Supporting Information

Facile Synthesis and Stereo-Resolution of Chiral 1,2,3-Triazole

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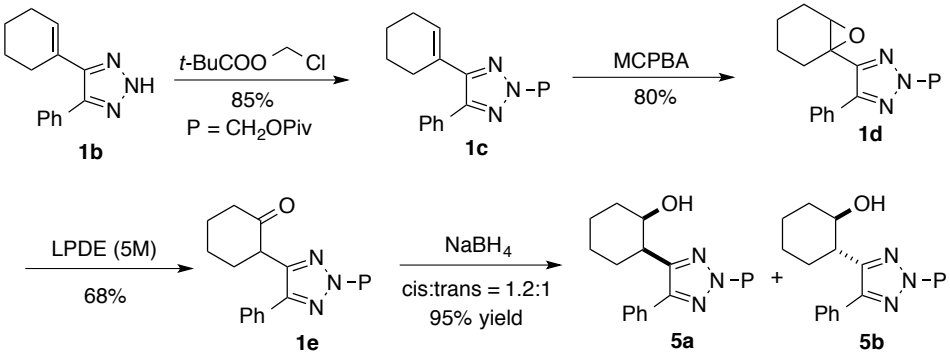
I. General Methods and Materials

General Information

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septum techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian 400 MHz spectrometers and Bruker 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm), CD_3CD (δ 3.31 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm), CD_3CD (δ 49.75 ppm) for ^{13}C. Flash column chromatography was performed on 300-400 mesh silica gels. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Optical rotations were measured on a commercial automatic polarimeter (WZZ-1S digital, Shanghai Physical Optics Instrument Factory) and reported as follows: $[\alpha]^{T}D$ (c = g/100 mL, solvent). Melting points were measured on a X-4 digital microscopy apparatus and uncorrected. HRMS were recorded on LTQ-FTUHRA spectrometer and Bruker Apexll mass spectrometer. Anhydrous Toluene was purchased from Beijing Chemical Reagent Co. and distilled with sodium, immediately before use.

General procedure for the preparation of 5a/5b



4-(cyclohex-1-en-1-yl)-5-phenyl-2H-1,2,3-triazole (1b) was synthesized according the following literature:
Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, *10*, 1493

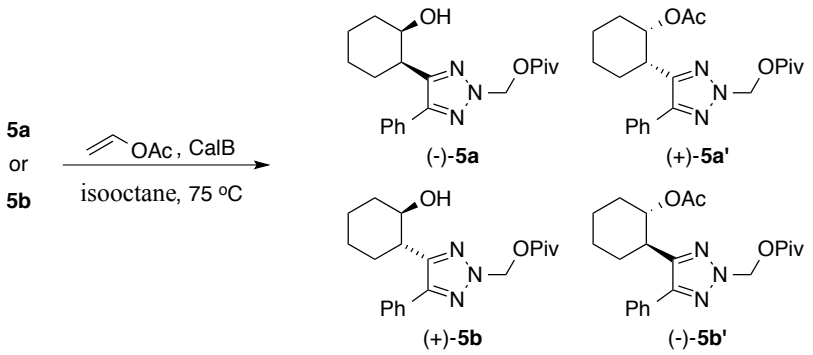
4-(cyclohex-1-en-1-yl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1c). To the solution of compound **1b** (30.0g, 0.13mol) in acetone (60 mL), chloromethylene pivalate (23.4g, 0.26mol) and K_2CO_3 (35.9g, 0.26mol) were added. The mixture was stirring at RT for 12h. The white solid was removed by filtrating. After removing the solvent under vacuum, the resulting crude product was purified by column chromatography on silica gel (petroleum ether: EtOAc= 10:1).

(4-(7-oxabicyclo[4.1.0]heptan-1-yl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1d). Compound **1c** (35.0g, 0.11mol) was dissolved in 50ml dry DCM at 0 ^{o}C in ice-both under N_2 atmosphere. And then the solution of m-CPBA(26.9g, 0.17mol) in 20 ml dry DCM was added dropwise over 10 mins. The reaction mixture was stirred for 3 hours at RT and monitored by TLC. After the completing of starting material, the reaction mixture was filtrated to remove the white solid. The filtrate was then washed with 10% Na_2CO_3 solution and brine. The organic phase was dried with $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether: EtOAc= 8:1).

(4-(2-oxocyclohexyl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1e). The compound **1d** (30.0g, 0.085mol) was added to an ice-cold 5 M LPDE solution (17 mL) under N_2 atmosphere and monitored by TLC. The mixture was quenched by 50 mL H_2O, and then extracted by 50 mL CH_2Cl_2 three times. The combined organic phase was washed by 50 mL brine twice, dried by $MgSO_4$. Solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether:EtOAc= 5:1)

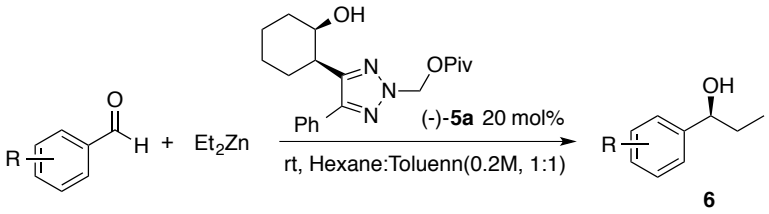
4-(2-hydroxycyclohexyl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (5a/5b) To the solution of compound **1e** (2.0g, 5.6mmol) into 20 mL MeOH at 0 ^{o}C, $NaBH_4$ (0.43g, 11.2mmol) was added. After stirring at 0 ^{o}C for 3h, the mixture was quenched by 50 mL H_2O, extracted by 50 mL EtOAc three times. The combined organic layer was washed by 100 mL brine twice, dried by $MgSO_4$. Solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether: EtOAc= 5:1).

General Procedure for kinetic resolution of 5a and 5b with CalB.



To the solution of racemic alcohols **5a or 5b** (1.07g, 3.0 mmol) in 30 mL of isooctane (HPLC grade), vinyl acetate (688 mg, 8.0 mmol) and lipase B (480 mg) were added. The mixture was then stirred in an orbital shaker (75 ℃, 160 rpm) at 24-72h. The mixture was then filtered and the solvent evaporated. The residue was purified by silica gel column chromatography gel (Hexane: EtOAc=4:1) to give desired enantiopure alcohols. The stereochemistry assignment is based on rules for *Pseudomonas cepacia lipases and Candida rugosa lipases* (R. J. Kazlauskas, A. N. E. Weissfloch, A.T. Rappaport and L.A. Cuccia, *J. Org. Chem.*, 1991, **56**, 2656-2665) thus, the stereochemical assignments are only tentative at this time. The crystal growing for the derivatives is undergoing in our lab, which will help for the conformation of stereochemical assignment

Asymmetric additions of diethylznic to aldehyes with Chiral *β*-hydroxyl TA ligand (5a'):



To a solution of Chiral *β*-hydroxyl TA ligand **5a'** (0.2 mmol) in toluene (1.0 ml) at 0 ºC, 2.0 ml (1.0M, 2 mmol) diethylzinc in hexane was added. After stirring for 30 min, aldehyde (1 mmol in 1 mL toluene) was added slowly. The mixture was then stirred for 48 h at room temperature. The reaction was quenched with saturated ammoniumchloride solution (10 ml), and extracted with diethyl ether (20ml) twice. The combined organic extracts were washed with 30 mL brine twice, and dried by $MgSO_4$. Evaporate the solvent under vacuum. The residue was purified by chromatography on silica gel (Hexane: EtOAc= 5:1) to give the desired product (**6a-6e)**.

II. Screening table for kinetic resolution of 5a and 5b with CalB.

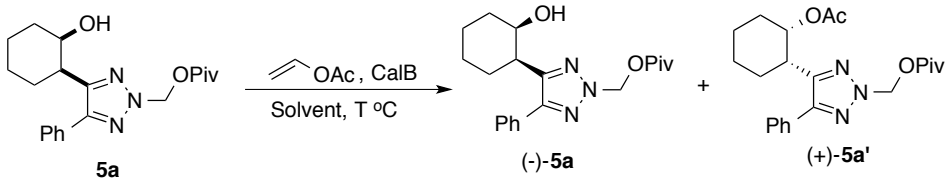
To the solution of racemic alcohols **5a or 5b** (89.2, 0.25 mmol) in 2 mL of isooctane (HPLC grade), vinyl acetate (57.3mg, 0.67 mmol) and lipase B (40 mg) were added. The mixture was then stirred in an orbital shaker (75 ℃, 160 rpm) at 24-72h. The mixture was then filtered and the solvent evaporated. The mixture was used directly for HPLC analysis.

The conversion was calculated by:

$c = \frac{ee_s}{ee_s + ee_p}$ where S for the substrate and P for the product.

The enatioselectivity, S was calculated by

$S = \frac{\ln[(1-c)(1-ee_s)]}{\ln[(1-c)(1+ee_s)]} = \frac{\ln[1-c(1+ee_p)]}{\ln[1-c(1-ee_p)]}$

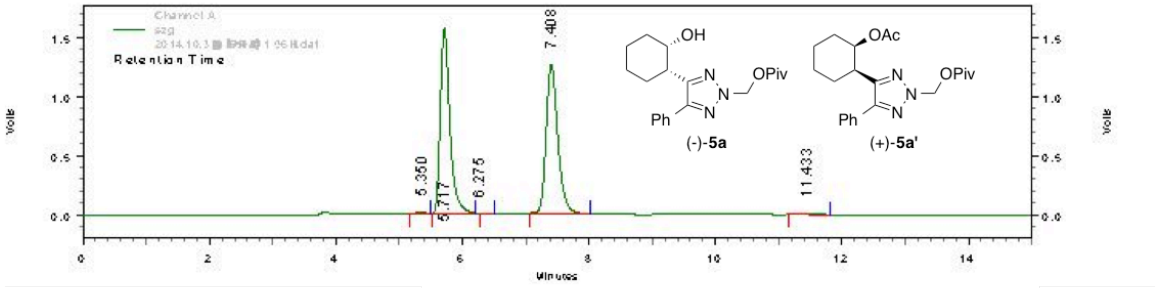


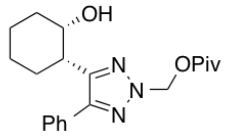
5a (-)-**5a** (+)-**5a'**

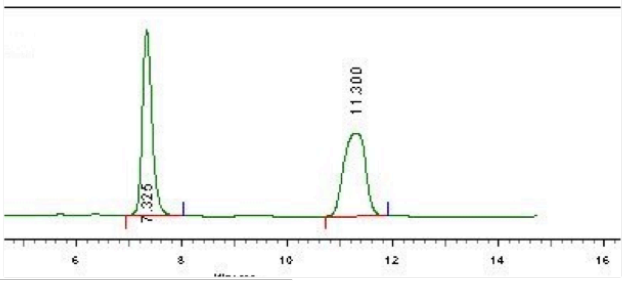
Entry	Solvent	T(°C)	Reaction time (h)	Conv.(%)	**(-)-5a** *ee*	**(+)-5a'** *ee*	S
1	H_2O	40 °C	24h	0	0	0	--
2	THF	40 °C	24h	0	0	0	--
3	acetone	40 °C	24h	0	0	0	--
4	1,4-dioxane	40 °C	24h	0	0	0	--
5	isooctane	40 °C	24h	<10	<10	>99	<10
6	isooctane	75 °C	24h	35	55	99	163
7	isooctane	75 °C	72h	50	99	99	>200
8[a]	isooctane	75 °C	72h	50	99	99	>200
9[b]	isooctane	75 °C	72h	49	95	99	>200
10[c]	isooctane	75 °C	72h	47	89	99	>200

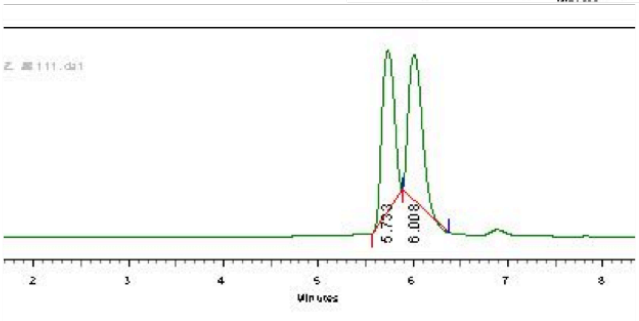
[a] reuse for the first time [b] reused for the second times [c] reused for the three times

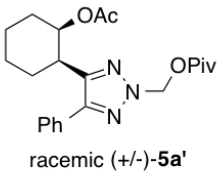
HPLC profile for entry 7

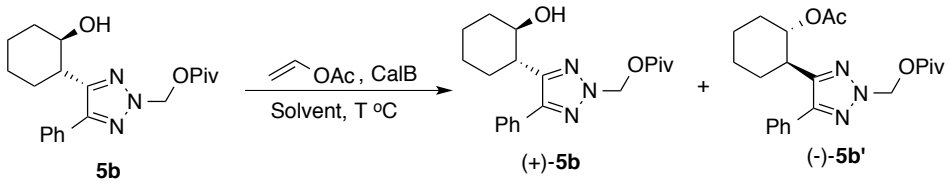








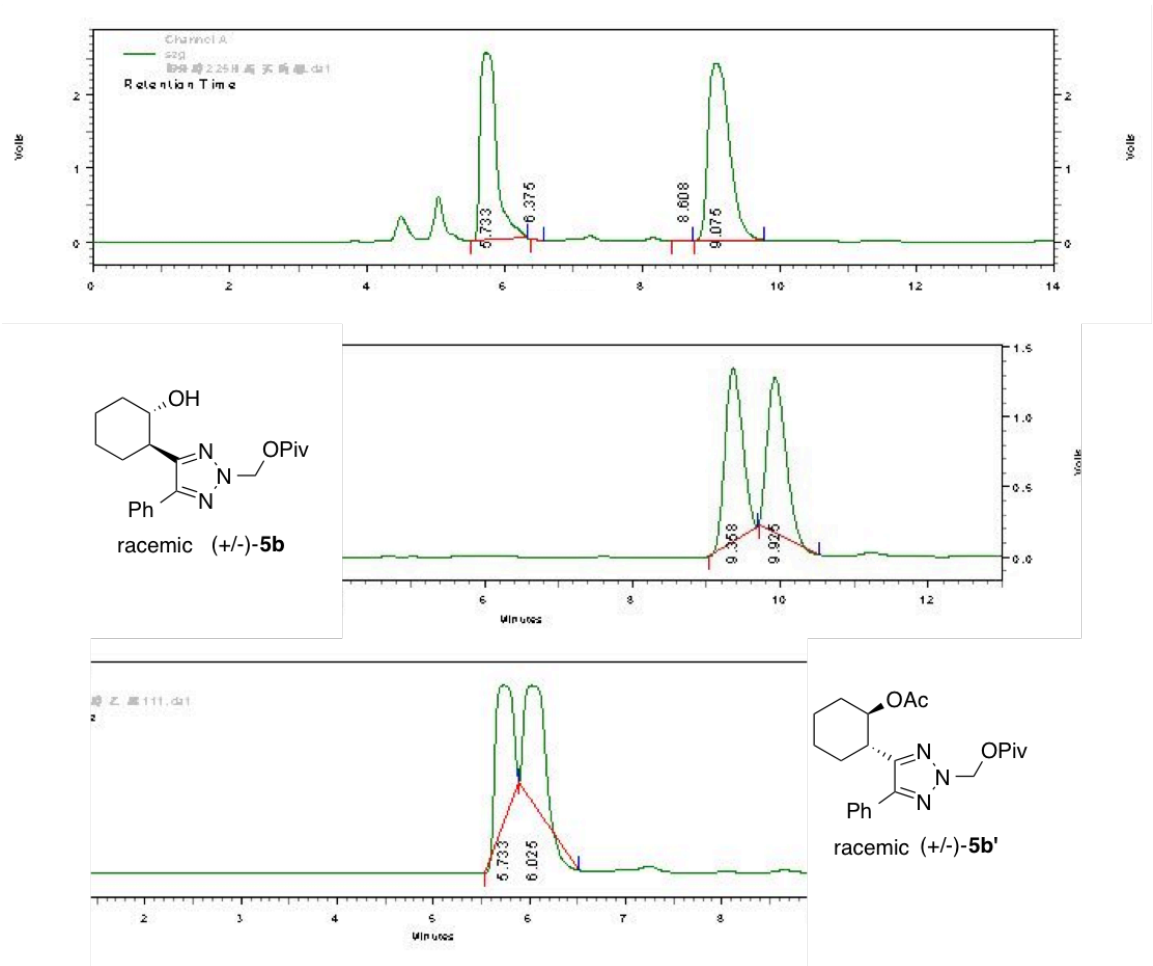




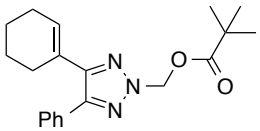
Entry	Solvent	T(°C)	Reaction time (h)	Conv.(%)	**(+)-5b** *ee*	**(-)-5b'** *ee*	*S*
1	H_2O	40 °C	24h	0	0	0	--
2	THF	40 °C	24h	0	0	0	--
3	acetone	40 °C	24h	<10	<10	>99	<10
4	1,4-dioxane	40 °C	24h	<10	<10	>99	<10
5	isooctane	40 °C	24h	49	98	95	152
6	isooctane	75 °C	24h	50	>99	99	>200
7[a]	isooctane	75 °C	24h	50	99	98	>200
8[b]	isooctane	75 °C	24h	50	99	98	>200
9[c]	isooctane	75 °C	24h	50	98	97	>200

[a] reuse for the first time [b] reused for the second times [c] reused for the three times

HPLC profile for entry 6



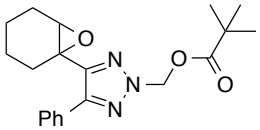
III. Compounds Characterization



1c

4-(cyclohex-1-en-1-yl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1c)

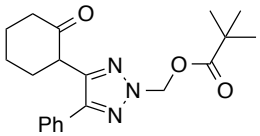
The product was obtained as white solid 35.3g (85% yield). m.p. 76-78 ^{o}C. ^{1}HNMR (400 MHz, CDCl3): δ 7.68-7.70 (d, J=7.2Hz, 2H), 7.36-7.48(m,3H), 6.26(s, 2H), 6.08(m, 1H), 2.32-2.38(m, 2H), 2.12-2.18(m, 2H), 1.66-1.80(m, 4H), 1.24(s,9H); 13C NMR(100 MHz, CDCl3): δ 177.0, 148.3, 145.7, 131.2, 130.2, 128.5, 128.5, 128.3, 128.2, 74.6, 38.9, 27.5, 27.0, 25.5, 22.6, 21.8. LC-MS(ESI) Calculated for $[C_{20}H_{25}N_3O_2H]^+$: 340.1947, Found: 340.1912.



1d

(4-(7-oxabicyclo[4.1.0]heptan-1-yl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1d).

The product was obtained as white solid 31.2g (80% yield). m.p. 40-42℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.84 (d, J=7.2Hz, 2H), 7.39-7.49 (m, 3H), 6.23 (s, 2H), 3.48-3.51(m, 1H), 2.20-2.30(m, 1H), 1.91-2.20(m, 3H), 1.50-1.51(m, 2H), 1.30-1.42(m, 2H), 1.21(s, 9H); ^{13}C NMR(100 MHz, CDCl3): δ 177.0, 147.1, 130.1, 128.9, 127.6, 128.1 74.4, 65.9, 58.4, 55.2, 38.9, 28.4, 24.2, 19.6, 19.1, 15.2. LC-MS(ESI) Calculated for $[C_{20}H_{25}N_3O_3H]^+$: 356.1896, Found: 356.1816.

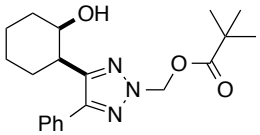


1e

(4-(2-oxocyclohexyl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (1e).

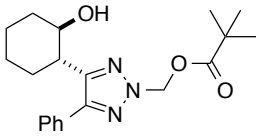
The product was obtained as light white solid 18.6 g, with 68% yield. m. p. 83-85 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.39-7.54 (m, 5H), 6.28 (s, 1H), 3.90 (t, J=8.5, 1H), 3.90 (t, J=8.5, 1H), 1.68-2.7 (m, 8H), 1.21 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 208.57, 177.013, 148.11, 144.71, 130.39, 128.72, 128.67, 128.06, 74.46, 48.68, 41.86, 38.91, 32.76, 27.34, 24.67. LC-MS(ESI): calculated for C20H27N3O3 $[C_{20}H_{25}N_3O_3H]^+$: 356.1896, Found: 356.1812.

4-(2-hydroxycyclohexyl)-5-phenyl-2H-1,2,3-triazol-2-yl)methyl pivalate (5a/5b)



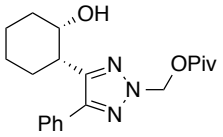
5a

cis-**5a** was obtained as light yellow oil 1.0 g, with 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4-7.65 (m, 5H), 6.28 (s, 1H), 4.17 (m, 1H), 3.10 (m, 1H), 1.25-2.1 (m, 8H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.92, 150.14, 146.89, 130.33, 128.86, 128.71, 128.08, 74.23, 67.91, 39.16, 38.92, 32.16, 26.91, 26.89, 25.88, 19.50. LC-MS(ESI): calculated for $[C_{20}H_{27}N_3O_3H]^+$: 358.2052, Found: 358.2119.



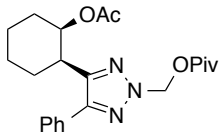
5b

trans-**5b** was obtained as light yellow oil 0.83 g, with 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4-7.65 (m, 5H), 6.28 (s, 1H), 4.15(m, 1H), 2.98 (m, 1H), 1.25-2.1 (m, 8H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.02, 149.19, 147.85, 130.56, 128.73, 128.58, 128.02, 74.39, 73.44, 43.57, 38.91, 34.41, 31.86, 26.92, 25.66, 24.84. LC-MS(ESI): calculated for $[C_{20}H_{27}N_3O_3H]^+$:358.2052, Found:358.2119.



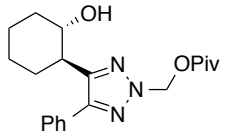
(-)-**5a**

cis-(-)-**5a** was obtained as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: (ppm) 7.4-7.65 (m, 5H), 6.28 (s, 2H), 4.17 (m, 1H), 3.10 (m, 1H), 1.25-2.1 (m, 8H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.92, 150.14, 146.89, 130.33, 128.86, 128.71, 128.08, 74.23, 67.91, 39.16, 38.92, 32.16, 26.91, 26.89, 25.88, 19.50. LC-MS(ESI): calculated for $[C_{20}H_{27}N_3O_3H]^+$: 358.2052, Found: 358.2119. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (hexane: 2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_{minor} = 11.93 min and t_{major} = 7.59 min. 99% *ee* . $[\alpha]_D^{20}$ = -33.9 (*c*=1.0, $CHCl_3$).



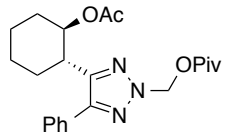
(+)-**5a'**

cis-(+)-**5a'** was obtained as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ δ 7.57 (dt, *J* = 8.1, 1.8 Hz, 2H), 7.47-7.37 (m, 3H), 6.24 (s, 2H), 5.21 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.24 (dt, *J* = 10.8, 3.4 Hz, 1H), 2.17-2.10 (m, 1H), 2.06 (s, 3H), 2.00-1.88 (m, 5H), 1.79-1.53 (m, 5H), 1.44-1.36 (m, 2H), 1.22-1.18 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 170.9, 170.1, 147.8, 147.2, 130.6, 128.58, 128.41, 128.1, 74.2, 70.5, 60.2, 38.7, 37.1, 29.7, 26.8, 26.5, 24.6, 20.98, 20.87, 20.7, 14.1. HRMS for $[C_{22}H_{30}N_3O_4]^+$: 400.2231, Found: 400.2233.



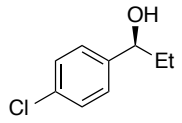
(+)-**5b**

trans-(+)-**5b** was obtained as colorless liquid.; ^{1}H NMR (400 MHz, $CDCl_3$) δ: (ppm) 7.4-7.65 (m, 5H), 6.28 (s, 2H), 4.15(m, 1H), 2.98 (m, 1H), 1.25-2.1 (m, 8H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: (ppm) 177.02, 149.19, 147.85, 130.56, 128.73, 128.58, 128.02, 74.39, 73.44, 43.57, 38.91, 34.41, 31.86, 26.92, 25.66, 24.84. LC-MS(ESI): calculated for $[C_{20}H_{27}N_3O_3H]^+$:358.2052, Found:358.2119. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (hexane: 2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_{minor} = 9.41 min and t_{major} = 9.88 min. 99% *ee*. $[\alpha]_D^{20}$ = + 32.3 (*c* 1.0, $CHCl_3$).



(-)-**5b'**

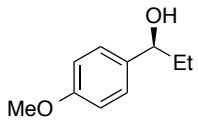
trans-(-)-**5b'** was obtained as yellow liquid ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.49-7.39 (m, 3H), 6.24 (d, *J* = 0.2 Hz, 2H), 5.29 (s, 2H), 5.08 (td, *J* = 10.6, 4.3 Hz, 1H), 3.12 (ddd, *J* = 11.9, 10.5, 3.9 Hz, 1H), 2.21-2.17 (m, 1H), 2.03 (d, *J* = 3.5 Hz, 1H), 1.99-1.94 (m, 1H), 1.86-1.74 (m, 5H), 1.53-1.25 (m, 5H), 1.24-1.19 (m, 8H). 13-C NMR (101 MHz; cdcl3): δ 176.7, 170.9, 169.6, 161.5, 148.3, 147.4, 130.6, 128.59, 128.55, 128.51, 128.36, 128.23, 128.20, 128.05, 127.99, 76.4, 74.2, 60.2, 53.3, 39.7, 38.7, 32.0, 31.8, 26.7, 25.2, 24.2, 20.8, 14.1. HRMS for $[C_{22}H_{30}N_3O_4]^+$: 400.2231, Found: 400.2233.



6a

(*S*)-1-(4-Chlorophenyl)-1-propanol

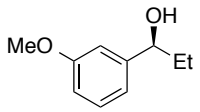
6a was obtained as light yellow oil. 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.4 Hz, 2H), 7.24(d, J = 8.4 Hz, 2H), 4.57 (t, J = 6.8 Hz, 1H), 2.12 (s, 1H), 1.82–1.66 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 133.0, 128.4, 127.3, 75.2, 31.9, 9.9. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (hexane: 2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_S = 27.10 min for (*S*) and t_R = 31.10 min for (*R*), 99% *ee* (S).



6b

(*S*)-1-(4-Methoxyphenyl)-1-propanol (6b)

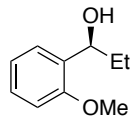
6b was obtained as light yellow oil. 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.25 (m, 2H), 6.90–6.86(m, 2H), 4.54 (t, J = 6.7 Hz, 1H), 3.80(s, 3H), 1.84–1.69 (m, 3H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 136.9, 127.2, 113.7, 75.4, 55.2, 31.7, 10.1. Enantiomeric excess was determined by HPLC analysis with a Daicel Chiralcel OD-H column, (hexane: 2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_S = 18.38 min for (*S*) and t_R = 15.79 min for (*R*), 60% *ee* (S)



6c

***(S)*-1-(3-Methoxyphenyl)-1-propanol (6c)**

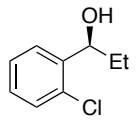
6c was obtained as yellow oil. 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.83-6.80 (m, 1H), 4.57 (t, *J* = 6.5 Hz, 1H), 3.81 (s, 3H), 1.85-1.71 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.3, 129.4, 118.3, 112.9, 111.4, 75.9, 55.2, 31.8, 10.1. Enantiomeric excess was determined by HPLC analysis with a Daicel Chiralcel OD-H column, (hexane: 2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_S = 23.21 min for (*S*) and t_R = 21.95 min for (*R*), 60% *ee* (S)



6d

(*S*)-1-(2-Methoxyphenyl)-1-propwwanol (6d)

6d was obtained as yellow oil. 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.23 (m, 1H), 6.95–6.86(m, 3H), 4.60 (t, J = 6.4 Hz, 1H), 3.84 (s, 3H), 1.77–1.86 (m and s overlap, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.3, 129.4, 118.3, 112.9, 111.5, 75.9, 55.3, 31.9, 10.1. Enantiomeric excess was determined by HPLC analysis with a Daicel Chiralcel OD-H column (hexane: ethanol = 97:3, 0.5 mL/min, 254 nm UV detector), t_S = 16.55 min for (*S*) and t_R = 18.41 min for (*R*). 90% *ee* (S)



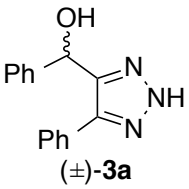
6e

(*S*)-1-(2-Chlorophenyl)-1-propanol (6e)

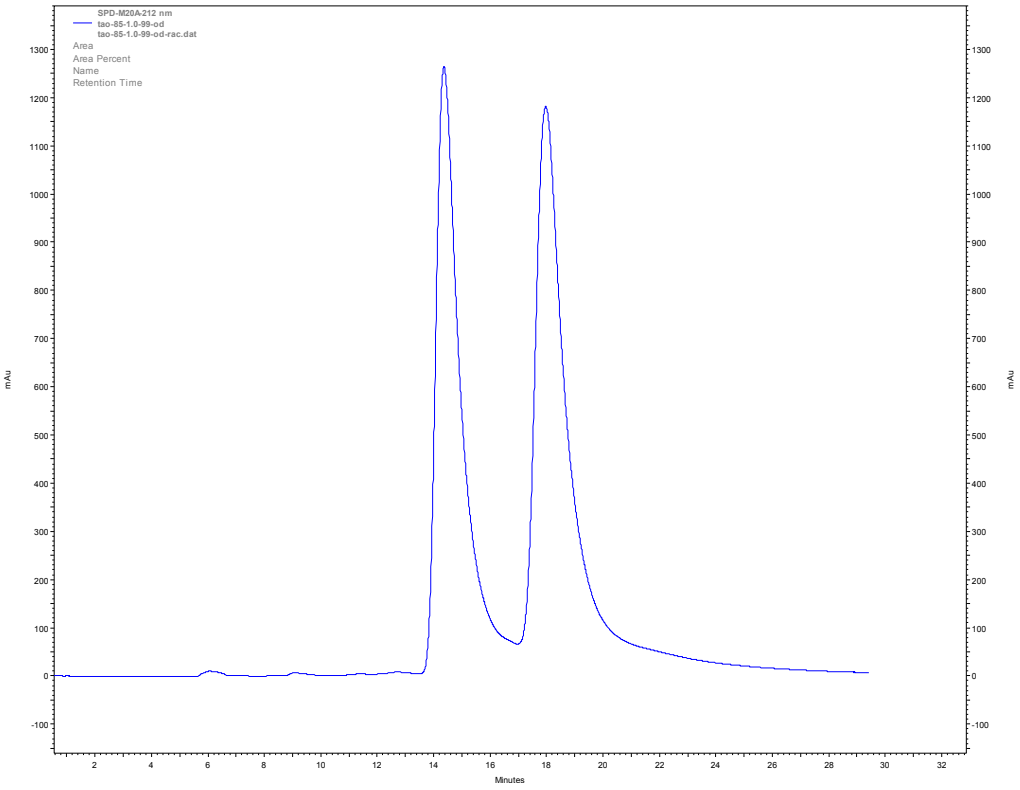
6e was obtained as yellow oil. 90% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.36–7.25 (m, 2H), 7.25–7.16 (m, 1H), 5.10-5.05 (dd, J = 4.8 Hz, J = 7.6 Hz, 1H), 2.14 (s, 1H), 1.90–1.71 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 131.9, 129.3,128.3, 127.1, 127.0, 71.9, 30.4, 10.1. Enantiomeric excess was determined by HPLC analysis with a Daicel Chiralcel OD-H column (hexane:

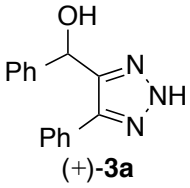
2-propanol = 97:3, 1.0 mL/min, 254 nm UV detector), t_S = 8.68 min for (*S*) and t_R = 10.19 min for (*R*). 60% *ee* (S)

HPLC Profile

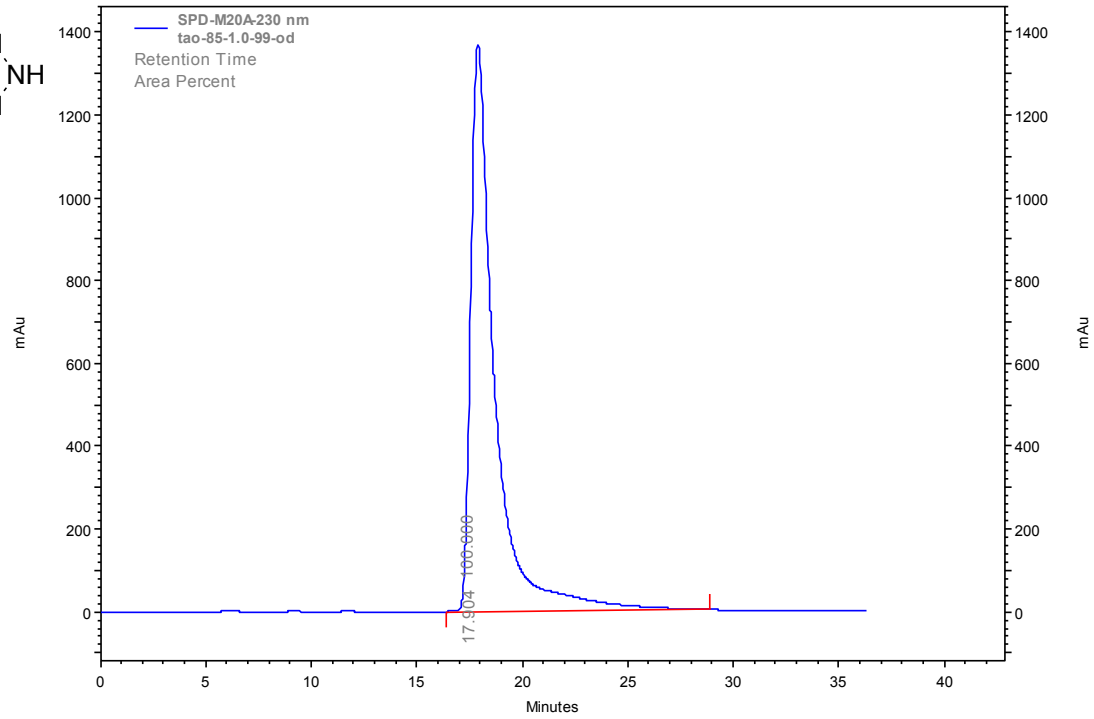

OH
Ph
N
NH
N
Ph

(±)-**3a**


SPD-M20A-212 nm
tao-85-1.0-99-od
tao-85-1.0-99-od-rac.dat
Area
Area Percent
Name
Retention Time
mAu
Minutes


OH
Ph
N
NH
N
Ph

(+)-**3a**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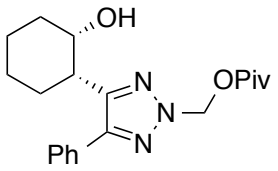
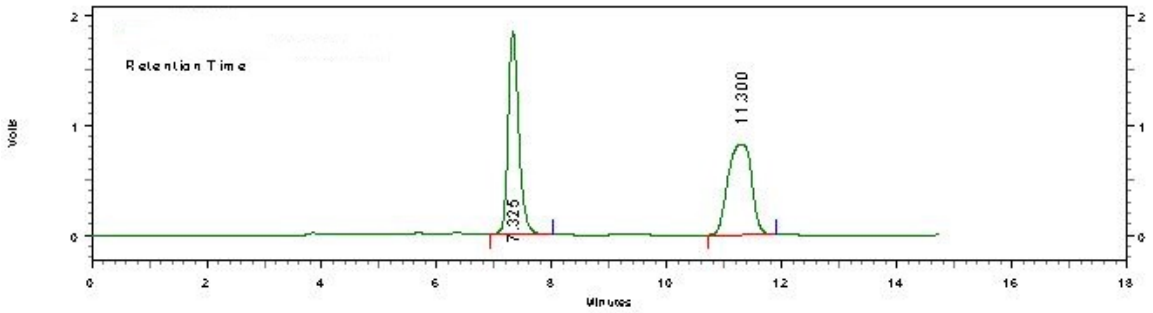
tao-85-1.0-99-od
Retention Time
Area Percent
17.904 100.000
mAu
Minutes

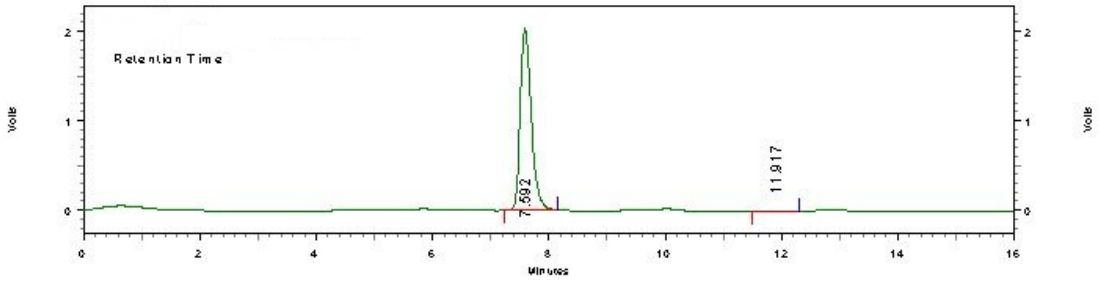


(-)-**5a**



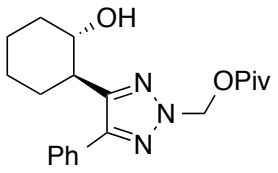
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	7.325	23877036	50.380	1848436	69.140
2	11.300	23516578	49.620	825032	30.860
Totals		47393614	100.000	2673468	100.000

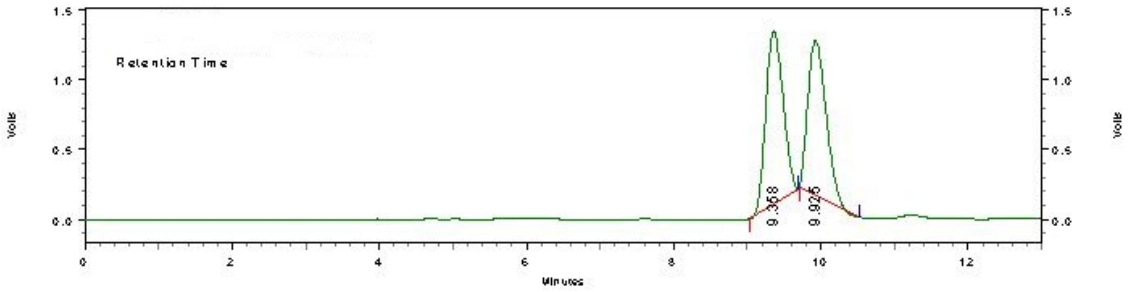


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	7.592	26617232	99.966	2028837	99.975
2	11.917	9069	0.034	500	0.025
Totals		26626301	100.000	2029337	100.000

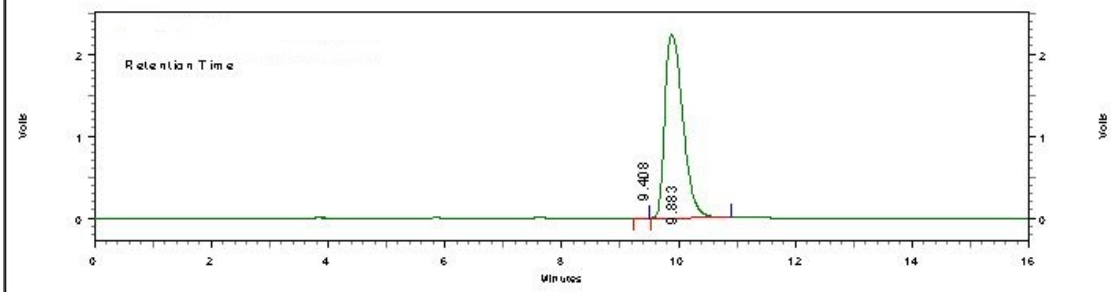


(+)-**5b**



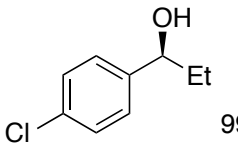
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	9.358	20207348	51.421	1237867	52.647
2	9.925	19090738	48.579	1113413	47.353
Totals		39298086	100.000	2351280	100.000

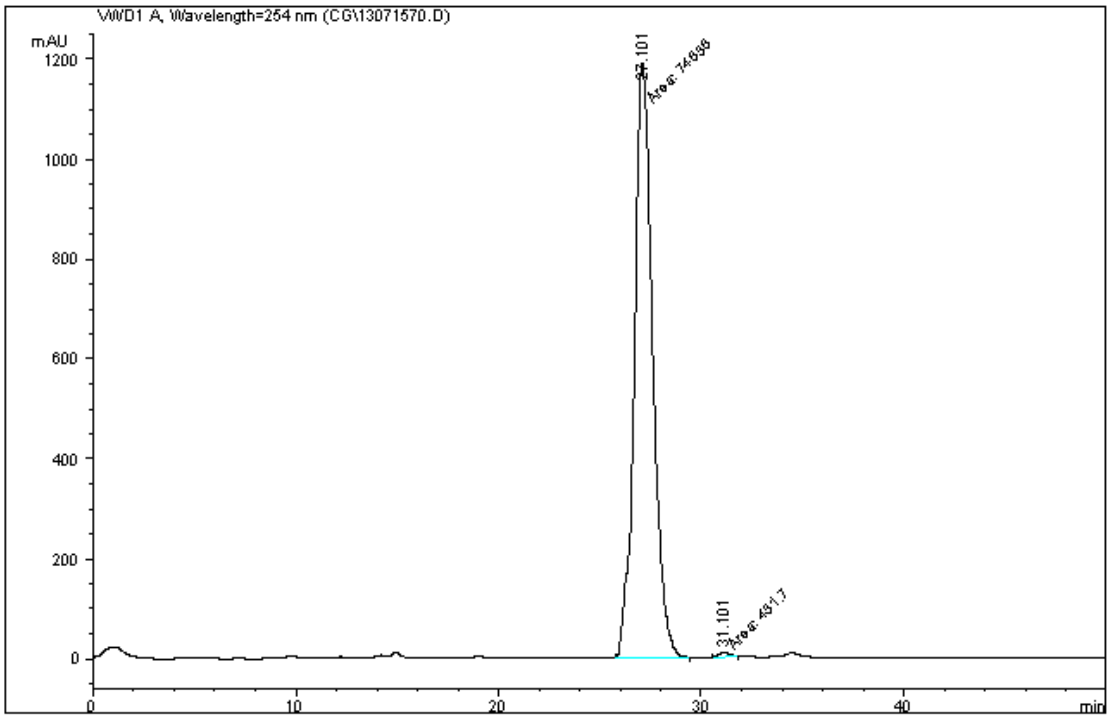


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	9.408	8345	0.017	842	0.038
2	9.883	47786490	99.983	2231787	99.962
Totals		47794835	100.000	2232629	100.000



6a
99% *ee* (S)

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Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime  Type    Width     Area      Area     Name
  #   [min]           [min]  mAU   *s       %
----|-------|------|-------|----------|--------|--------------------
   1   0.000         0.0000    0.00000   0.0000
   2  12.916         0.0000    0.00000   0.0000
   3  13.848         0.0000    0.00000   0.0000
   4  15.919         0.0000    0.00000   0.0000
   5  27.101 MM      1.0463 7.48380e4   99.4265 ?
   6  31.101 MM      0.7792  431.69977   0.5735 ?
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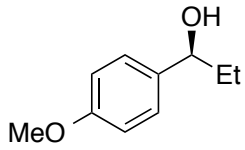
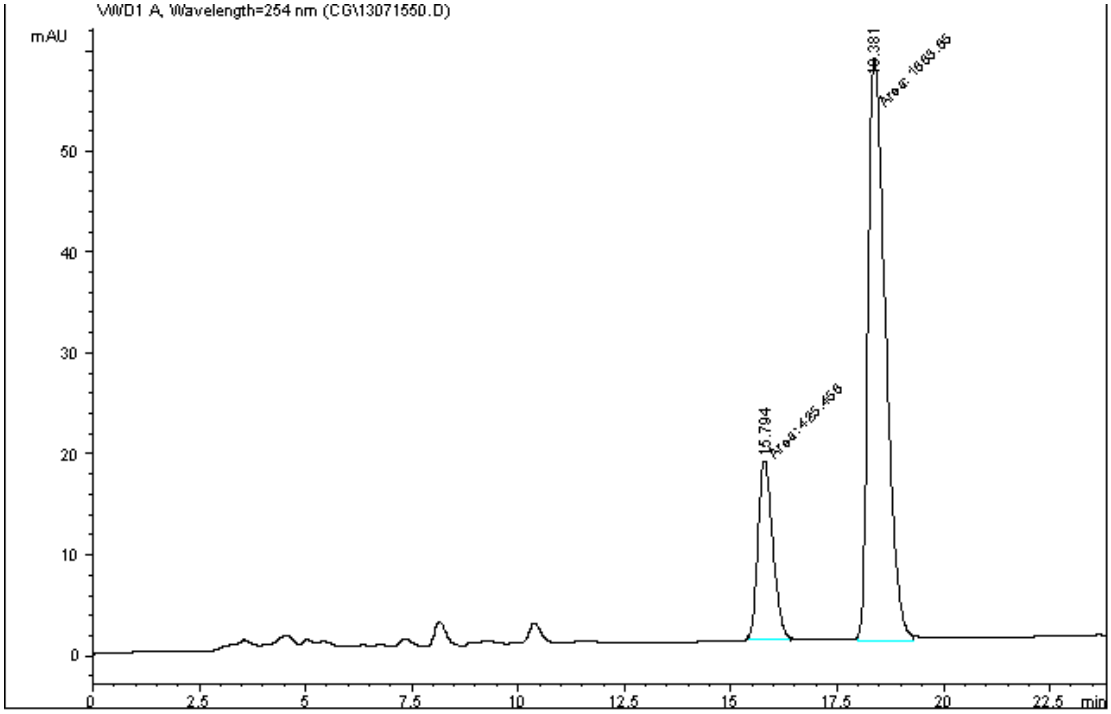


6b

59% *ee* (S)

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Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime  Type    Width     Area      Area     Name
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   3  13.848         0.0000    0.00000   0.0000
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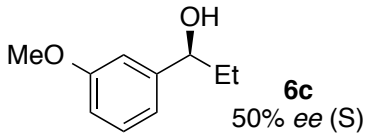
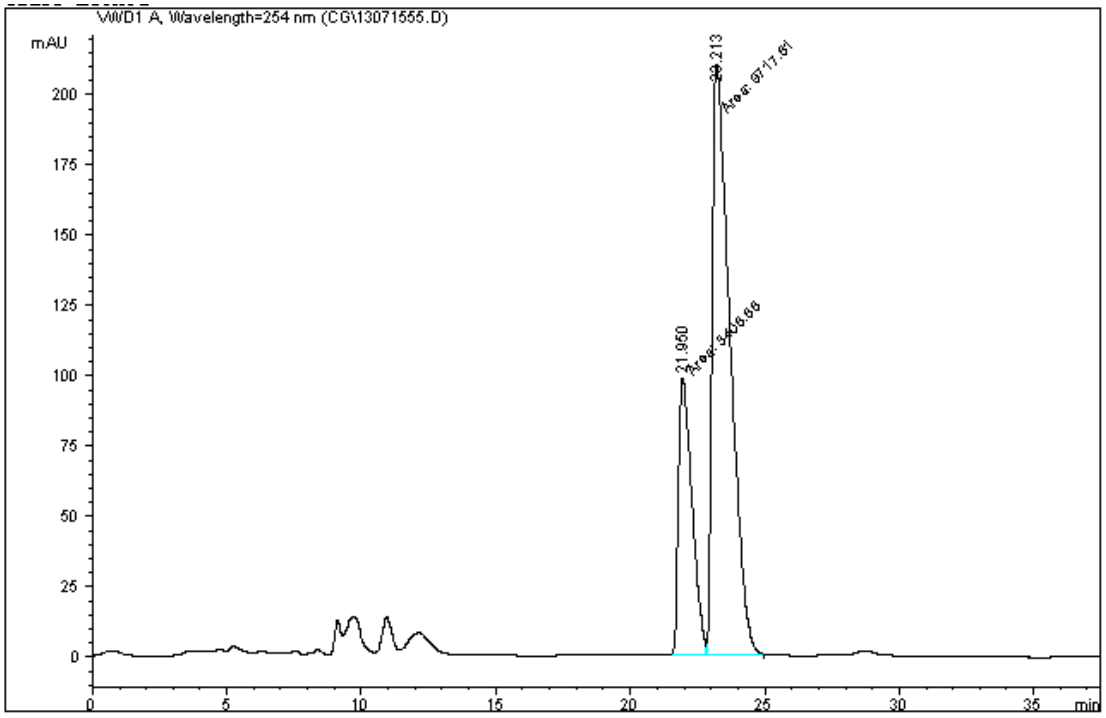


6c

50% *ee* (S)

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Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime  Type   Width     Area      Area    Name
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   3  13.848         0.0000    0.00000   0.0000
   4  15.919         0.0000    0.00000   0.0000
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   6  23.213 MM      0.7705 9717.60840  74.0306 ?
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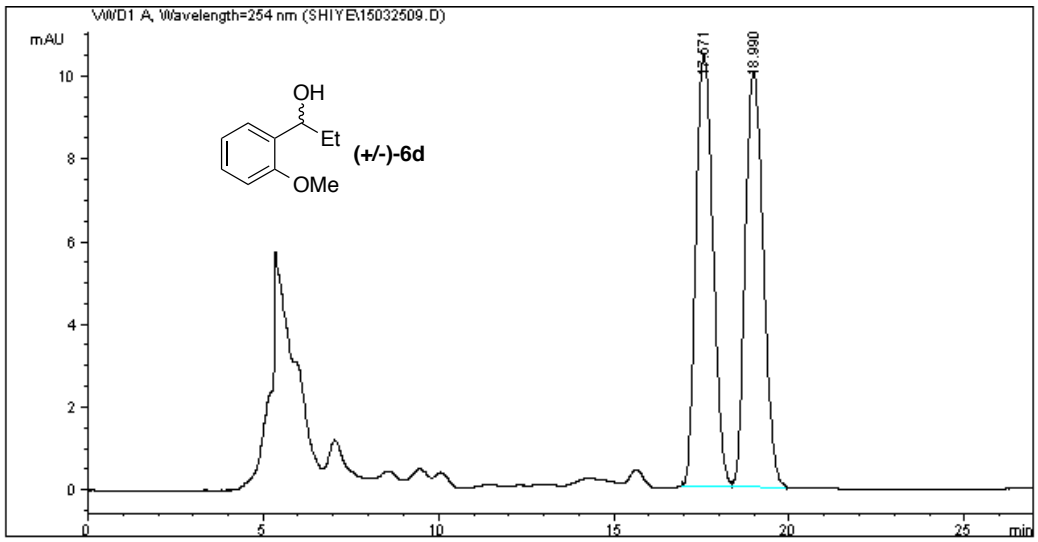

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2	18.990	VB	0.5627	360.02292	10.07078	50.2375
Totals :				716.64233	20.54357	

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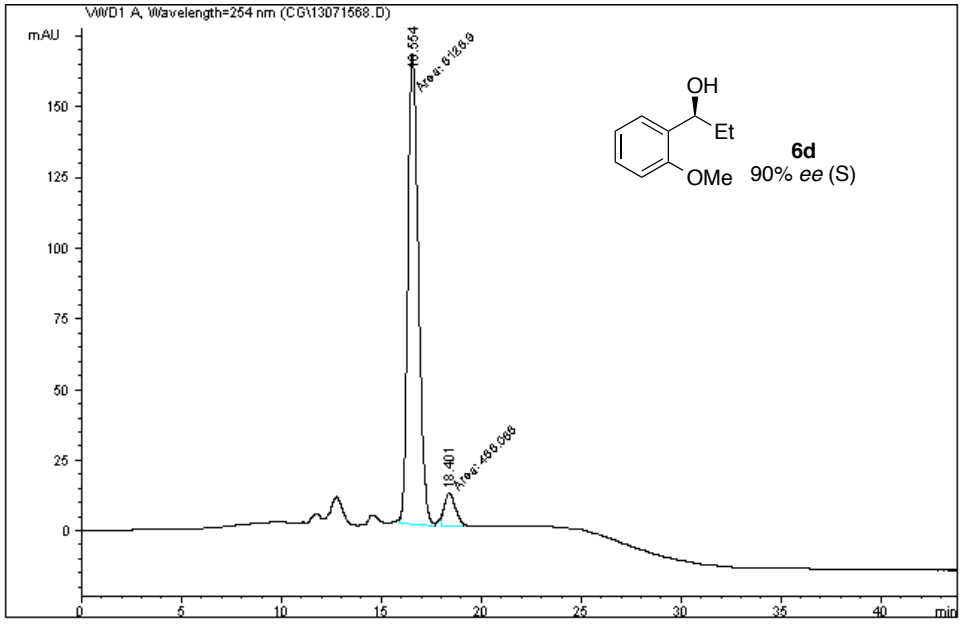
*** End of Report ***



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Area Percent Report

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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
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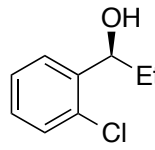
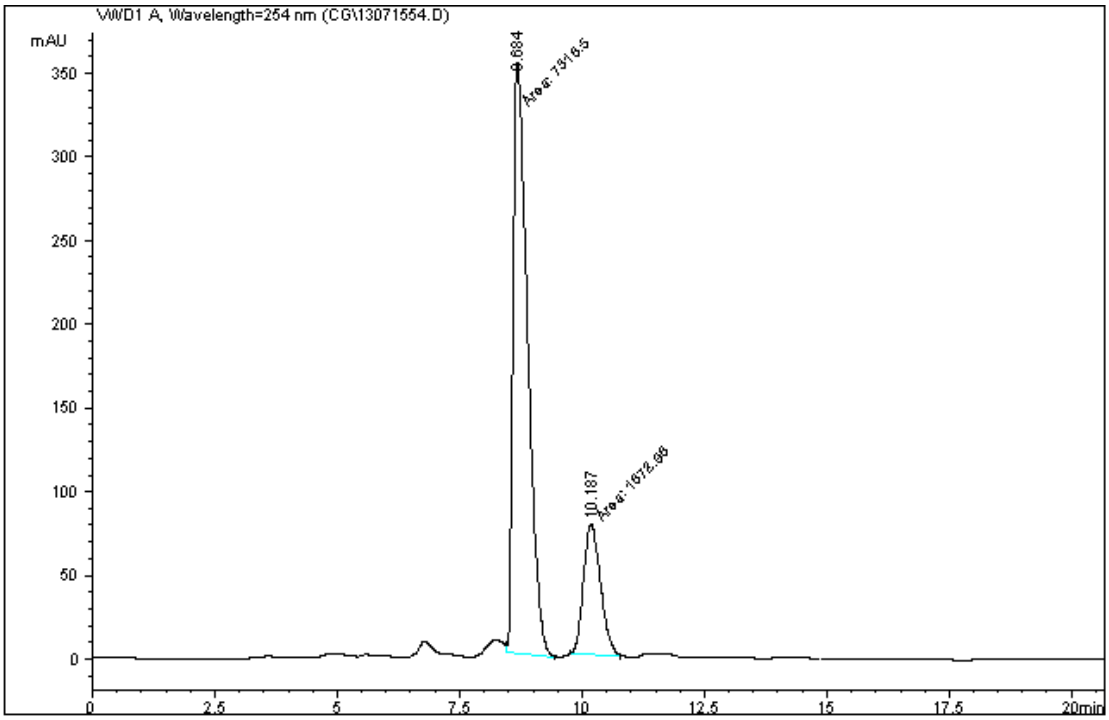
2	12.916		0.0000	0.00000	0.0000	
3	13.848		0.0000	0.00000	0.0000	
4	15.919		0.0000	0.00000	0.0000	
5	16.554	MM	0.6122	6128.90283	92.9330	?
6	18.401	MM	0.6426	466.06564	7.0670	?



6e

60% *ee* (S)

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Sorted By             :      Signal
Calib. Data Modified  :      12/15/2014 10:11:39 AM
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime  Type    Width     Area      Area     Name
  #   [min]           [min]   mAU   *s       %
----|-------|------|-------|----------|--------|--------------------
   1   0.000         0.0000    0.00000   0.0000
   2   8.684 MM      0.3449 7318.49512  79.6228 ?
   3  10.187 MM      0.4009 1872.96252  20.3772 ?
   4  12.916         0.0000    0.00000   0.0000
   5  13.848         0.0000    0.00000   0.0000
   6  15.919         0.0000    0.00000   0.0000
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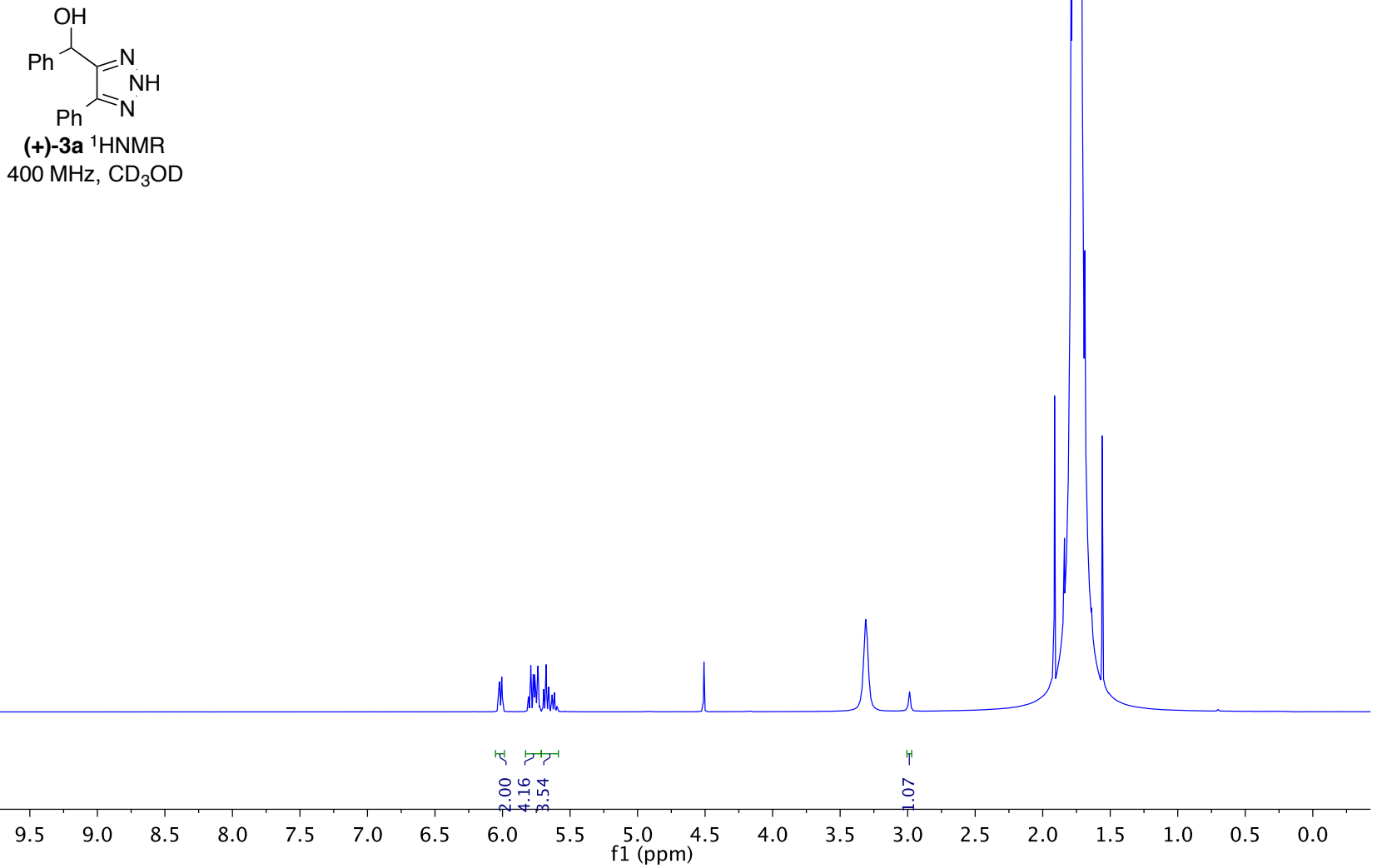
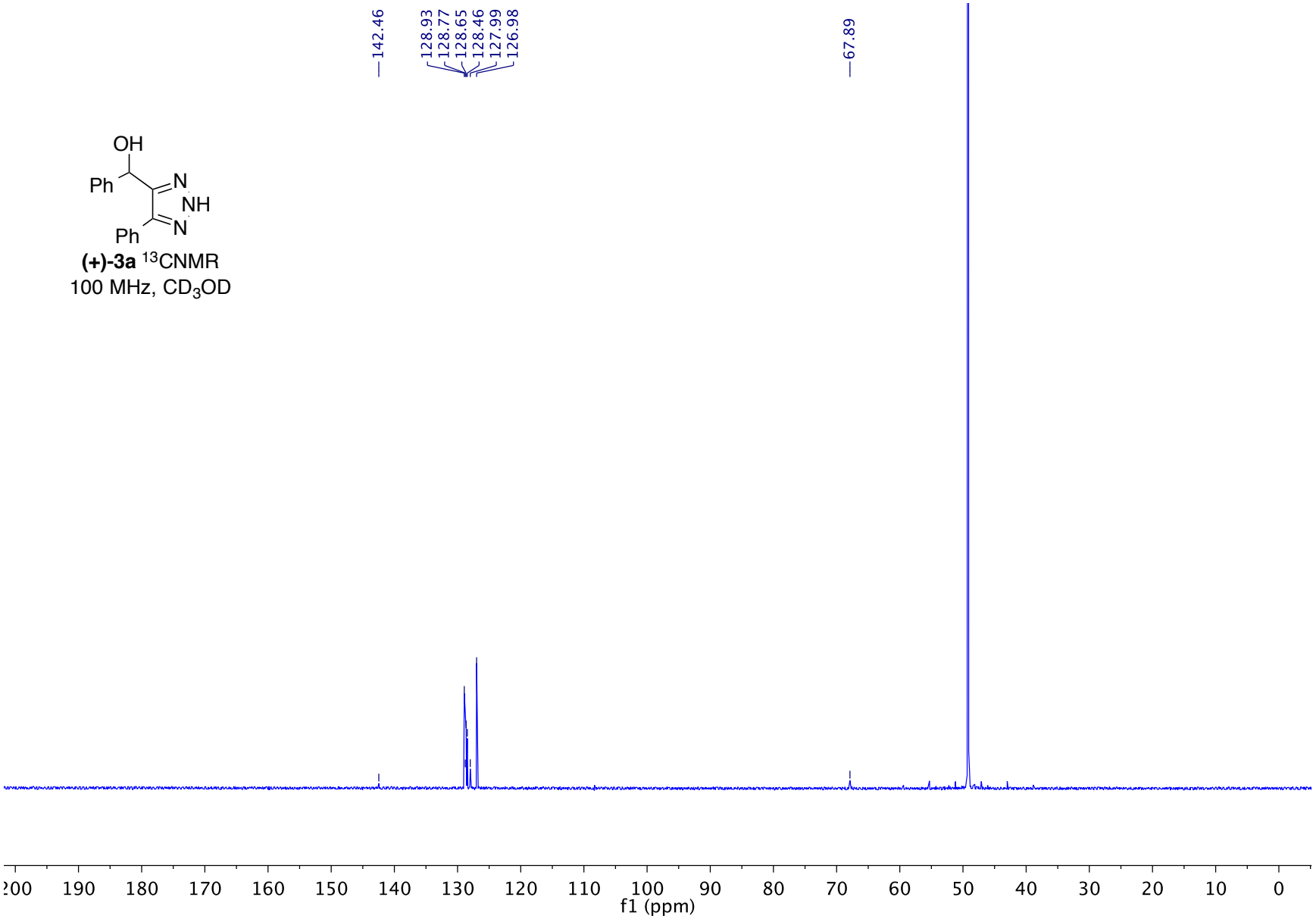
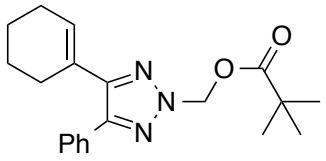
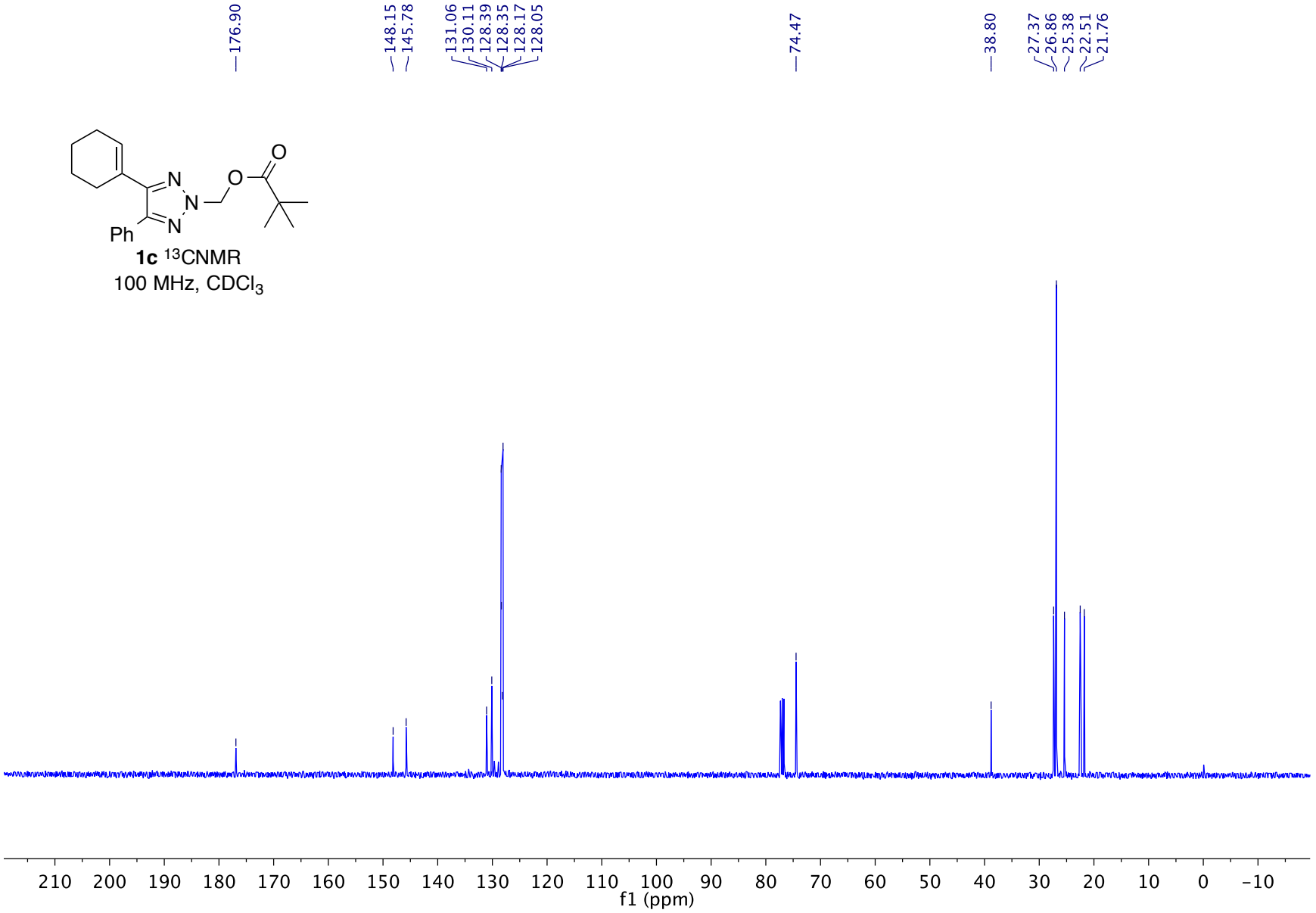
VI. NMR spectra data

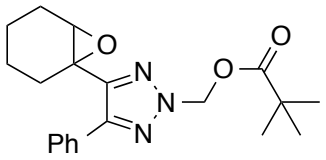

OH
Ph
N
NH
N
Ph
(+)-3a 1HNMR
400 MHz, CD3OD
2.00
4.16
3.54
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.46
128.93
128.77
128.65
128.46
127.99
126.98
67.89
OH
Ph
N
NH
N
Ph
(+)-3a 13CNMR
100 MHz, CD3OD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

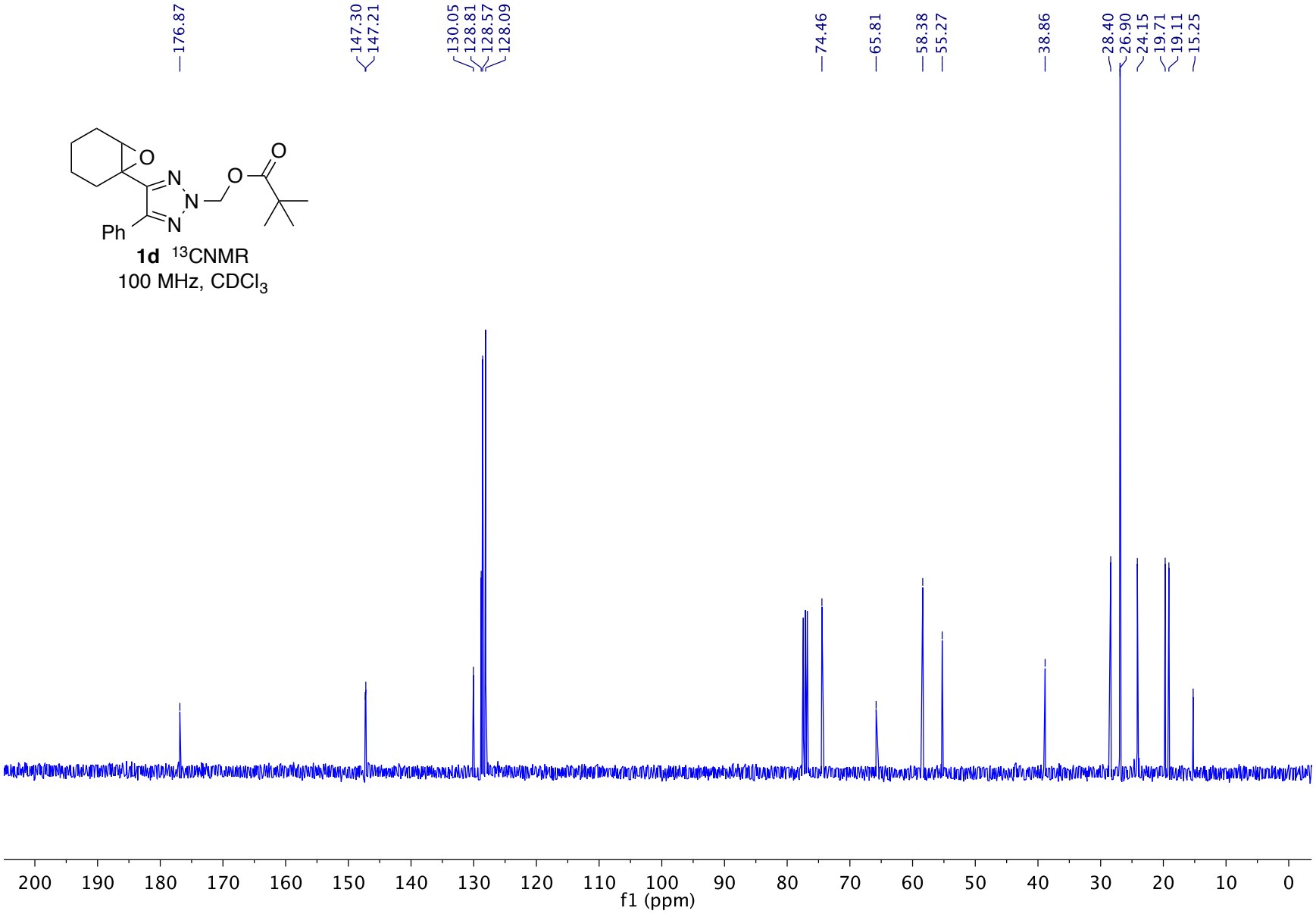


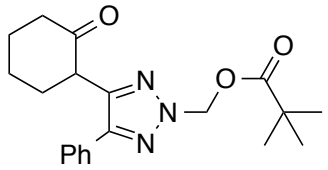
1c ^{1}HNMR
400 MHz, $CDCl_3$


176.90
148.15
145.78
131.06
130.11
128.39
128.35
128.17
128.05
74.47
38.80
27.37
26.86
25.38
22.51
21.76
N
N
N
O
O
Ph
1c 13CNMR
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

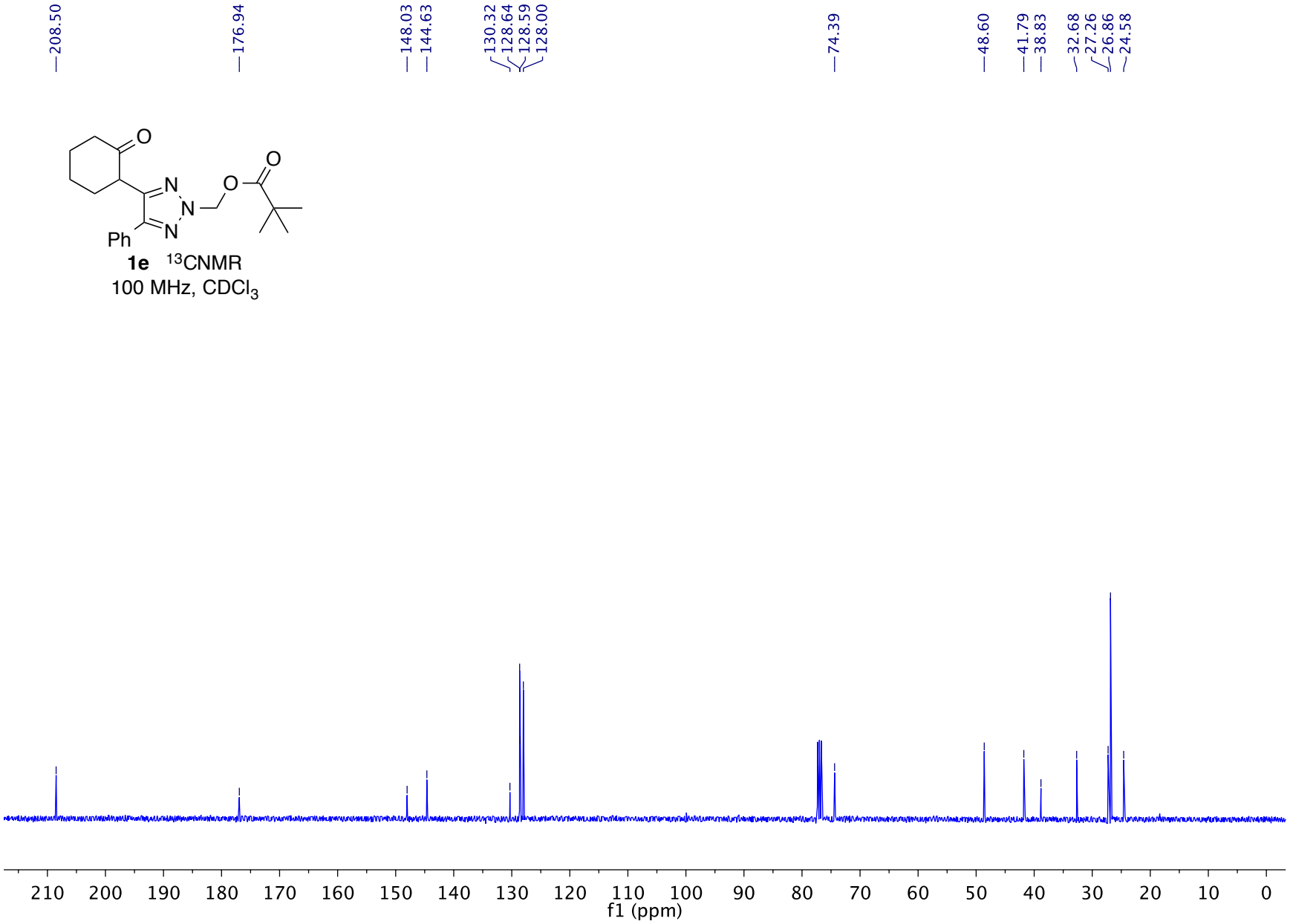


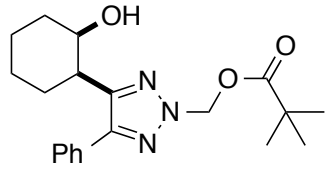
1d ^{1}HNMR
400 MHz, $CDCl_3$


176.87
147.30
147.21
130.05
128.81
128.57
128.09
74.46
65.81
58.38
55.27
38.86
28.40
26.90
24.15
19.71
19.11
15.25
O
N
N
N
O
O
Ph
1d 13CNMR
100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



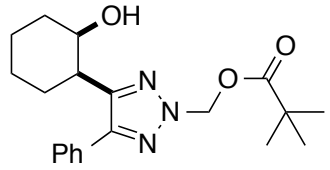
1e ^{1}HNMR
400 MHz, $CDCl_3$


208.50
176.94
148.03
144.63
130.32
128.64
128.59
128.00
74.39
48.60
41.79
38.83
32.68
27.26
26.86
24.58
O
O
N
N
N
O
Ph
1e 13CNMR
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

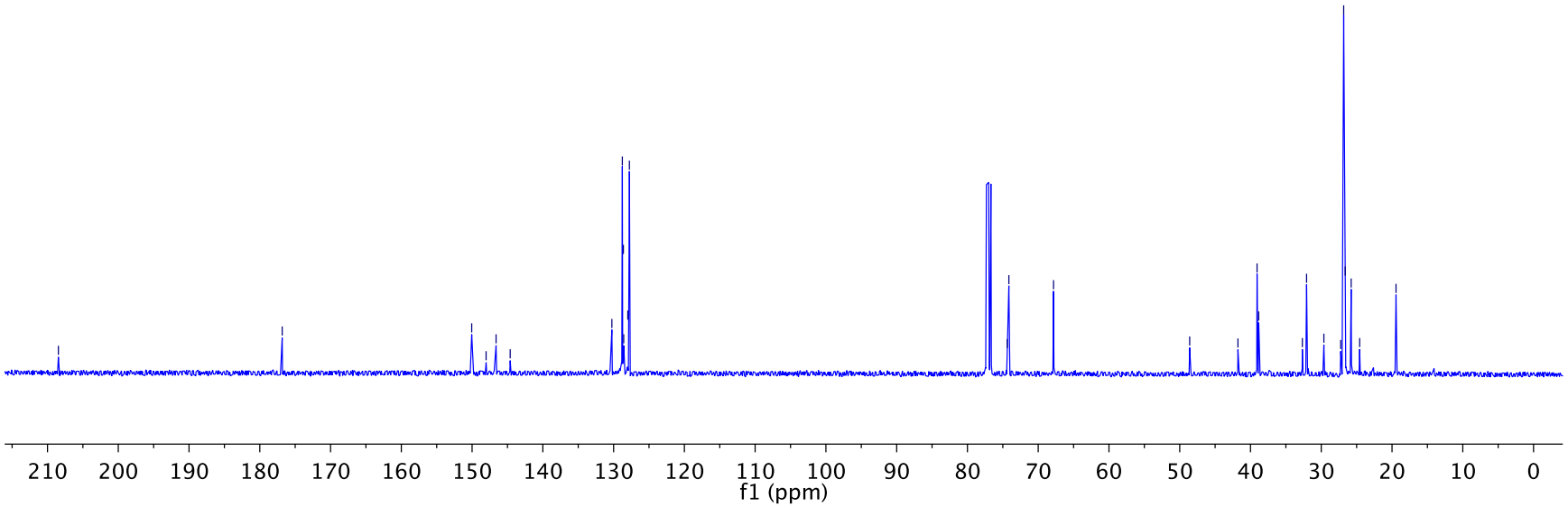


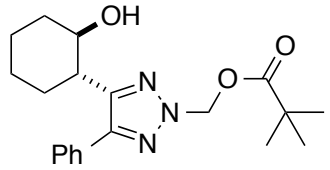
5a ^{1}HNMR
400 MHz, $CDCl_3$

208.46
176.83
150.05
148.02
146.61
144.62
130.25
128.77
128.62
128.57
128.00
127.77
74.37
74.15
67.83
48.59
41.77
39.07
38.84
32.67
32.07
29.63
27.25
26.83
26.61
25.77
24.57
19.43

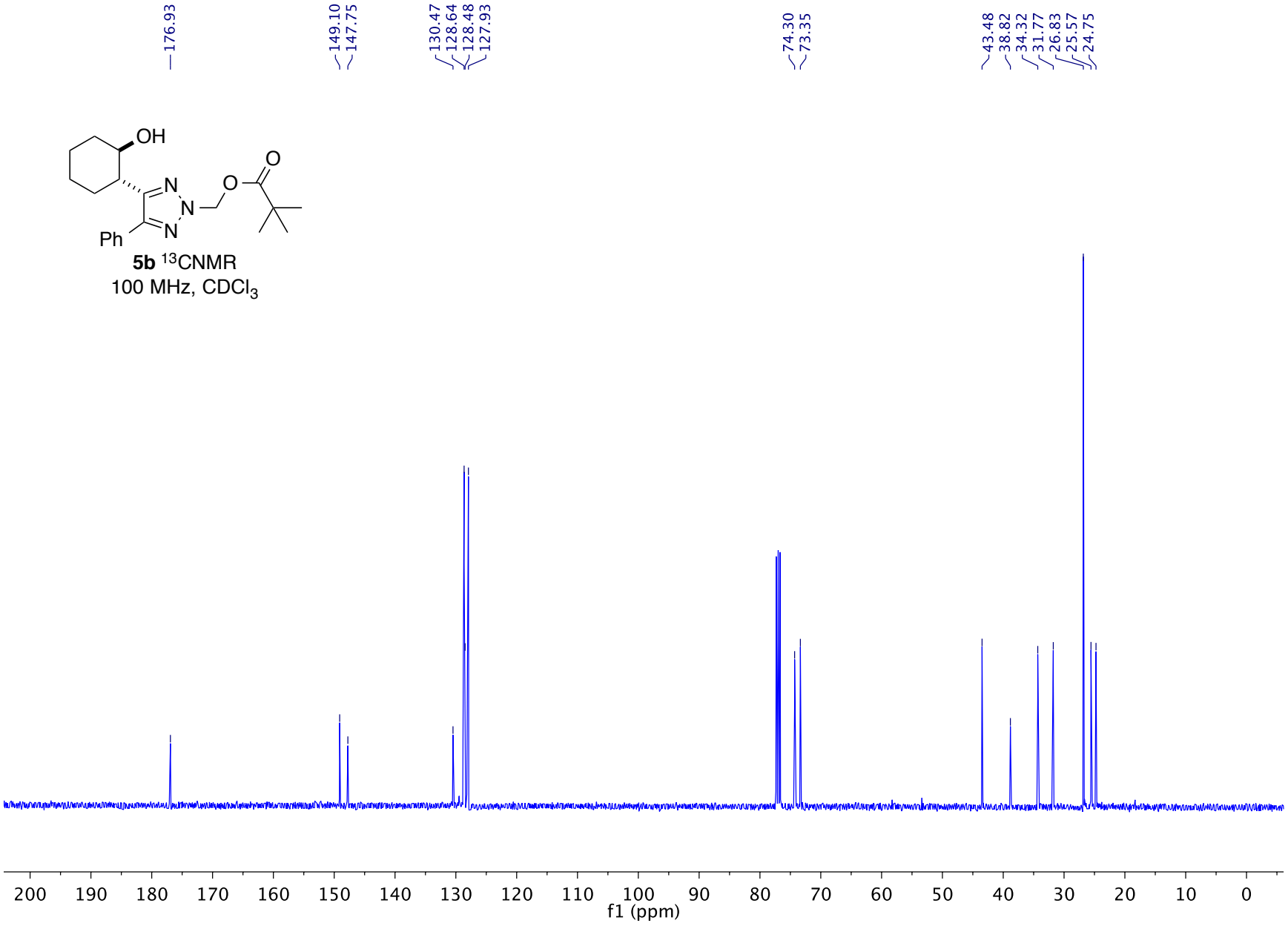


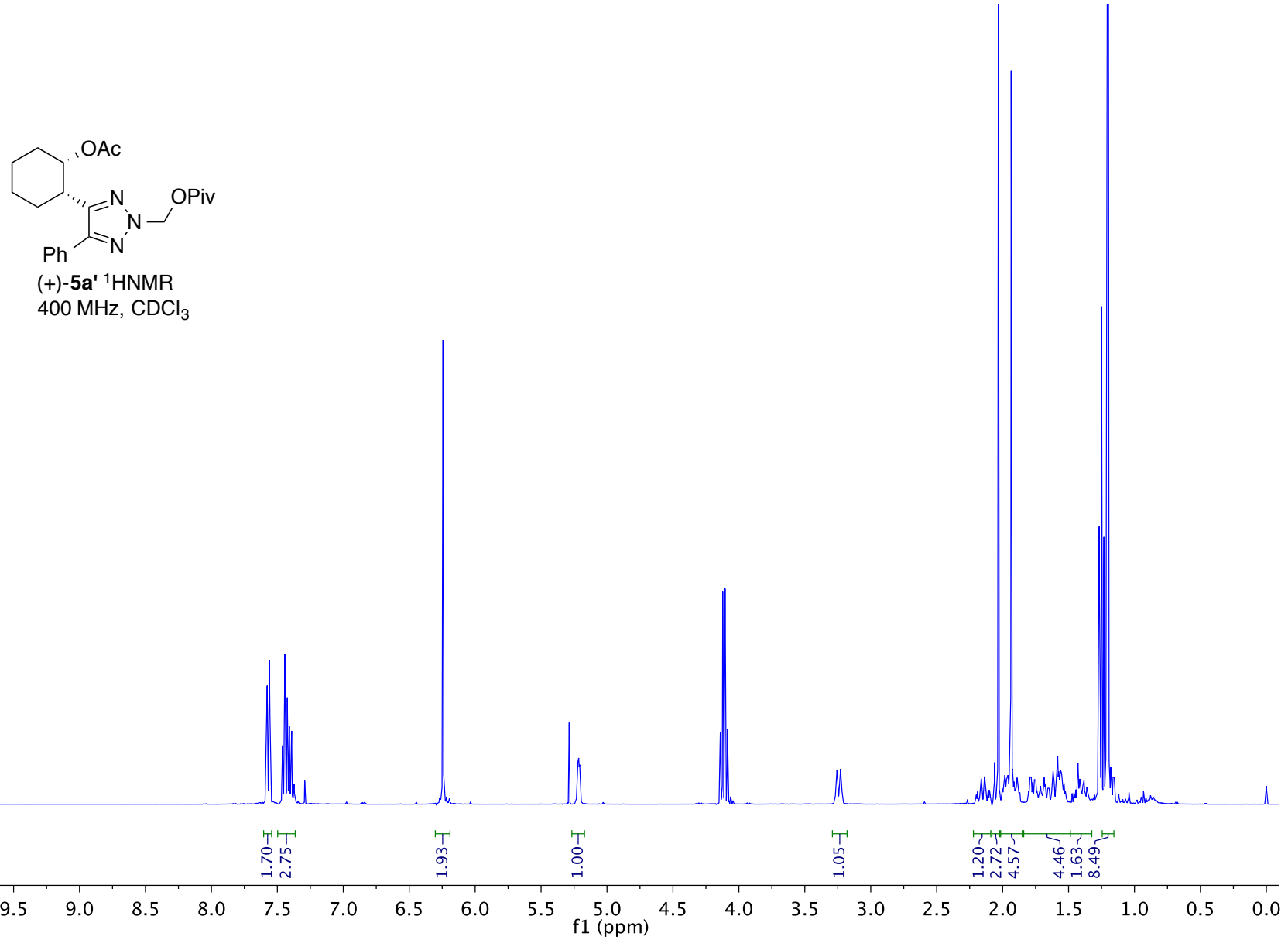
5a ^{13}CNMR
100 MHz, $CDCl_3$

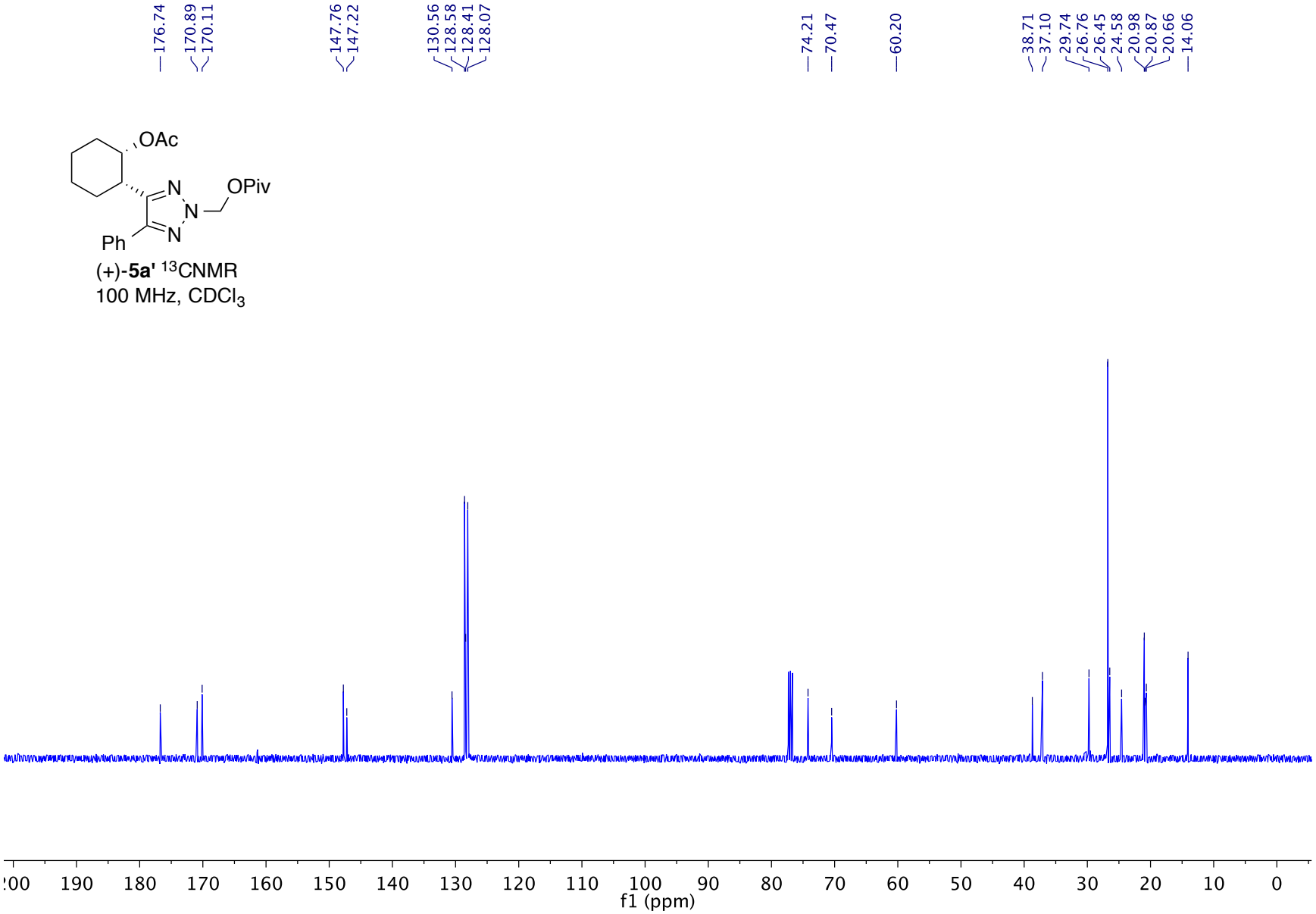


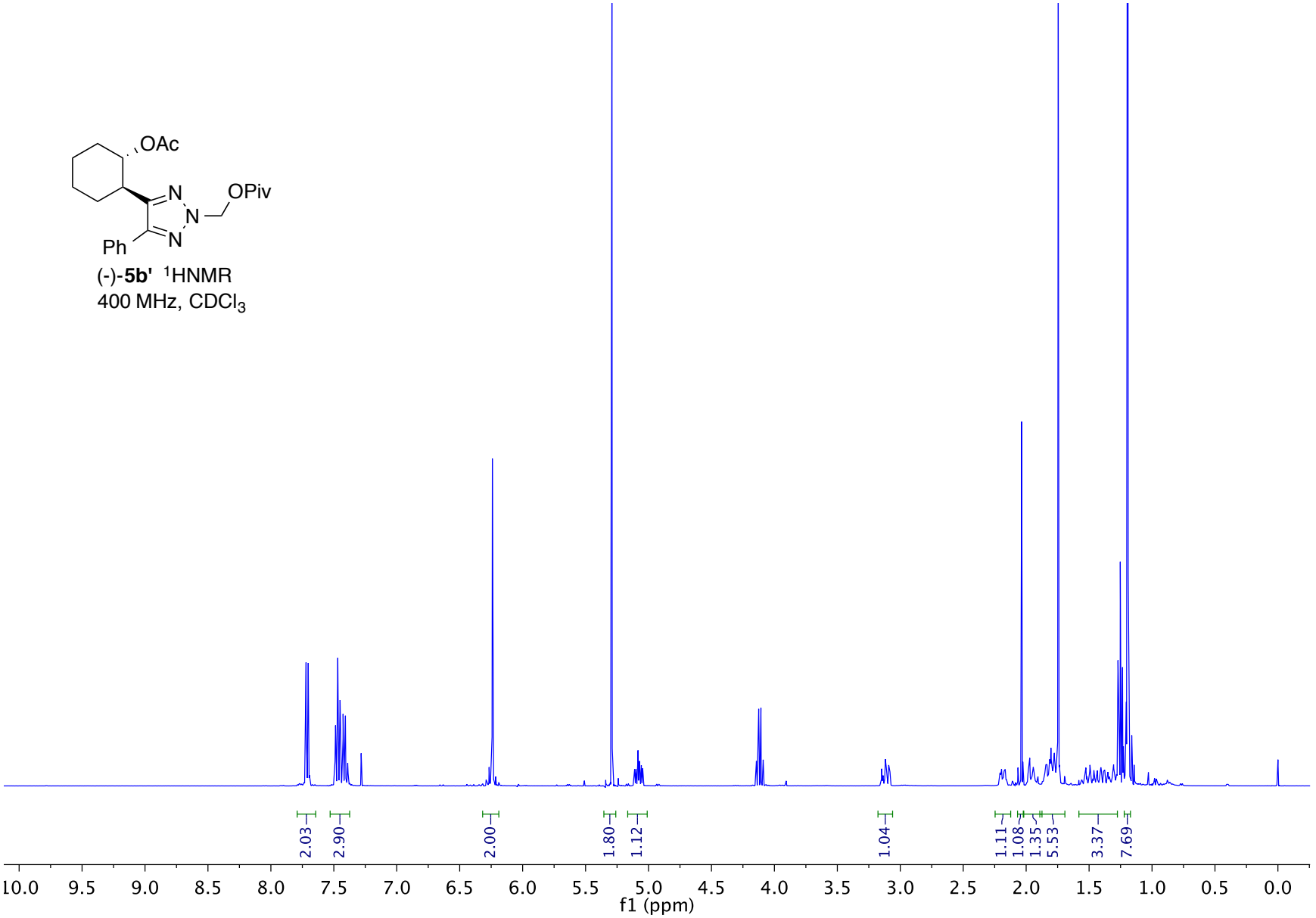


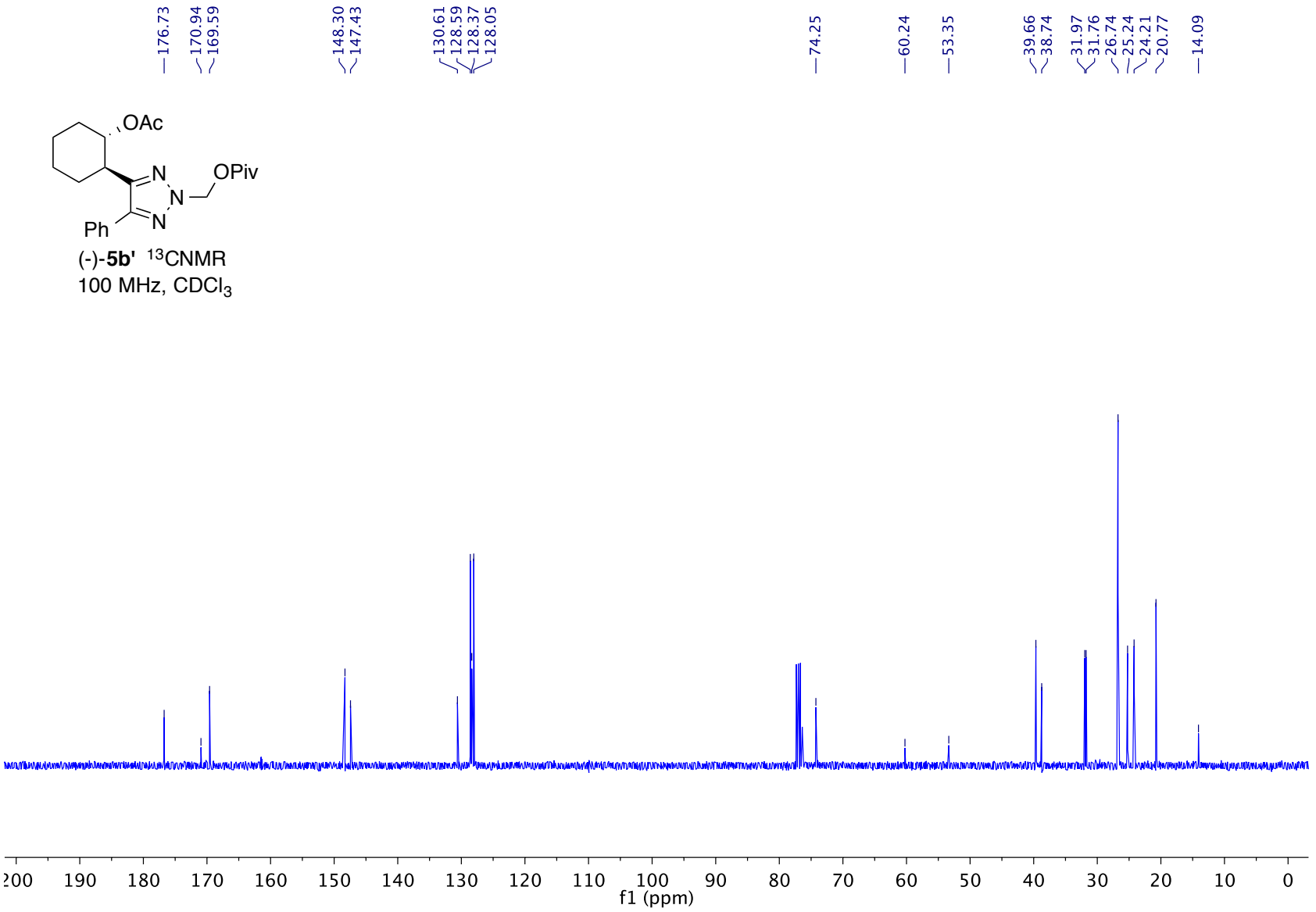
5b ^{1}HNMR
400 MHz, $CDCl_3$

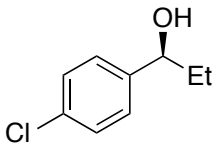

176.93
149.10
147.75
130.47
128.64
128.48
127.93
74.30
73.35
43.48
38.82
34.32
31.77
26.83
25.57
24.75
OH
O
N
N
O
N
Ph
5b 13CNMR
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
N
N
N
OPiv
Ph
(+)-5a' 1HNMR
400 MHz, CDCl3
1.70
2.75
1.93
1.00
1.05
1.20
2.72
4.57
4.46
1.63
8.49
f1 (ppm)

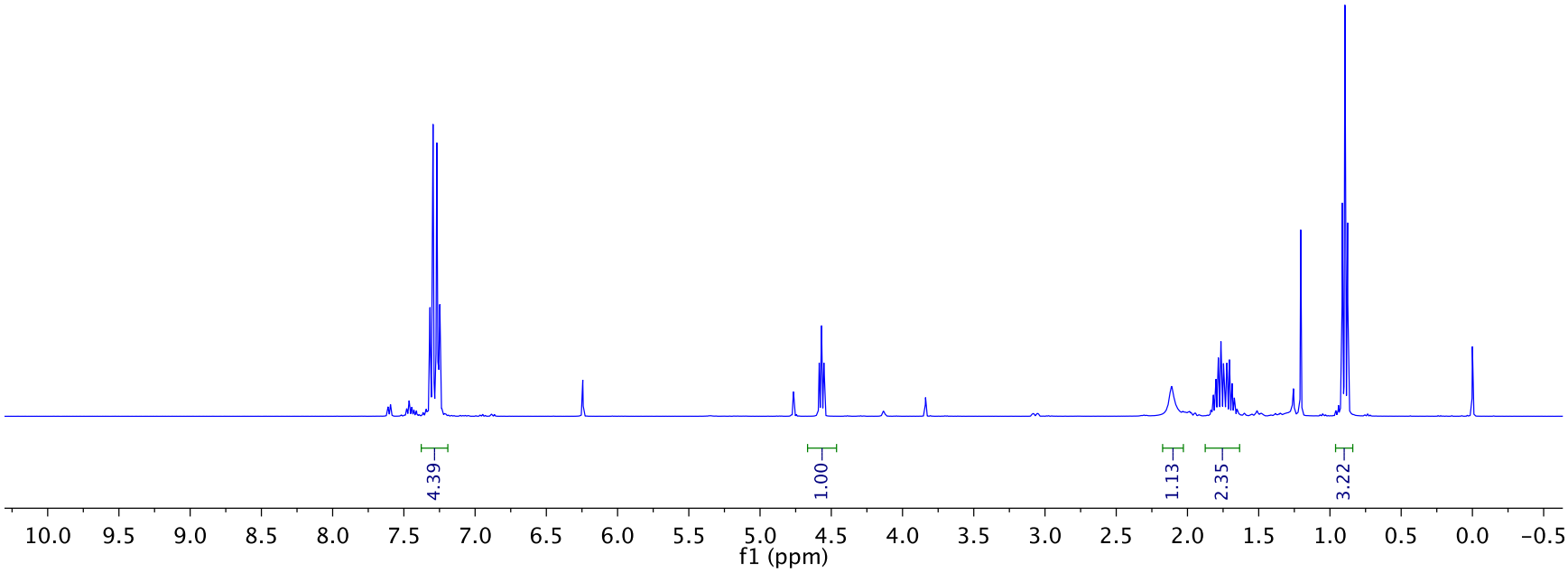

176.74
170.89
170.11
147.76
147.22
130.56
128.58
128.41
128.07
74.21
70.47
60.20
38.71
37.10
29.74
26.76
26.45
24.58
20.98
20.87
20.66
14.06
OAc
OPiv
N
N
N
Ph
(+)-5a' 13CNMR
100 MHz, CDCl3
f1 (ppm)

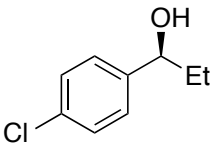

OAc
N
N
N
OPiv
Ph
(-)-5b' 1HNMR
400 MHz, CDCl3
2.03
2.90
2.00
1.80
1.12
1.04
1.11
1.08
1.35
5.53
3.37
7.69
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


176.73
170.94
169.59
148.30
147.43
130.61
128.59
128.37
128.05
74.25
60.24
53.35
39.66
38.74
31.97
31.76
26.74
25.24
24.21
20.77
14.09
OAc
OPiv
N
N
N
Ph
(-)-5b' 13CNMR
100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

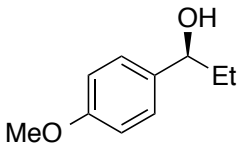


6a ^{1}HNMR
400 MHz, $CDCl_3$

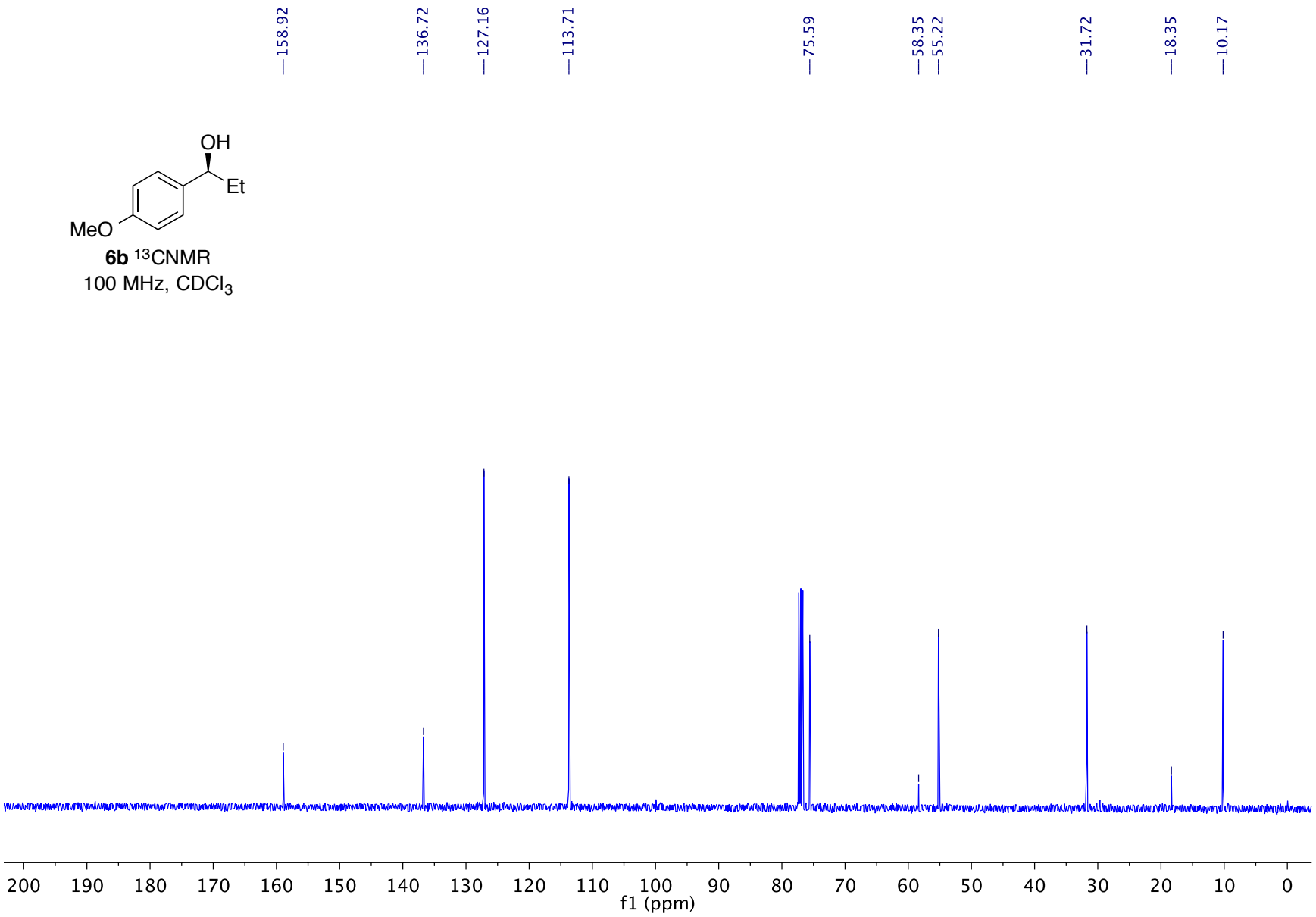




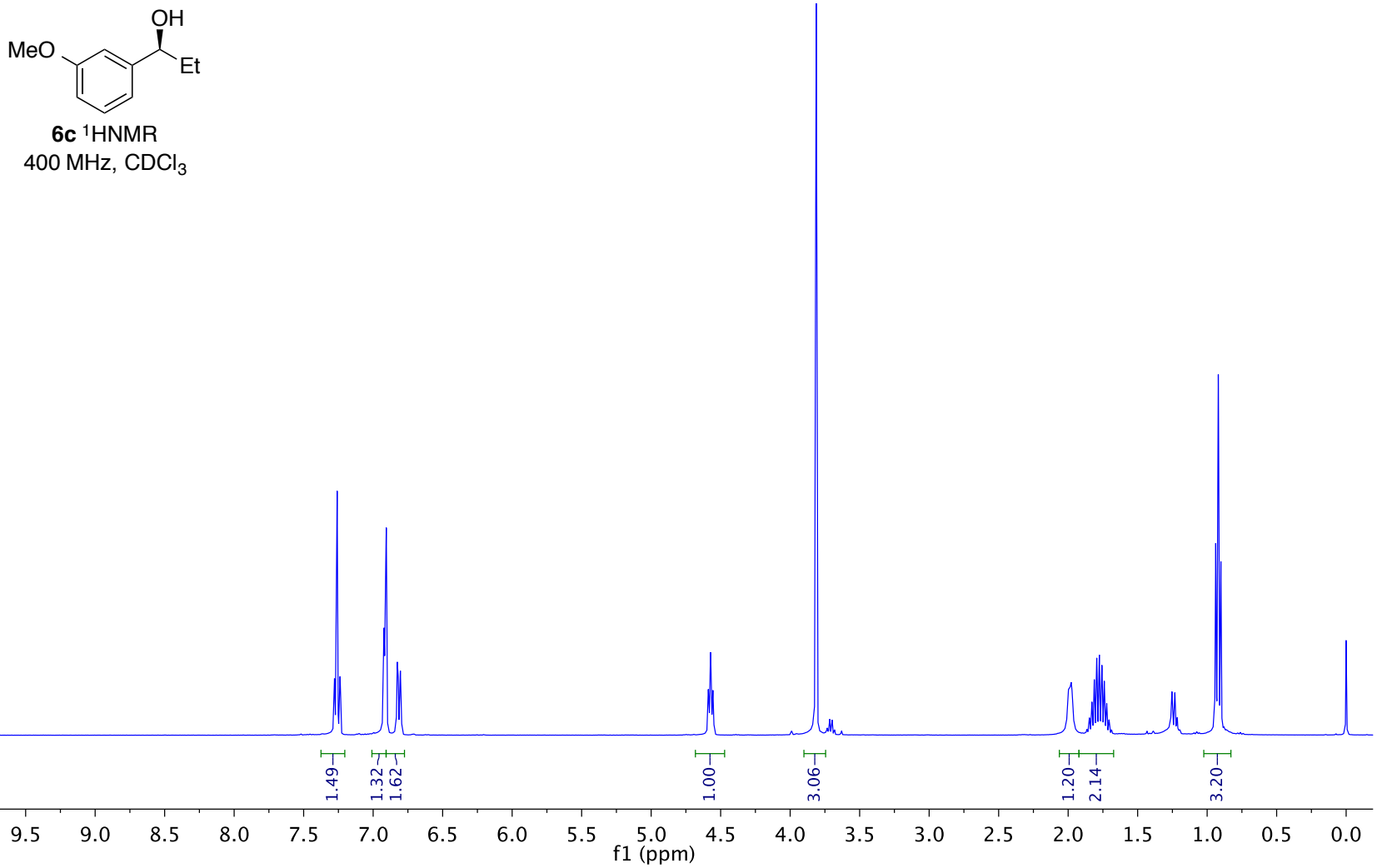
6a ^{13}CNMR
100 MHz, $CDCl_3$

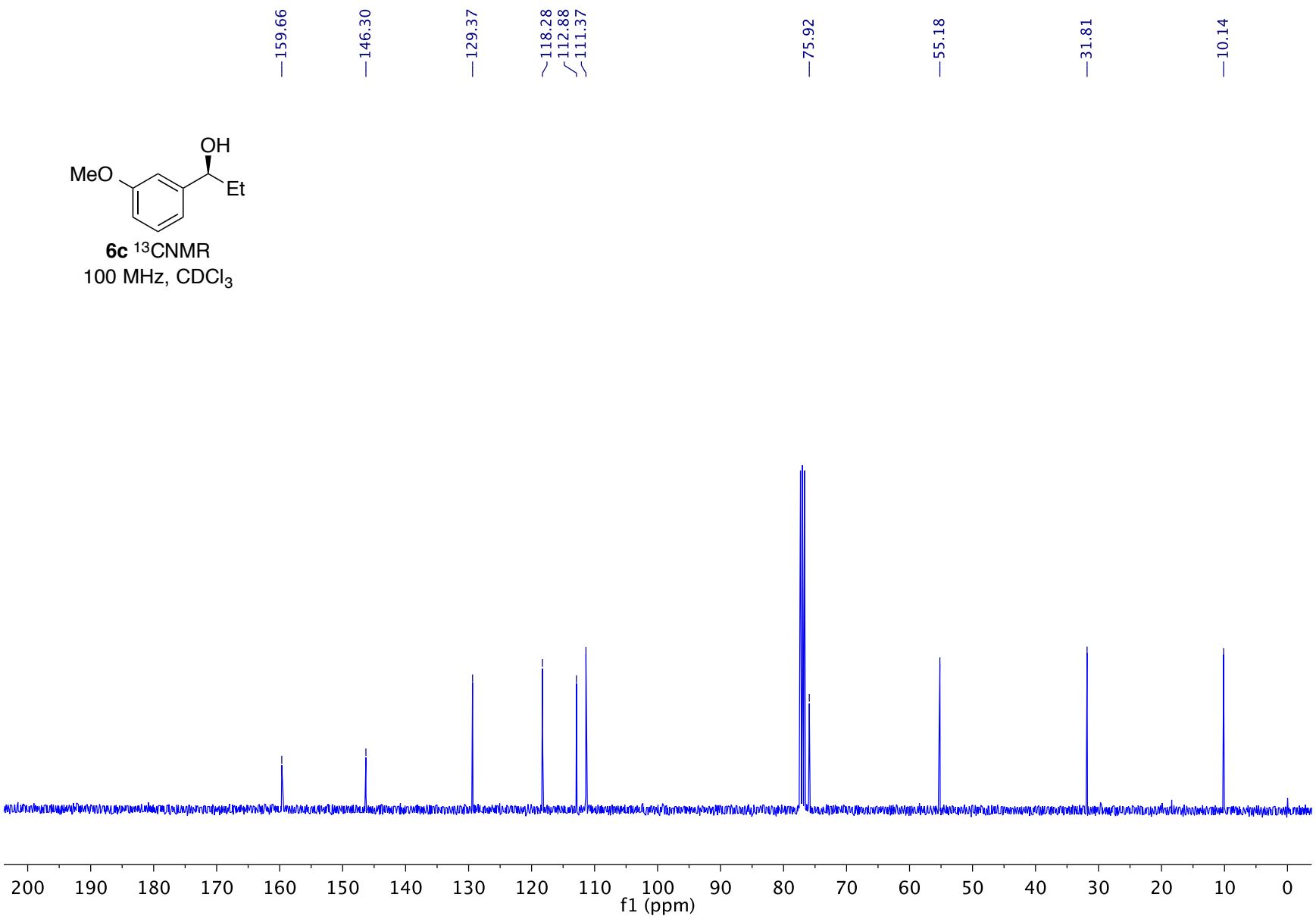


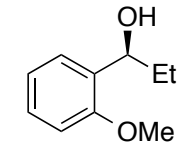
6b ^{1}HNMR
400 MHz, $CDCl_3$



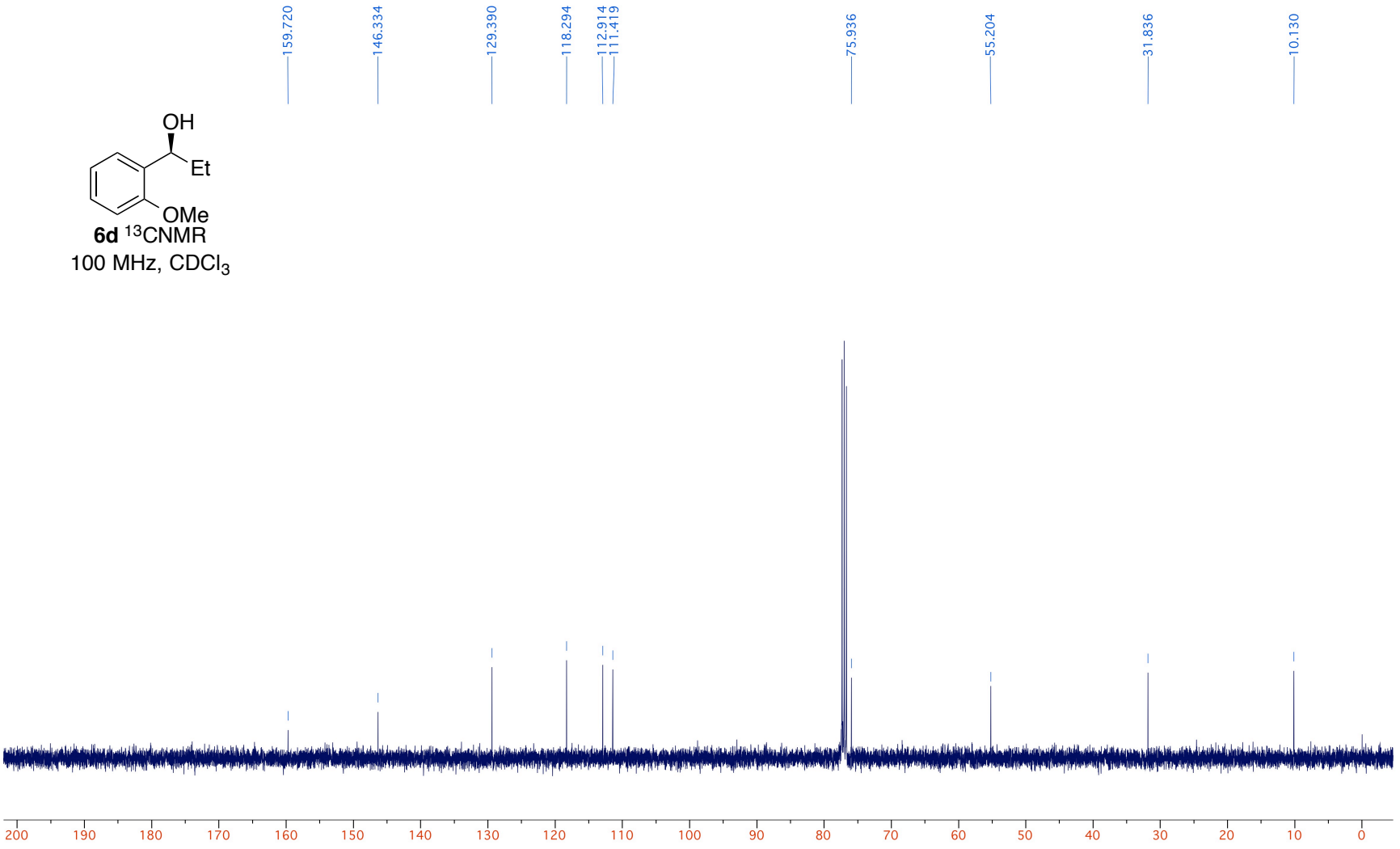
6b ^{13}CNMR
100 MHz, $CDCl_3$

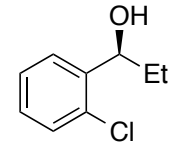

OH
MeO
Et
6c 1HNMR
400 MHz, CDCl3
1.49
1.32
1.62
1.00
3.06
1.20
2.14
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.66
146.30
129.37
118.28
112.88
111.37
75.92
55.18
31.81
10.14
OH
MeO
Et
6c 13CNMR
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

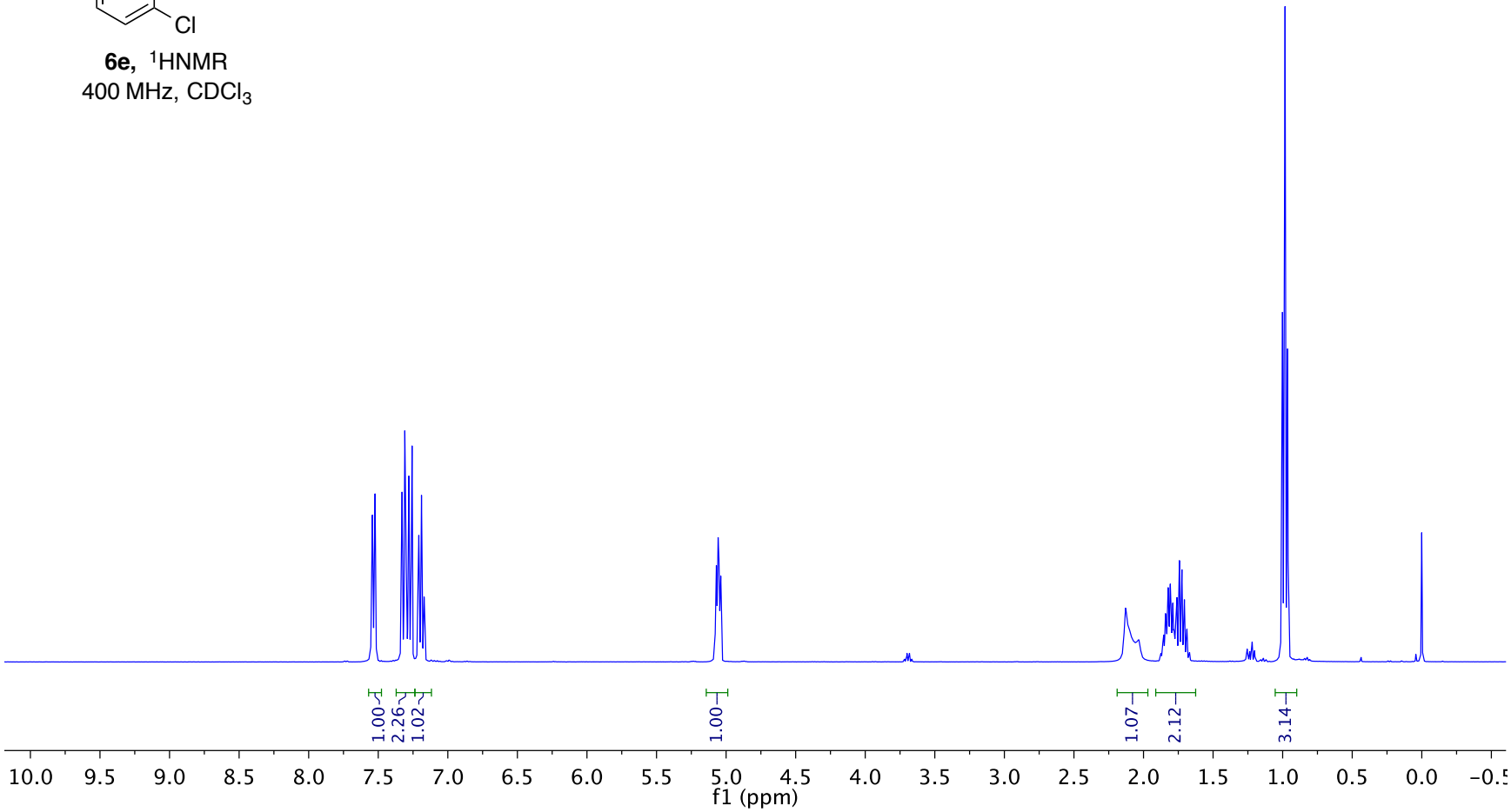


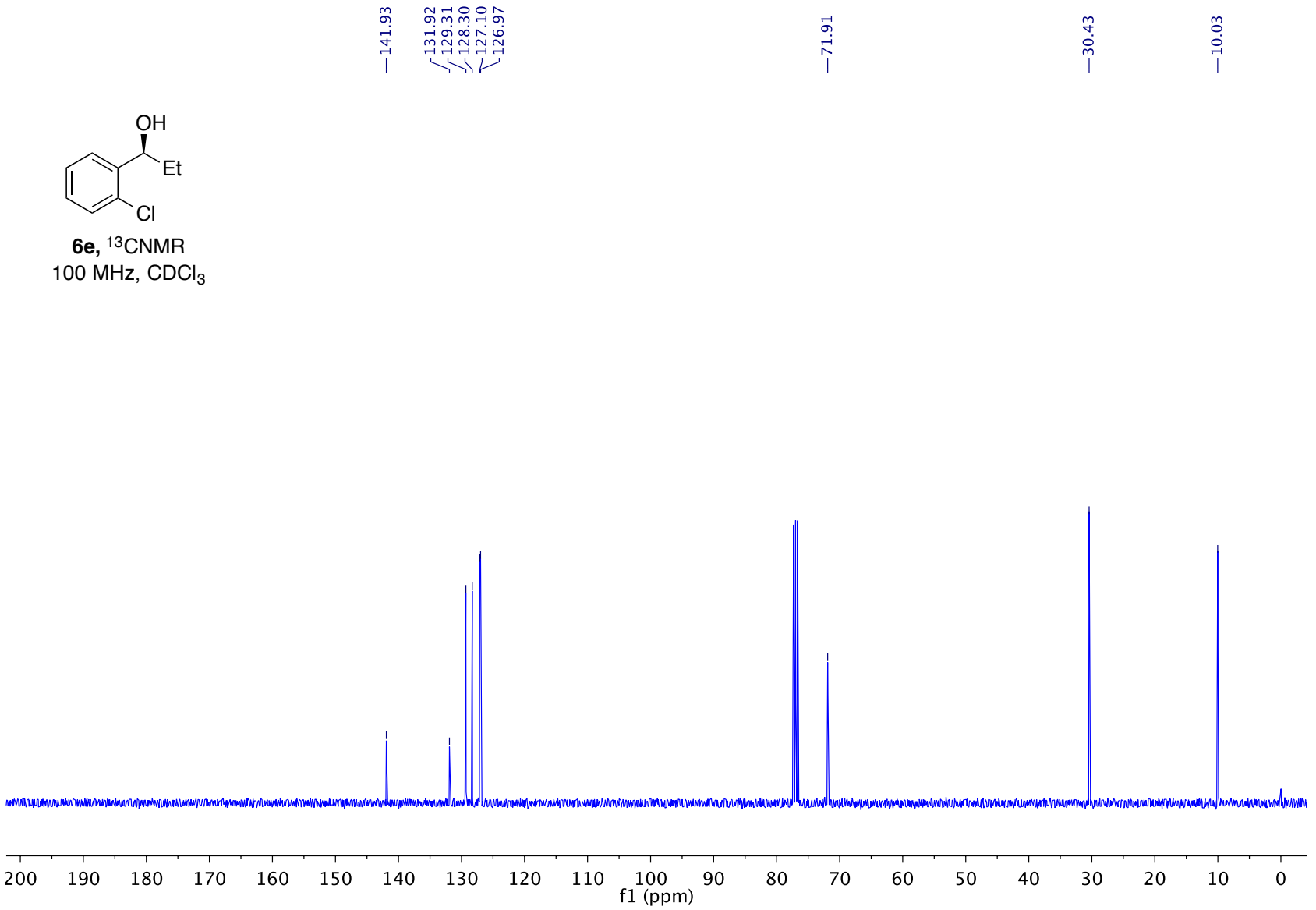
6d ^{1}HNMR
400 MHz, $CDCl_3$


159.720
146.334
129.390
118.294
112.914
111.419
75.936
55.204
31.836
10.130
OH
Et
OMe
6d 13CNMR
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



6e, ^{1}HNMR
400 MHz, $CDCl_3$





6e, ^{13}CNMR
100 MHz, $CDCl_3$