Electronic Supplementary Information

Visible light-mediated dehydrogenative β-arylsulfonylation of tertiary aliphatic amines with arylsulfonyl chlorides

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Content

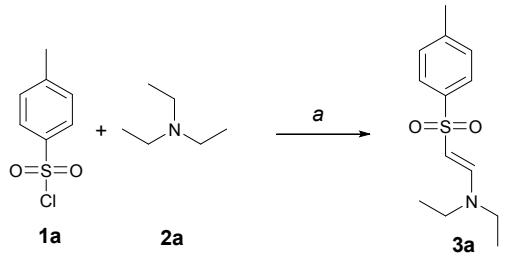
1. General methods

Unless specified noted, all reagents were purchased from commercial suppliers without further purification. Column chromatography was performed using 200-300 mesh silica gel (YanTai, China). ^{1}H NMR spectra were recorded on BRUKER 400 (400 MHz) spectrophotometer. Chemical shifts (δ) are reported in ppm from TMS as the internal standard (TMS 0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs=broad singlet, d = doublet, t = triplet, q =quartlet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on BRUKER 400 (100 MHz) with complete proton decoupling spectrophotometer. Mass spectra were measured on Bruker Apex IV FTMS (ESI), infrared spectroscopy was carried out on Nicolet iS460 FT-IR Thermo Fisher Scientific infrared spectrometer.

2. Optimization of the reaction of triethylamine with *p*-toluene sulfonyl chloride

A 25 ml round bottomed flask equipped with a stirring-bar was charged with *p*-tolylsulfonyl chloride (**1a,** 1 mmol), photocatalyst, and additives in solvent, and then pre-bathed in ice-salt -water mixtures for 5 minutes. Subsequently, triethylamine was added to the system when 23 w fluorescent light turned on with gentle stirring. With TsCl completely consumed, the reaction mixture was diluted with CH_2Cl_2, silica gel added to, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

Table S1 Evaluation of various parameters in the photoredox reaction



1a **2a** **3a**

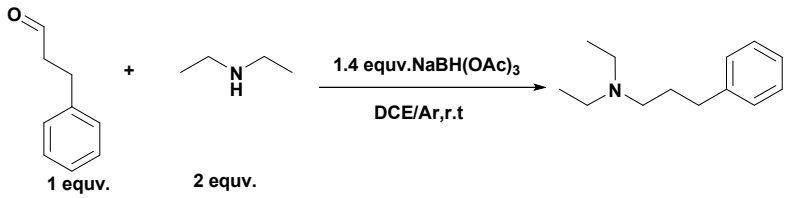
Entry[a]	Photocatalyst	Solvent	Ratio of **2a**/**1a**	Additive	Yield[b]

1	$Ru(bpy)_3(PF_6)_2$	CH_3CN	2	_	22%
2	$Ru(bpy)_3(PF_6)_2$	CH_3CN	3	_	37%
3	$Ru(bpy)_3(PF_6)_2$	CH_3CN	4	_	46%
4	$Ru(bpy)_3(PF_6)_2$	CH_3CN	6	_	46%
5	$Ru(bpy)_3(PF_6)_2$	CH_3CN	1/3	_	12%
6[c]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	4	_	22%
7[d]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	4	_	14%
8	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	47%
9[e]	$Ru(bpy)_3(PF_6)_2$	DMF	5	_	Trace
10[e]	$Ru(bpy)_3(PF_6)_2$	DMSO	4	_	Trace
11[e]	$Ru(bpy)_3(PF_6)_2$	NMP	4	_	Trace
12	$Ru(bpy)_3(PF_6)_2$	CH_3OH	4	_	Trace
13[e]	$Ru(bpy)_3(PF_6)_2$	Aceton/H_2O	4	_	40%
14	$Ru(bpy)_3(PF_6)_2$	Acetone	4	K_3PO_4	23%
15	$Ru(bpy)_3(PF_6)_2$	Acetone	4	K_2HPO_4	26%
16	$Ru(bpy)_3(PF_6)_2$	Acetone	4	MgSO4	46%
17	$Ru(bpy)_3(PF_6)_2$	Acetone	4	4Å MS	38%
18	$Ru(bpy)_3(PF_6)_2$	Acetone	4	Silica gel	30%
19	$Ru(bpy)_3(PF_6)_2$	Acetone	4	NBS	39%
20	$Ru(bpy)_3(PF_6)_2$	Acetone	4	$RuCl_3$	Trace
21	$Ru(bpy)_3(PF_6)_2$	Acetone	4	MV^{2+}	Trace
22[f]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	25%
23[g]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	37%
24[h]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	47%
25[i]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	47%
26[j]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	42%
27	$Ru(bpz)_3(PF6)_2$	Acetone	4	_	44%
28	$Ir(ppy)_2(bpy)PF_6$	Acetone	4	_	40%

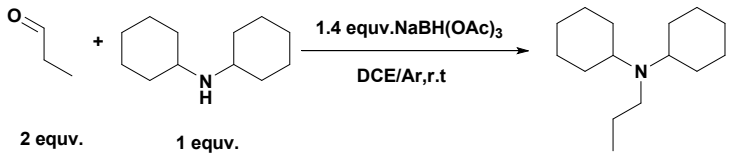
29	$Ir(ppy)_2(dtbbpy)PF_6$	Acetone	4	_	39%
30	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	Acetone	4	_	37%
31[k]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	_[l]
32	_	Acetone	4	_	Trace
33[m]	$Ru(bpy)_3(PF_6)_2$	Acetone	4	_	Trace

[a] Unless otherwise specified, all reactions were carried out with **2a**, **1a** (1 mmol), photocatalyst (2.5% mol), under 23 w fluorescent light at -5 to 5 °C open to air with gentle stirring for 5minutes. [b] Isolated yield. [c] At temperature of 25 °C. [d] At temperature of -30 °C, 8h. [e] the mixture was poured into ether and water after concentrated, then organic phase was washed by water and brine, and dried by Na_2SO_4 [f] at the concentration of 1M. [g] at the concentration of 0.02M. [h] 5 mol % photocatalyst. [i] 1 mol % photocatalys [j] 0.5 mol % photocatalyst [k] fierce stirring. [l] most of the product was sulfonamide. [m] No light

3. Synthesis of tertiary amines



According to the reference (*J. Org. Chem*. **1996**, *61*, 3849), to an round bottomed flask equipped with a stirring stir bar under Ar atmosphere was added 2 equiv of ethylamine and 1.0 equiv. of 3-phenylpropanal in 1,2- dichloroethane(DCE), and then treated with 1.4 equiv. of sodium triacetoxy borohydride($NaBH(OAc)_3$). After the complete consumption of the 3-phenylpropanal, the mixture was quenched by adding saturated aqueous $NaHCO_3$ solution and extracted with ether. The combined organic layer was washed with 1M HCl and then pH of aqueous phase was to adjust to 10 by 1M NaOH solution. Ether was added to extracted free amine, subsequently dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was used without further purification.



According to the reference (*J. Org. Chem*. **1996**, *61*, 3849), to an round bottomed flask equipped with a stirring stir bar under Ar atmosphere was added 2 equiv of propanal and 1.0 equiv. dicyclohexylamine in 1,2- dichloroethane(DCE), and then treated with 1.4 equiv. of sodium triacetoxy borohydride($NaBH(OAc)_3$). After 24h, the mixture was quenched by adding saturated aqueous $NaHCO_3$ solution and extracted with ether. The combined organic layer was washed with 1M HCl and then pH of aqueous phase was to adjust to 10 by 1M NaOH solution. Ether was added to extracted free amine, subsequently dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was used without further purification.

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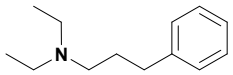
4. General procedure for β-arysulfonylation of tertiary aliphatic amines with arysulfonyl chlorides

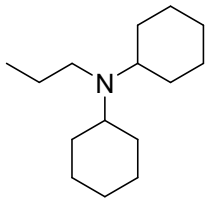
A 25ml round bottomed flask equipped with a stirring-bar was charged with arylsulfonyl chloride (1 mmol), photocatalyst (1 mol%), in acetone, and then pre-bathed in ice-salt - water mixtures for 5 minutes. Subsequently, tertiary amine was added to the system when 23 w fluorescent light turned on with gentle stirring. With arylsulfonyl chloride completely consumed, the reaction mixture was diluted with CH_2Cl_2, silica gel added to, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product.

5. Experimental data for the described substances



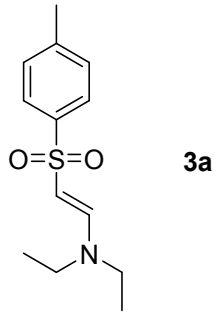
***N*, *N*-diethyl-3-phenylpropan-1-amine**

Yielding the title compound as light yellow oil in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, J = 7.5 Hz, 2H), 7.15-7.20 (m, 3H), 2.61 (t, J = 7.8 Hz, 2H), 2.52 (q, J = 7.1 Hz, 4H), 2.46 (t, J = 7.6 Hz, 2H), 1.74-1.82 (m, 2H), 1.00 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 128.6, 128.5, 125.9, 52.7, 47.1, 34.1, 28.9, 11.9. IR (film, cm^{-1}): ν 2928, 2853, 2809, 1450. HRMS (ESI): Calcd for $C_{13}H_{22}N$ $[MH]^+$: m/z 192.1747; found: 192.1744.



***N*-cyclohexyl-*N*-propylcyclohexanamine**

Yielding the title compound as light yellow oil in quantitative yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.49-2.54 (m, 2H), 2.40-2.44 (m, 2H), 1.70-1.75 (m, 7H), 1.57-1.61 (m, 3H), 1.37 (q, J = 7.5 Hz, 2H), 1.17-1.24 (m, 8H), 1.05-1.08 (m, 2H), 0.82 (q, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 58.3, 48.8, 31.9, 26.7, 26.6, 25.0, 11.9. IR (film, cm^{-1}): ν 2968, 2935, 2870, 2799. HRMS (ESI):Calcd for $C_{15}H_{30}N$ $[MH]^+$: m/z 224.2373; found: 224.2368.

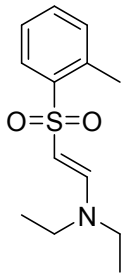


3a

(*E*)-*N*, *N*-diethyl-2-tosylethenamine

Prepared according to the general procedure from **1a** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 3minutes to provide the

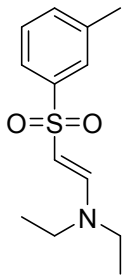
title compound as a white solid (47% yield). M.p.: 80-81°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 12.8. Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.90 (d, J = 12.8 Hz, 1H), 3.16(bs, 4H), 2.39 (s, 3H), 1.14 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ148.8, 142.6, 142.1, 129.5, 126.2, 91.8, 50.1(bs), 42.8(bs), 21.5, 14.8(bs), 11.3(bs) , **^{13}C NMR (125 MHz, DMSO, 100°C): 149.5, 144.2, 142.0, 129.9, 126.2, 92.8, 46.2, 21.3, 13.2.** IR (film, cm^{-1}): v 3076, 2977, 2935, 2876, 1617(vs), 1493, 1450. HRMS (ESI): Calcd for $C_{13}H_{20}O_2NS$ $[MH]^+$: m/z 254.1209; found: 254.1206.



3b

(*E*)-*N* , *N*-diethyl-2-(o-tolylsulfonyl)ethenamine

Prepared according to the general procedure from **2-methylbenzene-1-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (47% yield). M.p.: 51-52°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 1H), 7.36-7.40 (m, 1H), 7.23-7.30 (m, 3H), 4.92 (d, J = 12.8 Hz, 1H), 3.17(q, J = 8 Hz, 4H), 2.62 (s, 3H), 1.14 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ149.6, 142.8, 136.4, 132.2, 131.8, 127.6, 126.1, 90.6, 50.1(bs), 42.8(bs), 20.2, 14.8(bs), 11.3(bs) , IR (film, cm^{-1}): v 3066, 2976, 2922, 2871, 1613(vs), 1493, 1468. HRMS (ESI): Calcd for $C_{13}H_{20}O_2NS$ $[MH]^+$: m/z 254.1209; found: 254.1205.

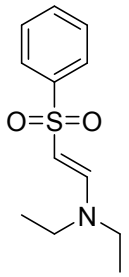


3c

(*E*)-*N*,*N*-diethyl-2-(m-tolylsulfonyl)ethenamine

Prepared according to the general procedure from **3-methylbenzene-1-sulfonyl chloride** (1

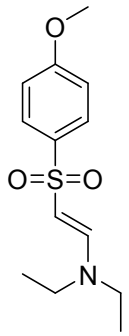
mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (45% yield). M.p.: 72-73°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.67 (m, 2H), 7.28-7.30 (m, 3H), 4.90 (d, J = 12.8 Hz, 1H), 3.17(broad doublet, 4H), 2.40 (s, 3H), 1.15 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ148.9, 145.2, 138.9, 132.3, 128.7, 126.4, 123.2, 91.3, 50.0(bs), 42.7(bs), 21.4, 14.2(bs), 11.2(bs) , IR (film, cm^{-1}): v 3063, 2976, 2935, 2872, 1614(vs), 1469. HRMS (ESI): Calcd for $C_{13}H_{20}O_2NS$ $[MH]^+$: m/z 254.1209; found: 254.1205.



3d

(*E*)-*N*,*N*-diethyl-2-(m-tolylsulfonyl)ethenamine

Prepared according to the general procedure from **benzenesulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (40% yield). M.p.: 45-46°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84-7.86 (m, 2H), 7.43-7.48 (m, 3H), 7.31 (d, J = 12.8 Hz, 1H), 4.91 (d, J = 12.8 Hz, 1H), 3.17(broad doublet, 4H), 1.14 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ149.1, 145.4, 131.5, 128.8, 126.0, 91.1, 50.1(bs), 42.7(bs), 14.7(bs), 11.2(bs) , IR (film, cm^{-1}): v 3069, 2977, 2936, 2875, 1614(vs), 1452, 1468. HRMS (ESI): Calcd for $C_{12}H_{18}O_2NS$ $[MH]^+$: m/z 240.1053; found: 254.1050.

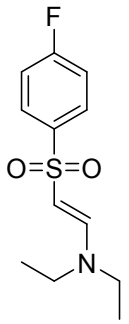


3e

(*E*)-*N*,*N*-diethyl-2-(4-methoxyphenylsulfonyl)ethenamine

Prepared according to the general procedure from **4-methoxybenzene-1-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light

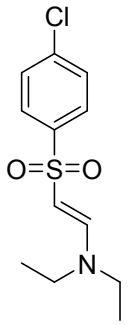
irradiation for 5 minutes to provide the title compound as a white solid (41% yield). M.p.: 74-75°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78(d, J = 8.4 Hz, 1H), 7.28 (d, J = 12.8 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.90 (d, J = 12.8 Hz, 1H), 3.84(s, 3H), 3.16 (bs, 4H), 1.14 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ162.1, 148.6, 137.4, 128.3, 114.1, 92.3, 55.7, 50.0(bs), 42.4(bs), 14.8(bs), 11.4(bs) , IR (film, cm^{-1}): v 3069, 2975, 2934, 2872, 1612(vs), 1495, 1460. HRMS (ESI): Calcd for $C_{13}H_{20}O_3NS$ $[MH]^+$: m/z 270.1158; found: 270.1155.



3f

(*E*)-*N*,*N*-diethyl-2-(4-methoxyphenylsulfonyl)ethenamine

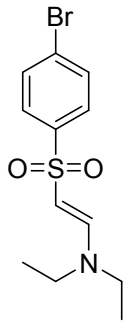
Prepared according to the general procedure from **4-fluorobenzene-1-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid (33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.87(m, 2H), 7.31 (d, J = 12.7 Hz, 1H), 7.12 (t, J = 8.6 Hz, 2H), 4.89 (d, J = 12.7 Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ165.6, 163.1, 149.2, 141.65, 141.62, 128.8, 128.7, 116.0, 115.8, 91.1, 50.2(bs), 42.7(bs), 14.7(bs), 11.1(bs) , IR (film, cm^{-1}): v 3073, 2979, 2934, 2881, 1615(vs), 1493, 1469. HRMS (ESI): Calcd for $C_{12}H_{17}O_2NFS$ $[MH]^+$: m/z 258.0959; found: 258.0956.



3g

(*E*)-2-(4-chlorophenylsulfonyl)-*N*,*N*-diethylethenamine

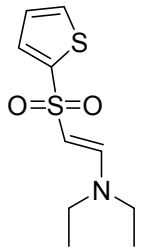
Prepared according to the general procedure from **4-chlorobenzene-1-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 3 minutes to provide the title compound as a white solid (42% yield). M.p.: 42-43°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 8.4 Hz, 2H), 7.29 (d, J = 12.8 Hz, 1H), 4.87 (d, J = 12.8 Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 144.1, 137.8, 129.1, 127.7, 90.9, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs) , IR (film, cm^{-1}): ν 3077, 2976, 2934, 2872, 1613(vs), 1507. HRMS (ESI): Calcd for $C_{12}H_{17}O_2N^{35}ClS$ $[MH]^+$: m/z 274.0663; found: 274.0659.



3h

(*E*)-2-(4-bromophenylsulfonyl)-*N,N*-diethylethenamine

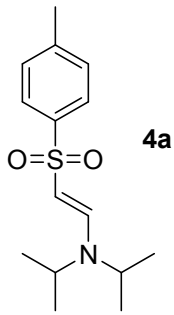
Prepared according to the general procedure from **4-bromobenzene-1-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (45% yield). M.p.: 94-95°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 12.8 Hz, 1H), 4.87 (d, J = 12.8 Hz, 1H), 3.18 (broad doublet, 4H), 1.15 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 144.6, 132.1, 127.9, 126.2, 90.8, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs) , IR (film, cm^{-1}): ν 3069, 2969, 2920, 2850, 1610(vs), 1569. HRMS (ESI): Calcd for $C_{12}H_{17}O_2N^{79}BrS$ $[MH]^+$: m/z 318.0158; found: 318.0155.



3i

(*E*)-*N,N*-diethyl-2-(thiophen-2-ylsulfonyl)ethenamine

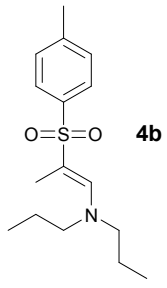
Prepared according to the general procedure from **thiophene-2-sulfonyl chloride** (1 mmol), **2a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 5 minutes to provide the title compound as a white solid (47% yield). M.p.: 75-77°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.52 (m, 2H), 7.33 (t, J = 12.8. Hz, 2H), 7.00-7.03 (m, 1H), 4.87 (d, J = 12.8 Hz, 1H), 3.18 (m, 4H), 1.17 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.2, 130.5, 130.0, 127.2, 92.1, 50.2(bs), 42.8(bs), 14.8(bs), 11.2(bs) , IR (film, cm^{-1}): ν 3078, 2976, 2934, 2875, 1613(vs), 1507. HRMS (ESI): Calcd for $C_{10}H_{16}O_2NS_2$ $[MH]^+$: m/z 246.0617; found: 246.0614.



4a

(*E*)-*N*, *N*-diethyl-2-tosylethenamine

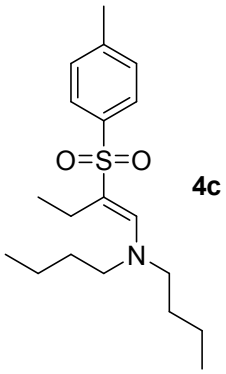
Prepared according to the general procedure from ***N*-ethyldiisopropylamine** (4 mmol), **1a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 3minutes to provide the title compound as a white solid (41% yield). M.p.: 133-134°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 12.8. Hz, 1H), 7.25 (d, J = 7.2 Hz, 2H), 4.96 (d, J = 12.8 Hz, 1H), 3.56(bs, 4H), 2.39 (s, 3H), 1.20 (bs, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 142.8, 142.0, 129.5, 126.3, 91.9, 49.4(bs), 47.7(bs), 21.7, 21.6(bs) , 19.7(bs) IR (film, cm^{-1}): ν 3074, 2976, 2925, 2869, 1607(vs), 1542. HRMS (ESI): Calcd for $C_{15}H_{24}O_2NS$ $[MH]^+$: m/z 282.1522; found: 282.1519.



4b

(*E*)-*N*,*N*-dipropyl-2-tosylprop-1-en-1-amine

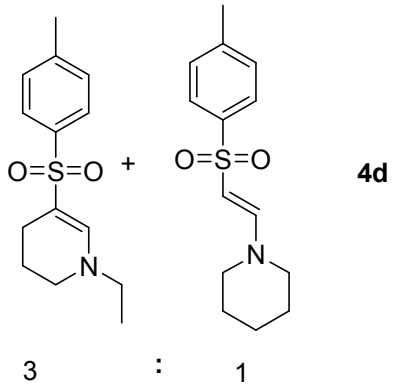
Prepared according to the general procedure from **tri-n-propylamine** (4 mmol), **1a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid (41% yield). M.p.: 86-87°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.0 Hz, 2H), 7.31 (s, 1H), 7.25 (d, J = 8 Hz, 2H), 3.15 (t, J = 7.6 Hz, 4H), 2.40(s, 3H), 1.87 (s, 3H), 1.56-1.61 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 142.3, 139.8, 129.5, 127.2, 97.1, 54.8, 22.8, 21.6, 11.1, 11.0. IR (film, cm^{-1}): v 2964, 2933, 2874, 1628(vs), 1495, 1457. HRMS (ESI): Calcd for $C_{16}H_{26}O_2NS$ $[MH]^+$: m/z 296.1679; found: 296.1678.



4c

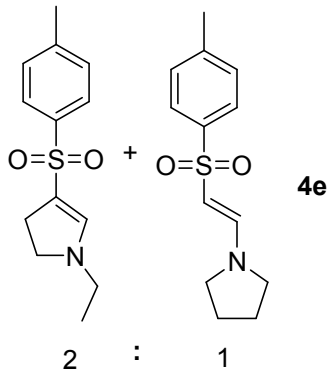
(*E*)-*N*,*N*-dibutyl-2-tosylbut-1-en-1-amine

Prepared according to the general procedure from **tri-n-butylamine** (4 mmol), **1a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 40 minutes in room temperature to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, providing a white solid (36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8 Hz, 2H), 7.31 (s, 1H), 7.25 (d, J = 8 Hz, 2H), 3.17 (t, J = 7.6 Hz, 4H) , 2.40(s, 3H), 2.21 (q, J = 8 Hz, 2H), 1.52-1.56(m, 4H), 1.28-1.33(m, 4H), 0.93 (t, J = 7.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 142.2, 140.8, 129.4, 127.2, 104.2, 52.8, 31.4, 21.6, 19.9, 18.8, 16.0, 13.9. IR (film, cm^{-1}): v 2959, 2929, 2872, 1620(vs), 1460. HRMS (ESI): Calcd for $C_{19}H_{32}O_2NS$ $[MH]^+$: m/z 338.2148; found: 338.2141.



4d

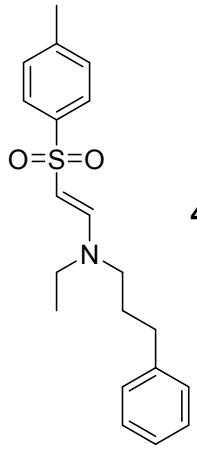
Prepared according to the general procedure from ***1-ethylpiperidine*** (4 mmol), **1a** (1 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid with two regioisomers (41% yield), and then the major isomer was separated from the other by semi-HPLC. Major isomer M.p.: 105-108°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J =8 Hz, 2H), 7.31 (s, 1H), 7.25 (d, J = 8 Hz, 2H), 3.19 (q, J = 7.2 Hz, 2H), 3.04 (q, J = 5.6 Hz, 2H), 2.40(s, 3H), 2.15 (q, J = 6.0 Hz, 2H), 1.80 (m, 2H), 1.16 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.3, 140.2, 129.6, 127.0, 100.1, 50.6, 45.0, 21.7, 21.3, 19.9, 14.0. IR (film, cm^{-1}): v 3048, 2963, 2923, 2852, 1616(vs), 1491, 1468. HRMS (ESI): Calcd for $C_{14}H_{20}O_2NS$ $[MH]^+$: m/z 266.1209; found: 266.1206. Minor isomer ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J =8 Hz, 2H), 7.23-7.26 (m, 3H), 4.95 (d, J = 12.8 Hz, 1H), 3.15 (bs, 3H), 2.40 (s, 3H), 1.60(bs, 7H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 142.5, 142.2, 129.5, 126.3, 92.5, 60.5, 23.9, 21.2, 14.3 . HRMS (ESI): Calcd for $C_{14}H_{20}O_2NS$ $[MH]^+$: m/z 266.1209; found: 266.1206.



4e

Prepared according to the general procedure from ***1-methylpiperidine*** (4 mmol), **1a** (1 mmol),

$Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the title compound as a white solid with two regioisomers (36% yield), and then the major isomer was separated from the other by semi-HPLC. Major isomer M.p.: 87-88°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J =8 Hz, 2H), 7.27 (d, J = 8 Hz, 2H), 7.00 (s, 1H), 3.46 (q, J = 6 Hz, 2H), 3.07 (q, J = 7.2 Hz, 2H), 2.68 (q, J = 6 Hz, 2H), 2.41(s, 3H), 1.15 (q, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 142.6, 139.9, 129.6, 126.7, 106.1, 52.2, 44.8, 27.7, 21.6, 13.6, IR (film, cm^{-1}): ν 3062, 2973, 2930, 2855, 1577(vs), 1493, HRMS (ESI): Calcd for $C_{13}H_{18}O_2NS$ $[MH]^+$: m/z 252.1053; found: 266.1050. Minor isomer M.p.: 123-125°C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J =8 Hz, 2H), .7.51(d, J =12.8 Hz, 1H), 7.25 (d, J =8 Hz, 2H), 4.82 (d, J = 12.8 Hz, 1H), 3.45 (bs, 2H), 3.03 (bs, 2H), 2.40(s, 3H), 1.92 (bs, 4H),.^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 142.7, 142.2, 129.6, 126.4, 93.1, 25.5, 21.6, 14.4. IR (film, cm^{-1}): ν 3062, 2955, 2921, 2852, 1612(vs), 1458, HRMS (ESI): Calcd for $C_{13}H_{18}O_2NS$ $[MH]^+$: m/z 2652.1051; found: 252.1053.

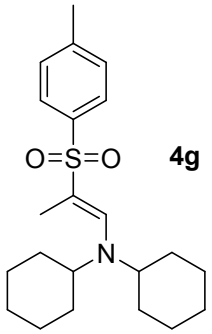


4f

(*E*)-N-ethyl-3-phenyl-N-(2-tosylvinyl)propan-1-amine

Prepared according to the general procedure from ***N*-ethyl-3-phenyl-N-propylpropan-1-amine** (4 mmol), **1a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 40 minutes to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, providing a white solid (25% yield). M.p.: 58-59°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2H), 7.12-7.29 (m, 8H), 4.90(bs, 1H), 3.13 (bs, 4H), 2.58 (d, J = 7.2 Hz, 2H), 2.39(s, 3H),

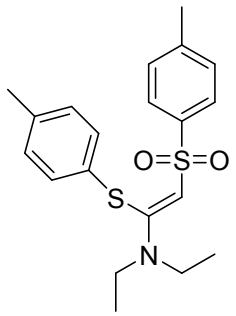
1.87 (d, J = 7.2 Hz, 2H), 1.11 (bs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 142.6, 142.2, 140.8, 129.5, 128.7, 128.4, 126.4, 126.3, 92.2, 32.9(bs), 21.6 . IR (film, cm^{-1}): v 3060, 3024, 2971, 2931, 2870, 1613(vs), 1495. HRMS (ESI): Calcd for $C_{20}H_{26}O_2NS$ $[MH]^+$: m/z 344.1679; found: 344.1674.



4g

(*E*)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine

Prepared according to the general procedure from ***N-cyclohexyl-N-propylcyclohexanamine*** (4 mmol), **1a** (4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.01 mmol) and acetone (5 mL) under visible light irradiation for 10 minutes to provide the crude product with little amine. Then it was dissolved in ether and washed with 1M HCl. Subsequently organic phase was washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, providing a white solid (36% yield). M.p.: 138-140^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.0 Hz, 2H), 7.45 (s,1H), 7.26 (d, J = 8.0 Hz, 2H), 3.34(bs, 2H), 2.40 (s, 3H), 1.89 (s, 3H), 1.80-1.83(m, 4H), 1.70-1.76(m, 4H), 1.63-1.66(m, 2H), 1.45-1.55(m, 4H), 1.22-1.32(m, 4H), 1.08-1.17(m, 2H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 142.0, 140.1, 129.5, 127.2, 96.2, 57.0, 33.3, 26.1, 25.4, 21.6, 12.3 . IR (film, cm^{-1}): v 2930, 2855, 1618(vs), 1492. HRMS (ESI): Calcd for $C_{20}H_{26}O_2NS$ $[MH]^+$: m/z 376.2305; found: 376.2299.

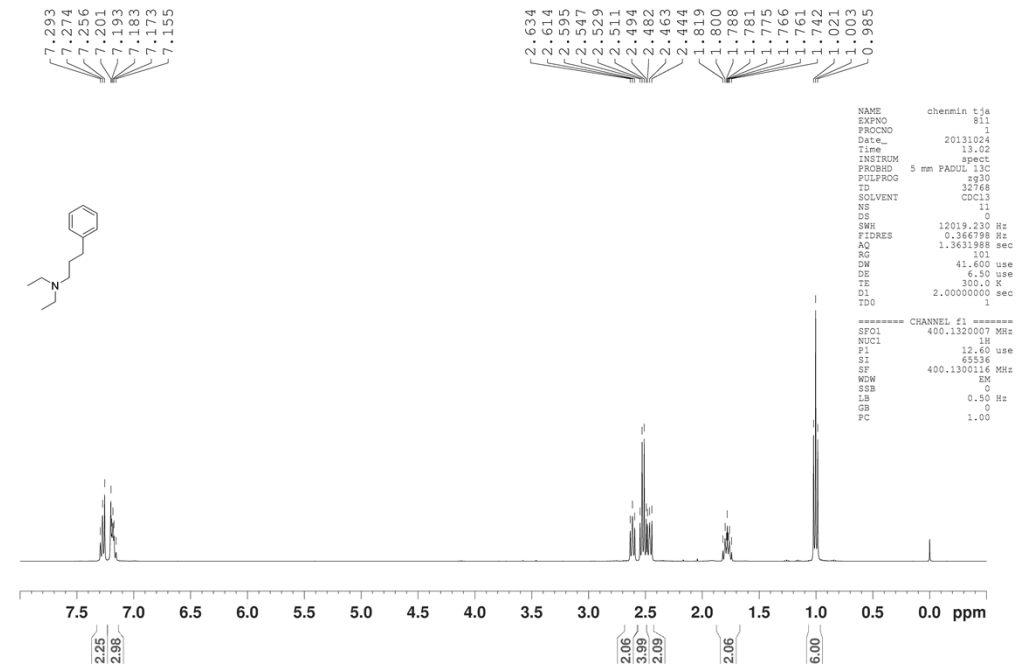


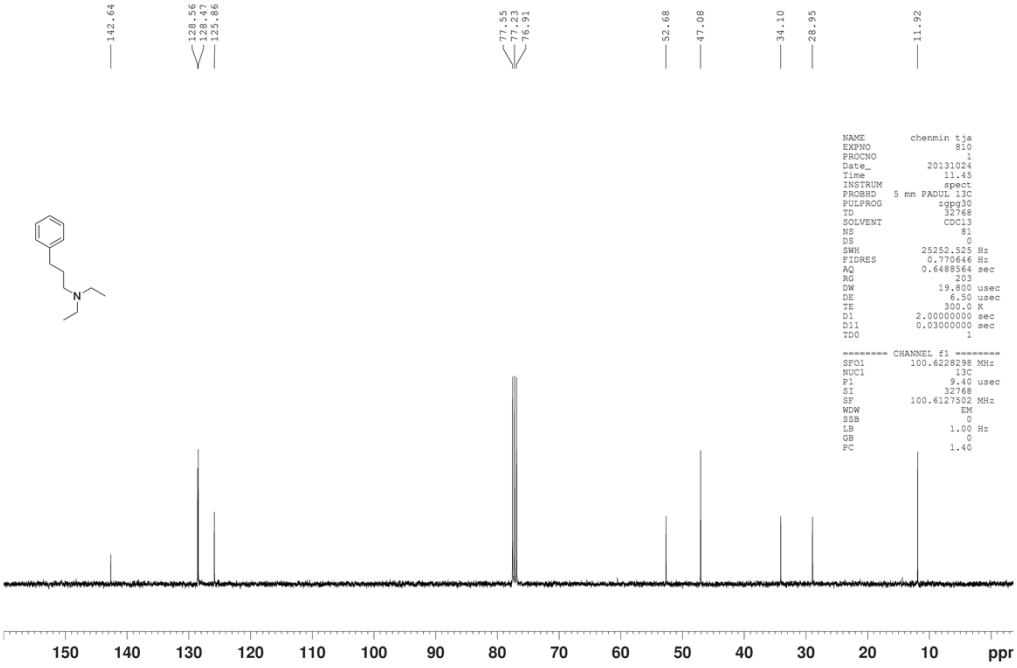
(*E*)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine

A 25 ml Schlenk tube equipped with stir-bar was charged with **1a** (1 mmol), photocatalyst $Ru(bpy)_3(PF_6)_2$ 1 mol %), the system was evacuated 3 times and backfilled with Ar ,then solvent 5 ml CH_3CN and **triethylamine** (4 mmol) were added by syringe. After 3h under 23 w fluorescent light, the reaction mixture was diluted with CH_2Cl_2 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product. M.p.: 85-86^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12(s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.92 (s, 4H), 3.58(bs, 2H), 3.33(bs, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.24 (bs, 3H), 1.08(m, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 142.4, 139.4, 135.3, 134.8, 129.5, 129.1, 127.9, 125.1, 91.8, 21.5, 21.0 . IR (film, cm^{-1}): v 2975, 2930, 2868, 1599(vs), 1491. HRMS (ESI): Calcd for $C_{20}H_{26}O_2NS_2$ $[MH]^+$: m/z 376.1390; found: 376.1395.

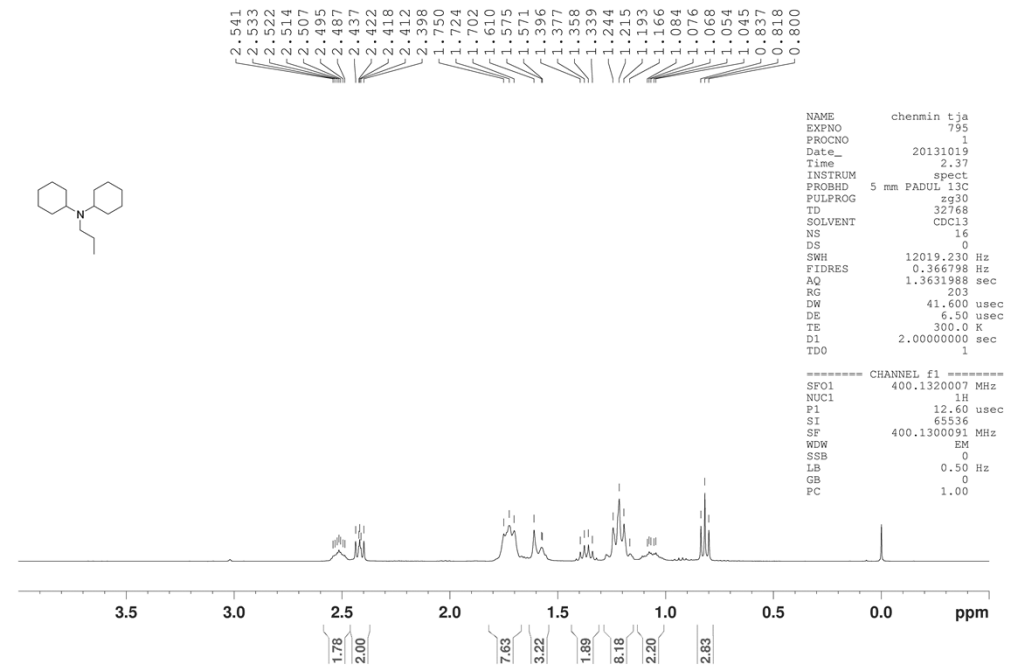
6. Copies of ^{1}H, ^{13}C NMR spectra and HRMS spectra

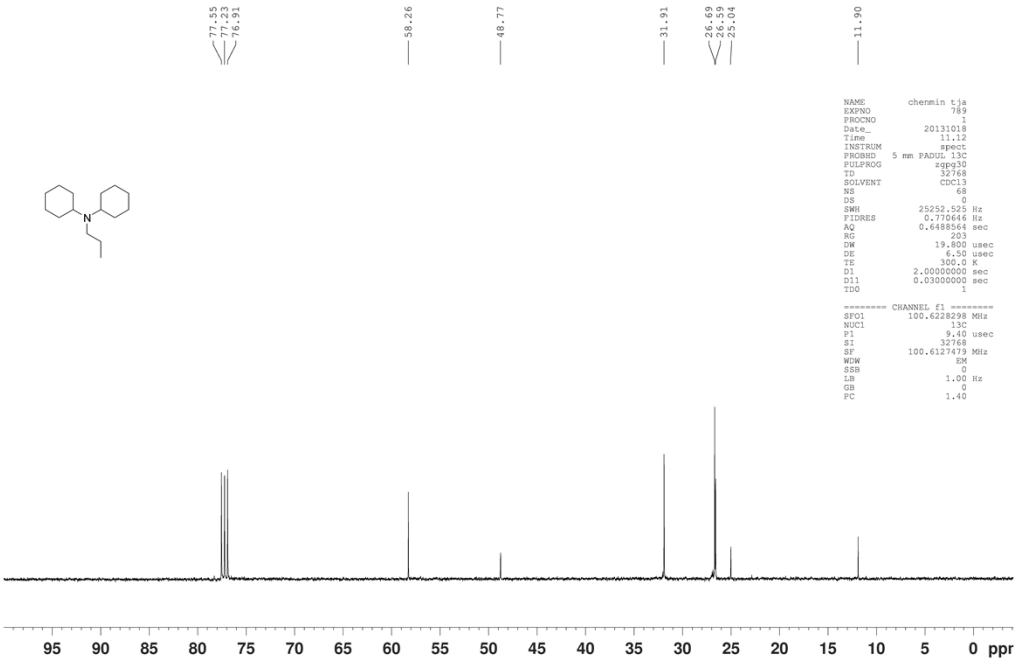
***N*, *N*-diethyl-3-phenylpropan-1-amine**



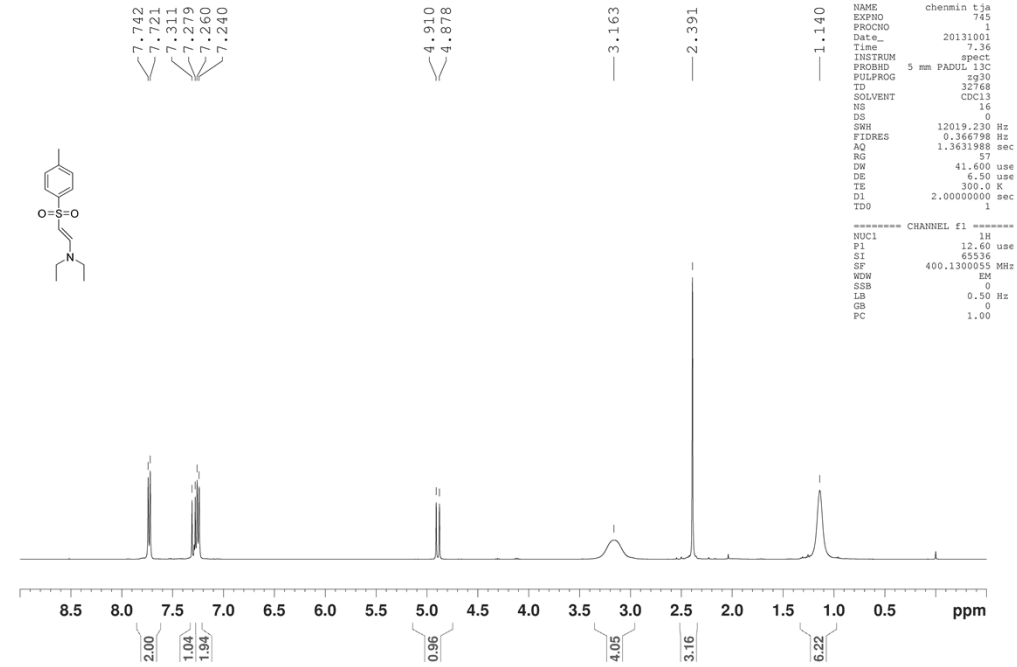


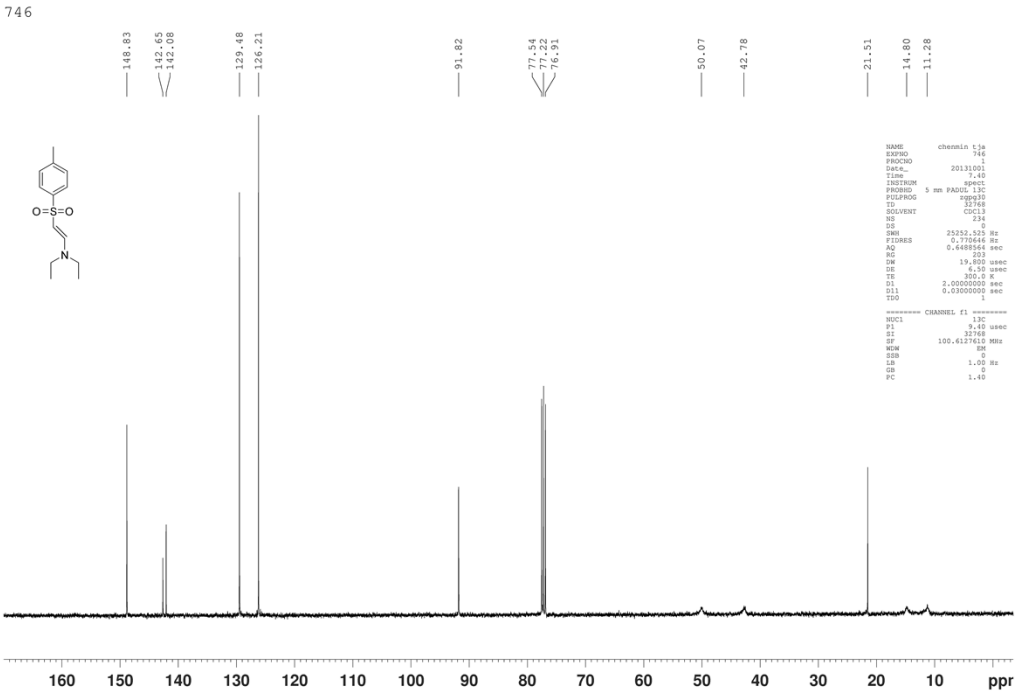
***N*-cyclohexyl-*N*-propylcyclohexanamine**



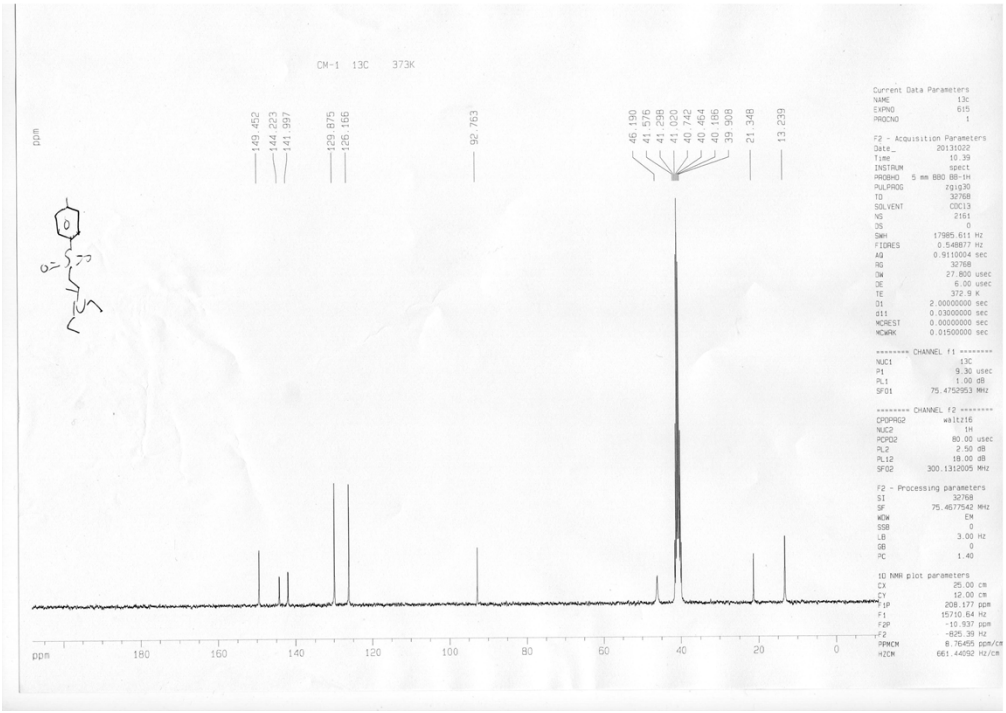


(*E*)-*N*, *N*-diethyl-2-tosylethenamine





373K(DMSO)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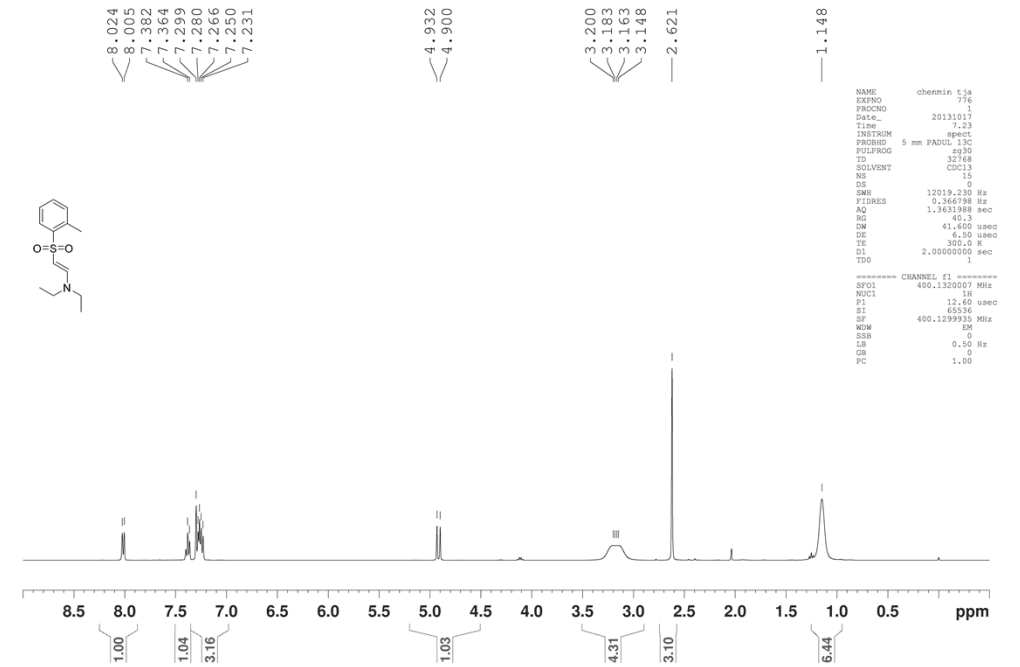
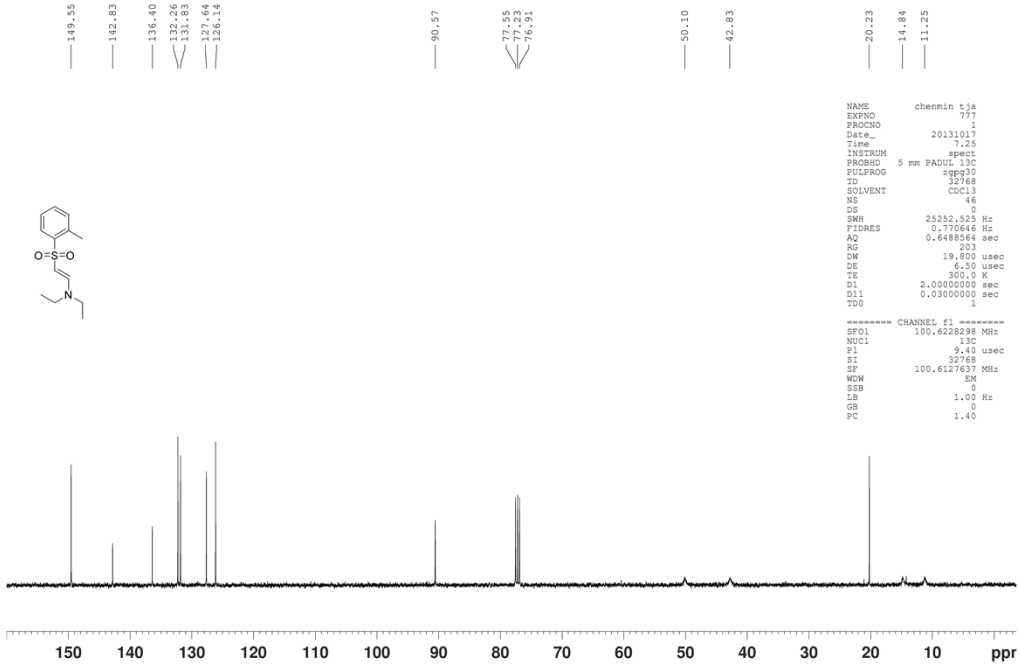
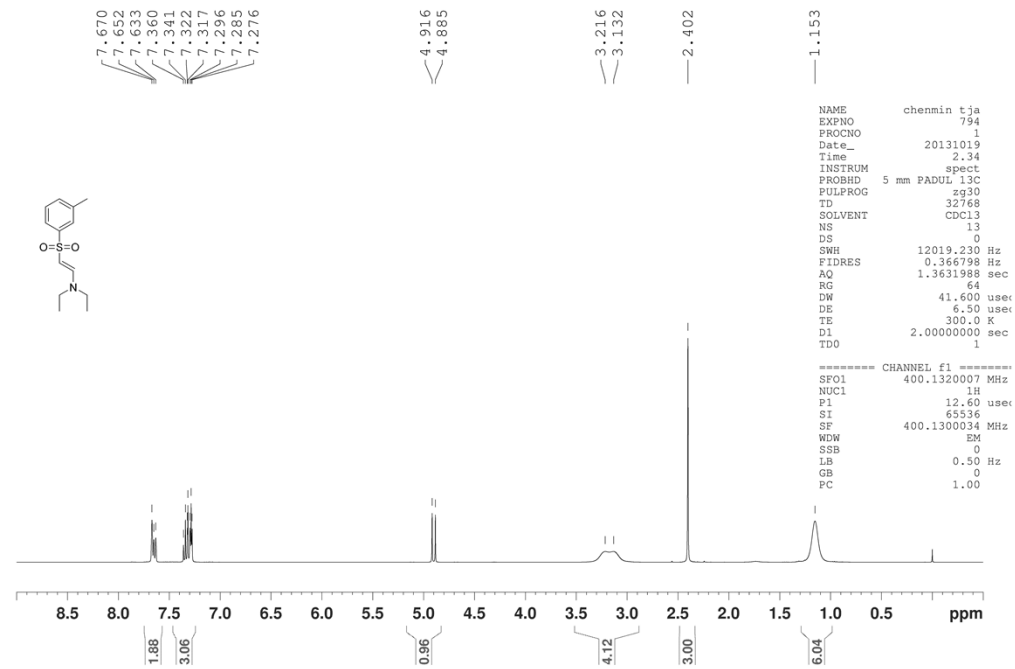
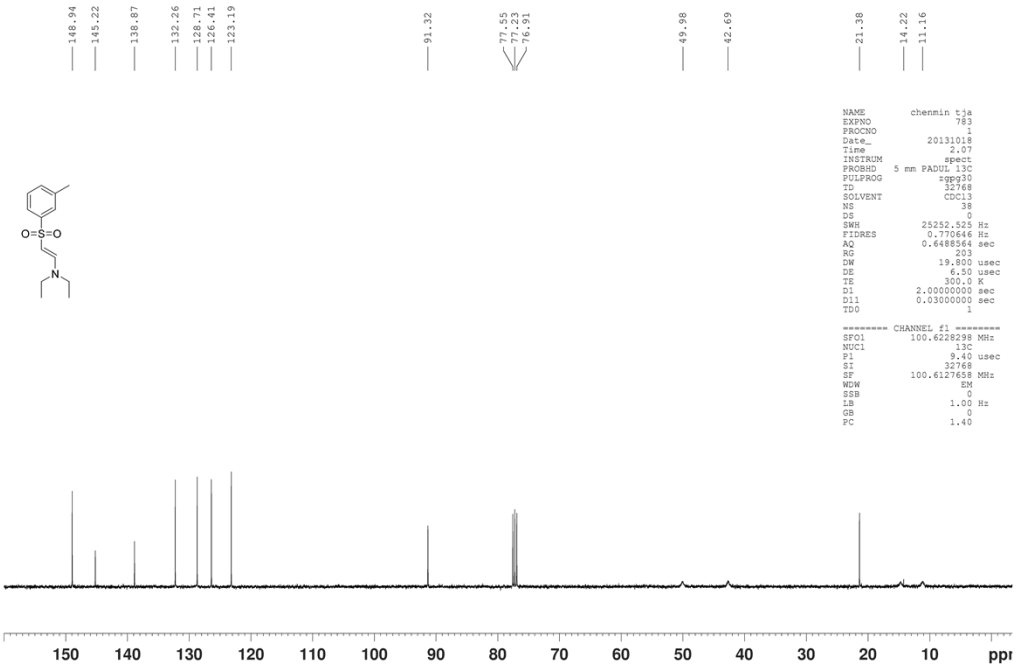
(*E*)-*N* , *N*-diethyl-2-(o-tolylsulfonyl)ethenamine



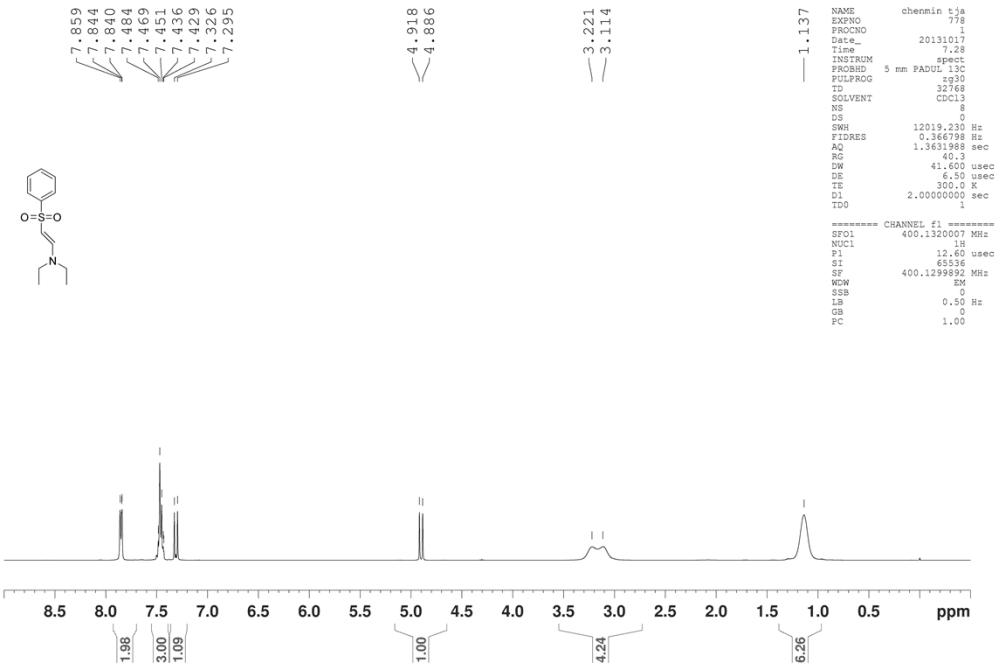


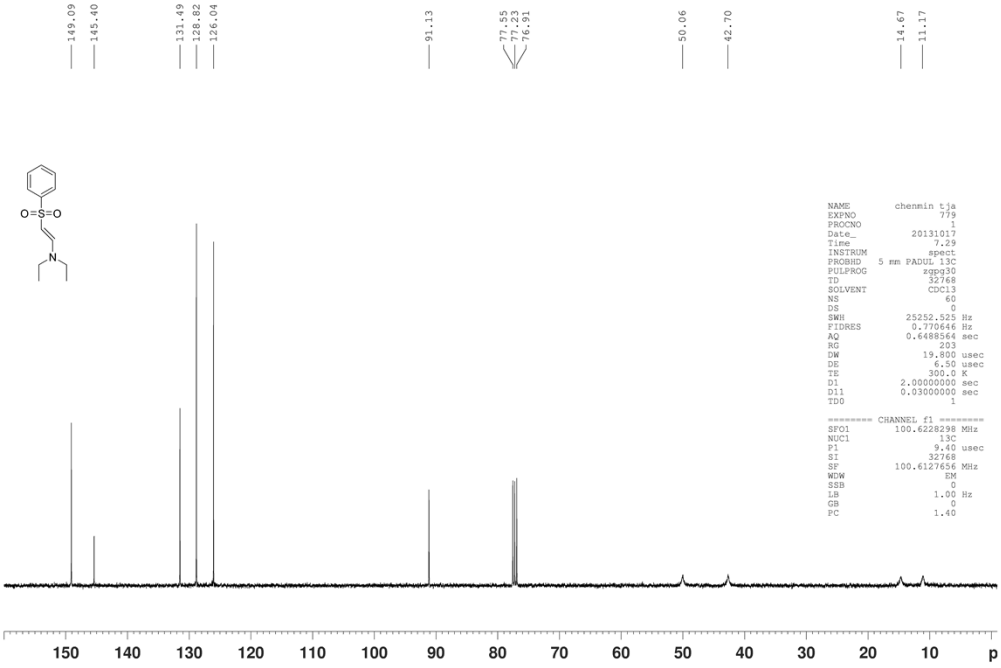
(*E*)-*N*,*N*-diethyl-2-(m-tolylsulfonyl)ethenamine



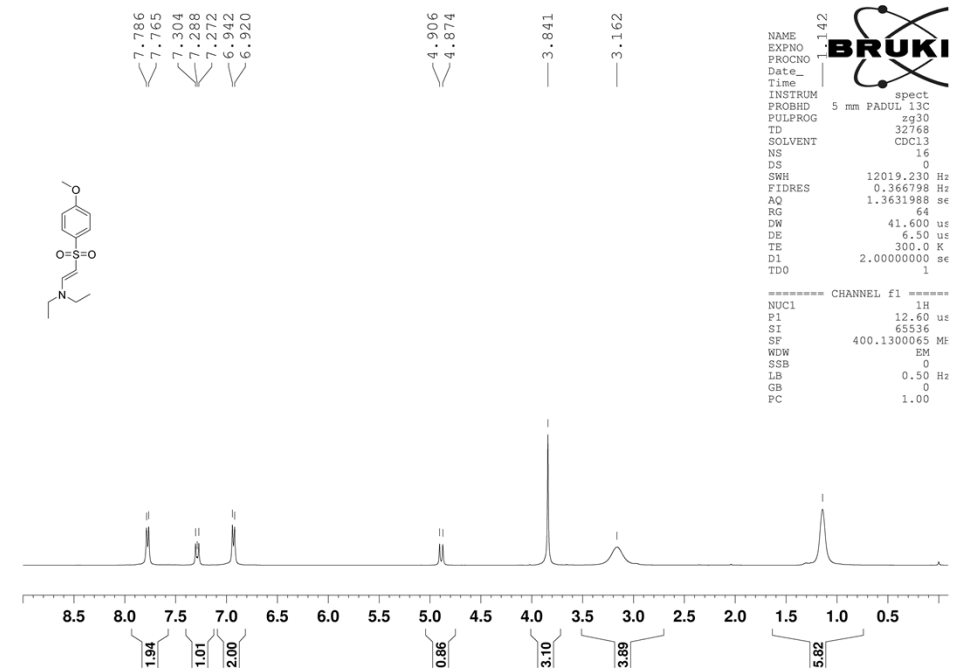


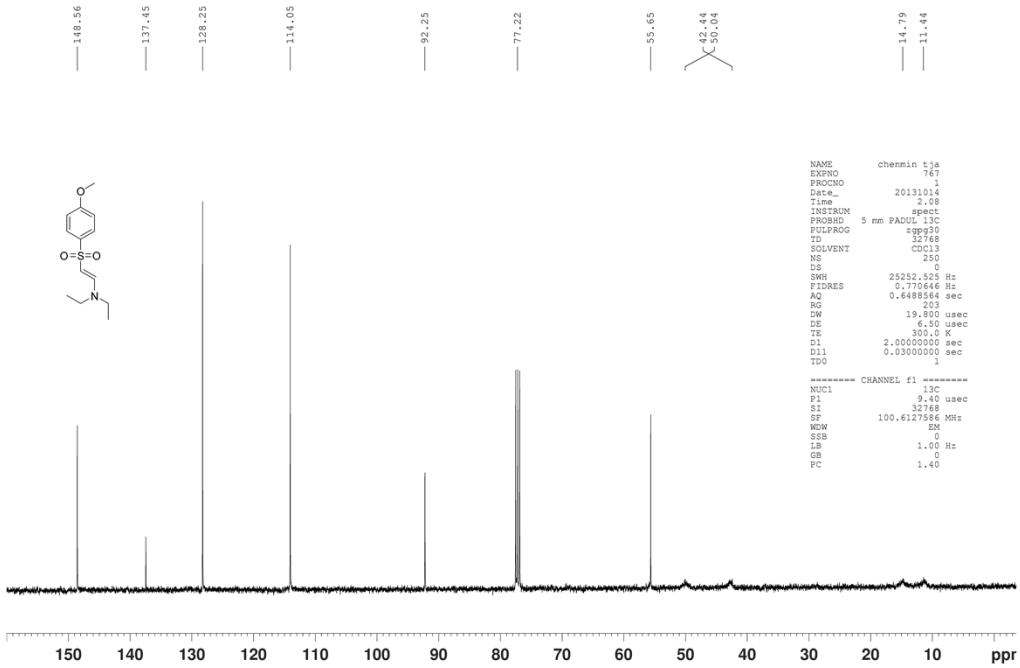
(*E*)-*N*,*N*-diethyl-2-(m-tolylsulfonyl)ethenamine



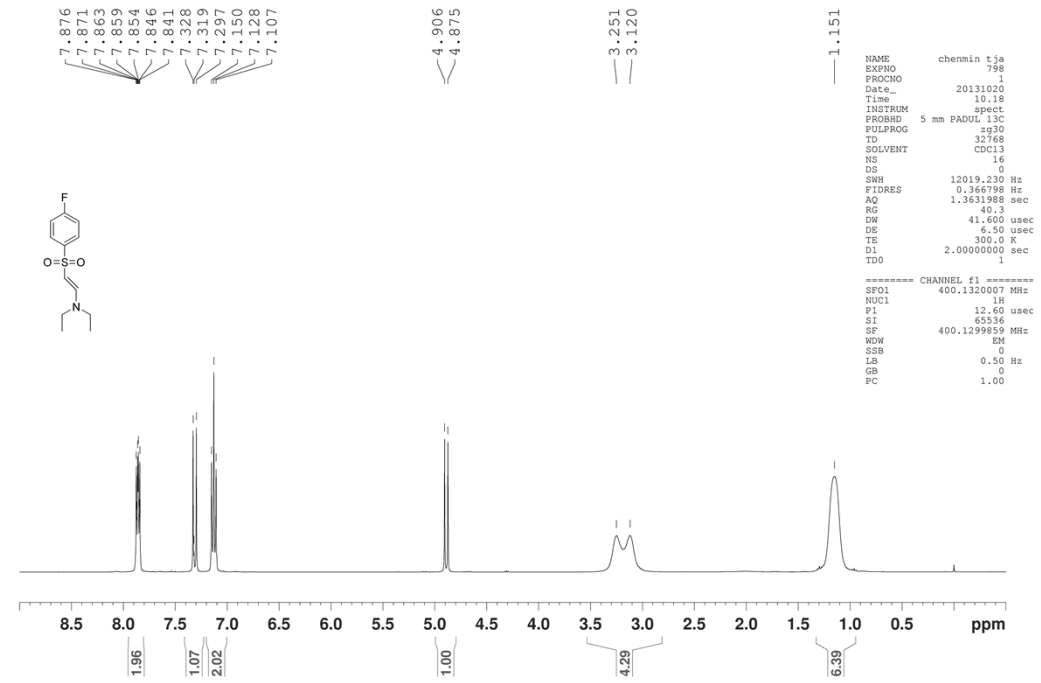


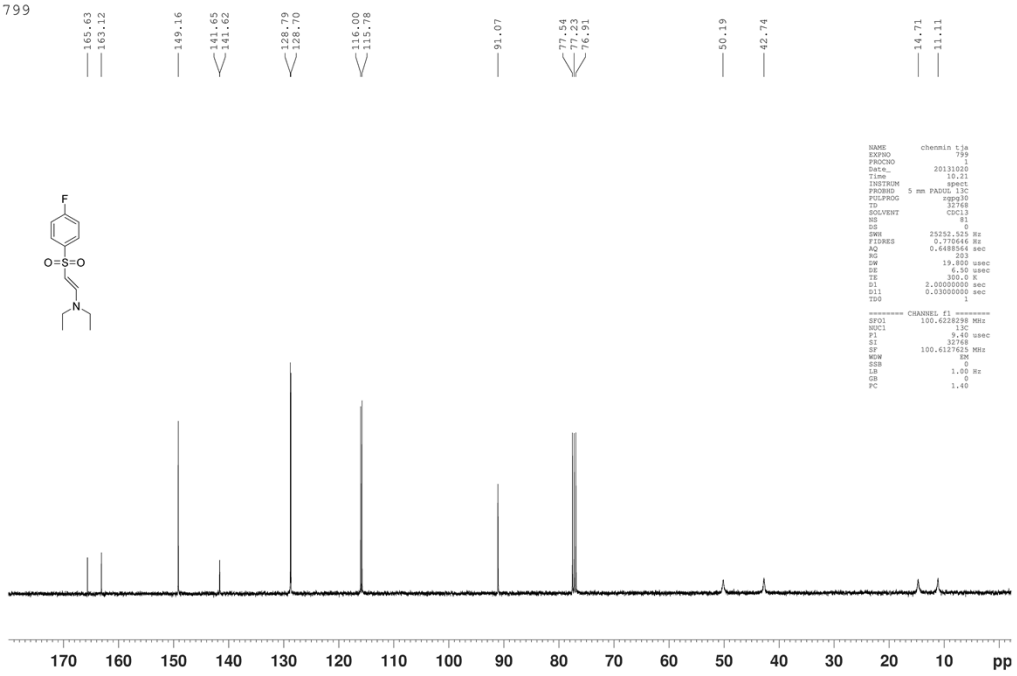
(*E*)-*N*,*N*-diethyl-2-(4-methoxyphenylsulfonyl)ethenamine



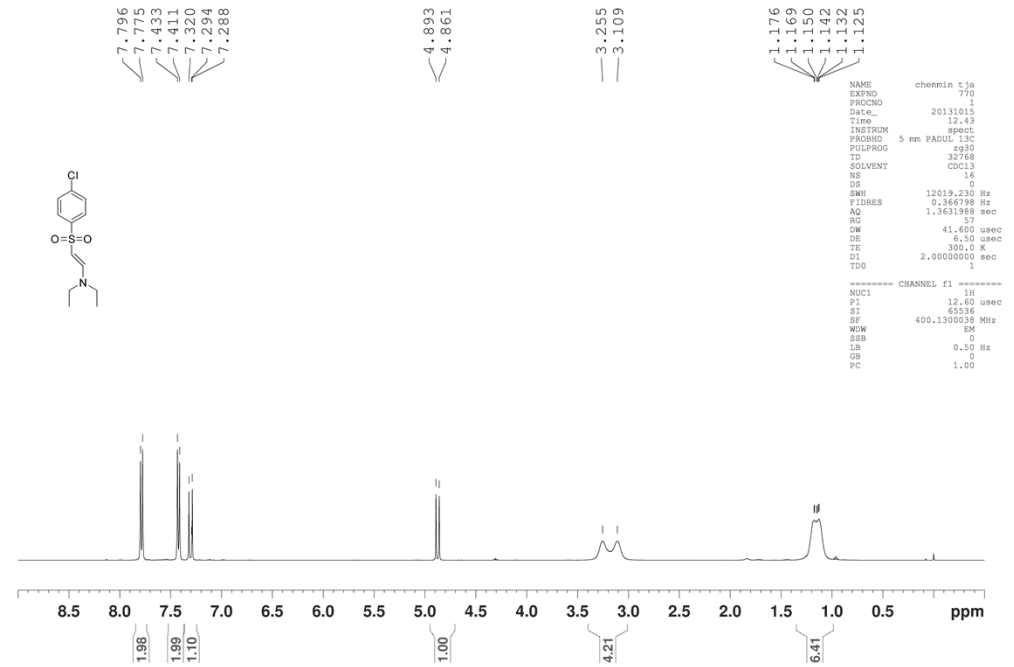


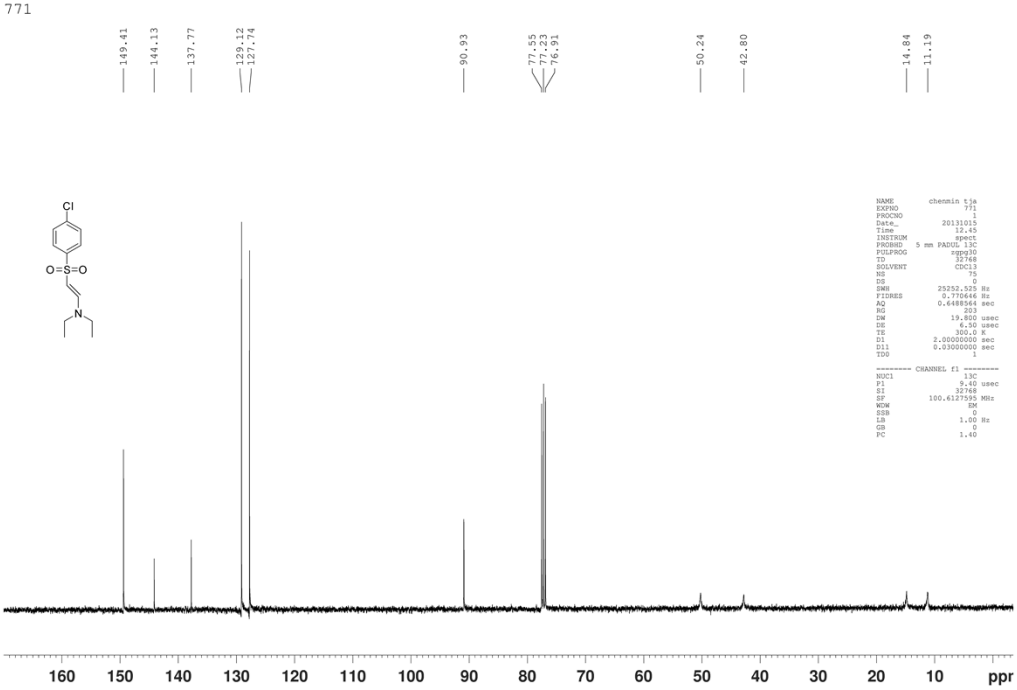
(*E*)-*N*,*N*-diethyl-2-(4-fluorophenylsulfonyl)ethenamine



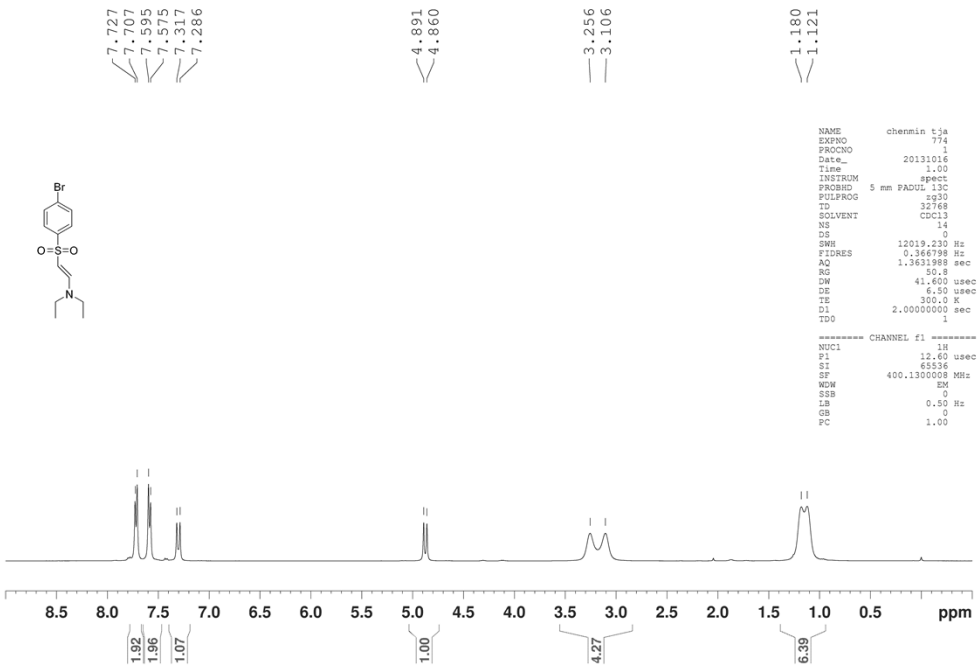


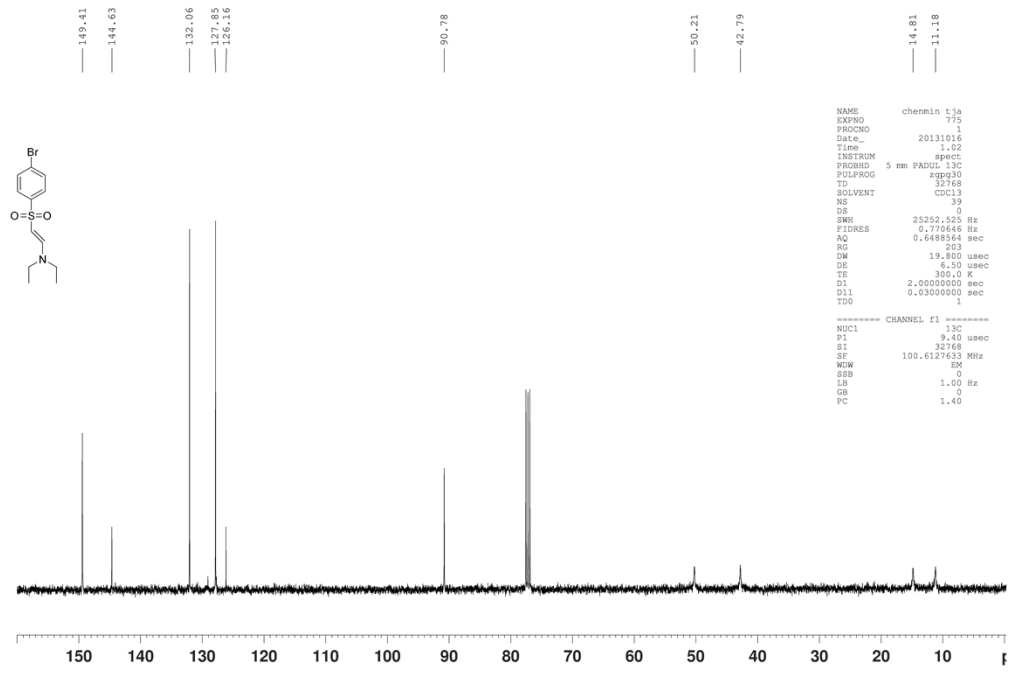
(*E*)-2-(4-chlorophenylsulfonyl)-*N*,*N*-diethylethenamine



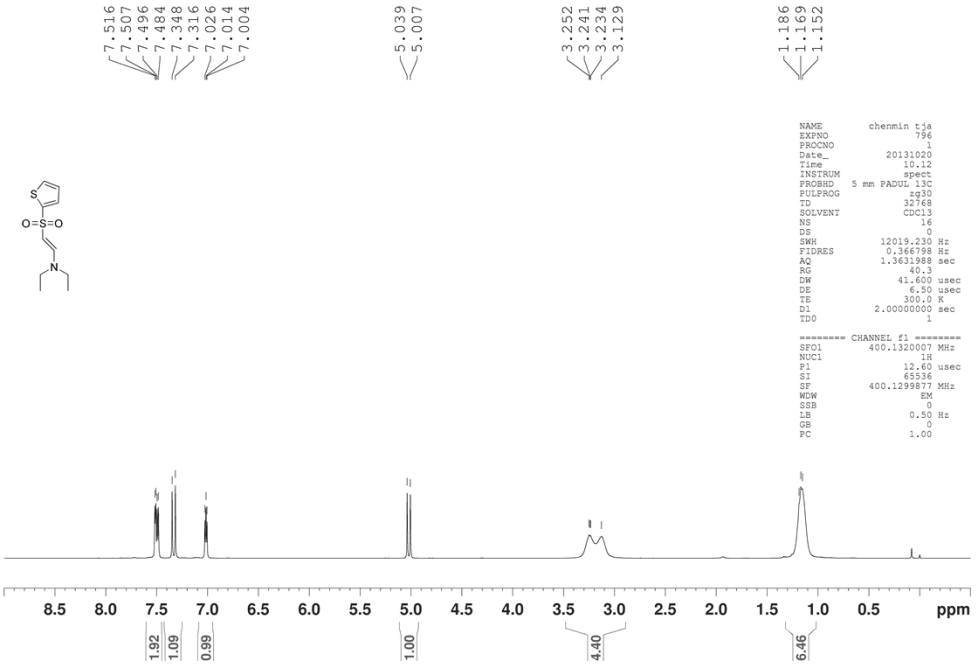


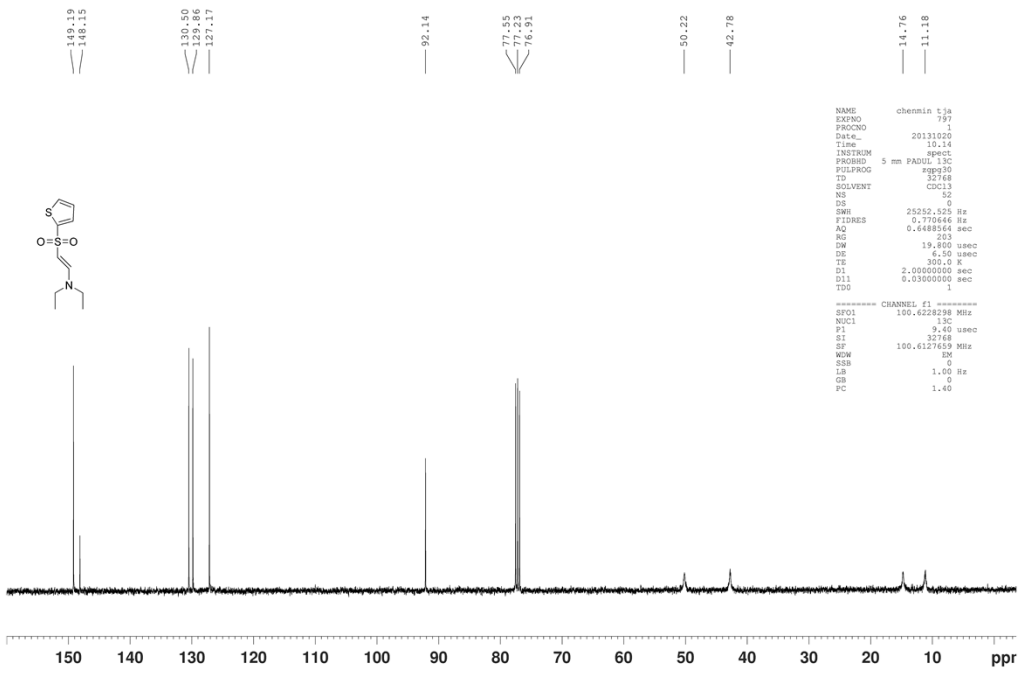
(*E*)-2-(4-bromophenylsulfonyl)-*N*,*N*-diethylethenamine



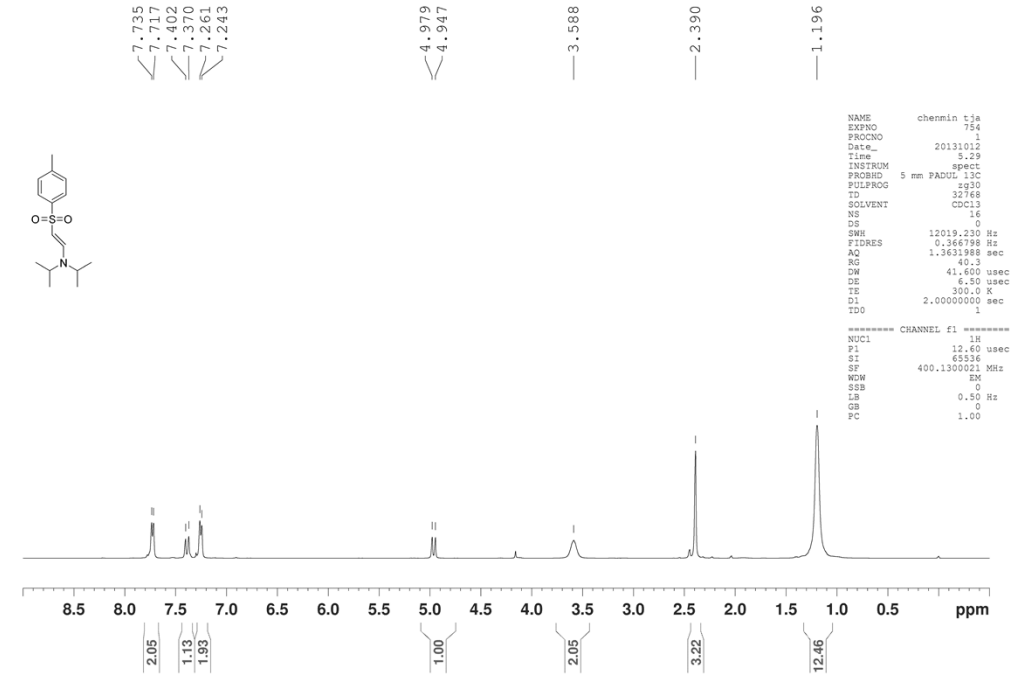


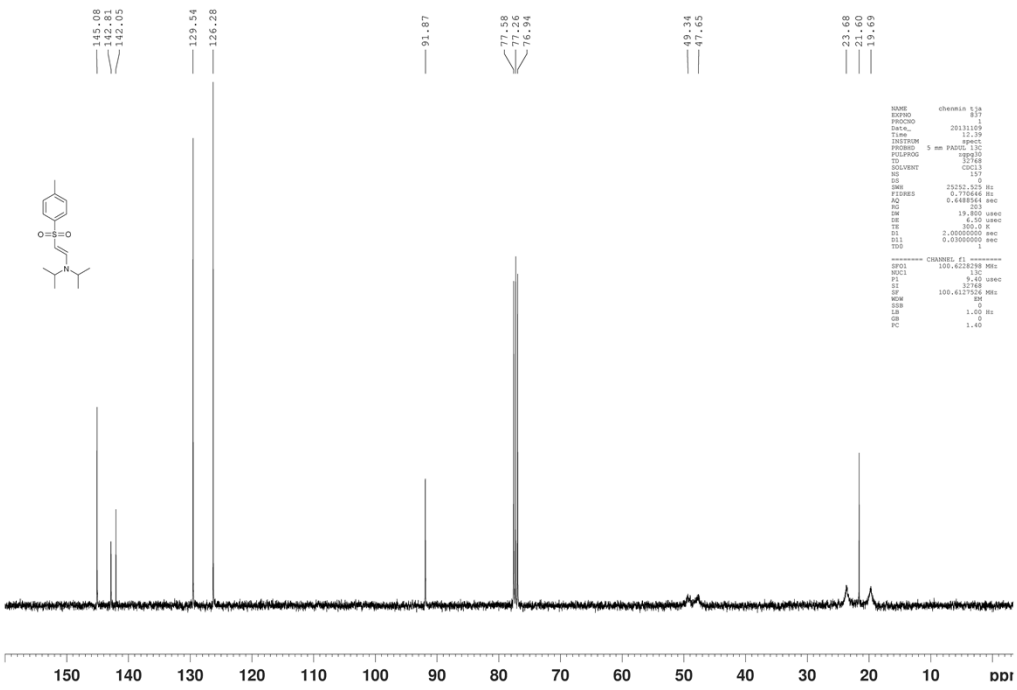
(*E*)-*N*,*N*-diethyl-2-(thiophen-2-ylsulfonyl)ethenamine



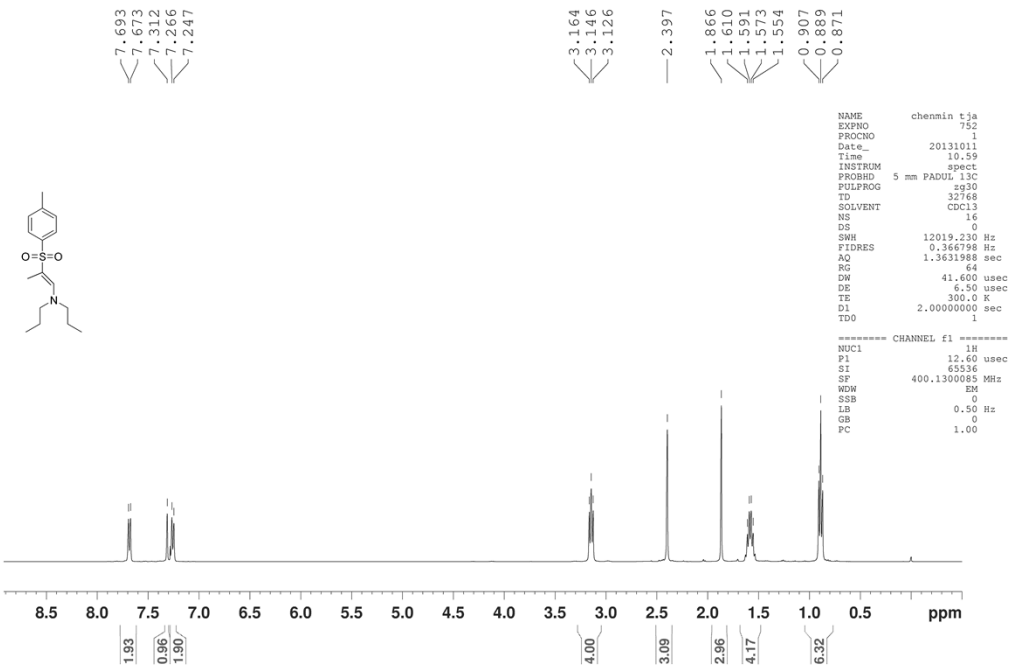


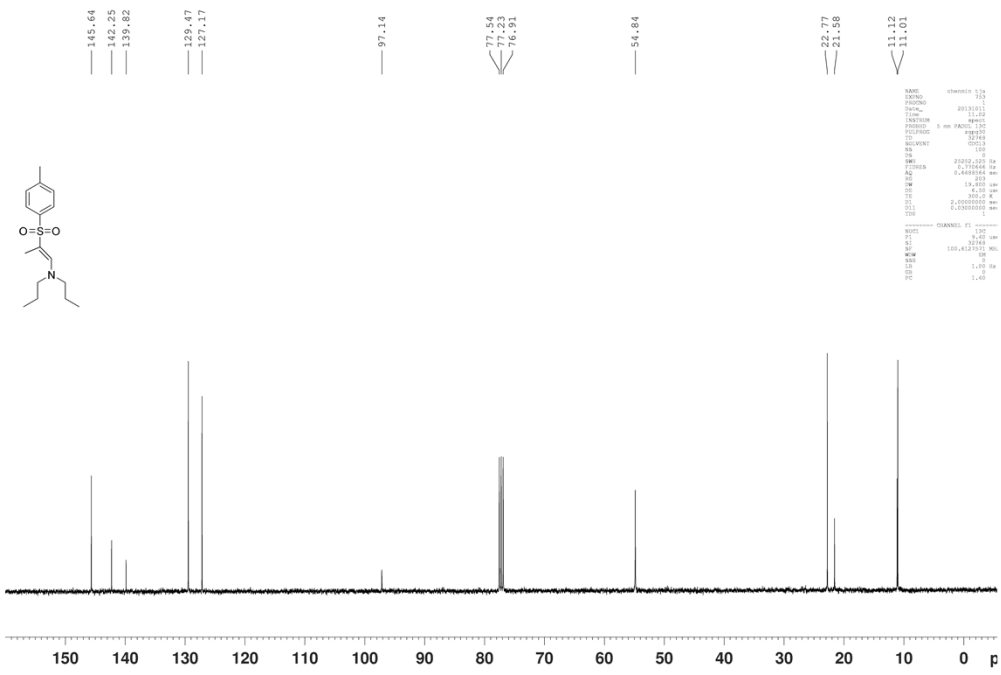
(*E*)-*N*-isopropyl-N-(2-tosylvinyl)propan-2-amine

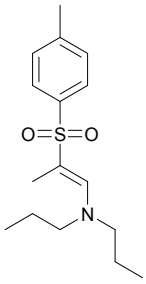




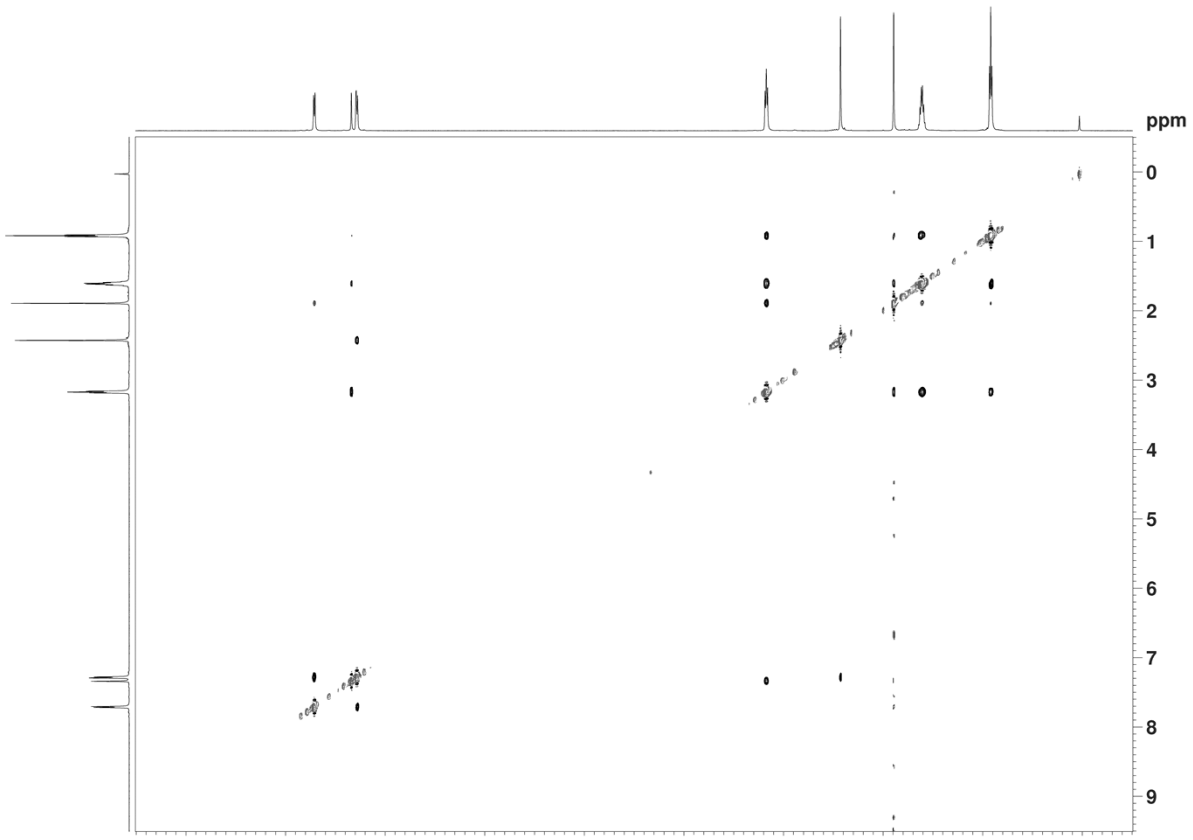
(*E*)-*N*,*N*-dipropyl-2-tosylprop-1-en-1-amine



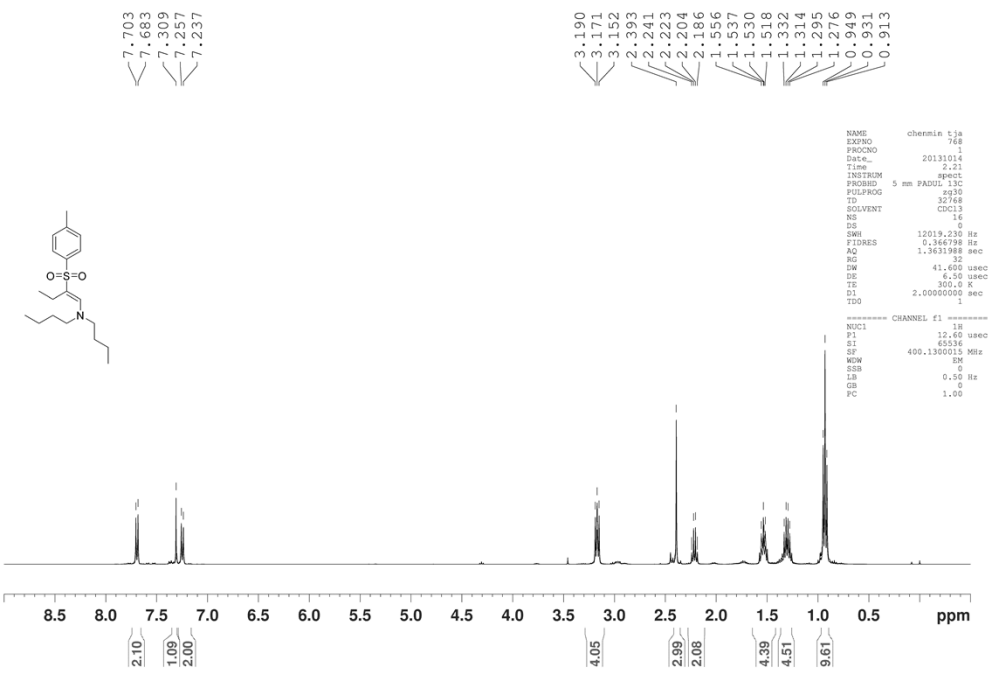


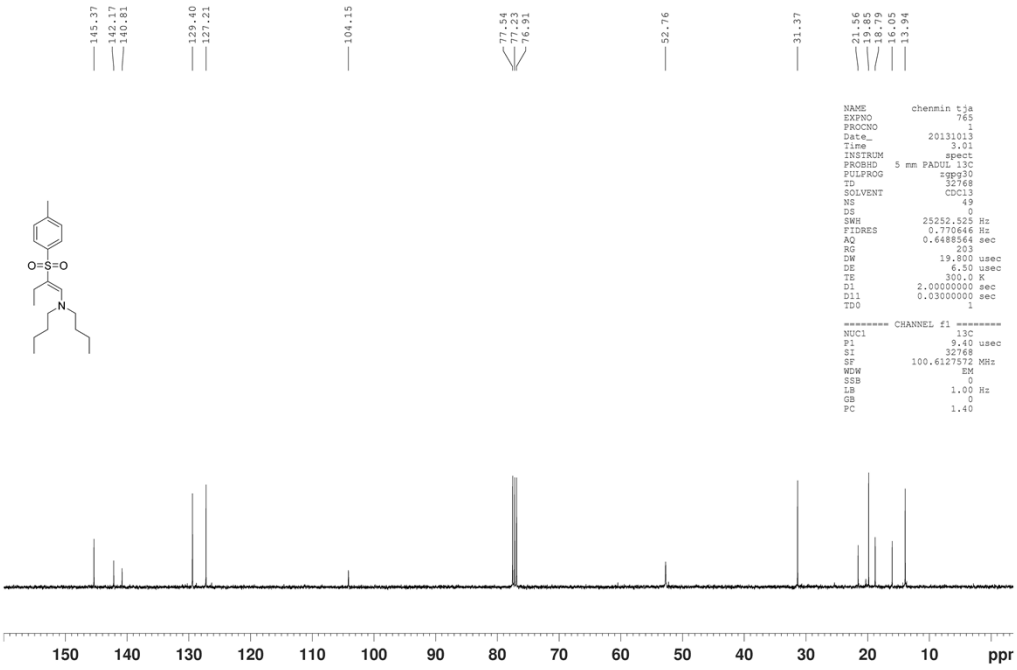


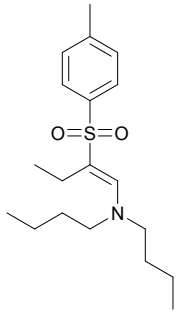
2D-**NOESY(600 MHz, $CDCl_3$)**



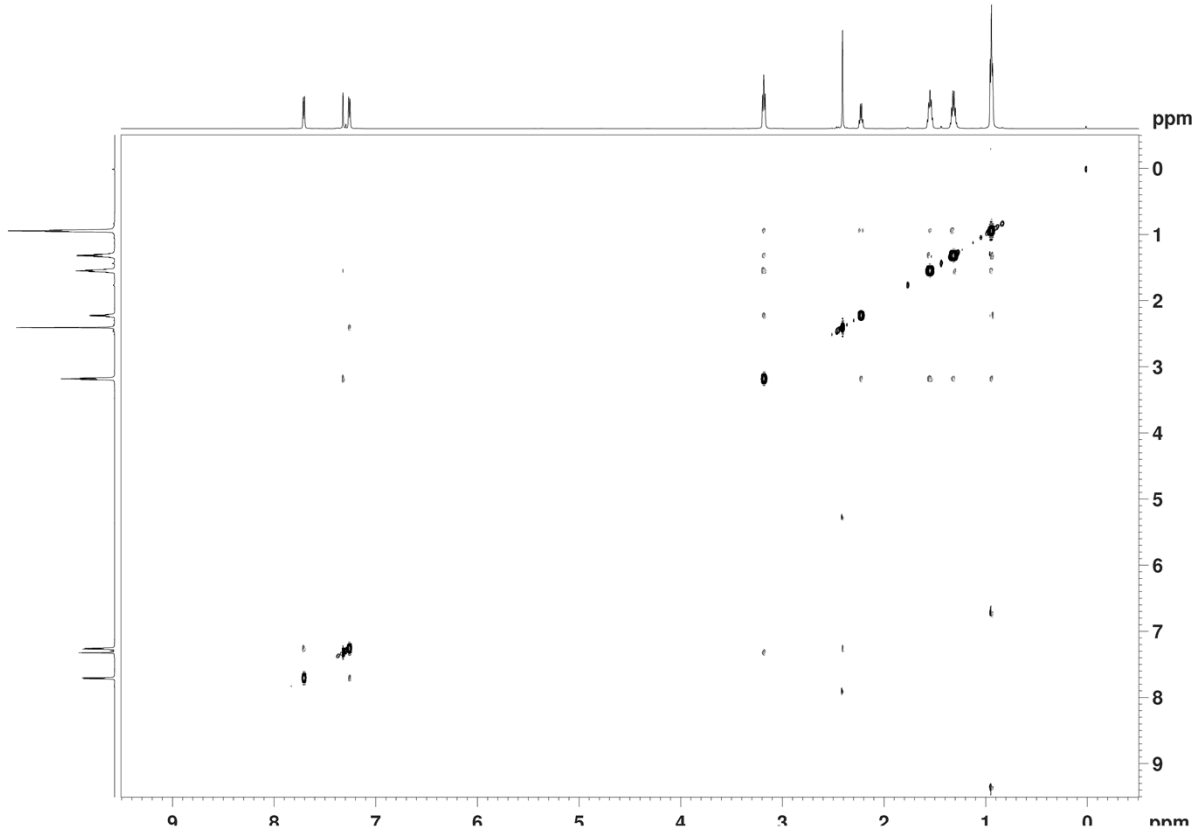
(*E*)-*N*,*N*-dibutyl-2-tosylbut-1-en-1-amine

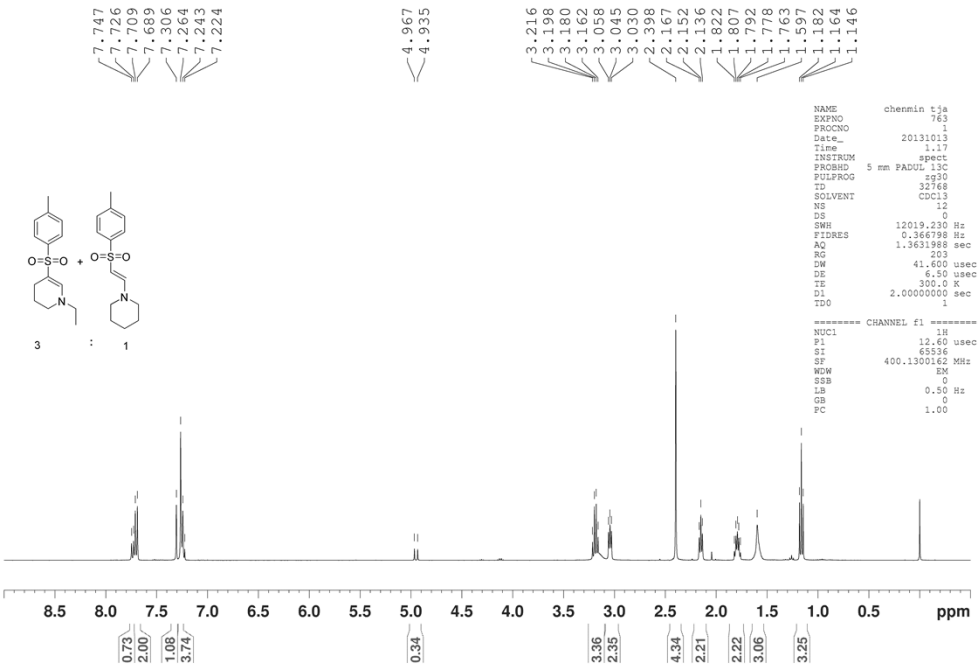

7.703
7.683
7.309
7.257
7.237
3.190
3.171
3.152
2.393
2.241
2.223
2.204
2.186
1.556
1.537
1.530
1.518
1.332
1.314
1.295
1.276
0.949
0.931
0.913
O=S=O
N
NAME chenmin tja
EXPNO 768
PROCNO 1
Date_ 20131014
Time 2.21
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 12019.230 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 32
DW 41.600 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.60 usec
SI 65536
SF 400.1300015 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.10
1.09
2.00
4.05
2.99
2.08
4.39
4.51
9.61

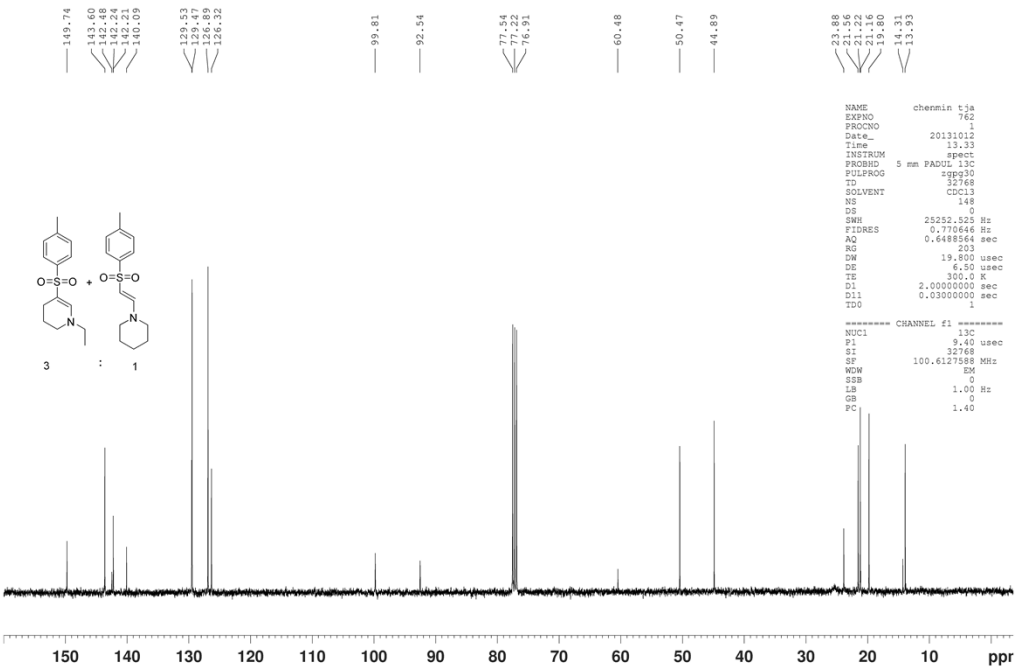

145.37
142.17
140.81
129.40
127.21
104.15
77.54
77.23
76.91
52.76
31.37
21.56
19.85
18.79
16.05
13.94
O=S=O
N
NAME chenmin tja
EXPNO 765
PROCNO 1
Date_ 20131013
Time 3.01
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 49
DS 0
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 0.6488564 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.40 usec
SI 32768
SF 100.6127572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



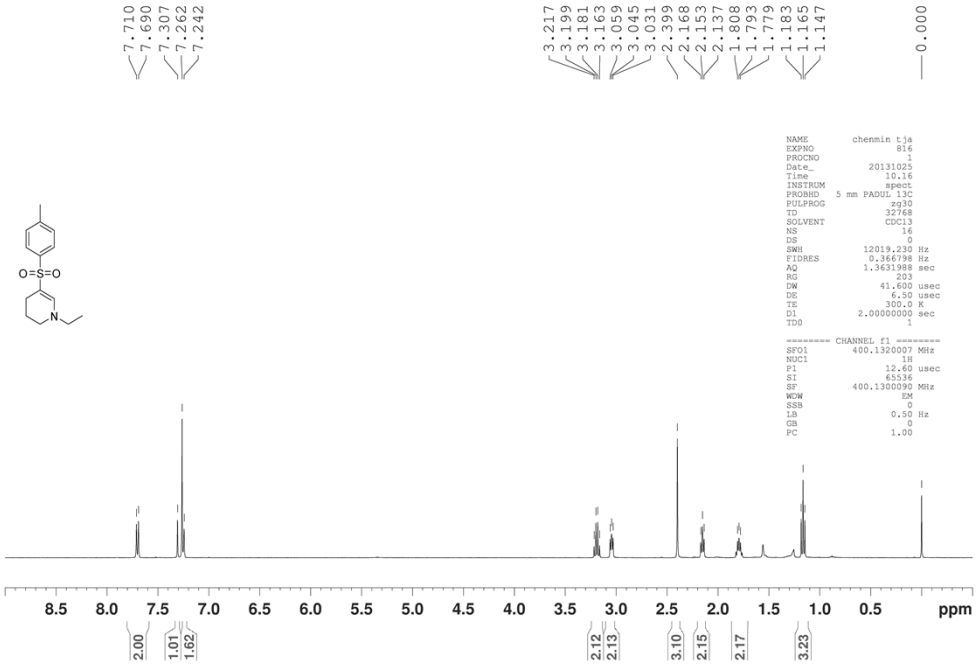
2D-NOESY(600 MHz, $CDCl_3$)

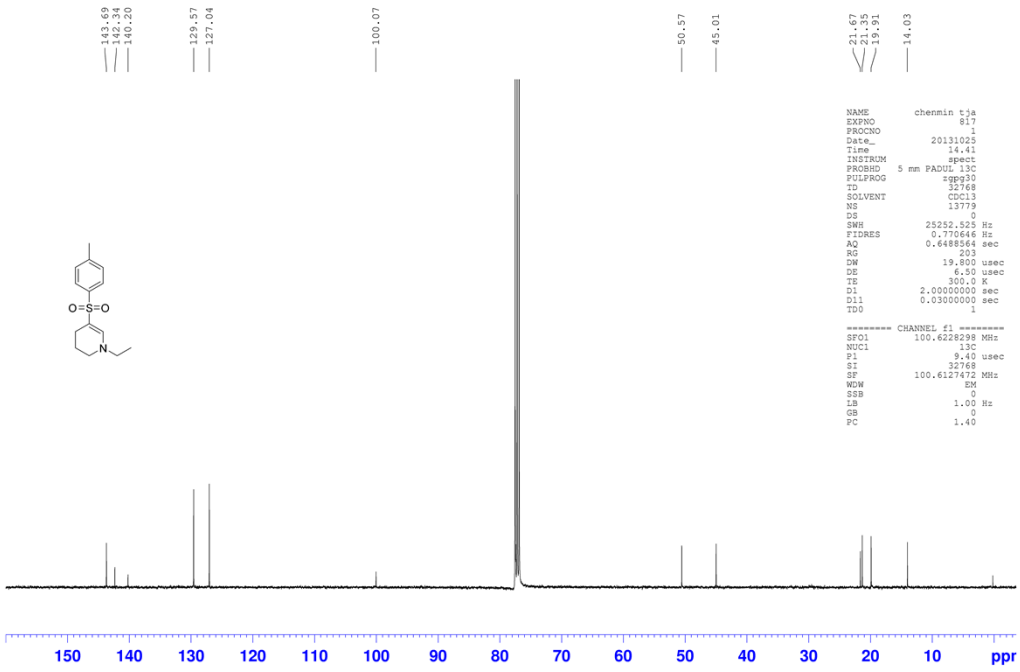



7.747
7.726
7.709
7.689
7.306
7.264
7.243
7.224
4.967
4.935
3.216
3.198
3.180
3.162
3.058
3.045
3.030
2.398
2.167
2.152
2.136
1.822
1.807
1.792
1.778
1.763
1.597
1.182
1.164
1.146
3 : 1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.73 2.00 1.08 3.74 0.34 3.36 2.35 4.34 2.21 2.22 3.06 3.25

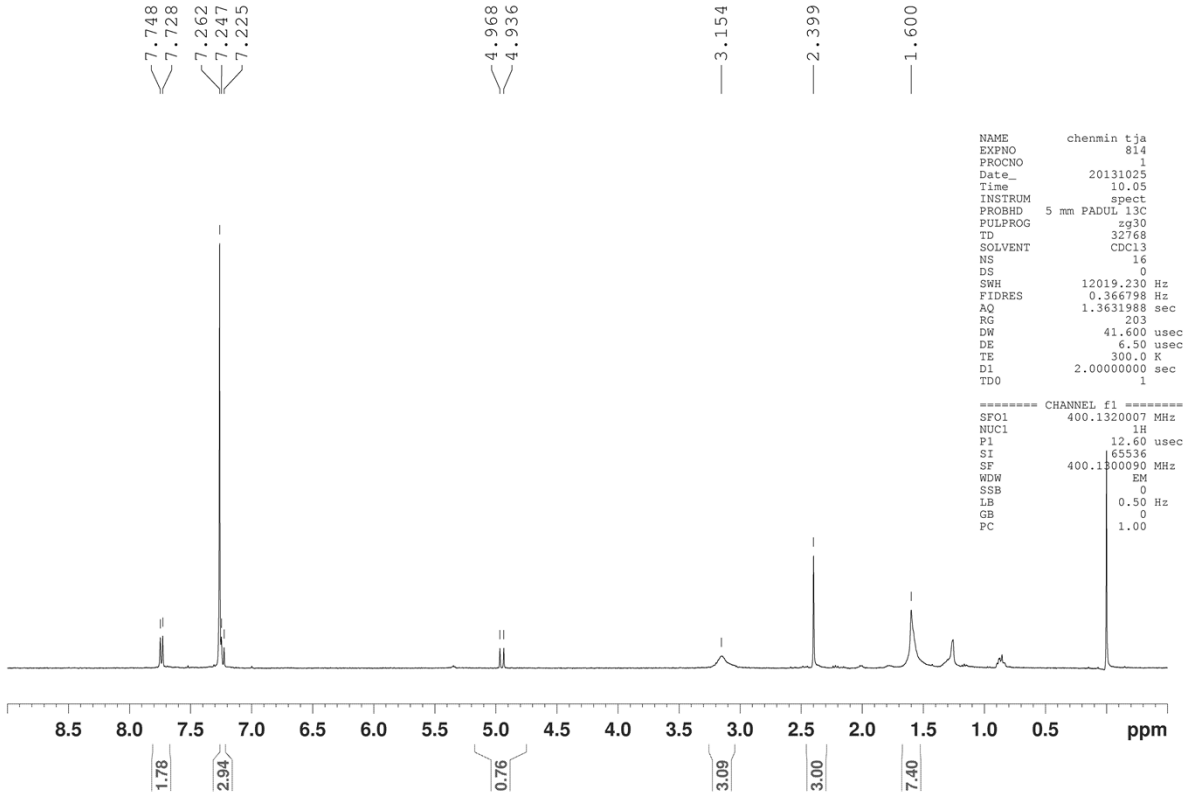

149.74
143.60
142.48
142.24
142.21
140.09
129.53
129.47
126.89
126.32
99.81
92.54
77.54
77.22
76.91
60.48
50.47
44.89
23.88
21.56
21.22
21.16
14.31
13.33
3 : 1
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Ethyl-5-tosyl-1,2,3,4-tetrahydropyridine

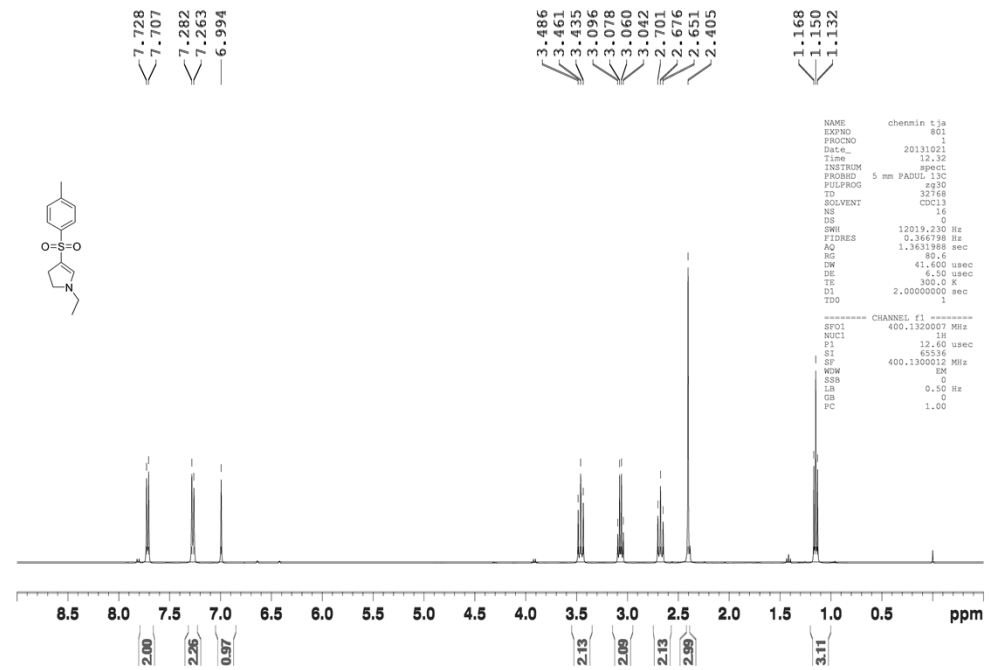


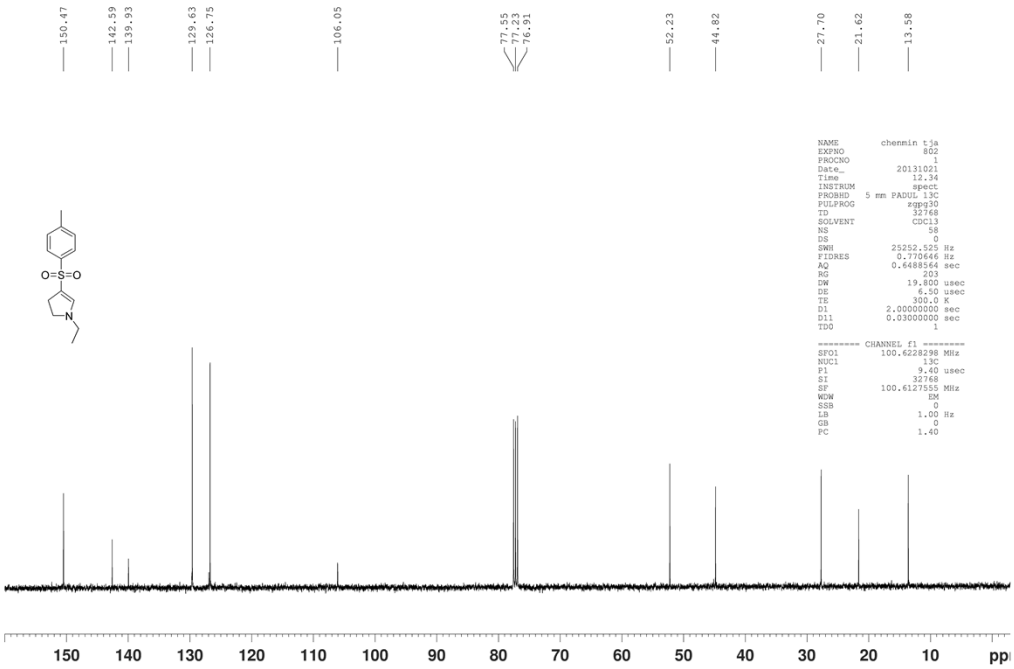


(*E*)-1-(2-tosylvinyl)piperidine

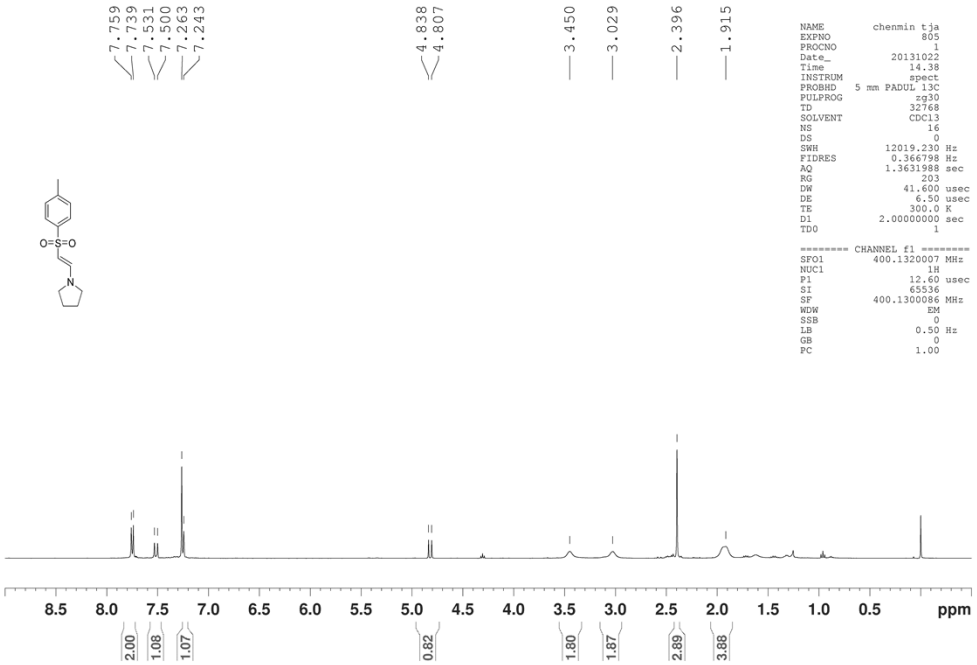


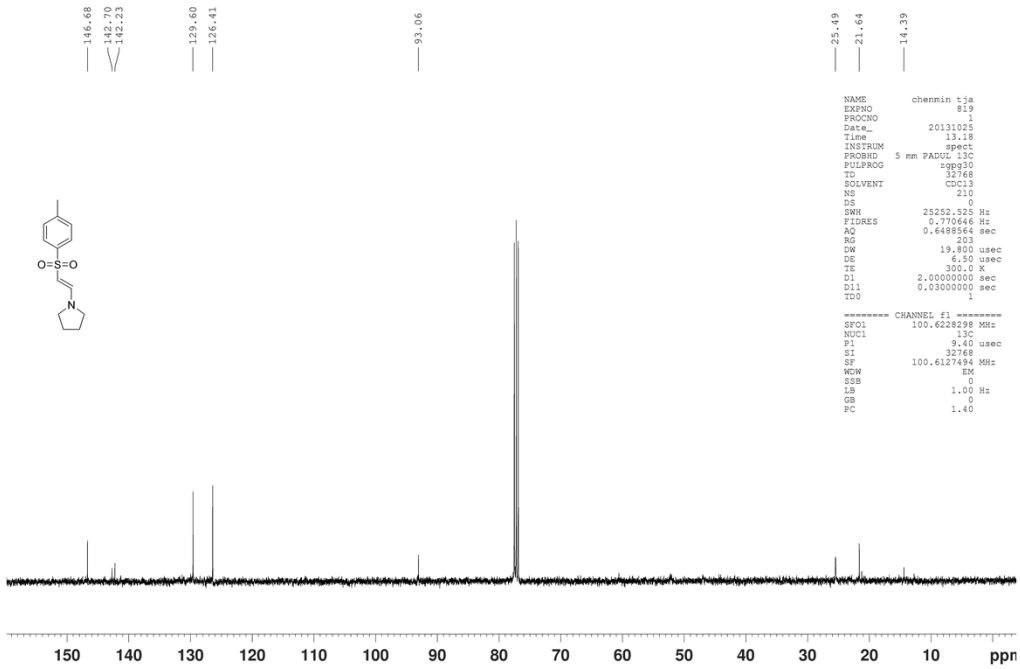
Ethyl-4-tosyl-2,3-dihydro-1H-pyrrole



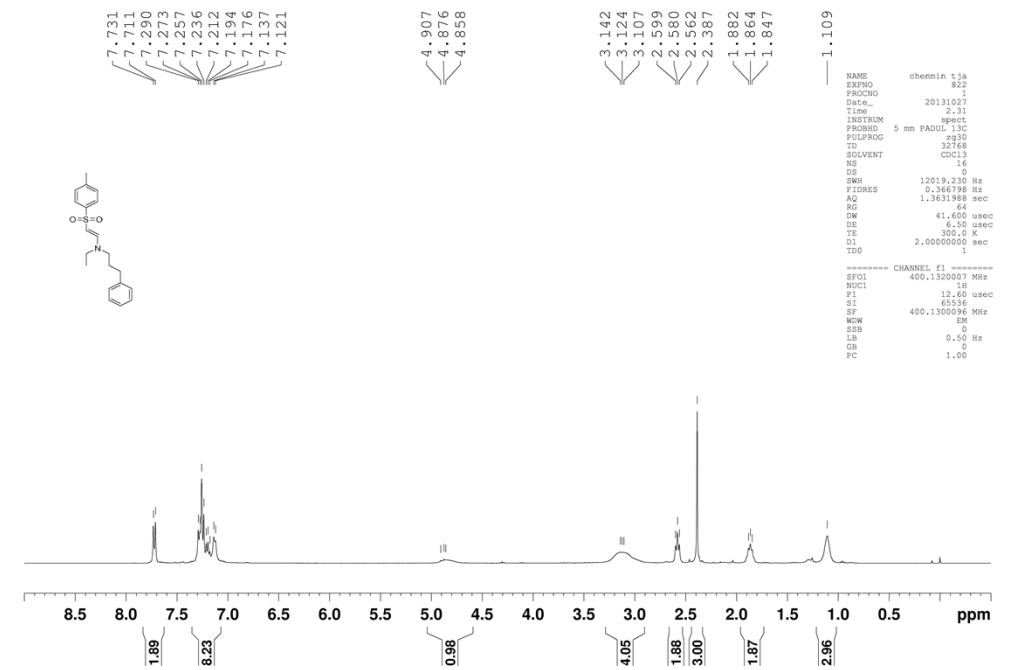


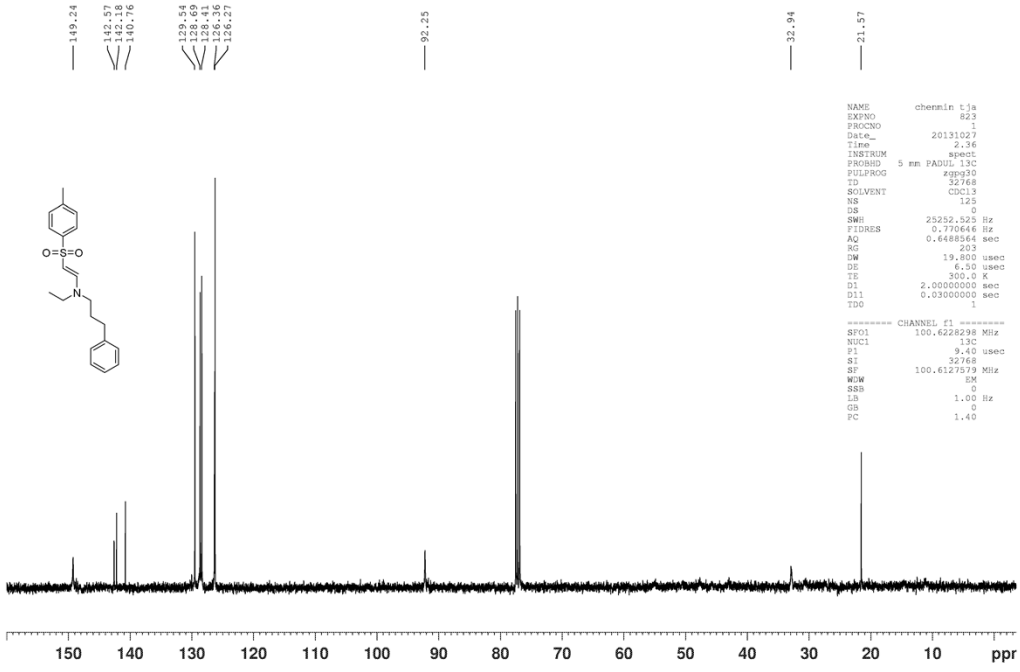
(*E*)-1-(2-tosylvinyl)pyrrolidine



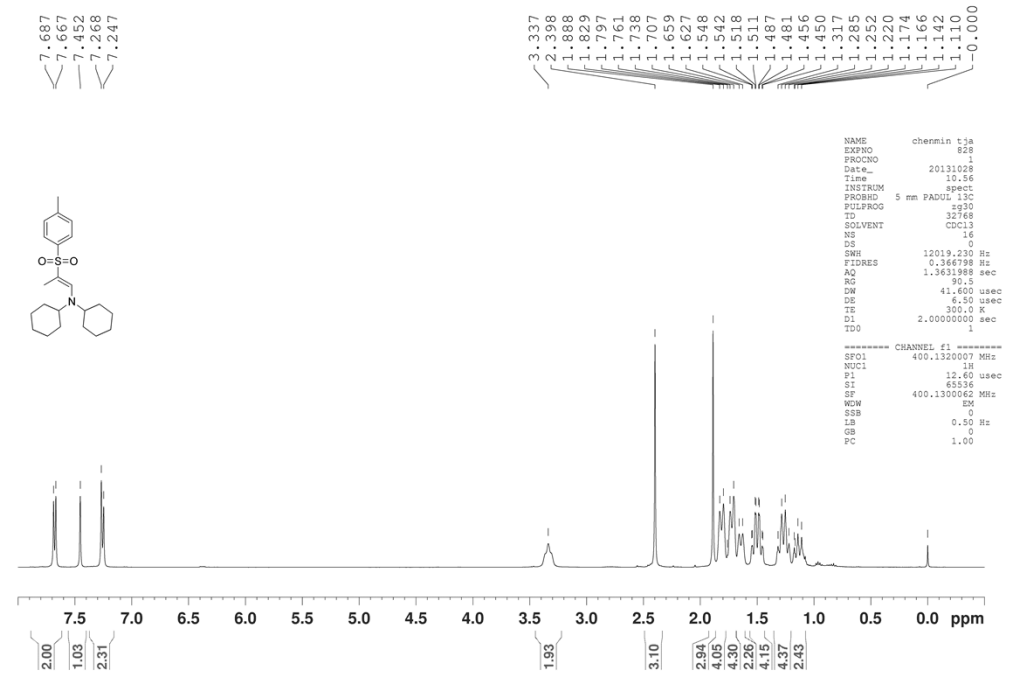


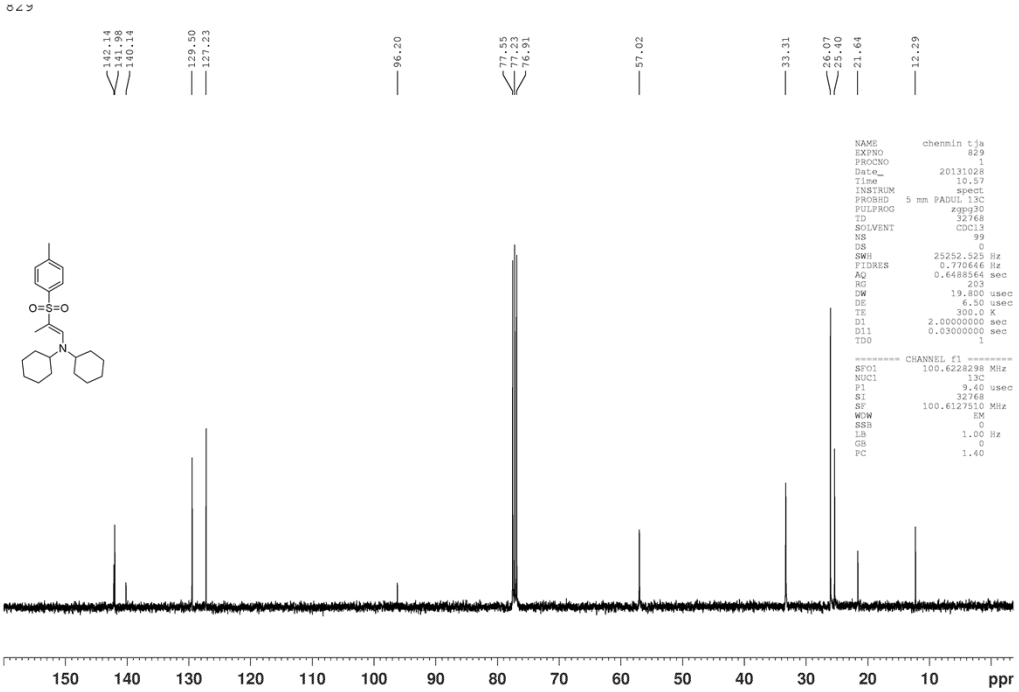
(*E*)-N-ethyl-3-phenyl-N-(2-tosylvinyl)propan-1-amine

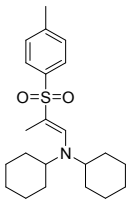




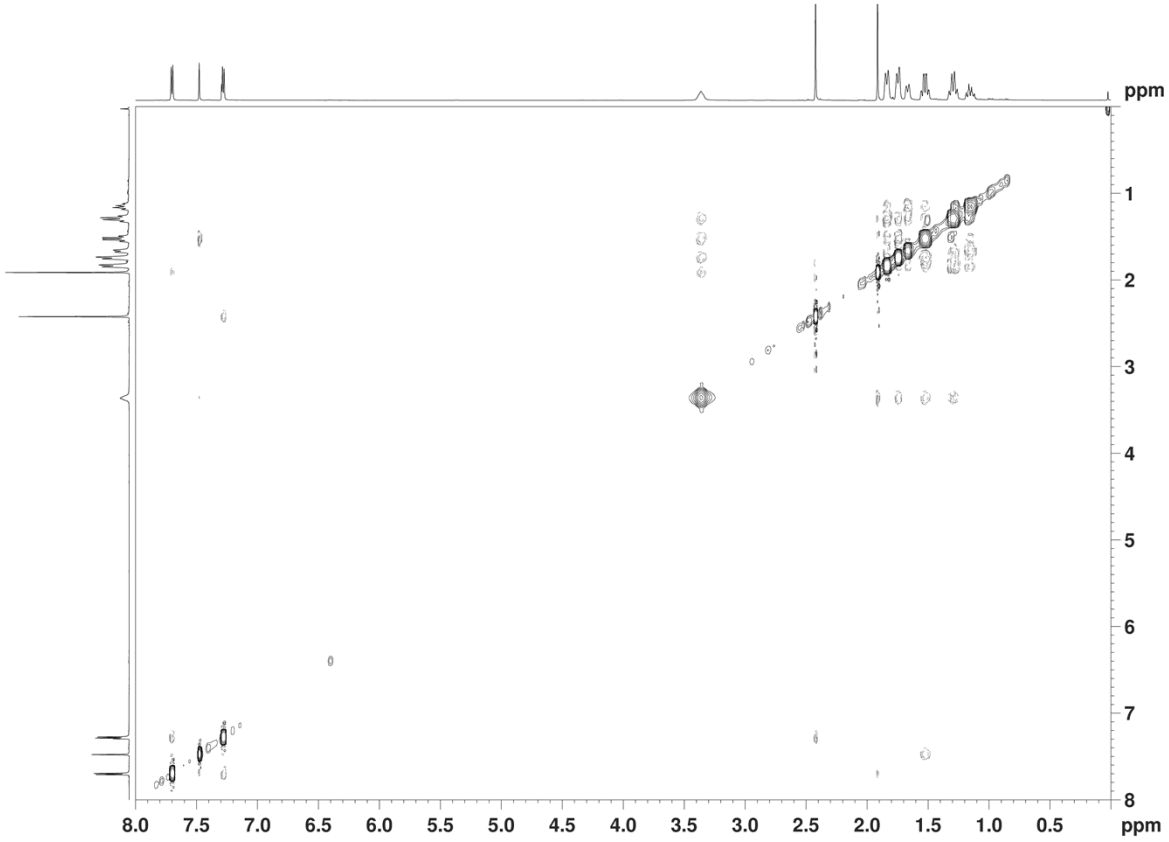
(*E*)-N-cyclohexyl-N-(2-tosylprop-1-enyl)cyclohexanamine



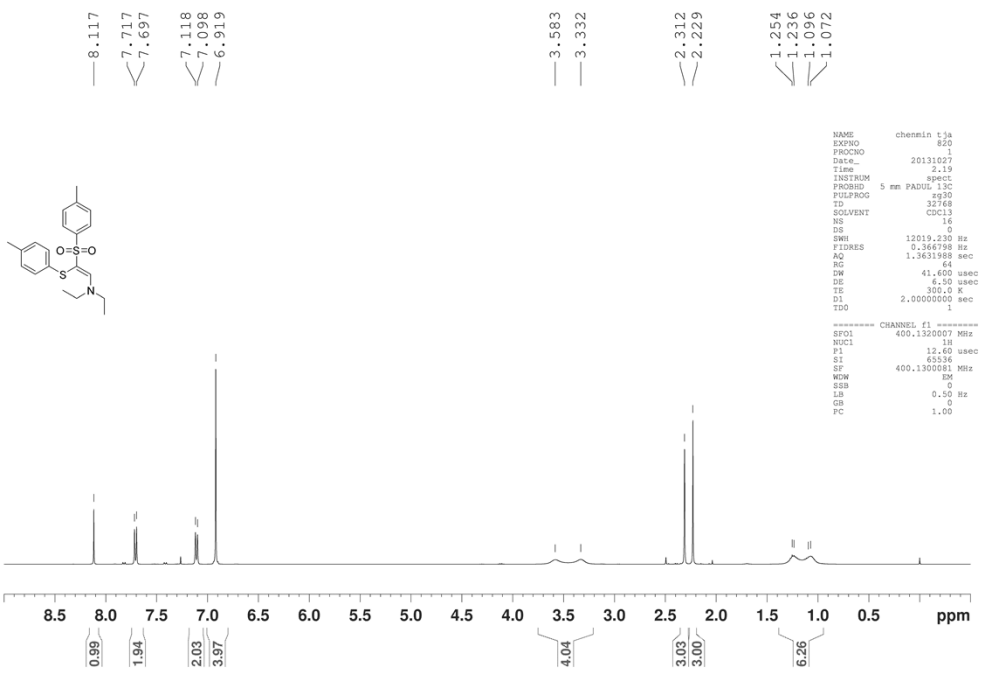


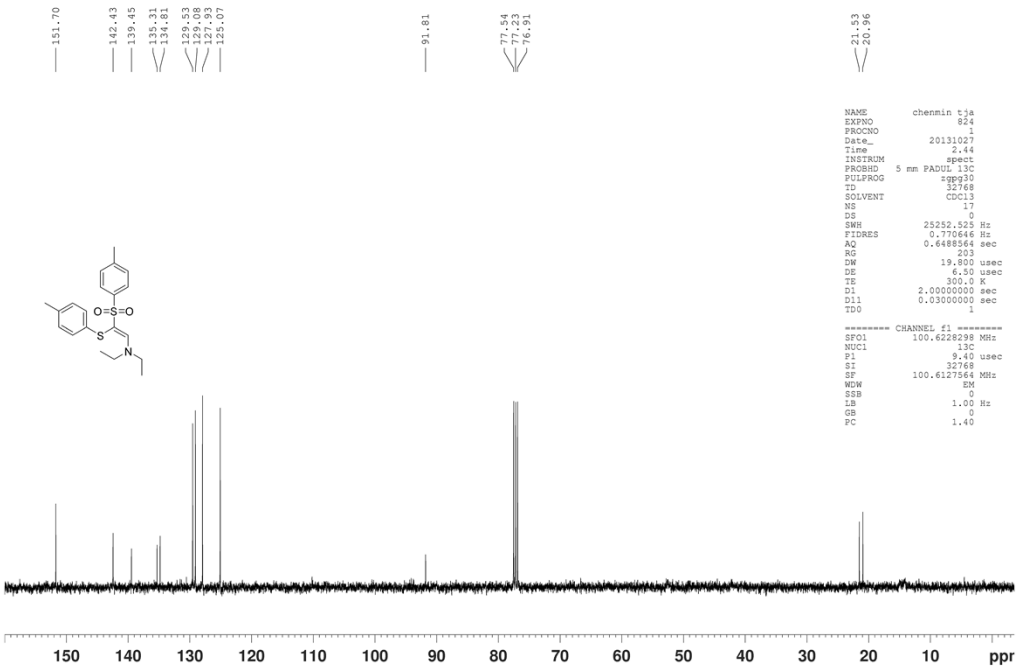


2D-NOESY(600M,$CDCl_3$)



(*Z*)-N,N-diethyl-1-(p-tolylthio)-2-tosylethenamine


8.117
7.717
7.697
7.118
7.098
6.919
3.583
3.332
2.312
2.229
1.254
1.236
1.096
1.072
ppm
0.99
1.94
2.03
3.97
4.04
3.03
3.00
6.26


151.70
142.43
139.45
135.31
134.81
129.53
129.08
127.93
125.07
91.81
77.54
77.23
76.91
21.53
20.96
ppr