Table of Contents

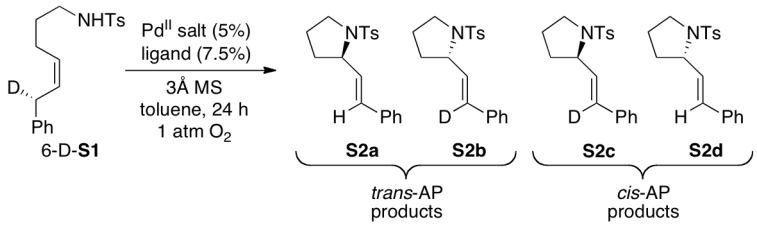
I. General Considerations

All commercially available compounds were purchased and used as received, unless otherwise noted. Solvents were dried over alumina columns prior to use; however, purification and drying of commercial solvents is not required for the catalytic reactions described here. ^{1}H and ^{13}C NMR spectra were recorded on Bruker or Varian 300 MHz spectrometers, or Varian 500 and 600 MHz spectrometers, and chemical shifts are given in parts per million relative to internal tetramethylsilane (0.00 ppm for ^{1}H) or $CDCl_3$ (77.23 ppm for ^{13}C). Chiral HPLC analysis and separations were carried out with a Shimadzu analytical HPLC system with a commercial Chiralcel column (OJ-H). Flash chromatography was performed using SiliaFlash® P60 (Silicycle, particle size 40-63 um, 230-400 mesh) or activated basic aluminum oxide (Brockmann I, standard grade, particle size 58Å, ~150 mesh) from Sigma Aldrich. Some chromatography was carried out using a CombiFlash Rf® system with reusable high performance silica columns (RediSep® Rf Gold Silica, 20-40 um spherical particles).

II. Experimental procedures and data for the determination of *trans*- vs. *cis*-AP

The catalytic aerobic oxidation reactions described in this report were carried out using a custom reaction apparatus that enabled several reactions to be performed simultaneously under a constant pressure of O_2 (approx 1 atm) with controlled temperature and orbital agitation. A control experiment demonstrated that similar results could be obtained using a standard round-bottom flask equipped with a stir bar and a balloon of O_2 (see previous publication[1]).

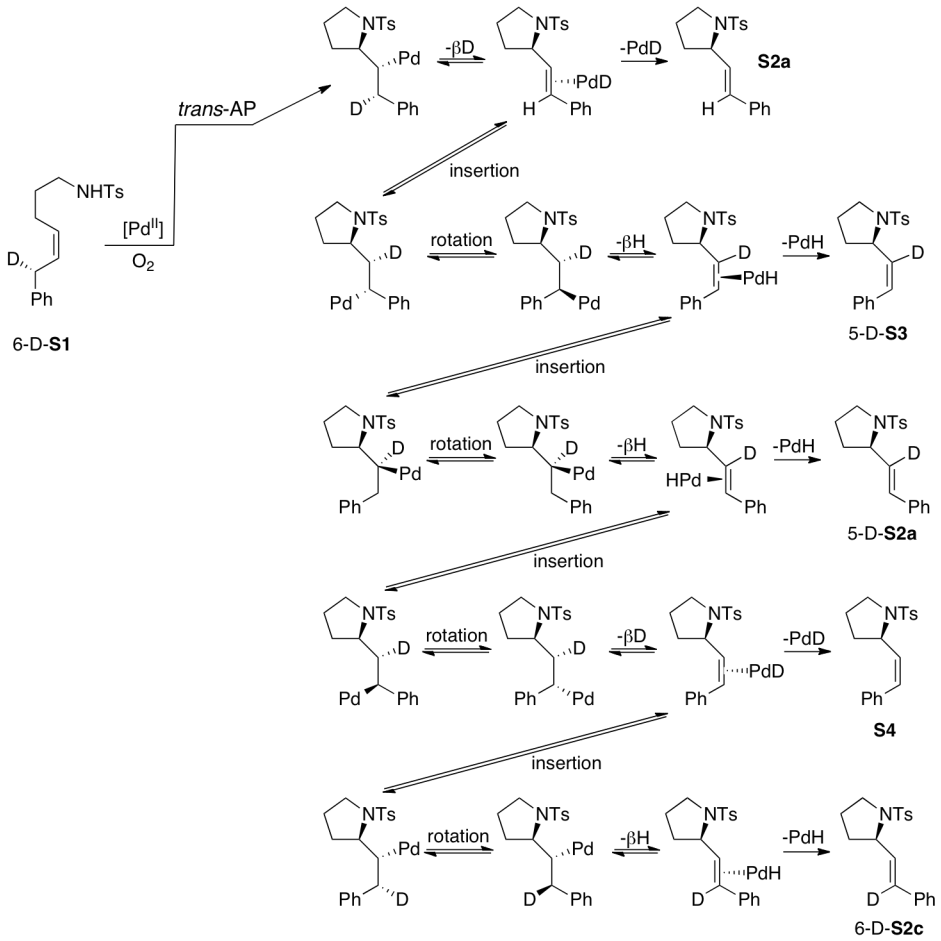
General procedure for catalytic aerobic oxidation reactions:



PdX_2 (0.00375 mmol, 0.05 equiv) and powdered 3Å molecular sieves (20 mg, 267 mg/mmol substrate) were weighed into a 10 ml glass vial (note: the powdered 3Å molecular sieves were stored on the benchtop; activation and glovebox storage was note required to achieve the beneficial effect[2]). The vial was placed in a custom parallel reactor and the headspace was purged with O_2 for 10 min and temperature set to be maintained at 23 °C. A 0.35 ml solution of ligand in toluene was added by syringe (0.0056 mmol, 0.075 equiv) and the reaction apparatus was set to shake vigorously for 15 min. A 0.4 ml solution of substrate in toluene was added by syringe (0.075 mmol, 1 equiv) and the reaction apparatus was set to shake vigorously for 24 hrs. The resulting reaction mixture was filtered over a plug of basic alumina, eluting with EtOAc and then concentrated. The material was analyzed by ^{1}H NMR using $CDCl_3$ spiked with an internal standard to determine yields. The mixture of products and residual starting material was then purified over basic alumina using 3:1 hexanes:EtOAc. The purified mixture of isotopologue/enantiomeric products was analyzed by ^{1}H NMR, ^{2}H NMR and chiral HPLC. HPLC conditions were the same as described in our previous report[1] (Chiralcel OJ-H, 15% iPrOH, 1 ml/min, 230 nm). Enantiomers were separated using the analytical chiral HPLC set up: the two desired peaks were collected manually into distinct test tubes by diverting the material eluting from the detector. Each peak was collected over five HPLC runs in order to obtain tens of micrograms of material, which was analyzed in a Shigemi tube on a 600 MHz NMR and by ESI-MS. For a depiction of potential isomerization pathways that could complicate interpretation of experimental results, see Scheme S1. The ^{2}H NMR analysis of the purified mixture of isotopologue/enantiomeric products was used as a measure of the extent of isomerization (only trace amounts of isomerization to 5-D-**S2a** was detected in each experiment presented in Table 2). For presentation of the raw data collected using substrate probe 6-D-**S1**, see Schemes S2-S8.

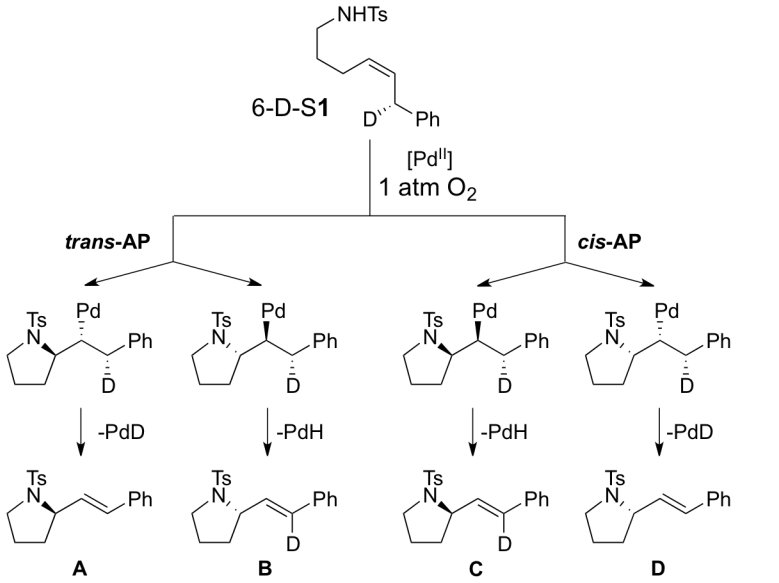
[1] McDonald, R. I.; White, P. B.; Weinstein, A. B.; Tam, C. P.; Stahl, S. S. *Org. Lett.* **2011**, *13*,
[2] Steinhoff, B. A.; King, A. E.; Stahl, S. S. *J. Org. Chem.* **2006**, *71*, 1861-1868.

Scheme S1. Potential isomerizations when using substrate probe 6-D-**S1**.



Scheme S2. Application of novel deuterated substrate probe

A. Mixture of four products derived from substrate probe 6-D-S**1**

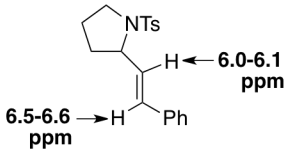


B. Four equations / four unknowns

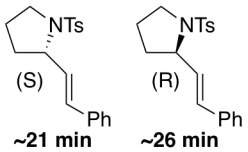
Eq 1.	**a**+**b**+**c**+**d** = 100	Defining **a**, **b**, **c**, **d** as % compositions	*trans*-AP:*cis*-AP (**a**+**b**):(**c**+**d**)
Eq 2.	(**a**+**d**) = x(**b**+**c**)	Isotopic distribution (H:D) of product mixture **a**+**b**+**c**+**d** (^{1}H NMR analysis)	
Eq 3.	(**a**+**c**) = y(**b**+**d**)	Enantiomeric ratio (*R*:*S*) of product mixture **a**+**b**+**c**+**d** (chiral HPLC analysis)	
Eq 4.	**a** = p**c** and/or **b** = q**d**	Isotopic distribution (H:D) of **a**+**c** or **b**+**d** after isolation with chiral HPLC (^{1}H NMR analysis)	

C. Analytical methods and key observables

^{1}H and ^{2}H NMR analysis

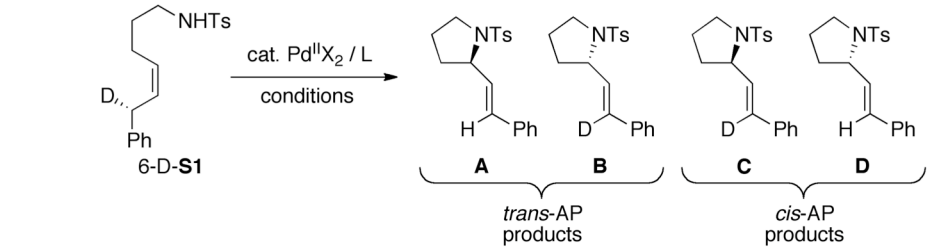


chiral HPLC analysis



~21 min retention **~26 min retention**

Scheme S3: Raw experimental data: $Pd(OAc)_2$ / pyridine catalyst system.



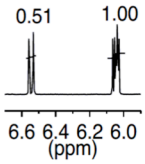
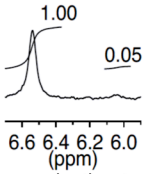
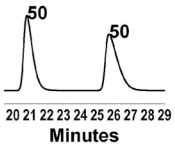
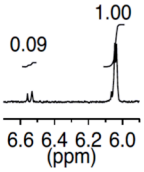
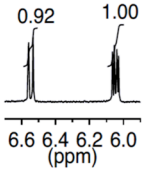
Catalyst system:

5% $Pd(OAc)_2$ / 10% 
toluene, 80 °C,
24 h, 1 atm O_2 (84% yield)

***trans*-AP:*cis*-AP**

(**a**+**b**):(**c**+**d**) = (4+4) : (46+46)

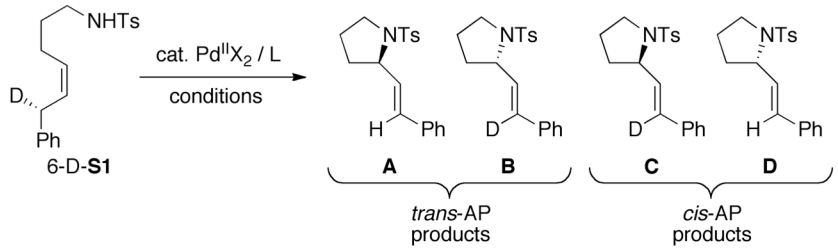
8:92

^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
				
H:D = 50:50 (x=1)	isomerization to 5-D-**S2a** = <5%	e.r. = 50:50 (y=1)	H:D = 9:91 (p=0.1)	92:8 (q=0.09)
			ESI-MS	ESI-MS
			H:D = 8 : 92	H:D = 87 : 13

The above experiment demonstrates that the new substrate probe, 6-D-**S1**, and the protocol for product analysis, are capable of reproducing the previous conclusions obtained from the use of cyclopentenyl substrate probe 3-D-**4** (i.e., the *cis*-AP pathway is favored under these conditions).[3]

[3] G. Liu, S. S. Stahl, *J. Am. Chem. Soc.* **2007**, *129*, 6328-6335.

Scheme S4: Raw experimental data: $Pd(TFA)_2$ / (*S*)-pyrox catalyst system.

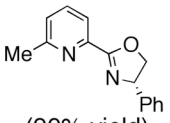


Catalyst system:

5% $Pd(TFA)_2$ / 7.5%

3Å M.S., toluene,

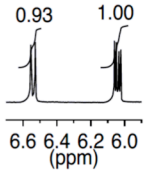
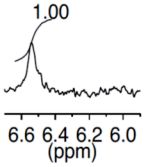
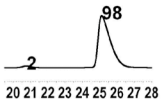
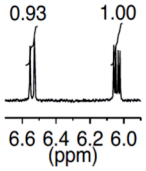
23 °C, 24 h, 1 atm O_2 (90% yield)



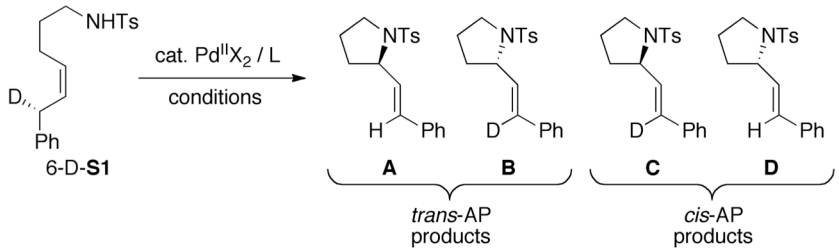
***trans*-AP:*cis*-AP**

(**a**+**b**):(**c**+**d**) = (91+0) : (7+2)

91:9

^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
				minor enantiomer not analyzed
H:D = 93:7 (x=13.3)	isomerization to 5-D-**S2a** = <5%	e.r. = 98:2 (y=49)	H:D = 93:7 (p=13.3) ESI-MS H:D = 89 : 11	nd

Scheme S5: Raw experimental data: $Pd(TFA)_2$ / (*R*)-pyrox catalyst system

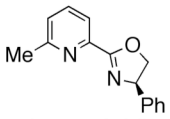


Catalyst system:

5% $Pd(TFA)_2$ / 7.5%

3Å M.S., toluene,

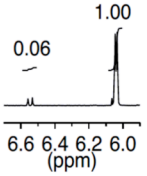
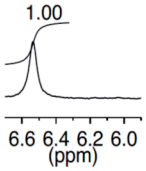
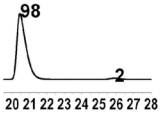
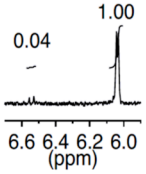
23 °C, 24 h, 1 atm O_2 (93% yield)



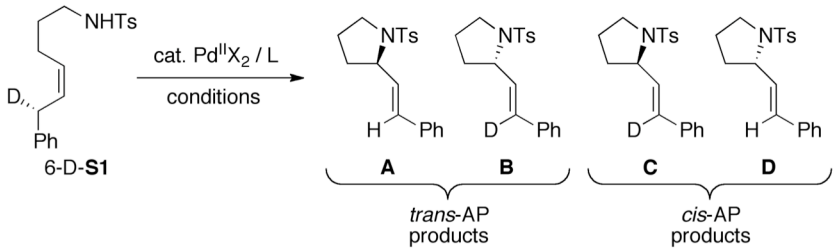
***trans*-AP:*cis*-AP**

(**a**+**b**):(**c**+**d**) = (2+94) : (0+4)

96:4

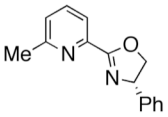
^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
			minor enantiomer not analyzed	
H:D = 6:94 (x=0.06)	isomerization to 5-D-**S2a** = <5%	e.r. = 2:98 (y=0.02)	nd	H:D = 4:96 (q=24) ESI-MS H:D = 8 : 92

Scheme S6: Raw experimental data: $Pd(OAc)_2$ / (*S*)-pyrox catalyst system



Catalyst system:

5% $Pd(OAc)_2$ / 7.5%



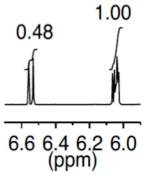
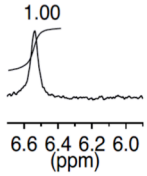
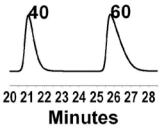
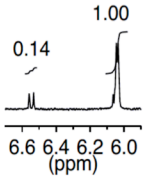
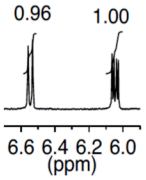
3Å M.S., toluene,

23 °C, 24 h, 1 atm O_2 (48% yield)

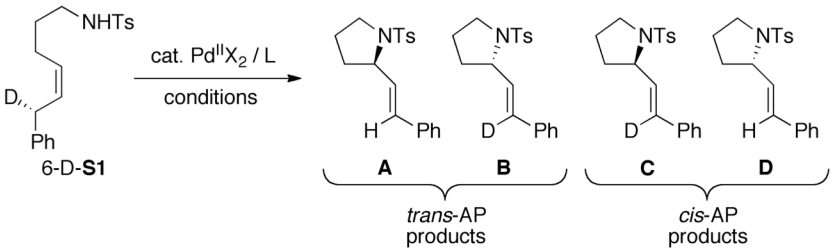
***trans*-AP:*cis*-AP**

(**a**+**b**):(**c**+**d**) = (9+1) : (51+39)

10:90

^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
				
H:D = 48:52 (x=0.92)	isomerization to 5-D-**S2a** = <5%	e.r. = 60:40 (y=1.5)	H:D = 14:86 (p=0.16) ESI-MS H:D = 18 : 82	H:D = 96:4 (q=0.04) ESI-MS H:D = 100 : 0

Scheme S7: Raw experimental data: $Pd(TFA)_2$ / no ligand catalyst system



Catalyst system:

5% $Pd(TFA)_2$ / no ligand

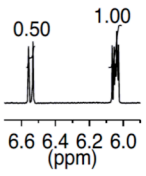
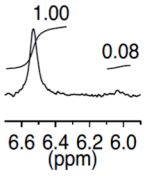
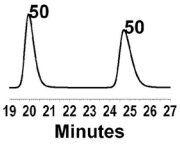
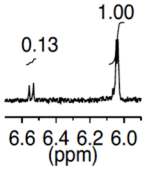
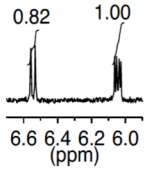
3Å M.S., toluene,

23 °C, 24 h, 1 atm O_2 (55% yield)

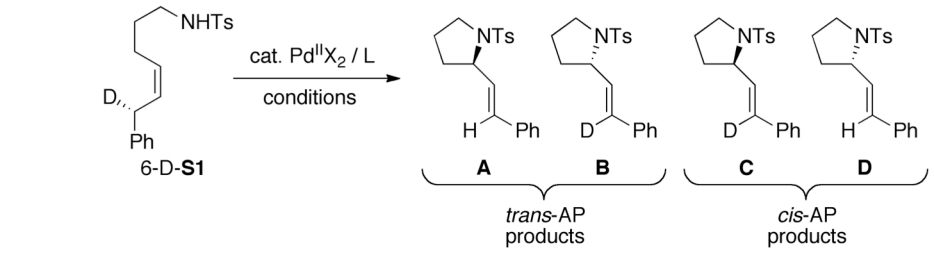
***trans*-AP:*cis*-AP**

(**a**+**b**):(**c**+**d**) = (8+8) : (42+42)

16:84

^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
				
H:D = 50:50 (x=1)	isomerization to 5-D-**S2a** = ~7%	e.r. = 50:50 (y=1)	H:D = 13:87 (p=0.15) ESI-MS H:D = 11 : 89	H:D = 82:18 (q=0.22) ESI-MS H:D = 85 : 15

Scheme S8: Raw experimental data: $Pd(OAc)_2$ / no ligand catalyst system



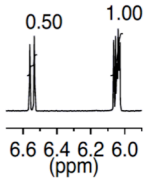
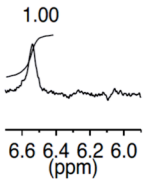
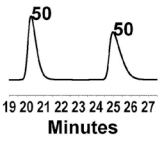
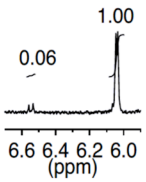
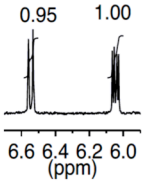
Catalyst system:

5% $Pd(OAc)_2$ / no ligand
3Å M.S., toluene,
23 °C, 24 h, 1 atm O_2 (15% yield)

***trans*-AP:*cis*-AP**

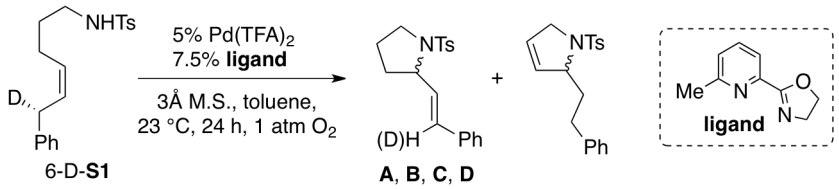
(**a**+**b**):(**c**+**d**) = (3+3) : (47+47)

6:94

^{1}H NMR analysis **A**+**B**+**C**+**D** (for eq 2)	^{2}H NMR analysis **A**+**B**+**C**+**D**	Chiral HPLC analysis **A**+**B**+**C**+**D** (for eq 3)	^{1}H NMR analysis **A**+**C** (for eq 4)	^{1}H NMR analysis **B**+**D** (for eq 4)
				
H:D = 50:50 (x=1)	isomerization to 5-D-**S2a** = <5%	e.r. = 50:50 (y=1)	H:D = 6:94 (p=0.06)	H:D = 95:5 (q=0.05)
			ESI-MS	ESI-MS
			H:D = 8 : 92	H:D = 89 : 11

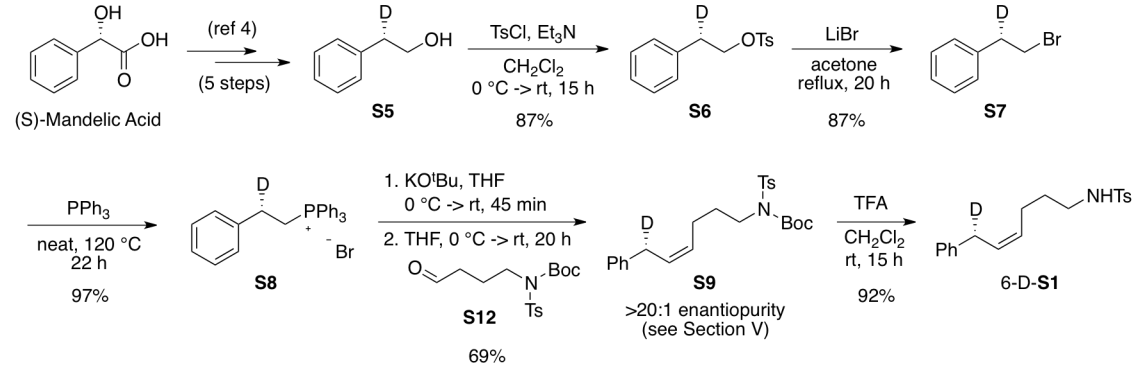
We were intrigued by the prospect of systematically studying the effect of the pyrox ligand structure on the amidopalladation pathway selectivity, and so an experiment in which the substrate probe was subjected to conditions with a pyrox ligand lacking a substituent on the oxazoline fragment was attempted (Scheme S9). Unfortunately, significant alkene isomerization associated with β-hydride elimination was observed (a 5:1 mixture of alkene isomers was isolated in 58% yield). This degree of isomerization prevents reliable interpretation of the result (cf. Scheme S1). This finding highlights the limitations of the experimental design presented in this work.

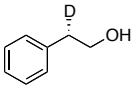
Scheme S9: Attempt to study reactivity with modified pyrox ligand.



58% yield
isolated as a 5:1 mixture of alkene isomers (favoring styrene)

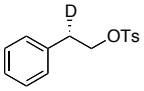
III. Stereoselective synthesis of deuterium labeled substrate probe





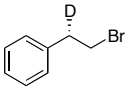
S5

Stereoselectively deuterated phenethanol **S5** was synthesized in five steps from commercially available (*S*)-Mandelic acid using known procedures. Characterization data matched the literature report.[4]



S6

A 250 ml round-bottom flask was charged with a stir bar and alcohol **S5** (608 mg, 4.94 mmol, 1 equiv), and then taken up in 49 ml of dichloromethane (0.1 M). The reaction mixture was submerged in an ice bath. Triethylamine (2.56 ml, 18.3 mmol, 3.7 equiv) was added via syringe, followed by *p*-toluenesulfonyl chloride (1.505 g, 7.9 mmol, 1.6 equiv). The reaction mixture was allowed to warm to room temperature and stir for 15 h. The pale yellow solution was washed twice with 2M HCl, then with saturated sodium bicarbonate solution, and then with brine. The organic layer was dried over $MgSO_4$ and concentrated to orange-yellow oil. Purification on silica with 9:1 hexanes : ethyl acetate afforded 1.198 g of tosylate **S6** as a clear oil (87% yield), which solidified at reduced temperature. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.33 – 7.18 (m, 5H), 7.14 – 7.06 (m, 2H), 4.20 (dt, J = 7.1, 0.9 Hz, 2H), 2.94 (ddd, J = 7.2, 5.2, 2.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 144.83, 136.34, 133.15, 129.95, 129.06, 128.75, 127.99, 127.03, 70.73, 35.19 (t, $J_{C\text{-}D}$ = 19.5 Hz), 21.79.

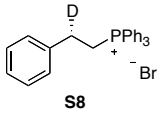


S7

This procedure was adapted from literature precedence.[5] A 50 ml round-bottom flask was charged with a stir bar and tosylate S6 (1.198 g, 4.32 mmol, 1 equiv), and taken up in 11 ml of acetone (0.4 M). Lithium bromide (1.876 g, 21.6 mmol, 5 equiv) was added in one portion, and the reaction mixture was heated to reflux for 20 h. After allowing to cool to room temperature, the reaction mixture was partitioned between 150 ml dichloromethane and 150 ml water. The

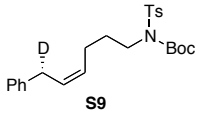
[4] M. N. Alberti, G. Vassilikogiannakis, M. Orfanopoulos, *Org. Lett.* **2008**, *10*, 3997-4000.
[5] J. Novak, I. Linhart, H. Dvorakova, V. Kubelka, *Org. Lett.* **2003**, *5*, 637-639.

aqueous layer was extracted once with additional dichloromethane, and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to a clear liquid. Purification on silica with hexanes afforded 700 mg of bromide **S7** as a clear liquid (87% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.40 – 7.09 (m, 5H), 3.56 (dt, J = 7.6, 1.1 Hz, 2H), 3.23 – 3.03 (m, 1H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 139.07, 128.86, 128.82, 127.13, 39.31 (t, $J_{C\text{-}D}$ = 19.5 Hz), 33.04; HRMS (ESI) calculated for $C_8H_8DBr^+$ $[M]^+$ requires *m/z* 184.9945, found 184.9938.



S8

This procedure was adapted from literature precedence.[6] A 5 ml thick walled pressure tube was charged with a stir bar and bromide **S7** (700 mg, 3.76 mmol, 1 equiv). Triphenylphosphine (987 mg, 3.76 mmol, 1 equiv) was added in one portion, and the vessel was sealed and heated to 120 °C behind a blast shield for 22 h. The resulting viscous oil was dried under vacuum at 105 °C for several hours, affording 1.635 g of a hard, glassy solid (97% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.94 – 7.74 (m, 10H), 7.74 – 7.62 (m, 5H), 7.36 – 7.12 (m, 5H), 4.28 – 4.16 (m, 2H), 3.06 (dt, J = 14.5, 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.23 (d, $J_{C\text{-}P}$ = 12.8 Hz), 135.24, 133.68 (d, $J_{C\text{-}P}$ = 9 Hz), 130.67 (d, $J_{C\text{-}P}$ = 12 Hz), 128.84 (d, $J_{C\text{-}P}$ = 18.8 Hz), 127.17, 118.69, 117.55, 28.12 (t, $J_{C\text{-}D}$ = 19.5 Hz), 24.76 (d, $J_{C\text{-}P}$ = 48 Hz); HRMS (ESI) calculated for $C_{26}H_{23}DP^+$ $[M\text{-}Br]^+$ requires *m/z* 368.1673, found 368.1682.



S9

This procedure was adapted from literature precedence.[1] Wittig salt **S8** was scraped to a white powder and added to a dry 100 ml round bottom flask with a stir bar (776 mg, 1.73 mmol, 1 equiv) under an atmosphere of N_2. Dry THF (10 ml) was added via syringe, and the reaction mixture was cooled to 0 °C. A solution of potassium *tert*-butoxide (2.0 ml of a 0.93 M solution in THF, 1.9 mmol, 1.1 equiv) was added dropwise via syringe. The mixture was allowed to stir at 0 °C for 15 min, then at room temperature for 45 min. The red-orange mixture was cooled back down to 0 °C, and a solution of aldehyde **S12** (886 mg, 2.6 mmol, 1.5 equiv) in 5 ml of dry THF was added dropwise via syringe (see below for synthesis of **S12**). The mixture was allowed to warm to room temperature and stir for 20 h. The pale yellow mixture was partitioned between 100 ml diethyl ether and 100 ml water. The aqueous layer was extracted an additional two times with diethyl ether, and the combined organics were washed with brine, dried over $MgSO_4$, and concentrated to oil (~9:1 mixture of *cis*:*trans* alkene products present). Purification on silica using 19:1 → 9:1 hexanes : ethyl acetate as the solvent system afforded 518 mg of **S9** as a clear oil (69% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 5.70 – 5.44 (m, 2H), 3.88 – 3.80 (m, 2H), 3.39 (d, J = 6.1 Hz, 1H), 2.44 (s, 3H), 2.23 (q, J = 7.3 Hz, 2H), 1.87 (p, J = 7.5 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 151.16, 144.23, 141.08, 137.71, 129.54, 129.43, 129.24, 128.64, 128.53, 128.00, 126.08, 84.31, 47.03, 33.38 (t, $J_{C\text{-}D}$ = 19.5 Hz), 30.25, 28.09, 24.74, 21.81; HRMS (ESI) calculated for $C_{24}H_{30}DNO_4SNa^+$ $[M+Na]^+$ requires *m/z* 453.1929, found 452.1942.

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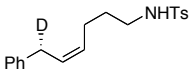
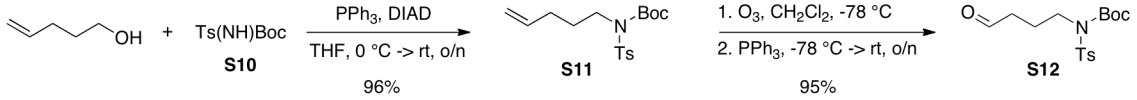
[6] Y. S. Angelis, M. Orfanopoulos, *J. Org. Chem.* **1997**, *62*, 6083-6085.

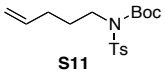


6-D-**S1**

This procedure was adapted from literature precedence.[7] A 100 ml round bottom flask was charged with a stir bar, protected amine **S9** (515 mg, 1.2 mmol, 1 equiv) and 20 ml of dichloromethane (0.06 M). Trifluoroacetic acid (0.92 ml, 12 mmol, 10 equiv) was added cautiously via syringe. The mixture was allowed to stir for 15 h at room temperature. The mixture was quenched with saturated sodium bicarbonate solution and partitioned between 50 ml of dichloromethane and 50 ml saturated sodium bicarbonate solution. The organic layer was washed with an additional volume of saturated sodium bicarbonate solution, then brine, and then dried over $MgSO_4$ and concentrated to oil. Purification on silica with 4:1 hexanes : ethyl acetate afforded 364 mg of 6-D-**S1** as a clear oil (92% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.10 (m, 3H), 5.59 (dd, *J* = 10.6, 7.7 Hz, 1H), 5.41 (dddd, *J* = 10.8, 8.8, 6.9, 1.5 Hz, 1H), 4.30 (t, *J* = 6.3 Hz, 1H), 3.32 (d, *J* = 6.9 Hz, 1H), 2.97 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.14 (q, *J* = 6.9 Hz, 2H), 1.57 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 143.56, 140.93, 137.18, 129.90, 129.52, 129.29, 128.66, 128.45, 127.28, 126.14, 43.05, 33.28 (t, $J_{C\text{-}D}$ = 19.5 Hz), 29.72, 24.52, 21.72; HRMS (ESI) calculated for $C_{19}H_{22}DNO_2SNa^+$ $[M+Na]^+$ requires *m/z* 353.1405, found 353.1391.

IV. Synthesis of protio intermediates and analogues





S11

Procedure adapted from literature precedence.[7] Triphenylphosphine (1.967 g, 7.5 mmol, 1.5 equiv) and **S10**[8] (1.899 g, 7 mmol, 1.4 equiv) were weighed into a 250 ml round bottom flask equipped with a stir bar and placed under an atmosphere of N_2. Dry THF (29 ml, 0.17 M) was added via syringe, followed by 4-penten-1-ol (0.52 ml, 5 mmol, 1 equiv). The reaction mixture was cooled to 0 °C in an ice bath, and diisopropyl azodicarboxylate (1.23 ml, 6.25 mmol, 1.25 equiv) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirred for 20 h. The reaction mixture was concentrated to oil and purified on silica with 10:1 → 8:1 hexanes : ethyl acetate to afford 1.634 g of **S11** as a clear oil that solidified at reduced temperature (96% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.84 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.00 (ddd, *J* = 10.2, 3.1, 1.2 Hz, 1H), 3.86 – 3.78 (m, 2H), 2.44 (s, 3H), 2.13 (q, *J* = 7.2 Hz, 3H), 1.86 (p, *J* = 7.5 Hz, 2H), 1.33 (s, 8H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 151.12, 144.20, 137.64, 129.39, 127.94, 115.38, 84.26, 46.93, 31.04, 29.38, 28.05, 21.75; HRMS (ESI) calculated for $C_{17}H_{25}NO_4SNa^+$ $[M+Na]^+$ requires *m/z* 362.1397, found 362.1390.

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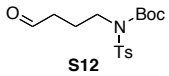
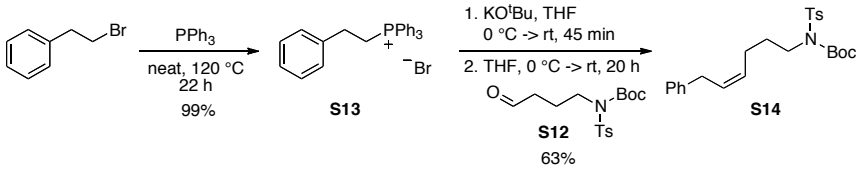
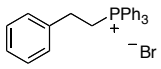
[7] W. E. Brenzovich, D. Benitez, A. D. Lackner, H. P. Shunatona, E. Tkatchouk, W. A. Goddard, D. F. Toste, *Angew. Chem. Int. Ed.* **2010**, *49*, 5519-5522; *Angew. Chem.* **2010**, *122*, 5651-5654.
[8] B. R. Neustadt, *Tet. Lett.* **1994**, *25*, 379-380.



S12

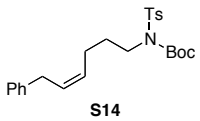
Starting alkene **S11** (1.162 g, 3.42 mmol, 1 equiv) was dissolved in 34 ml of dichloromethane in a 250 ml 3-neck flask equipped with a stir bar. The solution was cooled to -78 °C in a dry ice / acetone bath. An ozone generator was used to bubble ozone through the reaction mixture. After 10 min, the solution took on a characteristic lavender color. The ozone generator was turned off and O_2 was bubbled through the reaction mixture until the color disappeared (about 5 minutes). Triphenylphosphine (1.35 g, 5.13 mmol, 1.5 equiv) was added slowly and the reaction mixture was allowed to slowly warm to room temperature overnight, 15 h. The reaction mixture was concentrated to oil and purified on silica with 3:1 hexanes : ethyl acetate, affording 1.109 g of aldehyde **S12** as a clear oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 9.82 (t, J = 1.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.98 – 3.80 (m, 2H), 2.58 (td, J = 7.2, 1.1 Hz, 2H), 2.09 (p, J = 7.3 Hz, 2H), 1.34 (s, 10H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 201.43, 177.92, 151.16, 144.47, 137.44, 129.50, 127.99, 84.68, 46.48, 40.95, 31.08, 28.08, 25.27, 22.79, 21.82; HRMS (ESI) calculated for $C_{16}H_{23}NO_5SNa^+$ $[M+Na]^+$ requires *m/z* 364.1190, found 364.1183.





S13

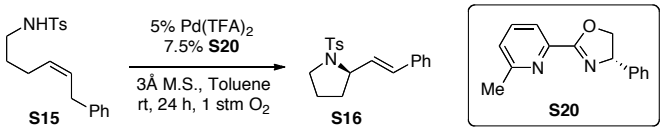
This procedure was reproduced from literature precedence.[6] A 5 ml thick walled pressure tube was charged with a stir bar and (2-bromoethyl)benzene (1.371 g, 7.41 mmol, 1 equiv). Triphenylphosphine (1.943 mg, 7.41 mmol, 1 equiv) was added in one portion, and the vessel was sealed and heated to 120 °C behind a blast shield for 22 h. The resulting viscous oil was dried under vacuum at 105 °C for several hours, affording 3.286 g of a hard, glassy solid (99% yield). Characterization data matched literature precedence. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 6H), 7.83 – 7.74 (m, 3H), 7.74 – 7.62 (m, 6H), 7.50 – 7.38 (m, 1H), 7.34 – 7.12 (m, 4H), 4.27 (ddd, J = 12.6, 8.3, 7.2 Hz, 2H), 3.08 (dt, J = 13.1, 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.33 (d, $J_{C\text{-}P}$ = 12.8 Hz), 135.24 (d, $J_{C\text{-}P}$ = 3 Hz), 133.94 (d, $J_{C\text{-}P}$ = 9.75 Hz), 130.66 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 17.3 Hz), 127.20, 118.83, 117.69, 28.54, 28.50, 24.89 (d, $J_{C\text{-}P}$ = 48 Hz); HRMS (ESI) calculated for $C_{26}H_{24}P^+$ $[M\text{-}Br]^+$ requires *m/z* 367.1611, found 367.1606.



S14

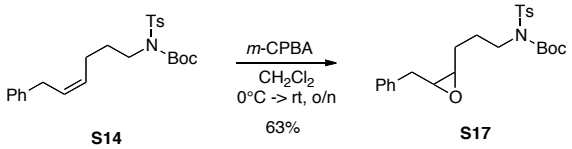
This procedure was adapted from literature precedence.[1] Wittig salt **S13** was scraped to a white powder and added to a dry 100 ml round bottom flask with a stir bar (502 mg, 1.12 mmol, 1 equiv) under an atmosphere of N_2. Dry THF (8 ml) was added via syringe, and the reaction mixture was cooled to 0 °C. A solution of potassium *tert*-butoxide (1.28 ml of a 0.96 M solution in THF, 1.23 mmol, 1.1 equiv) was added dropwise via syringe. The mixture was allowed to stir

at 0 °C for 15 min, then at room temperature for 45 min. The red-orange mixture was cooled back down to 0 °C, and a solution of aldehyde **S12** (575 mg, 1.68 mmol, 1.5 equiv) in 3 ml of dry THF was added dropwise via syringe. The mixture was allowed to warm to room temperature and stir for 20 h. The pale yellow mixture was partitioned between 100 ml diethyl ether and 100 ml water. The aqueous layer was extracted an additional two times with diethyl ether, and the combined organics were washed with brine, dried over $MgSO_4$, and concentrated to oil (~9:1 mixture of *cis*:*trans* alkene products present). Purification on silica using 19:1 → 9:1 hexanes : ethyl acetate as the solvent system afforded 301 mg of **S14** as a clear oil (63% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.34 – 7.24 (m, 4H), 7.22 – 7.16 (m, 3H), 5.69 – 5.47 (m, 2H), 3.89 – 3.80 (m, 2H), 3.41 (d, J = 6.7 Hz, 2H), 2.43 (s, 3H), 2.23 (q, J = 7.0 Hz, 2H), 1.87 (p, J = 7.5 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 151.16, 144.23, 141.12, 137.73, 129.53, 129.43, 129.28, 128.63, 128.53, 128.00, 126.07, 84.30, 47.04, 33.70, 30.25, 28.09, 24.74, 21.80; HRMS (ESI) calculated for $C_{24}H_{35}N_2O_4S^+$ $[M+NH_4]^+$ requires *m/z* 447.2313, found 447.2311.



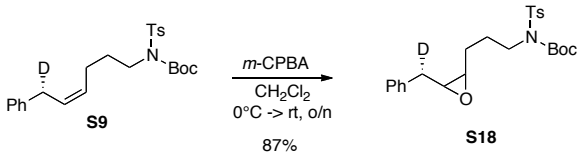
Substrate **S15** and pyrrolidine **S16** could be synthesized as previously described. Characterization data matched previous reports.[1]

V. Characterization of stereochemical purity of the deuterated substrate probe



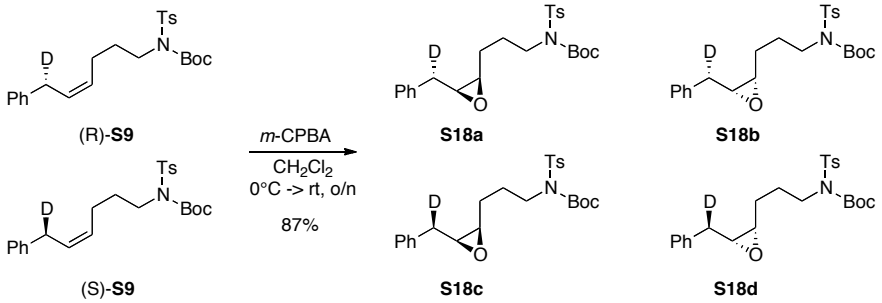
This procedure was adapted from literature precedence.[9] A 25 ml round bottom flask was charged with a stir bar and **S14** (61 mg, 0.142 mmol, 1 equiv) and dissolved in 1 ml of dichloromethane. The reaction vessel was submerged in an ice bath and 3-chloroperbenzoic acid (40 wt%) (122 mg, 0.283 mmol, 2 equiv) was added in one portion. The heterogeneous reaction mixture was allowed to warm to room temperature and stirred for 18 h. The dichloromethane was removed and the reaction mixture was dissolved in ethyl acetate and washed with 1M sodium bisulfite solution, saturated sodium bicarbonate solution, and then brine. The organic layer was dried over $MgSO_4$ and concentrated to an oil, which was purified on silica with 3:1 hexanes : ethyl acetate to afford 40 mg of epoxide **S17** as a clear oil (63% yield). HPLC analysis (Chiralcel, OJ-H, 10% iPrOH, 1 ml, min, 230 nm) achieved separation of enantiomers. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 1H), 7.43 – 7.17 (m, 4H), 4.04 – 3.80 (m, 2H), 3.20 (td, J = 6.3, 4.1 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.93 (dd, J = 14.7, 6.4 Hz, 1H), 2.81 (dd, J = 14.7, 6.2 Hz, 1H), 2.44 (s, 3H), 1.99 (dddd, J = 17.2, 10.8, 6.9, 4.0 Hz, 1H), 1.88 – 1.59 (m, 1H), 1.34 (s, 4H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 151.14, 144.31, 137.96, 137.61, 129.45, 128.99, 128.83, 127.99, 126.74, 84.45, 57.54, 56.95, 46.95, 34.47, 28.07, 27.64, 25.54, 21.79; HRMS (ESI) calculated for $C_{24}H_{35}N_2O_5S^+$ $[M+NH_4]^+$ requires *m/z* 463.2262, found 463.2258.

[9] R. M. Denton, X. Tang, A. Przeslak, *Org. Lett.* **2010**, *12*, 4678-4681.



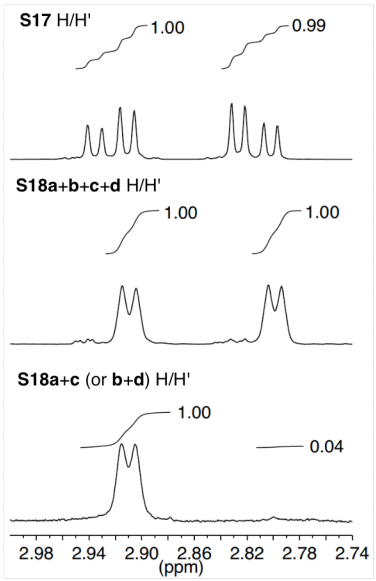
This procedure was adapted from literature precedence.[9] A 25 ml round bottom flask was charged with a stir bar and **S9** (52 mg, 0.12 mmol, 1 equiv) and dissolved in 1 ml of dichloromethane. The reaction vessel was submerged in an ice bath and 3-chloroperbenzoic acid (40 wt%) (104 mg, 0.24 mmol, 2 equiv) was added in one portion. The heterogeneous reaction mixture was allowed to warm to room temperature and stirred for 18 h. The dichloromethane was removed and the reaction mixture was dissolved in ethyl acetate and washed with 1M sodium bisulfite solution, saturated sodium bicarbonate solution, and then brine. The organic layer was dried over $MgSO_4$ and concentrated to an oil, which was purified on silica with 3:1 hexanes : ethyl acetate to afford 47 mg of epoxide **S18** as a clear oil (87% yield). HPLC analysis (Chiralcel, OJ-H, 10% iPrOH, 1 ml, min, 230 nm) achieved separation of enantiomers. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.40 – 7.17 (m, 7H), 4.07 – 3.76 (m, 2H), 3.19 (dd, J = 6.2, 4.1 Hz, 1H), 3.05 (dt, J = 7.4, 4.6 Hz, 1H), 2.91 (d, J = 6.4 Hz, 0.5H), 2.80 (d, J = 6.0 Hz, 0.5H), 2.44 (s, 3H), 2.11 – 1.87 (m, 2H), 1.86 – 1.60 (m, 2H), 1.34 (s, 9H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 151.15, 144.32, 137.93, 137.63, 129.46, 129.00, 128.84, 128.00, 126.75, 84.45, 57.48, 56.93, 46.96, 34.15 (t, $J_{C\text{-}D}$ = 19.5 Hz), 28.08, 27.65, 25.56, 21.80; HRMS (ESI) calculated for $C_{24}H_{34}DN_2O_5S^+$ $[M+NH_4]^+$ requires *m/z* 464.2324, found 464.2325.

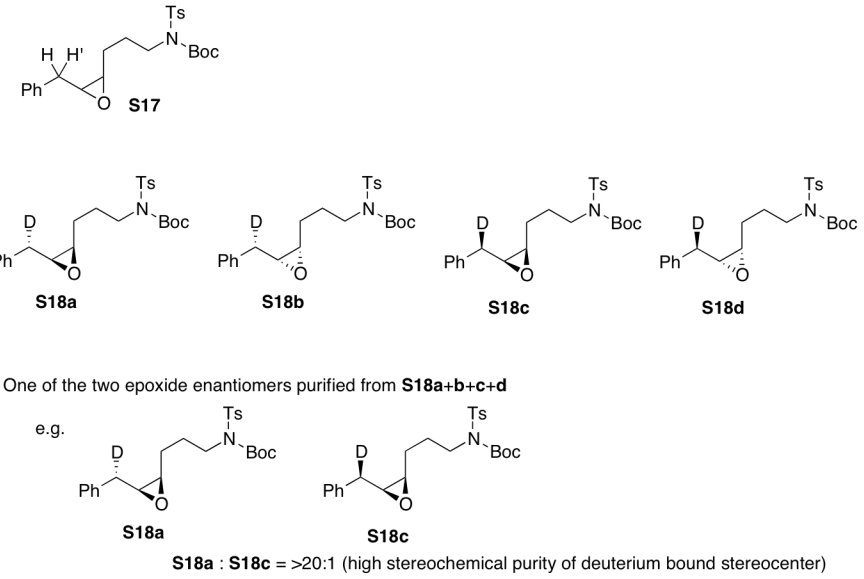
Supposing the deuterium label in **S9** is not perfectly stereopure, four stereoisomeric products are possible from the epoxidation:



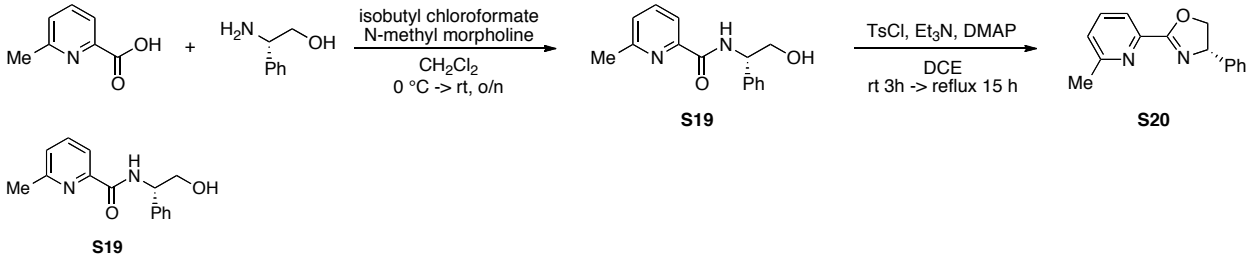
Epoxide enantiomers **S18a**+**c** and **S18b**+**d** were separated using the analytical chiral HPLC set up. One of the two enantiomers was collected manually into a test tube by diverting the material eluting from the detector. Material was collected over five HPLC runs in order to obtain tens of micrograms of material, which was analyzed in a Shigemi tube on a 600 MHz NMR. Below, this resulting spectrum is presented, zoomed in on the methylene proton(s) of interest and compared to spectra taken of protio compound **S17** and the mixture of **S18** products prior to separation of enantiomers. Note: the absolute configuration of the epoxide was not determined, so the configuration of the purified enantiomer that was analyzed is ambiguous. The results indicate that the substrate probe has a high degree of stereochemical purity (>20:1 desired stereochemistry, Scheme S10).

Scheme S10. Characterization of stereochemical purity of probe 6-D-**S1**

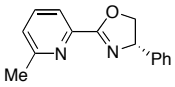




VI. Synthesis of pyridine-oxazoline ligand



This procedure was adapted from literature precedence.[1] A dry 250 ml round bottom flask was charged with a stir bar and 6-methylpicolinic acid (700 mg, 5.1 mmol, 1 equiv) and put under an atmosphere of N_2. Dry dichloromethane (50 ml, 0.1M) was added and the reaction vessel was submerged in a brine ice bath. 4-Methylmorpholine (0.84 ml, 7.65 mmol, 1.5 equiv) was added slowly by syringe and the mixture was stirred for 15 min. Isobutylchloroformate (0.77 ml, 5.87 mmol, 1.15 equiv) was added dropwise by syringe and stirred for 30 min. A solution of (S)-phenylglycinol (840 mg, 6.13 mmol, 1.2 equiv) in 10 ml of dichloromethane and with additional 4-methylmorpholine (0.64 ml, 5.87 mmol, 1.15 equiv) was added dropwise and stirred at reduced temperature for 1 h and then allowed to warm to room temperature and stir overnight (18 h). The reaction mixture was diluted with dichloromethane and washed twice with saturated ammonium chloride solution, then water, then brine. The organic layer was dried over $MgSO_4$ and concentrated to yellow-pink oil. The oil was purified on silica with a 25% ethyl acetate / 40% hexanes / 5% methanol / 30% dichloromethane solvent system to afford 1.253 g of amide **S19** as a clear oil (96% yield). Characterization data matched previous report. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.74 (d, J = 5.7 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.51 – 7.17 (m, 6H), 5.26 (ddd, J = 7.4, 6.1, 4.3 Hz, 1H), 4.13 – 3.93 (m, 2H), 2.80 (dd, J = 7.1, 5.3 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 165.24, 157.52, 149.03, 139.22, 137.69, 129.11, 128.07, 127.08, 126.31, 119.66, 67.04, 56.50, 24.49; HRMS (ESI) calculated for $C_{15}H_{17}N_2O_2^+$ $[M+H]^+$ requires *m/z* 257.1285, found 257.1280.

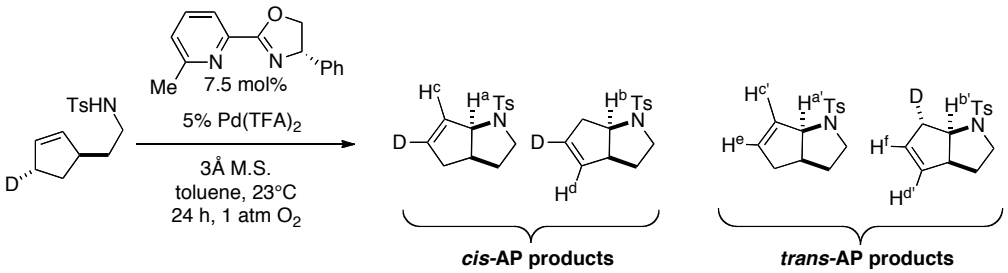


S20

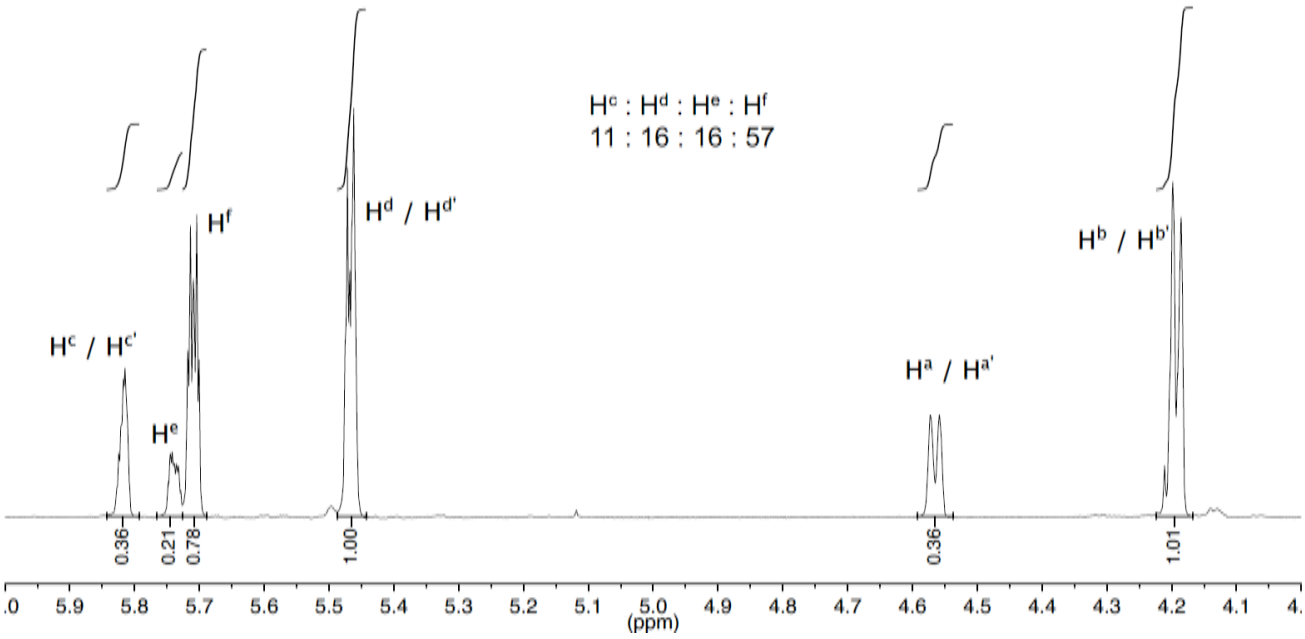
This procedure was adapted from literature precedence.[1] A dry 50 ml 2-neck round bottom flask equipped with a stir bar and reflux condenser was placed under N_2. 4-Dimethylaminopyridine (15 mg, 0.12 mmol, 0.1 equiv) and *p*-toluenesulfonylchloride (350 mg, 1.84 mmol, 1.5 equiv) were added to the reaction vessel under a positive pressure of N_2. Amide **S19** (314 mg, 1.23 mmol, 1 equiv) was added in a solution of 12 ml of dry 1,2-dichloroethane (0.1 M) to the reaction vessel by syringe. Triethylamine (0.98 ml, 7.04 mmol, 4 equiv) was added to the reaction mixture by syringe. The reaction mixture was stirred at room temperature for 3 h and then heated to reflux for 17 h. The deep red solution was cooled to room temperature, diluted with dichloromethane and washed twice with saturated sodium bicarbonate, then water, then brine. The organic layer was dried over $MgSO_4$ and concentrated to red oil. Purification on a CombiFlash Rf purification system using a high performance basic alumina column (Teledyne-Isco RediSep) and 5→35% ethyl acetate in hexanes gradient afforded 147 mg of **S20** as a pale red oil (50% yield). Note: this reaction proceeds with nearly complete conversion to product, but purification results in problematic decomposition. Use of activated basic alumina and dry-loading the crude mixture (pre-adsorb onto small amount of alumina for purification) are recommended for purification of this ligand. Characterization data matched the previous report. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.47 – 7.15 (m, 6H), 5.44 (dd, J = 10.3, 8.5 Hz, 1H), 4.96 – 4.82 (m, 1H), 4.39 (t, J = 8.5 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR: (75 MHz, $CDCl_3$) δ 164.21, 159.02, 146.30, 142.10, 136.99, 128.94, 127.88, 127.04, 125.74, 121.66, 75.56, 70.49, 24.87; HRMS (ESI) calculated for $C_{15}H_{15}N_2O^+$ $[M+H]^+$ requires *m/z* 239.1179, found 239.1175.

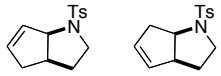
VII. Use of cyclopentenyl deuterated substrate probe

For the synthesis and characterization of the cyclopentenyl substrate probe, please see our previous publication. The catalytic reaction of the cyclopentenyl substrate probe was carried out as described in section II. The products and starting material were isolated using silica chromatography (hexanes/ethyl acetate solvent system). The product mixture was analyzed on a 600 MHz NMR spectrometer to obtain a ratio of the four products (see below).



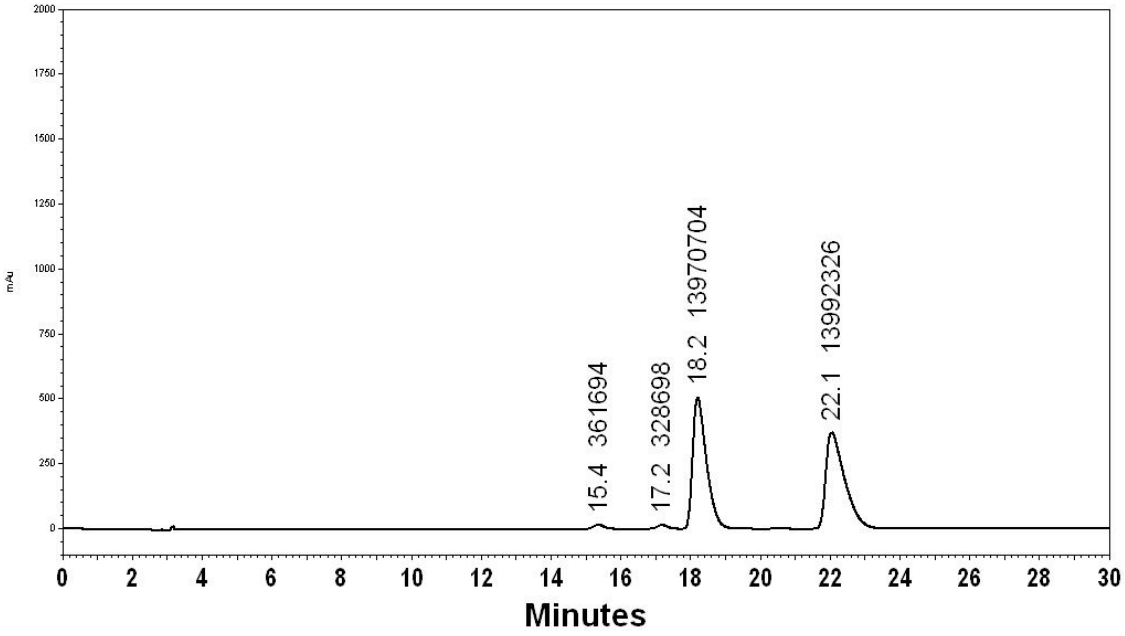
61% yield (^{1}H NMR yield, 0.075 mmol scale), 27% remaining starting material.



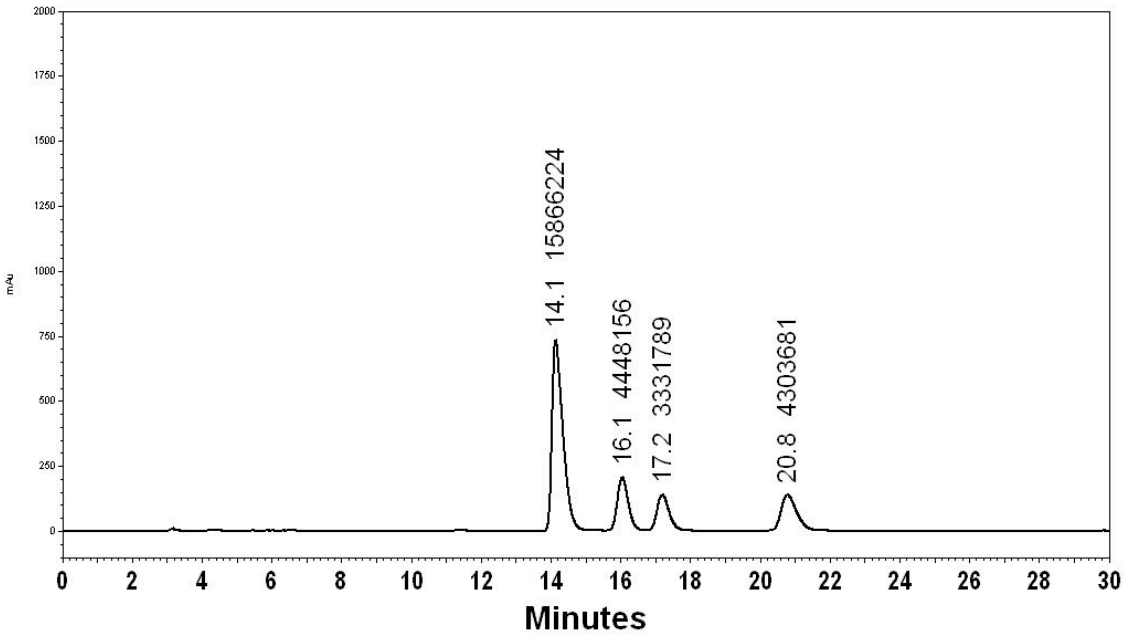


S21 *iso*-**S21**

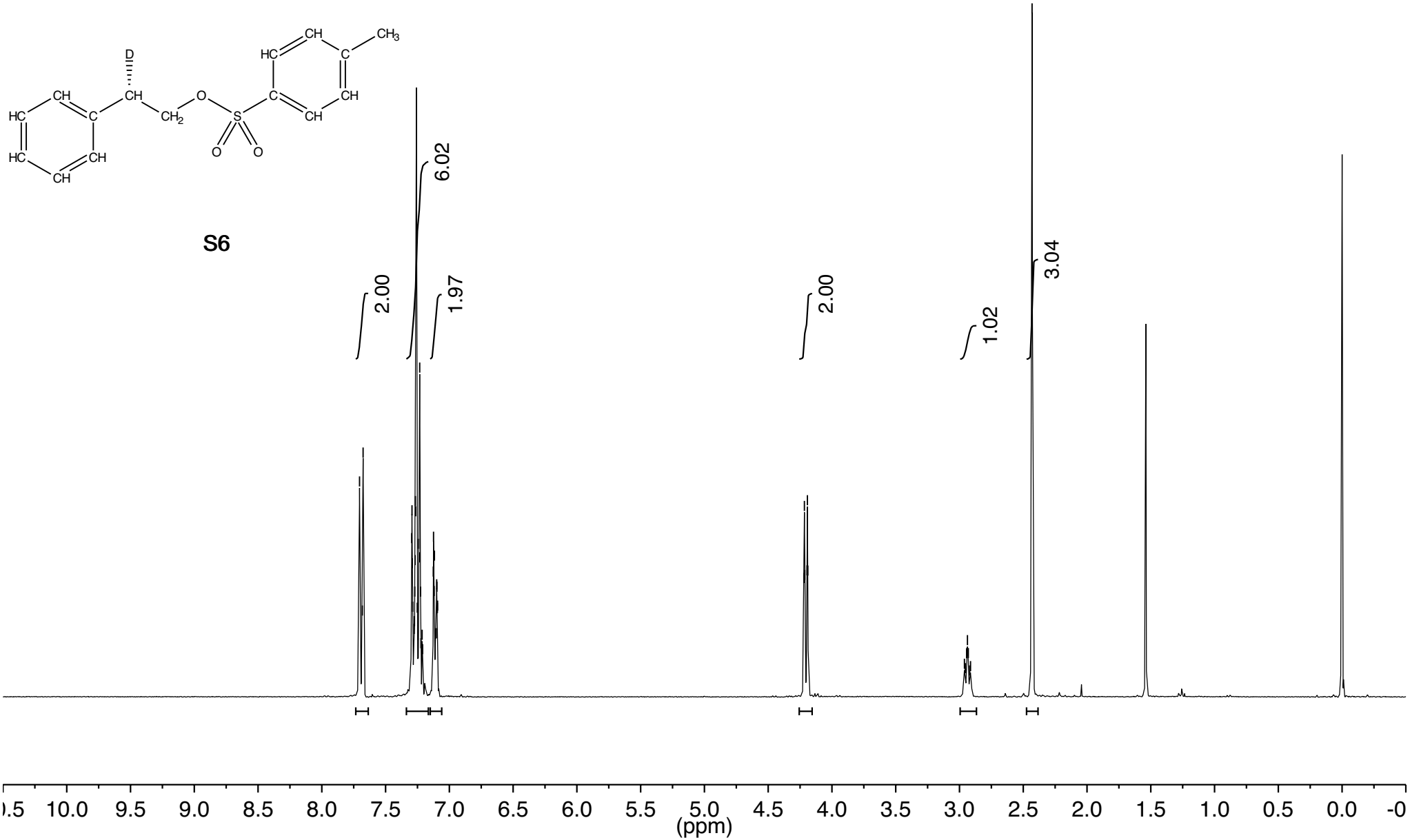
Racemic sample of predominantly **S21** with minor amount of iso-**S21**
Chiralcel *OJ-H*, 10% iPrOH, 1 ml/min, 230 nm

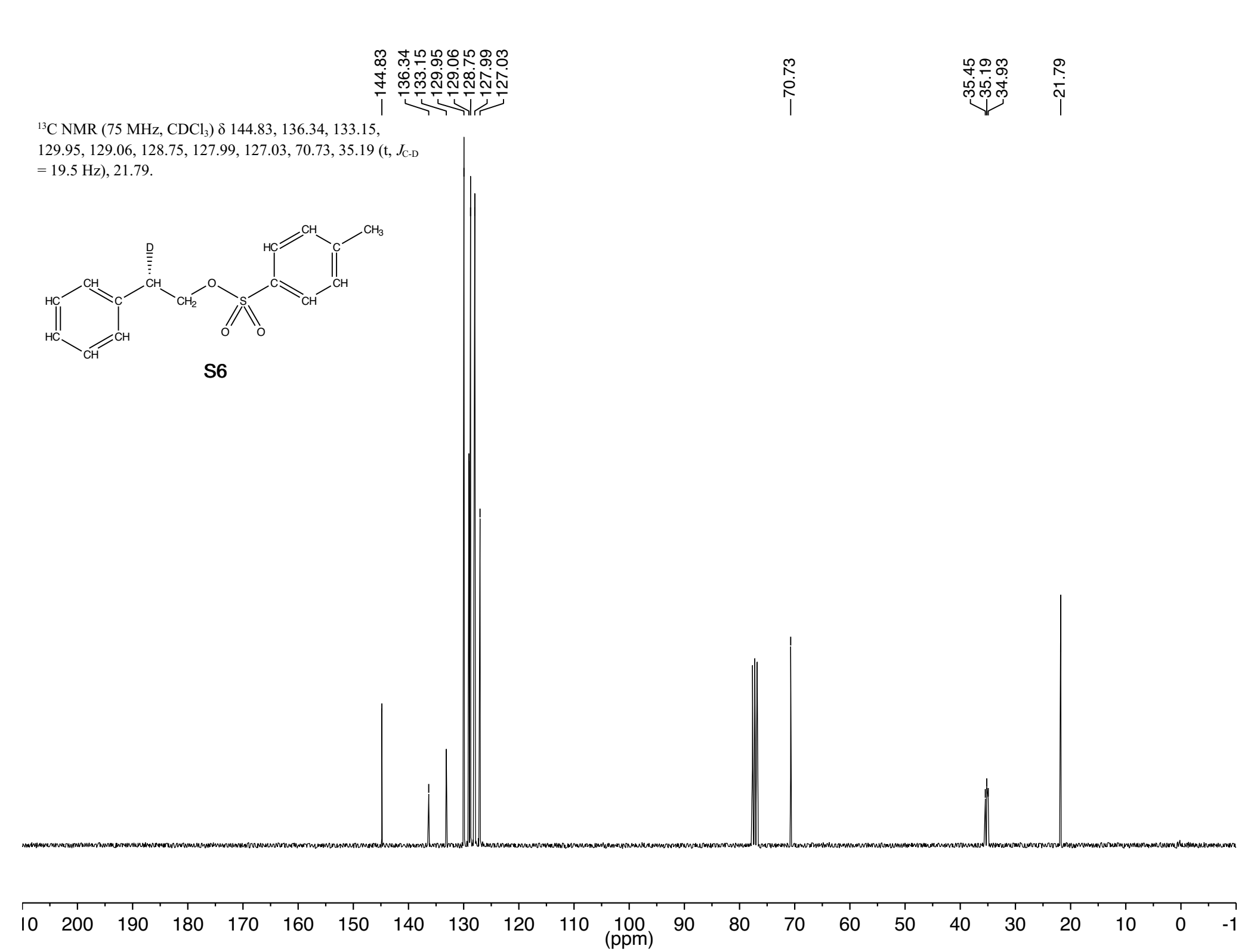


Product mixture from Table 1 entry 2:
13% ee of partially deuterated **S21**, 56% ee of partially deuterated iso-**S21**
Chiralcel *OJ-H*, 10% iPrOH, 1 ml/min, 230 nm



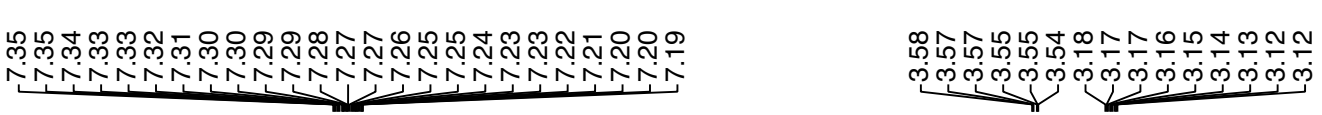
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.18 (m, 5H), 7.14 – 7.06 (m, 2H), 4.20 (dt, *J* = 7.1, 0.9 Hz, 2H), 2.94 (ddd, *J* = 7.2, 5.2, 2.0 Hz, 1H), 2.43 (s, 3H).



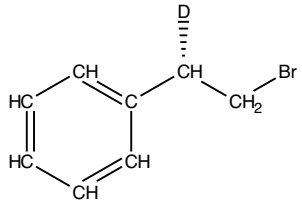


^{13}C NMR (75 MHz, $CDCl_3$) δ 144.83, 136.34, 133.15, 129.95, 129.06, 128.75, 127.99, 127.03, 70.73, 35.19 (t, $J_{C\text{-}D}$ = 19.5 Hz), 21.79.

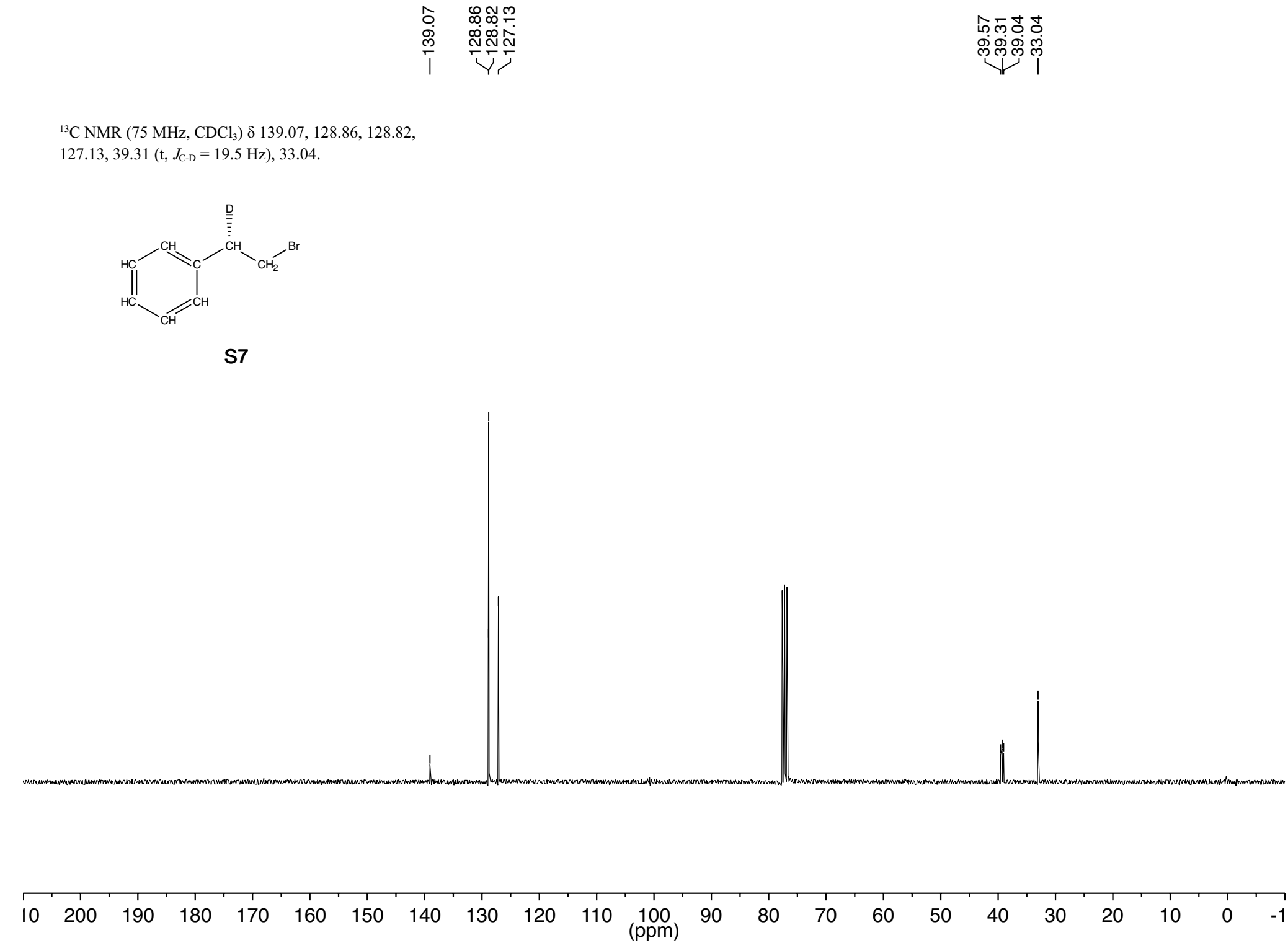
S6



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.09 (m, 5H), 3.56 (dt, *J* = 7.6, 1.1 Hz, 2H), 3.23 – 3.03 (m, 1H).

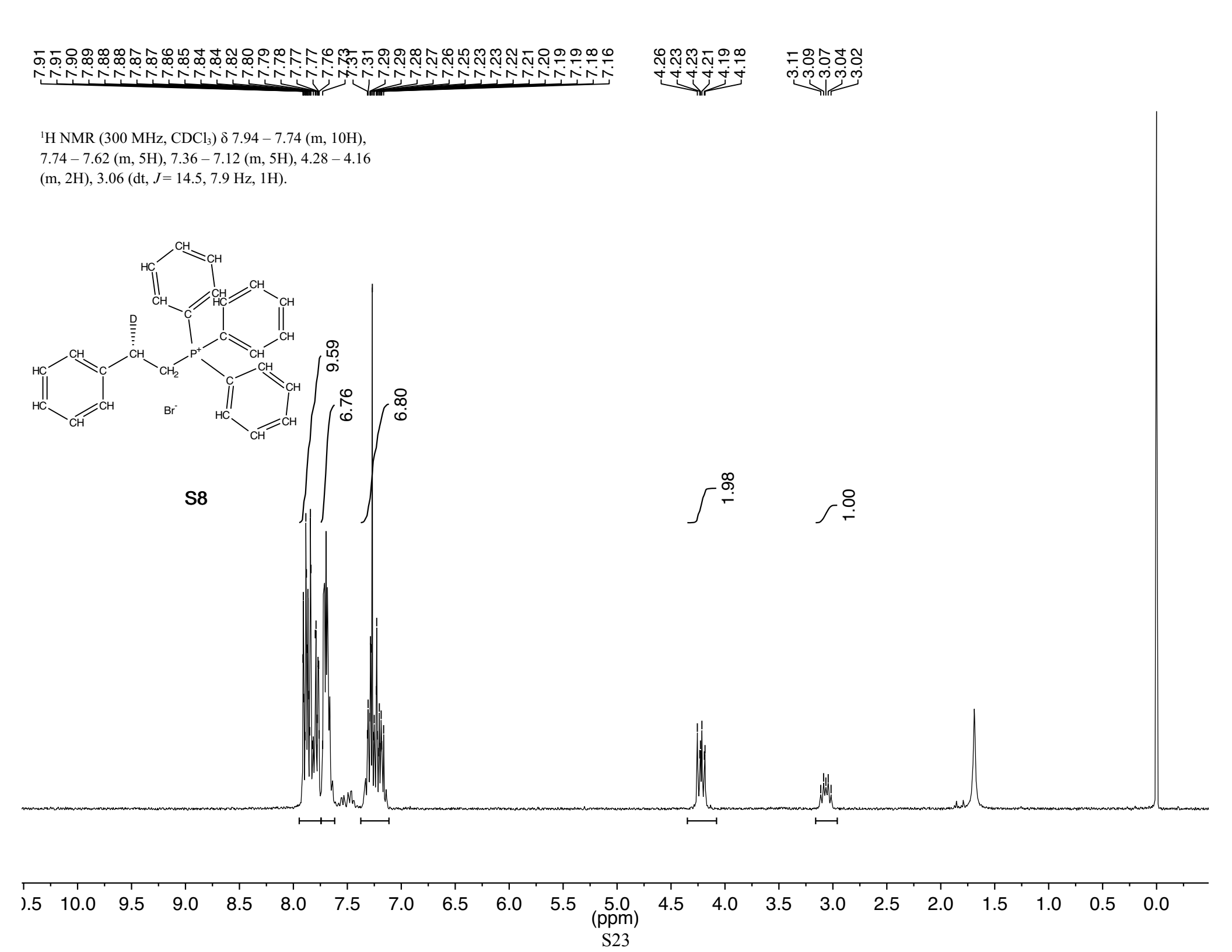


S7



^{13}C NMR (75 MHz, $CDCl_3$) δ 139.07, 128.86, 128.82, 127.13, 39.31 (t, $J_{C\text{-}D}$ = 19.5 Hz), 33.04.

S7


7.91
7.91
7.90
7.89
7.88
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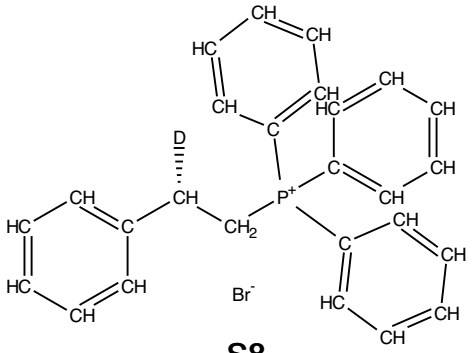
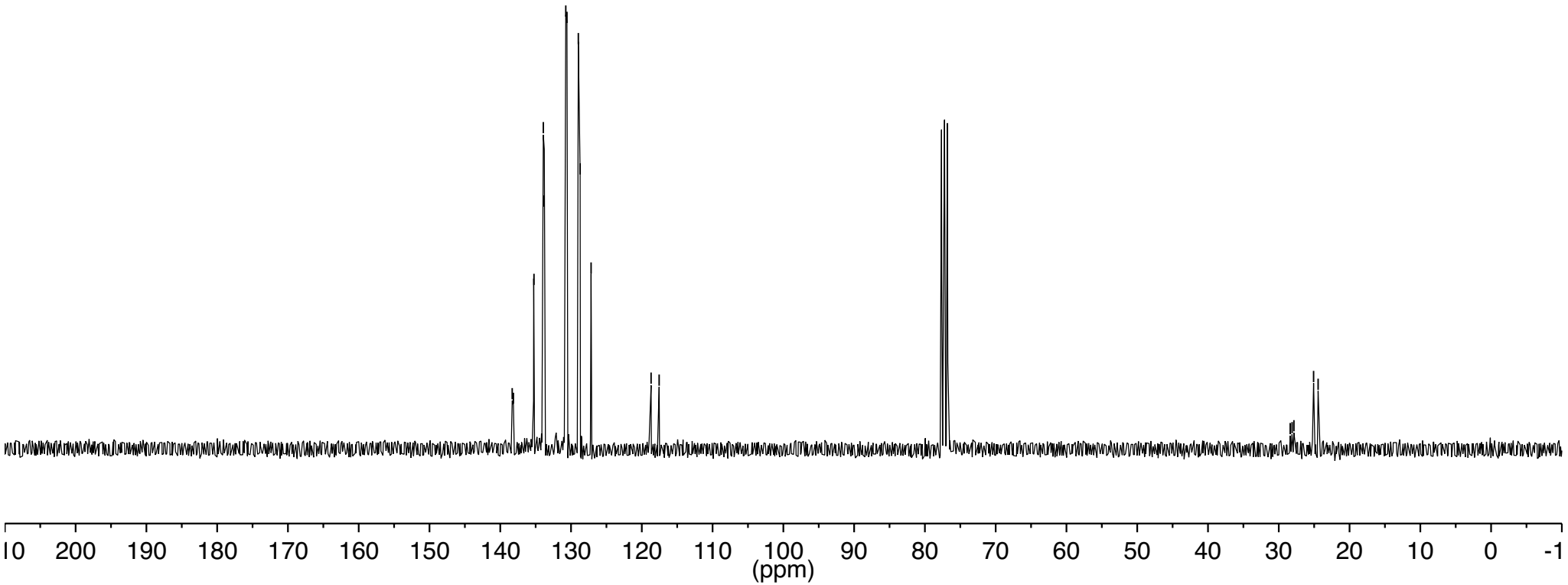
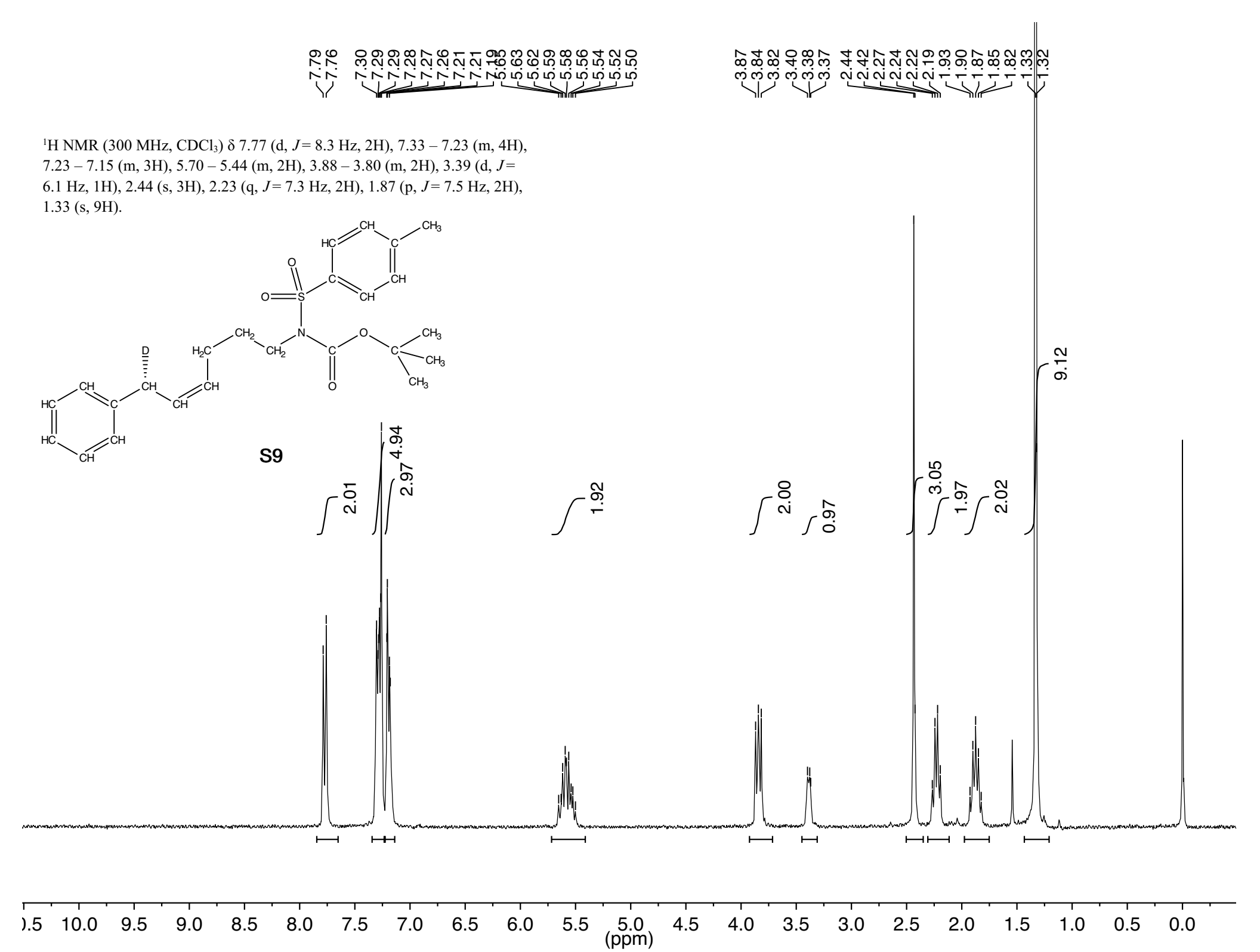
7.87
7.87
7.86
7.85
7.84
7.84
7.82
7.80
7.79
7.78
7.77
7.77
7.76
7.73
7.31
7.31
7.29
7.29
7.28
7.27
7.26
7.25
7.23
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.16
4.26
4.23
4.23
4.21
4.19
4.18
3.11
3.09
3.07
3.04
3.02
[1]H NMR (300 MHz, CDCl3) δ 7.94 – 7.74 (m, 10H),
7.74 – 7.62 (m, 5H), 7.36 – 7.12 (m, 5H), 4.28 – 4.16
(m, 2H), 3.06 (dt, J = 14.5, 7.9 Hz, 1H).
D
P+
CH2
Br-
S8
9.59
6.76
6.80
1.98
1.00
(ppm)

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.23 (d, $J_{C\text{-}P}$ = 12.8 Hz), 135.24, 133.68 (d, $J_{C\text{-}P}$ = 9 Hz), 130.67 (d, $J_{C\text{-}P}$ = 12 Hz), 128.84 (d, $J_{C\text{-}P}$ = 18.8 Hz), 127.17, 118.69, 117.55, 28.12 (t, $J_{C\text{-}D}$ = 19.5 Hz), 24.76 (d, $J_{C\text{-}P}$ = 48 Hz).



S8




7.79
7.76
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7.29
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7.28
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7.26
7.21
7.21
7.19
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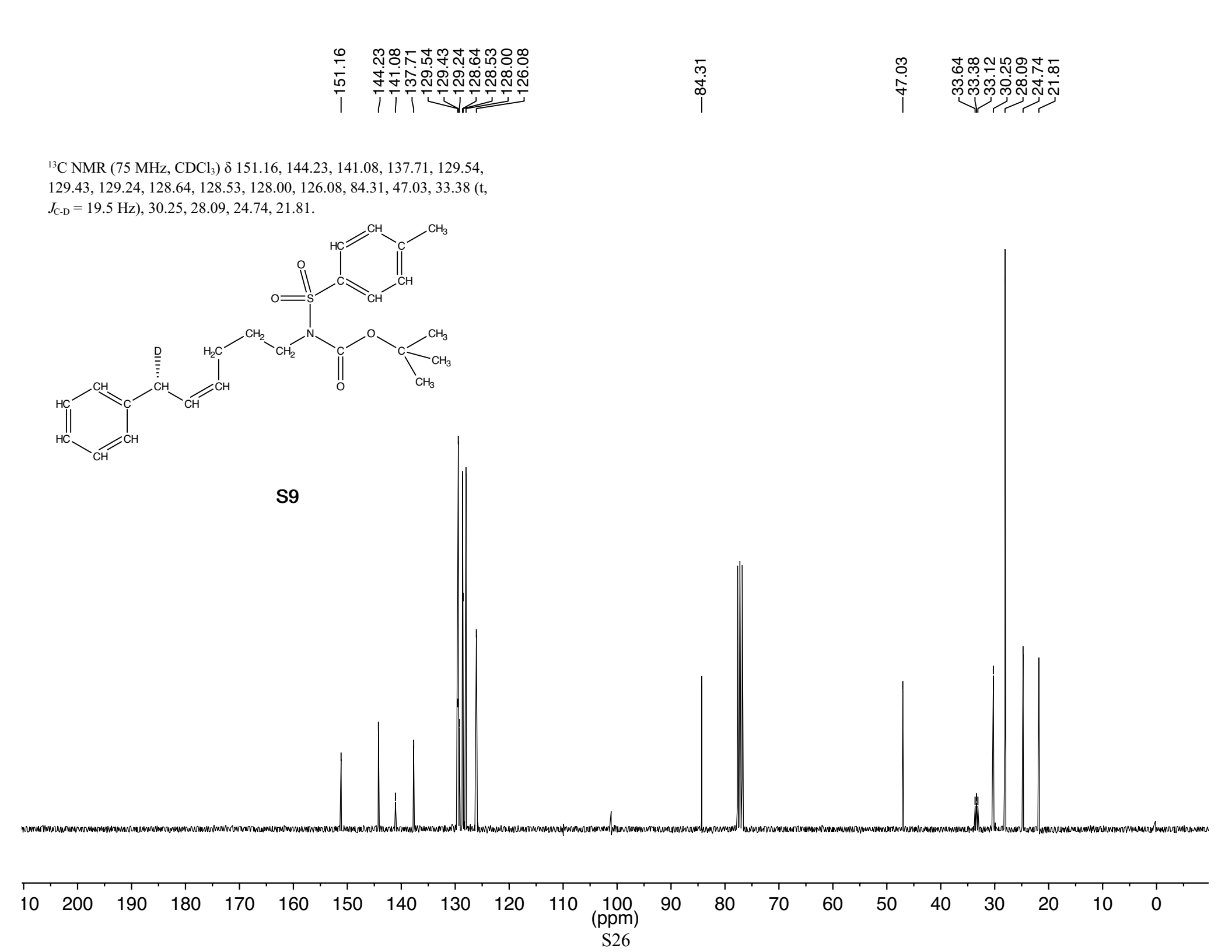
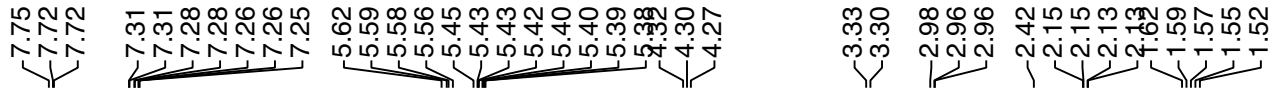
5.63
5.62
5.59
5.58
5.56
5.54
5.52
5.50
3.87
3.84
3.82
3.40
3.38
3.37
2.44
2.42
2.27
2.24
2.22
2.19
1.93
1.90
1.87
1.85
1.82
1.33
1.32
[1]H NMR (300 MHz, CDCl3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 5.70 – 5.44 (m, 2H), 3.88 – 3.80 (m, 2H), 3.39 (d, J = 6.1 Hz, 1H), 2.44 (s, 3H), 2.23 (q, J = 7.3 Hz, 2H), 1.87 (p, J = 7.5 Hz, 2H), 1.33 (s, 9H).
S9
2.01
4.94
2.97
1.92
2.00
0.97
3.05
1.97
2.02
9.12
(ppm)

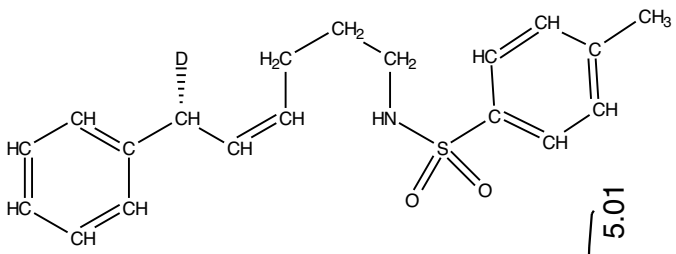


^{13}C NMR (75 MHz, $CDCl_3$) δ 151.16, 144.23, 141.08, 137.71, 129.54, 129.43, 129.24, 128.64, 128.53, 128.00, 126.08, 84.31, 47.03, 33.38 (t, $J_{C\text{-}D}$ = 19.5 Hz), 30.25, 28.09, 24.74, 21.81.

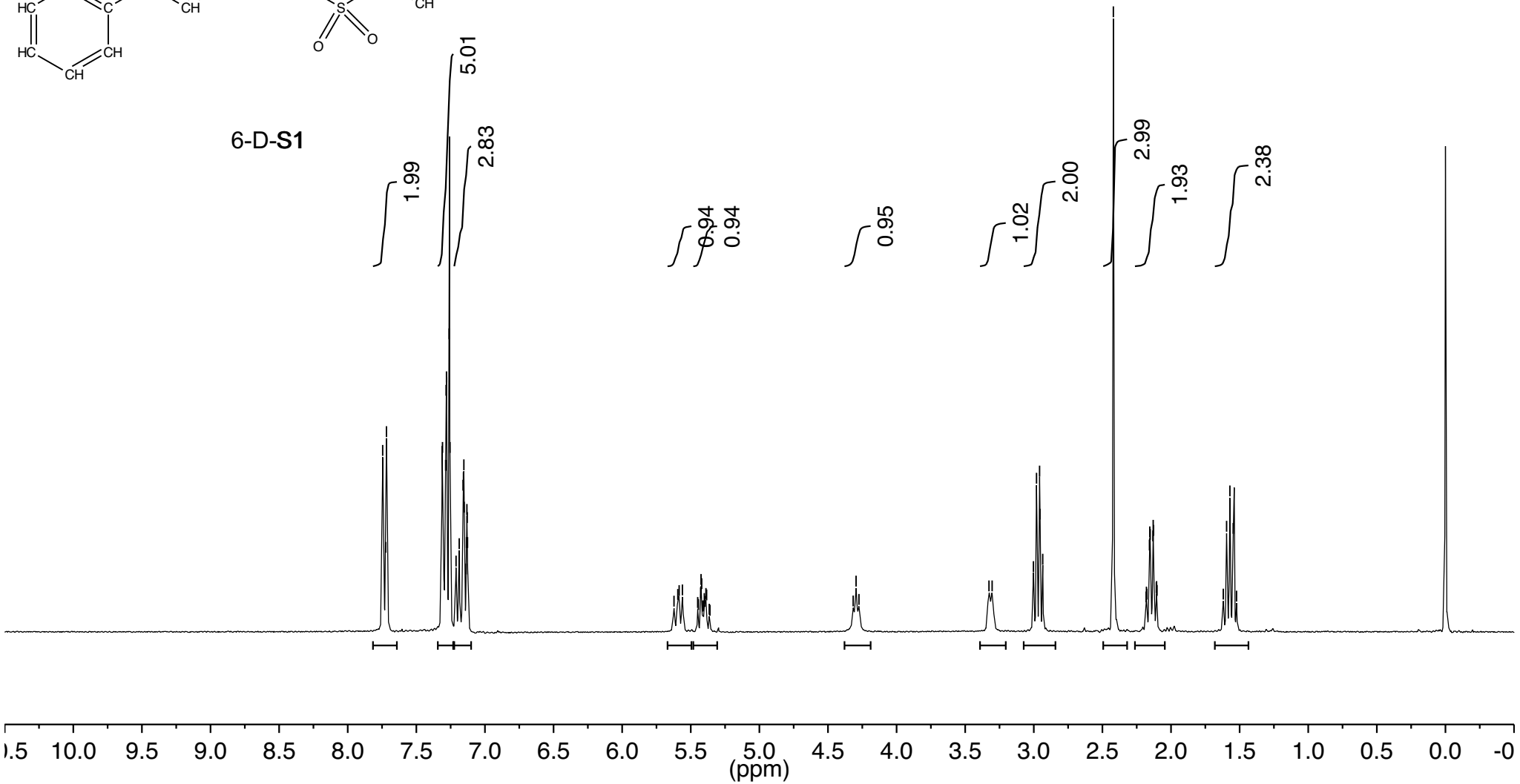
S9

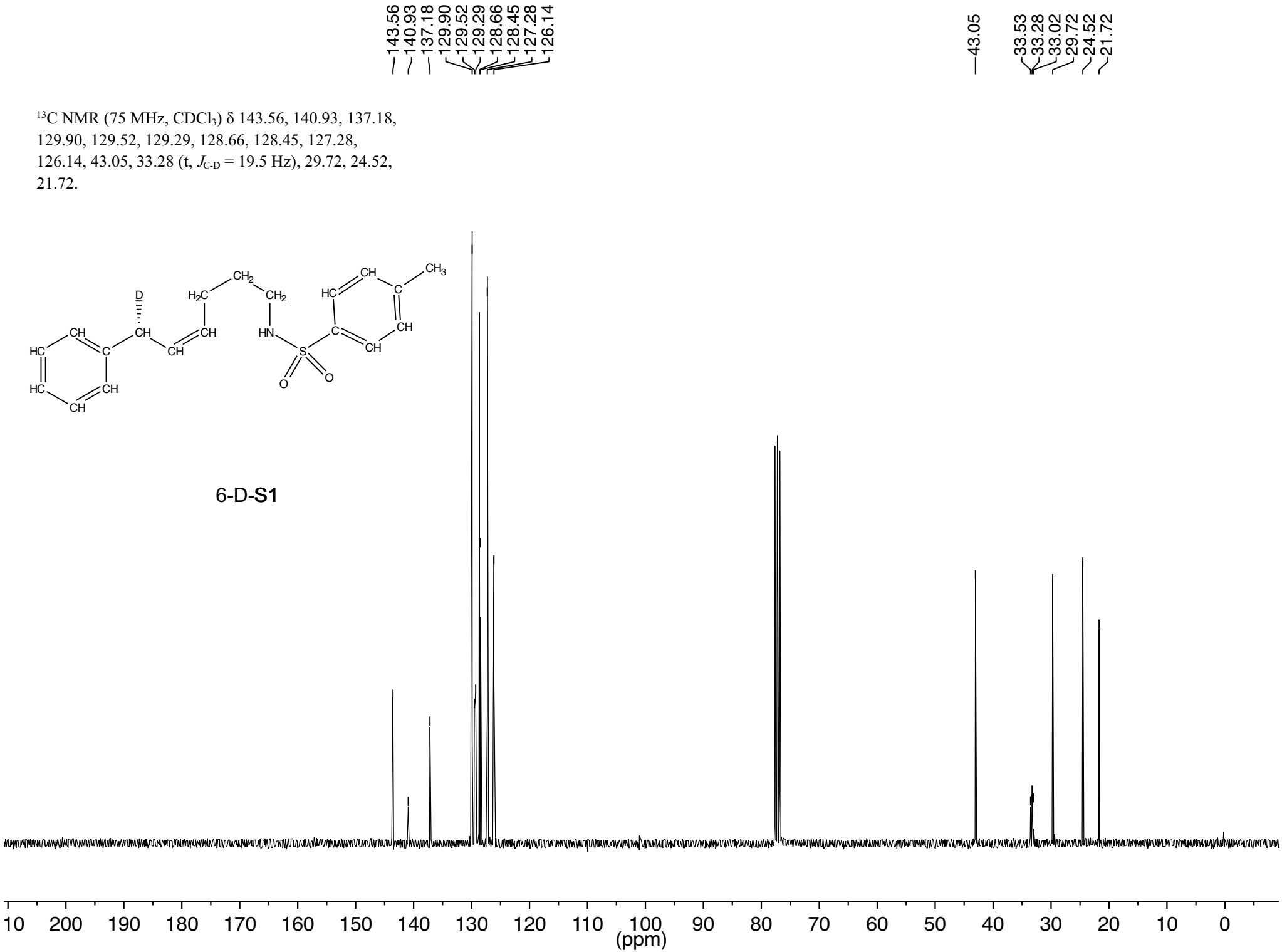


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.10 (m, 3H), 5.59 (dd, *J* = 10.6, 7.7 Hz, 1H), 5.41 (dddd, *J* = 10.8, 8.8, 6.9, 1.5 Hz, 1H), 4.30 (t, *J* = 6.3 Hz, 1H), 3.32 (d, *J* = 6.9 Hz, 1H), 2.97 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.14 (q, *J* = 6.9 Hz, 2H), 1.57 (p, *J* = 7.2 Hz, 2H).



6-D-**S1**

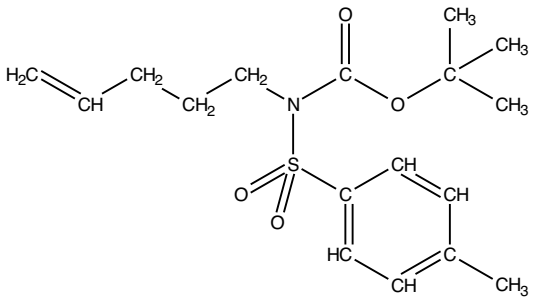




^{13}C NMR (75 MHz, $CDCl_3$) δ 143.56, 140.93, 137.18, 129.90, 129.52, 129.29, 128.66, 128.45, 127.28, 126.14, 43.05, 33.28 (t, $J_{C\text{-}D}$ = 19.5 Hz), 29.72, 24.52, 21.72.

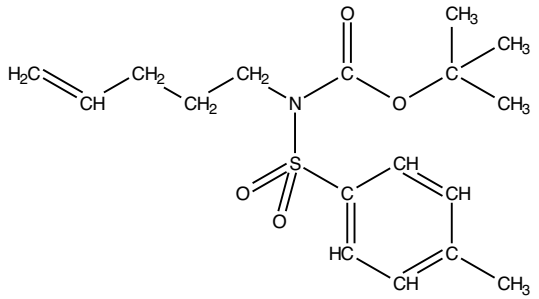
6-D-**S1**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.84 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.00 (ddd, *J* = 10.2, 3.1, 1.2 Hz, 1H), 3.86 – 3.78 (m, 2H), 2.44 (s, 3H), 2.13 (q, *J* = 7.2 Hz, 3H), 1.86 (p, *J* = 7.5 Hz, 2H), 1.33 (s, 8H).

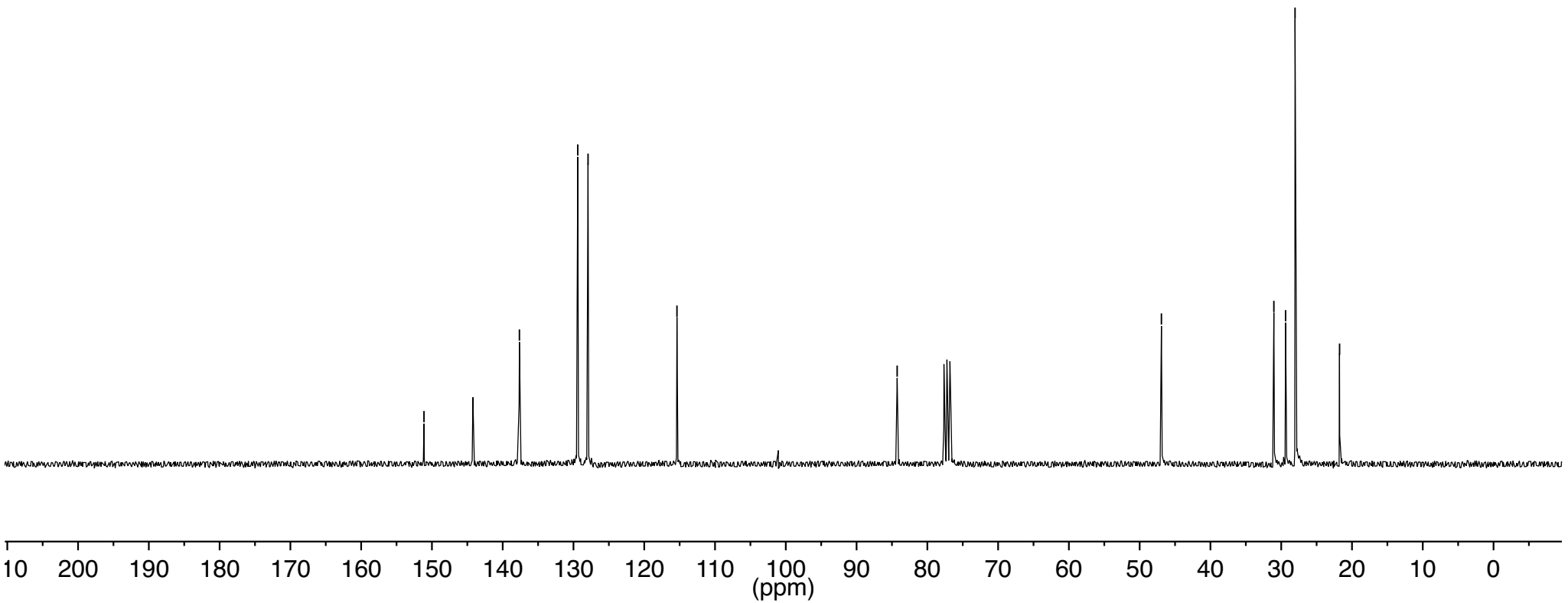


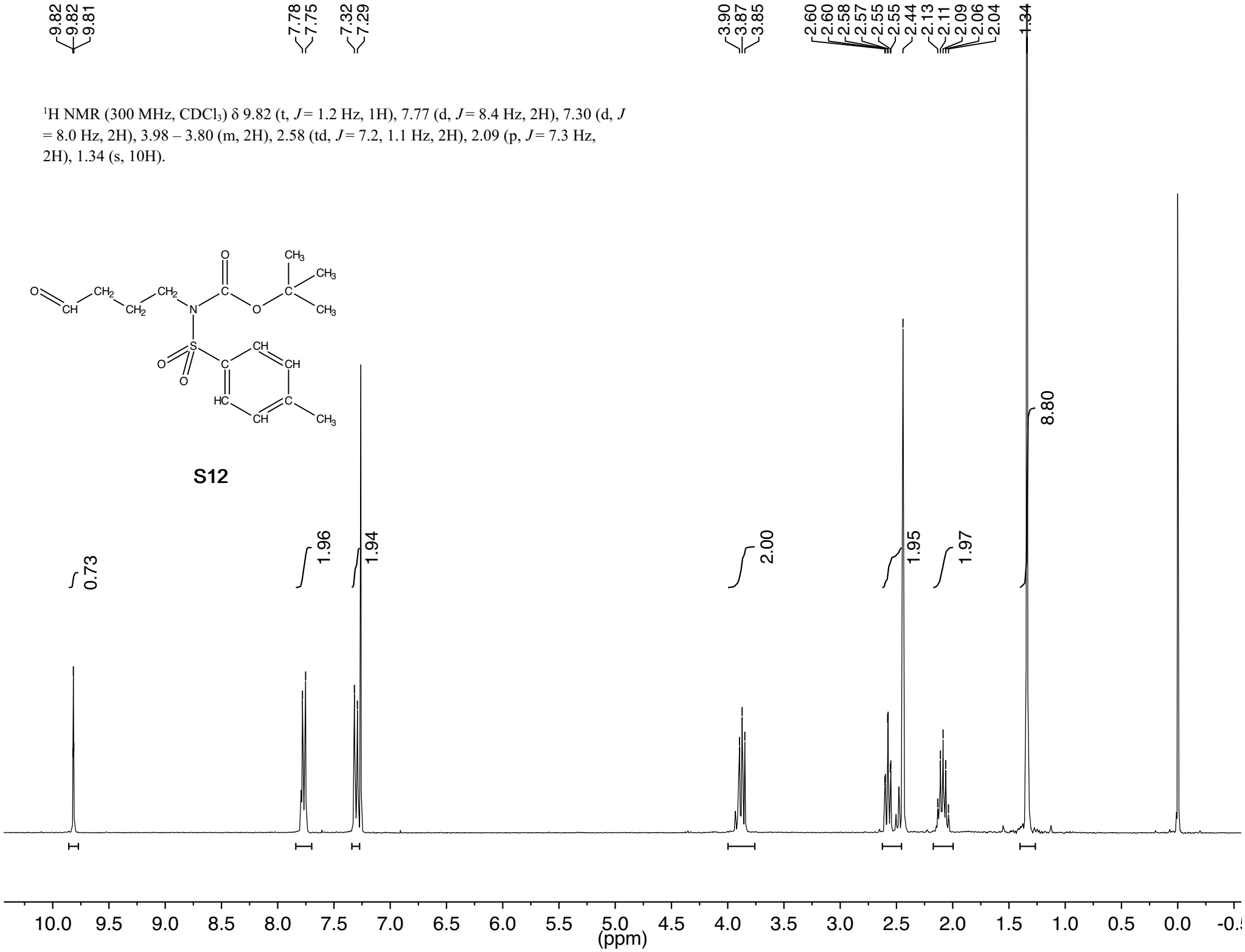
S11

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.12, 144.20, 137.64, 129.39, 127.94, 115.38, 84.26, 46.93, 31.04, 29.38, 28.05, 21.75.



S11

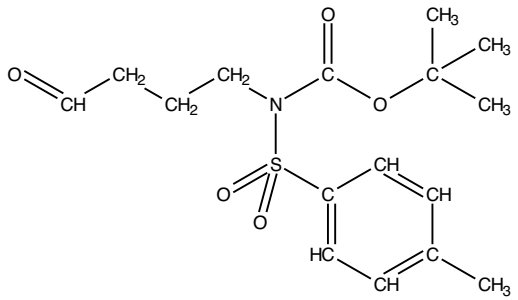




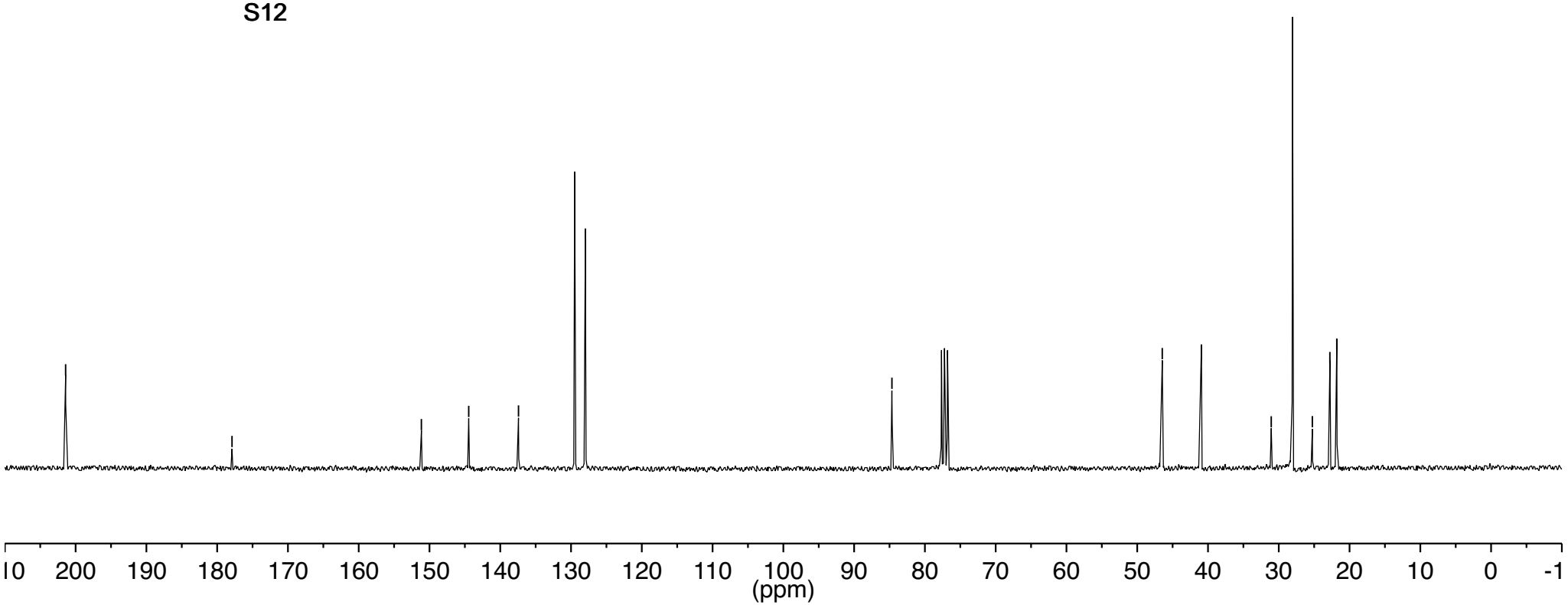
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.98 – 3.80 (m, 2H), 2.58 (td, *J* = 7.2, 1.1 Hz, 2H), 2.09 (p, *J* = 7.3 Hz, 2H), 1.34 (s, 10H).

201.41
177.90
151.14
144.46
137.42
129.48
127.98
84.66
46.46
40.93
31.06
28.06
25.26
22.78
21.80

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.43, 177.92, 151.16, 144.47, 137.44, 129.50, 127.99, 84.68, 46.48, 40.95, 31.08, 28.08, 25.27, 22.79, 21.82.

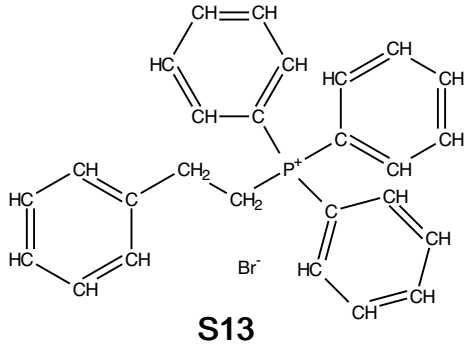


S12



^{1}H NMR (300 MHz, Chloroform-d) δ 7.96 – 7.83 (m, 6H), 7.83 – 7.74 (m, 3H), 7.74 – 7.62 (m, 6H), 7.50 – 7.38 (m, 1H), 7.34 – 7.12 (m, 4H).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 6H), 7.83 – 7.74 (m, 3H), 7.74 – 7.62 (m, 6H), 7.50 – 7.38 (m, 1H), 7.34 – 7.12 (m, 4H), 4.27 (ddd, *J* = 12.6, 8.3, 7.2 Hz, 2H), 3.08 (dt, *J* = 13.1, 7.8 Hz, 2H).

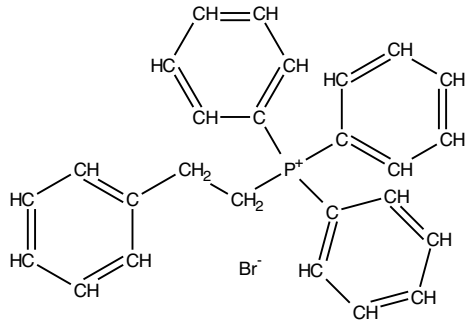


S13

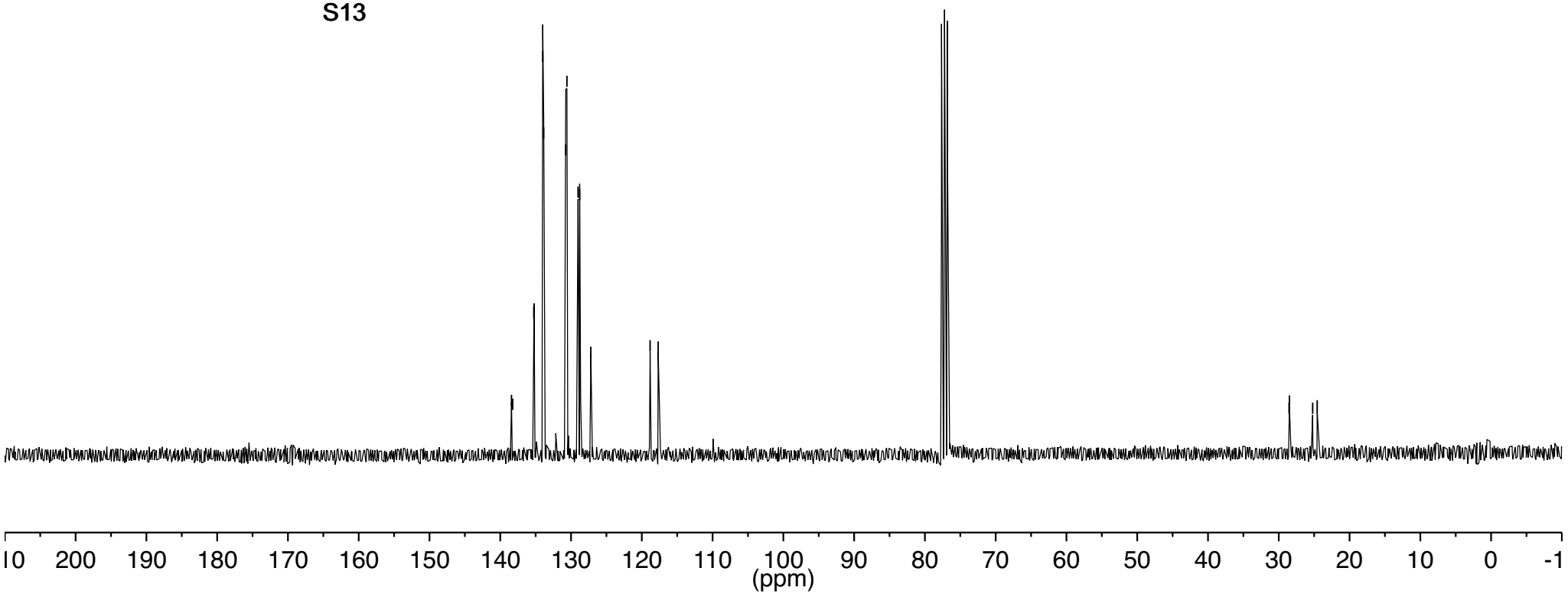
138.41
138.24
135.26
135.22
134.00
133.87
130.75
130.58
129.01
128.78
127.20
118.83
117.69

28.54
28.50
25.21
24.57

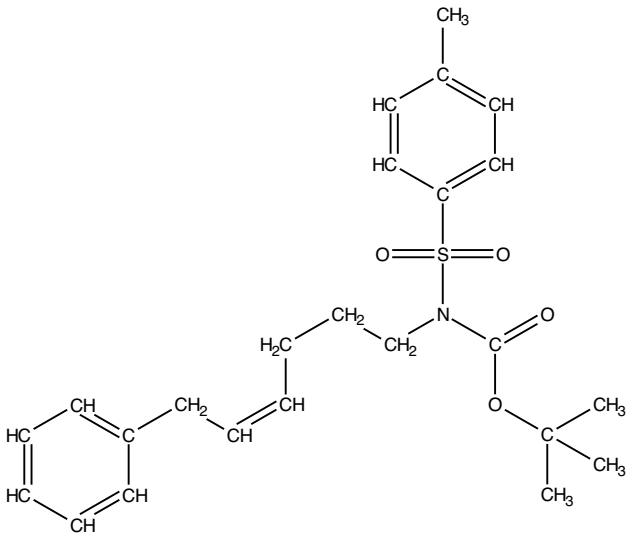
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.33 (d, $J_{C\text{-}P}$ = 12.8 Hz), 135.24 (d, $J_{C\text{-}P}$ = 3 Hz), 133.94 (d, $J_{C\text{-}P}$ = 9.75 Hz), 130.66 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.9 (d, $J_{C\text{-}P}$ = 17.3 Hz), 127.20, 118.83, 117.69, 28.54, 28.50, 24.89 (d, $J_{C\text{-}P}$ = 48 Hz).



S13

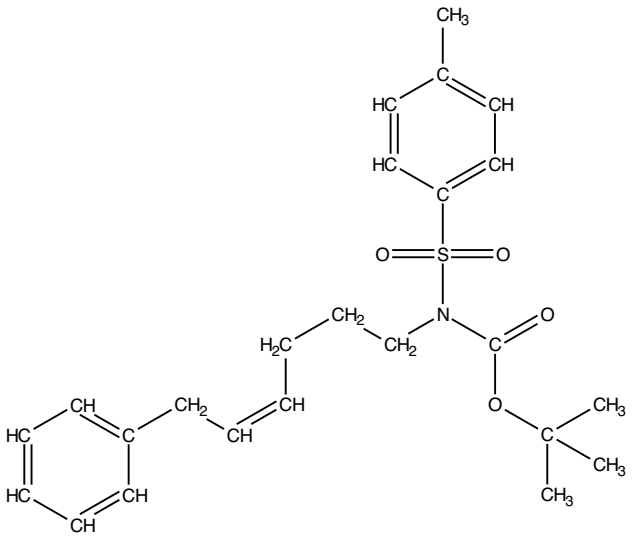


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.24 (m, 4H), 7.22 – 7.16 (m, 3H), 5.69 – 5.47 (m, 2H), 3.89 – 3.80 (m, 2H), 3.41 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 2.23 (q, *J* = 7.0 Hz, 2H), 1.87 (p, *J* = 7.5 Hz, 2H), 1.33 (s, 9H).

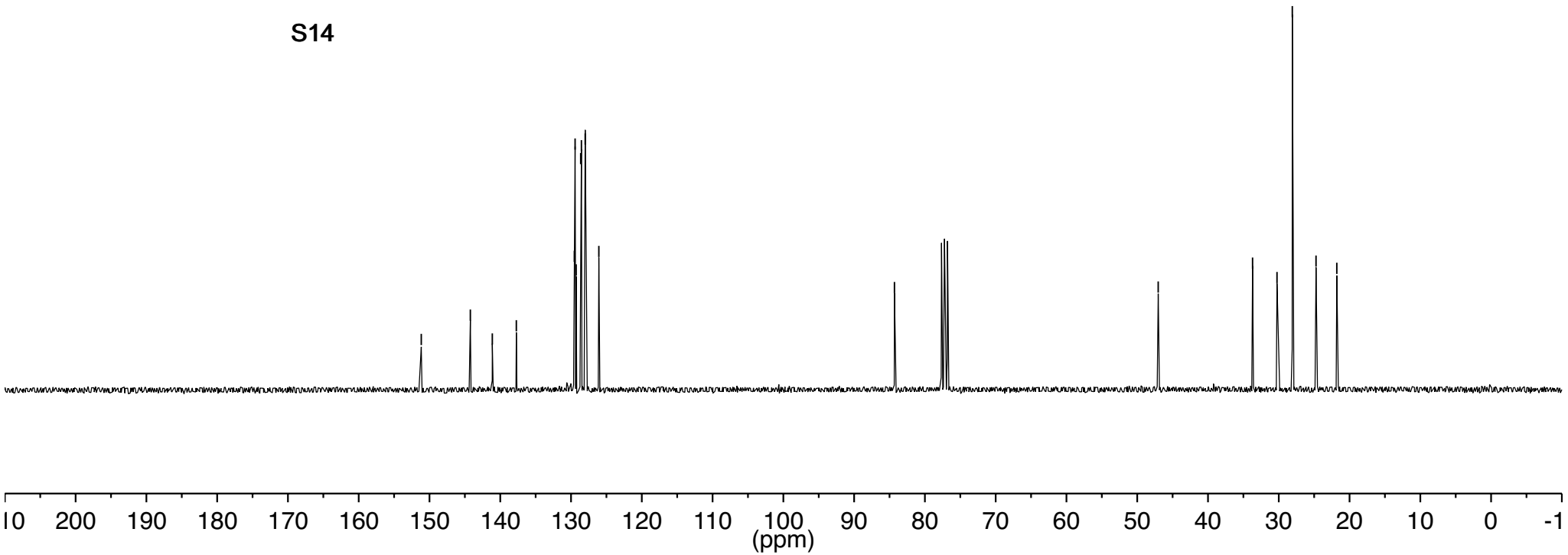


S14

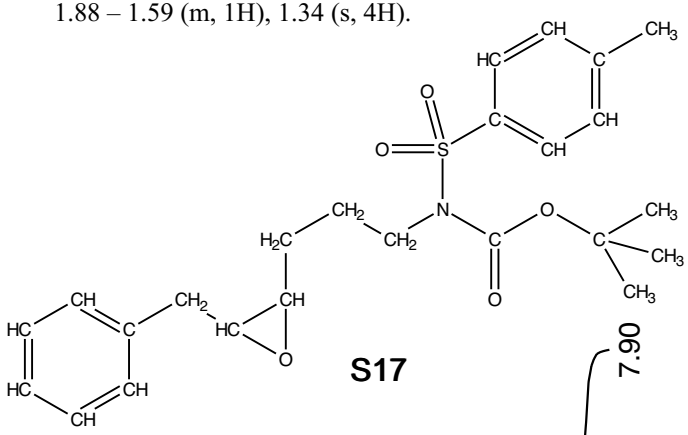
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.16, 144.23, 141.12, 137.73, 129.53, 129.43, 129.28, 128.63, 128.53, 128.00, 126.07, 84.30, 47.04, 33.70, 30.25, 28.09, 24.74, 21.80.



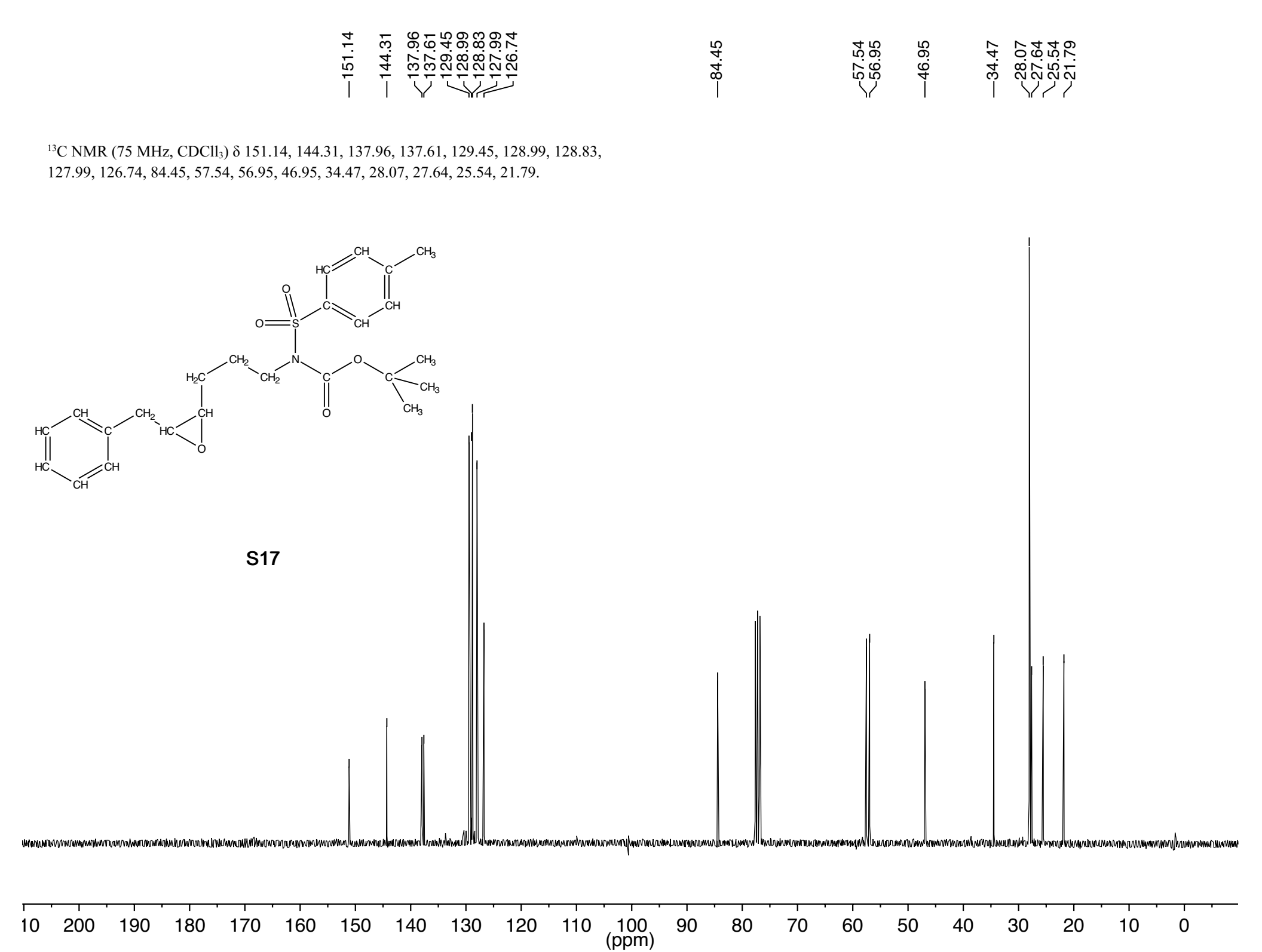
S14



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 1H), 7.43 – 7.17 (m, 4H), 4.04 – 3.80 (m, 2H), 3.20 (td, *J* = 6.3, 4.1 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.93 (dd, *J* = 14.7, 6.4 Hz, 1H), 2.81 (dd, *J* = 14.7, 6.2 Hz, 1H), 2.44 (s, 3H), 1.99 (dddd, *J* = 17.2, 10.8, 6.9, 4.0 Hz, 1H), 1.88 – 1.59 (m, 1H), 1.34 (s, 4H).

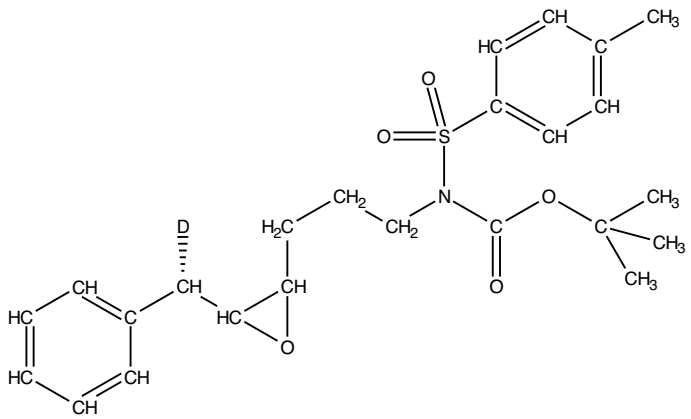


S17



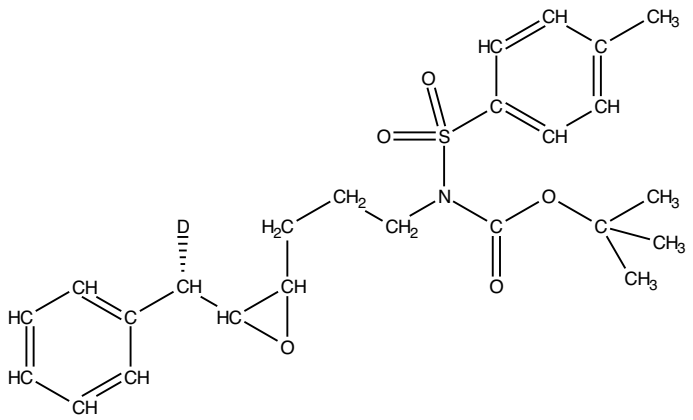
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.14, 144.31, 137.96, 137.61, 129.45, 128.99, 128.83, 127.99, 126.74, 84.45, 57.54, 56.95, 46.95, 34.47, 28.07, 27.64, 25.54, 21.79.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.17 (m, 7H), 4.07 – 3.76 (m, 2H), 3.19 (dd, *J* = 6.2, 4.1 Hz, 1H), 3.05 (dt, *J* = 7.4, 4.6 Hz, 1H), 2.91 (d, *J* = 6.4 Hz, 0.5H), 2.80 (d, *J* = 6.0 Hz, 0.5H), 2.44 (s, 3H), 2.11 – 1.87 (m, 2H), 1.86 – 1.60 (m, 2H), 1.34 (s, 9H).

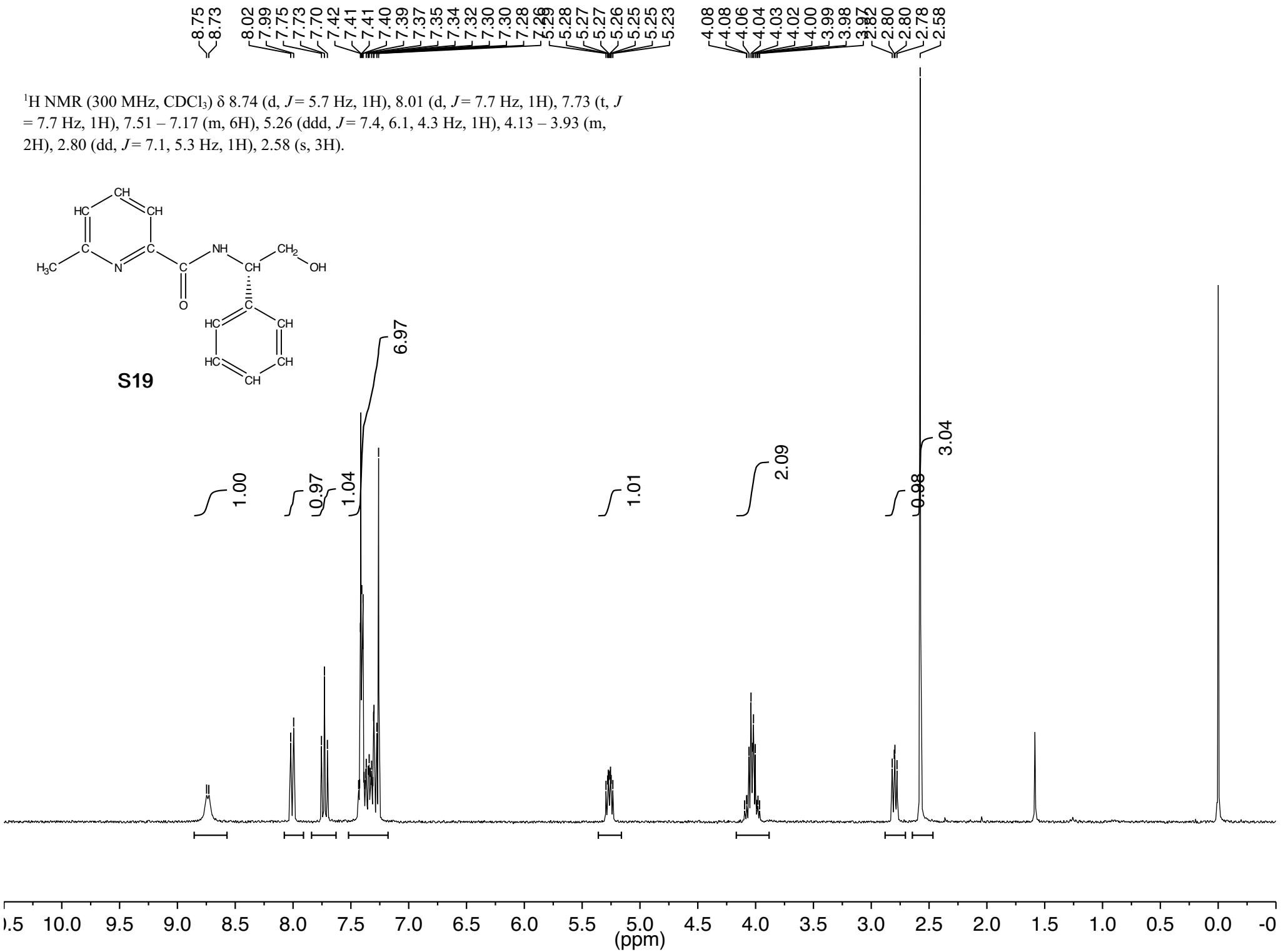


S18

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.15, 144.32, 137.93, 137.63, 129.46, 129.00, 128.84, 128.00, 126.75, 84.45, 57.48, 56.93, 56.92, 46.96, 34.15 (t, $J_{C\text{-}D}$ = 19.5 Hz), 28.08, 27.65, 25.56, 21.80.

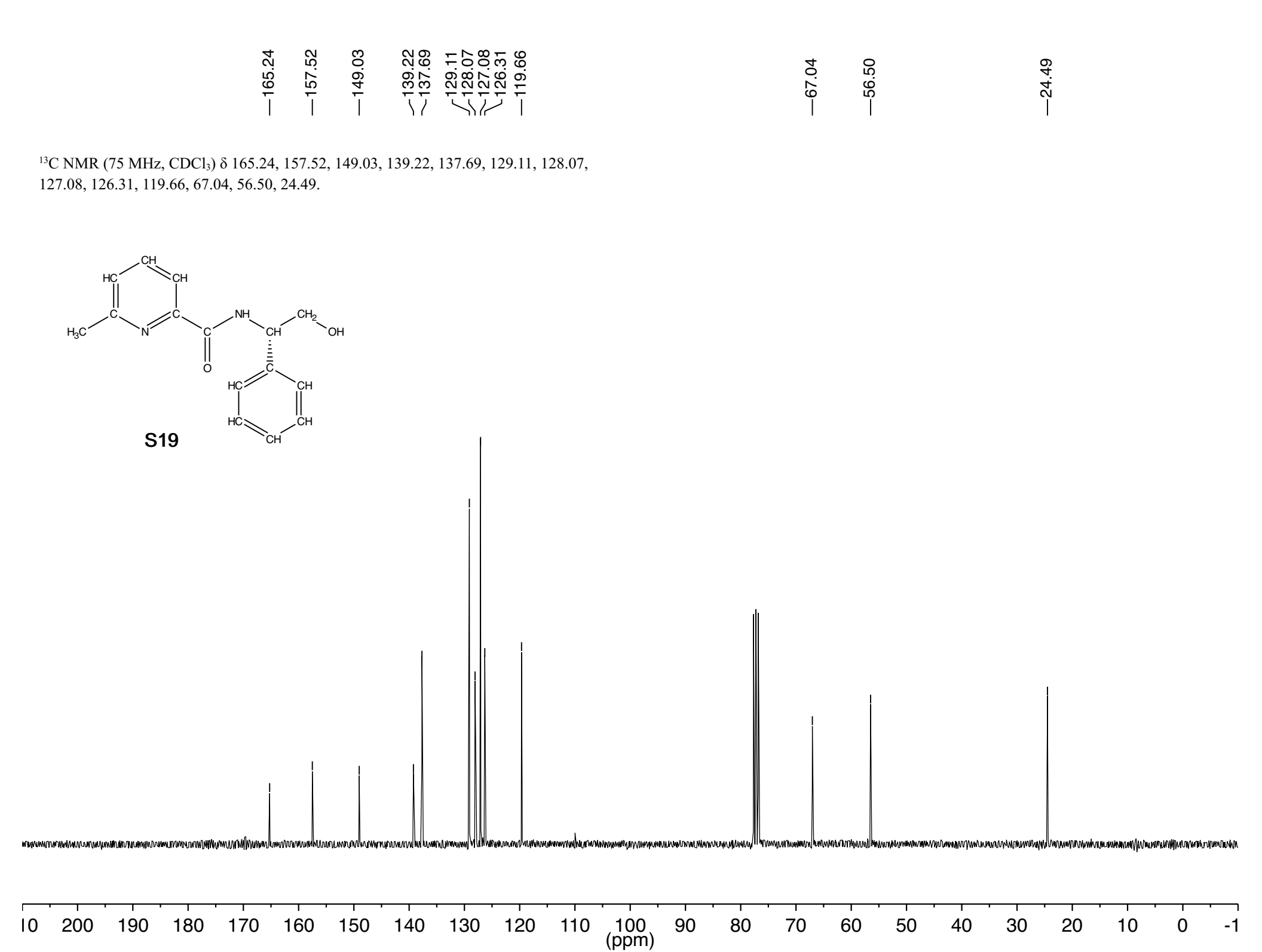


S18

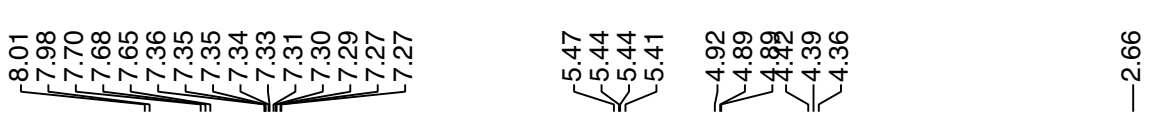


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.17 (m, 6H), 5.26 (ddd, *J* = 7.4, 6.1, 4.3 Hz, 1H), 4.13 – 3.93 (m, 2H), 2.80 (dd, *J* = 7.1, 5.3 Hz, 1H), 2.58 (s, 3H).

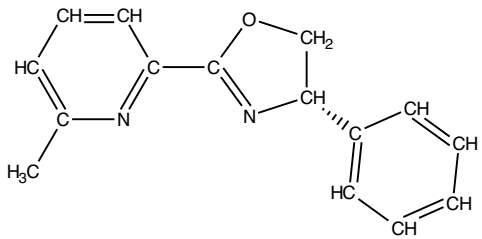
S19



^{13}C NMR (75 MHz, $CDCl_3$) δ 165.24, 157.52, 149.03, 139.22, 137.69, 129.11, 128.07, 127.08, 126.31, 119.66, 67.04, 56.50, 24.49.

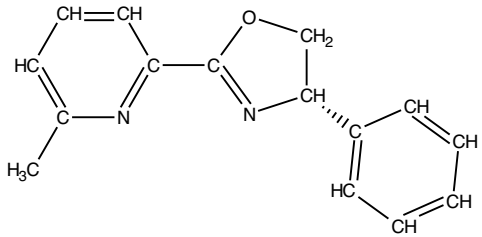


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.15 (m, 6H), 5.44 (dd, *J* = 10.3, 8.5 Hz, 1H), 4.96 – 4.82 (m, 1H), 4.39 (t, *J* = 8.5 Hz, 1H), 2.66 (s, 3H).



S20

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.21, 159.02, 146.30, 142.10, 136.99, 128.94, 127.88, 127.04, 125.74, 121.66, 75.56, 70.49, 24.87.



S20