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Palladium-catalyzed aerobic oxidative coupling of enantioenriched primary allylic amines with sulfonyl hydrazides leading to optically active allylic sulfones

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Supporting information

Table of contents

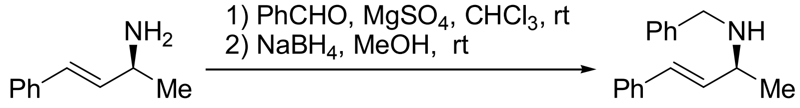
General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High-resolution mass spectrometry (HRMS) was recorded on a LC-TOF instrument (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump using a Daicel Chiralpak column (AD, OD, or IC, 250 x 4.6 mm) with hexane/isopropanol as mobile phase, and the UV detection was monitored at 220 or 254 nm. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,°C}$ (c = g/100 mL, solvent). Melting points were uncorrected.

Amines **1a-f** and **1i** were resolved from the corresponding racemic compounds (prepared by reductive amination of the corresponding α,β-unsaturated ketones with hydroxylamine in the presence of zinc and acetic acid)[1a] with (+)-tartaric acid, and their absolute configuration was assigned by comparison of the optical rotation (or the chiral HPLC trace for the derivative) with that reported in the literature.[1] Amine **1g**[2] was prepared from *L*-valine and amine **1h**[3] was prepared from the corresponding ketone according to known procedures. Sulfonyl hydrazides **2c-m**,[4] **4a**,[5] and **4b**[6] and sulfinic acids **7a** and **7b**[7] were prepared according to known procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

Abbreviations: Ac = acetyl; BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; BINOL = 1,1'-binaphthol; Boc = *tert*-butoxycarbonyl; dba = dibenzylideneacetone; Cy = cyclohexyl; DCE = 1,2-dichloroethane; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide; dppb = 1,4-bis(diphenylphosphino)butane; dppe = 1,2-bis(diphenylphosphino)ethane; dppf = 1,1'-bis(diphenylphosphino)ferrocene; Np = naphthyl; ee = enantiomeric excess; rt = room temperature; THF = tetrahydrofuran; TMEDA = *N,N,N',N'*-tetramethylethylenediamine; Ts = *p*-toluenesulfonyl; Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

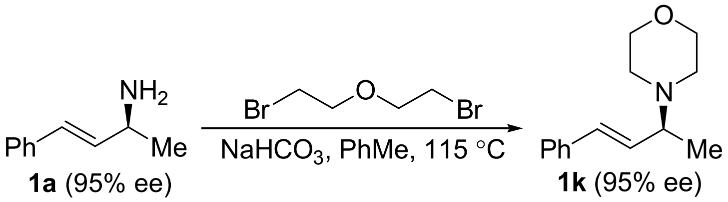
Preparation of amine 1j[1d]



1a (95% ee) **1j** (95% ee)

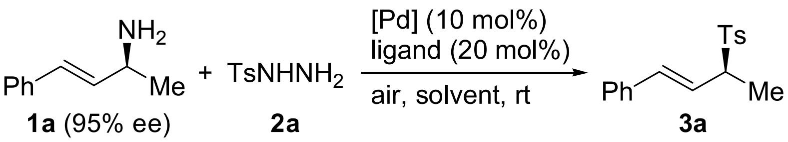
To a solution of amine **1a** (147 mg, 1.0 mmol)[1a] and benzaldehyde (106 mg, 1.0 mmol) in dry chloroform (5.0 mL) was added magnesium sulfate (500 mg). The mixture was stirred at room temperature for 5 h. After filtration, the solvent was evaporated under reduced pressure. The residue was dissolved in methanol (5.0 mL), and then $NaBH_4$ (37.8 mg, 1.0 mmol) was added. The mixture was stirred at room temperature for 1 h, added water (5.0 mL), and extracted with ethyl acetate (2 x 20 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give amine **1j** (142 mg, 60%) as a colorless oil.[8] $[\alpha]_D^{20}$ = -120.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.19 (m, 10H), 6.48 (d, J = 16.0 Hz, 1H), 6.11 (dd, J = 16.0, 8.0 Hz, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.73 (d, J = 13.2 Hz, 1H), 3.44-3.36 (m, 1H), 1.26 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.2, 134.3, 130.2, 128.6, 128.5, 128.2, 127.4, 126.9, 126.3, 55.6, 51.6, 22.1. The ee was determined to be 95% ee by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 99:1, flow rate = 0.5 mL/min): t_R (minor) = 23.7 min, t_R (major) = 26.2 min.

Preparation of amine 1k



A mixture of amine **1a** (58.8 mg, 0.40 mmol), 1-bromo-2-(2-bromoethoxy) ethane (102 mg, 0.44 mmol), and sodium bicarbonate (73.9 mg, 0.88 mmol) in toluene (0.50 mL) was heated under nitrogen at 115 °C for 23 h. The mixture was cooled to room temperature and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:2), to give amine **1k** (69.6 mg, 80%) as a colorless oil.[9] $[\alpha]_D^{20}$ = -60.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.34-7.27 (m, 2H), 7.25-7.18 (m, 1H), 6.46 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 8.0 Hz, 1H), 3.73 (t, J = 4.4 Hz, 4H), 3.05-2.98 (m, 1H), 2.61-2.51 (m, 4H), 1.26 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.0, 131.3, 128.6, 127.5, 126.3, 67.2, 63.1, 50.7, 17.7. The ee was determined to be 95% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 6.6 min, t_R (major) = 8.6 min.

Optimization of reaction conditions[a]

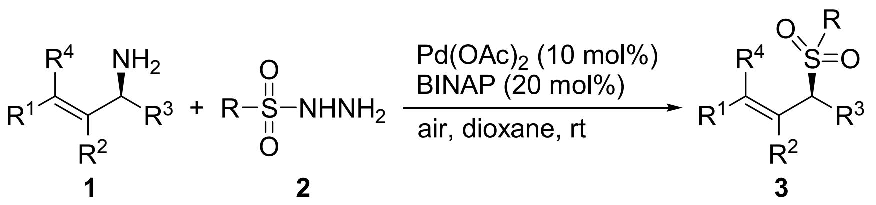


Entry	[Pd]	Ligand	Solvent	Yield[b] (%)	ee[c] (%)
1	$Pd(OAc)_2$	BINAP	Dioxane	79	95
2	$Pd(NO_3)_2\cdot 2H_2O$	BINAP	Dioxane	90	92
3	$PdCl_2$	BINAP	Dioxane	70	93
4	$Pd(PPh_3)_4$	None	Dioxane	0	–

5[d]	$Pd_2(dba)_3$	None	Dioxane	0	–
6	$Pd(OAc)_2$	Xantphos	Dioxane	0	–
7	$Pd(OAc)_2$	dppf	Dioxane	Trace	–
8	$Pd(OAc)_2$	dppe	Dioxane	0	–
9	$Pd(OAc)_2$	dppb	Dioxane	17	72
10	$Pd(OAc)_2$	TMEDA	Dioxane	0	–
11	$Pd(OAc)_2$	BINOL	Dioxane	0	–
12	$Pd(OAc)_2$	BINAP	Toluene	80	87
13	$Pd(OAc)_2$	BINAP	CH_2Cl_2	73	19
14	$Pd(OAc)_2$	BINAP	DCE	64	92
15	$Pd(OAc)_2$	BINAP	EtOAc	73	91
16	$Pd(OAc)_2$	BINAP	THF	32	95
17	$Pd(OAc)_2$	BINAP	MeCN	49	88
18	$Pd(OAc)_2$	BINAP	$MeNO_2$	13	95
19	$Pd(OAc)_2$	BINAP	DMSO	43	15
20	$Pd(OAc)_2$	BINAP	DMF	75	75
21	$Pd(OAc)_2$	BINAP	Ethanol	Trace	–
22[e]	$Pd(OAc)_2$	BINAP	Dioxane	60	95
23[f]	$Pd(OAc)_2$	BINAP	Dioxane	Trace	–
24[g]	$Pd(OAc)_2$	BINAP	Dioxane	65	95

[a] Reaction conditions: amine **1a** (0.20 mmol), sulfonyl hydrazide **2a** (0.30 mmol), [Pd] (10 mol%), ligand (if any, 20 mol%), solvent (1.2 mL), open to air, rt, 24 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] 5 mol% $Pd_2(dba)_3$ was used. [e] The reaction was run with 5 mol% $Pd(OAc)_2$ and 10 mol% BINAP. [f] The reaction was under nitrogen. [g] The reaction was under oxygen.

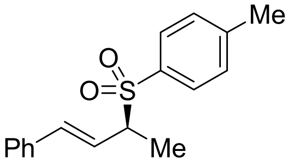
General procedure for the aerobic oxidative coupling of enantioenriched primary allylic amines with sulfonyl hydrazides



To a solution of amine **1** (0.20 mmol) in dioxane (1.2 mL) was added sulfonyl hydrazide **2** (0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol). The mixture was stirred under air at room temperature for 24 h, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:2 ~ 1:5), to give sulfone **3**.

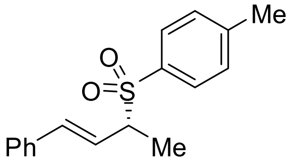
The absolute configuration of compound **3a**, **3b**, **3e**, **3j**, **3m**, **3n**, and **3p-r** was assigned to be *S* by comparison of the optical rotations with those reported in the literature, and that of the rest of products was assigned by analogy.

Analytical data for the products



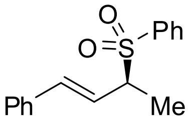
3a

Compound **3a**,[1c] white solid; m.p. 109-110 °C; 95% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 14.3 min, t_R (major) = 19.2 min; $[\alpha]_D^{20}$ = -120.3 (*c* = 1.0, acetone), Lit.[1c]: $[\alpha]_D^{20}$ = -116 (*c* = 0.58, acetone, 96% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.31-7.23 (m, 7H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.08 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.88-3.79 (m, 1H), 2.42 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 136.2, 136.0, 134.0, 129.5, 129.2, 128.7, 128.3, 126.5, 122.2, 64.0, 21.5, 13.6.



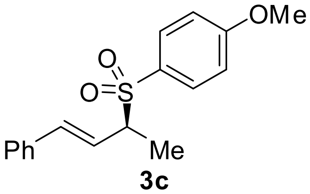
ent-3a

Compound **ent-3a**,[1c] white solid; m.p. 108-109 °C; 95% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (major) = 14.1 min, t_R (minor) = 18.9 min; $[\alpha]_D^{20}$ = +121.4 (*c* =1.0, acetone).



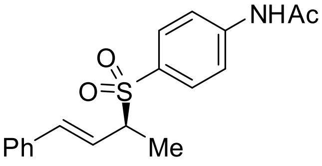
3b

Compound **3b**,[1c] white solid; m.p. 62-63 °C; 95% ee as determined by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90/10, flow rate 1.0 mL/min): t_R (minor) = 15.6 min, t_R (major) = 18.0 min; $[\alpha]_D^{20}$ = -82.7 (*c* = 1.0, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -85.3 (*c* = 0.82, $CHCl_3$, 94% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.64-7.59 (m, 1H), 7.53-7.48 (m, 2H), 7.33-7.23 (m, 5H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.07 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.90-3.81 (m, 1H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.5, 135.8, 133.7, 129.3, 128.8, 128.7, 128.4, 126.6, 122.1, 64.1, 13.7.



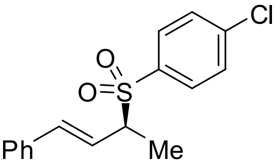
3c

Compound **3c**, white solid; m.p. 127-128 °C; 94% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 24.7 min, t_R (major) = 37.1 min; $[\alpha]_D^{20}$ = -63.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.2 Hz, 2H), 7.31-7.25 (m, 5H), 6.96 (d, *J* = 9.2 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.08 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.85-3.77 (m, 4H), 1.53 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 136.3, 136.1, 131.5, 128.7, 128.5, 128.4, 126.6, 122.6, 114.1, 64.3, 55.7, 13.7; HRMS (ESI) calcd for $C_{17}H_{18}O_3NaS^+$ $(M + Na)^+$ 325.0869, found 325.0861.



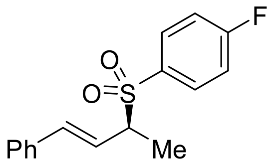
3d

Compound **3d**, white solid; m.p. 84-85 °C; 92% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 13.0 min, t_R (major) = 16.6 min; $[\alpha]_D^{20}$ = -86.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, br, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.33-7.27 (m, 5H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.88-3.80 (m, 1H), 2.18 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 143.2, 136.7, 135.8, 131.2, 130.5, 128.7, 128.5, 126.6, 121.9, 119.0, 64.2, 24.7, 13.7; HRMS (ESI) calcd for $C_{18}H_{19}O_3NNaS^+$ $(M + Na)^+$ 352.0978, found 352.0966.



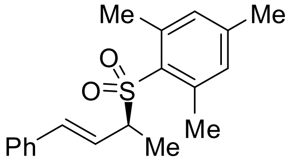
3e

Compound **3e**,[1c] white solid; m.p. 76-77 °C; 95% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 75/25, flow rate 1.0 mL/min): t_R (minor) = 10.1 min, t_R (major) = 13.3 min; $[\alpha]_D^{20}$ = -85.5 (*c* = 0.55, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -82.0 (*c* = 0.60, $CHCl_3$, 96% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.34-7.27 (m, 5H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.06 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.89-3.81 (m, 1H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.8, 135.7, 135.5, 130.8, 129.2, 128.7, 128.6, 126.6, 121.8, 64.2, 13.5.



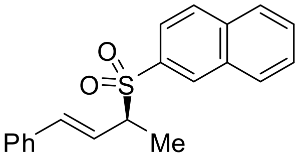
3f

Compound **3f**, white solid; m.p. 93-94 °C; 93% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 9.3 min, t_R (major) = 11.9 min; $[\alpha]_D^{20}$ = -13.3 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.32-7.27 (m, 5H), 7.25-7.13 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.88-3.80 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, *J* = 254.7 Hz), 136.7, 135.7, 133.0, 132.1 (d, *J* = 9.5 Hz), 128.7, 128.5, 126.6, 121.9, 116.2 (d, *J* = 22.4 Hz), 64.2, 13.5; HRMS (ESI) calcd for $C_{16}H_{15}O_2FNaS^+$ $(M + Na)^+$ 313.0669, found 313.0668.



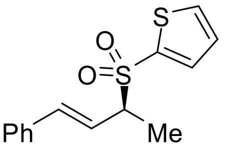
3g

Compound **3g**, white solid; m.p. 135-136 °C; 93% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min): t_R (major) = 16.8 min, t_R (minor) = 18.6 min; $[\alpha]_D^{20}$ = -205.7 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 5H), 6.91 (s, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.90-3.82 (m, 1H), 2.62 (s, 6H), 2.28 (s, 3H), 1.60 (d, *J* =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.6, 136.3, 136.0, 132.1, 131.6, 128.6, 128.3, 126.5, 122.4, 63.7, 23.1, 21.0, 12.6; HRMS (ESI) calcd for $C_{19}H_{22}O_2NaS^+$ $(M + Na)^+$ 337.1233, found 337.1227.



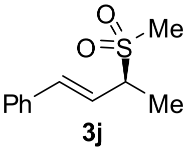
3h

Compound **3h**, white solid; m.p. 120-121 °C; 93% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 14.5 min, t_R (major) = 22.6 min; $[\alpha]_D^{20}$ = -54.0 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.95-7.89 (m, 3H), 7.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.69-7.57 (m, 2H), 7.30-7.22 (m, 5H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.99-3.90 (m, 1H), 1.58 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 135.9, 135.3, 134.1, 132.1, 131.2, 129.4, 129.2, 128.9, 128.6, 128.4, 127.9, 127.6, 126.6, 124.1, 122.2, 64.2, 13.7; HRMS (ESI) calcd for $C_{20}H_{18}O_2NaS^+$ $(M + Na)^+$ 345.0920, found 345.0912.



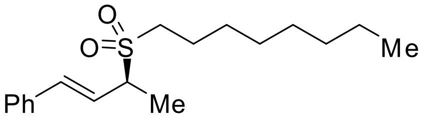
3i

Compound **3i**, white solid; m.p. 54-55 °C; 94% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 14.5 min, t_R (major) = 18.0 min; $[\alpha]_D^{20}$ = -75.1 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.69 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 3.6 Hz, 1H), 7.33-7.26 (m, 5H), 7.14-7.10 (m, 1H), 6.42 (d, *J* = 15.6 Hz, 3H), 6.14 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.98-3.90 (m, 1H), 1.60 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 137.6, 136.8, 135.8, 135.3, 134.4, 128.7, 128.5, 127.7, 126.7, 122.0, 65.2, 13.7; HRMS (ESI) calcd for $C_{14}H_{14}O_2NaS_2^+$ $(M + Na)^+$ 301.0327, found 301.0318.



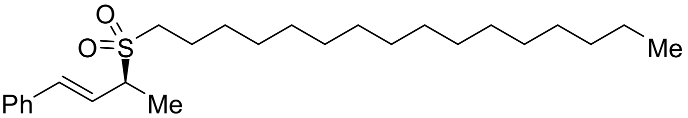
3j

Compound **3j**,[1c] white solid; m.p. 88-89 °C; 95% ee as determined by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min): t_R (minor) = 10.9 min, t_R (major) = 12.8 min; $[\alpha]_D^{20}$ = -21.1 (*c* = 0.80, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -19.5 (*c* = 0.84, $CHCl_3$, 92% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42 (d, *J* = 8.4 Hz, 2H), 7.37-7.28 (m, 3H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.83-3.75 (m, 1H), 2.85 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.4, 135.6, 128.9, 128.8, 126.8, 122.9, 63.2, 37.6, 12.8.



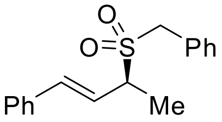
3k

Compound **3k**, white solid; m.p. 45-46 °C; 94% ee as determined by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min): t_R (minor) = 6.6 min, t_R (major) = 7.3 min; $[\alpha]_D^{20}$ = -70.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43-7.28 (m, 5H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 9.2 Hz, 1H), 3.84-3.75 (m, 1H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.91-1.78 (m, 2H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.42-1.23 (m, 10H), 0.86 (t, *J* =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.0, 135.7, 128.8, 128.7, 126.8, 123.2, 61.7, 49.8, 31.7, 29.1, 29.0, 28.6, 22.6, 21.5, 14.1, 12.7; HRMS (ESI) calcd for $C_{18}H_{28}O_2NaS^+$ $(M + Na)^+$ 331.1702, found 331.1701.



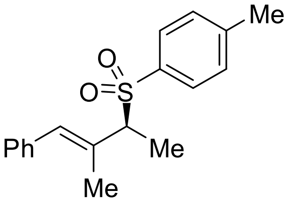
3l

Compound **3l**, white solid; m.p. 69-70 °C; 95% ee as determined by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min): t_R (minor) = 6.5 min, t_R (major) = 7.5 min; $[\alpha]_D^{20}$ = -53.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43-7.27 (m, 5H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.84-3.75 (m, 1H), 2.95 (t, *J* = 8.8 Hz, 2H), 1.91-1.79 (m, 2H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.40-1.23 (m, 26H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.0, 135.6, 128.9, 128.6, 126.7, 123.1, 61.6, 49.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 22.7, 21.4, 14.1, 12.6; HRMS (ESI) calcd for $C_{26}H_{44}O_2NaS^+$ (M + Na)$^+$ 443.2954, found 443.2952.



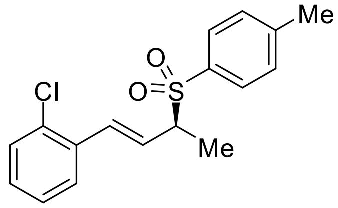
3m

Compound **3m**,[1c] white solid; m.p. 101-102 °C; 94% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (major) = 22.2 min, t_R (minor) = 24.5 min; $[\alpha]_D^{20}$ = -195.0 (*c* = 1.0, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -116.0 (*c* = 0.78, $CHCl_3$, 95% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44-7.29 (m, 10H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.29 (d, *J* = 14.0 Hz, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 3.77-3.69 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.4, 135.3, 130.7, 128.7, 128.6, 128.5, 127.4, 126.5, 122.6, 60.2, 56.3, 12.6.



3n

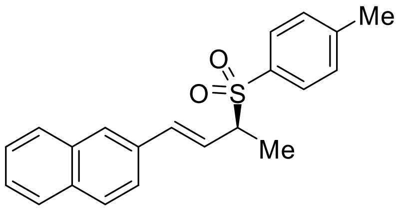
Compound **3n**,[1c] white solid; m.p. 65-66 °C; 96% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 13.0 min, t_R (major) = 14.6 min; $[\alpha]_D^{20}$ = -84.7 (*c* = 0.80, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -87.1 (*c* = 0.72, $CHCl_3$, 97% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.73 (d, *J* = 8.0 Hz, 2H), 7.32-7.25 (m, 4H), 7.22-7.18 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 3.83-3.77 (m, 1H), 2.42 (s, 3H), 1.90 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.5, 136.7, 134.4, 133.2, 131.5, 129.5, 129.2, 128.8, 128.1, 127.0, 69.3, 21.7, 15.8, 12.5.



3o

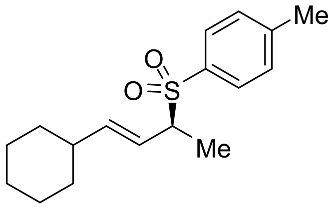
Compound **3o**, white solid; m.p. 59-60 °C; 96% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 16.2 min, t_R (major) = 24.0 min; $[\alpha]_D^{20}$ = -41.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.72 (d, *J* = 8.4 Hz, 2H), 7.48-7.45 (m, 1H), 7.33-7.29

(m, 3H), 7.25-7.17 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.93-3.85 (m, 1H), 2.42 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.8, 134.1, 133.9, 133.2, 132.5, 129.7, 129.6, 129.4, 129.2, 127.0, 125.3, 64.1, 21.7, 13.4; HRMS (ESI) calcd for $C_{17}H_{17}O_2ClNaS^+$ (M + Na)$^+$ 343.0530, found 343.0528.



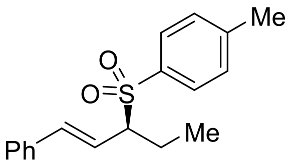
3p

Compound **3p**,[1c] white solid; m.p. 115-116 °C; 90% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 16.6 min, t_R (major) = 21.9 min; $[\alpha]_D^{20}$ = -103.5 (*c* = 0.95, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -109 (*c* = 0.60, 92% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.80-7.71 (m, 5H), 7.62 (s, 1H), 7.51-7.42 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.93-3.84 (m, 1H), 2.40 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.6, 136.3, 134.0, 133.4, 133.3, 129.5, 129.3, 128.4, 128.1, 127.7, 126.9, 126.4, 126.3, 123.3, 122.6, 64.2, 21.6, 13.6.



3q

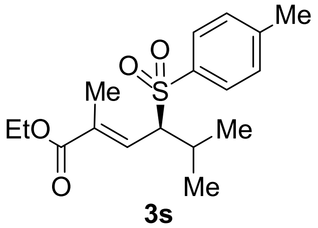
Compound **3q**,[1c] yellow oil; 95% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min): t_R (minor) = 16.6 min, t_R (major) = 20.3 min; $[\alpha]_D^{20}$ = -42.3 (*c* = 1.0, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -38.0 (*c* = 0.64, 98% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.67 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.36-5.25 (m, 2H), 3.62-3.54 (m, 1H), 2.42 (s, 3H), 1.89-1.81 (m, 1H), 1.67-1.52 (m, 5H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.25-1.01 (m, 3H), 0.94-0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.3, 143.9, 134.1, 129.3, 129.2, 120.8, 63.8, 40.5, 32.3, 32.2, 26.0, 25.7, 21.5, 13.3.



3r

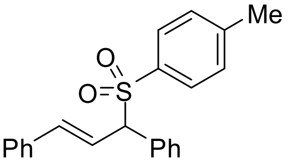
Compound **3r**,[1c] white solid; m.p. 66-67 °C; 98% ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 70/30, flow rate 1.0

mL/min): t_R (minor) = 17.5 min, t_R (major) = 21.4 min; $[\alpha]_D^{20}$ = -81.2 (*c* = 1.1, $CHCl_3$), Lit.[1c]: $[\alpha]_D^{20}$ = -80.8 (*c* = 0.88, 95% ee, *S*-enantiomer); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.33-7.24 (m, 7H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.90 (dd, *J* = 16.0, 9.6 Hz, 1H), 3.58-3.51 (m, 1H), 2.41 (s, 3H), 2.28-2.21 (m, 1H), 1.78-1.73 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.1, 136.0, 134.8, 129.5, 129.2, 128.6, 126.6, 121.2, 71.1, 21.6, 21.1, 11.4.



3s

Compound **3s**, white solid; m.p. 60-61 °C; 99% ee as determined by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90/10, flow rate 1.0 mL/min): t_R (minor) = 7.2 min, t_R (major) = 8.3 min; $[\alpha]_D^{20}$ = -52.0 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.73-6.69 (m, 1H), 4.24-4.18 (m, 2H), 3.72 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.76-2.70 (m, 1H), 2.43 (s, 3H), 1.37 (d, *J* = 1.6 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 144.8, 135.9, 135.4, 130.2, 129.6, 128.7, 70.1, 61.1, 28.2, 22.0, 21.6, 18.3, 14.2, 12.5; HRMS (ESI) calcd for $C_{17}H_{24}O_4NaS^+$ $(M + Na)^+$ 347.1288, found 347.1285.

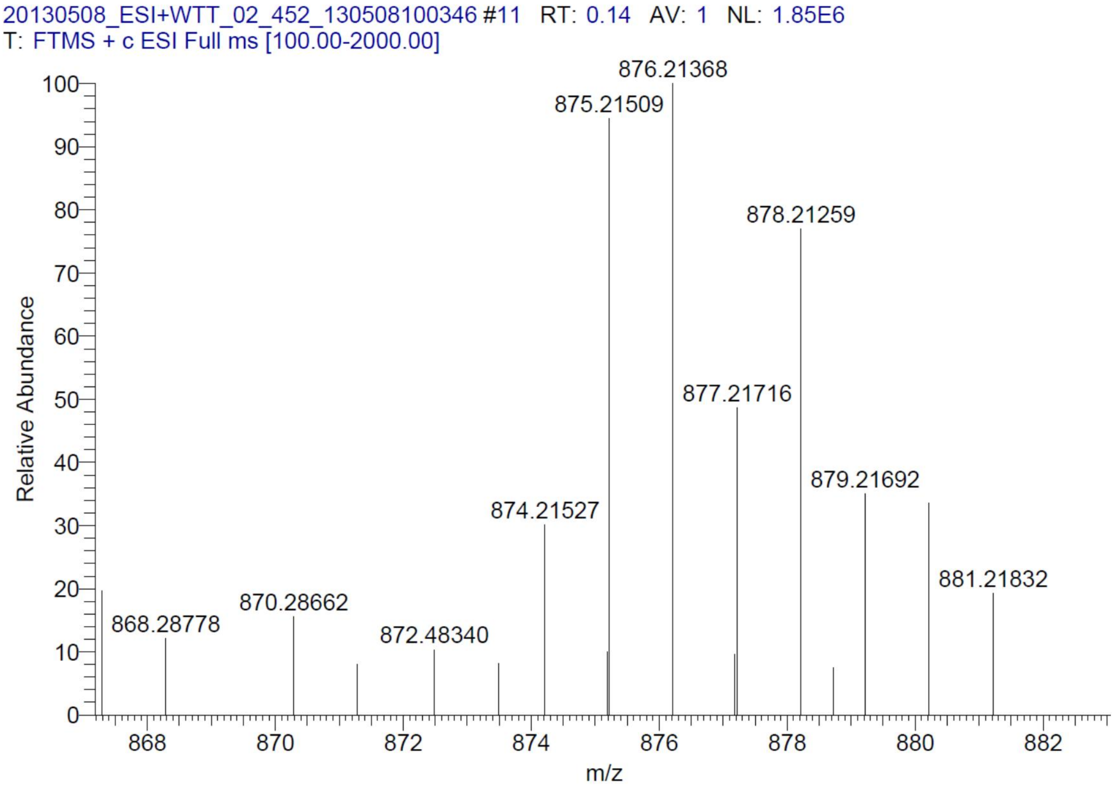


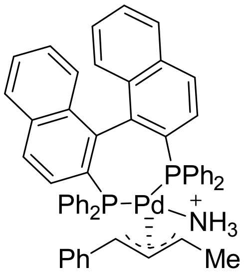
3t

Compound **3t**,[1c] white solid; m.p. 150-151 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.37-7.25 (m, 10H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.62-6.50 (m, 2H), 4.82 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 138.0, 136.0, 134.5, 132.5, 129.7, 129.4, 129.3, 128.9, 128.7, 128.6, 128.5, 126.8, 120.2, 75.4, 21.9.

ESI-MS analysis of the reaction mixture

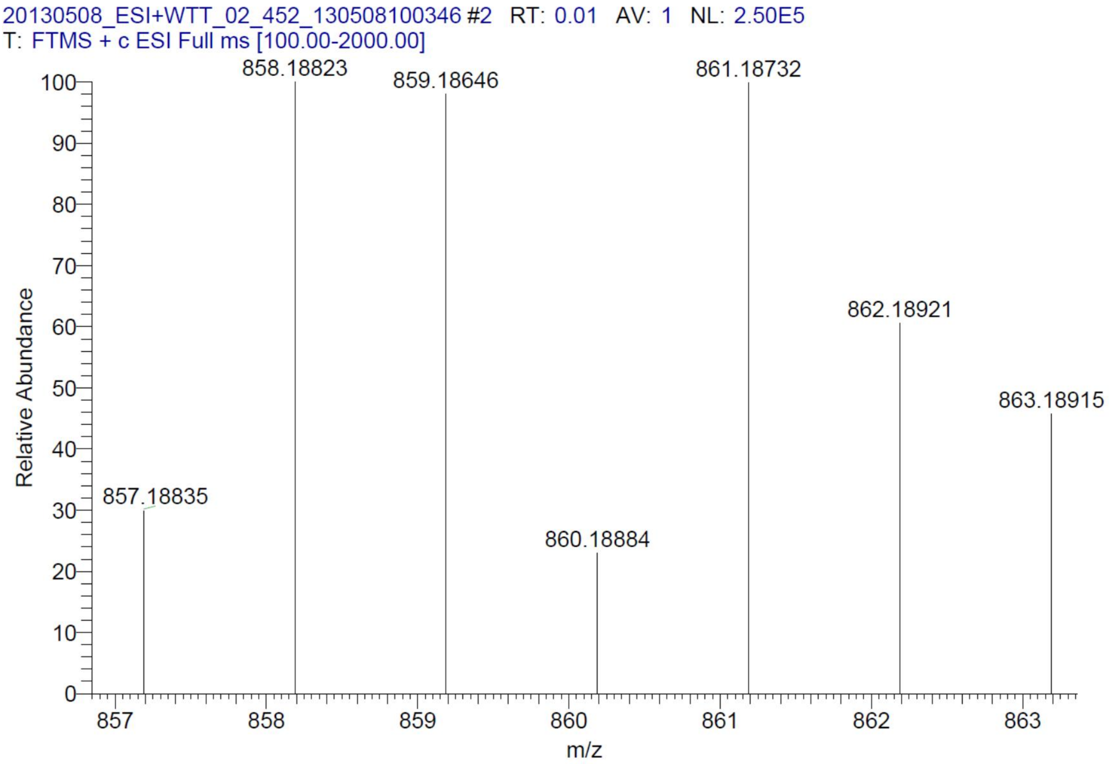
To a solution of amine **1a** (29.4 mg, 0.20 mmol) in dioxane (1.2 mL) was added sulfonyl hydrazide **2a** (55.9 mg， 0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol). The mixture was stirred under air at room temperature for 30 min, and directly subjected to ESI-MS (positive mode) analysis. Copied below is the spectrometry we obtained and the species shown below have been assigned according to the high resolution mass data.

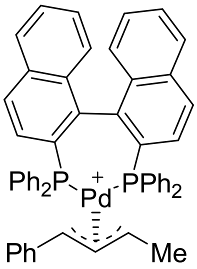




5a

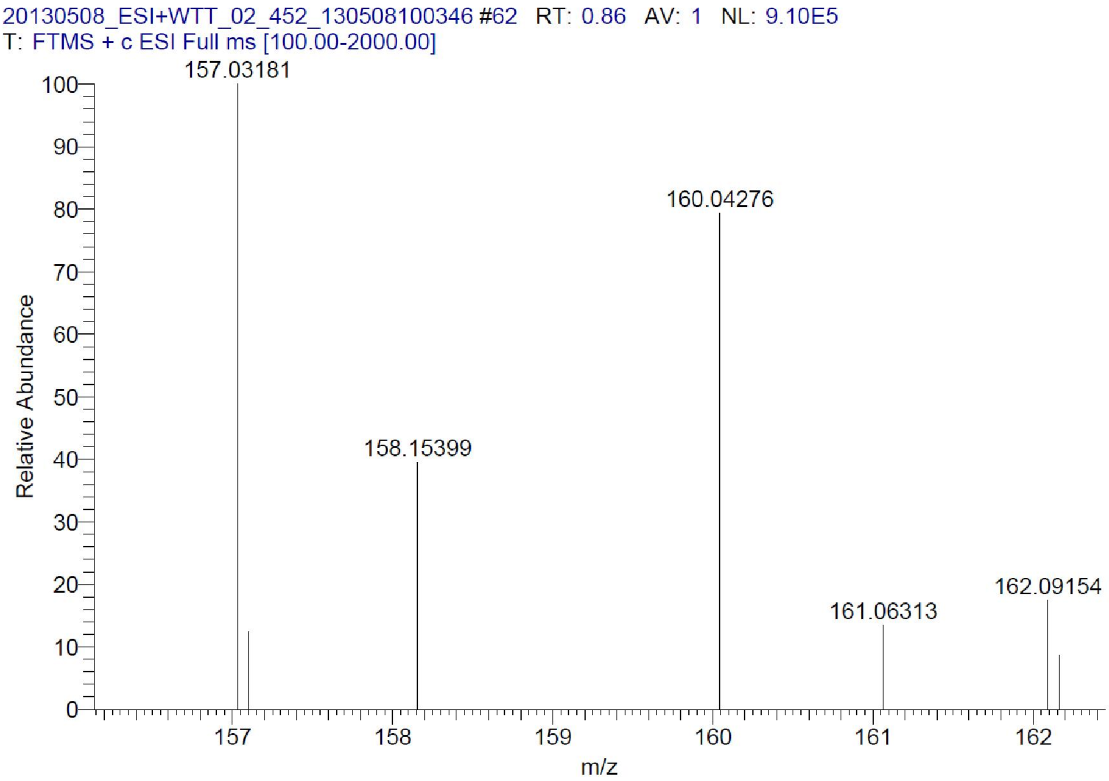
π-Allylpalladium **5a**: HRMS (ESI) calcd for $C_{54}H_{46}NP_2Pd^+$ (**5a** + H)$^+$ 876.21348, found 876.21368.

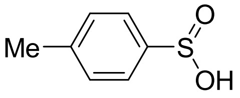




6a

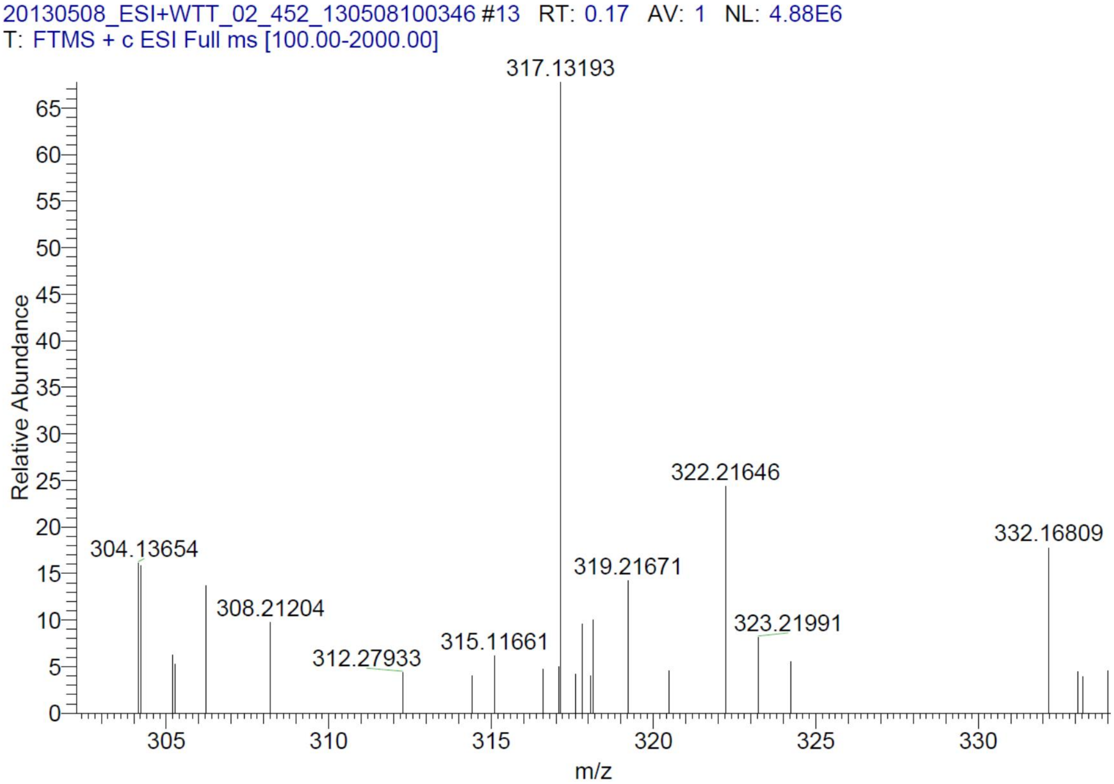
π-Allylpalladium **6a**: HRMS (ESI) calcd for $C_{54}H_{43}P_2Pd^+$ (**6a** + H)$^+$ 859.18693, found 859.18646.

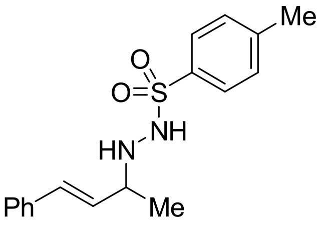




7a

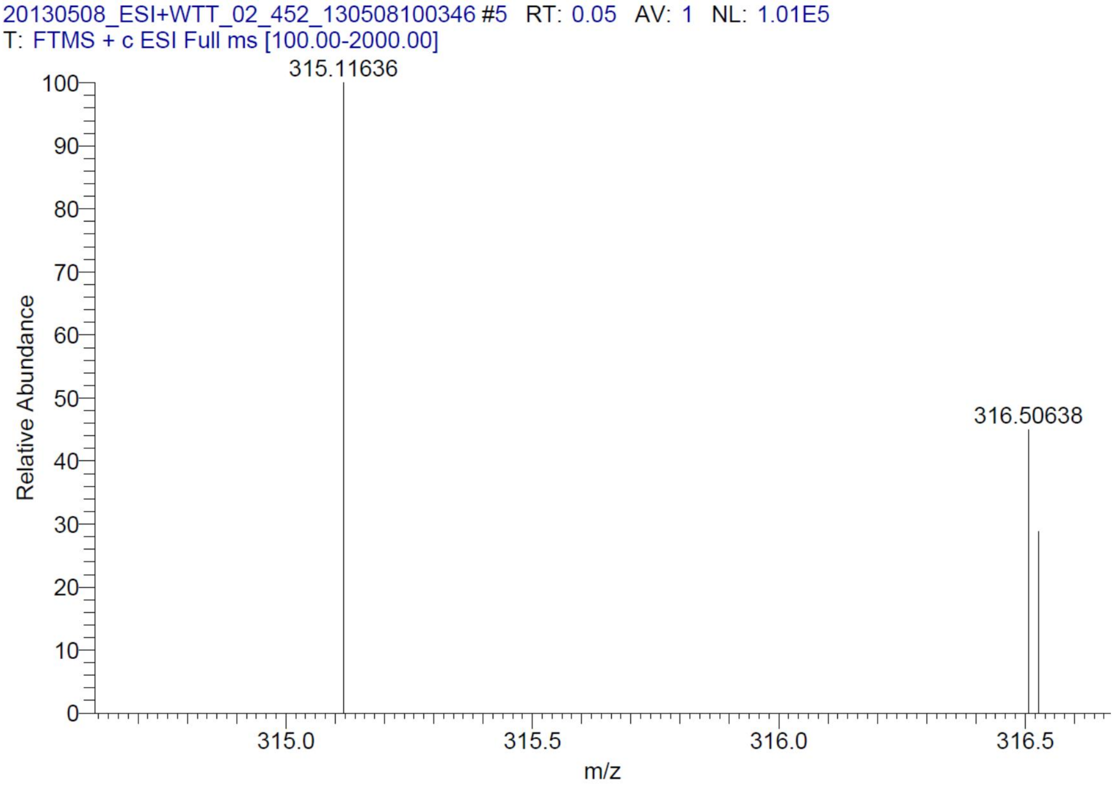
Sulfinic acid **7a**: HRMS (ESI) calcd for $C_7H_9O_2S^+$ (**7a** + H)$^+$ 157.03178, found 157.03181.

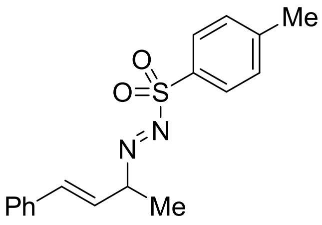




8a

Sulfonyl hydrazide **8a**: HRMS (ESI) calcd for $C_{17}H_{21}N_2O_2S^+$ (**8a** + H)$^+$ 317.13183, found 317.13193.

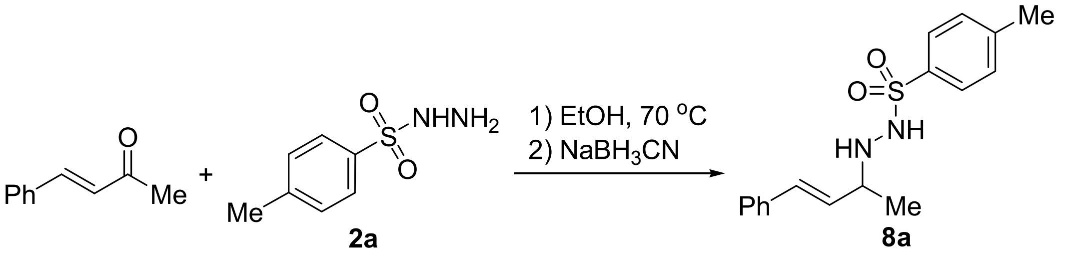




9a

Sulfonyl diazene **9a**: HRMS (ESI) calcd for $C_{17}H_{19}N_2O_2S^+$ (**9a** + H)$^+$ 315.11617, found 315.11636.

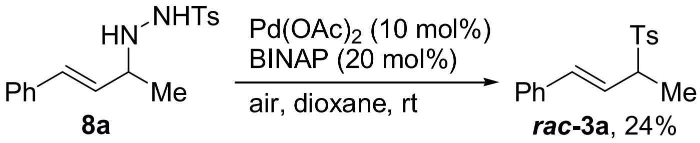
Preparation of sulfonyl hydrazide 8a[10a]



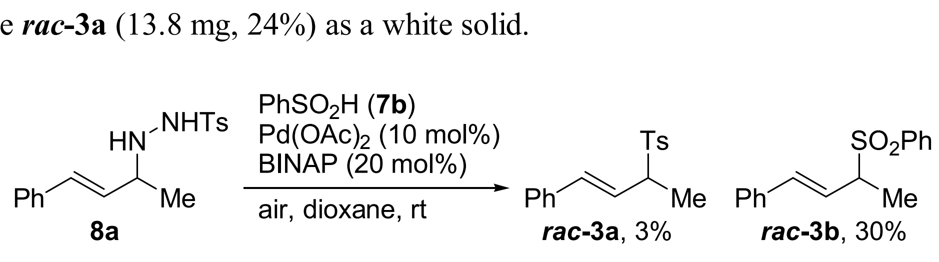
A mixture of (*E*)-4-phenylbut-3-en-2-one (1.47 g, 10.0 mmol) and sulfonyl hydrazine **2a** (1.77 g, 9.5 mmol) in absolute ethanol (15.0 mL) was heated with stirring at 70 °C for 2 h. The mixture was cooled to room temperature, then ether (20 mL) was added, and the solid was collected by filtration and washed thoroughly with ether (4 x 5 mL) to give the corresponding tosylhydrazone as a light yellow soild.

To a stirred solution of the tosylhydrazone and a trace of methyl orange (indicator) in a mixture of 1:1 THF-MeOH (80 mL) was added sodium cyanoborohydride (628 mg, 10.0 mmol) slowly at 0 °C. Methanol saturated with hydrogen chloride was then added dropwise, keeping the color of the solution at the red-yellow transition point (orange, pH = 3.8). A second portion of sodium cyanoborohydride (314 mg, 5.0 mmol) was added followed by the dropwise addition of methanol saturated with hydrogen chloride to maintain the pH at 3.8. The mixture was then stirred for 2 h at 25 °C and at pH 3.8. A saturated solution of sodium bicarbonate was then added, and the mixture (pH = 7) was concentrated in vacuo. Water (60 mL) was added, and the solution was extracted with dichloromethane (3 x 40 mL). The combined organic phases were successively washed with 6 N HCl (30 mL), saturated aqueous sodium bicarbonate (30 mL), and saturated brine (30 mL), dried over anhydrous sodium sulfate, and then evaporated in vacuo to dryness. The resulting solid was purified by recrystallization (dichloromethane/hexane) to give sulfonyl hydrazine **8a** (2.20 g, 73%) as a yellow solid.[10b] m.p. 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.36-7.22 (m, 7H), 6.30 (d, J = 16.0 Hz, 1H), 5.84 (s, br, 1H), 5.74 (dd, J = 16.0, 8.4 Hz, 1H), 3.37-3.29 (m, 1H), 2.43 (s, 3H), 1.10 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.1, 135.7, 132.9, 129.9, 129.6, 128.6, 128.2, 127.9, 126.5, 58.0, 21.6, 19.1; HRMS (ESI) calcd for $C_{17}H_{20}O_2N_2NaS^+$ $(M + Na)^+$ 339.1138, found 339.1133.

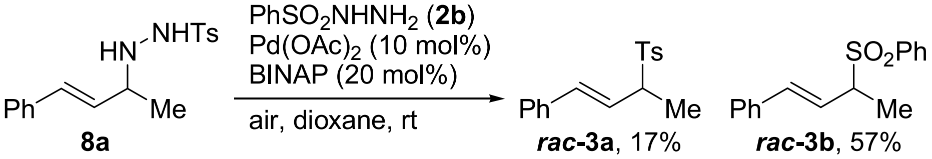
Reactions of sulfonyl hydrazide 8a



A mixture of sulfonyl hydrazide **8a** (63.3 mg, 0.20 mmol), $Pd(OAc)_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol) in dioxane (1.2 mL) was stirred under air at room temperature for 24 h. The mixture was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give sulfone ***rac*-3a** (13.8 mg, 24%) as a white solid.

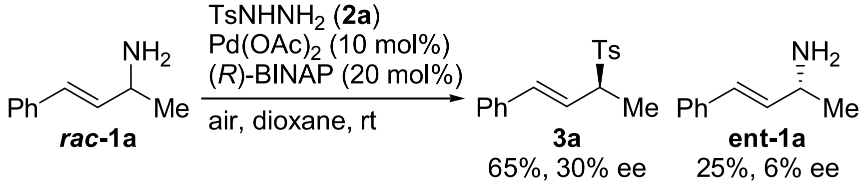


A mixture of sulfonyl hydrazide **8a** (63.3 mg, 0.20 mmol), sulfinic acid **7b** (42.7 mg, 0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol) in dioxane (1.2 mL) was stirred under air at room temperature for 24 h. The mixture was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give a mixture of sulfones ***rac*-3a** (1.7 mg, 3%) and ***rac*-3b** (16.3 mg, 30%). The ratio was determined by ^{1}H NMR spectroscopic analysis.

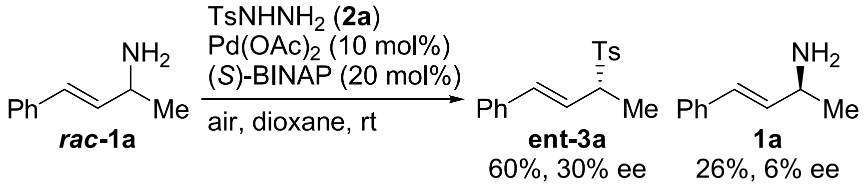


A mixture of sulfonyl hydrazide **8a** (63.3 mg, 0.20 mmol), sulfonyl hydrazide **2b** (51.6 mg, 0.30 mmol), Pd(OAc)$_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol) in dioxane (1.2 mL) was stirred under air at room temperature for 24 h. The mixture was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give a mixture of sulfones ***rac*-3a** (9.7 mg, 17%) and ***rac*-3b** (31.0 mg, 57%). The ratio was determined by ^{1}H NMR spectroscopic analysis.

Reactions of amine *rac*-1a in the presence of optically active BINAP

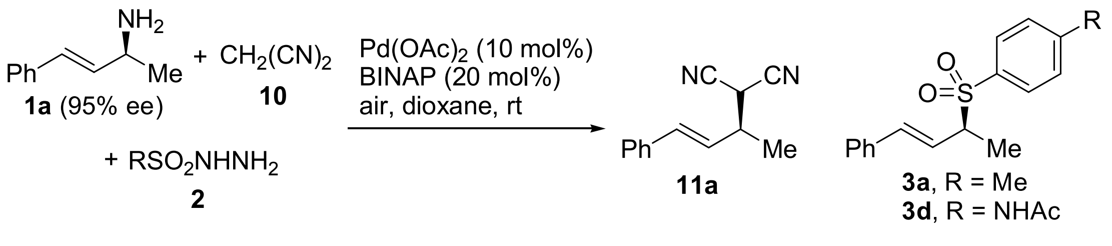


To a solution of racemic amine ***rac*-1a** (29.4 mg, 0.20 mmol) in dioxane (1.2 mL) was added sulfonyl hydrazide **2a** (55.9 mg, 0.30 mmol), Pd(OAc)$_2$ (4.4 mg, 0.020 mmol,) and (*R*)-BINAP (24.8 mg, 0.040 mmol). The mixture was stirred under air at room temperature for 24 h, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give sulfone **3a** (37.3 mg, 65%, 30% ee) as a white solid. Amine **ent-1a** was recovered (7.4 mg, 25%, 6% ee) as a yellowish oil by eluting with methanol/dichloromethane (1:5).



Replacing (*R*)-BINAP with (*S*)-BINAP in the above reaction led to the formation of sulfone **ent-3a** (34.4 mg, 60%, 30% ee) as a white solid and the recovery of amine **1a** (7.6 mg, 26%, 6% ee) as a yellowish oil.

Reactions of amine 1a with malononitrile (10) and sulfonyl hydrazide 2



To a solution of amine **1a** (29.4 mg, 0.20 mmol) in dioxane (1.2 mL) was added sulfonyl hydrazide **2** (0.02 or 0.30 mmol), malononitrile (**10**) (19.8 mg, 0.30 mmol), $Pd(OAc)_2$ (4.4 mg, 0.020 mmol), and racemic BINAP (24.8 mg, 0.040 mmol). The mixture was stirred under air at room temperature for 24 h, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5), to give substituted malononitrile **11a** and sulfone **3**. Compounds **11a** and **3a** were inseparable from each other, and their ratio was determined by ^{1}H NMR spectroscopic analysis.

Compound **11a**,[1d] colorless oil; 95% ee as determined by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 97/3, flow rate 1.0 mL/min): t_R (major) = 17.2 min, t_R (minor) = 19.5 min; $[\alpha]_D^{20}$ = -13.2 (*c* = 1.0, $CHCl_3$), Lit.[1d]: $[\alpha]_D^{20}$ = -11.1 (*c* = 1.0, $CHCl_3$, 95% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.26 (m, 5H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.11 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.74 (d, *J* = 5.6 Hz, 1H), 3.11-3.01 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 134.7, 128.7, 128.5, 126.7, 126.0, 111.7, 111.6, 39.3, 29.9, 17.7.

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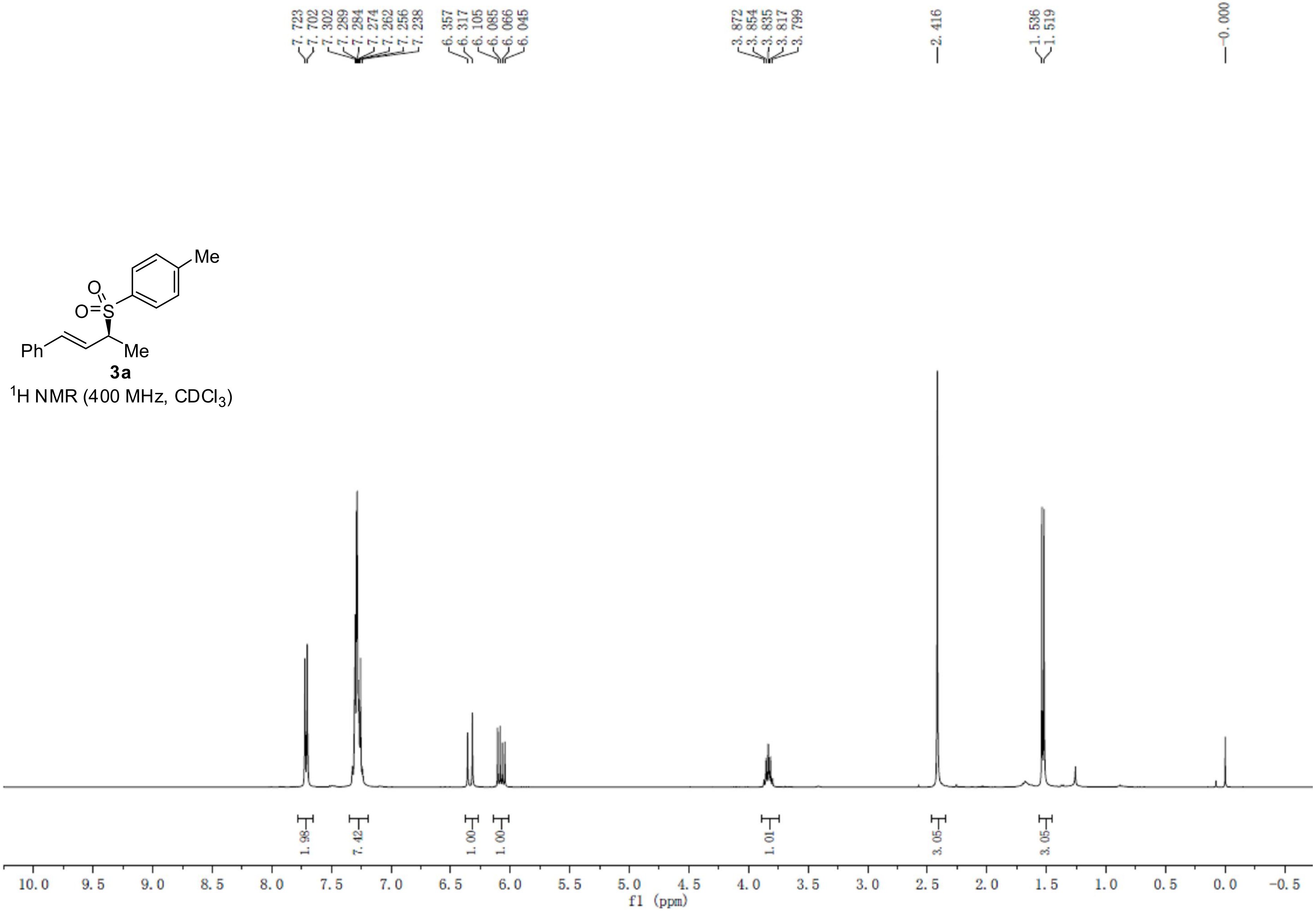
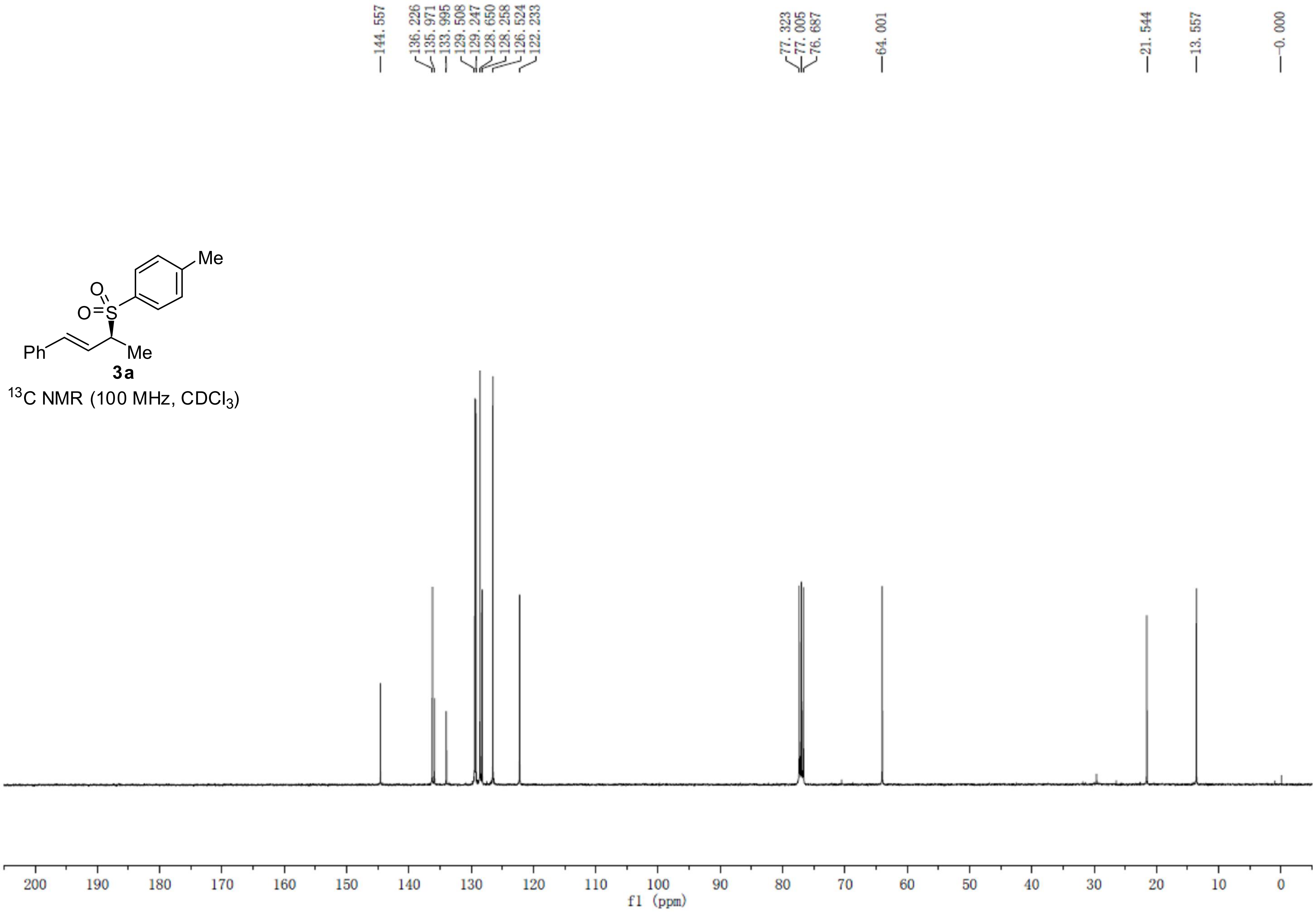


3a

^{1}H NMR (400 MHz, CDCl$_3$)



3a

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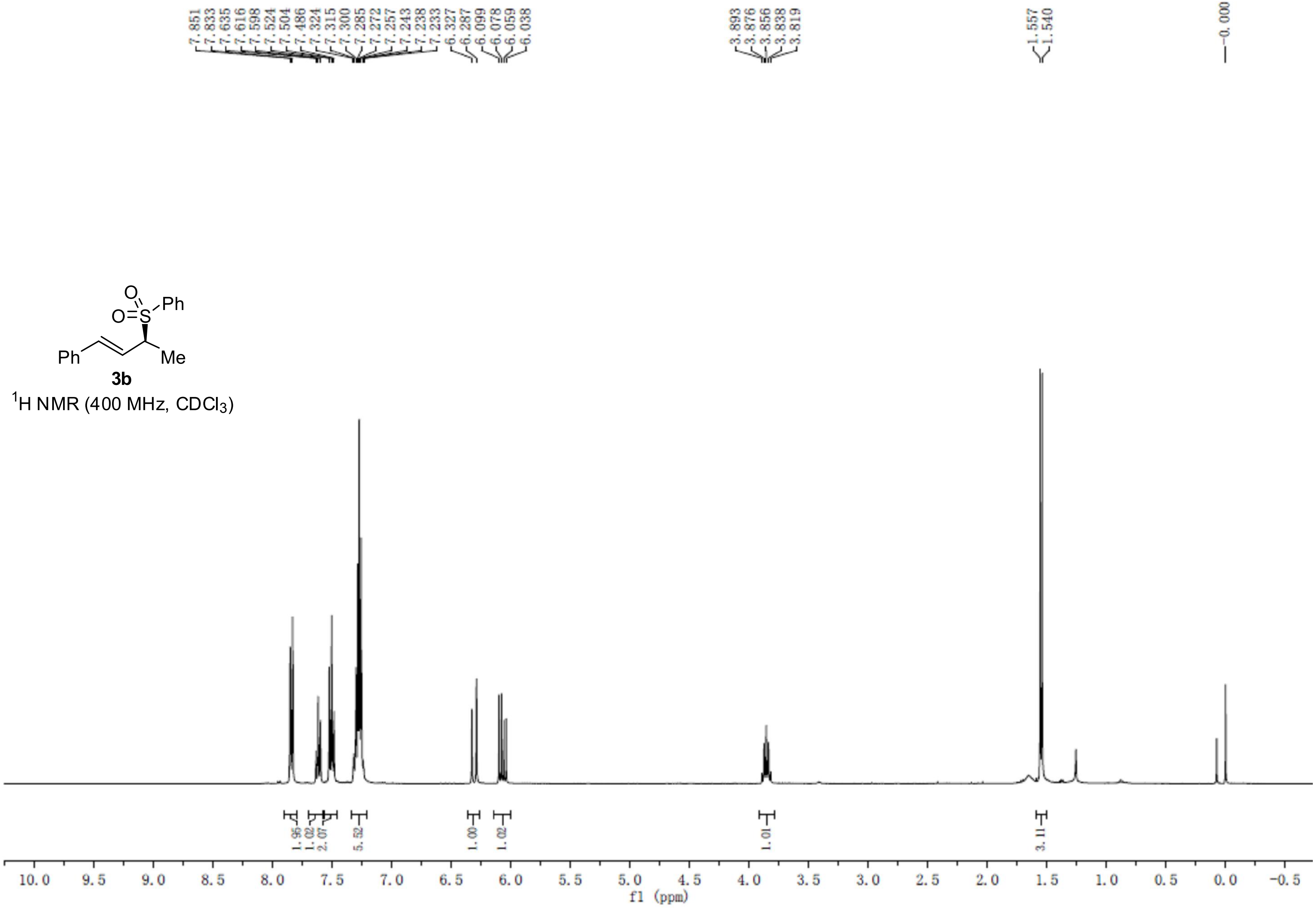

3b

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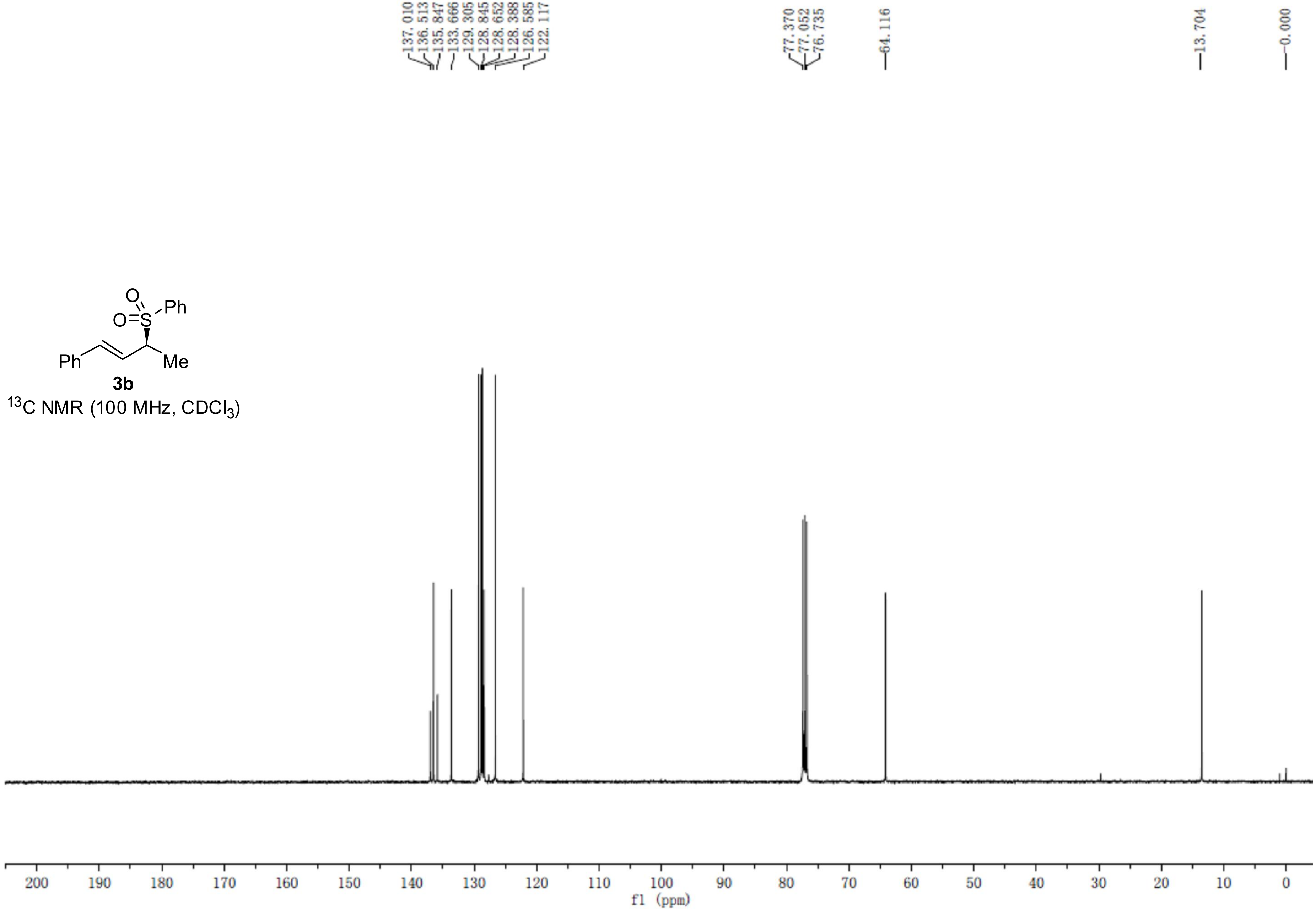

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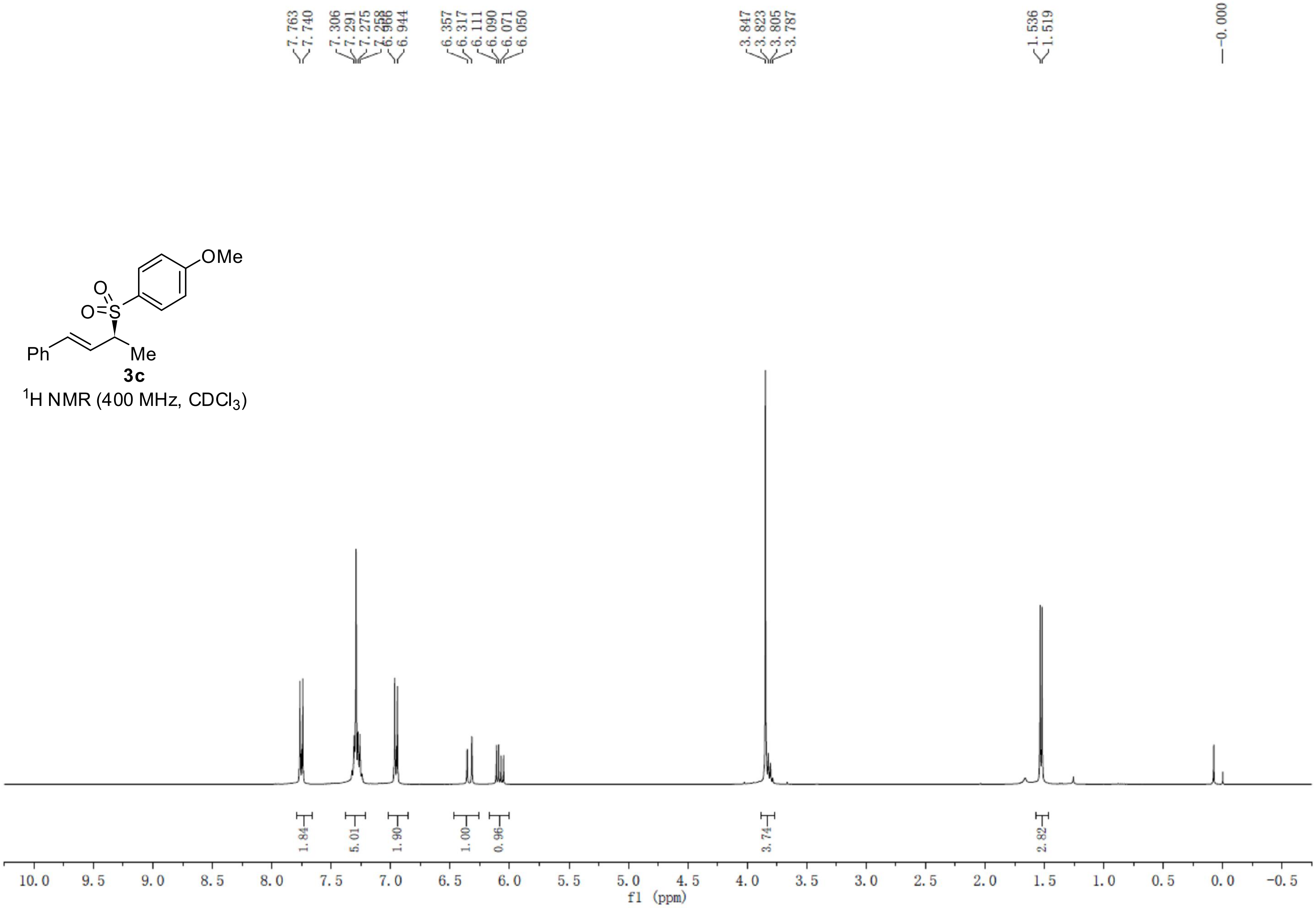

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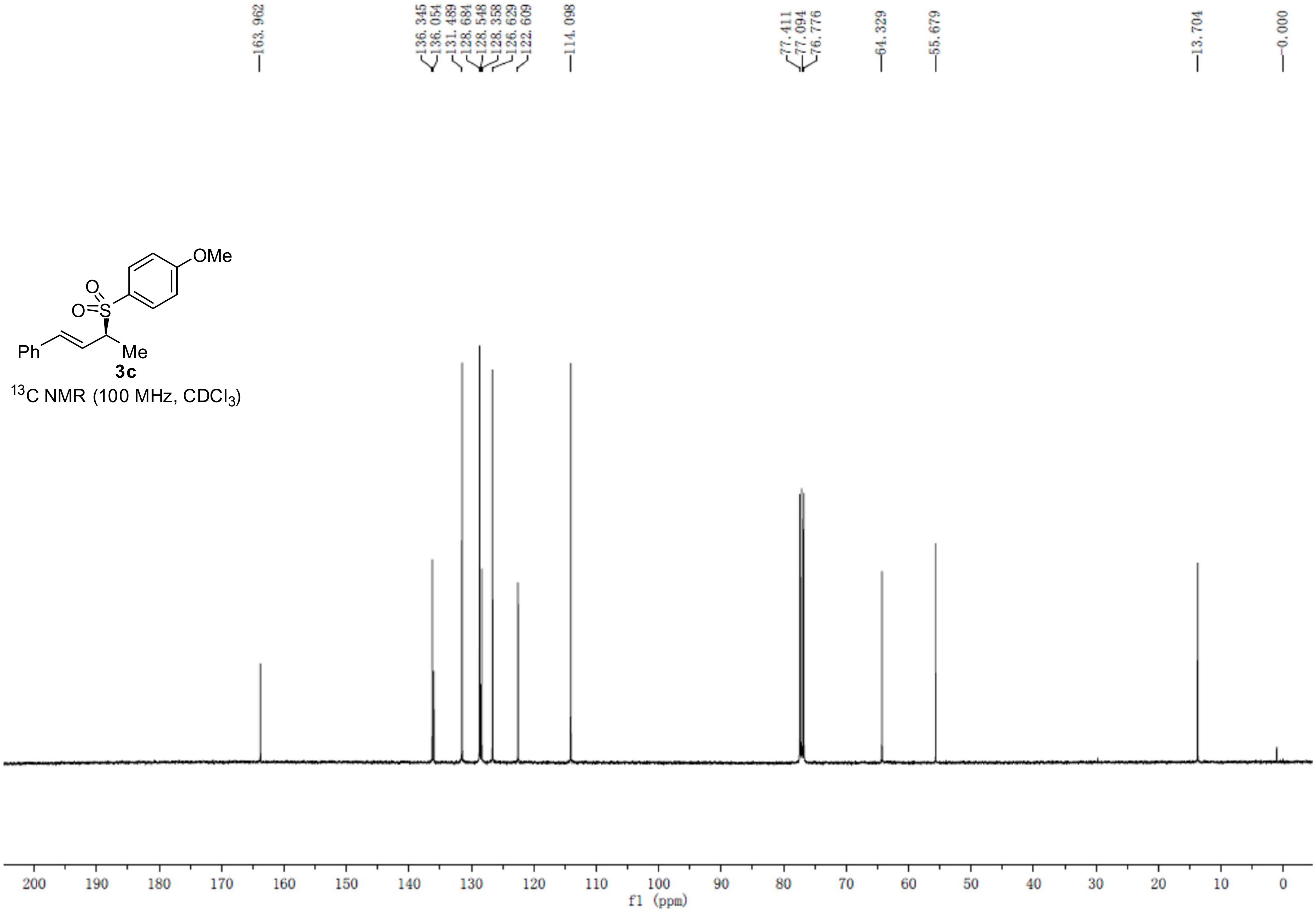

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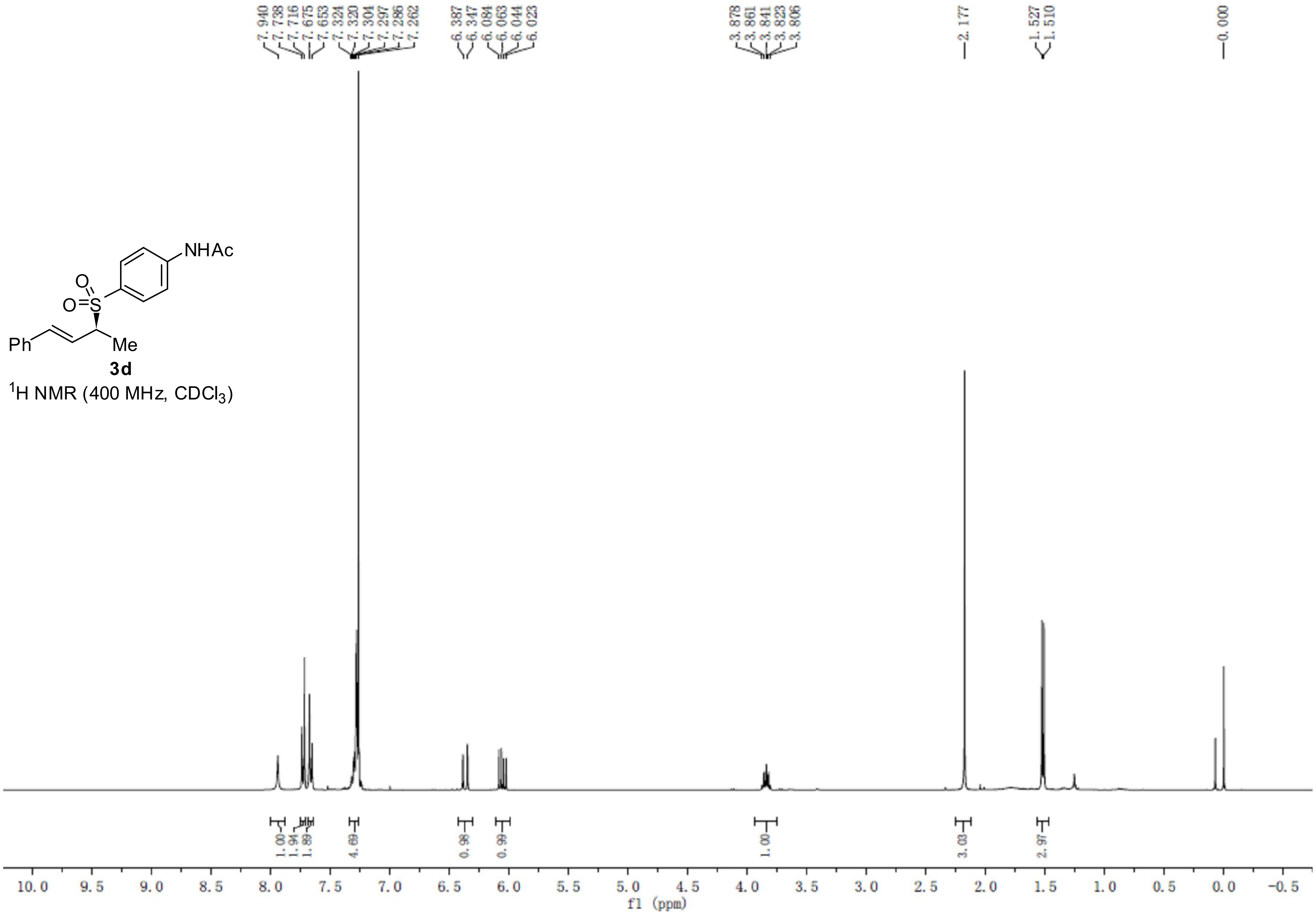
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6.084
6.063
6.044
6.023
3.878
3.861
3.841
3.823
3.806
2.177
1.527
1.510
0.000
NHAc
O
O=S
Ph
Me
3d
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.94
1.89
4.69
0.98
0.99
1.00
3.03
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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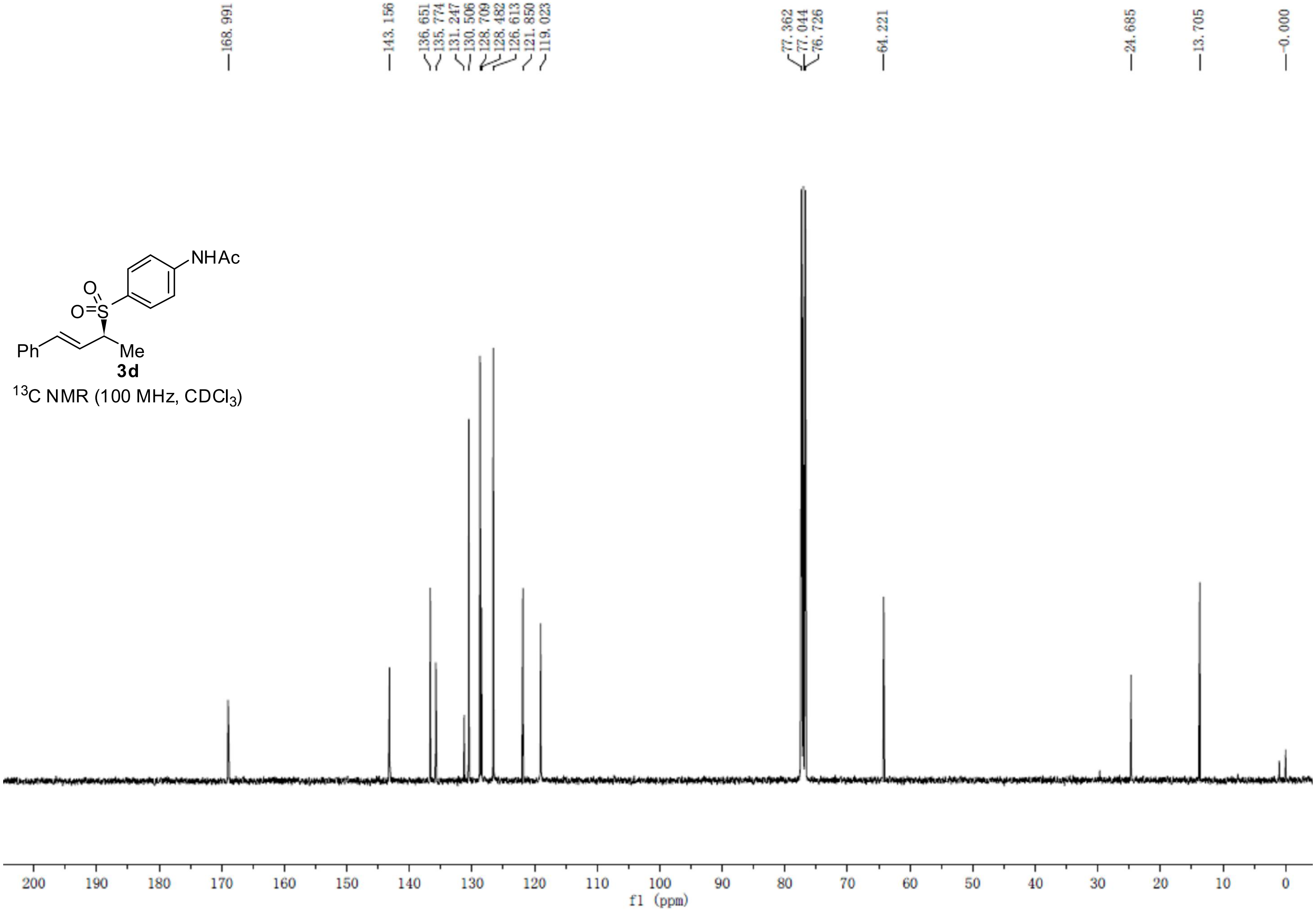
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


3d

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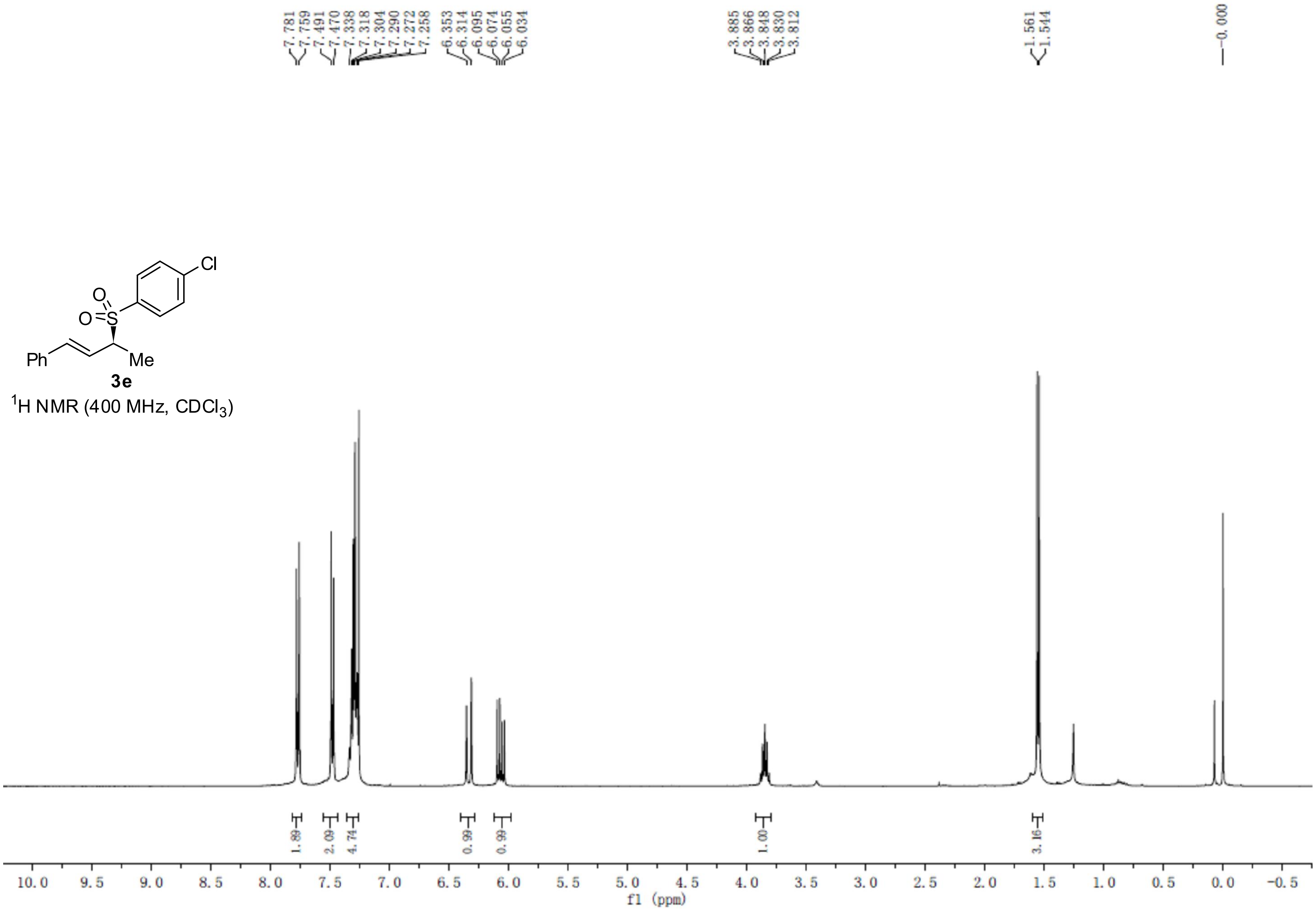

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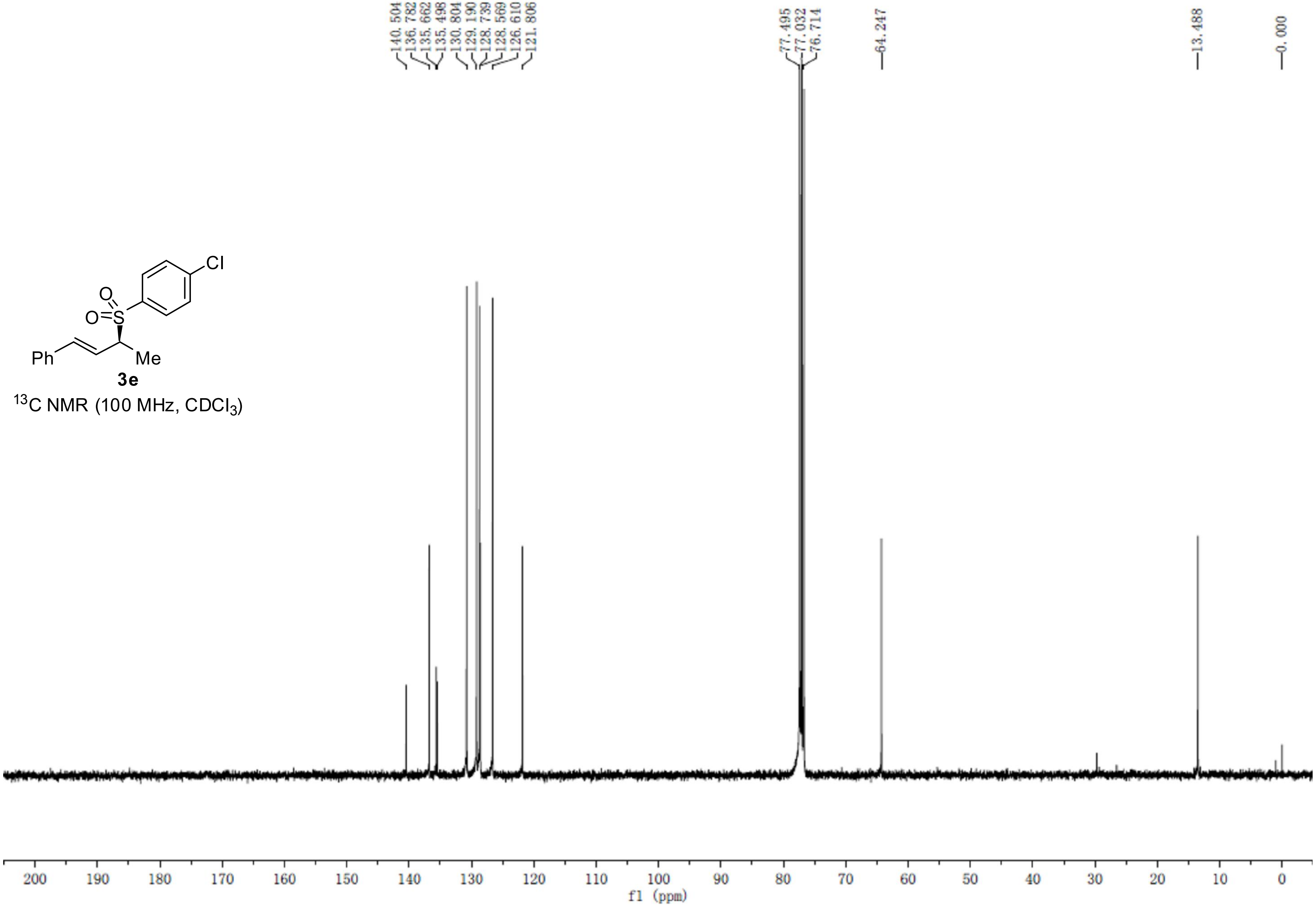

3e

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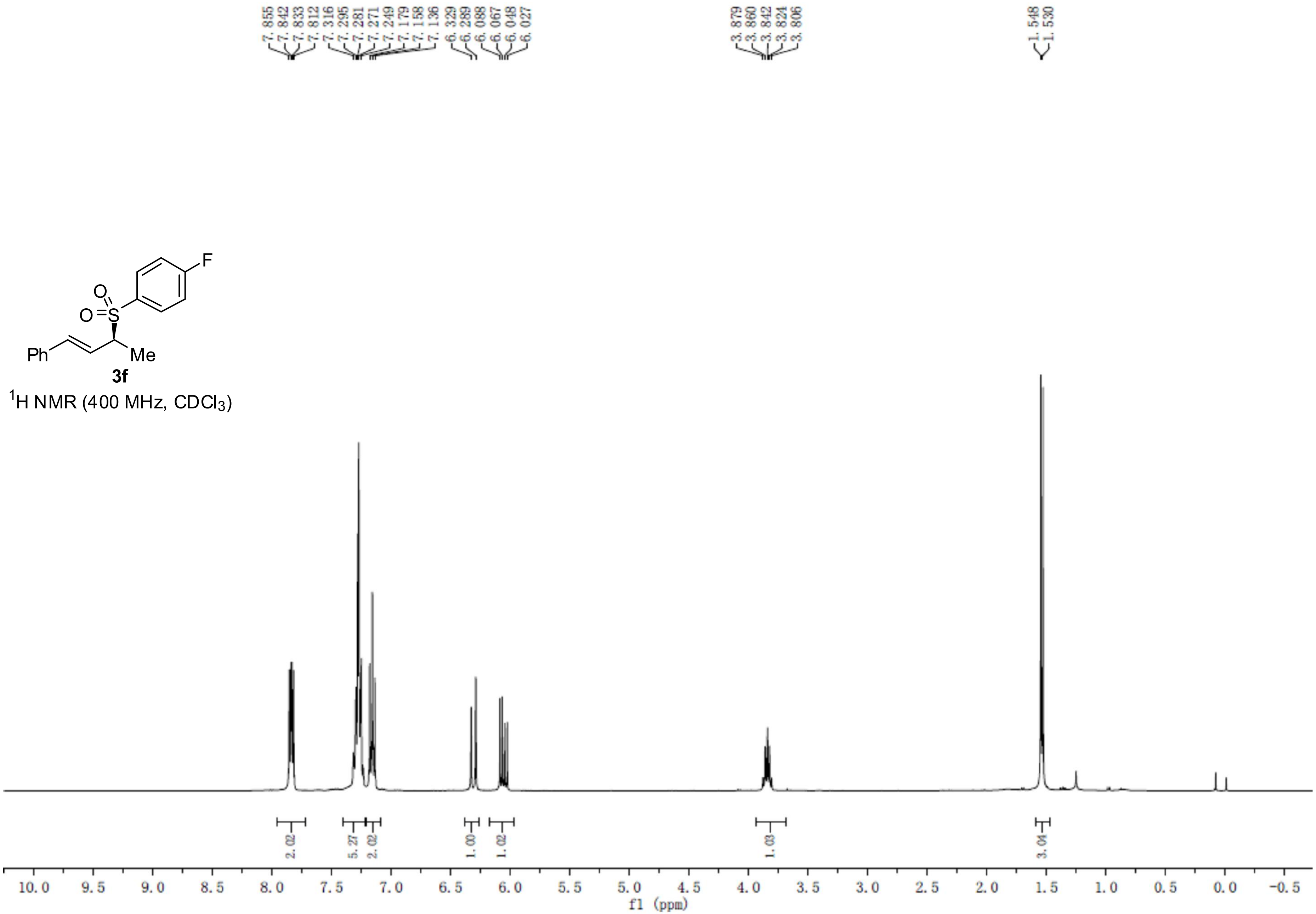

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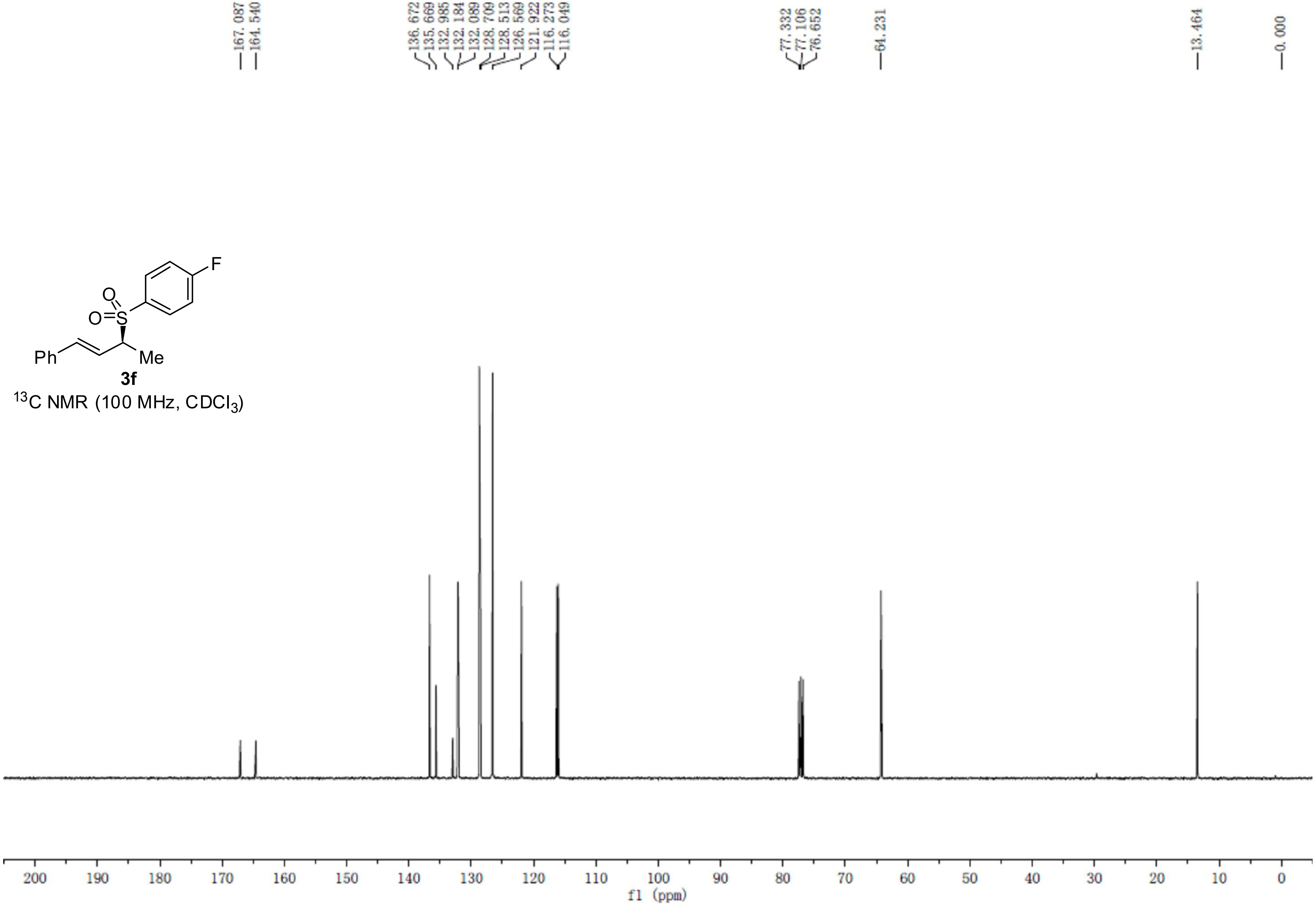

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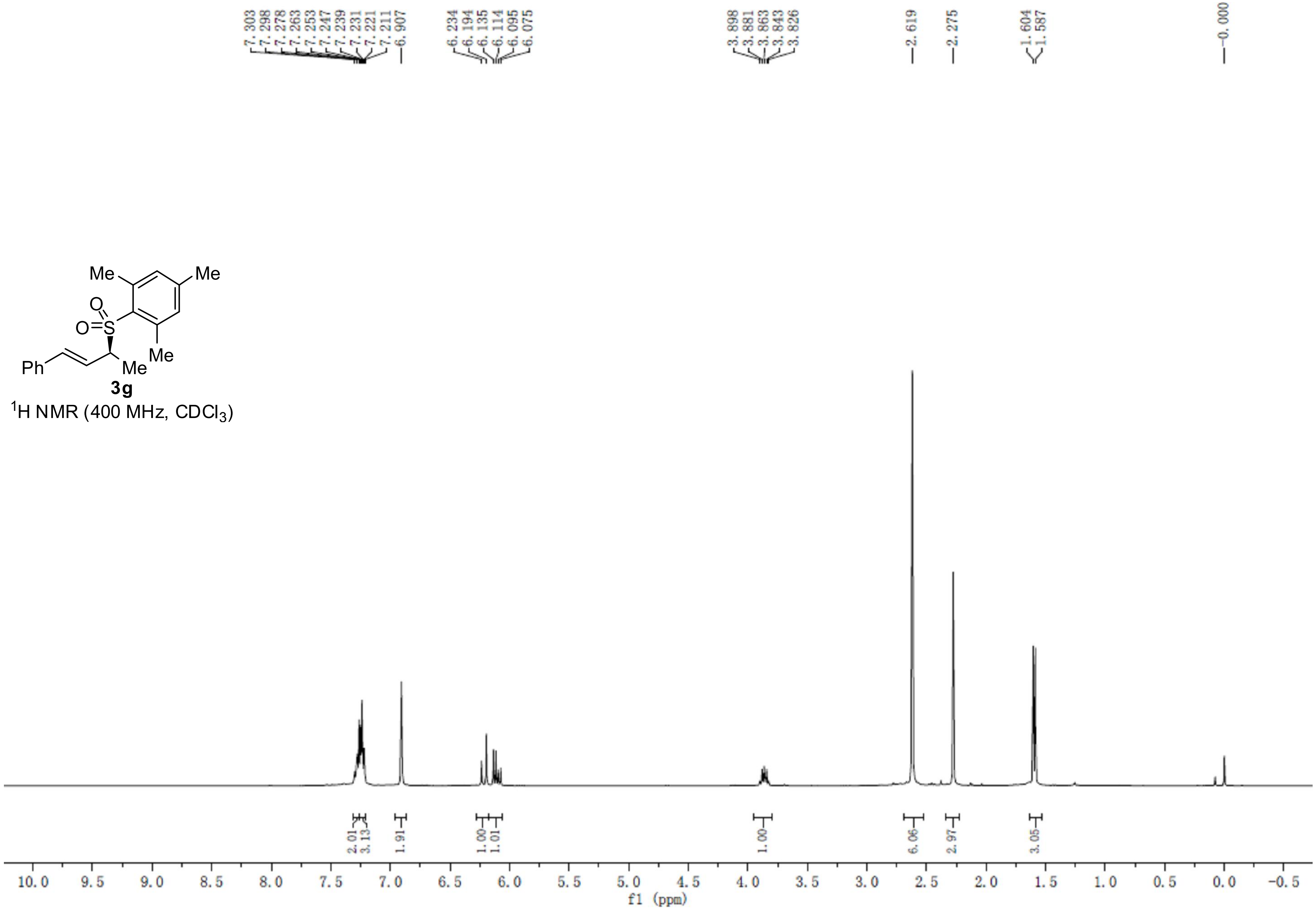

3g

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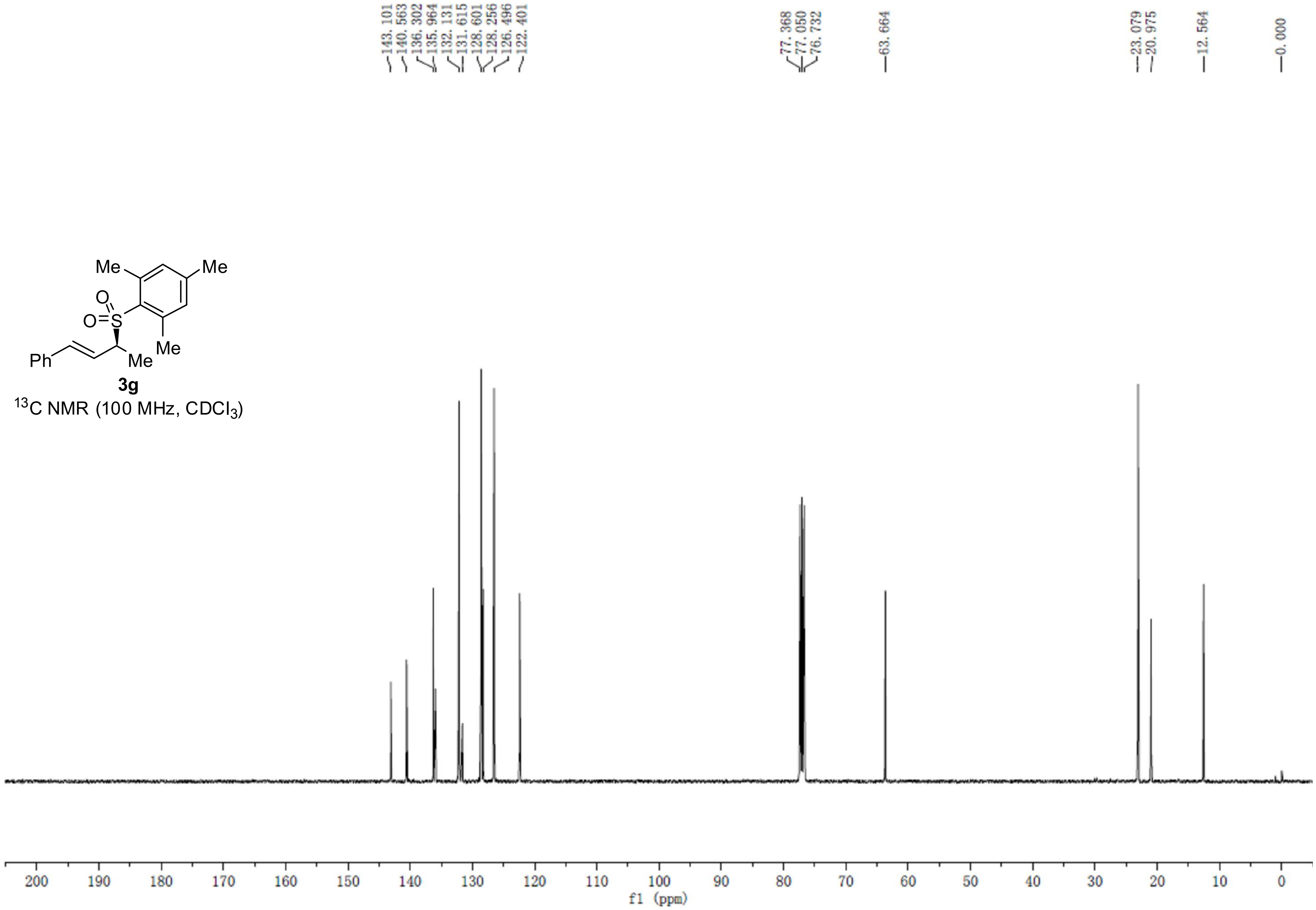

3g

^{13}C NMR (100 MHz, CDCl$_3$)

3h

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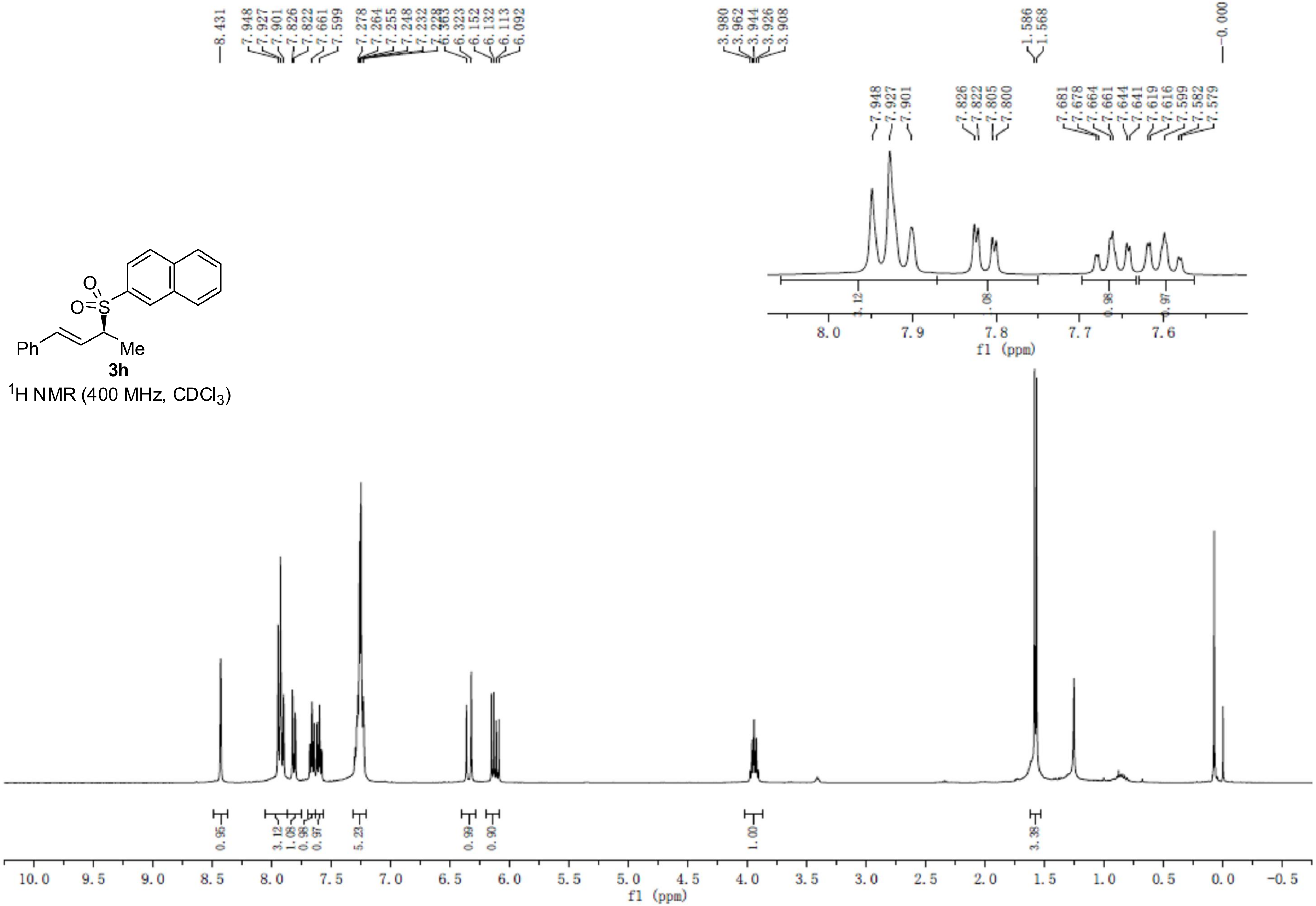

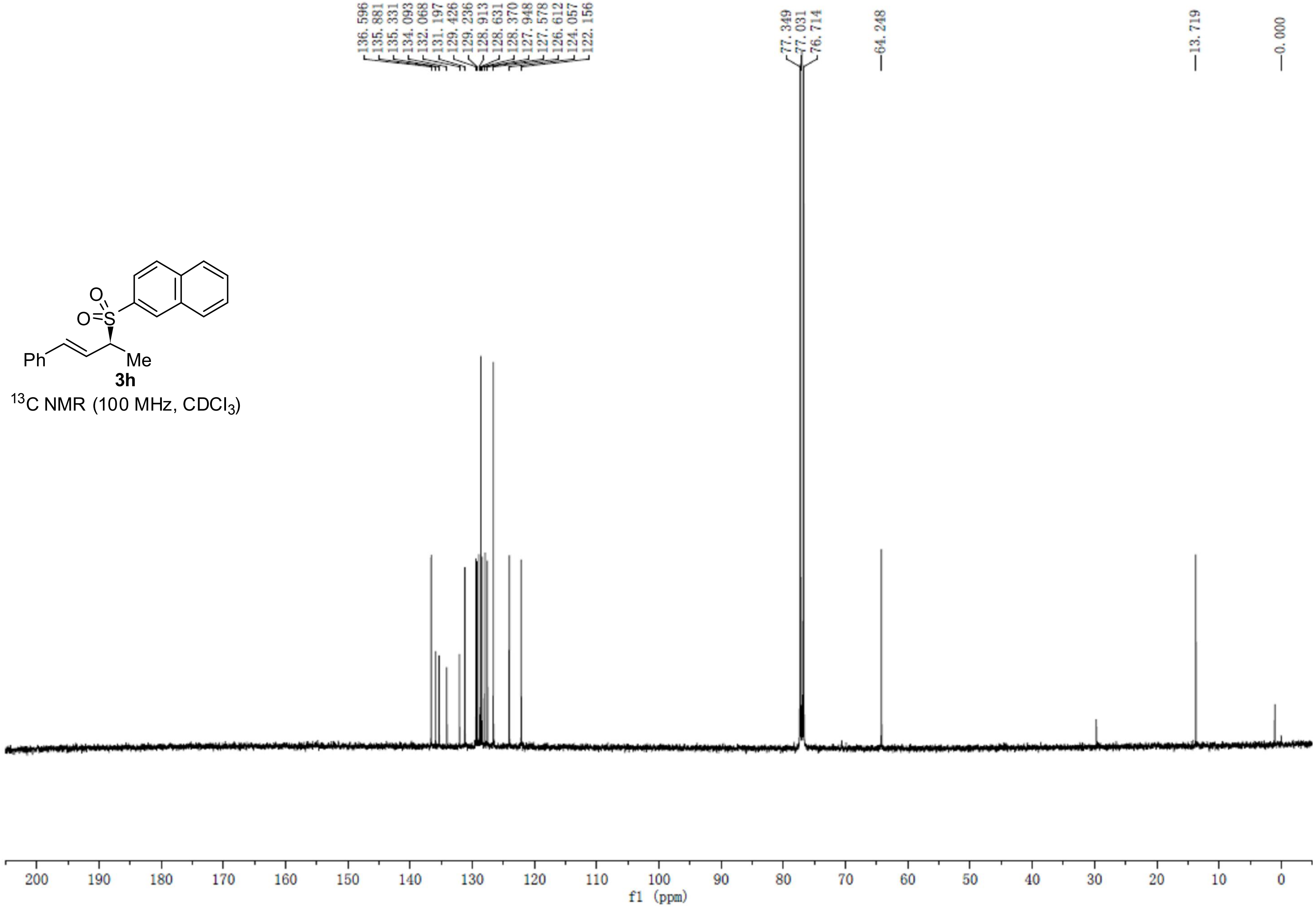

3h

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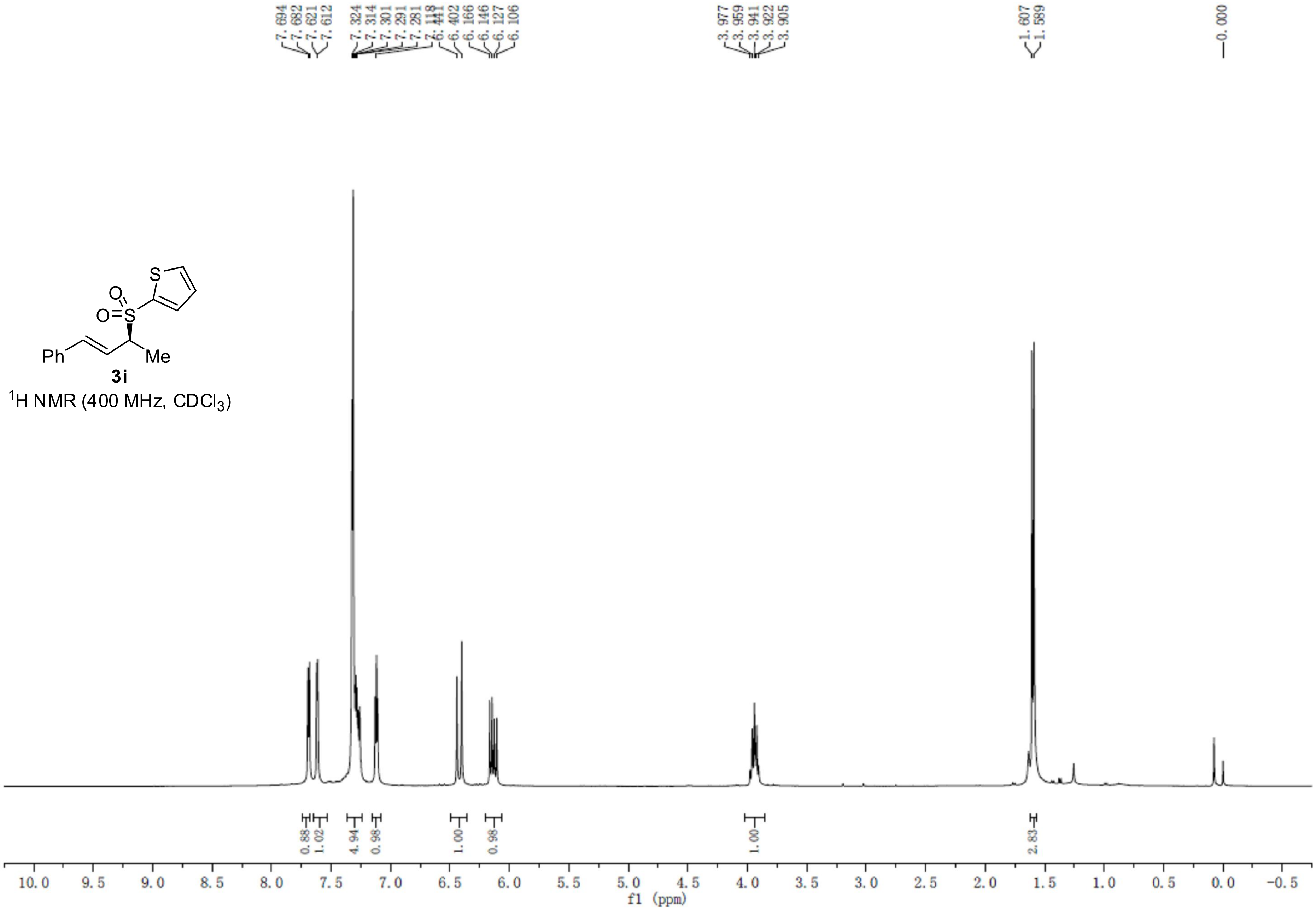

3i

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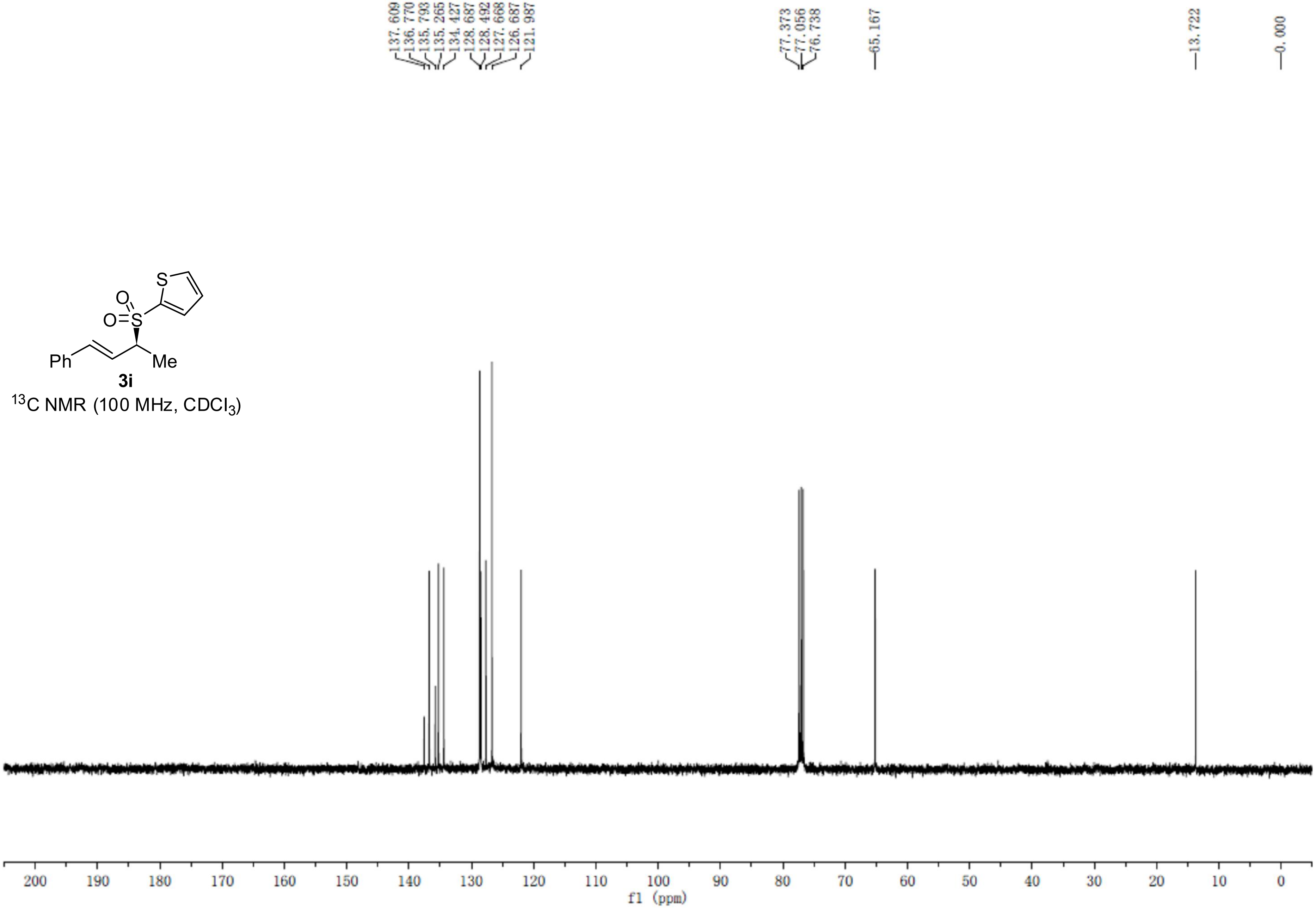

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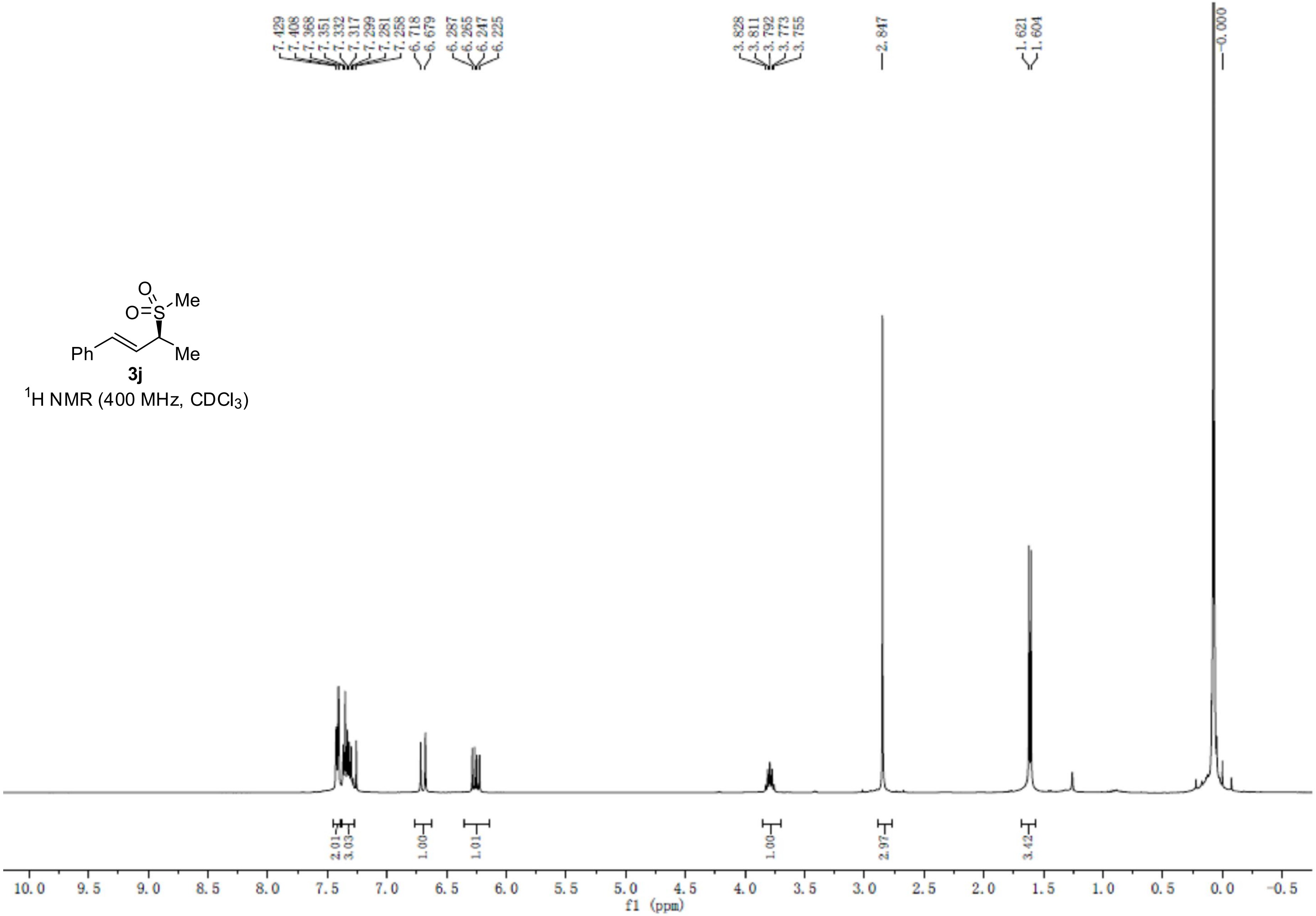

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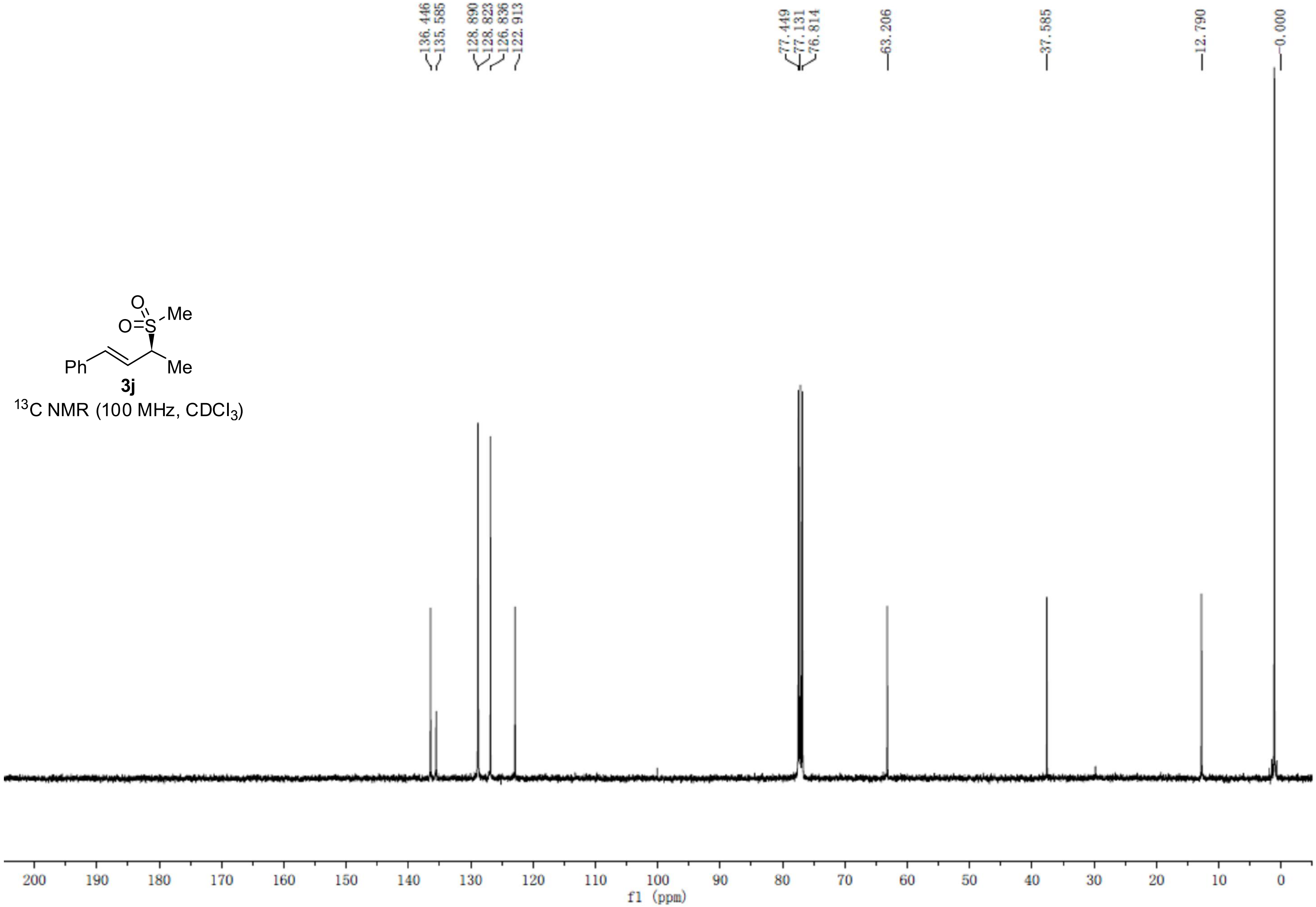

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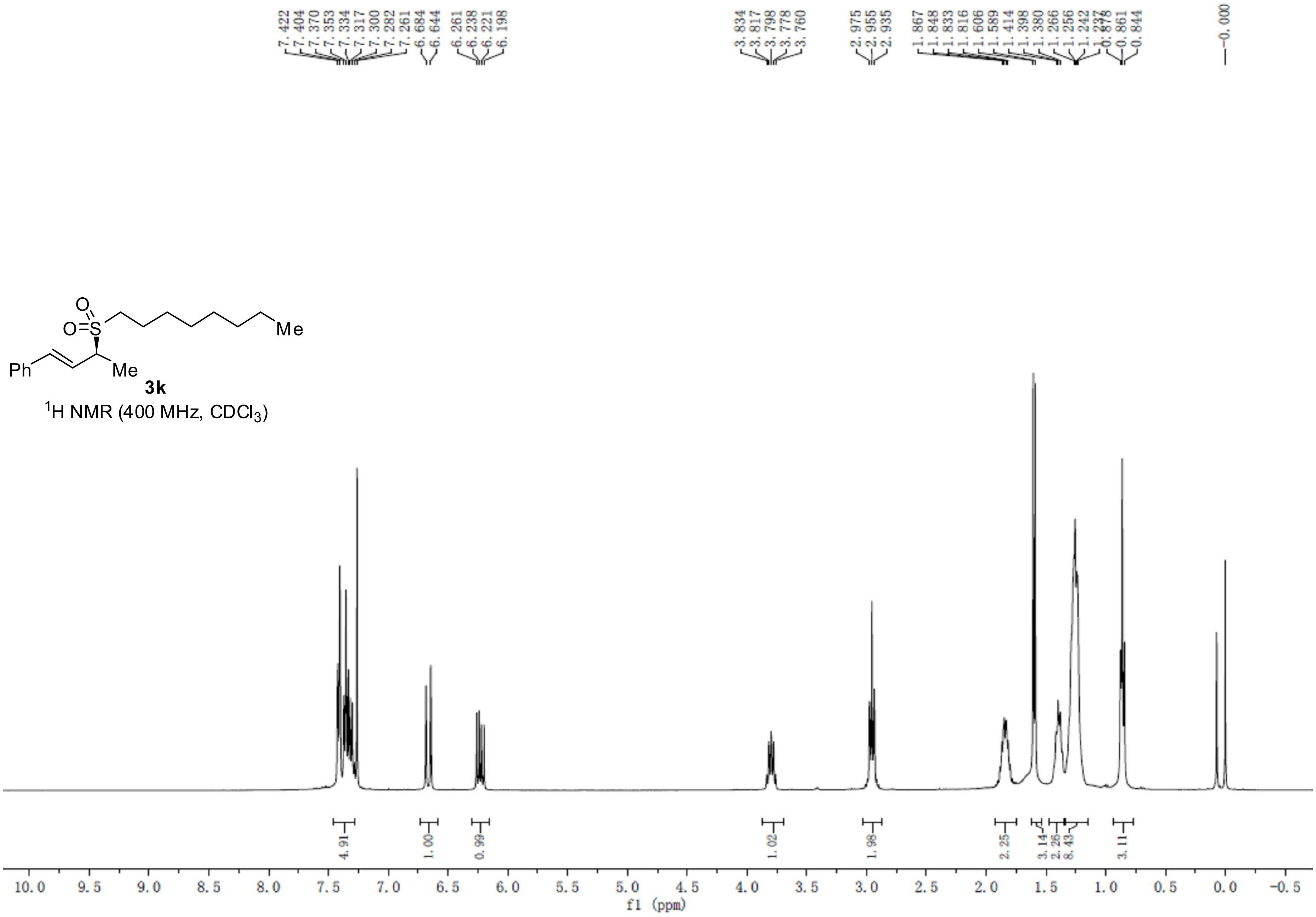

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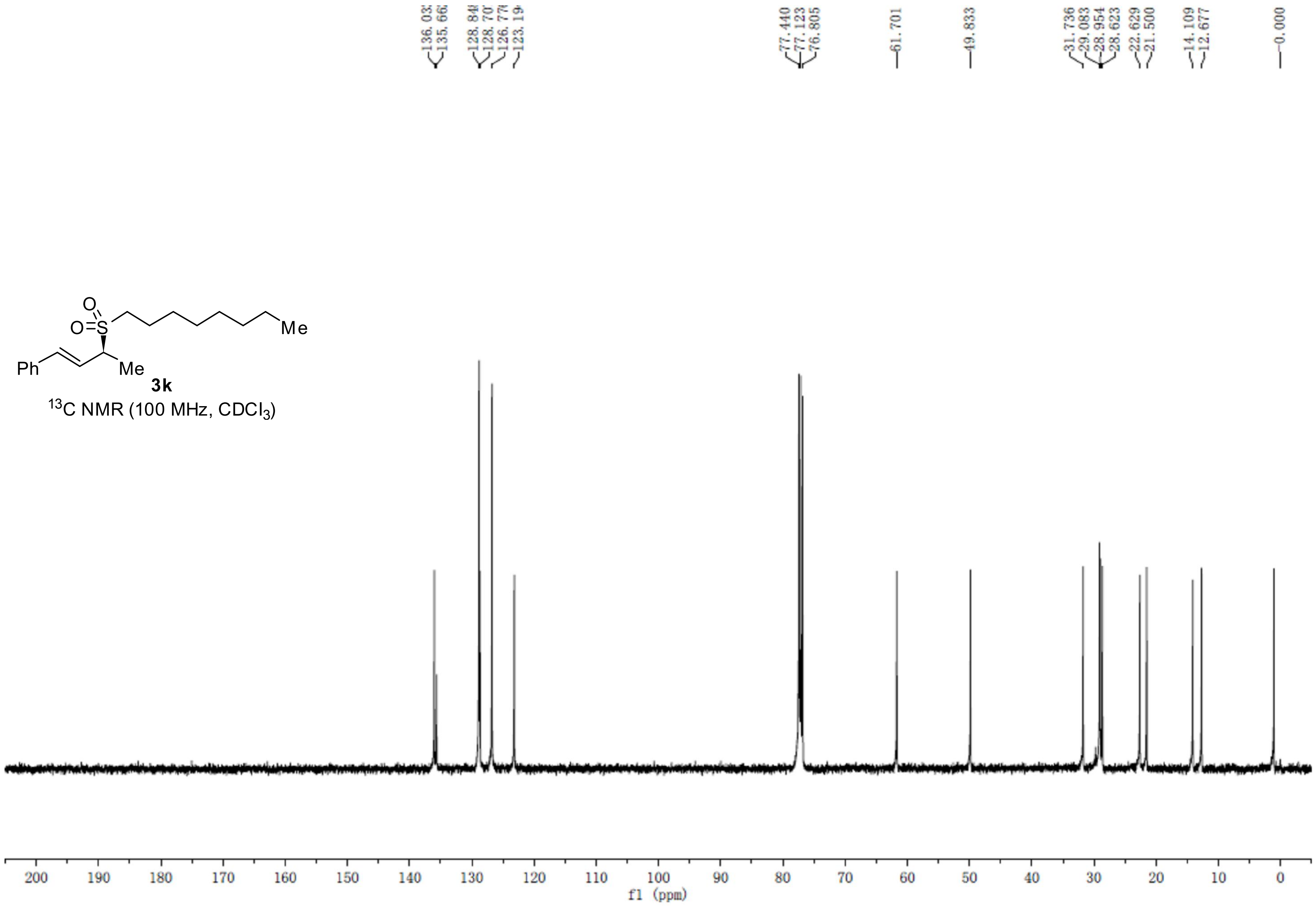

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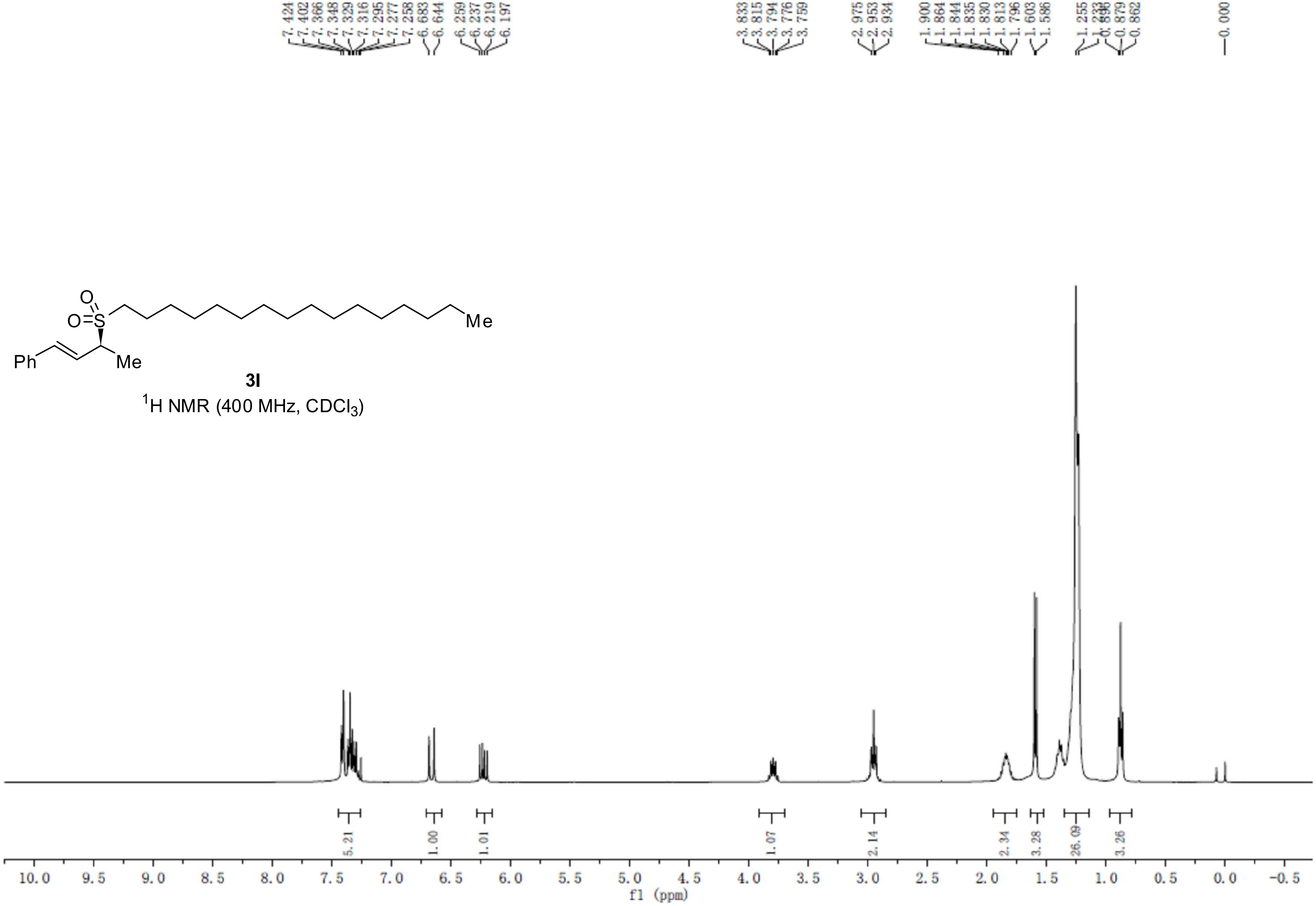

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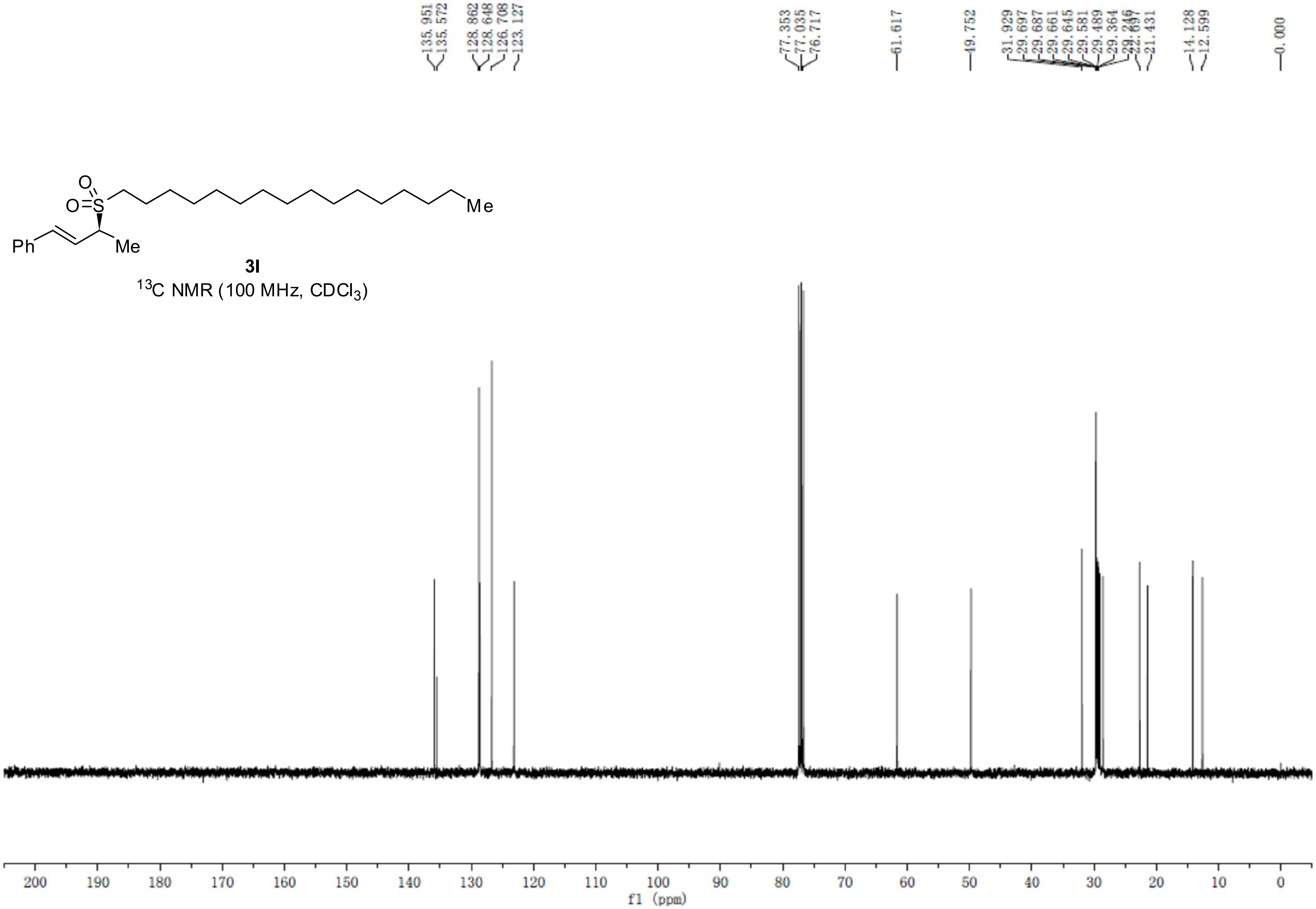

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3m

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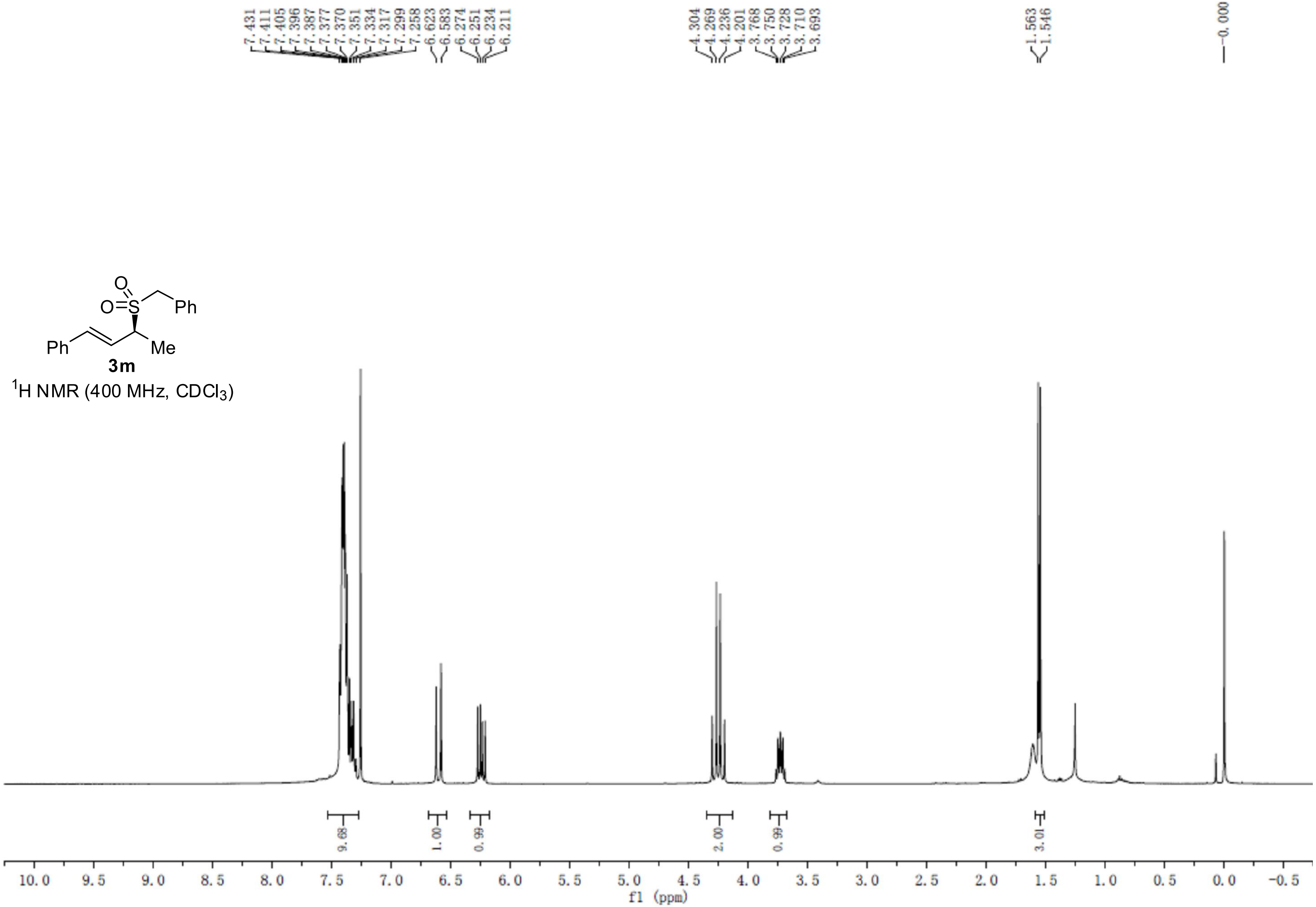

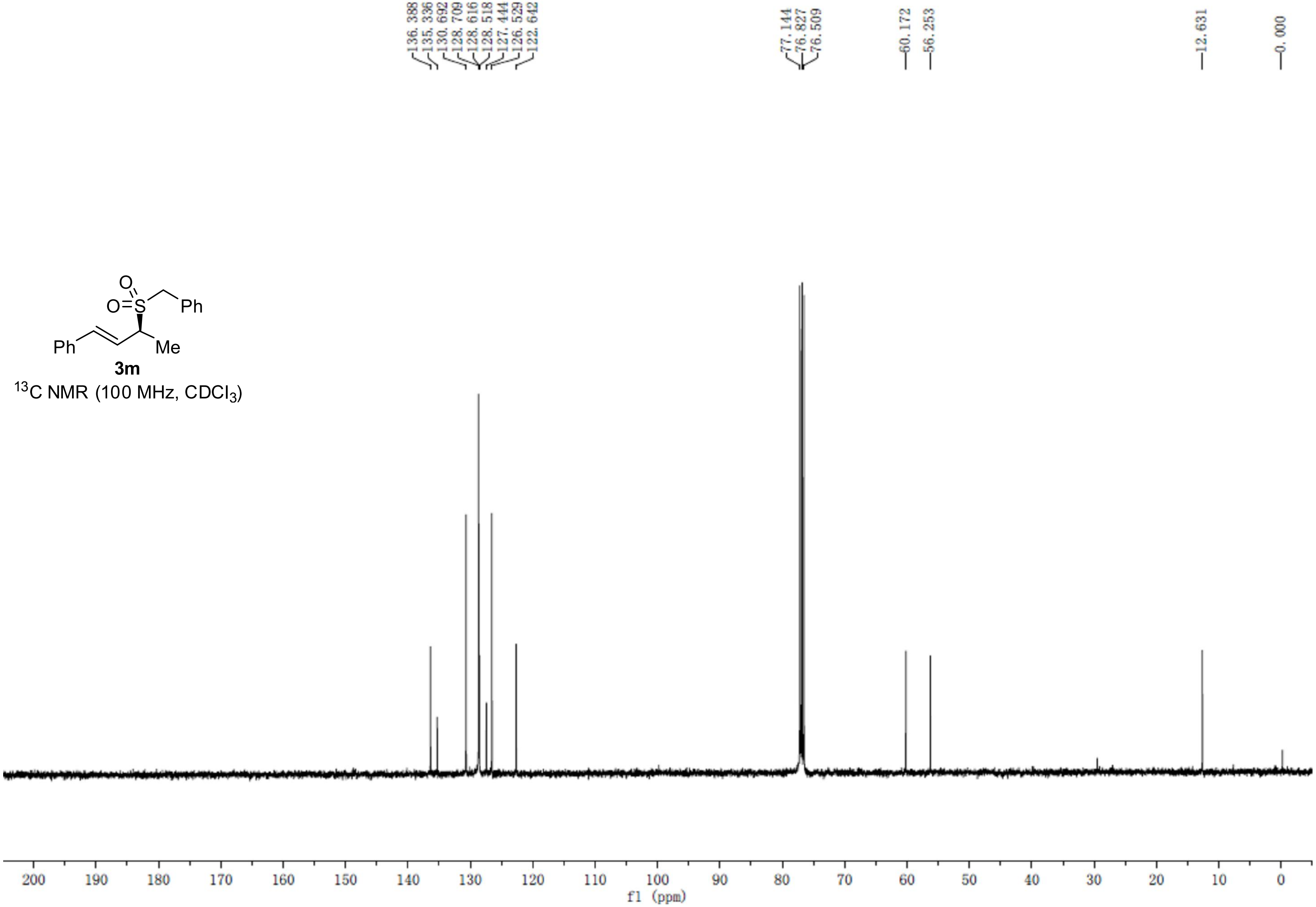

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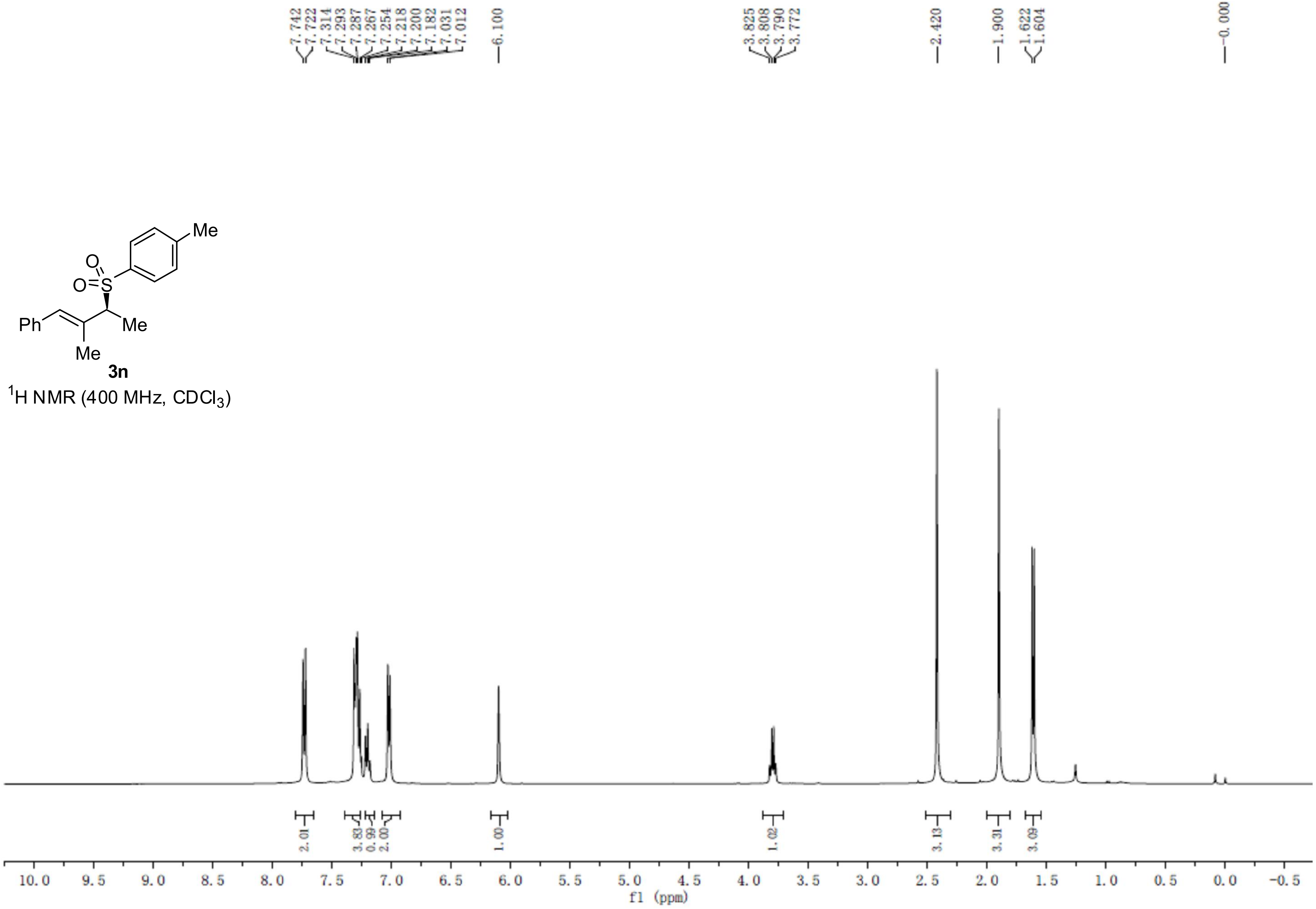

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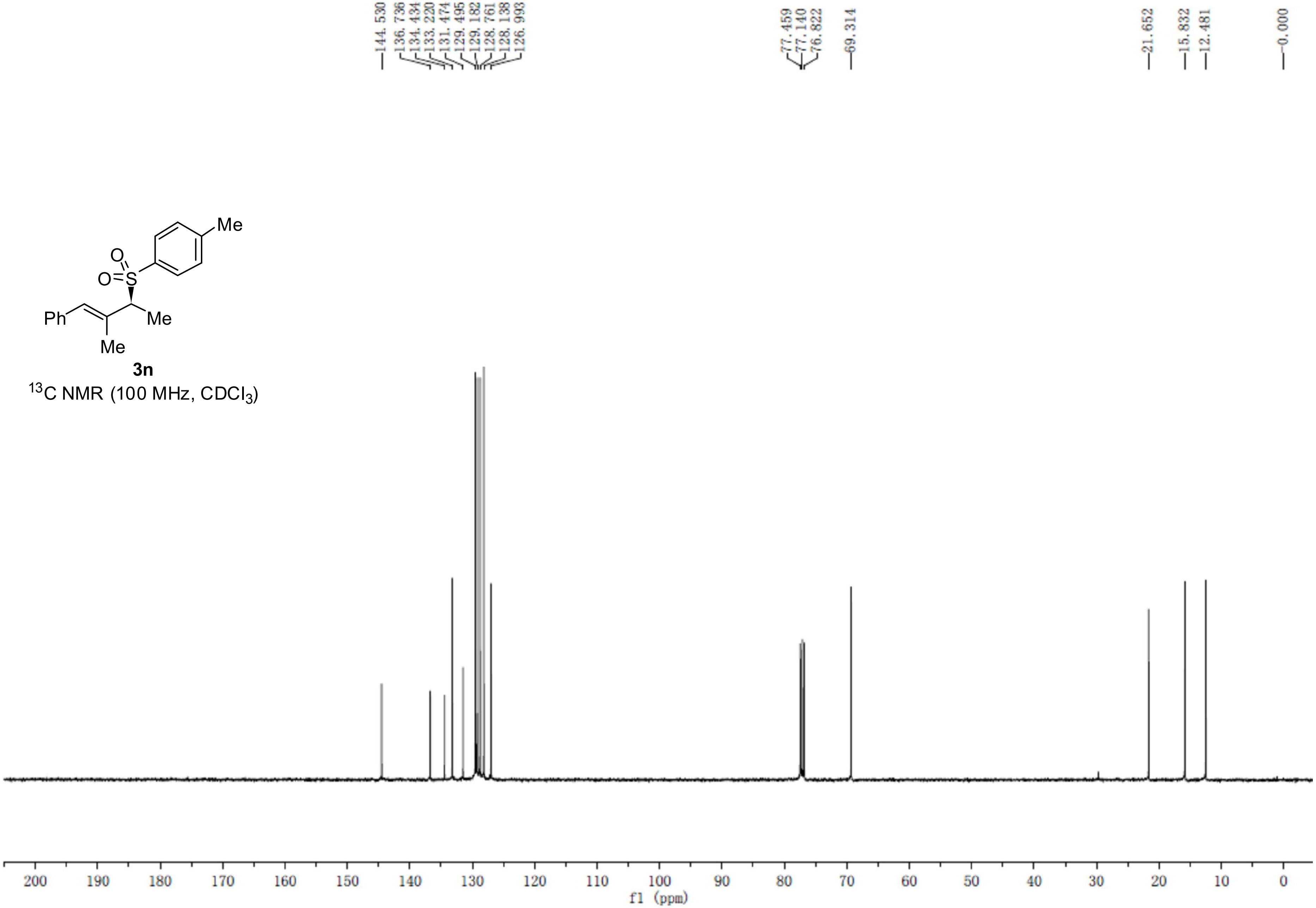

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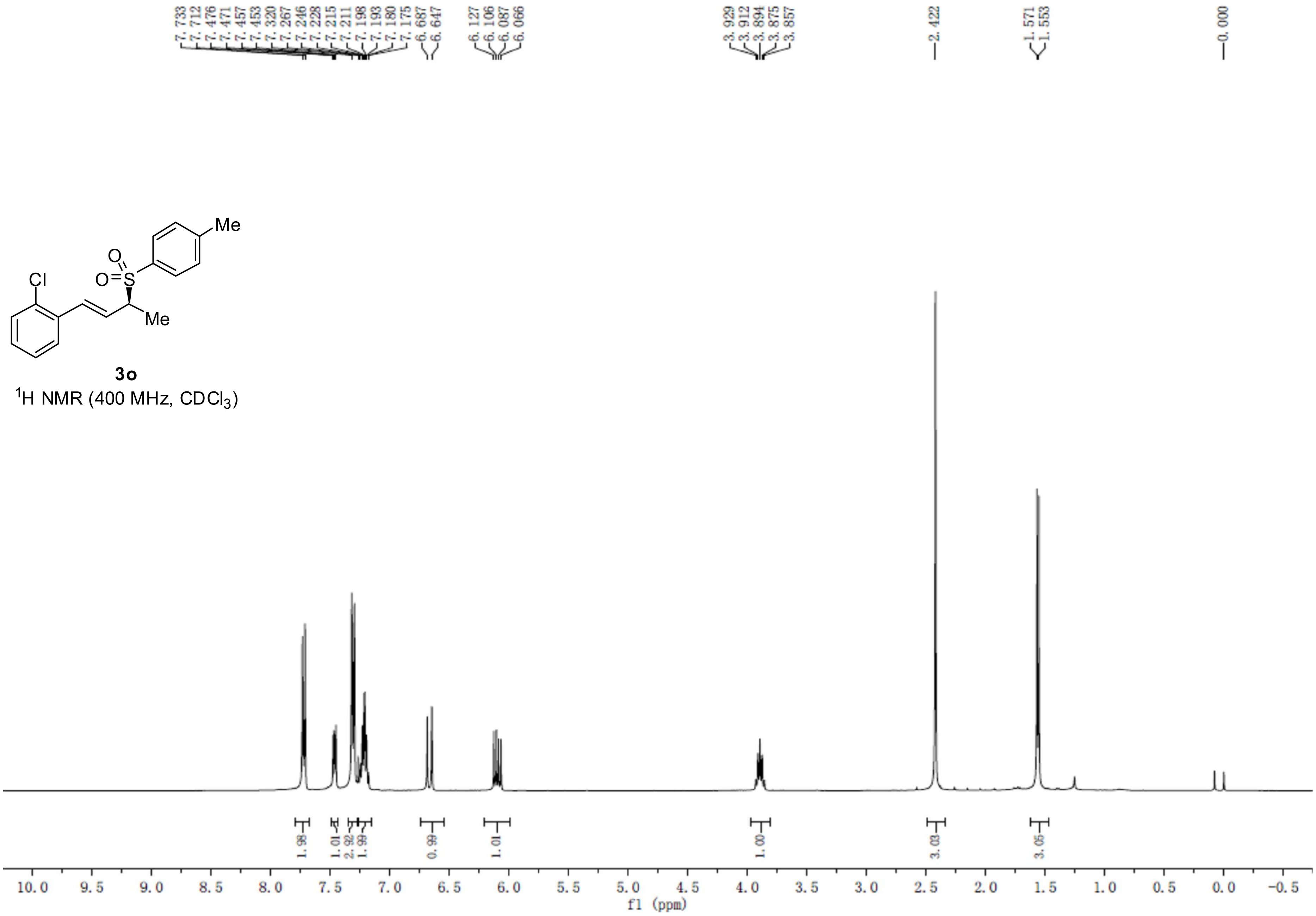

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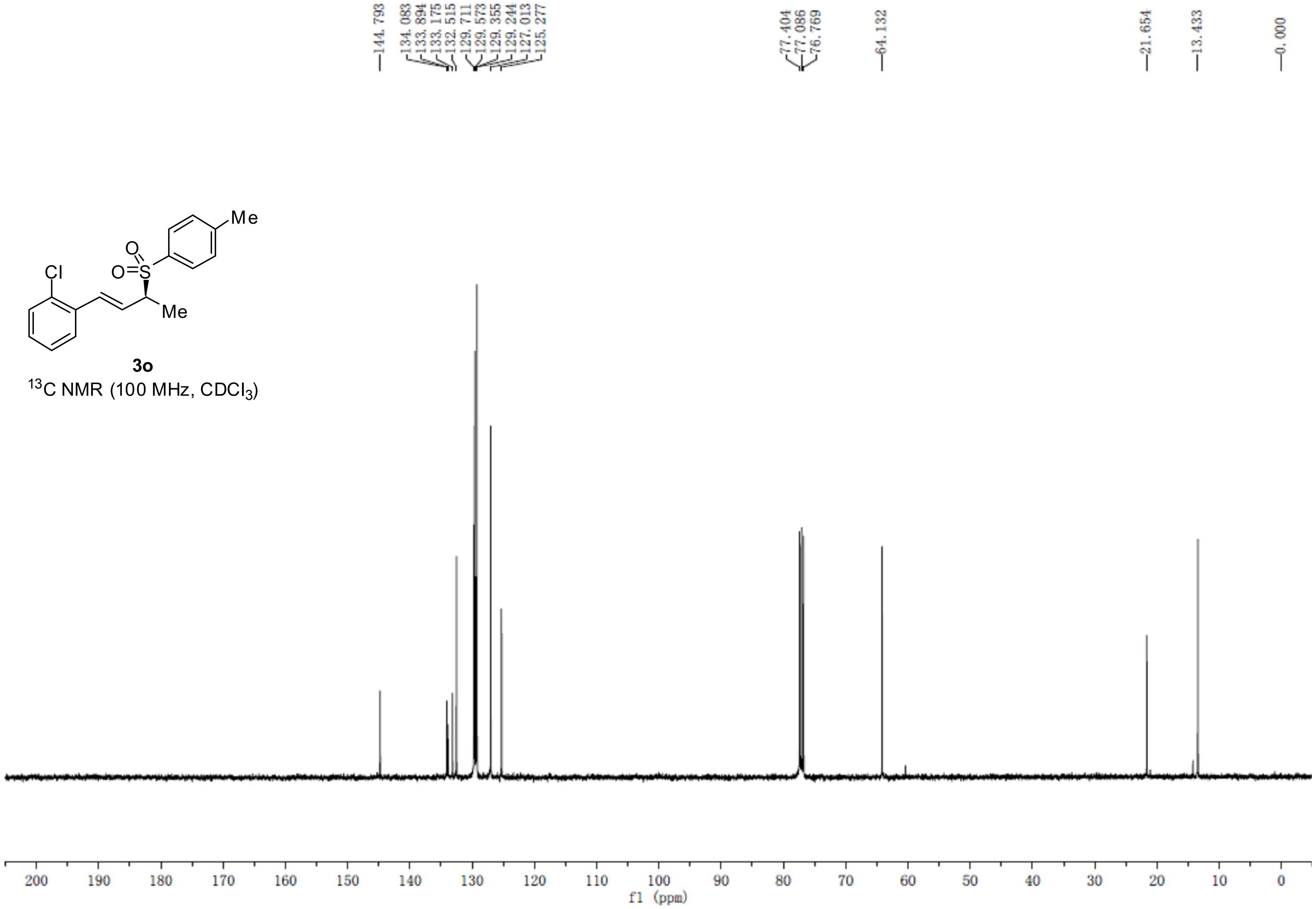

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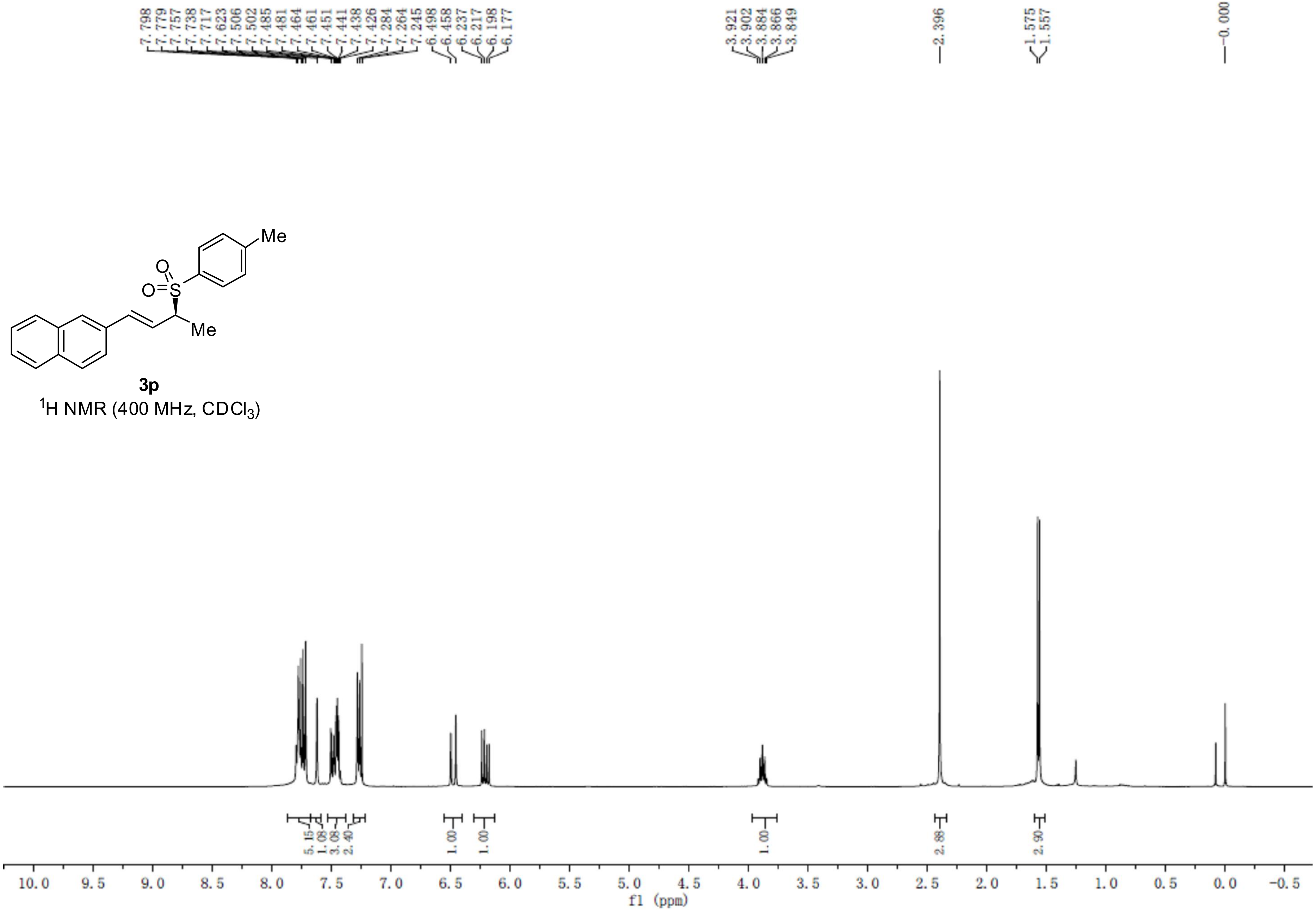

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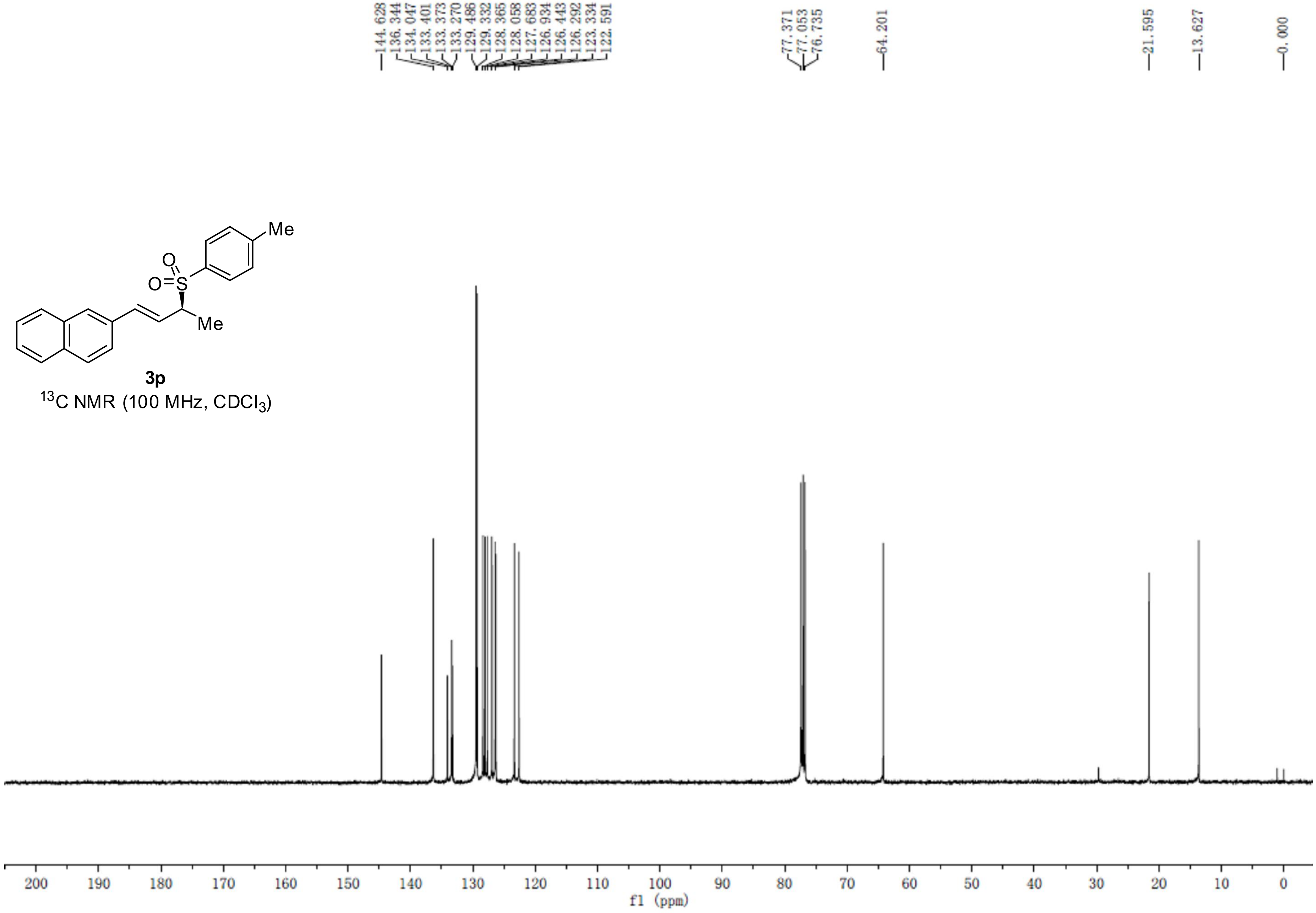

3p

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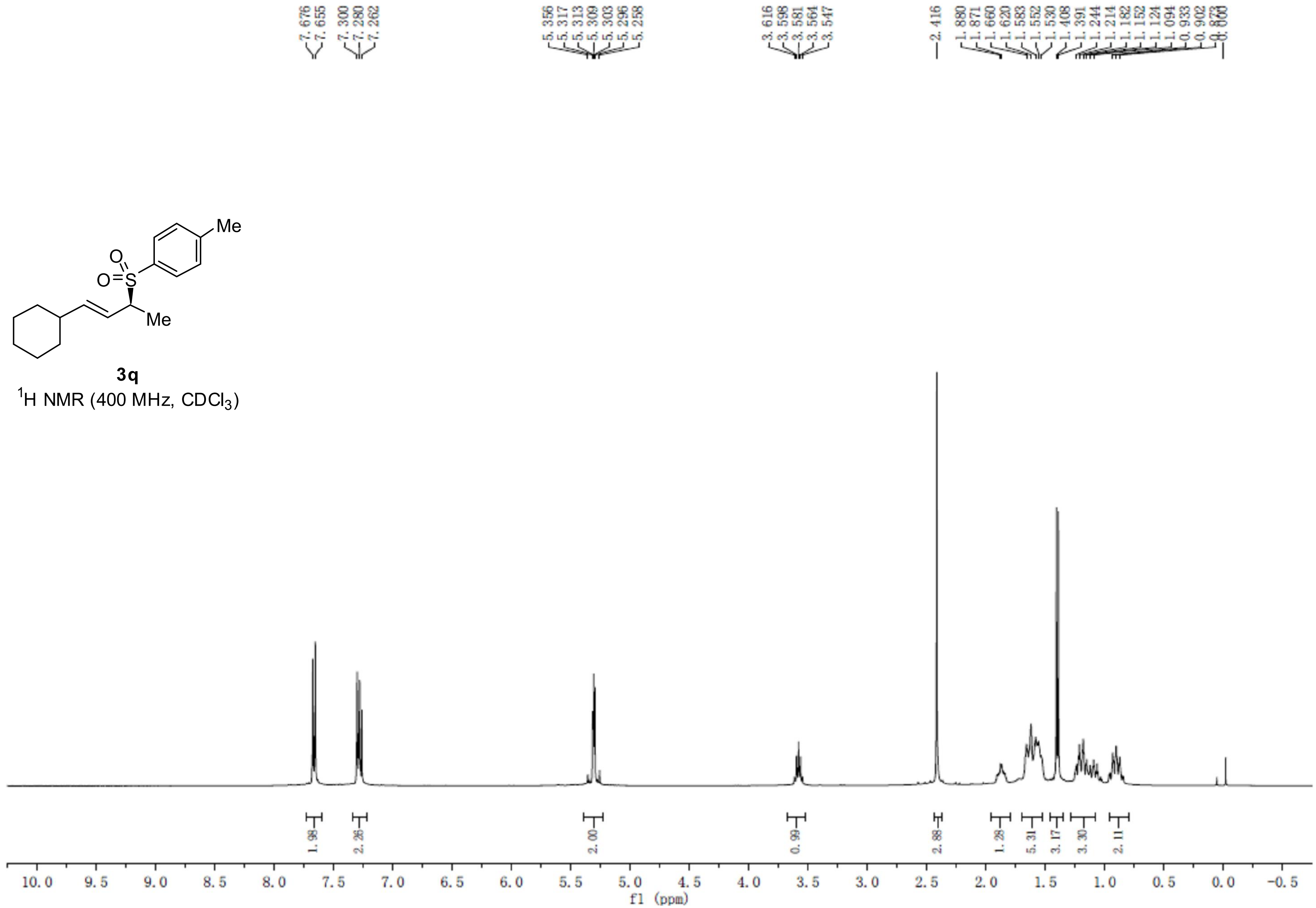

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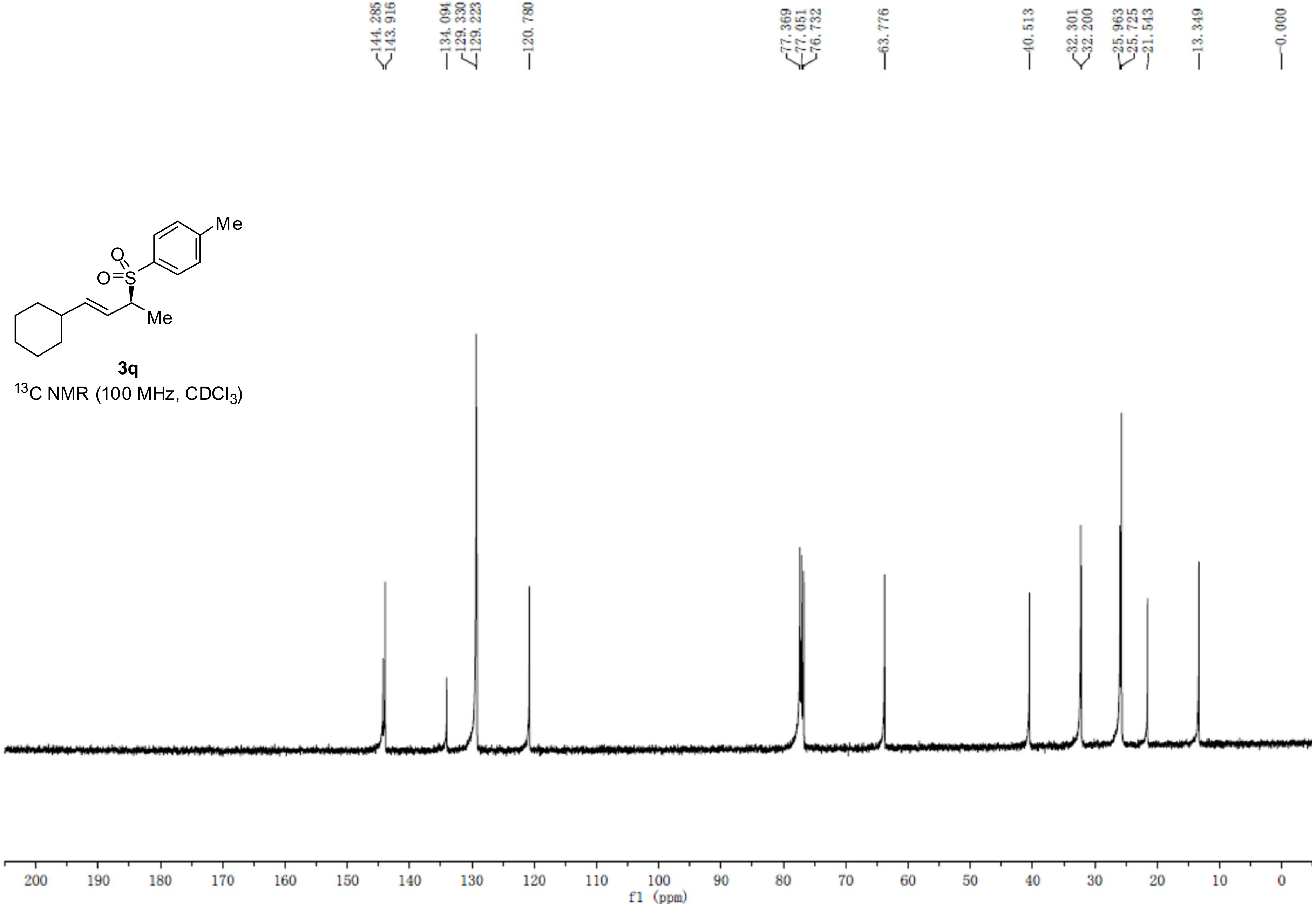

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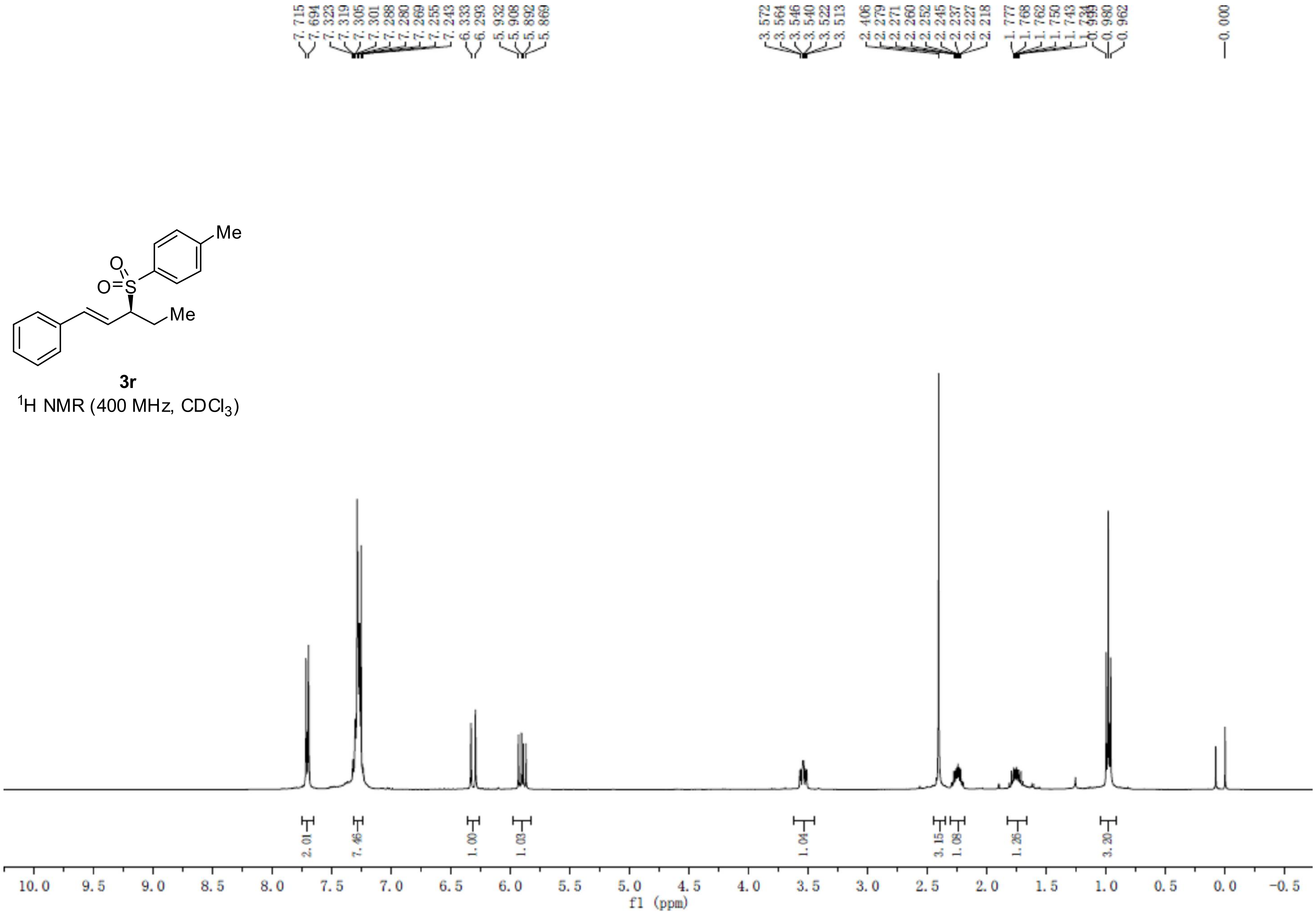

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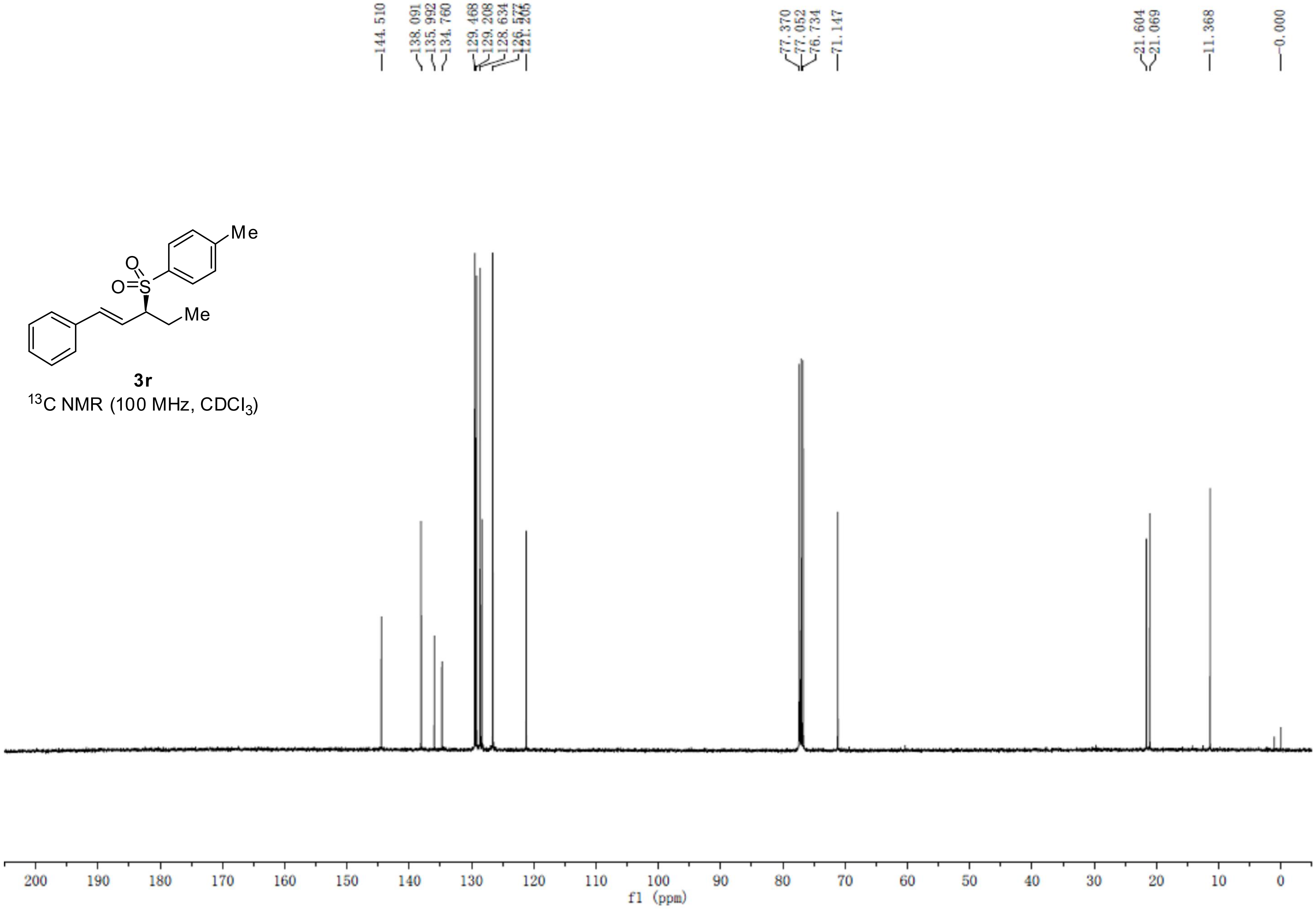

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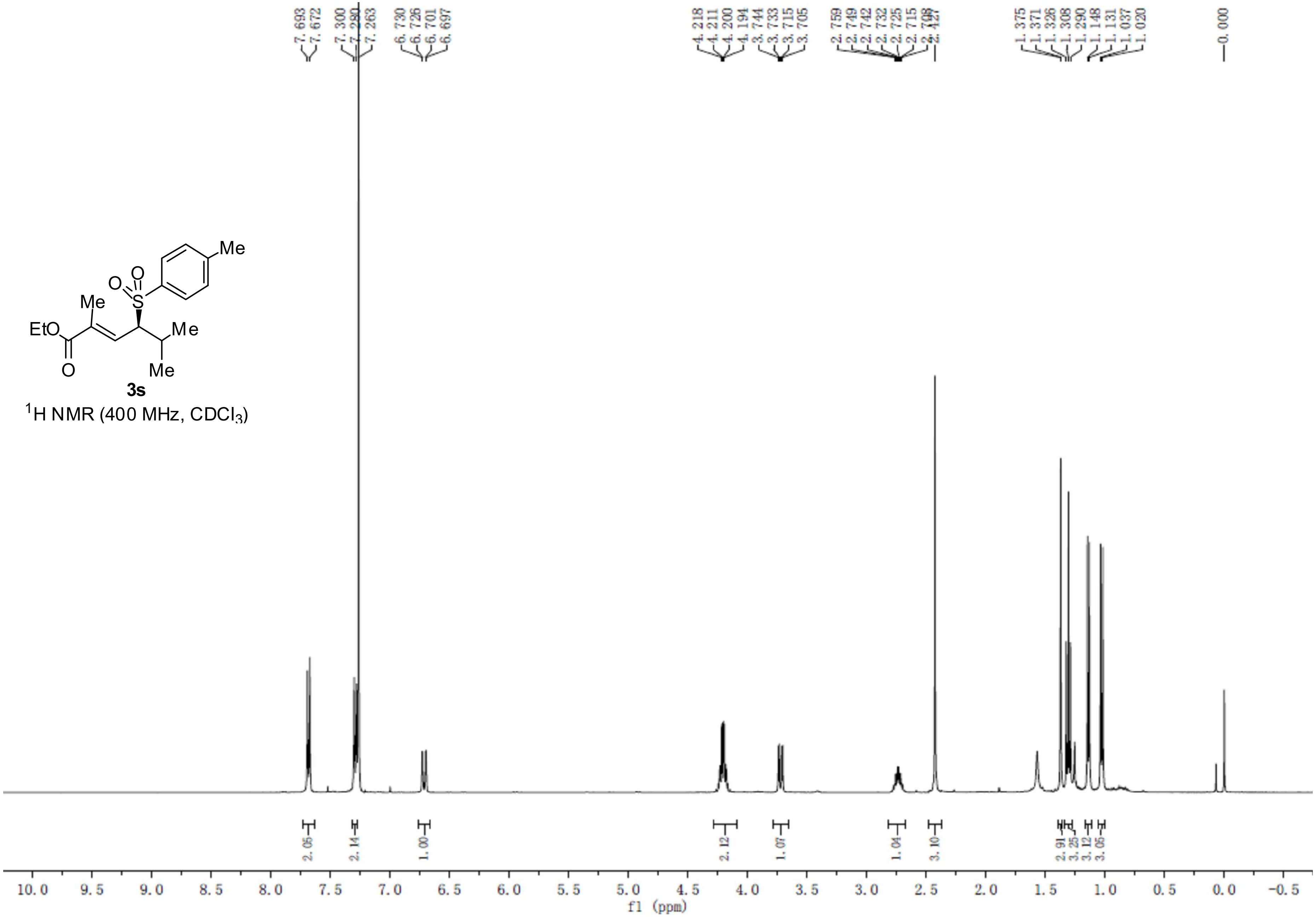

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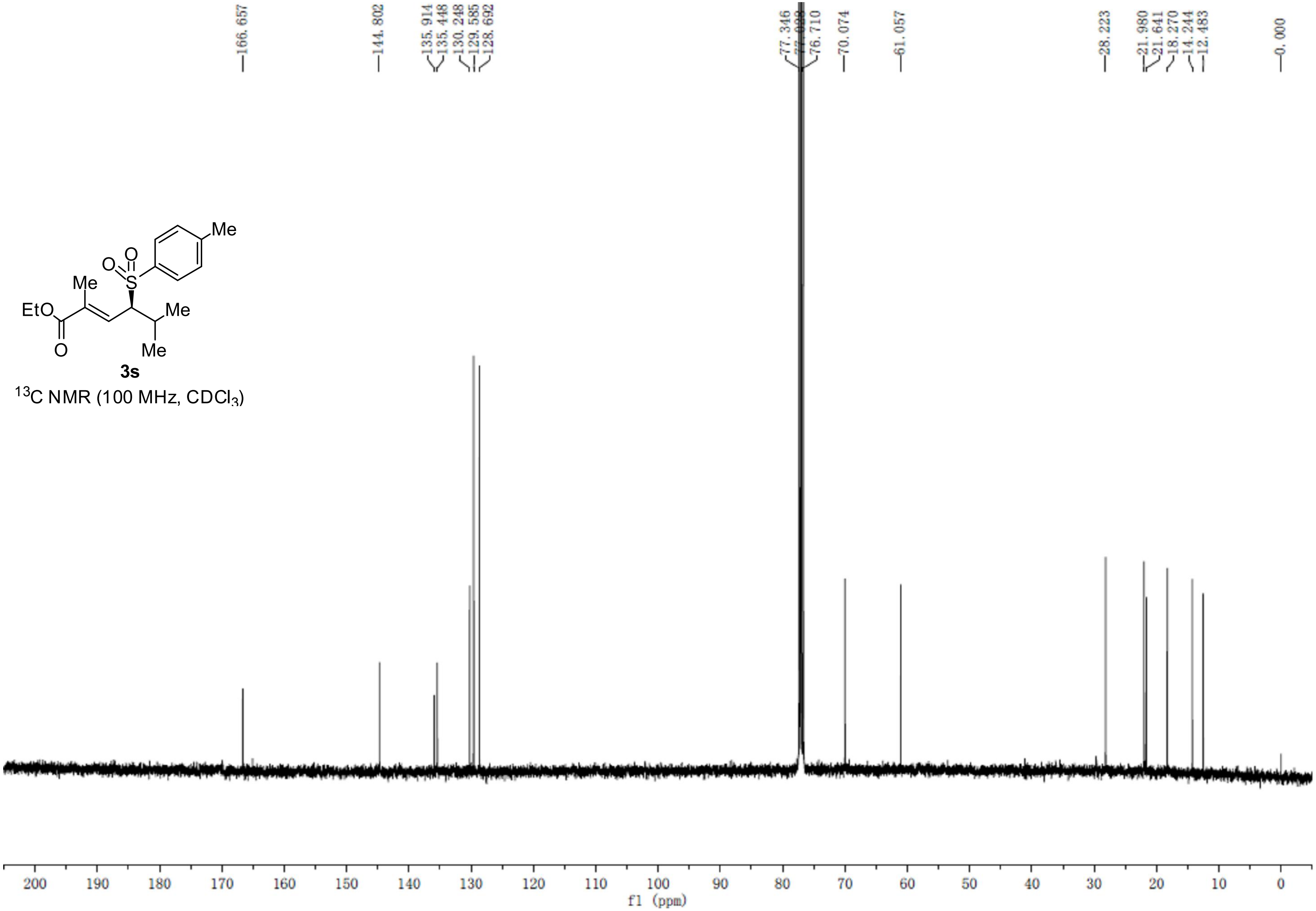

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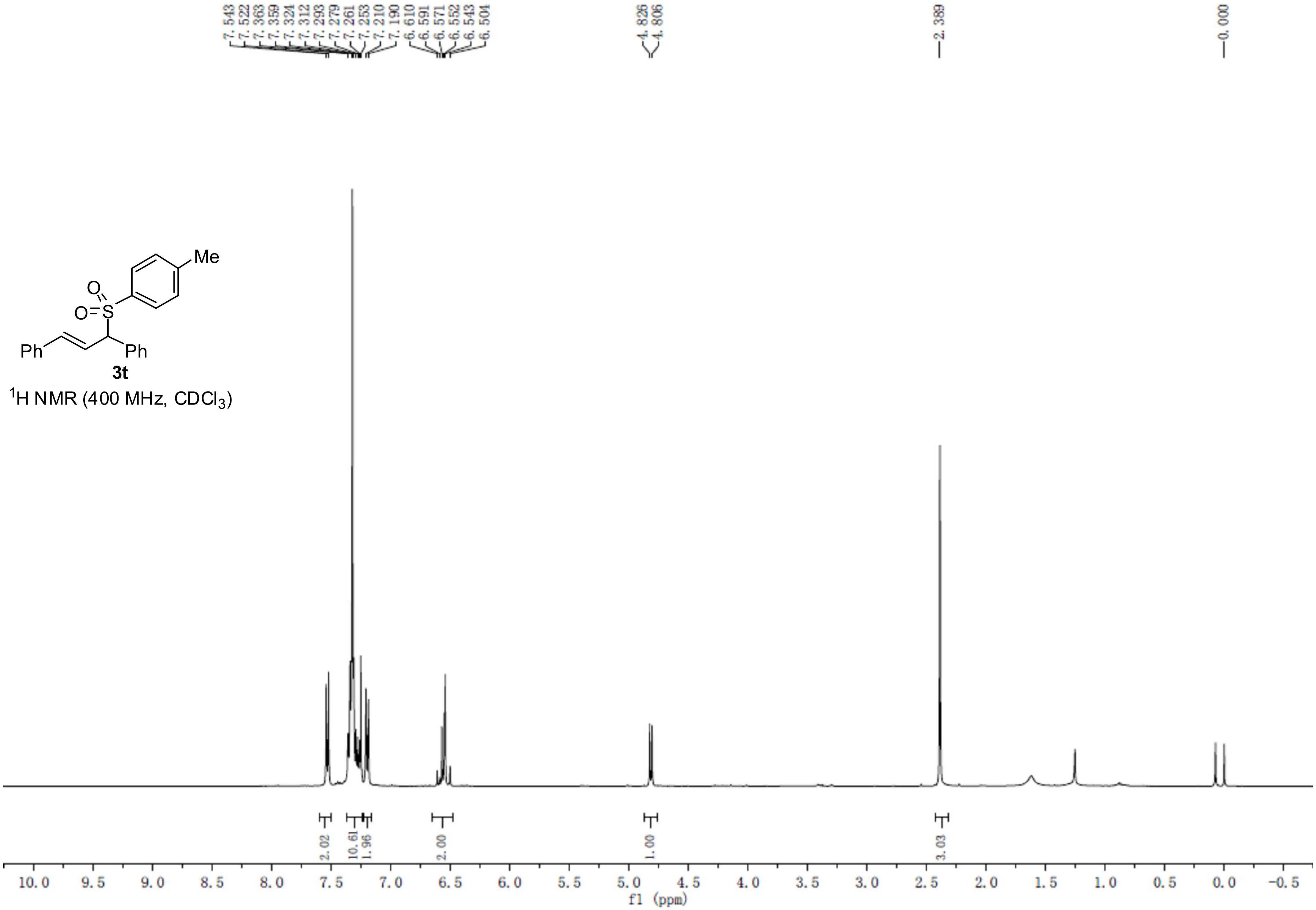
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6.591
6.571
6.552
6.543
6.504
4.826
4.806
2.389
0.000
Me
O
O=S
Ph
Ph
3t
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2.00
1.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
0.0
-0.5
f1 (ppm)

3t

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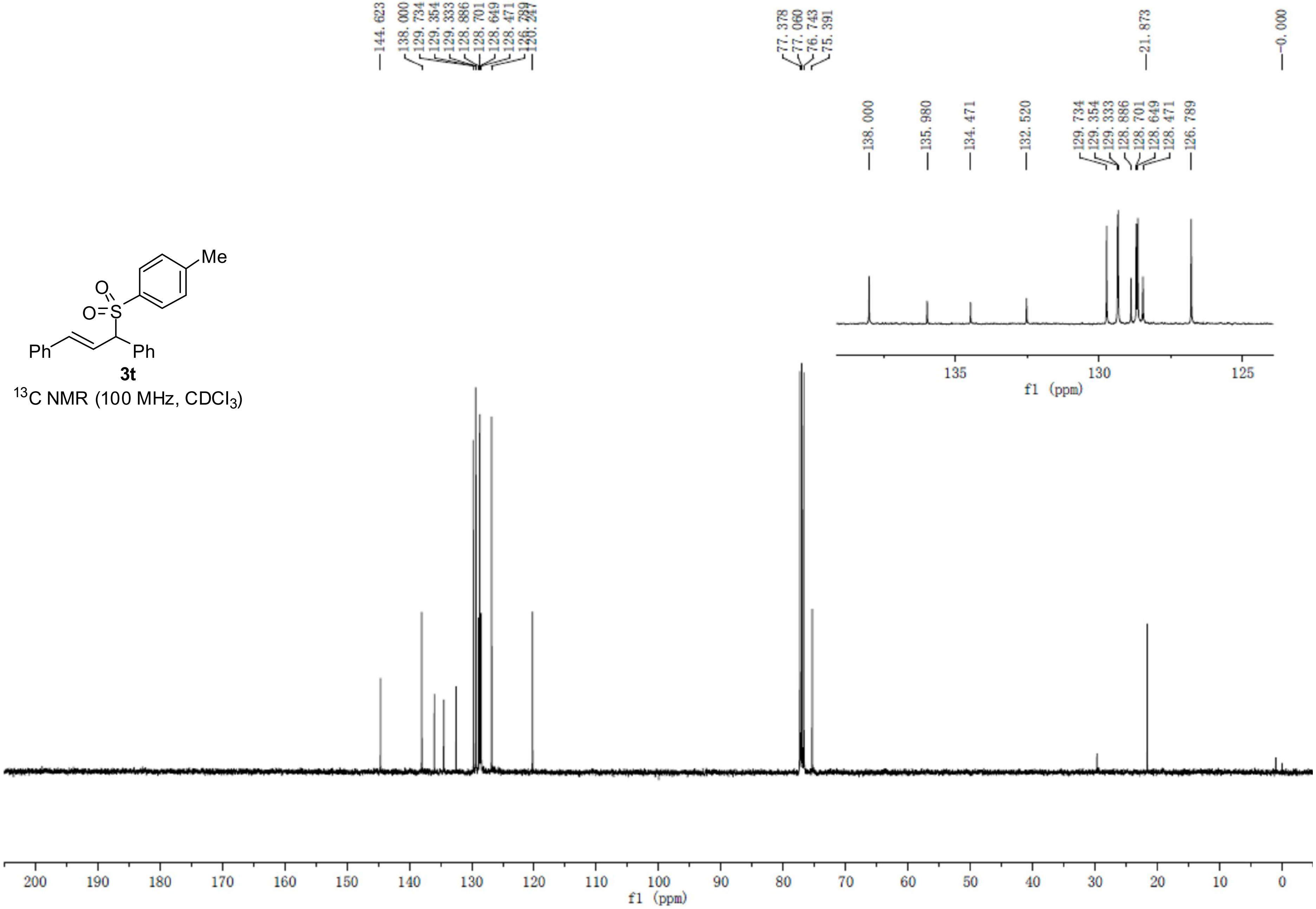

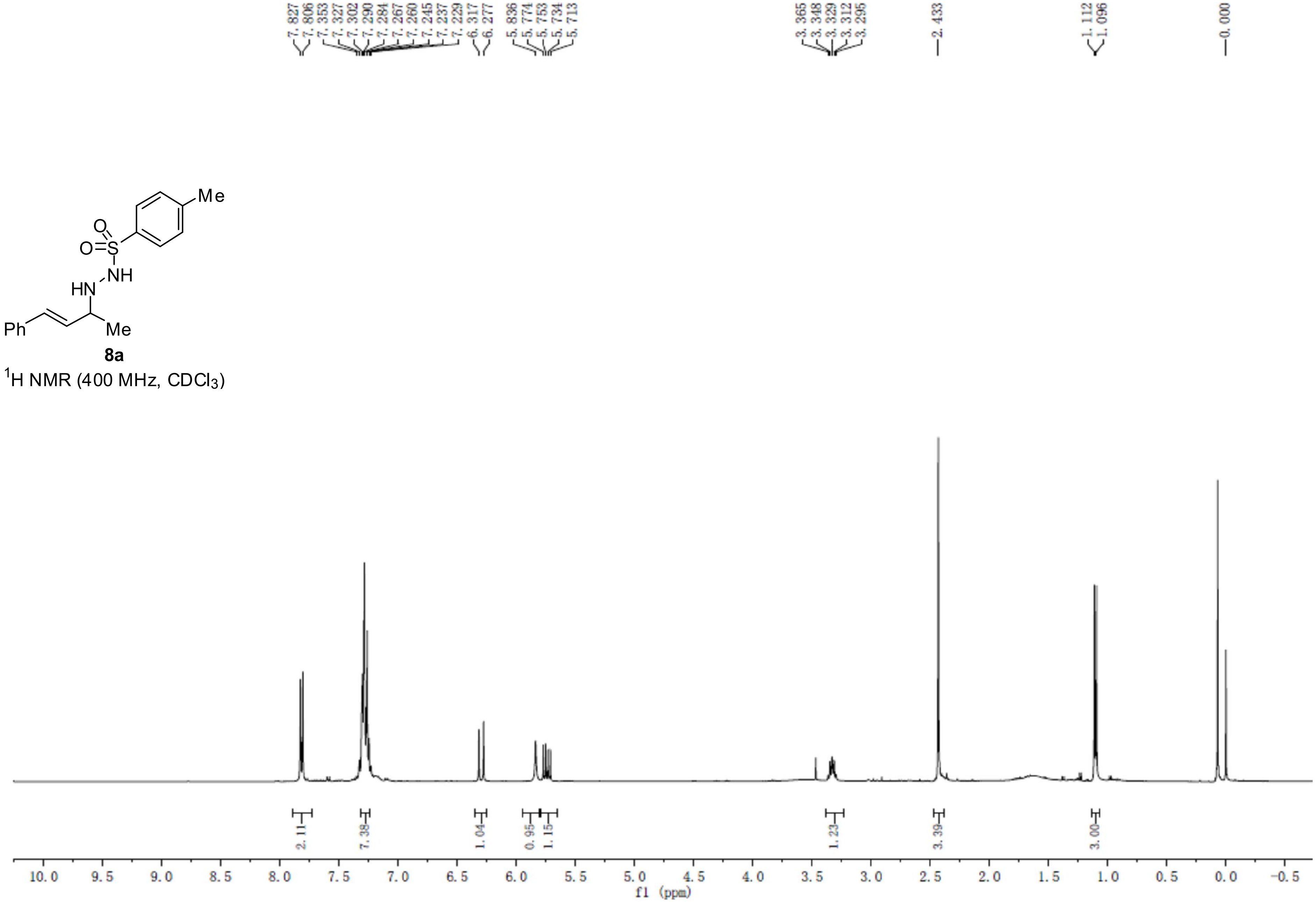

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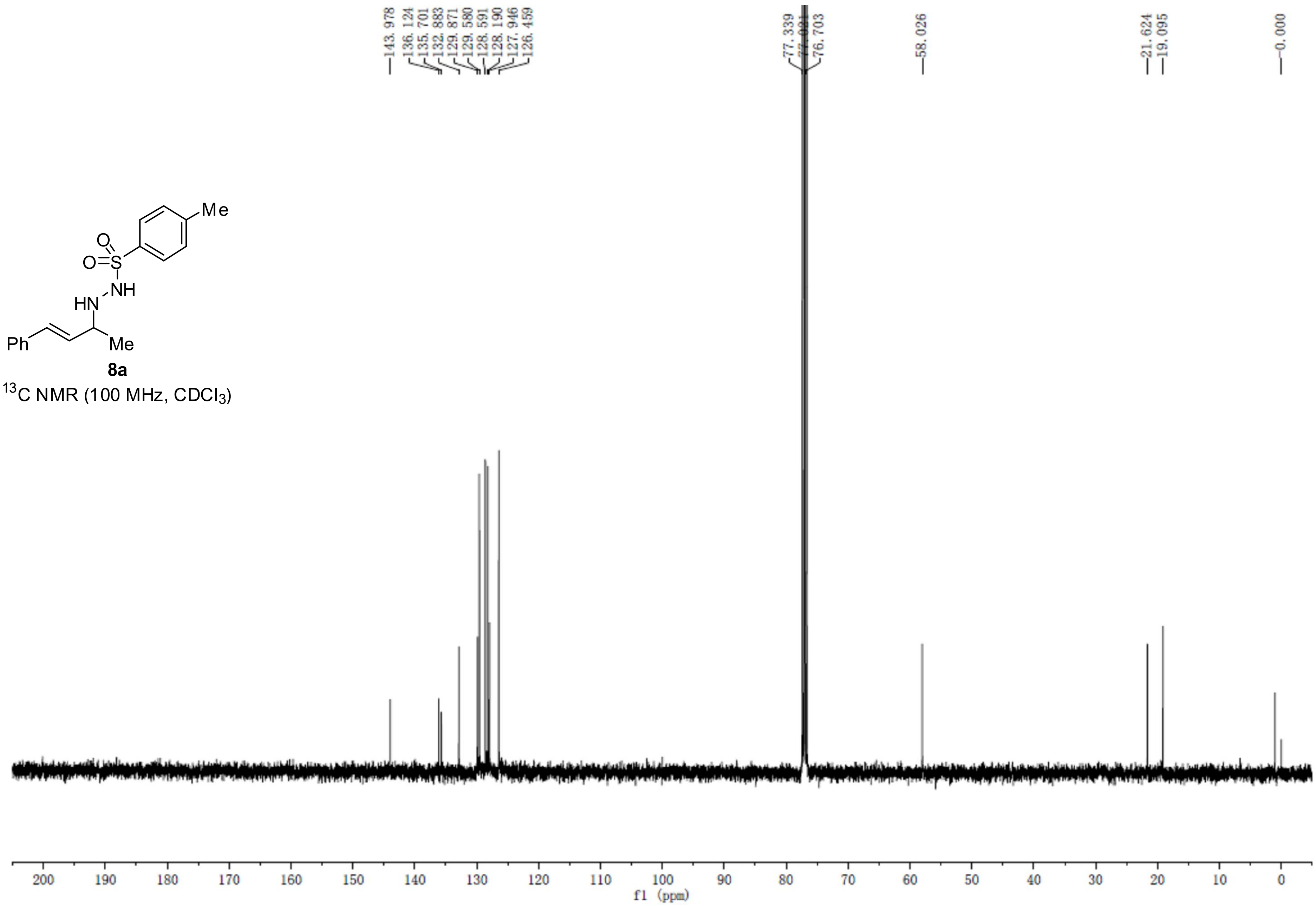
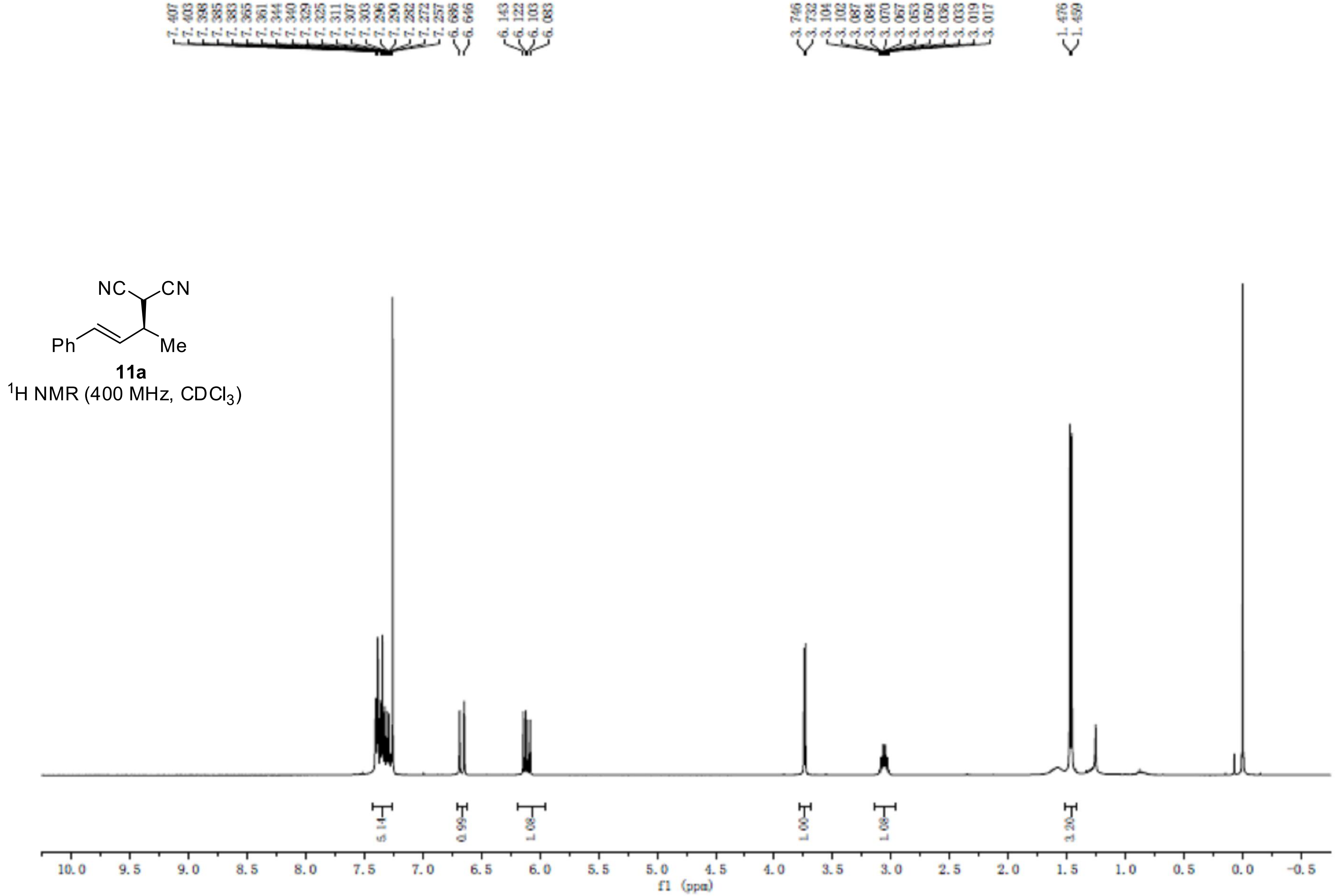


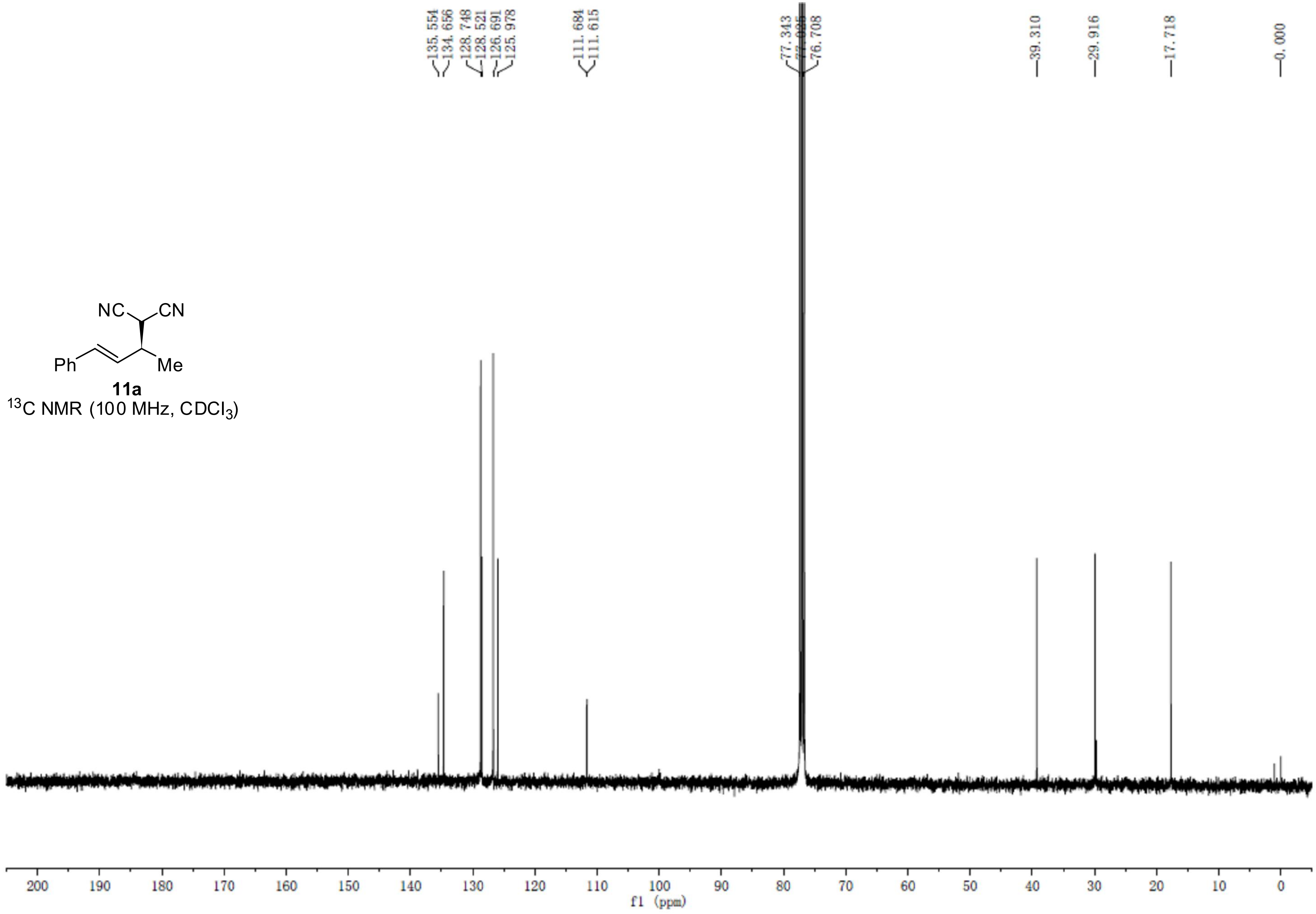
8a

^{13}C NMR (100 MHz, $CDCl_3$)



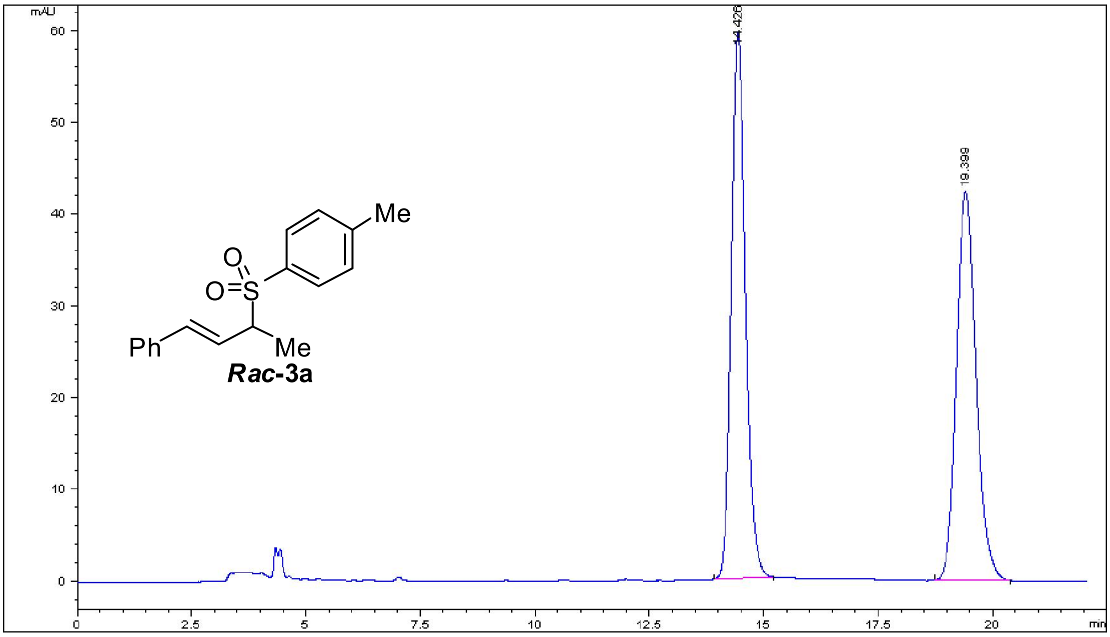
11a

^{1}H NMR (400 MHz, $CDCl_3$)

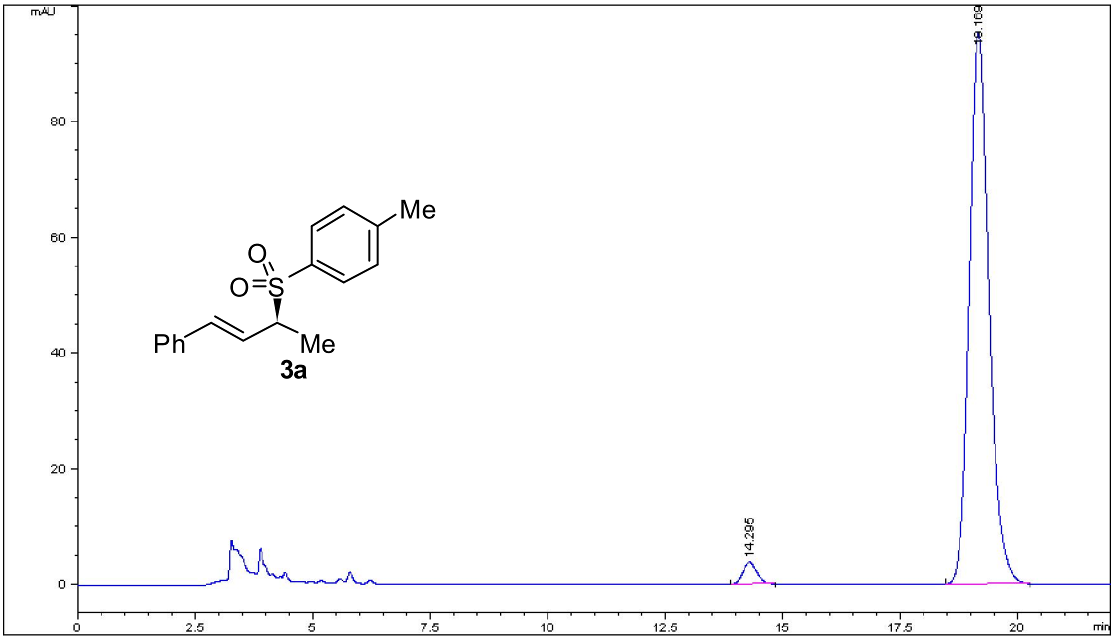


11a

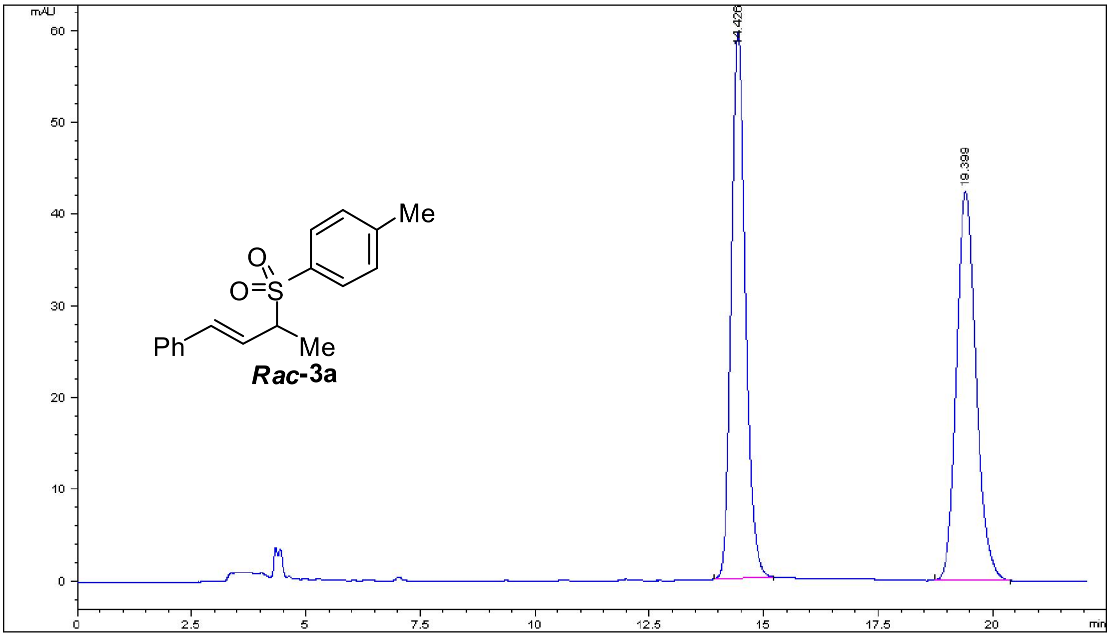
^{13}C NMR (100 MHz, $CDCl_3$)



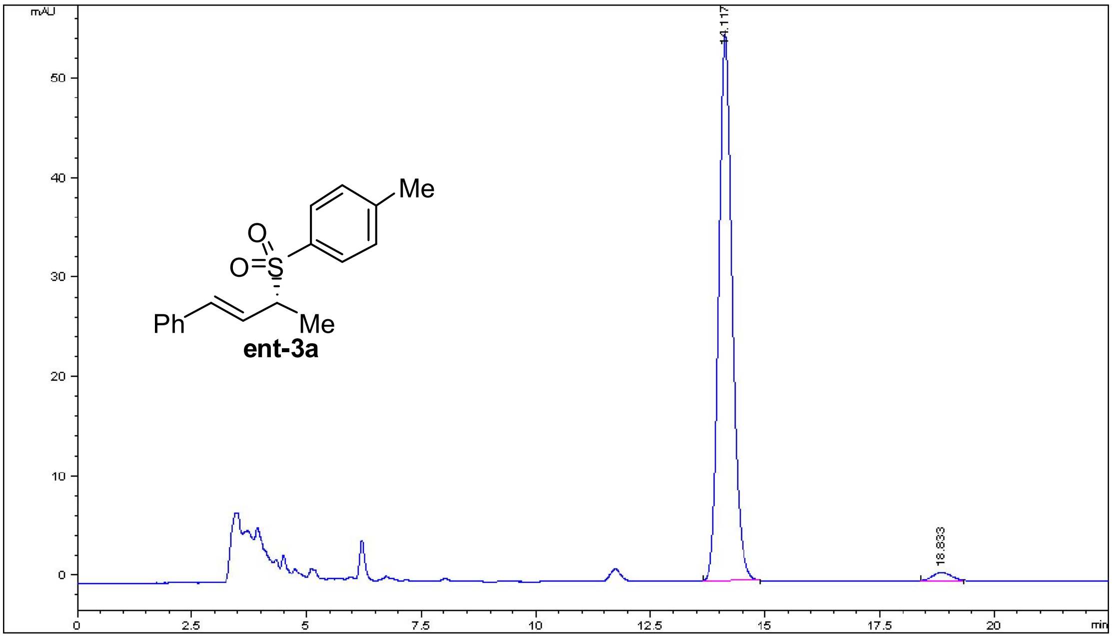
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.426	1290.2	59.6	0.3327	0.83	50.437
2	19.399	1267.8	42.5	0.4591	0.839	49.563



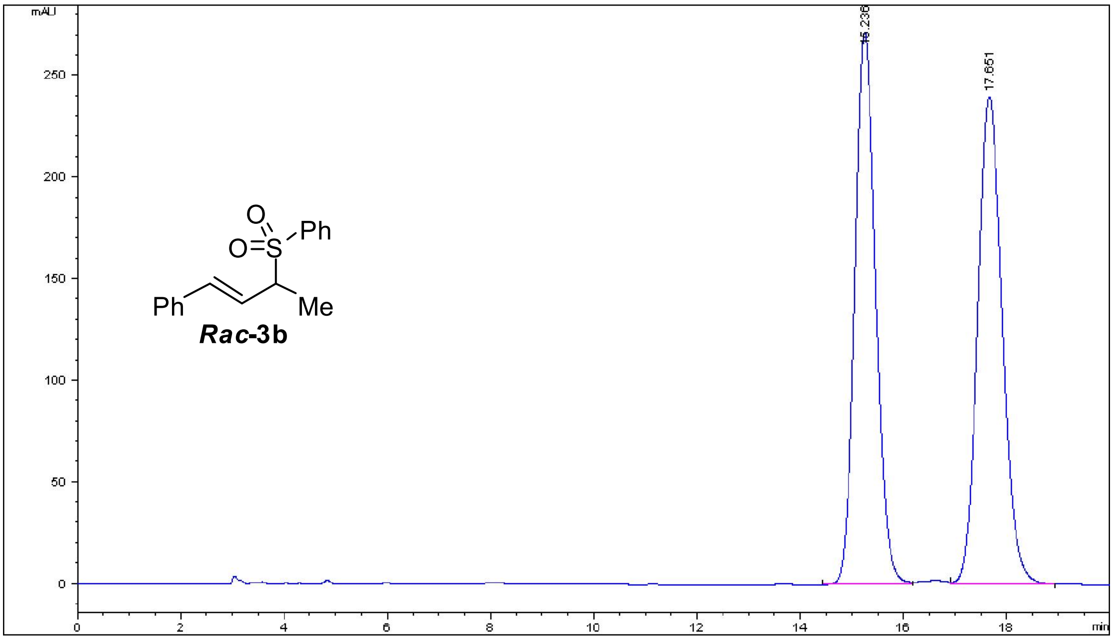
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.295	79	3.8	0.3203	0.872	2.747
2	19.169	2794.9	95.4	0.4483	0.831	97.253



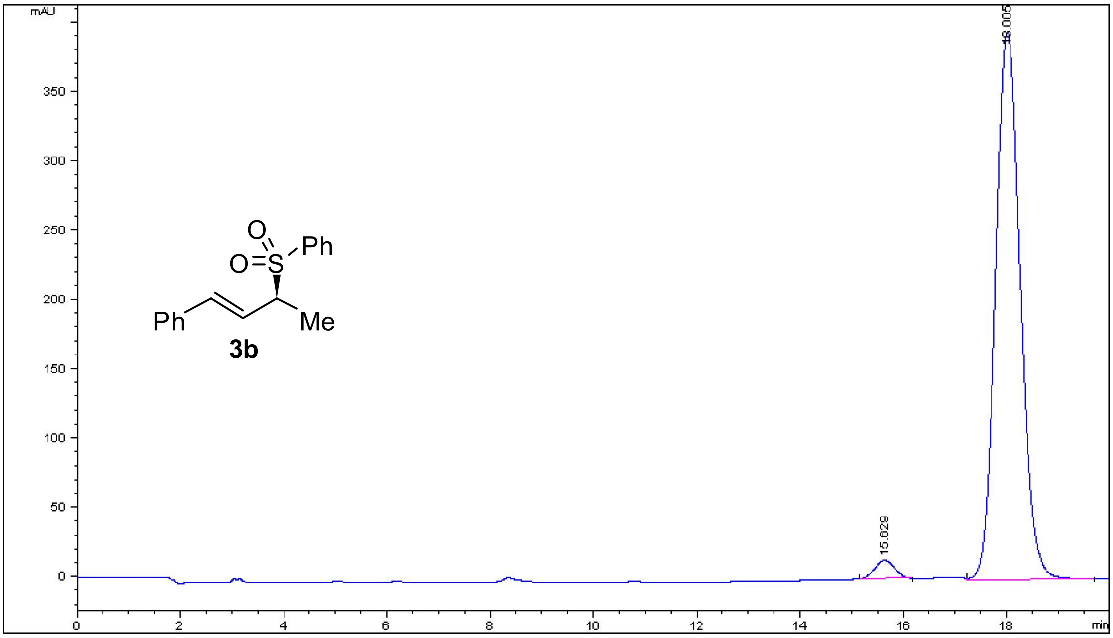
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.426	1290.2	59.6	0.3327	0.83	50.437
2	19.399	1267.8	42.5	0.4591	0.839	49.563



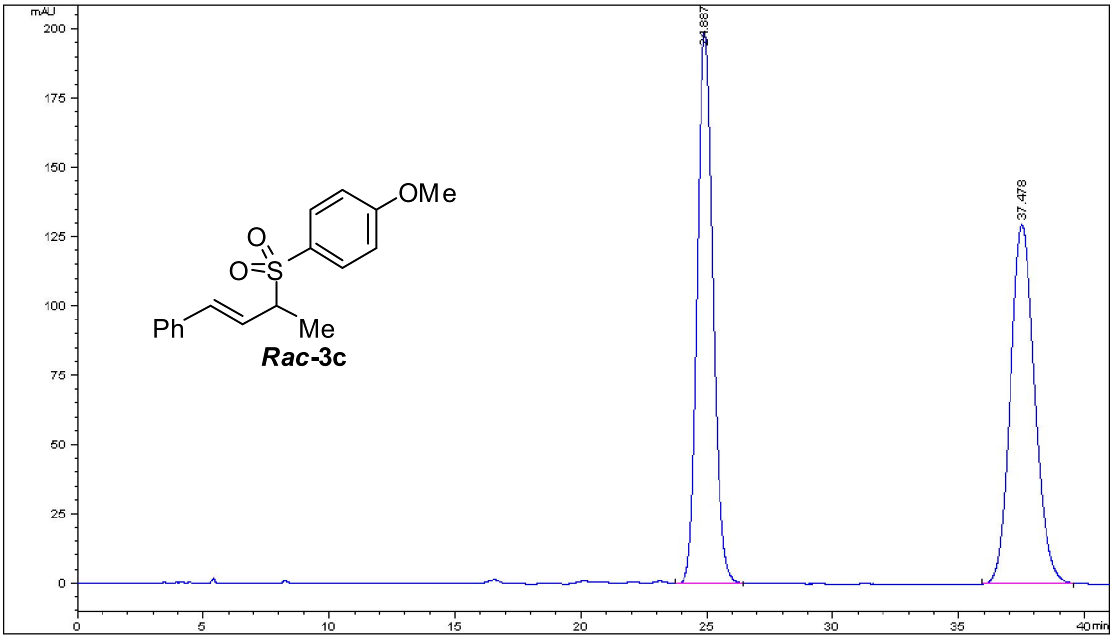
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.117	1142.1	55.2	0.3173	0.849	97.489
2	18.833	29.4	9.8E-1	0.4988	0.837	2.511



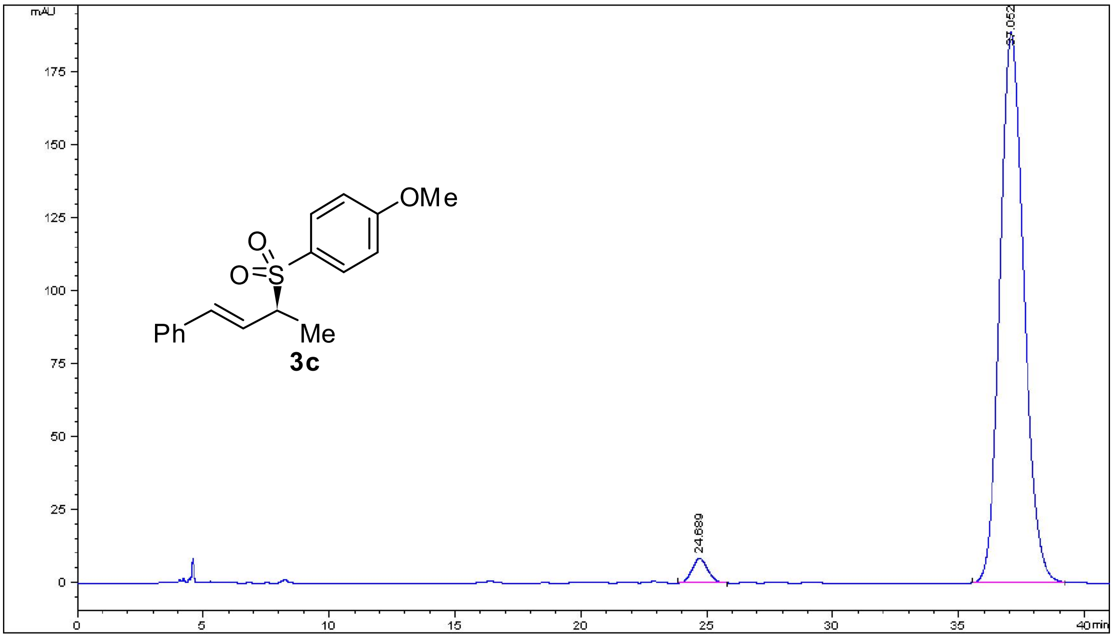
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.236	7650	271.5	0.4365	0.841	49.058
2	17.651	7943.7	240	0.5142	0.855	50.942



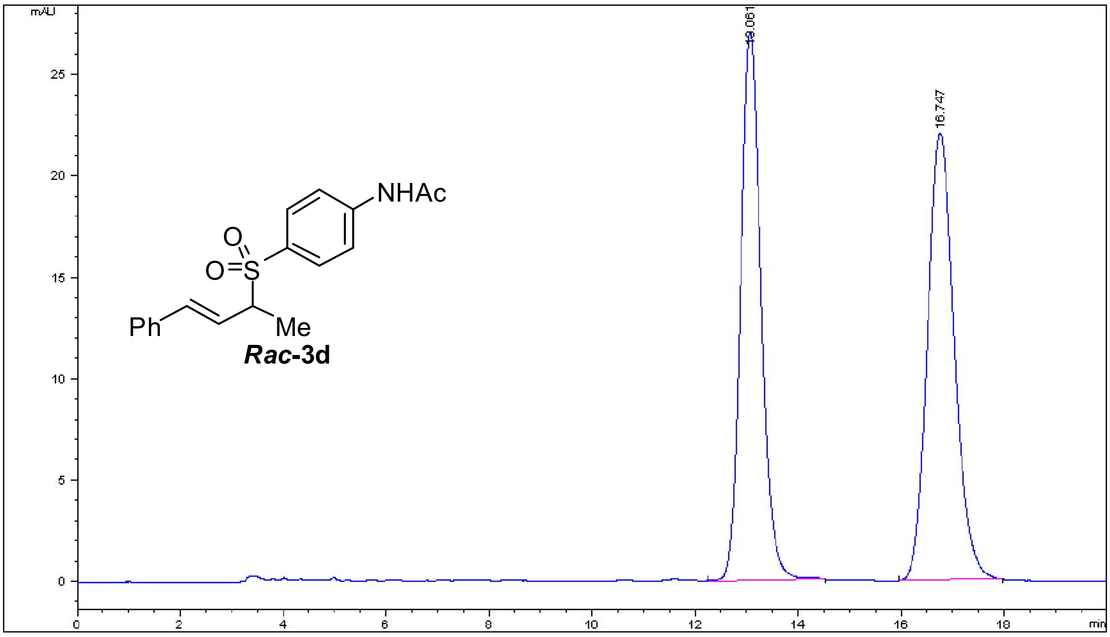
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.629	353.1	13.4	0.4403	0.964	2.637
2	18.005	13035.8	394.6	0.5136	0.85	97.363



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.887	8678.4	198.8	0.6767	0.859	49.995
2	37.478	8680	129.6	1.0346	0.851	50.005

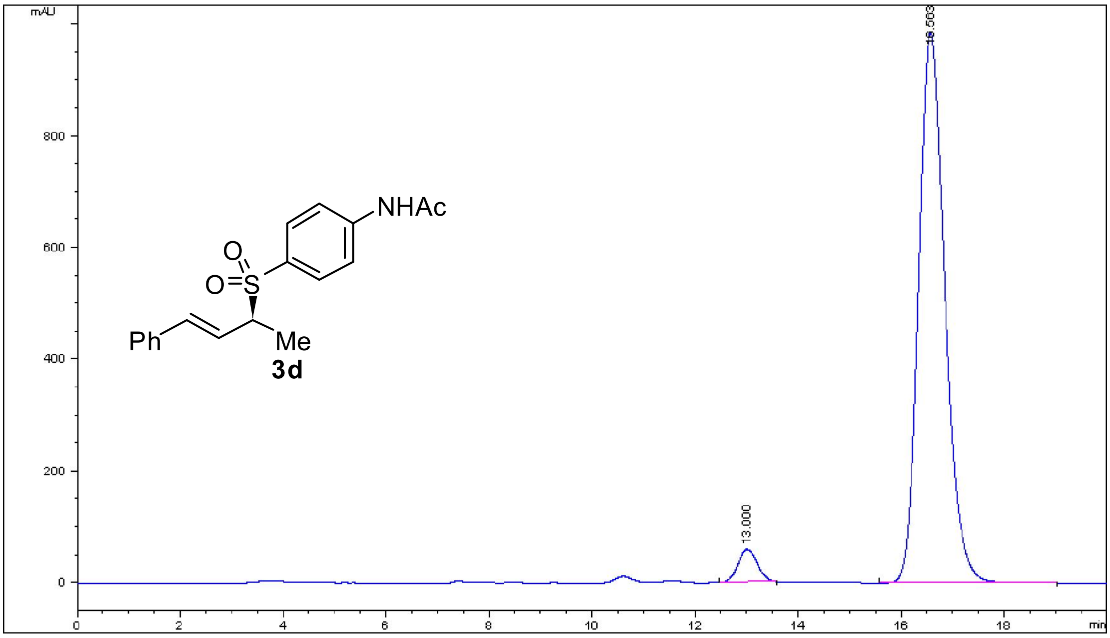


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.689	362.1	8.4	0.6653	0.894	2.810
2	37.052	12521.5	188.8	1.0271	0.843	97.190



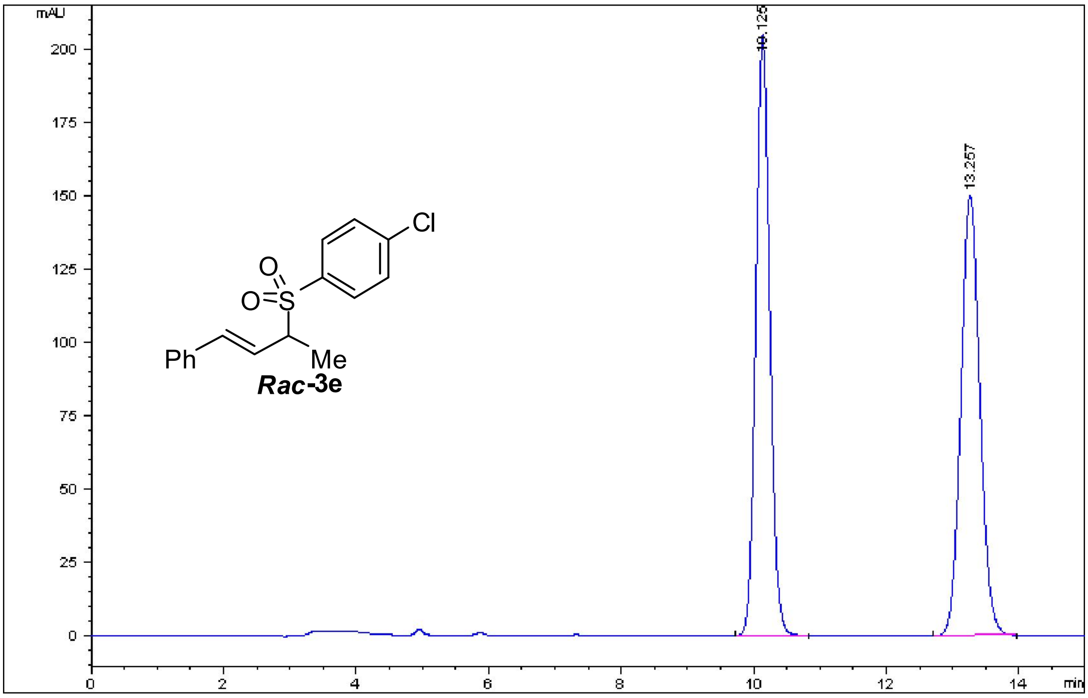
***Rac*-3d**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.061	750.9	27.1	0.4619	0.893	48.373
2	16.747	801.4	22	0.6058	0.837	51.627

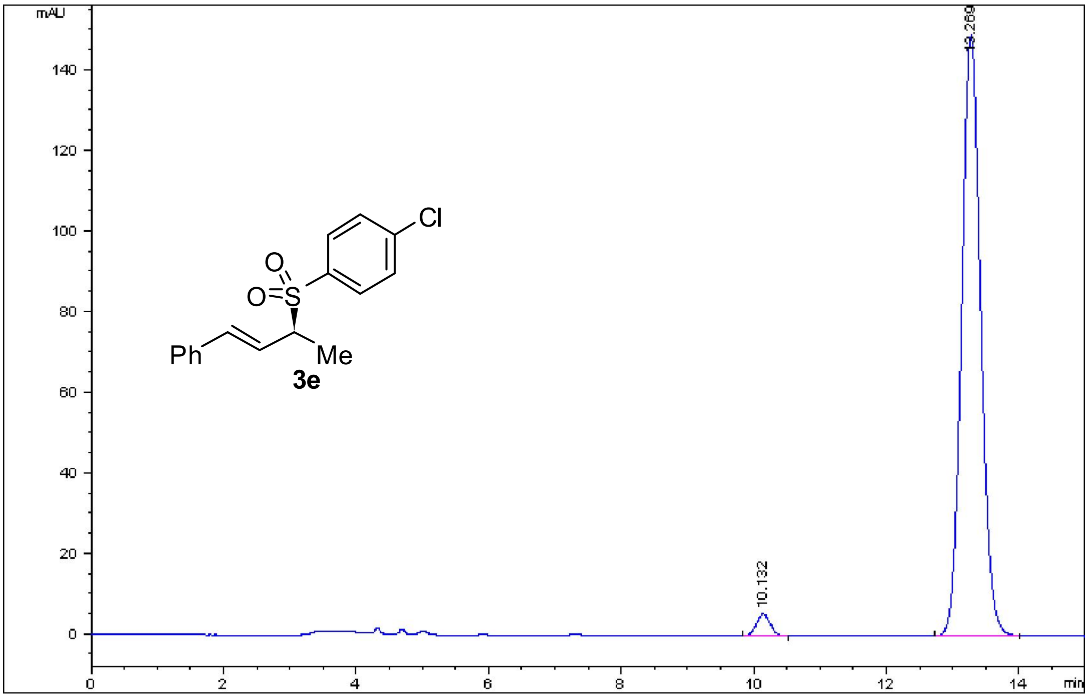


3d

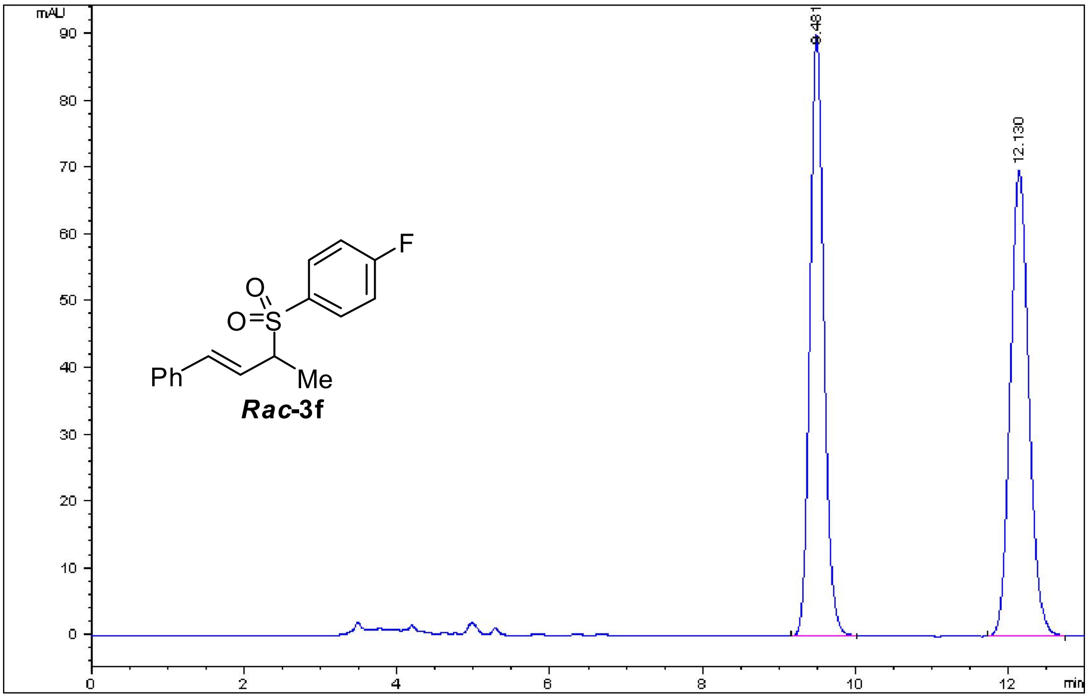
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13	1541.6	59.1	0.4347	0.885	4.239
2	16.563	34824.3	985.1	0.5464	0.781	95.761



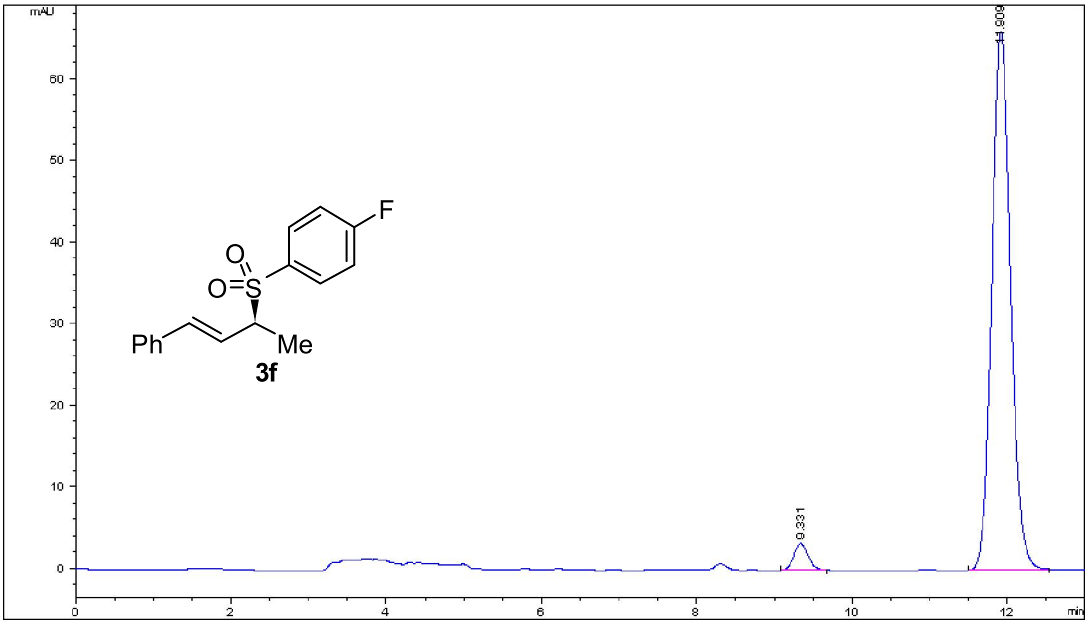
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.125	3000.7	204.7	0.2264	0.899	50.020
2	13.257	2998.2	149.9	0.3091	0.908	49.980



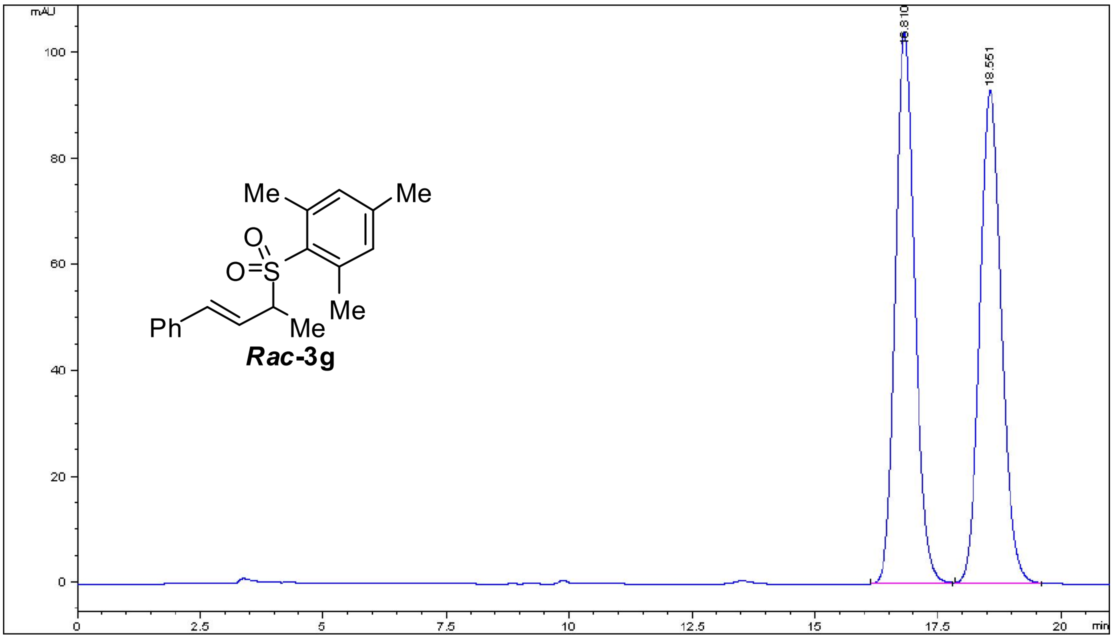
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.132	78.9	5.4	0.2245	0.921	2.572
2	13.269	2986.9	149.1	0.3109	0.907	97.428



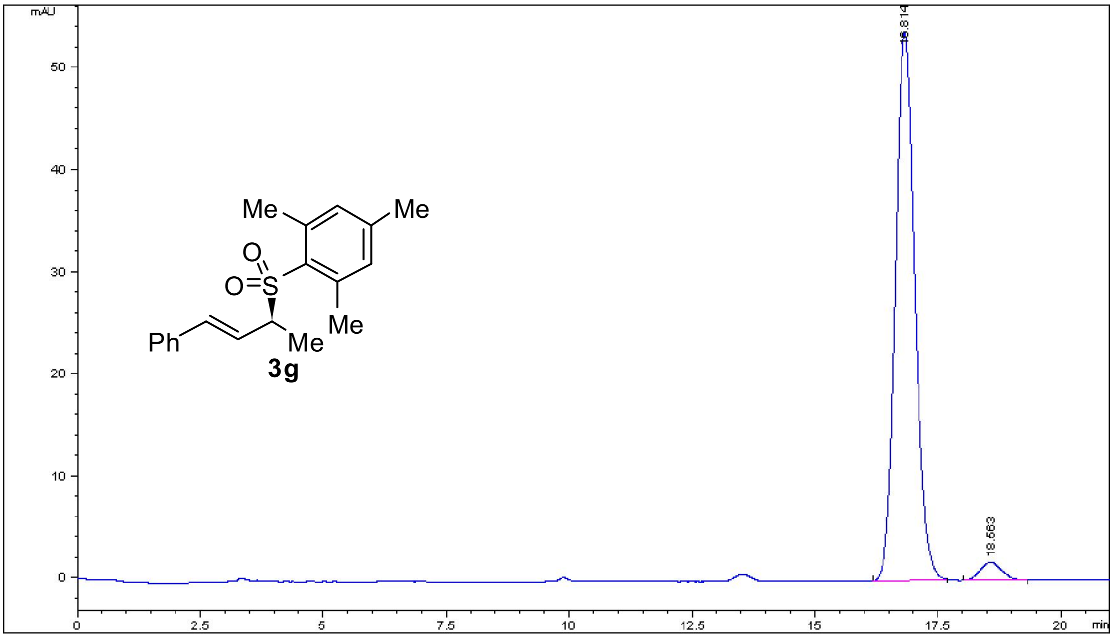
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.481	1147.6	90	0.1969	0.861	49.484
2	12.13	1171.5	69.7	0.2586	0.874	50.516



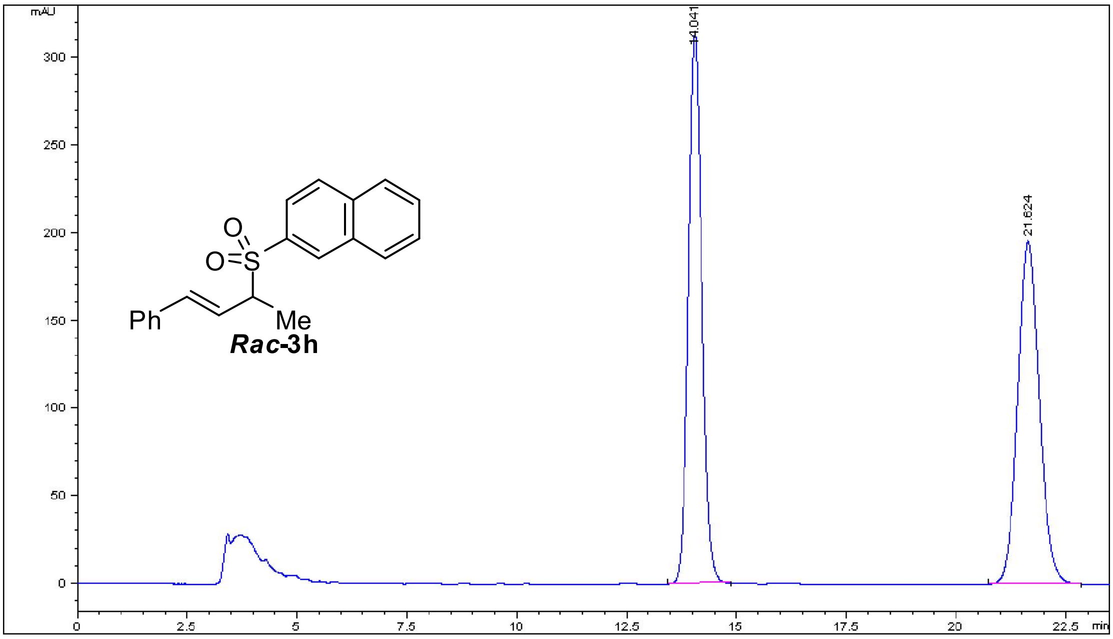
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.331	42.7	3.3	0.1977	0.876	3.713
2	11.909	1108.3	66	0.2585	0.877	96.287



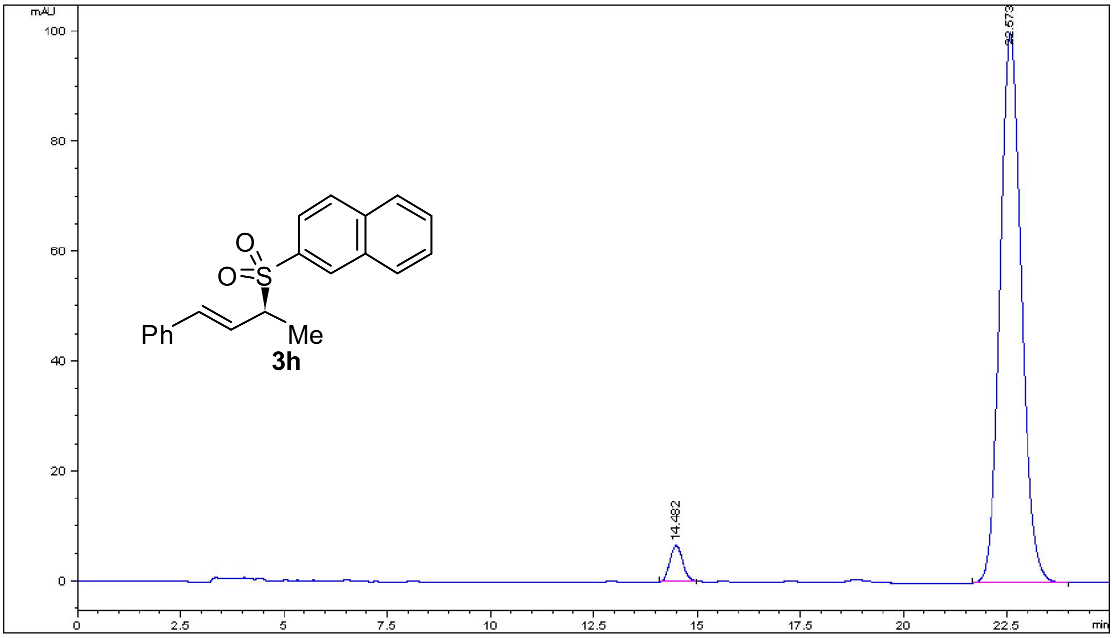
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.810	2873.2	104.1	0.4268	0.857	50.223
2	18.551	2847.7	93.1	0.4734	0.868	49.777



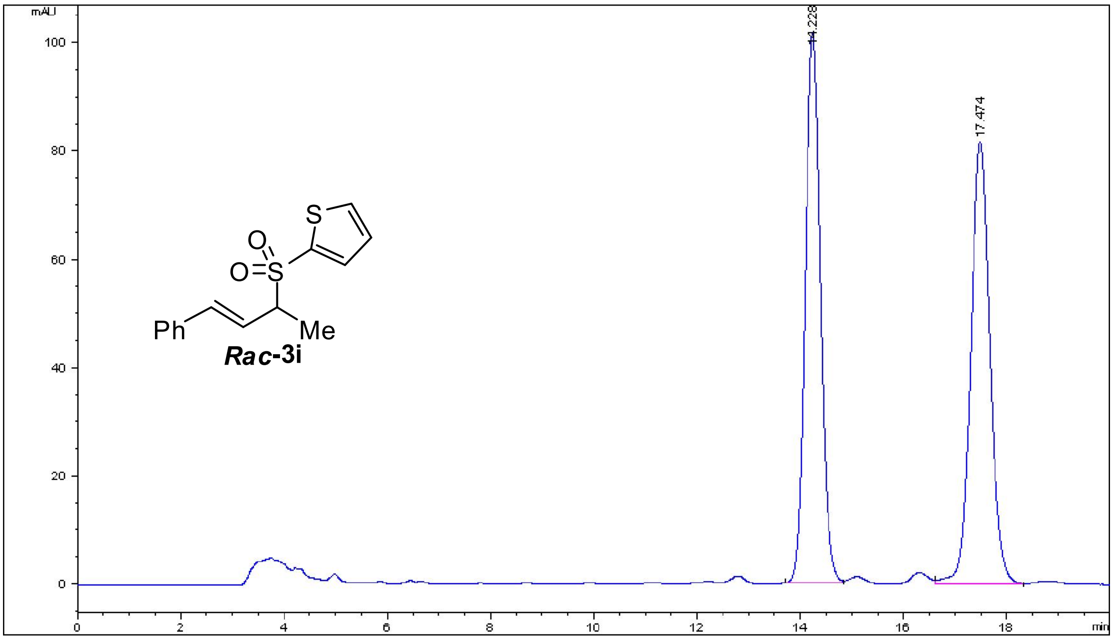
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.814	1477.3	53.7	0.4244	0.874	96.545
2	18.563	52.9	1.8	0.443	0.893	3.455



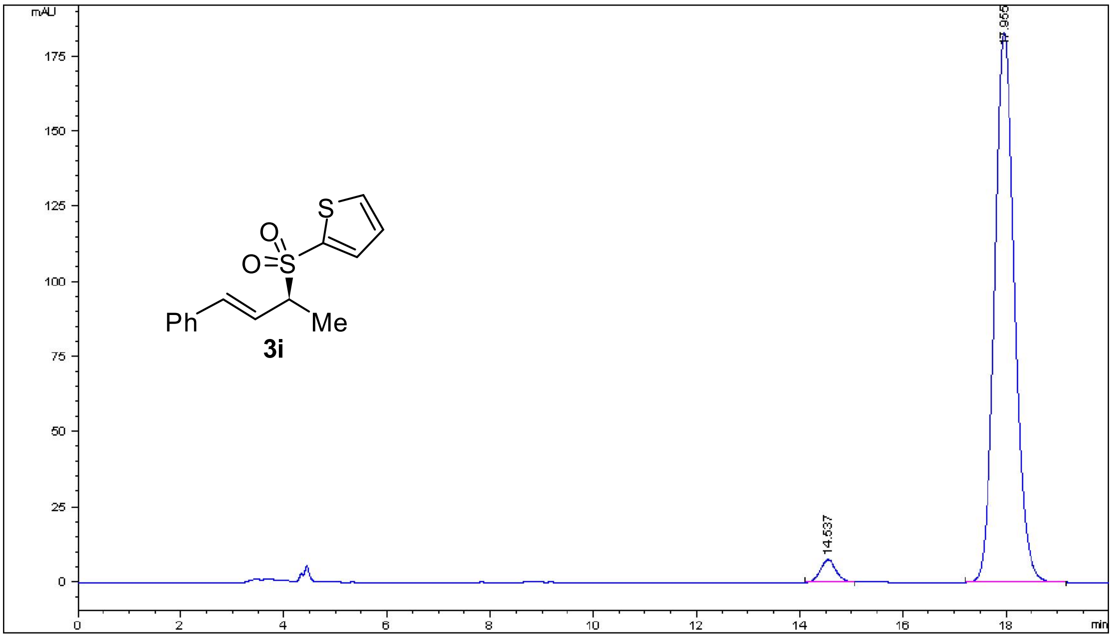
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.041	6708.7	314.3	0.3291	0.885	49.977
2	21.624	6714.8	195.8	0.5311	0.891	50.023



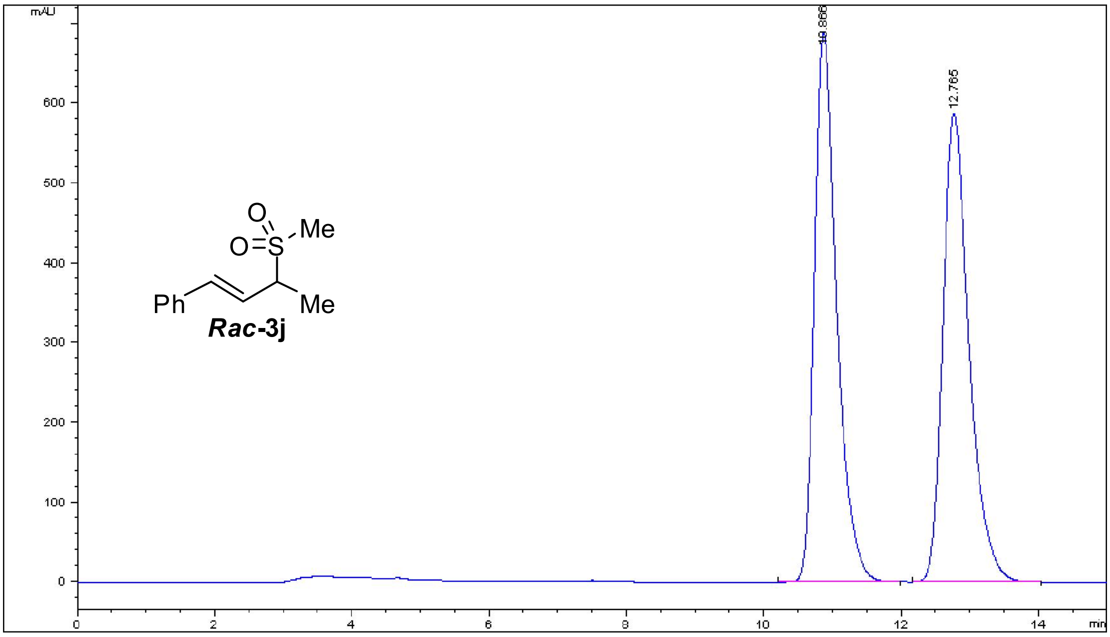
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.482	138.2	6.5	0.3534	0.948	3.681
2	22.573	3616.8	100.2	0.5611	0.878	96.319



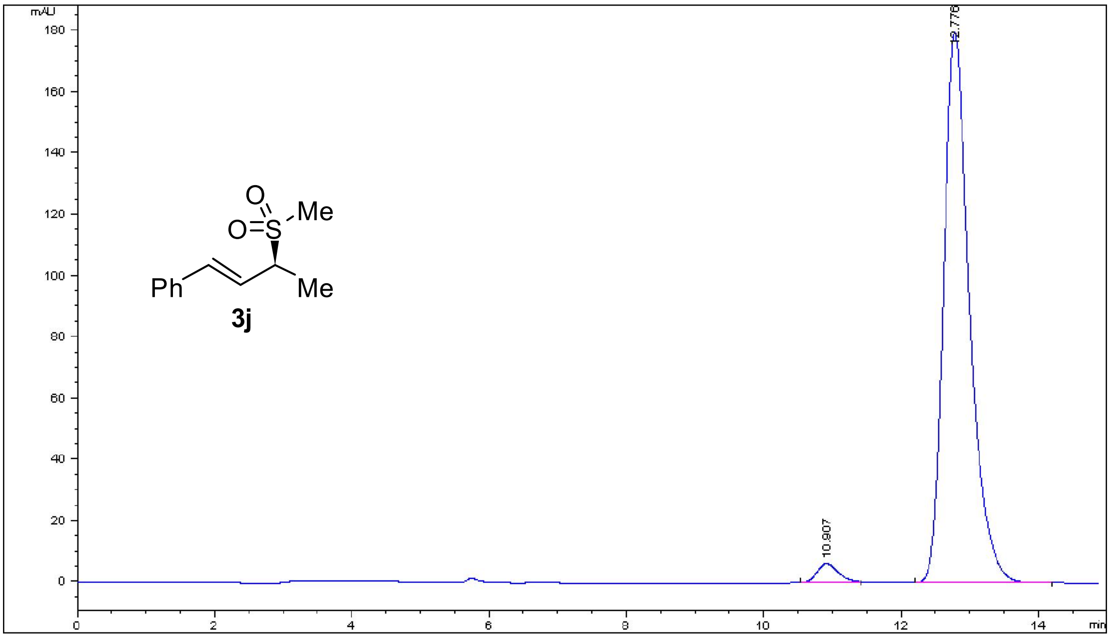
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.228	2076.3	101.8	0.3137	0.898	49.529
2	17.474	2115.8	81.6	0.3985	0.94	50.471



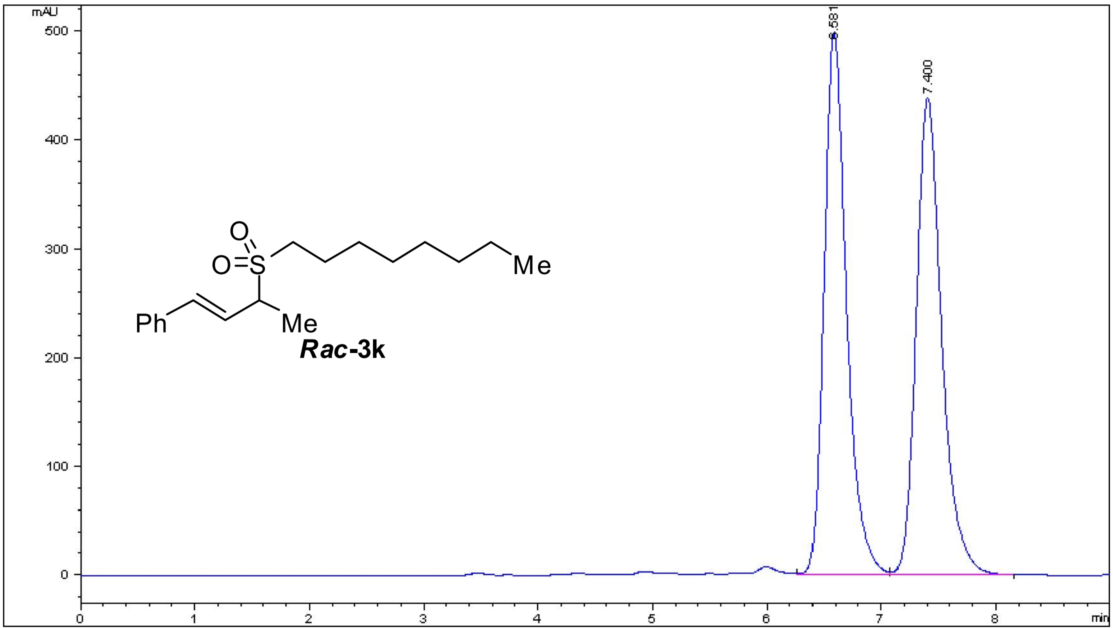
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.537	164.4	7.6	0.3333	0.862	3.221
2	17.955	4938.4	183.1	0.4195	0.86	96.779



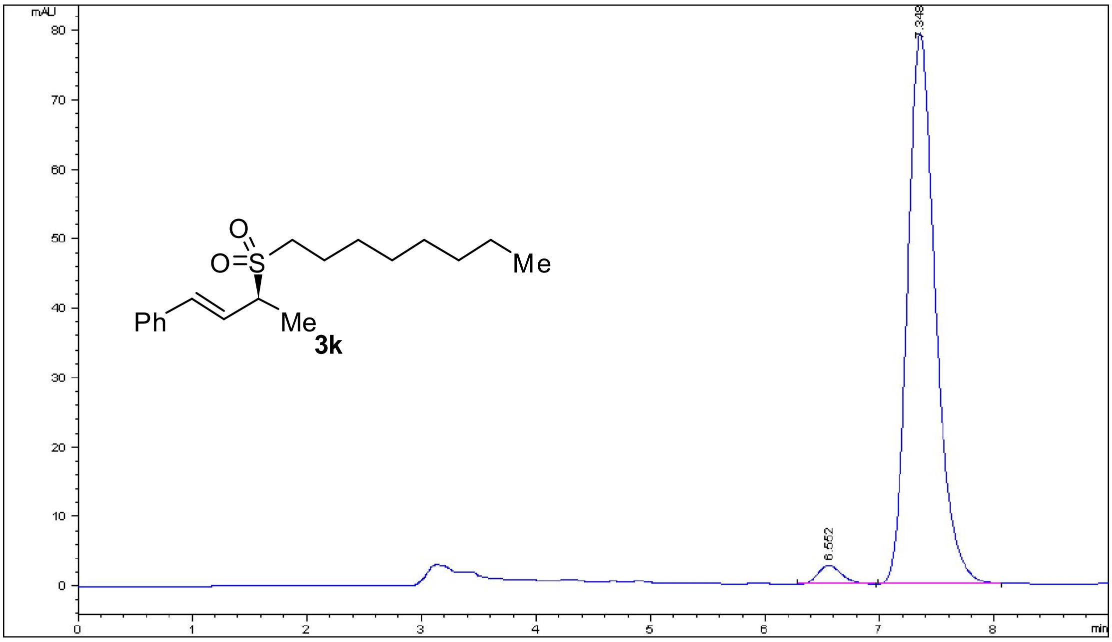
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.866	15511.5	688.7	0.3399	0.658	49.995
2	12.765	15514.7	586.6	0.3988	0.692	50.005



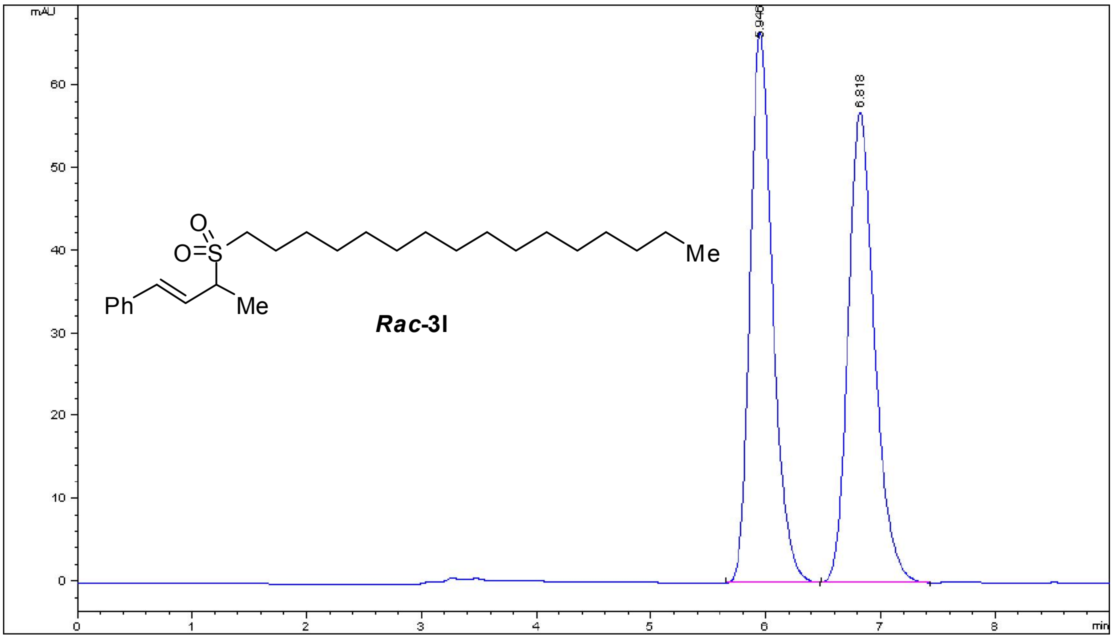
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.907	129.1	6.1	0.3512	0.778	2.662
2	12.776	4720.8	179.5	0.4	0.705	97.338



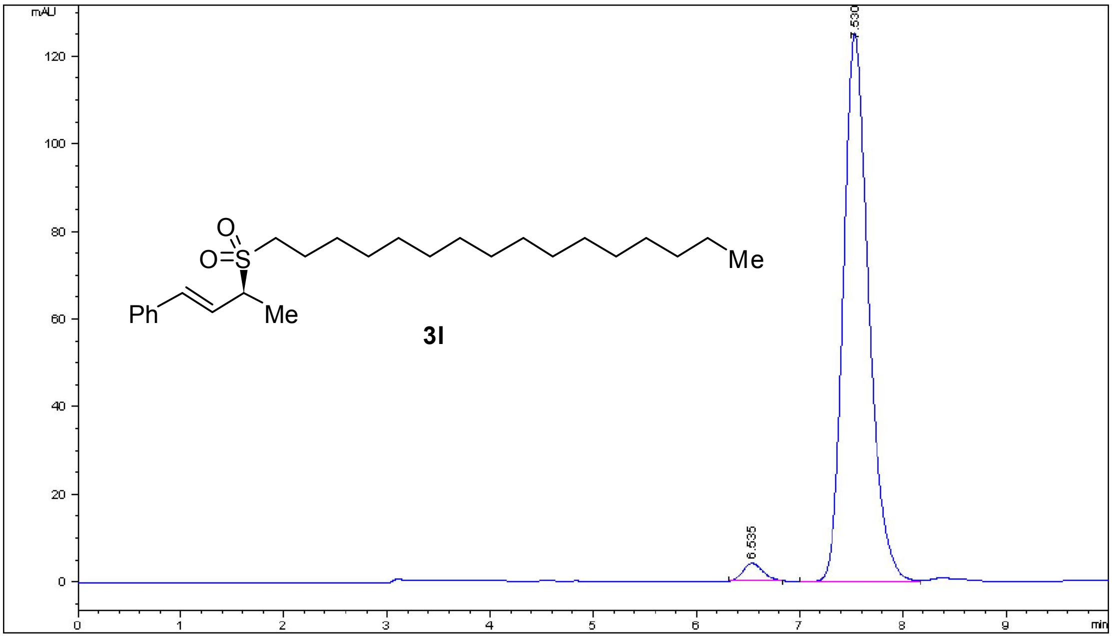
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.581	6871.8	499.7	0.2085	0.726	49.865
2	7.4	6909	439.1	0.2389	0.746	50.135



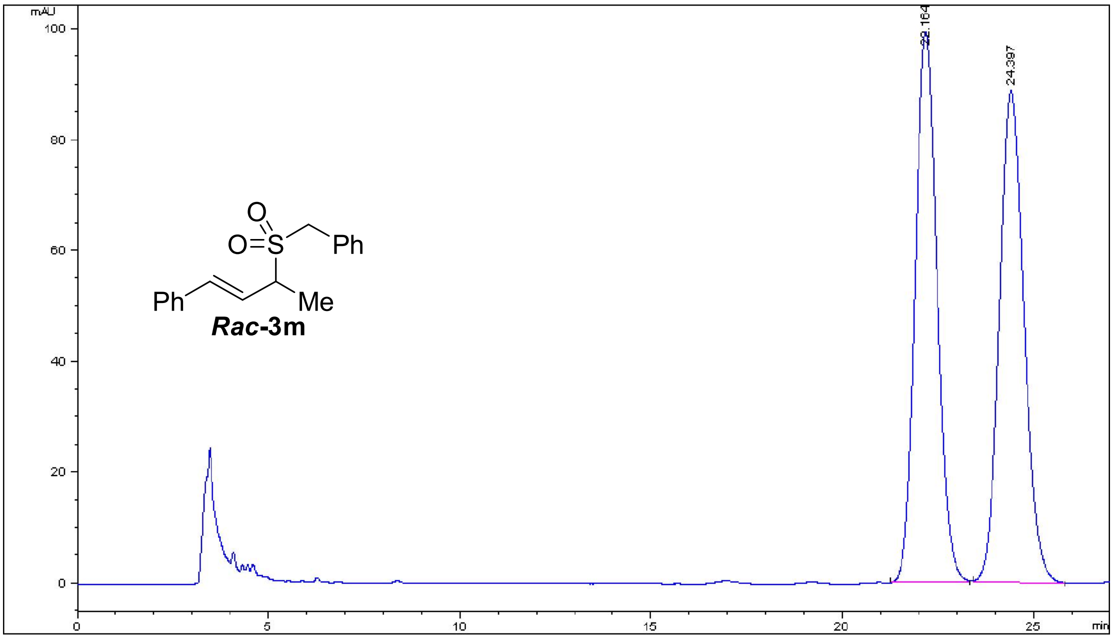
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.552	40.2	2.7	0.2269	0.818	2.909
2	7.348	1343	79.3	0.2586	0.773	97.091



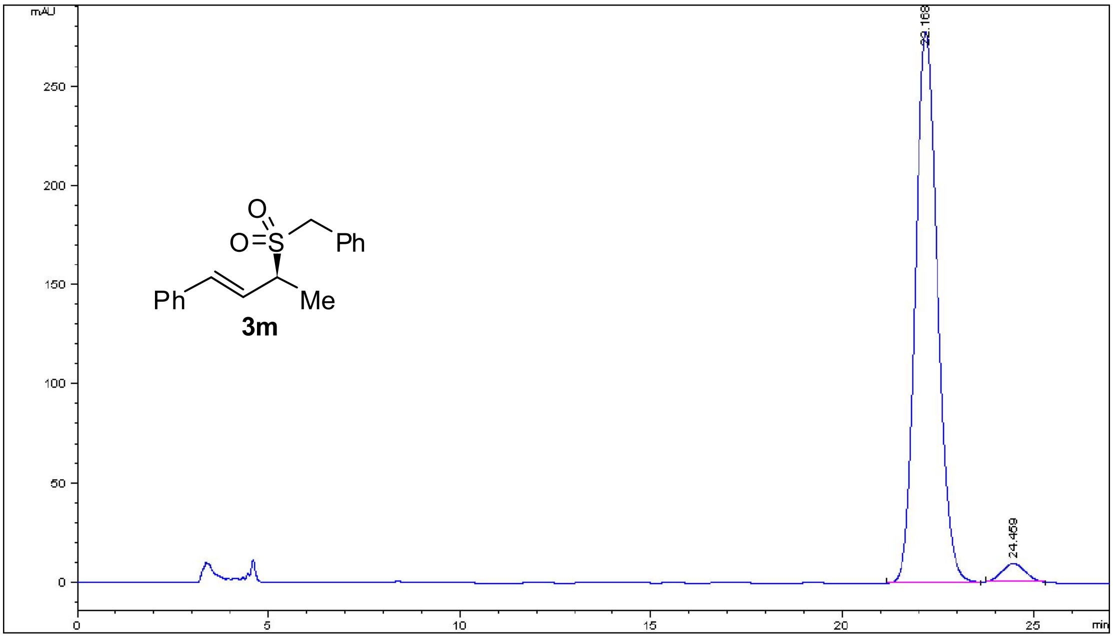
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.946	910.4	66.5	0.2077	0.749	50.062
2	6.818	908.2	56.8	0.2432	0.775	49.938



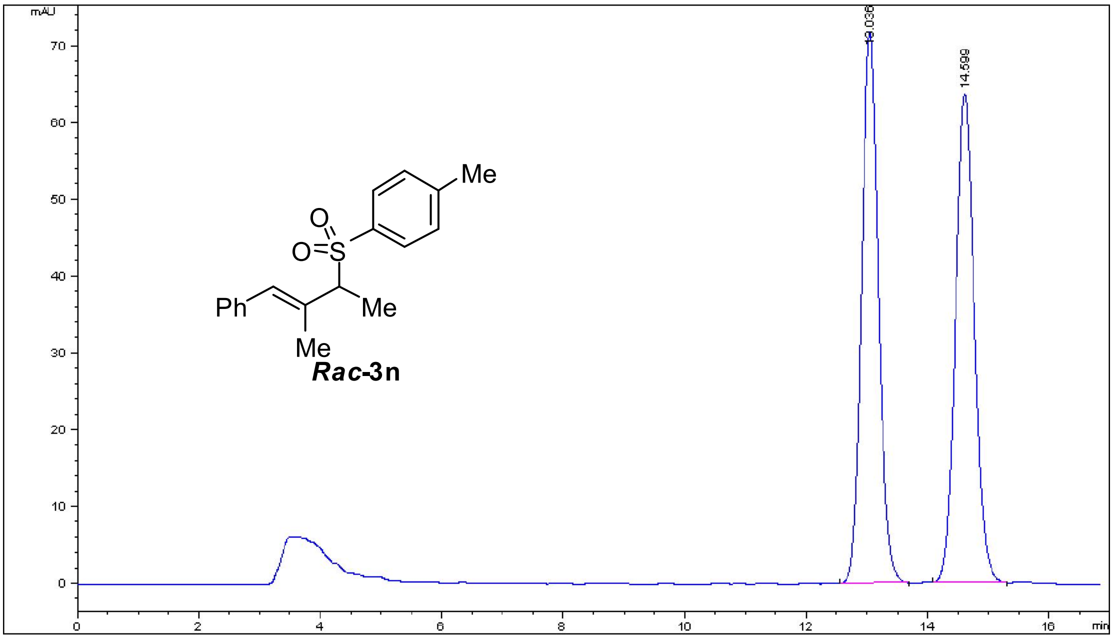
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.535	56.8	4.1	0.2324	0.807	2.582
2	7.53	2141.9	125.1	0.258	0.773	97.418



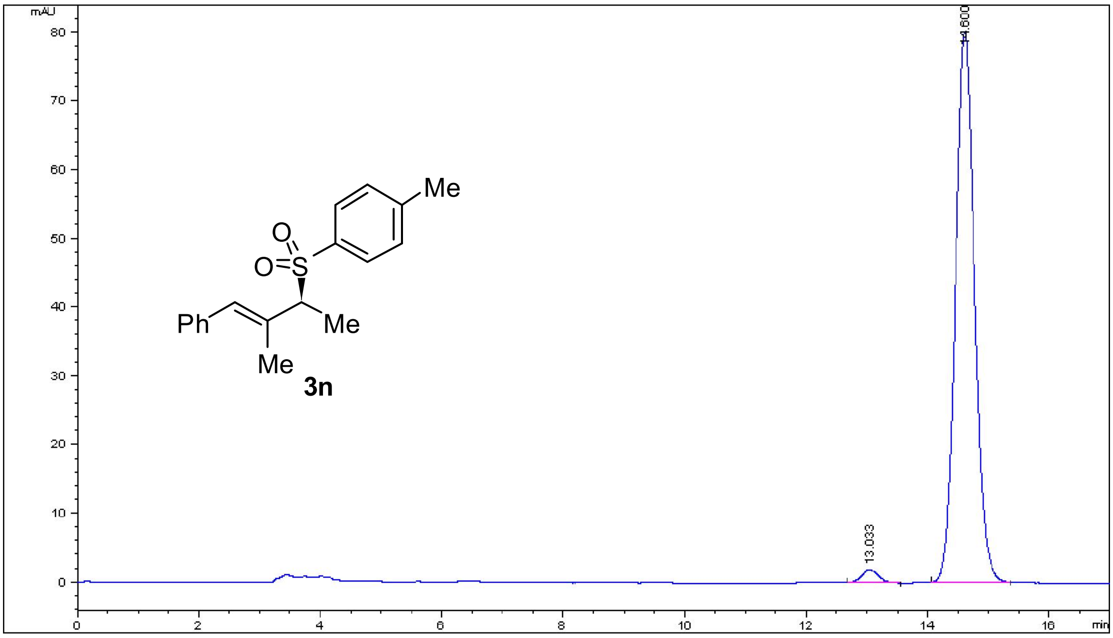
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.164	3966.1	99.3	0.6205	0.865	49.906
2	24.397	3981	88.9	0.693	0.863	50.094



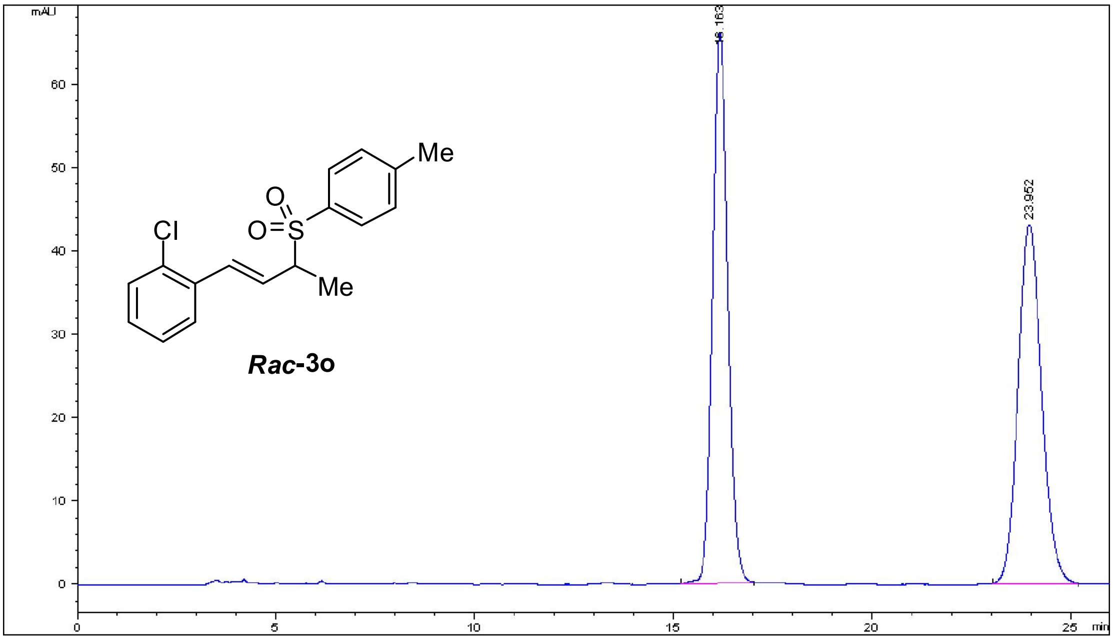
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.168	11186	277.4	0.6219	0.835	96.867
2	24.459	361.8	9	0.6712	0.954	3.133



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.036	1382.2	71.7	0.2978	0.901	50.084
2	14.599	1377.6	63.6	0.3357	0.907	49.916

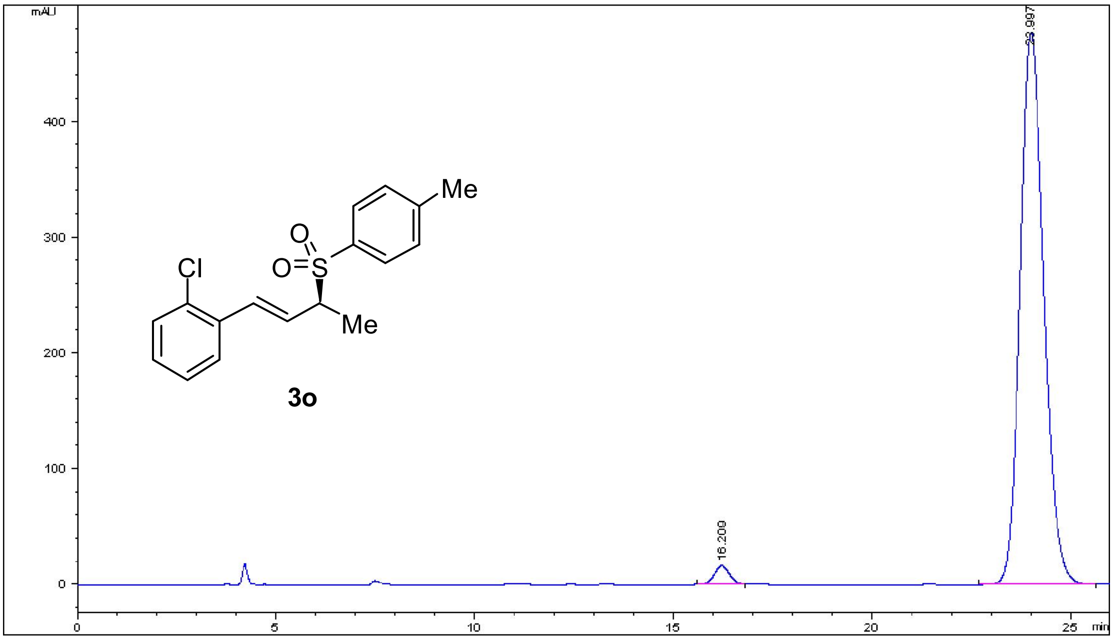


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.033	36.5	1.9	0.2961	0.888	2.043
2	14.6	1749.6	80	0.3382	0.902	97.957



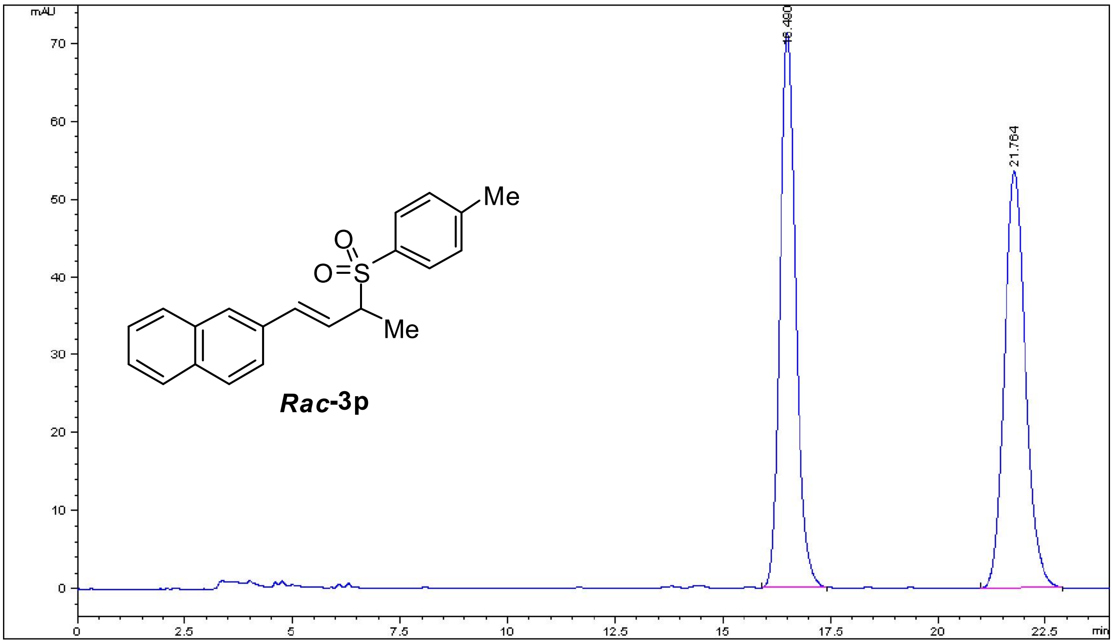
***Rac*-3o**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.163	1771.2	66.2	0.4128	0.892	49.808
2	23.952	1784.9	43.2	0.6395	0.867	50.192

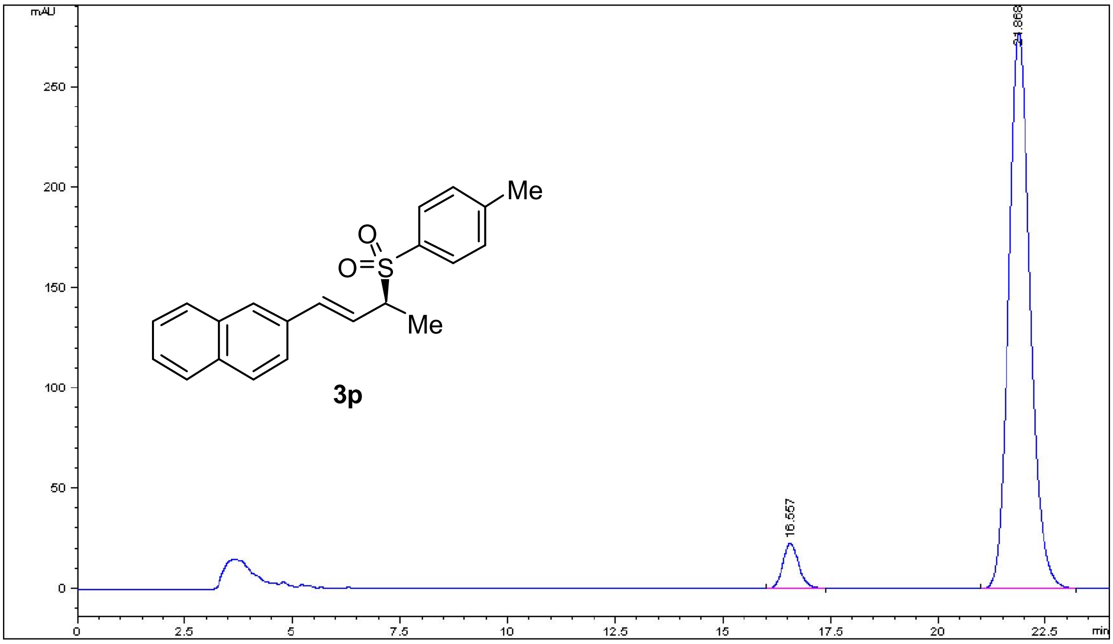


3o

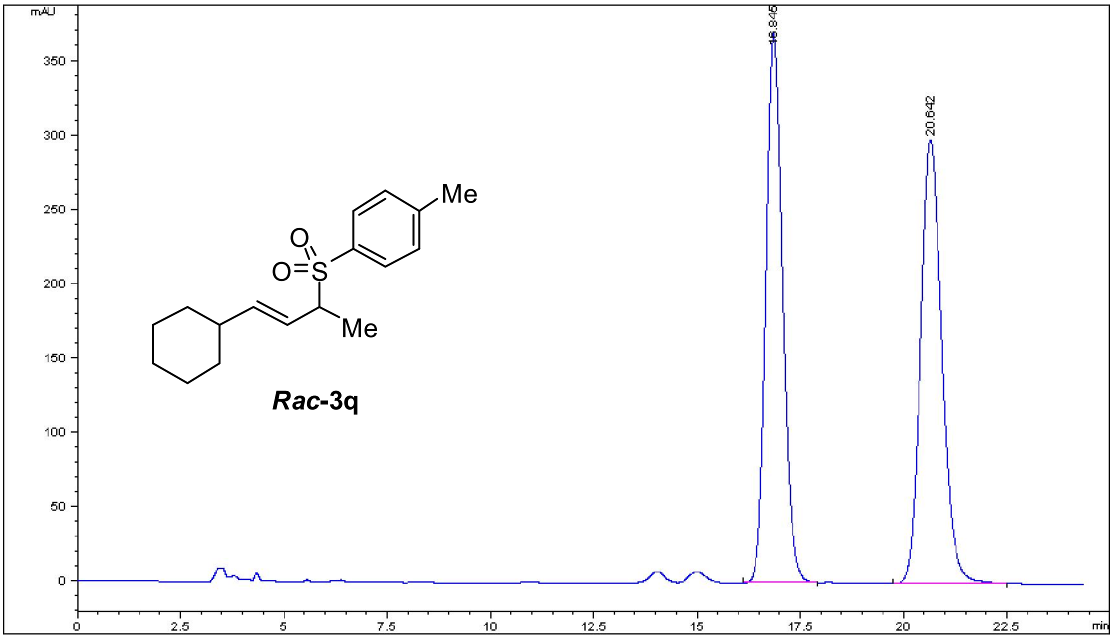
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.209	446.3	16.4	0.4203	0.911	2.208
2	23.997	19760.6	476.8	0.6407	0.812	97.792



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.49	1818.3	71.2	0.3926	0.84	49.828
2	21.764	1830.9	53.5	0.526	0.855	50.172

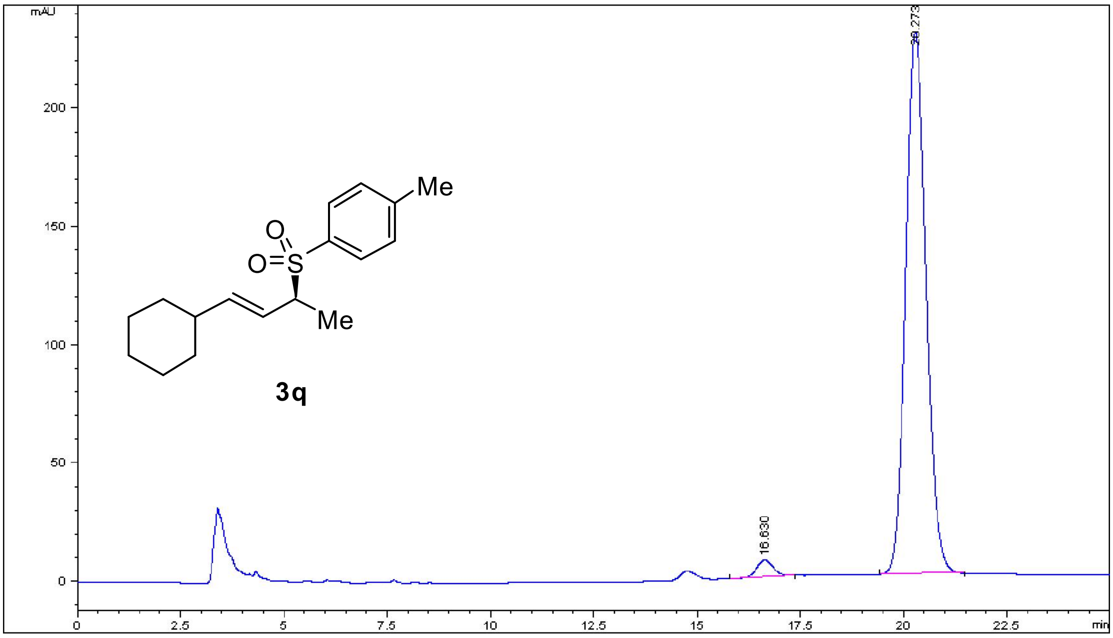


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.557	577	22.5	0.3941	0.841	5.685
2	21.868	9573.1	277	0.5313	0.839	94.315



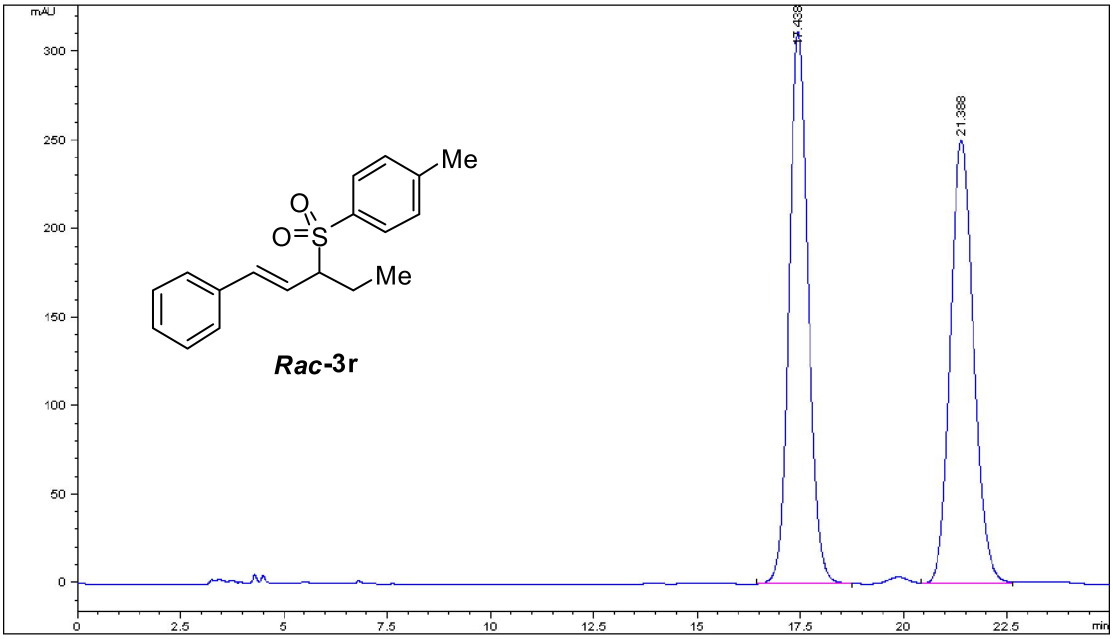
***Rac*-3q**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.845	10521.1	370.3	0.4392	0.83	49.682
2	20.642	10655.8	298.5	0.5504	0.815	50.318

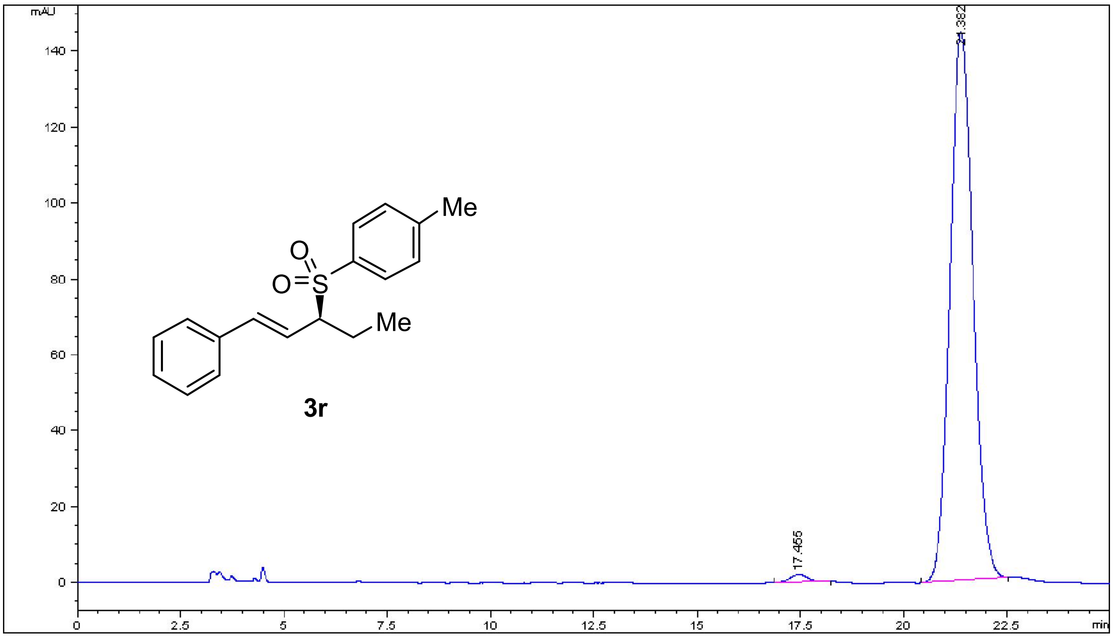


3q

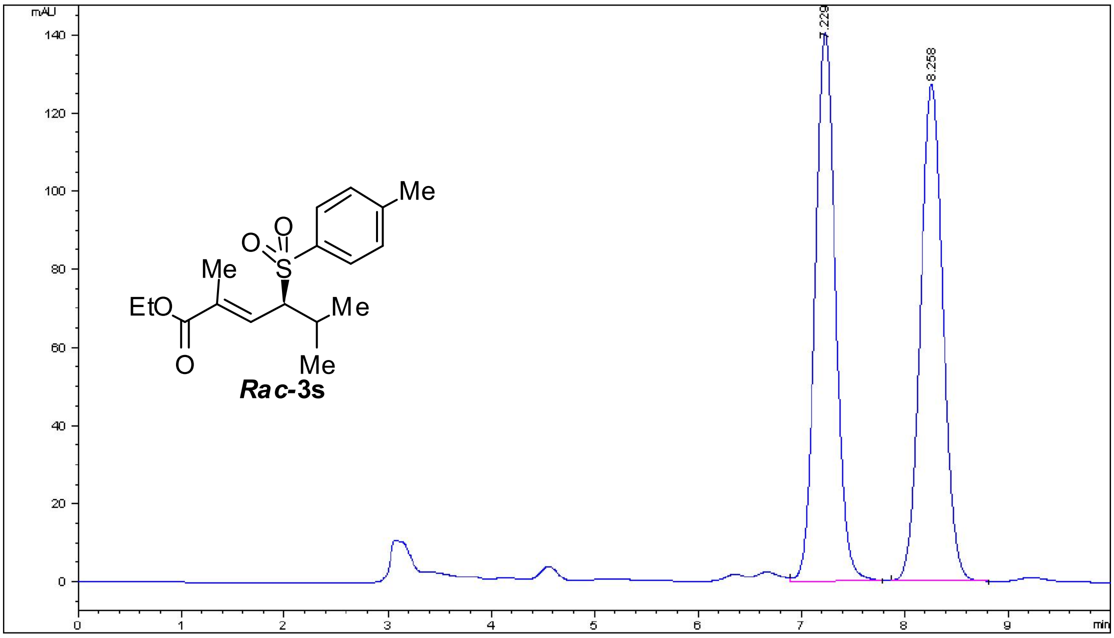
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.63	202.2	7	0.4395	0.892	2.515
2	20.273	7837.1	228.9	0.5305	0.847	97.485



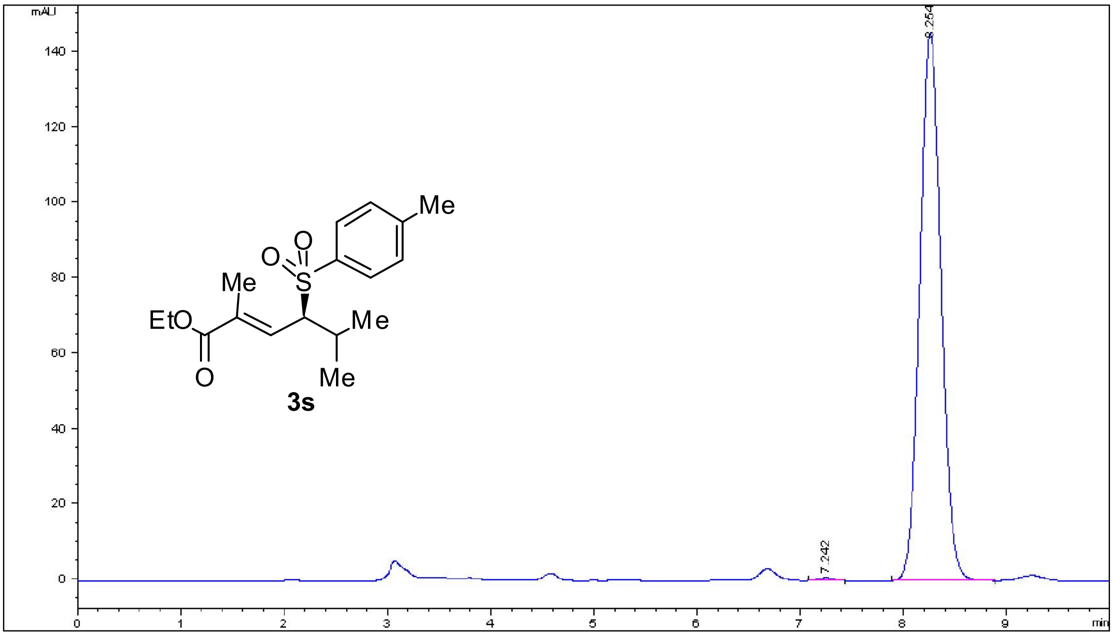
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.438	9989.4	311.4	0.4952	0.869	50.267
2	21.388	9883.2	250.4	0.6104	0.854	49.733



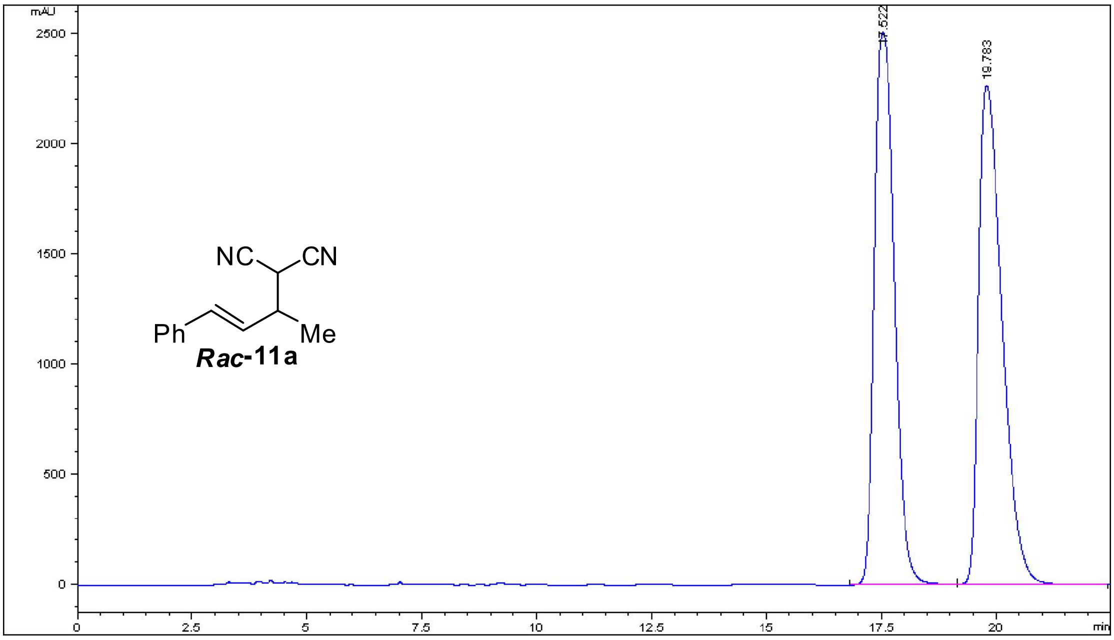
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.455	63.7	1.9	0.4997	0.826	1.117
2	21.382	5641.1	144.5	0.6083	0.881	98.883



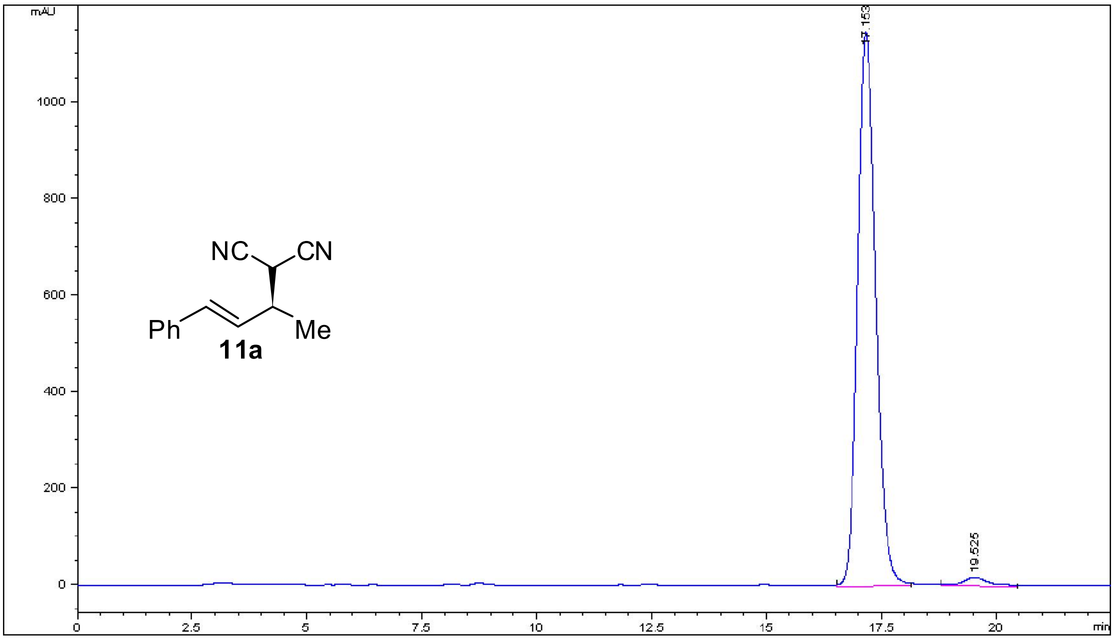
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.229	1935.2	140.7	0.2129	0.923	49.903
2	8.258	1942.7	127.1	0.2365	0.95	50.097



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.242	8.2	7.2E-1	0.1894	0.876	0.390
2	8.254	2090.1	145.2	0.2262	0.924	99.610



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.522	76117	2504.9	0.4783	0.697	48.563
2	19.783	80622.7	2265.9	0.5491	0.493	51.437



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.153	31565.5	1146.5	0.4589	0.811	97.659
2	19.525	756.7	17.8	0.7101	0.726	2.341