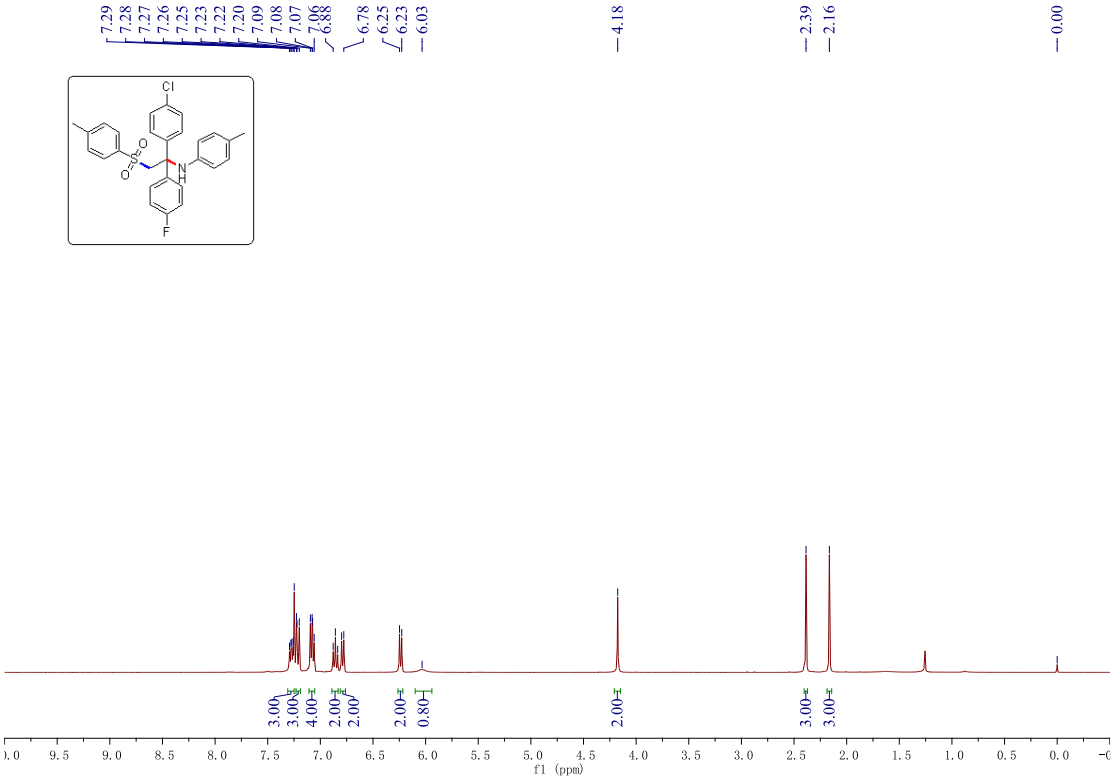


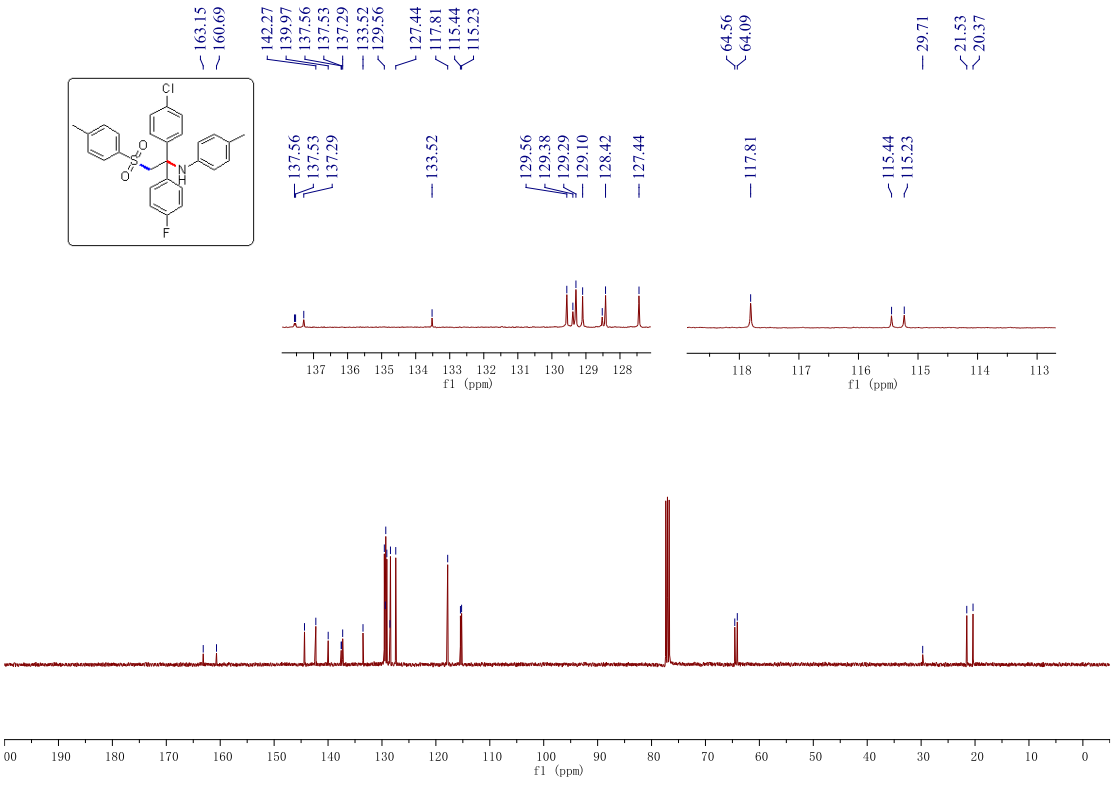
N-(1-(4-bromophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4v)

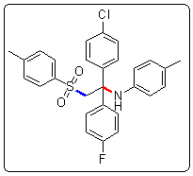




N-(1-(4-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4w)

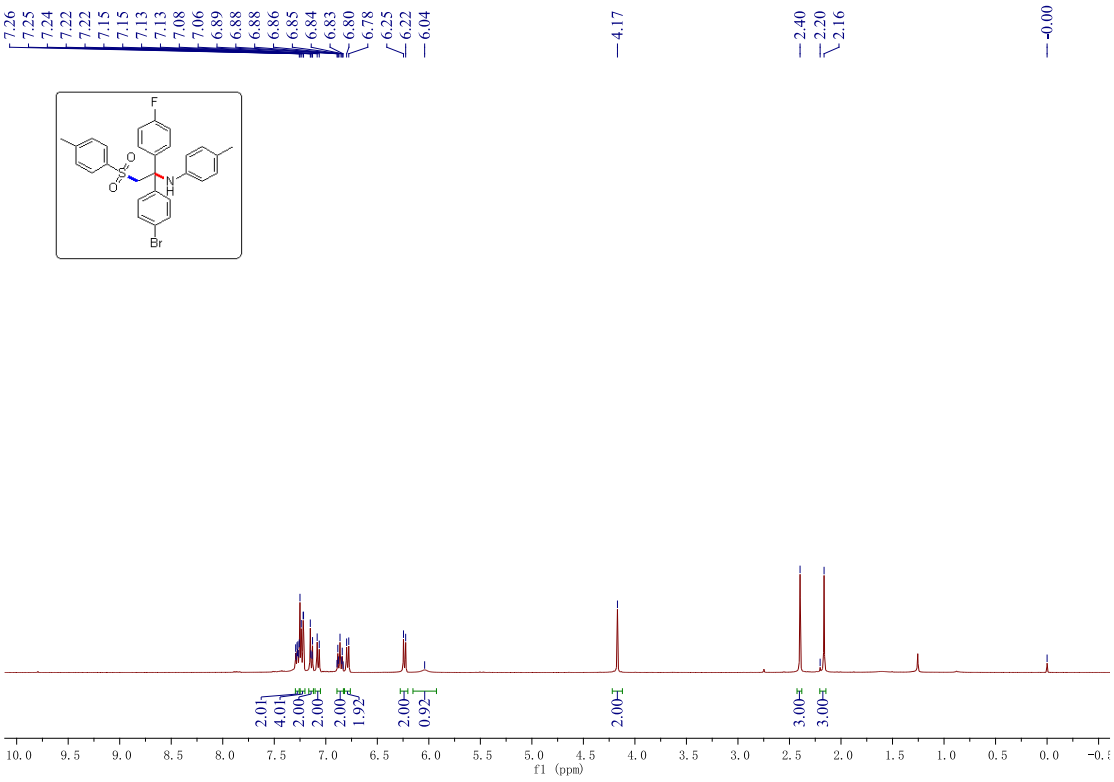


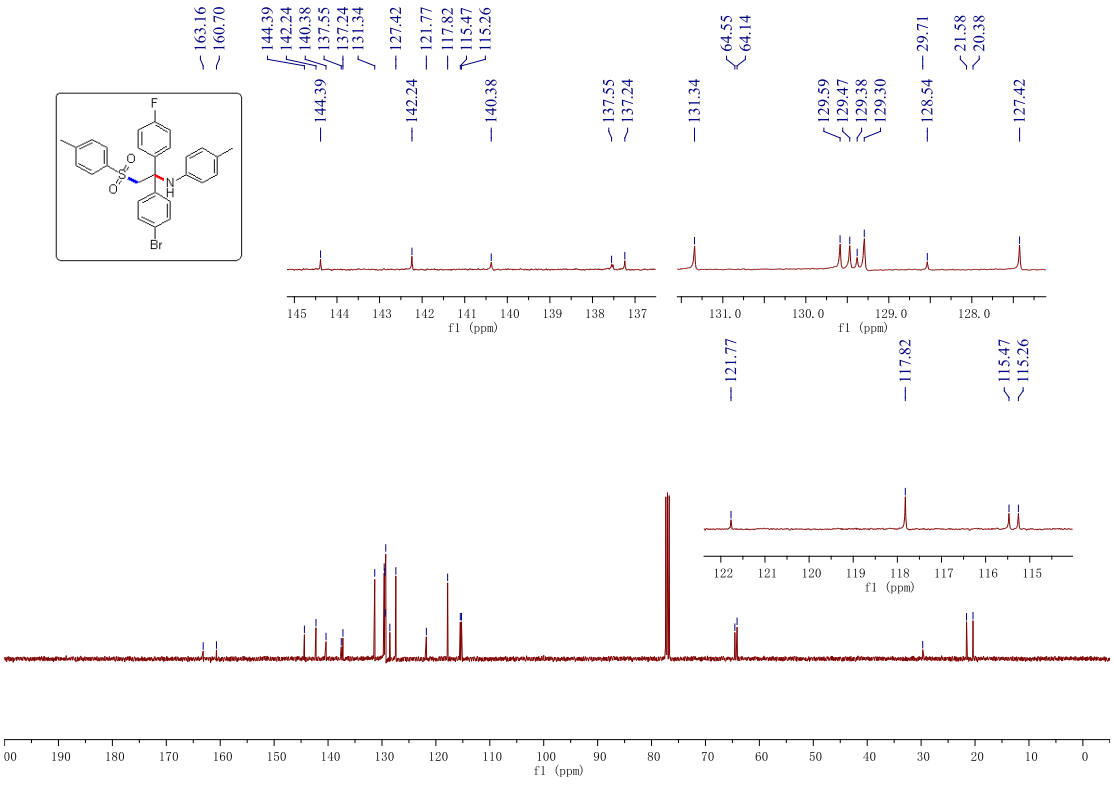


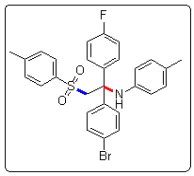

Cl
O
S
O
N
H
F

-114.52
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

N-(1-(4-bromophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4x)

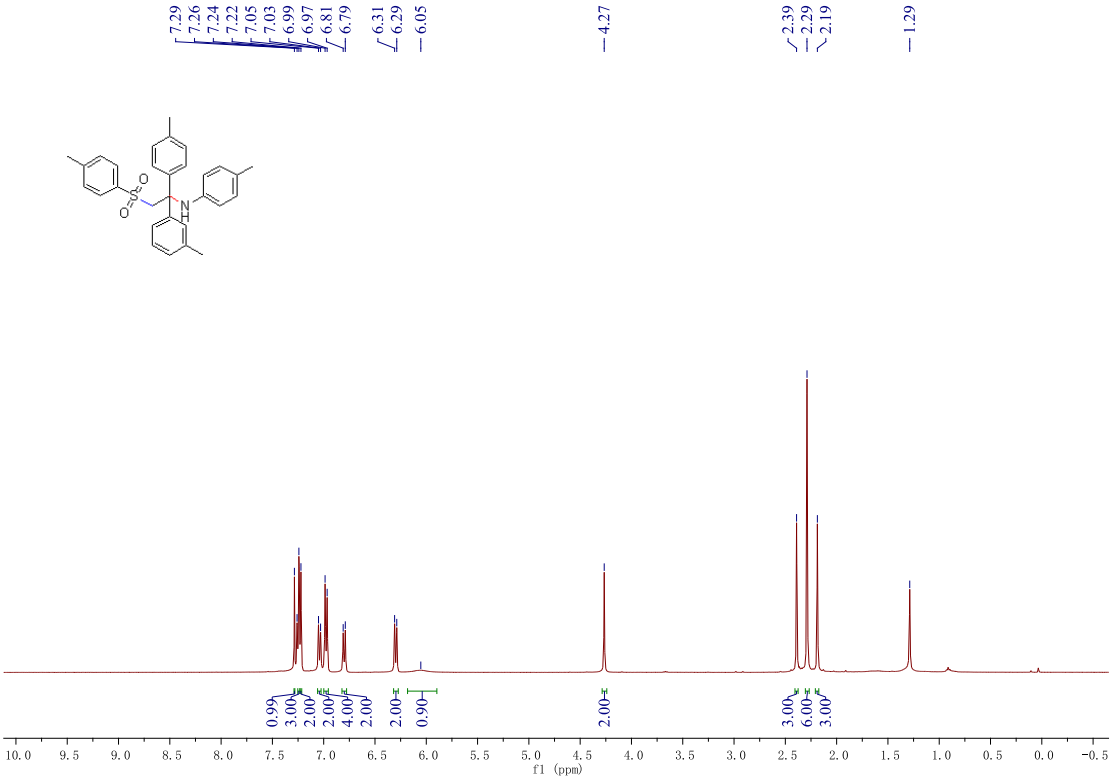


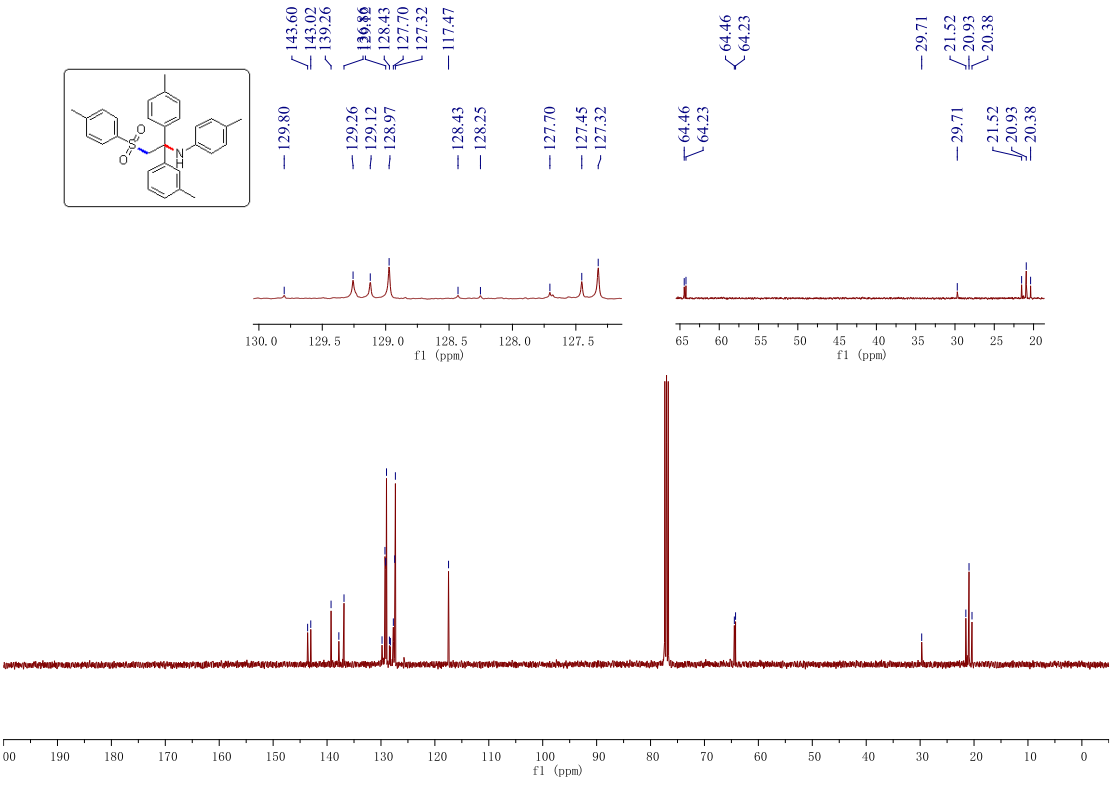



F
O
S
O
N
H
Br

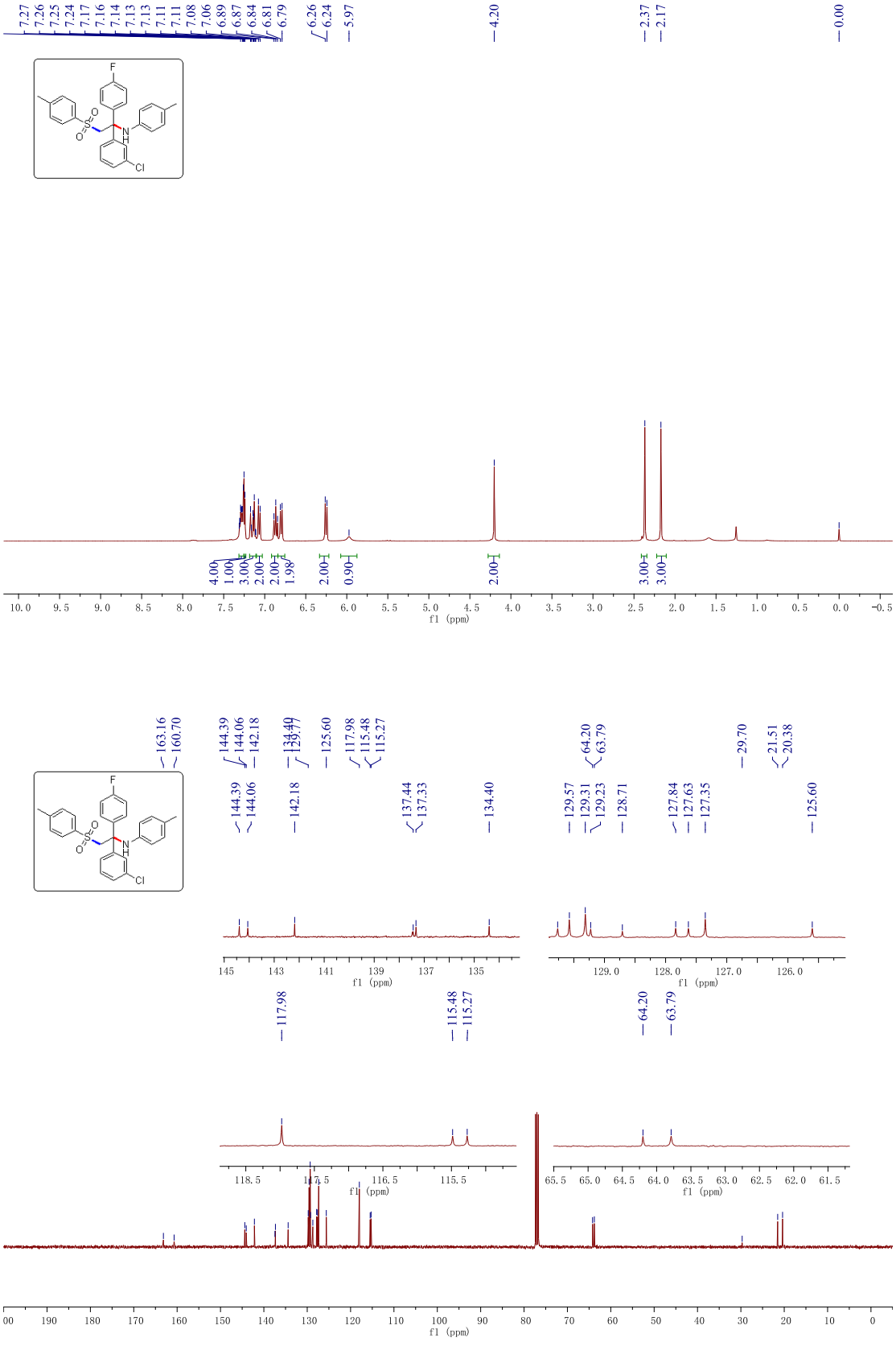
-114.41
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

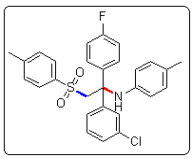
4-methyl-*N*-(1-(m-tolyl)-1-(p-tolyl)-2-tosylethyl)aniline (4y)





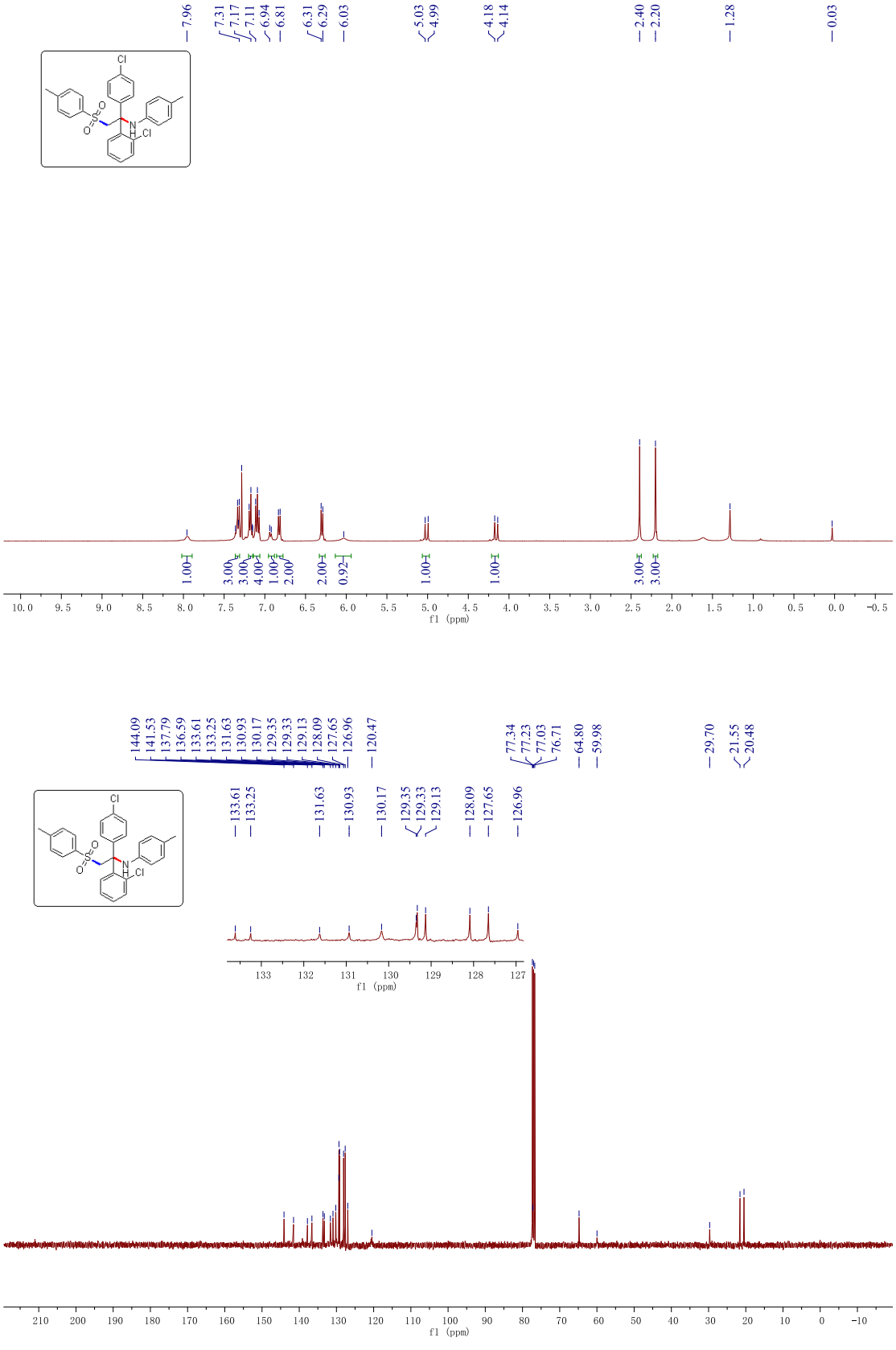
N-(1-(3-chlorophenyl)-1-(4-fluorophenyl)-2-tosylethyl)-4-methylaniline (4z)



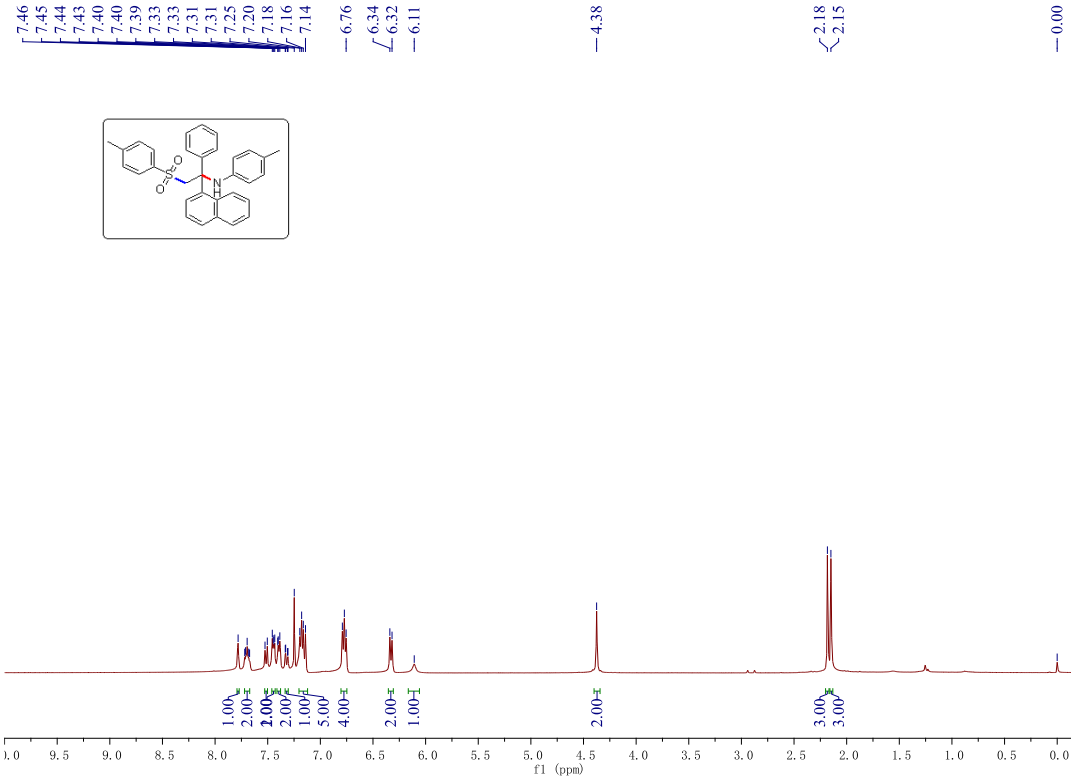

F
O
O
S
N
H
Cl

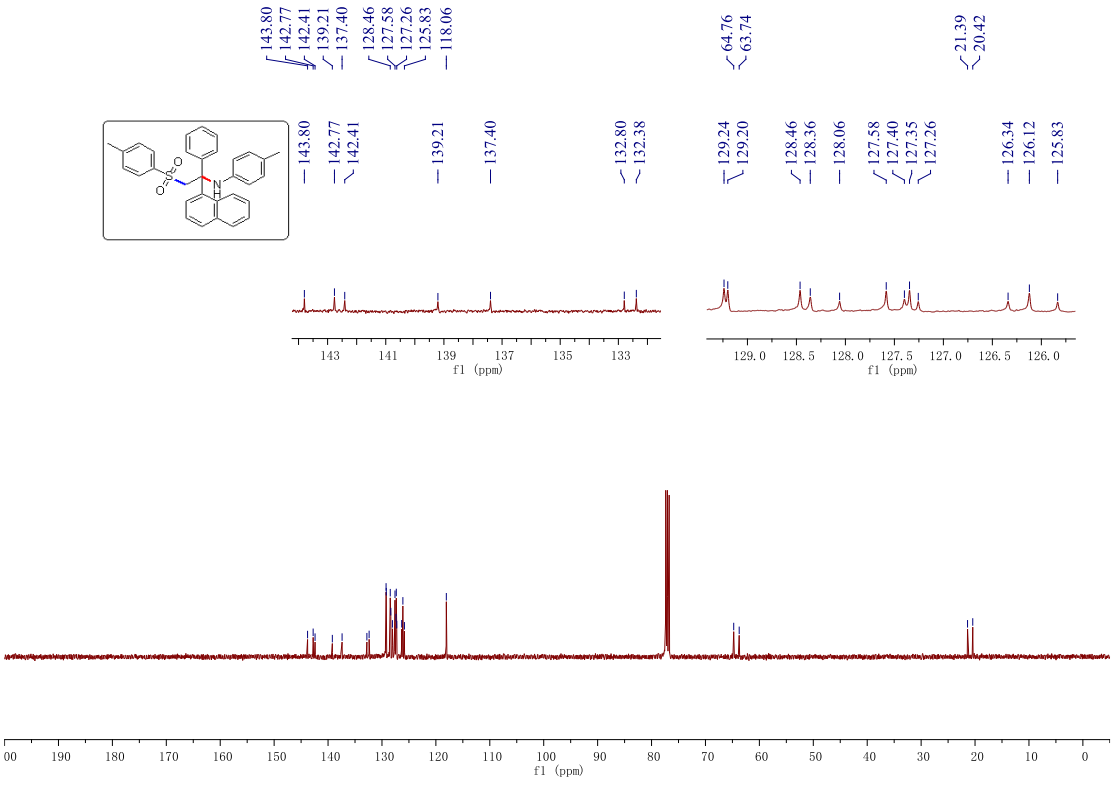
-114.52
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

N-(1-(2-chlorophenyl)-1-(4-chlorophenyl)-2-tosylethyl)-4-methylaniline (4a')

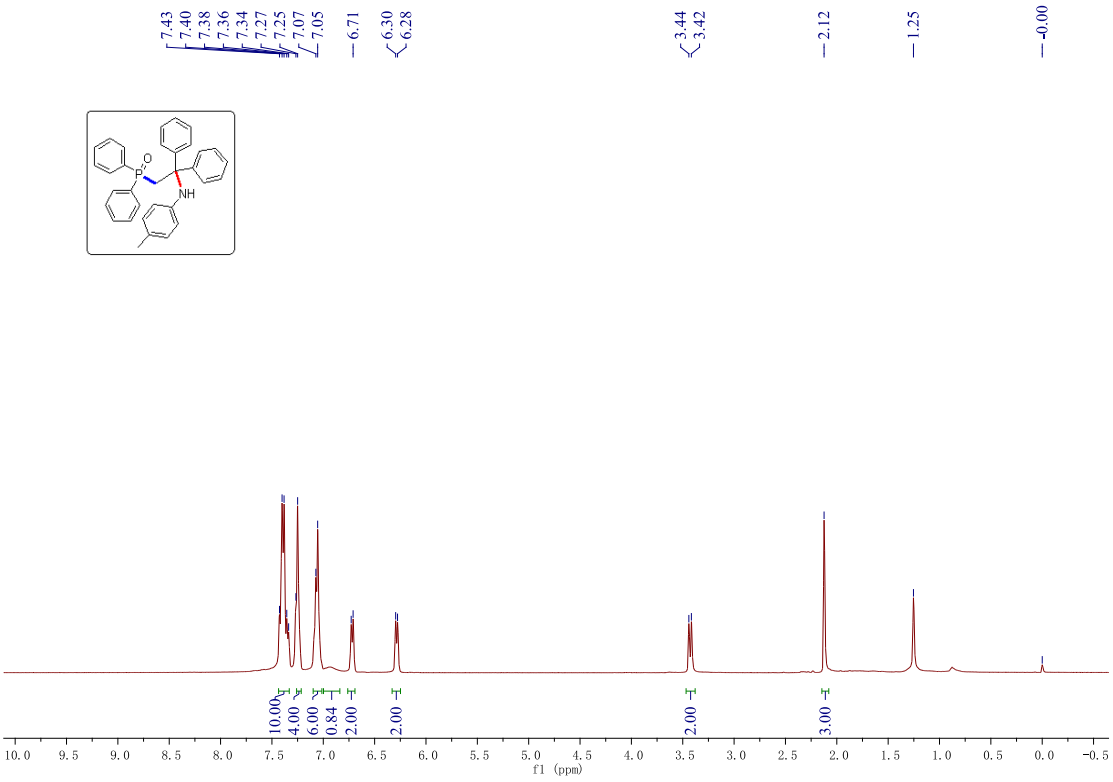


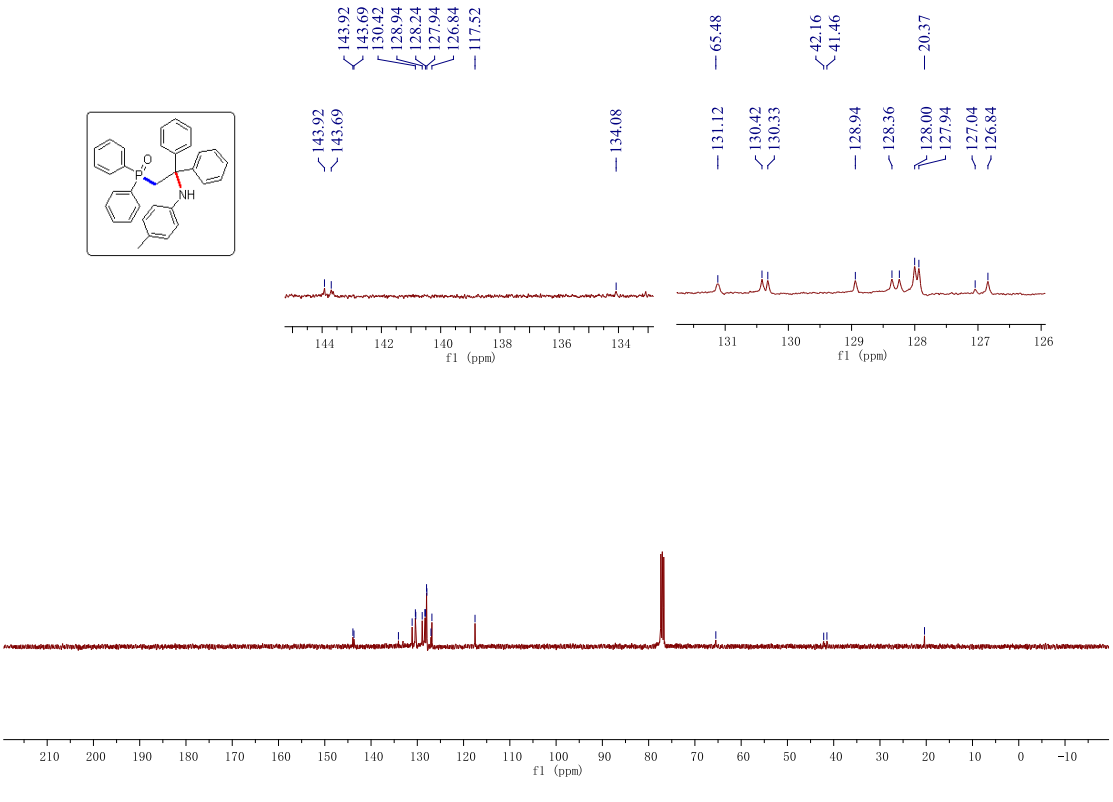
4-methyl-*N*-(1-(naphthalen-1-yl)-1-phenyl-2-tosylethyl)aniline (4b’)

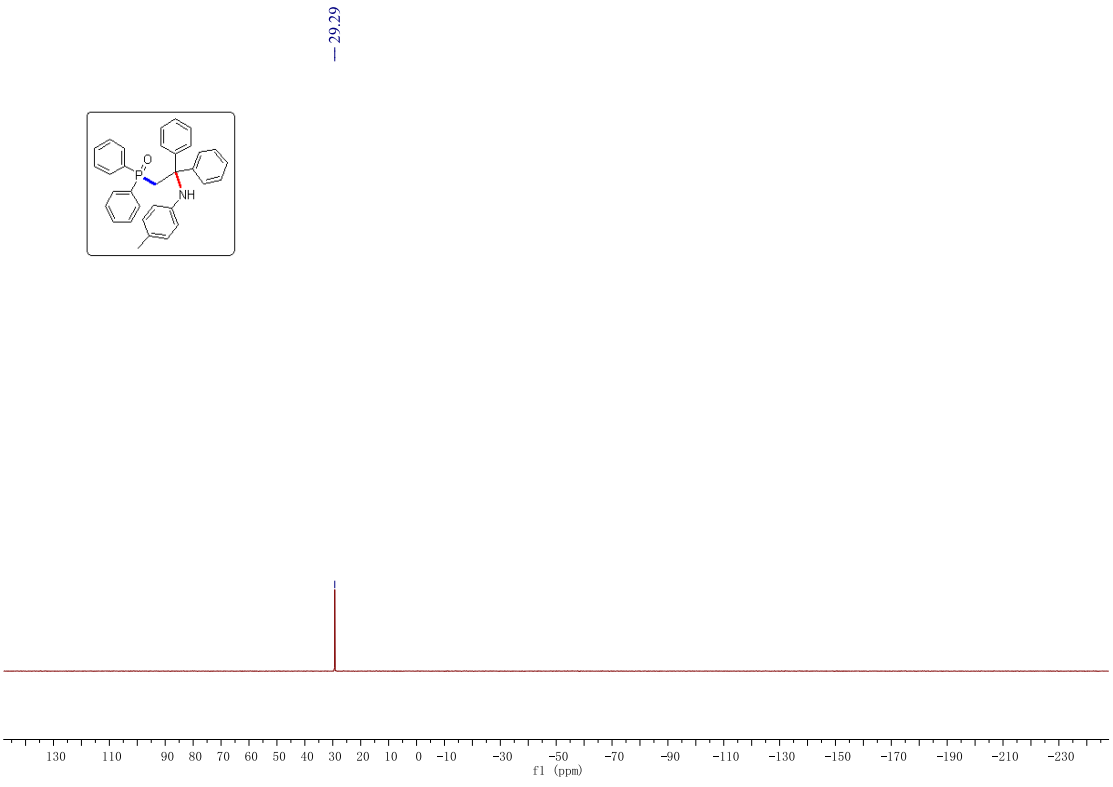




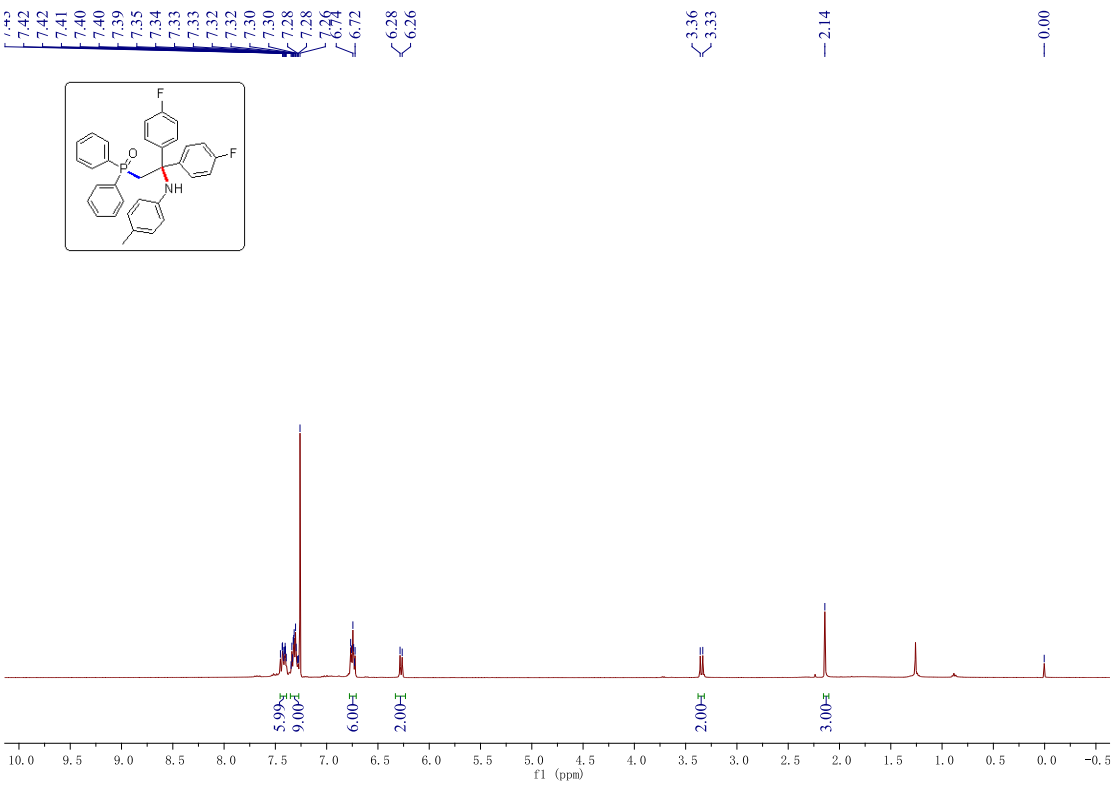
(2,2-diphenyl-2-(p-tolylamino)ethyl)diphenylphosphine oxide (6a)

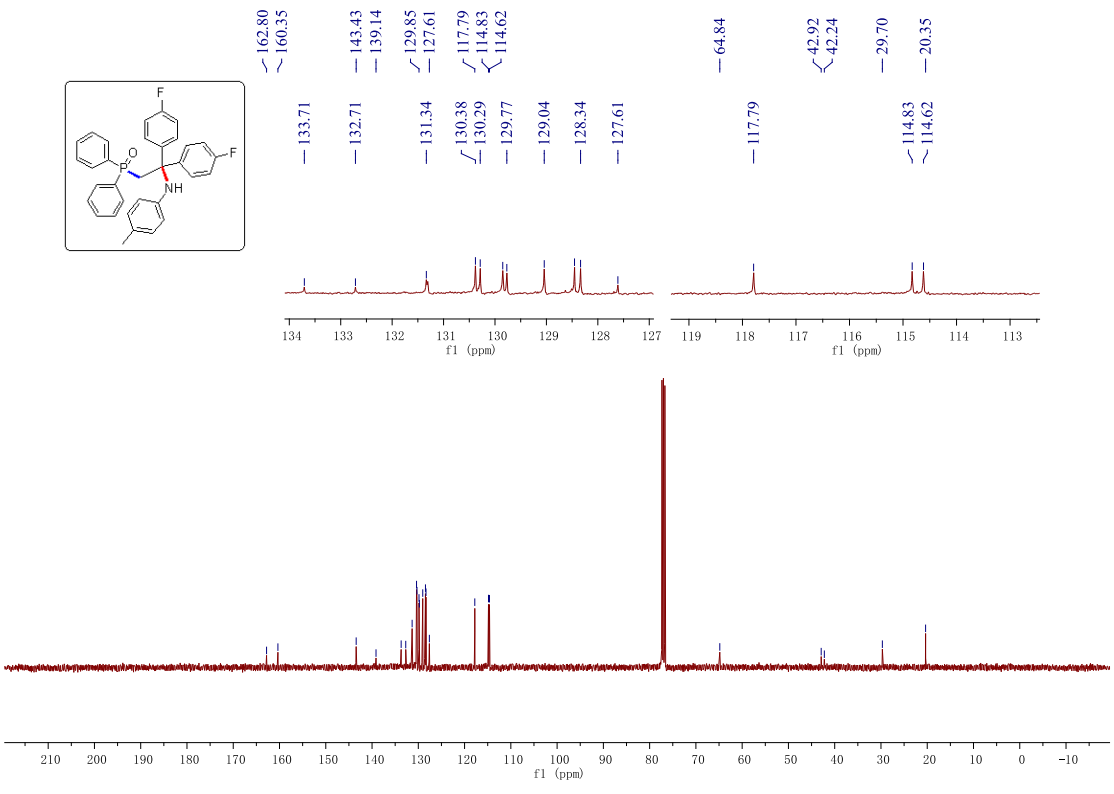


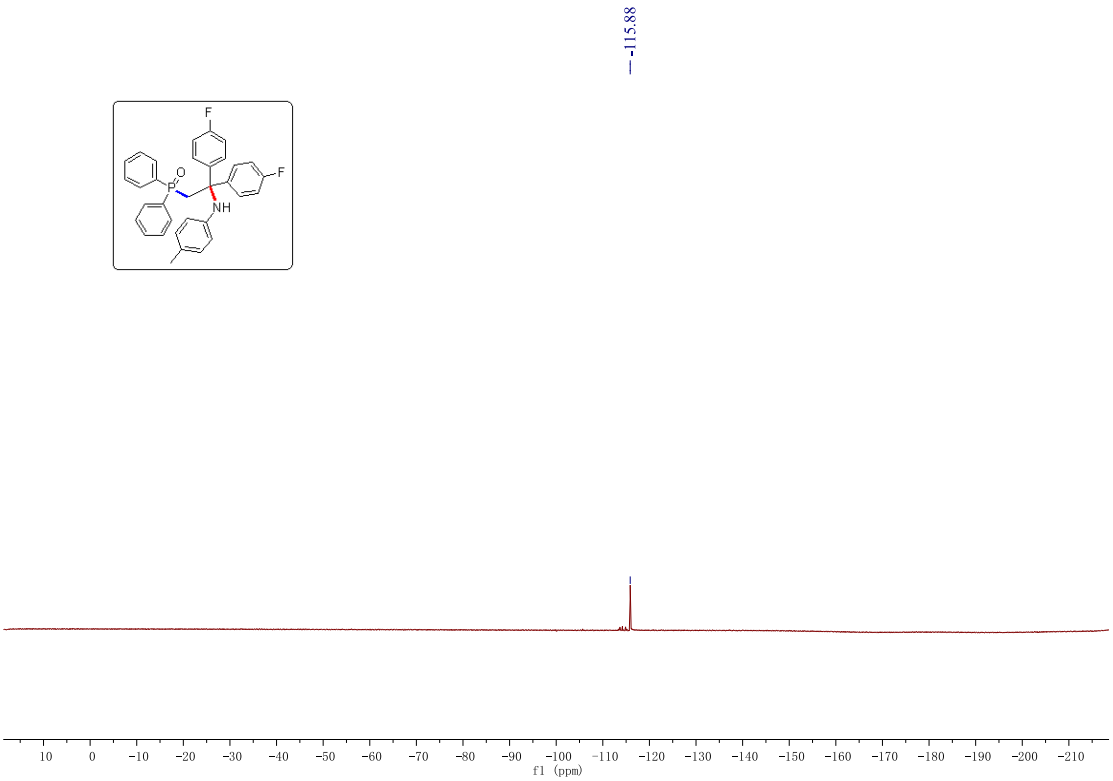


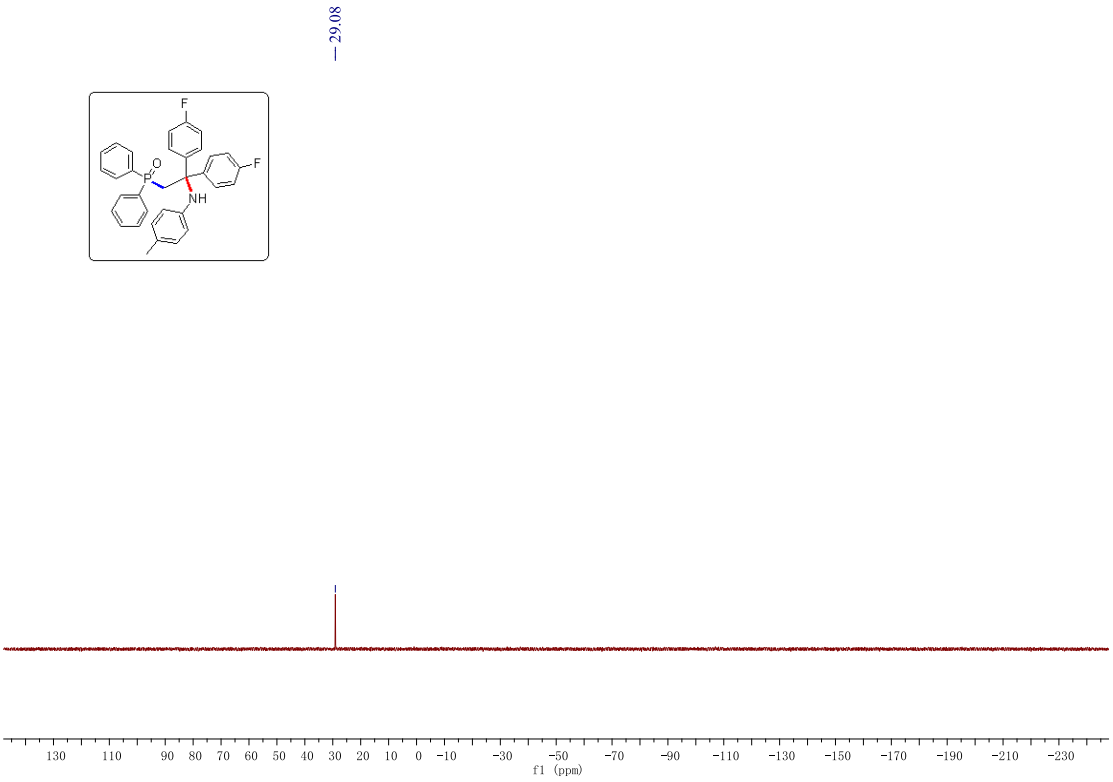

29.29
O
P
NH
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

(2,2-bis(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6b)

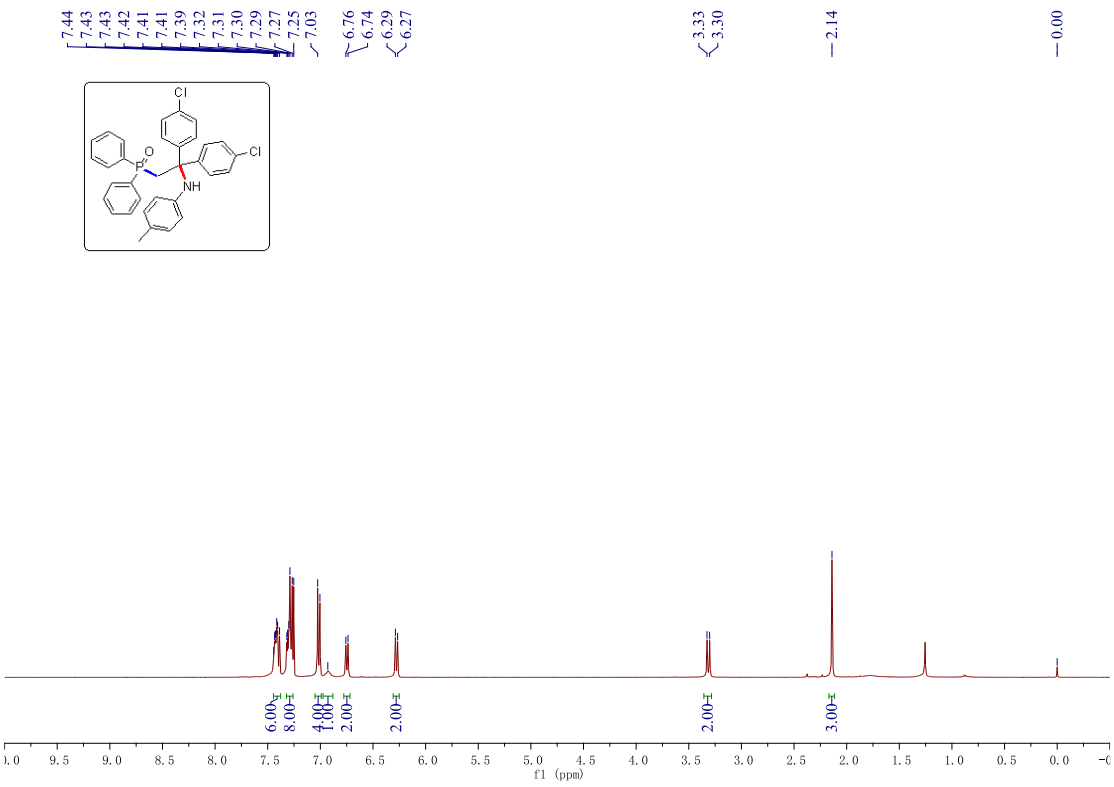


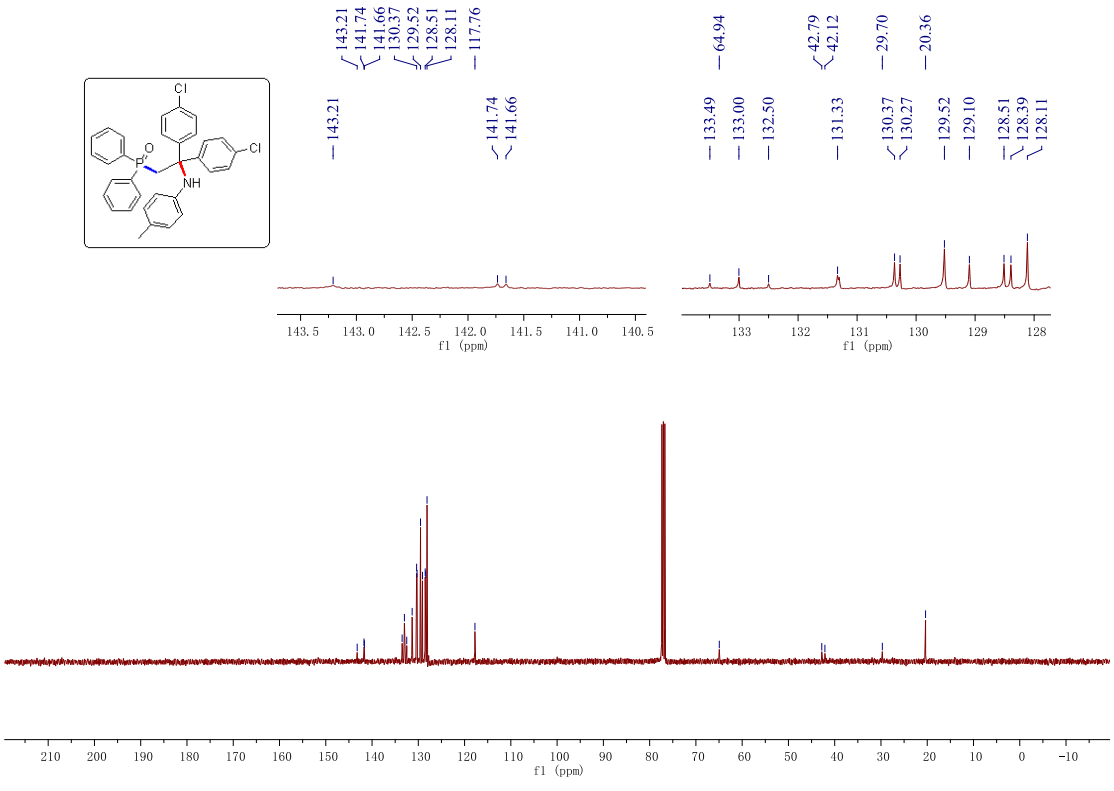


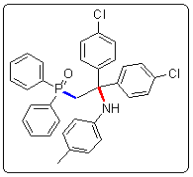

-115.88
F
O
P
NH
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


29.08
F
O
P
NH
F
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

(2,2-bis(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6c)

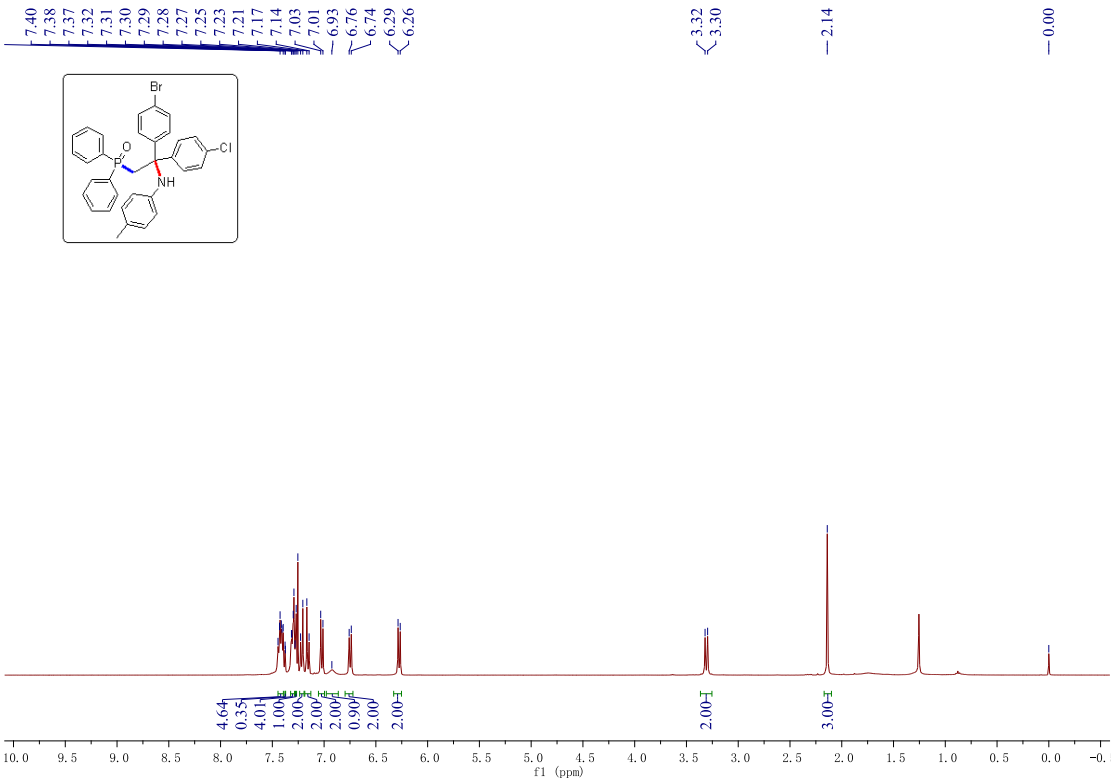


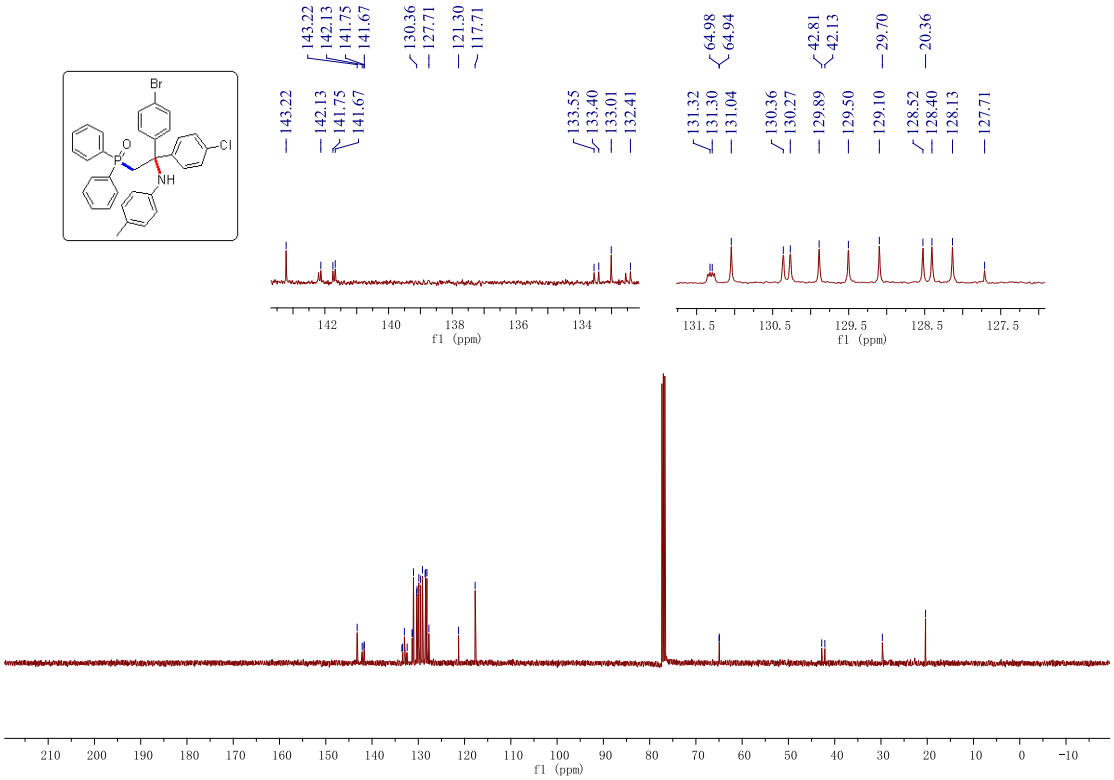


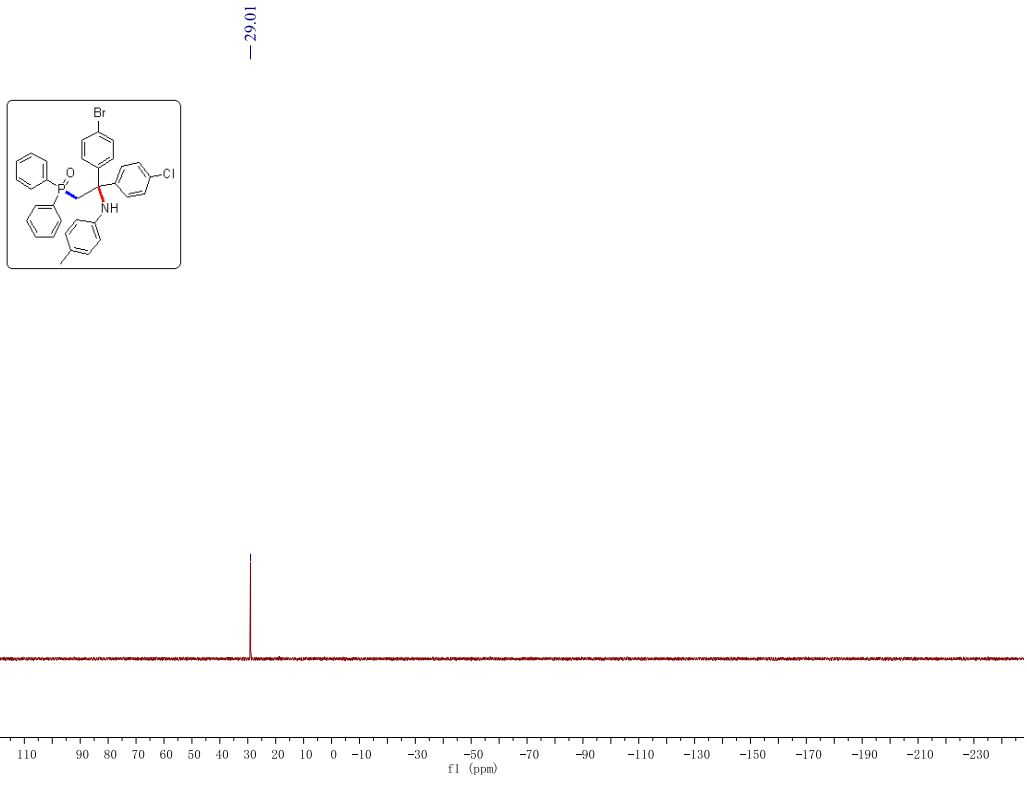

Cl
O
P
NH
Cl

29.03
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

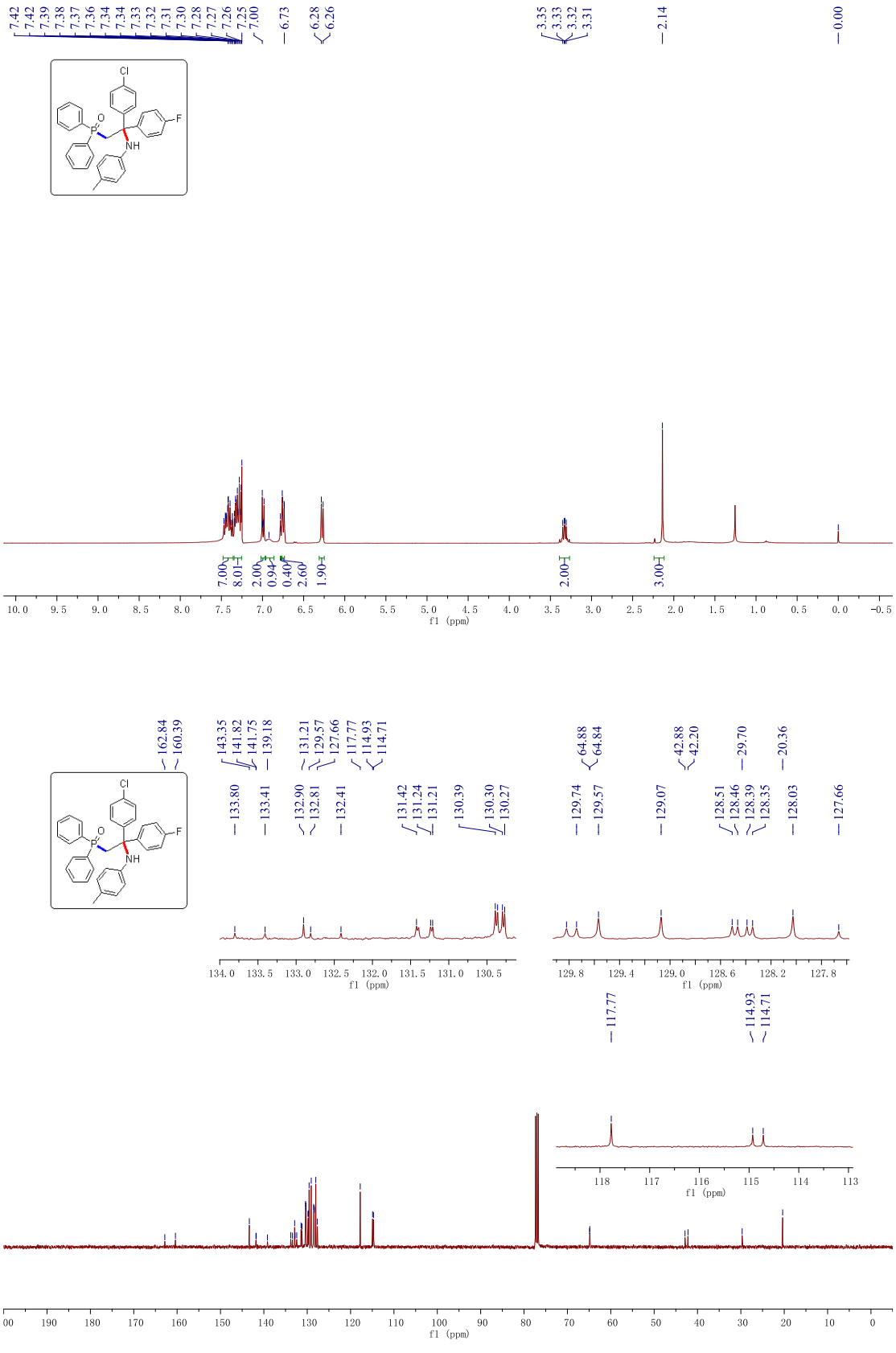
(2-(4-bromophenyl)-2-(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6d)

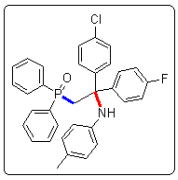




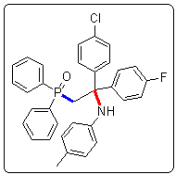

29.01
Br
Cl
O
P
NH
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

(2-(4-chlorophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6e)



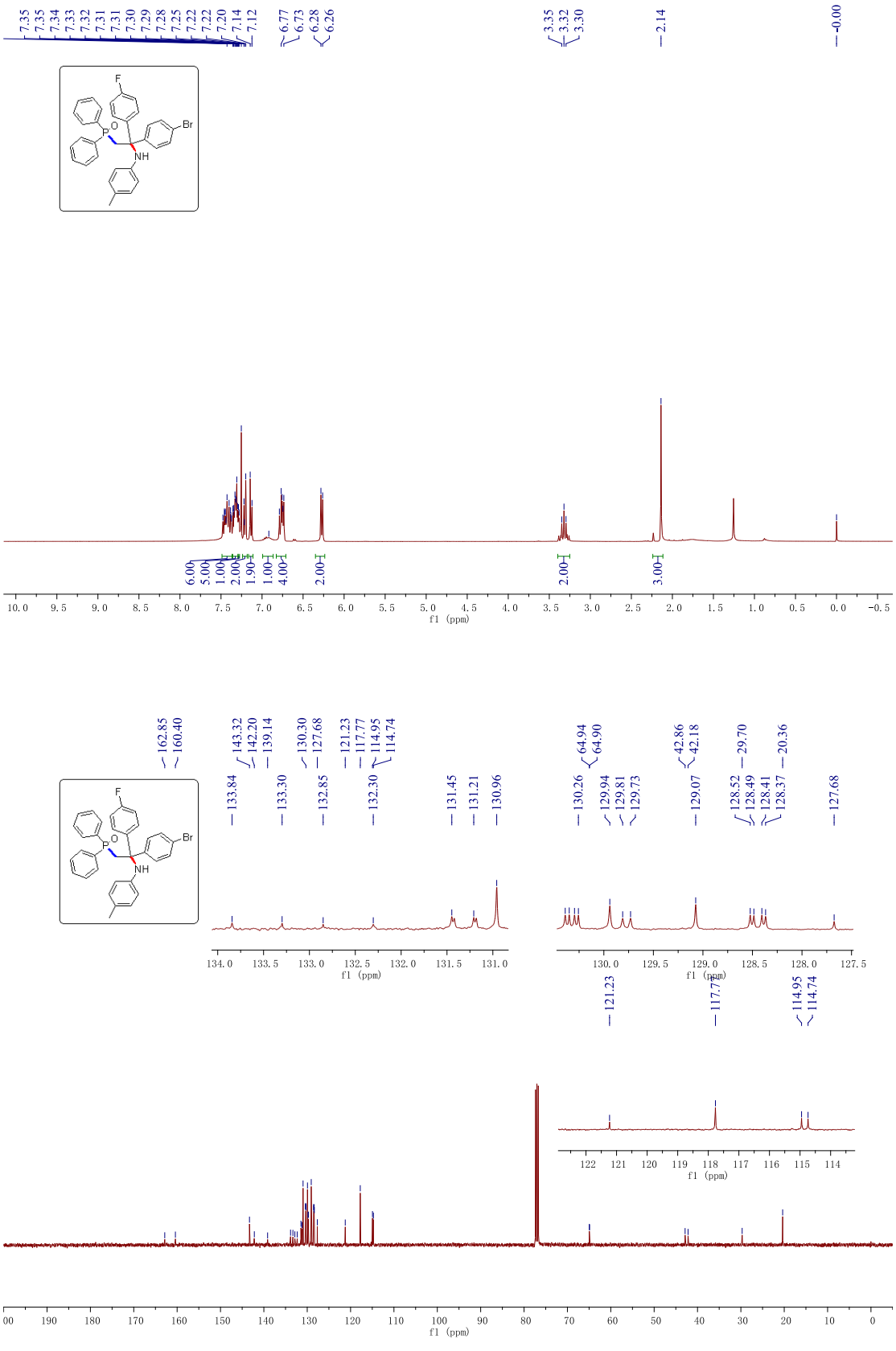

Cl
O
P
F
NH

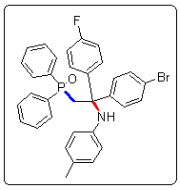
-115.64
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


Cl
O
P
F
NH

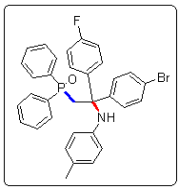
29.03
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

(2-(4-bromophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6f)



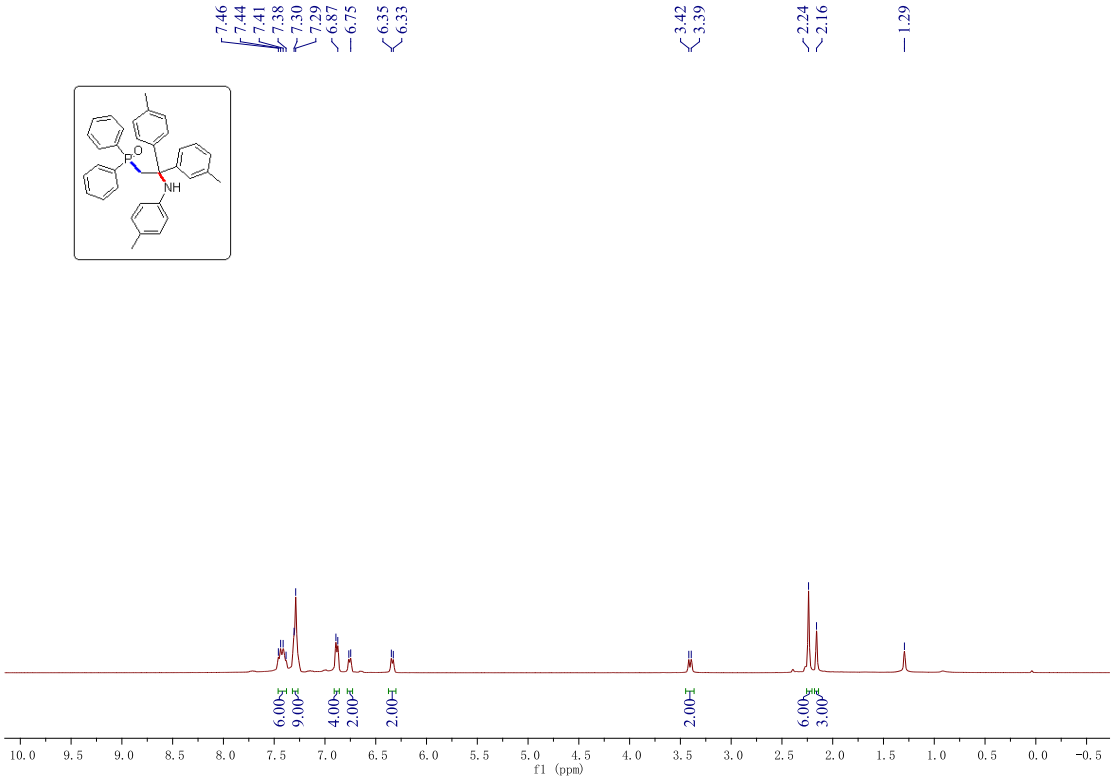

F
O
P
Br
NH

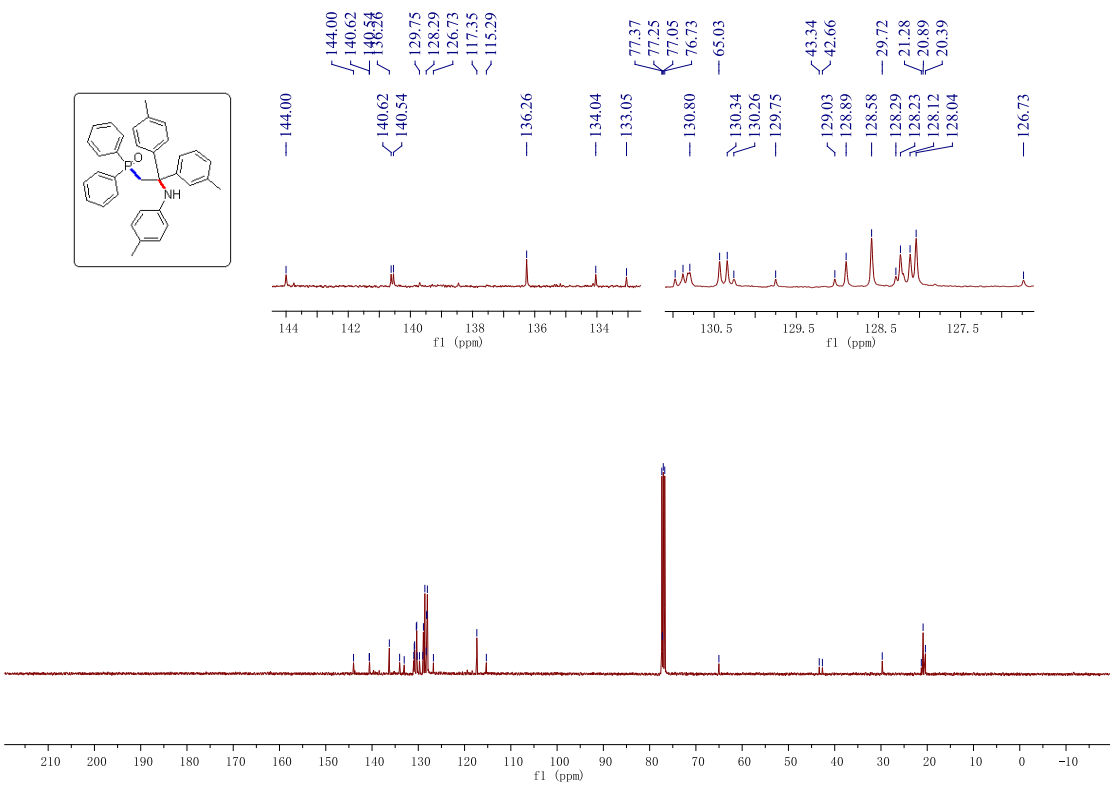
-115.59
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

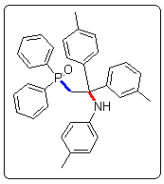

F
O
P
Br
NH

29.03
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

diphenyl(2-(*m*-tolyl)-2-(*p*-tolyl)-2-(*p*-tolylamino)ethyl)phosphine oxide (6g)

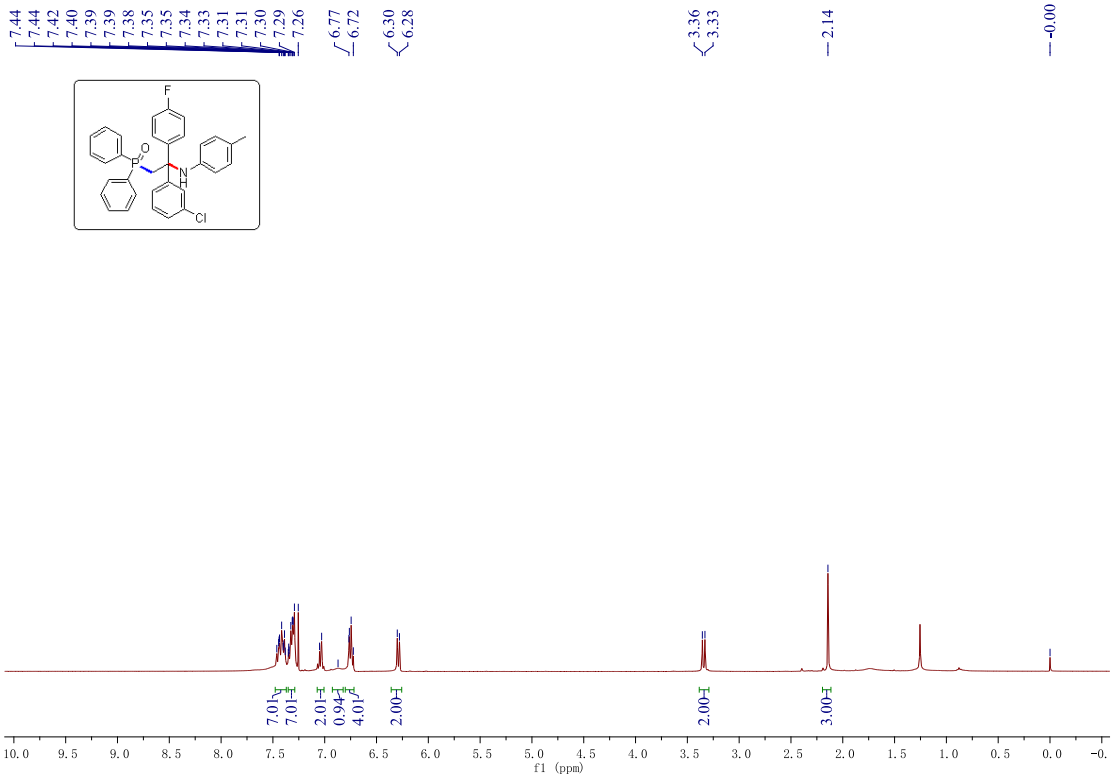


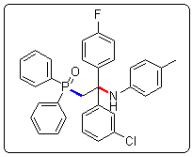



O
P
NH

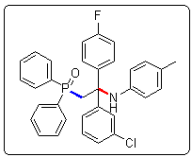
29.27
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

(2-(3-chlorophenyl)-2-(4-fluorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6h)



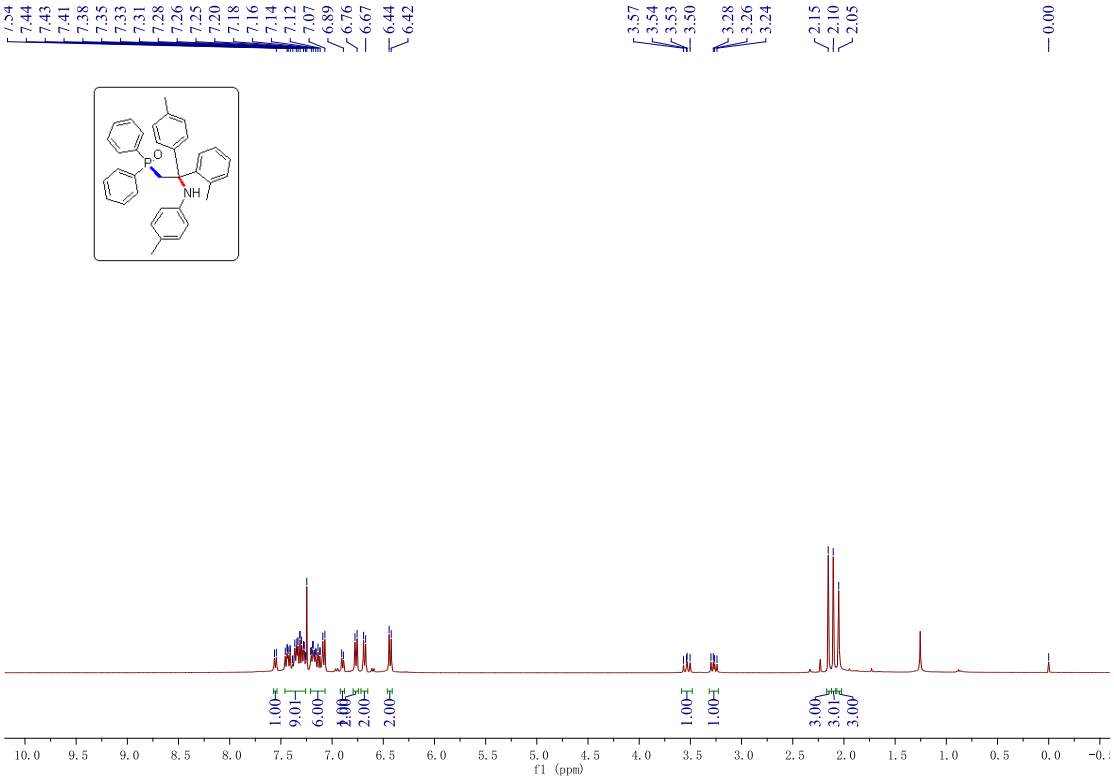

F
O
P
N
H
Cl

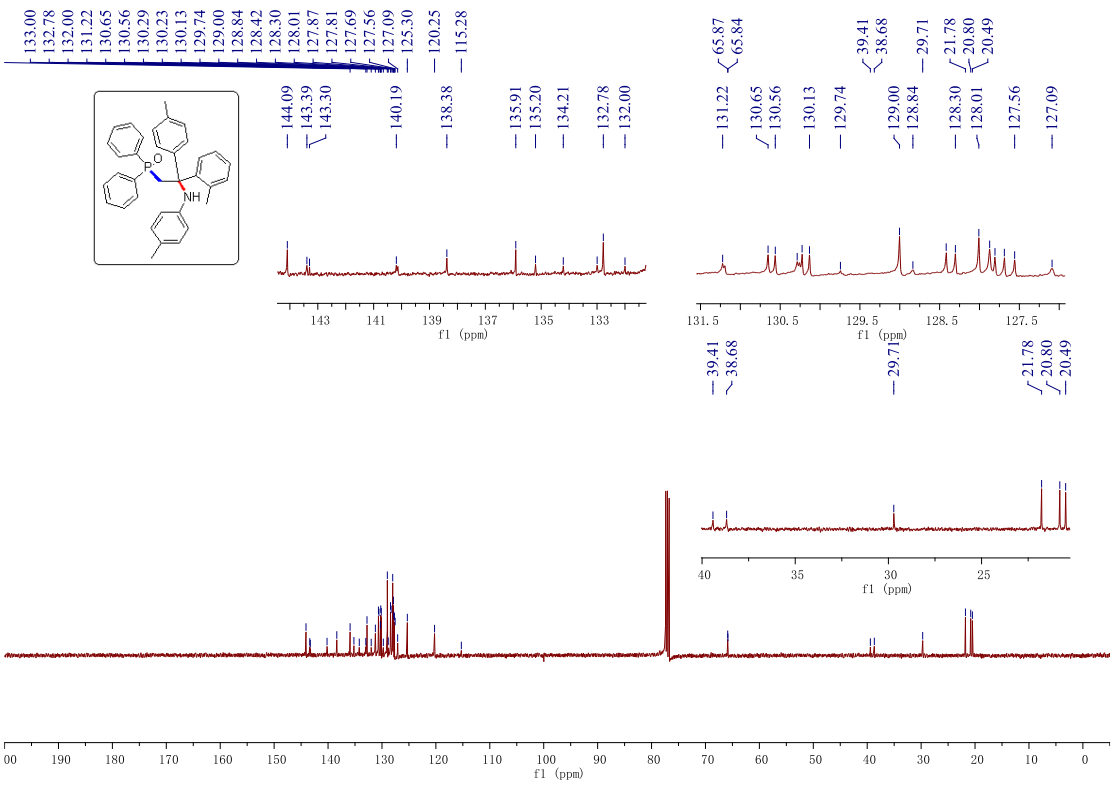
-115.71
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

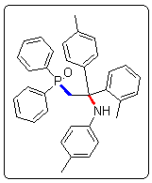

F
O
P
N
H
Cl

28.94
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

diphenyl(2-(*o*-tolyl)-2-(*p*-tolyl)-2-(*p*-tolylamino)ethyl)phosphine oxide (6i)

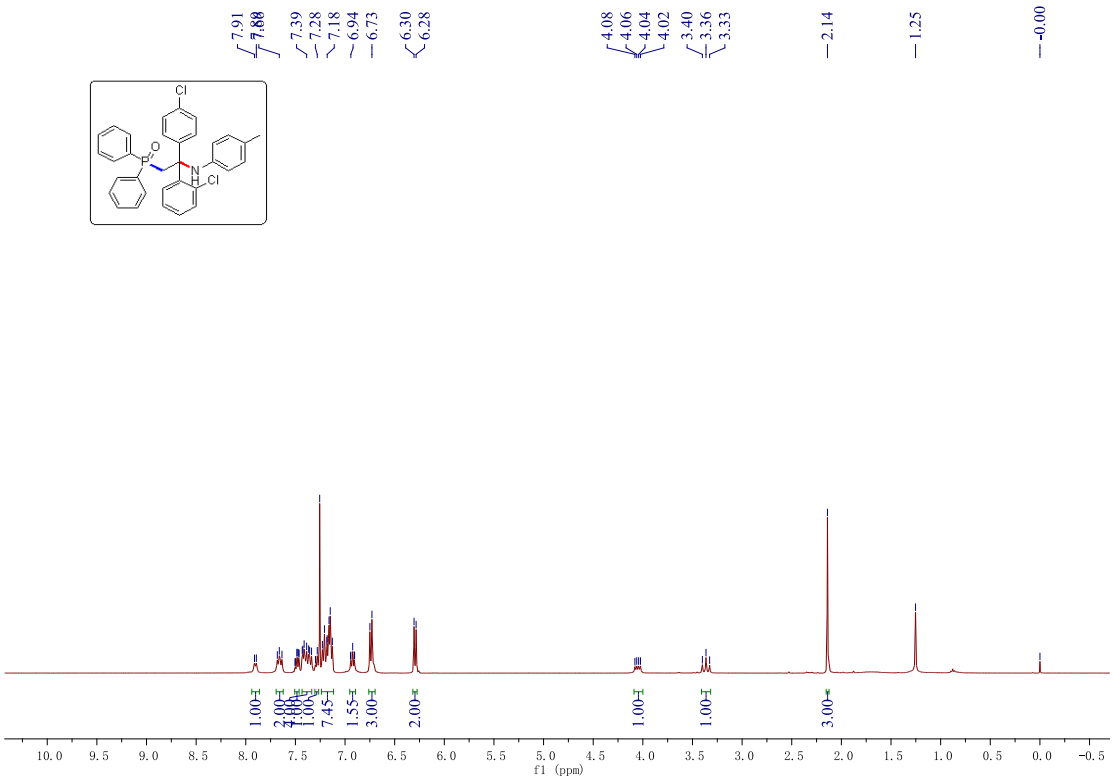


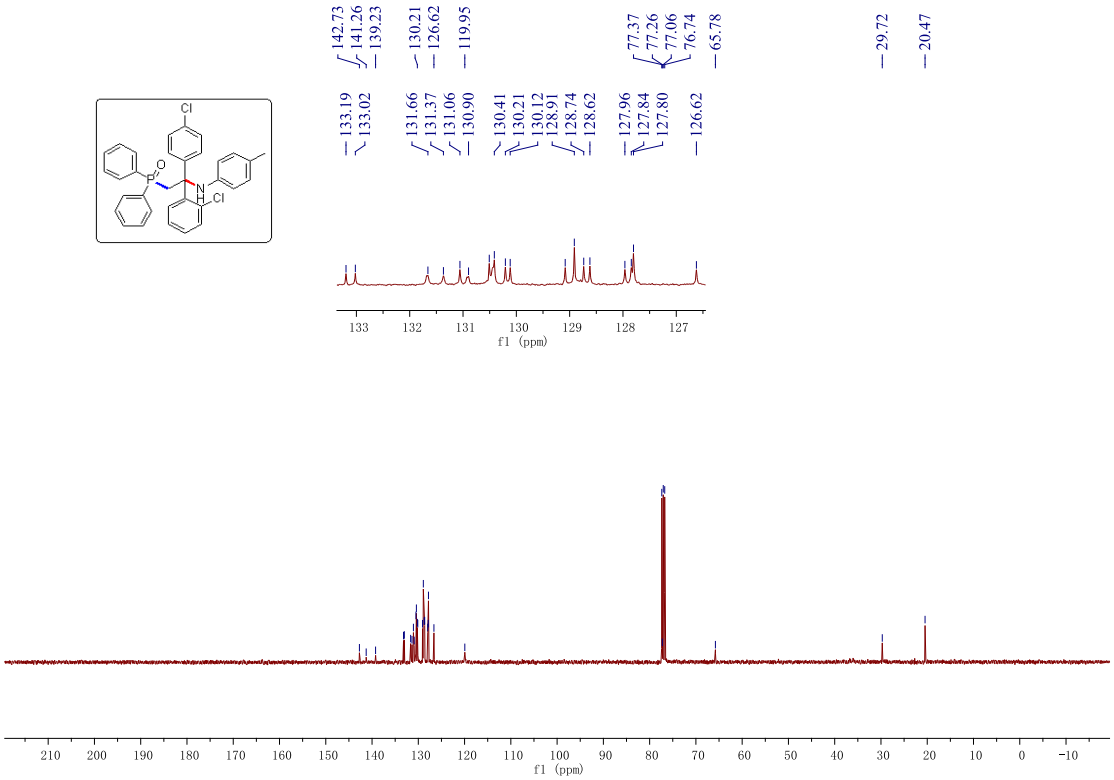


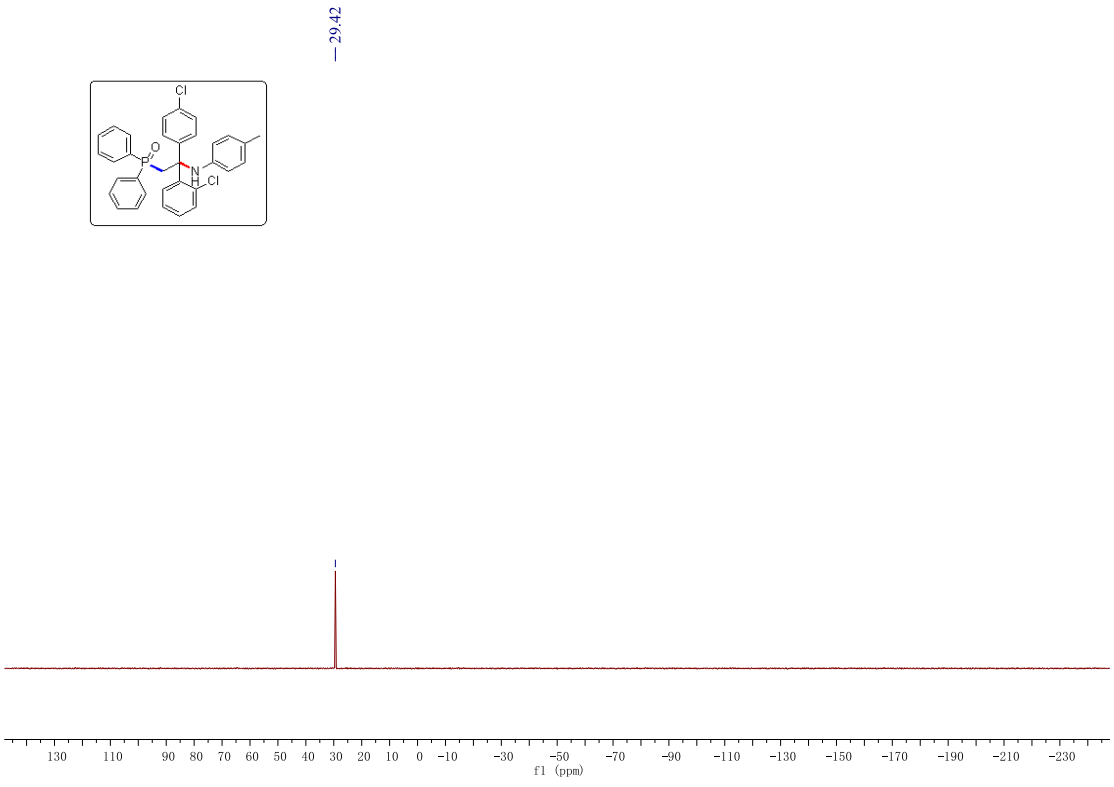

O
P
NH

29.32
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

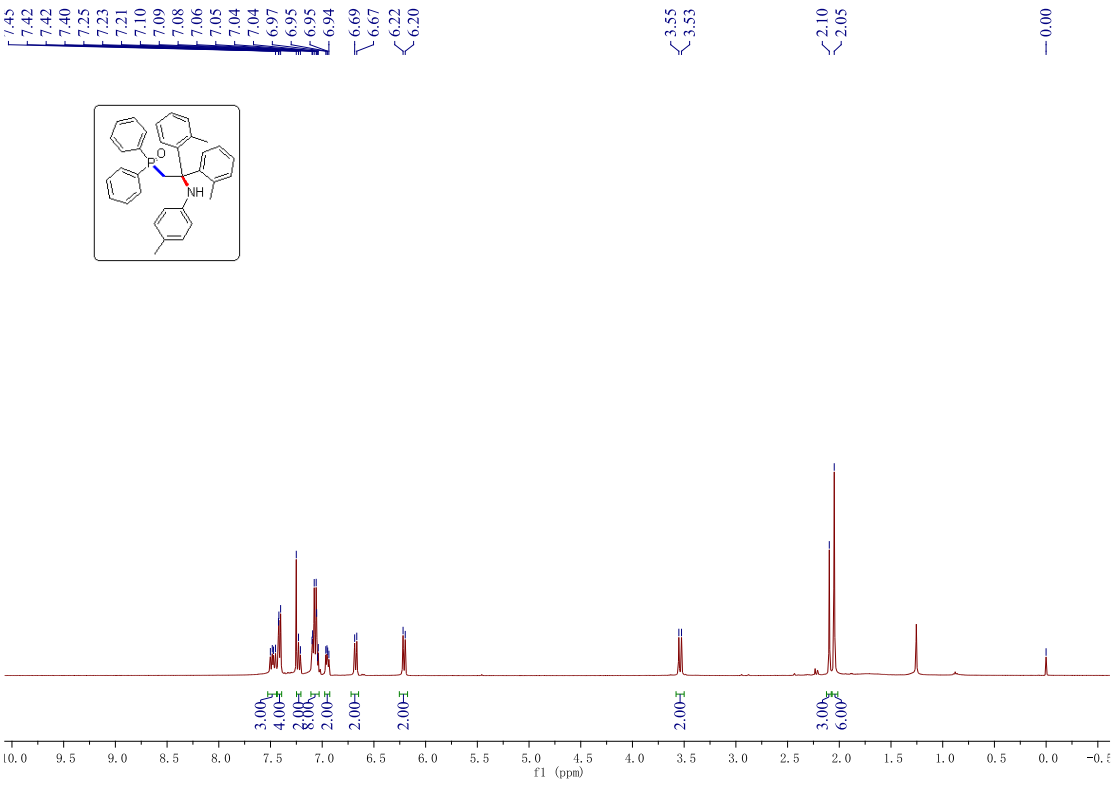
(2-(2-chlorophenyl)-2-(4-chlorophenyl)-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6j)

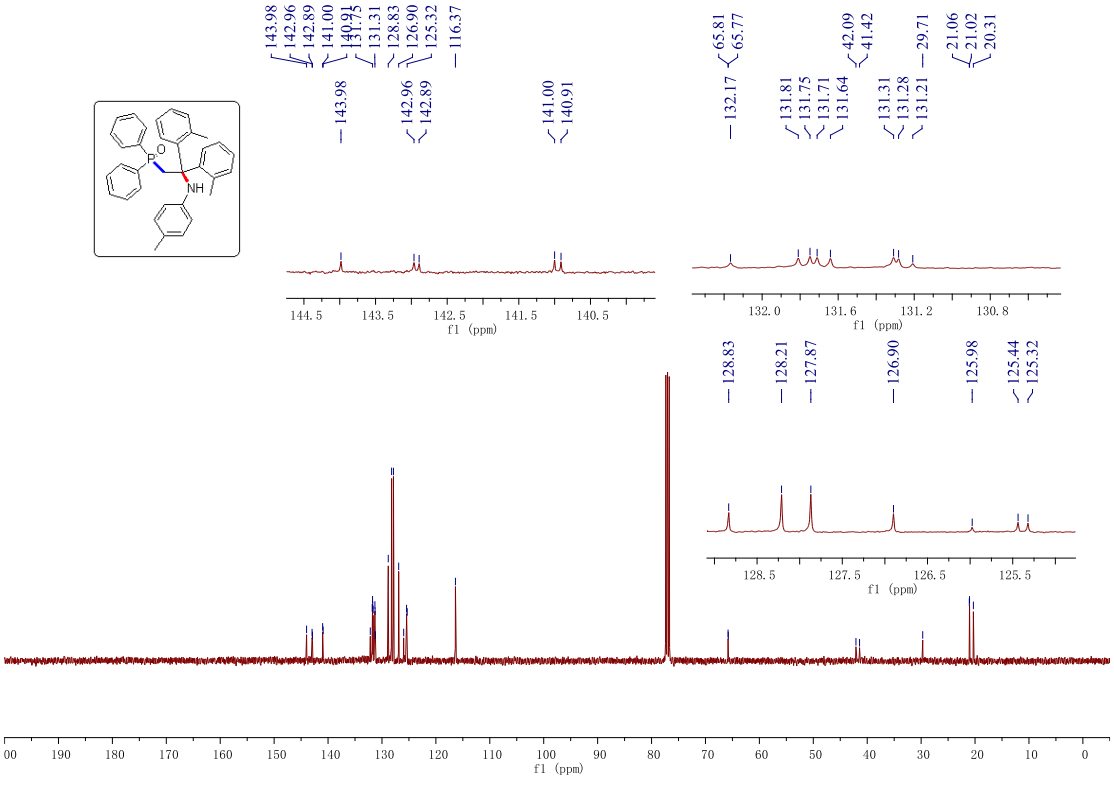


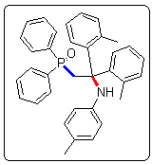



29.42
Cl
O
P
N
H
Cl
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

(2,2-di-*o*-tolyl-2-(*p*-tolylamino)ethyl)diphenylphosphine oxide (6k)






O
P
NH

28.80
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)