Supporting Information

Enantioselective C–H Functionalization of Allylic and Benzylic sp^3 C–H Bonds using *N*-Sulfonyl-1,2,3-triazoles

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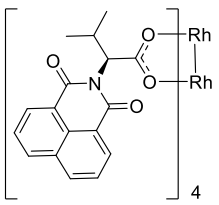
1. Experimental Section

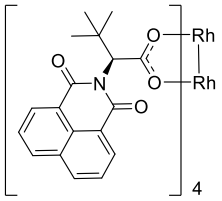
1.1 General Considerations

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers, unless otherwise stated. All solvents were purchased from Sigma Aldrich, dried over calcium hydride, and freshly distilled prior to use in synthesis. Proton (^{1}H) NMR spectra were recorded at 400 or 500 MHz on a Varian-400 or an Inova-500 spectrometer, respectively. Carbon-13 (^{13}C) NMR spectra were recorded at 100 or 125 MHz on a Varian-400 or an Inova-500 spectrometer, respectively. NMR spectra were recorded in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.26 ppm for ^{1}H NMR and δ 77.16 ppm for ^{13}C NMR) as the internal standard, and were reported in parts per million (ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sep, septet; and m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. Infrared (IR) Spectra were collected on a Nicolet Impact Series 10 FT-IR. Mass spectrometric determinations were carried out on a Thermo Finnigan LTQ-FTMS spectrometer with nano-spray ionization (NSI). Optical rotations were measured on a PerkinElmer 341 polarimeter. High performance liquid chromatography (HPLC) analysis was performed on a Varian Prostar 350 with hexanes/isopropanol as eluent. Analytical thin layer chromatography (TLC) was performed on silica gel plates using ultraviolet (UV) light or stained with either $KMnO_4$ or phosphomolybdic acid (PMA). Flash column chromatography was performed with silica gel 60 Å (230 – 400 mesh) according to the literature procedure.[1] 4-Phenyl-*N*-mesyltriazole,[2] Rh_2(*S*-NTV)$_4$,[3] Rh_2(*S*-NTTL)$_4$,[4] Rh_2(*S*-4-Cl-NTTL)$_4$,[5] Rh_2(*S*-PTTL)$_4$,[6] Rh_2(*S*-TCPTTL)$_4$,[7] Rh_2(*S*-PTAD)$_4$,[8] and Rh_2(*S*-TCPTAD)$_4$[9] were all prepared according to literature procedures.

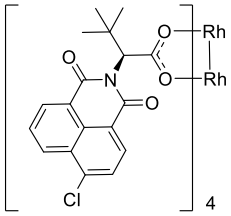
1.2 Catalyst Structures



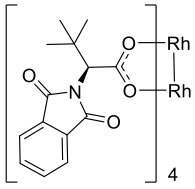
S1. Rh_2(*S*-NTV)$_4$
MW = 1391.02



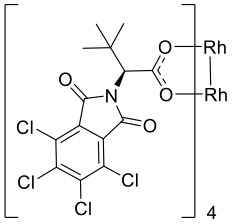
S2. Rh_2(*S*-NTTL)$_4$
MW = 1447.13



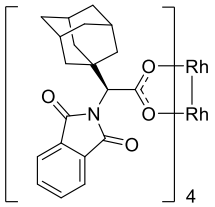
S3. Rh_2(*S*-4-Cl-NTTL)$_4$
MW = 1584.90



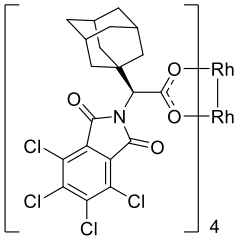
S4. Rh_2(*S*-PTTL)$_4$
MW = 1250.92



S5. Rh_2(*S*-TCPTTL)$_4$
MW = 1801.99



S6. Rh_2(*S*-PTAD)$_4$
MW = 1563.38



S7. Rh_2(*S*-TCPTAD)$_4$
MW = 2114.45

1.3 General Procedures

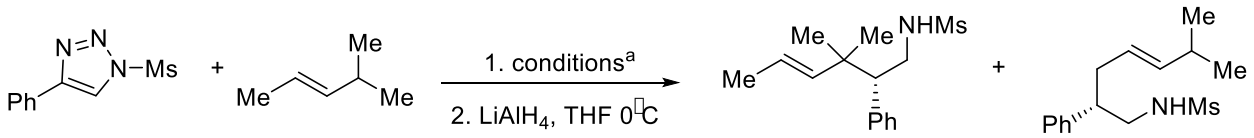
1.3.1 Triazole Reactions

The same general procedure was used for both the allylic and benzylic systems, unless otherwise indicated. Two 10 mL round bottom flasks (RBF), one with magnetic stir bar, were flamed dried under vacuum then purged with dry argon and allowed to cool to room temperature (rt). This was repeated three times followed by an additional 15 min under vacuum. The RBF with the magnetic stir bar was then charged with 4-phenyl-*N*-mesyltriazole (224 mg, 1.0 mmol, 1 equiv) and dirhodium catalyst (1 mol %) followed by three successive vacuum/argon cycles. Both flasks were transferred from Schlenk line to argon balloon. The other RBF was charged with the respective substrate (4.0 mmol, 4 equiv) and chlorinated solvent (2 mL) via syringes equipped with oven dried needles. The respective substrate and solvent were then added to the RBF containing the 4-phenyl-*N*-mesyltriazole and dirhodium catalyst and allowed to react at rt for 18 - 24 h. Solvent was removed via rotary evaporation. The reaction mixture was diluted with 4 mL THF and reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0º C for 1 h. The reaction mixture was quenched by slowly adding $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped and maintaining 0º C for an additional 15 min. The crude product was isolated by vacuum filtration using a 60 mL medium porosity fritted funnel with a smoothly packed layer of Celite® and DCM (50 mL) as the eluent. DCM was removed via rotary evaporation. The desired product was purified via flash chromatography eluting with either hexane/ethyl acetate (EtOAc) or hexane/isopropanol (IPA) to afford the analytically pure allylic or benzylic product.

1.3.2 Diazo Reactions

The same procedural guidelines were followed for reactions using methyl phenyl diazoacetate in place of the 4-phenyl-*N*-mesyltriazole substrate. Two 10 mL round bottom flasks (RBF), one with magnetic stir bar, were flamed dried under vacuum then purged with dry argon and allowed to cool to room temperature (rt). This was repeated three times followed by an additional 15 min under vacuum. The RBF with the magnetic stir bar was then charged with the dirhodium catalyst (1 mol %) followed by three successive vacuum/argon cycles. Both flasks were transferred from Schlenk line to argon balloon. The RBF containing the catalyst was charged with chlorinated solvent (1 mL) and the respective substrate (4.0 mmol, 4 equiv). The other RBF was charged with methyl phenyl diazoacetate (176.2 mg, 1.0 mmol, 1 equiv) and chlorinated solvent (1 mL) via syringes equipped with oven dried needles. The diazoacetate and chlorinated solvent mixture was added dropwise over 1 h to the solution of catalyst, substrate, and chlorinated solvent. After addition, the reaction was allowed to proceed an additional 17 – 23 h until reaction completion. The crude product was isolated by vacuum filtration using a 60 mL medium porosity fritted funnel with a smoothly packed layer of Celite® and DCM (50 mL) as the eluent. DCM was removed via rotary evaporation. The desired product was purified via flash chromatography eluting with either hexane/EtOAc or hexane/IPA to afford the analytically pure allylic or benzylic product.

1.4 Optimization of the Allylic System



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

Optimization Procedure: Performed using General Procedure 1.3.1 with variations of catalyst, solvent, substrate, and conditions.

Table 1. Screening of Rh(II)-catalysts for enantioselective sp^3 functionalization of the alkenes[a]

entry	catalyst	3°:1°	3° % yield[b]	% ee
1	Rh_2(*S*-NTTL)$_4$	>30:1	83	84
2	Rh_2(*S*-PTTL)$_4$	>30:1	57	78
3	Rh_2(*S*-PTAD)$_4$	>30:1	54	79
4	Rh_2(*S*-TCPTAD)$_4$	>30:1	29	73

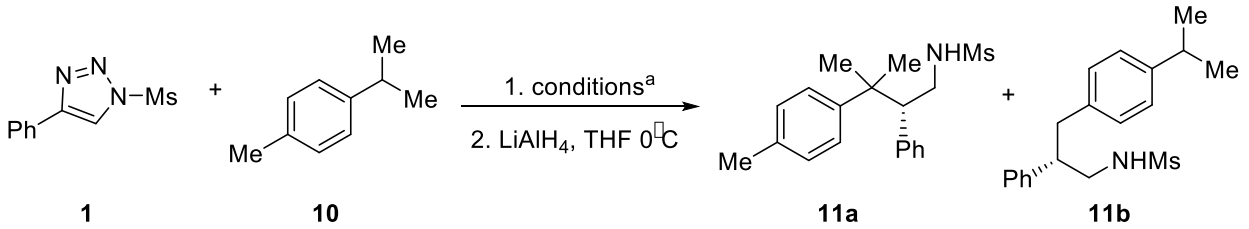
[a]Rh(II)-catalyst (1 mol %), $CHCl_3$ (2 mL), *trans*-4-methyl-2-pentene (4 equiv), rt, 18h. [b]Isolated yields.

Table 2. Screening of the reaction conditions[a,b]

entry	solvent	alkene equiv	T °C	c, M	3°:1°	3° % yield[c]	% ee
1	$CHCl_3$	2	rt	0.5	>30:1	74	77
2	$CHCl_3$	4	rt	0.5	>30:1	83	84
3	$CHCl_3$	8	rt	0.5	>30:1	77	84
4	$CHCl_3$	4	rt	1.0	>30:1	77	83
5	$CHCl_3$	4	rt	0.25	>30:1	76	83
6	$CHCl_3$	4	40	0.5	>30:1	78	83
7	$CHCl_3$	4	0	0.5	n/a	0	n/a
8[d]	$CHCl_3$	4	rt	0.5	>30:1	74	84
9[e]	$CHCl_3$	4	rt	0.5	>30:1	82	83
10[f]	$CHCl_3$	4	rt	0.5	>30:1	80	83
11	DCM	4	rt	0.5	>30:1	73	85
12	DCM	4	reflux	0.5	>30:1	70	82
13	1,2-DCE	4	rt	0.5	>30:1	63	86
14	1,2-DCE	4	40	0.5	>30:1	72	67
15	TFT	4	rt	0.5	n/a	0	n/a
16	TFT	4	40	0.5	>30:1	69	79
17	EtOAc	4	rt	0.5	n/a	0	n/a
18	EtOAc	4	40	0.5	n/a	0	n/a

[a]Rh_2(*S*-NTTL)$_4$ (1 mol %) and t*rans*-4-methyl-2-pentene were used for this optimization. [b]18 h reaction time unless otherwise indicated. [c]Isolated yields. [d]4 Å molecular sieves. [e]6 h reaction time. [f]12 h reaction time.

1.5 Optimization of the Benzylic System



Optimization Procedure: Performed using General Procedure 1.3.1 with variations of catalyst, solvent, substrate, and conditions.

Table 3. Screening of Rh(II)-catalysts for enantioselective sp^3 functionalization of arenes[a]

entry	catalyst	3º:1º	3º % yield[b]	% ee
1	Rh_2(*S*-NTTL)$_4$	80:20	52	74
2	Rh_2(S-4-Cl-NTTL)$_4$	n/a	0	n/a
3	Rh_2(S-PTTL)$_4$	71:29	20	65
4[c]	Rh_2(S-TCPTTL)$_4$	80:20	28	43
5	Rh_2(S-PTAD)$_4$	64:36	10	70
6	Rh_2(S-TCPTAD)$_4$	67:33	9	50
7[d]	Rh_2(S-NTV)$_4$	83:17	53	62
8[d]	Rh_2(S-NTAD)$_4$	78:22	55	66

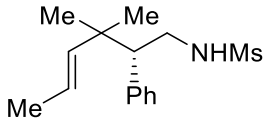
[a]Rh(II)-catalyst (1 mol %), 1,2-DCE (2 mL), *p*-cymene (4 equiv), rt, 24 h. [b]Isolated yields. [c]Reaction ran at 45 ºC. [d]Reaction ran for 18 h.

Table 4. Screening of the reaction conditions[a,b]

entry	solvent	arene equiv	T ºC	c, M	3º:1º	3º % yield[c]	% ee
1	$CHCl_3$	4	rt	0.5	79:21	59	68
2	1,2-DCE	4	rt	0.5	80:20	52	74
3[d]	1,2-DCE	4	rt	0.5	80:20	43	77
4[e]	1,2-DCE	4	rt	0.5	83:17	54	65
5	DMB	4	50	0.5	n/a	0	n/a

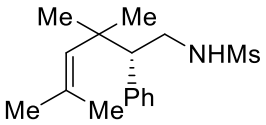
[a]Rh_2(*S*-NTTL)$_4$ and *p*-cymene were used for this screening. [b]24 h reaction time unless otherwise stated. [c]Isolated yields. [d]3 h reaction time. [e]4 Å molecular sieves.

2. Procedures and Characterization Data



(*S,E*)-*N*-(3,3-dimethyl-2-phenylhex-4-en-1-yl)methanesulfonamide (3a)
Prepared by General Procedure 1.3.1 with **1** (224 mg, 1.0 mmol, 1.0 equiv), *trans*-4-methyl-2-pentene (337 mg, 4.0 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1 mol %), and $CHCl_3$ (2 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3; R_f 0.26) afforded the title compound as a tan oil (235 mg, 83% yield). Crystal structure to confirm stereochemistry was obtained by dissolving 30 mg of the tan oil in 2 mL hexanes and allowing the title compound to crash out of solution as pure white needles over a 24 h period. Crystallographic analysis confirmed the suspected *S* stereochemistry at the chiral center (see attached crystallographic file for further information).

MP = 74 °C
$[\alpha]^{20}_D$ -17.1° (*c* 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.24 (m, 3H), 7.15 (dd, *J* = 8.5, 3.5, 1.7 Hz, 2H), 5.47-5.42 (m, 1H), 5.40-5.32 (m, 1H), 3.85 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.57 (ddd, *J* = 12.9, 8.8, 4.2 Hz, 1H), 3.36 (td, *J* = 12.2, 3.6 Hz, 1H), 2.75 (s, 3H), 2.65 (dd, *J* = 11.7, 4.1 Hz, 1H), 1.70 (dd, *J* = 6.4, 1.6 Hz, 3H), 0.97 (s, 3H), 0.89 (s, 3H)
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 138.4, 129.8, 128.6, 128.5, 127.4, 123.3, 56.5, 44.2, 40.3, 38.7, 27.9, 24.3, 18.3
FTIR (neat): ν_{max}/cm^{-1} 3289, 3027, 2863, 1542, 1409, 1364, 1319, 1150, 1072, 972, 855, 778, 751, 704
HRMS (NSI): *m/z* 282.1518 [$(M-H)^+$ requires 282.1522], Calcd for $C_{15}H_{24}NO_2S$
HPLC: 84% ee, Chiralcel OD column, 2% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, t_r: 36.0 min (major), 25.6 min (minor)



(*S*)-*N*-(3,3,5-trimethyl-2-phenylhex-4-en-1-yl)methanesulfonamide (7a)

Prepared by General Procedure 1.3.1 with **1** (224 mg, 1.0 mmol, 1.0 equiv), *trans*-2,4-dimethyl-2-pentene (393 mg, 4.0 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1 mol %), and $CHCl_3$ (2 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3; R_f 0.30) afforded a tan oil containing a 1.5:1 mixture of the title compound and the 1° insertion product (**7b**), respectively (154 mg, 52% combined yield). Further purification for characterization purposes were performed by additional flash chromatography (SiO_2; hexanes/EtOAc, 7:3): The leading fractions contained the excess of **7a** while the tail fractions contained an inseparable mix of the regioisomers (in all cases the R_f values were identical).

$[\alpha]^{20}_D$ +8.7° (*c* 0.5, $CHCl_3$)

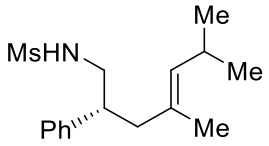
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.24 (m, 3H), 7.19-7.16 (m, 2H), 5.11 (quin, *J* = 2.7 Hz, 1H), 3.85 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.66 (ddd, *J* = 12.5, 8.6, 4.1 Hz, 1H), 3.47 (td, *J* = 11.9, 3.7 Hz, 1H), 2.85 (dd, *J* = 11.7, 3.9 Hz, 1H), 2.78 (s, 3H), 1.73 (d, *J* = 1.4, 3H), 1.67 (d, *J* = 1.3, 3H), 1.05-1.01 (m, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 132.4, 131.9, 129.9, 128.5, 127.4, 56.6, 44.1, 40.4, 38.9, 28.8, 28.6, 26.4, 19.2

FTIR (neat): ν_{max}/cm^{-1} 3287, 2964, 2928, 1602, 1494, 1452, 1409, 1365, 1316, 1147, 1094, 1071, 967, 909, 931, 781, 733, 702

HRMS (NSI): *m/z* 296.1677 [$(M-H)^+$ requires 296.1679], Calcd for $C_{16}H_{26}NO_2S$

HPLC: 74% ee, Chiralcel OD column, 1% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, t_r: 49.6 min (major), 41.6 min (minor)



(*R*,*E*)-*N*-(4,6-dimethyl-2-phenylhept-4-en-1-yl)methanesulfonamide (7b)

Prepared by General Procedure 1.3.1 with **1** (224 mg, 1.0 mmol, 1.0 equiv), *trans*-2,4-dimethyl-2-pentene (393 mg, 4.0 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1 mol %), and $CHCl_3$ (2 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3; R_f 0.30) afforded a tan oil containing a 1.5:1 mixture of **7a** and the title compound, respectively (154 mg, 52% combined yield). Further purification for characterization purposes were performed by additional flash chromatography (SiO_2; hexanes/EtOAc, 7:3): The leading fractions contained **7a** while the tail fractions contained an inseparable mix of the regioisomers (in all cases the R_f values were identical).

$[\alpha]^{20}_D$ -12.2° (*c* 0.5, $CHCl_3$)

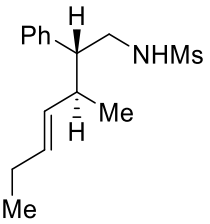
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.14 (m, 10H), 5.11 (s, 1H), 4.92 – 4.86 (d, *J* = 8.9 Hz, 1H), 4.24 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.99 (dd, *J* = 8.6, 3.7 Hz, 1H), 3.65 (ddd, *J* = 12.4, 8.3, 3.9 Hz, 1H), 3.52 – 3.47 (dd, *J* = 12.0, 3.8 Hz, 2H) 3.46 – 3.37 (m, 1H), 3.20 (ddd, *J* = 12.8, 9.3, 4.9 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.85 (dd, *J* = 11.7, 3.9 Hz, 1H), 2.77 – 2.75 (m, 4H), 2.72 (s, 3H), 2.46 – 2.28 (m, 2H), 2.23 (dd, *J* = 13.5, 7.6 Hz, 1H), 1.73 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.04 (d, *J* = 7.9 Hz, 6H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8, 138.8, 136.1, 132.3, 131.9, 129.9, 129.3, 128.9, 128.4, 128.0, 127.3, 127.2, 56.5, 48.2, 44.4, 44.3, 44.1, 40.2, 38.8, 28.7, 28.6, 27.2, 26.3, 23.1, 22.9, 19.2, 16.0

FTIR (neat): ν_{max}/cm^{-1} 3289, 2957, 1602, 1495, 1453, 1410, 1364, 1316, 1148, 1094, 1074, 969, 833, 758, 702

HRMS (NSI): *m/z* 296.1677 [$(M–H)^+$ requires 296.1679], Calcd for $C_{16}H_{26}NO_2S$

HPLC: 1° - 94% ee, Chiralcel OD column, 1% isopropanol/hexanes, 1.0 mL/min, UV: 230 nm, t_r: 100.3 min (major), 63.5 min (minor) 3° - See S7.



***N*-((2R,3S,E)-3-methyl-2-phenylhept-4-en-1-yl)methanesulfonamide (8 - major)**

Prepared by General Procedure 1.3.1 with **1** (224 mg, 1.0 mmol, 1.0 equiv), *trans*-3-heptene (336 mg, 4.0 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1 mol %), and $CHCl_3$ (2 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 6:4; R_f 0.32) afforded a tan oil containing a 7:3 diastereomeric ratio of the title compound and **8 - minor**, respectively (225 mg, 80% combined yield). Further purification for characterization purposes were performed by additional flash chromatography (SiO_2; hexanes/EtOAc, 6:4): The leading fractions contained the minor diastereomer, the tail fractions contained the major diastereomer, and the middle fractions contained a mix of the diastereomers (in all cases the Rf values were identical).

$[\alpha]^{20}_D$ -2.7° (*c* 0.5, $CHCl_3$)

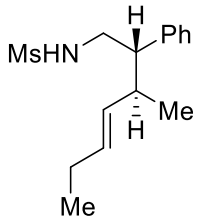
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 7.14 – 7.09 (m, 2H), 5.36 (dtd, *J* = 15.4, 6.4, 0.9 Hz, 1H), 5.11 (ddt, *J* = 15.3, 8.4, 1.5 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.52 (ddd, *J* = 12.6, 8.4, 5.1 Hz, 1H), 3.36 (ddd, *J* = 12.6, 10.3, 3.9 Hz, 1H), 2.82 (s, 3H), 2.78 – 2.71 (m, 1H), 2.44 (h, *J* = 6.8 Hz, 1H), 1.98 – 1.88 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 139.4, 133.0, 131.1, 129.1, 128.7, 127.3, 51.8, 46.2, 40.4, 40.0, 29.9, 25.7, 18.9, 14.0

FTIR (neat): ν_{max}/cm^{-1} 3291, 3028, 2961, 2927, 2872, 2853, 1454, 1411, 1374, 1320, 1079, 972, 847, 758, 703

HRMS (NSI): *m/z* 282.1522 [$(M–H)^+$ requires 282.1522], Calcd for $C_{15}H_{24}NO_2S$

HPLC: 97% ee, Chiralcel OD column, 1% isopropanol/hexanes for 80 minutes then 10% isopropanol/hexanes to flush out major enantiomer, 1 mL/min, UV: 230 nm, t_r: 71.2 min (minor), 133.3 min (major)



***N*-((2S,3S,E)-3-methyl-2-phenylhept-4-en-1-yl)methanesulfonamide (8 - minor)**

Prepared by General Procedure 1.3.1 with **1** (224 mg, 1.0 mmol, 1.0 equiv), *trans*-3-heptene (336 mg, 4.0 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1 mol %), and $CHCl_3$ (2 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 6:4; R_f 0.32) afforded a tan oil containing a 7:3 diastereomeric ratio of **8 - major** and the title compound, respectively (225 mg, 80% combined yield). Further purification for characterization purposes were performed by additional flash chromatography (SiO_2; hexanes/EtOAc, 6:4): The leading fractions contained the minor diastereomer, the tail fractions contained the major diastereomer, and the middle fractions contained a mix of the diastereomers (in all cases the Rf values were identical).

$[\alpha]^{20}_D$ -45.0° (*c* 0.5, $CHCl_3$)

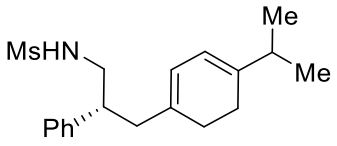
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 2H), 7.26 (tt, *J* = 6.6, 1.3 Hz, 1H), 7.19 – 7.14 (m, 2H), 5.56 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.30 (ddt, *J* = 15.3, 9.0, 1.5 Hz, 1H), 3.92 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.56 (ddd, *J* = 13.0, 8.7, 4.6 Hz, 1H), 3.20 – 3.12 (m, 1H), 2.72 (s, 3H), 2.53 (td, *J* = 10.2, 4.4 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.10 – 2.00 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.77 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.8, 133.3, 132.7, 129.1, 128.5, 127.4, 52.2, 47.6, 41.4, 40.2, 29.8, 25.7, 20.0, 14.0

FTIR (neat): ν_{max}/cm^{-1} 3286, 3027, 2966, 2923, 1494, 1453, 1430, 1330, 1319, 1087, 968, 849, 782, 766, 701

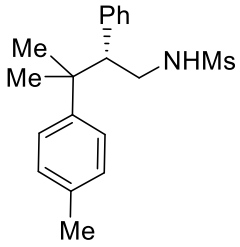
HRMS (NSI): *m/z* 282.1522 [$(M–H)^+$ requires 282.1522], Calcd for $C_{15}H_{24}NO_2S$

HPLC: 89% ee, Chiralcel OD column, 1% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_r: 59.8 min (major), 51.5 min (minor)



***R*-*N*-(3-(4-isopropylcyclohexa-1,3-dien-1-yl)-2-phenylpropyl)methanesulfonamide (9)**
Prepared by General Procedure 1.3.1 with **1** (67 mg, 0.3 mmol, 1.0 equiv), α-terpinene (168 mg, 1.2 mmol, 4.0 equiv), {Rh_2(*S*-NTTL)$_4$} (4.3 mg, 0.003 mmol, 1 mol %), and $CHCl_3$ (0.6 mL) at rt for 18 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 1.2 mL THF then reduced with 1 M $LiAlH_4$ in THF (0.36 mL, 0.36 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 6.75:3.25; R_f 0.25) afforded the title compound as a tan oil (52 mg, 51% yield). Upon separation a mix of insertion products were acquired in such minor yields that further characterization was unable to be performed (3 mg, < 3% combined yield of minor products).

$[\alpha]^{20}_D$ +3.3° (*c* 0.5, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.30 (m, 2H), 7.27-7.18 (m, 3H), 5.62 (d, *J* = 5.42 Hz, 1H), 5.55 (d, *J* = 5.42 Hz, 1H), 4.12 (t, *J* = 6.5 Hz, 1H), 3.48-3.42 (m, 1H), 3.24-3.17 (m, 1H), 3.01 (m, 1H), 2.74 (s, 3H), 2.48-2.36 (m, 2H), 2.31-2.21 (m, 1H), 2.10-1.95 (m, 4H), 1.00 (d, *J* = 7 Hz, 6H)
^{13}C MR (125 MHz, $CDCl_3$): δ 144.2, 141.8, 133.4, 129.0, 127.9, 127.3, 122.1, 116.3, 48.3, 47.8, 44.5, 41.6, 40.3, 34.6, 27.4, 25.5, 24.1, 21.2
FTIR (neat): ν_{max}/cm^{-1} 3288, 3028, 2959, 2928, 2870, 1653, 1603,1495, 1454, 1432, 1316, 1234, 1147, 1077, 970, 909, 831, 759, 730, 700
HRMS (NSI): *m/z* 334.1833 [$(M-H)^+$ requires 334.1835], Calcd for $C_{19}H_{28}NO_2S$
HPLC: 96% ee, Chiralcel OD column, 2% isopropanol/hexanes, 1 mL/min, UV: 254 nm, t_r: 66.9 min (major), 48.0 min (minor)



(*S*)-*N*-(3-methyl-2-phenyl-3-(p-tolyl)butyl)methanesulfonamide (11a)

Prepared by General Procedure 1.3.1 using with **1** (223 mg, 1.00 mmol), *p*-cymene (626 µL, 4.00 mmol), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and 1,2-DCE (2.0 mL) at room temperature for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer (1.27 cm) of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Crude ^{1}H NMR revealed a 4:1 regioselective ratio for tertiary over primary insertion. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3, R_f 0.31) afforded the title compound as a clear oil (157 mg, 47%). Combined yield with the primary C–H insertion product (249 mg, 75%).

$[\alpha]^{20}_D$ +1.8° (*c* 1.0, $CHCl_3$)

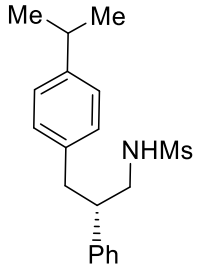
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 3H), 7.28 – 7.25 (m, 2H), 7.15 – 7.11 (m, 2H), 7.08 – 7.05 (m, 2H), 3.71 (br d, J = 4.9 Hz, 1H), 3.35 (td, J = 12.2, 11.7, 3.6 Hz, 1H), 3.27 (ddd, J = 12.6, 8.3, 4.1 Hz, 1H), 3.05 (dd, J = 11.5, 4.1 Hz, 1H), 2.64 (s, 3H), 2.34 (s, 3H), 1.29 (s, 3H), 1.21 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 138.3, 135.9, 130.1, 129.1, 128.4, 127.6, 126.3, 57.5, 43.9, 40.4, 40.2, 29.3, 23.8, 21.0

FTIR (neat): ν_{max}/cm^{-1} 3287, 3027, 2968, 1513, 1453, 1407, 1315, 1146

HRMS (NSI) *m/z* 332.16774 [$(M+H)^+$ requires 332.16788], Calcd for $C_{19}H_{26}O_2NS$

HPLC: 74% ee, Chiralcel OD-H column, 3% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 25.9 min (minor), t_R: 30.9 min (major)



(*S*)-*N*-(3-(4-isopropylphenyl)-2-phenylpropyl)methanesulfonamide (11b)

Prepared by General Procedure 1.3.1 using with **1** (223 mg, 1.00 mmol), *p*-cymene (626 µL, 4.00 mmol), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and 1,2-DCE (2.0 mL) at room temperature for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer (1.27 cm) of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Crude ^{1}H NMR revealed a 4:1 regioselective ratio for tertiary over primary insertion. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3, R_f 0.27) afforded the title compound as a clear oil. Combined yield with the tertiary C–H insertion product (249 mg, 75%).

$[\alpha]^{20}_D$ +9.1° (*c* 0.4, $CHCl_3$)

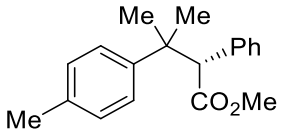
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H, coincidental with $CDCl_3$), 7.22 – 7.18 (m, 2H), 7.12 – 7.08 (m, 2H), 7.03 – 6.99 (m, 23.43 (ddd, *J* = 12.7, 7.7, 4.9 Hz, 1H), 3.35 – 3.25 (m, 1H), 3.14 – 3.05 (m, 2H), 3.00 – 2.81 (m, 3H), 2.71 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1, 141.4, 136.3, 129.1, 129.0, 128.0, 127.5, 126.7, 48.0, 47.8, 40.3, 39.9, 33.8, 24.1

FTIR (neat): ν_{max}/cm^{-1} 3288, 2959, 2929, 1514, 1453, 1410, 1316, 1148

HRMS (NSI) *m/z* 332.16773 [$(M+H)^+$ requires 332.16788], Calcd for $C_{19}H_{26}O_2NS$

HPLC: 95% ee, Chiralcel OD-H column, 5% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 26.3 min (minor), t_R: 46.4 min (major)



methyl (*S*)-3-methyl-2-phenyl-3-(*p*-tolyl)butanoate (13)

Prepared by General Procedure 1.3.2 with methyl phenyl diazoacetate (176.2 mg, 1.0 mmol, 1 equiv), *p*-cymene (536 mg, 4.0 mmol, 4.0 equiv), Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and 1,2-DCE (2.0 mL) at room temperature for 18 h. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/isopropanol, 9.5:0.5, R_f 0.20) afforded the title compound as a clear oil (144 mg, 51%).

$[\alpha]^{20}_D$ -20.3° (*c* 0.5, $CHCl_3$)

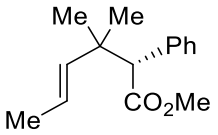
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.17 (m, 7H), 7.11 – 7.06 (m, 2H), 3.91 – 3.86 (m, 1H), 3.46 (d, J = 1.1 Hz, 3H), 2.37 – 2.29 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 144.3, 135.7, 130.2, 128.7, 127.8, 127.3, 126.4, 62.4, 51.5, 41.0, 26.7, 24.9, 21.1

FTIR (neat): ν_{max}/cm^{-1} 3089, 3060, 3027, 2971, 2949, 2877, 1733, 1599, 1582, 1515, 1495, 1454, 1480, 1432, 1409, 1362, 1326, 1267, 1198, 1163, 1138, 1115, 1095, 1079,1019, 815, 749, 701

HRMS (method NSI): *m/z* 283.16916 [$(M–H)^+$ requires 283.16926], Calcd for $C_{19}H_{23}O_2$

HPLC: 20% ee, Chiralcel ODR, 2.5% isopropanol/hexanes, 1 mL/min, UV: 254 nm, t_r: 4.09 min (major), 5.11 min (minor)



methyl (*R*,*E*)-3,3-dimethyl-2-phenylhex-4-enoate (14)

Prepared by General Procedure 1.3.2 with methyl phenyl diazoacetate (176.2 mg, 1.0 mmol, 1 equiv), *trans*-4-methyl-2-pentene (337 mg, 4.0 mmol, 4.0 equiv), Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and $CHCl_3$ (2.0 mL) at room temperature for 18 h. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3, R_f 0.70) afforded the title compound as a clear oil (96 mg, 41%).

$[\alpha]^{20}_D$ -3.0° (*c* 0.5, $CHCl_3$)

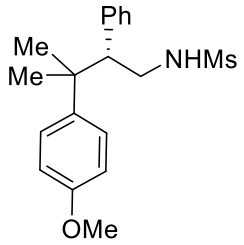
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.35 (m, 2H), 7.32 – 7.24 (m, 3H), 5.62 (dd, *J* = 15.9, 1.9 Hz, 1H), 5.28 (dq, *J* = 15.1, 6.2 Hz, 1H), 3.63 (d, *J* = 0.7 Hz, 3H), 3.50 (s, 1H), 1.67 (ddd, *J* = 6.4, 1.6, 0.6 Hz, 3H), 1.06 (d, *J* = 5.6 Hz, 6H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 138.0, 135.9, 130.2, 127.7, 127.3, 122.9, 61.5, 51.5, 39.5, 26.6, 24.5, 18.2

FTIR (neat): ν_{max}/cm^{-1} 3029, 2963, 1736, 1497, 1454, 1433, 1363, 1199, 1165, 1140, 1021, 974

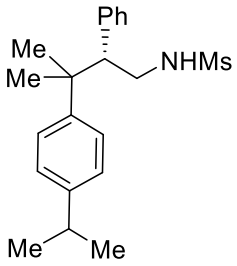
HRMS (NSI): *m/z* 233.15353 [$(M+H)^+$ requires 233.15361], Calcd for $C_{15}H_{21}O_2$

HPLC: 20% ee, Chiralcel OD column, 0.1% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm, t_r: 13.3 min (major), 39.3 min (minor)



(*S*)-*N*-(3-(4-methoxyphenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (15)
Prepared by General Procedure 1.3.1 using with **1** (223 mg, 1.00 mmol), 4-isopropylanisole (639 μL, 4.00 mmol), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and 1,2-DCE (2.0 mL) at room temperature for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer (1.27 cm) of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3, R_f 0.16) afforded the title compound as a colorless solid (154 mg, 44%).

$[\alpha]^{20}_D$ +3.0° (*c* 0.984, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 3H), 7.22 – 7.19 (m, 2H), 7.06 – 7.02 (m, 2H), 6.87 – 6.83 (m, 2H), 3.81 (s, 3H), 3.77 – 3.68 (br m, 1H), 3.38 – 3.26 (m, 2H), 3.02 (dd, *J* = 11.0, 4.6 Hz, 1H), 2.65 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H)
^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 139.2, 138.3, 130.0, 128.4, 127.5, 113.6, 57.6, 55.4, 43.9, 40.2, 40.1, 29.2, 24.2
FTIR (neat): ν_{max}/cm^{-1} 3286, 2965, 2836, 1609, 1512, 1453, 1409, 1316, 1250, 1146
HRMS (NSI) *m/z* 348.16279 [$(M+H)^+$ requires 348.16279], Calcd for $C_{19}H_{26}O_3NS$
HPLC: 77% ee, Chiralcel OD-H column, 3% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 50.6 min (minor), t_R: 55.5 min (major)



(*S*)-*N*-(3-(4-isopropylphenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (16)

Prepared by General Procedure 1.3.1 using with **1** (223 mg, 1.00 mmol), *p*-cymene (626 µL, 4.00 mmol), {Rh_2(*S*-NTTL)$_4$} (14.5 mg, 0.01 mmol, 1.00 mol %) and 1,2-DCE (2.0 mL) at room temperature for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer (1.27 cm) of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/*i*-Pr, 2:1, R_f 0.39) afforded the title compound as waxy and amorphous yellow solid over time (215 mg, 64%).

$[\alpha]^{20}_D$ +1.8° (*c* 1.005, $CHCl_3$)

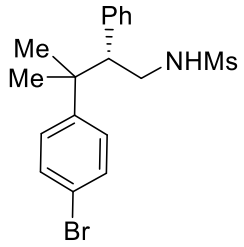
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 7.20 – 7.16 (m, 2H), 7.08 – 7.04 (m, 2H), 3.71 – 3.57 (br m, 1H), 3.36 (ddd, *J* = 12.6, 11.5, 3.8 Hz, 1H), 3.27 (ddd, *J* = 12.6, 8.3, 4.0 Hz, 1H), 3.04 (dd, *J* = 11.4, 4.0 Hz, 1H), 2.90 (sep, *J* = 6.9 Hz, 1H), 2.63 (s, 3H), 1.30 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.21 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 144.6, 138.4, 130.0, 128.4, 127.6, 126.4, 126.4, 57.6, 43.9, 40.4, 40.1, 33.7, 29.3, 24.1, 23.7

FTIR (neat): ν_{max}/cm^{-1} 3261, 2959, 2869, 1510, 1441, 1388, 1145

HRMS (NSI) *m/z* 360.19921 [$(M+H)^+$ requires 360.19918], Calcd for $C_{21}H_{30}O_2NS$

HPLC: 66% ee, Chiralcel OD-R column, 5% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 11.8 min (minor), t_R: 14.6 min (major)



(*S*)-*N*-(3-(4-bromophenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (17)

Prepared by General Procedure 1.3.1 with **1** (223 mg, 1.0 mmol, 1.0 equiv), 1-bromo-4-isopropylbenzene (796 mg, 0.61 mL, 4.0 mmol, 4.0 equiv), Rh_2(*S*-NTTL)$_4$ (14.5 mg, 0.01 mmol, 0.01 equiv), and 1,2-DCE (2 mL) at rt for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3; R_f 0.25) afforded the title compound as an amorphous white solid (160 mg, 40% yield).

$[\alpha]^{20}_D$ +8.1° (*c* 0.4, $CHCl_3$)

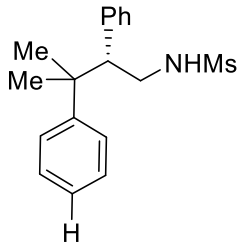
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 2H), 7.30 – 7.24 (m, 3H), 7.17 – 7.13 (m, 2H), 7.04 – 7.00 (m, 2H), 3.87 – 3.68 (br m, 1H), 3.39 – 3.25 (m, 2H), 3.04 (dd, *J* = 11.5, 4.5 Hz, 1H), 2.66 (s, 3H), 1.30 (s, 3H), 1.22 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 137.7, 131.3, 130.0, 128.5, 128.4, 127.7, 120.4, 57.2, 43.6, 40.6, 40.4, 28.7, 24.3

FTIR (neat): ν_{max}/cm^{-1} 3286, 2969, 1492, 1453, 1396, 1317, 1147

HRMS (NSI) *m/z* 396.06294 [$(M+H)^+$ requires 396.06274], Calcd for $C_{18}H_{23}O_2NBrS$

HPLC: 82% ee, Chiralcel OD-H column, 5% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 24.4 min (minor), t_R: 38.8 min (major)



(*S*)-*N*-(3-methyl-2,3-diphenylbutyl)methanesulfonamide (18a)

Prepared by General Procedure 1.3.1 with **1** (223 mg, 1.0 mmol, 1.0 equiv), cumene (481 mg, 0.56 mL, 4.0 mmol, 4.0 equiv), Rh_2(*S*-NTTL)$_4$ (14.5 mg, 0.01 mmol, 0.01 equiv), and 1,2-DCE (2 mL) at rt for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3) afforded the title compound **18a** (R_f 0.23) as a clear oil (77 mg, 24% yield) and **18b** (R_f 0.58) as a crystalline solid (31 mg, 10%).

$[\alpha]^{20}_D$ +6.3° (*c* 0.65, $CHCl_3$)

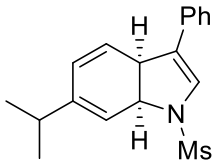
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.21 (m, 8H), 7.08 – 7.04 (m, 2H), 3.76 (br dd, *J* = 7.9, 3.3 Hz, 1H), 3.37 (td, *J* = 12.2, 3.8 Hz, 1H), 3.26 (ddd, *J* = 12.4, 8.3, 3.9 Hz, 1H), 3.07 (dd, *J* = 11.6, 3.9 Hz, 1H) 2.62 (s, 3H), 1.33 (s, 3H), 1.23 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.4, 138.2, 130.0, 128.38, 128.36, 127.6, 126.43, 126.41, 57.5, 43.8, 40.7, 40.1, 29.0, 23.8

FTIR (neat): ν_{max}/cm^{-1} 3286, 2967, 1601, 1496, 1408, 1315, 1145

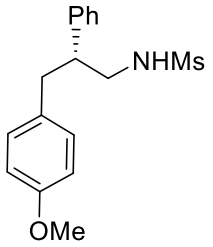
HRMS (NSI) *m/z* 318.15194 [$(M+H)^+$ requires 318.15223], Calcd for $C_{18}H_{24}O_2NS$

HPLC: 72% ee, Chiralcel OD-H column, 2% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 50.4 min (minor), t_R: 58.2 min (major)



(3a*S*,7a*S*)-6-isopropyl-1-(methylsulfonyl)-3-phenyl-3a,7a-dihydro-1H-indole (18b)
See procedure for **18a**.

[α]$^{20}_{D}$ -142° (*c* 0.3, $CHCl_3$)
^{1}H NMR (500 MHz, $CDCl_3$): *δ* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 4H), 7.26 – 7.23 (m, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 5.97 – 5.84 (m, 1H), 5.76 (dd, *J* = 7.3, 2.1 Hz, 2H), 4.88 (dd, *J* = 12.8, 5.2 Hz, 1H), 4.46 – 4.16 (m, 1H), 2.93 (s, 3H), 2.37 (sep, *J* = 6.8 Hz, 1H), 1.08 (dd, *J* = 6.8, 3.3 Hz, 6H)
^{13}C NMR (125 MHz, $CDCl_3$): *δ* 144.3, 132.8, 129.0, 127.3, 126.1, 125.3, 124.9, 124.3, 123.9, 113.1, 59.6, 42.5, 39.0, 33.7, 21.3, 21.0
FTIR (neat): ν_{max}/cm^{-1} 2961, 2929, 1629, 1447, 1342, 1152
HRMS (NSI) *m/z* 316.13646 [$(M+H)^+$ requires 316.13658], Calcd for $C_{18}H_{22}O_2NS$
HPLC: 92% ee, Chiralcel *SS*-Whelk column, 7.5% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 20.3 min (major), t_R: 24.2 min (minor)



(*R*)-*N*-(3-(4-methoxyphenyl)-2-phenylpropyl)methanesulfonamide (20)

Prepared by General Procedure 1.3.1 with **1** (223 mg, 1.0 mmol, 1.0 equiv), 4-methylanisole (489 mg, 0.50 mL, 4.0 mmol, 4.0 equiv), Rh_2(*S*-NTTL)$_4$ (14.5 mg, 0.01 mmol, 0.01 equiv), and 1,2-DCE (2 mL) at rt for 24 h. Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with 1 M $LiAlH_4$ in THF (1.2 mL, 1.2 mmol, 1.2 equiv) at 0 °C for 1 h. The reaction mixture was quenched by slow addition of $Na_2SO_4 \cdot 10H_2O$ until bubbling stopped followed by 15 additional min at 0 °C. The crude brown product was obtained via vacuum filtration over a thin layer of Celite® packed atop a 60 mL medium porosity fritted funnel using DCM (50 mL) as eluent. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 7:3; R_f 0.26) afforded the title compound as a tan oil (118 mg, 37% yield).

$[\alpha]^{20}_D$ +19.4° (*c* 0.40, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 2H), 7.29 – 7.25 (m, 1H, coincidental with $CDCl_3$), 7.20 – 7.17 (m, 2H) 7.01 – 6.97 (m, 2H), 6.81 – 6.77 (m, 2H), 4.06 – 3.90 (br m, 1H), 3.78 (s, 3H), 3.49 – 3.41 (m, 1H), 3.32 (ddd, *J* = 12.8, 9.3, 4.8 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.91 (d, *J* = 7.5 Hz, 2H), 2.76 (s, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 141.2, 131.0, 130.1, 129.1, 128.0, 127.5, 114.0, 55.4, 48.3, 47.8, 40.4, 39.5

FTIR (neat): ν_{max}/cm^{-1} 3286, 2928, 1611, 1511, 1316, 1244, 1146

HRMS (NSI) *m/z* 320.13159 [$(M+H)^+$ requires 320.13149], Calcd for $C_{17}H_{22}O_3NS$

HPLC: 93%, Chiralcel AD-H column, 8% isopropanol/hexanes, 1 mL/min, UV: 210 nm, t_R: 18.1 min (minor), t_R:19.7 min (major)

3. References

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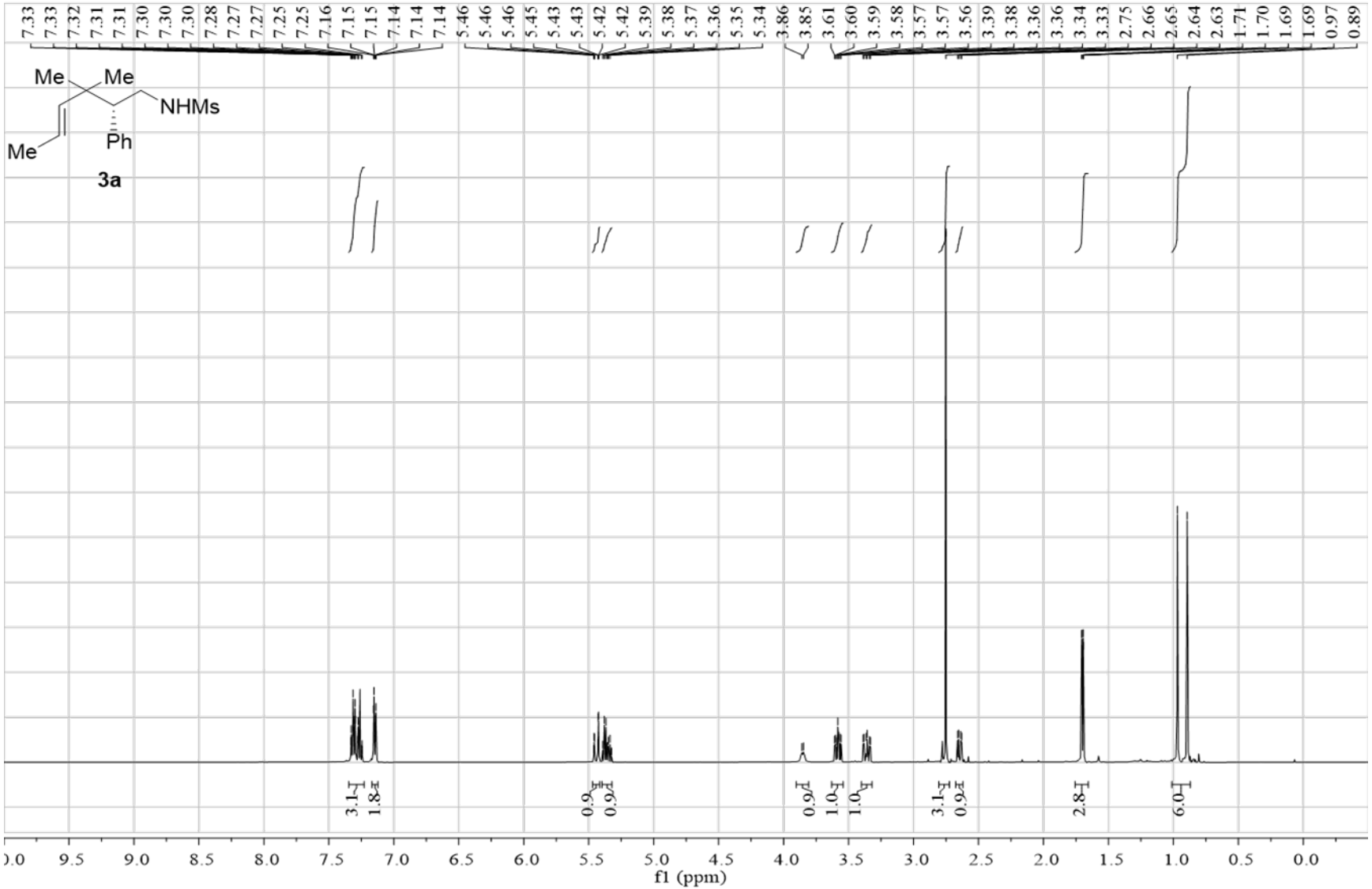
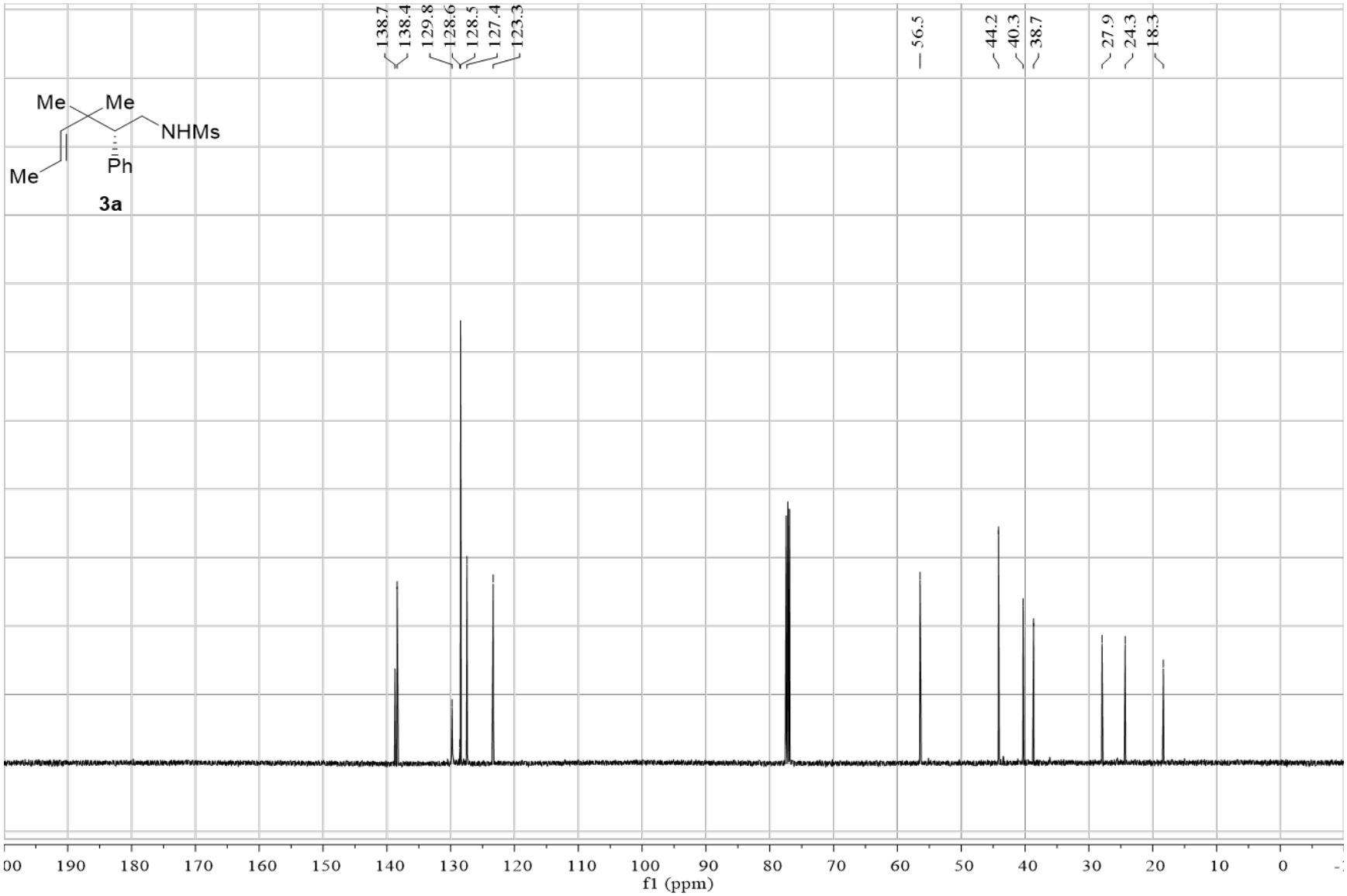
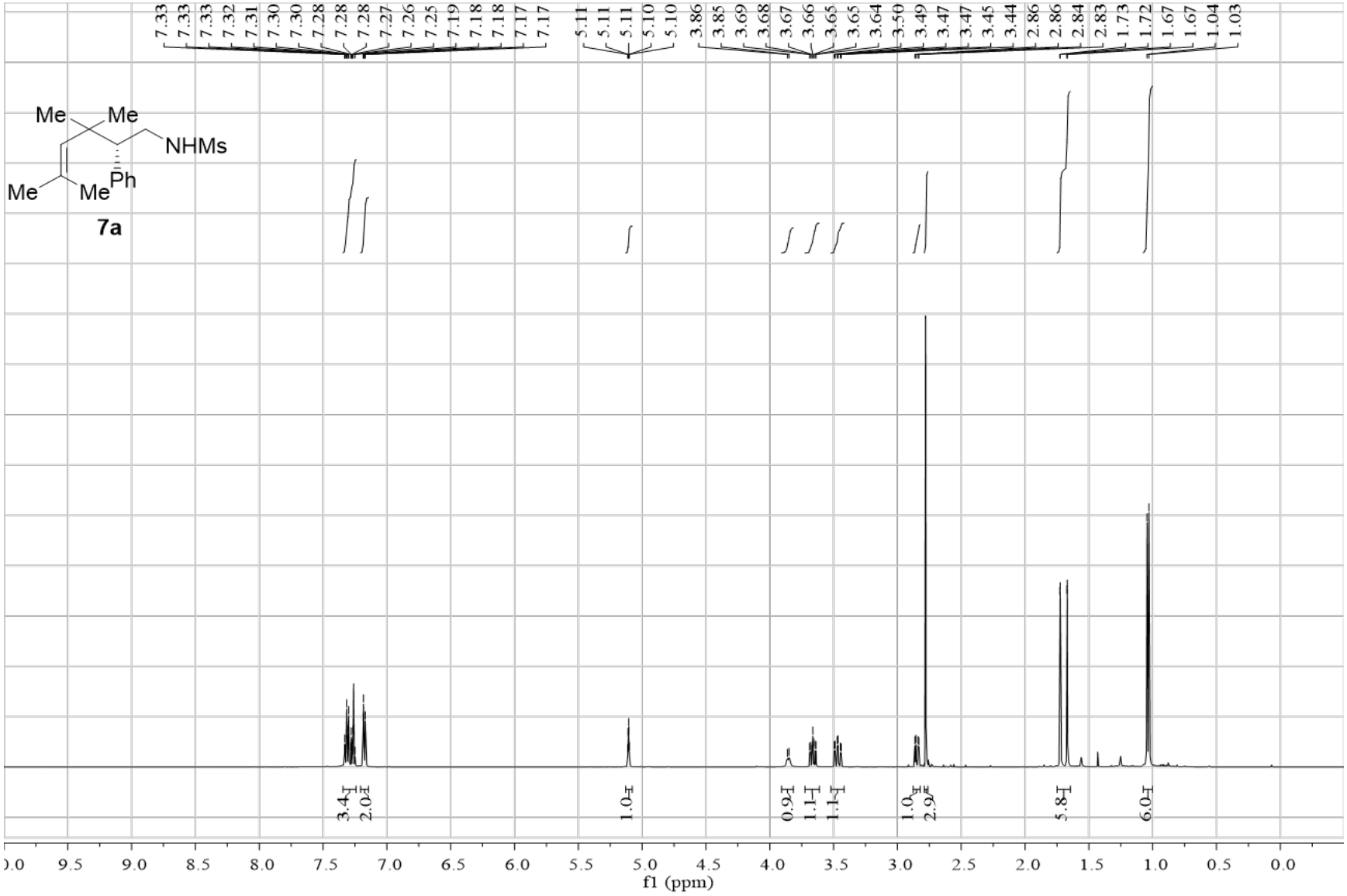
4. NMR Data for New Compounds



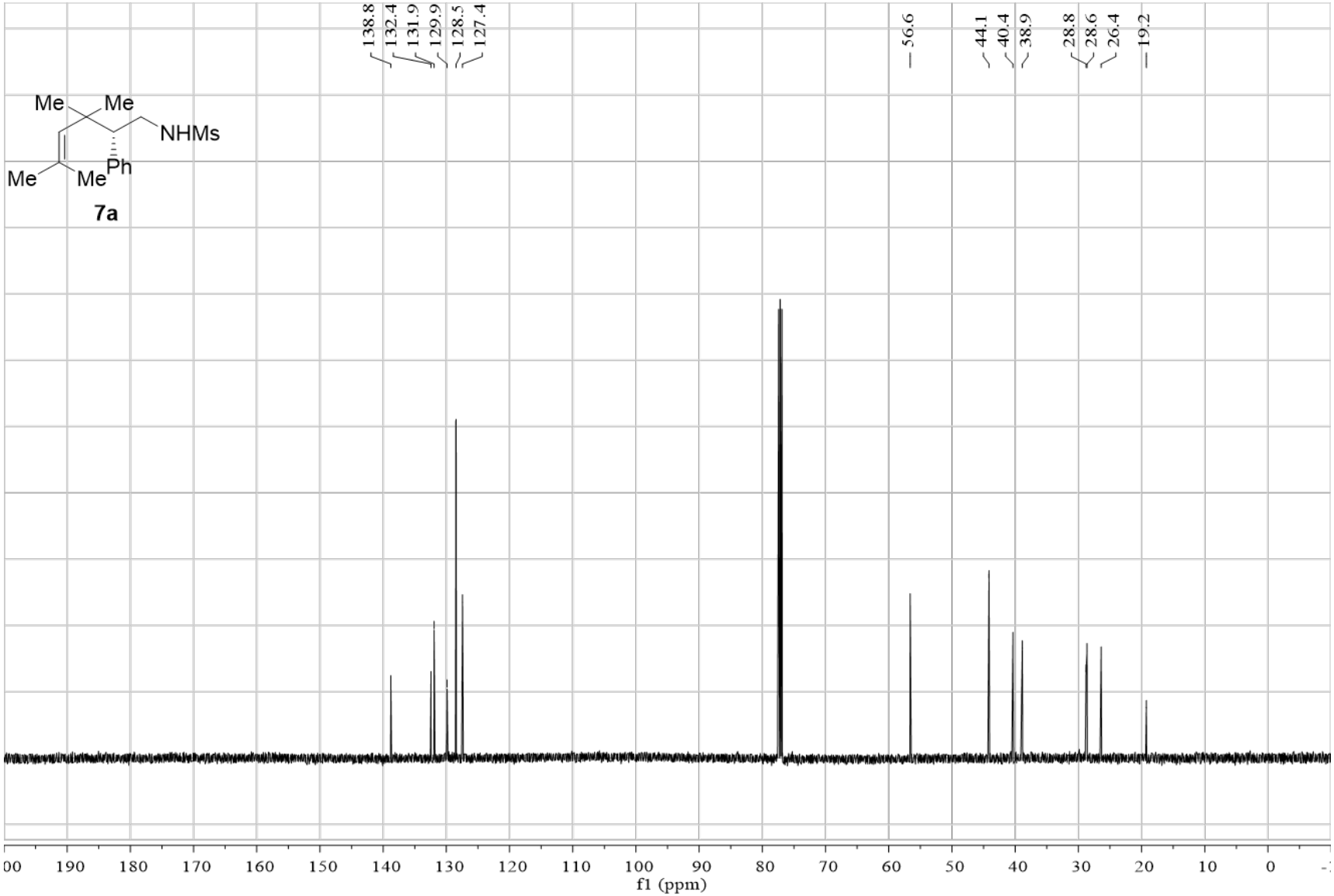
Supporting Information Figure 1. ^{1}H NMR Spectrum of **3a**, 500 MHz, $CDCl_3$



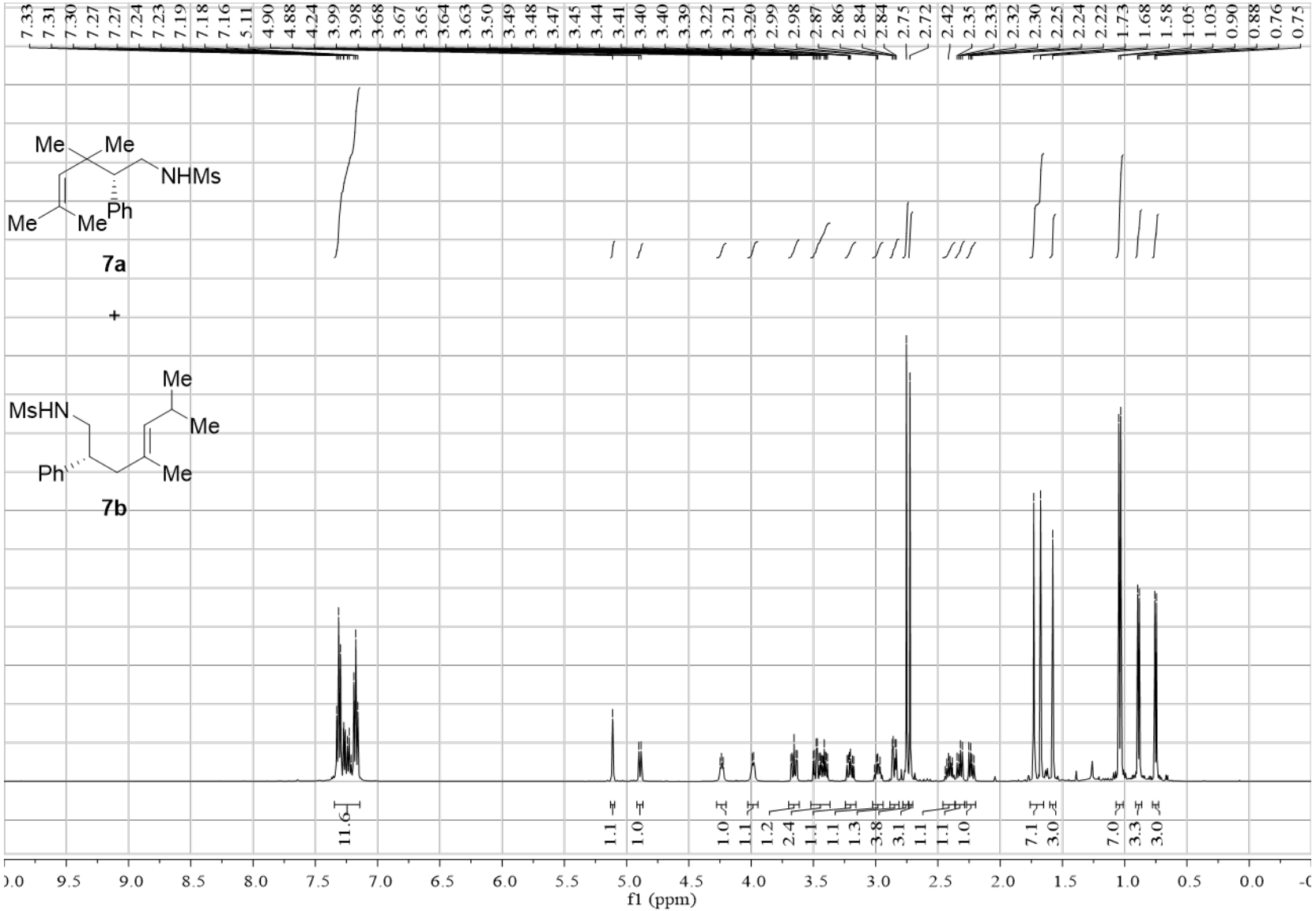
Supporting Information Figure 2. ^{13}C NMR Spectrum of **3a**, 125 MHz, $CDCl_3$



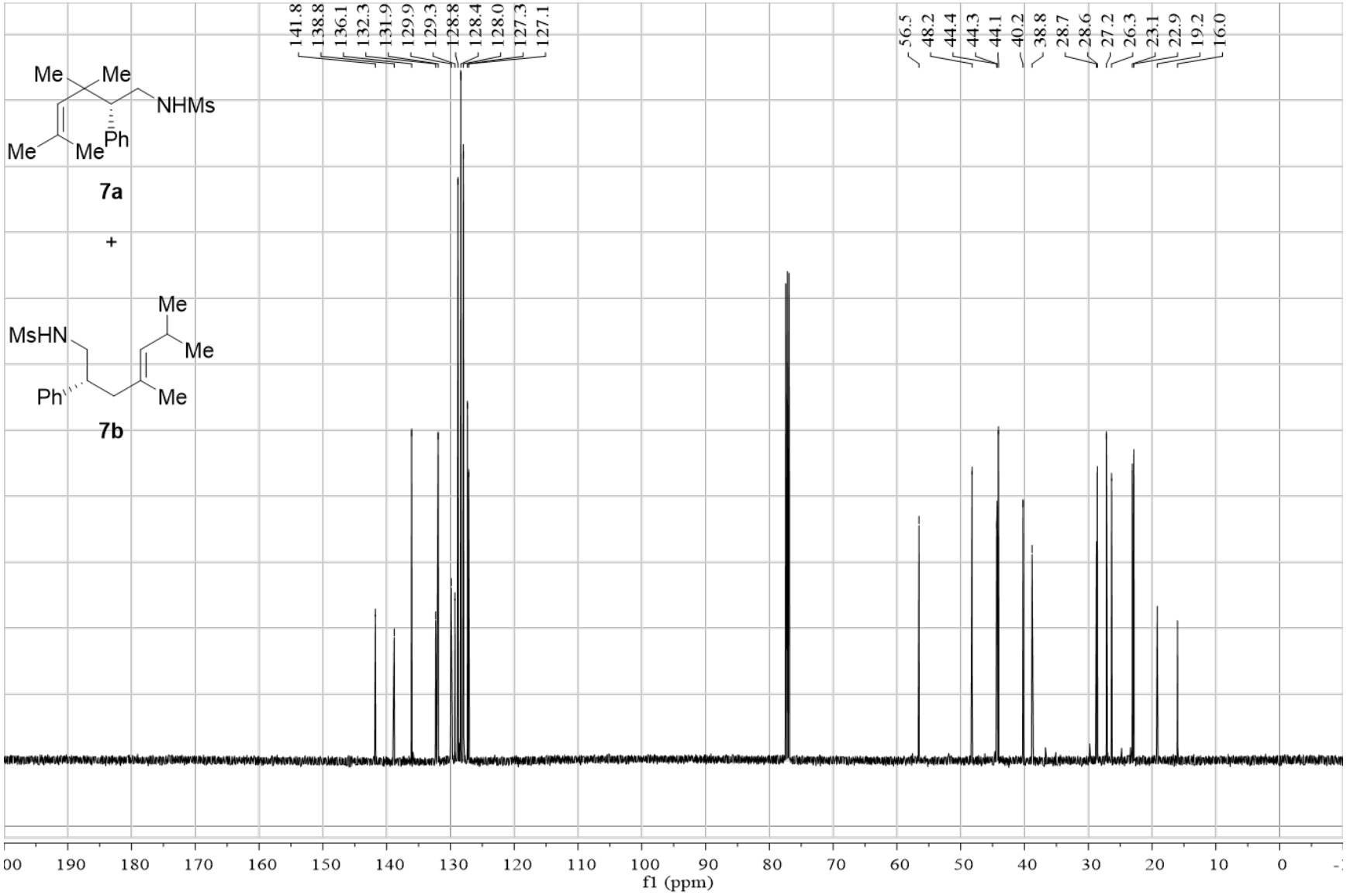
Supporting Information Figure 3. ^{1}H NMR Spectrum of **7a**, 500 MHz, $CDCl_3$



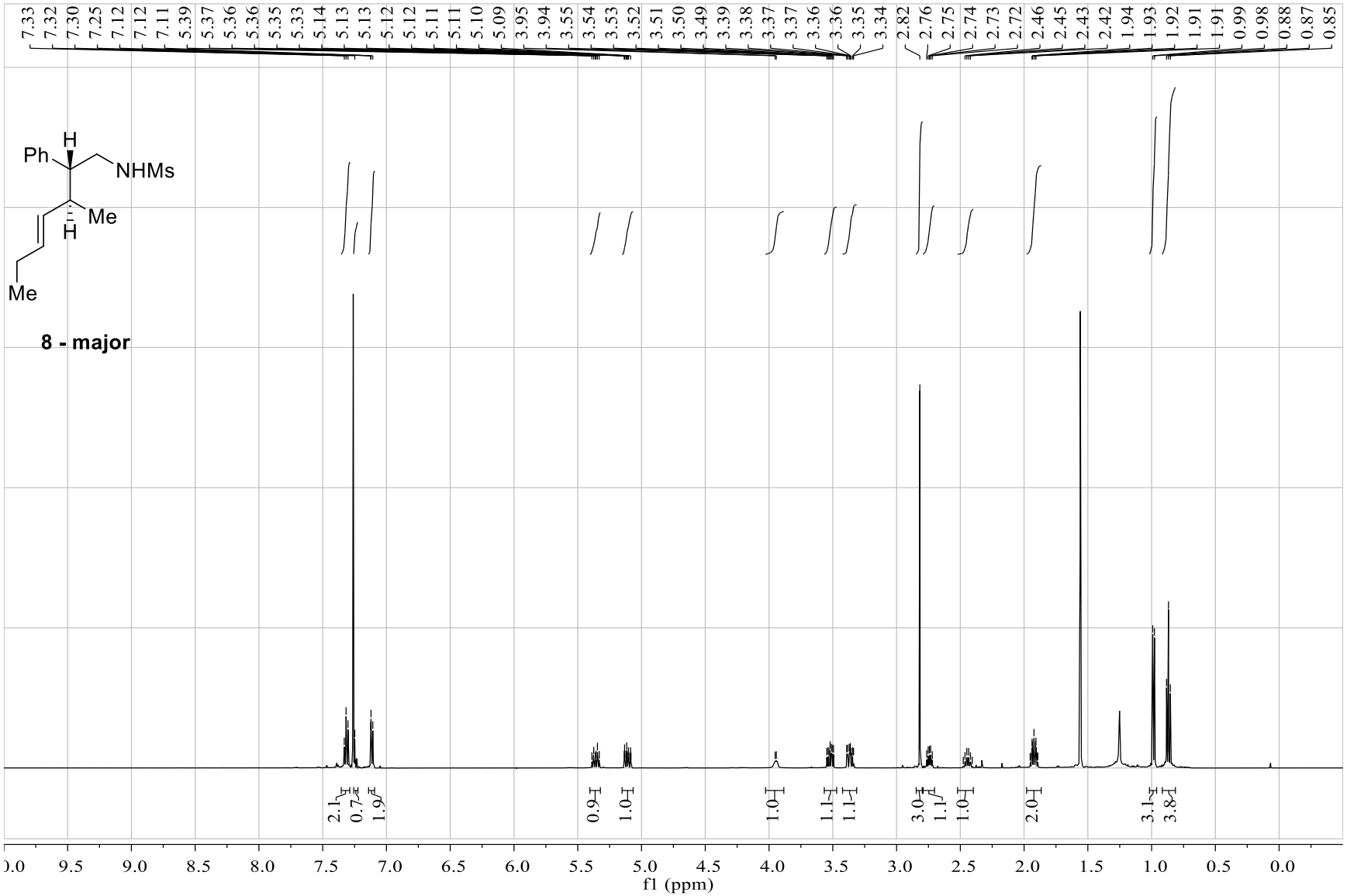
Supporting Information Figure 4. ^{13}C NMR Spectrum of **7a**, 125 MHz, $CDCl_3$



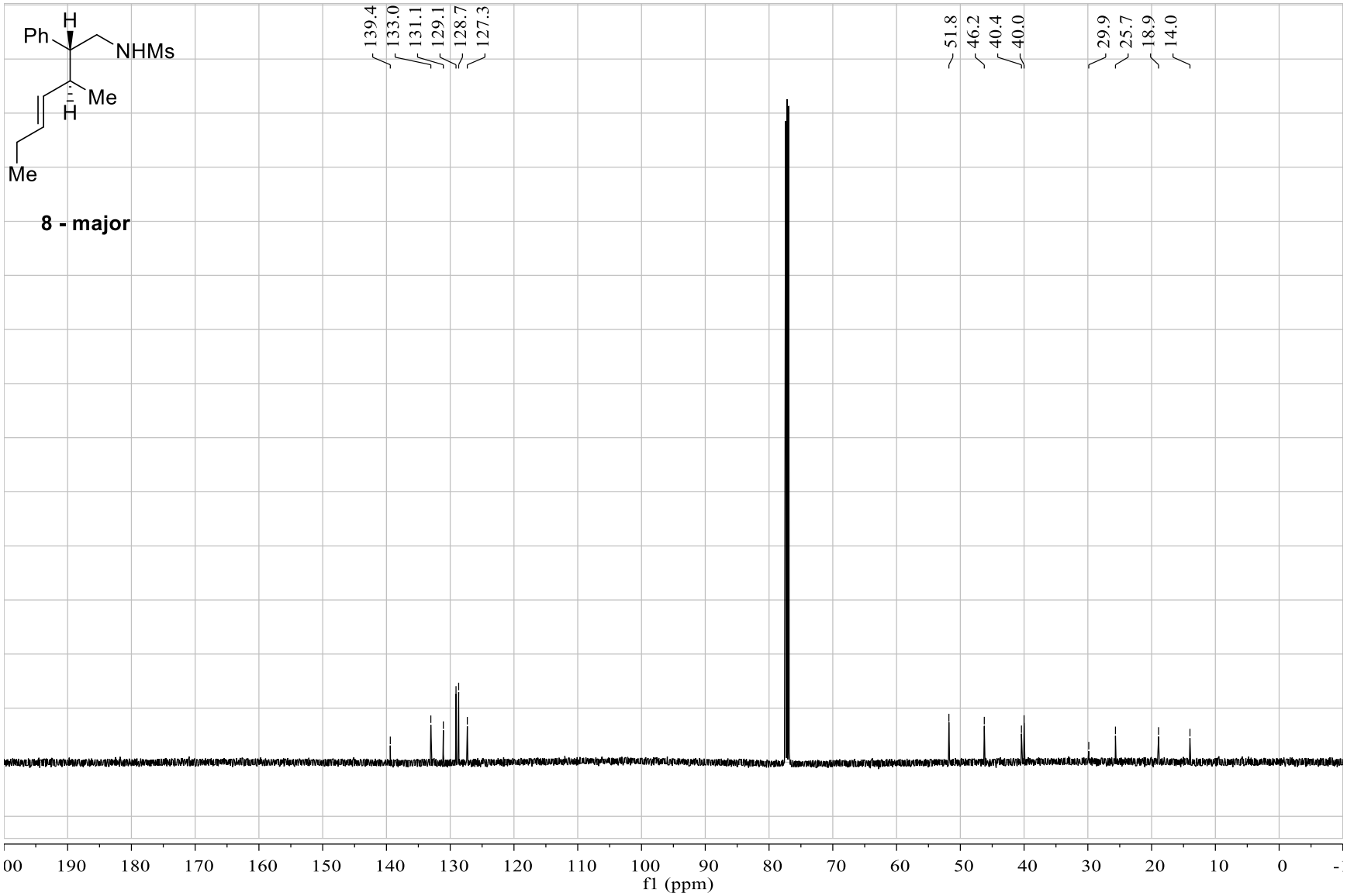
Supporting Information Figure 5. ^{1}H NMR Spectrum of **7a** and **7b** mix, 500 MHz, $CDCl_3$



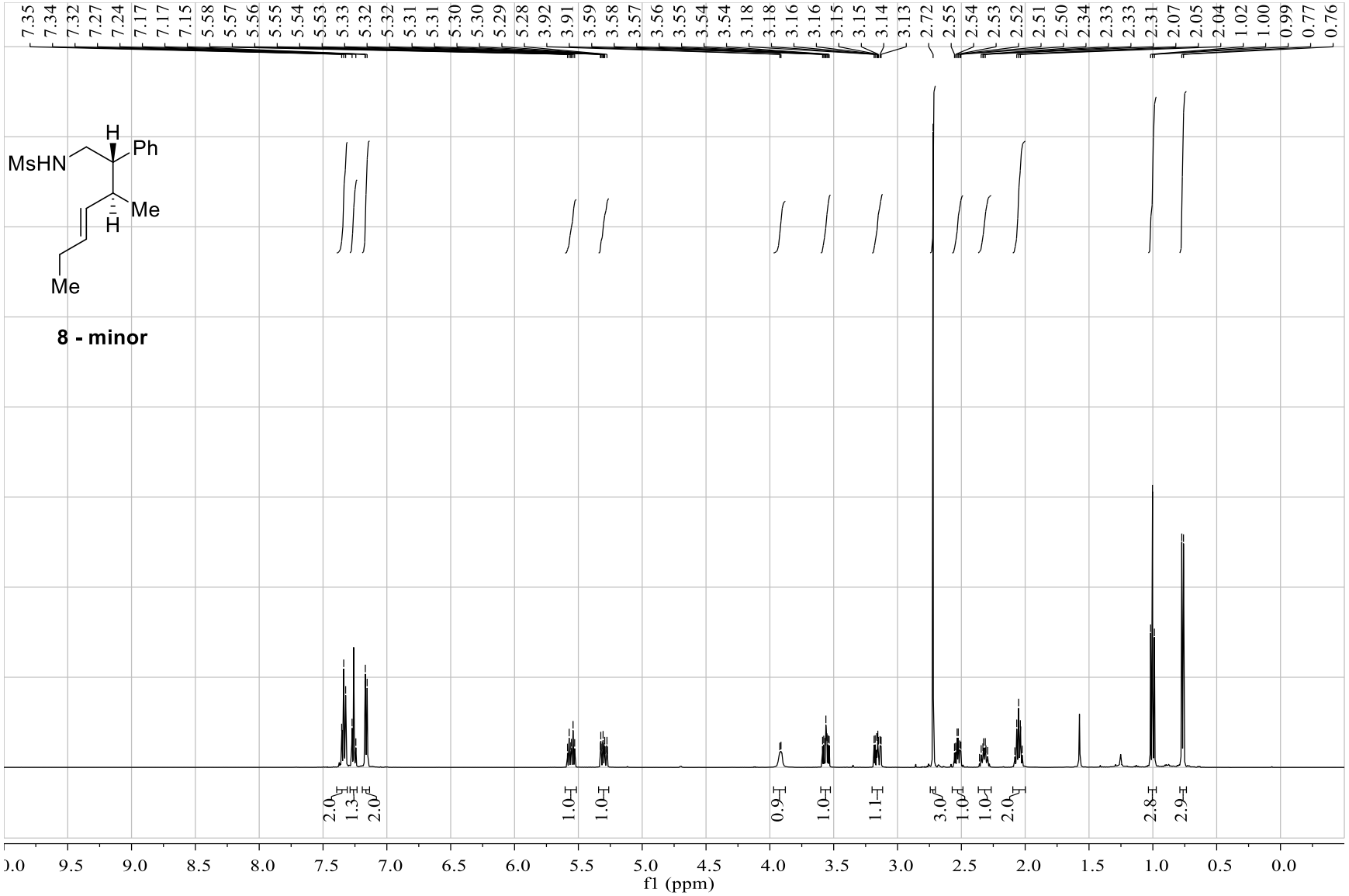
Supporting Information Figure 6. ^{13}C NMR Spectrum of **7a** and **7b** mix, 125 MHz, $CDCl_3$



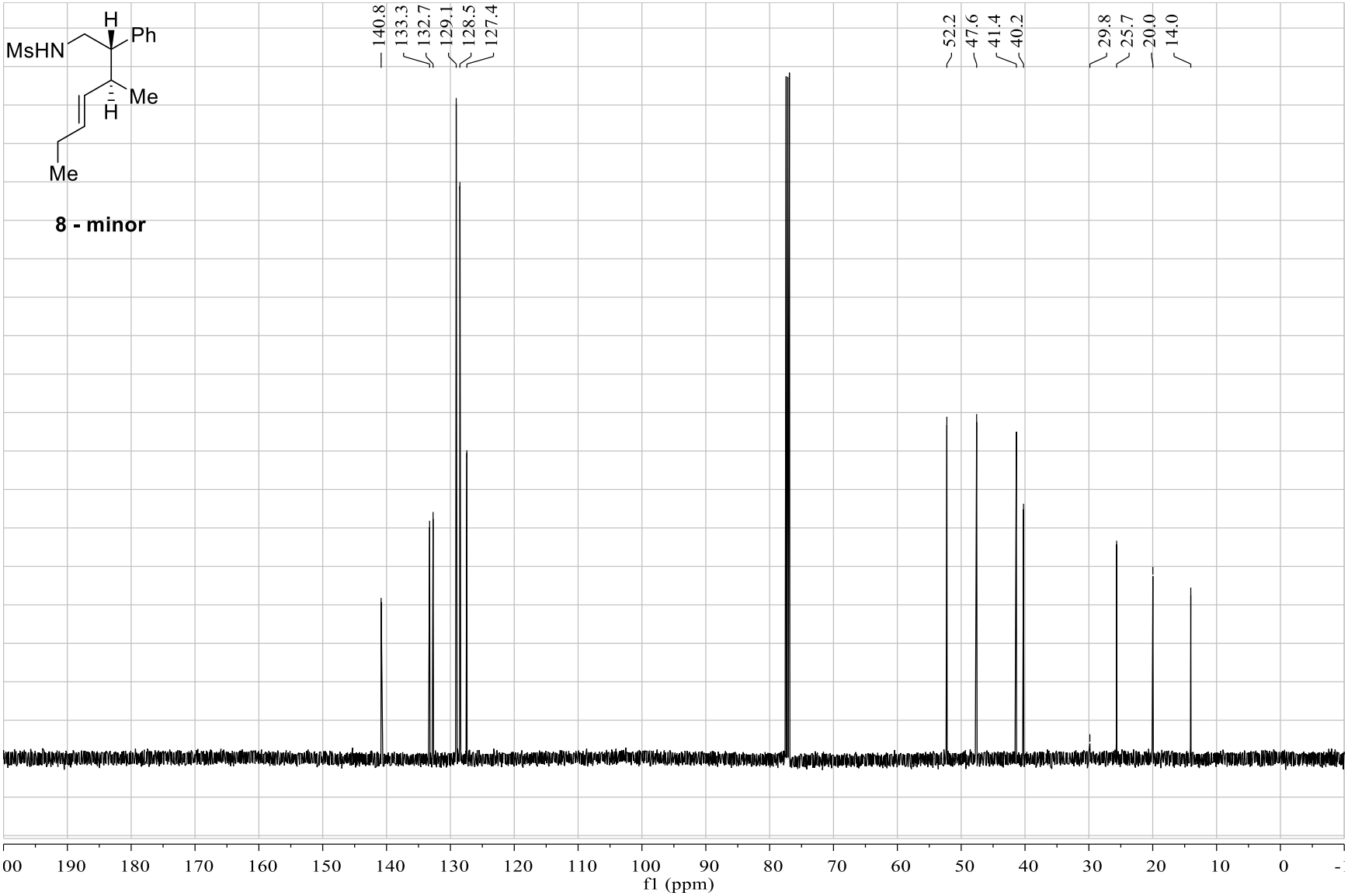
Supporting Information Figure 7. ^{1}H NMR Spectrum of Major Diastereomer of **8**, 500 MHz, $CDCl_3$



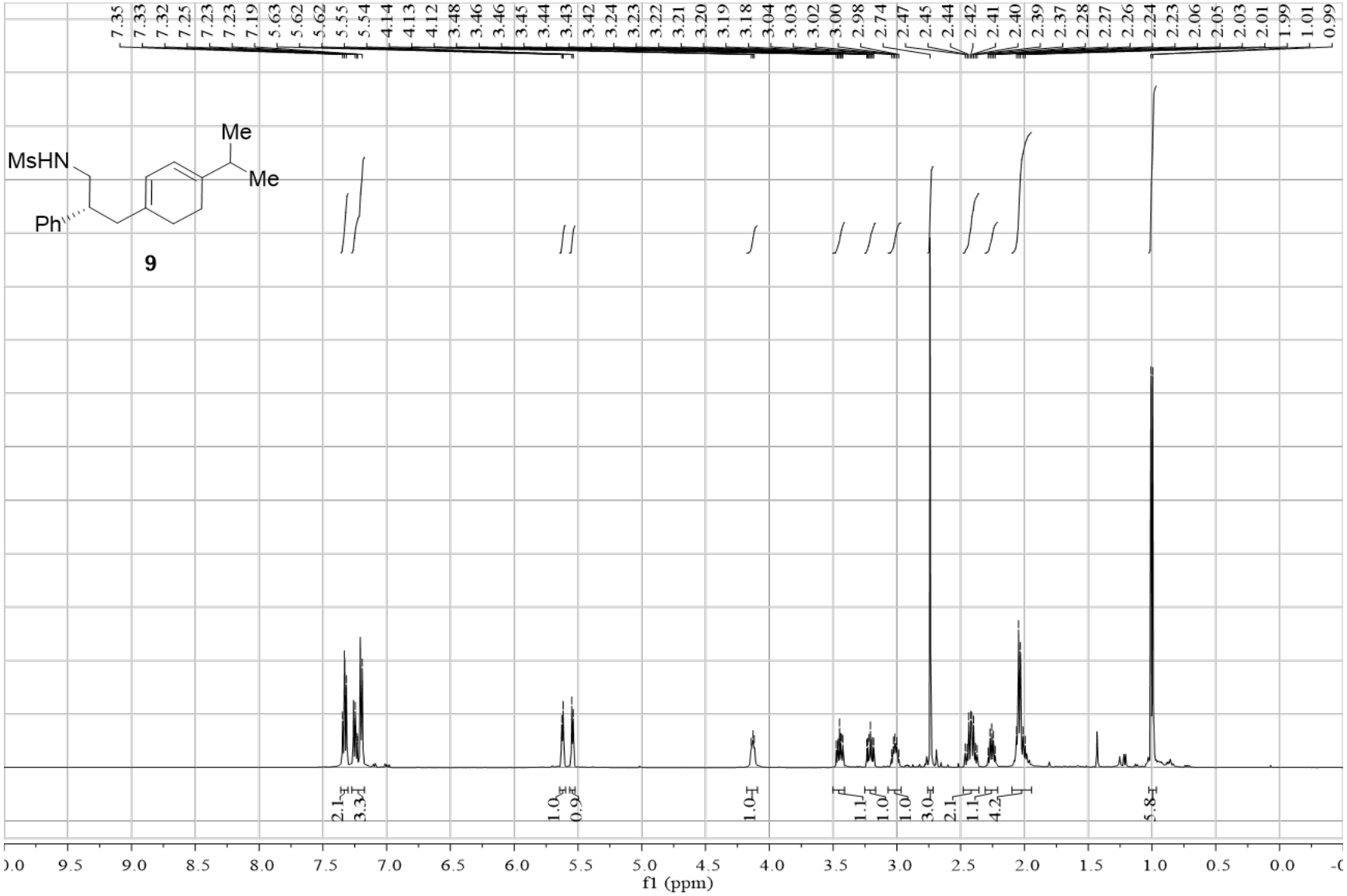
Supporting Information Figure 8. ^{13}C NMR Spectrum of Major Diastereomer of **8**, 125 MHz, $CDCl_3$



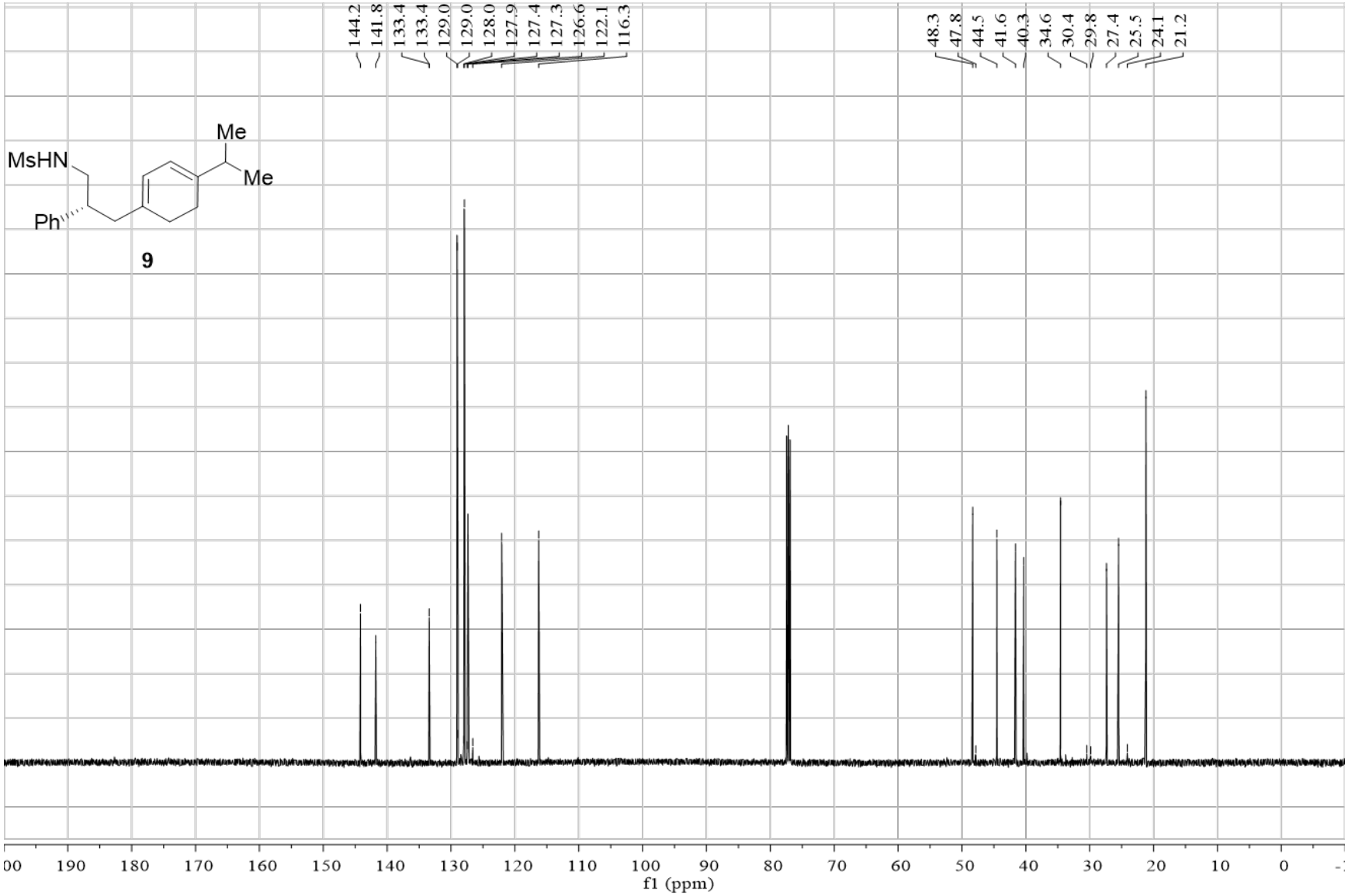
Supporting Information Figure 9. ^{1}H NMR Spectrum of Minor Diastereomer of **8**, 500 MHz, $CDCl_3$



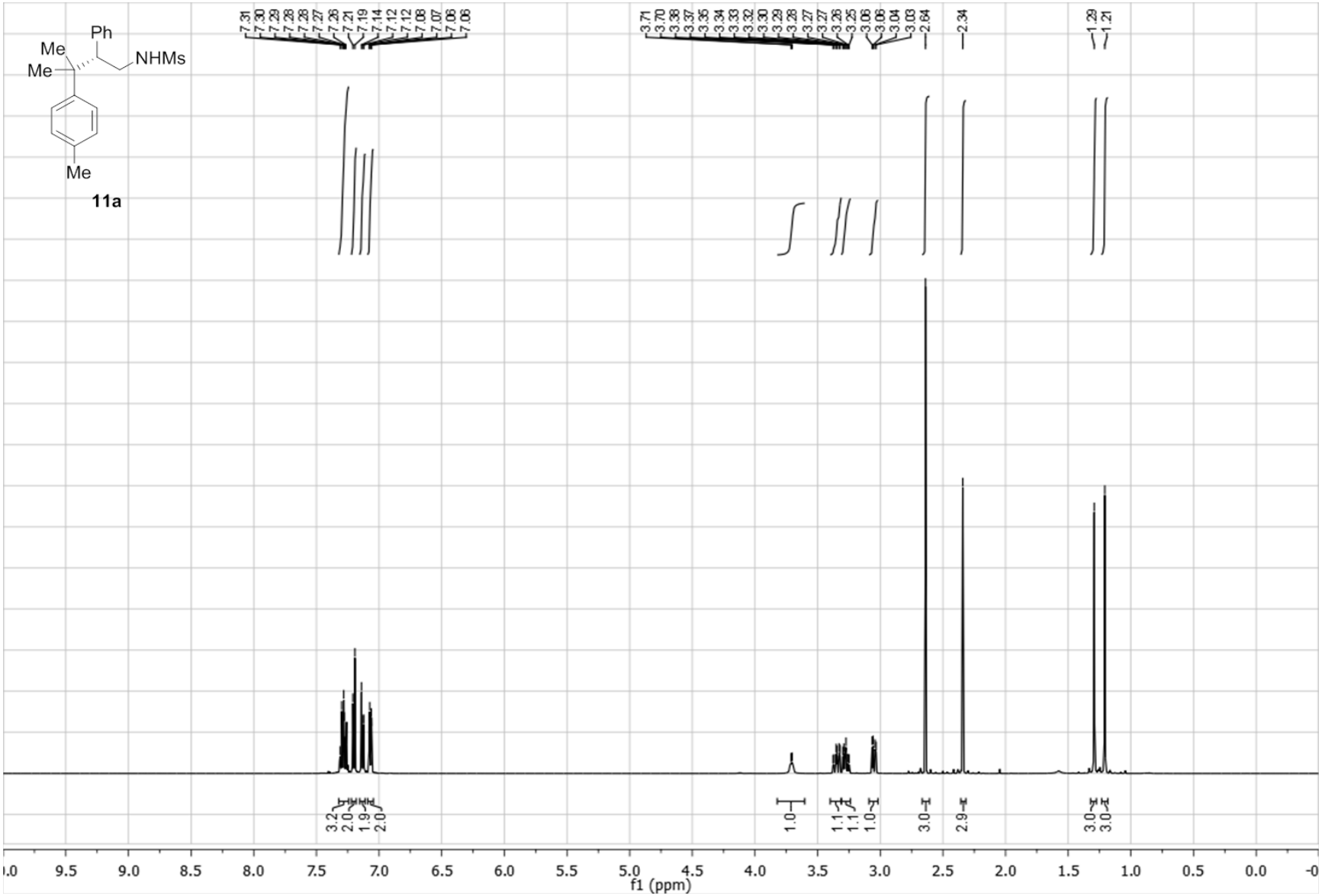
Supporting Information Figure 10. ^{13}C NMR Spectrum of Minor Diastereomer of **8**, 125 MHz, $CDCl_3$



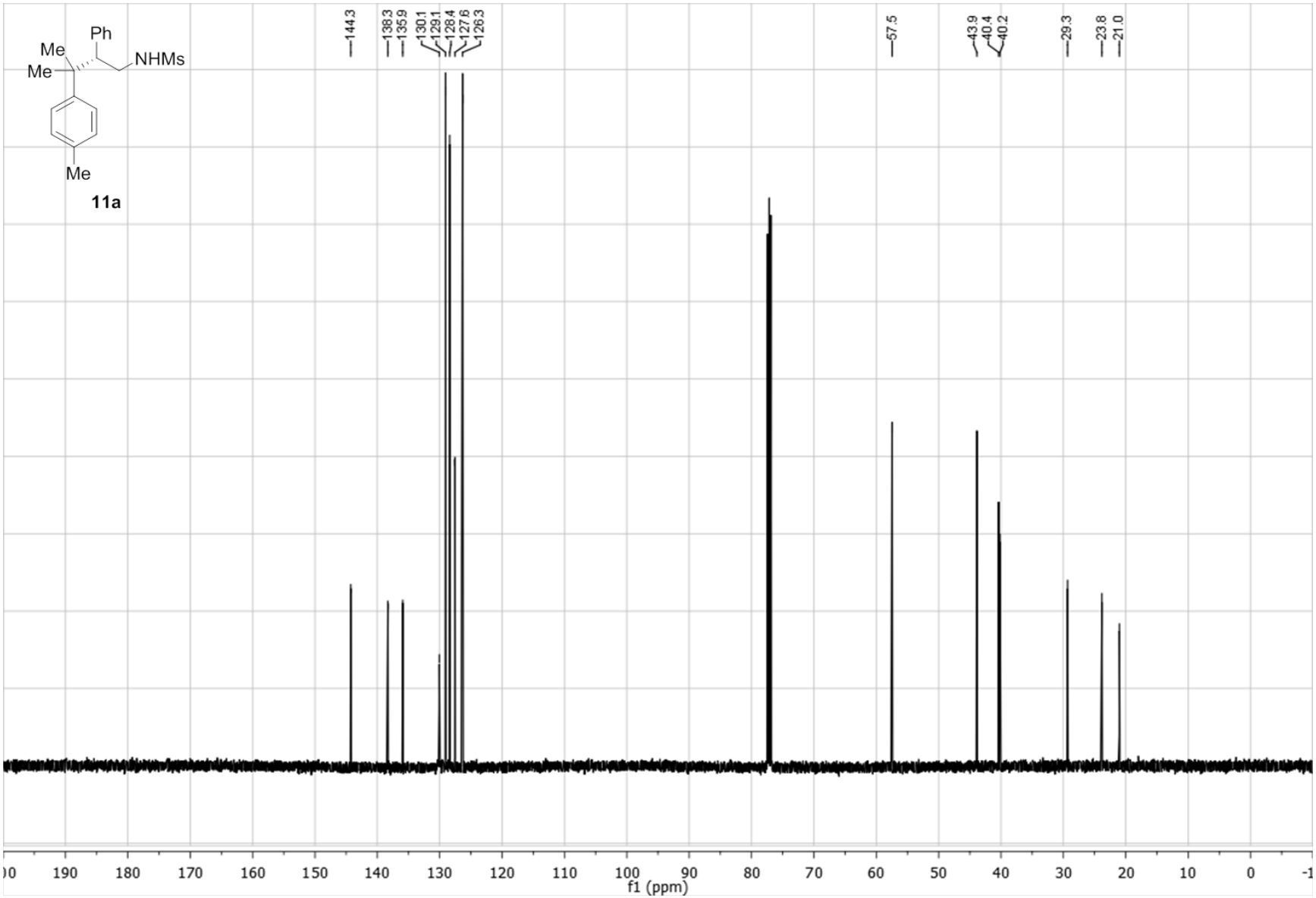
Supporting Information Figure 11. ^{1}H NMR Spectrum of **9**, 500 MHz, $CDCl_3$



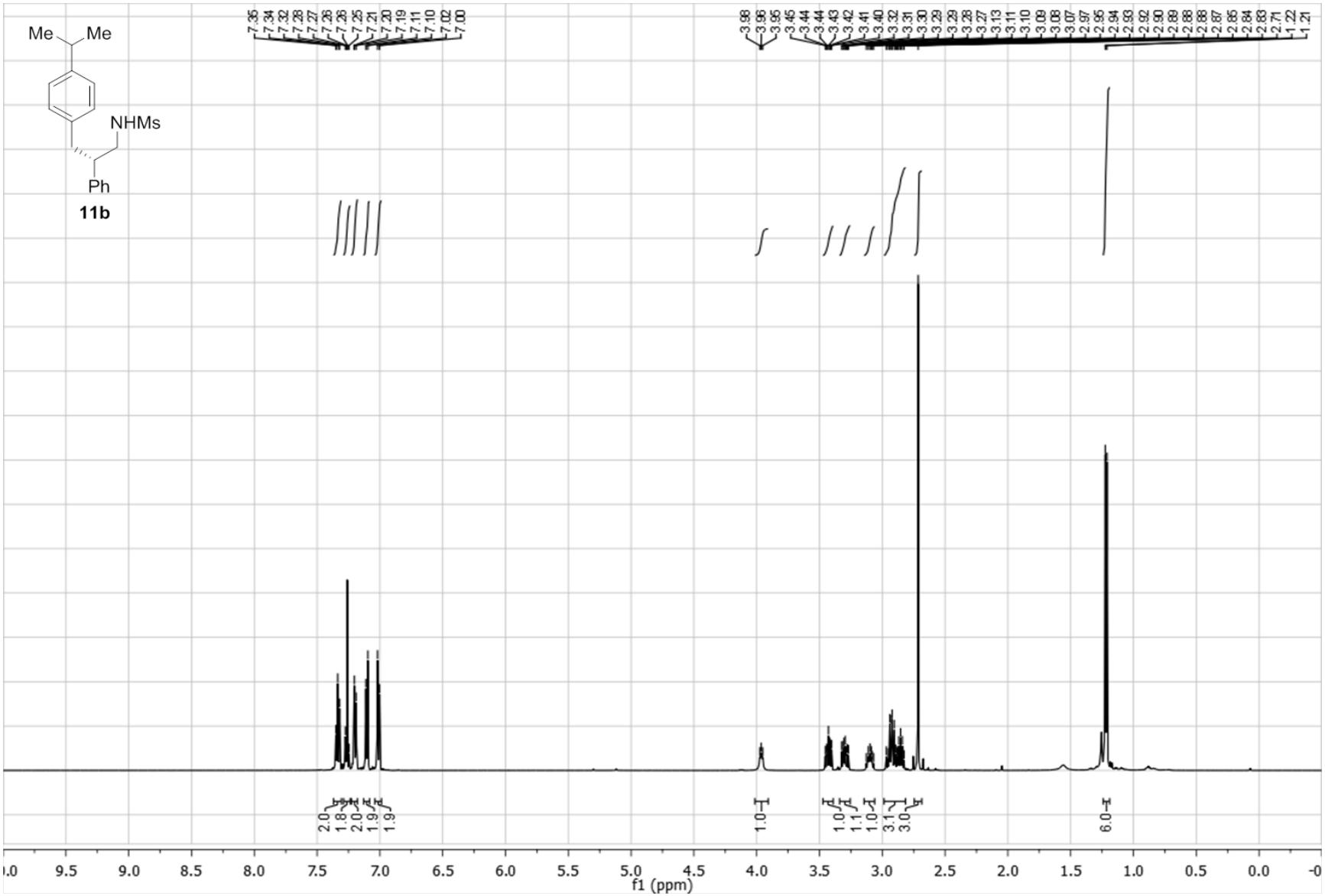
Supporting Information Figure 12. ^{13}C NMR Spectrum of **9**, 125 MHz, $CDCl_3$



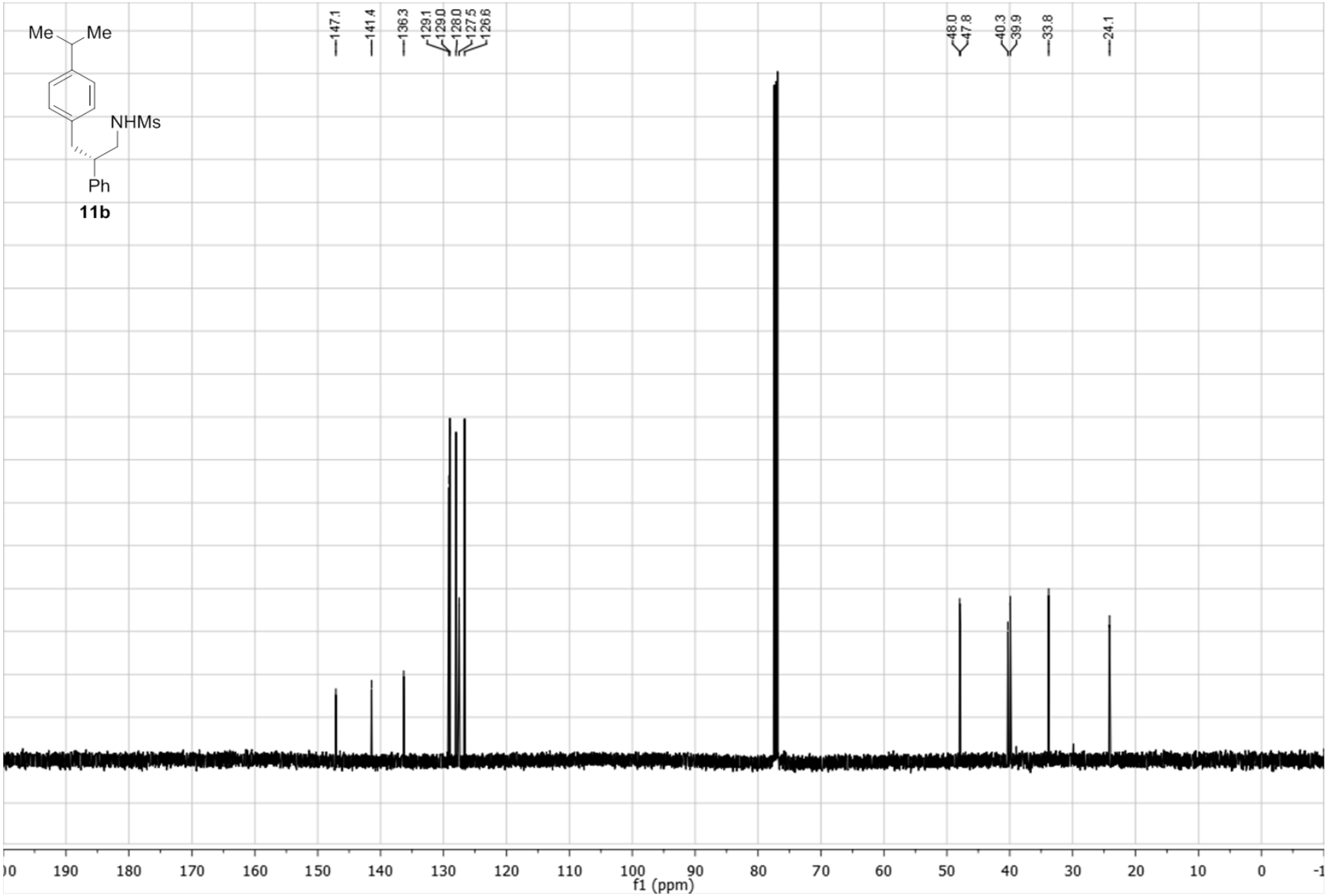
Supporting Information Figure 13. ^{1}H NMR Spectrum of **11a**, 500 MHz, $CDCl_3$



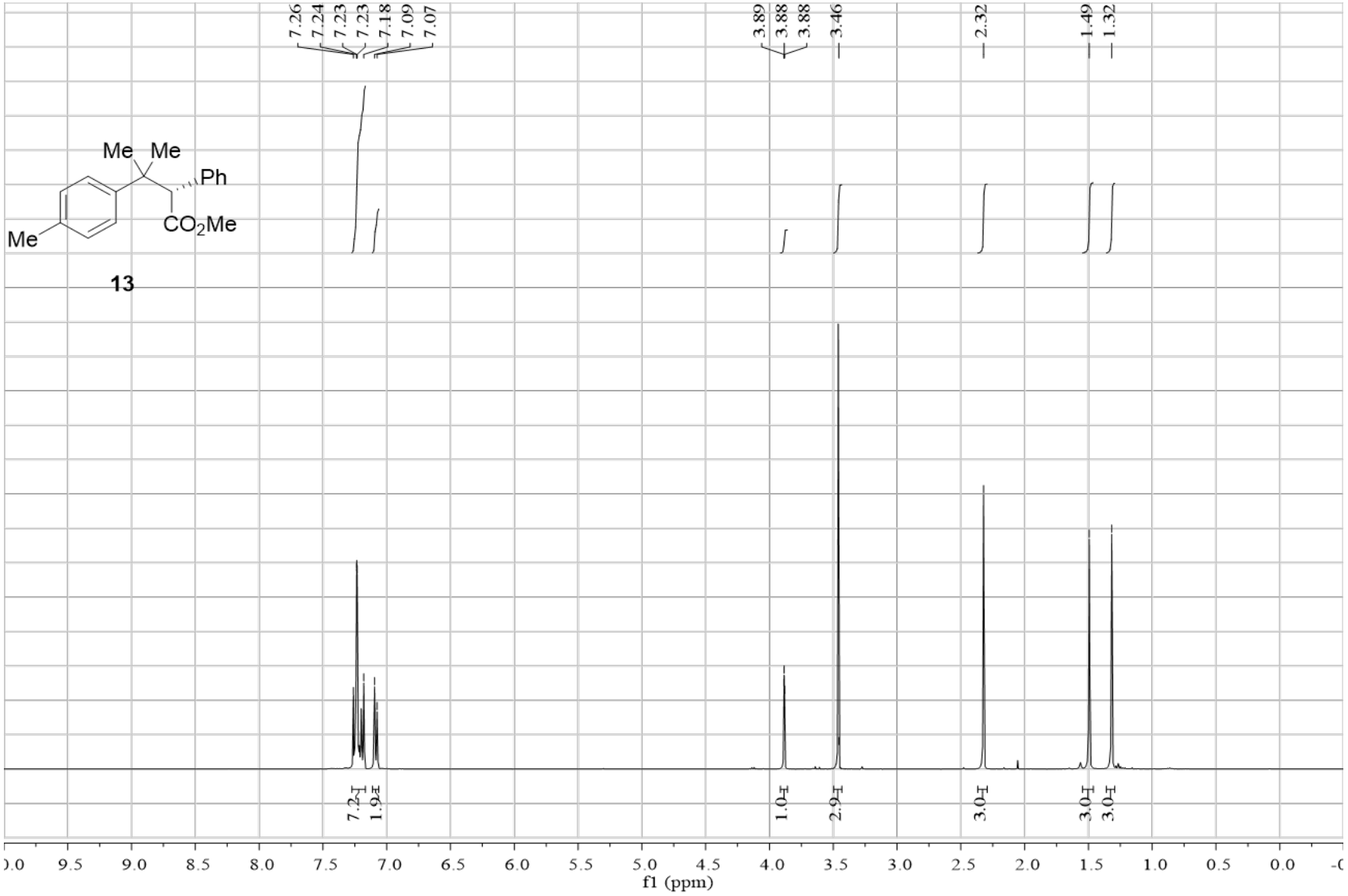
Supporting Information Figure 14. ^{13}C NMR Spectrum of **11a**, 125 MHz, $CDCl_3$



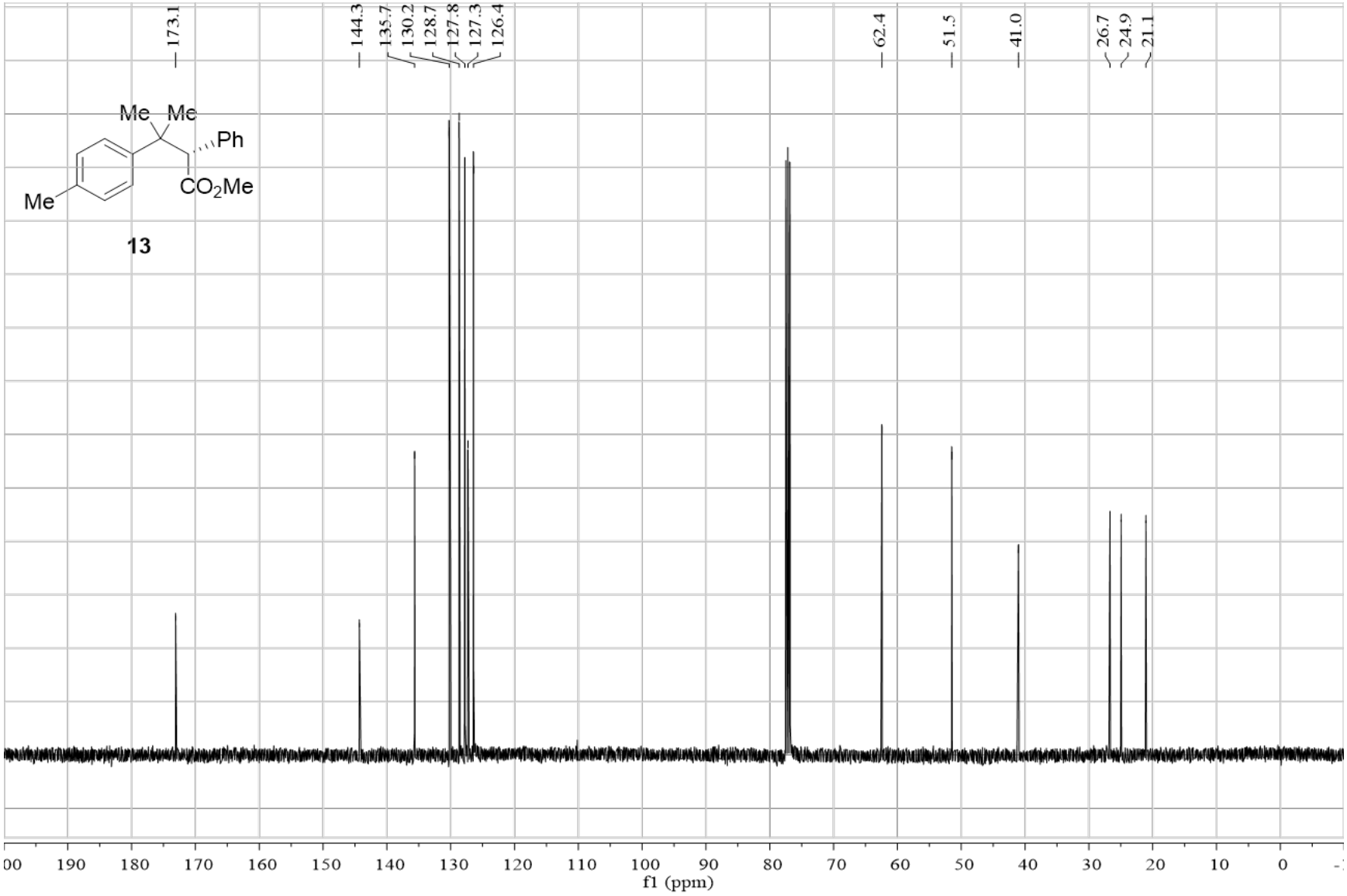
Supporting Information Figure 15. ^{1}H NMR Spectrum of **11b**, 500 MHz, $CDCl_3$



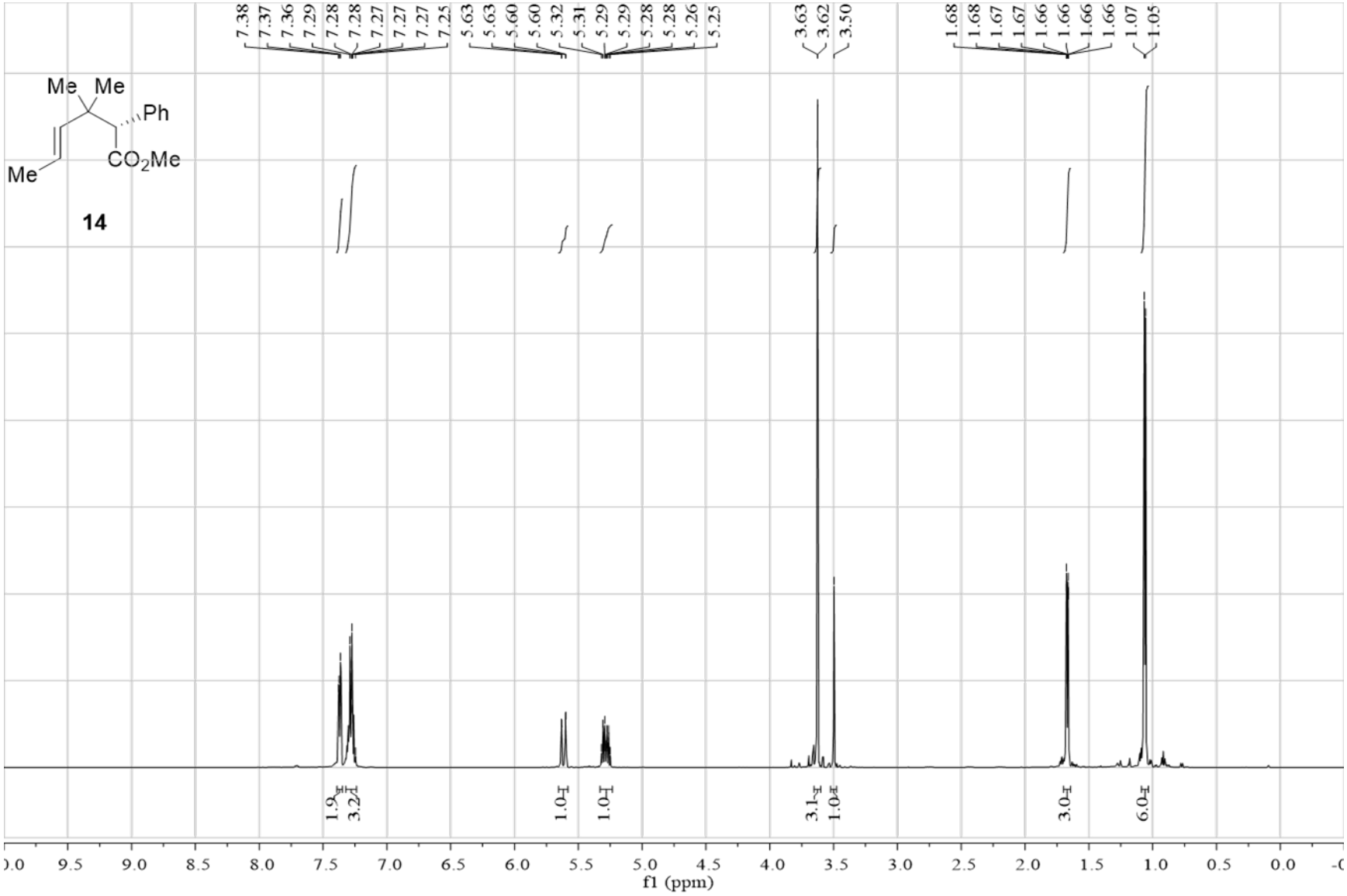
Supporting Information Figure 16. ^{13}C NMR Spectrum of **11b**, 125 MHz, $CDCl_3$



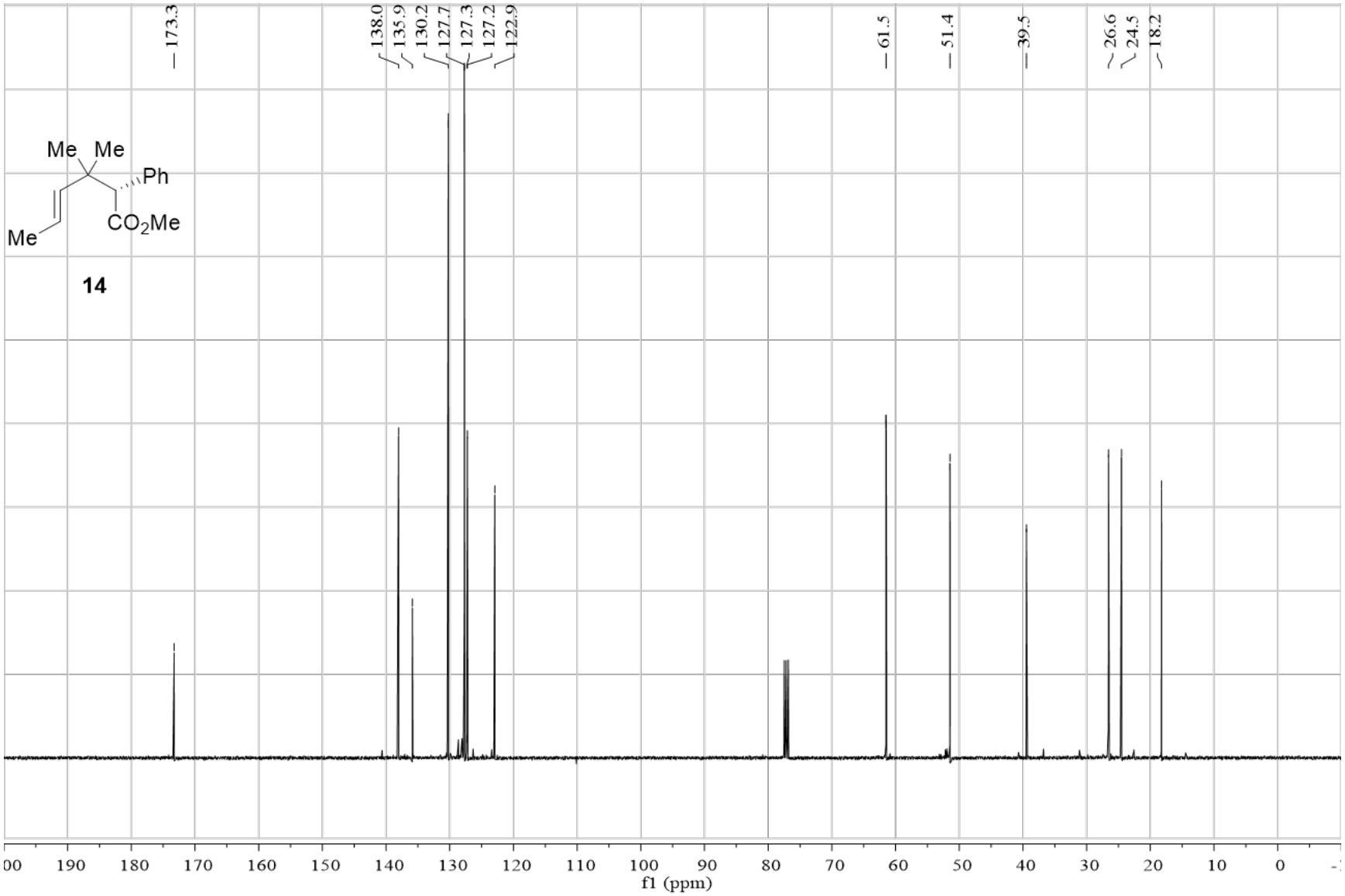
Supporting Information Figure 17. ^{1}H NMR Spectrum of **13**, 400 MHz, $CDCl_3$



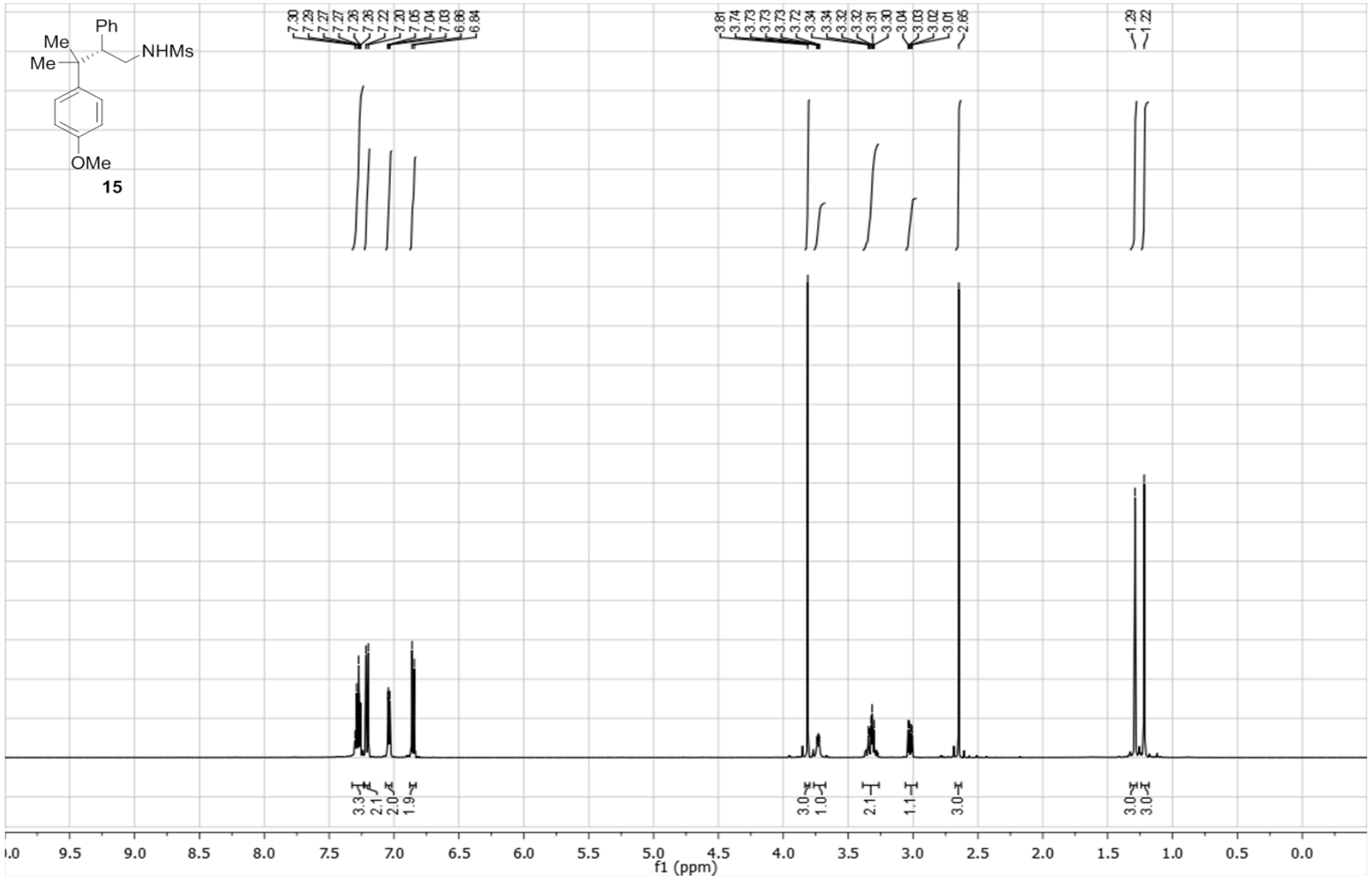
Supporting Information Figure 18. ^{13}C NMR Spectrum of **13**, 100 MHz, $CDCl_3$



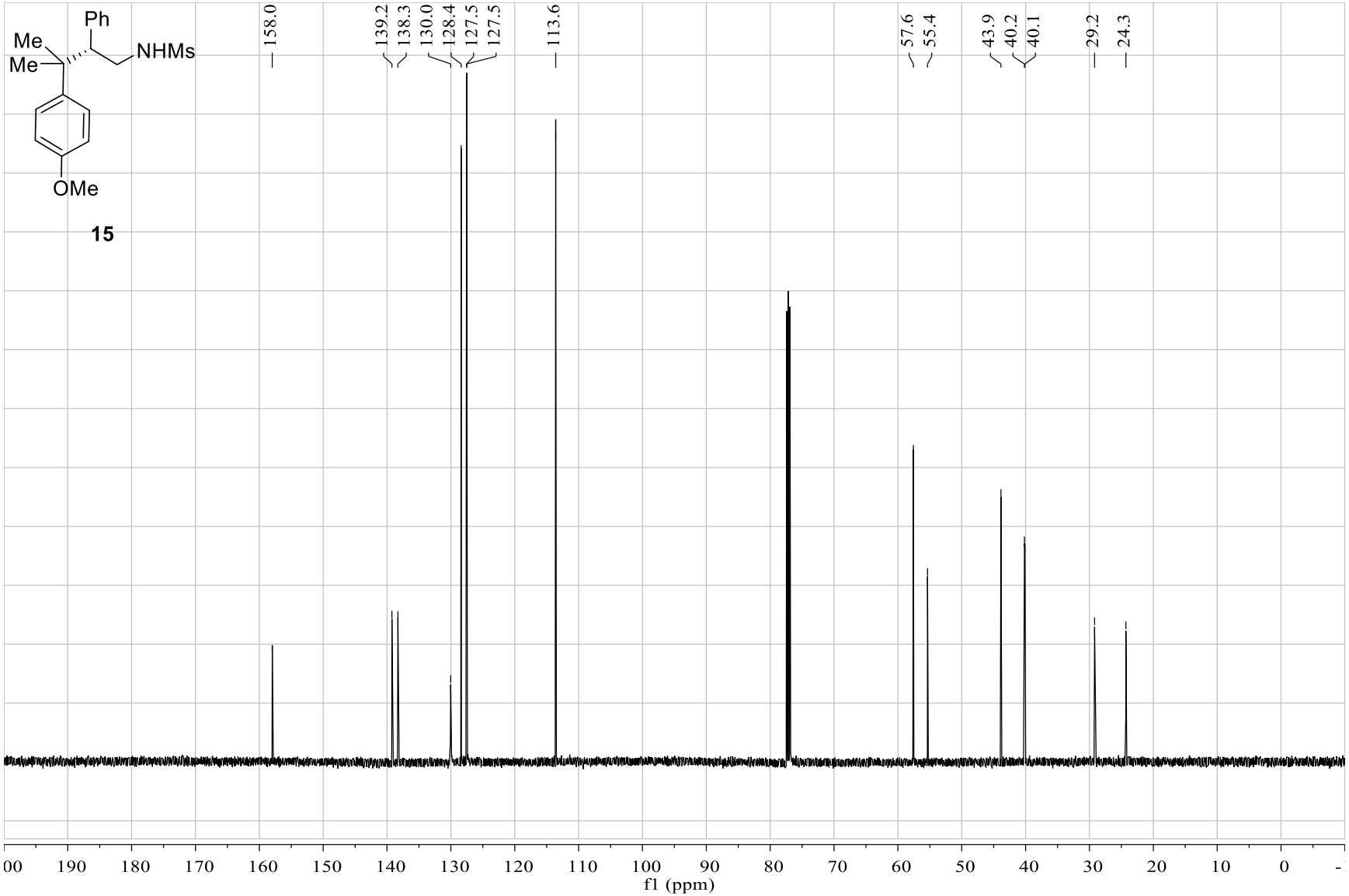
Supporting Information Figure 19. ^{1}H NMR Spectrum of **14**, 500 MHz, $CDCl_3$



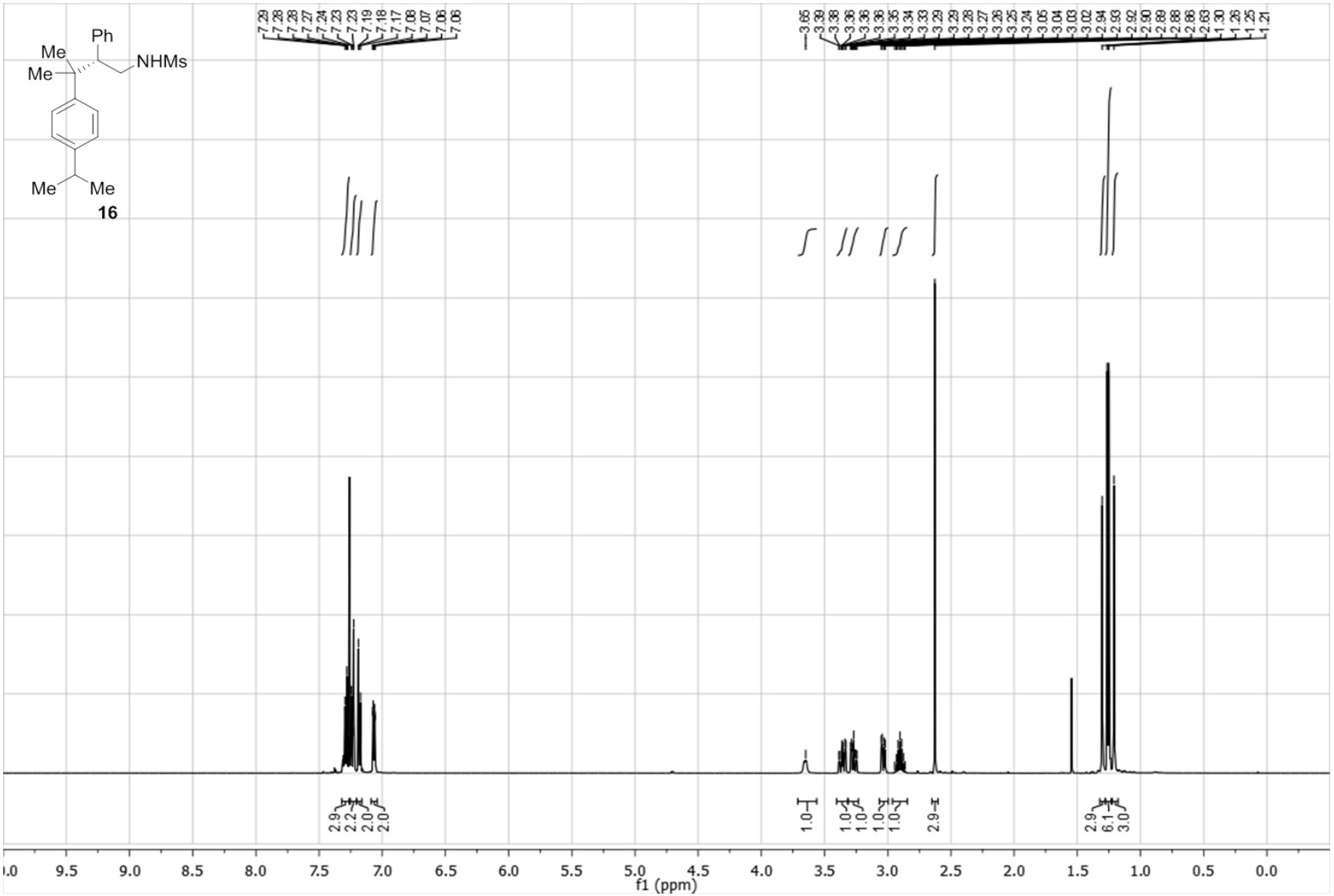
Supporting Information Figure 20. ^{13}C NMR Spectrum of **14**, 100 MHz, $CDCl_3$



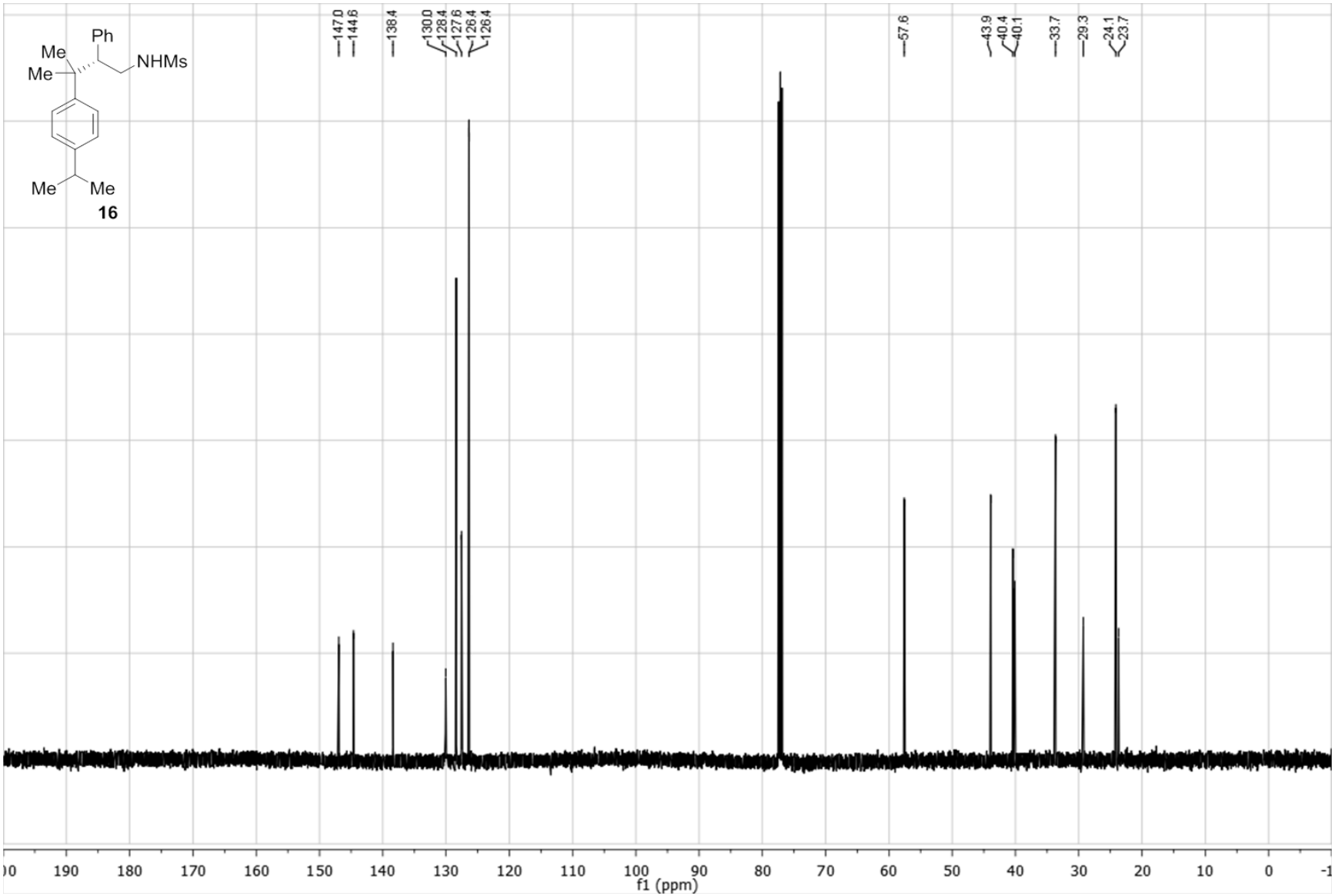
Supporting Information Figure 21. ^{1}H NMR Spectrum of **15**, 500 MHz, $CDCl_3$



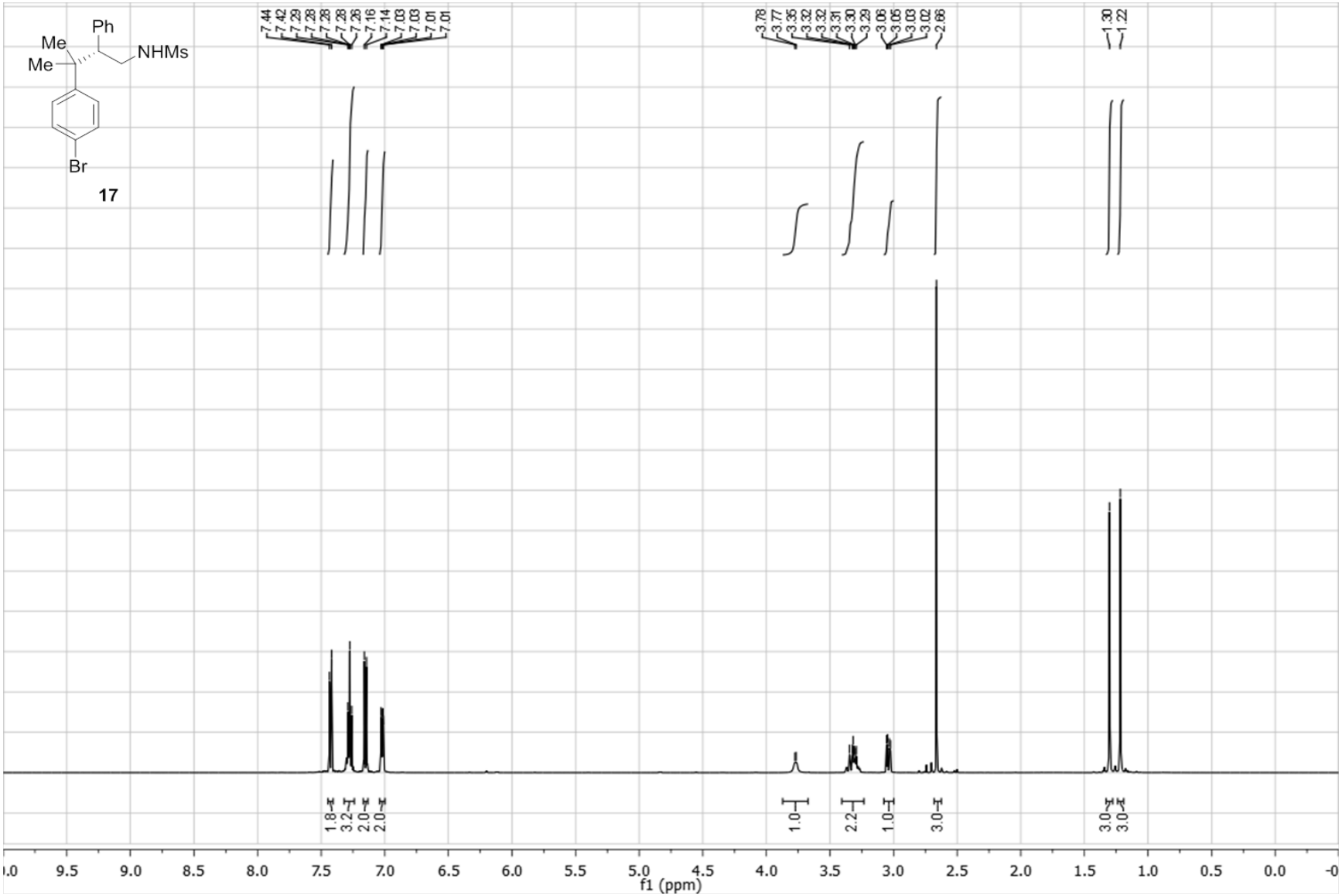
Supporting Information Figure 22. ^{13}C NMR Spectrum of **15**, 125 MHz, $CDCl_3$



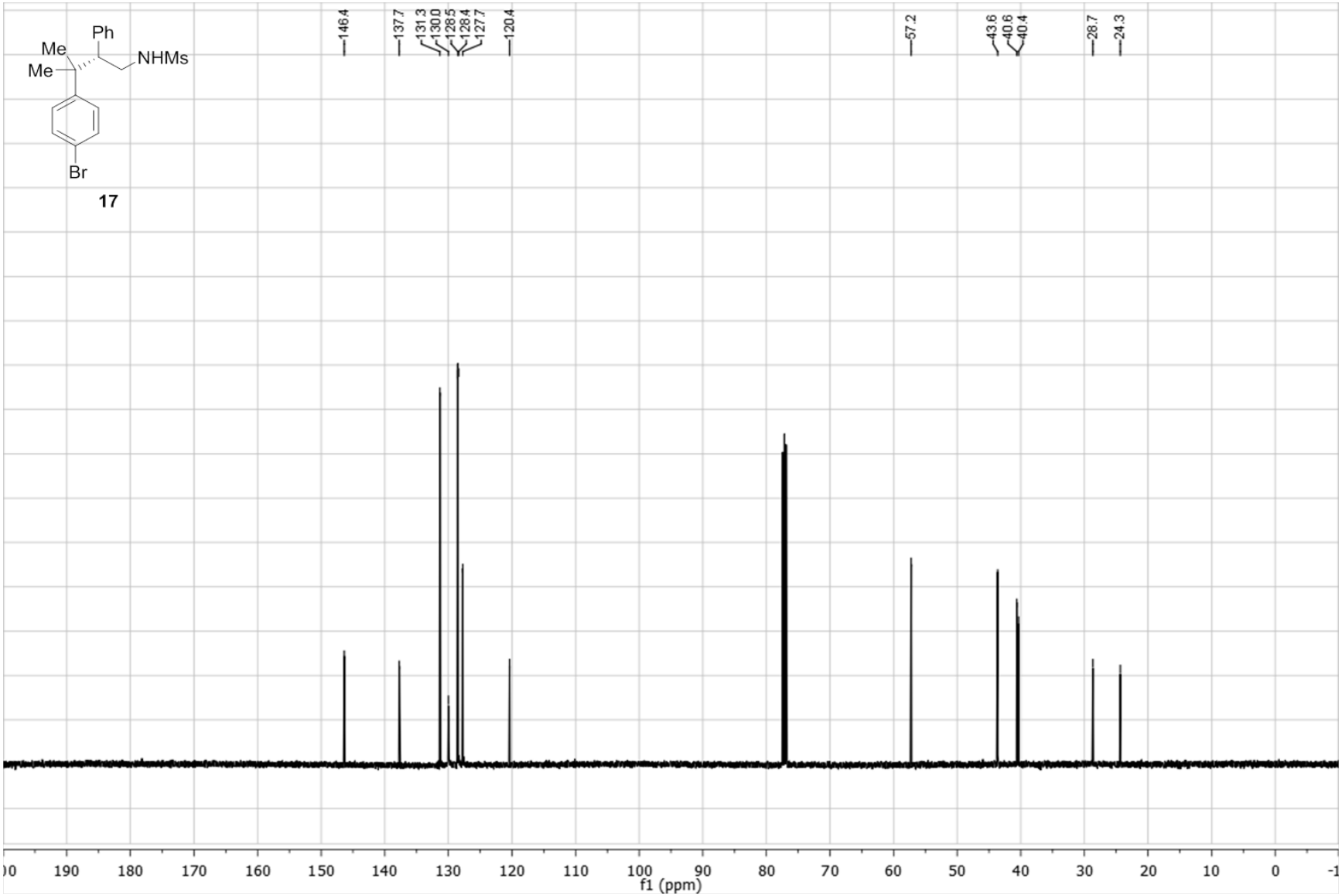
Supporting Information Figure 23. ^{1}H NMR Spectrum of **16**, 500 MHz, $CDCl_3$



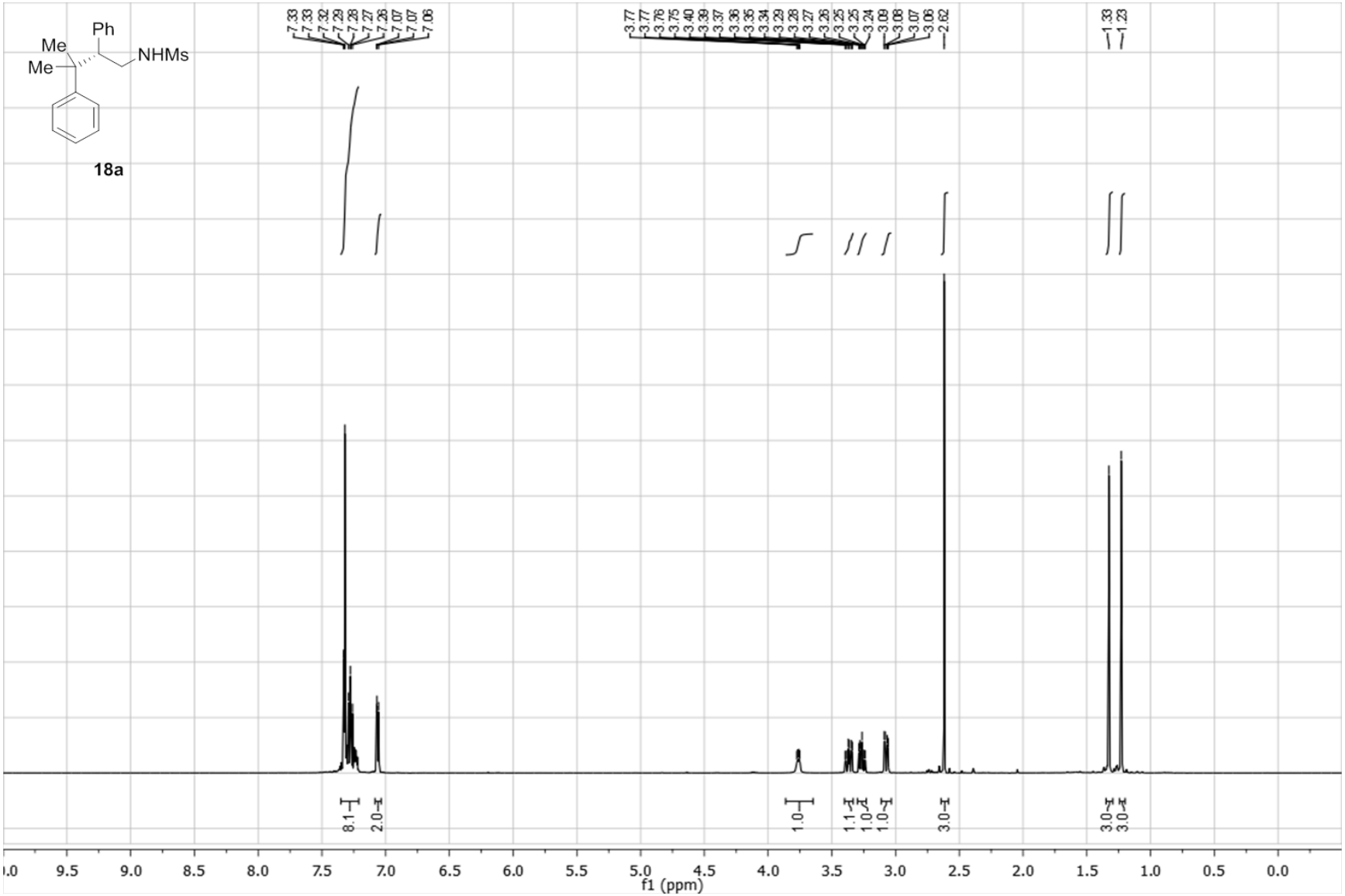
Supporting Information Figure 24. ^{13}C NMR Spectrum of **16**, 125 MHz, $CDCl_3$



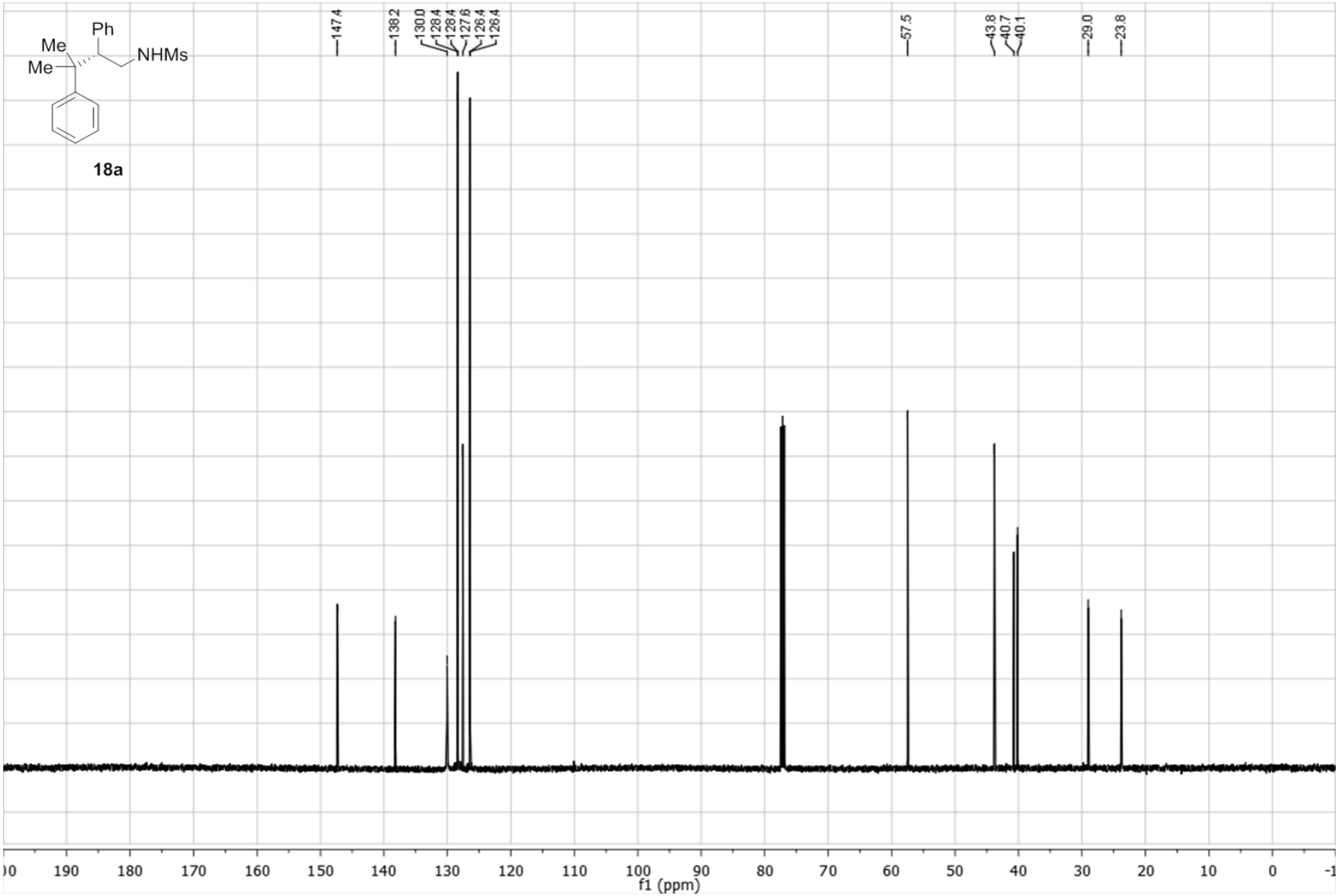
Supporting Information Figure 25. ^{1}H NMR Spectrum of **17**, 500 MHz, $CDCl_3$



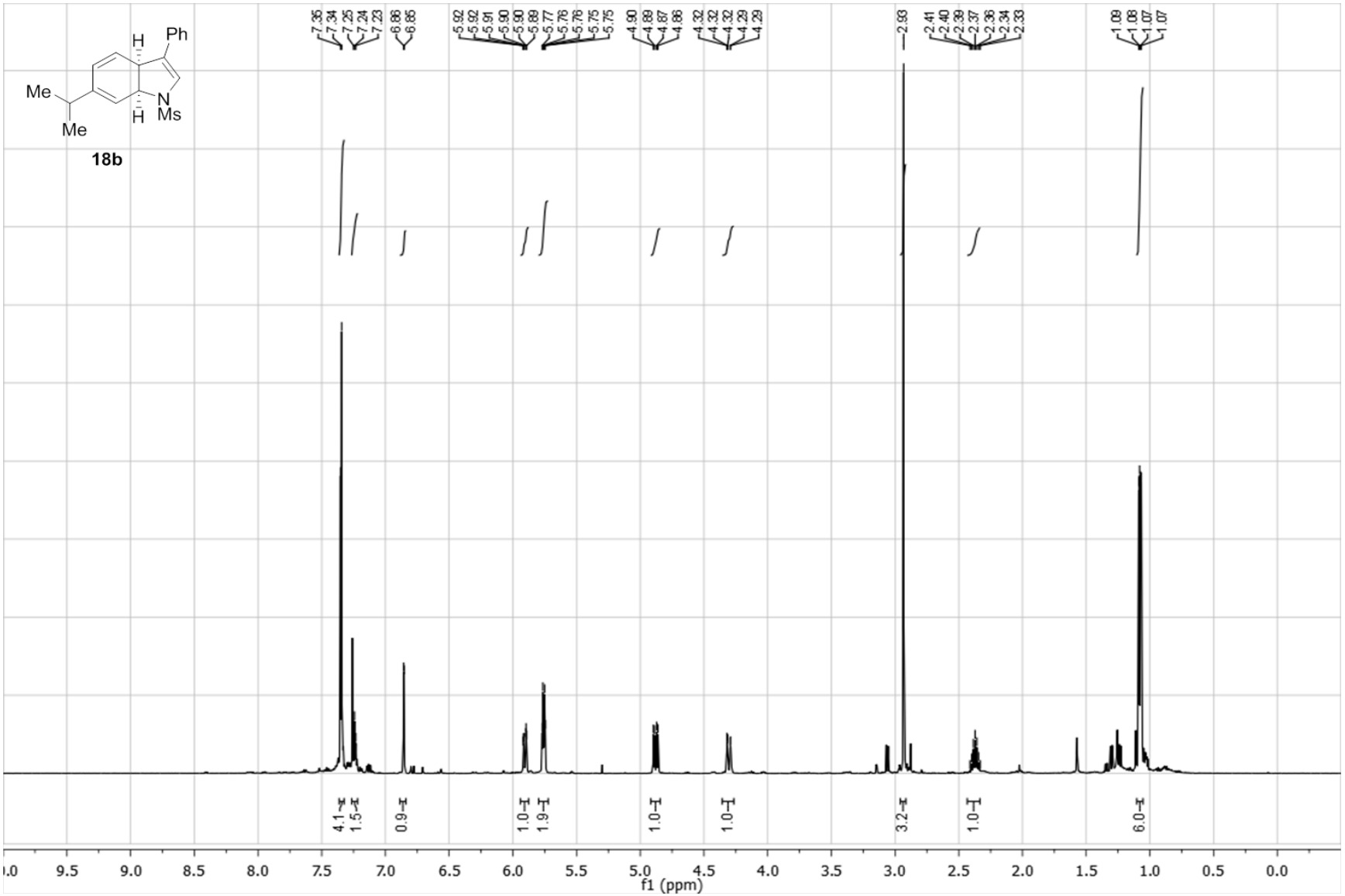
Supporting Information Figure 26. ^{13}C NMR Spectrum of **17**, 125 MHz, $CDCl_3$



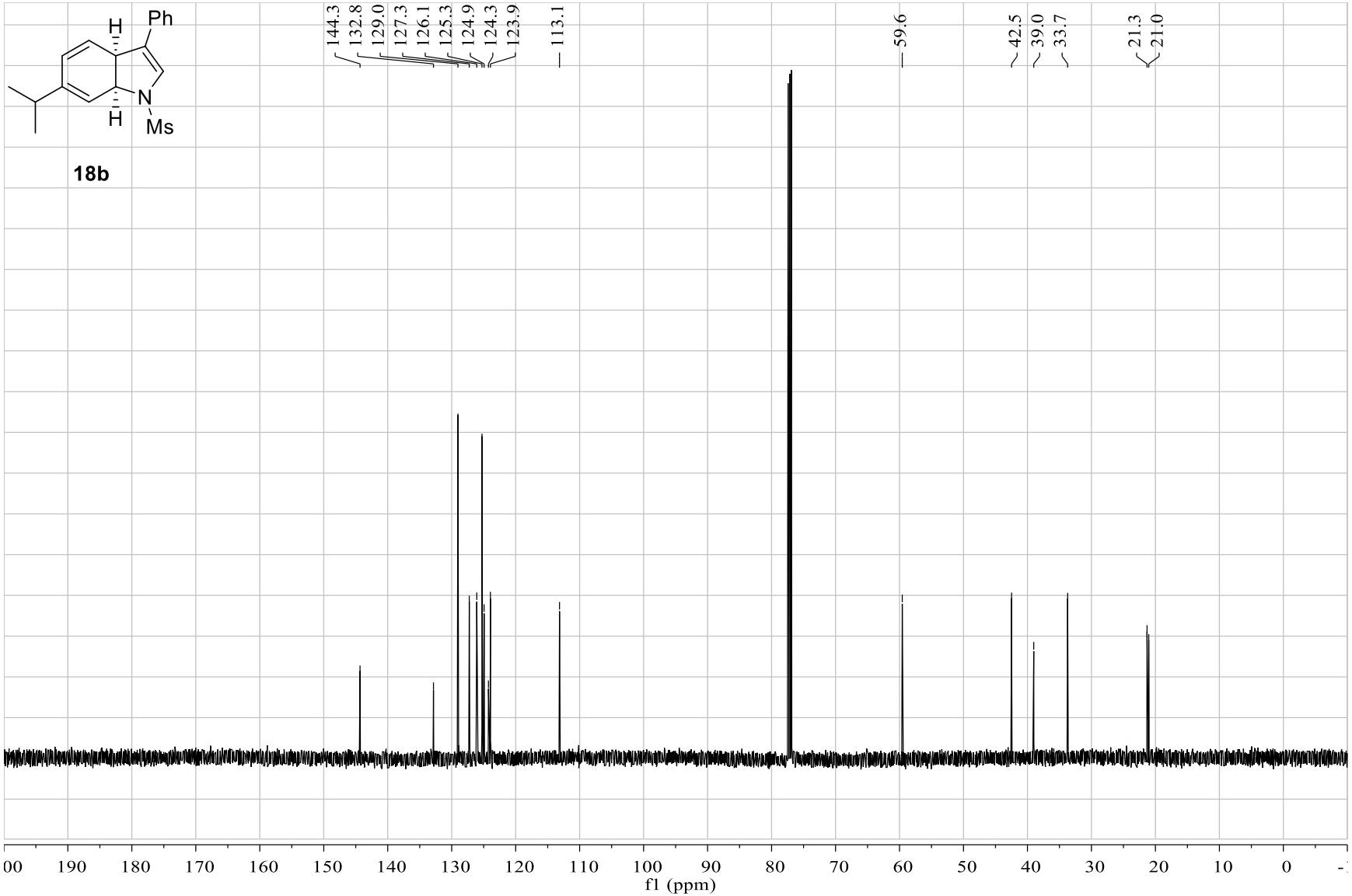
Supporting Information Figure 27. ^{1}H NMR Spectrum of **18a**, 500 MHz, $CDCl_3$



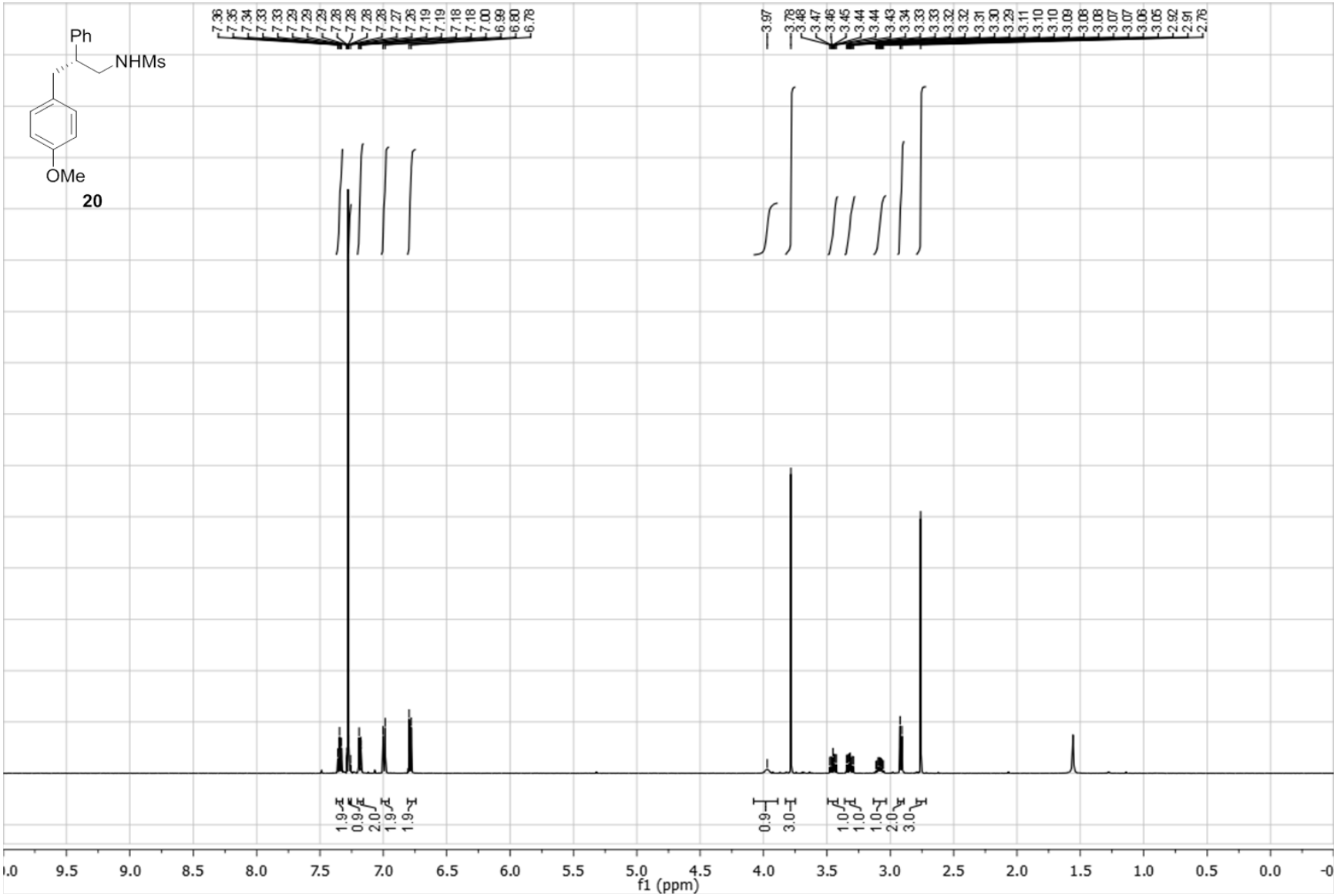
Supporting Information Figure 28. ^{13}C NMR Spectrum of **18a**, 125 MHz, $CDCl_3$



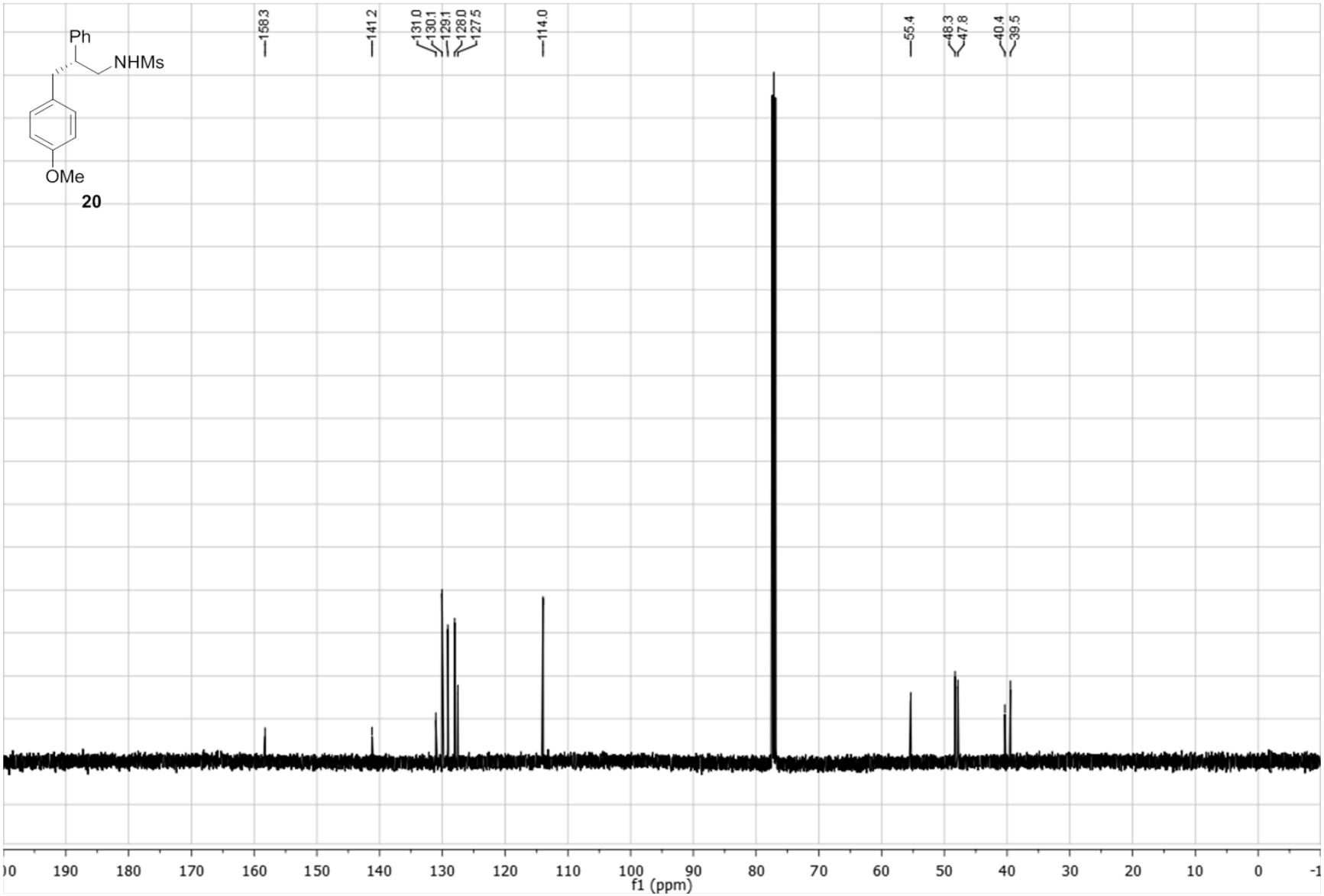
Supporting Information Figure 29. ^{1}H NMR Spectrum of **18b**, 500 MHz, $CDCl_3$



Supporting Information Figure 30. ^{13}C NMR Spectrum of **18b**, 125 MHz, $CDCl_3$

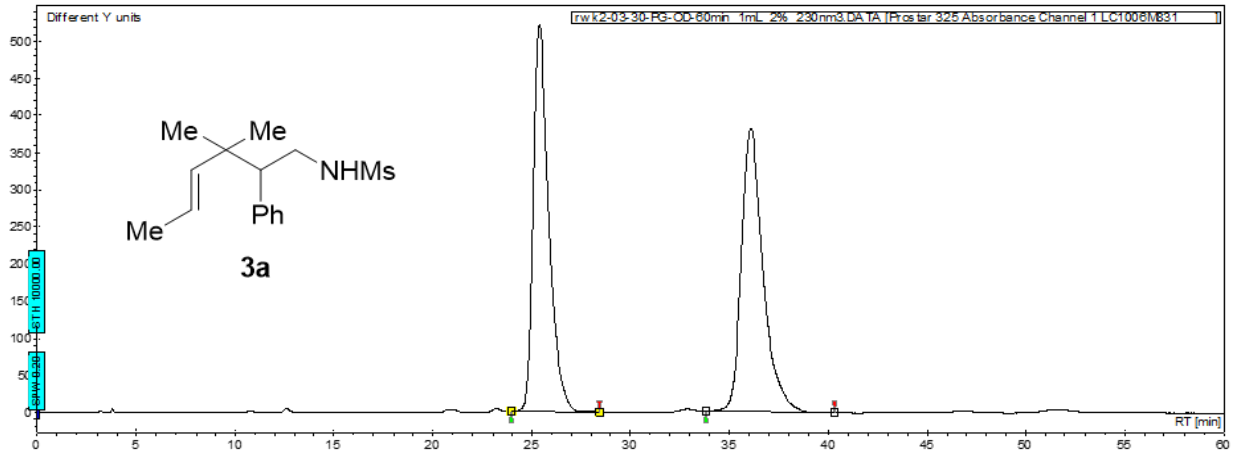


Supporting Information Figure 31. ^{1}H NMR Spectrum of **20**, 500 MHz, $CDCl_3$

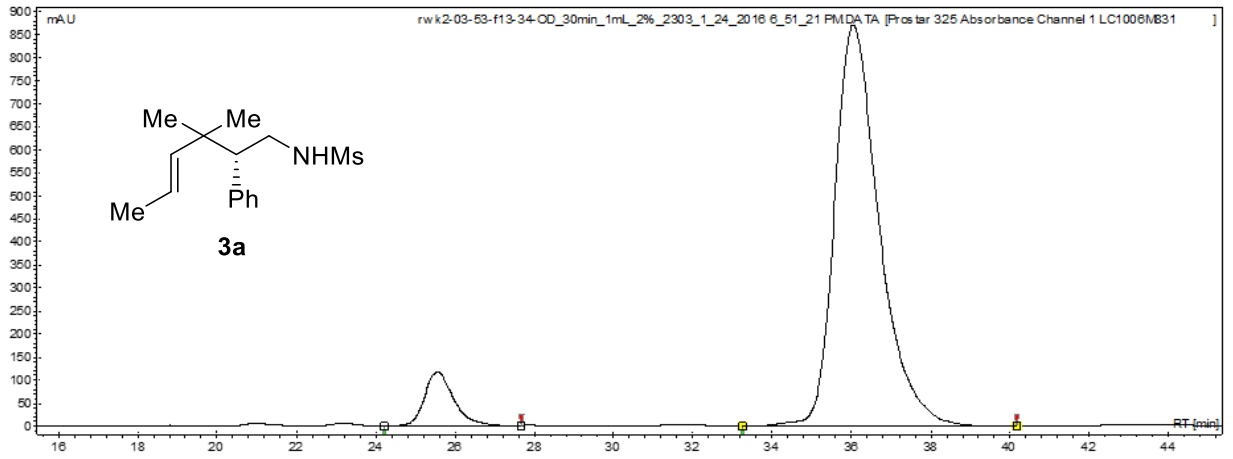


Supporting Information Figure 32. ^{13}C NMR Spectrum of **20**, 125 MHz, $CDCl_3$

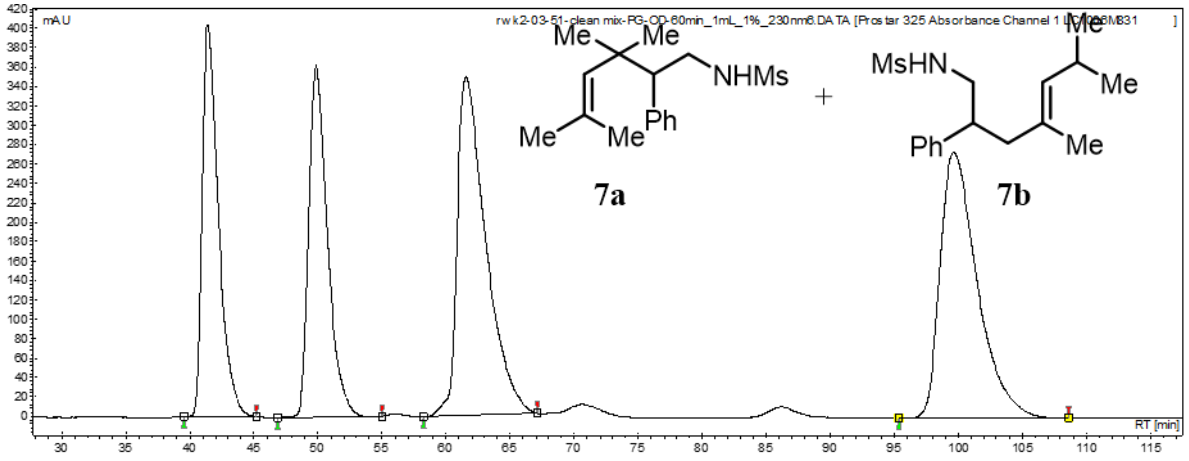
5. HPLC Traces



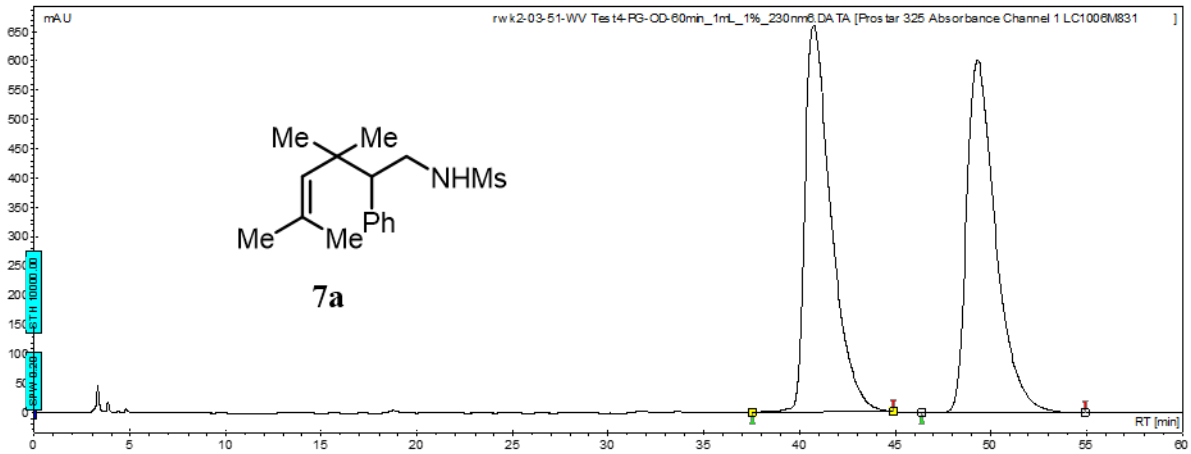
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.38	49.35	521.4	471.8	49.347
2	UNKNOWN	36.07	50.65	382.0	484.3	50.653
Total			100.00	903.4	956.2	100.000



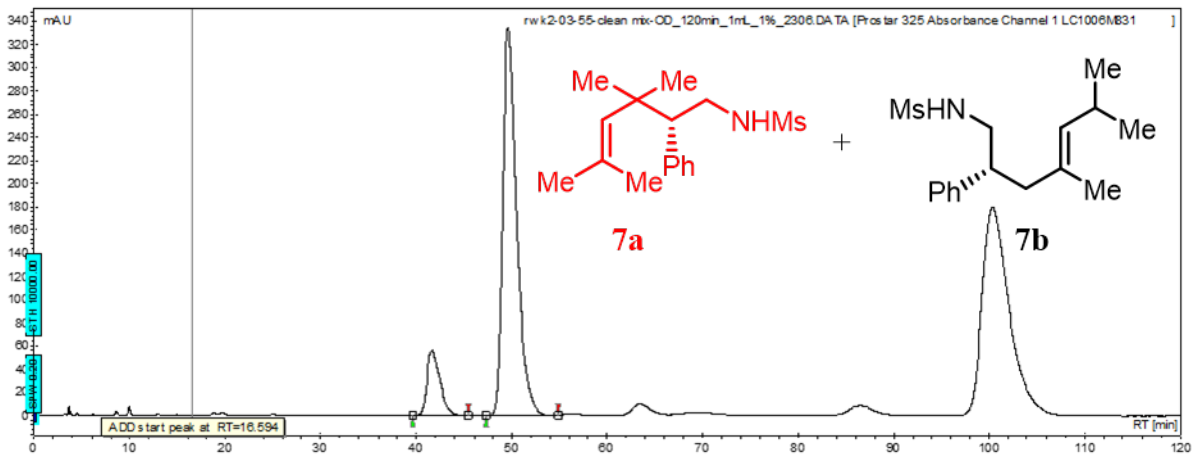
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	25.55	8.04	117.5	98.8	8.037
1	UNKNOWN	36.04	91.96	871.2	1131.0	91.963
Total			100.00	988.7	1229.9	100.000



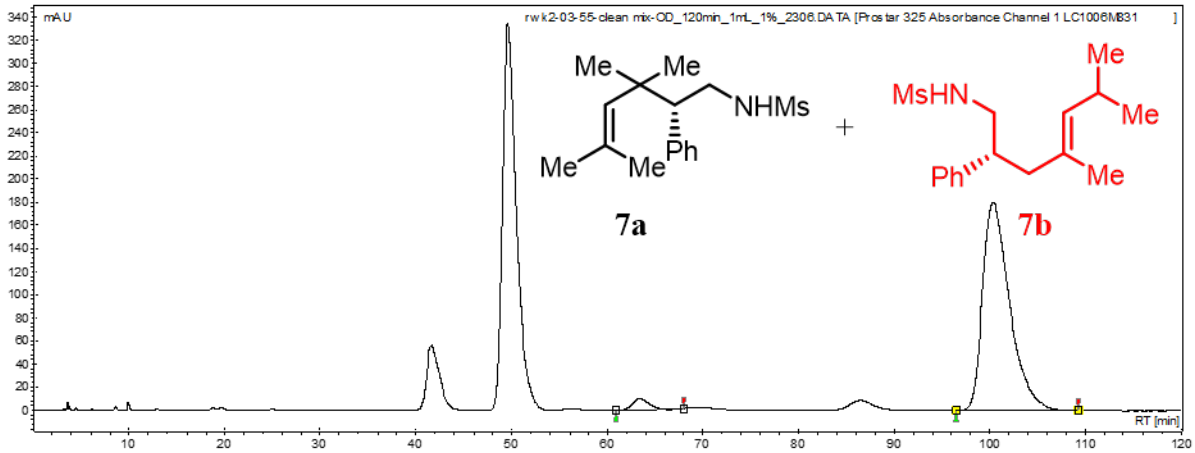
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
3	UNKNOWN	41.38	19.80	404.5	600.9	19.799
2	UNKNOWN	49.83	20.17	362.6	612.1	20.166
4	UNKNOWN	61.55	29.81	348.7	904.7	29.809
1	UNKNOWN	99.65	30.23	273.4	917.4	30.226
Total			100.00	1389.2	3035.1	100.000



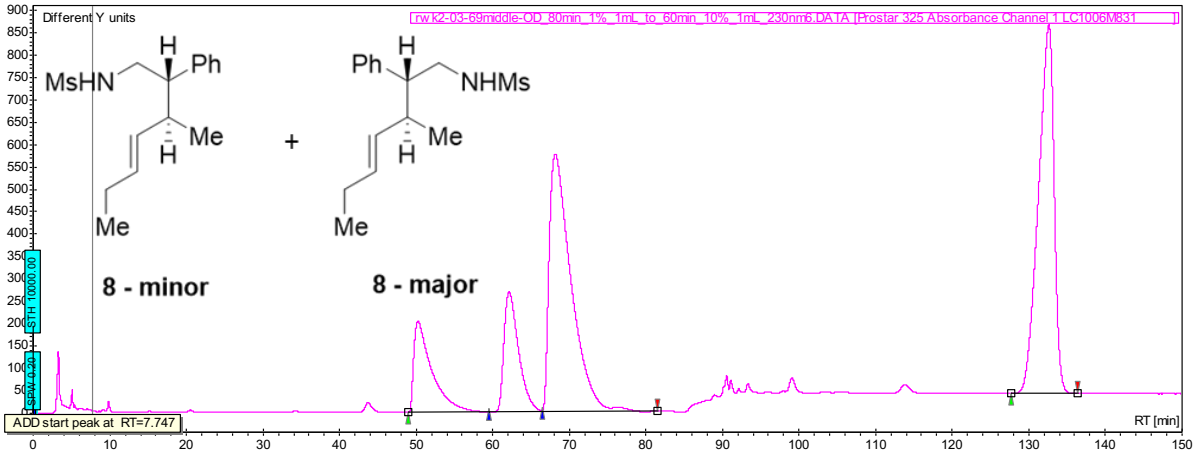
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	40.73	49.79	658.9	1046.5	49.793
2	UNKNOWN	49.29	50.21	601.3	1055.2	50.207
Total			100.00	1260.3	2101.7	100.000



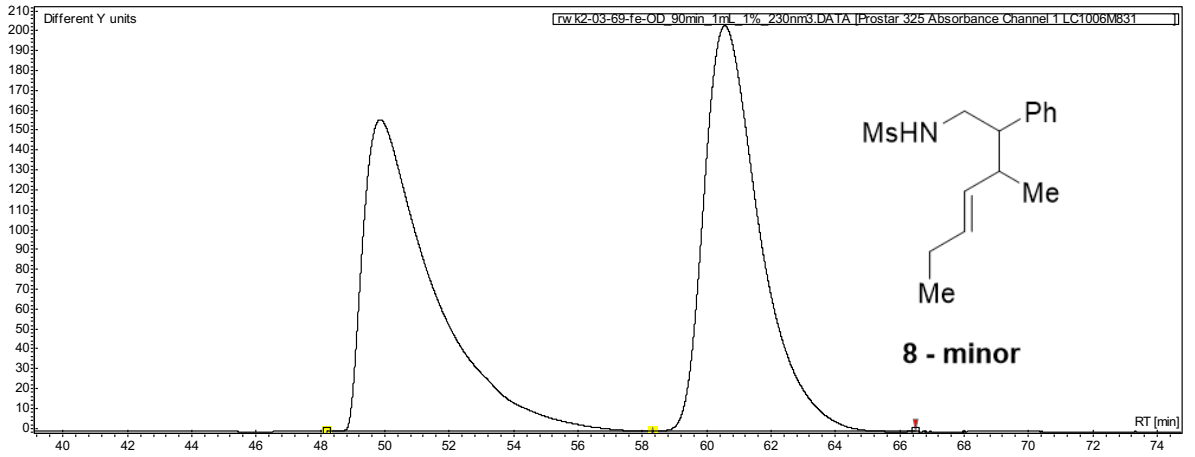
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	41.63	13.24	56.0	86.0	13.238
1	UNKNOWN	49.64	86.76	334.7	563.9	86.762
Total			100.00	390.7	650.0	100.000



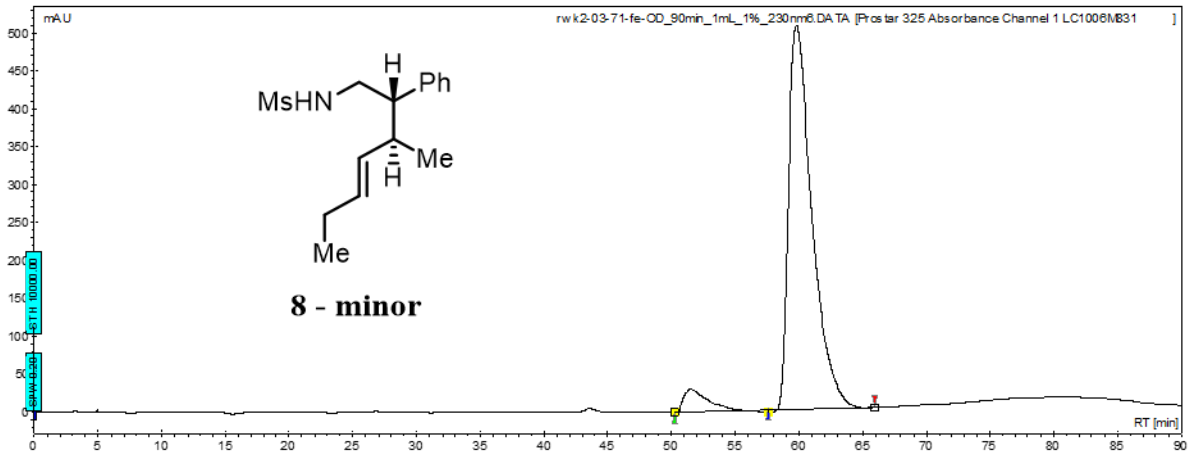
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	63.47	2.80	9.7	17.0	2.802
1	UNKNOWN	100.34	97.20	180.4	590.0	97.198
Total			100.00	190.1	607.0	100.000



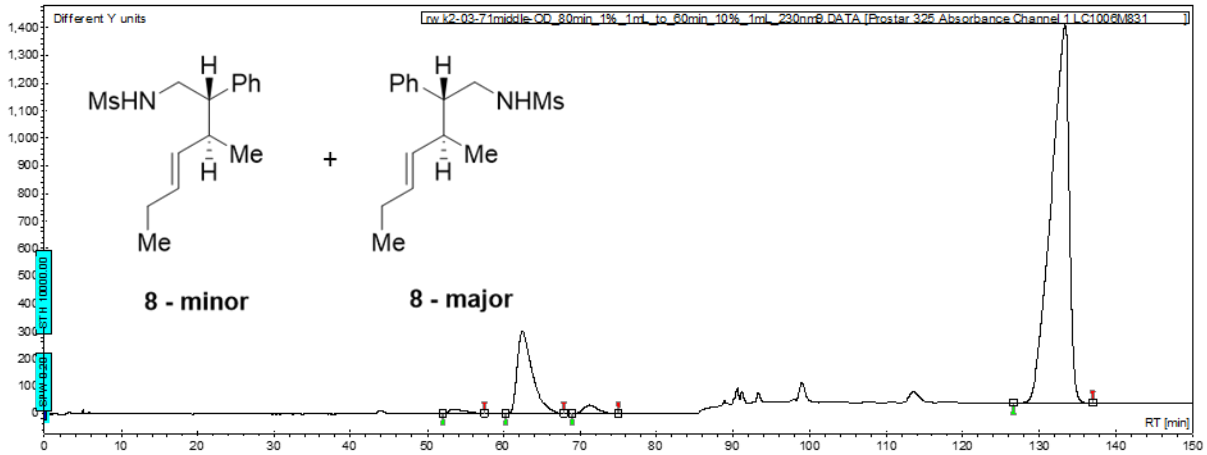
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	50.25	11.01	203.7	552.5	11.005
2	UNKNOWN	62.13	11.80	268.5	592.6	11.805
3	UNKNOWN	68.16	38.01	576.3	1908.4	38.014
4	UNKNOWN	132.60	39.18	825.4	1966.8	39.176
Total			100.00	1874.0	5020.3	100.000



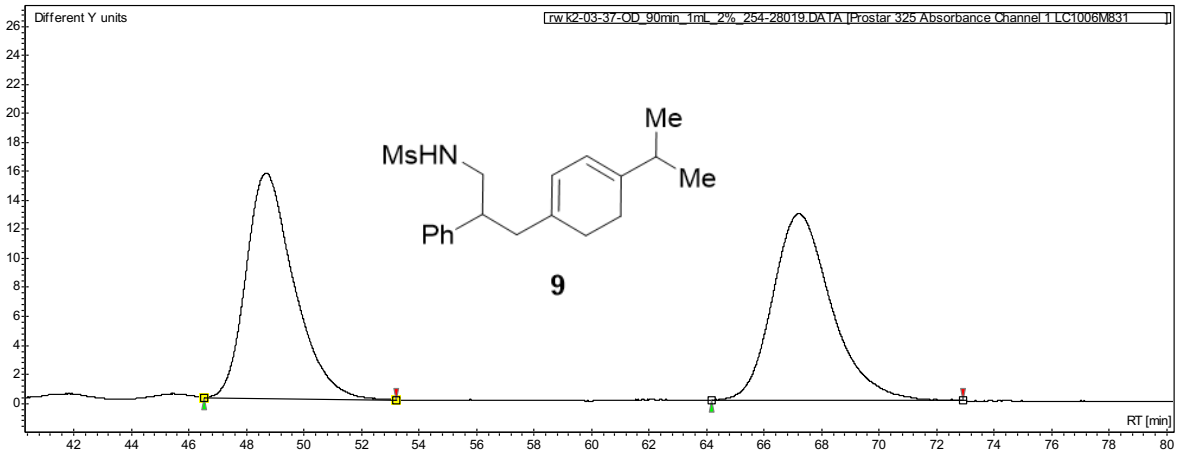
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	49.85	49.18	156.8	395.3	49.180
2	UNKNOWN	60.56	50.82	204.2	408.5	50.820
Total			100.00	361.0	803.9	100.000



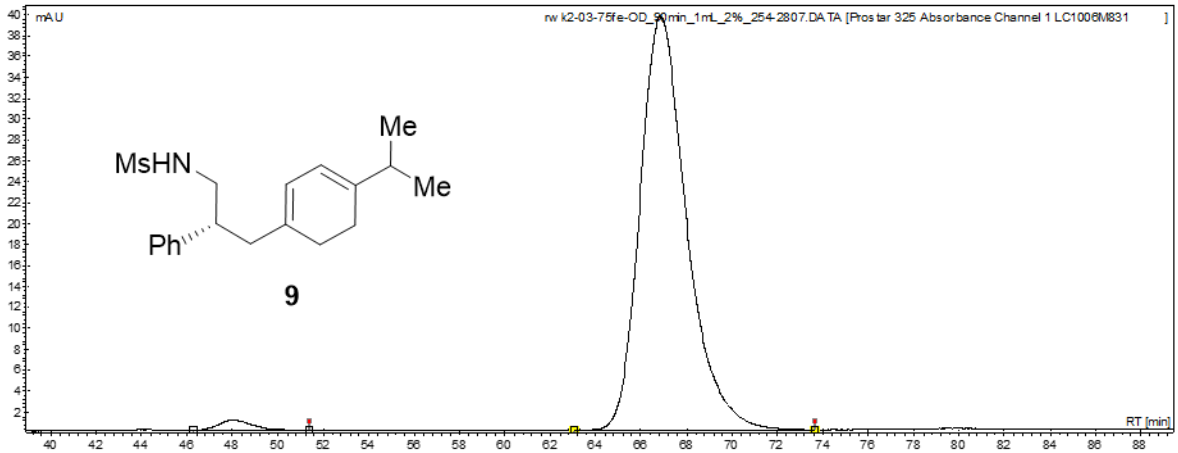
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	51.50	5.54	29.3	63.3	5.535
2	UNKNOWN	59.81	94.46	507.4	1080.4	94.465
Total			100.00	536.6	1143.7	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	53.49	0.84	16.3	38.6	0.845
2	UNKNOWN	62.46	15.12	300.5	690.6	15.115
3	UNKNOWN	71.17	1.45	29.3	66.3	1.451
4	UNKNOWN	133.32	82.59	1368.9	3773.4	82.589
Total			100.00	1715.0	4568.9	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	48.71	49.59	15.5	29.9	49.586
2	UNKNOWN	67.19	50.41	12.9	30.4	50.414
Total			100.00	28.4	60.4	100.000



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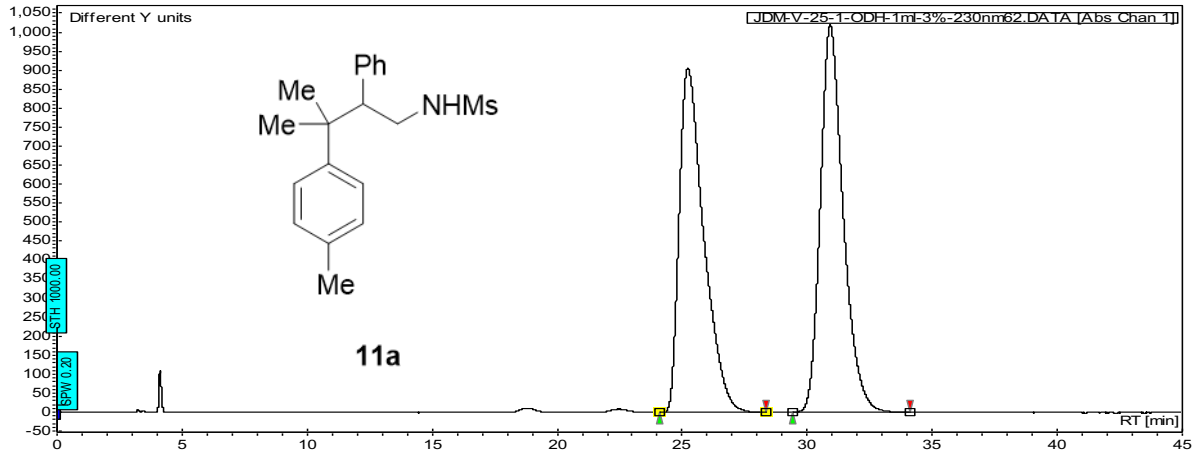
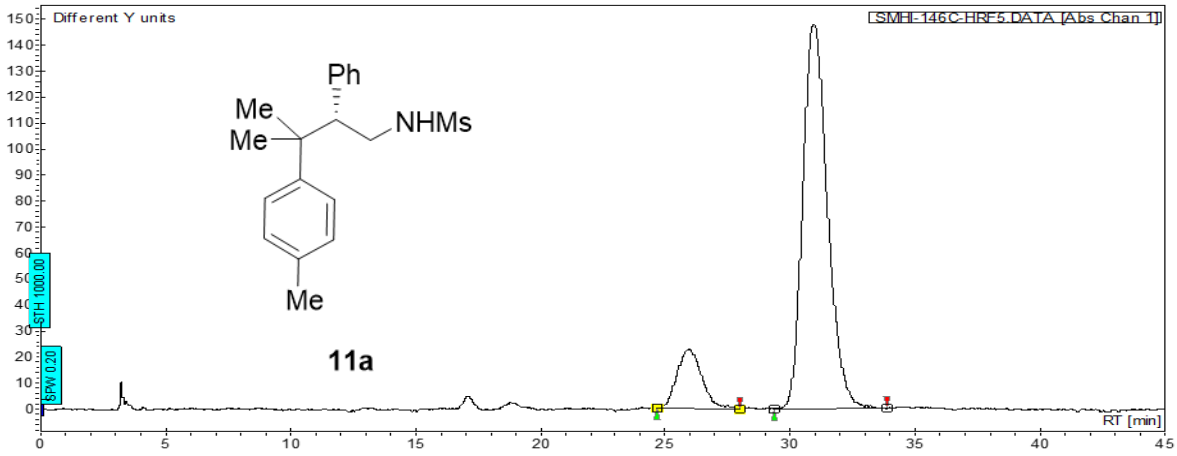
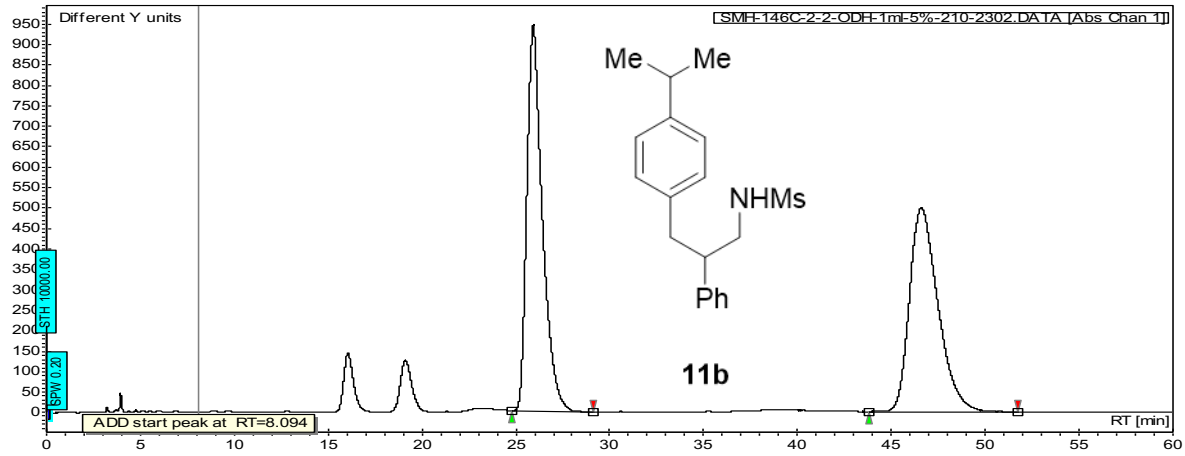
2	UNKNOWN	48.01	1.68	0.9	1.6	1.678
1	UNKNOWN	66.85	98.32	39.6	93.8	98.322
Total			100.00	40.5	95.4	100.000



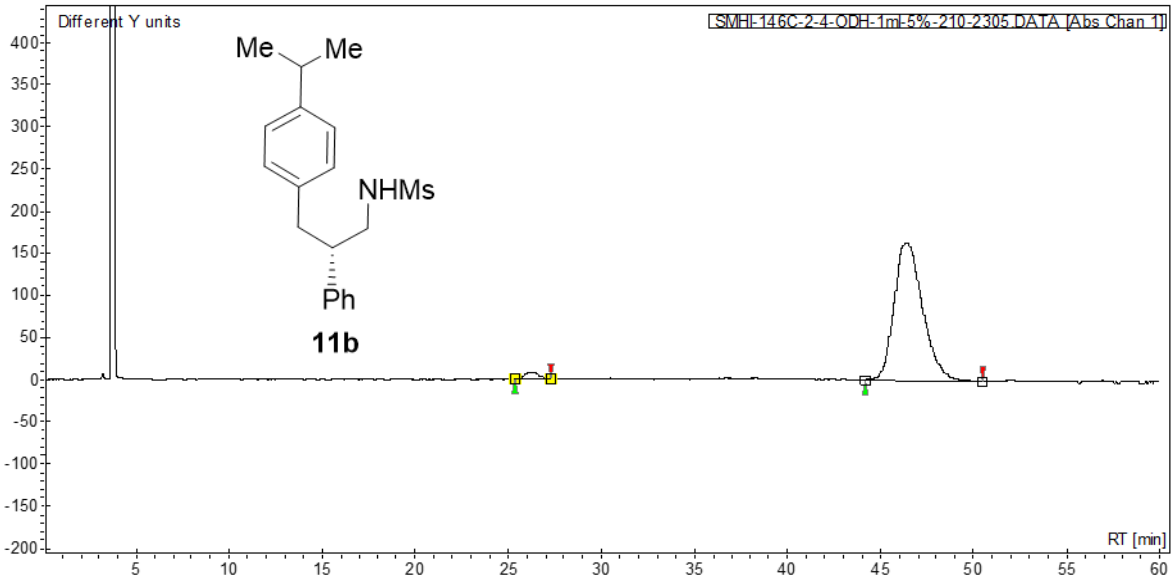
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.22	48.82	905.8	1030.2	48.822
2	UNKNOWN	30.92	51.18	1018.9	1079.9	51.178
Total			100.00	1924.7	2110.1	100.000



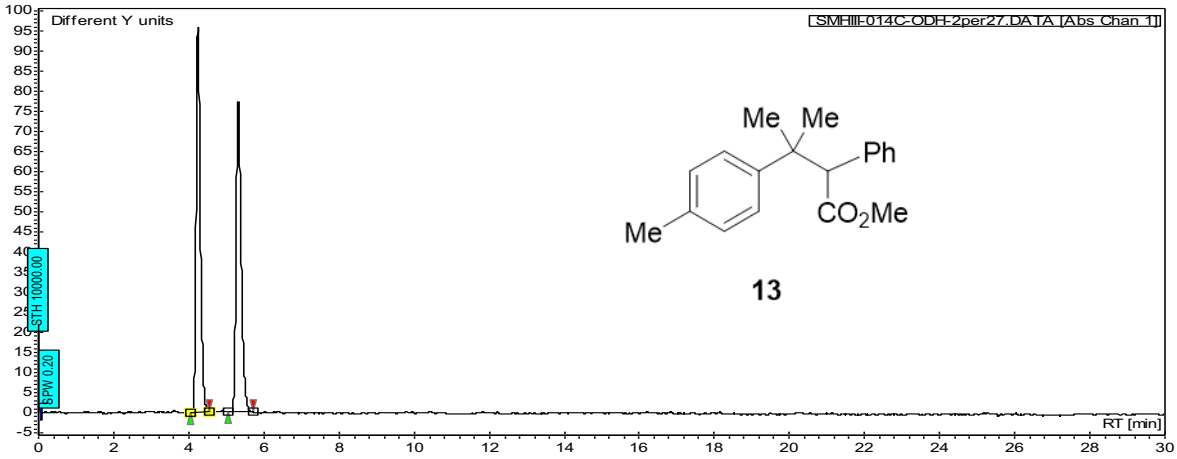
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.91	13.42	22.7	26.2	13.419
2	UNKNOWN	30.93	86.58	147.4	169.2	86.581
Total			100.00	170.1	195.4	100.000



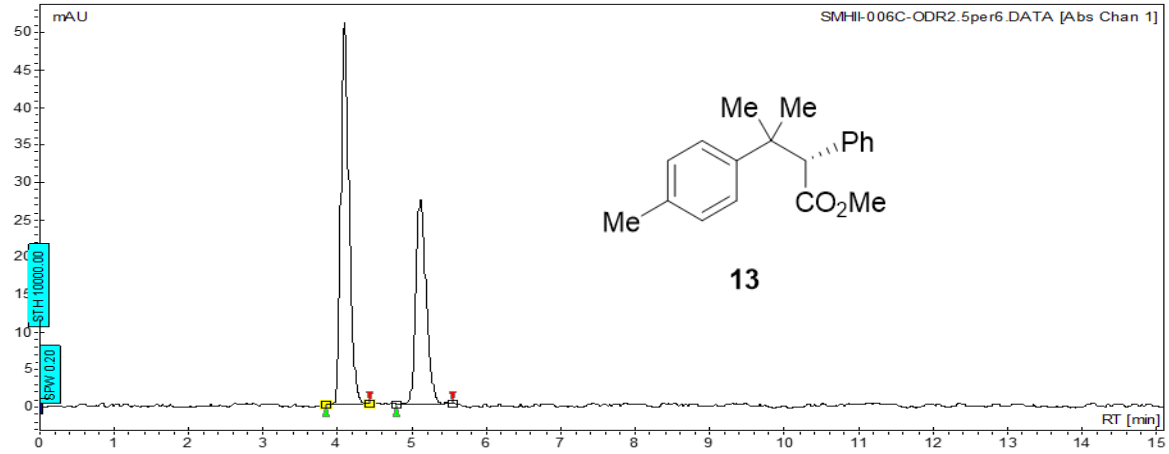
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25.92	50.68	944.1	902.2	50.678
2	UNKNOWN	46.57	49.32	498.1	878.1	49.322
Total			100.00	1442.3	1780.3	100.000



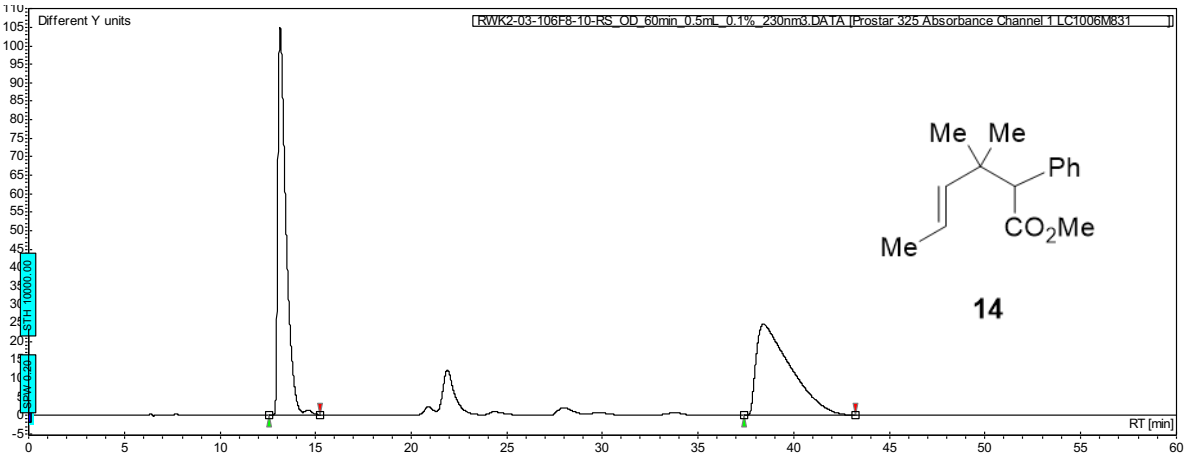
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.30	2.34	7.5	7.0	2.343
2	UNKNOWN	46.36	97.66	163.2	290.3	97.657
Total			100.00	170.7	297.2	100.000



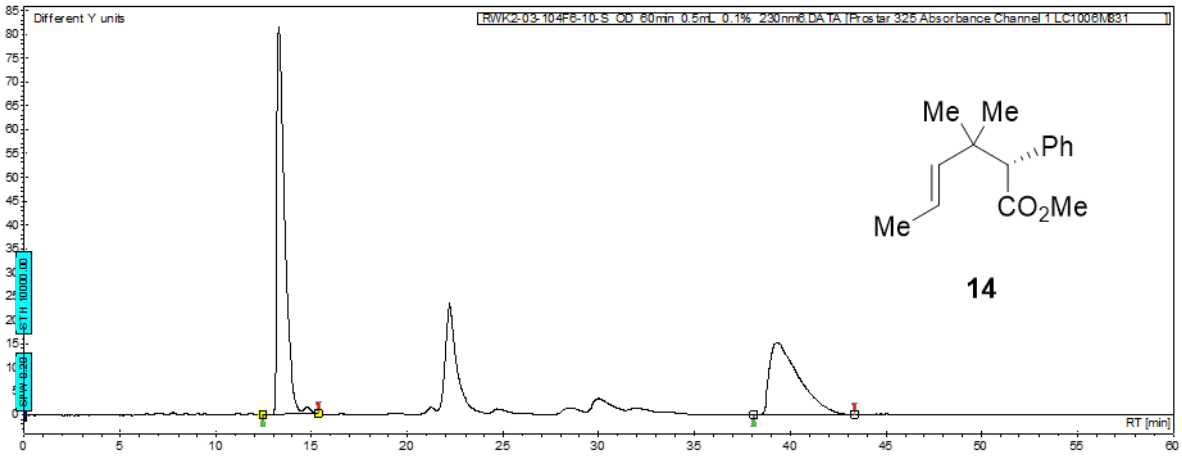
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.24	50.57	95.7	12.3	50.565
2	UNKNOWN	5.32	49.43	77.1	12.1	49.435
Total			100.00	172.7	24.4	100.000



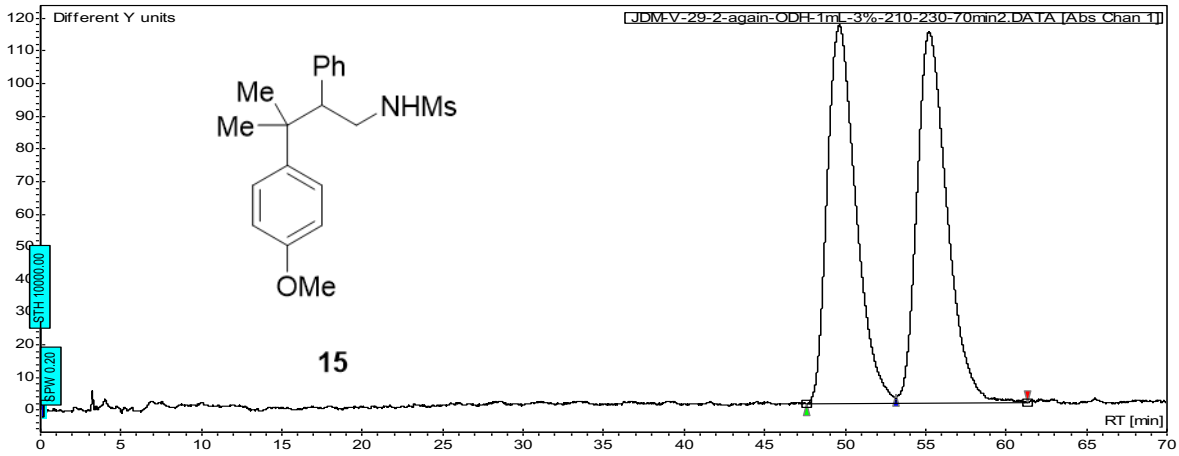
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.09	60.39	50.9	6.7	60.389
2	UNKNOWN	5.11	39.61	27.2	4.4	39.611
Total			100.00	78.1	11.0	100.000



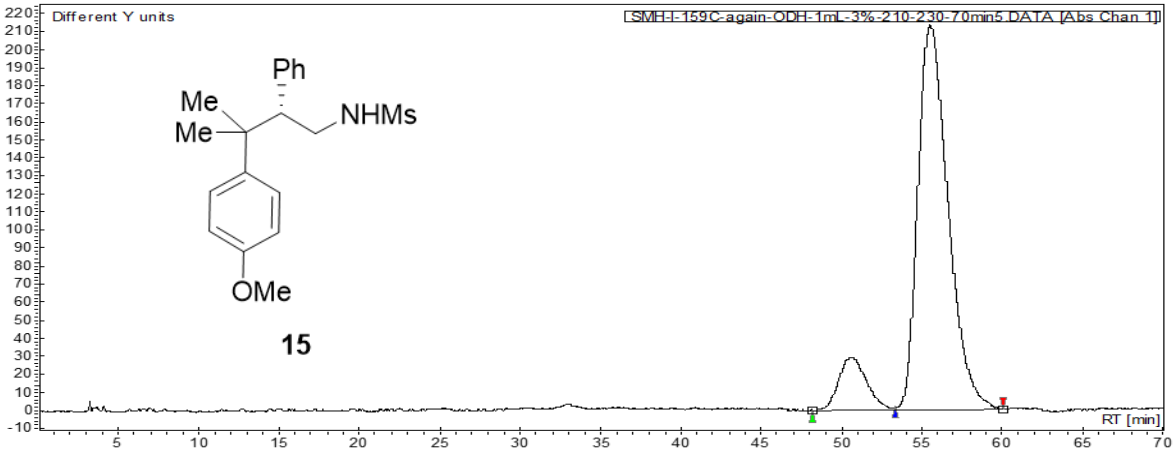
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.15	50.47	104.8	52.2	50.468
2	UNKNOWN	38.41	49.53	24.7	51.2	49.532
Total			100.00	129.5	103.4	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.31	59.84	81.5	39.5	59.836
2	UNKNOWN	39.30	40.16	15.1	26.5	40.164
Total			100.00	96.6	65.9	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	49.64	49.25	116.0	240.1	49.254
2	UNKNOWN	55.18	50.75	113.6	247.4	50.746
Total			100.00	229.7	487.4	100.000



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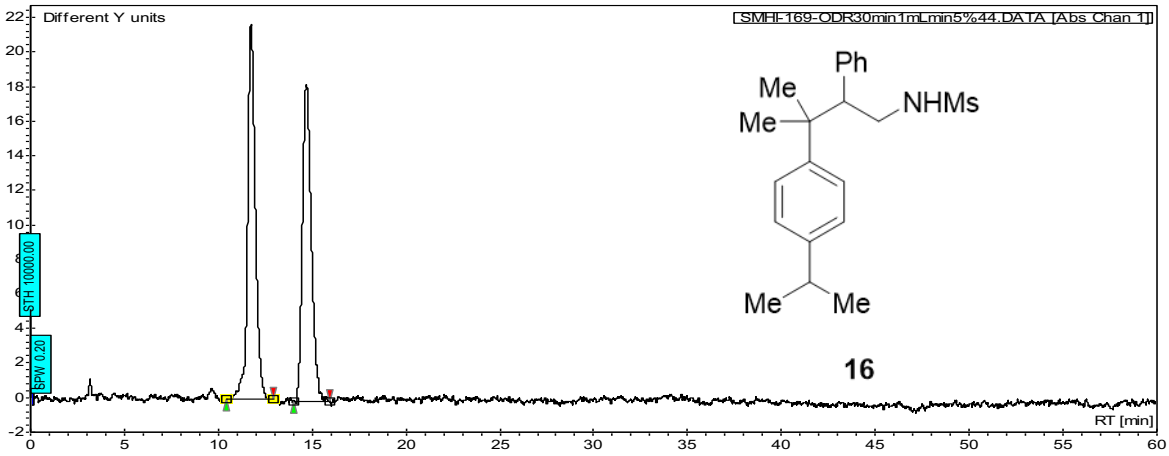
1	UNKNOWN	50.63	11.30	29.5	59.5	11.296
2	UNKNOWN	55.52	88.70	213.8	467.1	88.704
Total			100.00	243.4	526.5	100.000



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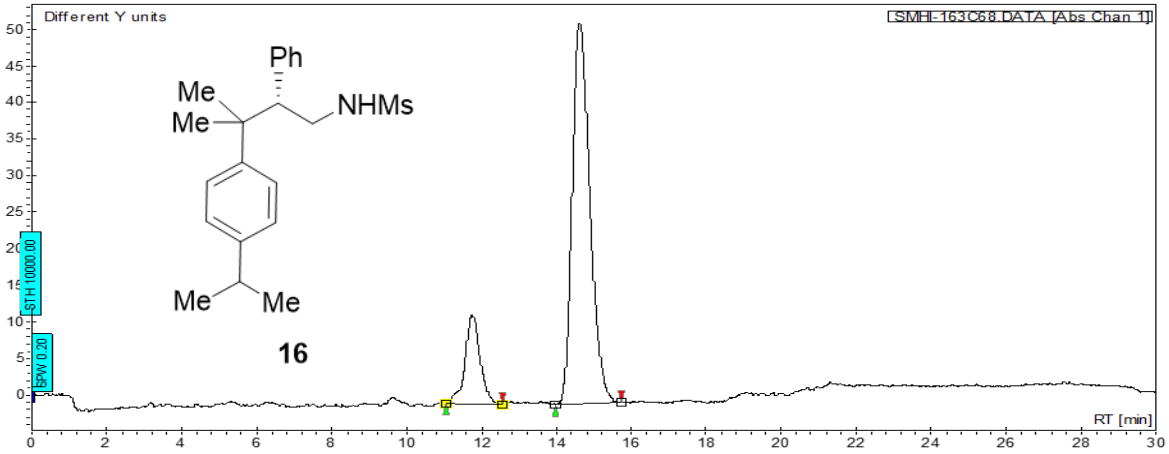
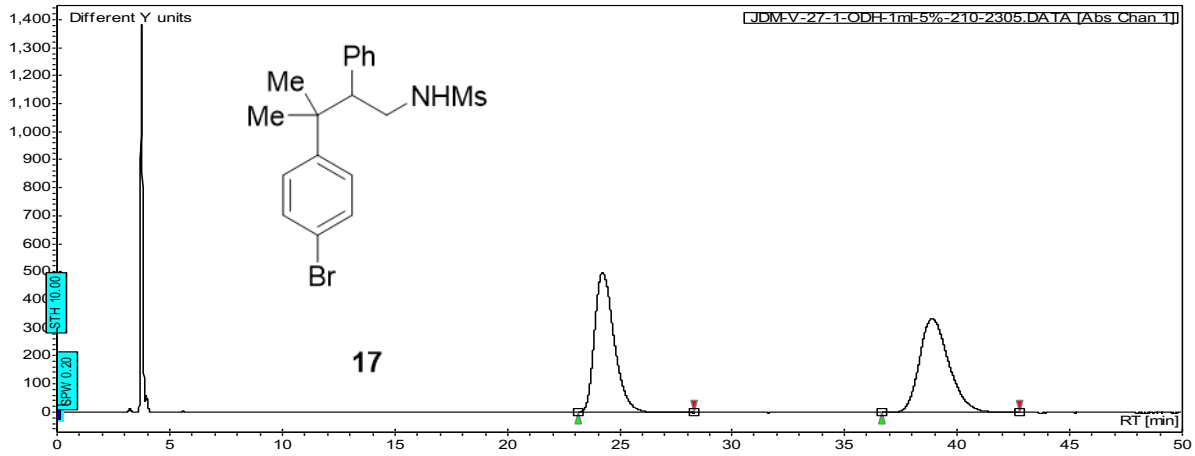
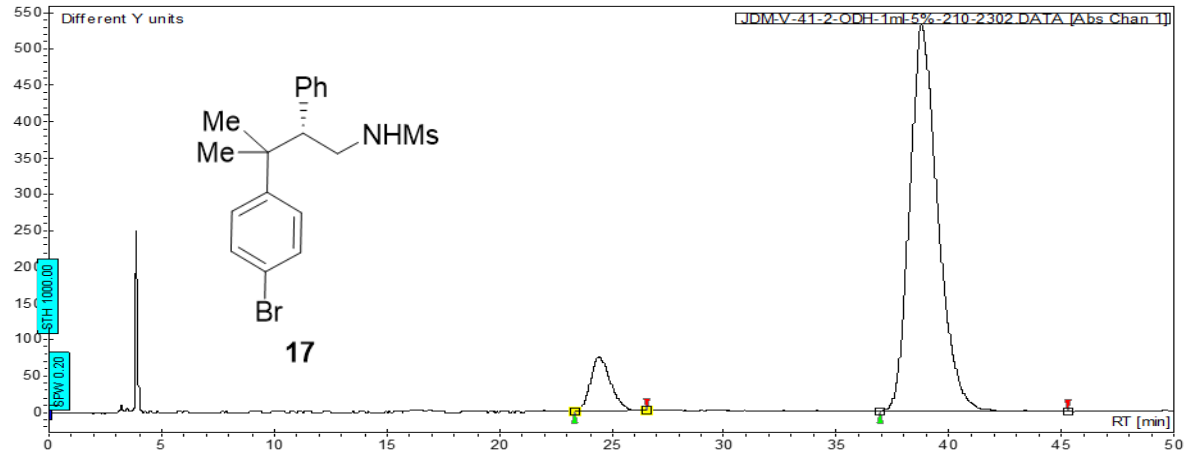
1	UNKNOWN	11.74	50.57	21.7	10.3	50.566
2	UNKNOWN	14.68	49.43	18.3	10.1	49.434
Total			100.00	40.0	20.4	100.000



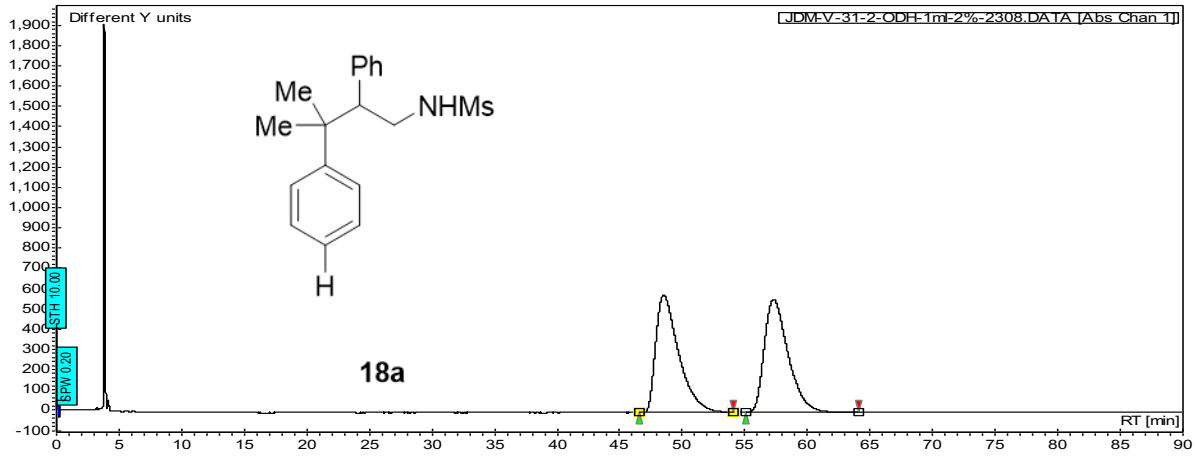
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.75	16.65	12.2	5.7	16.649
2	UNKNOWN	14.62	83.35	52.0	28.4	83.351
Total			100.00	64.2	34.1	100.000



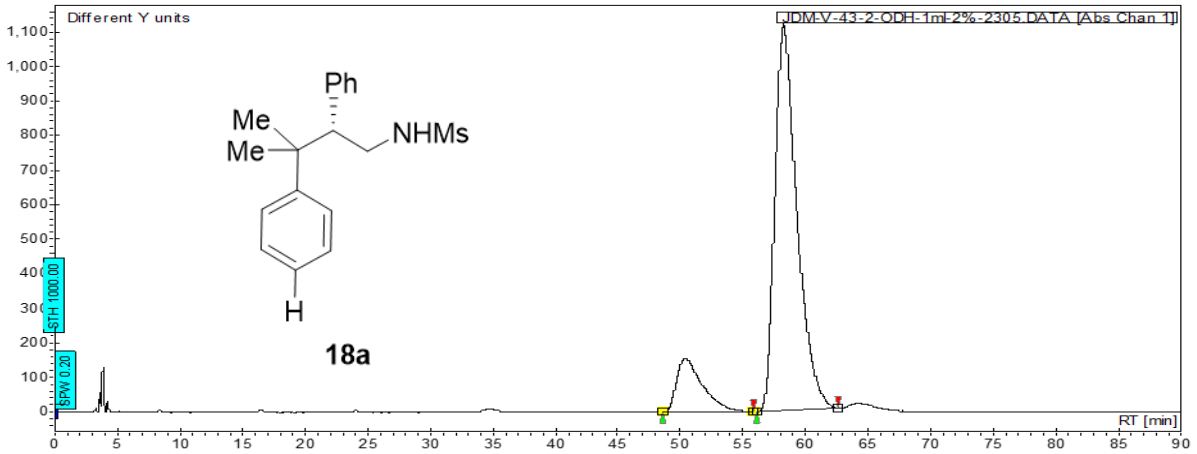
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	24.24	49.77	500.3	505.9	49.766
2	UNKNOWN	38.88	50.23	334.1	510.6	50.234
Total			100.00	834.4	1016.5	100.000



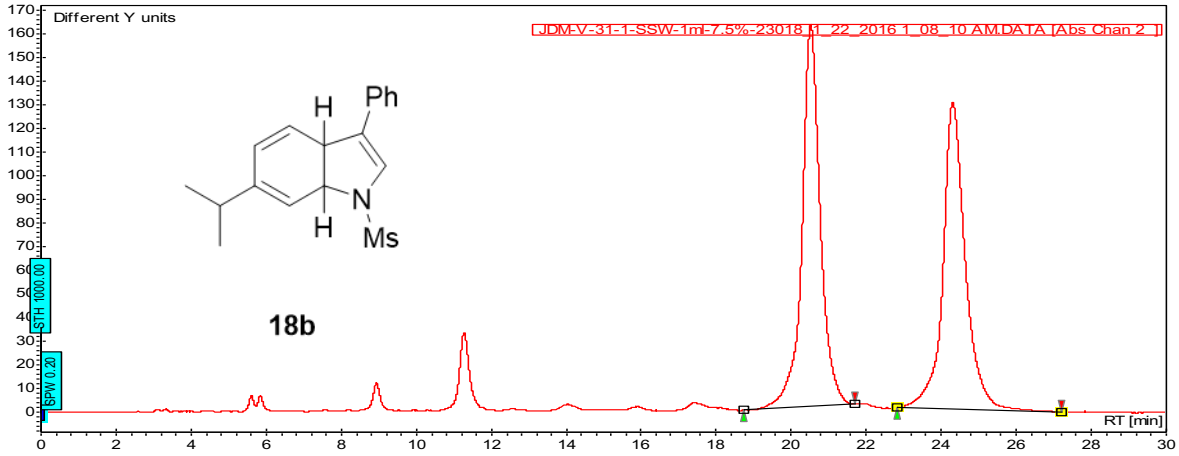
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	24.44	9.10	73.8	77.1	9.100
2	UNKNOWN	38.76	90.90	531.1	770.0	90.900
Total			100.00	604.9	847.1	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	48.49	50.11	578.3	1232.3	50.106
2	UNKNOWN	57.28	49.89	557.4	1227.1	49.894
Total			100.00	1135.7	2459.4	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	50.37	13.90	155.9	368.0	13.895
2	UNKNOWN	58.21	86.10	1117.6	2280.5	86.105
Total			100.00	1273.4	2648.6	100.000



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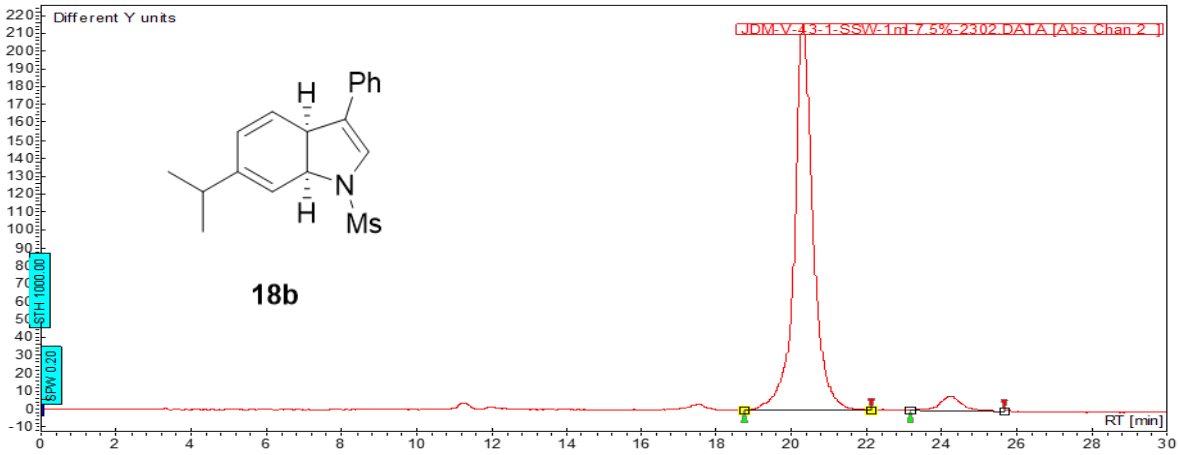
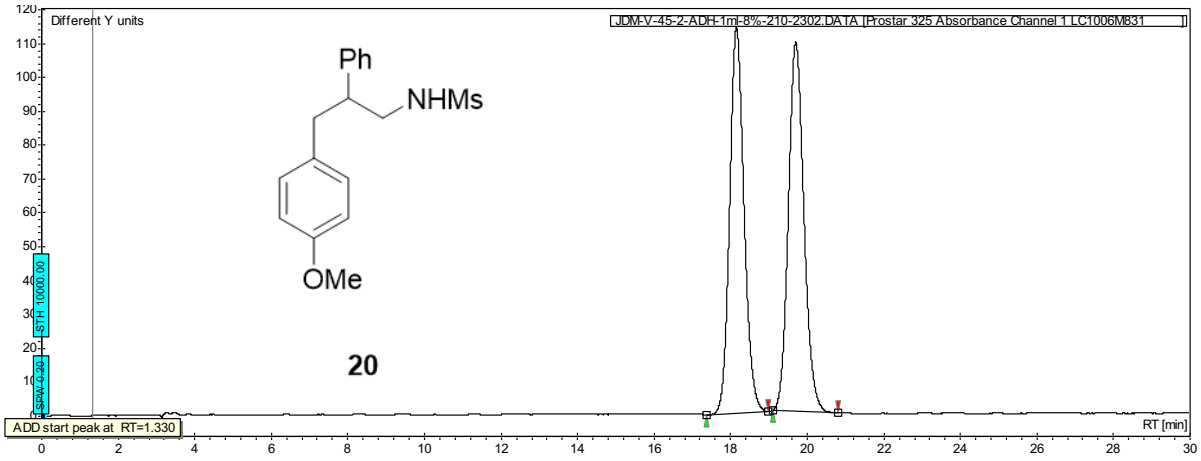
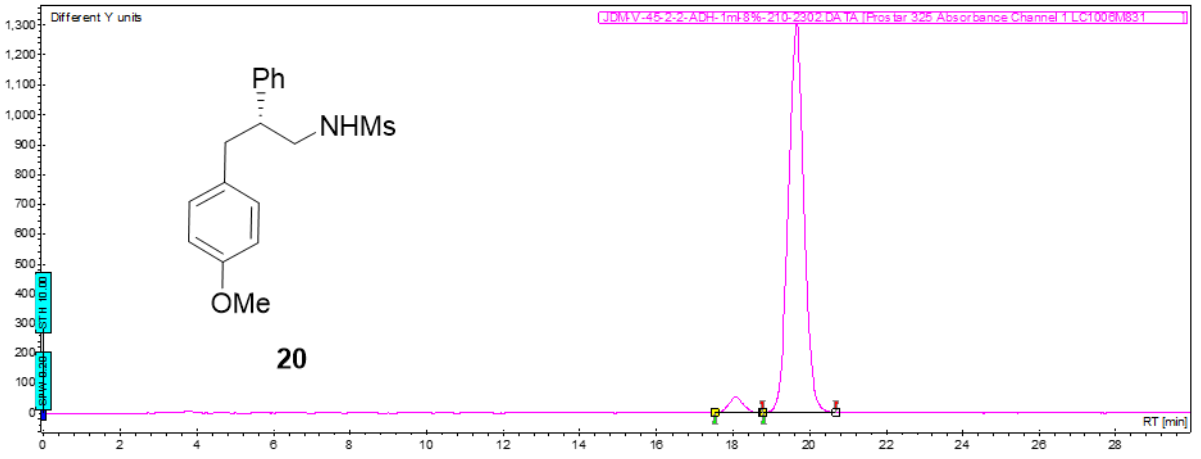
2	UNKNOWN	20.52	50.46	161.5	91.6	50.458
1	UNKNOWN	24.31	49.54	129.8	90.0	49.542
Total			100.00	291.2	181.6	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.30	95.90	215.3	124.0	95.898
2	UNKNOWN	24.23	4.10	8.2	5.3	4.102
Total			100.00	223.5	129.3	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.15	49.13	113.9	49.6	49.134
2	UNKNOWN	19.70	50.87	109.1	51.4	50.866
Total			100.00	223.1	101.0	100.000



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.06	3.49	52.1	22.4	3.495
2	UNKNOWN	19.66	96.51	1300.5	619.6	96.505
Total			100.00	1352.6	642.1	100.000